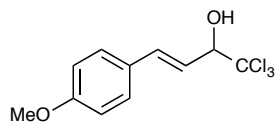


**Organocatalytic Michael Addition-Lactonisation of Carboxylic Acids  
and  $\alpha,\beta$ -Unsaturated Trichloromethyl Ketones: A Route to  
Stereodefined Diesters**

*Supporting Information*

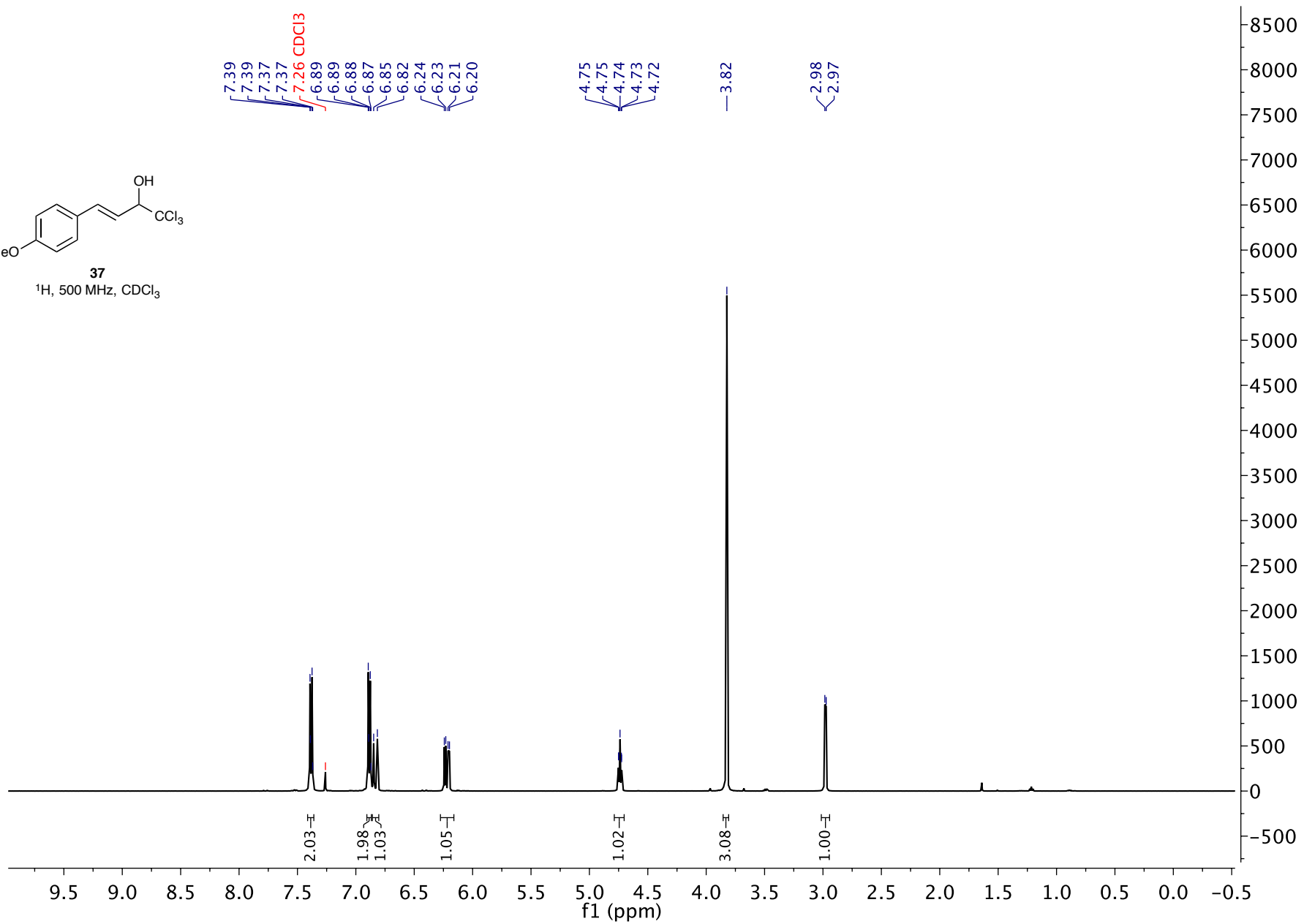
*Louis C. Morrill,<sup>a</sup> Daniel. G. Stark,<sup>a</sup> James. E. Taylor,<sup>a</sup> Siobhan R. Smith,<sup>a</sup> James A. Squires,<sup>a</sup> Agathe D'Hollander,<sup>a</sup> Carmen Simal,<sup>a</sup> Peter Shapland,<sup>b</sup> Timothy. J. C. O'Riordan<sup>c</sup> and Andrew D. Smith\*<sup>a</sup>*

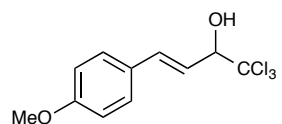
<b>1.0</b>	<b><sup>1</sup>H and <sup>13</sup>C NMR Data.....</b>	<b>S2</b>
<b>2.0</b>	<b>HPLC Data.....</b>	<b>S41</b>



37

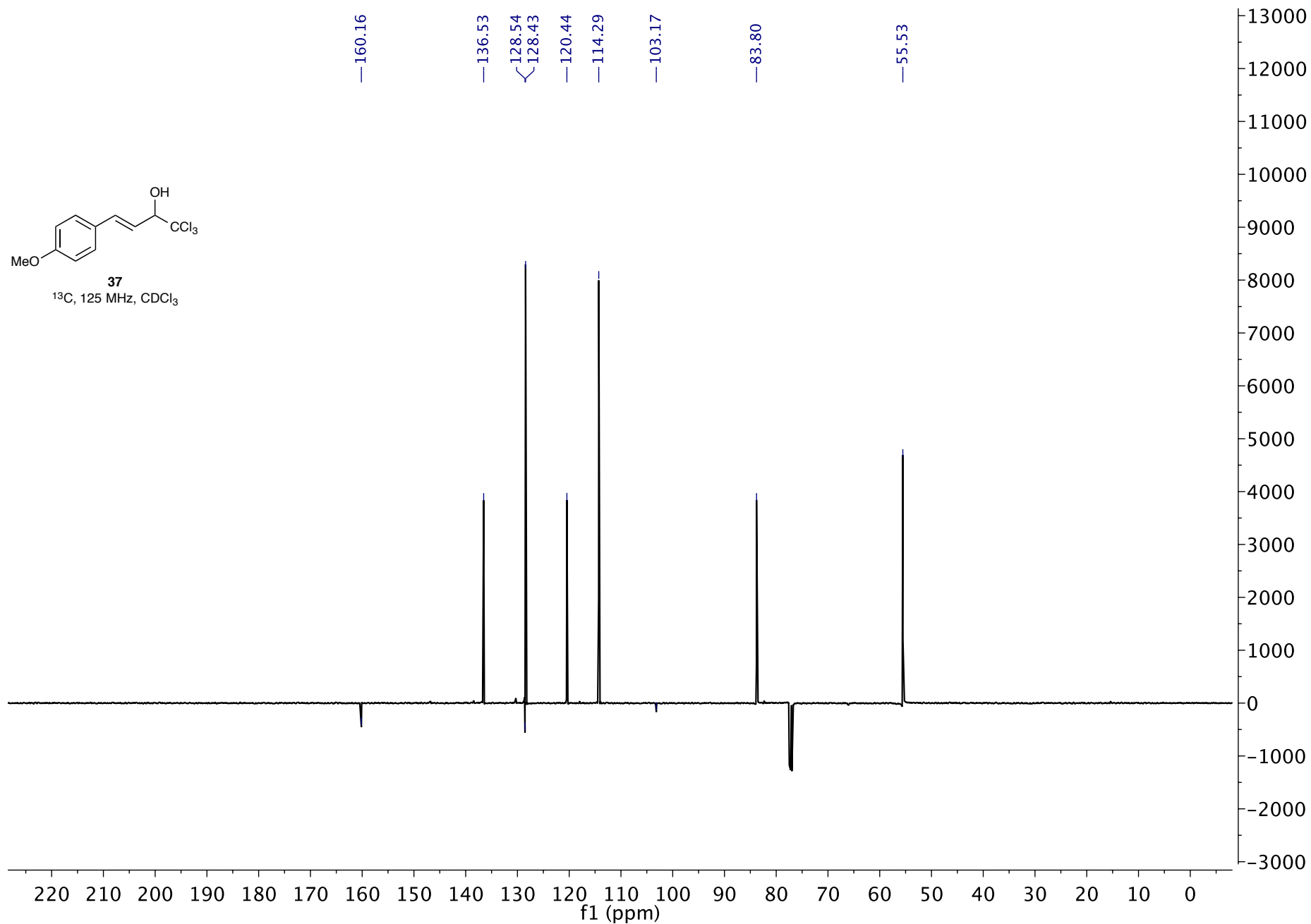
<sup>1</sup>H, 500 MHz, CDCl<sub>3</sub>



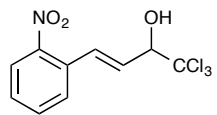


37

<sup>13</sup>C, 125 MHz, CDCl<sub>3</sub>

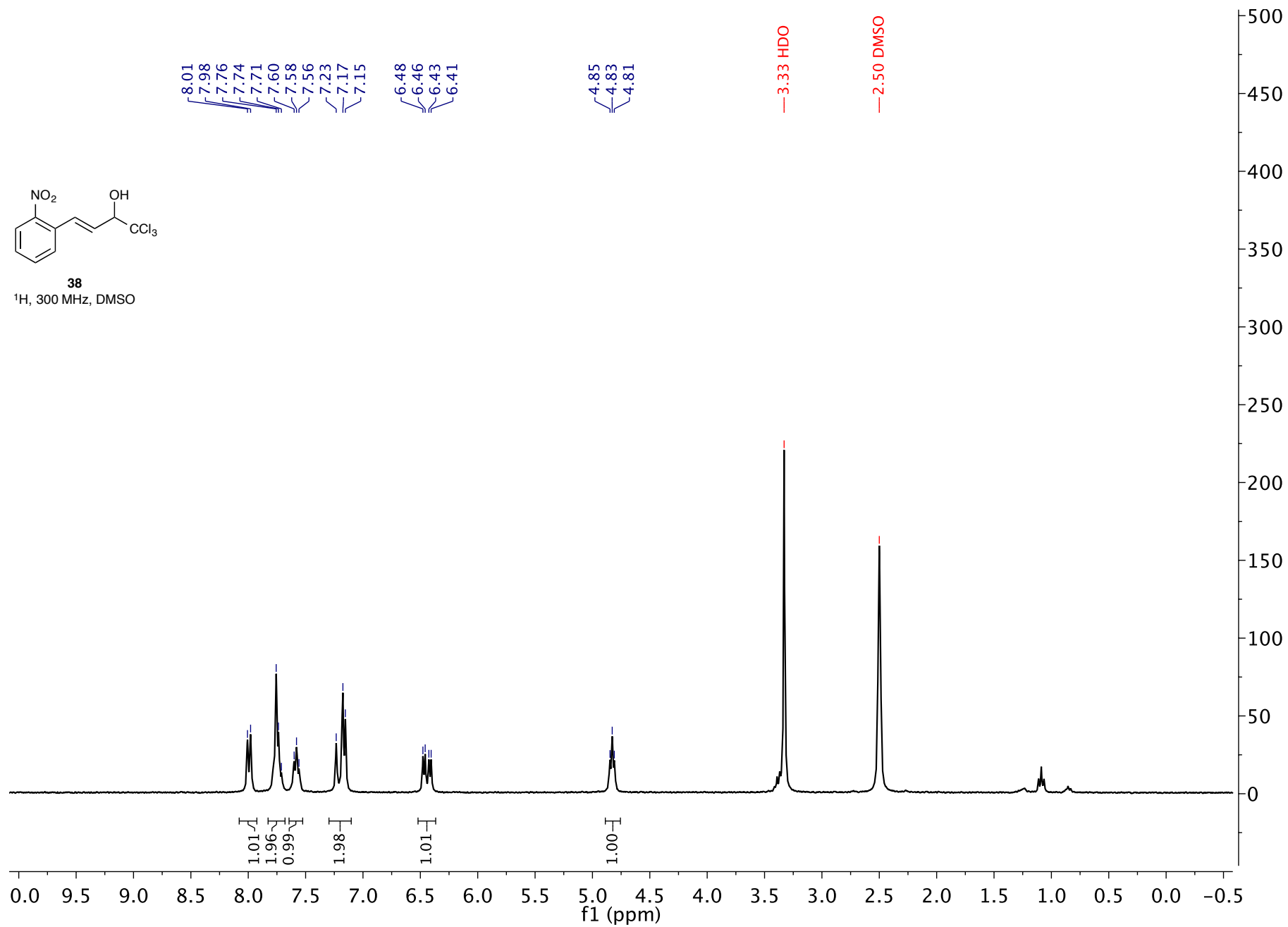


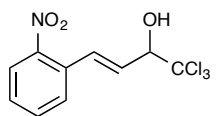
S3



**38**

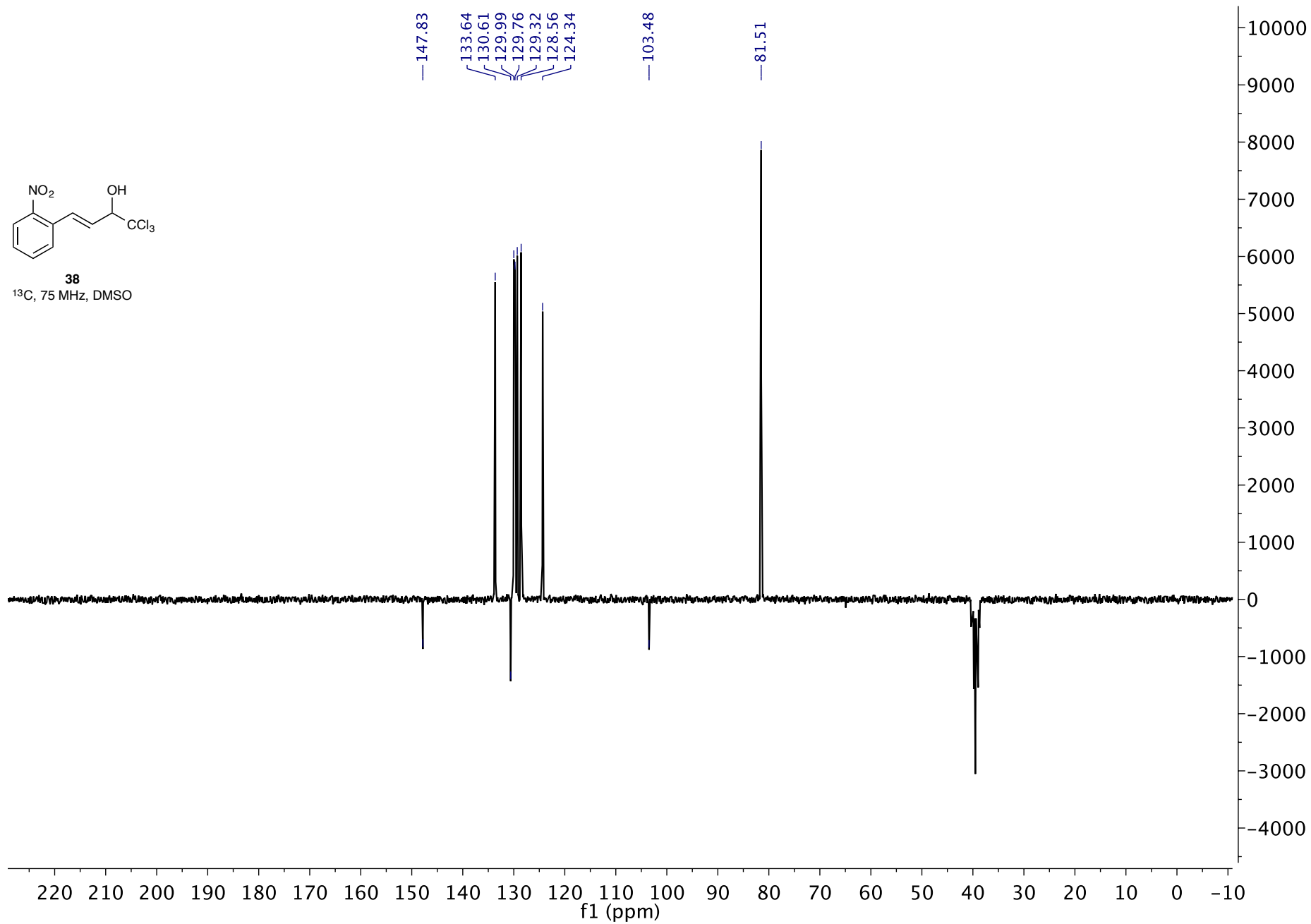
<sup>1</sup>H, 300 MHz, DMSO

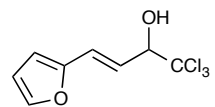




**38**

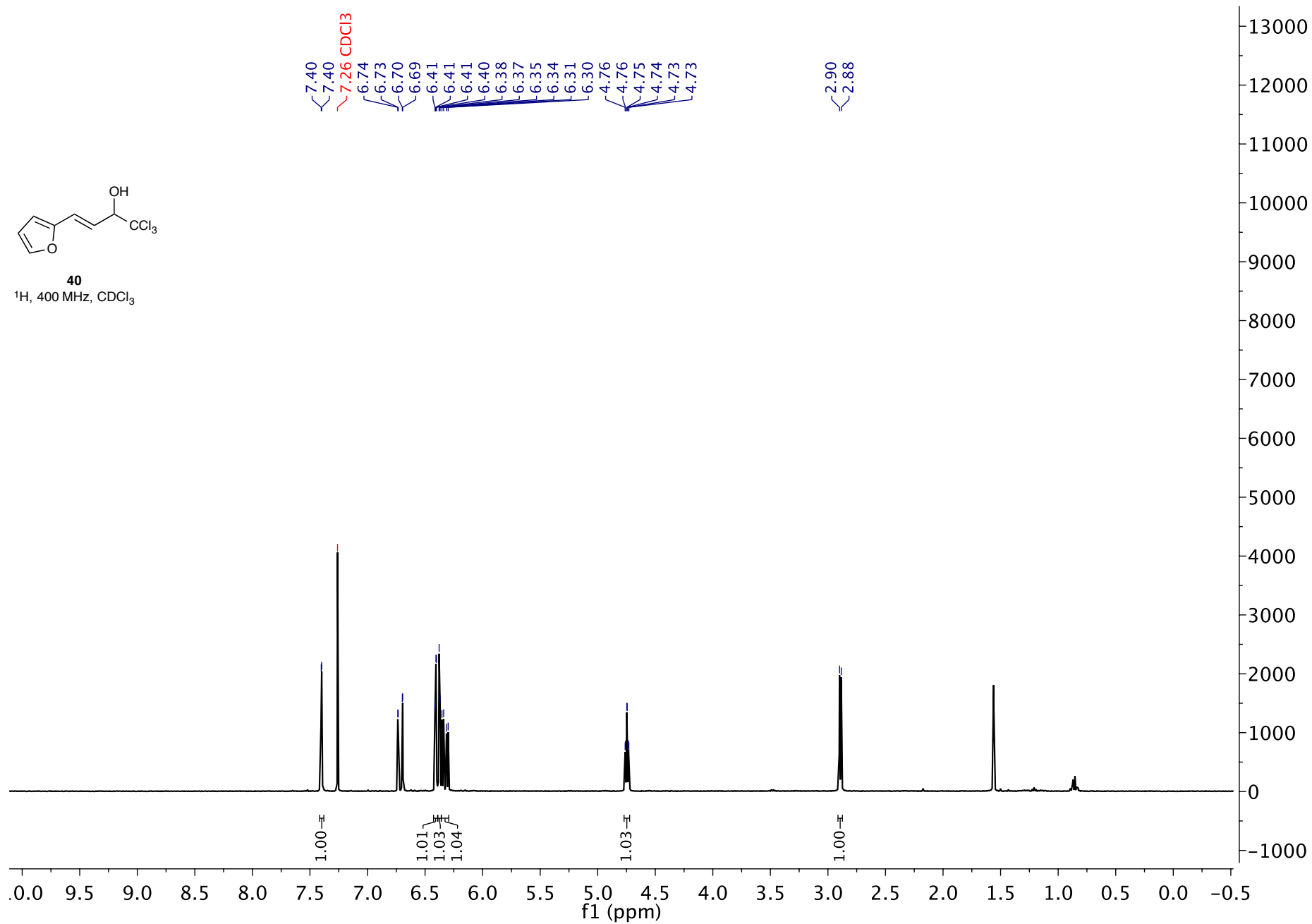
$^{13}\text{C}$ , 75 MHz, DMSO

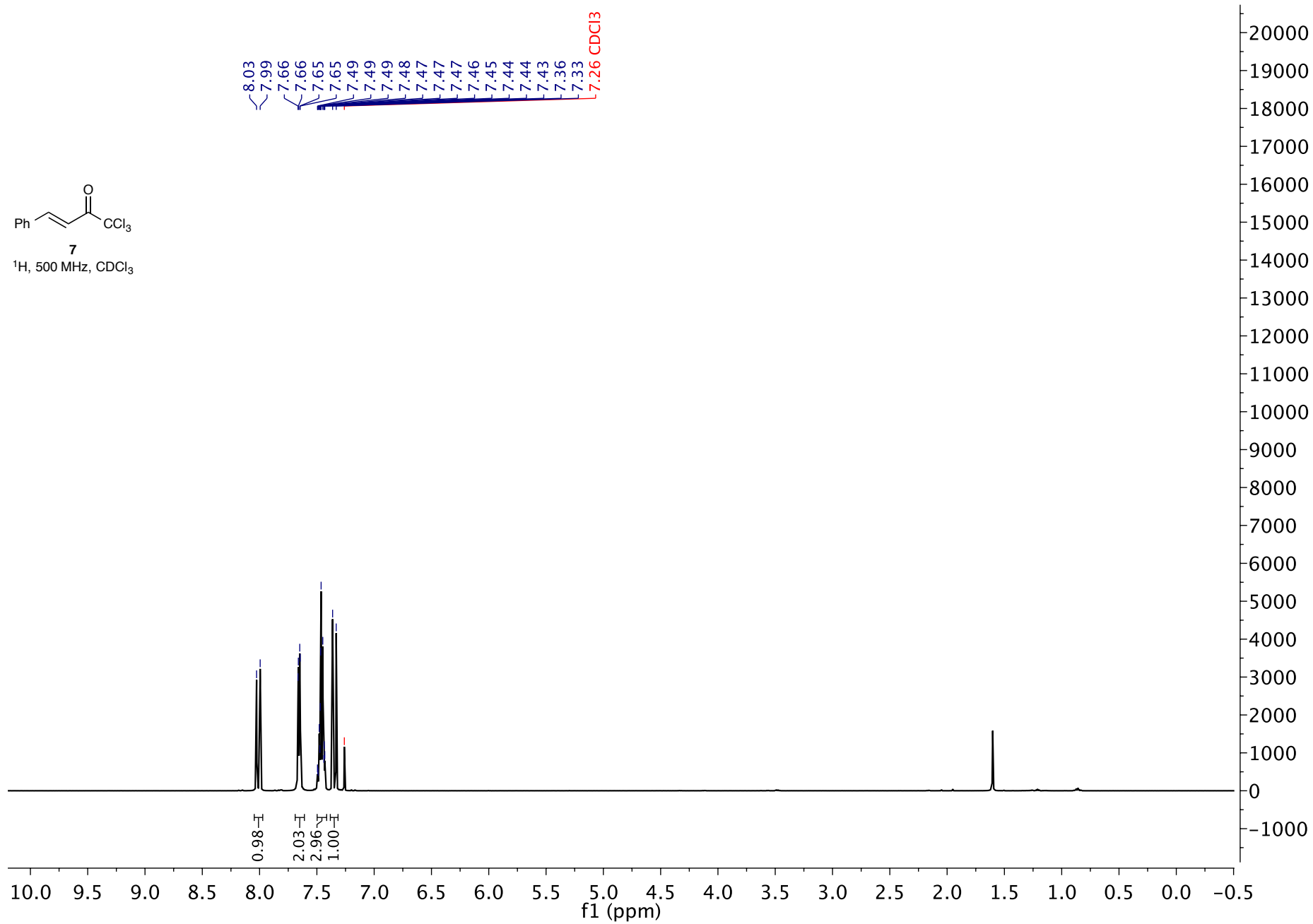
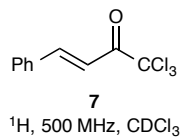


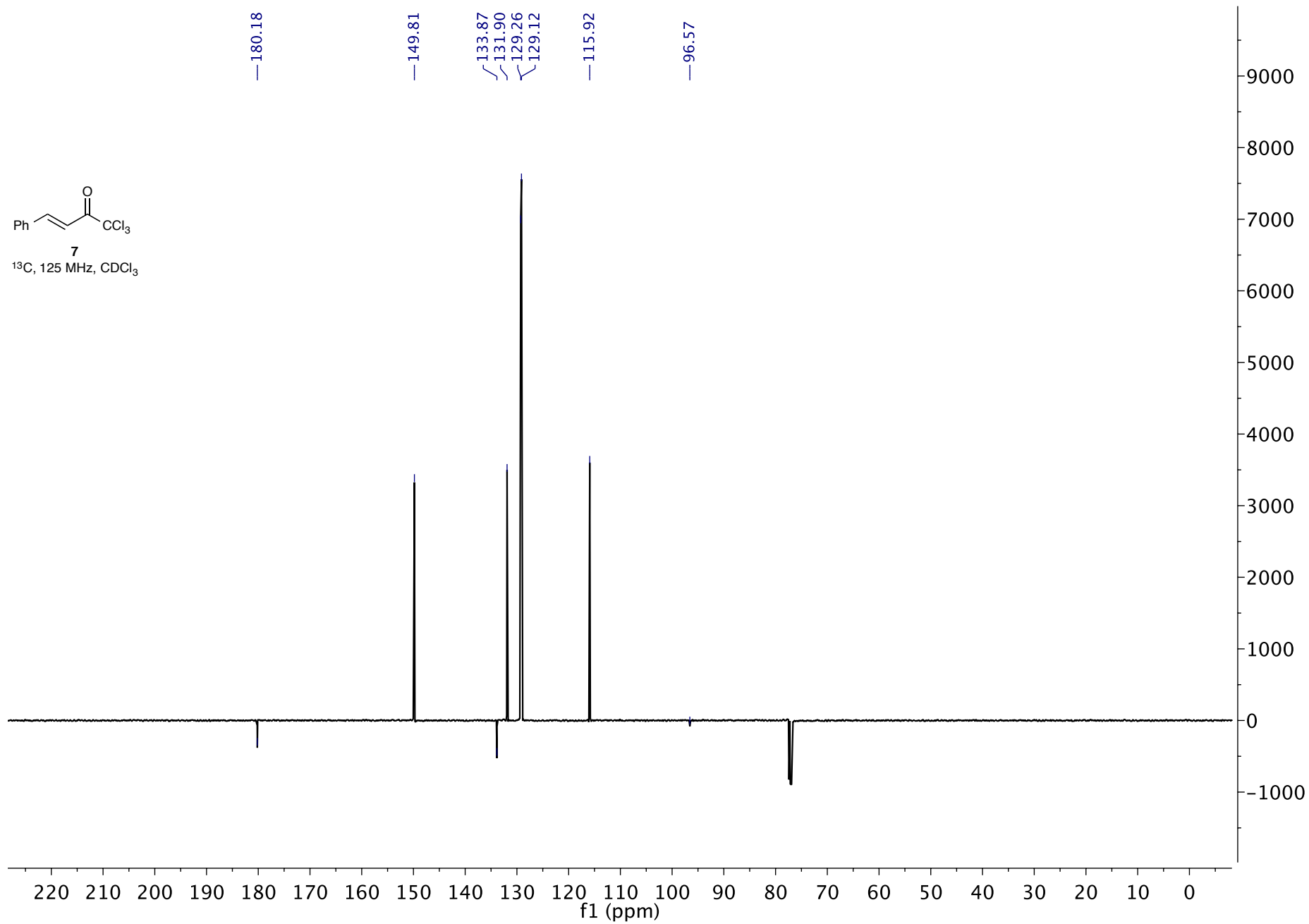
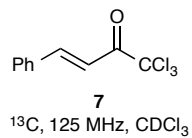


**40**

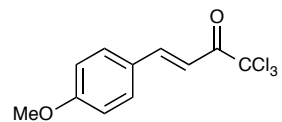
<sup>1</sup>H, 400 MHz, CDCl<sub>3</sub>





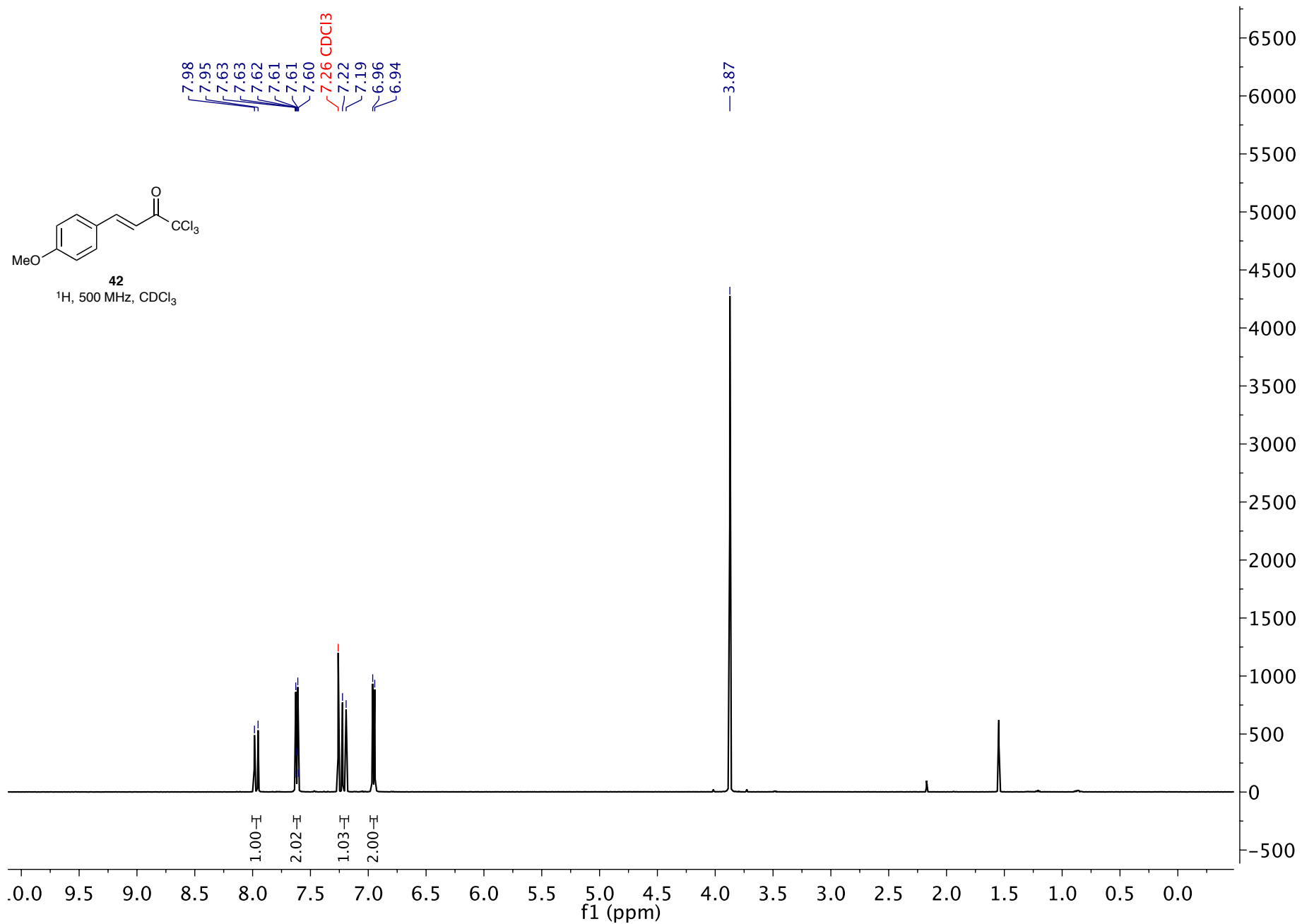


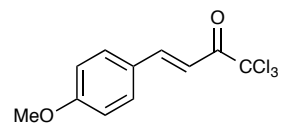




42

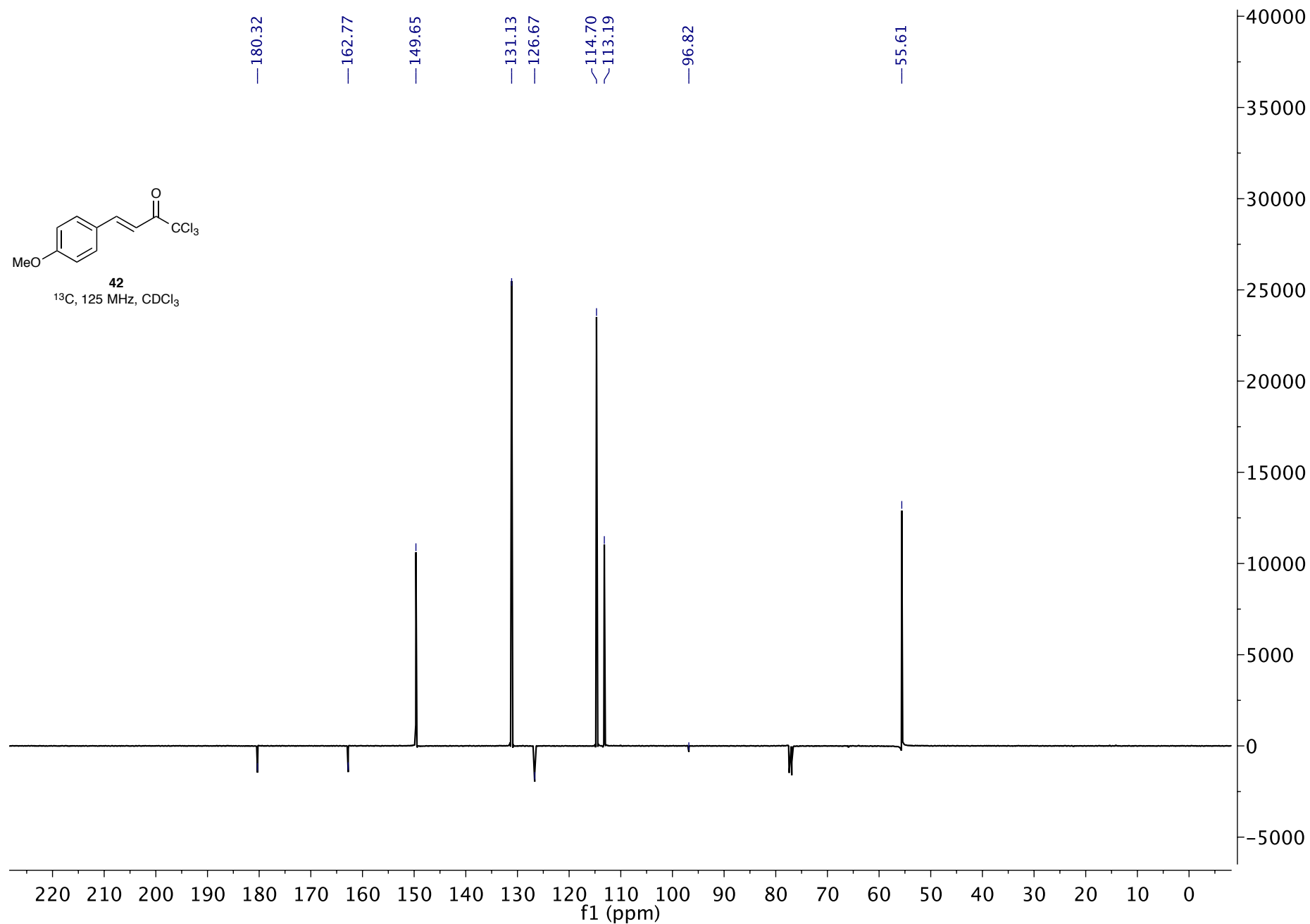
<sup>1</sup>H, 500 MHz, CDCl<sub>3</sub>



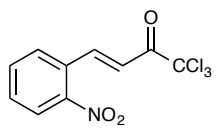


42

<sup>13</sup>C, 125 MHz, CDCl<sub>3</sub>

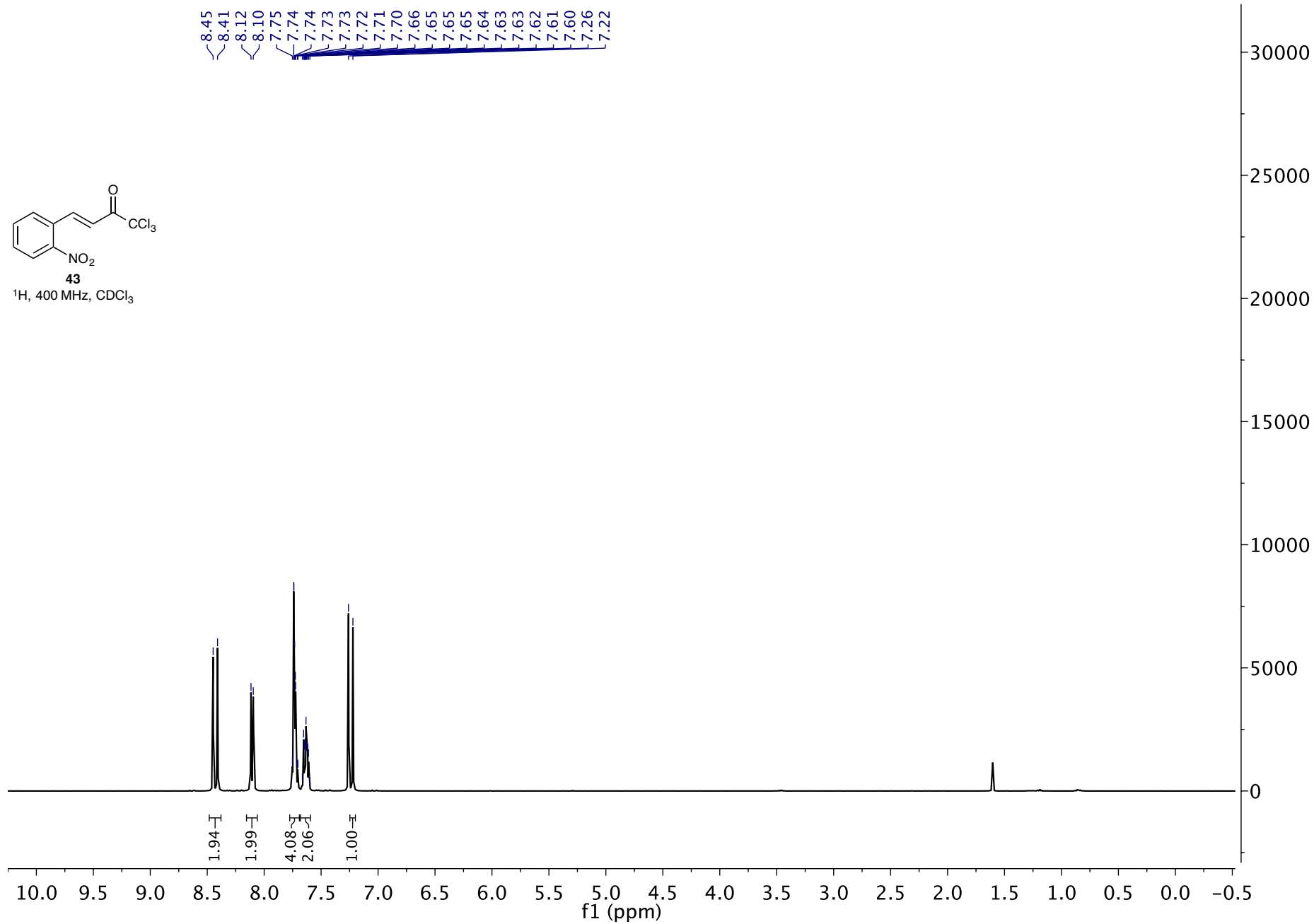


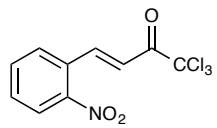
S10



**43**

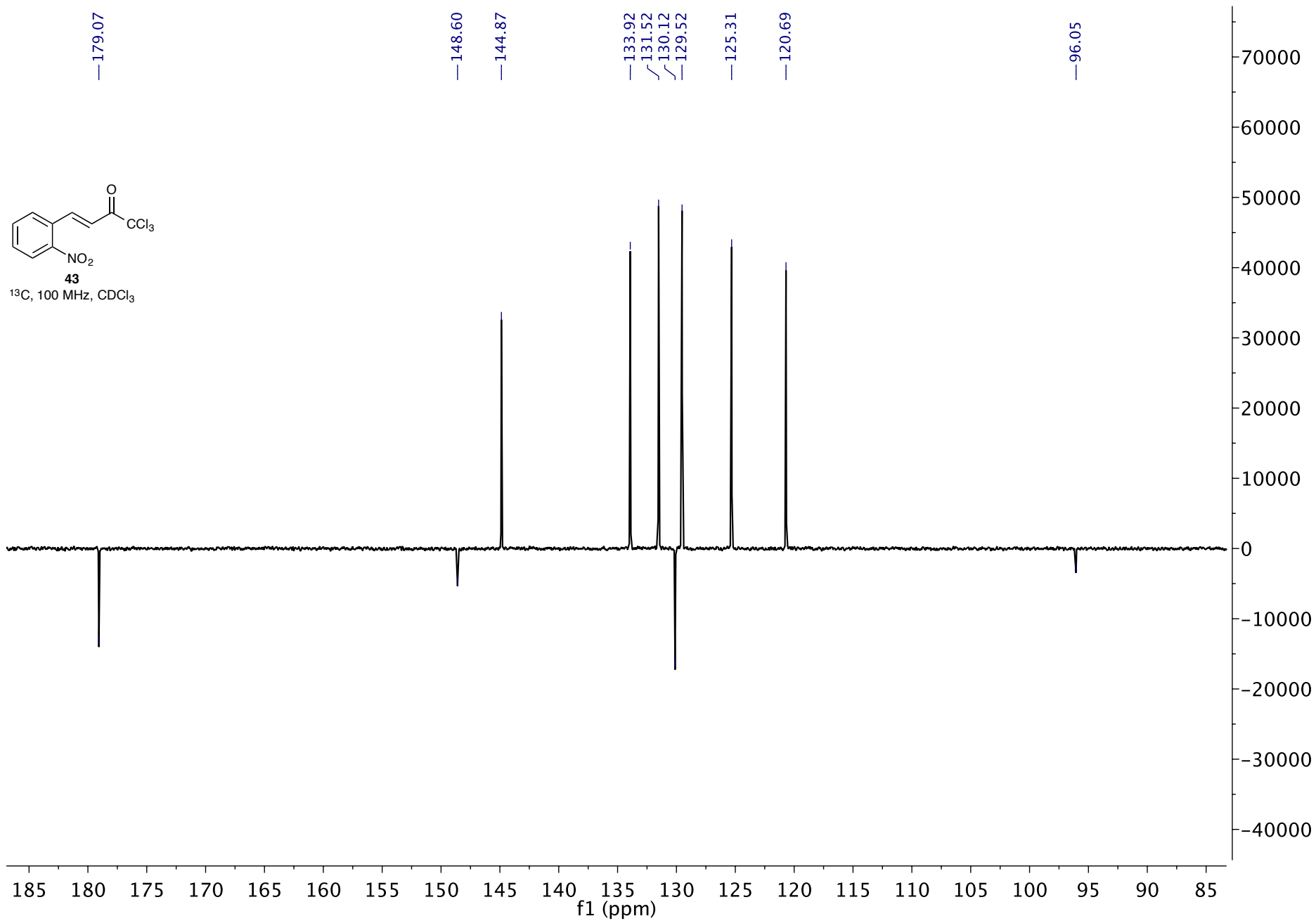
<sup>1</sup>H, 400 MHz, CDCl<sub>3</sub>



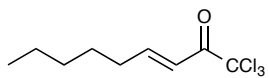


43

<sup>13</sup>C, 100 MHz, CDCl<sub>3</sub>

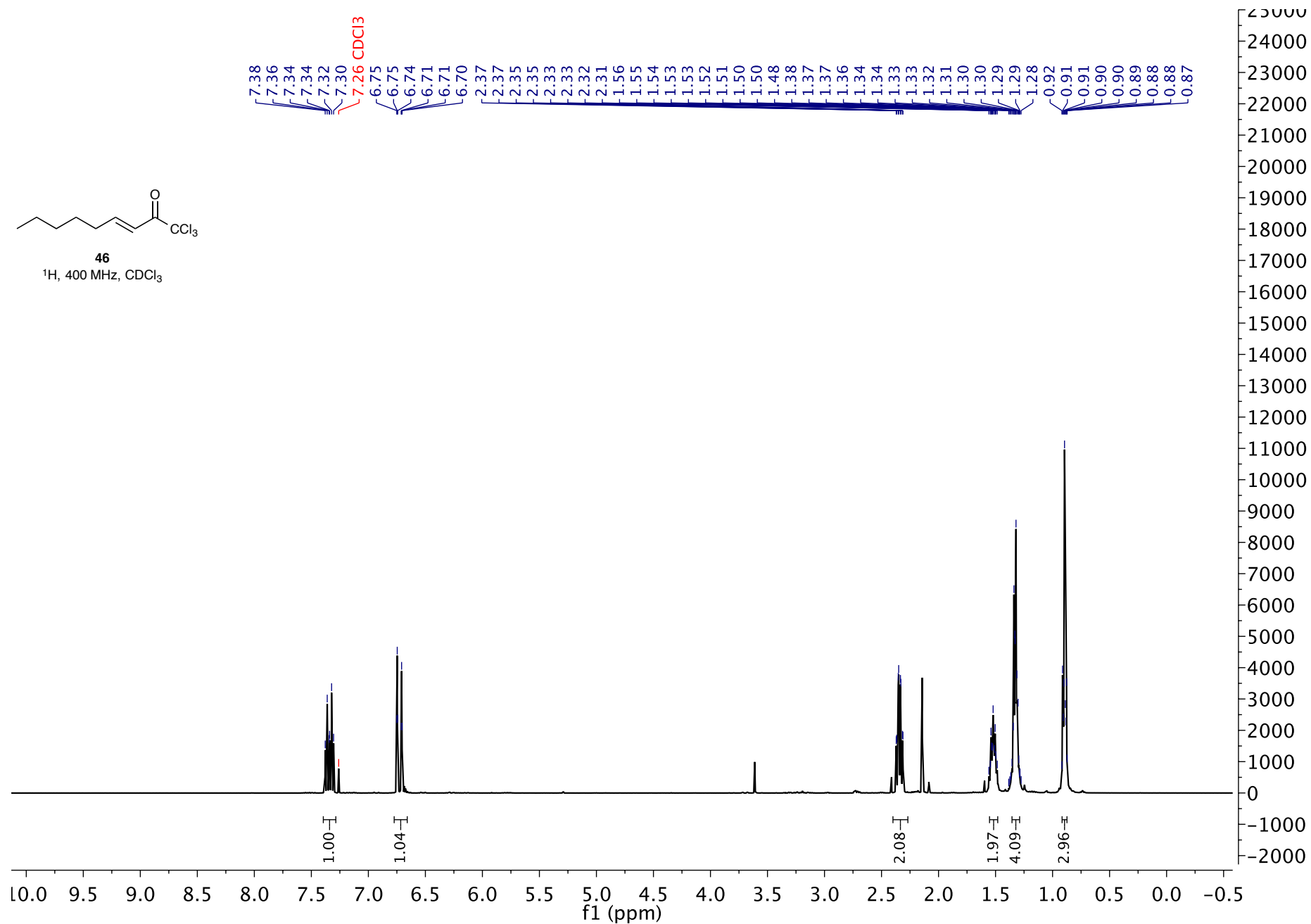


S12

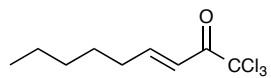


46

<sup>1</sup>H, 400 MHz, CDCl<sub>3</sub>

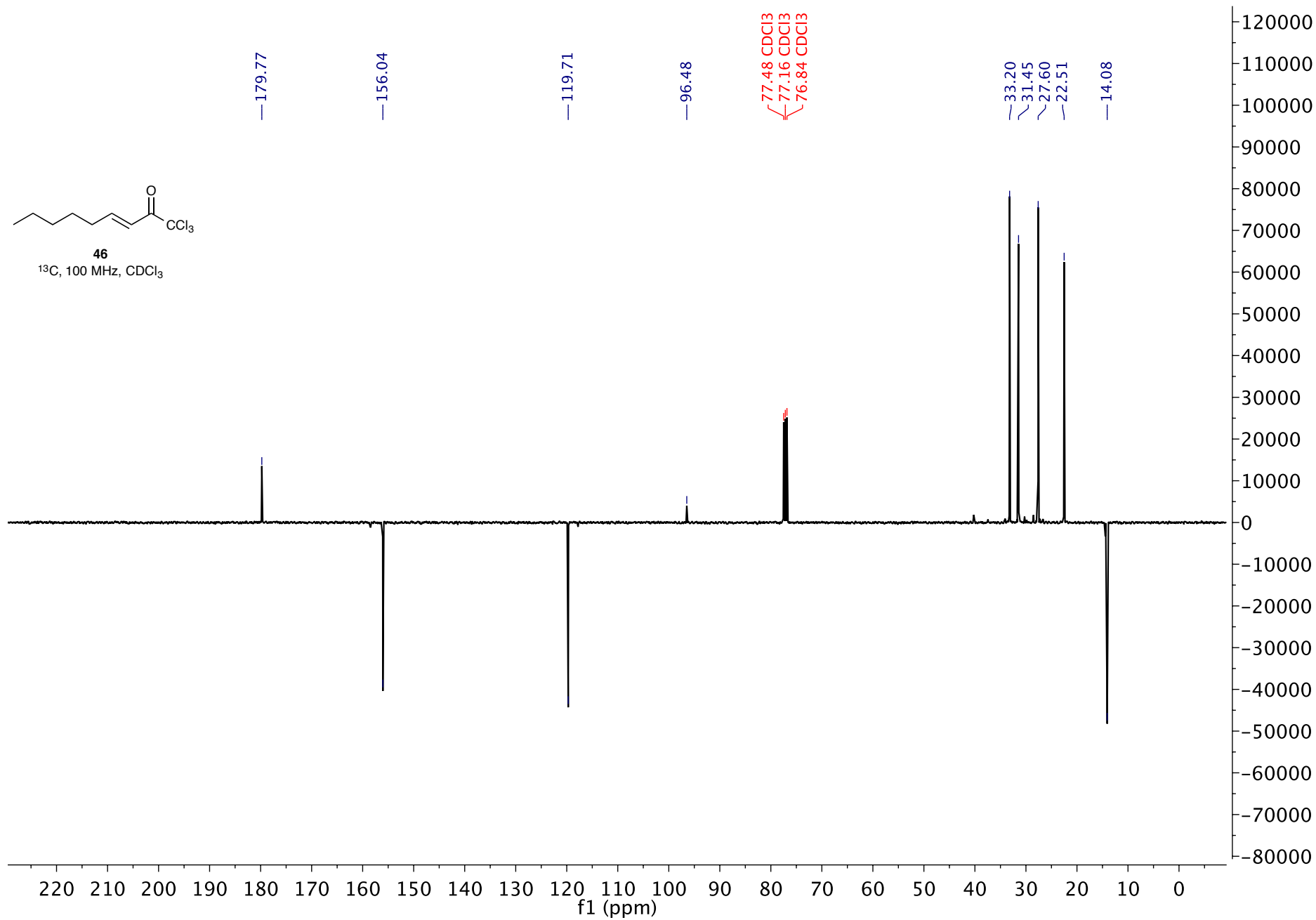


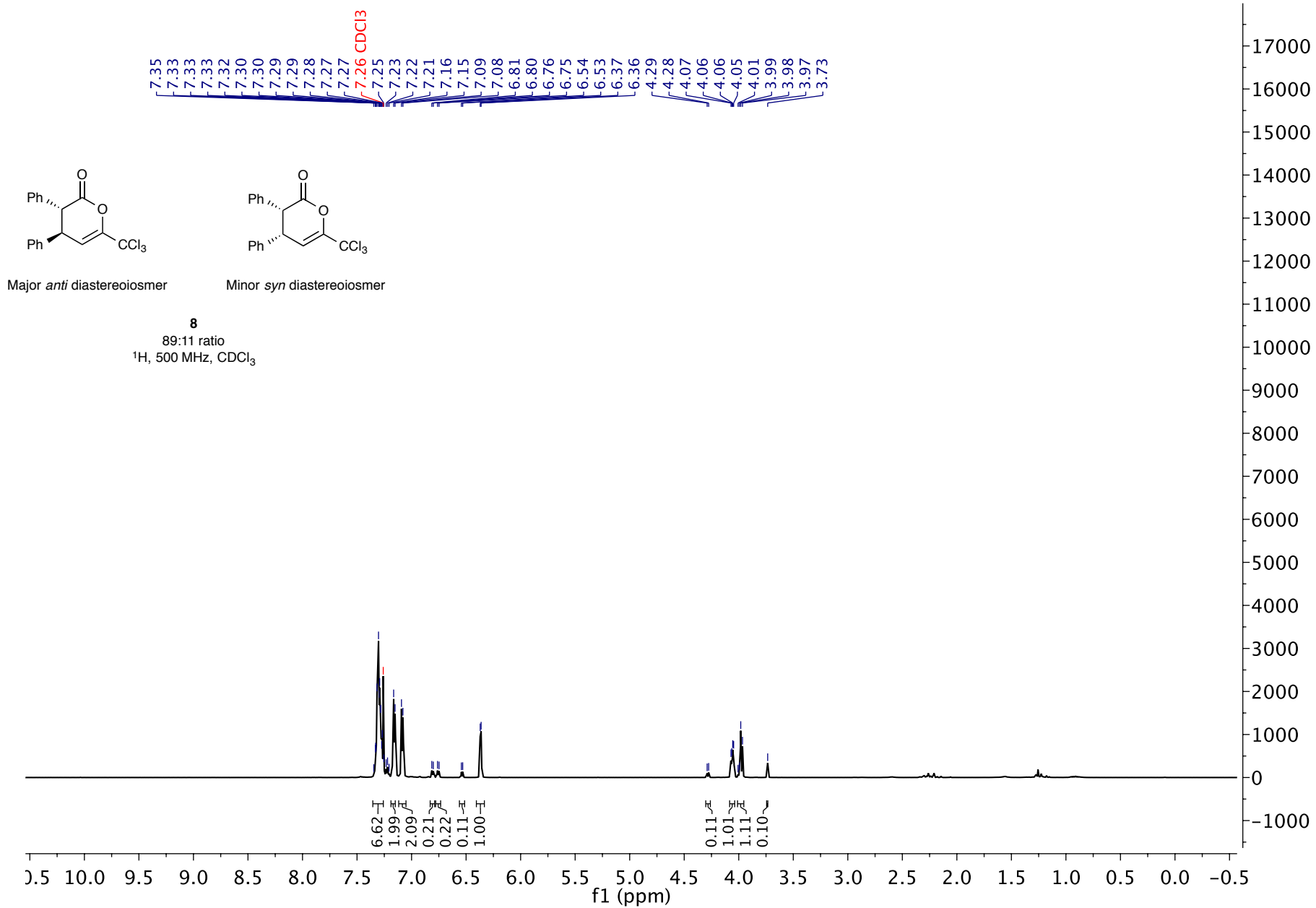
S13

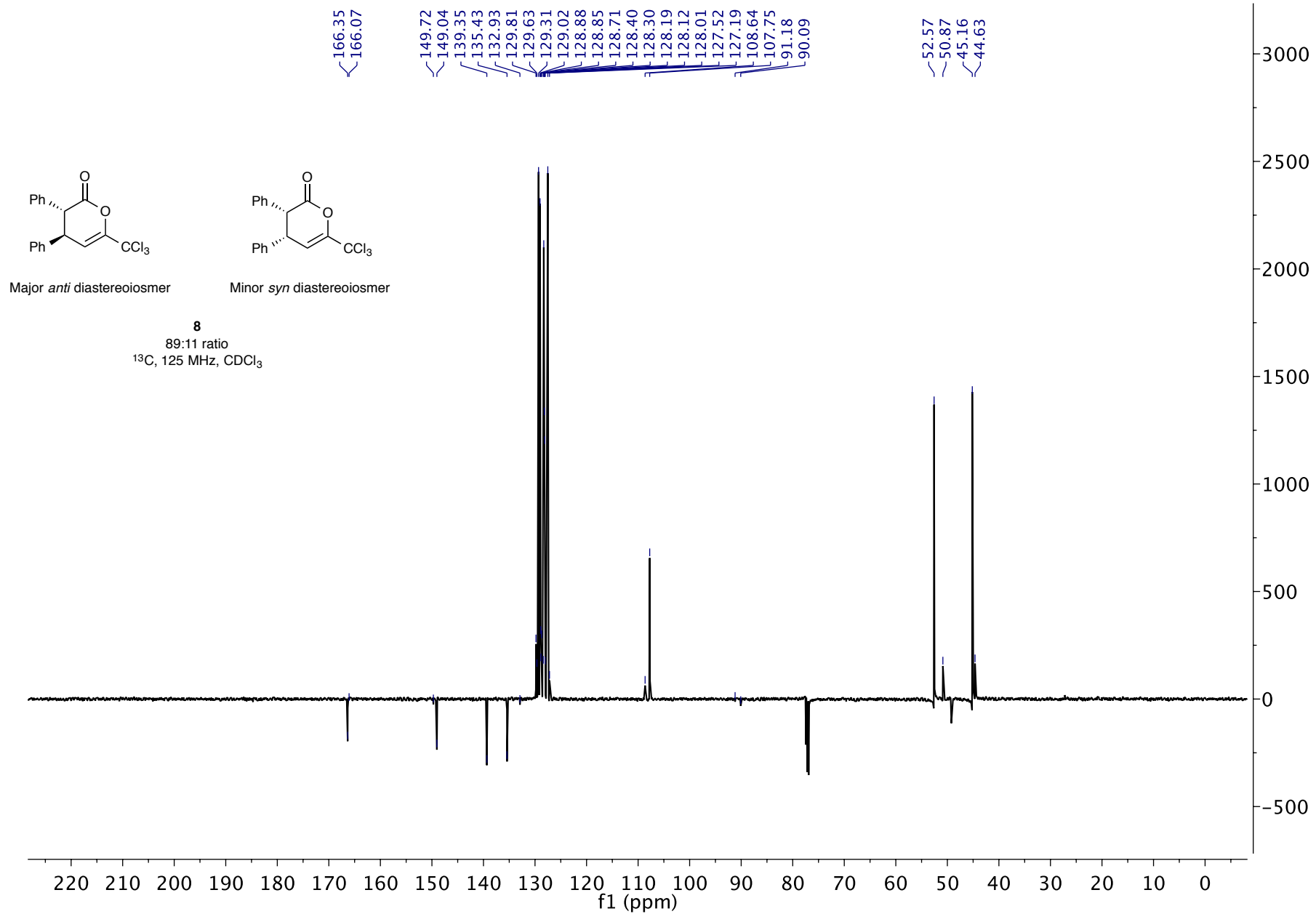


46

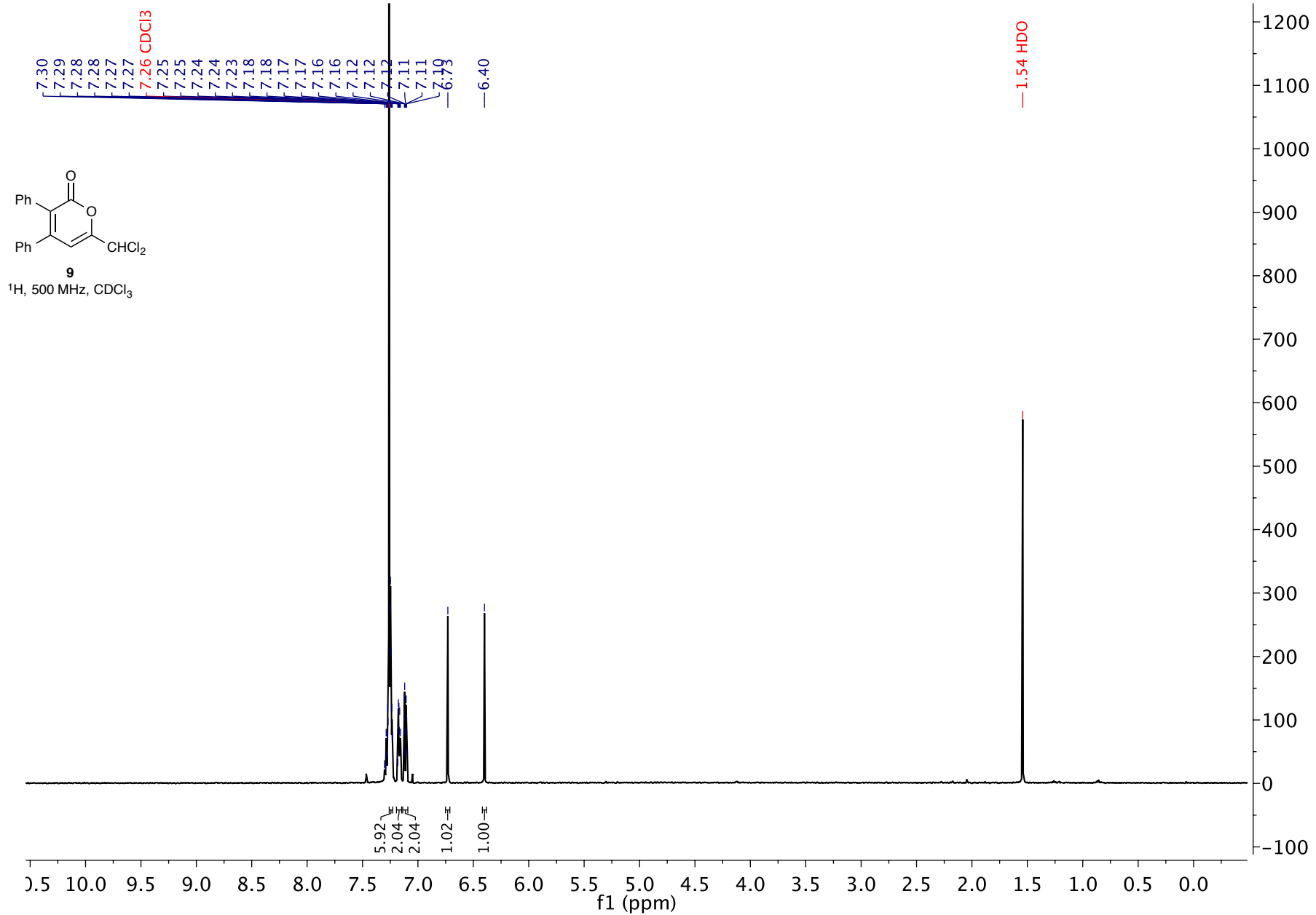
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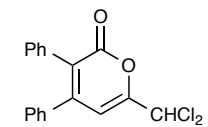






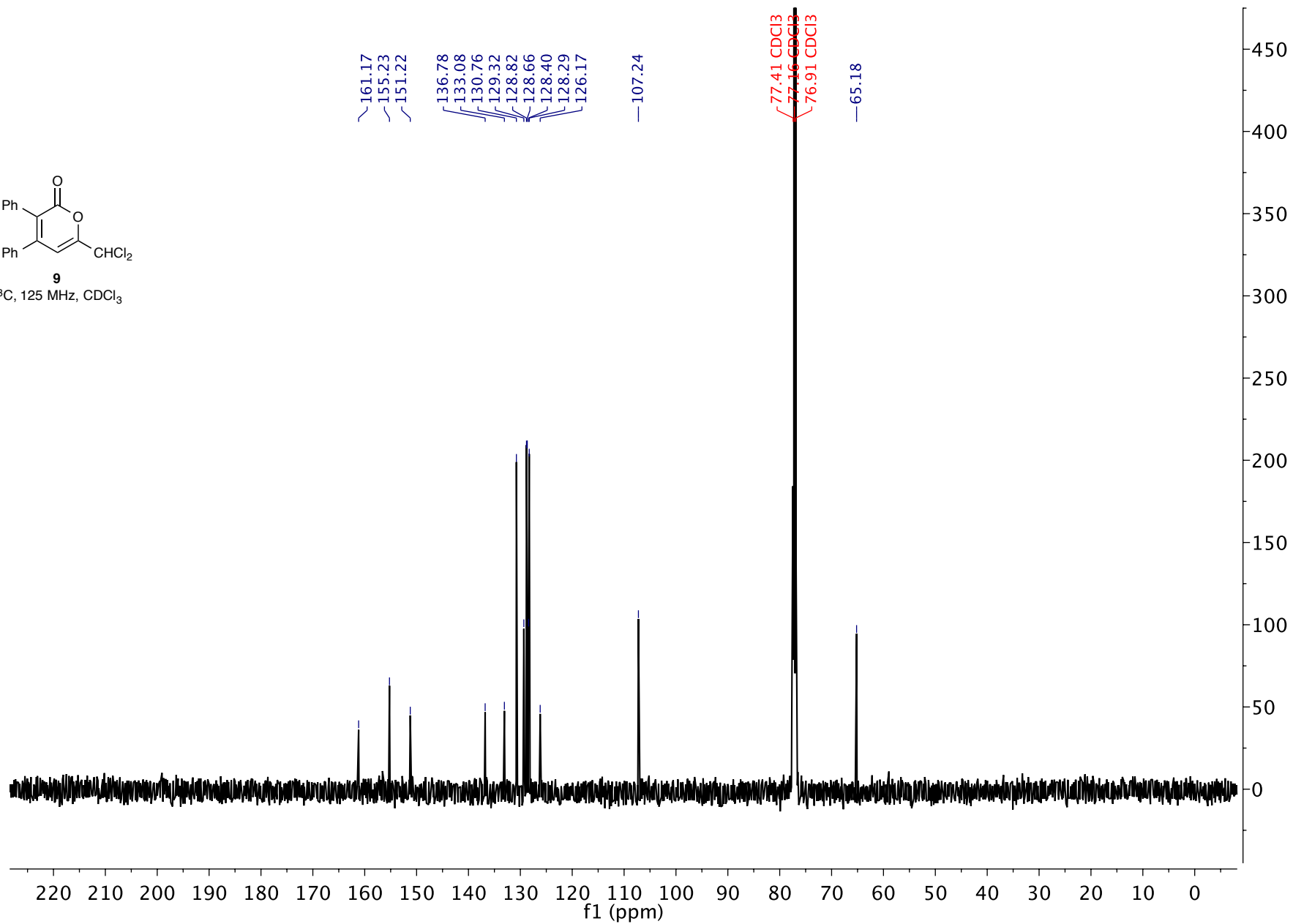


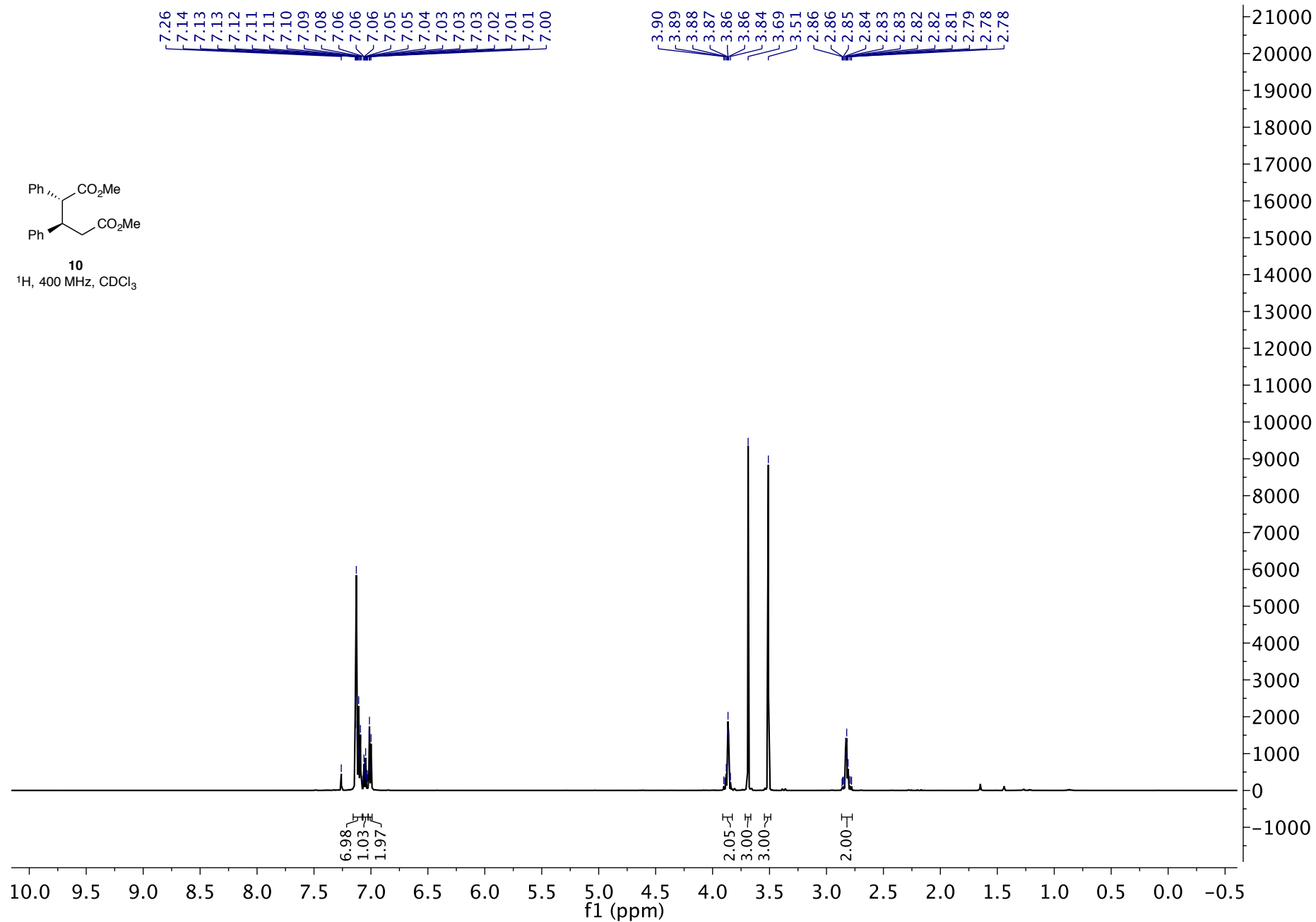
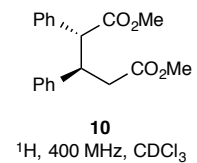


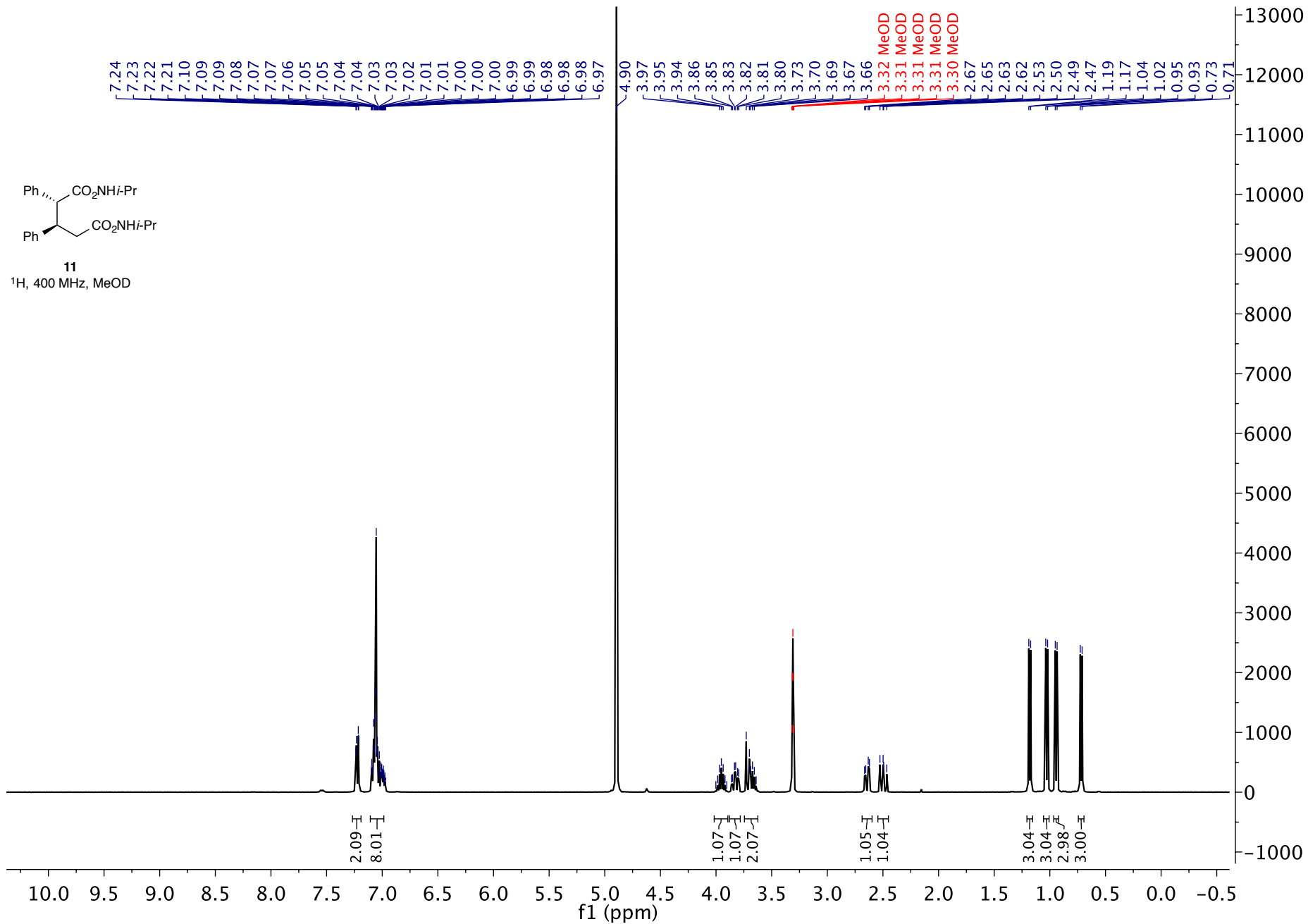
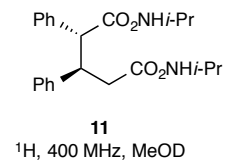


**9**

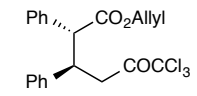
$^{13}\text{C}$ , 125 MHz,  $\text{CDCl}_3$





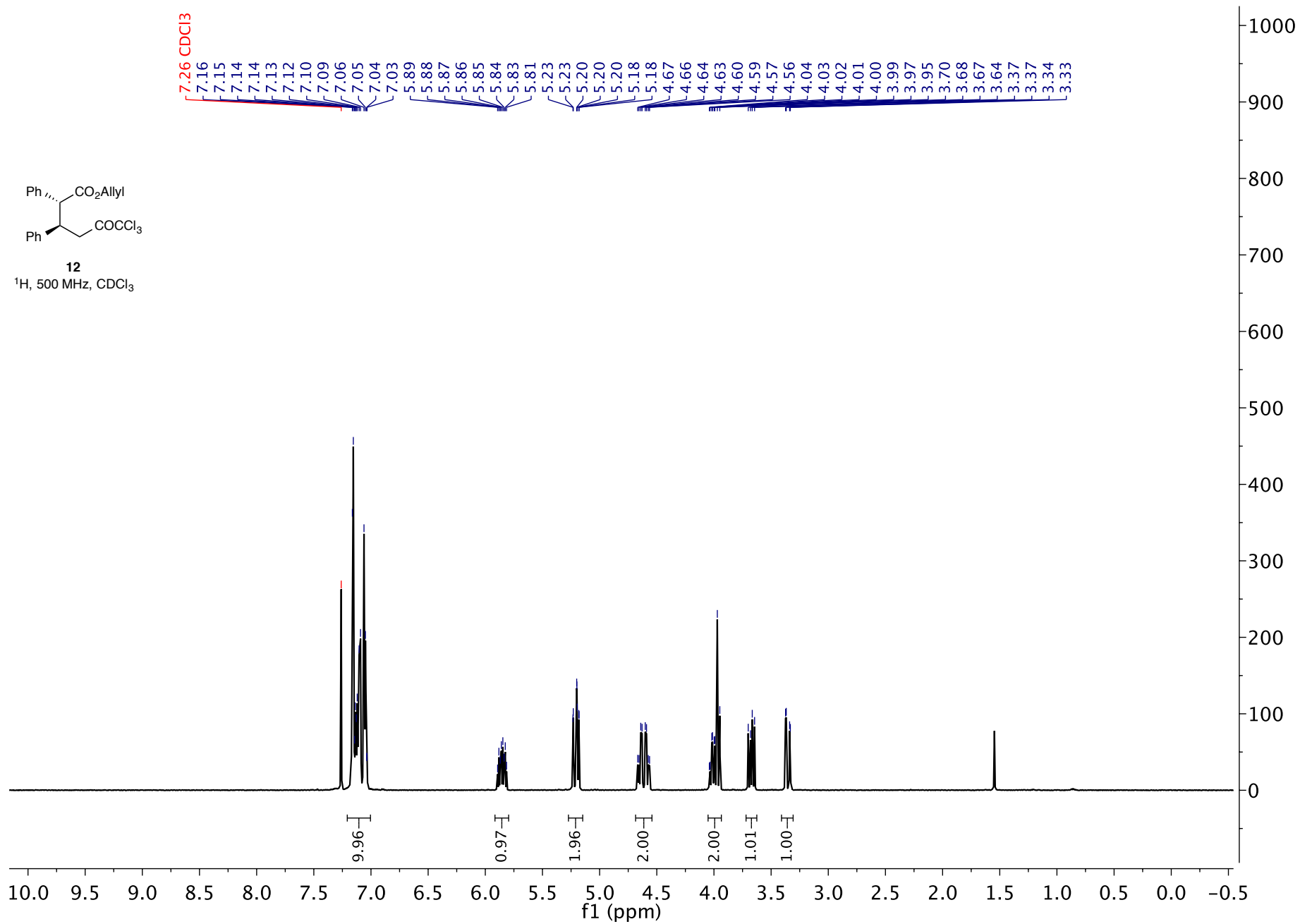


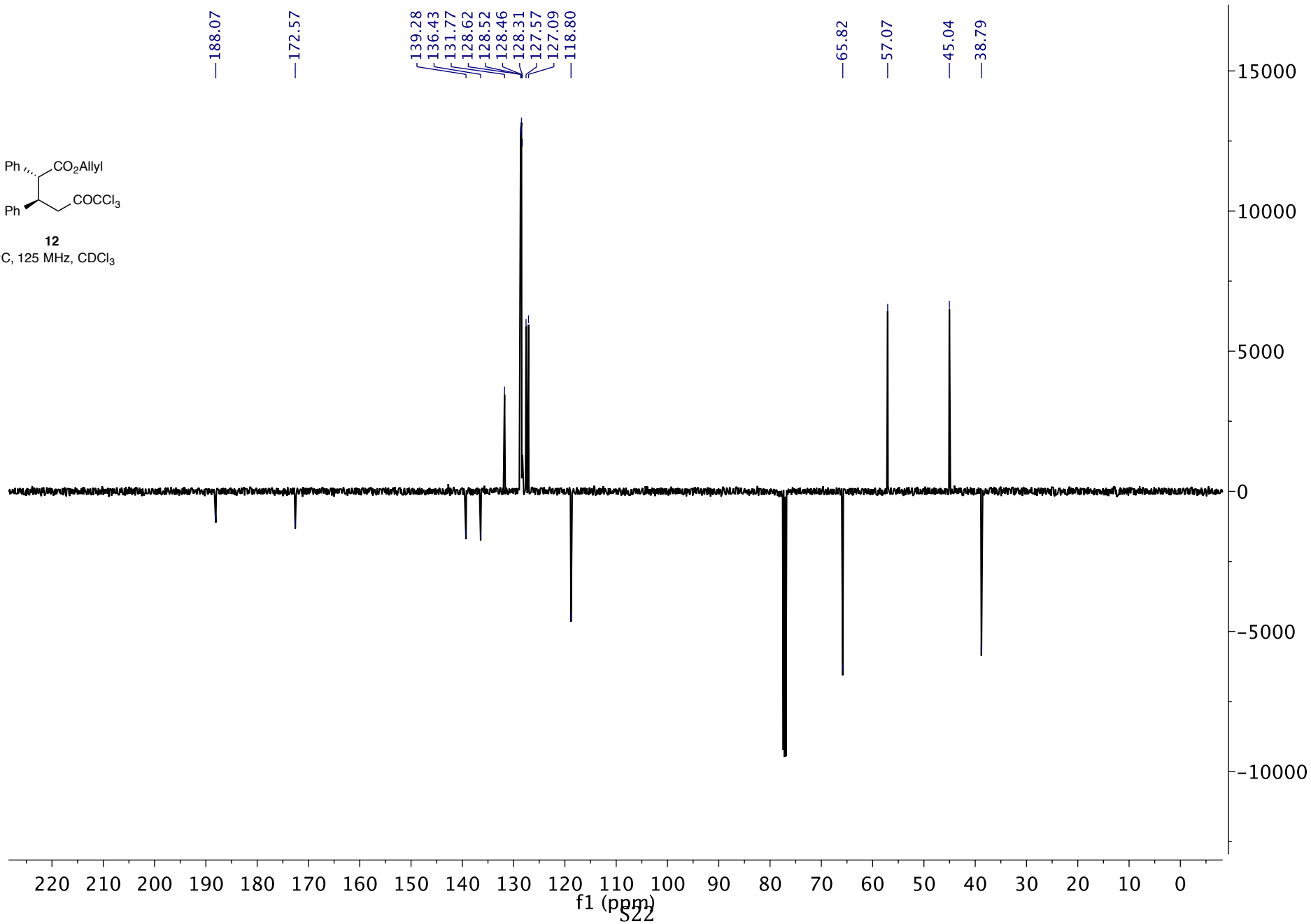
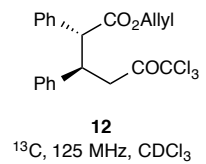
S20

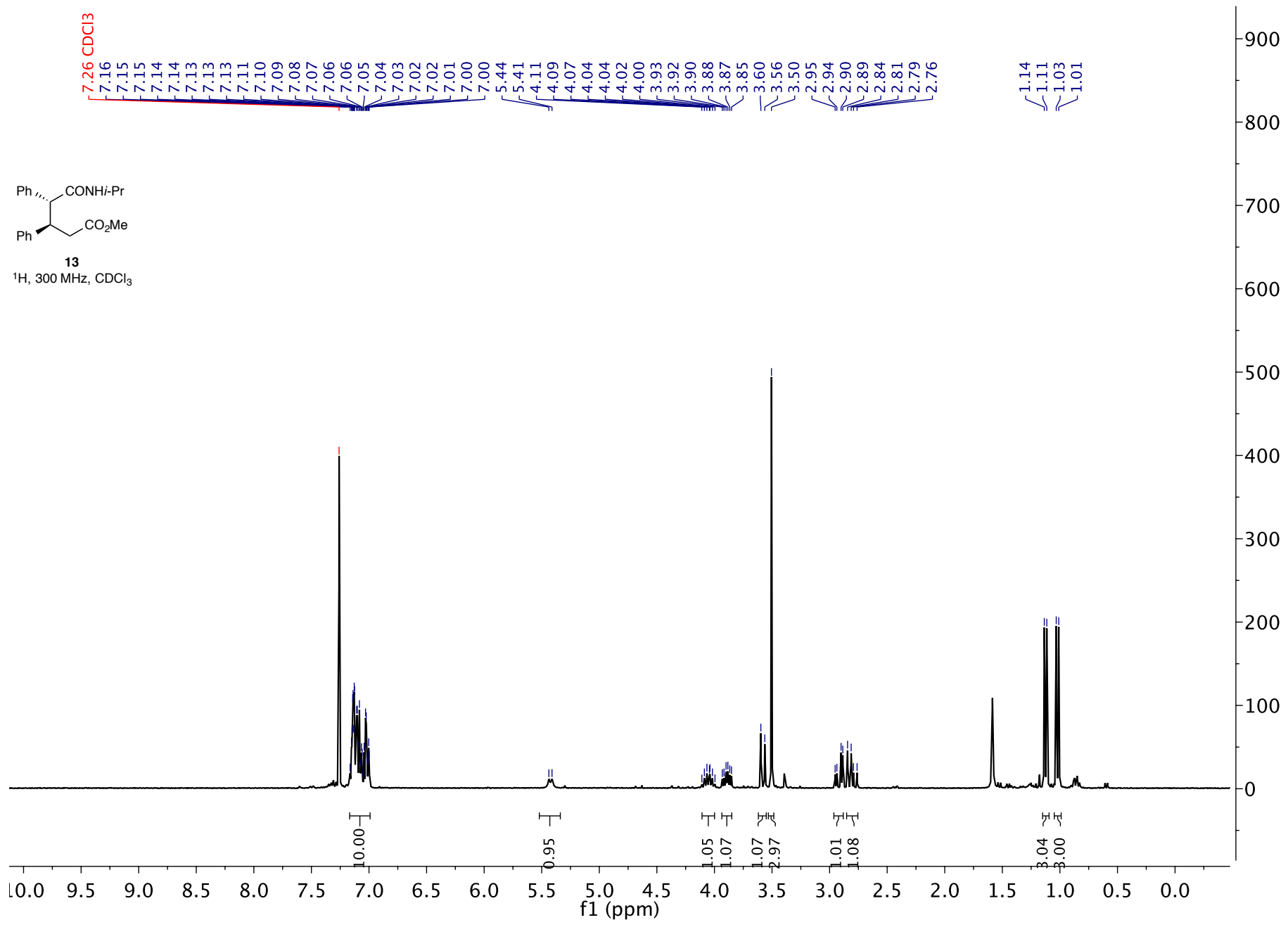
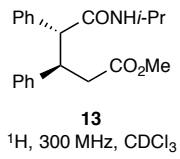


**12**

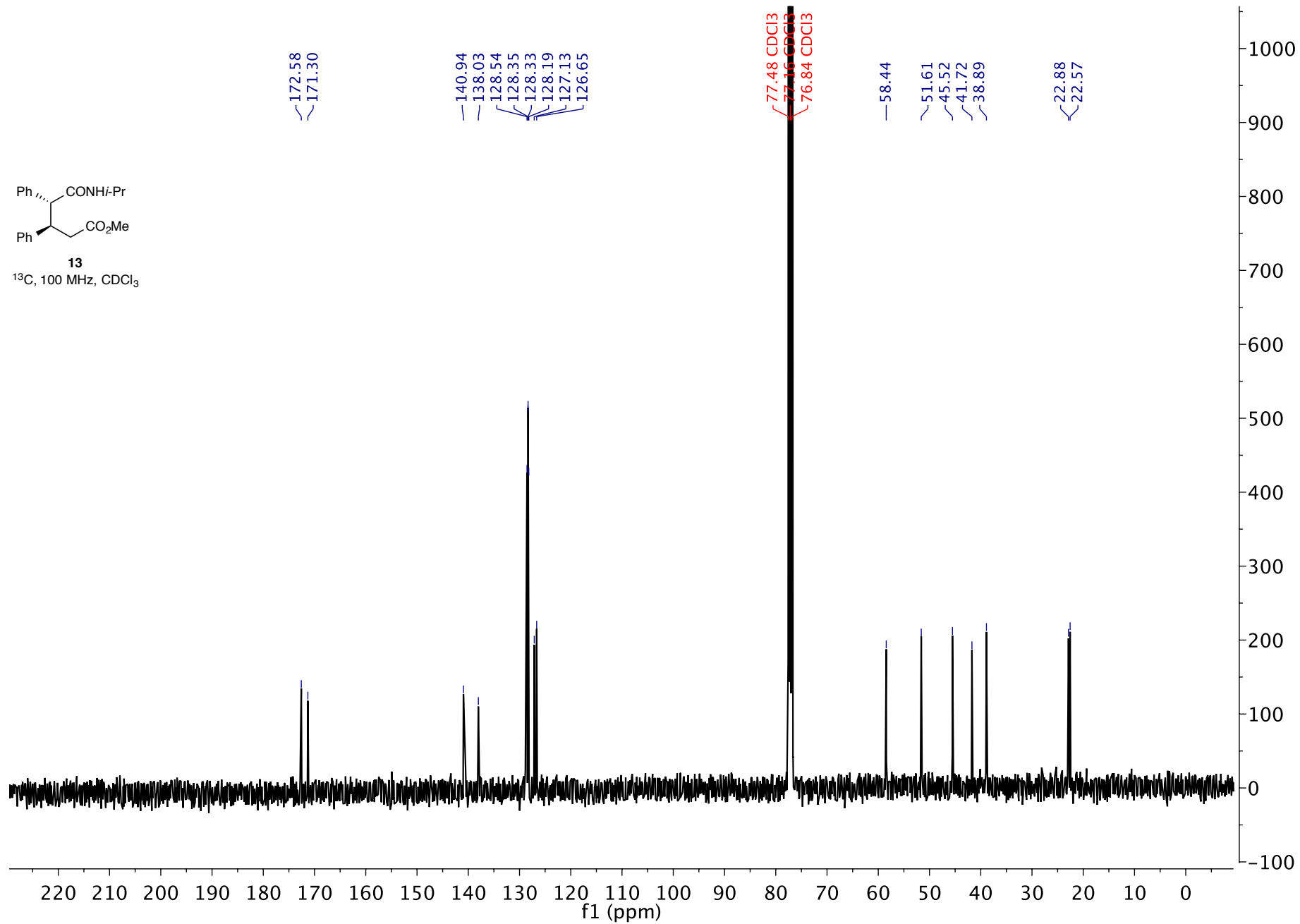
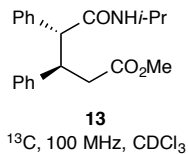
<sup>1</sup>H, 500 MHz, CDCl<sub>3</sub>



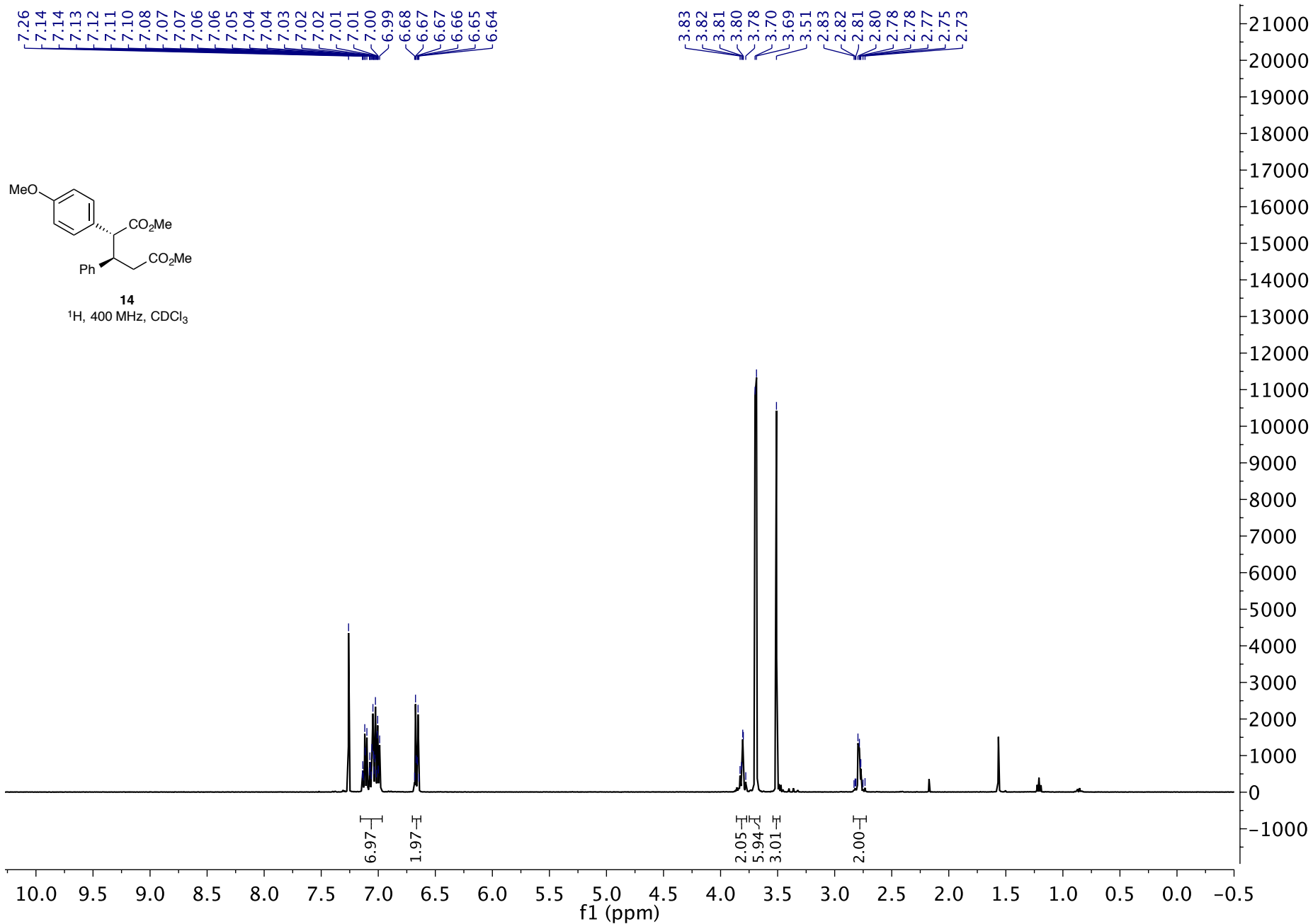


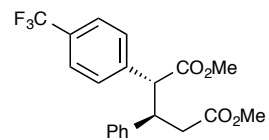


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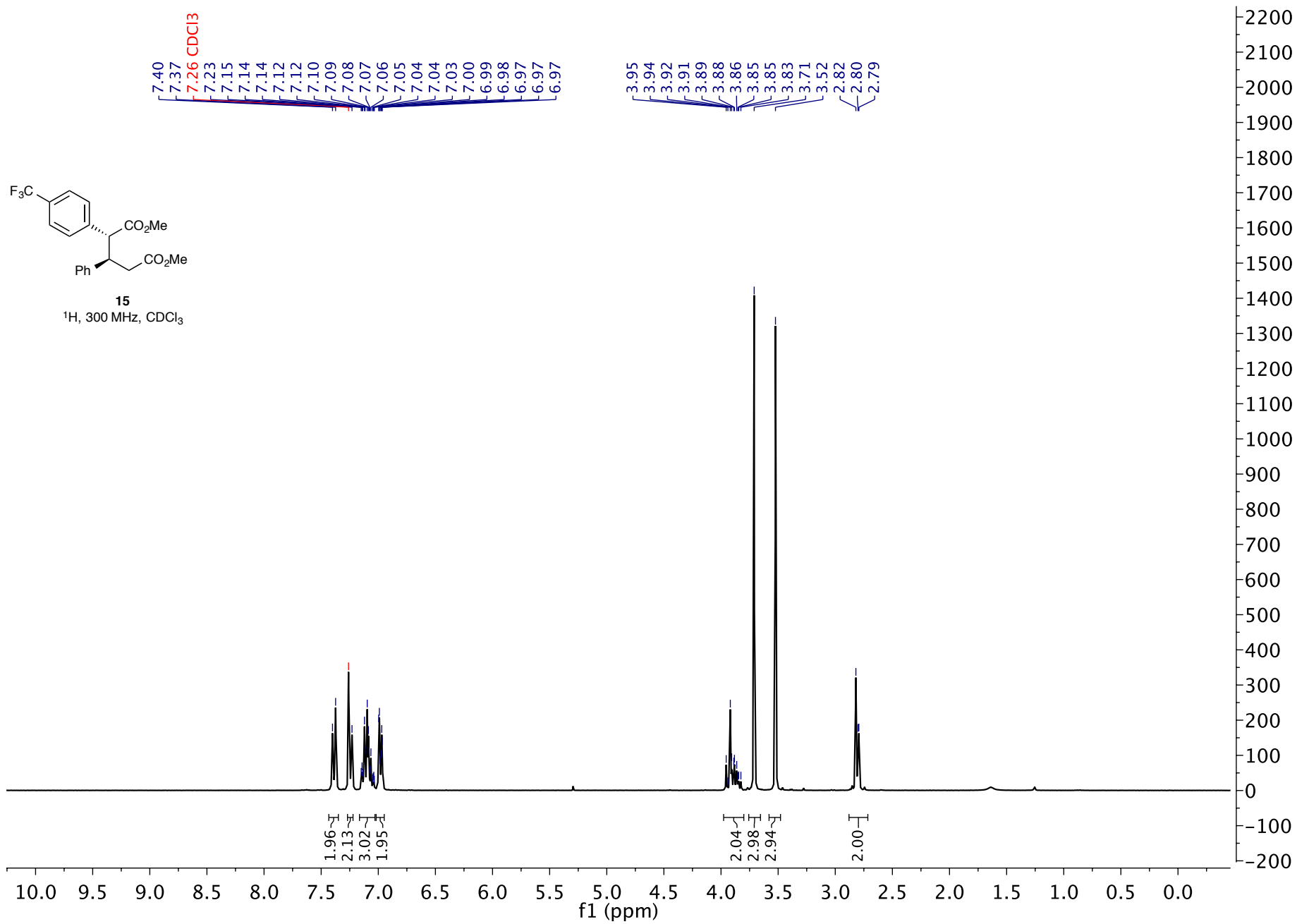


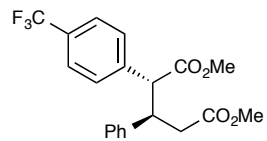




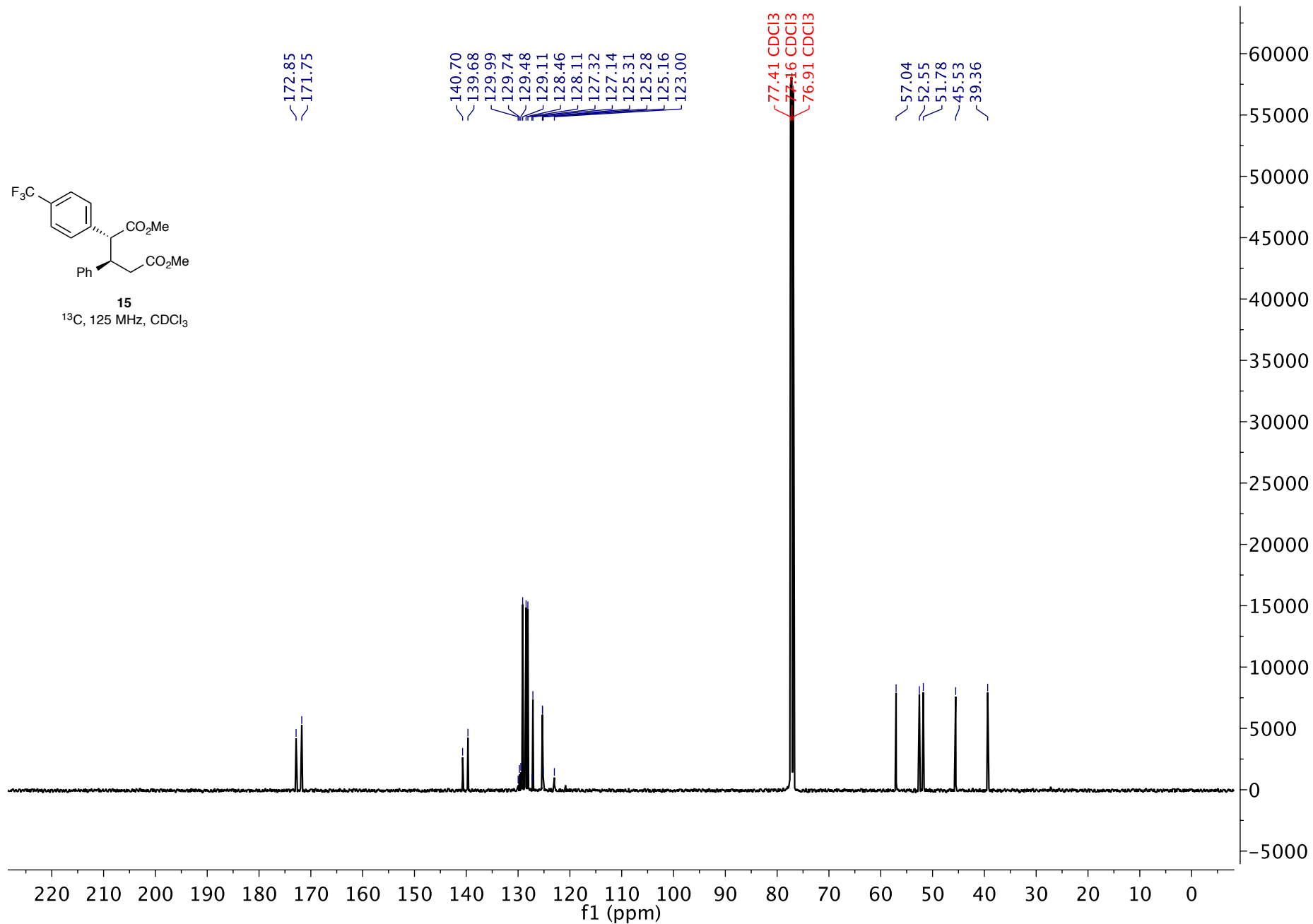


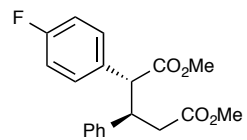
**15**  
<sup>1</sup>H, 300 MHz, CDCl<sub>3</sub>





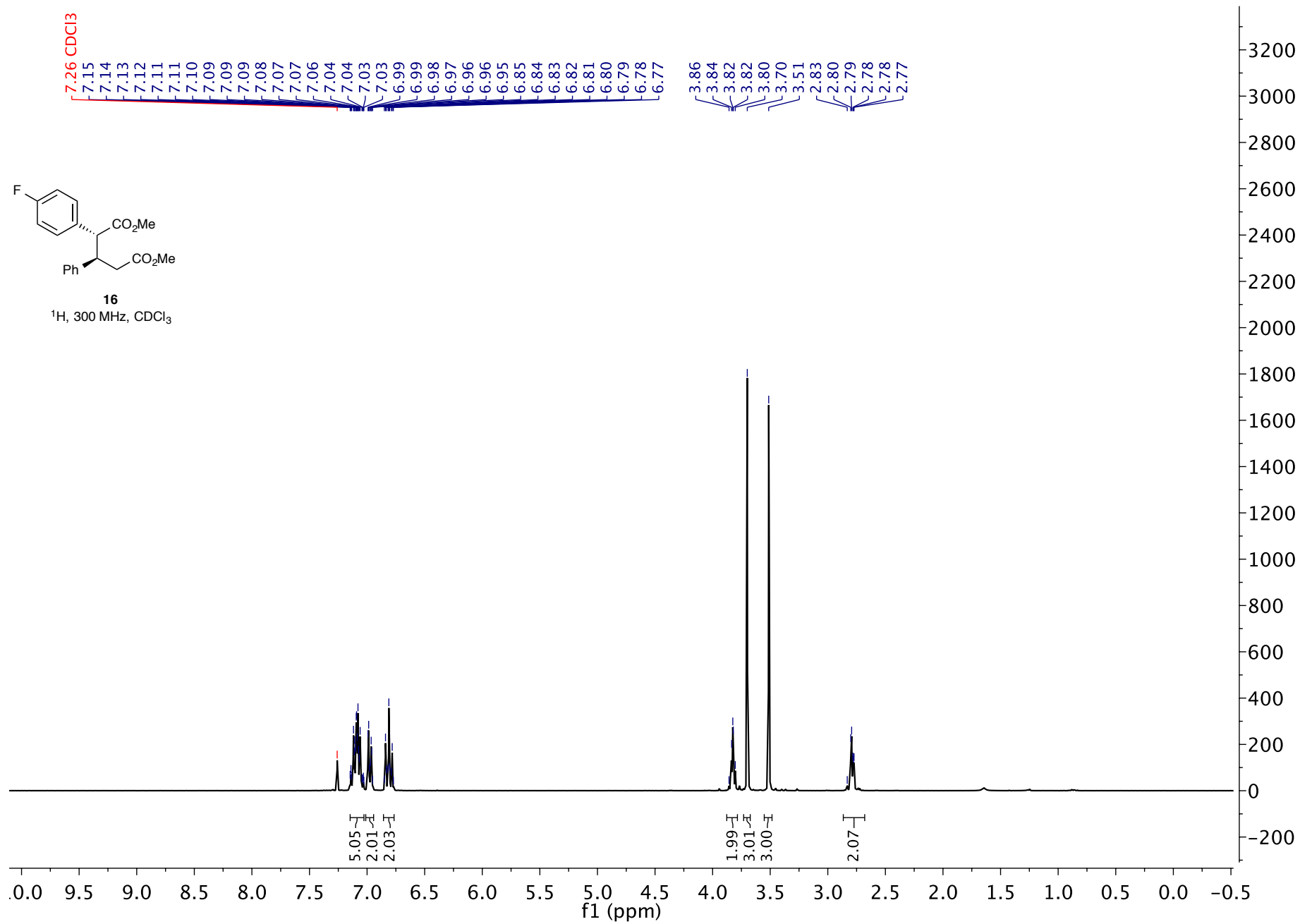
**15**  
<sup>13</sup>C, 125 MHz, CDCl<sub>3</sub>



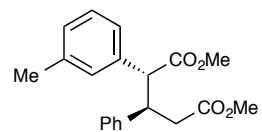


16

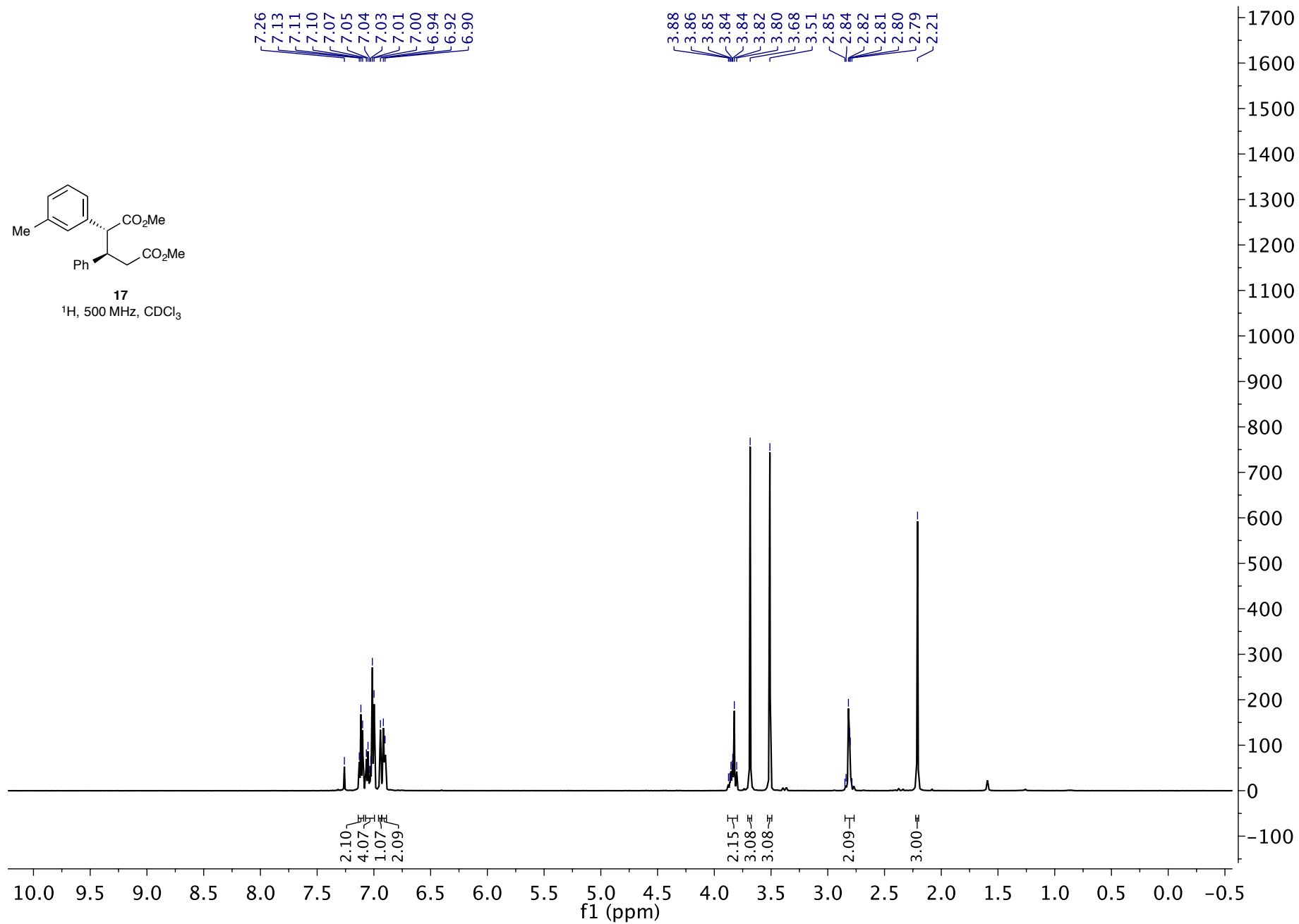
<sup>1</sup>H, 300 MHz, CDCl<sub>3</sub>

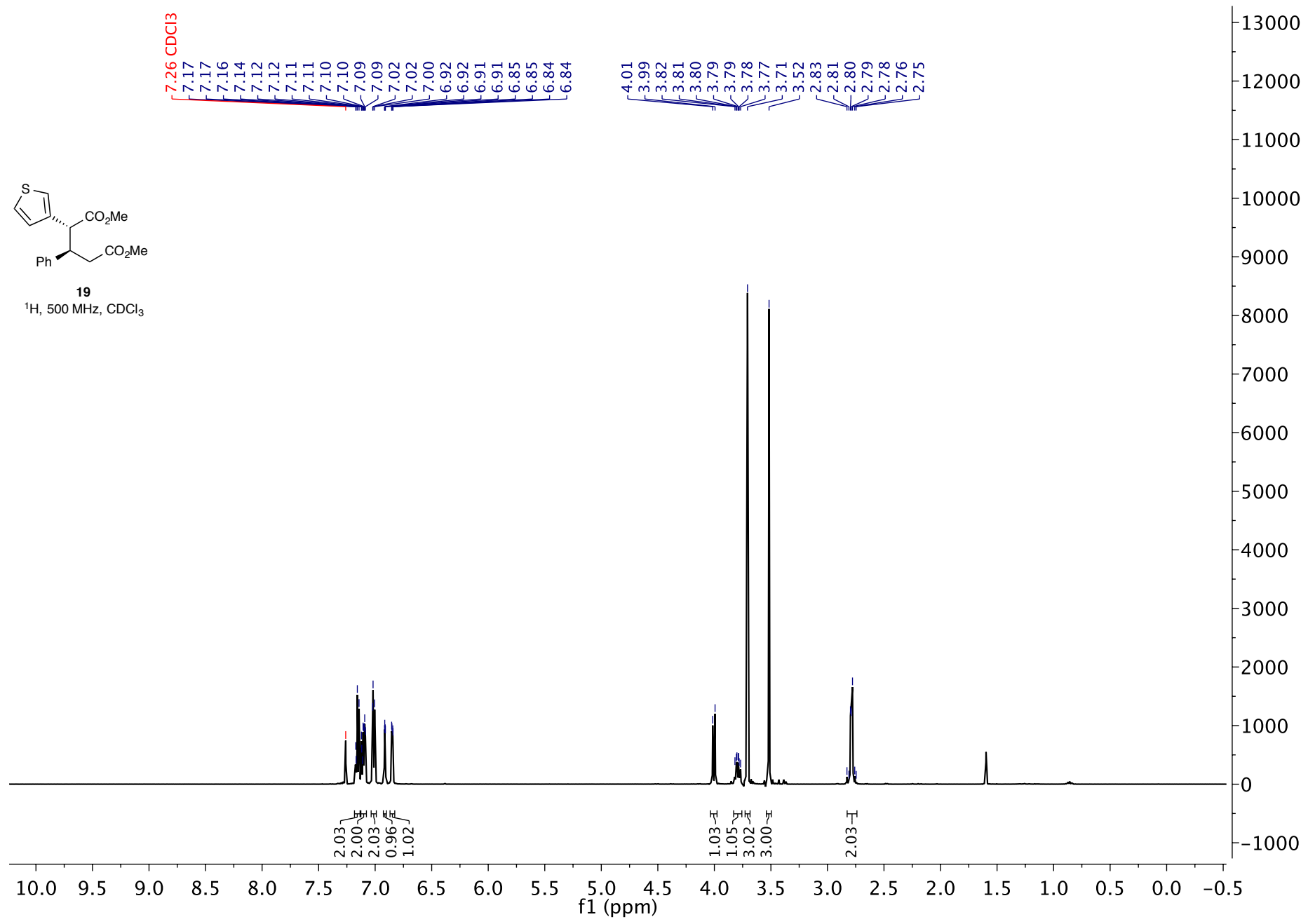
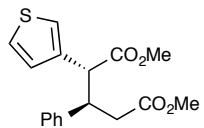


S28

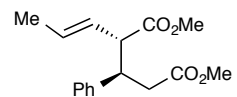


**17**  
 $^1\text{H}$ , 500 MHz,  $\text{CDCl}_3$

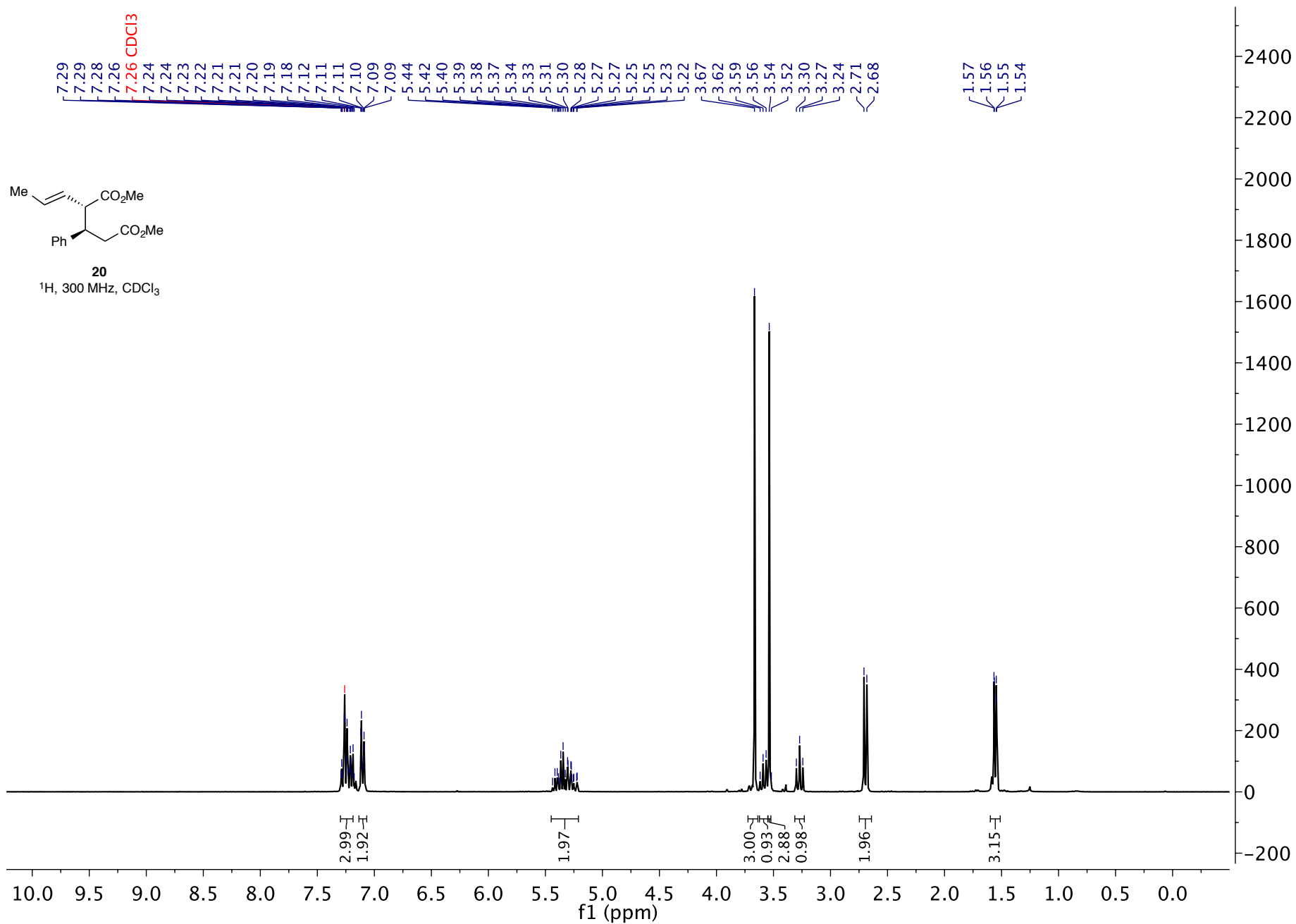


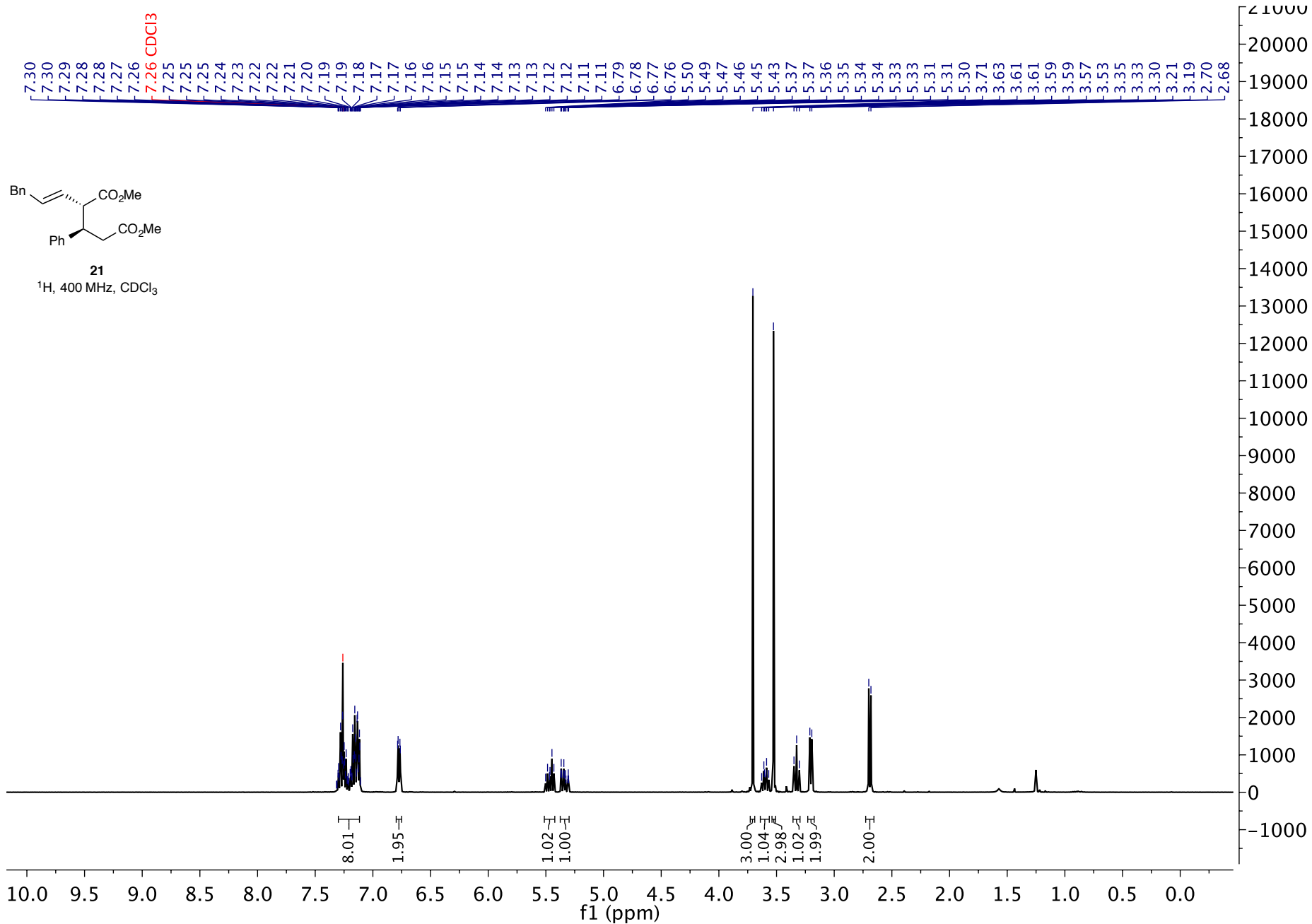


S30

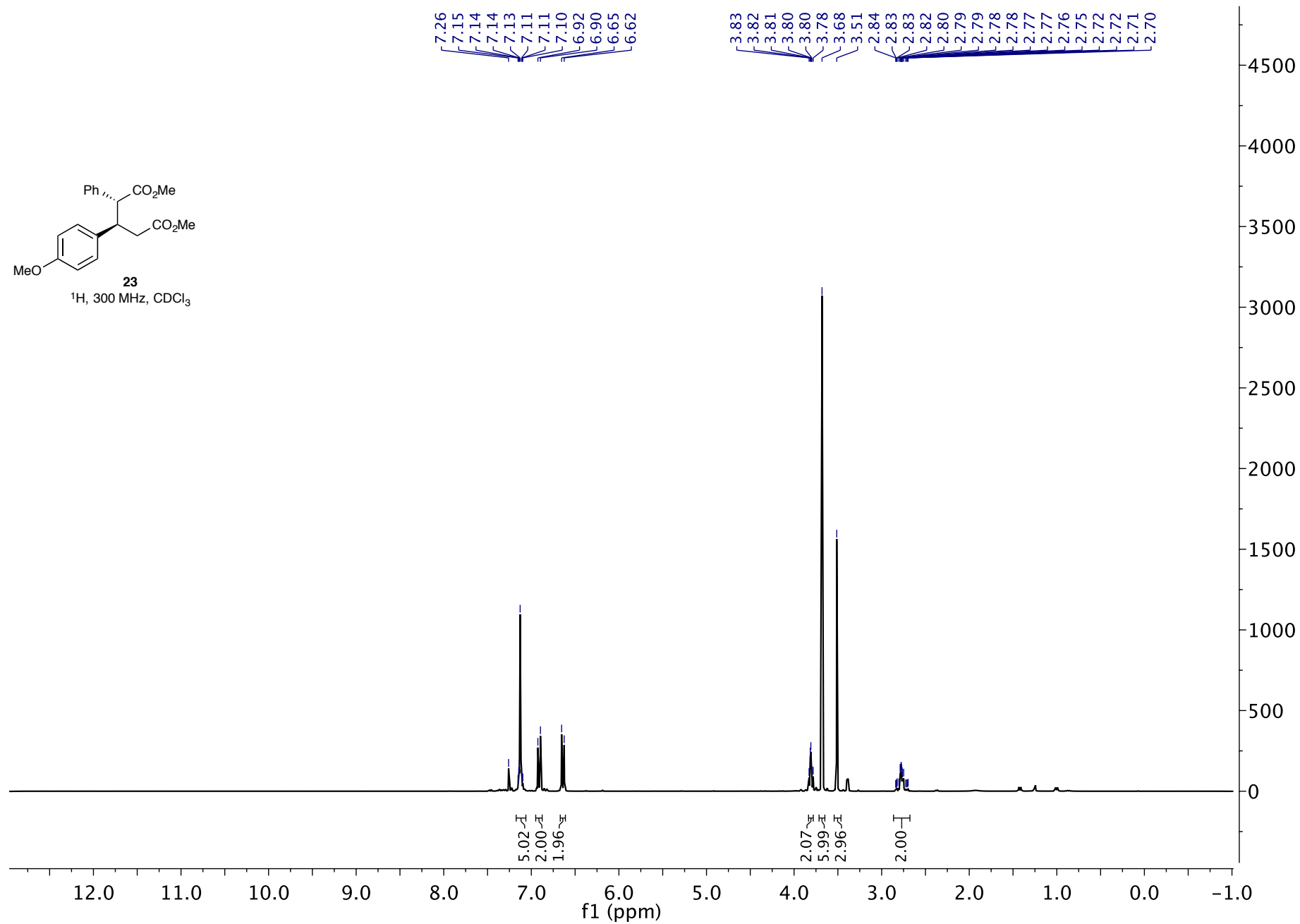
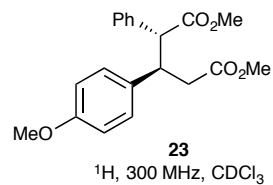


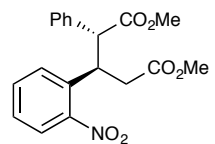
**20**  
<sup>1</sup>H, 300 MHz, CDCl<sub>3</sub>





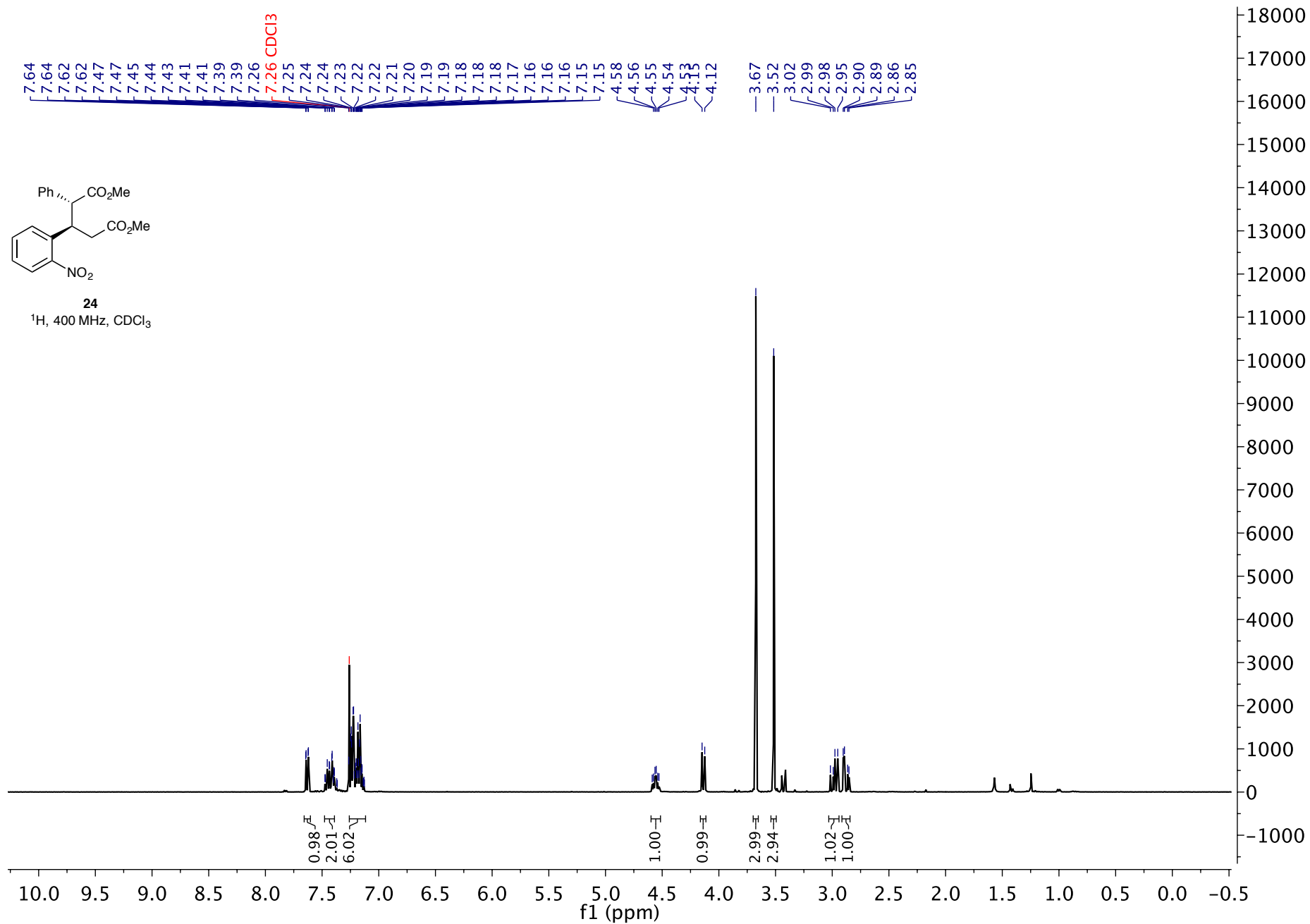




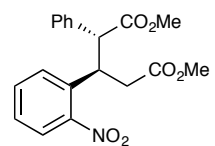


**24**

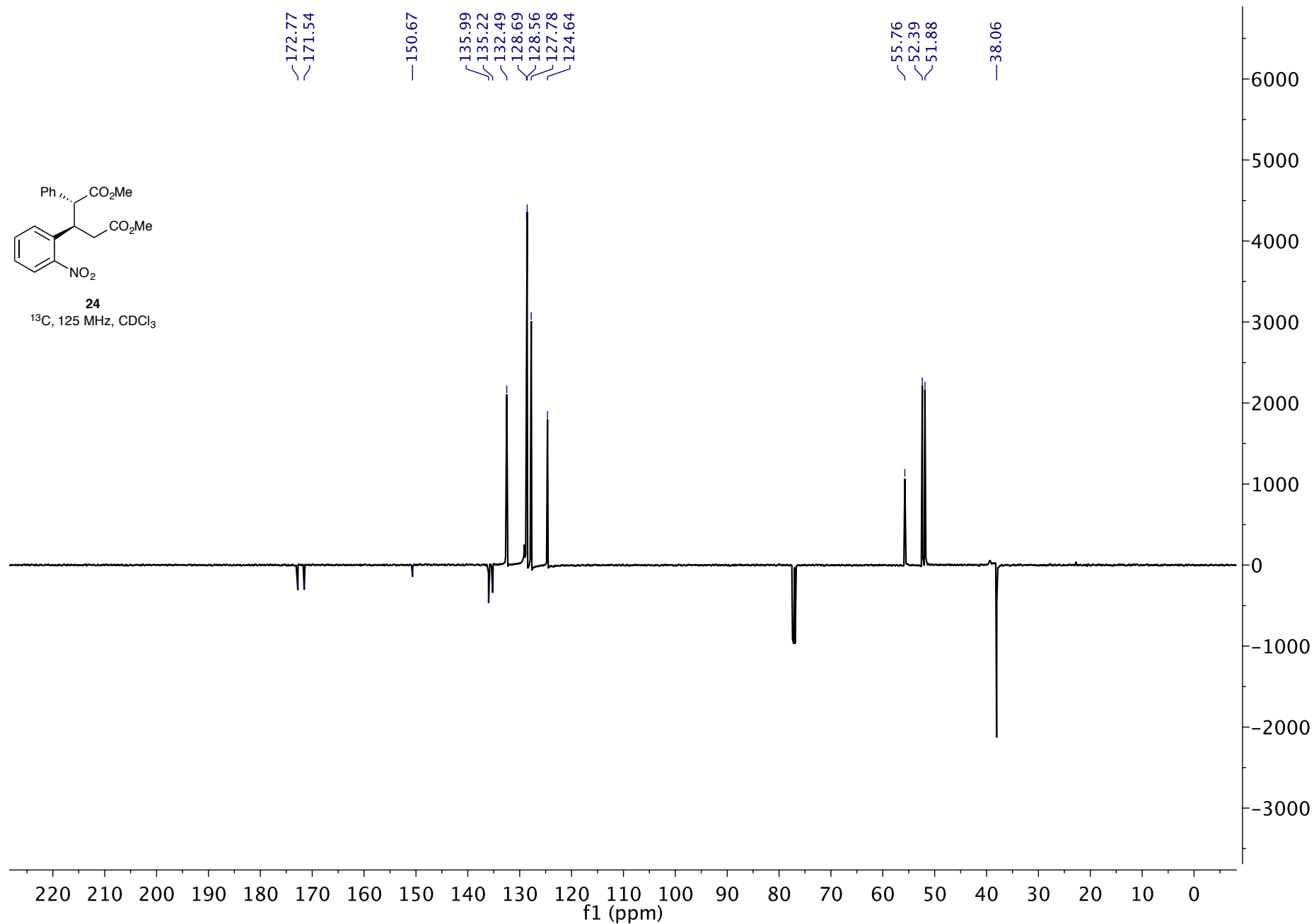
<sup>1</sup>H, 400 MHz, CDCl<sub>3</sub>

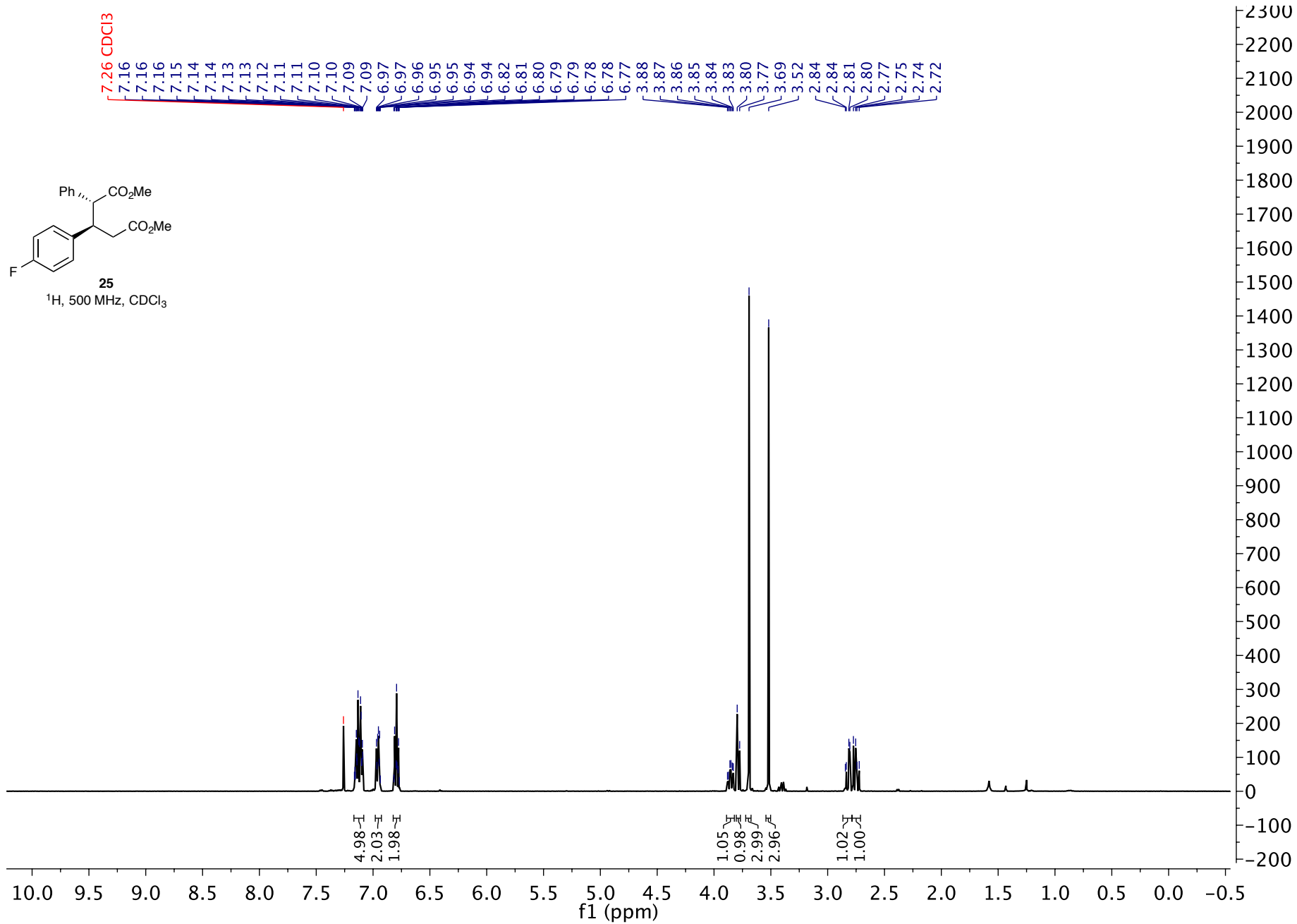


S34

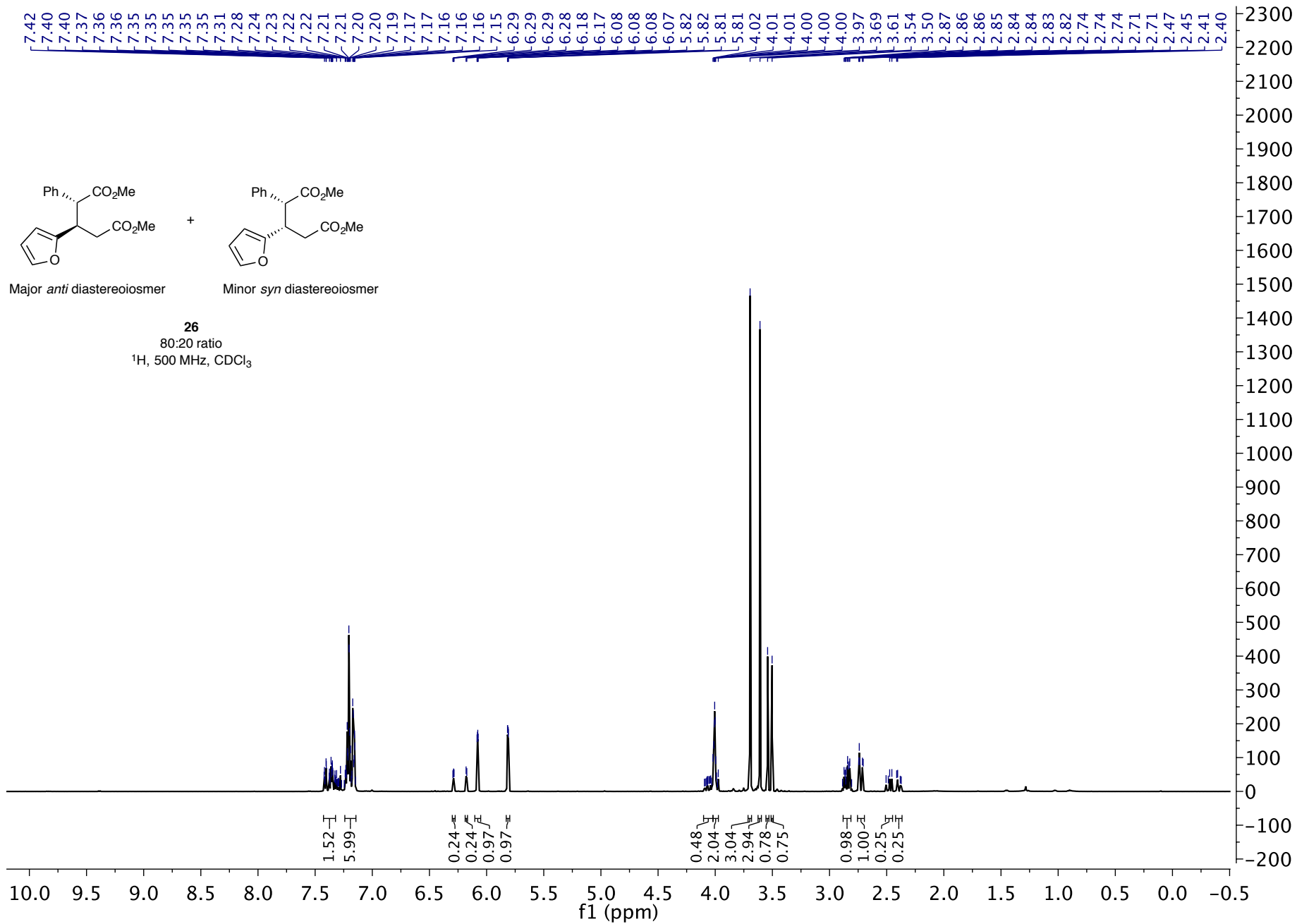


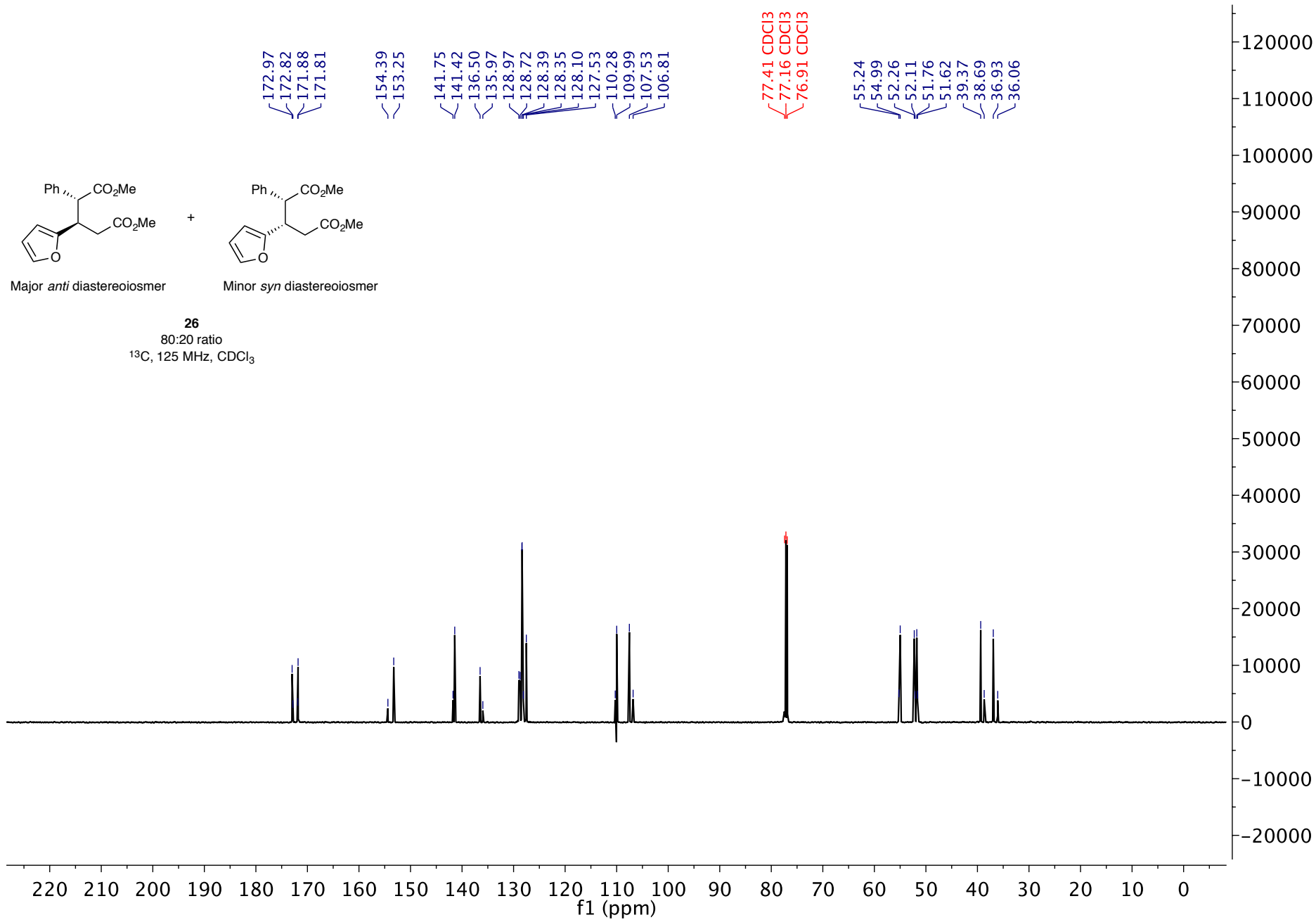
**24**  
<sup>13</sup>C, 125 MHz, CDCl<sub>3</sub>

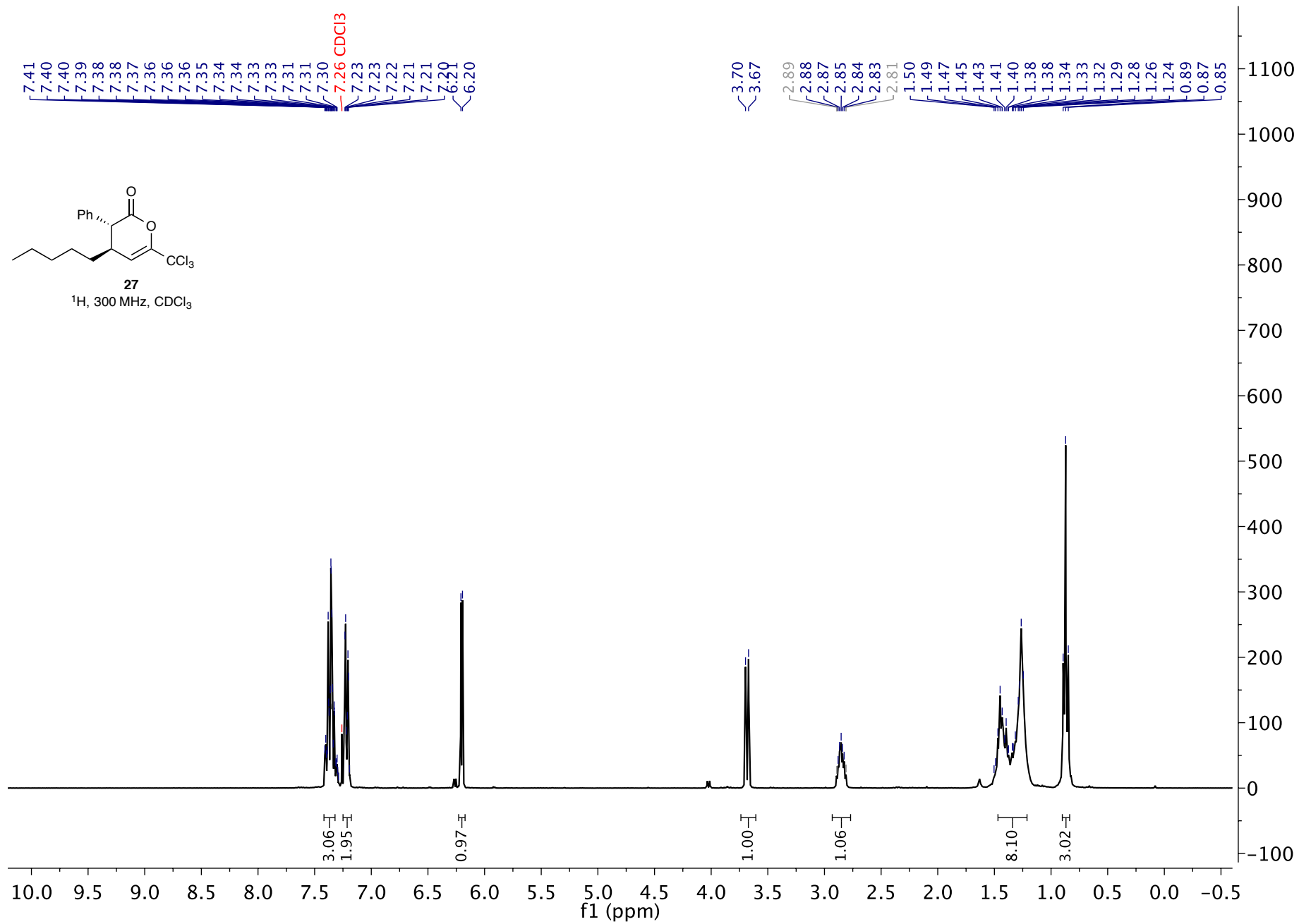
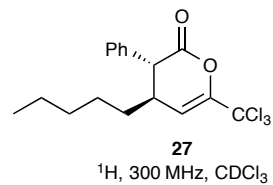


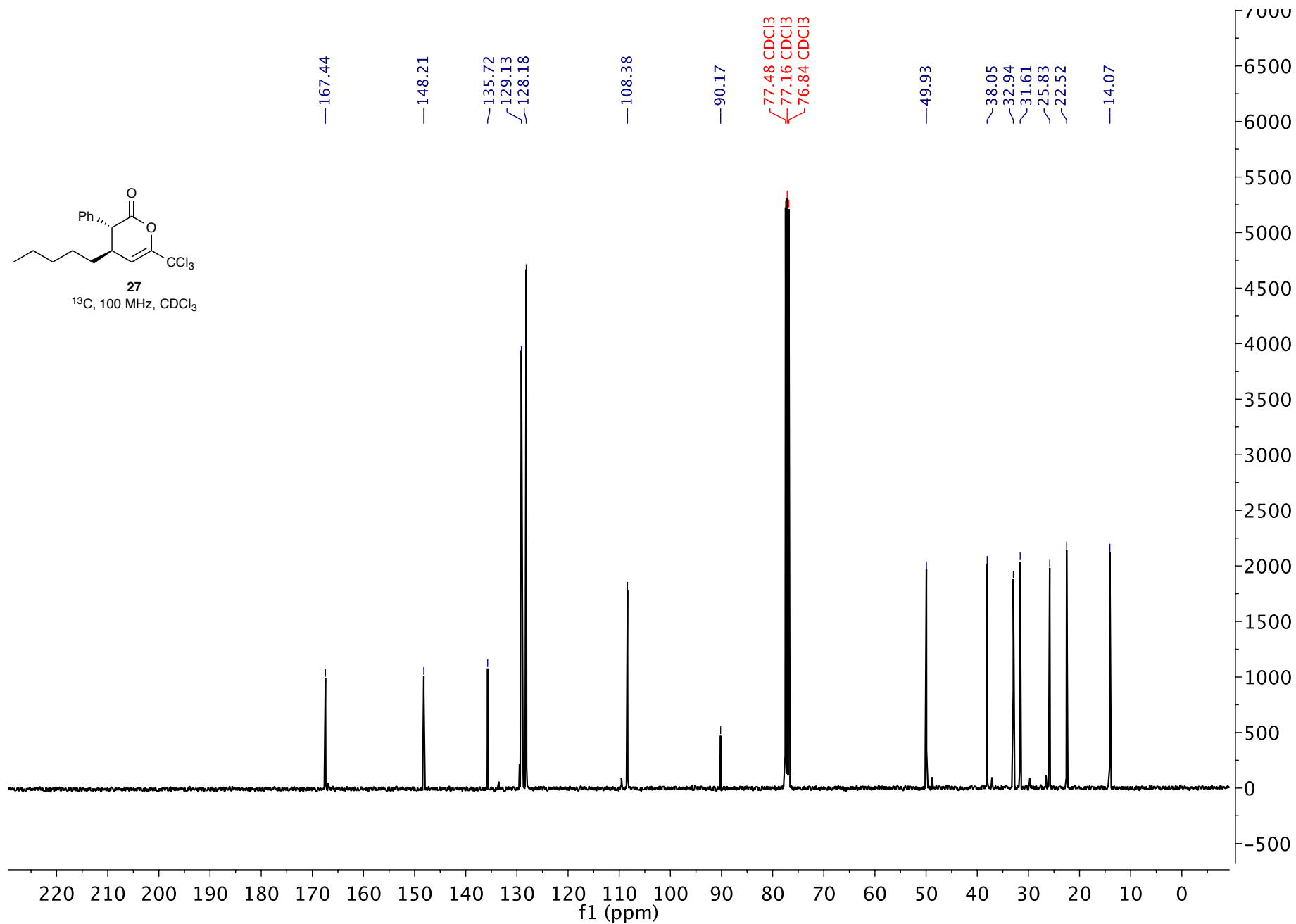
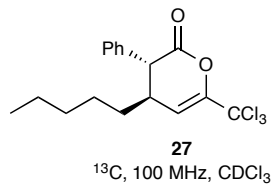


S36







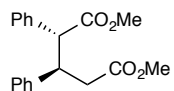




## 2.0 HPLC Data

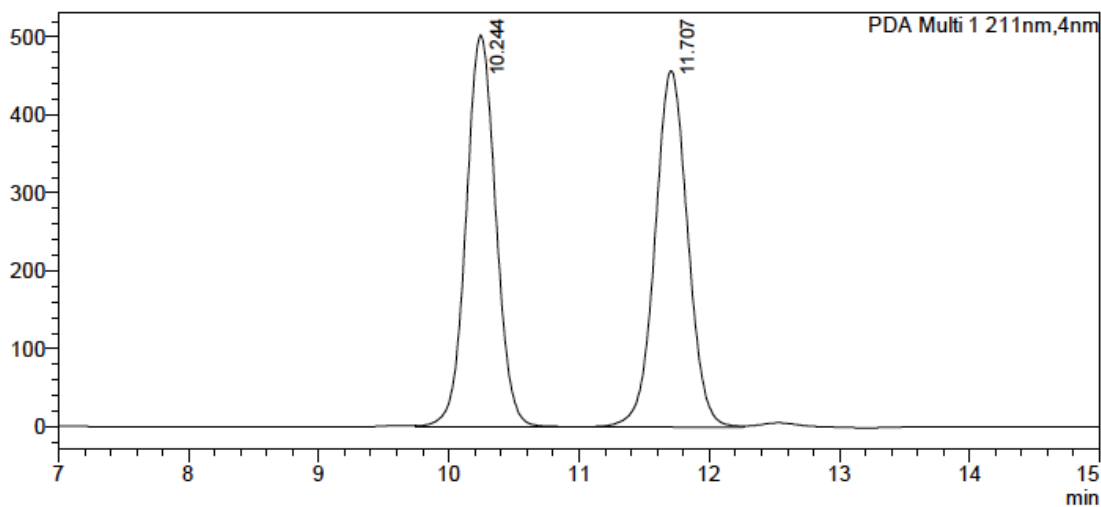
HPLC data for **10**: Chiralpak AD-H (95:5 hexane:IPA, flow rate 1mLmin<sup>-1</sup>, 211 nm, 30 °C)

$t_R(2S,3S)$ : 16.7 min,  $t_R(2R,3R)$ : 22.9 min; >99% ee;



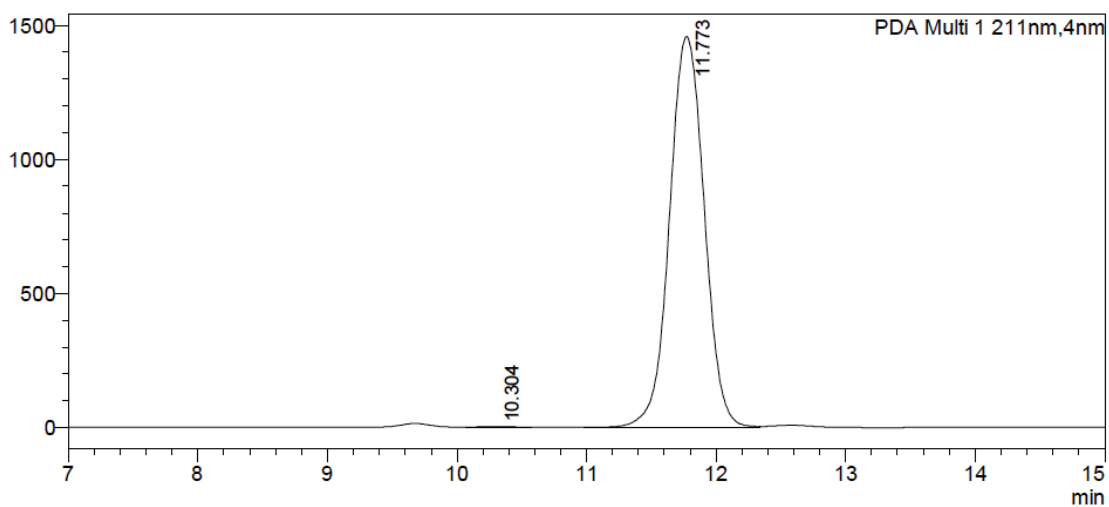
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	10.244	49.885
2	11.707	50.115
Total		100.000



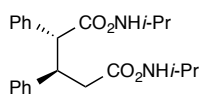
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	10.304	0.149
2	11.773	99.851
Total		100.000



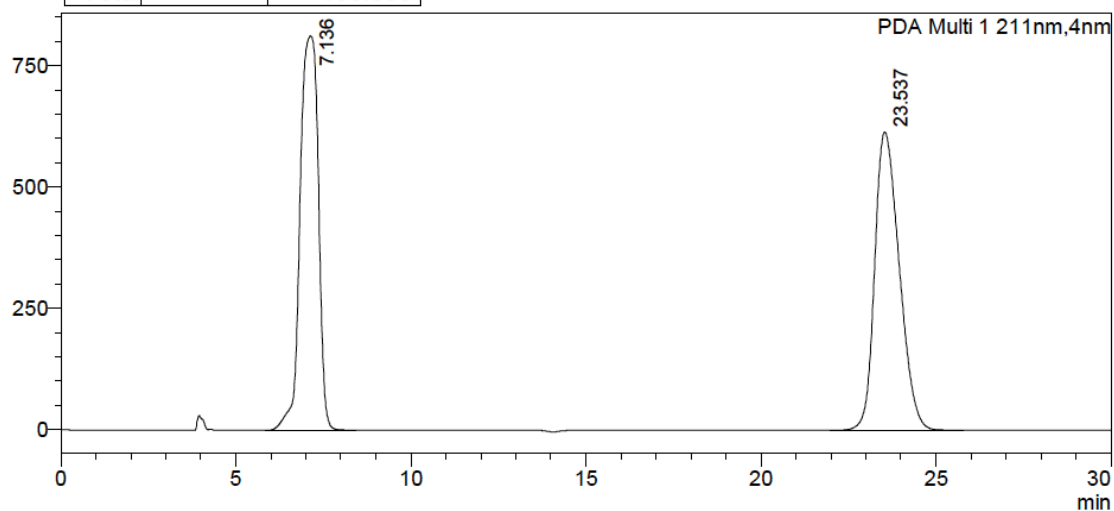
HPLC data for **11**: Chiralpak AD-H (95:5 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C)

t<sub>R</sub>(2*S*,3*S*): 7.1 min, t<sub>R</sub>(2*R*,3*R*): 23.5 min, >99% ee;



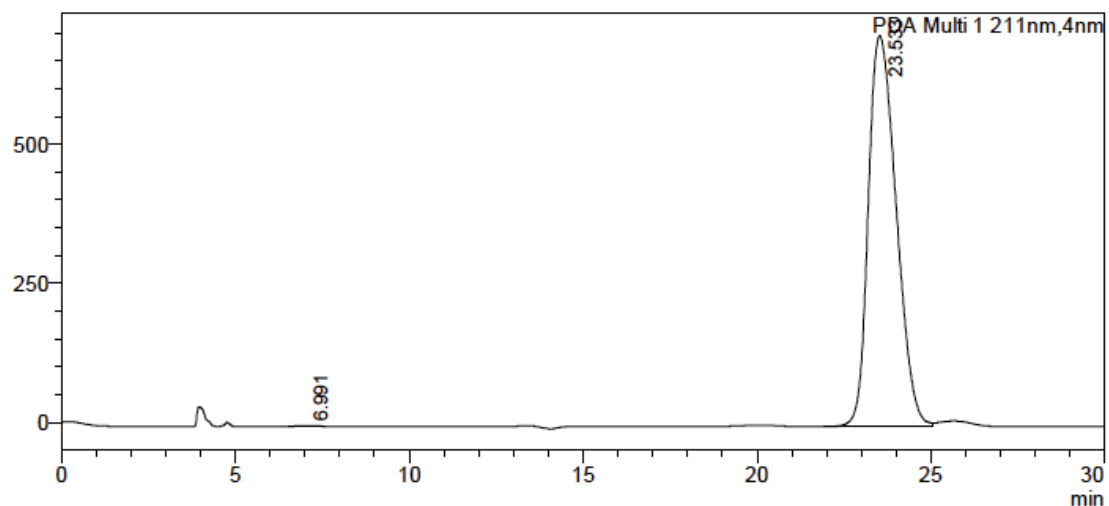
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	7.136	49.655
2	23.537	50.345
Total		100.000

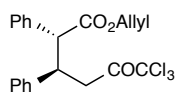


PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	6.991	0.099
2	23.533	99.901
Total		100.000

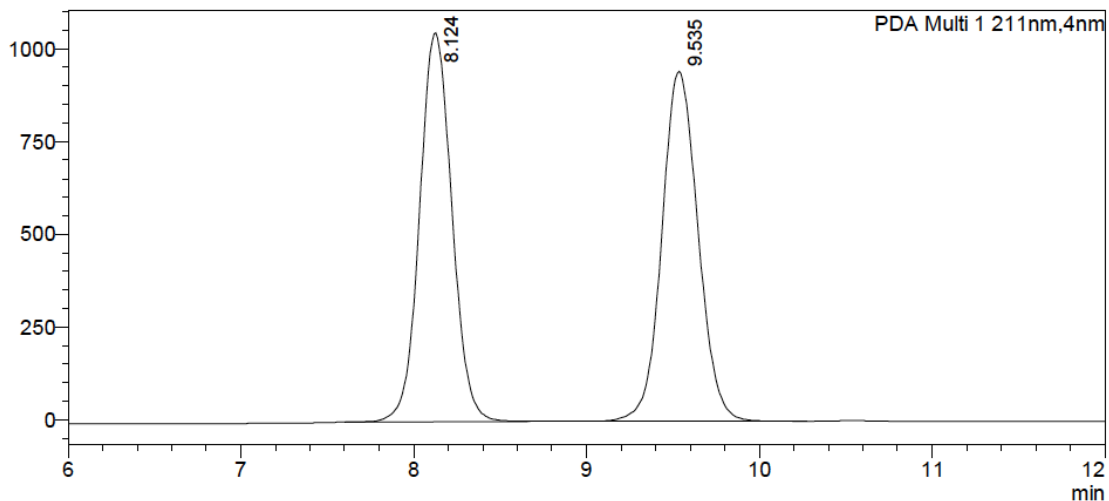


HPLC data for **12**: Chiral HPLC analysis, Chiralpak AD-H (95:5 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C) t<sub>R</sub>(2*S*,3*S*): 8.1 min, t<sub>R</sub>(2*R*,3*R*): 9.5 min, 99% ee;



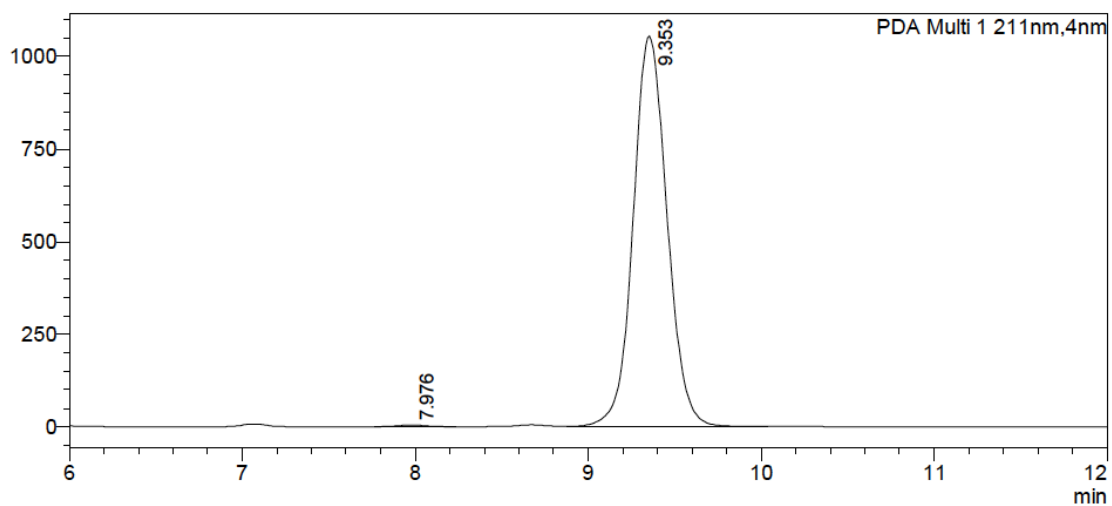
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	8.124	49.736
2	9.535	50.264
Total		100.000



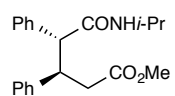
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	7.976	0.338
2	9.353	99.662
Total		100.000



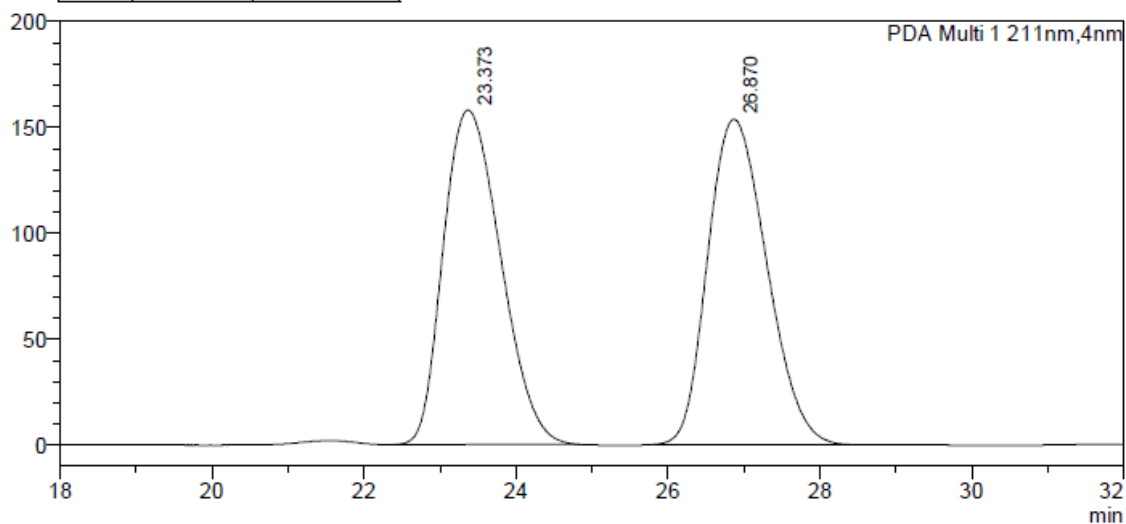
HPLC Data for **13**: Chiralpak AD-H (95:5 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C)

$t_R(2S,3S)$ : 23.6 min,  $t_R(3R,4R)$ : 26.7 min, 99% ee;



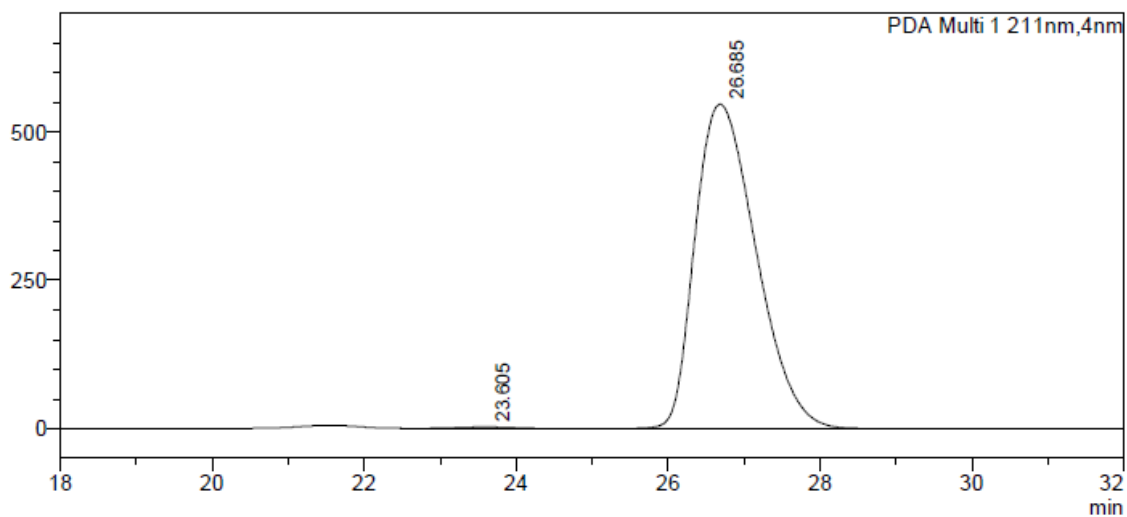
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	23.373	50.064
2	26.870	49.936
Total		100.000



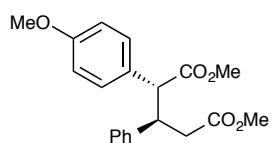
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	23.605	0.387
2	26.685	99.613
Total		100.000



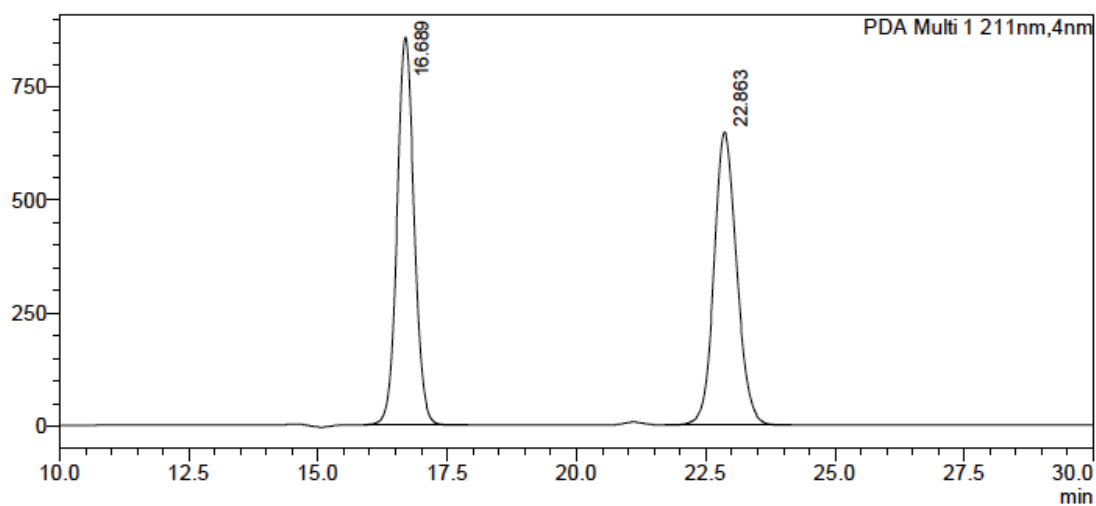
HPLC data for **14**: Chiralpak AD-H (95:5 hexane:IPA, flow rate 1mLmin<sup>-1</sup>, 211 nm, 30 °C)

$t_R(2S,3S)$ : 16.7 min,  $t_R(2R,3R)$ : 22.9 min; >99% ee;



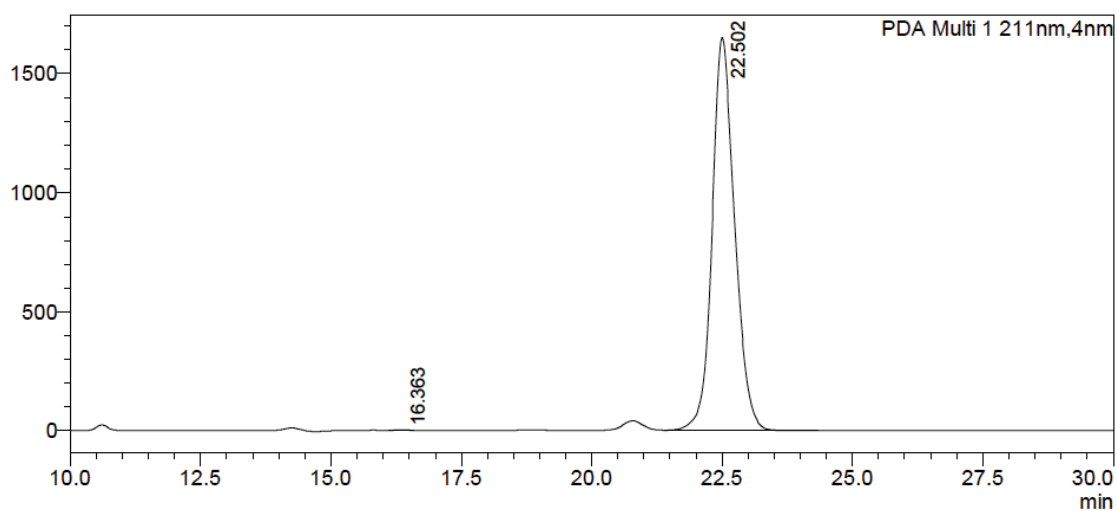
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	16.689	49.829
2	22.863	50.171
Total		100.000



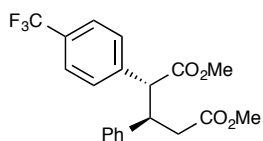
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	16.363	0.035
2	22.502	99.965
Total		100.000



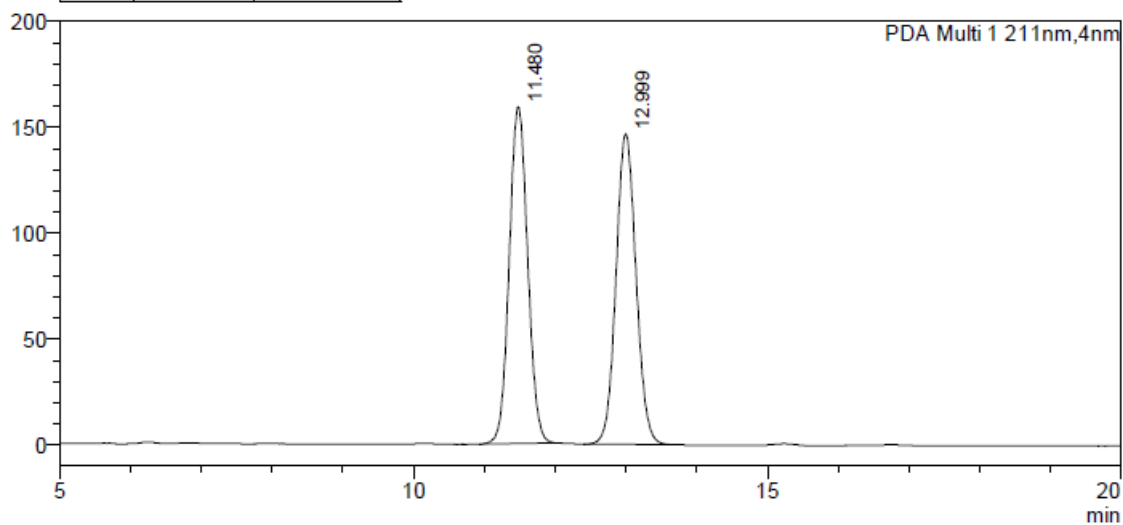
HPLC Data for **15**: Chiralpak AD-H (95:5 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C)

$t_R(2S,3S)$ : 11.4 min,  $t_R(2R,3R)$ : 12.9 min, 91% ee;



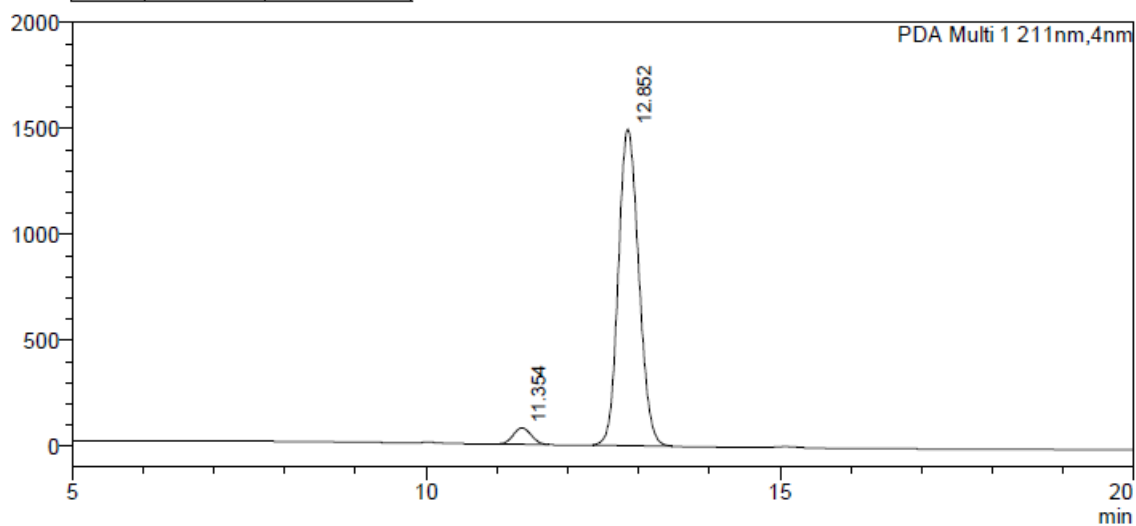
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	11.480	50.045
2	12.999	49.955
Total		100.000

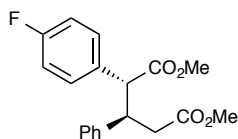


PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	11.354	4.343
2	12.852	95.657
Total		100.000

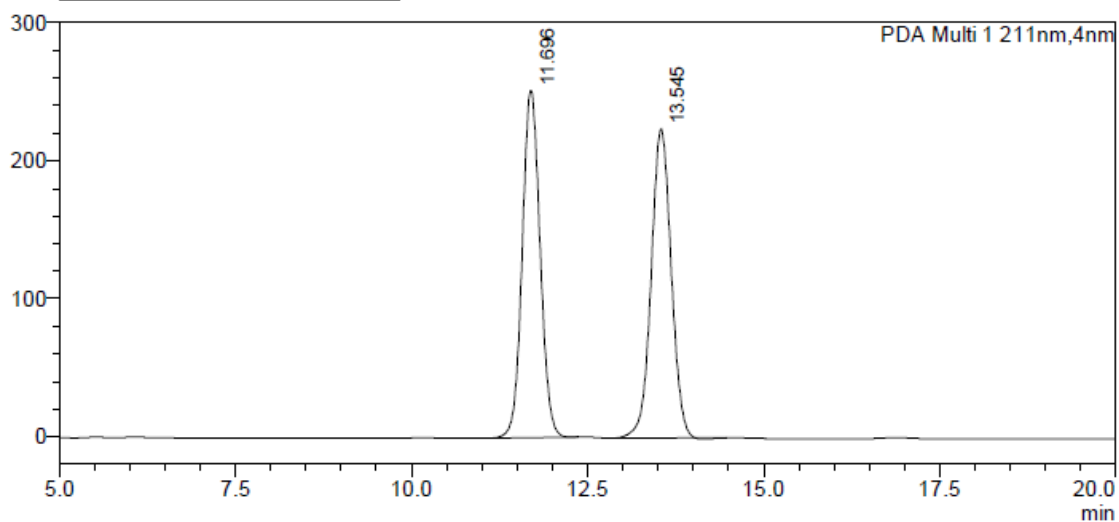


HPLC Data for **16**: Chiralpak AD-H (95:5 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C)  $t_R(2S,3S)$ : 11.7 min,  $t_R(2R,3R)$ : 13.5 min, 99% ee;



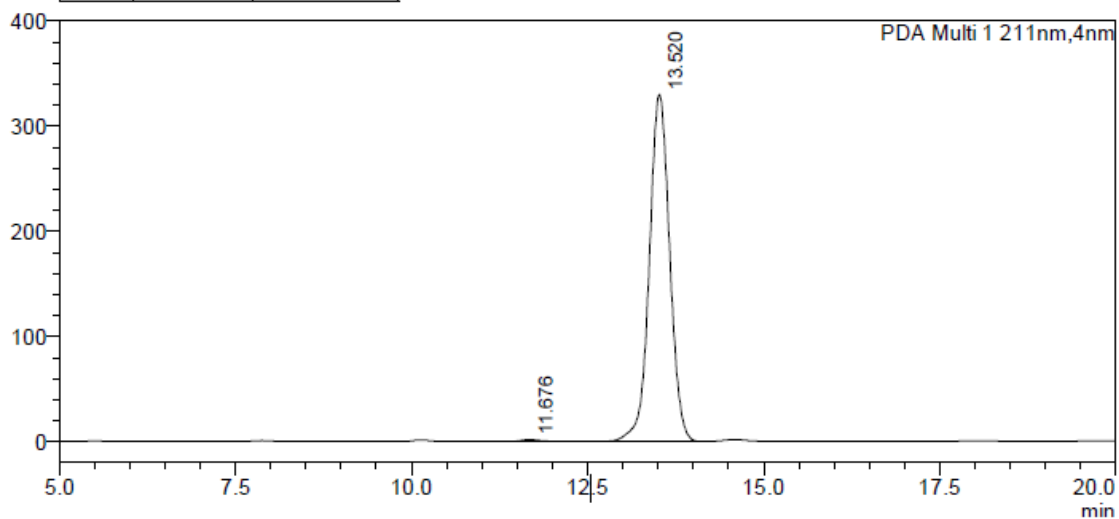
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	11.696	50.072
2	13.545	49.928
Total		100.000



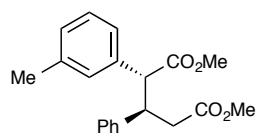
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	11.676	0.479
2	13.520	99.521
Total		100.000



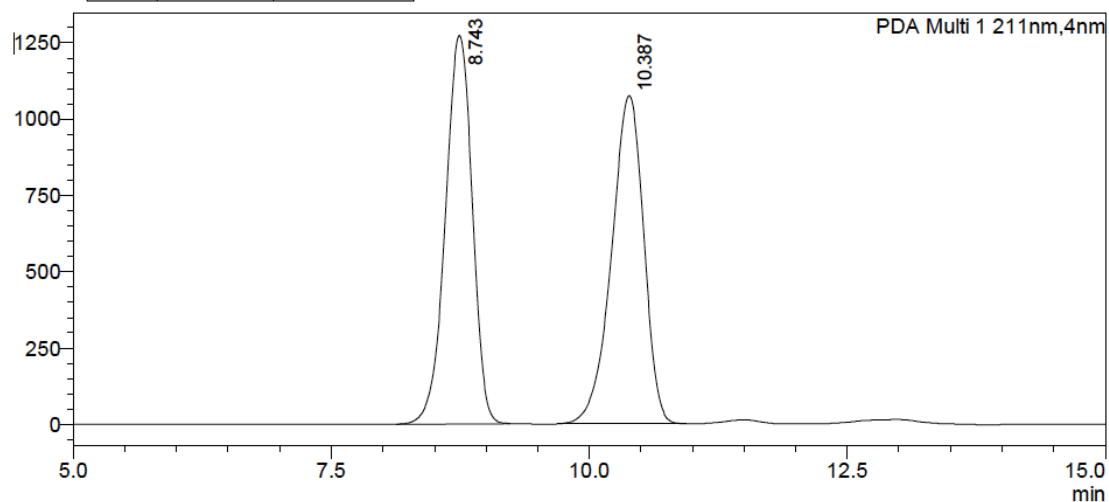
HPLC data for **17**: Chiralpak AD-H (95:5 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C)

t<sub>R</sub>(2*S*, 3*S*): 8.7 min, t<sub>R</sub> (2*R*, 3*R*): 10.4 min, 99% ee;



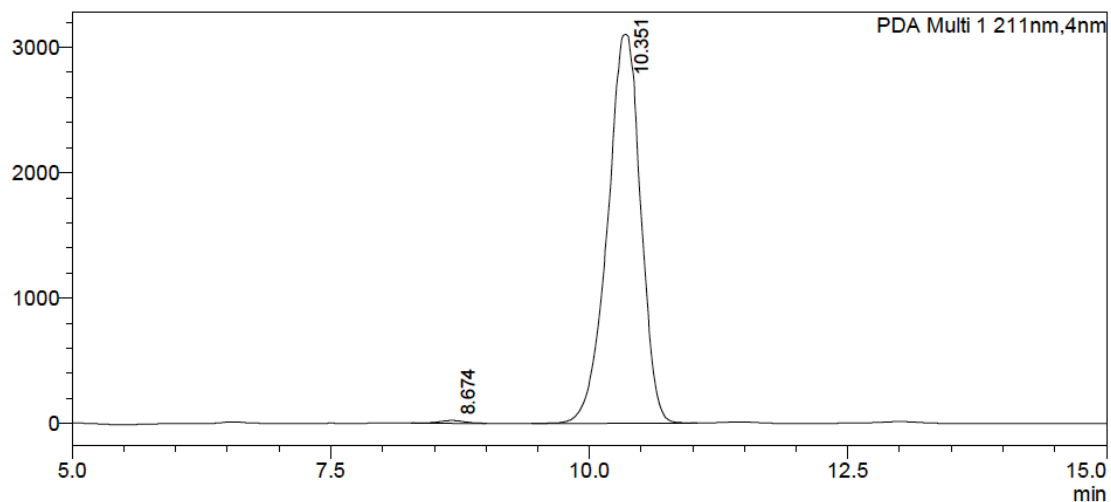
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	8.743	49.705
2	10.387	50.295
Total		100.000



PDA Ch1 211nm

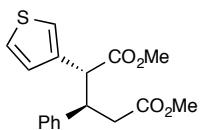
Peak#	Ret. Time	Area%
1	8.674	0.552
2	10.351	99.448
Total		100.000





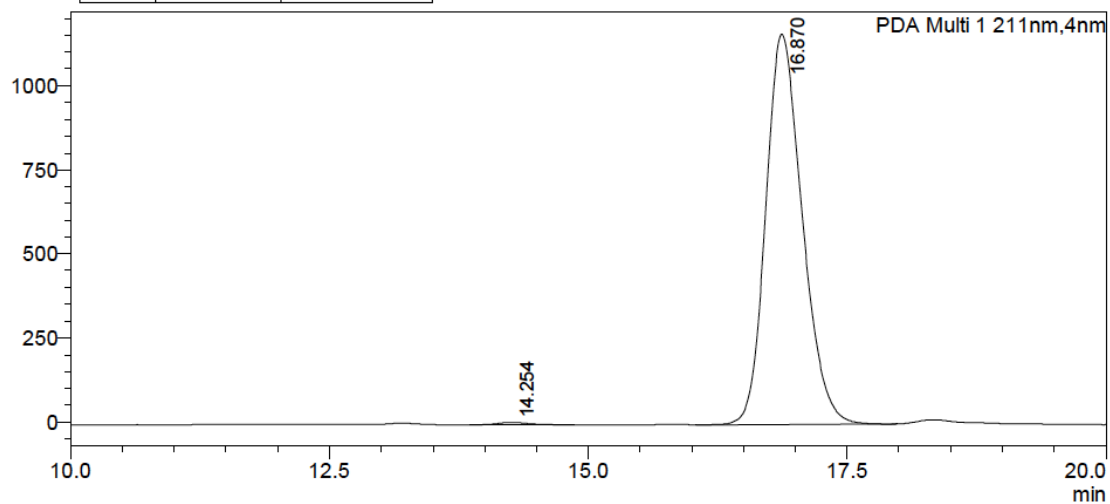
HPLC data for **19**: Chiralpak AD-H (95:5 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C)

t<sub>R</sub>(2*R*, 3*R*): 16.9 min, t<sub>R</sub> (2*S*, 3*S*): 18.3 min, >99% ee;



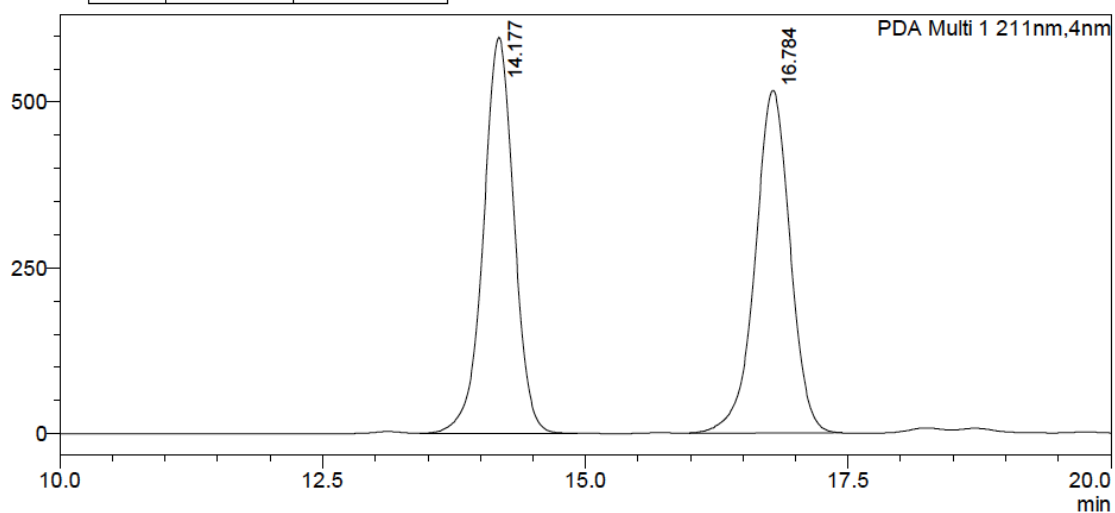
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	14.177	50.245
2	16.784	49.755
Total		100.000



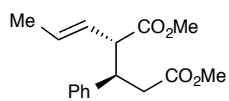
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	14.254	0.486
2	16.870	99.514
Total		100.000



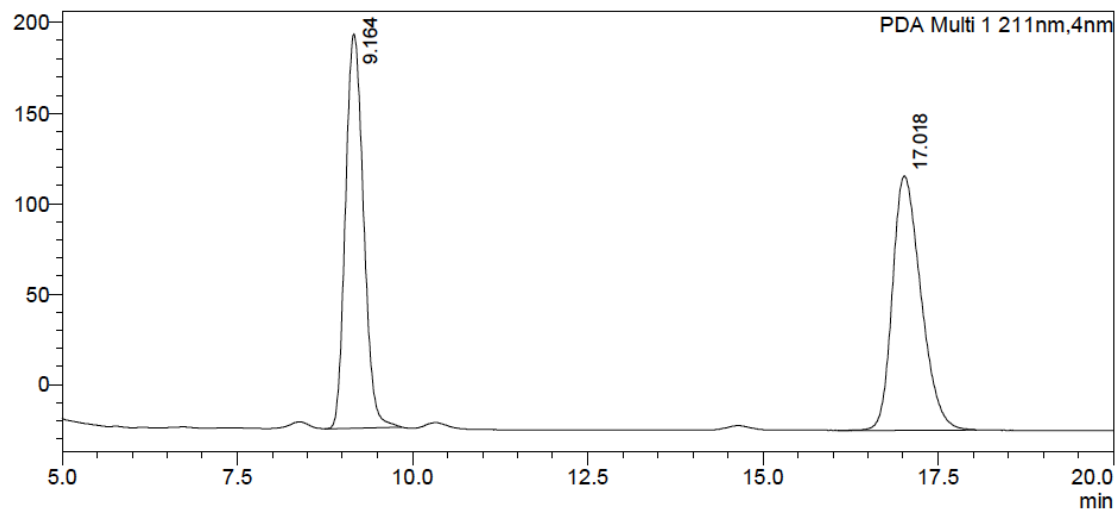
HPLC data for **20**: Chiralpak OD-H (97:3 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 220 nm, 30 °C)

t<sub>R</sub>(2*S*,3*S*): 9.82 min, t<sub>R</sub> (2*R*,3*R*): 15.5 min, >99% ee;



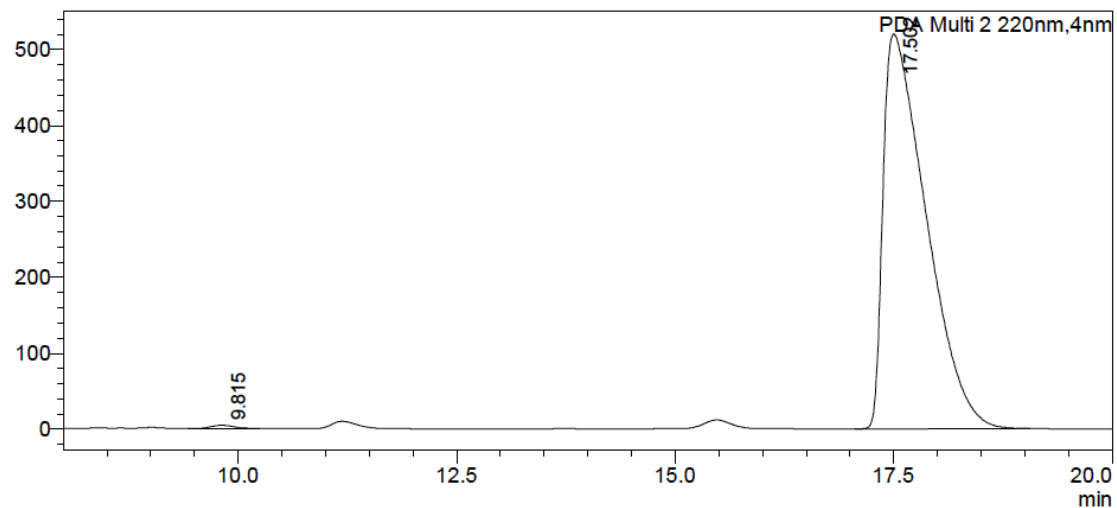
PDA Ch1 211nm

Ret. Time	Area%
9.164	49.549
17.018	50.451
	100.000

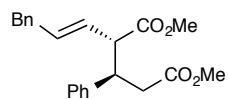


PDA Ch2 220nm

Ret. Time	Area%
9.815	0.373
17.502	99.627
	100.000

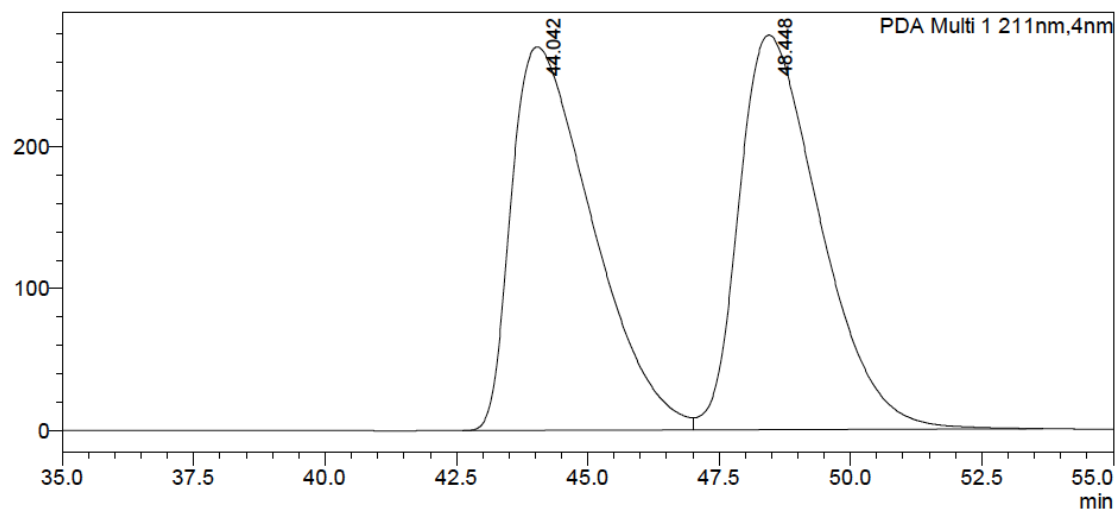


HPLC data for **21**: Chiral HPLC analysis, Chiralcel OJ-H (99:1 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 40 °C)  $t_R(2S,3R)$ : 44.0 min,  $t_R(2R,3S)$ : 48.4 min, 99% ee;



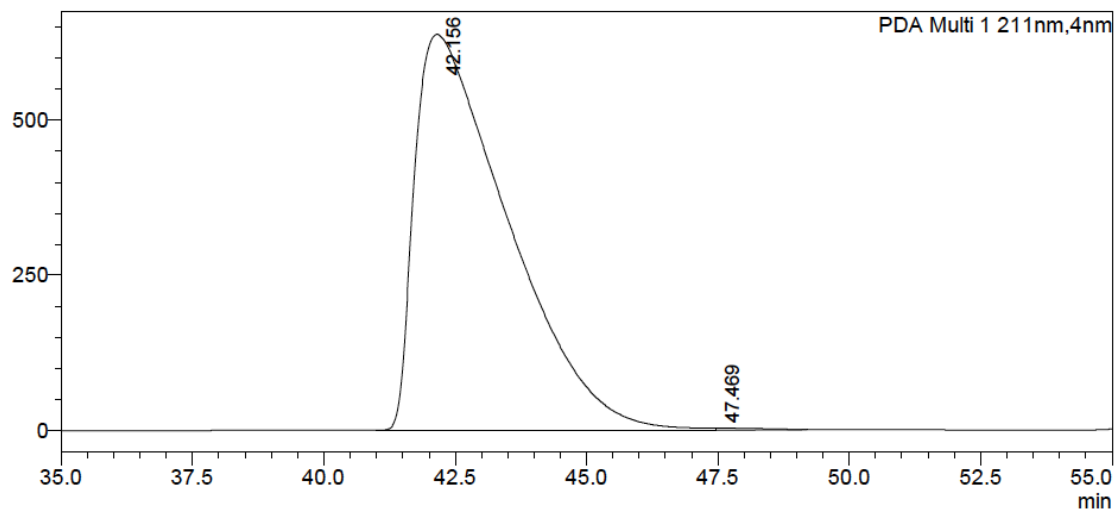
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	44.042	49.322
2	48.448	50.678
Total		100.000

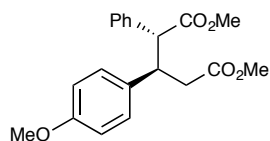


PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	42.156	99.712
2	47.469	0.288
Total		100.000

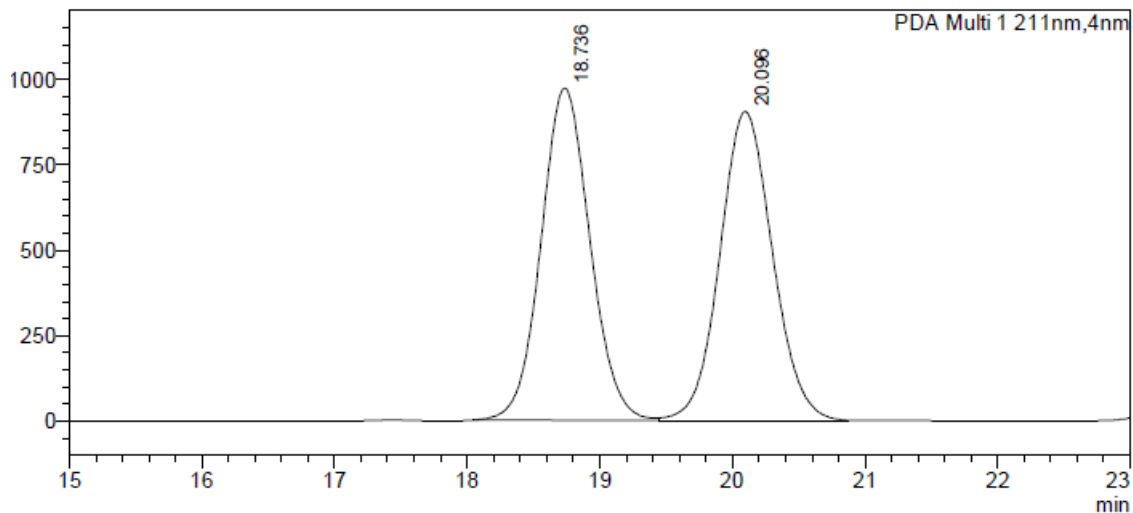


HPLC Data for **23**: Chiralpak AD-H (95:5 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C)  $t_R(2S,3S)$ : 18.7 min,  $t_R(2R,3R)$ : 20.1 min, >99% ee;



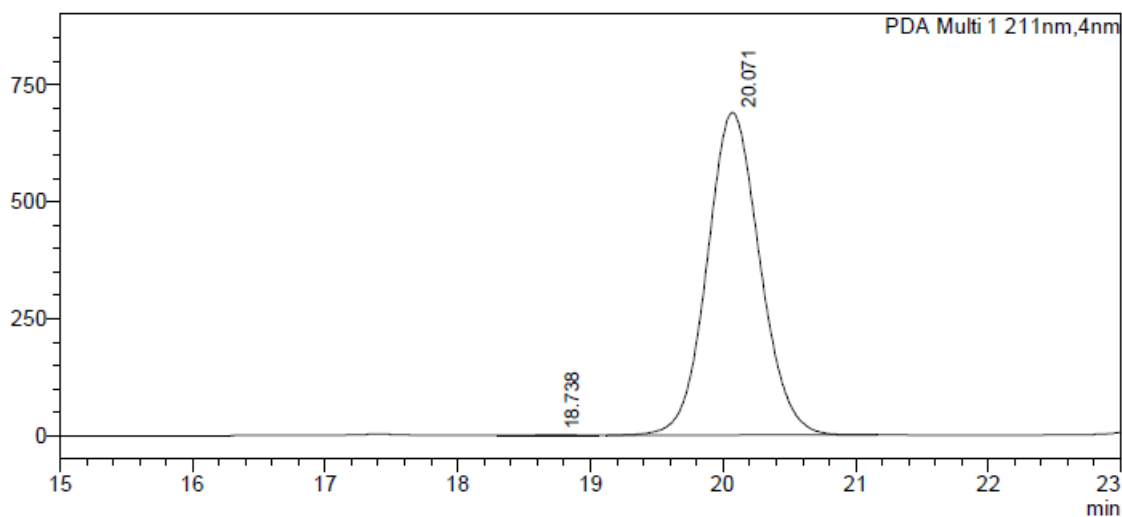
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	18.736	50.027
2	20.096	49.973
Total		100.000

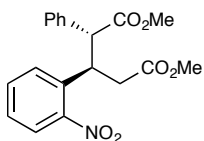


PDA Ch1 211nm

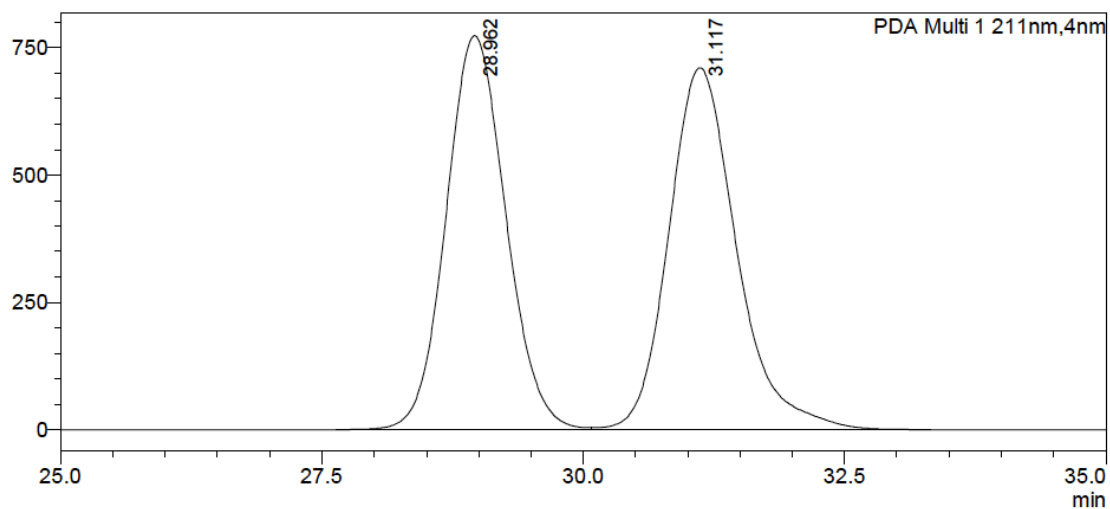
Peak#	Ret. Time	Area%
1	18.738	0.132
2	20.071	99.868
Total		100.000



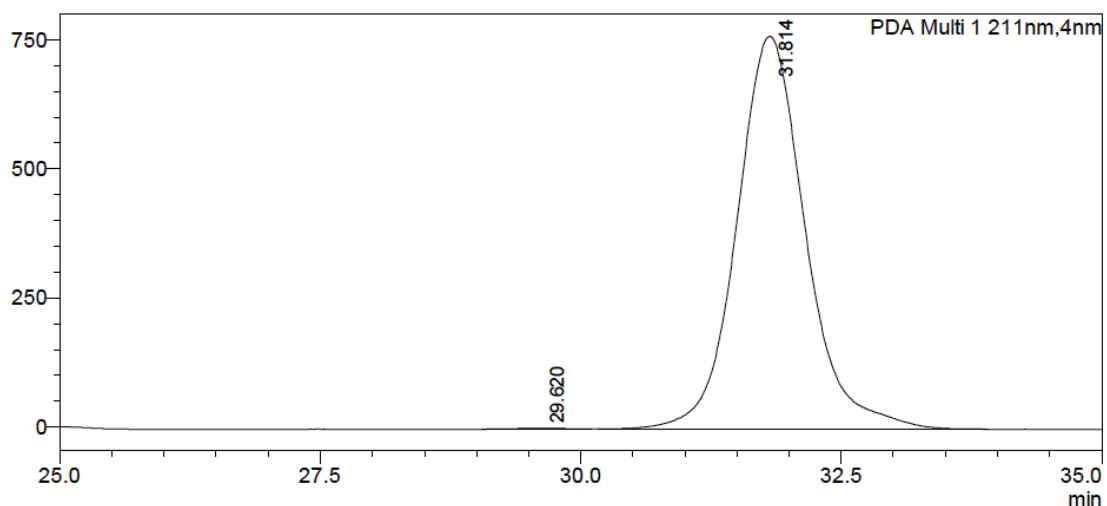
HPLC data for **24**: Chiral HPLC analysis, Chiralpak AD-H (95:5 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C)  $t_R(2S,3S)$ : 29.0 min,  $t_R(2R,3R)$ : 31.1 min, >99% ee;



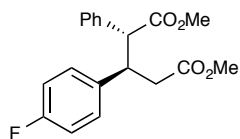
PDA Ch1 211nm		
Peak#	Ret. Time	Area%
1	28.962	49.007
2	31.117	50.993
Total		100.000



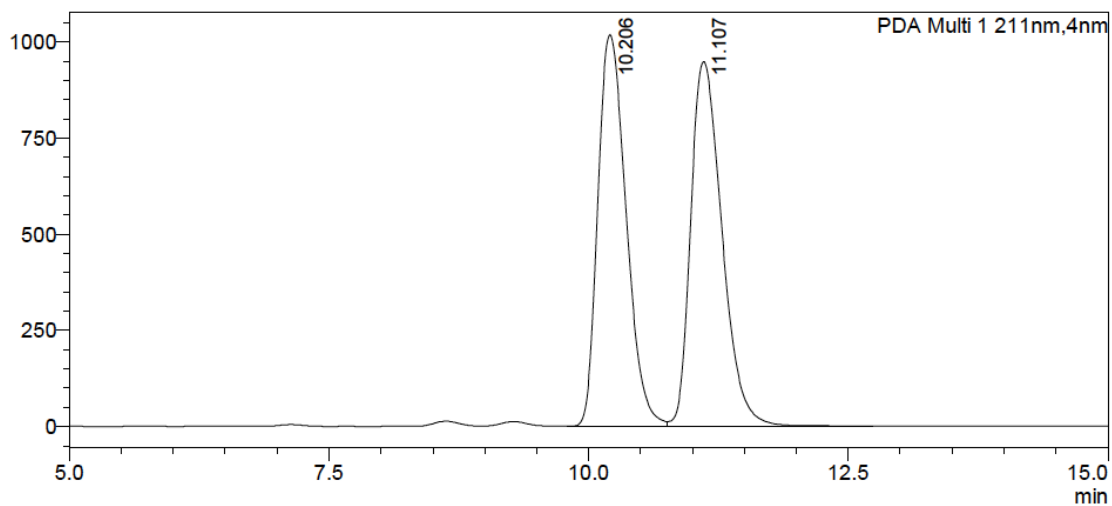
PDA Ch1 211nm		
Peak#	Ret. Time	Area%
1	29.620	0.218
2	31.814	99.782
Total		100.000



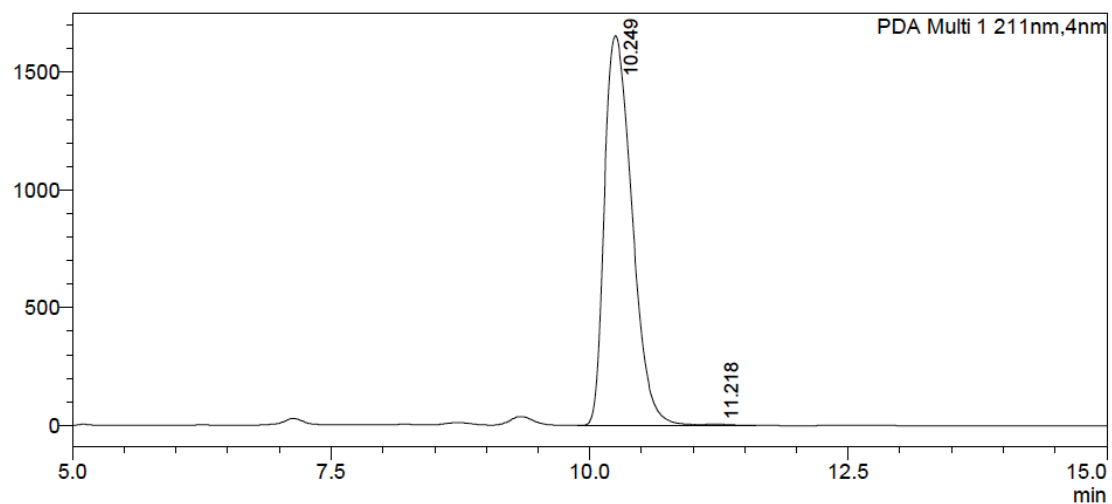
HPLC data for **25**: Chiral HPLC analysis, Chiralcel OD-H (95:5 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C)  $t_R(2R,3R)$ : 10.2 min,  $t_R(2S,3S)$ : 11.1 min, 99% ee;



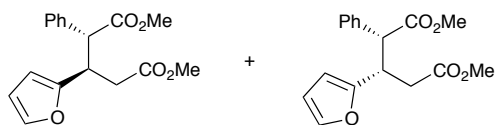
PDA Ch1 211nm		
Peak#	Ret. Time	Area%
1	10.206	49.311
2	11.107	50.689
Total		100.000



PDA Ch1 211nm		
Peak#	Ret. Time	Area%
1	10.249	99.660
2	11.218	0.340
Total		100.000

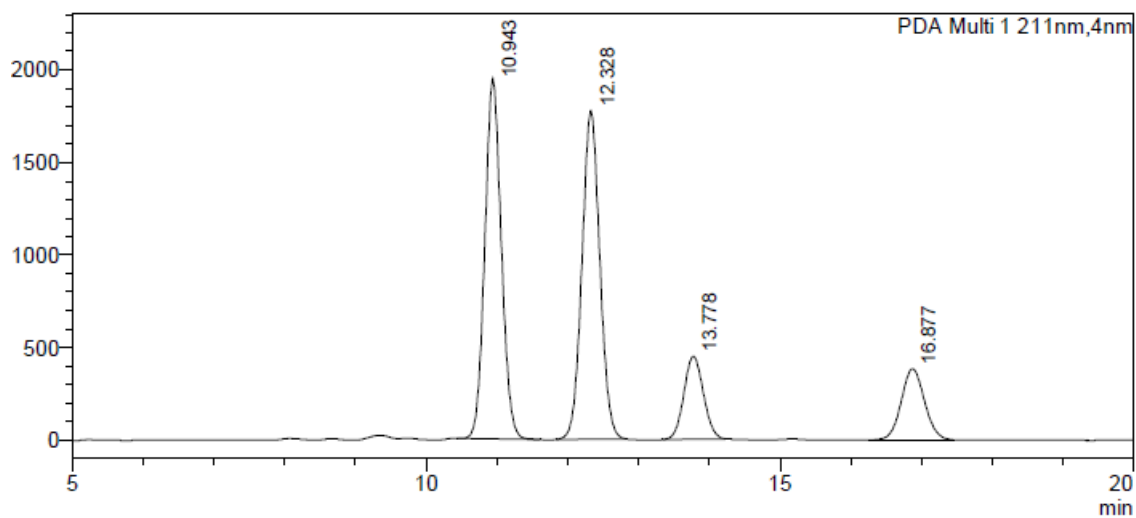


HPLC Data for *anti*-**26**: Chiralpak AD-H (95:5 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C) *t<sub>R</sub>*(*2S,3S*): 10.9 min, *t<sub>R</sub>*(*2R,3R*): 12.3 min, 98% ee; *syn*-**26**: *t<sub>R</sub>*(major): 13.8 min, *t<sub>R</sub>*(minor): 16.9 min, 23% ee;



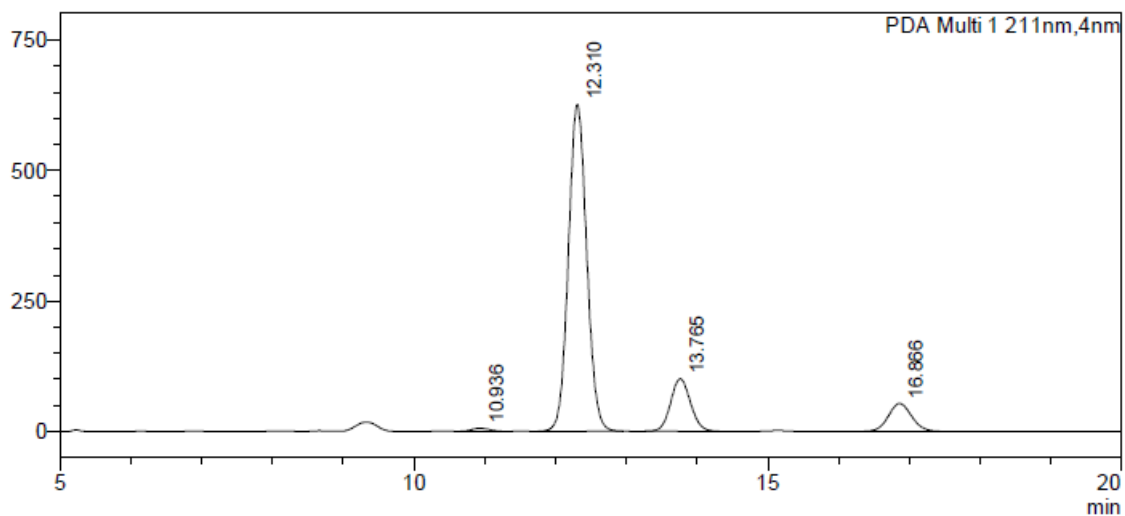
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	10.943	39.284
2	12.328	38.880
3	13.778	10.782
4	16.877	11.054
Total		100.000



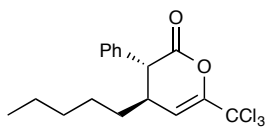
PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	10.936	0.694
2	12.310	77.226
3	13.765	13.563
4	16.866	8.517
Total		100.000



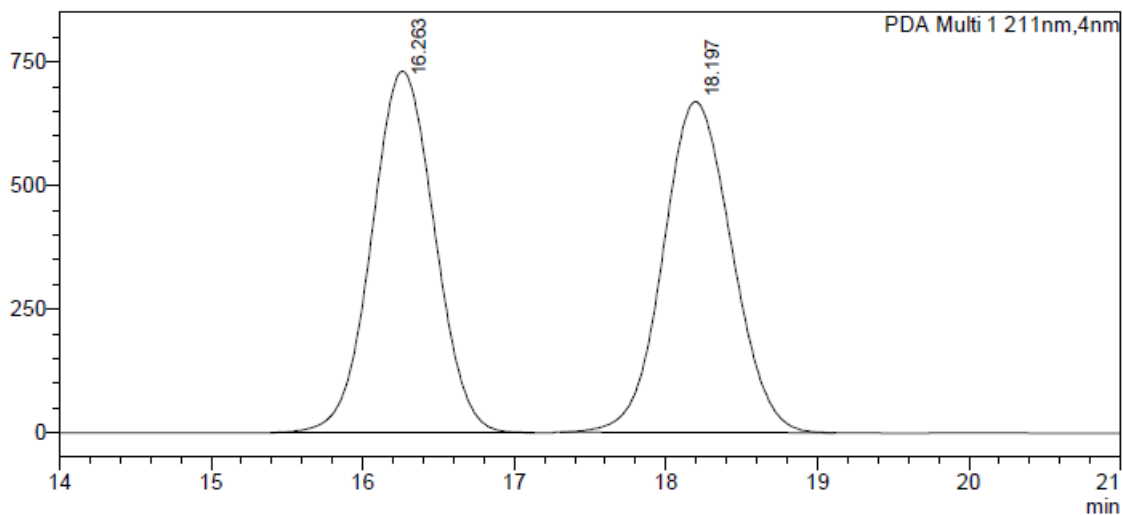
HPLC Data for **27**: Chiralpak AD-H (99:1 hexane:IPA, flow rate 1 mLmin<sup>-1</sup>, 211 nm, 30 °C)

$t_R(2R,3R)$ : 15.9 min,  $t_R(2S,3S)$ : 17.7 min, 86% ee;



PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	16.263	50.013
2	18.197	49.987
Total		100.000



PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	15.851	93.246
2	17.683	6.754
Total		100.000

