Supporting Information for:

Synthesis of pyrazole containing α-amino acids via a highly regioselective condensation/aza-Michael reaction of β-aryl α,β-unsaturated ketones

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1. Experimental Procedures and Data of All Known Compounds

Dimethyl (2*S*)-2-aminobutandioate hydrochloride.[1] To a suspension of L-aspartic acid (**4**) (5.00 g, 37.6 mmol) in methanol (30 mL) at 0 °C under argon was added dropwise thionyl chloride (4.00 mL, 52.6 mmol). The reaction mixture was warmed to room temperature and then heated under reflux for 3 h. The solution was concentrated *in vacuo* to give a colourless oil and triturated with diethyl ether to give dimethyl (2*S*)-2-aminobutandioate hydrochloride as a colourless solid (7.55 g, 100%). Mp 115–116 °C (lit.[1] 114–115 °C); $[\alpha]_D^{24}$ +22.0 (*c* 1.0, MeOH); δ_H (400 MHz, DMSO-d_6) 2.99 (1H, dd, *J* 18.0, 5.5 Hz, 3-*H*H), 3.05 (1H, dd, *J* 18.0, 5.5 Hz, 3-H*H*), 3.66 (3H, s, OMe), 3.74 (3H, s, OMe), 4.35 (1H, t, *J* 5.5 Hz, 2-H), 8.72 (3H, s, CHNH_3^+); δ_C (101 MHz, DMSO-d_6) 34.0 (CH_2), 48.4 (CH), 52.2 (CH_3), 53.0 (CH_3), 168.7 (C), 169.6 (C); *m/z* (CI) 162 (MH^+, 100%), 148 (5), 102 (20).

Dimethyl (2*S*)-2-(tritylamino)butandioate (5).[2] To a solution of dimethyl (2*S*)-2-aminobutandioate hydrochloride (7.46 g, 37.7 mmol) in dichloromethane (150 mL) at 0 °C was added dropwise triethylamine (11.0 mL, 75.4 mmol) and triphenylmethyl chloride (10.5 g, 37.7 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was washed with 2 M citric acid (100 mL), water (100 mL), brine (100 mL), then dried ($MgSO_4$) and concentrated *in vacuo* to give a colourless oil. The crude product was purified by column chromatography (elution with 50% diethyl ether in petroleum ether) to give **5** as a colourless solid (15.2 g, 100%). Mp 71–72 °C (lit.[2] 70–71 °C); $[\alpha]_D^{24}$ +36.6 (*c* 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.51 (1H, dd, *J* 14.7, 7.0 Hz, 3-*H*H), 2.66 (1H, dd, *J* 14.7, 5.4 Hz, 3-H*H*), 2.93 (1H, d, *J* 10.1 Hz, NH), 3.25 (3H, s, OMe), 3.67 (3H, s, OMe), 3.68–3.73 (1H, m, 2-H), 7.15–7.20 (3H, m, ArH), 7.23–7.28 (6H, m, ArH), 7.46–7.51 (6H, m, ArH); δ_C (101 MHz, $CDCl_3$) 39.0 (CH_2), 50.5 (CH), 50.7 (CH_3), 52.4 (CH_3), 69.9 (C), 125.2 (3 × CH), 126.6 (6 × CH), 127.5 (6 × CH), 144.4 (3 × C), 169.7 (C), 172.6 (C); *m/z* (EI) 403 (M^+, 1%), 326 (35), 243 (100), 165 (30), 83 (70).

Methyl (2*S*)-5-(dimethoxyphosphoryl)-4-oxo-2-(tritylamino)pentanoate (6).[2] A solution of dimethyl methylphosphonate (3.00 mL, 27.3 mmol) in THF (50 mL) was cooled to –78 °C under an argon atmosphere. *n*-Butyl lithium (2.5 M in hexane, 11.0 mL, 28.6 mmol) was added dropwise and the reaction mixture stirred for 1 h. In a separate reaction vessel, a solution of dimethyl (2*S*)-2-(tritylamino)butandioate (**5**) (5.00 g, 12.4 mmol) in THF (100 mL) was cooled to –78 °C and then the dimethyl methylphosphonate/*n*-butyl lithium solution was cannulated into the flask and the reaction mixture stirred at –78 °C for 2 h to give a yellow solution. The reaction was quenched with a saturated solution of ammonium chloride (3 mL) and allowed to warm to room temperature. The mixture was concentrated *in*

vacuo. The resulting residue was diluted with ethyl acetate (100 mL), washed with water (2 × 100 mL), brine (100 mL) then dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by column chromatography (elution with 75% ethyl acetate in petroleum ether) to give **6** as a colourless solid (5.65 g, 92%). Mp 117–118 °C (lit.[2] 117–118.5 °C); $[\alpha]_D^{24}$ +31.1 (*c* 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.78 (1H, dd, *J* 16.7, 6.9 Hz, 3-*H*H), 2.85–2.95 (2H, m, 3-H*H* and NH), 3.06 (2H, d, $J_{H–C–P}$ 22.7 Hz, 5-H_2), 3.29 (3H, s, OMe), 3.65–3.73 (1H, m, 2-H), 3.76 (3H, s, OMe), 3.79 (3H, s, OMe), 7.15–7.21 (3H, m, ArH), 7.26 (6H, t, *J* 7.7 Hz, ArH), 7.47 (6H, d, *J* 7.7 Hz, ArH); δ_C (101 MHz, $CDCl_3$) 41.8 (d, $J_{C–P}$ 128 Hz, CH_2), 48.8 (CH_2), 52.0 (CH_3), 52.9 (CH_3), 53.0 (CH_3), 53.1 (CH), 71.3 (C), 126.6 (3 × CH), 127.9 (6 × CH), 128.8 (6 × CH), 145.7 (3 × C), 174.0 (C), 199.3 (C); *m/z* (CI) 496 (MH^+, 1%), 301 (5), 254 (90), 243 (100), 237 (55), 167 (45).

General Procedure for the Horner-Wadsworth-Emmons Reaction:[3] Methyl (2*S*)-5-(dimethoxyphosphoryl)-4-oxo-2-(tritylamino)pentanoate (**6**) (0.20 g, 0.40 mmol) was dissolved in acetonitrile (4 mL) at room temperature under argon. Anhydrous potassium carbonate (0.06 g, 0.42 mmol) was added to the solution and stirred for 0.5 h. An aldehyde (0.80 mmol) was added to the suspension and heated at 50 °C until the reaction was complete by TLC. The reaction mixture was allowed to cool to room temperature and then concentrated *in vacuo*. The resultant residue was dissolved in ethyl acetate (30 mL) and washed with water (20 mL), brine (30 mL) then dried ($MgSO_4$) and concentrated *in vacuo*. The products were purified by column chromatography on eluting with 20–40% diethyl ether in petroleum ether.

Methyl (2*S*,5*E*)-4-oxo-6-phenyl-2-(tritylamino)hex-5-enoate (7).[3] Using the general procedure above gave **7** after 36 h as a yellow oil (0.18 g, 95%). Spectroscopic data was consistent with the literature.[3] ν_{max}/cm^{-1} (NaCl) 3023 (NH), 2950 (CH), 1737 (C=O), 1657 (C=C), 1608, 1205; $[\alpha]_D^{25}$ +111.0 (*c* 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.80 (1H, dd, *J* 15.2, 7.0 Hz, 3-*H*H), 2.88–2.97 (2H, m, 3-H*H* and NH), 3.28 (3H, s, OMe), 3.79–3.89 (1H, m, 2-H), 6.69 (1H, d, *J* 16.2 Hz, 5-H), 7.14–7.29 (10H, m, ArH and 6-H), 7.37–7.41 (3H, m, ArH), 7.44–7.53 (8H, m, ArH); δ_C (101 MHz, $CDCl_3$) 45.7 (CH_2), 52.0 (CH_3), 53.7 (CH), 71.3 (C), 126.4 (3 × CH), 127.9 (6 × CH), 128.1 (2 × CH), 128.4 (6 × CH), 128.8 (2 × CH), 129.0 (CH), 130.6 (CH), 134.4 (C), 143.3 (CH), 145.8 (3 × C), 174.5 (C), 197.5 (C); *m/z* (FAB) 476.2231 (MH^+. $C_{32}H_{30}NO_3$ requires 476.2226), 398 (15%), 259 (6), 243 (100), 232 (25), 166 (23), 132 (24).

Methyl (2*S*,5*E*)-6-(4-nitrophenyl)-4-oxo-2-(tritylamino)hex-5-enoate (8).[4] Using the general procedure above gave **8** after 24 h as an off-white solid (0.15 g, 72%). Spectroscopic data was consistent with the literature.[4] Mp 139–141 °C; ν_{max}/cm^{-1} (neat) 2951 (CH), 1742

(C=O), 1712 (C=O), 1490, 1509, 1341; $[\alpha]_D^{25}$ +43.3 (*c* 0.2, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.80 (1H, dd, *J* 15.5, 6.9 Hz, 3-*H*H), 2.91 (1H, dd, *J* 15.5, 5.1 Hz, 3-H*H*), 2.95 (1H, br s, NH), 3.31 (3H, s, OMe), 3.55–3.76 (1H, m, 2-H), 6.77 (1H, d, *J* 16.2 Hz, 5-H), 7.17–7.32 (10H, m, 2 × Ph), 7.41–7.53 (6H, m, 6-H and Ph), 7.66 (2H, d, *J* 8.8 Hz, 2'-H and 6'-H), 8.25 (2H, d, *J* 8.8 Hz, 3'-H and 5'-H); δ_C (101 MHz, $CDCl_3$) 46.2 (CH_2), 52.1 (CH_3), 53.7 (CH), 71.3 (C), 124.3 (CH), 126.6 (3 × CH), 128.0 (6 × CH), 128.8 (6 × CH), 128.9 (2 × CH), 129.6 (2 × CH), 139.9 (CH), 140.6 (C), 145.7 (3 × C), 148.6 (C), 174.3 (C), 197.0 (C); *m/z* (FAB) 543.1903 (MNa^+. $C_{32}H_{28}N_2O_5Na$ requires 543.1896), 443 (9%), 413 (9), 351 (19), 329 (58), 243 (100), 176 (78), 154 (32).

Methyl (2*S*,5*E*)-6-(4'-methoxyphenyl)-4-oxo-2-(tritylamino)hex-5-enoate (9).[5] Using the general procedure above gave **9** after 36 h as a colourless oil (0.16 g, 76%). Spectroscopic data was consistent with the literature.[5] ν_{max}/cm^{-1} (neat) 3320 (NH), 3057, 3021, 2951 (CH), 1736 (C=O), 1653 (C=O), 1595 (C=C), 1510, 1447, 1252, 1171, 1028; $[\alpha]_D^{23}$ +54.1 (*c* 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.78 (1H, dd, *J* 15.0, 7.0 Hz, 3-*H*H), 2.84–2.99 (2H, m, 3-H*H* and NH), 3.27 (3H, s, OMe), 3.71–3.93 (4H, m, 2-H and OMe), 6.59 (1H, d, *J* 16.1 Hz, 5-H), 6.92 (2H, d, *J* 8.7 Hz, ArH), 7.11–7.35 (9H, m, ArH), 7.39–7.59 (9H, m, 6-H and ArH); δ_C (101 MHz, $CDCl_3$) 45.7 (CH_2), 52.0 (CH_3), 54.0 (CH), 55.4 (CH_3), 71.3 (C), 114.5 (2 × CH), 124.3 (CH), 126.6 (3 × CH), 127.1 (C), 128.0 (6 × CH), 128.9 (6 × CH), 130.2 (2 × CH), 143.2 (CH), 145.9 (3 × C), 161.8 (C), 174.6 (C), 197.5 (C); *m/z* (FAB) 506.2329 (MH^+. $C_{33}H_{32}NO_4$ requires 506.2331), 428 (5%), 262 (11), 243 (100), 162 (18), 86 (5).

Methyl (2*S*,5*E*)-6-(naphthalen-2-yl)-4-oxo-2-(tritylamino)hex-5-enoate (10).[3] Using the general procedure above gave **10** after 48 h as a yellow solid (0.19 g, 89%). Spectroscopic data was consistent with the literature.[3] Mp 62–63 °C; ν_{max}/cm^{-1} (NaCl) 3055 (NH), 2982 (CH), 1734 (C=O), 1655 (C=C), 1604, 1593, 1489, 1172; $[\alpha]_D^{24}$ +64.1 (*c* 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.84 (1H, dd, *J* 15.1, 7.0 Hz, 3-*H*H), 2.92–3.00 (2H, m, 3-H*H* and NH), 3.29 (3H, s, OMe), 3.79–3.86 (1H, m, 2-H), 6.80 (1H, d, *J* 16.2 Hz, 5-H), 7.15–7.30 (9H, m, ArH), 7.50–7.55 (8H, m, ArH), 7.62–7.69 (2H, m, 6-H and ArH), 7.84–7.89 (3H, m, ArH), 7.94 (1H, br s, ArH); δ_C (101 MHz, $CDCl_3$) 45.8 (CH_2), 52.0 (CH_3), 53.9 (CH), 71.3 (C), 123.5 (CH), 126.5 (CH), 126.6 (3 × CH), 126.8 (CH), 127.4 (CH), 127.8 (CH), 127.9 (6 × CH), 128.1 (CH), 128.6 (CH), 128.8 (6 × CH), 130.6 (CH), 131.9 (C), 133.3 (C), 134.4 (C), 143.4 (CH), 145.8 (3 × C), 174.5 (C), 197.5 (C); *m/z* (FAB) 526.2388 (MH^+. $C_{36}H_{32}NO_3$ requires 526.2382), 448 (7%), 273 (8), 243 (100), 181 (19), 165 (24).

Methyl (2*S*,5*E*)-6-(3'-nitrobiphen-4-yl)-4-oxo-2-(tritylamino)hex-5-enoate (11).[3] Using the general procedure above gave **11** after 72 h as a yellow foam (0.20 g, 84%). Spectroscopic data was consistent with the literature.[3] ν_{max}/cm^{-1} (neat) 3030 (NH), 1736 (C=O), 1657 (C=C), 1603, 1530,

1514, 1348; $[\alpha]_D^{23}$ +61.7 (*c* 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.82 (1H, dd, *J* 15.2, 6.9 Hz, 3-*H*H), 2.90–3.02 (2H, m, 3-H*H* and NH), 3.30 (3H, s, OMe), 3.77–3.88 (1H, m, 2-H), 6.75 (1H, d, *J* 16.2 Hz, 5-H), 7.12–7.32 (9H, m, ArH), 7.45–7.73 (12H, m, ArH and 6-H), 7.93 (1H, d, *J* 7.9 Hz, ArH), 8.23 (1H, d, *J* 7.9 Hz, ArH), 8.48 (1H, s, ArH); δ_C (101 MHz, $CDCl_3$) 45.8 (CH_2), 52.0 (CH_3), 53.8 (CH), 71.3 (C), 121.9 (CH), 122.6 (CH), 126.5 (3 × CH), 126.9 (CH), 127.7 (2 × CH), 127.9 (6 × CH), 128.8 (6 × CH), 129.1 (2 × CH), 129.9 (CH), 132.9 (CH), 134.6 (C), 140.6 (C), 141.7 (C), 142.1 (CH), 145.7 (3 × C), 148.8 (C), 174.4 (C), 197.4 (C); *m/z* (FAB) 597.2384 (MH^+. $C_{38}H_{33}N_2O_5$ requires 597.2389), 519 (23%), 419 (5), 353 (32), 243 (100), 194 (9), 166 (54).

2. References

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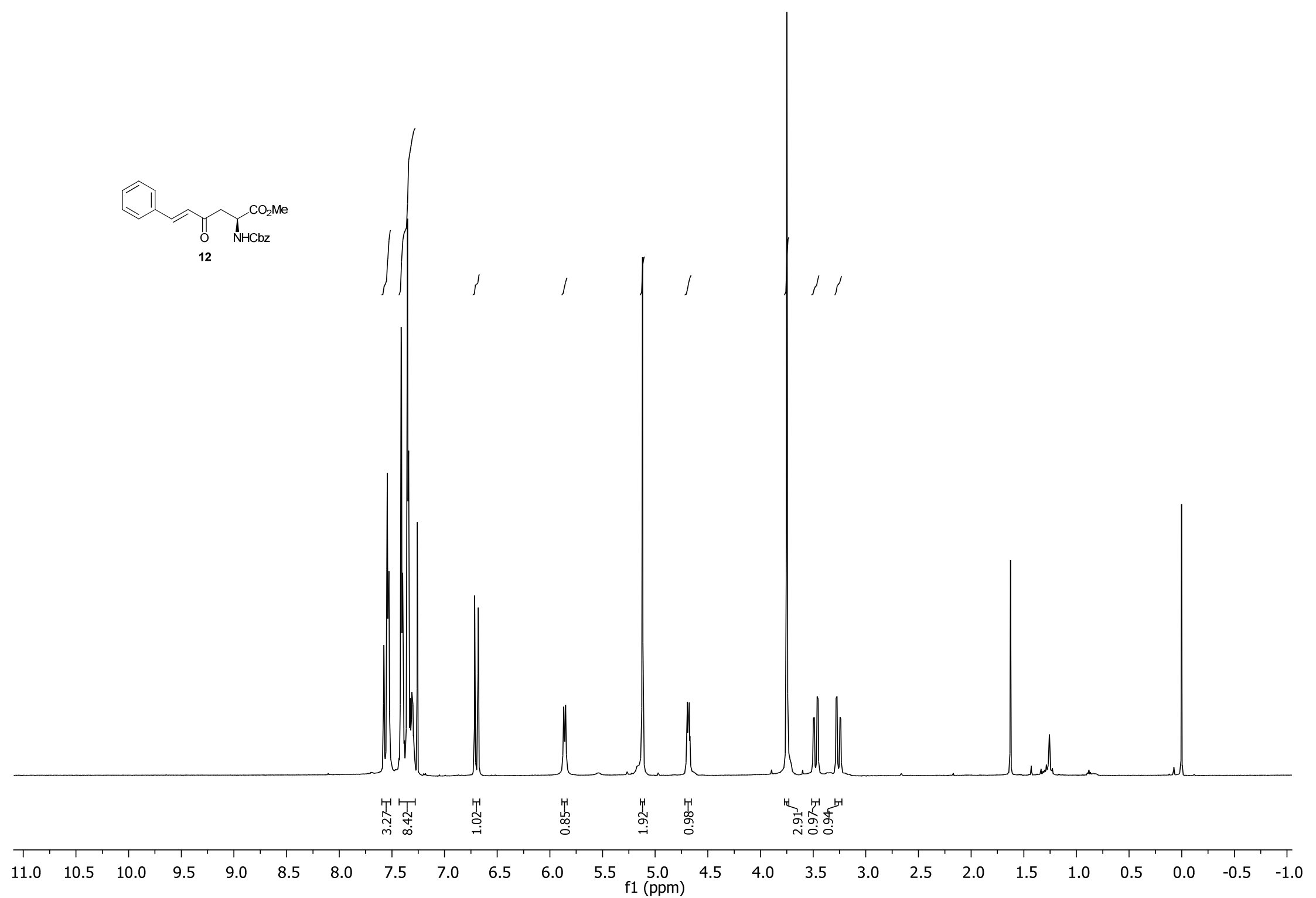
5. L. S. Fowler, L. H. Thomas, D. Ellis and A. Sutherland, *Chem. Commun*., 2011, **47**, 6569.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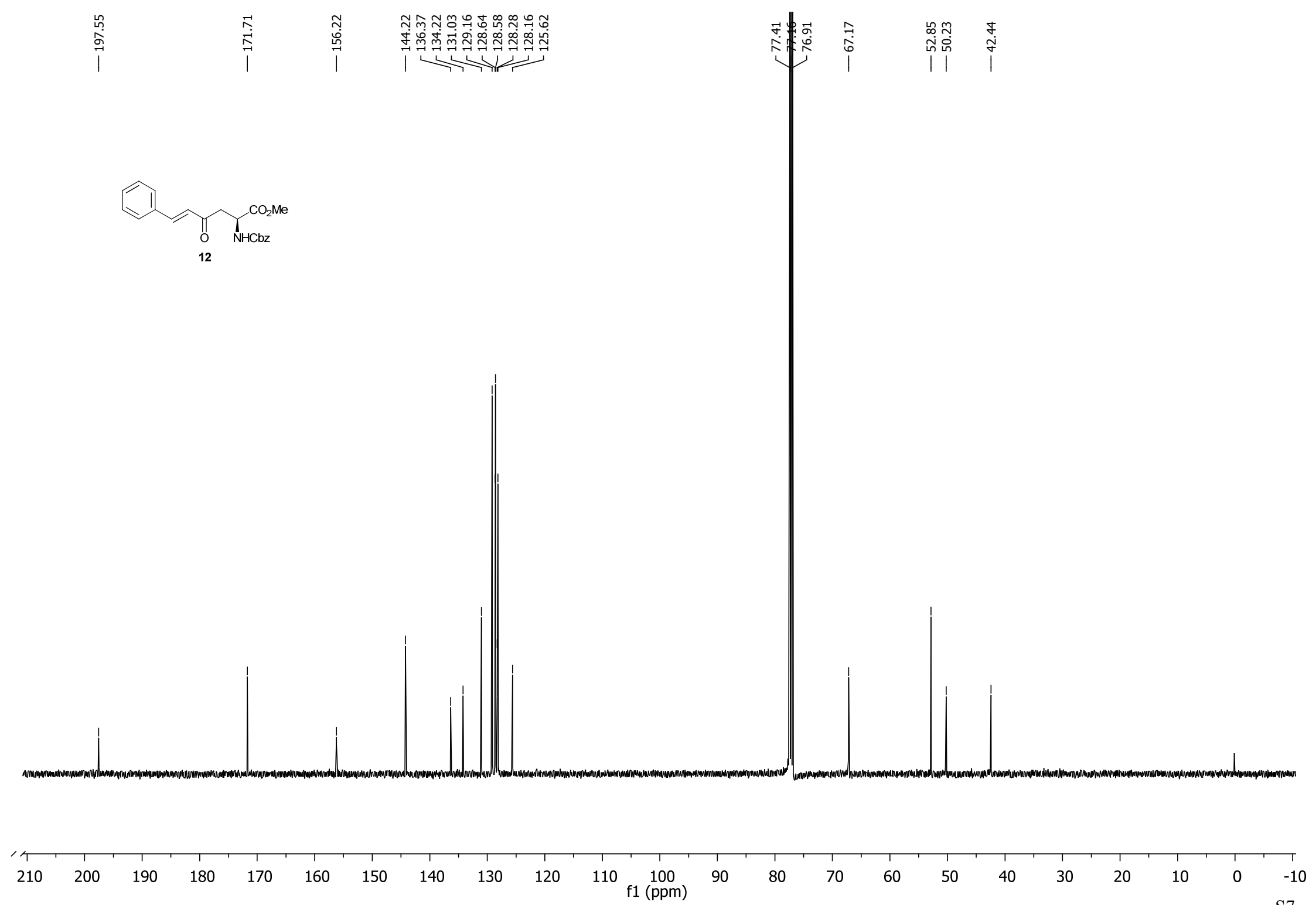
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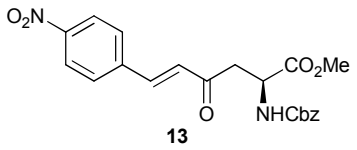
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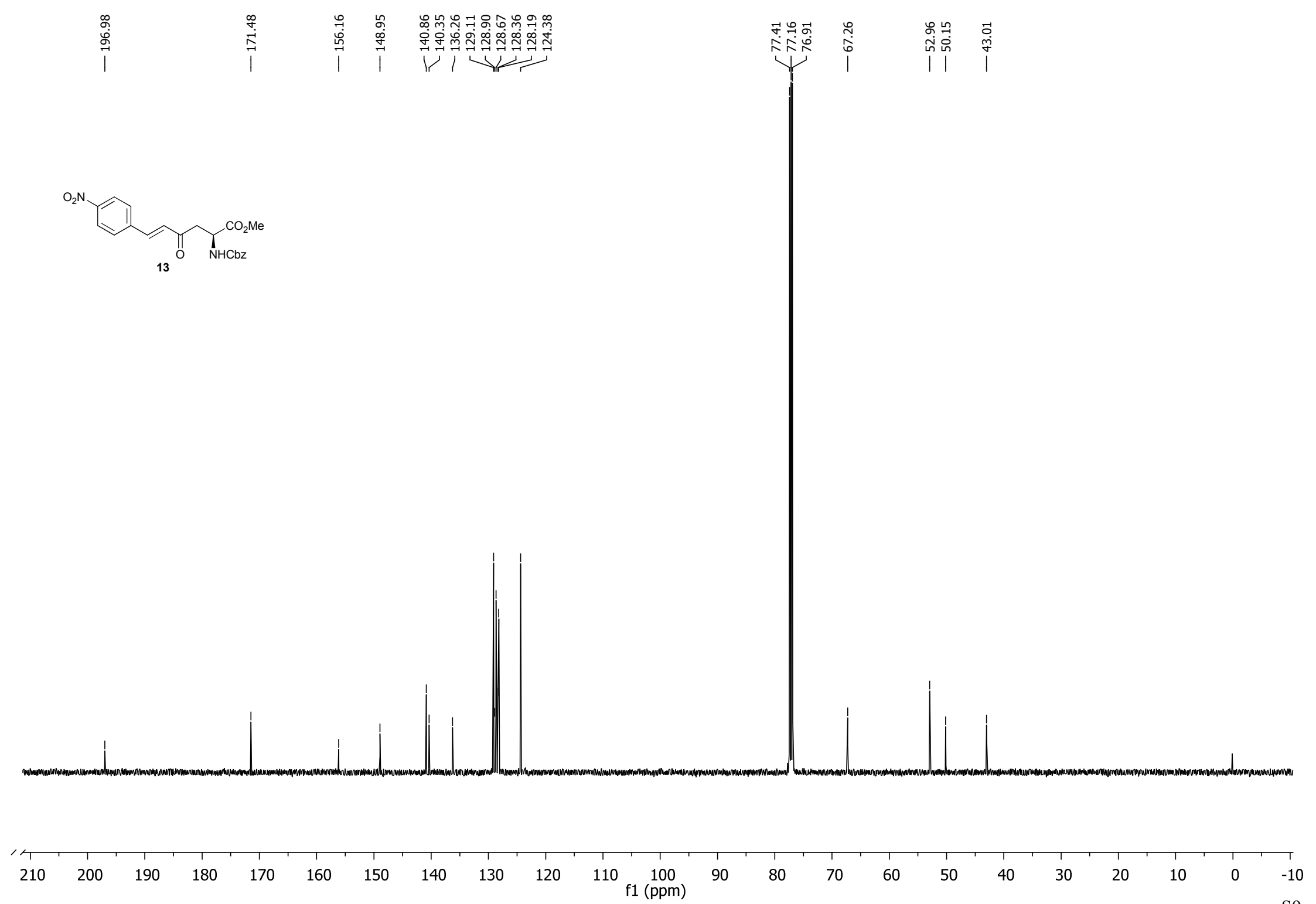
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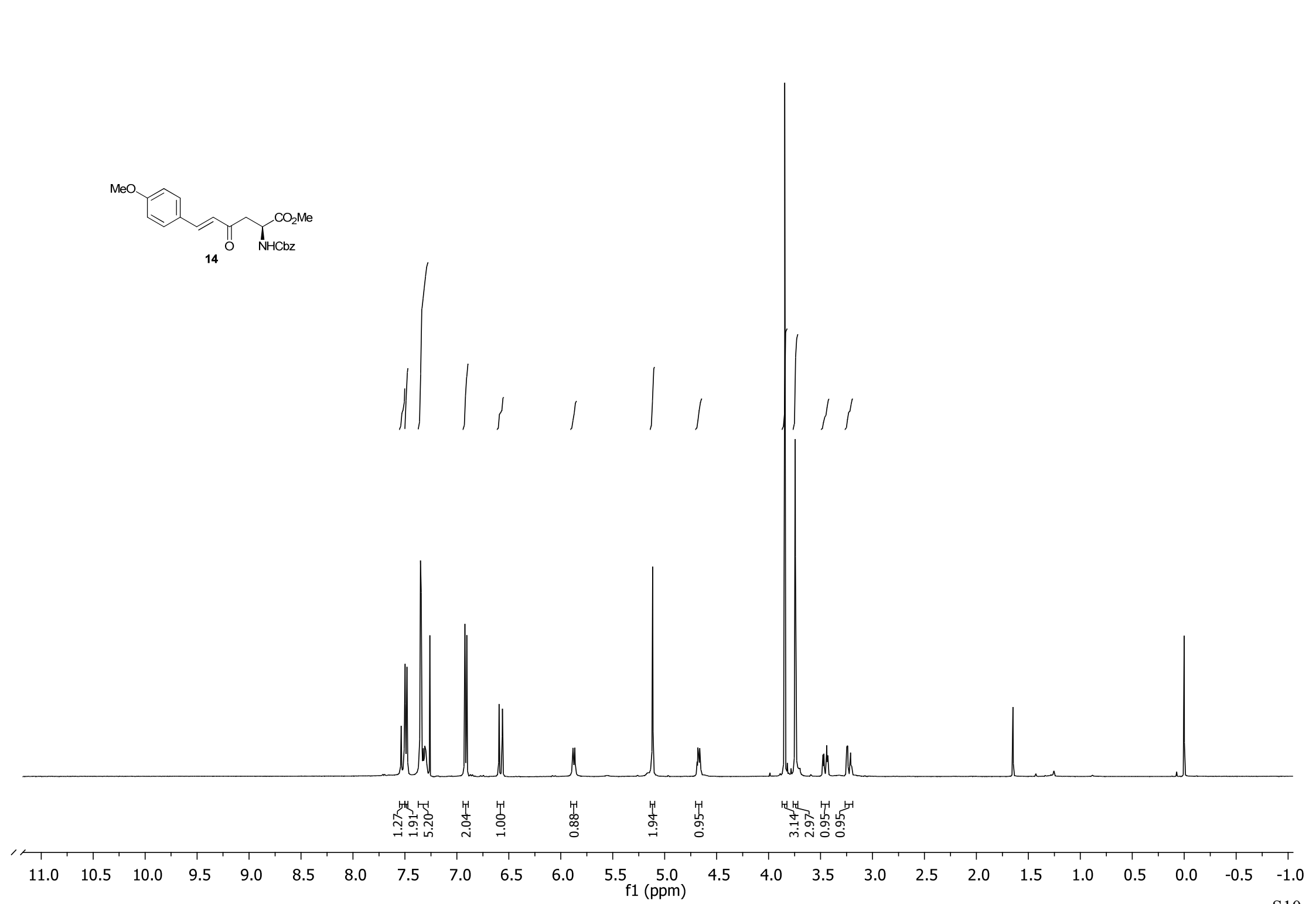
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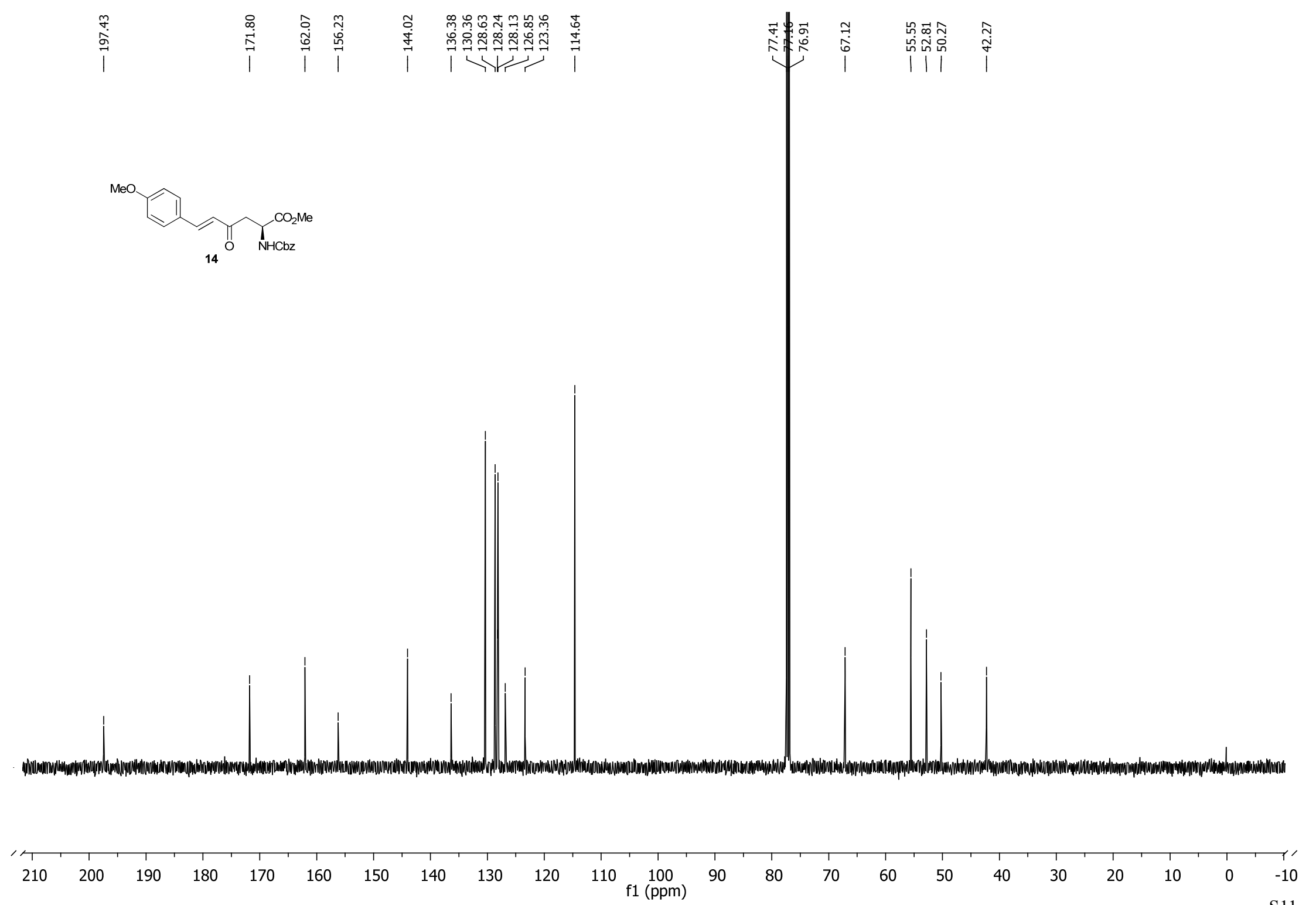
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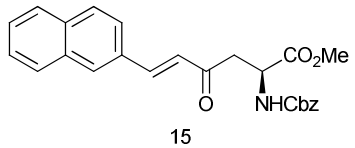
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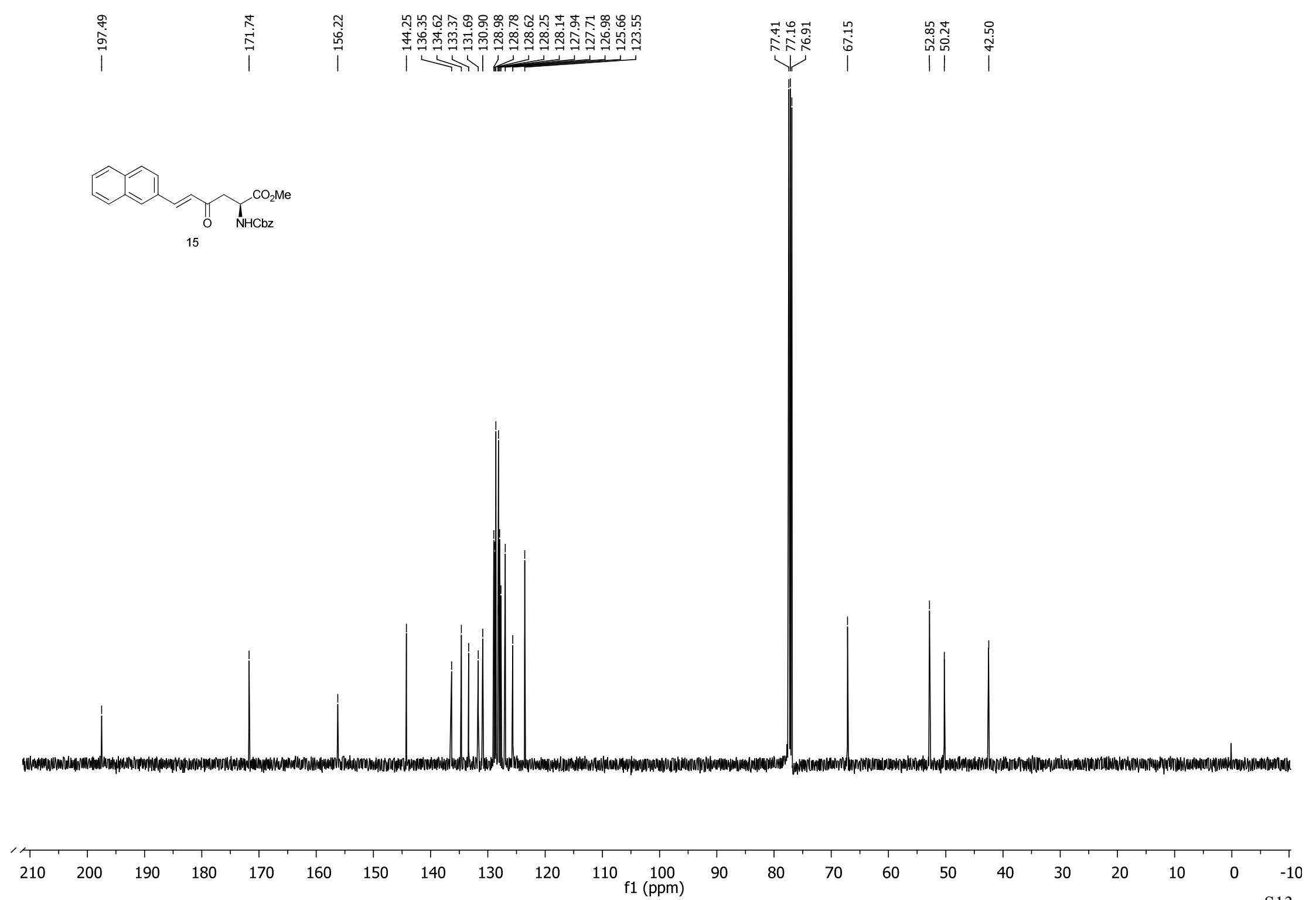
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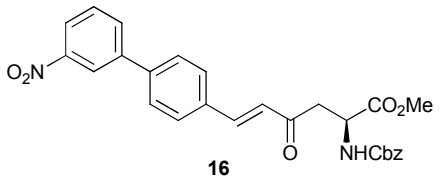
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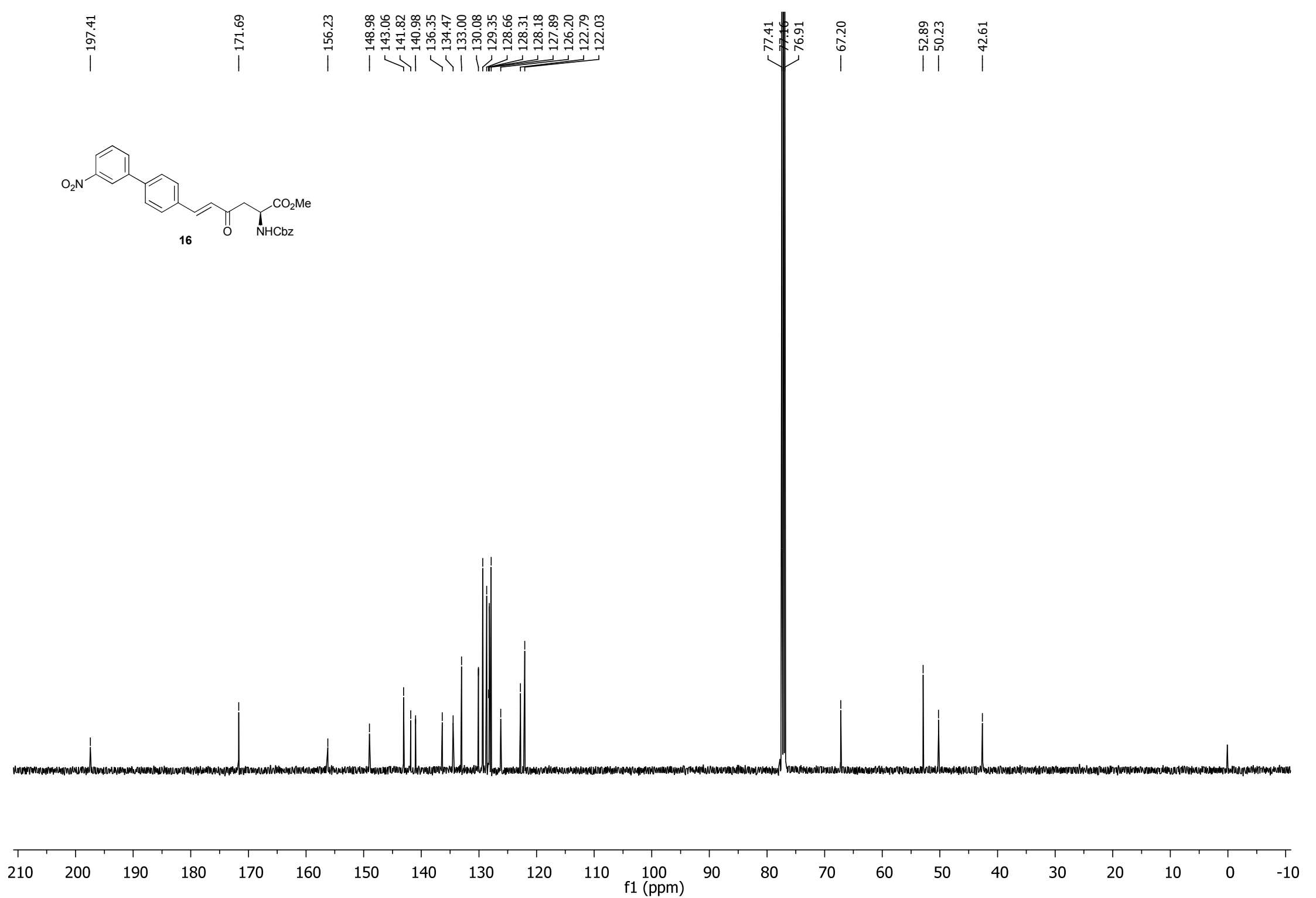
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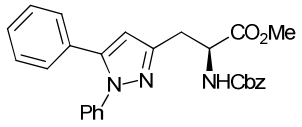
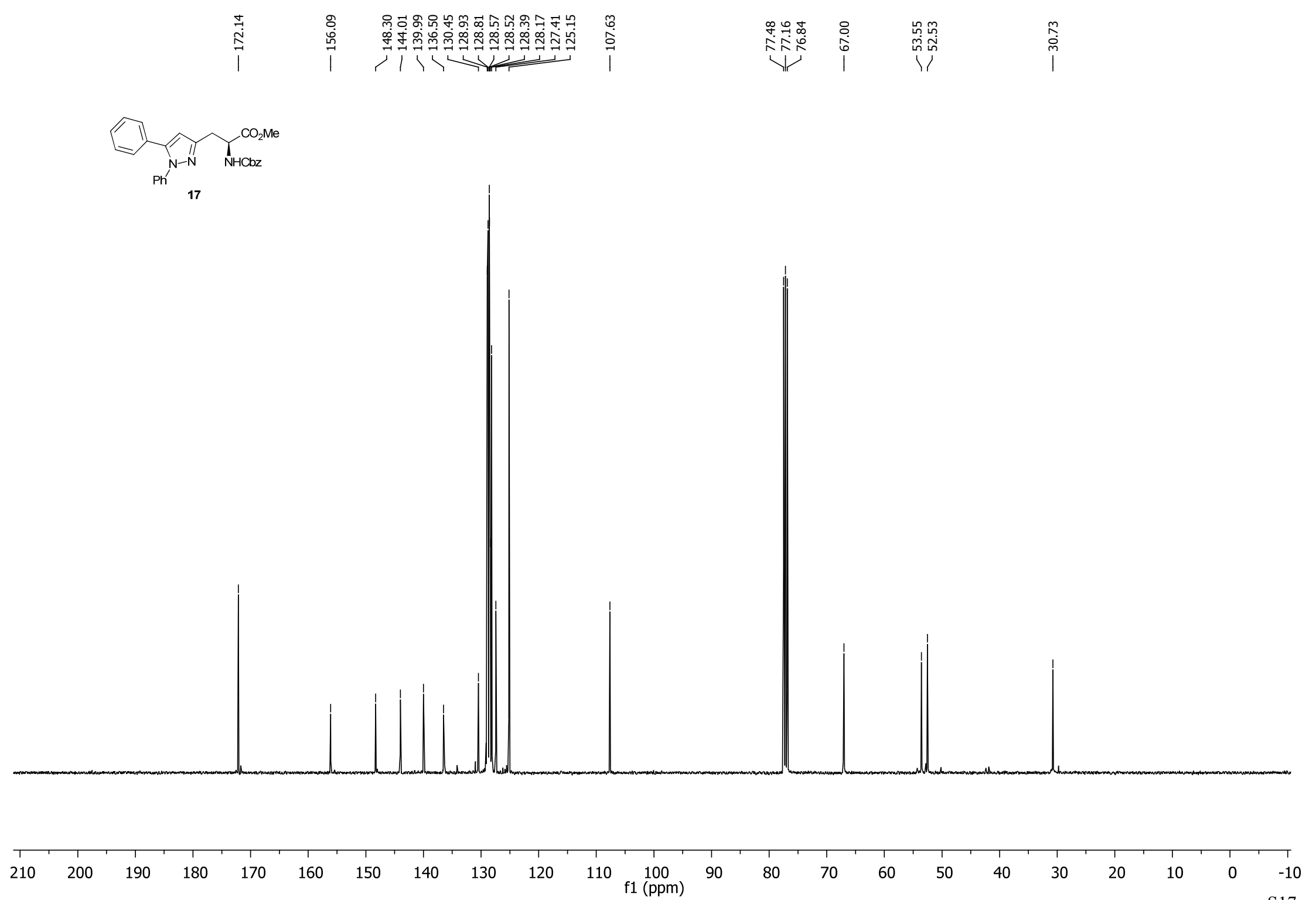
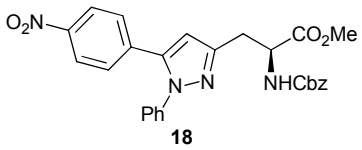
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CO2Me
NHCbz
N
N
Ph

17

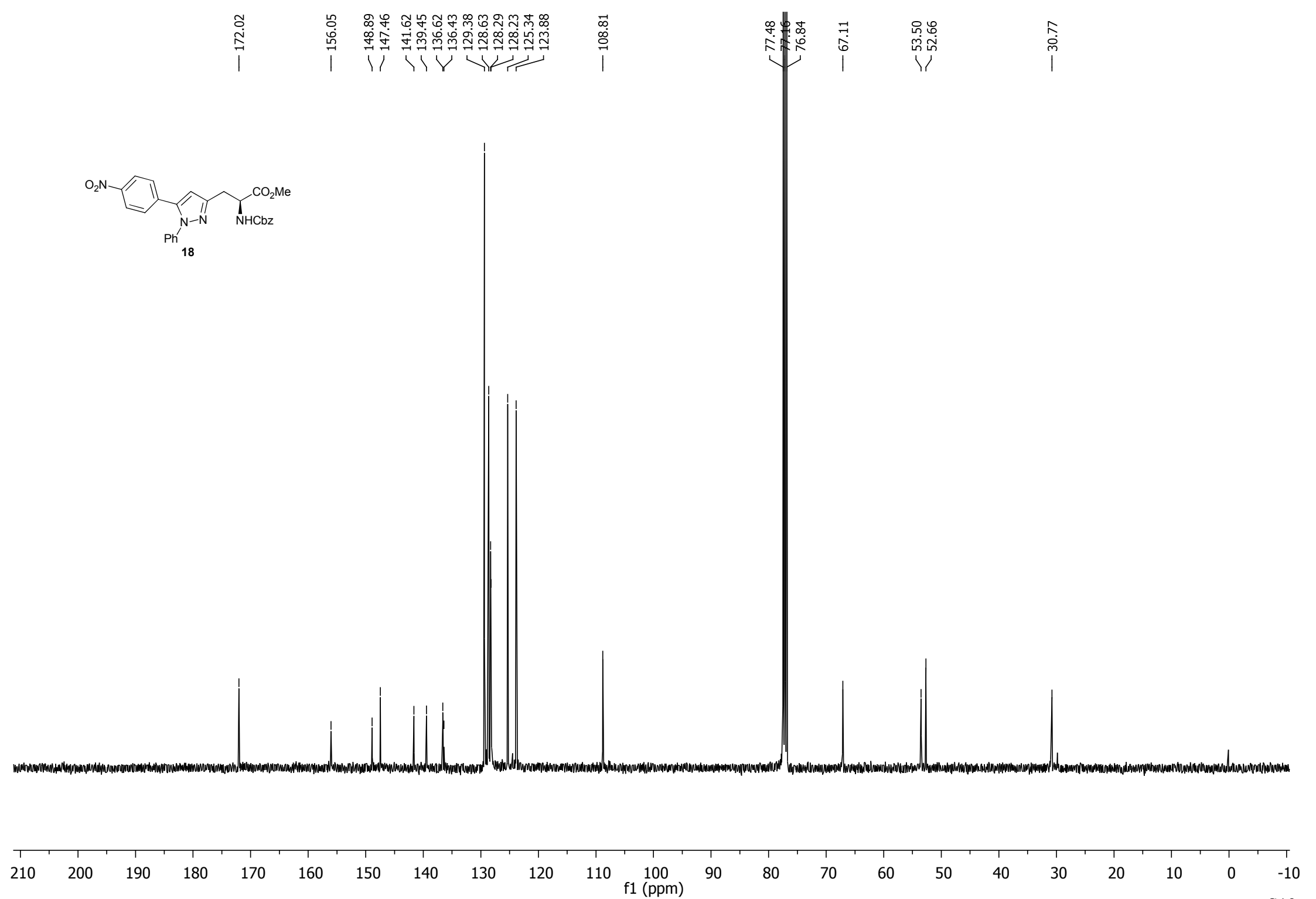
14.89
0.85
0.71
1.91
0.78
2.47
0.77
1.07
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

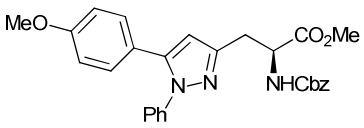

172.14
156.09
148.30
144.01
139.99
136.50
130.45
128.93
128.81
128.57
128.52
128.39
128.17
127.41
125.15
107.63
77.48
77.16
76.84
67.00
53.55
52.53
30.73
CO2Me
NHCbz
N
N
Ph
17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O2N
CO2Me
N
N
NHCbz
Ph

18

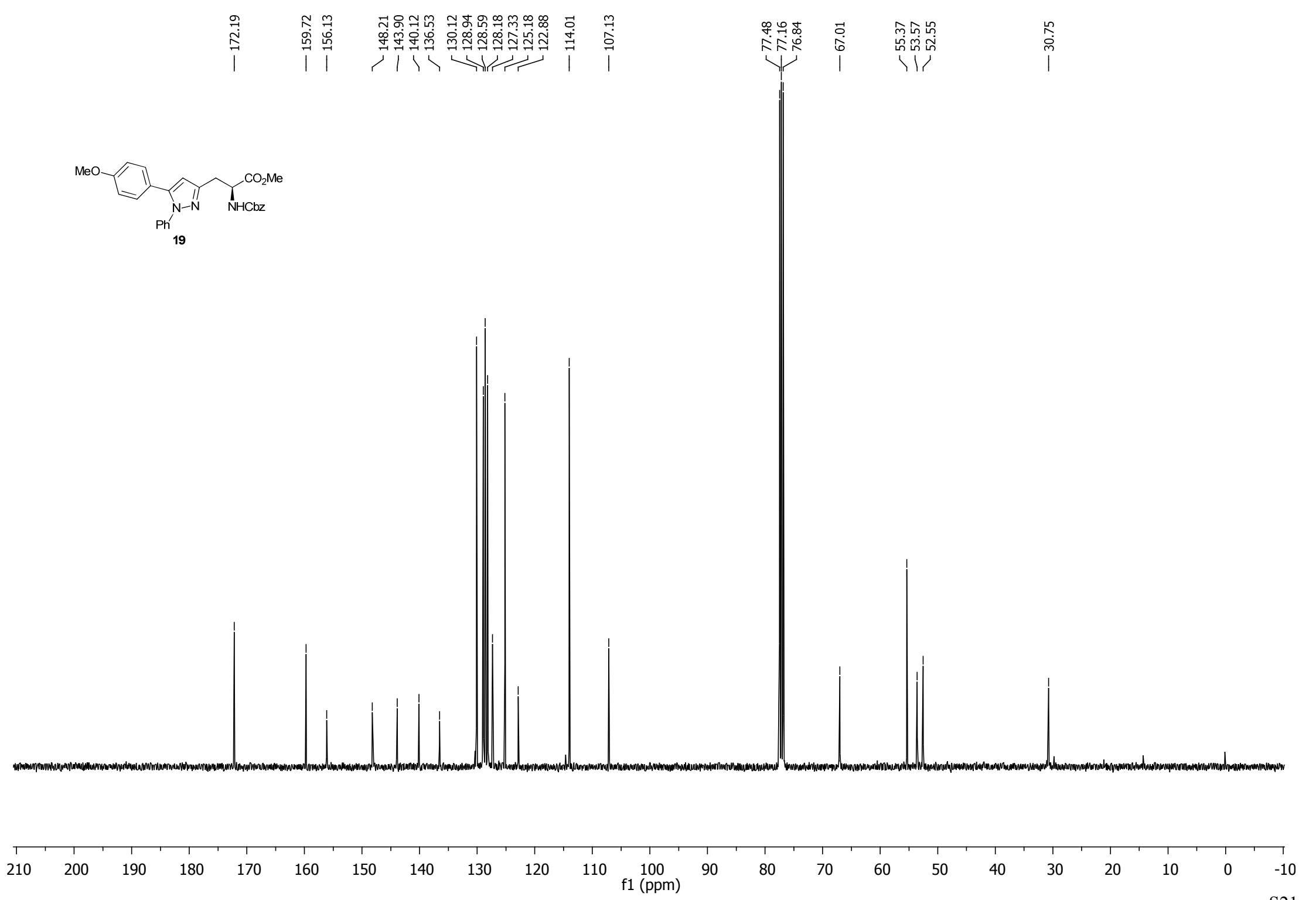
1.88
10.00
1.93
0.90
0.74
2.05
0.78
2.55
1.87
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

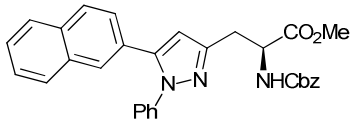

172.02
156.05
148.89
147.46
141.62
139.45
136.62
136.43
129.38
128.63
128.29
128.23
125.34
123.88
108.81
77.48
77.16
76.84
67.11
53.50
52.66
30.77
O2N
CO2Me
NHCbz
N
N
Ph
18
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
CO2Me
N–N
NHCbz
Ph

19

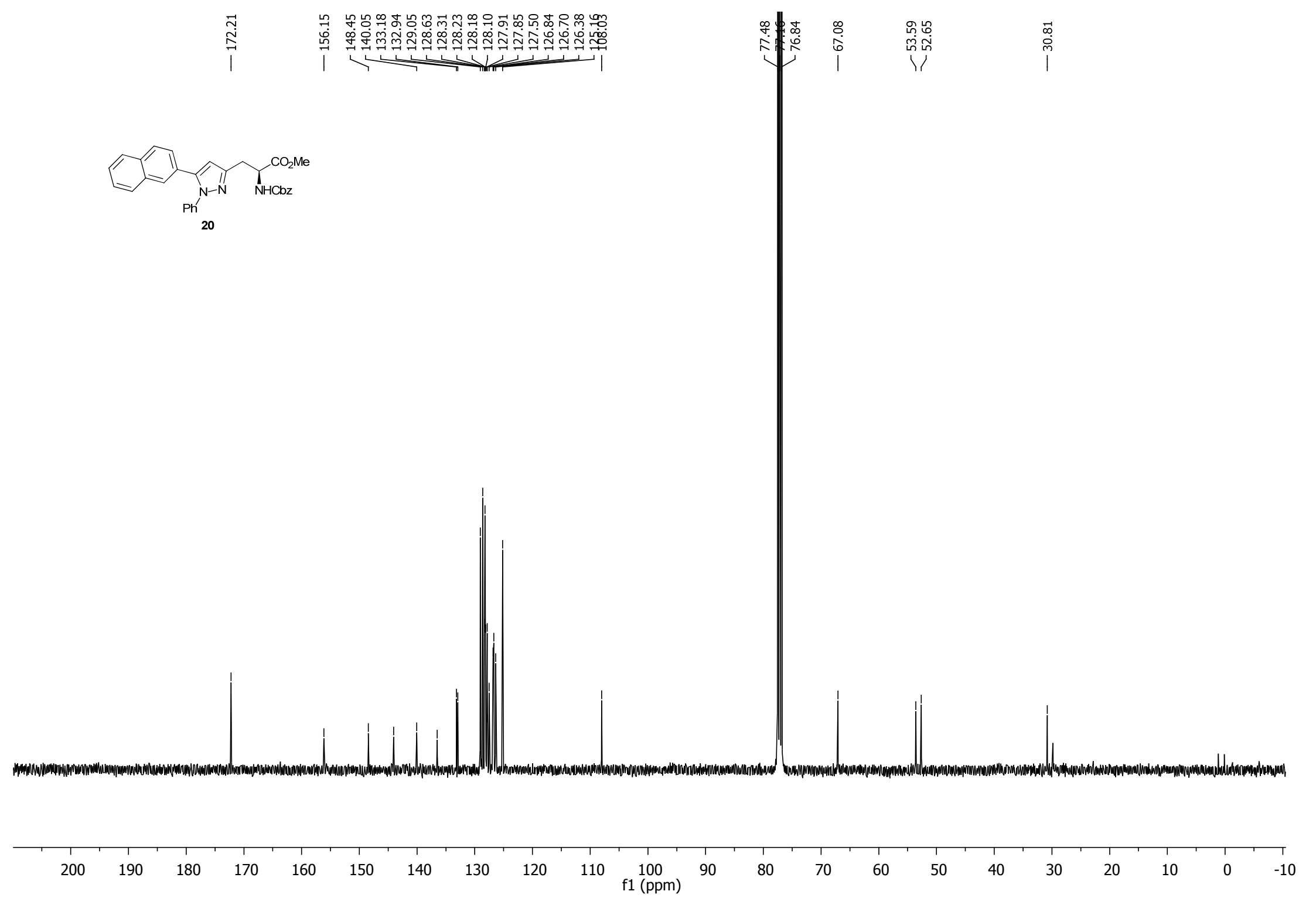
10.01
1.95
1.82
0.88
0.69
1.82
0.75
2.65
2.37
0.74
1.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

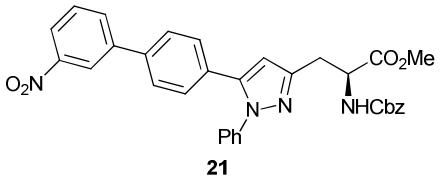

172.19
159.72
156.13
148.21
143.90
140.12
136.53
130.12
128.94
128.59
128.18
127.33
125.18
122.88
114.01
107.13
77.48
77.16
76.84
67.01
55.37
53.57
52.55
30.75
MeO
CO2Me
NHCbz
N
N
Ph
19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CO2Me
NHCbz
N
N
Ph

20

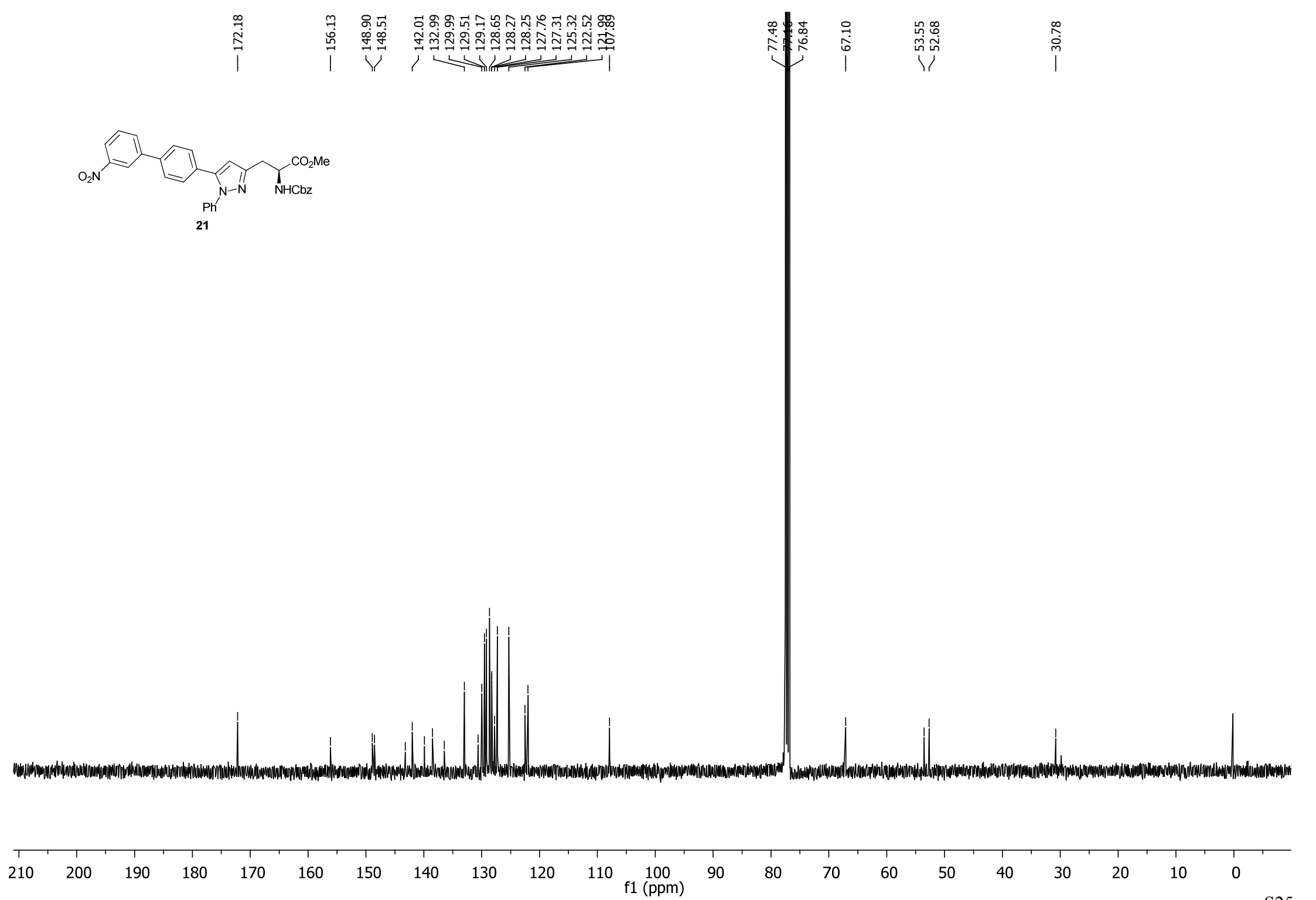
3.69
1.90
10.00
0.83
0.82
0.67
1.71
0.72
2.31
0.74
0.94
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

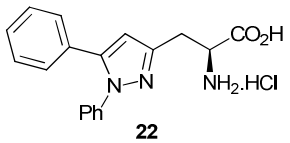

172.21
156.15
148.45
140.05
133.18
132.94
129.05
128.63
128.31
128.23
128.18
128.10
127.91
127.85
127.50
126.84
126.70
126.38
125.16
108.03
77.48
77.16
76.84
67.08
53.59
52.65
30.81
CO2Me
NHCbz
N
N
Ph
20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O2N
CO2Me
NHCbz
N
N
Ph

21

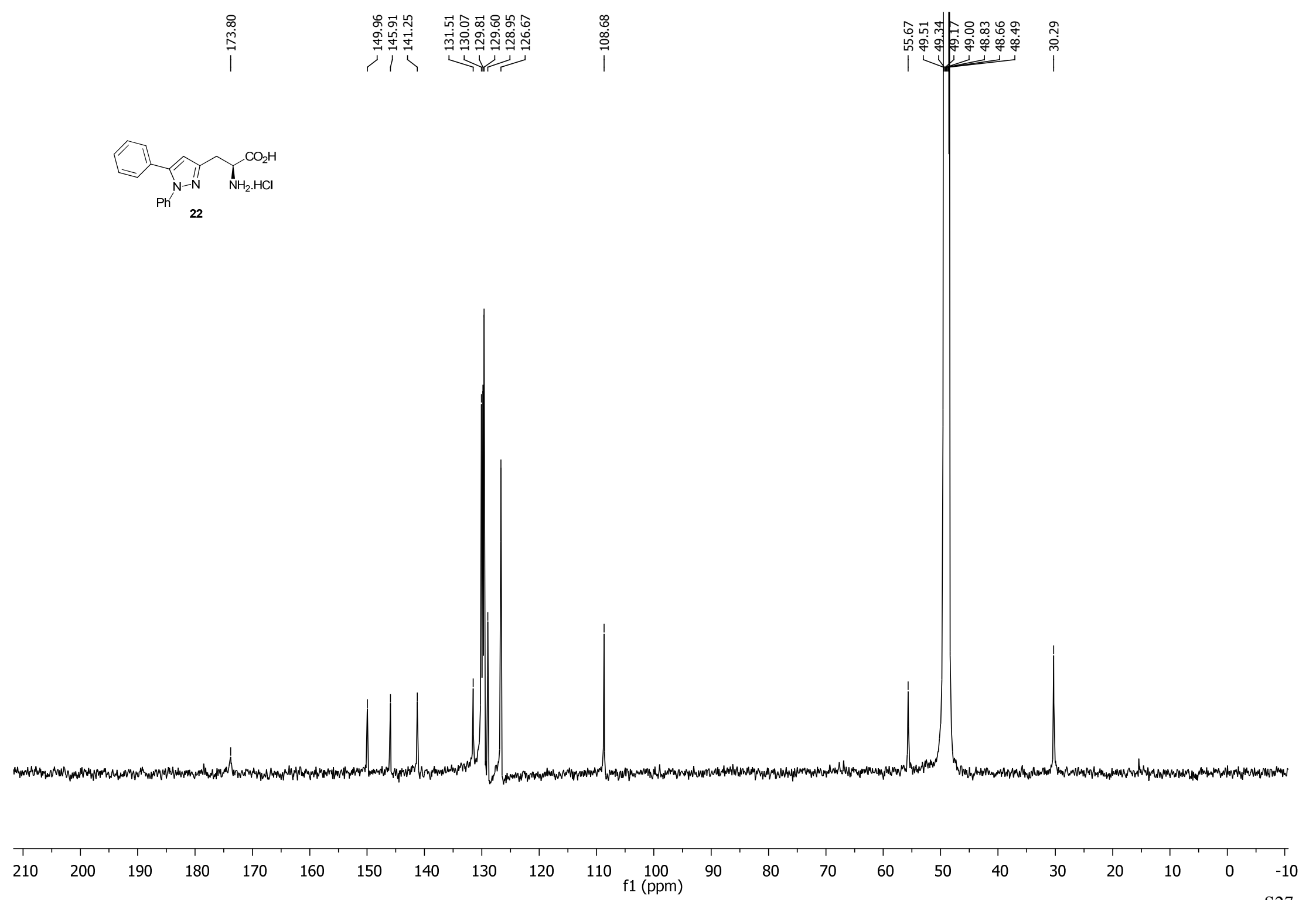
0.79
0.82
0.83
0.95
1.68
11.81
0.76
0.64
1.62
0.68
2.25
0.67
0.89
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

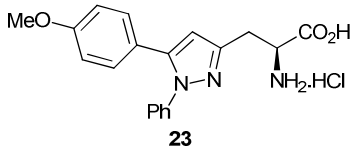

172.18
156.13
148.90
148.51
142.01
132.99
129.99
129.51
129.17
128.65
128.27
128.25
127.76
127.31
125.32
122.52
77.48
76.84
67.10
53.55
52.68
30.78
O2N
CO2Me
NHCbz
N
N
Ph
21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CO2H
NH2.HCl
N
N
Ph

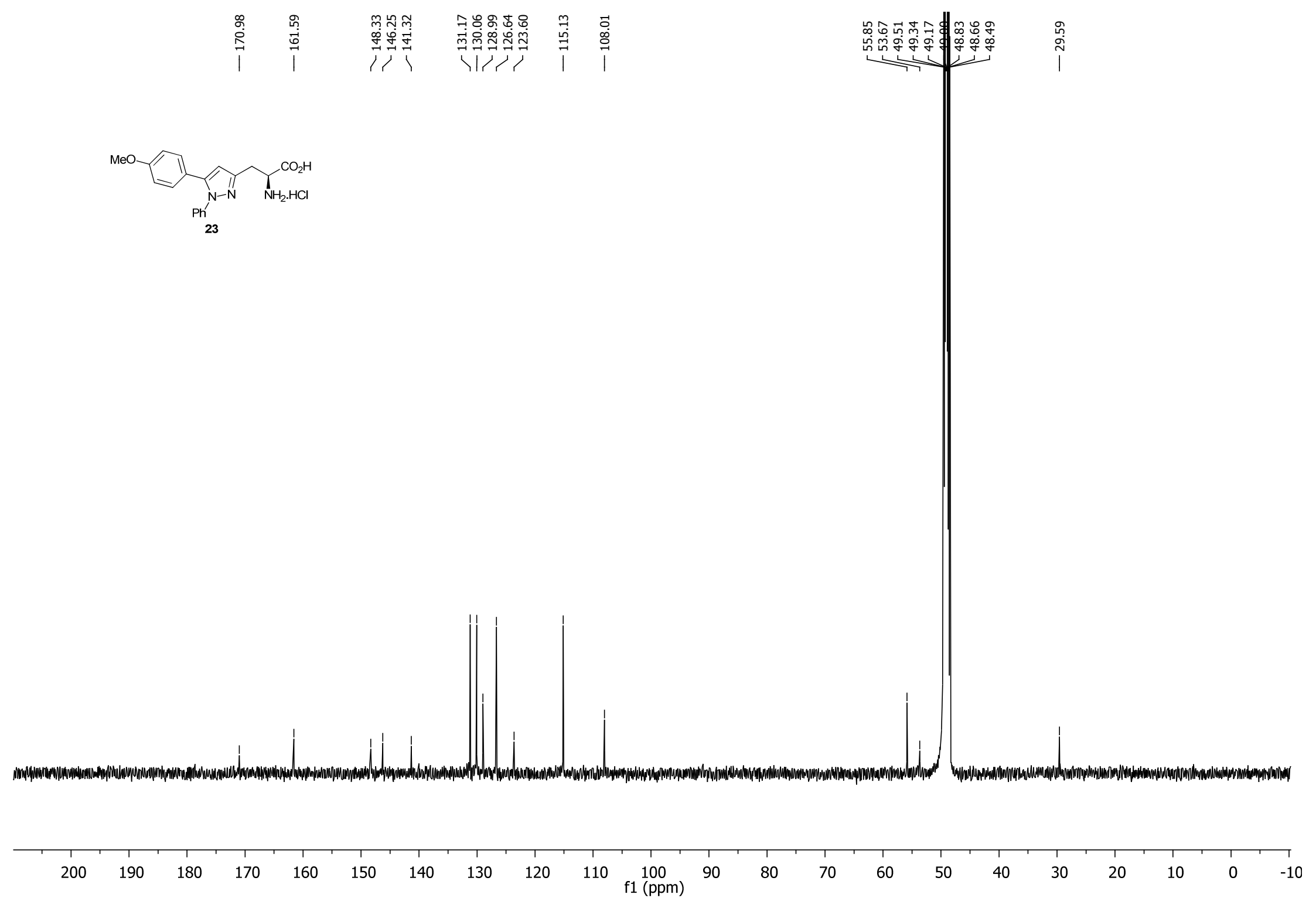
22

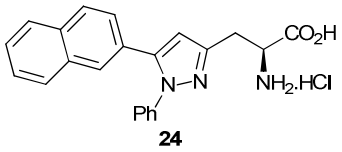
9.88
0.92
0.85
0.98
0.83
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


173.80
149.96
145.91
141.25
131.51
130.07
129.81
129.60
128.95
126.67
108.68
55.67
49.51
49.34
49.17
49.00
48.83
48.66
48.49
30.29
CO2H
NH2.HCl
N
N
Ph
22
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)



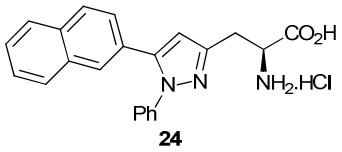
23


170.98
161.59
148.33
146.25
141.32
131.17
130.06
128.99
126.64
123.60
115.13
108.01
55.85
53.67
49.51
49.34
49.17
48.83
48.66
48.49
29.59
MeO
CO2H
NH2.HCl
N
N
Ph
23
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CO2H
NH2.HCl
N
N
Ph

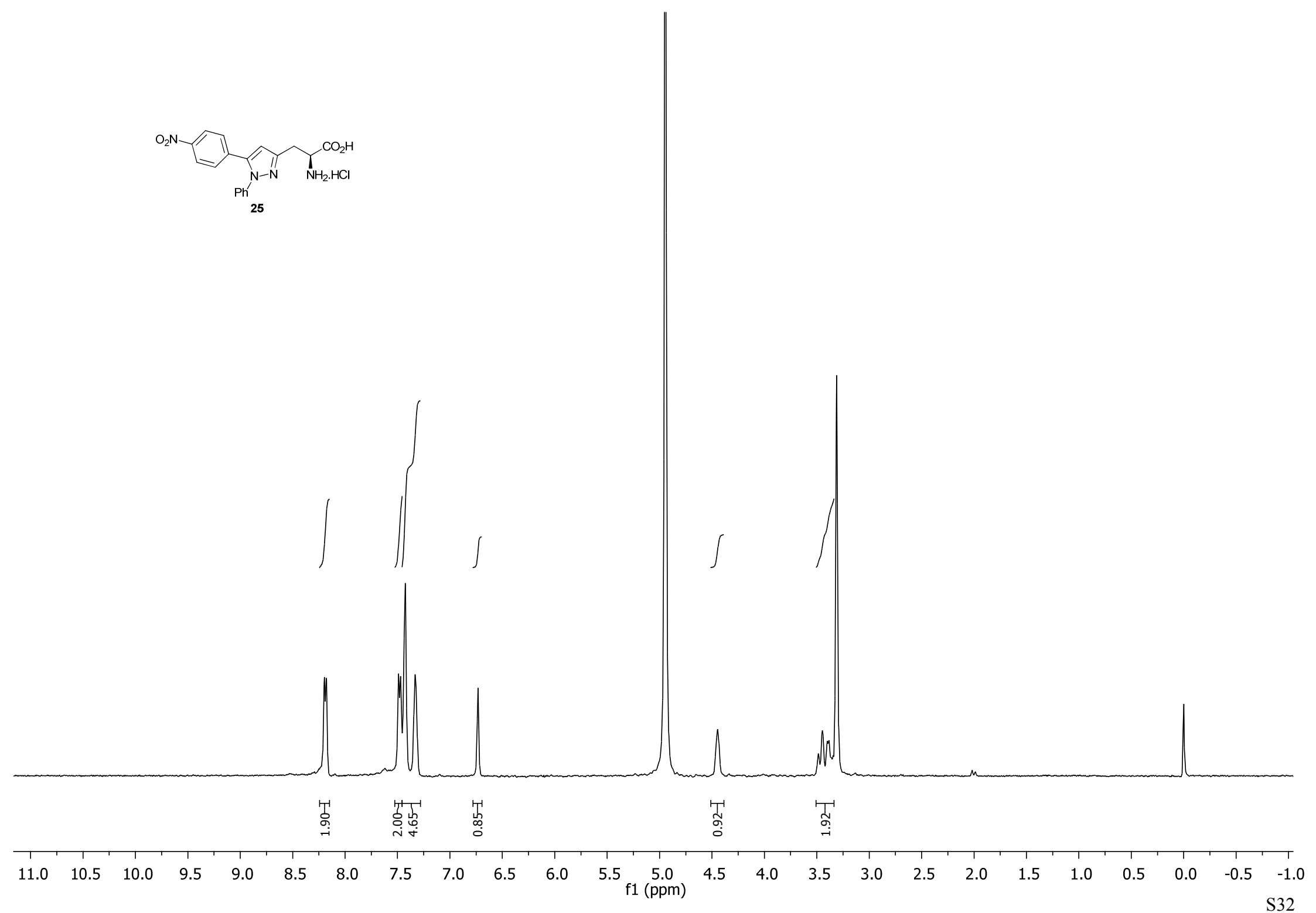
24

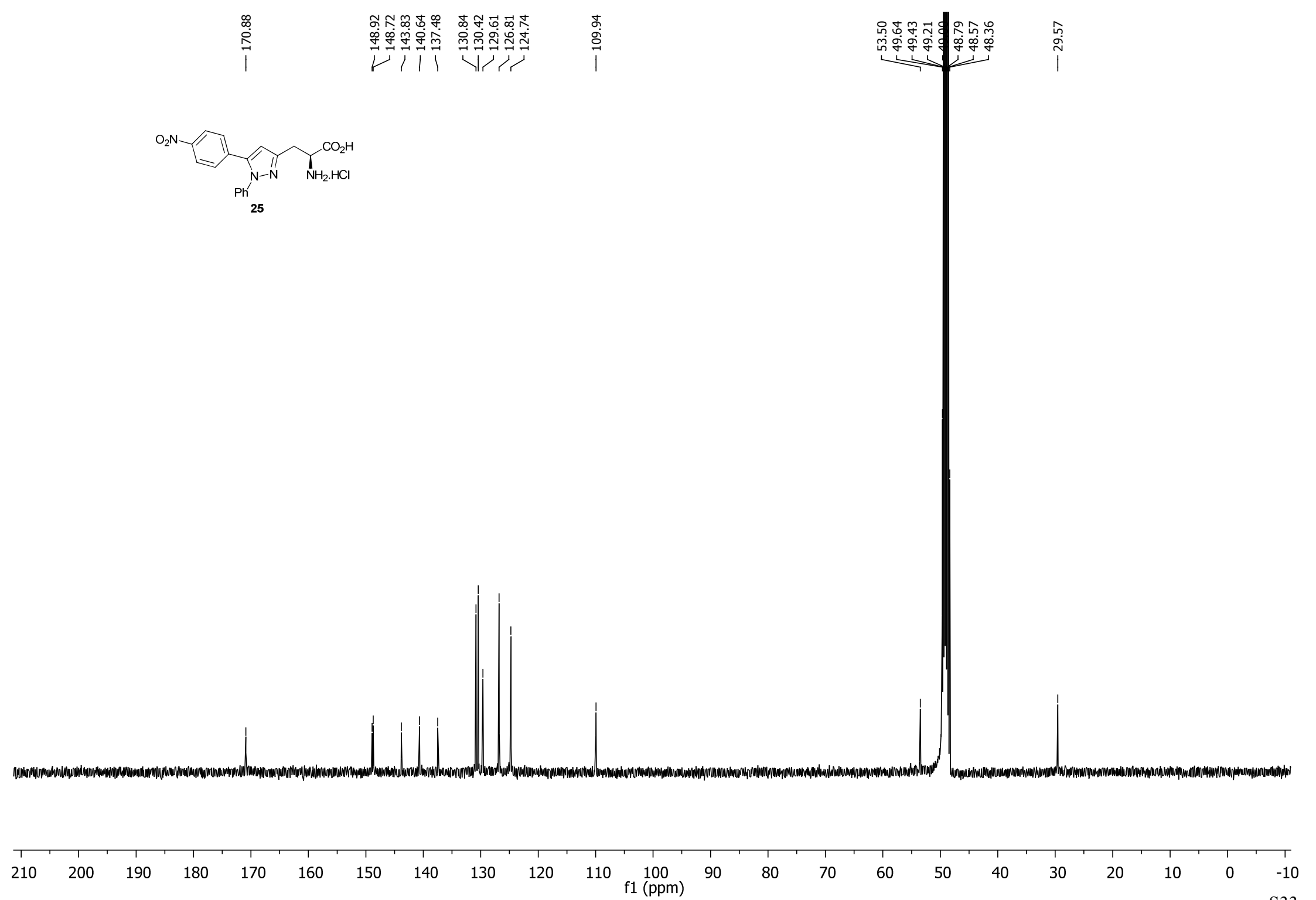
4.18
2.31
5.00
0.94
0.89
1.00
0.92
1.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

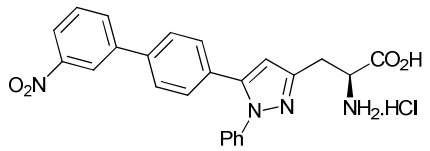

CO2H
NH2.HCl
N
N
Ph

24

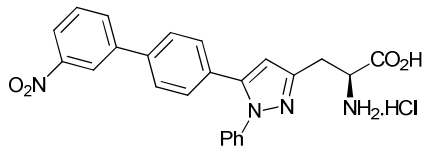
170.99
148.37
146.32
140.93
134.44
130.22
129.31
129.27
129.17
128.74
128.46
128.05
127.82
127.02
126.69
109.00
53.53
49.64
49.43
49.21
48.79
48.57
48.36
29.55
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O2N
CO2H
N
N
NH2.HCl
Ph
25
1.90
2.00
4.65
0.85
0.92
1.92
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
-0.5
-1.0
f1 (ppm)


170.88
148.92
148.72
143.83
140.64
137.48
130.84
130.42
129.61
126.81
124.74
109.94
53.50
49.64
49.43
49.21
48.79
48.57
48.36
29.57
O2N
CO2H
NH2.HCl
N
N
Ph
25
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)



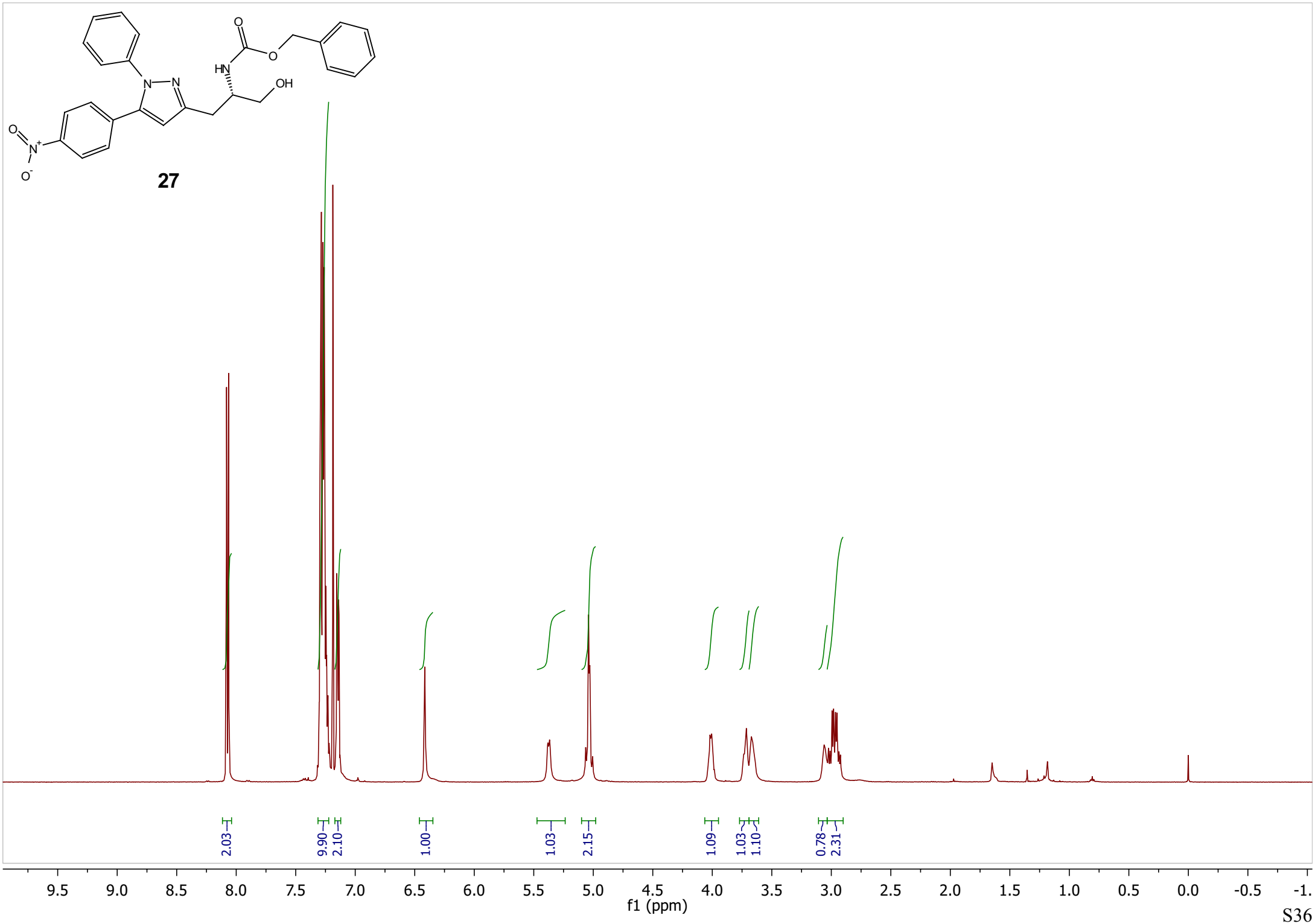
26

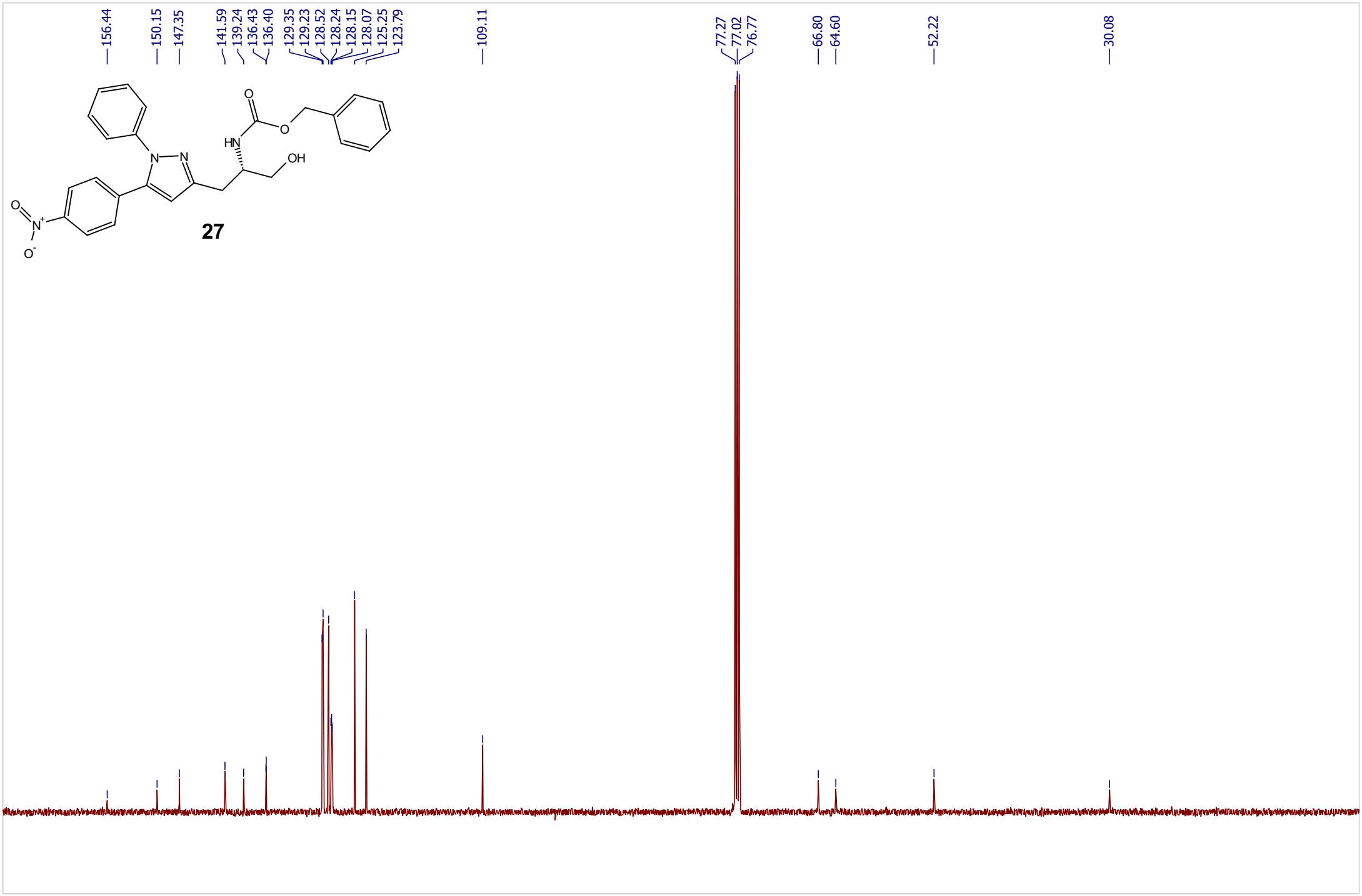


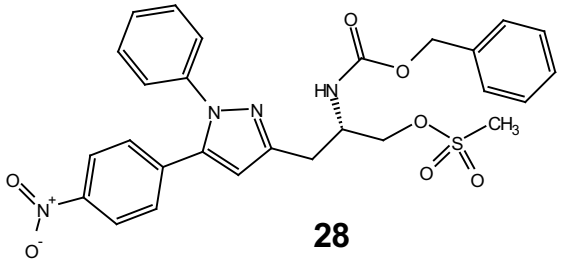
26

171.03
150.26
148.53
145.47
143.04
141.12
140.19
134.08
131.46
131.34
130.61
130.27
129.29
128.37
126.75
123.41
122.47
108.83
53.55
49.64
49.43
49.21
48.79
48.57
48.36
29.61

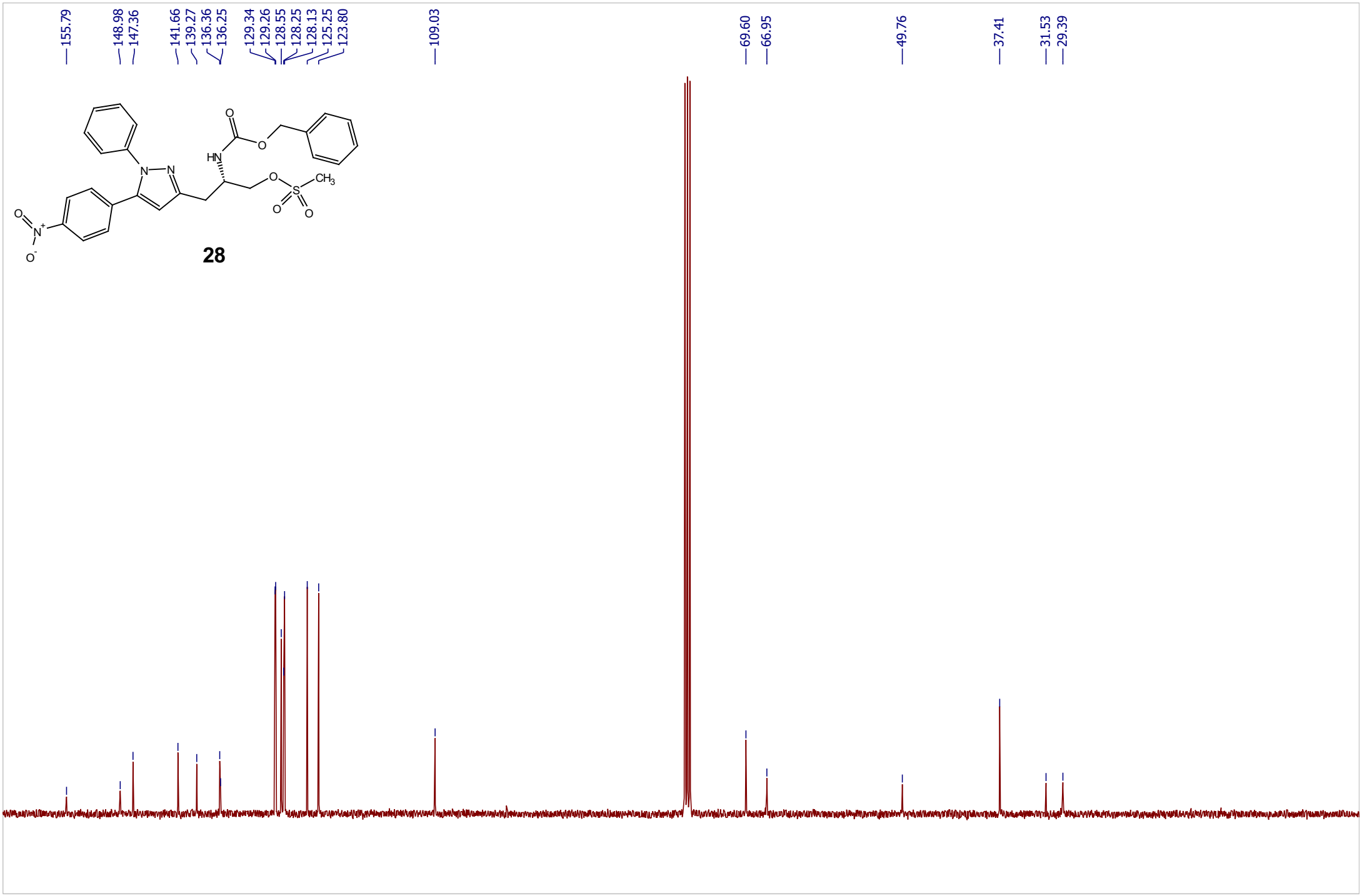
f1 (ppm)

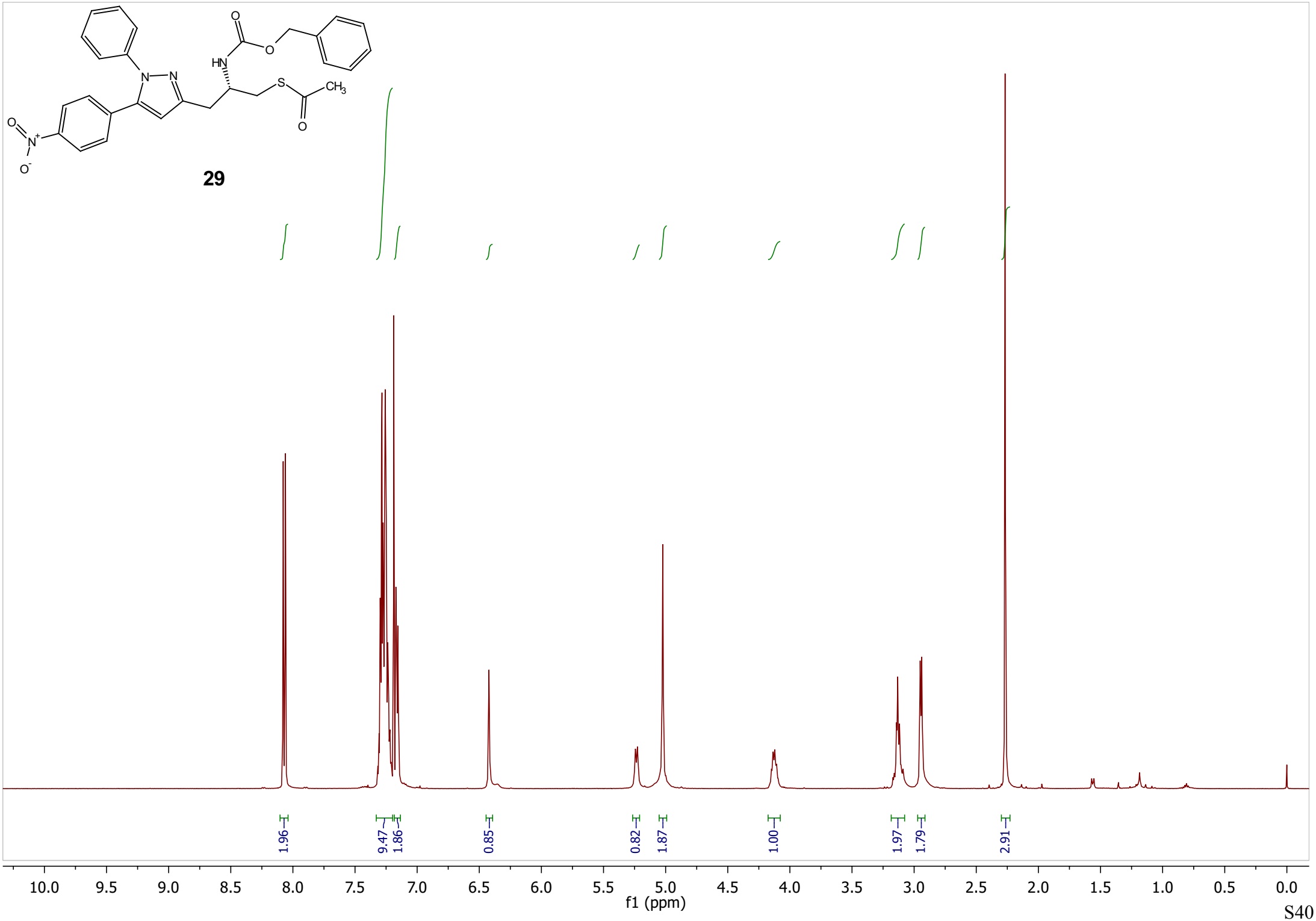

27
2.03
9.90
2.10
1.00
1.03
2.15
1.09
1.03
1.10
0.78
2.31
f1 (ppm)

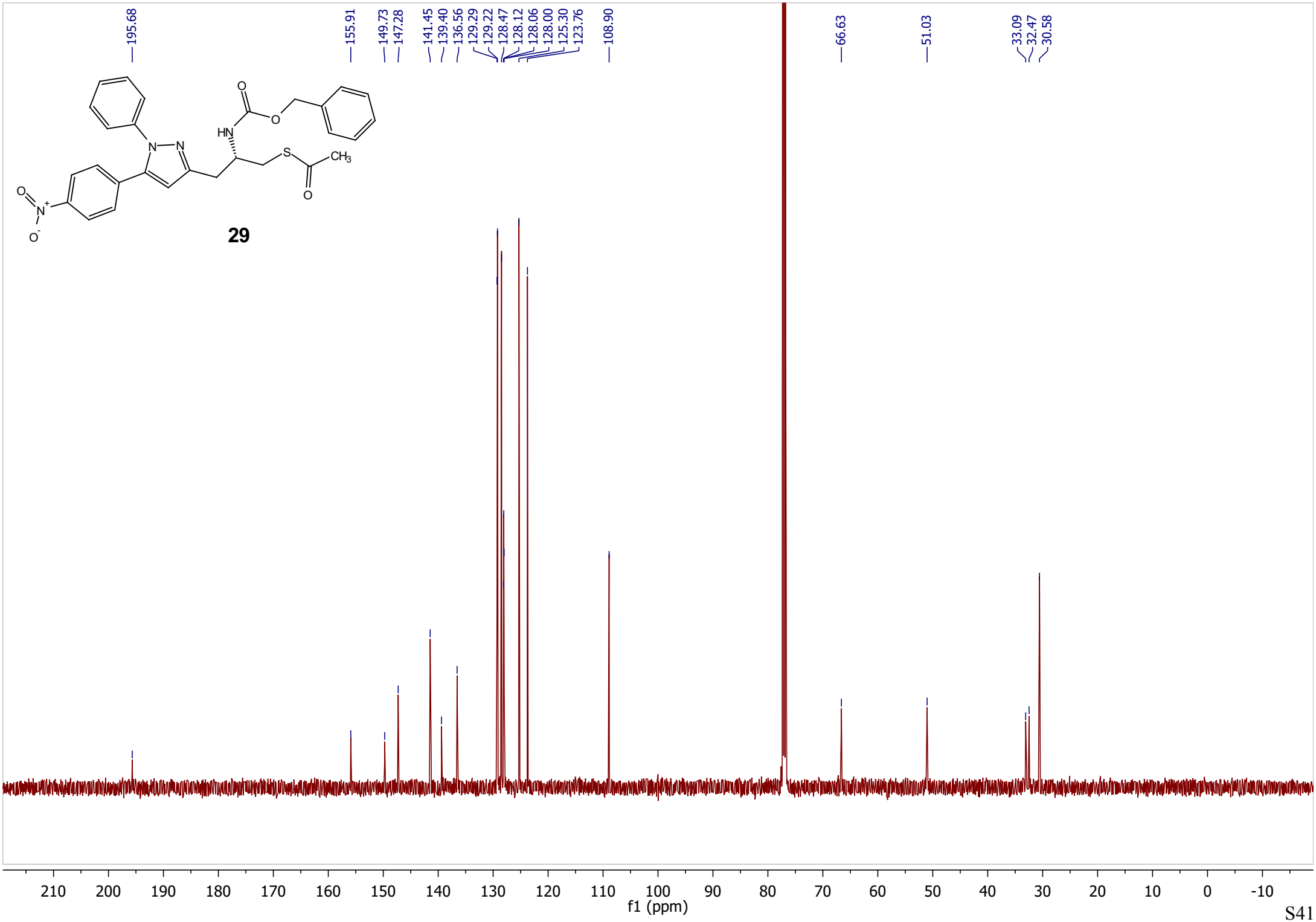

156.44
150.15
147.35
141.59
139.24
136.43
136.40
129.35
129.23
128.52
128.24
128.15
128.07
125.25
123.79
109.11
77.27
77.02
76.77
66.80
64.60
52.22
30.08
O
HN
O
OH
N
N
O
N+
O-
27
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

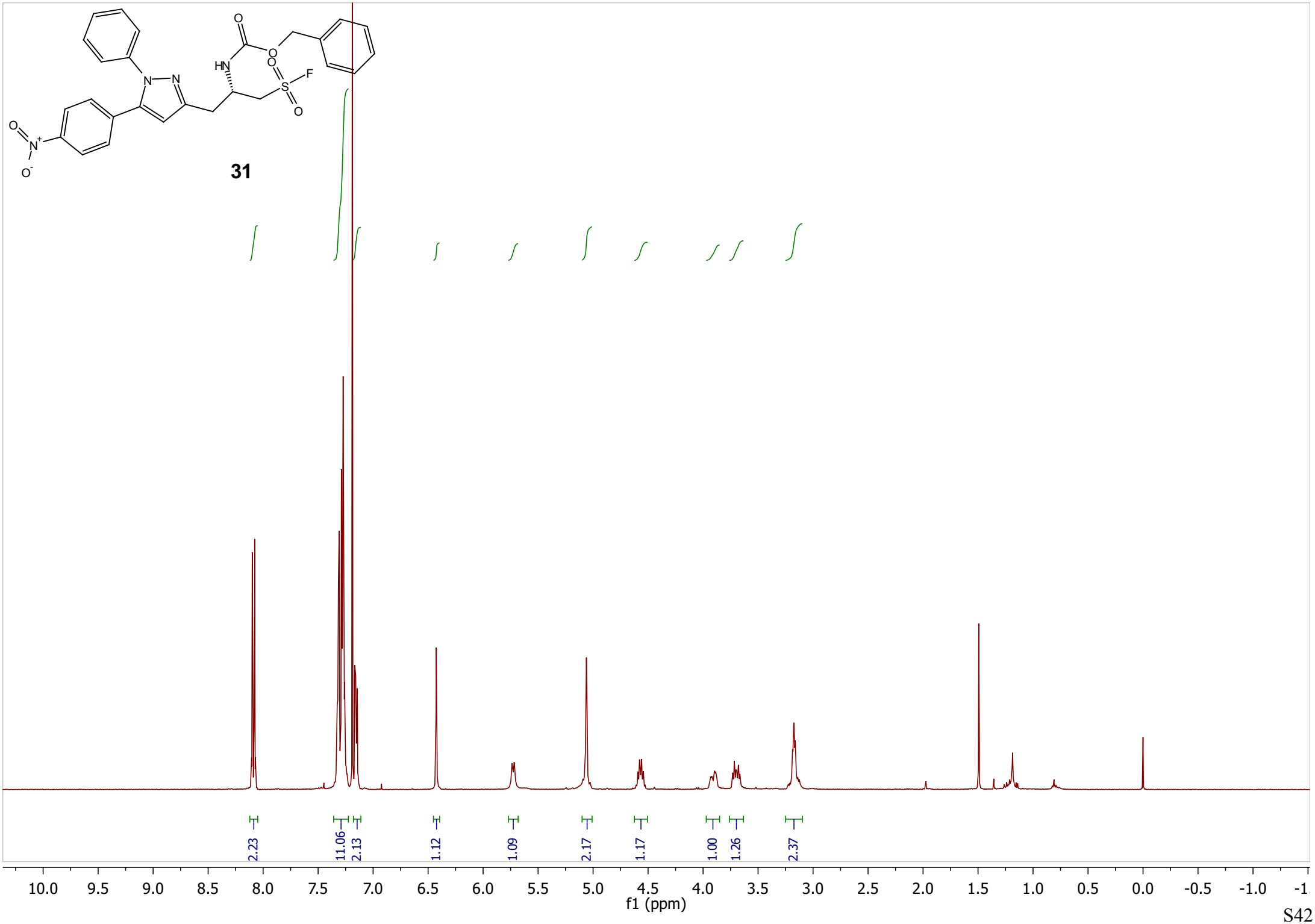

28

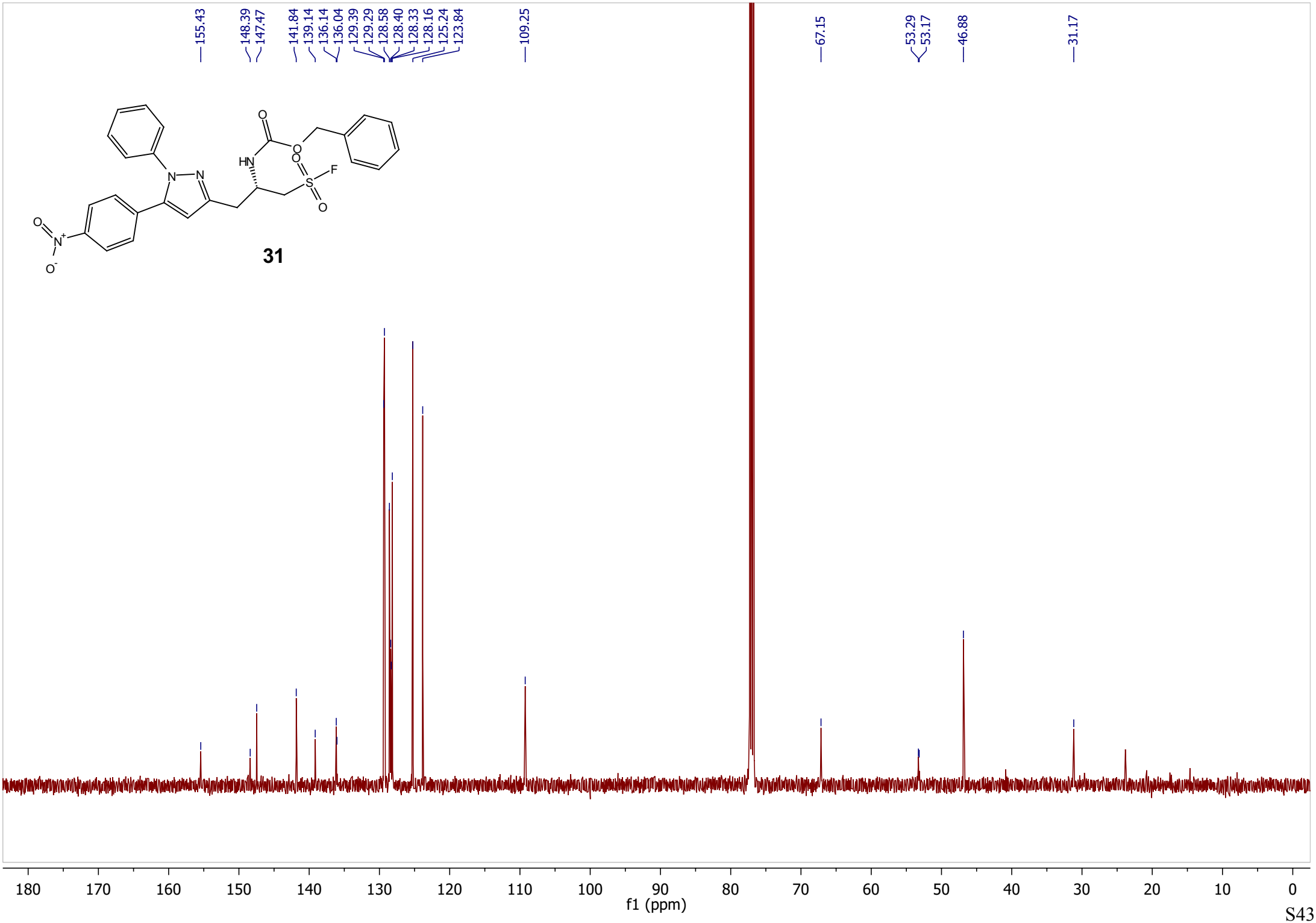
2.06
10.16
2.04
1.00
0.98
2.15
3.56
2.16
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


155.79
148.98
147.36
141.66
139.27
136.36
136.25
129.34
129.26
128.55
128.25
128.13
125.25
123.80
109.03
69.60
66.95
49.76
37.41
31.53
29.39
28
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


29
1.96
9.47
1.86
0.85
0.82
1.87
1.00
1.97
1.79
2.91
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)


195.68
155.91
149.73
147.28
141.45
139.40
136.56
129.29
129.22
128.47
128.12
128.06
128.00
125.30
123.76
108.90
66.63
51.03
33.09
32.47
30.58
29
f1 (ppm)


31
2.23
11.06
2.13
1.12
1.09
2.17
1.17
1.00
1.26
2.37
f1 (ppm)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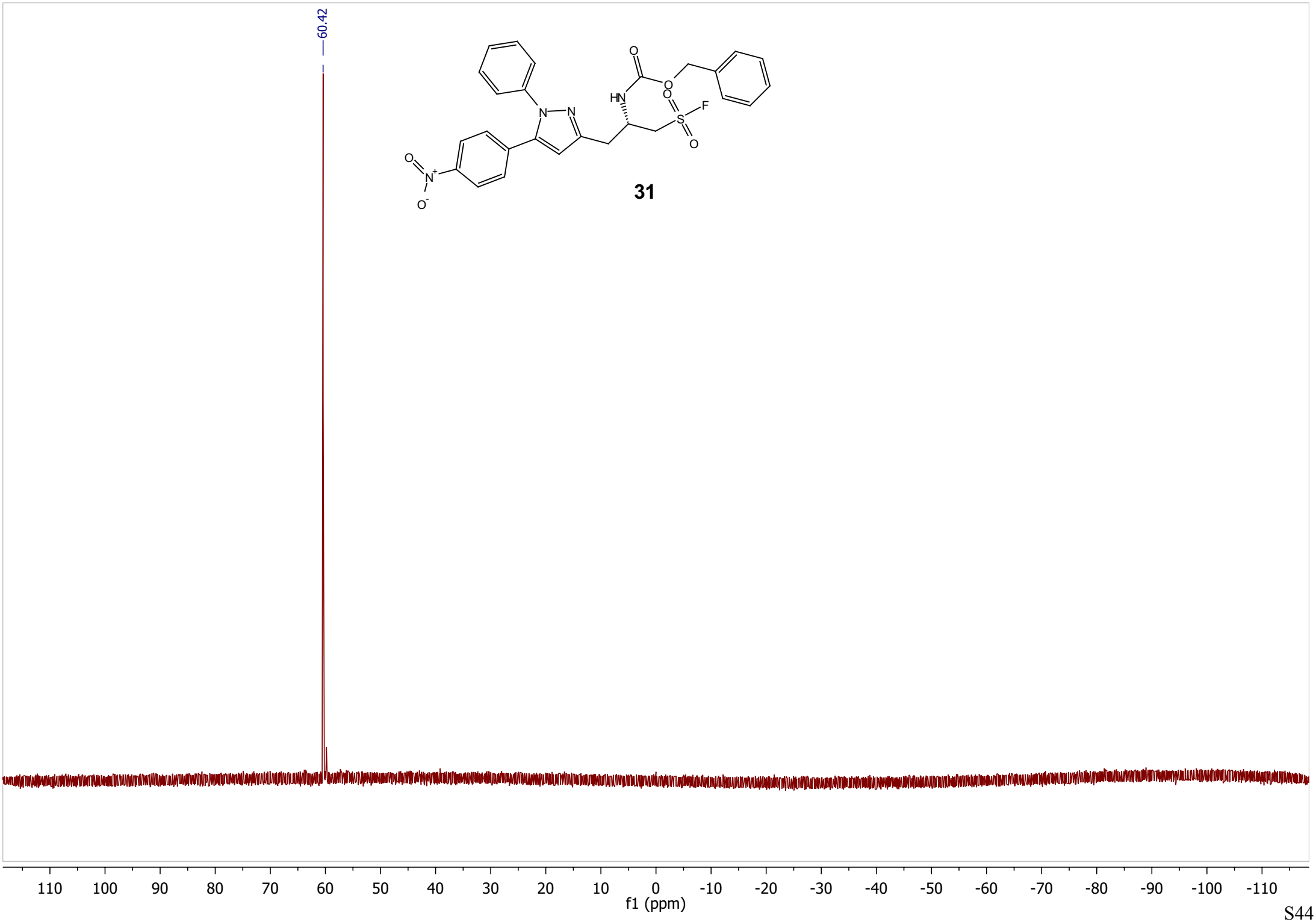
148.39
147.47
141.84
139.14
136.14
136.04
129.39
129.29
128.58
128.40
128.33
128.16
125.24
123.84
109.25
67.15
53.29
53.17
46.88
31.17
31
f1 (ppm)


60.42
31
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100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)