Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
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Supporting Information

One-pot catalytic asymmetric borylation of unsaturated aldehyde-derived imines; functionalisation to homoallylic boronate carboxylate ester derivatives.

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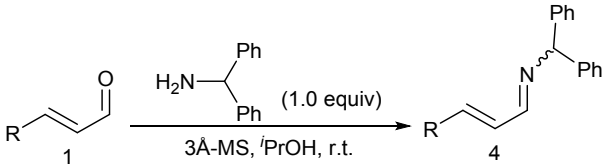
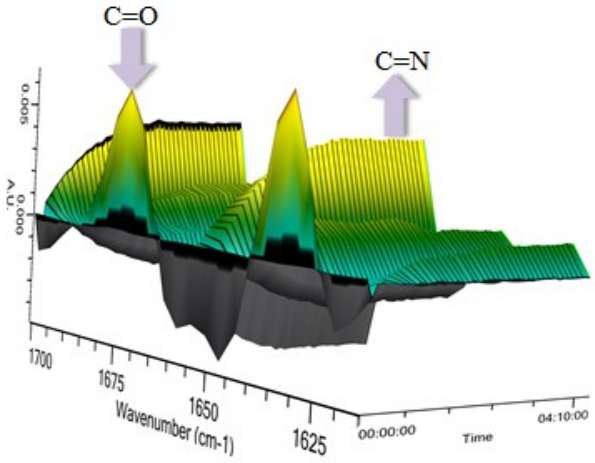
1. ReactIR studies on *in situ* imine formation

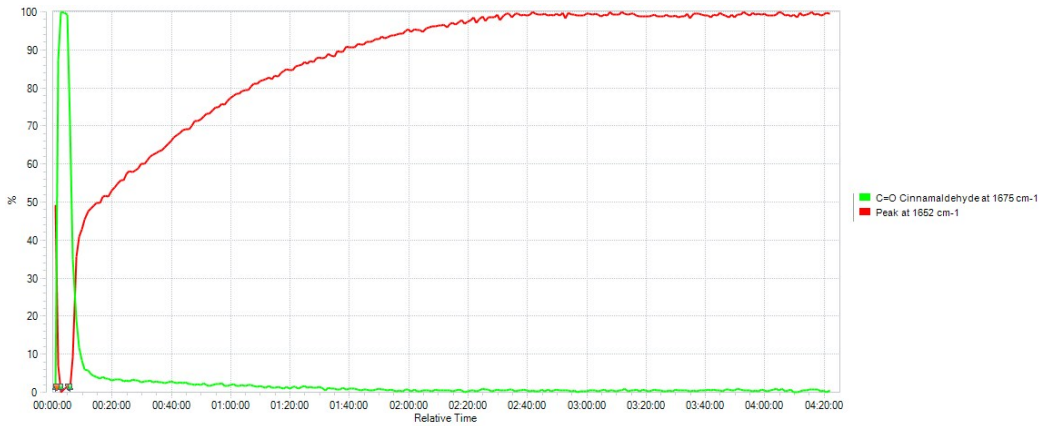


Scheme 1 Formation of α,β-unsaturated imines in ^{i}PrOH.

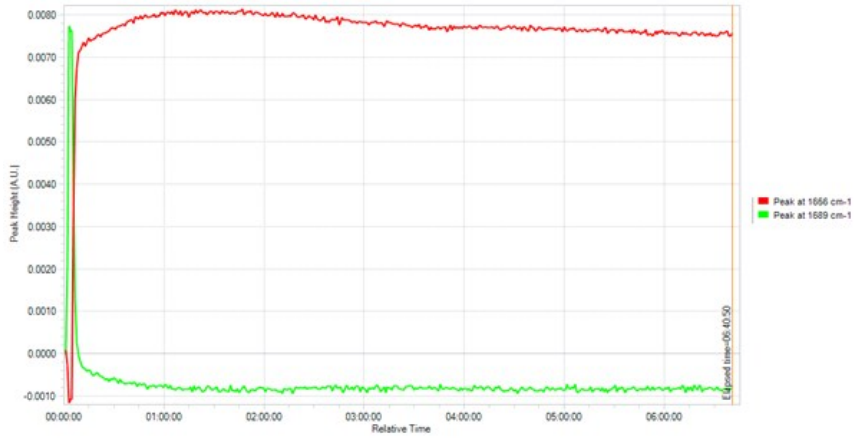
Standard conditions: To an oven-dried two-necked flask, fitted with the IR probe, enal (2.0 mmol) was added to a stirring solution of solvent (8.0 mL) and 3 Å-molecular sieve beads (2.0 g, oven-dried at 250 ºC for >48 h prior to use), under argon at 25 ºC. Once the C=O peak had plateaued (observed through PC-interface), showing maximum intensity, amine (2.0 mmol) was added and the reaction was carried out for 0.5 – 24 h. The *in situ*-formed imine was then utilised without purification by using a needle-syringe combination.

Representative graphical output of the reaction between Cinnamaldehyde **1a** and benzhydryl amine (see standard conditions).



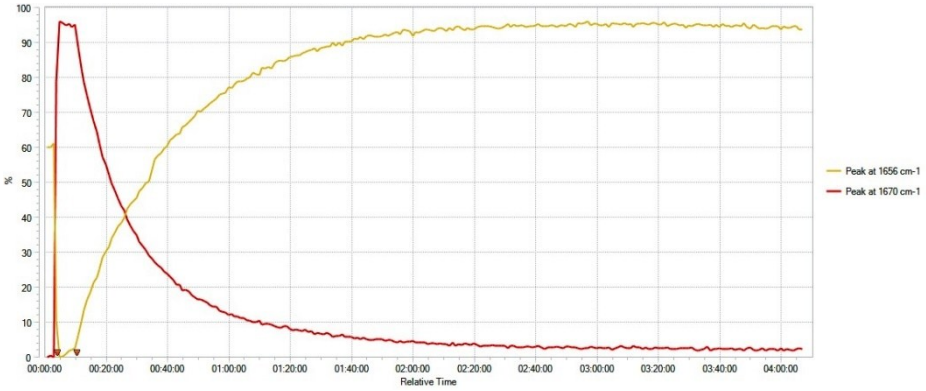


Reaction profile of 2-Hexenal **1d** and benzhydryl amine (see standard conditions).



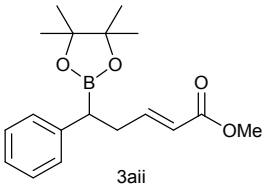
Reaction profile of Crotonaldehyde **1g** and benzhydryl amine (see standard conditions).

Reaction profile of (2*E*)-3-(Thiophen-2-yl)prop-2-enal **1j** and benzhydryl amine (see standard conditions).



2. Chiral HPLC

Sample chromatograms: 1) Racemic standard; 2) Optimised asymmetric reaction (IPA, (*R*)-DM BINAP as ligand, unless otherwise stated).



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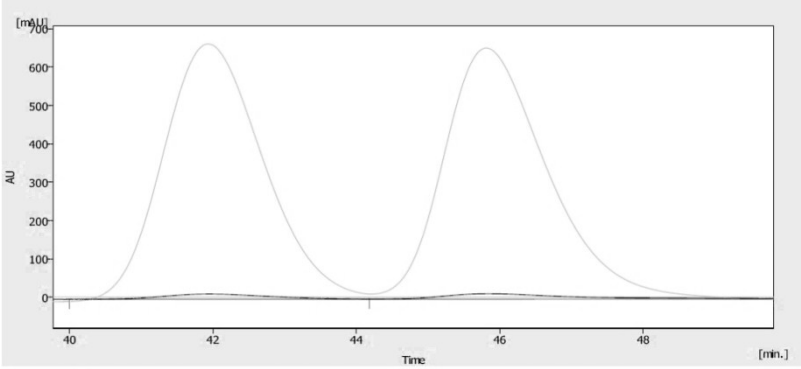
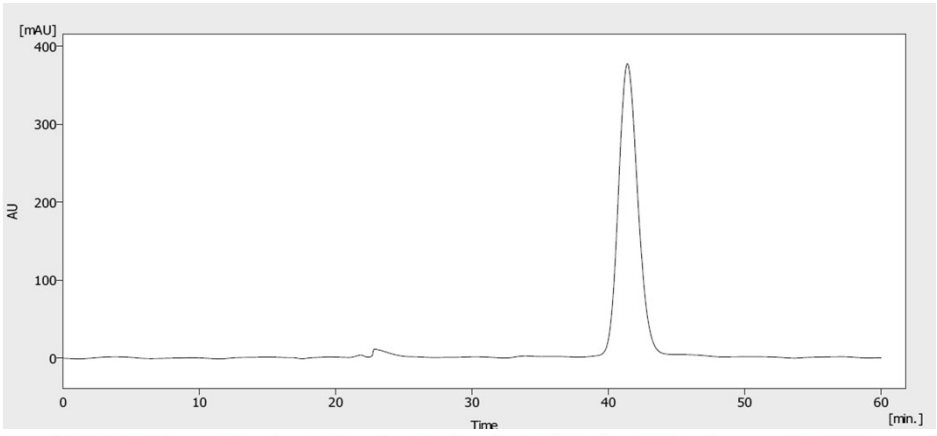
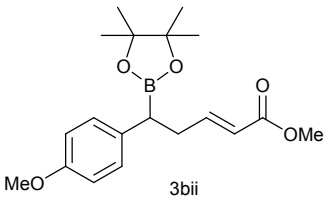


	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.127	23.010	0.282	0.0	0.0	1.41	
2	13.173	457.230	2.414	0.3	0.2	3.59	
3	17.120	830.722	11.873	0.6	0.9	0.79	
4	19.033	228.956	5.204	0.2	0.4	0.65	
5	22.893	1443.336	16.585	1.0	1.2	1.05	
6	26.980	1390.905	8.311	1.0	0.6	2.36	
7	36.413	1025.105	4.705	0.7	0.3	2.58	
8	41.933	66252.971	673.329	47.2	48.6	1.54	
9	45.813	68767.519	662.387	48.9	47.8	1.55	
10	54.047	67.081	0.791	0.0	0.1	1.51	
	Total	140486.834	1385.880	100.0	100.0		



	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	3.893	479.949	2.604	1.1	0.6	3.06	
2	9.560	262.330	1.375	0.6	0.3	3.21	
3	14.900	546.002	2.262	1.2	0.5	4.65	
4	19.593	325.961	2.209	0.7	0.5	2.78	
5	21.793	260.632	4.627	0.6	1.1	0.93	
6	22.847	1365.509	12.089	3.1	2.9	1.43	
7	30.213	496.113	2.238	1.1	0.5	4.52	
8	33.847	741.091	3.185	1.7	0.8	4.78	
9	41.393	39118.242	377.873	88.2	91.7	1.55	
10	50.893	456.305	1.916	1.0	0.5	4.21	
11	57.107	319.777	1.675	0.7	0.4	3.34	
	Total	44371.910	412.054	100.0	100.0		



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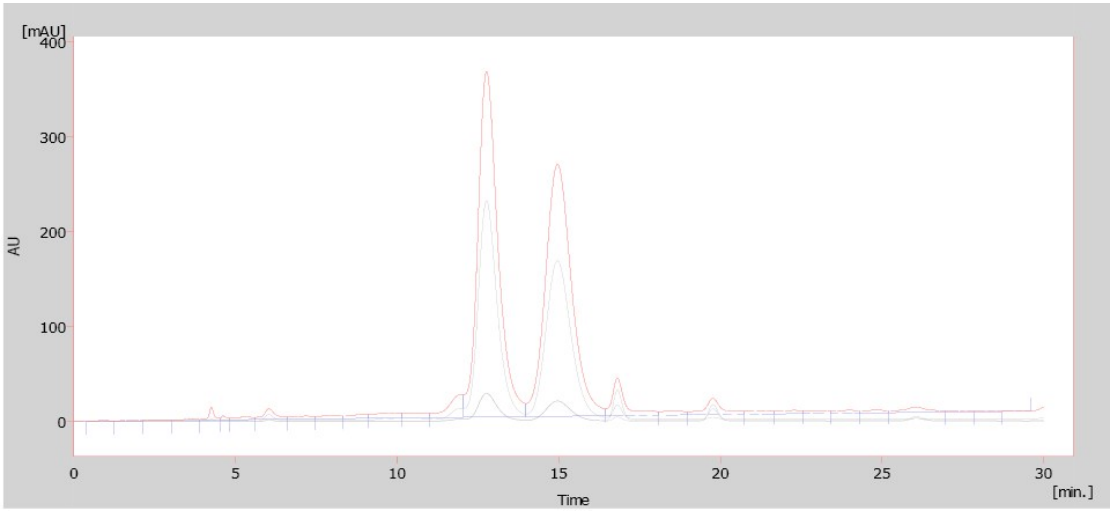
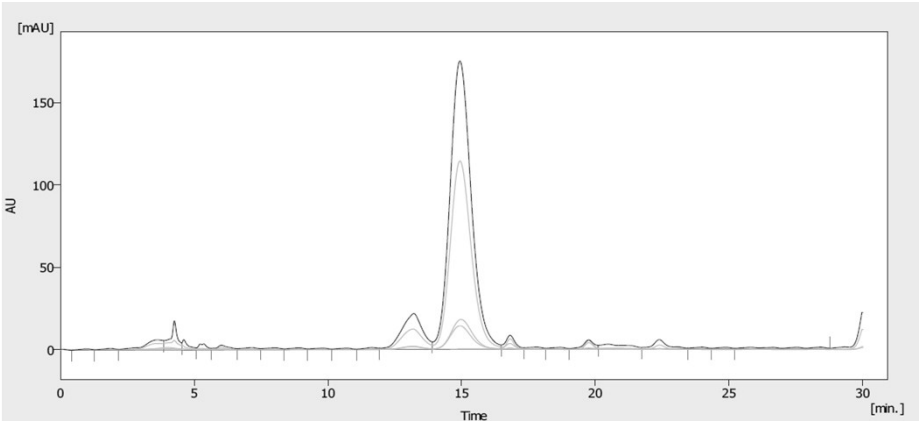
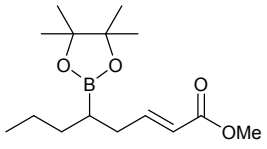


	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	4.247	17.614	1.941	0.1	0.4	0.13	
2	4.580	4.838	0.505	0.0	0.1	0.19	
3	5.327	13.070	0.611	0.1	0.1	0.30	
4	6.027	128.701	6.447	0.6	1.5	0.29	
5	9.780	112.939	0.722	0.6	0.2	1.74	
6	11.947	326.622	12.364	1.6	2.8	0.41	
7	12.767	9699.683	230.617	48.8	52.7	0.63	
8	14.960	9172.587	167.331	46.2	38.2	0.84	
9	16.813	328.515	15.239	1.7	3.5	0.32	
10	19.753	33.832	1.573	0.2	0.4	0.34	
11	26.013	20.094	0.522	0.1	0.1	0.55	
	Total	19858.494	437.873	100.0	100.0		

Optimised asymmetric reaction (THF/MeOH, *(R)*-DM-BINAP as ligand)



	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	0.980	26.145	0.871	0.2	0.3	0.53	
2	1.873	39.001	1.100	0.3	0.4	0.67	
3	3.607	301.871	6.245	2.3	2.3	0.68	
4	4.260	331.373	17.712	2.5	6.6	0.19	
5	4.607	99.678	6.291	0.8	2.3	0.21	
6	5.360	81.983	3.695	0.6	1.4	0.35	
7	6.020	95.396	2.901	0.7	1.1	0.51	
8	7.140	54.667	1.373	0.4	0.5	0.86	
9	8.020	50.192	1.222	0.4	0.5	0.83	
10	8.900	43.740	1.182	0.3	0.4	0.69	
11	9.787	37.110	0.967	0.3	0.4	0.70	
12	10.667	32.973	0.915	0.3	0.3	0.62	
13	11.620	41.378	1.229	0.3	0.5	0.59	
14	13.207	1180.689	21.785	9.0	8.1	0.85	
15	14.933	9691.124	175.071	73.9	65.0	0.85	
16	16.813	212.967	8.414	1.6	3.1	0.37	
17	17.793	47.631	1.231	0.4	0.5	0.75	
18	18.653	38.252	1.010	0.3	0.4	0.69	
19	19.747	154.338	5.487	1.2	2.0	0.43	
20	20.473	202.823	2.869	1.5	1.1	1.41	
21	22.387	202.408	5.516	1.5	2.0	0.44	
22	23.960	31.769	0.909	0.2	0.3	0.60	
23	24.860	25.673	0.805	0.2	0.3	0.54	
24	28.393	89.221	0.720	0.7	0.3	0.48	
	Total	13112.402	269.521	100.0	100.0		



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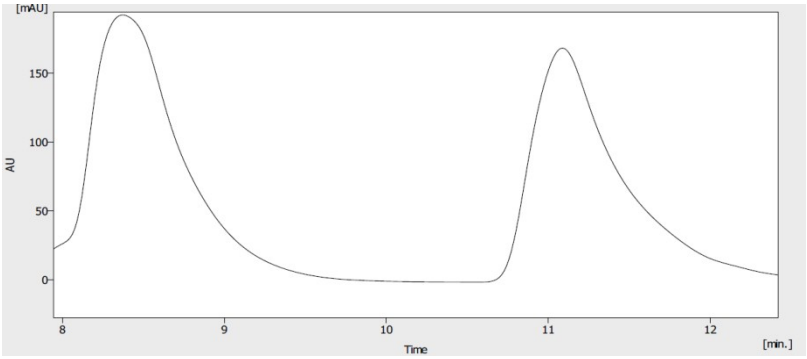
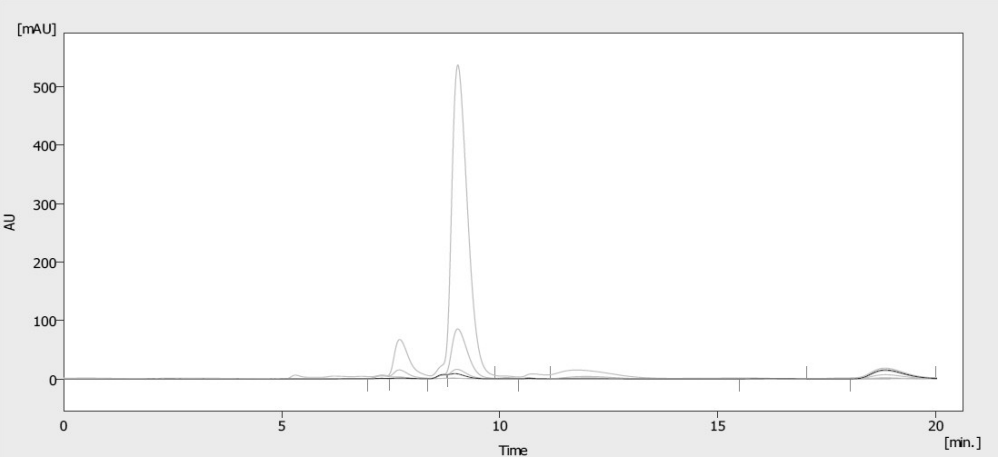
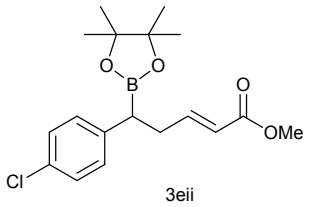


	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.360	134.678	5.939	0.2	0.3	0.43	
2	6.627	584.507	12.656	0.9	0.7	0.60	
3	7.593	1987.348	86.184	3.1	4.9	0.31	
4	7.953	2755.013	108.175	4.4	6.1	0.52	
5	8.720	28100.181	805.924	44.5	45.7	0.49	
6	11.140	25813.031	710.028	40.8	40.3	0.49	
7	18.340	1372.991	16.792	2.2	1.0	1.15	
8	20.653	375.514	3.268	0.6	0.2	1.98	
9	24.347	561.743	4.599	0.9	0.3	2.47	
10	26.880	483.170	3.243	0.8	0.2	2.78	
11	30.180	607.202	3.502	1.0	0.2	2.60	
12	36.273	431.676	3.377	0.7	0.2	2.13	
	Total	63207.052	1763.686	100.0	100.0		



	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	0.460	28.780	0.509	0.1	0.1	0.81	
2	5.313	139.995	6.885	0.7	1.0	0.37	
3	6.200	239.348	5.271	1.2	0.8	0.94	
4	6.807	117.488	4.876	0.6	0.7	0.43	
5	7.313	121.319	6.029	0.6	0.9	0.38	
6	7.707	1733.689	67.953	8.9	10.1	0.37	
7	9.040	14151.492	537.899	72.3	79.8	0.40	
8	10.753	278.325	9.209	1.4	1.4	0.53	
9	11.740	1473.713	15.782	7.5	2.3	1.53	
10	15.560	295.103	2.248	1.5	0.3	2.42	
11	18.827	984.683	17.554	5.0	2.6	0.84	
	Total	19563.935	674.216	100.0	100.0		



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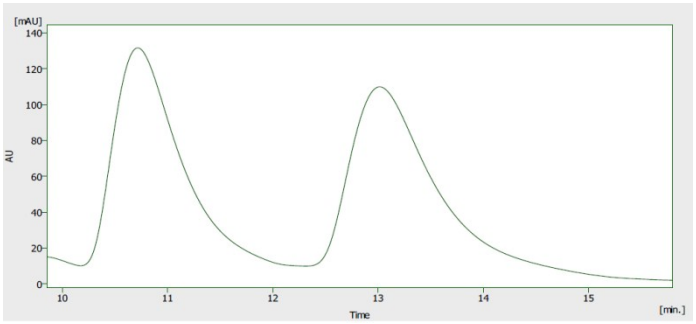
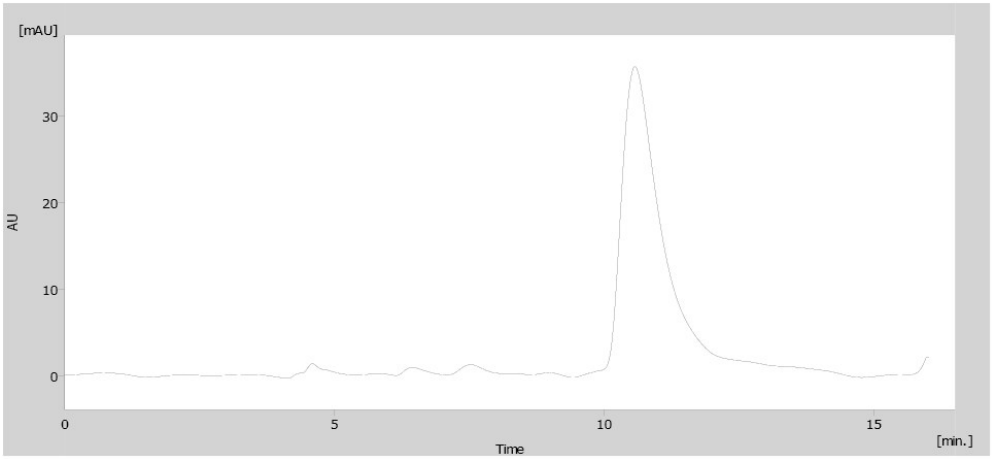
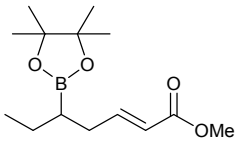


	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	4.340	23.179	1.994	0.1	0.4	0.21	
2	4.567	30.451	2.277	0.1	0.5	0.27	
3	4.913	136.719	7.006	0.6	1.5	0.30	
4	6.487	2036.963	60.083	8.5	13.0	0.53	
5	7.813	1469.235	23.349	6.2	5.1	1.11	
6	9.133	1257.949	37.276	5.3	8.1	0.57	
7	9.800	532.680	16.758	2.2	3.6	0.59	
8	10.720	6790.915	133.139	28.5	28.8	0.72	
9	13.013	7253.222	111.483	30.4	24.1	0.88	
10	16.573	4331.460	68.344	18.2	14.8	0.91	
	Total	23862.772	461.709	100.0	100.0		

Optimised asymmetric reaction (THF/MeOH, *(R)*-DM-BINAP as ligand)



	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	10.567	1801.379	35.358	100.0	100.0	0.74	
	Total	1801.379	35.358	100.0	100.0		



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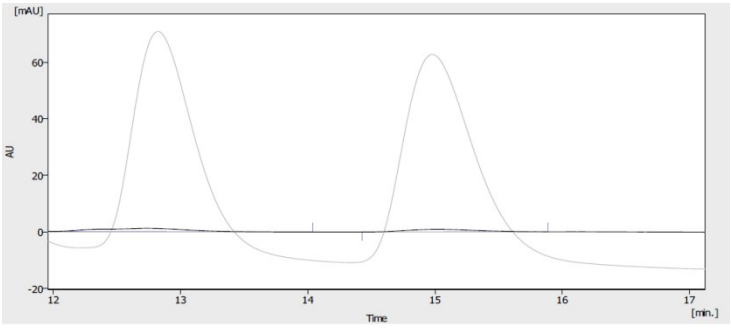
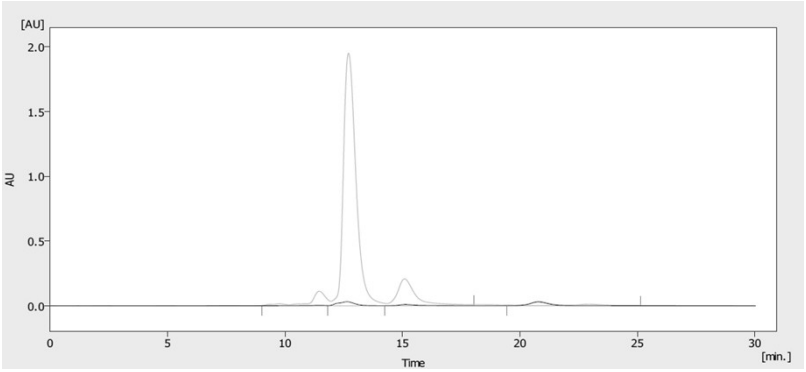
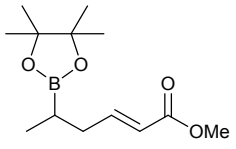


	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	9.320	215.216	6.403	2.9	3.5	0.44	
2	10.540	277.863	6.489	3.7	3.5	0.81	
3	11.680	467.868	10.517	6.3	5.7	0.79	
4	12.820	3049.955	82.030	40.9	44.4	0.54	
5	14.980	3173.051	75.331	42.6	40.8	0.62	
6	20.967	86.455	1.939	1.2	1.0	0.67	
7	22.820	185.952	2.142	2.5	1.2	0.84	
	Total	7456.360	184.851	100.0	100.0		



	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	2.207	44.382	0.567	0.0	0.0	1.81	
2	7.587	44.971	0.608	0.0	0.0	0.97	
3	9.767	788.026	16.016	0.9	0.7	0.99	
4	10.833	592.012	15.608	0.6	0.7	0.72	
5	11.460	3956.487	112.525	4.3	4.8	0.57	
6	12.707	72404.547	1950.740	78.2	82.9	0.56	
7	15.087	11400.206	207.151	12.3	8.8	0.70	
8	18.260	785.413	8.348	0.8	0.4	2.02	
9	20.807	1743.984	31.305	1.9	1.3	0.81	
10	22.933	816.927	10.153	0.9	0.4	1.19	
	Total	92576.954	2353.022	100.0	100.0		



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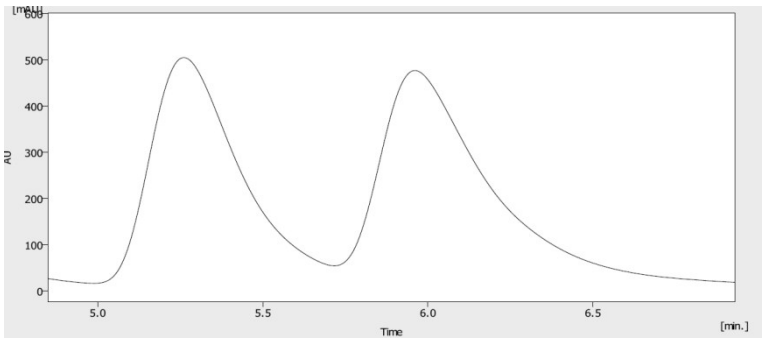
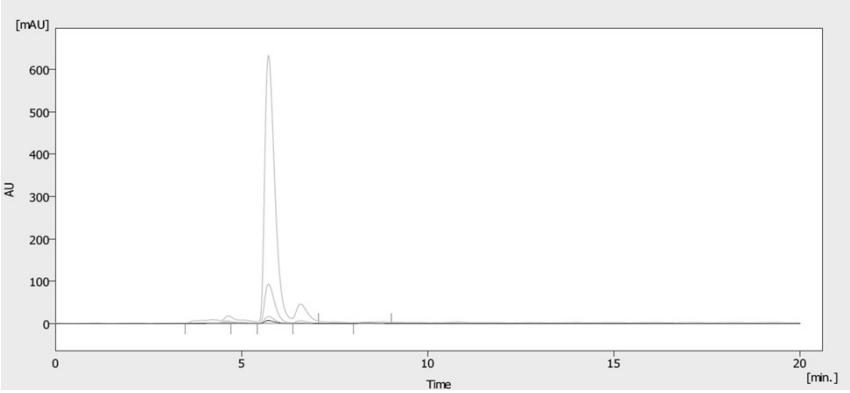
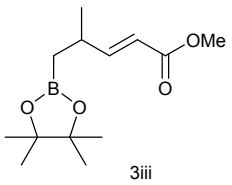


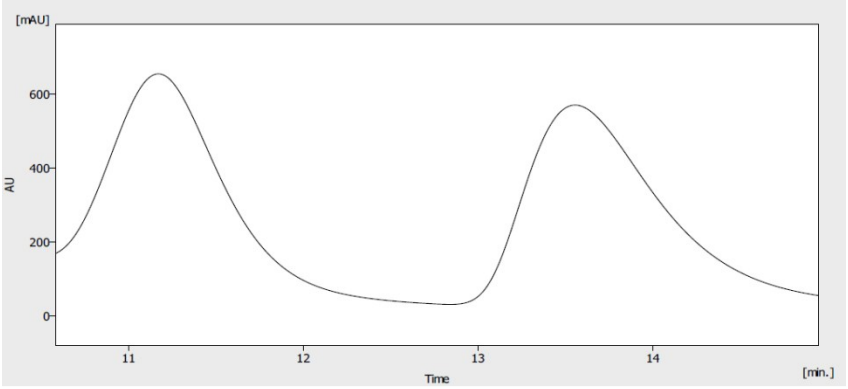
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	0.647	115.671	3.268	0.4	0.2	0.61	
2	1.720	134.089	3.574	0.4	0.3	0.64	
3	2.780	126.562	3.341	0.4	0.2	0.65	
4	3.713	120.668	6.485	0.4	0.5	0.29	
5	4.607	2291.768	82.083	7.1	6.1	0.39	
6	5.260	11425.595	580.508	35.2	43.3	0.30	
7	5.960	13810.201	549.013	42.6	41.0	0.35	
8	7.220	284.934	20.056	0.9	1.5	0.24	
9	7.620	1052.632	30.417	3.2	2.3	0.65	
10	8.300	740.600	13.110	2.3	1.0	1.07	
11	10.227	258.751	5.105	0.8	0.4	0.90	
12	11.607	222.092	5.191	0.7	0.4	0.77	
13	12.387	296.516	5.425	0.9	0.4	1.00	
14	13.380	264.268	4.795	0.8	0.4	0.98	
15	14.553	191.145	4.022	0.6	0.3	0.94	
16	15.660	285.354	5.723	0.9	0.4	0.96	
17	16.700	276.380	5.480	0.9	0.4	0.98	
18	17.787	271.215	5.712	0.8	0.4	0.84	
19	18.820	196.149	4.439	0.6	0.3	0.82	
20	19.967	81.873	2.554	0.3	0.2	0.53	
	Total	32446.463	1340.300	100.0	100.0		



	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	4.633	22.407	0.696	9.9	6.5	0.31	
2	4.900	28.343	1.251	12.5	11.7	0.38	
3	5.727	142.493	7.400	63.1	69.0	0.30	
4	6.567	10.686	0.512	4.7	4.8	0.34	
5	8.353	22.039	0.870	9.8	8.1	0.41	
	Total	225.968	10.729	100.0	100.0		



3iii



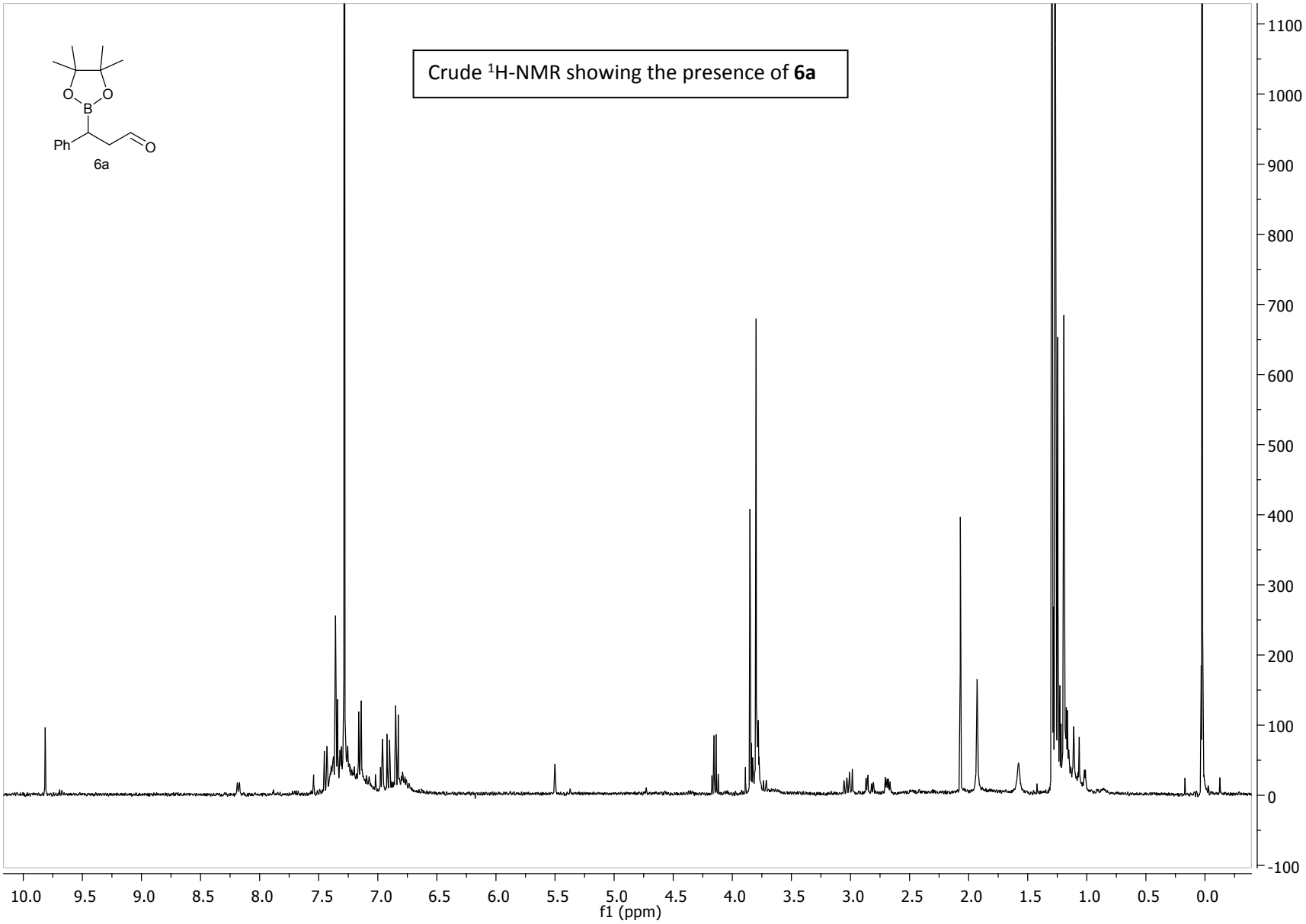
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.933	69.146	2.895	0.1	0.2	0.35	
2	7.313	66.652	2.910	0.1	0.2	0.45	
3	7.760	65.026	2.245	0.1	0.2	0.56	
4	9.040	487.742	13.722	0.6	1.0	0.52	
5	9.847	3435.056	138.793	4.2	9.7	0.40	
6	11.173	39065.008	654.134	47.3	45.6	0.77	
7	13.553	34625.812	569.474	41.9	39.7	0.86	
8	16.980	3478.394	33.751	4.2	2.4	1.68	
9	20.127	1366.296	17.889	1.7	1.2	1.11	
	Total	82659.132	1435.813	100.0	100.0		

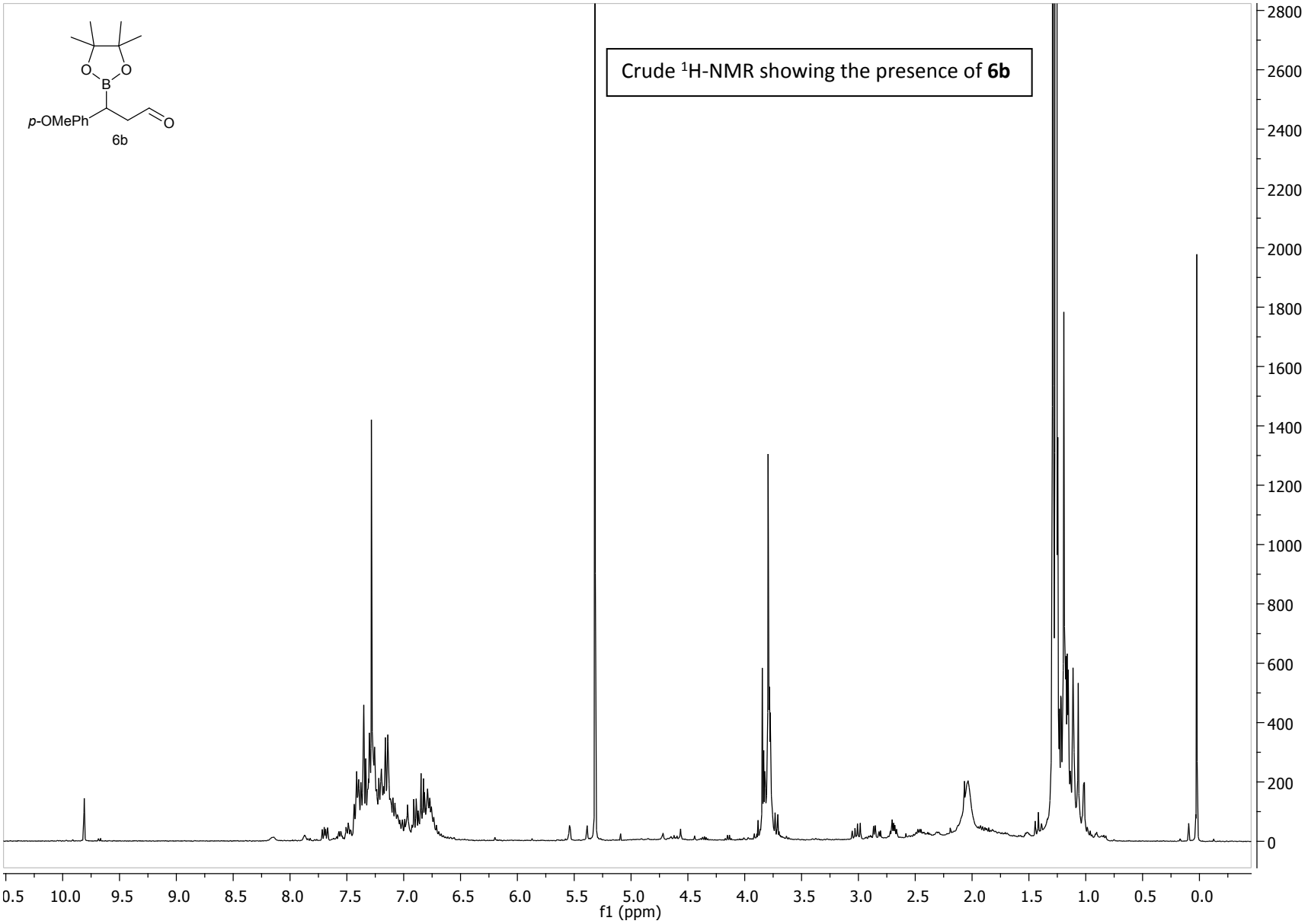
Stereochemical assignments

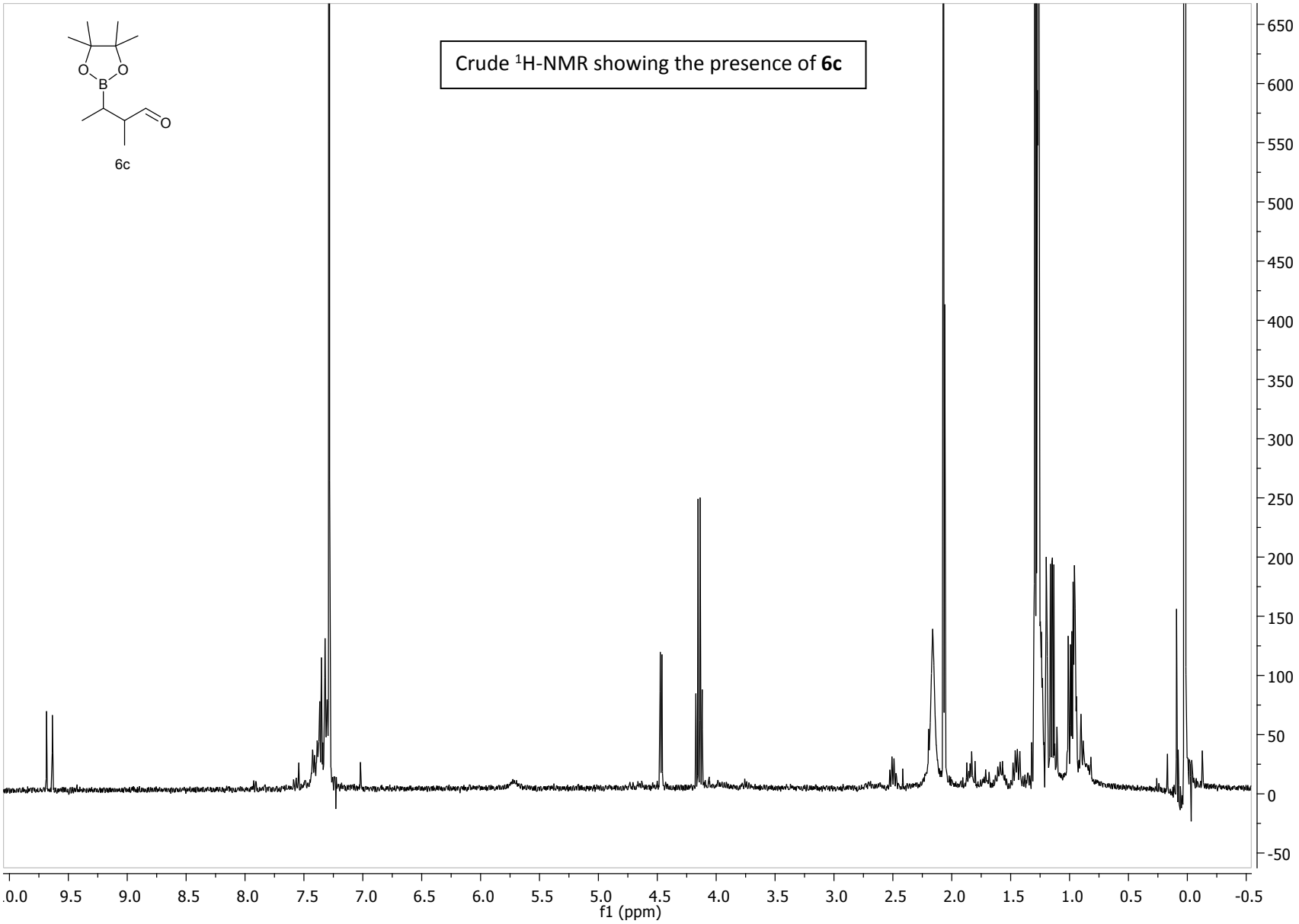
The relative stereochemistry of each chiral compound can be determined through the use of chiral HPLC (see above). In addition, the absolute stereochemistry of each product is assumed to be consistent with previous studies in our group,[1] whereby derivatisation and X-ray analysis allowed for the absolute stereochemistry of the respective compounds to be assigned. This was later supported by derivatisation of such compounds into known pharmaceuticals,[2] whereby the absolute stereochemistry was consistent with those independently verified by this work.1

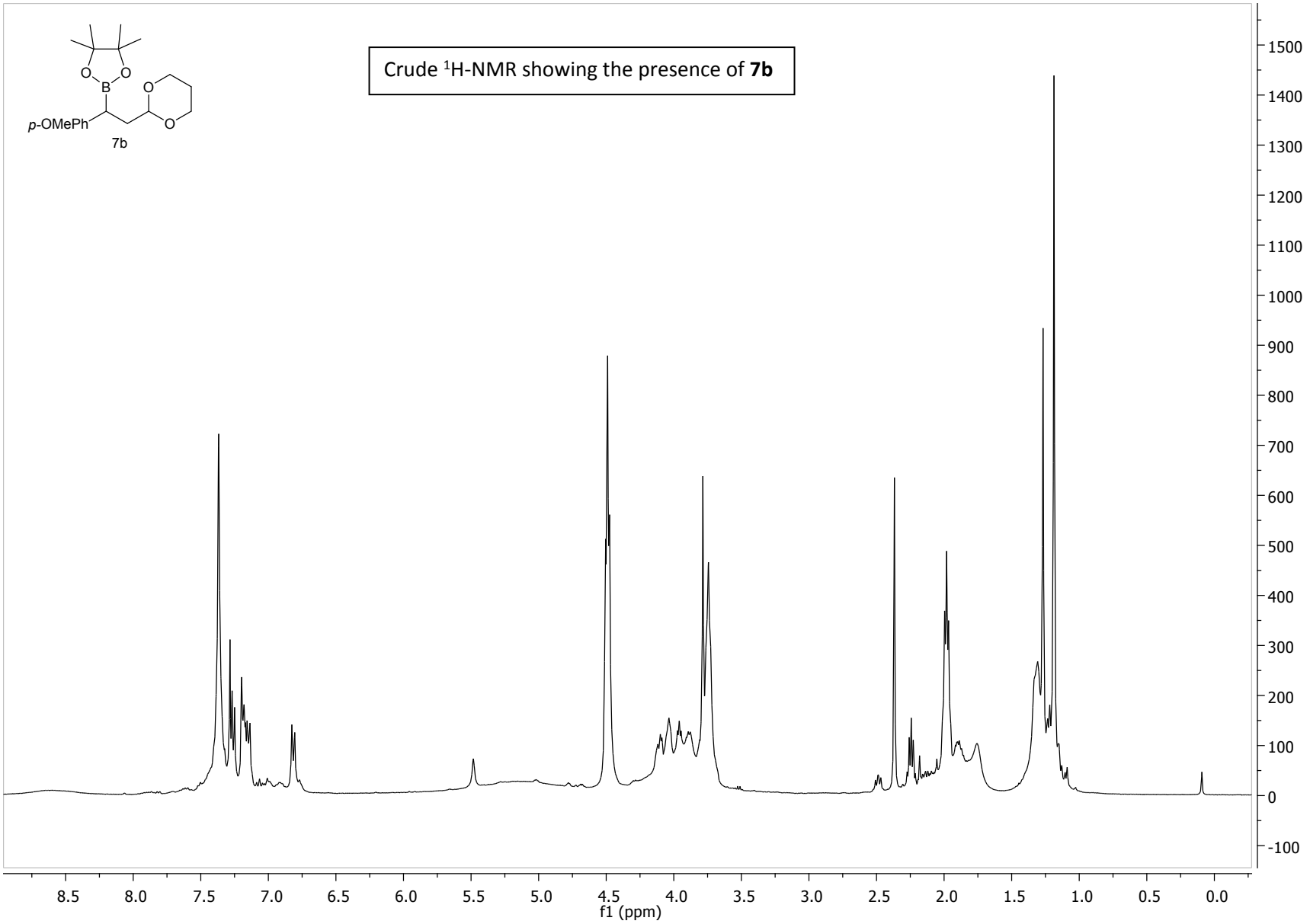
3. ^{1}H, ^{13}C and ^{11}B NMR spectra

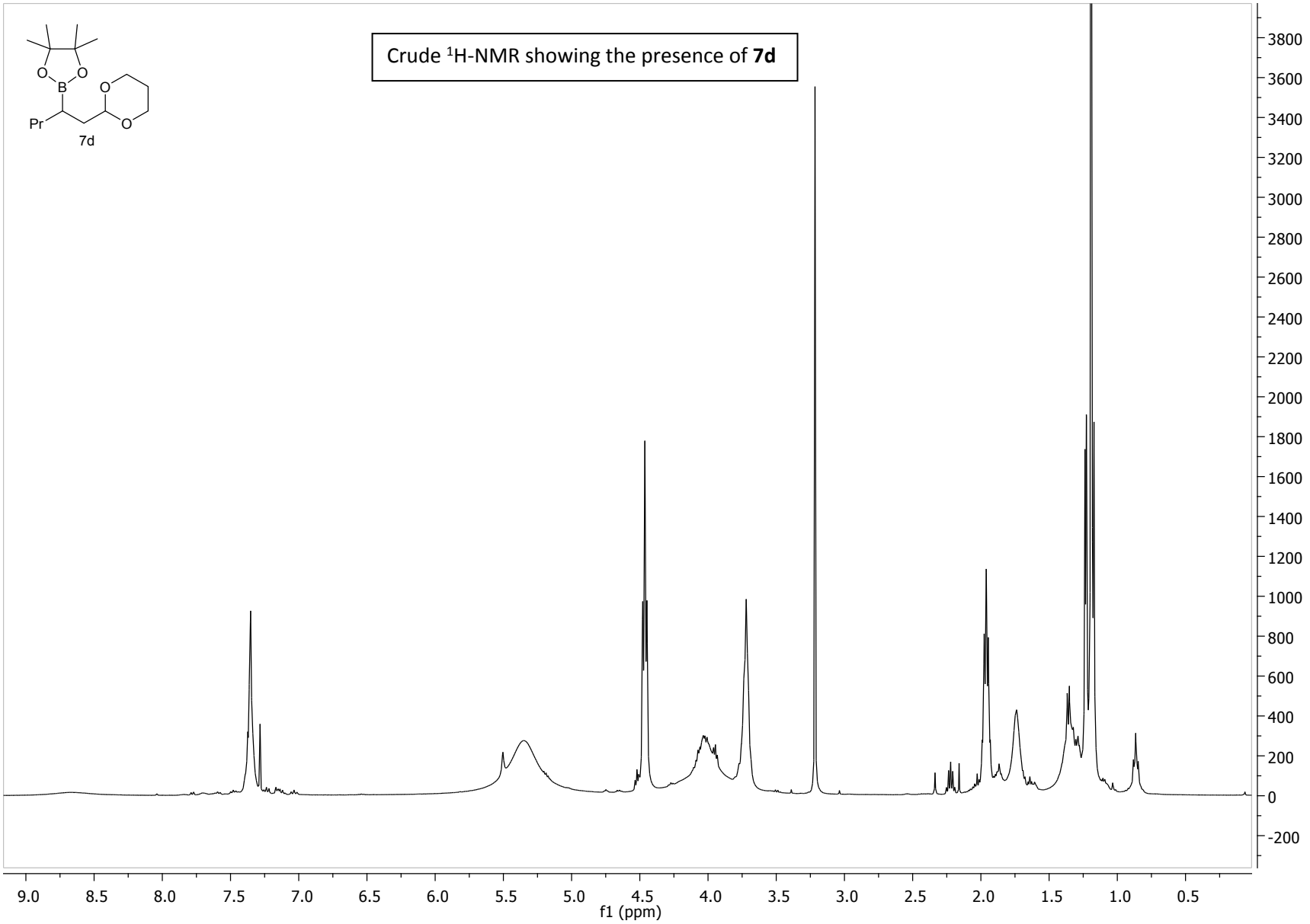
It is important to note that samples **6a-c**, **7b** and **7d** could not be purified due to their inherent instability. Therefore, the crude ^{1}H-NMR spectra of **6a-c**, **7b** and **7d** are listed below.

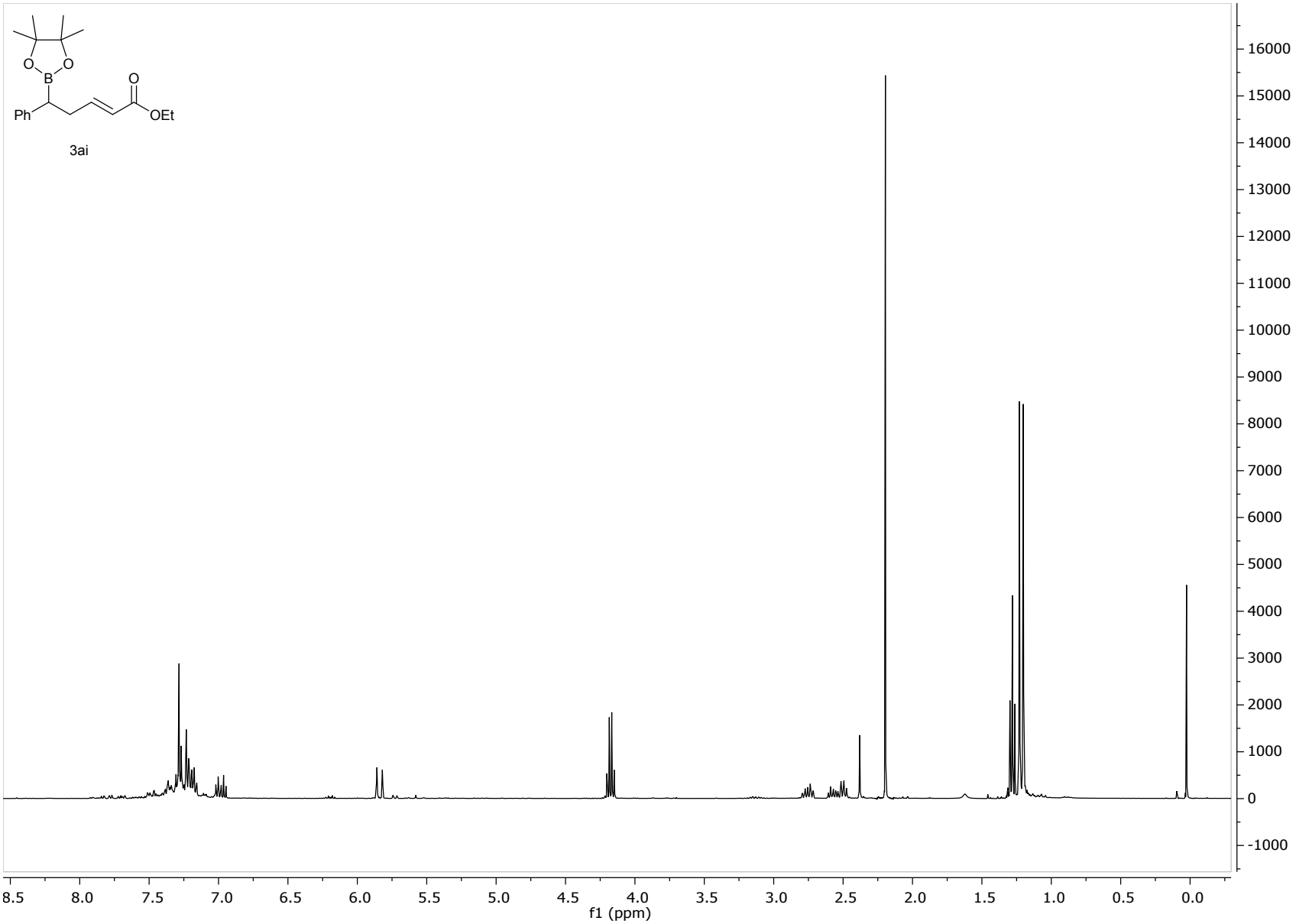

Crude ^{1}H-NMR showing the presence of **6a**
O
B
O
Ph
O
6a
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

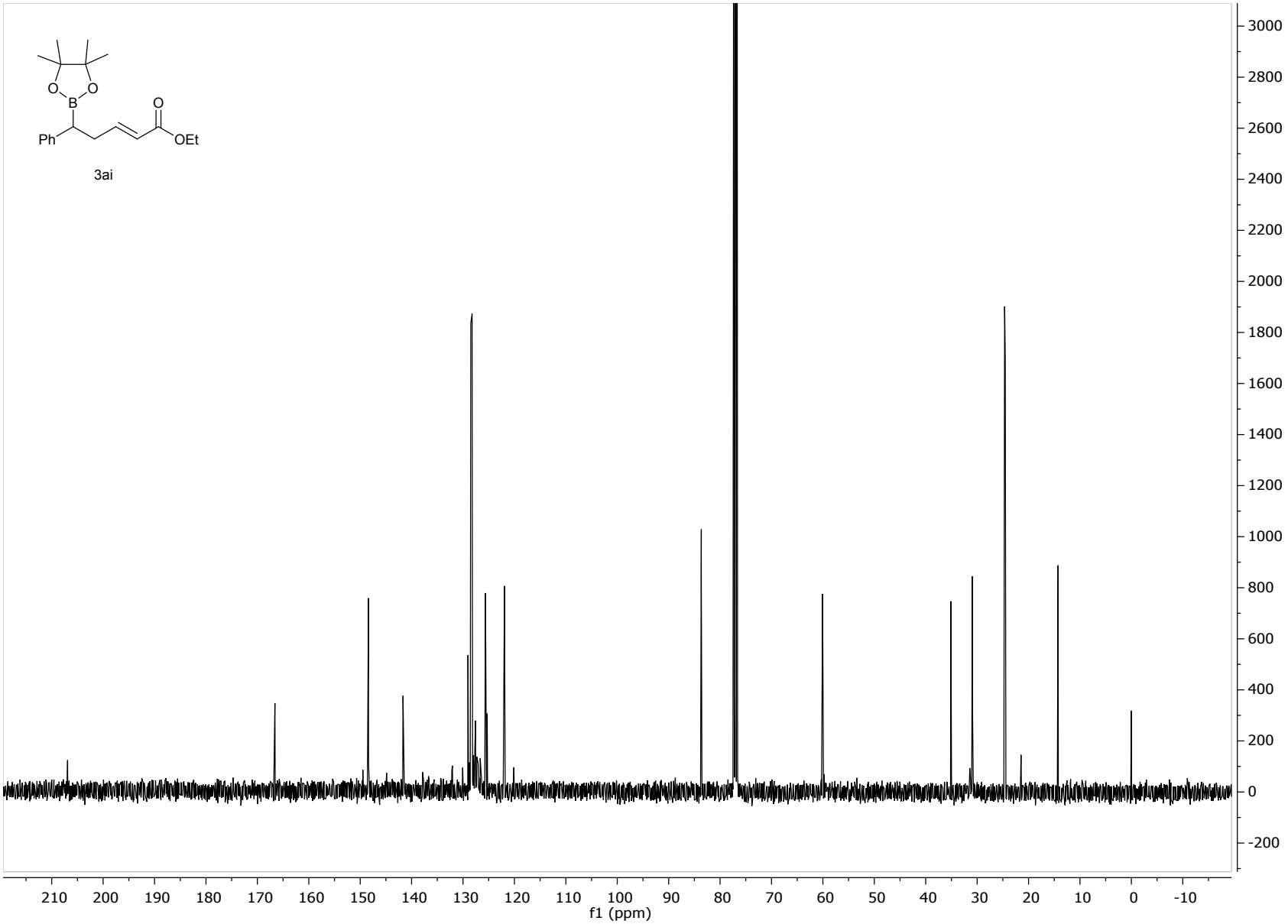

Crude ^{1}H-NMR showing the presence of **6b**
p-OMePh
6b
f1 (ppm)

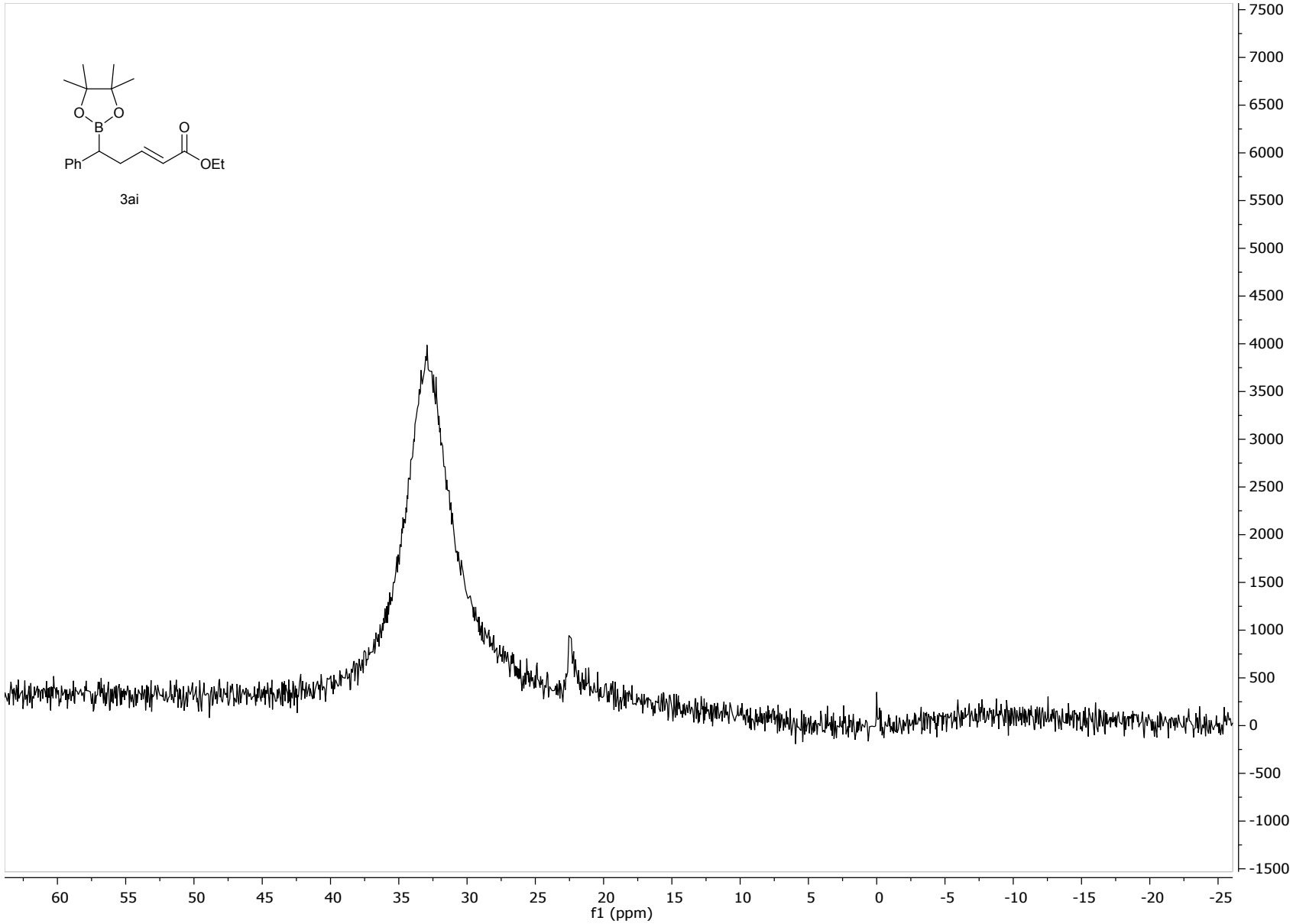

Crude ^{1}H-NMR showing the presence of **6c**
O
B
O
O
6c
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
.0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

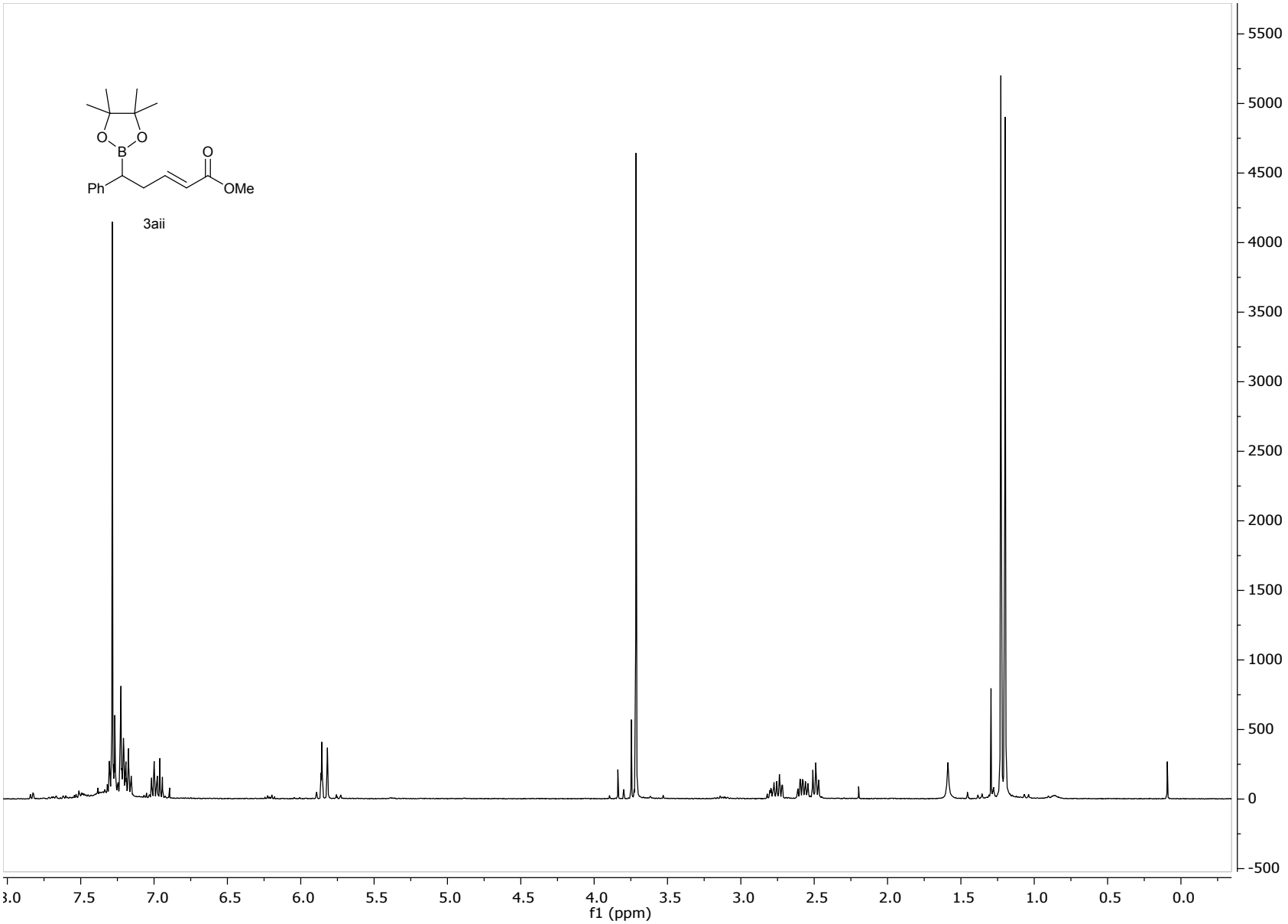

Crude ^{1}H-NMR showing the presence of **7b**
p-OMePh
7b
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

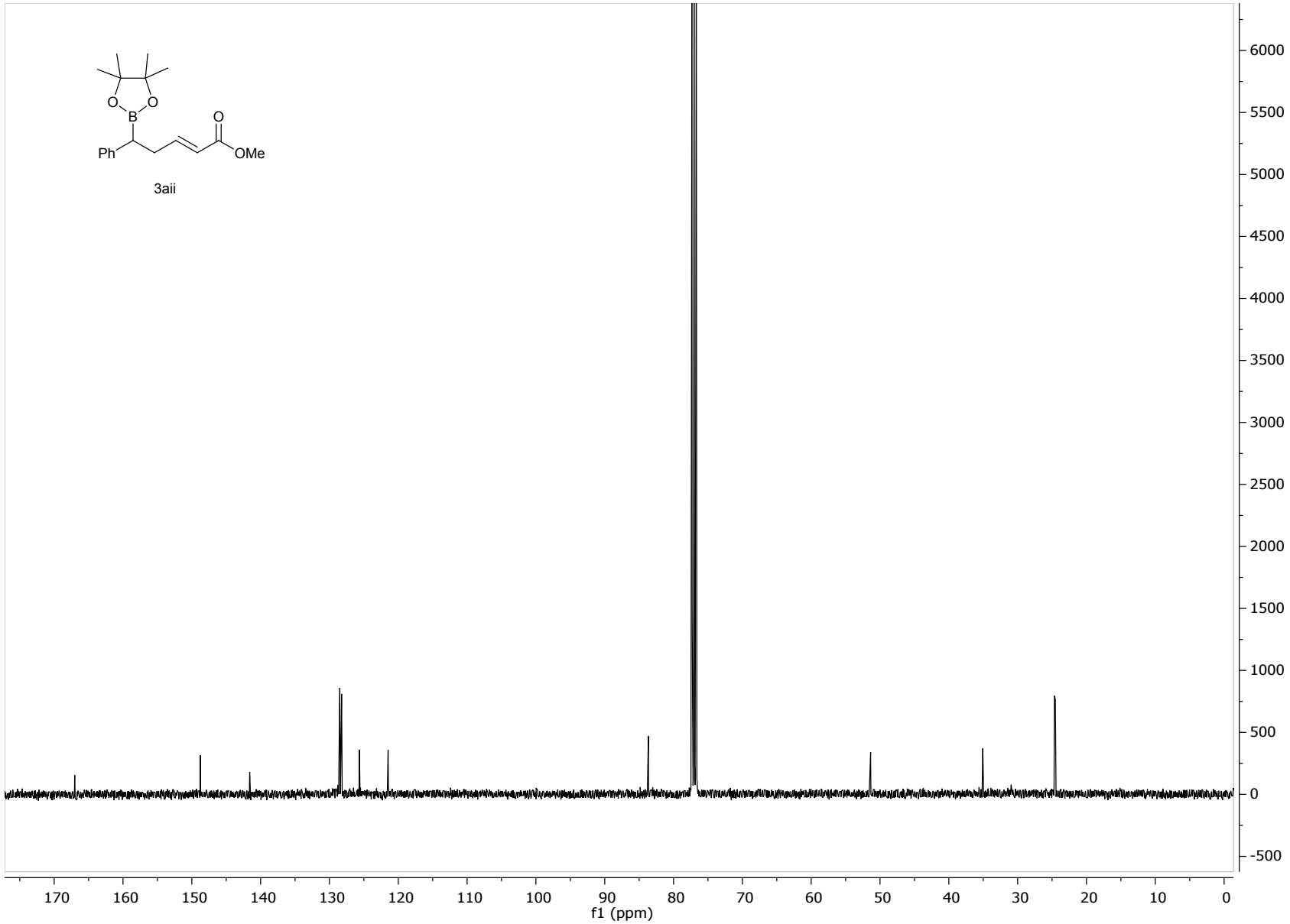

Crude ^{1}H-NMR showing the presence of **7d**
Pr
7d
f1 (ppm)

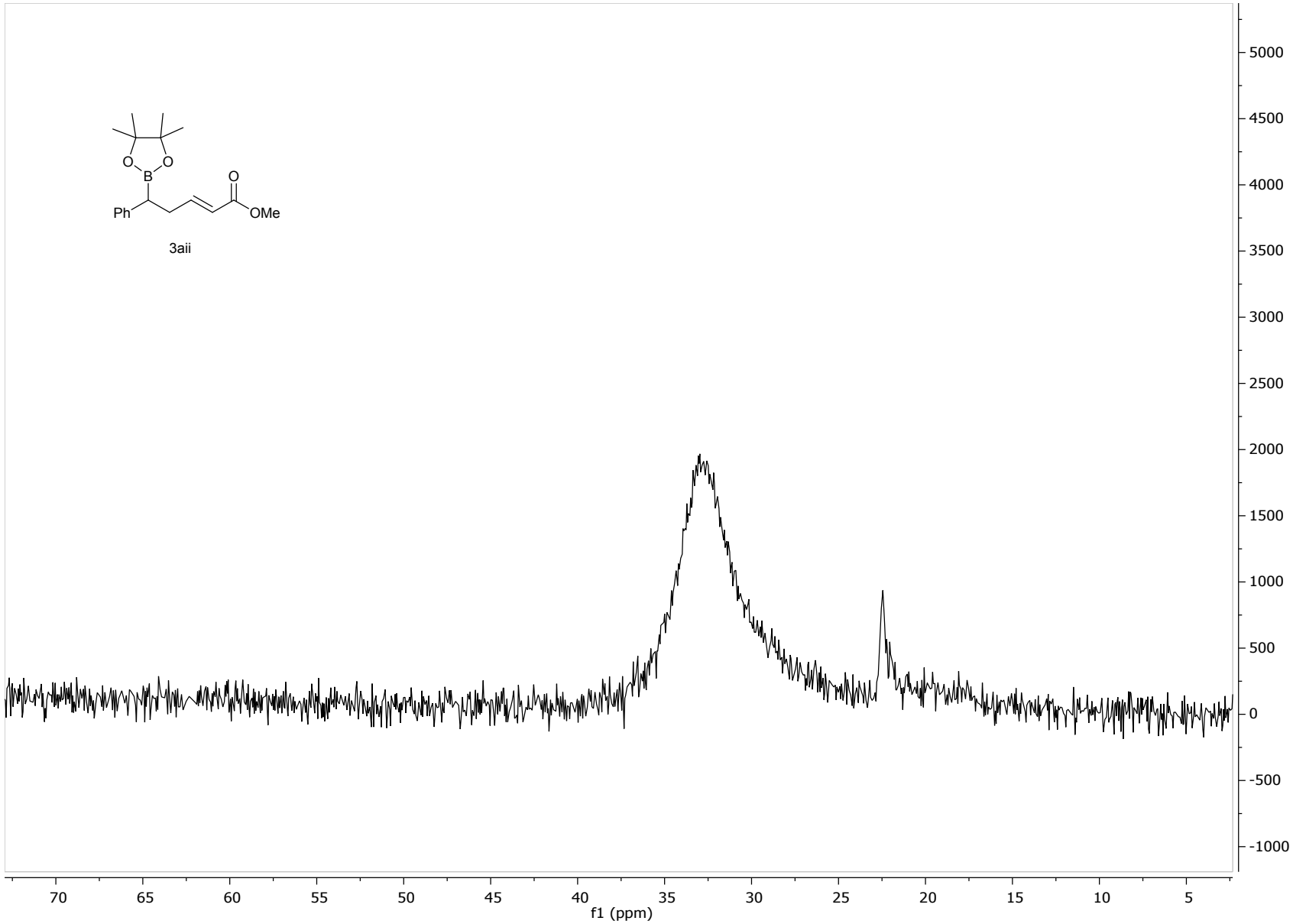

O
O
B
O
Ph
OEt
3ai
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

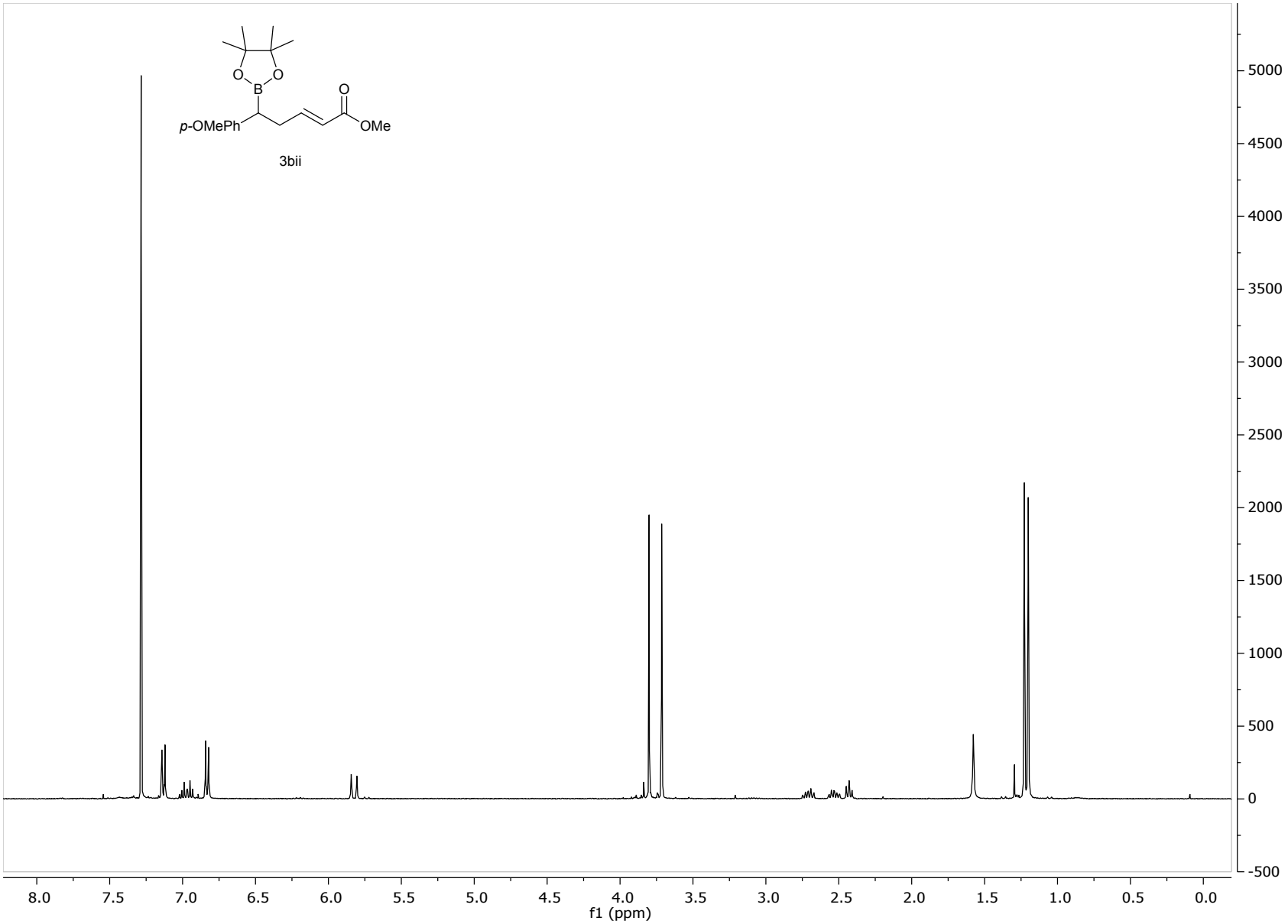

O
B
O
O
Ph
OEt
3ai
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

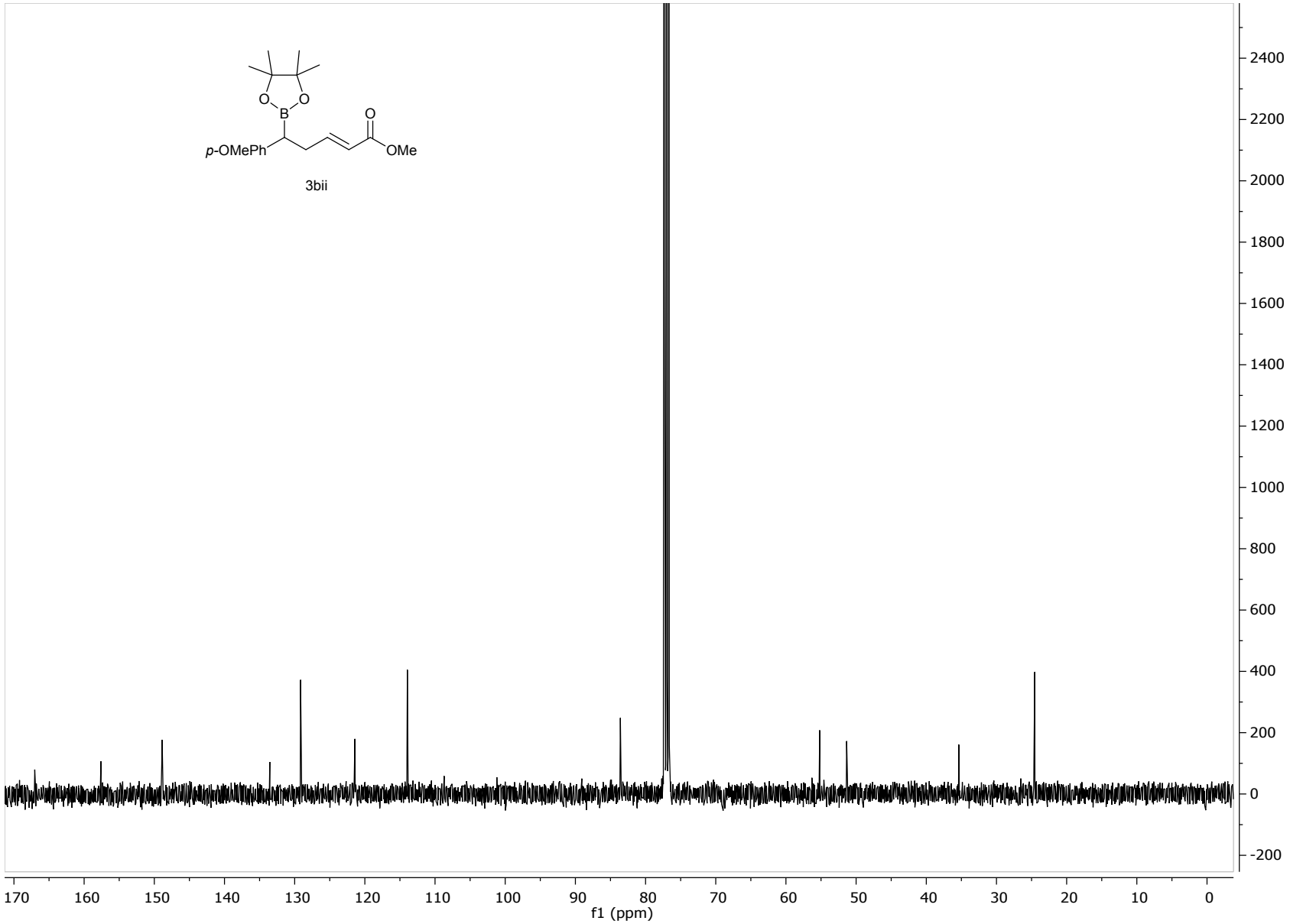

O
B
O
O
Ph
OEt
3ai
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

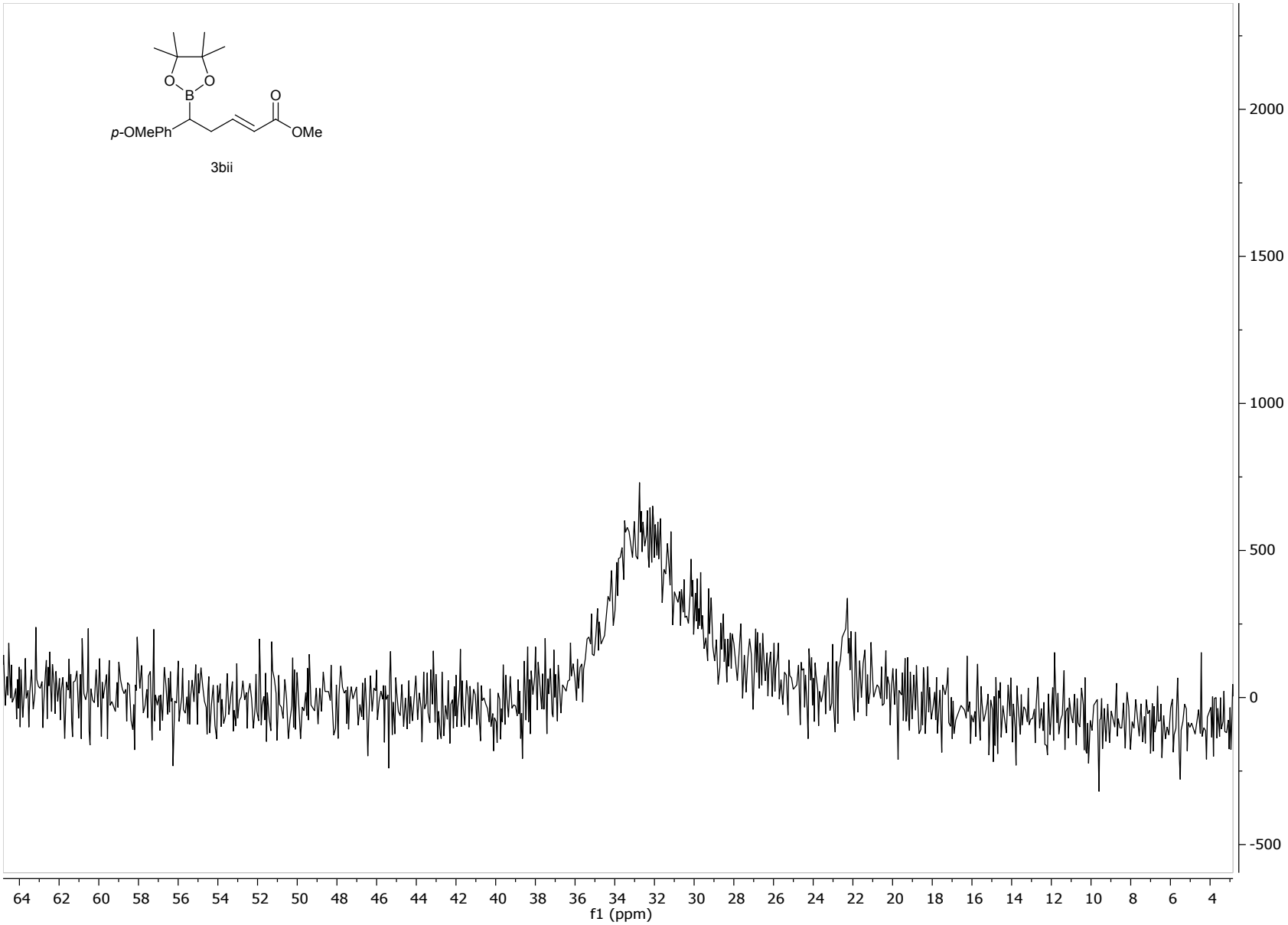

O
B
O
O
Ph
OMe
3aii
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

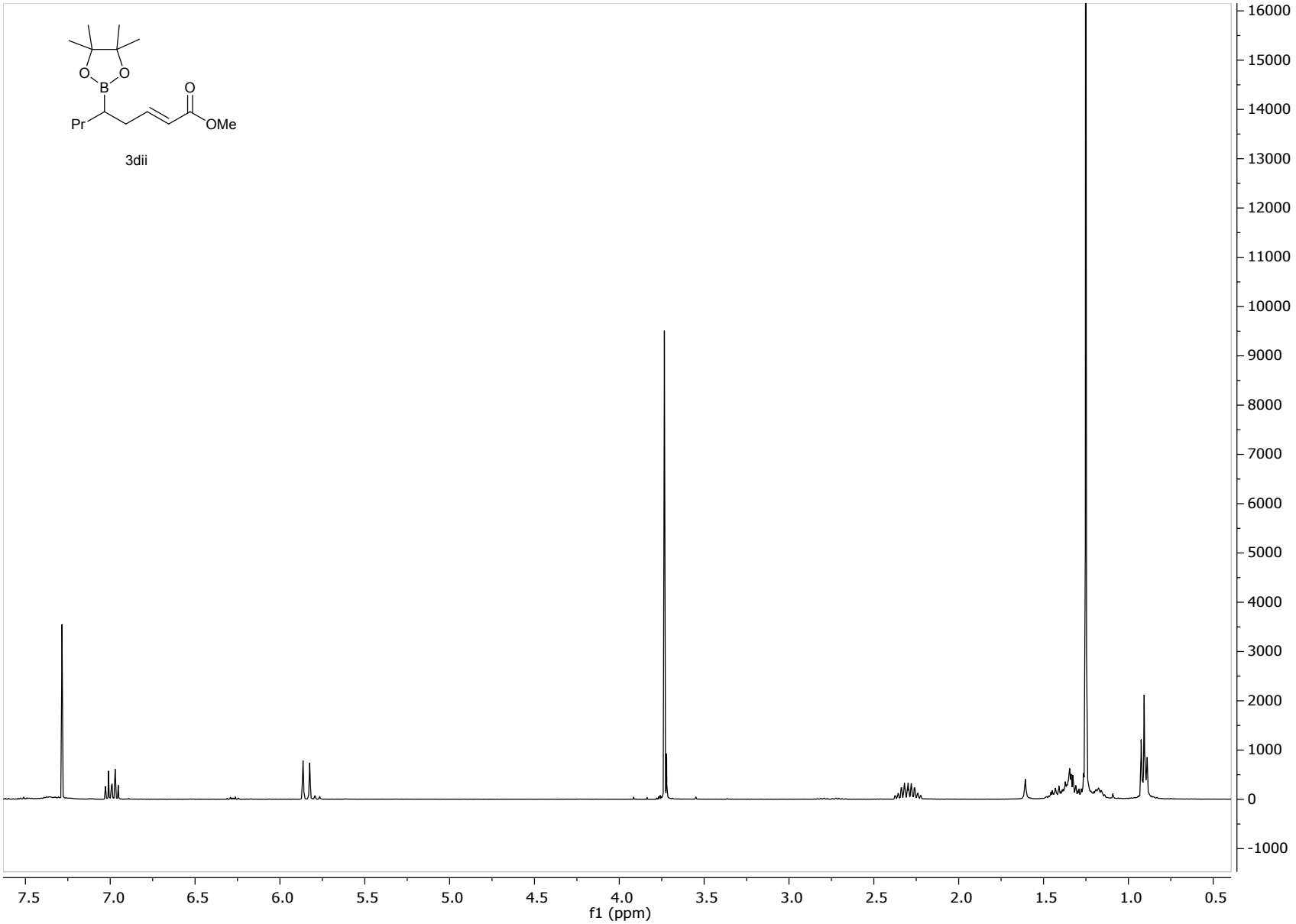

O
B
O
O
Ph
OMe
3aii
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

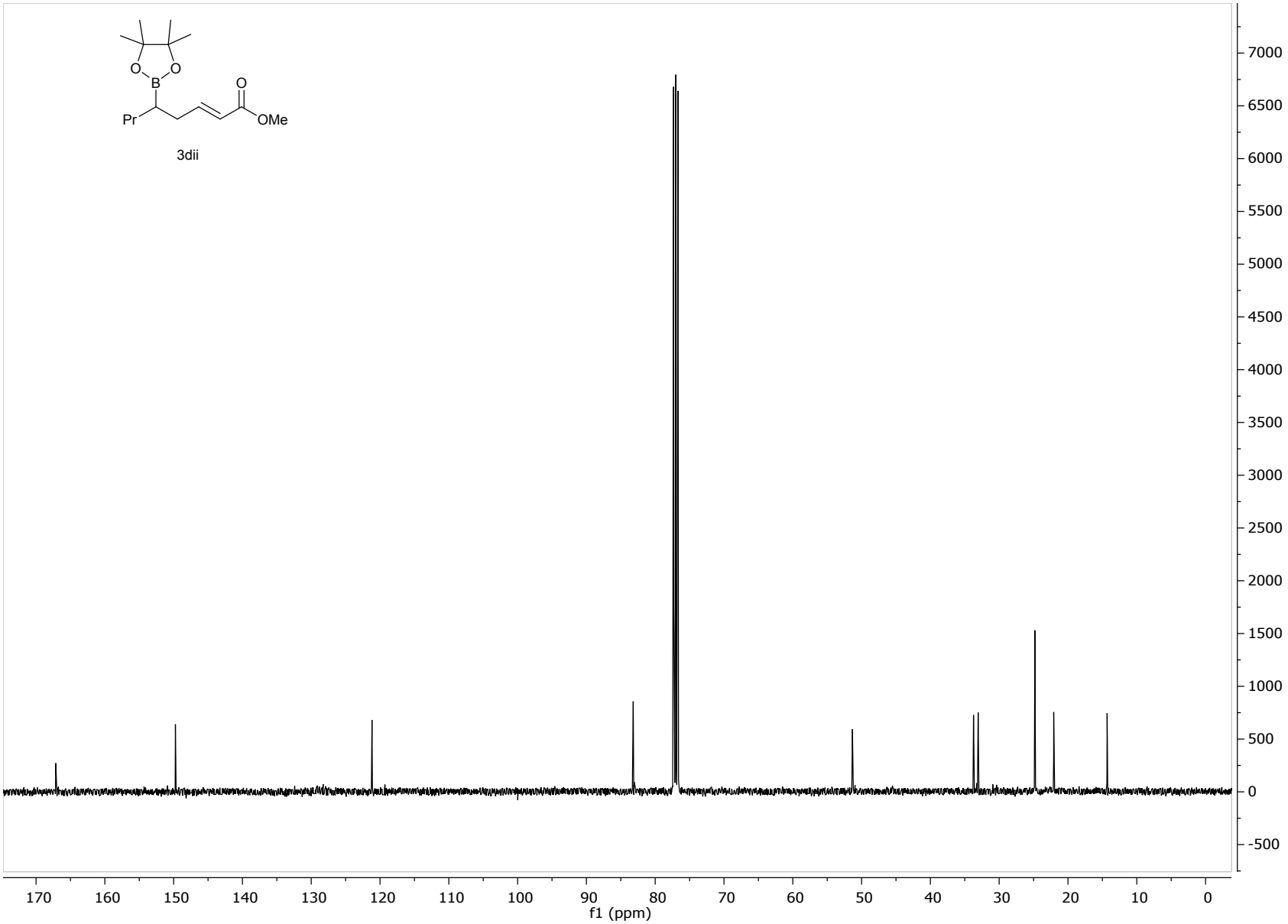

O
B
O
Ph
O
OMe
3aii
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

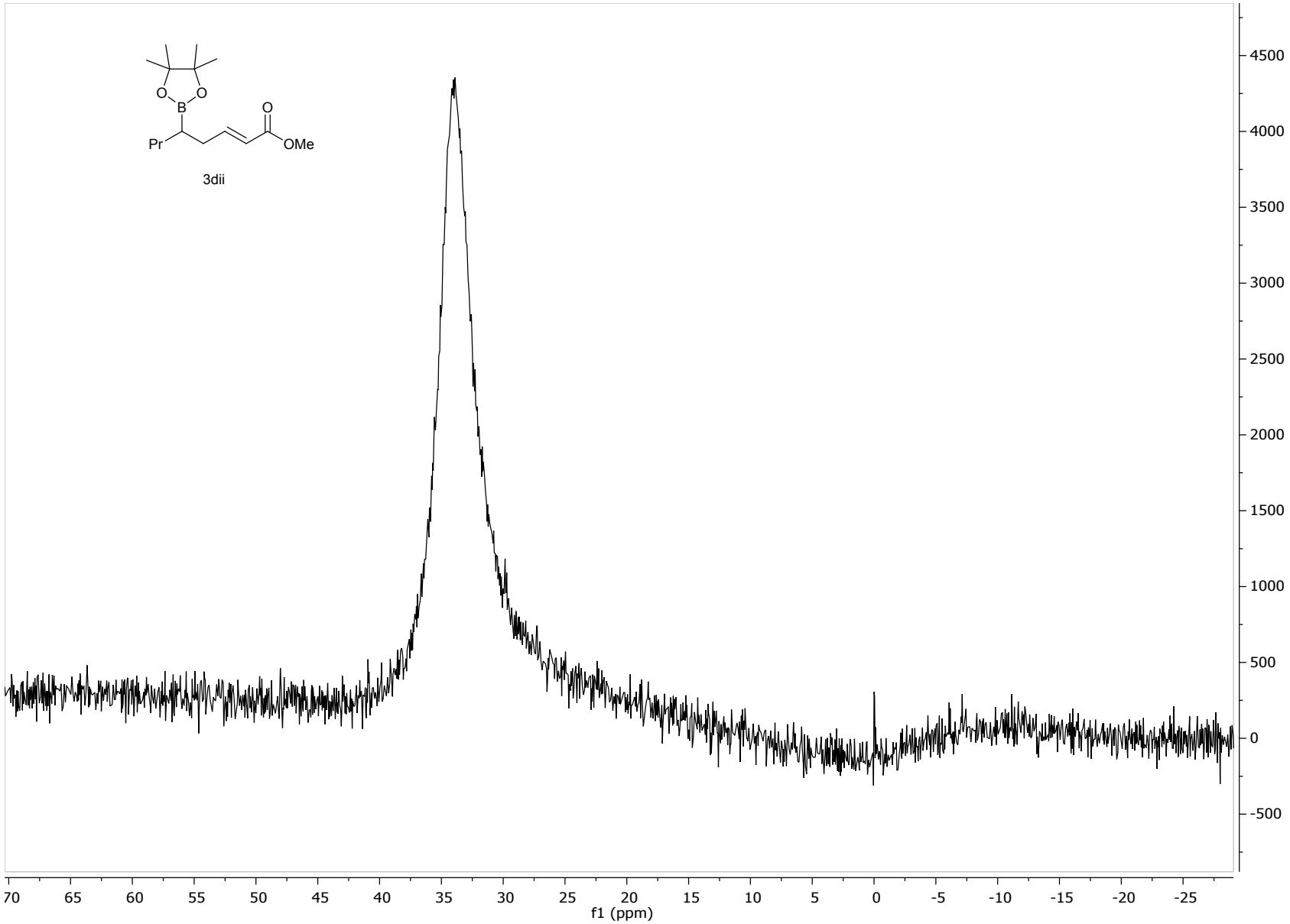

O
B
O
O
p-OMePh
OMe
3bii
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

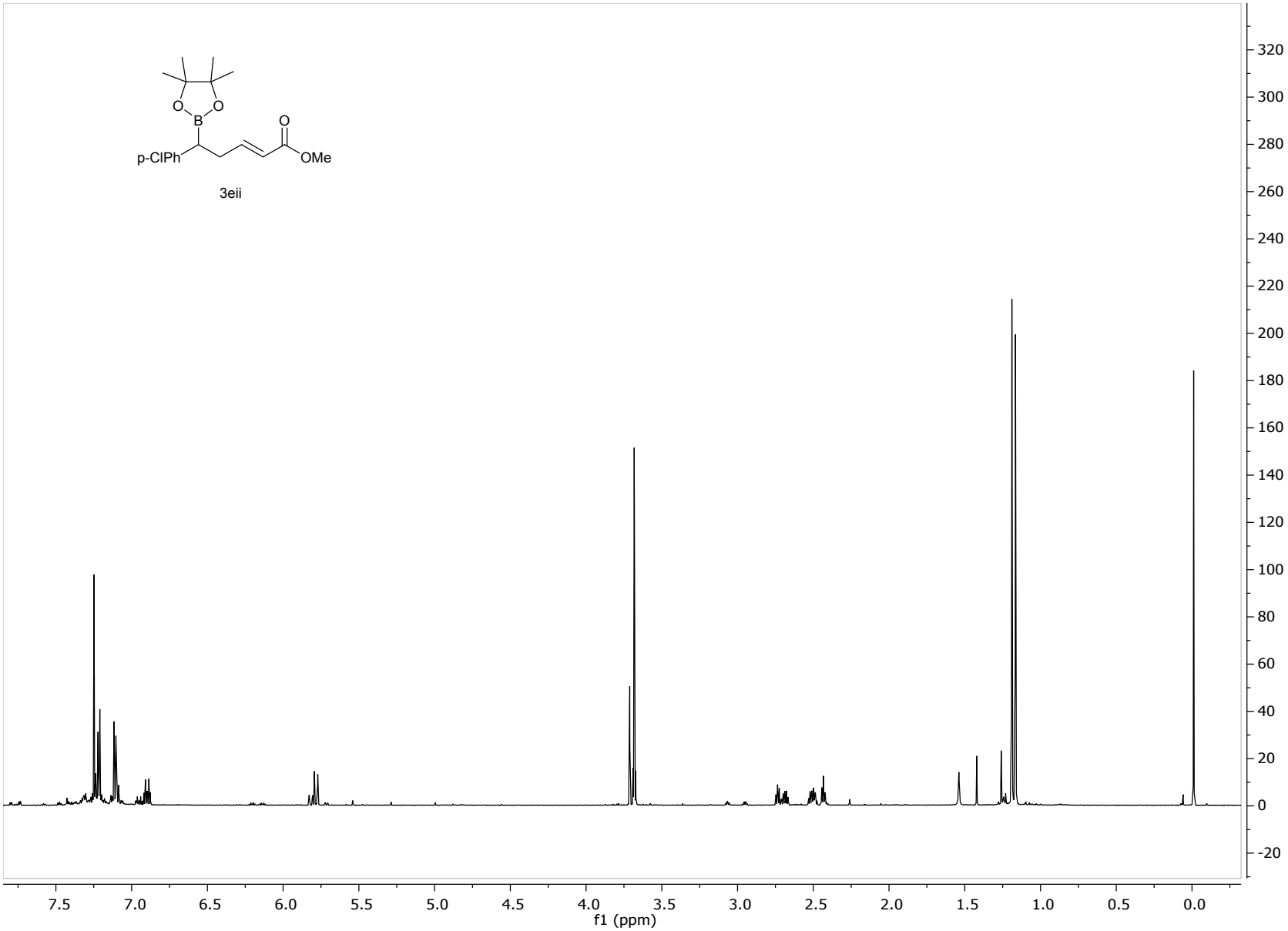

O
B
O
O
p-OMePh
OMe
3bii
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

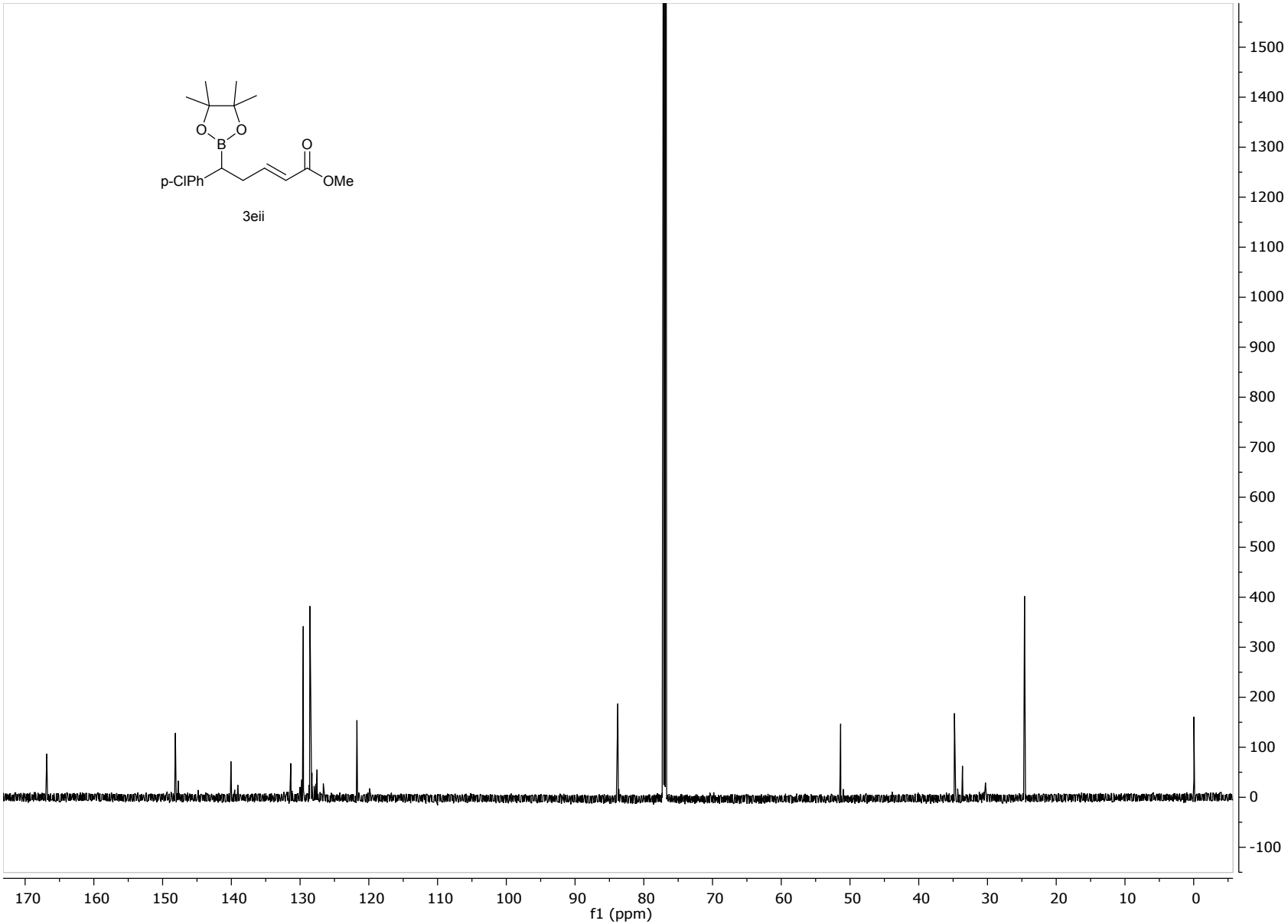

O
B
O
O
p-OMePh
OMe
3bii
2000
1500
1000
500
0
-500
64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4
f1 (ppm)

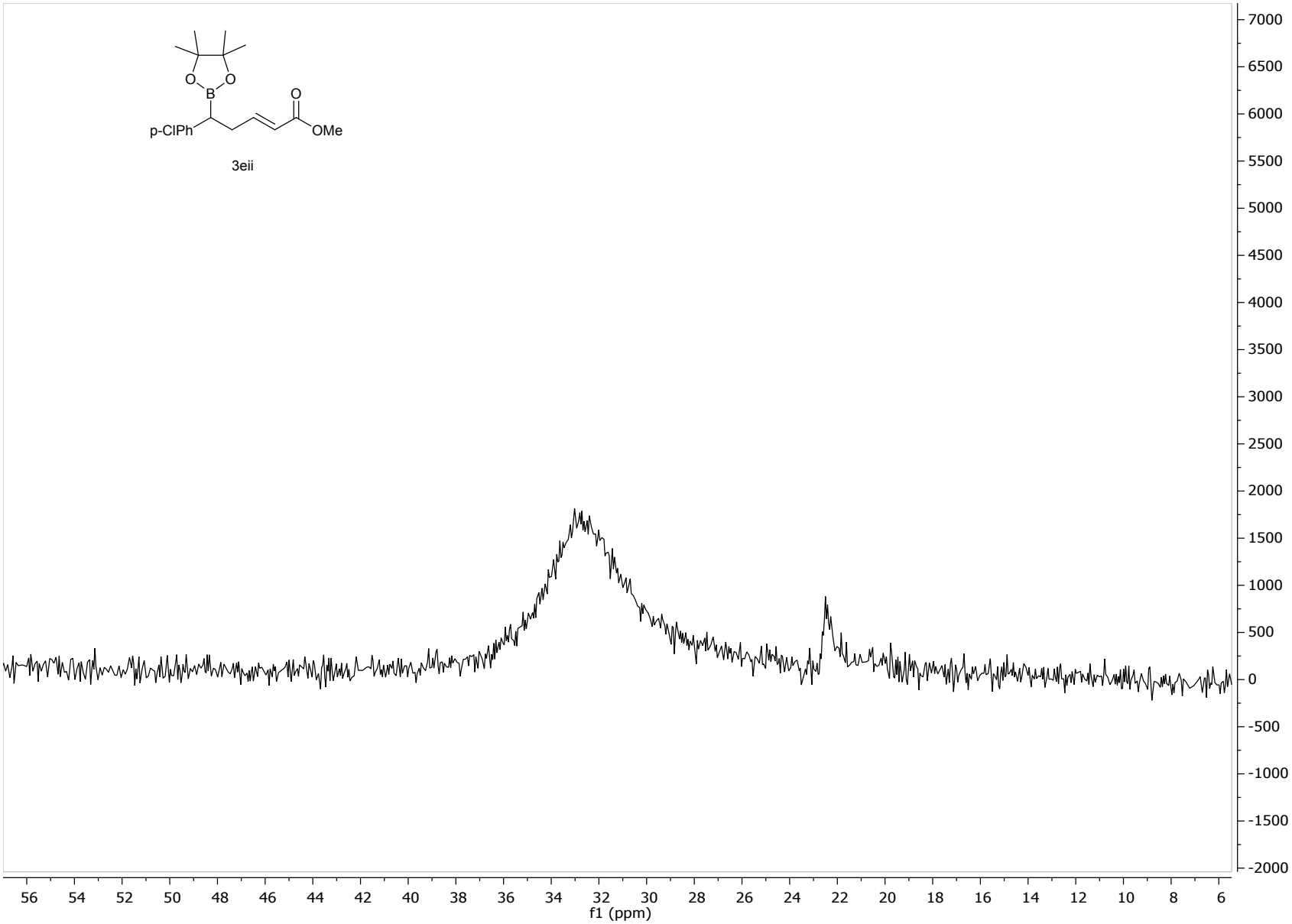

O
B
O
O
Pr
OMe
3dii
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

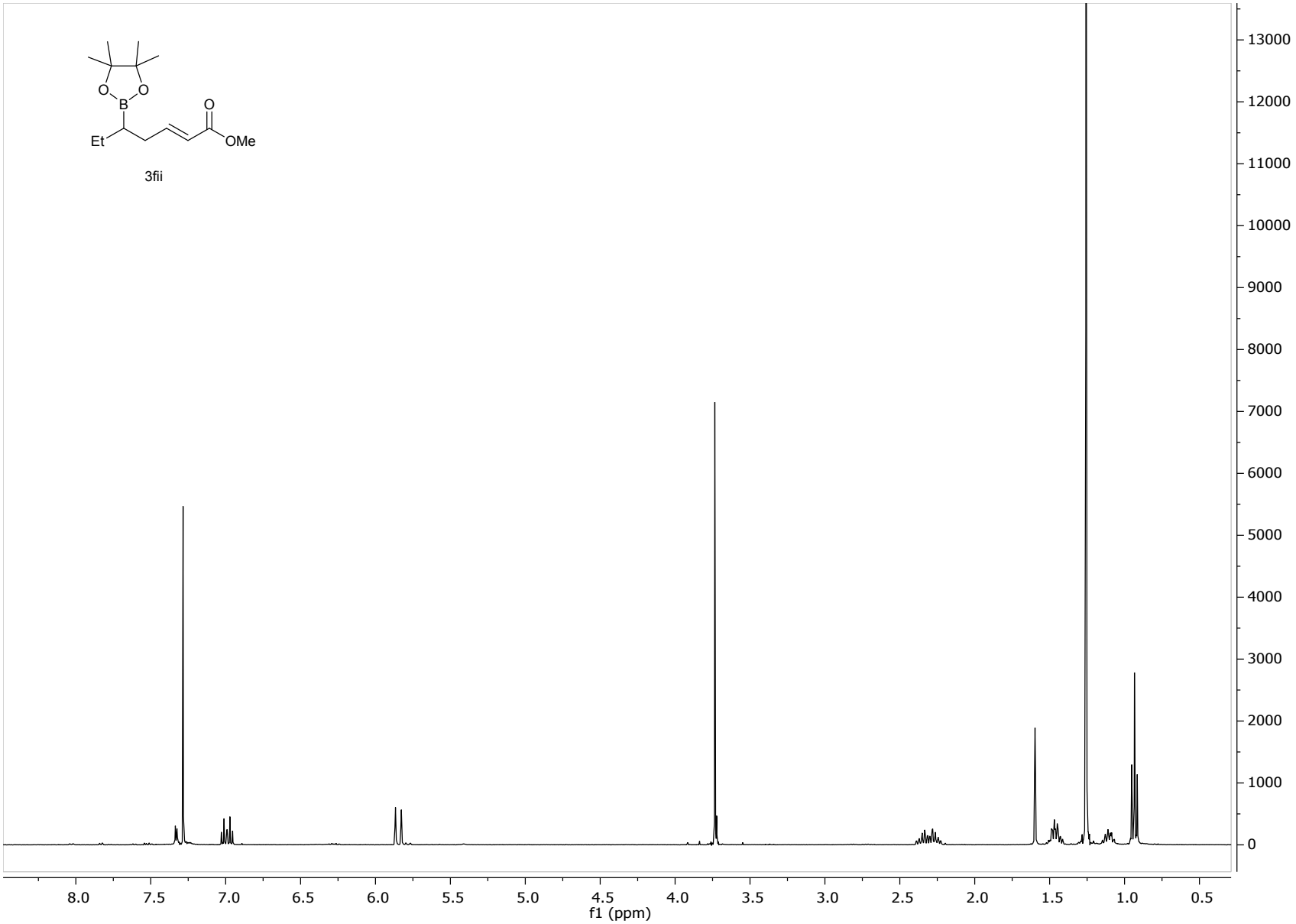

O
B
O
O
Pr
OMe
3dii
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

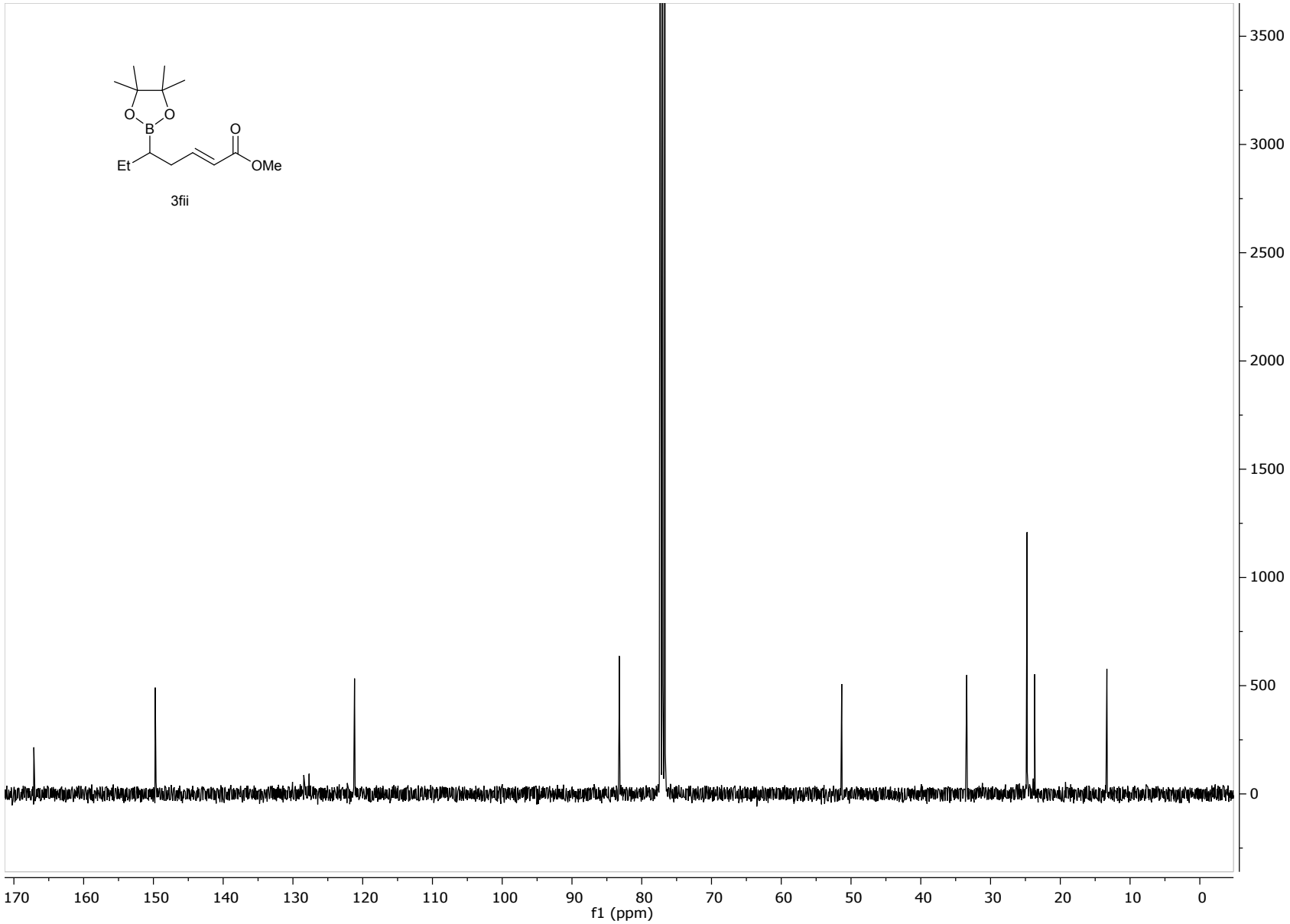

O
B
O
O
Pr
OMe
3dii
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

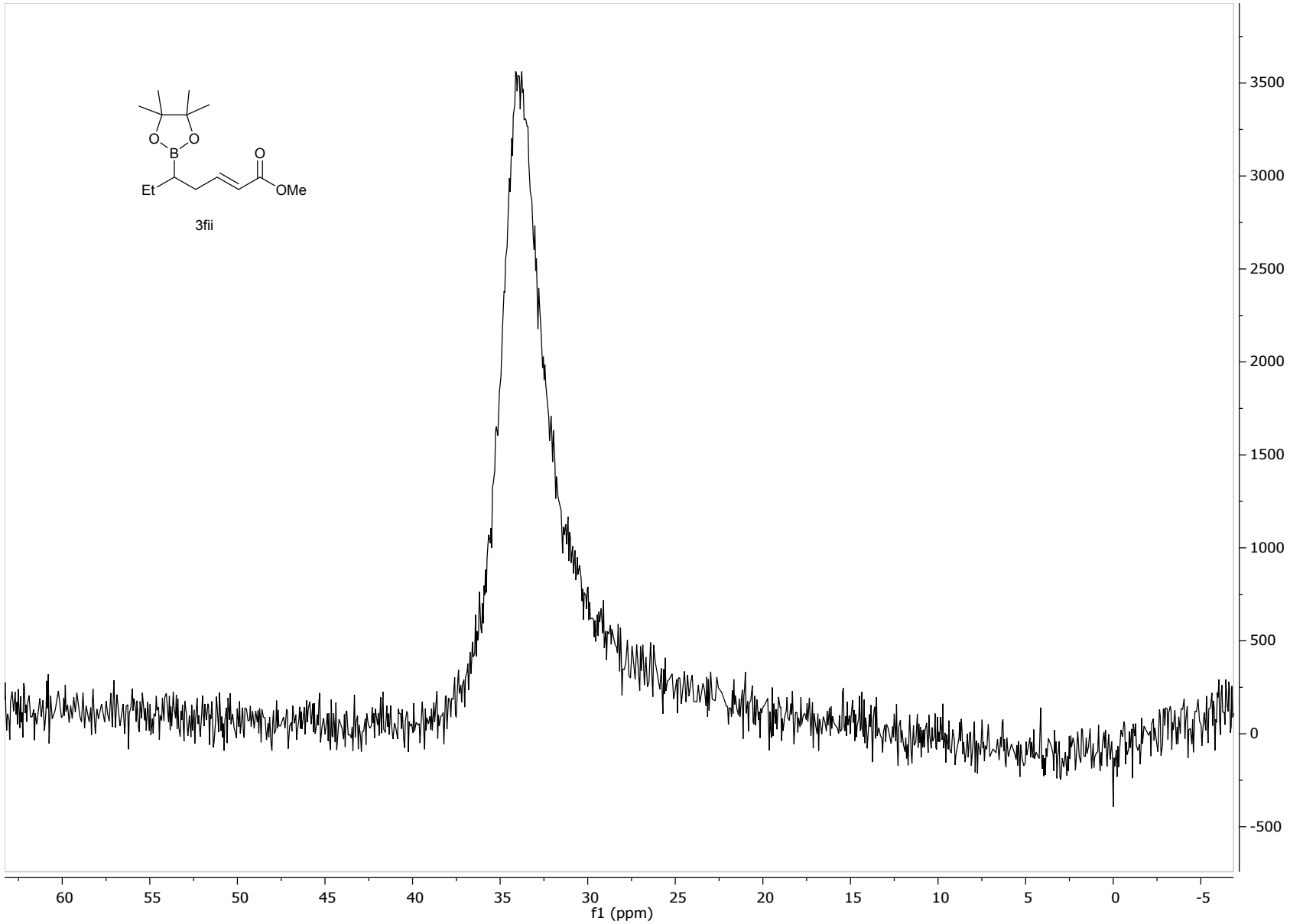

O
B
O
O
p-ClPh
OMe
3eii
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

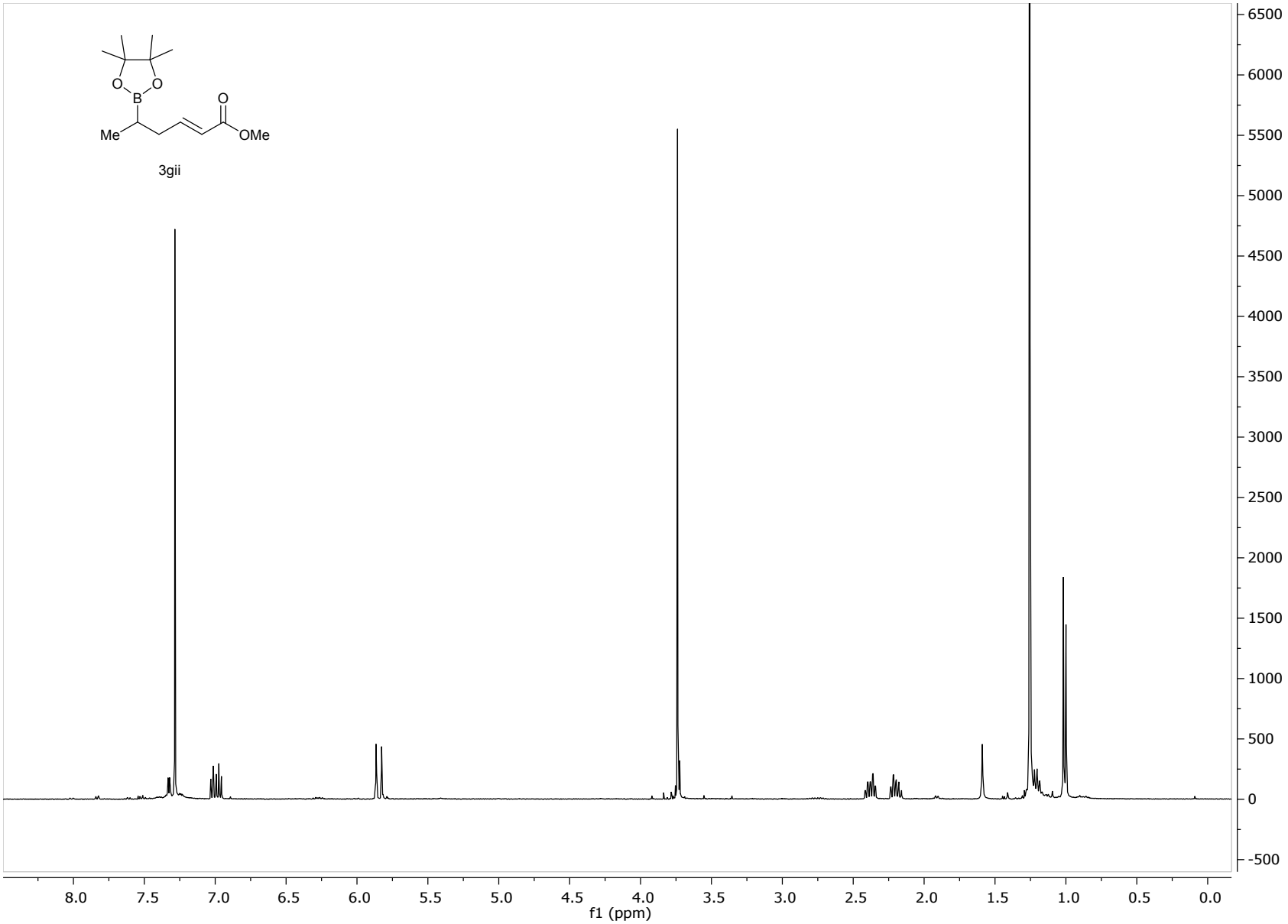

O
B
O
O
p-ClPh
OMe
3eii
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

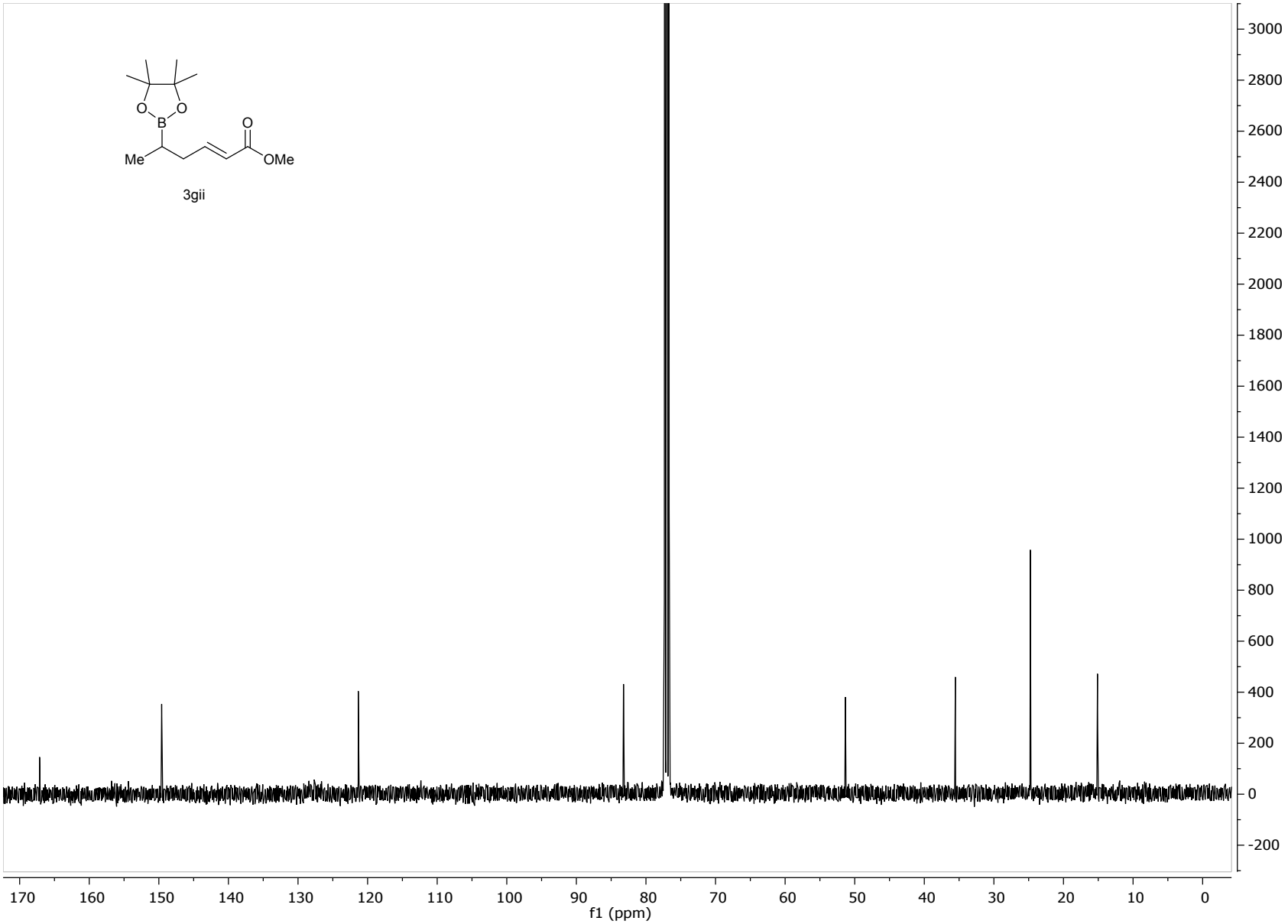

O
B
O
O
p-ClPh
OMe
3eii
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6
f1 (ppm)


O
B
O
Et
O
OMe
3fii
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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
f1 (ppm)


O
B
O
O
Et
OMe
3fii
3500
3000
2500
2000
1500
1000
500
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
B
O
O
Et
OMe
3fii
3500
3000
2500
2000
1500
1000
500
0
-500
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
f1 (ppm)


O
O
B
O
Me
OMe
3gii
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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
f1 (ppm)


O
O
B
O
Me
OMe
3gii
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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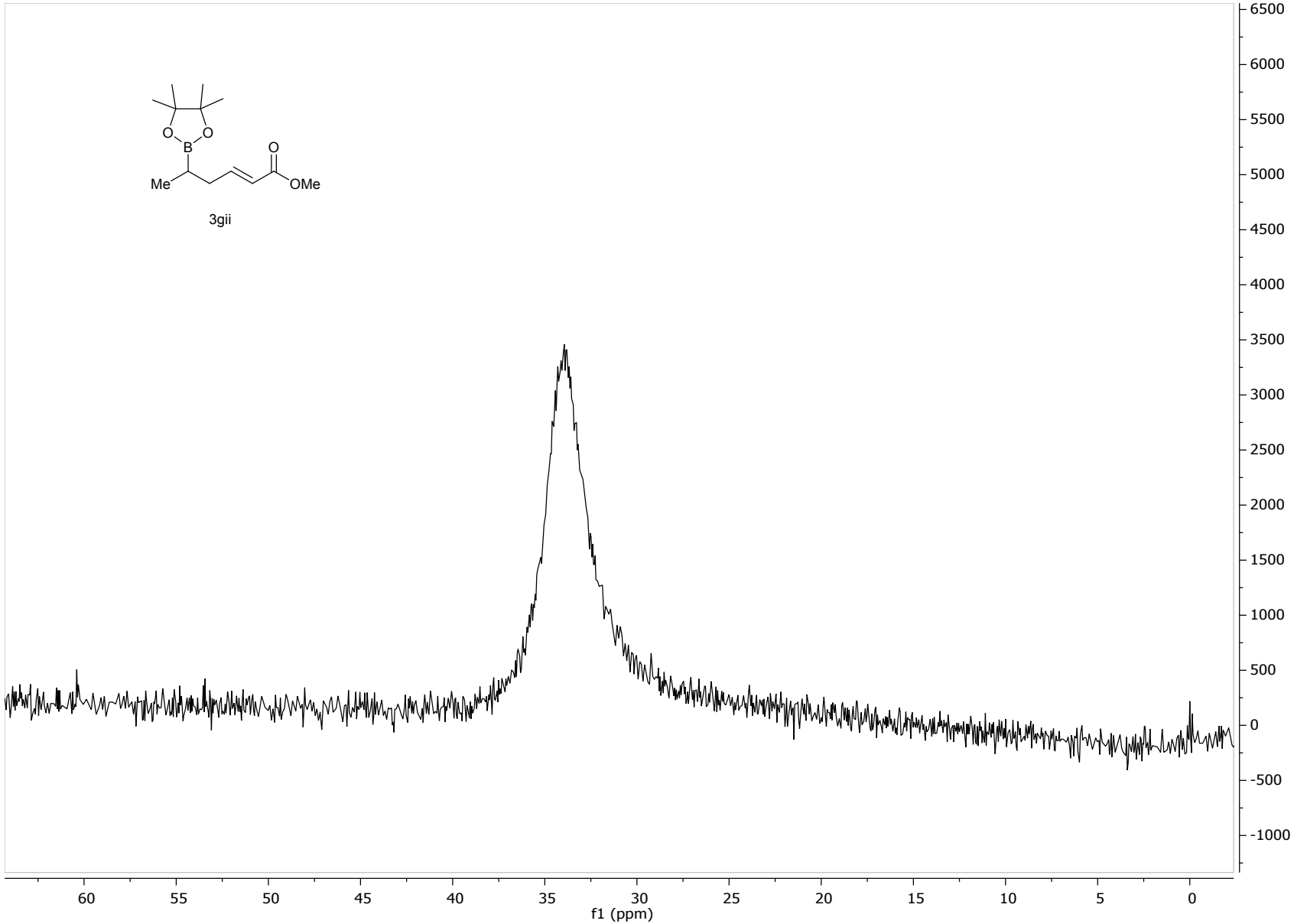
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Me
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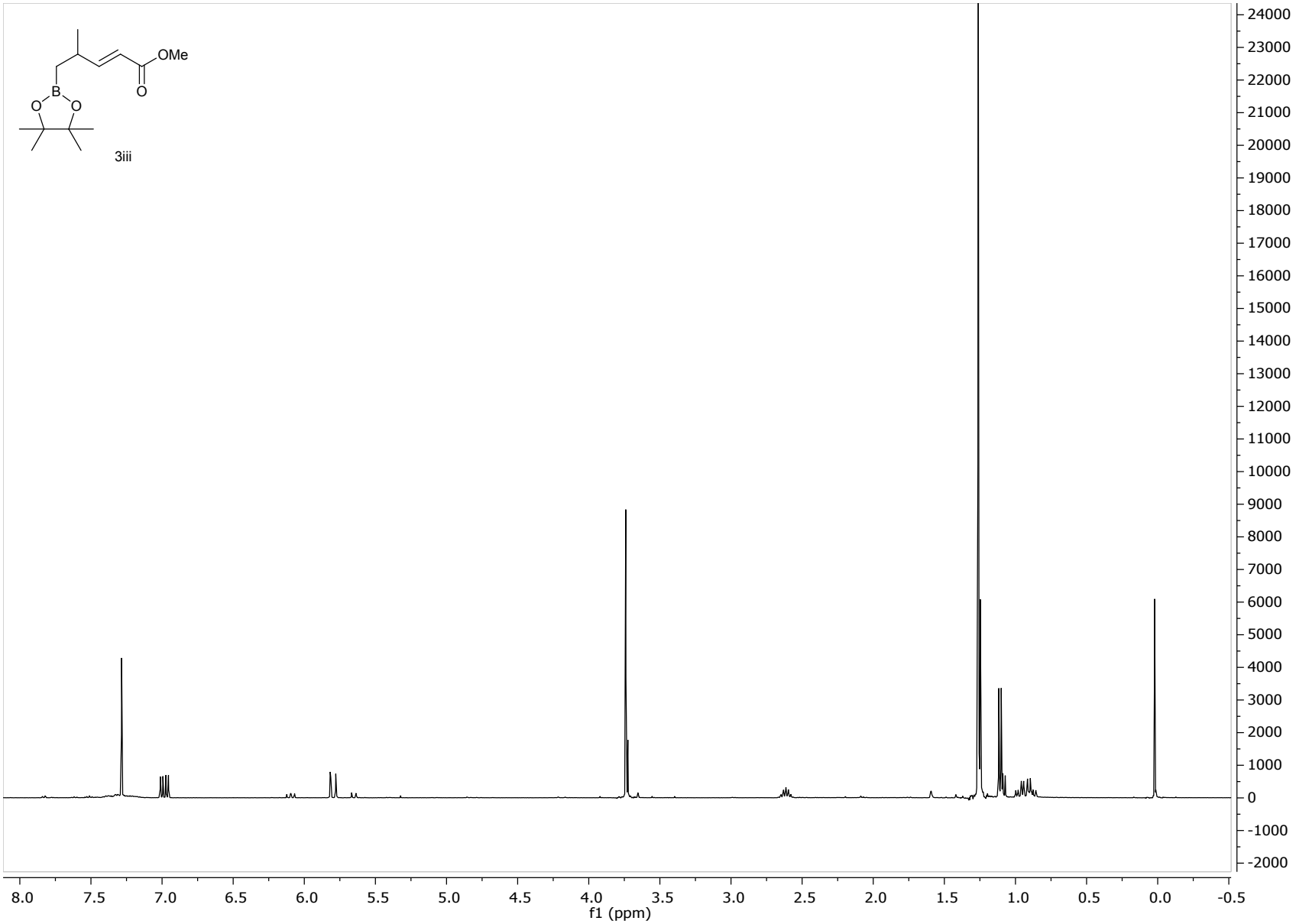
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6000
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4000
3000
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7.5
7.0
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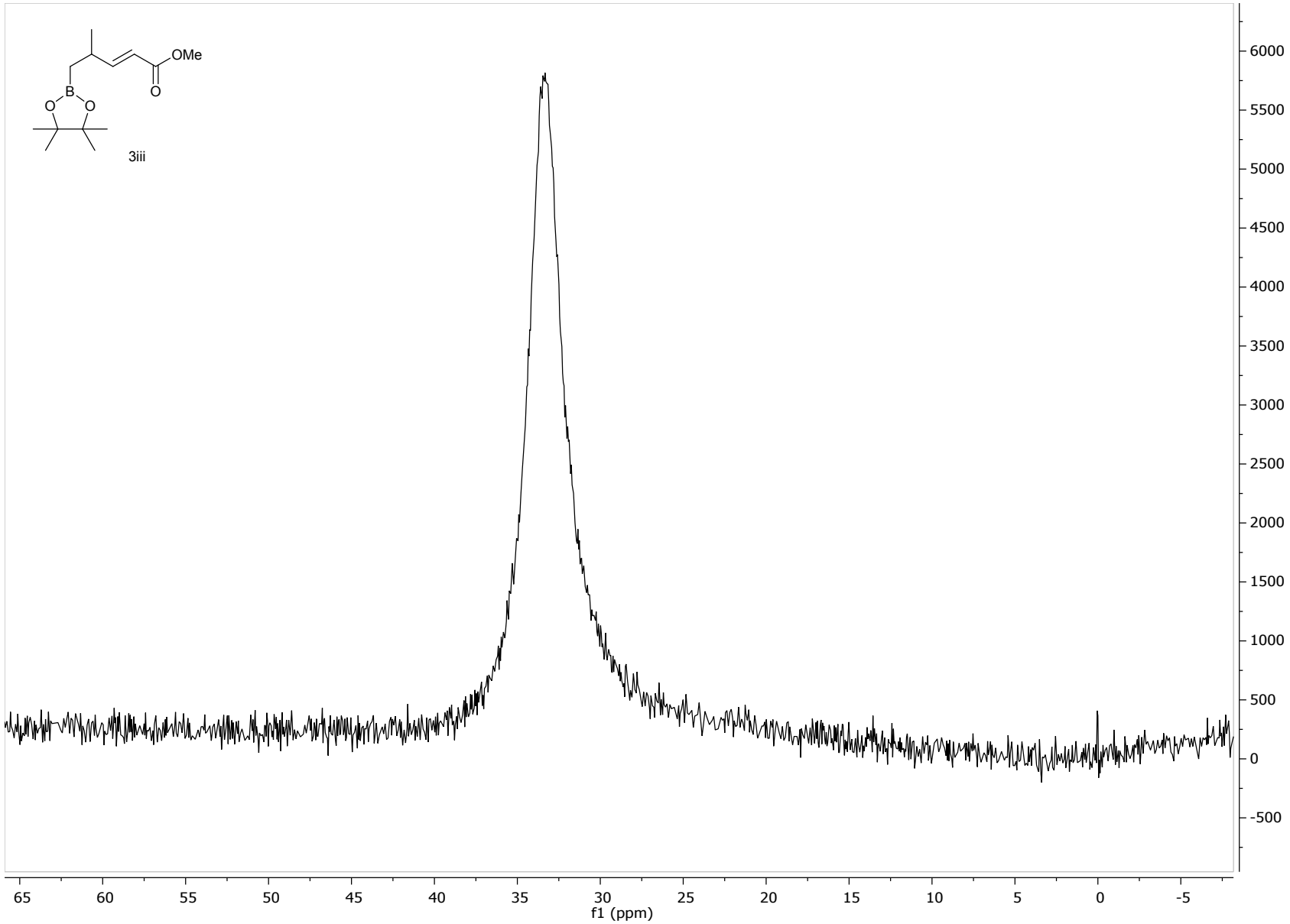
f1 (ppm)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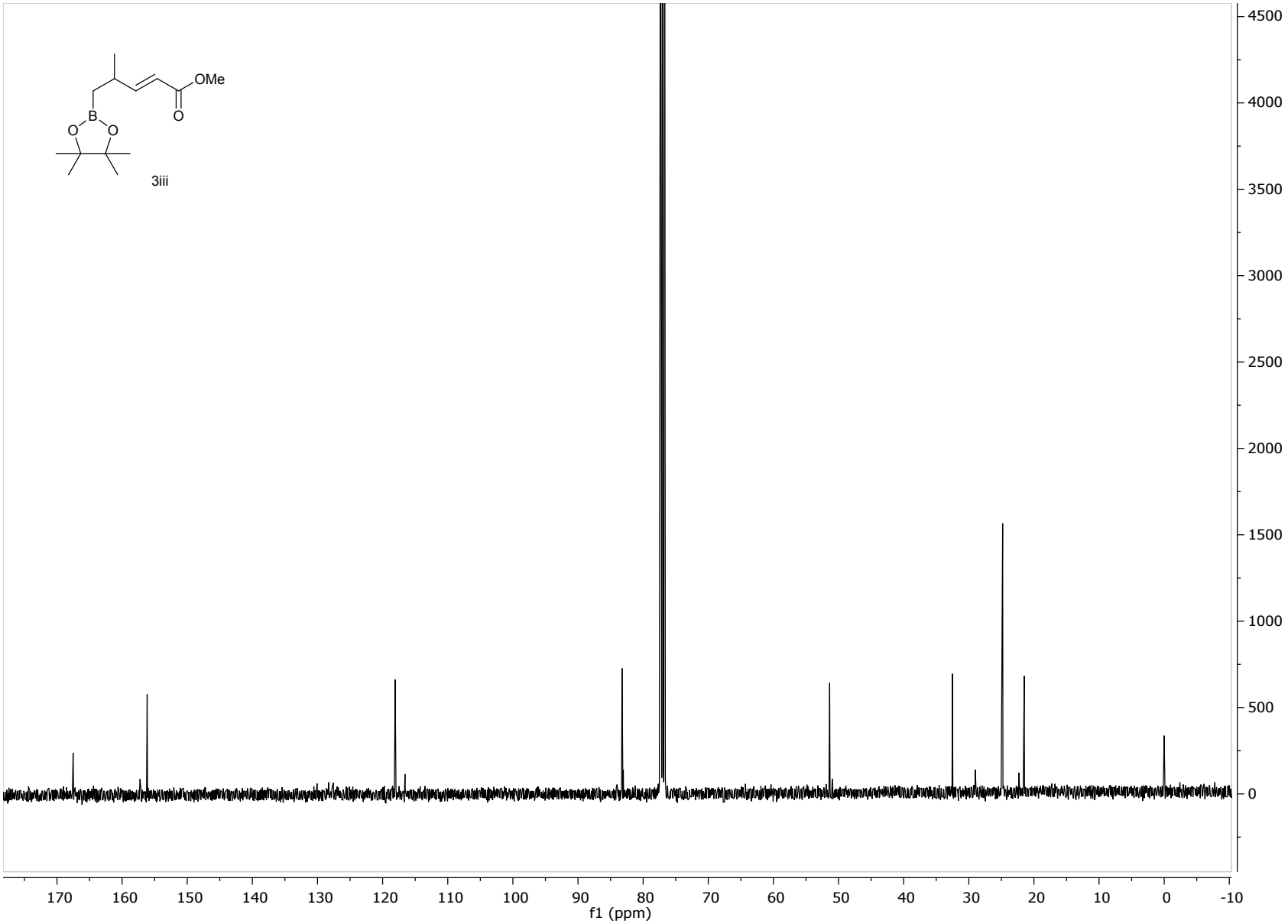
-5
f1 (ppm)


OMe
O
B
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3iii
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140
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10
0
-10
f1 (ppm)

4. Crystallographic data

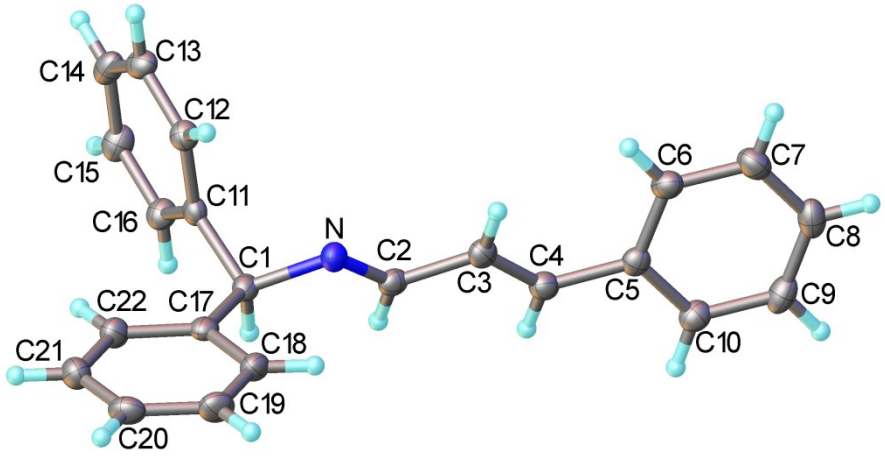

Figure X1. X-ray molecular structure of compound **4a** at 120 K. Here and below, atomic displacement ellipsoids are drawn at 50% probability level.

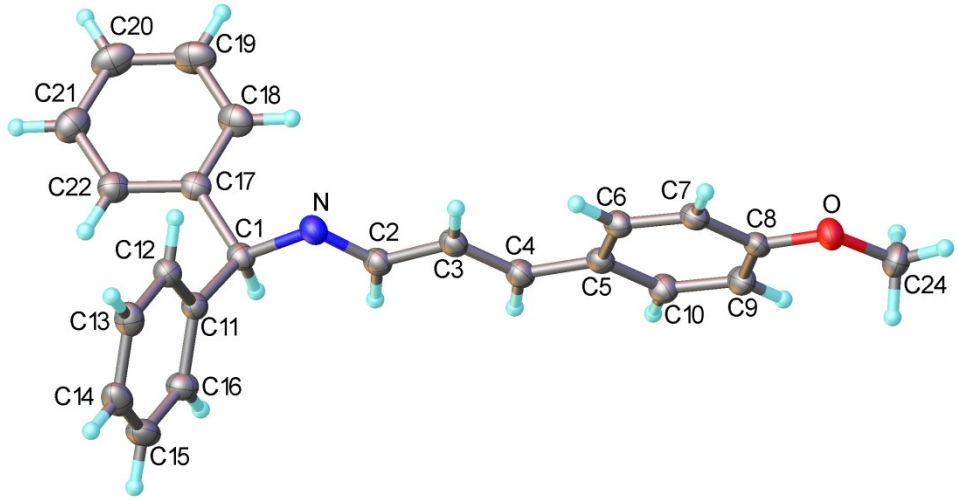

Figure X2. X-ray molecular structure of compound **4b** at 120 K.

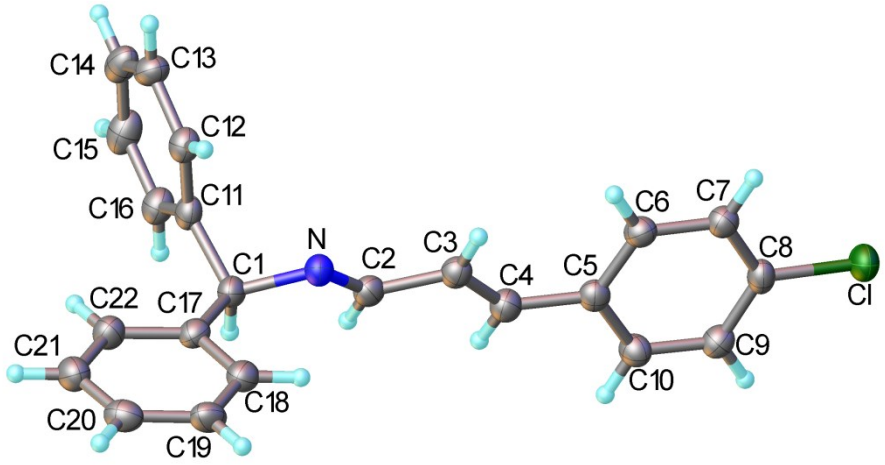

Figure X3. X-ray molecular structure of compound **4e** at 120 K.

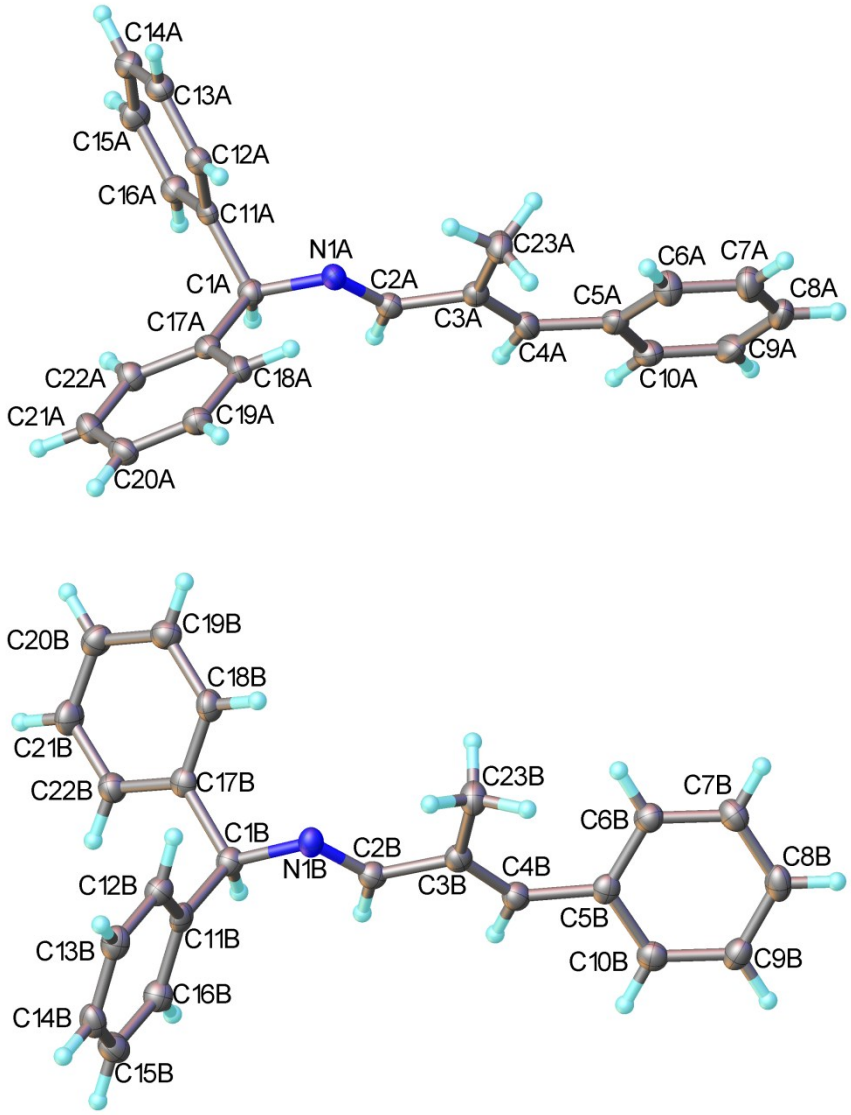

Figure X4. Two independent molecules in the crystal structure of compound **4h** at 120 K.

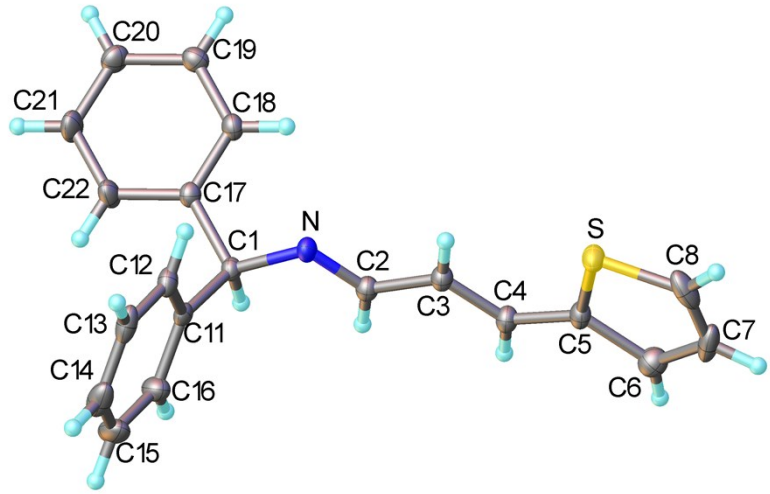

Figure X5. X-ray molecular structure of compound **4j** at 120 K; the thiophene ring is disordered between two opposite orientations in 4:1 ratio (minor atom positions are primed).

5. References

1. A. D. J. Calow, A. Batsanov, A. Pujol, C. Solé, E. Fernández, A. Whiting, *Org. Lett.*, 2013, **15**, 4810-4813
2. A. D. J. Calow, E. Fernández, A. Whiting, *Org. Biomol. Chem*., 2014, **12**, 6121-6127.