

Supporting Information

TMSOTf-mediated Synthesis of Skipped Dienes Through the Addition of Olefins to Imines and Semicyclic *N, O*-Acetals

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I. X-Ray Structure for compounds 3ea and 6aa

ORTEP drawing of the X-ray crystallographic structure of compound 3ea (50% probability ellipsoids, ddz20103 is the original test number for 3ea):

The single crystal of compound 3ea was prepared from its solution in petroleum ether by slow evaporation of the solvent (**Table S1**)

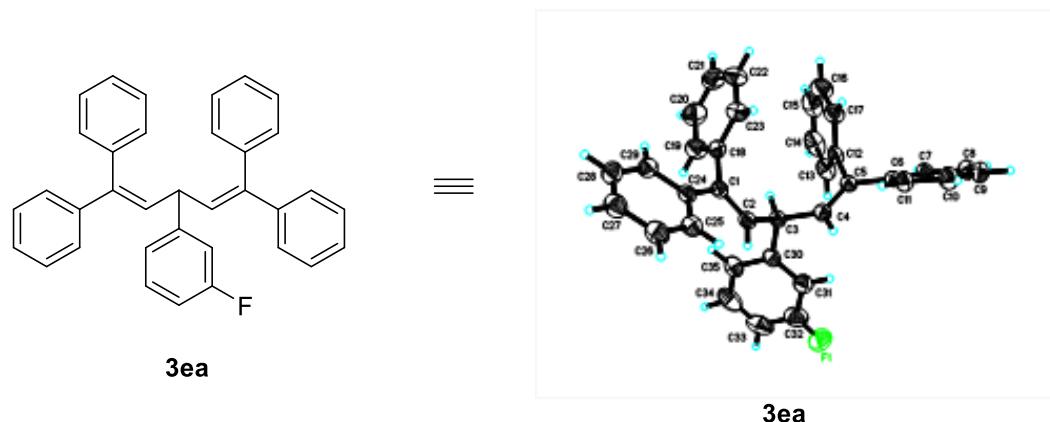


Table S1. Crystal data and structure refinement for 3ea.

Identification code	3ea	
Empirical formula	C ₃₅	H ₂₇ F
Formula weight	466.56	
Temperature	293(2)	K
Wavelength	0.71073	Å
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 18.4643(12) Å	= 90°.
	b = 8.6875(6) Å	= 90°.
	c = 32.046(2) Å	= 90°.
Volume	5140.4(6) Å ³	
Z	8	
Density (calculated)	1.206 Mg/m ³	
Absorption coefficient	0.073 mm ⁻¹	
F(000)	1968	

Crystal size	0.180 x 0.110 x 0.070 mm ³
Theta range for data collection	2.546 to 25.494 °
Index ranges	-22<=h<=22, -10<=k<=10, -38<=l<=38
Reflections collected	70059
Independent reflections	4788 [R(int) = 0.0963]
Completeness to theta = 25.242 °	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6846
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4788 / 0 / 335
Goodness-of-fit on F ²	1.078
Final R indices [I>2sigma(I)]	R1 = 0.0524, wR2 = 0.1000
R indices (all data)	R1 = 0.1079, wR2 = 0.1268
Extinction coefficient	0.0036(3)
Largest diff. peak and hole	0.129 and -0.136 e.Å ⁻³

CCDC 2090252. For detailed crystallographic data, please refer to the Cambridge Crystallographic Data Centre at <http://ccdc.cam.ac.uk>.

ORTEP drawing of the X-ray crystallographic structure of compound 6aa (50% probability ellipsoids, mo_dd20131_0m is the original test number for 6aa):

The single crystal of compound **6aa** was prepared from its solution in petroleum ether/ethylacetate (4:1) by slow evaporation of the solvent (**Table S2**)

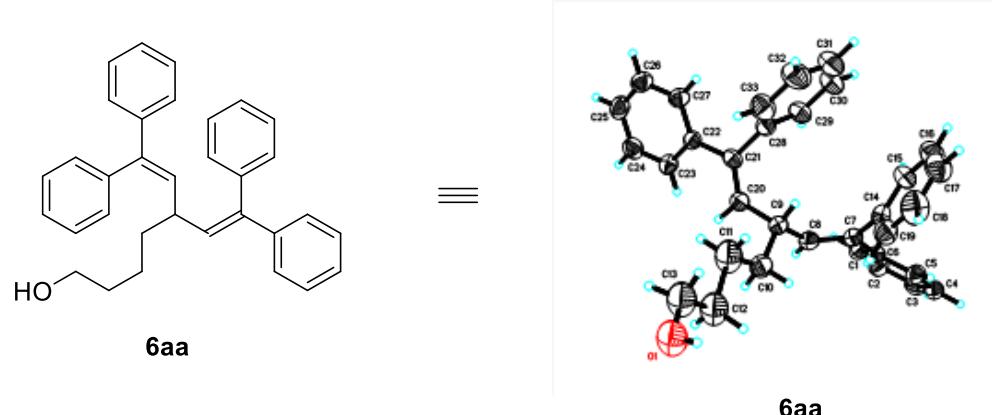
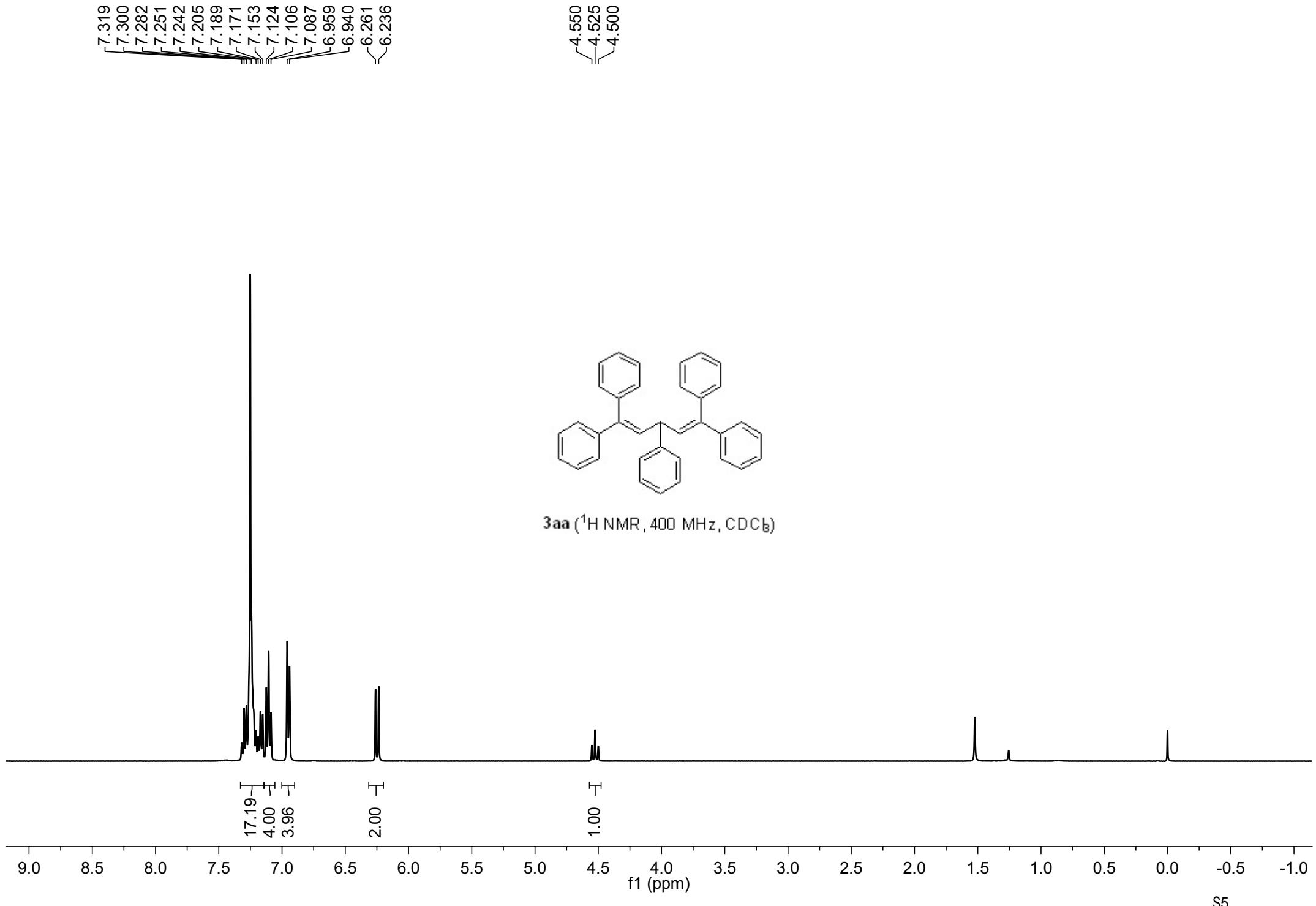


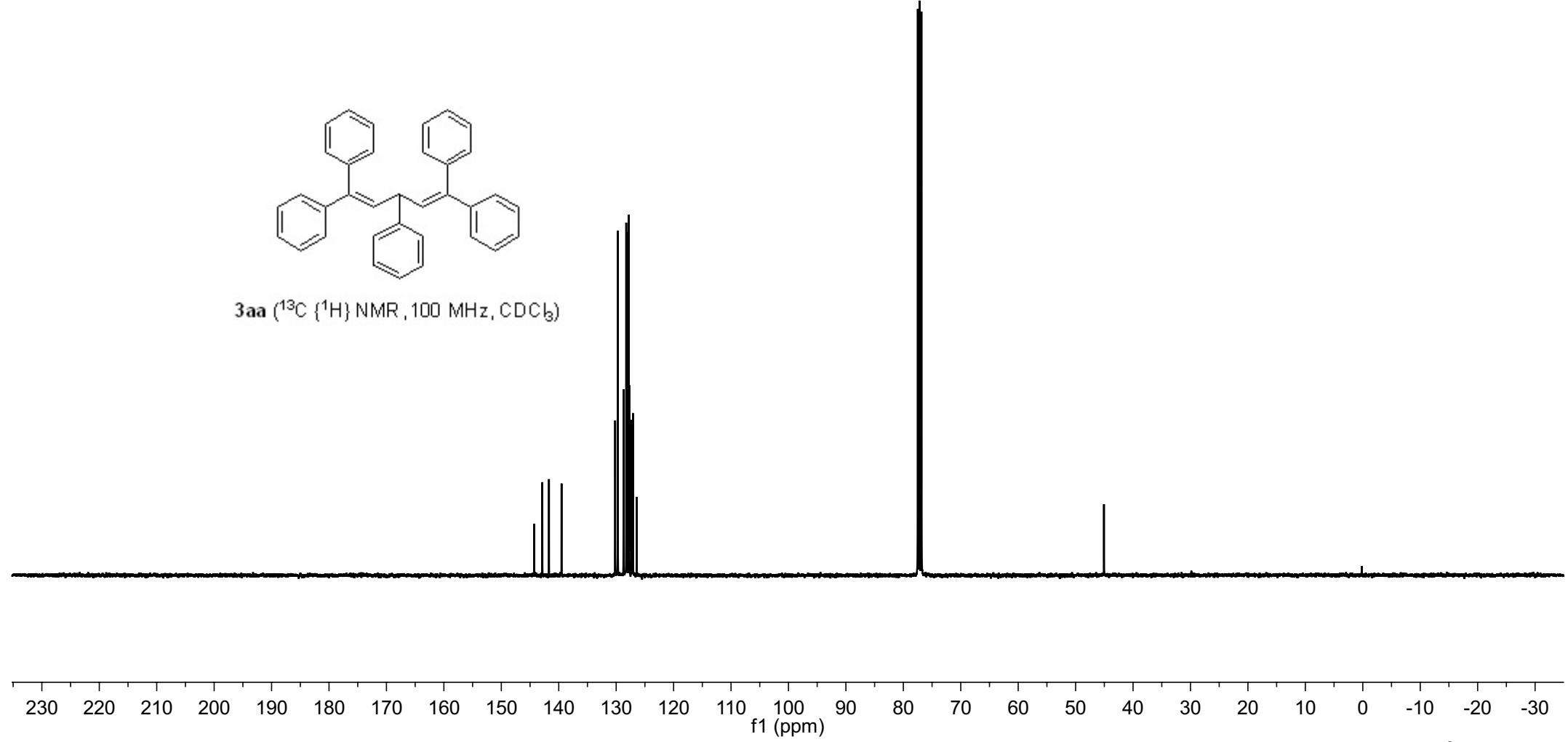
Table S2. Crystal data and structure refinement for **6aa**.

Identification code	6aa					
Empirical formula	C ₃₃ H ₃₂ O					
Formula weight	444.58					
Temperature	293.06 K					
Wavelength	0.71073 Å					
Crystal system	Orthorhombic					
Space group	P b c n					
Unit cell dimensions	a = 36.302(8) Å	a= 90 °	b = 17.985(4) Å	b= 90 °	c = 8.873(2) Å	g = 90 °
Volume	5793(2) Å ³					
Z	8					
Density (calculated)	1.019 Mg/m ³					
Absorption coefficient	0.060 mm ⁻¹					
F(000)	1904					
Crystal size	0.18 x 0.15 x 0.1 mm ³					

Theta range for data collection	2.028 to 24.998 °
Index ranges	-43<=h<=35, -21<=k<=21, -10<=l<=10
Reflections collected	40663
Independent reflections	5099 [R(int) = 0.1790]
Completeness to theta = 25.242 °	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5131
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5099 / 104 / 346
Goodness-of-fit on F ²	0.995
Final R indices [I>2sigma(I)]	R1 = 0.0989, wR2 = 0.2551
R indices (all data)	R1 = 0.1704, wR2 = 0.3205
Extinction coefficient	0.018(3)
Largest diff. peak and hole	0.373 and -0.396 e.Å ⁻³

CCDC 2090251. For detailed crystallographic data, please refer to the Cambridge Crystallographic Data Centre at <http://ccdc.cam.ac.uk>.

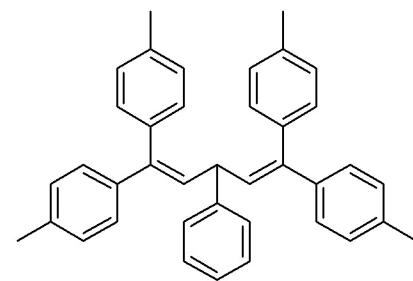




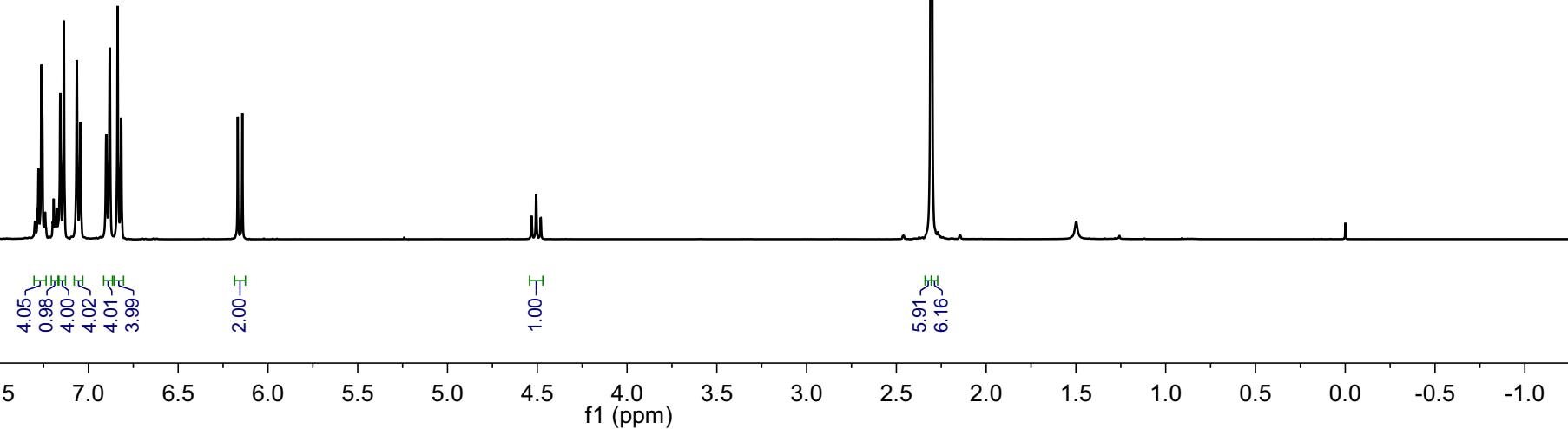
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7.278
7.262
7.257
7.241
7.199
7.193
7.188
7.182
7.177
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7.137
7.064
7.044
6.901
6.881
6.837
6.817
6.168
6.143

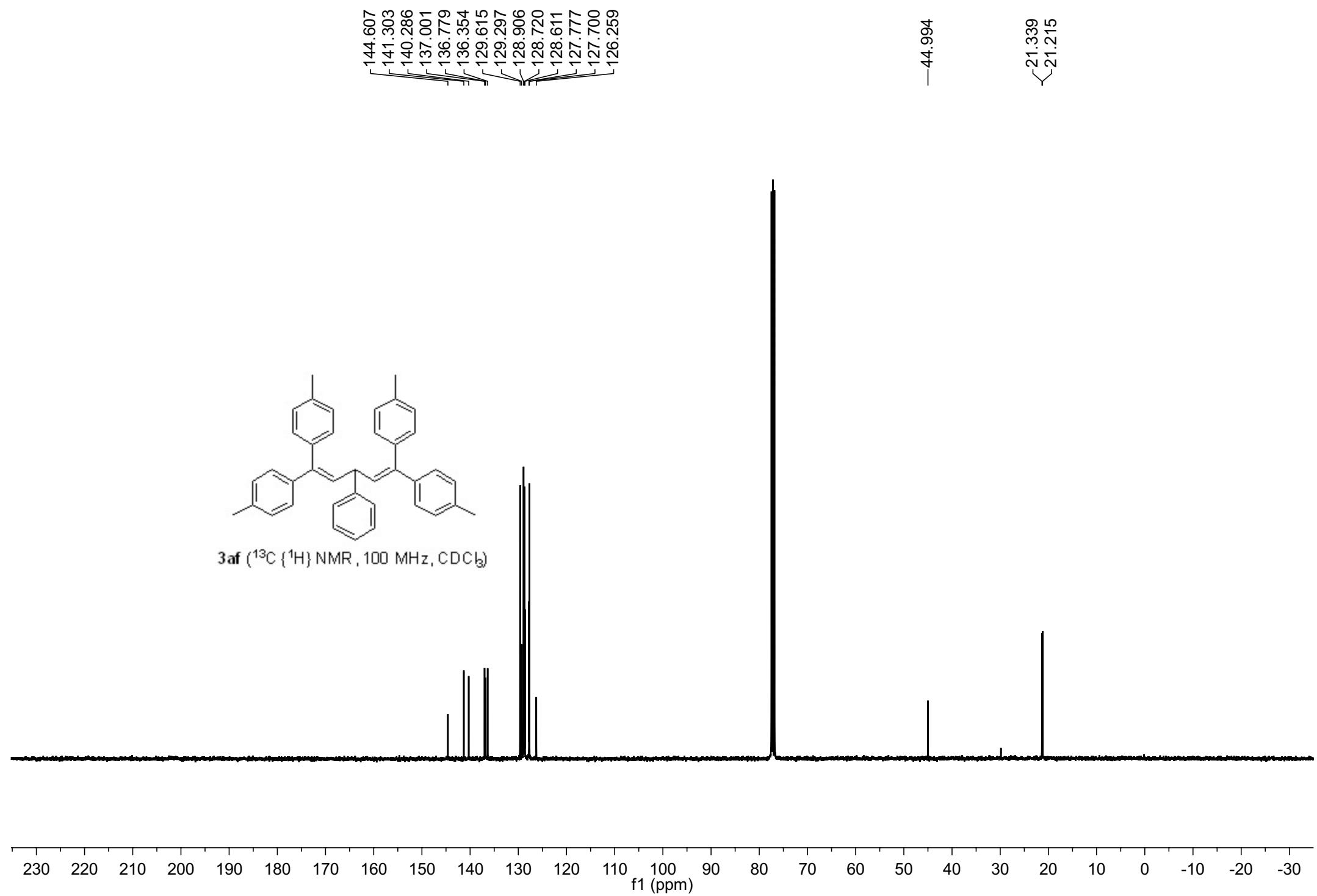
4.532
4.506
4.481

2.308
2.303



3af (^1H NMR, 400 MHz, CDCl_3)

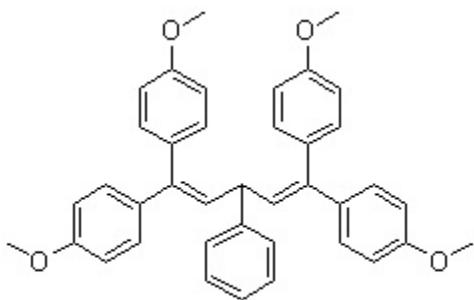




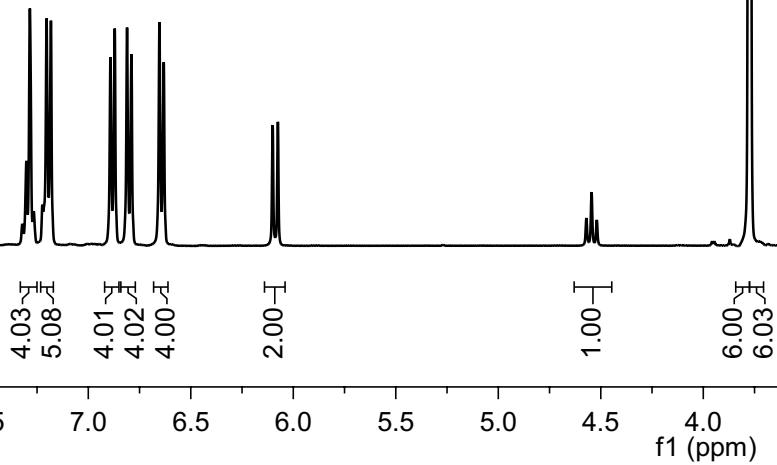
7.322
7.302
7.285
7.266
7.224
7.203
7.182
6.892
6.871
6.811
6.789
6.653
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6.100
6.075

4.570
4.545
4.519

3.780
3.768



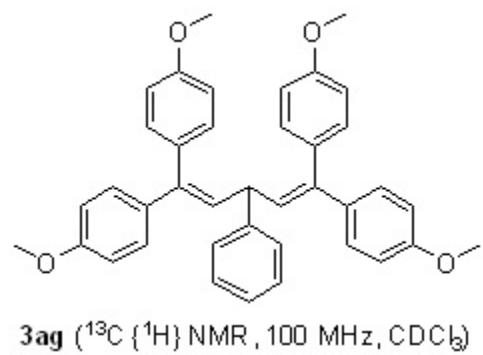
3ag (^1H NMR, 400 MHz, CDCl_3)



9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

f1 (ppm)

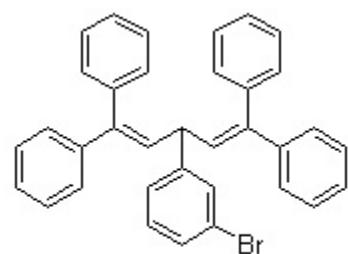
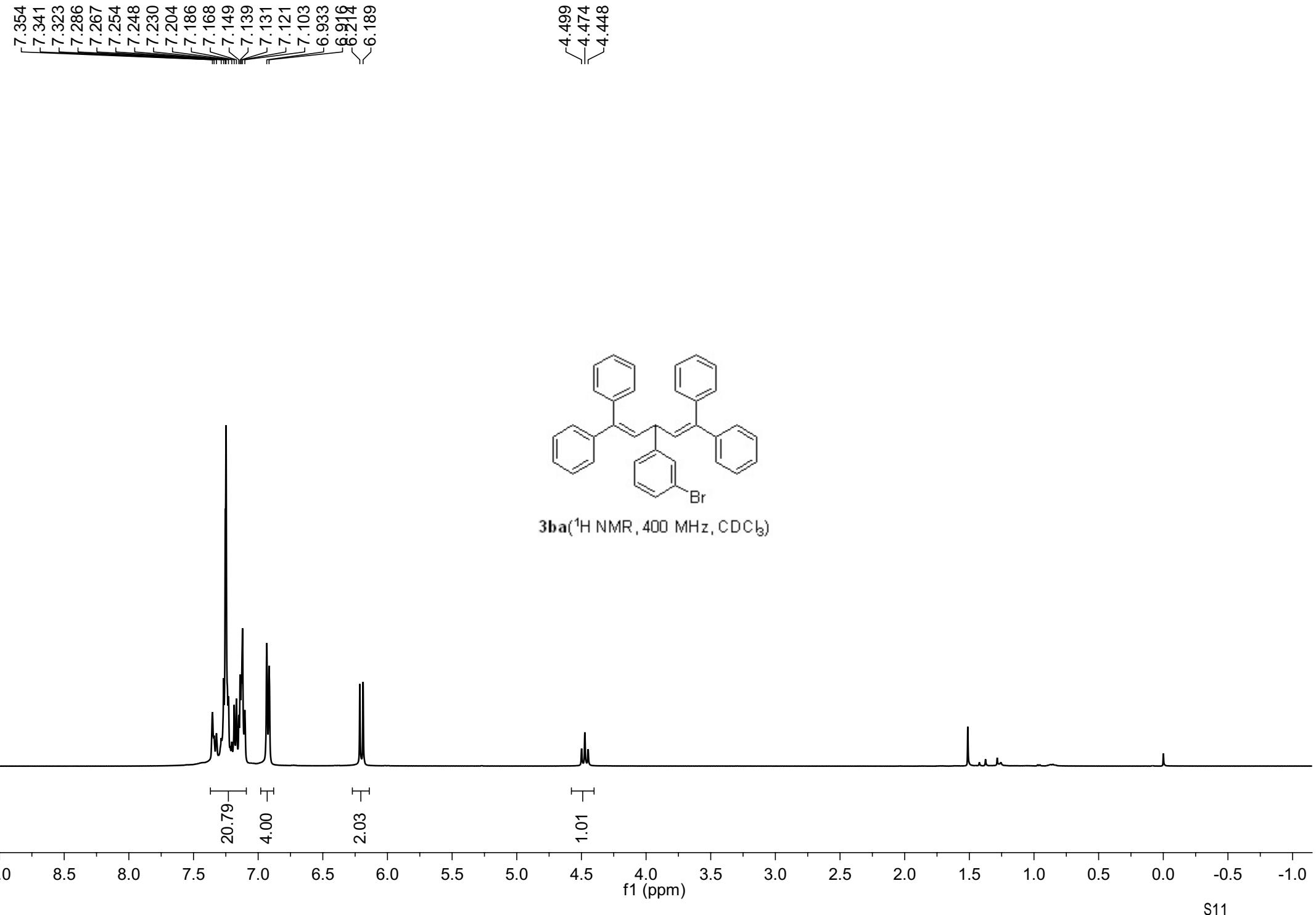
S9

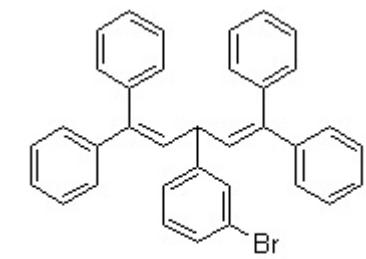


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

f1 (ppm)

S10





3ba (^{13}C { ^1H } NMR, 100 MHz, CDCl_3)

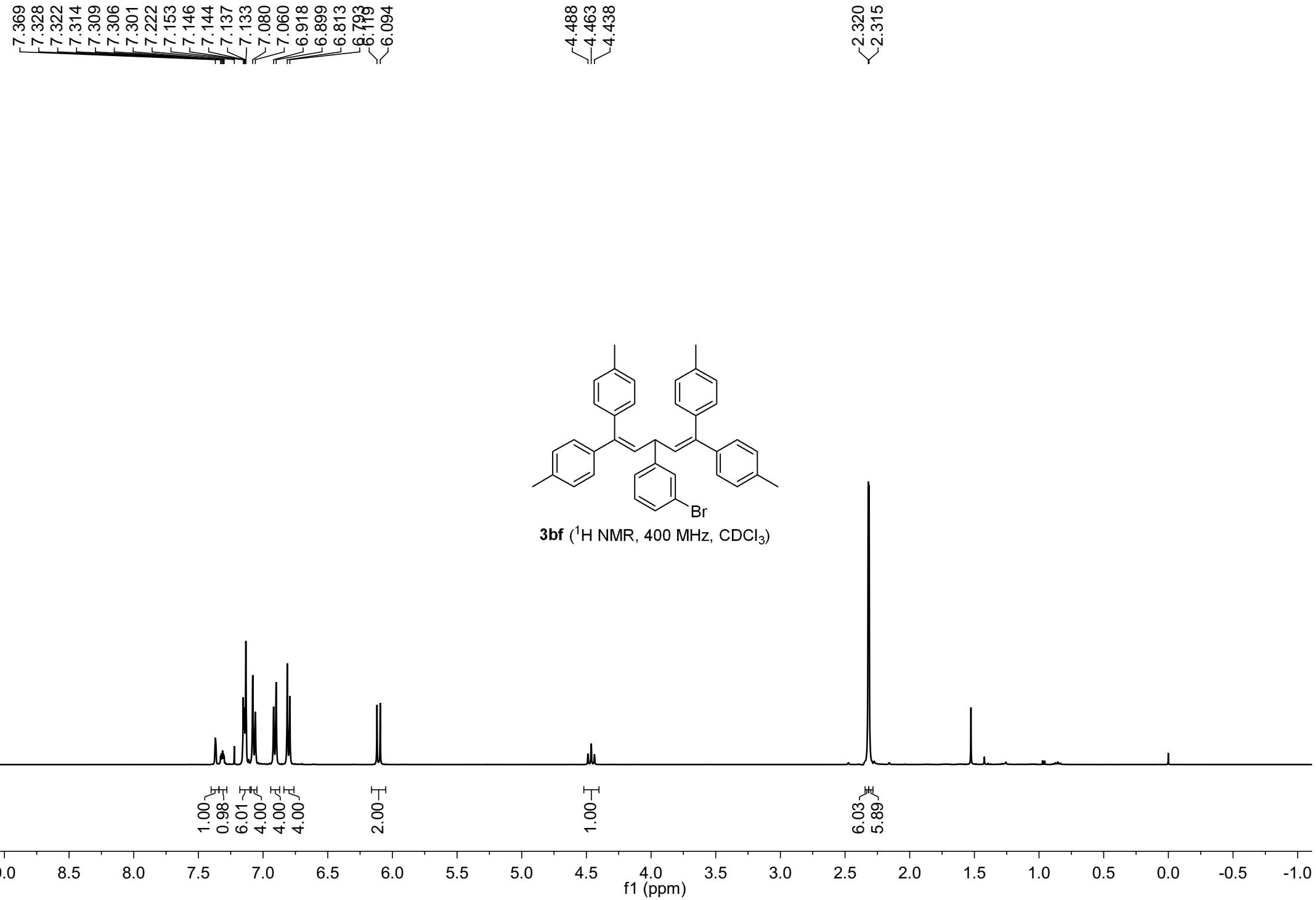
146.749
142.517
142.304
139.255
130.663
130.262
129.606
129.574
129.246
128.293
128.249
127.782
127.529
127.225
126.410
122.885

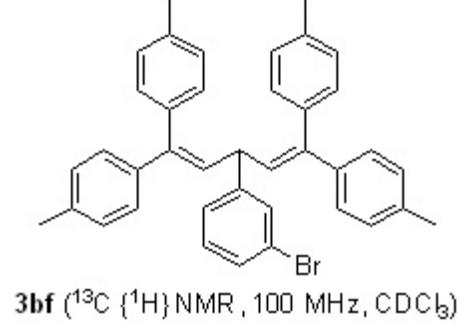
—44.879

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

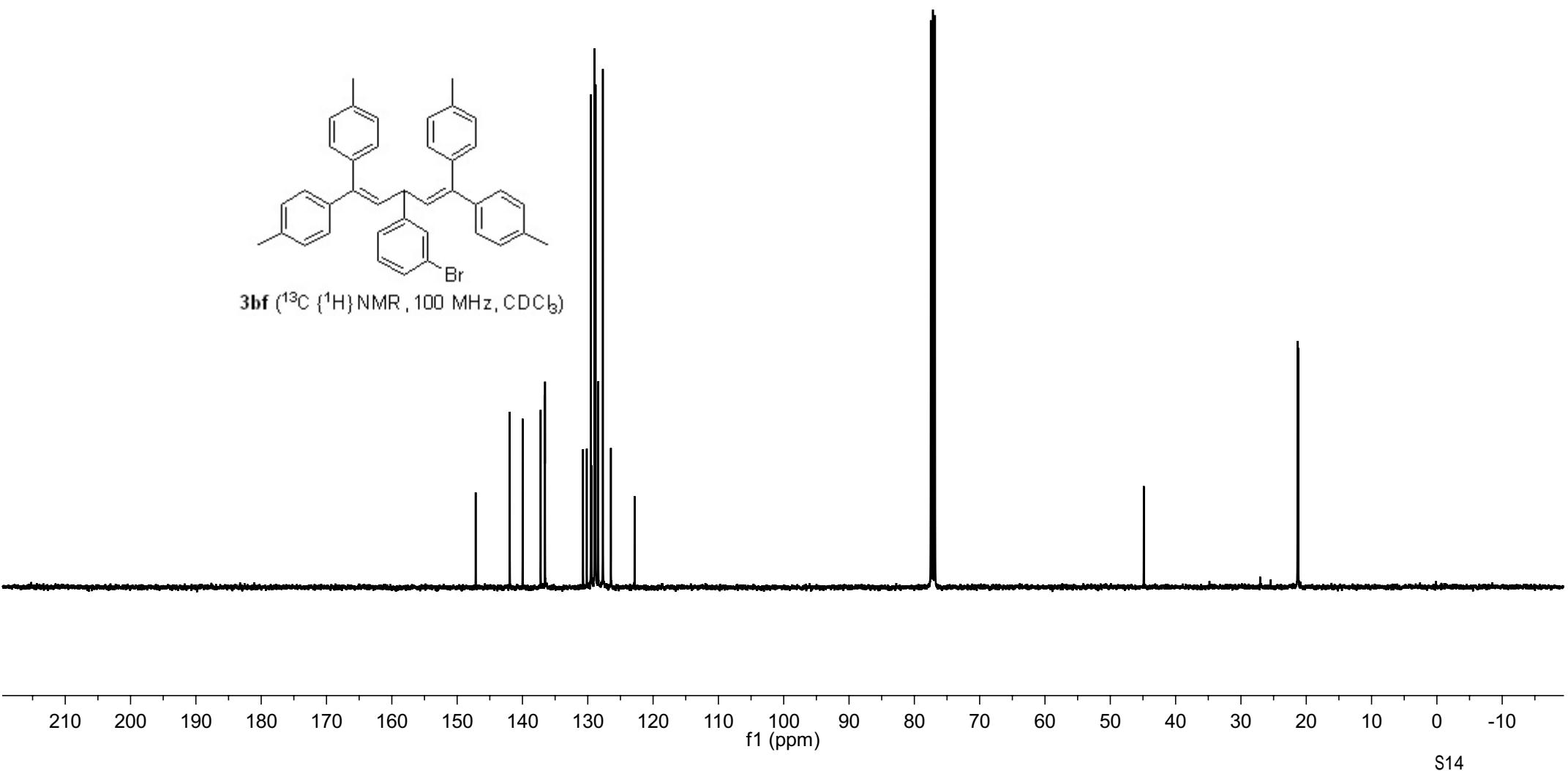
f1 (ppm)

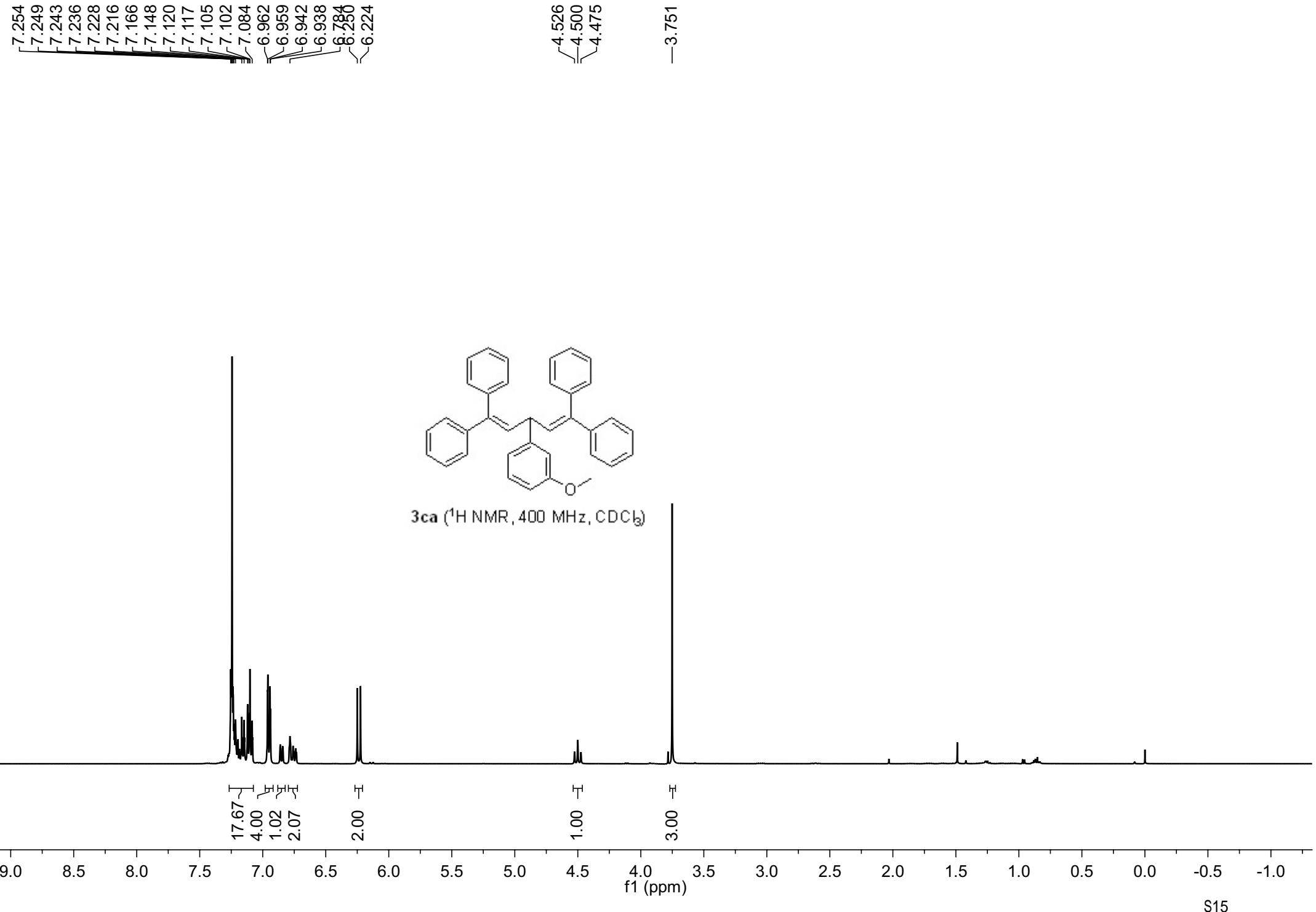
S12

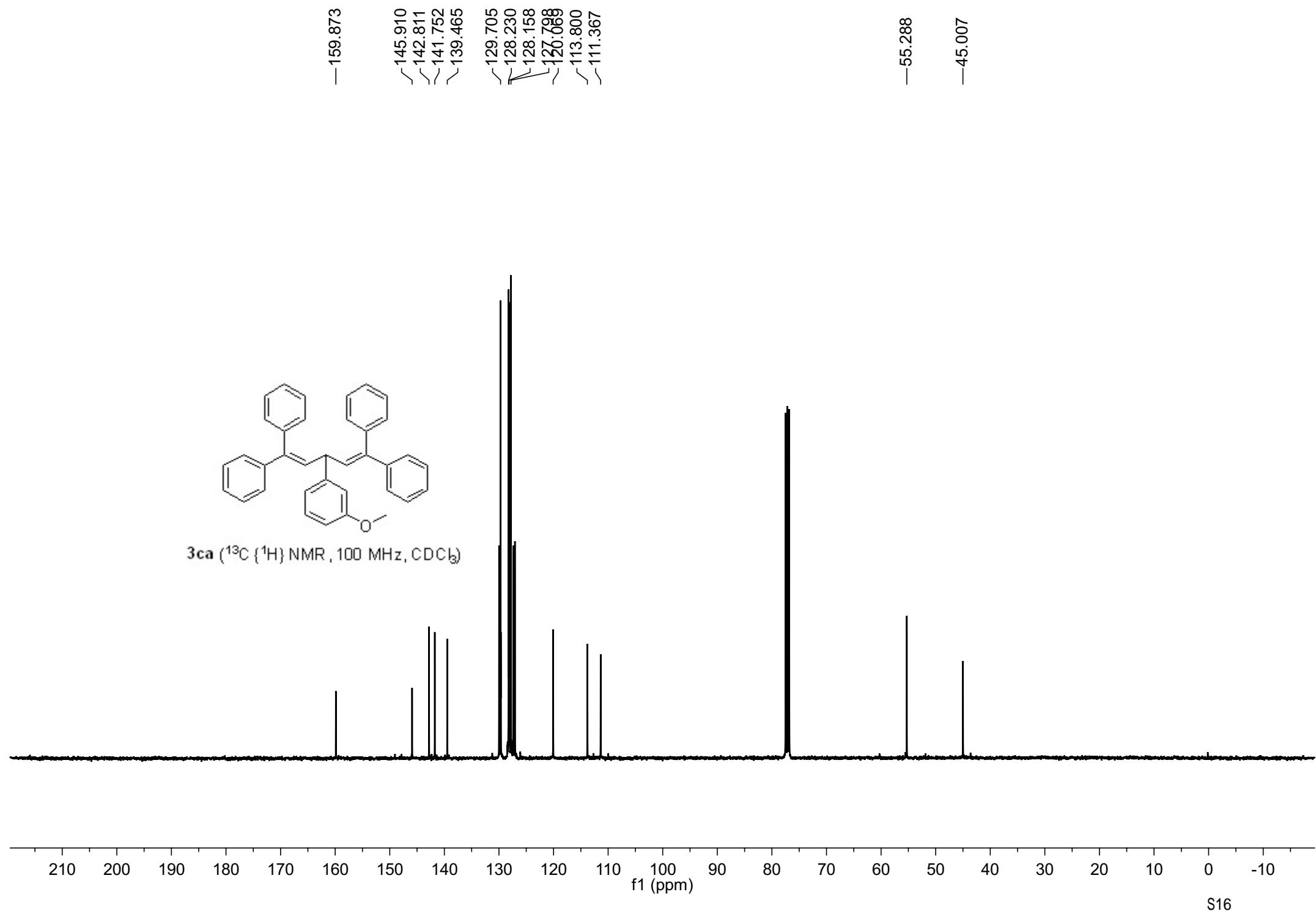


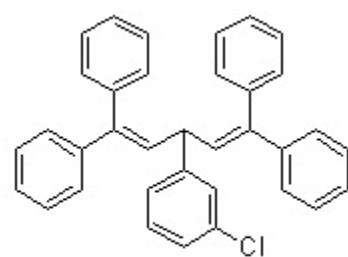
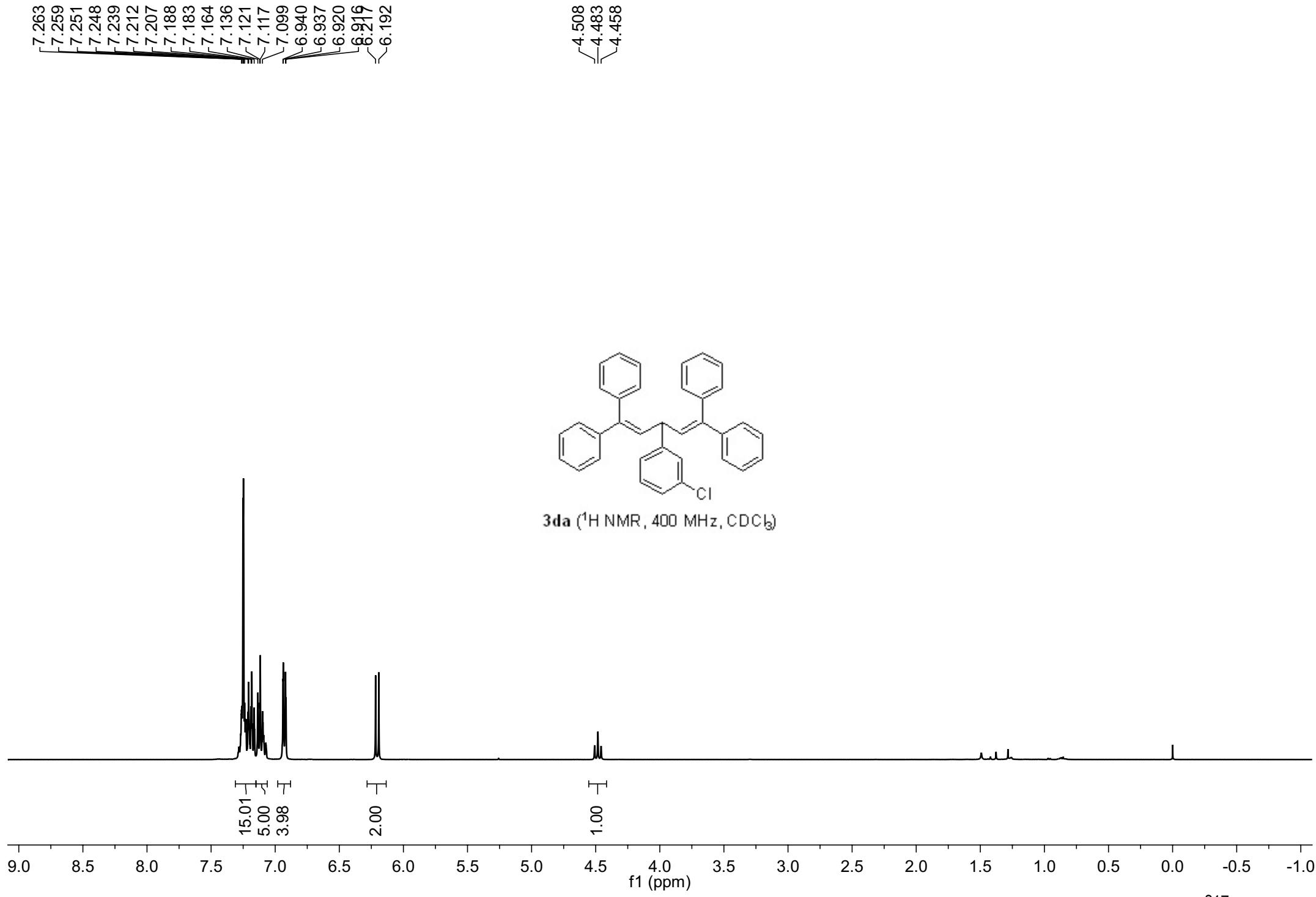


3bf (^{13}C { ^1H } NMR, 100 MHz, CDCl_3)

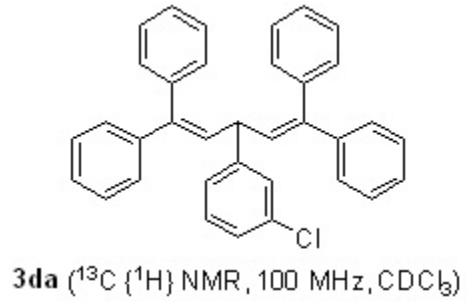








3da (^1H NMR, 400 MHz, CDCl_3)

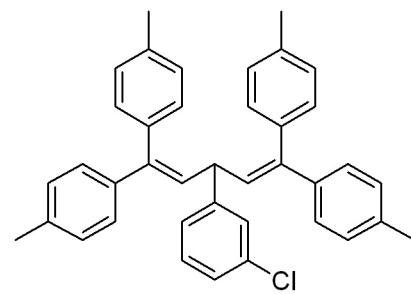


—44.898

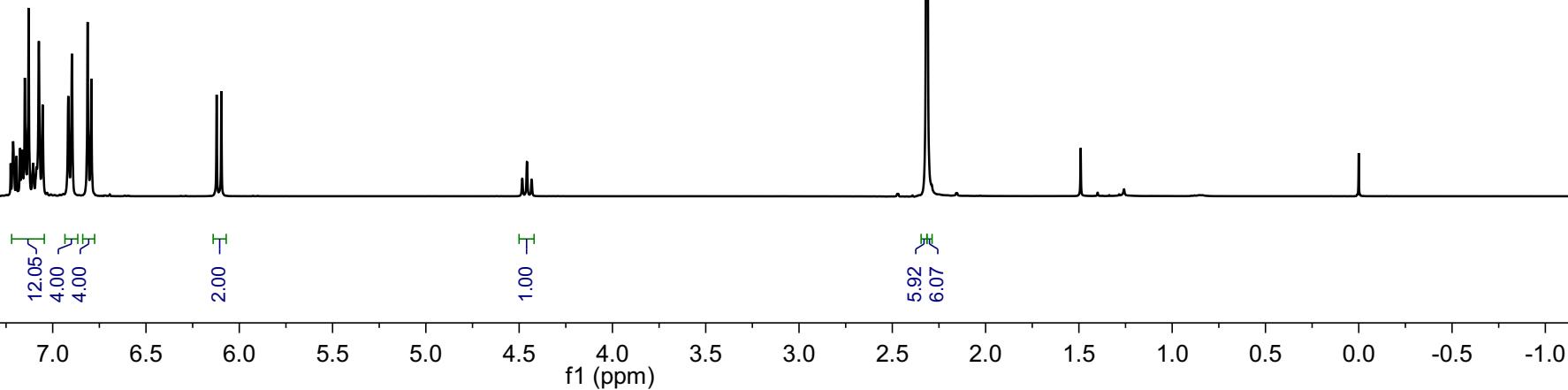
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7.165
7.160
7.149
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7.054
6.917
6.897
6.813
6.793
6.121
6.096

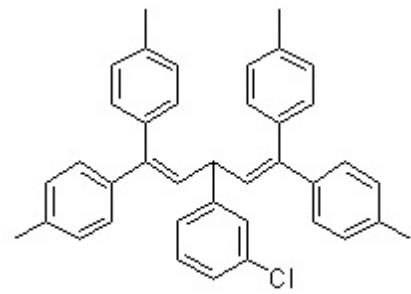
4.483
4.458
4.433

2.317
2.312

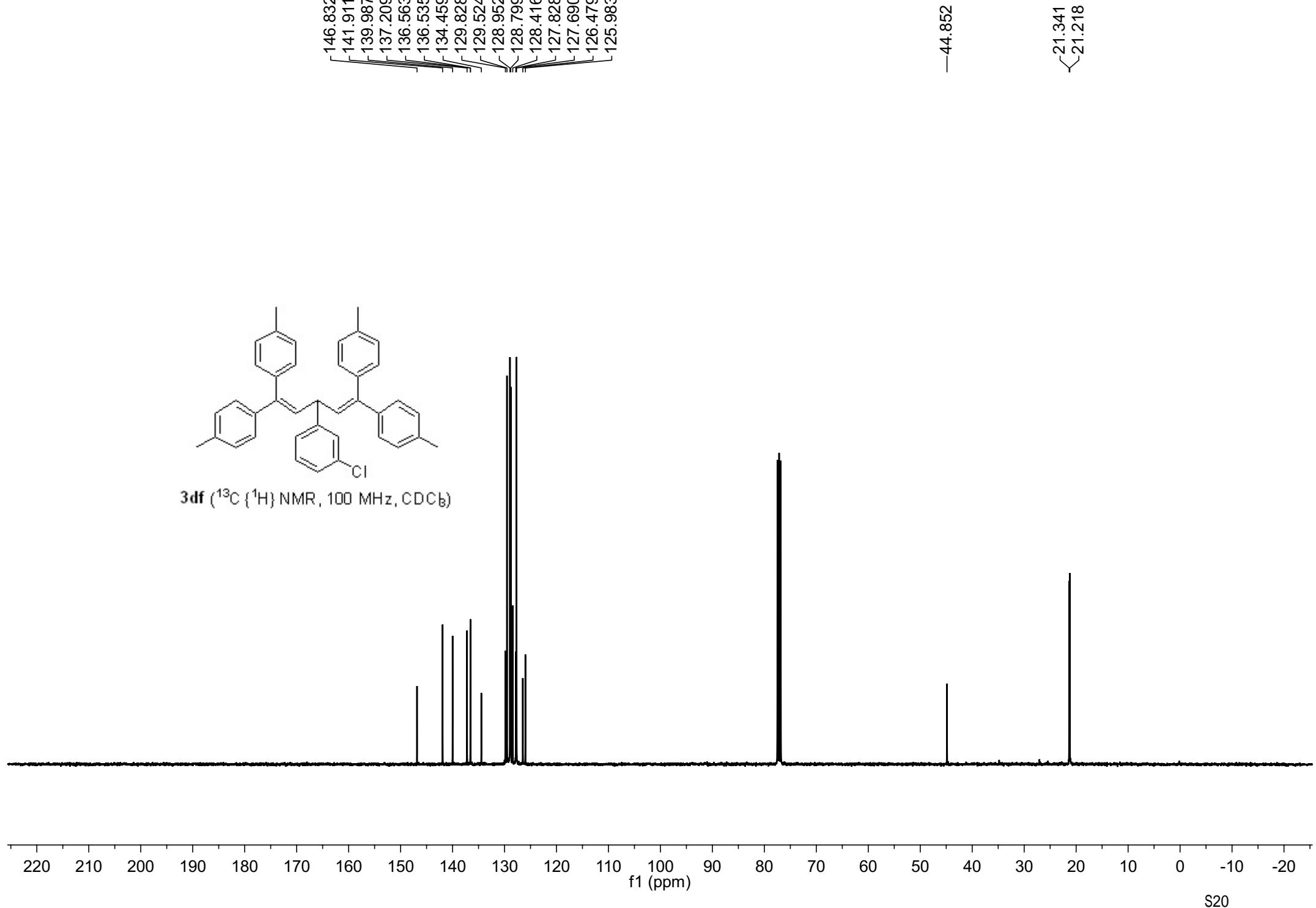


3df (^1H NMR, 400 MHz, CDCl_3)



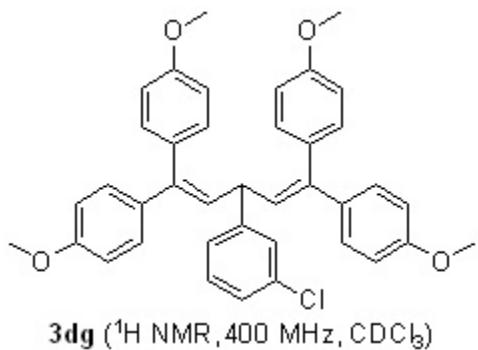


3df (^{13}C { ^1H } NMR, 100 MHz, CDCl_3)

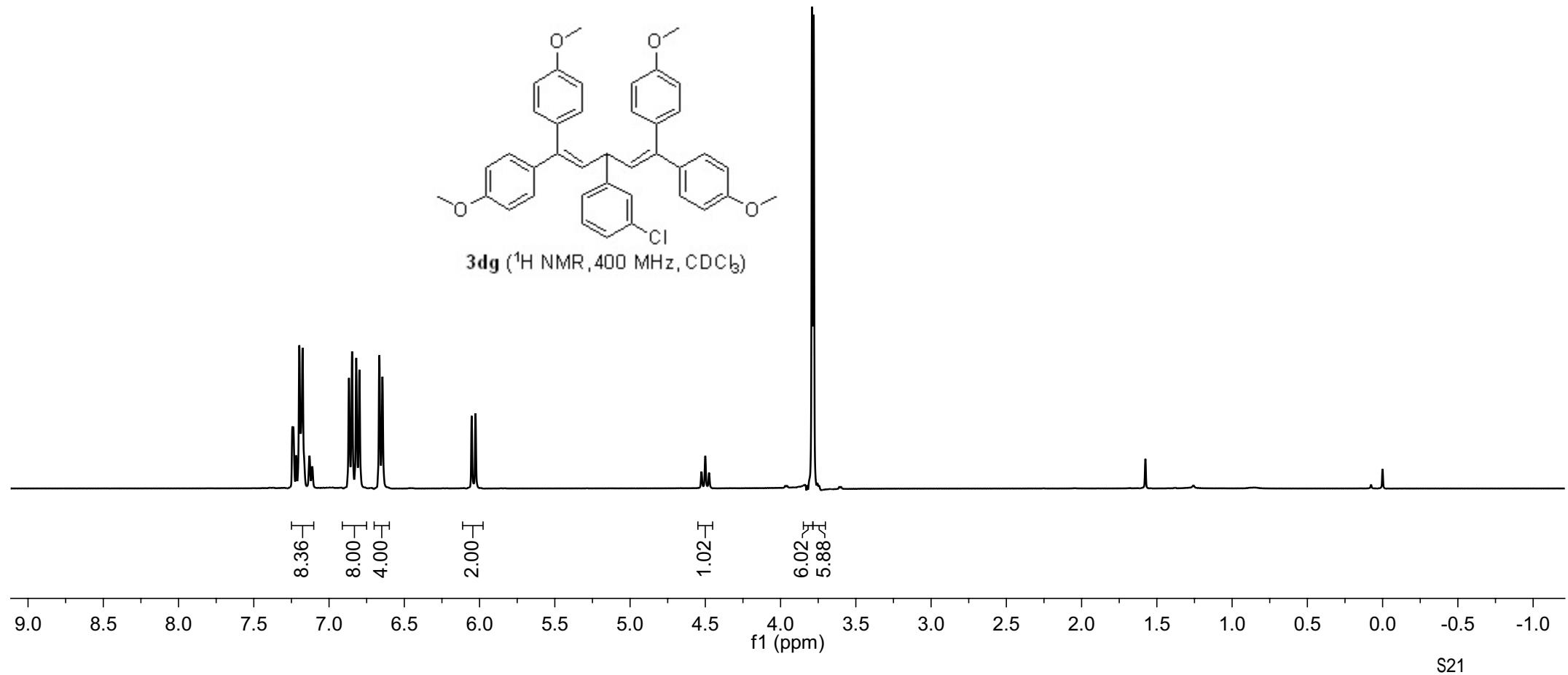


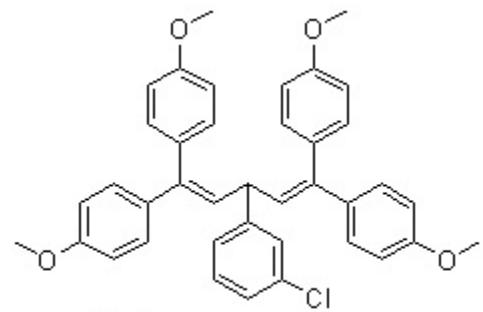
7.243
7.238
7.218
7.197
7.176
7.150
7.112
6.868
6.847
6.819
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6.052
6.027

4.525
4.500
4.475
3.791
3.780

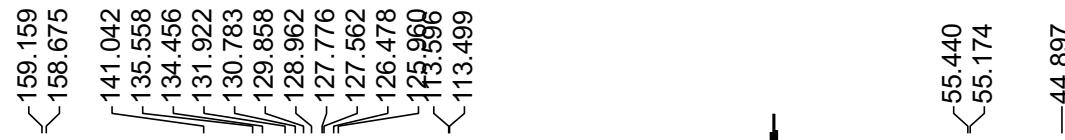


3dg (^1H NMR, 400 MHz, CDCl_3)





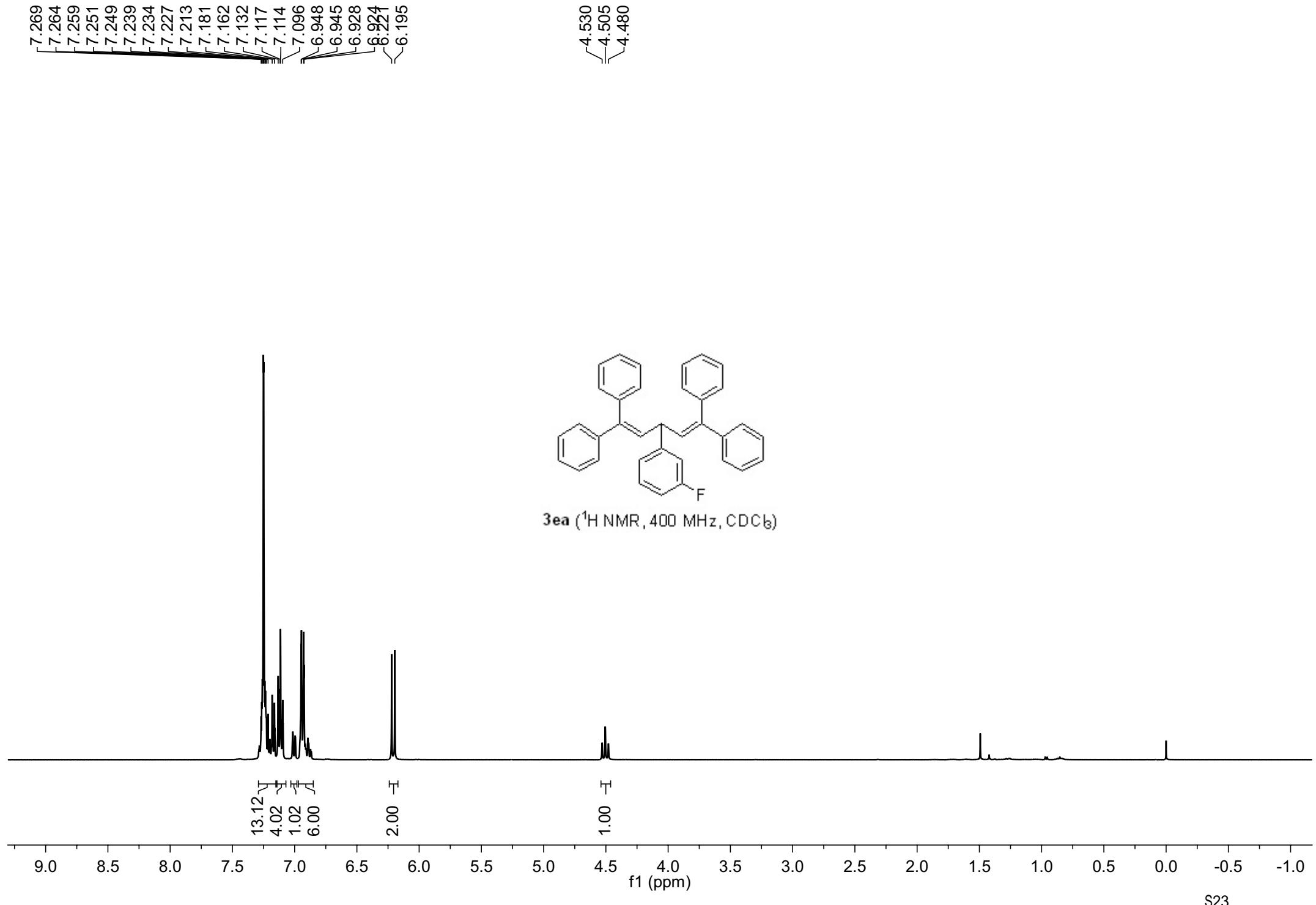
3dg (^{13}C { ^1H } NMR, 100 MHz, CDCl_3)

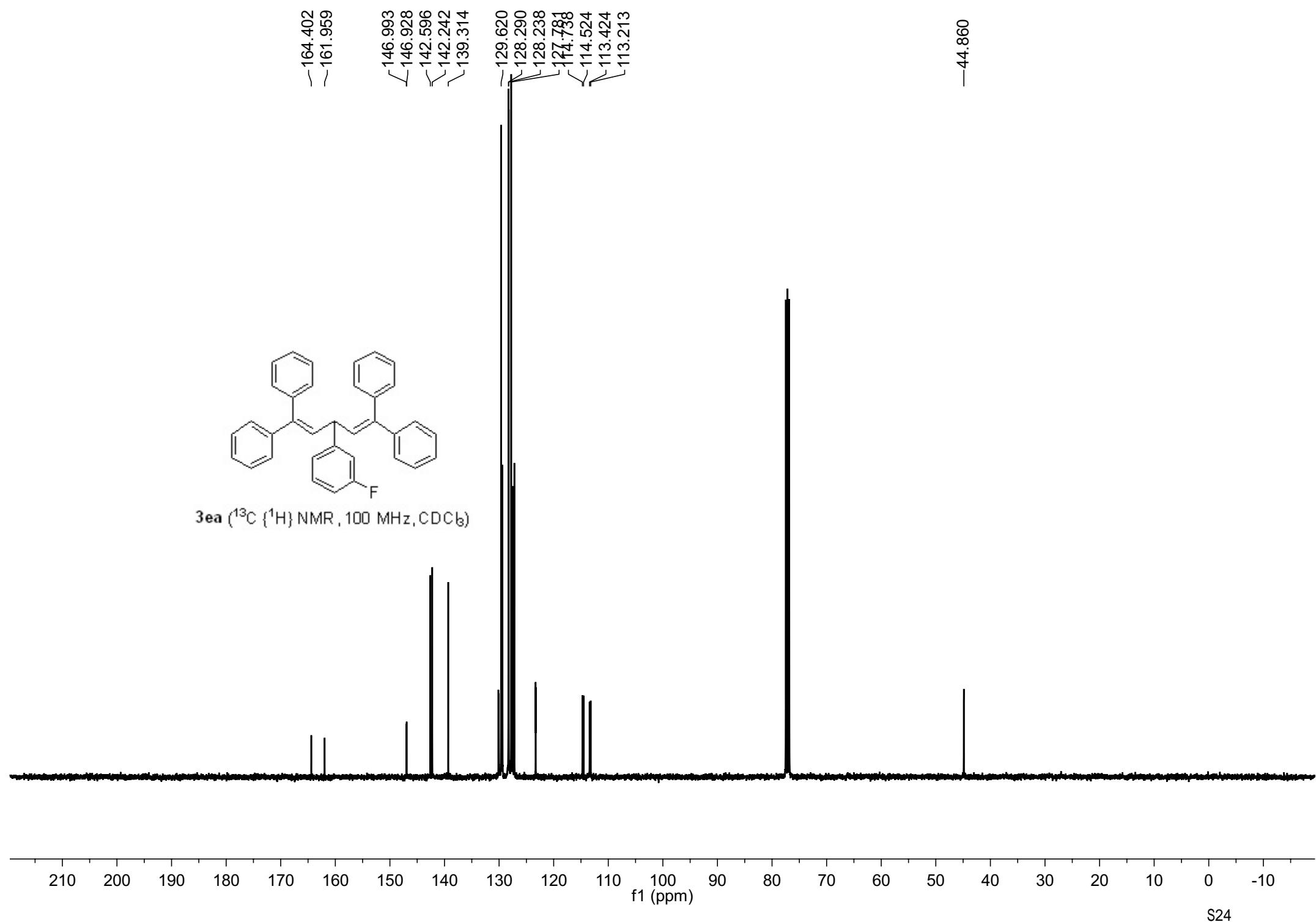


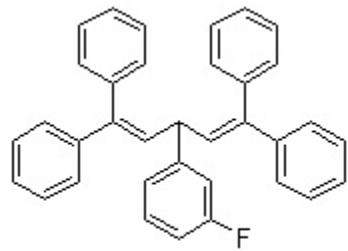
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f1 (ppm)

S22

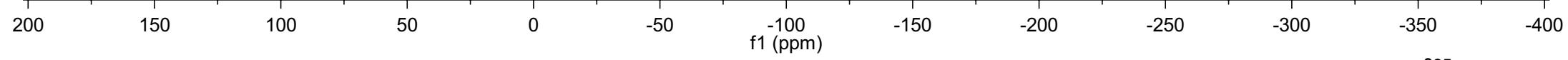


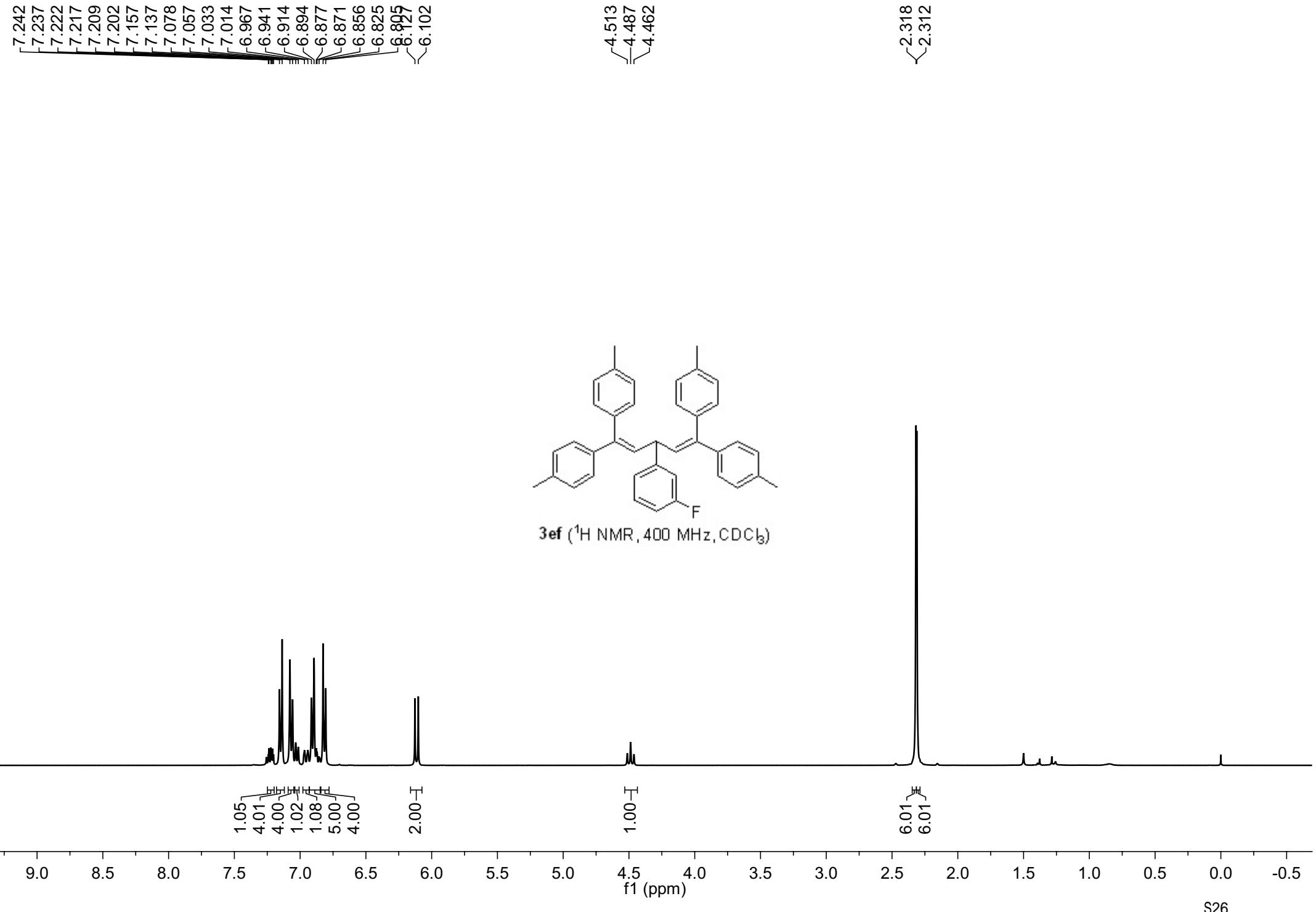




3ea (^{19}F NMR, 376 MHz, CDCl_3)

-112.732





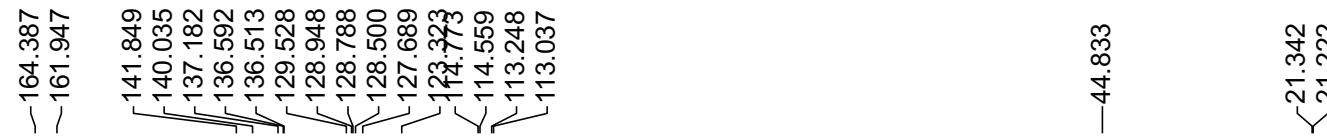
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4.487
4.462

2.318
2.312

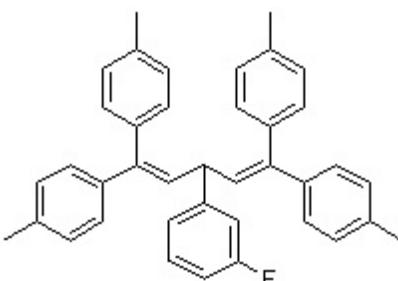
3ef (^1H NMR, 400 MHz, CDCl_3)



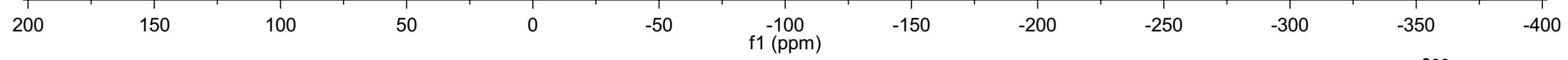
^{13}C { ^1H } NMR, 100 MHz, CDCl_3)

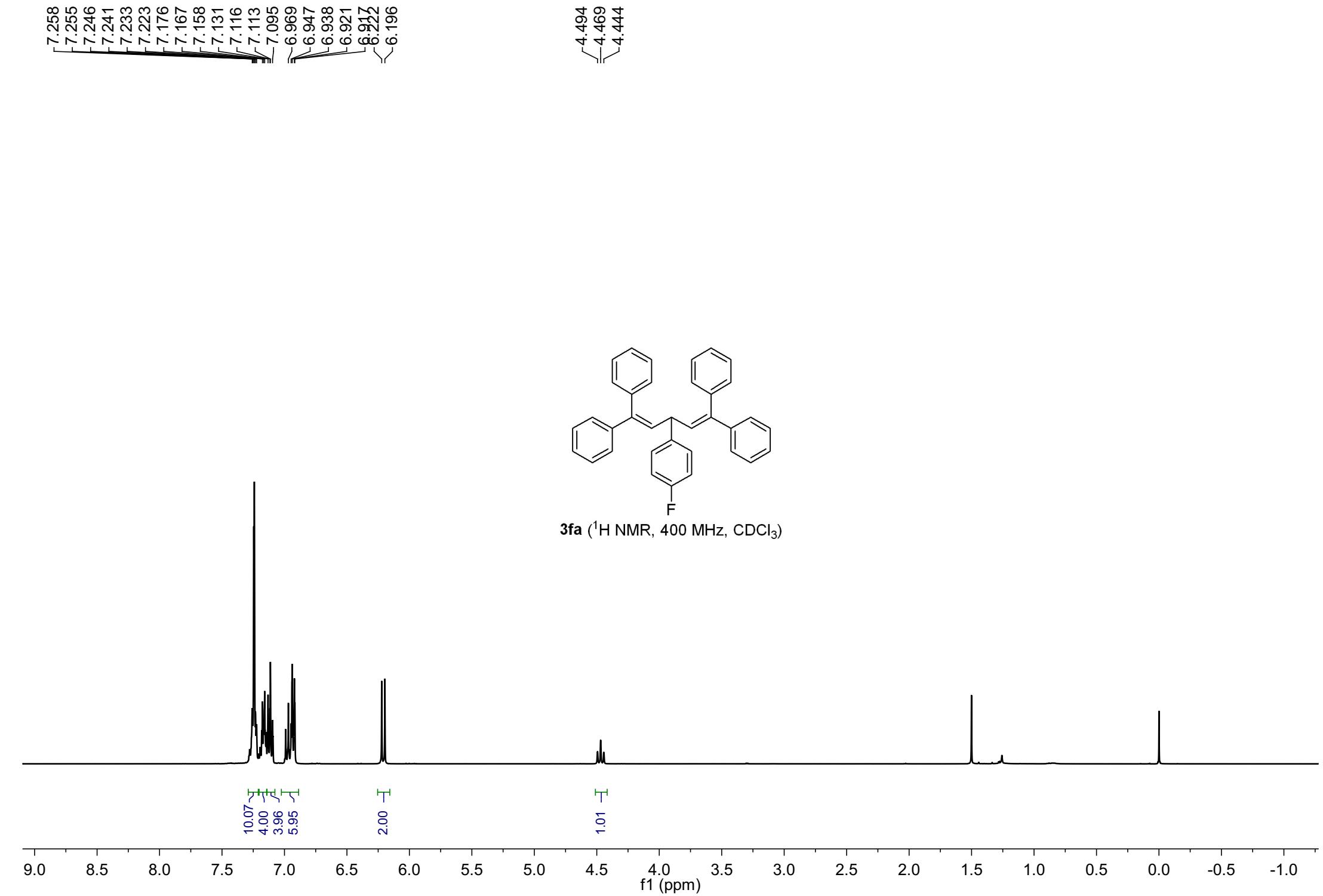


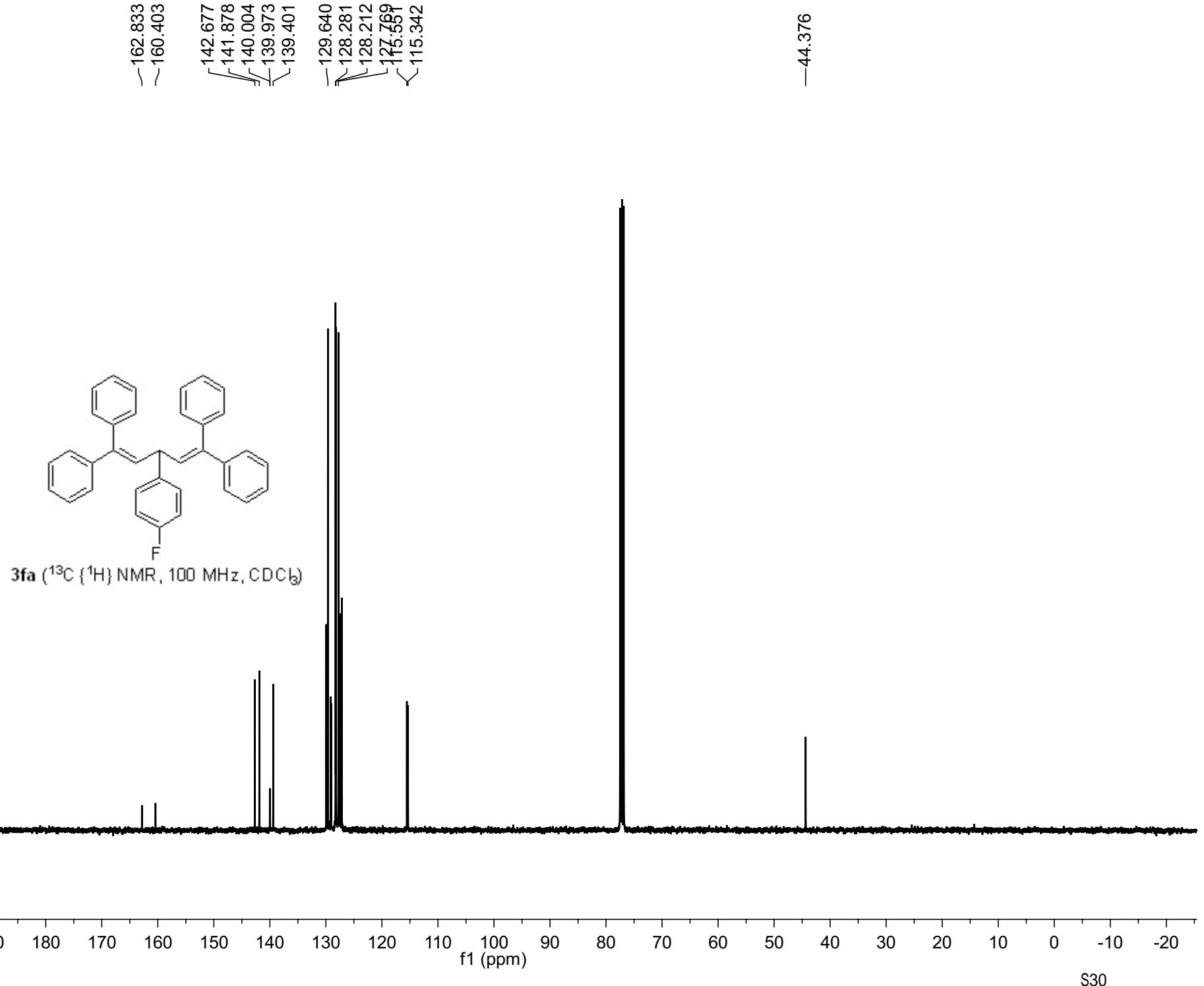
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-113.028



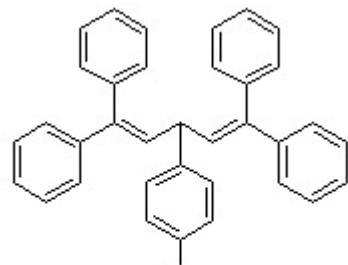
3ef (^{19}F NMR, 376 MHz, CDCl_3)



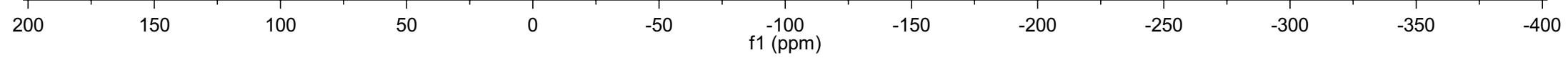




-116.884



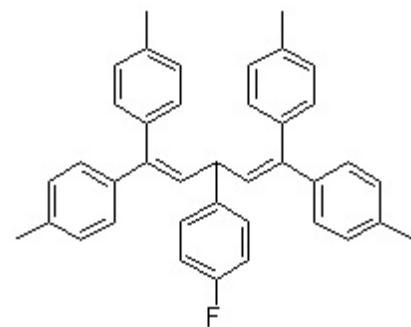
3fa (${}^{19}\text{F}$ NMR, 376 MHz, CDCl_3)



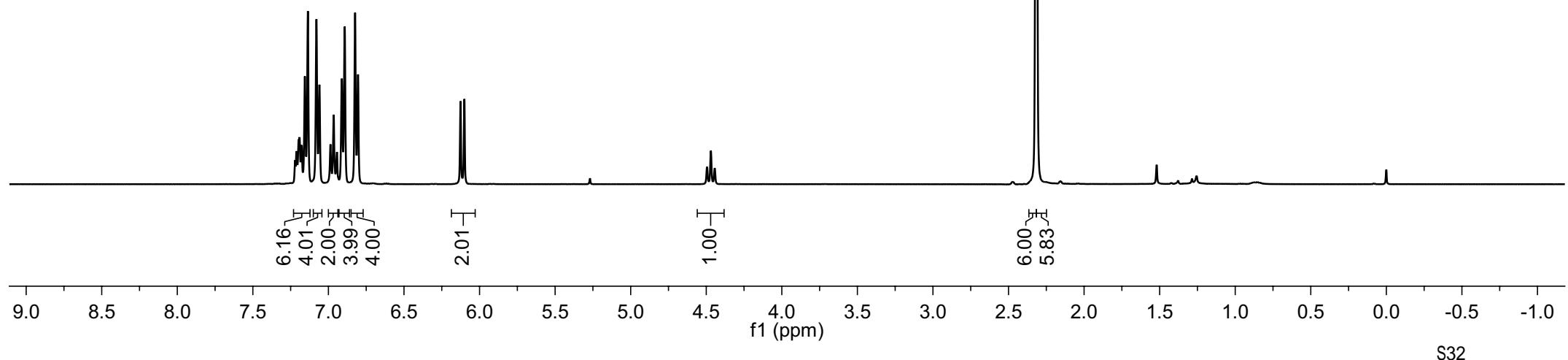
7.220
7.212
7.196
7.191
7.177
7.156
7.136
7.079
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6.987
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6.912
6.892
6.823
6.804
6.126
6.100

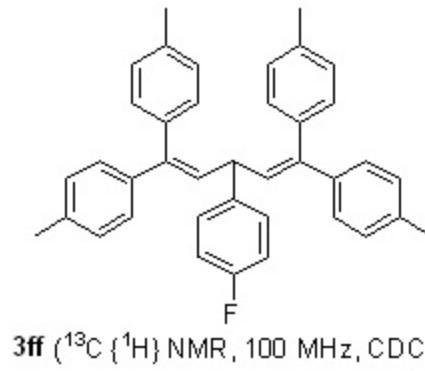
4.495
4.469
4.444

2.320
2.312



3ff (^1H NMR, 400 MHz, CDCl_3)





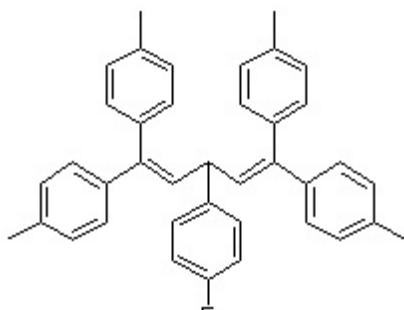
(^{13}C { ^1H } NMR, 100 MHz, CDCl_3)

—162.752
—160.324
141.454
140.097
137.133
136.636
136.472
129.530
129.016
128.935
128.756
127.884
115.205

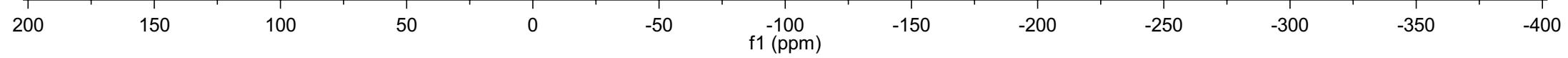
—44.269

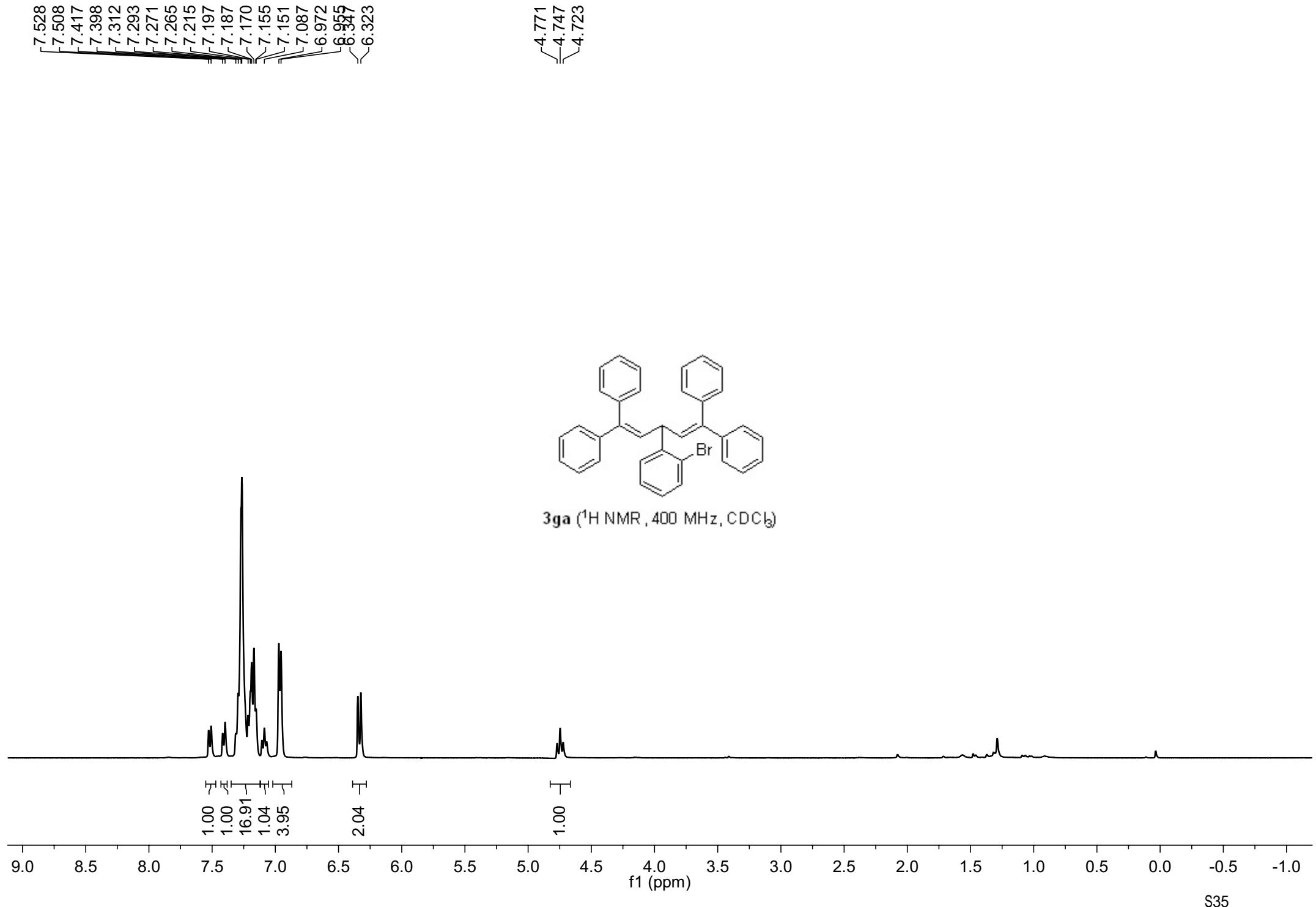
—21.347
—21.227

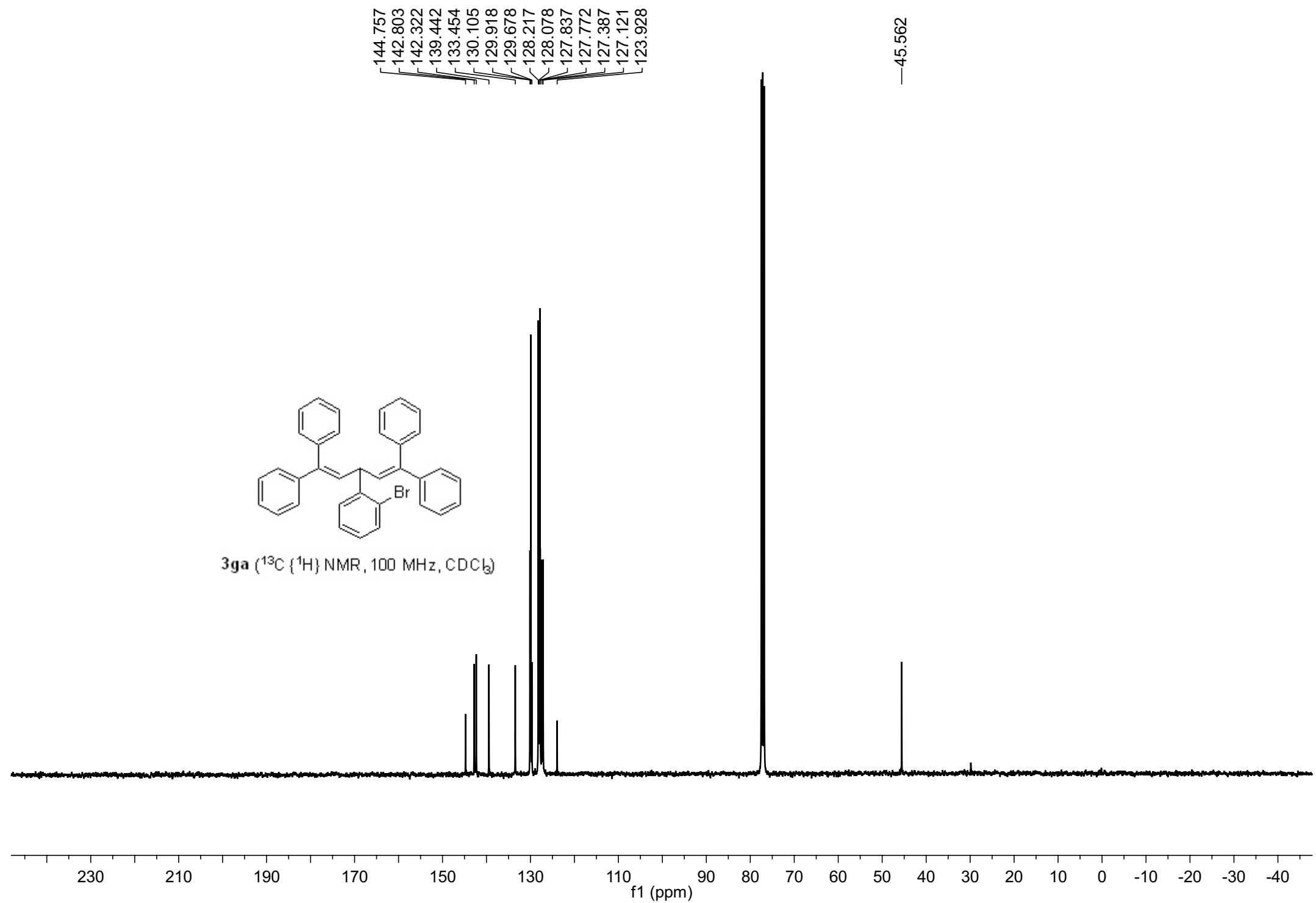
-117.183



3ff (^{19}F NMR, 376 MHz, CDCl_3)



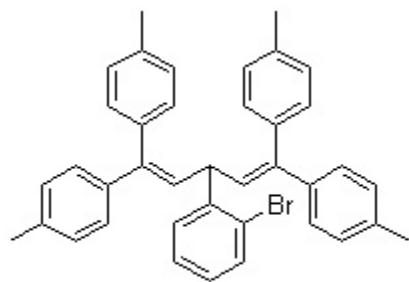




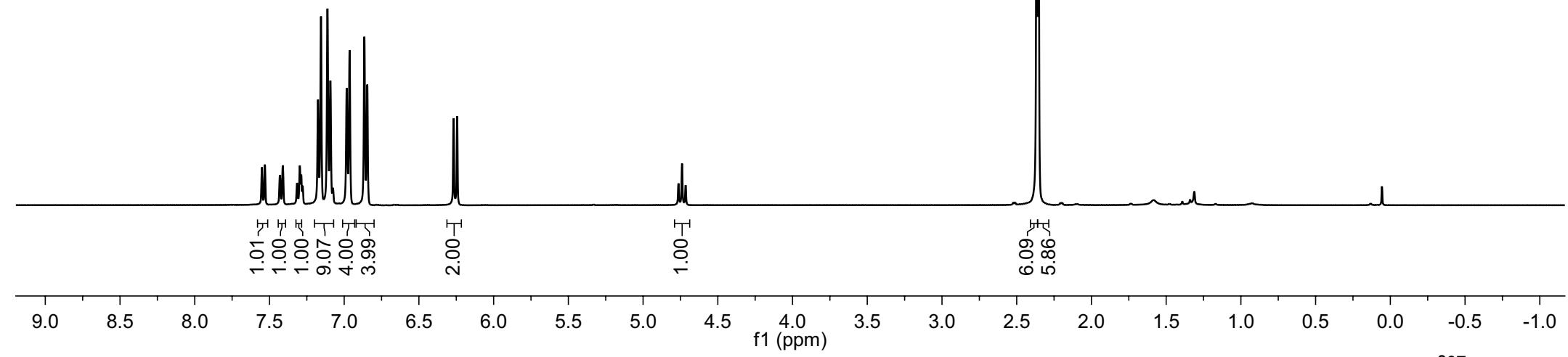
7.550
7.531
7.430
7.411
7.315
7.297
7.287
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7.112
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6.964
6.944
6.865
6.846
6.268
6.244

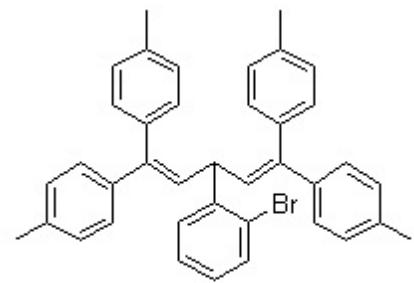
4.763
4.739
4.715

2.366
2.354



3gf (^1H NMR, 400 MHz, CDCl_3)



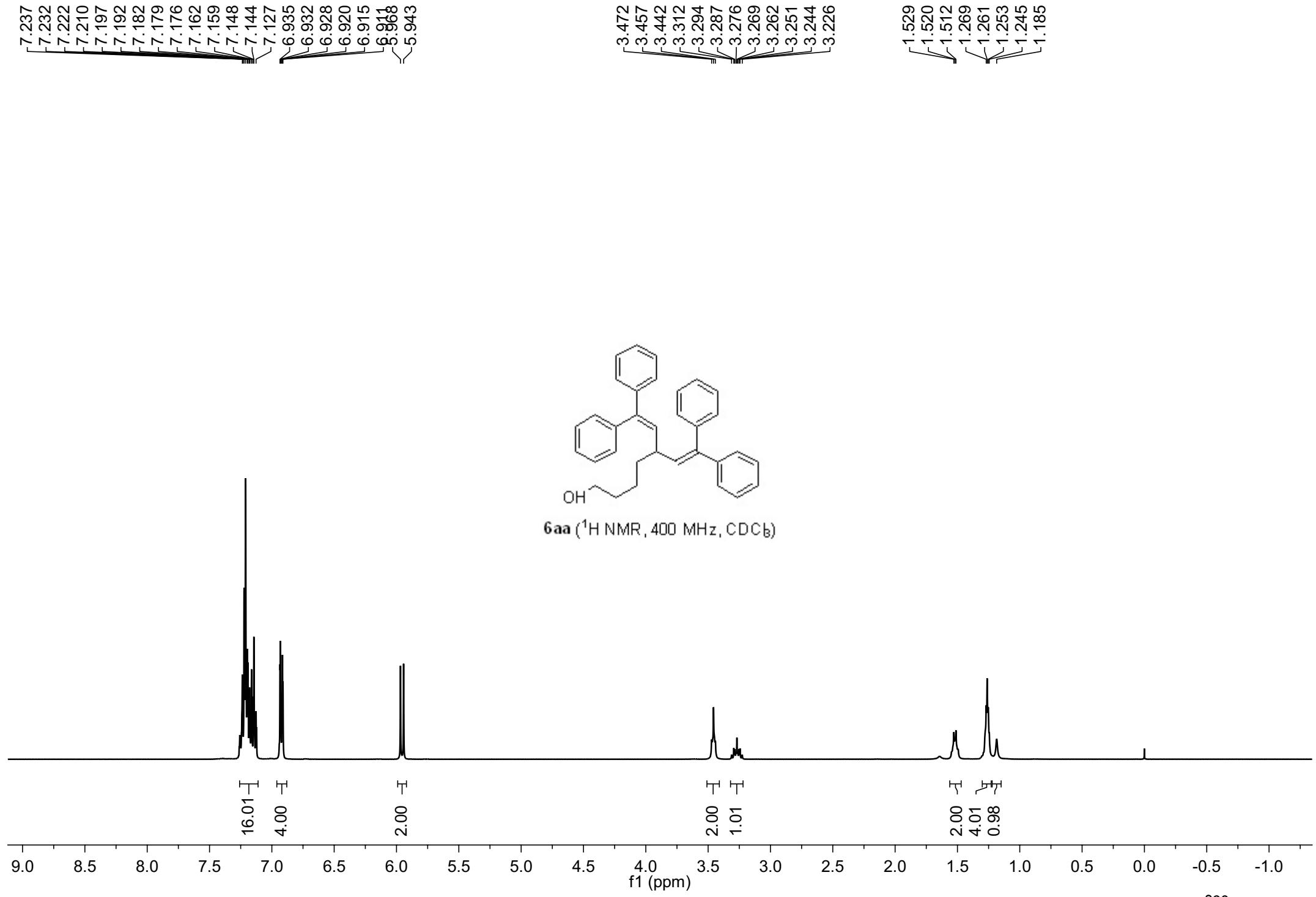


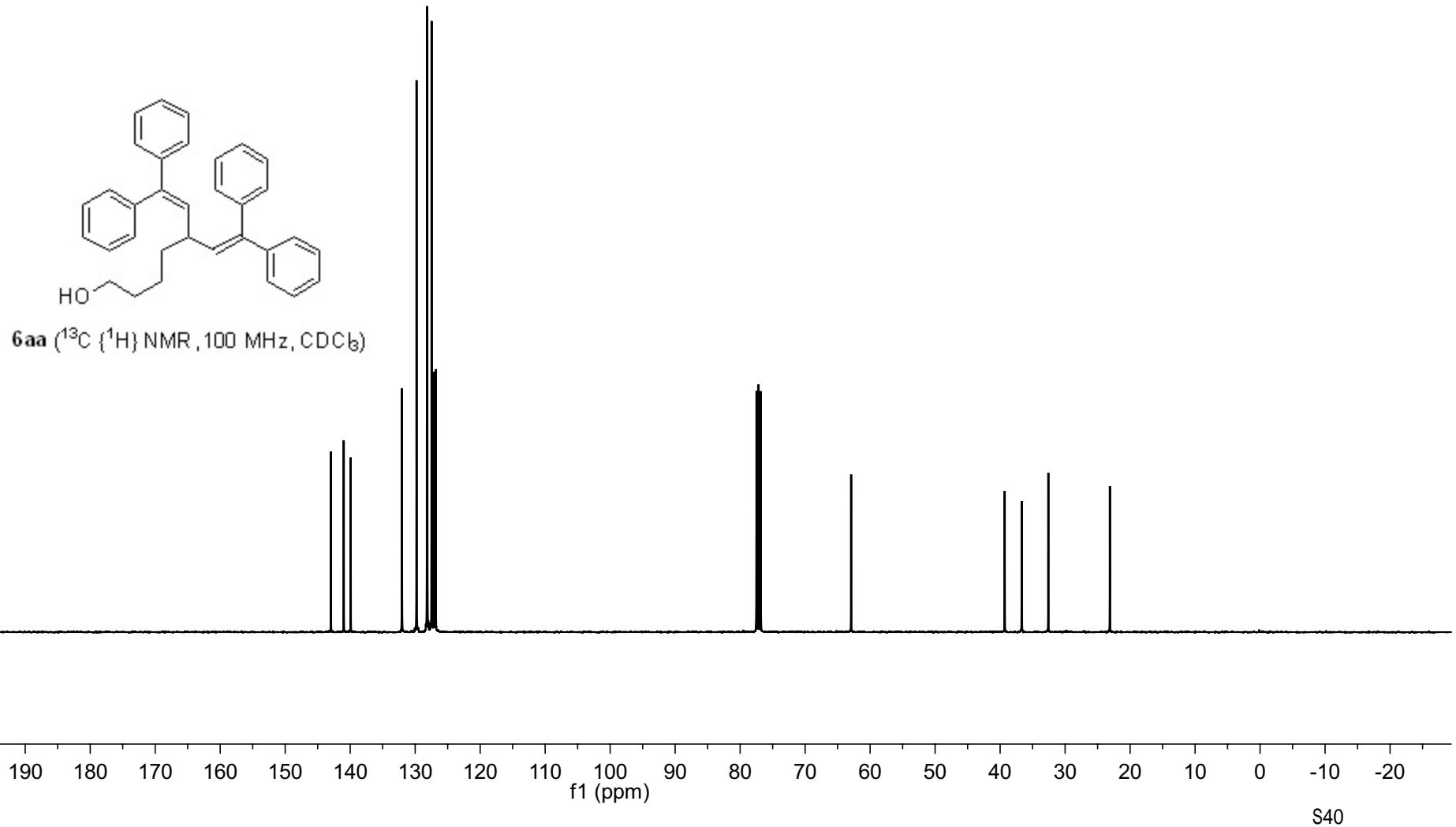
3gf (^{13}C { ^1H } NMR, 100 MHz, CDCl_3)

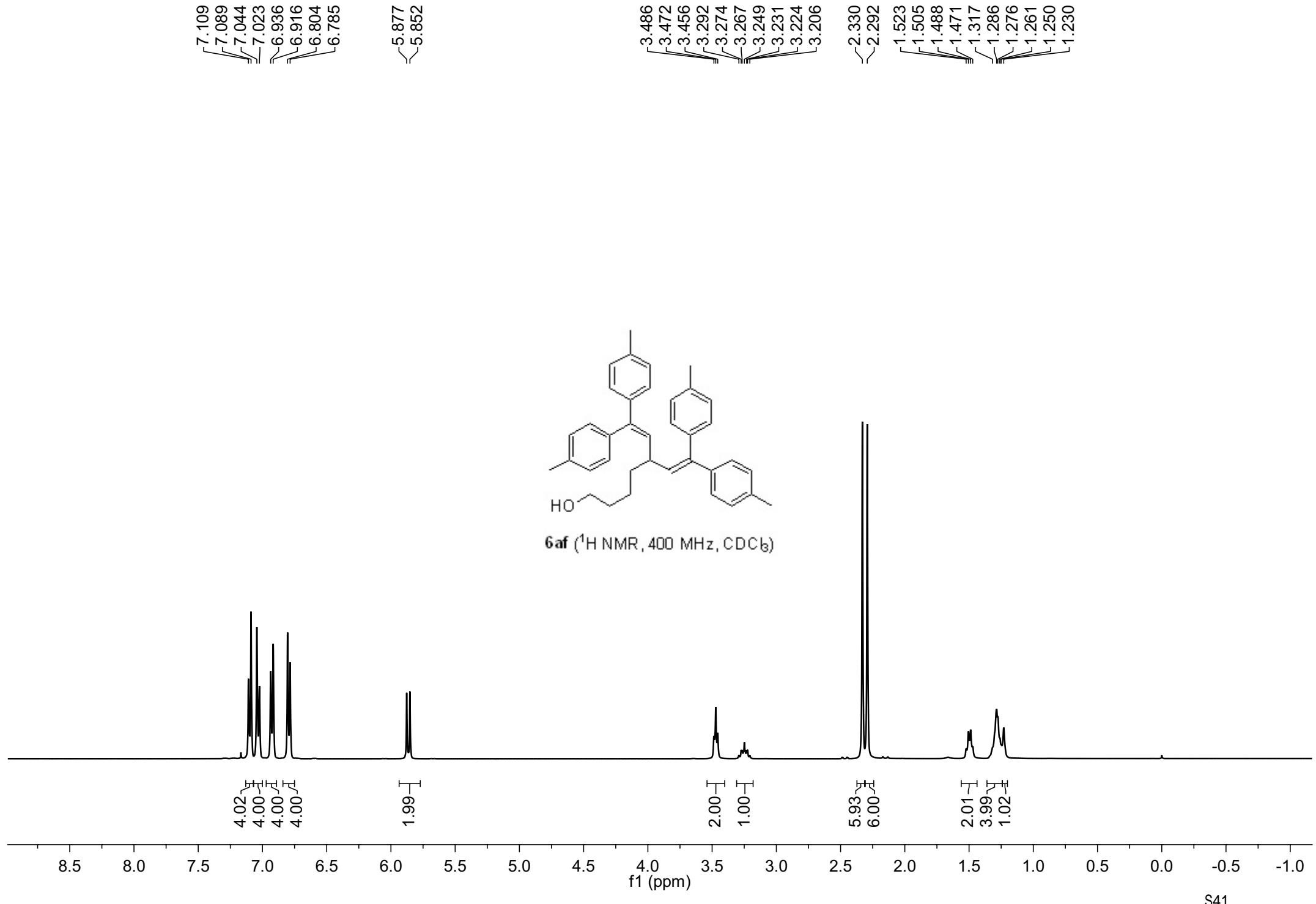


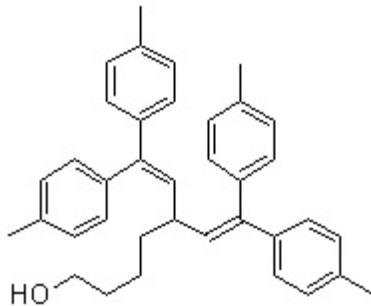
—45.597

<21.370
<21.210

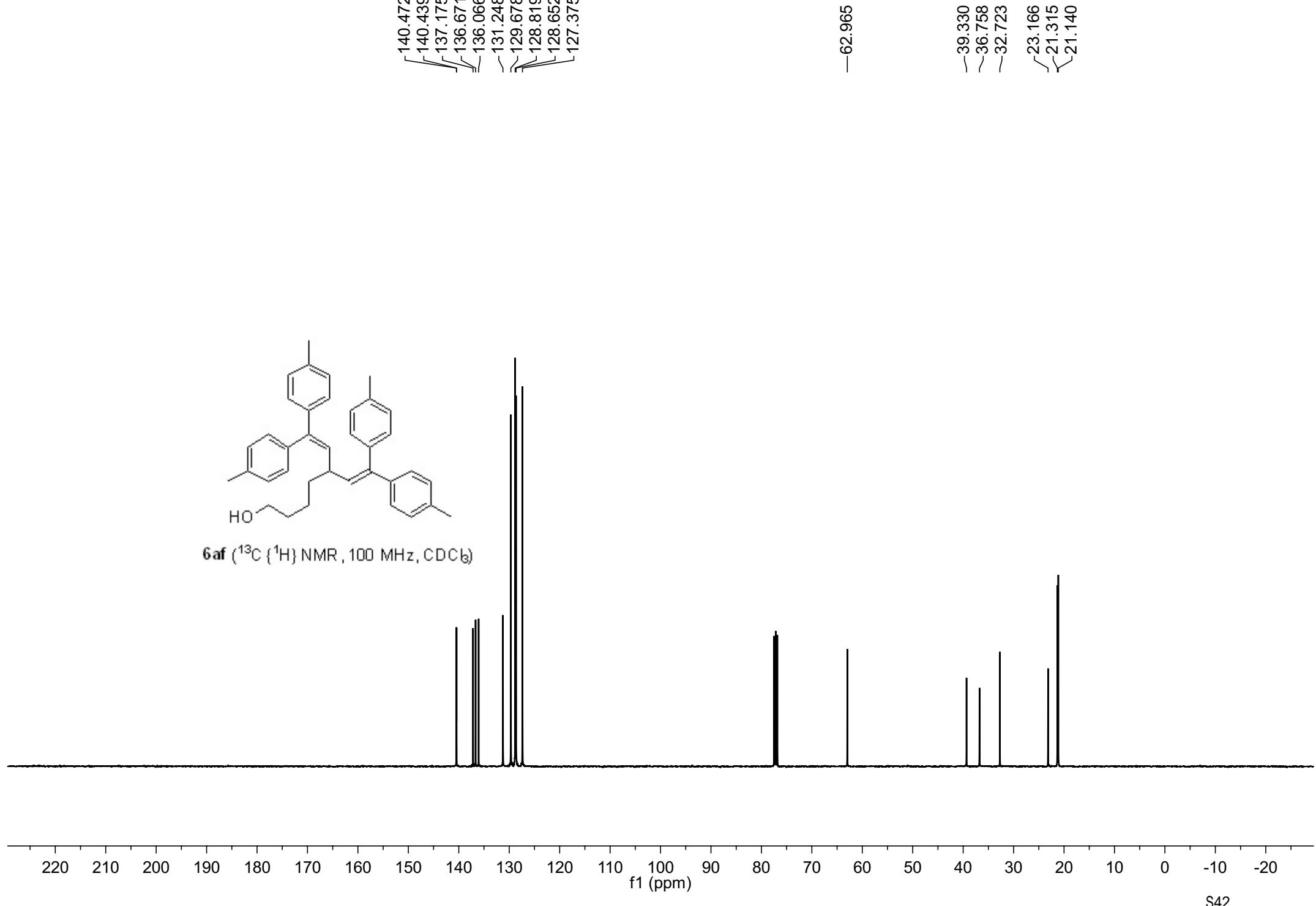


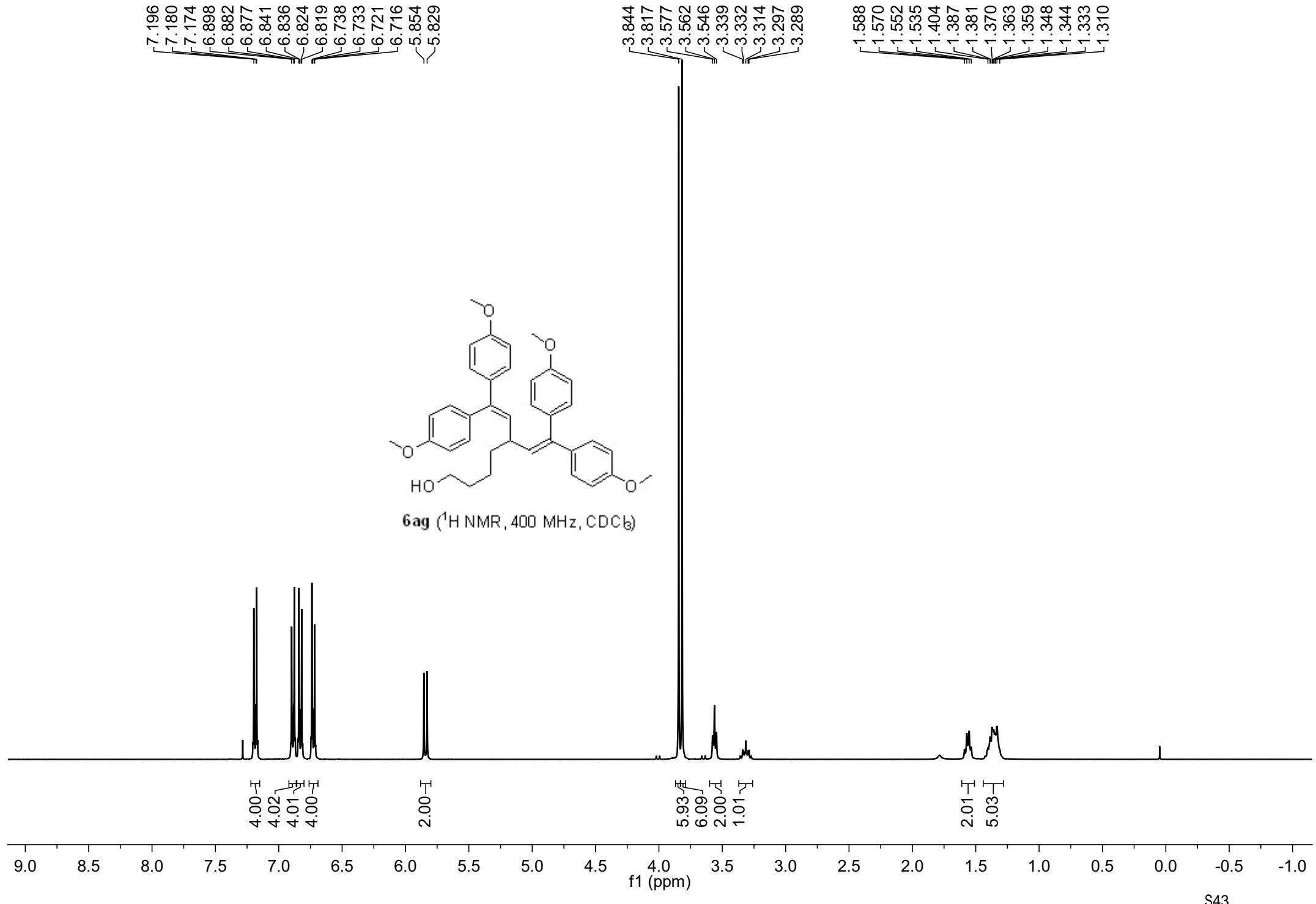


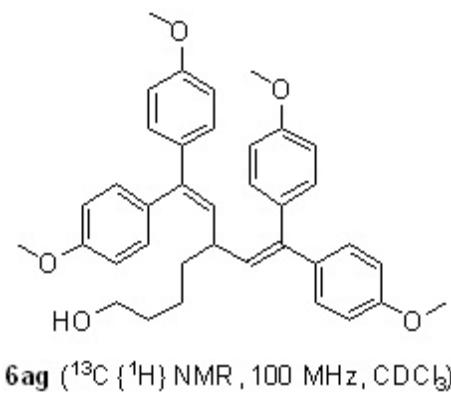


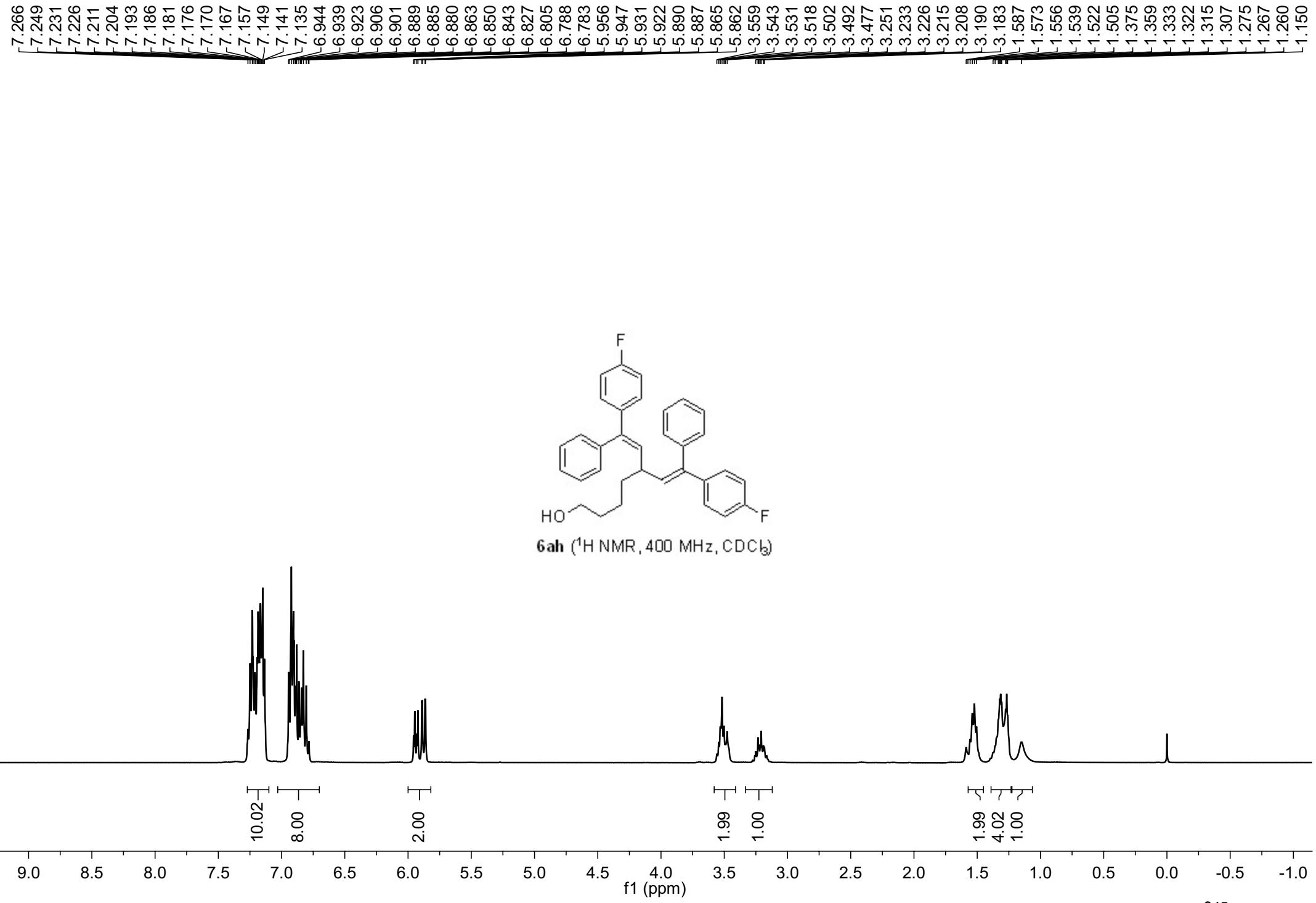


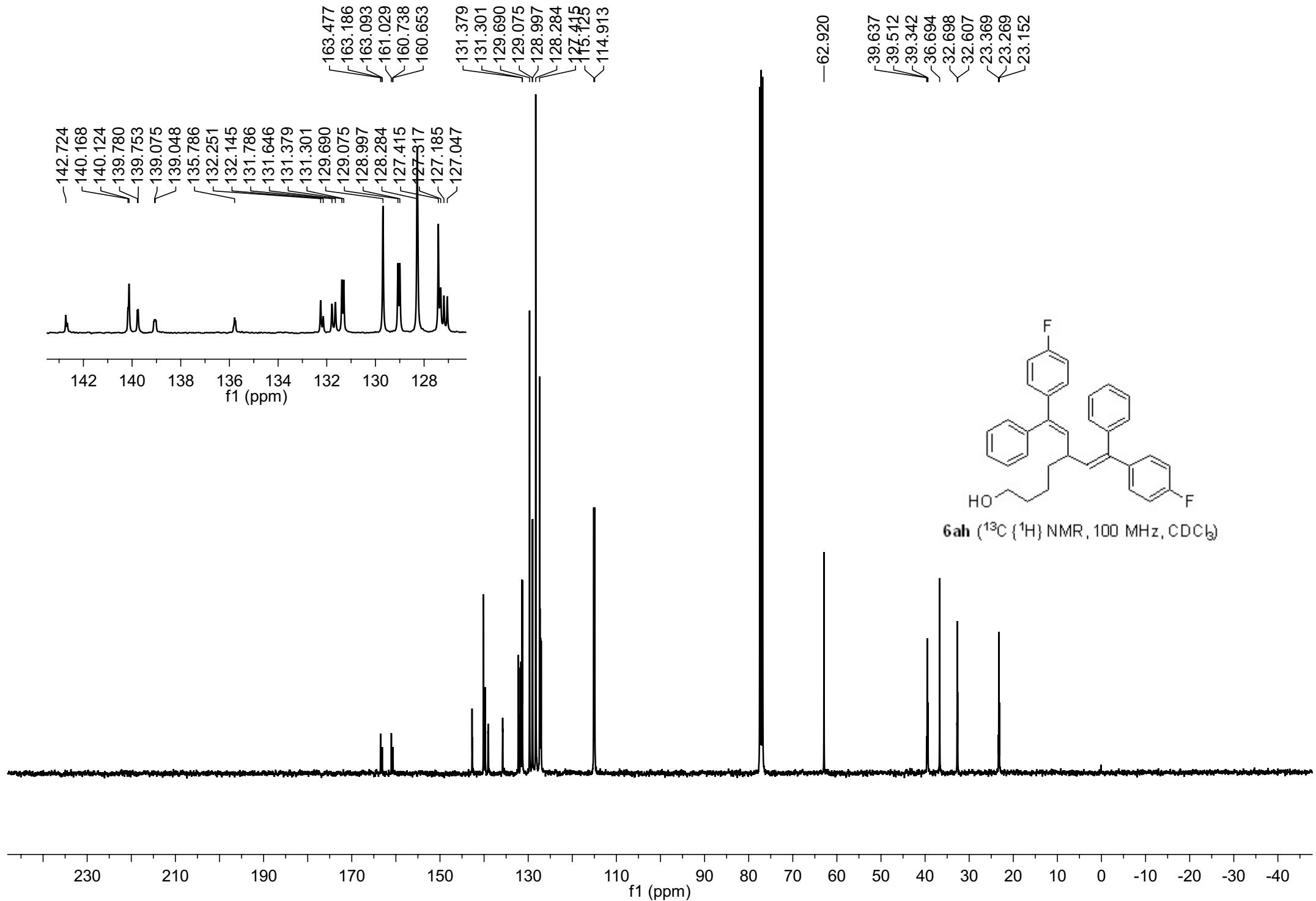
6af (¹³C {¹H} NMR, 100 MHz, CDCl₃)

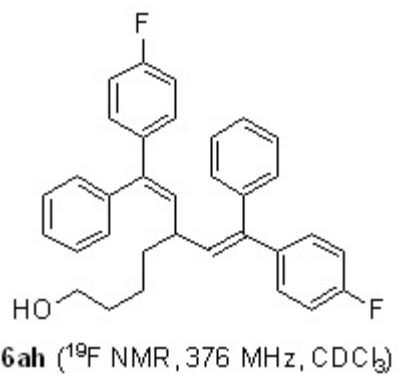




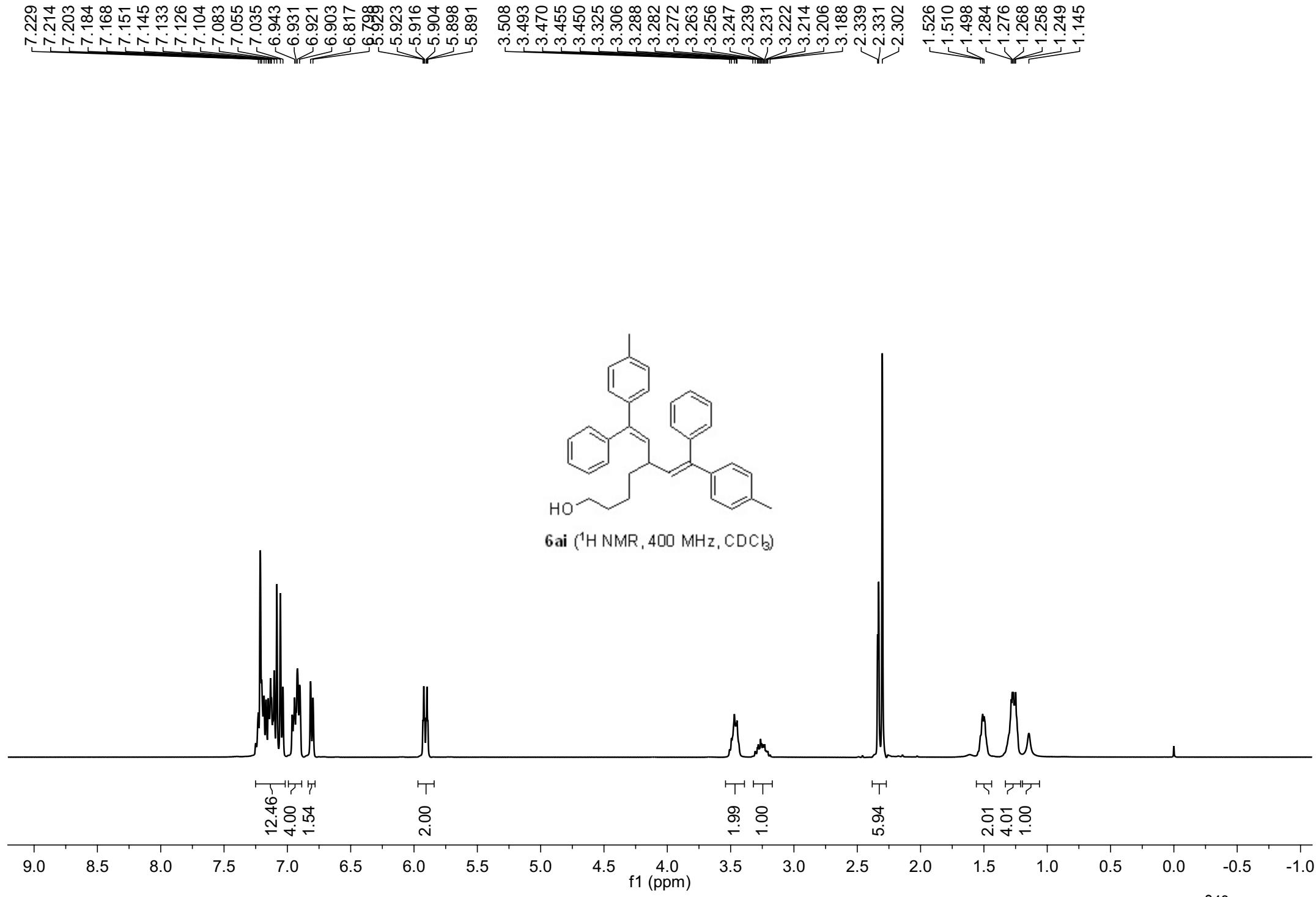


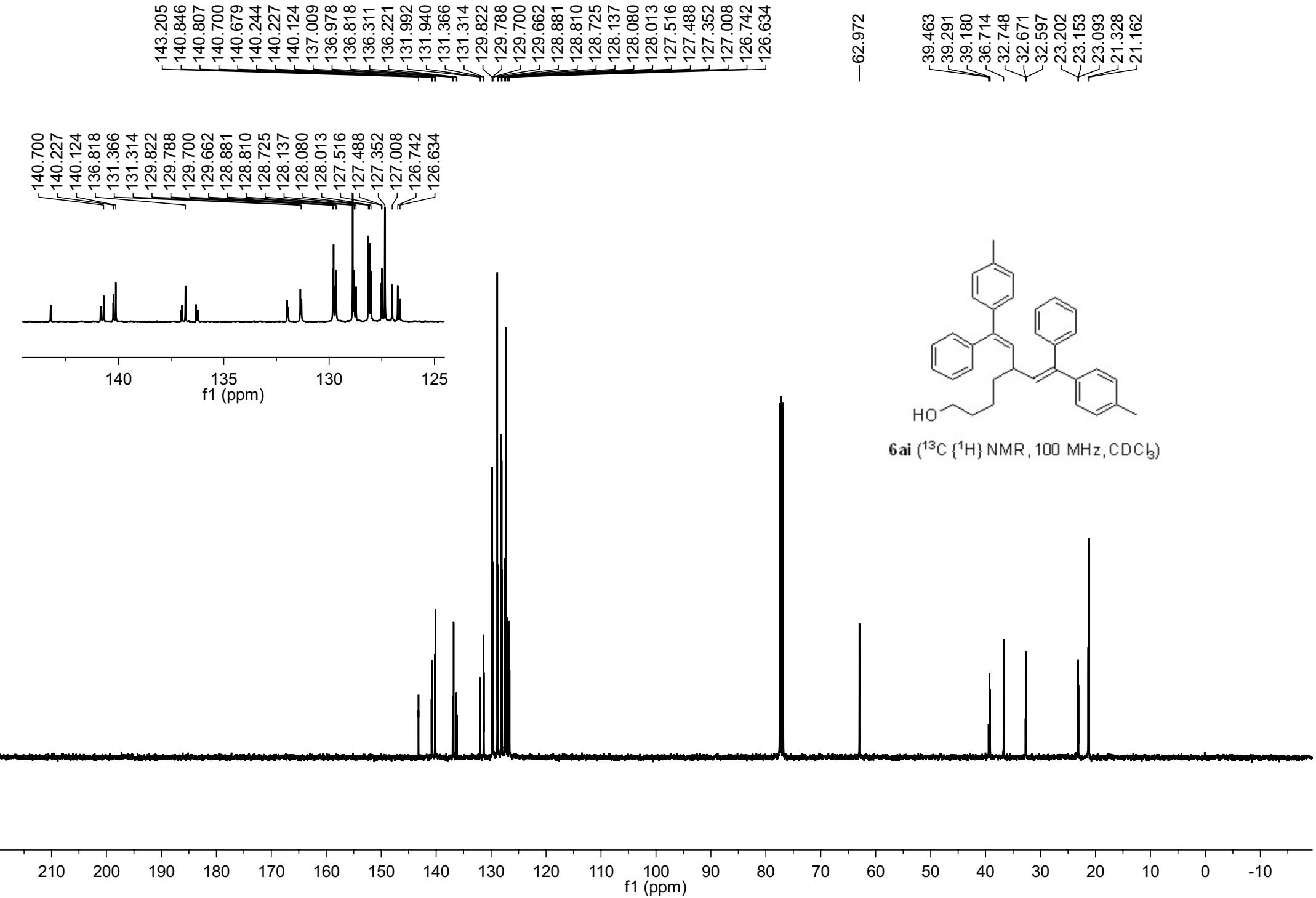


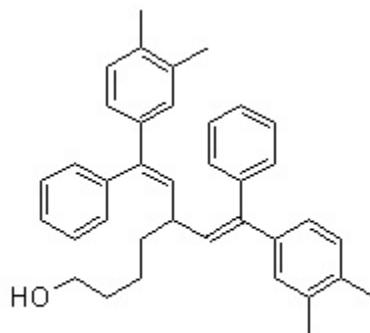
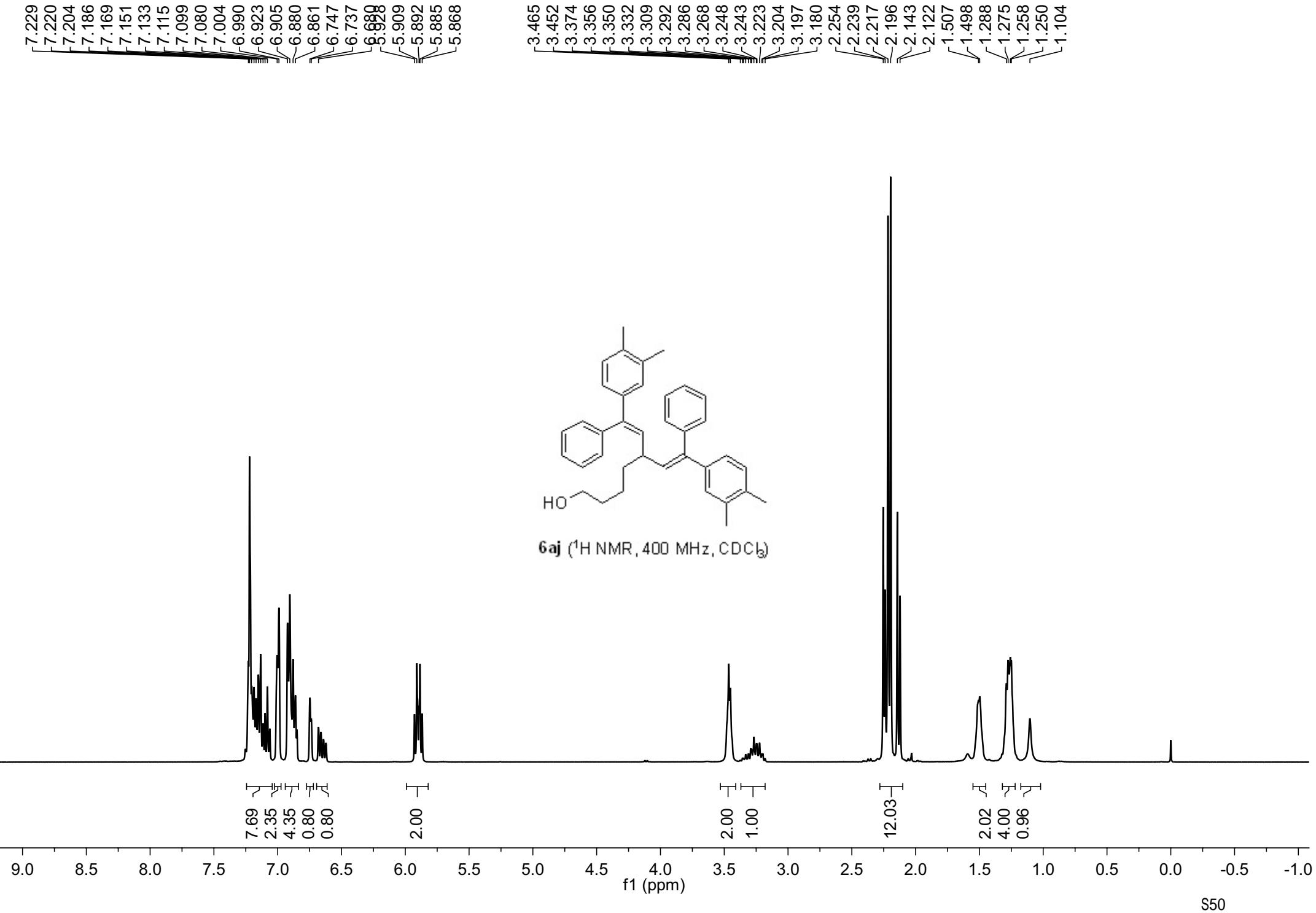




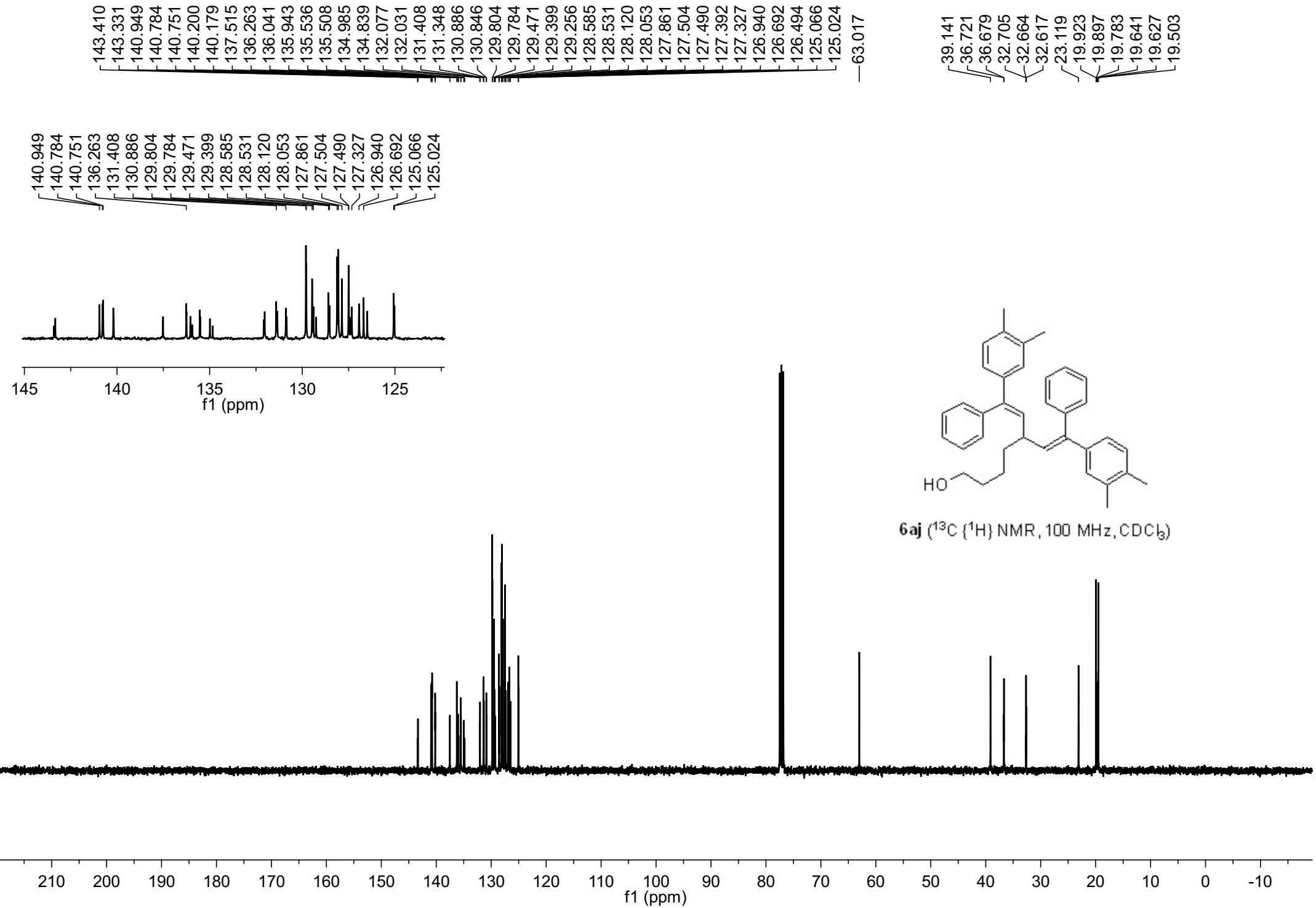
-115.30
-115.65
-115.69
-115.74

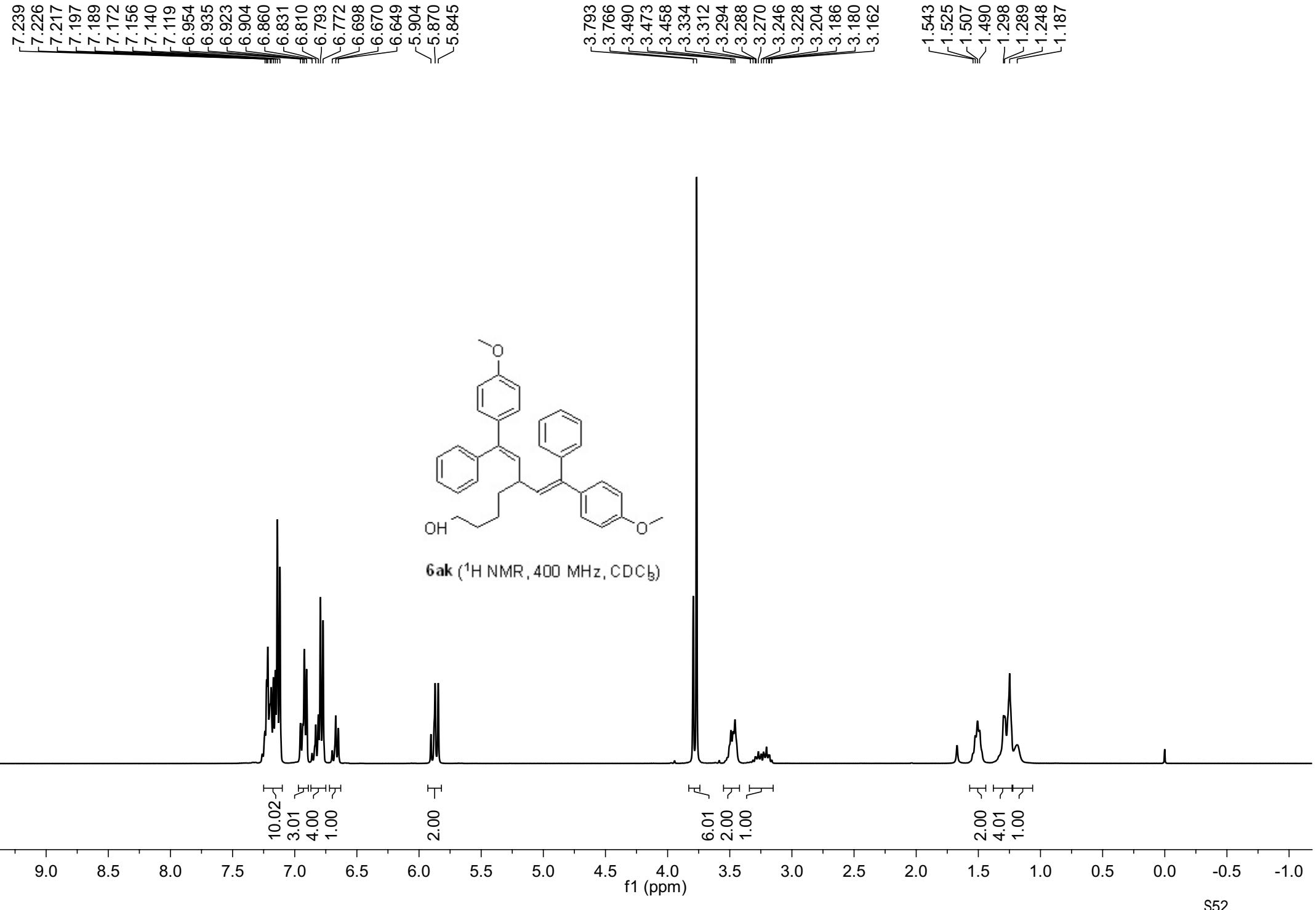


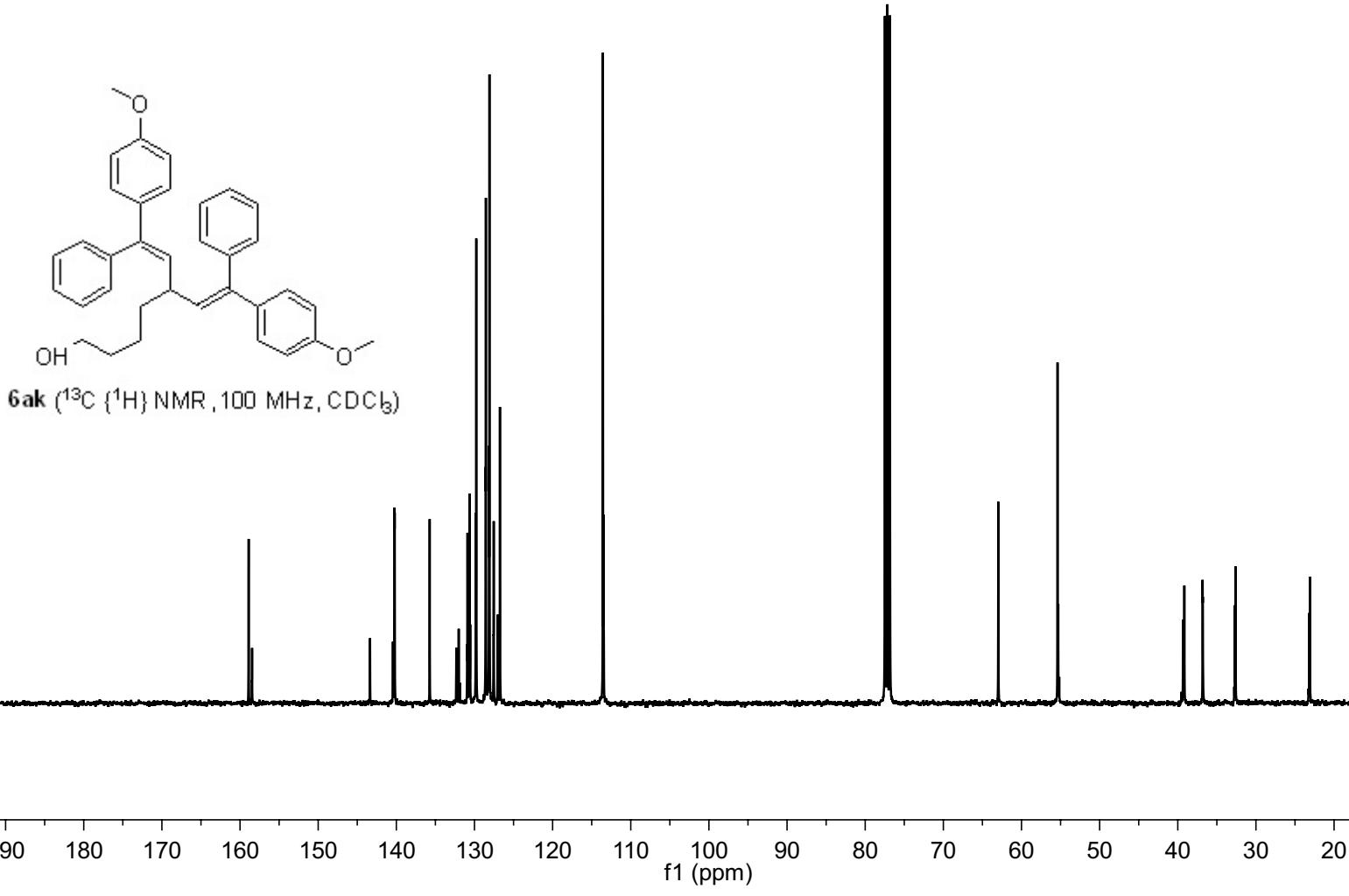




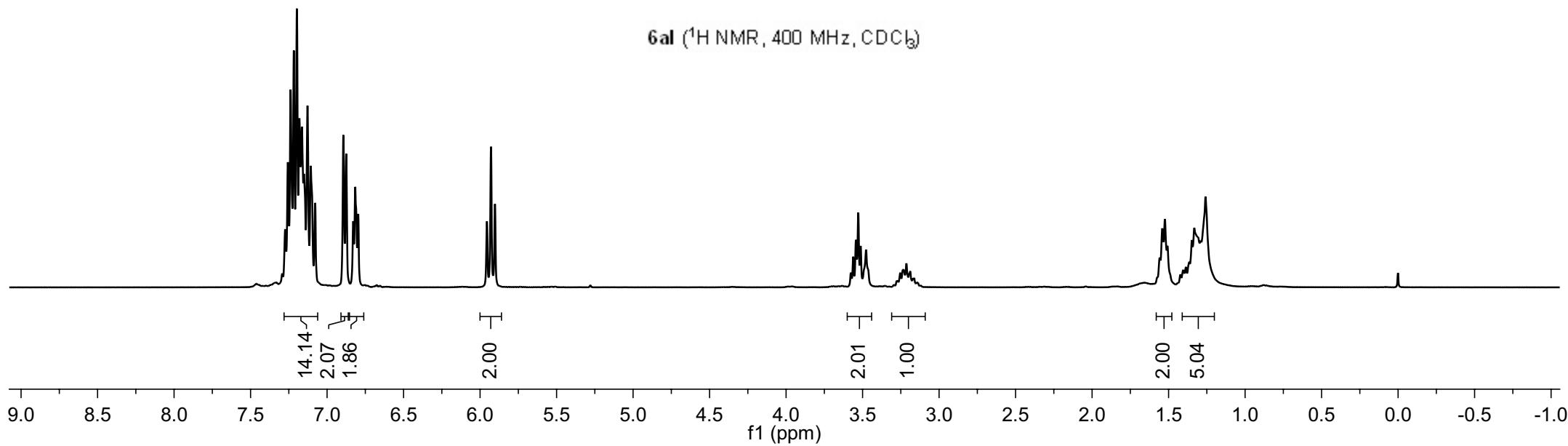
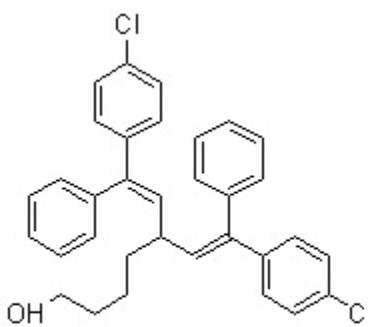
6aj (¹H NMR, 400 MHz, CDCl₃)

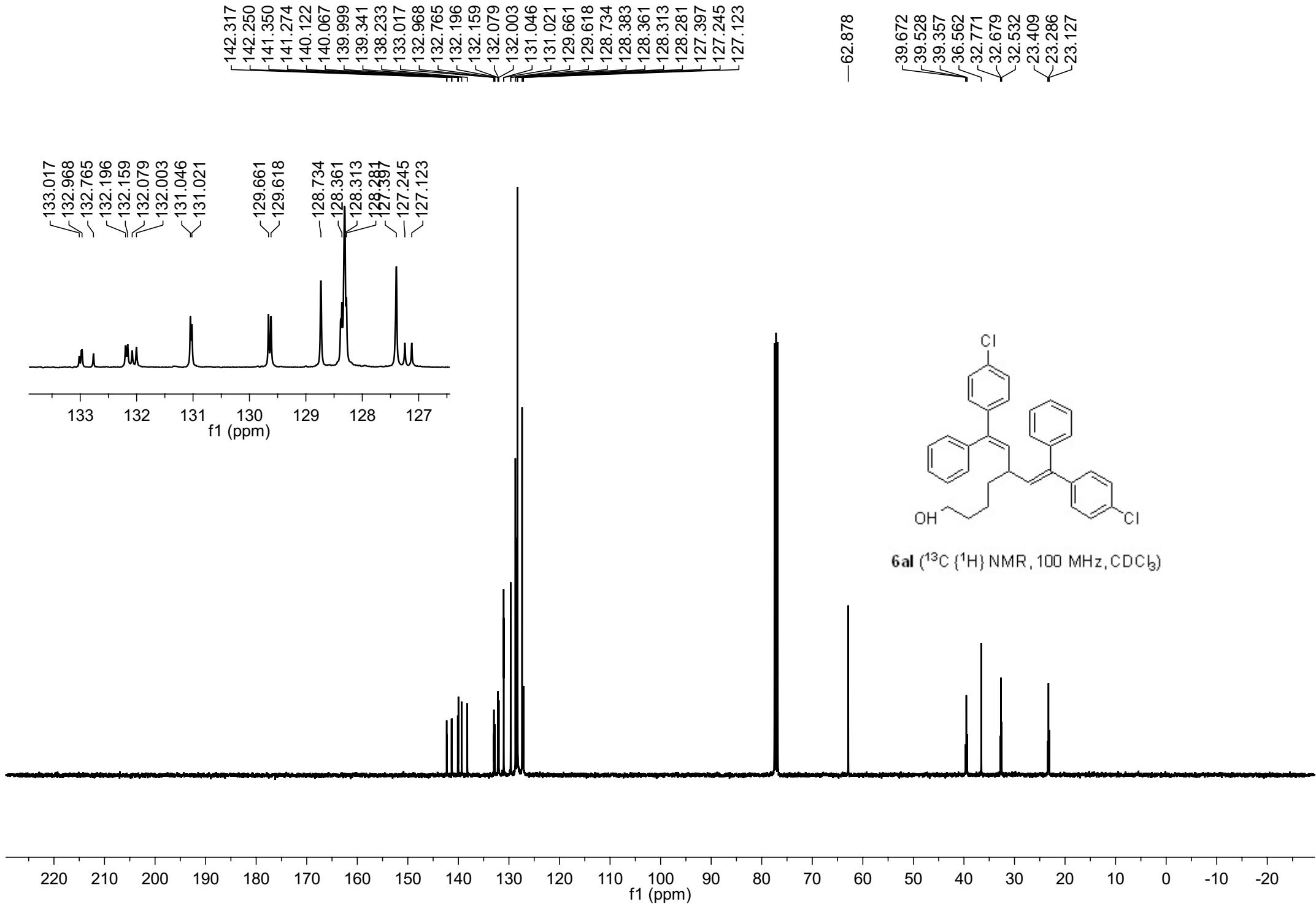


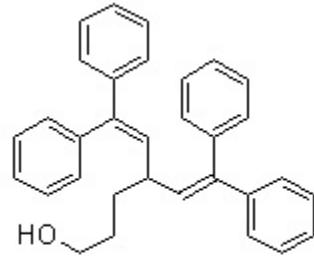
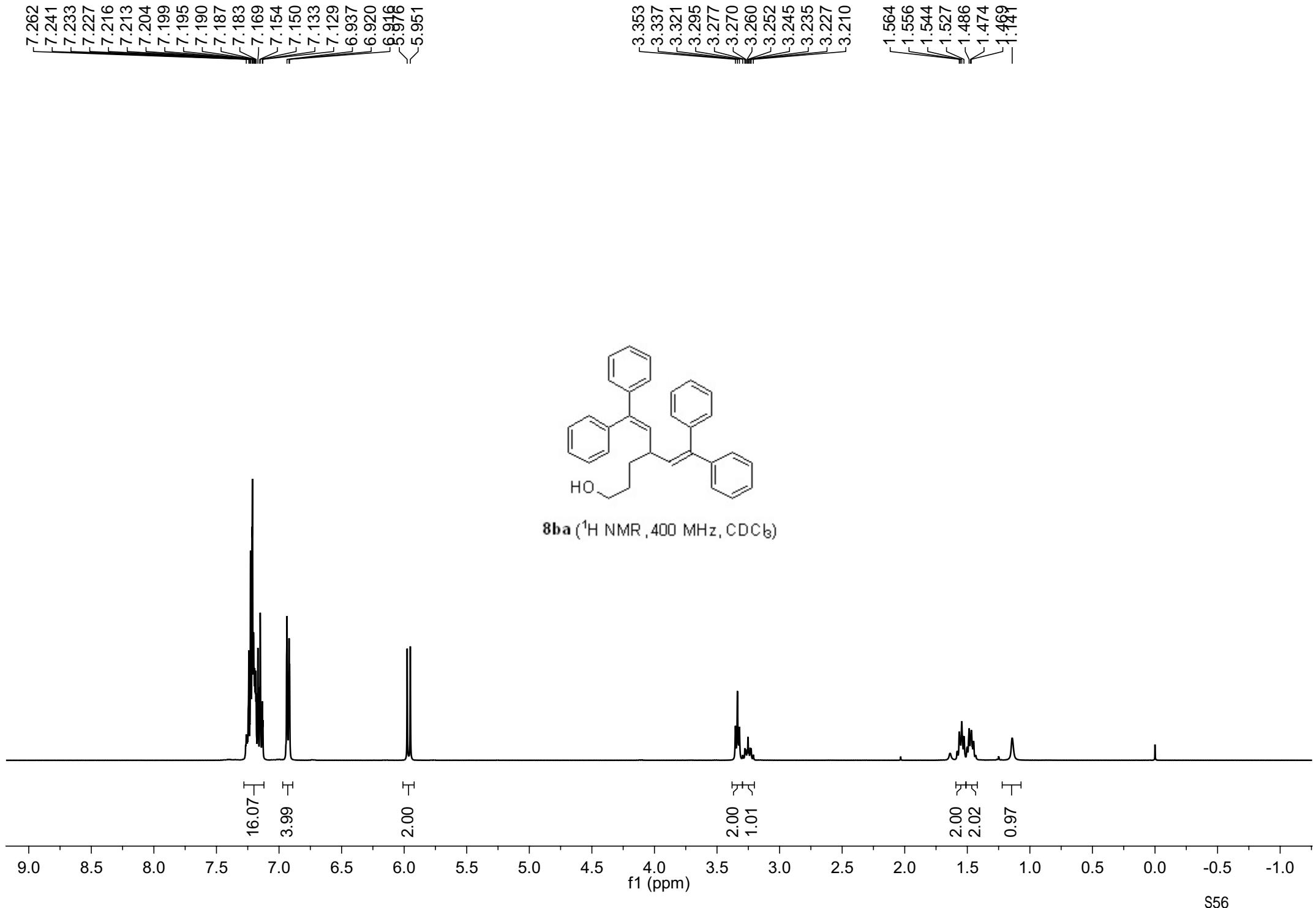


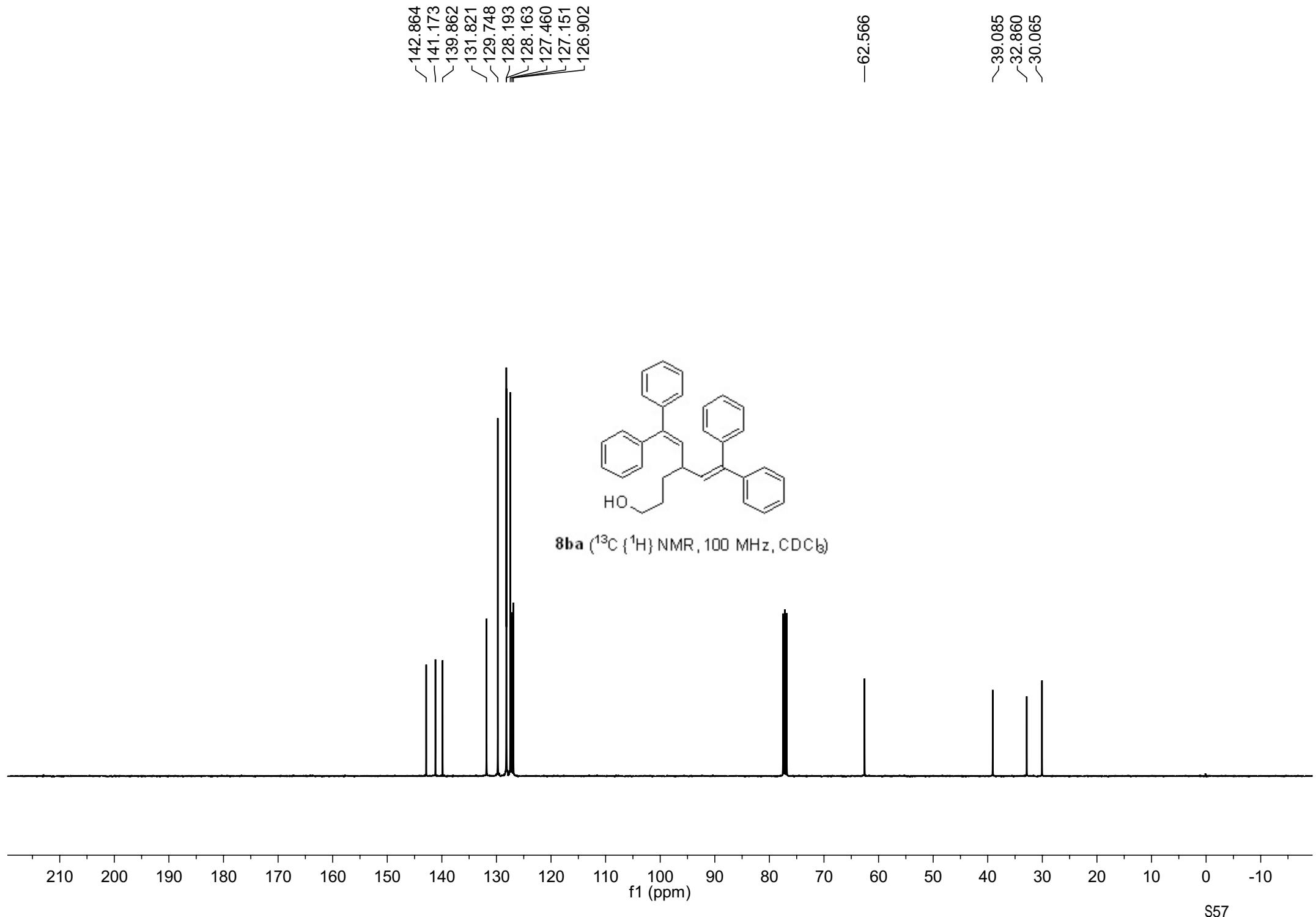


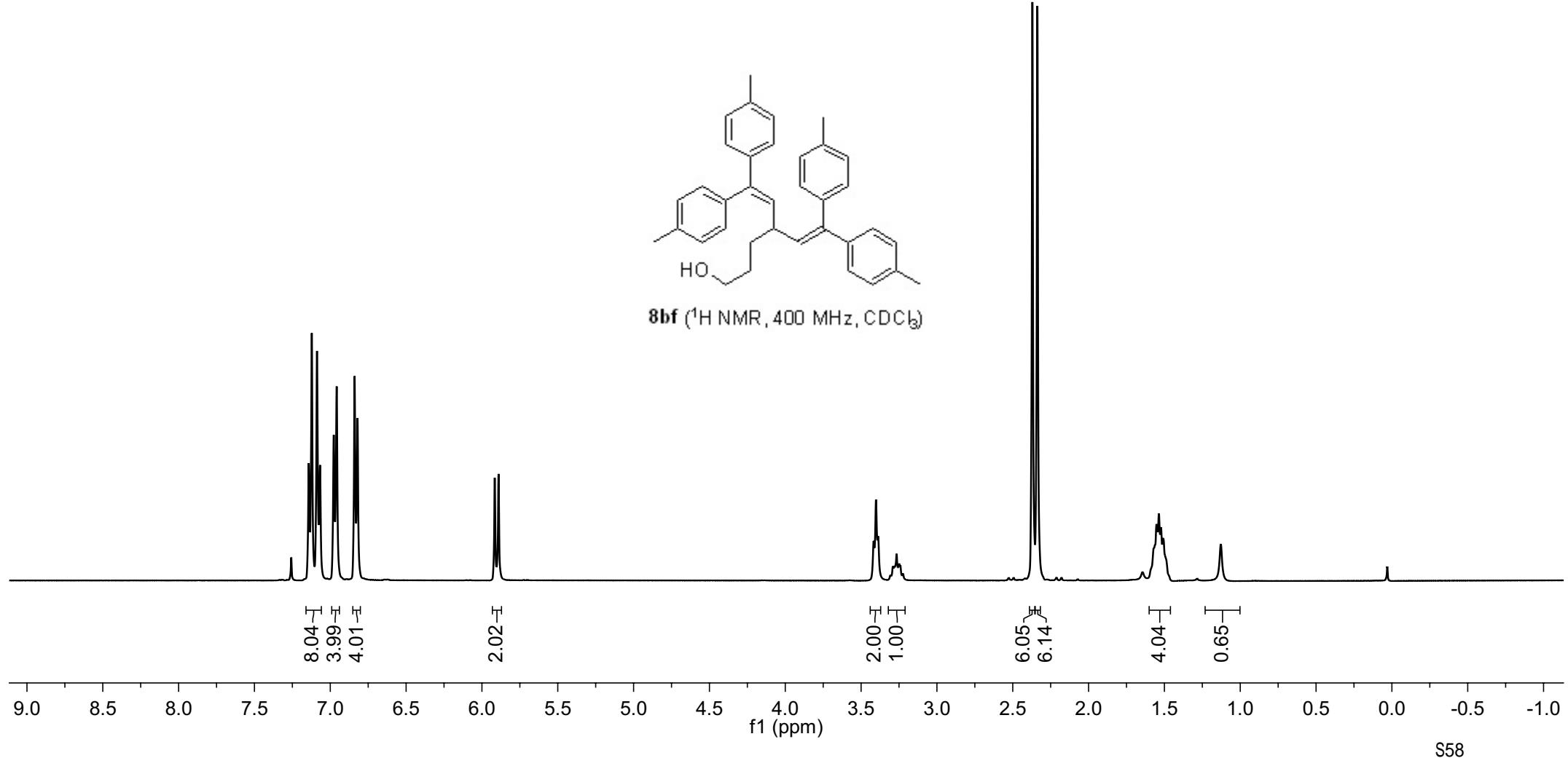
7.274
7.256
7.238
7.217
7.197
7.181
7.164
7.151
7.128
7.106
7.078
6.894
6.875
6.829
6.816
6.797
5.955
5.929
5.903
3.661
3.648
3.633
3.615
3.577
3.561
3.544
3.528
3.512
3.477
3.383
3.351
3.295
3.277
3.270
3.253
3.232
3.213
3.189
3.170
3.163
3.145
3.120
1.574
1.558
1.541
1.524
1.507
1.423
1.404
1.387
1.365
1.348
1.332
1.291
1.258

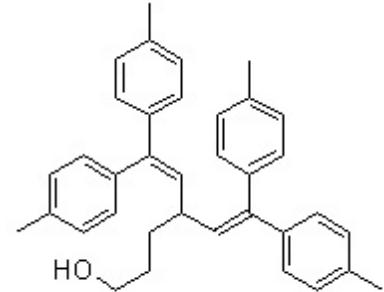




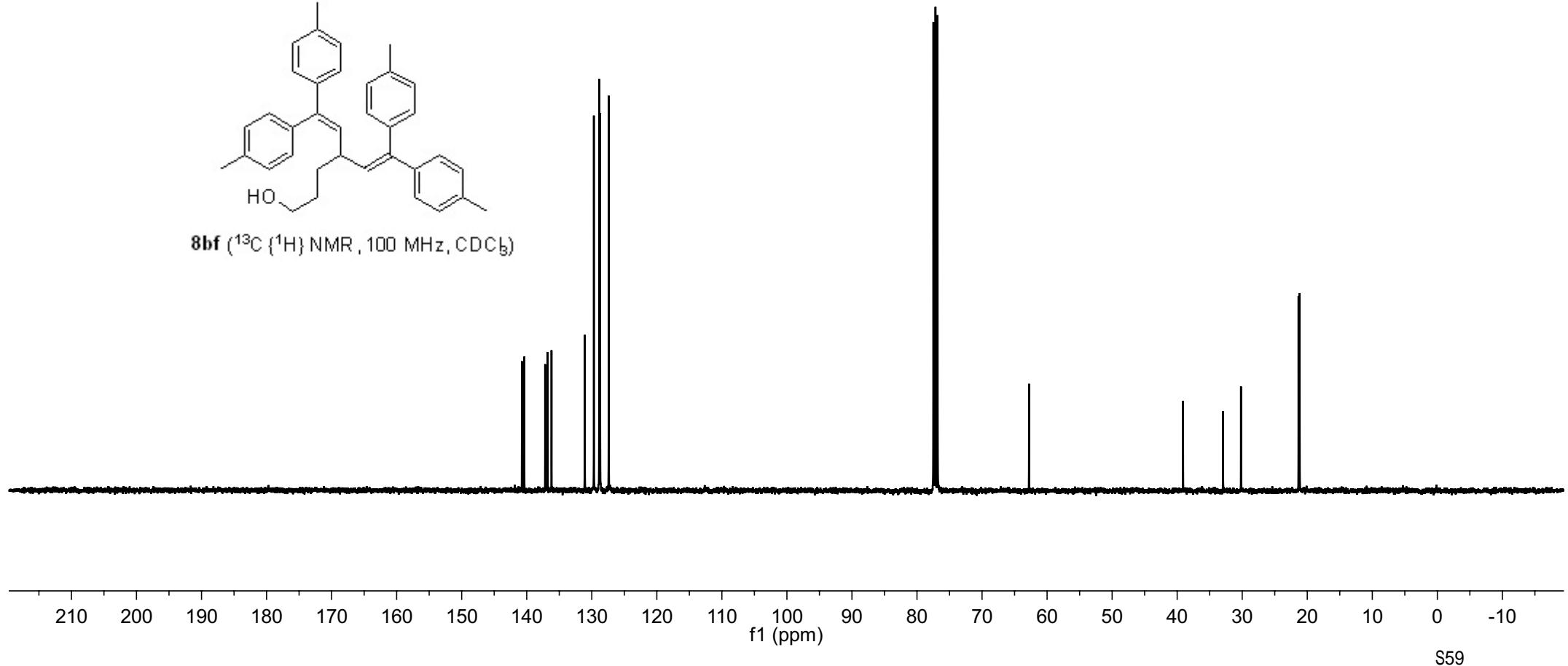


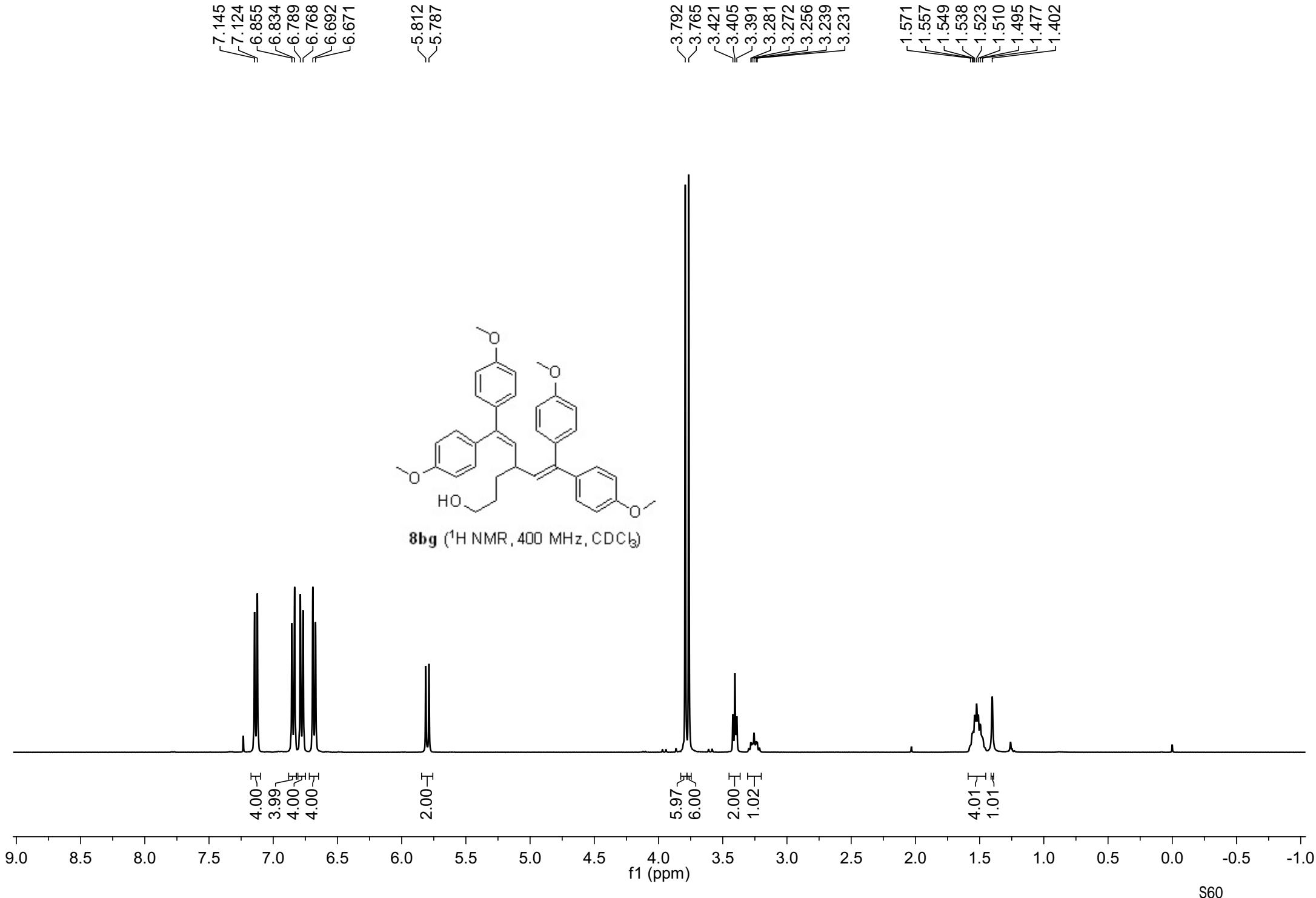


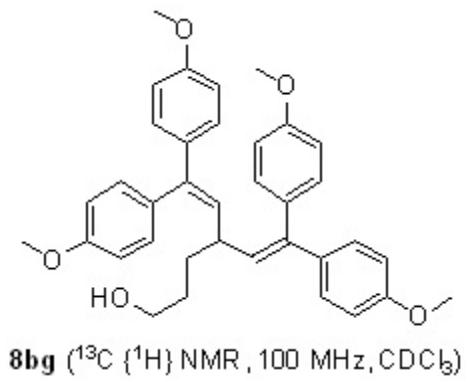




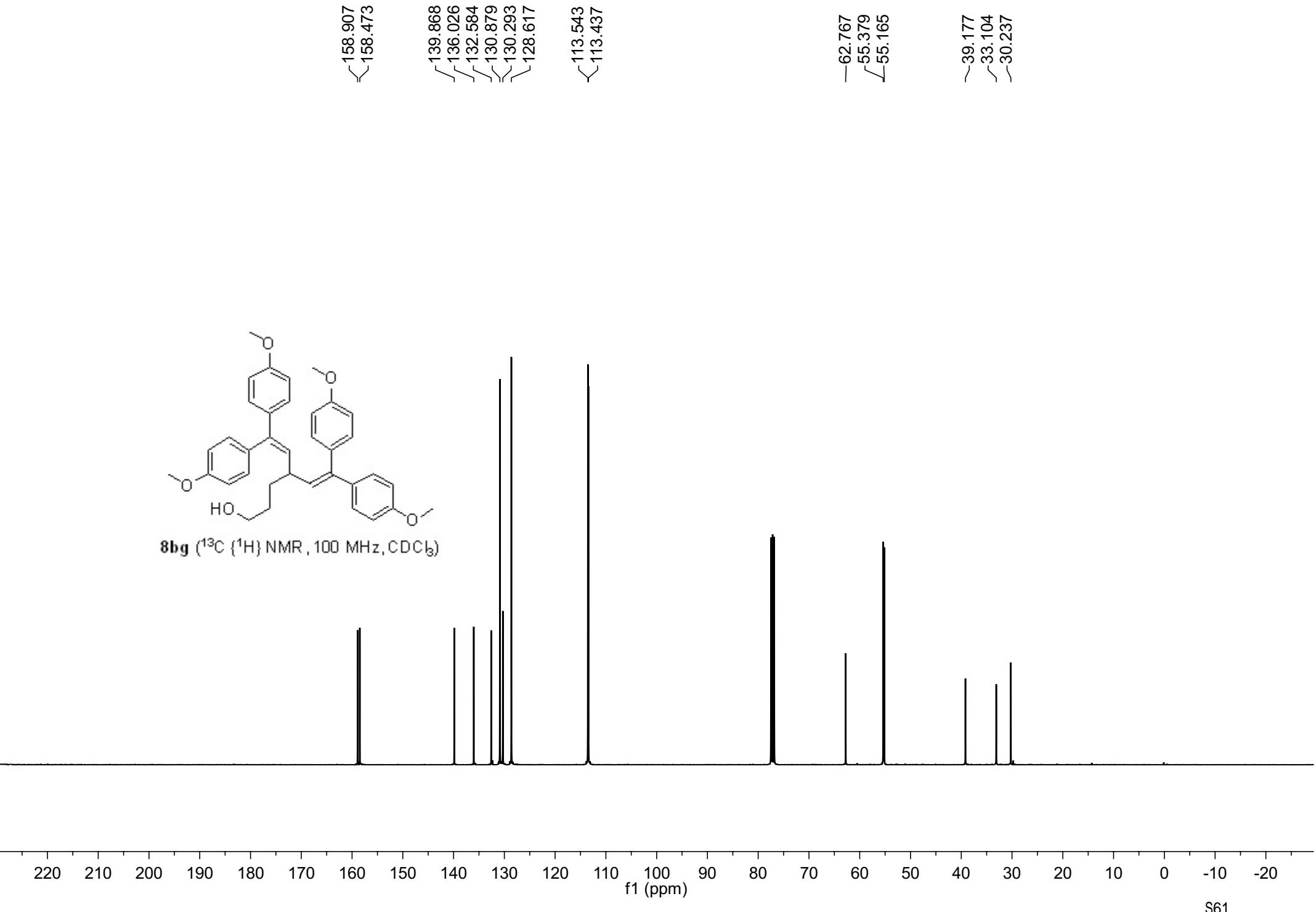
8bf (^{13}C { ^1H } NMR, 100 MHz, CDCl_3)

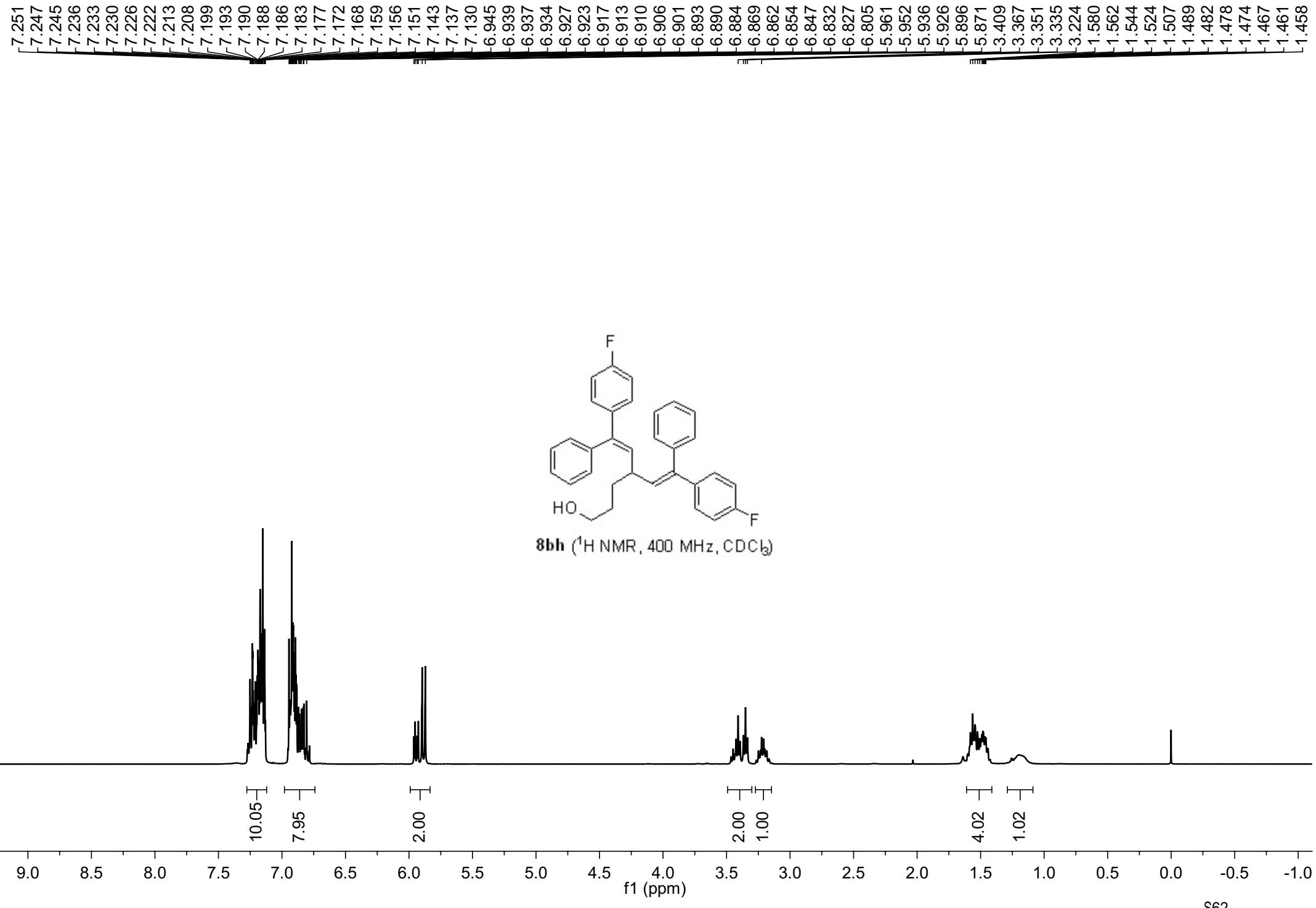


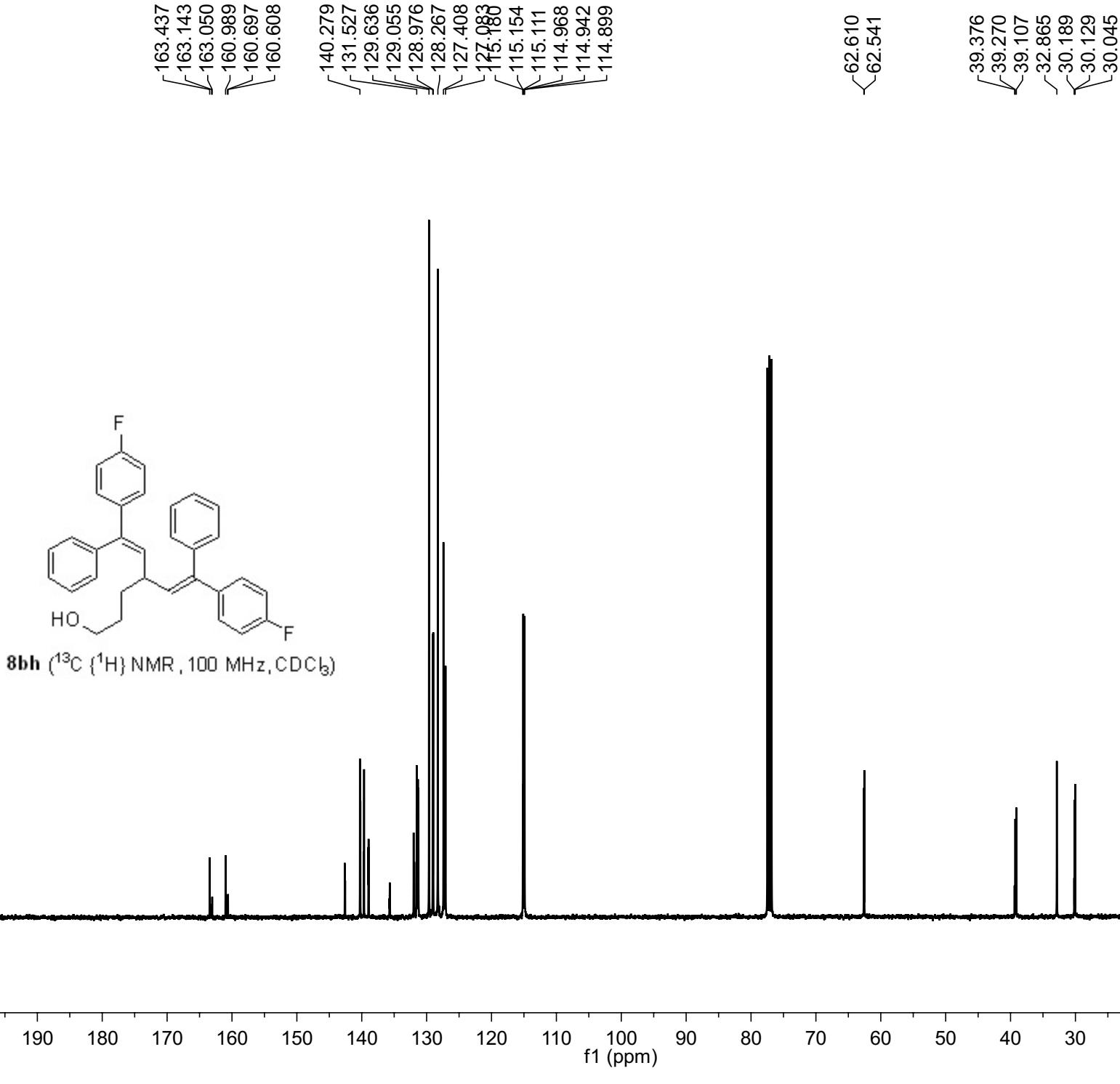


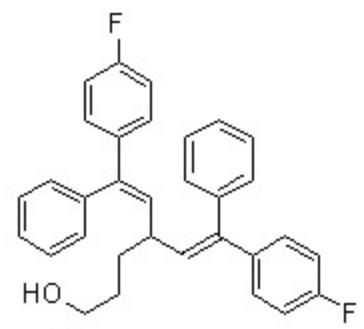


(^{13}C { ^1H } NMR, 100 MHz, CDCl_3)

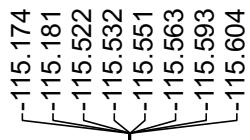






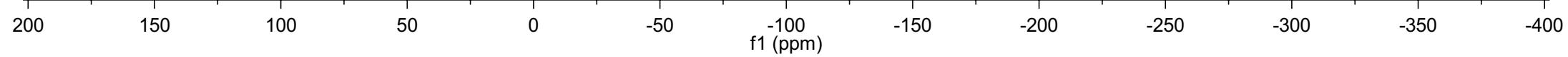


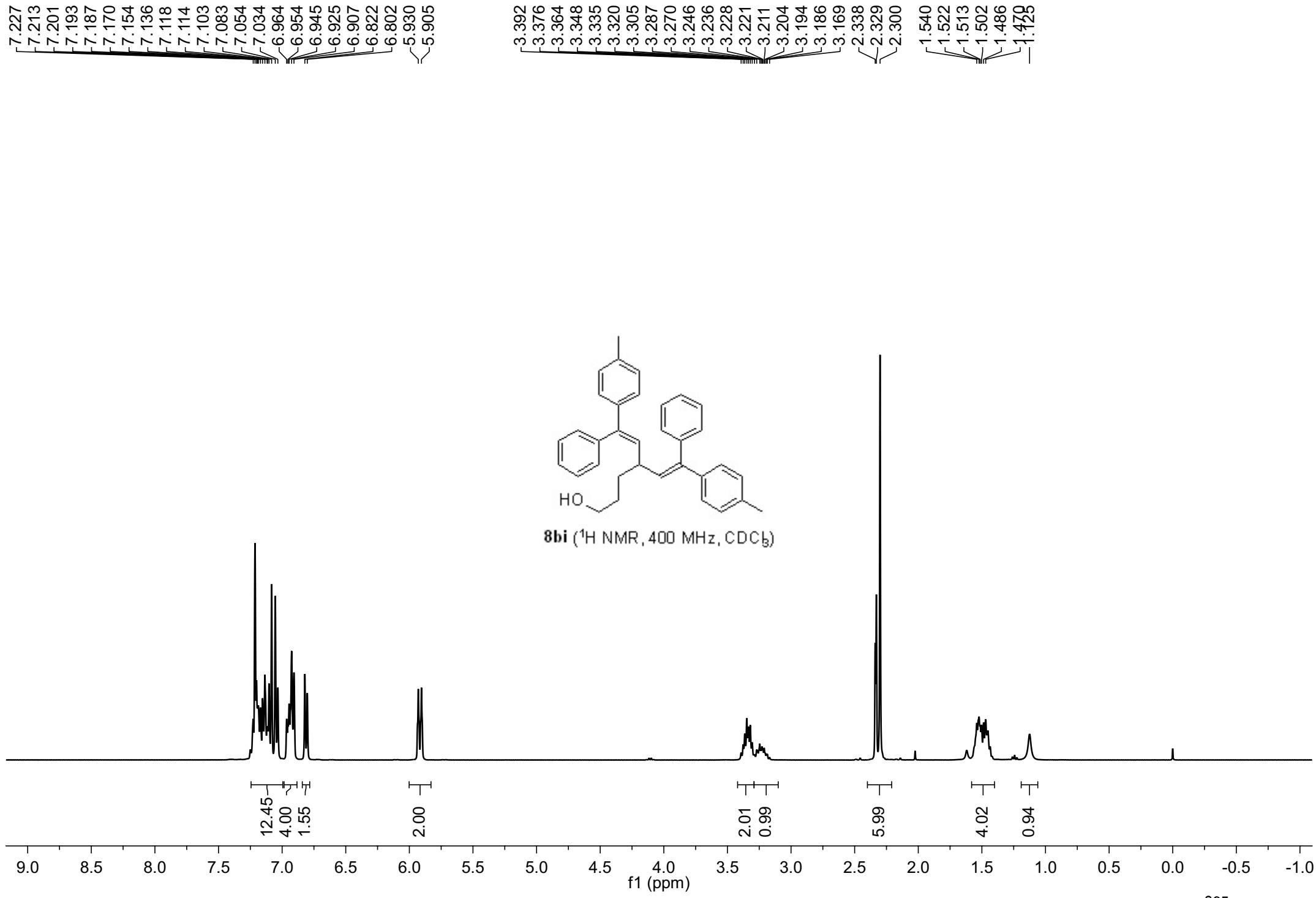
8bh (¹⁹F NMR, 376 MHz, CDCl₃)

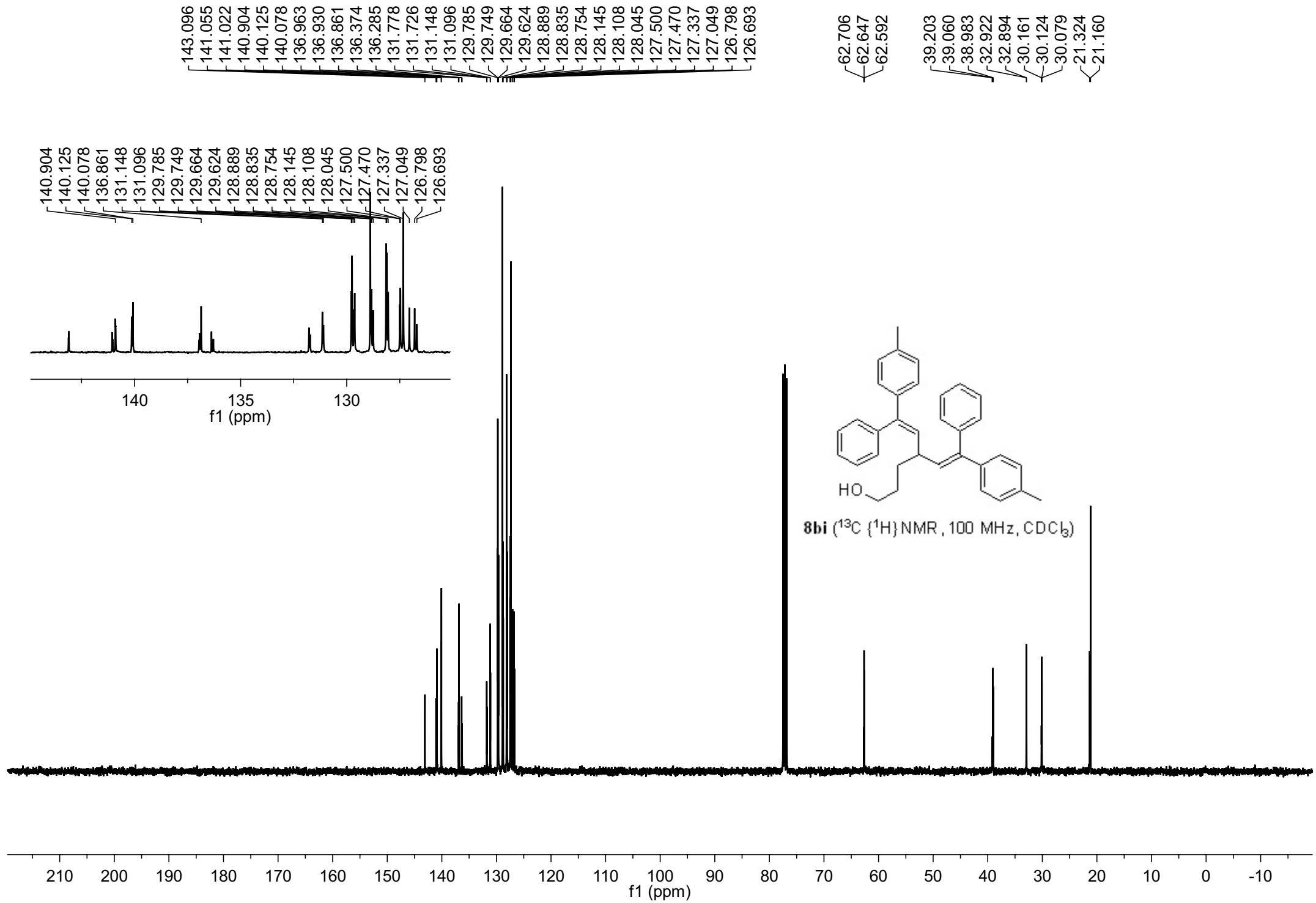


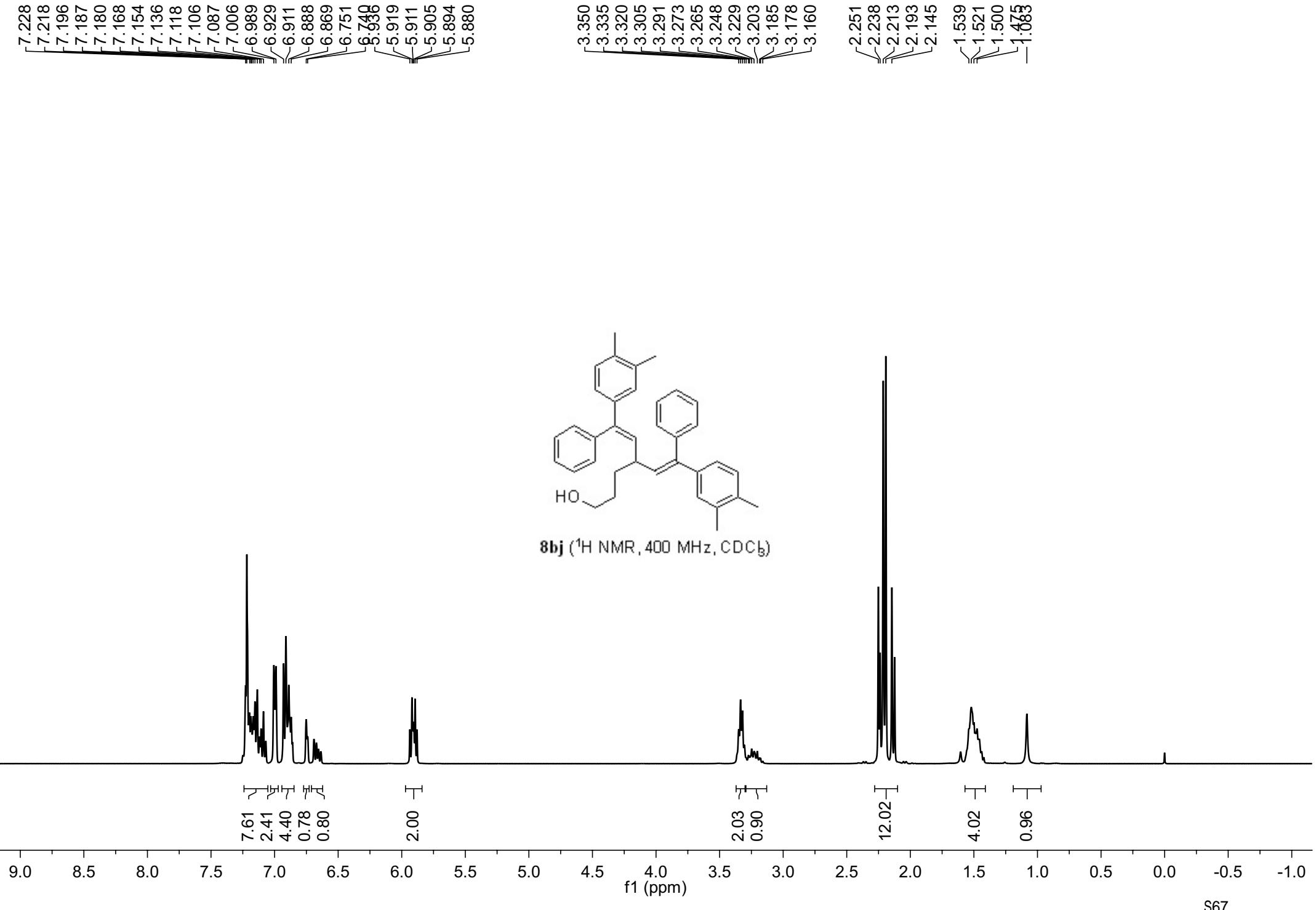
A bracketed group of chemical shifts for the allyl carbons of compound **8bh**, ranging from -115.174 ppm to -115.604 ppm.

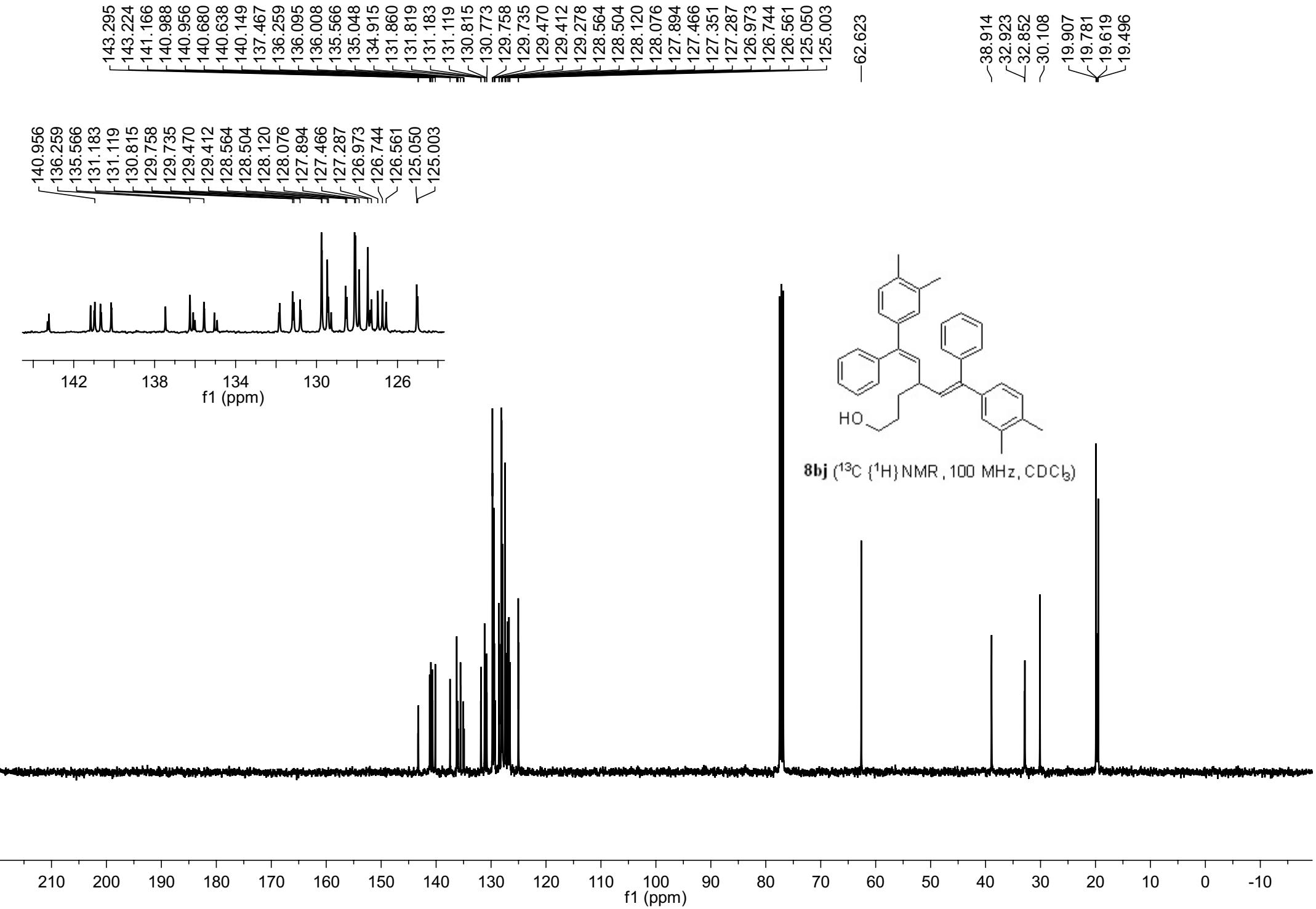
-115.174
-115.181
-115.522
-115.532
-115.551
-115.563
-115.593
-115.604

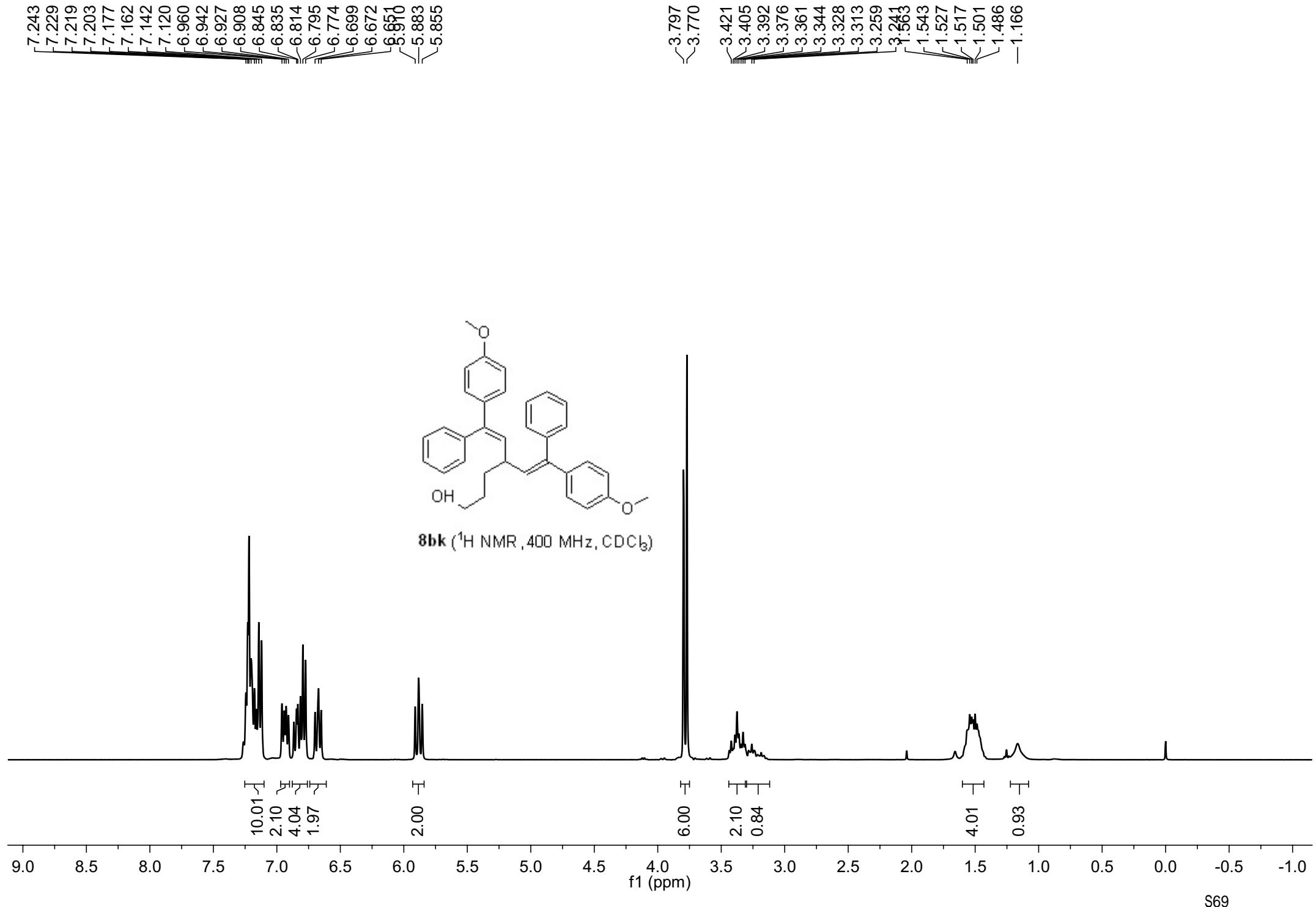


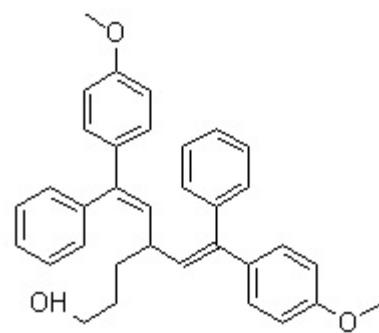






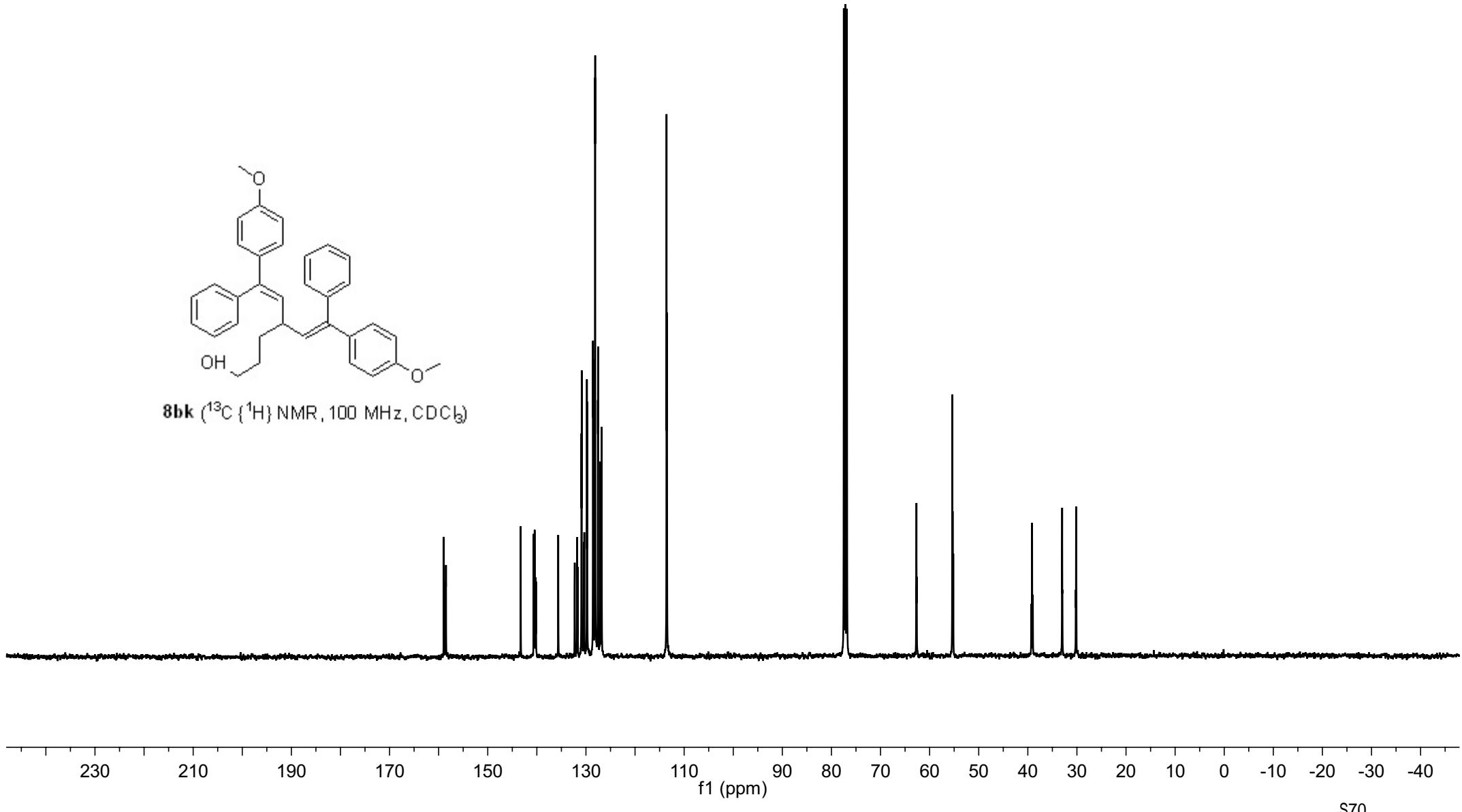


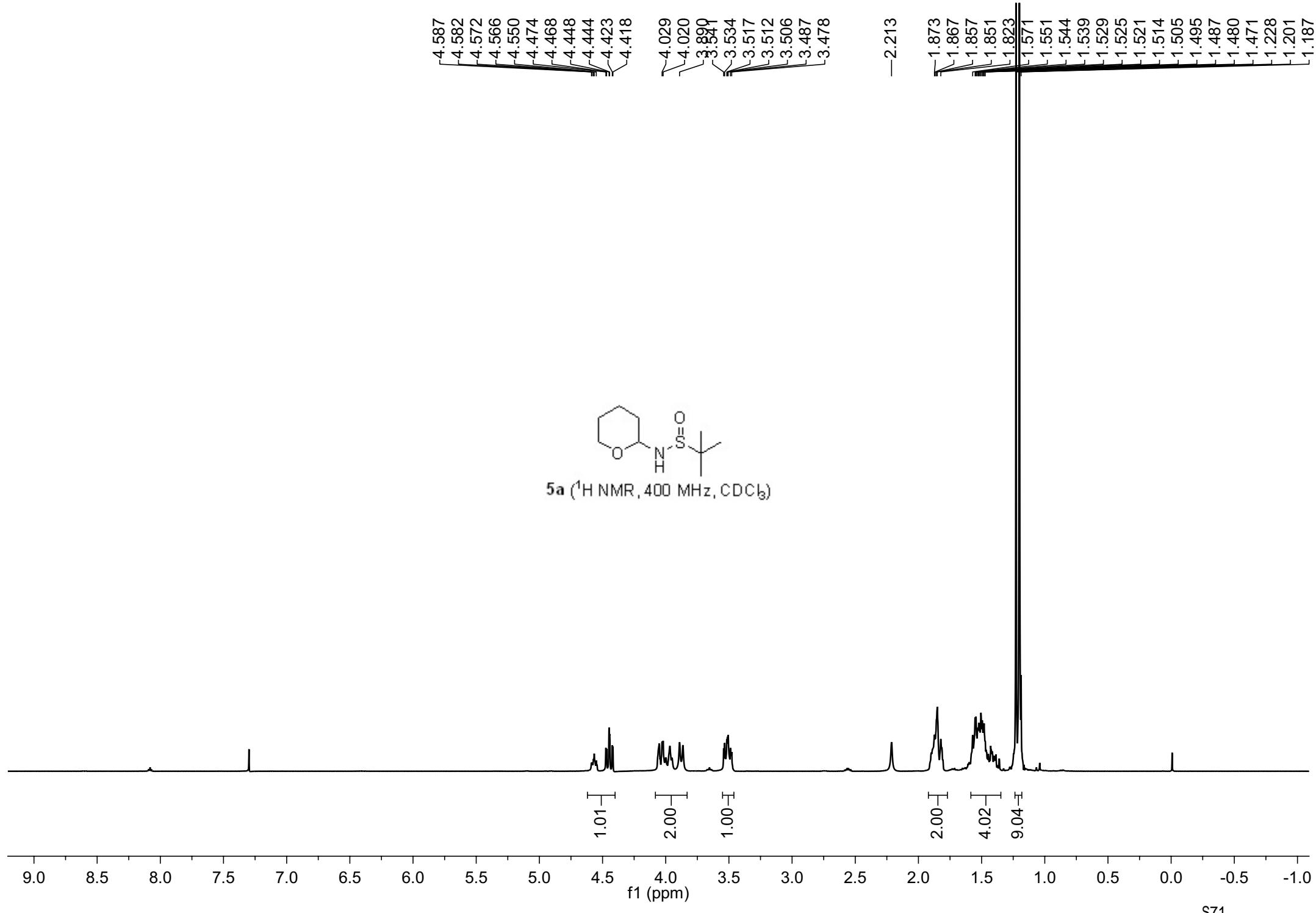


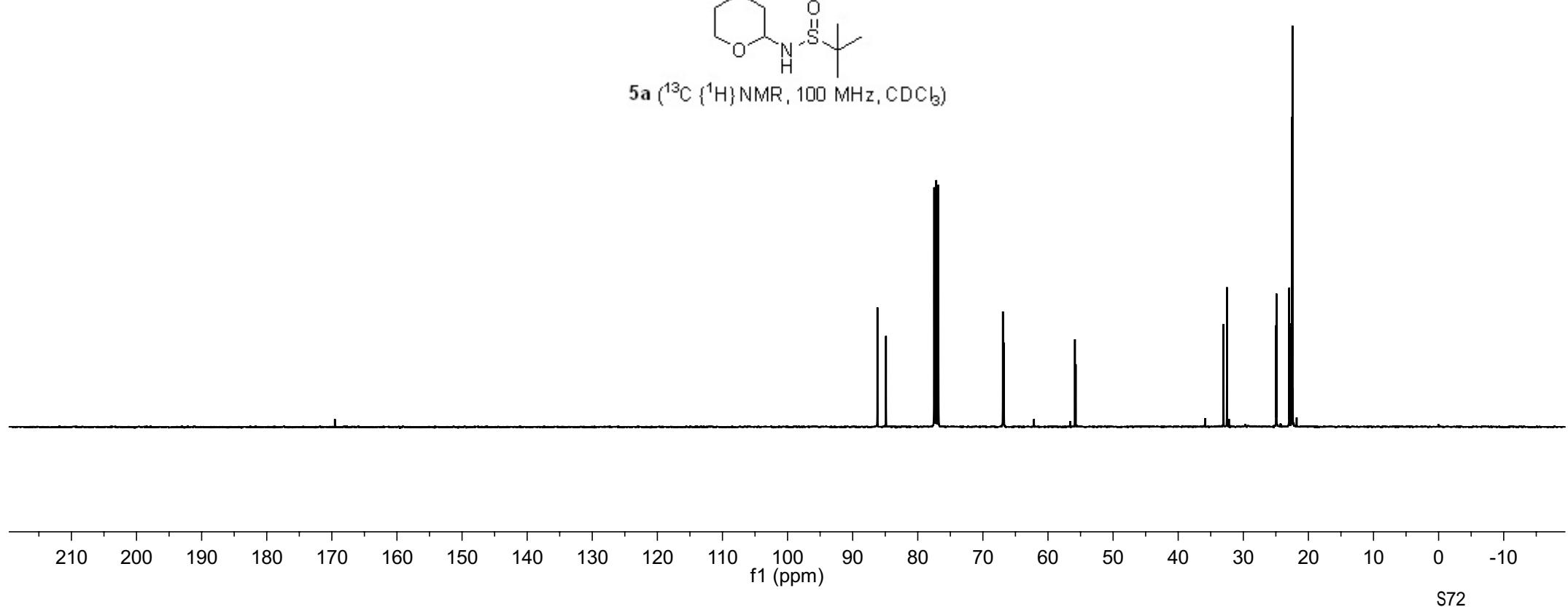
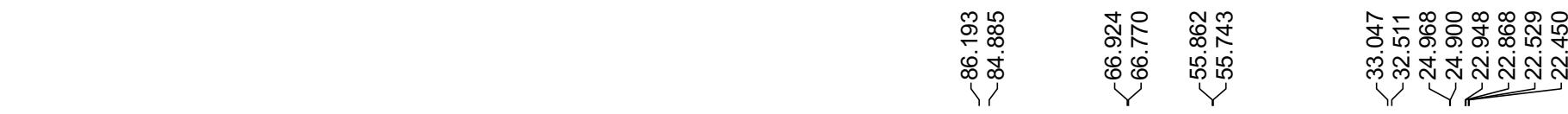


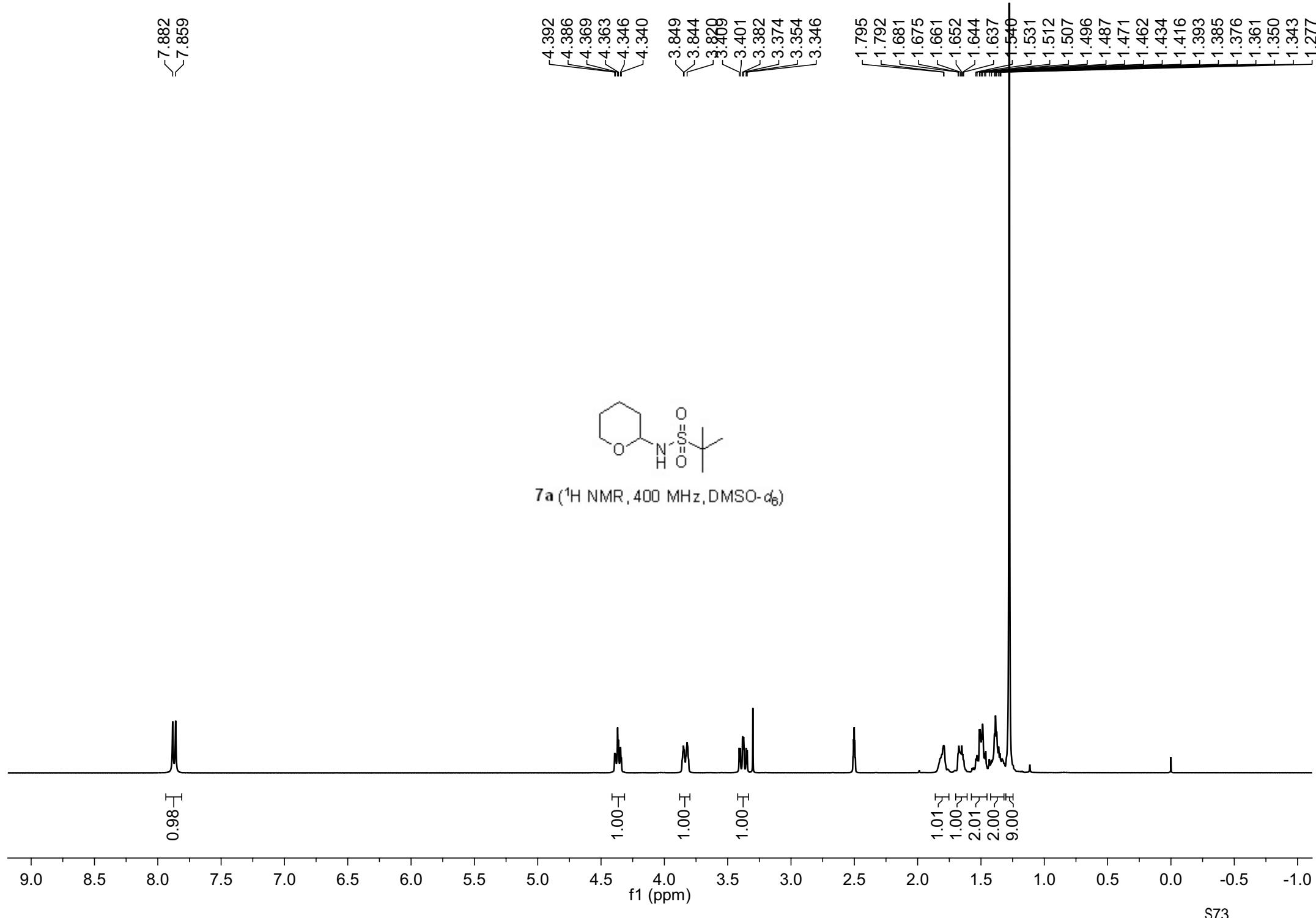
8bk (¹³C {¹H} NMR, 100 MHz, CDCl₃)

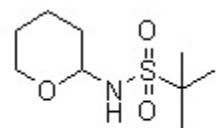
158.944	130.867	62.737
158.536	129.807	62.684
158.507	128.568	62.622
	128.531	55.390
	128.147	55.300
	128.116	55.179
	127.584	39.296
	113.525	39.127
	113.486	38.977



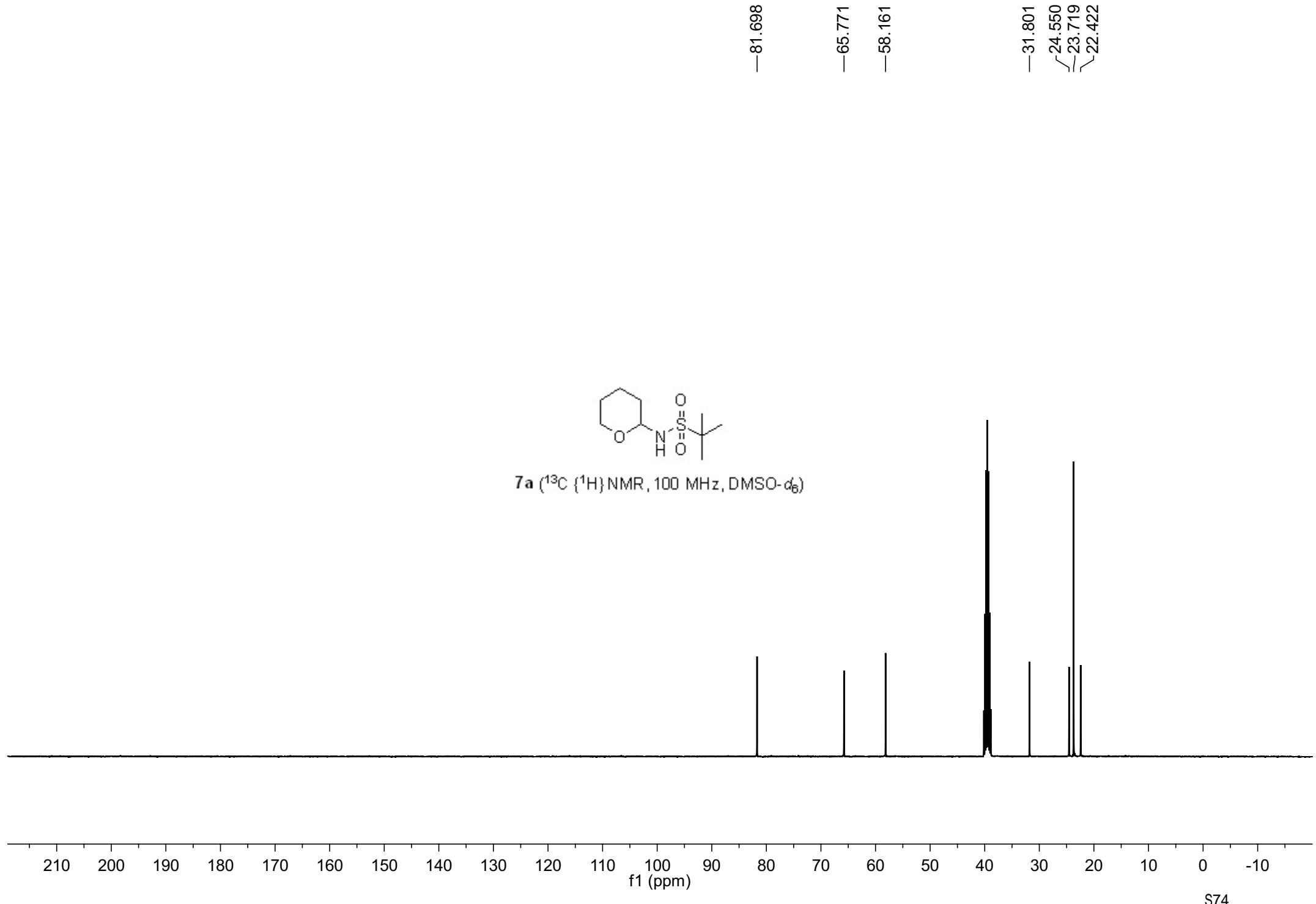


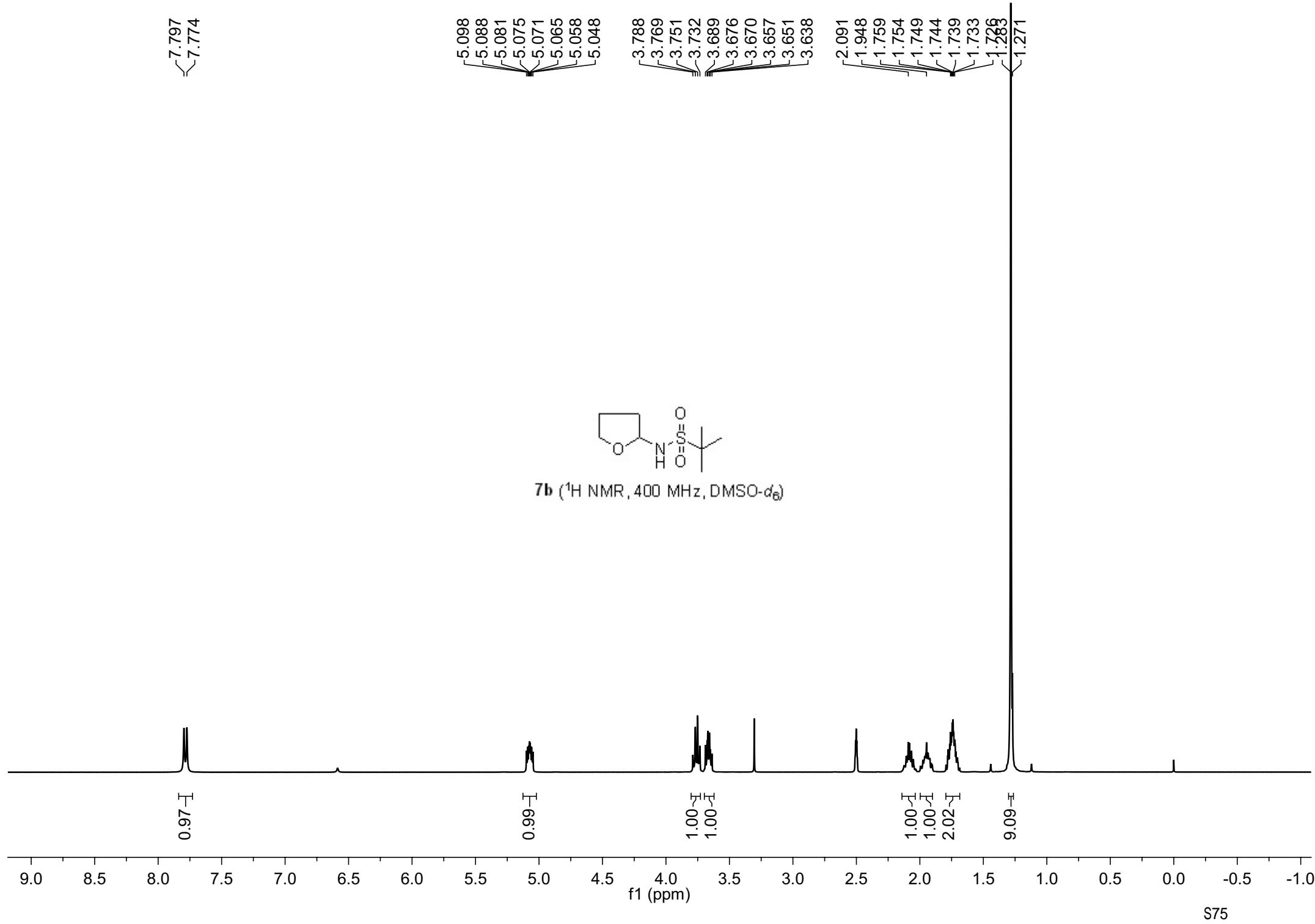




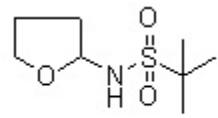


7a (¹³C {¹H} NMR, 100 MHz, DMSO-*d*₆)

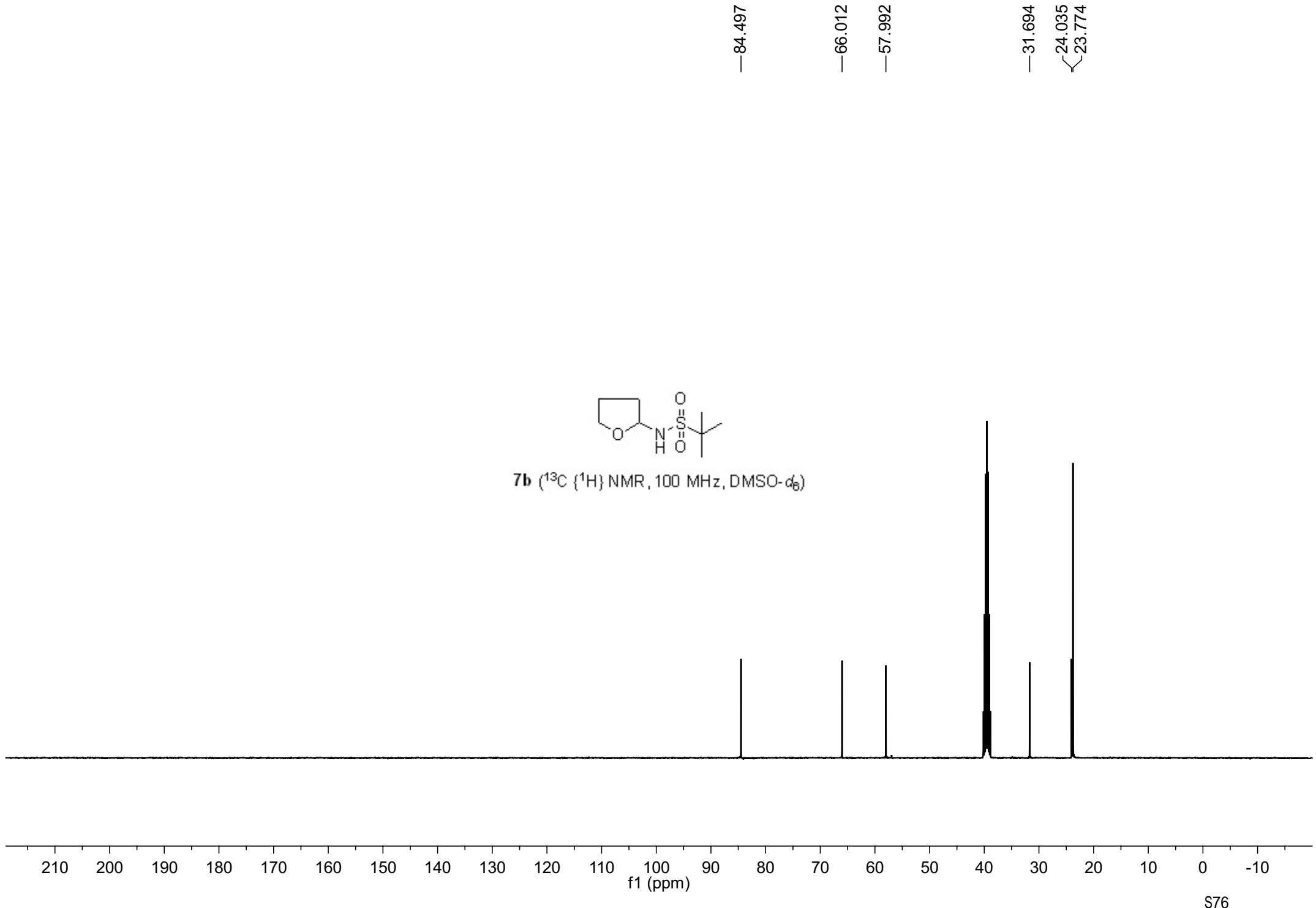


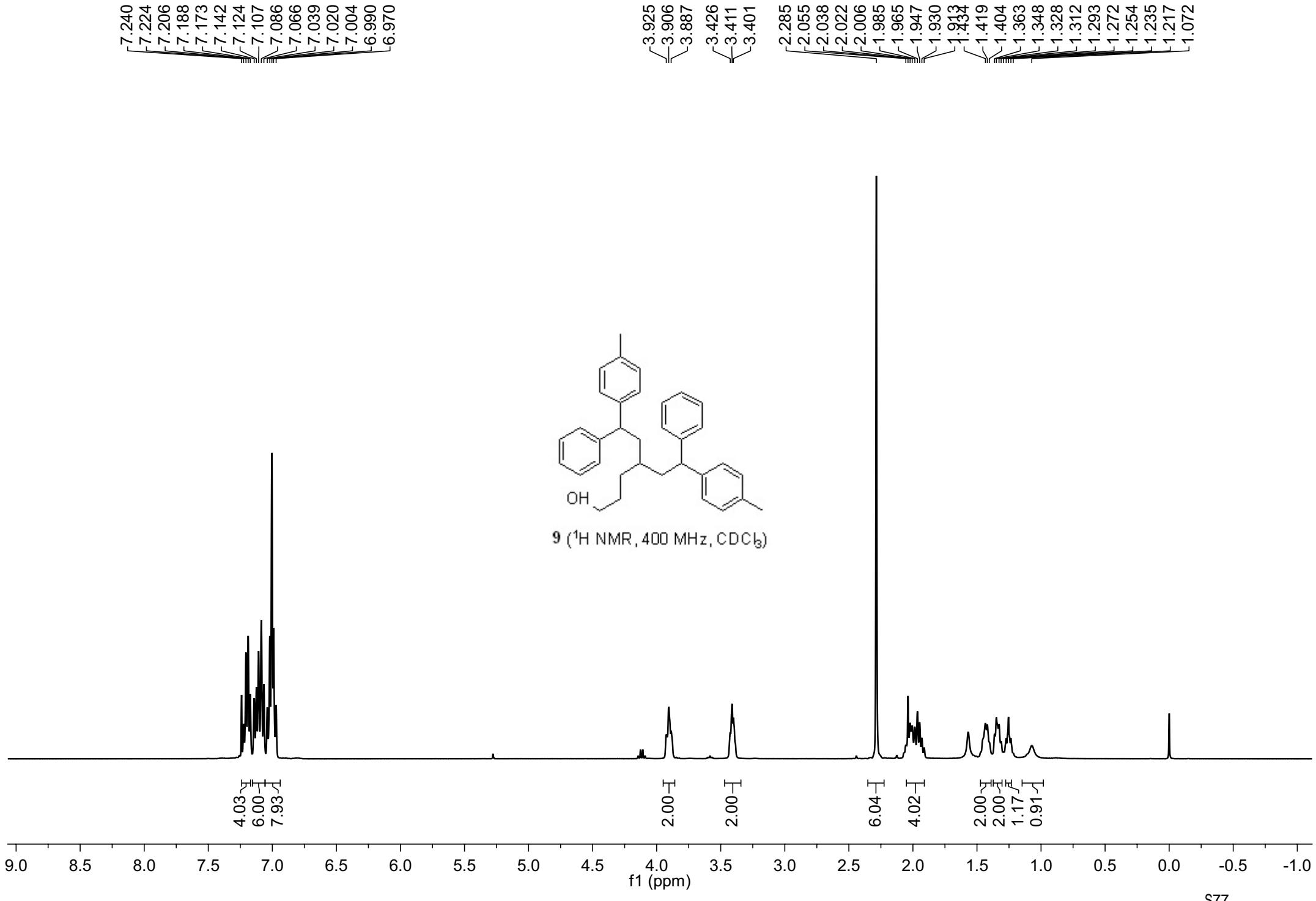


7b (^1H NMR, 400 MHz, $\text{DMSO}-d_6$)



7b (^{13}C (^1H) NMR, 100 MHz, DMSO- d_6)

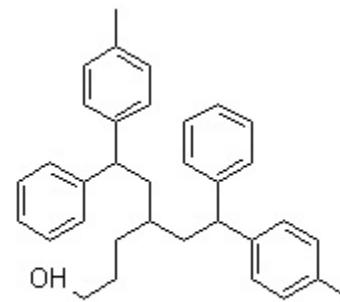




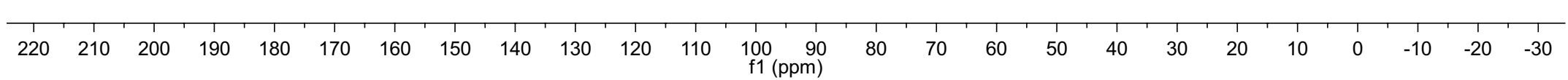
145.351
145.052
145.028
142.122
141.869
141.836
135.498
129.099
128.385
128.367
127.878
127.797
127.771
125.971

-63.036
-48.172

40.575
40.511
32.095
29.263
28.995



9 (^{13}C { ^1H } NMR, 100 MHz, CDCl_3)

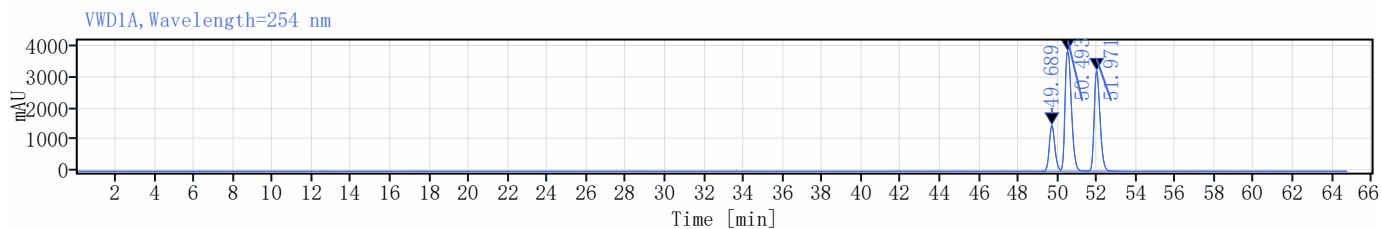


Single Injection Report



Agilent Technologies

Data file: FD_HPLC_012-2021-01-07 19-16-03+08-00. dx
Inj. volume: 5.000
Sequence Name: Single Sample
Sample name: 6aj
Instrument: FD_HPLC_012
Processing method: Method 1.pmx
Location: P1-A3



Signal: VWD1A, Wavelength=254 nm

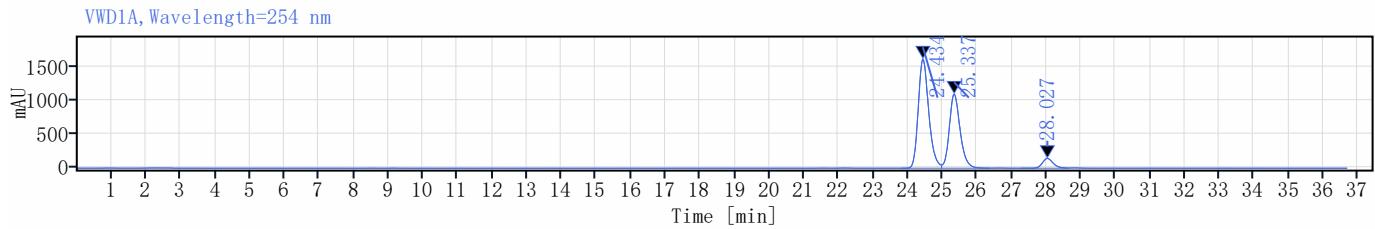
RT[min]	Type	Width[min]	Area	Height	Area%
49.689	BV	0.98	28955.91	1465.71	15.93
50.493	VB	1.38	86601.74	3838.79	47.64
51.971	BB	1.61	66217.99	3212.39	36.43
Sum			181775.64		

Single Injection Report



Agilent Technologies

Data file: FD_HPLC_010-2021-01-11 16-20-53+08-00. dx
Inj. volume: 2.000
Sequence Name: Single Sample
Sample name: 6ak
Instrument: FD_HPLC_010
Processing method: Method 1.pmx
Location: P1-A1



Signal: VWD1A, Wavelength=254 nm

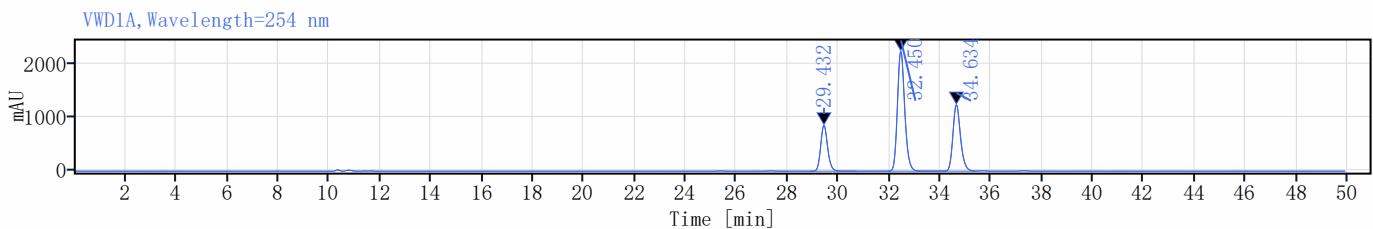
RT[min]	Type	Width[min]	Area	Height	Area%
24.434	BV	1.16	34085.54	1619.52	55.79
25.337	VV	1.40	23881.28	1099.14	39.09
28.027	BV	1.37	3124.86	144.43	5.12
Sum			61091.68		

Single Injection Report



Agilent Technologies

Data file: FD_HPLC_012-2021-01-08 12-34-18+08-00. dx
Inj. volume: 5.000
Sequence Name: Single Sample
Sample name: 6al
Instrument: FD_HPLC_012
Processing method: Method 1.pmx
Location: P1-A7



Signal: VWD1A, Wavelength=254 nm

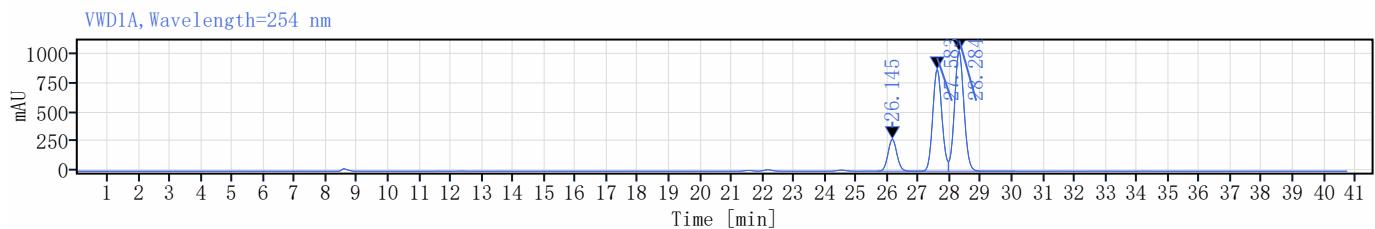
RT[min]	Type	Width[min]	Area	Height	Area%
29.432	BB	1.83	16058.57	847.26	18.76
32.450	VB	1.99	43979.51	2221.47	51.38
34.634	BV	1.48	25550.45	1230.71	29.85
Sum			85588.53		

Single Injection Report



Agilent Technologies

Data file: FD_HPLC_010-2021-01-11 17-39-47+08-00. dx
Inj. volume: 2.000
Sequence Name: Single Sample
Sample name: 8bh
Instrument: FD_HPLC_010
Processing method: Method 1.pmx
Location: P1-A3



Signal: VWD1A, Wavelength=254 nm

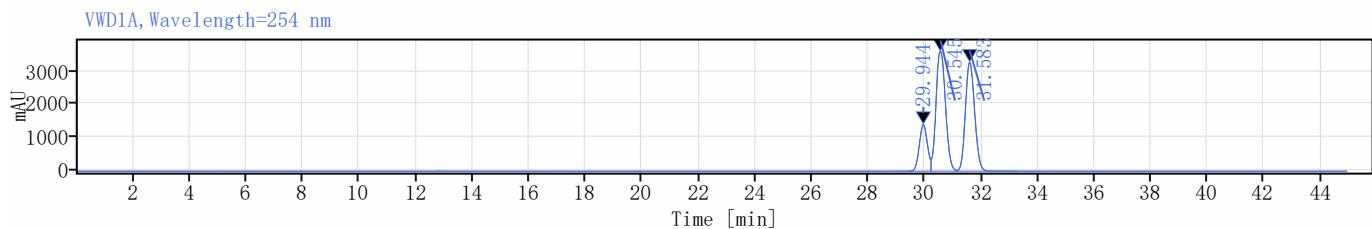
RT[min]	Type	Width[min]	Area	Height	Area%
26.145	VB	1.21	5418.12	270.91	12.14
27.583	BV	1.10	17684.43	865.86	39.62
28.284	VB	2.13	21536.93	1020.37	48.25
Sum			44639.48		

Single Injection Report



Agilent Technologies

Data file: FD_HPLC_010-2021-01-11 20-02-28+08-00. dx
Inj. volume: 5.000
Sequence Name: Single Sample
Sample name: 8bi
Instrument: FD_HPLC_010
Processing method: Method 1.pmx
Location: P1-A5



Signal: VWD1A, Wavelength=254 nm

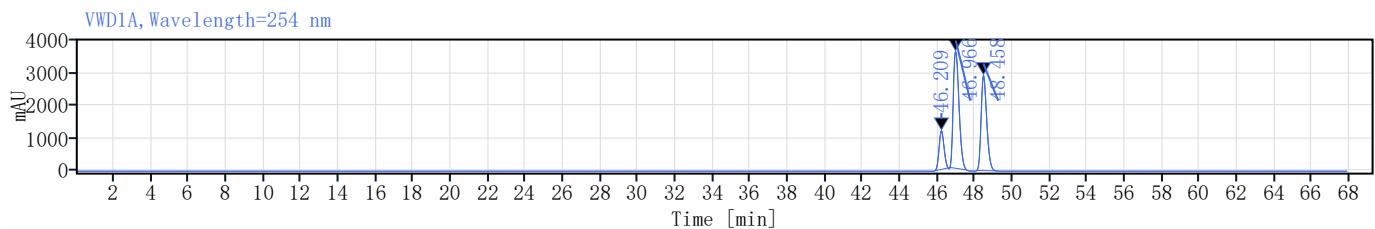
RT[min]	Type	Width[min]	Area	Height	Area%
29.944	BV	0.82	27946.27	1397.99	15.01
30.545	VV	0.91	83885.05	3591.13	45.06
31.583	VB	2.14	74342.66	3264.77	39.93
Sum			186173.98		

Single Injection Report



Agilent Technologies

Data file: FD_HPLC_012-2021-01-07 18-12-28+08-00. dx
Inj. volume: 5.000
Sequence Name: Single Sample
Sample name: 8bj
Instrument: FD_HPLC_012
Processing method: Method 1.pmx
Location: P1-A2



Signal: VWD1A, Wavelength=254 nm

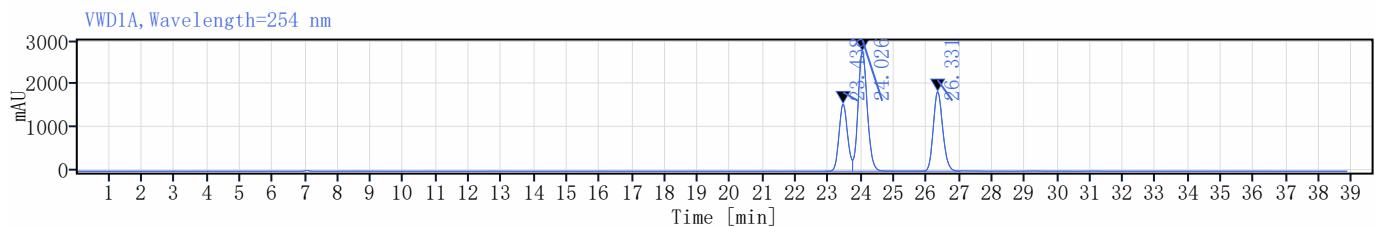
RT[min]	Type	Width[min]	Area	Height	Area%
46.209	MM m	0.83	21618.30	1189.40	13.57
46.966	MM m	0.88	76876.80	3589.03	48.25
48.458	MM m	1.02	60833.05	2927.07	38.18
Sum			159328.15		

Single Injection Report



Agilent Technologies

Data file: FD_HPLC_010-2021-01-11 16-58-59+08-00. dx
Inj. volume: 0.700
Sequence Name: Single Sample
Sample name: 8bk
Instrument: FD_HPLC_010
Processing method: Method 1.pmx
Location: P1-A2



Signal: VWD1A, Wavelength=254 nm

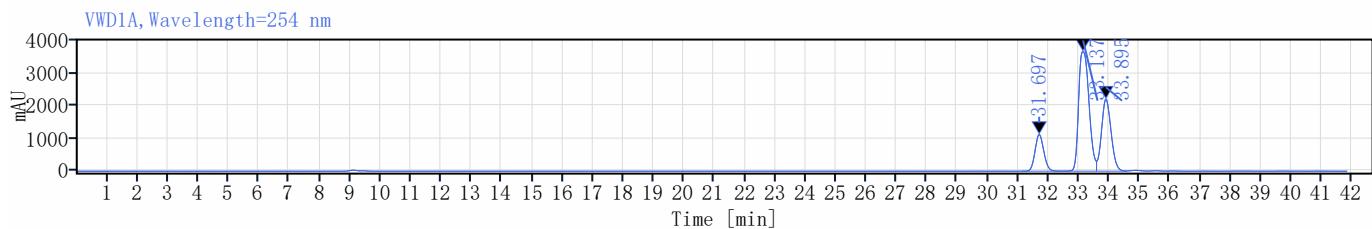
RT[min]	Type	Width[min]	Area	Height	Area%
23.438	BV	0.85	28179.94	1552.03	23.59
24.026	VB	2.03	54345.32	2769.35	45.49
26.331	BV	1.26	36942.33	1836.68	30.92
Sum			119467.59		

Single Injection Report



Agilent Technologies

Data file: FD_HPLC_010-2021-01-11 21-25-40+08-00. dx
Inj. volume: 5.000
Sequence Name: Single Sample
Sample name: 6ah
Instrument: FD_HPLC_010
Processing method: Method 1.pmx
Location: P1-A6



Signal: VWD1A, Wavelength=254 nm

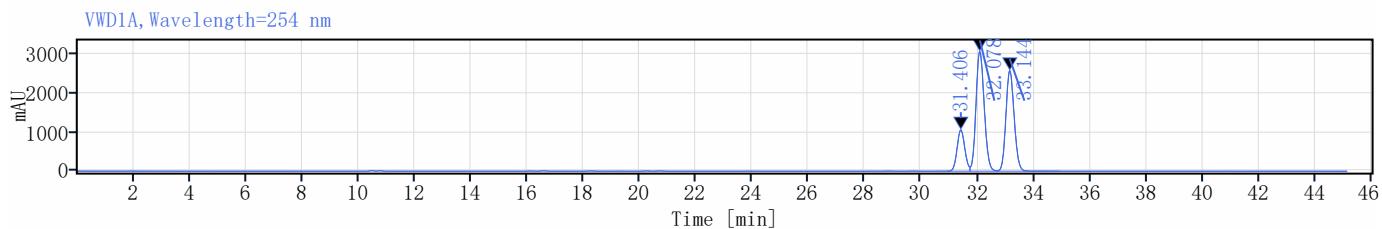
RT[min]	Type	Width[min]	Area	Height	Area%
31.697	BB	1.33	22689.41	1129.91	14.29
33.137	BV	1.15	87256.84	3683.78	54.96
33.895	VV	0.99	48817.07	2217.64	30.75
Sum			158763.32		

Single Injection Report



Agilent Technologies

Data file: FD_HPLC_010-2021-01-11 19-15-20+08-00. dx
Inj. volume: 5.000
Sequence Name: Single Sample
Sample name: 6ai
Instrument: FD_HPLC_010
Processing method: Method 1.pmx
Location: P1-A4



Signal: VWD1A, Wavelength=254 nm

RT[min]	Type	Width[min]	Area	Height	Area%
31.406	BV	0.83	20310.43	1067.21	14.90
32.078	VV	0.96	63020.27	3095.30	46.25
33.144	VB	2.23	52938.48	2601.55	38.85
Sum			136269.18		