Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Synthesis and structural feature of a series of Cu(I) furan-2-thiocarboxylate complexes act as an efficient "click" catalyst for the synthesis of glycoconjugates and glycocluster

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Contents in supporting information

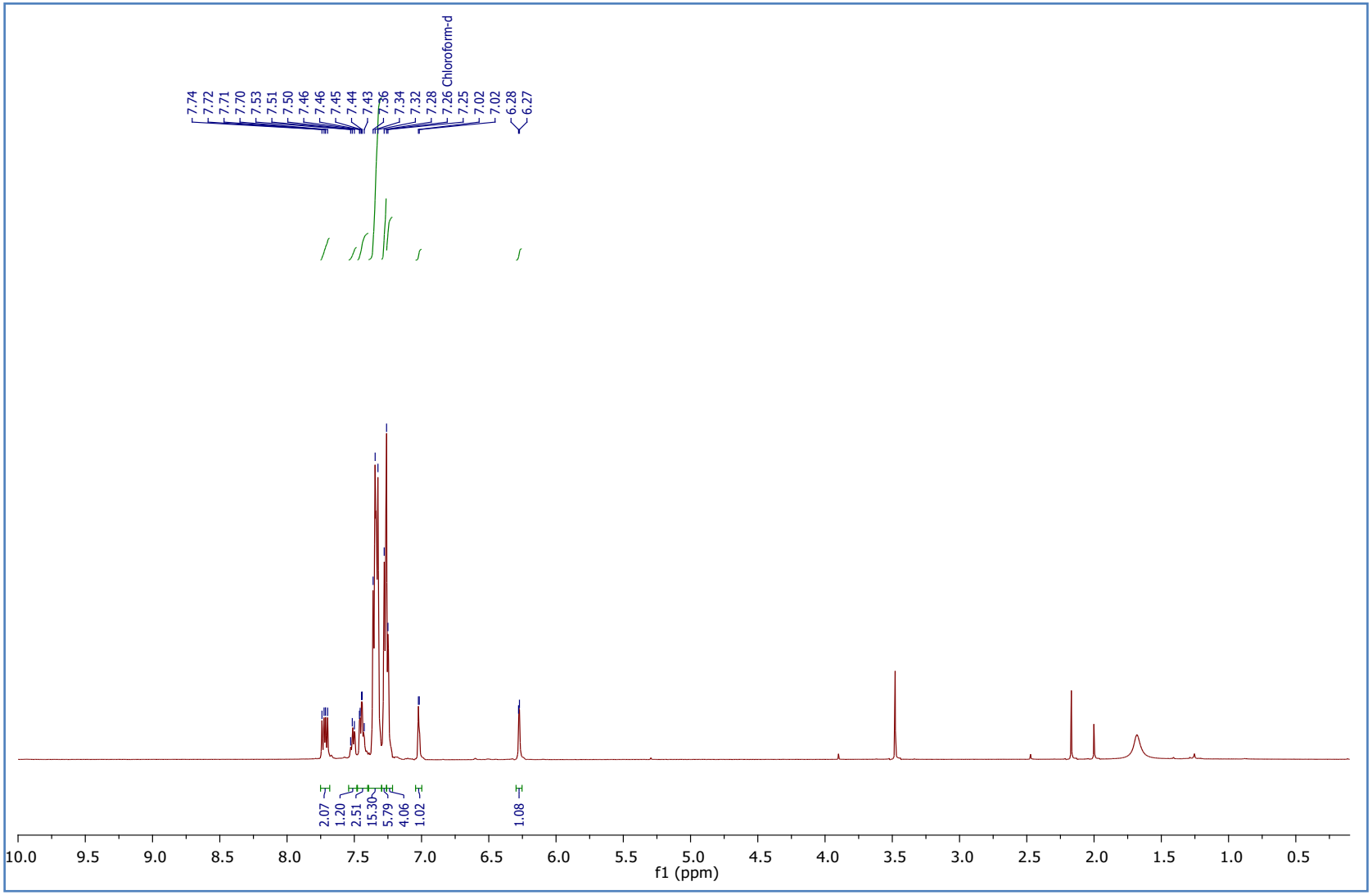


Figure SI 1(a) ^{1}HNMR spectra of complex **1**

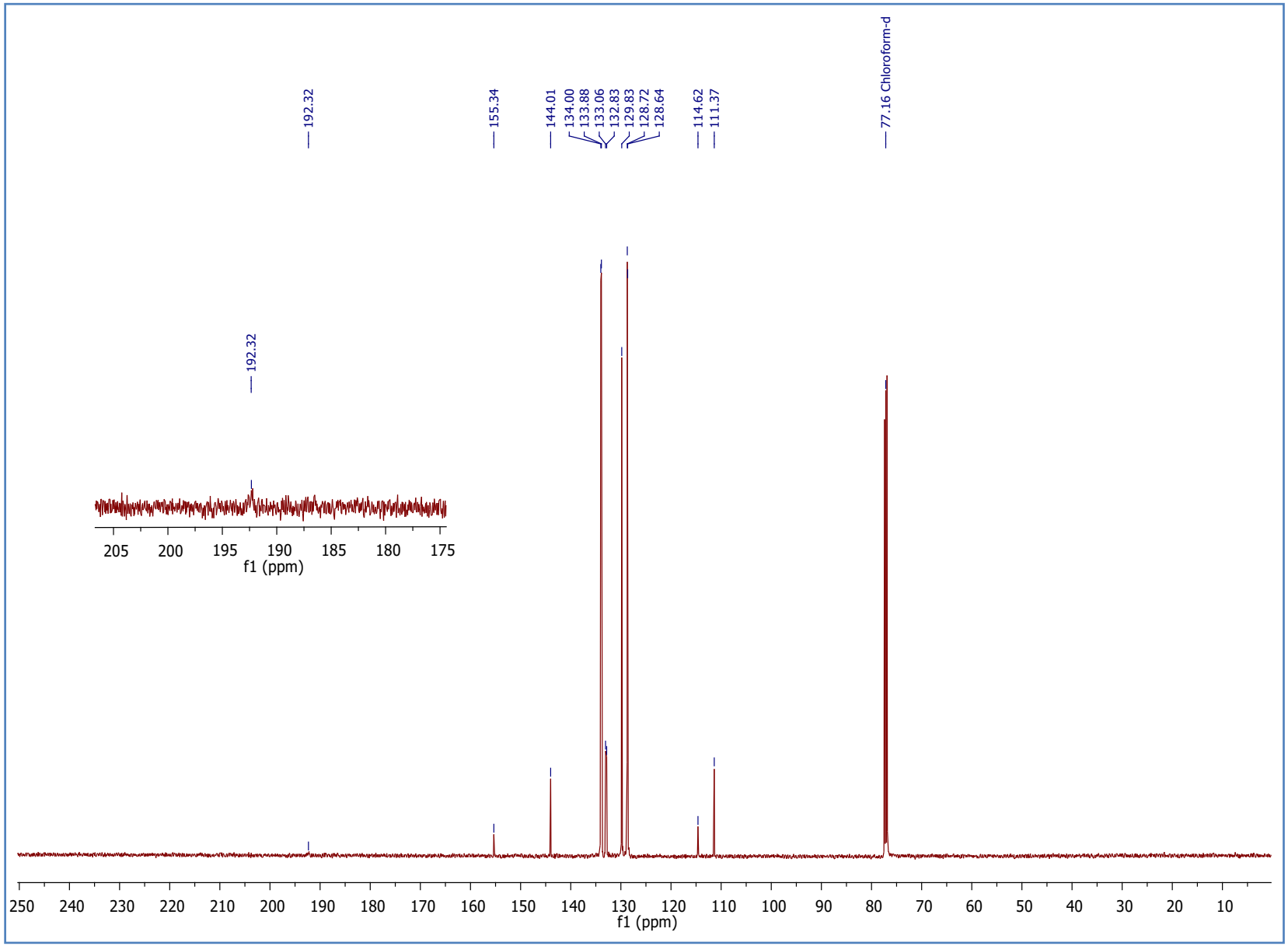


Figure SI 1(b) ^{13}CNMR spectra of complex **1**

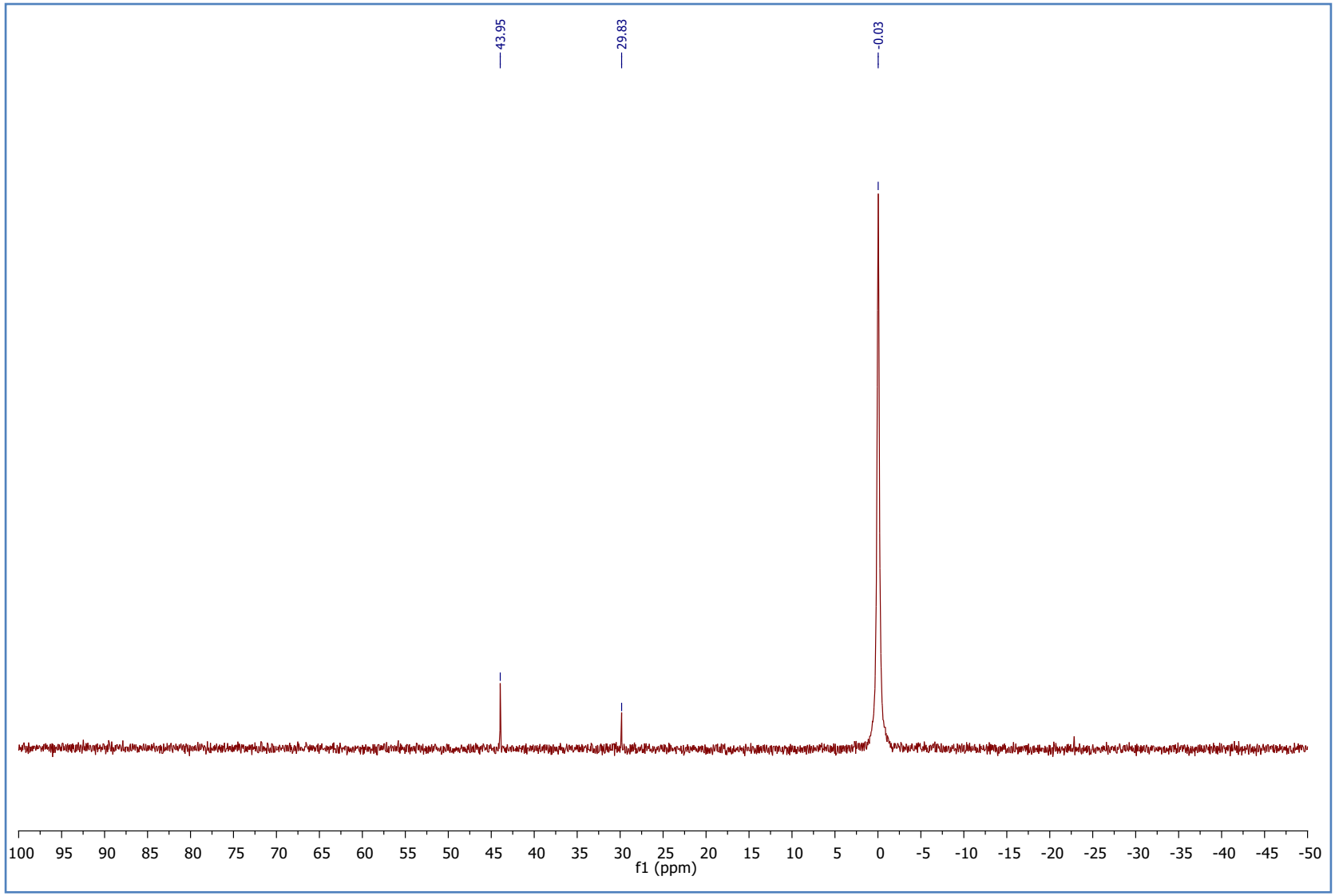


Figure SI 1(c) ^{31}P NMR spectra of complex **1**

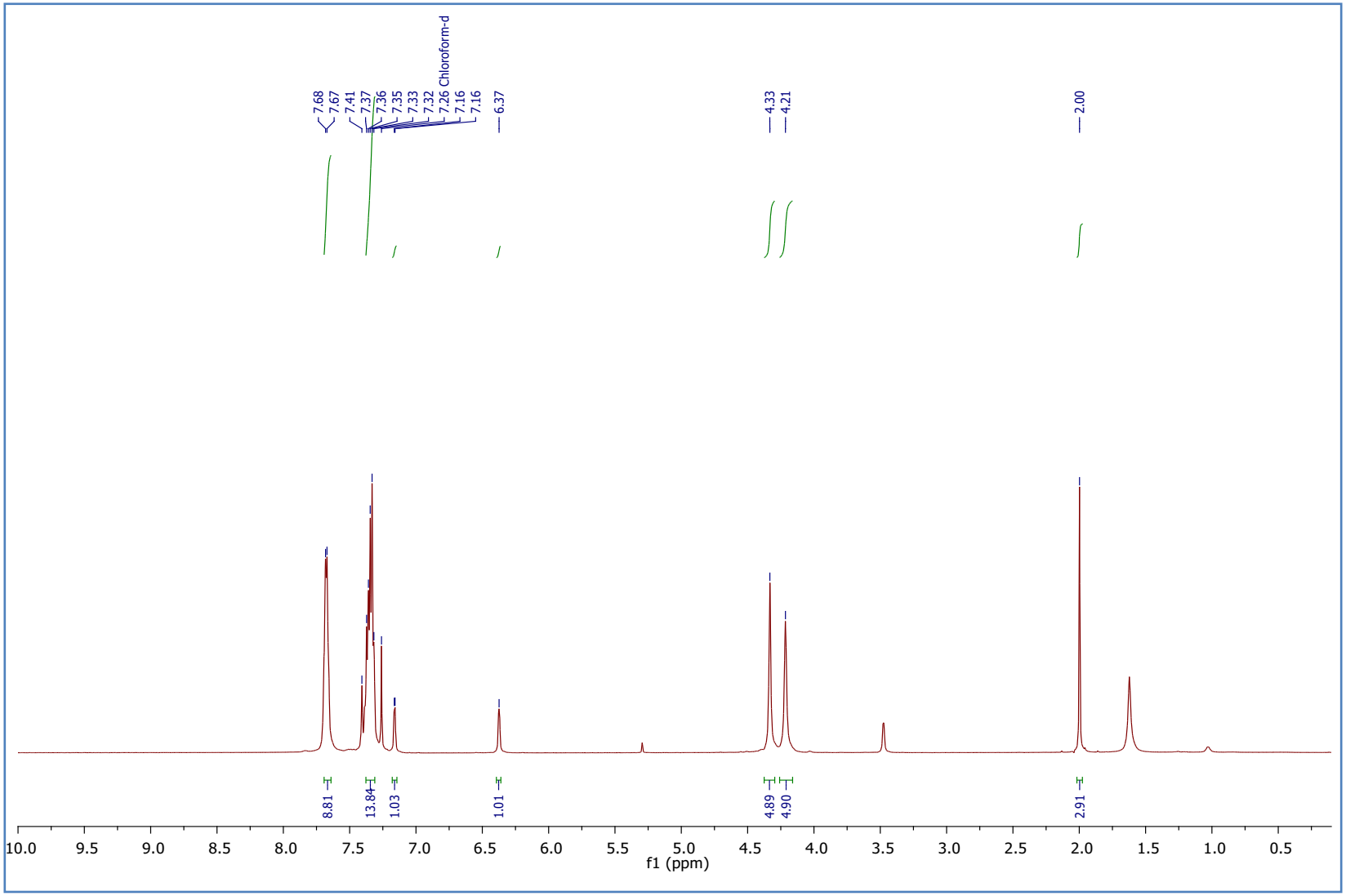


Figure SI 2(a) ^{1}HNMR spectra of complex **3**

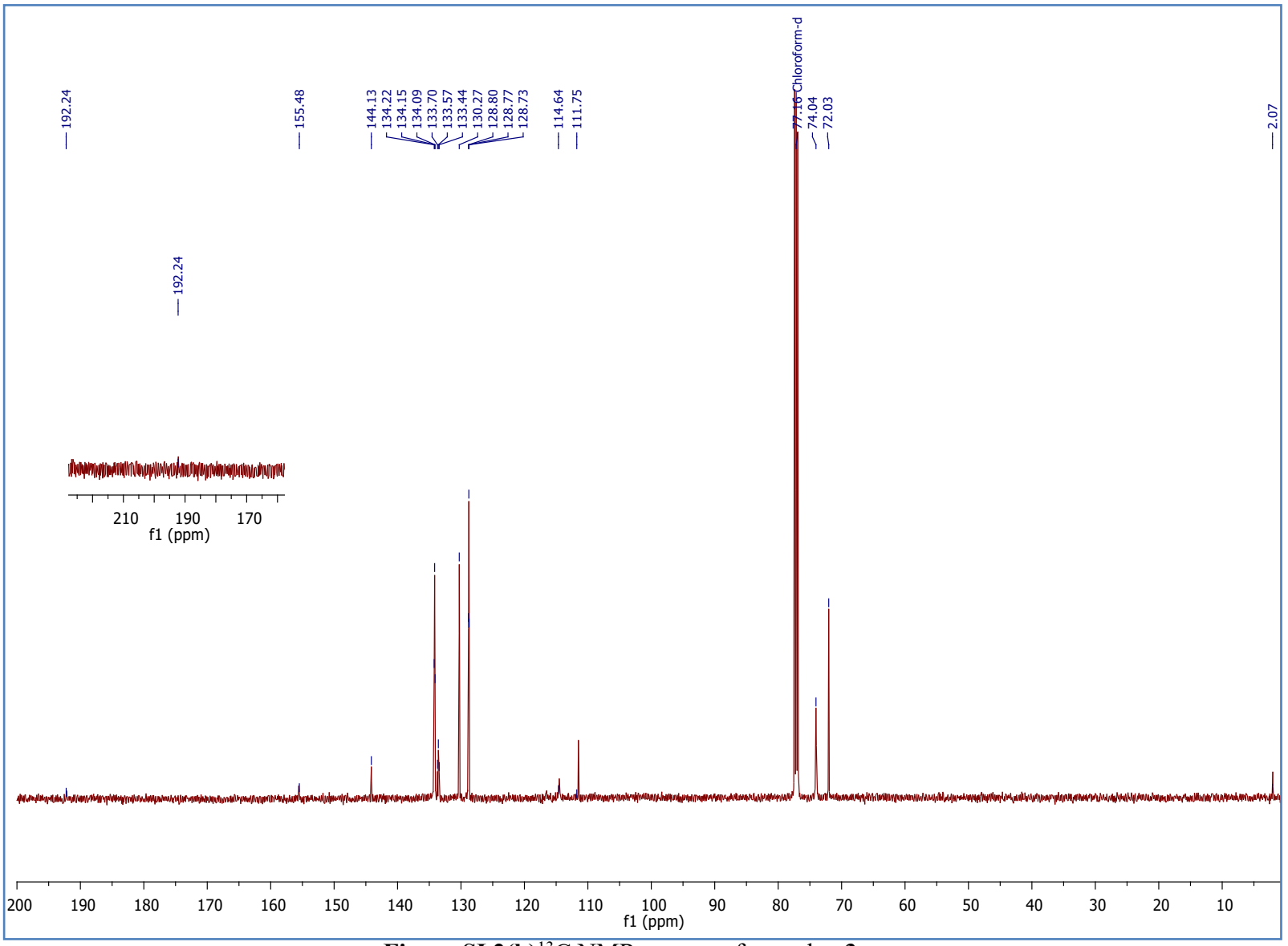


Figure SI 2(b) ^{13}C NMR spectra of complex **3**

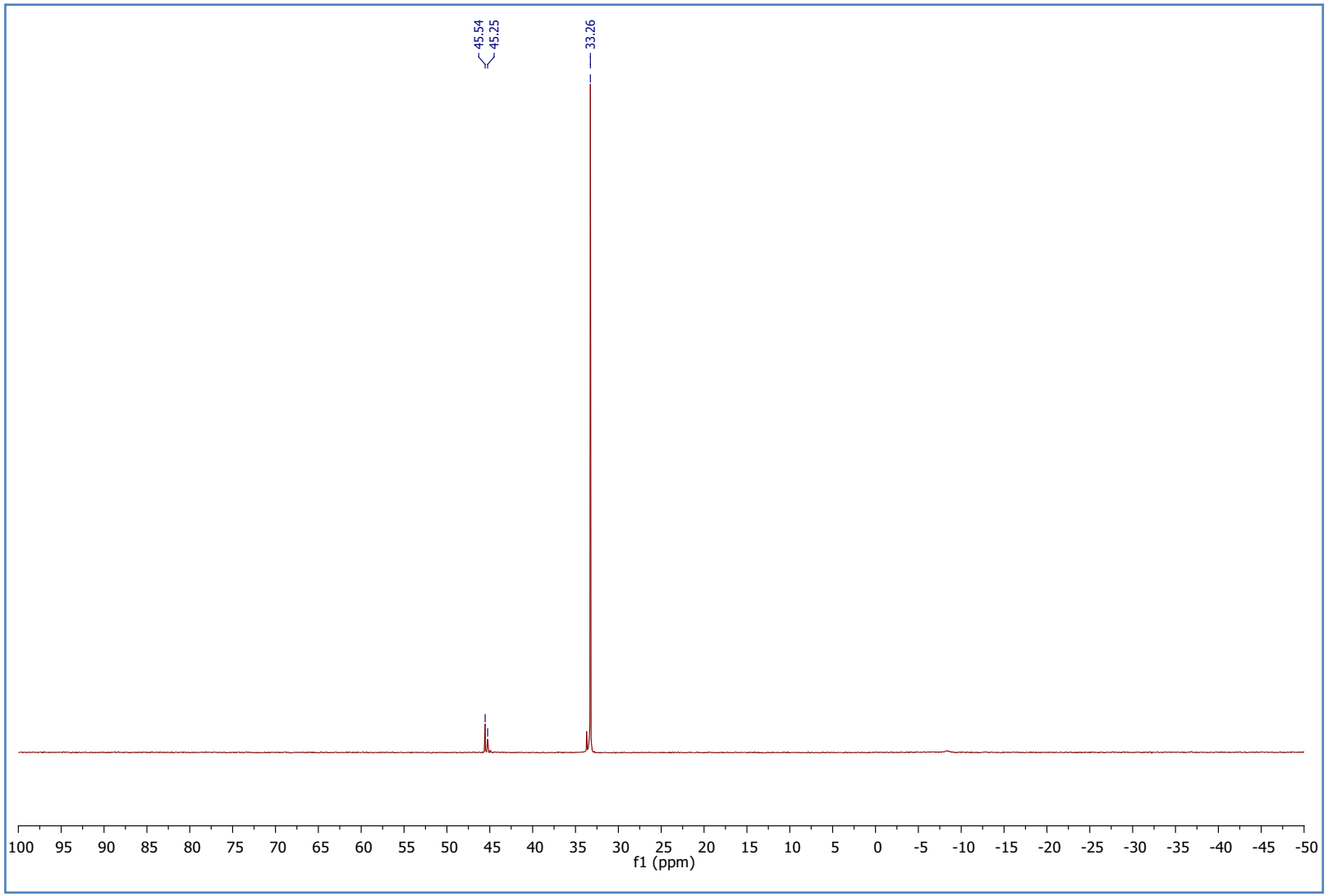


Figure SI 2(c) ^{31}P NMR spectra of complex **3**

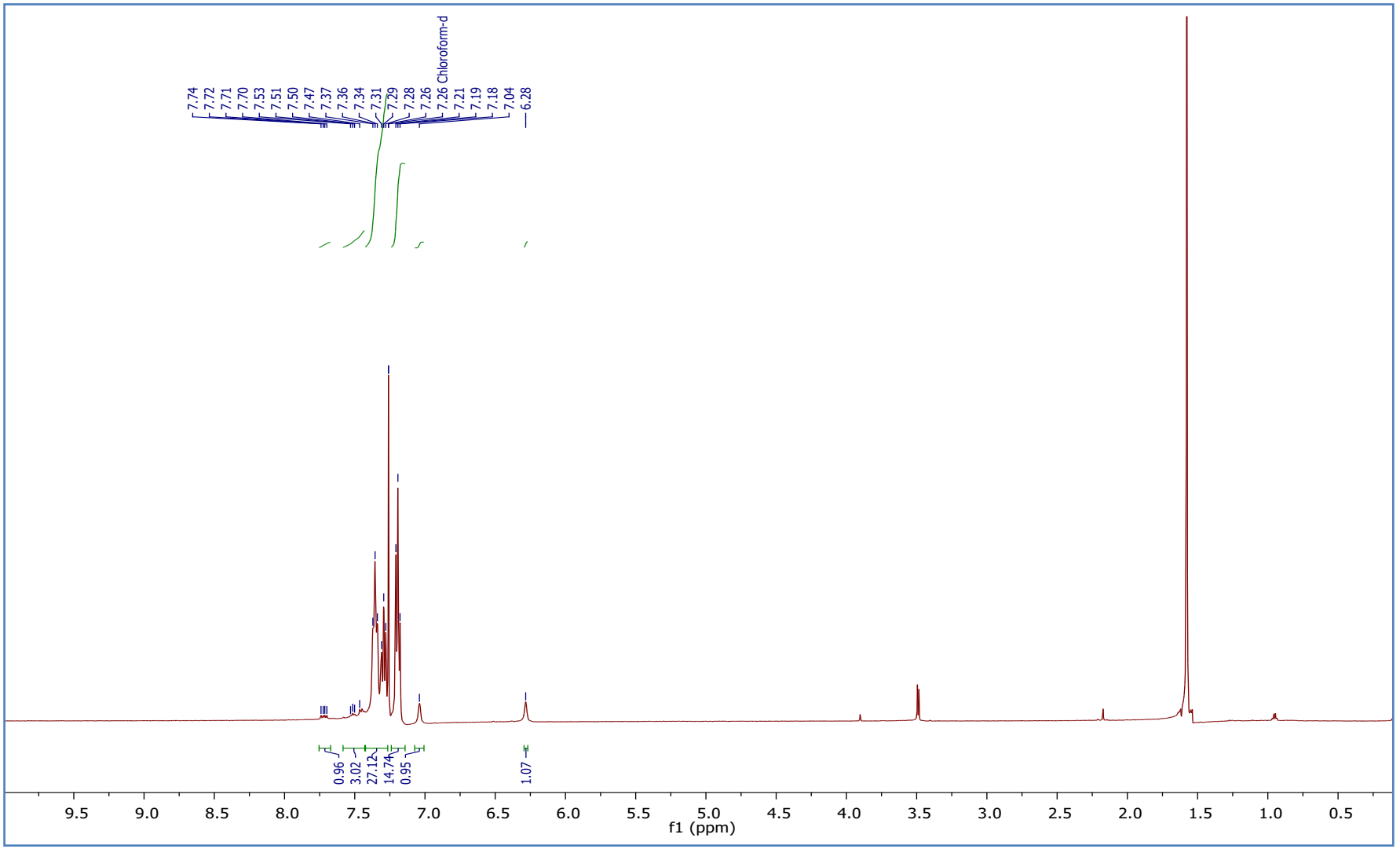


Figure SI 3(a) ^{1}H NMR spectra of complex **4**

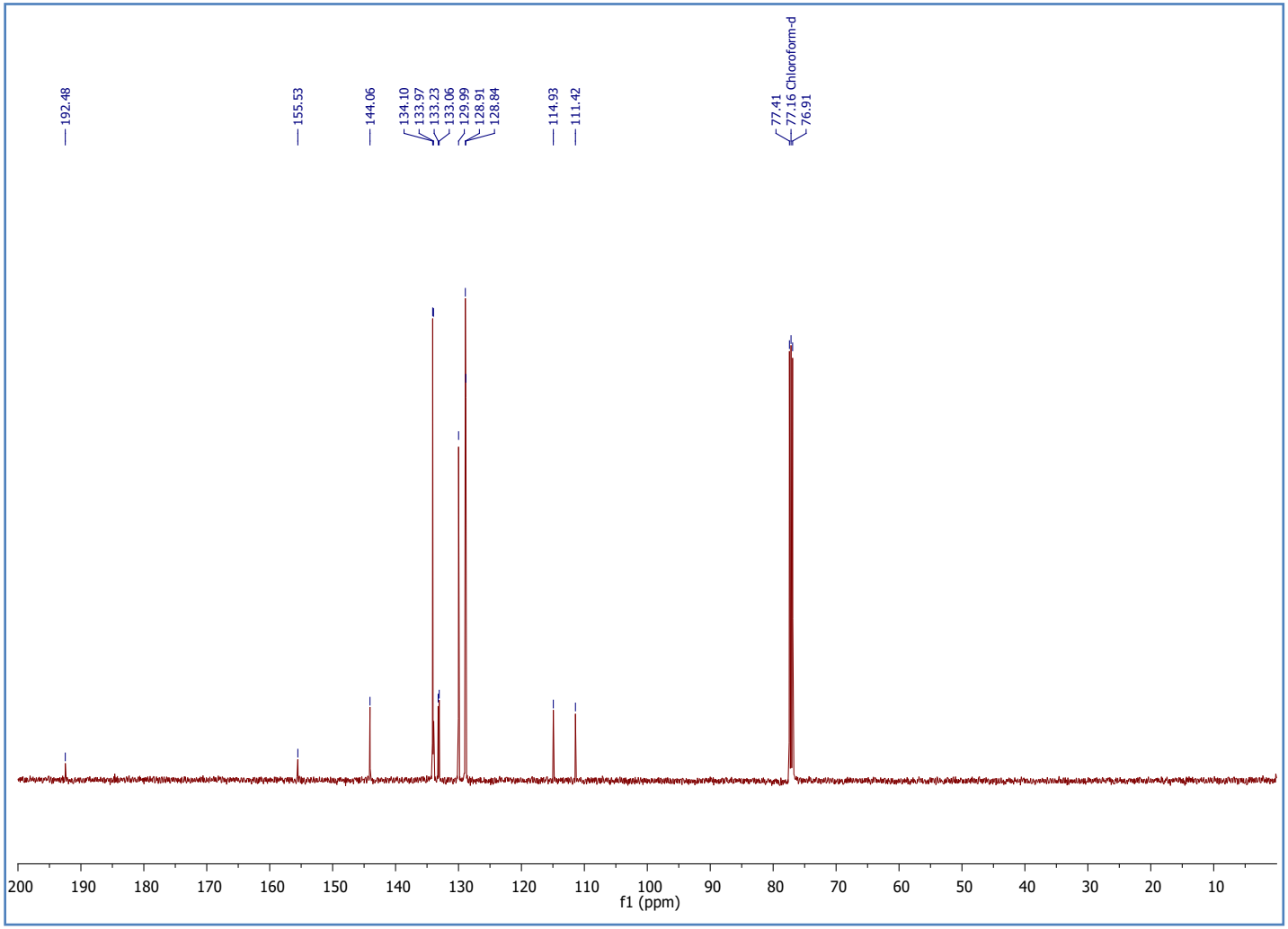


Figure SI 3(b) ^{13}C NMR spectra of complex **4**

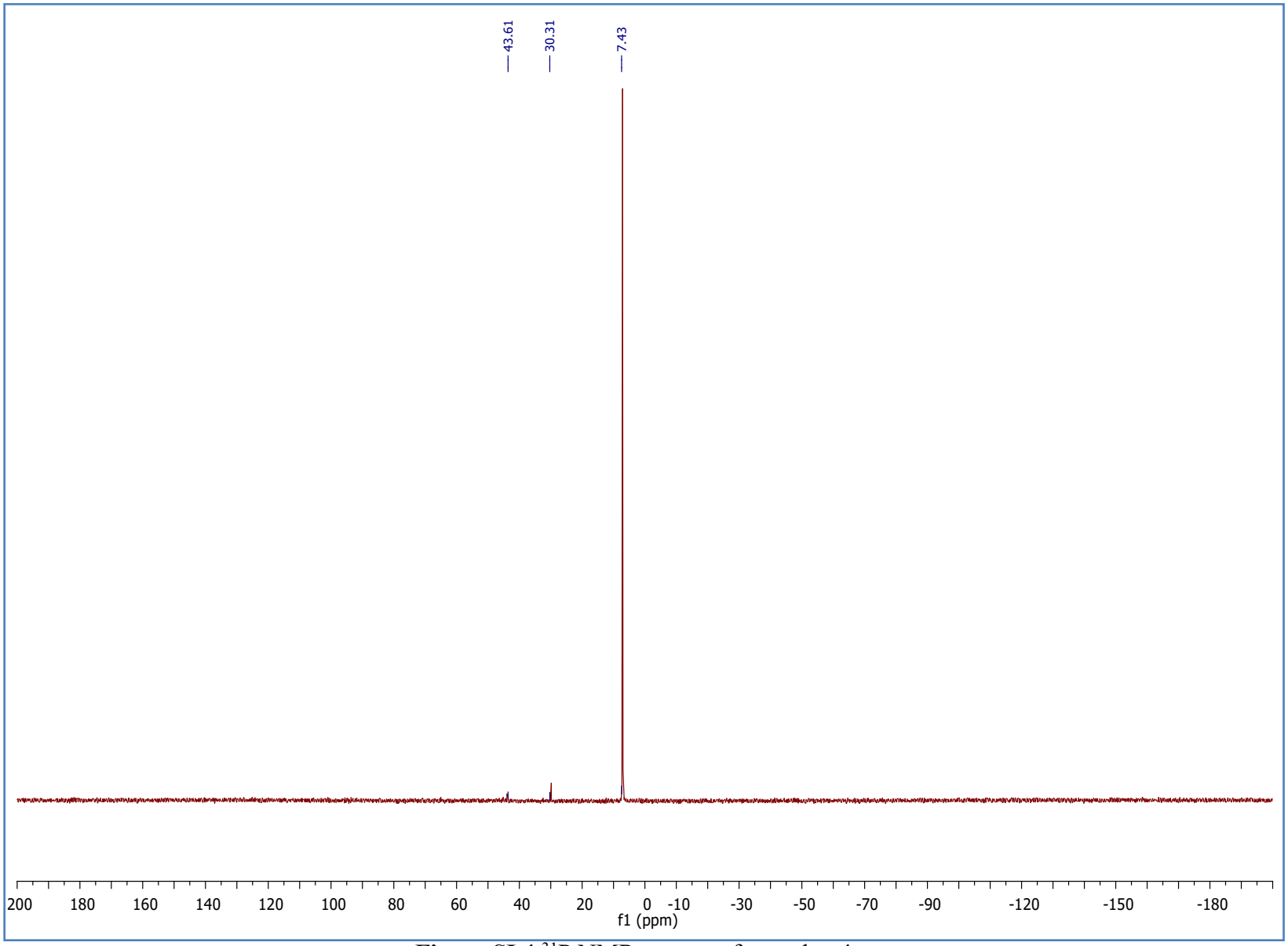


Figure SI 4 ^{31}P NMR spectra of complex **4**

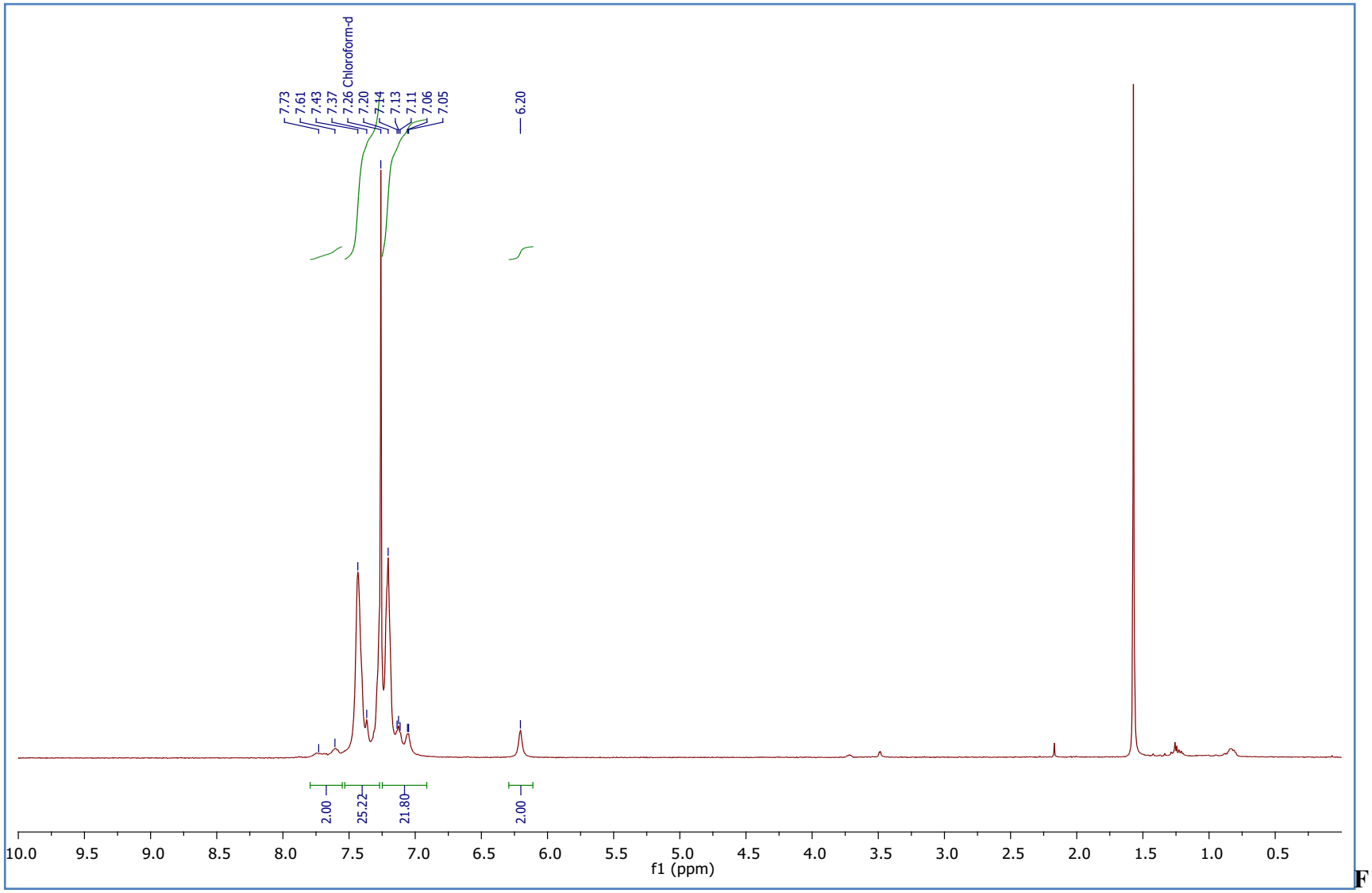
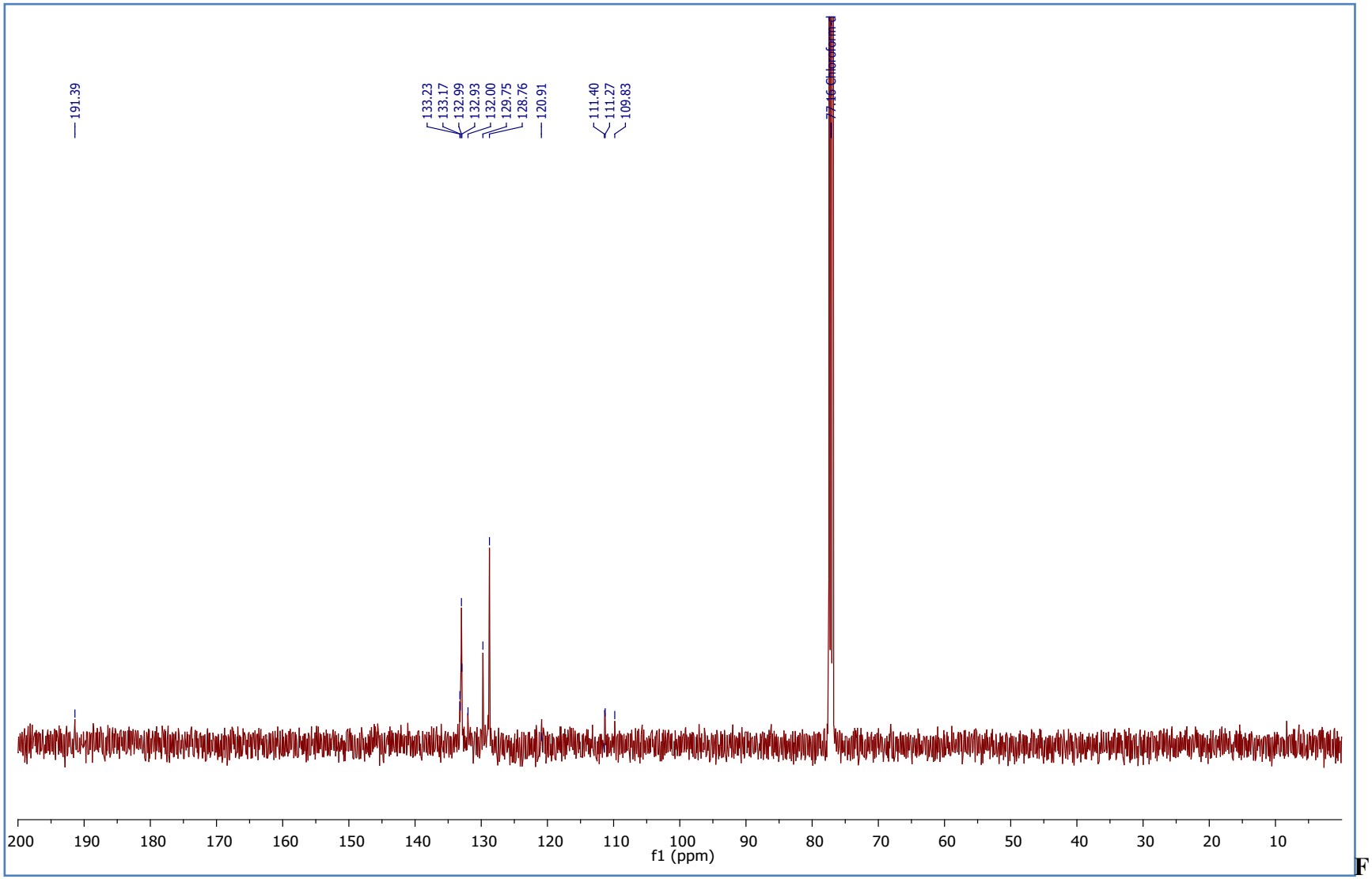


Figure SI 5(a) ^{1}H NMR spectra of complex **5**



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igure SI 5(b) ^{13}C NMR spectra of complex **5**

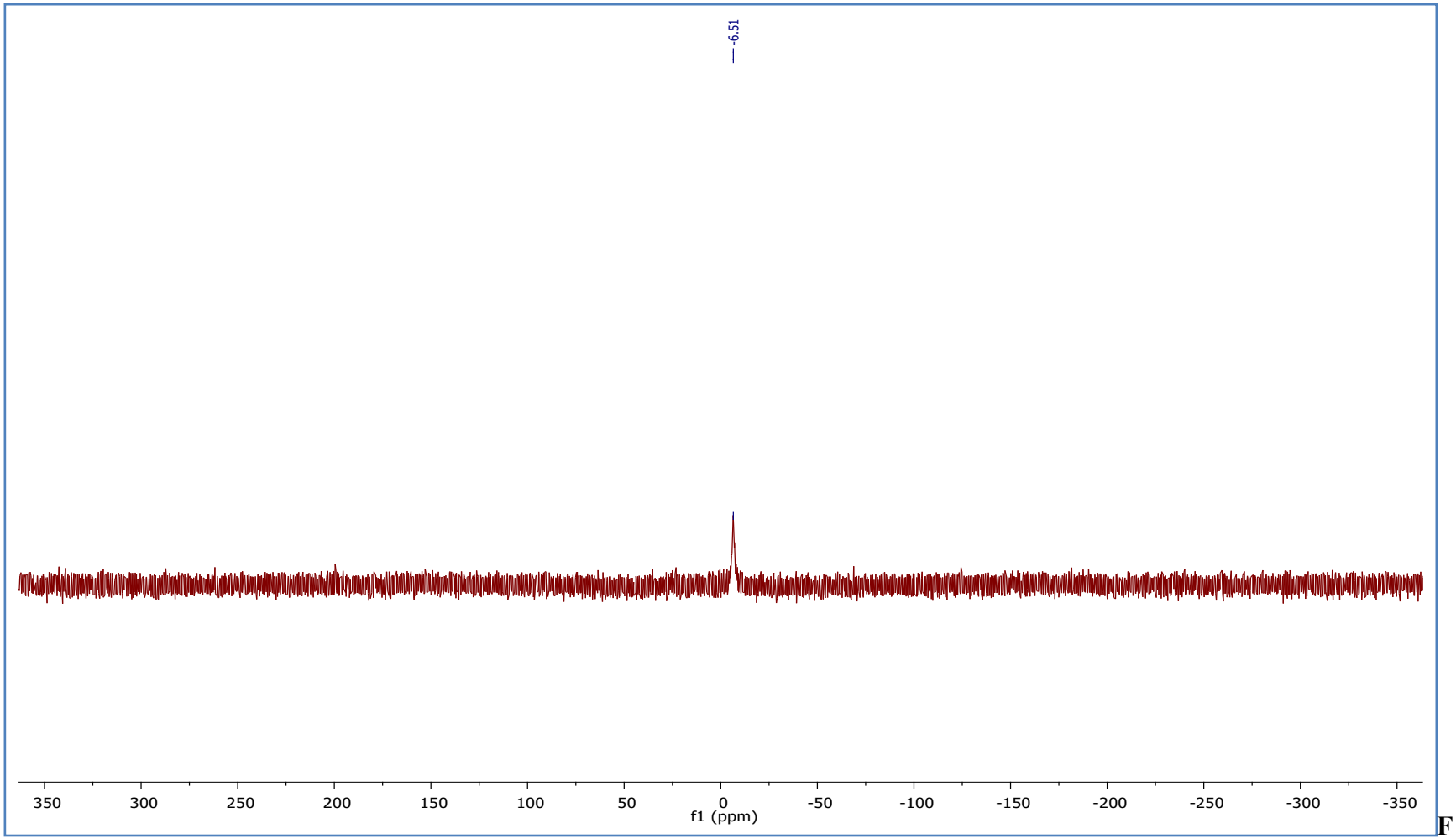


Figure SI 5(c) ^{31}P NMR spectra of complex **5**

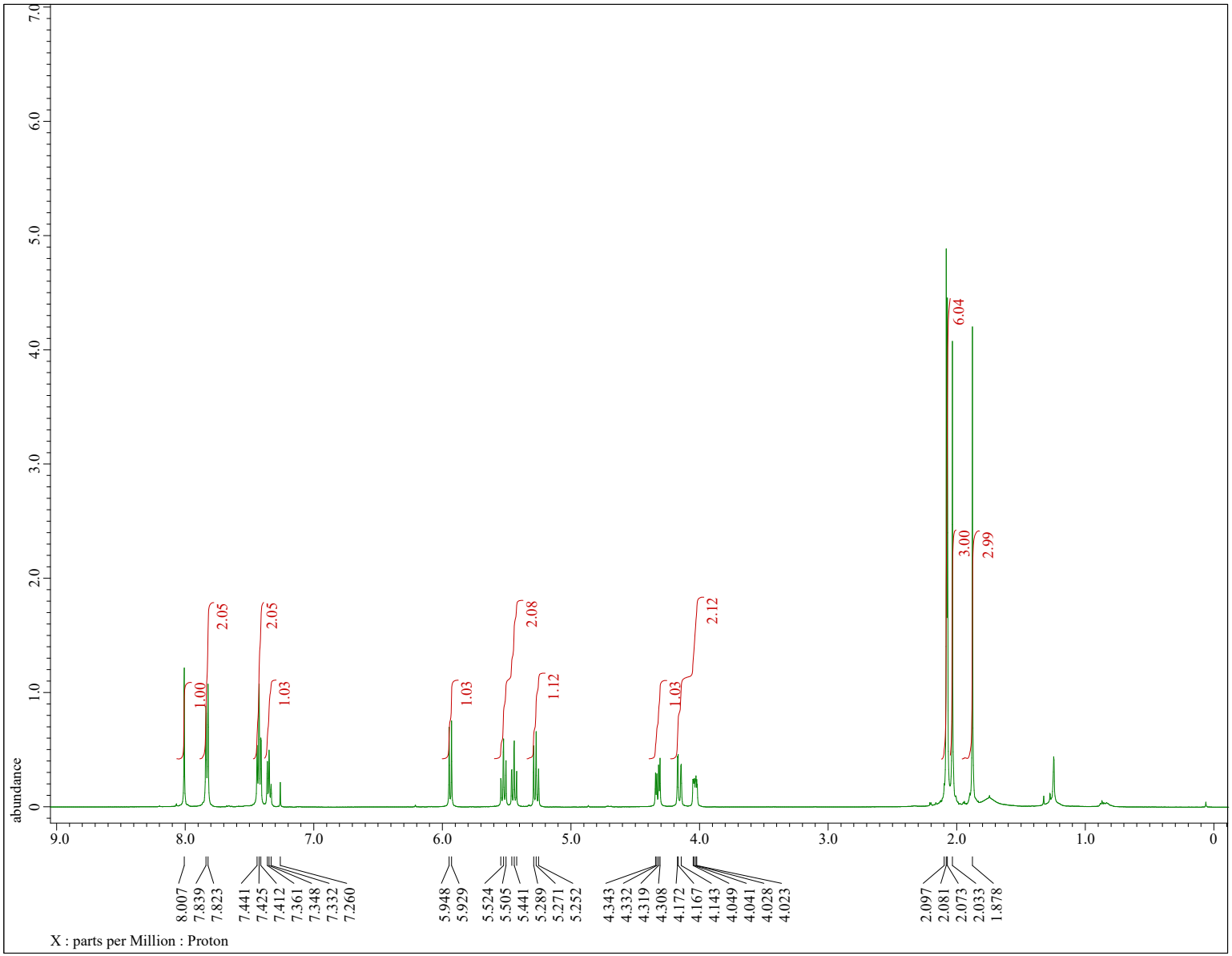


Figure SI 6(a): ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **7a**

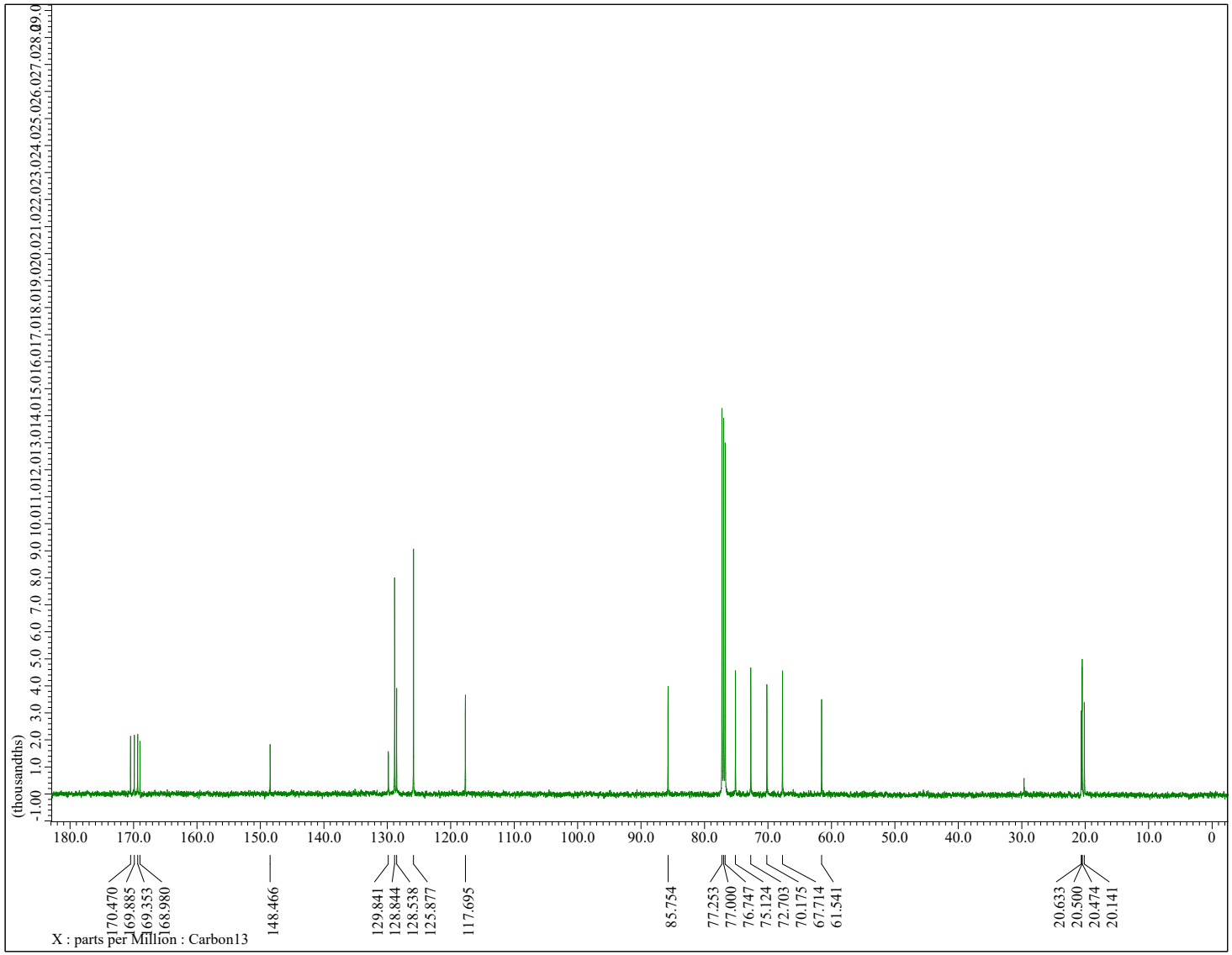
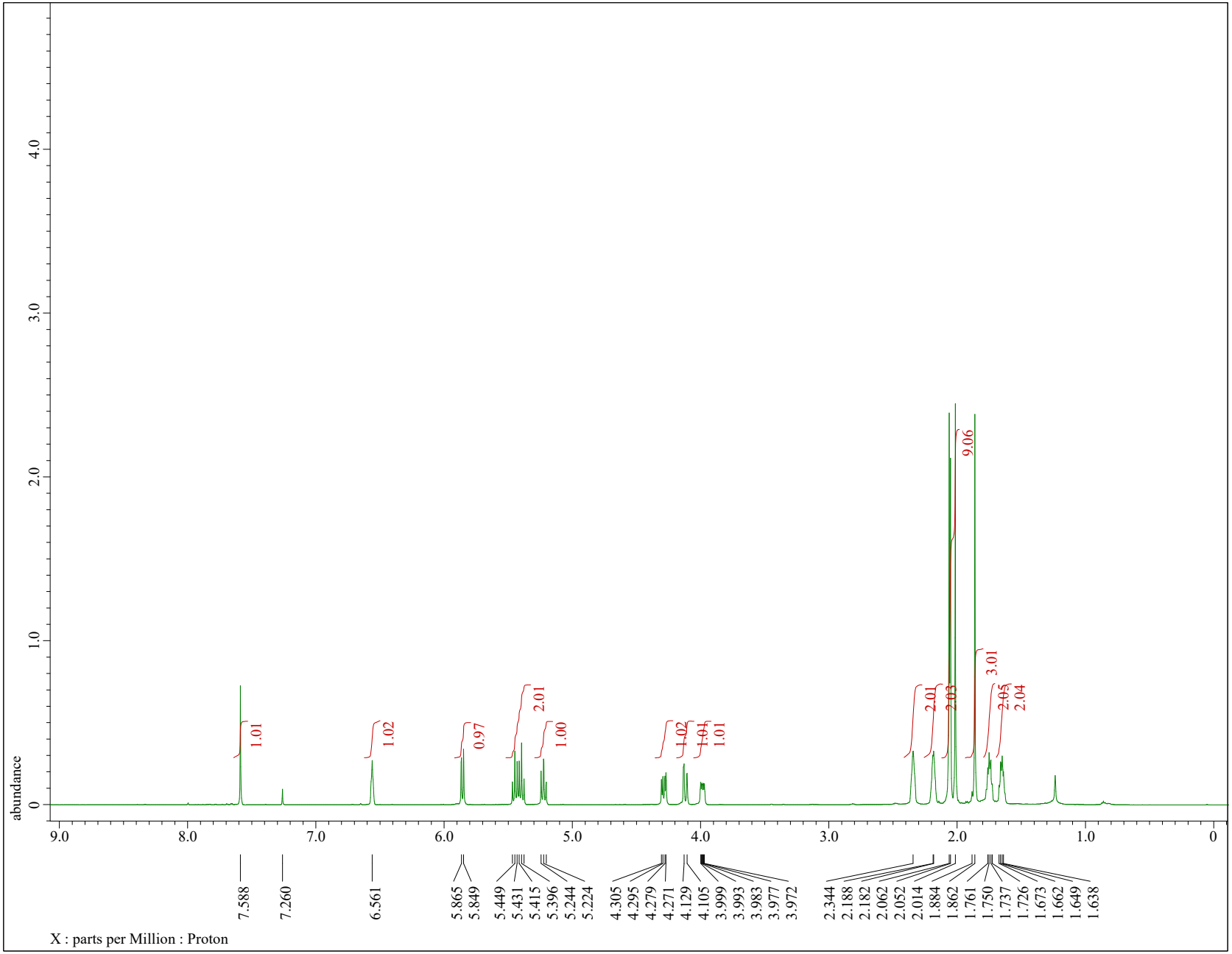


Figure SI 6(b): ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **7a**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3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.01
1.02
0.97
2.01
1.00
1.02
1.01
1.01
2.01
2.03
9.06
3.01
2.05
2.04
7.588
7.260
6.561
5.865
5.849
5.449
5.431
5.415
5.396
5.244
5.224
4.305
4.295
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4.271
4.129
4.105
3.999
3.993
3.983
3.977
3.972
2.344
2.188
2.182
2.062
2.052
2.014
1.884
1.862
1.761
1.750
1.737
1.726
1.673
1.662
1.649
1.638
X : parts per Million : Proton

Fig

ure SI 7(a): ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **7b**

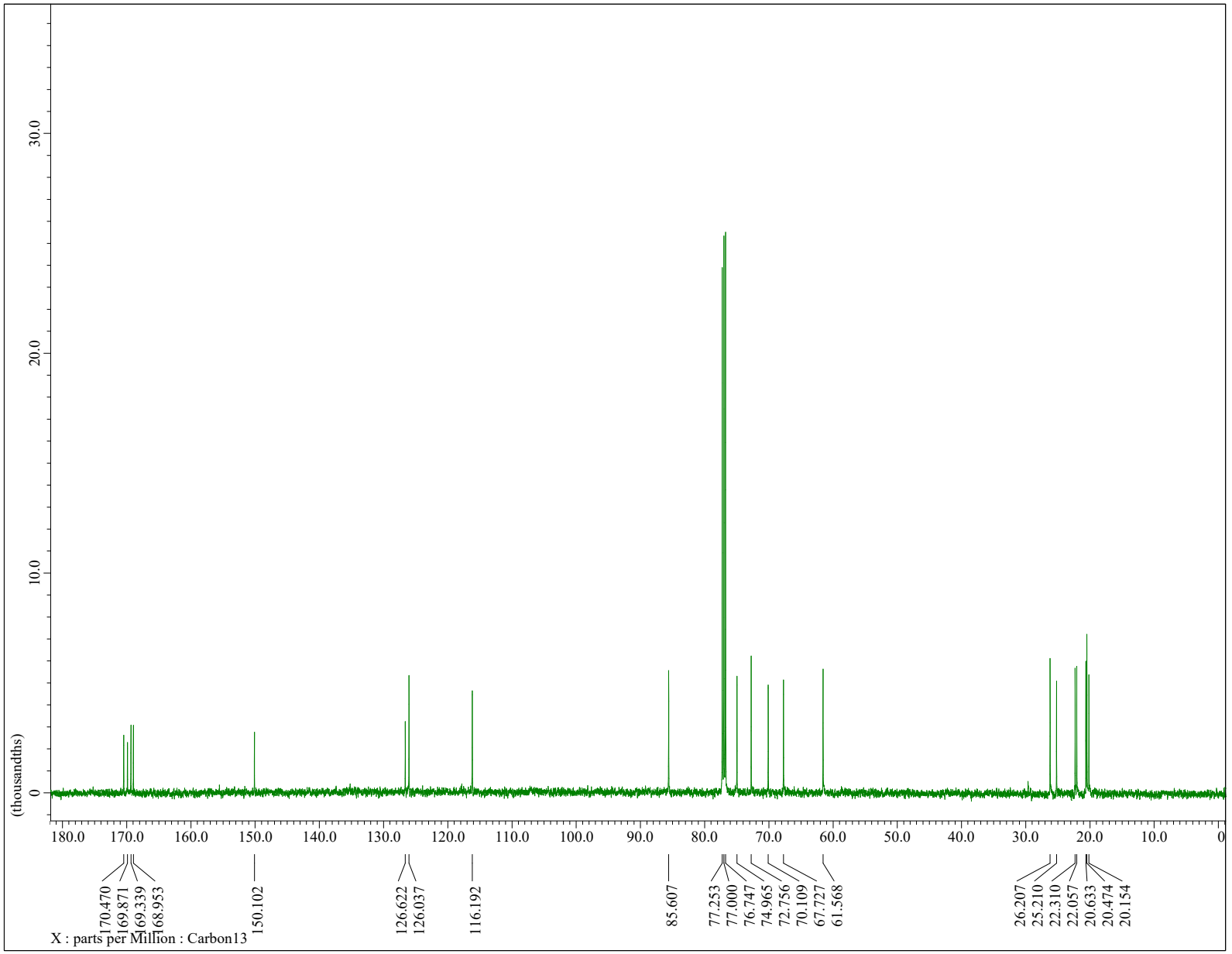


Figure SI 7(b): ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **7b**

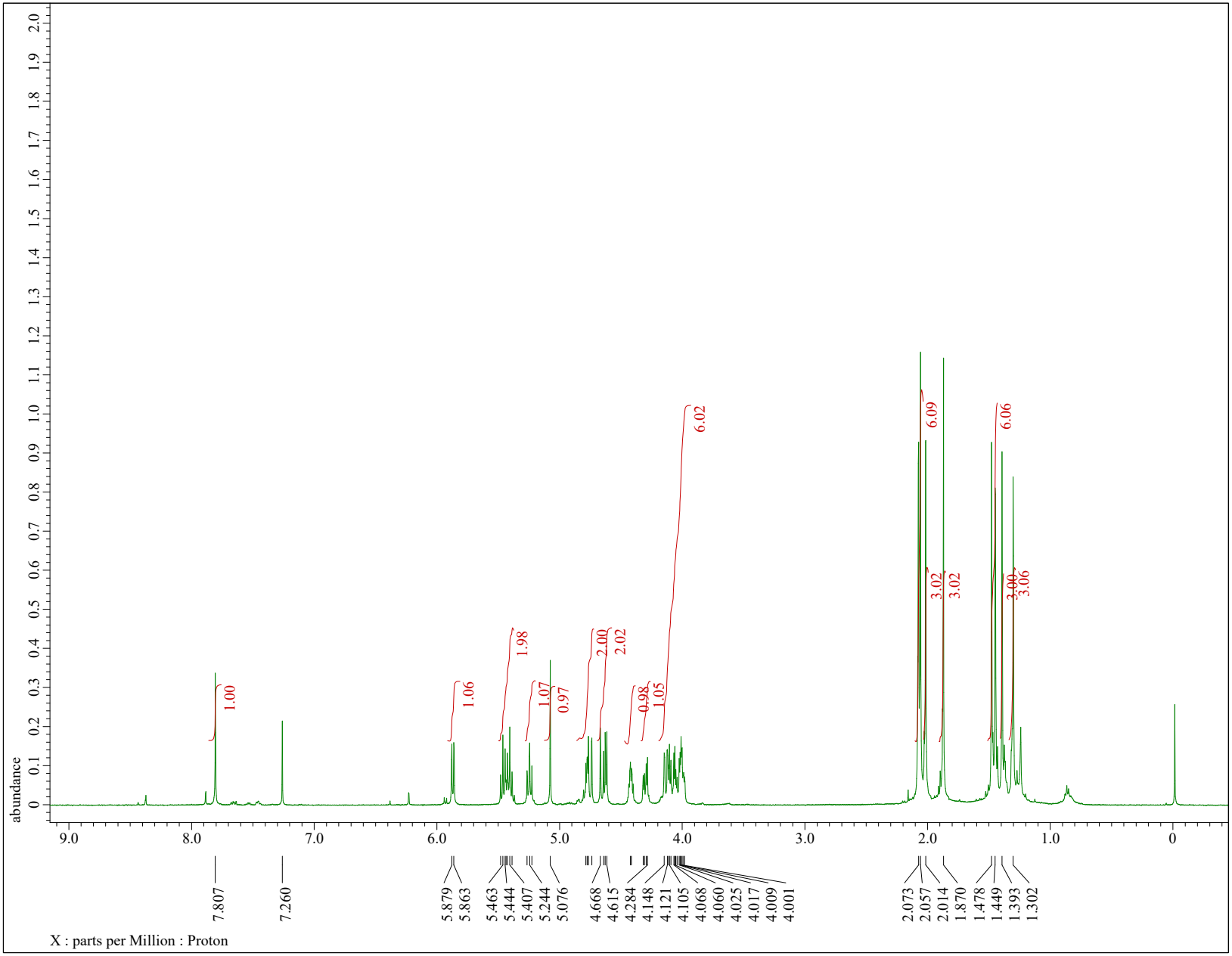


Figure SI 8(a): ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **7c**

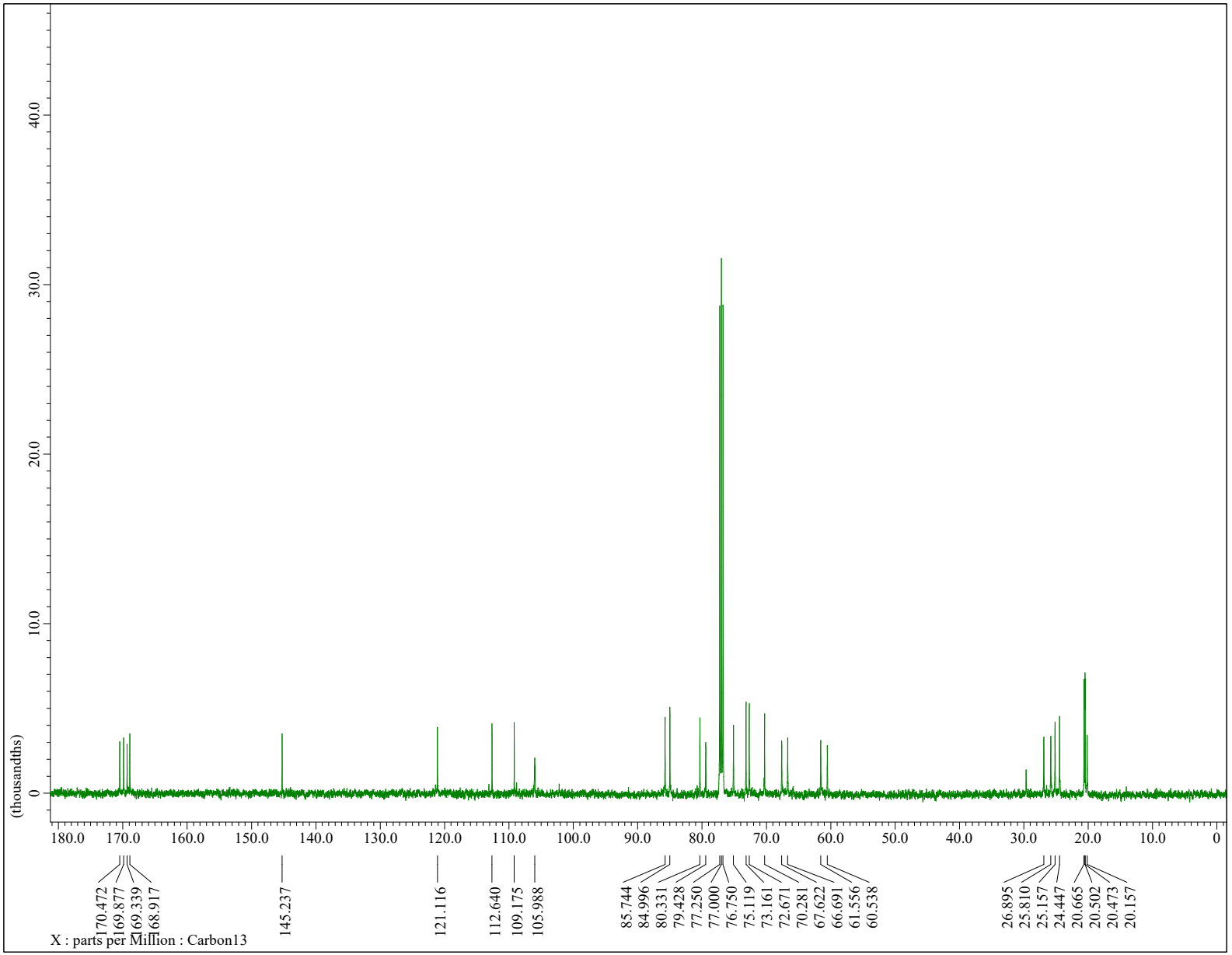


Figure SI 8(b): ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **7c**

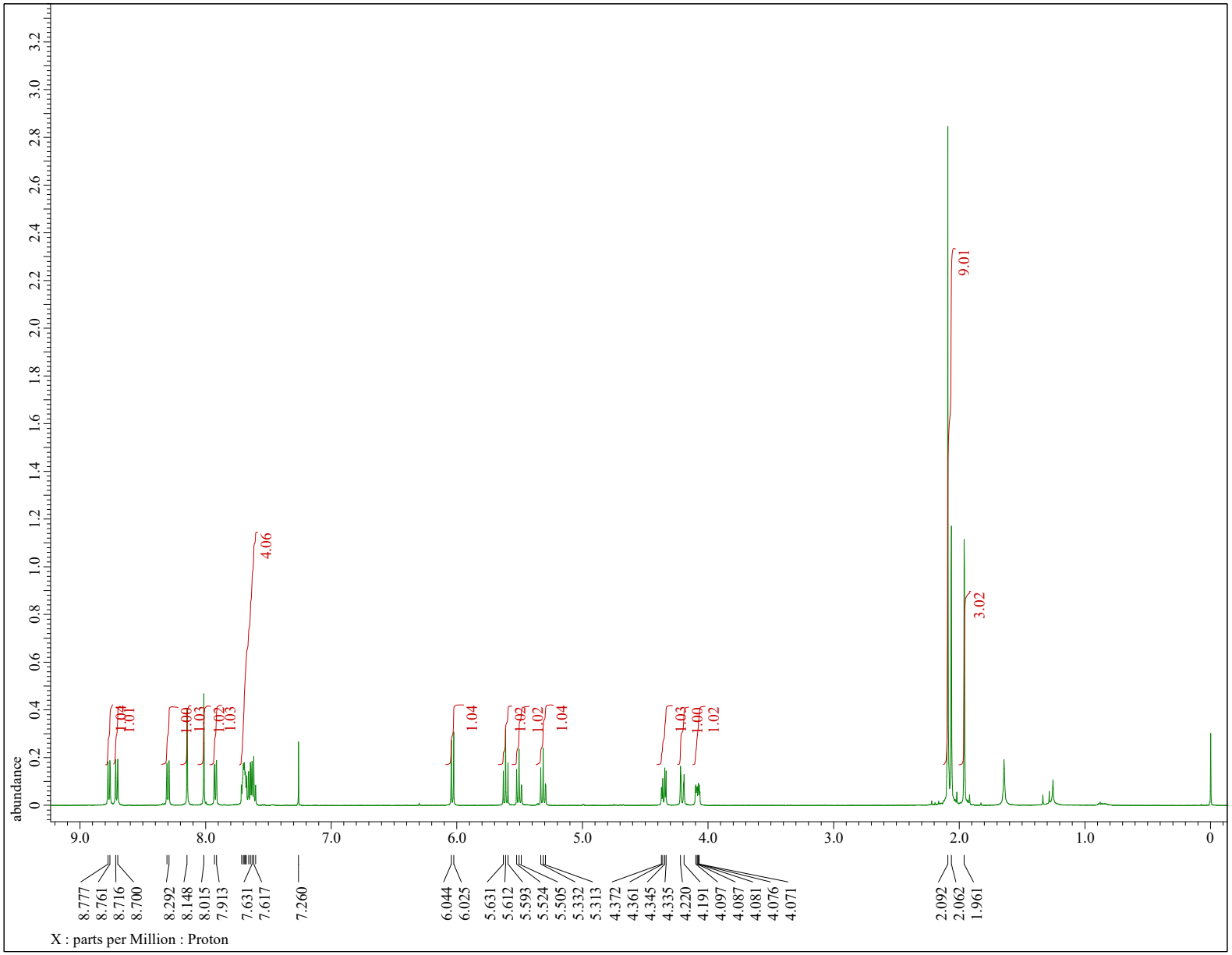


Figure SI 9(a): ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **7d**

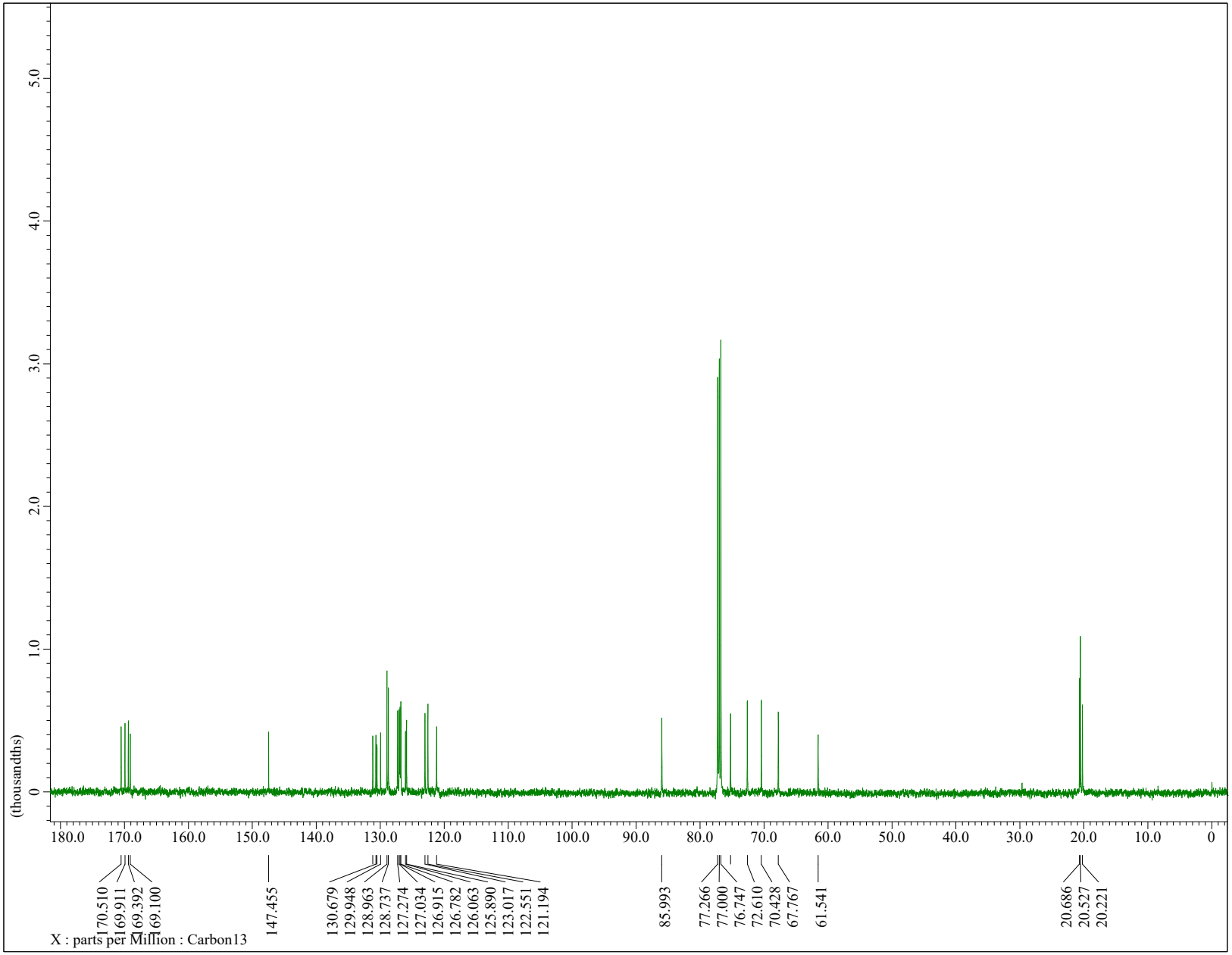


Figure SI 9(b): ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **7d**

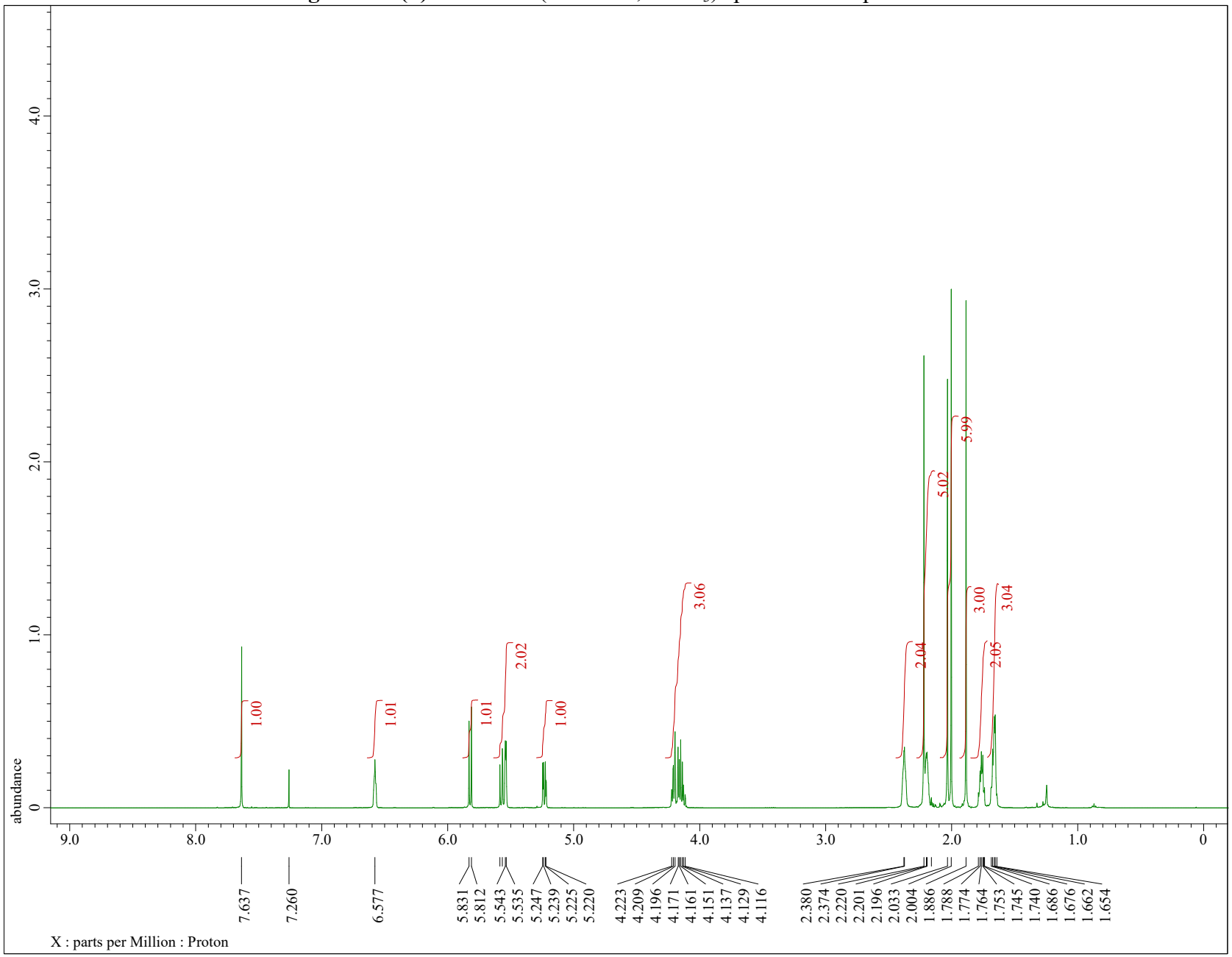


Figure SI 10(a): ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **7e**

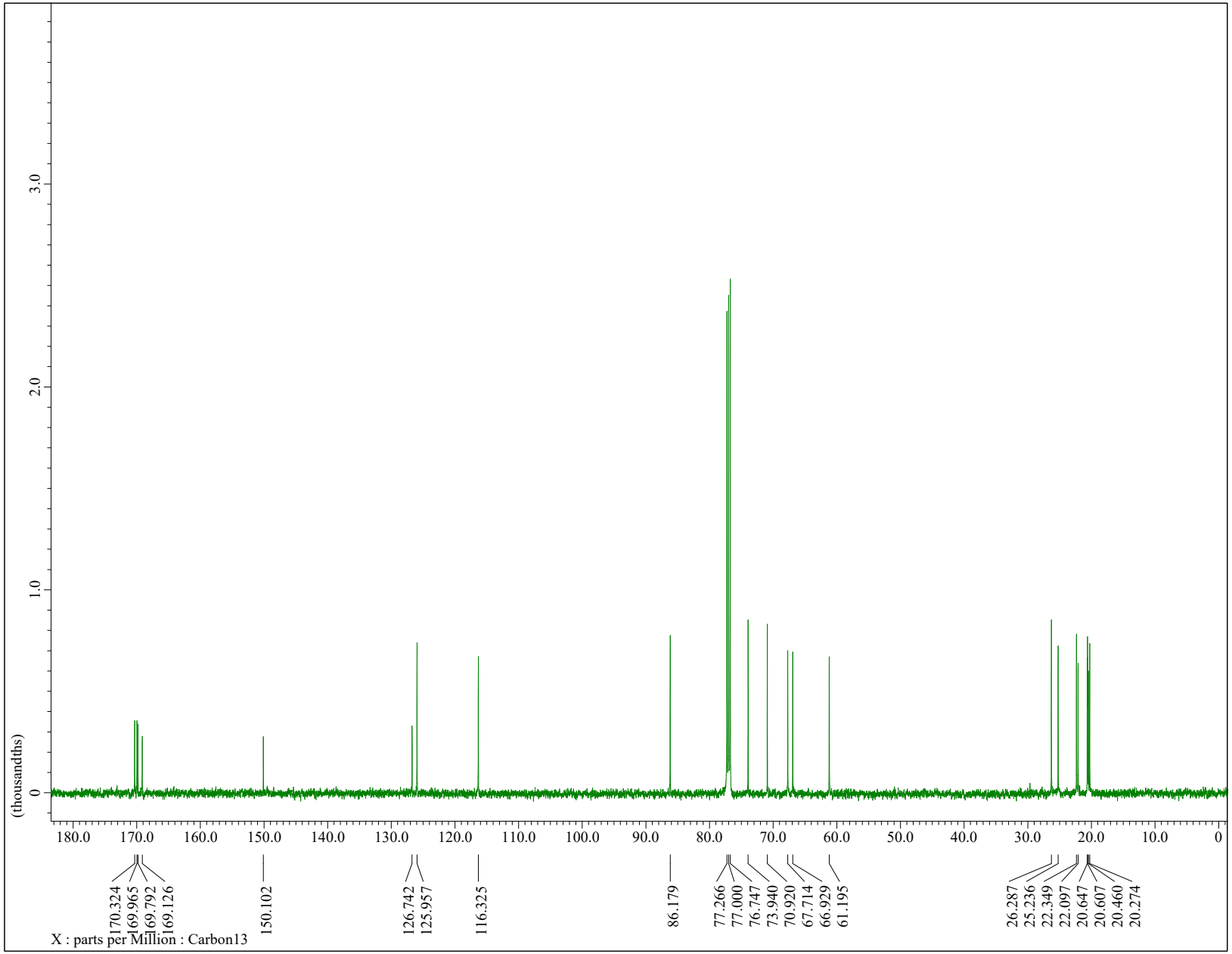


Figure SI 10(b): ^{13}C NMR (125 MHz, $CDCl_3$) of compound **7e**

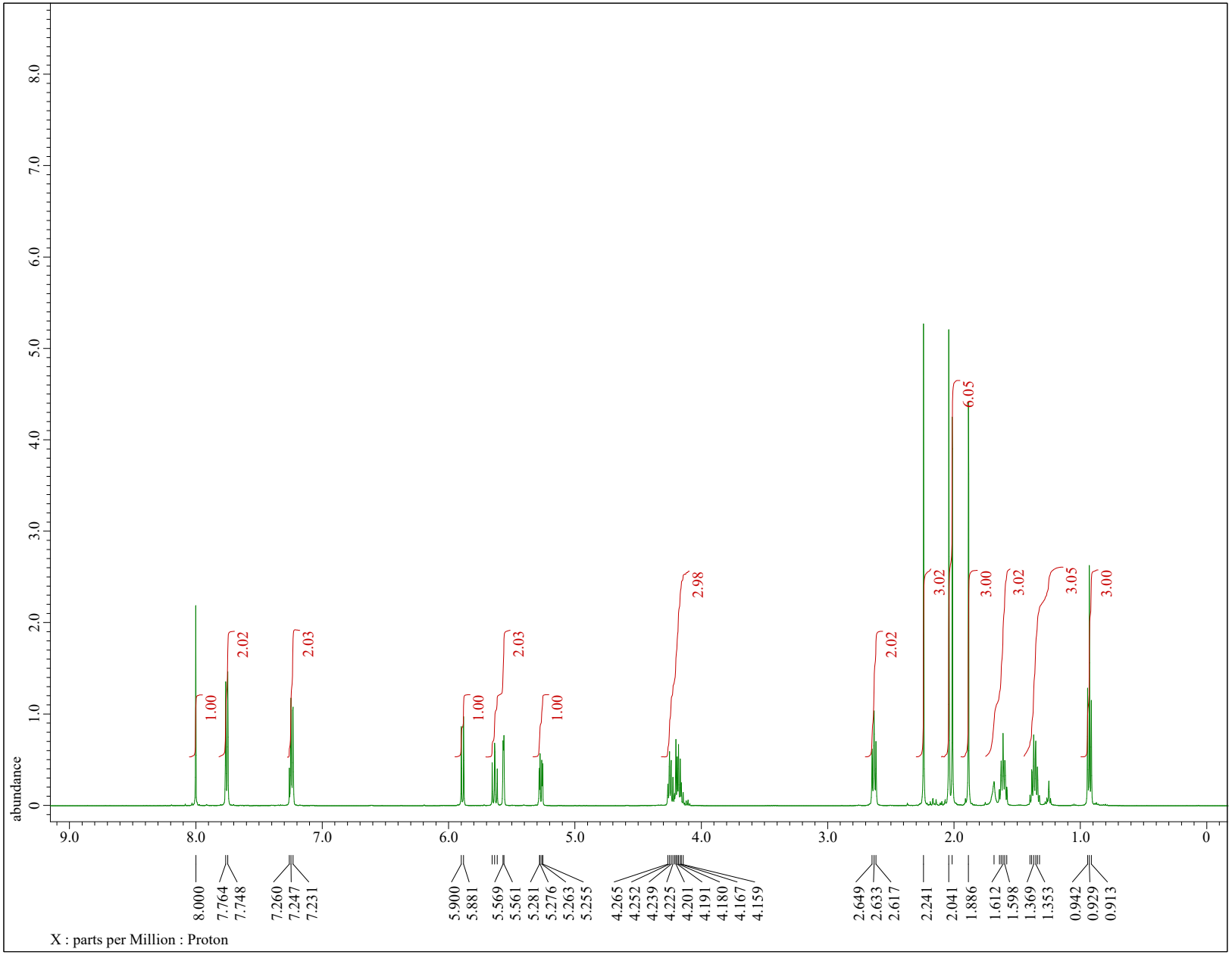


Figure SI 11(a): ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **7f**

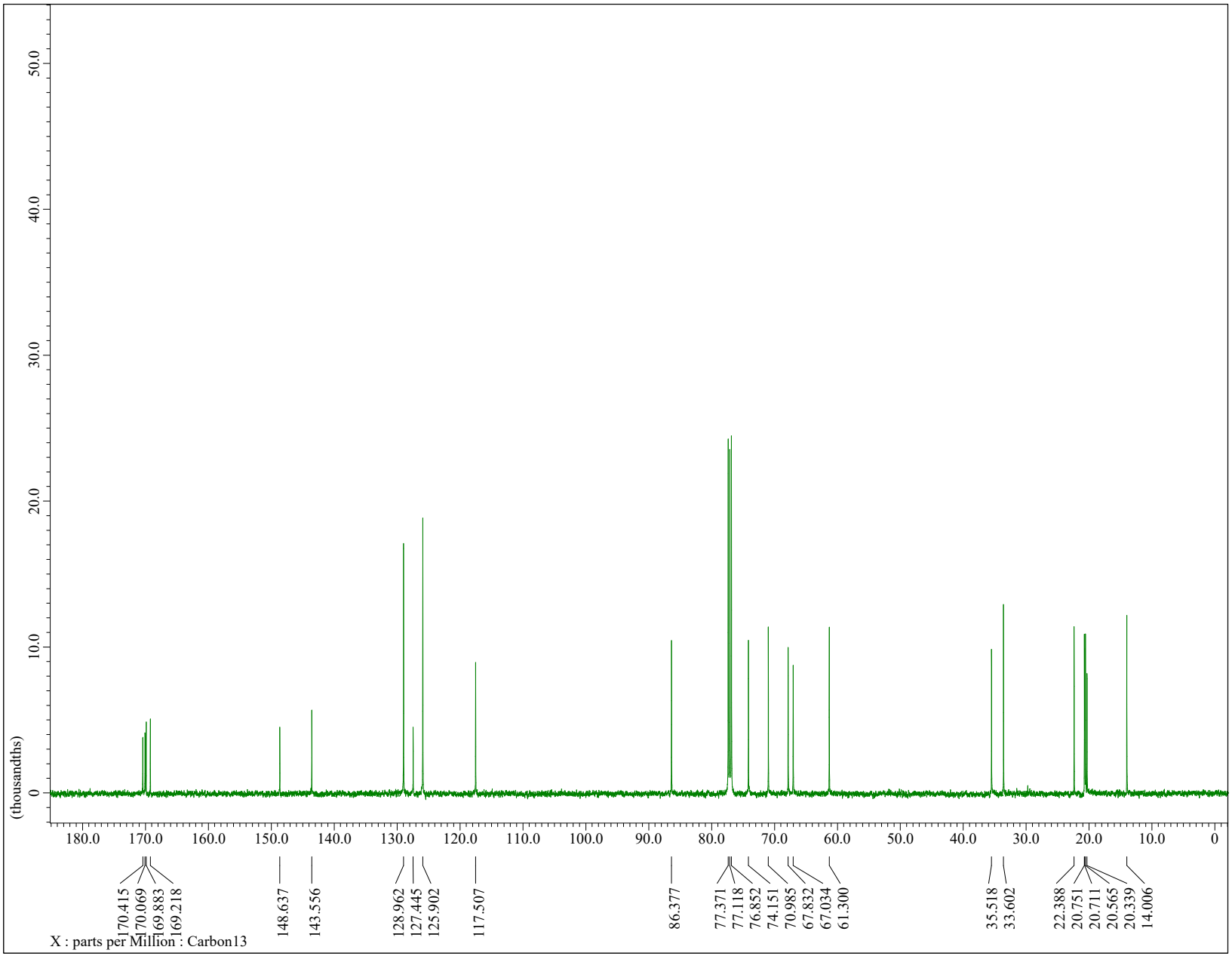


Figure SI 11(b): ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **7f**

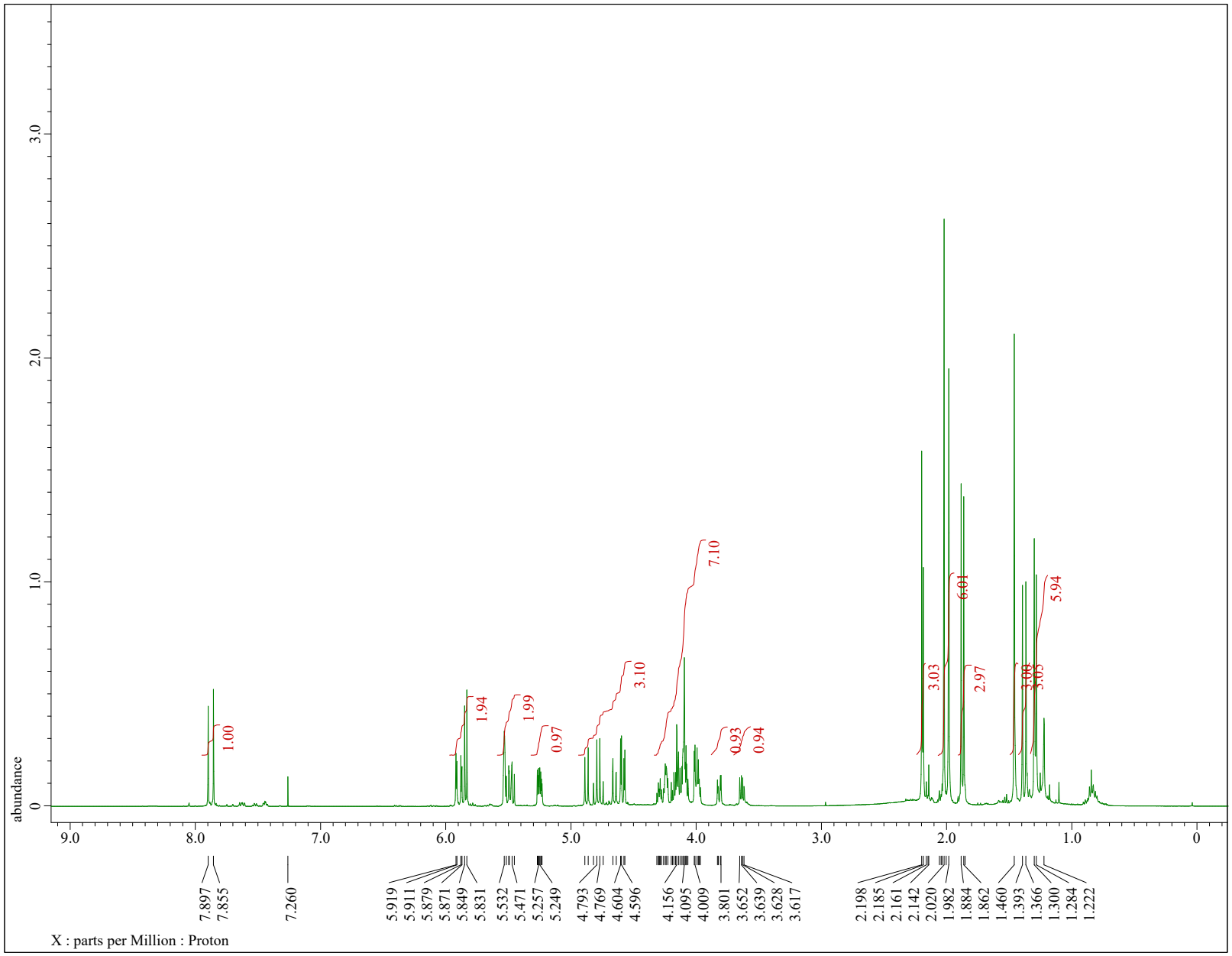


Figure SI 12(a): ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **7g**

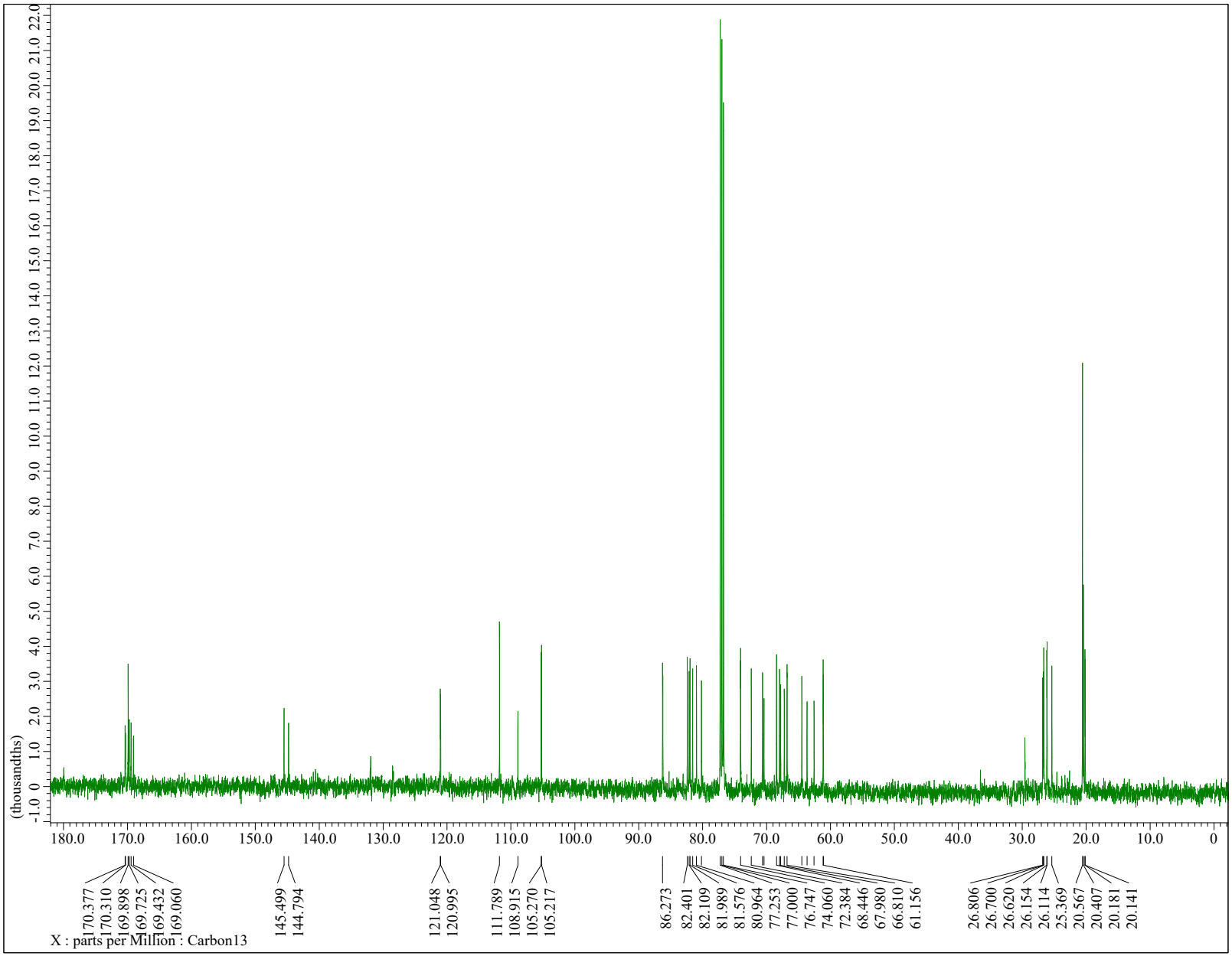


Figure SI 12(b): ^{13}C NMR (125 MHz, $CDCl_3$) of compound **7g**

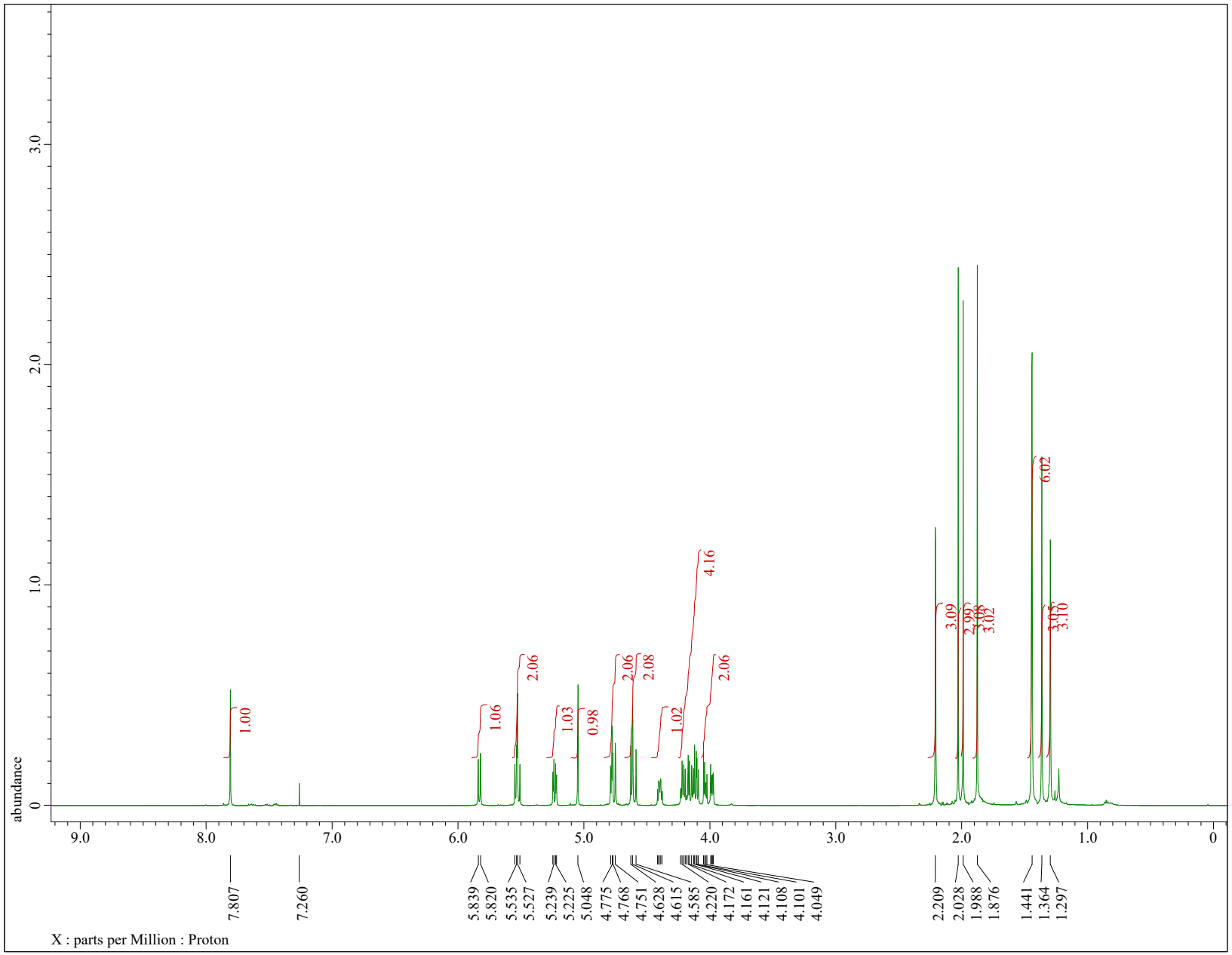


Figure SI 13(a): ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **7h**

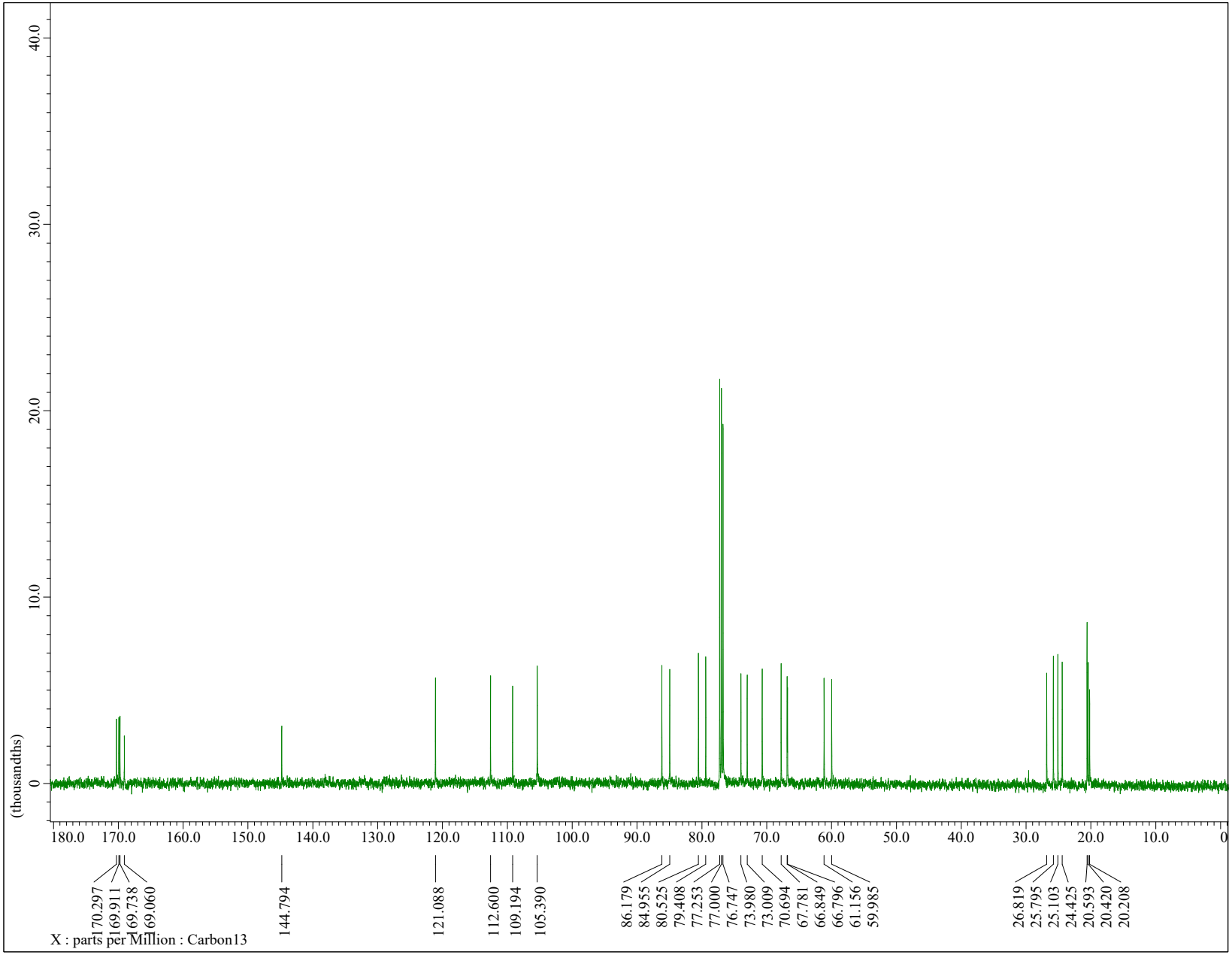


Figure SI 13(b): ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **7h**

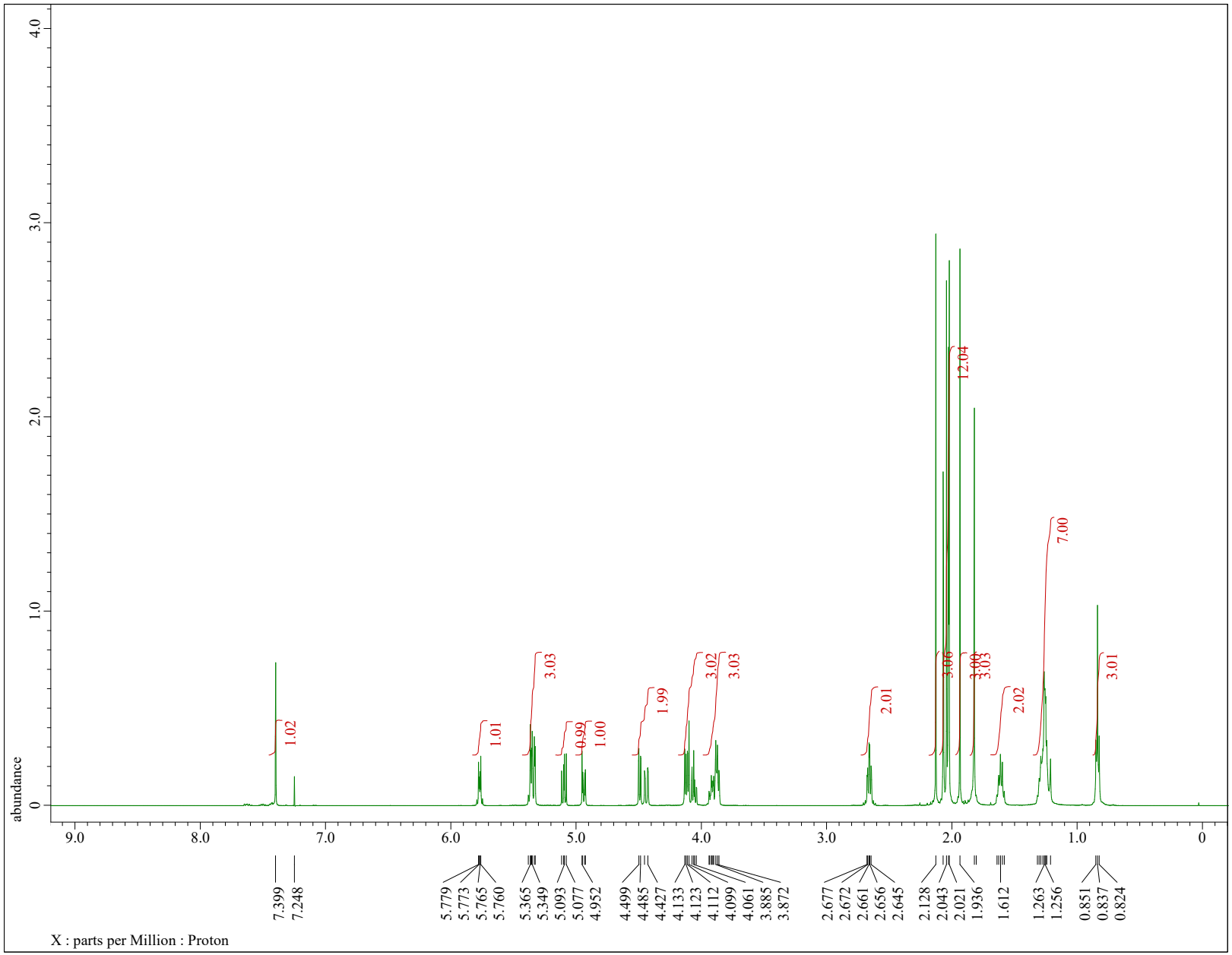


Figure SI 14(a): ^{1}H NMR (500 MHz, $CDCl_3$) of compound **7i**

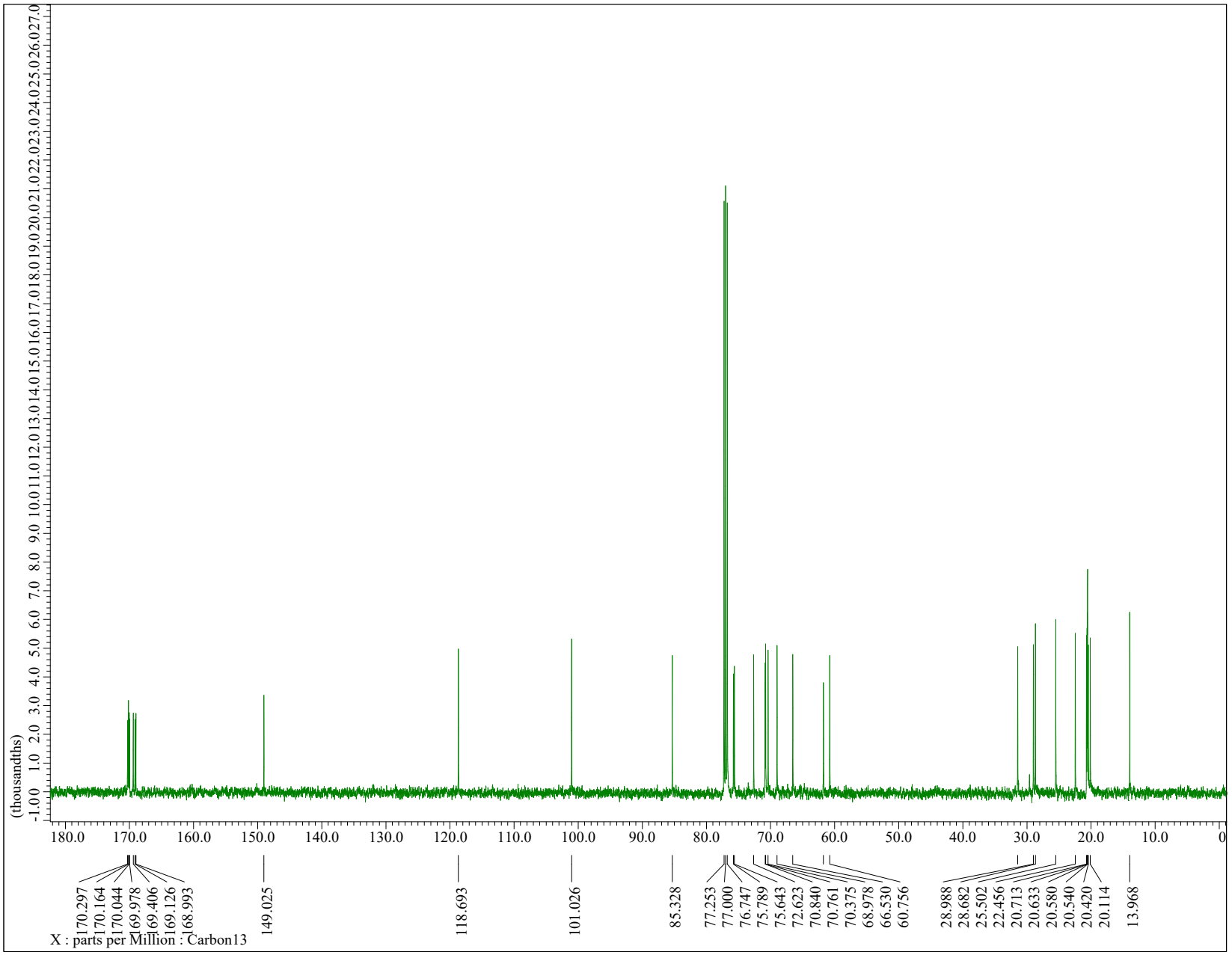


Figure SI 14(b): ^{13}C NMR (125 MHz, $CDCl_3$) of compound **7i**

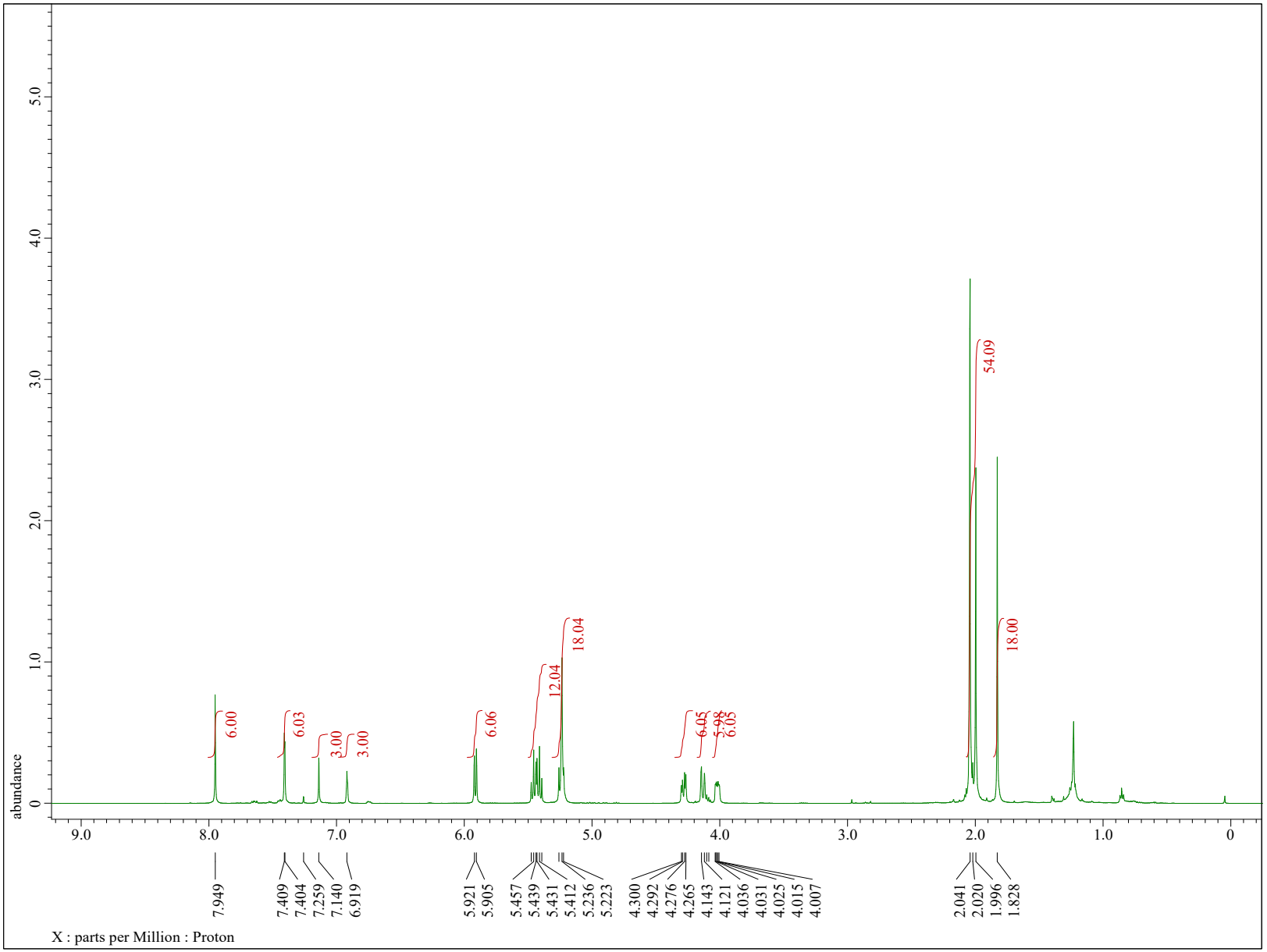


Figure SI 15(a): ^{1}H NMR (500 MHz, $CDCl_3$) of compound **7j**

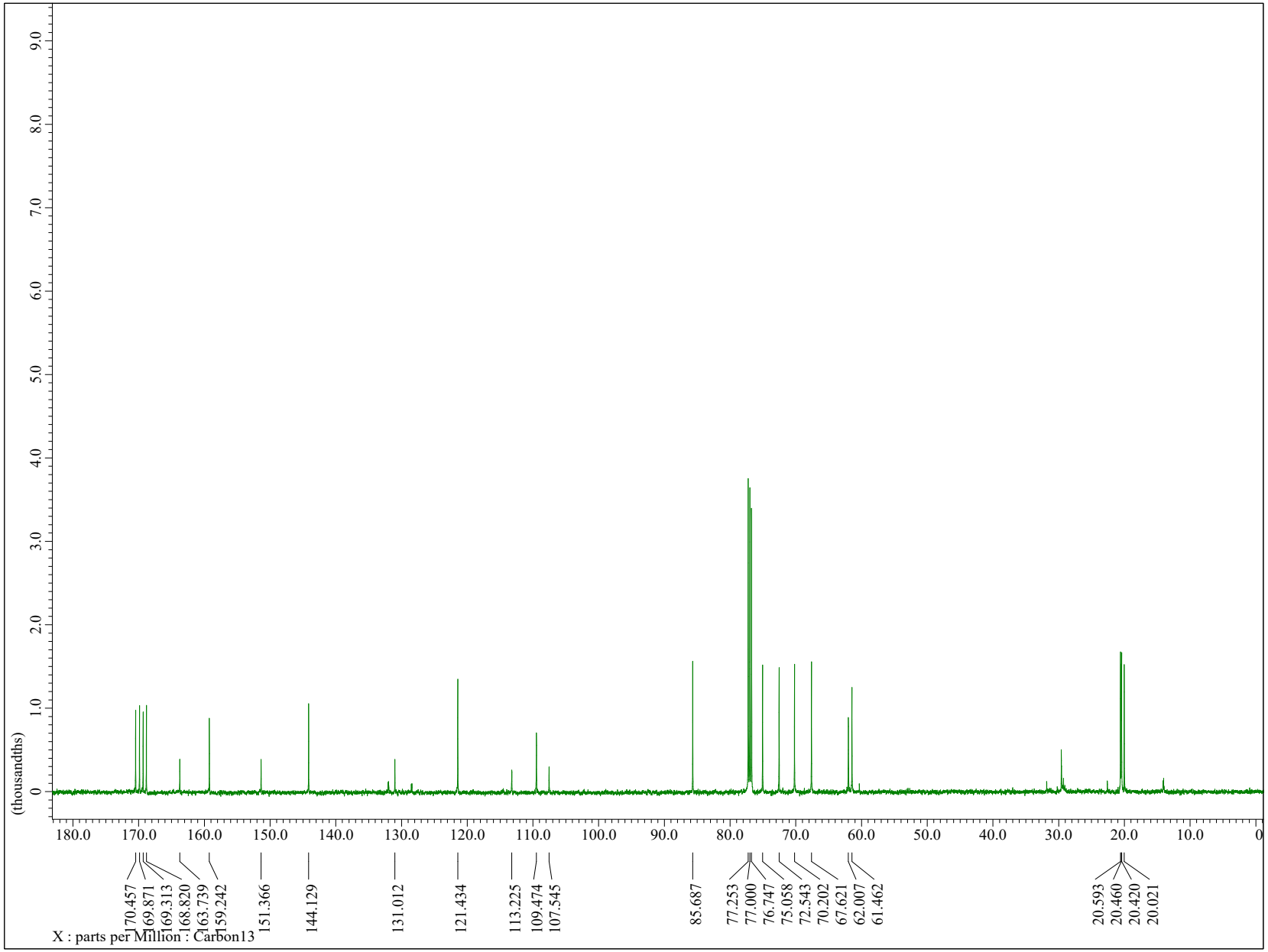


Figure SI 15 (b): ^{13}C NMR (125 MHz, $CDCl_3$) of compound **7j**

Synthesis and spectral characterization of Compounds 7a-7i

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranos-1-yl)-4-phenyl-[1,2,3]-triazole (7a)[1]

2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl azide (100 mg, 0.268 mmol) was reacted with phenylacetylene (32.4 μL, 0.295 mmol) using Cu-catalyst **1** (11.8 mg, 0.013 mmol) according to the general procedure A which afford triazole derivative **7a**. Yield (95%), white solid, m.p. 200-202 ^{o}C, R_f= 0.6, (55% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.0 (s, 1H); 7.83-7.82 (m, 2H), 7.44-7.41 (m, 2H), 7.36-7.33 (m, 1H), 5.93 (d, *J* = 9.0 Hz, 1H), 5.54-5.42 (m, 2H), 5.28-5.25 (m, 1H), 4.34-4.30 (m, 2H), 4.17-4.02 (m, 2H), 2.09-2.07 (m, 6H), 2.03 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 169.8, 169.3, 168.9, 148.4, 129.8, 128.8, 128.5, 125.8, 117.6, 85.7, 75.1, 72.7, 70.1, 67.7, 61.5, 20.6, 20.5, 20.4 and 20.1 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranos-1-yl)-4-(3-cyclohexene)-[1,2,3]-triazole (7b)[1]

2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl azide (100 mg, 0.268 mmol) was reacted with 1-ethynylcyclohexene (34.6 μL, 0.295 mmol) using Cu-catalyst **1** (11.8 mg, 0.016 mmol) according to the general procedure to afford triazole derivative **7b**. Yield (95%). off white solid, 196-198^{o}C; R_f= 0.5, (50% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (s, 1H), 6.56 (s, 1H), 5.85 (d, J = 8.0 Hz, 1H), 5.46-5.37 (m, 2H), 5.24-5.20 (m, 1H), 4.30-4.27 (m, 1H), 4.19-4.10 (m, 1H), 3.99-3.97 (m, 1H), 2.34 (s, 2H), 2.18-2.18 (m, 2H), 2.06-2.01 (m, 9H), 1.88-1.86 (m, 3H), 1.76-1.72 (m, 2H), 1.67-1.63 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 169.8, 169.3, 168.9, 150.1, 126.6, 126.0, 116.1, 85.6, 74.9, 72.7, 70.1, 67.7, 61.5, 26.2, 25.2, 25.1, 22.3, 22.0, 20.6, 20.4, and 20.1 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranos-1-yl)-4-(2,3;5,6-di-*O*-isopropylidene-1-*O*-methyl-*β*-D-mannofuranos-1-yl)-[1,2,3]-triazole (7c)

2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl azide (100 mg, 0.268 mmol) was reacted with 2,3;5,6-di-*O*-isopropylidene-1-*O*-propargyloxy-*β*-D-mannofuranos-1-yl (87.9 mg, 0.295 mmol) using Cu-catalyst **1** (11.8 mg, 0.016 mmol) according to the general

procedure to afford triazole derivative **7c**. Yield (94%); solid, m.p. 108°C, R_f= 0.5, (50% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 1H), 5.86 (d, *J* = 8.0 Hz, 1H), 5.48-5.38 (m, 2H), 5.26-5.22 (m, 1H), 5.07 (s, 1H), 4.78-4.73 (m, 2H), 4.66-4.61 (m, 2H), 4.42-4.41 (m, 1H), 4.31-4.28 (m, 1H), 4.14-3.98 (m, 6H), 2.07-2.05 (m, 6H), 2.01 (s, 3H), 1.87 (s, 3H), 1.47-1.44 (s, 6H), 1.39 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 169.8, 169.3, 168.9, 145.2, 121.1, 112.6, 109.1, 105.9, 85.7, 84.9, 80.3, 79.4, 75.1, 73.1, 72.6, 70.2, 67.6, 66.6, 61.5, 60.5, 26.8, 25.8, 25.1, 24.4, 20.6, 20.5, 20.4 and 20.1 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranos-1-yl)-4-(9-phenanthrene)- [1,2,3]-triazole (7d)

2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl azide (100 mg, 0.268 mmol) was reacted with 9-ethynylphenanthrene (1.1 equiv.) using Cu-catalyst **1** (11.8 mg, 0.016 mmol) according to the general procedure to afford triazole derivative **7d**. Yield (94%), white solid, m.p.; 168-170°C; R_f= 0.45, (40% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.77 (d, *J* = 7.5 Hz, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.14 (s, 1H), 8.01 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.70-7.61 (m, 4H), 6.03 (d, *J* = 9.5 Hz, 1H), 5.61 (t, *J* = 9.5 Hz, 1H), 5.52-5.48 (m, 1H), 5.33-5.29 (m, 1H), 4.37-4.33 (m, 1H), 4.22-4.19 (m, 1H), 4.09-4.07 (m, 2H), 2.09-2.06 (m, 9H), 1.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ170.5, 169.9, 169.3, 169.1, 147.4, 130.6, 129.9, 128.9, 128.7, 127.2, 127.0, 126.9, 126.7, 126.0, 125.8, 123.0, 122.5, 121.1, 85.9, 75.2, 72.6, 70.4, 67.7, 61.5, 20.6, 20.5, and 20.2 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranos-1-yl)-4-(3-cyclohexene)-[1,2,3]-triazole (7e)[1]

2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl azide (100 mg, 0.268 mmol) was reacted with 1-ethynylcyclohexene (34.6 μL, 0.295 mmol) using Cu-catalyst **1** (11.8 mg, 0.016 mmol) according to the general procedure to afford triazole derivative **7e**. Yield (95%). off white solid, 196-198°C; R_f= 0.5, (50% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1H), 6.57 (s, 1H), 5.82 (d, *J* = 9.5 Hz, 1H), 5.58-5.53 (m, 2H), 5.24-5.22 (m, 1H), 4.22-4.11 (m, 3H), 2.38-2.37 (m, 2H), 2.22-2.16 (m, 5H), 2.03-2.00 (m, 6H), 1.88 (s, 3H), 1.78-1.74 (m, 2H), 1.68-1.65 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ

170.3, 169.9, 169.7, 169.1, 150.1, 126.7, 125.9, 116.3, 86.1, 73.9, 70.9, 67.7, 66.9, 61.1, 26.2, 25.2, 22.3, 22.0, 20.6, 20.60, 20.4 and 20.2 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl)-4-(4-*n*-pentylphenyl)-[1,2,3]-triazole (7f)[1]

2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl azide (100 mg, 0.268 mmol) was reacted with 1-ethynyl-4-pentylbenzene (57.3 µl, 0.321 mmol) using Cu-catalyst **1** (11.8 mg, 0.016 mmol) according to the general procedure A to afford triazole derivative **7f**. Yield (96%). solid; m.p. 170-176°C; R_f= 0.4, (35% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.26-7.23 (m, 2H), 5.89 (d, *J* = 9.5 Hz, 1H), 5.65-5.56 (m, 2H), 5.28-5.25 (m, 1H), 4.26-4.14 (m, 3H), 2.63 (t, J = 8.0 Hz, 2H), 2.24 (s, 3H), 2.04-2.01 (m, 6H), 1.88 (s, 3H), 1.68-1.58 (m, 3H), 1.39-1.32 (m, 3H), 0.94-0.91 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 170.0, 169.8, 169.2, 148.6, 143.5, 128.9, 127.4, 125.9, 117.5, 86.3, 74.1, 70.9, 67.8, 67.0, 61.3, 35.5, 33.6, 30.9, 22.3, 20.75, 20.71, 20.5, 20.3 and 14.0 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranos-1-yl)-4-(1,2;5,6-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranos-3-yl)-[1,2,3]-triazole (7g)

2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactocopyranosyl azide (100 mg, 0.268 mmol) was reacted with 1,2;5,6-*O*-isopropylidene-3-*O*-propargyloxy-α-D-glucofuranos-3-yl (87.9 mg, 0.295 mmol) using Cu-catalyst **1** (11.8 mg, 0.016 mmol) according to the general procedure A to afford triazole derivative **7g**. Yield (94%), off white solid; m.p. 36-38 °C; R_f= 0.5, (50% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, J = 21.0 Hz, 1H), 5.91-5.831 (m, 2H), 5.53-5.47 (m, 2H), 5.26-5.23 (m, 1H), 4.88-4.56 (m, 3H), 4.31-3.98 (m, 7H), 3.83-3.80 (m, 1H), 3.62-3.61 (m, 1H), 2.19-2.18 (m, 3H), 2.05-1.98 (m, 6H), 1.88-1.85 (m, 3H), 1.46 (s, 3H), 1.39-1.36 (m, 3H), 1.30-1.22 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.37, 170.3, 169.8, 169.7, 169.4, 169.0, 145.4, 144.7, 121.0, 120.9, 111.7, 108.9, 105.27, 105.2, 86.2, 82.4, 82.1, 81.9, 81.5, 80.9, 74.0, 72.3, 68.4, 67.9, 66.8, 61.1, 26.8, 26.7, 26.6, 26.15, 26.11, 25.3, 20.5, 20.4 and 20.1 ppm.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranos-1-yl)-4-(2,3;5,6-di-*O*-isopropylidene-1-*O*-methyl-*β*-D-mannofuranos-1-yl)-[1,2,3]-triazole (7h)

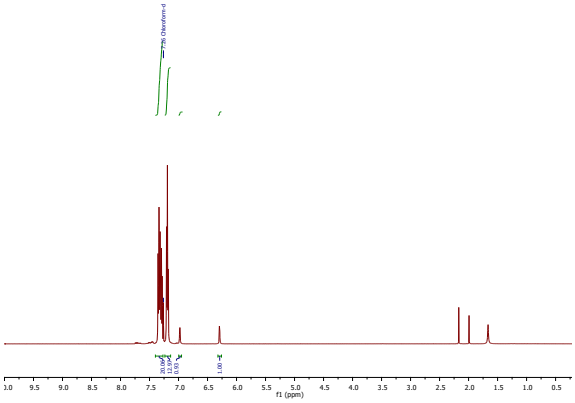
2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl azide (100 mg, 0.268 mmol) was reacted with 2,3;5,6-di-*O*-isopropylidene-1-*O*-propargyloxy-*β*-D-mannofuranos-1-yl (87.9 mg, 0.295 mmol) using Cu-catalyst **1** (11.8 mg, 0.016 mmol) according to the general procedure A to afford triazole derivative **7h**. Yield (93%); m.p.106 ^{o}C R_f= 0.5, (50% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 1H), 5.83 (d, *J* = 9.5 Hz, 1H), 5.54-5.50 (m, 2H), 5.24-5.21 (m, 1H), 5.04 (s, 1H), 4.78-4.75 (m, 2H), 4.62-4.58 (m, 2H), 4.41-4.38 (m, 1H), 4.23-4.09 (m, 4H), 4.04-3.97 (m, 2H), 2.20 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.87 (s, 3H), 1.44 (s, 6H), 1.36 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 169.8, 169.7, 169.0, 144.7, 121.0, 112.6, 109.1, 105.3, 86.1, 84.9, 80.5, 79.4, 73.9, 73.0, 70.6, 67.7, 66.8, 66.7, 61.1, 59.9, 26.8, 25.7, 25.1, 24.4, 20.5, 20.4 and 20.2 ppm.

1-(2,3,4,6-Tri-*O*-acetyl-4-*O*(2',3',4',6'-tetra-*O*-acetyl-*β*-D-galacopyranosyl)-*β*-D-glucopyranos-1-yl)4-(n-hexane)-[1,2,3]-triazole (7i)

2,3,4,6-Tri-*O*-acetyl-4-*O*(2',3',4',6'-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-*β*-D-glucopyranosyl azide (100 mg, 0.151 mmol) was reacted with 1-octyne (24.7 µl, 0.179 mmol) using Cu-catalyst **1** (7.5 mg, 0.010 mmol) according to the general procedure A to afford triazole derivative **7i**. Yield (96%); white solid; m.p. 102^{o}C; R_f= 0.45, (50% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (s, 1H), 5.77-5.76 (m, 1H), 5.38-5.32 (m, 3H), 5.1-5.07 (m, 1H), 4.95-4.92 (m, 1H), 4.49-4.42 (m, 2H), 4.13-4.04 (m, 3H), 3.93-3.85 (m, 3H), 2.67-2.64 (m, 2H), 2.12 (s, 3H), 2.06-2.02 (m, 12H), 1.93 (s, 3H), 1.82-1.80 (m, 3H), 1.64-1.58 (m, 2H), 1.31-1.21 (m, 7H), 0.85-0.82 (m, 3H); δ 170.3, 170.1, 170.0, 169.9, 169.4, 169.1, 168.9, 149.0, 118.6, 101.0, 85.3, 75.7, 75.6, 72.6, 70.8, 70.7, 70.3, 68.9, 66.5, 61.7, 60.7, 31.4, 28.9, 28.6, 25.5, 22.4, 20.7, 20.6, 20.58, 20.54, 20.4, 20.1 and 13.96 ppm.

Figure S16 ^{1}H NMR spectra of catalyst **1** up to 4 runs

RUN 1



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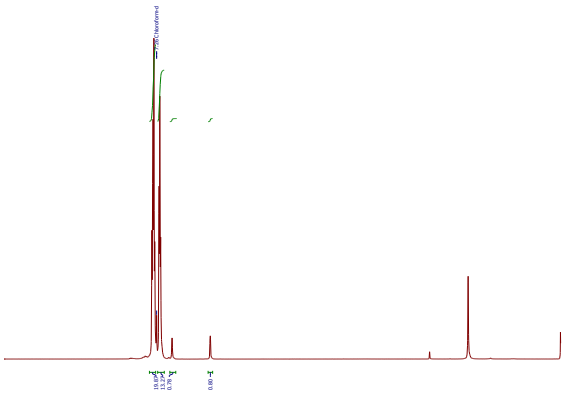
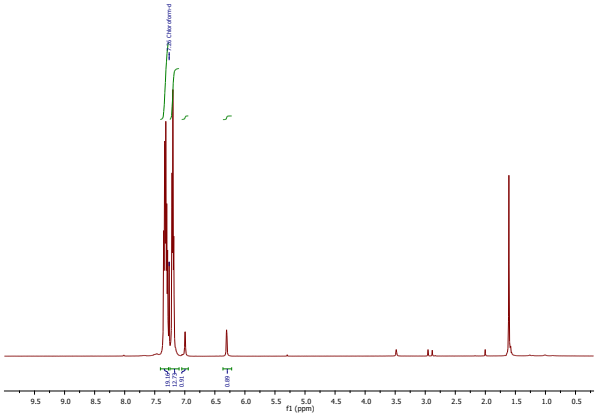


RUN 3



RUN 4