Chiral α-Amino Acid/Palladium-Catalyzed Asymmetric Allylation of α-Branched β-Ketoesters with Allylic Amines: Highly Enantioselective Construction of All-Carbon Quaternary Stereocenters

Ya-Nan Xu,[†] Meng-Zeng Zhu,[†] and Shi-Kai Tian*[,†,‡]

[†]Hefei National Laboratory for Physical Sciences at the Microscale, Center for Excellence in Molecular Synthesis, and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China
E-mail: tiansk@ustc.edu.cn
[‡]Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Supporting Information

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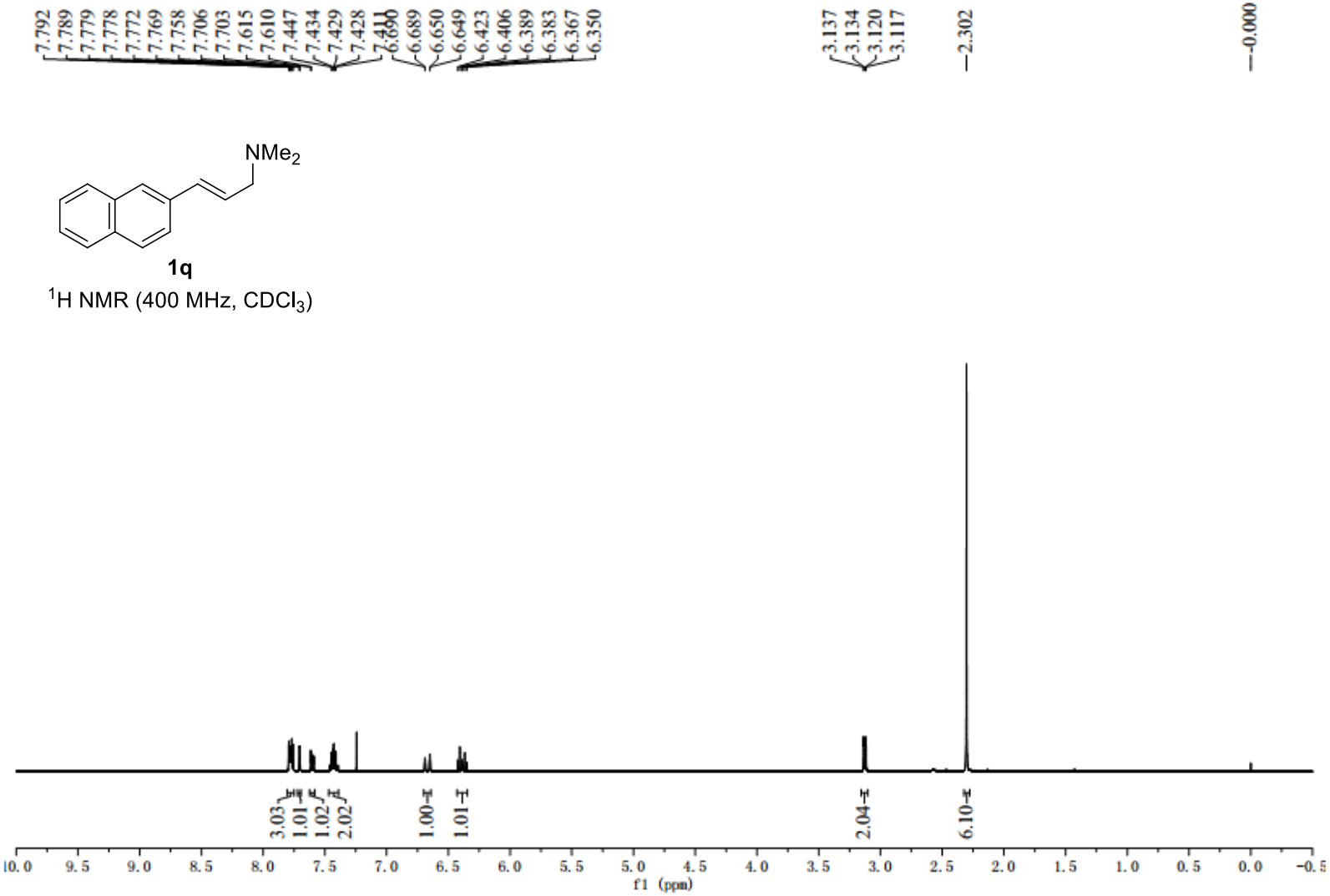
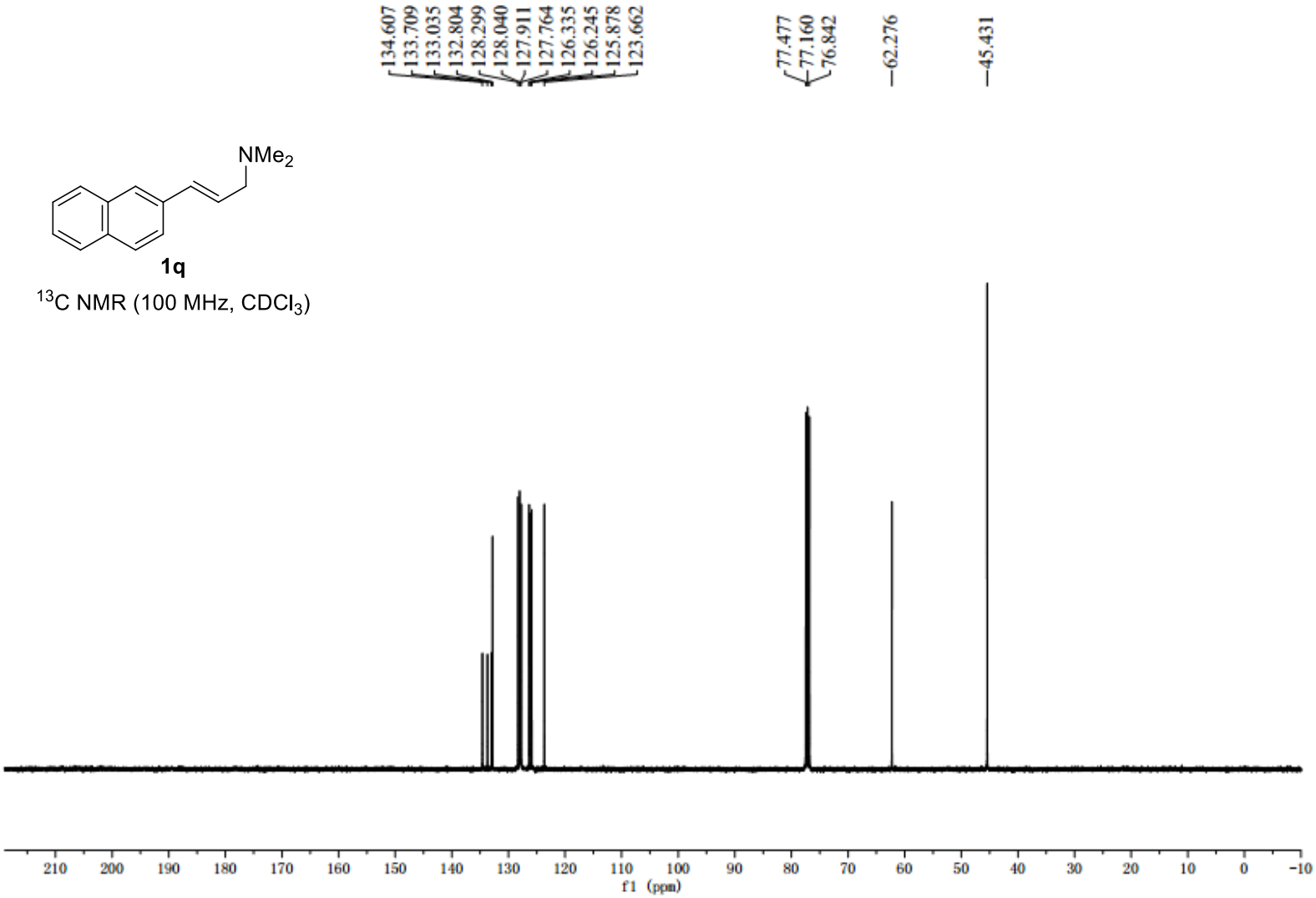


1q

^{1}H NMR (400 MHz, $CDCl_3$)

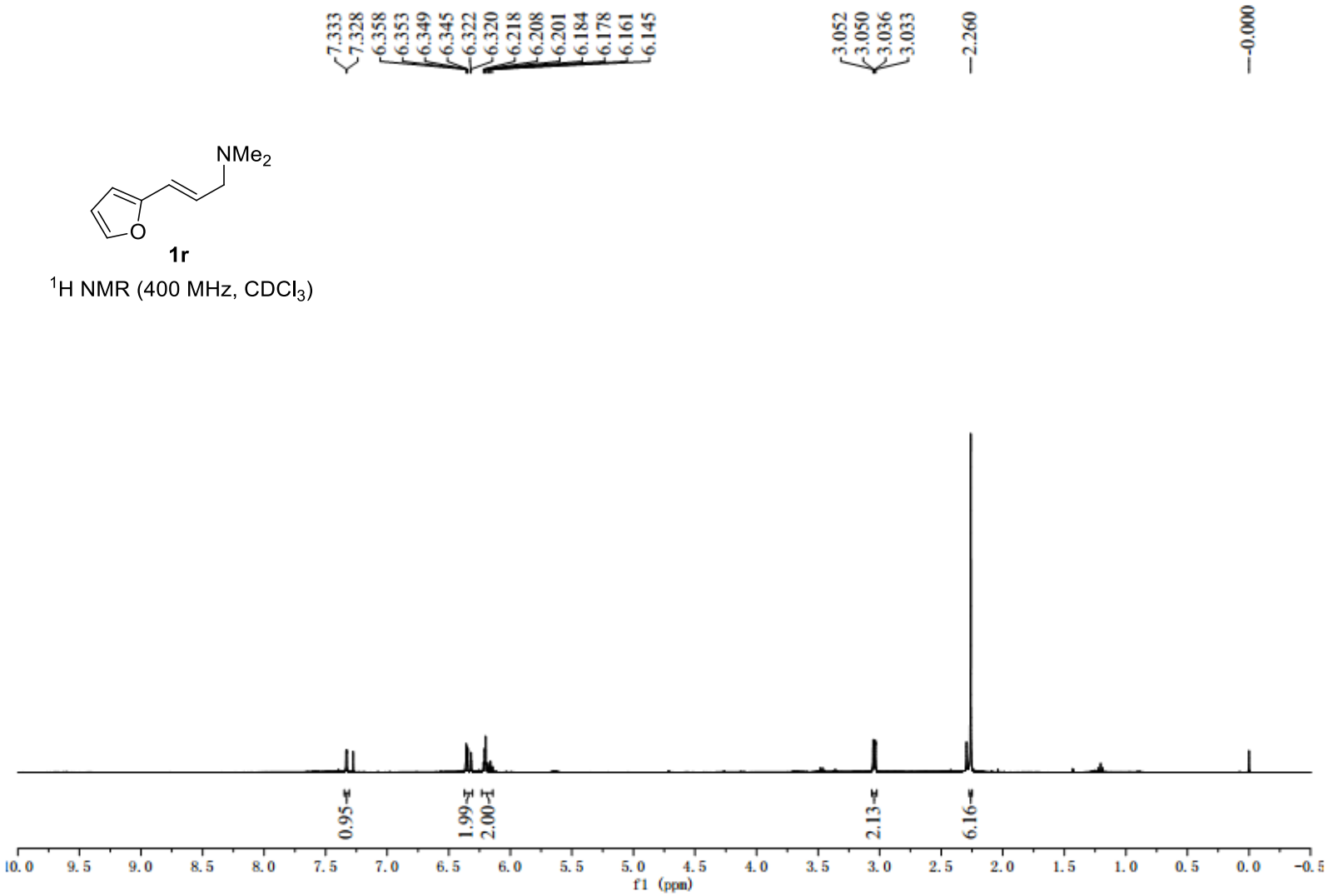
1q

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



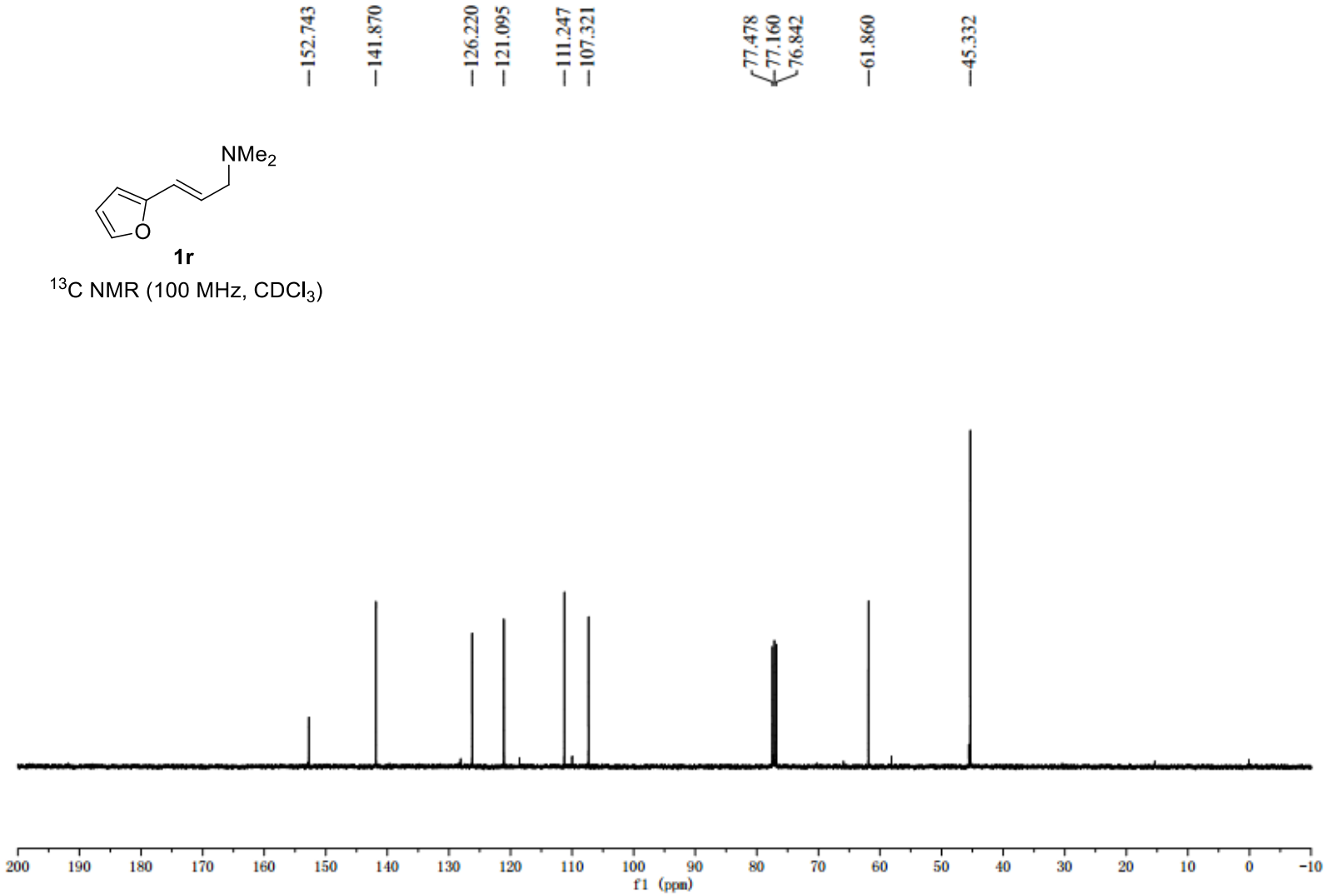
1r

^{1}H NMR (400 MHz, $CDCl_3$)



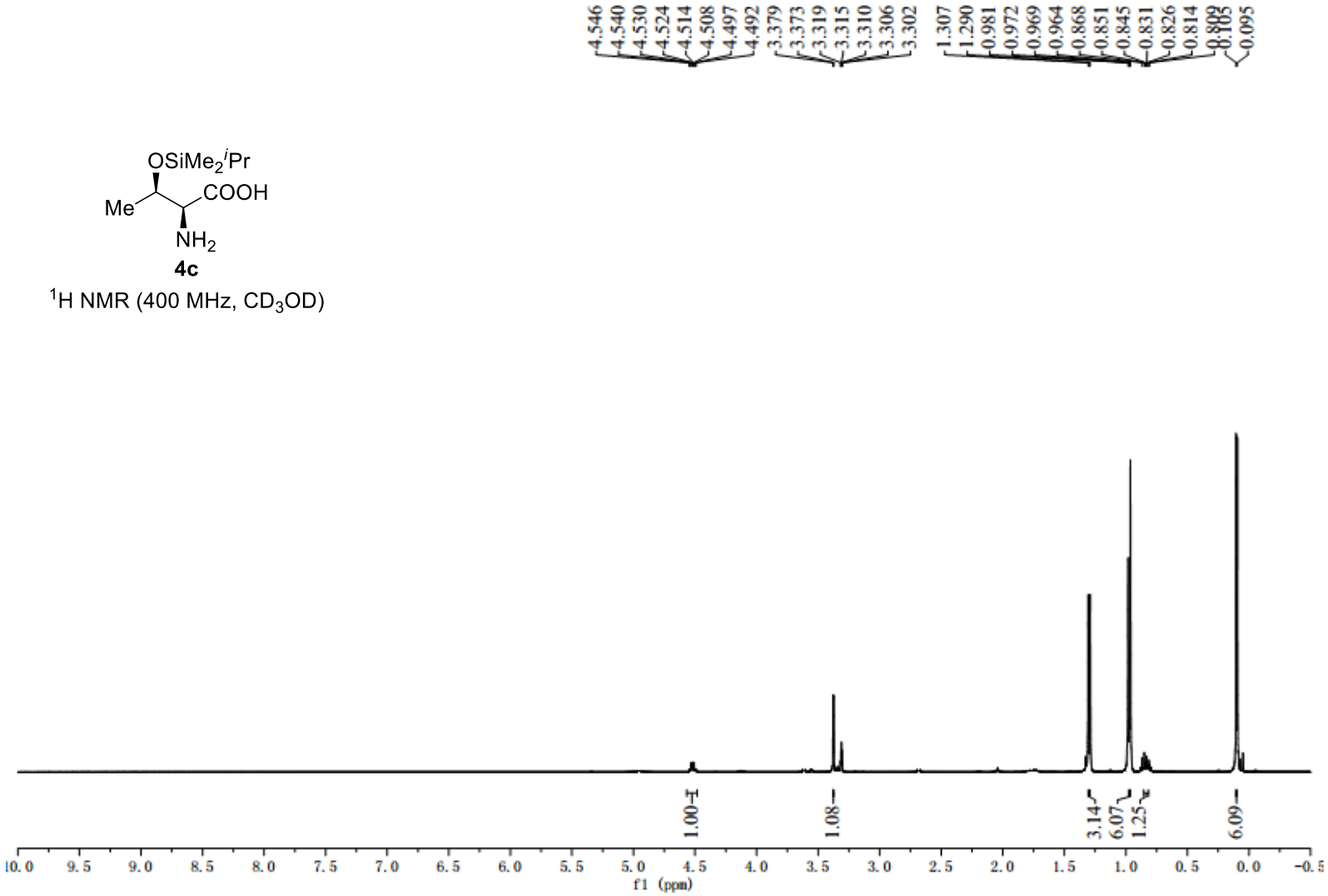
1r

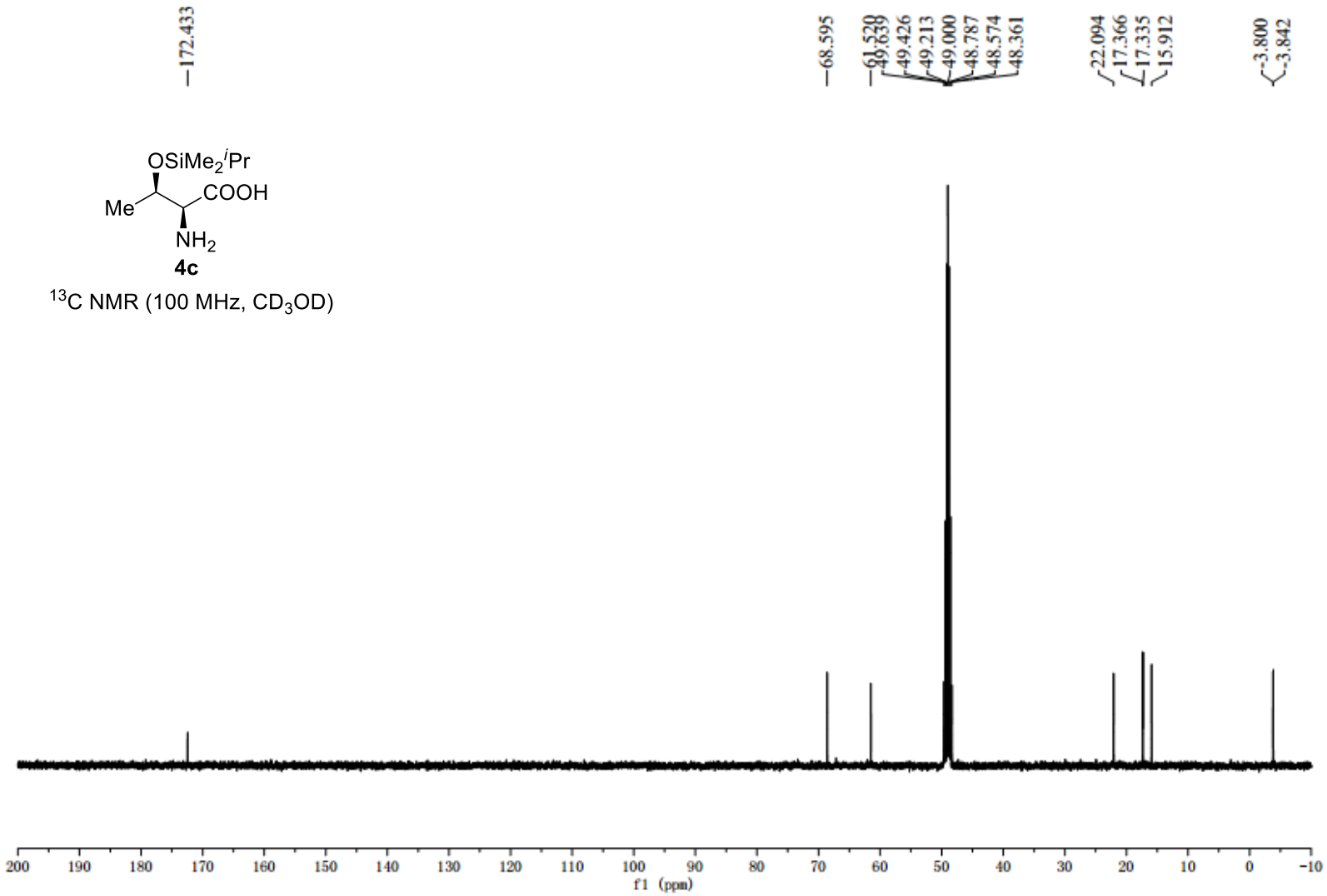
^{13}C NMR (100 MHz, $CDCl_3$)

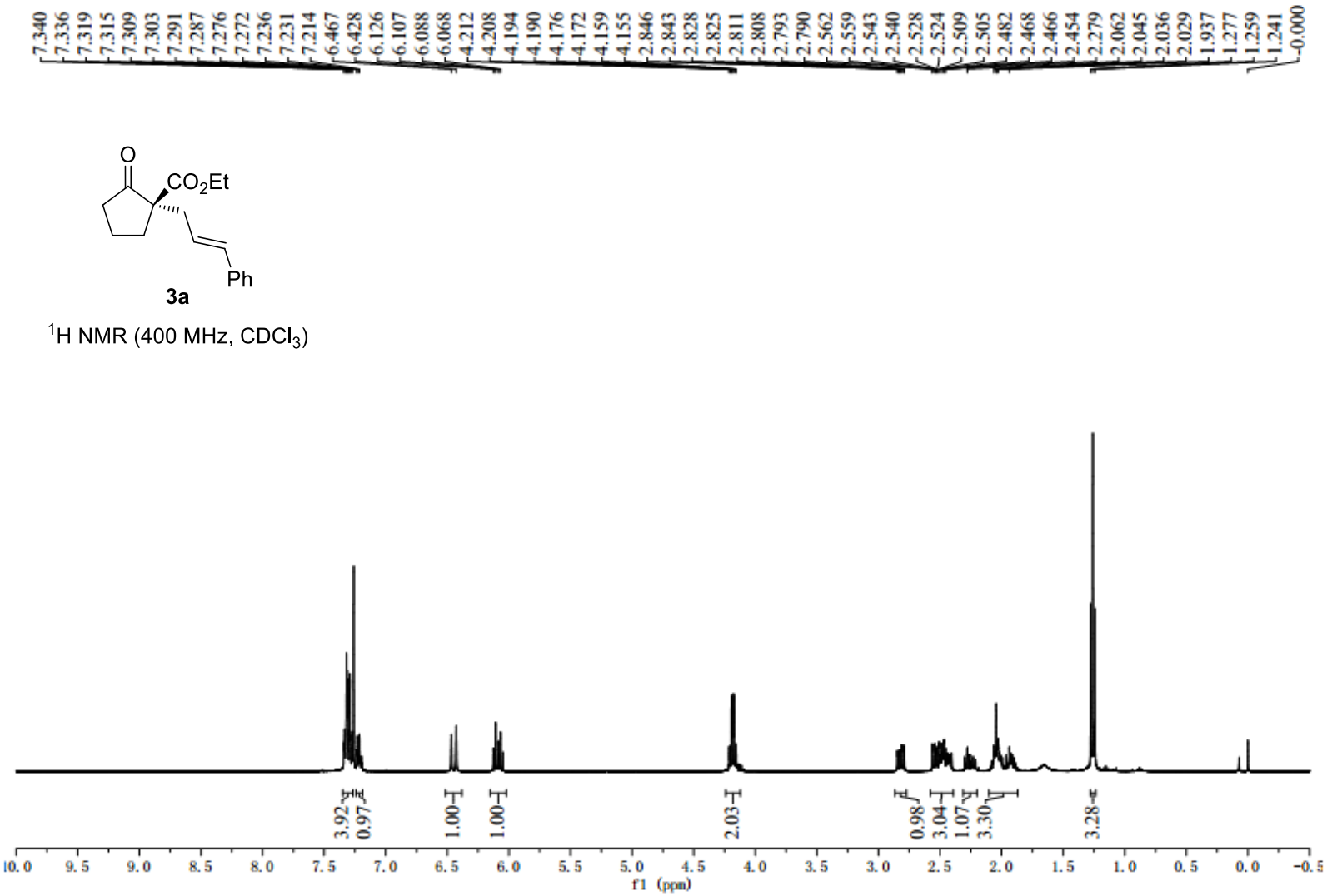


4c

^{1}H NMR (400 MHz, CD_3OD)




OSiMe2iPr
COOH
Me
NH2
4c
13C NMR (100 MHz, CD3OD)
172.433
68.595
61.520
49.639
49.426
49.213
49.000
48.787
48.574
48.361
22.094
17.366
17.335
15.912
-3.800
-3.842
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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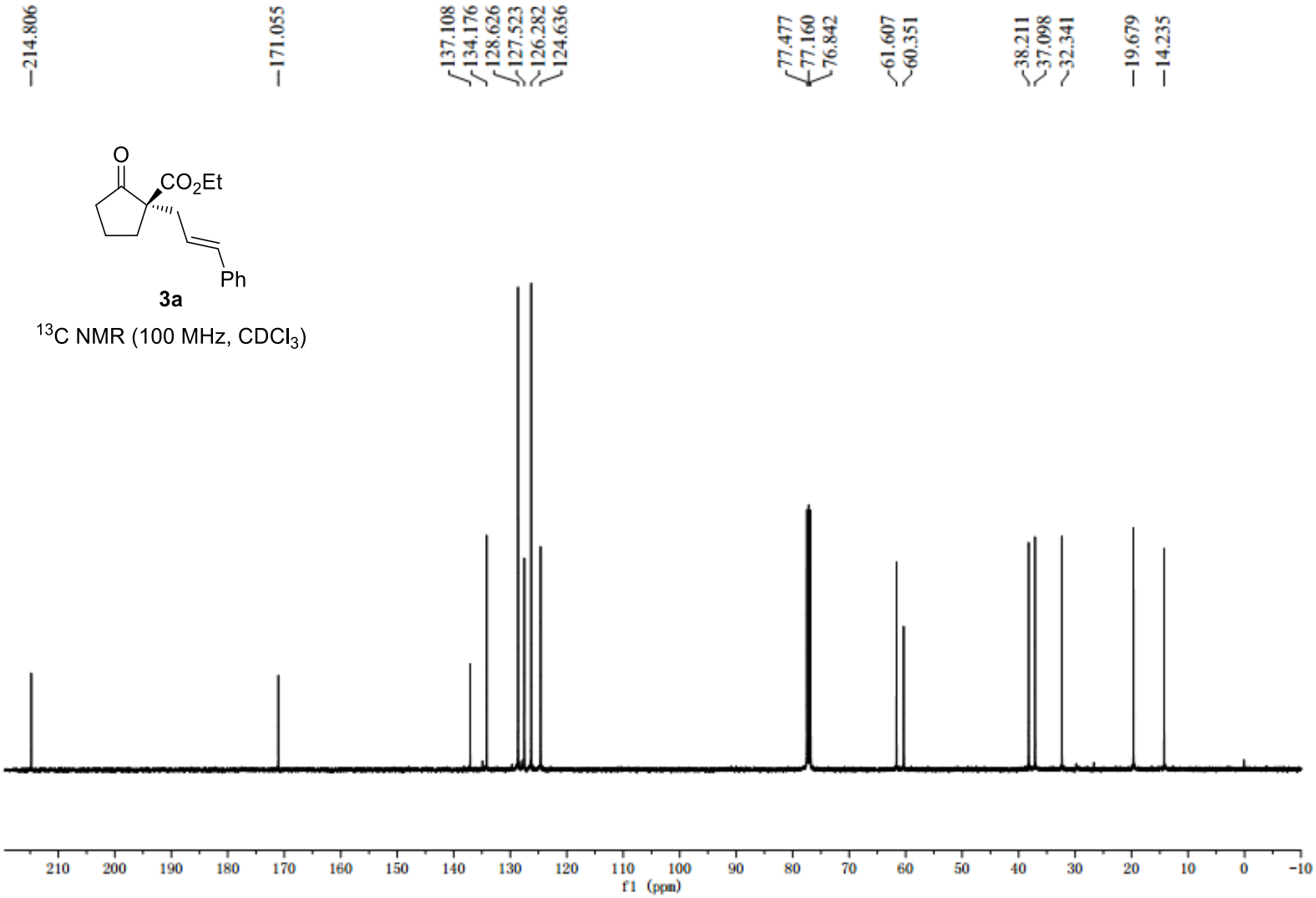
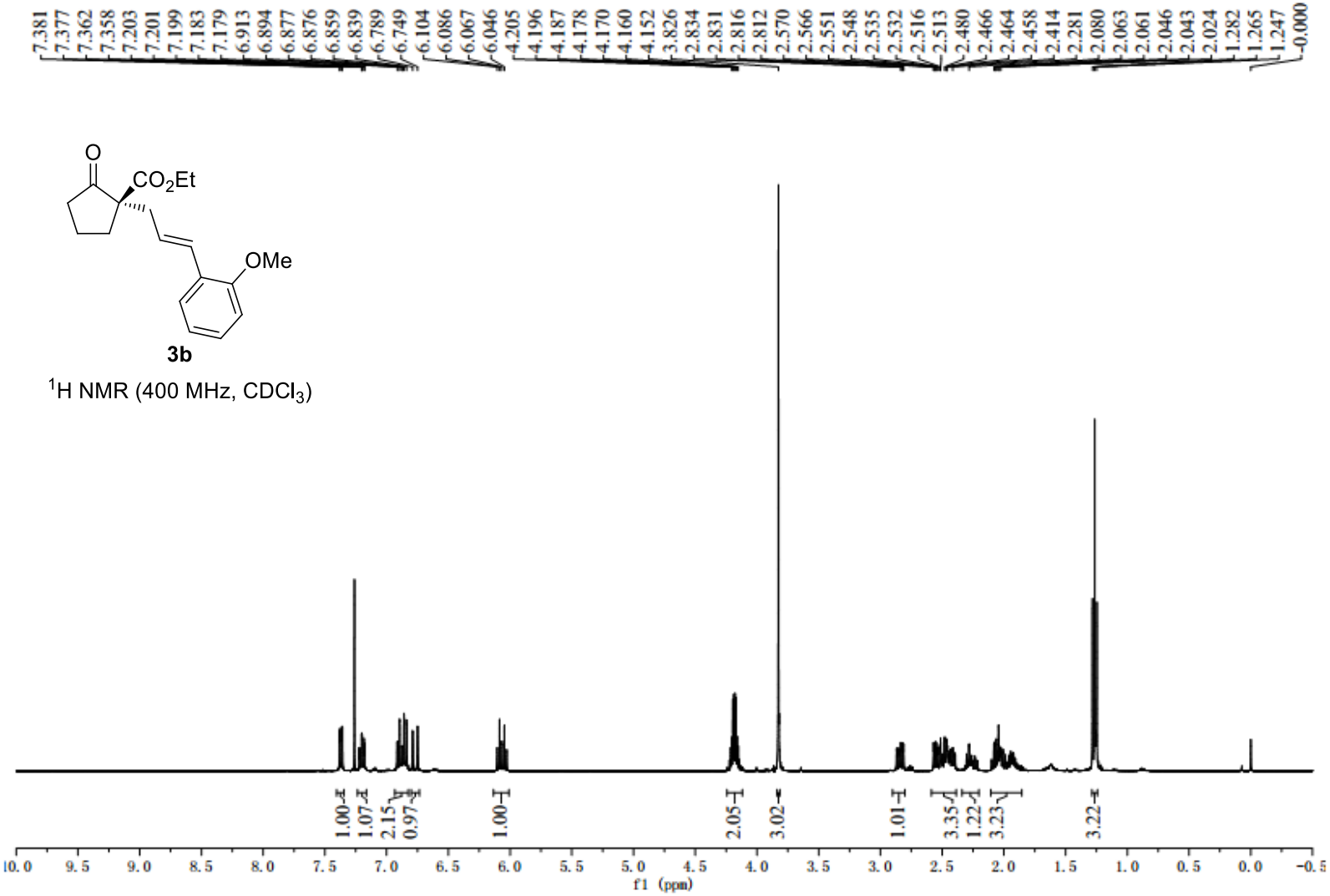
7.336
7.319
7.315
7.309
7.303
7.291
7.287
7.276
7.272
7.236
7.231
7.214
6.467
6.428
6.126
6.107
6.088
6.068
4.212
4.208
4.194
4.190
4.176
4.172
4.159
4.155
2.846
2.843
2.828
2.825
2.811
2.808
2.793
2.790
2.562
2.559
2.543
2.540
2.528
2.524
2.509
2.505
2.482
2.468
2.466
2.454
2.279
2.062
2.045
2.036
2.029
1.937
1.277
1.259
1.241
-0.000
O
CO2Et
Ph
3a
1H NMR (400 MHz, CDCl3)
3.92
0.97
1.00
1.00
2.03
0.98
3.04
1.07
3.30
3.28
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
-0.5
f1 (ppm)


214.806
171.055
137.108
134.176
128.626
127.523
126.282
124.636
77.477
77.160
76.842
61.607
60.351
38.211
37.098
32.341
19.679
14.235
O
CO2Et
Ph
3a
13C NMR (100 MHz, CDCl3)
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)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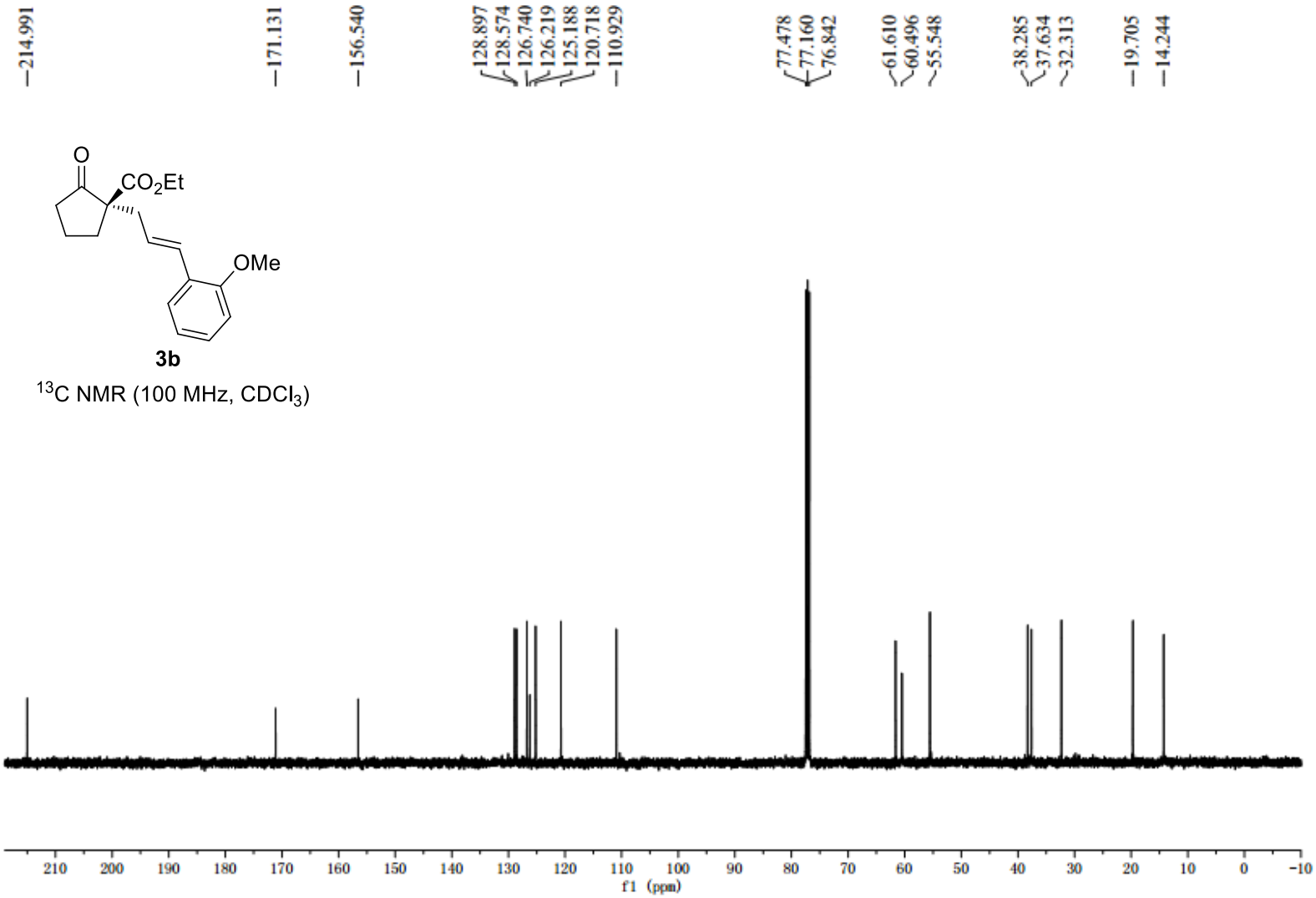
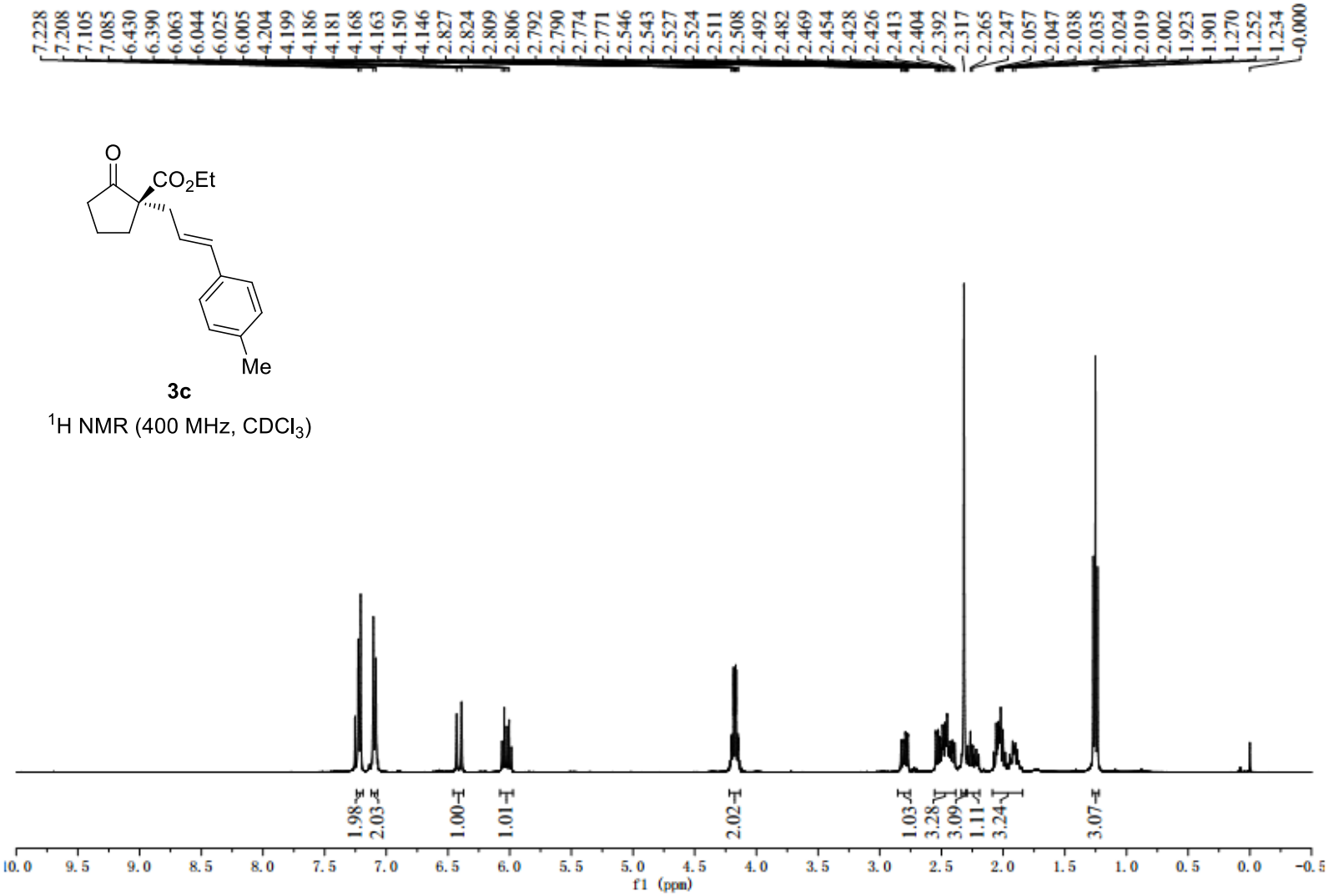
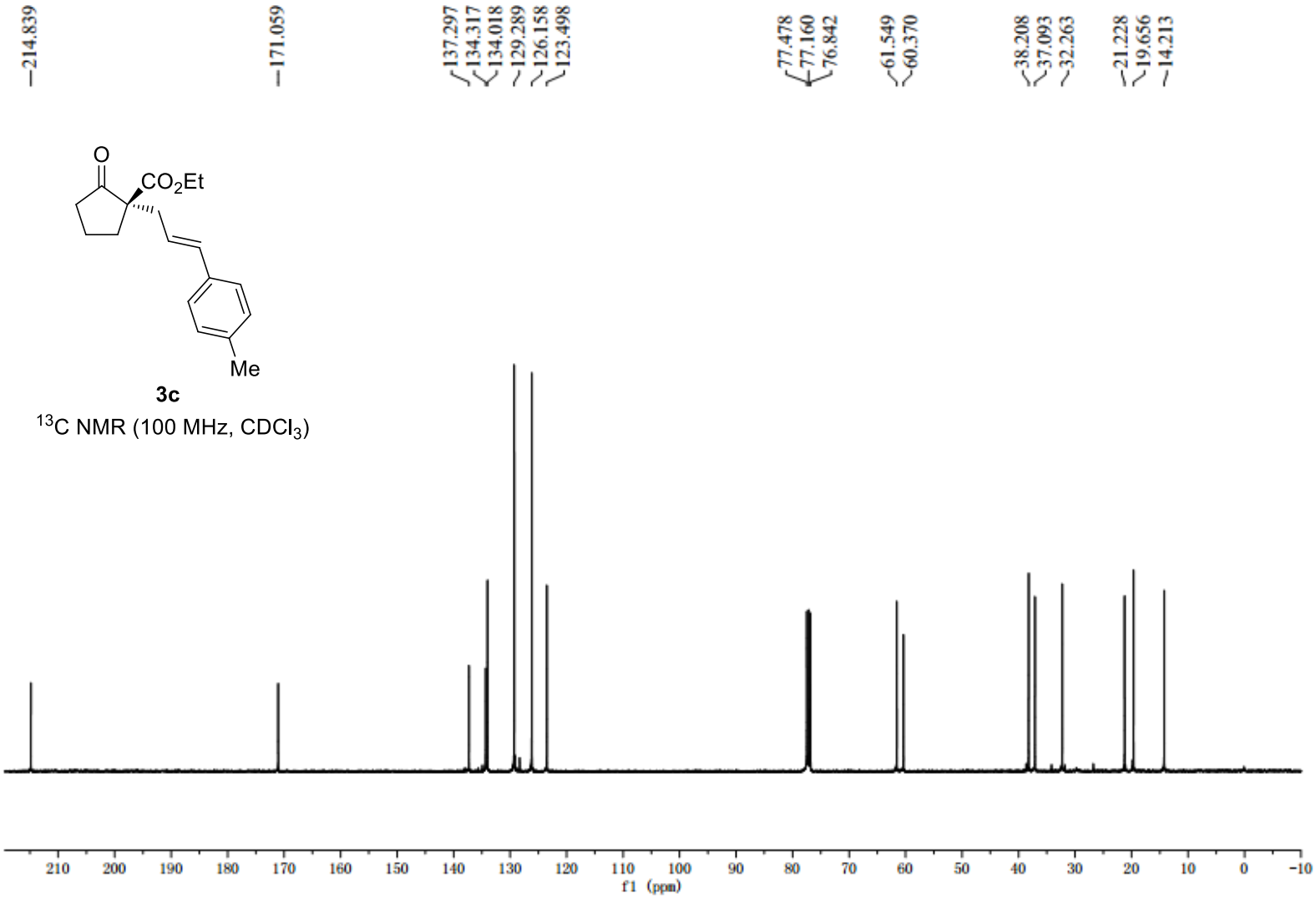
7.377
7.362
7.358
7.203
7.201
7.199
7.183
7.179
6.913
6.894
6.877
6.876
6.859
6.839
6.789
6.749
6.104
6.086
6.067
6.046
4.205
4.196
4.187
4.178
4.170
4.160
4.152
3.826
2.834
2.831
2.816
2.812
2.570
2.566
2.551
2.548
2.535
2.532
2.516
2.513
2.480
2.466
2.464
2.458
2.414
2.281
2.080
2.063
2.061
2.046
2.043
2.024
1.282
1.265
1.247
-0.000
O
CO2Et
OMe
3b
1H NMR (400 MHz, CDCl3)
1.00
1.07
2.15
0.97
1.00
2.05
3.02
1.01
3.35
1.22
3.23
3.22
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
-0.5
f1 (ppm)


214.991
171.131
156.540
128.897
128.574
126.740
126.219
125.188
120.718
110.929
77.478
77.160
76.842
61.610
60.496
55.548
38.285
37.634
32.313
19.705
14.244
O
CO2Et
OMe
3b
13C NMR (100 MHz, CDCl3)
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)



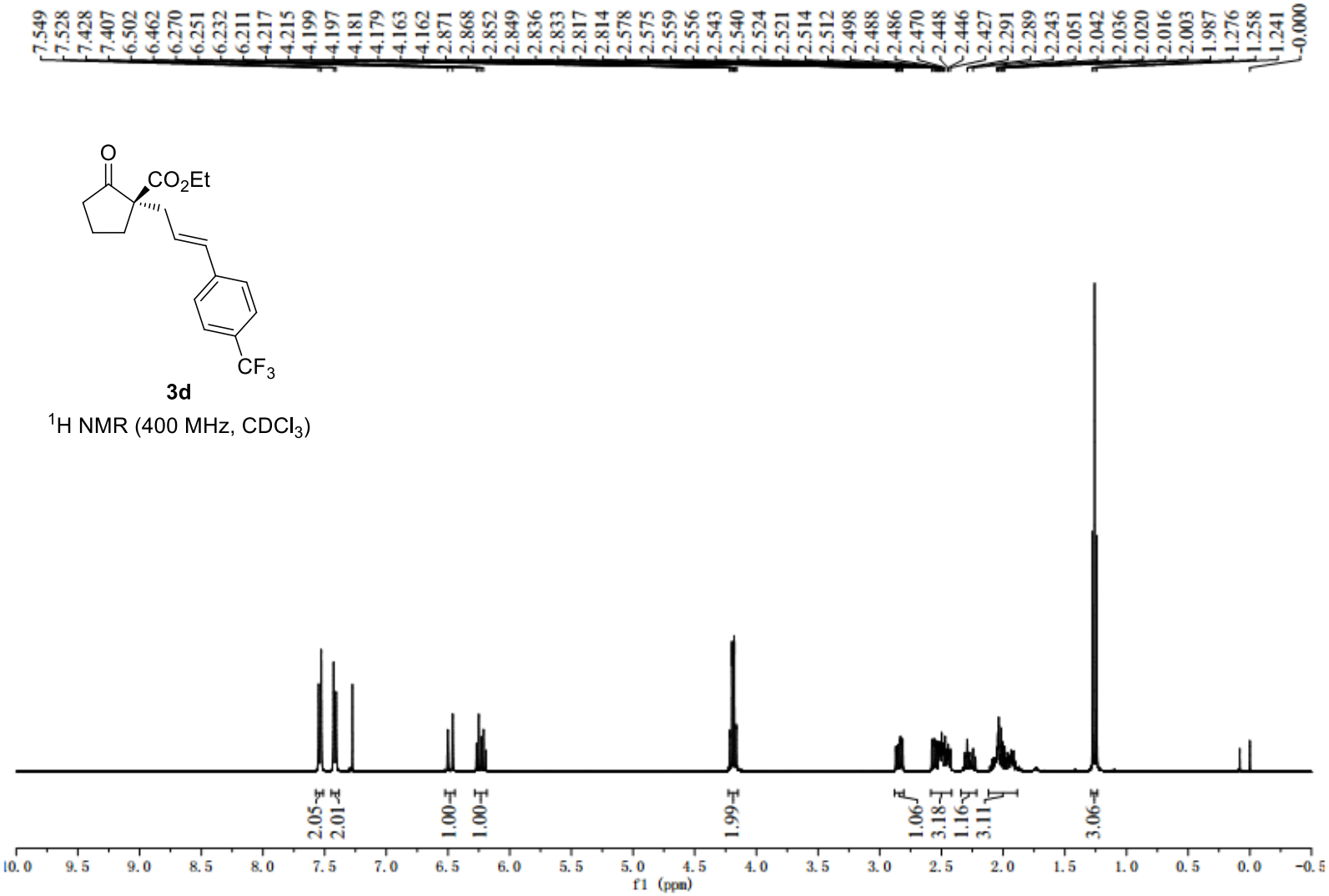
3c

^{1}H NMR (400 MHz, $CDCl_3$)



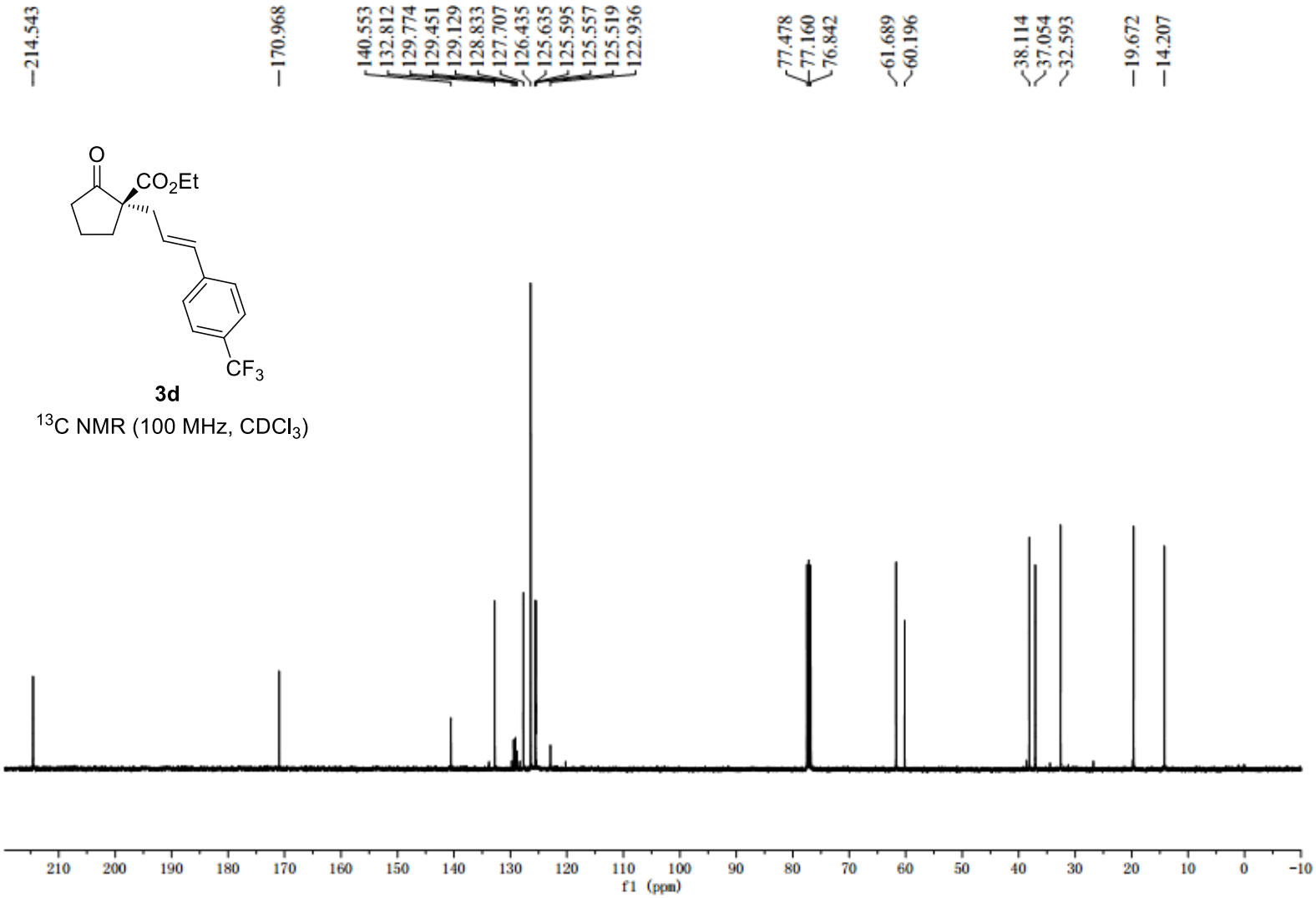
3c

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



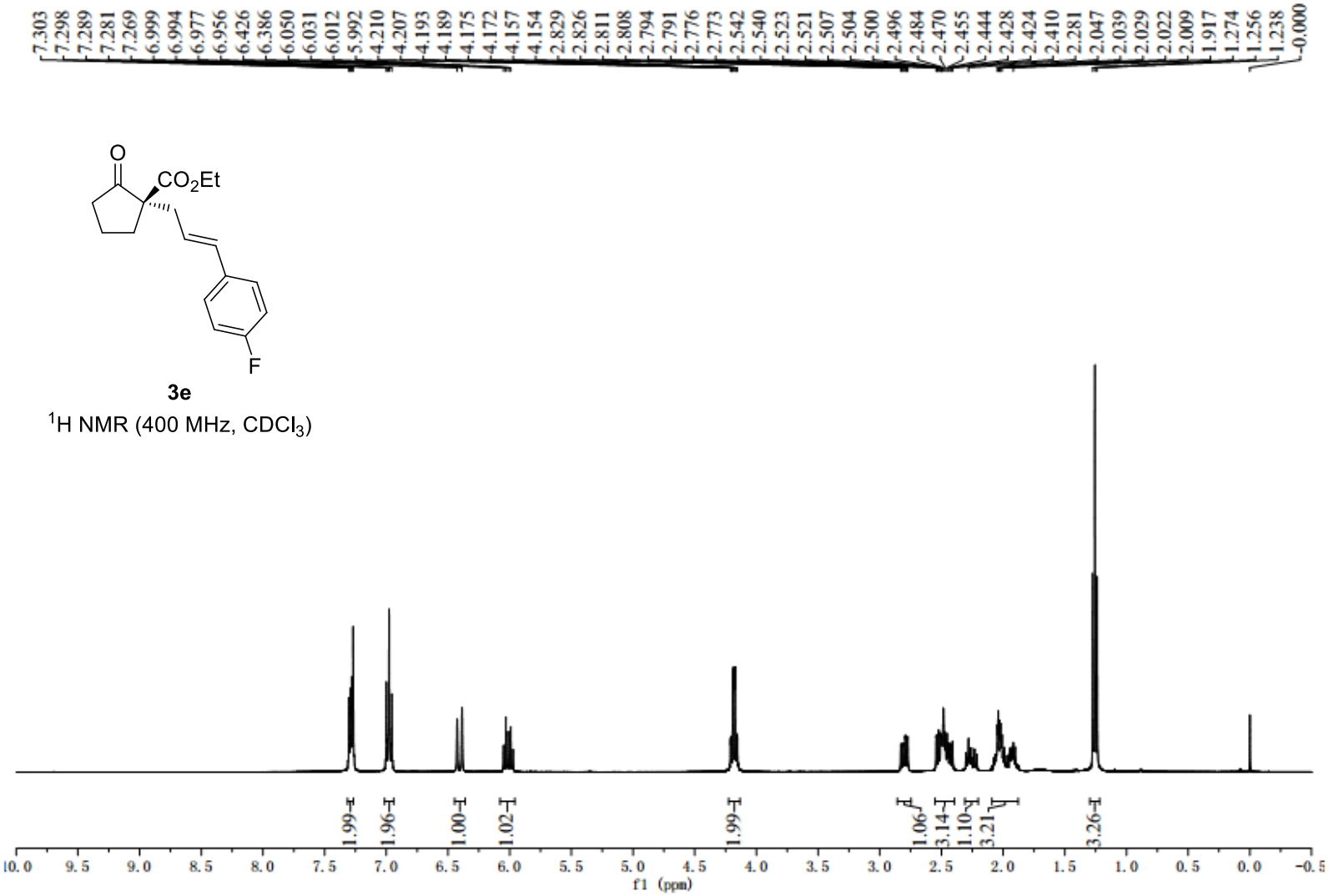
3d

^{1}H NMR (400 MHz, $CDCl_3$)



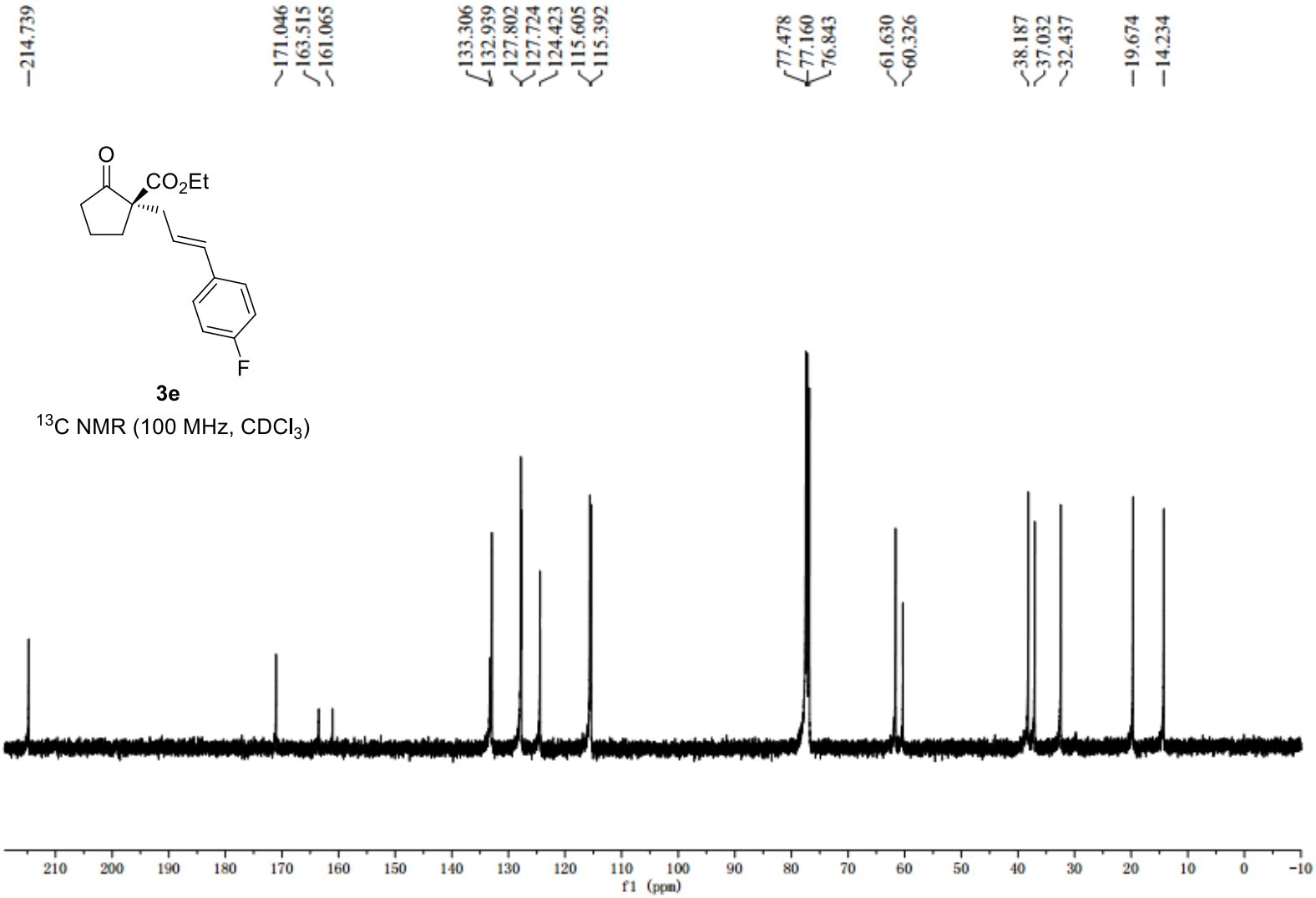
3d

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



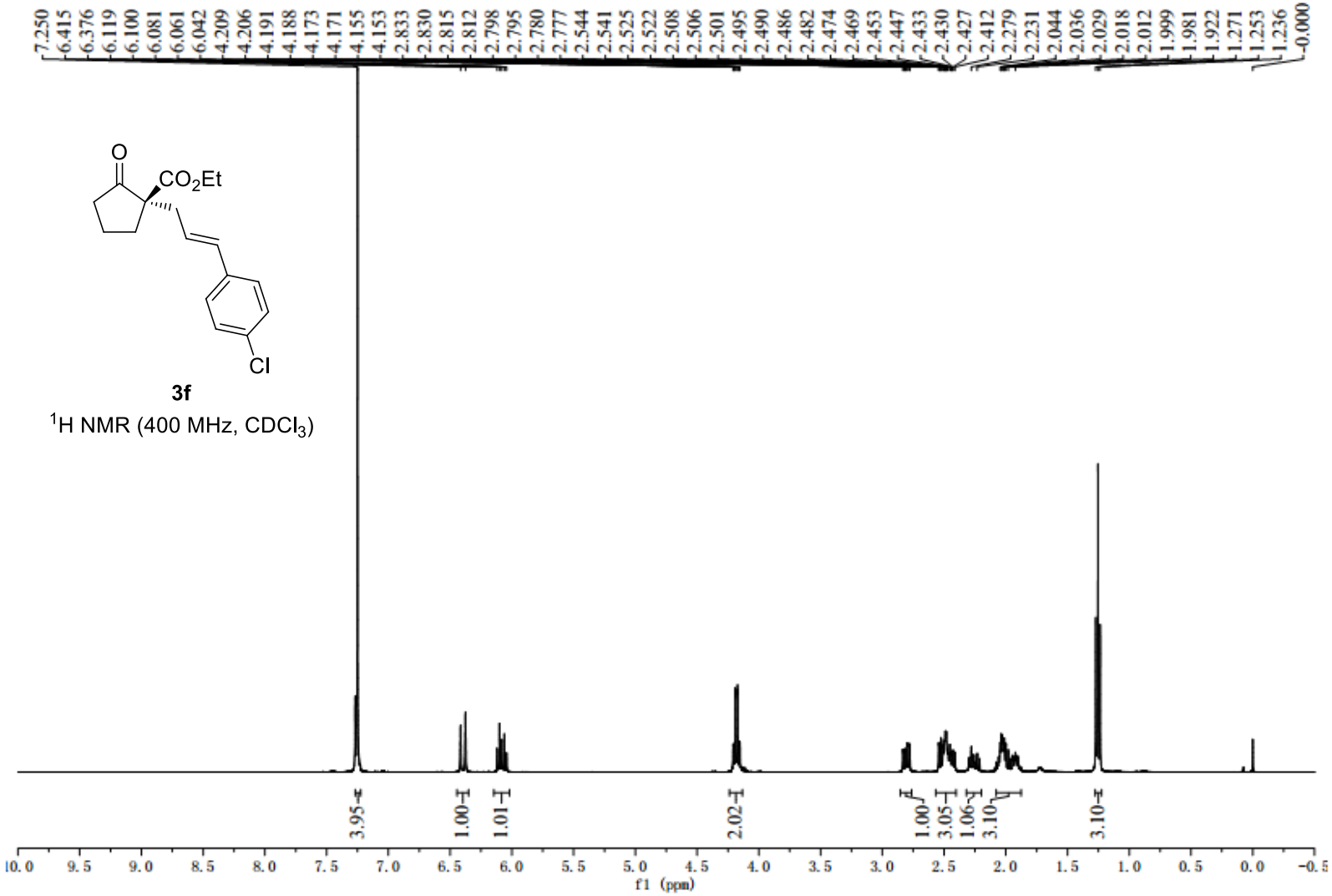
3e

^{1}H NMR (400 MHz, $CDCl_3$)



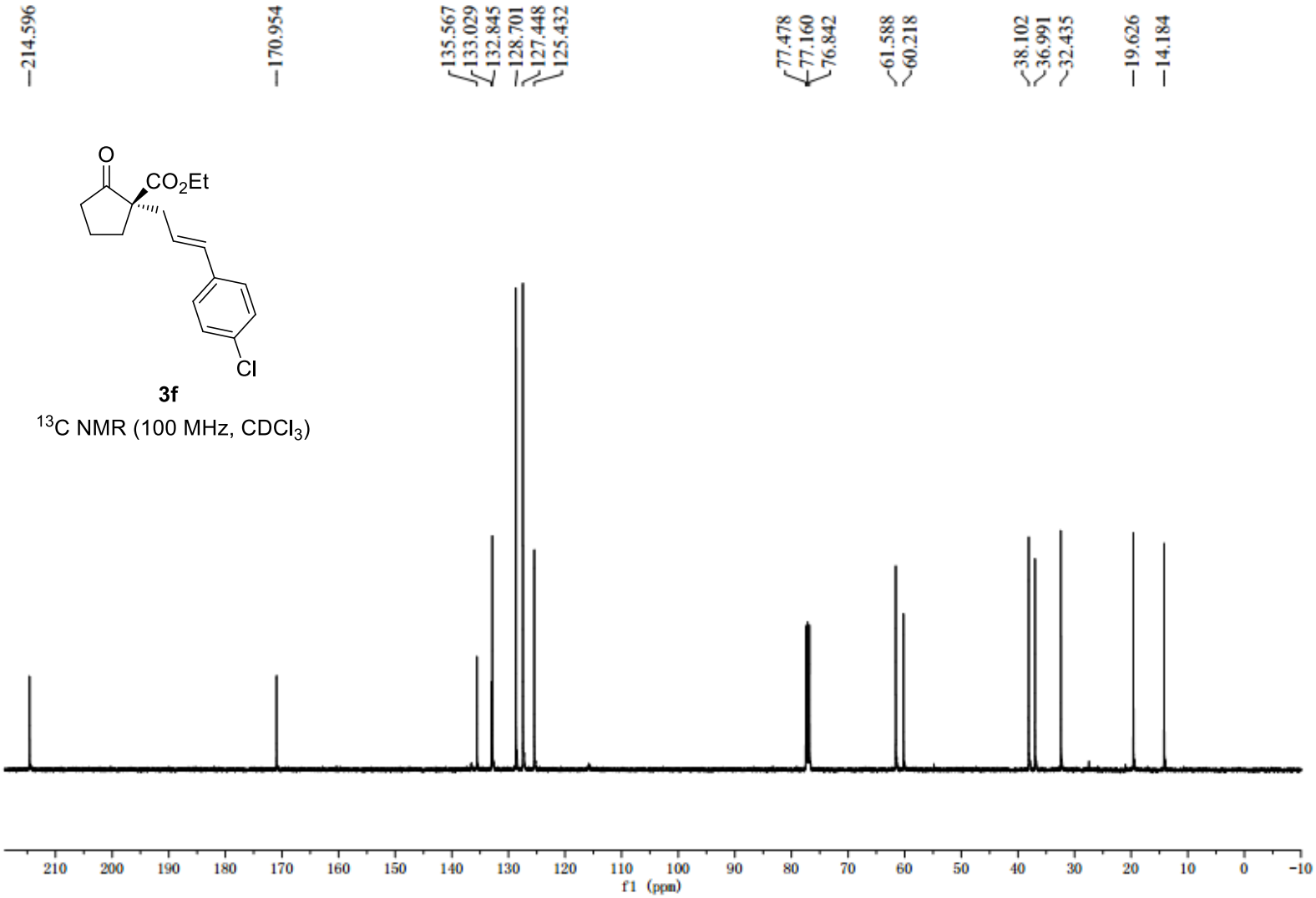
3e

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



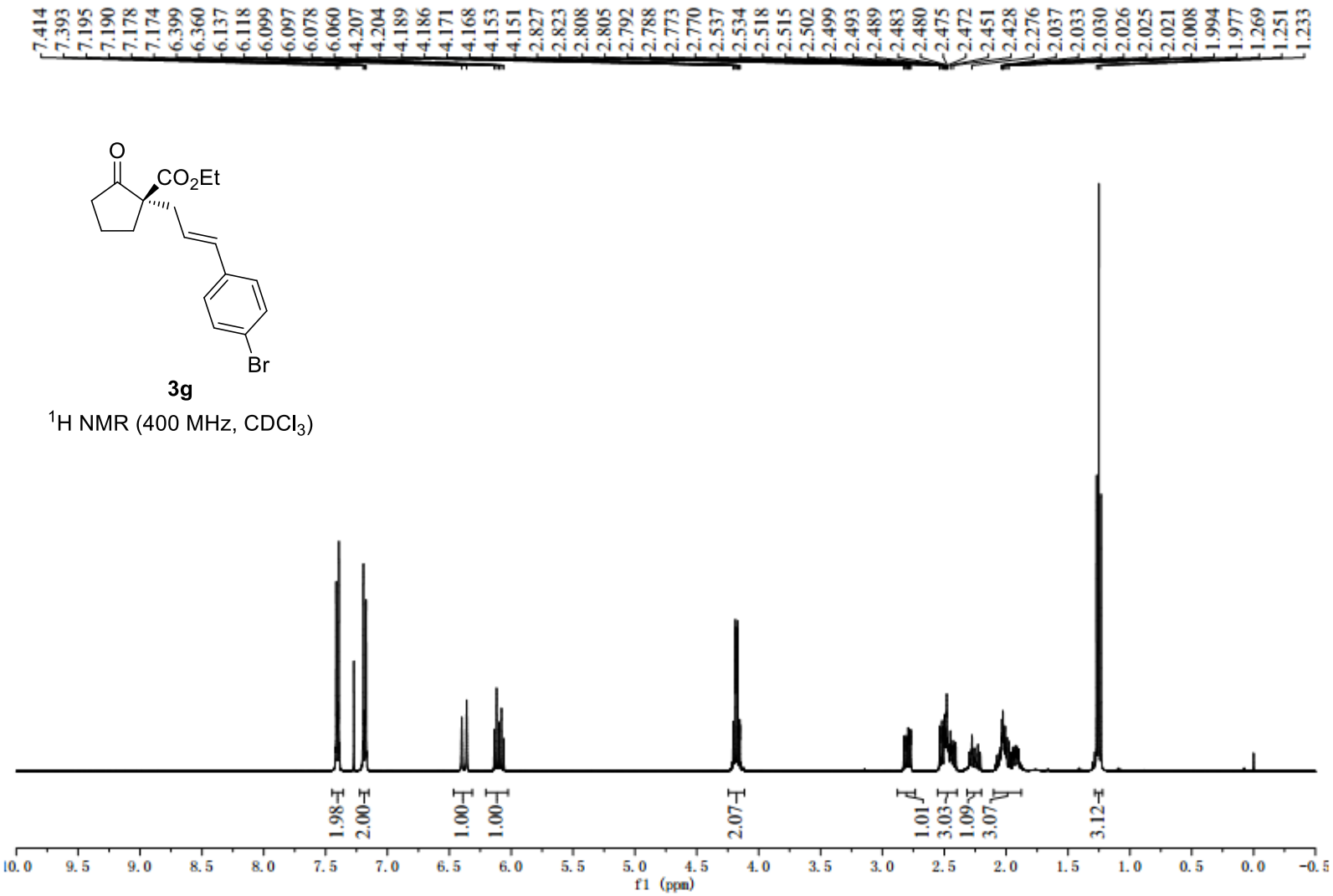
3f

^{1}H NMR (400 MHz, $CDCl_3$)



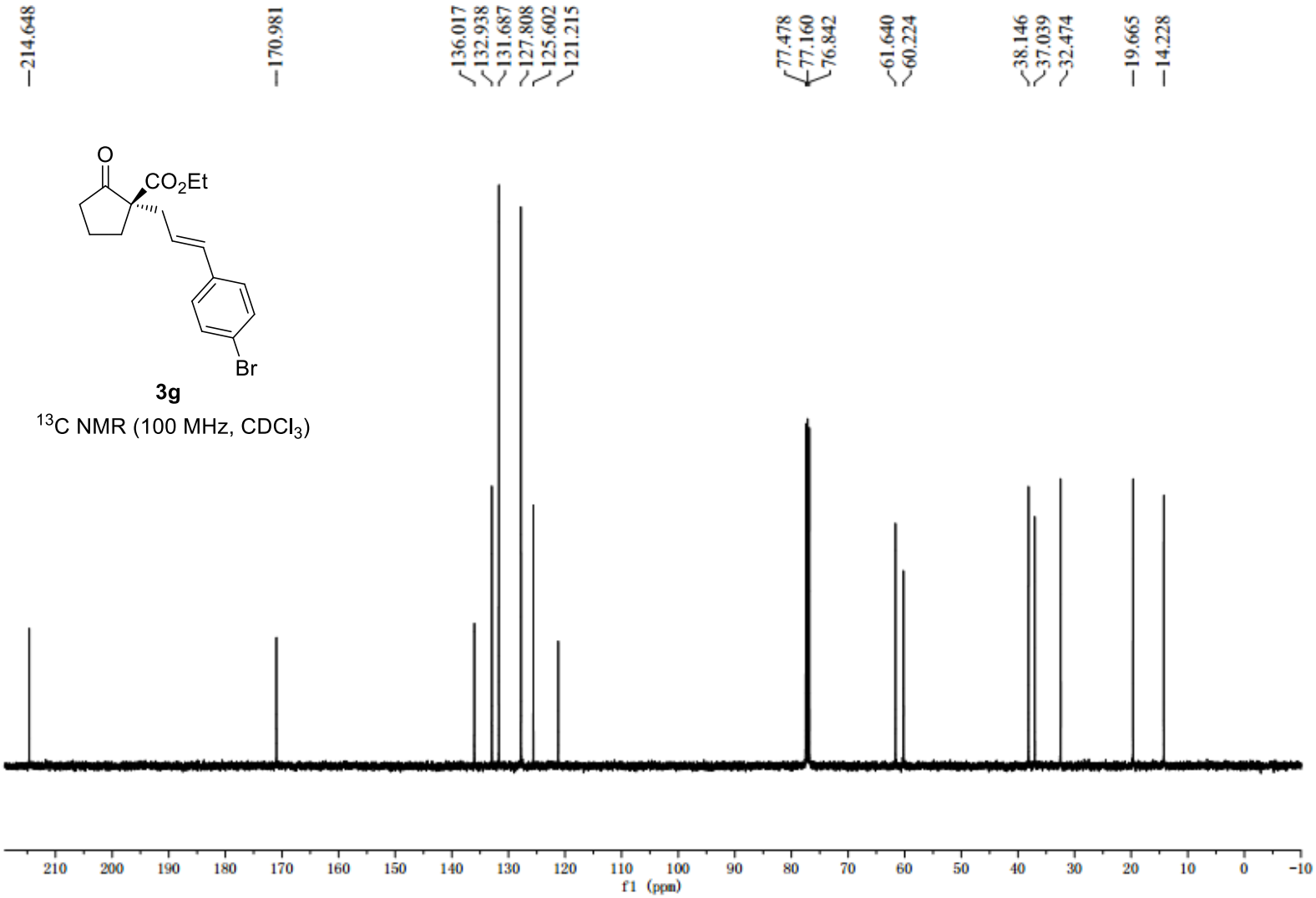
3f

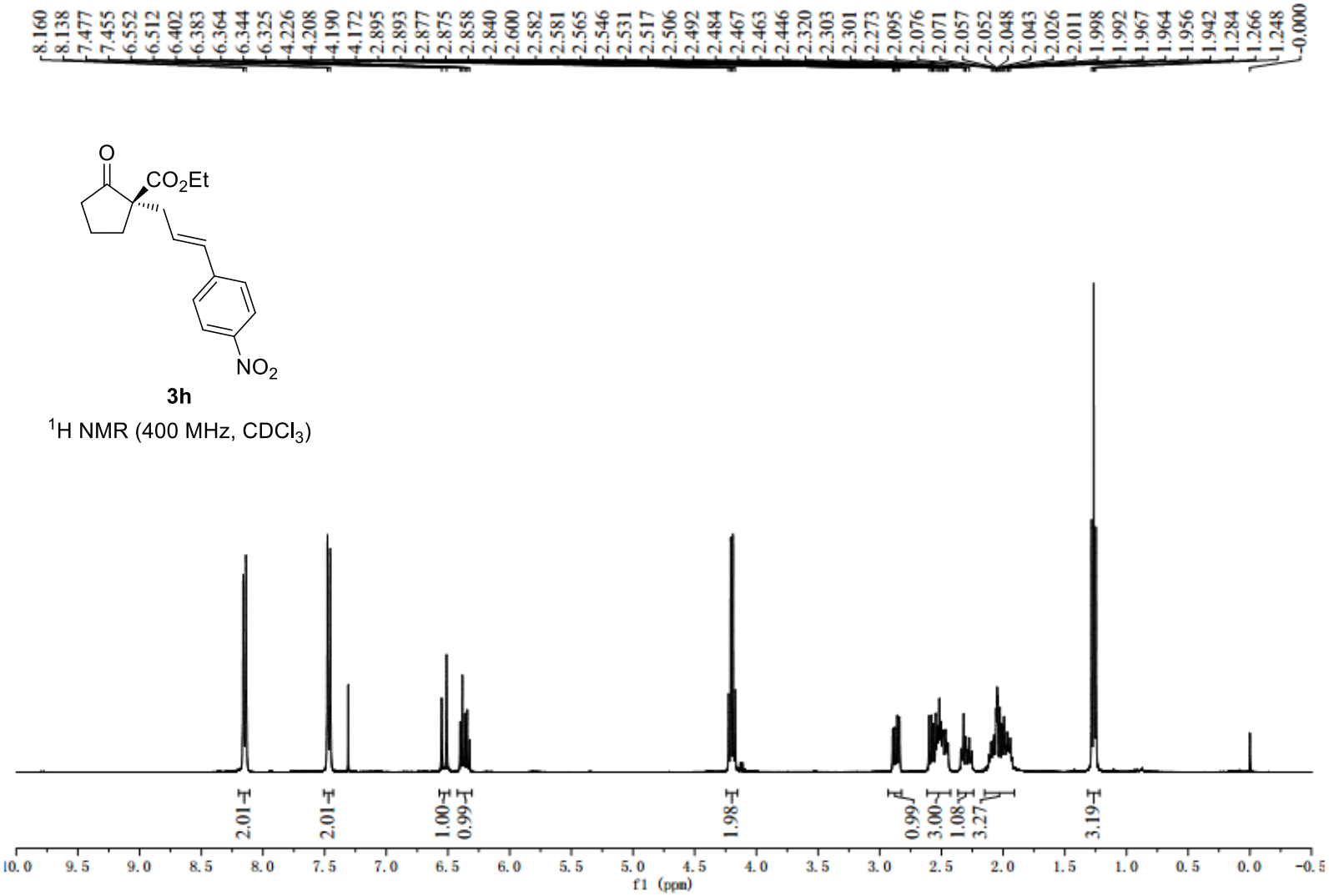
^{13}C NMR (100 MHz, $CDCl_3$)



3g

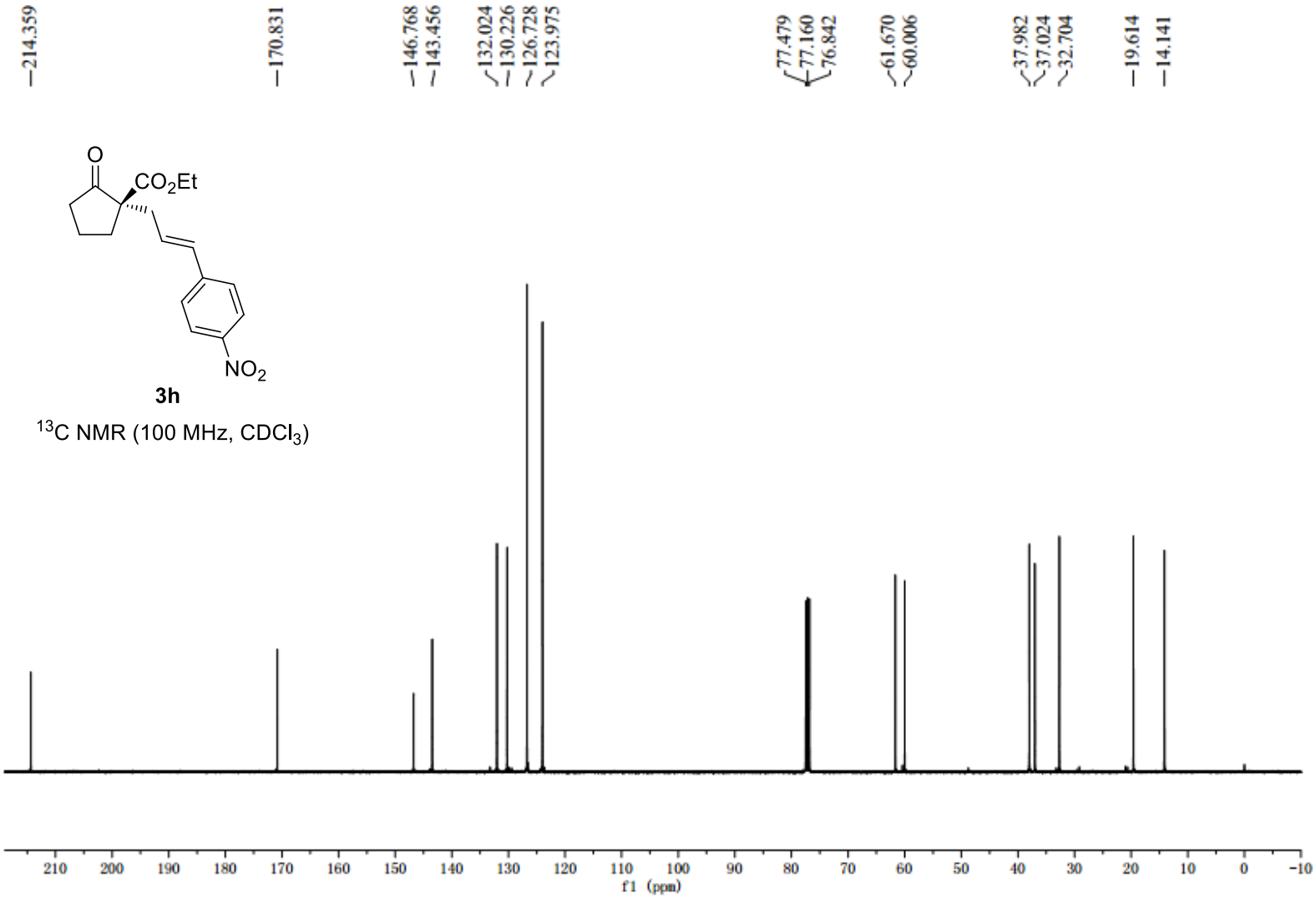
^{1}H NMR (400 MHz, $CDCl_3$)


214.648
170.981
136.017
132.938
131.687
127.808
125.602
121.215
77.478
77.160
76.842
61.640
60.224
38.146
37.039
32.474
19.665
14.228
O
CO2Et
Br
3g
13C NMR (100 MHz, CDCl3)
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)



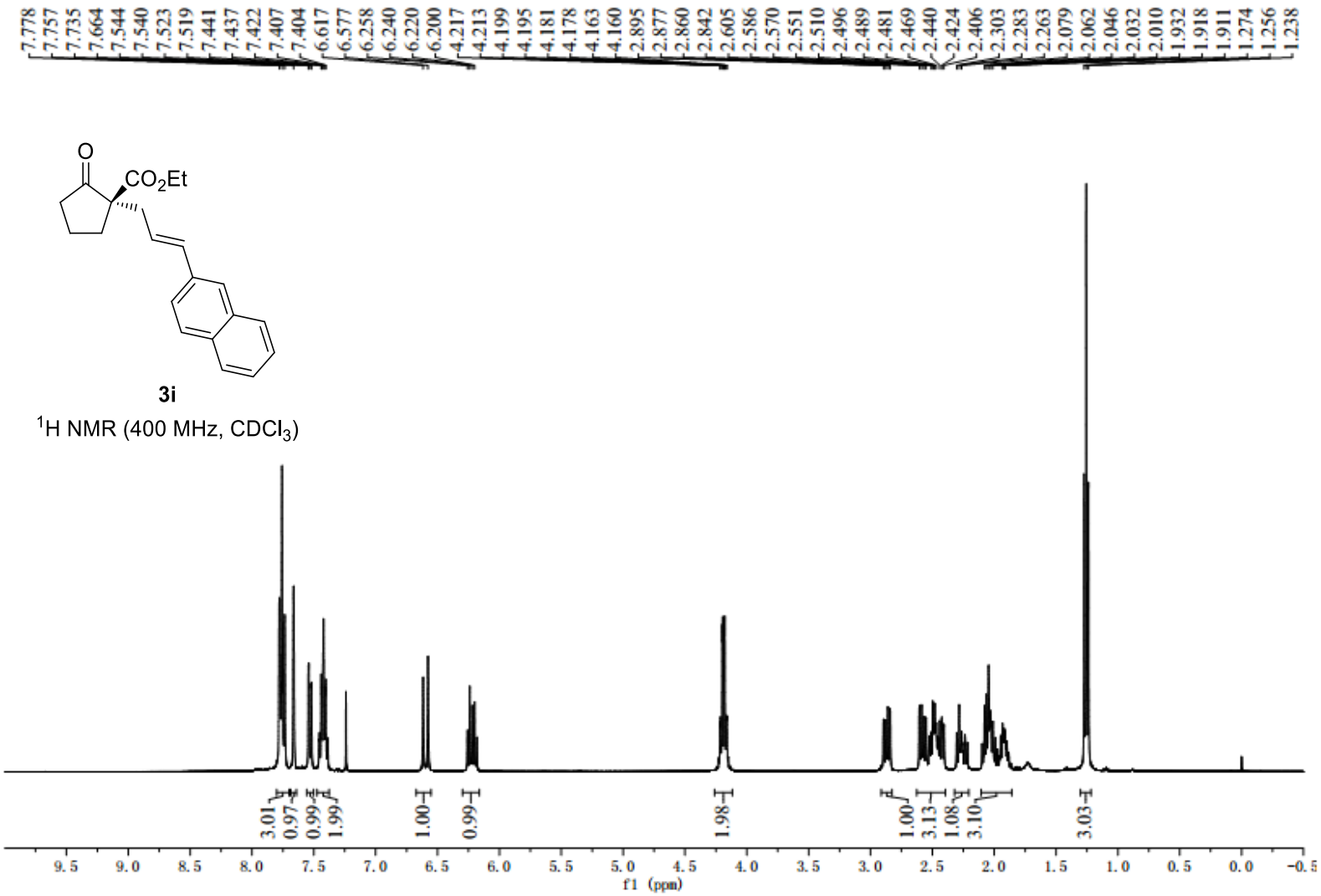
3h

^{1}H NMR (400 MHz, $CDCl_3$)



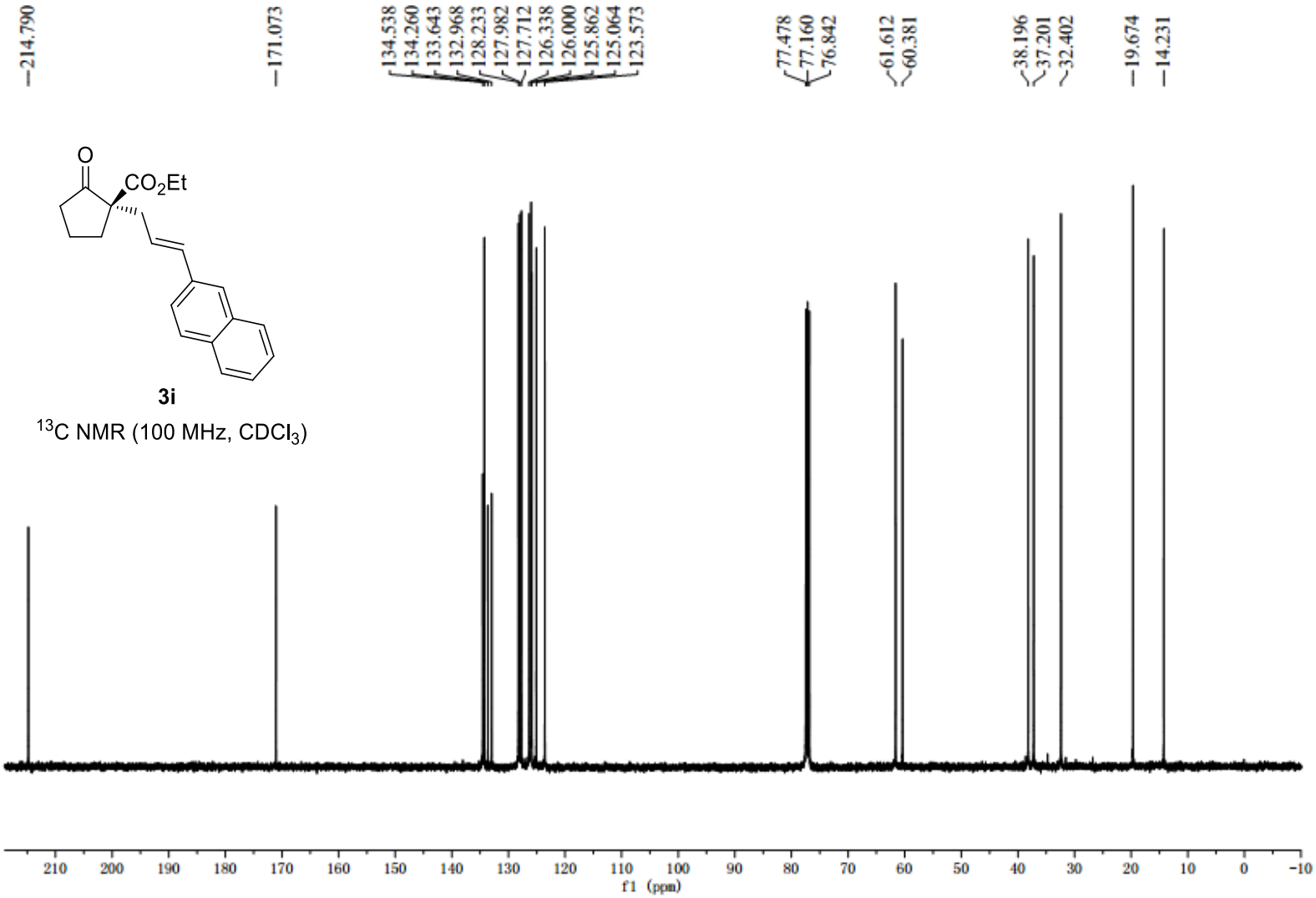
3h

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



3i

^{1}H NMR (400 MHz, $CDCl_3$)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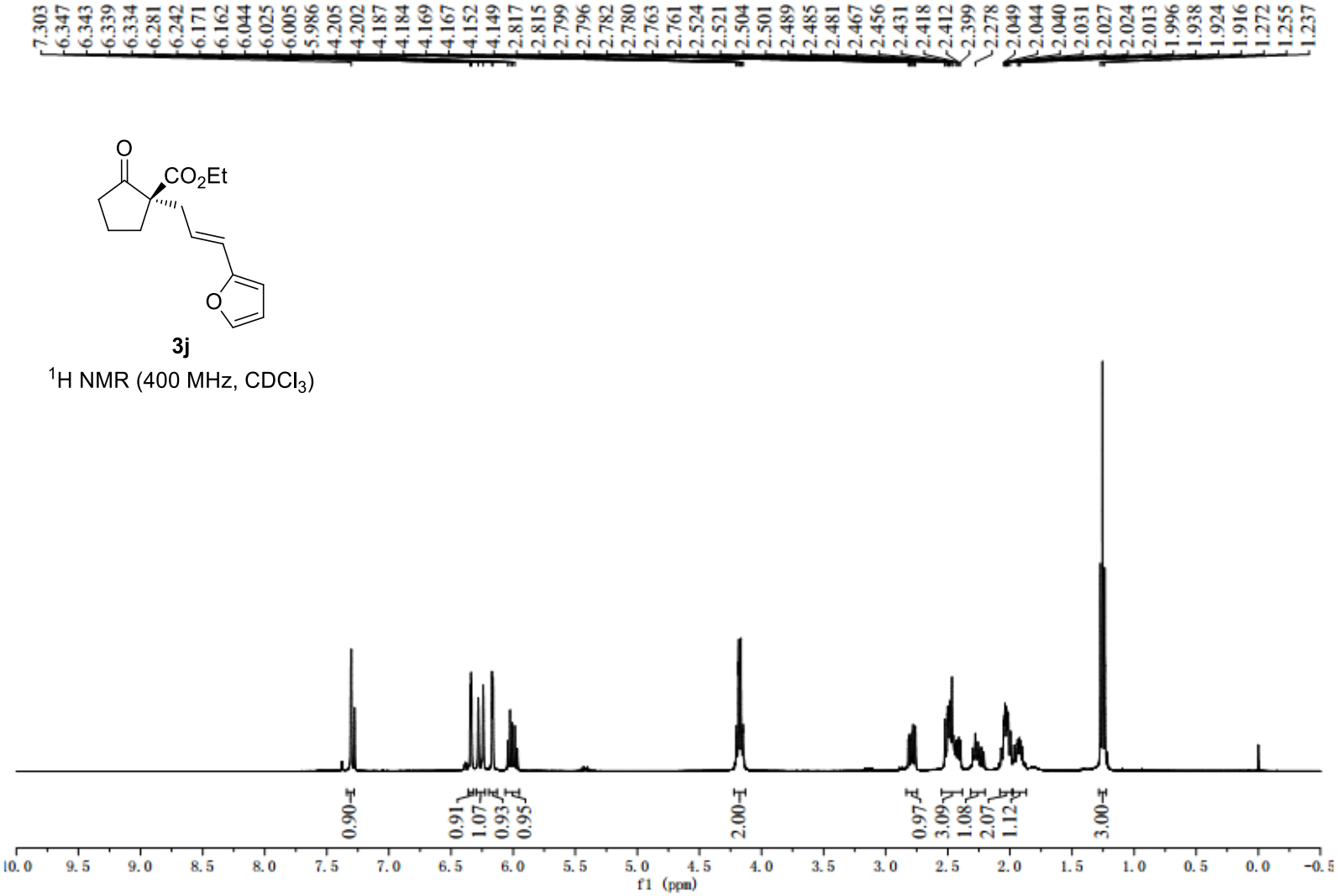
171.073
134.538
134.260
133.643
132.968
128.233
127.982
127.712
126.338
126.000
125.862
125.064
123.573
77.478
77.160
76.842
61.612
60.381
38.196
37.201
32.402
19.674
14.231
O
CO2Et
3i
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.303
6.347
6.343
6.339
6.334
6.281
6.242
6.171
6.162
6.044
6.025
6.005
5.986
4.205
4.202
4.187
4.184
4.169
4.167
4.152
4.149
2.817
2.815
2.799
2.796
2.782
2.780
2.763
2.761
2.524
2.521
2.504
2.501
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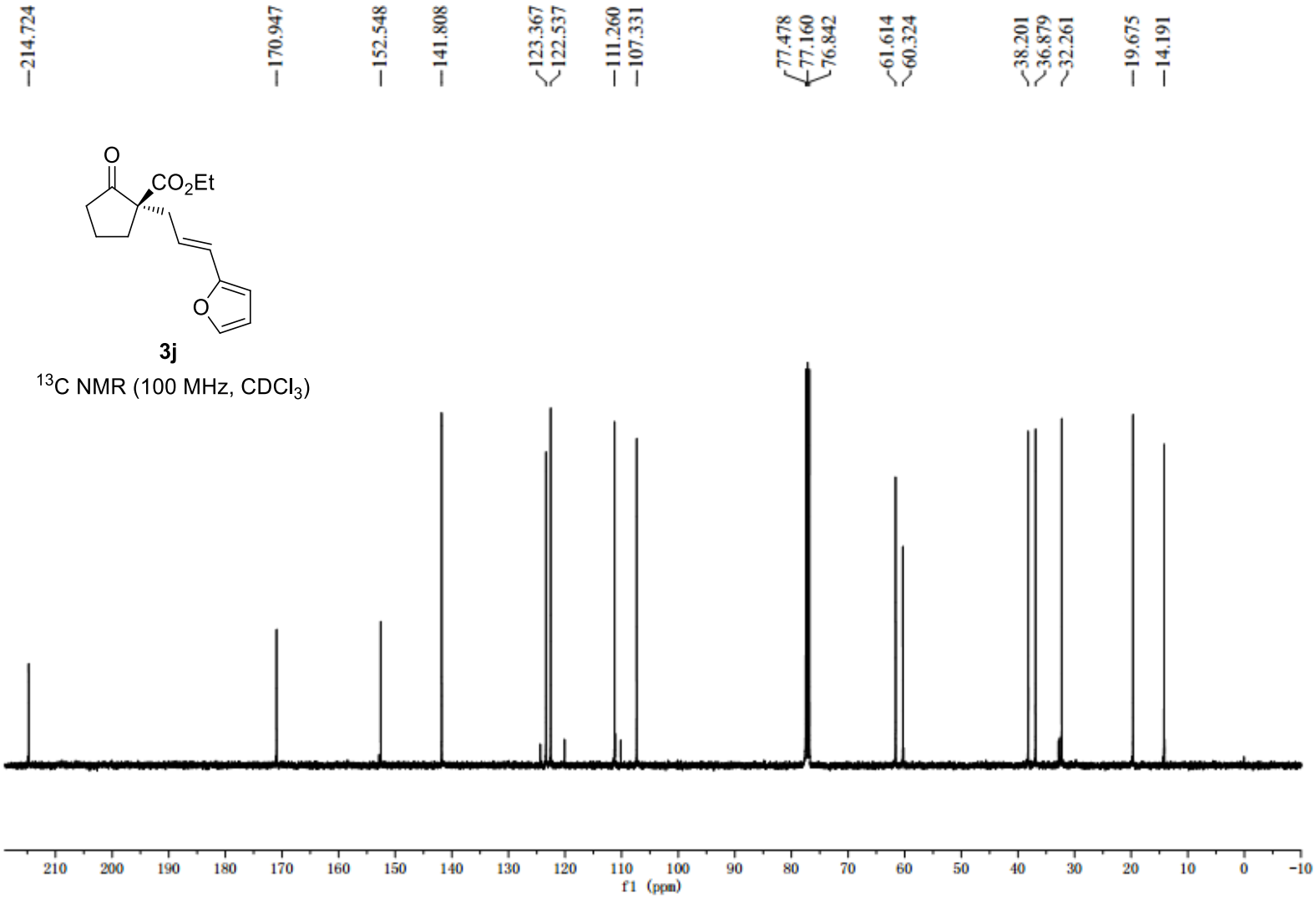
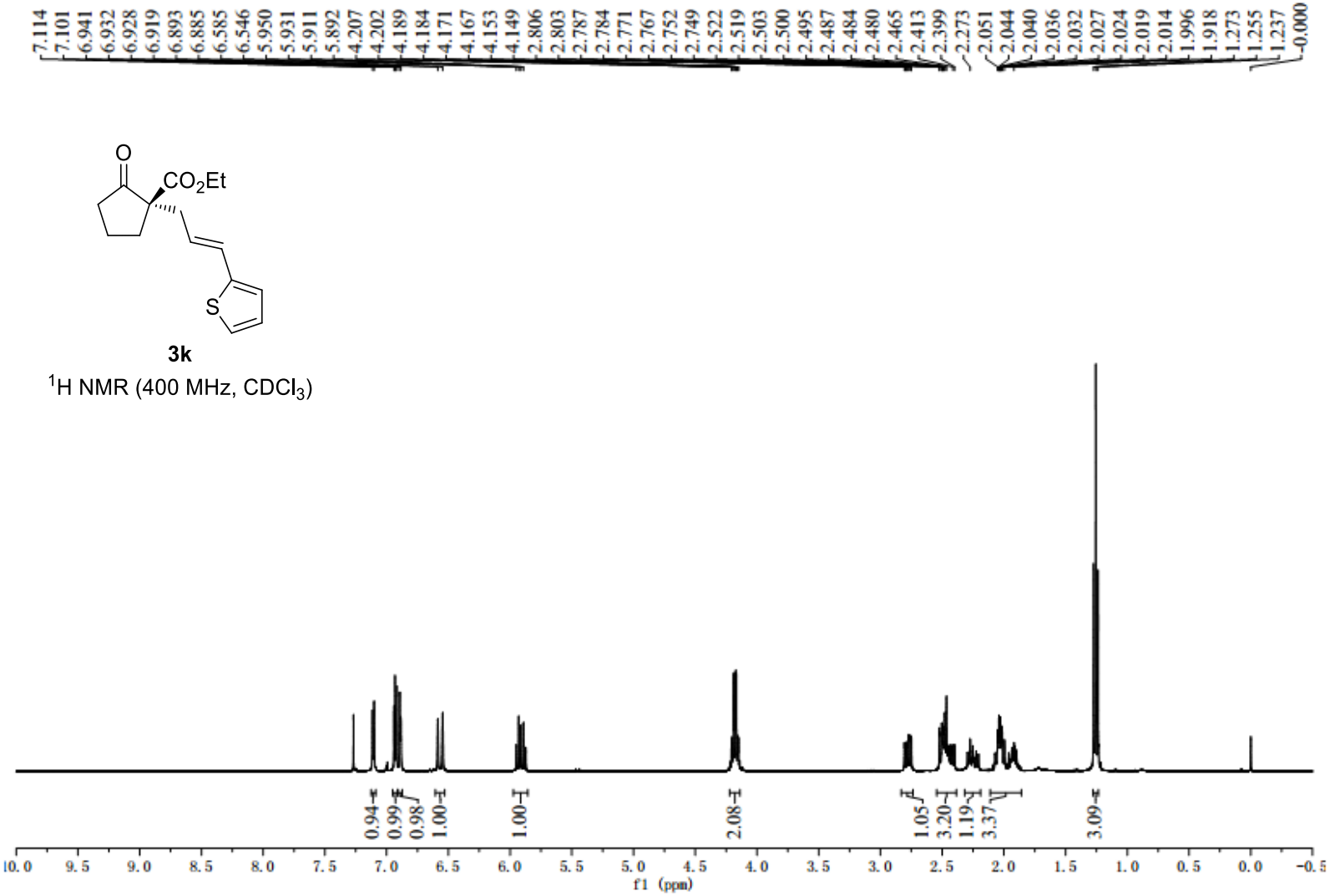
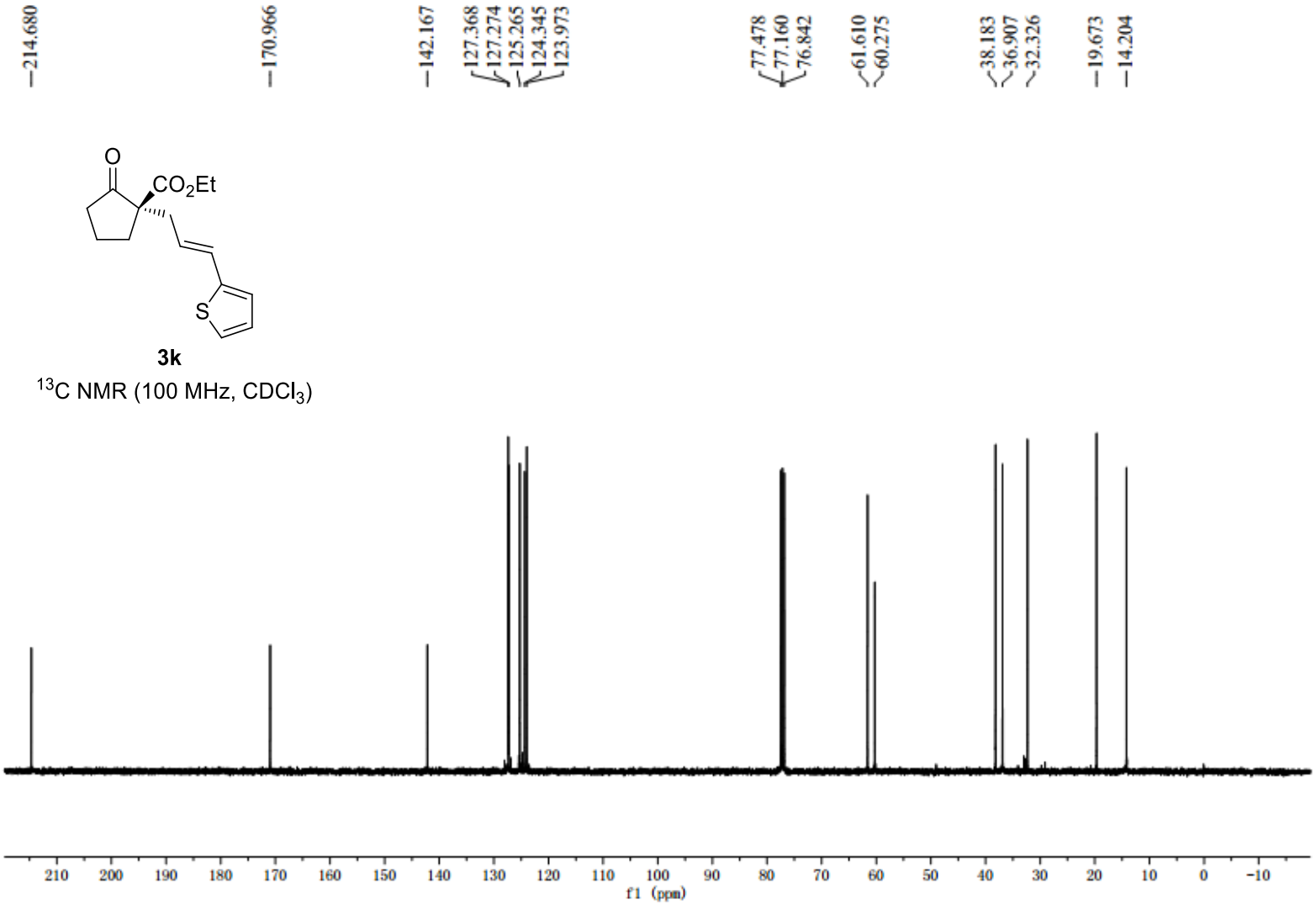
2.024
2.013
1.996
1.938
1.924
1.916
1.272
1.255
1.237
O
CO2Et
O
3j
1H NMR (400 MHz, CDCl3)
0.90
0.91
1.07
0.93
0.95
2.00
0.97
3.09
1.08
2.07
1.12
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


214.724
170.947
152.548
141.808
123.367
122.537
111.260
107.331
77.478
77.160
76.842
61.614
60.324
38.201
36.879
32.261
19.675
14.191
O
CO2Et
O
3j
13C NMR (100 MHz, CDCl3)
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)



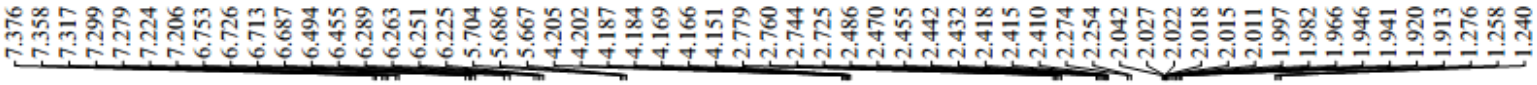
3k

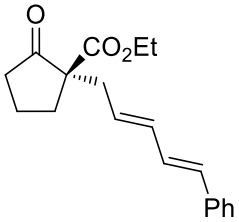
^{1}H NMR (400 MHz, $CDCl_3$)



3k

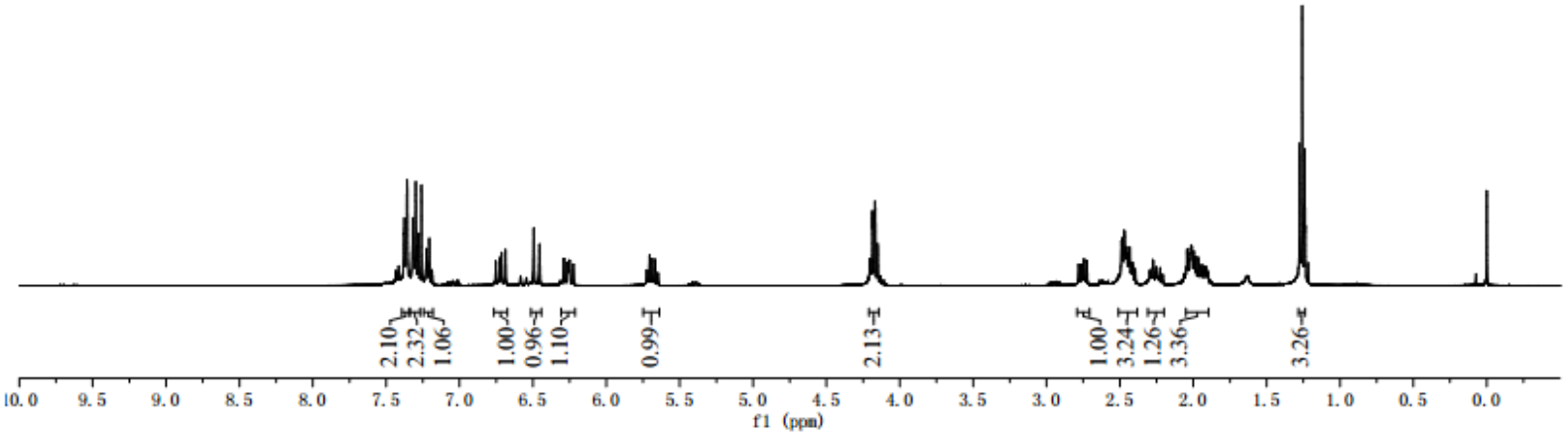
^{13}C NMR (100 MHz, $CDCl_3$)

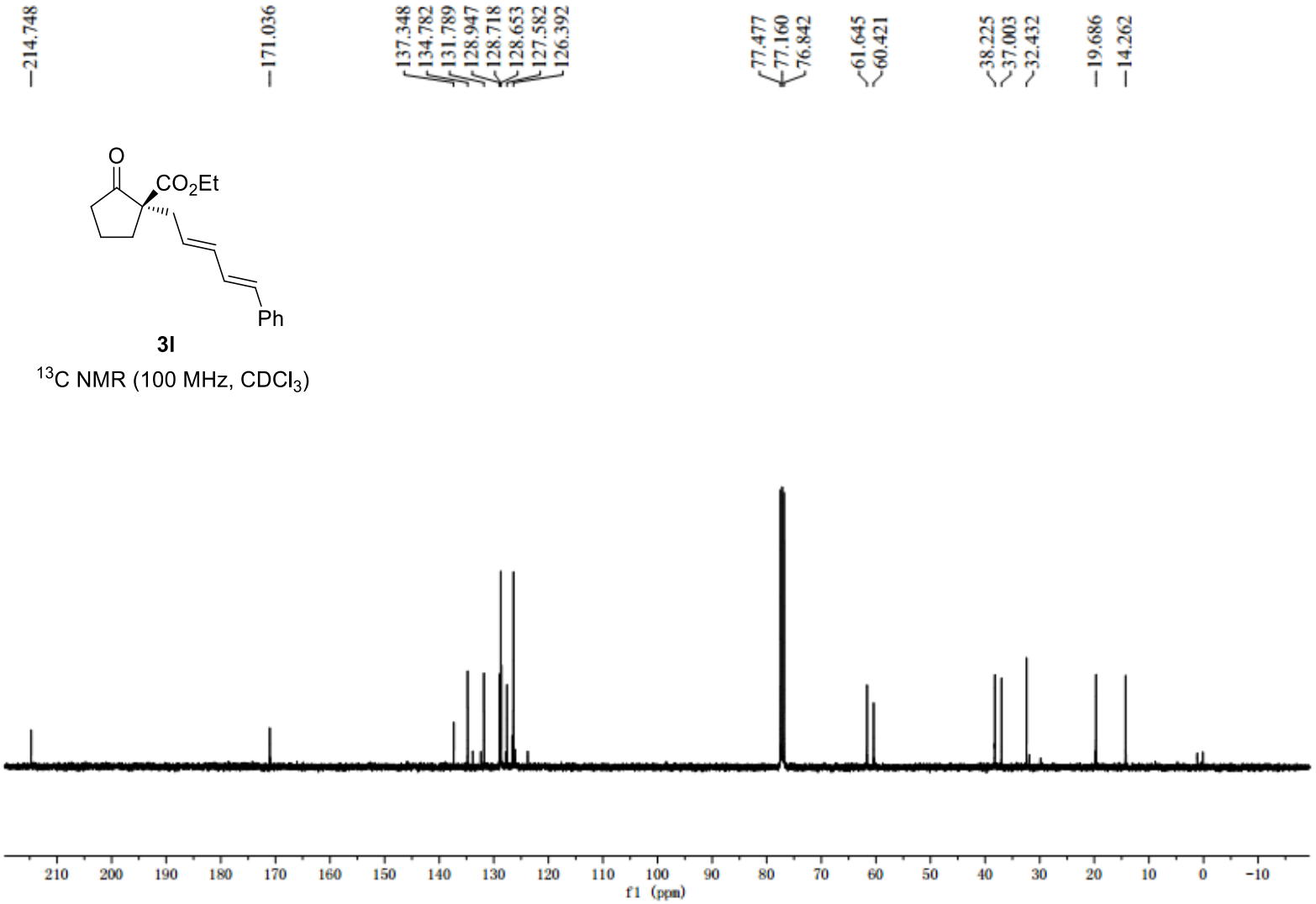




3l

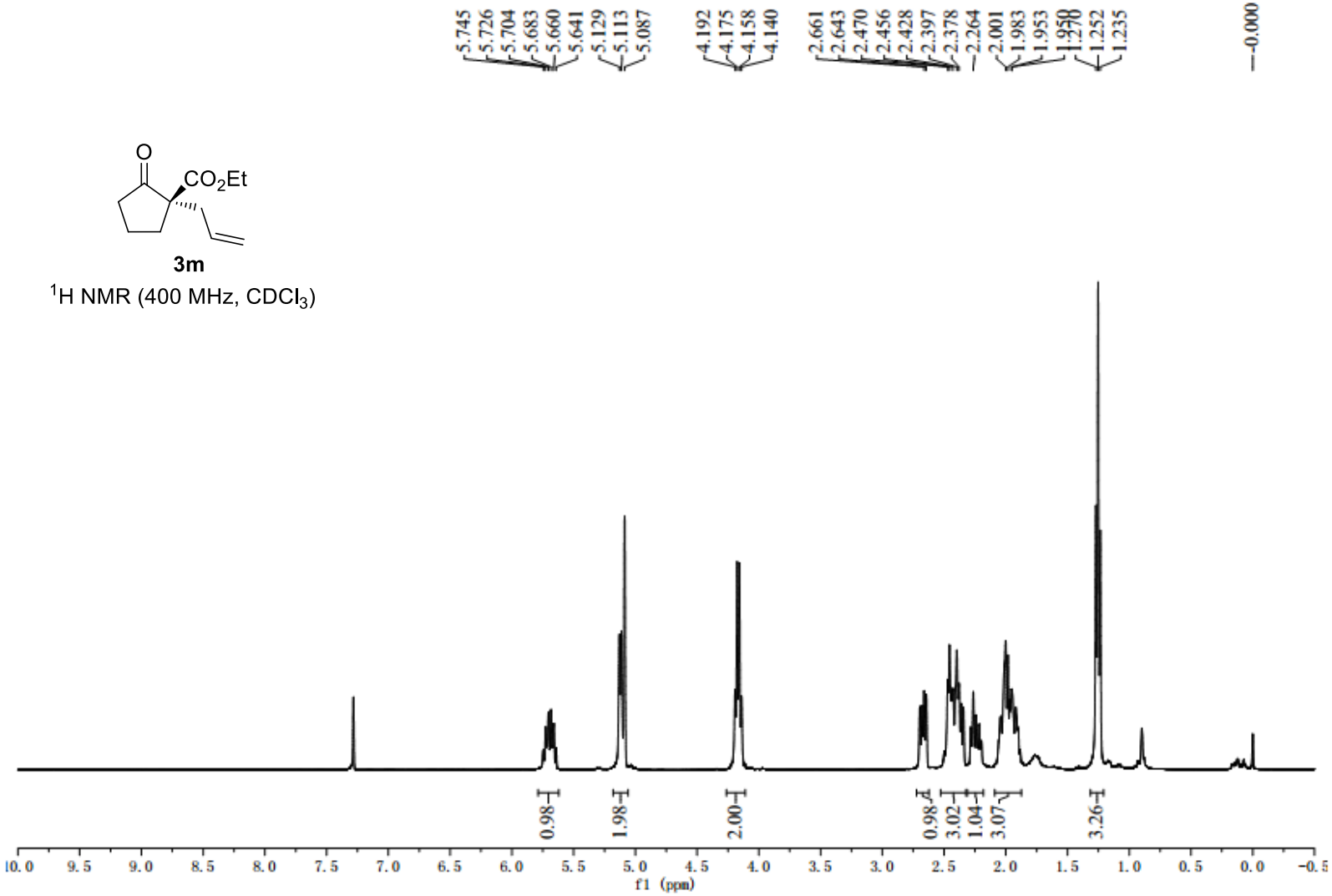
^{1}H NMR (400 MHz, $CDCl_3$)





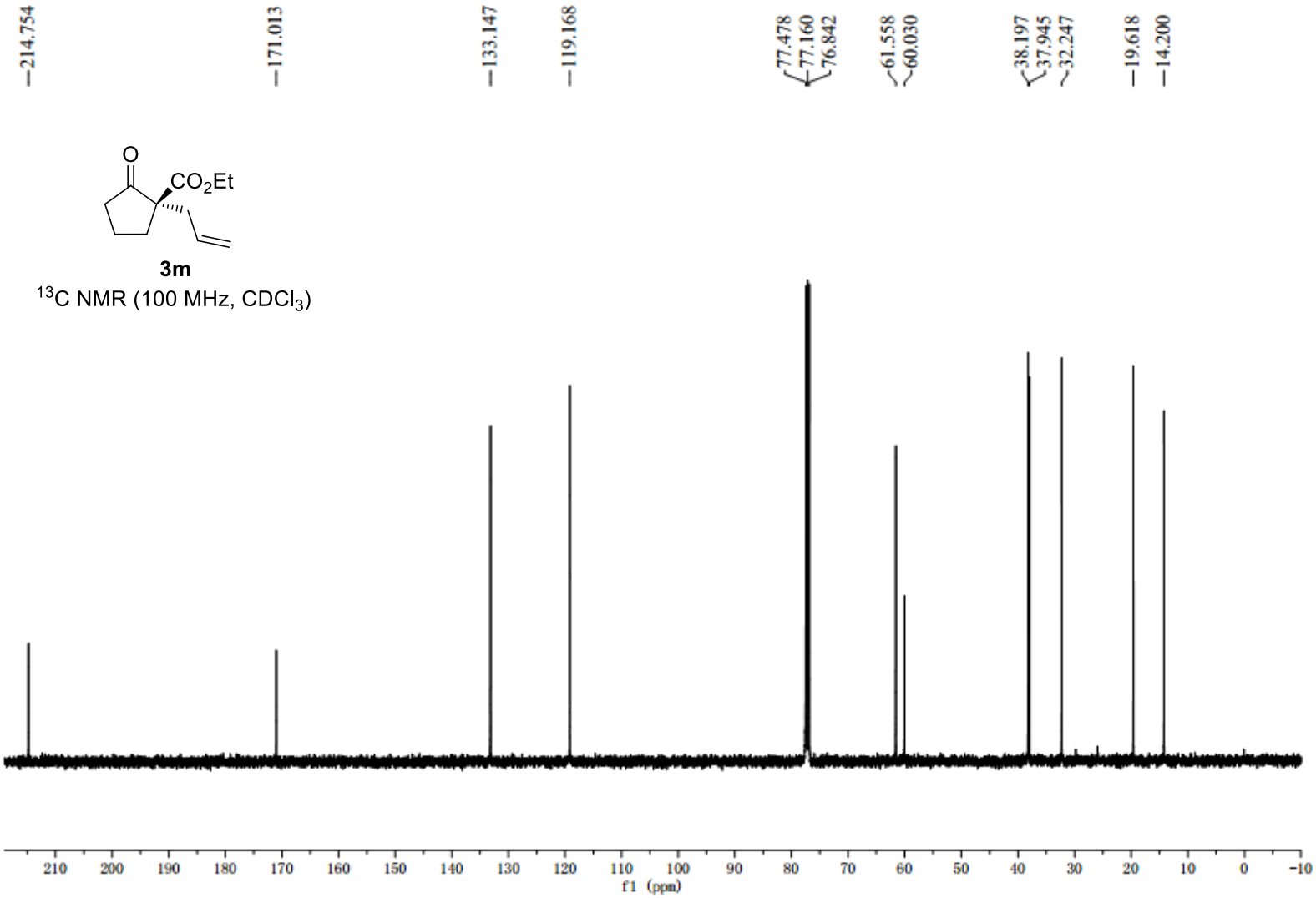
3l

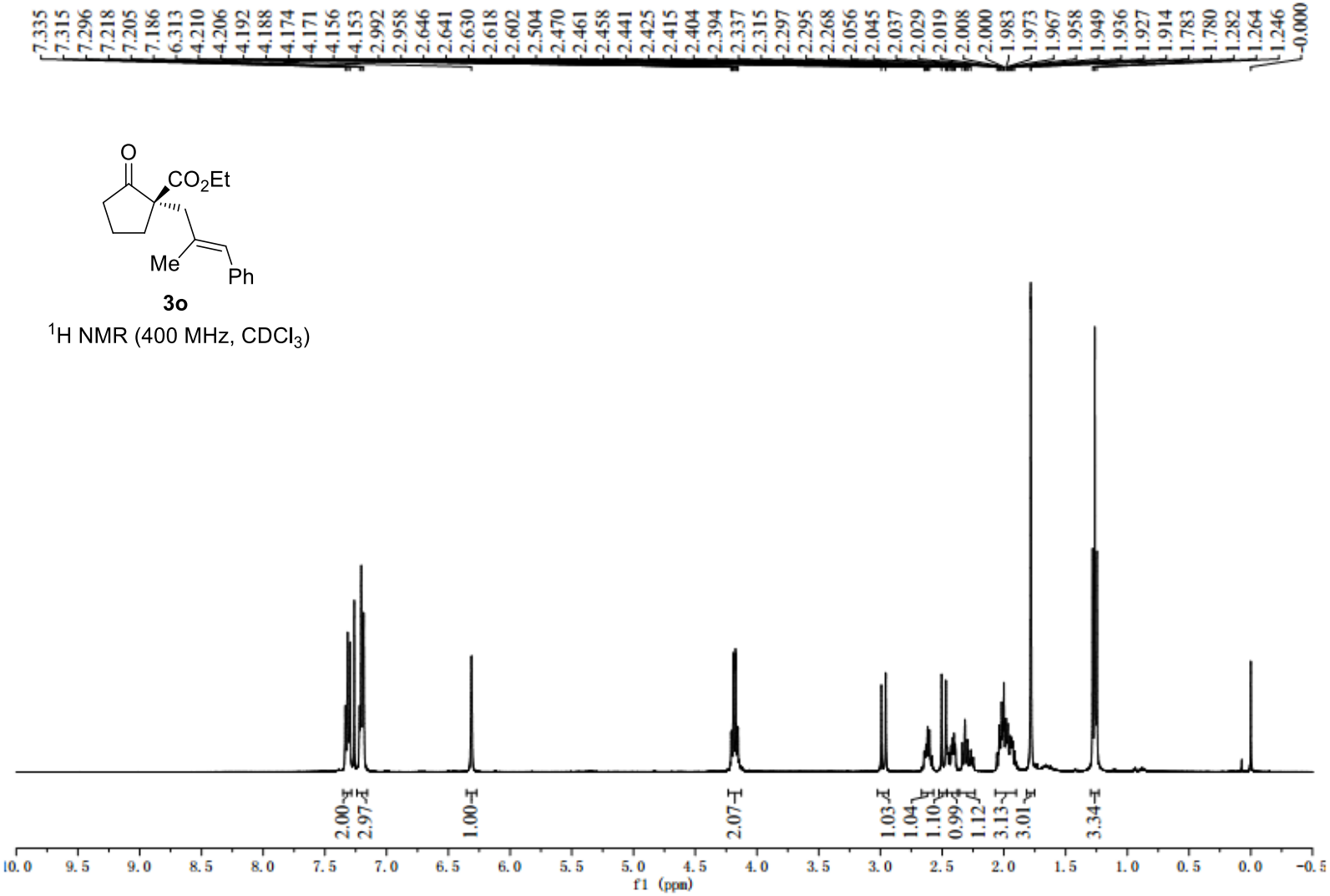
^{13}C NMR (100 MHz, $CDCl_3$)

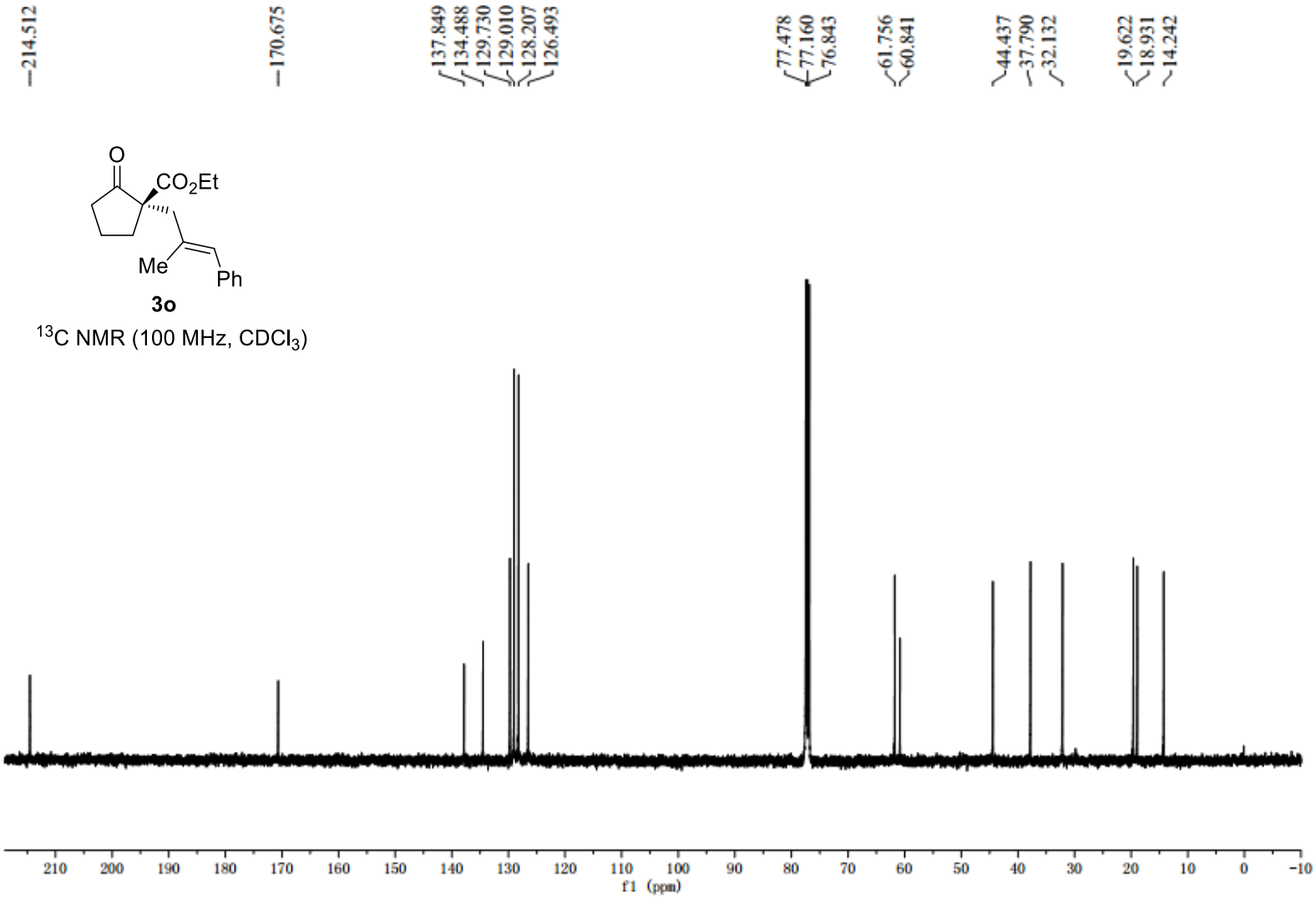


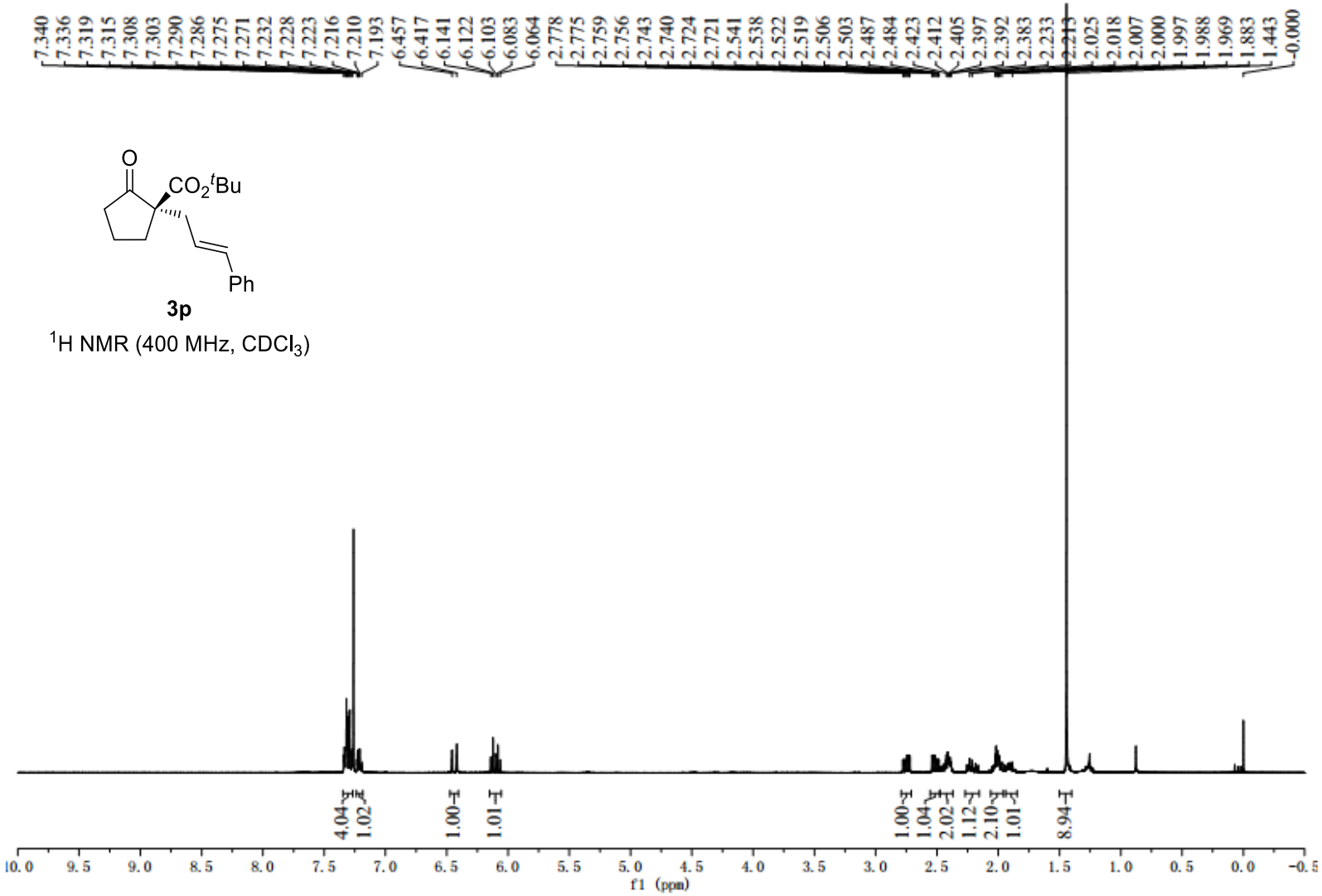
3m

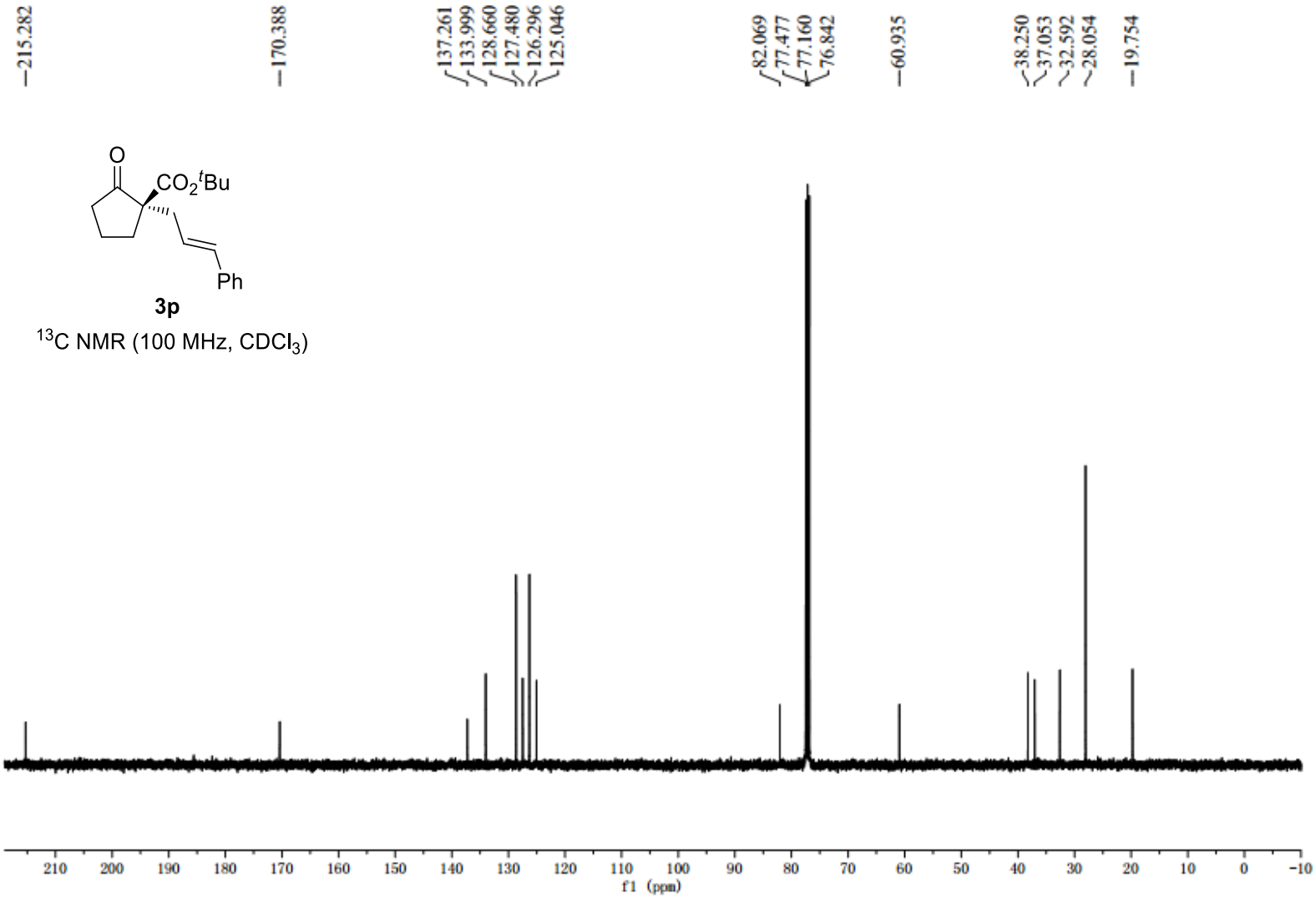
^{1}H NMR (400 MHz, $CDCl_3$)


214.754
171.013
133.147
119.168
77.478
77.160
76.842
61.558
60.030
38.197
37.945
32.247
19.618
14.200
O
CO2Et
3m
13C NMR (100 MHz, CDCl3)
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)


7.335
7.315
7.296
7.218
7.205
7.186
6.313
4.210
4.206
4.192
4.188
4.174
4.171
4.156
4.153
2.992
2.958
2.646
2.641
2.630
2.618
2.602
2.504
2.470
2.461
2.458
2.441
2.425
2.415
2.404
2.394
2.337
2.315
2.297
2.295
2.268
2.056
2.045
2.037
2.029
2.019
2.008
2.000
1.983
1.973
1.967
1.958
1.949
1.936
1.927
1.914
1.783
1.780
1.282
1.264
1.246
-0.000
O
CO2Et
Me
Ph
3o
1H NMR (400 MHz, CDCl3)
2.00
2.97
1.00
2.07
1.03
1.04
1.10
0.99
1.12
3.13
3.01
3.34
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
-0.5
f1 (ppm)

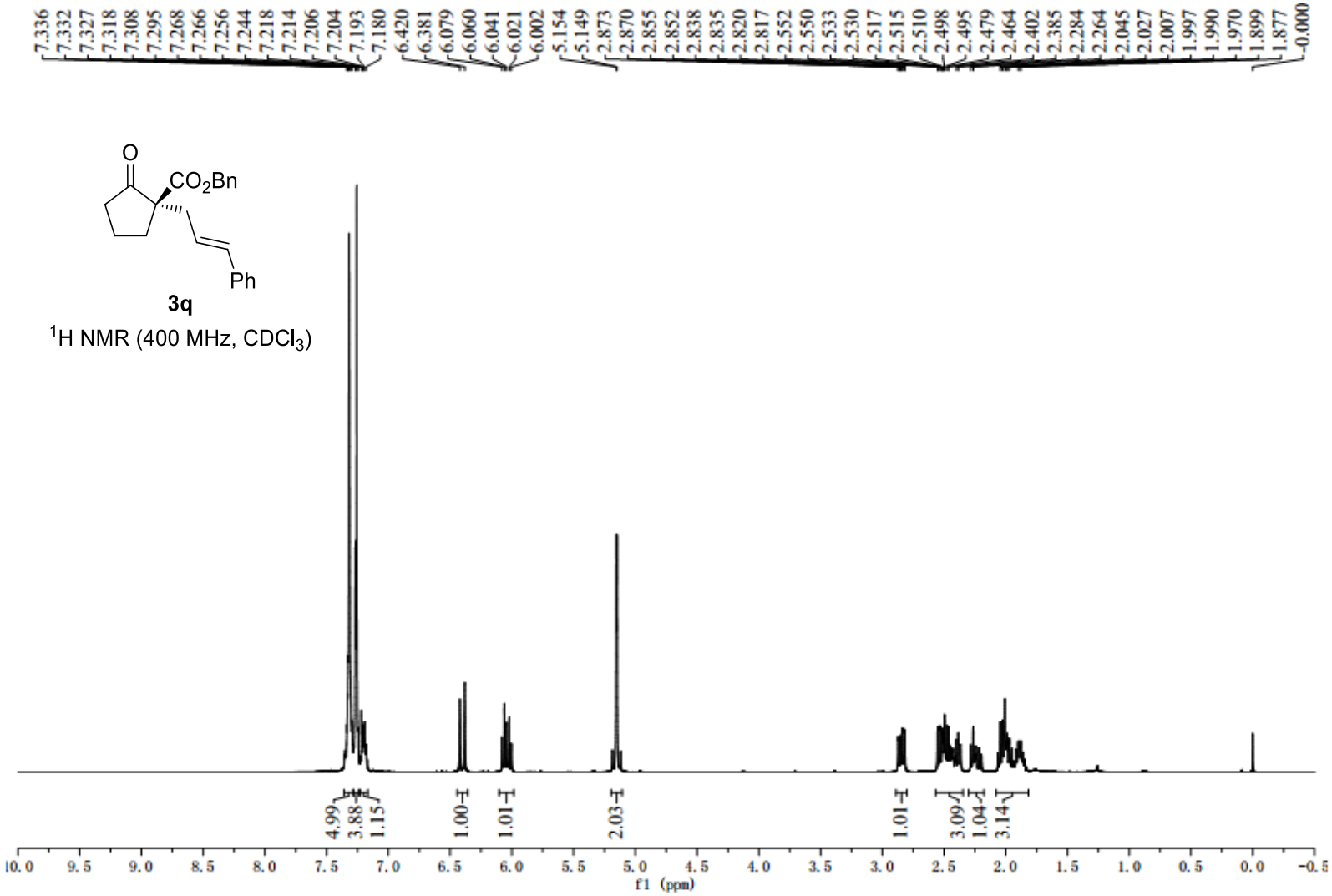

214.512
170.675
137.849
134.488
129.730
129.010
128.207
126.493
77.478
77.160
76.843
61.756
60.841
44.437
37.790
32.132
19.622
18.931
14.242
O
CO2Et
Me
Ph
3o
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

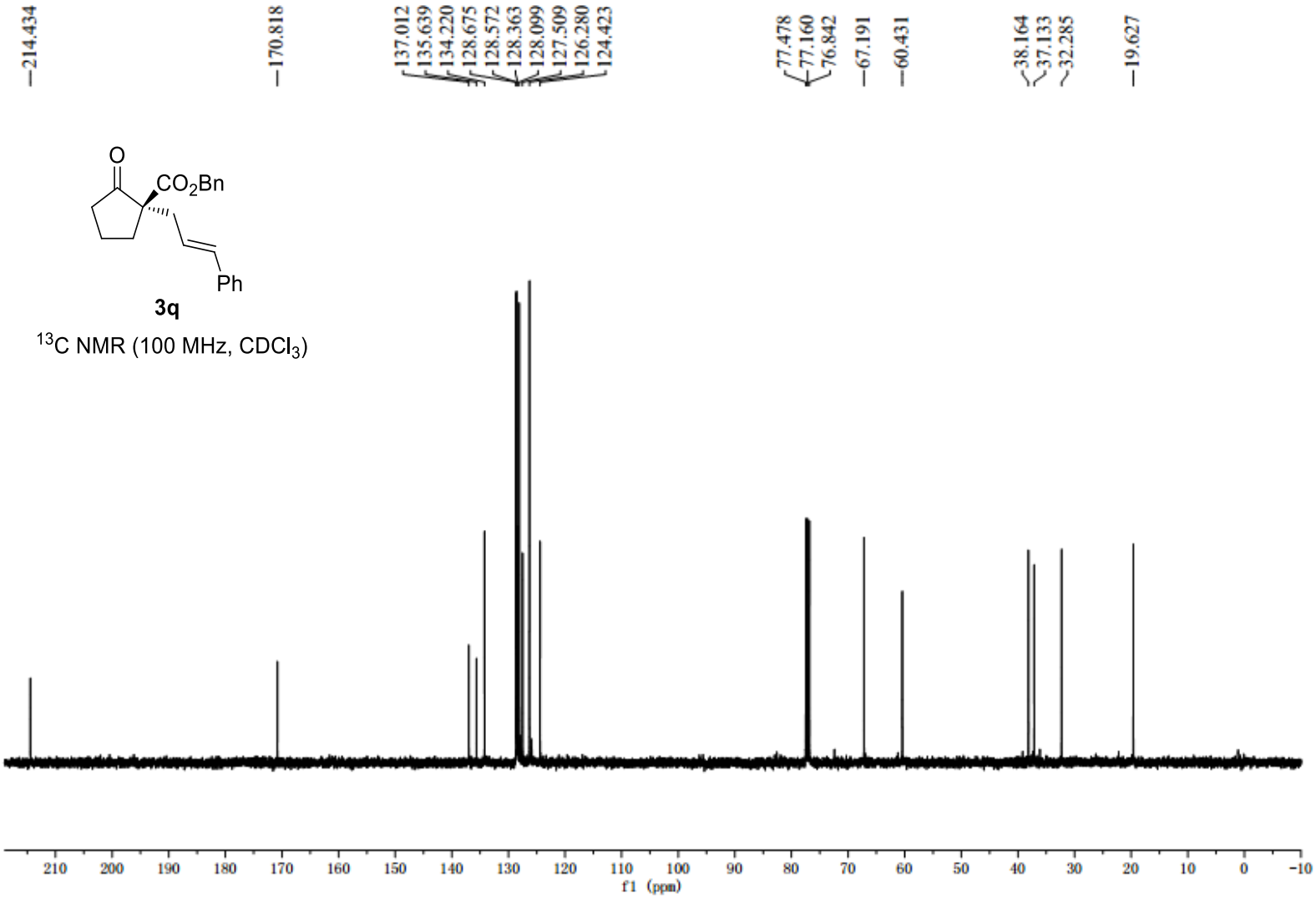

7.340
7.336
7.319
7.315
7.308
7.303
7.290
7.286
7.275
7.271
7.232
7.228
7.223
7.216
7.210
7.193
6.457
6.417
6.141
6.122
6.103
6.083
6.064
2.778
2.775
2.759
2.756
2.743
2.740
2.724
2.721
2.541
2.538
2.522
2.519
2.506
2.503
2.487
2.484
2.423
2.412
2.405
2.397
2.392
2.383
2.233
2.213
2.025
2.018
2.007
2.000
1.997
1.988
1.969
1.883
1.443
-0.000
O
CO2tBu
Ph
3p
1H NMR (400 MHz, CDCl3)
4.04
1.02
1.00
1.01
1.00
1.04
2.02
1.12
2.10
1.01
8.94
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
-0.5
f1 (ppm)

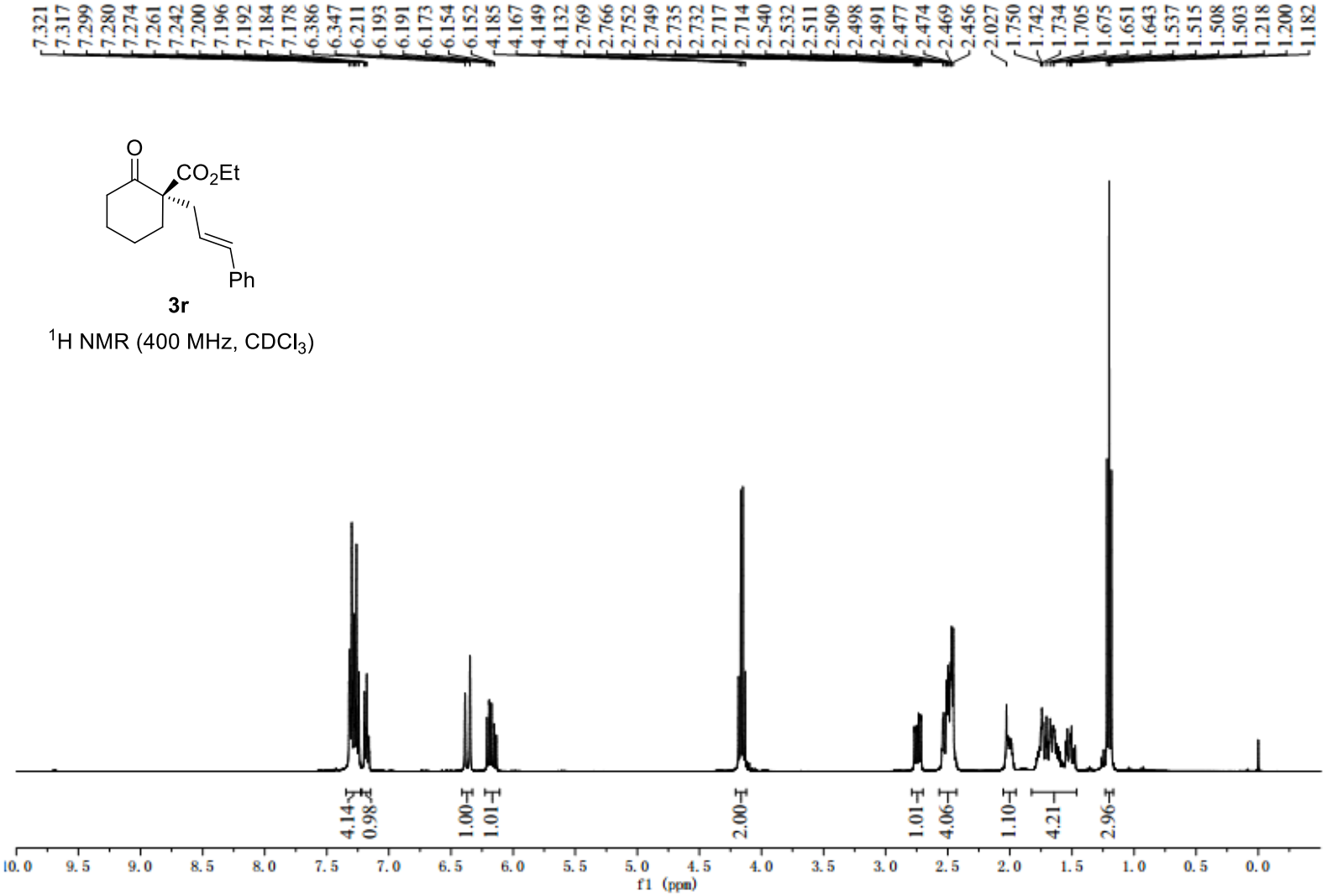


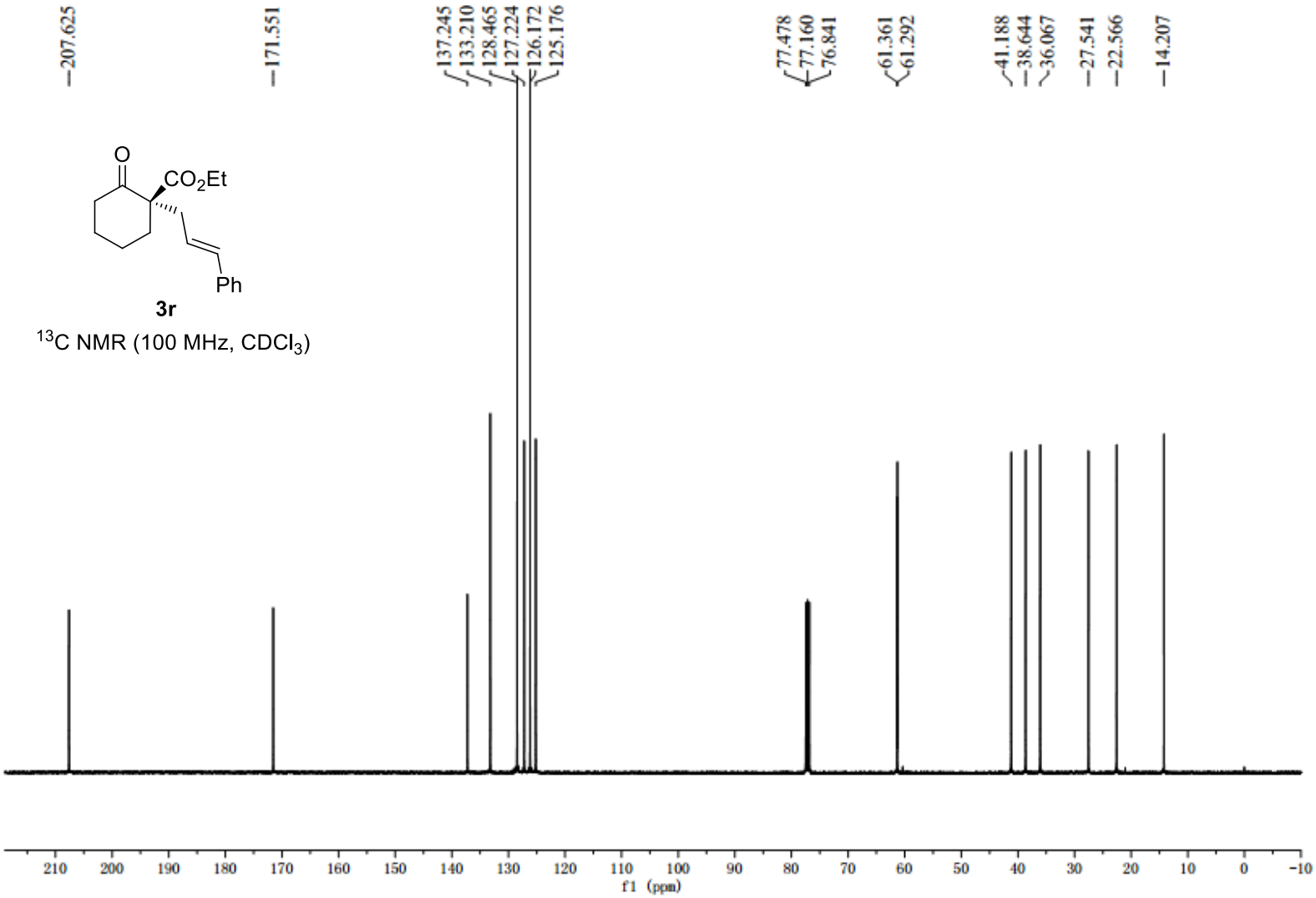
3p

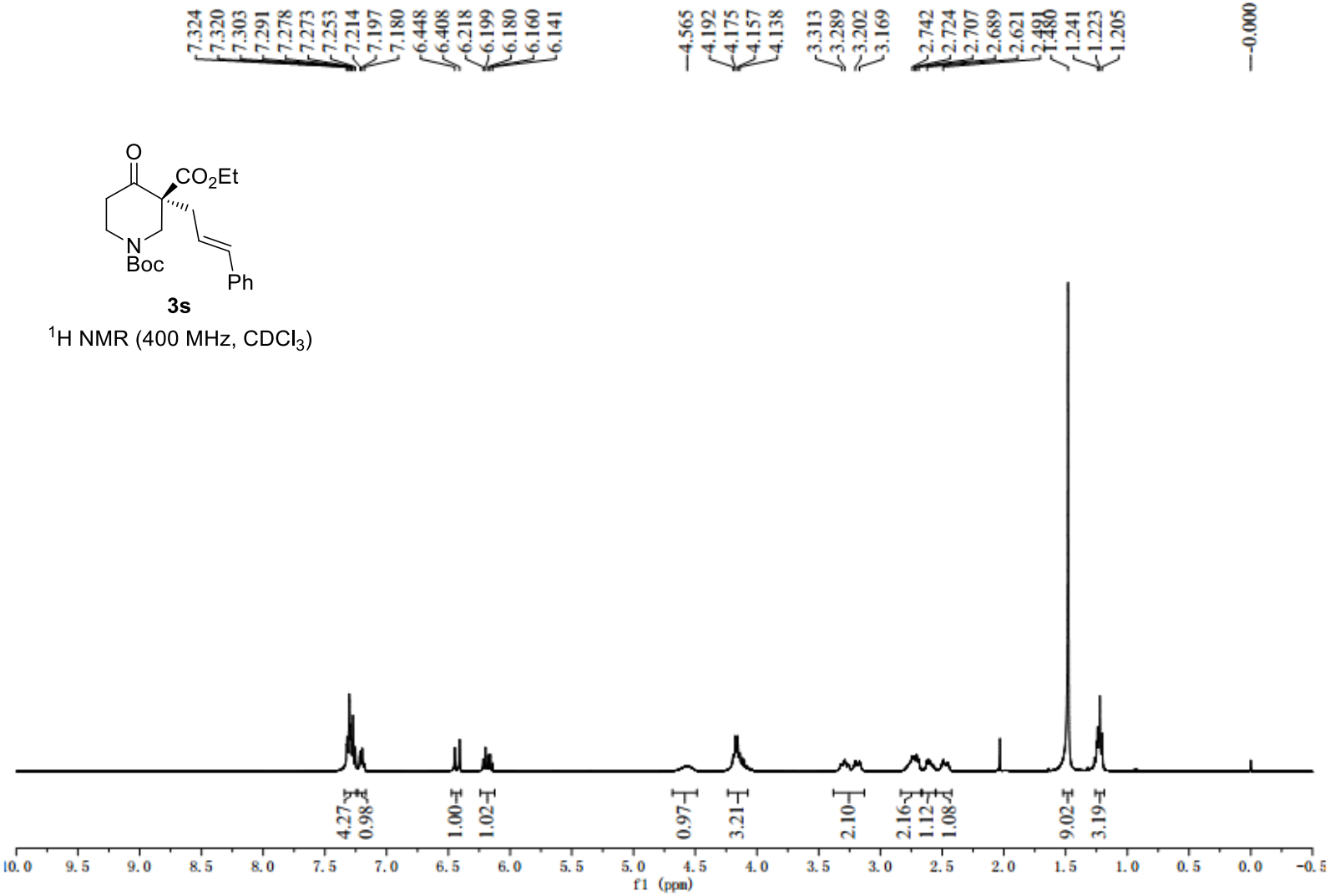
^{13}C NMR (100 MHz, $CDCl_3$)


7.336
7.332
7.327
7.318
7.308
7.295
7.268
7.266
7.256
7.244
7.218
7.214
7.206
7.204
7.193
7.180
6.420
6.381
6.079
6.060
6.041
6.021
6.002
5.154
5.149
2.873
2.870
2.855
2.852
2.838
2.835
2.820
2.817
2.552
2.550
2.533
2.530
2.517
2.515
2.510
2.498
2.495
2.479
2.464
2.402
2.385
2.284
2.264
2.045
2.027
2.007
1.997
1.990
1.970
1.899
1.877
-0.000
O
CO2Bn
Ph
3q
1H NMR (400 MHz, CDCl3)
4.99
3.88
1.15
1.00
1.01
2.03
1.01
3.09
1.04
3.14
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
-0.5
f1 (ppm)


214.434
170.818
137.012
135.639
134.220
128.675
128.572
128.363
128.099
127.509
126.280
124.423
77.478
77.160
76.842
67.191
60.431
38.164
37.133
32.285
19.627
O
CO2Bn
Ph
3q
13C NMR (100 MHz, CDCl3)
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)

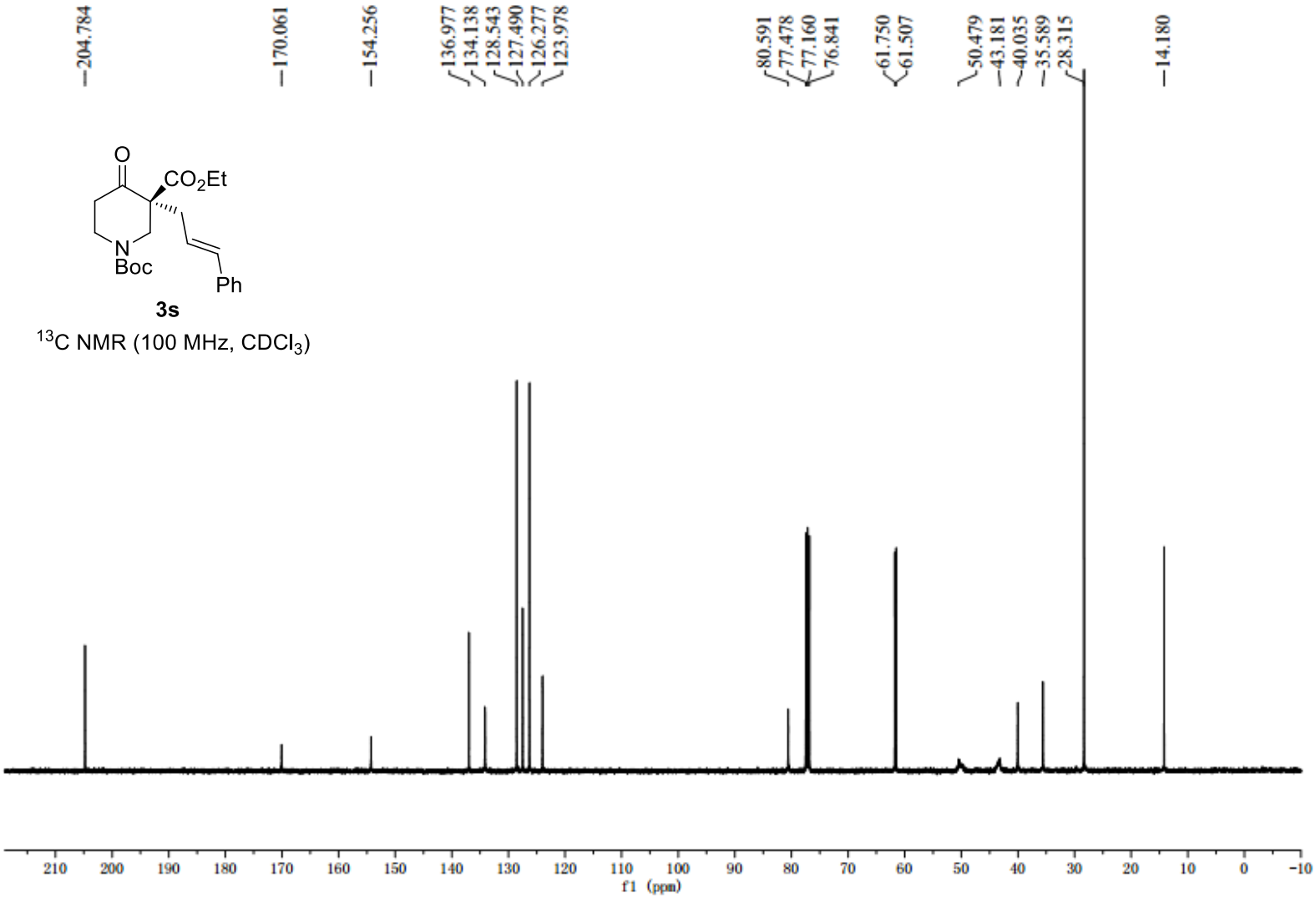

7.321
7.317
7.299
7.280
7.274
7.261
7.242
7.200
7.196
7.192
7.184
7.178
6.386
6.347
6.211
6.193
6.191
6.173
6.154
6.152
4.185
4.167
4.149
4.132
2.769
2.766
2.752
2.749
2.735
2.732
2.717
2.714
2.540
2.532
2.511
2.509
2.498
2.491
2.477
2.474
2.469
2.456
2.027
1.750
1.742
1.734
1.705
1.675
1.651
1.643
1.537
1.515
1.508
1.503
1.218
1.200
1.182
O
CO2Et
Ph
3r
1H NMR (400 MHz, CDCl3)
4.14
0.98
1.00
1.01
2.00
1.01
4.06
1.10
4.21
2.96
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)


207.625
171.551
137.245
133.210
128.465
127.224
126.172
125.176
77.478
77.160
76.841
61.361
61.292
41.188
38.644
36.067
27.541
22.566
14.207
O
CO2Et
Ph
3r
13C NMR (100 MHz, CDCl3)
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)



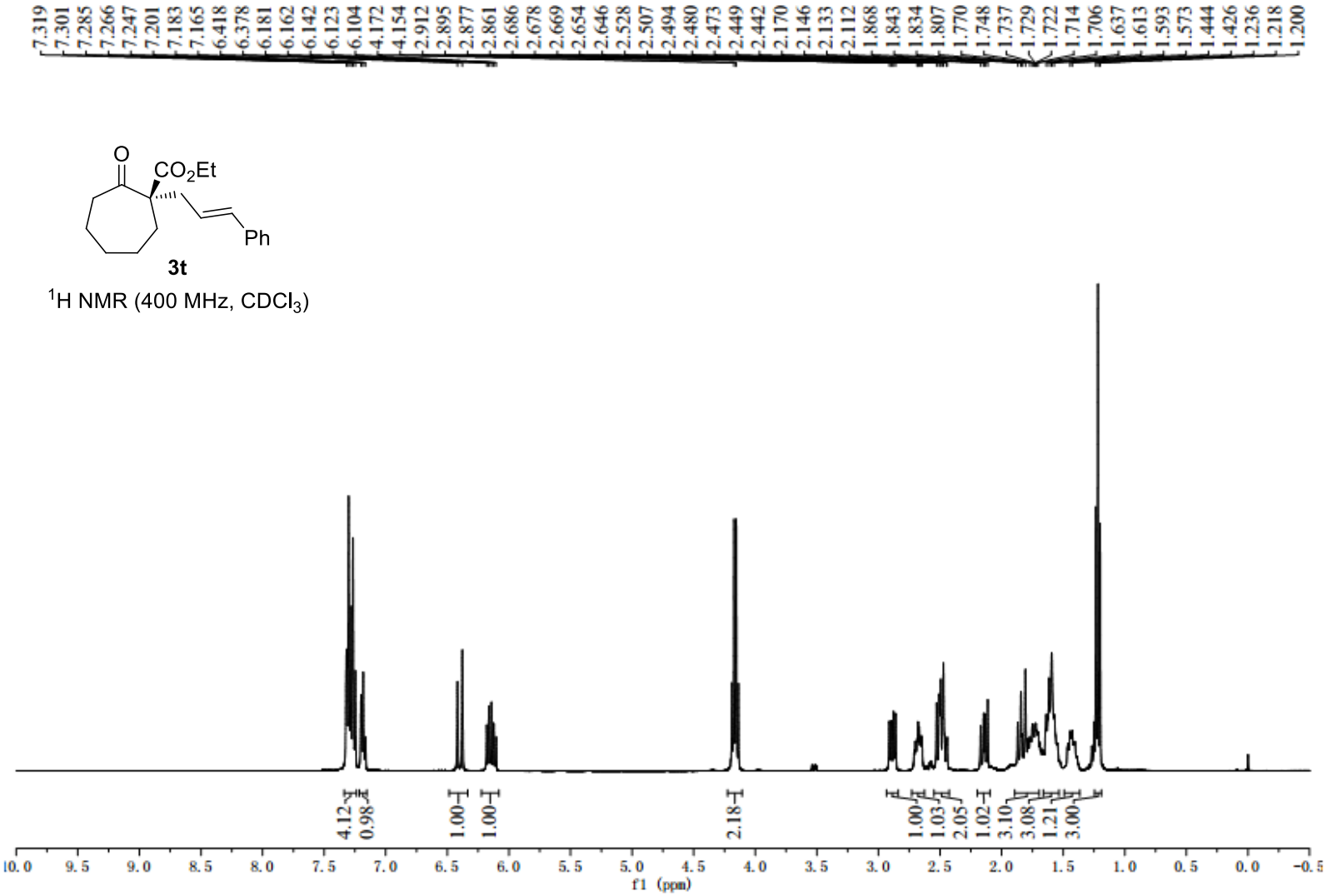
3s

^{1}H NMR (400 MHz, $CDCl_3$)



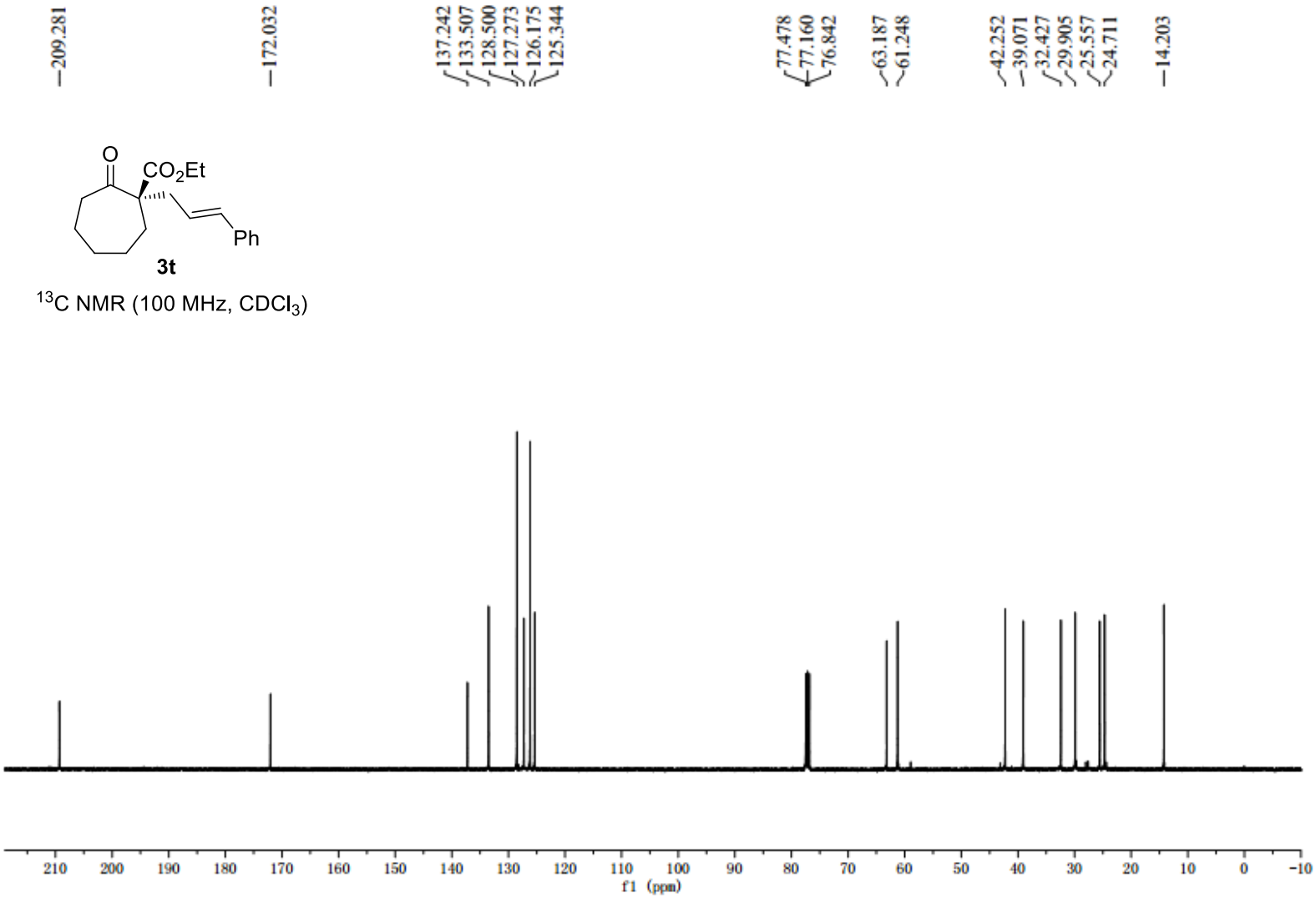
3s

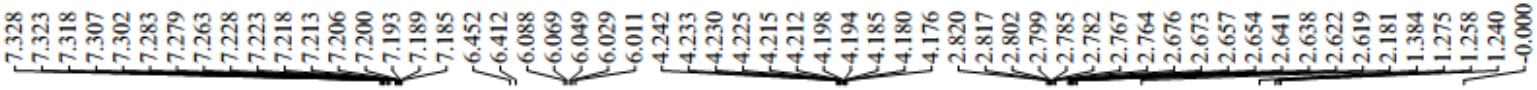
^{13}C NMR (100 MHz, $CDCl_3$)

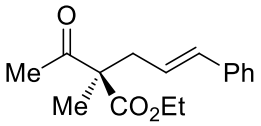

7.319
7.301
7.285
7.266
7.247
7.201
7.183
7.165
6.418
6.378
6.181
6.162
6.142
6.123
6.104
4.172
4.154
2.912
2.895
2.877
2.861
2.686
2.678
2.669
2.654
2.646
2.528
2.507
2.494
2.480
2.473
2.449
2.442
2.170
2.146
2.133
2.112
1.868
1.843
1.834
1.807
1.770
1.748
1.737
1.729
1.722
1.714
1.706
1.637
1.613
1.593
1.573
1.444
1.426
1.236
1.218
1.200
O
CO2Et
Ph
3t
1H NMR (400 MHz, CDCl3)
4.12
0.98
1.00
1.00
2.18
1.00
1.03
2.05
1.02
3.10
3.08
1.21
3.00
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
-0.5
f1 (ppm)

3t

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

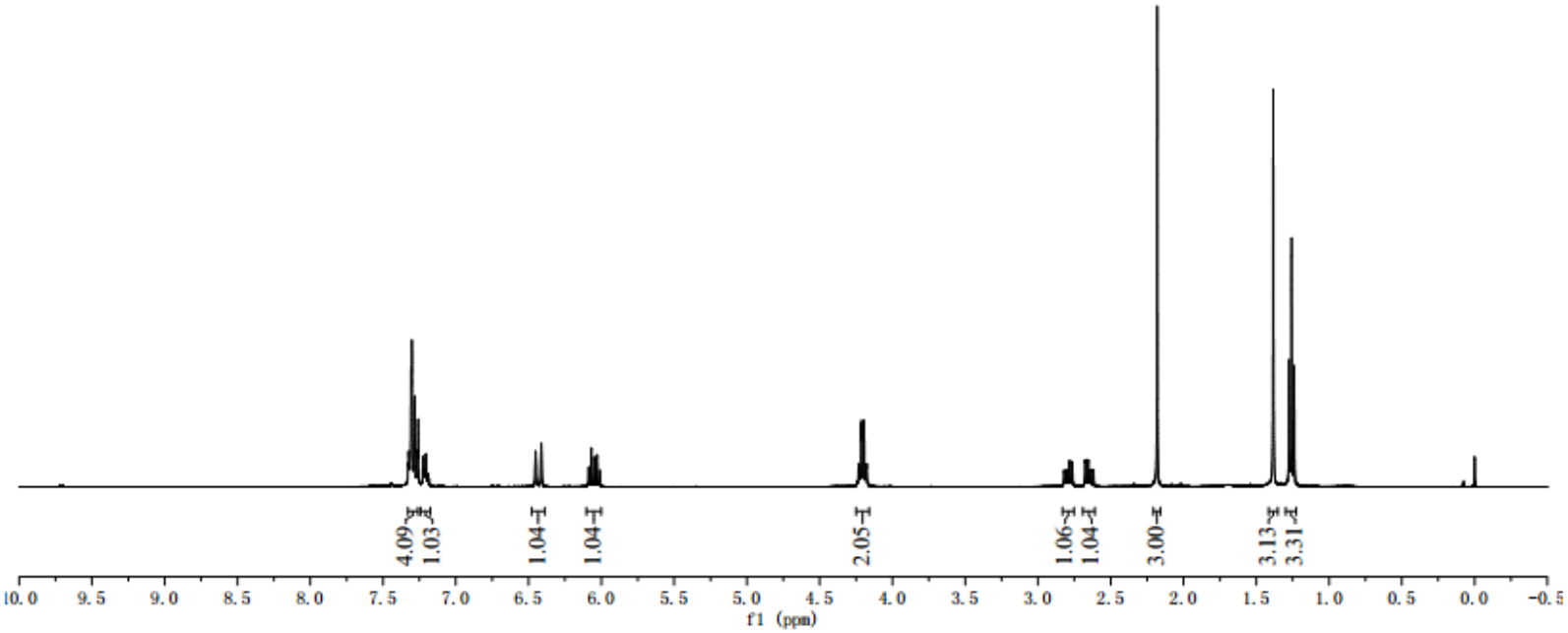


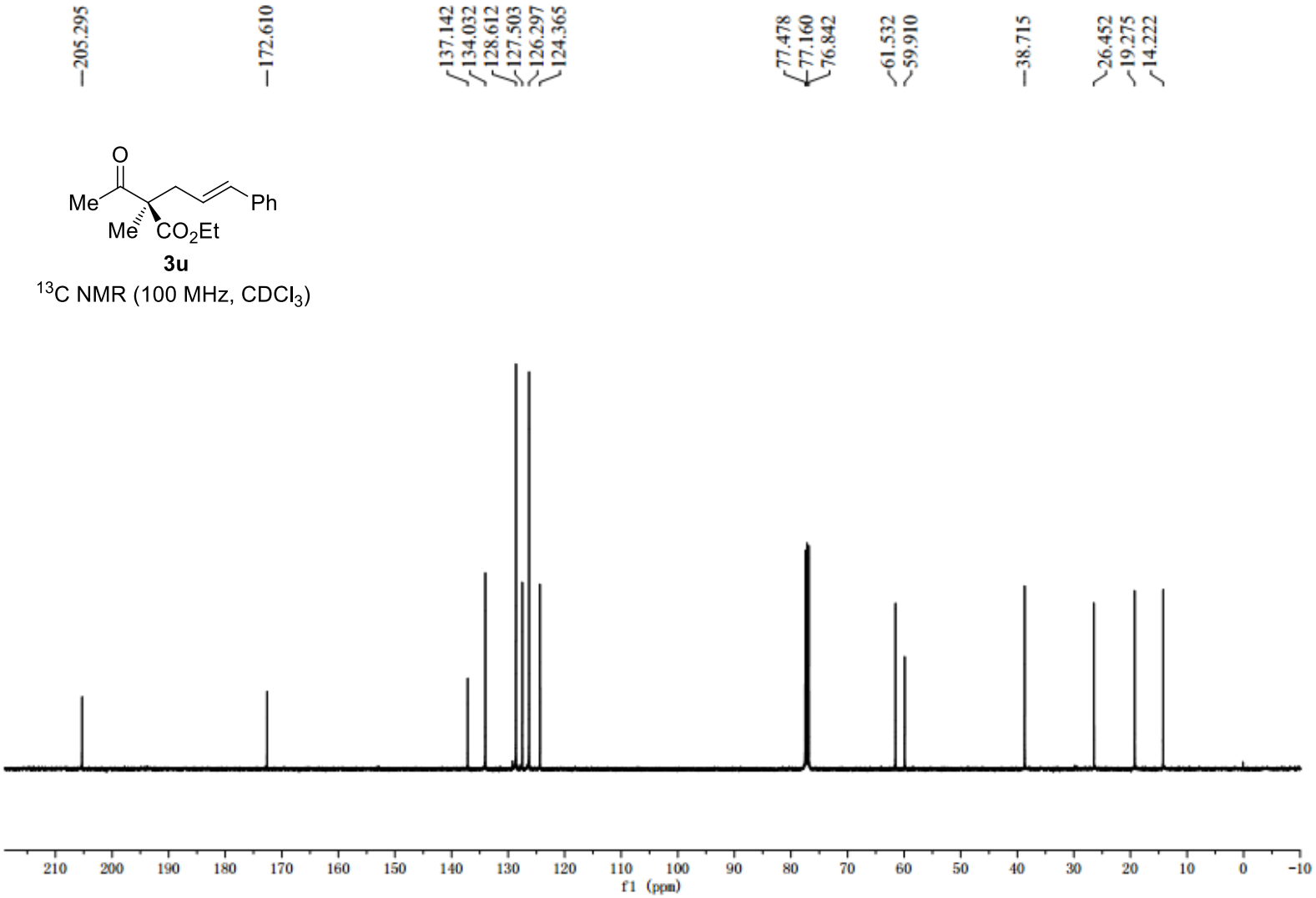




3u

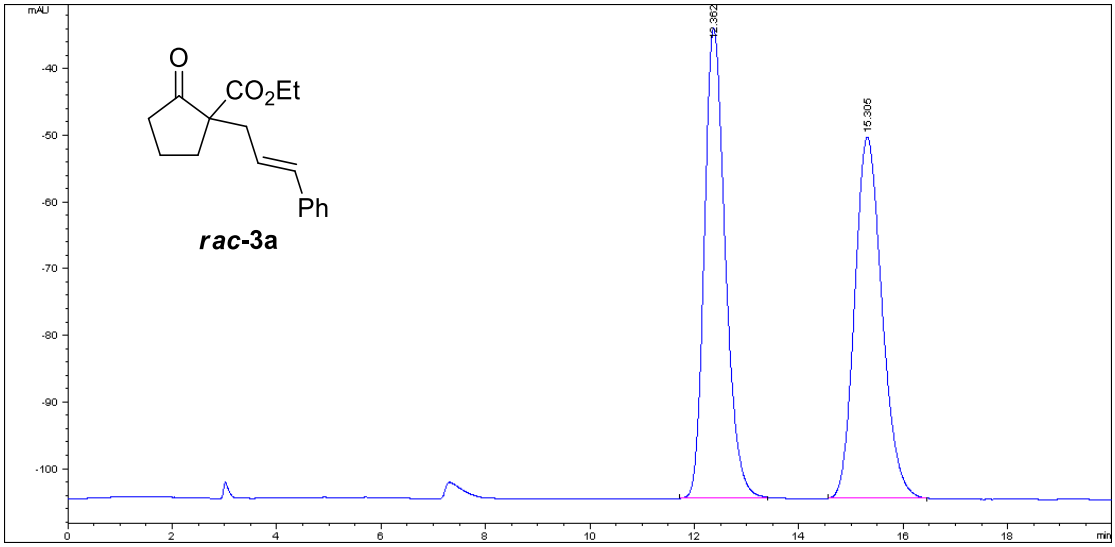
^{1}H NMR (400 MHz, $CDCl_3$)



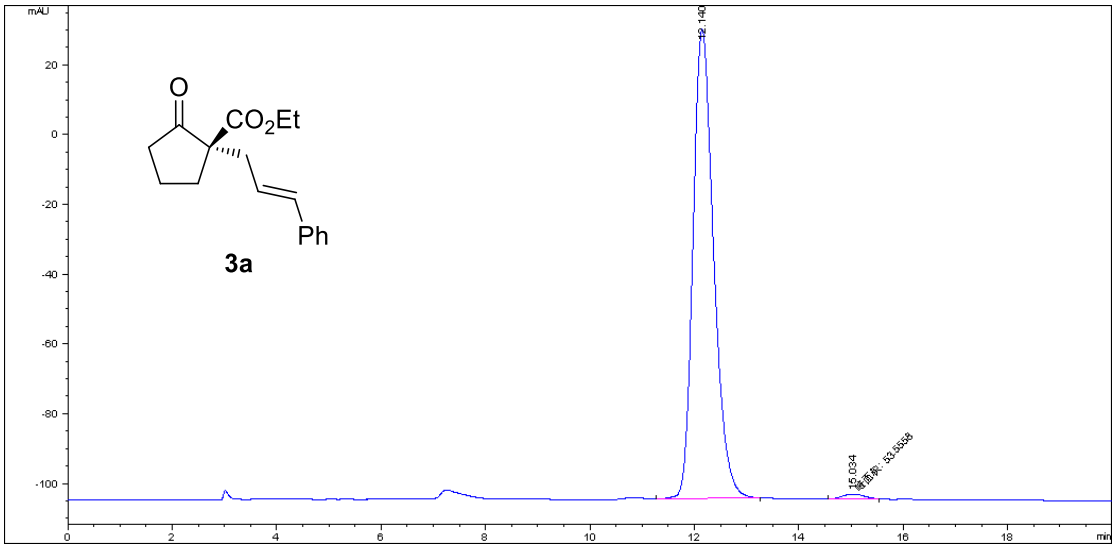


3u

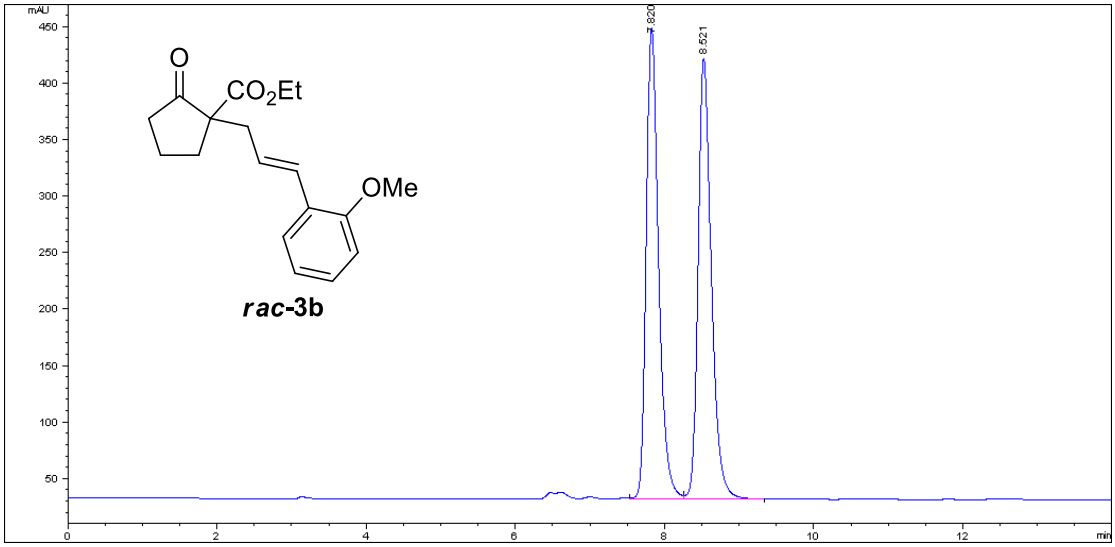
^{13}C NMR (100 MHz, $CDCl_3$)



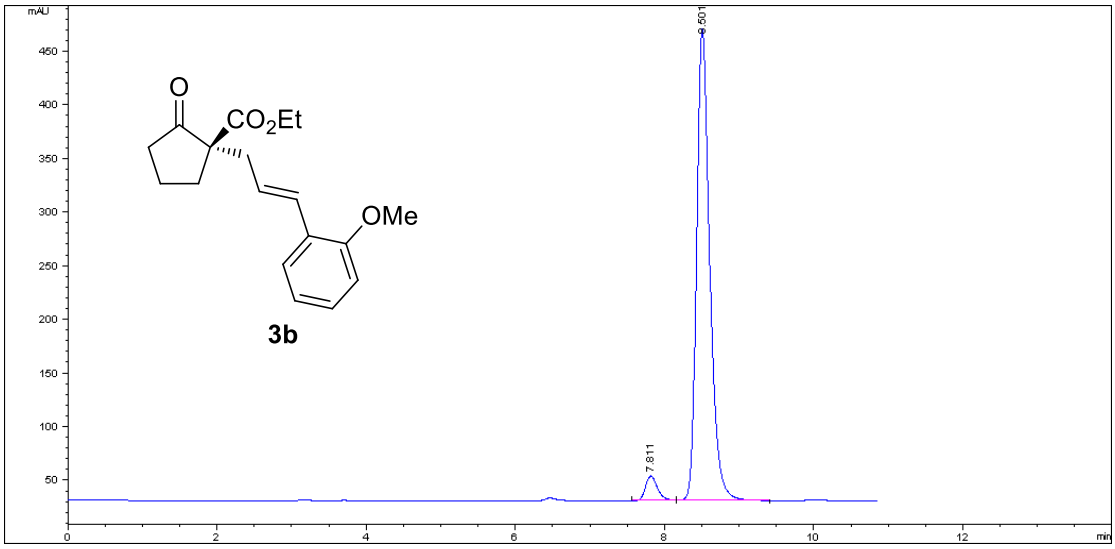
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.362	1970.3	70.5	0.4278	0.757	49.999
2	15.305	1970.3	54.2	0.561	0.817	50.001



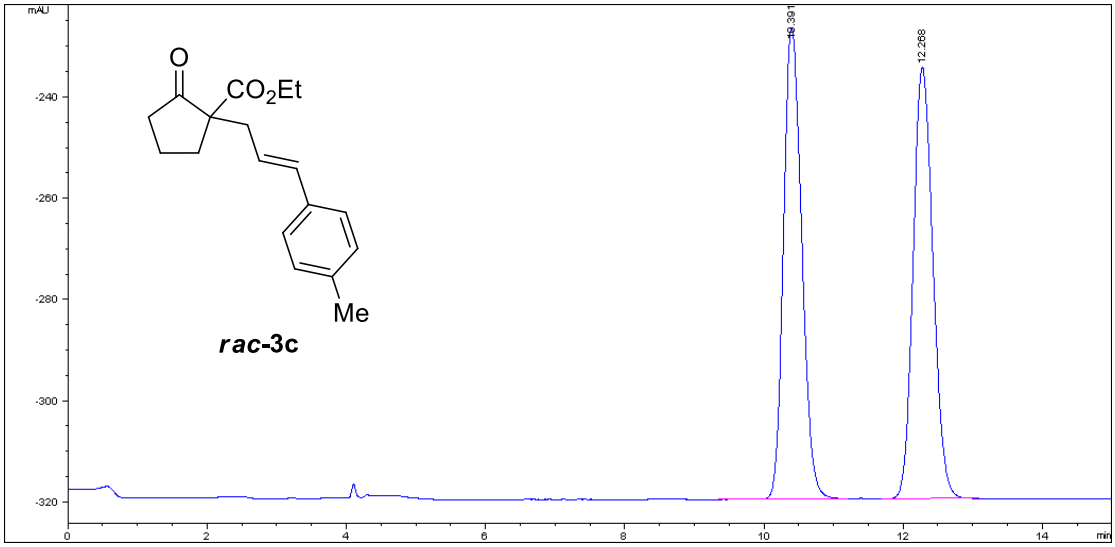
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.14	3694	134.7	0.422	0.739	98.571
2	15.034	53.6	1.6	0.5454	0.938	1.429



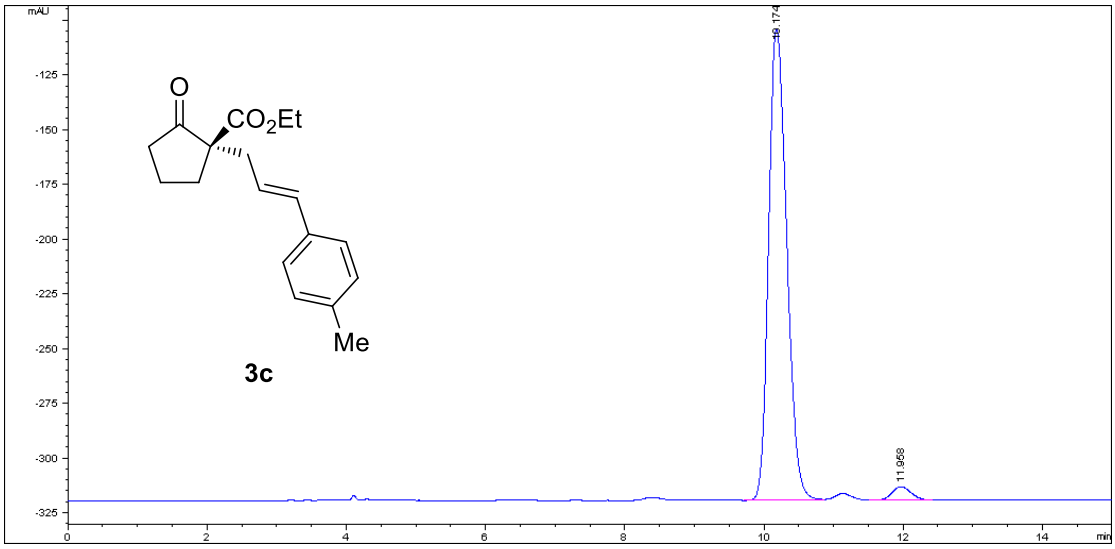
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	7.82	4801.9	416.8	0.1752	0.695	49.838
2	8.521	4833.2	389.9	0.1883	0.705	50.162



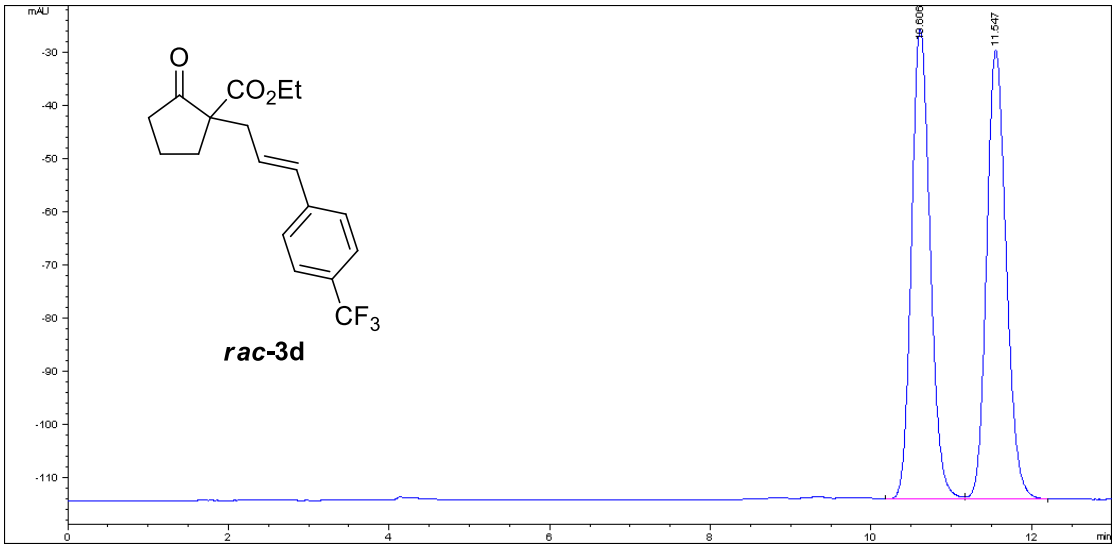
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	7.811	259.8	23.1	0.172	0.736	4.589
2	8.501	5400.6	439.9	0.1869	0.705	95.411



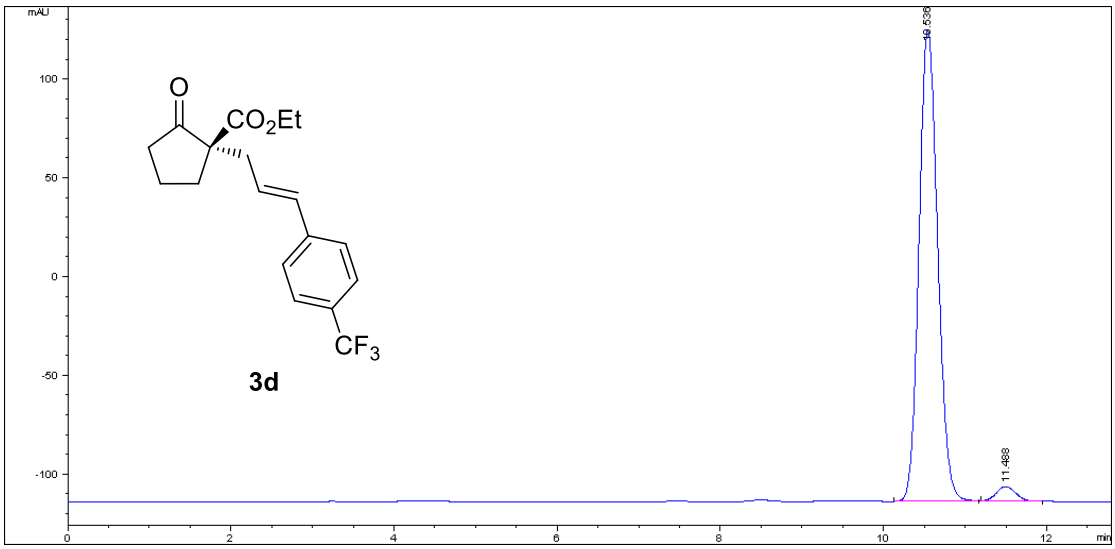
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.391	1699.7	93	0.2888	0.766	50.176
2	12.268	1687.8	85.2	0.3097	0.819	49.824



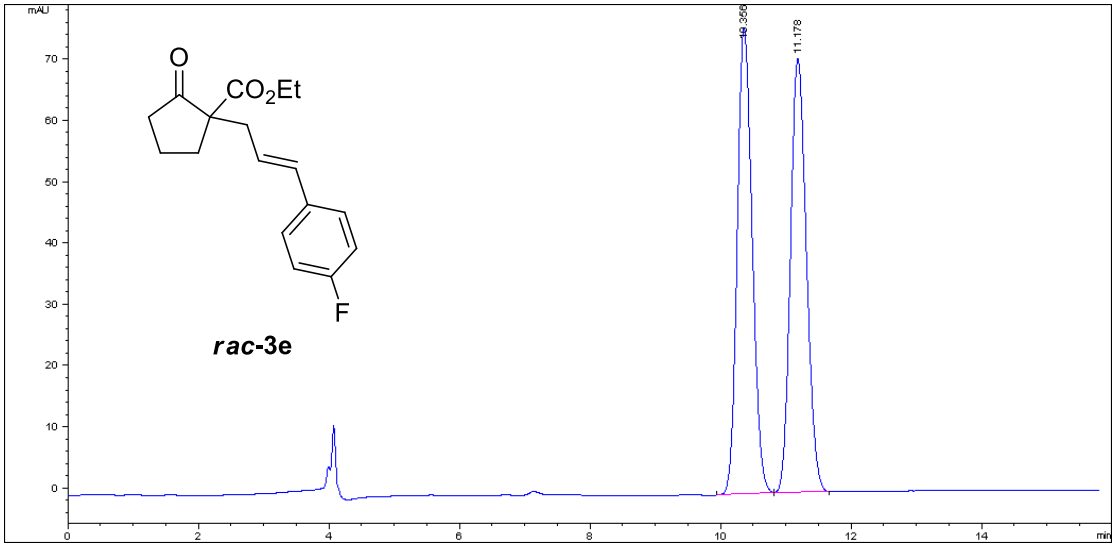
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.174	3895.8	215.3	0.2839	0.733	96.984
2	11.958	121.1	6.2	0.307	0.849	3.016



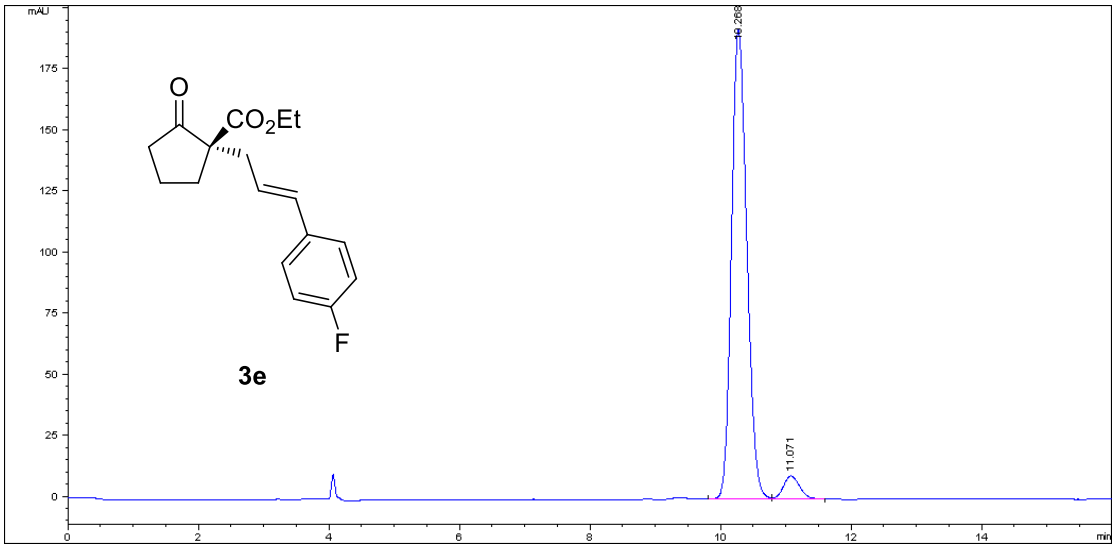
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.606	1432.6	88.4	0.2516	0.827	50.010
2	11.547	1432	84.4	0.2649	0.821	49.990



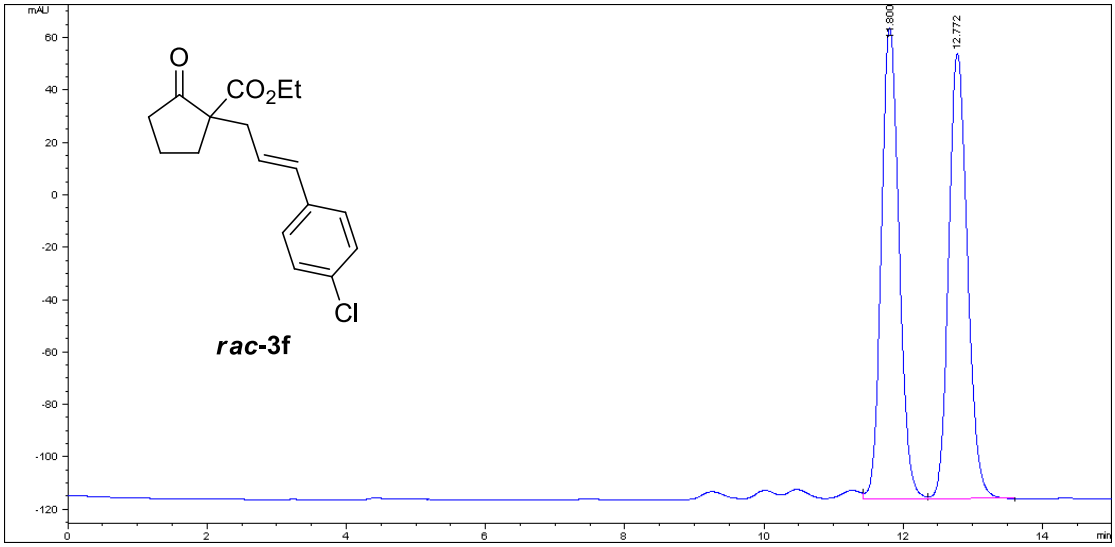
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.536	3799.6	238.7	0.2498	0.835	96.766
2	11.488	127	7.5	0.2631	0.897	3.234



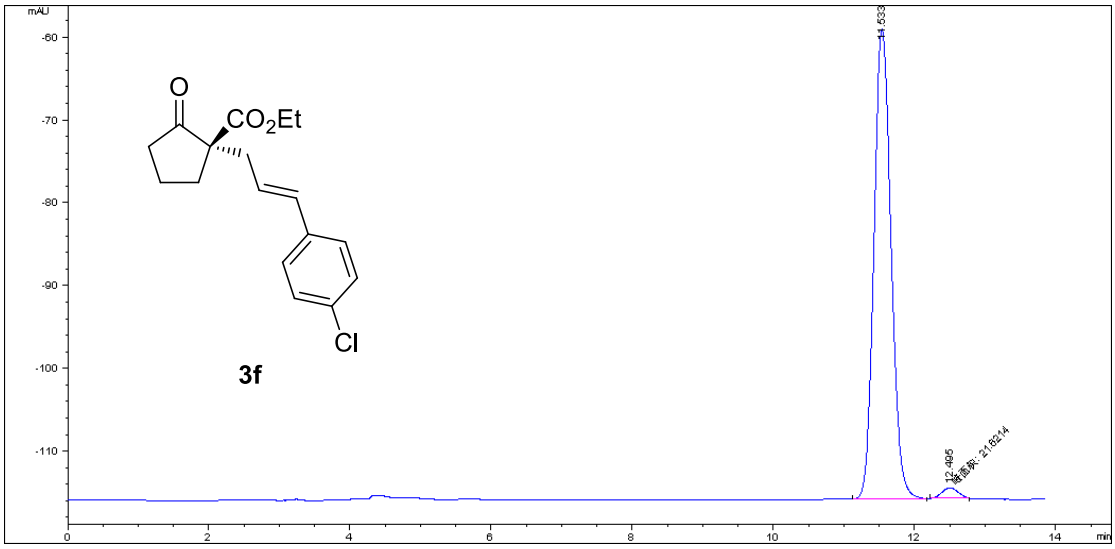
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.356	1213.8	76.1	0.2487	0.807	50.175
2	11.178	1205.3	70.9	0.2654	0.809	49.825



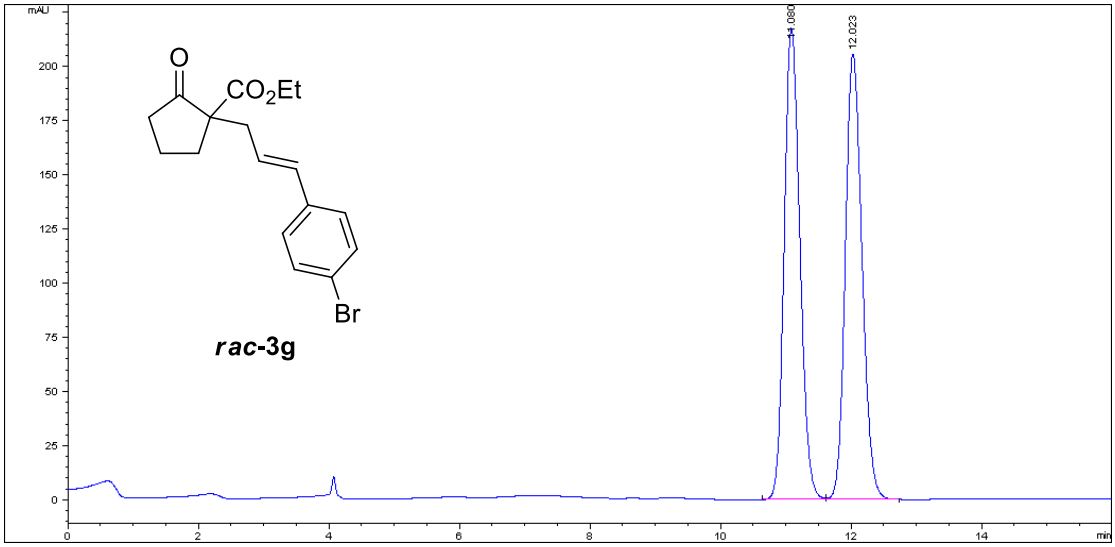
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.268	3142.8	192.5	0.256	0.782	94.964
2	11.071	166.7	9.6	0.2702	0.806	5.036



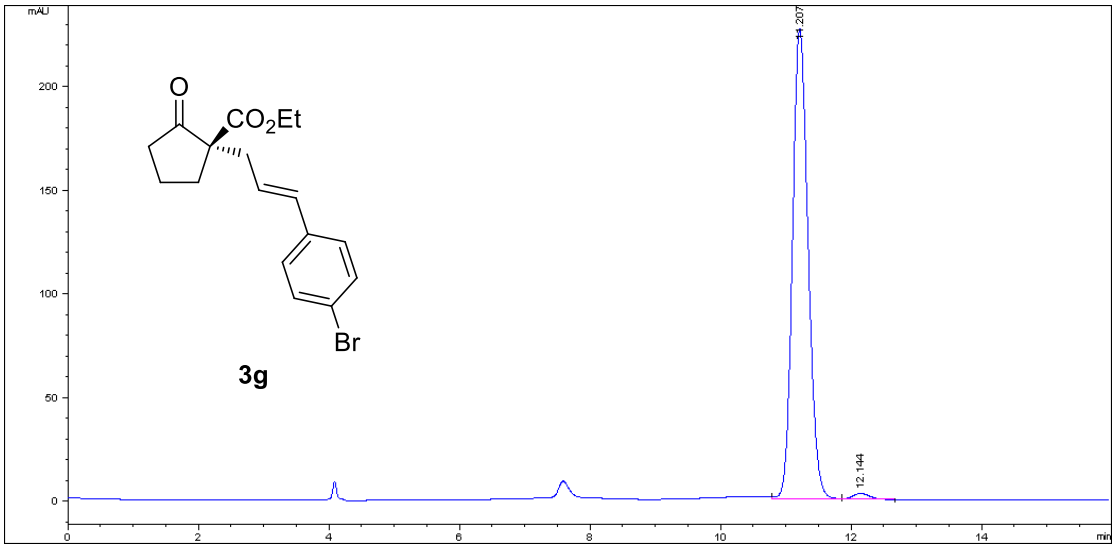
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.8	3198.6	179.7	0.279	0.848	50.039
2	12.772	3193.6	169.9	0.2921	0.815	49.961



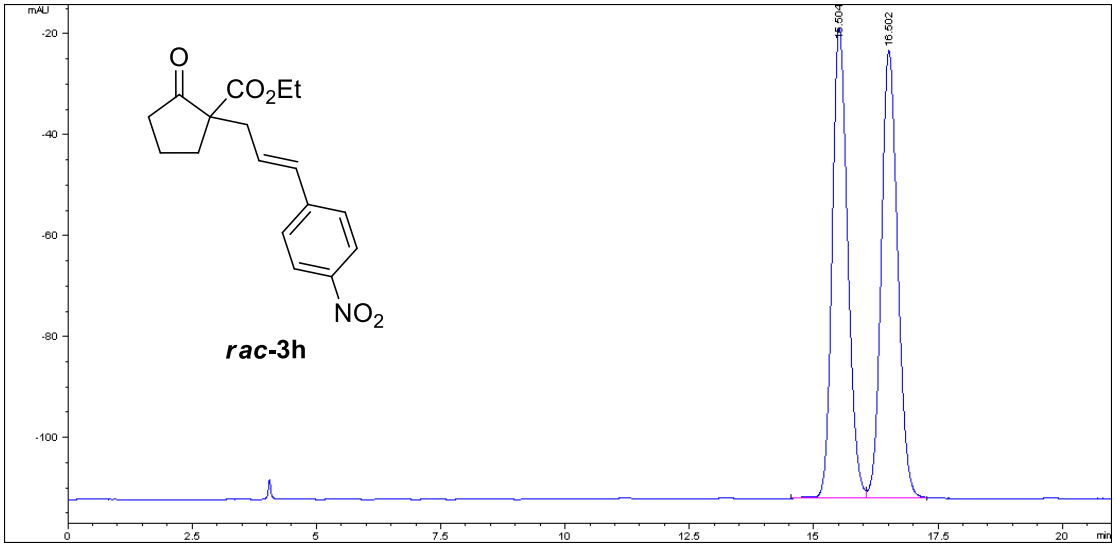
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.533	955.8	56.8	0.2619	0.844	97.788
2	12.495	21.6	1.3	0.281	0.945	2.212



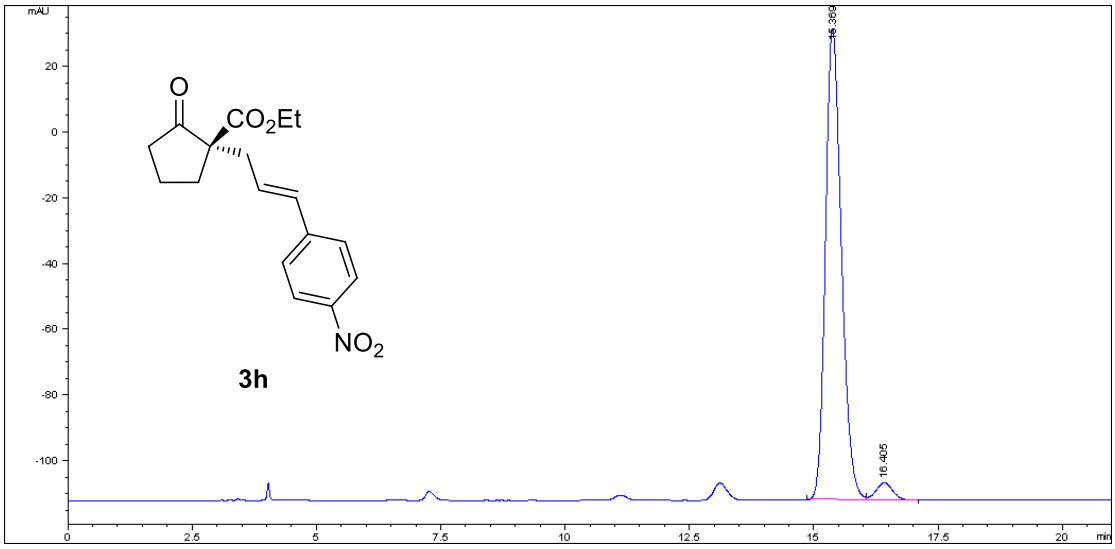
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.08	3630.7	217.6	0.2587	0.803	49.888
2	12.023	3647	205.6	0.2754	0.799	50.122



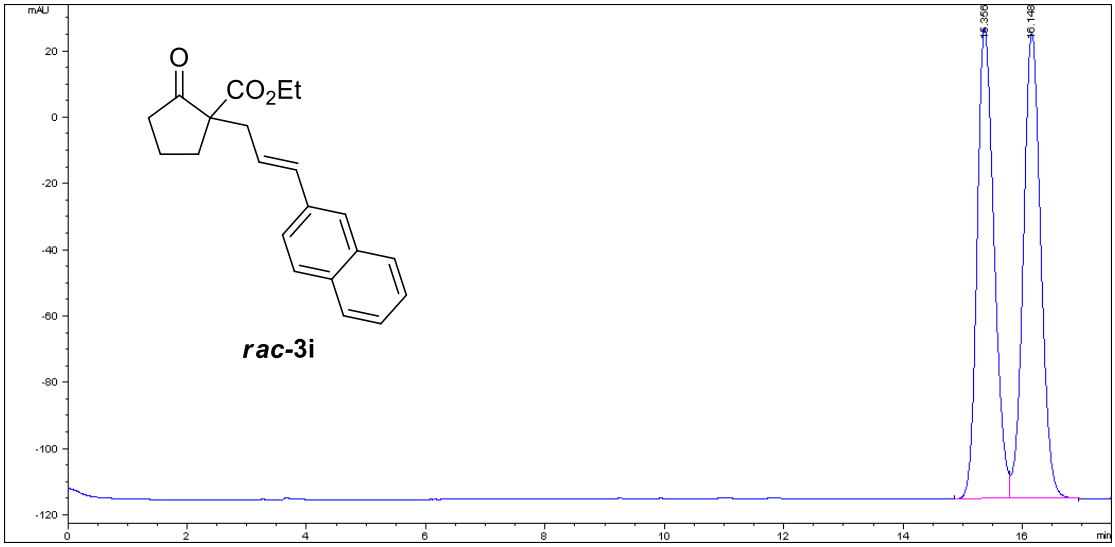
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.207	3792.9	226.9	0.2605	0.812	98.559
2	12.144	55.4	3	0.2815	0.876	1.441



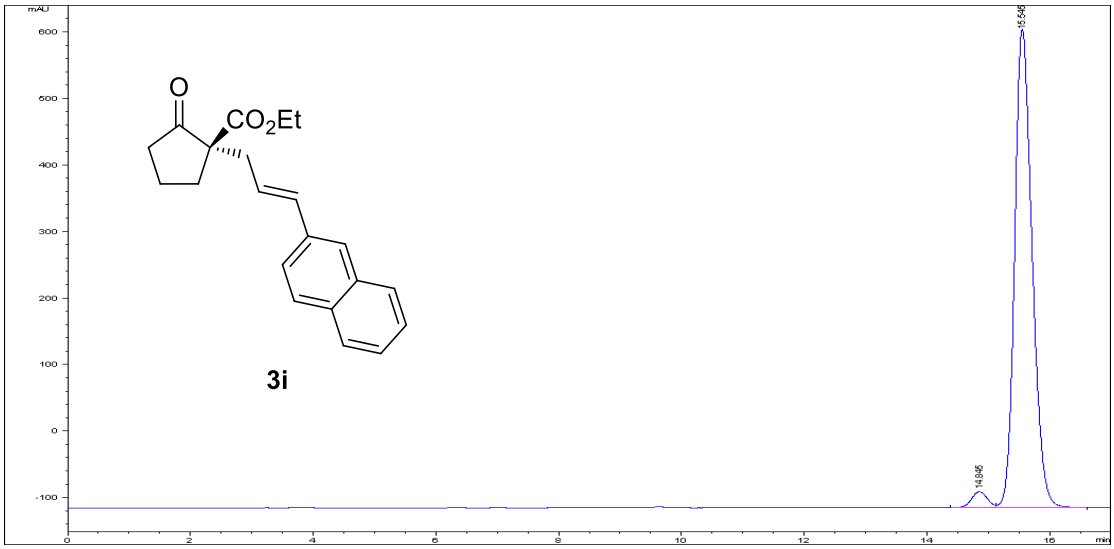
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.504	2024	93.2	0.3363	0.795	49.946
2	16.502	2028.4	88.7	0.3557	0.827	50.054



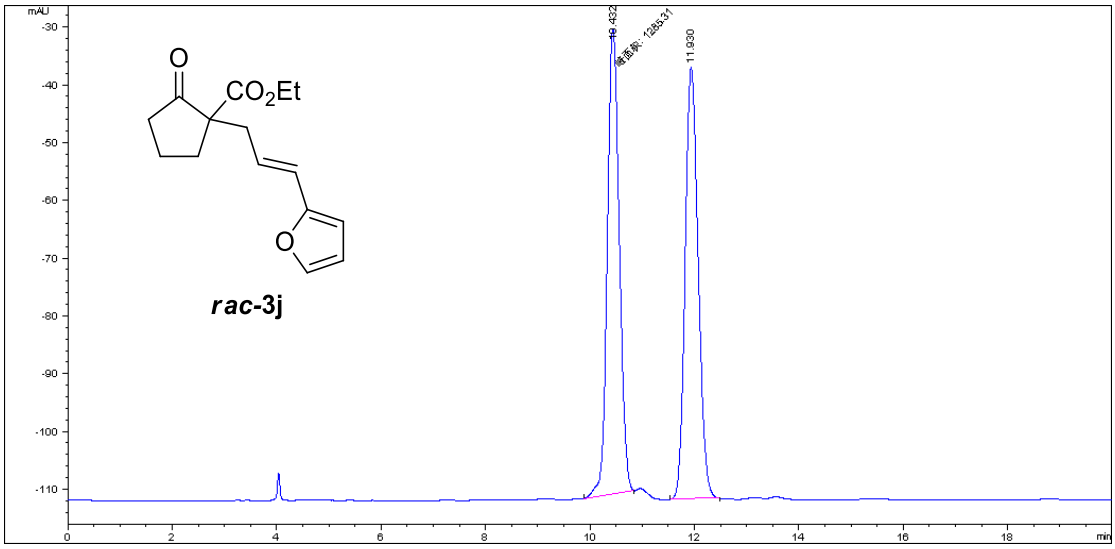
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.369	3195.5	143.2	0.3418	0.749	96.308
2	16.405	122.5	5.3	0.3609	0.922	3.692



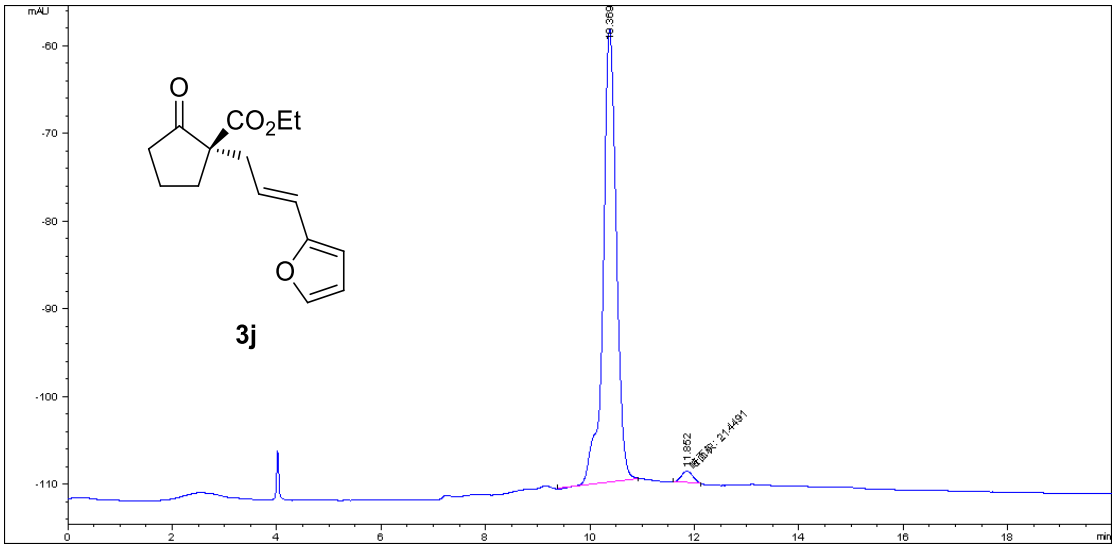
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	15.356	2809.9	142.1	0.3065	0.741	49.606
2	16.148	2854.6	140.6	0.3126	0.892	50.394



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.845	430.4	24.1	0.277	0.947	2.946
2	15.545	14177.8	719.4	0.3028	0.728	97.064

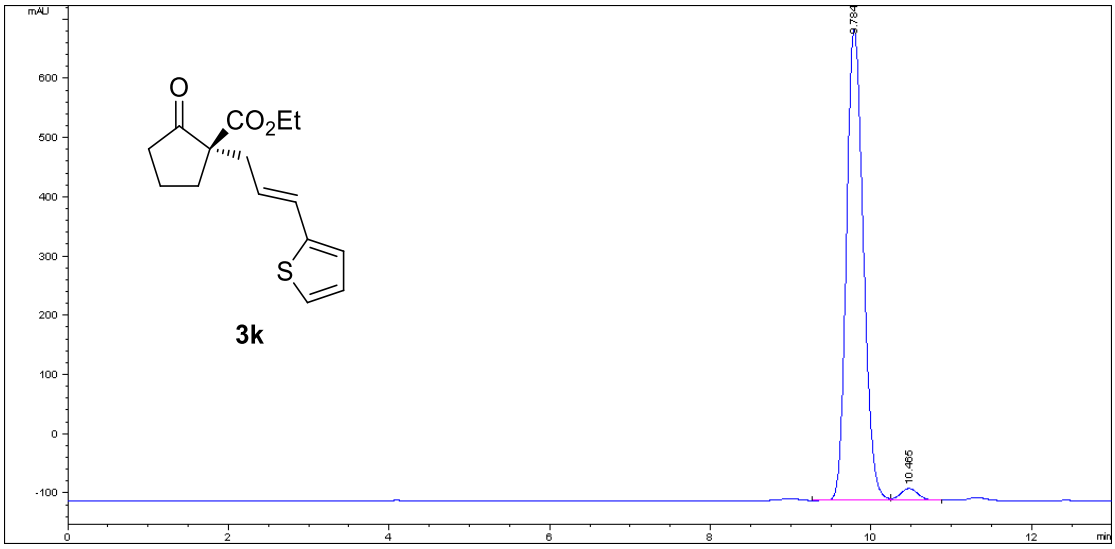


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.432	1285.3	80.6	0.2659	0.856	49.802
2	11.93	1295.5	74.7	0.2709	0.815	50.198

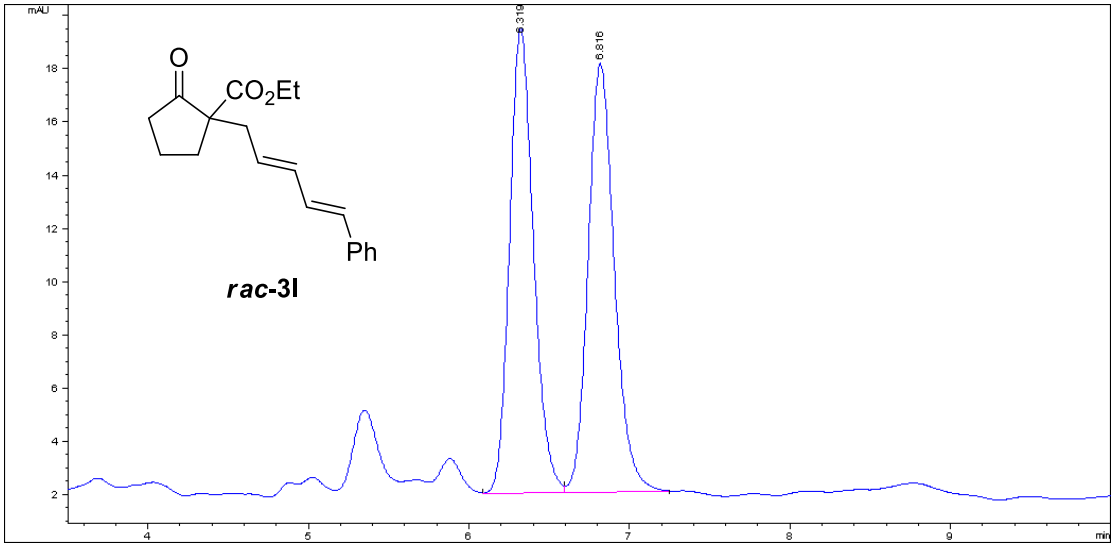


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.369	913.9	51.7	0.2672	0.971	97.707
2	11.852	21.4	1.3	0.2661	0.898	2.293

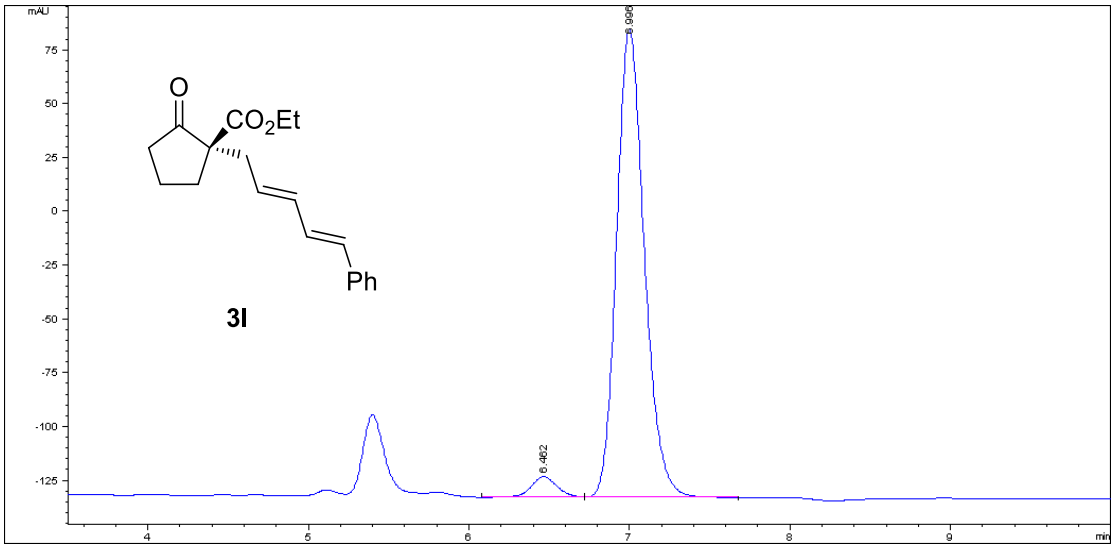
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.751	1167.5	81.5	0.2223	0.846	50.042
2	10.417	1165.5	78.2	0.232	0.837	49.958



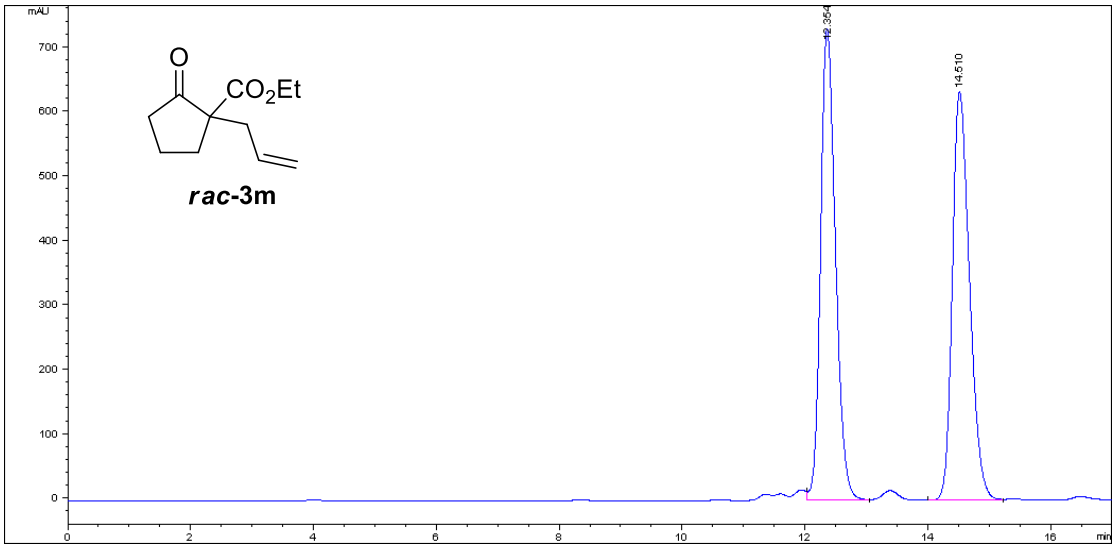
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.784	1166.7	796.3	0.2292	0.796	97.303
2	10.465	323.4	20.4	0.2445	0.868	2.697



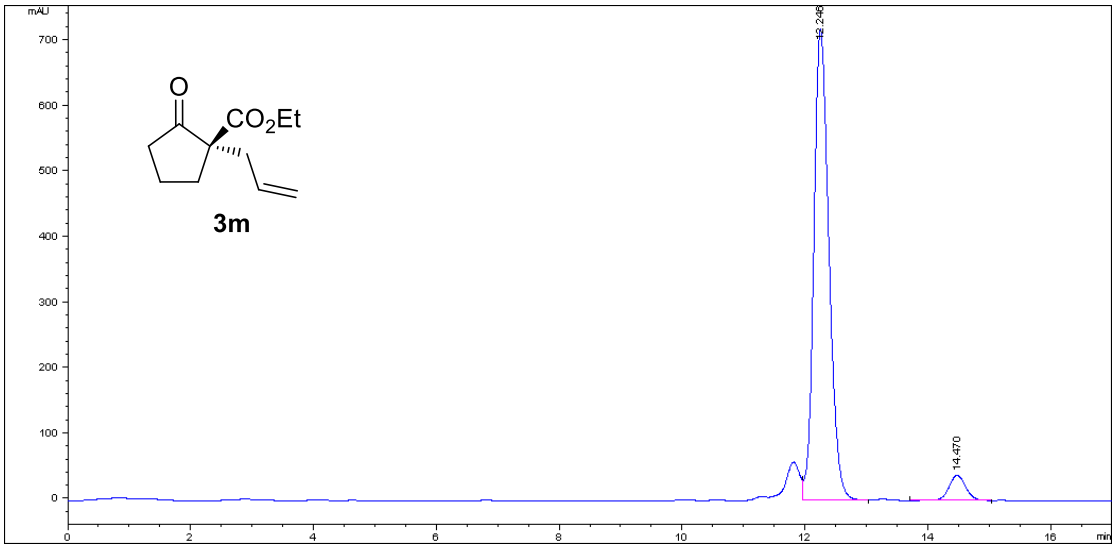
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.319	182.3	17.5	0.1607	0.818	49.660
2	6.816	184.8	16.2	0.1756	0.818	50.340



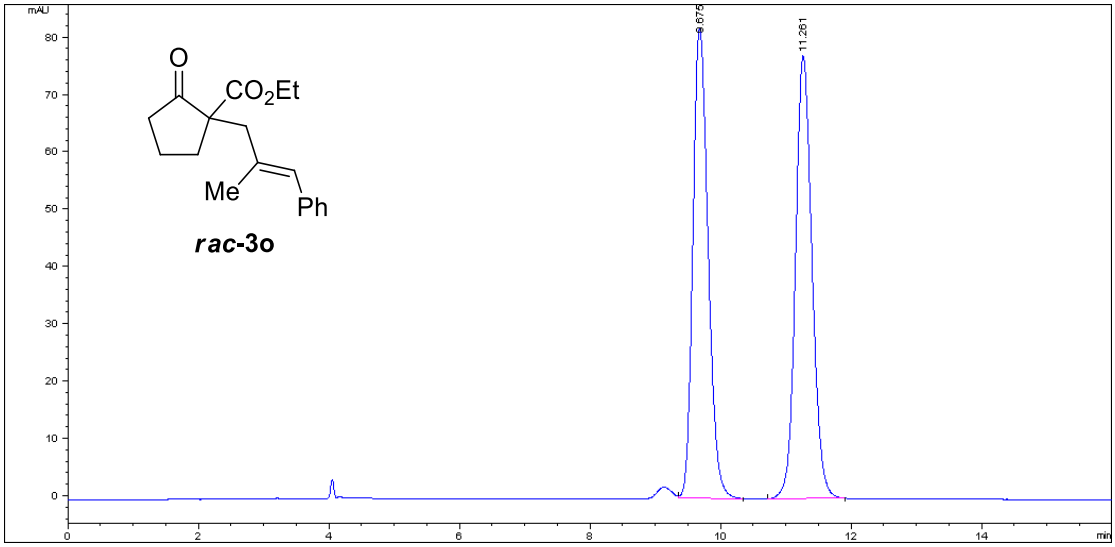
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.462	110.3	9.7	0.1741	0.912	4.039
2	6.996	2620.5	217.8	0.1841	0.798	95.961



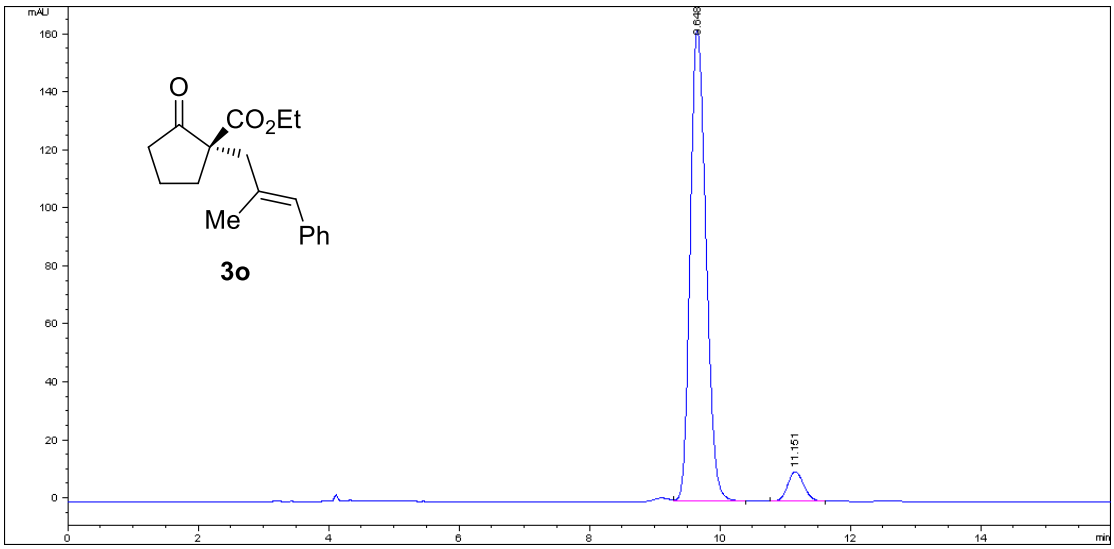
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.354	12360.0	731.3	0.2598	0.735	50.059
2	14.51	12331.7	633.7	0.2998	0.685	49.941



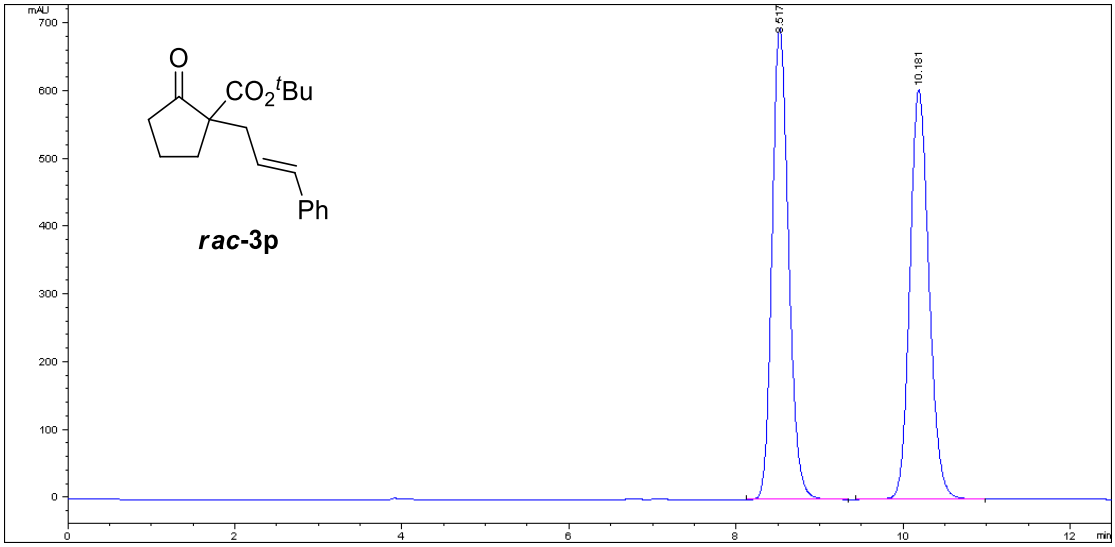
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.246	12264.8	719.7	0.2629	0.742	94.405
2	14.47	726.9	38.3	0.2944	0.942	5.595



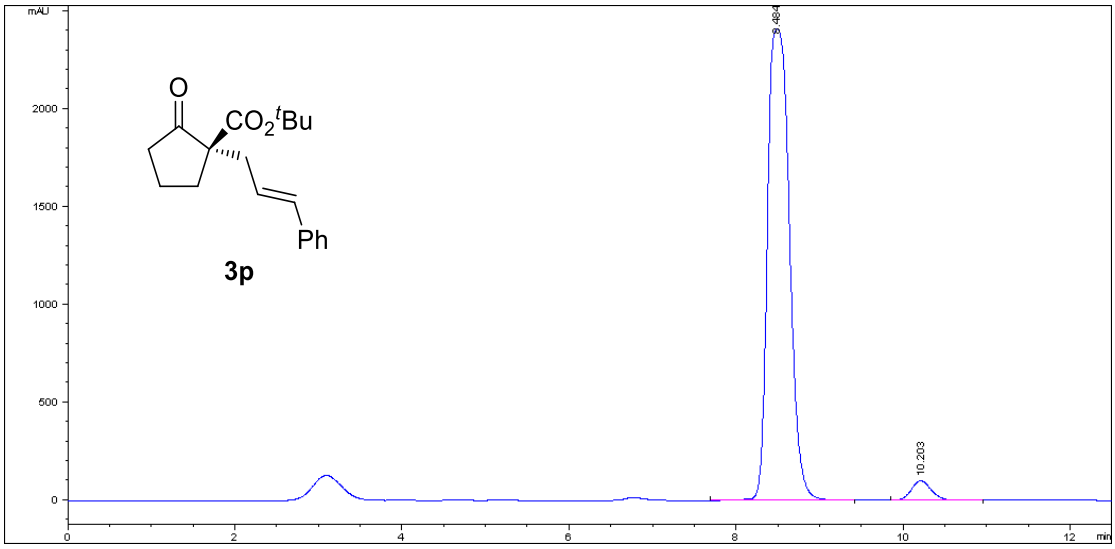
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.675	1333.2	82.1	0.2535	0.758	49.442
2	11.261	1363.3	77.2	0.2729	0.839	50.558



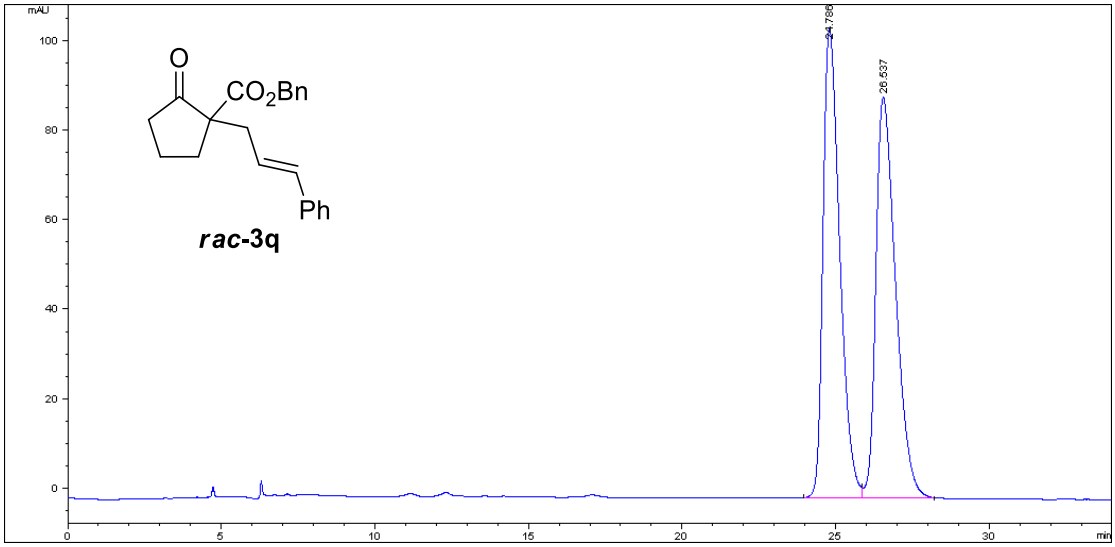
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.648	2740	162.6	0.2665	0.767	93.971
2	11.151	175.8	10.2	0.2692	0.862	6.029



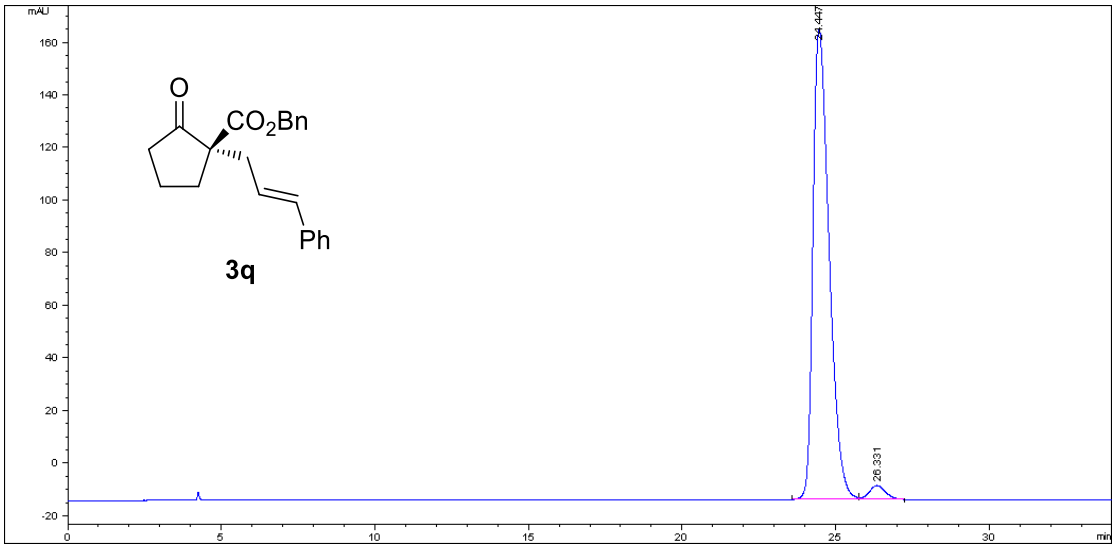
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	8.517	9561.5	695.9	0.2113	0.799	49.811
2	10.181	9634.2	603.9	0.2473	0.83	50.189



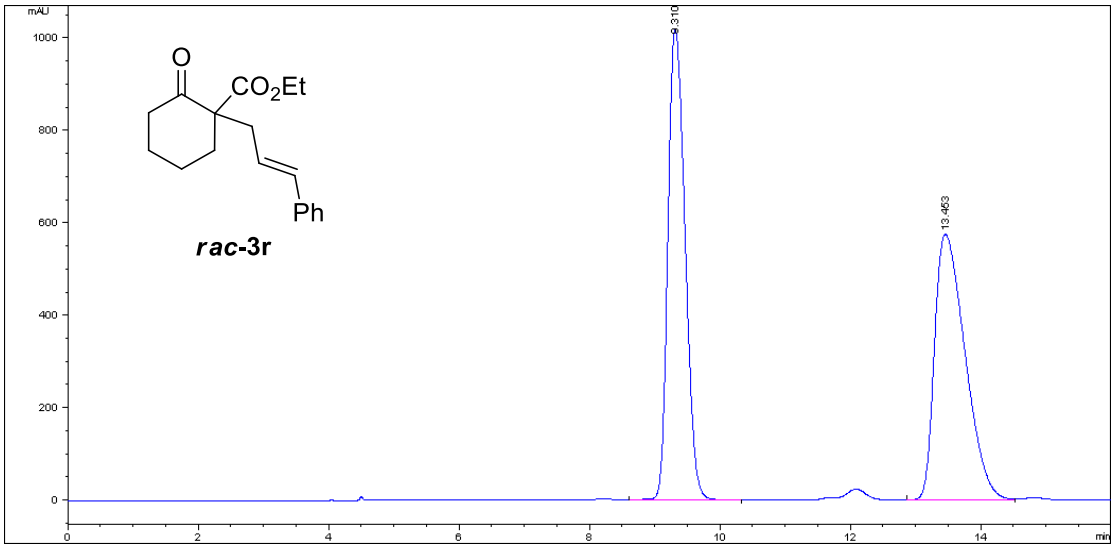
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	8.484	43769.1	2410.6	0.289	0.721	96.122
2	10.203	1765.7	101.7	0.2652	0.796	3.878



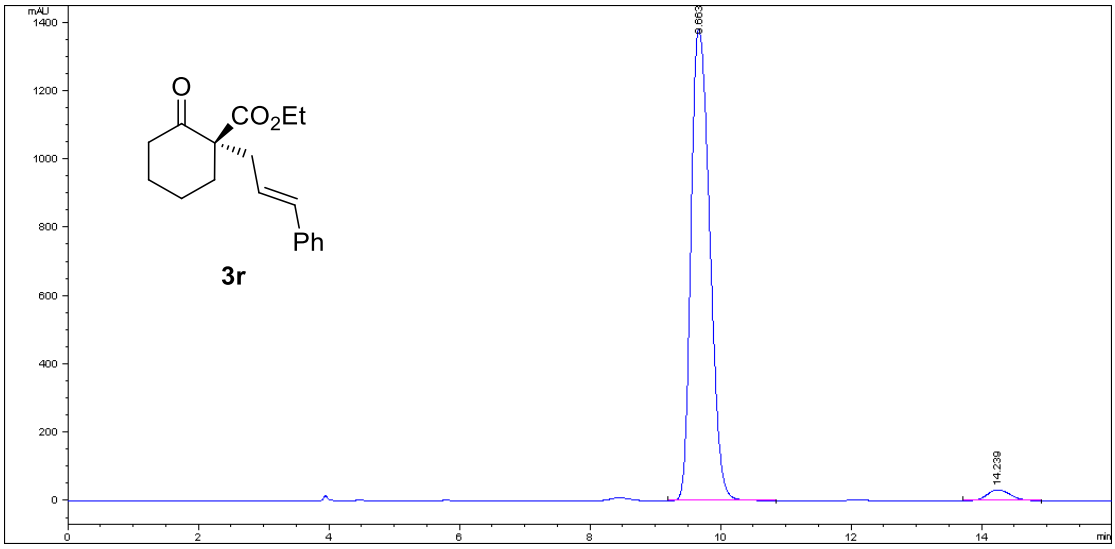
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	24.786	3984.7	105	0.8524	0.591	49.887
2	26.537	4002.7	89.5	0.6831	0.565	50.113



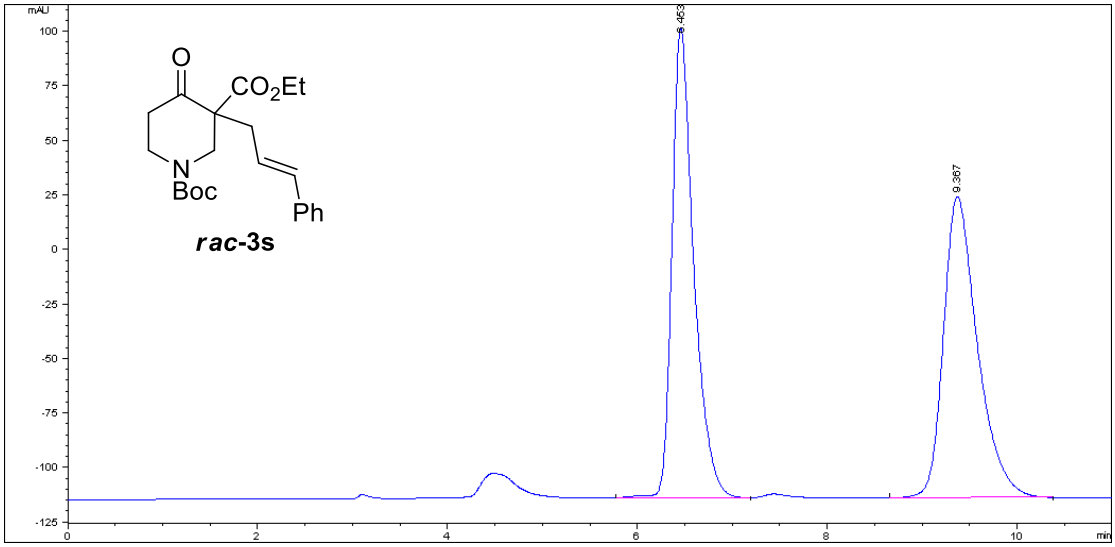
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	24.447	6547.1	178.9	0.562	0.573	97.016
2	26.331	201.2	5.4	0.5494	0.866	2.984



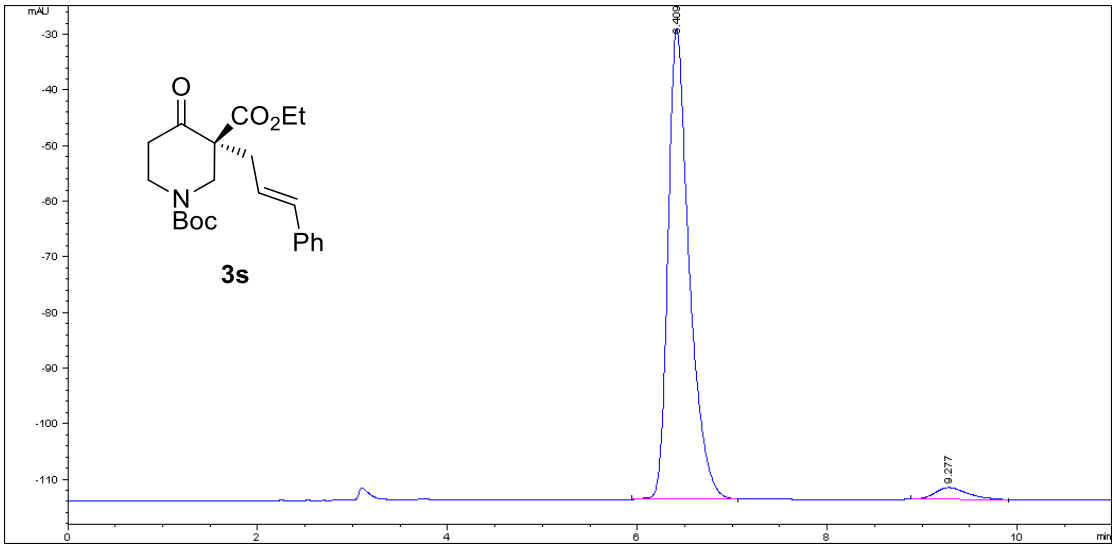
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.31	18634	1019.2	0.2934	0.706	49.847
2	13.453	18748.5	575.5	0.514	0.518	50.153



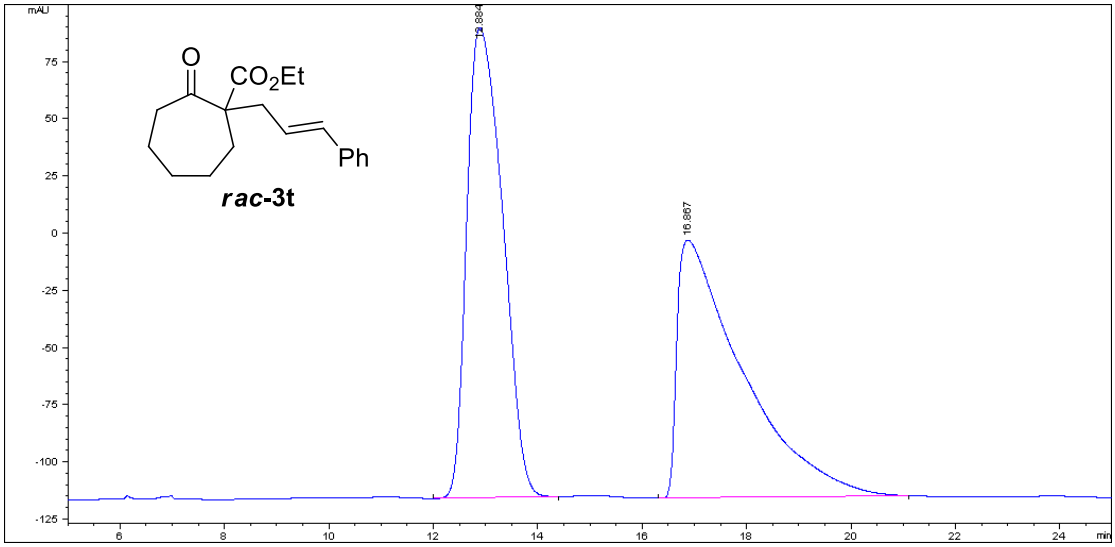
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.663	27505.3	1380.6	0.3213	0.692	97.202
2	14.239	791.6	31.7	0.3889	0.791	2.798



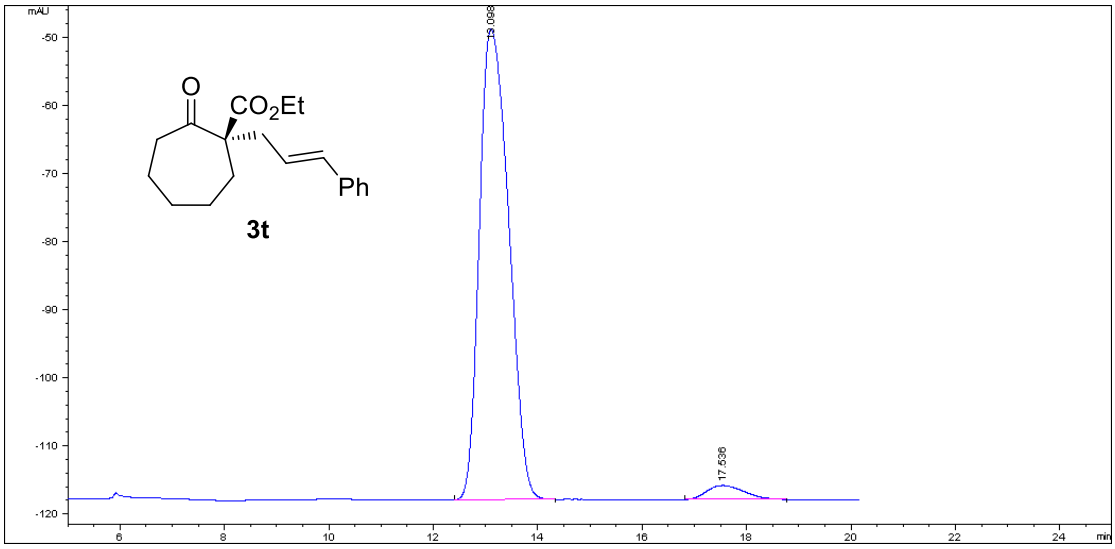
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.453	3432.6	215.4	0.2369	0.635	49.976
2	9.367	3435.9	138	0.3721	0.654	50.024



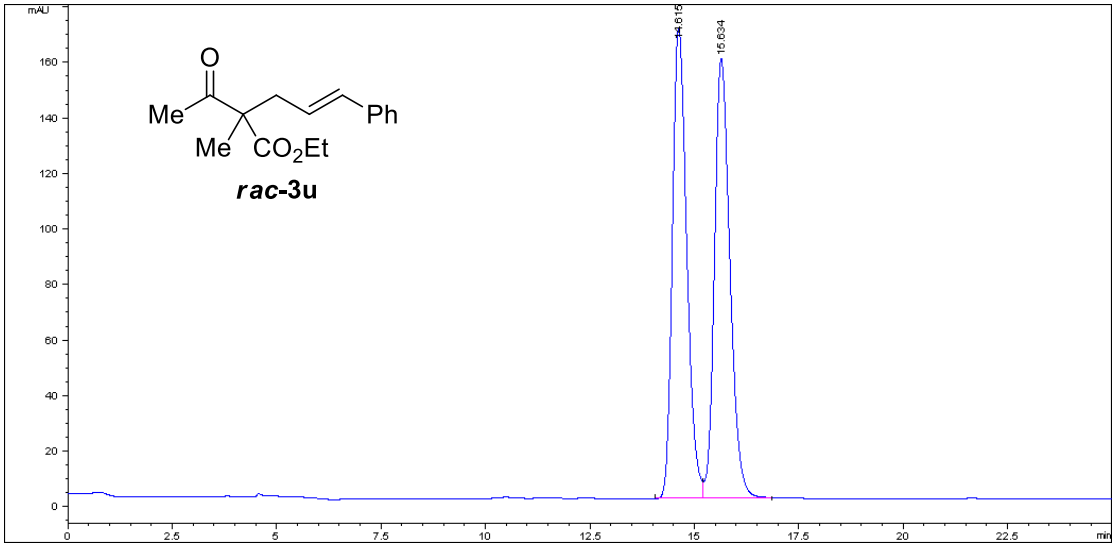
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.409	1313.5	84.6	0.2306	0.638	96.082
2	9.277	53.6	2.2	0.3583	0.714	3.918



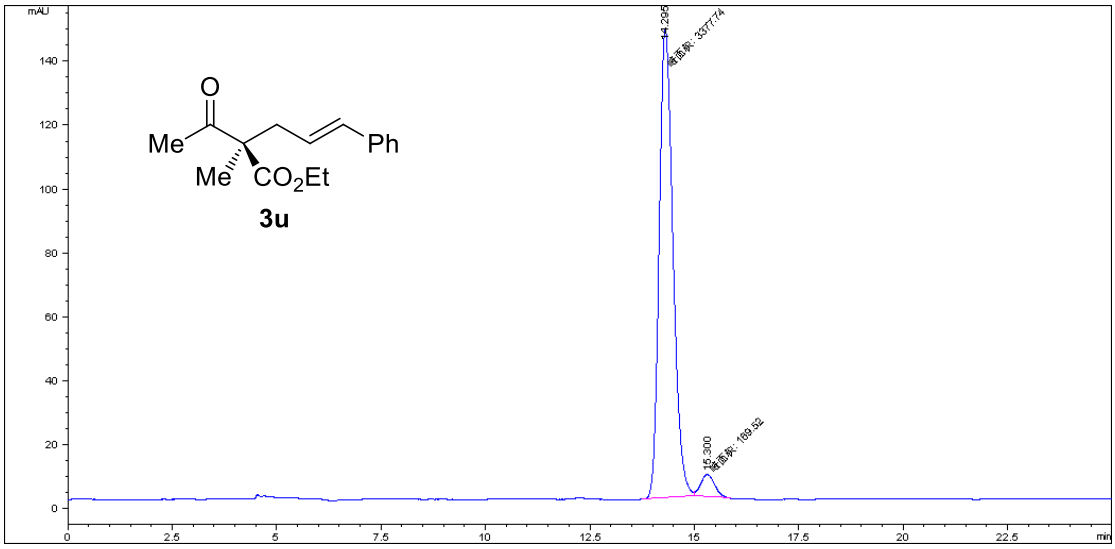
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.884	9800.7	205.4	0.8026	0.557	49.971
2	16.867	9812.2	112.7	1.1903	0.177	50.029



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.098	2696.5	69.2	0.6397	0.641	96.194
2	17.536	106.7	2.1	0.6174	0.718	3.806



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.615	4056.3	169.4	0.371	0.734	49.825
2	15.634	4084.9	158.3	0.3972	0.732	50.175



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.295	3377.7	146.7	0.3837	0.757	95.221
2	15.3	169.5	7.2	0.3949	0.859	4.779