

Supporting Information

Copper(I)-catalyzed enantioselective hydroboration of cyclopropenes: facile synthesis of optically active cyclopropylboronates

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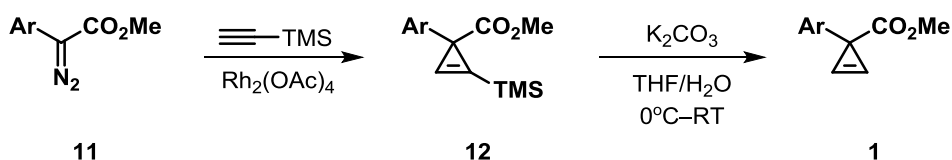
1. GENERAL INFORMATION

All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. The ^1H and ^{13}C NMR spectra were recorded on Bruker AV-400 MHz in the indicated solvents. Chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for ^1H NMR and CDCl_3 ($\delta = 77.10$ ppm) for ^{13}C NMR. Coupling constants (J) are quoted in Hz. Optical rotations were measured on a JASCO P-1030 polarimeter. IR spectra were recorded on Nicolet iN 10 MX. ESI mass spectra were recorded on Agilent1200/G6100A. HRMS of boron-containing compounds is based on ^{10}B .

2. SUBSTRATE PREPARATION

Cyclopropene **1o** was prepared according to the literature procedure.^[1]

General procedures for the preparation of other cyclopropenes substrates^[2–3]

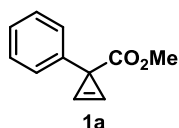


Starting material, methyl diazoarylacrylate **11** was prepared according to the literature procedure^[3].

A solution of methyl diazoarylacrylate (**11**, 7 mmol, 1.0 equiv) in trimethylsilylacetylene (10 mL) was added via syringe pump over 16 h to a stirred mixture of Rh₂(OAc)₄ (1 mol%) in trimethylsilylacetylene (5 mL). After the addition was complete, the reaction mixture was stirred at room temperature for additional 12 h. Then the trimethylsilylacetylene was removed under reduced pressure to give the crude product **12**.

Crude material **12** was dissolved in THF (15 mL) and stirred at 0 °C. 10% aqueous K₂CO₃ (10 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 5 h, when the reaction completed. Ethyl acetate (20 mL) and water (20 mL) were added to the mixture, aqueous phase was separated, and the water layer was extracted with ethyl acetate (50 mL × 3), the combined organic phase was washed by brine (100 mL), dried (MgSO₄), filtered, and evaporated. The residue was purified by silica gel column chromatography (eluent: *n*-hexane / EtOAc = 15:1) to give pure cyclopropene products **1**.

Methyl 1-phenylcycloprop-2-enecarboxylate (**1a**)^[3]



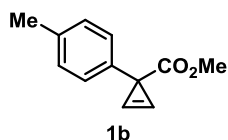
Light yellow oil, 640 mg, 52% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.33–7.24 (m, 5H), 7.22 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 175.52, 141.44, 128.16, 128.13, 126.59, 107.68 (2C), 52.25, 30.58 ESI-MS: $[\text{M}+\text{Na}]^+$ 197.1; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_{10}\text{O}_2\text{Na}^+$ 197.0573, found 197.0565; IR (KBr) ν (cm^{-1}) 3155, 3113, 3058, 3025, 2951, 1724, 1662, 1601, 1495, 1435, 1228, 1113, 1021, 1009, 998, 892, 791, 762, 738, 699.

[1] D. H. T. Phan, K. G. M. Kou and V. M. Dong, *J. Am. Chem. Soc.*, 2010, **132**, 16354.

[2] H. M. L. Davies, T. Hansen and M. R. Churchill, *J. Am. Chem. Soc.*, 2000, **122**, 3063.

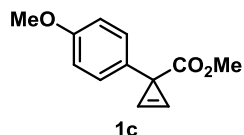
[3] M. Rubina, M. Rubin and V. Gevorgyan, *J. Am. Chem. Soc.*, 2003, **125**, 7198.

Methyl 1-*p*-tolylcycloprop-2-enecarboxylate (1b)



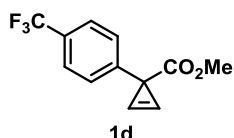
Light yellow oil, 315 mg, 24% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.20(s, 2H), 7.17–7.10 (m, 4H), 3.69 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 175.71, 138.50, 136.22, 128.86, 128.03, 107.84 (2C), 52.24, 30.28, 21.05; ESI-MS: $[\text{M}+\text{Na}]^+$ 211.1; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2\text{Na}^+$ 211.0730, found 211.0734; IR (KBr) ν (cm^{-1}) 3128, 3088, 3053, 3001, 2948, 2925, 2840, 1710, 1651, 1515, 1434, 1292, 1219, 1033, 1019, 1003, 899, 863, 812, 741, 638, 547.

Methyl 1-(4-methoxyphenyl)cycloprop-2-enecarboxylate (1c)



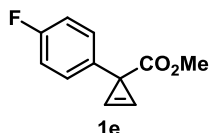
Yellow oil, 250 mg, 18% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.21 (s, 2H), 7.18 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 175.81, 158.25, 133.66, 129.23, 113.57, 107.92 (2C), 55.23, 52.25, 29.92; ESI-MS: $[\text{M}+\text{Na}]^+$ 227.1; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3\text{Na}^+$ 227.0679, found 227.0677; IR (KBr) ν (cm^{-1}) 3151, 3109, 3005, 2958, 2840, 1713, 1663, 1611, 1516, 1442, 1436, 1250, 1223, 1119, 926, 829, 806, 771, 626, 550.

Methyl 1-(4-(trifluoromethyl)phenyl)cycloprop-2-enecarboxylate (1d)



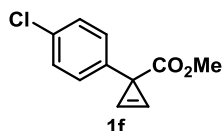
Yellow oil, 863 mg, 51% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.56 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.21(s, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.79, 145.41, 129.02, 128.90, 125.15 (q, J_{CF} = 3.8 Hz), 122.95, 107.24 (2C), 52.47, 30.42; ESI-MS: $[\text{M}+\text{H}]^+$ 243.0; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_9\text{F}_3\text{O}_2\text{Na}^+$ 265.0447, found 265.0447; IR (KBr) ν (cm^{-1}) 3120, 2955, 1727, 1666, 1618, 1436, 1409, 1327, 1292, 1225, 1165, 1120, 1069, 1014, 872, 833, 796, 767, 606.

Methyl 1-(4-fluorophenyl)cycloprop-2-enecarboxylate (1e)

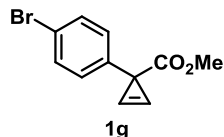


Yellow oil, 445 mg, 34% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.26–7.20 (m, 2H), 7.20 (s, 2H), 7.00–6.95 (m, 2H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 175.32, 161.55 (d, J_{CF} = 243.7 Hz), 137.23 (d, J_{CF} = 3.8 Hz), 129.80 (d, J_{CF} = 8.3 Hz, 2C), 114.92 (d, J_{CF} = 20.5 Hz, 2C), 107.67 (2C), 52.30, 29.89; ESI-MS: $[\text{M}+\text{Na}]^+$ 215.1; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_9\text{FO}_2\text{Na}^+$ 215.0479, found 215.0488; IR (KBr) ν (cm^{-1}) 3433, 3158, 3117, 2999, 2953, 2844, 1724, 1660, 1604, 1510, 1435, 1293, 1224, 1030, 1006, 870, 832, 625, 544.

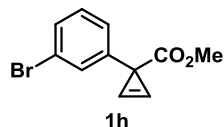
Methyl 1-(4-chlorophenyl)cycloprop-2-enecarboxylate (1f)



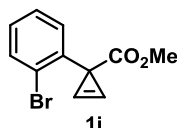
Light yellow oil, 728 mg, 50% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.27 (d, J = 8.0 Hz, 2H), 7.22–7.19 (m, 4H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 175.05, 139.96, 132.37, 129.61, 128.22, 107.42 (2C), 52.32, 29.98; ESI-MS: $[\text{M}+\text{H}]^+$ 209.1; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_9\text{ClO}_2\text{Na}^+$ 231.0183, found 231.0186; IR (KBr) ν (cm^{-1}) 3432, 3153, 3114, 2959, 2849, 1725, 1686, 1657, 1488, 1436, 1280, 1236, 1086, 1005, 996, 875, 789, 748, 614, 548, 464.

Methyl 1-(4-bromophenyl)cycloprop-2-enecarboxylate (1g)

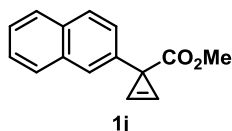
Light yellow oil, 243 mg, 35% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.42 (d, $J = 8.4$ Hz, 2H), 7.19 (s, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.98, 140.49, 131.16, 129.99, 120.50, 107.36 (2C), 52.33, 30.05; ESI-MS: $[\text{M}+\text{Na}]^+$ 274.9; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_9\text{BrO}_2\text{Na}^+$ 274.9678, found 274.9687; IR (KBr) ν (cm^{-1}) 3152, 3114, 3043, 3025, 2956, 1725, 1656, 1483, 1436, 1412, 1280, 1237, 1069, 1030, 1005, 897, 876, 788, 746, 718, 612.

Methyl 1-(3-bromophenyl)cycloprop-2-enecarboxylate (1h)

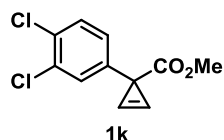
Light yellow oil, 413 mg, 24% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.40 (s, 1H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.23–7.14 (m, 4H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.80, 143.80, 131.33, 129.68, 129.65, 126.95, 122.16, 107.32 (2C), 52.36, 30.17; ESI-MS: $[\text{M}+\text{H}]^+$ 253.0; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_9\text{BrO}_2\text{Na}^+$ 274.9678, found 274.9671; IR (KBr) ν (cm^{-1}) 3157, 3116, 2997, 2950, 2848, 1940, 1724, 1661, 1593, 1564, 1476, 1434, 1223, 1033, 1011, 738, 711, 604.

Methyl 1-(2-bromophenyl)cycloprop-2-enecarboxylate (1i)

Light yellow oil, 552 mg, 32% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.54–7.51 (m, 1H), 7.33 (s, 2H), 7.29–7.09 (m, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 175.07, 141.71, 132.60, 130.23, 128.65, 127.63, 125.18, 108.78 (2C), 52.55, 32.31; ESI-MS: $[\text{M}+\text{Na}]^+$ 275.0; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_9\text{BrO}_2\text{Na}^+$ 274.9678, found 274.9683; IR (KBr) ν (cm^{-1}) 3430, 3139, 3097, 3065, 2950, 2838, 1731, 1651, 1589, 1466, 1432, 1285, 1225, 1051, 1023, 877, 745, 650, 562.

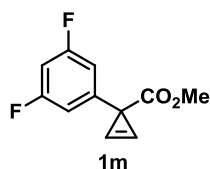
Methyl 1-(naphthalen-2-yl)cycloprop-2-enecarboxylate (1j)

Light yellow oil, 564 mg, 36% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.81–7.60 (m, 3H), 7.66 (s, 1H), 7.45–7.41 (m, 3H), 7.29 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 175.60, 139.08, 133.31, 132.28, 127.72, 127.65, 127.59, 126.73, 126.61, 125.99, 125.67, 107.89 (2C), 52.33, 30.77; ESI-MS: $[\text{M}+\text{H}]^+$ 225.1; HRMS (FTMS-ESI): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2$ 225.0910, found 225.0905; IR (KBr) ν (cm^{-1}) 3155, 3114, 3055, 3019, 1950, 1724, 1661, 1631, 1434, 1243, 1214, 1186, 1035, 1013, 818, 749, 635, 613.

Methyl 1-(3,4-dichlorophenyl)cycloprop-2-enecarboxylate (1k)

Light yellow oil, 300 mg, 20% yield for two steps. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.37–7.35 (m, 2H), 7.18 (s, 2H), 7.14–7.12 (m, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.57, 141.88, 130.43, 130.09, 127.84, 107.19 (2C), 52.52, 29.82; ESI-MS: $[\text{M}+\text{Na}]^+$ 265.0; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_8\text{Cl}_2\text{O}_2\text{Na}^+$ 264.9794, found 264.9788; IR (KBr) ν (cm^{-1}) 3429, 3160, 3119, 2951, 2848, 1726, 1663, 1471, 1435, 1292, 1252, 1223, 1135, 1031, 887, 813, 741, 616, 598, 440.

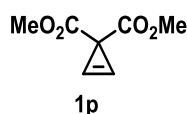
Methyl 1-(3,5-difluorophenyl)cycloprop-2-enecarboxylate (1m)



Yellow oil, 350 mg, 23% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.15 (s, 2H), 6.81 (d, $J = 7.2$ Hz, 2H), 6.60 (t, $J = 9.2$ Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.30, 164.14, 145.63, 111.36, 106.82 (2C), 102.44, 52.49, 30.19; ESI-MS: $[\text{M}+\text{H}]^+$ 211.2; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_8\text{F}_2\text{O}_2\text{Na}^+$ 233.0385, found 233.0377; IR (KBr) ν (cm^{-1}) 3716, 3219, 3084, 2957, 2484, 1724, 1625, 1594, 1469, 1430, 1253, 1150, 1120, 988, 883, 854, 745, 867, 629, 531, 515, 493.

Ethyl 1-methylcycloprop-2-enecarboxylate (1n). Preparation of this cyclopropene used the same procedure with literature.^[1]

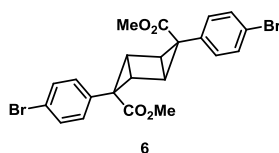
Dimethyl cycloprop-2-ene-1,1-dicarboxylate (1p).^[2]



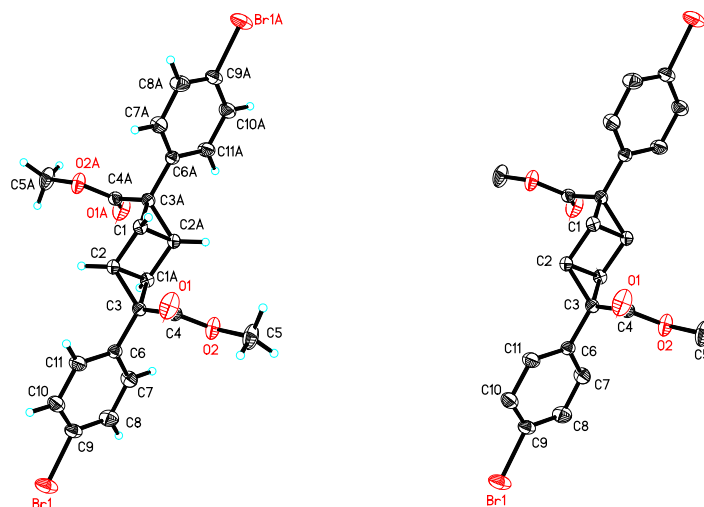
Light yellow oil, 568 mg, 52% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 6.91 (s, 2H), 3.74 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 171.33, 102.41 (2C), 52.45, 29.83; ESI-MS: $[\text{M}+\text{Na}]^+$ 179.1; HRMS (FTMS-ESI): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_7\text{H}_8\text{O}_4\text{Na}^+$ 179.0315, found 179.0312; IR (KBr) ν (cm^{-1}) 3617, 3167, 3122, 3004, 2956, 2847, 1728, 1671, 1436, 1293, 1192, 1143, 1069, 987, 950, 883, 817, 766, 720, 635, 519.

3. X-RAY CRYSTAL STRUCTURE OF 6

Preparation of the crystal: To a one-neck round-bottomed flask was added 30 mg of product **3g**, dissolved with 0.5 mL dichloromethane, added 5.0 mL *n*-hexane. Then the flask was sealed with rubber plug for two weeks to gives the crystal **6**. CCDC 1004894 (**6**) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

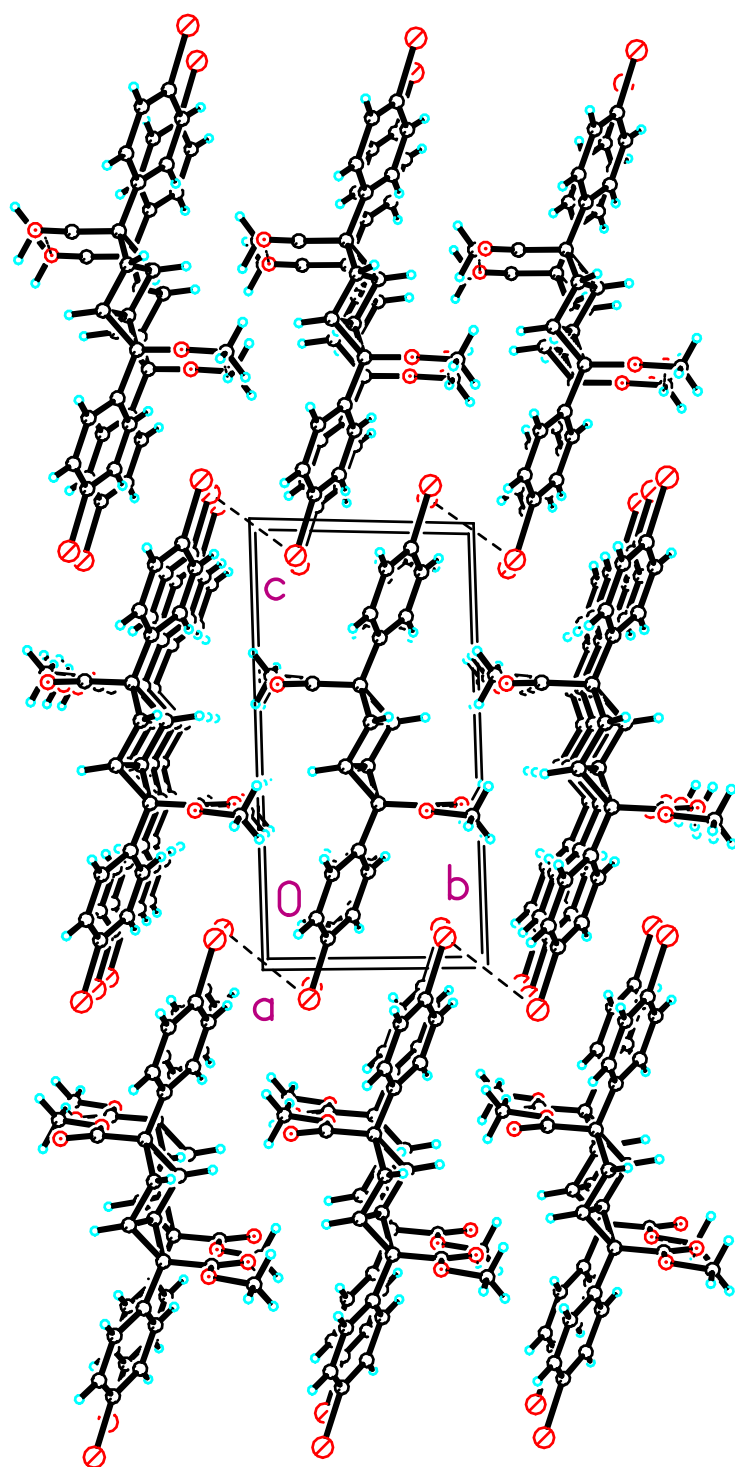


Colorless crystal, 5 mg. ^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.50–7.28 (m, 6H), 7.21–7.15 (m, 2H), 3.72 (s, 6H), 2.36 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 169.85, 132.20, 131.33, 130.18, 127.85, 122.59, 54.15, 52.55, 30.09.



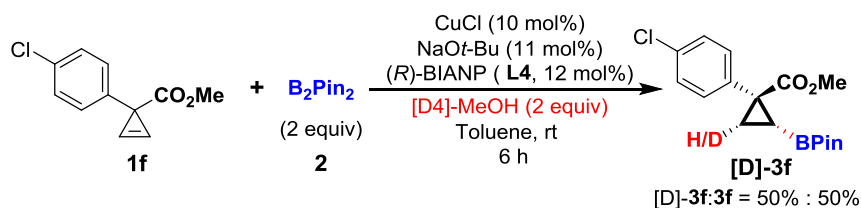
[1] Z. Yu, Y. Pan, Z. Wang, J. Wang and Q. Lin, *Angew. Chem. Int. Ed.*, 2012, **51**, 10600.

[2] M. Rubina, M. Rubin and V. Gevorgyan, *J. Am. Chem. Soc.*, 2003, **125**, 7198.

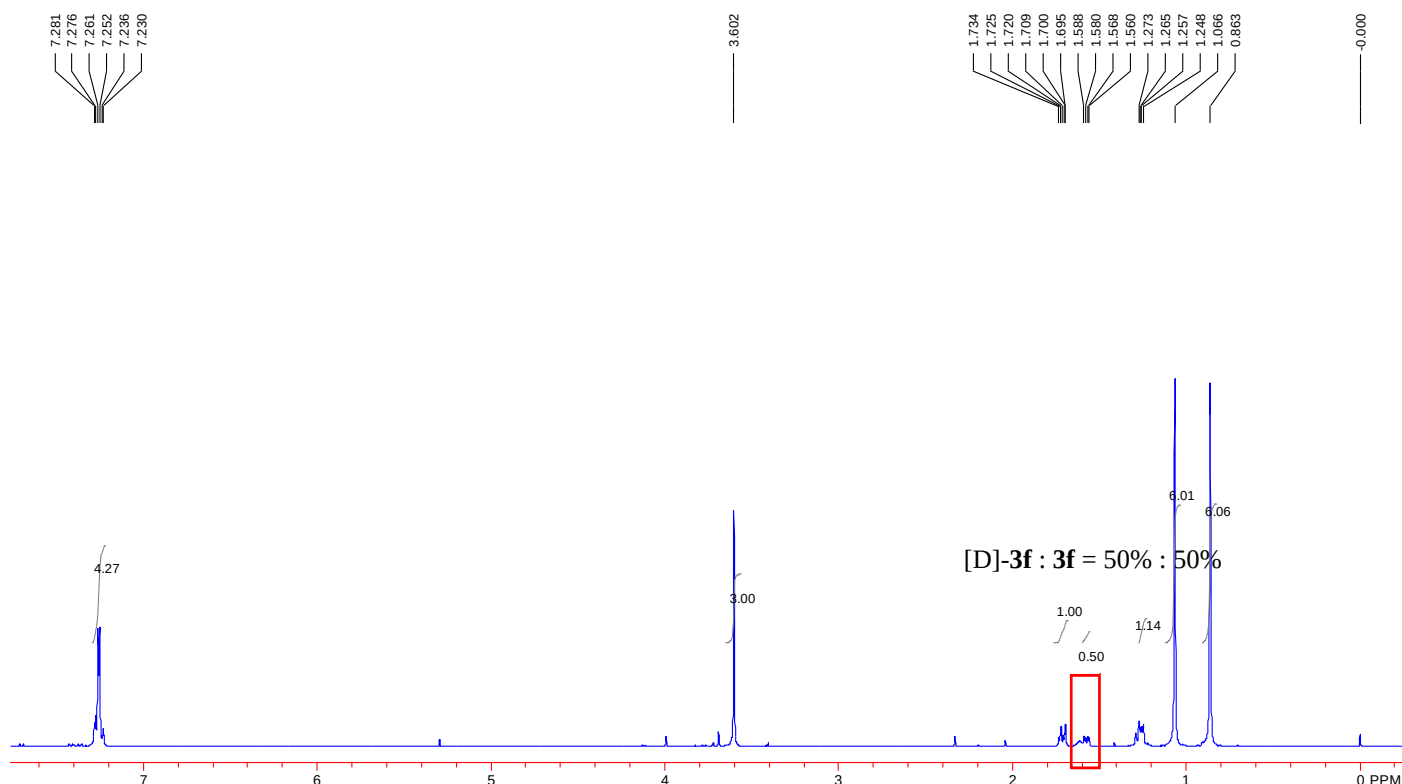


4. DEUTERATED EXPERIMENT

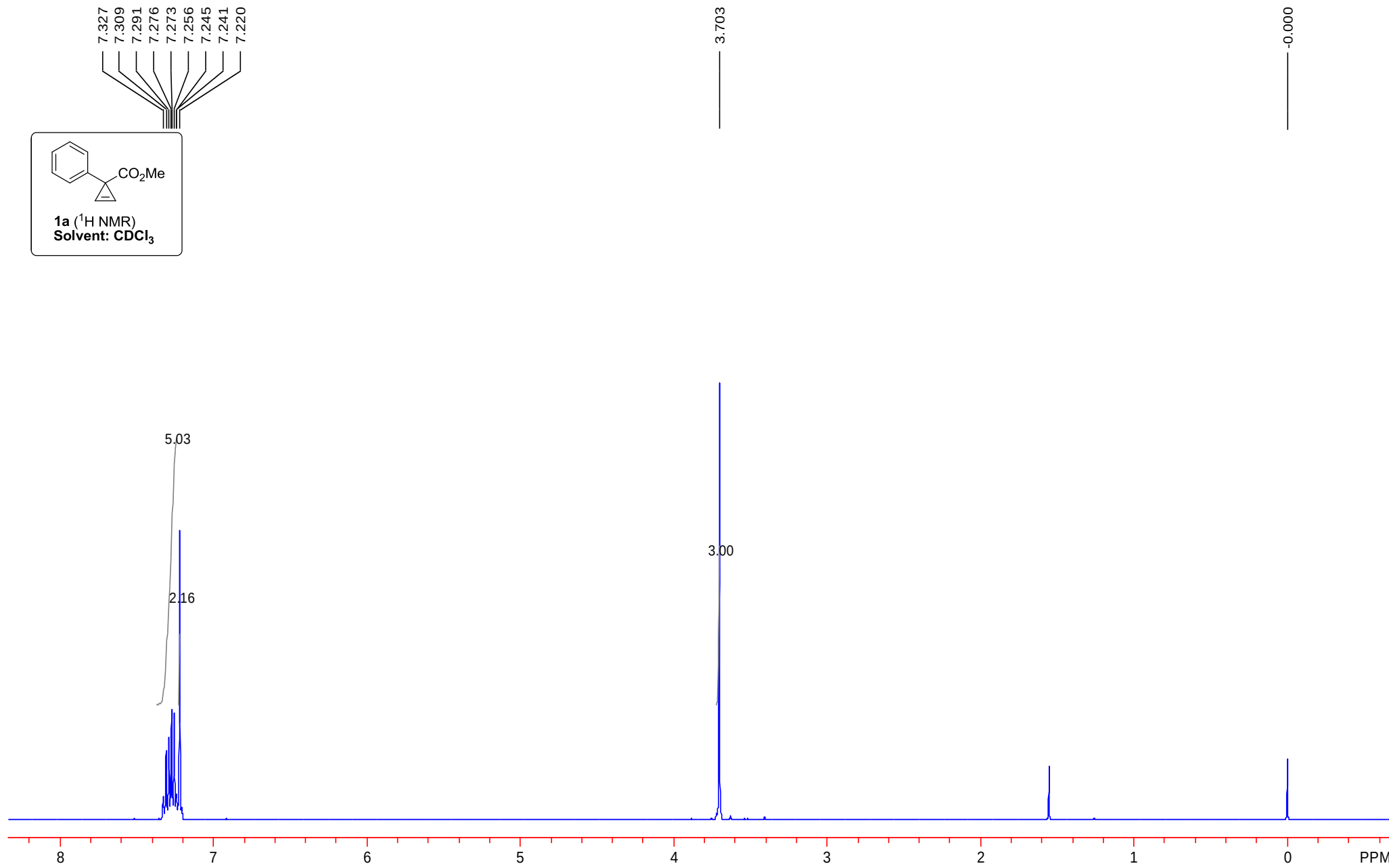
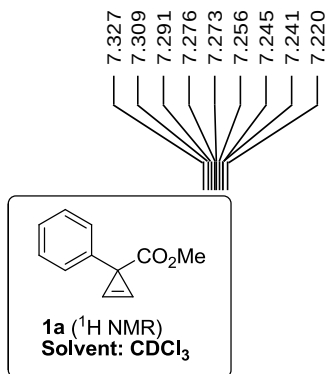
To probe the 'hydrogen' source of this hydroboration reaction, [D4]-methanol experiment was investigated.



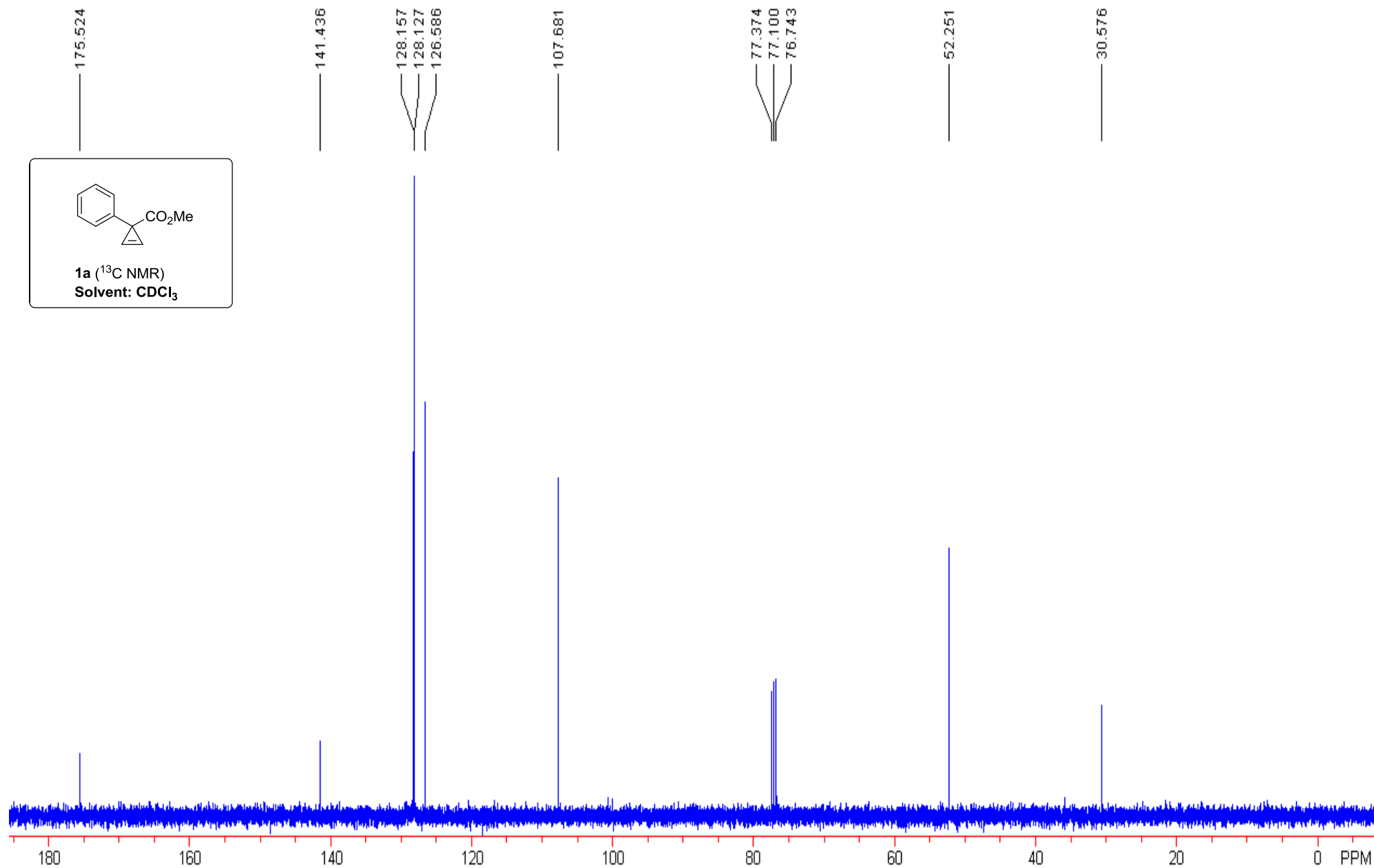
Procedure: A dried Schlenk flask was charged with CuCl (1.5 mg, 0.015mmol, 10 mol%), (R)-(+)-BINAP (14 mg, 0.0225mmol, 15 mol%), B₂Pin₂ (2, 76.2 mg, 0.3 mmol, 2.0 equiv), NaOtBu (1.6 mg, 0.0165mmol, 11 mol%) and anhydrous toluene (1.0 mL) under nitrogen atmosphere. After the mixture was stirred at room temperature for 40 min, a solution of cyclopropene **1f** (0.15 mmol) in anhydrous toluene (0.5 mL) was added, followed by anhydrous [D4]-MeOH (12.2 μ L, 0.30 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 6h, then filtered through Celite®, and concentrated in vacuo. The residue was purified by silica gel (300–400 mesh) column chromatography to afford the desired product **3f**. Deuterated product **3f** (50%) was observed, which was proved that the proton partially came from methanol.

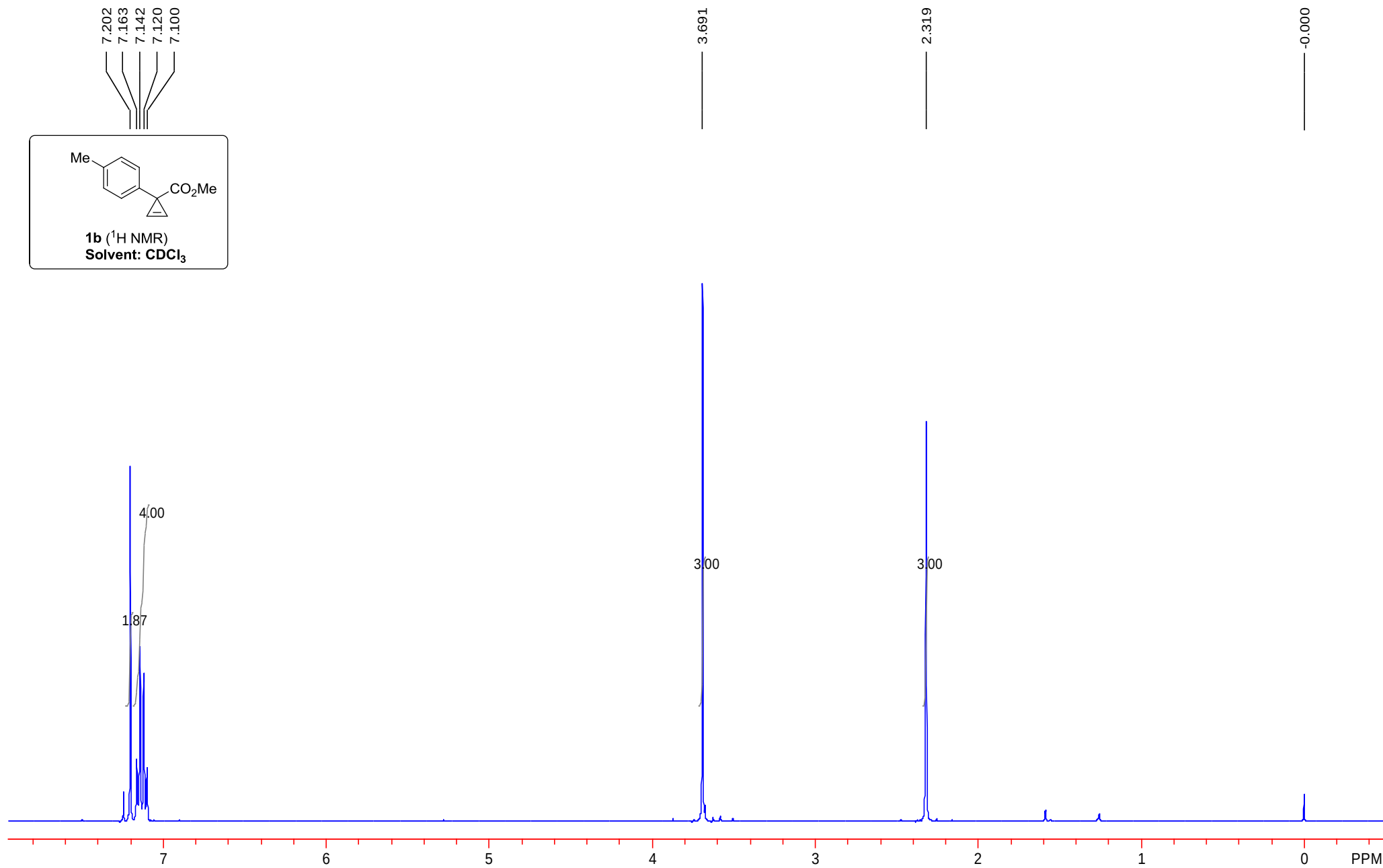
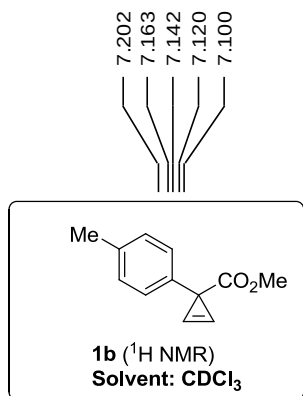


5. ^1H NMR, ^{13}C NMR, NOSEY & HPLC

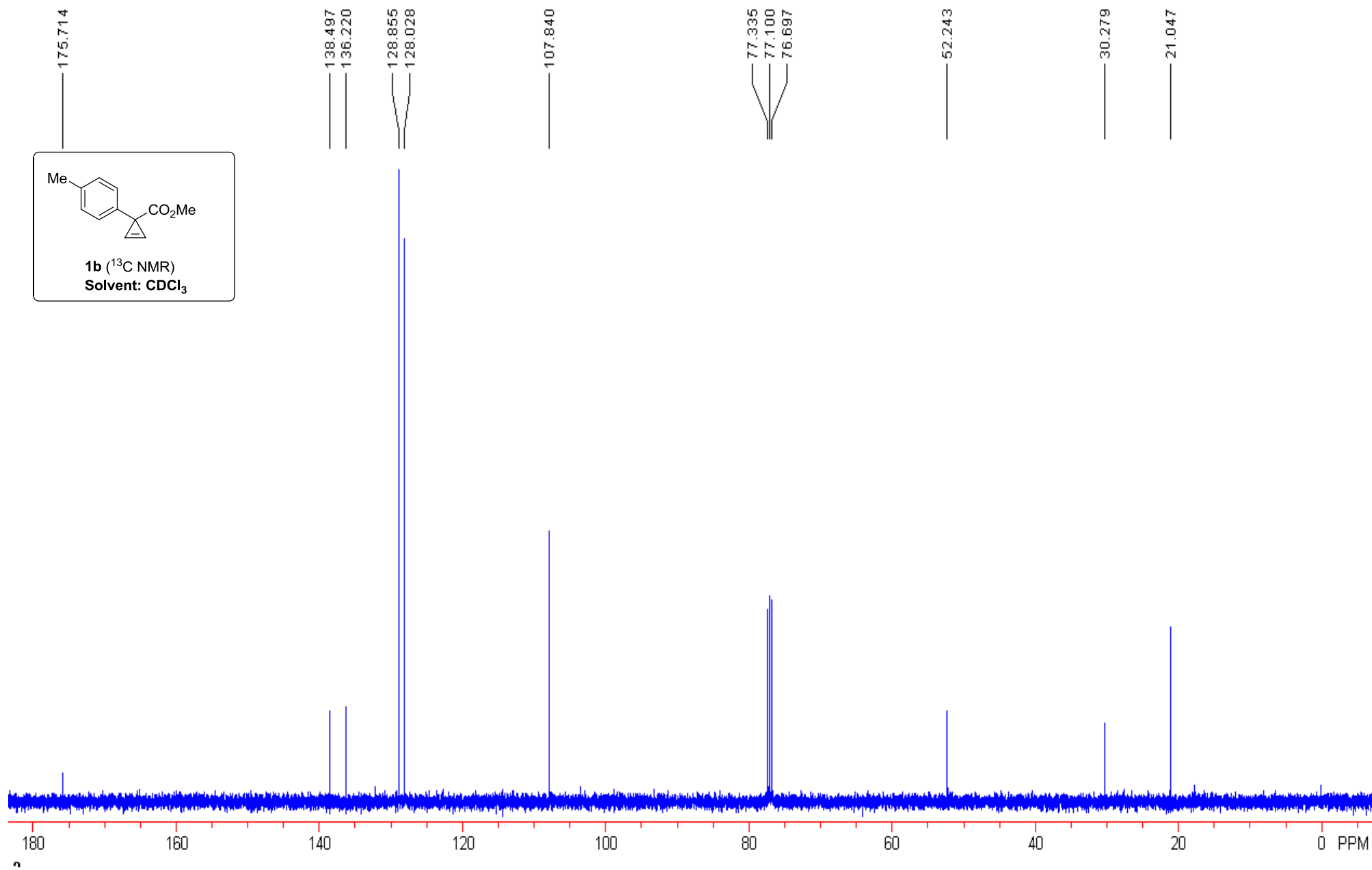


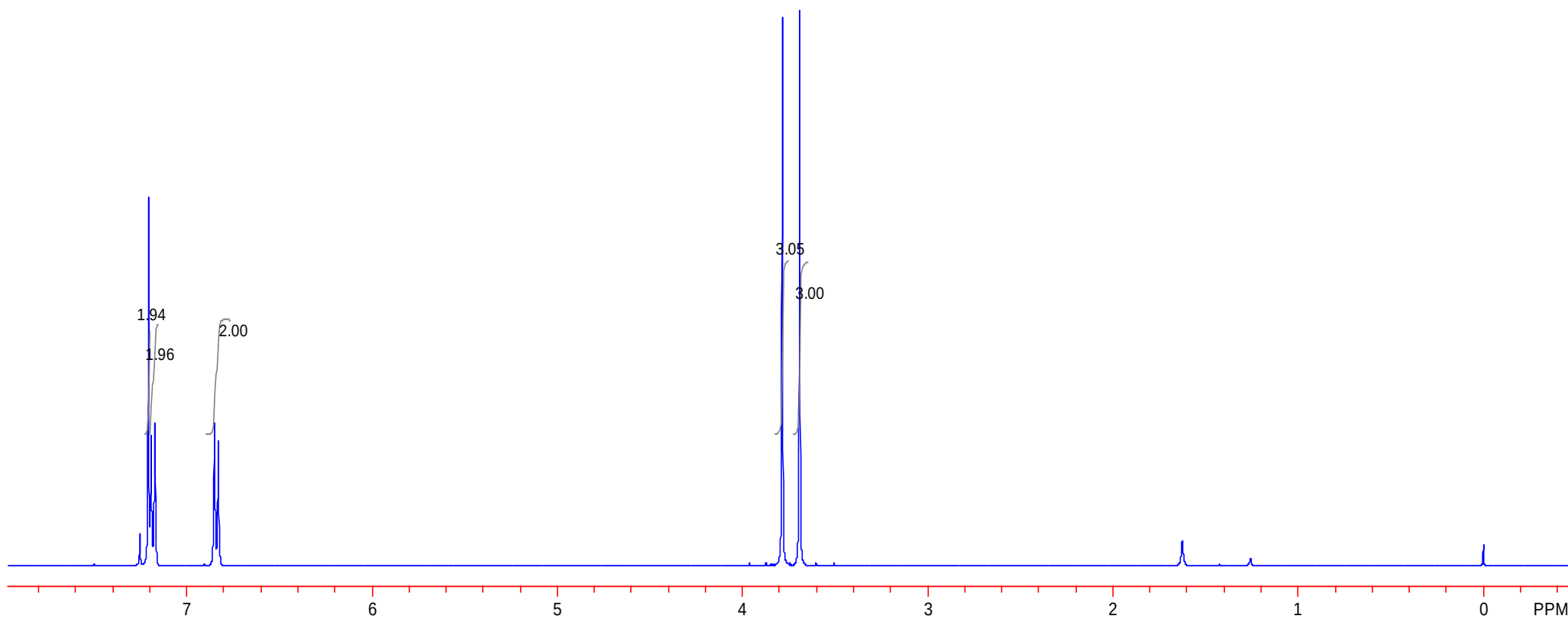
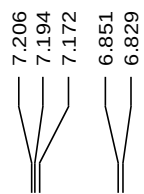
S10



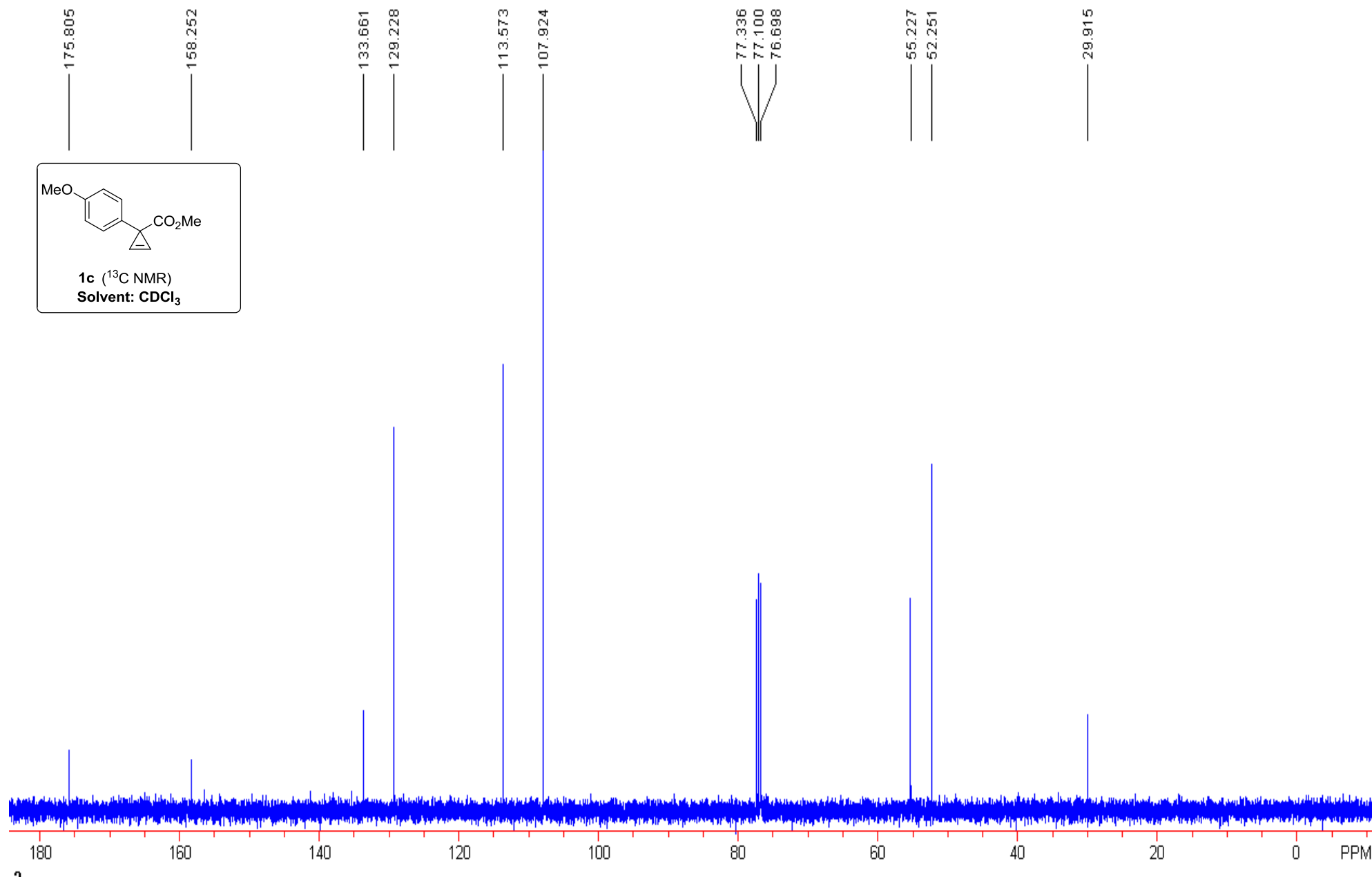


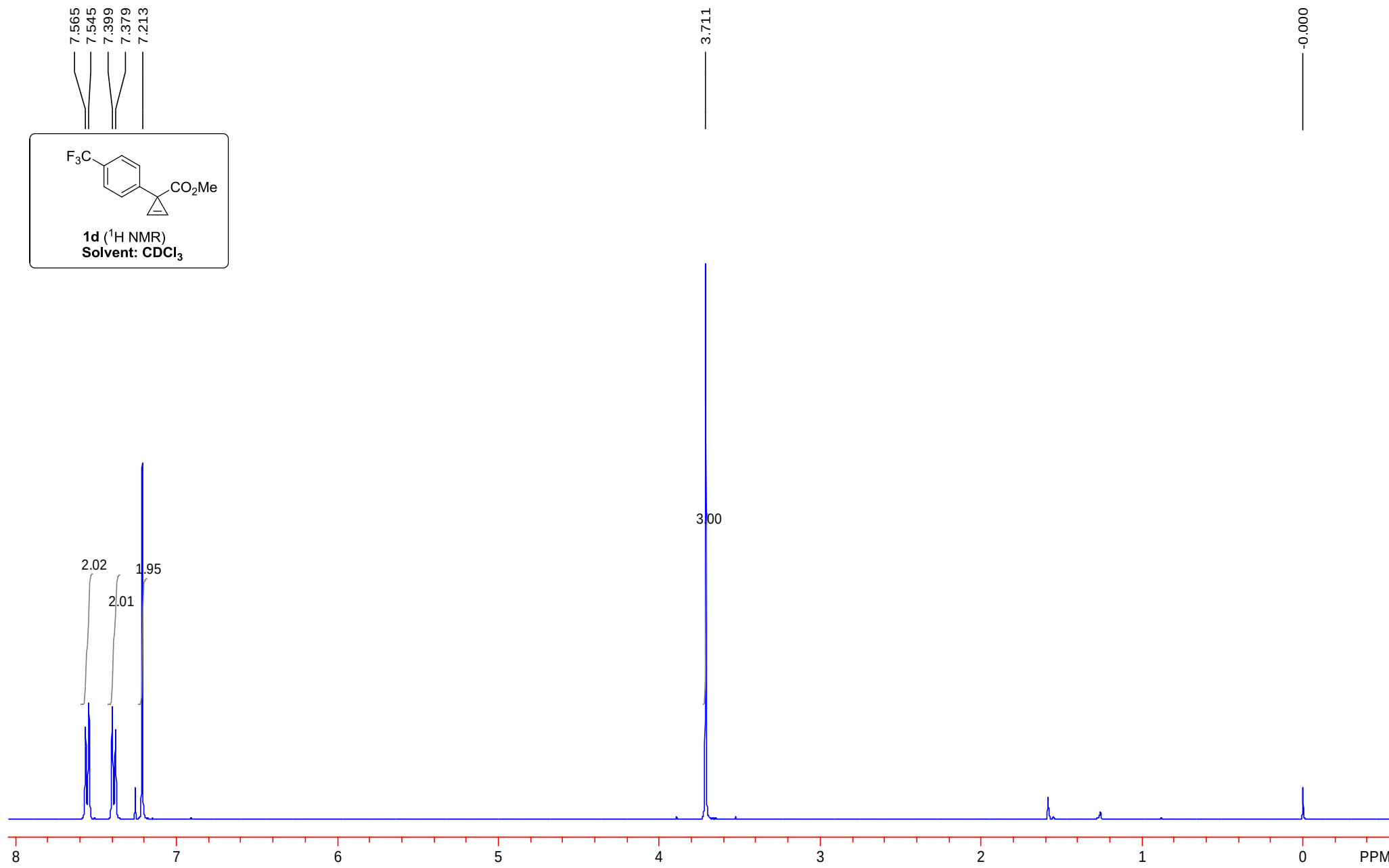
S12



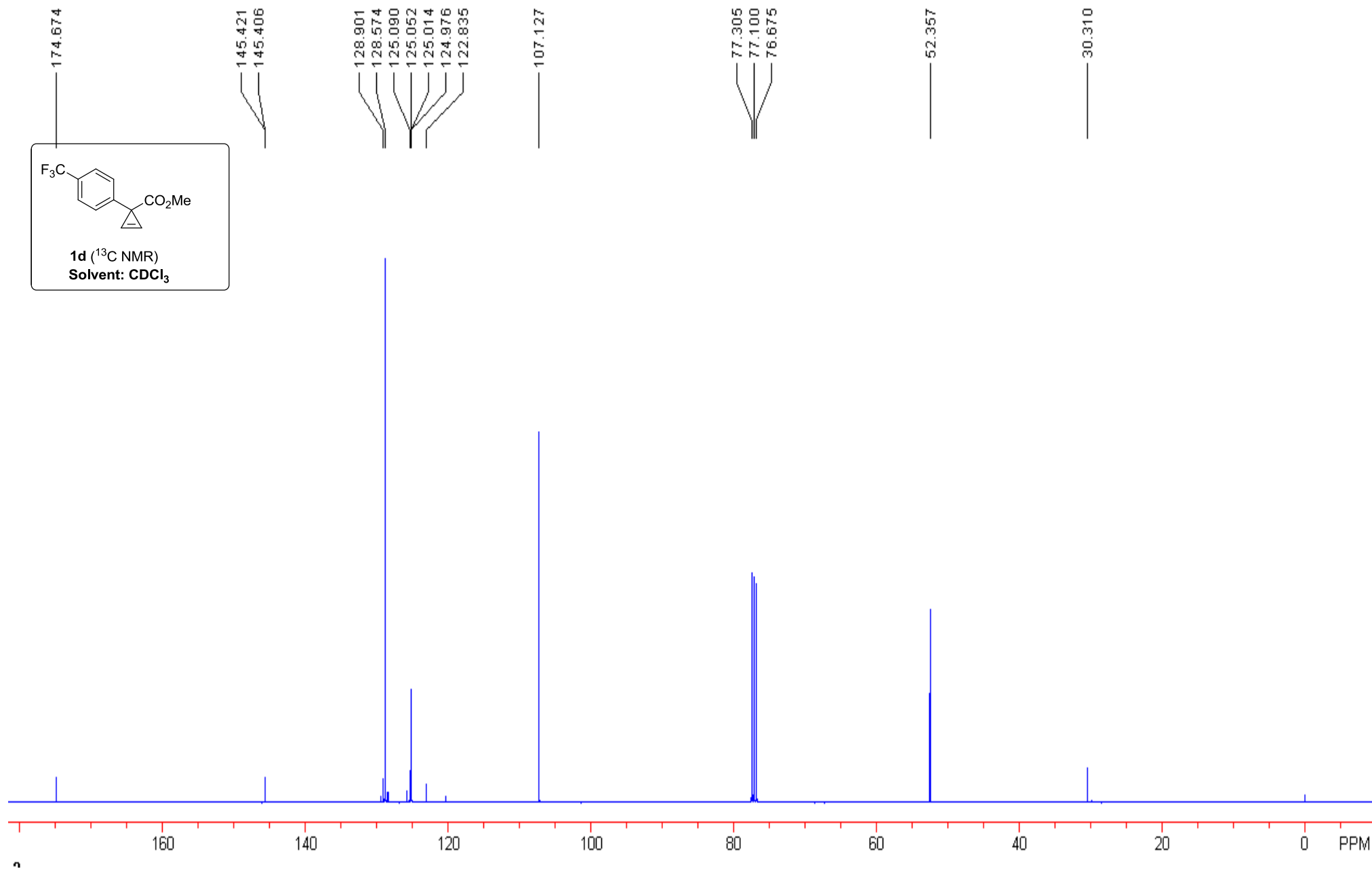


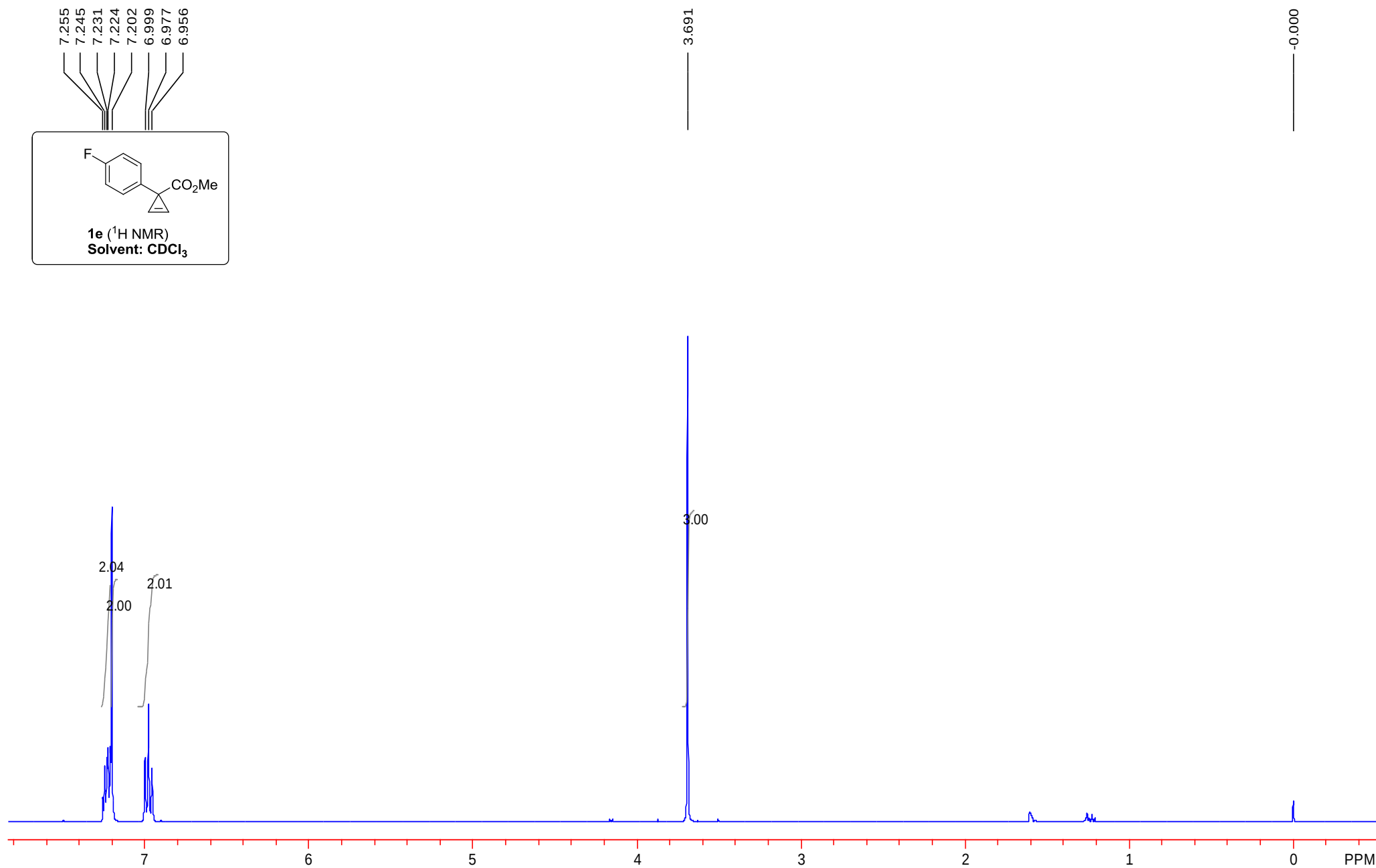
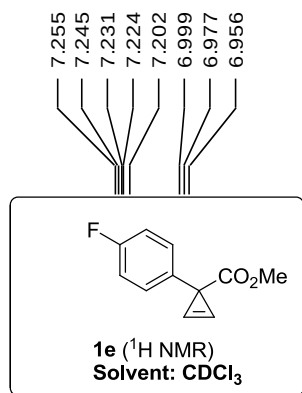
S14



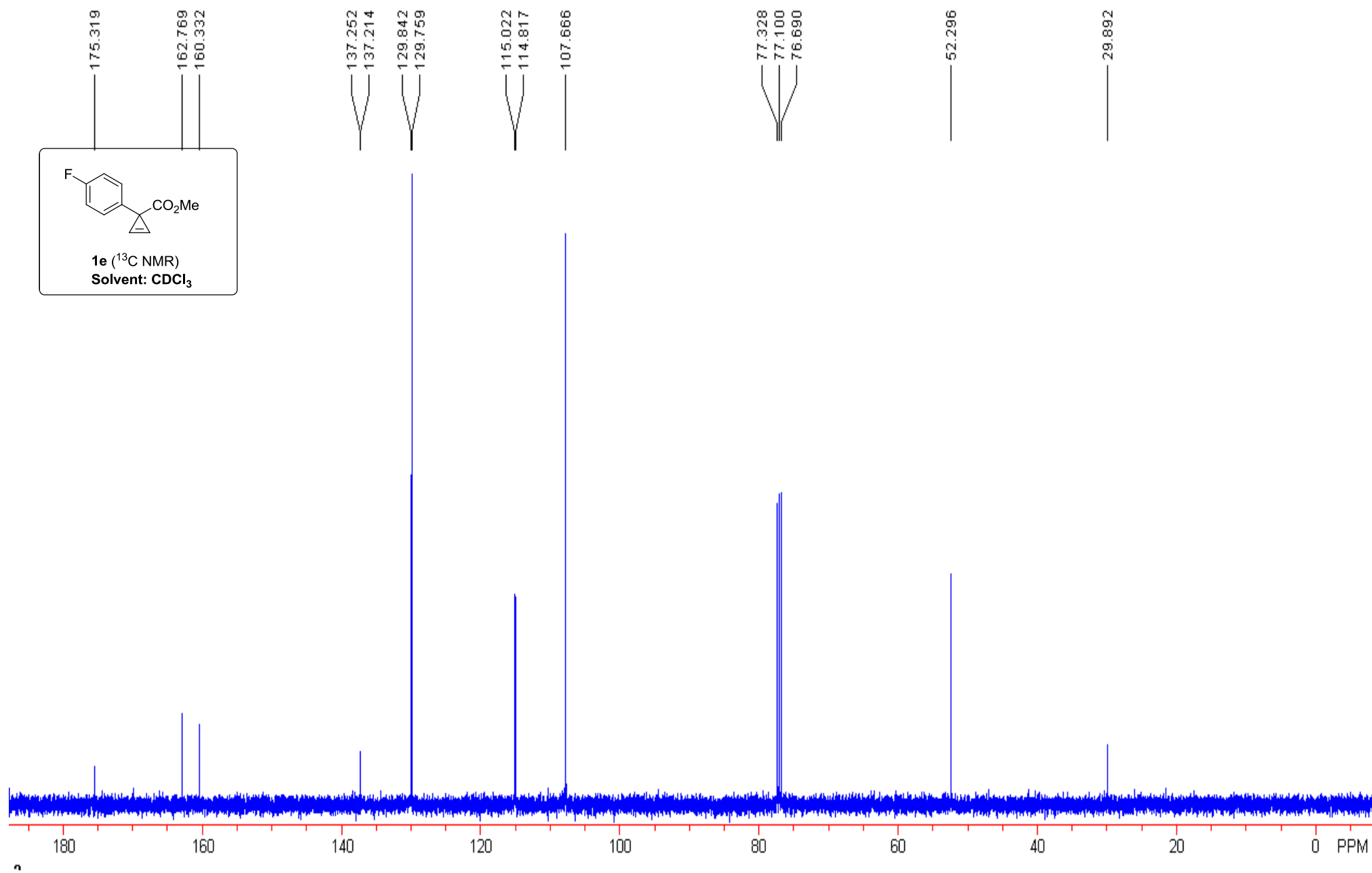


S16

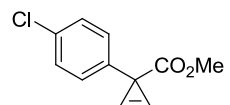




S18



7.279
7.259
7.212
7.207
7.197
7.192



1f (¹H NMR)
Solvent: CDCl₃

3.698

-0.000

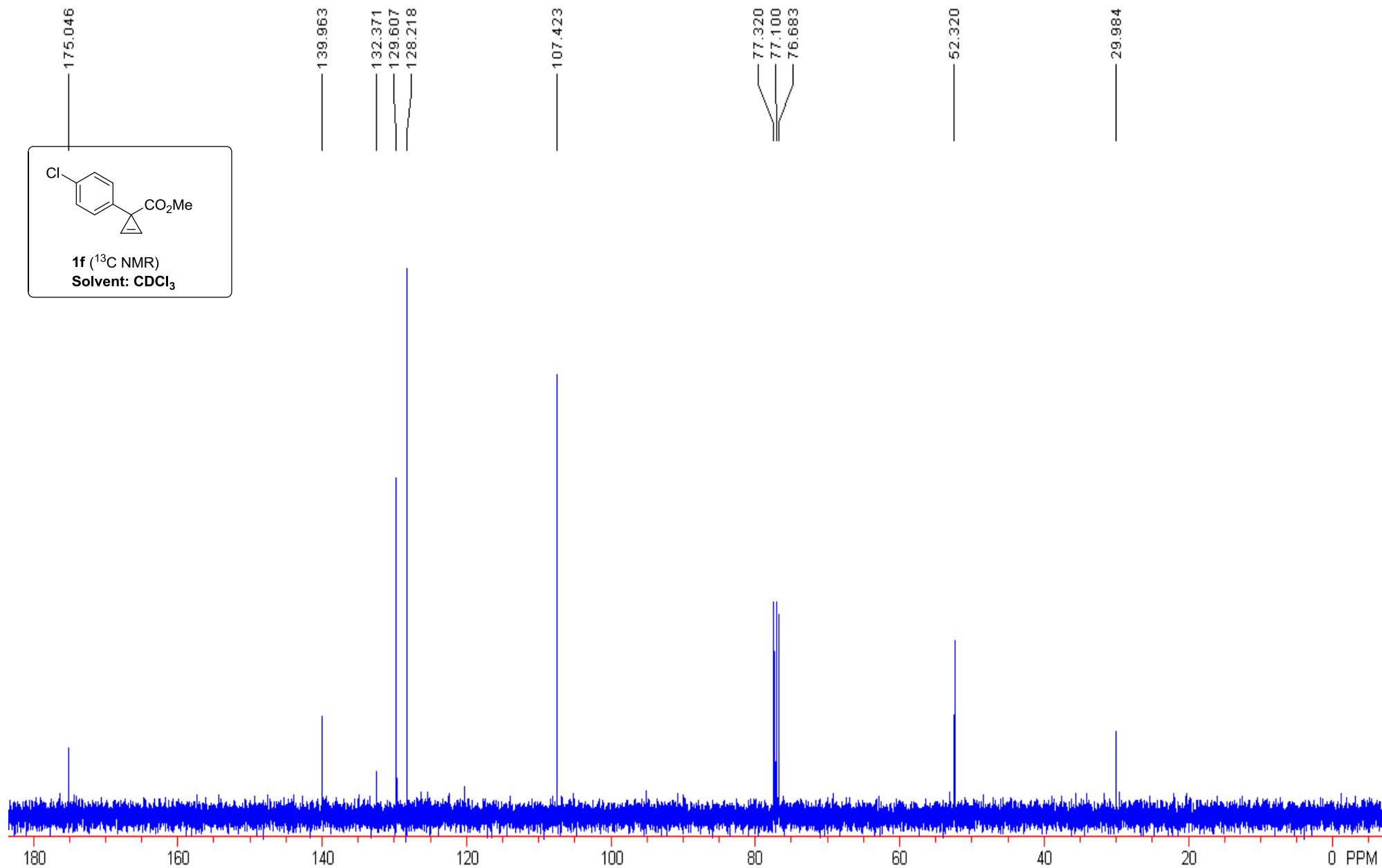
3.94

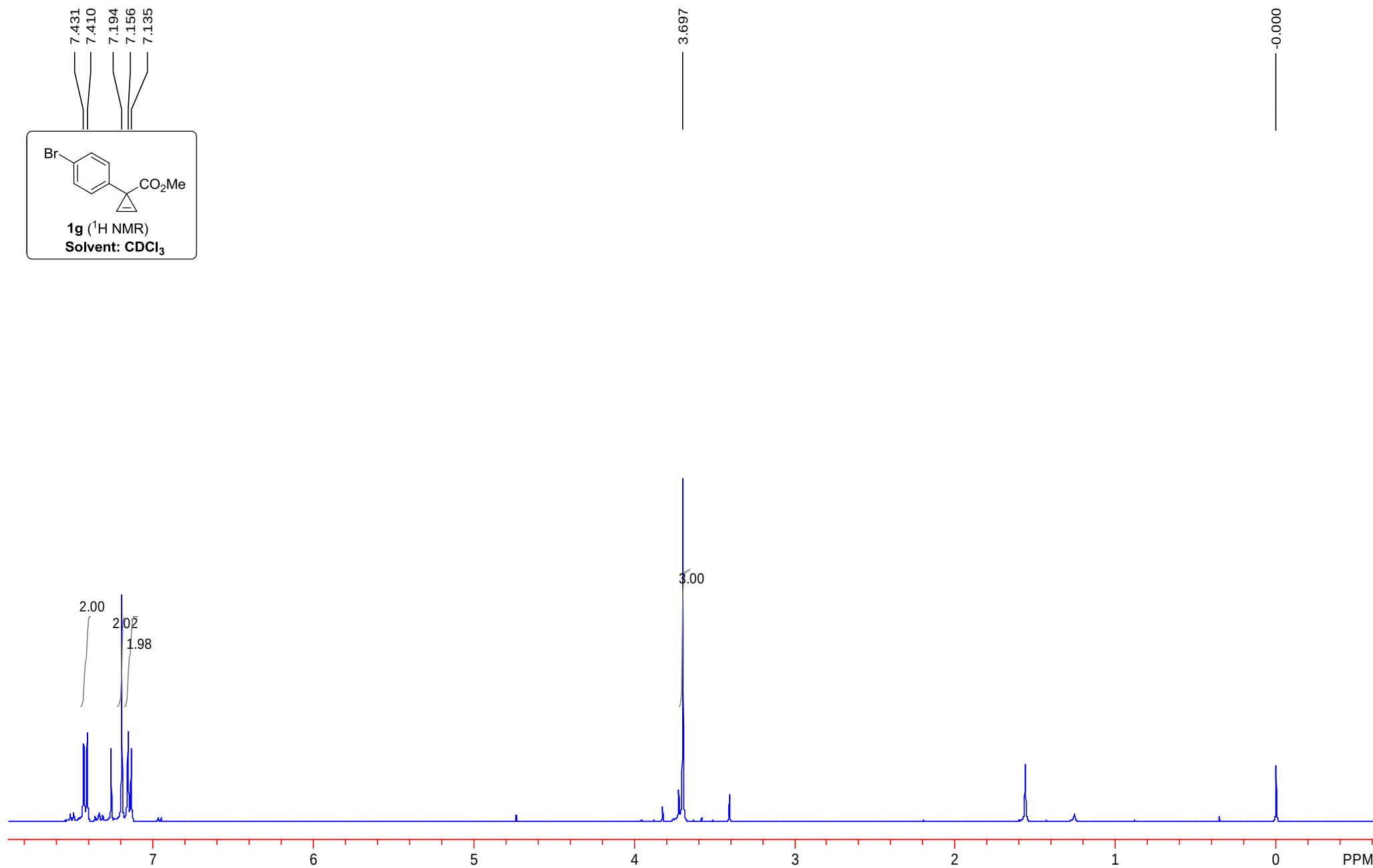
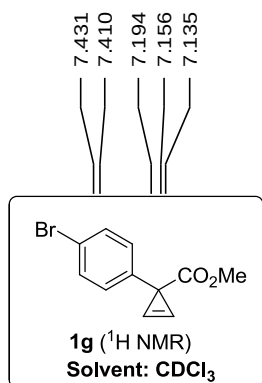
2.11

3.00

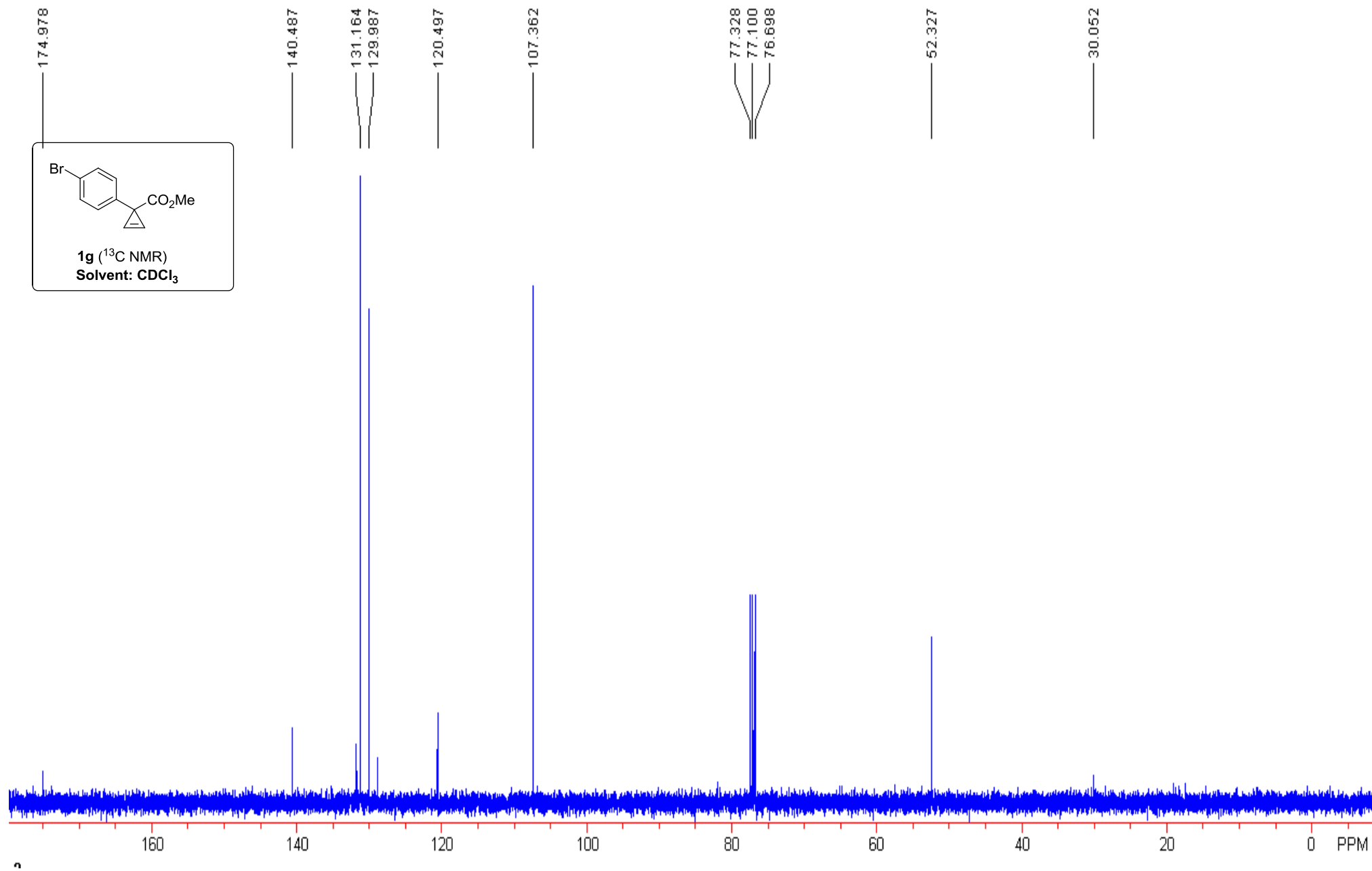
7 6 5 4 3 2 1 0 PPM

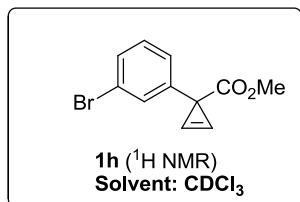
S20





S22

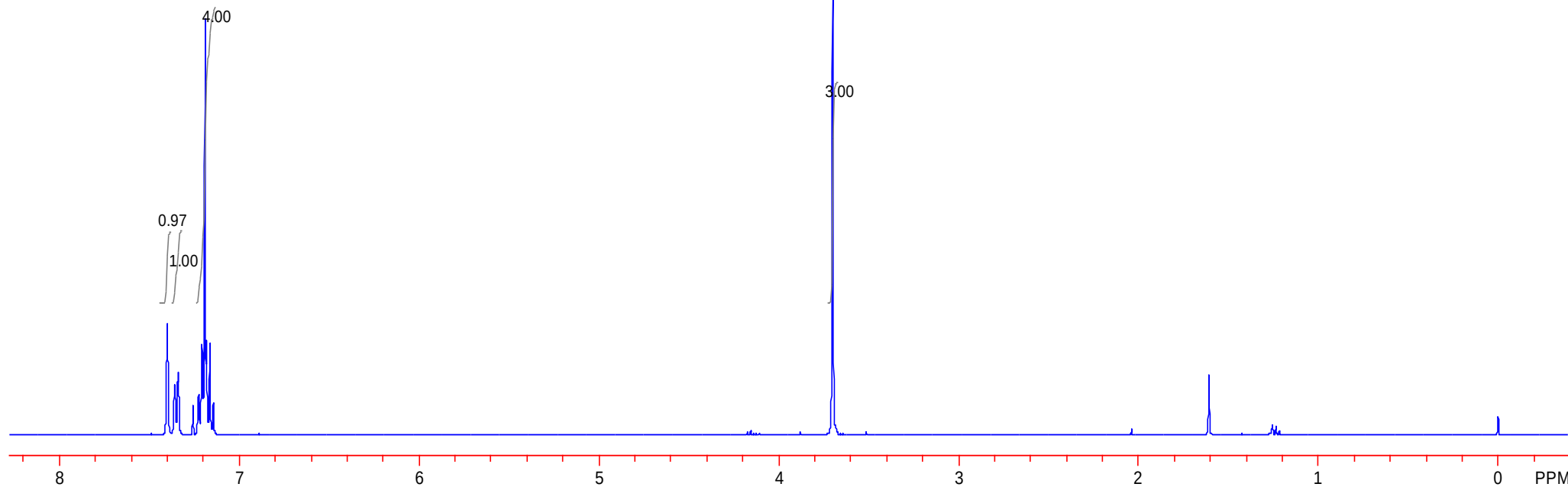




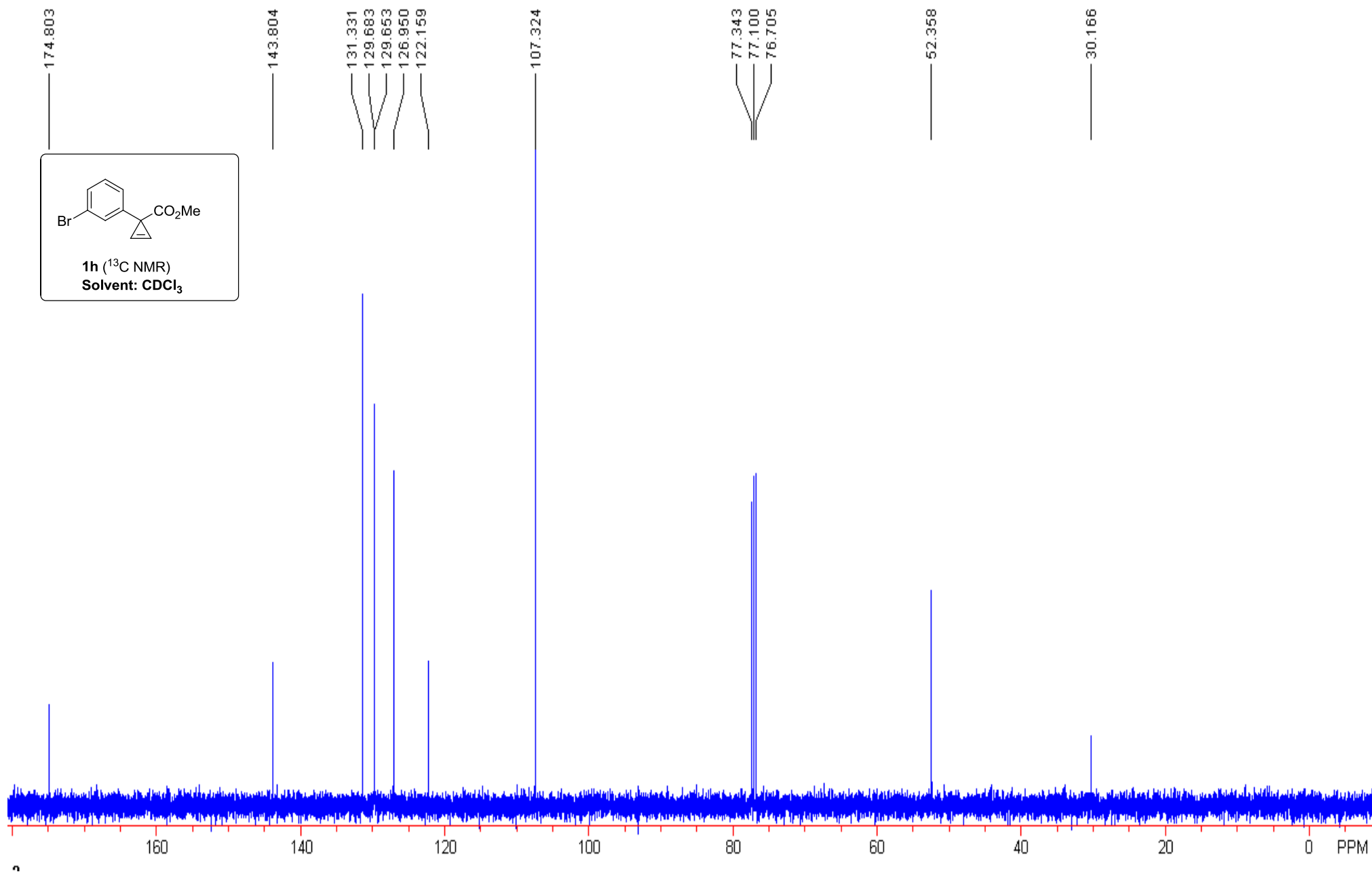
7.399
7.358
7.339
7.226
7.207
7.190
7.182
7.163
7.144

3.699

0.000



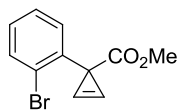
S24



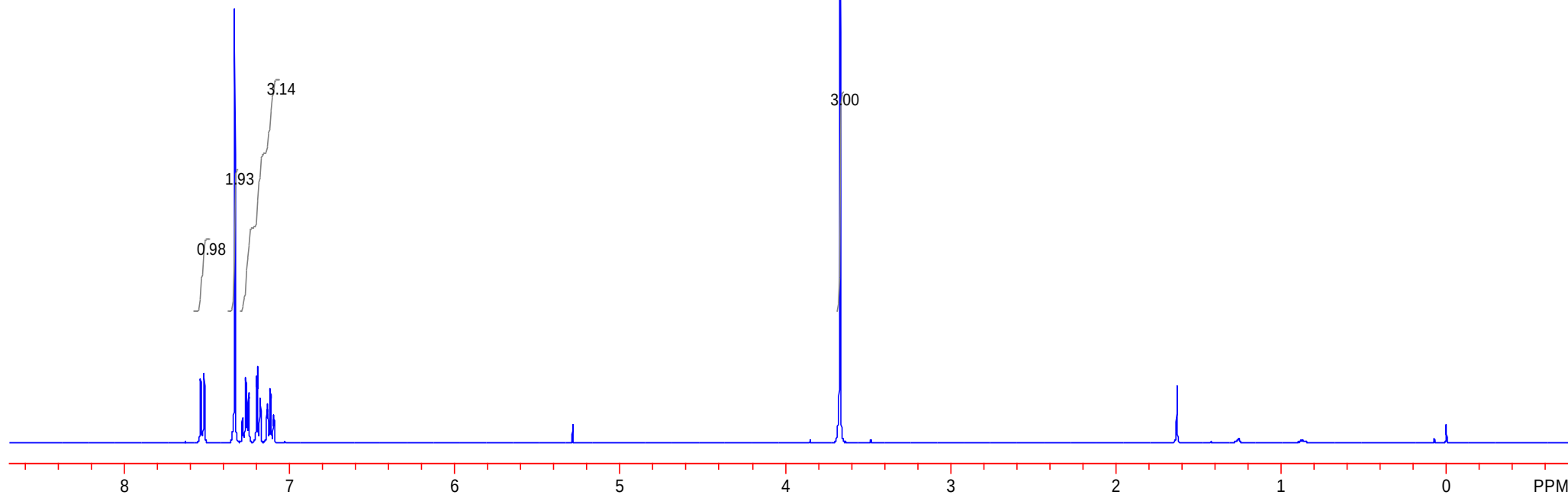
7.538
7.536
7.518
7.516
7.331
7.284
7.282
7.265
7.264
7.255
7.247
7.245
7.198
7.194
7.180
7.175
7.136
7.131
7.116
7.113
7.098
7.094

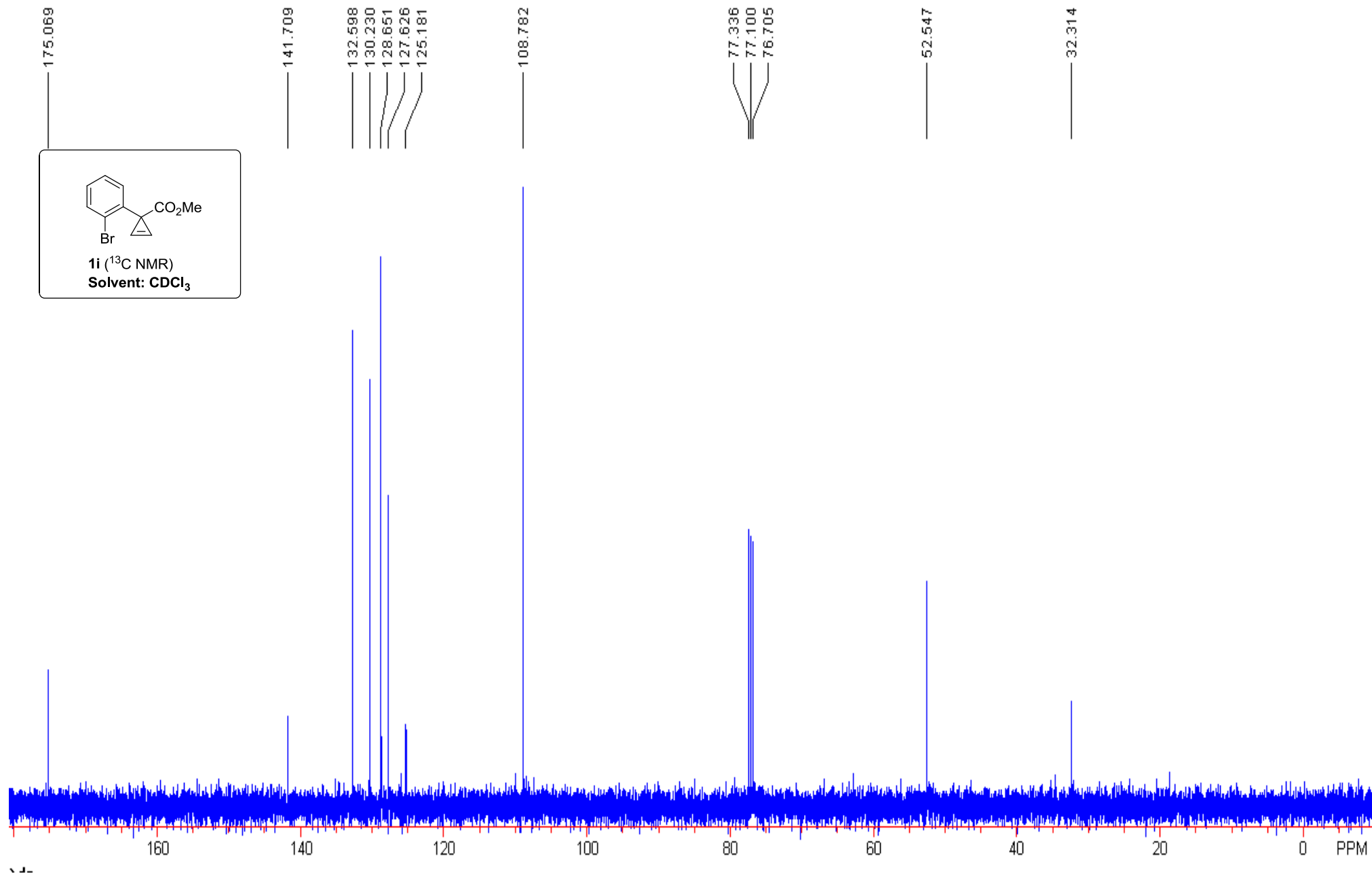
3.669

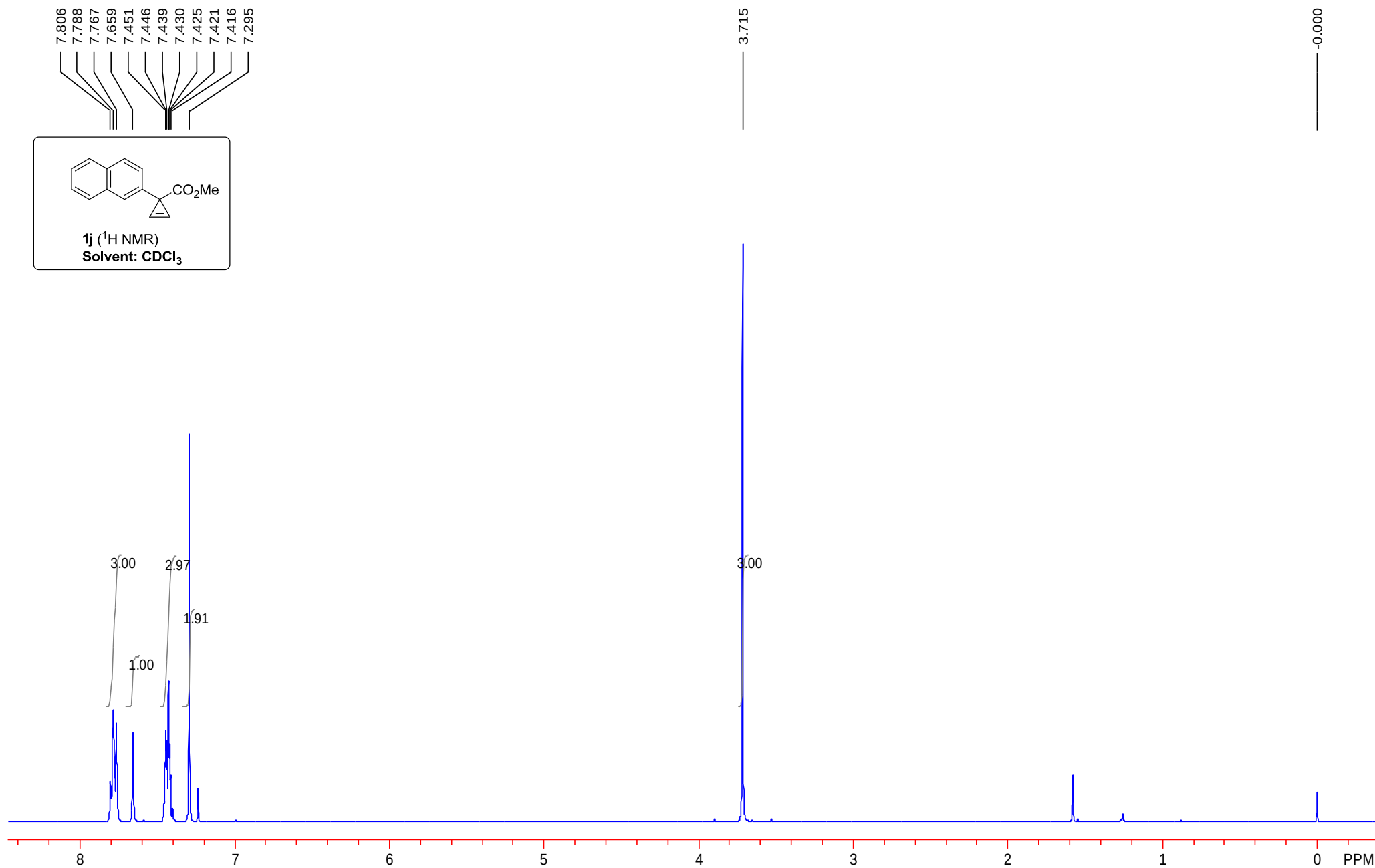
0.000



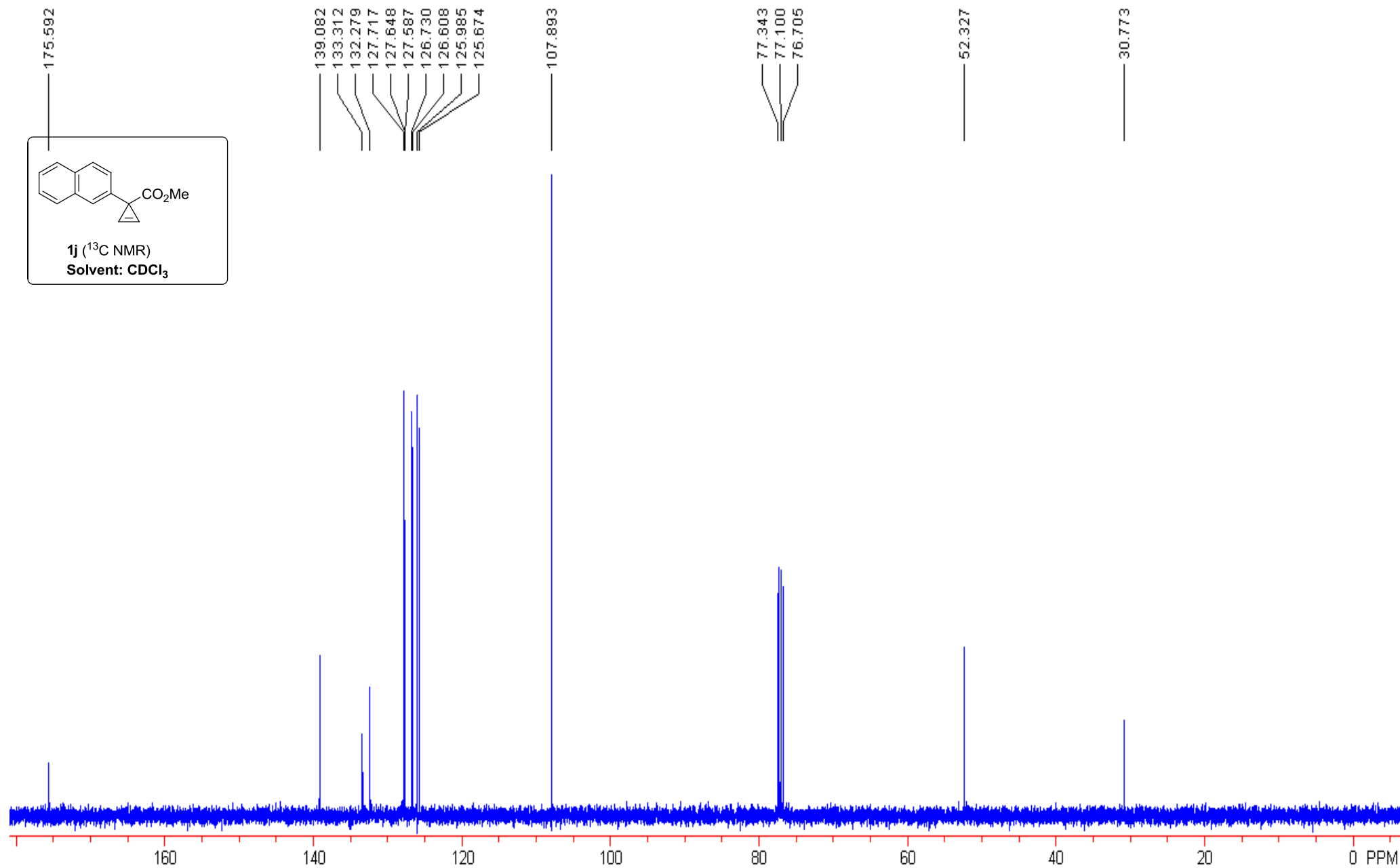
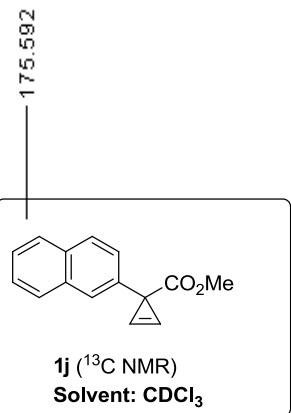
1i (^1H NMR)
Solvent: CDCl_3

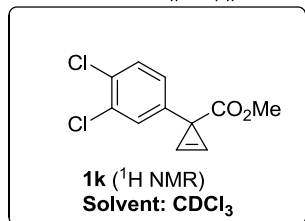






S28

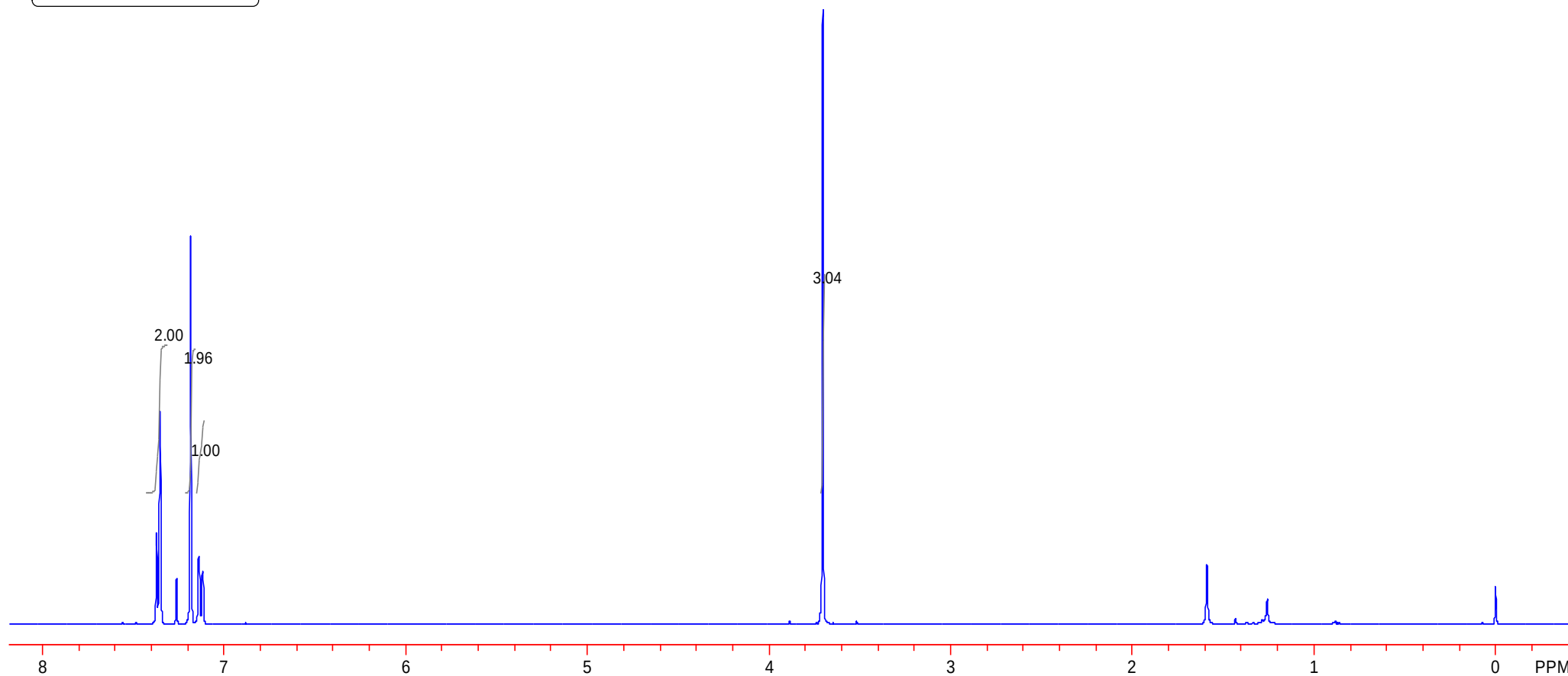




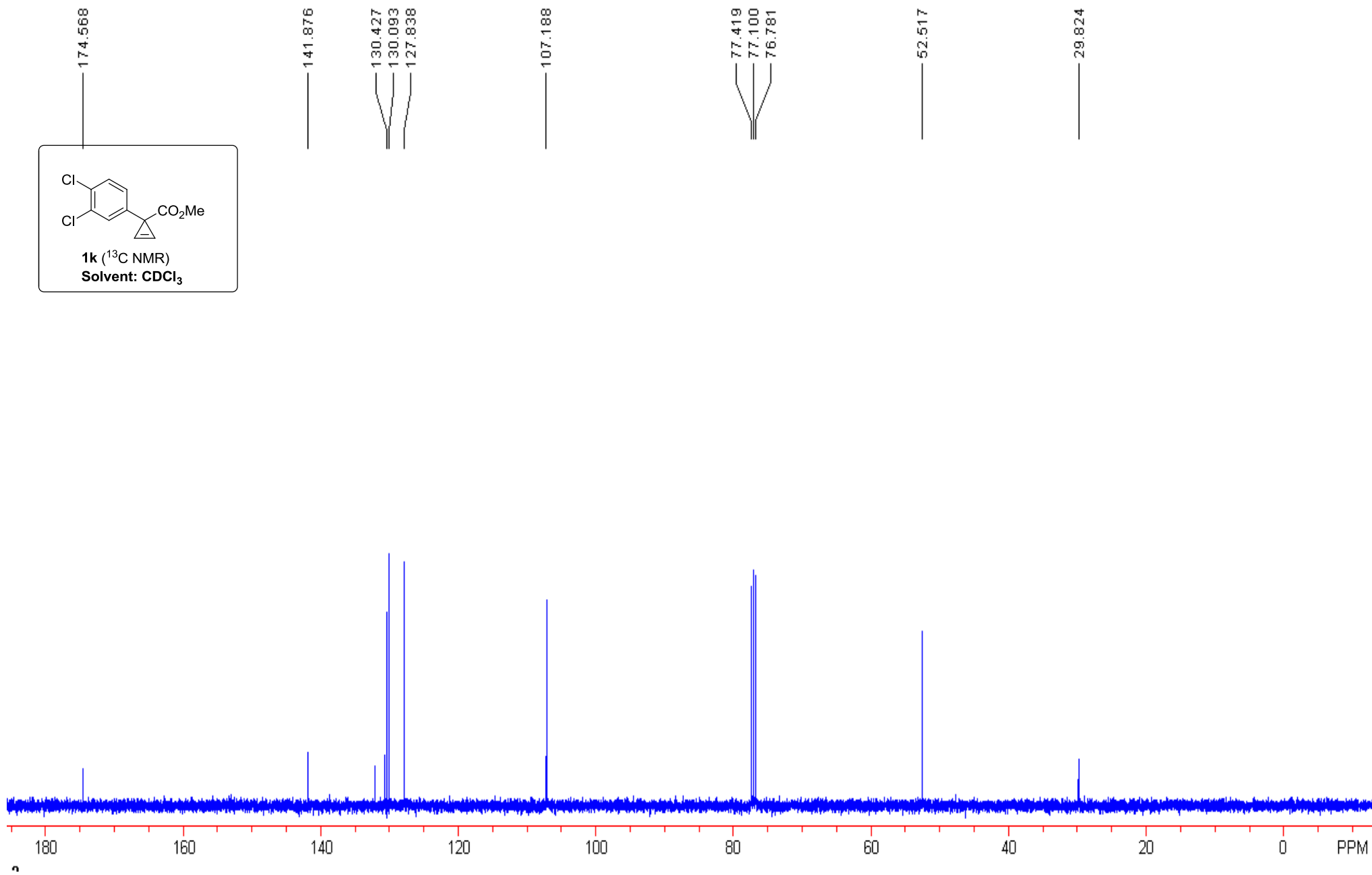
7.371
7.350
7.183
7.140
7.119

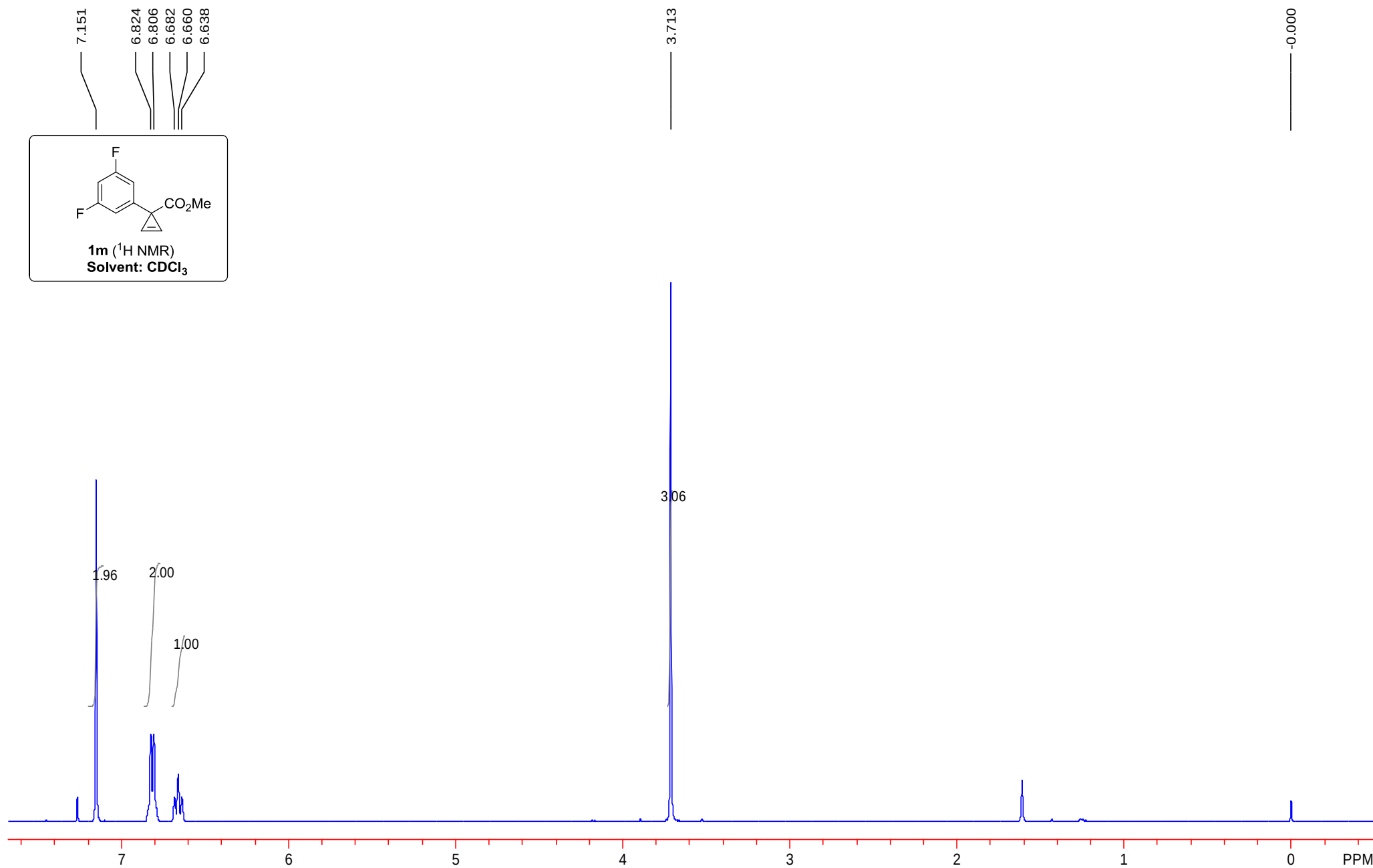
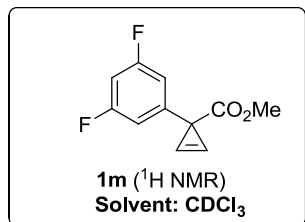
3.703

-0.000

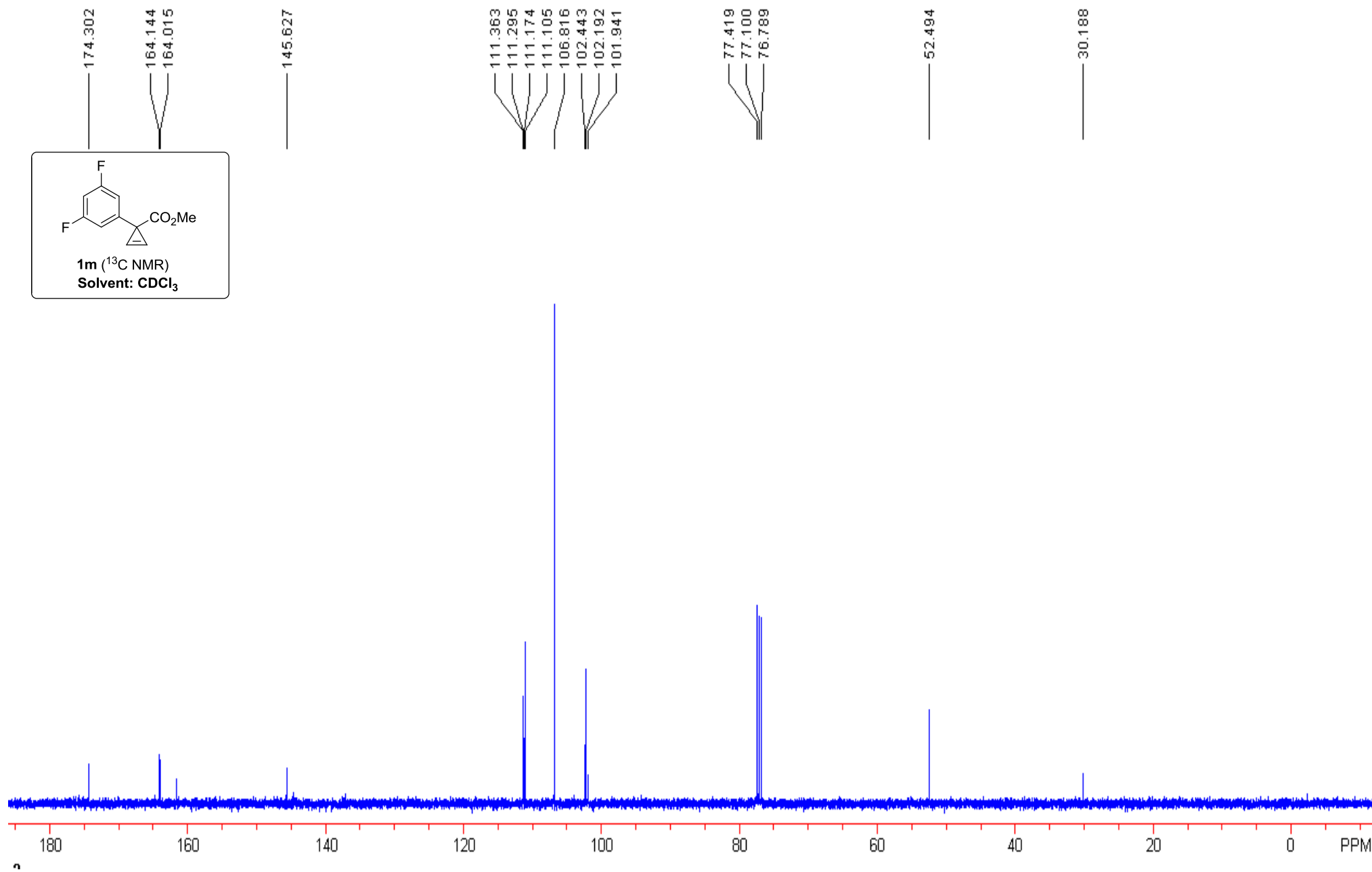


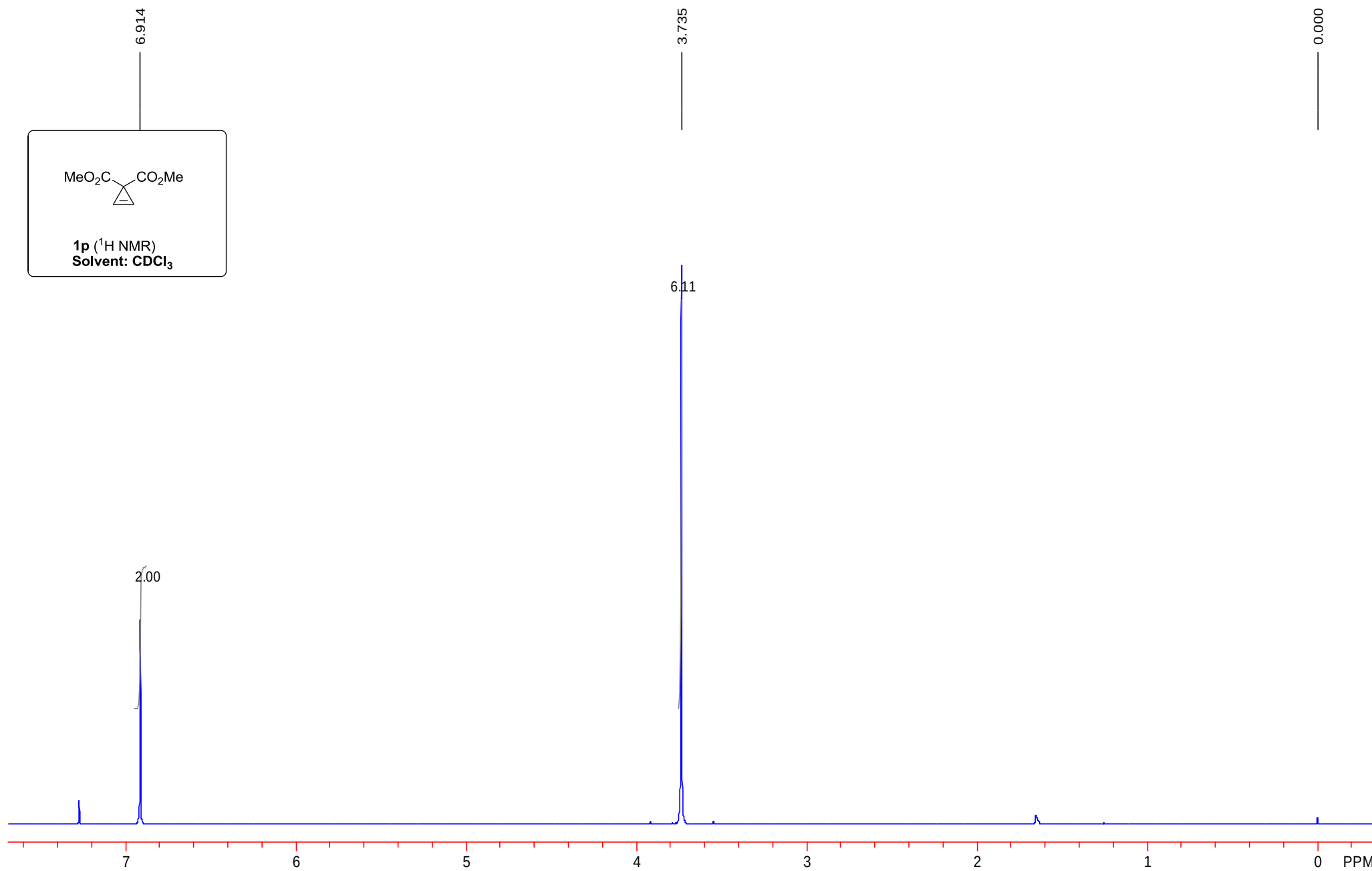
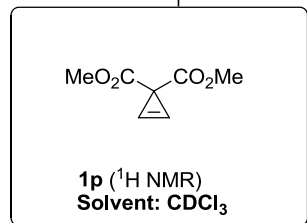
S30



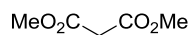


S32

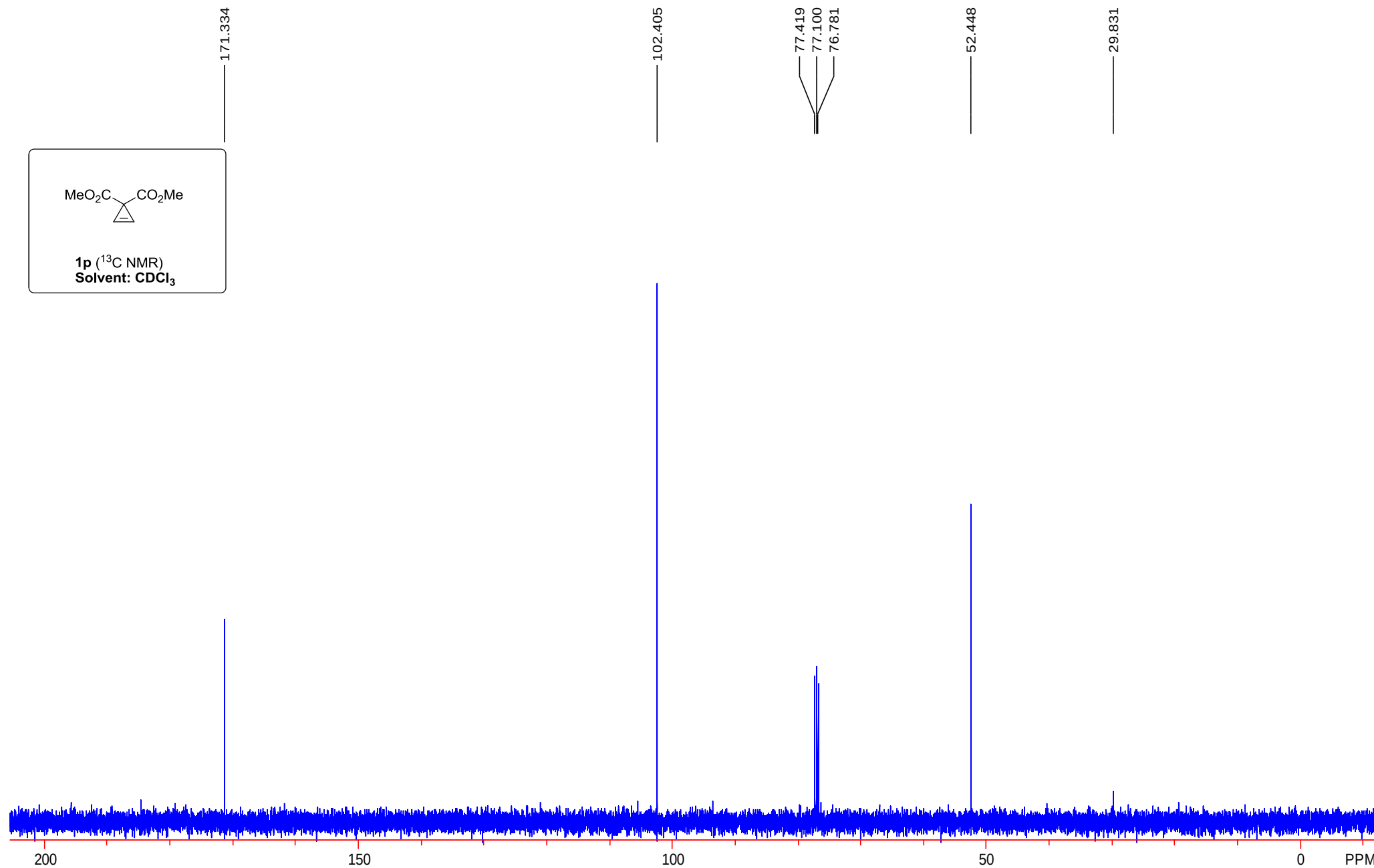




S34

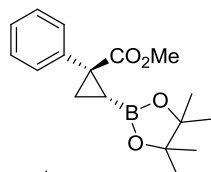


1p (^{13}C NMR)
Solvent: CDCl_3



S35

7.344
7.326
7.281
7.262
7.245
7.231
7.213

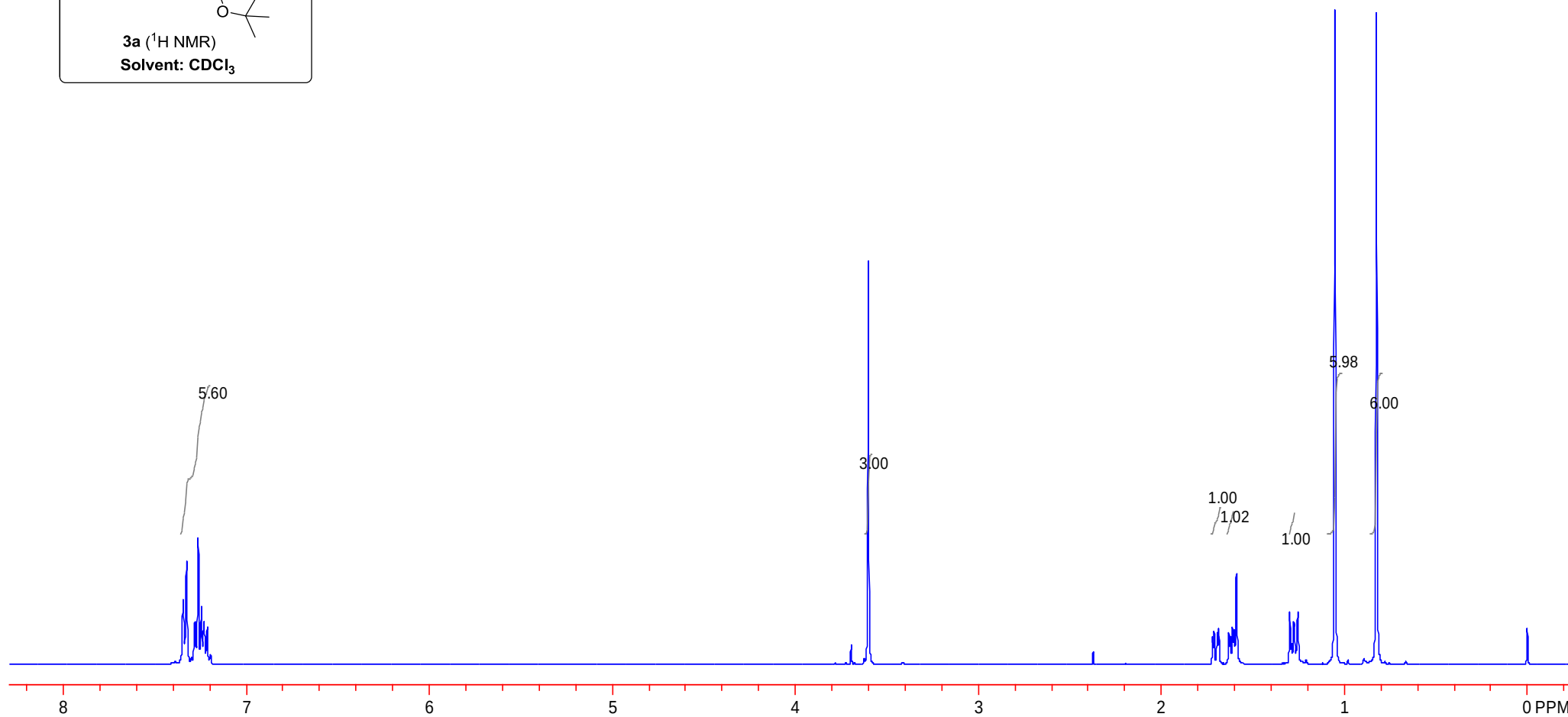


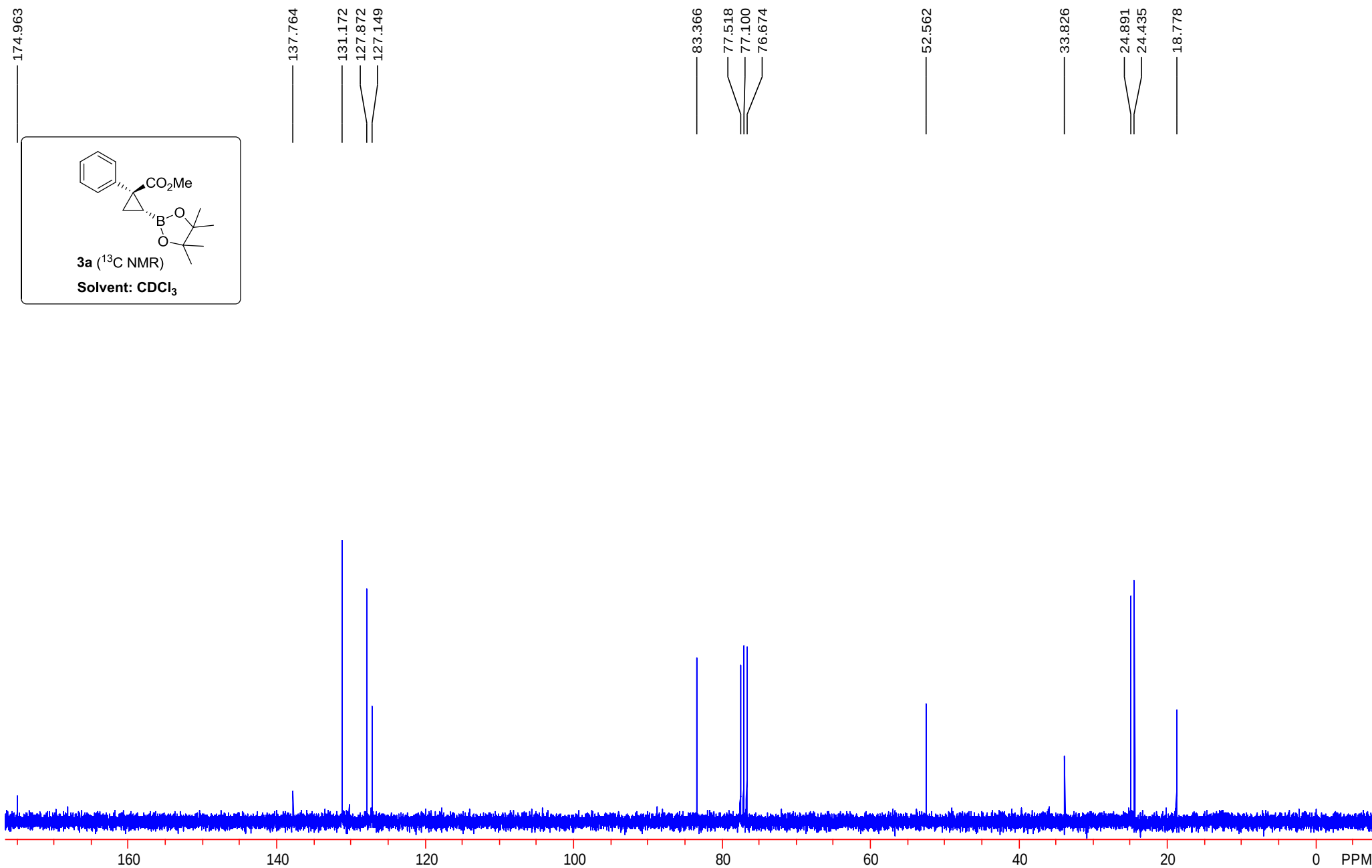
3a (^1H NMR)
Solvent: CDCl_3

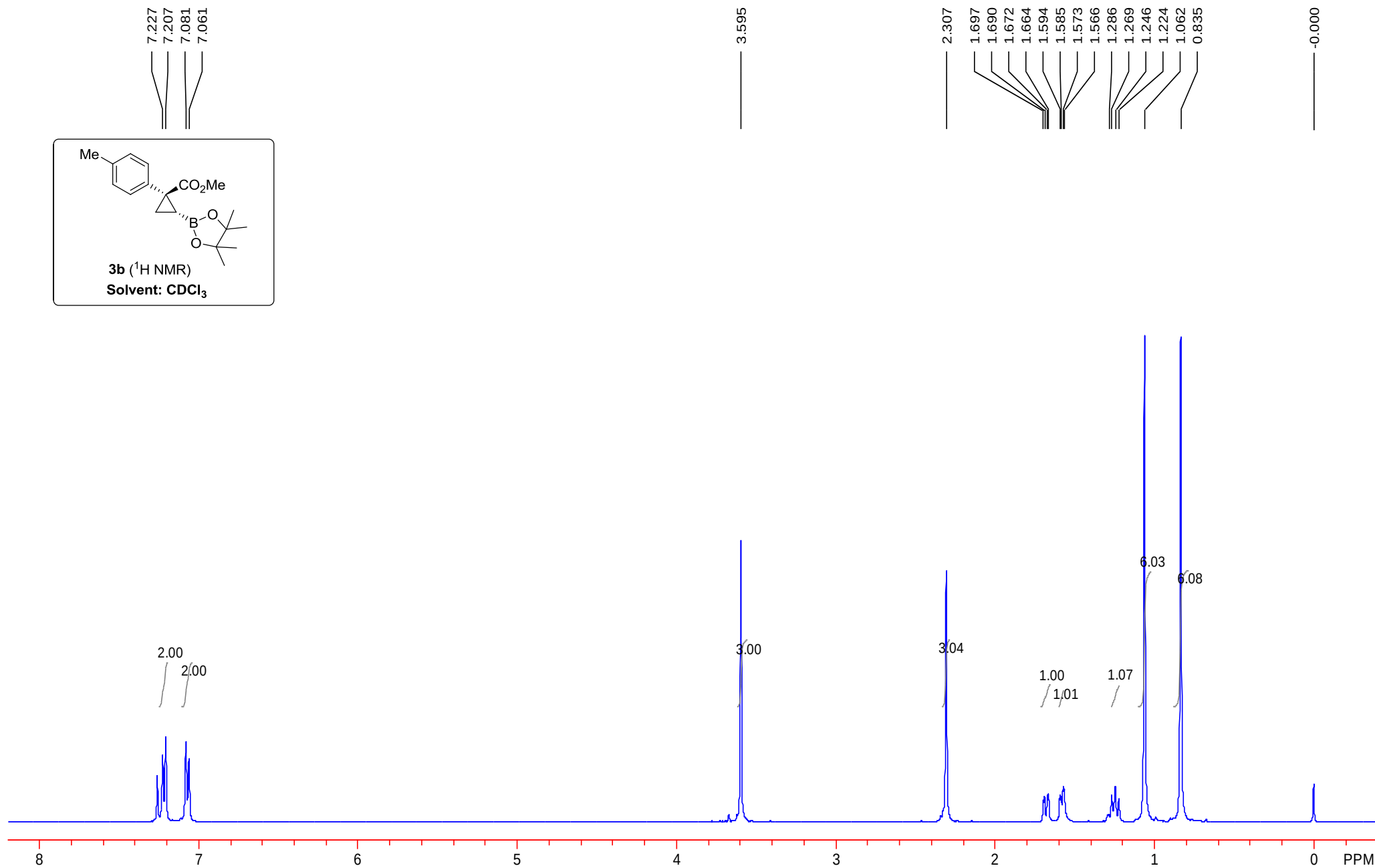
3.601

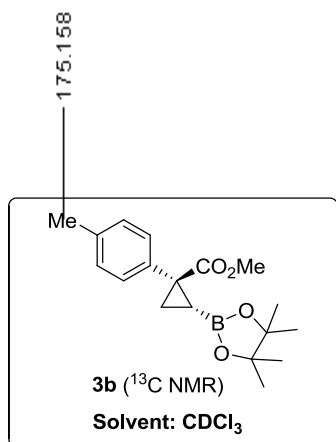
1.720
1.712
1.695
1.686
1.632
1.624
1.612
1.604
1.298
1.289
1.278
1.273
1.052
0.825

-0.000









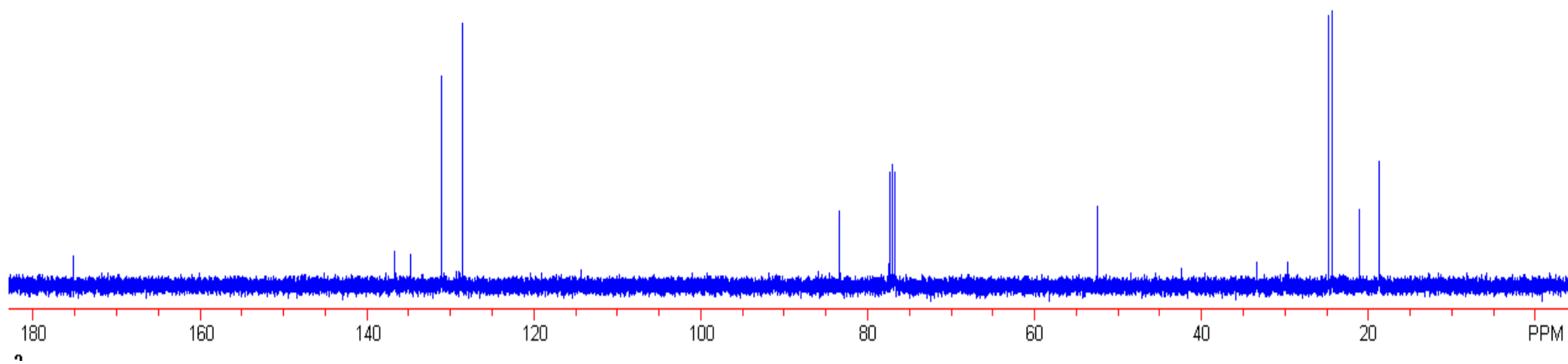
175.158
 136.735
 134.735
 131.005
 128.563

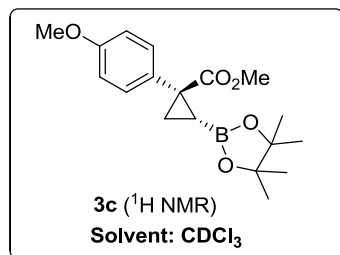
83.365
 77.416
 77.100
 76.784

52.575

33.427

24.886
 24.448
 21.213
 18.856





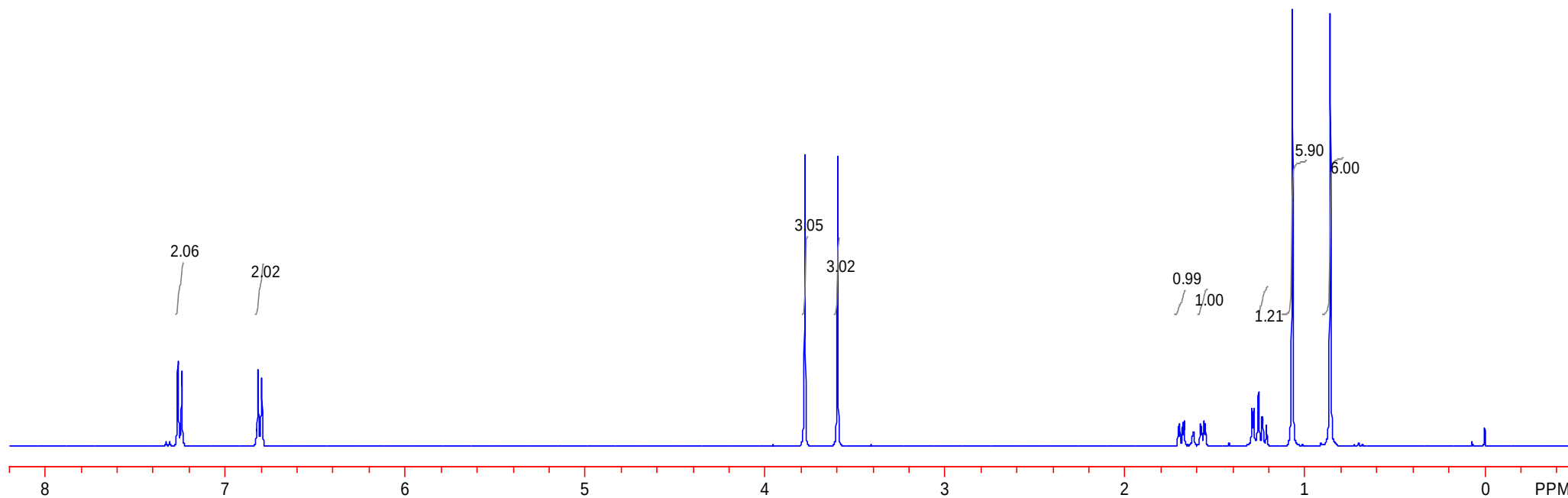
7.262
7.241

6.818
6.797

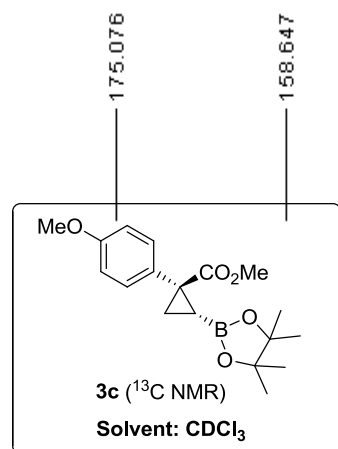
3.779
3.596

1.705
1.696
1.680
1.671
1.582
1.574
1.562
1.553
1.258
1.239
1.234
1.214
1.071
0.859

-0.000



S40



132.082
129.949

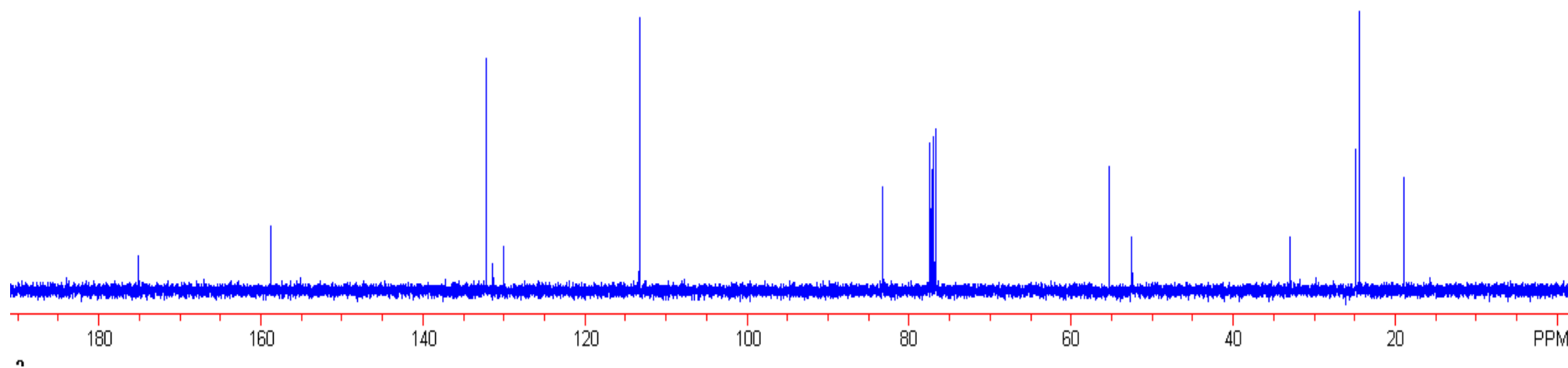
113.200

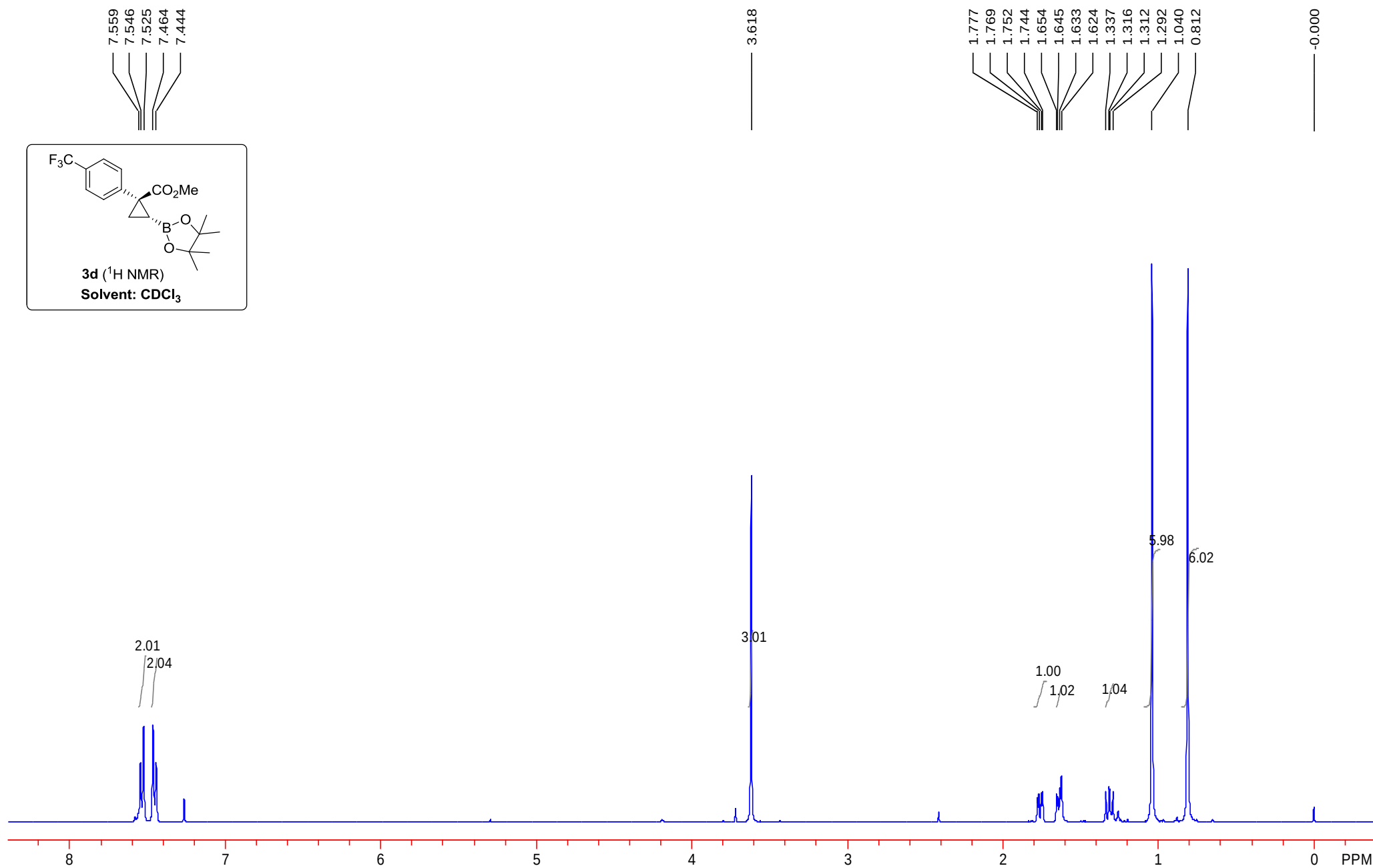
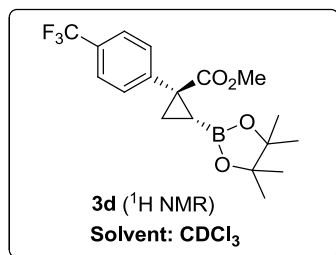
83.257
77.320
77.100
76.682

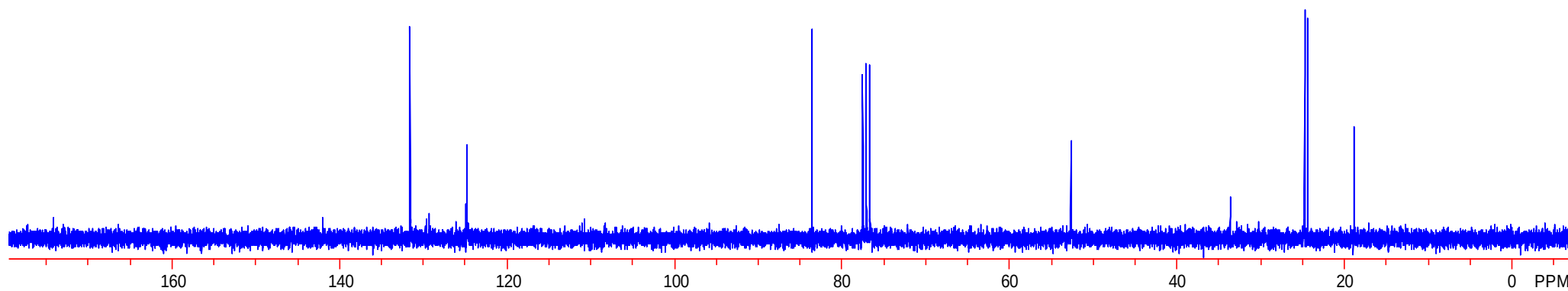
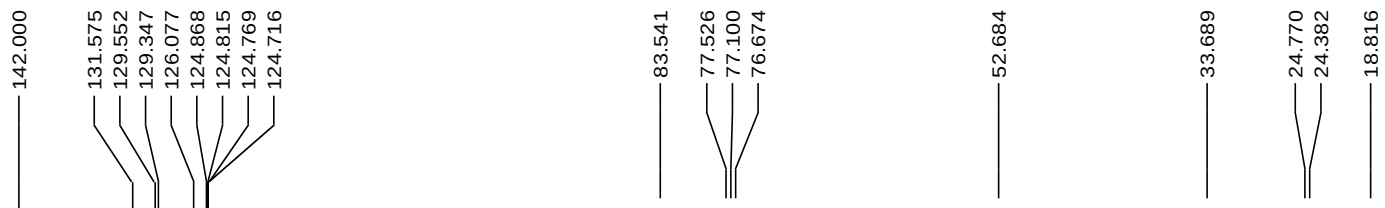
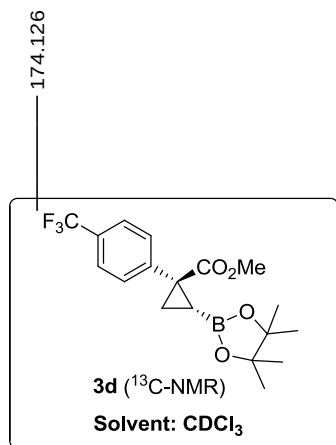
55.257
52.418

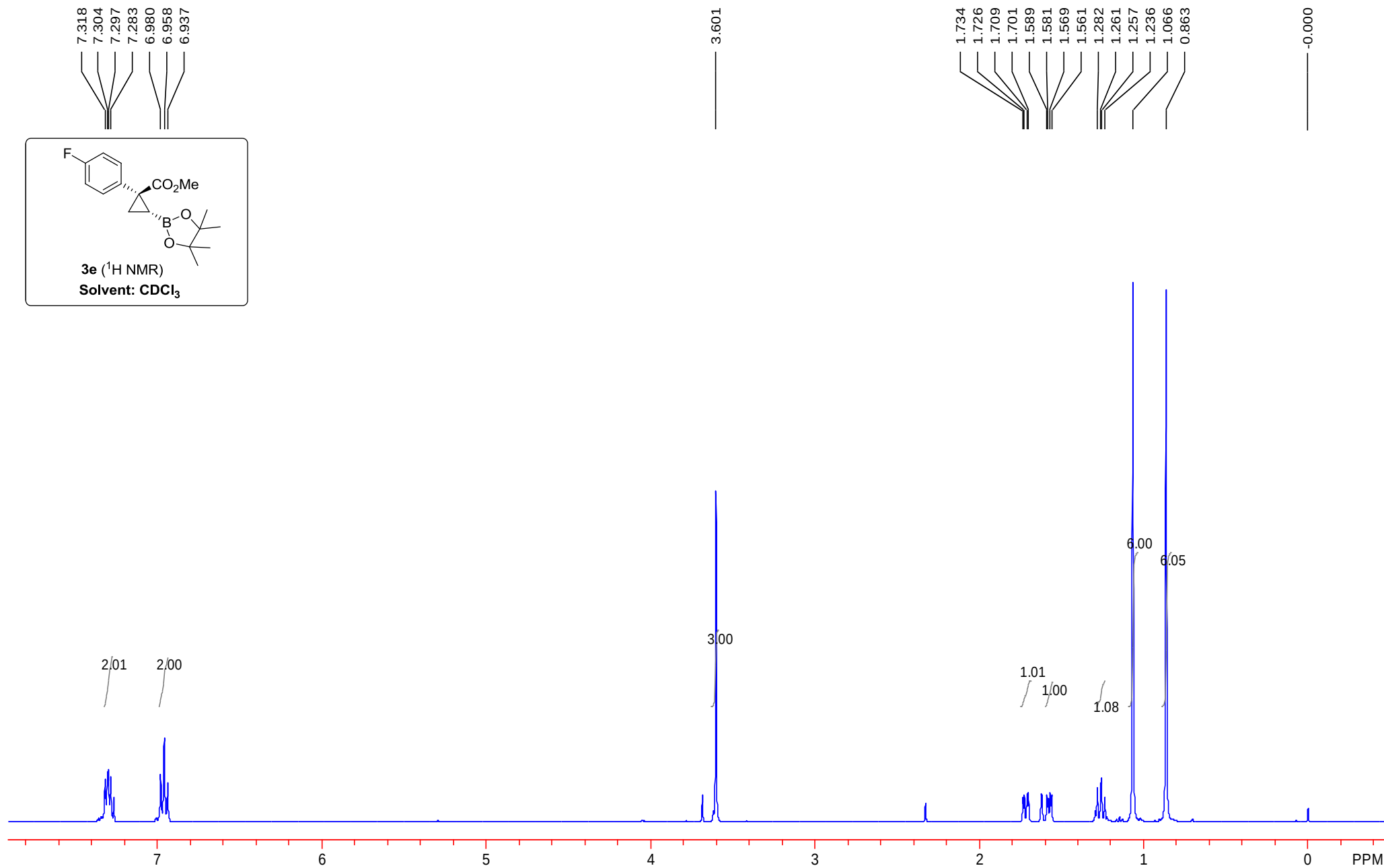
32.929

24.866
24.357
18.815

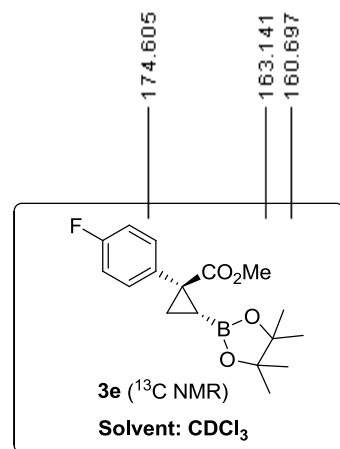








S44



133.623
133.593
132.697
132.613

114.666
114.453

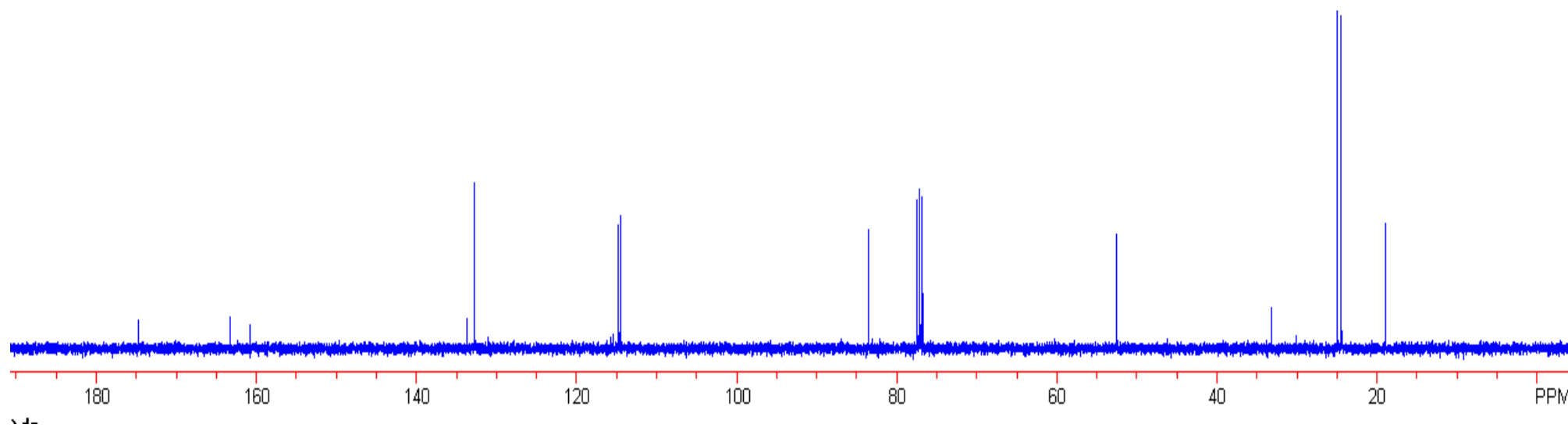
83.363
77.312
77.100
76.675

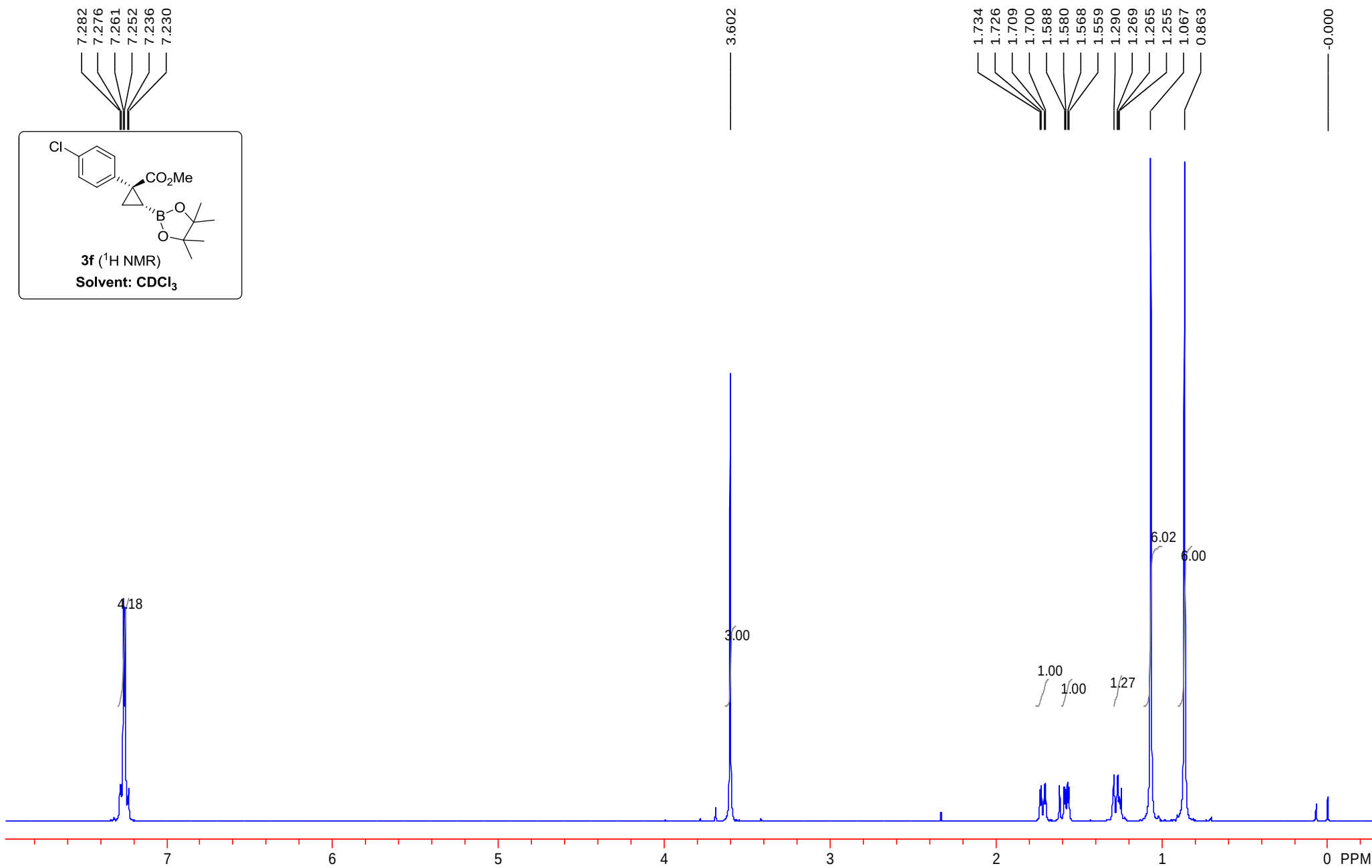
52.463

33.012

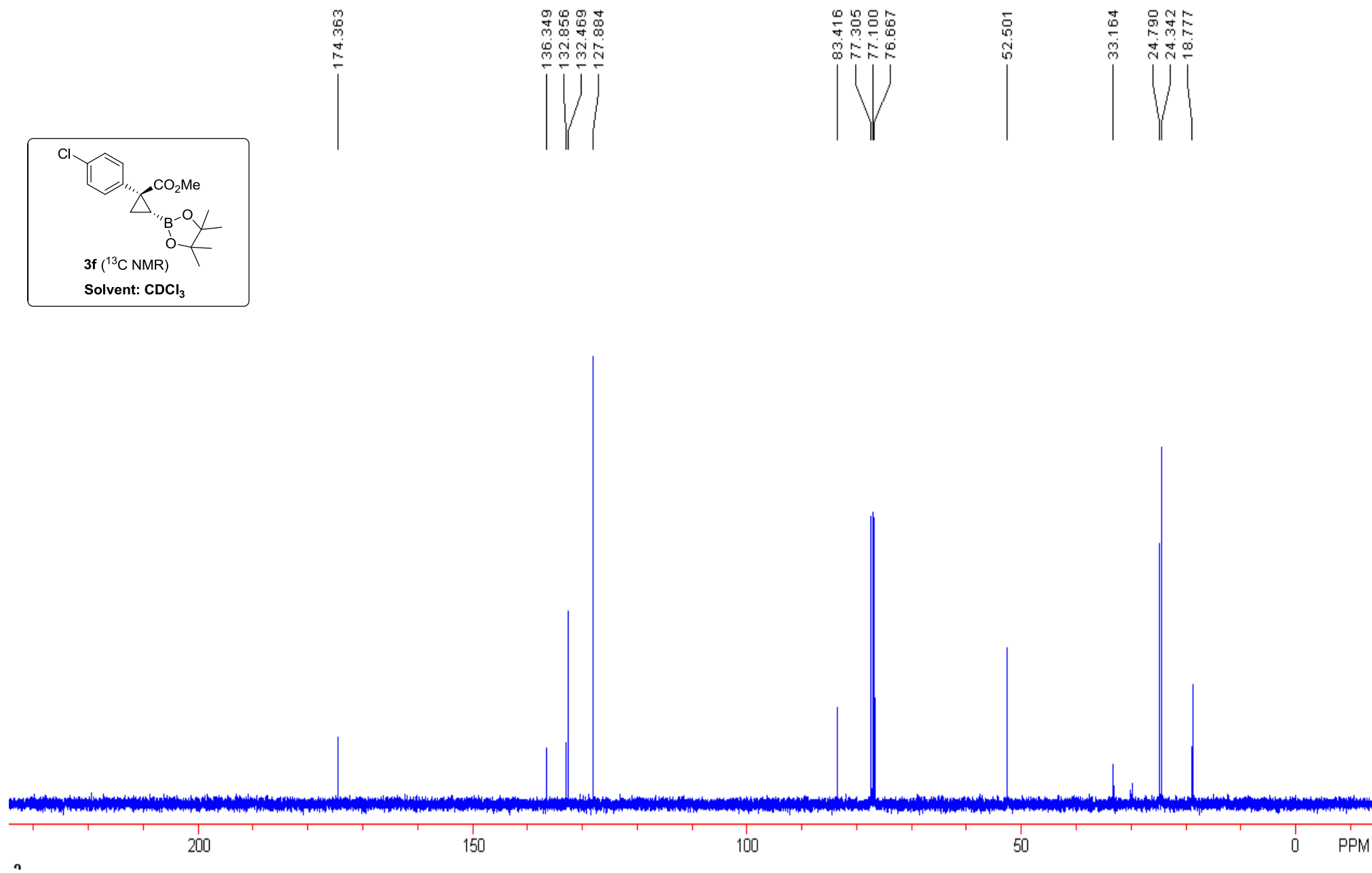
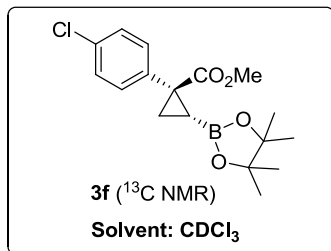
24.813
24.342

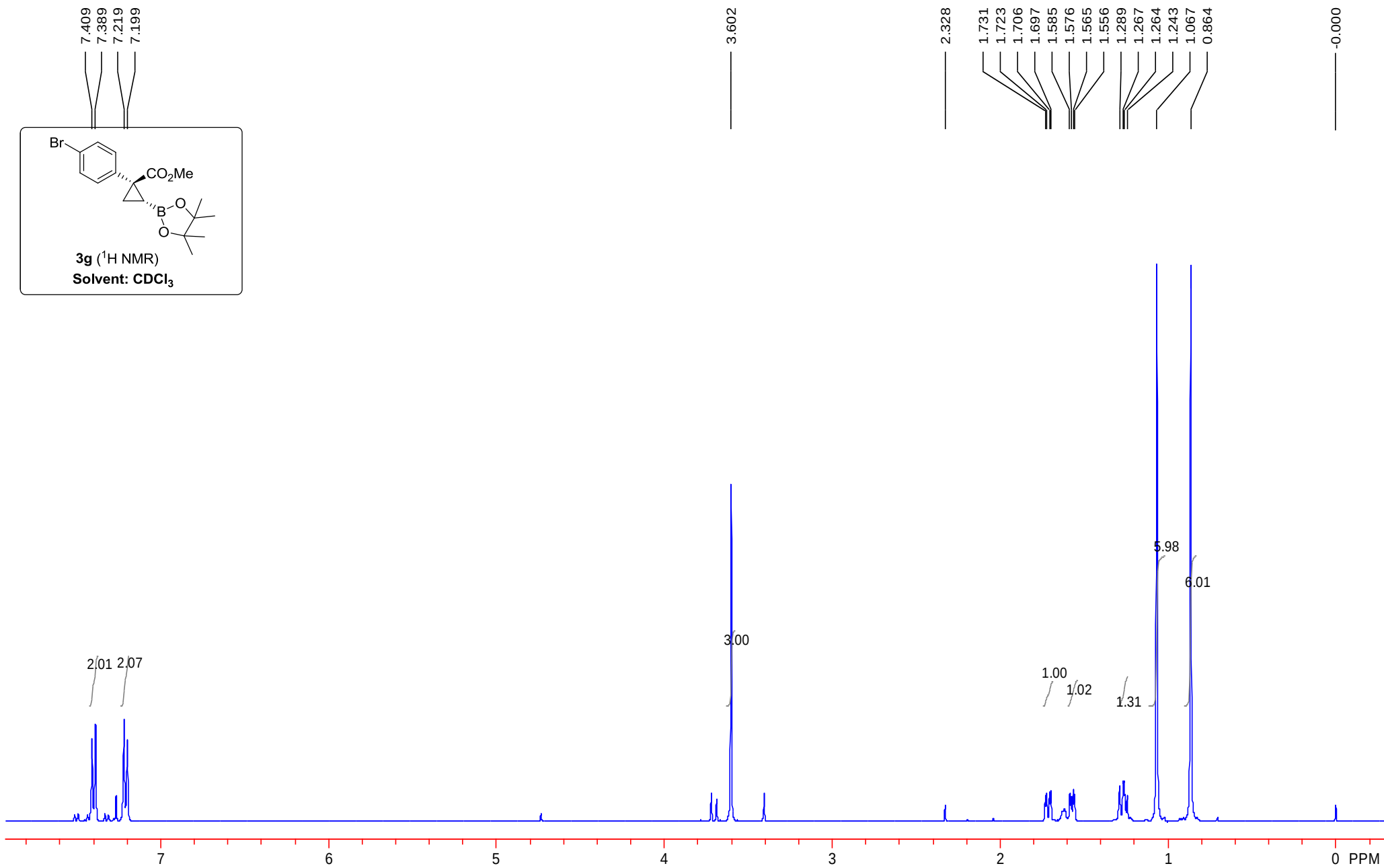
18.861



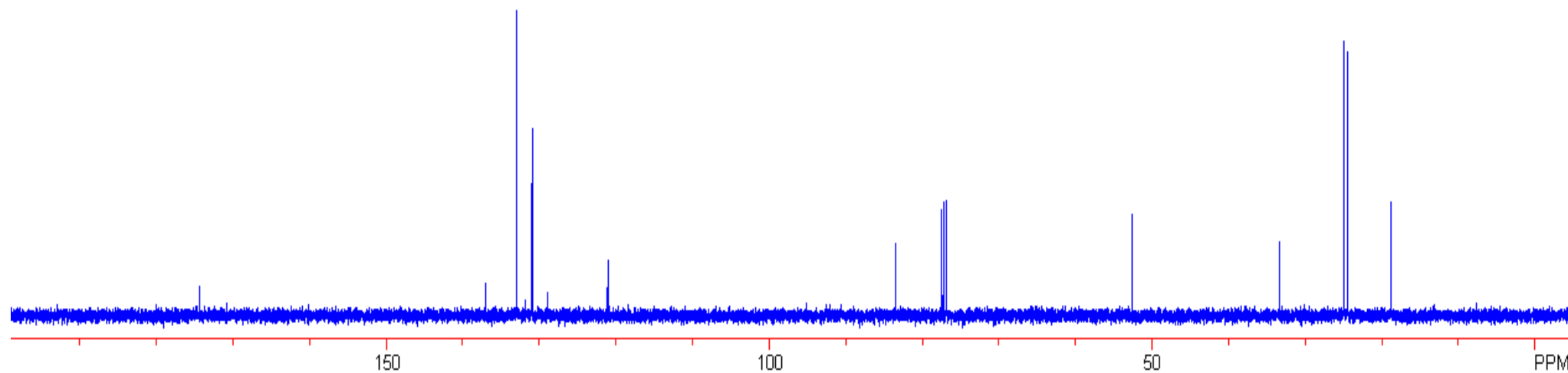
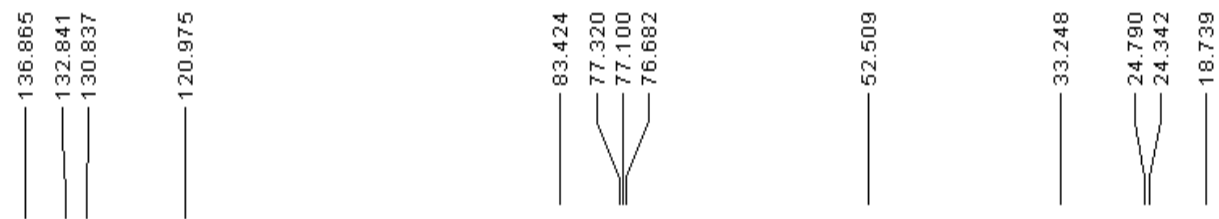
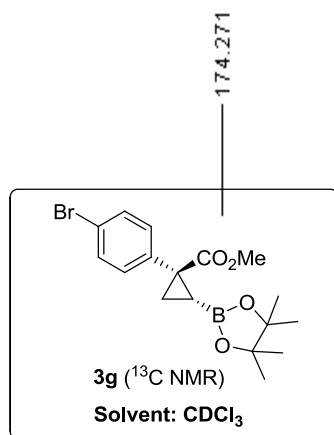


S46





S48



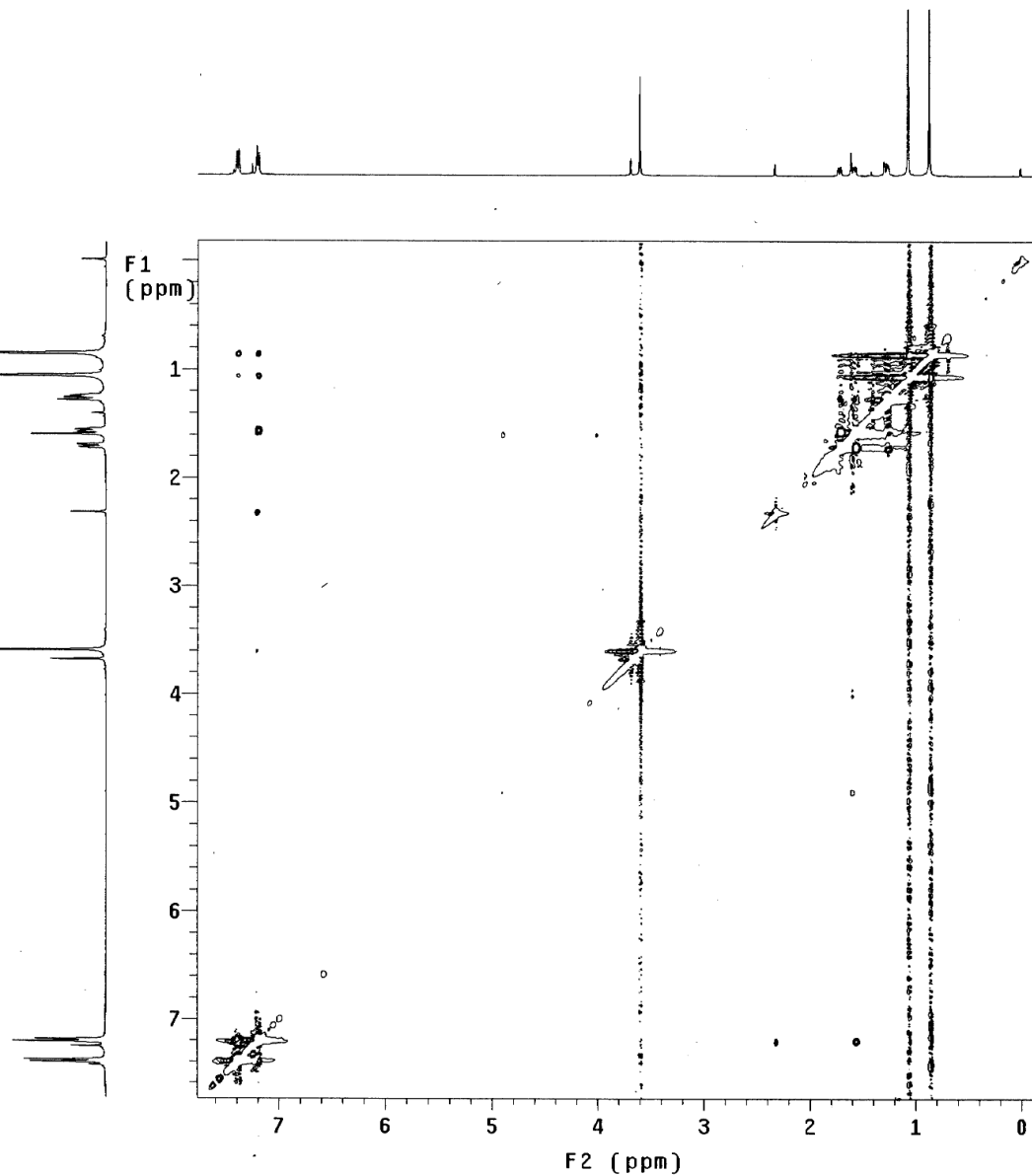
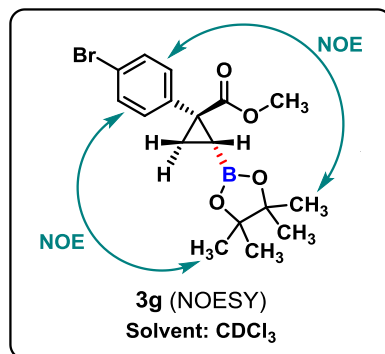
20135681qtb-br

Sample Name:
20135681qtb-br
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
20135681qtb-br_20140903_01
FidFile: NOESY_01

Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Sep 3 2014

Temp. 25.0 C / 298.1 K
Operator: sioc

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3858.0 Hz
2D Width 3858.0 Hz
8 repetitions
2 x 200 increments
OBSERVE H1, 399.6538482 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.048 sec
FT size 2048 x 2048
Total time 1 hr, 41 min

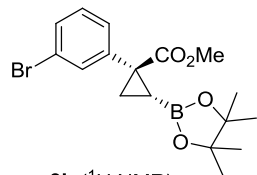


7.484
7.370
7.350
7.271
7.264
7.161
7.141
7.122

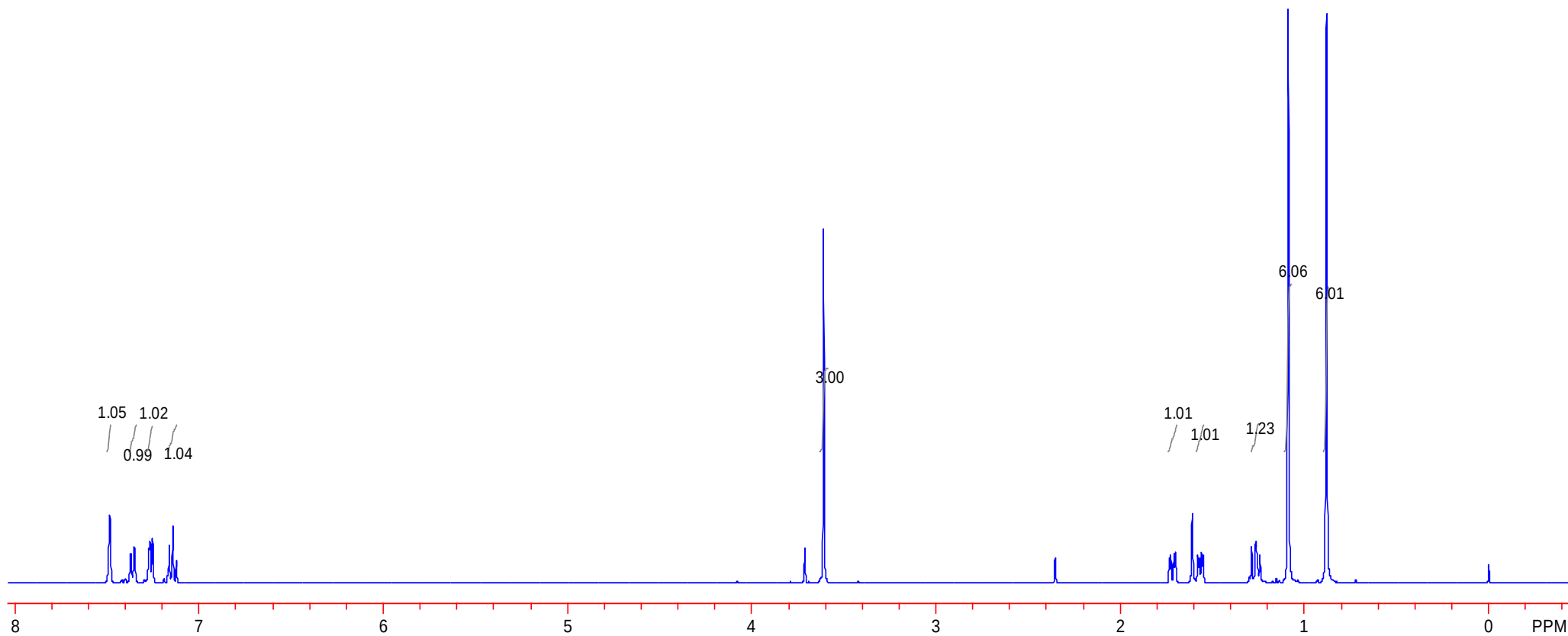
1.734
1.725
1.708
1.700
1.579
1.571
1.559
1.551
1.288
1.266
1.262
1.242
1.089
0.881

-0.000

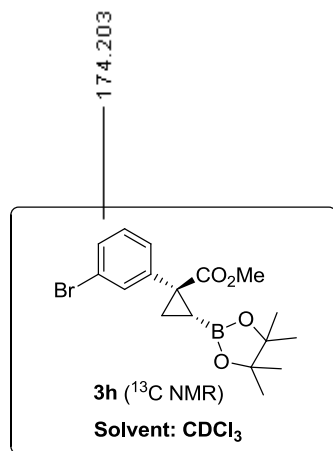
3.609



3h (^1H NMR)
Solvent: CDCl_3



S51



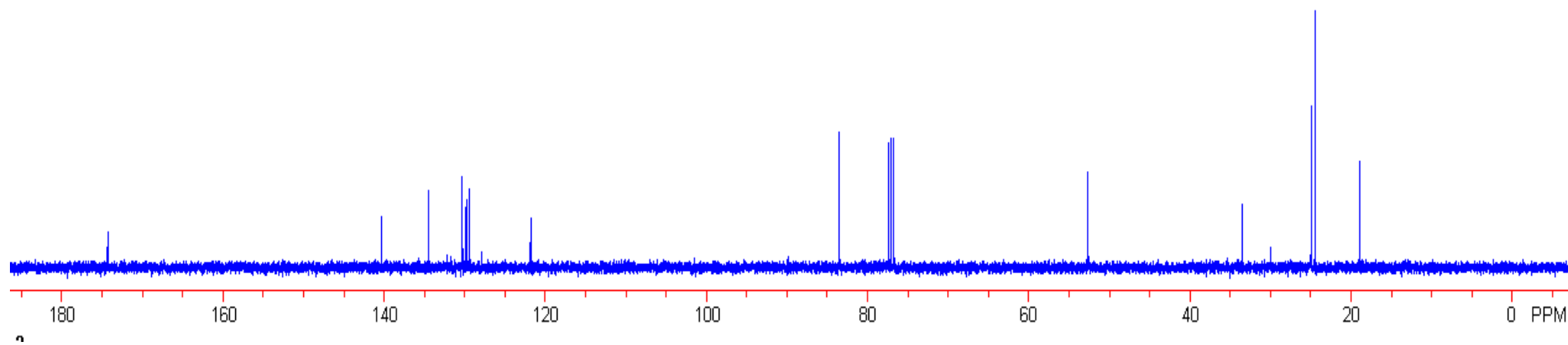
140.190
 134.337
 130.169
 129.698
 129.334
 121.711

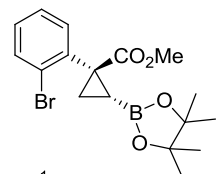
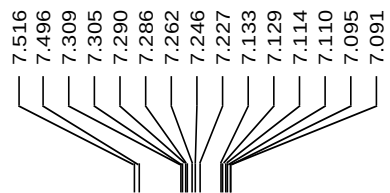
83.462
 77.312
 77.100
 76.682

52.555

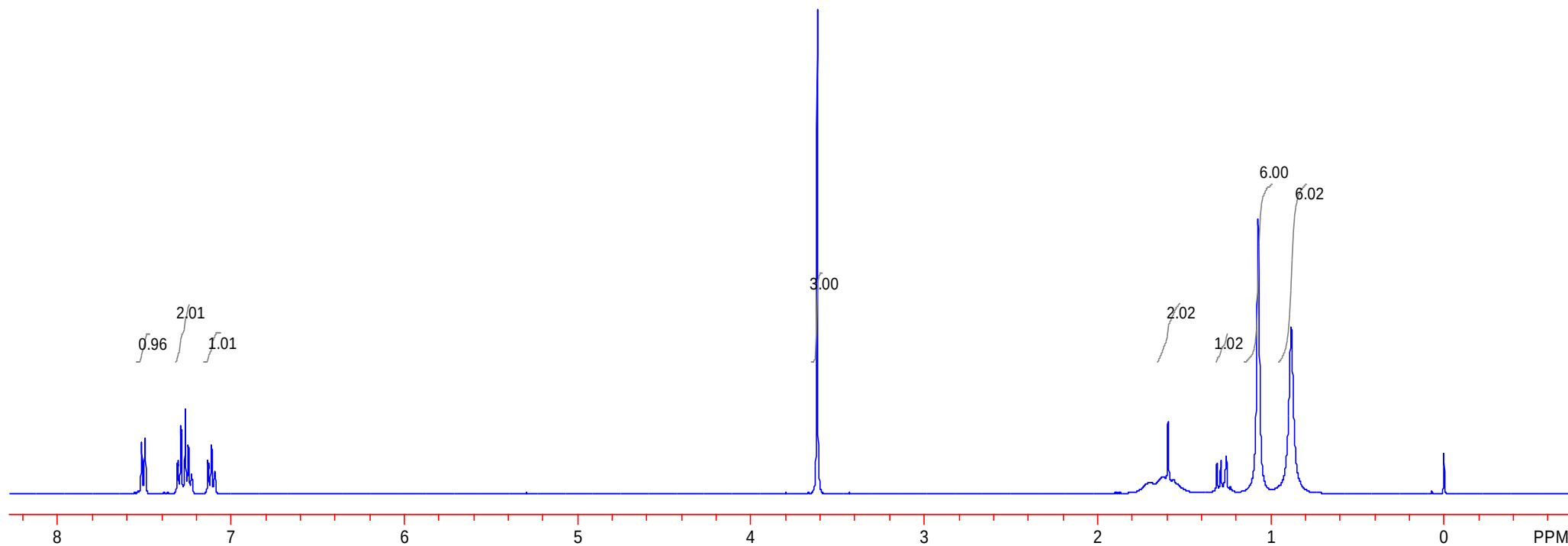
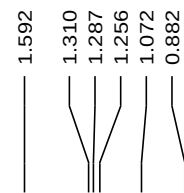
33.483

24.866
 24.418
 18.846

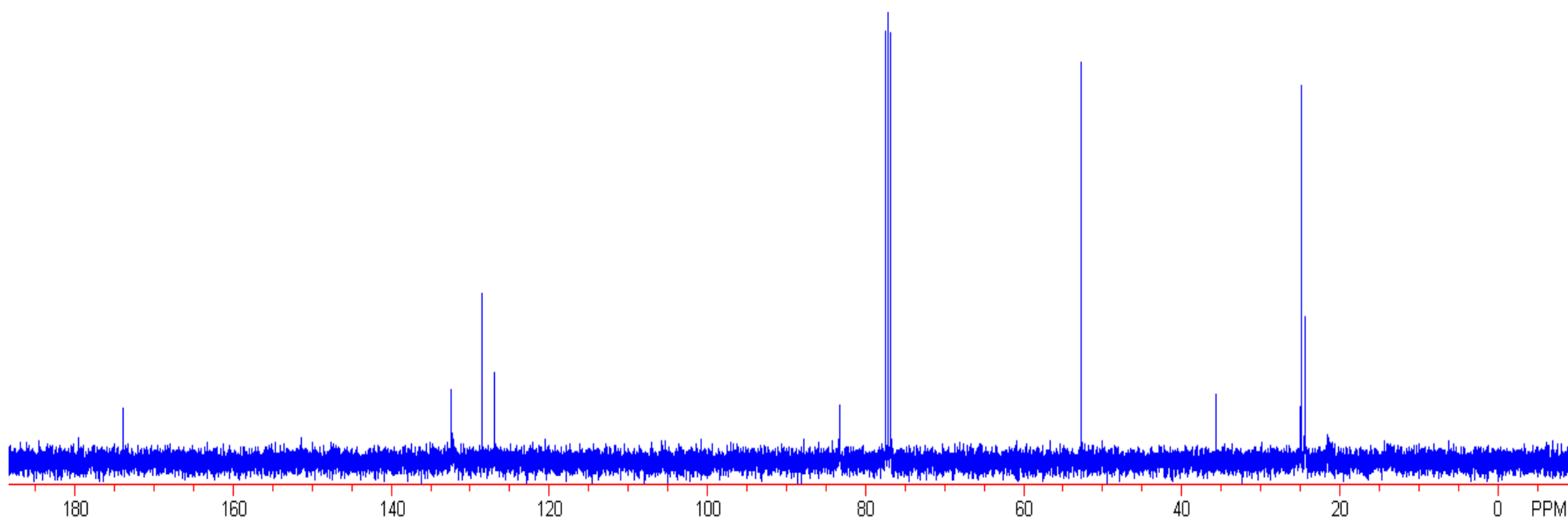
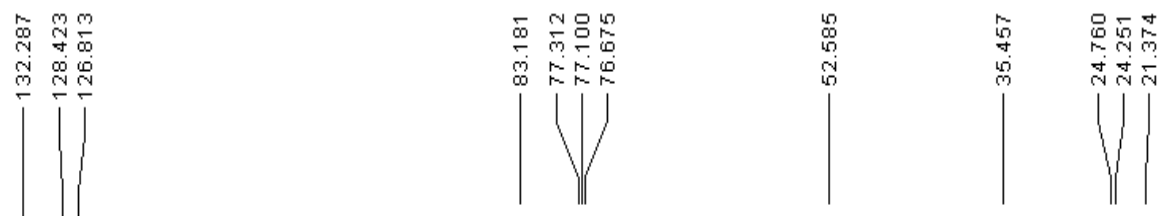
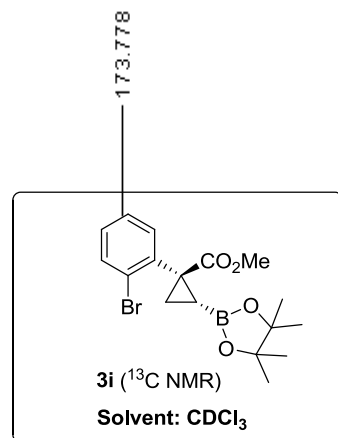


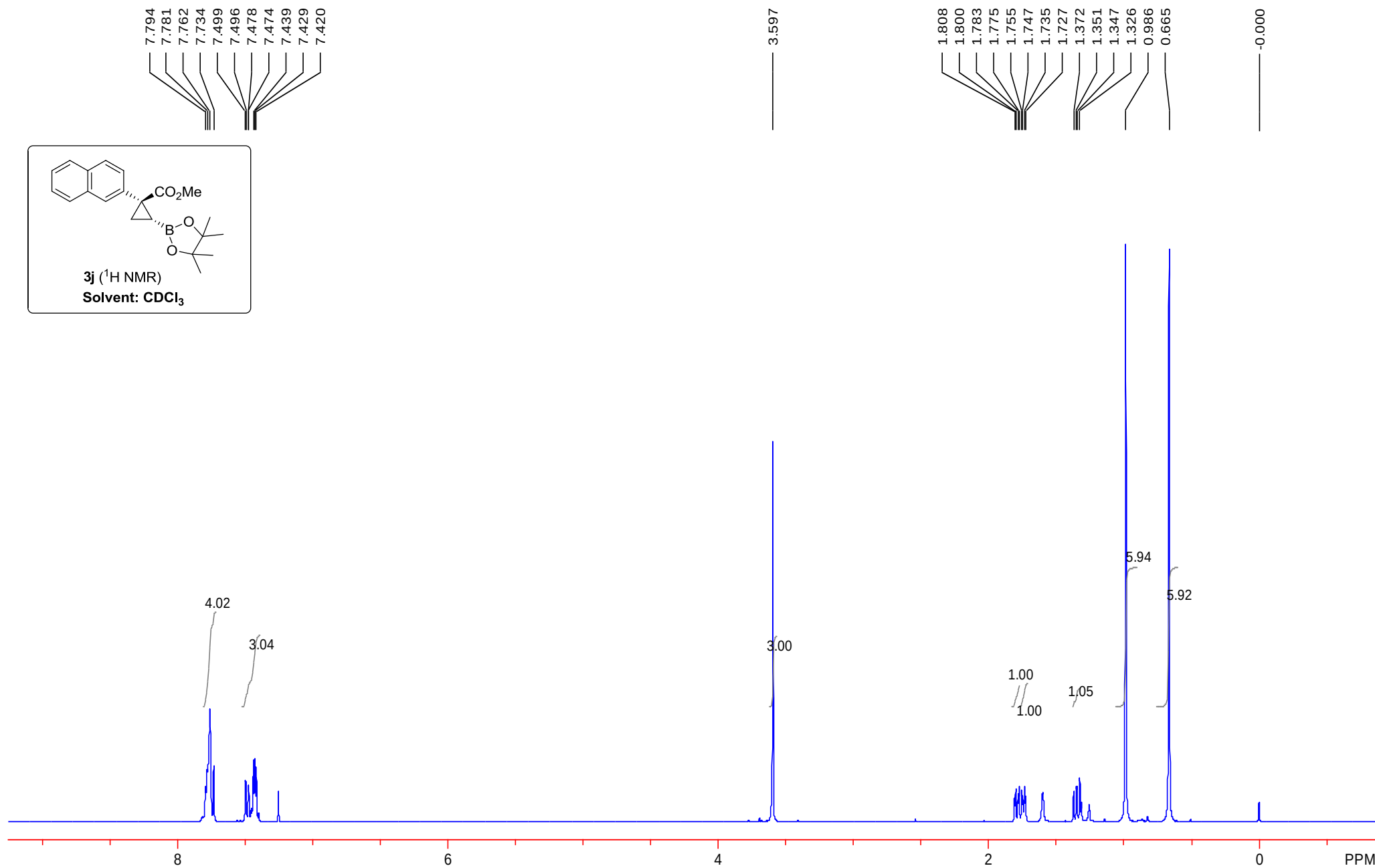
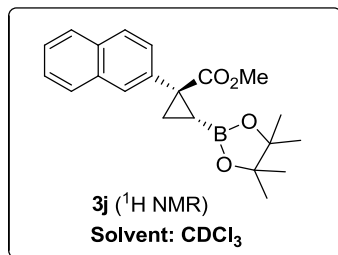


3i (^1H NMR)
Solvent: CDCl_3

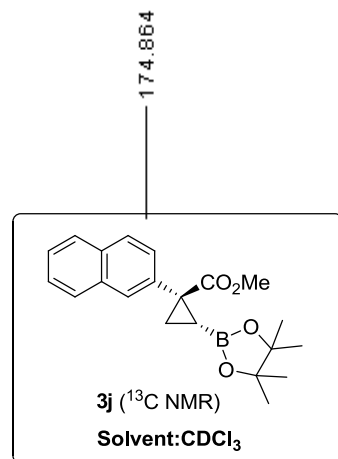


S53





S55



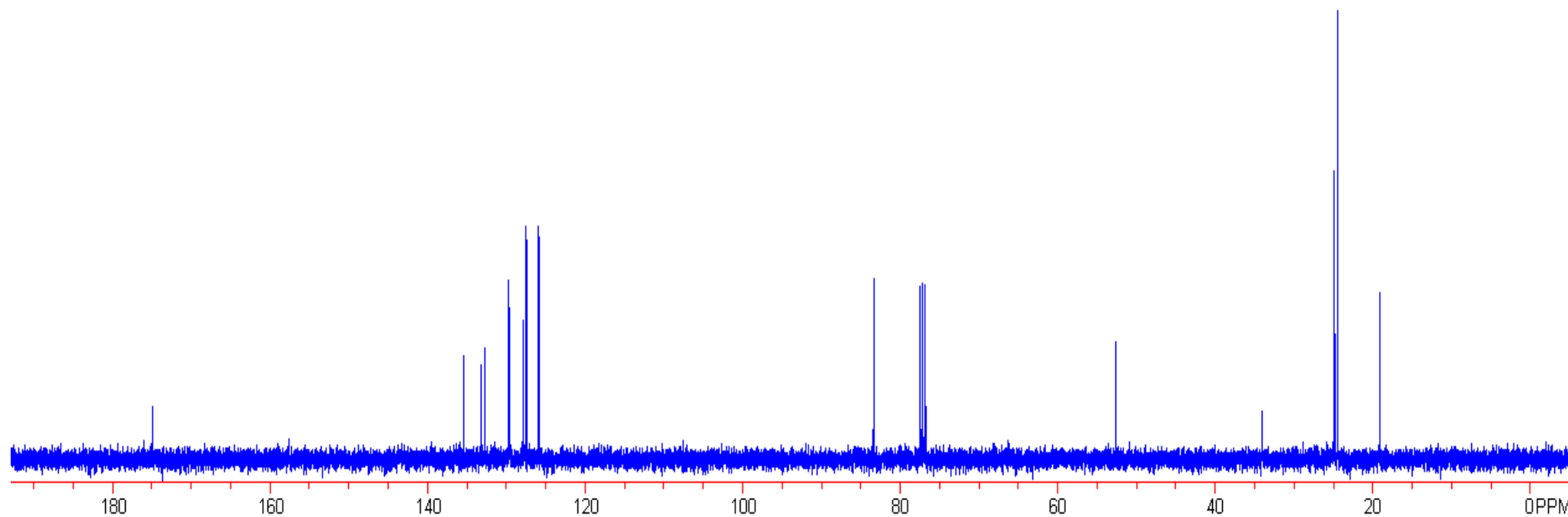
135.278
 133.046
 132.613
 129.577
 129.432
 127.762
 127.496
 127.246
 125.803
 125.651

83.280
 77.328
 77.100
 76.690

52.471

33.923

24.729
 24.266
 18.944



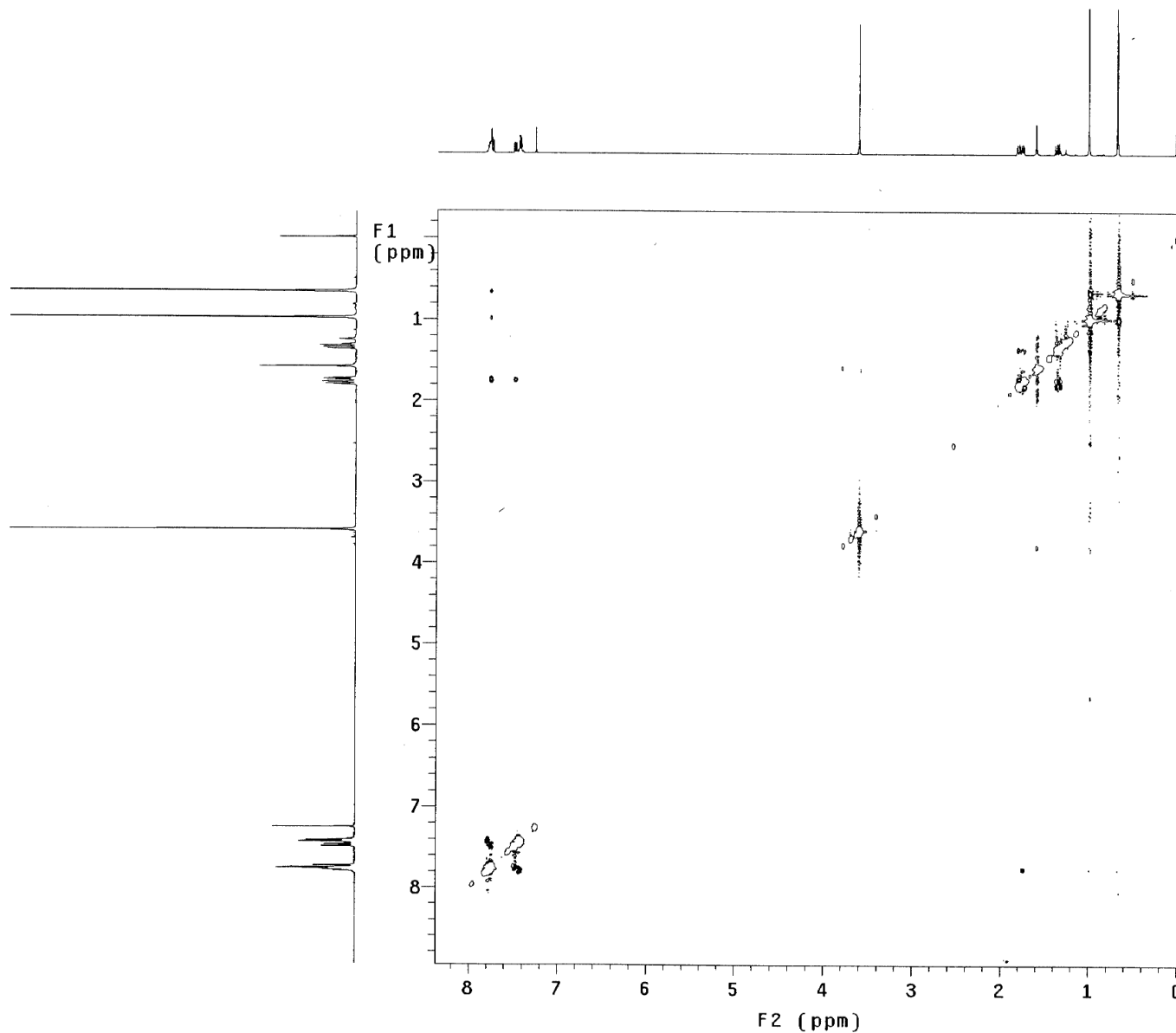
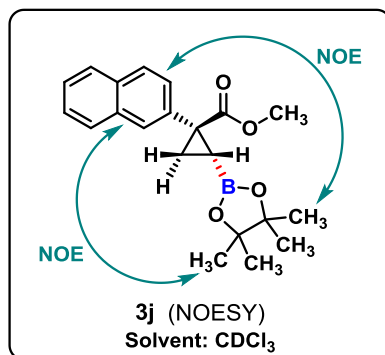
20135681qtb-cf3

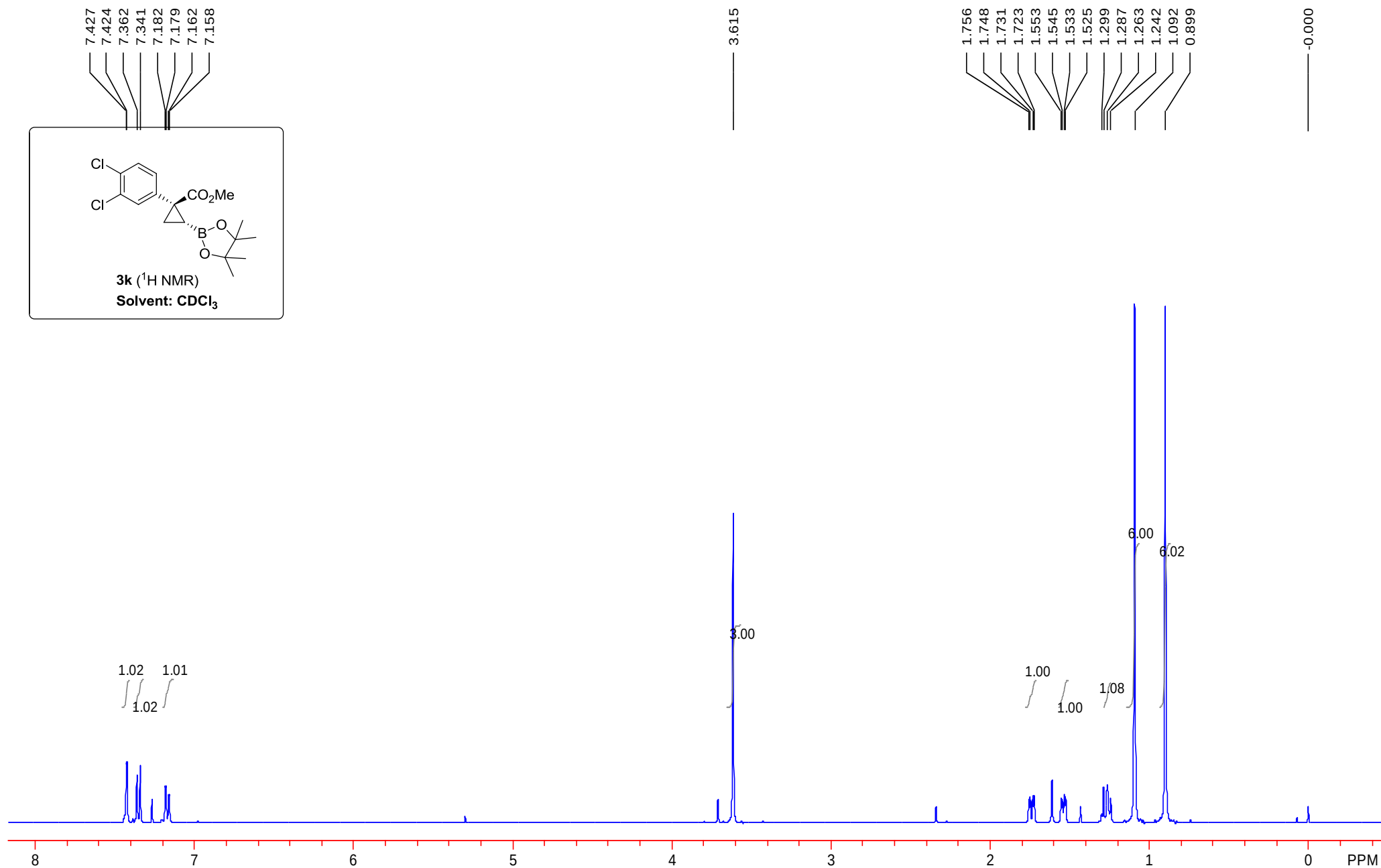
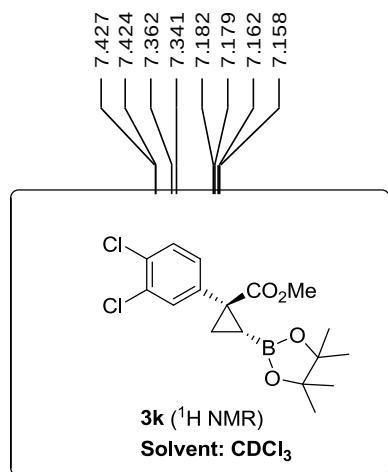
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20135681qtb-cf3
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
20135681qtb-cf3_20140904_01
FidFile: NOESY_01

Pulse Sequence: NOESY
Solvent: cdc13
Data collected on: Sep 4 2014

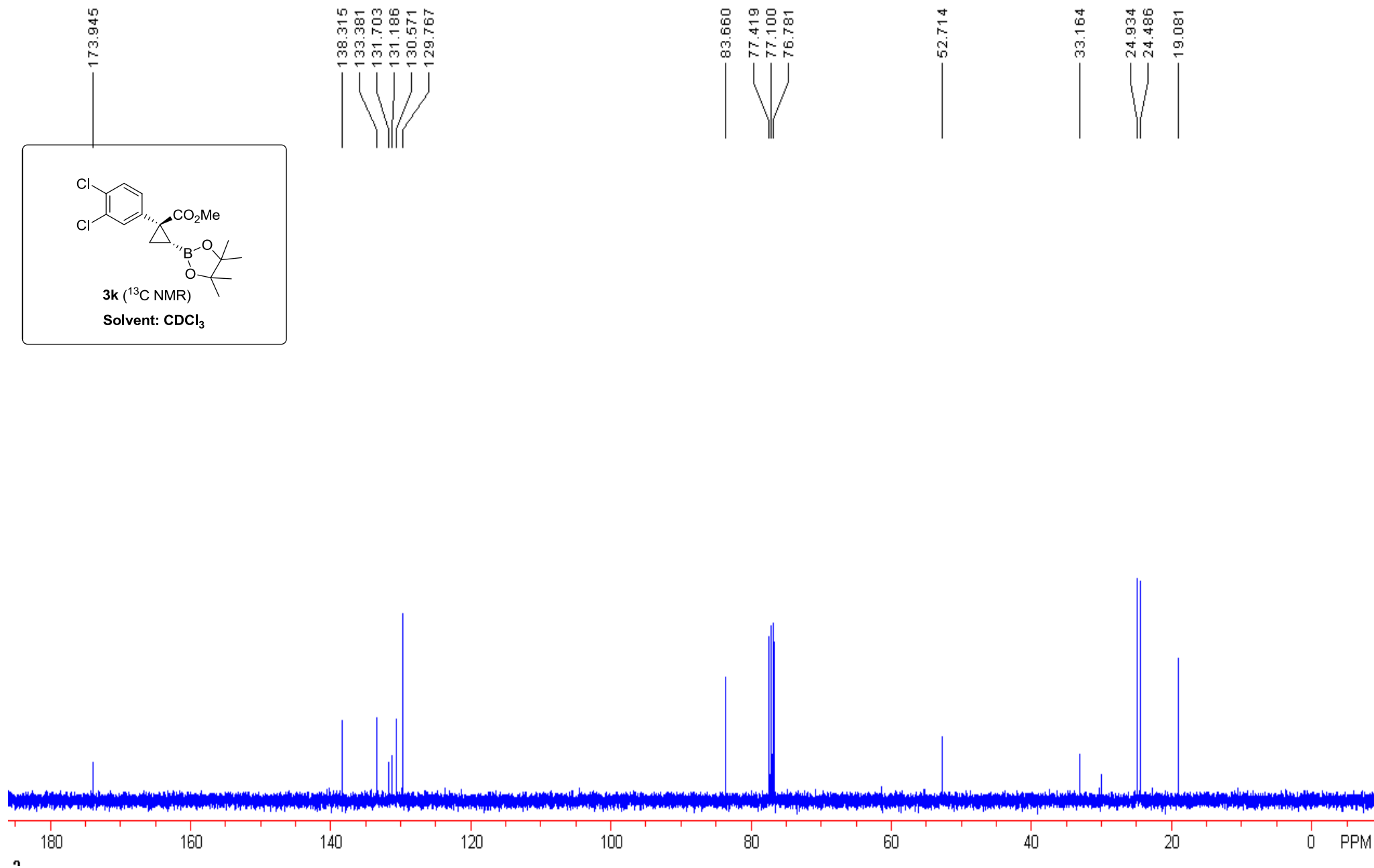
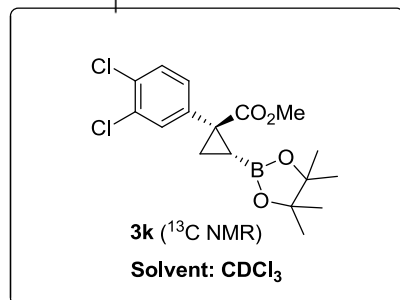
Temp. 25.0 C / 298.1 K
Operator: sioc

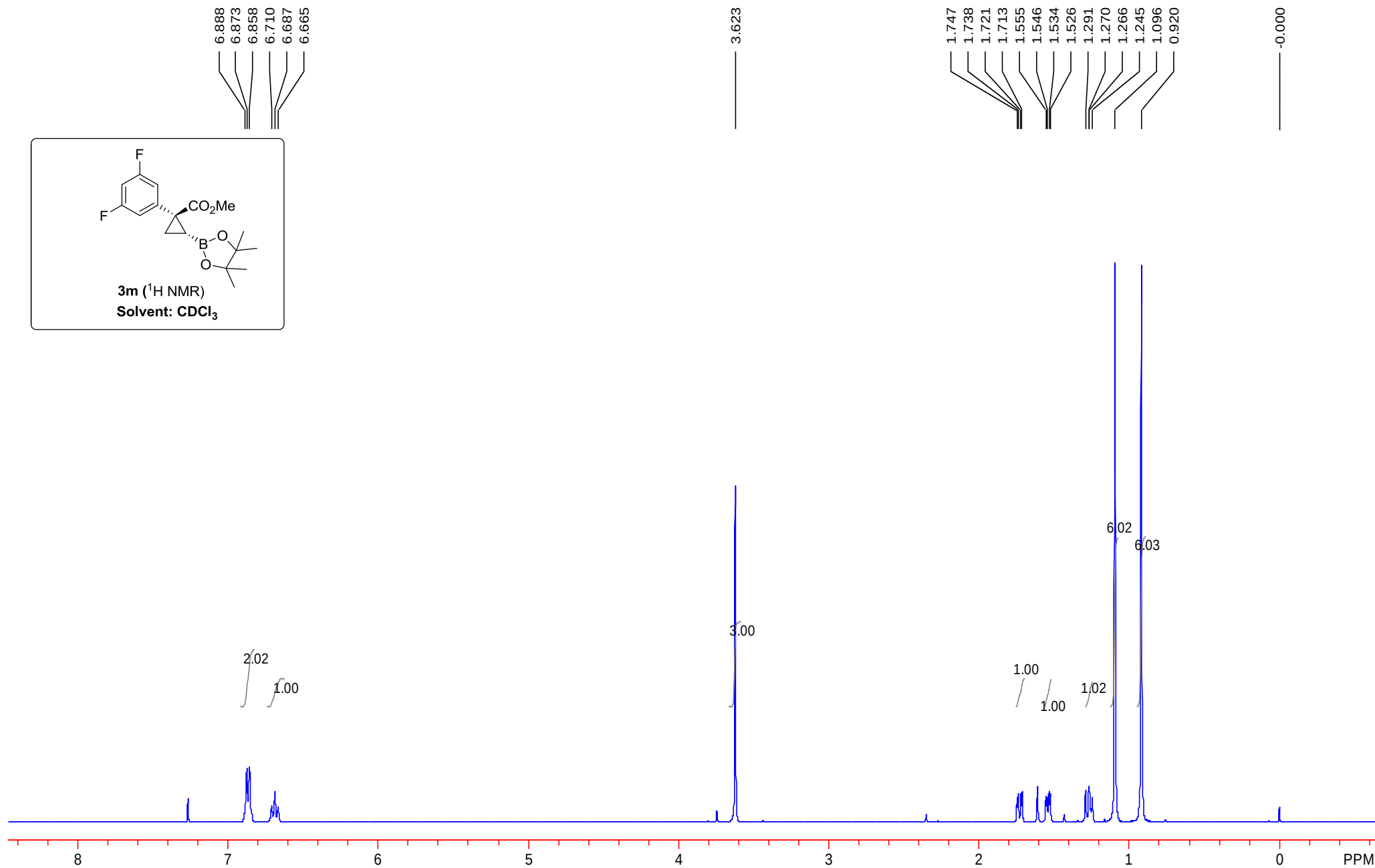
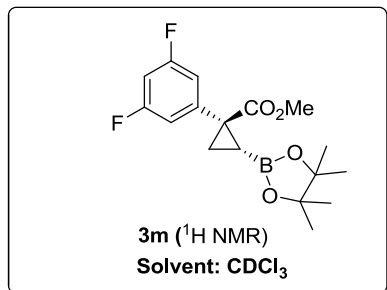
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4921.3 Hz
2D Width 4921.3 Hz
8 repetitions
2 x 256 increments
OBSERVE H1, 399.6538482 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.037 sec
FT size 2048 x 2048
Total time 2 hr, 9 min



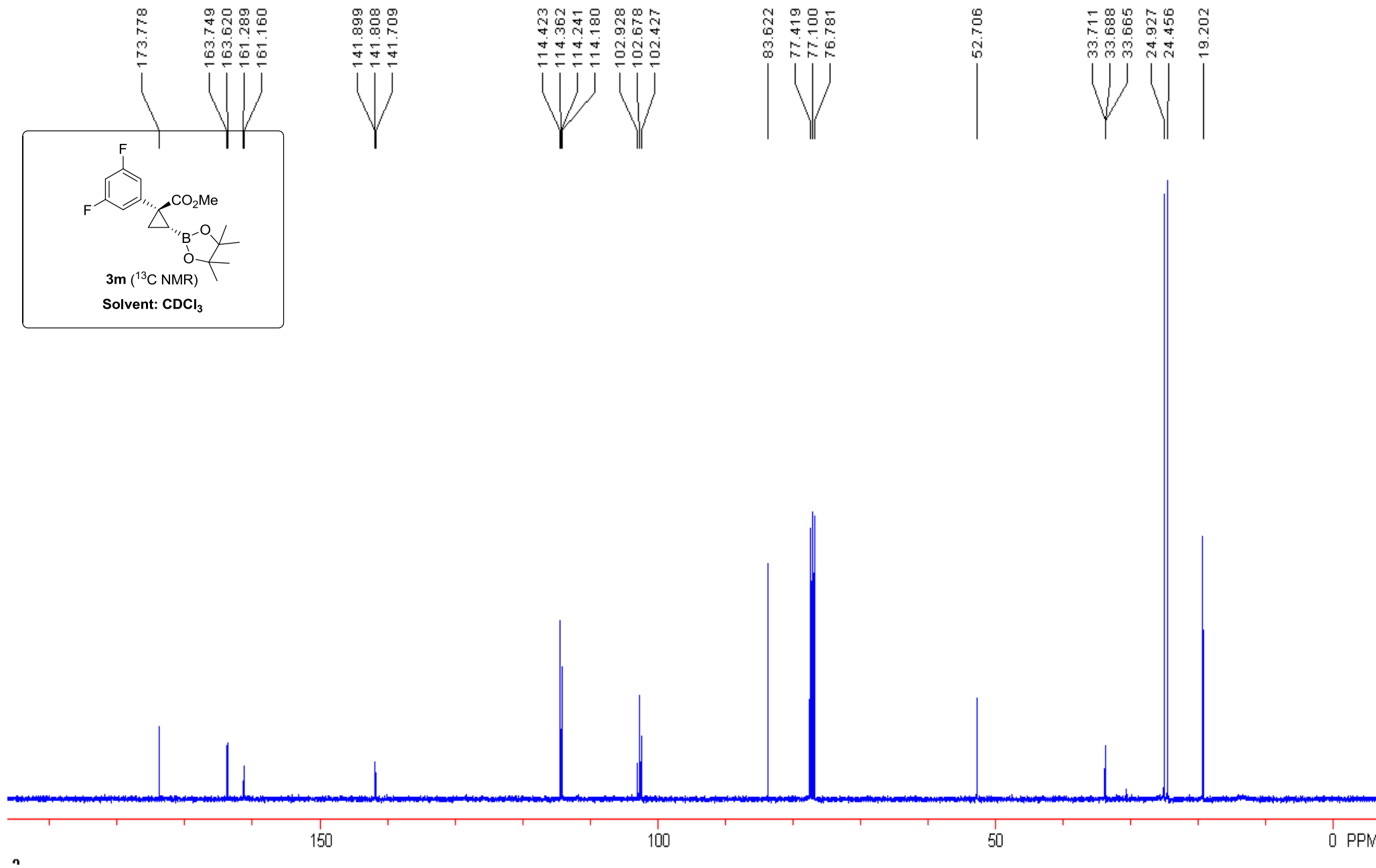


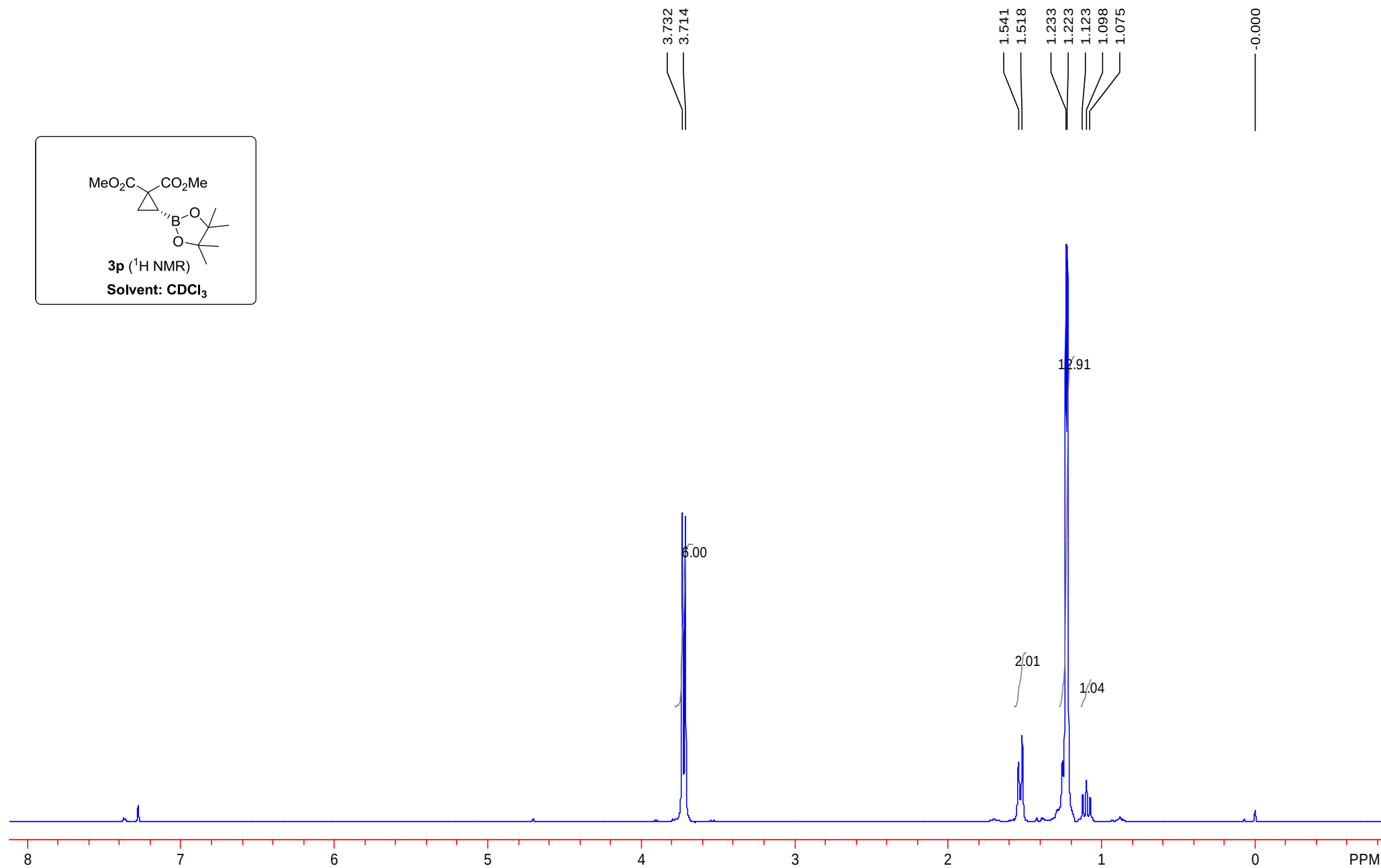
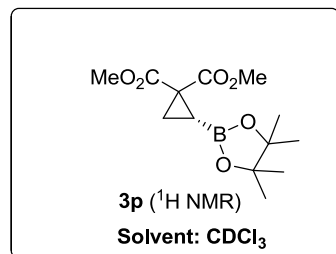
S58



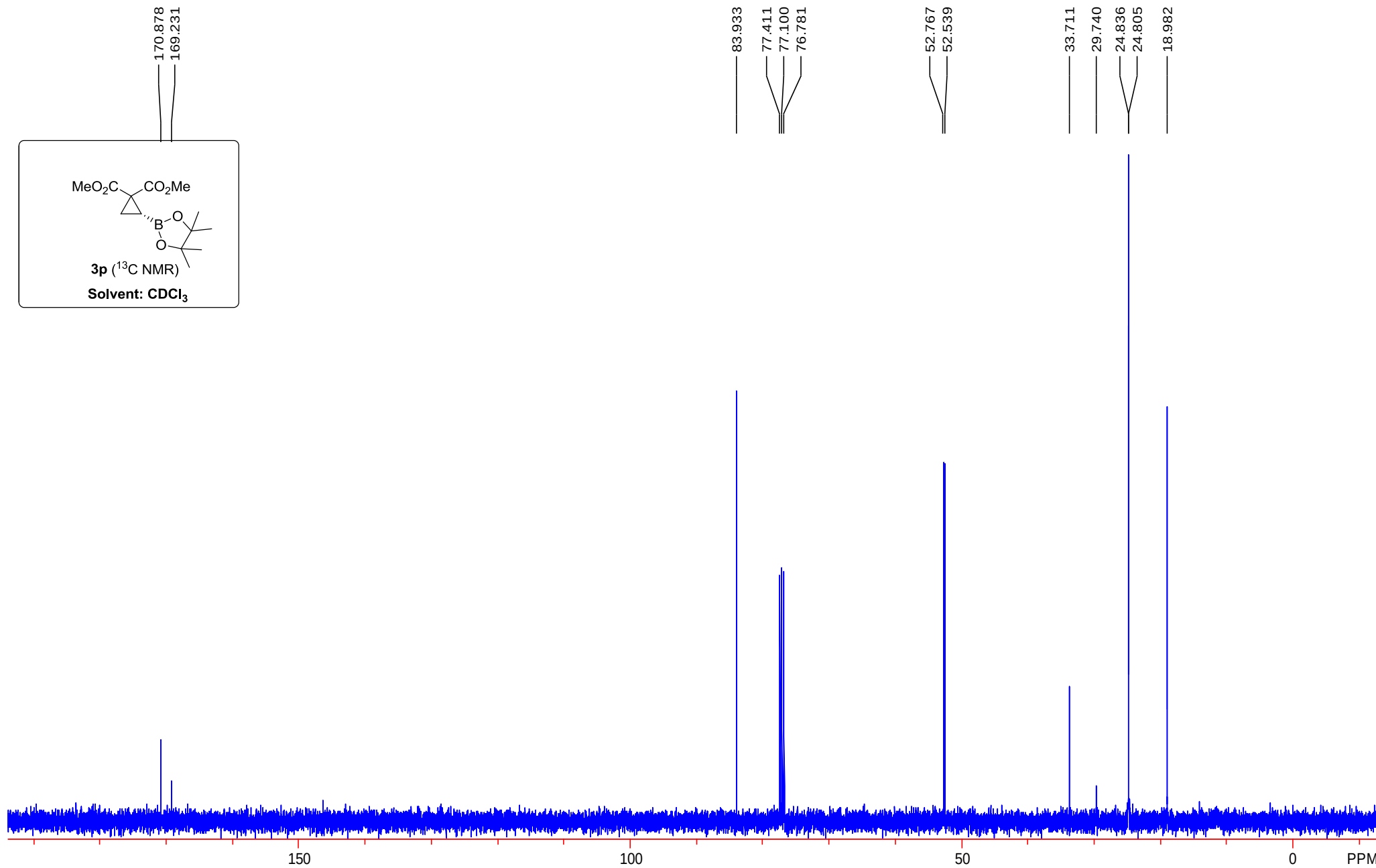
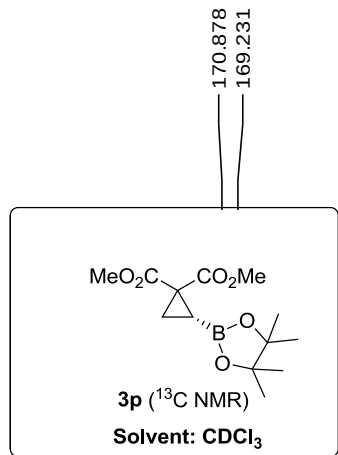


S60





S62



S63

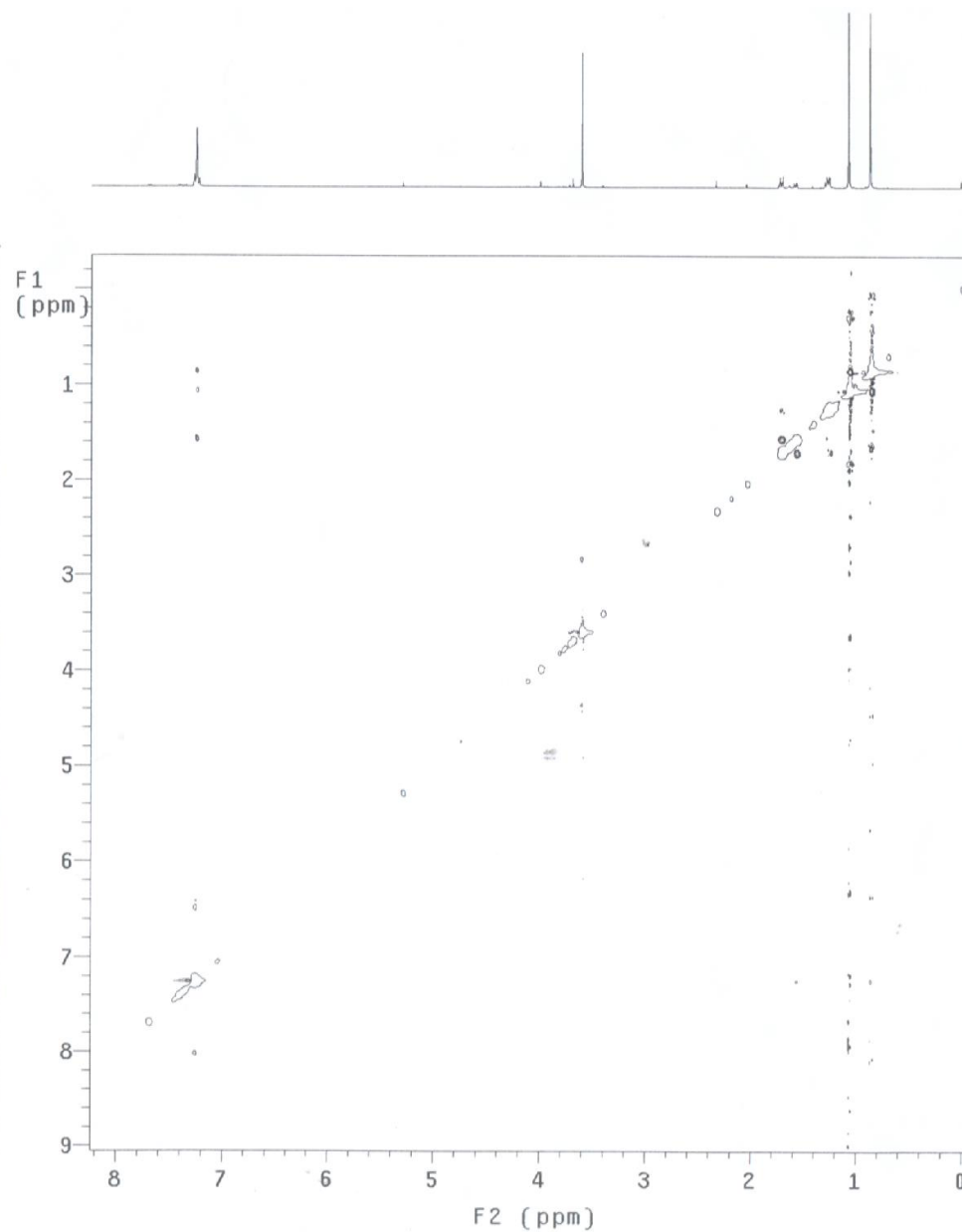
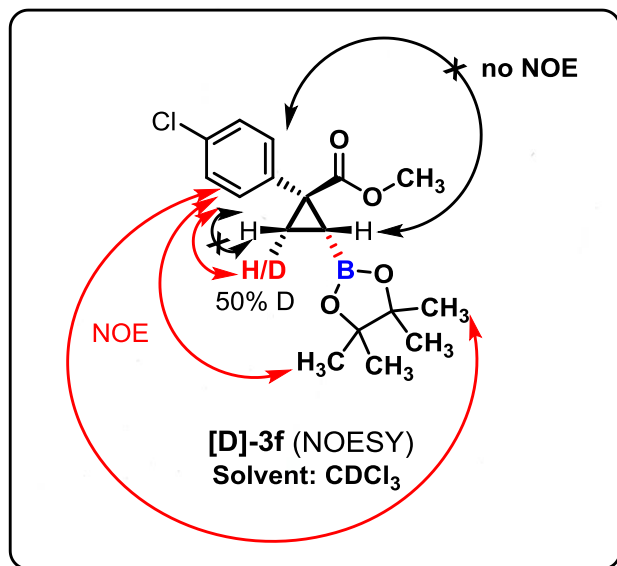
2012442tb06-55

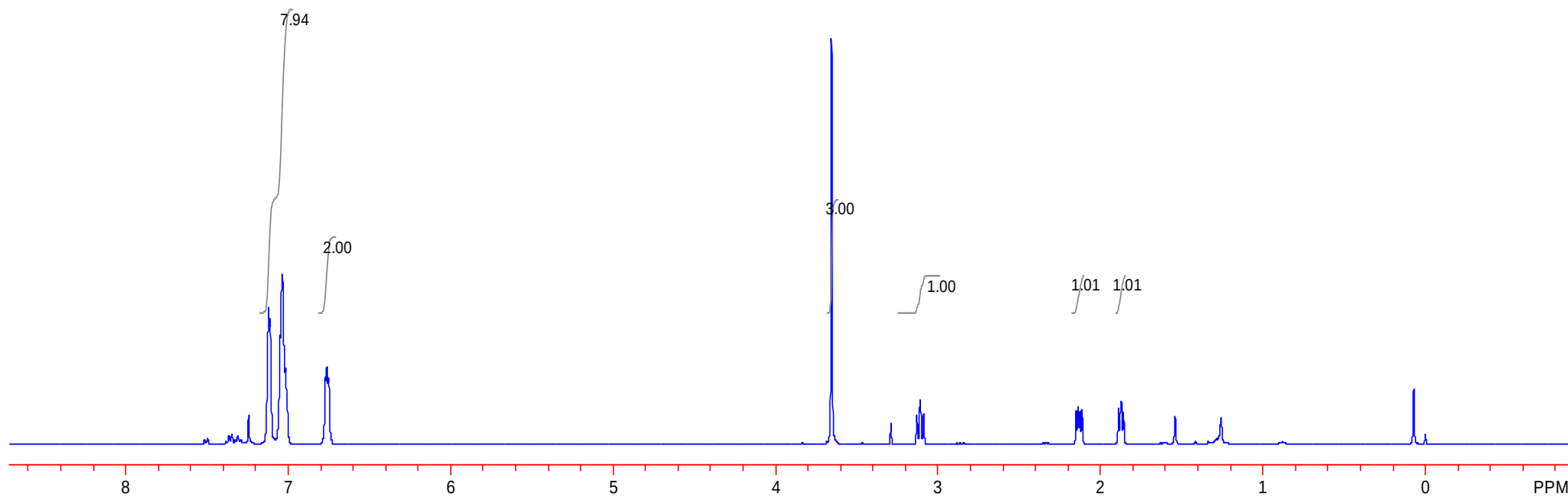
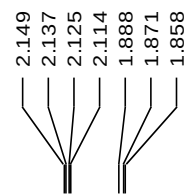
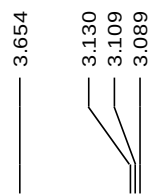
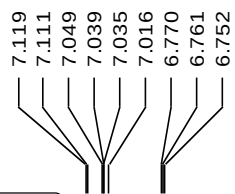
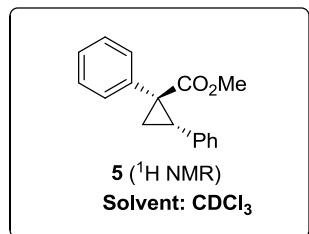
Sample Name:
2012442tb06-55
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012442tb06-55_20140516_01
FidFile: NOESY_01

Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: May 16 2014

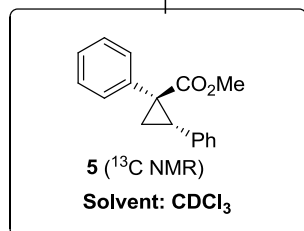
Temp. 25.0 C / 298.1 K
Operator: sioc

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 5458.5 Hz
2D Width 5458.5 Hz
8 repetitions
2 x 200 increments
OBSERVE H1, 399.6556605 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.034 sec
FT size 2048 x 2048
Total time 1 hr, 40 min





S65



136.418
134.793
131.999
128.400
128.104
127.755
127.087
126.366

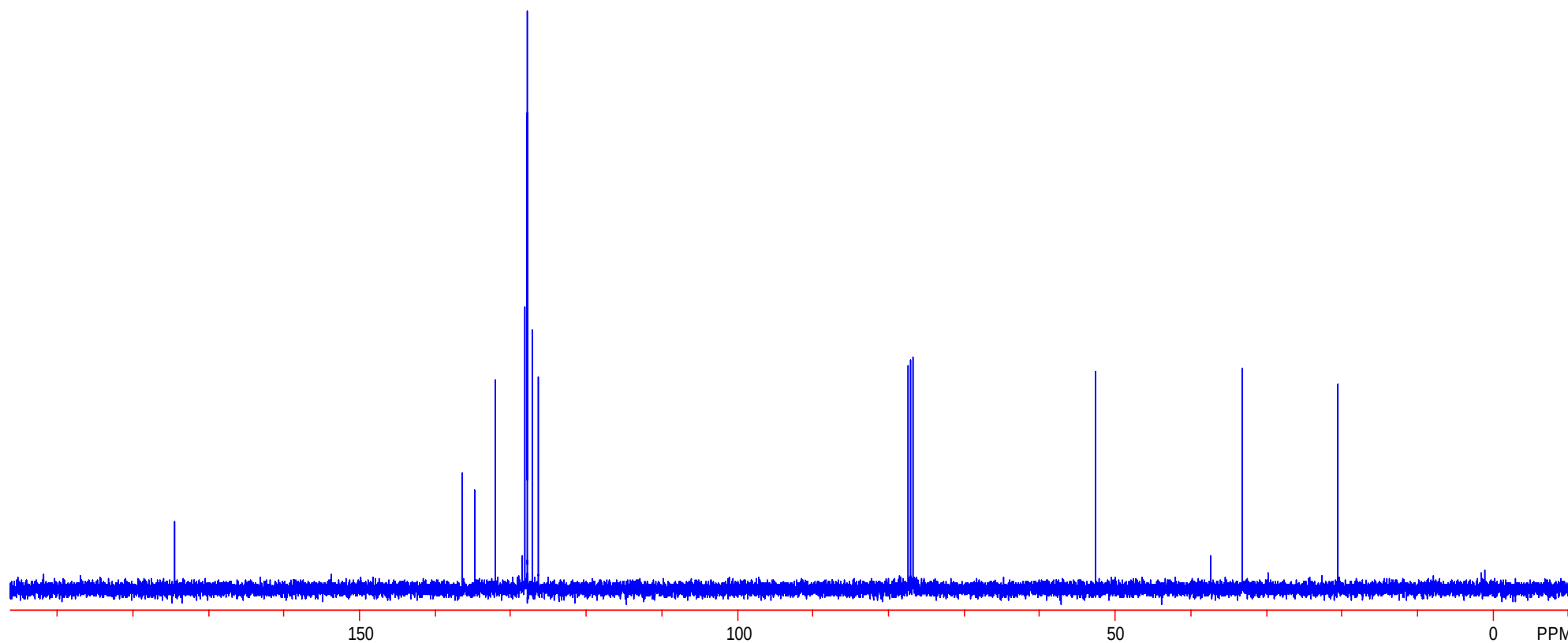
77.419
77.100
76.781

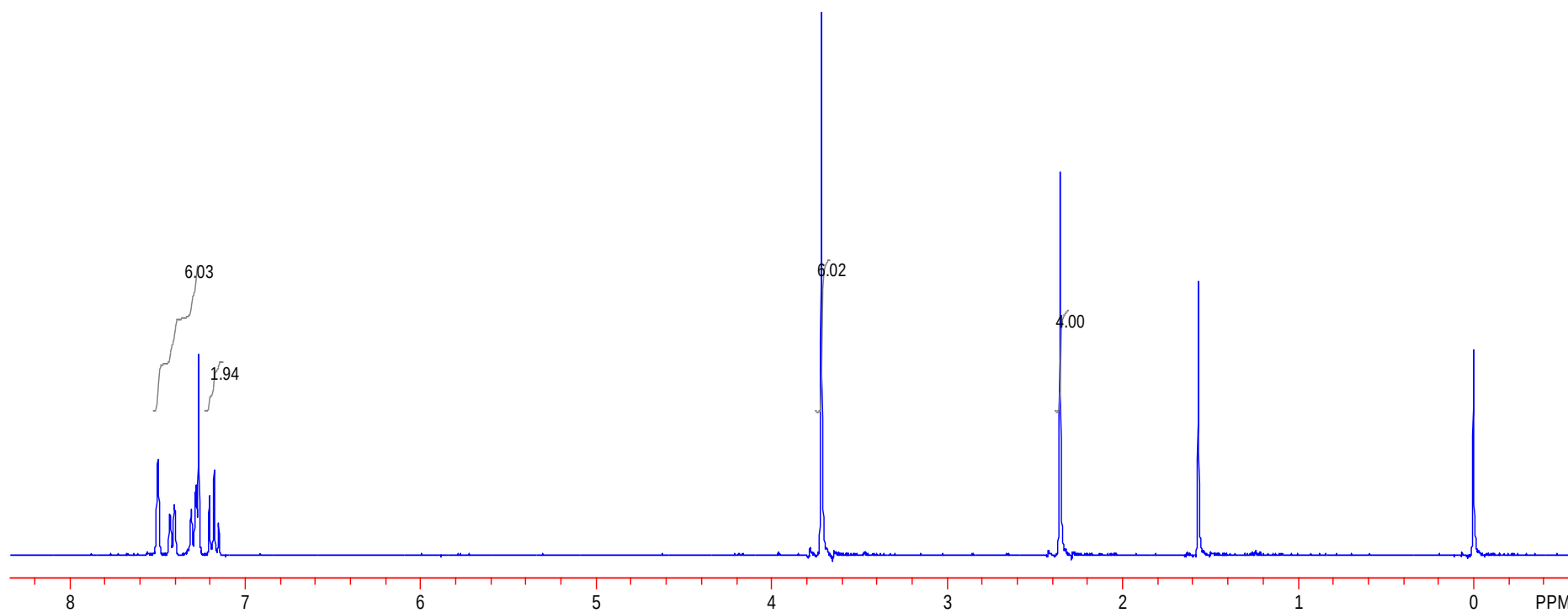
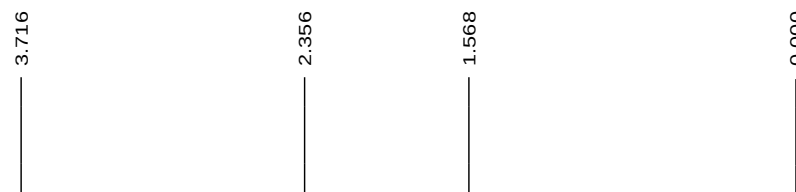
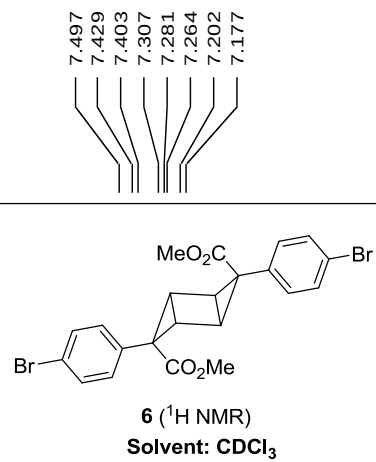
52.684

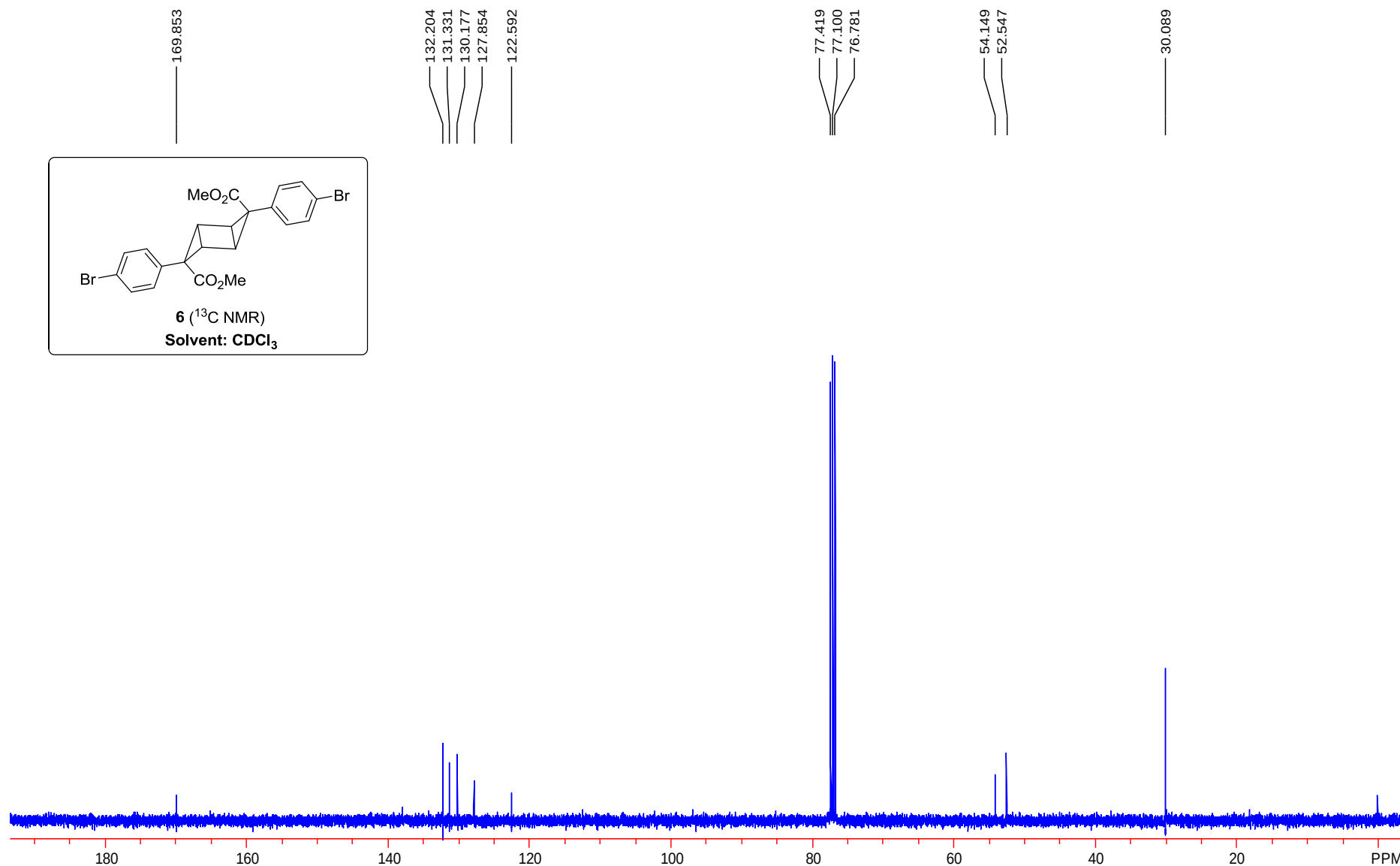
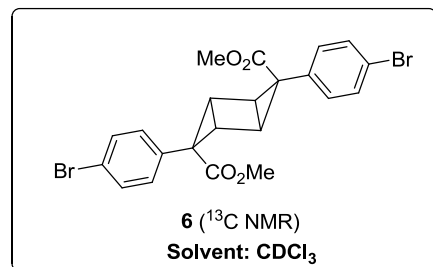
37.454

33.187

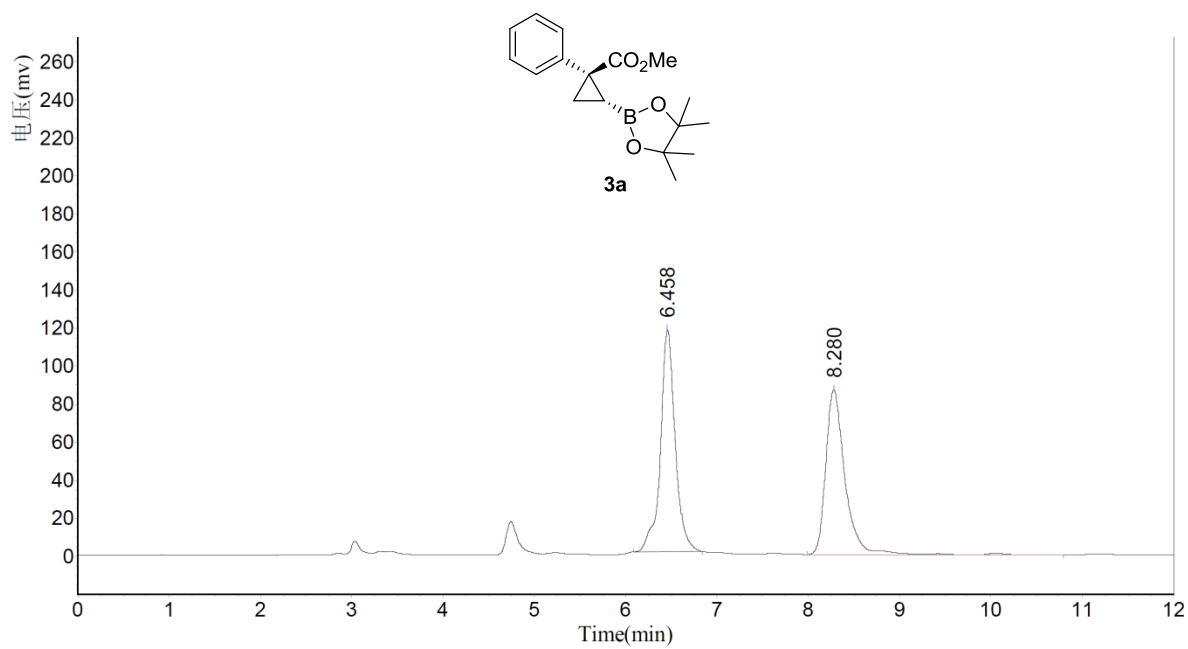
20.538





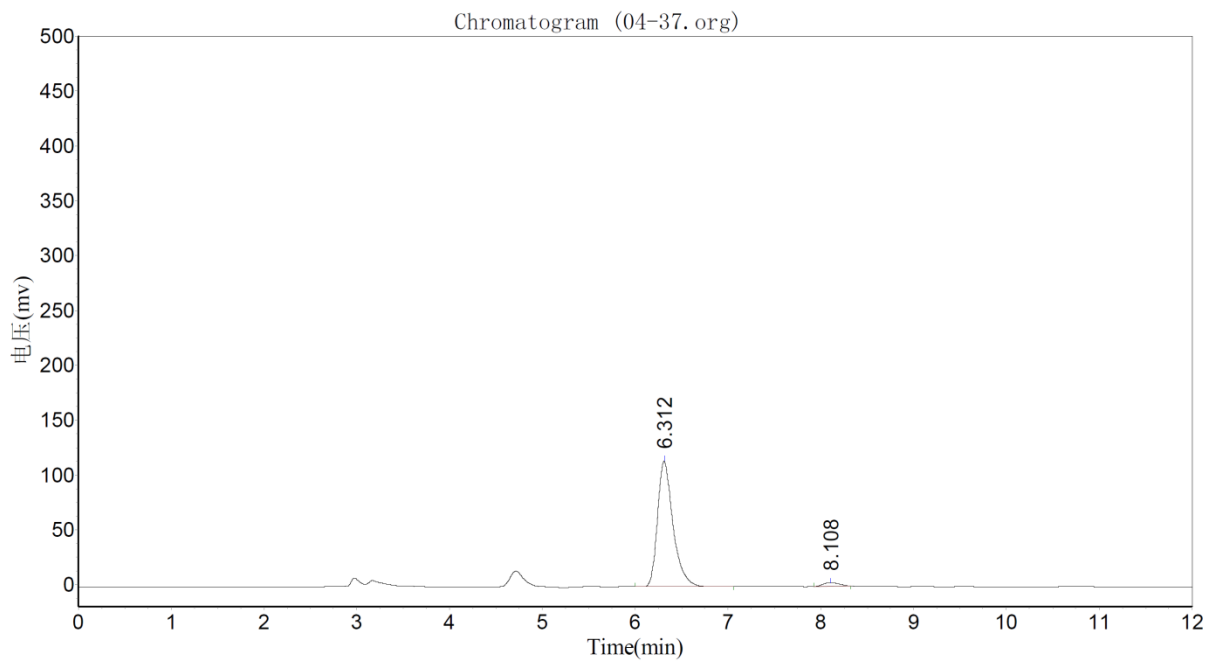


(1*R*,2*R*)-Methyl 1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate (3a)



Results

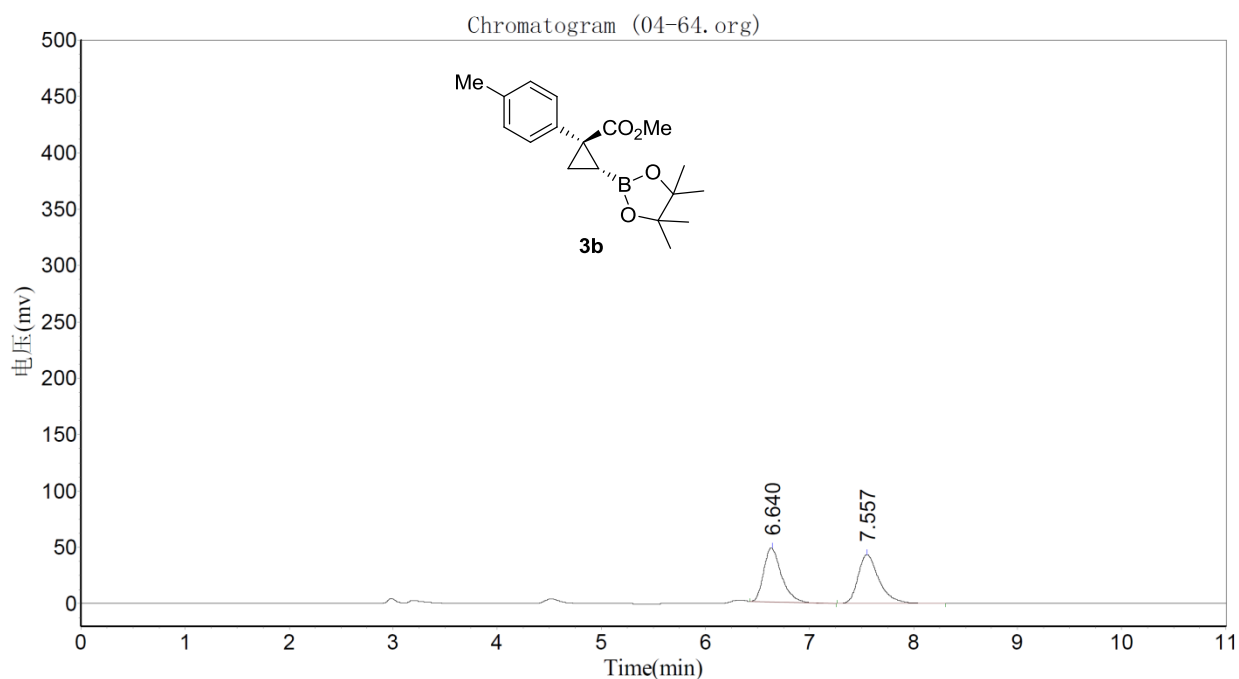
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.458	116572.070	1309002.125	50.6992
2		8.280	86462.656	1272896.875	49.3008
Total			203034.727	2581899.000	100.0000



Results

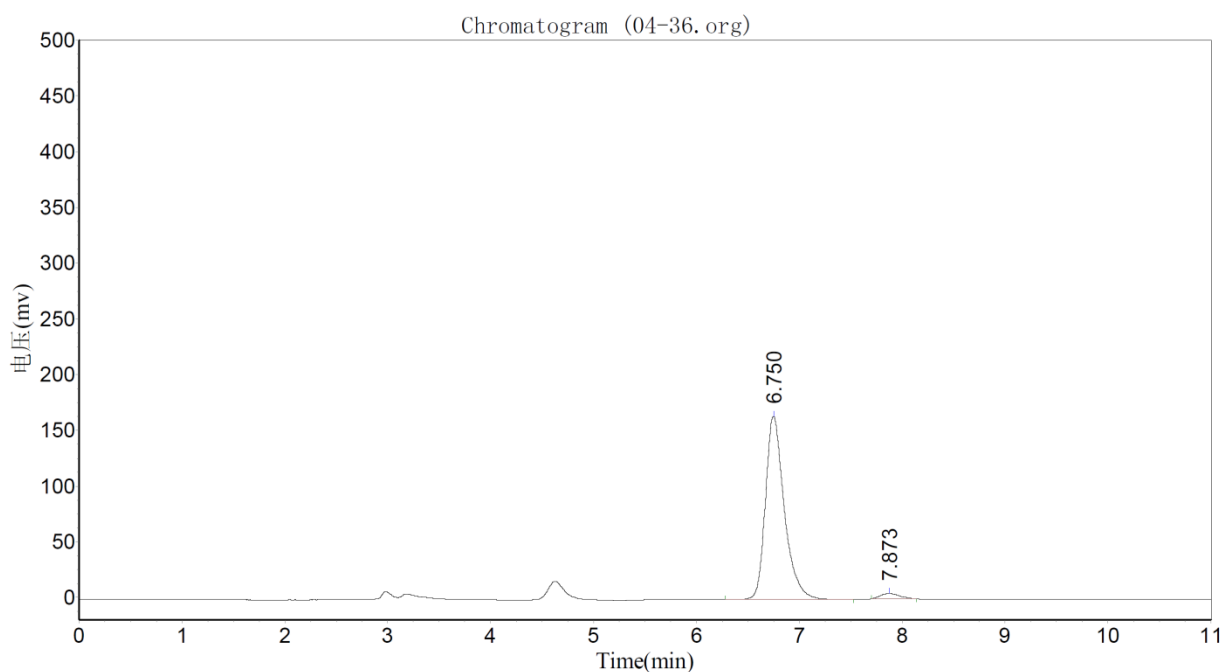
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.312	114378.969	1330611.125	97.2773
2		8.108	3001.004	37242.652	2.7227
Total			117379.973	1367853.777	100.0000

(1*R*,2*R*)-Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-*p*-tolylcyclopropanecarboxylate (3b)



Results

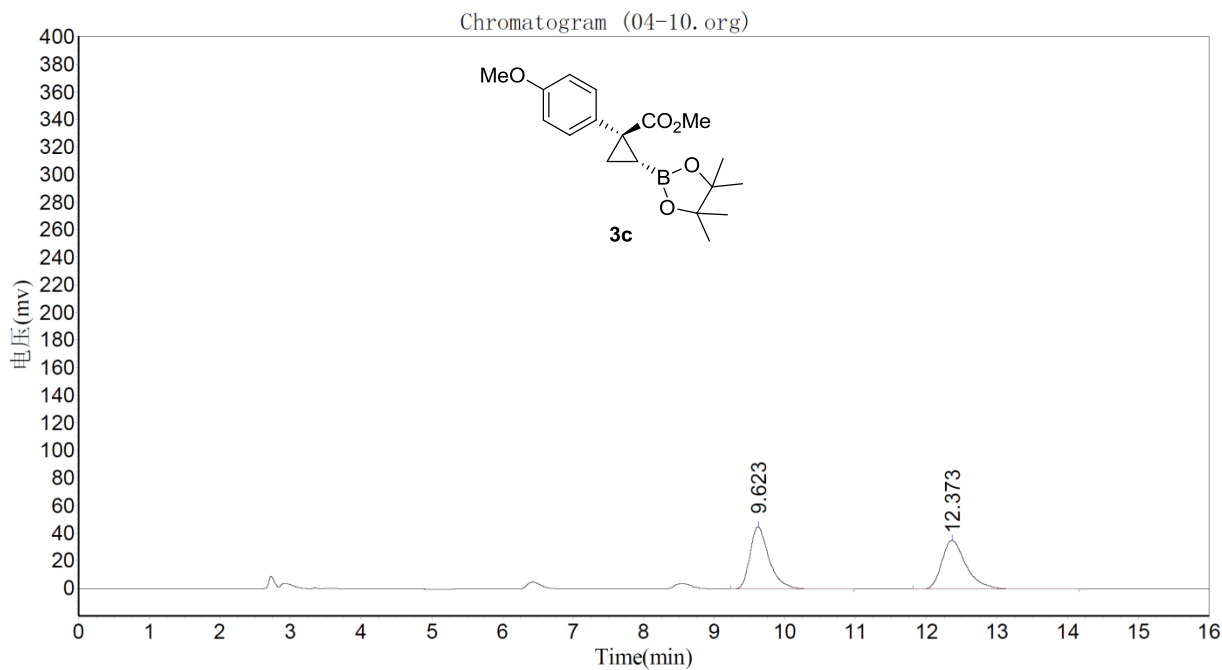
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.640	49345.270	615000.000	50.3441
2		7.557	43474.520	606592.313	49.6559
Total			92819.789	1221592.313	100.0000



Results

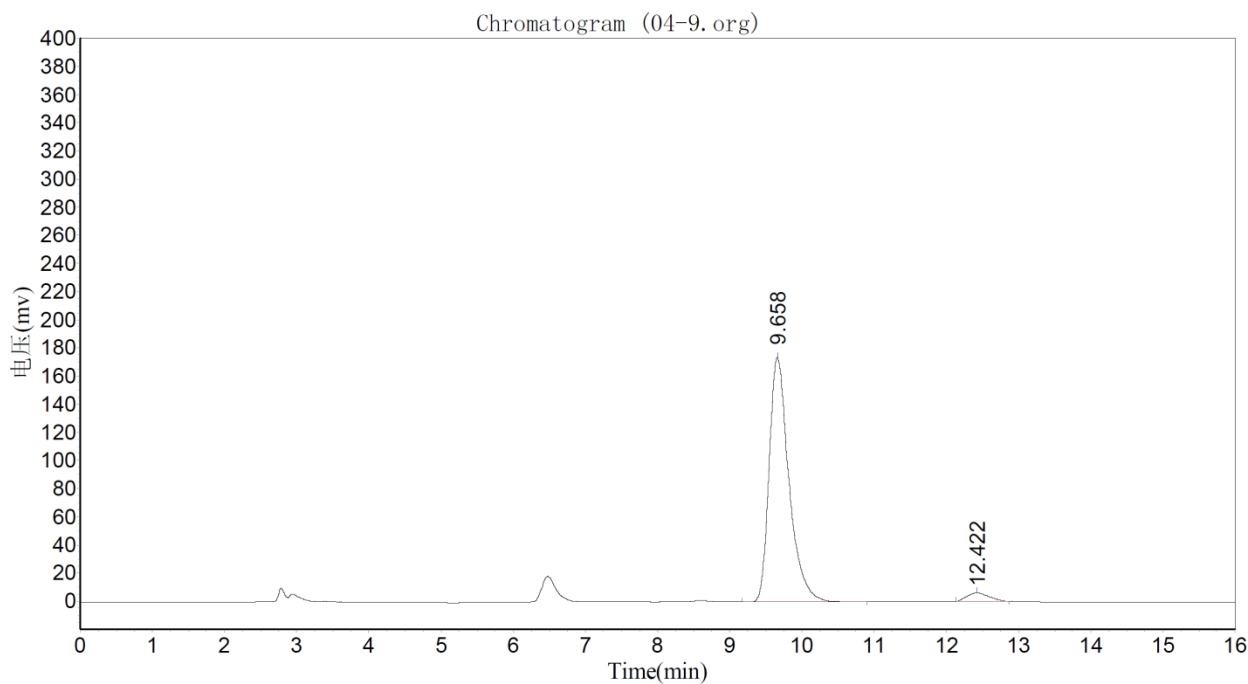
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.750	164177.375	2098171.500	97.1788
2		7.873	4890.031	60911.500	2.8212
Total			169067.406	2159083.000	100.0000

(1*R*,2*R*)-Methyl 1-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (3c)



Results

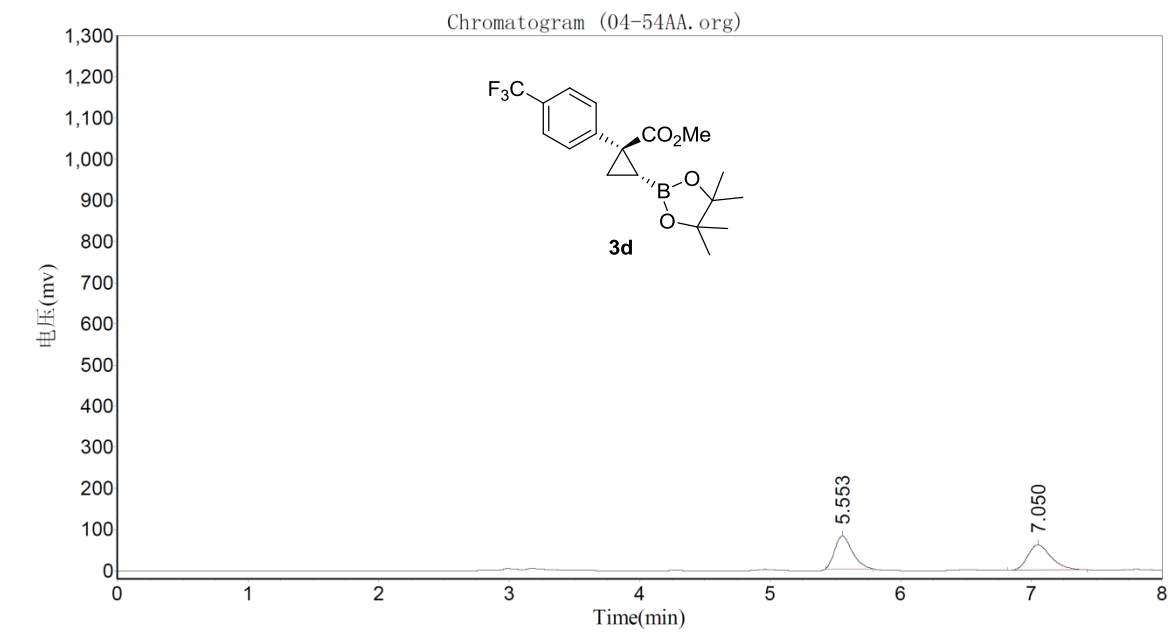
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.623	44988.973	844058.375	49.9452
2		12.373	35401.379	845910.875	50.0548
Total			80390.352	1689969.250	100.0000



Results

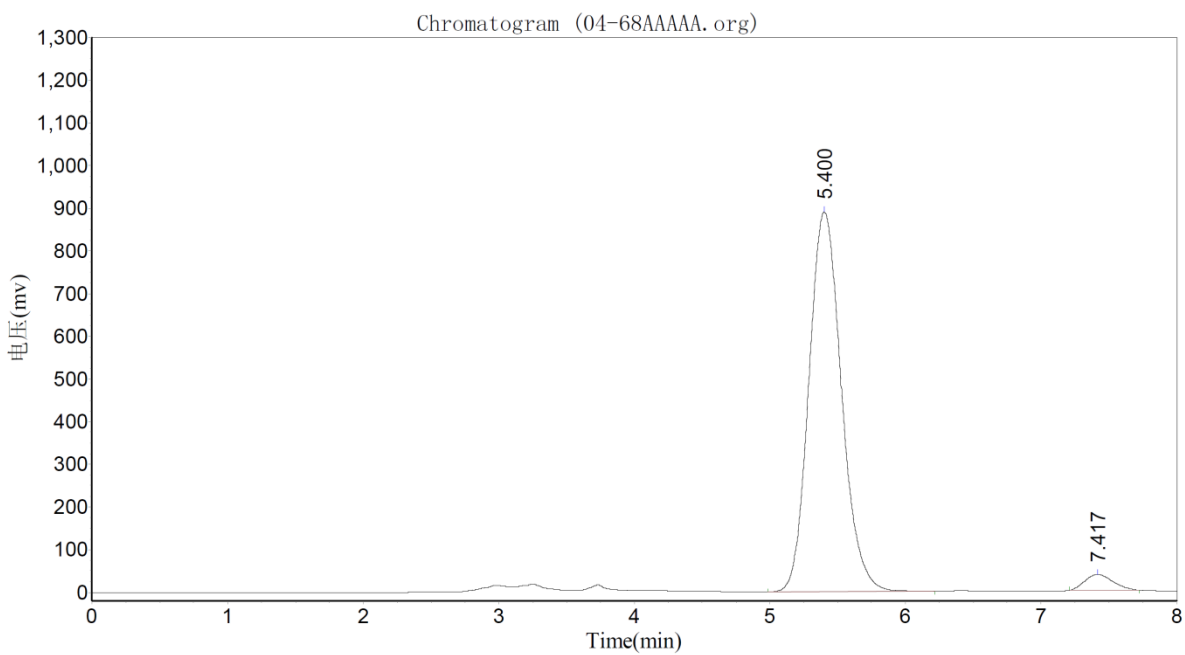
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.658	173736.938	3306299.250	96.4440
2		12.422	5879.554	121906.297	3.5560
Total			179616.492	3428205.547	100.0000

(1*R*,2*R*)-Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-(trifluoromethyl)phenyl)cyclopropanecarboxylate (**3d**)



Results

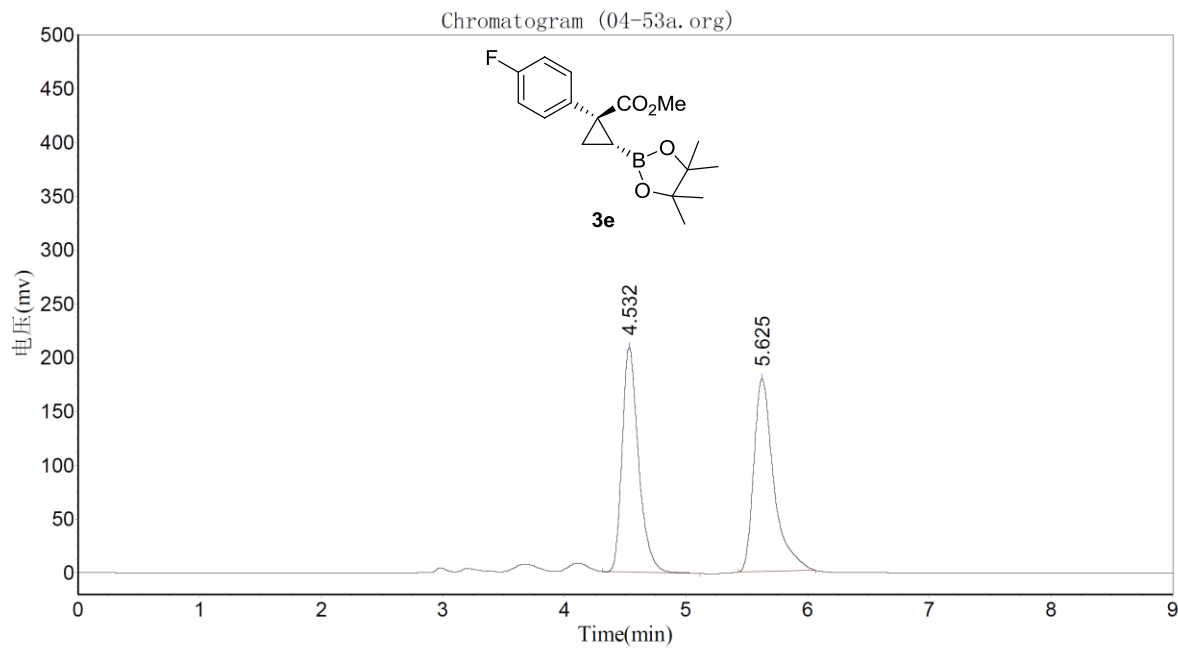
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.553	79736.586	739423.063	49.2303
2		7.050	61355.023	762544.938	50.7697
Total			141091.609	1501968.000	100.0000



Results

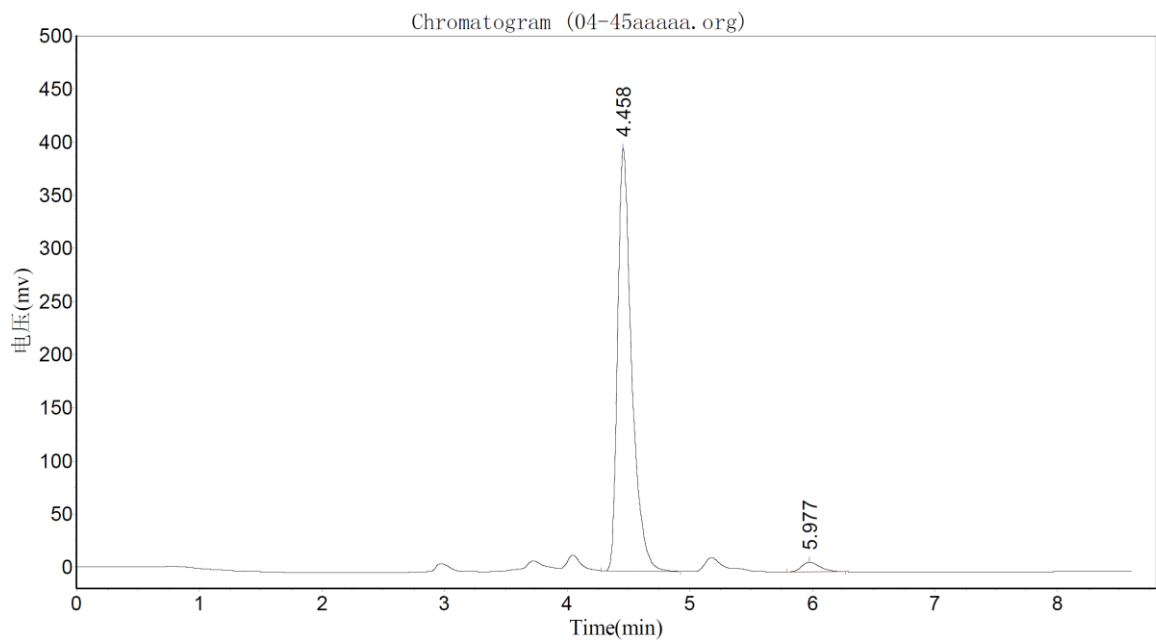
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.400	889776.500	14841171.000	96.5931
2		7.417	36571.199	523453.000	3.4069
Total			926347.699	15364624.000	100.0000

(1*R*,2*R*)-Methyl 1-(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (3e)



Results

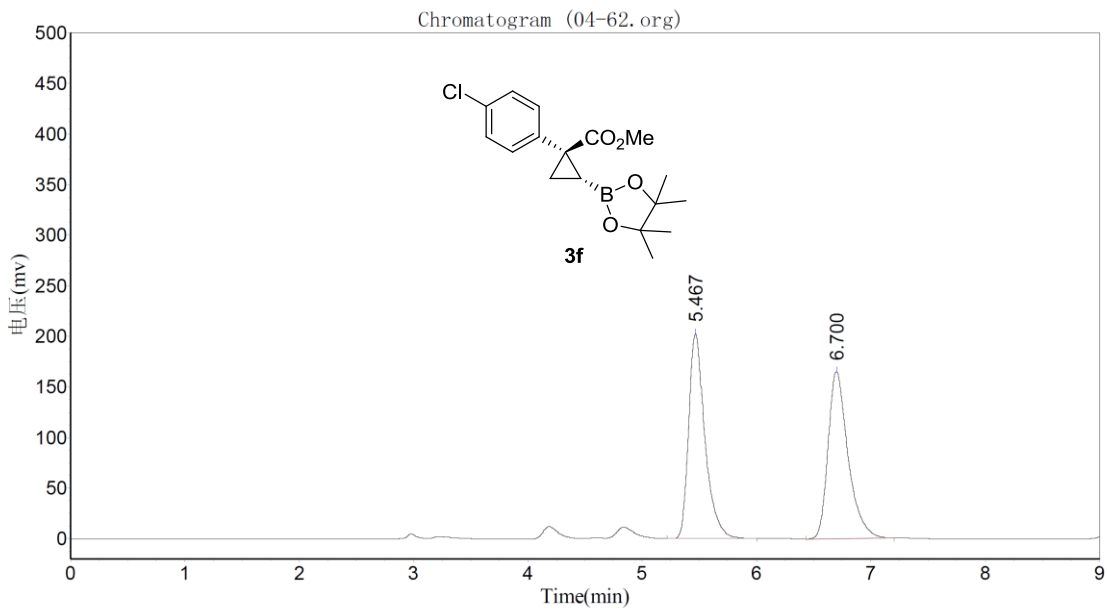
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.532	208747.313	1967327.375	48.9368
2		5.625	179538.953	2052813.125	51.0632
Total			388286.266	4020140.500	100.0000



Results

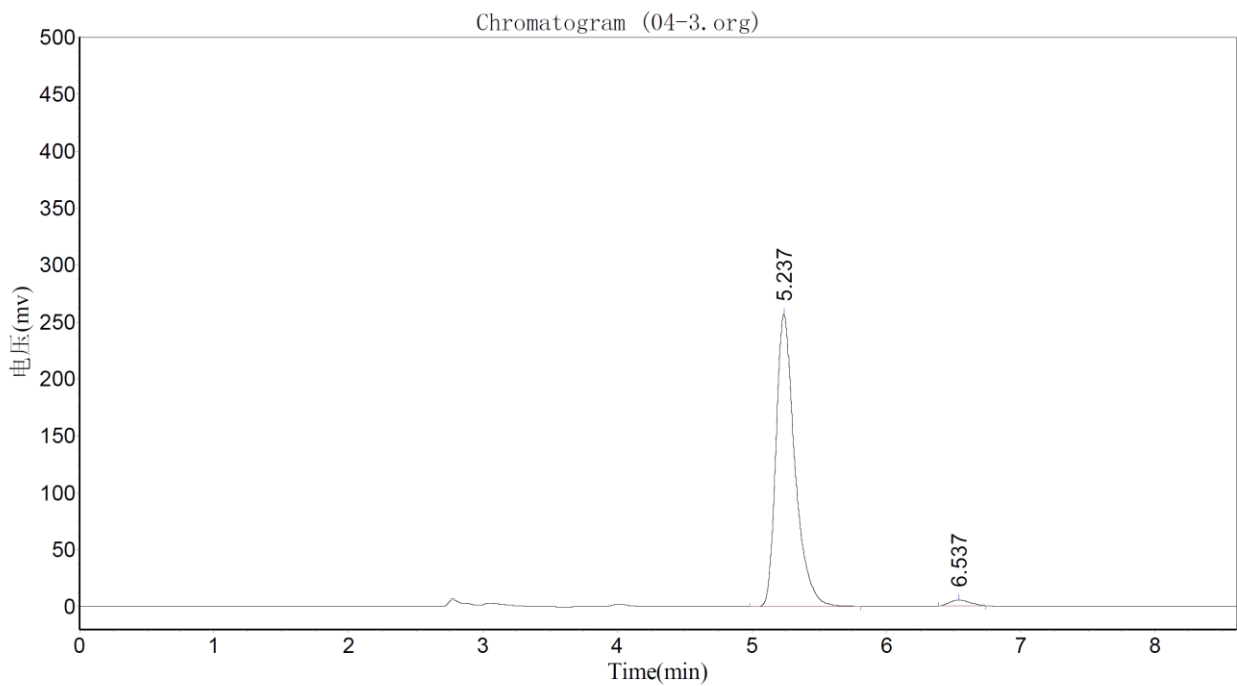
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.458	397386.375	3157529.000	97.0913
2		5.977	9145.035	94593.945	2.9087
Total			406531.410	3252122.945	100.0000

(1*R*,2*R*)-Methyl 1-(4-chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (3f)



Results

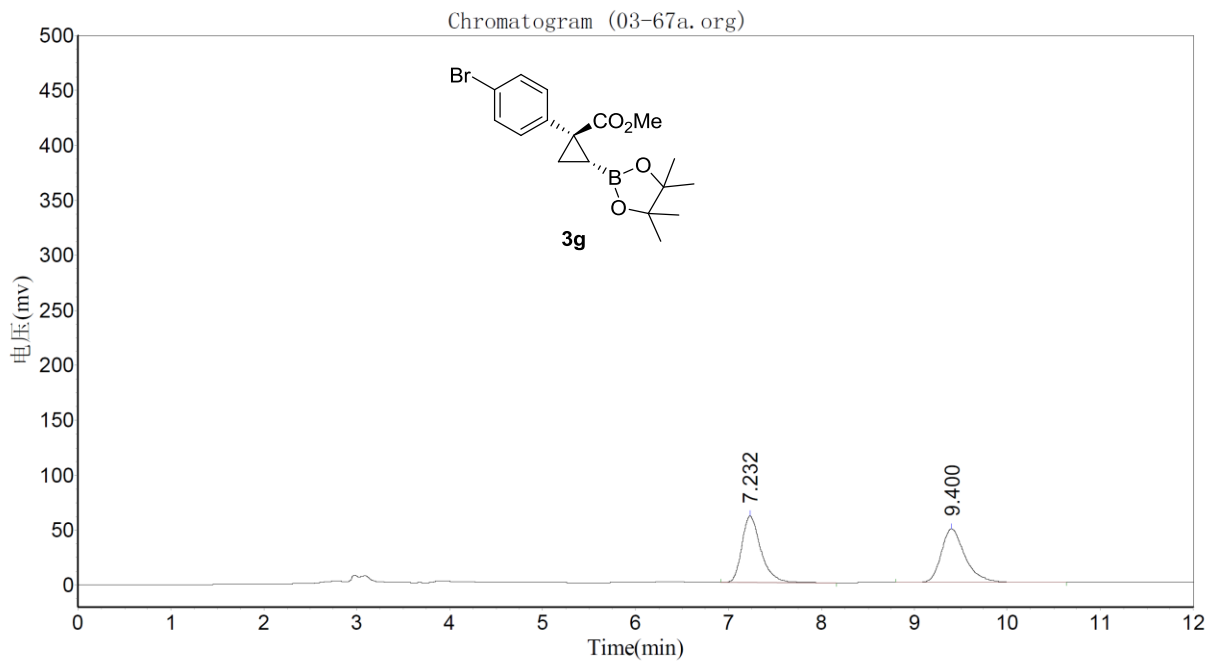
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.467	202831.969	2006685.750	49.9623
2		6.700	165151.688	2009715.125	50.0377
Total			367983.656	4016400.875	100.0000



Results

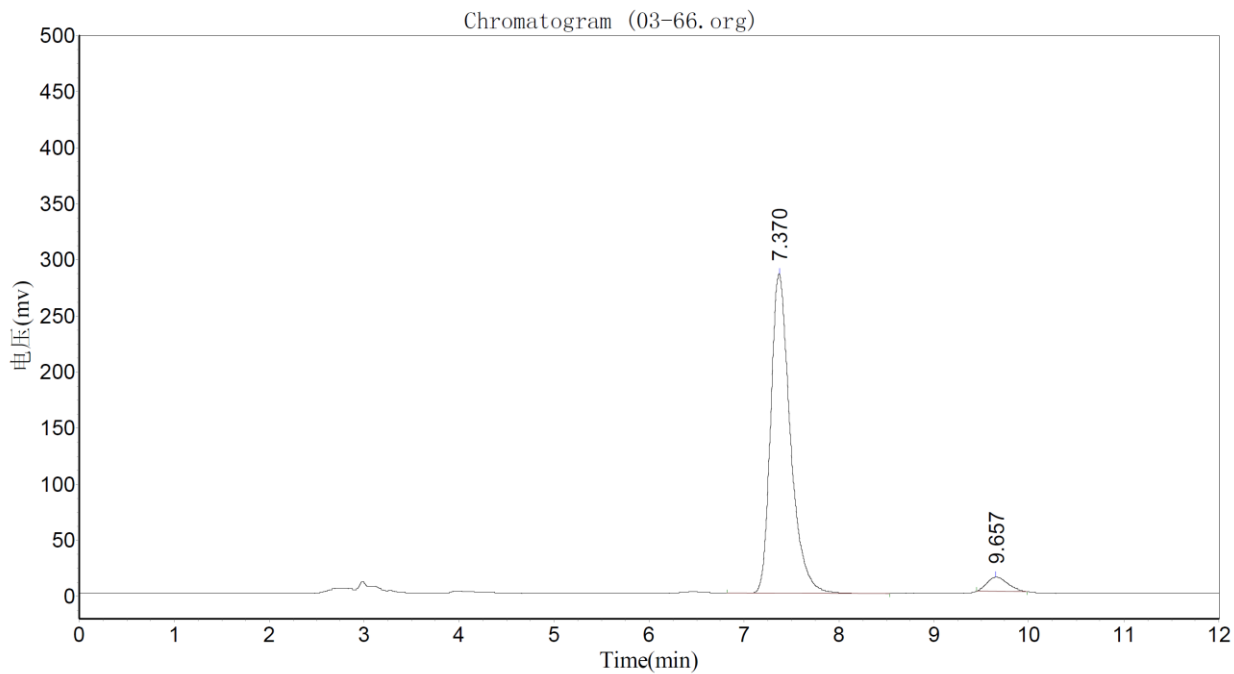
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.237	256793.281	2501006.500	97.8061
2		6.537	5470.327	56100.047	2.1939
Total			262263.608	2557106.547	100.0000

(1*R*,2*R*)-Methyl 1-(4-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (**3g**)



Results

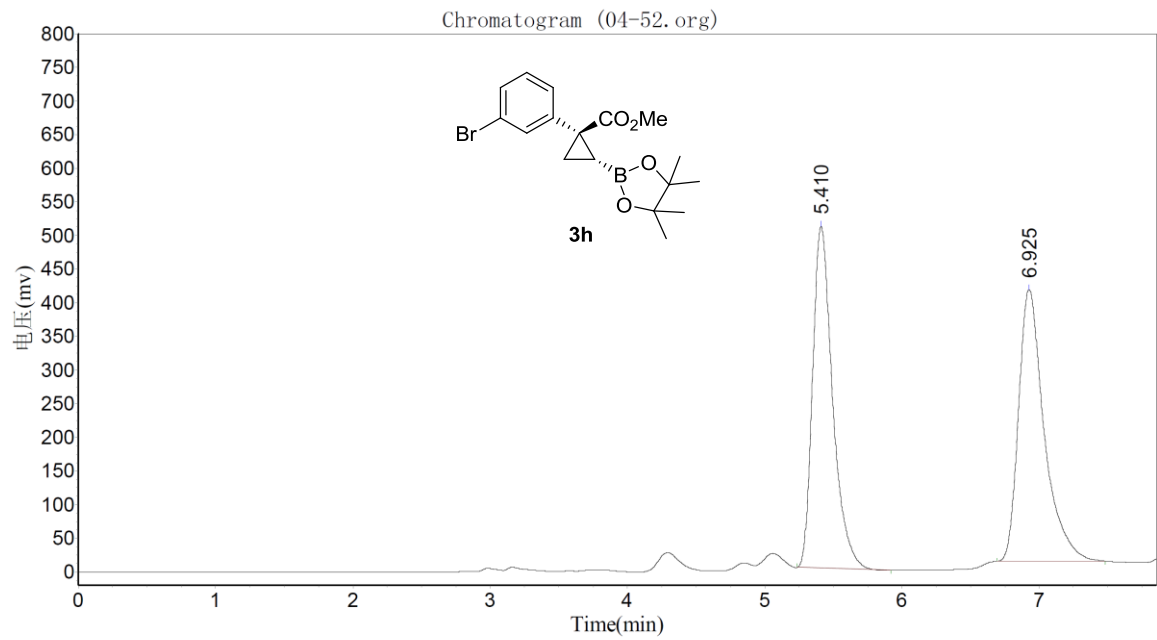
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.232	60576.539	866571.813	49.7521
2		9.400	48777.621	875208.688	50.2479
Total			109354.160	1741780.500	100.0000



Results

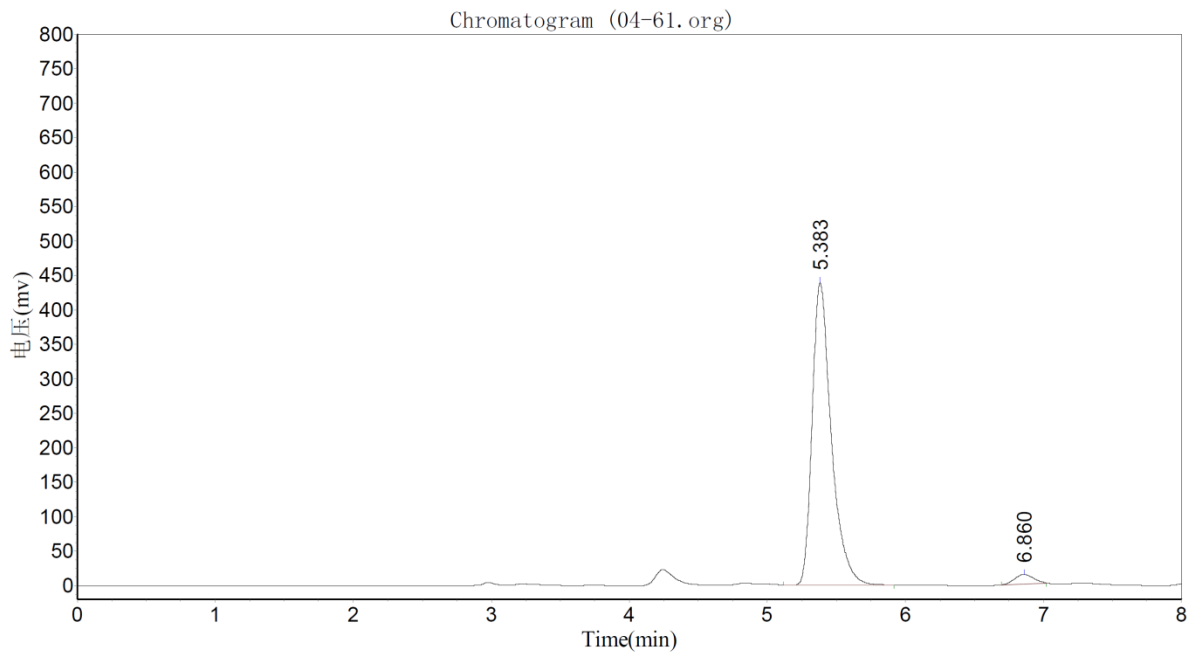
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.370	284587.781	4060744.500	95.5031
2		9.657	12635.659	191205.594	4.4969
Total			297223.440	4251950.094	100.0000

(1*R*,2*R*)-Methyl 1-(3-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (3h)



Results

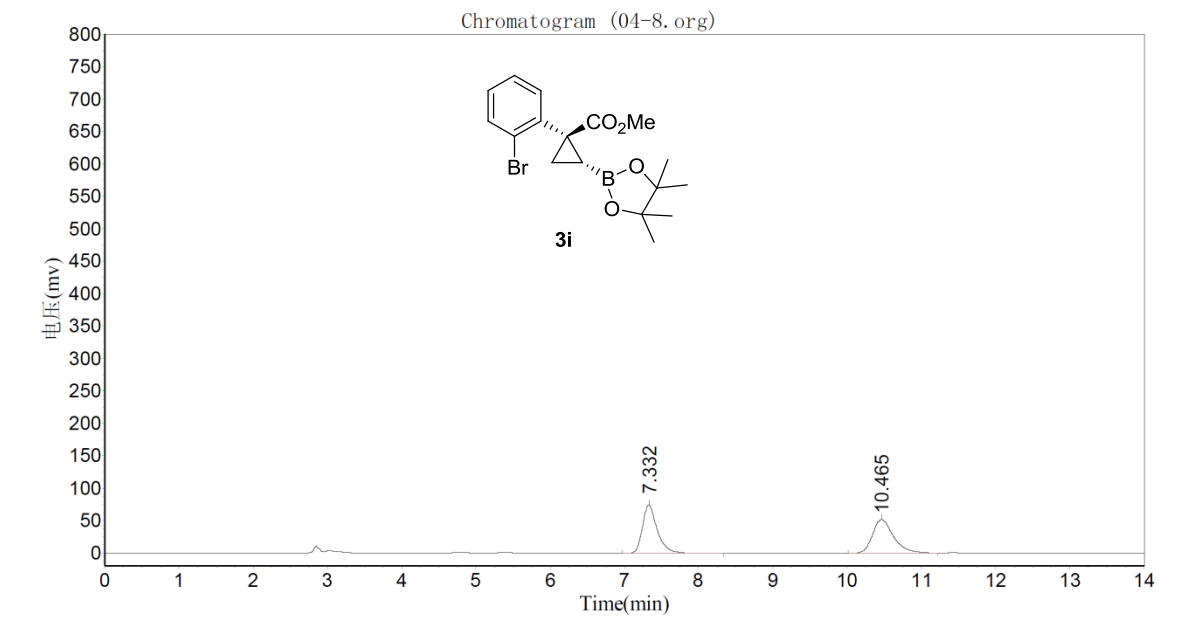
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.410	507967.063	5130262.000	49.4841
2		6.925	404073.844	5237237.000	50.5159
Total			912040.906	10367499.000	100.0000



Results

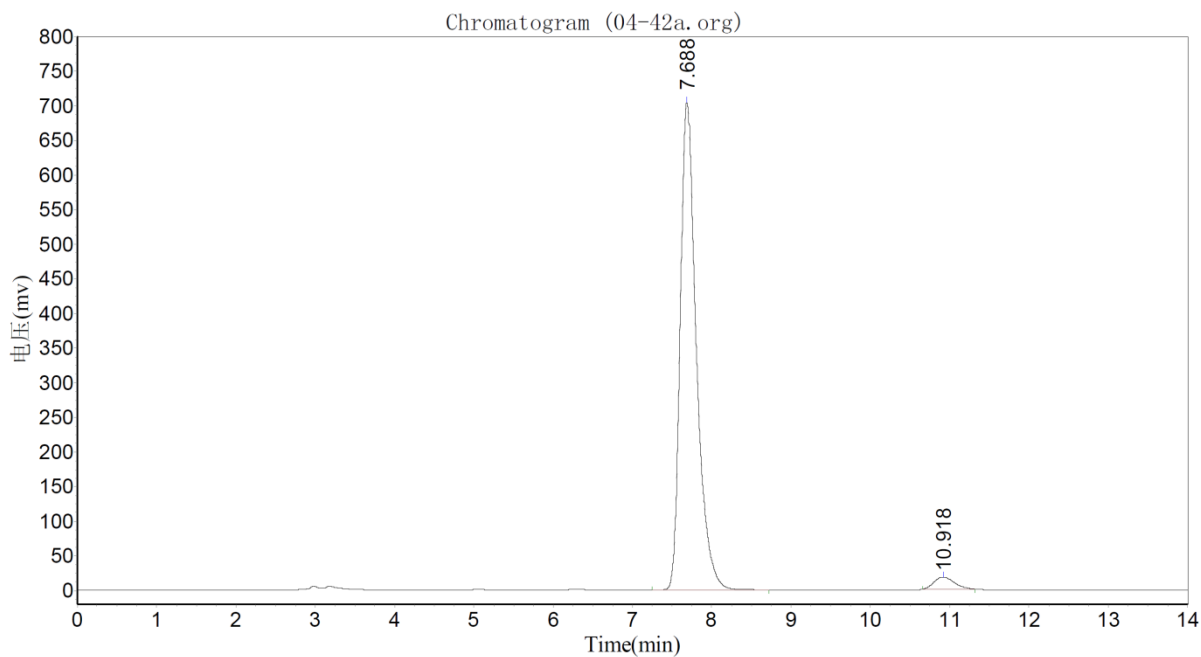
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.383	439026.688	4229278.500	97.0151
2		6.860	13452.745	130121.805	2.9849
Total			452479.433	4359400.305	100.0000

(1*R*,2*R*)-Methyl 1-(2-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (3i)



Results

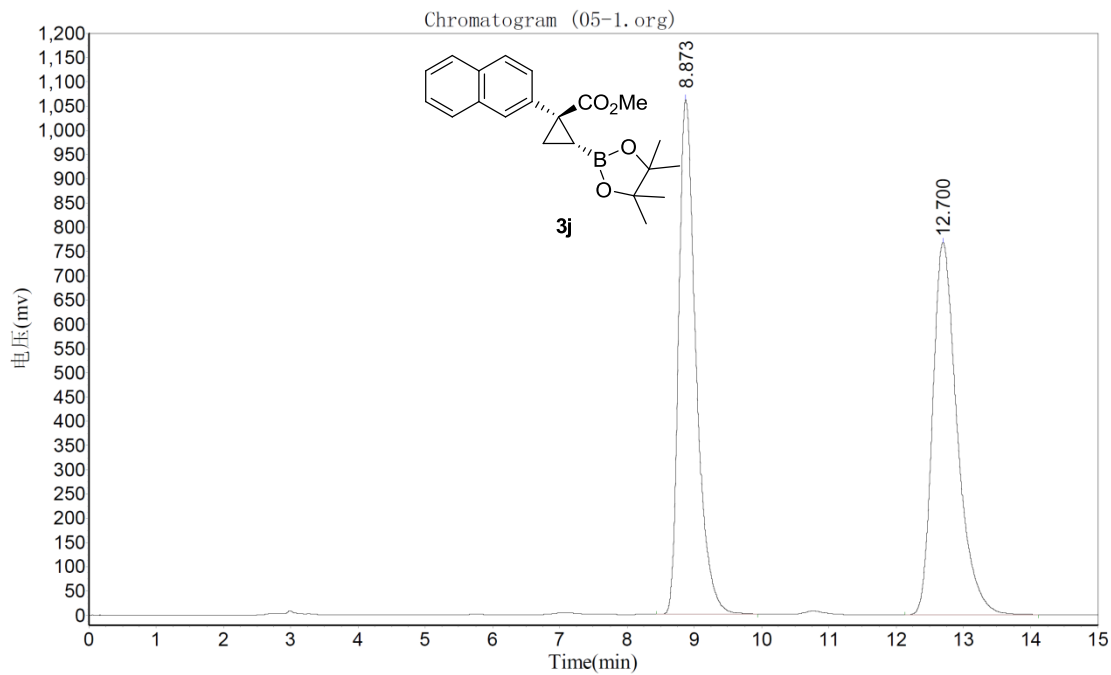
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.332	73764.633	1015637.125	49.9145
2		10.465	51737.223	1019116.188	50.0855
Total			125501.855	2034753.313	100.0000



Results

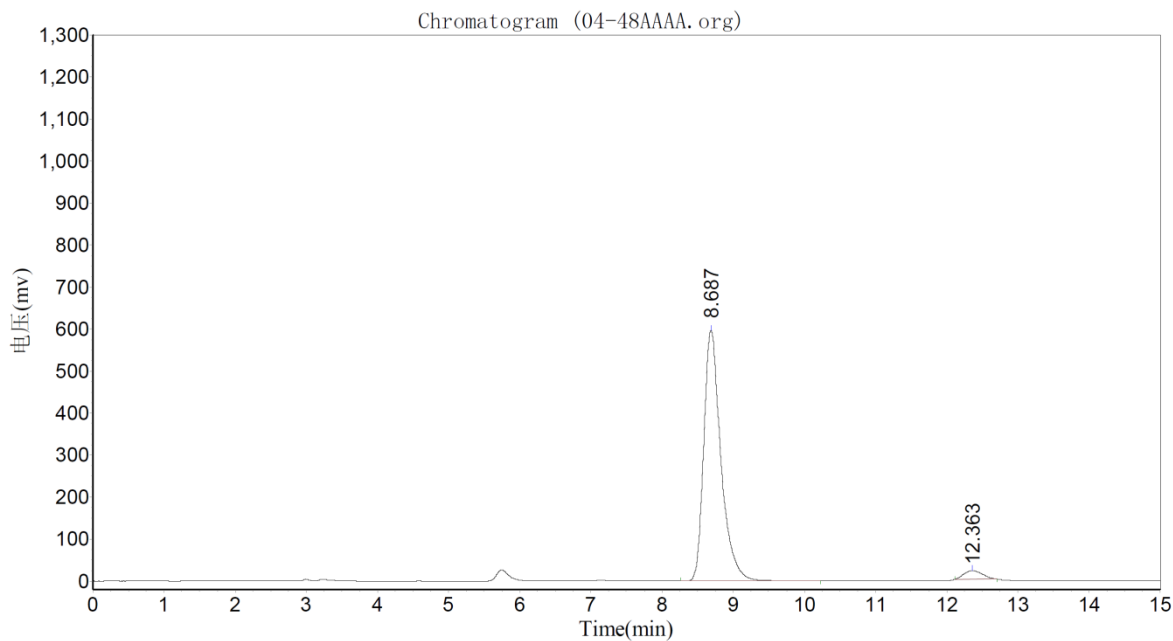
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.688	704335.750	9943681.000	96.9136
2		10.918	17944.900	316671.375	3.0864
Total			722280.650	10260352.375	100.0000

(1*R*,2*R*)-Methyl 1-(naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (**3j**)



Results

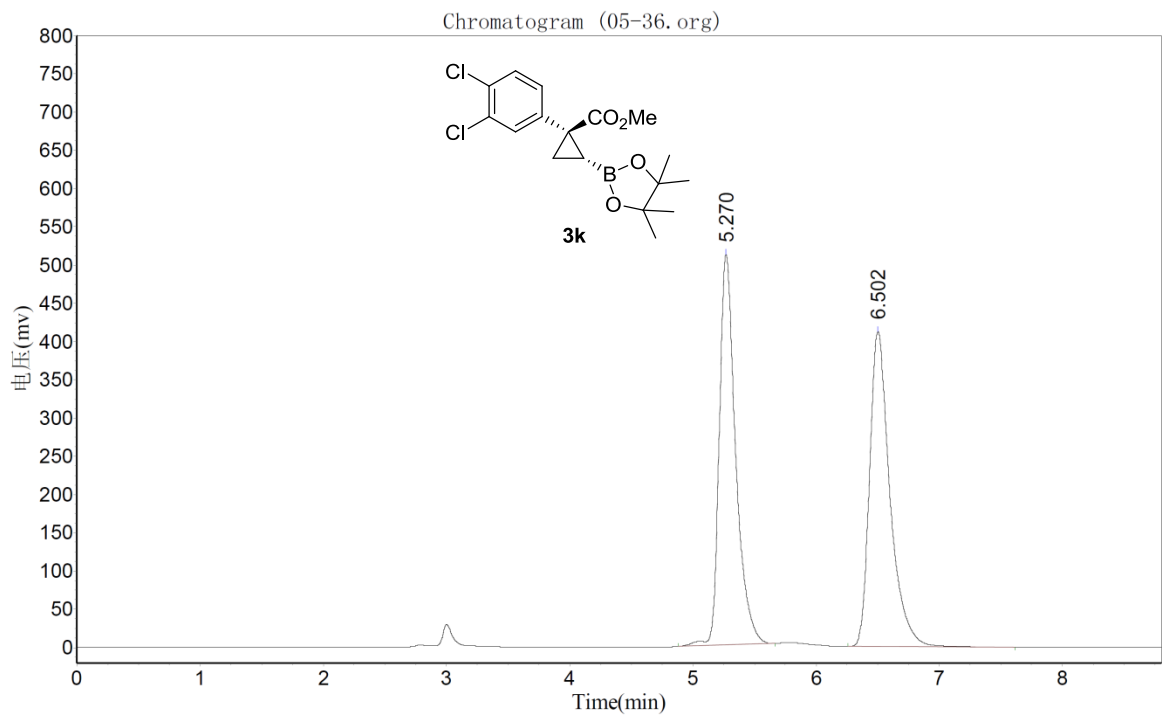
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.873	1061924.750	19054004.000	49.3895
2		12.700	767961.688	19525076.000	50.6105
Total			1829886.438	38579080.000	100.0000



Results

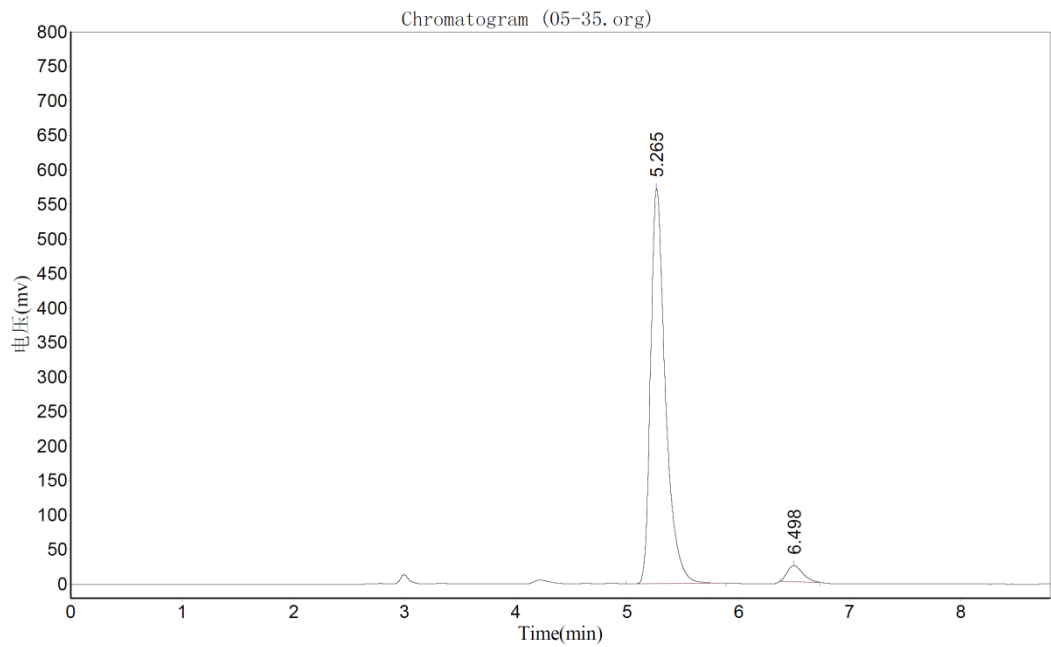
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.687	596291.938	9960564.000	96.4901
2		12.363	20132.539	362323.688	3.5099
Total			616424.477	10322887.688	100.0000

(1*R*,2*R*)-Methyl 1-(3,4-dichlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (3k)



Results

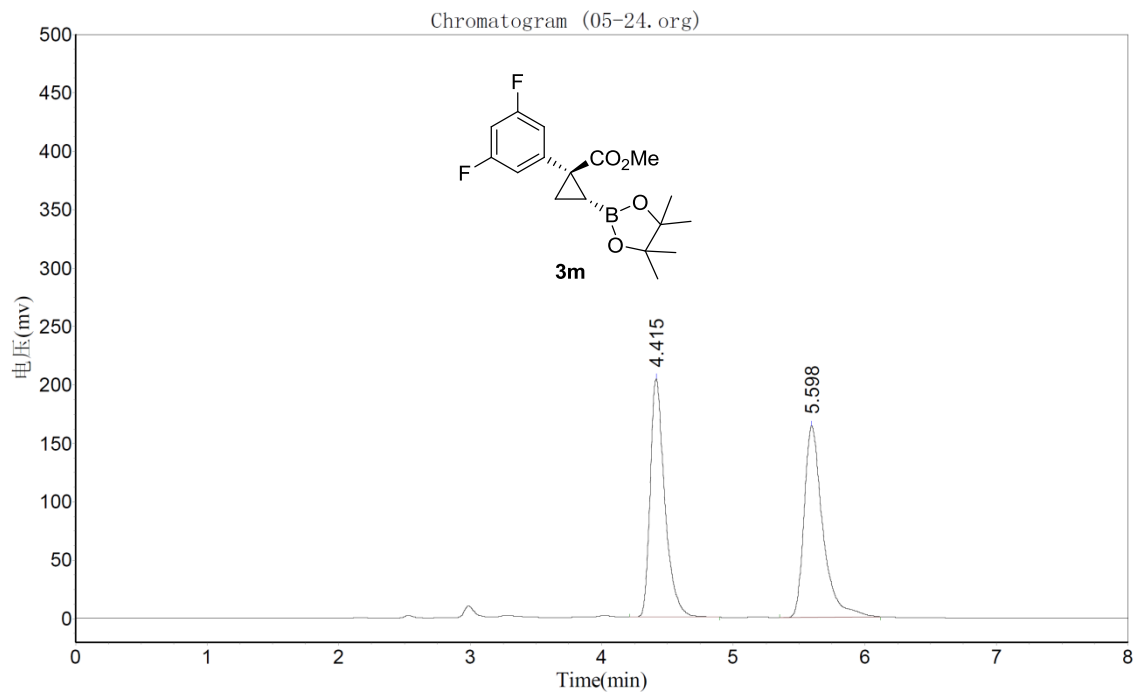
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.270	510356.500	4717506.000	49.9098
2		6.502	412098.219	4734558.500	50.0902
Total			922454.719	9452064.500	100.0000



Results

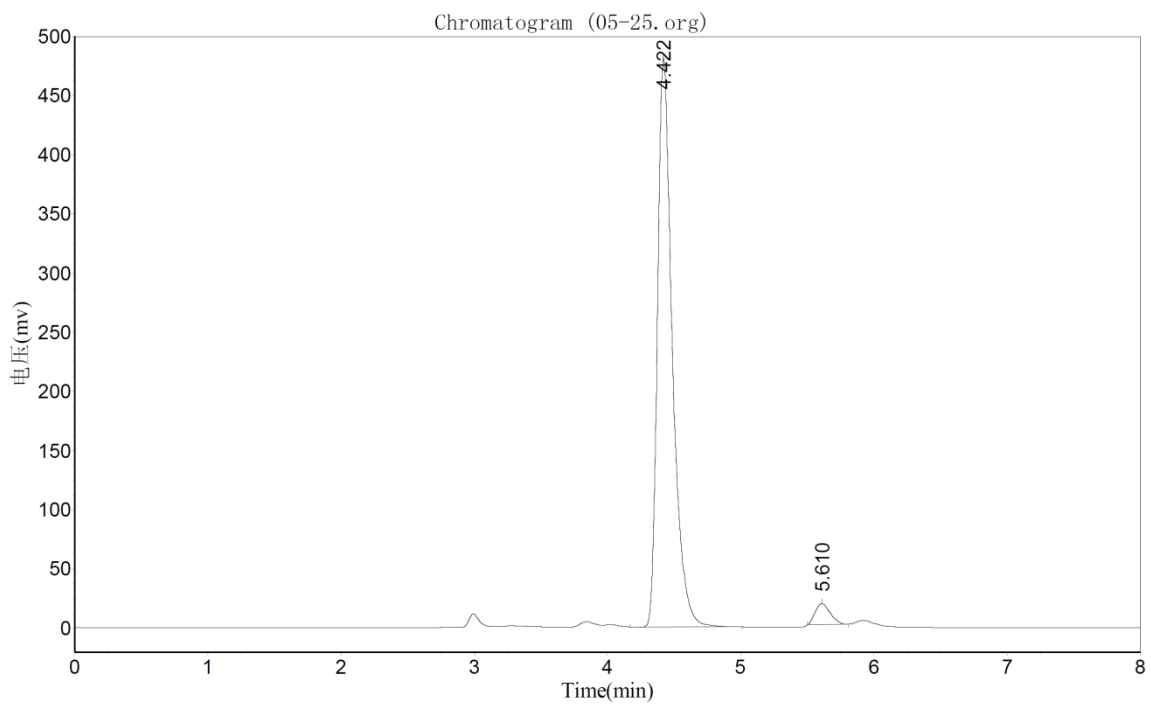
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.265	572598.313	5268845.500	95.8538
2		6.498	23473.000	227908.391	4.1462
Total			596071.313	5496753.891	100.0000

(1*R*,2*R*)-Methyl 1-(3,5-difluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-carboxylate (3m)



Results

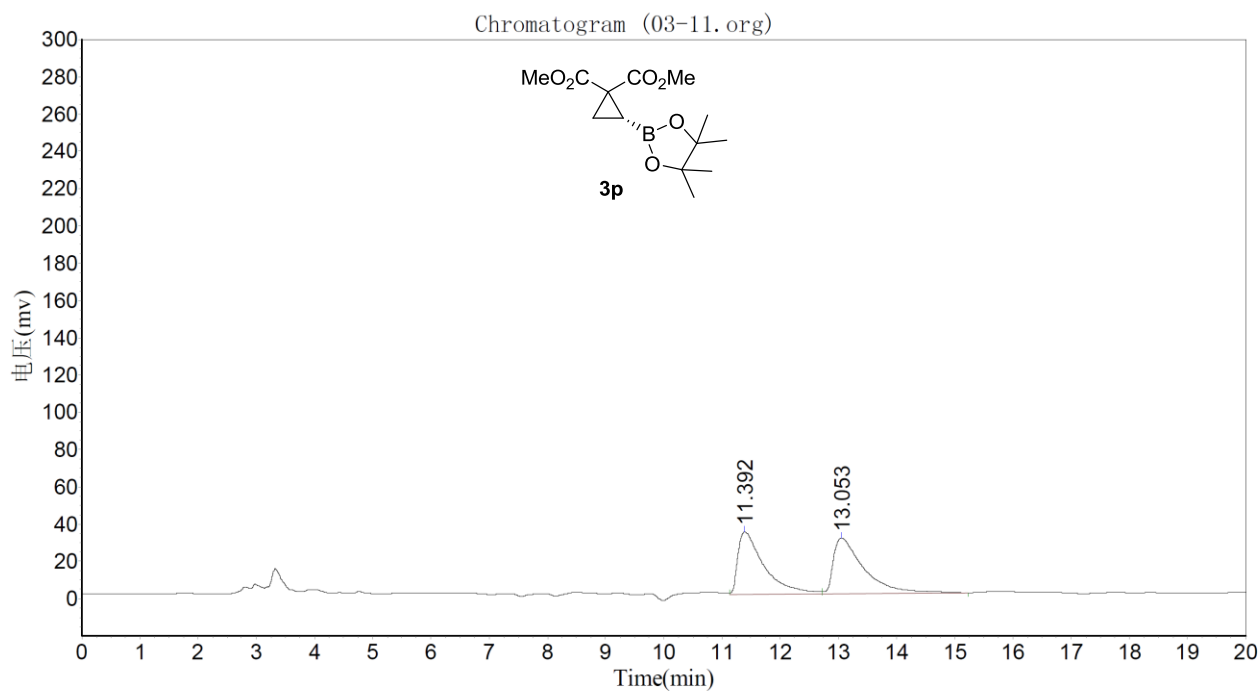
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.415	204051.234	1570528.625	49.2951
2		5.598	164095.063	1615441.625	50.7049
Total			368146.297	3185970.250	100.0000



Results

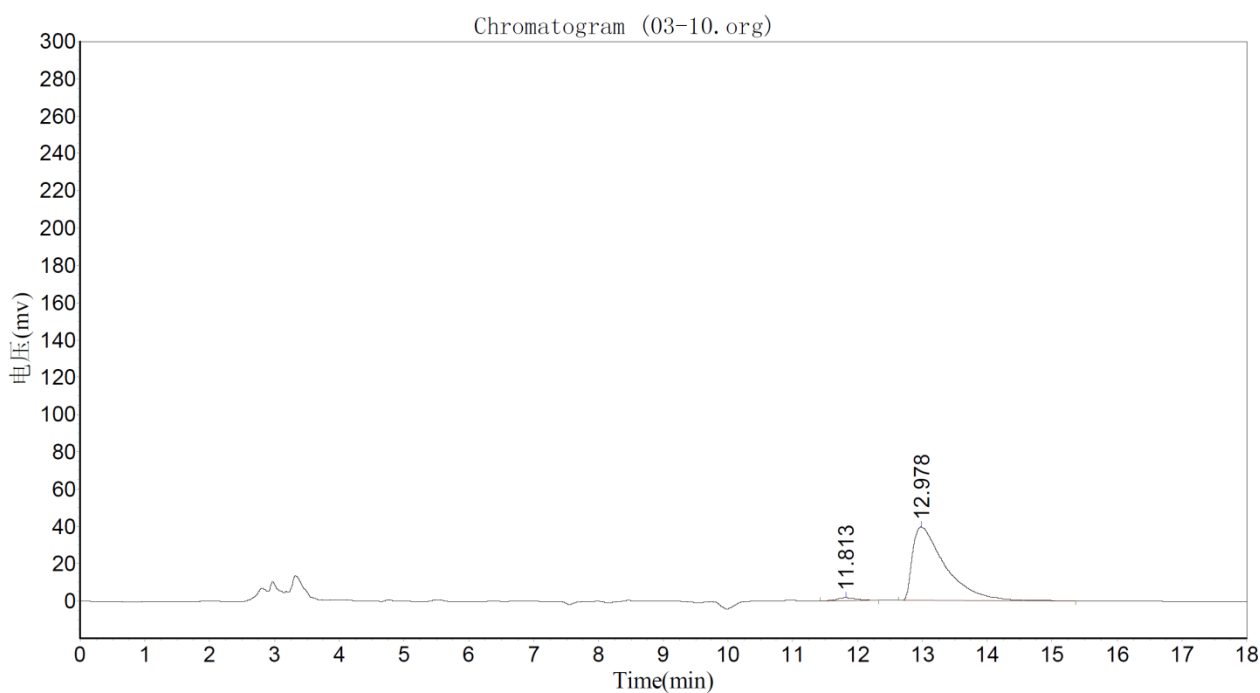
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.422	480571.531	3714432.250	96.3744
2		5.610	17728.537	139735.297	3.6256
Total			498300.068	3854167.547	100.0000

(R)-Dimethyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropane-1,1-dicarboxylate (3p)



Results

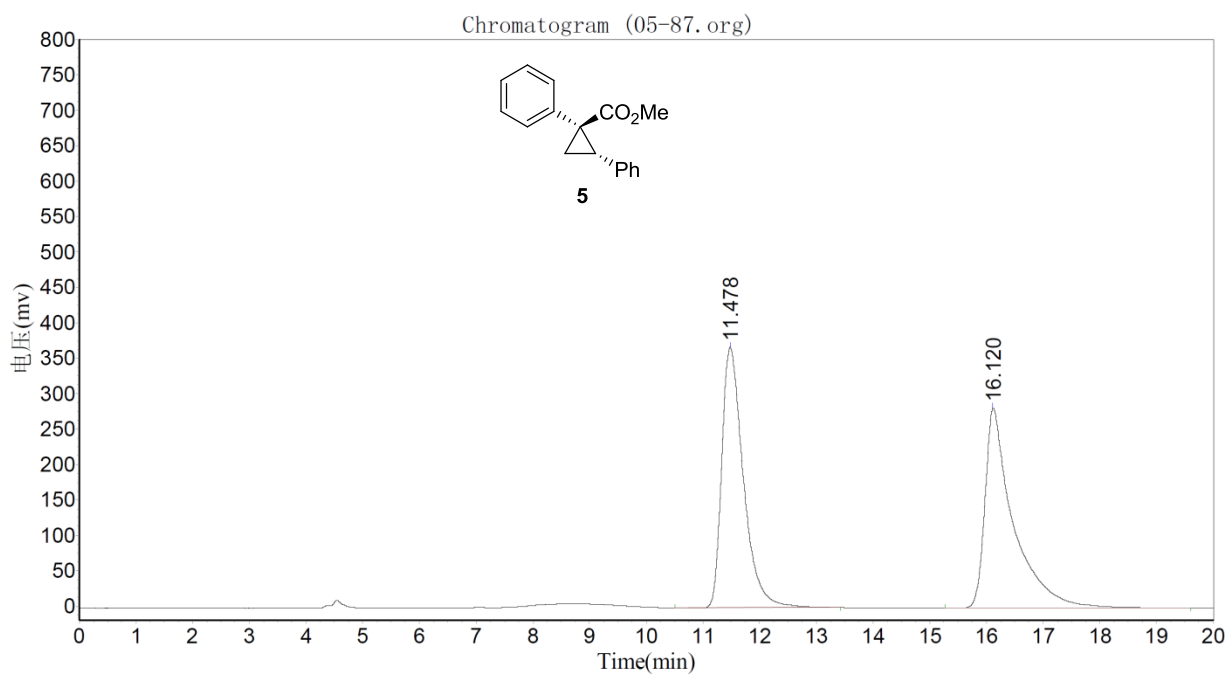
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.392	33715.301	1063152.250	49.0988
2		13.053	30026.555	1102178.125	50.9011
Total			63741.855	2165330.375	100.0000



Results

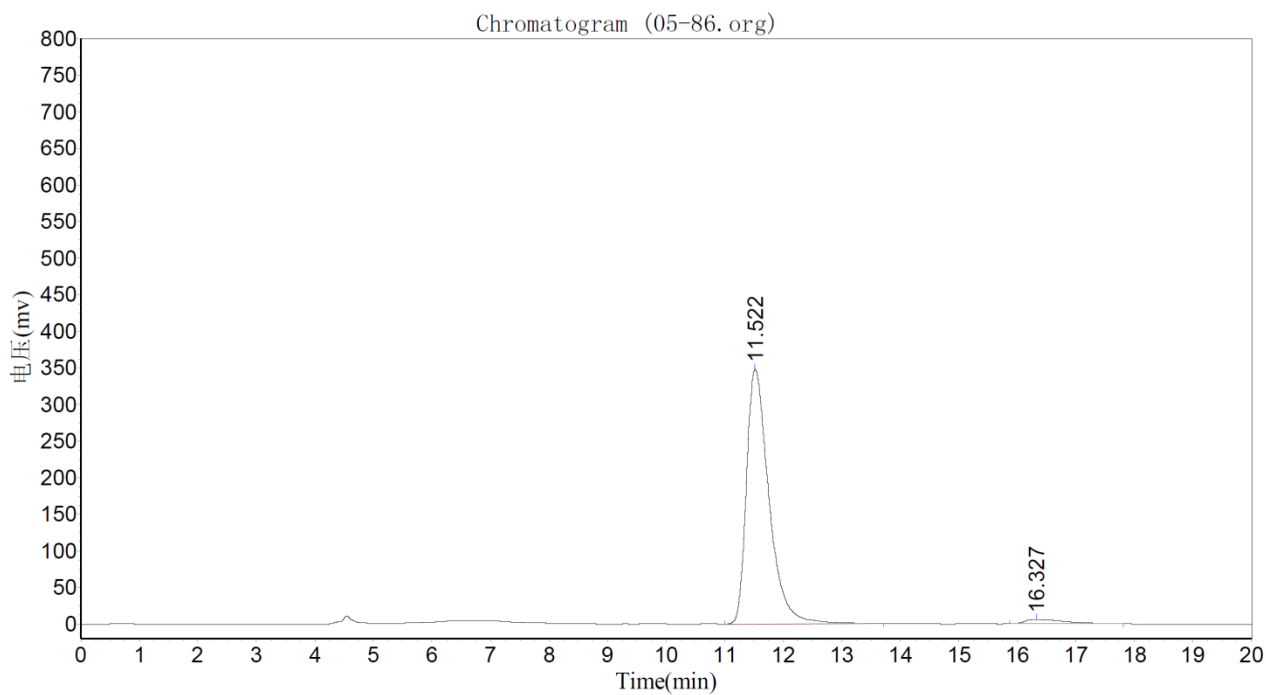
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.813	1526.219	35190.750	2.4737
2		12.978	39417.293	1387382.375	97.5263
Total			40943.512	1422573.125	100.0000

(1R,2S)-Methyl 1,2-diphenylcyclopropanecarboxylate (5)



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.478	367557.656	9726735.000	49.8654
2		16.120	281591.313	9779263.000	50.1346
Total			649148.969	19505998.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.522	348305.125	9299768.000	97.0302
2		16.327	6018.578	284638.719	2.9698
Total			354323.703	9584406.719	100.0000