Supporting Information

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High-Temperature Polymer Components Reimagined: Scalable Syntheses and *de novo* Routes to Structurally Versatile Precursors

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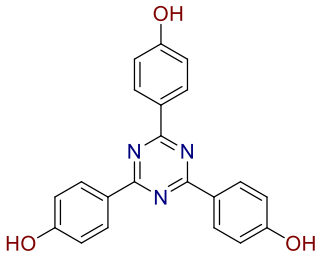
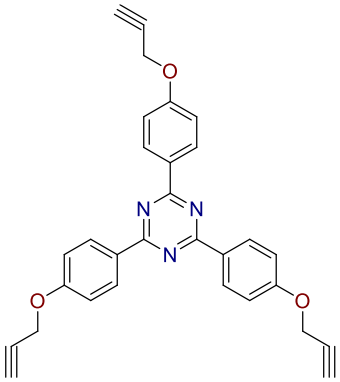
Analytical data



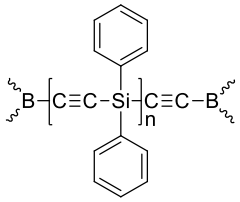
4,4',4''-(1,3,5-triazine-2,4,6-triyl)triphenol (2)

Yellow powder. ^{1}H NMR (302 MHz, DMSO-d_6) δ 11.46 (s, 3H), 7.90 (dd, J = 11.0, 8.2 Hz, 4H), 7.39 – 7.15 (m, 8H). LCMS, positive mode, m/z: 358.2 $[M+H]^+$. Anal. calcd. for $C_{21}H_{15}N_3O_3$: C 70.58; H 4.23; N 11.76. Found: C 70.38; H 3.87; N 12.14.



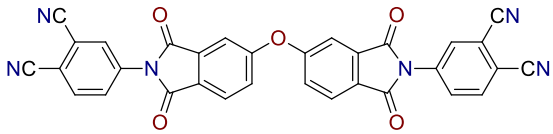
2,4,6-tris(4-(prop-2-yn-1-yloxy)phenyl)-1,3,5-triazine (3):

Yellow powder. ^{1}H NMR (302 MHz, DMSO-d_6) δ 8.67 (d, J = 8.6 Hz, 6H), 7.21 (d, J = 8.7 Hz, 6H), 4.96 (s, 6H), one peak is overlapped with the peaks of the solvent. LCMS, positive mode, m/z: 472.2 $[M+H]^+$. Anal. calcd. for $C_{30}H_{21}N_3O_3$: C 76.42; H 4.49; N 8.91. Found: C 76.34; H 4.71; N 8.82.



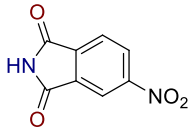
bis((dimethylboraneyl)ethynyl)diphenylsilane oligomer (9c):

Brown powder. ^{1}H NMR (302 MHz, DMSO-d_6) δ 7.71 – 7.64 (m, 4H), 7.57 – 7.39 (m, 6H), one peak is overlapped with the peaks of the solvent. ^{1}H NMR (302 MHz, Chloroform-d) δ 7.77 – 7.75 (m, 4H), 7.42 – 7.34 (m, 6H), 1.60 (s, 12H).



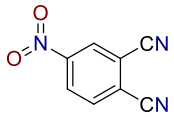
4,4'-(Oxybis(1,3-dioxoisoindoline-5,2-diyl))diphthalonitrile (11)

Yellow powder. ^{1}H NMR (500 MHz, DMSO-d6) δ 8.40 – 8.27 (m, 2H), 8.27 – 8.19 (m, 2H), 8.19 – 8.09 (m, 2H), 8.09 – 7.95 (m, 2H), 7.77 – 7.60 (m, 4H). ^{13}C NMR (126 MHz, DMSO) 165.1, 165.0, 161.0, 136.3, 134.9, 134.2, 131.6, 131.1, 126.9, 126.6, 125.5, 115.6, 115.3, 114.1, 113.4. Anal. calcd. for $C_{32}H_{12}N_6O_5$: C 68.57; H 2.16; N 14.99. Found: C 68.93; H 2.50; N 15.00.



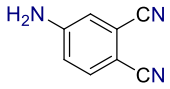
5-nitroisoindoline-1,3-dione (13)

Yellow crystalline powder. M.p. = 202 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.83 (s, 1H), 8.61 (dd, J = 8.1, 1.9 Hz, 1H), 8.44 (d, J = 1.7 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.4, 167.1, 151.3, 137.2, 134.0, 129.3, 124.4, 117.7. LCMS, negative mode, m/z: 191.0 $[M-H]^-$. Anal. calcd. for $C_8H_4N_2O_4$: C 50.01; H 2.10; N 14.58. Found: C 49.62; H 2.00; N 14.81.



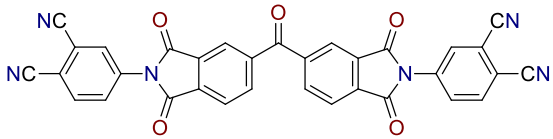
4-nitrophthalonitrile (14)

White powder. M.p. = 139 – 144 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.04 (d, J = 1.8 Hz, 1H), 8.71 – 8.64 (m, 1H), 8.44 (d, J = 8.6 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 149.7, 135.6, 128.8, 128.5, 120.2, 116.6, 114.9, 114.5. EIMS, 70eV, m/z (rel. int.): 173 $[M]^+$ (51); 127 (91); 115 (19); 101 (17); 100 (100); 98 (27); 76 (46); 75 (53); 64 (13); 63 (14); 62 (12); 51 (20); 50 (34); 48 (10); 45 (17); 37 (10); 36 (11). Anal. calcd. for $C_8H_3N_3O_2$: C 55.50; H 1.75; N 24.27. Found: C 55.77; H 1.89; N 24.31.



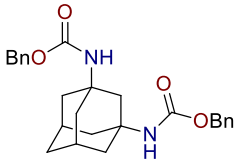
4-aminophthalonitrile (15)

Yellow crystalline powder. M.p. = 179 – 182 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.63 (d, J = 8.7 Hz, 1H), 7.01 (d, J = 2.2 Hz, 1H), 6.87 (dd, J = 8.7, 2.2 Hz, 1H), 6.69 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.0, 134.9, 117.4, 117.2, 116.9, 116.4, 115.4, 97.7. LCMS, negative mode, m/z: 142.0 $[M-H]^-$. Anal. calcd. for $C_8H_5N_3$: C 67.12; H 3.52; N 29.35. Found: C 67.04; H 3.37; N 29.50.



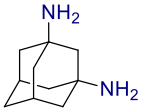
4,4'-(Carbonylbis(1,3-dioxoisoindoline-5,2-diyl))diphthalonitrile (17)

Yellow powder. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.40 – 8.16 (m, 10H), 8.08 (d, J = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 193.1, 165.2, 142.0, 136.2, 136.2, 134.9, 134.3, 131.7, 131.5, 131.2, 124.3, 124.2, 115.6, 115.4, 115.3, 113.6. Anal. calcd. for $C_{33}H_{12}N_6O_5$: C 69.23; H 2.11; N 14.68. Found: C 69.50; H 2.23; N 15.05.



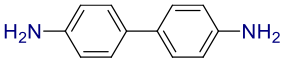
Dibenzyl ((1s,3s,5s,7s)-adamantane-1,3-diyl)dicarbamate (20)

Yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.45 – 7.19 (m, 8H), 7.09 – 6.80 (m, 2H), 4.99 – 4.81 (m, 4H), 4.27 (q, J = 4.5 Hz, 1H), 3.40 (h, J = 5.6 Hz, 2H), 3.26 – 3.21 (m, 1H), 2.15 – 1.92 (m, 4H), 1.88 – 1.59 (m, 8H), 1.45 (s, 2H), 1.12 – 0.85 (m, 3H). Anal. calcd. for $C_{26}H_{30}N_2O_4$: C 71.87; H 6.96; N 6.45. Found: C 71.57; H 7.33; N 6.40.



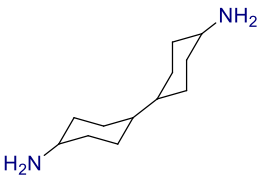
(1s,3s,5s,7s)-Adamantane-1,3-diamine (21)

White powder. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.42 (s, 4H), 2.25 (s, 2H), 2.02 (s, 2H), 1.82 – 1.67 (m, 8H), 1.49 (s, 2H). ^{13}C NMR (151 MHz, DMSO) δ 52.1, 42.8, 38.7, 33.8, 28.8. LCMS, positive mode, m/z: 167.2 $[M+H]^+$. Anal. calcd. for $C_{10}H_{18}N_2$: C 72.24; H 10.91; N 16.85. Found: C 72.60; H 11.23; N 17.24.



Benzidine (23)

Beige powder. M.p. = 128 – 130 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.18 (d, J = 8.2 Hz, 4H), 6.56 (d, J = 8.2 Hz, 4H), 5.00 (s, 4H). ^{13}C NMR (126 MHz, DMSO) δ 146.7, 128.7, 125.9, 114.3. LCMS, positive mode, m/z: 185.2 $[M+H]^+$. Anal. calcd. for $C_{12}H_{12}N_2$: C 78.23; H 6.57; N 15.21. Found: C 78.54; H 6.32; N 15.08.

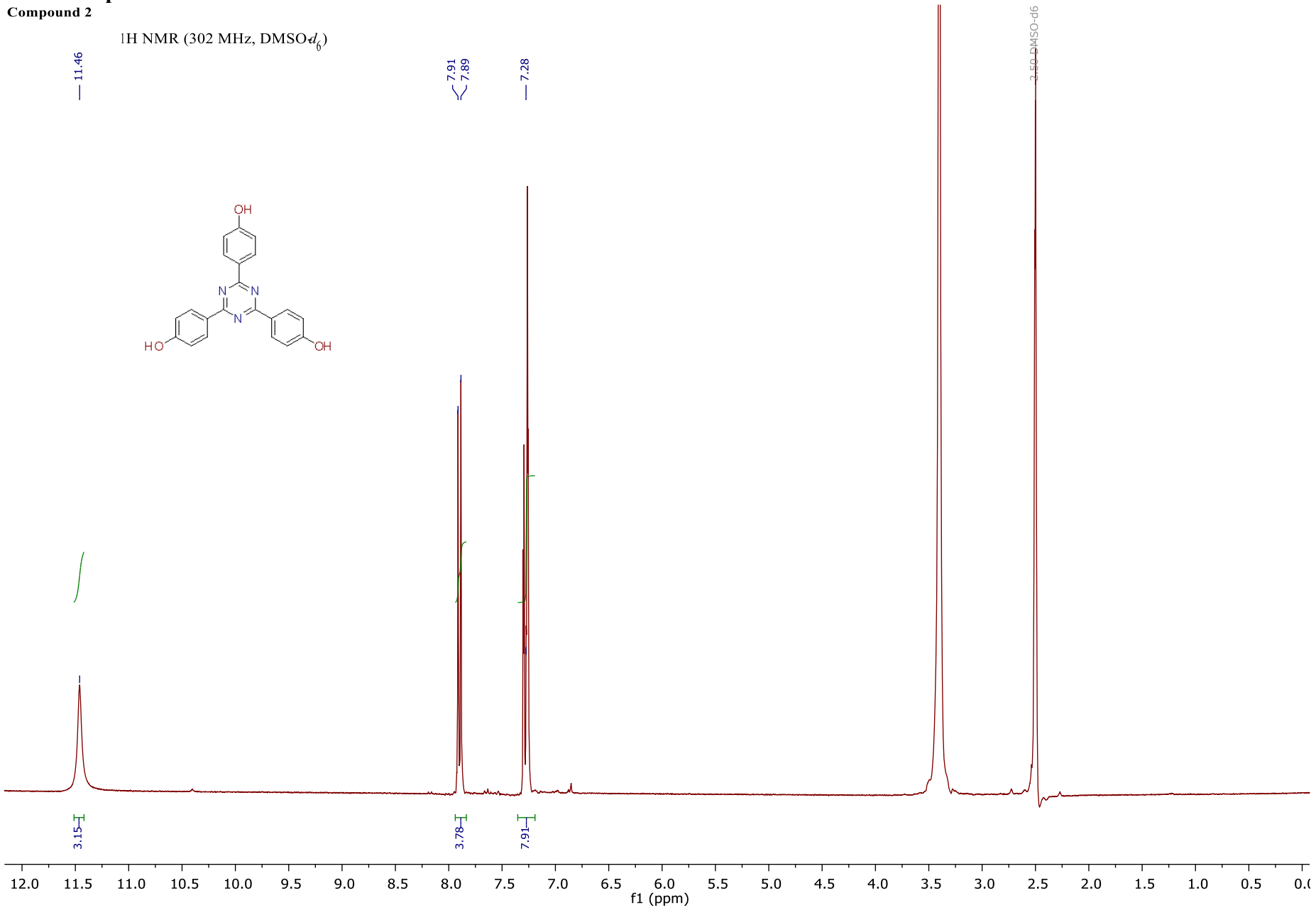


1,1'-bi(cyclohexane)]-4,4'-diamine (26)

White powder. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.13 (s, 4H), 3.45 – 2.75 (m, 4H), 2.03 – 0.60 (m, 16H). ^{13}C NMR (126 MHz, DMSO) δ 47.3, 45.2, 26.8, 23.6. LCMS, positive mode, m/z: 197.2 $[M+H]^+$. Anal. calcd. for $C_{12}H_{24}N_2$: C 73.41; H 12.32; N 14.27. Found: C 73.53; H 12.05; N 13.93.

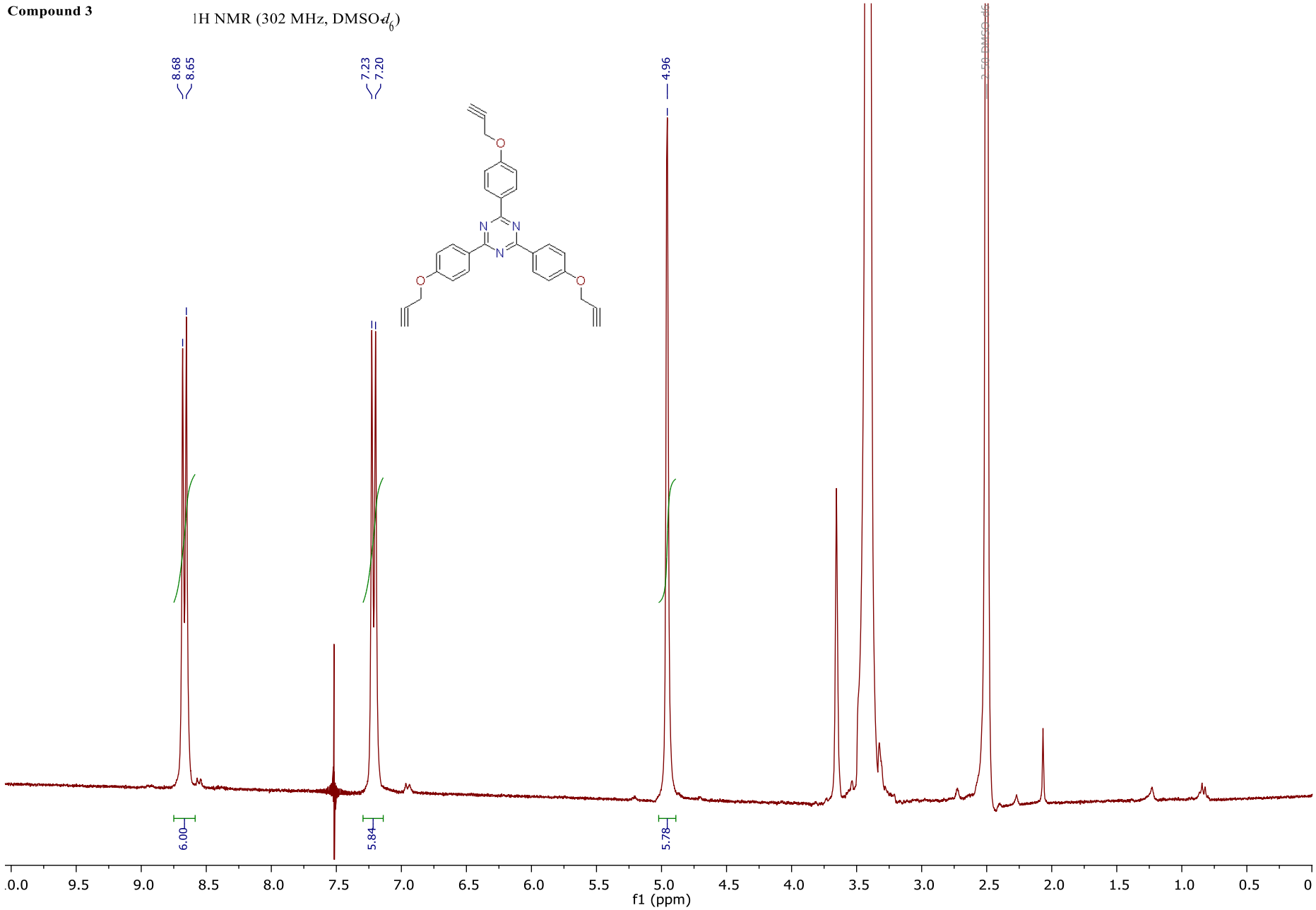
Copies of NMR spectra

Compound 2



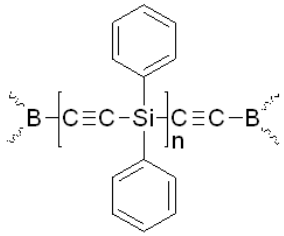
Compound 3

^{1}H NMR (302 MHz, DMSO-d_6)



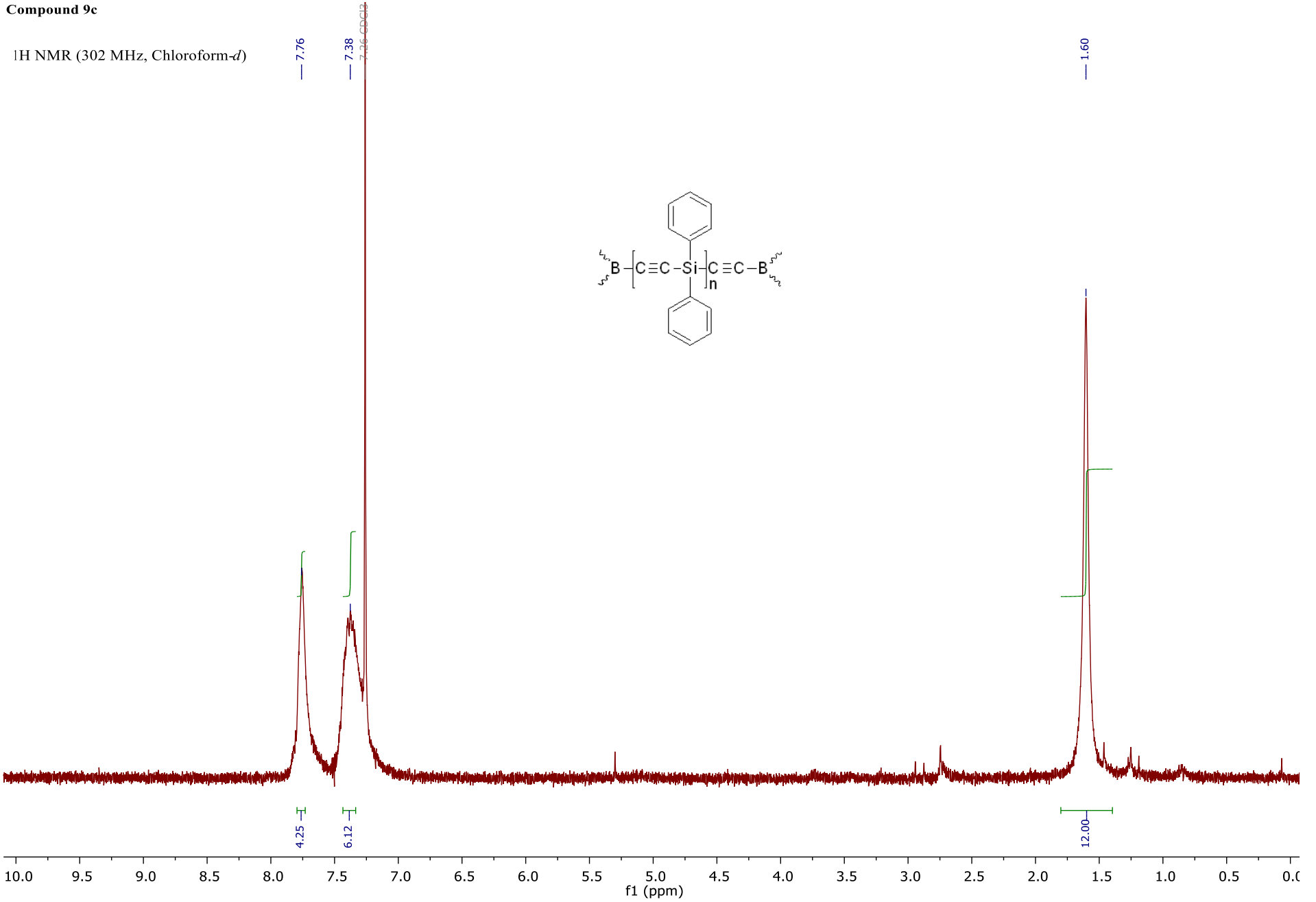
Compound 9c

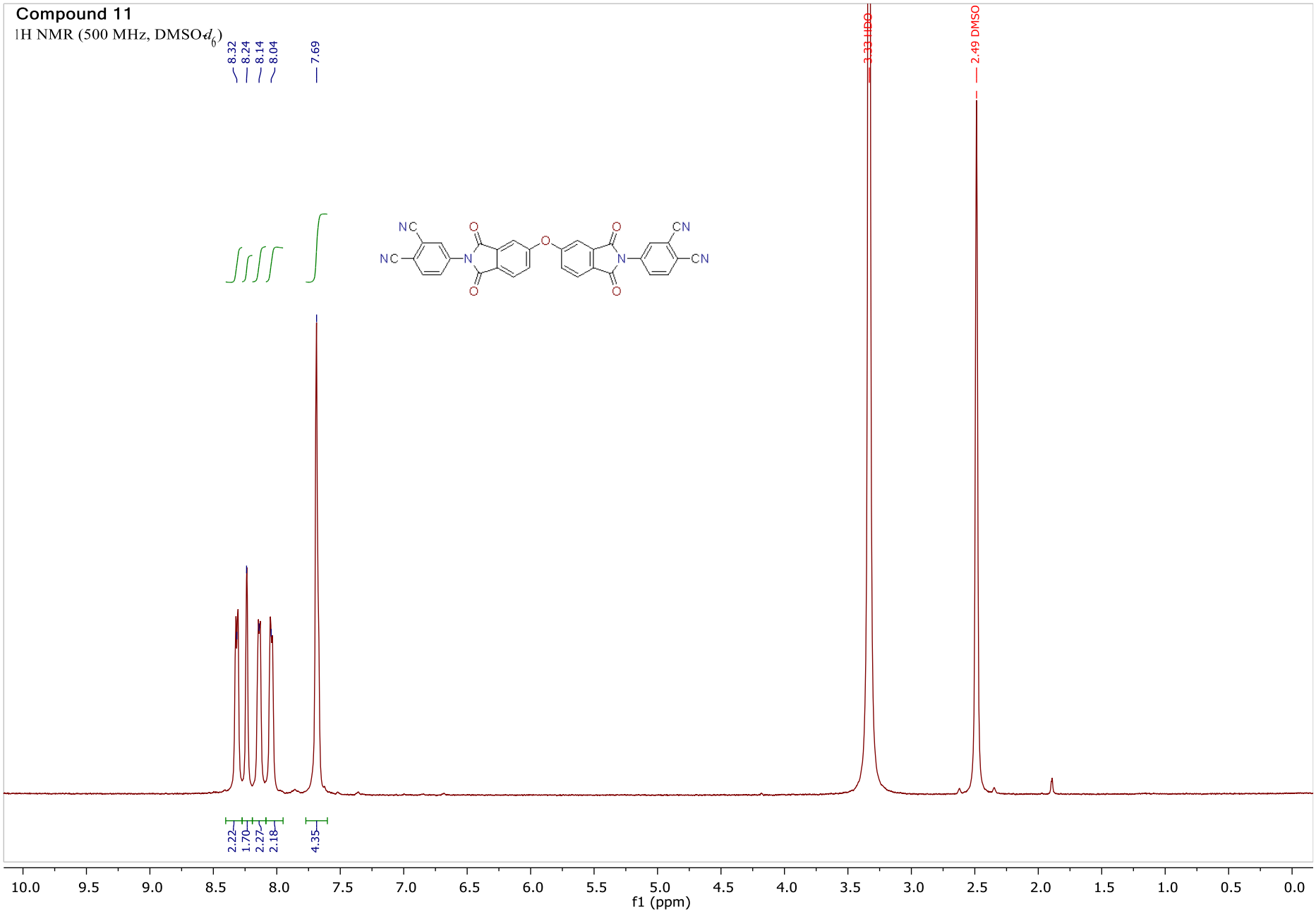
^{1}H NMR (302 MHz, DMSO-d_6)



Compound 9c

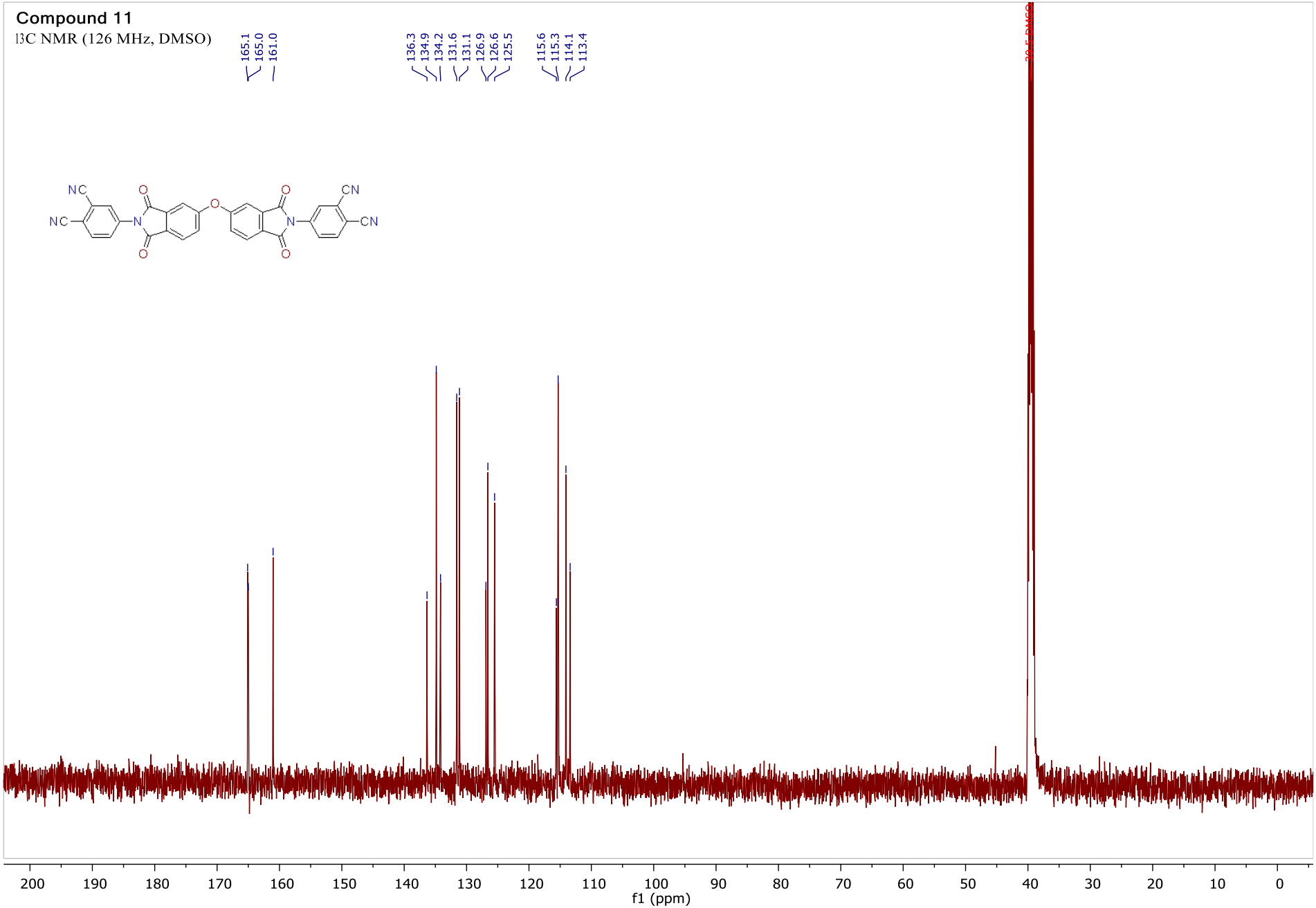
1H NMR (302 MHz, Chloroform-*d*)




Compound 11
1H NMR (500 MHz, DMSO-d_6)
8.32
8.24
8.14
8.04
7.69
3.33 HDO
2.49 DMSO
NC
NC
CN
CN
2.22
1.70
2.27
2.18
4.35
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)

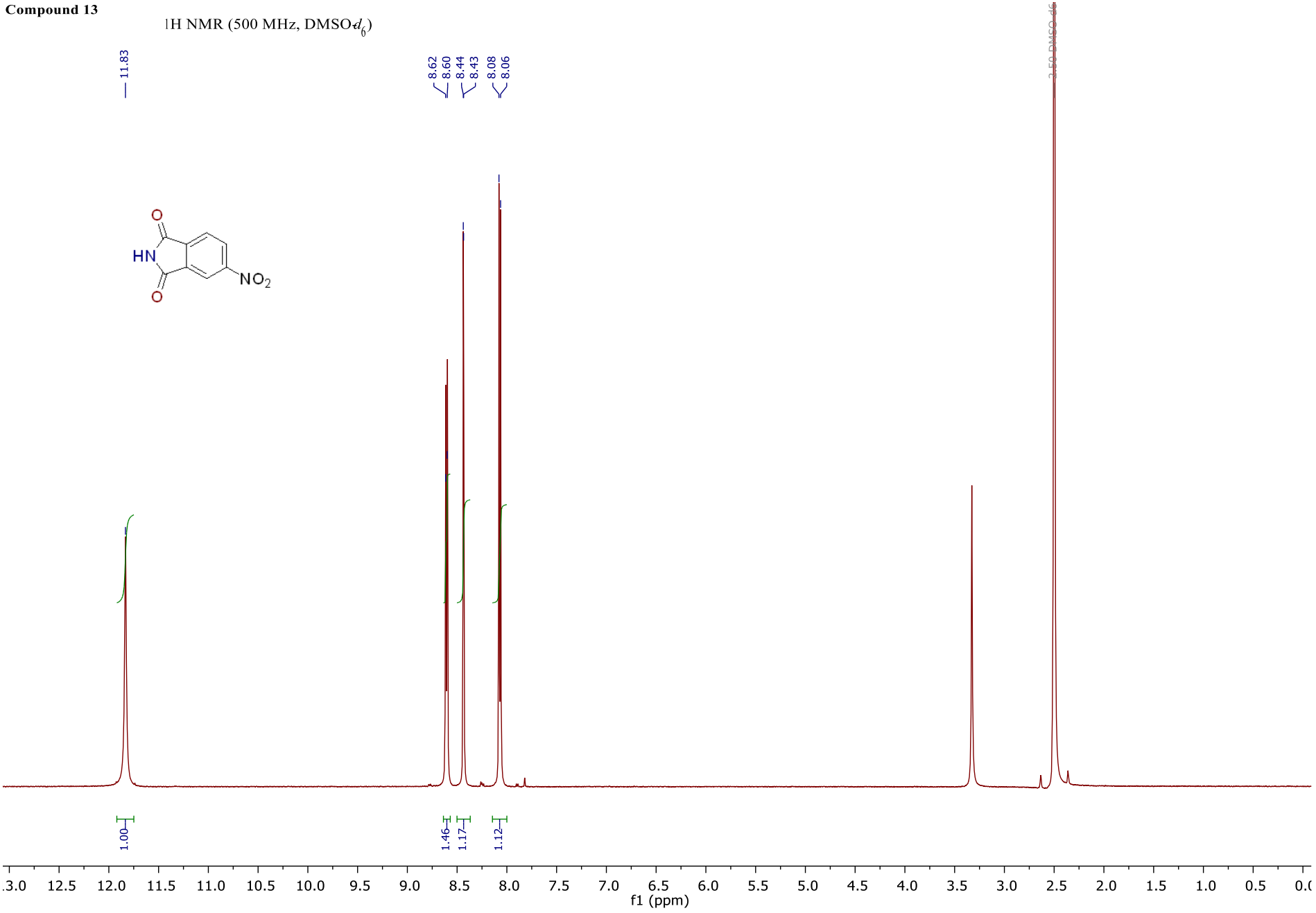
Compound 11

13C NMR (126 MHz, DMSO)



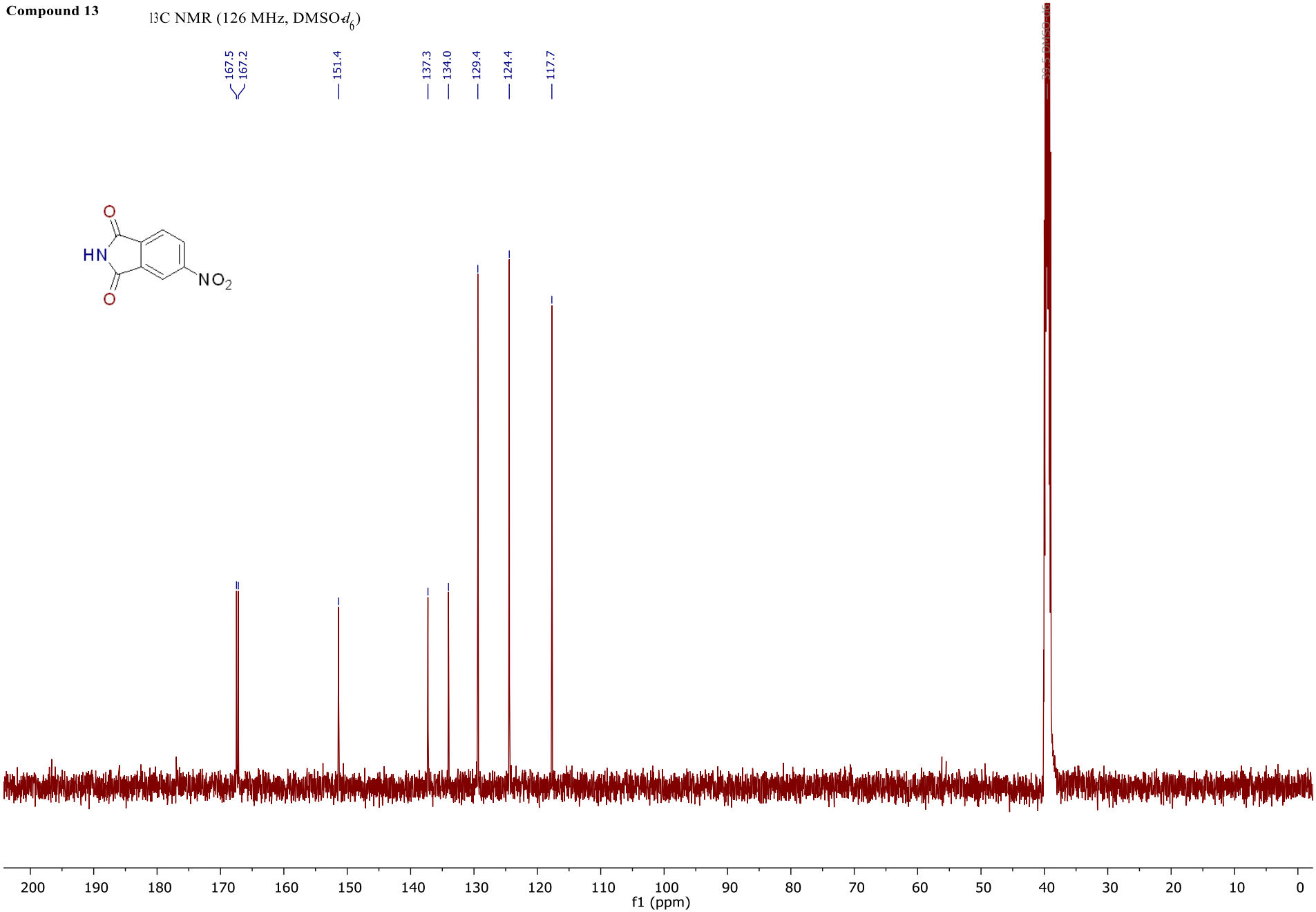
Compound 13

^{1}H NMR (500 MHz, DMSO-d_6)

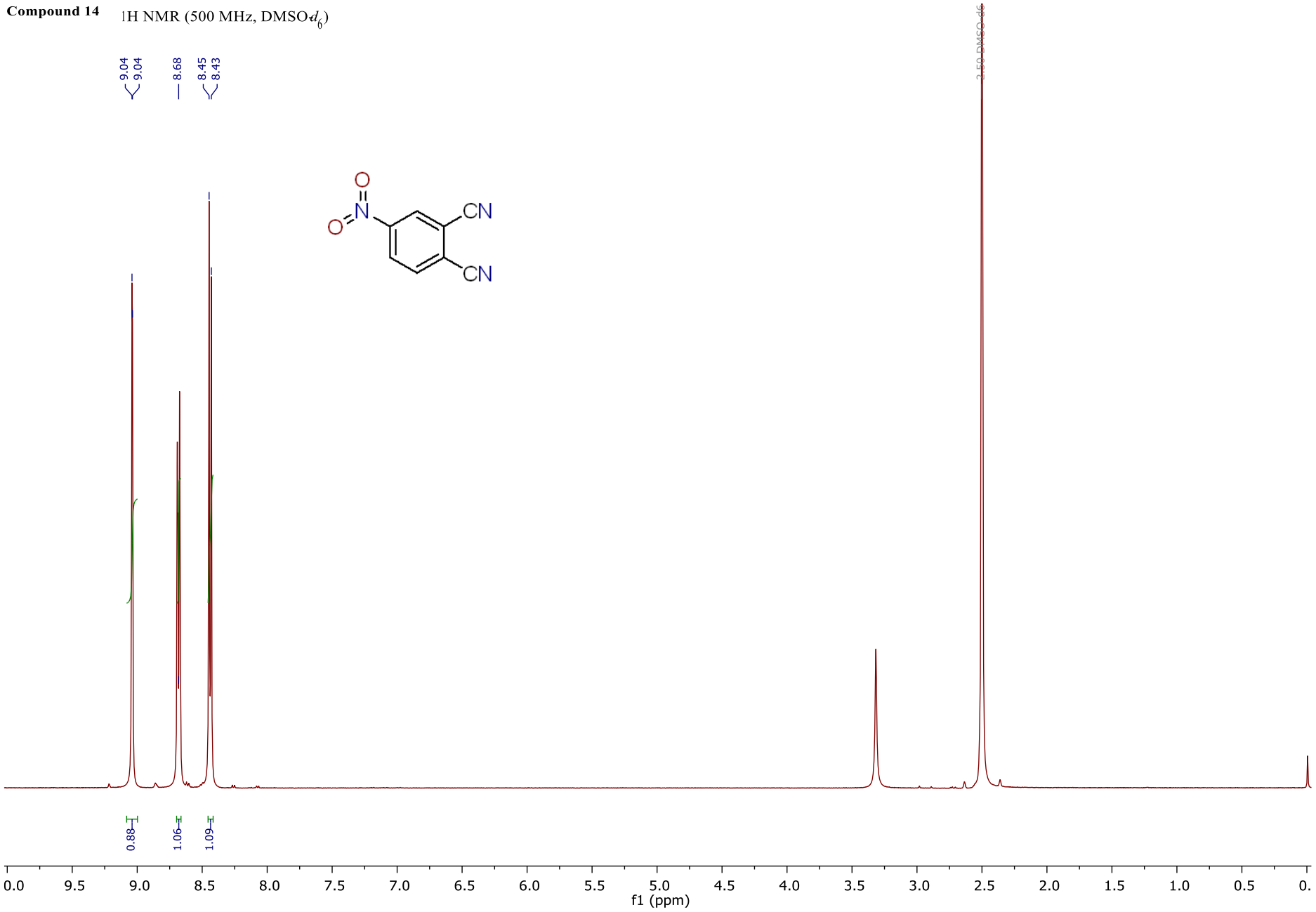


Compound 13

^{13}C NMR (126 MHz, DMSO-d_6)

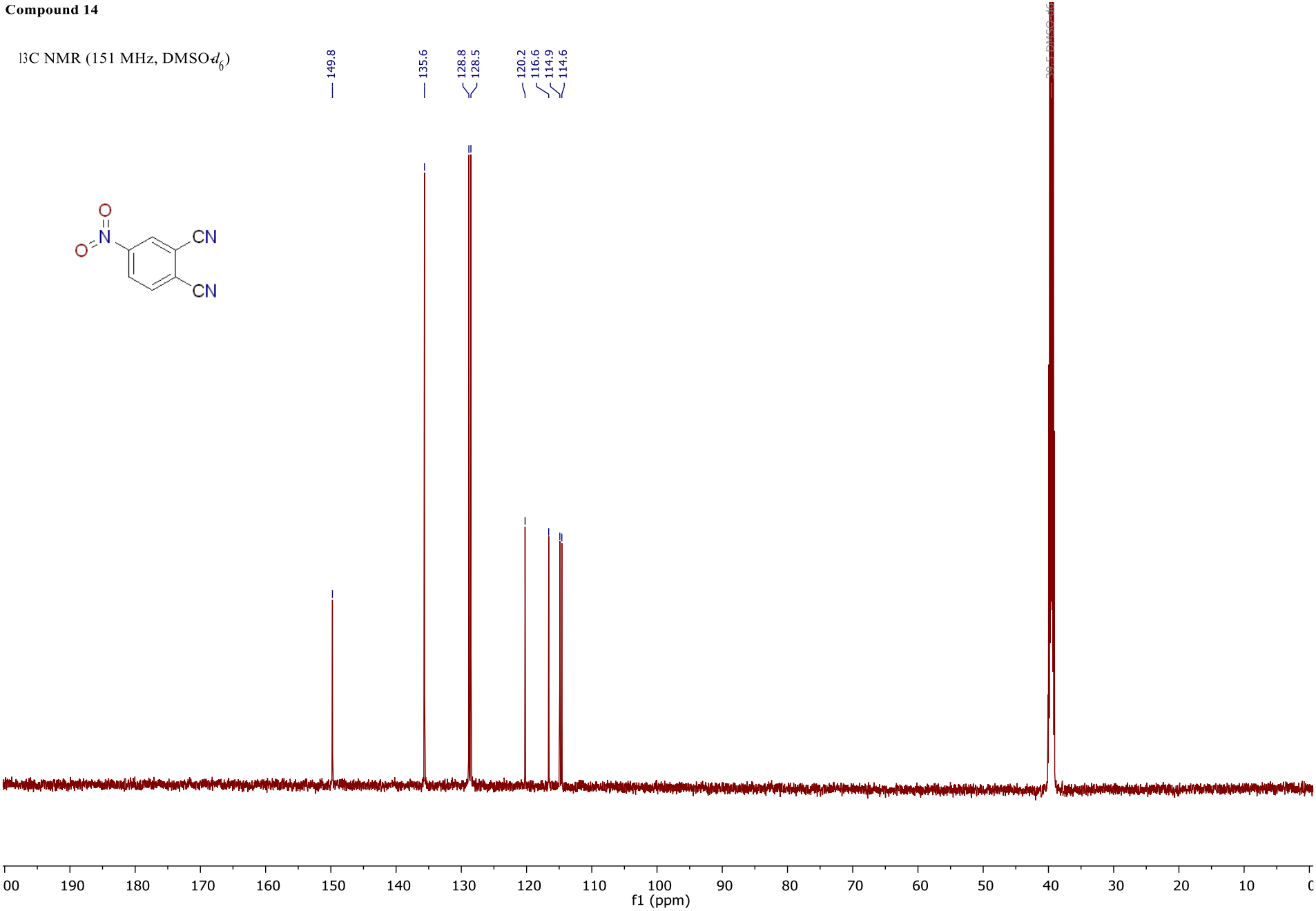


Compound 14 ^{1}H NMR (500 MHz, DMSOd_6)



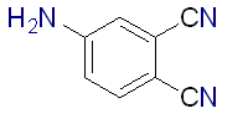
Compound 14

^{13}C NMR (151 MHz, DMSO-d_6)



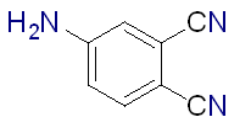
Compound 15

^{1}H NMR (500 MHz, DMSO-d_6)



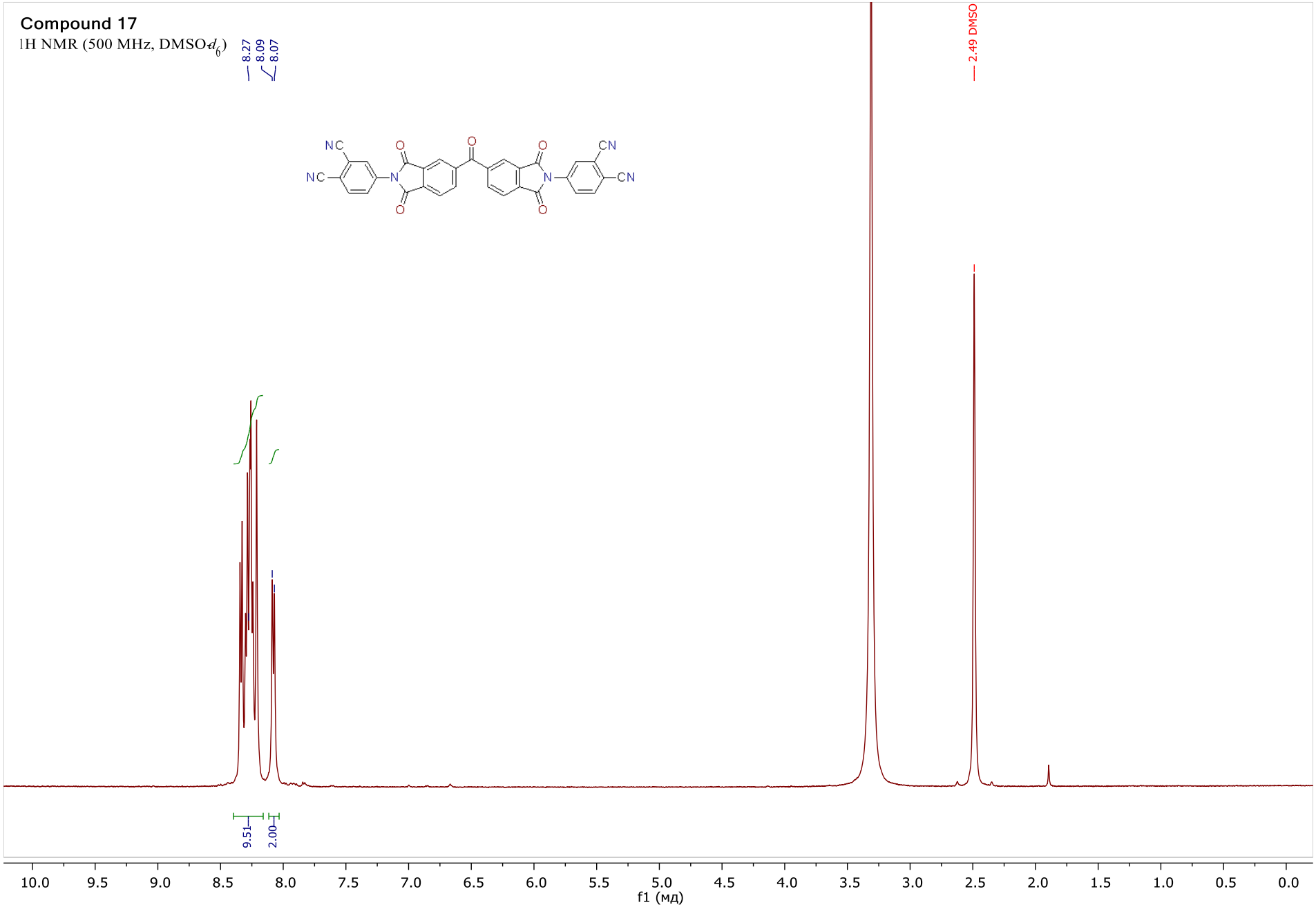
Compound 15

^{13}C NMR (126 MHz, DMSO-d_6)



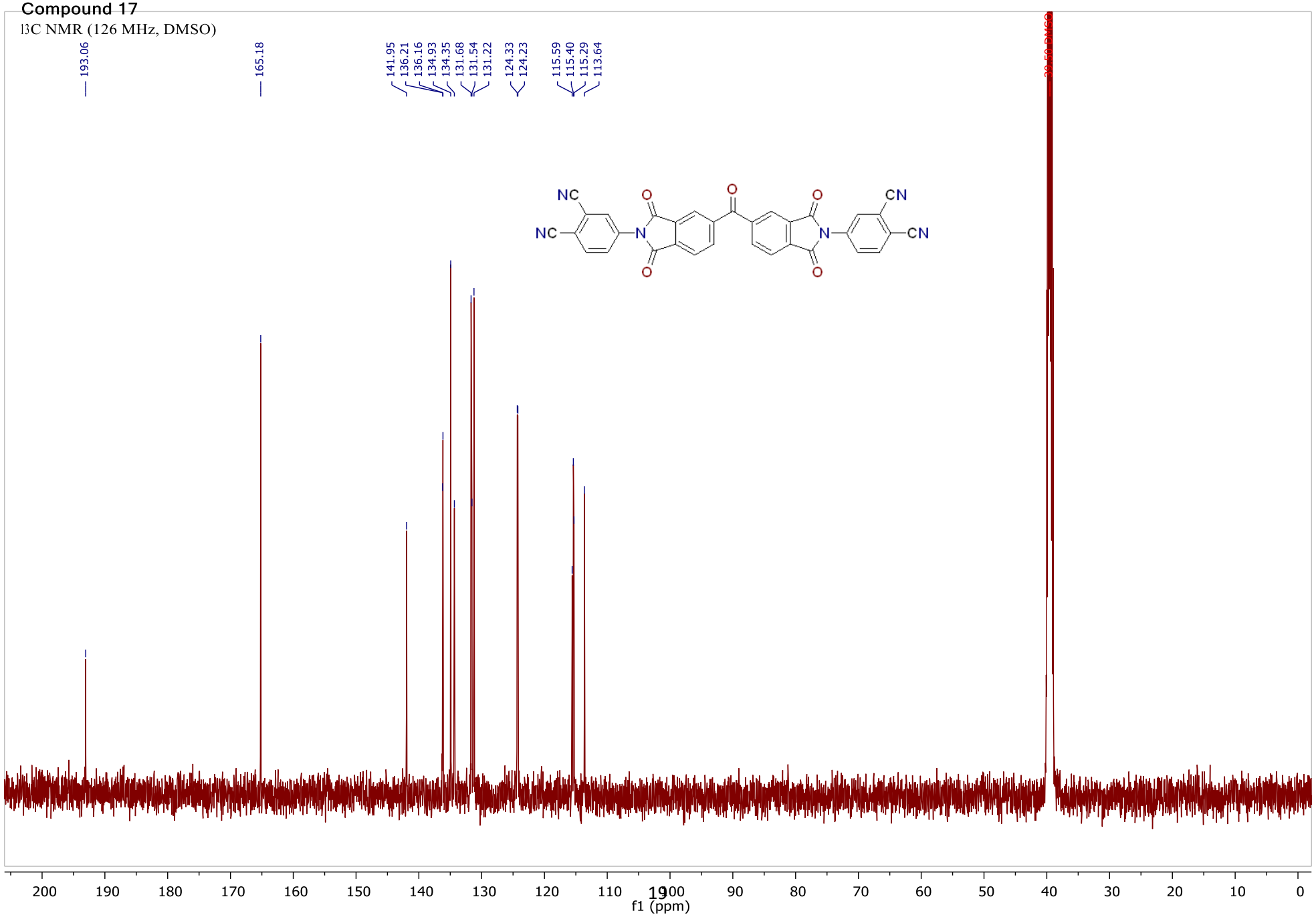
Compound 17

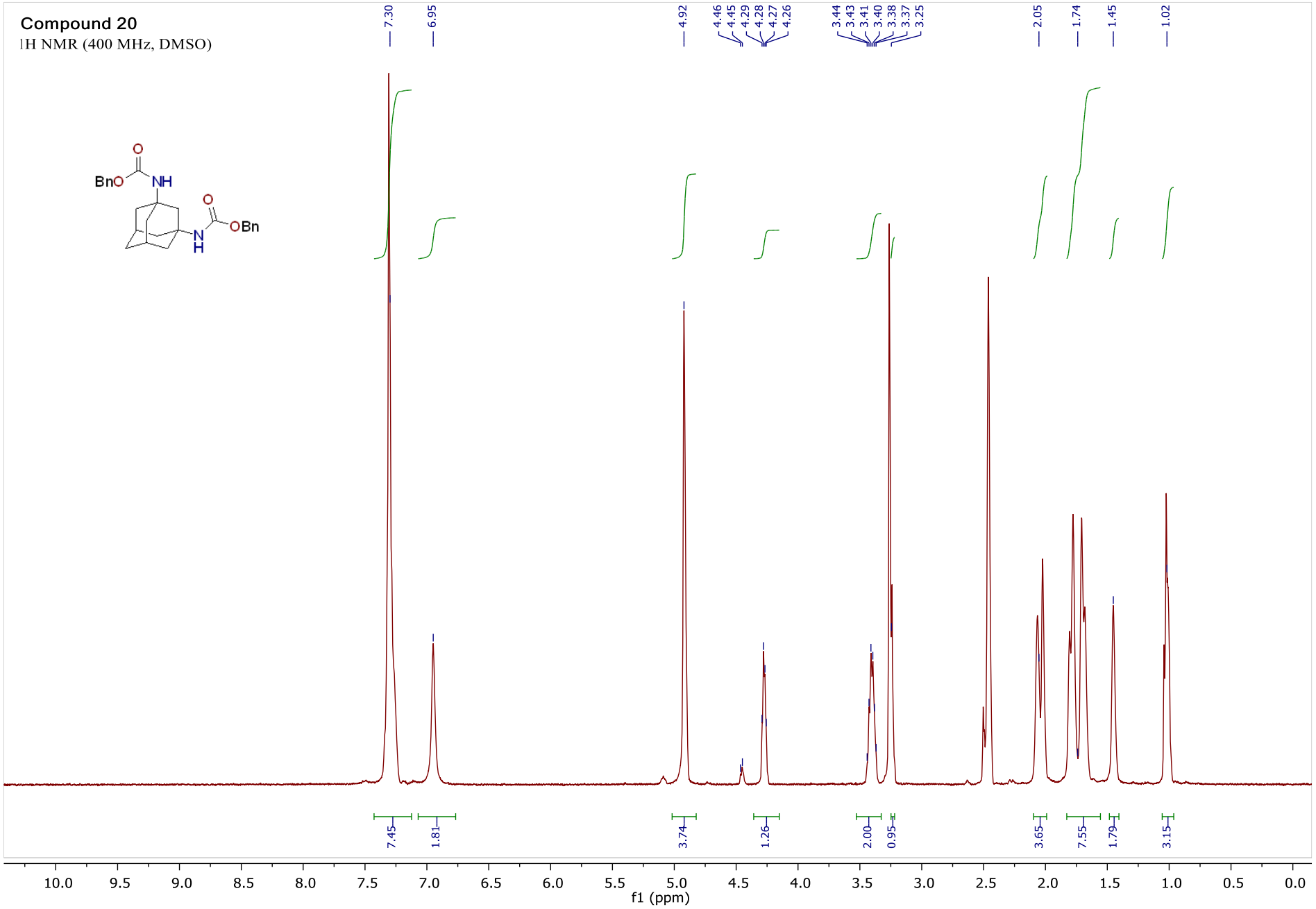
^{1}H NMR (500 MHz, DMSO-d_6)

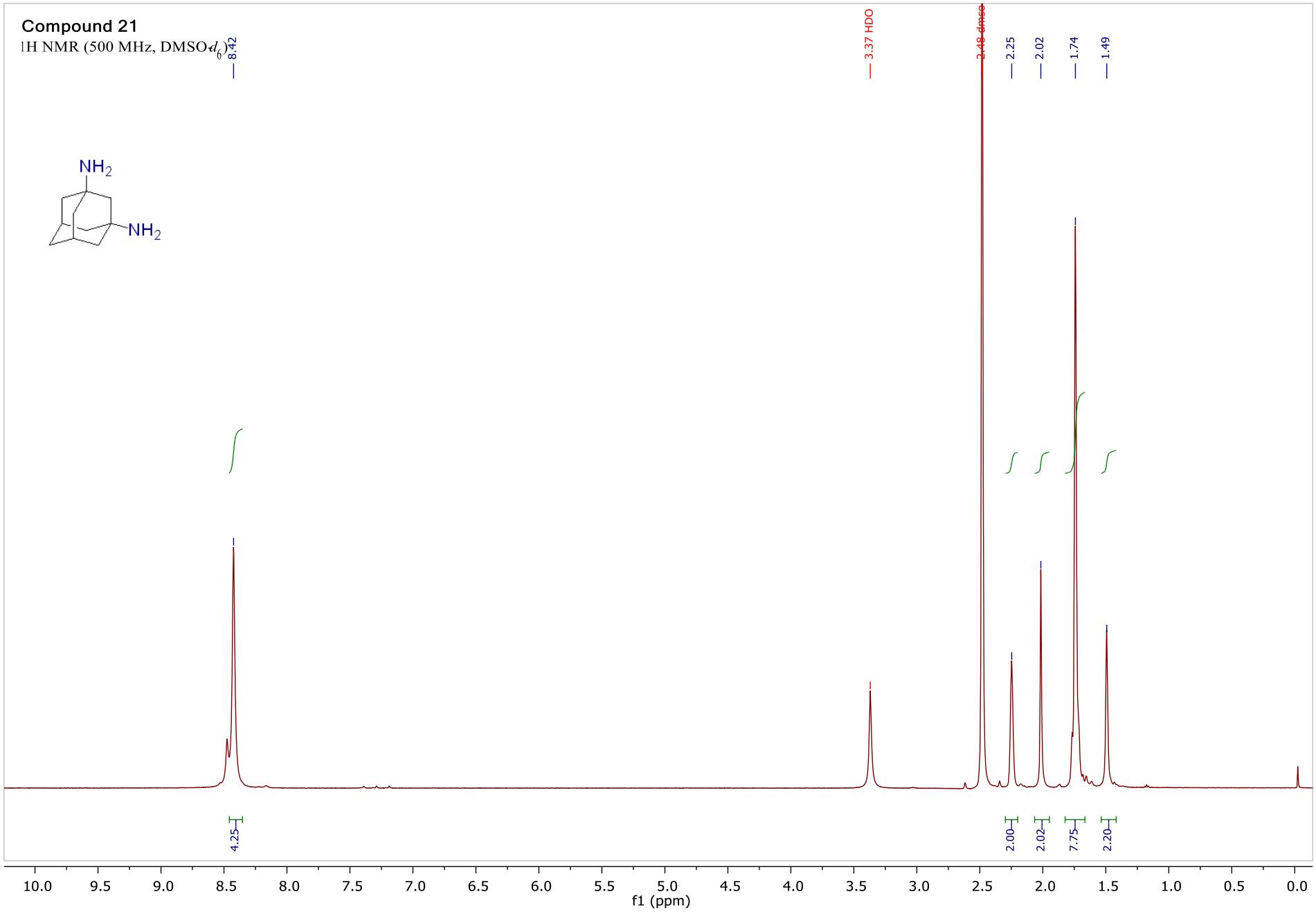


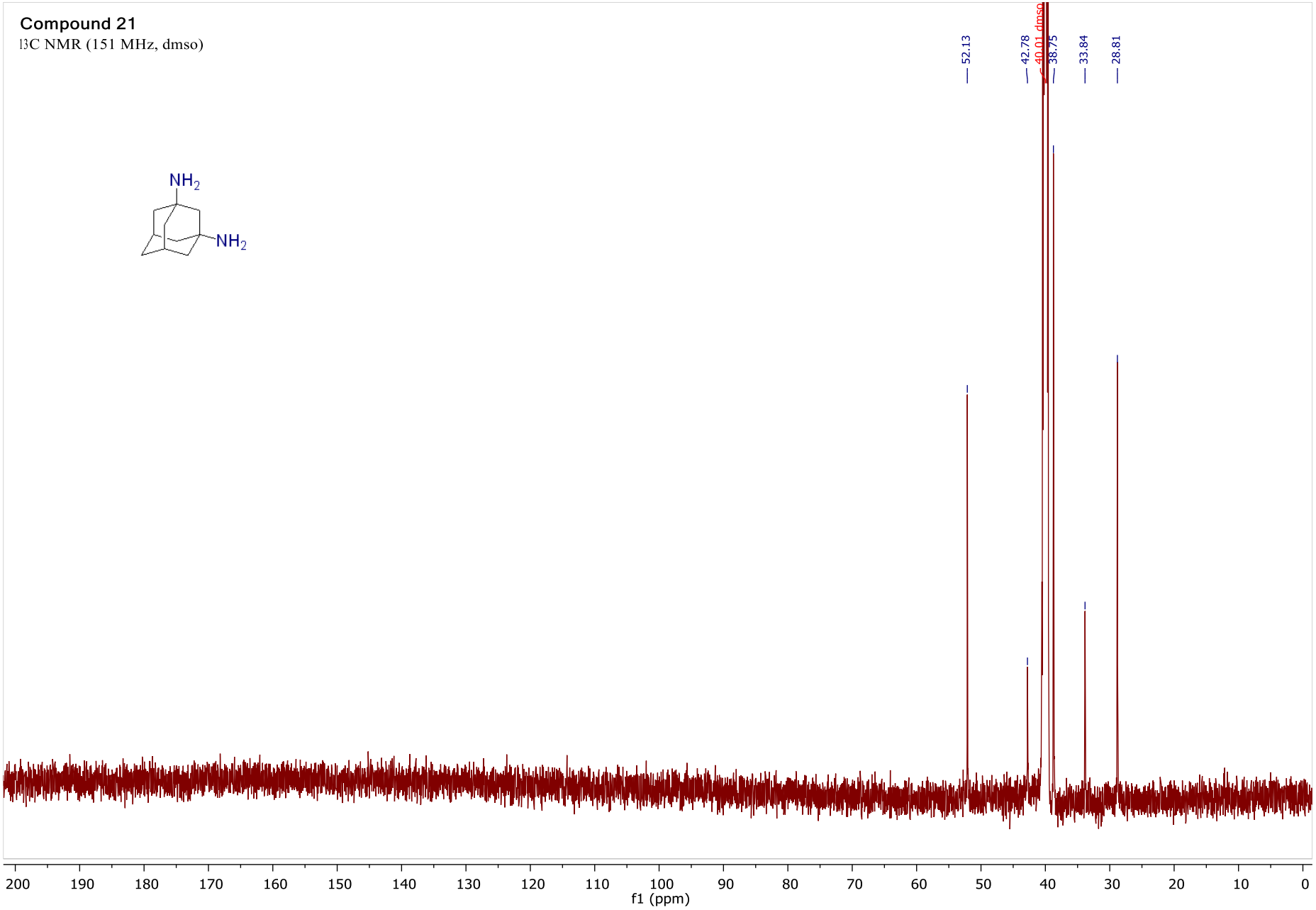
Compound 17

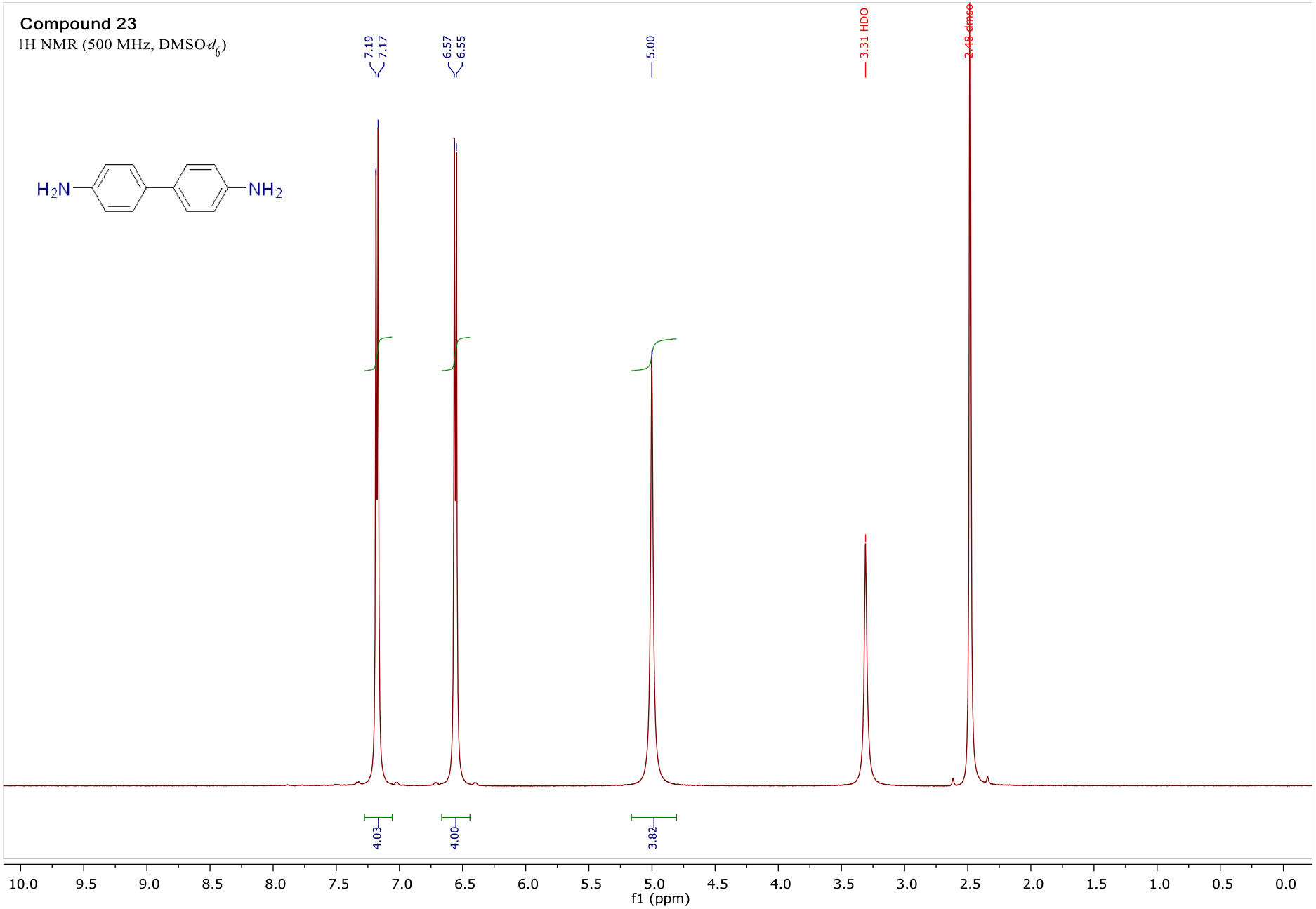
13C NMR (126 MHz, DMSO)

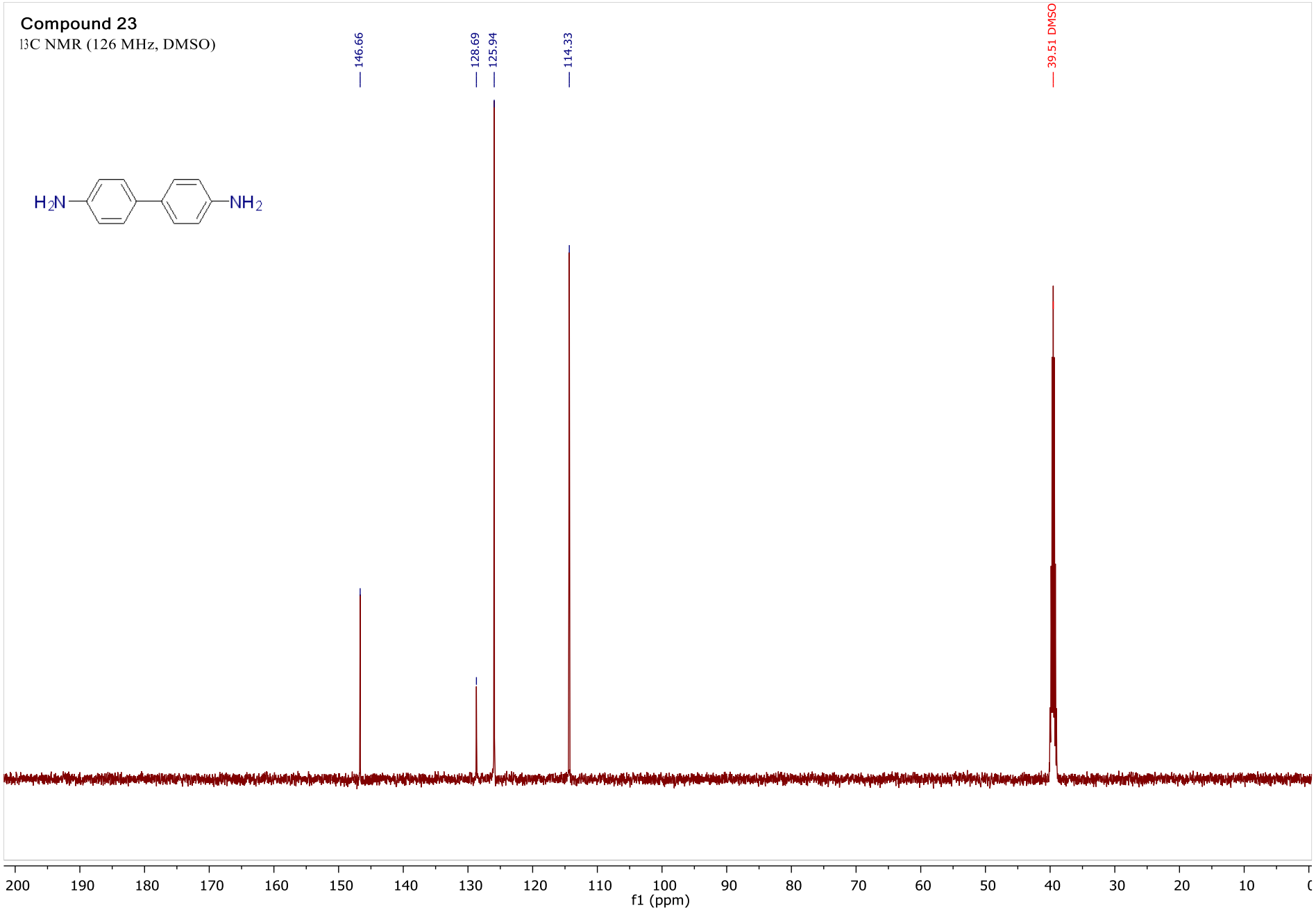


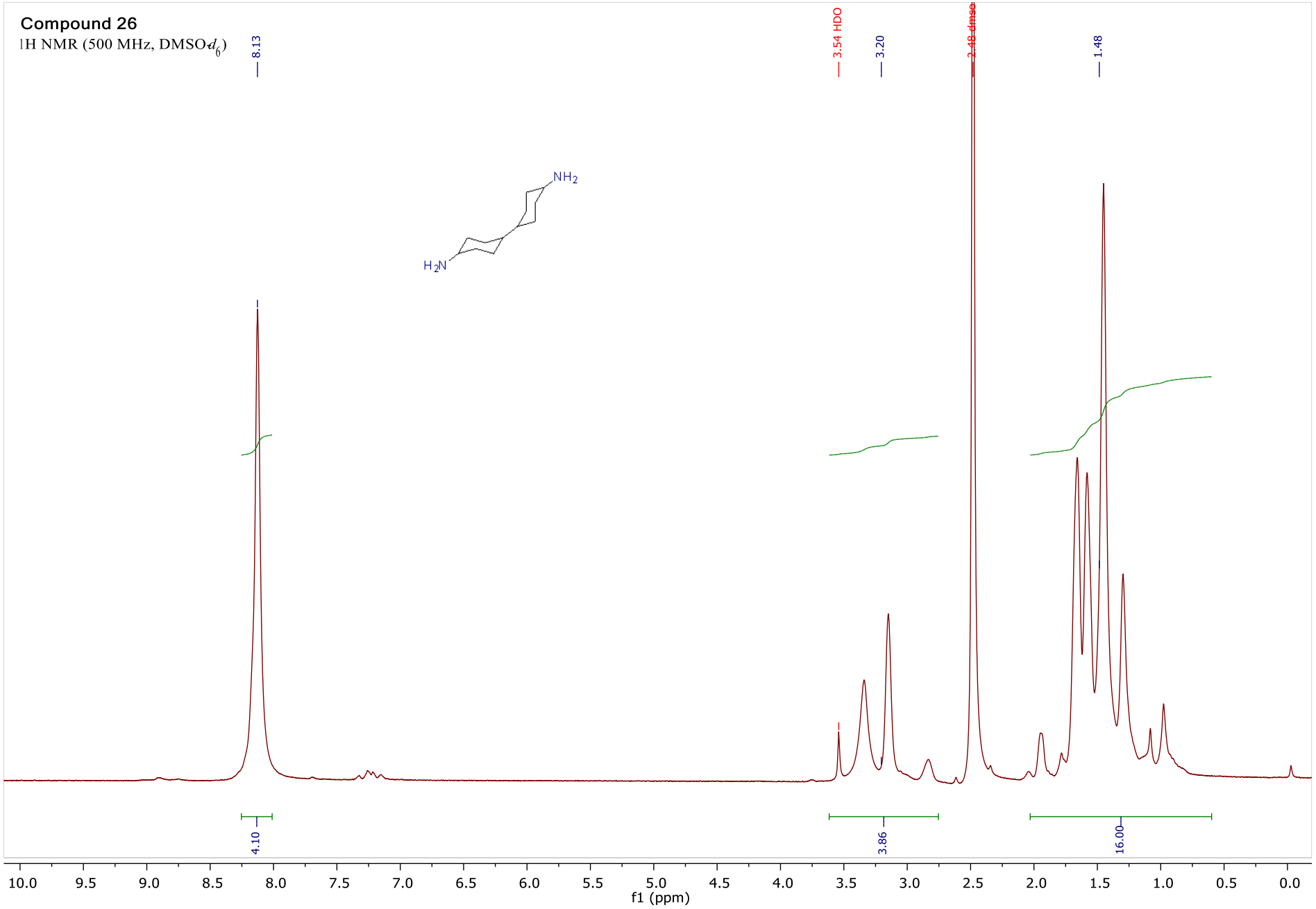

Compound 20
1H NMR (400 MHz, DMSO)
7.30
6.95
4.92
4.46
4.45
4.29
4.28
4.27
4.26
3.44
3.43
3.41
3.40
3.38
3.37
3.25
2.05
1.74
1.45
1.02
BnO
NH
O
N
H
OBn
7.45
1.81
3.74
1.26
2.00
0.95
3.65
7.55
1.79
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

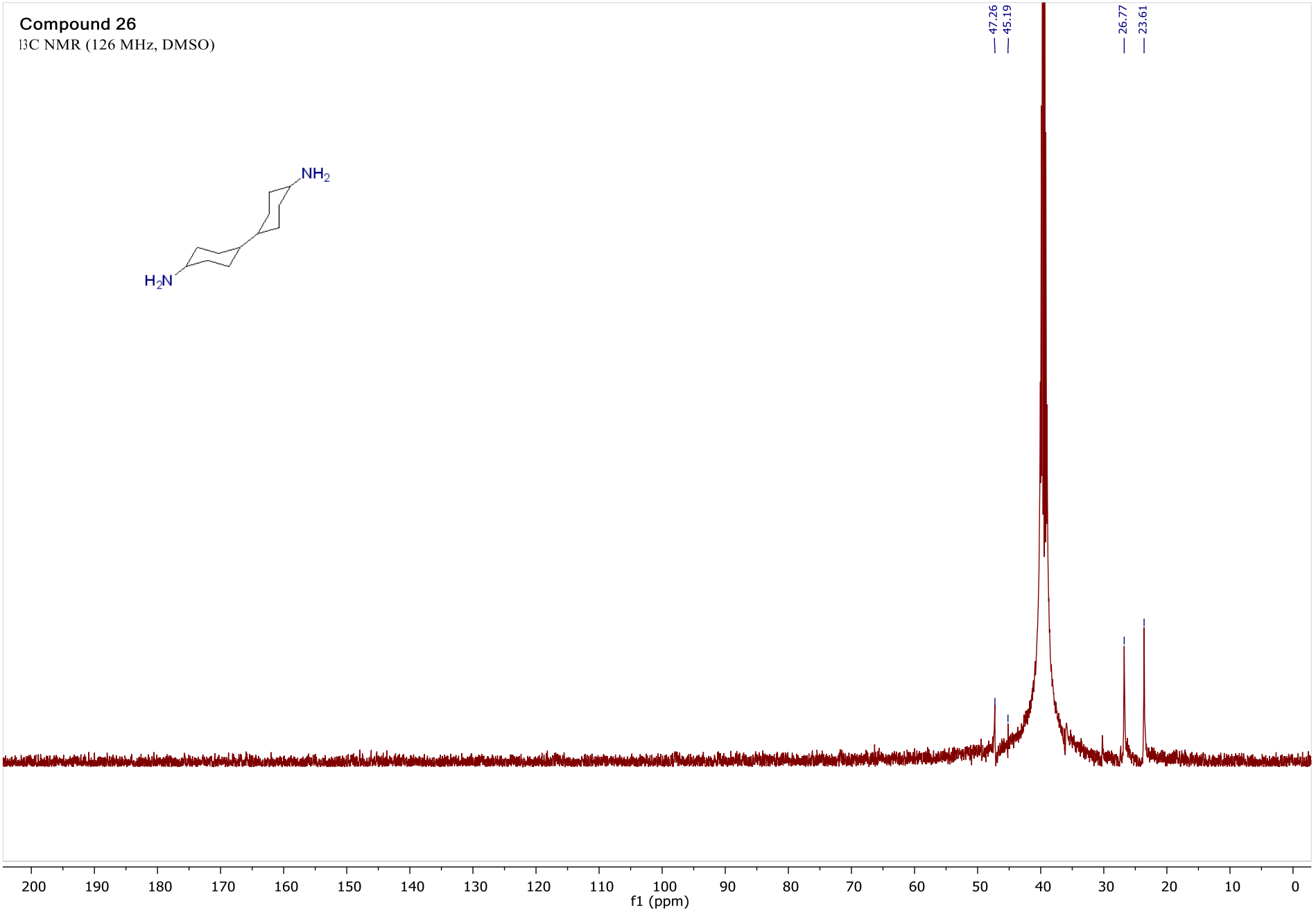

Compound 21
1H NMR (500 MHz, DMSO-d_6)
8.42
3.37 HDO
2.48 dmso
2.25
2.02
1.74
1.49
NH2
NH2
4.25
2.00
2.02
7.75
2.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Compound 21
13C NMR (151 MHz, dmso)
NH2
NH2
52.13
42.78
40.01 dmso
38.75
33.84
28.81
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Compound 23
1H NMR (500 MHz, DMSO-d_6)
H_2N
NH_2
7.19
7.17
6.57
6.55
5.00
3.31 HDO
2.49 dmso
4.03
4.00
3.82
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)


Compound 23
13C NMR (126 MHz, DMSO)
146.66
128.69
125.94
114.33
39.51 DMSO
H2N
NH2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Compound 26
1H NMR (500 MHz, DMSO-d_6)
8.13
3.54 HDO
3.20
2.49 dmso
1.48
NH_2
H_2N
4.10
3.86
16.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Compound 26
13C NMR (126 MHz, DMSO)
NH2
H2N
47.26
45.19
26.77
23.61
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)