SUPPLEMENTARY MATERIAL

Chemical Constituents from the Leaves of *Elaeocarpus floribundus*

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Abstract

The genus Elaeocarpus belongs to the Elaeocarpaceae family. It consists of about 350 species distributed in the tropical and subtropical regions. Plants in the genus, reportedly, contain compounds known for various biological activities such as affinity for the δ-opioid receptor, antioxidant, cytotoxicity and antimicrobial activities. Elaeocarpus floribundus, commonly known in India as 'Indian Olive' is a medicinal plant widely distributed through Eastern Asia and the pacific. In this study, we report the isolation and spectroscopic characterization of fifteen compounds (**1-15**) and an additional three compounds (**16-18**) were obtained as mixtures. This includes three fatty acids, three diterpenoids, one triterpene alcohol, two fatty alcohols, three phaeophytins, two phytosterols, one sesquiterpene, and three hydrocarbons from the hexane extract of the leaves. Compounds **1-18** are reported for the first time from this source. To the best of our knowledge, this is an initial report of the isolation of compounds **1-11**, and **14-18** from the genus Elaeocarpus.

Keywords: *Elaeocarpus floribundus*; Indian Olive; Elaeocarpaceae; Pheophytins

Experimental

General methods

Silica gel of mesh sizes 60-120 and 100-200 (Merck) was used as an adsorbent for column chromatographic isolation of the compounds while the purity of the compounds was determined by analytical TLC using silica gel 60 F_{254} plates (Merck) and subsequently visualized using UV light and p-anisaldehyde stain reagent. Infrared spectra were taken with a Perkin Elmer, Model: Spectrum 100. High-resolution electrospray ionization mass spectrometry (HRMS) were recorded on Xevo XS QTof mass spectrometer, Waters ACQUITY UHPLC. Nuclear magnetic resonance spectra were recorded on BRUKER, AVANCE III 500 MHz (Switzerland) 500 MHz (^{1}H) and 125 MHz (^{13}C). Chemical shifts of ^{1}H and ^{13}C were recorded in ppm with respect to deuterated chloroform that was used to dissolve the compounds prior to measurement.

Plant Material

The leaves of *Elaeocarpus floribundus* were collected from CSIR-NEIST campus, Jorhat, India, at coordinates 26.7378° N, 94.1570° E, in January 2018. Dr. Dipanwita Banik, a botanist at the medicinal, aromatic and economical plants group, CSIR-NEIST, identified the plant and a voucher's specimen (Ref. no: NEIST/1893) was deposited at the divisional herbarium for future reference.

Extraction and Isolation

The leaves were air-dried at room temperature and pulverized into 3700.0 g of fine powder. The powdered leaves were soaked three times for three days each in solvents of increasing polarity, as follows: hexane (Hex), chloroform, ethyl acetate (EtOAc) and methanol MeOH. Thereafter, the extracts were filtered using Whatman No. 1 filter paper and solvents were removed under reduced pressure with a rotatory evaporator. The yield of the extracts obtained correspond to

34.7 g (HEL), 42.3 g (CEL), 11.5 g (EEL), and 85.4 g (MEL) for hexane, chloroform, ethyl acetate, and methanol respectively.

The hexane extract (32 g) was subjected to a silica gel (60-120 mesh) open column chromatography (CC) and eluted with Hex/EtOAc (100:1 to 1:100, v/v) and finally with 100% methanol to give 100 fractions. The fractions were combined into four super fractions (HELA-HELD) pooled together based on TLC similarities. Column chromatography of HELA with Hex yielded a white compound **1** (1.6 g) and **2** (43 mg). Sub-fraction HELA-3 eluted with 3% EtOAc in Hex yielded a white solid that was further purified by crystallization to obtain compound **3 (**72.3 mg). Super fraction HELB (26.8 g) was subjected to column chromatography on silica gel, eluting with Hex/EtOAc gradient to obtain seven subfractions (HELB1 –HEL B7). Sub-fraction HEL-B1 (256.7 mg) was purified by CC on silica gel with Hex to obtain compound **4 (**30 mg). Subfraction HEL-B2 (7.6 g) was subjected to silica gel CC and separated with Pet ether to give three sub-fractions (B2a-B2c). Sub-fraction B2a (2.8 g) was purified again on silica gel with Pet ether to obtain compound **5** (29 mg). All efforts to isolate compounds from other sub-fractions of HEL-B2 proved abortive due to their complex and oily nature. Sub-fraction HEL-B3 (2.6 g) was purified repeatedly by silica gel (100-200 mesh) CC with Hex-EtOAc (gradient from 1% to 3% v/v) to afford compound **6** (40 mg). Sub-fraction HEL-B4 (2.27 g) was subjected to a silica gel (100-200 mesh) CC, eluting with Hex/ EtOAc (gradient from 1% EtOAc to 10% EtOAc) to yield sub-fractions (B4a-B4d). Compound **7** (63 mg) was isolated by purification of sub-fraction B4c using solvent system (1%-4%) EtOAc on silica gel (100-200 mesh) CC. Successive purification of sub-fractions resulting from B4c led to the isolation of compounds **8** (4mg). Repeated chromatography of sub-fraction B4d (427 mg) on silica gel (100-200 mesh) CC with hexane-DCM (99:1 to 95:5) afforded compound **9** (11 mg).Sub-fraction HEL-B5 (3.6 g) was

fractionated on silica gel (100-200 mesh) CC using gradient elution of 5% EtOAc in hexane up to 100% methanol to obtain three sub-fractions (Fr. B5A-B5C). Sub-fraction B5B (2.8 g) was further chromatographed to obtain five fractions (Fr. B5B1-B5B5) using the same procedure.Fr.B5B1 (237.2 mg) was purified by using silica gel CC with 5% EtOAc in hexane to afford compound **10** (20 mg). Fr B5B2 (824.6 mg) was re-chromatographed on silica gel (100-200 mesh) CC with 5% EtOAc to give four sub-fractions (B2A-B2D). Sub-fraction B2C (709 mg) was subjected to further purification by silica gel CC, followed by precipitation, afforded compounds **11** (348mg)**.** Sub-fraction B2D (117 mg) was submitted to another silica gel chromatography with hexane-EtOAc (97:3) to yield compounds **12** (7 mg) and **13** (11 mg). Fraction HEL-B6 (3.8 g) was subjected to CC using hexane-EtOAc (95:5-0:100) gradient as a mobile phase to afford seven sub-fractions (B6a-B6g). B6c was submitted to repeated CC using the same chromatographic conditions described above, afforded compounds **14** (41 mg), **15** (4 mg)**, 16** (196 mg), **17** (44 mg) and **18** (71 mg).

Characterization of Decene (1), $C_{10}H_{20}$, colourless liquid, Yields, 1.6 g; **IR** (υ_{max}, cm^{-1}): 2924 (C-H), 1636 (C=C), 909 (C-H bending vib.); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.81 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.03 – 4.89 (m, 1H), 2.08 – 1.99 (m, 1H), 1.38 (q, *J* = 7.1 Hz, 1H), 1.26 (d, *J* = 6.1 Hz, 13H), 0.91 – 0.79 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.15, 113.96, 37.00, 33.74, 31.84, 30.07, 29.95, 29.61, 29.60, 29.58, 29.53, 29.42, 29.28, 29.07, 28.86, 27.00, 26.63, 22.60, 19.61, 14.02 (sdbs).

Characterization of Hexadecane (2), $C_{16}H_{34}$, colourless liquid, Yields, 43 mg; **IR** (υ_{max}, cm^{-1}): 2918, 2849 (C-H), 1463 (C-H bending vib.); **^{1}H NMR** (500 MHz, Chloroform-d) δ 1.32 – 1.25 (m, 1H), 1.25 (s, 3H), 0.91 – 0.81 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 31.84, 29.61, 29.57, 29.28, 22.61, 14.04 (Jatoi et al., 2007).

Characterization of 1-docosanol (3), $C_{22}H_{46}O$, white solid, Yields, 72.3 mg, M.pt=70-72 ^{o}C; **IR** (υ_{max}, cm^{-1}): 3401 (O-H), 2917, 2849 (C-H), 1473, 1462 (C-H bending vib.); **^{1}H NMR** (500 MHz, Chloroform-d) δ 1.27 (s, 2H), 1.25 (s, 6H), 0.88 (t, J = 6.9 Hz, 0H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 63.02, 32.71, 31.82, 29.60, 29.56, 29.51, 29.33, 29.26, 25.63, 22.59, 14.02; **HR-ESI-MS (-ve mode)**: 325.1813 $[M-H]^-$ (Mahmood et al. 2002).

Characterization of Heptane (4), C_7H_{16}, colourless liquid, Yields, 30 mg; **IR** (υ_{max}, cm^{-1}): 2918, 2849 (C-H), 1462 (C-H bending vib.); **^{1}H NMR** (500 MHz, Chloroform-d) δ 1.27 (s, 1H), 1.25 (s, 3H), 0.92 – 0.79 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 31.83, 29.61, 29.57, 29.27, 22.60, 22.56, 14.02 (sdbs).

Characterization of Tanacetene (5), $C_{15}H_{26}$, colourless oil, Yields, 29 mg; **IR** (υ_{max}, cm^{-1}): 2924, 2854 (C-H), 1449, 1377 (C-H bending vib.); **^{1}H NMR** (500 MHz, Chloroform-d) δ 5.16 (d, J = 6.6 Hz, 1H), 5.15 – 5.06 (m, 2H), 2.07 (p, J = 7.5 Hz, 4H), 2.04 – 1.94 (m, 6H), 1.68 (s, 2H), 1.60 (d, J = 1.7 Hz, 5H), 1.32 – 1.27 (m, 1H), 1.26 (s, 4H), 1.24 (s, 1H), 0.86 (dt, J = 18.0, 6.6 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 134.98, 134.78, 131.12, 124.30, 124.20, 39.65, 29.63, 29.60, 29.56, 28.17, 26.66, 26.55, 25.58, 17.56, 15.88 (Mahmood et al., 2002).

Characterization of α-tocopherolquinone (6), $C_{29}H_{50}O_3$, Yellow oil, Yields 40 mg; **IR** (υ_{max}, cm^{-1}): 3494 (O-H), 2926, 2867 (C-H), 1731, 1643 (C=O); **^{1}H NMR** (500 MHz, Chloroform-d) δ 2.58 – 2.51 (m, 1H), 2.07 (s, 1H), 2.04 (s, 1H), 2.01 (s, 2H), 1.58 – 1.48 (m, 1H), 1.50 – 1.32 (m, 1H), 1.34 – 1.27 (m, 1H), 1.30 – 1.22 (m, 3H), 1.24 – 1.10 (m, 1H), 1.10 – 0.98 (m, 1H), 1.00 – 0.79 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 187.60, 187.14, 144.32, 140.43, 140.32, 140.07, 72.58, 42.16, 40.13, 39.25, 37.48, 37.32, 37.17, 32.69, 32.66, 29.60, 27.86, 26.46, 24.69, 24.38, 22.61, 22.52, 21.30, 21.20, 19.64, 19.59, 12.28, 12.20, 11.87; **HR-ESI-MS (+ve mode)**: 469.3642 $[M+ Na]^+$ (Sung et al. 1999).

Characterization of Decanol (7), $C_{10}H_{22}O$, Colourless liquid, Yields 63 mg; **IR** (υ_{max}, cm^{-1}): 3324 (O-H), 2917, 2849 (C-H); **^{1}H NMR** (500 MHz, Chloroform-d) δ 3.64 (t, J = 6.7 Hz, 1H), 1.56 (dt, J = 8.3, 6.6 Hz, 1H), 1.29 (s, 3H), 1.28 (d, J = 5.0 Hz, 1H), 1.25 (s, 12H), 0.88 (t, J = 7.0 Hz, 1H); **^{13}C NMR** (125 MHz, CDCl3) δ 63.33, 33.02, 32.14, 29.91, 29.82, 29.65, 29.58, 25.95, 22.91, 14.34; **HR-ESI-MS (+ve mode)**: 158.0958 $[M]^+$ (de Brito-Filho et al. 2017).

Characterization of Phytol (8), $C_{20}H_{40}O$, Colourless oil, Yields 4 mg; **IR** (υ_{max}, cm^{-1}): 3400 (O-H), 2918, 2849 (C-H), 1631 (C=C); **^{1}H NMR** (500 MHz, Chloroform-d) δ 3.64 (t, J = 6.6 Hz, 1H), 1.62 (s, 0H), 1.55 (dq, J = 14.5, 7.3, 6.9 Hz, 1H), 1.32 (s, 10H), 1.31 – 1.27 (m, 2H), 1.25 (d, J = 9.4 Hz, 2H), 1.25 (s, 12H), 0.92 – 0.81 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.37, 123.06, 63.13, 39.88, 37.44, 37.37, 37.30, 36.67, 35.04, 32.81, 32.70, 29.45, 25.14, 24.81, 24.48, 22.71, 22.64, 19.76, 19.73 (Itoh et al. 2018).

Characterization of Euphorbol (9), $C_{31}H_{52}O$, Solid, Yields 11 mg, Mpt: 122-125 °C; **IR** (υ_{max}, cm^{-1}): 3336 (O-H), 2928, 2867 (C-H), 1641 (C=C); **^{1}H NMR** (500 MHz, Chloroform-d) δ 3.32 – 3.24 (m, 1H), 2.18 – 2.06 (m, 0H), 2.04 – 1.90 (m, 1H), 1.88 (ddd, J = 16.1, 11.8, 7.2 Hz, 1H), 1.81 – 1.70 (m, 1H), 1.68 (d, J = 1.4 Hz, 1H), 1.69 – 1.53 (m, 6H), 1.56 – 1.46 (m, 1H), 1.46 – 1.20 (m, 7H), 1.27 (s, 1H), 1.20 – 1.07 (m, 1H), 1.10 – 1.00 (m, 3H), 0.96 (d, J = 2.4 Hz, 5H), 0.92 – 0.70 (m, 10H), 0.55 (d, J = 4.1 Hz, 1H), 0.33 (d, J = 4.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.52, 136.94, 134.52, 106.38, 78.71, 51.30, 50.81, 50.29, 45.15, 39.31, 37.10, 35.71, 35.66, 34.74, 34.13, 33.85, 31.02, 30.75, 30.69, 28.35, 28.14, 22.06, 21.94, 21.64, 21.06, 19.20, 18.74, 18.40, 15.7; **HR-ESI-MS (+ve mode)**: 485.3698 $[M\text{-}H\text{-}CO_2]^+$ (Akihisa et al. 2002).

Characterization of rel-(2R,4aR,8aR)-3,4,4a,8a-Tetrahydro-4a-hydroxy-2,6,7,8a-tetramethyl-2-(4,8,12-trimethyltridecyl)-2H-chromene-5,8-dione (10), $C_{29}H_{50}O4$, Colourless oil, Yields 20 mg; **IR** (υ_{max}, cm^{-1}): 3440 (O-H), 2918, 2849 (C-H), 1712, 1678 (C=O), 1108 (C-O); **^{1}H NMR**

(500 MHz, Chloroform-d) δ 3.83 (s, 1H), 2.30 (s, 1H), 2.09 – 2.04 (m, 5H), 2.02 (s, 1H), 2.06 – 1.86 (m, 1H), 1.86 – 1.79 (m, 2H), 1.75 – 1.67 (m, 1H), 1.70 – 1.62 (m, 1H), 1.61 (s, 6H), 1.64 – 1.53 (m, 1H), 1.55 – 1.43 (m, 1H), 1.36 (d, J = 18.2 Hz, 5H), 1.33 – 1.24 (m, 2H), 1.25 (s, 12H), 1.19 – 1.10 (m, 2H), 1.10 – 1.00 (m, 3H), 1.00 – 0.79 (m, 18H), 0.07 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.90, 197.03, 140.72, 139.70, 83.54, 73.86, 72.78, 40.64, 37.77, 37.68, 37.55, 36.47, 35.96, 35.04, 33.16, 32.93, 30.73, 27.79, 27.21, 24.83, 24.74, 22.64, 21.39, 20.76, 19.84, 19.24, 13.13, 13.02; **HR-ESI-MS (+ve mode)**: 463.3806 $[M+H]^+$ (Tan et al. 2009).

Characterization of β-sitosterol (11), $C_{29}H_{50}O$, White solid, Yields 348 mg, Mpt: 132-138 °C; **IR** (υ_{max}, cm^{-1}): 3366 (O-H), 2960, 2936 (C-H); **^{1}H NMR** (500 MHz, Chloroform-d) δ 2.34 – 2.18 (m, 1H), 2.05 – 1.93 (m, 1H), 1.84 (td, J = 8.5, 6.8, 3.5 Hz, 1H), 1.73 – 1.39 (m, 3H), 1.38 – 1.20 (m, 1H), 1.22 – 1.12 (m, 1H), 1.12 – 1.02 (m, 1H), 1.01 (s, 1H), 1.02 – 0.88 (m, 2H), 0.88 – 0.75 (m, 3H), 0.68 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.96, 121.45, 70.19, 56.09, 55.67, 49.60, 45.88, 42.37, 42.34, 39.71, 36.73, 36.51, 36.20, 33.94, 31.91, 31.69, 30.36, 29.43, 28.25, 26.15, 24.21, 23.25, 21.06, 19.50, 19.29, 18.64, 12.24, 11.92. **EI-MS:** 414 $[M]^+$ (Cha et al. 2018).

Characterization of Stearic acid (12), $C_{18}H_{36}O_2$, White solid, Yields 7 mg, Mpt: 70 °C; **IR** (υ_{max}, cm^{-1}): 3418 (O-H), 2918, 2850 (C-H), 1705 (C=O), 1214 (C-O); **^{1}H NMR** (500 MHz, Chloroform-d) δ 2.35 (t, J = 7.5 Hz, 1H), 1.66 – 1.60 (m, 1H), 1.36 – 1.30 (m, 0H), 1.30 (s, 2H), 1.27 (s, 3H), 1.25 (s, 9H), 0.91 – 0.82 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.83, 34.38, 31.75, 29.93, 29.83, 29.73, 29.63, 29.59, 29.54, 29.49, 29.43, 29.35, 29.24, 29.11, 25.97, 22.86, 14.17; **HR-ESI-MS (-ve mode)**: 283.2648 $[M-H]^-$ (Bus et al. 1976).

Characterization of Oleic acid (13), $C_{18}H_{34}O_2$, Cream paste, Yields 11 mg, Mpt: 13 °C; **IR** (υ_{max}, cm^{-1}): 3755 (O-H), 2918, 2850 (C-H), 1705 (C=O), 1463 (C=C), 1215 (C-O); **^{1}H NMR**

(500 MHz, Chloroform-d) δ 2.29 (t, J = 7.6 Hz, 1H), 1.60 – 1.54 (m, 1H), 1.31 – 1.19 (m, 6H), 1.19 (s, 6H), 0.85 – 0.76 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.83, 130.34, 130.23, 34.38, 31.75, 29.78, 29.68, 29.40, 29.32, 29.15, 28.91, 28.85, 28.70, 27.46, 27.36, 25.97, 22.86, 14.17; **HR-ESI-MS (-ve mode)**: 281.2517 $[M-H]^-$ (Hamid et al. 2016).

Characterization of Elaidic acid (14), $C_{18}H_{34}O_2$, Waxy solid, Yields 41 mg, Mpt: 47 °C; **IR** (υ_{max}, cm^{-1}): 3736 (O-H), 2918, 2850 (C-H), 1704 (C=O), 1465 (C=C), 1293 (C-O); **^{1}H NMR** (500 MHz, Chloroform-d) δ 2.35 (t, J = 7.6 Hz, 1H), 1.66 – 1.60 (m, 1H), 1.36 – 1.25 (m, 4H), 1.25 (s, 6H), 0.88 (t, J = 6.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.83, 130.34, 130.23, 34.38, 33.24, 33.14, 31.75, 29.78, 29.68, 29.40, 29.32, 29.15, 28.91, 28.85, 28.70, 25.97, 22.86, 14.17; **HR-ESI-MS (-ve mode)**: 281.2523 $[M-H]^-$ (Yang et al., 2014).

Characterization of Linolenic acid (15), $C_{18}H_{30}O_2$, Colourless liquid, Yields 4 mg; **IR** (υ_{max}, cm^{-1}): 3656 (O-H), 2925, 2854 (C-H), 1712 (C=O), 1463 (C=C), 1259 (C-O); **^{1}H NMR** (500 MHz, Chloroform-d) δ 5.44 – 5.27 (m, 2H), 2.84 – 2.74 (m, 1H), 2.35 (t, J = 7.6 Hz, 1H), 2.13 – 2.01 (m, 2H), 1.67 – 1.60 (m, 1H), 1.40 – 1.24 (m, 8H), 0.98 (t, J = 7.5 Hz, 1H), 0.88 (td, J = 6.9, 4.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.83, 131.61, 129.97, 128.95, 128.78, 128.50, 127.32, 35.47, 35.37, 34.38, 33.14, 29.40, 29.34, 29.32, 29.15, 26.02, 25.97, 14.30; **HR-ESI-MS (+ve mode)**: 279.0868 $[M+H]^+$ (Yang et al. 2014).

Characterization of 13^2-hydroxyl-(13^{2-}s)-phaeophytin a (16), $C_{55}H_{74}N_4O_6$, Brown liquid, Yields 196 mg; **IR** (υ_{max}, cm^{-1}): 3391 (O-H), 2926, (C-H), 1739, 1700 (C=O), 1619 (N-H), 1297 (C-O); **^{1}H NMR** (500 MHz, Chloroform-d) δ 9.44 (d, J = 17.8 Hz, 1H), 9.30 (s, 1H), 8.54 (s, 1H), 7.93 (ddd, J = 19.3, 11.6, 7.8 Hz, 1H), 6.25 (d, J = 18.0 Hz, 2H), 6.18 – 6.12 (m, 1H), 5.13 (tq, J = 7.1, 1.3 Hz, 1H), 4.54 – 4.39 (m, 3H), 4.24 – 4.18 (m, 1H), 3.89 (s, 3H), 3.82 (s, 1H), 3.69 – 3.57 (m, 5H), 3.37 (d, J = 7.7 Hz, 3H), 3.16 (d, J = 7.2 Hz, 3H), 2.63 (dddd, J = 13.9, 9.9, 6.2, 3.4 Hz,

1H), 2.49 (ddd, J = 15.9, 9.8, 6.2 Hz, 1H), 2.40 – 2.29 (m, 1H), 2.31 (s, 1H), 2.25 – 2.15 (m, 1H), 2.10 – 2.01 (m, 1H), 1.99 (d, J = 9.2 Hz, 0H), 1.95 – 1.83 (m, 2H), 1.81 (d, J = 7.3 Hz, 2H), 1.66 (t, J = 7.7 Hz, 3H), 1.65 – 1.56 (m, 4H), 1.50 (ddt, J = 13.2, 11.8, 6.5 Hz, 1H), 1.37 – 1.06 (m, 11H), 1.06 – 0.92 (m, 3H), 0.96 (s, 3H), 0.92 – 0.73 (m, 14H), 0.52 (s, 1H), -1.66 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.52, 173.37, 170.58, 168.82, 168.30, 156.63, 149.56, 142.71, 141.54, 140.86, 138.19, 137.69, 136.47, 136.07, 131.13, 130.22, 127.55, 125.29, 125.10, 122.71, 117.81, 109.15, 107.26, 103.85, 100.49, 83.22, 61.46, 53.58, 53.24, 49.20, 39.80, 37.55, 37.37, 36.64, 36.47, 35.96, 35.04, 32.64, 32.50, 30.73, 27.83, 24.83, 24.80, 24.74, 22.64, 20.76, 19.71, 19.60, 18.00, 15.34, 15.17, 14.62, 11.71, 10.15 ; **HR-ESI-MS (+ve mode)**: 505.2652 $[M+3ACN+2H]^+$ (Jerz et al. 2007).

Characterization of phaeophytin a (17), $C_{55}H_{74}N_4O_5$, Green powder, Yields 44 mg; **IR** (υ_{max}, cm^{-1}): 3397 (N-H), 2926, 2868 (C-H), 1737, 1715 (C=O), 1618 (N-H), 1220 (C-O); **^{1}H NMR** (500 MHz, Chloroform-d) δ 9.57 (d, J = 15.2 Hz, 1H), 9.45 – 9.38 (m, 1H), 8.62 (d, J = 14.5 Hz, 1H), 7.99 (ddd, J = 17.1, 11.4, 4.8 Hz, 1H), 6.29 (d, J = 17.7 Hz, 1H), 6.18 (d, J = 11.5 Hz, 1H), 5.42 – 5.30 (m, 1H), 5.24 – 5.07 (m, 1H), 4.62 – 4.50 (m, 1H), 4.48 (t, J = 7.1 Hz, 1H), 4.16 (dd, J = 9.2, 2.9 Hz, 0H), 3.73 (s, 1H), 3.72 – 3.62 (m, 3H), 3.61 (s, 1H), 3.41 (d, J = 3.6 Hz, 2H), 3.24 – 3.17 (m, 2H), 2.36 – 2.23 (m, 2H), 2.15 – 1.95 (m, 2H), 1.95 – 1.84 (m, 1H), 1.68 (dq, J = 7.8, 3.6 Hz, 4H), 1.61 (d, J = 1.2 Hz, 1H), 1.58 (d, J = 6.9 Hz, 1H), 1.58 – 1.45 (m, 1H), 1.43 (s, 1H), 1.36 – 1.26 (m, 10H), 1.25 (s, 8H), 1.25 – 1.04 (m, 5H), 1.06 – 0.68 (m, 22H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.99, 173.37, 170.22, 170.12, 169.82, 152.36, 149.56, 142.71, 142.09, 135.85, 134.85, 133.44, 132.06, 131.23, 130.59, 130.11, 129.39, 125.29, 123.79, 122.71, 117.81, 108.42, 105.83, 96.92, 94.62, 67.20, 61.46, 52.27, 52.21, 48.99, 39.80, 37.55, 37.37, 36.64, 36.47, 35.96, 35.04, 32.64, 31.98, 30.73, 27.83, 24.83, 24.80, 24.74, 22.64, 20.76, 19.71, 19.60,

18.58, 15.17, 14.62, 12.10, 11.71, 10.15; **HR-ESI-MS (+ve mode)**: 889.5843 $[M+H+H_2O]^+$ (Kapewangolo et al. 2017).

***Characterization of** phaeophytin b (18)*, $C_{55}H_{72}N_4O_6$, Green powder, Yields 71 mg; **IR** (υ_{max}, cm^{-1}): 3397 (N-H), 2926, 2868 (C-H), 1736, 1705 (C=O), 1664 (N-H), 1161 (C-O); **^{1}H NMR** (500 MHz, Chloroform-d) δ 11.06 – 10.99 (m, 1H), 10.23 (t, J = 4.3 Hz, 1H), 9.53 – 9.45 (m, 1H), 8.53 (s, 1H), 7.96 (ddd, J = 18.0, 11.6, 3.5 Hz, 1H), 6.35 (d, J = 17.9 Hz, 1H), 6.30 – 6.17 (m, 2H), 5.60 (s, 1H), 5.37 (dq, J = 11.3, 5.4 Hz, 1H), 5.25 – 5.13 (m, 1H), 5.11 (s, 2H), 4.56 – 4.41 (m, 4H), 4.33 – 4.26 (m, 1H), 4.23 – 4.14 (m, 1H), 3.92 (s, 2H), 3.91 (s, 2H), 3.90 – 3.82 (m, 2H), 3.70 – 3.60 (m, 4H), 3.43 – 3.34 (m, 4H), 3.20 (dt, J = 8.5, 4.1 Hz, 1H), 2.80 (d, J = 5.8 Hz, 1H), 2.66 (dtd, J = 13.3, 6.3, 3.1 Hz, 1H), 2.53 (ddd, J = 15.9, 9.3, 6.5 Hz, 1H), 2.35 (dt, J = 9.5, 4.8 Hz, 1H), 2.34 – 2.20 (m, 2H), 2.06 (s, 1H), 1.90 (t, J = 4.3 Hz, 1H), 1.86 (dd, J = 18.8, 6.9 Hz, 4H), 1.75 (h, J = 5.2, 4.2 Hz, 4H), 1.70 – 1.66 (m, 1H), 1.69 – 1.59 (m, 5H), 1.57 (s, 1H), 1.55 – 1.41 (m, 2H), 1.36 – 1.19 (m, 40H), 1.19 (dd, J = 6.3, 2.9 Hz, 1H), 1.19 – 1.06 (m, 3H), 1.06 – 0.99 (m, 1H), 1.02 – 0.94 (m, 6H), 0.96 – 0.91 (m, 1H), 0.91 – 0.84 (m, 3H), 0.84 (d, J = 6.6 Hz, 10H), 0.83 – 0.70 (m, 9H), 0.45 (s, 1H), -1.63 (d, J = 6.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.99, 187.21, 173.37, 170.22, 170.12, 169.82, 152.36, 149.56, 142.71, 142.09, 141.29, 137.70, 135.85, 134.85, 134.39, 133.04, 130.79, 130.59, 129.39, 123.79, 122.71, 117.81, 108.42, 105.83, 96.56, 94.62, 67.20, 61.46, 52.27, 52.21, 48.99, 39.80, 37.55, 37.37, 36.64, 36.47, 35.96, 35.04, 32.64, 31.98, 30.73, 27.83, 24.83, 24.80, 24.74, 22.64, 20.76, 19.71, 19.60, 19.12, 14.99, 14.62, 12.10, 11.71; **HR-ESI-MS (+ve mode):** 885.5585 $[M+H]^+$ (Schwikkard et al. 1998).

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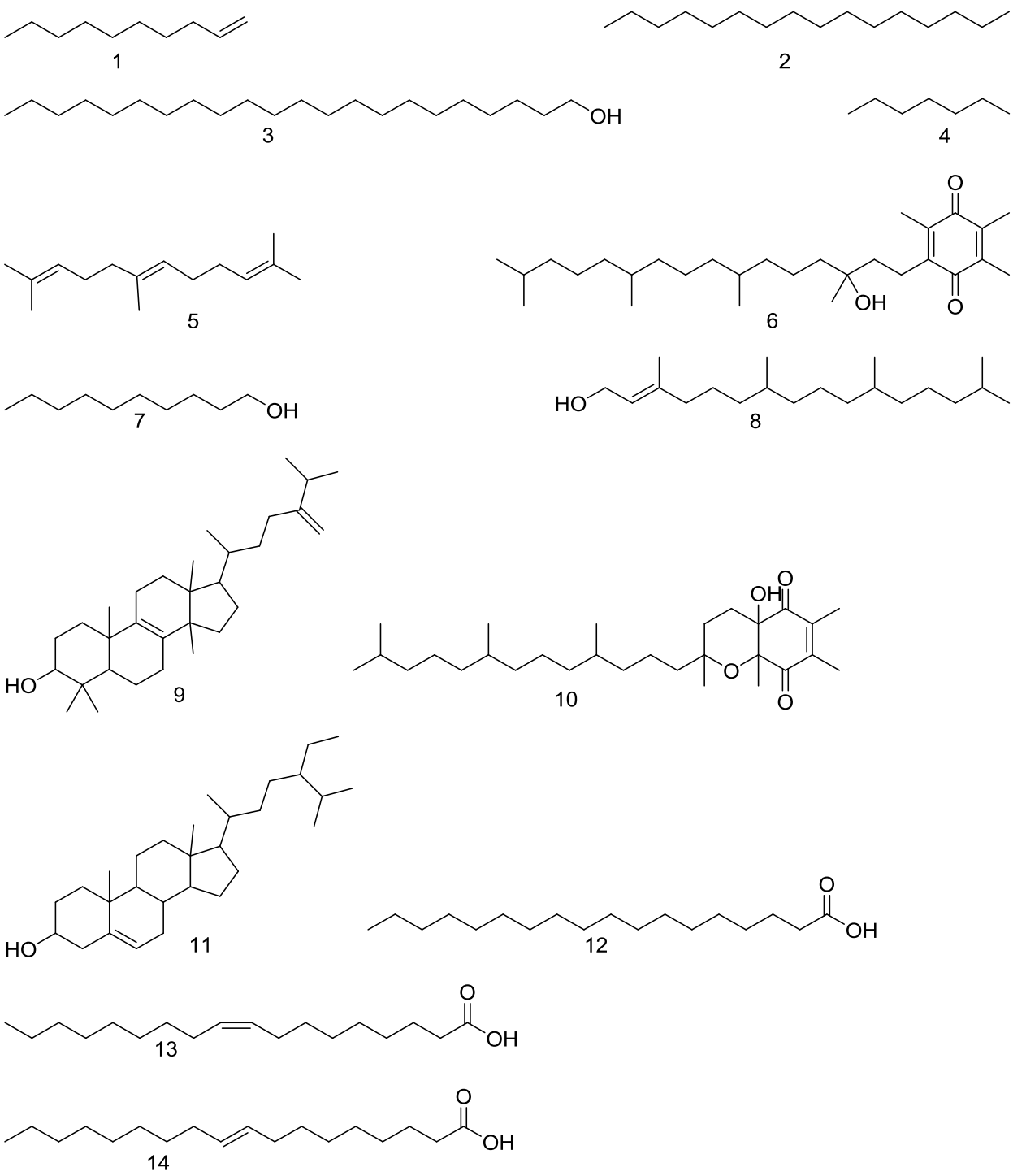
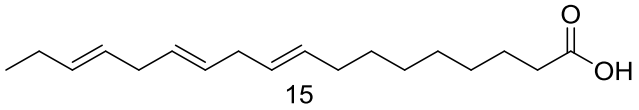
Figure S1 Structures of compounds **1-18.**





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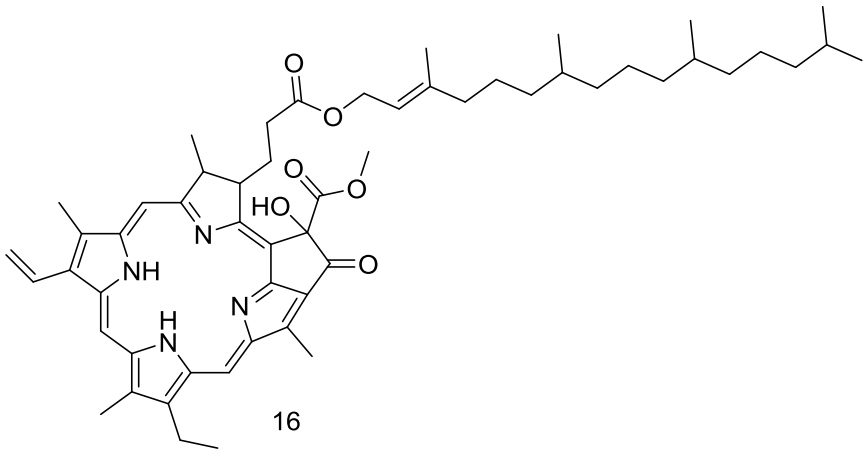

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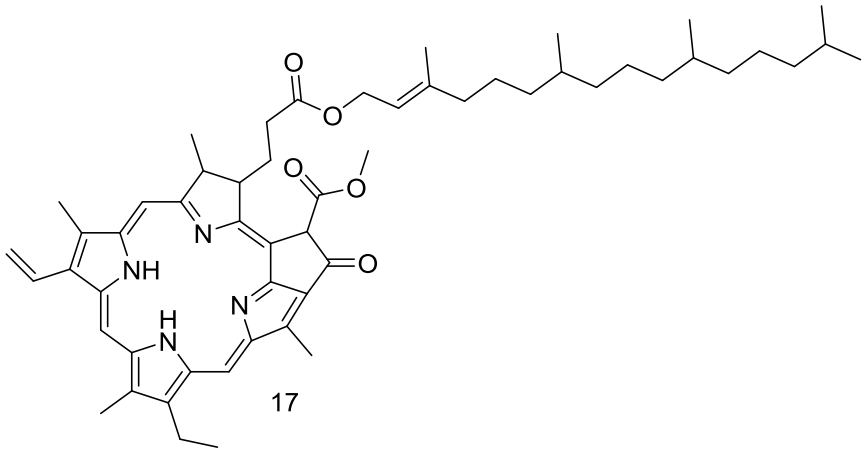

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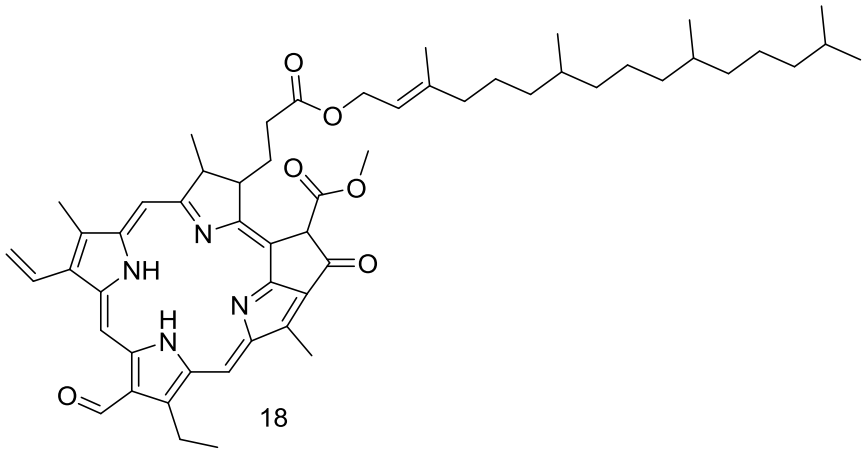

18

Figure S2 ^{1}H NMR spectrum of compound **1** in $CDCl_3$

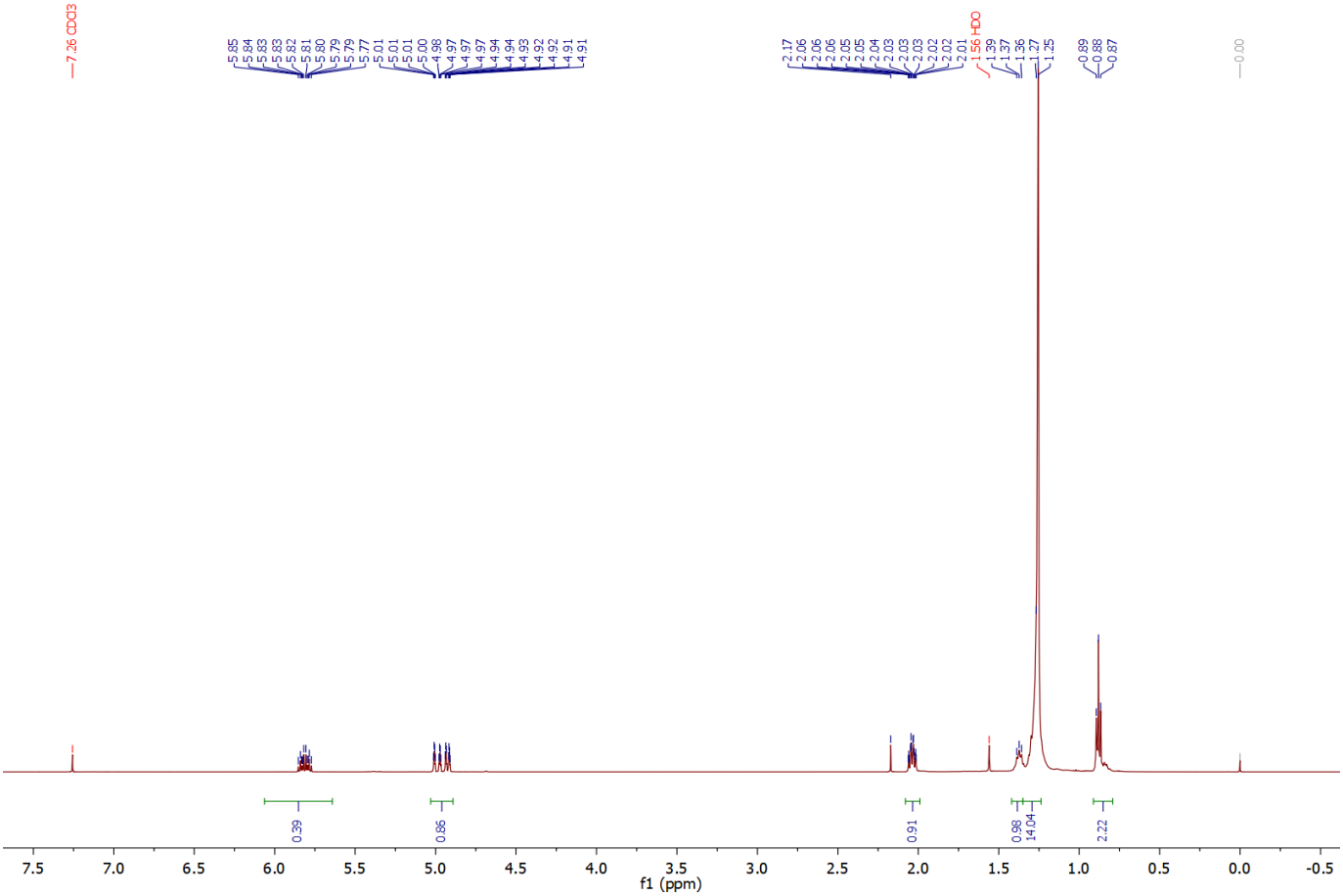

Figure S3 ^{13}C NMR spectrum of compound **1** in $CDCl_3$

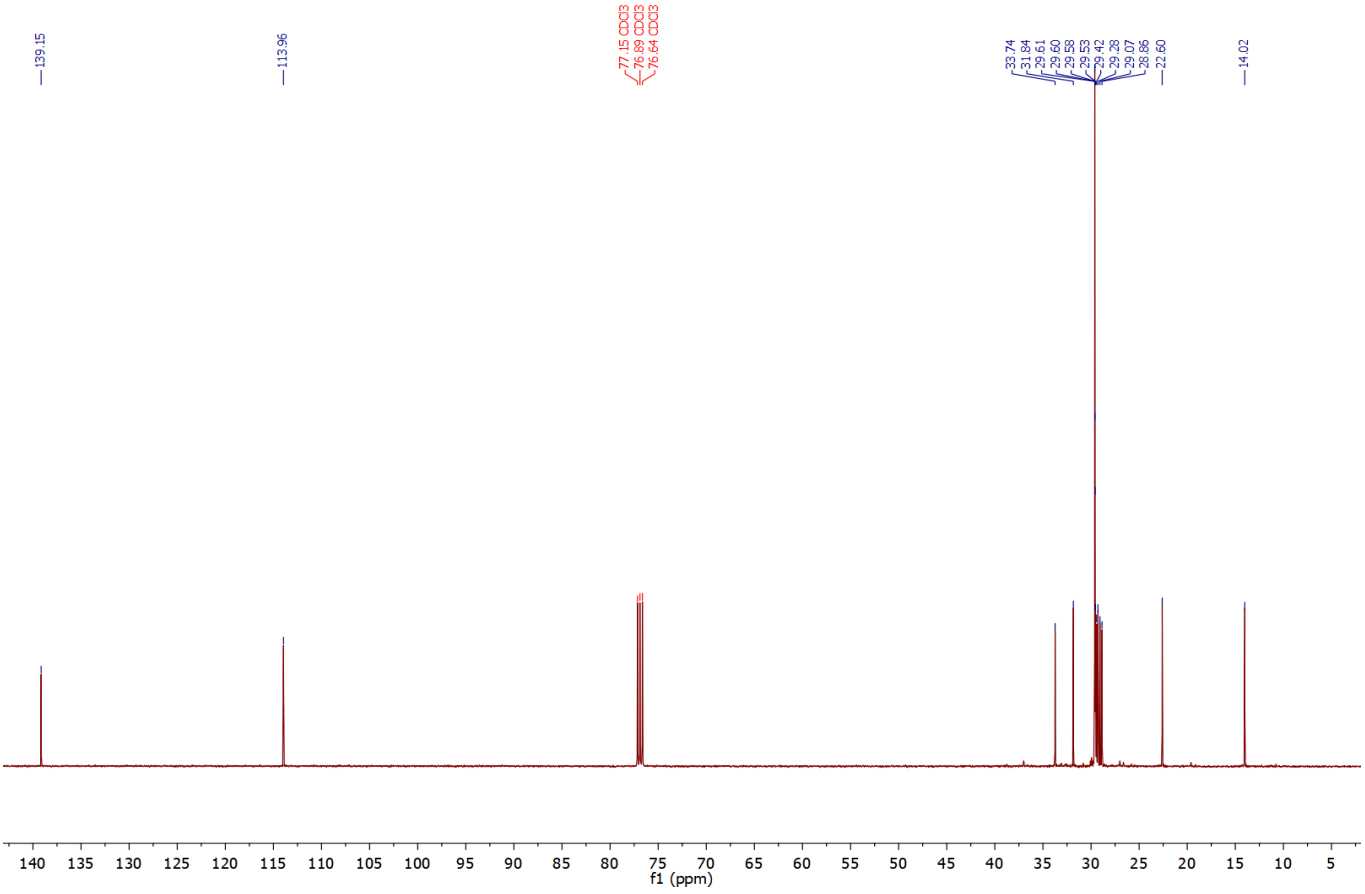

Figure S4 ^{1}H NMR spectrum of compound **2** in $CDCl_3$

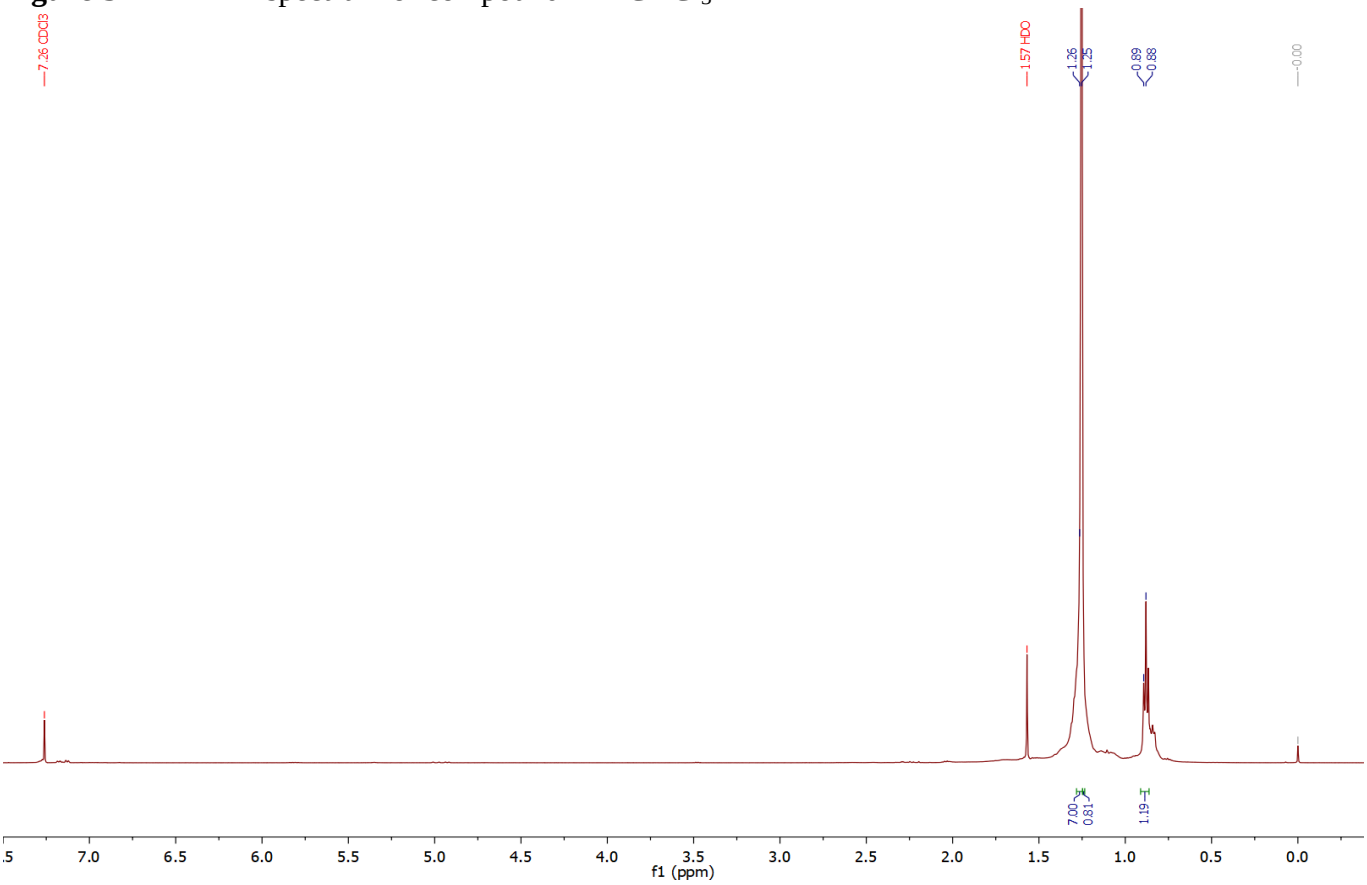

Figure S5 ^{13}C NMR spectrum of compound **2** in $CDCl_3$

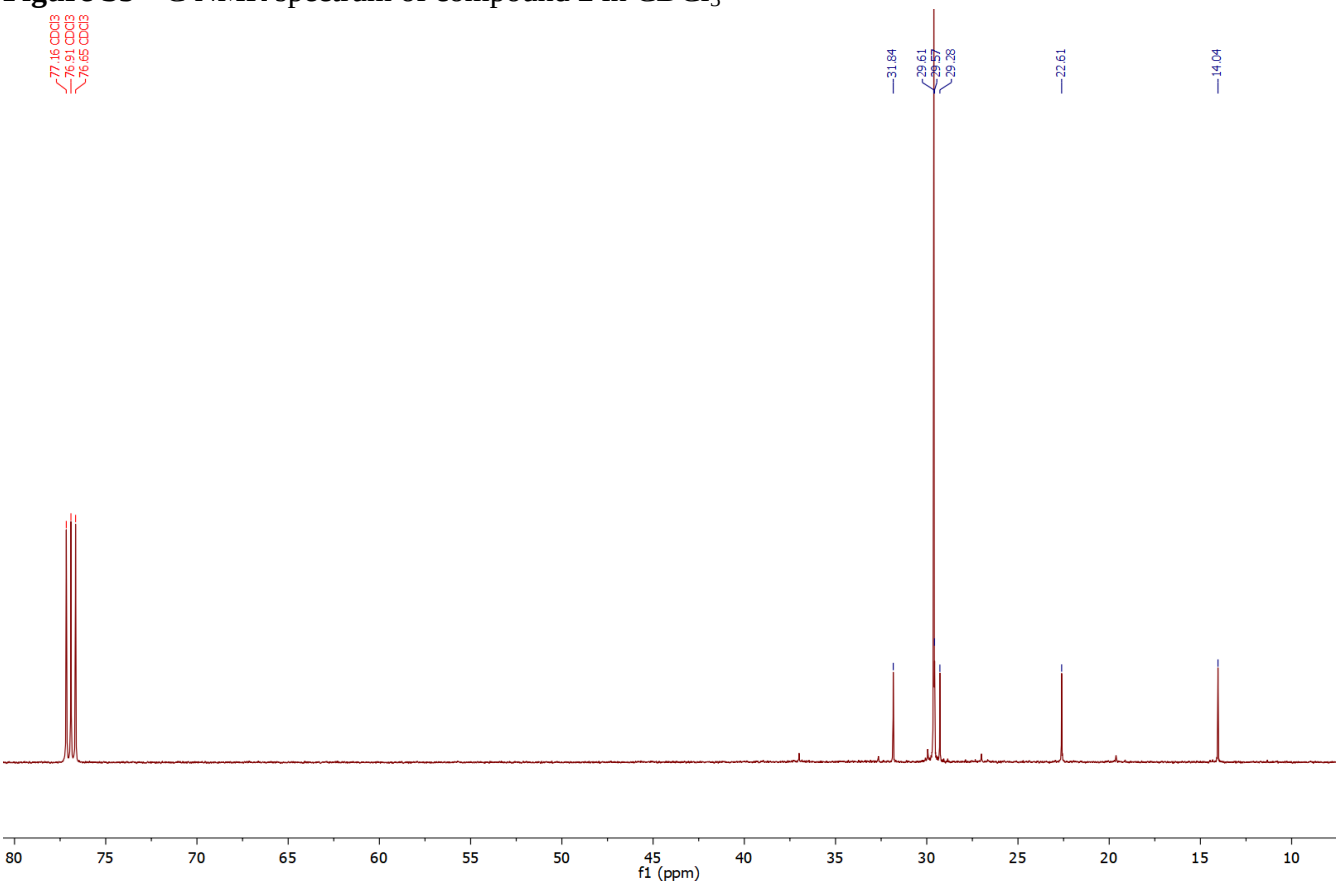

Figure S6 ^{1}H NMR spectrum of compound **3** in $CDCl_3$

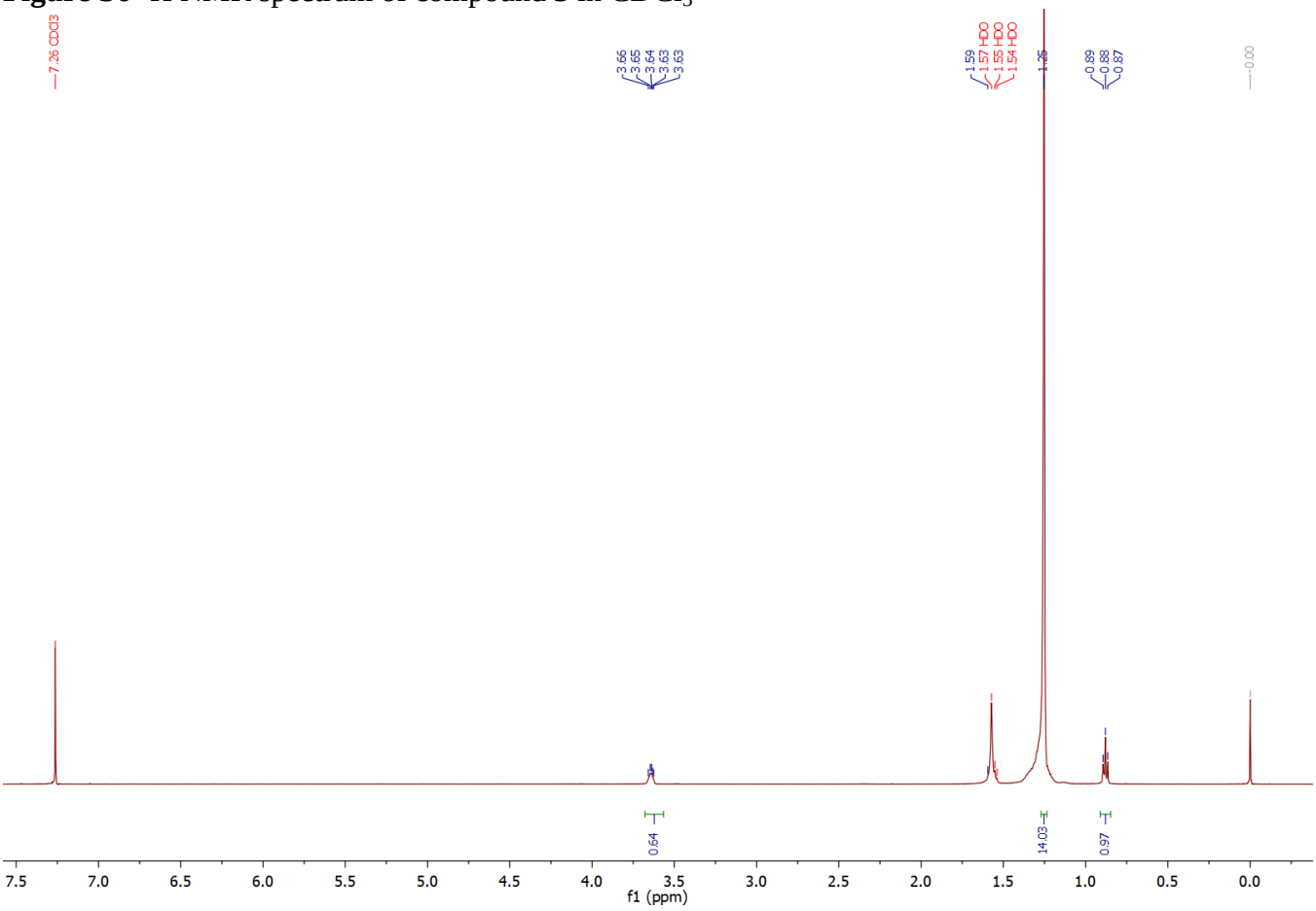

Figure S7 ^{13}C NMR spectrum of compound **3** in $CDCl_3$

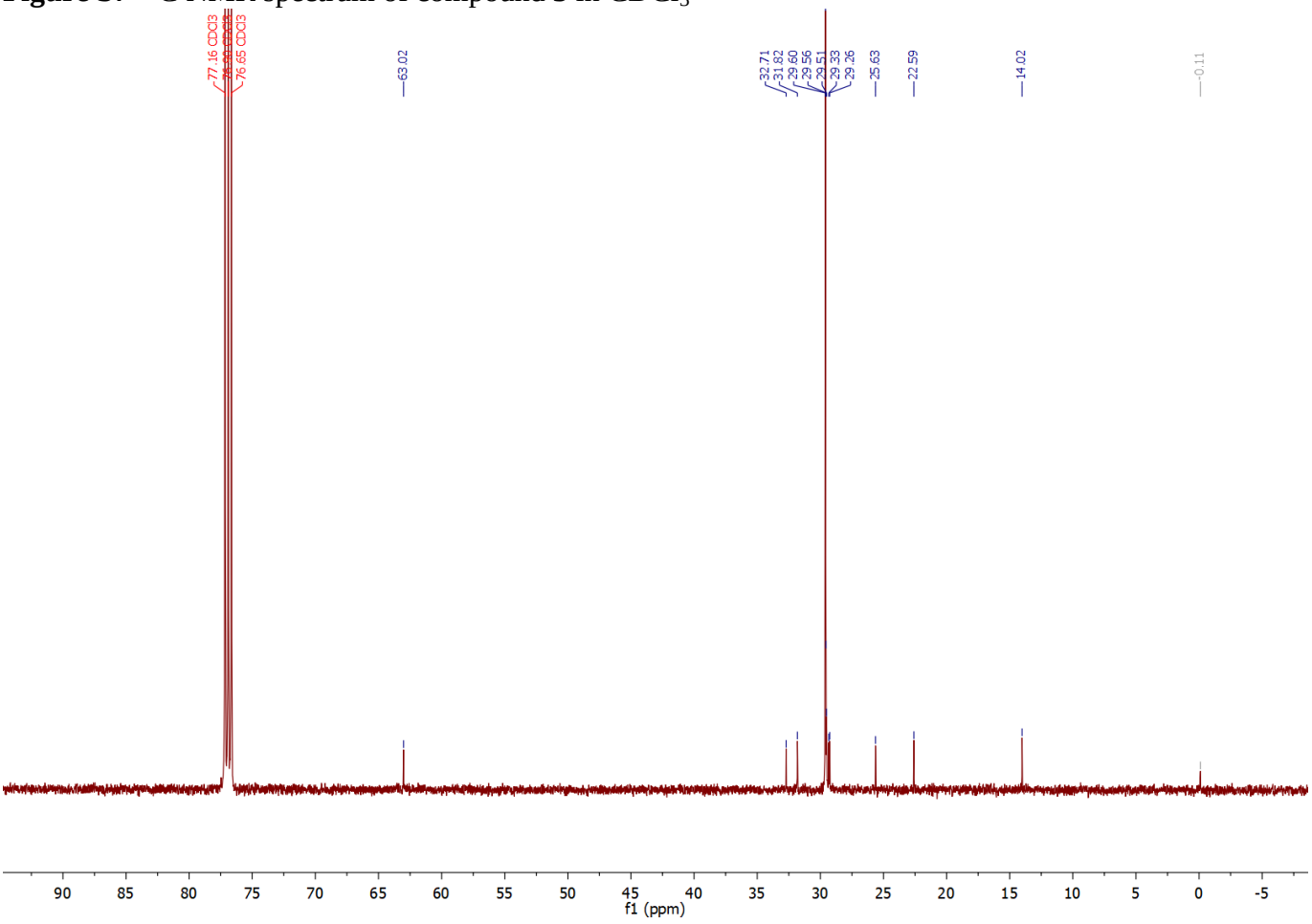

Figure S8 ^{1}H NMR spectrum of compound **4** in $CDCl_3$

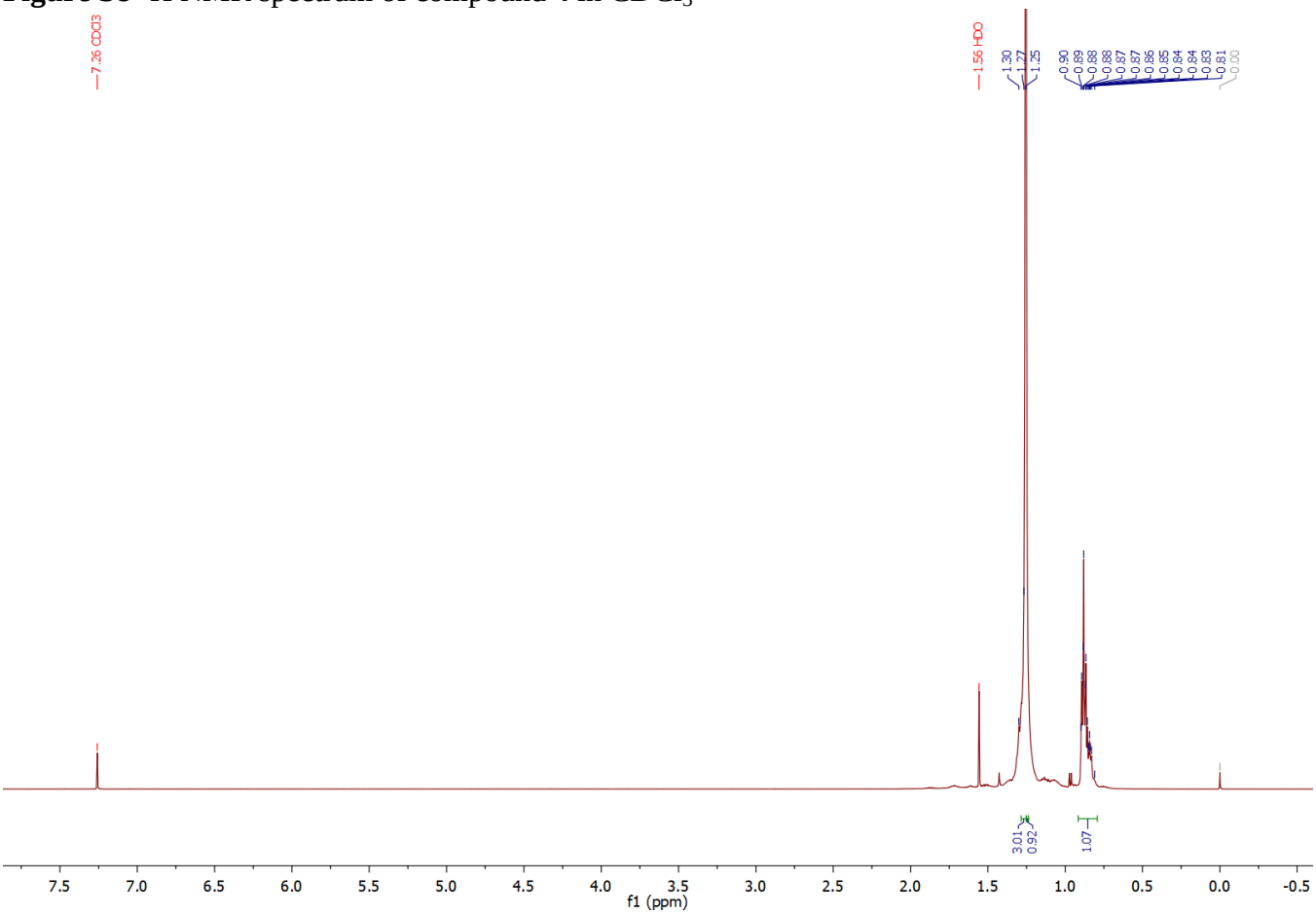

Figure S9 ^{13}C NMR spectrum of compound **4** in $CDCl_3$

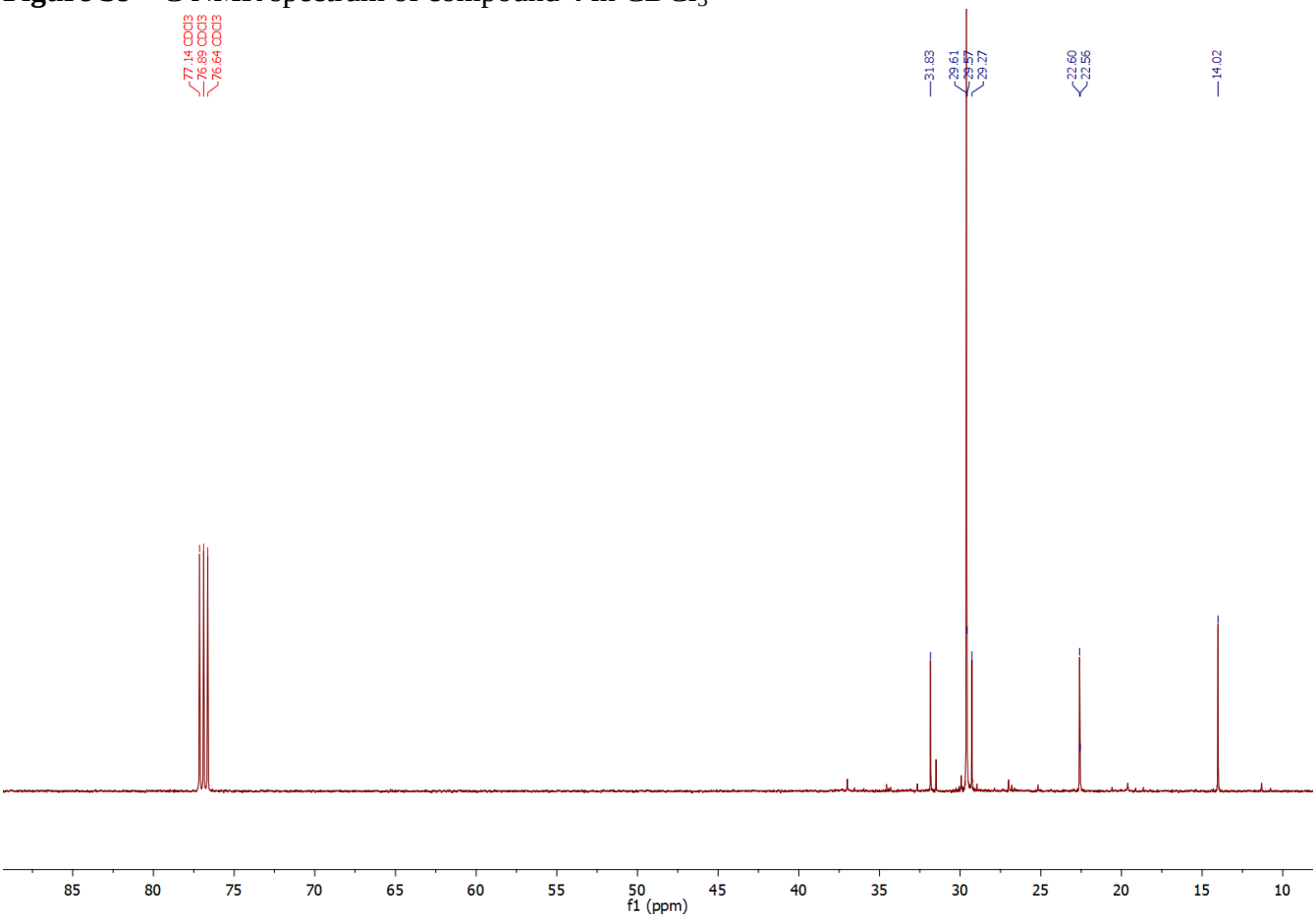

Figure S10 ^{1}H NMR spectrum of compound **5** in $CDCl_3$

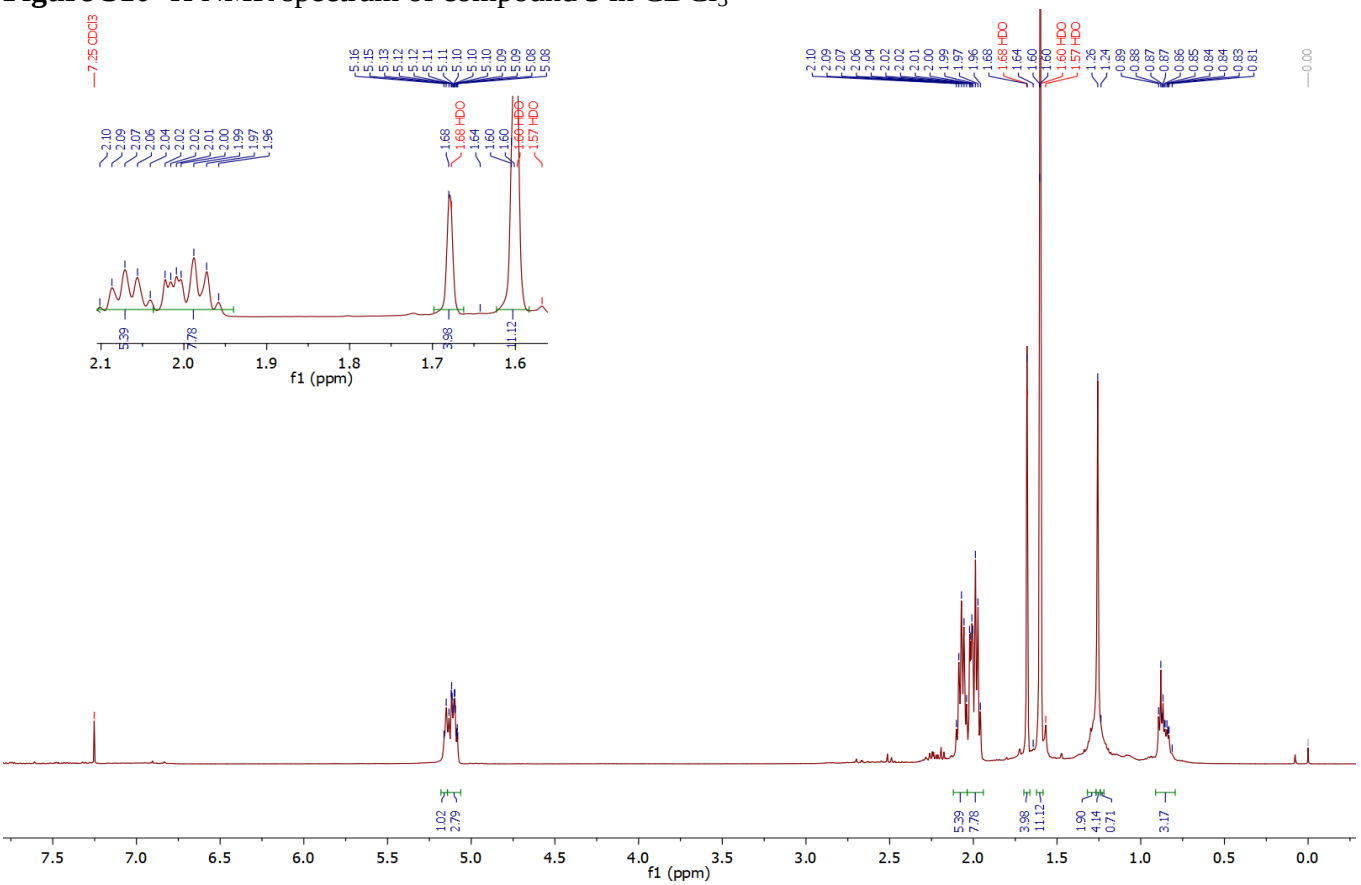

Figure S11 ^{13}C NMR spectrum of compound **5** in $CDCl_3$

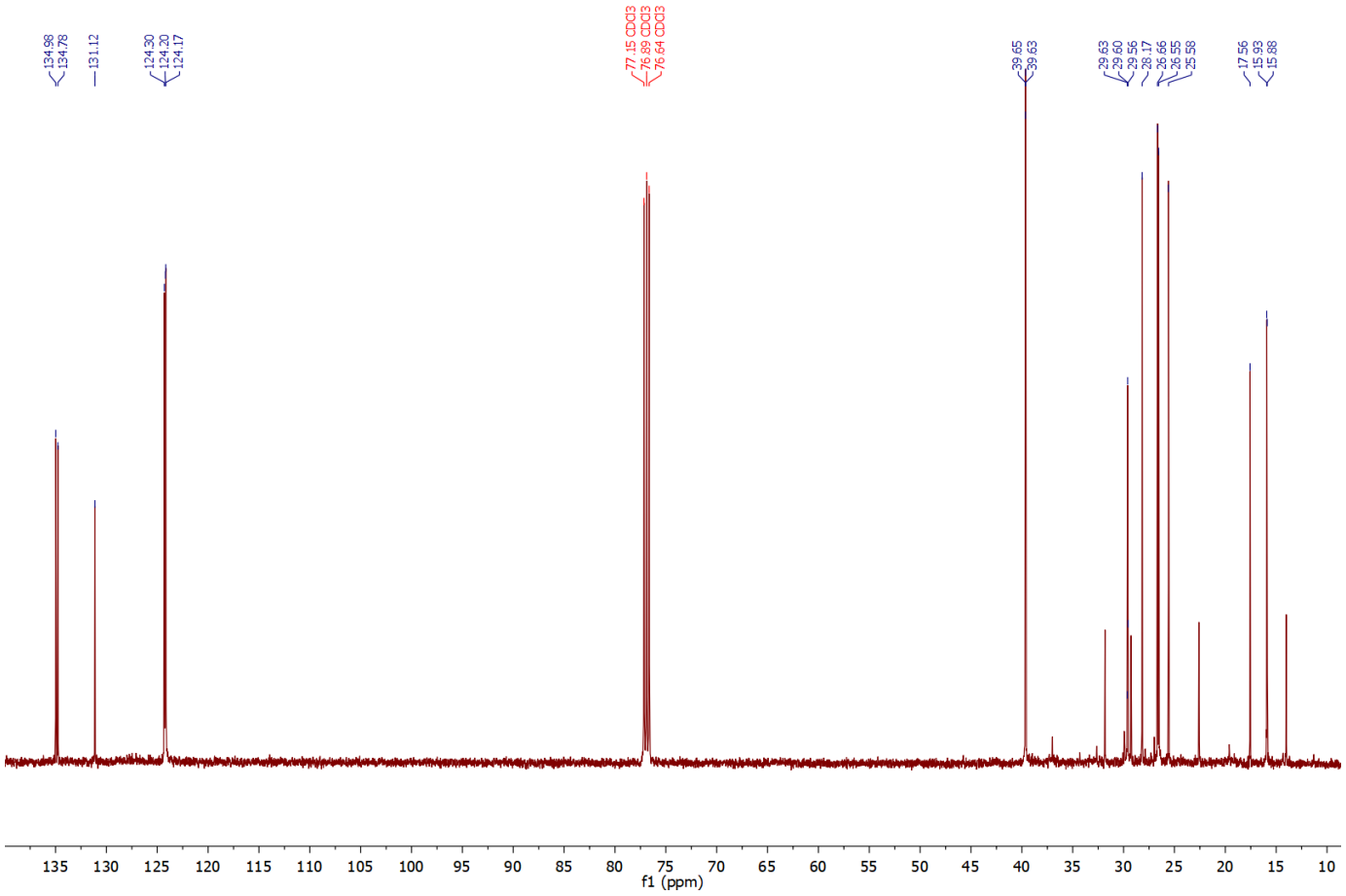

Figure S12 ^{1}H NMR spectrum of compound **6** in $CDCl_3$

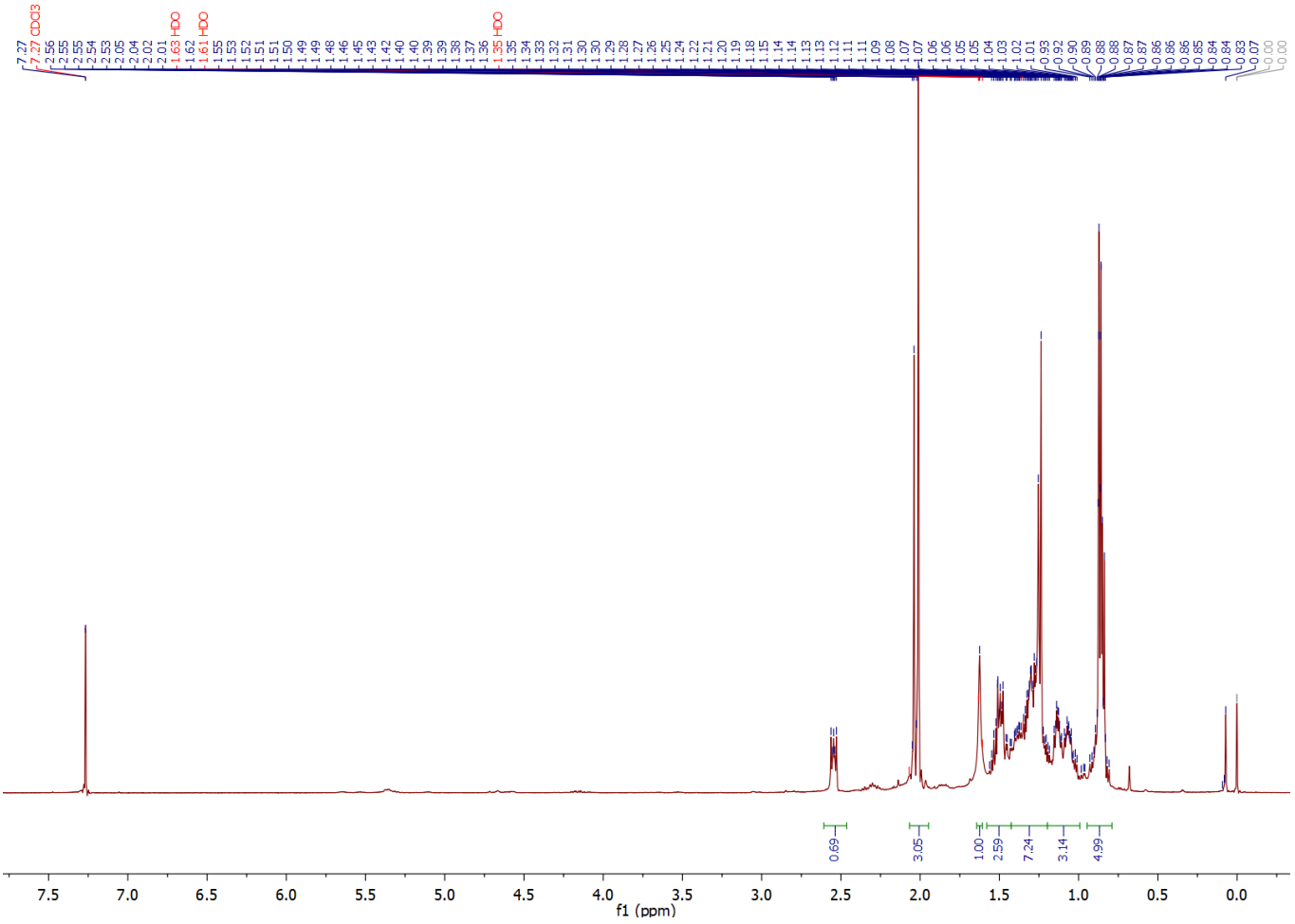

Figure S13 ^{13}C NMR spectrum of compound **6** in $CDCl_3$

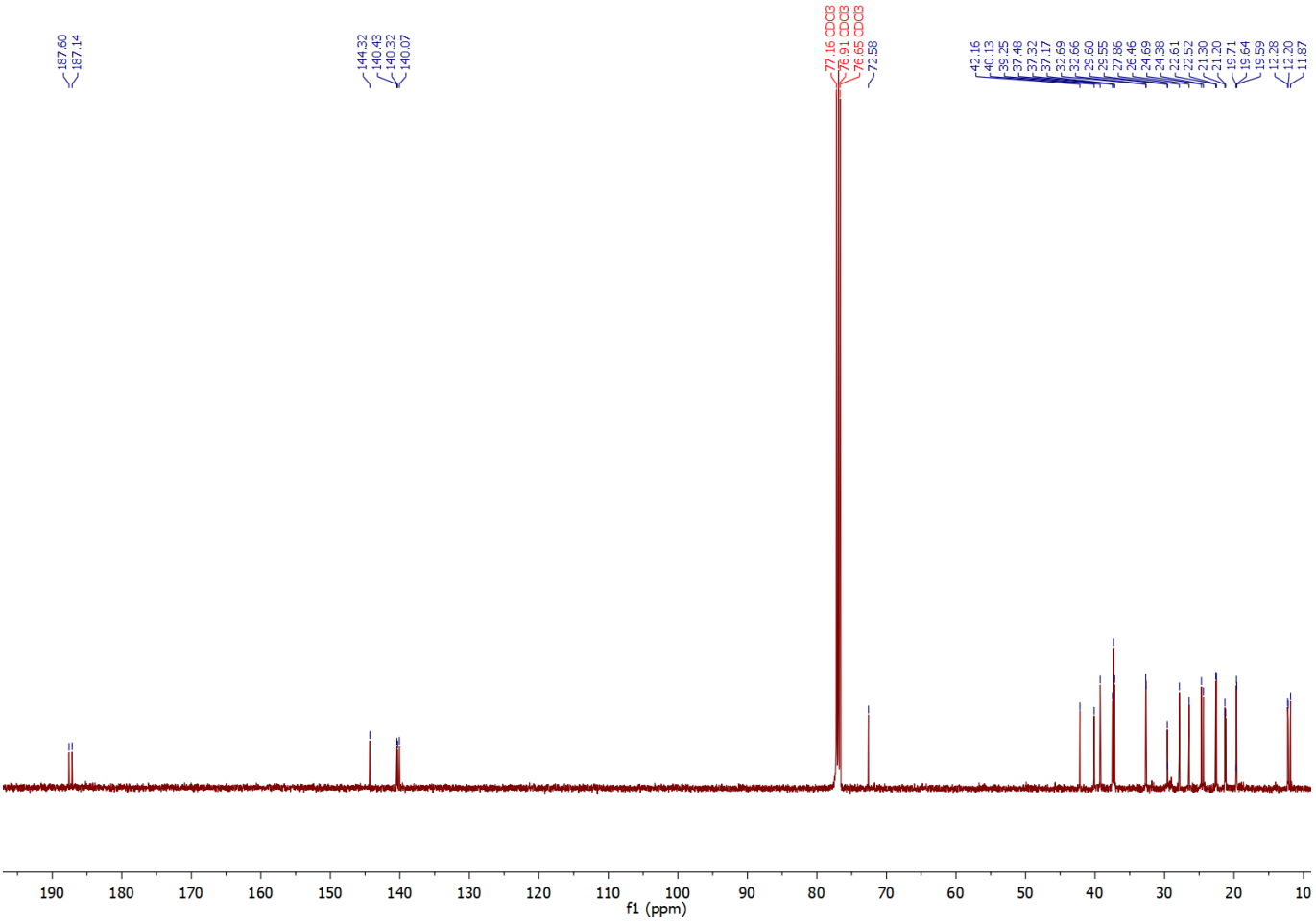

Figure S14 ^{1}H NMR spectrum of compound **7** in $CDCl_3$

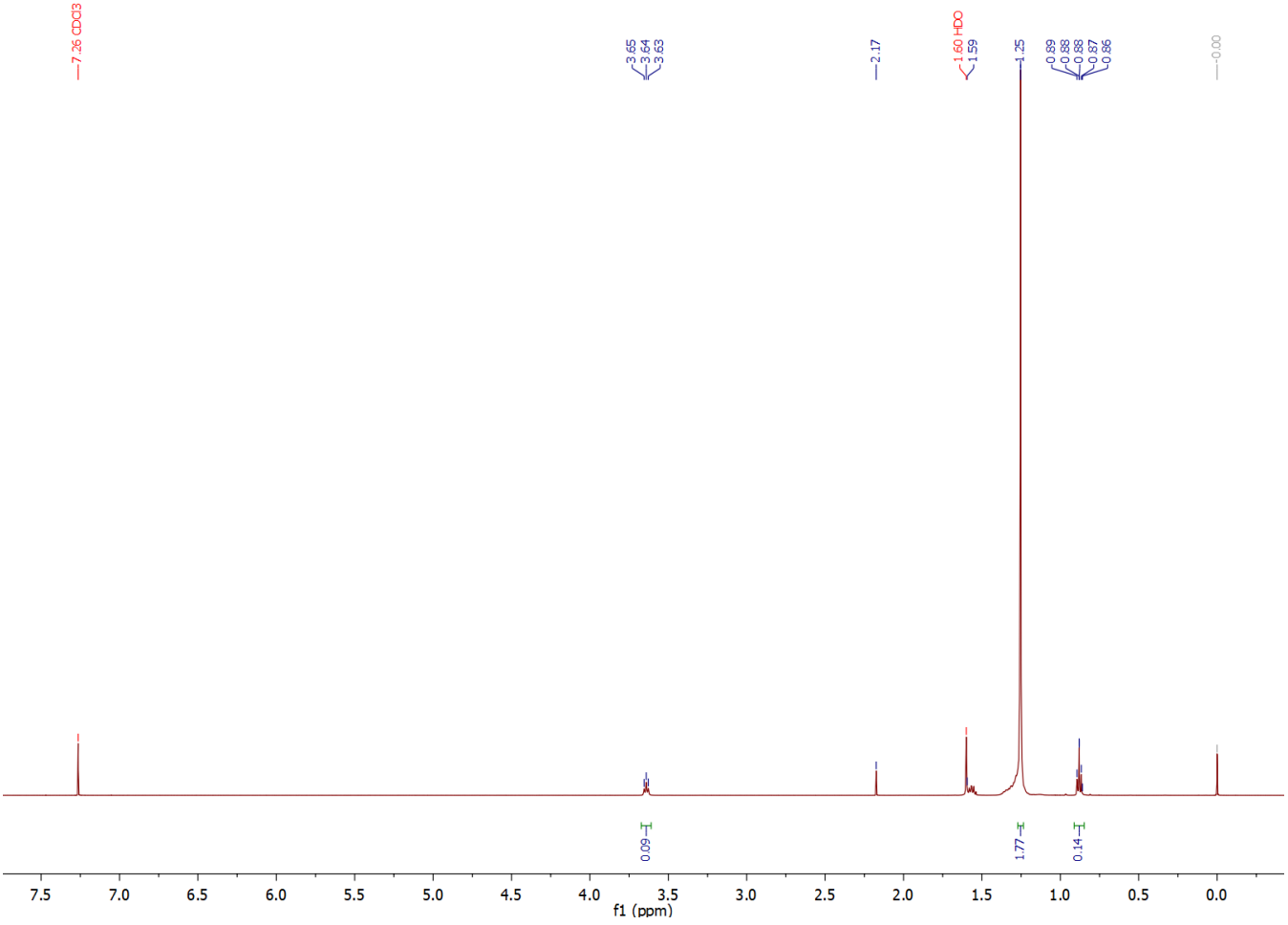

Figure S15 ^{13}C NMR spectrum of compound **7** in $CDCl_3$

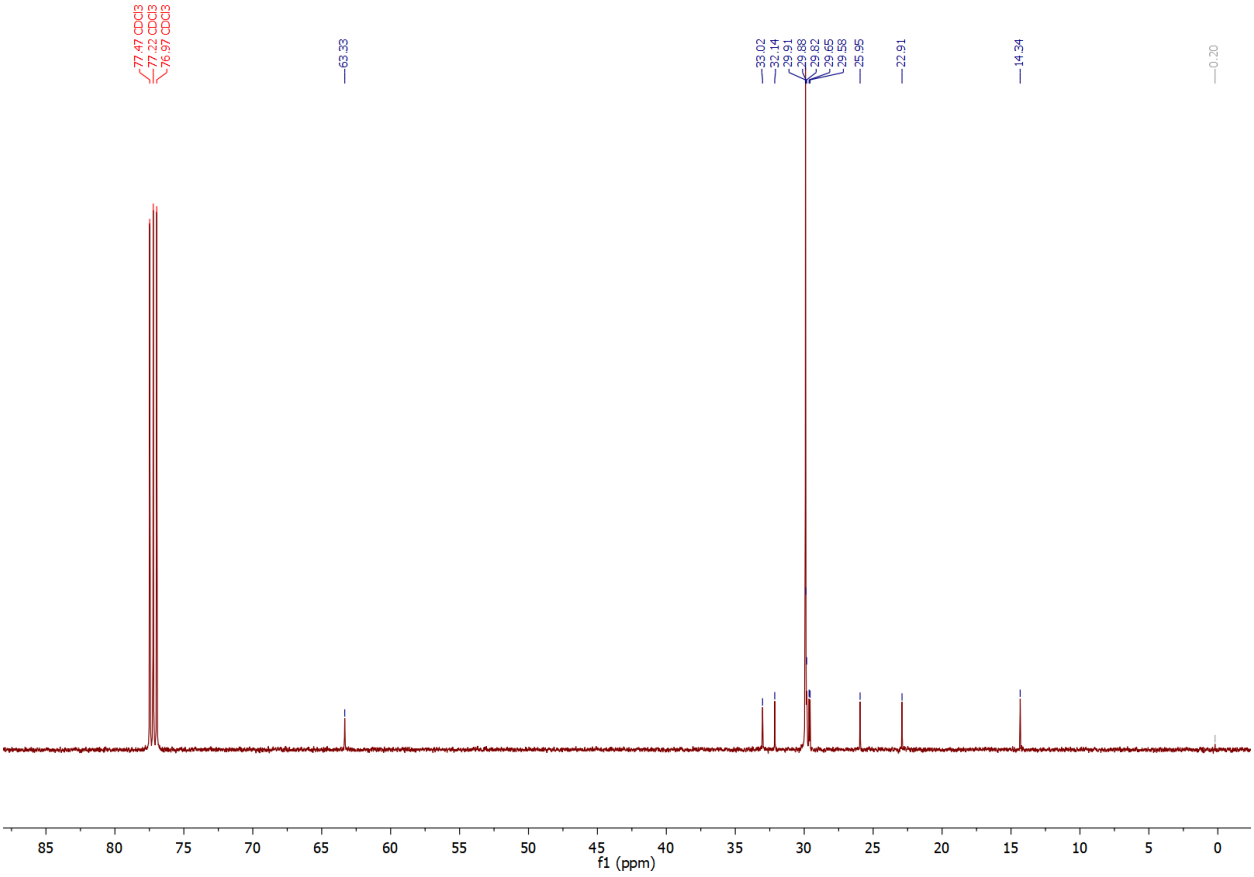

Figure S16 ^{1}H NMR spectrum of compound **8** in $CDCl_3$

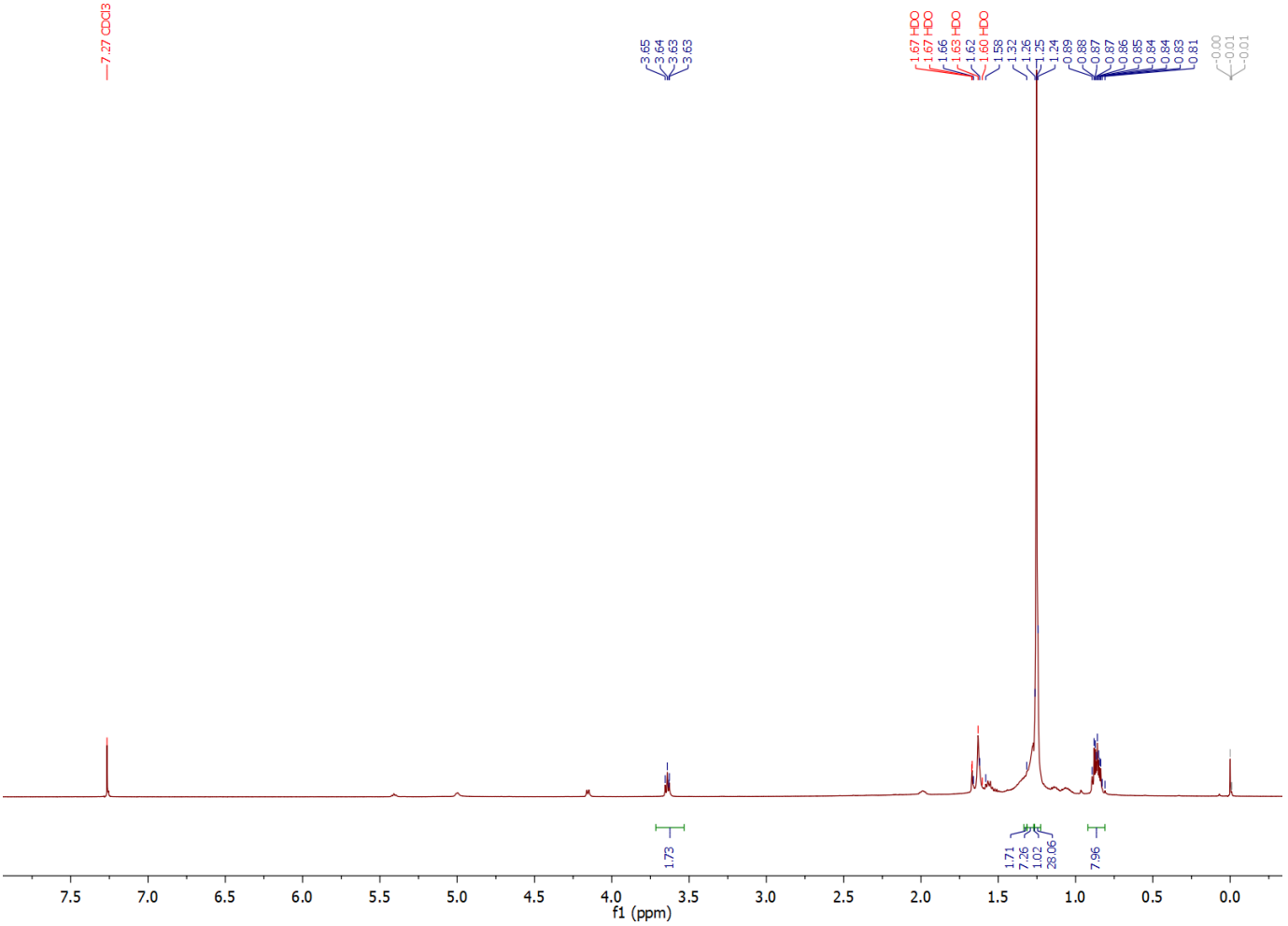

Figure S17 ^{13}C NMR spectrum of compound **8** in $CDCl_3$

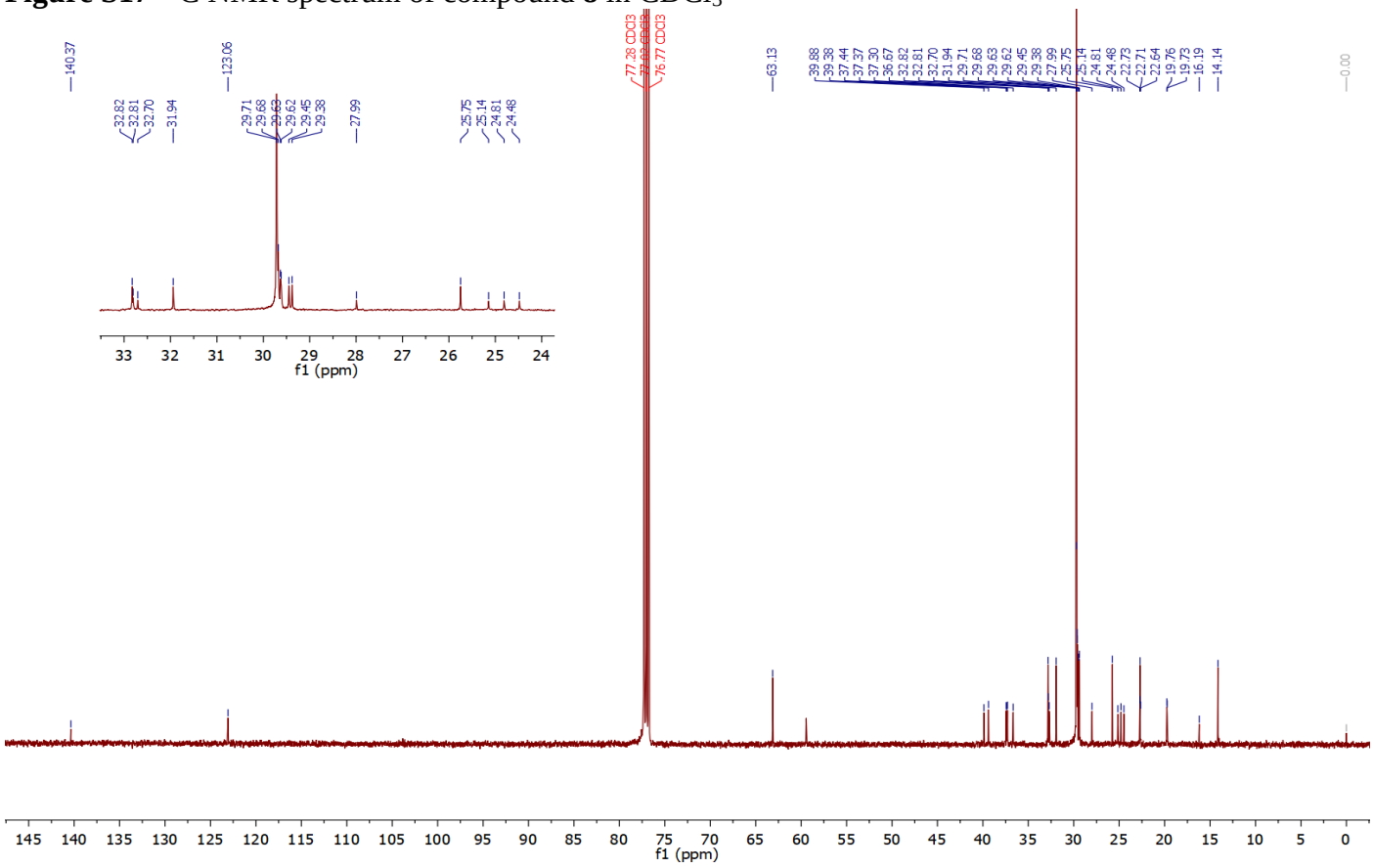

Figure S18 ^{1}H NMR spectrum of compound **9** in $CDCl_3$

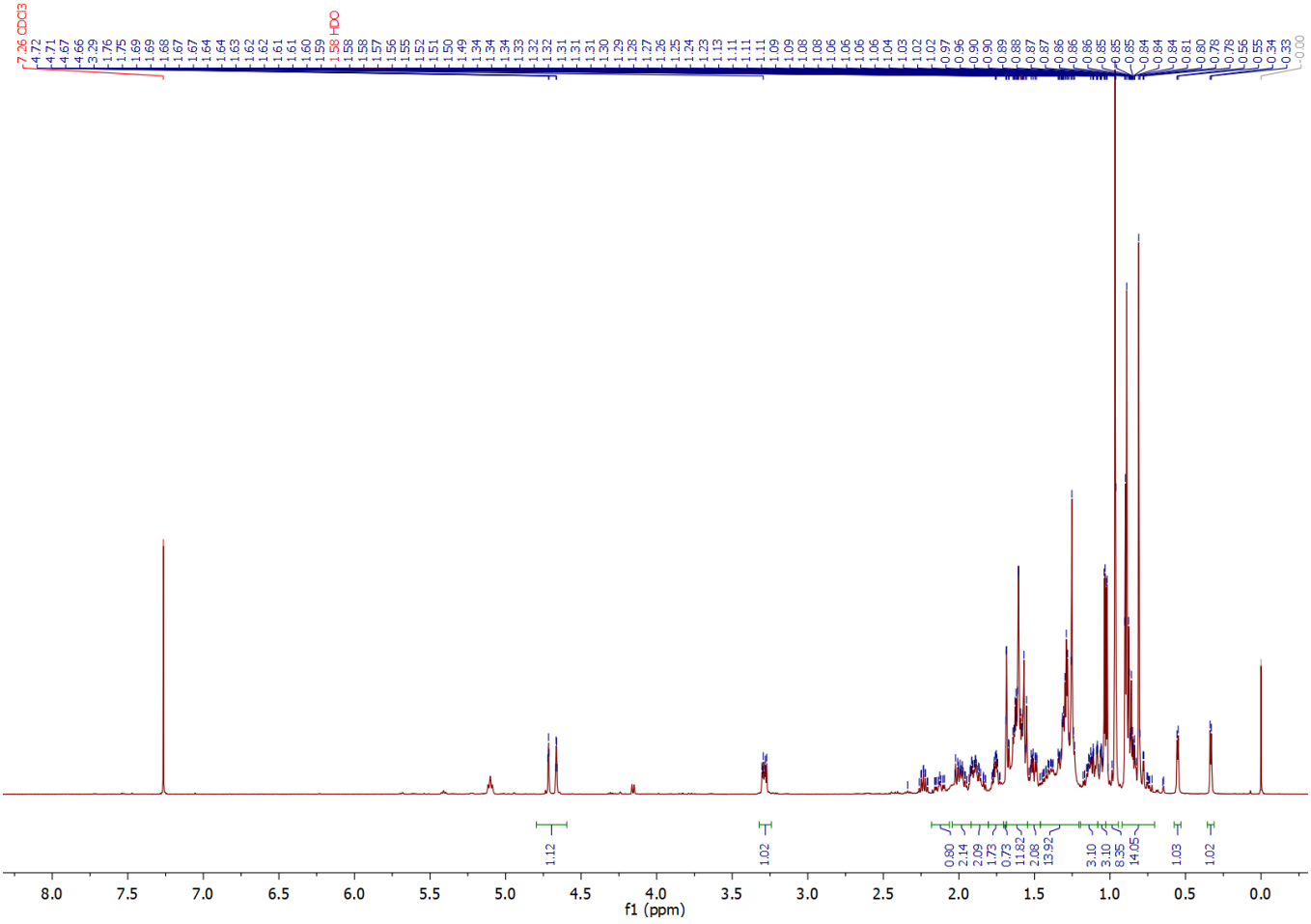

Figure S19 ^{13}C NMR spectrum of compound **9** in $CDCl_3$

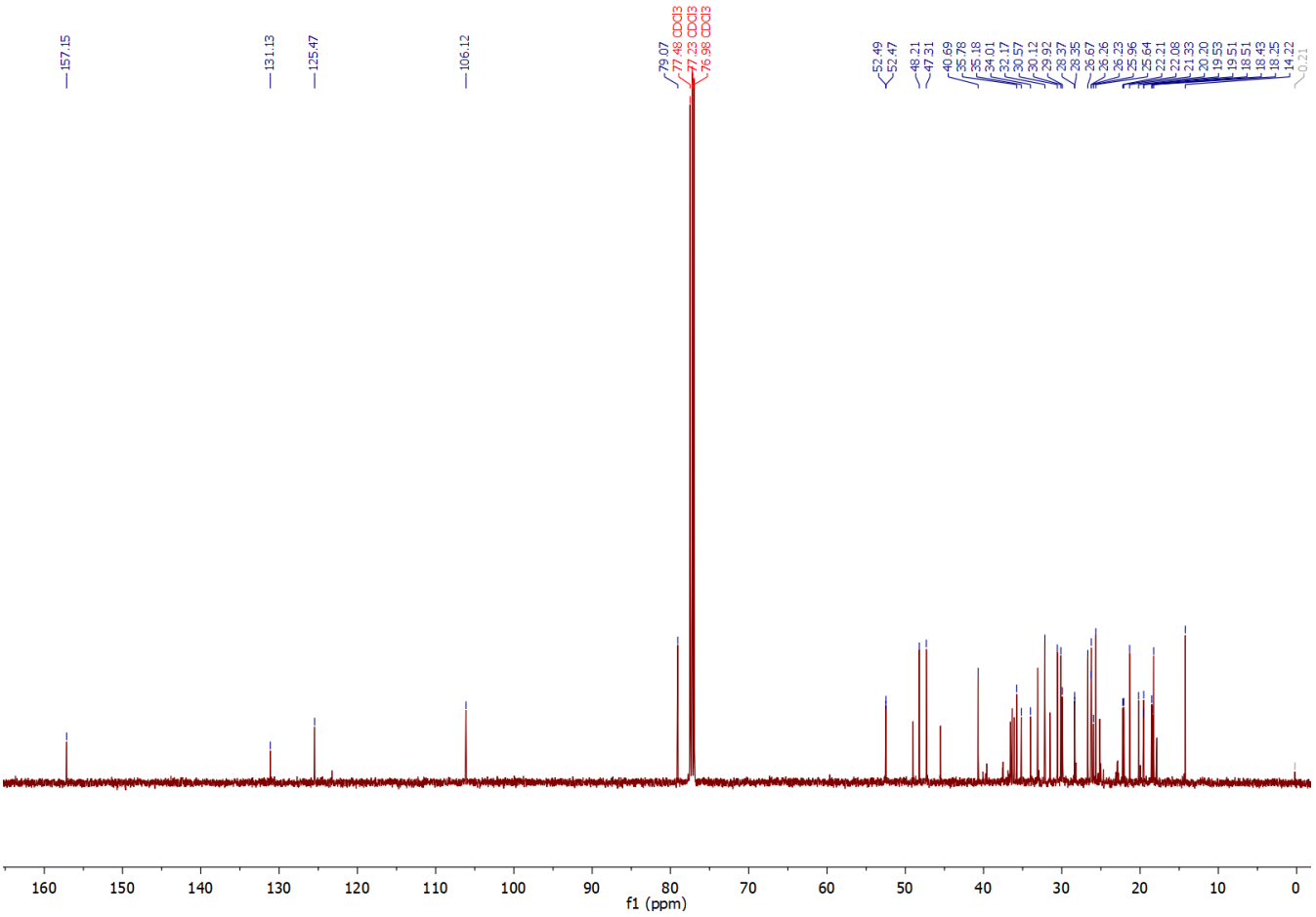

Figure S20 ^{1}H NMR spectrum of compound **10** in $CDCl_3$

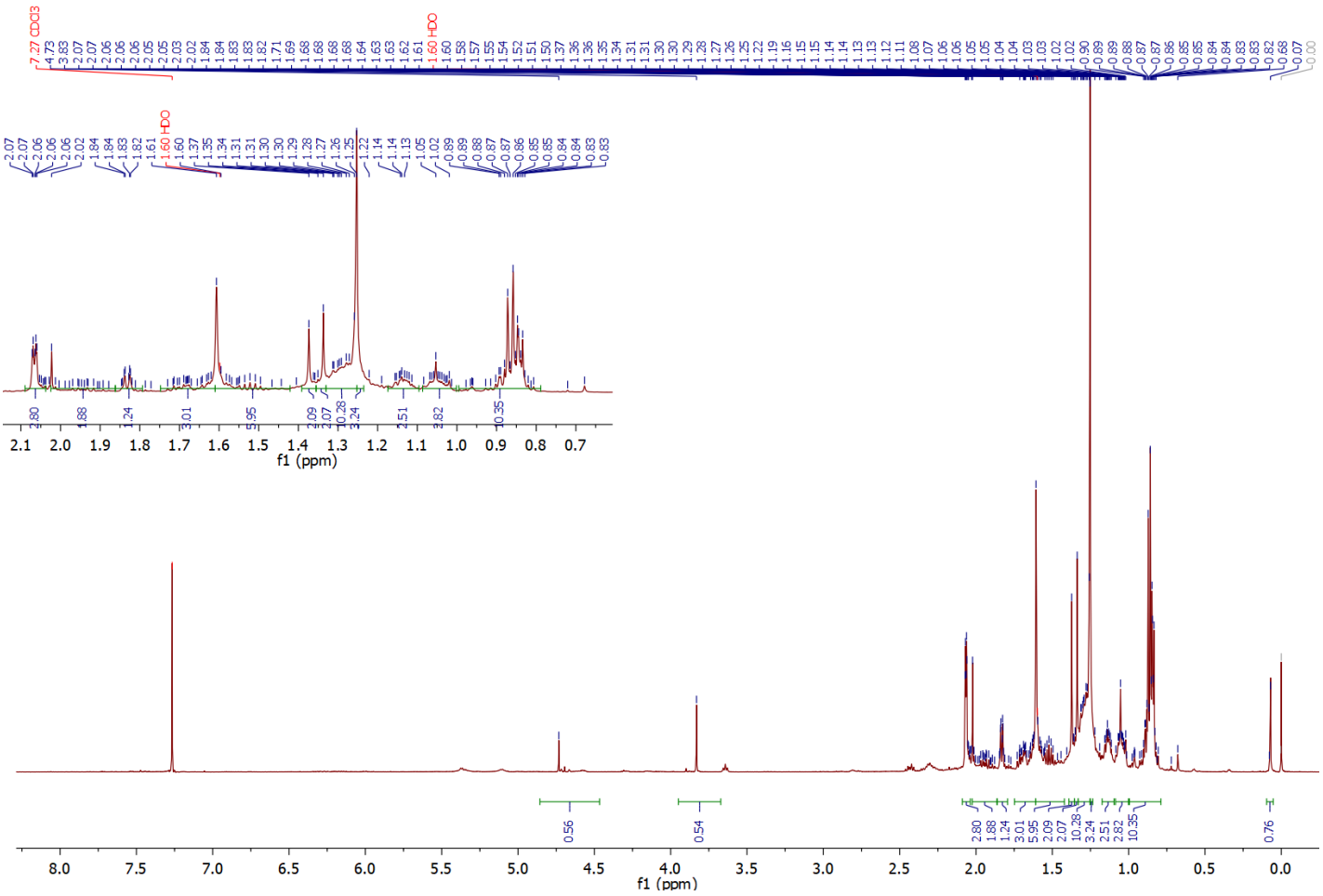

Figure S21 ^{13}C NMR spectrum of compound **10** in $CDCl_3$

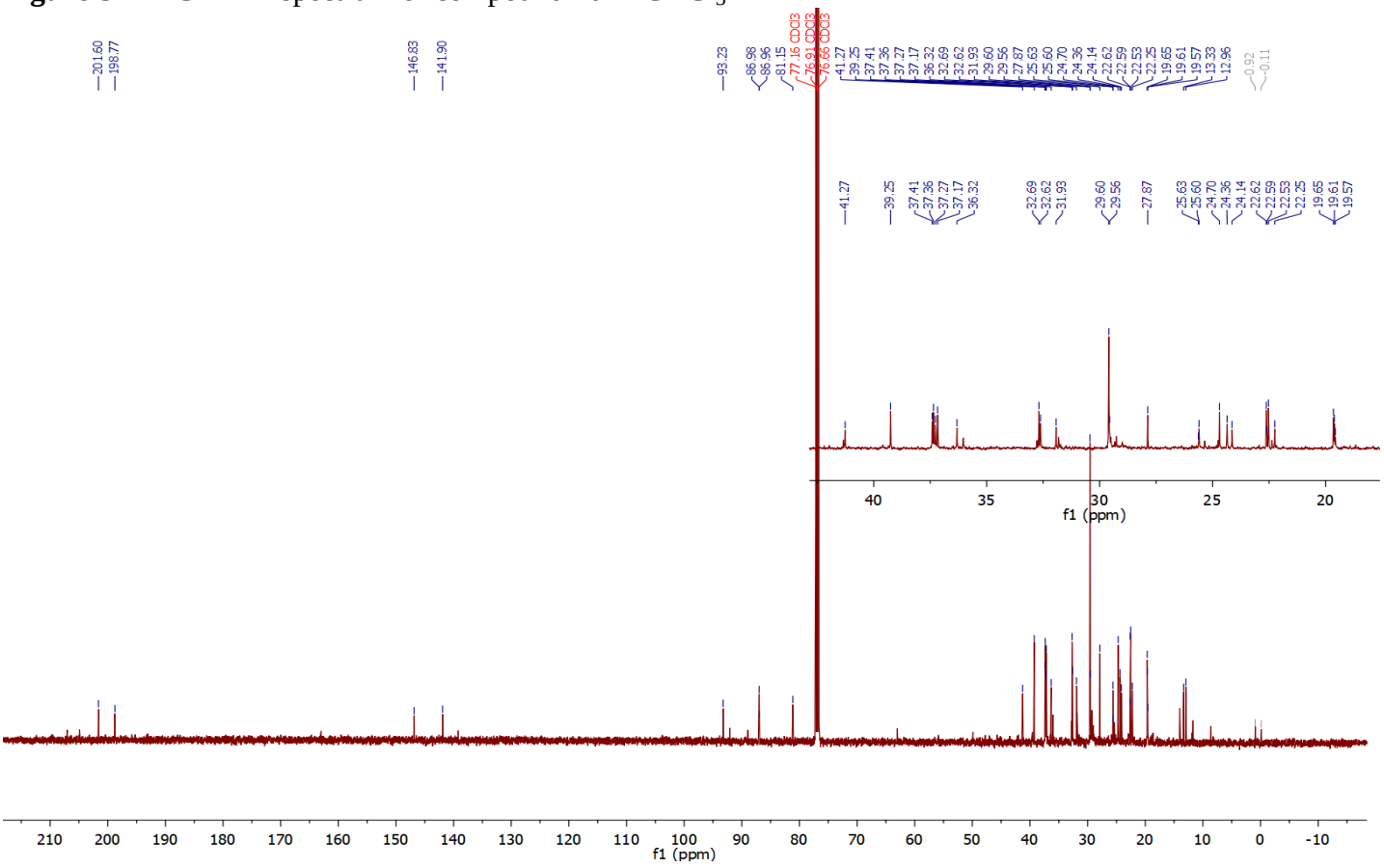

Figure S22 ^{1}H NMR spectrum of compound **11** in $CDCl_3$

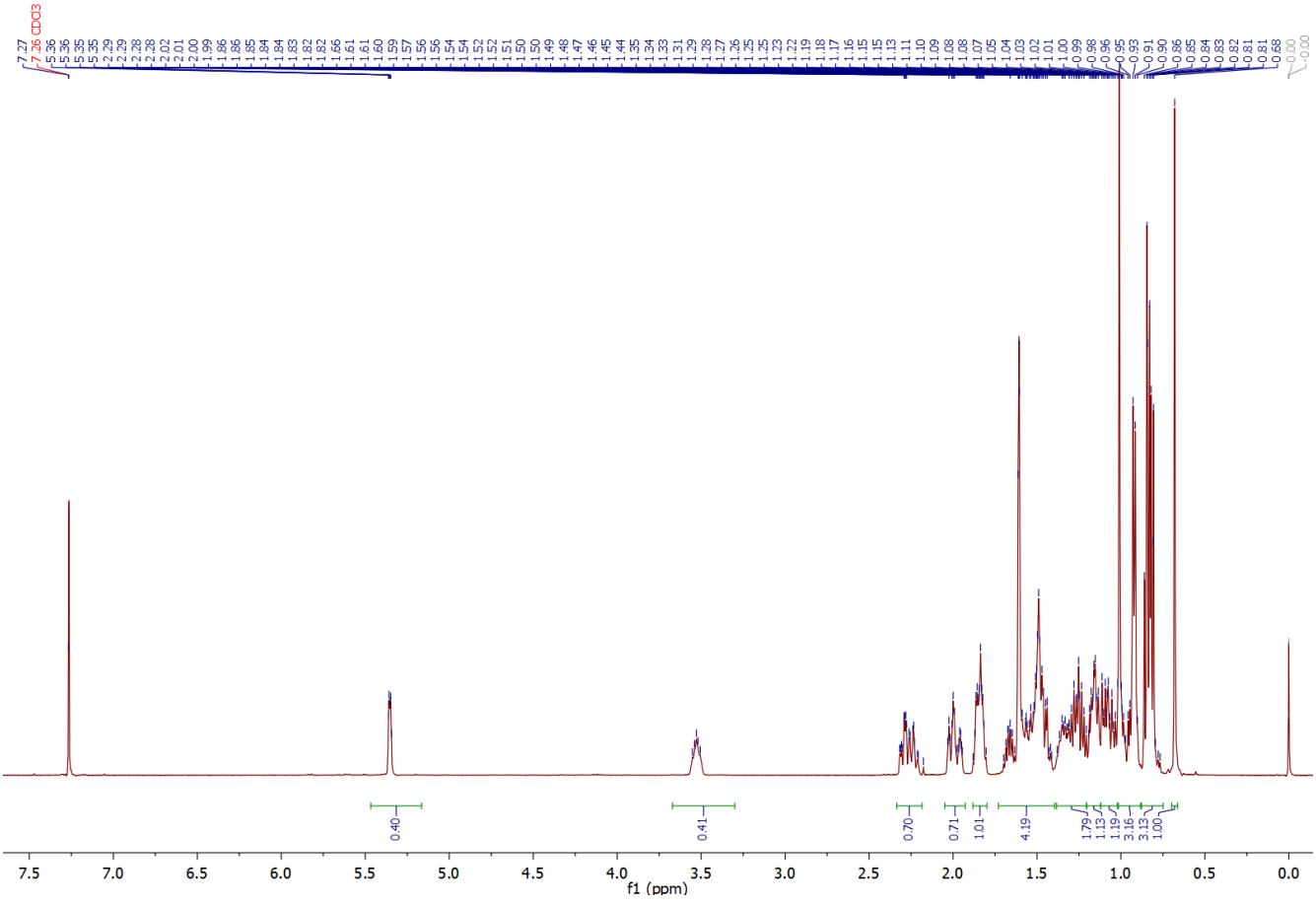

Figure S23 ^{13}C NMR spectrum of compound **11** in $CDCl_3$

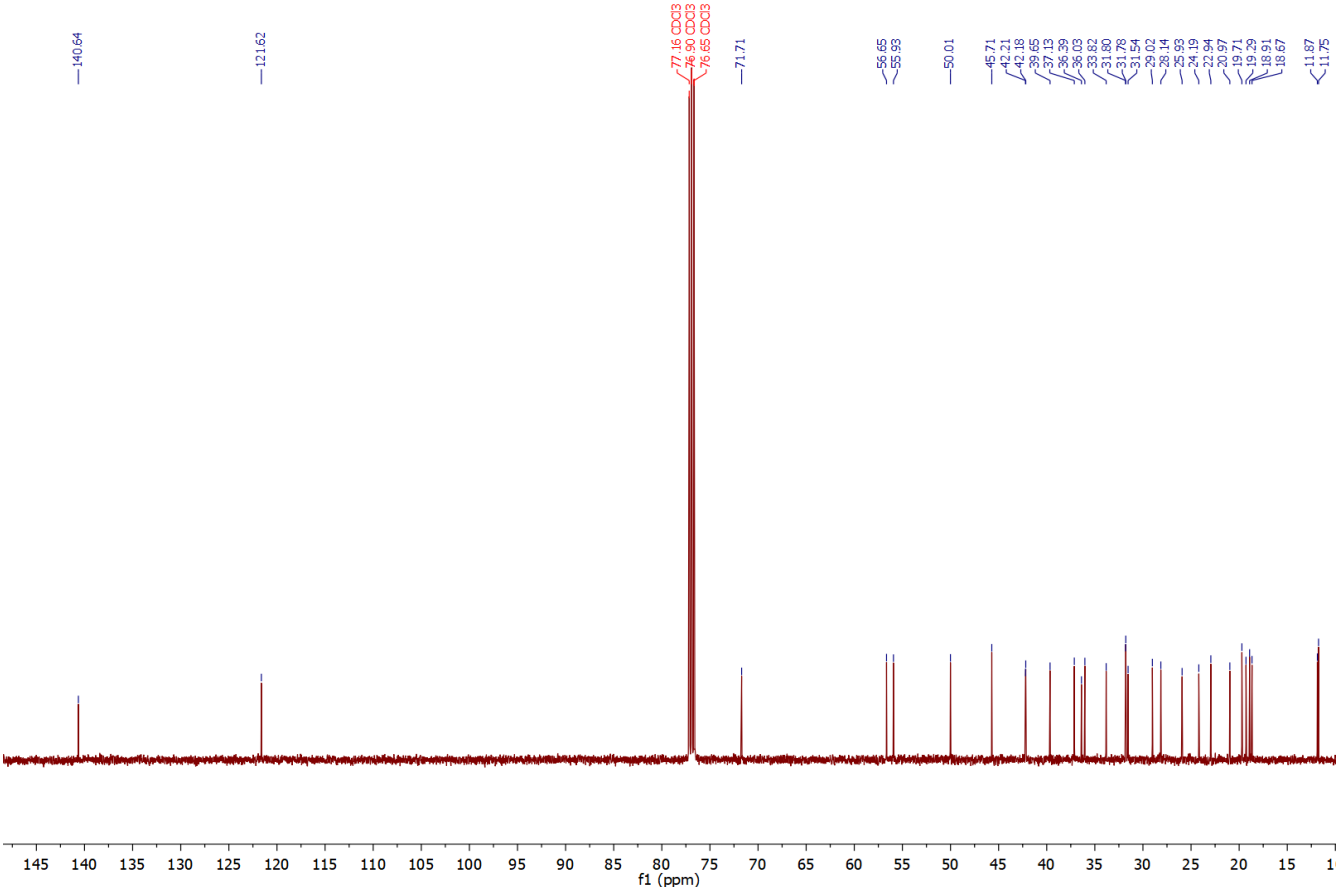

Figure S24 ^{1}H NMR spectrum of compound **12** in $CDCl_3$

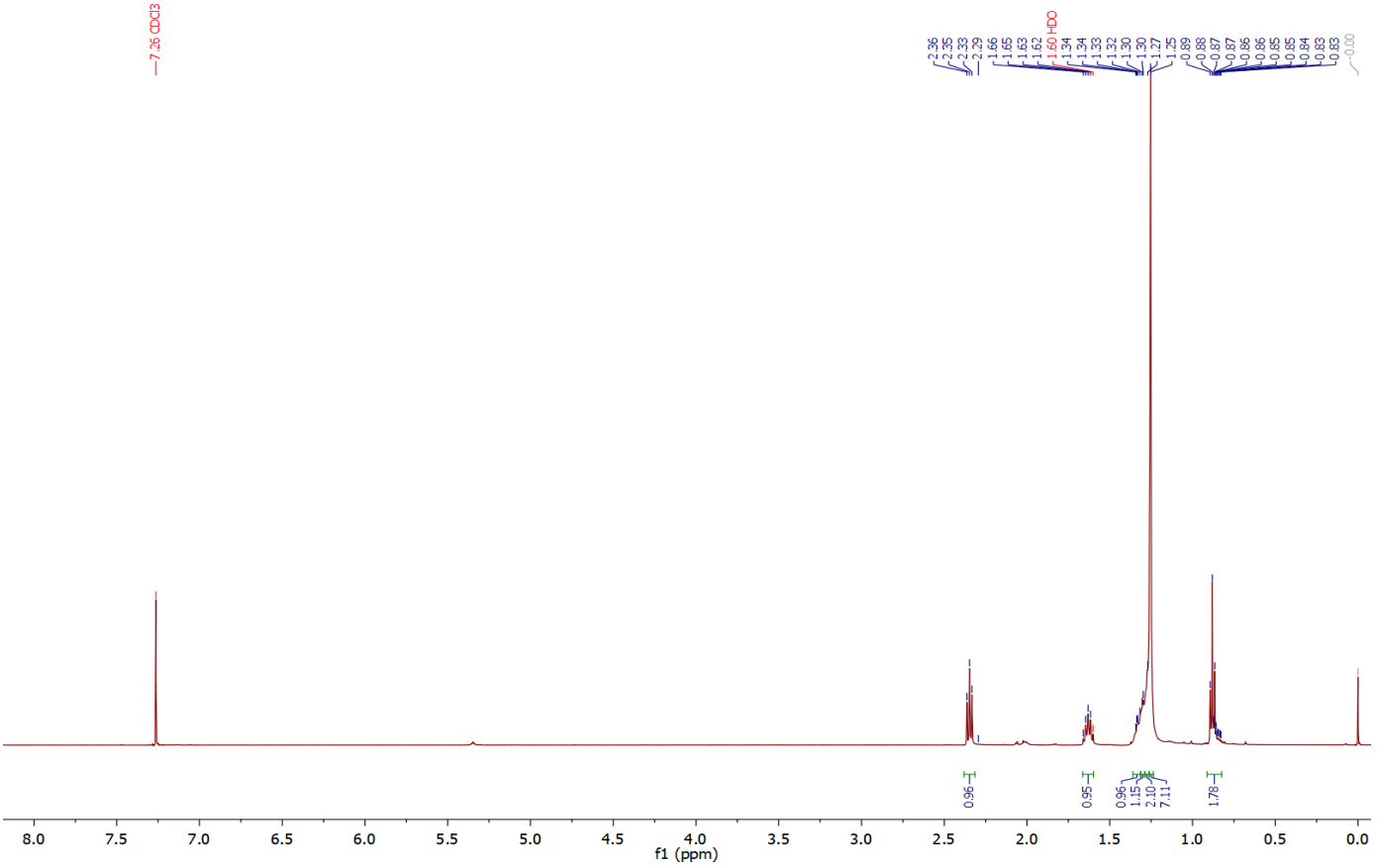

Figure S25 ^{13}C NMR spectrum of compound **12** in $CDCl_3$

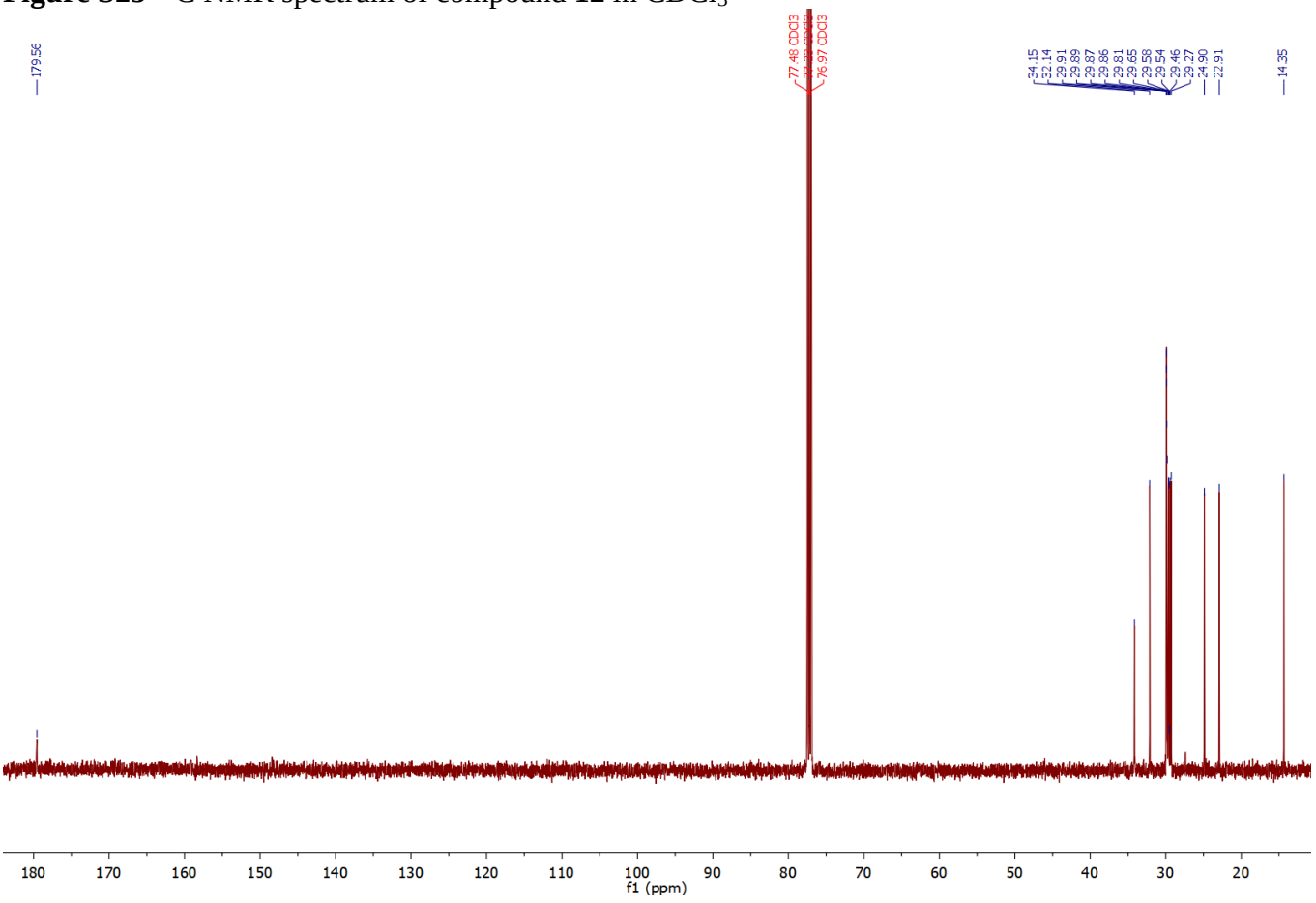

Figure S26 ^{1}H NMR spectrum of compound **13** in $CDCl_3$

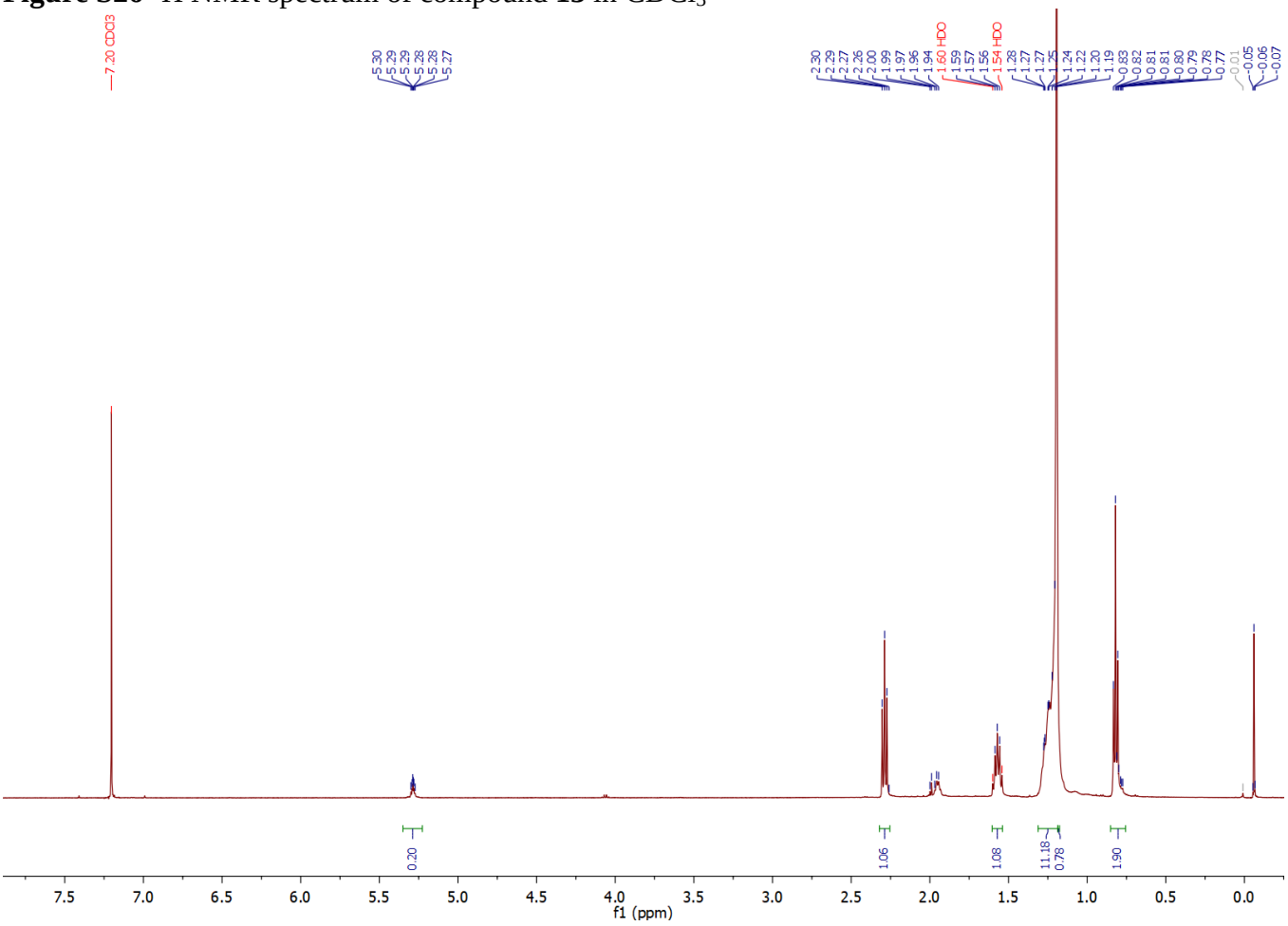

Figure S27 ^{13}C NMR spectrum of compound **13** in $CDCl_3$

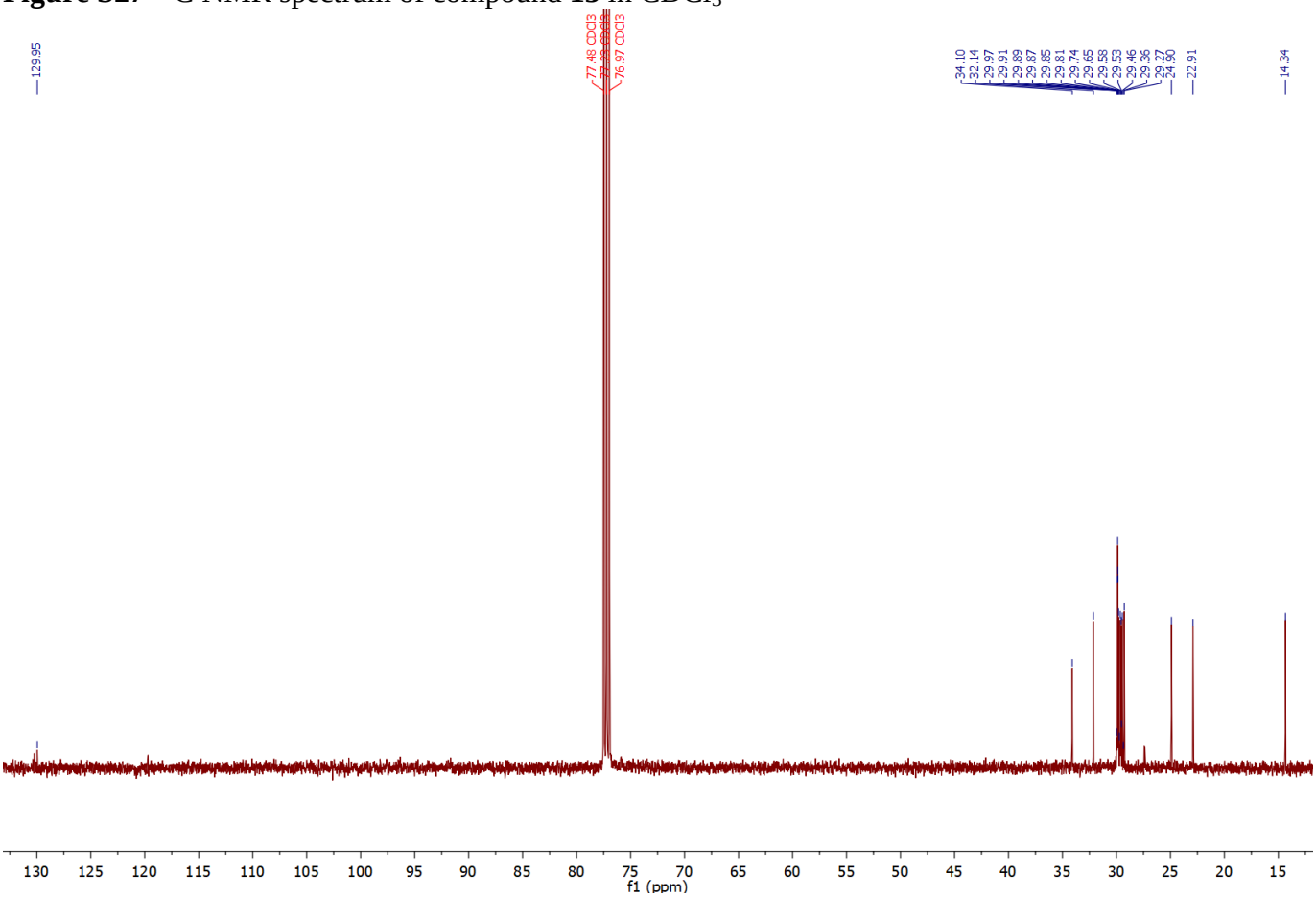

Figure S28 ^{1}H NMR spectrum of compound **14** in $CDCl_3$

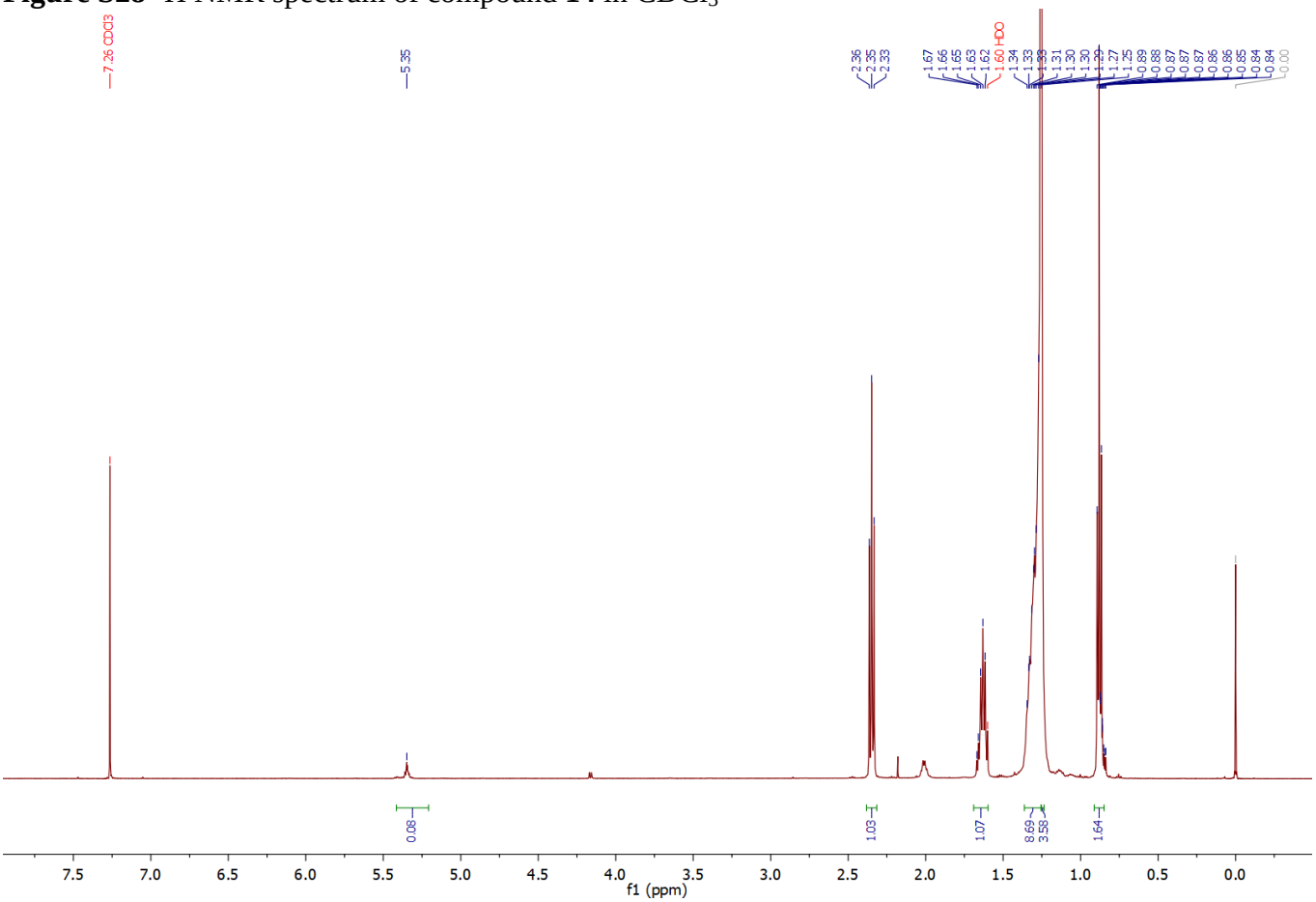

Figure S29 ^{13}C NMR spectrum of compound **14** in $CDCl_3$

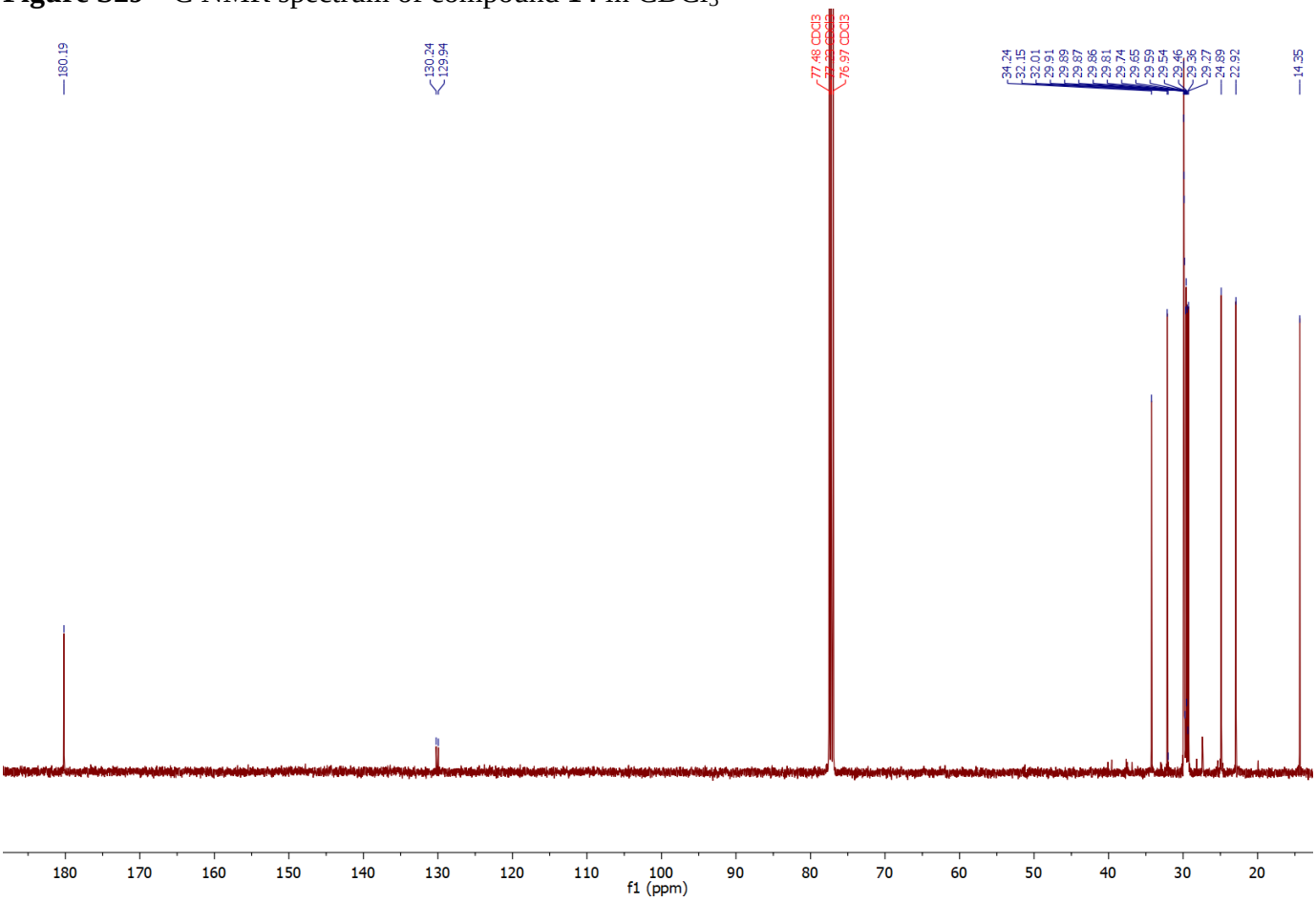

Figure S30 ^{1}H NMR spectrum of compound **15** in $CDCl_3$

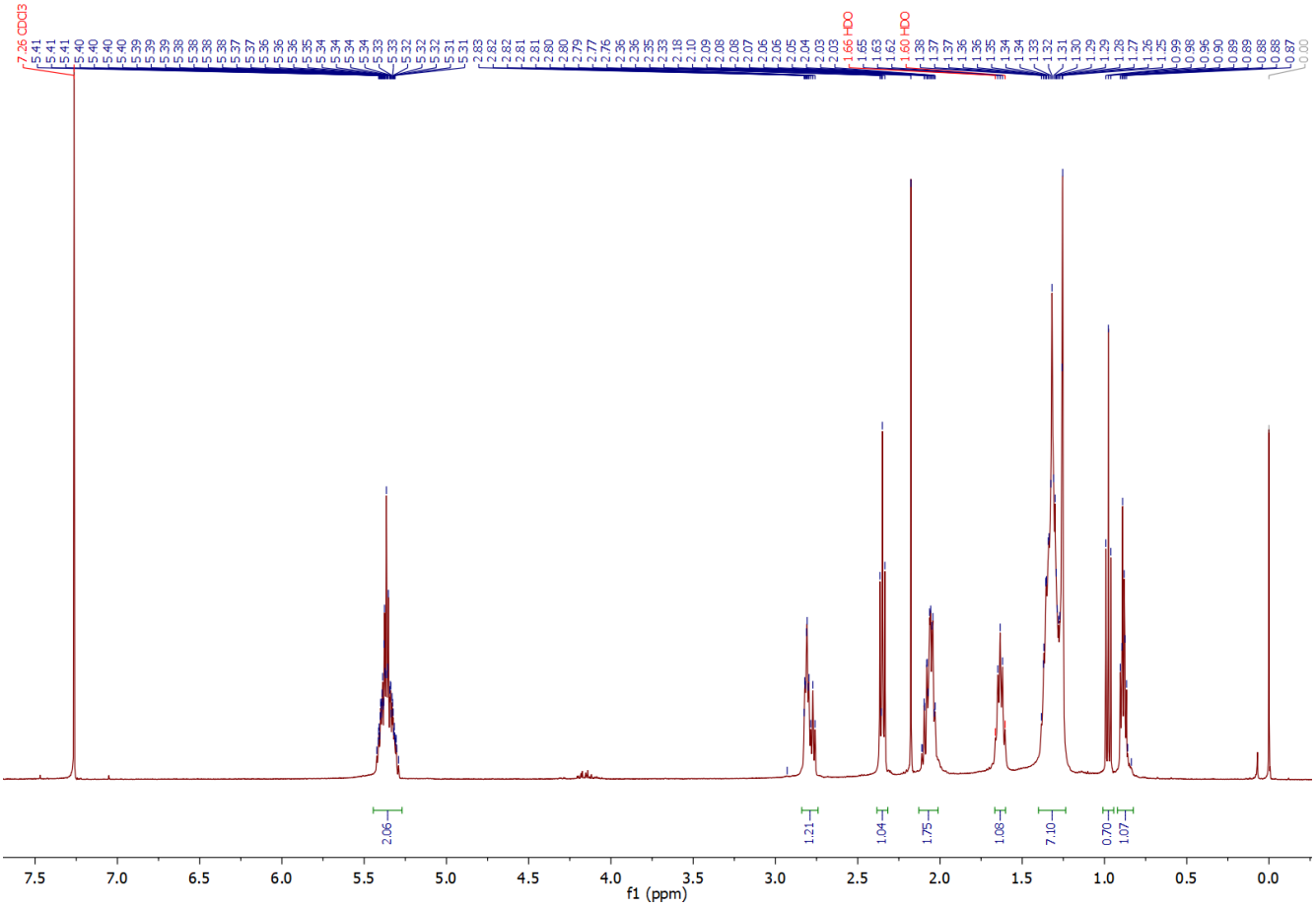

Figure S31 ^{13}C NMR spectrum of compound **15** in $CDCl_3$

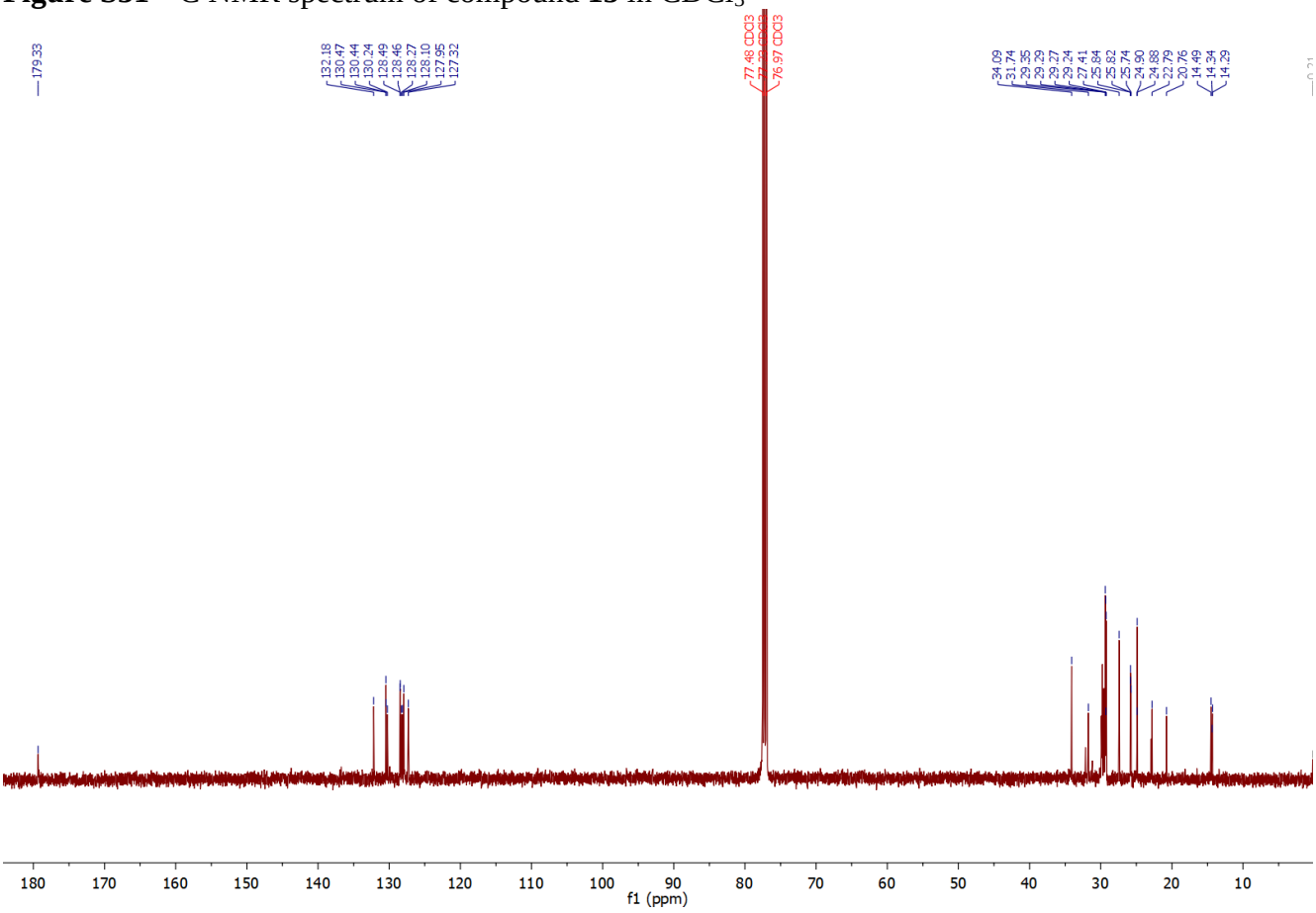

Figure S32 ^{1}H NMR spectrum of compound **16** in $CDCl_3$

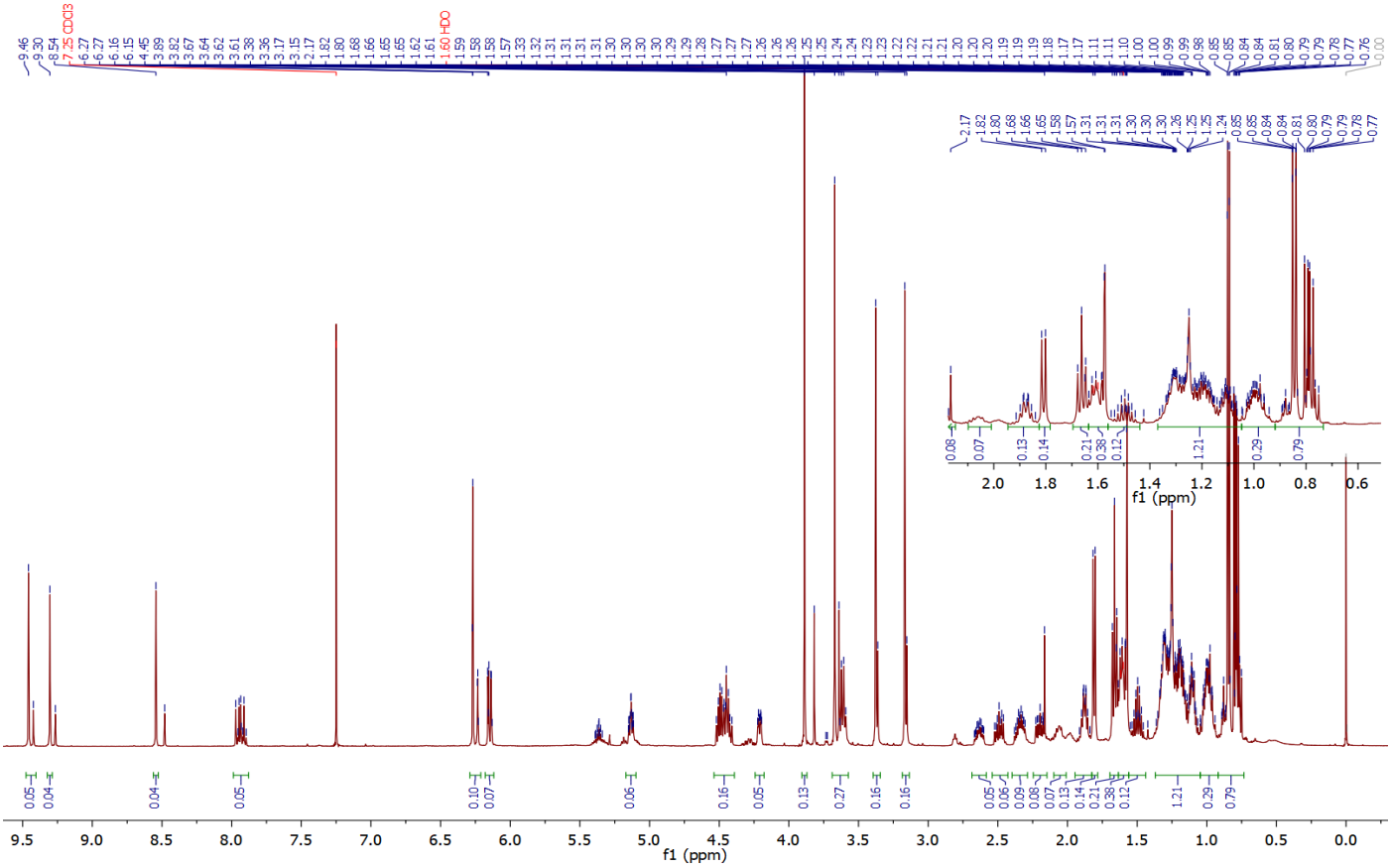

Figure S33 ^{13}C NMR spectrum of compound **16** in $CDCl_3$

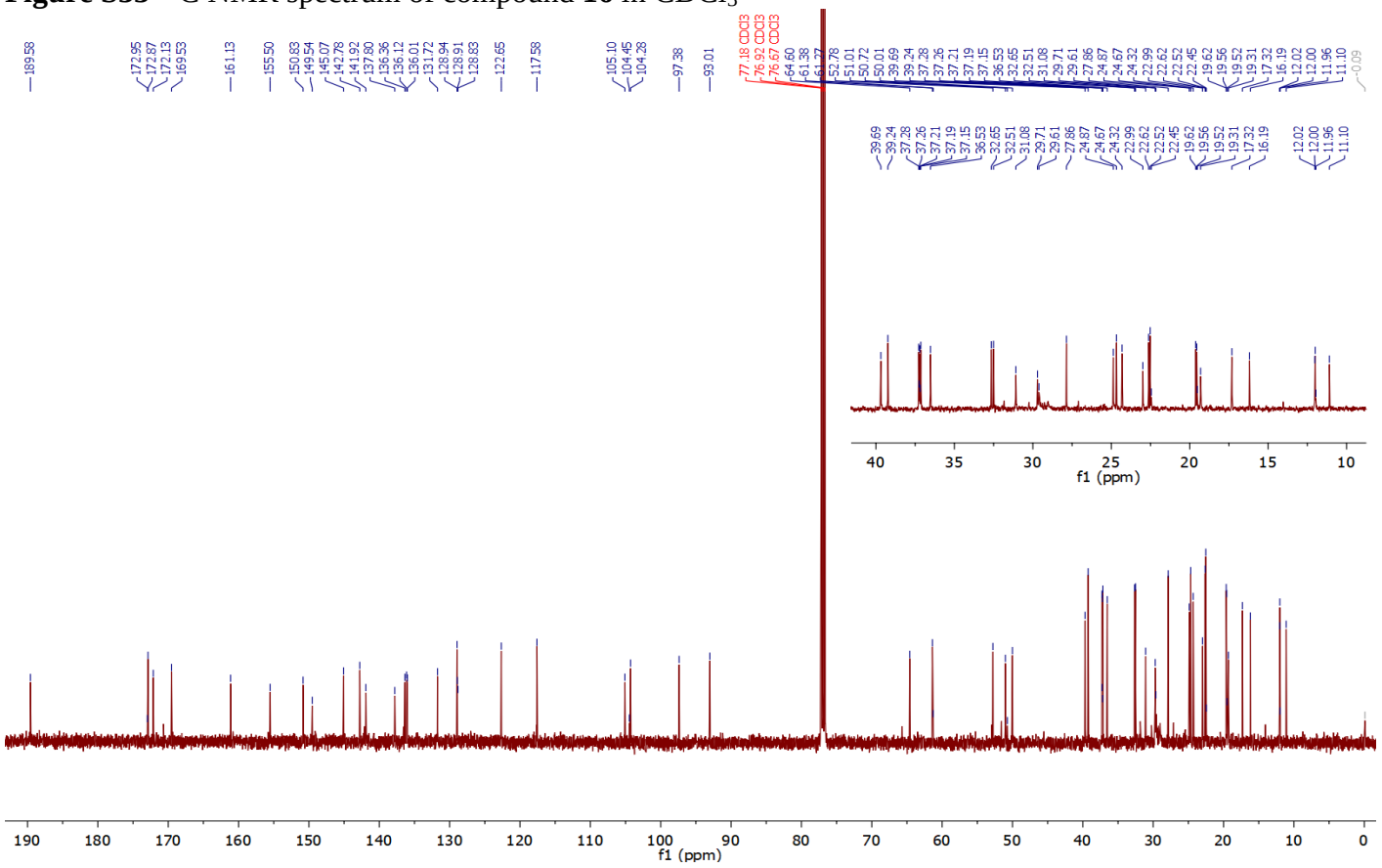

Figure S34 HRMS spectrum of compound **16**

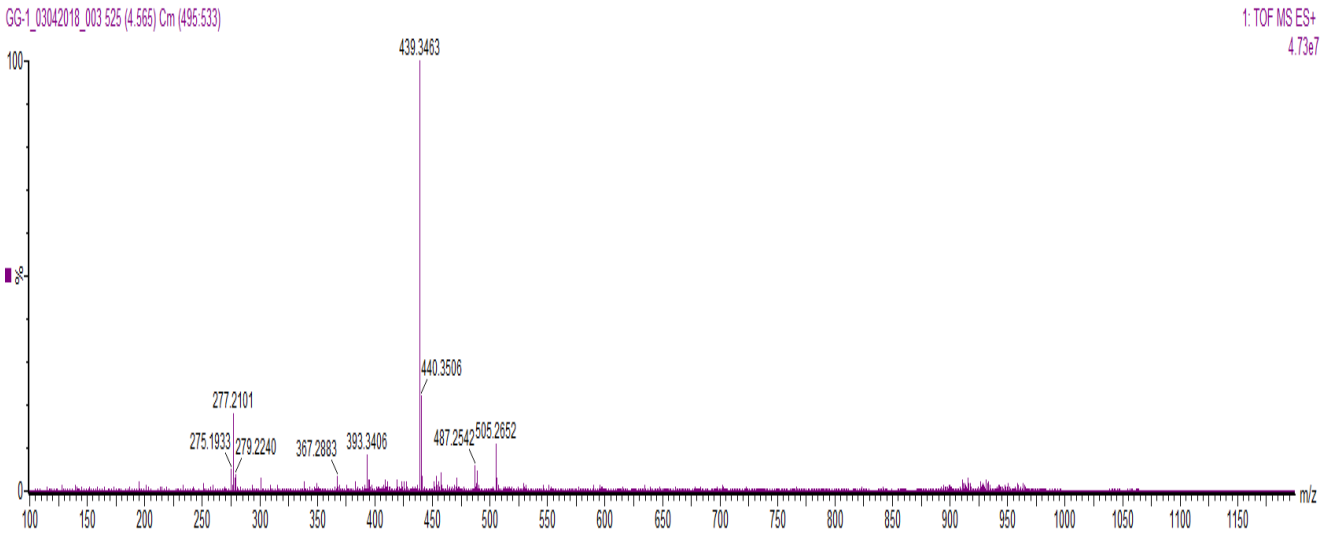

Figure S35 ^{1}H NMR spectrum of compound **17** in $CDCl_3$

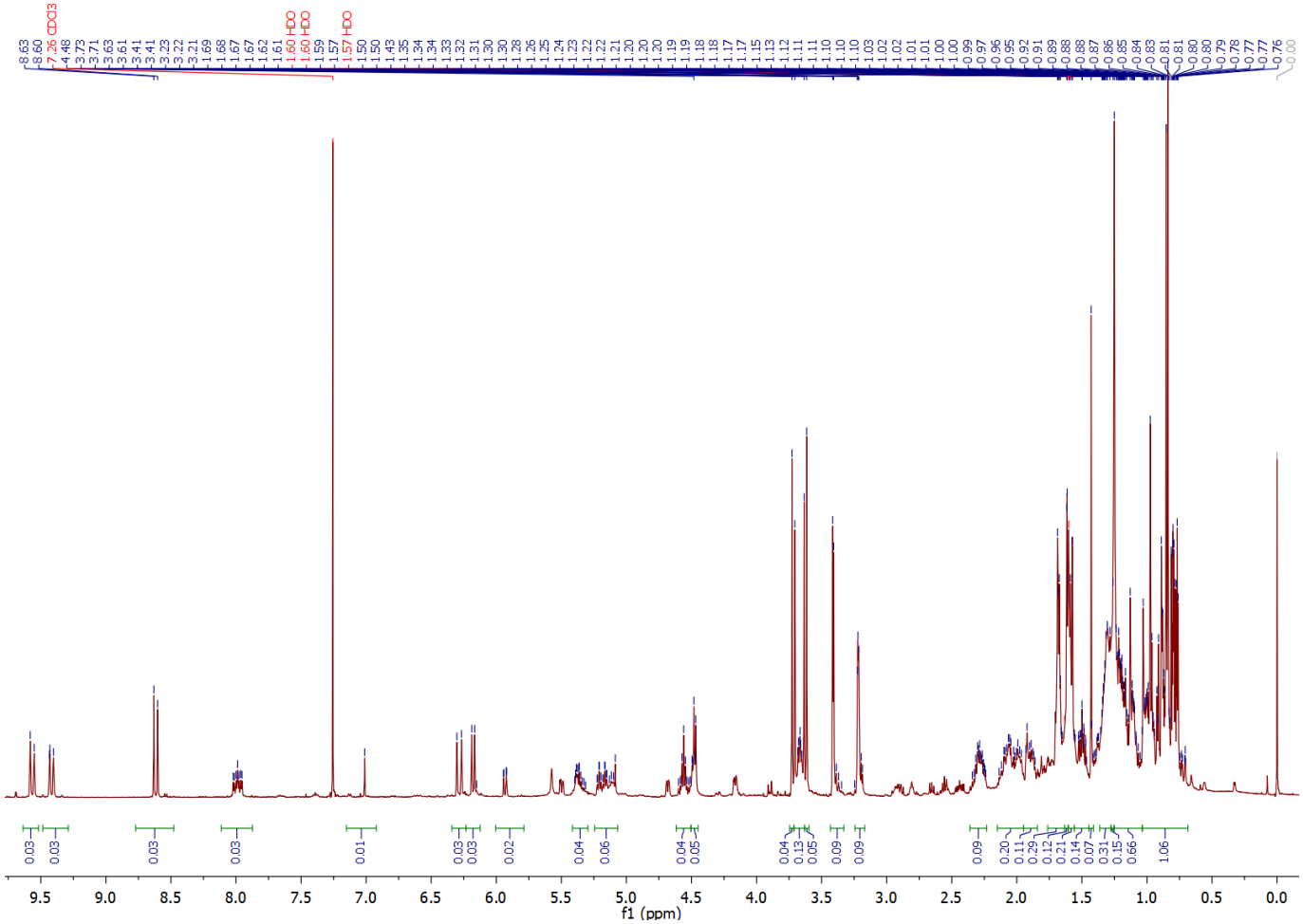

Figure S36 ^{13}C NMR spectrum of compound **17** in $CDCl_3$

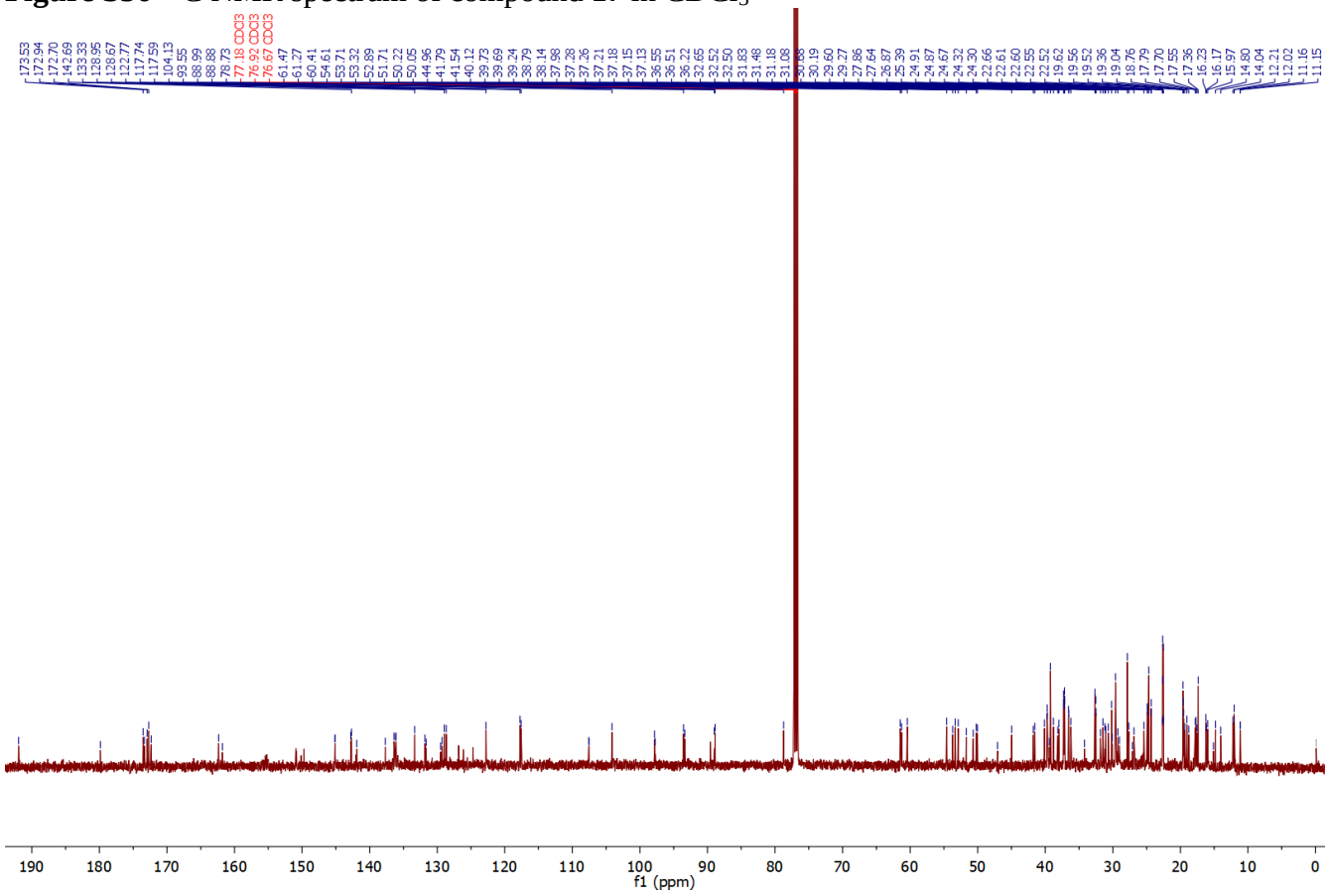

Figure S37 HRMS spectrum of compound **17**

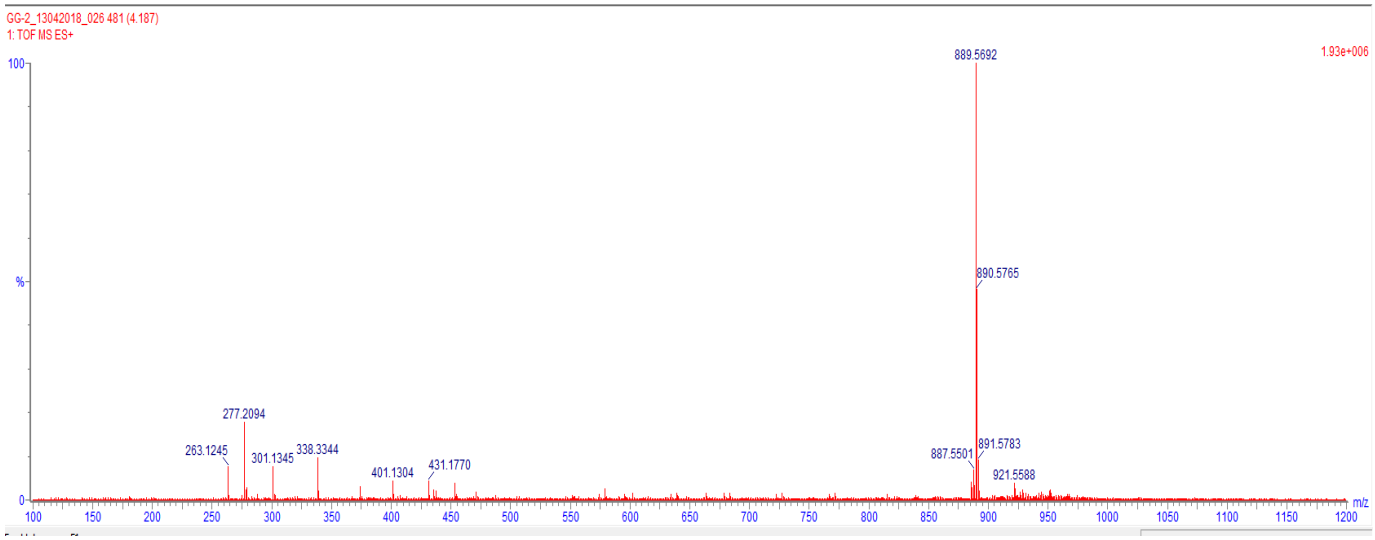

Figure S38 ^{1}H NMR spectrum of compound **18** in $CDCl_3$

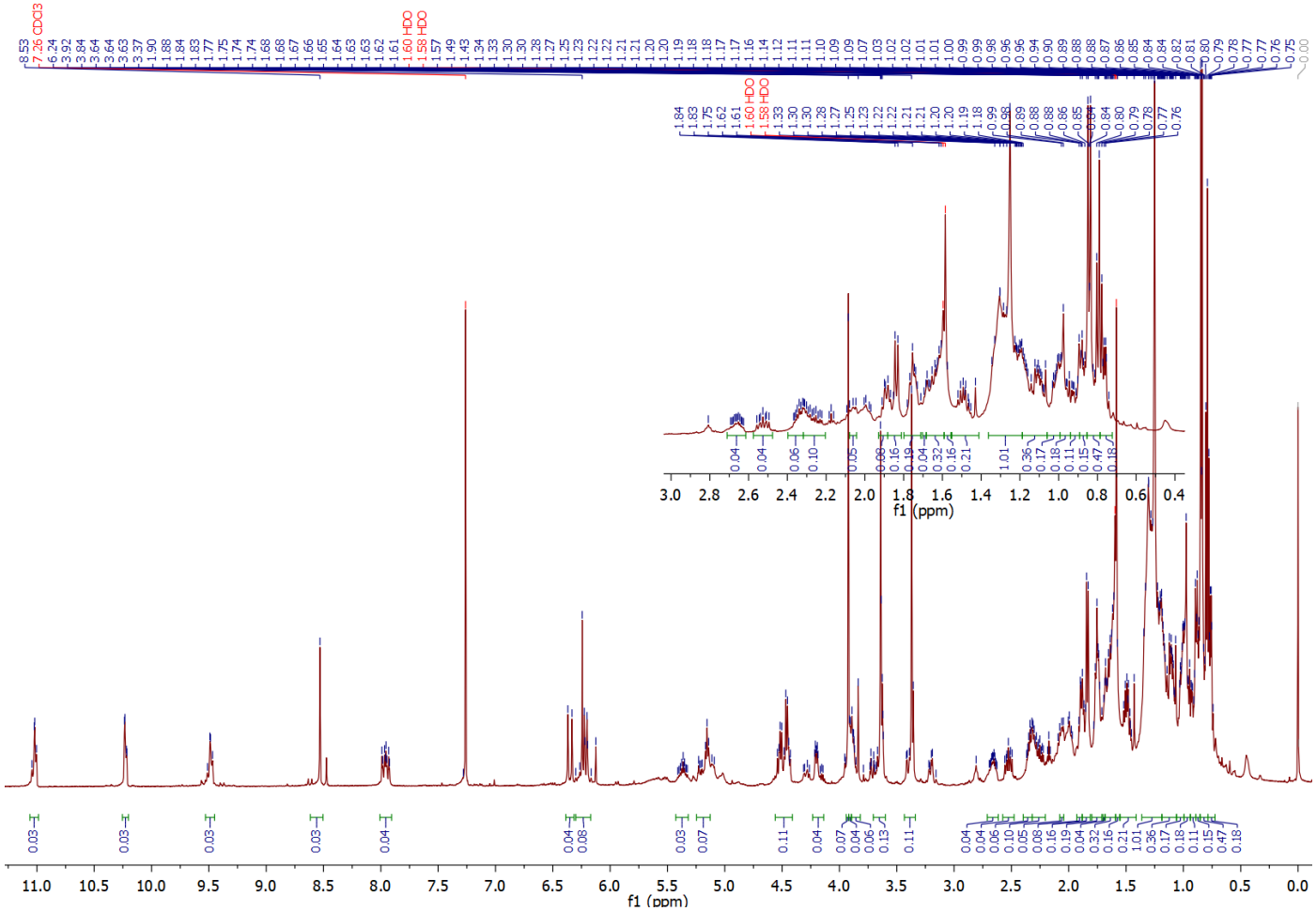

Figure S39 ^{13}C NMR spectrum of compound18 in $CDCl_3$

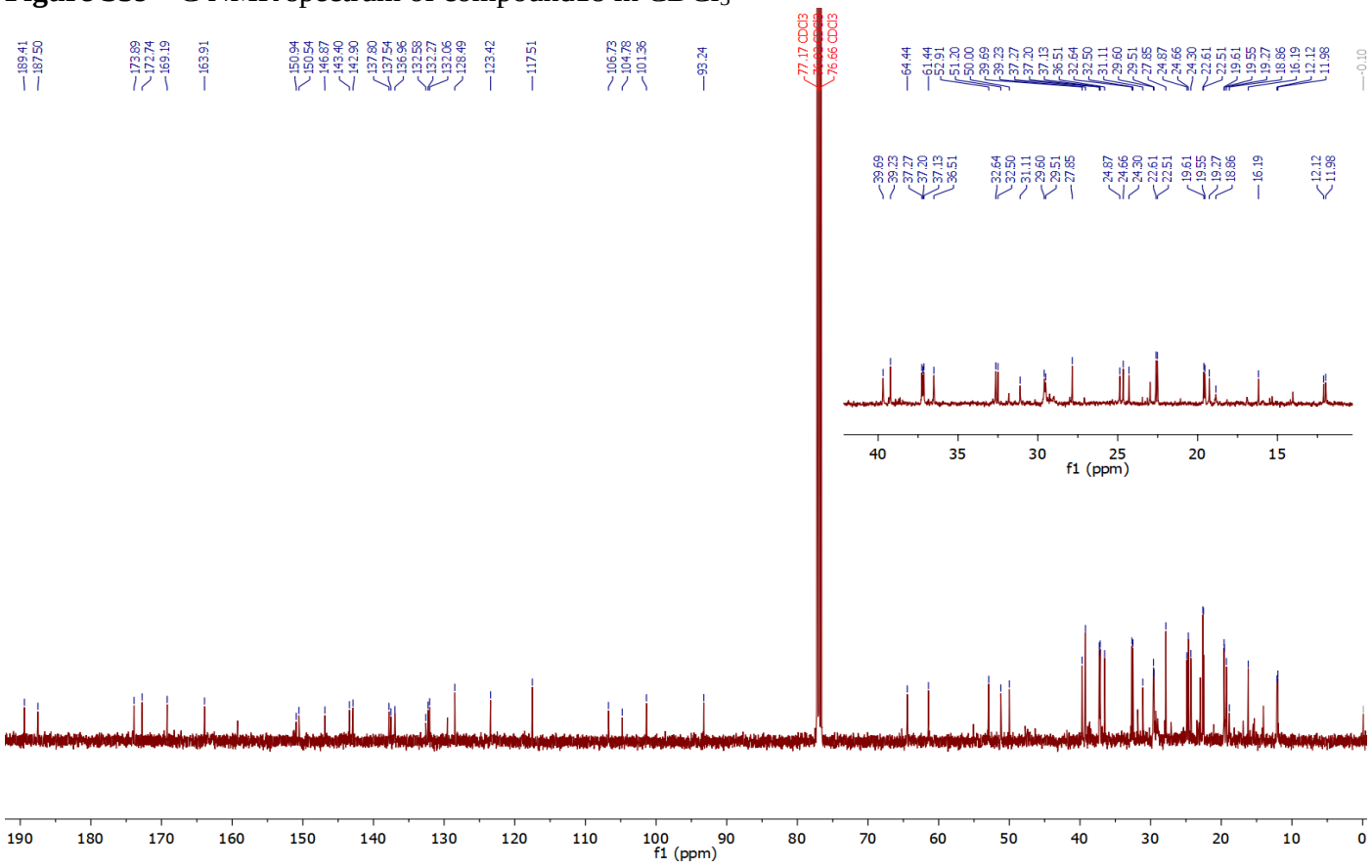

Figure S40 HRMS spectrum of compound18