Electronic Supplementary Information

Ultrasound mediated efficient synthesis of spironaphthoquinolines

Manas M. Sarmah, Somadrita Borthakur, Debajyoti Bhuyan, and Dipak Prajapati*

Medicinal Chemistry Division, CSIR-North-East Institute of Science & Technology, Jorhat, Assam 785006, India

E-mail: dr_dprajapati2003@yahoo.co.uk

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General information

All the commercially available reagents were used as received. Melting points were measured with a Buchi M-560 melting point apparatus and are uncorrected. IR spectra were recorded on a SHIMADZU FTIR-8400 instrument. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on Avance DPX 500 MHz FT-NMR spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are given from TMS (0 ppm) and coupling constants are expressed in Hertz (Hz). ^{13}C NMR spectra were recorded on an Avance DPX 75 MHz FT-NMR spectrometer and Chemical shifts (δ) are given from $CDCl_3$ (77.0 ppm). Mass spectra were recorded on ESQUIRE 3000 Mass spectrometer. All experiments were monitored by thin layer chromatography (TLC). TLC was performed on a pre-coated silica gel plates (Merck). After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by stating $KMnO_4$ and warming in a hot air oven. Column chromatography was performed on silica gel (100-200 mesh, Merck) using ethyl acetate-hexane as eluent.

Ultrasound instrumentation

All ultrasound reactions were carried out in a Cole-Parmer 130-Watt ultrasonic processor (Model 04714-51) at 70% amplitude. The instrument is microprocessor controlled and can tune automatically to eliminate the need for constant adjustment. The amount of power delivered to the probe is displayed by the digital wattmeter. The variable power output control permits the ultrasonic vibrations at the probe tip to be put to any desired amplitude. The timer controls the processing time from 1 sec to 10 h and a pulser enables safe treatment of temperature-sensitive samples of high intensity.

Experimental data

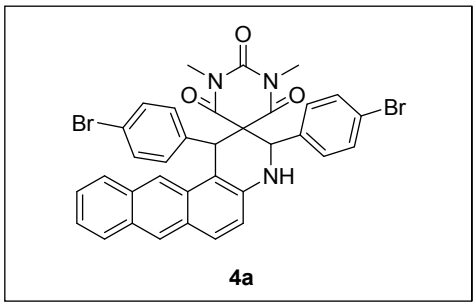
General procedure

(a) **Under ultrasound conditions**: A mixture of 2-aminoanthracene (**1**, 1 mmol), 4-bromobenzaldehyde (**2a**, 1 mmol), and 5-(4-bromobenzylidene)-1,3-dimethylpyrimidine-2,4,6-trione (**3a**, 1 mmol) was dissolved in ethanol (10 ml) by warming and the reddish brown solution was irradiated with ultrasounds for 45 min without catalyst in a Cole-Parmer 130-Watt ultrasonic processor (Model 04714-51) at 70% amplitude. After reaction the reaction mixture was allowed settle down at room temperature which was followed by the addition of cold distilled water (10 ml) to the reaction mixture. The yellow solid so formed was separated from solvents by simple Buchner filtration, washed with cold ethanol (3×20 ml), and dried to obtain pure 1,3-bis(4-bromophenyl)-1′,3′-dimethyl-3,4-dihydrospiro[naphtho[2,3-*f*]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione(**4a**).
Similar processes were performed to obtain products **4b-v**.

(b) **Under classical conditions**: A mixture of 2-aminoanthracene (**1**, 1 mmol), 4-bromobenzaldehyde (**2a**, 1 mmol), and 5-(4-bromobenzylidene)-1,3-dimethylpyrimidine-2,4,6-trione (**3a**, 1 mmol) was dissolved in ethanol (10 ml) and the reaction mixture was refluxed for 5 hours without catalyst.

After reaction, as indicated by TLC, the reaction mixture was allowed settle down at room temperature which was followed by the addition of cold distilled water (10 ml) to the reaction mixture. The yellow solid so formed was separated from solvents by simple Buchner filtration, washed with cold ethanol (3×20 ml), and dried to obtain pure 1,3-bis(4-bromophenyl)-1′,3′-dimethyl-3,4-dihydrospiro[naphtho[2,3-*f*]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione(**4a**).

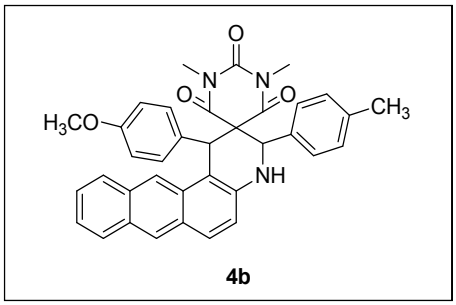
Characterization data of the products



4a

*1,3-bis(4-bromophenyl)-1′,3′-dimethyl-3,4-dihydrospiro[naphtho[2,3-f]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione**4a***

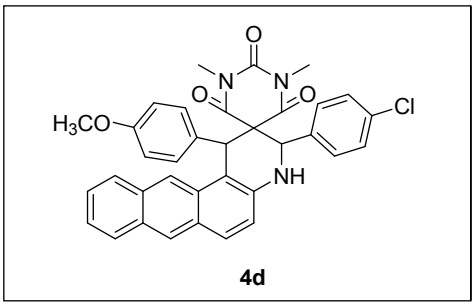
Yield: 87%. m. p. 247-249 ^{o}C; greenish yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29-6.34 (m,16H), 5.69 (s, 1H), 4.92 (s, 1H), 4.64 (s, 1H), 3.14 (s, 3H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.36, 164.61, 149.55, 141.81, 138.29, 134.81, 132.15, 131.49, 131.45, 131.32, 129.84, 129.65, 129.37, 128.93, 128.51, 127.95, 127.54, 127.00, 125.33, 124.27, 123.74, 123.08, 121.22, 119.83, 110.20, 63.07, 62.10, 48.66, 28.65, 27.69. IR ($CHCl_3$): 3393.2, 1745.4, 1676.1, 1629.6 cm^{-1}. MS (GC-MS): *m/z* = 683 $[M]^+$. Anal.Calcd for $C_{34}H_{25}Br_2N_3O_3$: C, 59.76; H, 3.69;N, 6.15. Found: C, 59.78; H, 3.68;N, 6.13.



4b

*1-(4-methoxyphenyl)-1′,3′-dimethyl-3-(p-tolyl)-3,4-dihydrospiro[naphtho[2,3-f]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione**4b***

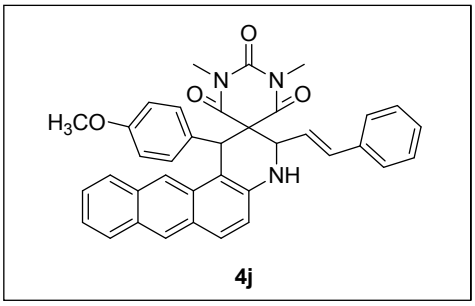
Yield: 86%. m. p. 215-217 ^{o}C; greenish yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27-7.00 (m, 16H), 5.65 (s, 1H), 4.91 (s, 1H), 4.68 (s, 1H), 3.79 (s, 3H), 3.12 (s, 3H), 2.81 (s, 3H), 2.18 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 170.95, 165.19, 160.18, 158.36, 150.06, 141.93, 139.39, 136.66, 136.10, 132.99, 131.24, 131.21, 131.17, 130.33, 129.52, 128.92, 128.13, 127.52, 126.75, 124.94, 123.92, 123.44, 120.17, 114.13, 113.54, 63.29, 55.17, 54.95, 48.69, 28.47, 27.61, 20.92. IR ($CHCl_3$): 3390.0, 1742.7, 1674.6, 1628.4cm^{-1}. MS (GC-MS): *m/z* = 569 $[M]^+$. Anal.Calcd for $C_{36}H_{31}N_3O_4$: C, 75.90; H, 5.49; N, 7.38; O. Found: C, 75.88; H, 5.47; N, 7.37.



4d

*3-(4-chlorophenyl)-1-(4-methoxyphenyl)-1′,3′-dimethyl-3,4-dihydrospiro[naphtho[2,3-f]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione**4d***

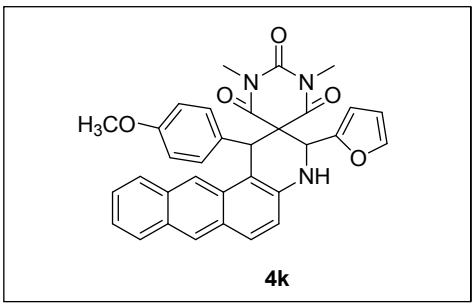
Yield: 88%. m. p. 229-231°C; greenish yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29-6.40(m, 16H), 5.71 (s, 1H), 4.94 (s, 1H), 4.66 (s, 1H), 3.80 (s, 3H), 3.12 (s, 3H), 2.81 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 170.56, 164.82, 160.33, 142.09, 141.82, 138.11, 137.79, 135.57, 134.31, 133.04, 132.81, 131.32, 129.34, 129.18, 128.37, 128.24, 128.06, 127.95, 127.54, 126.99, 126.91, 125.31, 125.22, 124.26, 124.14, 123.10, 119.93, 119.84, 114.17,62.99, 55.21, 48.59, 48.13, 28.63, 27.67.IR ($CHCl_3$): 3387.9, 1744.3, 1675.2, 1628.8 cm^{-1}. MS (GC-MS): *m/z* = 589 $[M]^+$. Anal.Calcd for $C_{35}H_{28}ClN_3O_4$: C, 71.24; H, 4.78;N, 7.12. Found: C, 71.20; H, 4.77;N, 7.10.



4j

*1-(4-methoxyphenyl)-1′,3′-dimethyl-3-styryl-3,4-dihydrospiro[naphtho[2,3-f]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione **4j***

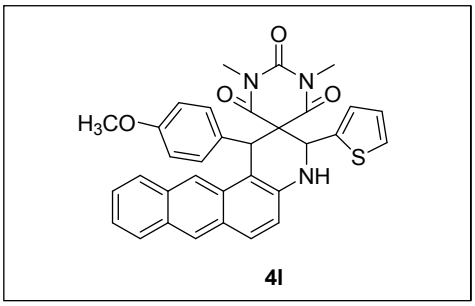
Yield: 85%. m. p. 204-206°C; brownish yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51-6.11 (m, 19H), 5.65 (s, 1H), 4.90 (s, 1H), 4.66 (s, 1H), 3.79 (s, 3H), 3.12 (s, 3H), 2.81 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 170.94, 165.19, 160.17, 158.35, 157.25, 154.22, 150.01, 141.91, 131.23, 131.15, 130.75, 130.28, 129.14, 129.04, 129.00, 128.93, 128.76, 128.64, 128.07, 127.87, 127.49, 126.66, 124.94, 123.97, 123.43, 120.12, 114.12, 113.54, 113.46, 110.92, 62.97, 55.18, 54.95, 48.67, 28.51, 27.61. IR ($CHCl_3$): 3383.3, 1742.0, 1673.9, 1627.8, cm^{-1}. MS (GC-MS): *m/z* = 581 $[M]^+$. Anal.Calcd for $C_{37}H_{31}N_3O_4$: C, 76.40; H, 5.37; N, 7.22. Found: C, 76.39; H, 5.36; N, 7.20.



4k

3-(furan-2-yl)-1-(4-methoxyphenyl)-1′,3′-dimethyl-3,4-dihydrospiro[naphtho[2,3-f]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione ***4k***

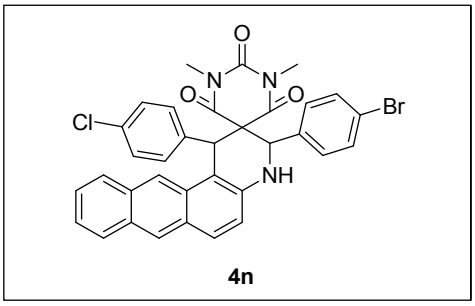
Yield: 83%. m. p. 223-225°C; blackish brown solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24-6.79 (m, 15H), 5.65 (s, 1H), 4.90 (s, 1H), 4.66 (s, 1H), 3.79 (s, 3H), 3.12 (s, 3H), 2.81 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 170.94, 165.19, 160.17, 158.34, 150.01, 141.90, 131.22, 131.14, 130.74, 130.27, 129.13, 128.93, 128.75, 128.06, 127.86, 127.49, 126.65, 124.94, 123.97, 123.43, 120.11, 114.13, 113.54, 113.46, 110.92, 62.97, 55.18, 54.95, 48.66, 28.51, 27.61. IR ($CHCl_3$): 3384.0, 1743.0, 1674.8, 1627.4 cm^{-1}. MS (GC-MS): *m/z* = 545 $[M]^+$. Anal.Calcd for $C_{33}H_{27}N_3O_5$: C, 72.65; H, 4.99; N, 7.70. Found: C, 72.61; H, 4.96; N, 7.68.



4l

1-(4-methoxyphenyl)-1′,3′-dimethyl-3-(thiophen-2-yl)-3,4-dihydrospiro[naphtho[2,3-f]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione ***4l***

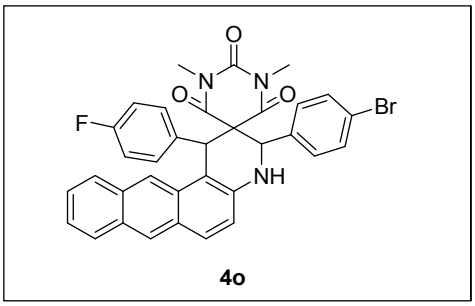
Yield: 83%. m. p. 197-199°C; golden yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30-6.83 (m, 15H), 5.65 (s, 1H), 4.90 (s, 1H), 4.66 (s, 1H), 3.80 (s, 3H), 3.12 (s, 3H), 2.81 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 152.68, 148.86, 145.35, 141.79, 132.27, 130.75, 130.41, 129.27, 129.14, 128.92, 128.11, 127.87, 127.76, 127.48, 126.65, 126.11, 125.52, 125.16, 123.96, 123.42, 121.35, 120.12, 117.81, 114.12, 113.54, 113.46, 62.97, 55.17, 54.94, 48.67, 28.81, 28.01.IR ($CHCl_3$): 3378.7, 1728.7, 1668.4, 1629.0 cm^{-1}. MS (GC-MS): *m/z* = 561 $[M]^+$. Anal.Calcd for $C_{33}H_{27}N_3O_4S$: C, 70.57; H, 4.85; N, 7.48. Found C, 70.55; H, 4.80; N, 7.46.



4n

3-(4-bromophenyl)-1-(4-chlorophenyl)-1′,3′-dimethyl-3,4-dihydrospiro[naphtho[2,3-f]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione ***4n***

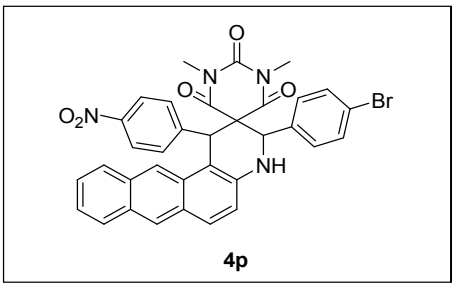
Yield: 88%. m. p. 243-245°C; greenish yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29-7.08 (m,16H), 5.70 (s, 1H), 4.92 (s, 1H), 4.64 (s, 1H), 3.14 (s, 3H), 2.81 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 170.38, 164.60, 149.56, 141.81, 138.30, 137.79, 135.57, 134.81, 134.31, 133.04, 132.14, 131.45, 131.33, 129.67, 129.35, 129.18, 128.52, 128.37, 128.23, 127.95, 127.55, 127.00, 125.33, 124.27, 123.73, 123.10, 121.22, 119.83, 110.18, 63.05, 62.25, 48.65, 28.64, 27.68. IR ($CHCl_3$):3391.8, 1745.3, 1675.8, 1629.4 cm^{-1}. MS (GC-MS): *m/z* = 637 $[M]^+$. Anal.Calcd for $C_{34}H_{25}BrClN_3O_3$: C, 63.91; H, 3.94; N, 6.58. Found: C, 63.88; H, 3.93; N, 6.55.



4o

3-(4-bromophenyl)-1-(4-fluorophenyl)-1′,3′-dimethyl-3,4-dihydrospiro[naphtho[2,3-f]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione ***4o***

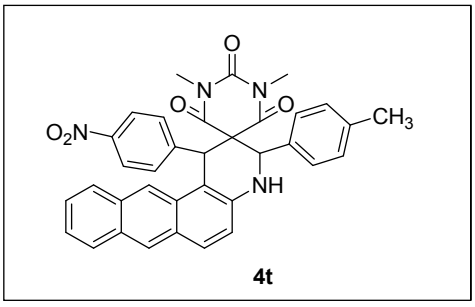
Yield: 87%.brown solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29-6.96 (m, 16H), 5.69 (s, 1H), 4.91 (s, 1H), 4.65 (s, 1H), 3.14 (s, 3H), 2.81 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 170.36, 164.61, 149.60, 141.81, 138.41, 134.82, 132.14, 131.59, 131.45, 131.30, 129.84, 129.66, 129.36, 128.93, 128.51, 127.95, 127.53, 126.98, 125.32, 124.24, 123.73, 123.20, 123.08, 121.22, 119.82, 116.10, 115.93, 110.19, 63.07, 62.10, 48.67, 28.60, 27.65. IR ($CHCl_3$): 3394.1, 1743.9, 1676.3, 1628.7 cm^{-1}. MS (GC-MS): *m/z* = 621 $[M]^+$. Anal.Calcd for $C_{34}H_{25}BrFN_3O_3$: C, 65.60; H, 4.05;N, 6.75. Found: C, 65.58; H, 4.02;N, 6.71.



4p

3-(4-bromophenyl)-1′,3′-dimethyl-1-(4-nitrophenyl)-3,4-dihydrospiro[naphtho[2,3-f]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione ***4p***

Yield: 87%. m. p. 246-248^{o}C; yellowsolid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25-7.03(m, 16H), 5.92 (s, 1H), 4.91 (s, 1H), 4.69 (s, 1H), 3.15 (s, 3H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.00, 165.79, 150.48, 146.75, 141.46, 136.95, 131.82, 131.51, 131.24, 129.80, 128.98, 128.42, 128.17, 127.95, 127.67, 127.46, 127.09, 125.87, 123.51, 122.15, 120.23, 117.84, 104.62, 64.19, 62.84, 55.43, 54.61, 46.68, 31.02, 28.91, 28.56, 27.84.IR ($CHCl_3$): 3394.6, 1745.7, 1677.5, 1629.8 cm^{-1}. MS (GC-MS): *m/z* = 248 $[M]^+$. Anal.Calcd for $C_{34}H_{25}BrN_4O_5$: C, 62.88; H, 3.88; N, 8.63. Found: C, 62.84; H, 3.86;N, 8.62.



4t

1′,3′-dimethyl-1-(4-nitrophenyl)-3-(p-tolyl)-3,4-dihydrospiro[naphtho[2,3-f]quinoline-2,5′-pyrimidine]-2′,4′,6′-trione ***4t***

Yield: 82%. m. p. 268-270^{o}C; yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29-7.07 (m, 16H), 5.96 (s, 1H), 4.86 (s, 1H), 4.76 (s, 1H), 3.11 (s, 3H), 2.81 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.07,

165.88, 151.30, 150.50, 149.60, 146.62, 141.64, 139.22, 138.31, 134.23, 132.29, 131.98, 131.34, 130.33, 129.20, 128.16, 127.46, 125.84, 124.04, 117.80, 107.39, 104.89, 64.84, 63.15, 55.59, 47.05, 46.41, 31.02, 29.01, 28.80, 28.49, 27.78, 20.99.IR ($CHCl_3$): 3400.2, 1745.2, 1676.4, 1628.8 cm^{-1}.MS (GC-MS): *m/z* = 584$[M]^+$. Anal.Calcd for $C_{35}H_{28}N_4O_5$: C, 71.91; H, 4.83; N, 9.58. Found:C,71.88; H, 4.81; N, 9.57.

NMR spectra of the products

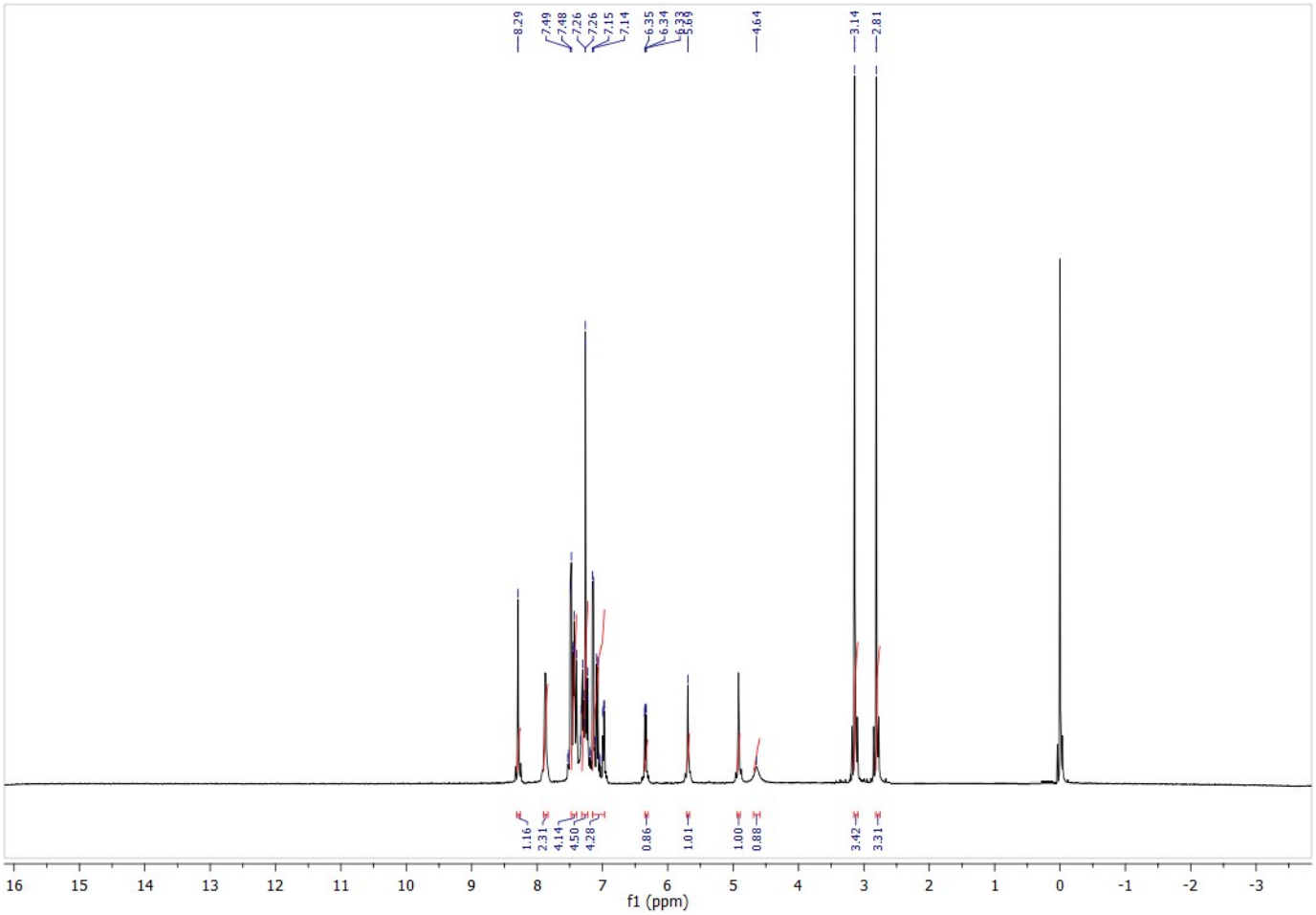


Fig S-1: ^{1}H NMR Spectrum of Product **4a**

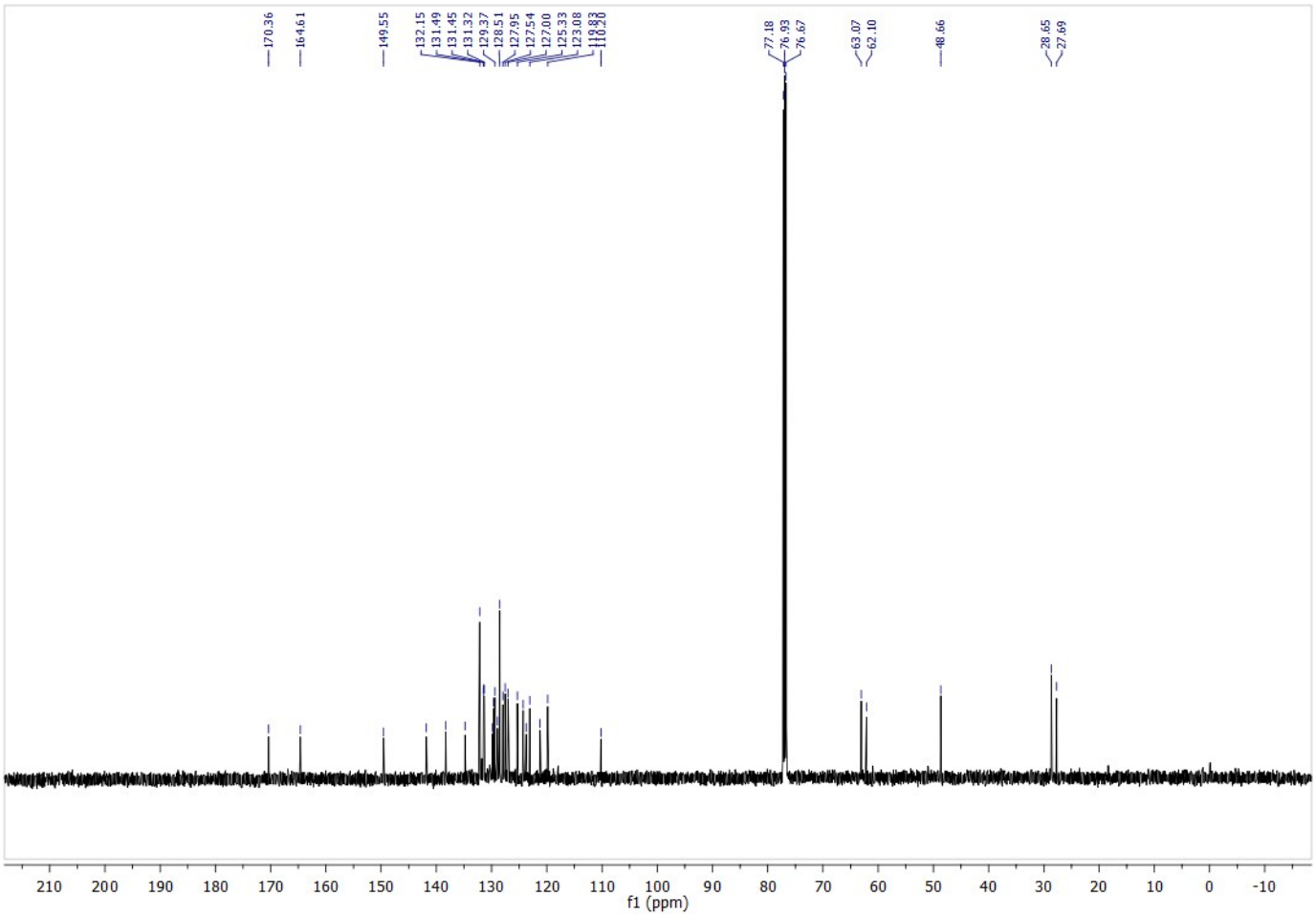


Fig S-2: ^{13}C NMR Spectrum of Product **4a**

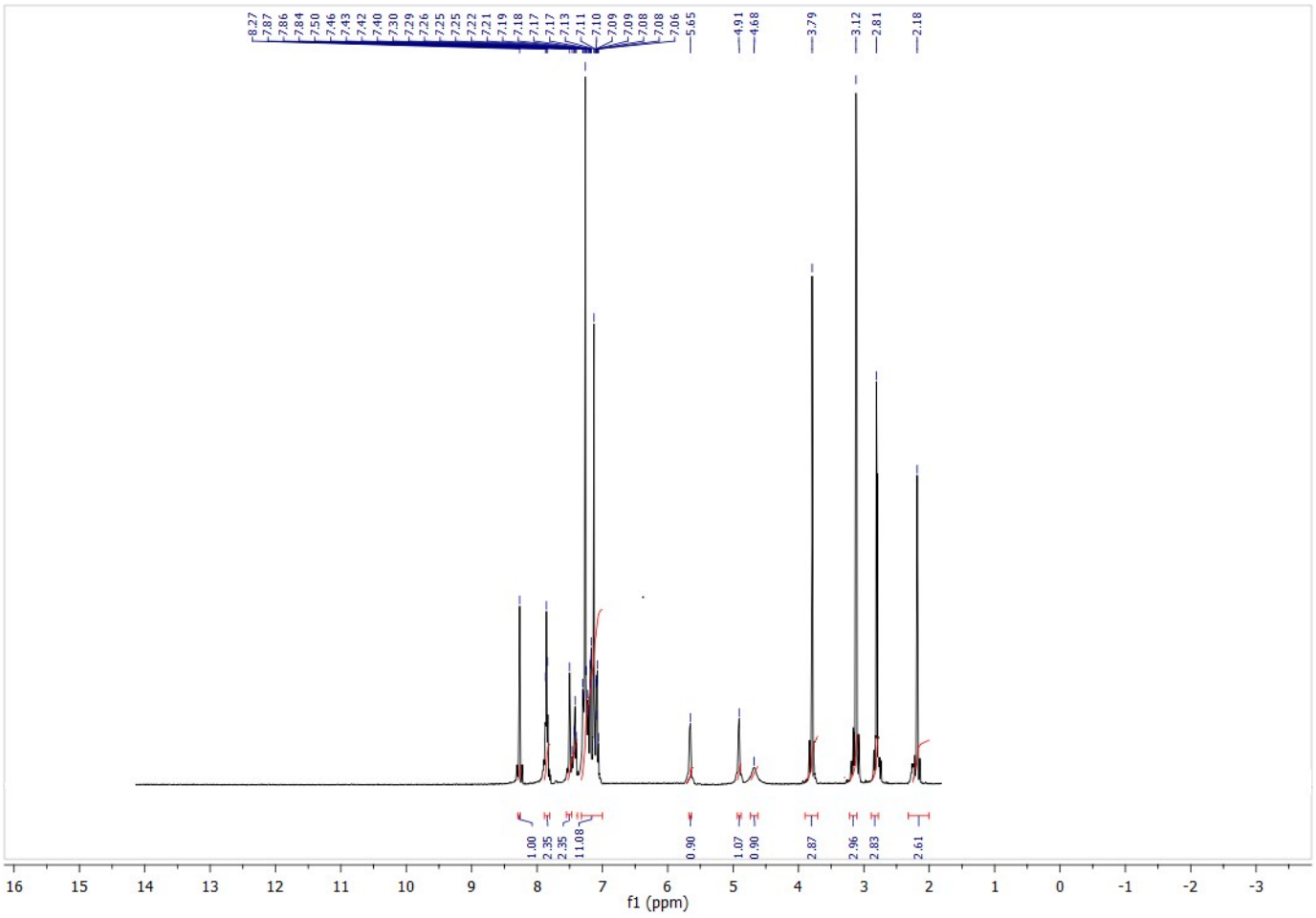


Fig S-3: ^{1}H NMR Spectrum of Product **4b**

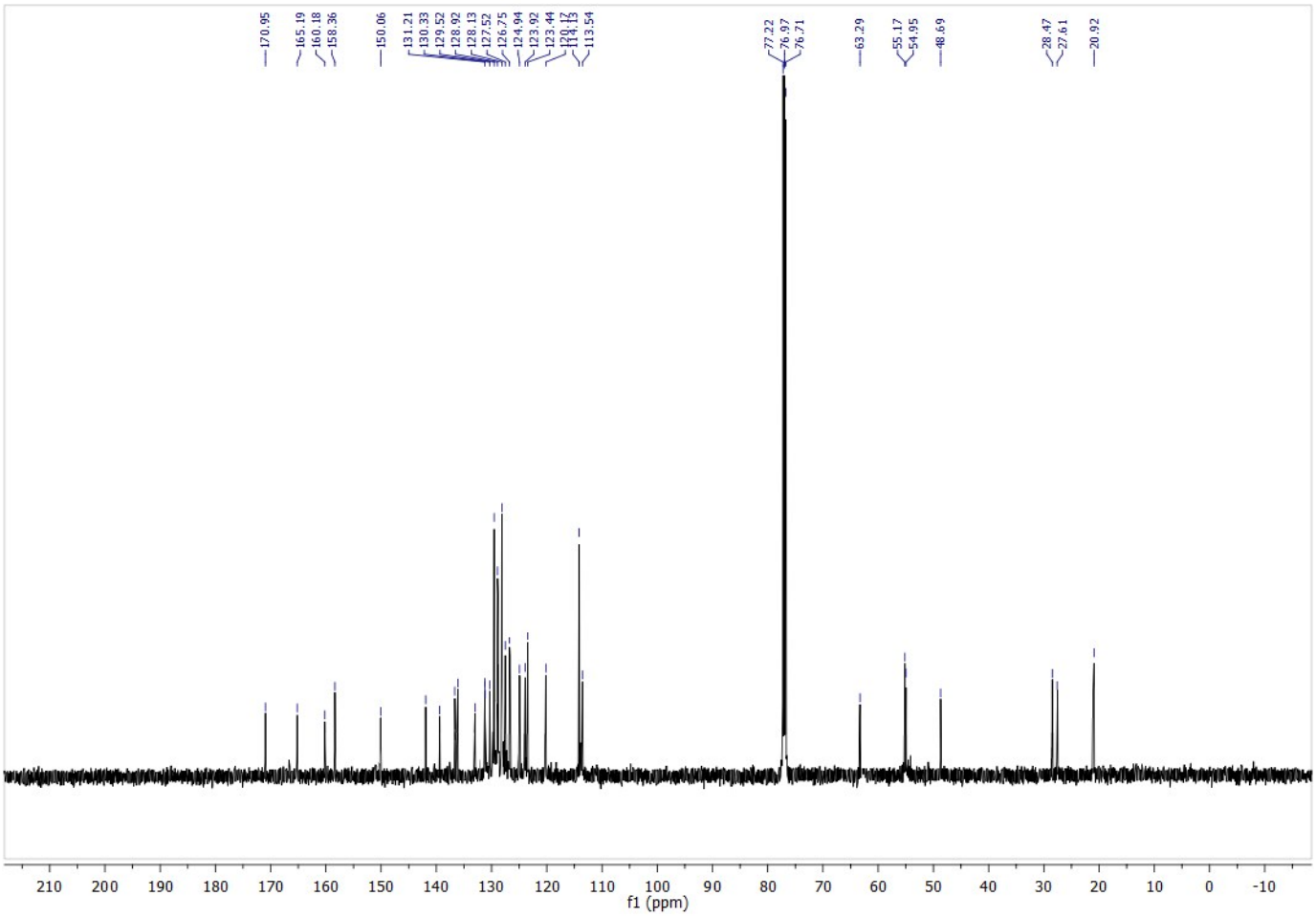


Fig S-4: ^{13}C NMR Spectrum of Product **4b**

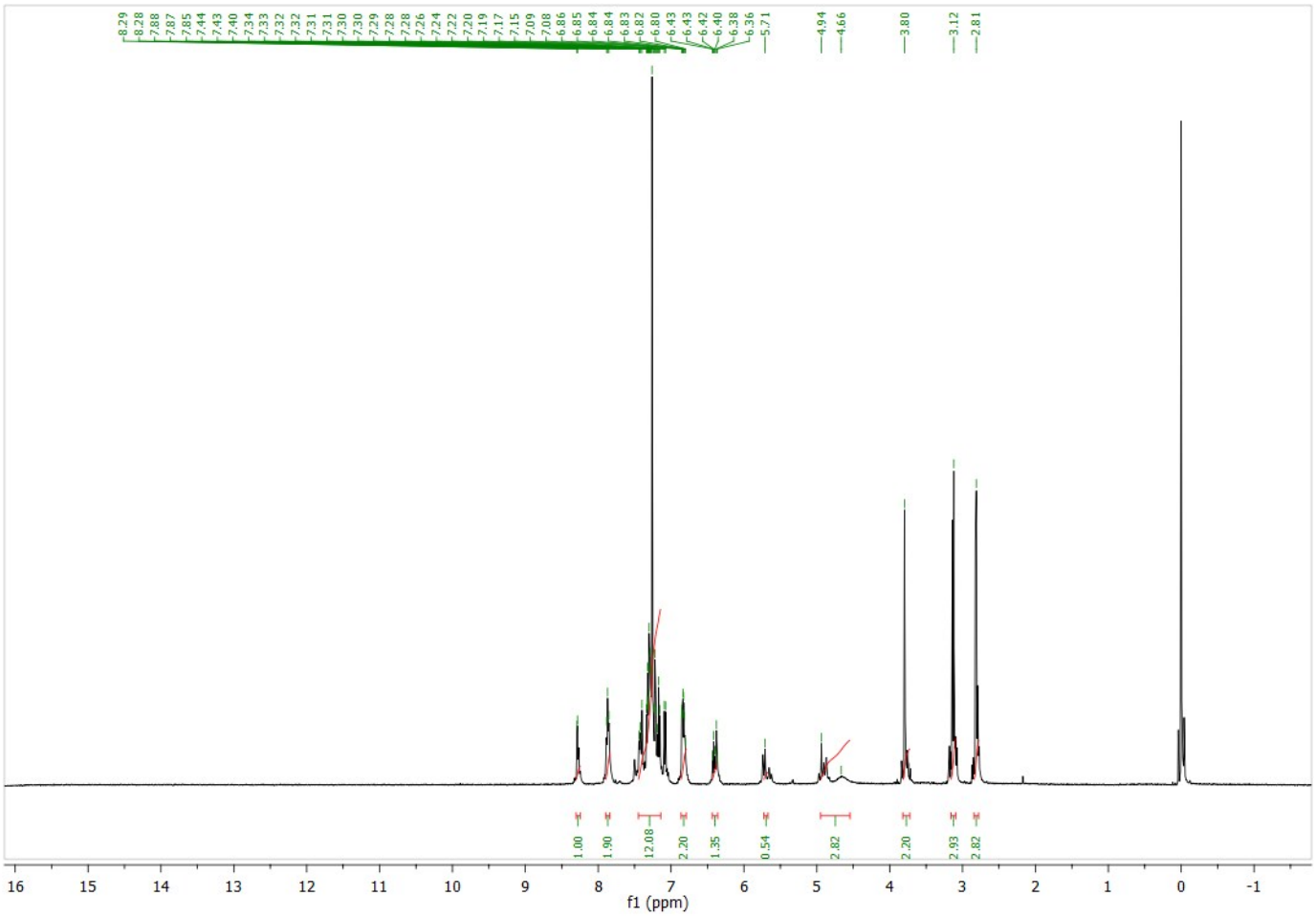


Fig S-5: [1]H NMR Spectrum of Product **4d**

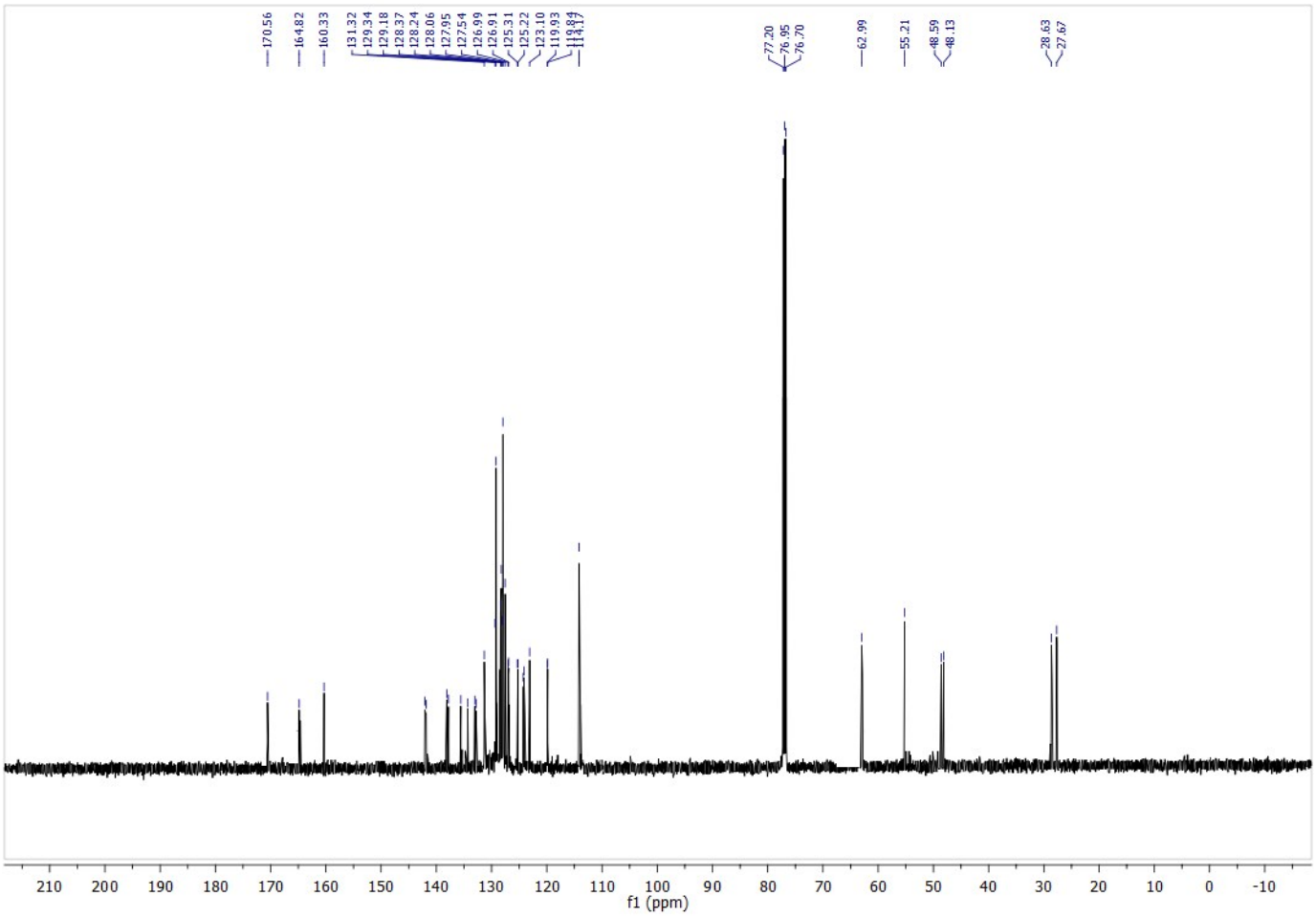


Fig S-6: ^{13}C NMR Spectrum of Product **4d**

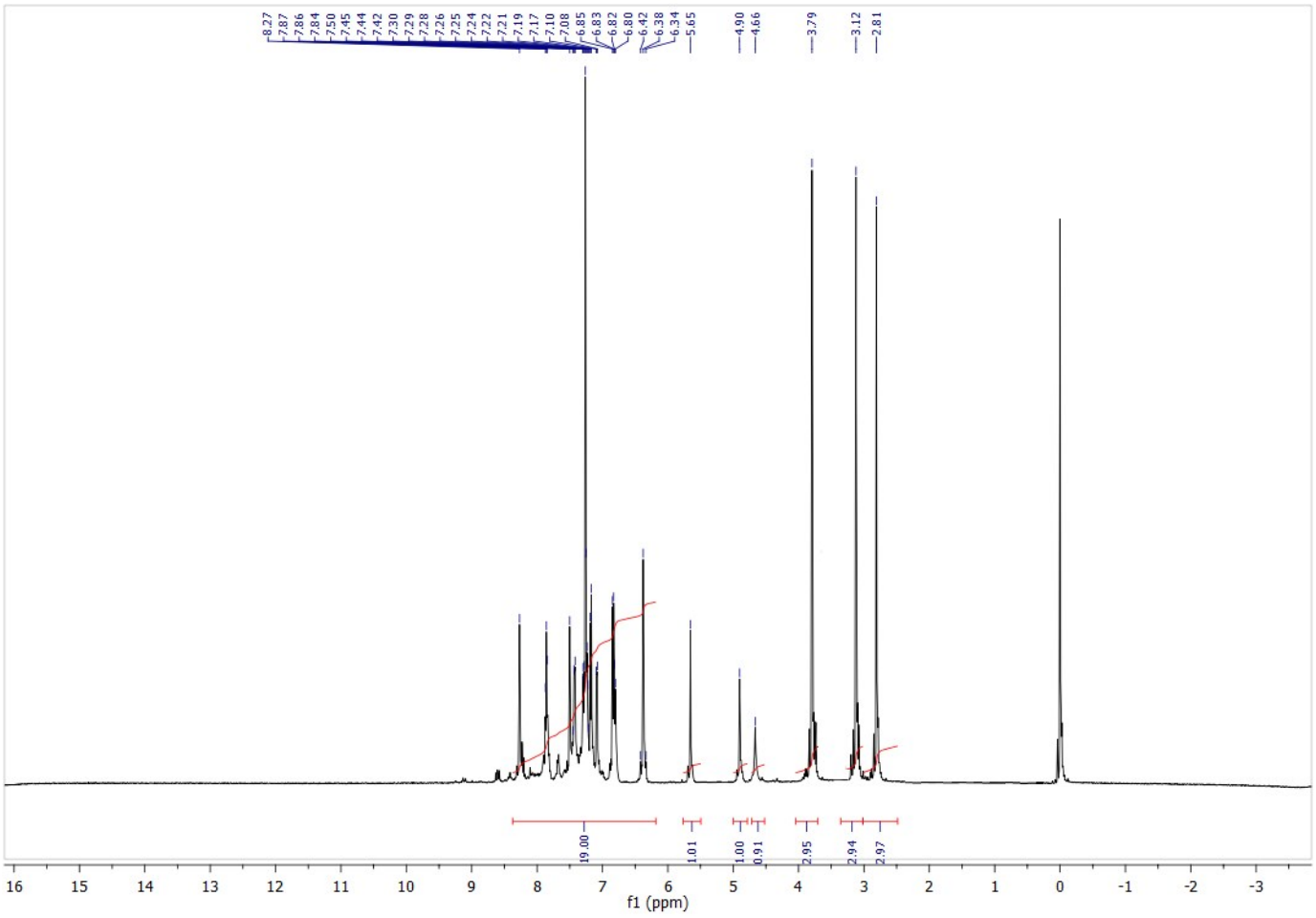


Fig S-7: ^{1}H NMR Spectrum of Product **4j**

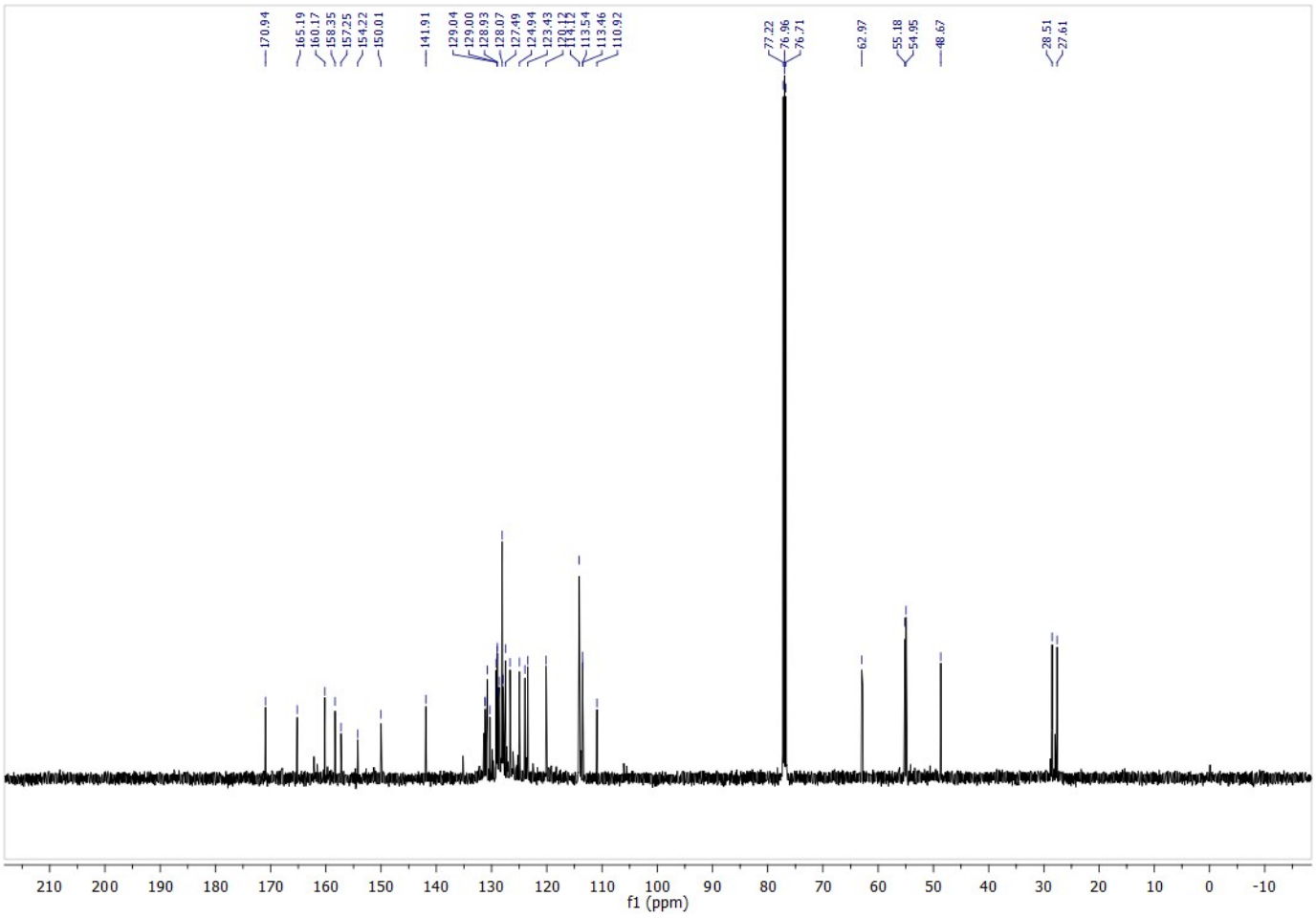


Fig S-8: ^{13}C NMR Spectrum of Product **4j**

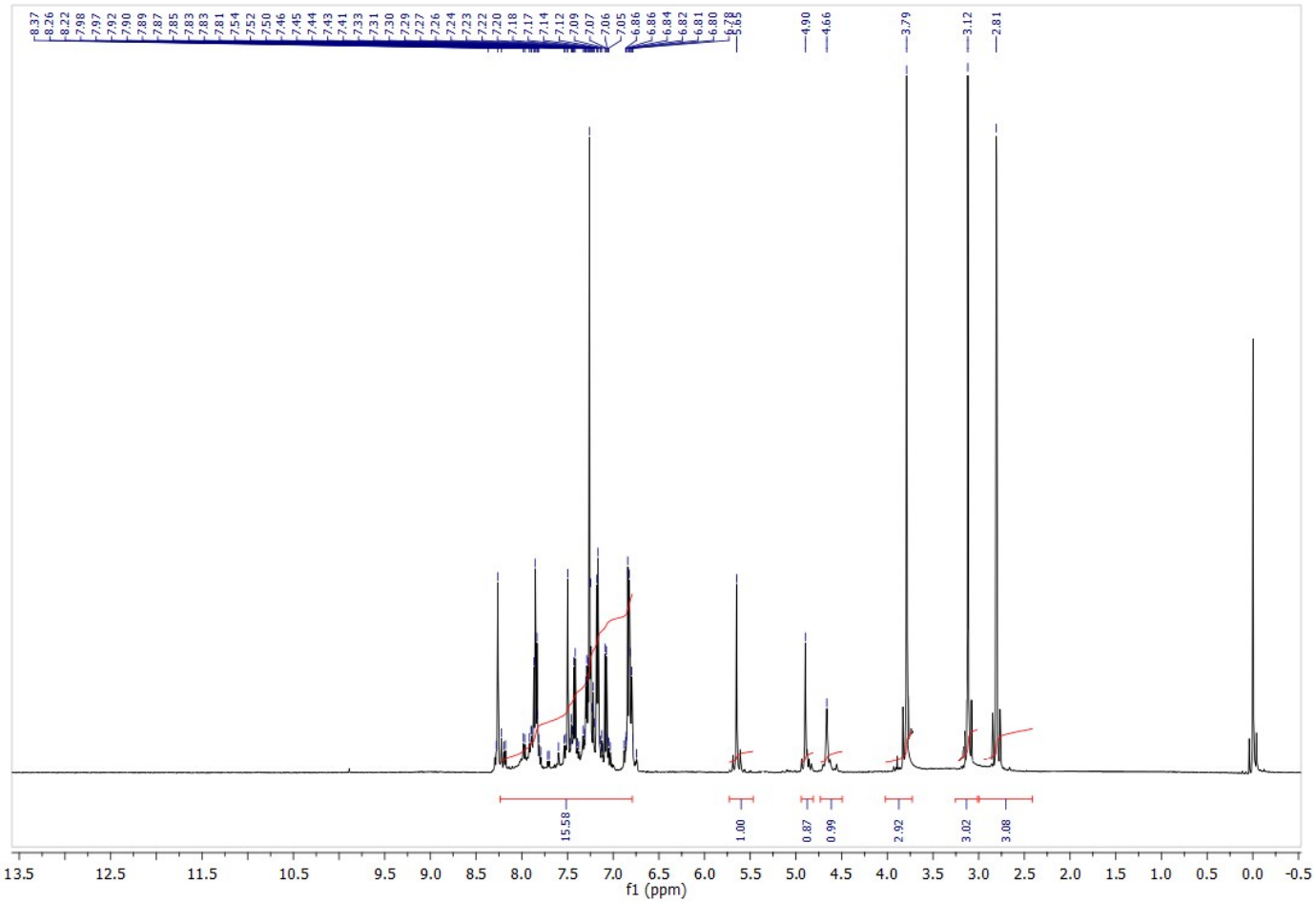


Fig S-9: ^{1}H NMR Spectrum of Product **4k**

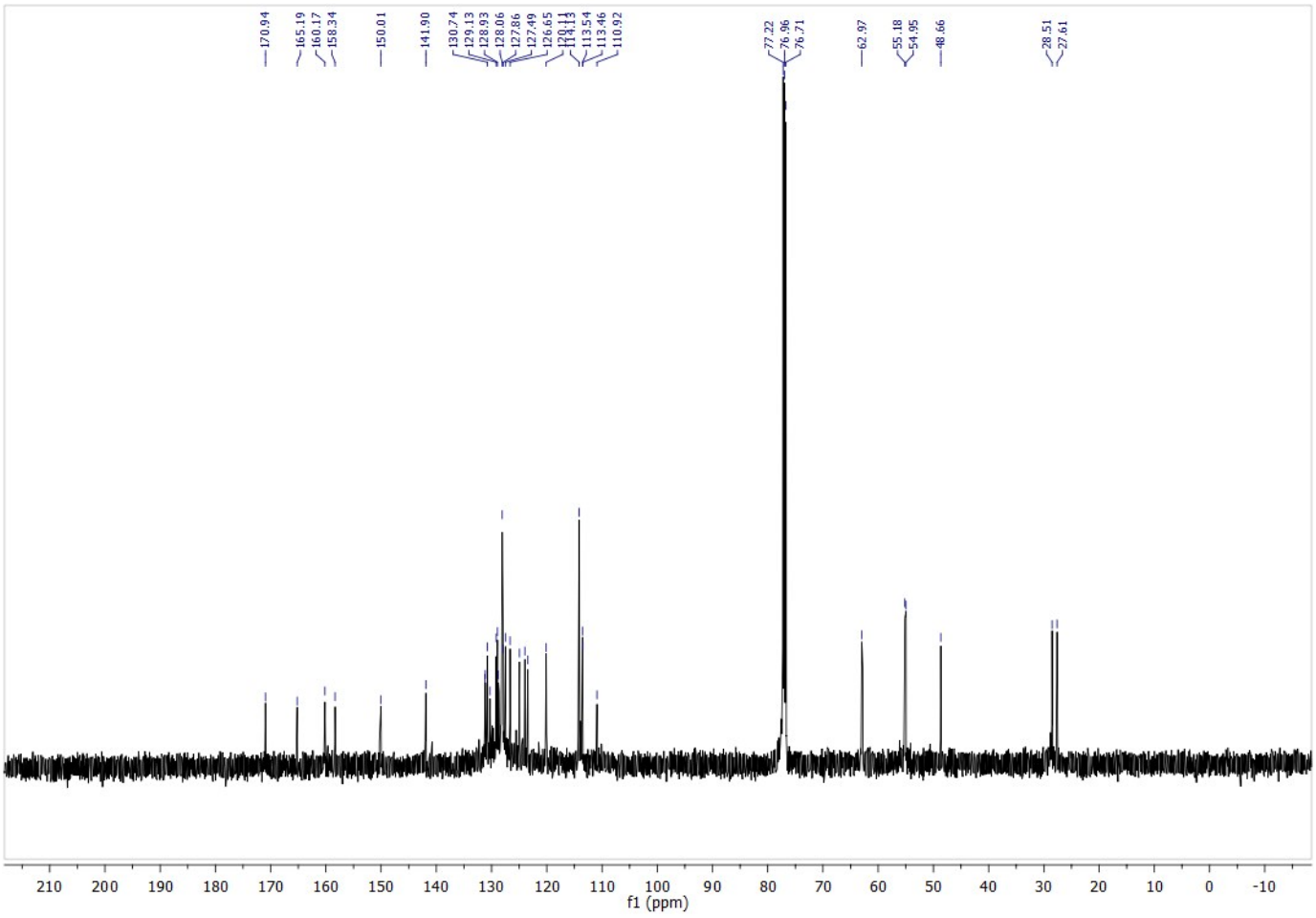


Fig S-10: ^{13}C NMR Spectrum of Product **4k**

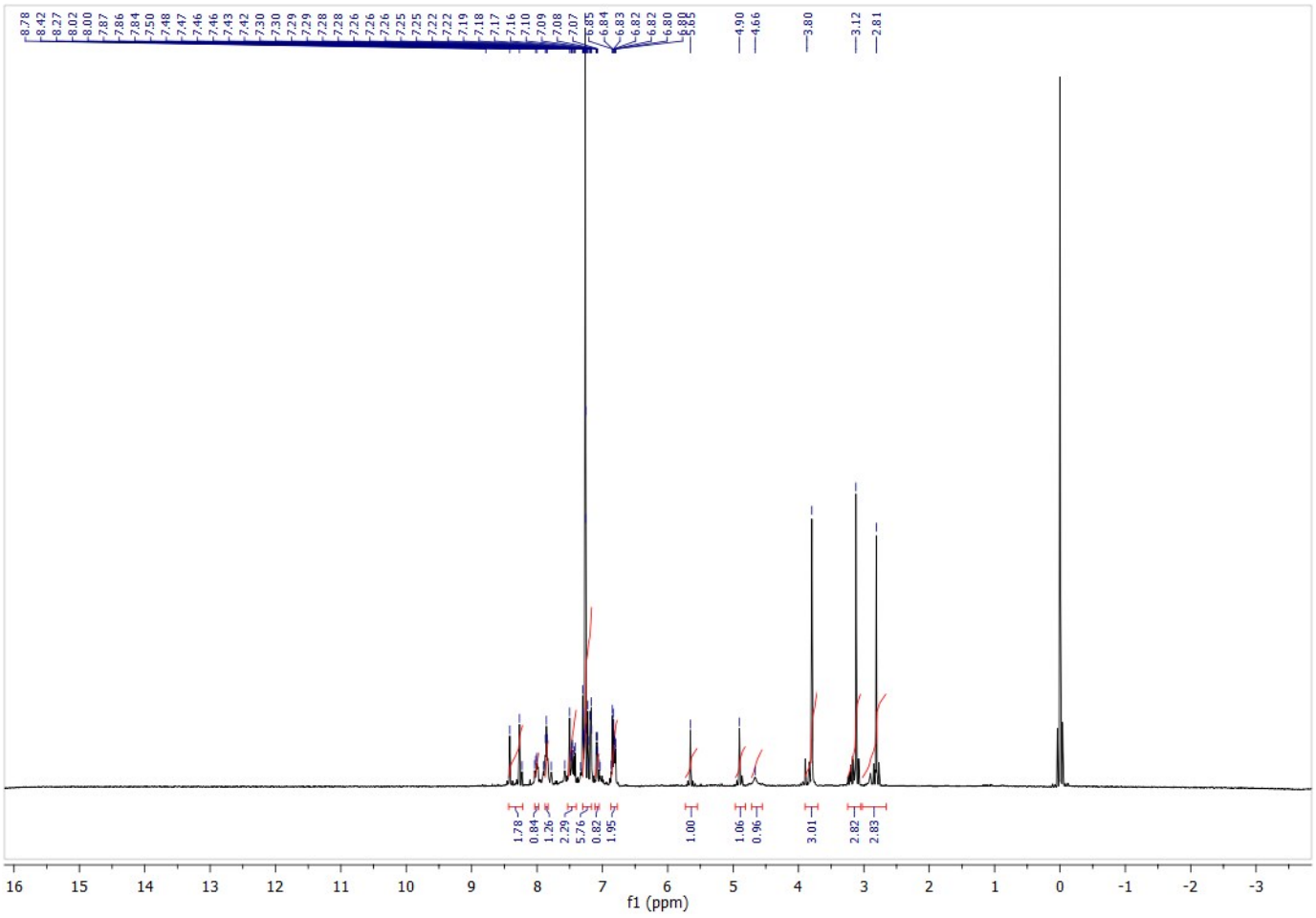


Fig S-11: ^{1}H NMR Spectrum of Product **4l**

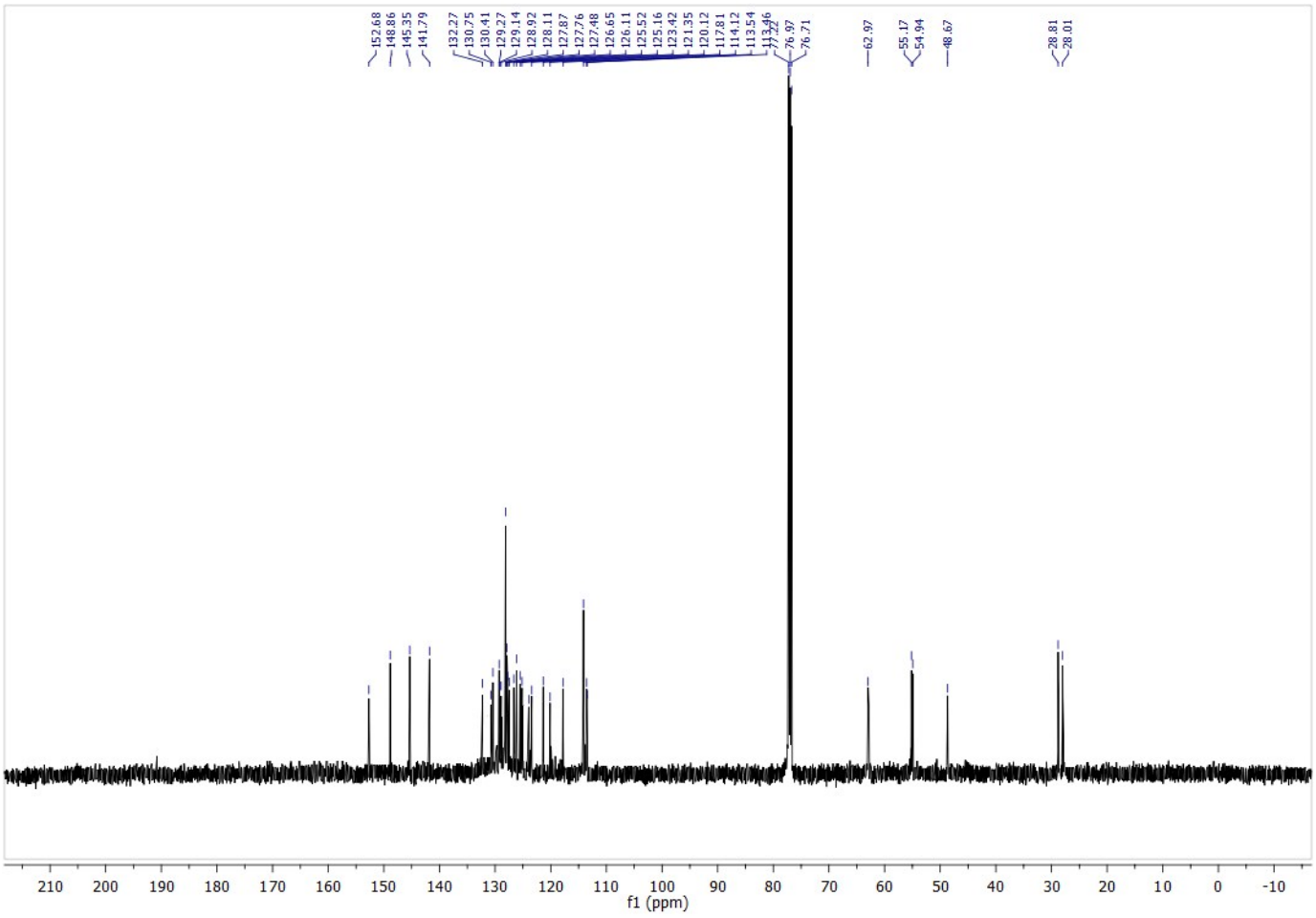


Fig S-12: ^{13}C NMR Spectrum of Product **4l**

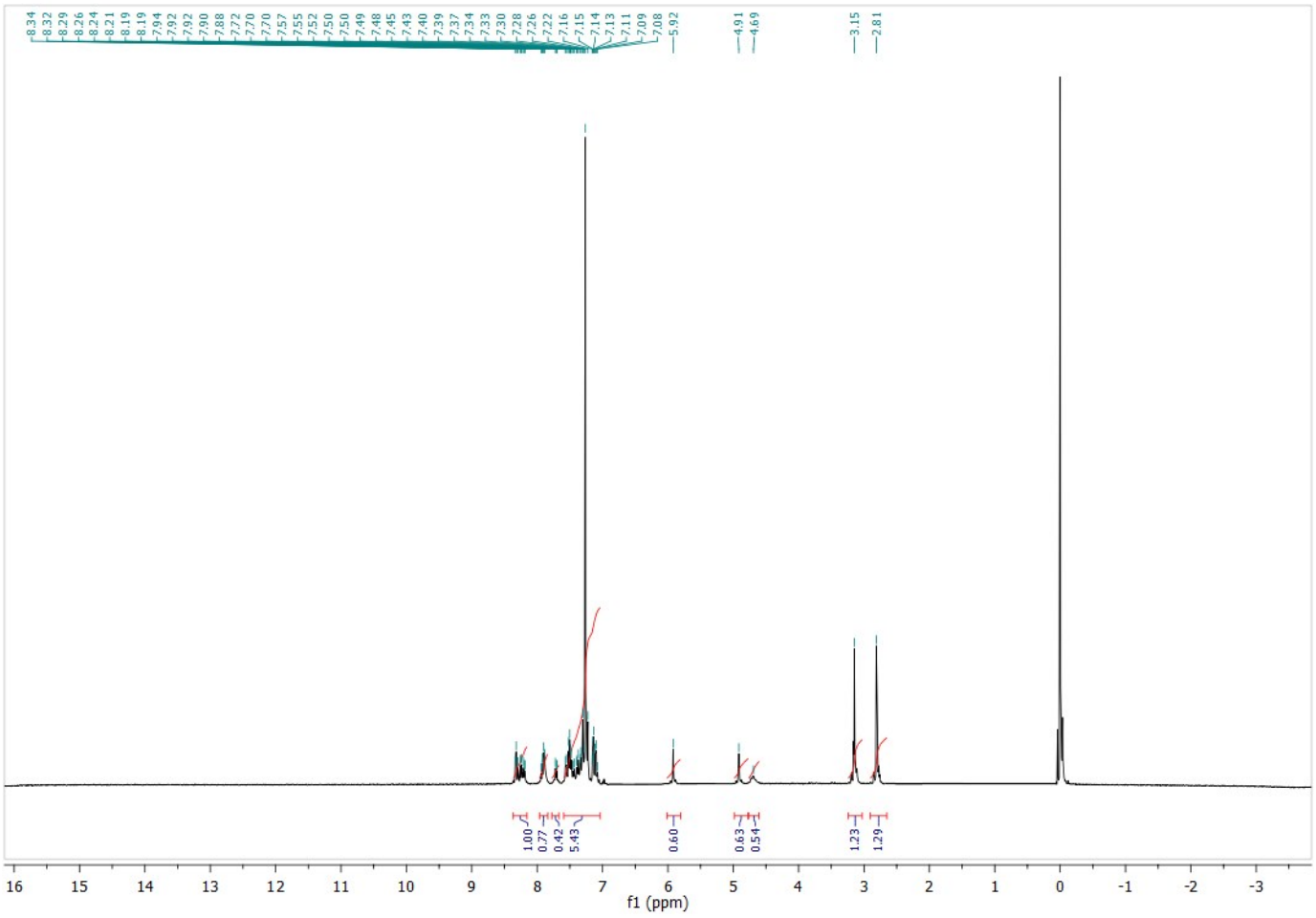


Fig S-13: ^{1}H NMR Spectrum of Product 4n

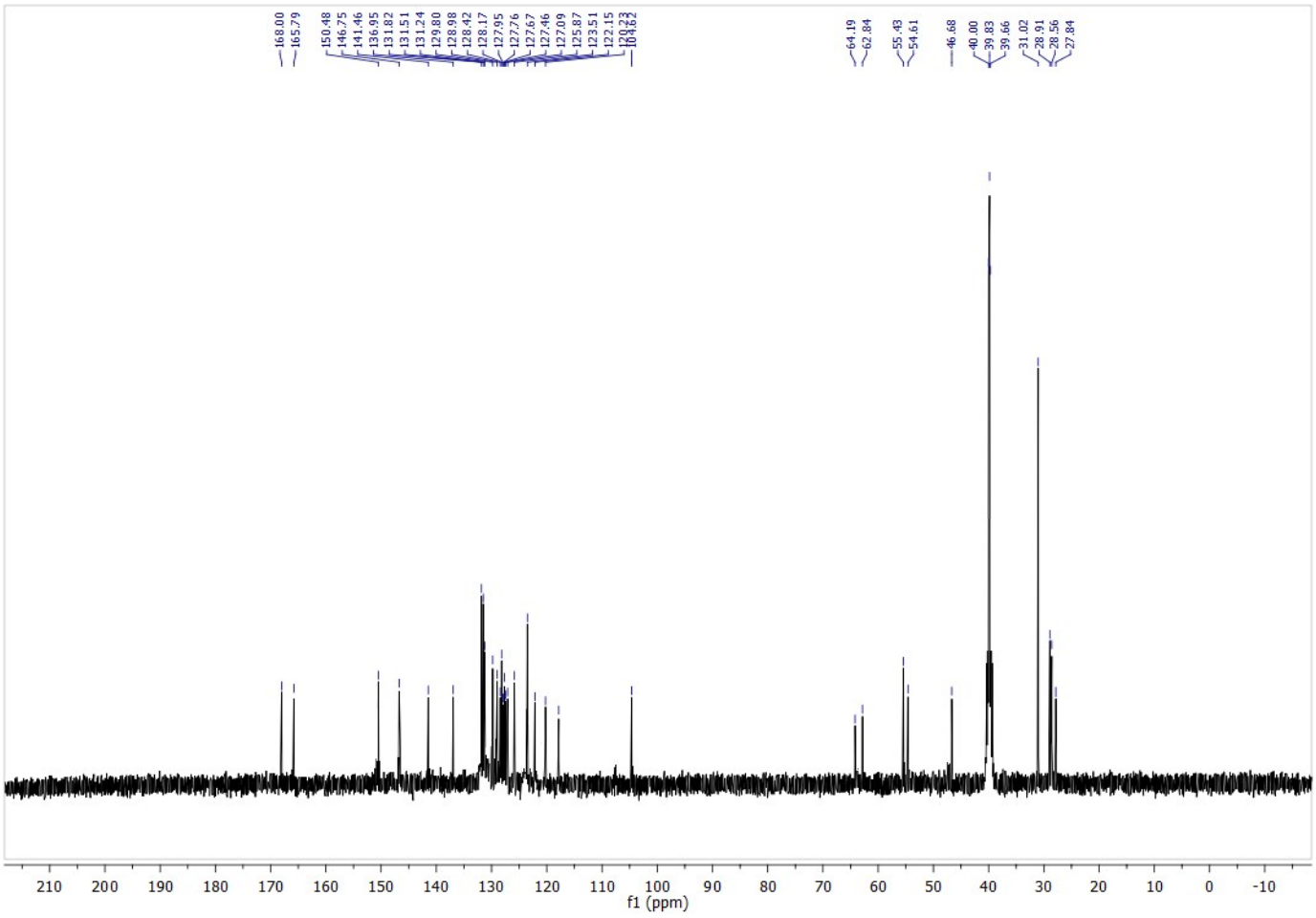


Fig S-14: ^{13}C NMR Spectrum of Product 4n

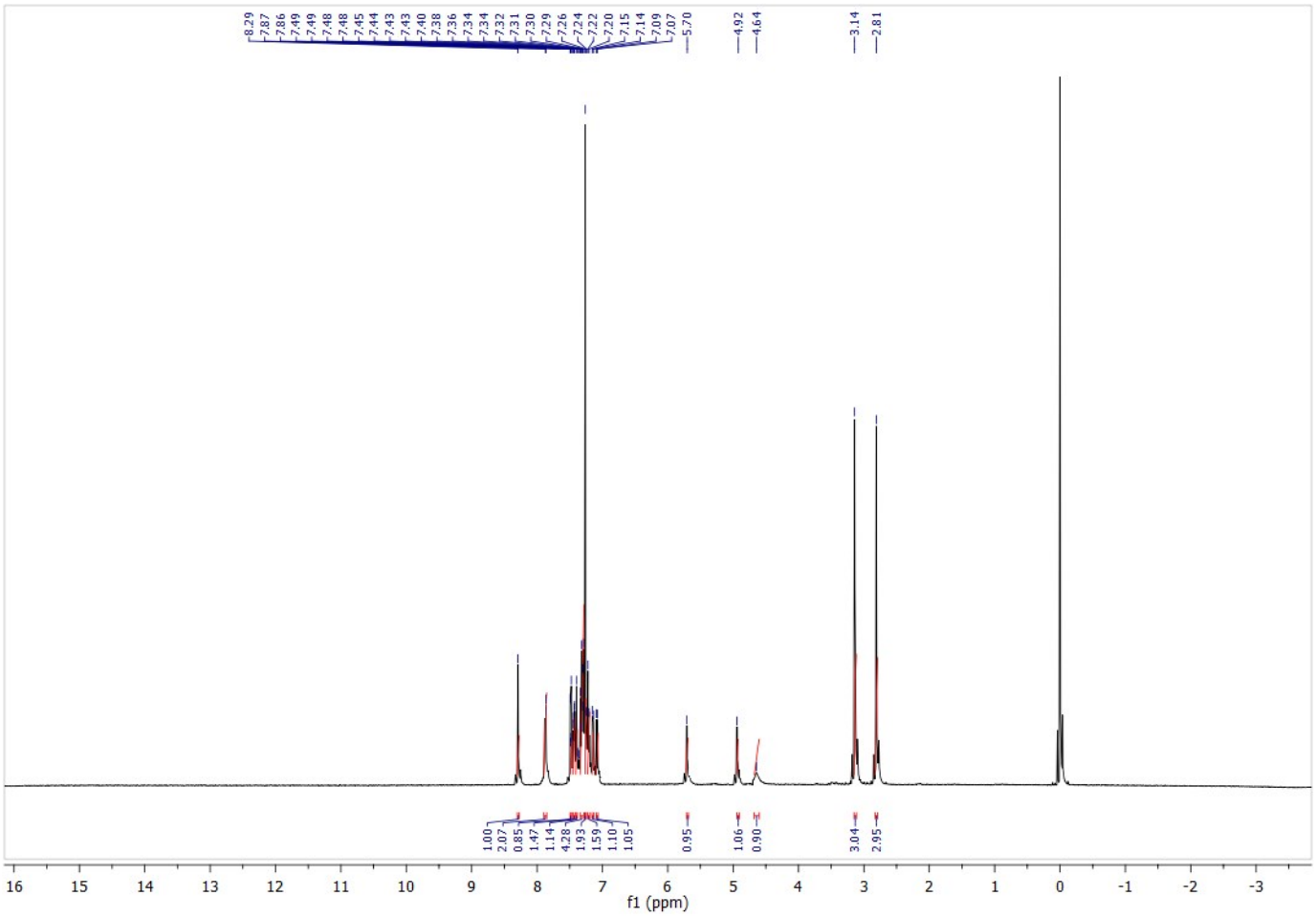


Fig S-15: ^{1}H NMR Spectrum of Product **4o**

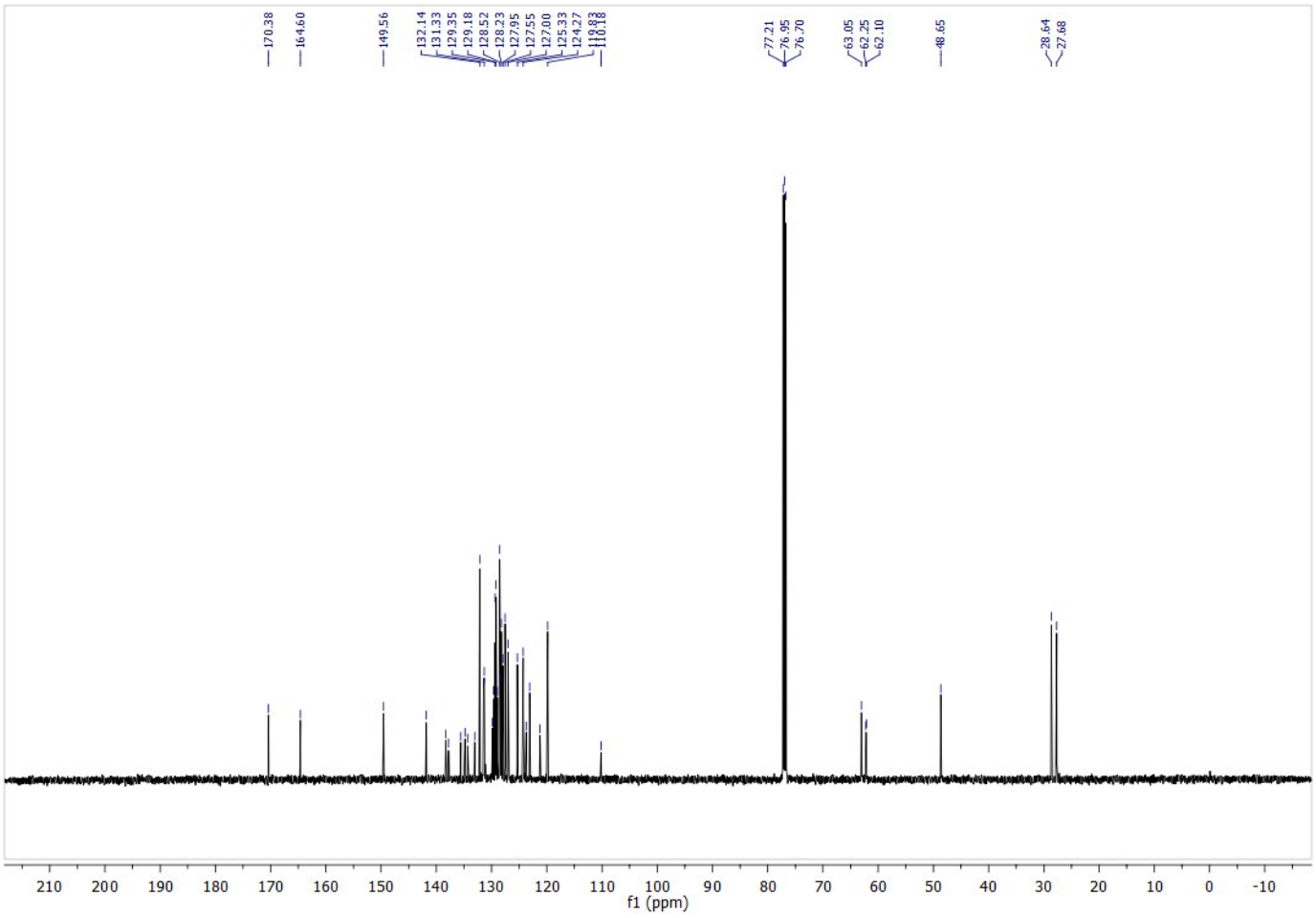


Fig S-16: ^{13}C NMR Spectrum of Product **4o**

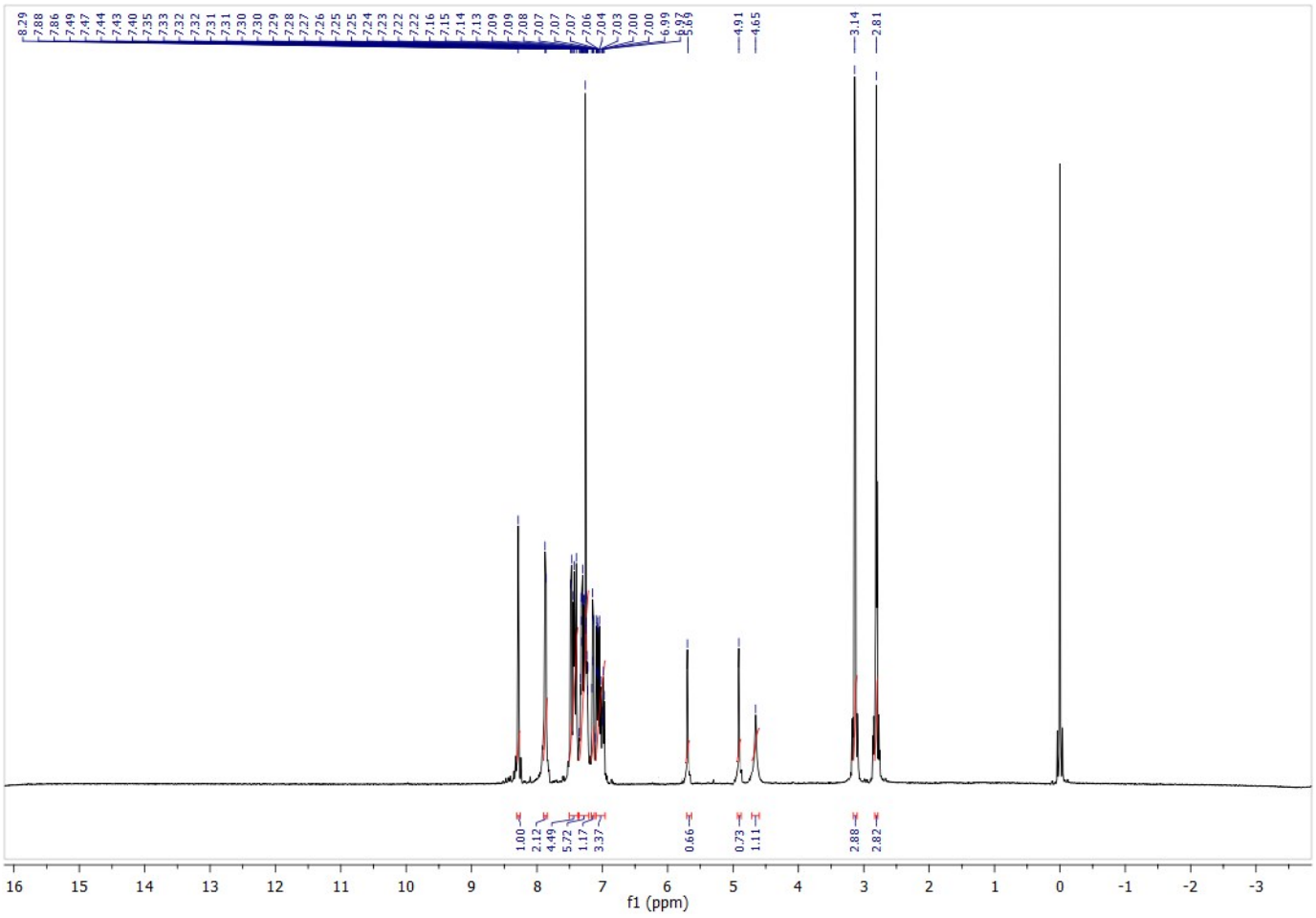


Fig S-17: ^{1}H NMR Spectrum of Product **4p**

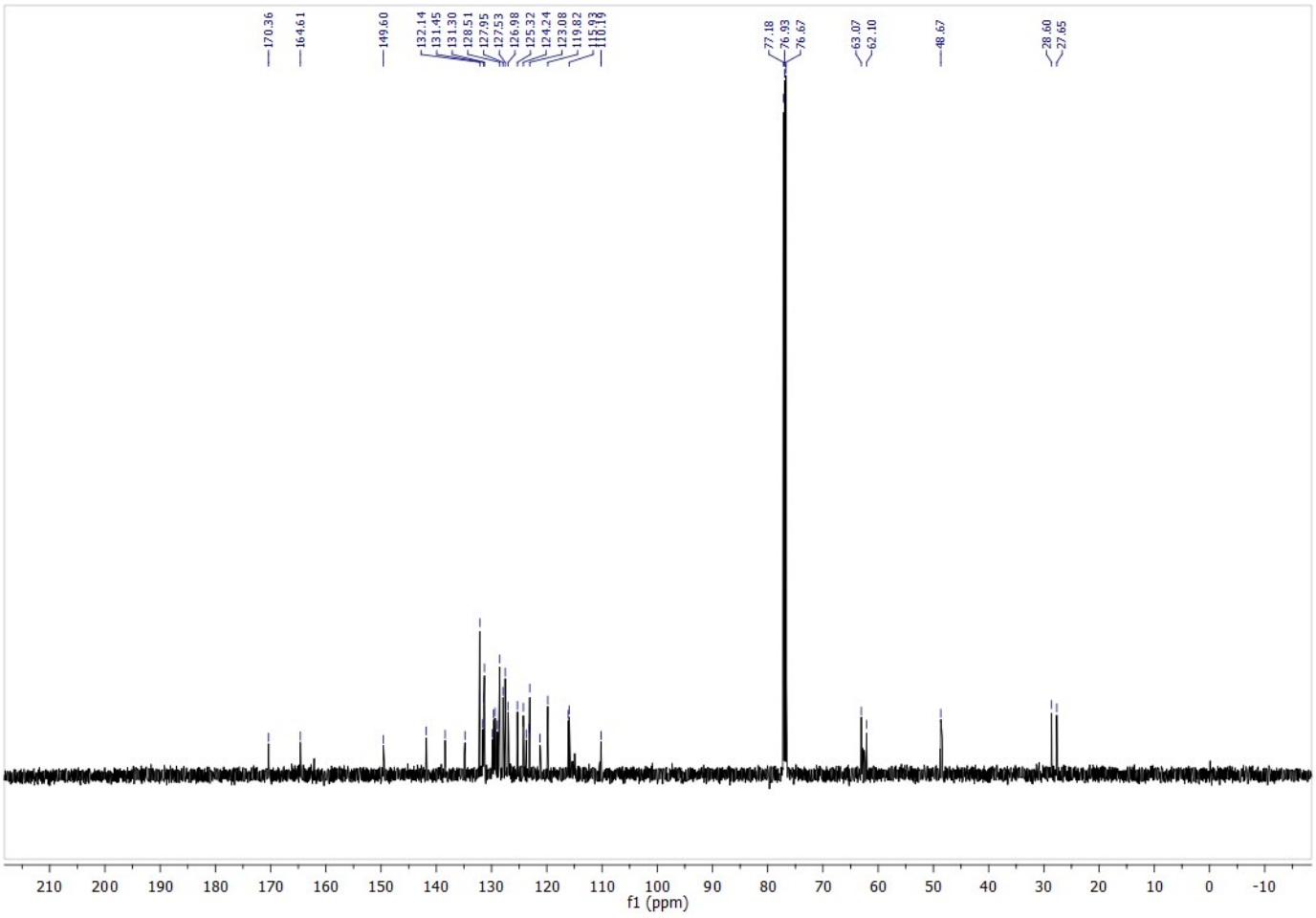


Fig S-18: ^{13}C NMR Spectrum of Product **4p**

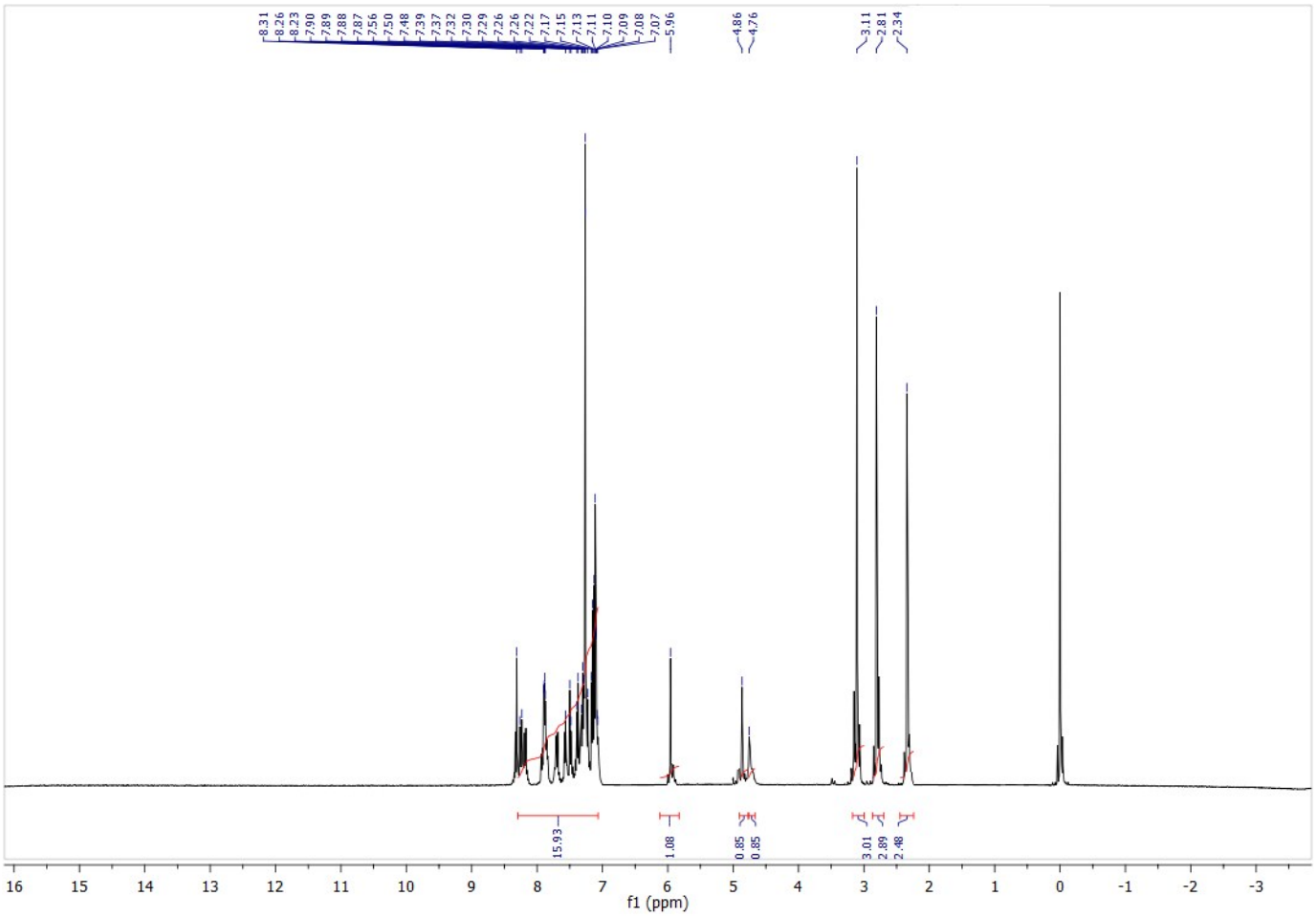


Fig S-19: ^{1}H NMR Spectrum of Product **4t**

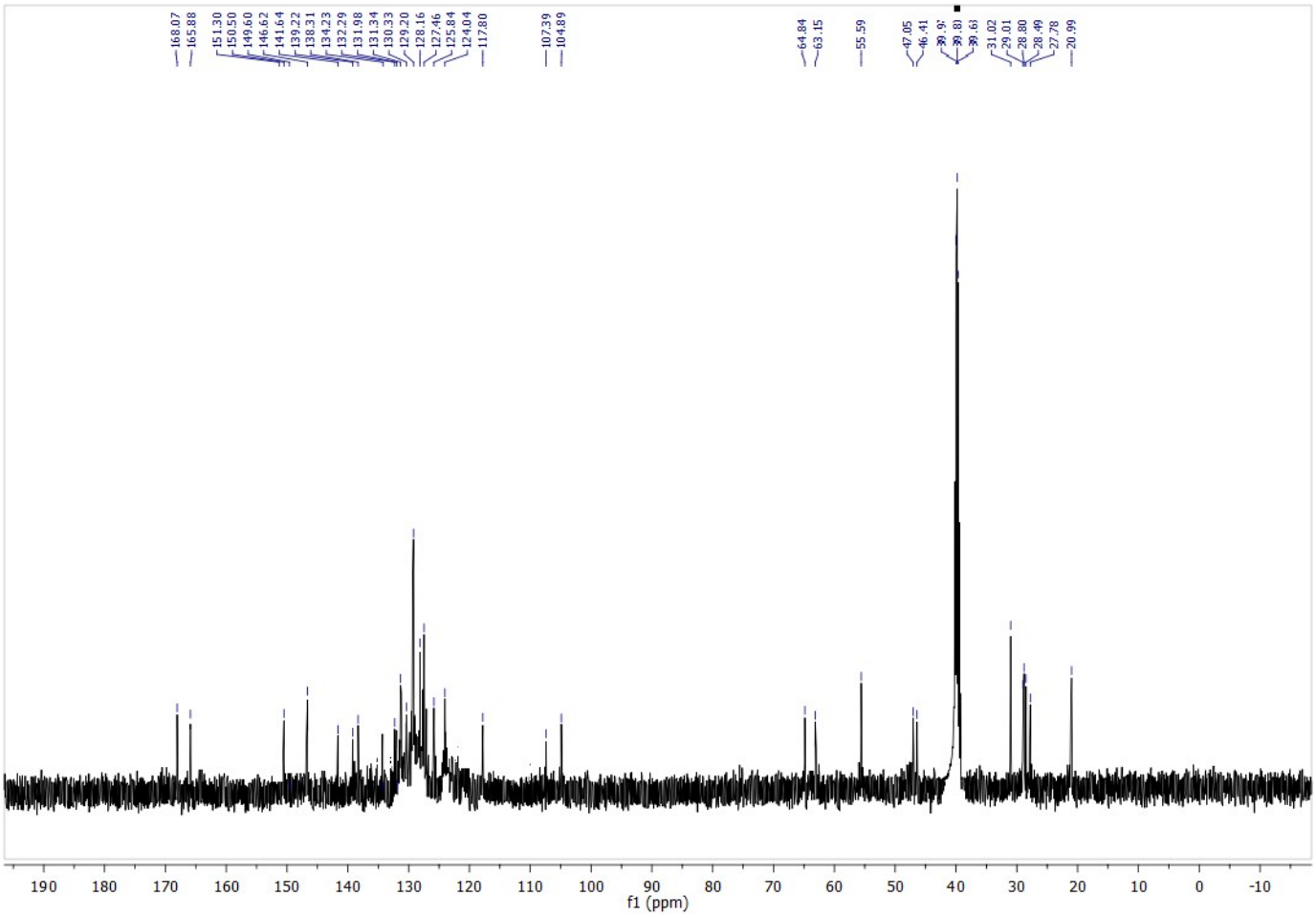


Fig S-20: ^{13}C NMR Spectrum of Product **4t**