Graphene Oxide (GO) Catalysed MW-assisted One-Pot Synthesis of Densely Substituted Furan

Anupam Jana,* Nirmal Das Adhikary and Animesh Pramanik*

Department of Chemistry, University of Calcutta, 92, A. P. C. Road, Kolkata 700009, India.
Fax: +91-33-2351-9755; Tel: +91 9830107470
Corresponding E-mail: anupamjana2@gmail.com; pramanikanimesh61@gmail.com

Experimental Section

General information

All chemicals and solvents were purchased from commercial suppliers and used without further purification. All reactions were carried out in oven-dried glassware with magnetic stirring. Commercially available chemicals were used without further purification. The starting materials aryl glyoxals (**1**)[1] and graphene oxide[2] were synthesized according to the reported procedure. Monitoring of the reaction was performed by thin-layer chromatography using TLC silica gel 60 F254 plates. Melting points were measured in open capillary tubes and were uncorrected. Flash column chromatography was performed using silica gel 60 (particle size 0.040–0.063 mm) typically using a n-hexane/ethyl acetate eluent system. FT-IR spectra were recorded with PerkinElmer 782 spectrophotometer. NMR spectra were calibrated to the solvent residual signals of $CDCl_3$. ^1H NMR spectra were recorded at a 300 MHz and 500 MHz Bruker instrument. Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, qui: quintuplet, m: multiplet), coupling constant (*J* in Hz) and integration. ^{13}C NMR spectra were recorded at 75 MHz and 125 MHz using broadband proton decoupling and chemicals shifts are reported in ppm using residual solvent peaks as reference. High resolution mass spectra (HRMS) were recorded on a QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray–electrospray interface. Reported yields are based upon isolation following purification by silica gel column chromatography; isolated material was judged to be homogeneous based upon TLC and NMR.

General procedure of the one-pot furan synthesis: Glyoxal **1** (2.0 mmol), 1,3 diketone **2** (2.0 mmol) and compound **3** (0.8 mmol) were taken in a MW-tube and radiated in MW reactor at 150W for 6 min (3 min X 2). Then, graphene oxide (60 mg) was added to the reaction vessel and whole mixture was heated at 70 ^oC for 5 h. Then, EtOH (5 mL) was added to the reaction vessel and the product was extracted from the surface of graphene oxide (GO) by ultrasonication. The graphene oxide (GO) was separated by decantation. The separated organic layer was evaporated to get the crude mass which was purified by column chromatography (20% ethyl acetate/n-hexane) to afford the desired product.

Compound **4a**: Yellow solid, mp 170 ^oC. δ_H (500 MHz, Chloroform-*d*) 8.47 (1 H, s), 7.44-7.39 (2 H, m), 7.31 – 7.21 (3 H, m), 7.18 – 7.05 (2 H, m), 6.95 (2 H, d, *J* 8.0), 2.68 (3 H, s), 2.23 (3 H, s), 1.84 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 157.5, 148.9, 137.2, 136.3, 129.1, 128.0, 127.9, 125.4, 125.2, 123.8, 122.8, 120.5, 119.9, 112.5, 111.5, 108.9, 30.1, 21.3, 14.8. **ESI-MS**: *m/z* =$[M+H]^+$calcd. for $C_{22}H_{20}NO_2$: 330.1489; found 330.1487.

Compound **4b**: δ_H (300 MHz, Chloroform-*d*) 8.54 (1 H, s), 7.36 – 7.25 (3 H, m), 7.24 – 7.08 (2 H, m), 7.06 – 6.96 (5 H, m), 2.60 (3 H, s), 1.76 (3 H, s). δ_C (75 MHz, Chloroform-*d*) 197.1, 157.8, 148.6, 136.3, 133.0, 130.6, 128.5, 127.9, 127.3, 126.4, 125.2, 123.8, 122.7, 120.5, 119.8, 113.3, 111.5, 108.5, 30.1, 14.9 . **ESI-MS**: *m/z* =$[M+H]^+$calcd. for $C_{22}H_{18}NO_2$: 316.1332; found 316.1334.

Compound **4c**: Brown viscous liquid. δ_H (300 MHz, Chloroform-*d*) 8.50 (1 H, s), 7.36 (1 H, dt, *J* 8.2, 0.9), 7.30-7.26 (1 H, m), 7.24 – 7.13 (3 H, m), 7.09 – 6.95 (4 H, m), 2.60 (3 H, s), 1.76 (3 H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 158.0, 147.9, 136.2, 133.0, 129.2, 128.6, 127.5, 126.5, 125.7, 123.7, 123.0, 120.6, 119.9, 113.8, 111.5, 108.2, 30.0, 14.9. **ESI-MS**: *m/z* =$[M+H]^+$calcd. for $C_{21}H_{17}ClNO_2$: 350.0942; found 350.0942.

Compound **4d**: Yellow solid, mp 180 ^oC.. δ_H (500 MHz, Chloroform-*d*) 8.51 (1 H, s), 7.46 (1 H, d, *J* 8.2), 7.37 (1 H, d, *J* 7.9), 7.32 – 7.20 (5 H, m), 7.18 – 7.08 (2 H, m), 2.68 (3 H, s), 1.84 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 158.0, 147.7, 136.3, 131.5, 129.5, 127.6, 126.7, 125.6, 123.7, 123.0, 121.2, 120.8, 119.8, 114.0, 111.6, 108.4, 30.1, 14.9. **ESI-MS**: *m/z* =$[M+H]^+$calcd. for $C_{21}H_{17}BrNO_2$: 394.0437; found 394.0436.

Compound **4e**: Yellow solid, mp 180 ^oC. δ_H (300 MHz, Chloroform-*d*) 8.3 (1 H, s), 7.4 – 7.3 (4 H, m), 7.2 – 7.1 (2 H, m), 7.06 - 7.01 (1 H, m), 6.8 – 6.6 (2 H, m), 4.0 (2 H, q, *J* 7.1), 3.7 (3 H, s), 2.7 (3 H, s), 0.9 (3 H, t, *J* 7.1). δ_C (75 MHz, Chloroform-*d*) 164.5, 158.8, 157.9, 148.7, 136.1, 128.0, 126.9, 123.9, 123.7, 122.0, 120.3, 119.8, 116.4, 113.8, 112.7, 111.1, 108.6, 55.3, 14.7, 59.9, 13.7. **ESI-MS**: *m/z* =$[M+H]^+$calcd. for $C_{23}H_{22}NO_4$: 376.1543; found 376.1545.

Compound **4f**: Light yellow solid, mp 140 ^oC. δ_H (500 MHz, Chloroform-*d*) 8.35 (1 H, s), 7.38 (1 H, d, *J* 8.2), 7.3-7.25 (4 H, m), 7.21 – 6.99 (4 H, m), 4.01 (2 H, q, *J* 7.1), 2.70 (3 H, s), 0.86 (3 H, t, *J* 7.1). δ_C (126 MHz, Chloroform-*d*) 164.2, 158.7, 147.6, 136.2, 131.4, 129.7, 127.6, 126.9, 123.9, 122.2, 121.1, 120.2, 120.0, 116.7, 115.1, 111.2, 107.9, 60.0, 29.9, 14.5, 13.7. **ESI-MS**: *m/z* =$[M+H]^+$calcd. for $C_{22}H_{19}BrNO_3$: 424.0543; found 424.0542.

Compound **4g**: Yellow liquid. δ_H (500 MHz, Chloroform-*d*) 8.41 (1 H, s), 7.47 (1 H, d, *J* 8.2), 7.40 (1 H, d, *J* 7.9), 7.30 – 7.24 (2 H, m), 7.20 (1 H, d, *J* 2.4), 7.16 – 7.06 (2 H, m), 6.93 (1 H, dd, *J* 5.1, 1.3), 2.68 (3 H, s), 1.87 (3 H, s). δ_C (126 MHz, Chloroform-*d*) 196.6, 157.4, 146.7, 136.3, 131.7, 127.9, 125.5, 125.2, 125.0, 123.9, 122.9, 120.7, 120.4, 120.0, 112.1, 111.5, 108.7, 30.2, 14.9. **ESI-MS**: *m/z* =$[M+H]^+$calcd. for $C_{19}H_{16}NO_2S$: 322.0896; found 322.0895.

Compound **4h**: Yellow solid, mp 210 ^oC. δ_H (300 MHz, Chloroform-*d*) 8.52 (1 H, s), 7.46 - 7.43 (1 H, m), 7.29 – 7.18 (4 H, m), 7.17 – 7.05 (3 H, m), 2.61 (3 H, s), 1.79 (3 H, s). δ_C (75 MHz, Chloroform-*d*) 196.2, 158.3, 148.0, 134.9, 131.6, 129.4, 129.3, 126.7, 126.0, 125.4, 124.9, 122.2, 121.5, 114.1, 113.2, 108.2, 100.1, 30.2, 15.0. **ESI-MS**: *m/z* =$[M+H]^+$calcd. for $C_{21}H_{16}Br_2NO_2$: 471.9542; found 471.9542.

Compound **4i**: Brown viscous liquid. δ $_H$ (300 MHz, Chloroform-*d*) 8.29 (1 H, s), 7.37-7.30 (2 H, m), 7.20 – 7.13 (1 H, m), 7.11 – 7.00 (2 H, m), 2.51 (3 H, s), 2.08 (3 H, s), 1.83 (3 H, s). δ $_C$ (75 MHz, Chloroform-*d*) 197.0, 156.7, 148.3, 136.1, 128.1, 123.6, 122.6, 120.3, 119.8, 112.6, 111.4, 108.9, 30.0, 14.6, 12.0. **ESI-MS**: *m/z* =[M+H]$^+$calcd. for $C_{16}H_{16}NO_2$: 254.1176; found 254.1175.

Compound **4j**: Yellow viscous liquid. δ $_H$ (300 MHz, Chloroform-*d*) 7.98 – 7.81 (2 H, m), 7.09 – 6.98 (4 H, m), 6.94 – 6.87 (2 H, m), 3.81 (3 H, s), 2.64 (3 H, s), 2.50 (3 H, s), 2.28 (3 H, s). δ $_C$ (75 MHz, Chloroform-*d*) 195.8, 160.1, 158.5, 155.6, 135.4, 133.9, 130.2, 128.3, 125.8, 124.8, 122.1, 114.0, 105.1, 55.4, 30.6, 21.0, 15.0. **ESI-MS**: *m/z* =[M+H]$^+$calcd. for $C_{21}H_{21}O_3S$: 353.1206; found 353.1204.

Compound **4k**: White solid, mp 110 ^{o}C. δ $_H$ (300 MHz, Chloroform-*d*) 7.98 – 7.87 (2 H, m), 7.44 – 7.33 (3 H, m), 7.25 – 7.18 (2 H, m), 7.10 – 7.01 (2 H, m), 2.66 (3 H, s), 2.48 (3 H, s). δ $_C$ (75 MHz, Chloroform-*d*) 195.3, 159.3, 155.6, 135.9, 131.6, 129.6, 129.2, 129.1, 128.7, 127.0, 126.8, 124.8, 106.1, 30.7, 15.1. **ESI-MS**: *m/z* =[M+H]$^+$calcd. for $C_{19}H_{16}ClO_2S$: 343.0554; found 343.0555.

Compound **4l**: Yellow viscous liquid. δ $_H$ (300 MHz, Chloroform-*d*) 7.60 – 7.46 (2 H, m), 7.43 – 7.18 (3 H, m), 6.32 (1 H, d, *J* 3.1), 6.14 – 6.12 (1 H, m), 2.66 (3 H, s), 2.40 (3 H, s), 2.07 (3 H, s). δ $_C$ (75 MHz, Chloroform-*d*) 195.7, 157.8, 152.8, 150.1, 143.5, 129.8, 128.5, 128.2, 125.7, 124.1, 112.1, 111.2, 107.5, 29.7, 14.6, 13.8. **ESI-MS**: *m/z* =[M+H]$^+$calcd. for $C_{18}H_{17}O_3$: 281.1172; found 281.1172.

Compound **4m**: Yellow viscous liquid. δ $_H$ (300 MHz, Chloroform-*d*) 7.36 – 7.26 (2 H, m), 7.24 – 7.12 (2 H, m), 6.20 (1 H, d, *J* 3.1), 6.12 – 5.92 (1 H, m), 2.54 (3 H, s), 2.29 (3 H, s), 1.96 (3 H, s). δ $_C$ (75 MHz, Chloroform-*d*) 195.4, 158.0, 153.0, 149.0, 143.1, 134.0, 128.8, 128.2, 126.9, 124.2, 112.2, 111.9, 107.5, 29.7, 14.6, 13.8. **ESI-MS**: *m/z* =[M+H]$^+$calcd. for $C_{18}H_{16}ClO_3$: 315.0782; found 315.0783.

Compound **4n**: Yellow viscous liquid. δ $_H$ (300 MHz, Chloroform-*d*) 7.46 – 7.33 (2 H, m), 6.89 – 6.76 (2 H, m), 6.27 (1 H, d, *J* 3.1), 6.09 (1 H, dq, *J* 3.1, 1.0), 3.80 (3 H, s), 2.62 (3 H, s), 2.37 (3 H, s), 2.03 (3 H, s). δ $_C$ (75 MHz, Chloroform-*d*) 195.8, 159.6, 157.3, 152.6, 150.3, 143.8, 127.2, 125.3, 124.0, 122.6, 114.3, 112.0, 109.9, 107.4, 55.4, 29.7, 14.6, 13.8. **ESI-MS**: *m/z* =[M+H]$^+$calcd. for $C_{19}H_{19}O_4$: 311.1278; found 311.1274.

Compound **4o**: Brown viscous liquid. δ $_H$ (300 MHz, Chloroform-*d*) 7.49 – 7.37 (2 H, m), 7.36 – 7.28 (2 H, m), 6.28 (1 H, d, *J* 3.1), 6.10 (1 H, dq, *J* 3.1, 1.0), 2.62 (3 H, s), 2.36 (3 H, s), 2.03 (3 H, s). δ $_C$ (75 MHz, Chloroform-*d*) 195.4, 158.1, 153.0, 149.0, 143.1, 131.7, 128.7, 127.1, 124.2, 122.2, 112.2, 112.0, 107.5, 29.7, 14.6, 13.8. **ESI-MS**: *m/z* =[M+H]$^+$calcd. for $C_{18}H_{16}BrO_3$: 359.0277; found 359.0278.

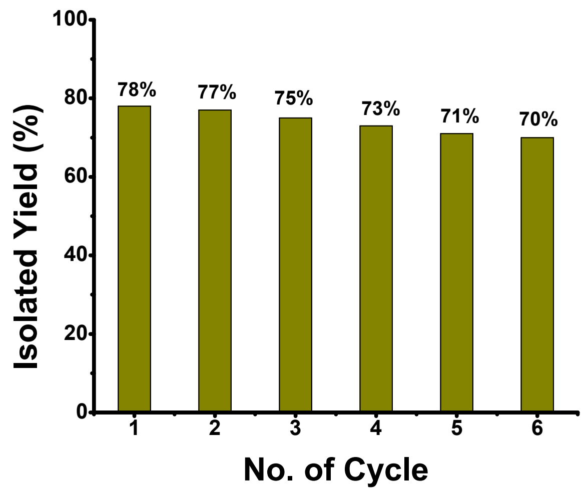
General procedure of the one-pot pyrrole synthesis: Glyoxal **1** (2.0 mmol), 1,3 diketone **2a** (2.0 mmol) and indole (2.0 mmol) were taken in a MW-tube and radiated in MW reactor at 150W for 6 min (3 min X 2). Then, aniline **5** (2.0 mmol) was added to the reaction vessel and whole mixture was heated at 70 ^{o}C for 5 h. Then, the crude mass was purified by column chromatography (25% ethyl acetate/n-hexane) to afford the desired product.

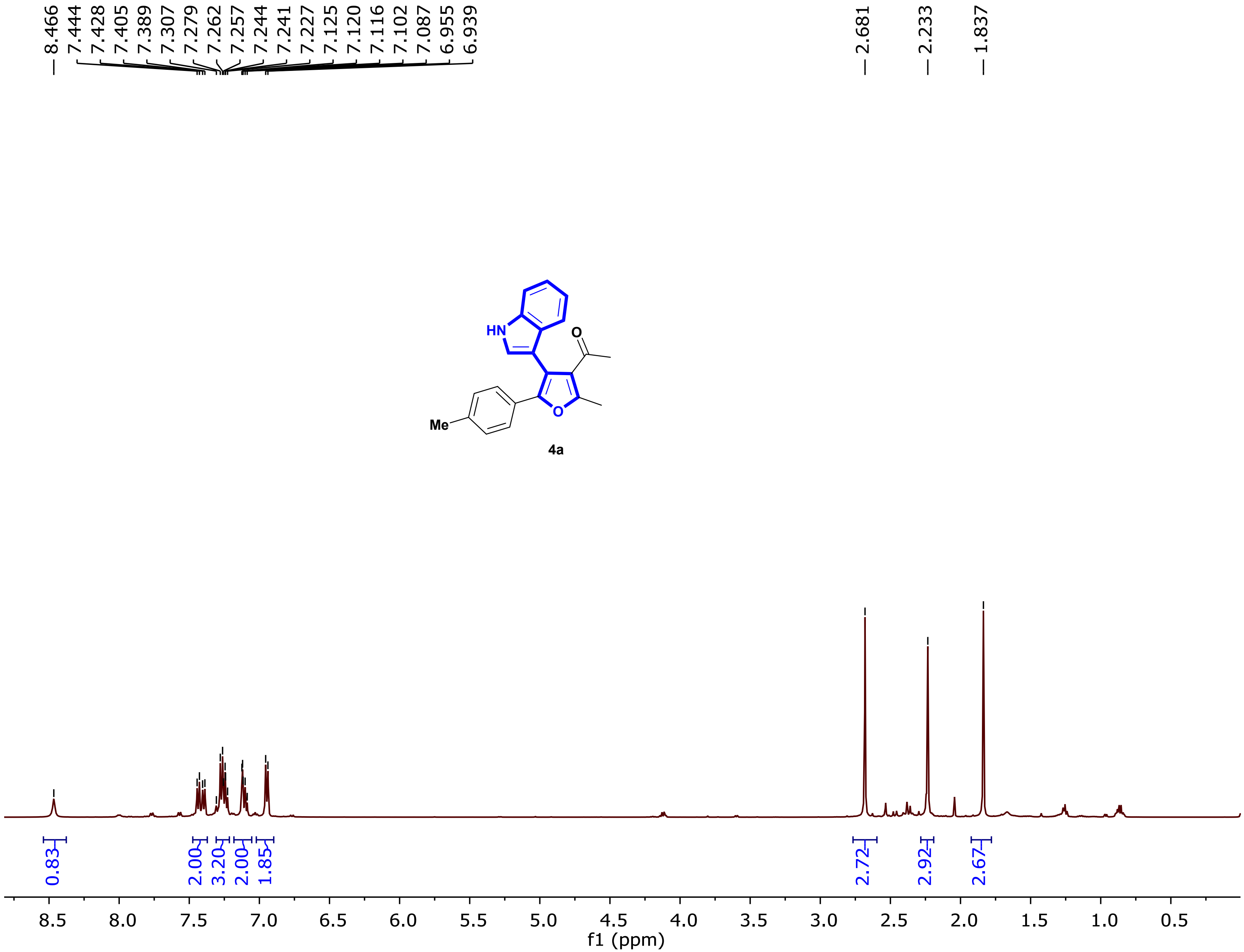
Compound **5a**: Light yellow solid, mp 205 ^{o}C. δ_H (300 MHz, DMSO-d_6) 11.00 (1 H, s), 7.33 (1 H, d, *J* 8.0), 7.26 (1 H, d, *J* 7.8), 7.22 – 7.09 (5 H, m), 7.05 (1 H, t, *J* 7.5), 6.93 (3 H, dd, *J* 12.5, 8.0), 6.54 (2 H, d, *J* 8.4), 3.56 (3 H, s), 2.29 (6 H, s), 1.74 (3 H, s). δ_C (75 MHz, DMSO-d_6) 195.9, 157.8, 137.5, 135.7, 134.9, 134.8, 132.4, 131.9, 129.6, 128.7, 128.4, 125.0, 122.4, 120.0, 119.0, 118.9, 114.8, 112.8, 111.5, 109.4, 54.7, 29.6, 20.6, 13.0 . **ESI-MS**: *m/z* =[M+H]$^+$calcd. for $C_{29}H_{27}N_2O_2$: 435.2067; found 435.2067.

Compound **5b**: Off white solid, mp 275 ^{o}C. δ_H (300 MHz, DMSO-d_6) 11.34 – 10.78 (1 H, m), 7.35 (1 H, d, *J* 8.1), 7.29 – 7.11 (6 H, m), 7.10 – 6.90 (6 H, m), 2.30 (6 H, s), 1.75 (3 H, s). δ_C (75 MHz, DMSO-d_6) 195.8, 137.8, 135.8, 134.6, 132.2, 131.4, 131.2, 130.9, 129.7, 128.5, 128.3, 127.4, 125.2, 123.9, 122.5, 121.1, 119.1, 118.7, 115.6, 111.6, 108.8, 29.7, 20.6, 12.9 . **ESI-MS**: *m/z* =[M+H]$^+$calcd. for $C_{28}H_{24}ClN_2O$: 439.1572; found 439.1570.

Compound **5c**: Light red solid, mp 288 ^{o}C. δ_H (300 MHz, DMSO-d_6) 11.03 (1 H, s), 7.55 – 7.40 (2 H, m), 7.40 – 7.29 (3 H, m), 7.30 – 7.15 (2 H, m), 7.14 – 6.87 (7 H, m), 2.32 (3 H, s), 1.76 (3 H, d, *J* 1.4). δ_C (75 MHz, DMSO-d_6) 196.0, 136.3, 136.1, 135.7, 135.4, 135.0, 132.7, 132.4, 132.2, 131.6, 130.7, 130.5, 129.1, 129.3, 127.6, 127.4, 125.1,122.8, 121.0, 119.0, 118.7, 115.4, 111.5, 108.9, 108.7, 29.7, 12.9 . **ESI-MS**: *m/z* =[M+H]$^+$calcd. for $C_{27}H_{22}ClN_2O$: 425.1415; found 425.1416.

Figure 1. Reusability test of GO for the synthesis 4a

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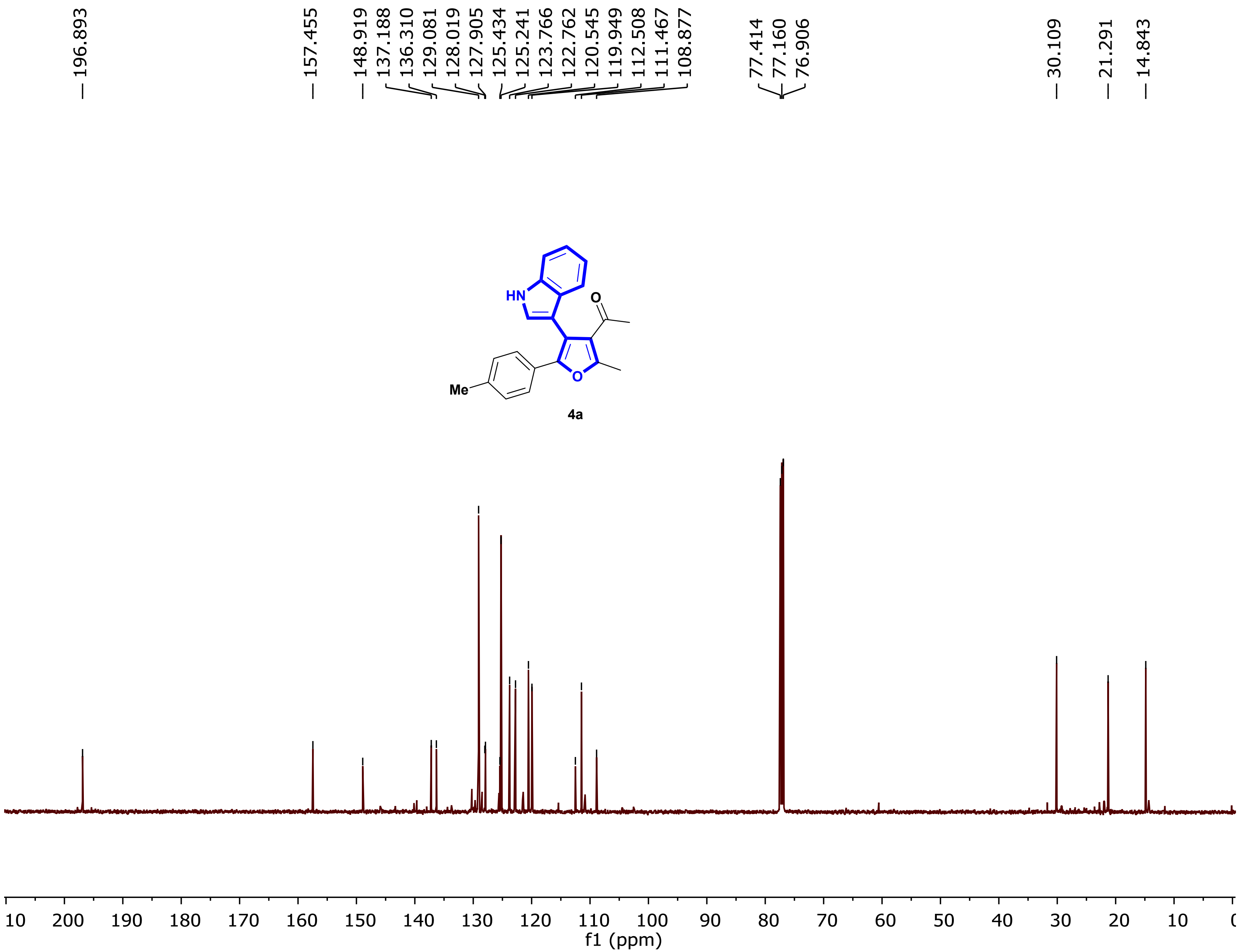
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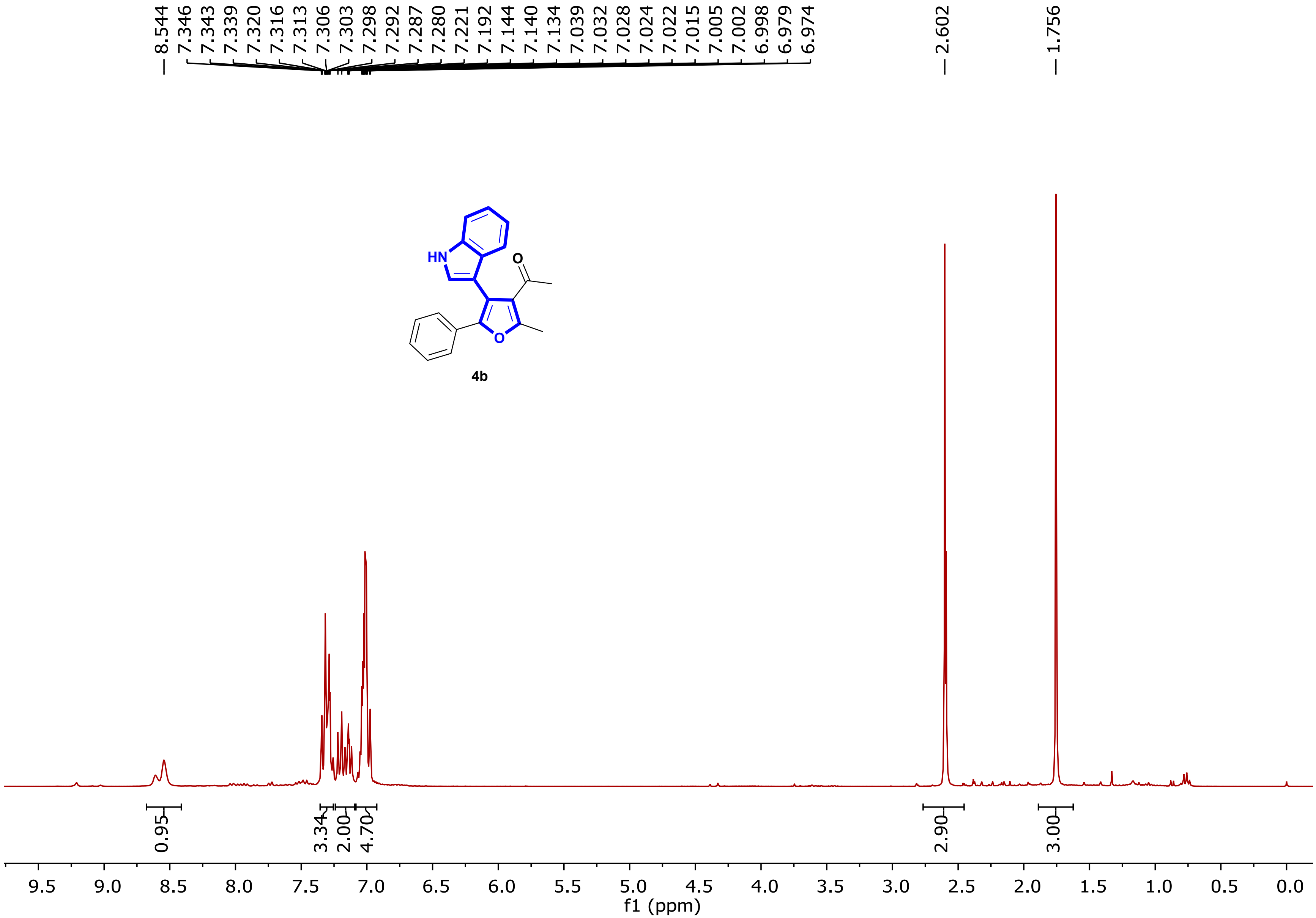
f1 (ppm)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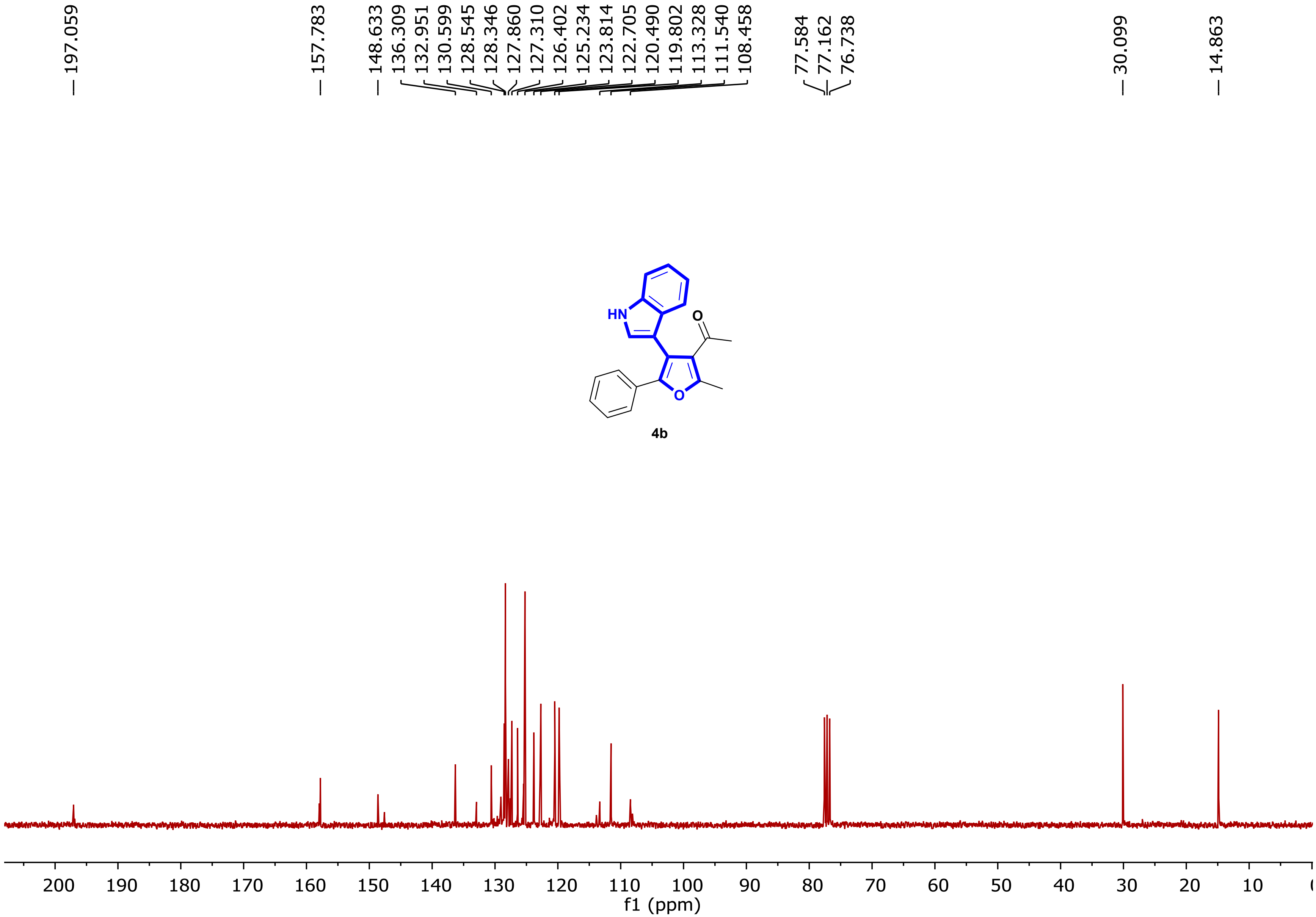
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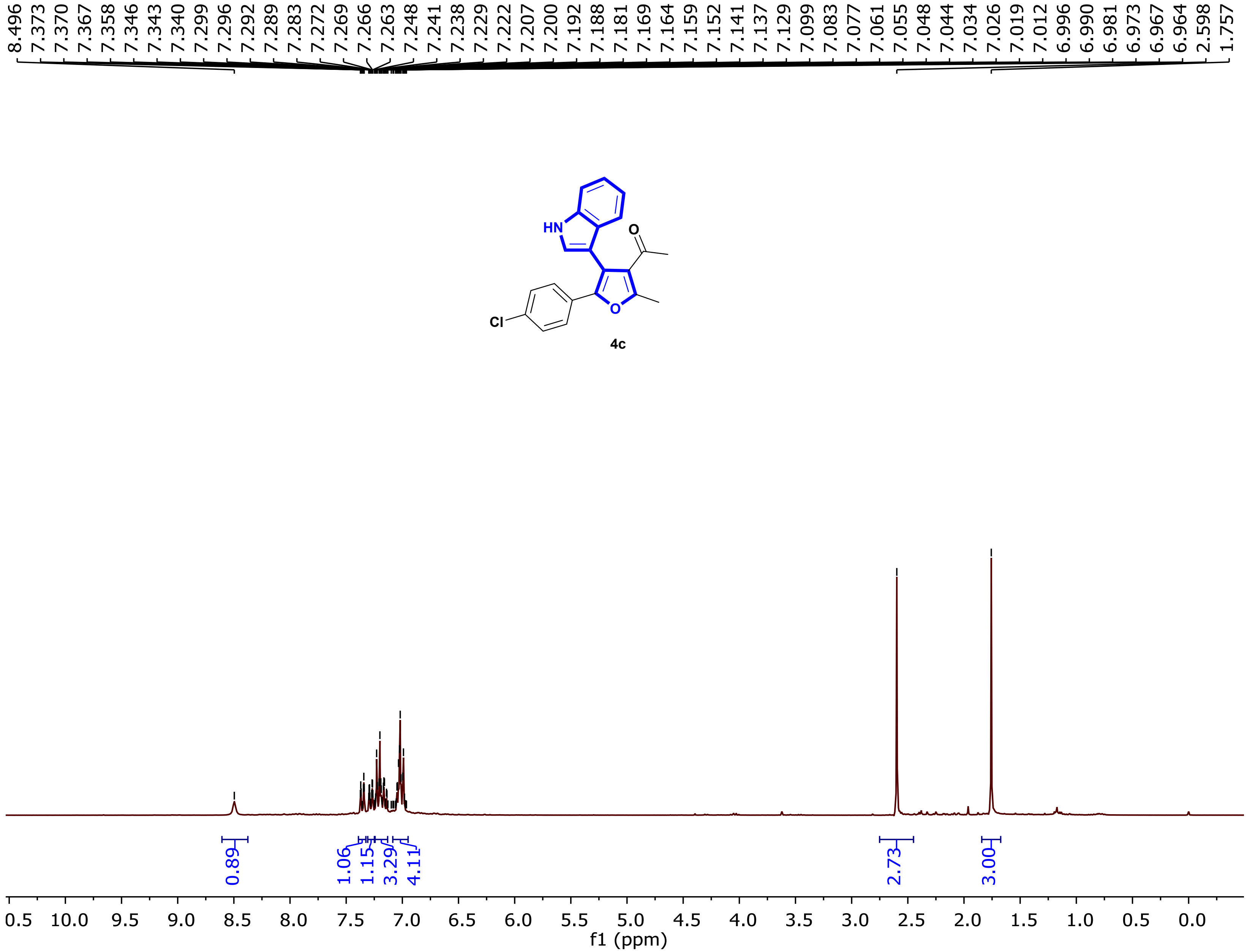
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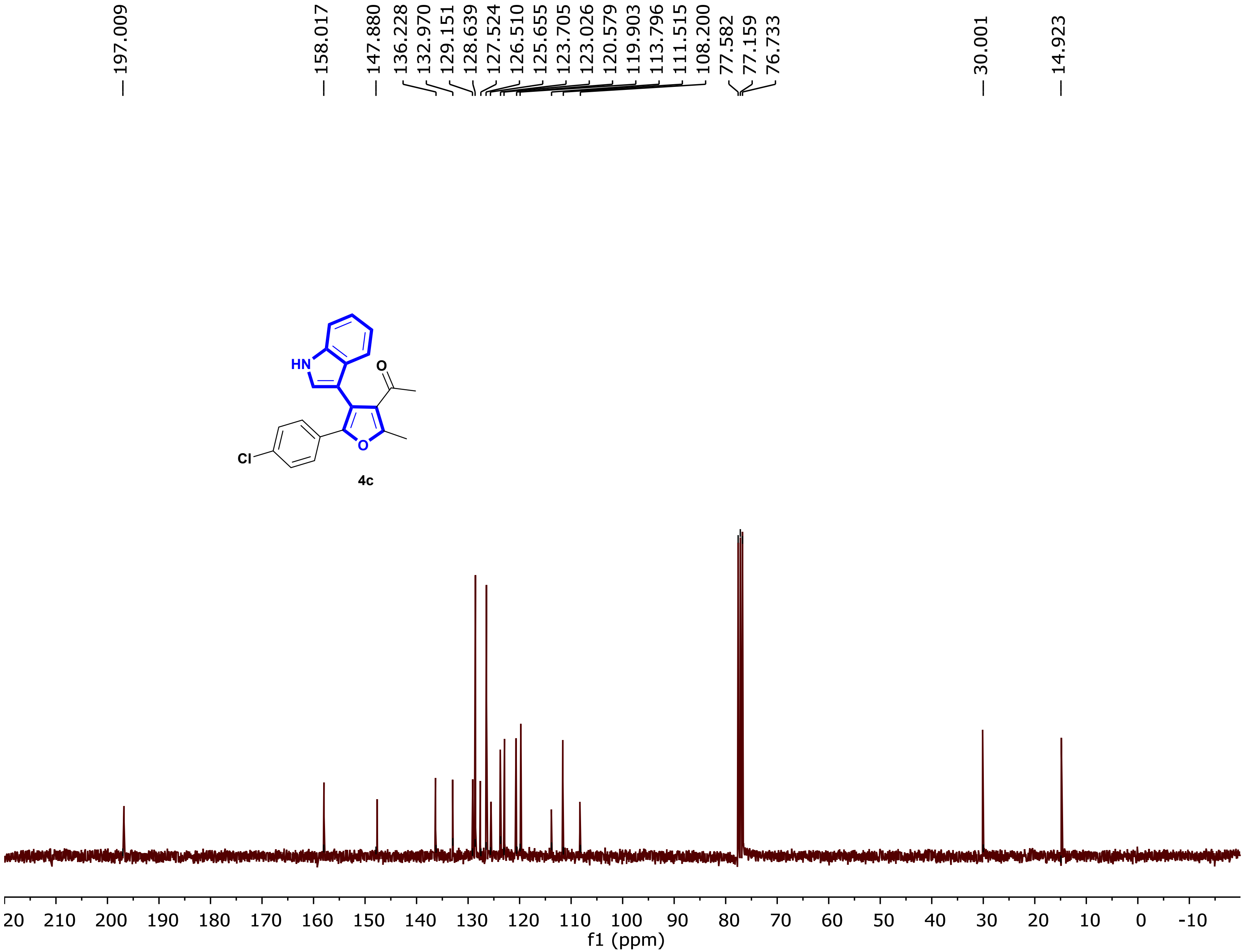
f1 (ppm)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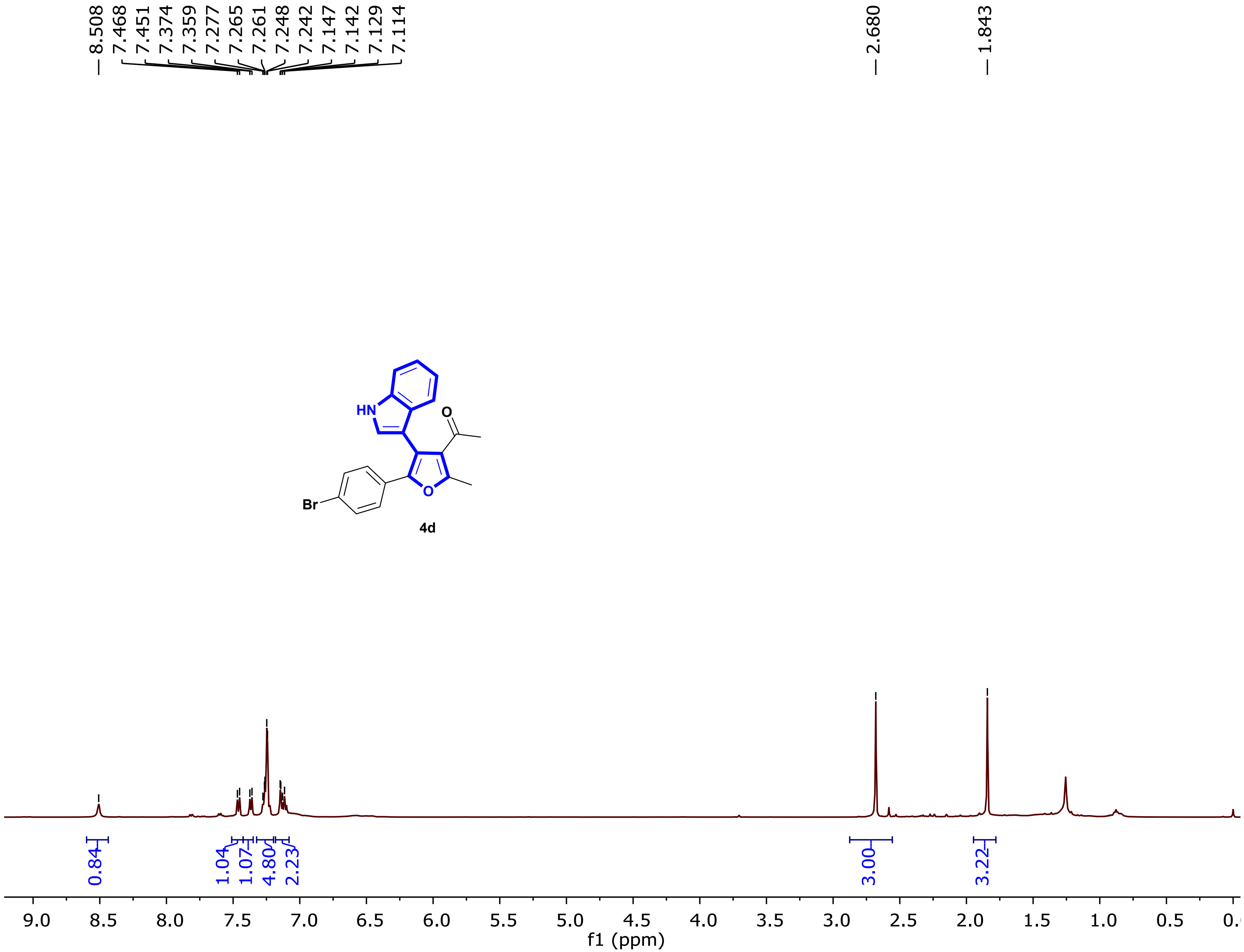
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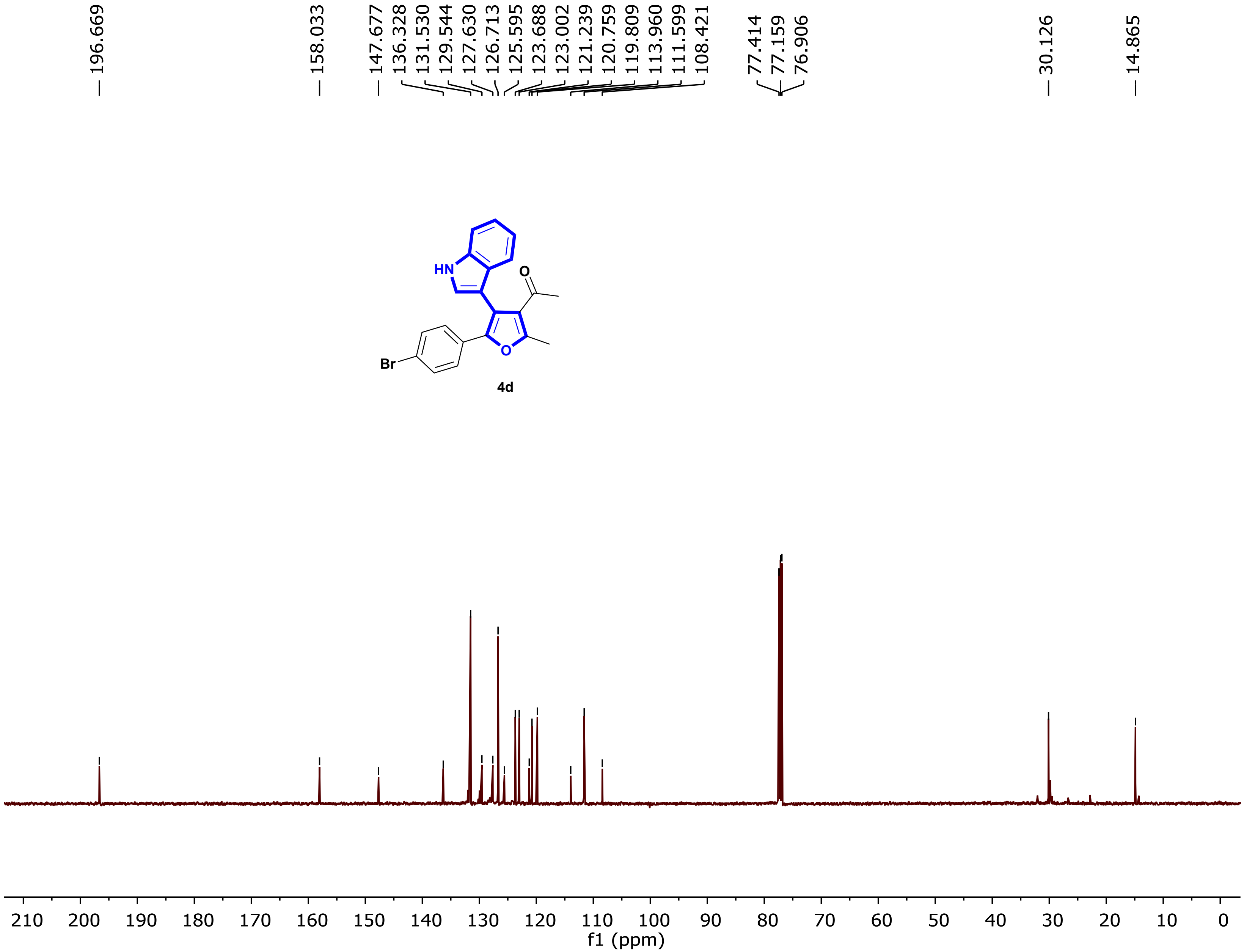
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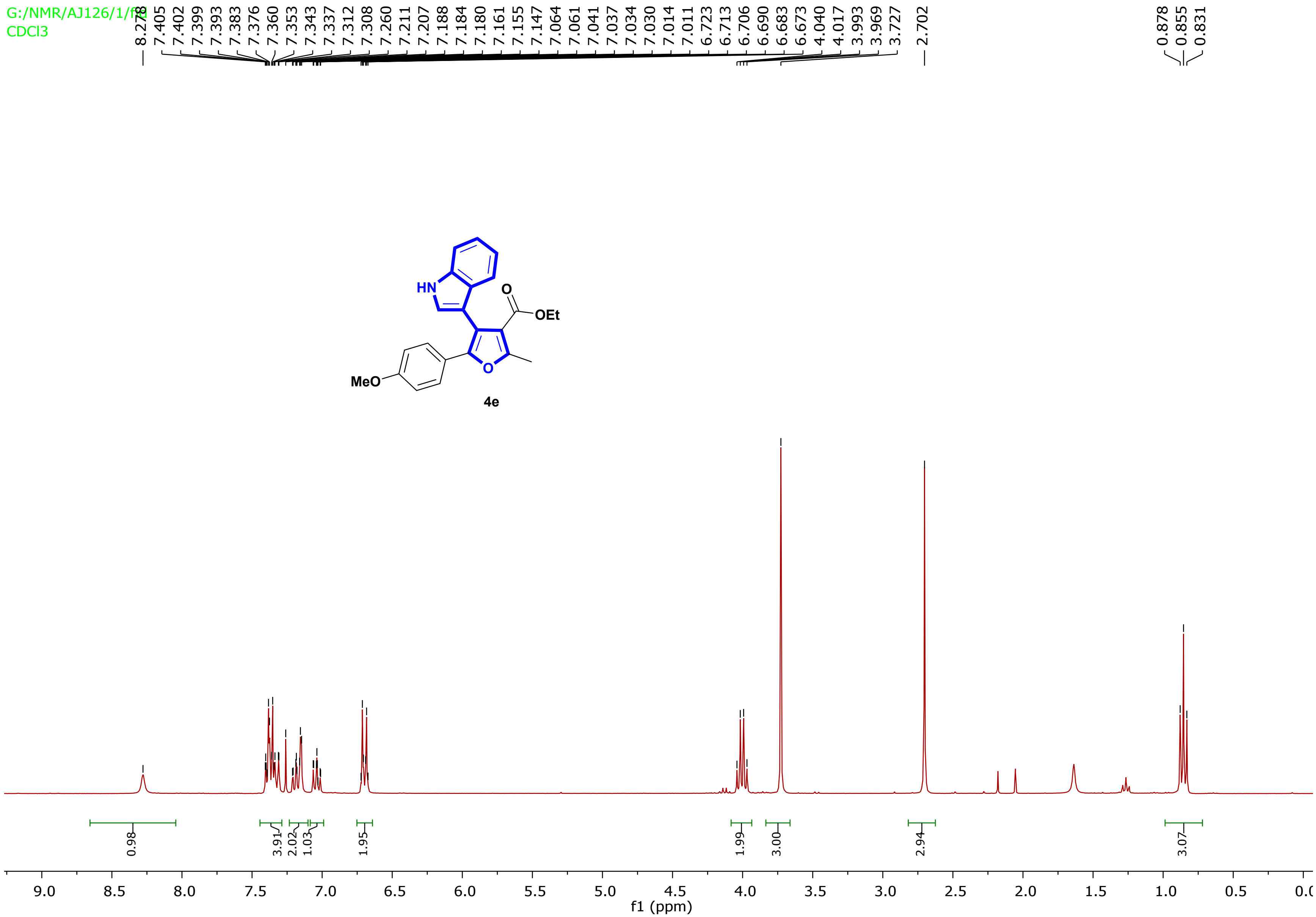
108.421
77.414
77.159
76.906
30.126
14.865
HN
O
O
Br
4d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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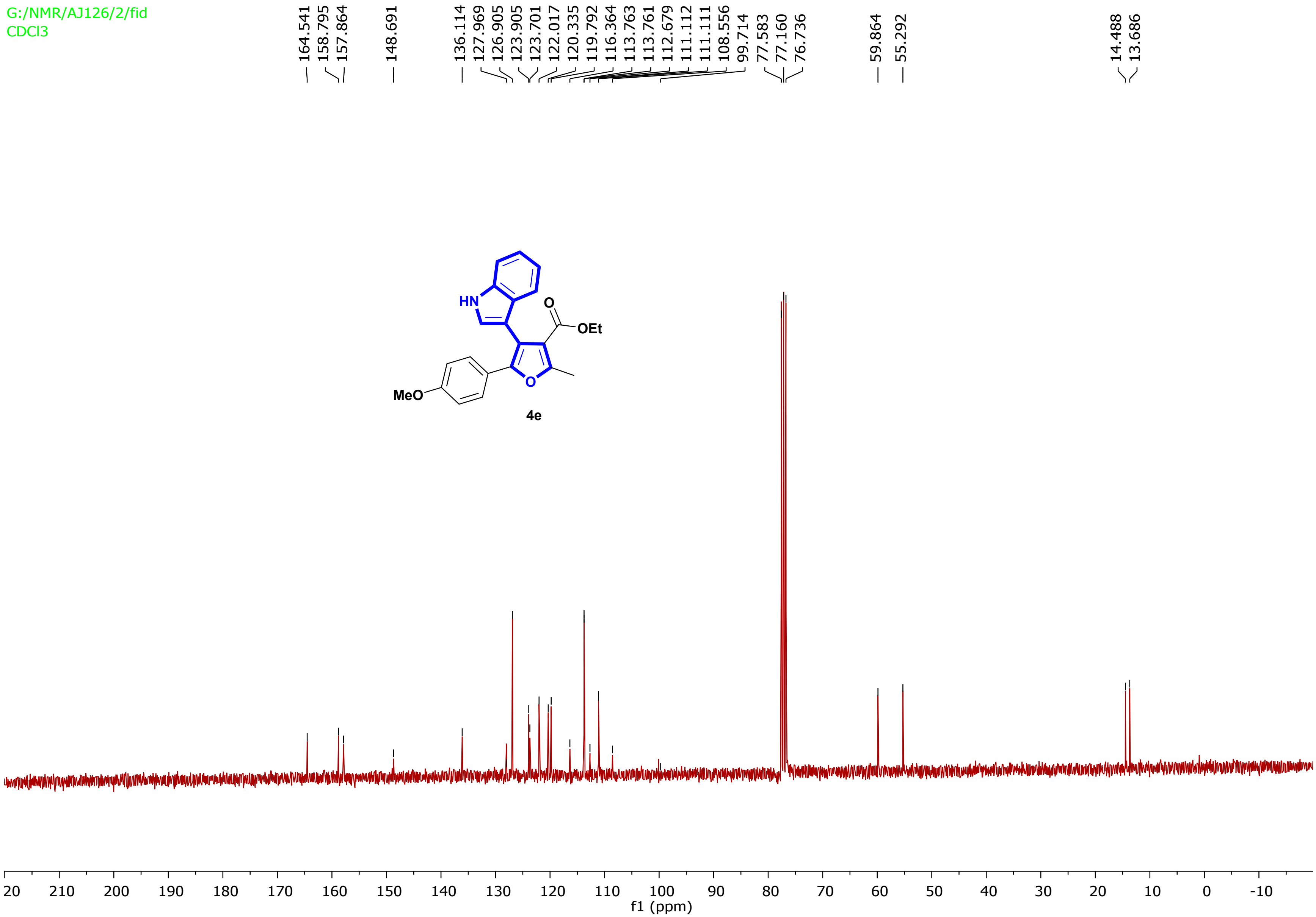
CDCl3
8.278
7.405
7.402
7.399
7.393
7.383
7.376
7.360
7.353
7.343
7.337
7.312
7.308
7.260
7.211
7.207
7.188
7.184
7.180
7.161
7.155
7.147
7.064
7.061
7.041
7.037
7.034
7.030
7.014
7.011
6.723
6.713
6.706
6.690
6.683
6.673
4.040
4.017
3.993
3.969
3.727
2.702
0.878
0.855
0.831
HN
O
OEt
MeO
O
4e
0.98
3.91
2.02
1.03
1.95
1.99
3.00
2.94
3.07
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)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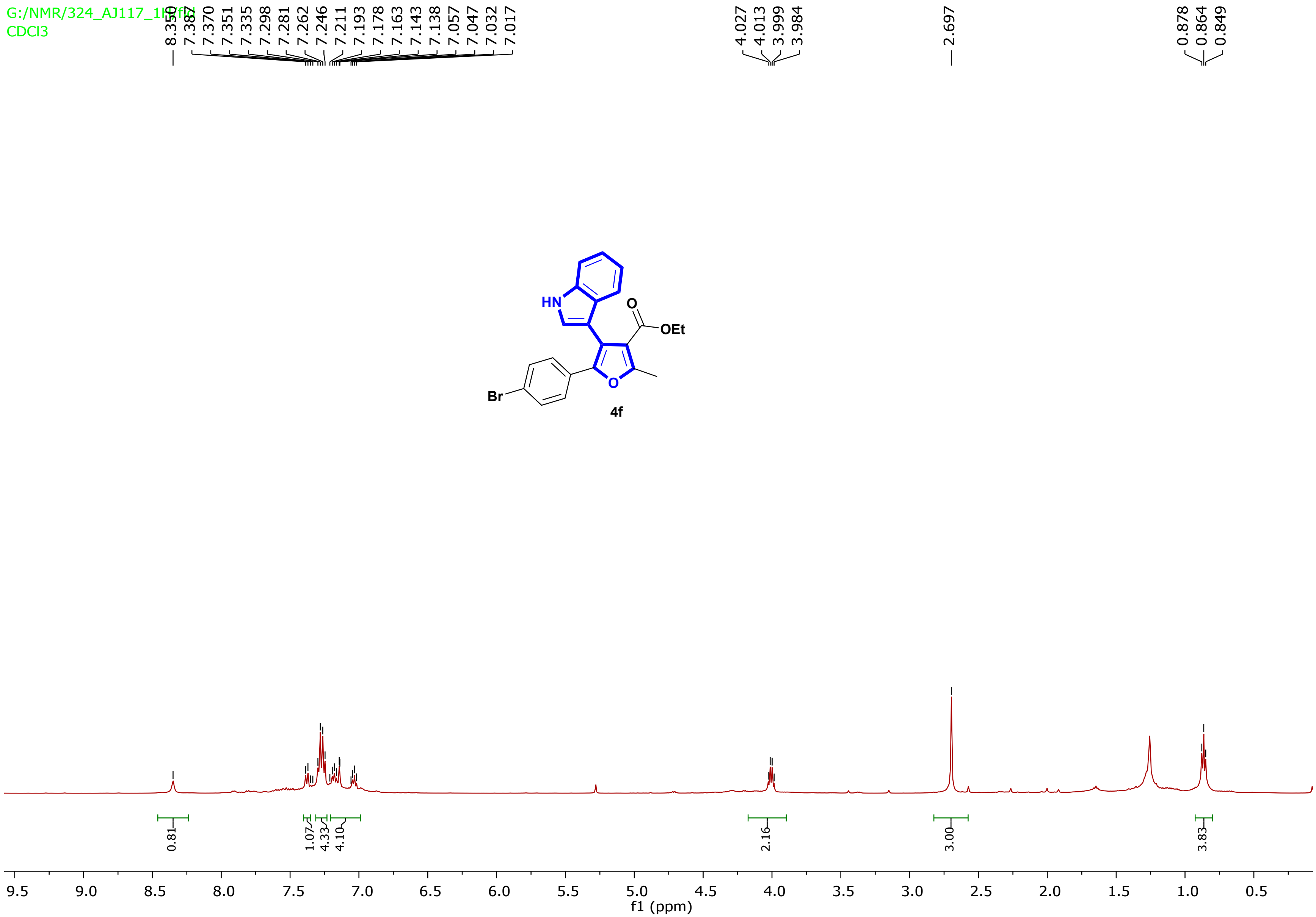
157.864
148.691
136.114
127.969
126.905
123.905
123.701
122.017
120.335
119.792
116.364
113.763
113.761
112.679
111.112
111.111
108.556
99.714
77.583
77.160
76.736
59.864
55.292
14.488
13.686
HN
O
OEt
MeO
O
4e
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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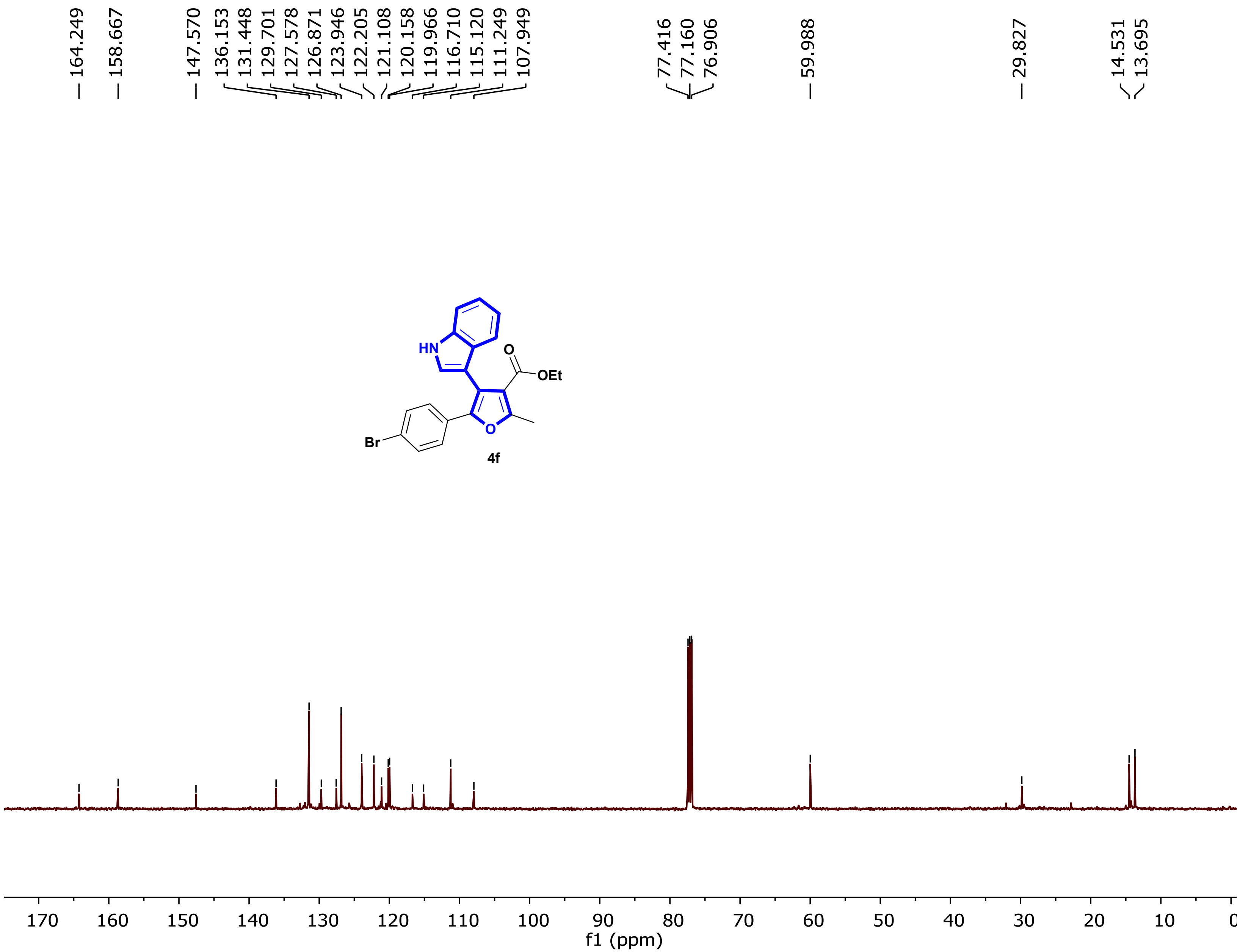
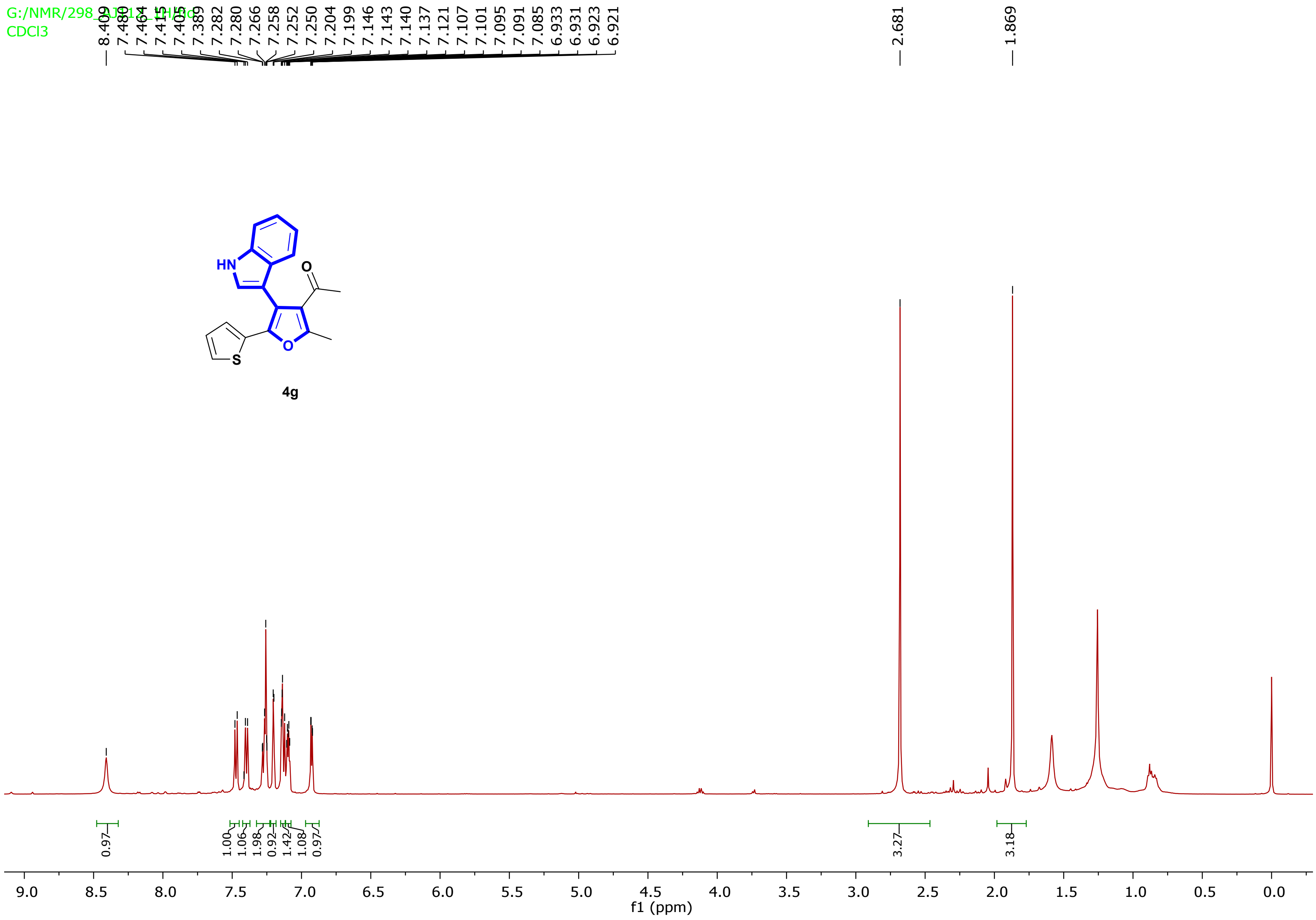
7.387
7.370
7.351
7.335
7.298
7.281
7.262
7.246
7.211
7.193
7.178
7.163
7.143
7.138
7.057
7.047
7.032
7.017
4.027
4.013
3.999
3.984
2.697
0.878
0.864
0.849
HN
O
OEt
Br
O
4f
0.81
1.07
4.33
4.10
2.16
3.00
3.83
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


164.249
158.667
147.570
136.153
131.448
129.701
127.578
126.871
123.946
122.205
121.108
120.158
119.966
116.710
115.120
111.249
107.949
77.416
77.160
76.906
59.988
29.827
14.531
13.695
HN
O
OEt
O
Br
4f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



G:/NMR/298_AJ11_15H/10
CDCl3
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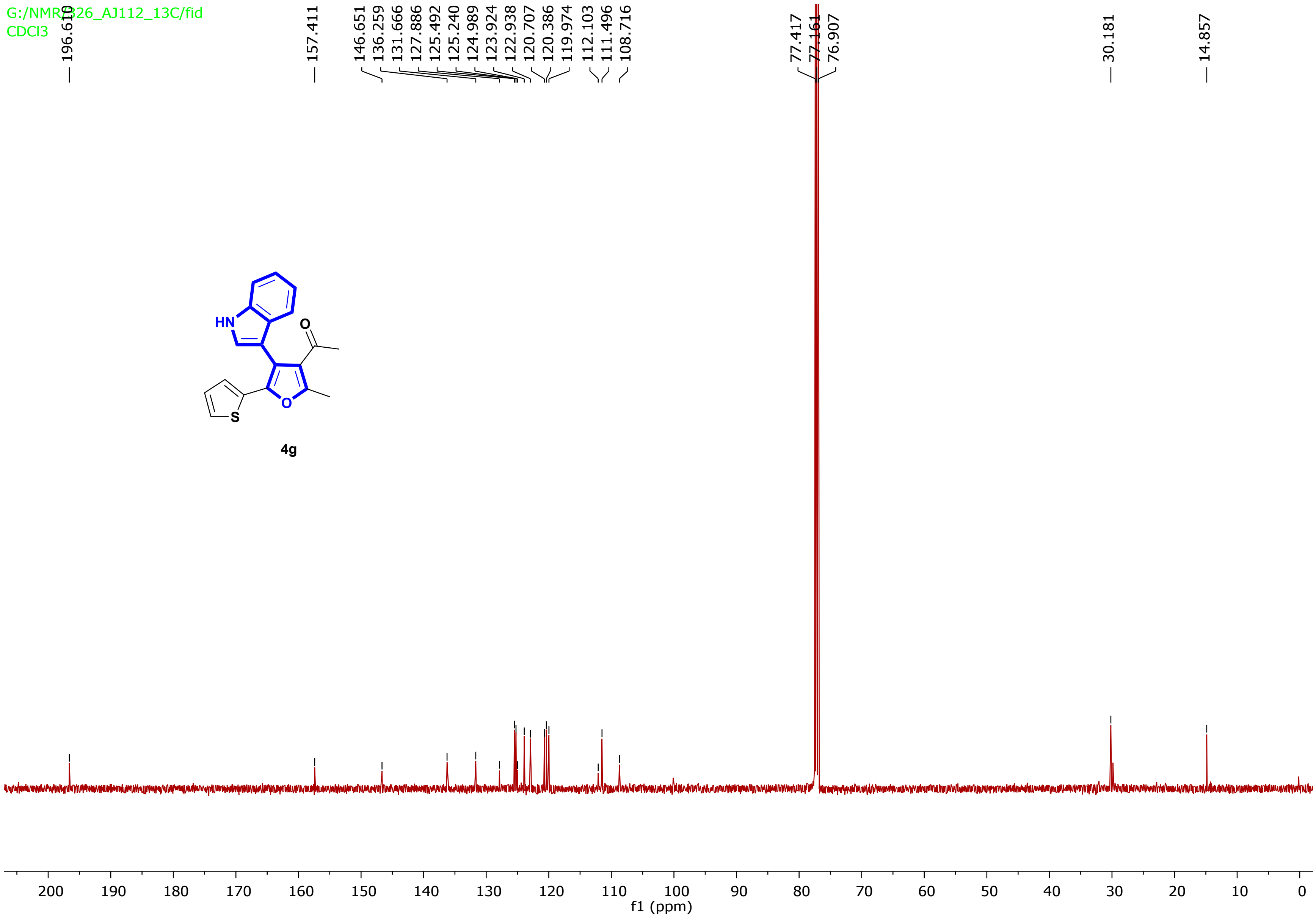
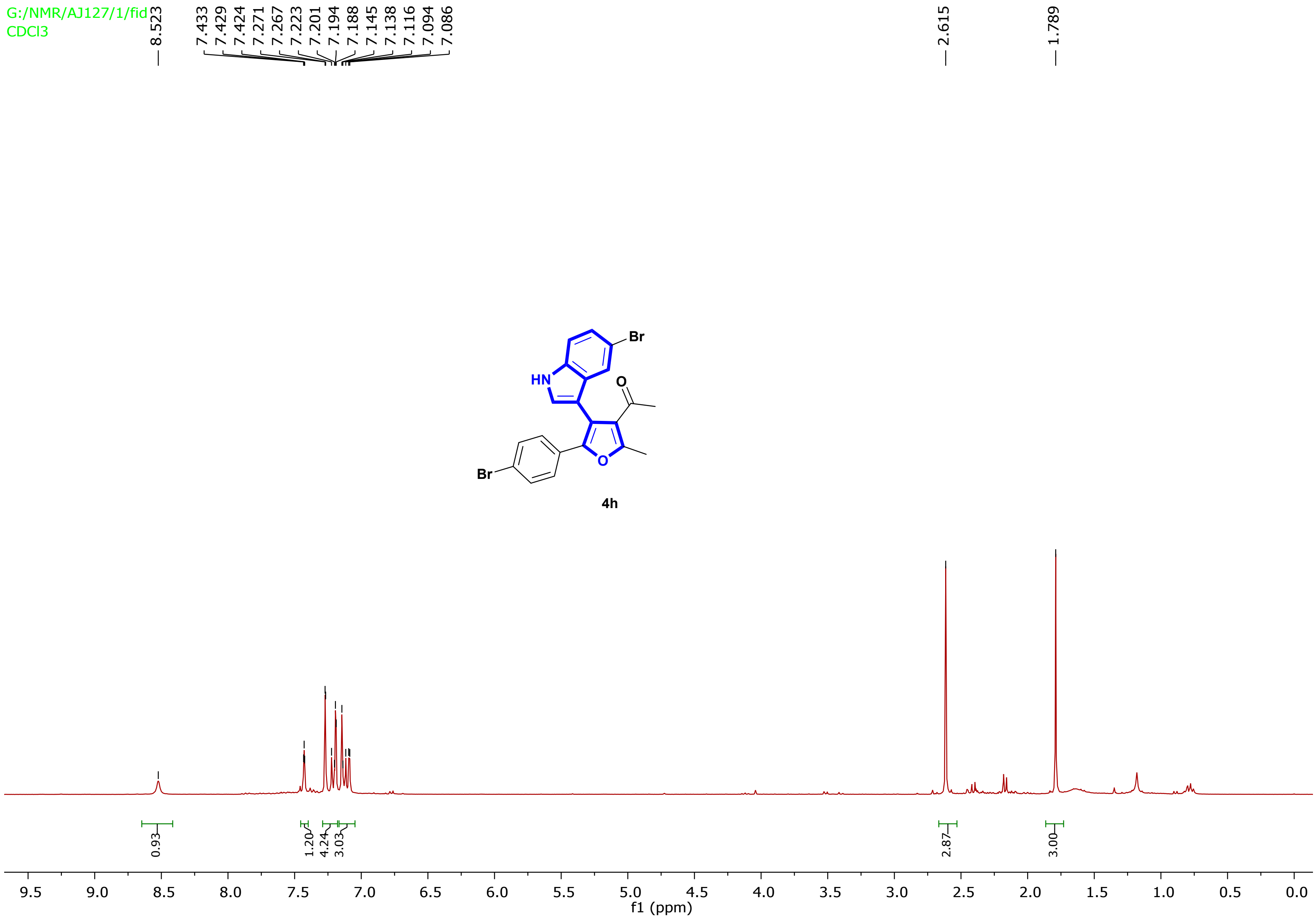
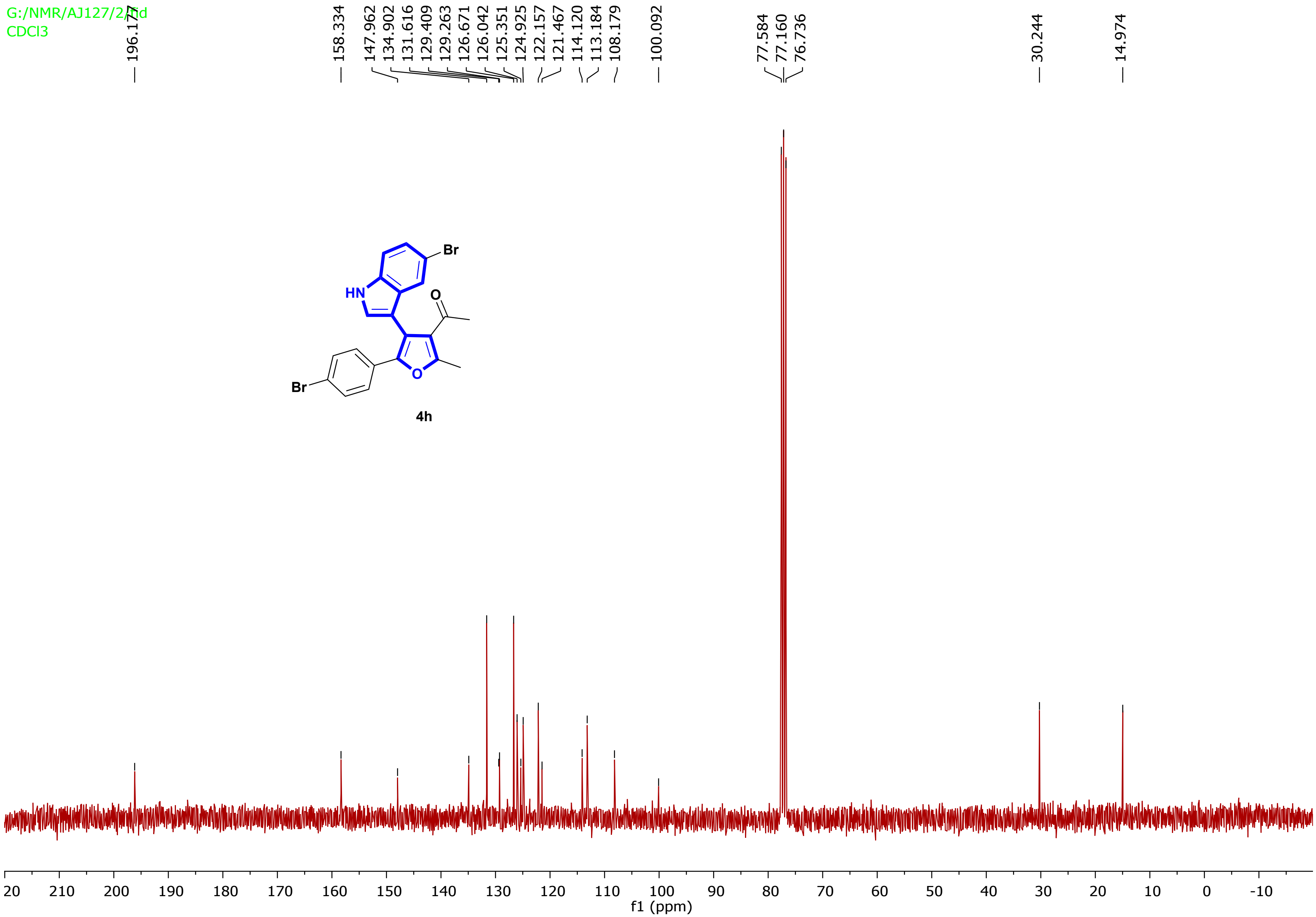
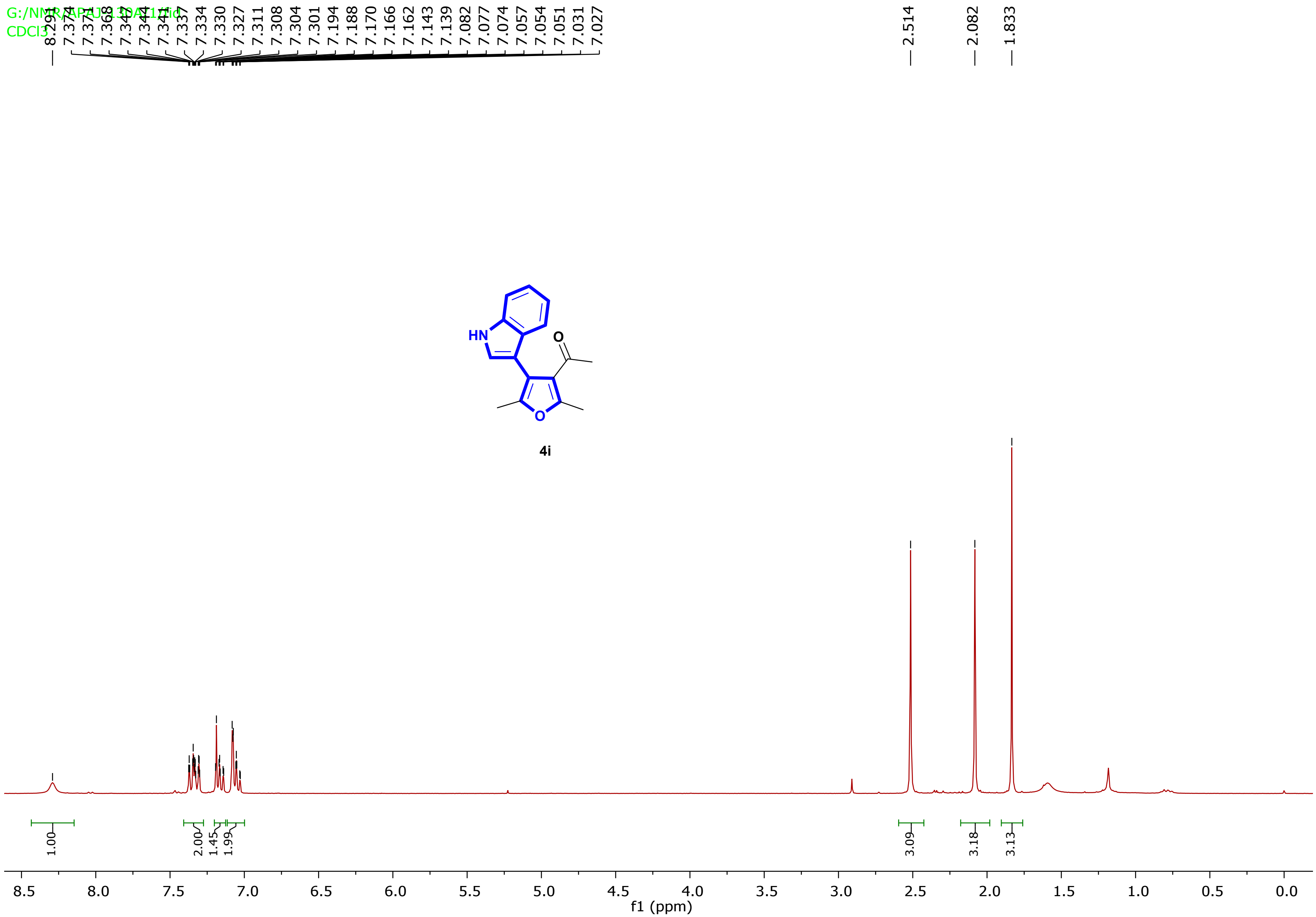
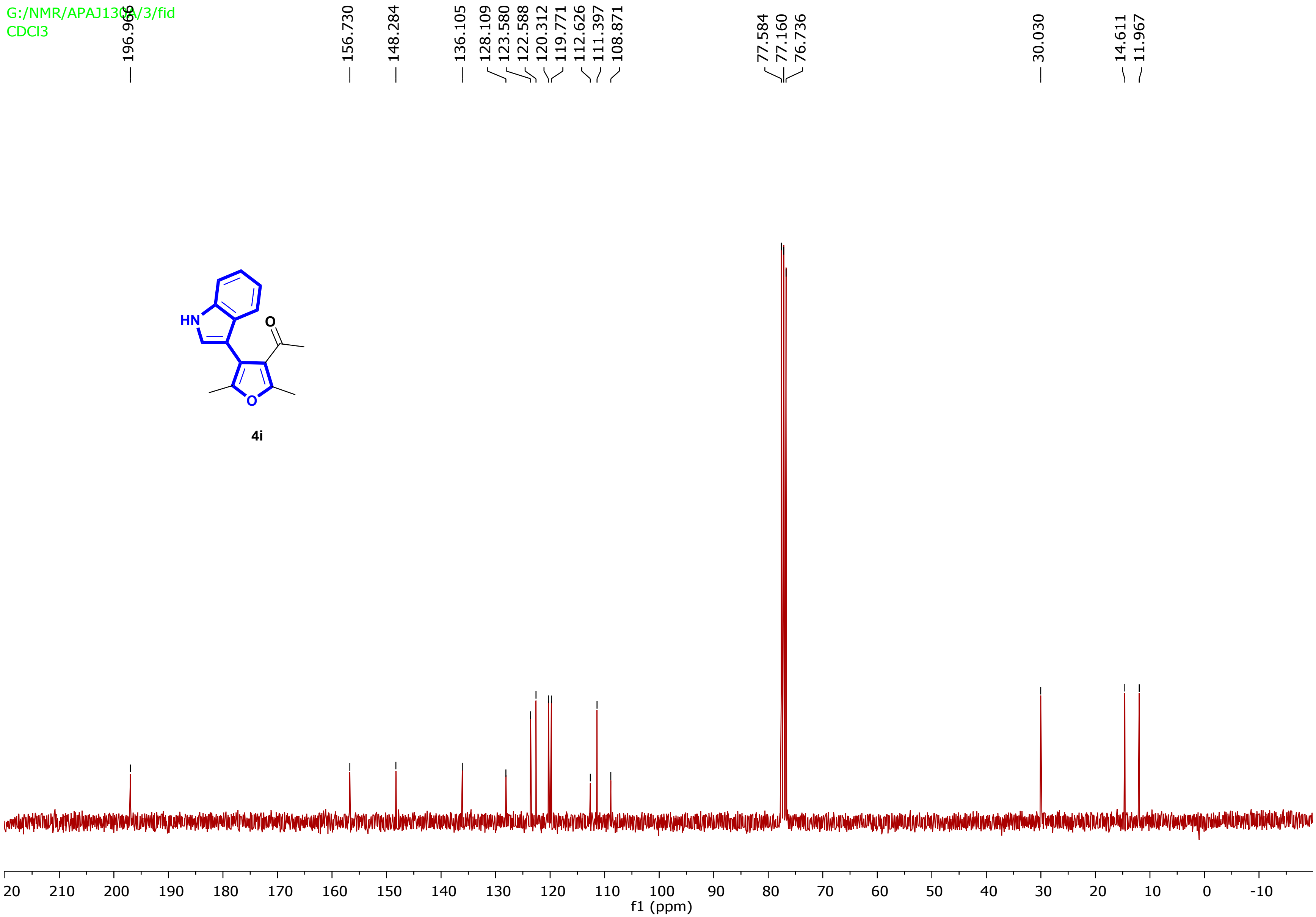
7.480
7.464
7.415
7.405
7.389
7.282
7.280
7.266
7.258
7.252
7.250
7.204
7.199
7.146
7.143
7.140
7.137
7.121
7.107
7.101
7.095
7.091
7.085
6.933
6.931
6.923
6.921
2.681
1.869
HN
O
S
4g
0.97
1.00
1.06
1.98
0.92
1.42
1.08
0.97
3.27
3.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

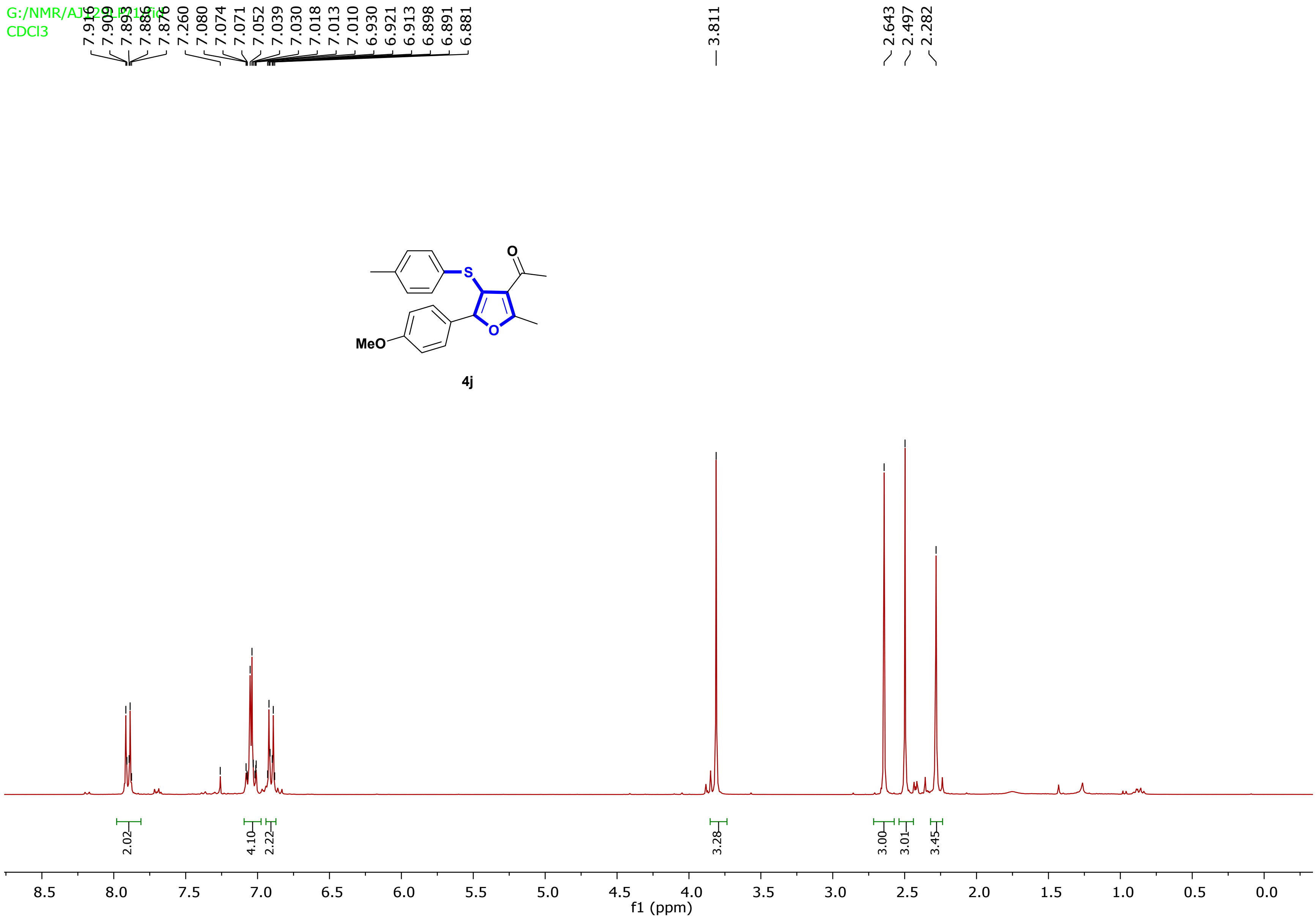

G:/NMR/326_AJ112_13C/fid
CDCl3
196.610
157.411
146.651
136.259
131.666
127.886
125.492
125.240
124.989
123.924
122.938
120.707
120.386
119.974
112.103
111.496
108.716
77.417
77.161
76.907
30.181
14.857
HN
O
S
4g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

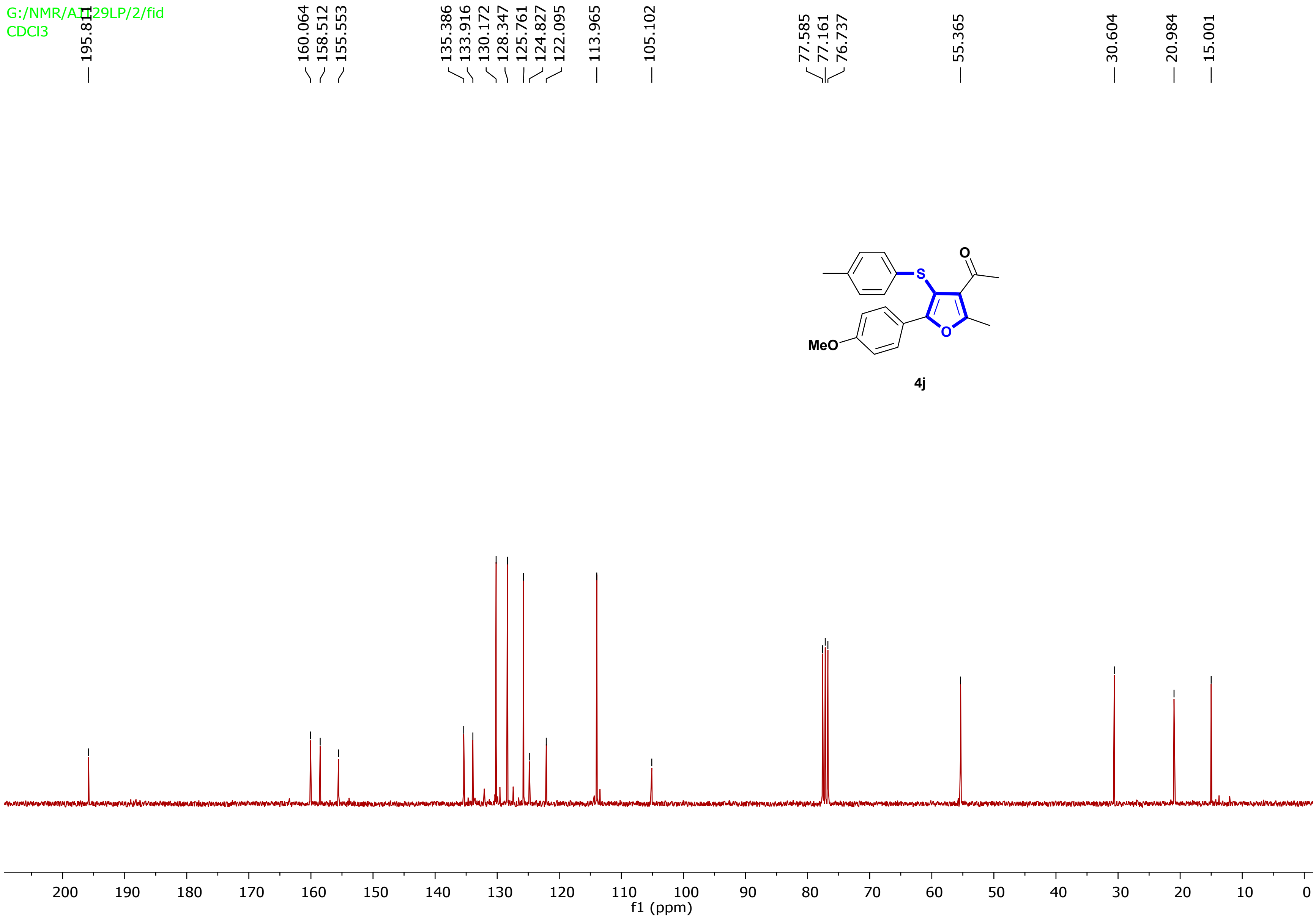

G:/NMR/AJ127/1/fid
CDCl3
8.523
7.433
7.429
7.424
7.271
7.267
7.223
7.201
7.194
7.188
7.145
7.138
7.116
7.094
7.086
2.615
1.789
Br
HN
O
Br
O
4h
0.93
1.20
4.24
3.03
2.87
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


G:/NMR/AJ127/2/fid
CDCl3
196.177
158.334
147.962
134.902
131.616
129.409
129.263
126.671
126.042
125.351
124.925
122.157
121.467
114.120
113.184
108.179
100.092
77.584
77.160
76.736
30.244
14.974
HN
Br
O
Br
4h
f1 (ppm)

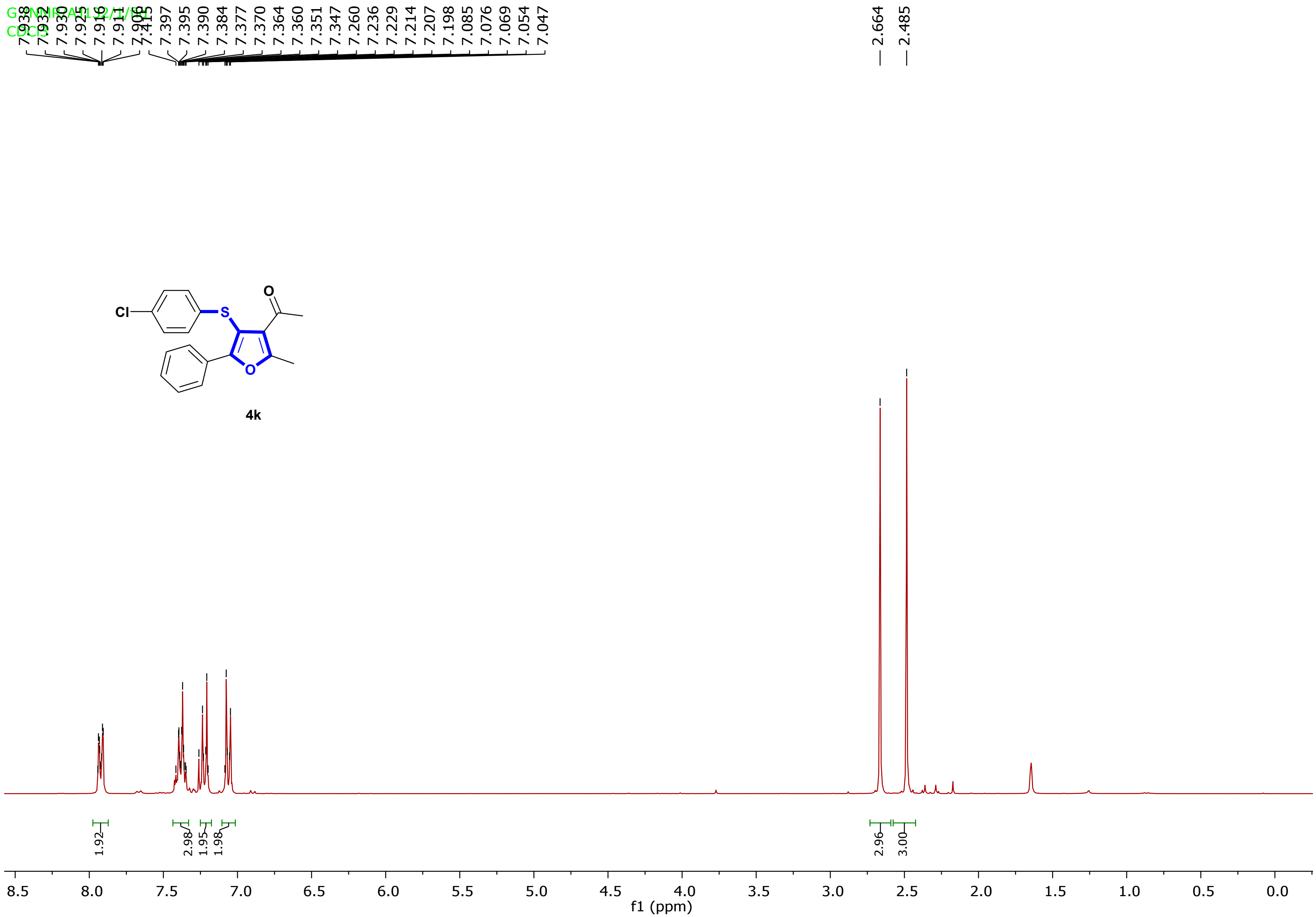

CDCl3
8.291
7.374
7.371
7.368
7.347
7.344
7.341
7.337
7.334
7.330
7.327
7.311
7.308
7.304
7.301
7.194
7.188
7.170
7.166
7.162
7.143
7.139
7.082
7.077
7.074
7.057
7.054
7.051
7.031
7.027
2.514
2.082
1.833
HN
O
O
4i
1.00
2.00
1.45
1.99
3.09
3.18
3.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

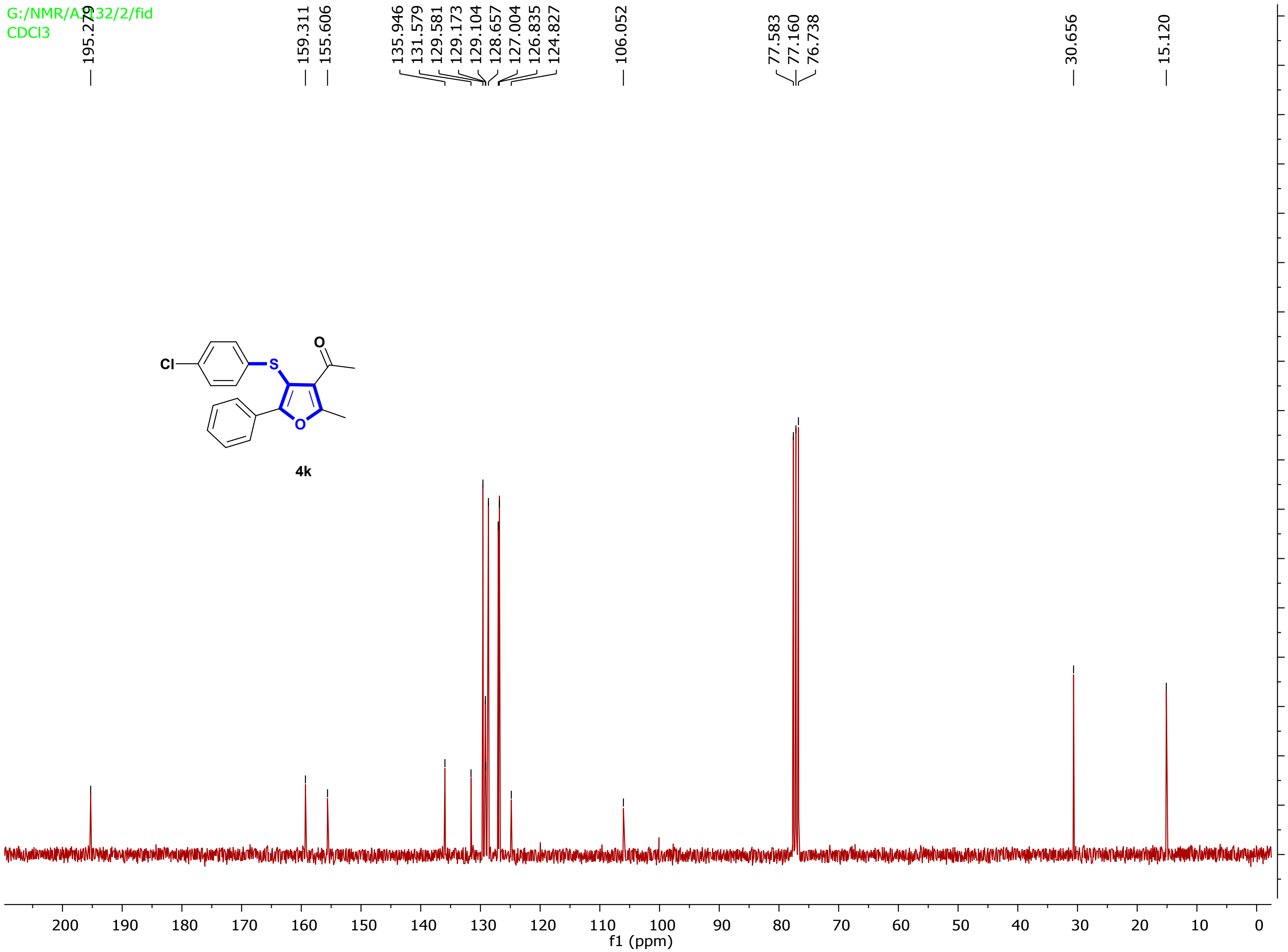

CDCl3
196.966
156.730
148.284
136.105
128.109
123.580
122.588
120.312
119.771
112.626
111.397
108.871
77.584
77.160
76.736
30.030
14.611
11.967
HN
O
4i
f1 (ppm)


CDCl3
7.916
7.909
7.893
7.886
7.876
7.260
7.080
7.074
7.071
7.052
7.039
7.030
7.018
7.013
7.010
6.930
6.921
6.913
6.898
6.891
6.881
3.811
2.643
2.497
2.282
O
S
O
MeO
4j
2.02
4.10
2.22
3.28
3.00
3.01
3.45
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)



G:/NMR/AJ129LP/2/fid
CDCl3
195.811
160.064
158.512
155.553
135.386
133.916
130.172
128.347
125.761
124.827
122.095
113.965
105.102
77.585
77.161
76.737
55.365
30.604
20.984
15.001
O
S
O
MeO
4j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.938
7.932
7.930
7.925
7.916
7.911
7.906
7.415
7.397
7.395
7.390
7.384
7.377
7.370
7.364
7.360
7.351
7.347
7.260
7.236
7.229
7.214
7.207
7.198
7.085
7.076
7.069
7.054
7.047
2.664
2.485
Cl
S
O
O
4k
1.92
2.98
1.95
1.98
2.96
3.00
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)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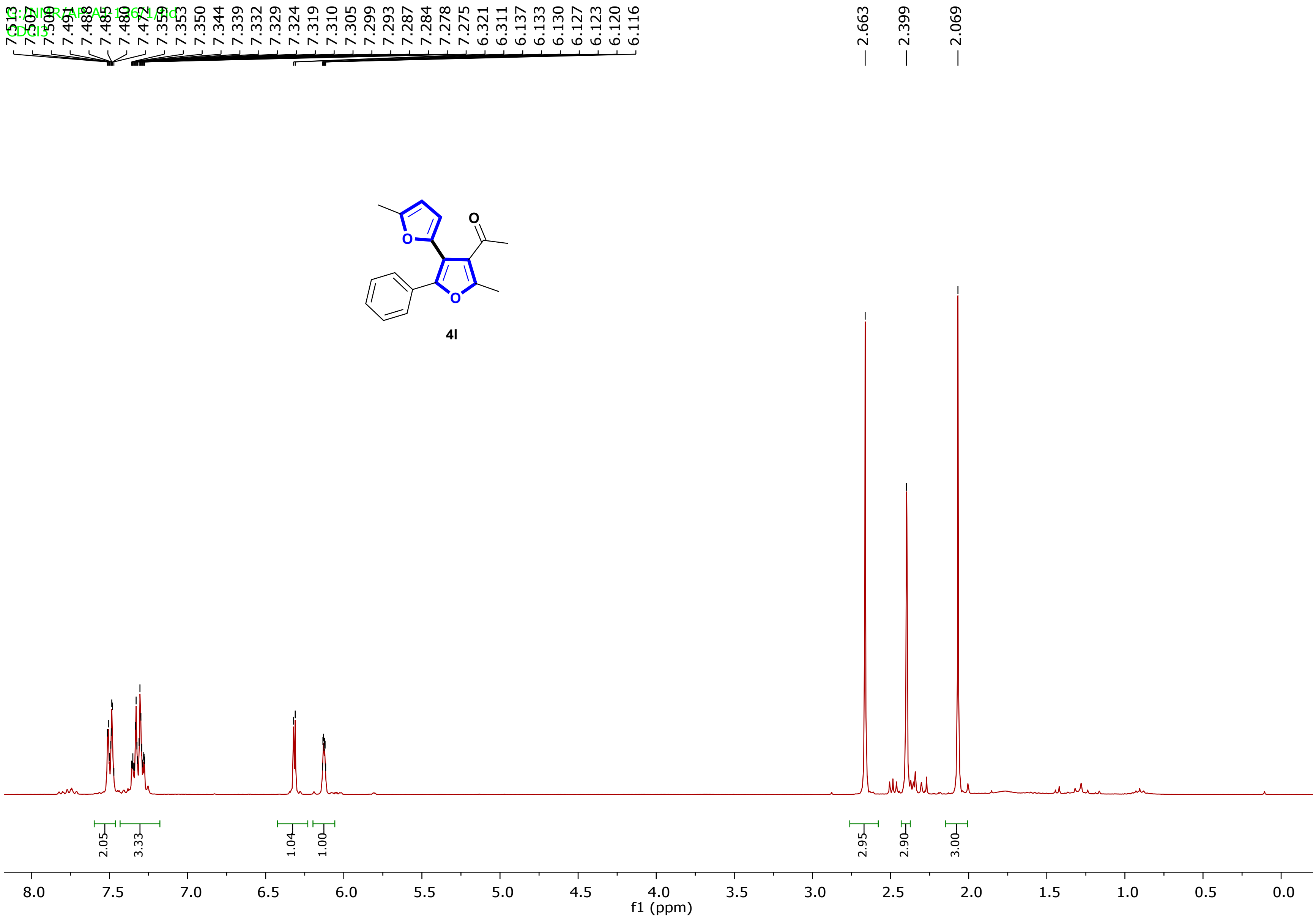
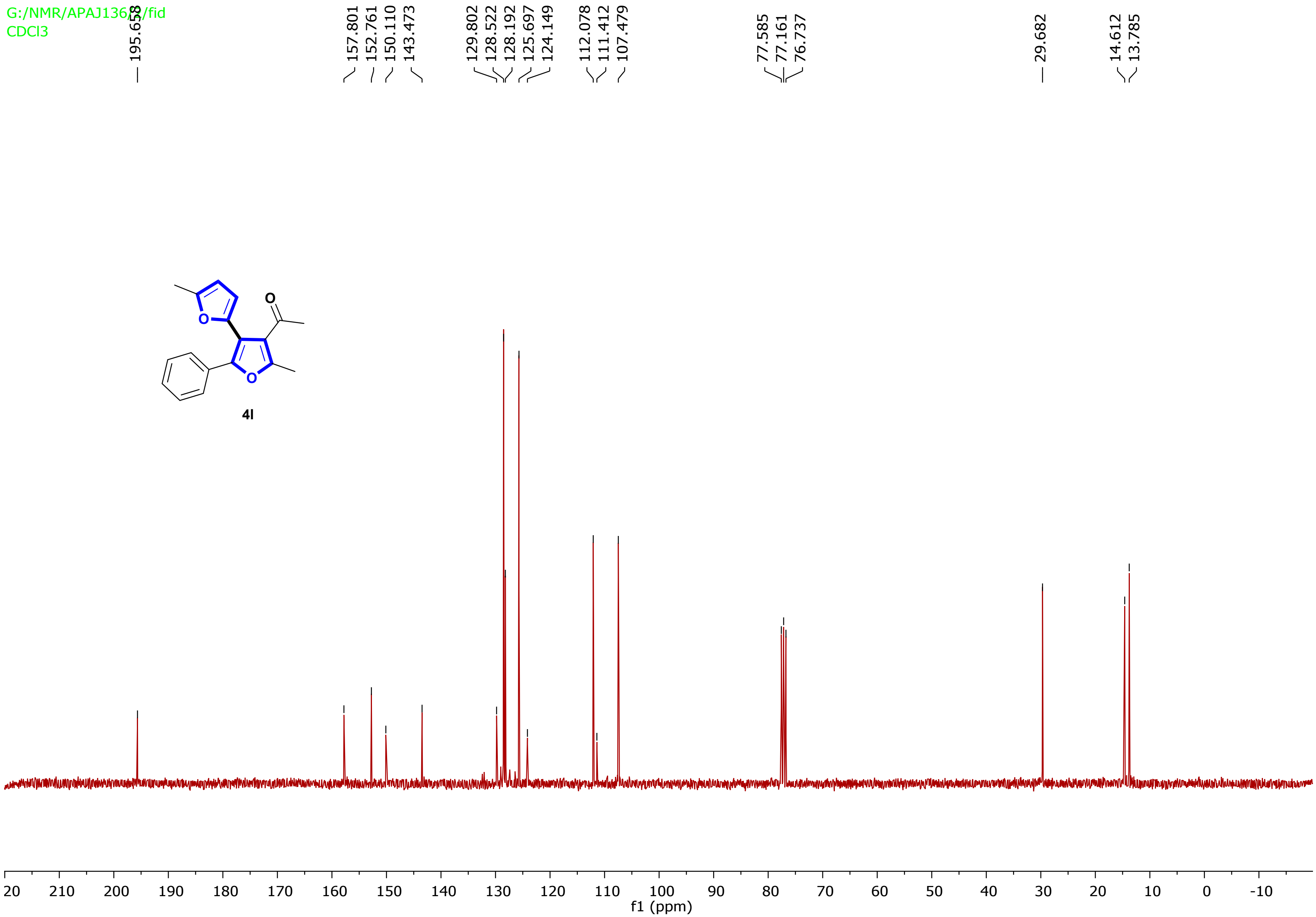
CDCl3
195.279
159.311
155.606
135.946
131.579
129.581
129.173
129.104
128.657
127.004
126.835
124.827
106.052
77.583
77.160
76.738
30.656
15.120
Cl
S
O
O
4k
f1 (ppm)


7.513
7.507
7.500
7.491
7.488
7.485
7.480
7.472
7.359
7.353
7.350
7.344
7.339
7.332
7.329
7.324
7.319
7.310
7.305
7.299
7.293
7.287
7.284
7.278
7.275
6.321
6.311
6.137
6.133
6.130
6.127
6.123
6.120
6.116
2.663
2.399
2.069
O
O
O
4l
2.05
3.33
1.04
1.00
2.95
2.90
3.00
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)


G:/NMR/APAJ136
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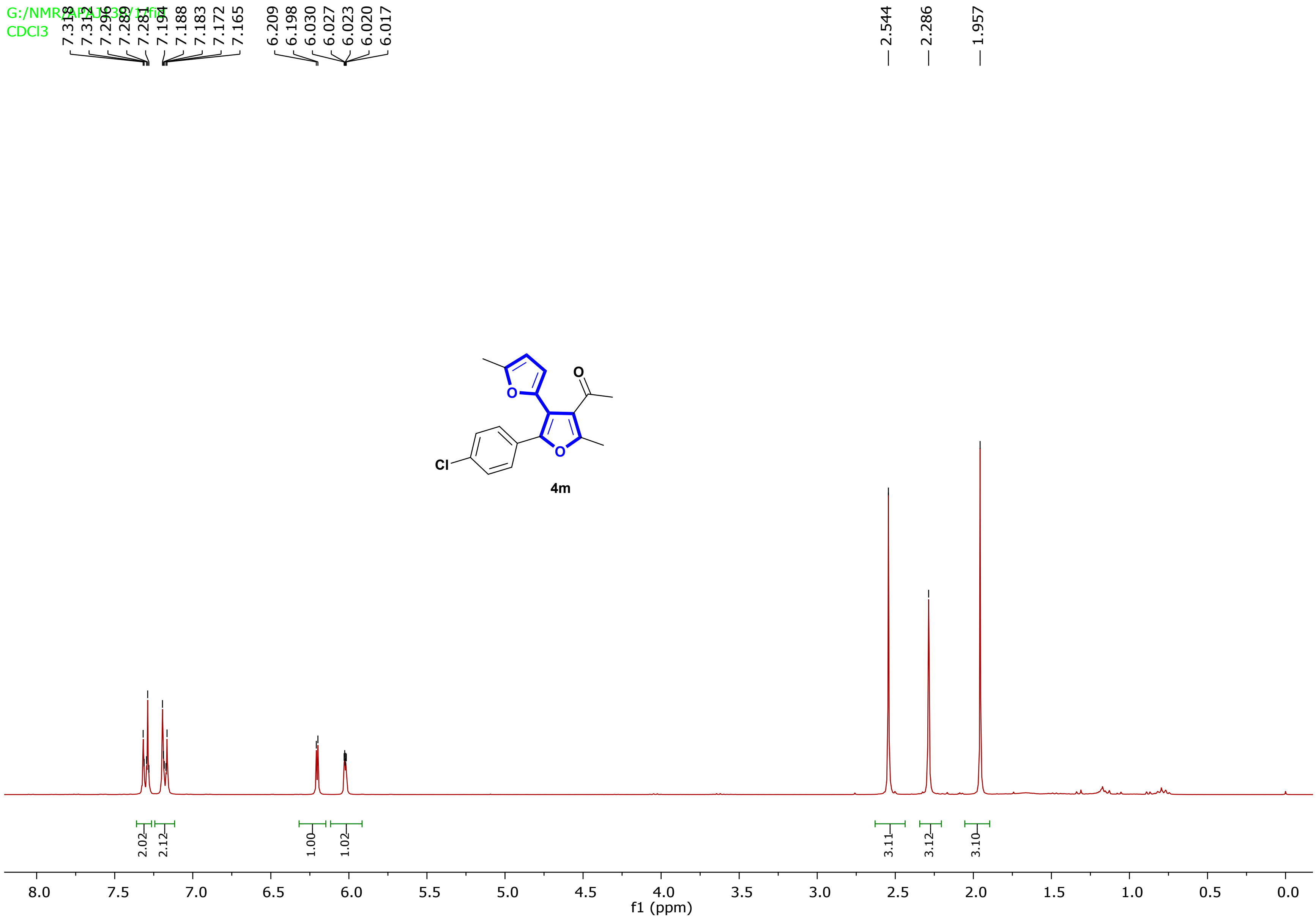
157.801
152.761
150.110
143.473
129.802
128.522
128.192
125.697
124.149
112.078
111.412
107.479
77.585
77.161
76.737
29.682
14.612
13.785
O
O
O
4l
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.312
7.296
7.289
7.281
7.194
7.188
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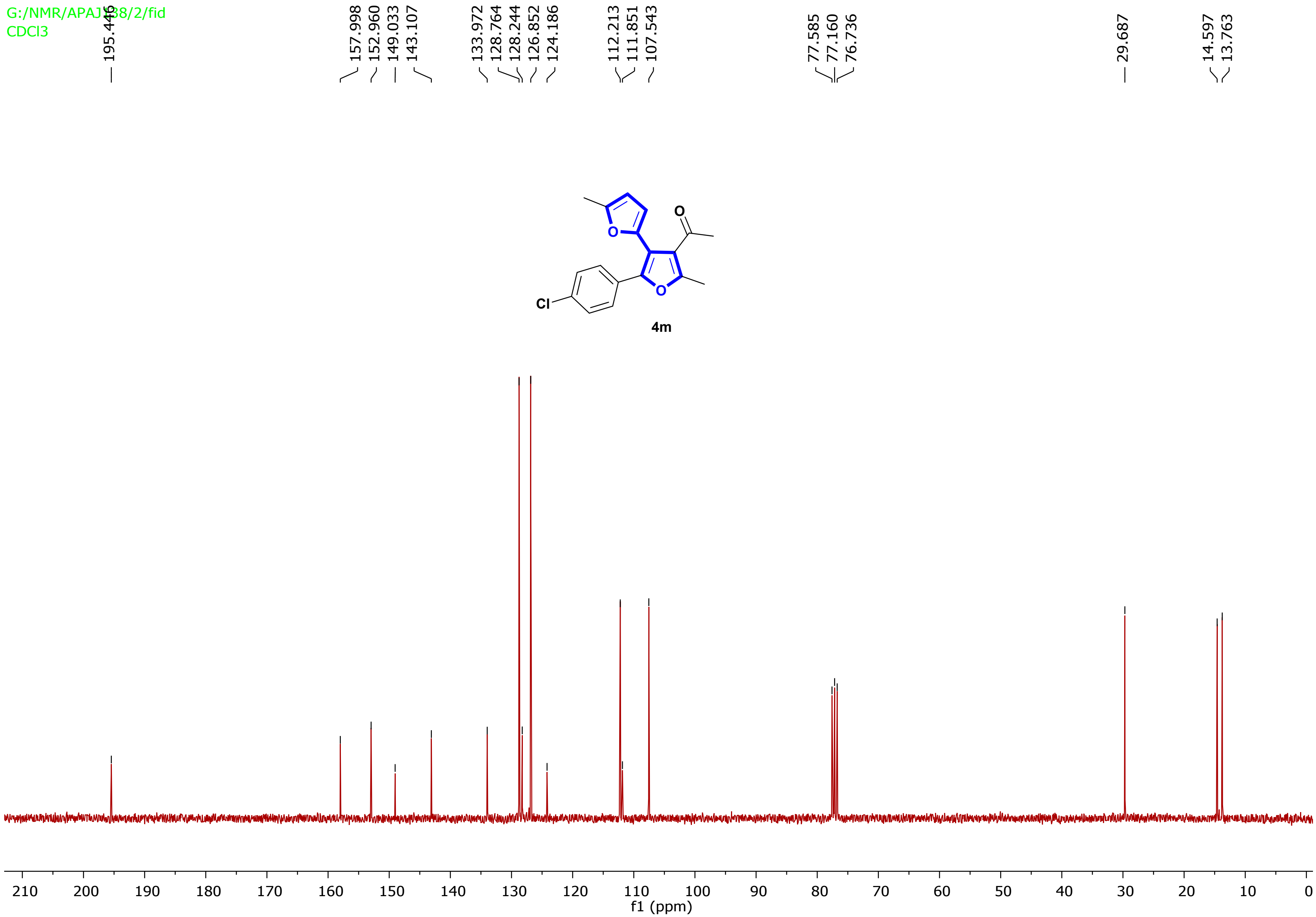
7.172
7.165
6.209
6.198
6.030
6.027
6.023
6.020
6.017
2.544
2.286
1.957
O
O
O
Cl
4m
2.02
2.12
1.00
1.02
3.11
3.12
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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157.998
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143.107
133.972
128.764
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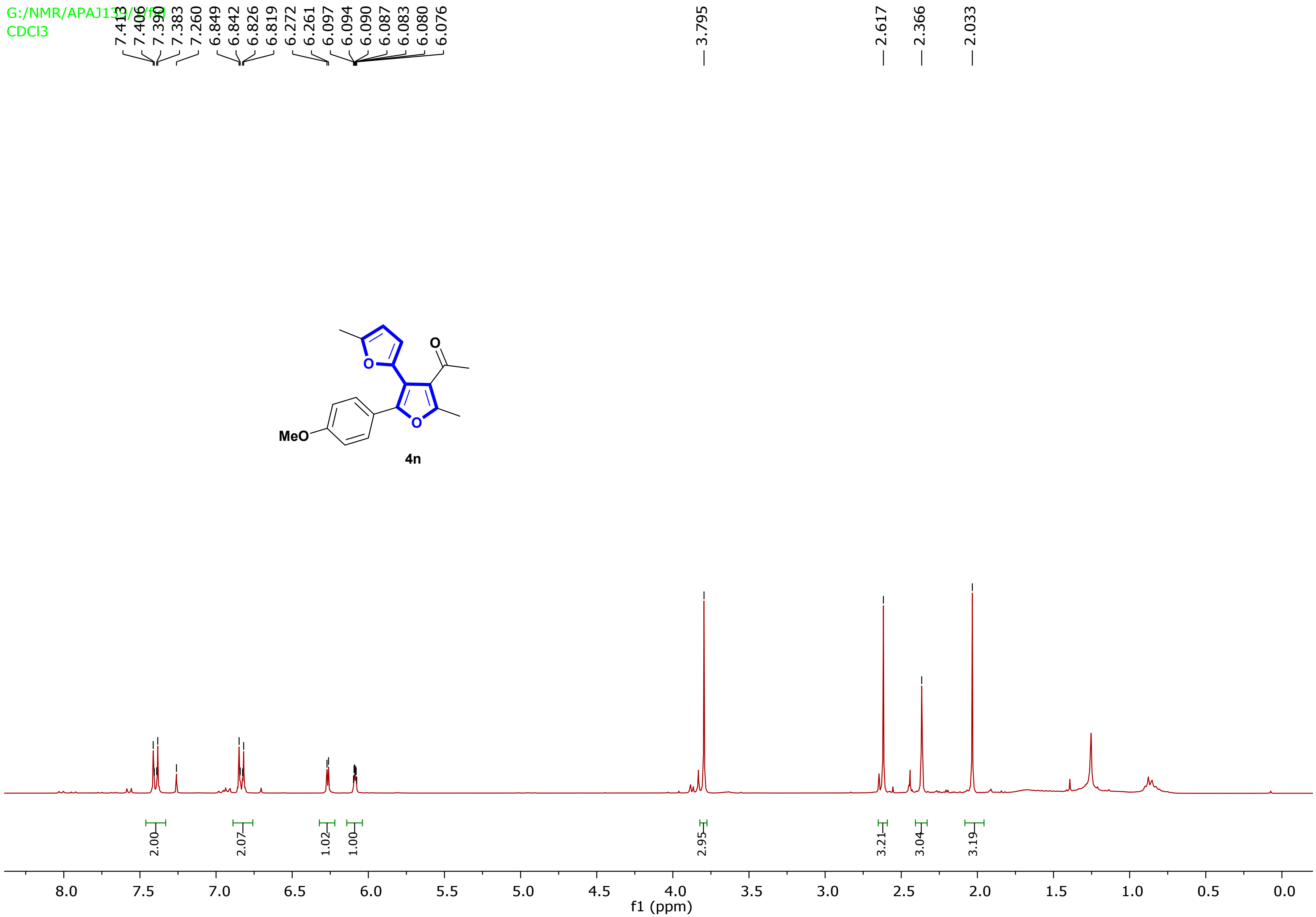
126.852
124.186
112.213
111.851
107.543
77.585
77.160
76.736
29.687
14.597
13.763
O
O
O
Cl
4m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CDCl3
7.413
7.406
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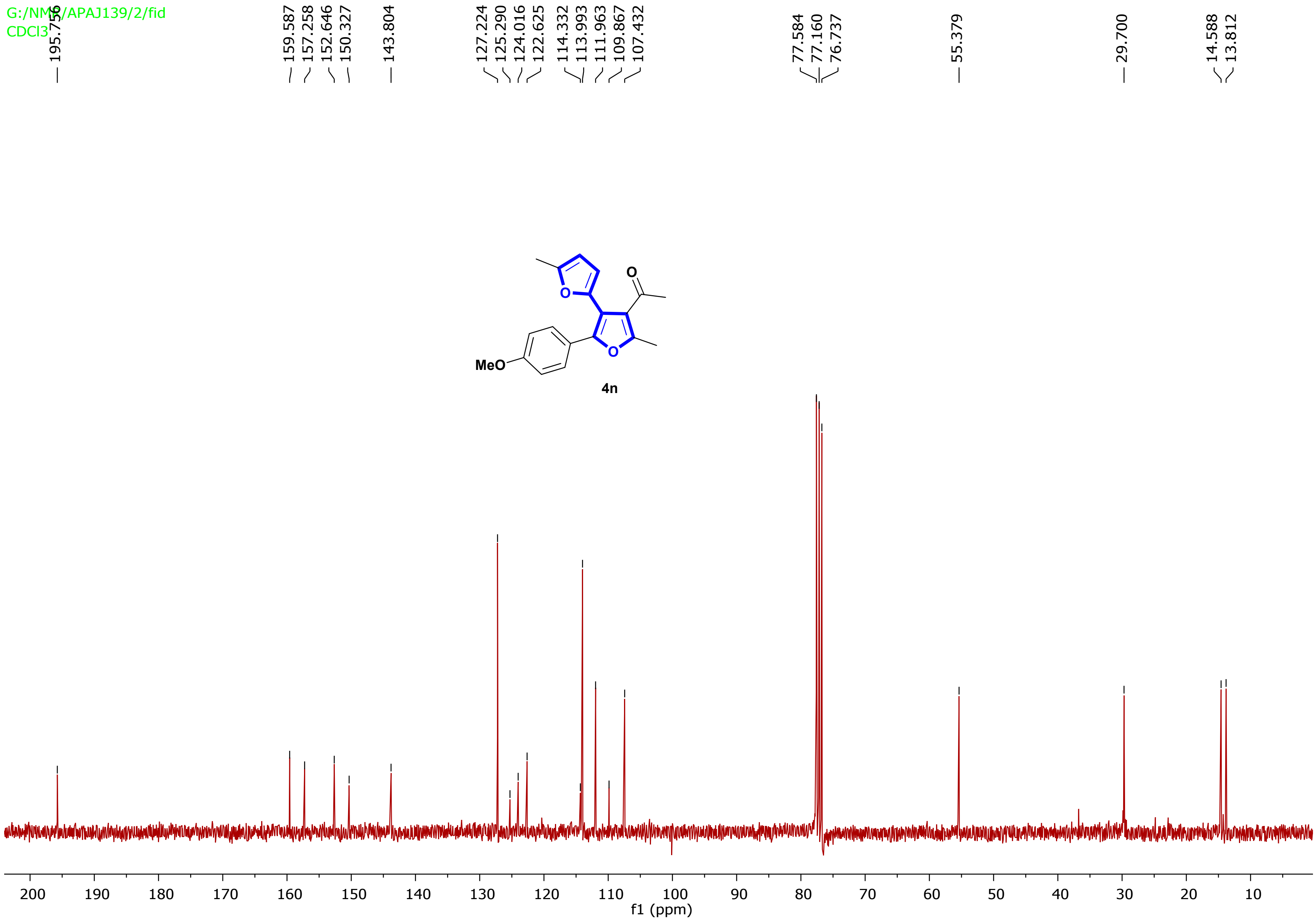
7.383
7.260
6.849
6.842
6.826
6.819
6.272
6.261
6.097
6.094
6.090
6.087
6.083
6.080
6.076
3.795
2.617
2.366
2.033
MeO
O
4n
2.00
2.07
1.02
1.00
2.95
3.21
3.04
3.19
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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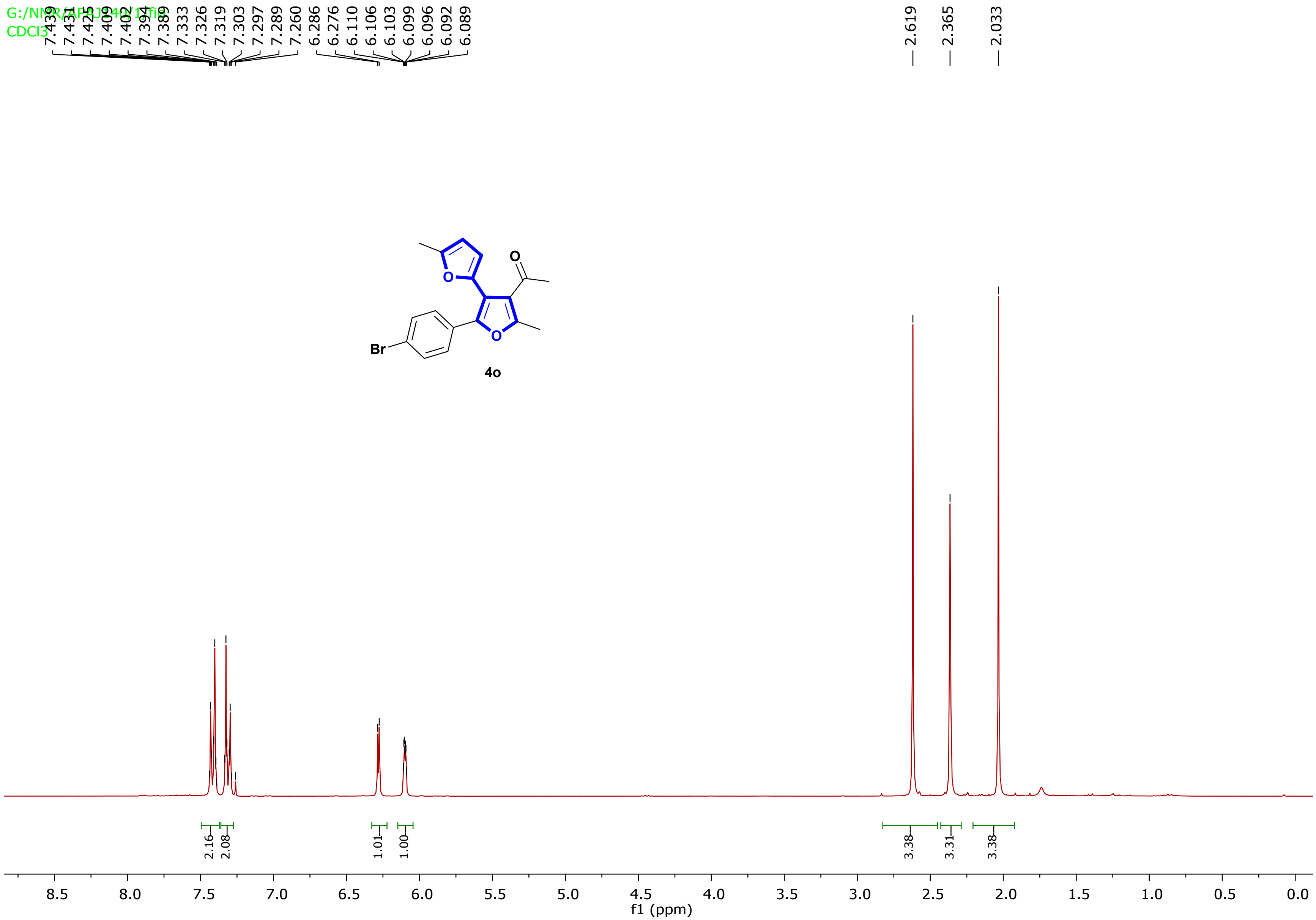
195.756
159.587
157.258
152.646
150.327
143.804
127.224
125.290
124.016
122.625
114.332
113.993
111.963
109.867
107.432
77.584
77.160
76.737
55.379
29.700
14.588
13.812
MeO
O
O
O
4n
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


CDCl3
7.439
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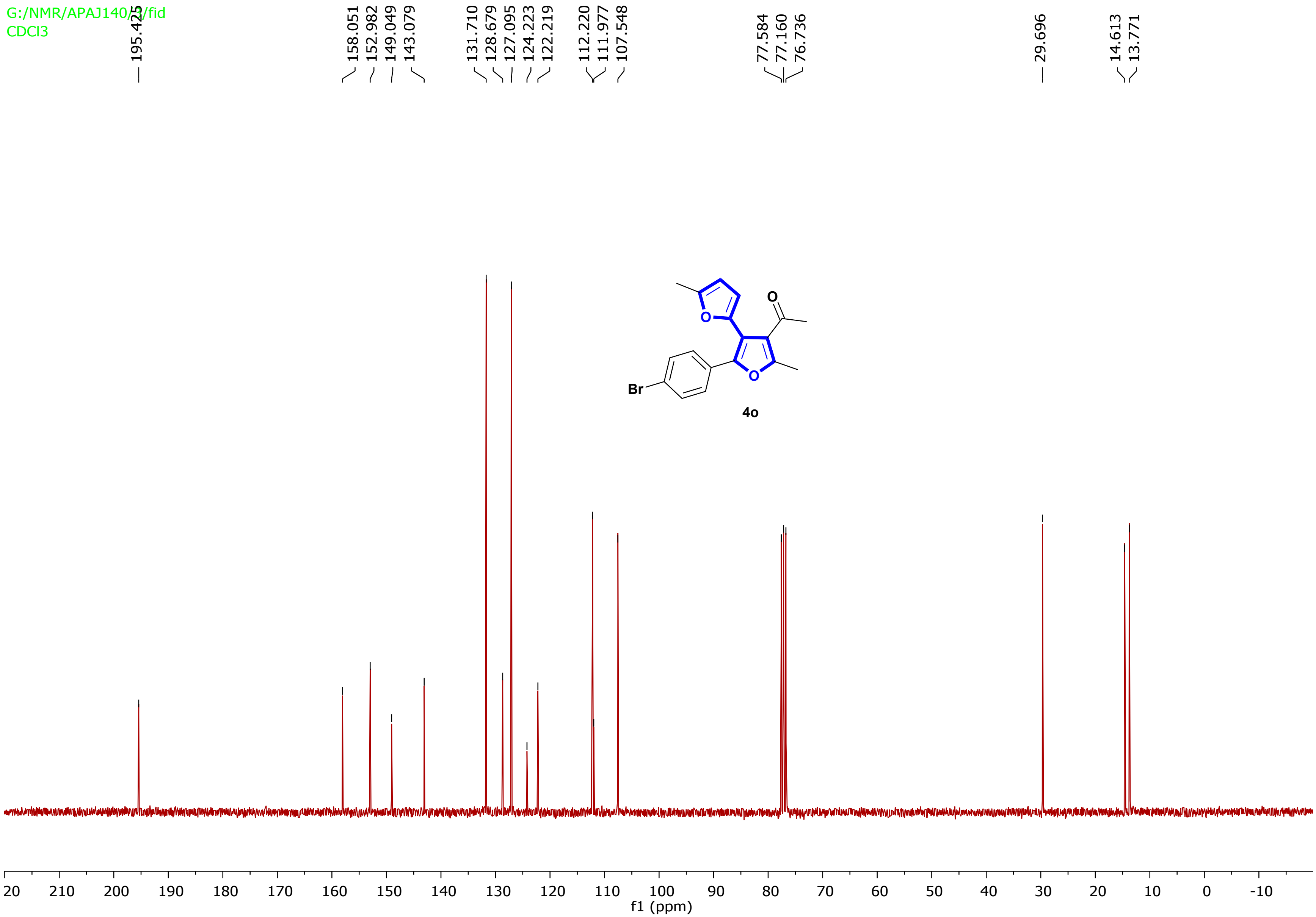
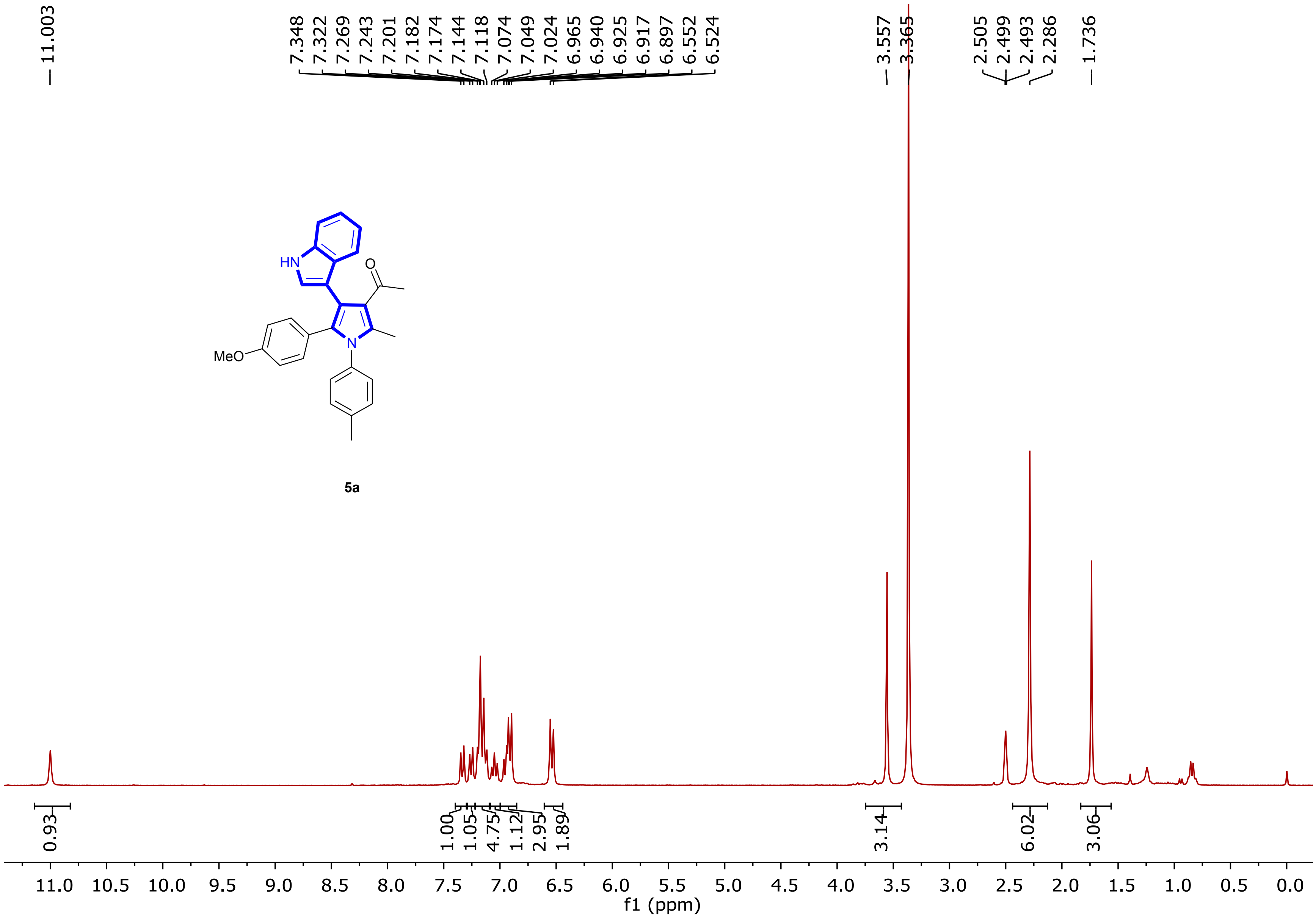
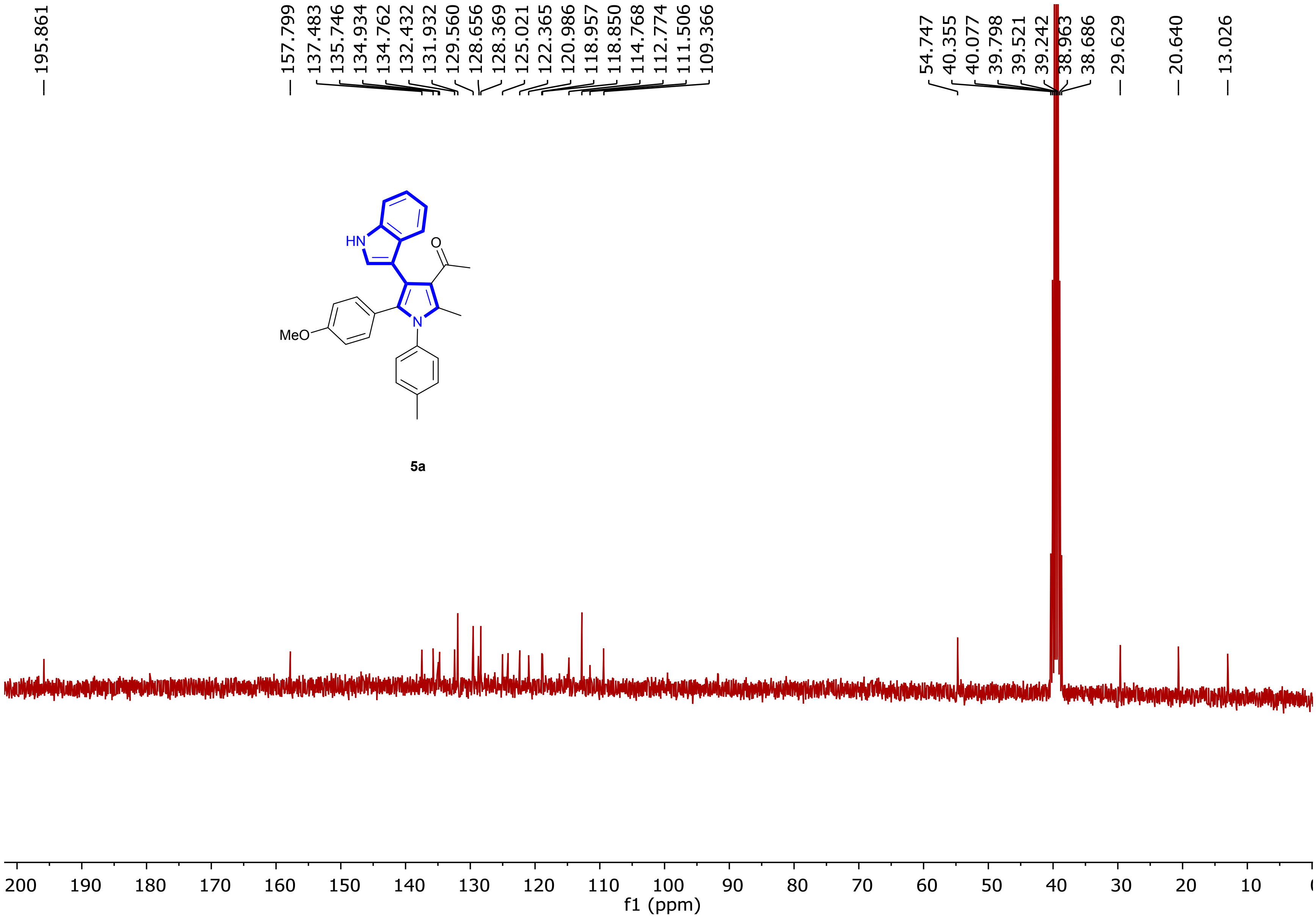
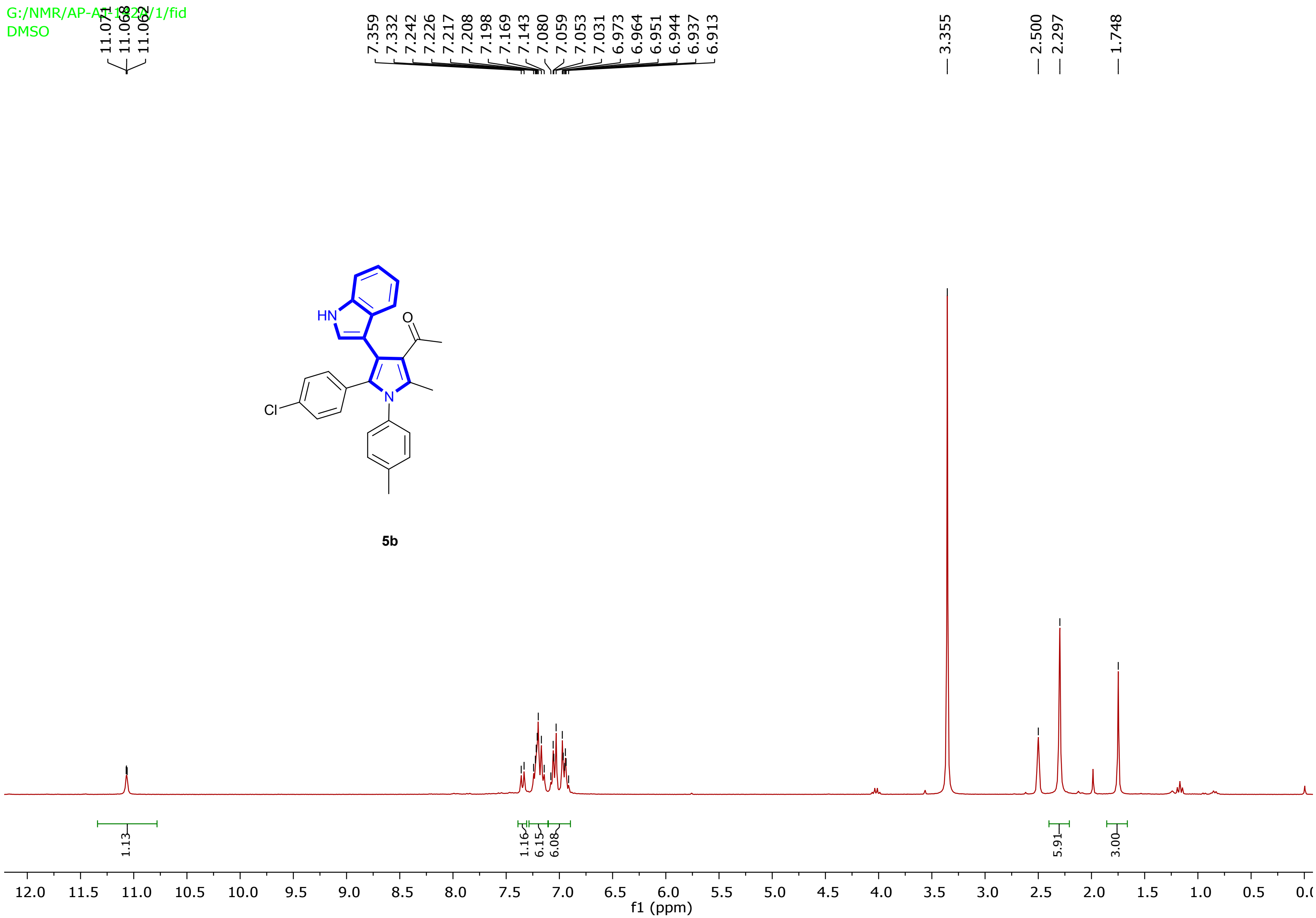
7.409
7.402
7.394
7.389
7.333
7.326
7.319
7.303
7.297
7.289
7.260
6.286
6.276
6.110
6.106
6.103
6.099
6.096
6.092
6.089
2.619
2.365
2.033
O
O
O
Br
4o
2.16
2.08
1.01
1.00
3.38
3.31
3.38
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CDCl3
195.425
158.051
152.982
149.049
143.079
131.710
128.679
127.095
124.223
122.219
112.220
111.977
107.548
77.584
77.160
76.736
29.696
14.613
13.771
O
O
O
Br
4o
f1 (ppm)


11.003
7.348
7.322
7.269
7.243
7.201
7.182
7.174
7.144
7.118
7.074
7.049
7.024
6.965
6.940
6.925
6.917
6.897
6.552
6.524
3.557
3.365
2.505
2.499
2.493
2.286
1.736
HN
O
N
MeO
5a
0.93
1.00
1.05
4.75
1.12
2.95
1.89
3.14
6.02
3.06
11.0
10.5
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)



195.861
157.799
137.483
135.746
134.934
134.762
132.432
131.932
129.560
128.656
128.369
125.021
122.365
120.986
118.957
118.850
114.768
112.774
111.506
109.366
54.747
40.355
40.077
39.798
39.521
39.242
38.963
38.686
29.629
20.640
13.026
HN
O
N
MeO
5a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


DMSO
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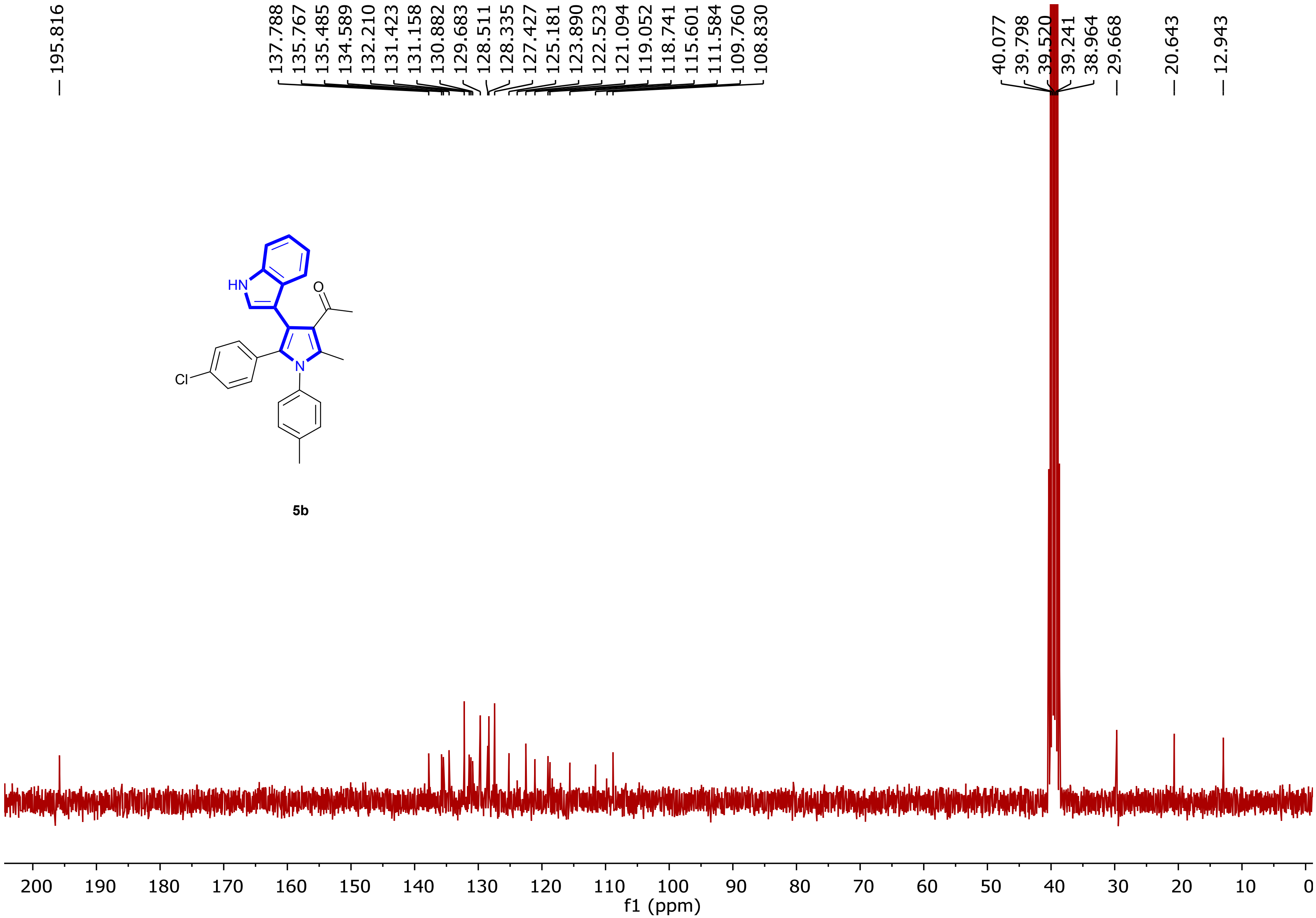
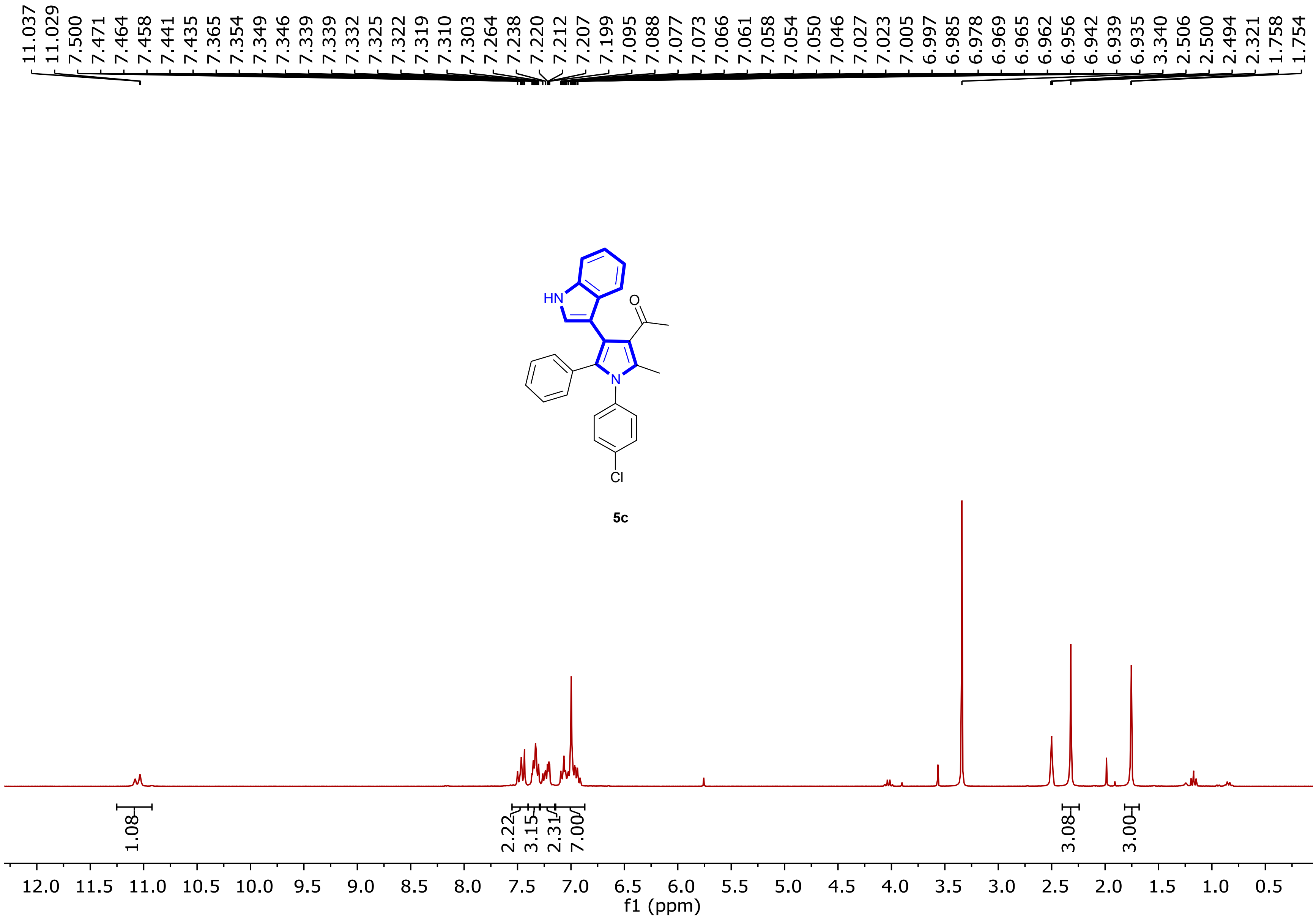
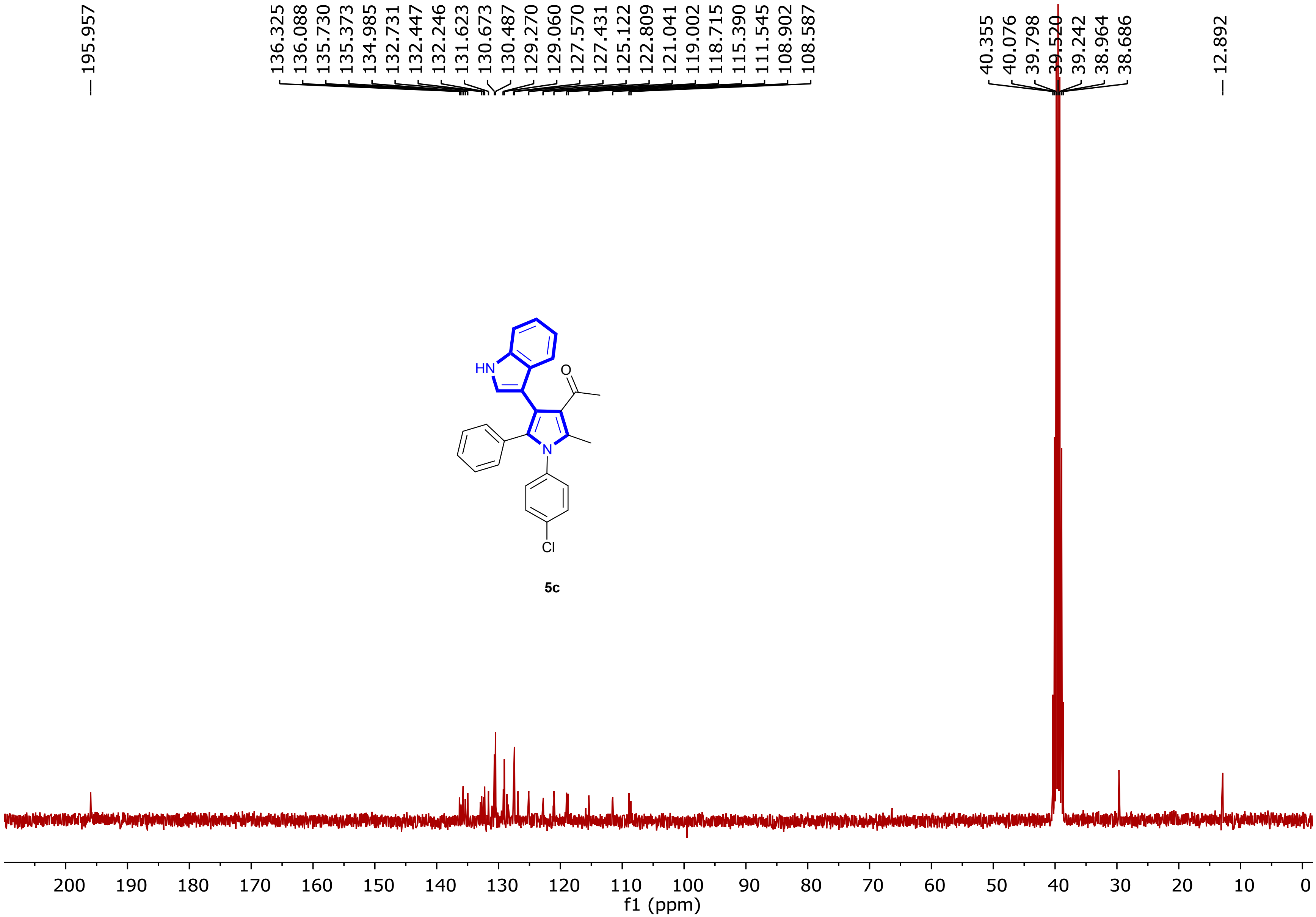
11.068
11.062
7.359
7.332
7.242
7.226
7.217
7.208
7.198
7.169
7.143
7.080
7.059
7.053
7.031
6.973
6.964
6.951
6.944
6.937
6.913
3.355
2.500
2.297
1.748
HN
O
N
Cl
5b
1.13
1.16
6.15
6.08
5.91
3.00
f1 (ppm)


195.816
137.788
135.767
135.485
134.589
132.210
131.423
131.158
130.882
129.683
128.511
128.335
127.427
125.181
123.890
122.523
121.094
119.052
118.741
115.601
111.584
109.760
108.830
40.077
39.798
39.520
39.241
38.964
29.668
20.643
12.943
HN
O
Cl
N
5b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


11.037
11.029
7.500
7.471
7.464
7.458
7.441
7.435
7.365
7.354
7.349
7.346
7.339
7.339
7.332
7.325
7.322
7.319
7.310
7.303
7.264
7.238
7.220
7.212
7.207
7.199
7.095
7.088
7.077
7.073
7.066
7.061
7.058
7.054
7.050
7.046
7.027
7.023
7.005
6.997
6.985
6.978
6.969
6.965
6.962
6.956
6.942
6.939
6.935
3.340
2.506
2.500
2.494
2.321
1.758
1.754
HN
O
N
Cl
5c
1.08
2.22
3.15
2.31
7.00
3.08
3.00
12.0 11.5 11.0 10.5 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
f1 (ppm)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136.325
136.088
135.730
135.373
134.985
132.731
132.447
132.246
131.623
130.673
130.487
129.270
129.060
127.570
127.431
125.122
122.809
121.041
119.002
118.715
115.390
111.545
108.902
108.587
40.355
40.076
39.798
39.520
39.242
38.964
38.686
12.892
HN
O
N
Cl
5c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

References

1. (a) B. Eftekhari-Sis, M. Zirak, A. Akbari, *Chem. Rev.* **2013**, *113*, 2958-3043. (b) F. Kipnis, J. Ornfelt, *J. Am. Chem. Soc.***1946**, *68*, 2734.

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