Supporting Information for

Sulfonamide Trapping Reactions of Thermally Generated Benzynes

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I. General Experimental Protocols

^{1}H (and ^{13}C NMR) spectra were measured on Bruker Avance 400 or 500 spectrometers at 400 (or 101) or 500 (or 126) MHz, respectively. ^{1}H chemical shifts for spectra taken in $CDCl_3$ are referenced to TMS (δ 0.00 ppm) and for benzene-d_6 to C_6HD_5 (δ 7.15 ppm). Non-first order multiplets in the ^{1}H NMR spectra are identified by the designation "nfom". The following format is used to report resonances: chemical shift in ppm [multiplicity, coupling constant(s) (in Hz), integral (to the nearest whole integer), and assignment]. Assignments are designated by the proximity to neighboring atoms, e.g., CH*aHb*. Coupling constant analysis was done using methods we have reported earlier.[1] ^{13}C chemical shifts for spectra taken in $CDCl_3$ are referenced to the carbon in TMS (δ 0.00 ppm). The carbon skeletons of some structures are numbered to allow for easier specification of the proton assignment.

Infrared (IR) spectra were recorded using a Nicolet iS5 spectrometer. Thin film (neat) samples were solvent cast onto a NaCl plate and spectra were taken in the transmission mode. Absorptions are reported in wavenumbers (reciprocal cm).

HRMS data were recorded in the positive electron spray ionization (ESI) mode using a Thermo Orbitrap Velos instrument [external standard (Pierce™ LTQ); mass accuracy < 3 ppm; samples were introduced as a dilute methanol solution].

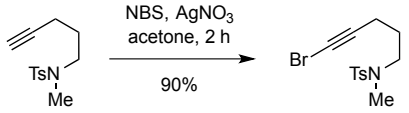
Medium pressure liquid chromatography (MPLC) was performed at 25-200 psi in hand-packed, glass columns of silica gel (25-35 μm, 60 Å pore size). The instrument was fitted with a Waters HPLC pump and a differential refractive index (RI) detector (Water R401). Flash chromatography was carried out on columns packed with larger sized silica gel (40-63 μm).

GCMS data were taken in the electron ionization (EI) mode using an Agilent 5975 MSD at 70 eV. The column was an ~30 m HP-5 column with an internal diameter of 0.32 mm and a film thickness of 0.25 μm.

Reaction temperatures refer to the external temperature of the heating or cooling bath. Some reactions were performed at temperatures above the solvent's boiling point of the solvent. These were done in a threaded, capped vial or culture tube fitted with an inert, Teflon®-lined screw-cap. Chloroform was passed through a silica gel plug prior to use as a reaction solvent in order to remove the ethanol stabilizer.

II. Preparation procedures and characterization data for all new compounds

N-(5-Bromopent-4-yn-1-yl)-*N*,4-dimethylbenzenesulfonamide (S2)



S1 ***S2***

N-Bromosuccinimide (NBS, 1.23 g, 6.93 mmol) was added to an acetone (15 mL) solution of alkyne **S1**[2] (0.87 g, 3.47 mmol) and silver nitrate (59 mg, 0.35 mmol). After being stirred for 2 h the mixture was filtered through Celite® and concentrated. The residue was purified by flash chromatography (12:1 hexanes:EtOAc elution) to provide the bromoalkyne **S2** (1.03 g, 2.0 mmol, 90%) as a colorless oil.

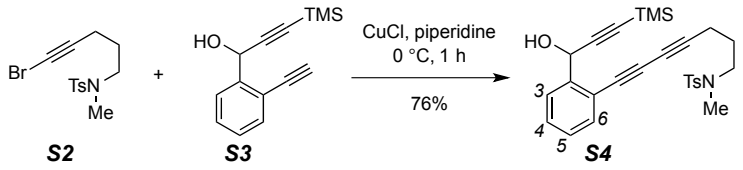
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.2 Hz, 2H, Ts aromatic *H* meta to Me), 7.32 (d, *J* = 8.2 Hz, 2H, Ts aromatic *H* ortho to Me), 3.06 (t, *J* = 7.0 Hz, 2H, C*H*$_2$NTsMe), 2.73 (s, 3H, N*Me*), 2.43 (s, 3H, Me on Ts), 2.29 (t, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NTsMe), and 1.76 (tt, *J* = 7.1, 7.1 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NTsMe).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 134.6, 129.8, 127.6, 79.2, 49.3, 38.8, 35.3, 26.8, 21.7, and 17.1.

IR (neat): 2938, 2870, 1647, 1458, 1339, 1161, 1090, 716, and 653 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{13}H_{17}{}^{79}BrNO_2S^+$ (M•H$^+$) 330.0158, found 330.0153.

N-(7-(2-(1-Hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hepta-4,6-diyn-1-yl)-*N*,4-dimethylbenzenesulfonamide (S4)



Terminal alkyne **S3** (595mg, 2.6 mmol) and bromoalkyne **S2** (1.03 g, 3.13 mmol) were mixed in piperidine (9.0 mL) at 0 ^{o}C under a nitrogen atmosphere. Catalytic CuCl (13 mg, 0.13 mmol) was then added. After being stirred for 1 h, the reaction mixture was quenched by the addition of saturated NH_4Cl aqueous solution (30 mL), and the mixture was then extracted with Et_2O (three times). The organic phases were combined, dried over Na_2SO_4, and concentrated. The crude product was purified by flash chromatography (5:1 hexanes:EtOAc elution) to provide the triyne alcohol **S4** (942 mg, 1.97 mmol, 76 %) as a yellow oil.

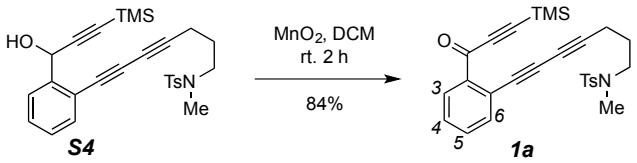
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (dd, *J* = 7.7, 1.4 Hz, 1H, *H6*), 7.68 (d, *J* = 8.3 Hz, 1H, 2H, Ts aromatic *H* meta to Me), 7.50 (dd, *J* = 7.7, 1.3 Hz, 1H, *H3*), 7.39 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H5*), 7.33 (d, *J* = 8.1, Hz, 2H, Ts aromatic *H* ortho to Me), 7.29 (ddd, J = 7.7, 7.7, 1.3 Hz, 1H, *H4*), 5.82 (d, *J* = 5.5 Hz, 1H, ArC*H*OH), 3.10 (t, *J* = 6.9 Hz, 2H, CH_2NTsMe), 2.75 (s, 3H, N*Me*), 2.482 (d, *J* = 5.8 Hz, 1H, O*H*), 2.480 (t, *J* = 7.2 Hz, 2H, CH_2CH_2CH_2NTsMe), 2.43 (s, 3H, *Me* on Ts), 1.84 (tt, *J* = 7.1, 7.1 Hz, 2H, CH$_2$CH_2CH$_2$NTsMe), and 0.19 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 143.5, 134.5, 133.7, 129.9, 129.6, 128.5, 127.6, 127.1, 120.7, 104.2, 91.9, 84.9, 79.5, 72.3, 65.8, 63.5, 49.4, 35.3, 26.8, 21.7, 17.1, and -0.1.

IR (neat): 3483, 2959, 2239, 2173, 1598, 1450, 1339, 1240, 1160, 1039, 984, 845, and 762cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{27}H_{31}NNaO_3SSi^+$ 500.1686, found 500.1673.

_N_,4-Dimethyl-_N_-(7-(2-(3-(trimethylsilyl)propioloyl)phenyl)hepta-4,6-diyn-1-yl)benzenesulfonamide (1a)



S4 **1a**

Triyne alcohol **S4** (942 mg, 1.97 mmol) and MnO_2 (1.7 g, 19.7 mmol) were mixed in DCM (5 mL) at room temperature. After being stirred for 2 h, the mixture was filtered through Celite®, and the filtrate was concentrated. The crude product was purified by flash chromatography (5:1 hexanes:EtOAc elution) to provide the triyne ketone **1a** (786 mg, 1.65 mmol, 84 %) as a yellow oil.

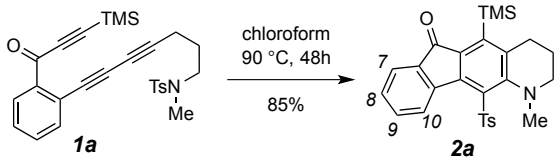
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 7.6, 1.5 Hz, 1H, *H3*), 7.68 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.60 (dd, *J* = 7.6, 1.5 Hz, 1H, *H6*), 7.50 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H, *H5*), 7.44 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H, *H4*), 7.33 (d, *J* = 8.2 Hz, 2H, Ts aromatic *H* ortho to Me), 3.09 (t, *J* = 7.0 Hz, 2H, C*H*$_2$NTsMe), 2.75 (s, 3H, N*Me*), 2.47 (t, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NTsMe), 2.43 (s, 3H, *Me* on Ts), 1.83 (tt, *J* = 7.1, 7.1 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NTsMe), and 0.30 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.6, 143.5, 139.1, 135.8, 134.5, 132.7, 132.0, 129.9, 128.6, 127.6, 122.0, 101.5, 101.4, 85.6, 80.4, 73.3, 66.4, 49.4, 35.4, 26.9, 21.6, 17.2, and -0.6.

IR (neat): 2960, 2241, 2152, 1647, 1480, 1341, 1236, 1161, 1015, 849, and 756 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{27}H_{30}NO_3SSi^+$ 476.1710, found 476.1699.

1-Methyl-11-tosyl-5-(trimethylsilyl)-1,2,3,4-tetrahydro-6H-indeno[2,1-g]quinolin-6-one (2a)



Triyne ketone **1a** (786 mg, 1.65 mmol) was dissolved in 35 mL of chloroform in a screw-capped vial. This solution was heated in an oil bath held at 90 °C for 48 h. After concentration and flash chromatography (10:1 Hex:EtOAc elution), the tetrahydroquinoline **2a** (668 mg, 1.41 mmol, 85%) was obtained as a crystalline orange solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 7.7 Hz, 1H, *H10*), 7.54 (d, *J* = 8.0 Hz, 2H, Ts aromatic *H* meta to Me), 7.43 (d, *J* = 7.2 Hz, 1H, *H7*), 7.34 (ddd, *J* = 7.7, 7.7, 1.3 Hz, 1H, *H9*), 7.22–7.12 (m, 3H, Ts aromatic *H* ortho to Me and *H8*), 3.22 (s, 3H, N*Me*), 2.80 (t, *J* = 5.8 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NMe), 3.09–2.46 (br m, 2H, CH$_2$CH$_2$C*H*$_2$NMe), 2.34 (s, 3H, *Me* on Ts), 2.05–1.36 (br m, 2H, CH$_2$C*H*$_2$CH$_2$NMe), and 0.42 (s, 9H, TMS).

^{1}H NMR (400 MHz, Benzene-d_6) δ 8.68 (ddd, *J* = 7.7, 0.9, 0.9 Hz, 1H, *H10*), 7.54 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.44 (ddd, *J* = 7.1, 0.9, 0.8 Hz, 1H, *H7*), 6.98 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H, *H9*), 6.70 (ddd, *J* = 7.5, 7.5, 0.9 Hz, 1H, *H8*), 6.53 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* ortho to Me), 3.13 (s, 3H, N*Me*), 3.03–1.97 (br m, 4H, CH$_2$CH$_2$C*H*$_2$NMe and C*H*$_2$CH$_2$CH$_2$NMe), 1.66 (s, 3H, *Me* on Ts), 1.44–1.03 (br m, 2H, CH$_2$C*H*$_2$CH$_2$NMe), and 0.61 (s, 9H, TMS).

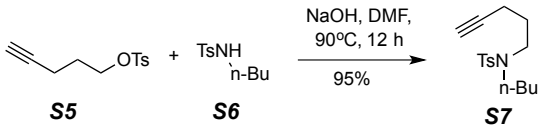
^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.1, 153.1, 147.9, 143.3, 142.4, 141.4, 140.5, 136.3, 134.4, 133.3, 129.8, 129.1, 128.9, 126.9, 126.7, 122.31, 122.26, 51.5, 47.7, 30.2, 22.2, 21.6, and 3.2.

IR (neat): 3055, 2949, 2895, 1700, 1604, 1534, 1445, 1337, 1299, 1286, 1137, 845, 752, and 652 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{27}H_{30}NO_3SSi^+$ 476.1710, found 476.1695.

m.p.: 192–194 °C.

N-Butyl-4-methyl-*N*-(pent-4-yn-1-yl)benzenesulfonamide (S7)



S5 ***S6*** ***S7***

Tosylate **S5** (536 mg, 2.25 mmol) was mixed with tosylamide **S6** (240 mg, 1.5 mmol) and NaOH (72 mg, 1.8 mmol) in DMF (15 mL) in a sealed tube. The mixture was heated at 90 °C for 16 hours. After addition of saturated NH_4Cl (15 mL), the quenched reaction mixture was extracted with EtOAc (20 mL three times). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography (10:1 hexanes:EtOAc elution) to provide the terminal alkyne **S7** (416 mg, 1.43 mmol, 95 %) as a colorless oil.

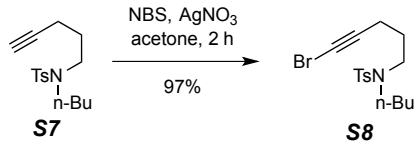
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.29 (d, *J* = 8.0 Hz, 2H, Ts aromatic *H* ortho to Me), 3.19 (t, *J* = 7.0 Hz, 2H, NC*H*$_2$CH_2CH_2Me), 3.10 (t, *J* = 7.0 Hz, 2H, C*H*$_2$N(Ts)Bu), 2.42 (s, 3H, *Me* on Ts), 2.21 (td, *J* = 7.0, 2.7 Hz, 2H, C*H*$_2$CH_2CH_2N(Ts)Bu), 1.96 (t, *J* = 2.6 Hz, 1H, C≡C*H*), 1.78 (tt, *J* = 7.1, 7.1 Hz, 2H, CH$_2$C*H*$_2$CH$_2$N(Ts)Bu), 1.51 (tt, *J* = 7.8, 7.0 Hz, 2H, CH$_2$*CH*$_2$CH$_2$Me), 1.29 (tq, *J* = 7.7, 7.3 Hz, 2H, CH$_2$*CH*$_2$Me), and 0.90 (t, *J* = 7.3 Hz, 3H, CH$_2$*Me*).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.2, 136.9, 129.7, 127.3, 83.4, 69.1, 48.7, 47.4, 30.8, 27.9, 21.6, 20.0, 16.0, and 13.8.

IR (neat): 3285, 2958, 2933, 2873, 2118, 1599, 1460, 1339, 1157, 1091, 925, and 816 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{16}H_{24}NO_2S^+$ 294.1522, found 294.1518.

N-(5-bromopent-4-yn-1-yl)-*N*-butyl-4-methylbenzenesulfonamide (S8)



S7 ***S8***

Bromoalkyne **S8** (351 mg, 0.95 mmol, 97 %) was obtained from alkyne **S7** (283 mg, 0.98 mmol), NBS (346 mg, 1.95 mmol) and $AgNO_3$ (17mg, 0.1 mmol) by following the procedure used to prepare bromoalkyne **S2** as a yellow oil.

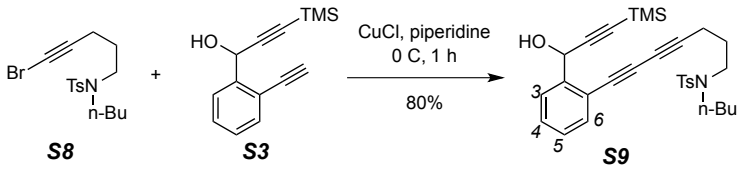
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.2 Hz, 2H, Ts aromatic *H* meta to Me), 7.30 (d, *J* = 8.1 Hz, 2H, Ts aromatic *H* ortho to Me), 3.15 (t, *J* = 7.0 Hz, 2H, NC*H*$_2$*C*H$_2$CH$_2$Me), 3.09 (t, *J* = 7.0 Hz, 2H, C*H*$_2$N(Ts)Bu), 2.42 (s, 3H, *Me* on Ts), 2.23 (t, *J* = 7.0 Hz, 2H, C*H*$_2$CH$_2$CH$_2$N(Ts)Bu), 1.76 (tt, *J* = 7.1, 7.1 Hz, 2H, CH$_2$C*H*$_2$CH$_2$N(Ts)Bu), 1.51 (tt, *J* = 7.7, 7.0 Hz, 2H, CH$_2$*CH*$_2$CH$_2$Me), 1.30 (tq, *J* = 7.7, 7.3 Hz, 2H, CH$_2$*CH*$_2$Me), and 0.90 (t, *J* = 7.3 Hz, 3H, CH$_2$*Me*).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.2, 136.8, 129.8, 127.3, 79.2, 48.7, 47.3, 38.8, 30.8, 27.8, 21.6, 20.0, 17.2, and 13.8.

IR (neat): 2958, 2933, 2872, 2216, 1646, 1599, 1459, 1339, 1157, 1091, 922, and 815 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{16}H_{23}BrNO_2S^+$ 372.0627, found 372.0622.

_N_-Butyl-_N_-(7-(2-(1-hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hepta-4,6-diyn-1-yl)-4-methylbenzenesulfonamide (S9)



S8 ***S3*** ***S9***

Triyne alcohol **S9** (206 mg, 0.40 mmol, 80 %) was obtained from terminal alkyne **S3** (114 mg, 0.50 mmol), and bromoalkyne **S8** (223mg, 0.6 mmol) by following the procedure used to prepare triyne alcohol **S4** as a yellow oil.

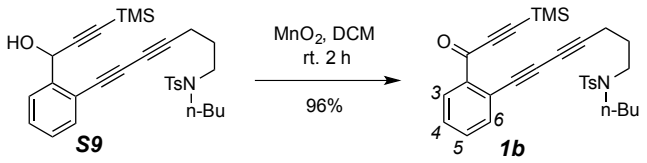
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.702 (d, partially overlapped, *J* = 7.7 Hz, 1H, *H6*), 7.698 (d, *J* = 8.3 Hz, 1H, 2H, Ts aromatic *H* meta to Me), 7.50 (dd, *J* = 7.8, 1.4 Hz, 1H, *H3*), 7.39 (td, *J* = 7.6, 1.4 Hz, 1H, *H5*), 7.31 (d, *J* = 8.1, Hz, 2H, Ts aromatic *H* ortho to Me), 7.28 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H, *H4*), 5.82 (d, *J* = 5.5 Hz, 1H, ArC*H*OH), 3.19 (t, *J* = 7.3 Hz, 2H, NC*H*$_2$*C*H$_2$CH$_2$Me), 3.12 (t, *J* = 7.6 Hz, 2H, C*H*$_2$N(Ts)Bu), 2.46 (d, *J* = 5.7 Hz, 1H, O*H*), 2.422 (s, 3H, *Me* on Ts), 2.420 (t, *J* = 7.0 Hz, 2H, C*H*$_2$CH$_2$CH$_2$N(Ts)Bu), 1.84 (tt, *J* = 7.1, 7.1 Hz, 2H, CH$_2$C*H*$_2$CH$_2$N(Ts)Bu), 1.53 (tt, *J* = 7.6, 6.4 Hz, 2H, CH$_2$*CH*$_2$CH$_2$Me), 1.30 (tq, *J* = 7.4, 7.4 Hz, 2H, CH$_2$*CH*$_2$Me), 0.92 (t, *J* = 7.3 Hz, 3H, CH$_2$*Me*), and 0.19 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.3, 143.2, 136.6, 133.6, 129.7, 129.5, 128.4, 127.2, 127.0, 120.6, 104.1, 91.8, 84.8, 79.3, 72.2, 65.7, 63.4, 48.7, 47.5, 30.8, 27.7, 21.5, 19.9, 17.2, 13.7, and -0.2.

IR (neat): 3463, 2959, 2873, 2238, 2173, 1646, 1336, 1250, 1156, 1090, 1038, 845, and 761 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{30}H_{37}NNaO_3SSi^+$ 542.2156, found 542.2146.

_N_-Butyl-4-methyl-_N_-(7-(2-(3-(trimethylsilyl)propioloyl)phenyl)hepta-4,6-diyn-1-yl)benzene sulfonamide (111)



Triyne ketone **1b** (164 mg, 0.32 mmol, 96 %) was obtained from triyne alcohol **S9** (173 mg, 0.33 mmol), and MnO_2 (290 mg, 3.3 mmol) by following the procedure used to prepare triyne ketone **1a** as a yellow oil.

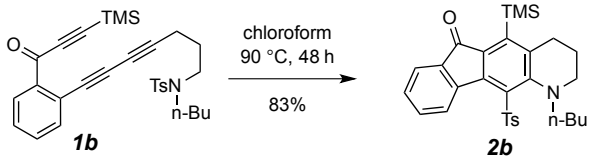
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.6, 1.3 Hz, 1H, *H3*), 7.69 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.60 (dd, J = 7.6, 1.3 Hz, 1H, *H6*), 7.50 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1H, *H5*), 7.44 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H, *H4*), 7.32 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* ortho to Me), 3.21 (t, *J* = 7.1 Hz, 2H, NC*H*$_2$*C*H$_2$CH$_2$Me), 3.10 (t, *J* = 7.6 Hz, 2H, C*H*$_2$N(Ts)Bu), 2.42 (s, 3H, Ts*Me*), 2.41 (t, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_2$CH$_2$N(Ts)Bu), 1.83 (tt, *J* = 7.2, 7.2 Hz, 2H, CH$_2$C*H*$_2$CH$_2$N(Ts)Bu), 1.57–1.49 (m, 2H, CH$_2$*CH*$_2$CH$_2$Me), 1.32 (tq, *J* = 7.7, 7.4 Hz, 2H, CH$_2$*CH*$_2$Me), 0.91 (t, *J* = 7.3 Hz, 3H, CH$_2$*Me*), and 0.30 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 143.3, 139.1, 136.7, 135.8, 132.6, 132.0, 129.8, 128.6, 127.3, 122.0, 101.5, 101.4, 85.6, 80.3, 73.3, 66.4, 48.9, 47.6, 31.0, 27.8, 21.6, 20.1, 17.4, 13.8, and -0.6.

IR (neat): 2959, 2872, 2241, 2152, 1647, 1339, 1236, 1157, 1015, 849, and 756 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{30}H_{36}NO_3SSi^+$518.2180, found 518.2167.

1-Butyl-11-tosyl-5-(trimethylsilyl)-1,2,3,4-tetrahydro-6H-indeno[2,1-g]quinolin-6-one (2b)



1b *2b*

Triyne ketone **1b** (78 mg, 0.15 mmol) was dissolved in 5 mL of chloroform (ethanol-free) in a screw-capped vial. This solution was heated in an oil bath held at 90 °C for 48 h. After concentration and flash chromatography (10:1 Hex:EtOAc elution), the tetrahydroquinoline **2b** (65 mg, 0.13 mmol, 83%) was obtained as a crystalline orange solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 7.6 Hz, 1H, *H10*), 7.54 (d, *J* = 8.0 Hz, 2H, Ts aromatic *H* meta to Me), 7.44 (d, *J* = 7.5 Hz, 1H, *H7*), 7.36 (dd, *J* = 7.6, 7.6 Hz, 1H, *H9*), 7.19 (dd, *J* = 7.6, 7.6 Hz, 1H, *H8*), 7.17 (d, *J* = 8.0 Hz, 2H, Ts aromatic *H* ortho to Me), 4.10–3.78 (br m, 1H), 3.34–3.10 (br m, 1H), 3.10–2.84 (br m, 2H), 2.64–2.4 (br m, 2H), 2.35 (s, 3H, *Me* on Ts), 2.06–1.80 (br m, 1H), 1.60–1.38 (br m, 2H), 1.36–1.21 (br m, 1H), 1.21–1.04 (br m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H, $NCH_2CH_2CH_2$*Me*), and 0.42 (s, 9H, TMS).

^{1}H NMR (400 MHz, Benzene-d_6) δ 8.73 (d, *J* = 7.7 Hz, 1H, *H10*), 7.56 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.43 (d, *J* = 7.4 Hz, 1H, *H7*), 6.98 (dd, *J* = 7.6, 7.6 Hz, 1H, *H9*), 6.70 (dd, *J* = 7.6, 7.6 Hz, 1H, *H8*), 6.57 (d, *J* = 8.0 Hz, 2H, Ts aromatic *H* ortho to Me), 4.31–3.99 (br m, 1H), 3.50–3.21 (br m, 1H), 3.02–2.77 (br m, 1H), 2.67–2.47 (br m, 1H), 2.47–2.32 (br m, 1H), 2.32–2.12 (br m, 1H), 1.70 (s, 3H, *Me* on Ts), 1.57–1.48 (br m, 1H), 1.40–1.23 (br m, 2H), 1.23–1.10 (br m, 1H), 1.10–0.94 (br m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H, $NCH_2CH_2CH_2$Me), and 0.61 (s, 9H, TMS).

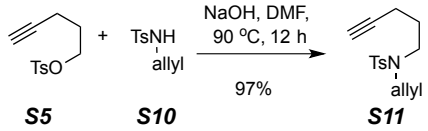
^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.3, 152.9, 147.9, 143.3, 141.9, 141.6, 140.5, 137.9, 134.5, 133.4, 130.1, 129.2, 129.0, 127.02, 126.98, 123.3, 122.4, 59.1, 47.8, 30.2, 30.1, 23.1, 21.6, 20.0, 13.9, and 3.2.

IR (neat): 2956, 2931, 2872, 1700, 1527, 1299, 1138, 979, and 848 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{30}H_{36}NO_3SSi^+$518.2180, found 518.2167.

m.p.: 174–175 °C.

N-Allyl-4-methyl-*N*-(pent-4-yn-1-yl)benzenesulfonamide (S11)



Alkyne **S11** (540 mg, 1.94 mmol, 97 %) was obtained as a colorless oil from the tosylate **S5** (714 mg, 3.0 mmol) and sulfonamide **S10** (422 mg, 2.0 mmol) by following the procedure used to prepare alkyne **S7**.

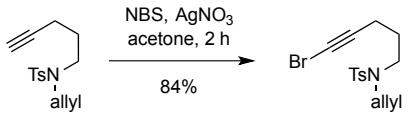
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.30 (d, *J* = 8.0 Hz, 2H, Ts aromatic *H* ortho to Me), 5.64 (ddt, *J* = 16.6, 10.1, 6.4 Hz, 1H, CH_2CH=CH_2), 5.18 (ddt, *J* = 17.1, 1.4, 1.4 Hz, 1H, CH_2CH=CH_ZH_E), 5.14 (ddt, *J* = 10.0, 1.4, 1.4 Hz, 1H, CH_2CH=CH_EH_Z), 3.80 (ddd, *J* = 6.5, 1.4, 1.4 Hz, 2H, CH_2CH=CH_2), 3.21 (t, *J* = 7.1 Hz, 2H, $CH_2CH_2CH_2$NTs), 2.43 (s, 3H, *Me* on Ts), 2.20 (td, *J* = 7.0, 2.6 Hz, 2H, $CH_2CH_2CH_2$NTs), 1.94 (t, *J* = 2.7 Hz, 1H, C≡C*H*), and 1.77 (tt, *J* = 7.1, 7.1 Hz, 2H, $CH_2CH_2CH_2$NTs(allyl)).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.4, 137.0, 133.2, 129.8, 127.3, 119.2, 83.4, 69.1, 51.2, 46.5, 27.5, 21.6, and 15.9.

IR (neat): 3288, 2926, 2872, 2118, 1598, 1449, 1341, 1160, 992, 929 and 816 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{15}H_{20}NO_2S^+$ 278.1209, found 278.1203.

N-Allyl-N-(5-bromopent-4-yn-1-yl)-4-methylbenzenesulfonamide (S12)



S11 ***S12***

Bromoalkyne **S12** (300 mg, 0.84 mmol, 84 %) was obtained as a colorless oil from alkyne **S11** (277 mg, 1.0 mmol), NBS (356 mg, 2.0 mmol), and $AgNO_3$ (17mg, 0.1 mmol) by following the procedure used to prepare bromoalkyne **S2**.

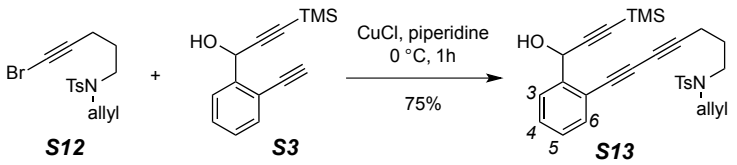
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.31 (d, *J* = 8.0 Hz, 2H, Ts aromatic *H* ortho to Me), 5.64 (ddt, *J* = 16.9, 10.1, 6.5 Hz, 1H, CH_2CH=CH_2), 5.18 (ddt, *J* = 17.0, 1.4, 1.4 Hz, 1H, CH_2CH=C$H_Z$$H_E$), 5.16 (ddt, *J* = 10.1, 1.4, 1.4 Hz, 1H, one of allyl CH_2CH=C$H_E$$H_Z$), 3.79 (ddd, *J* = 6.6, 1.4, 1.4 Hz, 2H, CH_2CH=CH_2), 3.17 (t, *J* = 7.1 Hz, 2H, $CH_2CH_2CH_2$NTs), 2.43 (s, 3H, *Me* on Ts), 2.22 (t, *J* = 7.1 Hz, 2H, C$H_2CH_2CH_2$NTs), and 1.75 (tt, *J* = 7.1, 7.1 Hz, 2H, $CH_2CH_2CH_2$NTs).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.4, 136.9, 133.2, 129.8, 127.4, 119.3, 79.2, 51.3, 46.4, 38.8, 27.4, 21.7, and 17.2.

IR (neat): 2925, 2871, 2216, 1643, 1598, 1341, 1160, 1093, 930, and 815 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{15}H_{19}BrNO_2S^+$ 356.0314, found 356.0313.

_N_-Allyl-N-(7-(2-(1-hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hepta-4,6-diyn-1-yl)-4-methylbenzenesulfonamide (S13)



Triyne alcohol **S13** (188 mg, 0.38 mmol, 75 %) was obtained as a yellow oil from the terminal alkyne **S3** (114 mg, 0.50 mmol) and the bromoalkyne **S12** (213mg, 0.6 mmol) by following the procedure used to prepare triyne alcohol **S4**.

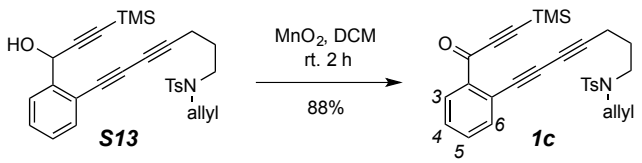
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.4 Hz, 2H, Ts aromatic *H* meta to Me), 7.70 (dd, *J* = 7.5, 1.3 Hz, 1H, *H6*), 7.50 (dd, *J* = 7.7, 1.3 Hz, 1H, *H3*), 7.40 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H4*), 7.32 (d, *J* = 8.3 Hz, 1H, Ts aromatic *H* ortho to Me), 7.29 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 1H, *H5*), 5.82 (d, *J* = 5.7 Hz, 1H, ArC*H*OH), 5.66 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H, CH_2CH=CH_2), 5.22 (ddt, *J* = 17.0, 1.4, 1.4 Hz, 1H, CH_2CH=C$H_Z$$H_E$), 5.18 (ddt, *J* = 10.1, 1.4, 1.4 Hz, 1H, one of allyl CH_2CH=C$H_E$$H_Z$), 3.81 (ddd, *J* = 6.5, 1.3, 1.3 Hz, 1H, CH_2CH=CH_2), 3.21 (t, *J* = 7.2 Hz, 2H, CH_2NTsMe), 2.45 (d, *J* = 5.7 Hz, 1H, O*H*), 2.43 (s, 3H, *Me* on Ts), 2.40 (t, *J* = 7.1 Hz, 2H, C$H_2$$CH_2$$CH_2$NTsMe), 1.83 (tt, *J* = 7.1, 7.1 Hz, 2H, CH_2C$H_2$$CH_2$NTsMe), and 0.19 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.50, 143.47, 136.8, 133.7, 133.2, 129.9, 129.6, 128.5, 127.4, 127.1, 120.7, 119.4, 104.2, 91.9, 85.0, 79.5, 72.3, 65.8, 63.5, 51.4, 46.6, 27.4, 21.7, 17.2, and -0.5.

IR (neat): 3482, 2958, 2239, 2173, 1380, 1250, 1158, 1038, 987, and 845 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{29}H_{33}NNaO_3SSi^+$ 526.1843, found 526.1832.

_N_-Allyl-4-methyl-N-(7-(2-(3-(trimethylsilyl)propioloyl)phenyl)hepta-4,6-diyn-1-yl)benzenes ulfonamide (1c)



Triyne ketone **1c** (81 mg, 0.16 mmol, 88 %) was obtained as a yellow oil from the triyne alcohol **S13** (93 mg, 0.18 mmol) and MnO_2 (160 mg, 1.9 mmol) by following the procedure used to prepare the triyne ketone **1a**.

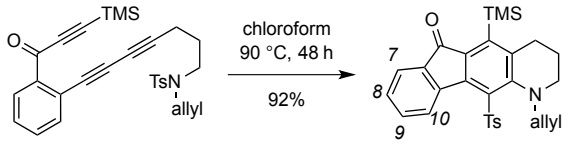
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.5, 1.5 Hz, 1H, *H3*), 7.71 (d, *J* = 8.1, Hz, 2H, Ts aromatic *H* meta to Me), 7.60 (dd, *J* = 7.5, 1.5 Hz 1H, *H6*), 7.50 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H, *H5*), 7.44 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H, *H4*), 7.32 (d, *J* = 8.1, Hz, 2H, Ts aromatic *H* ortho to Me), 5.66 (ddt, J = 16.6, 10.1, 6.5 Hz, 1H, CH_2CH=CH_2), 5.22 (ddt, J = 16.8, 1.4, 1.4 Hz, 1H, CH_2CH=CH_ZH_E), 5.19 (ddt, J = 10.1, 2.7, 1.5 Hz, 1H, CH_2CH=CH_EH_Z), 3.81 (ddd, J = 6.5, 1.4, 1.3 Hz, 2H, CH_2CH=CH_2), 3.20 (t, *J* = 7.0 Hz, 2H, CH_2NTsMe), 2.43 (s, 3H, *Me* on Ts), 2.40 (t, J = 7.1 Hz, 2H, C$H_2CH_2CH_2$NTsMe), 1.82 (tt, J = 7.0, 7.0 Hz, 2H, $CH_2CH_2CH_2$NTsMe), and 0.30 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 143.5, 139.1, 136.8, 135.8, 133.1, 132.6, 132.0, 129.9, 128.6, 127.3, 122.0, 119.5, 101.5, 101.4, 85.7, 80.4, 73.3, 66.4, 51.5, 46.6, 27.4, 21.7, 17.3, and -0.5.

IR (neat): 3428, 2959, 2241, 2152, 1647, 1340, 1236, 1160, 1015, 849, and 757 cm-1.

HRMS (ESI-TOF): calculated for $C_{29}H_{32}NO_3SSi^+$ 502.1867, found 502.1856.

1-Allyl-11-tosyl-5-(trimethylsilyl)-1,2,3,4-tetrahydro-6H-indeno[2,1-g]quinolin-6-one (2c)



1c *2c*

Triyne ketone **1c** (65 mg, 0.13 mmol) was dissolved in 5 mL of chloroform (ethanol-free) in a screw-capped vial. This solution was heated in an oil bath held at 90 °C for 48 h. After concentration and flash chromatography (10:1 Hex:EtOAc elution), the tetrahydroquinoline **2c** (60 mg, 0.12 mmol, 92%) was obtained as a crystalline orange solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 7.8 Hz, 1H, *H10*), 7.56 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.47 (d, *J* = 7.2 Hz, 1H, *H7*), 7.39 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H9*), 7.22 (dd, *J* = 7.6, 7.6 Hz, 1H, *H8*), 7.19 (d, *J* = 8.0 Hz, 2H, Ts aromatic *H* ortho to Me), 5.77 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H, CH_2CH=CH_2), 5.17 (ddt, J = 17.1, 1.4, 1.4 Hz, 1H, CH_2CH=CH_ZH_E), 5.15 (ddt, J = 10.1, 1.5, 1.5 Hz, 1H, CH_2CH=CH_EH_Z), 4.62–4.18 (br m, 1H), 4.03–3.55 (br m, 1H), 3.13–2.66 (br m, 2H), 2.66–2.15 (br m, 2H), 2.43 (s, 3H, *Me* on Ts), 2.01–1.65 (br m, 1H), 1.47–1.09 (br m, 1H), and 0.42 (s, 9H, TMS).

^{1}H NMR (400 MHz, Benzene-d_6) δ 8.71 (d, *J* = 7.7 Hz, 1H, *H10*), 7.55 (d, *J* = 8.4 Hz, 2H, Ts aromatic *H* meta to Me), 7.46 (dd, *J* = 7.4, 1.2 Hz, 1H, *H7*), 6.99 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, *H9*), 6.70 (dd, *J* = 7.6, 7.6 Hz, 1H, *H8*), 6.56 (d, *J* = 8.1 Hz, 2H, Ts aromatic *H* ortho to Me), 5.68 (ddt, *J* = 16.8, 10.0, 6.6 Hz, 1H, CH_2CH=CH_2), 4.97 (ddt, J = 17.0, 1.5, 1.5 Hz, 1H, CH_2CH=CH_ZH_E), 4.92 (ddt, J = 10.0, 1.5, 1.5 Hz, 1H, CH_2CH=CH_EH_Z), 4.65–4.25 (br m, 1H), 4.25–3.79 (br m, 1H), 3.01–1.96 (br m's, 4H), 1.71 (s, 3H, Me on Ts), 1.58–0.91 (br m, 2H), and 0.58 (s, 9H, TMS).

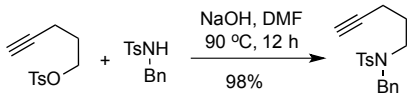
^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.4, 152.5, 147.6, 143.3, 142.9, 141.6, 140.6, 138.6, 134.5, 134.4, 133.6, 131.5, 129.3, 129.0, 127.3, 126.9, 124.9, 122.5, 118.9, 62.6, 47.1, 30.2, 22.5, 21.6, and 3.2.

IR (neat): 3063, 2950, 2897, 1703, 1526, 1411, 1299, 1139, 1082, 985, and 852 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{29}H_{32}NO_3SSi^+$ 502.1867, found 502.1857.

m.p.: 193–195 °C.

N-Benzyl-4-methyl-*N*-(pent-4-yn-1-yl)benzenesulfonamide (S15)



S5 ***S14*** ***S15***

Alkyne **S15** (320 mg, 0.98 mmol, 98 %) was obtained as a colorless oil from the tosylate **S5** (357 mg, 1.5 mmol) sulfonamide **S14** (261 mg, 1.0 mmol) by following the procedure used to prepare the alkyne **S7**.

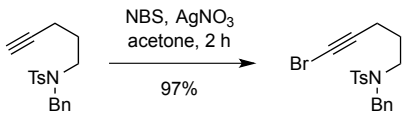
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.35–7.27 (m, 7H, Ts aromatic *H* ortho to Me and Ph*H*$_5$), 4.31 (s, 2H, PhC*H*$_2$), 3.18 (t, *J* = 7.5 Hz, 2H, $CH_2CH_2CH_2NTs$), 2.44 (s, 3H, *Me* on Ts), 2.01 (td, *J* = 7.0, 2.6 Hz, 2H, $CH_2CH_2CH_2NTs$), 1.86 (t, *J* = 2.6 Hz, 1H, C≡C*H*), and 1.56 (tt, *J* = 7.5, 6.9 Hz, 2H, $CH_2CH_2CH_2NTs$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.4, 136.9, 136.5, 129.9, 128.7, 128.5, 128.0, 127.4, 83.2, 69.0, 52.5, 47.4, 27.2, 21.7, and 15.9.

IR (neat): 3290, 3031, 2925, 2872, 2117, 1598, 1338, 1159, 816, 734, and 656 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{19}H_{22}NO_2S^+$ 328.1366, found 328.1360.

N-Benzyl-*N*-(5-bromopent-4-yn-1-yl)-4-methylbenzenesulfonamide (S16)



S15 ***S16***

Bromoalkyne **S16** (316 mg, 0.78 mmol, 97 %) was obtained as a colorless oil from the alkyne **S15** (262 mg, 0.80 mmol), NBS (285 mg, 1.6 mmol), and $AgNO_3$ (14mg, 0.08 mmol) by following the procedure used to prepare bromoalkyne **S2**.

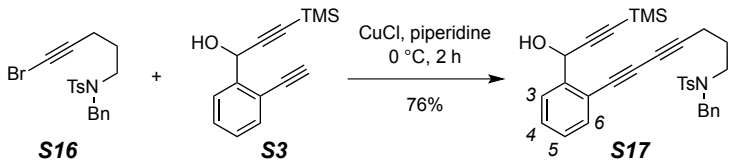
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.30 (m, 7H, Ts aromatic *H* ortho to Me and PhH_5), 4.31 (s, 2H, PhCH_2), 3.14 (t, *J* = 7.5 Hz, 2H, $CH_2CH_2CH_2NTs$), 2.45 (s, 3H, *Me* on Ts), 2.02 (t, *J* = 6.9 Hz, 2H, $CH_2CH_2CH_2NTs$), and 1.55 (tt, *J* = 7.5, 6.9 Hz, 2H, $CH_2CH_2CH_2NTs$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 136.8, 136.3, 129.9, 128.8, 128.6, 128.0, 127.4, 79.1, 52.6, 47.2, 38.7, 27.1, 21.7, and 17.1.

IR (neat): 3030, 2922, 2871, 1598, 1455, 1338, 1159, 1104, 937, and 734 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{19}H_{20}BrNNaO_2S^+$ 428.0290, found 428.0281.

_N_-Benzyl-_N_-(7-(2-(1-hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hepta-4,6-diyn-1-yl)-4-methylbenzenesulfonamide (S17)



S16 ***S3*** ***S17***

Triyne alcohol **S17** (210 mg, 0.38 mmol, 76 %) was obtained as a yellow oil from the terminal alkyne **S3** (114 mg, 0.50 mmol) and the bromoalkyne **S16** (243 mg, 0.6 mmol) by following the procedure used to prepare triyne alcohol **S4**.

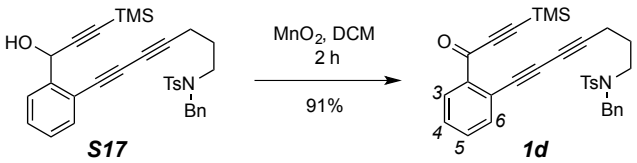
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.71 (dd, *J* = 7.7, 1.2 Hz, 1H, *H6*), 7.50 (dd, *J* = 7.7, 1.4 Hz, 1H, *H3*), 7.40 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H4*), 7.37–7.27 (m, 8H, Ts aromatic *H* ortho to Me, *H* on Bn, and *H5*), 5.82 (d, *J* = 5.7 Hz, 1H, ArC*H*OH), 4.32 (s, 2H, PhCH_2), 3.18 (t, *J* = 7.3 Hz, 2H, CH_2NTsBn), 2.45 (s, 3H, *Me* on Ts), 2.43 (d, *J* = 5.7 Hz, 1H, O*H*), 2.20 (t, *J* = 7.0 Hz, 2H, CH_2CH$_2$CH$_2$NTs), 1.61 (tt, *J* = 7.1, 7.1 Hz, 2H, CH$_2$CH_2CH$_2$NTs), and 0.19 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 143.4, 136.7, 136.3, 133.7, 130.0, 129.6, 128.8, 128.6, 128.5, 128.1, 127.4, 127.2, 120.8, 104.2, 92.0, 84.8, 79.5, 72.2, 65.7, 63.4, 52.8, 47.4, 27.2, 21.7, 17.1, and -0.1.

IR (neat): 3482, 3065, 2958, 2238, 2172, 1337, 1159, 1038, 984, and 845 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{33}H_{35}NNaO_3SSi^+$ 576.1999, found 576.1986.

_N_-Benzyl-4-methyl-_N_-(7-(2-(3-(trimethylsilyl)propioloyl)phenyl)hepta-4,6-diyn-1-yl)benzen esulfonamide (1d)



S17 ***1d***

Triyne ketone **1d** (161 mg, 0.29 mmol, 91 %) was obtained as a yellow oil from the triyne alcohol **S17** (177 mg, 0.32 mmol) and MnO_2 (278 mg, 3.2 mmol) by following the procedure used to prepare the triyne ketone **1a**.

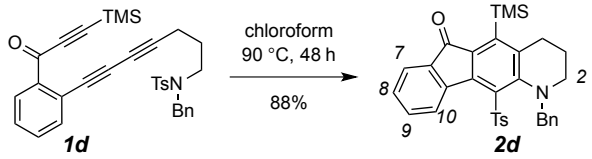
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.6, 1.5 Hz, 1H, *H3*), 7.75 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.60 (dd, *J* = 7.5, 1.4 Hz, 1H, *H6*), 7.50 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H, *H5*), 7.45 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H, *H4*), 7.38–7.28 (m, 7H, Ts aromatic *H* ortho to Me and PhH_5), 4.32 (s, 2H, PhCH_2), 3.17 (t, *J* = 7.0 Hz, 2H, CH_2NTsMe), 2.45 (s, 3H, *Me* on Ts), 2.19 (t, *J* = 7.0 Hz, 2H CH_2CH$_2$CH$_2$NTsMe), 1.60 (tt, *J* = 7.0, 7.0 Hz, 2H, CH$_2$CH_2CH$_2$NTsMe), and 0.29 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 143.5, 139.1, 136.7, 136.3, 135.8, 132.7, 132.1, 130.0, 128.8, 128.7, 128.6, 128.1, 127.4, 122.0, 101.5, 101.4, 85.5, 80.4, 73.2, 66.3, 52.8, 47.5, 27.3, 21.7, 17.2, and -0.6.

IR (neat): 3064, 2958, 2919, 2240, 2152, 1646, 1339, 1236, 1159, 1015, and 848 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{33}H_{34}NO_3SSi^+$ 552.2023, found 552.2012.

1-Benzyl-11-tosyl-5-(trimethylsilyl)-1,2,3,4-tetrahydro-6H-indeno[2,1-g]quinolin-6-one (2d)



1d ***2d***

Triyne ketone **1d** (77 mg, 0.14 mmol) was dissolved in 5 mL of chloroform in a screw-capped vial. This solution was heated in an oil bath held at 90 °C for 48 h. After concentration and flash chromatography (10:1 Hex:EtOAc elution), the tetrahydroquinoline **2d** (68 mg, 0.12 mmol, 88 %) was obtained as a crystalline orange solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 7.7 Hz, 1H, *H10*), 7.61 (d, *J* = 8.2 Hz, 2H, Ts *H* meta to Me), 7.47 (d, *J* = 7.4 Hz, 1H, *H7*), 7.38 (ddd, *J* = 7.5, 7.5, 1.3 Hz, 1H, *H9*), 7.27–7.18 (m, 6H, *H8*, Ts *H* ortho to Me and *o, p-H* on Bn), 7.02–6.96 (nfom, 2H, *m-H* on Bn), 5.37–5.19 (br m, 1H, one of PhCH_2), 4.23–4.06 (br m, 1H, one of PhCH_2), 3.05–2.84 (br m, 1H), 2.84–2.62 (br m, 1H), 2.57–2.40 (br m, 1H), 2.36 (s, 3H, *Me* on Ts), 2.25–2.03 (br m, 1H), 1.87–1.67 (br m, 1H), 1.36–1.14 (br m, 1H), and 0.42 (s, 9H, TMS).

^{1}H NMR (400 MHz, Benzene-d_6) δ 8.74 (ddd, *J* = 7.7, 0.9, 0.9 Hz, 1H, *H10*), 7.61 (d, *J* = 8.3 Hz, 2H, Ts *H* meta to Me), 7.46 (ddd, *J* = 7.4, 1.3, 0.7 Hz, , 1H, *H7*), 7.02–6.94 (m, 4H, *H9* and *o-, p- H* on Bn), 6.86–6.81 (m, 2H, *m-H* on Bn), 6.71 (dd, *J* = 7.4, 7.4 Hz, 1H, *H8*), 6.59 (d, *J* = 8.1 Hz, 2H, Ts *H* ortho to Me), 5.76–5.44 (br m, 1H, one of PhCH_2), 4.51–4.21 (br m, 1H, one of PhCH_2), 2.94–2.68 (br m, 1H), 2.67–2.49 (br m, 1H), 2.49–2.27 (br m, 1H), 2.15–1.85 (br m, 1H), 1.70 (s, 3H, *Me* on Ts), 1.41–1.21 (br m, 1H), 1.21–0.99 (br m, 1H), and 0.59 (s, 9H, TMS).

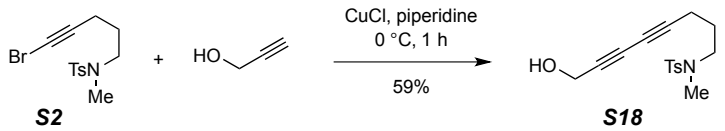
^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.4, 152.9, 148.0, 143.5, 142.2, 141.5, 140.5, 139.1, 137.9, 134.4, 133.5, 130.7, 129.2, 129.2, 128.6, 128.4, 127.8, 127.0, 126.9, 123.6, 122.5, 63.2, 47.4, 29.9, 23.3, 21.6, and 3.2.

IR (neat): 3062, 2949, 2896, 1703, 1526, 1300, 1287, 1138, 1081, 848, and 702 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{33}H_{34}NO_3SSi^+$ 552.2023, found 552.2026.

m.p.: 206–208 °C.

N-(8-Hydroxyocta-4,6-diyn-1-yl)-*N*,4-dimethylbenzenesulfonamide (S18)



Diyne alcohol **S18** (180 mg, 0.59 mmol, 59 %) was obtained as a yellow oil from propargyl alcohol (56 mg, 1.5 mmol) and bromoalkyne **S2** (247 mg, 1.0 mmol) by following the procedure used to prepare triyne alcohol **S4**.

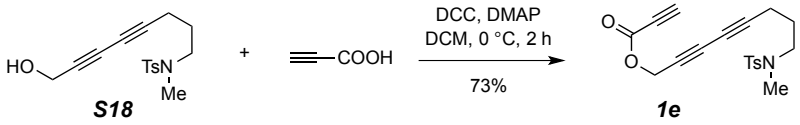
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.32 (d, *J* = 8.0 Hz, 2H, Ts aromatic *H* ortho to Me), 4.32 (d, *J* = 6.2 Hz, 2H, C*H*$_2$OH), 3.06 (t, *J* = 6.9 Hz, 2H, C*H*$_2$NTsMe), 2.73 (s, 3H, N*Me*), 2.43 (s, 3H, *Me* on Ts), 2.39 (t, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NTsMe), 1.79 (tt, *J* = 7.0, 7.0 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NTsMe), and 1.57 (t, *J* = 6.2 Hz, 1H, O*H*).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 134.4, 129.8, 127.5, 80.2, 74.2, 70.7, 65.3, 51.5, 49.3, 35.3, 26.7, 21.6, and 16.7.

IR (neat): 3497, 2925, 2867, 2256, 1597, 1335, 1159, 1019, 965, 816, and 716 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{16}H_{20}NO_3S^+$ 306.1158, found 306.1152.

8-((*N*,4-Dimethylphenyl)sulfonamido)octa-2,4-diyn-1-yl propiolate (1e)



A solution of DCC* (110 mg, 0.53 mmol) and DMAP (6 mg, 0.05 mmol) in CH_2Cl_2 (1 mL) was added slowly to a DCM (5 mL) solution containing alcohol **S18** (150 mg, 0.49 mmol) and propiolic acid (45 mg, 0.64 mmol) at 0 ^oC. After 2 h, the mixture was filtered through Celite® and concentrated under reduced pressure. After flash chromatography (3:1 Hex:EtOAc elution), the propiolate **1e** (128 mg, 0.39 mmol, 73%) was obtained as a colorless oil.

*CAUTION: Dicyclohexylcarbodiimide (DCC) is a known sensitizer that can lead to systemic reaction upon exposure. The reagent should be handled in a fume hood and in a manner that avoids any skin contact with the solid and exposure to microparticulates.

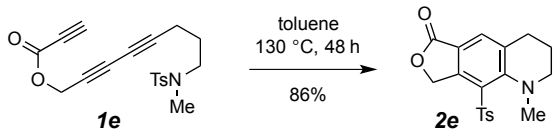
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.3 Hz, 2H, Ts *H* meta to Me), 7.32 (d, *J* = 8.0 Hz, 2H, Ts *H* ortho to Me), 4.83 (s, 2H, CH_2O), 3.06 (t, *J* = 6.9 Hz, 2H, CH_2NTsMe), 2.94 (s, 1H, C≡C*H*), 2.73 (s, 3H, N*Me*), 2.43 (s, 3H, *Me* on Ts), 2.38 (t, *J* = 7.1 Hz, 2H, CH_2CH$_2$CH$_2$NTsMe), and 1.79 (tt, *J* = 7.0, 7.0 Hz, 2H, CH$_2$CH_2CH$_2$NTsMe).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.8, 143.6, 134.4, 129.8, 127.5, 81.4, 76.2, 73.9, 72.6, 68.3, 64.9, 54.1, 49.3, 35.3, 26.6, 21.6, and 16.7.

IR (neat): 3255, 2939, 2260, 2121, 1722, 1338, 1211, 1160, 962, and 716 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{19}H_{20}NO_4S^+$ 358.1108, found 358.1102.

1-Methyl-9-tosyl-2,3,4,8-tetrahydrofuro[3,4-*g*]quinolin-6(1*H*)-one (2e)



1e ***2e***

Triyne ester **1e** (49 mg, 0.14 mmol) was dissolved in 14 mL of toluene in a screw-capped vial. This solution was heated in an oil bath held at 130 °C for 48 h. After concentration and purification by MPLC (2:1 Hex:EtOAc elution), the tetrahydroquinoline **2e** (42 mg, 0.12 mmol, 86 %) was obtained as a crystalline white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.2 Hz, 2H, Ts *H* meta to Me), 7.62 (s, 1H, Ar*H*), 7.25 (d, *J* = 8.2 Hz, 2H, Ts *H* ortho to Me), 5.59 (s, 2H, CH_2O), 3.09 (s, 3H, N*Me*), 2.82–2.76 (m, 4H, CH_2NMe and CH_2CH$_2$CH$_2$NMe), 2.41 (s, 3H, *Me* on Ts), and 1.81 (tt, *J* = 6.3, 6.3 Hz, 2H, CH$_2$CH_2CH$_2$NMe).

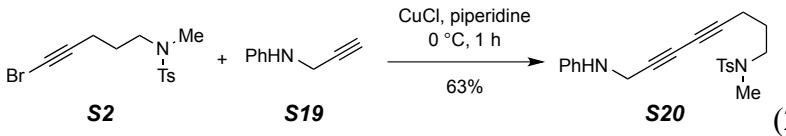
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.3, 154.8, 148.3, 144.3, 139.2, 134.1, 129.3, 129.2, 127.0, 125.6, 118.5, 71.0, 51.3, 47.9, 28.1, 21.7, and 18.7.

IR (neat): 2947, 2868, 1759, 1603, 1347, 1146, 1012, 669, and 659 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{19}H_{20}NO_4S^+$ 358.1108, found 358.1102.

m.p.: 162–164 ^{o}C

_N_,4-Dimethyl-_N_-(8-(phenylamino)octa-4,6-diyn-1-yl)benzenesulfonamide (S20)



S2 ***S19*** ***S20*** (221)

Triyne amine **S20** (242 mg, 0.64 mmol, 63 %) was obtained as a yellow oil from the terminal alkyne **S19**[3] (157 mg, 1.2 mmol) and the bromoalkyne **S2** (247 mg, 1.0 mmol) by following the procedure used to prepare triyne alcohol **S4**.

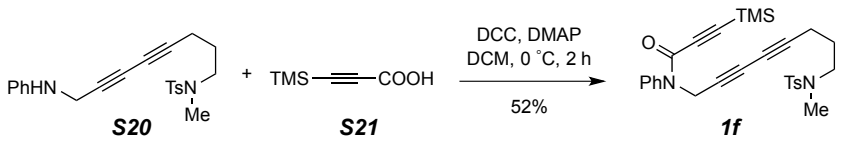
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.3 Hz, 2H, Ts *H* meta to Me), 7.31 (d, *J* = 8.3 Hz, 2H, Ts *H* ortho to Me), 7.21 (dd, *J* = 8.4, 7.5 Hz, 2H, Ph*H*m), 6.79 (tt, *J* = 7.4, 1.3 Hz, 1H, Ph*H*p), 6.67 (dd, *J* = 8.4, 1.3 Hz, 2H, Ph*H*o), 3.99 (s, 2H, NHCH_2), 3.86 (s, 1H, N*H*), 3.04 (t, *J* = 6.9 Hz, 2H, CH_2NTsMe), 2.72 (s, 3H, N*Me*), 2.43 (s, 3H, *Me* on Ts), 2.34 (t, *J* = 7.1 Hz, 2H, CH_2CH$_2$CH$_2$NTsMe), and 1.76 (tt, *J* = 7.0,7.0 Hz, 2H, CH$_2$CH_2CH$_2$NTsMe).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.8, 143.5, 134.4, 129.8, 129.3, 127.5, 118.7, 113.6, 78.5, 73.8, 68.0, 65.6, 49.3, 35.2, 34.3, 26.7, 21.6, and 16.6.

IR (neat): 3400, 3052, 2925, 2254, 1603, 1506, 1337, 1160, 1090, 751 and 694 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{22}H_{25}N_2O_2S^+$ 381.1631, found 381.1619.

_N_-(8-((_N_,4-Dimethylphenyl)sulfonamido)octa-2,4-diyn-1-yl)-_N_-phenyl-3-(trimethylsilyl)propiolamide (1f)



*DCC(150 mg, 0.72 mmol) was added slowly into a DCM (7 mL) solution containing amine **S20** (230 mg, 0.61 mmol), acid **S21** (129 mg, 0.91 mmol), and DMAP (11 mg, 0.09 mmol) at 0 ^{o}C. The mixture was allowed to warm to room temperature. After 2 hours of being stirred, the mixture was filtered through Celite® and concentrated under reduced pressure. After flash chromatography (5:1 Hex:EtOAc elution), the amide **1f** (157 mg, 0.31 mmol, 52%) was obtained as a yellow oil.

*CAUTION: Dicyclohexylcarbodiimide (DCC) is a known sensitizer that can lead to systemic reaction upon exposure. The reagent should be handled in a fume hood and in a manner that avoids any skin contact with the solid and exposure to microparticulates.

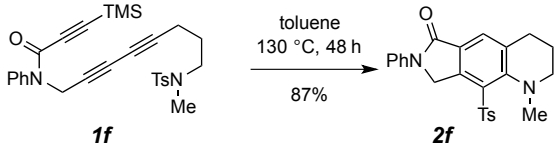
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.3 Hz, 2H, Ts *H* meta to Me), 7.44–7.29 (m, 7H, Ph*H* & Ts*H* ortho to Me), 4.56 (s, 2H, PhNC*H*$_2$), 3.05 (t, *J* = 6.9 Hz, 2H, C*H*$_2$NTsMe), 2.73 (s, 3H, N*Me*), 2.43 (s, 3H, *Me* on Ts), 2.35 (t, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NTsMe), 1.77 (tt, *J* = 7.0, 7.0 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NTsMe), and -0.04 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.2, 143.5, 141.0, 134.5, 129.8, 129.2, 128.7, 128.5, 127.5, 99.6, 96.1, 79.0, 70.7, 69.2, 65.5, 49.3, 38.5, 35.3, 26.7, 21.6, 16.7, and -1.0.

IR (neat): 3063, 2960, 2258, 2167, 1642, 1379, 1341, 1161, 849, and 698 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{28}H_{33}N_2O_3SSi^+$ 505.1975, found 505.1965.

1-Methyl-7-phenyl-9-tosyl-1,2,3,4,7,8-hexahydro-6*H*-pyrrolo[3,4-*g*]quinolin-6-one (2f)



1f ***2f***

Triyne amide **1f** (90 mg, 0.18 mmol) was dissolved in 18 mL of toluene in a screw-capped vial. This solution was heated in an oil bath held at 130 °C for 48 h. After concentration and purification by chromatography (10:1 Hex:EtOAc elution), the tetrahydroquinoline **2f** (78 mg, 0.15mmol, 87 %) was obtained as a crystalline pale yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.7, 1.2 Hz, 2H, Ph*H*o), 7.70 (d, *J* = 8.3 Hz, 2H, Ts *H* meta to Me), 7.41 (dd, *J* = 8.6, 7.3 Hz, 2H, Ph*H*m), 7.25 (d, *J* = 8.3 Hz, 2H, Ts *H* ortho to Me), 7.16 (tt, *J* = 7.4, 1.2 Hz, 1H, Ph*H*p), 5.26 (s, 2H, PhNCH_2), 3.00 (s, 3H, N*Me*), 2.82 (t, *J* = 6.5 Hz, 2H, $CH_2CH_2CH_2$NMe), 2.52 (t, *J* = 6.0 Hz, 2H, $CH_2CH_2CH_2$NMe), 2.41 (s, 3H, *Me* on Ts), 1.67 (tt, *J* = 6.5, 6.0 Hz, 2H, $CH_2CH_2CH_2$NMe), and 0.48 (s, 9H).

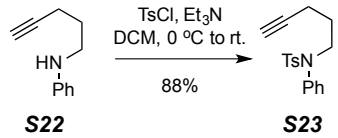
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 151.5, 144.2, 143.7, 141.8, 140.6, 139.9, 139.5, 132.4, 129.2, 129.0, 128.4, 127.3, 124.3, 119.7, 51.3, 50.4, 48.0, 30.0, 21.7, 20.7, and 3.8.

IR (neat): 2946, 2894, 2868, 1697, 1599, 1500, 1298, 1146, 847, and 662 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{28}H_{33}N_2O_3SSi^+$ 505.1976, found 505.1954.

m.p.: 204–205 °C

N-Phenyl-4-methyl-*N*-(pent-4-yn-1-yl)benzenesulfonamide (S23)



S22 ***S23***

Amine **S22**[4] (127 mg, 0.8 mmol) was mixed with triethylamine (0.14 mL, 1.0 mmol) in DCM (4 mL) at 0 °C. Tosyl chloride (182 mg, 0.96 mmol) was added in portions and the mixture was stirred and allowed to warm to room temperature overnight. After addition of 1% NaOH aqueous solution (3 mL), the quenched reaction mixture was extracted with EtOAc (8 mL three times). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography (10:1 hexanes:EtOAc elution) to provide the terminal alkyne **S23** (220 mg, 1.43 mmol, 88 %) as a white solid.

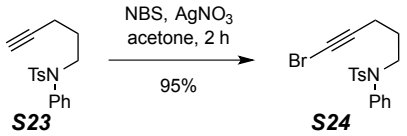
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.3 Hz, 2H, Ts *H* meta to Me), 7.34–7.27 (m, 3H, *o*- and *p*-*H* on Ph), 7.23 (d, *J* = 8.3 Hz, 2H, Ts *H* ortho to Me), 7.06–7.01 (nfom, 2H, *m*-*H* on Ph), 3.63 (t, *J* = 7.0 Hz, 2H, $CH_2CH_2CH_2NTs$), 2.42 (s, 3H, *Me* on Ts), 2.24 (td, *J* = 7.2, 2.7 Hz, 2H, $CH_2CH_2CH_2NTs$), 1.91 (t, *J* = 2.6 Hz, 1H, C≡C*H*), and 1.67 (tt, *J* = 7.1, 7.1 Hz, 1H, $CH_2CH_2CH_2NTs$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 139.2, 135.3, 129.5, 129.2, 128.8, 128.1, 127.9, 83.3, 69.1, 49.7, 27.4, 21.7, and 15.8.

IR (neat): 3291, 3063, 2935, 2872, 2118, 1596, 1492, 1347, 1163, 1106, 925, and 815 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{18}H_{19}NNaO_2S^+$ 336.1029, found 336.1024.

N-Phenyl-*N*-(5-bromopent-4-yn-1-yl)-4-methylbenzenesulfonamide (S24)



S23 ***S24***

Bromoalkyne **S24** (212 mg, 0.54 mmol, 95 %) was obtained as a white amorphous solid from alkyne **S23** (178 mg, 0.57 mmol), NBS (202 mg, 1.14 mmol), and $AgNO_3$ (10 mg, 0.06 mmol) by following the procedure used to prepare bromoalkyne **S2**.

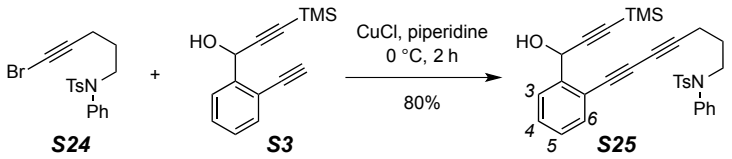
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.3 Hz, 2H, Ts *H* meta to Me), 7.34–7.26. (m, 3H, *p*- and *o*-*H* on Ph), 7.25 (d, *J* = 8.3 Hz, 1H, Ts *H* ortho to Me), 7.07–7.02 (nfom, 2H, *m*-*H* on Ph), 3.60 (t, *J* = 7.0 Hz, 2H, $CH_2CH_2CH_2NTs$), 2.42 (s, 3H, *Me* on Ts), 2.26 (t, *J* = 7.2 Hz, 2H, $CH_2CH_2CH_2NTs$), and 1.65 (tt, *J* = 7.1, 7.1 Hz, 1H, $CH_2CH_2CH_2NTs$).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 139.2, 135.2, 129.5, 129.2, 128.8, 128.1, 127.9, 79.1, 49.7, 38.7, 27.3, 21.7, and 17.1.

IR (neat): 2936, 2872, 1644, 1492, 1348, 1163, 1106, 815, 711, and 697 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{18}H_{19}BrNO_2S^+$ 392.0314, found 392.0311.

_N_-Phenyl-_N_-(7-(2-(1-hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hepta-4,6-diyn-1-yl)-4-methylbenzenesulfonamide (S25)



S24 ***S3*** ***S25***

Triyne alcohol **S25** (172 mg, 0.32 mmol, 80 %) was obtained as a colorless oil from terminal alkyne **S3** (92 mg, 0.4 mmol) and bromoalkyne **S24** (188 mg, 0.48 mmol) by following the procedure used to prepare triyne alcohol **S4**.

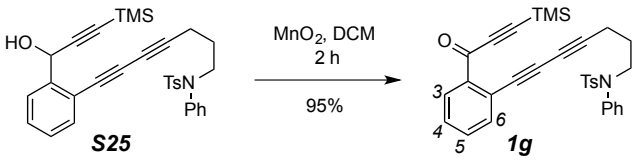
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (dd, *J* = 7.8, 1.2 Hz, 1H, *H3*), 7.48 (m, 3H, *H6* and Ts aromatic *H* meta to Me), 7.38 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, *H5*), 7.35–7.23 (m, 6H, *o*-, *p*-*H* on Ph, *H4* and Ts *H* ortho to Me), 7.08–7.04 (nfom, 2H, *m*-*H* on phenyl), 5.80 (d, *J* = 5.5 Hz, 1H, C*H*OH), 3.64 (t, *J* = 6.8 Hz, 2H, CH_2NTsMe), 2.45 (d, *J* = 5.5 Hz, 1H, O*H*), 2.45 (t, *J* = 7.3 Hz, 2H, CH_2CH$_2$CH$_2$NTsMe), 2.42 (s, 3H, N*Me*), 1.72 (tt, *J* = 7.0, 7.0 Hz, 2H, CH$_2$CH_2CH$_2$NTsMe), and 0.19 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 143.5, 139.1, 135.2, 133.7, 129.6, 129.5, 129.3, 128.8, 128.4, 128.2, 127.9, 127.1, 120.7, 104.2, 91.9, 84.9, 79.5, 72.3, 65.7, 63.5, 49.7, 27.2, 21.7, 17.1, and -0.1.

IR (neat): 3489, 3064, 2958, 2899, 2239, 2173, 1596, 1348, 1163, 1058, 984, and 845 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{32}H_{33}NNaO_3SSi^+$ 562.1843, found 562.1828.

_N_-Phenyl-4-methyl-_N_-(7-(2-(3-(trimethylsilyl)propioloyl)phenyl)hepta-4,6-diyn-1-yl)benzenesulfonamide (1g)



Triyne ketone **1g** (139 mg, 0.26 mmol, 95 %) was obtained as an oil from triyne alcohol **S25** (147 mg, 0.27 mmol) and MnO_2 (237 mg, 2.7 mmol) by following the procedure used to prepare triyne ketone **1a**.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.7, 1.5 Hz, 1H, *H3*), 7.58 (dd, *J* = 7.6, 1.4 Hz, 1H, *H6*), 7.52–7.41 (m, 4H, *H4*, *H5*, and Ts *H* meta to Me), 7.36–7.29 (m, 3H, *o*-*H* and *p*-*H* on phenyl), 7.25 (d, *J* = 8.2 Hz, 2H, Ts *H* ortho to Me), 7.08–7.03 (br dd, *J* = 7.6, 1.4 Hz, 2H, *m*-*H* on phenyl), 3.63 (t, *J* = 7.0 Hz, 2H, C*H*$_2$NTsMe), 2.45 (d, *J* = 7.3 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NTsMe), 2.42 (s, 3H, N*Me*), 1.72 (tt, *J* = 7.1, 7.1 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NTsMe), and 0.29 (s, 9H, TMS).

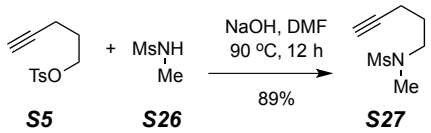
^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 143.6, 139.1, 139.0, 135.8, 135.2, 132.6, 131.9, 129.6, 129.3, 128.8, 128.5, 128.2, 127.9, 122.0, 101.5, 101.4, 85.6, 80.4, 73.2, 66.2, 49.8, 27.2, 21.7, 17.2, and -0.6.

IR (neat): 3064, 2959, 2242, 2152, 1647, 1493, 1481, 1349, 1237, 1164, 1016, 850, and 757 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{32}H_{32}NO_3SSi^+$ 538.1867, found 538.1857.

Heating this substrate under the standard conditions used throughout this study resulted in a very complex product mixture, as indicated by tlc analysis showing a multitude of discreet spots. This mixture was not further pursued.

N-Methyl-*N*-(pent-4-yn-1-yl)methanesulfonamide (S27)



Terminal alkyne **S27** (310 mg, 1.77 mmol, 89 %) was obtained as a colorless oil from the tosylate **S5** (714 mg, 3.0 mmol) and *N*-methyl methanesulfonamide (**S26**, 218 mg, 2.0 mmol) by following the procedure used to prepare the terminal alkyne **S7**.

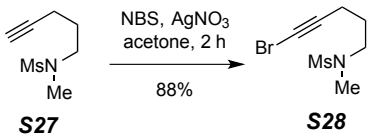
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.24 (t, *J* = 7.0 Hz, 2H, C*H*$_2$NMsMe), 2.87 (s, 3H, *Me* on Ms), 2.81 (s, 3H, N*Me*), 2.29 (td, *J* = 7.0, 2.7 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NMsMe), 1.99 (t, *J* = 2.7 Hz, 1H, C≡C*H*), and 1.83 (tt, *J* = 7.1, 7.1 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NMsMe).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 83.2, 69.3, 49.2, 35.6, 35.1, 27.1, and 15.8.

IR (neat): 3283, 3023, 2937, 2876, 2116, 1456, 1314, 1145, 1000, 978, 921, 789, and 675 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_7H_{14}NO_2S^+$ 176.0740, found 176.0737.

N-(5-Bromopent-4-yn-1-yl)-*N*-methylmethanesulfonamide (S28)



S27 ***S28***

The bromoalkyne **S28** (328 mg, 1.29 mmol, 88 %) was obtained as a colorless oil from the alkyne **S27** (255 mg, 1.46 mmol), NBS (519 mg, 2.9 mmol), and $AgNO_3$ (26 mg, 0.15 mmol) by following the procedure used to prepare the bromoalkyne **S2**.

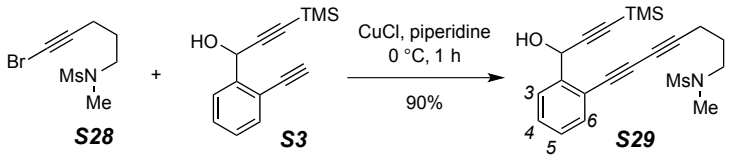
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.20 (t, *J* = 7.0 Hz, 2H, C*H*$_2$NMsMe), 2.85 (s, 3H, *Me* on Ms), 2.80 (s, 3H, N*Me*), 2.30 (t, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NMsMe), and 1.81 (tt, *J* = 7.1, 7.1 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NMsMe).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 79.0, 49.2, 39.0, 35.5, 35.0, 26.9, and 17.0.

IR (neat): 3014, 2934, 2871, 2290, 2216, 1459, 1322, 1147, 962, and 784 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_7H_{13}BrNO_2S^+$ 253.9845, found 253.9840.

_N_-(7-(2-(1-Hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hepta-4,6-diyn-1-yl)-_N_-methyl methanesulfonamide (S29)



The triyne alcohol **S29** (180 mg, 0.45 mmol, 90 %) was obtained as a yellow oil from terminal alkyne **S3** (114 mg, 0.5 mmol) and the bromoalkyne **S28** (152 mg, 0.6 mmol) by following the procedure used to prepare the triyne alcohol **S4**.

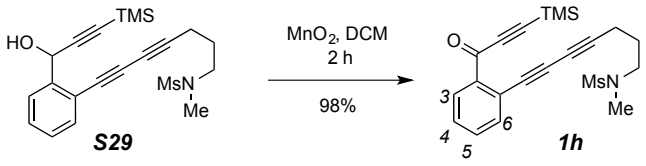
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (dd, *J* = 7.8, 1.2 Hz, 1H, *H6*), 7.50 (dd, *J* = 7.7, 1.3 Hz, 1H, *H3*), 7.40 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H4*), 7.29 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, *H5*), 5.83 (d, *J* = 5.7 Hz, 1H, ArC*H*OH), 3.25 (t, *J* = 6.9 Hz, 2H, CH_2NMsMe), 2.89 (s, 3H, Me on Ms), 2.82 (s, 3H, N*Me*), 2.50 (d, *J* = 5.7 Hz, 1H, O*H*), 2.49 (t, *J* = 6.9 Hz, 2H, CH_2CH$_2$NMsMe), 1.89 (tt, *J* = 7.0, 7.0 Hz, 2H, CH$_2$CH_2CH$_2$NMsMe), and 0.20 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 133.7, 129.6, 128.5, 127.1, 120.7, 104.2, 92.0, 84.7, 79.4, 72.4, 65.9, 63.5, 49.3, 35.5, 35.2, 27.0, 17.0, and -0.1.

IR (neat): 3471, 3066, 2959, 2900, 2239, 2172, 1329, 1250, 1150, 1038, 964, 845, and 761 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{21}H_{27}NNaO_3SSi^+$ 424.1373, found 424.1362.

_N_-(Methylsulfonyl)-_N_-(7-(2-(3-(trimethylsilyl)propioloyl)phenyl)hepta-4,6-diyn-1-yl)methanesulfonamide (1h)



The triyne ketone **1h** (160 mg, 0.40 mmol, 98 %) was obtained as a yellow oil from the triyne alcohol **S29** (165 mg, 0.41 mmol) and MnO_2 (358 mg, 4.1 mmol) by following the procedure used to prepare the triyne ketone **1a**.

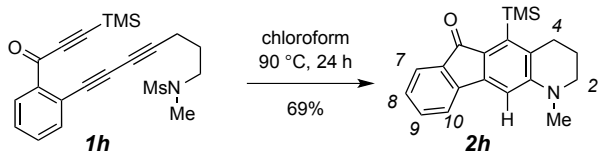
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.7, 1.5 Hz, 1H, *H3*), 7.60 (dd, *J* = 7.7, 1.4 Hz, 1H, *H6*), 7.50 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H, *H5*), 7.45 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H, *H4*), 3.24 (t, *J* = 7.0 Hz, 2H, C*H*$_2$NMsMe), 2.88 (s, 3H, *Me* on Ms), 2.82 (s, 3H, N*Me*), 2.48 (t, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NMsMe), 1.88 (tt, *J* = 7.0, 7.0 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NMsMe), and 0.30 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 139.1, 135.8, 132.7, 132.1, 128.6, 121.9, 101.45, 101.42, 85.4, 80.2, 73.4, 66.5, 49.3, 35.5, 35.2, 27.0, 17.1, and -0.1.

IR (neat): 3065, 2960, 2901, 2241, 2152, 1646, 1480, 1378, 1237, 1152, 1015, 963, 850, and 757 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{21}H_{26}NO_3SSi^+$ 400.1397, found 400.1386.

1-Methyl-5-(trimethylsilyl)-1,2,3,4-tetrahydro-6*H*-indeno[2,1-*g*]quinolin-6-one (2h)



1h ***2h***

The triyne ketone **1h** (90 mg, 0.23 mmol) was dissolved in 7 mL of chloroform in a screw-capped vial. This solution was heated for 48 h in an oil bath held at 90 °C. After concentration and flash chromatography (10:1 Hex:EtOAc elution), the tetrahydroquinoline **2h** (50 mg, 0.16 mmol, 69 %) was obtained as a crystalline orange solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.3 Hz, 1H, *H7*), 7.42–7.32 (m, 2H, *H9* and *H10*), 7.21 (dd, *J* = 7.2, 7.2 Hz, 1H, *H8*), 6.70 (s, 1H, *H11*), 3.36 (t, *J* = 5.8 Hz, 2H, *H2*), 3.09 (s, 3H, N*Me*), 2.85 (t, *J* = 6.2 Hz, 2H, *H4*), 1.93 (tt, *J* = 6.2, 5.8 Hz, 2H, *H3*), and 0.42 (s, 9H, TMS).

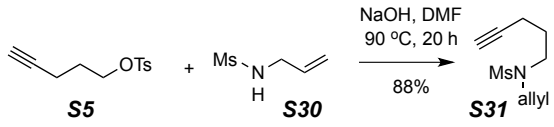
^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.1, 150.6, 146.4, 143.3, 141.7, 136.1, 132.9, 128.6, 128.4, 127.0, 122.8, 118.7, 103.0, 51.2, 39.7, 30.0, 22.8, and 3.0.

IR (neat): 3044, 2953, 2892, 1675, 1587, 1511, 1280, 1239, 1181, 1039, 836, and 737 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{20}H_{24}NOSi^{+}$ 322.1620, found 322.1606.

m.p.: 184–186 °C

N-Allyl-*N*-(pent-4-yn-1-yl)methanesulfonamide (S31)



The mesylamide **S31** (371 mg, 2.0 mmol, 88 %) was obtained as a colorless oil from the tosylate **S5** (597 mg, 2.51 mmol) and the mesyl amide **S30** (282 mg, 2.09 mmol) by following the procedure used to prepare the alkyne **S7**.

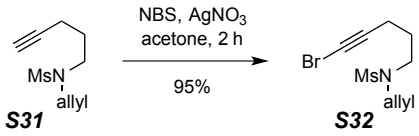
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.84 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H, CH_2CH=CH_2), 5.30 (ddt, *J* = 17.1, 1.4, 1.4 Hz, 1H, CH_2CH=CH_ZH_E), 5.27 (ddt, *J* = 10.1, 1.5, 1.5 Hz, 1H, CH_2CH=CH_EH_Z), 3.86 (ddd, *J* = 6.5, 1.4, 1.4 Hz, 2H, CH_2CH=CH_2), 3.30 (t, *J* = 7.2 Hz, 2H, CH_2NMs(allyl)), 2.86 (s, 3H, *Me* on Ms), 2.25 (td, *J* = 7.0, 2.6 Hz, 2H, $CH_2CH_2CH_2$NMs(allyl)), 1.98 (t, *J* = 2.6 Hz, 1H, C≡C*H*), and 1.83 (tt, *J* = 7.1, 7.1 Hz, 2H, $CH_2CH_2CH_2$NMs).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.7, 119.5, 83.1, 69.2, 50.4, 46.1, 39.0, 27.4, and 15.7.

IR (neat): 3281, 3082, 2934, 2873, 2117, 1642, 1324, 1145, 963, 929, and 790 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_9H_{16}NO_2S^+$ 202.0896, found 202.0893.

N-Allyl-*N*-(5-bromopent-4-yn-1-yl)methanesulfonamide (S32)



S31 ***S32***

The bromoalkyne **S32** (267 mg, 0.95 mmol, 95 %) was obtained as a colorless oil from the alkyne **S31** (201 mg, 1.0 mmol), NBS (352 mg, 2.0 mmol), and $AgNO_3$ (17 mg, 0.1 mmol) by following the procedure used to prepare the bromoalkyne **S2**.

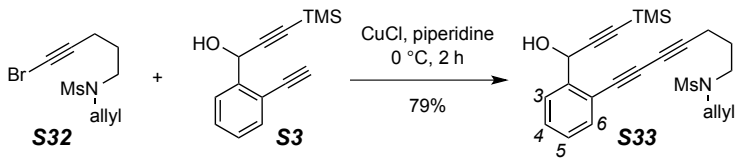
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.84 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H, CH_2CH=CH_2), 5.31 (ddt, *J* = 17.1, 1.4, 1.4 Hz, 1H, CH_2CH=CH_ZH_E), 5.28 (ddt, *J* = 10.1, 1.5, 1.5 Hz, 1H, CH_2CH=CH_EH_Z), 3.85 (ddd, *J* = 6.6, 1.4, 1.4 Hz, 1H, CH_2CH=CH_2), 3.26 (t, *J* = 7.2 Hz, 2H, CH_2NMs(allyl)), 2.86 (s, 3H, *Me* on Ms), 2.27 (t, *J* = 7.0 Hz, 3H, C$H_2CH_2CH_2$NMs(allyl)), and 1.81 (tt, *J* = 7.1, 7.1 Hz, 2H, $CH_2CH_2CH_2$NMs).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.7, 119.7, 79.0, 50.6, 46.1, 39.03, 39.01, 27.3, and 17.1.

IR (neat): 3082, 2934, 2872, 2288, 2216, 1326, 1146, 963, 933, and 792 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_9H_{15}BrNO_2S^+$ 280.0001, found 279.9997.

_N_-Allyl-_N_-(7-(2-(1-hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hepta-4,6-diyn-1-yl)methanesulfonamide (S33)



The triyne alcohol **S33** (145 mg, 0.4 mmol, 79 %) was obtained as a yellow oil from the terminal alkyne **S3** (97 mg, 0.43 mmol) and the bromoalkyne **S32** (143 mg, 0.51 mmol) by following the procedure used to prepare the triyne alcohol **S4**.

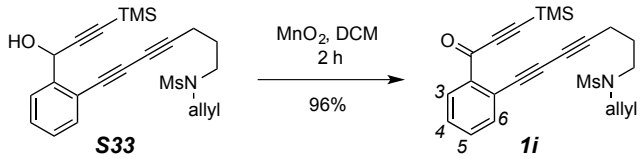
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 7.7, 1.3 Hz, 1H, *H6*), 7.50 (dd, *J* = 7.7, 1.4 Hz, 1H, *H3*), 7.40 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 1H, *H4*), 7.29 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H5*), 5.86 (ddt, *J* = 16.7, 10.1, 6.5 Hz, 1H, CH_2CH=CH_2), 5.82 (d, *J* = 5.7 Hz, 1H, ArC*H*OH), 5.34 (ddt, *J* = 16.9, 1.4, 1.4 Hz, 1H, CH_2CH=CH_ZH_E), 5.31 (ddt, *J* = 10.1, 1.5, 1.5 Hz, 1H, CH_2CH=CH_EH_Z), 3.88 (ddd, *J* = 6.5, 1.4, 1.4 Hz, 1H, CH_2CH=CH_2), 3.31 (t, *J* = 7.3 Hz, 2H, CH_2NMs(allyl)), 2.88 (s, 3H, *Me* on Ms), 2.46 (d, *J* = 5.7 Hz, 1H, O*H*), 2.45 (t, *J* = 7.1 Hz, 2H, CH_2CH$_2$CH$_2$NMs(allyl)), 1.89 (tt, *J* = 7.1, 7.1 Hz, 2H, CH_2CH$_2$NMs(allyl)), and 0.20 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 133.7, 132.7, 129.6, 128.5, 127.1, 120.7, 119.9, 104.2, 91.9, 84.7, 79.4, 72.4, 65.9, 63.5, 50.7, 46.3, 39.0, 27.4, 17.1, and -0.1.

IR (neat): 3474, 3069, 2958, 2899, 2238, 2172, 1327, 1250, 1147, 1038, 845, and 761 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{23}H_{29}NNaO_3SSi^+$ 450.1530, found 450.1514.

_N_-Allyl-_N_-(7-(2-(3-(trimethylsilyl)propioloyl)phenyl)hepta-4,6-diyn-1-yl)methanesulfonamide (1i)



The triyne ketone **1i** (104 mg, 0.24 mmol, 96 %) was obtained as a yellow oil from the triyne alcohol **S33** (108 mg, 0.25 mmol) and MnO_2 (217 mg, 2.5 mmol) by following the procedure used to prepare the triyne ketone **1a**.

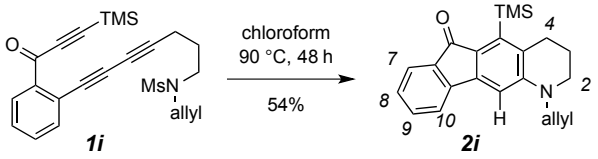
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.6, 1.5 Hz, 1H, *H3*), 7.61 (dd, *J* = 7.6, 1.5 Hz, 1H, *H6*), 7.50 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H, *H5*), 7.45 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H, *H4*), 5.85 (ddt, *J* = 16.7, 10.0, 6.5 Hz, 1H, CH_2CH=CH_2), 5.34 (ddt, *J* = 17.1, 1.4, 1.4 Hz, 1H, CH_2CH=CH_ZH_E), 5.30 (ddt, *J* = 10.1, 1.5, 1.5 Hz, 1H, CH_2CH=CH_EH_Z), 3.87 (ddd, *J* = 6.5, 1.4, 1.4 Hz, 1H, CH_2CH=CH_2), 3.31 (t, *J* = 7.3 Hz, 2H, CH_2NMs(allyl)), 2.87 (s, 3H, *Me* on Ms), 2.45 (t, *J* = 7.1 Hz, 2H, $CH_2CH_2CH_2$NMs(allyl)), 1.88 (tt, *J* = 7.1, 7.1 Hz, 2H, CH_2CH_2NMs(allyl)), and 0.20 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 139.0, 135.8, 132.7, 132.6, 132.1, 128.6, 121.9, 119.9, 101.42, 101.35, 85.4, 80.2, 73.4, 66.5, 50.7, 46.3, 38.9, 27.4, 17.2, and -0.6.

IR (neat): 3067, 2959, 2241, 2152, 1647, 1480, 1332, 1237, 1148, 1015, 849, and 757 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{23}H_{27}NNaO_3SSi^+$ 448.1373, found 448.1363.

1-Allyl-5-(trimethylsilyl)-1,2,3,4-tetrahydro-6*H*-indeno[2,1-*g*]quinolin-6-one (2i)



Triyne ketone **1i** (73 mg, 0.17 mmol) was dissolved in 3.4 mL of chloroform in a screw-capped vial. This solution was heated for 48 h in an oil bath held at 90 °C. After concentration and flash chromatography (10:1 Hex:EtOAc elution), the tetrahydroquinoline **2i** (32 mg, 0.09 mmol, 54 %) was obtained as an orange crystalline solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (dd, *J* = 7.2, 1.0 Hz, 1H, *H7*), 7.37–7.33 (m, 2H, *H9* and *H10*), 7.21 (nfom, 1H, *H8*), 6.67 (s, 1H, *H11*), 5.88 (ddt, *J* = 16.9, 10.1, 4.5 Hz, 1H), 5.23 (ddt, *J* = 10.1, 1.5, 1.5 Hz, 1H, $CH_2CH{=}C\mathit{H}_EH_Z$), 5.22 (ddt, *J* = 17.1, 1.4, 1.4 Hz, 1H, $CH_2CH{=}C\mathit{H}_ZH_E$), 4.02 (ddd, *J* = 4.5, 1.5, 1.5 Hz, 1H, $C\mathit{H}_2CH{=}CH_2$), 3.36 (tt, *J* = 5.9 Hz, 2H, *H2*), 2.88 (t, *J* = 6.2 Hz, 2H, *H4*), 1.95 (tt, *J* = 6.1, 6.1 Hz, 2H, *H3*), and 0.42 (s, 9H, TMS).

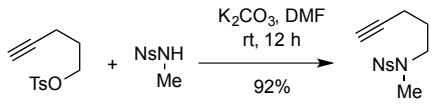
^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.0, 149.7, 146.2, 143.3, 142.2, 136.1, 132.9, 132.0, 128.6, 128.1, 127.1, 122.8, 118.7, 116.4, 103.5, 54.2, 49.4, 30.3, 22.8, and 3.0.

IR (neat): 2946, 2896, 2859, 1687, 1589, 1499, 1282, 1243, 1181, 843, and 766 cm^{-1}.

HRMS (ESI-TOF): calculated for C22H26NOSi+ 348.1778, found 348.1767.

m.p.: 129–131 °C

N-Methyl-4-nitro-*N*-(pent-4-yn-1-yl)benzenesulfonamide (S35)



S5 ***S34*** ***S35***

Tosylate **S5** (428 mg, 1.8 mmol) was mixed with tosylamide **S34** (324 mg, 1.5 mmol) and K_2CO_3 (72 mg, 1.8 mmol) in DMF (15 mL) in a sealed tube. The mixture was stirred for 16 hours. After addition of water (15 mL), the quenched reaction mixture was extracted with EtOAc (20 mL, 3x). The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography (3:1 hexanes:EtOAc elution) to provide the terminal alkyne **S35** (388 mg, 1.38 mmol, 92 %) as a crystalline pale yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 8.8 Hz, 2H, Ns aromatic *H* ortho to NO_2), 7.98 (d, *J* = 8.8 Hz, 2H, Ns aromatic *H* meta to NO_2), 3.18 (t, *J* = 7.1 Hz, 2H, C*H*$_2$NNsMe), 2.82 (s, 3H, N*Me*), 2.28 (td, *J* = 6.9, 2.6 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NNsMe), 1.98 (t, *J* = 2.7 Hz, 1H, C≡C*H*), and 1.80 (tt, *J* = 7.0, 7.0 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NNsMe).

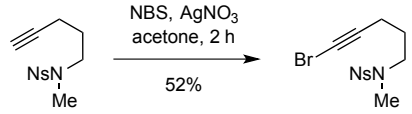
^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 143.8, 128.6, 124.5, 82.9, 69.5, 49.3, 35.2, 26.9, and 15.8.

IR (neat): 3288, 3103, 2974, 2867, 2291, 2116, 1527, 1346, 1167, 930, and 866 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{12}H_{15}N_2O_4S^+$ 283.0747, found 283.0744.

m.p.: 143–145 °C.

N-(5-Bromopent-4-yn-1-yl)-*N*-methyl-4-nitrobenzenesulfonamide (S36)



S35 ***S36***

Bromoalkyne **S36** (106 mg, 0.29 mmol, 52 %) was obtained from alkyne **S35** (160 mg, 0.57 mmol), NBS (202 mg, 1.13 mmol), and $AgNO_3$ (10 mg, 0.06 mmol) by following the procedure used to prepare bromoalkyne **S2** as a crystalline yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 8.9 Hz, 2H, Ns *H* ortho to NO_2), 7.98 (d, *J* = 8.8 Hz, 2H, Ns *H* meta to NO_2), 3.16 (t, *J* = 7.0 Hz, 2H, C*H*$_2$NNsMe), 2.82 (s, 3H, N*Me*), 2.30 (t, *J* = 7.0 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NNsMe), and 1.79 (tt, *J* = 7.0, 7.0 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NNsMe).

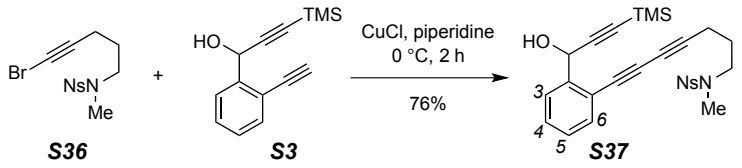
^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 143.8, 128.6, 124.6, 78.7, 49.4, 39.3, 35.2, 26.7, and 17.0.

IR (neat): 3099, 2981, 2953, 2864, 1639, 1531, 1348, 1165, 931, 857, and 743 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{12}H_{14}BrN_2O_4S^+$ 360.9852, found 360.9846.

m.p.: 135–137 °C.

N-(7-(2-(1-Hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hepta-4,6-diyn-1-yl)-*N*-methyl-4-nitrobenzenesulfonamide (S37)



Triyne alcohol **S37** (135 mg, 0.27 mmol, 76 %) was obtained from terminal alkyne **S3** (80 mg, 0.35 mmol) and bromoalkyne **S36** (152 mg, 0.42 mmol) by following the procedure used to prepare triyne alcohol **S4** as a colorless oil.

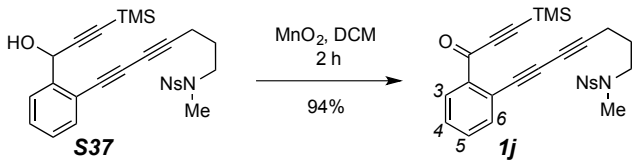
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 8.9 Hz, 2H, Ns *H* ortho to NO_2), 8.00 (d, *J* = 8.8 Hz, 2H, Ns *H* meta to NO_2), 7.71 (dd, *J* = 7.7, 1.5 Hz, 1H, *H6*), 7.50 (dd, *J* = 7.7, 1.4 Hz, 1H, *H3*), 7.40 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H5*), 7.30 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H4*), 5.82 (d, *J* = 5.7 Hz, 1H, C*H*OH), 3.19 (t, *J* = 7.0 Hz, 2H, CH_2NTsMe), 2.85 (s, 3H, N*Me*), 2.49 (t, *J* = 6.9 Hz, 2H, CH_2CH$_2$NNsMe), 2.46 (d, *J* = 5.7 Hz, 1H, O*H*), 1.87 (tt, *J* = 7.0, 7.0 Hz, 2H, CH$_2$CH_2CH$_2$NTsMe), and 0.19 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 143.7, 143.5, 133.7, 129.7, 128.6, 128.5, 127.1, 124.6, 120.6, 104.2, 92.0, 84.3, 79.3, 72.6, 66.1, 63.4, 49.4, 35.2, 26.7, 17.0, and -0.1.

IR (neat): 3506, 3104, 2959, 2899, 2239, 2173, 1531, 1350, 855, and 761 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{26}H_{28}N_2NaO_5SSi^+$ 531.1380, found 531.1362.

_N_-Methyl-4-nitro-_N_-(7-(2-(3-(trimethylsilyl)propioloyl)phenyl)hepta-4,6-diyn-1-yl)benzenesulfonamide (1j)



Triyne ketone **1j** (98 mg, 0.19 mmol, 94 %) was obtained as a yellow oil from triyne alcohol **S37** (104 mg, 0.20 mmol) and MnO_2 (178 mg, 2.0 mmol) by following the procedure used to prepare triyne ketone **1a**.

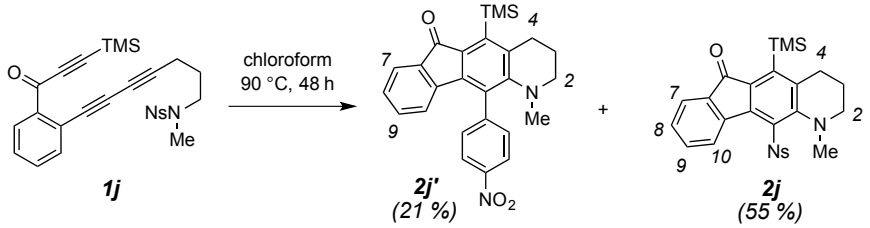
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 8.8 Hz, 2H, Ns *H* ortho to NO_2), 8.13 (dd, *J* = 7.7, 1.5 Hz, 1H, *H3*), 8.01 (d, *J* = 8.9 Hz, 1H, Ns *H* meta to NO_2), 7.60 (dd, *J* = 7.7, 1.5 Hz, 1H, *H6*), 7.51 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H, *H5*), 7.46 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H, *H4*), 3.19 (t, *J* = 7.0 Hz, 2H, C*H*$_2$NTsMe), 2.85 (s, 3H, N*Me*), 2.48 (t, *J* = 6.9 Hz, 2H, C*H*$_2$CH$_2$CH$_2$NNsMe), 1.86 (tt, *J* = 7.0, 7.0 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NTsMe), and 0.30 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.6, 143.5, 139.1, 135.8, 134.5, 132.7, 132.0, 129.9, 128.6, 127.6, 122.0, 101.5, 101.4, 85.6, 80.4, 73.3, 66.4, 49.4, 35.4, 26.9, 17.2, and -0.6.

IR (neat): 2960, 2917, 2241, 2152, 1645, 1530, 1349, 1237, 1165, 1015, 854, and 758 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{26}H_{27}N_2O_5SSi^+$ 507.1404, found 507.1396.

1-Methyl-11-(4-nitrophenyl)-5-(trimethylsilyl)-1,2,3,4-tetrahydro-6*H*-indeno[2,1-*g*]quinolin-6-one (2j') and
1-Methyl-11-((4-nitrophenyl)sulfonyl)-5-(trimethylsilyl)-1,2,3,4-tetrahydro-6*H*-indeno[2,1-*g*]quinolin-6-one (2j)



1j *2j'* (21 %) *2j* (55 %)

Triyne ketone **1j** (76 mg, 0.15 mmol) was dissolved in 5 mL of chloroform in a screw-capped vial. This solution was heated for 48 h in an oil bath held at 90 °C. After concentration and flash chromatography (10:1 Hex:EtOAc elution), in order of elution the tetrahydroquinolines **2j'** (14 mg, 0.03 mmol, 21 %) and **2j** (46 mg, 0.08 mmol, 55 %) were obtained as a yellow crystalline solid and an orange crystalline solid, respectively.

Data for **2j'**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 8.7 Hz, 2H, Ns *H* ortho to NO_2), 7.61 (d, *J* = 8.7 Hz, 2H, Ns *H* meta to NO_2), 7.52 (d, *J* = 7.2 Hz, 1H, *H7*), 7.13 (dd, *J* = 7.4, 7.4 Hz, 1H, *H9*), 7.01 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1H, *H8*), 6.06 (d, *J* = 7.6 Hz, 1H, *H10*), 3.09 (t, *J* = 5.7 Hz, 2H, *H2*), 2.87 (t, *J* = 6.2 Hz, 2H, *H4*), 2.32 (s, 3H, N*Me*), 1.90 (tt, *J* = 6.0, 6.0 Hz, 2H, *H3*), and 0.46 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.3, 151.5, 147.3, 147.1, 143.2, 142.8, 141.8, 136.3, 135.6, 133.2, 132.2, 130.9, 128.5, 126.5, 124.2, 123.3, 122.2, 52.9, 44.1, 31.6, 22.0, and 3.1.

IR (neat): 3073, 2946, 2895, 2864, 1694, 1516, 1346, 1299, 1042, 852, and 755 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{26}H_{27}N_2O_3Si^+$ 443.1785, found 443.1772.

m.p.: 228–230 °C

Data for **2j**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.8 Hz, 2H, Ns aromatic *H* ortho to NO_2), 8.18 (d, *J* = 7.7 Hz, 1H, *H10*), 7.82 (d, *J* = 8.8 Hz, 2H, Ns aromatic *H* meta to NO_2), 7.47 (d, *J* = 7.2 Hz, 1H, *H7*), 7.38 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, *H9*), 7.23 (ddd, *J* = 7.4, 7.4, 0.9 Hz, 1H, *H8*), 3.21 (s, 3H, N*Me*), 3.12–2.86 (br m, 1H), 2.86–2.49 (br m, 1H), 2.75 (br m, 2H, *H4*), 2.15–1.73 (br m, 1H), 1.63–1.36 (br m, 1H), and 0.43 (s, 9H, TMS).

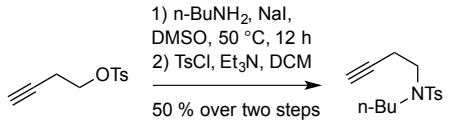
^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.7, 152.7, 149.8, 149.6, 147.4, 144.3, 140.8, 136.8, 134.3, 133.7, 130.9, 129.8, 127.6, 126.7, 123.6, 122.9, 121.4, 51.2, 47.9, 30.2, 21.6, and 3.2.

IR (neat): 3104, 2950, 2896, 2868, 1703, 1530, 1348, 1302, 1141, 855, and 735 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{26}H_{27}N_2O_5SSi^+$ 507.1404, found 507.1397.

m.p.: 195–197 ^oC

N-(But-3-yn-1-yl)-*N*-butyl-4-methylbenzenesulfonamide (S39)



S38 ***S39***

Tosylate **S38** (1.12 g, 5.0 mmol) was mixed with butylamine (1.5 mL, 15 mmol) and NaI (20 mg, 0.13 mmol) in DMSO (5 mL). After heating for 12 hours at 50 °C, the mixture was poured into aqueous NaOH (2 M, 10 mL) and extracted with ethyl ether (three times). The combined organic phase was washed with brine, dried, and concentrated to give a yellow oil. This crude amine product was dissolved in DCM (5 mL) containing triethylamine (360 mg, 3.6 mmol). Tosyl chloride (600 mg, 3.15 mmol) was added in portions, and the mixture was stirred for 3 hours. The reaction mixture was then diluted with another 20 mL of DCM and washed with brine. The organic layer was dried over $MgSO_4$ and concentrated. After flash chromatography (10:1 Hex:EtOAc elution), the tosylamide **S39** (630 mg, 2.5 mmol, 50 % over two steps) was obtained as a colorless oil.

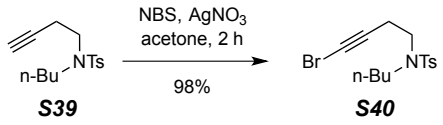
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.2 Hz, 2H, Ts aromatic *H* meta to Me), 7.29 (d, *J* = 8.2 Hz, 2H, Ts aromatic *H* ortho to Me), 3.28 (t, *J* = 7.0 Hz, 2H, NC*H*$_2$C*H*$_2$CH$_2$Me), 3.14 (t, *J* = 7.0 Hz, 2H, C*H*$_2$N(Ts)Bu), 2.50 (td, *J* = 7.8, 2.8 Hz, 2H, C*H*$_2$CH$_2$N(Ts)Bu), 2.42 (s, 3H, *Me* on Ts), 1.98 (t, *J* = 2.7 Hz, 1H, C≡C*H*), 1.52 (tt, *J* = 7.4, 7.0 Hz, 2H, CH$_2$*CH*$_2$CH$_2$Me), 1.30 (tq, *J* = 7.4, 7.4 Hz, 2H, CH$_2$*CH*$_2$Me), and 0.91 (t, *J* = 7.3 Hz, 3H, CH$_2$*Me*).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.4, 136.8, 129.8, 127.2, 81.1, 70.3, 48.8, 47.1, 30.8, 21.6, 19.9, 19.8, and 13.8.

IR (neat): 3287, 2959, 2933, 2873, 2120, 1920, 1599, 1339, 1158, 1091, 816, and 727 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{15}H_{22}NO_2S^+$ 280.1366, found 280.1360.

N-(4-Bromobut-3-yn-1-yl)-*N*-butyl-4-methylbenzenesulfonamide (S40)



S39 ***S40***

Bromoalkyne **S40** (333 mg, 0.37 mmol, 86 %) was obtained as a colorless oil from alkyne **S39** (120 mg, 0.43 mmol), NBS (153 mg, 0.86 mmol), and $AgNO_3$ (8 mg, 0.05 mmol) by following the procedure used to prepare bromoalkyne **S2**.

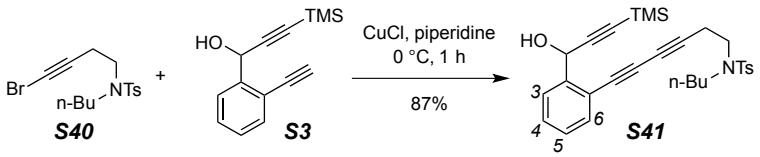
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.3 Hz, 2H, Ts aromatic *H* meta to Me), 7.30 (d, *J* = 8.0 Hz, 2H, Ts aromatic *H* ortho to Me), 3.36 (t, *J* = 7.0 Hz, 2H, NC*H*$_2$*C*H$_2$CH$_2$Me), 3.13 (t, *J* = 7.4 Hz, 2H, C*H*$_2$N(Ts)Bu), 2.50 (t, *J* = 7.4 Hz, 2H, C*H*$_2$CH$_2$N(Ts)Bu), 2.42 (s, 3H, *Me* on Ts), 1.52 (tt, *J* = 7.4, 7.0 Hz, 2H, CH$_2$*CH*$_2$CH$_2$Me), 1.30 (tq, *J* = 7.4, 7.4 Hz, 2H, CH$_2$*CH*$_2$Me), and 0.91 (t, *J* = 7.3 Hz, 3H, CH$_2$*Me*).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.4, 136.7, 129.8, 127.2, 77.2, 48.9, 46.9, 40.4, 30.9, 21.6, 21.0, 20.0, and 13.8.

IR (neat): 2959, 2932, 2872, 2219, 1598, 1339, 1158, 1091, 815, and 726 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{15}H_{21}BrNO_2S^+$ 358.0471, found 358.0467.

_N_-Butyl-_N_-(6-(2-(1-hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hexa-3,5-diyn-1-yl)-4-methylbenzenesulfonamide (S41)



Triyne alcohol **S41** (140 mg, 0.38 mmol, 87 %) was obtained as a yellow oil from terminal alkyne **S3** (73 mg, 0.32 mmol) and bromoalkyne **S40**(115 mg, 0.32 mmol) by following the procedure used to prepare triyne alcohol **S4**.

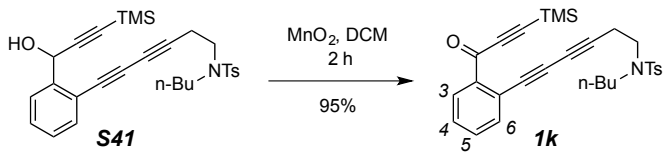
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73–7.69 (m, 3H, Ts aromatic *H* meta to Me & *H6*), 7.49 (dd, *J* = 7.6, 1.3 Hz, 1H, *H3*), 7.40 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 1H, *H4*), 7.33 (d, *J* = 8.1, Hz, 2H, Ts aromatic *H* ortho to Me), 7.29 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H, *H5*), 5.80 (d, *J* = 5.5 Hz, 1H, ArC*H*OH), 3.31 (t, *J* = 7.5 Hz, 2H, NC*H*$_2$*C*H$_2$CH$_2$Me C*H*$_2$NTsMe), 3.15 (t, *J* = 7.8 Hz, 2H, C*H*$_2$N(Ts)Bu), 2.67 (t, *J* = 8.1 Hz, 2H, C*H*$_2$CH$_2$N(Ts)Bu), 2.43 (overlapping s, 3H, *Me* on Ts and 1H, O*H*), 1.55 (tt, *J* = 7.4, 7.4 Hz, 2H, CH$_2$*CH*$_2$CH$_2$Me), 1.32 (tq, *J* = 7.4, 7.4 Hz, 2H, CH$_2$*CH*$_2$Me), and 0.92 (t, *J* = 7.3 Hz, 3H, CH$_2$*Me*), and 0.20 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.53, 143.51, 136.6, 133.7, 129.9, 129.7, 128.4, 127.2, 127.0, 120.4, 104.2, 91.9, 82.4, 79.2, 72.8, 66.9, 63.4, 49.0, 46.8, 30.8, 21.6, 21.1, 20.0, 13.8, and -0.08.

IR (neat): 3487, 2959, 2873, 2240, 2173, 1338, 1249, 1157, 1039, 844, and 760 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{29}H_{35}NNaO_3SSi^+$ 528.1999, found 528.1985.

_N_-Butyl-4-methyl-_N_-(6-(2-(3-(trimethylsilyl)propioloyl)phenyl)hexa-3,5-diyn-1-yl)benzenes ulfonamide (1k)



Triyne ketone **1k** (100 mg, 0.20 mmol, 95 %) was obtained as a yellow oil from triyne alcohol **S41** (106 mg, 0.21 mmol) and MnO_2 (183 mg, 2.1 mmol) by following the procedure used to prepare triyne ketone **1a**.

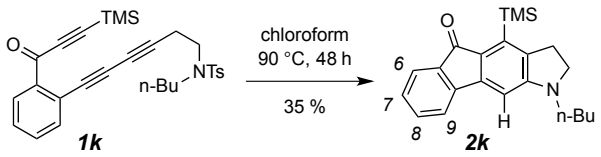
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.6, 1.7 Hz, 1H, *H3*), 7.70 (d, *J* = 8.3 Hz, 2H, Ts *H* meta to Me), 7.59 (dd, *J* = 7.6, 1.4 Hz, 1H, *H6*), 7.50 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H, *H5*), 7.45 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H, *H4*), 7.32 (d, *J* = 8.3 Hz, 2H, Ts *H* ortho to Me), 3.31 (t, *J* = 7.7 Hz, 2H, NC*H*$_2$CH$_2$CH$_2$Me), 3.15 (t, *J* = 7.8 Hz, 2H, C*H*$_2$N(Ts)Bu), 2.66 (t, *J* = 7.8 Hz, 2H, C*H*$_2$CH$_2$N(Ts)Bu), 2.42 (s, 3H, *Me* on Ts), 1.54 (tt, *J* = 7.7, 7.4 Hz, 2H, CH$_2$*CH*$_2$CH$_2$Me), 1.32 (tq, *J* = 7.3, 7.3 Hz, 2H, CH$_2$*CH*$_2$Me), 0.92 (t, *J* = 7.3 Hz, 3H, CH$_2$*Me*), and 0.30 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 143.5, 139.1, 136.6, 135.8, 132.7, 132.1, 129.9, 128.7, 127.3, 121.8, 101.44, 101.43, 83.1, 79.9, 73.8, 67.5, 49.0, 46.8, 30.9, 21.6, 21.2, 20.0, 13.8, and -0.5.

IR (neat): 2959, 2872, 2242, 2152, 1648, 1341, 1237, 1158, 1016, 849, and 757 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{29}H_{34}NO_3SSi^+$ 504.2023, found 504.2008.

1-Butyl-4-(trimethylsilyl)-2,3-dihydroindeno[2,1-*f*]indol-5(1*H*)-one (2k)



Triyne ketone **1k** (82 mg, 0.16 mmol) was dissolved in 3 mL of chloroform in a screw-capped vial. This solution was heated in an oil bath held at 90 °C for 48 h. After concentration and purification by MPLC (10:1 Hex:EtOAc elution), the indoline **2k** (20 mg, 0.057 mmol, 35 %) was obtained as a crystalline orange solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.2 Hz, 1H, *H6*), 7.37–7.34 (m, 2H, *H8* and *H9*), 7.21 (ddd, *J* = 7.0, 7.0, 2.1 Hz, 1H, *H7*), 6.47 (s, 1H, *H10*), 3.56 (t, *J* = 8.6 Hz, 2H, *H2*), 3.25 (t, *J* = 7.3 Hz, 2H, NC*H*$_2$CH$_2$CH$_2$Me), 3.09 (t, *J* = 8.7 Hz, 2H, *H3*), 1.63 (tt, *J* = 7.3, 7.3 Hz, 2H, NCH$_2$C*H*$_2$CH$_2$Me), 1.43 (tq, *J* = 7.3, 7.3 Hz, 2H, NCH$_2$CH$_2$C*H*$_2$Me), 0.99 (t, *J* = 7.3 Hz, 3H, NCH$_2$CH$_2$CH$_2$*Me*), and 0.39 (s, 9H, TMS).

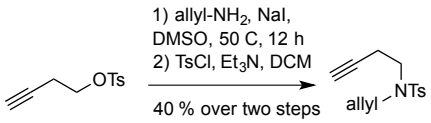
^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.5, 156.6, 148.9, 143.1, 137.0, 136.3, 135.4, 132.8, 128.7, 127.2, 122.6, 118.7, 97.8, 52.1, 47.0, 29.7, 29.3, 20.5, 14.1, and 1.5.

IR (neat): 2956, 2931, 2862, 1685, 1572, 1241, 865, 841, 766, and 735 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{22}H_{28}NOSi^{+}$ 350.1935, found 350.1923.

m.p.: 148–150 °C.

N-Allyl-*N*-(but-3-yn-1-yl)-4-methylbenzenesulfonamide (S42)



S38 ***S42***

Tosylate **S38** (1.12 g, 5 mmol) was mixed with allylamine (855 mg, 15 mmol) and NaI (20 mg, 0.13 mmol) in DMSO (8 mL). After heating for 12 hours at 50 °C, the mixture was poured into aqueous NaOH and extracted with ethyl ether (3x). The combined organic phase was washed with brine, dried, and concentrated to give a yellow oil. The crude amine product was dissolved in DCM (8 mL) containing triethylamine (320 mg, 3.2 mmol). Tosyl chloride (500 mg, 2.63 mmol) was added in portions, and the mixture was stirred for 3 hours. The reaction mixture was diluted with another 40 mL of DCM and washed with brine. The organic layer was dried over $MgSO_4$ and concentrated. After flash chromatography (10:1 Hex:EtOAc elution), the tosylamide **S42** (520 mg, 2.0 mmol, 40%) was obtained as a colorless oil.

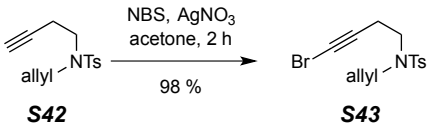
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.0 Hz, 2H, Ts *H* meta to Me), 7.30 (d, *J* = 8.0 Hz, 2H, Ts *H* ortho to Me), 5.66 (ddt, *J* = 16.7, 10.1, 6.4 Hz, 1H, CH_2CH=CH_2), 5.19 (ddt, J = 17.1, 1.4, 1.4 Hz, 1H, CH_2CH=C$H_Z$$H_E$), 5.16 (ddt, J = 10.1, 1.5, 1.5 Hz, 1H, CH_2CH=C$H_E$$H_Z$), 3.84 (ddd, *J* = 6.5, 1.4, 1.4 Hz, 2H, CH_2CH=CH_2), 3.28 (t, *J* = 7.4 Hz, 2H, CH_2N(Ts)allyl), 2.45 (td, *J* = 7.4, 2.7 Hz 2H, C$H_2$$CH_2$N(Ts)allyl), 2.43 (s, 3H, *Me* on Ts), and 1.96 (t, *J* = 2.7 Hz, 1H, C≡C*H*).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 136.8, 133.0, 129.8, 127.2, 119.3, 81.0, 70.2, 51.3, 46.0, 21.5, and 19.4.

IR (neat): 3289, 3067, 2925, 2871, 2120, 1922, 1598, 1452, 1343, 1157, 1093, 985, 920, 816, and 747 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{14}H_{18}NO_2S^+$ 264.1053, found 264.1048.

N-Allyl-*N*-(4-bromobut-3-yn-1-yl)-4-methylbenzenesulfonamide (S43)



S42 ***S43***

Bromoalkyne **S43** (337 mg, 0.98 mmol, 98 %) was obtained as a colorless oil from alkyne **S42** (260 mg, 1.0 mmol), NBS (352 mg, 2.0 mmol), and $AgNO_3$ (17 mg, 0.1 mmol) by following the procedure used to prepare bromoalkyne **S2**.

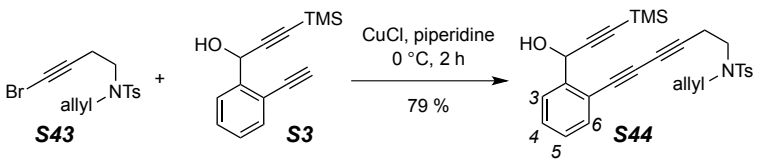
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.3 Hz, 2H, Ts *H* meta to Me), 7.30 (d, *J* = 8.0 Hz, 2H, Ts *H* ortho to Me), 5.66 (ddt, *J* = 16.7, 10.1, 6.4 Hz, 1H, CH_2CH=CH_2), 5.19 (ddt, *J* = 17.1, 1.4, 1.4 Hz, 1H, CH_2CH=CH_ZH_E), 5.18 (ddt, *J* = 10.2, 1.4, 1.4 Hz, 1H, CH_2CH=CH_EH_Z), 3.83 (ddd, *J* = 6.4, 1.3, 1.3 Hz, 2H, CH_2CH=CH_2), 3.27 (t, *J* = 7.4 Hz, 2H, CH_2N(Ts)allyl), 2.48 (t, *J* = 7.4 Hz, 2H, CH_2CH_2N(Ts)allyl), and 2.43 (s, 3H, *Me* on Ts).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 136.8, 133.0, 129.9, 127.3, 119.4, 77.1, 51.5, 45.8, 40.3, 21.6, and 20.7.

IR (neat): 3066, 2924, 2870, 2219, 1598, 1342, 1158, 1092, 922, and 815 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{14}H_{17}BrNO_2S^+$ 342.0158, found 342.0155.

_N_-Allyl-_N_-(6-(2-(1-hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hexa-3,5-diyn-1-yl)-4-methylbenzenesulfonamide (S44)



Triyne alcohol **S44** (193 mg, 0.4 mmol, 79 %) was obtained as a yellow oil from the terminal alkyne **S3** (114 mg, 0.5 mmol) and bromoalkyne **S43** (204 mg, 0.6 mmol) by following the procedure used to prepare triyne alcohol **S4**.

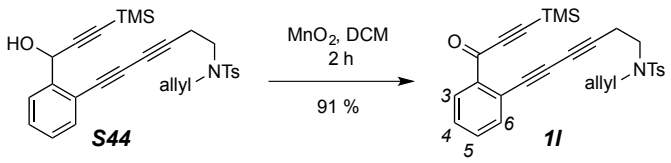
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.0 Hz, 2H, Ts *H* meta to Me), 7.70 (dd, *J* = 7.7, 1.3 Hz, 1H, *H6*), 7.50 (dd, *J* = 7.7, 1.3 Hz, 1H, *H3*), 7.40 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 1H, *H4*), 7.32 (d, *J* = 8.0 Hz, 2H, Ts *H* ortho to Me), 7.29 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H, *H5*), 5.80 (d, *J* = 4.9 Hz, 1H, ArC*H*OH), 5.68 (ddt, *J* = 16.6, 10.1, 6.4 Hz, 1H, CH_2CH=CH_2), 5.23 (ddt, *J* = 17.1, 1.4, 1.4 Hz, 1H, CH_2CH=C$H_Z H_E$), 5.20 (ddt, *J* = 10.1, 1.5, 1.5 Hz, 1H, CH_2CH=C$H_E H_Z$), 3.85 (ddd, *J* = 6.5, 1.4, 1.4 Hz, 1H, CH_2CH=CH_2), 3.32 (t, *J* = 7.5 Hz, 2H, CH_2N(Ts)allyl), 2.66 (dd, *J* = 7.5 Hz, 2H, C$H_2$$CH_2$N(Ts)allyl), 2.43 (s, 3H, *Me* on Ts), 2.42 (d, *J* = 5.0 Hz, 1H, O*H*), and 0.20 (s, 9H,TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.7, 143.5, 136.7, 133.7, 133.0, 130.0, 129.7, 128.5, 127.3, 127.1, 120.5, 119.7, 104.2, 92.0, 82.4, 79.2, 72.8, 66.9, 63.5, 51.6, 45.8, 21.7, 20.8, and -0.1.

IR (neat): 3486, 3067, 2959, 2240, 2173, 1341, 1250, 1157, 1092, 985, 845, and 761 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{28}H_{31}NNaO_3SSi^+$ 512.1686, found 512.1674.

_N_-Allyl-4-methyl-_N_-(6-(2-(3-(trimethylsilyl)propioloyl)phenyl)hexa-3,5-diyn-1-yl)benzenesulfonamide (1l)



Triyne ketone **1l** (90 mg, 0.18 mmol, 91 %) was obtained as a yellow oil from triyne alcohol **S44** (98 mg, 0.2 mmol) and MnO_2 (174 mg, 2.0 mmol) by following the procedure used to prepare triyne ketone **1a**.

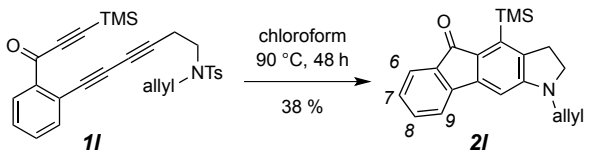
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.7, 1.5 Hz, 1H, *H3*), 7.72 (d, *J* = 8.0 Hz, 2H, Ts *H* meta to Me), 7.60 (dd, *J* = 7.6, 1.4 Hz, 1H, *H6*), 7.50 (ddd, *J* = 7.6, 7.6 1.5 Hz, 1H, *H5*), 7.45 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H, *H4*), 7.32 (d, *J* = 8.0 Hz, 2H, Ts *H* ortho to Me), 5.68 (ddt, *J* = 16.6, 9.9, 6.4 Hz, 1H, CH_2CH=CH_2), 5.23 (ddt, *J* = 17.1, 1.4, 1.4 Hz, 1H, CH_2CH=CH_ZH_E), 5.20 (ddt, *J* = 10.1, 1.5, 1.5 Hz, 1H, CH_2CH=CH_EH_Z), 3.85 (ddd, *J* = 6.4, 1.4, 1.4 Hz, 2H, CH_2CH=CH_2), 3.32 (t, *J* = 7.5 Hz, 2H, CH_2N(Ts)allyl), 2.66 (dd, *J* = 7.5 Hz, 2H, CH_2CH_2N(Ts)allyl), 2.43 (s, 3H, *Me* on Ts), and 0.30 (s, 9H,TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.5, 143.7, 139.1, 136.7, 135.8, 133.0, 132.7, 132.1, 129.9, 128.7, 127.3, 121.8, 119.7, 101.44, 101.43, 83.0, 80.0, 73.8, 67.4, 51.6, 45.8, 21.7, 20.8, and -0.6.

IR (neat): 3066, 2961, 2871, 2243, 2152, 1647, 1344, 1237, 1159, 1016, 849, and 756 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{28}H_{30}NO_3SSi^+$ 488.1710, found 488.1700.

1-Allyl-4-(trimethylsilyl)-2,3-dihydroindeno[2,1-*f*]indol-5(1*H*)-one (2l)



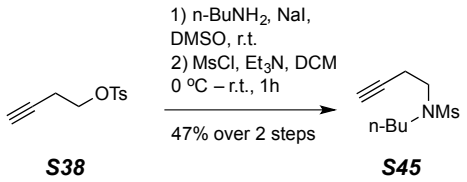
1l *2l*

Triyne ketone **1l** (80 mg, 0.17 mmol) was dissolved in 3 mL of chloroform in a screw-capped vial. This solution was heated for 48 h in an oil bath held at 90 °C. After concentration and MPLC (10:1 Hex:EtOAc elution), the indoline **2l** (20 mg, 0.045 mmol, 38 %) was obtained as a crystalline orange solid. This reaction gave a number of other compounds, some of which co-eluted with **2l**, the major product. To obtain the ^{1}H NMR spectrum below, the sample was purified by two subsequent rounds of HPLC purification. The small amount of resulting material still contained impurities and also gave a low quality 1D ^{13}C NMR spectrum. There was evidence for the presence of *p*-TsOH in the sample, which was likely leading to degradation reactions (e.g., desilylation and allyl migration). The reaction of this substrate was not pursued further.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.2 Hz, 1H, *H6*), 7.37–7.34 (m, 2H, *H8* and *H9*), 7.21 (nfom, 1H, *H7*), 6.51 (s, 1H, *H10*), 5.87 (ddt, *J* = 16.2, 10.7, 5.6 Hz, 1H, CH_2CH=CH_2), 5.29 (ddt, *J* = 16.1, 1.4, 1.4 Hz, 1H, CH_2CH=CH_ZH_E), 5.25 (ddt, *J* = 10.5, 1.5, 1.5 Hz, 1H, CH_2CH=CH_EH_Z), 3.81 (ddd, *J* = 5.6, 1.4, 1.4 Hz, 2H, CH_2CH=CH_2), 3.56 (t, *J* = 8.6 Hz, 2H, *H2*), 3.10 (t, *J* = 8.7 Hz, 2H, *H3*), and 0.39 (s, 9H, TMS).

HRMS (ESI-TOF): calculated for $C_{21}H_{24}NOSi^{+}$ 334.1622, found 334.1609.

N-(But-3-yn-1-yl)-*N*-butylmethanesulfonamide (S45)



S38 ***S45***

The mesylamide **S45** (300 mg, 1.75 mmol, 47 % from **S38** over two steps) was obtained as a colorless oil from tosylate **S38** (960 mg, 3.7 mmol), *n*-butylamine (352 mg, 2.0 mmol), and mesyl chloride (240 mg, 2.1 mmol) by following the procedure used to prepare the alkyne **S39**.

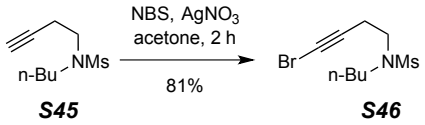
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.37 (t, *J* = 7.2 Hz, 2H, C*H*$_2$NMsBu), 3.23 (t, *J* = 7.5 Hz, 2H, NC*H*$_2$CH$_2$CH$_2$Me), 2.87 (s, 3H, *Me* on Ms), 2.51 (td, *J* = 7.2, 2.7 Hz, 2H, C*H*$_2$CH$_2$NMsBu), 2.02 (t, *J* = 2.7 Hz, 1H, C≡C*H*), 1.60 (tt, *J* = 7.4, 7.2 Hz, 2H, CH$_2$C*H*$_2$CH$_2$Me), 1.34 (tq, *J* = 7.4, 7.4 Hz, 1H, CH$_2$CH$_2$C*H*$_2$Me), and 0.94 (t, *J* = 7.3 Hz, 3H, CH$_2$CH$_2$*C*H$_2$*Me*).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 81.1, 70.5, 48.2, 46.5, 39.0, 30.8, 19.9, 19.5, and 13.8.

IR (neat): 3279, 2960, 2934, 2874, 2119, 1460, 1330, 1147, 967, and 776 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_9H_{18}NO_2S^+$ 204.1053, found 204.1050.

N-(But-3-yn-1-yl)-*N*-butylmethanesulfonamide (S46)



S45 ***S46***

The bromoalkyne **S46** (244 mg, 0.87 mmol, 81 %) was obtained as a colorless oil from the alkyne **S45** (217 mg, 1.07 mmol), NBS (380 mg, 2.14 mmol), and $AgNO_3$ (18 mg, 0.11 mmol) by following the procedure used to prepare the bromoalkyne **S2**.

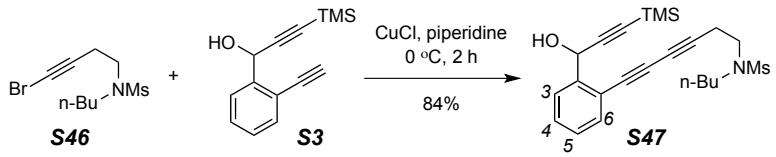
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.36 (t, *J* = 7.2 Hz, 2H, NC*H*$_2$CH$_2$CH$_2$Me), 3.23 (t, *J* = 7.2 Hz, 2H, C*H*$_2$NMsBu), 2.87 (s, 3H, *Me* on Ms), 2.54 (t, *J* = 7.2 Hz, 2H, C*H*$_2$CH$_2$NMsBu), 1.60 (tt, *J* = 7.4, 7.2 Hz, 2H, CH$_2$C*H*$_2$CH$_2$Me), 1.34 (tq, *J* = 7.4, 7.4 Hz, 2H, CH$_2$CH$_2$C*H*$_2$Me), and 0.95 (t, *J* = 7.4 Hz, 3H, CH$_2$CH$_2$CH$_2$*Me*).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 77.2, 48.2, 46.4, 40.7, 38.9, 30.9, 20.8, 20.0, and 13.8.

IR (neat): 2959, 2933, 2873, 2219, 1331, 1147, 966, and 773 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_9H_{17}BrNO_2S^+$ 282.0158, found 282.0153.

_N_-Butyl-_N_-(6-(2-(1-hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hexa-3,5-diyn-1-yl)methanesulfonamide (S47)



The triyne alcohol **S47** (183 mg, 0.42 mmol, 84 %) was obtained as a yellow oil from the terminal alkyne **S3** (114 mg, 0.5 mmol) and the bromoalkyne **S46** (282 mg, 0.6 mmol) by following the procedure used to prepare the triyne alcohol **S4**.

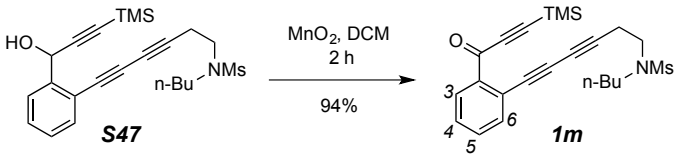
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 7.8, 1.2 Hz, 1H, *H6*), 7.50 (dd, *J* = 7.7, 1.3 Hz, 1H, *H3*), 7.41 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H4*), 7.29 (ddd, *J* = 7.7, 7.7, 1.2 Hz, 1H, *H5*), 5.80 (d, *J* = 4.9 Hz, 1H, ArC*H*OH), 3.42 (t, *J* = 7.2 Hz, 2H, NCH_2CH_2CH_2Me), 3.25 (t, *J* = 6.9 Hz, 2H, CH_2NMsBu), 2.90 (s, 3H, *Me* on Ms), 2.71 (t, *J* = 7.2 Hz, 2H, CH_2CH_2NMsBu), 2.45–2.41 (m, 1H, O*H*), 1.61 (tt, *J* = 7.4, 7.2 Hz, 2H, CH$_2$CH_2CH$_2$Me), 1.37 (tq, *J* = 7.4, 7.4 Hz, 2H, CH$_2$CH$_2$CH_2Me), 0.96 (t, *J* = 7.3 Hz, 3H, CH$_2$CH$_2$CH$_2$*Me*), and 0.20 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 133.7, 129.8, 128.5, 127.1, 120.4, 104.2, 91.9, 82.3, 79.0, 73.0, 67.2, 63.4, 48.4, 46.3, 39.0, 30.9, 20.9, 20.0, 13.9, and -0.1.

IR (neat): 3474, 2960, 2933, 2873, 2240, 2173, 1330, 1250, 1147, 1048, 968, 845, and 761 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{23}H_{31}NNaO_3SSi^+$ 452.1686, found 452.1672.

_N_-Butyl-_N_-(6-(2-(3-(trimethylsilyl)propioloyl)phenyl)hexa-3,5-diyn-1-yl)methanesulfonamide (1m)



The triyne ketone **1m** (106 mg, 0.25 mmol, 94 %) was obtained as a yellow oil from the triyne alcohol **S47** (114 mg, 0.27 mmol) and MnO_2 (231 mg, 2.7 mmol) by following the procedure used to prepare the triyne ketone **1a**.

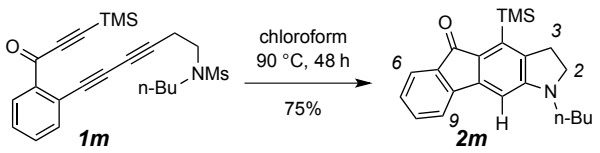
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 7.6, 1.5 Hz, 1H, *H3*), 7.60 (dd, *J* = 7.6, 1.5 Hz, 1H, *H6*), 7.51 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H, *H5*), 7.46 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H, *H4*), 3.43 (t, *J* = 7.2 Hz, 2H, NC*H*$_2$CH$_2$CH$_2$Me) 3.24 (t, *J* = 7.6 Hz, 2H, C*H*$_2$NMsBu), 2.91 (s, 3H, *Me* on Ms), 2.71 (t, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_2$NMsBu), 2.43 (s, 3H, *Me* on Ts), 1.63 (tt, *J* = 7.1, 7.1 Hz, 2H, CH$_2$C*H*$_2$CH$_2$Me), 1.36 (tq, *J* = 7.4, 7.4 Hz, 2H, CH$_2$CH$_2$C*H*$_2$Me), 0.96 (t, *J* = 7.3 Hz, 3H, CH$_2$CH$_2$CH$_2$*Me*) and 0.30 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.4, 139.1, 135.8, 132.7, 132.2, 128.8, 121.6, 101.39, 101.38, 83.0, 79.7, 74.0, 67.8, 48.3, 46.3, 39.1, 30.9, 20.9, 20.0, 13.9, and -0.6.

IR (neat): 2960, 2873, 2243, 2152, 1647, 1481, 1334, 1237, 1149, 1015, 1015, 849, and 757 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{23}H_{29}NNaO_3SSi^+$ 450.1530, found 450.1515.

1-Butyl-4-(trimethylsilyl)-2,3-dihydroindeno[2,1-*f*]indol-5(1*H*)-one (2m)



The triyne ketone **1m** (100 mg, 0.23 mmol) was dissolved in 23 mL of chloroform (0.01 M) and bubbled with nitrogen gas for 5 min before being sealed in a screw-capped vial. This solution was heated in an oil bath held at 90 °C for 48 h. After concentration and flash chromatography (30:1 Hex:EtOAc elution), the indoline **2m** (60 mg, 0.171 mmol, 75%) was obtained as an orange crystalline solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (ddd, *J* = 7.1, 1.0, 1.0 Hz, 1H, *H6*), 7.39–7.31 (m, 2H, *H8* and *H9*), 7.21 (ddd, *J* = 7.2, 6.1, 2.6 Hz, 1H, *H7*), 6.47 (s, 1H, *H10*), 3.56 (t, *J* = 8.7 Hz, 2H, *H2*), 3.25 (t, *J* = 7.3 Hz, 2H, NCH_2CH$_2$CH$_2$Me), 3.09 (t, *J* = 8.7 Hz, 2H, *H3*), 1.63 (tt, *J* = 7.7, 6.3 Hz, 2H, CH$_2$CH_2CH$_2$NTsMe), 1.43 (tq, *J* = 7.3, 7.3 Hz, 2H, NCH$_2$CH$_2$CH_2Me), 0.99 (t, *J* = 7.3 Hz, 2H, NCH$_2$CH$_2$CH$_2$*Me*), and 0.39 (s, 9H, TMS).

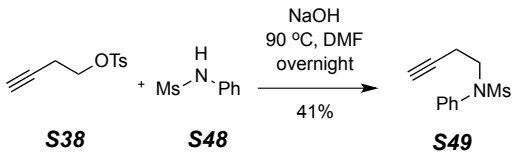
^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.5, 156.6, 148.9, 143.1, 137.0, 136.3, 135.4, 132.8, 128.7, 127.2, 122.6, 118.7, 97.8, 52.1, 47.0, 29.7, 29.3, 20.5, 14.1, and 1.5.

IR (neat): 2957, 2861, 1677, 1574, 1239, 1110, 865, 767, and 737 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{22}H_{28}NOSi^{+}$ 350.1935, found 350.1920.

m.p.: 149–150 °C

N-(But-3-yn-1-yl)-*N*-phenylmethanesulfonamide (S49)



S38 ***S48*** ***S49***

The terminal alkyne **S49** (495 mg, 2.22 mmol, 41 %) was obtained as a white, needle-like, crystalline solid from the tosylate **S38** (1.91 g, 8.53 mmol) and the *N*-phenyl methanesulfonamide (**S48**, 926 mg, 5.41 mmol) by following the procedure used to prepare the terminal alkyne **S7**.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46–7.33 (m, 5H, Ph*H*), 3.85 (t, *J* = 7.3 Hz, 2H, MsNC*H*$_2$), 2.95 (s, 3H, Me on Ms), 2.41 (td, *J* = 7.2, 2.6 Hz, 2H, MsNCH$_2$C*H*$_2$), and 2.00 (t, *J* = 2.7 Hz, 1H, C≡C*H*).

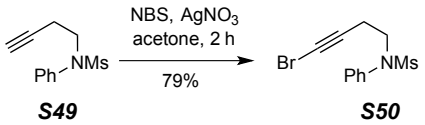
^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9, 129.8, 129.0, 128.6, 80.8, 70.6, 49.9, 38.3, and 19.5.

IR (neat): 3278, 3058, 2928, 2119, 1490, 1340, 1148, 1100, 968, 896, and 780 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{11}H_{13}NNaO_2S^+$ 246.0559, found 246.0552.

m.p.: 100–101 °C

N-(4-Bromobut-3-yn-1-yl)-*N*-phenylmethanesulfonamide (S50)



S49 ***S50***

The bromoalkyne **S50** (318 mg, 1.05 mmol, 79 %) was obtained as a white crystalline solid from the terminal alkyne **S49** (300 mg, 1.34 mmol) by following the procedure used to prepare the bromoalkyne **S2**.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46–7.40 (nfom, 2H, Ph*Hm*), 7.39–7.33 (m, 3H, Ph*Hp* & Ph*Ho*), 3.84 (t, *J* = 7.1 Hz, 2H, MsNCH_2), 2.94 (s, 3H, Me on Ms), and 2.44 (t, *J* = 7.2 Hz, 2H, $MsNCH_2CH_2$).

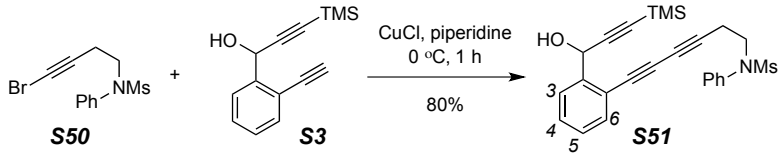
^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9, 129.8, 129.0, 128.7, 76.9, 49.8, 40.8, 38.4, and 20.8.

IR (neat): 3059, 3012, 2926, 2219, 1492, 1339, 1147, 1104, 968, 899, and 781 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{11}H_{12}BrNNaO_2S^+$ 323.9664, found 323.9658.

m.p.: 102–104 °C

_N_-(6-(2-(1-Hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenyl)hexa-3,5-diyn-1-yl)-_N_-phenylmethanesulfonamide (S51)



The triyne alcohol **S51** (334 mg, 0.74 mmol, 80 %) was obtained as a yellow oil from the terminal alkyne **S3** (221 mg, 0.93 mmol) and the bromoalkyne **S50** (280 mg, 0.93 mmol) by following the procedure used to prepare the triyne alcohol **S4**.

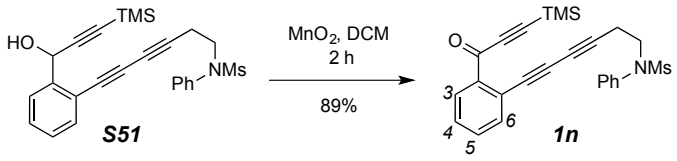
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 7.7, 1.3 Hz, 1H, *H6*), 7.50 (dd, *J* = 7.7, 1.4 Hz, 1H, *H3*), 7.48–7.42 (nfom, 2H, Ph*H*m), 7.42–7.36 (m, 4H, Ph*H*o, Ph*H*p and *H4*), 7.29 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H5*), 5.80 (d, *J* = 4.9 Hz, 1H, ArC*H*OH), 3.90 (t, *J* = 7.3 Hz, 2H, C*H*$_2$NMsPh), 2.97 (s, 3H, *Me* on Ms), 2.63 (t, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_2$NMsPh), 2.41 (d, *J* = 4.9 Hz, 1H, O*H*), and 0.20 (s, 9H, TMS).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 138.8, 133.7, 129.9, 129.7, 129.0, 128.8, 128.5, 127.1, 120.4, 104.2, 91.9, 82.1, 79.1, 72.9, 67.2, 63.4, 49.7, 38.3, 20.9, and -0.05.

IR (neat): 3478, 3064, 2959, 2899, 2240, 2172, 1492, 1339, 1152, 963, 845, and 763 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{25}H_{27}NNaO_3SSi^+$ 472.1373, found 472.1364.

_N_-Phenyl-_N_-(6-(2-(3-(trimethylsilyl)propioloyl)phenyl)hexa-3,5-diyn-1-yl)methanesulfonamide (1n)



The triyne ketone **7d** (222 mg, 0.50 mmol, 89%) was obtained as a pale yellow solid from the triyne alcohol **S51** (250 mg, 0.56 mmol) and MnO_2 (484 mg, 5.60 mmol) by following the procedure used to prepare the triyne ketone **1a**.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 7.6, 1.5 Hz, 1H, *H3*), 7.60 (dd, *J* = 7.6, 1.5 Hz, 1H, *H6*), 7.51 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H, *H5*), 7.48–7.33 (m, 7H, *H4* & Ph*H*), 3.89 (t, *J* = 7.3 Hz, 2H, C*H*$_2$NMsPh), 3.00 (s, 3H, C*H*$_3$SO$_2$), 2.61 (t, *J* = 7.3 Hz, 2H, C*H*$_2$CH$_2$NMsPh), and 0.20 (s, 9H, TMS).

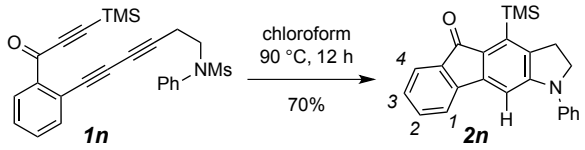
^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.3, 139.0, 138.7, 135.7, 132.7, 132.1, 129.8, 129.0, 128.72, 128.67, 121.6, 101.33, 101.31, 82.8, 79.8, 73.9, 67.7, 49.6, 38.5, 20.7, and -0.6.

IR (neat): 3063, 2960, 2902, 2243, 2152, 1646, 1492, 1343, 1237, 1154, 1016, 849, and 761 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{25}H_{26}NO_3SSi^+$ 448.1397, found 448.1382.

m.p.: 111–113 °C

1-Phenyl-4-(trimethylsilyl)-2,3-dihydroindeno[2,1-*f*]indol-5(1*H*)-one (2n)



Triyne ketone **1n** (80 mg, 0.18 mmol) was dissolved in 18 mL of chloroform in a screw-capped vial and nitrogen was bubbled through the solution for a few minutes. This solution was heated for 48 h in an oil bath held at 90 °C. After concentration and flash chromatography (10:1 Hex:EtOAc elution), the indoline derivative **2n** (46 mg, 0.10 mmol, 70 %) was obtained as an orange crystalline solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 7.3, 1.1 Hz, 1H, *H4*), 7.43 (br t, *J* = 8.0 Hz, 2H, Ph*H*m), 7.35 (ddd, *J* = 7.3, 7.3, 1.2 Hz, 1H, *H2*), 7.33–7.28 (m, 3H, Ph*H*o and Ph*H*p), 7.21 (ddd, *J* = 7.1, 7.1, 1.3 Hz, 1H, *H3*), 7.14 (ddd, *J* = 7.1, 1.2, 1.2 Hz, 1H, *H1*), 7.11 (s, 1H, Ar*H*), 4.03 (t, *J* = 8.5 Hz, 1H, PhNCH_2), 3.22 (t, *J* = 8.5 Hz, 2H, PhNCH$_2$CH_2), and 0.43 (s, 9H, TMS).

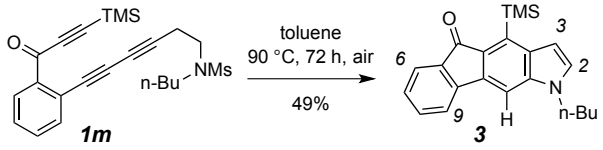
^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.9, 152.3, 148.0, 143.2, 142.6, 138.0, 136.9, 135.8, 133.2, 129.65, 129.63, 128.8, 123.6, 122.9, 120.4, 119.0, 100.3, 53.0, 29.8, and 1.5.

IR (neat): 3053, 2947, 2897, 1691, 1569, 1497, 1231, 865, 841, and 767 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{24}H_{24}NOSi^{+}$ 370.1622, found 370.1608.

m.p.: 170–171 °C.

1-Butyl-4-(trimethylsilyl)indeno[2,1-*f*]indol-5(1*H*)-one (3)



The triyne ketone **1m** (69 mg, 0.16 mmol) was dissolved in 13 mL of toluene (0.01 M) in a round-bottomed flask fitted with a condenser open to the air. This solution was heated in an oil bath at 90 °C for 72 h. After concentration and flash chromatography (20:1 Hex:EtOAc elution), the indole derivative **3** (27 mg, 0.08 mmol, 49%) was obtained as a yellow crystalline powder.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (ddd, *J* = 7.1, 1.0, 1.0 Hz, 1H, *H6*), 7.52 (br d, *J* = 7.8 Hz, 1H, *H9*), 7.42 (ddd, *J* = 7.5, 7.5 1.2 Hz, 1H, *H8*), 7.38 (d, *J* = 0.8 Hz, 1H, *H10*), 7.21 (ddd, *J* = 7.2, 1.0, 1.0 Hz, 1H, *H7*), 7.07 (d, *J* = 3.3 Hz, 1H, *H2*), 6.85 (dd, *J* = 3.3, 0.8 Hz, 1H, *H3*), 3.56 (t, *J* = 8.7 Hz, 2H, NC*H*$_2$CH$_2$CH$_2$Me), 1.84 (tt, *J* = 8.7, 7.4 Hz, 2H, CH$_2$C*H*$_2$CH$_2$NTsMe), 1.40 (tq, *J* = 7.4, 7.4 Hz, 2H, NCH$_2$CH$_2$C*H*$_2$Me), 0.98 (t, *J* = 7.4 Hz, 2H, NCH$_2$CH$_2$CH$_2$*Me*), and 0.52 (s, 9H, TMS).

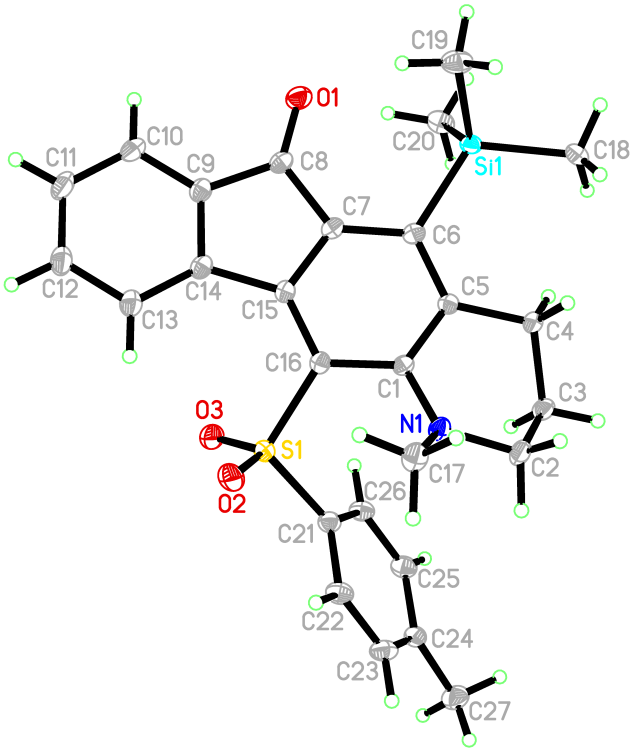
^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.8, 145.0, 138.7, 138.2, 137.3, 135.9, 134.11, 134.07, 132.9, 129.1, 128.1, 123.6, 119.2, 106.5, 102.6, 46.4, 32.5, 20.4, 13.8, and 1.5.

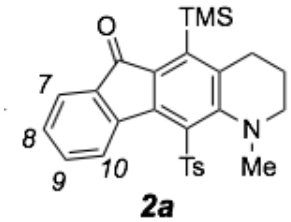
IR (neat): 2957, 2898, 2873, 1698, 1605, 1370, 999, 867, and 730 cm^{-1}.

HRMS (ESI-TOF): calculated for $C_{22}H_{26}NOSi^{+}$ 348.1778, found 348.1767.

m.p.: 89–91 °C

III. X-ray structure for 2a (CCDC deposition number: 1857242)





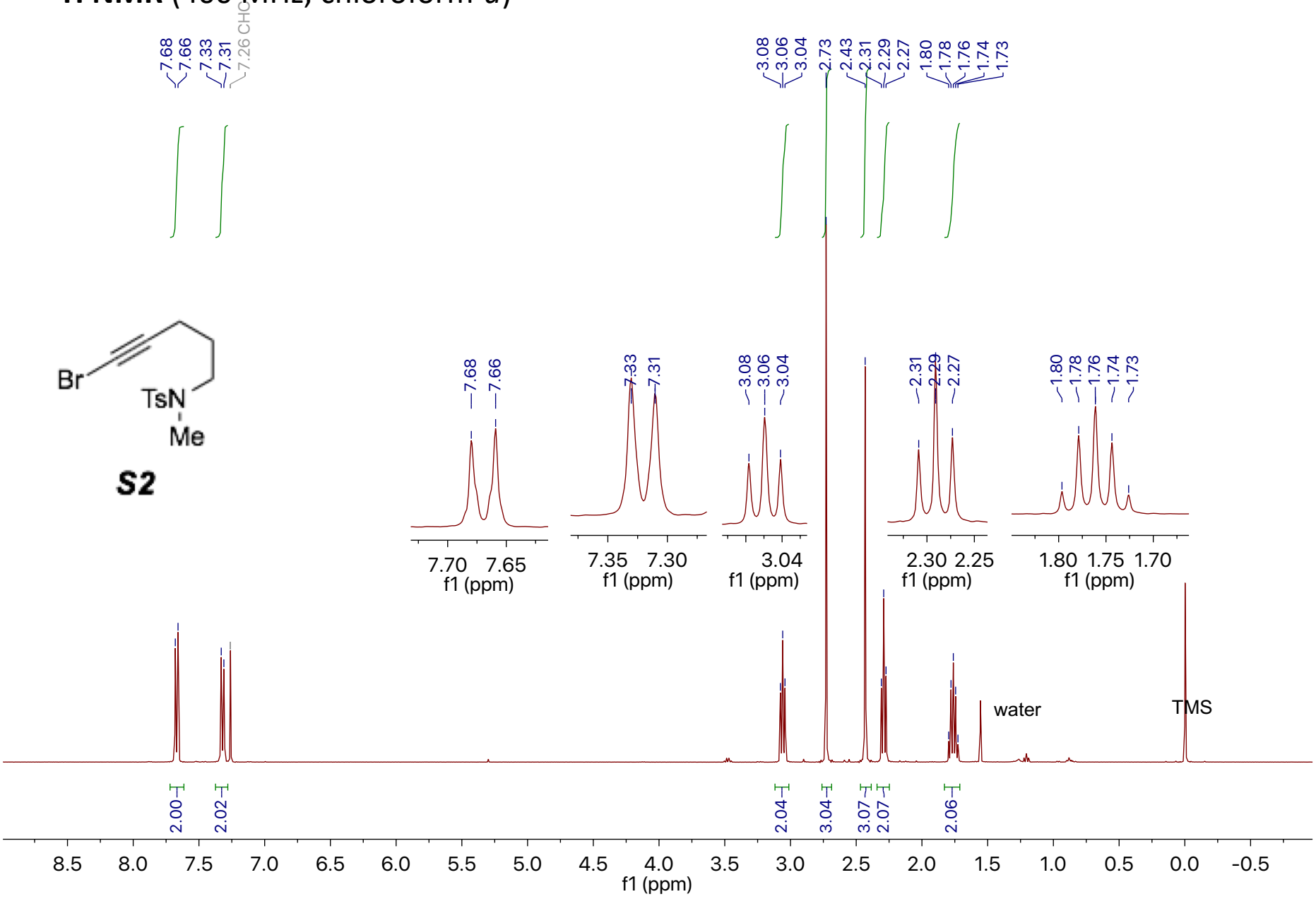
2a

IV. References

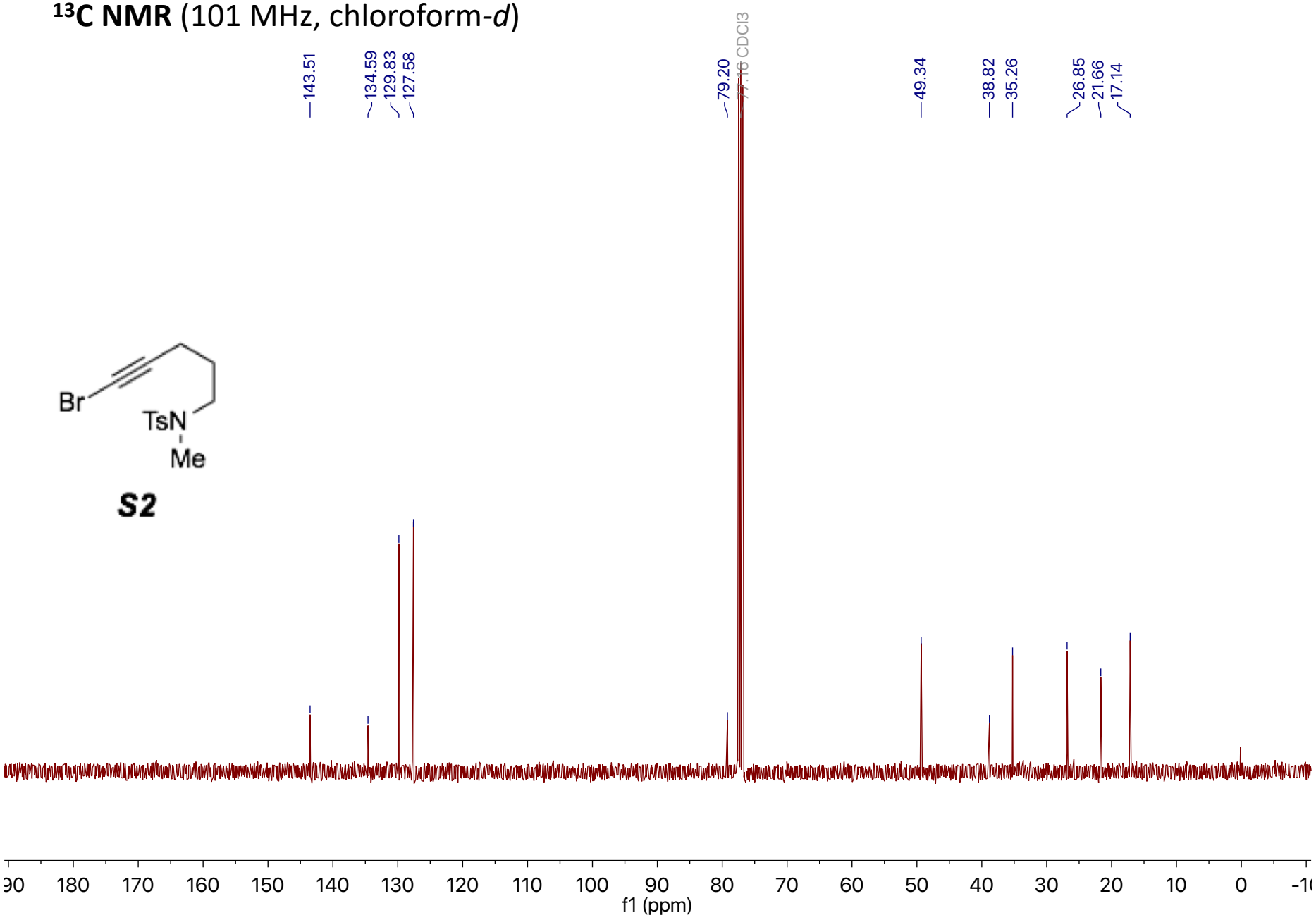
1. (a) Hoye, T. R.; Hanson, P. R.; Vyvyan, J. R. *J. Org. Chem*. **1994**, *59*, 4096-4103. (b) Hoye,T. R.; Zhao, H. *J. Org. Chem*. **2002**, *67*, 4014–4016.
2. Uehling, M. R.; Suess, A. M.; Lalic, G. *J. Am. Chem. Soc*. **2015**, *137*, 1424–1427.
3. Capella, L.; Montevecchi, P. C.; Nanni, D. *J. Org. Chem*. **1994**, *59*, 3368–3374.
4. Chevalier, A.; Massif, C.; Renard, P. Y.; Romieu, A. *Chem.– Eur. J*. **2013**, *19*, 1686−1699.

V. Copies of ^{1}H , ^{13}C NMR spectra

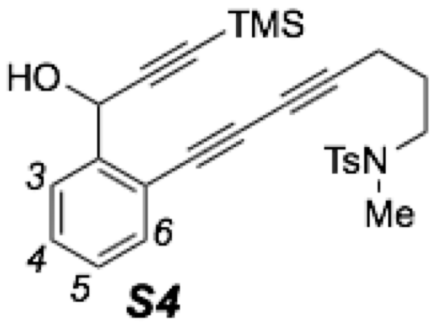
^{1}H NMR (400 MHz, chloroform-*d*)

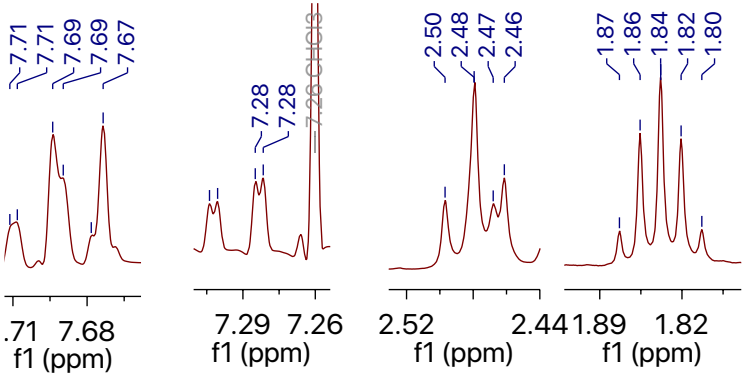


^{13}C NMR (101 MHz, chloroform-*d*)

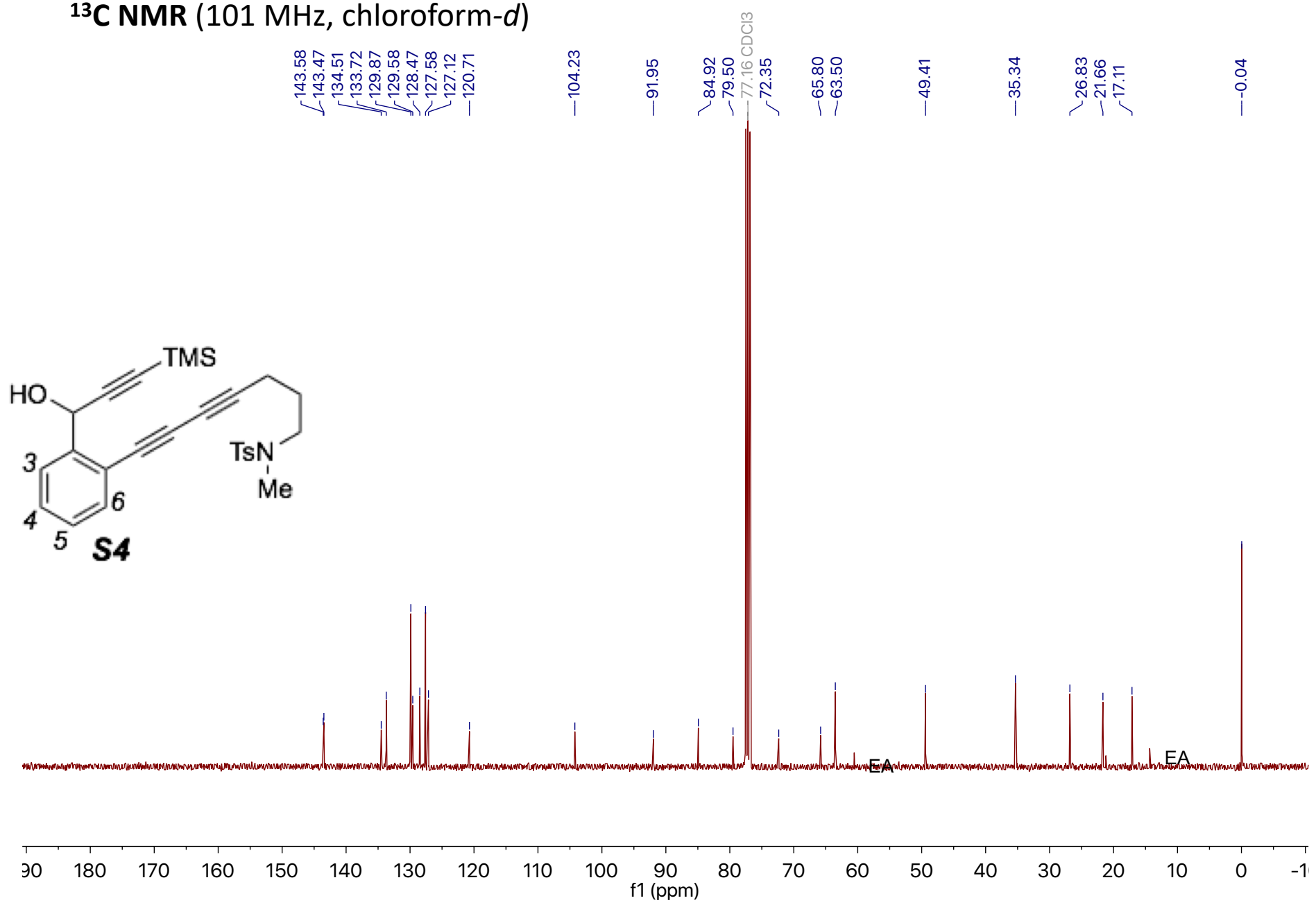


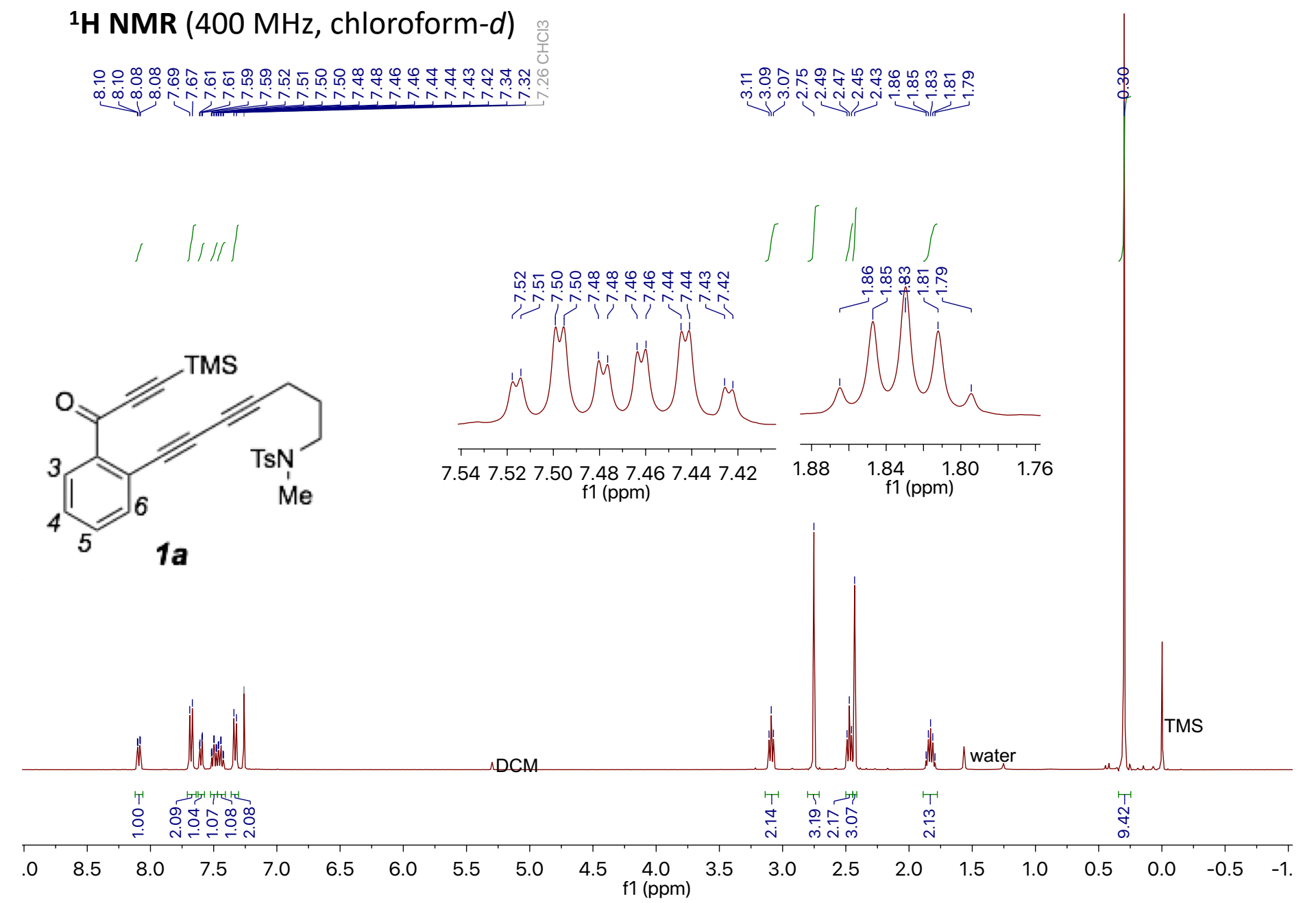
^{1}H NMR (400 MHz, chloroform-*d*)



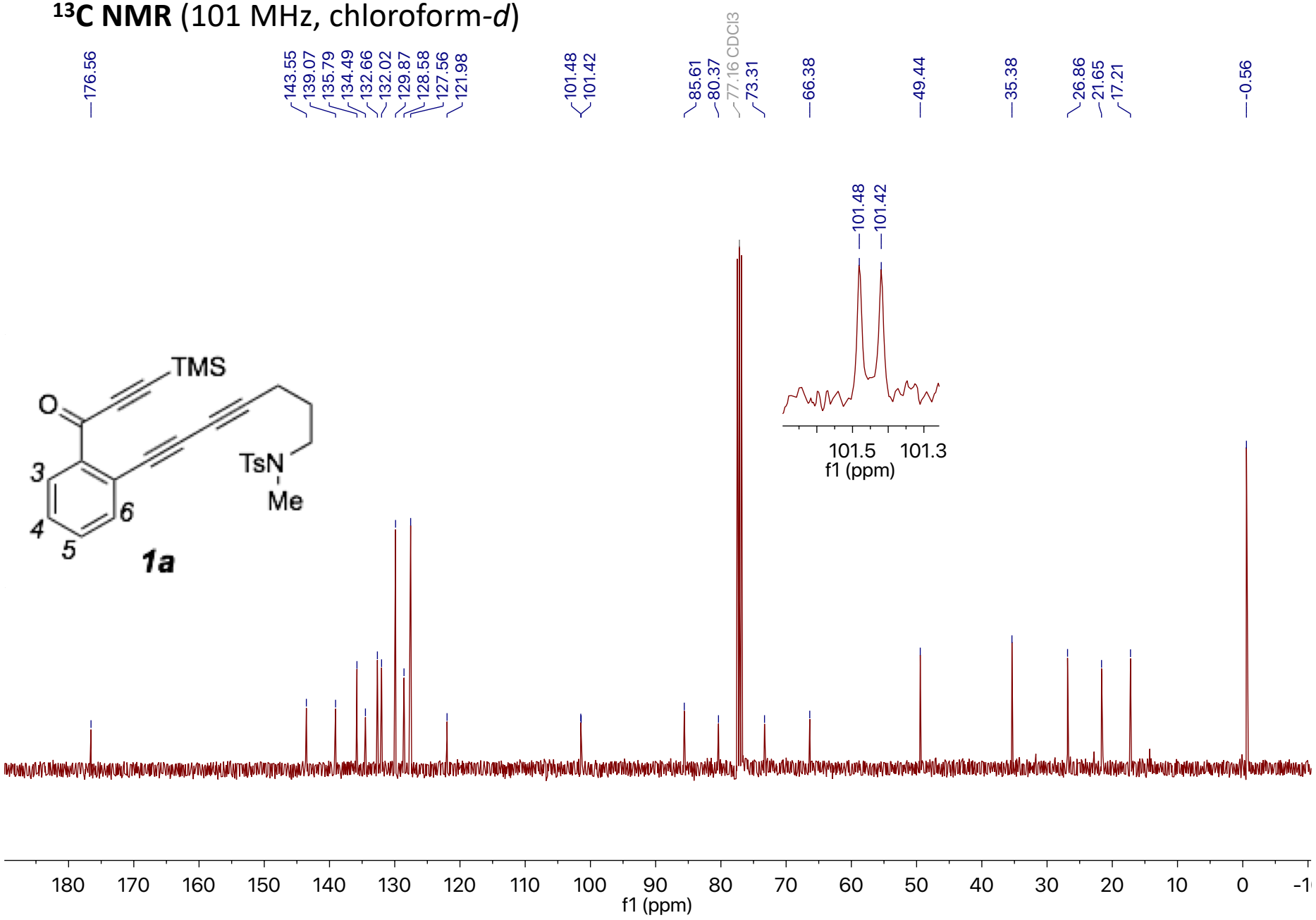


^{13}C NMR (101 MHz, chloroform-*d*)

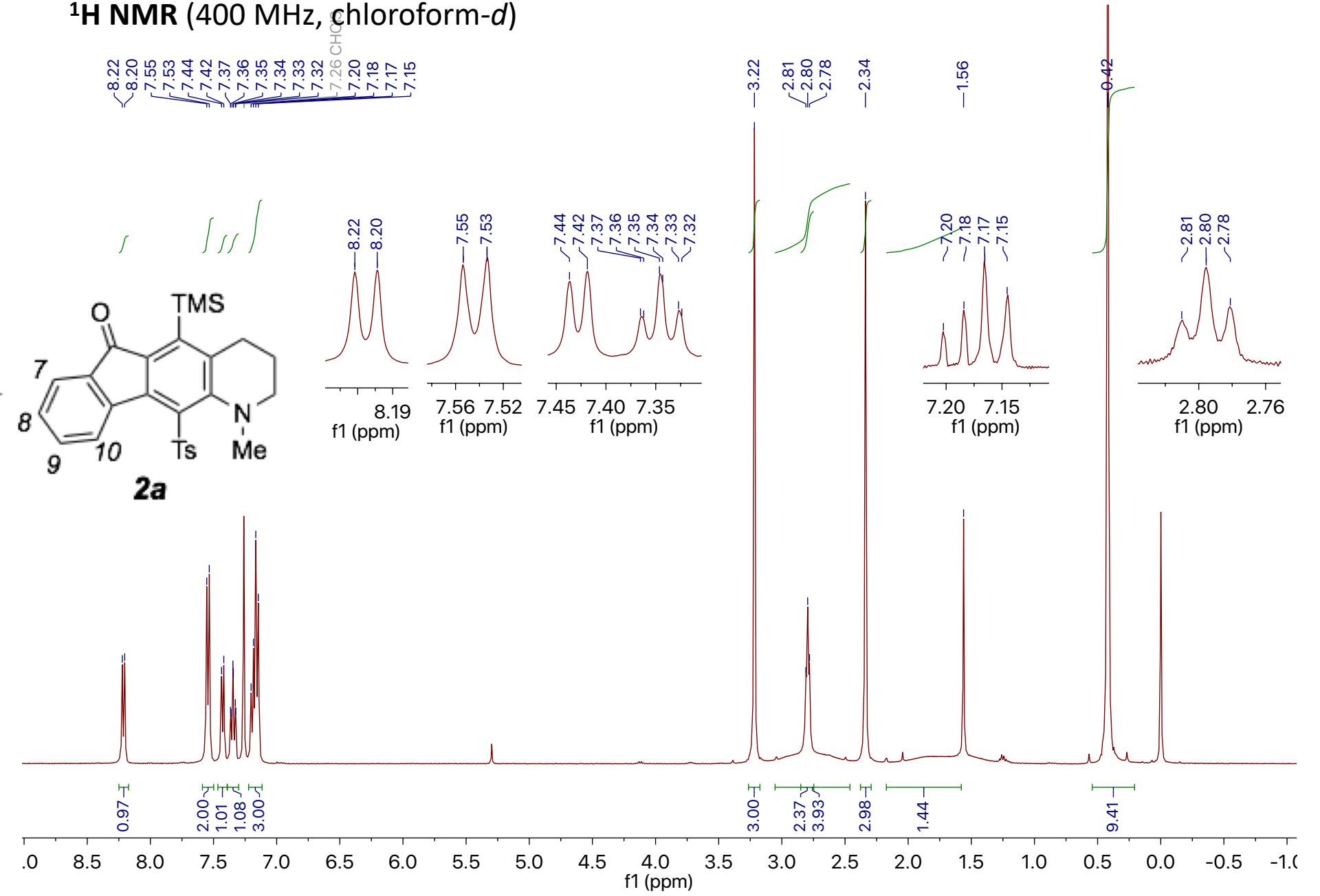



1H NMR (400 MHz, chloroform-d)
8.10 8.10 8.08 8.08 7.69 7.67 7.61 7.61 7.59 7.59 7.52 7.51 7.50 7.50 7.48 7.48 7.46 7.46 7.44 7.44 7.43 7.42 7.34 7.32
7.26 CHCl3
3.11 3.09 3.07 2.75 2.49 2.47 2.45 2.43 1.86 1.85 1.83 1.81 1.79
0.30
TMS
O
TsN
Me
3
4
5
6
1a
7.52 7.51 7.50 7.50 7.48 7.48 7.46 7.46 7.44 7.44 7.43 7.42
7.54 7.52 7.50 7.48 7.46 7.44 7.42
f1 (ppm)
1.86 1.85 1.83 1.81 1.79
1.88 1.84 1.80 1.76
f1 (ppm)
DCM
water
TMS
1.00 2.09 1.04 1.07 1.08 2.08
2.14 3.19 2.17 3.07 2.13 9.42
f1 (ppm)

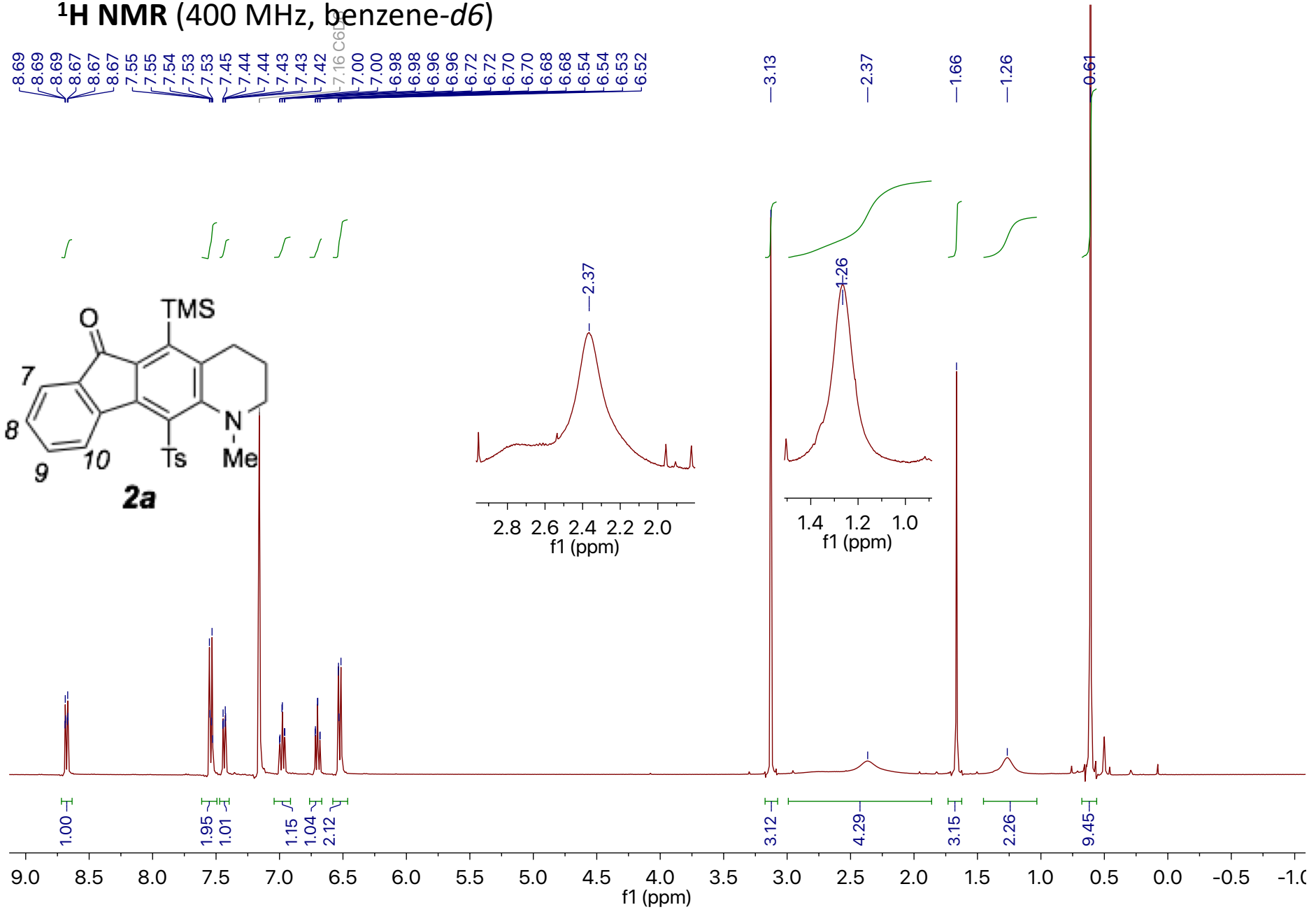
^{13}C NMR (101 MHz, chloroform-*d*)



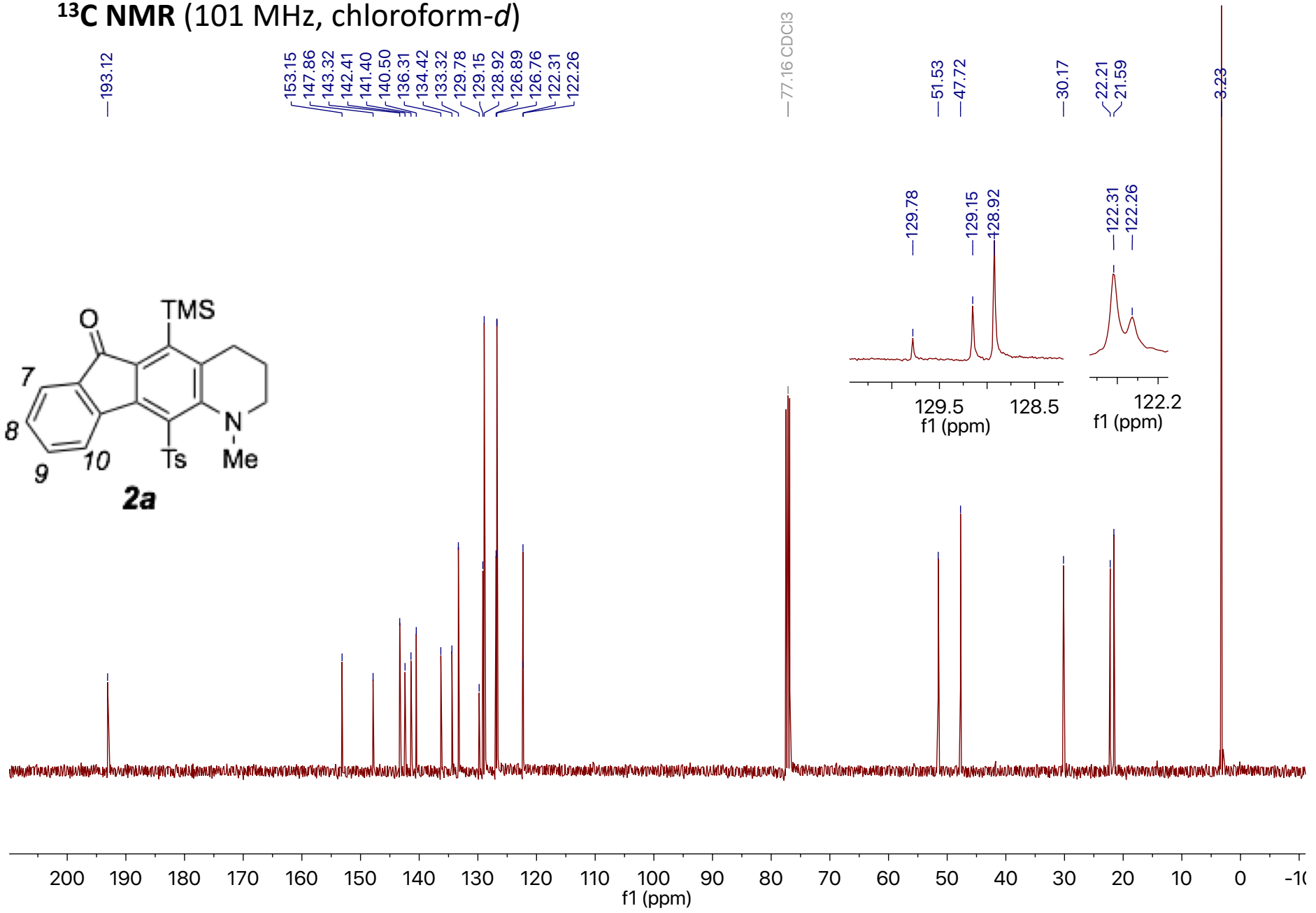
^{1}H NMR (400 MHz, chloroform-*d*)



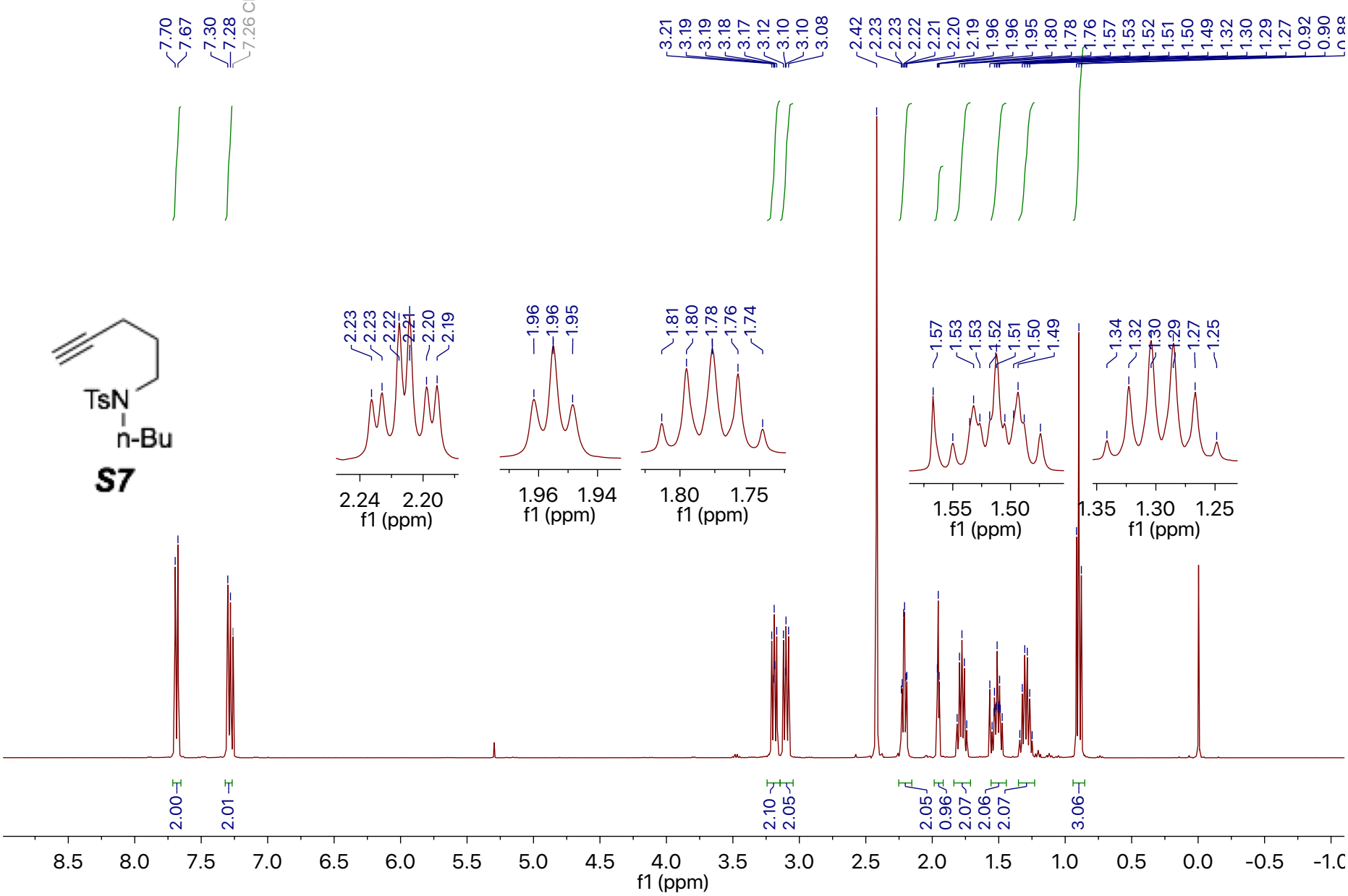
^{1}H NMR (400 MHz, benzene-*d6*)



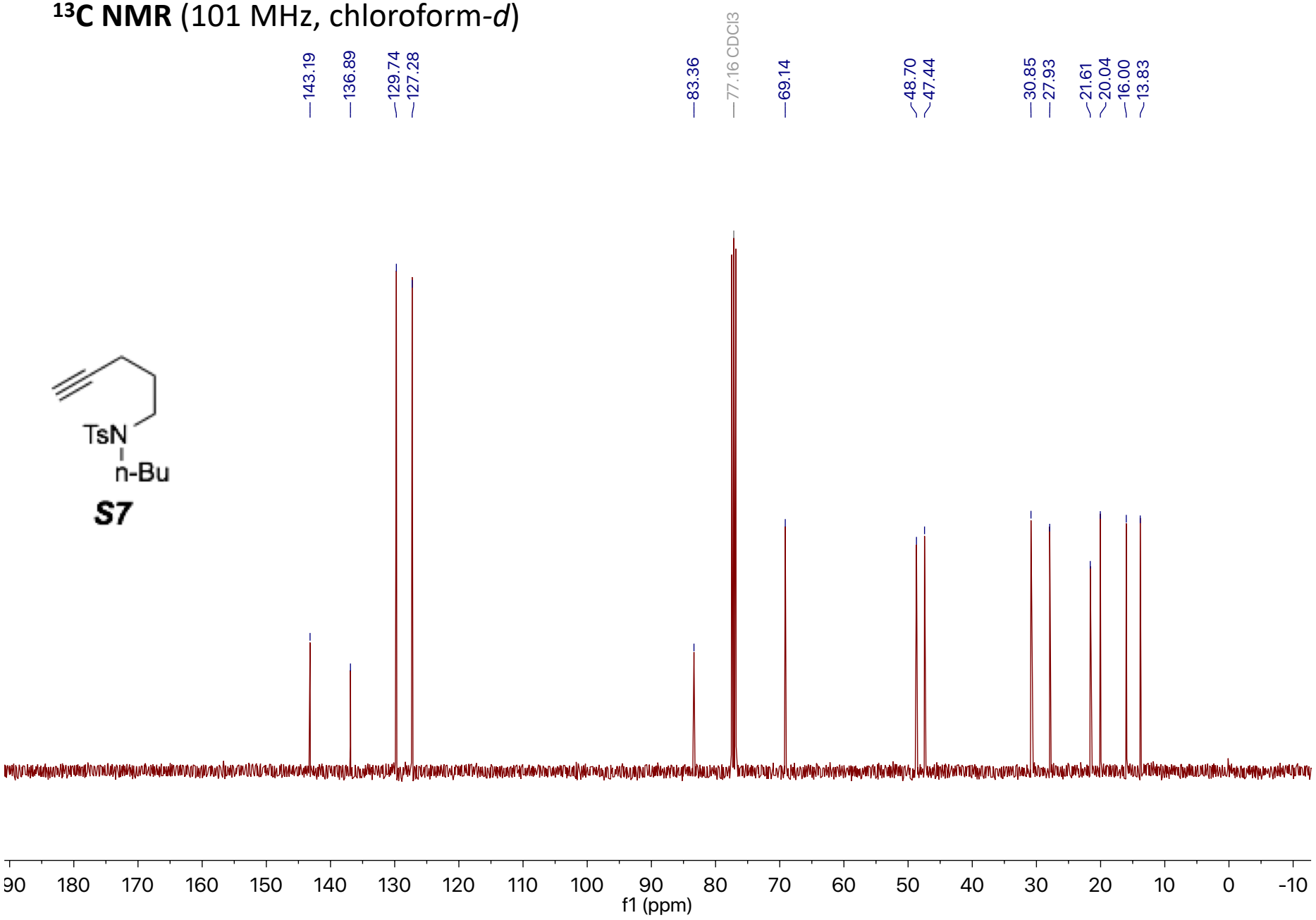
^{13}C NMR (101 MHz, chloroform-*d*)



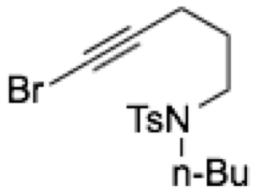
^{1}H NMR (400 MHz, chloroform-*d*)



^{13}C NMR (101 MHz, chloroform-*d*)

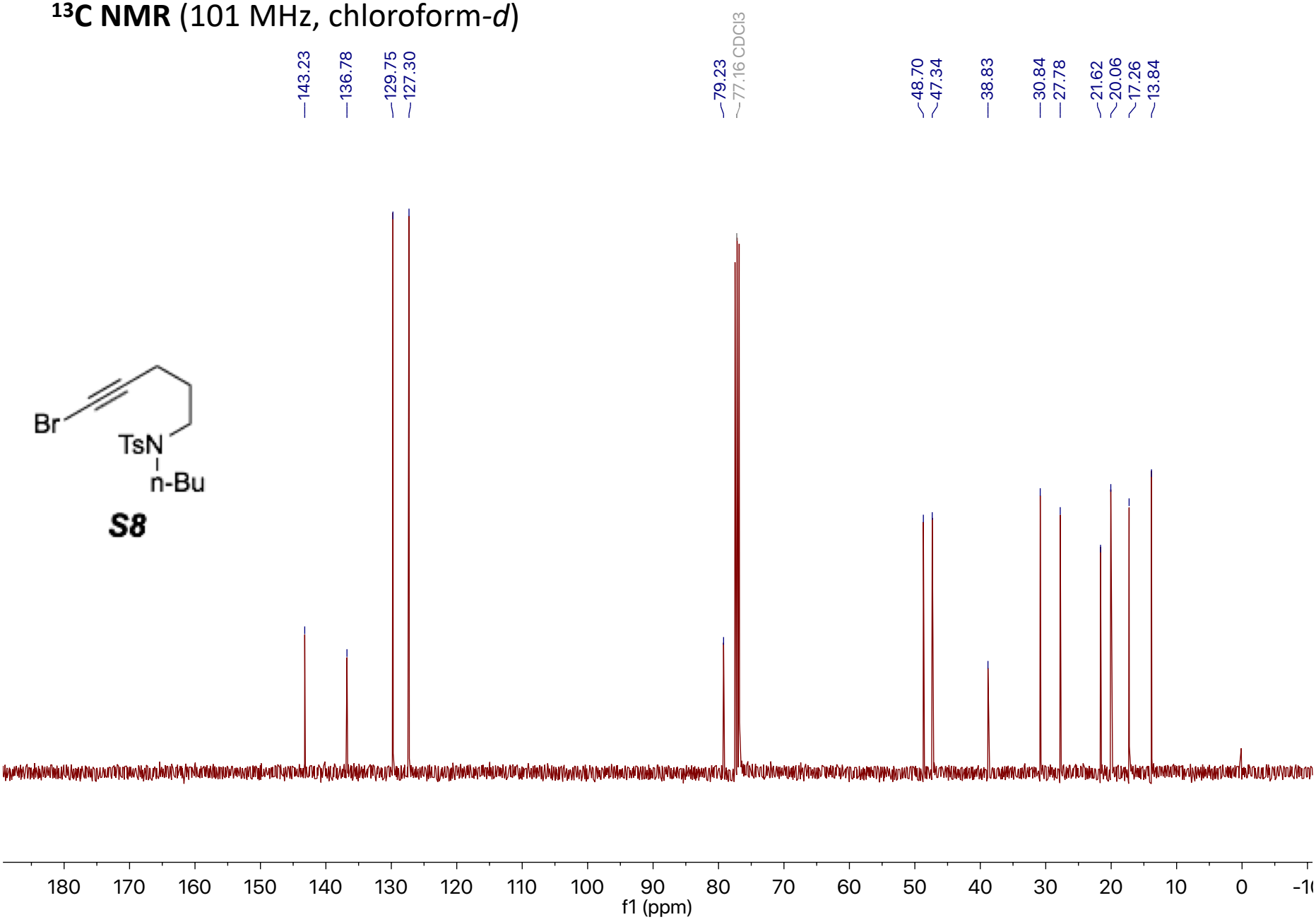


^{1}H NMR (400 MHz, chloroform-*d*)

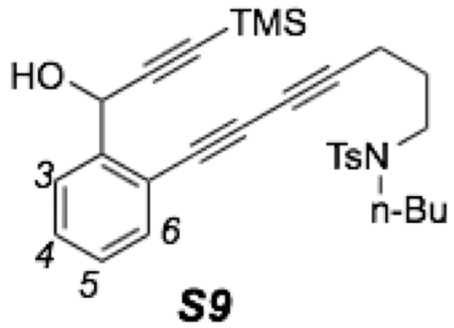


S8

^{13}C NMR (101 MHz, chloroform-*d*)



^{1}H NMR (400 MHz, chloroform-*d*)



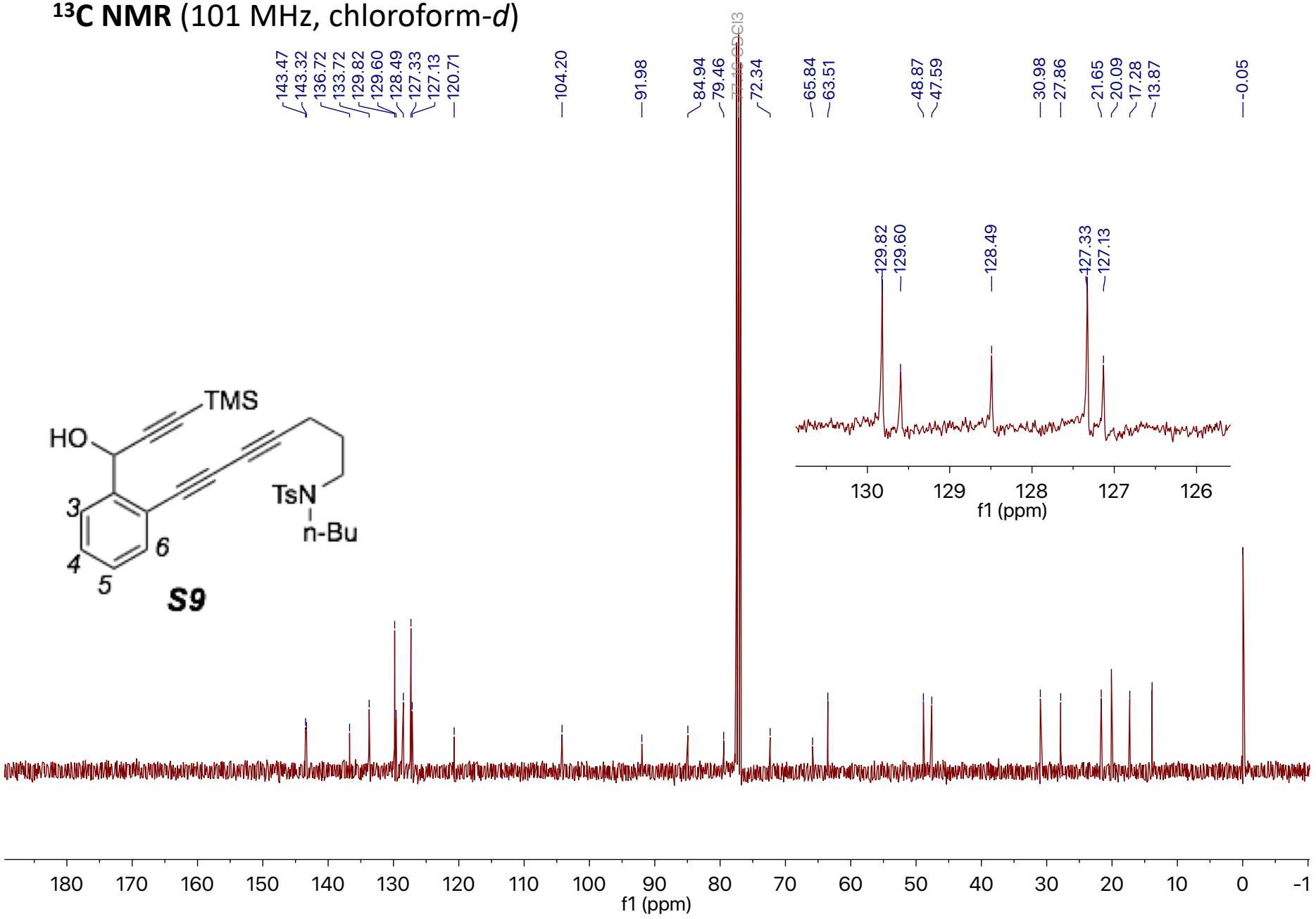
S9

TMS

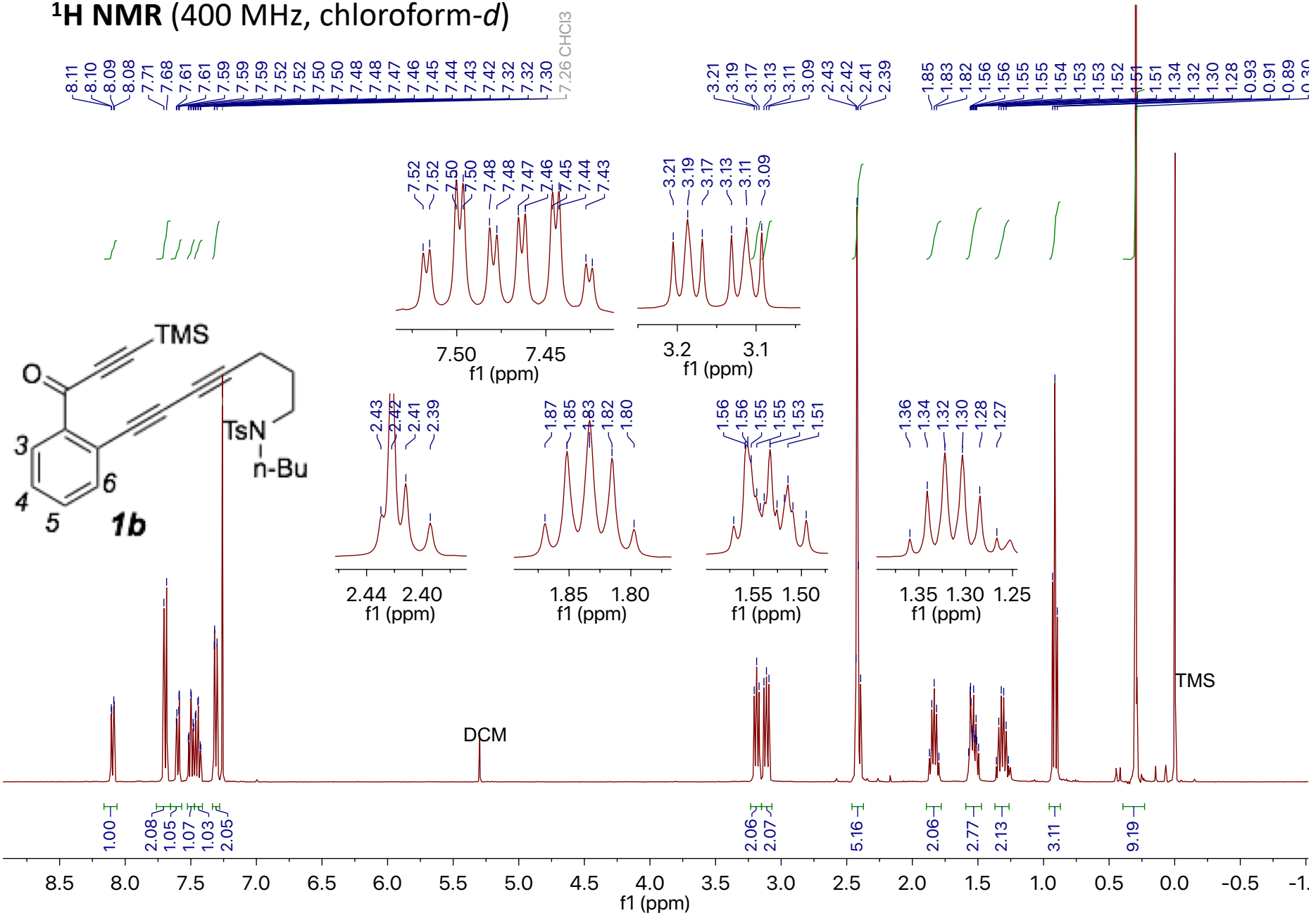
DCM

f1 (ppm)

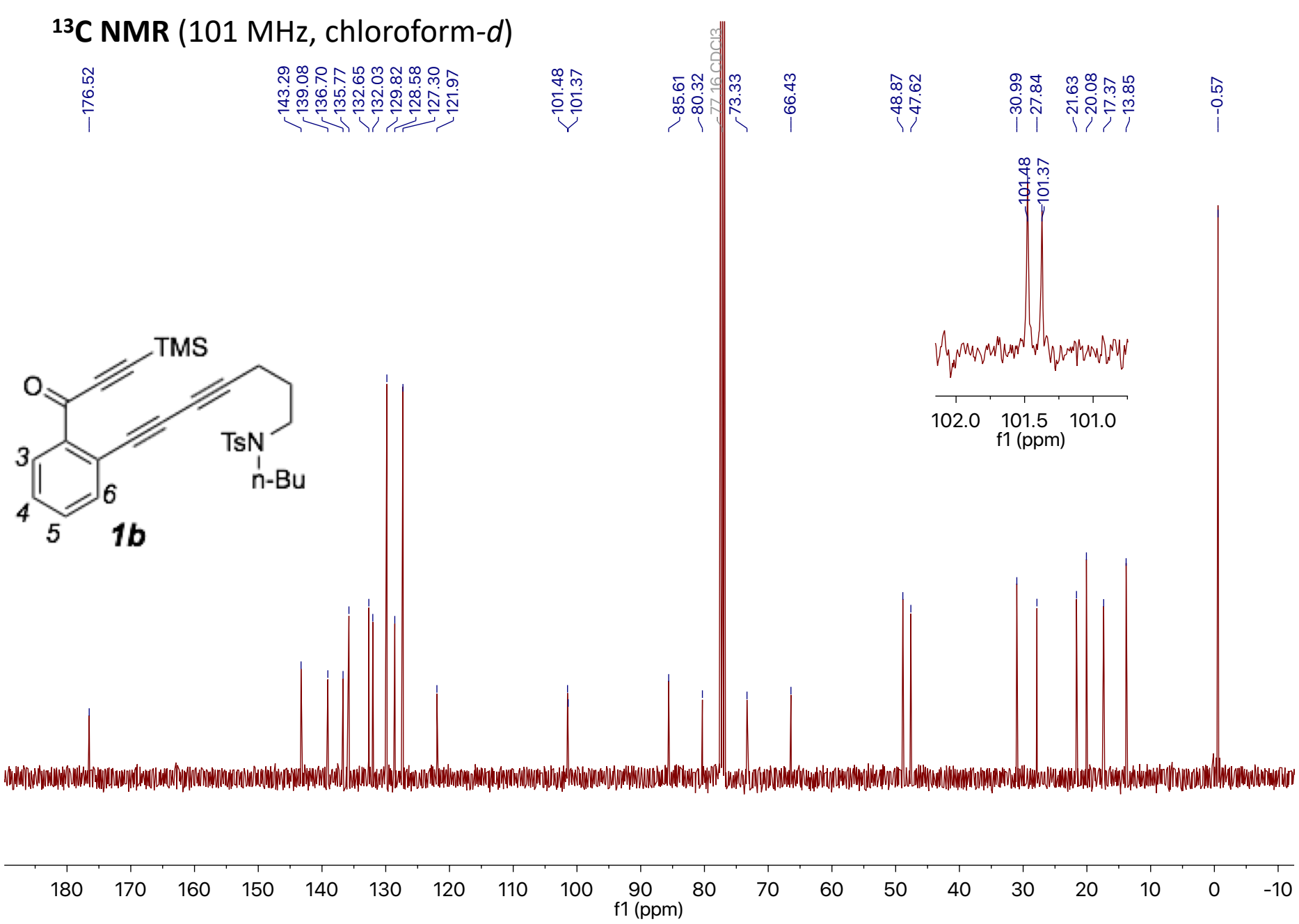
^{13}C NMR (101 MHz, chloroform-*d*)



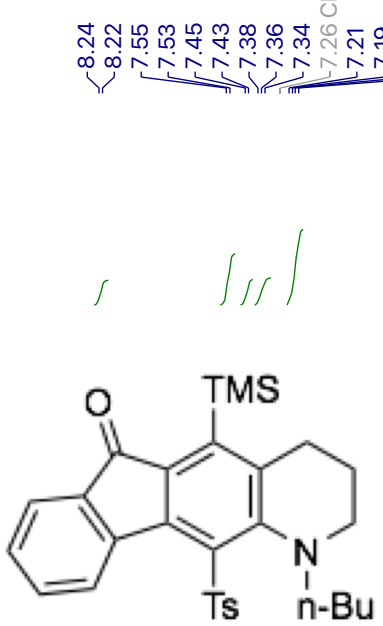
^{1}H NMR (400 MHz, chloroform-*d*)



^{13}C NMR (101 MHz, chloroform-*d*)

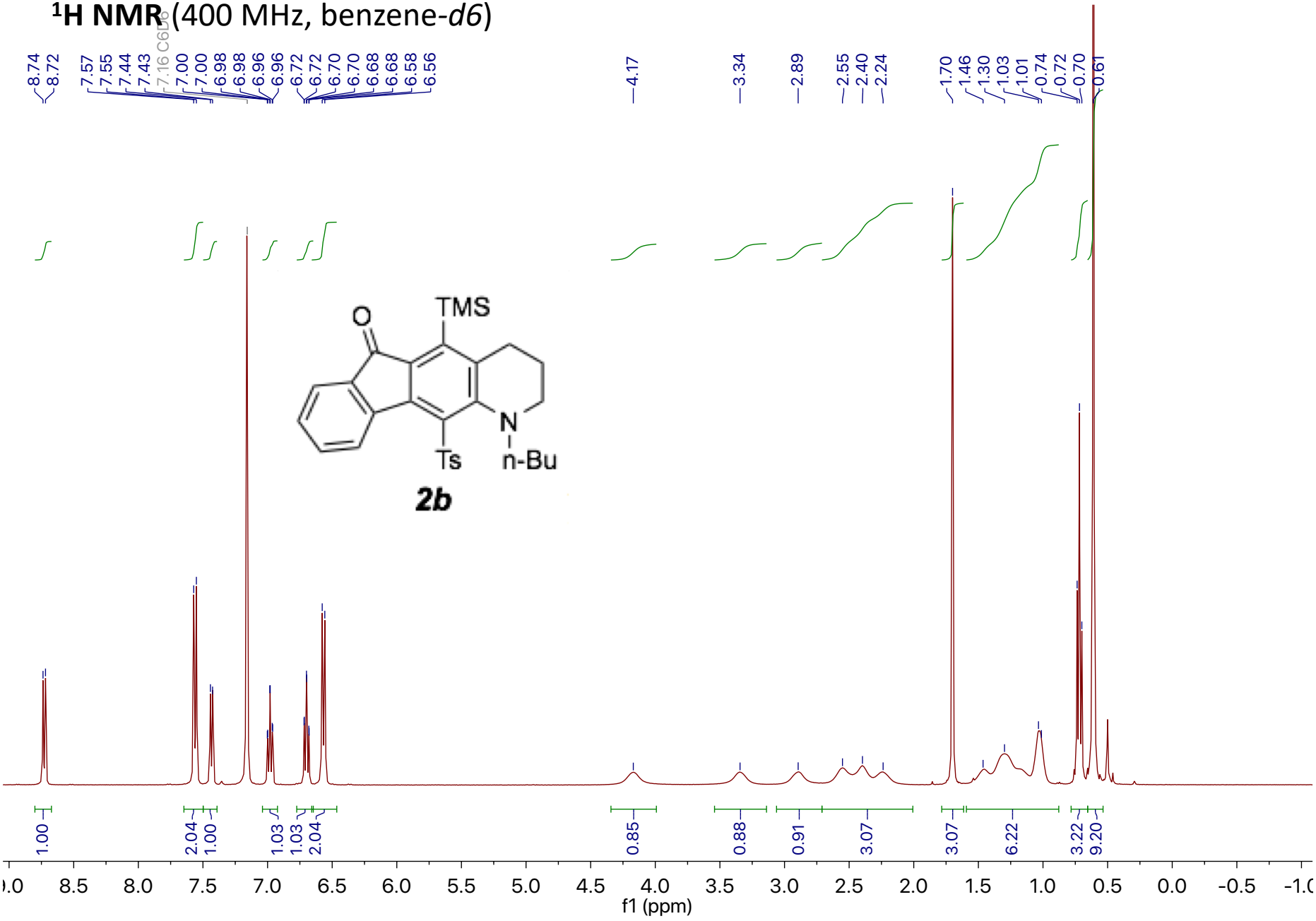


^{1}H NMR (400 MHz, chloroform-*d*)



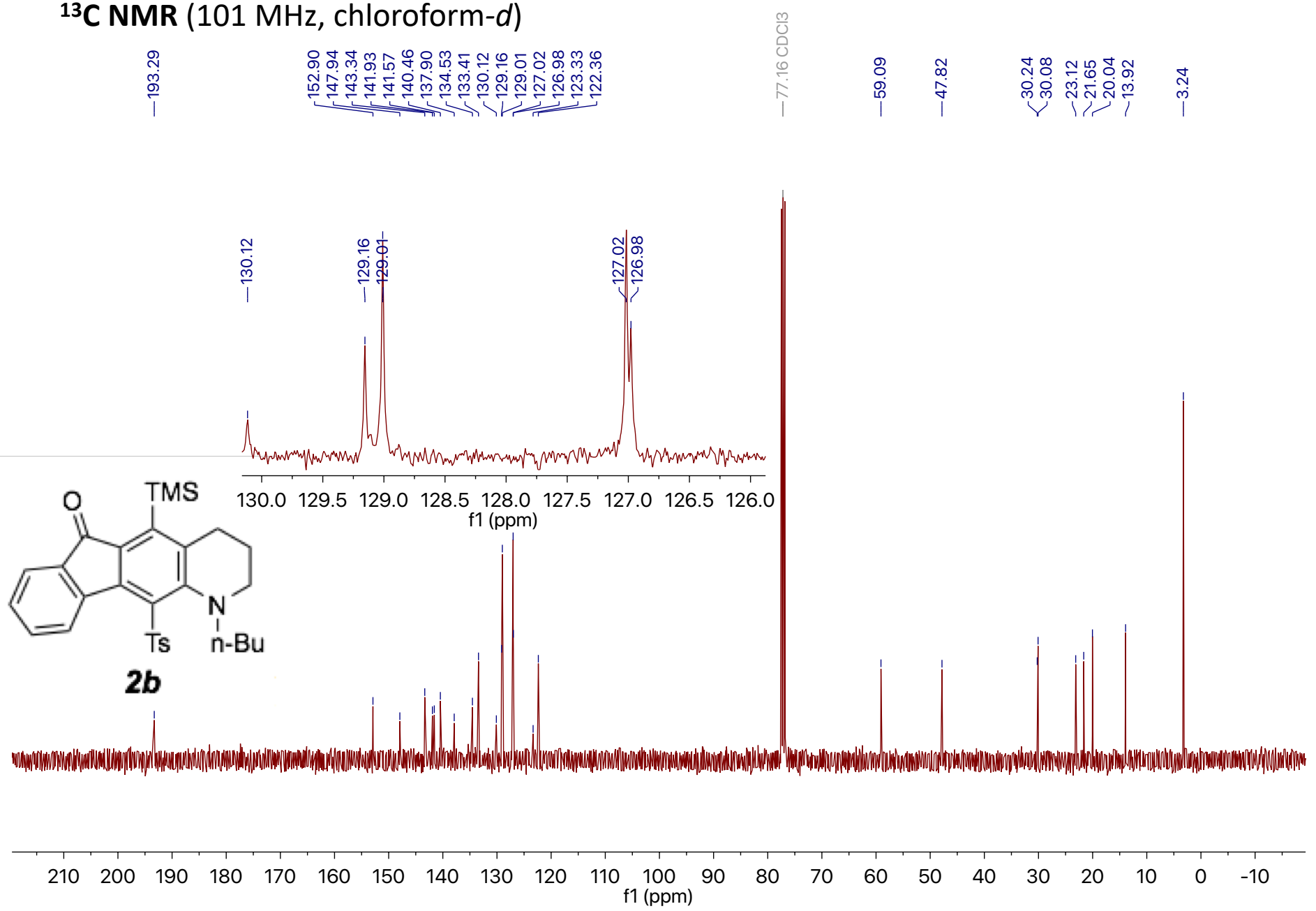
2b

^{1}H NMR (400 MHz, benzene-*d6*)

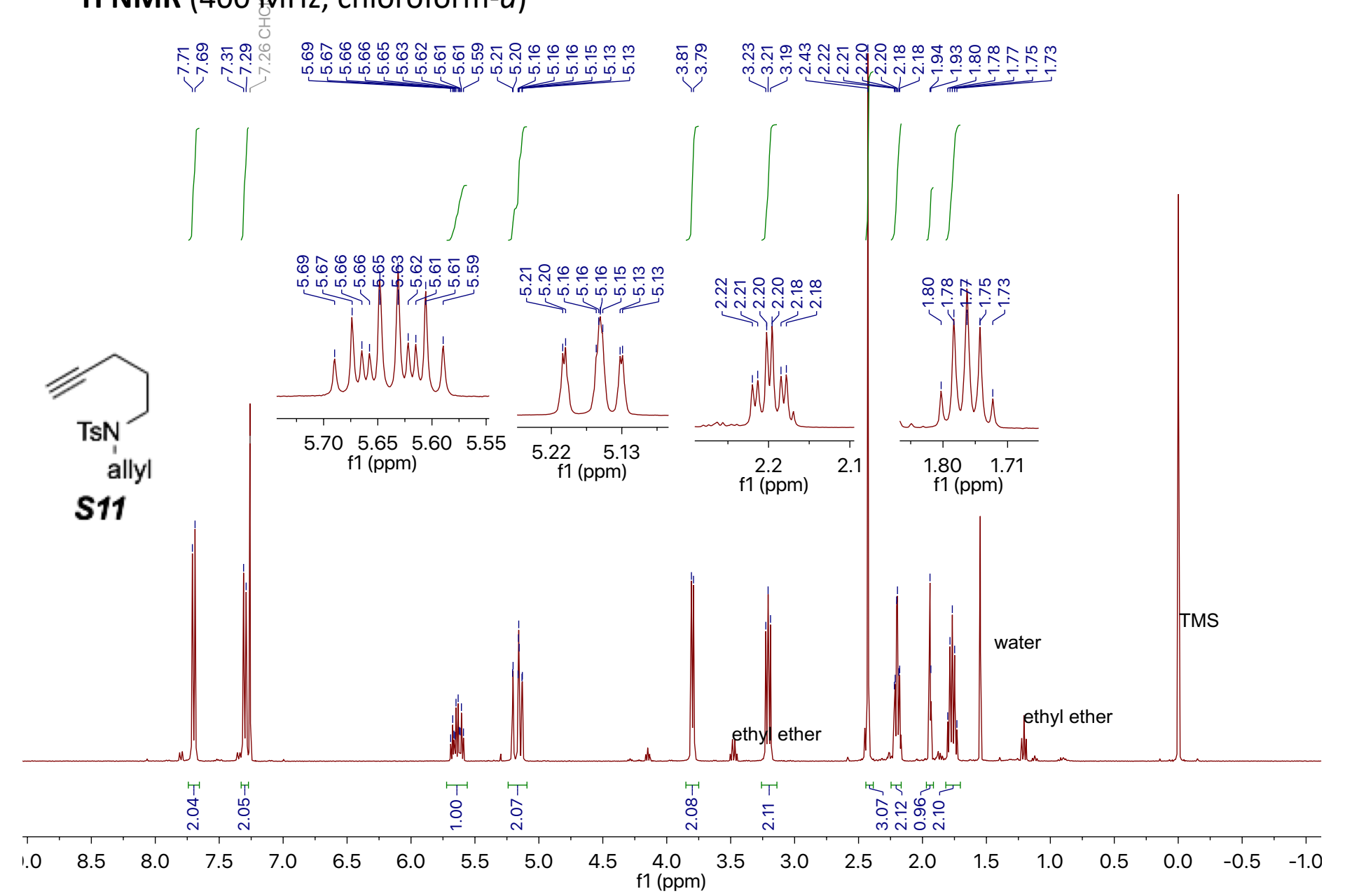


2b

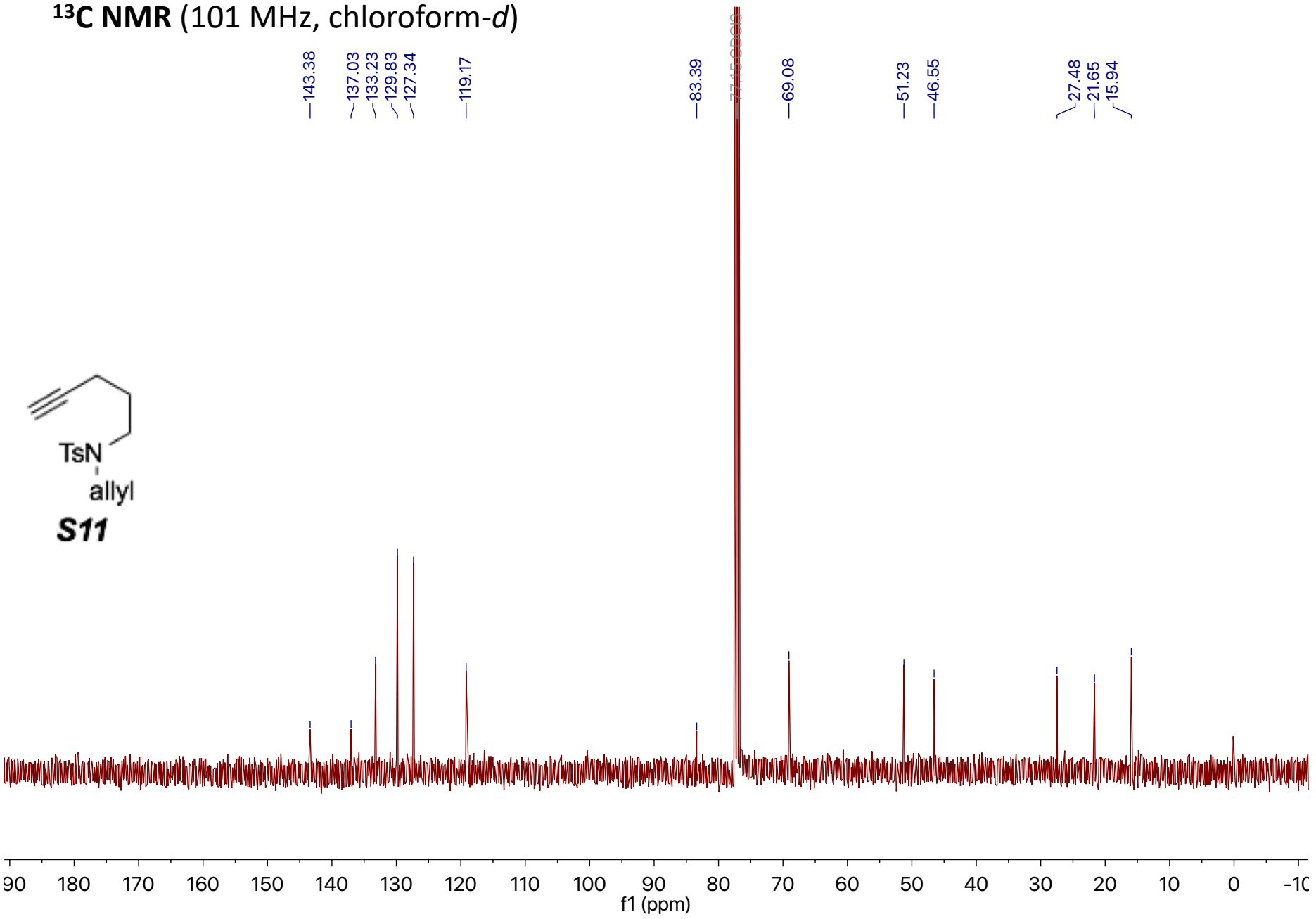
^{13}C NMR (101 MHz, chloroform-*d*)



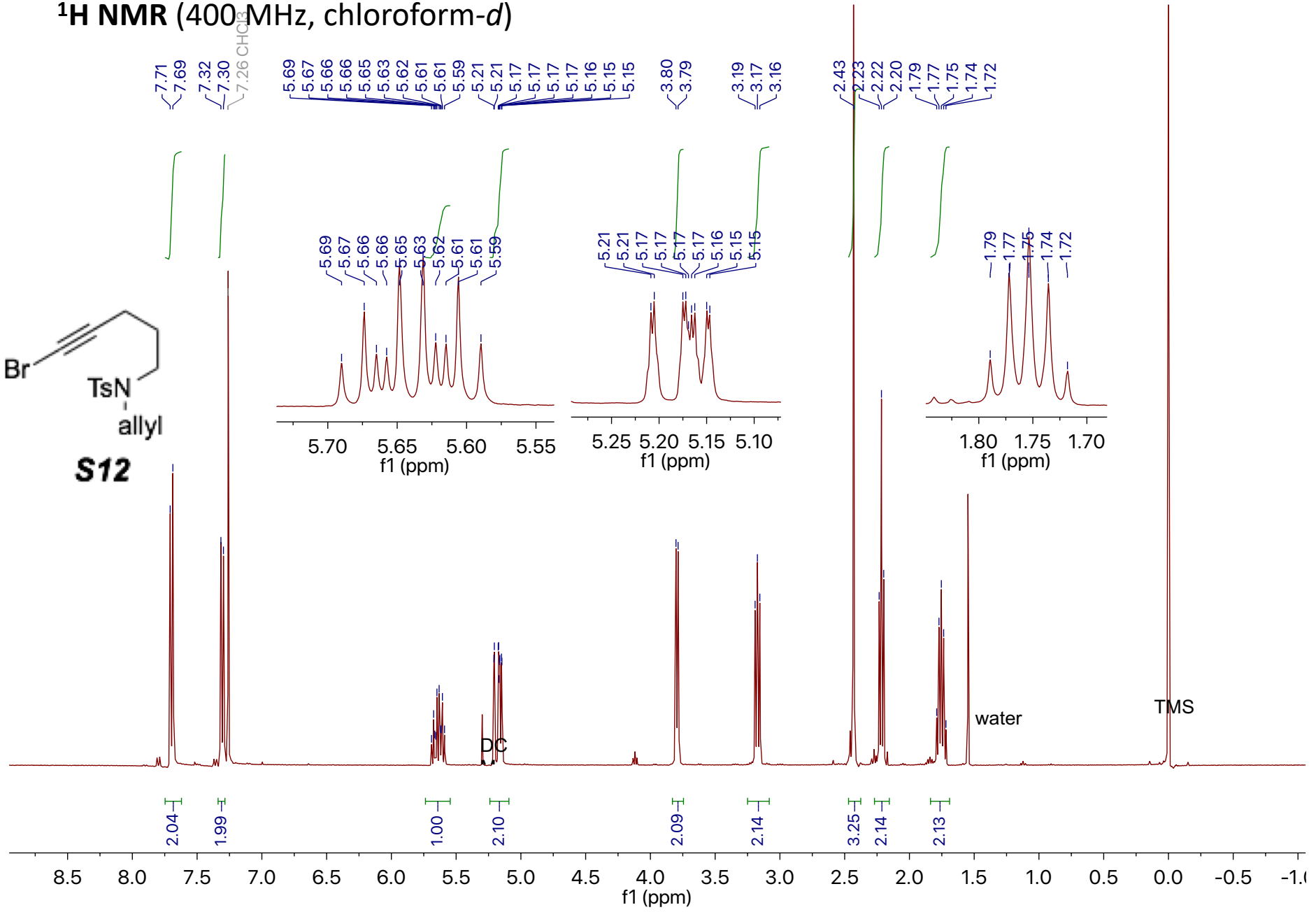
^{1}H NMR (400 MHz, chloroform-*d*)



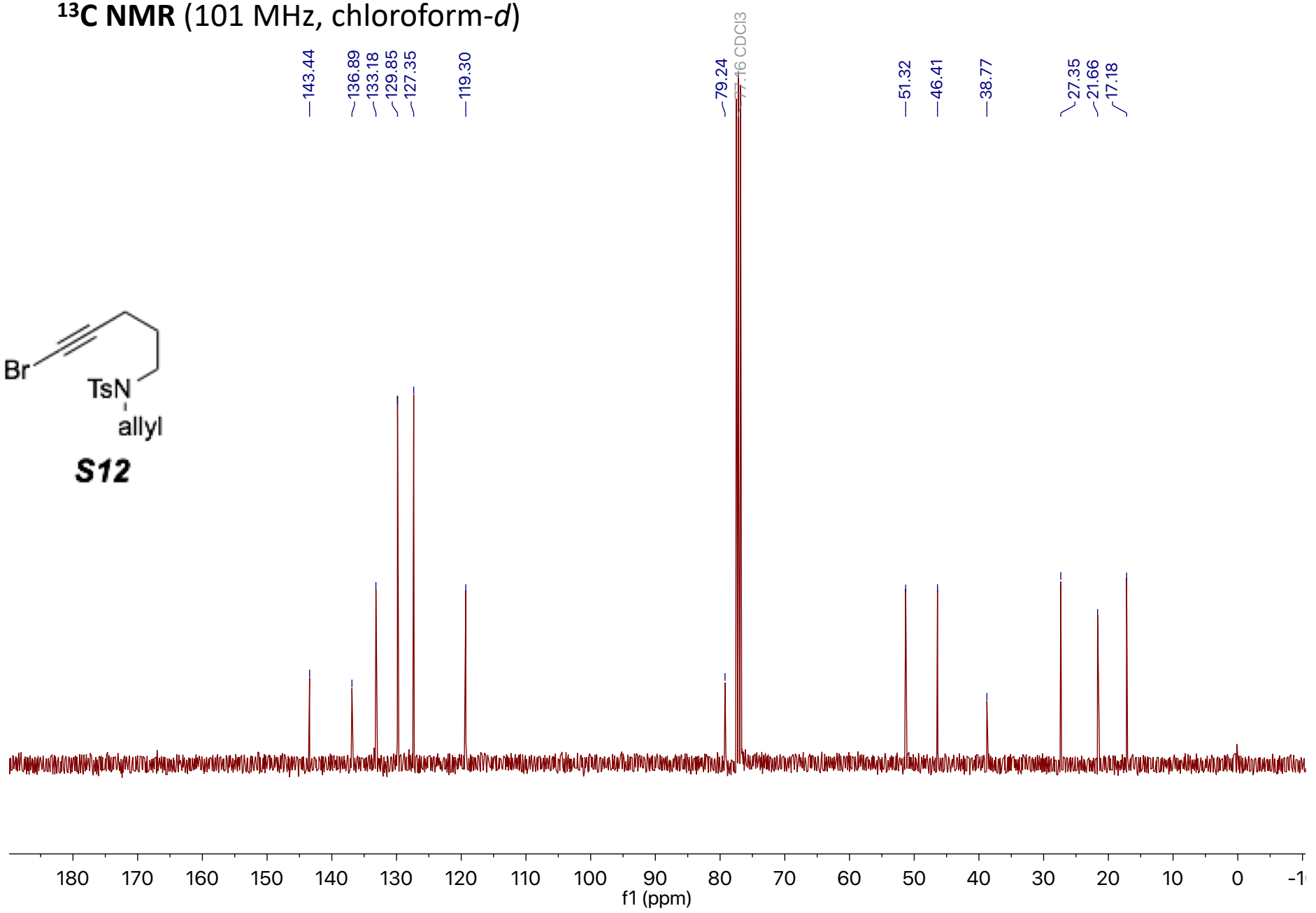
^{13}C NMR (101 MHz, chloroform-*d*)



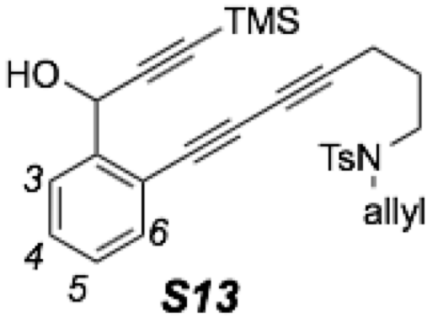
^{1}H NMR (400 MHz, chloroform-*d*)



^{13}C NMR (101 MHz, chloroform-*d*)

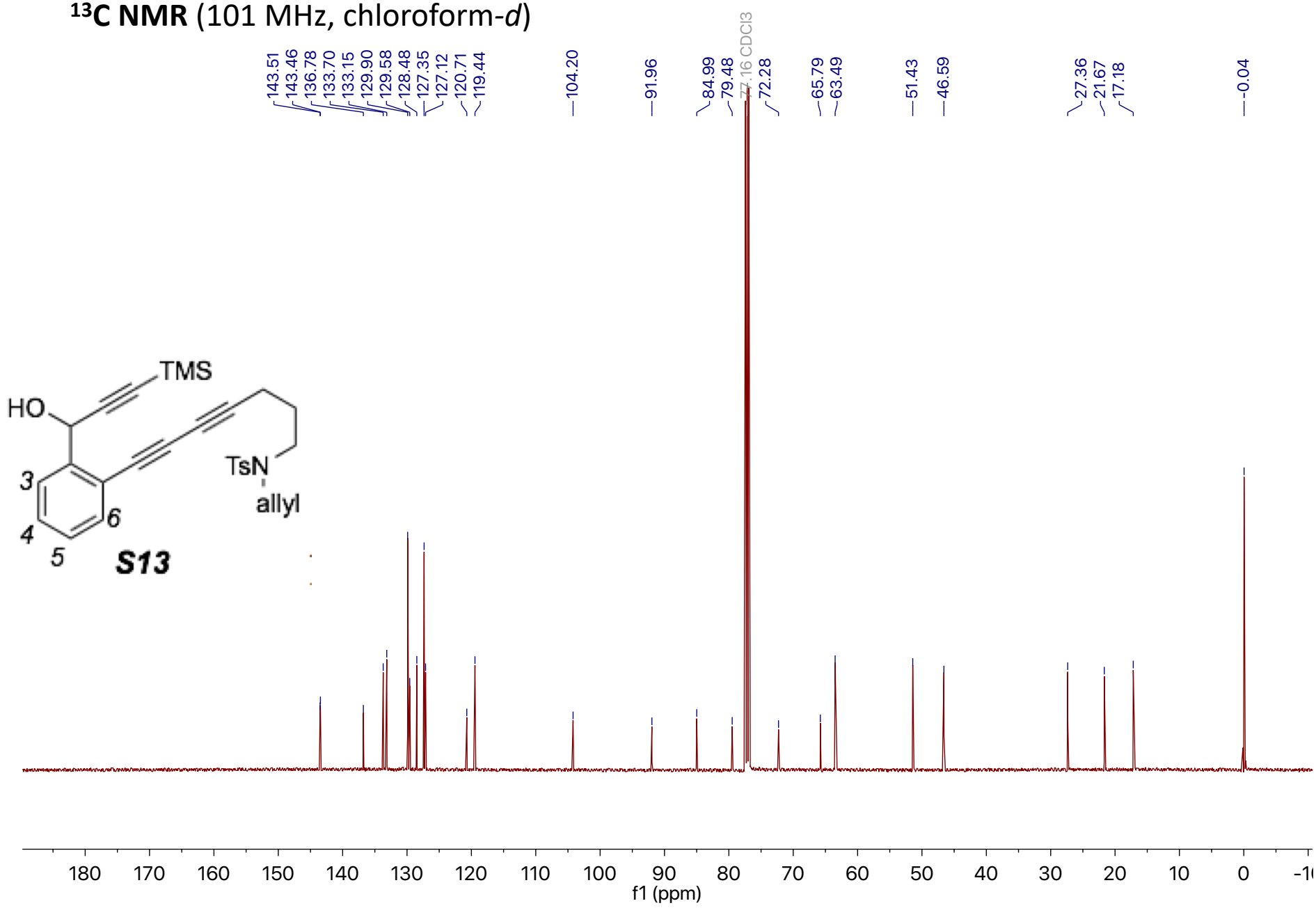


^{1}H NMR (500 MHz, chloroform-*d*)

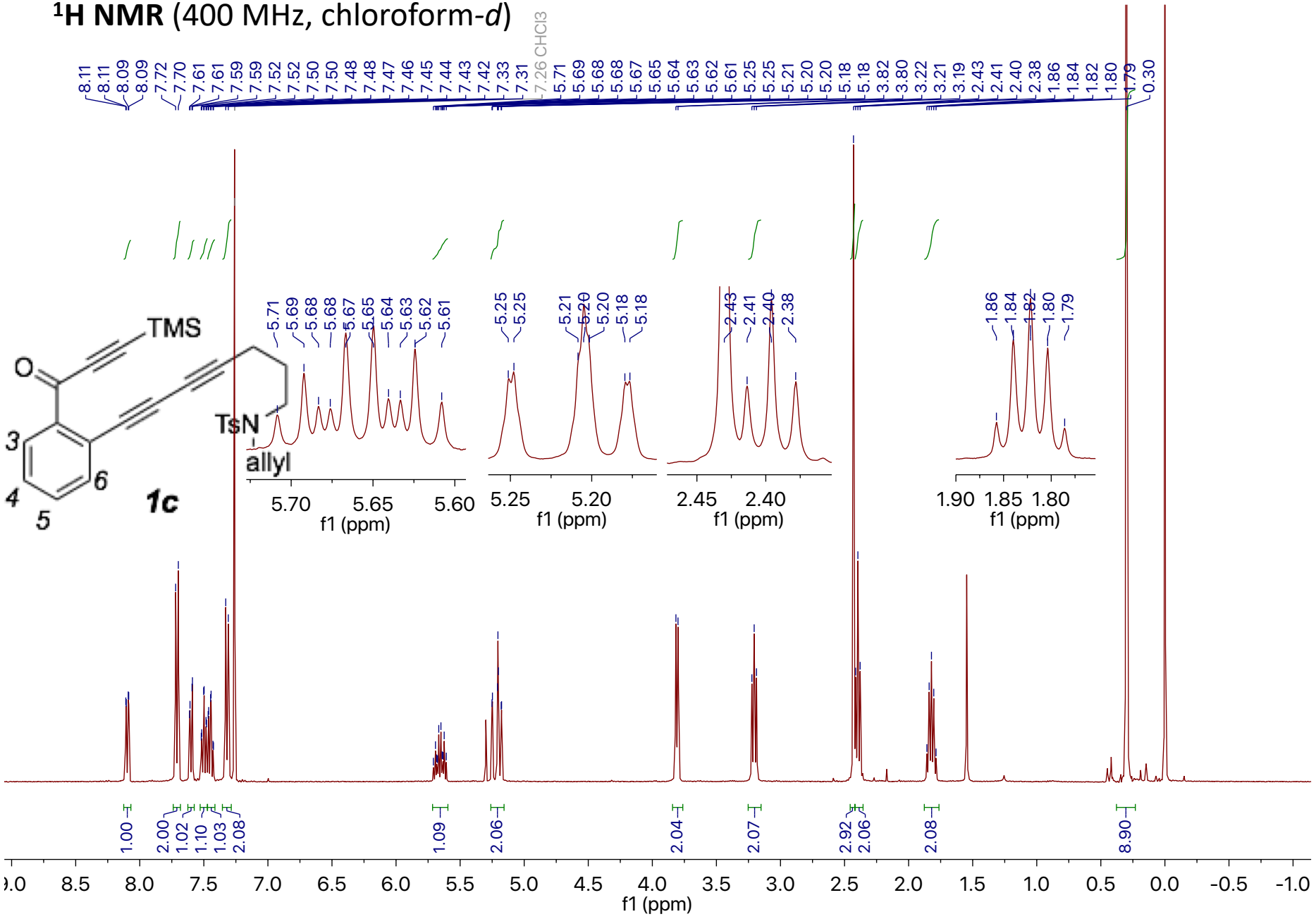


S13

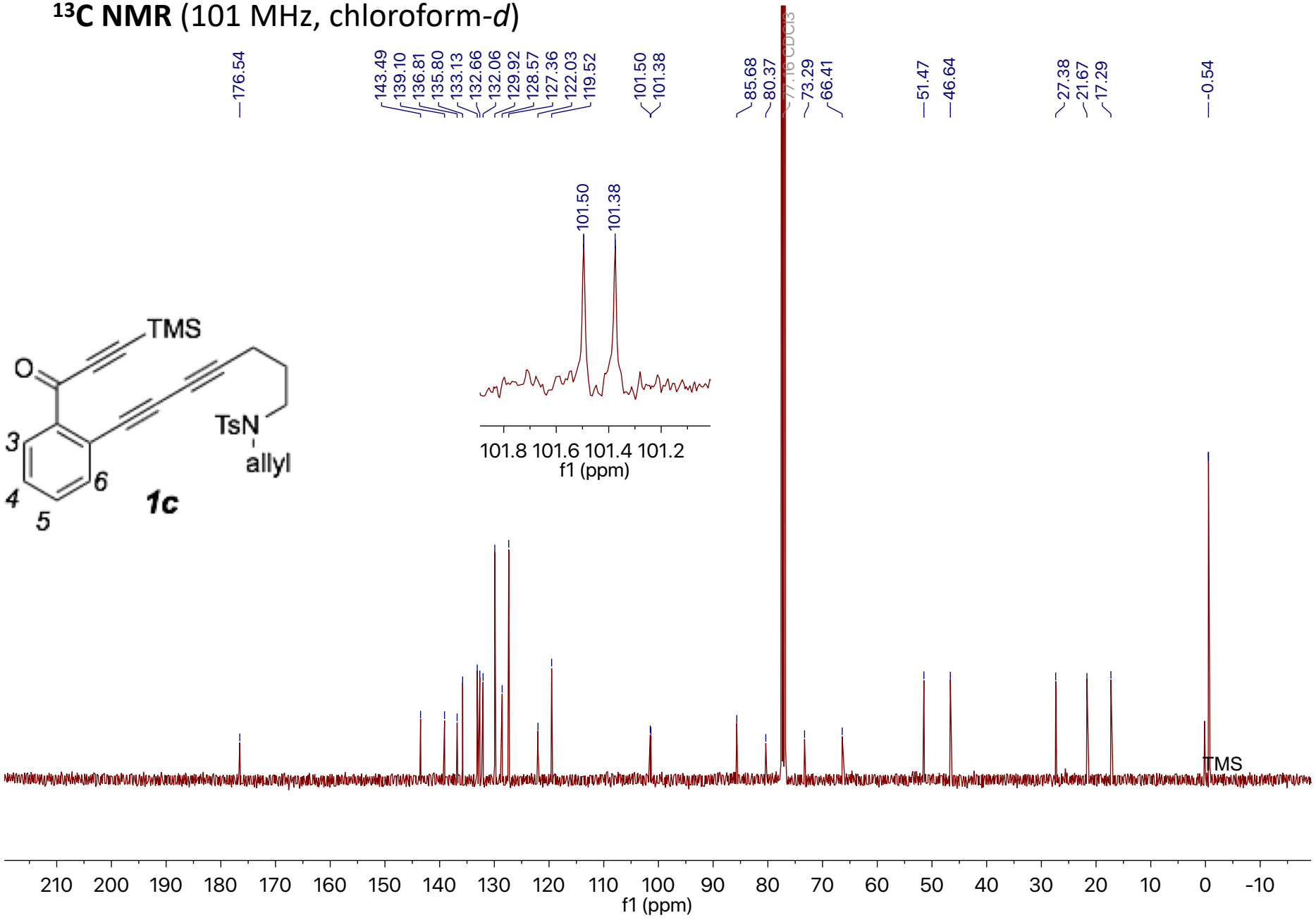
^{13}C NMR (101 MHz, chloroform-*d*)



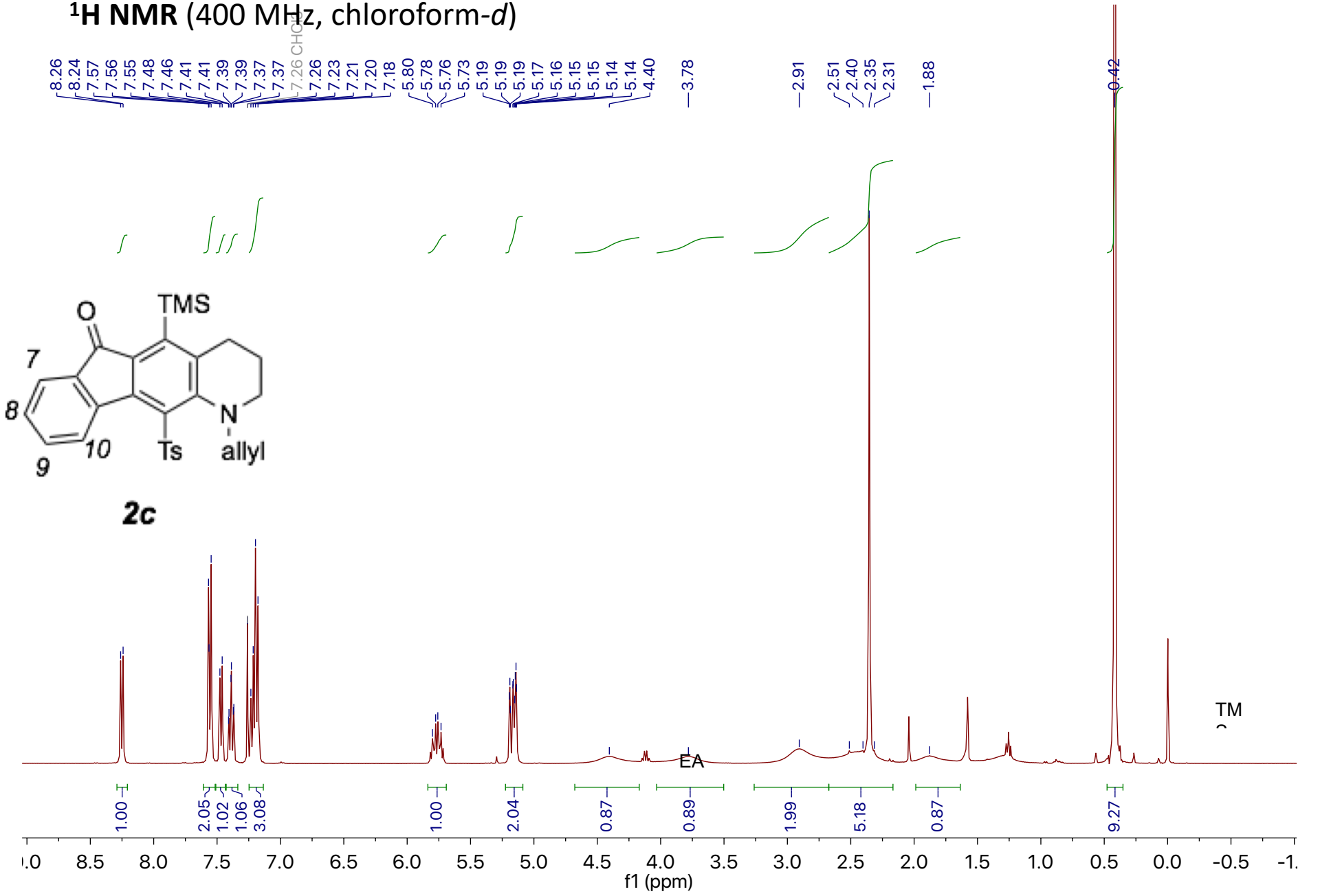
^{1}H NMR (400 MHz, chloroform-*d*)



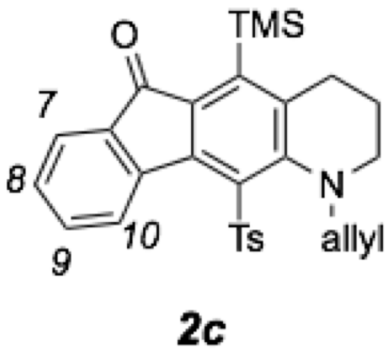
^{13}C NMR (101 MHz, chloroform-*d*)



^{1}H NMR (400 MHz, chloroform-*d*)



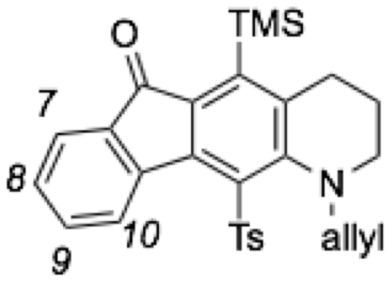
^{1}H NMR (400 MHz, benzene-*d6*)



2c

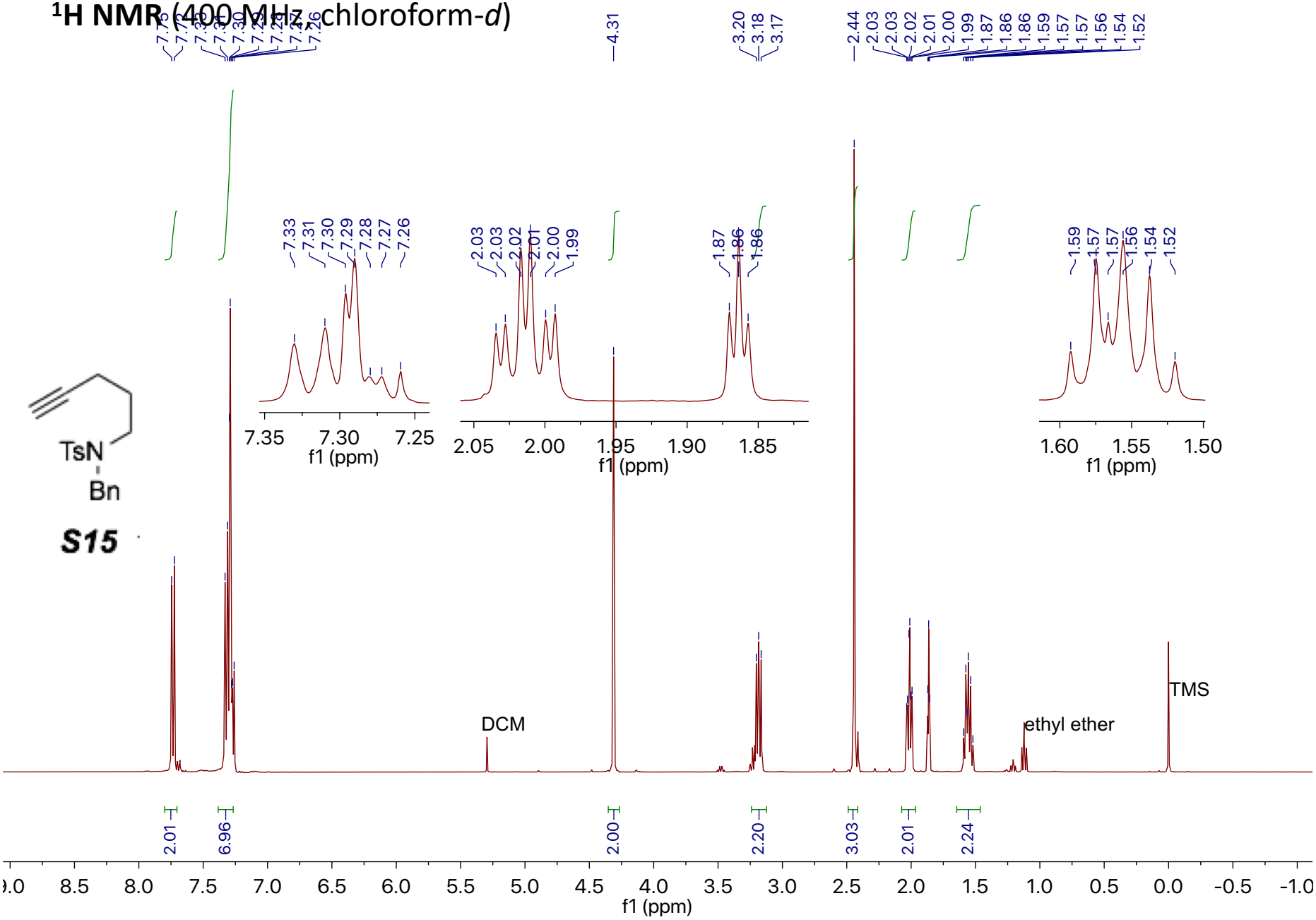
^{13}C NMR (101 MHz, chloroform-*d*)

193.37
152.47
147.65
143.34
142.92
141.62
140.56
138.55
134.51
134.39
133.61
131.47
129.29
129.02
127.29
126.93
124.92
122.55
118.91
77.16 CDCl3
62.62
47.13
30.20
22.55
21.64
3.19

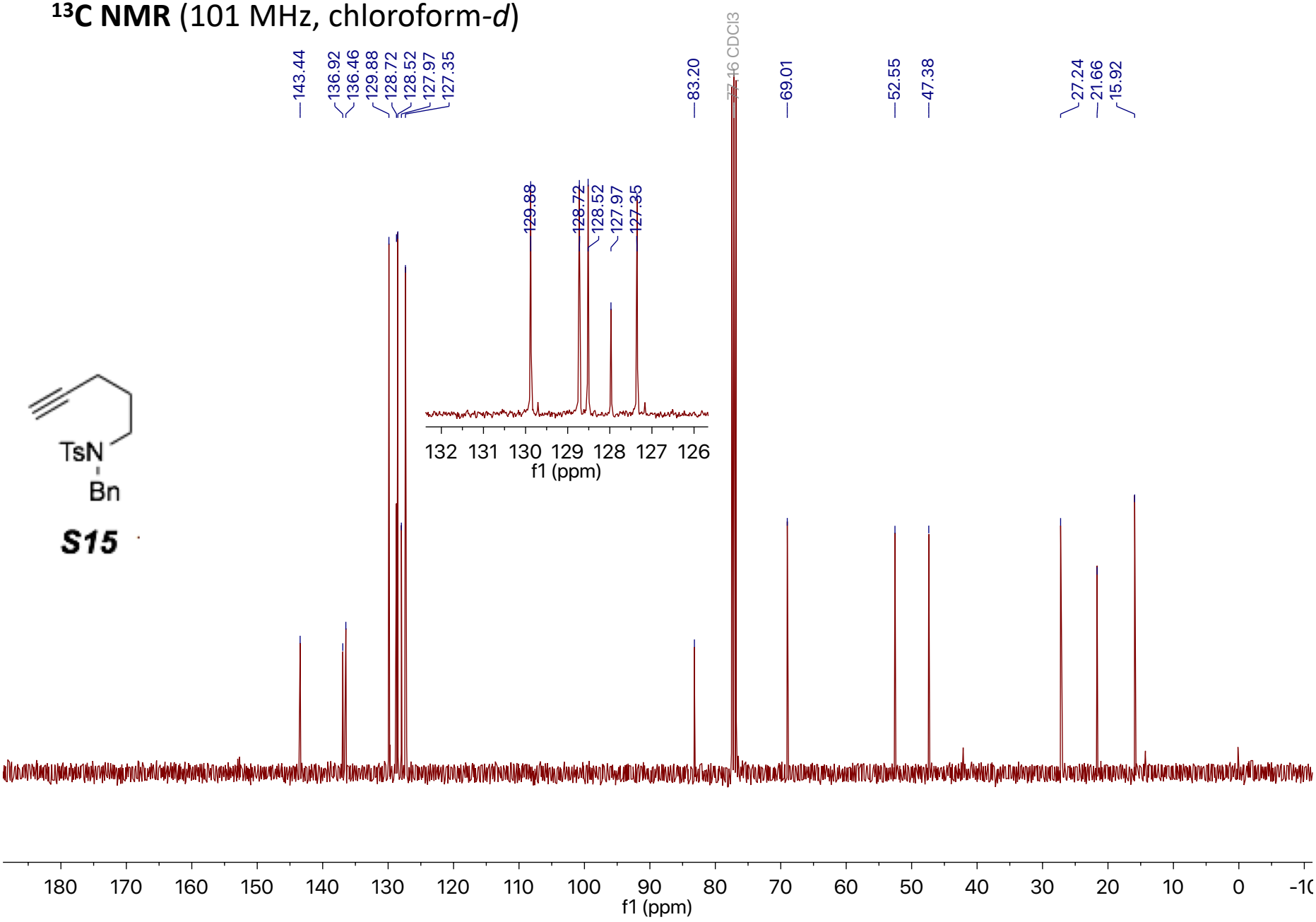


2c

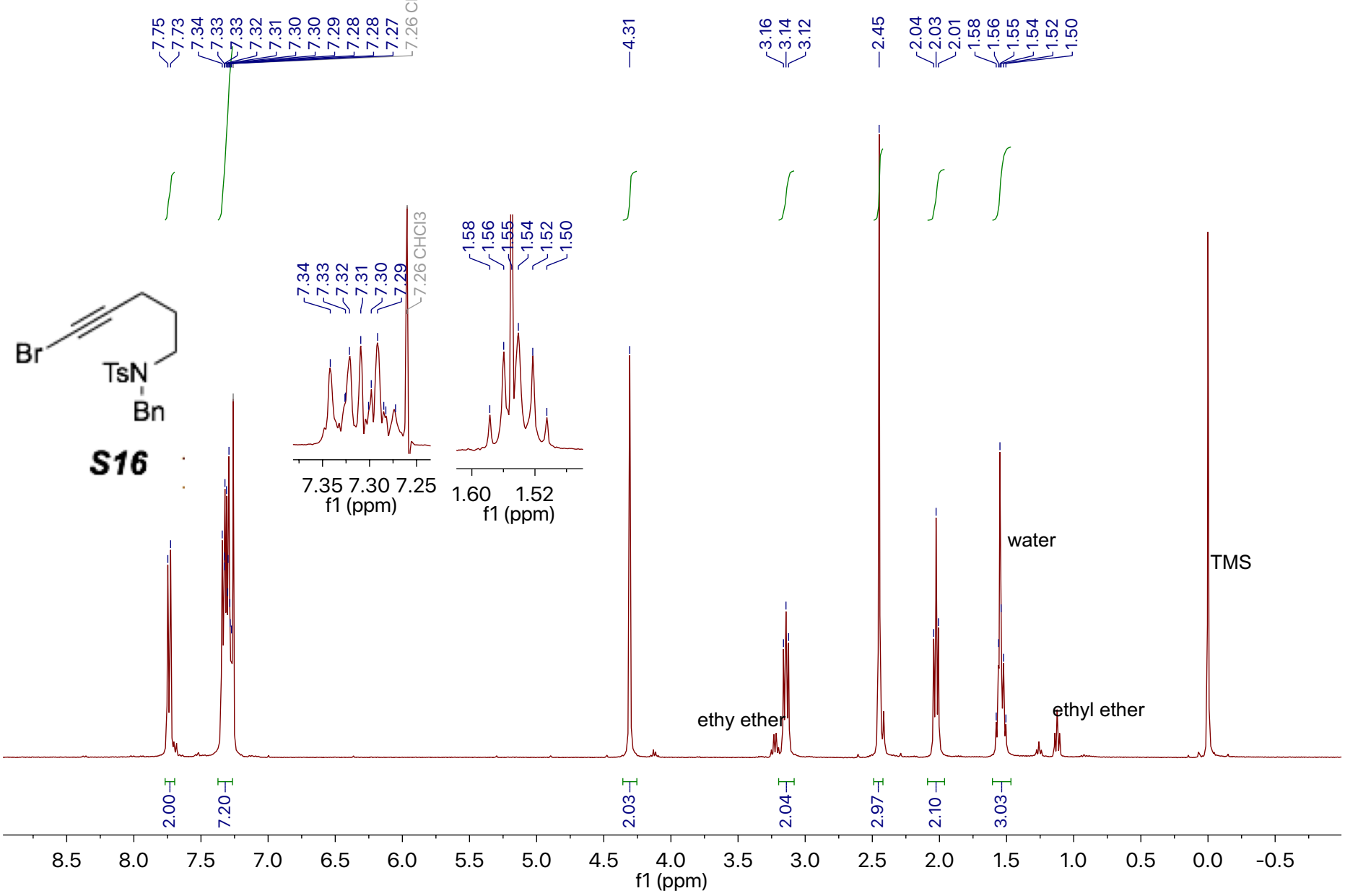
^{1}H NMR (400 MHz, chloroform-*d*)



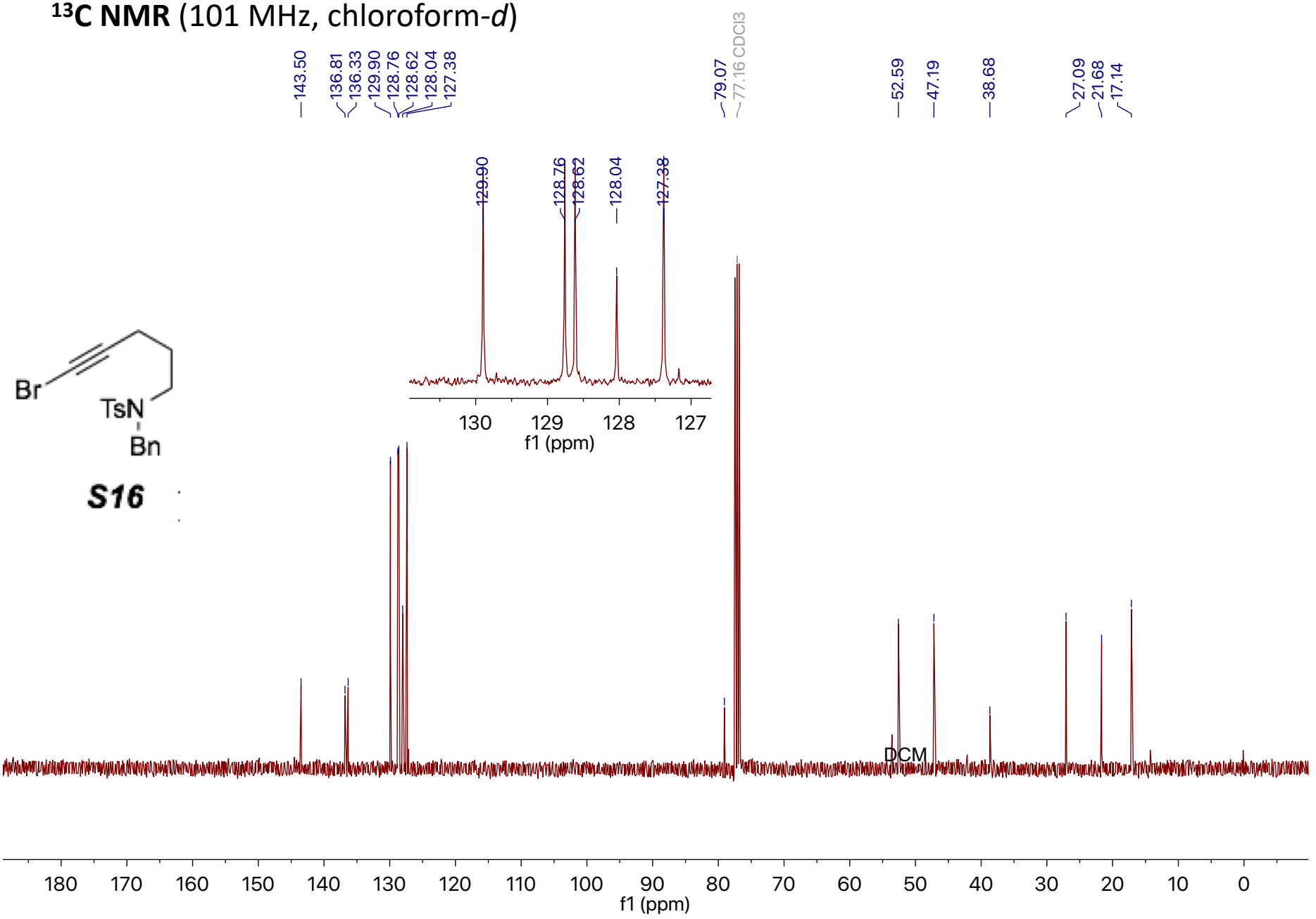
^{13}C NMR (101 MHz, chloroform-*d*)



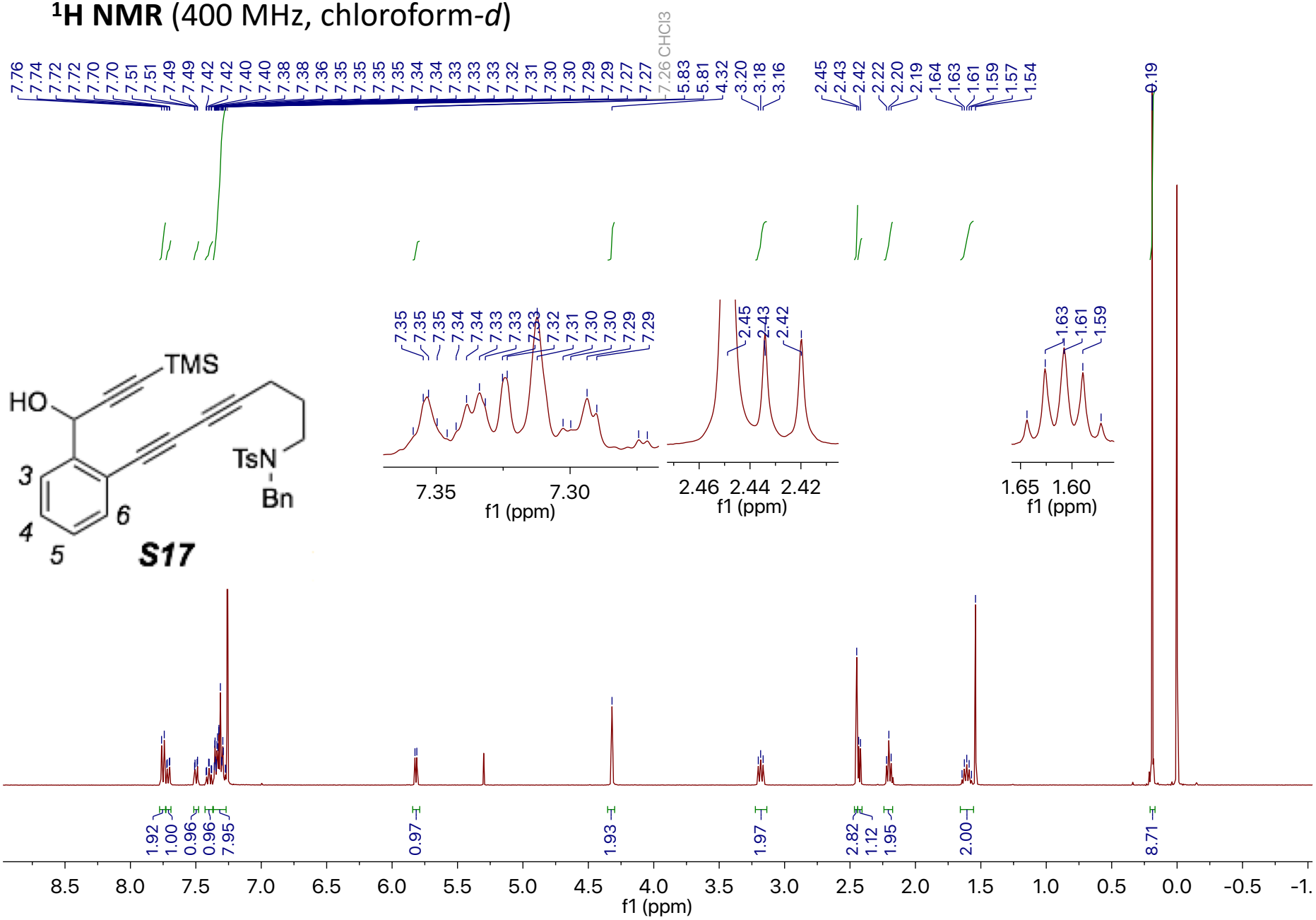
^{1}H NMR (400 MHz, chloroform-*d*)



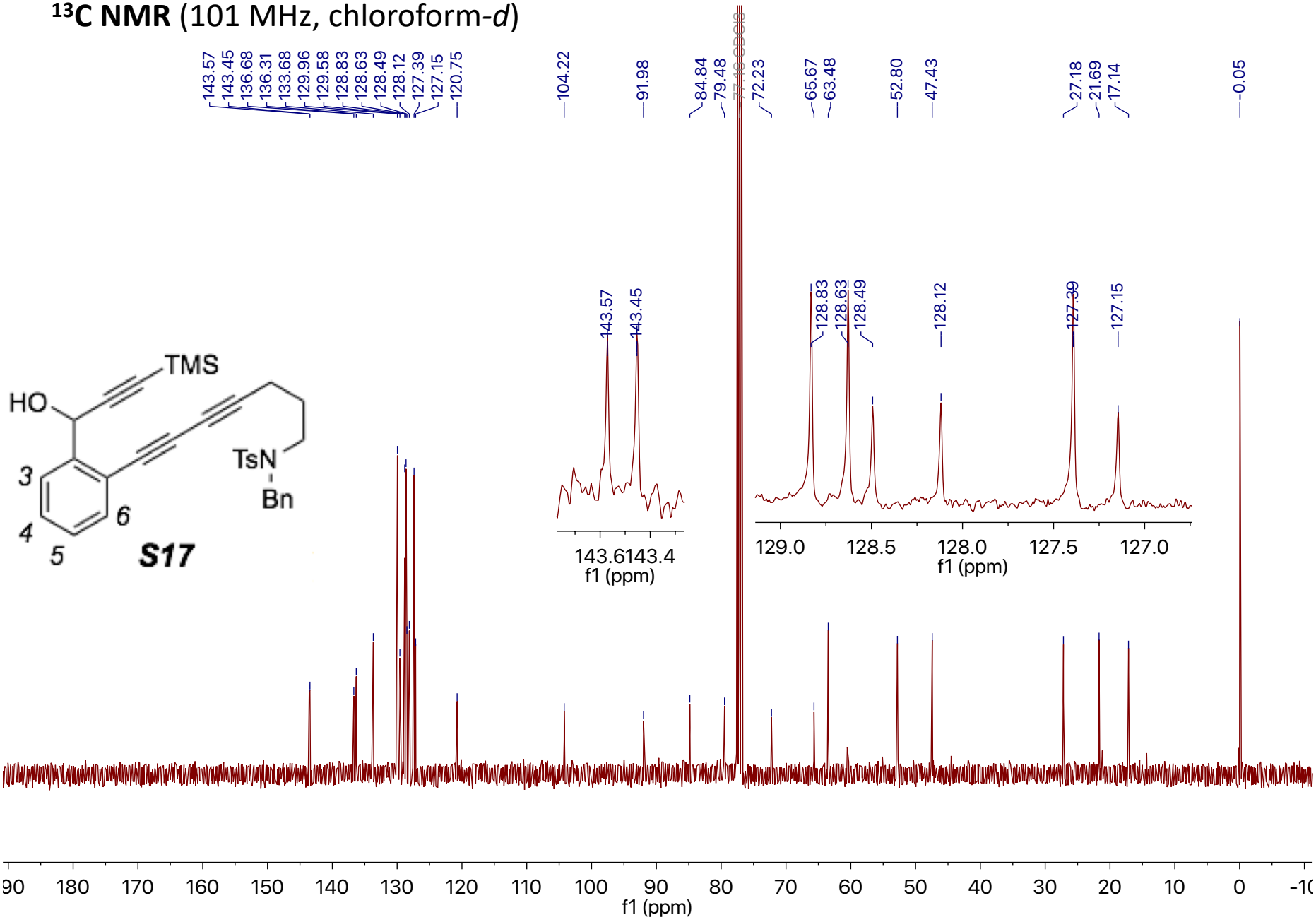
^{13}C NMR (101 MHz, chloroform-*d*)



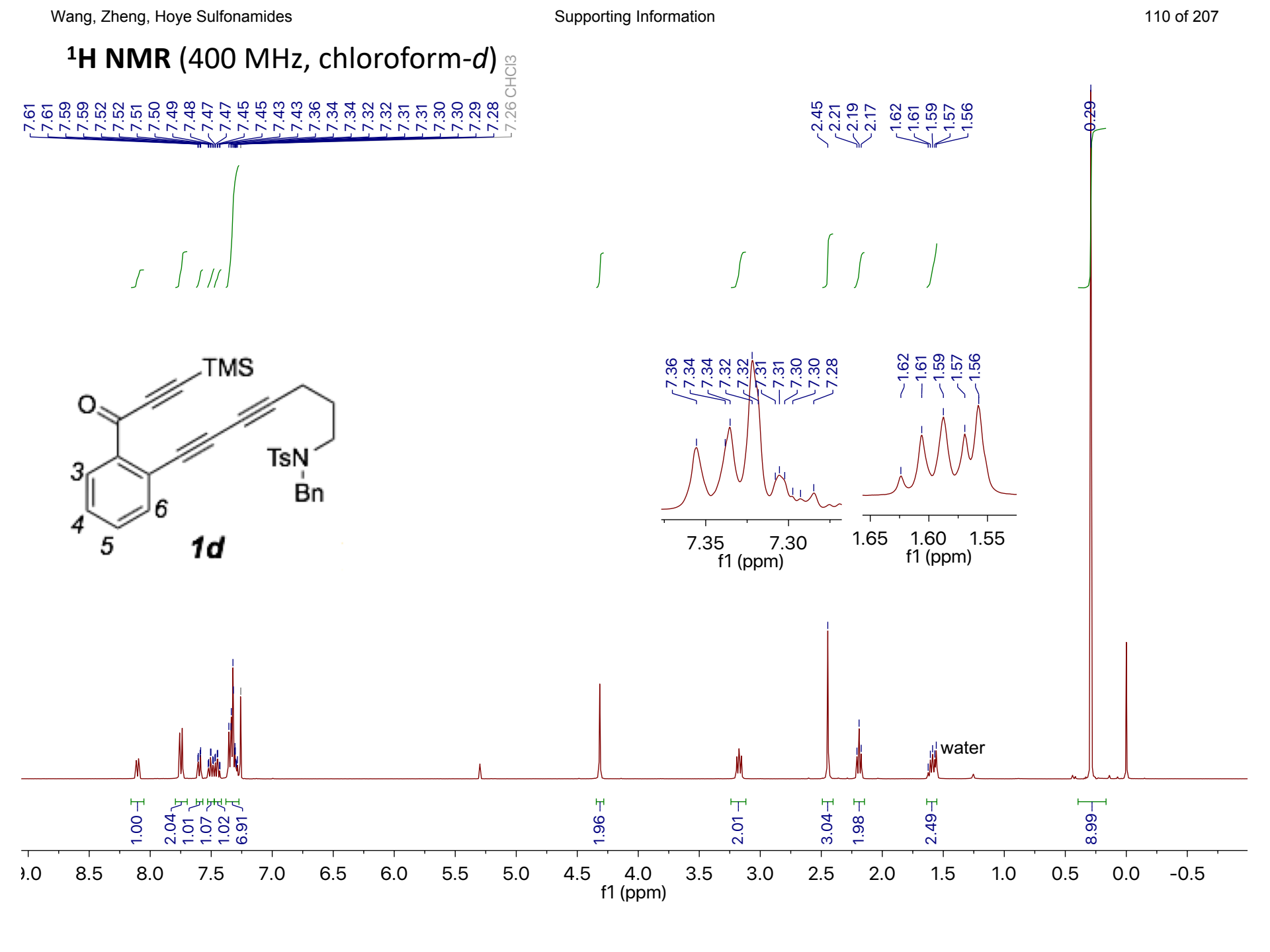
^{1}H NMR (400 MHz, chloroform-*d*)



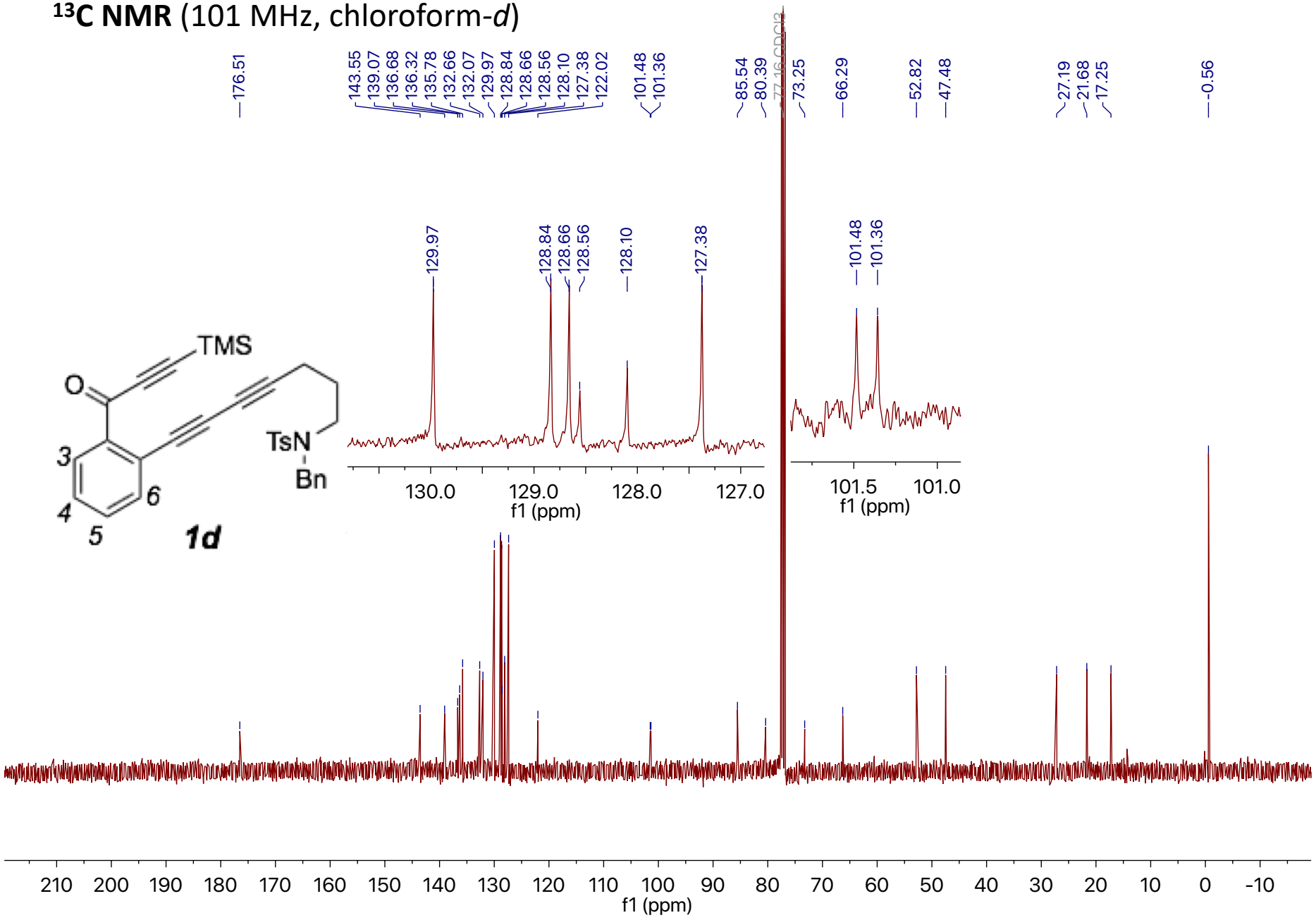
^{13}C NMR (101 MHz, chloroform-*d*)



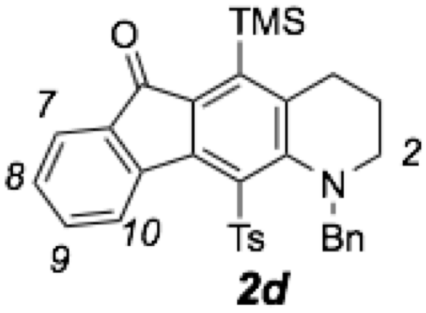
^{1}H NMR (400 MHz, chloroform-*d*)



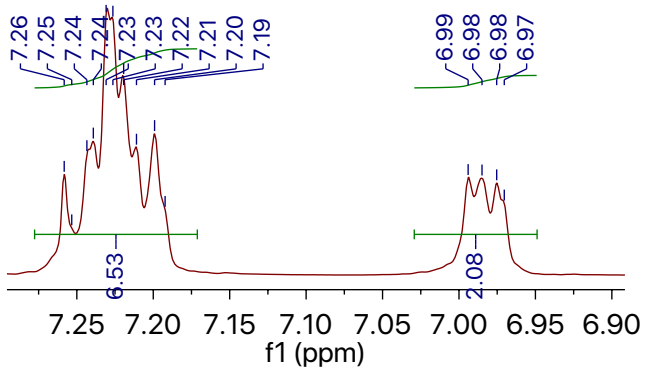
^{13}C NMR (101 MHz, chloroform-*d*)



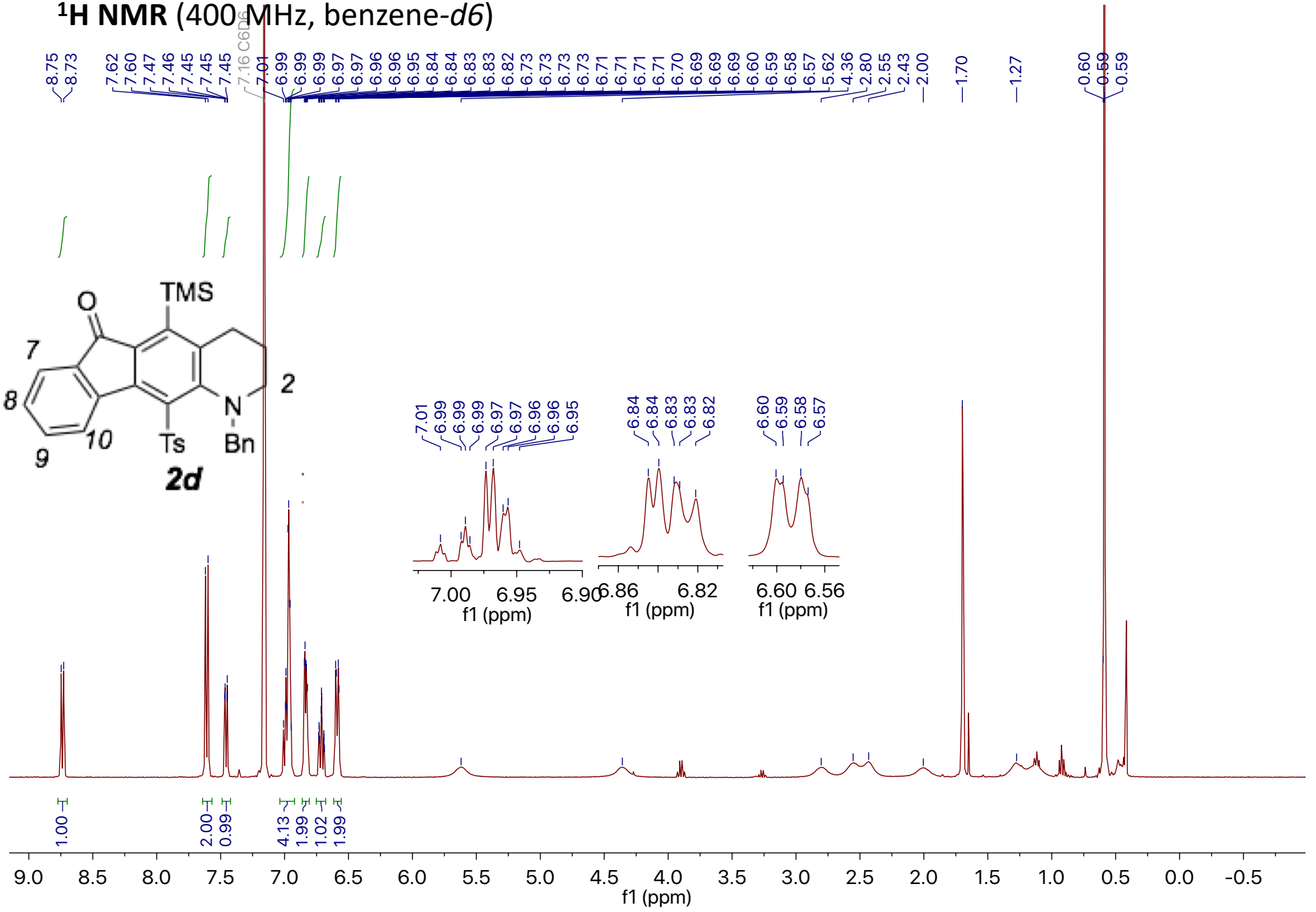
^{1}H NMR (400 MHz, chloroform-*d*)



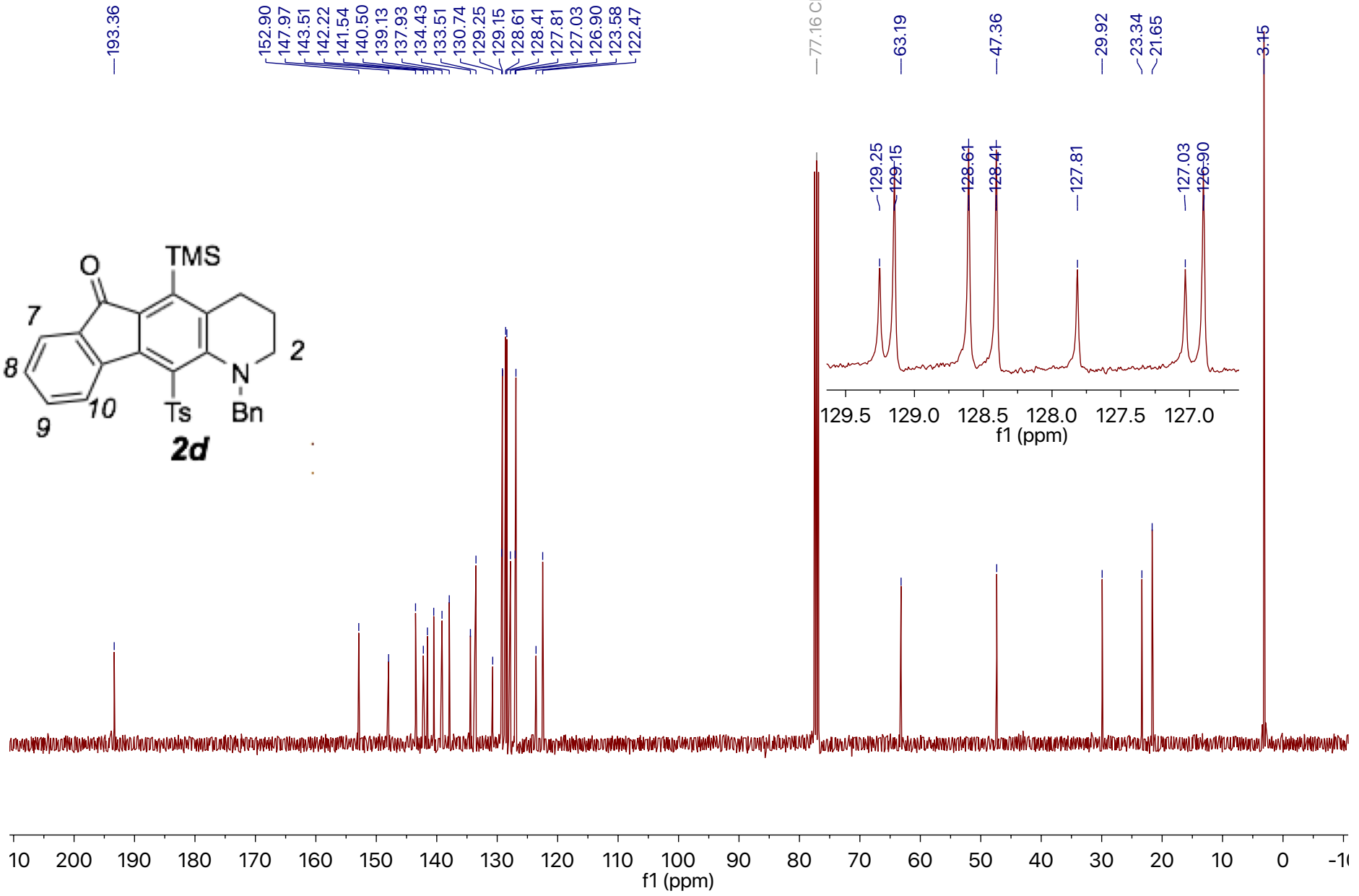
2d



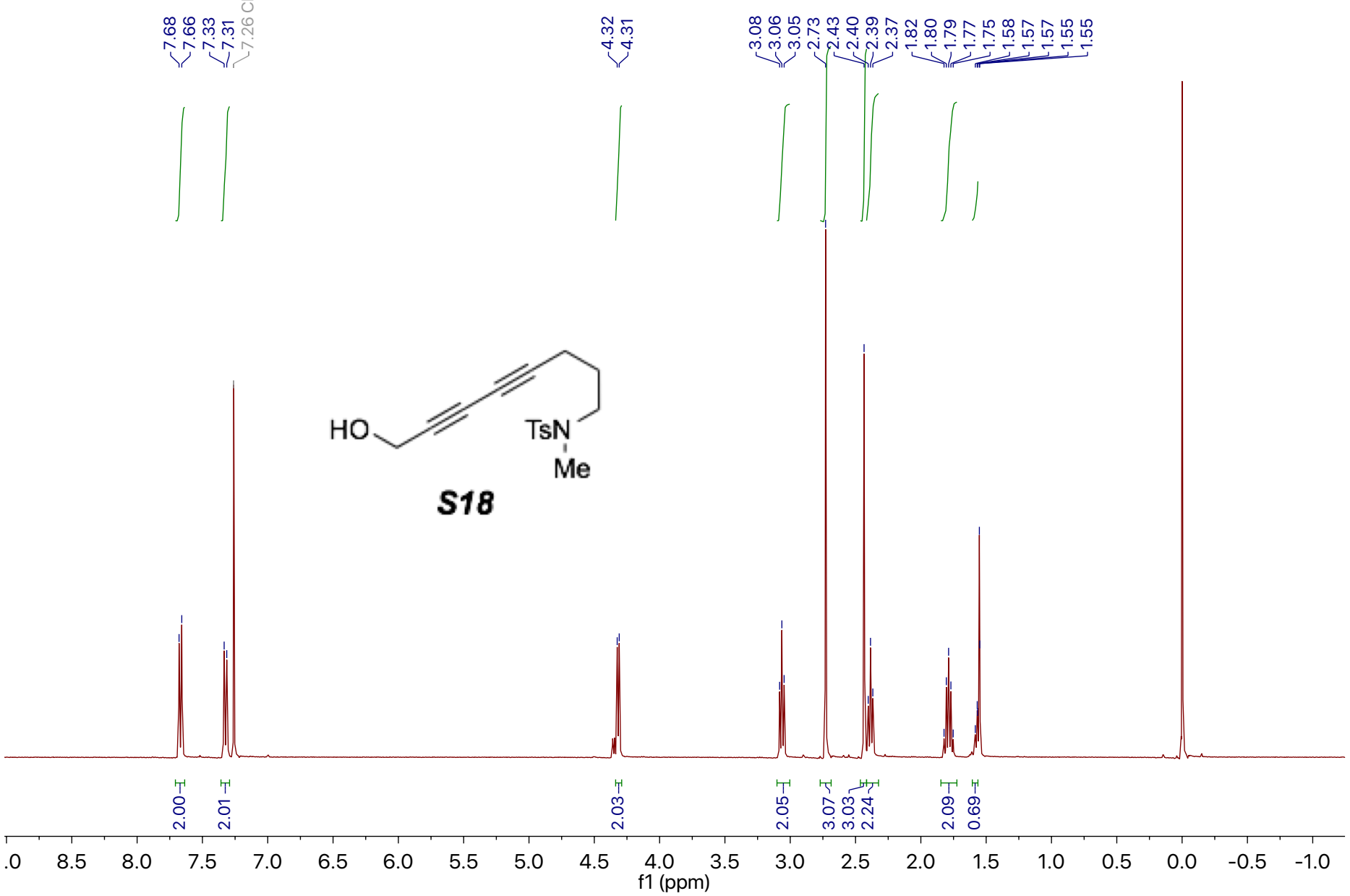
^{1}H NMR (400 MHz, benzene-*d6*)



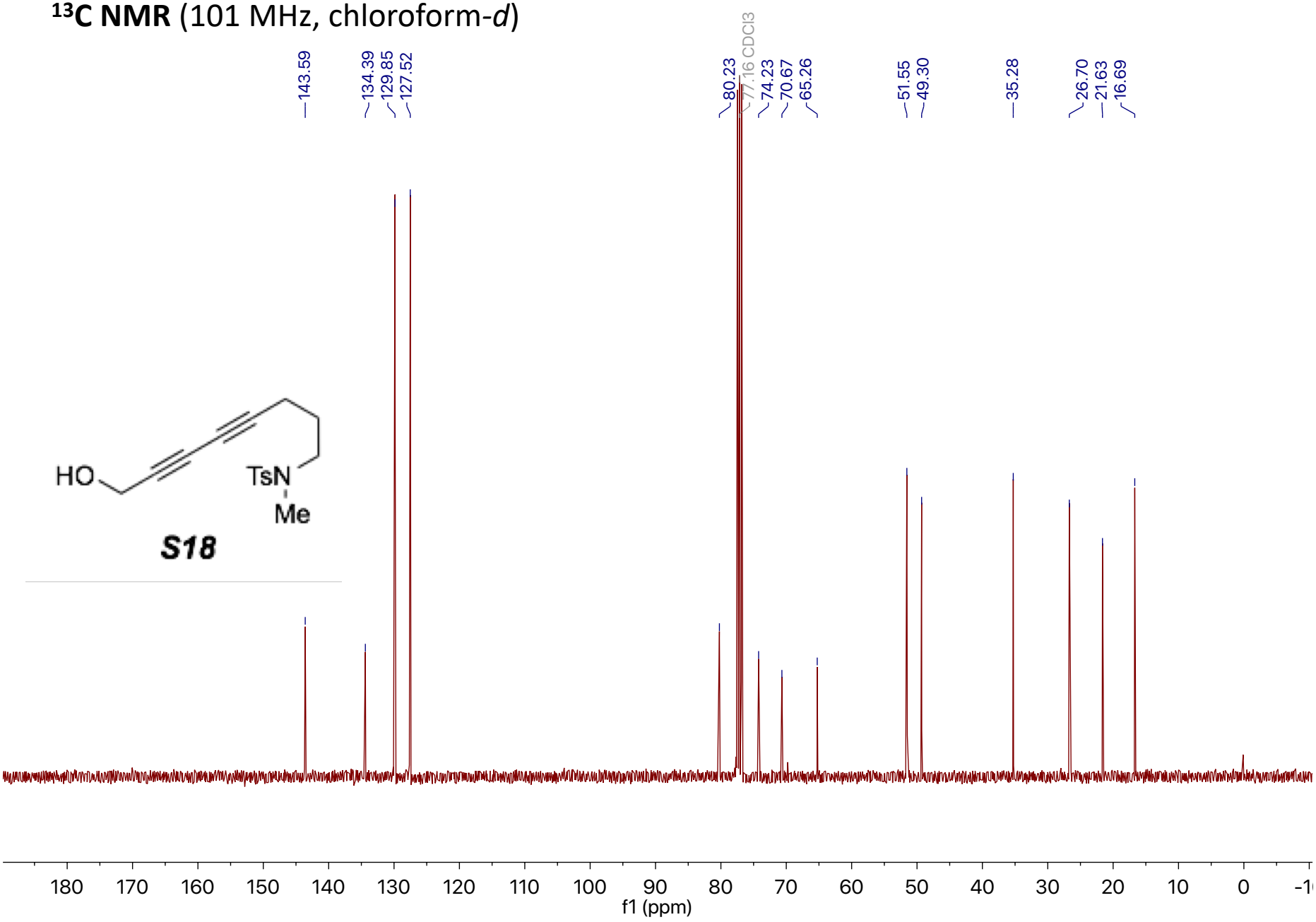
^{13}C NMR (101 MHz, chloroform-*d*)



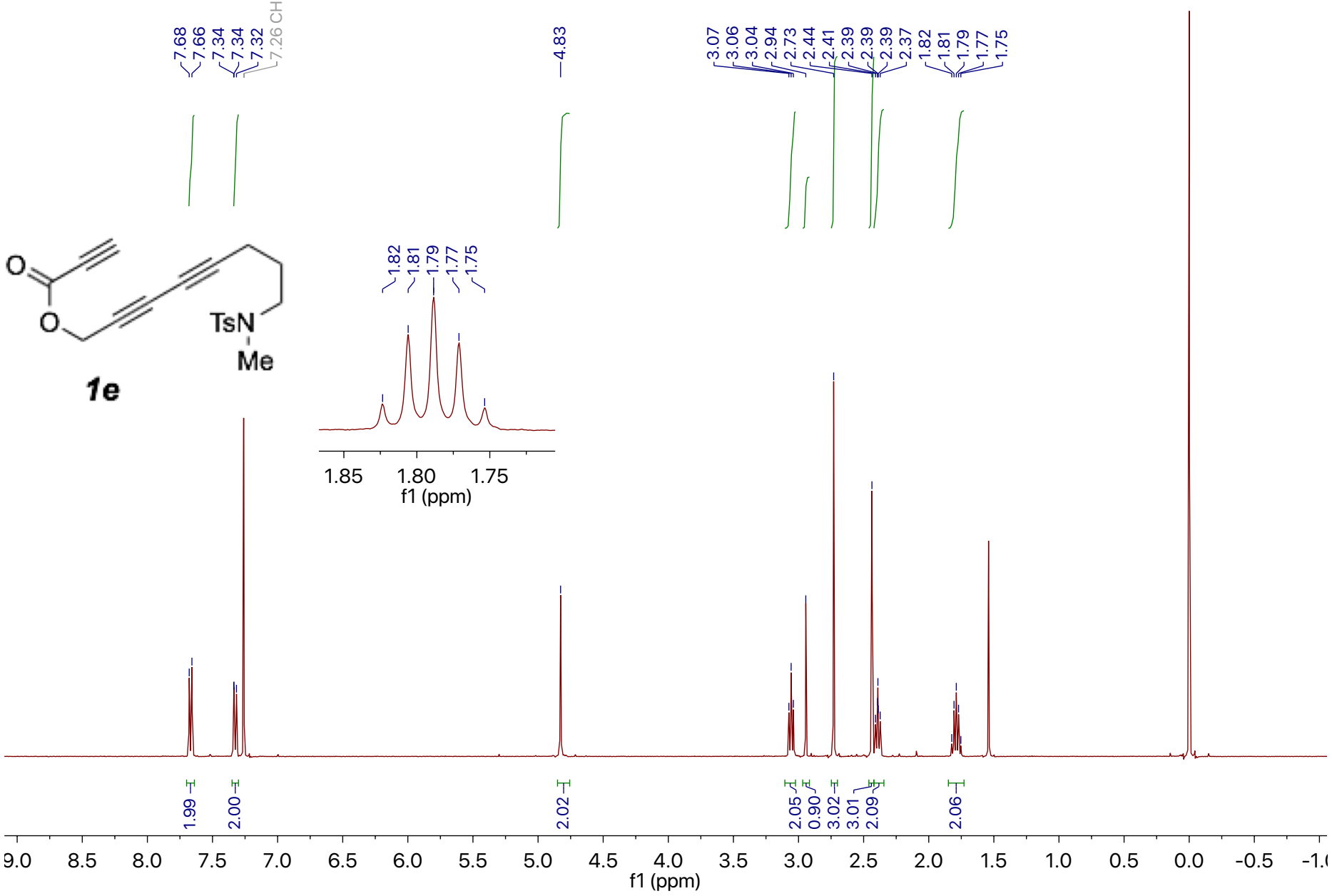
^{1}H NMR (400 MHz, chloroform-*d*)



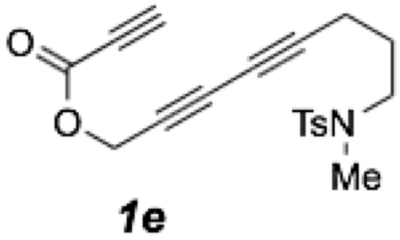
^{13}C NMR (101 MHz, chloroform-*d*)



^{1}H NMR (400 MHz, chloroform-*d*)

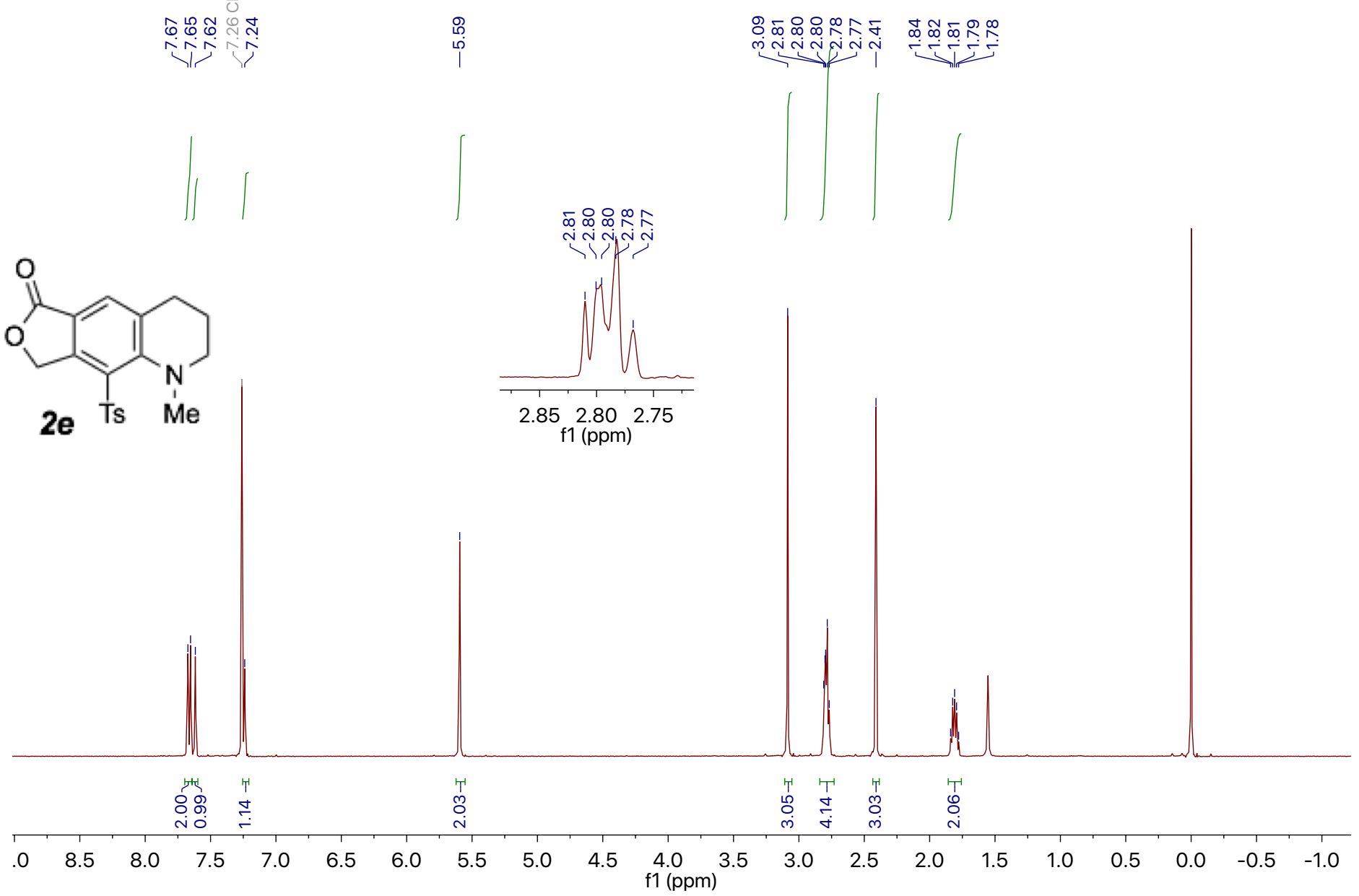


^{13}C NMR (101 MHz, chloroform-*d*)

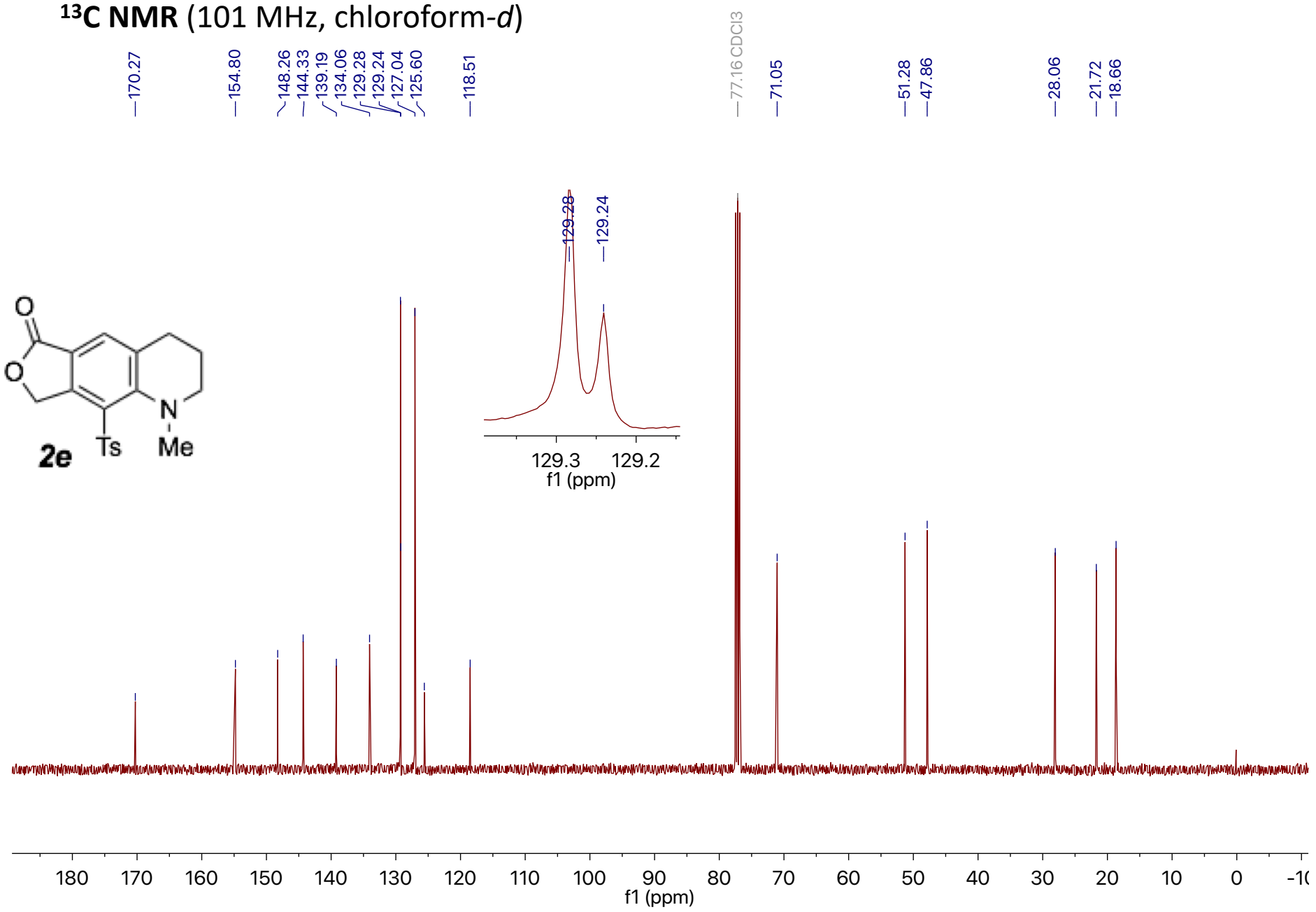


1e

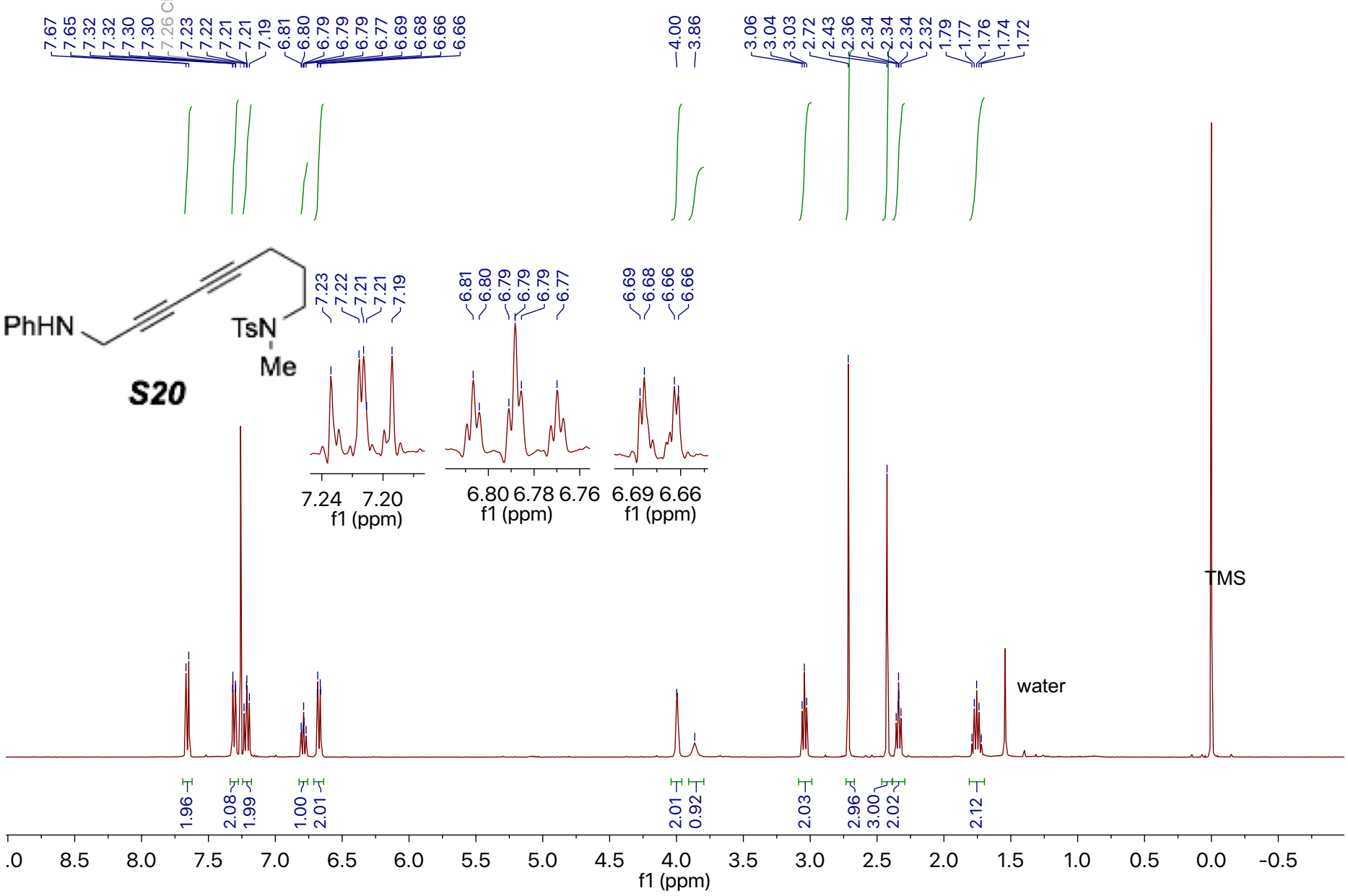
^{1}H NMR (400 MHz, chloroform-*d*)



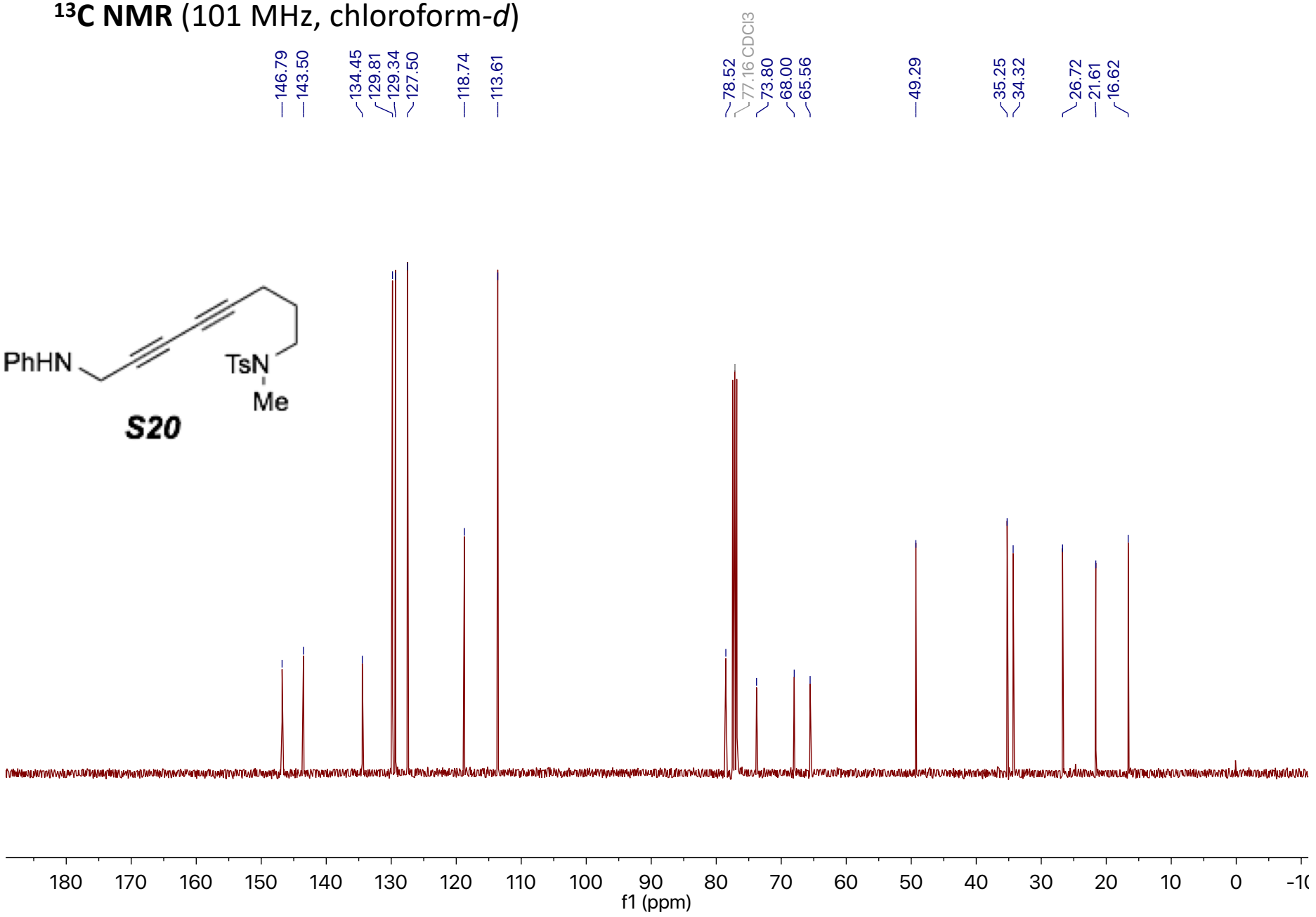
^{13}C NMR (101 MHz, chloroform-*d*)



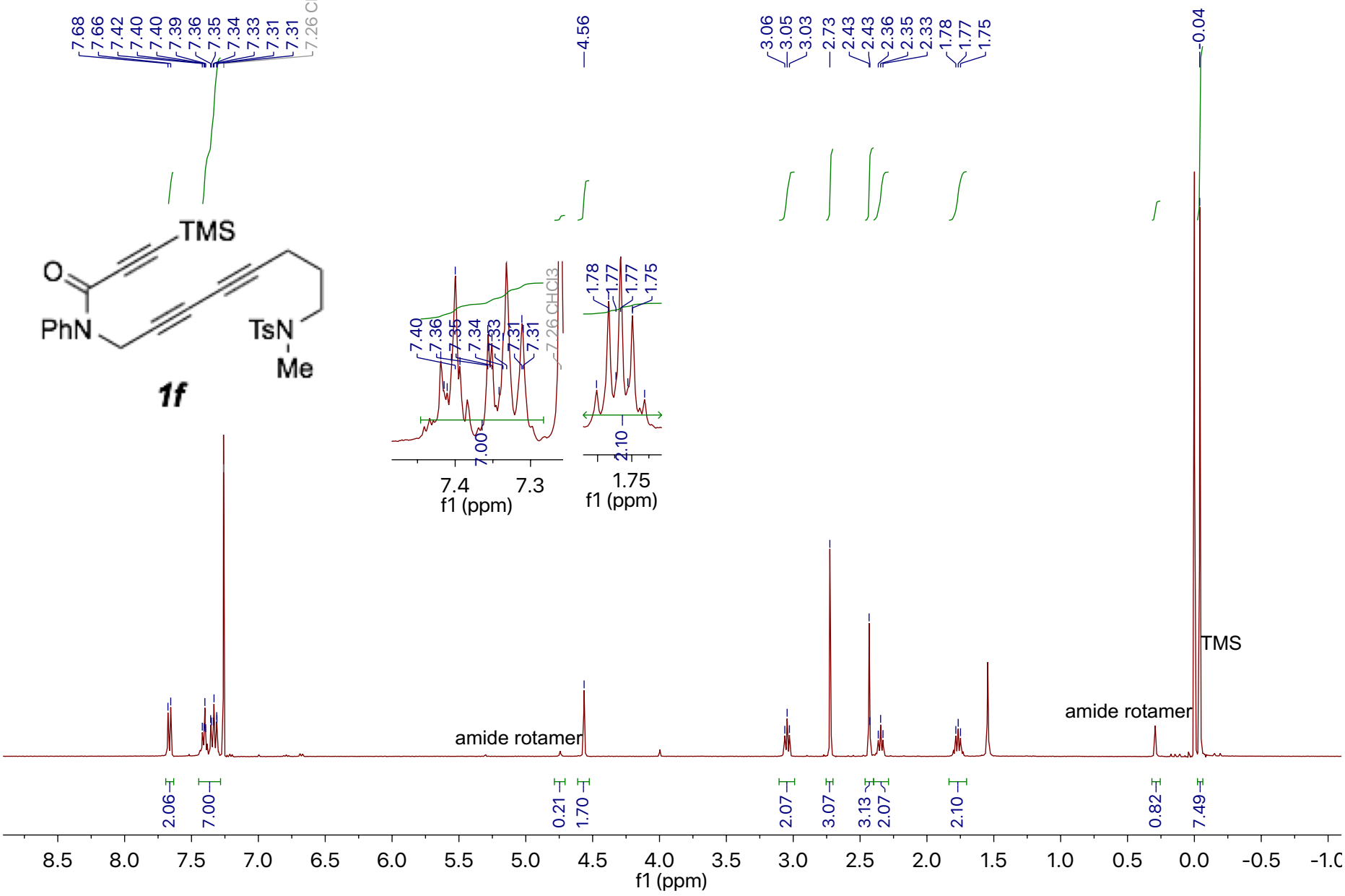
^{1}H NMR (400 MHz, chloroform-*d*)



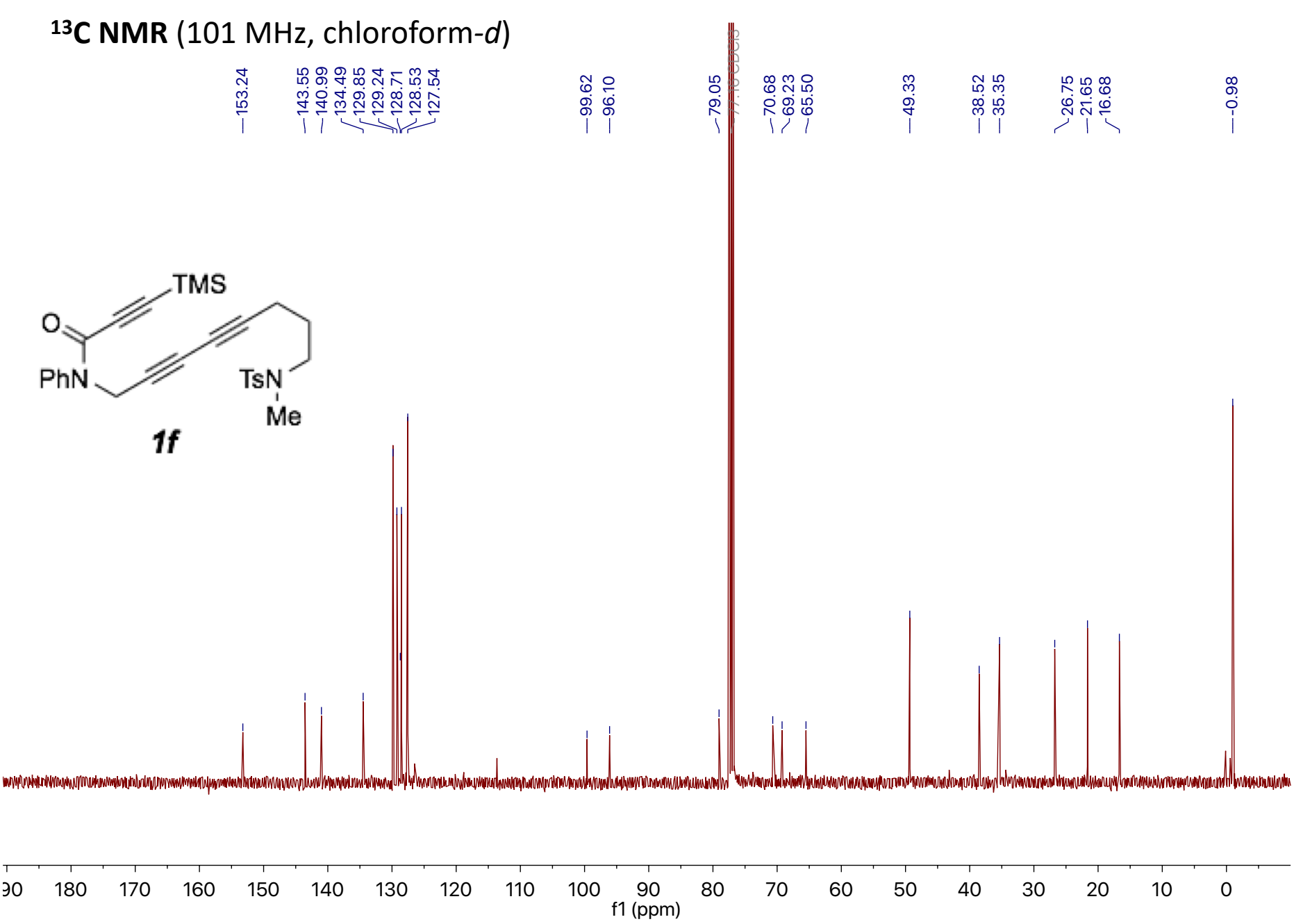
^{13}C NMR (101 MHz, chloroform-*d*)



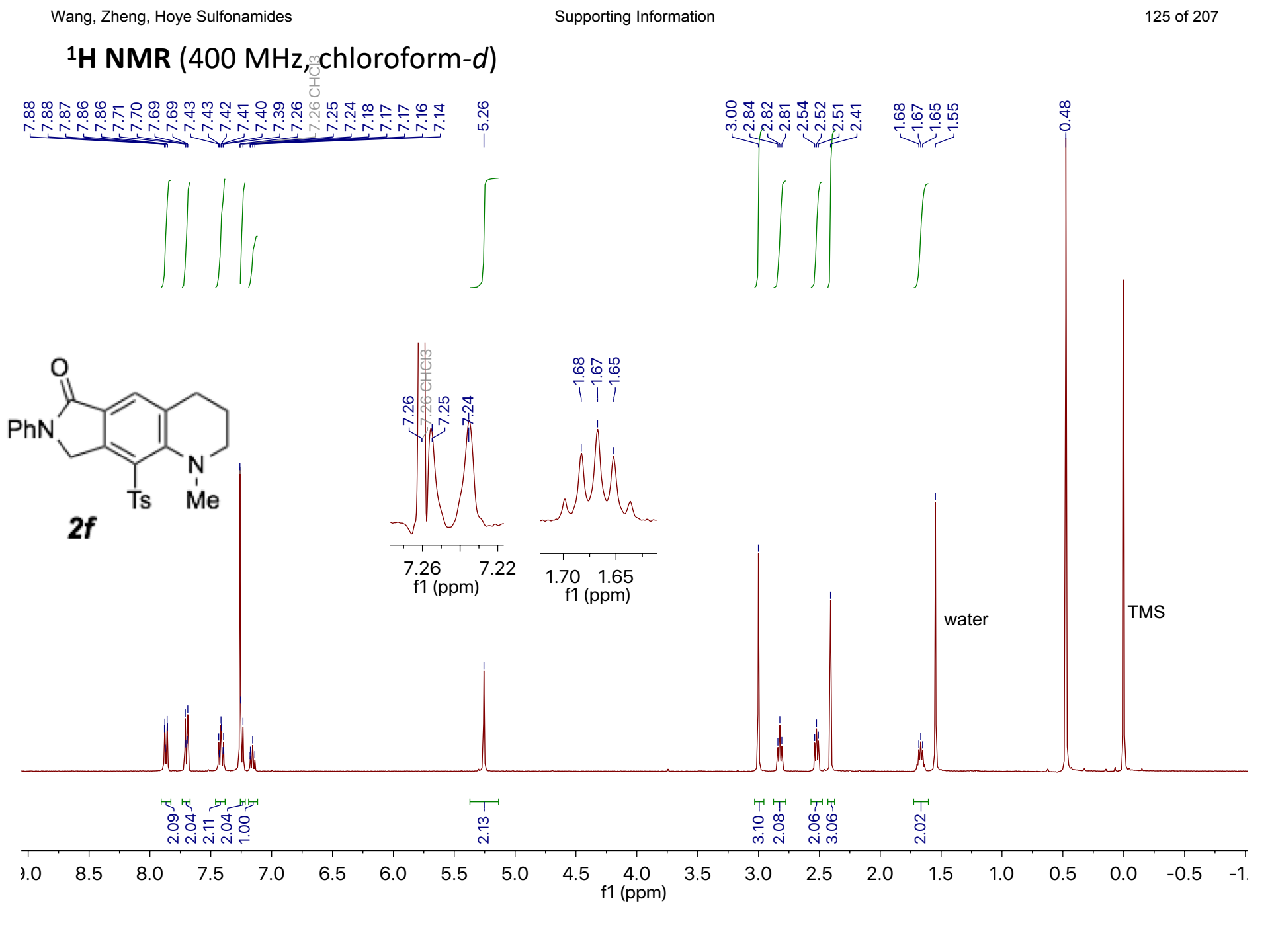
^{1}H NMR (400 MHz, chloroform-*d*)



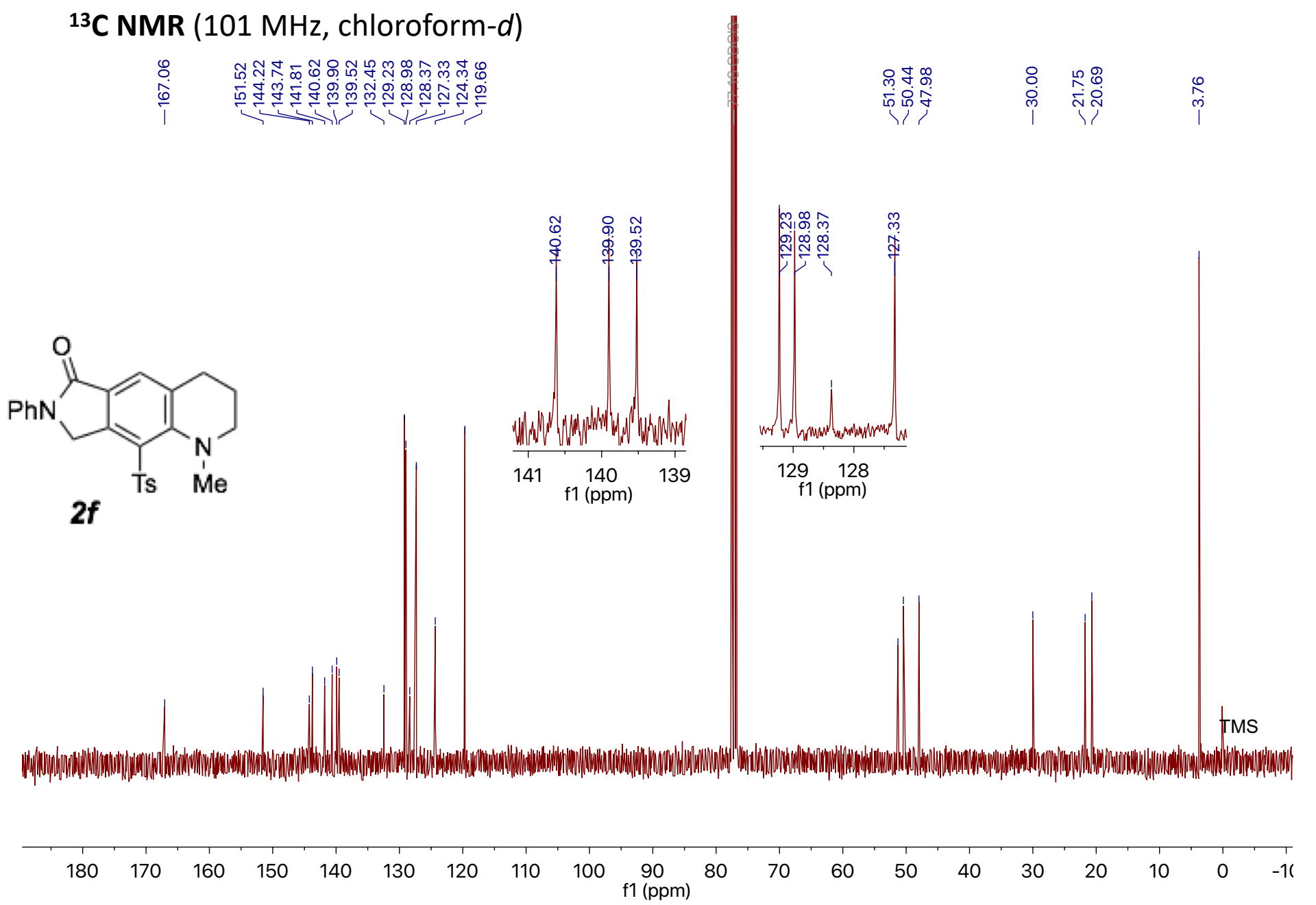
^{13}C NMR (101 MHz, chloroform-*d*)



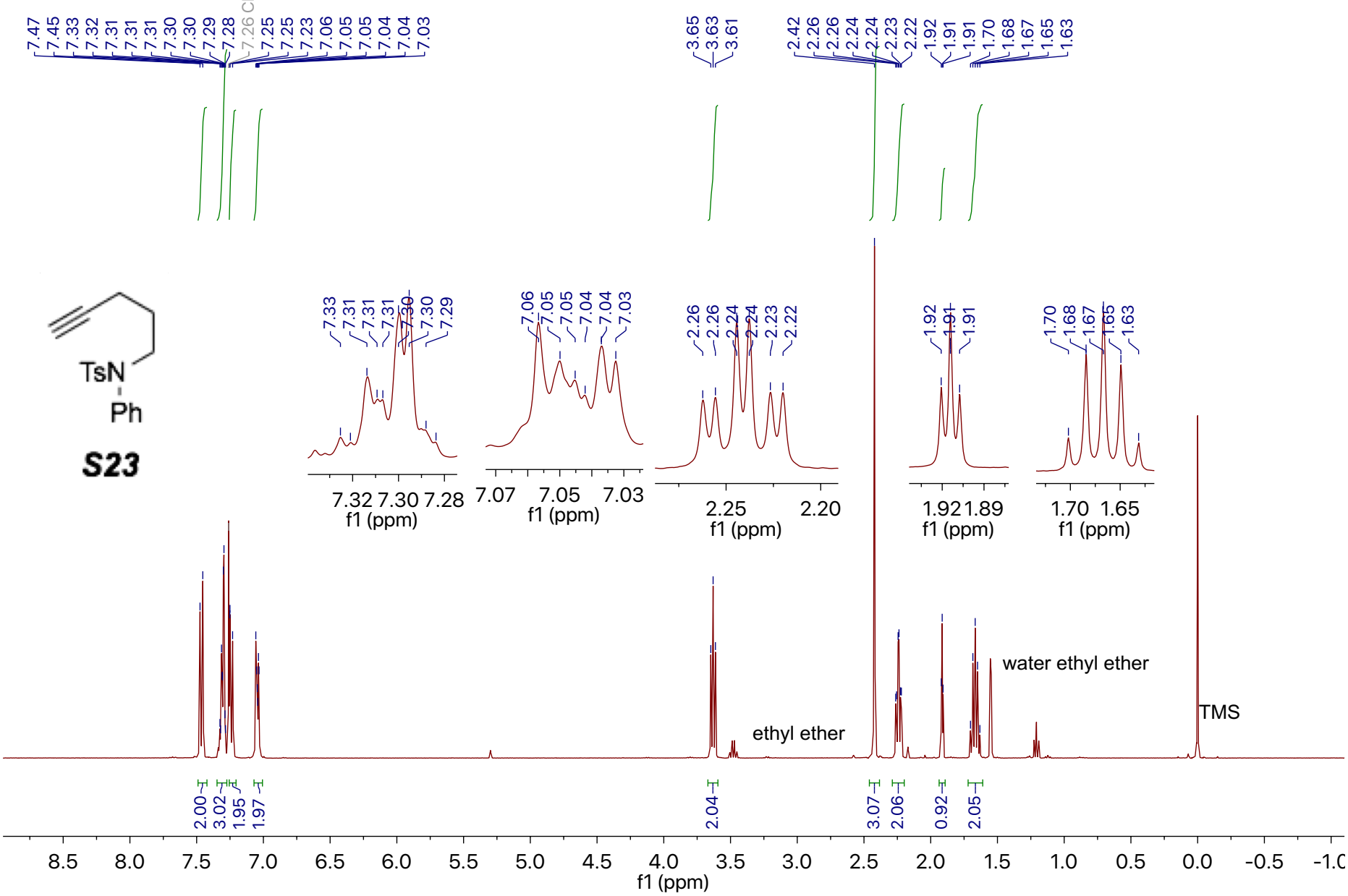
^{1}H NMR (400 MHz, chloroform-*d*)



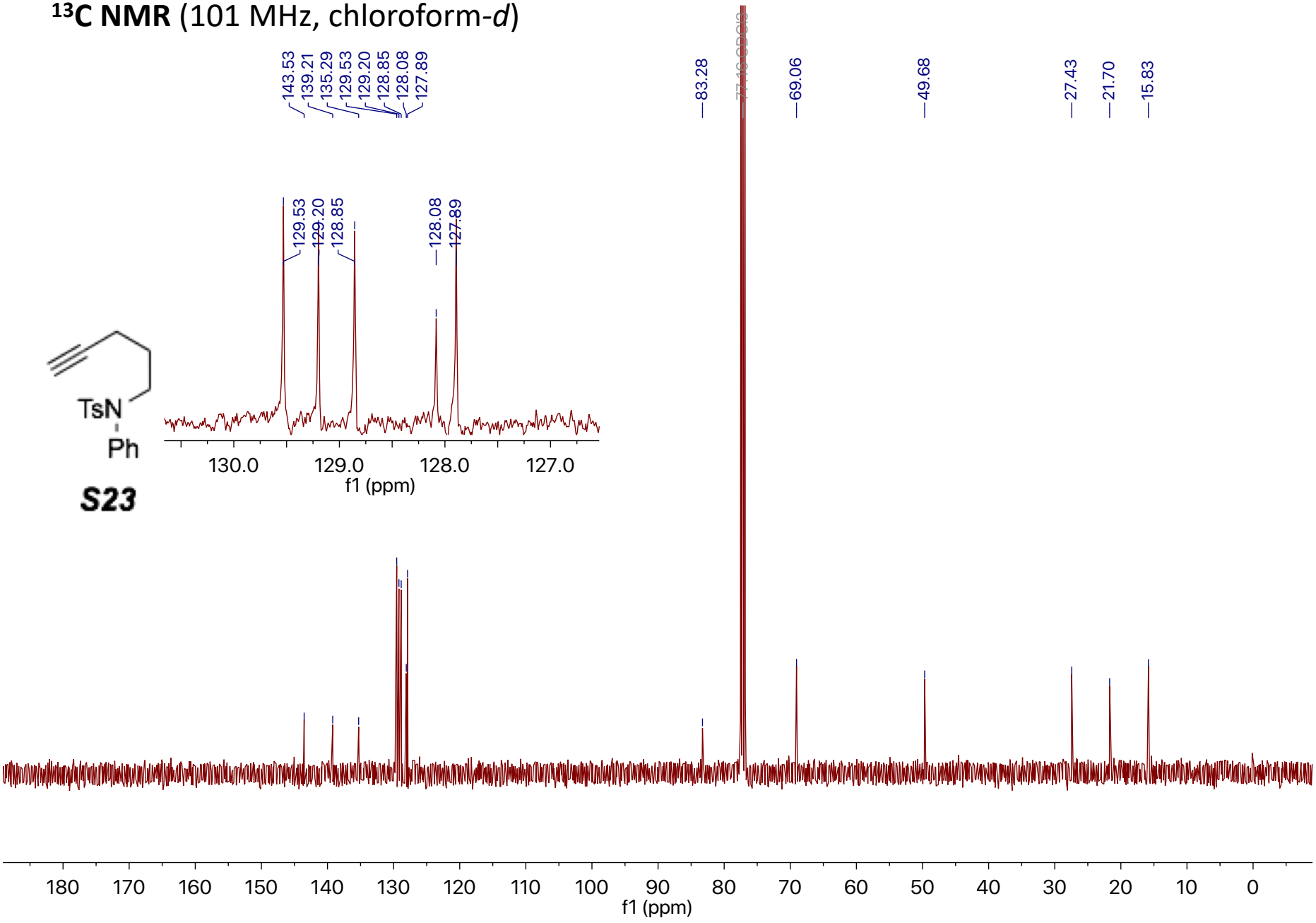
^{13}C NMR (101 MHz, chloroform-*d*)



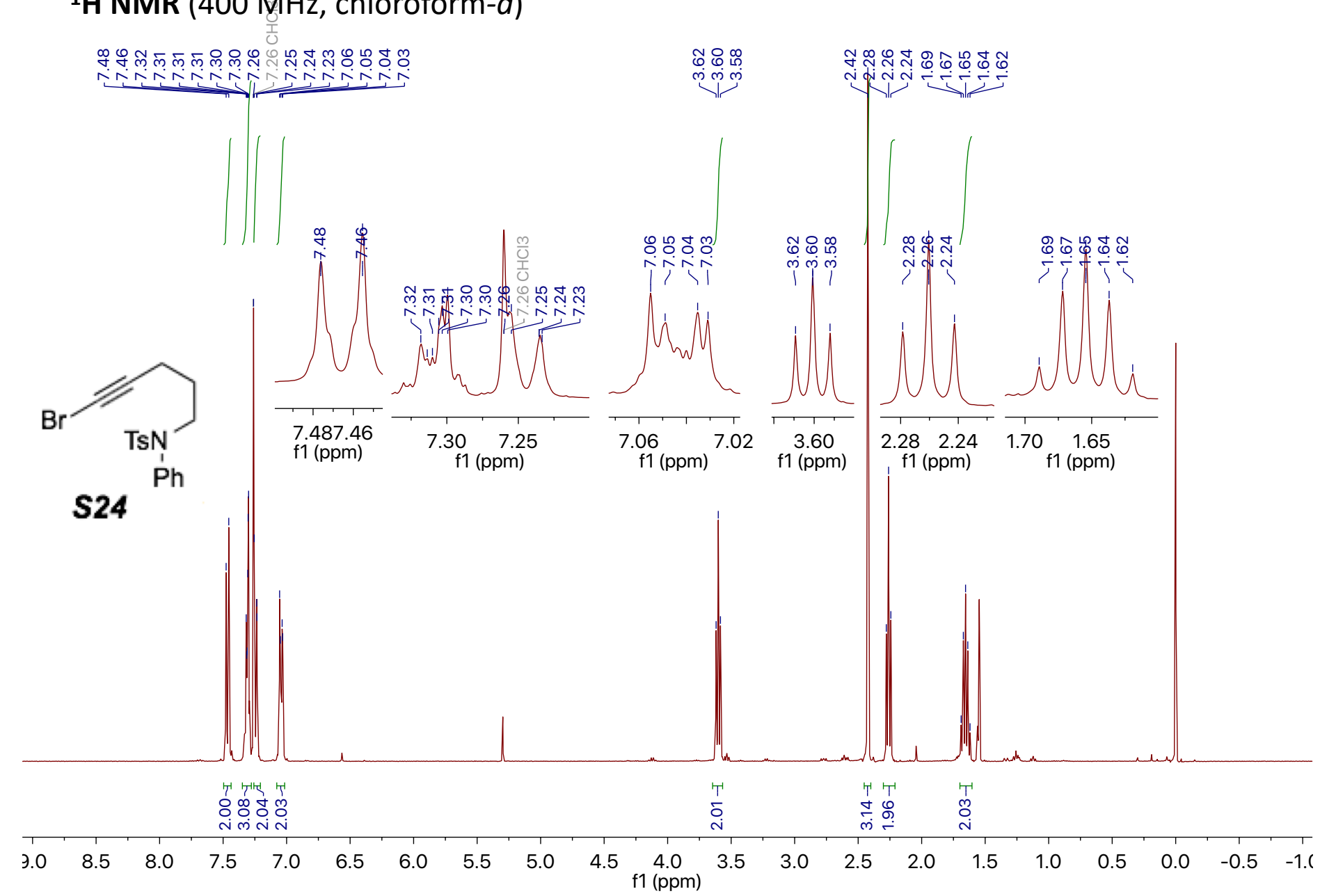
^{1}H NMR (400 MHz, chloroform-*d*)



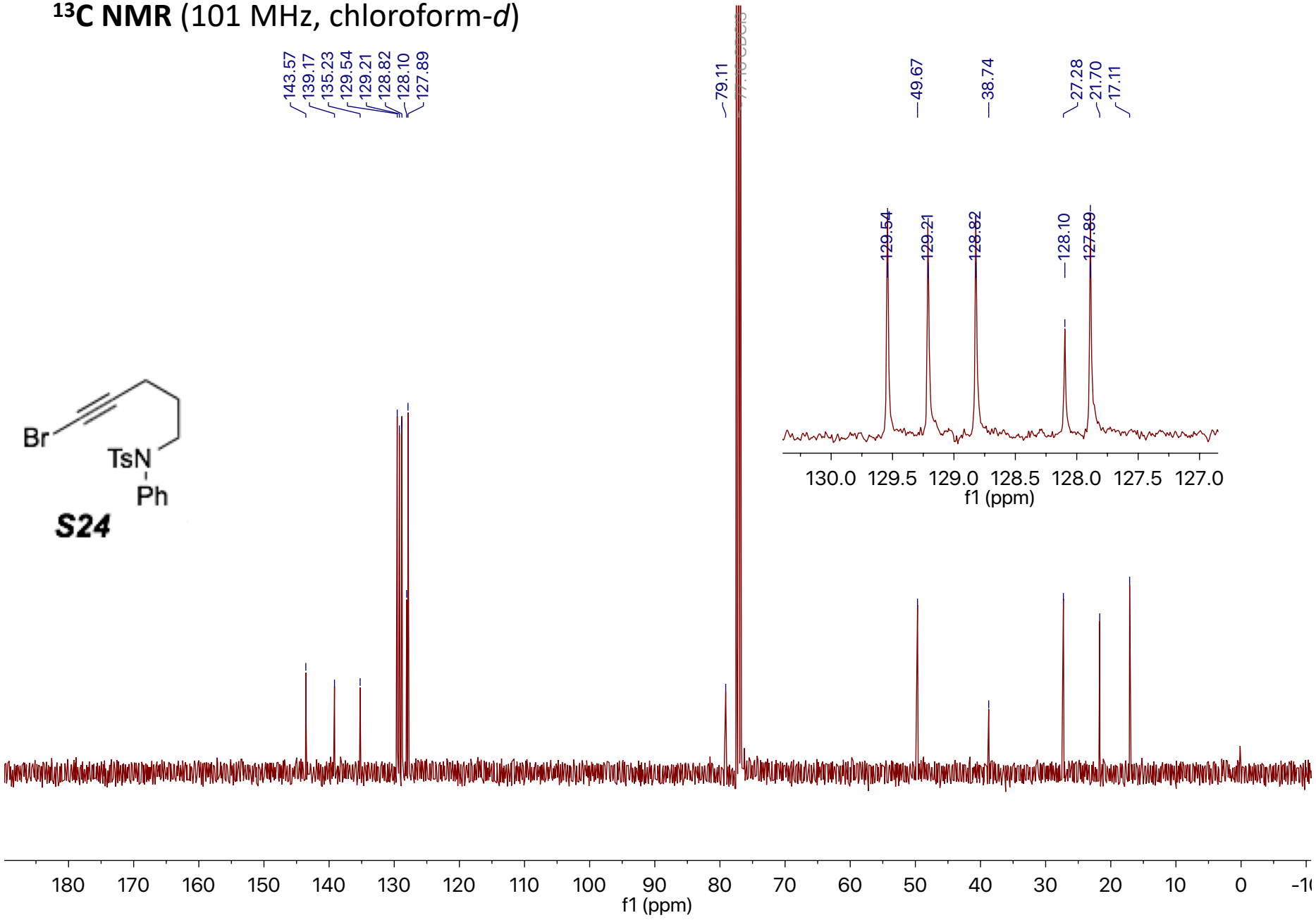
^{13}C NMR (101 MHz, chloroform-*d*)



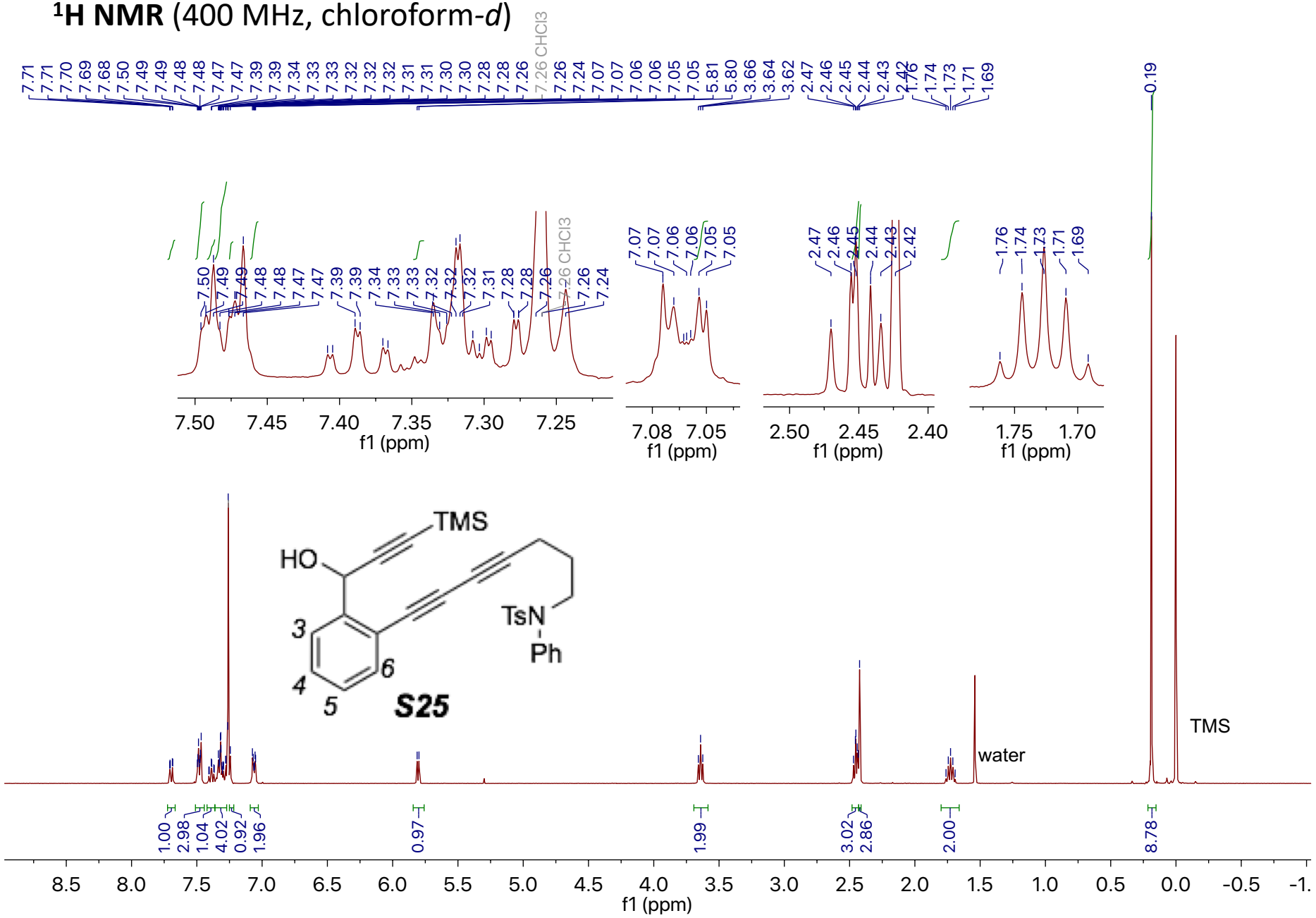
^{1}H NMR (400 MHz, chloroform-*d*)



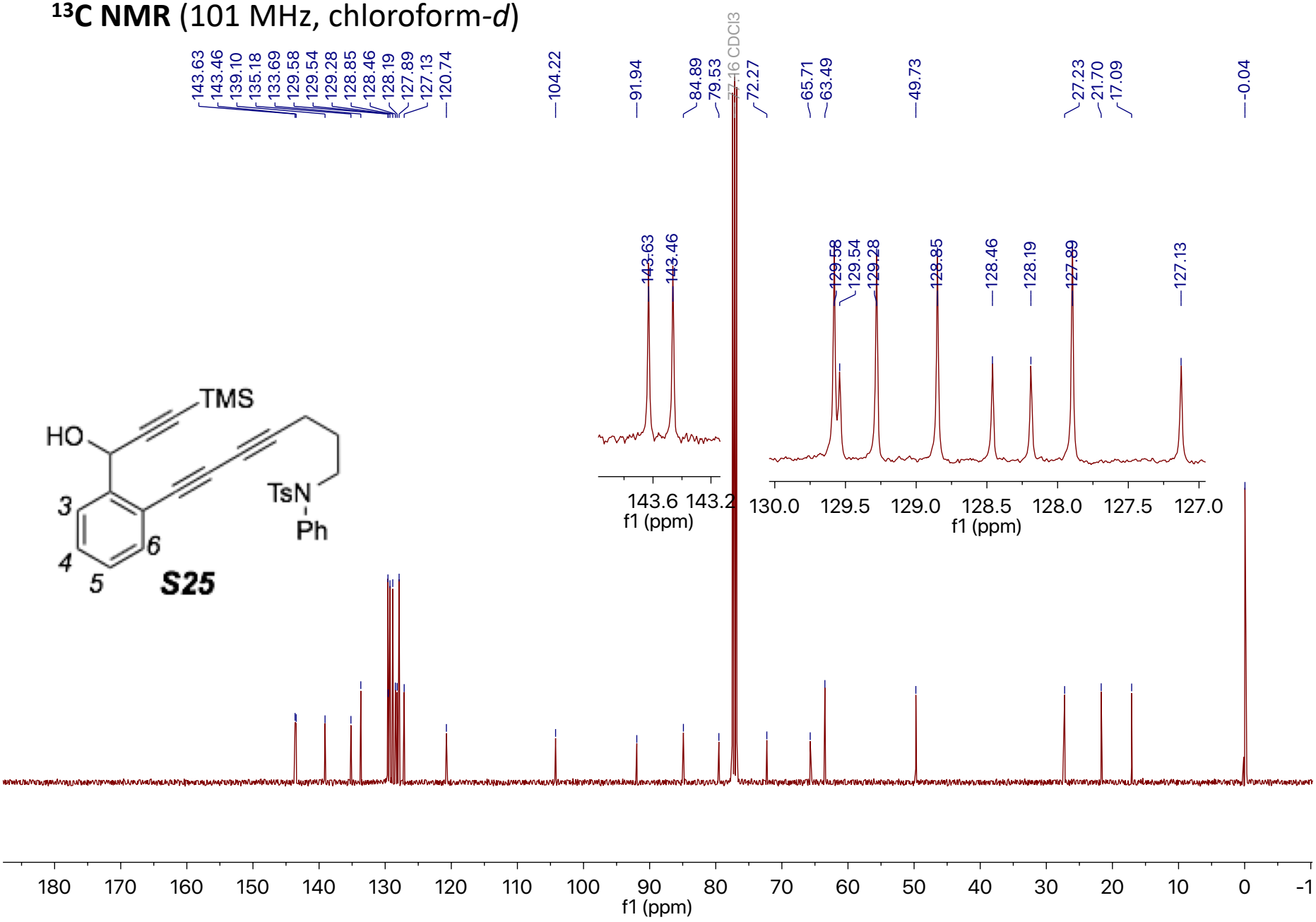
^{13}C NMR (101 MHz, chloroform-*d*)



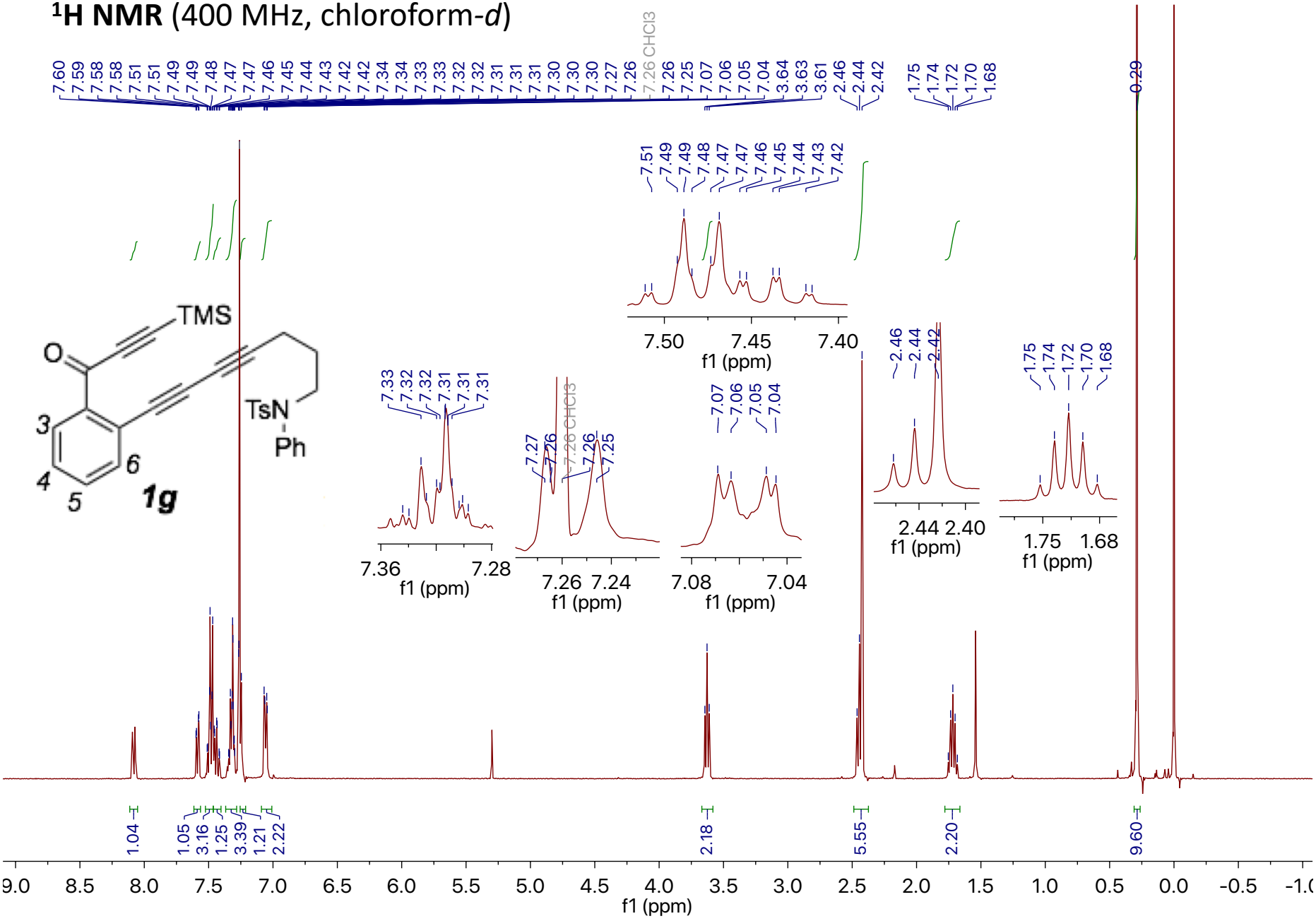
^{1}H NMR (400 MHz, chloroform-*d*)



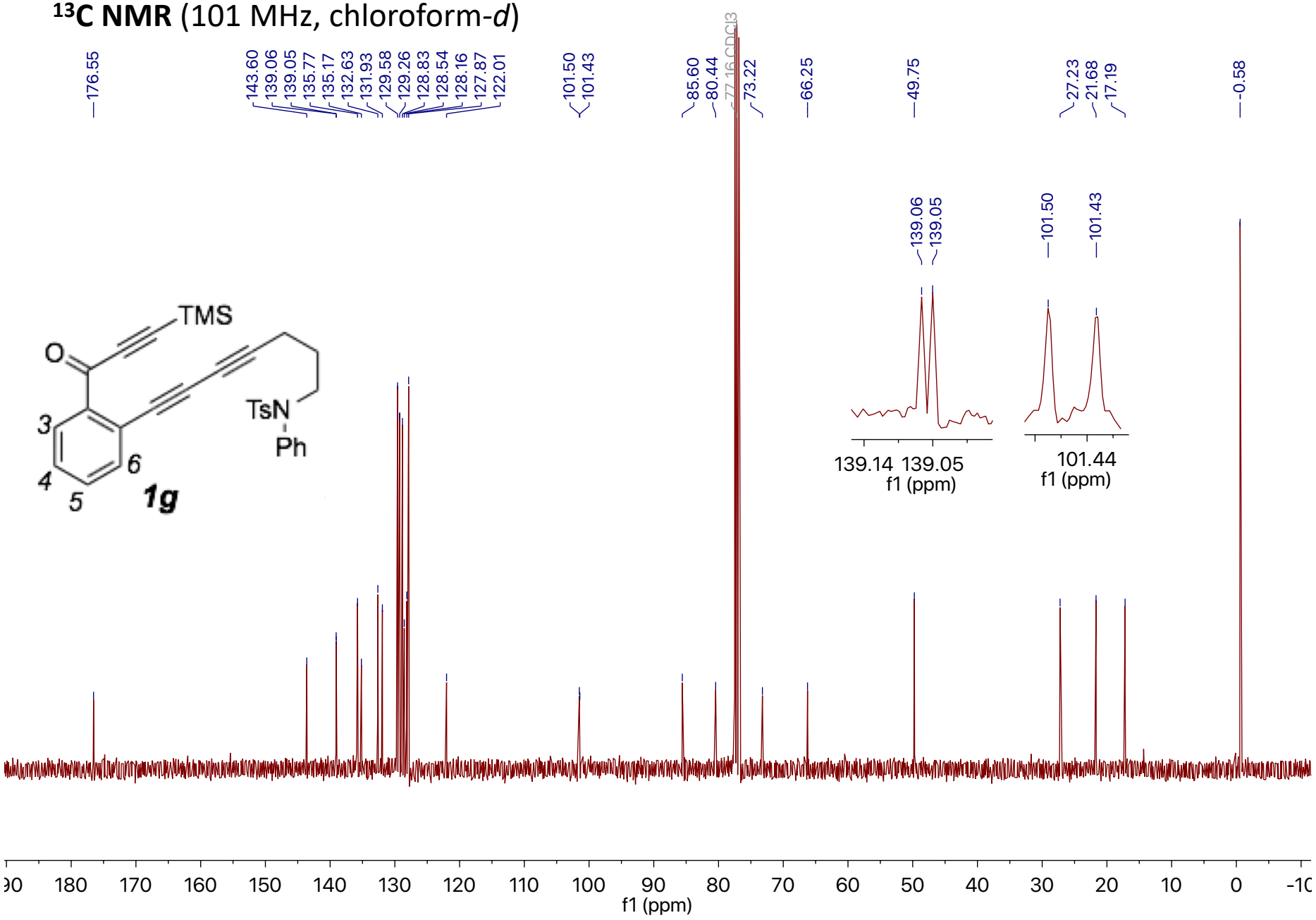
^{13}C NMR (101 MHz, chloroform-*d*)



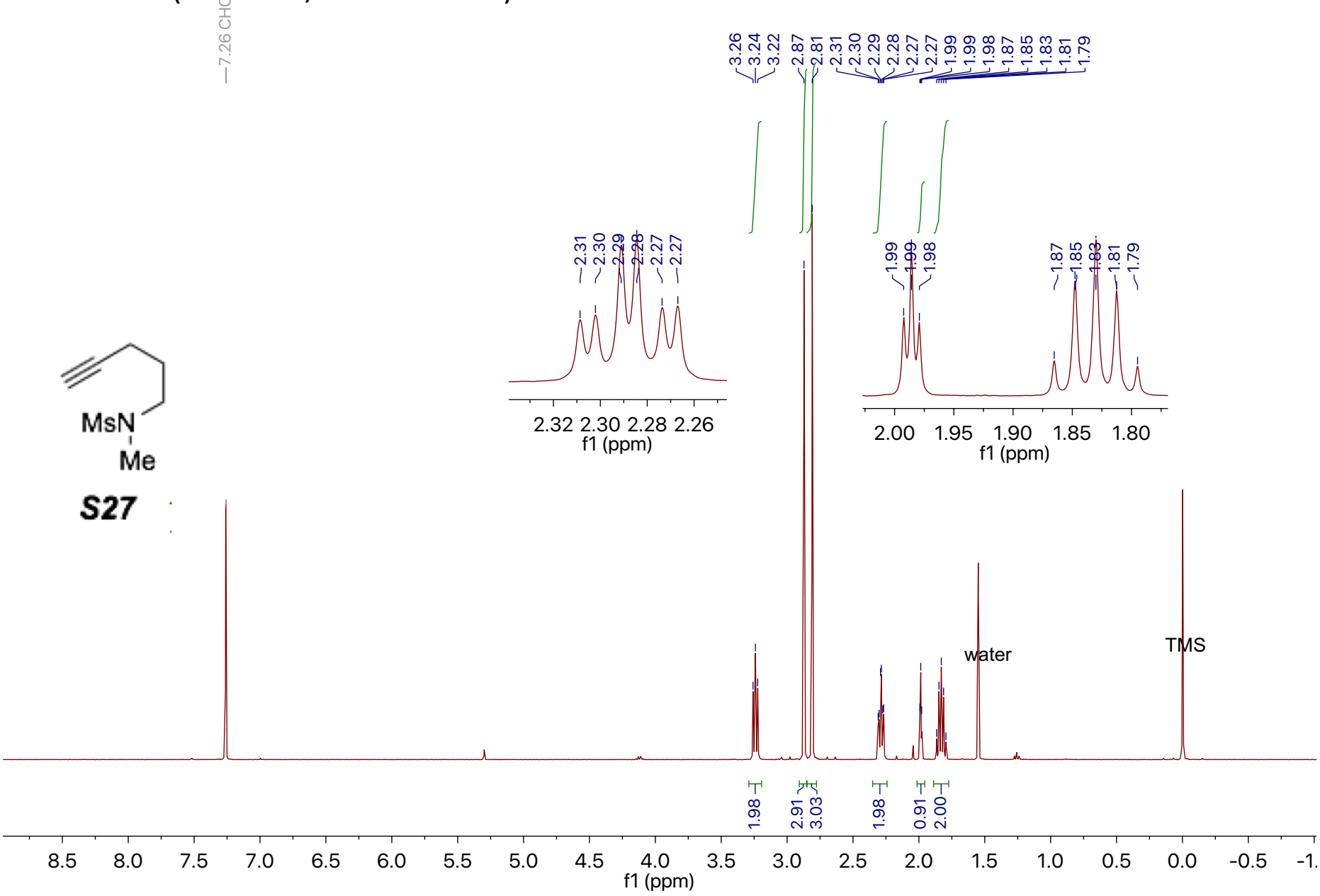
^{1}H NMR (400 MHz, chloroform-*d*)



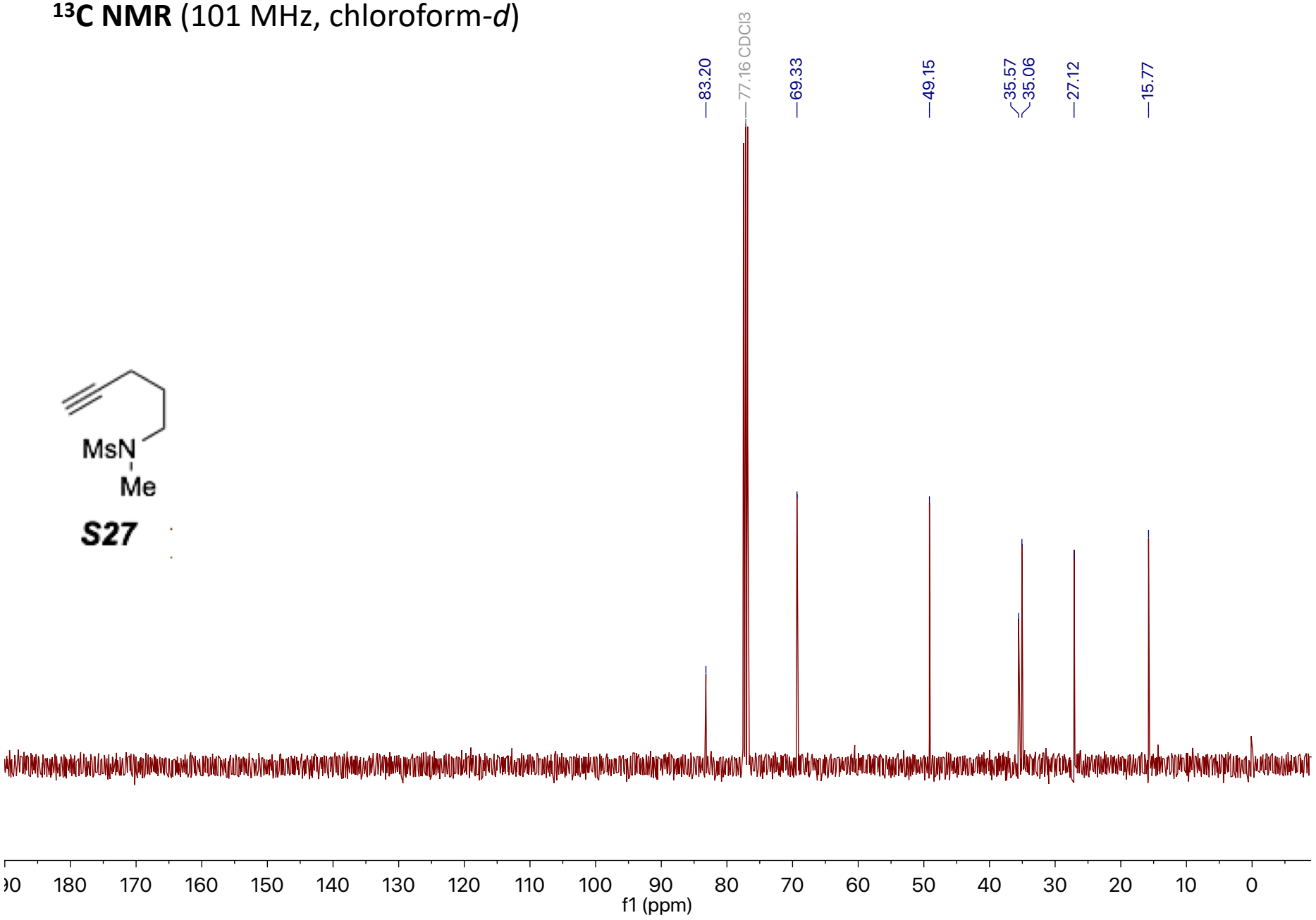
^{13}C NMR (101 MHz, chloroform-*d*)



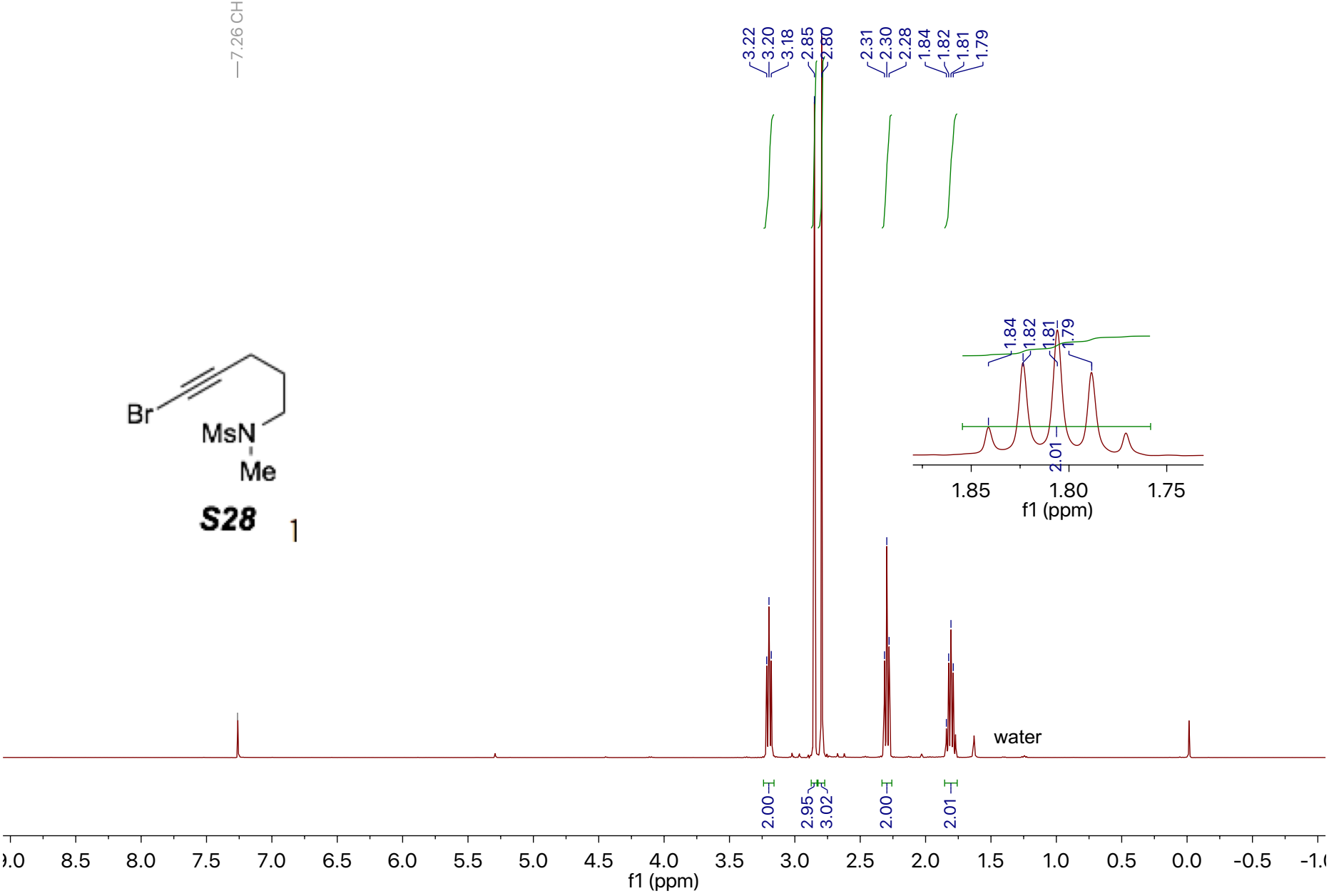
^{1}H NMR (400 MHz, chloroform-*d*)



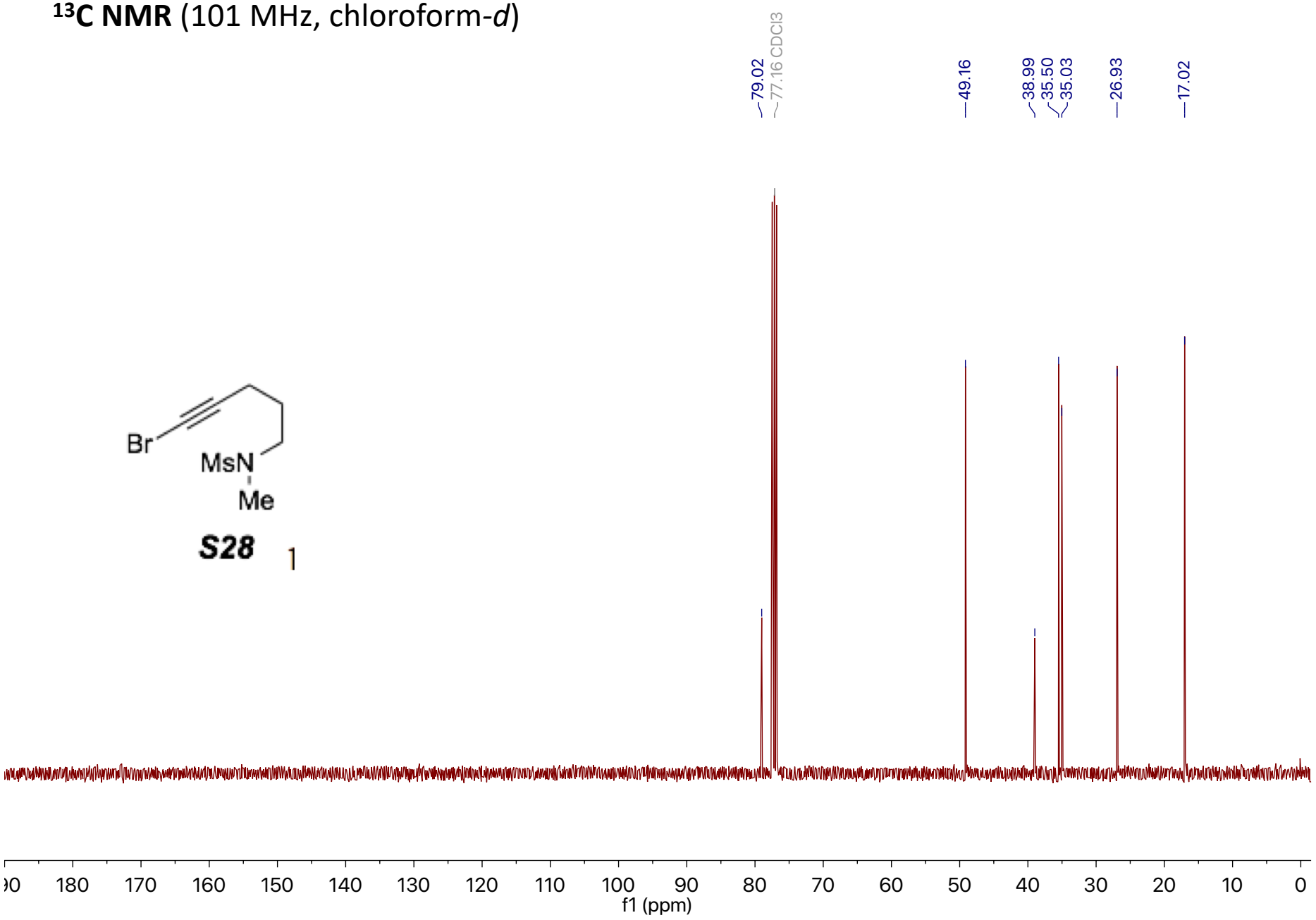
^{13}C NMR (101 MHz, chloroform-*d*)



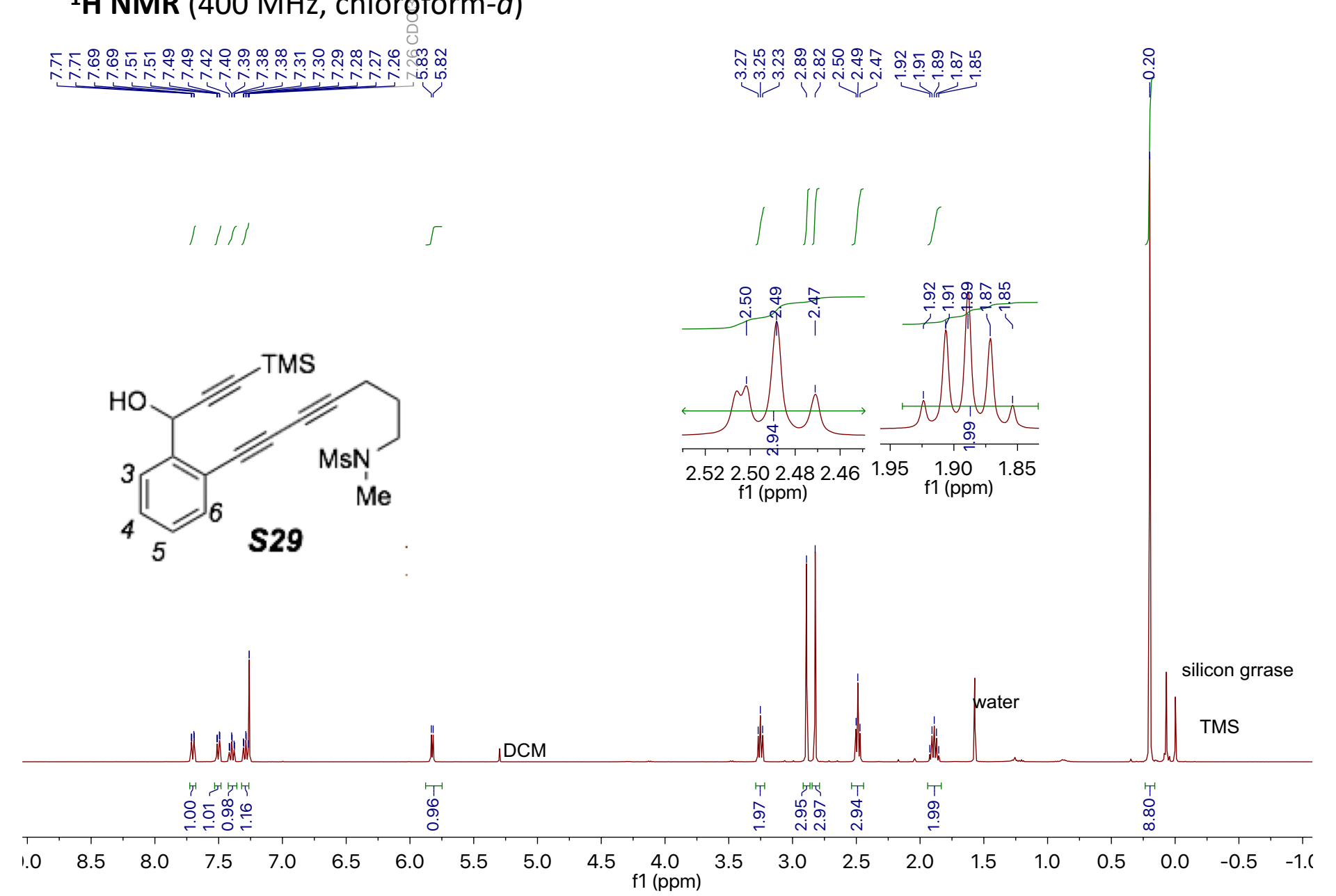
^{1}H NMR (400 MHz, chloroform-*d*)



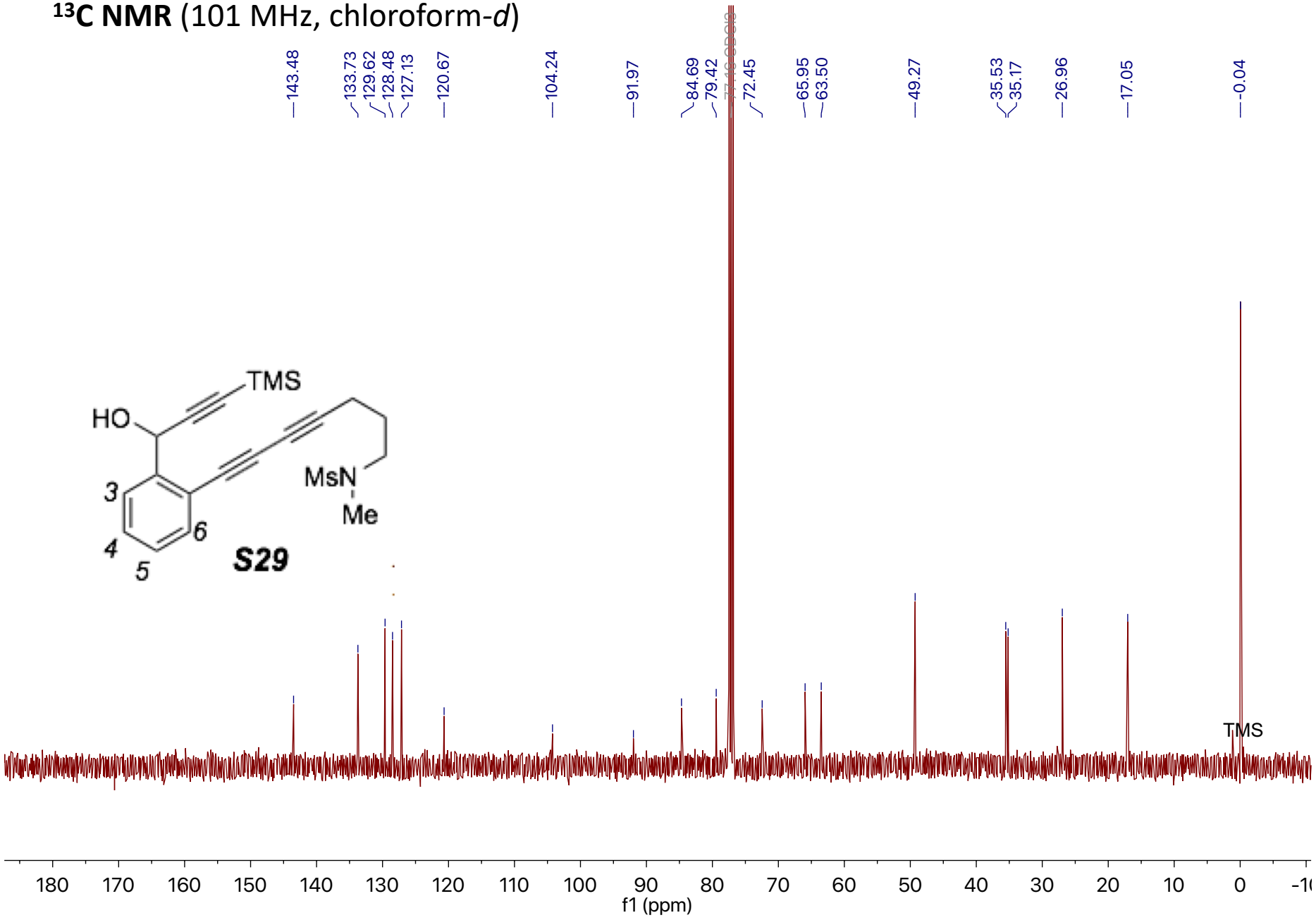
^{13}C NMR (101 MHz, chloroform-*d*)



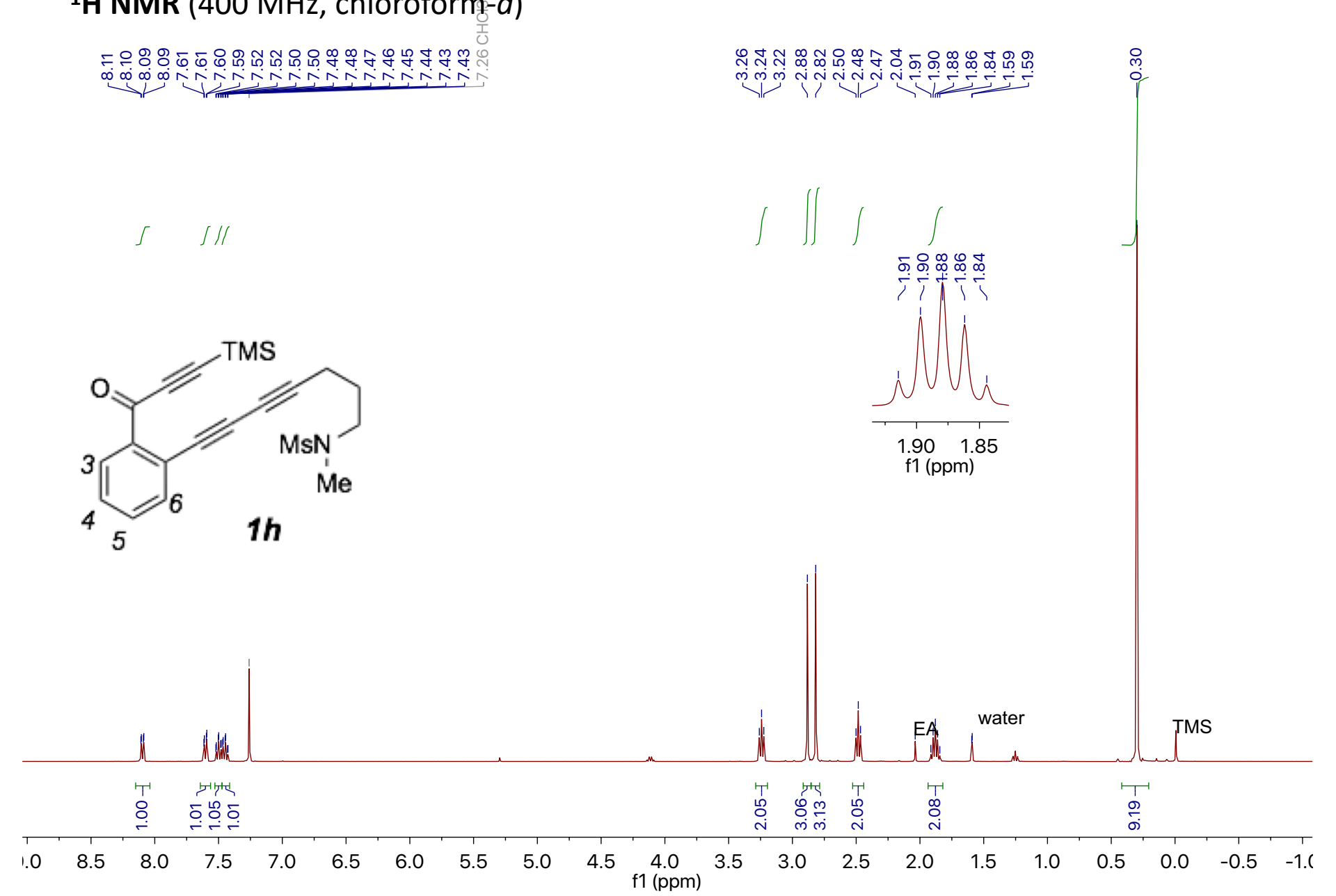
^{1}H NMR (400 MHz, chloroform-*d*)



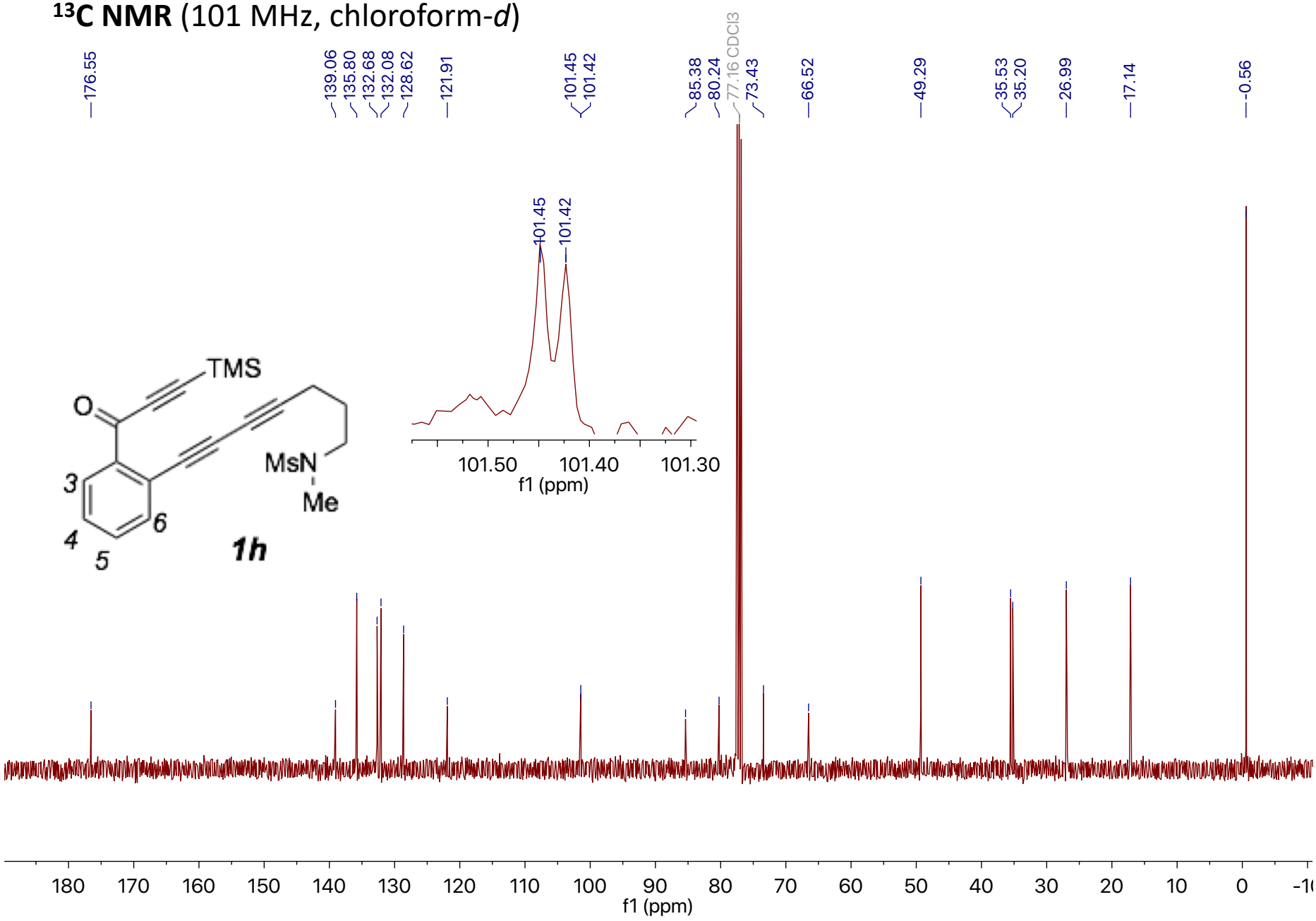
^{13}C NMR (101 MHz, chloroform-*d*)



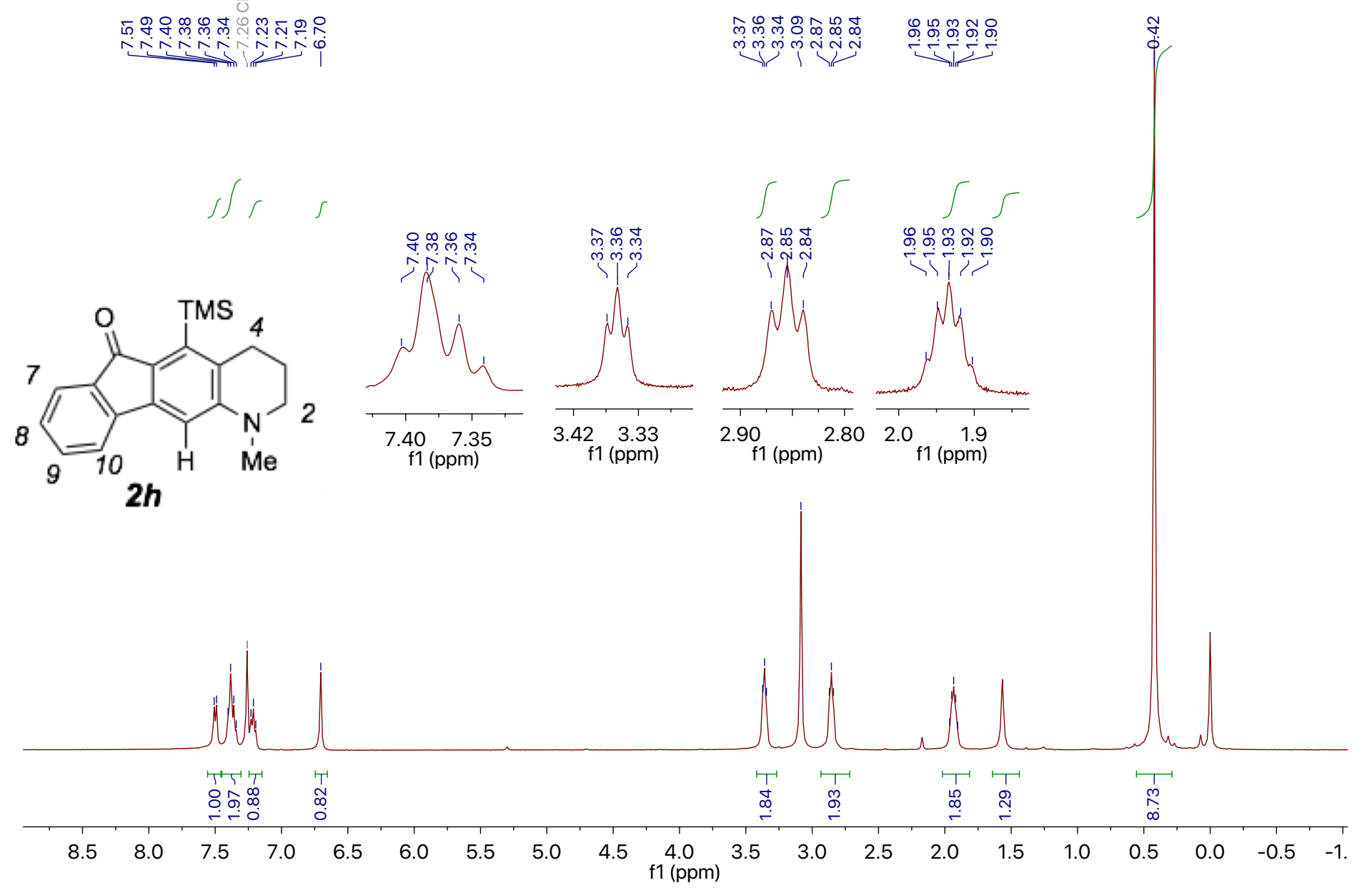
^{1}H NMR (400 MHz, chloroform-*d*)



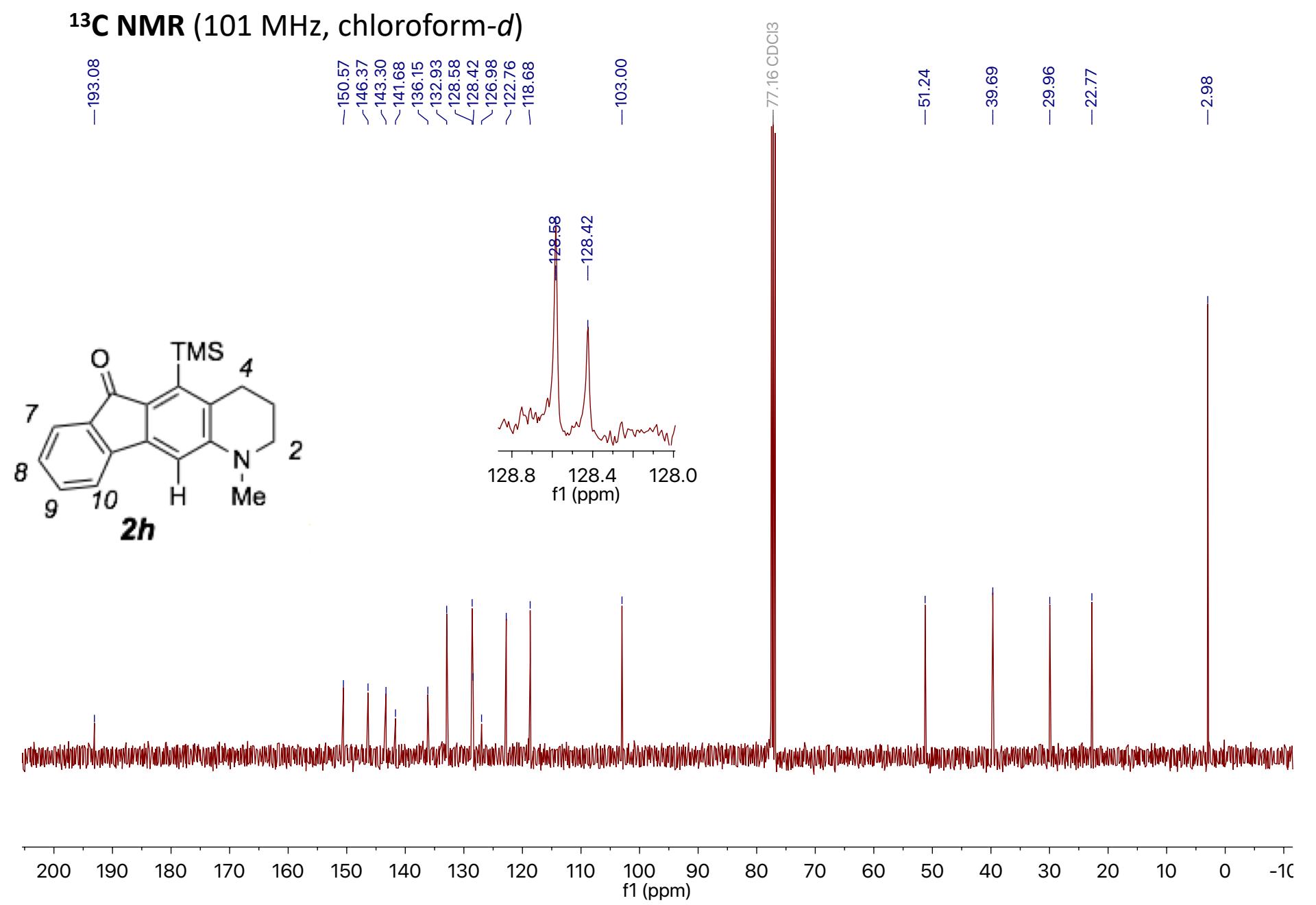
^{13}C NMR (101 MHz, chloroform-*d*)



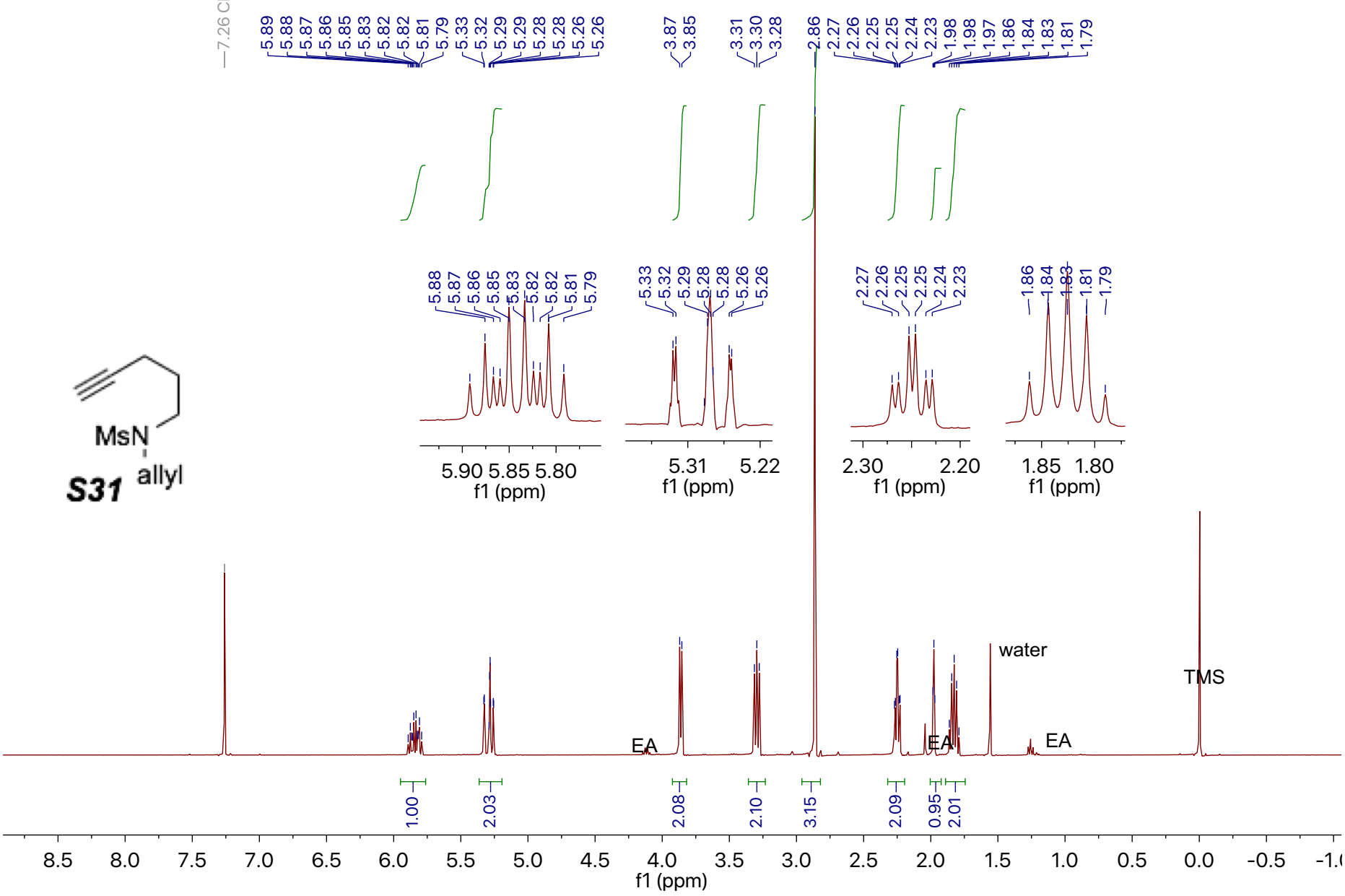
^{1}H NMR (400 MHz, chloroform-*d*)



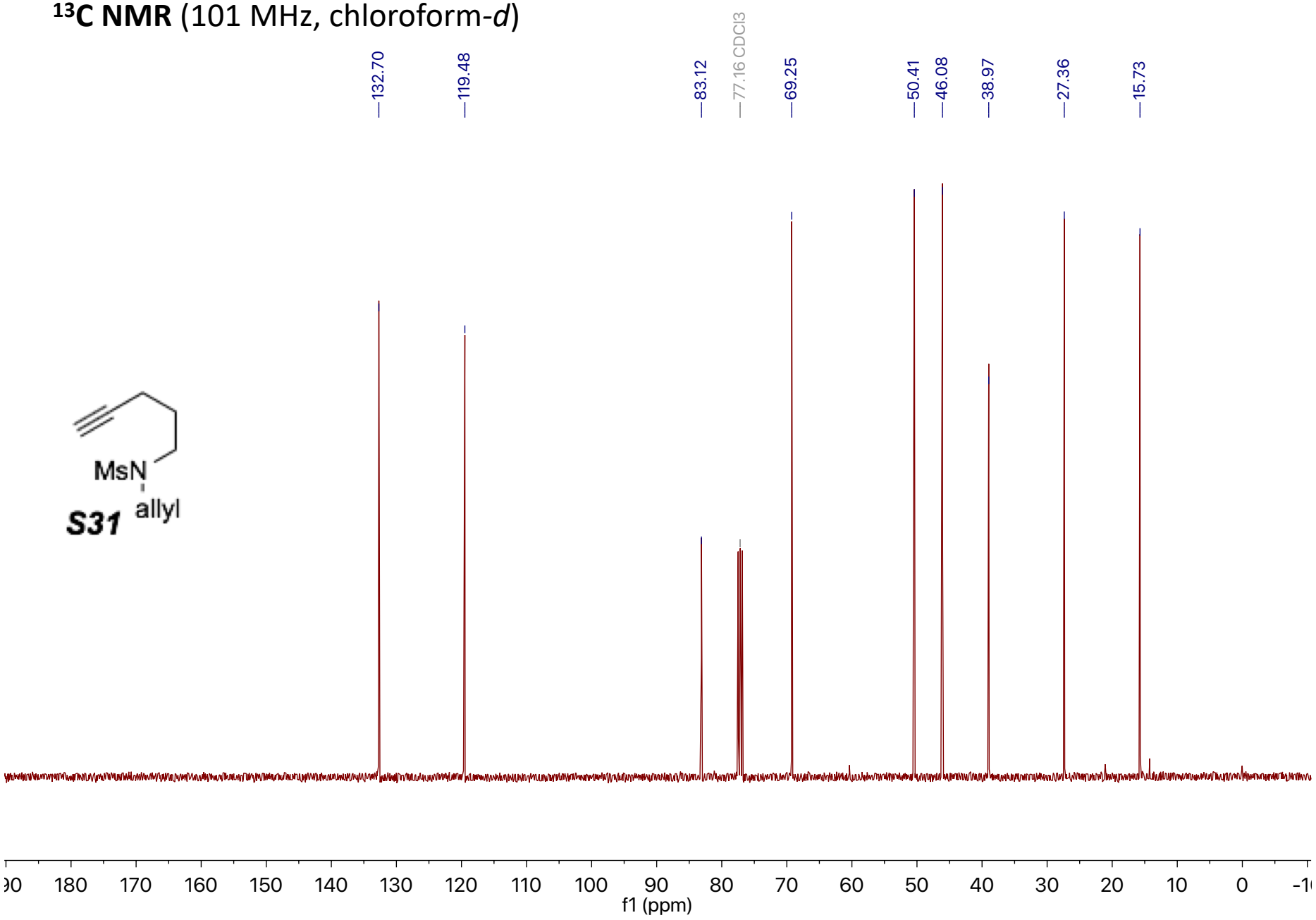
^{13}C NMR (101 MHz, chloroform-*d*)



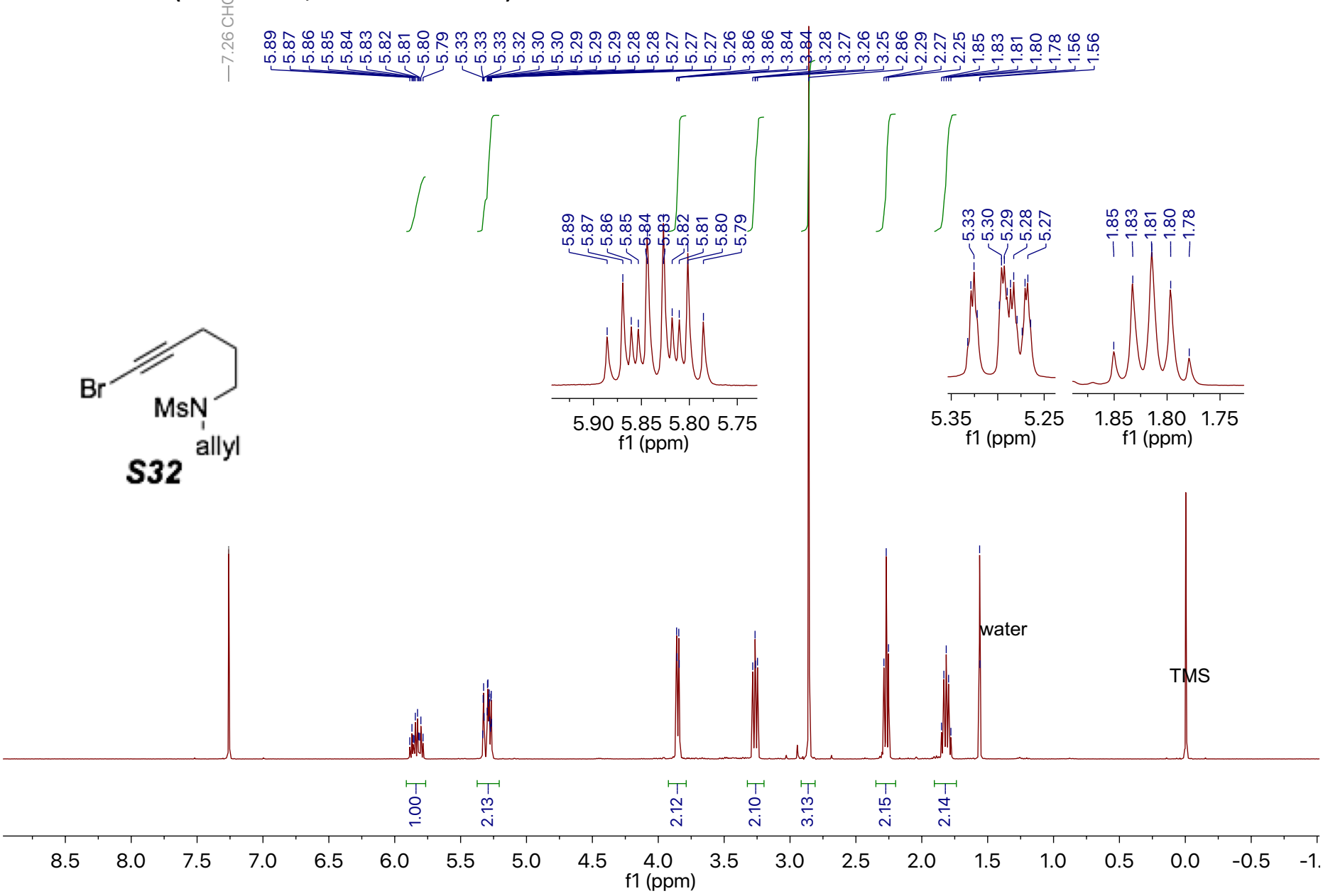
^{1}H NMR (400 MHz, chloroform-*d*)



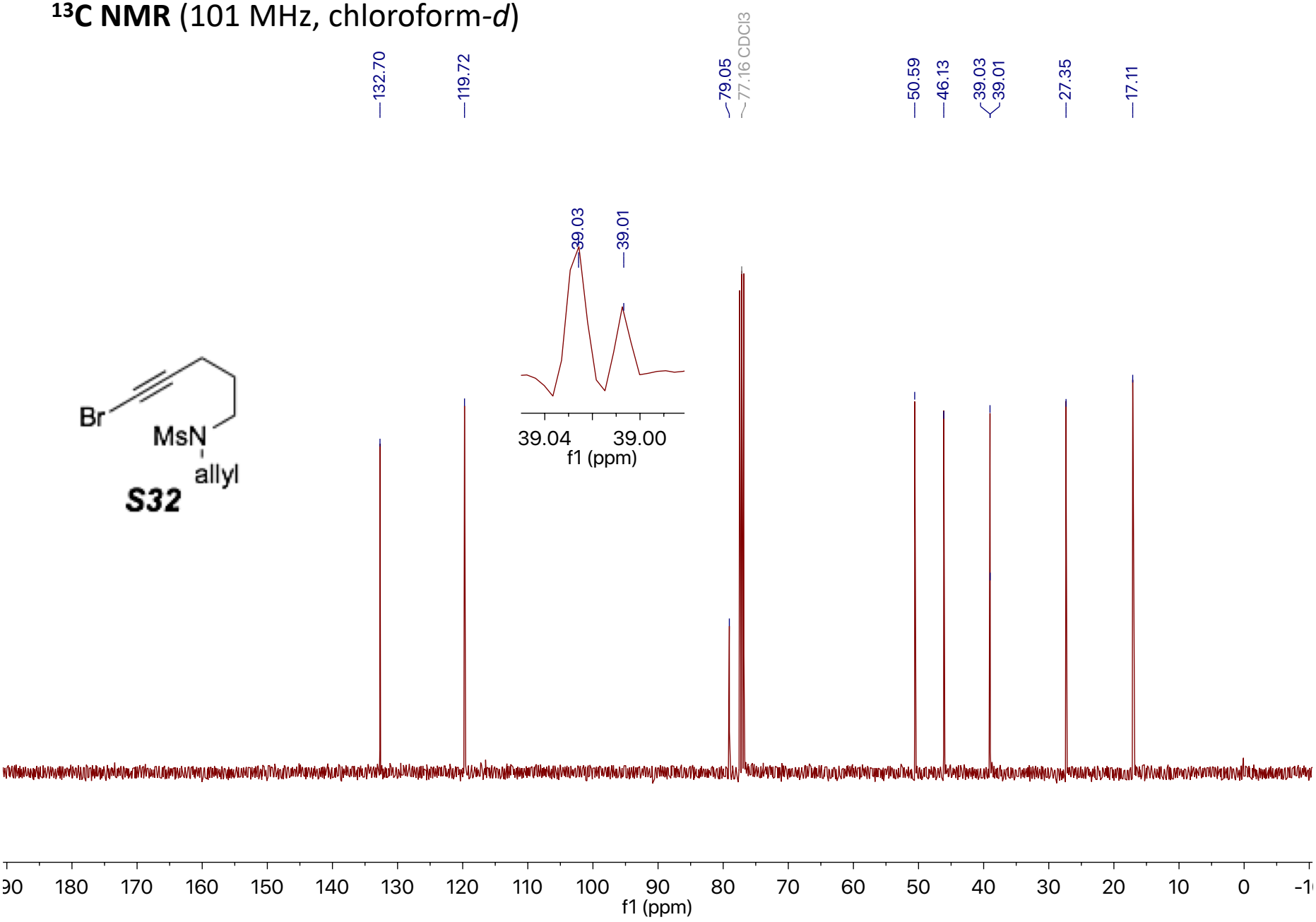
^{13}C NMR (101 MHz, chloroform-*d*)



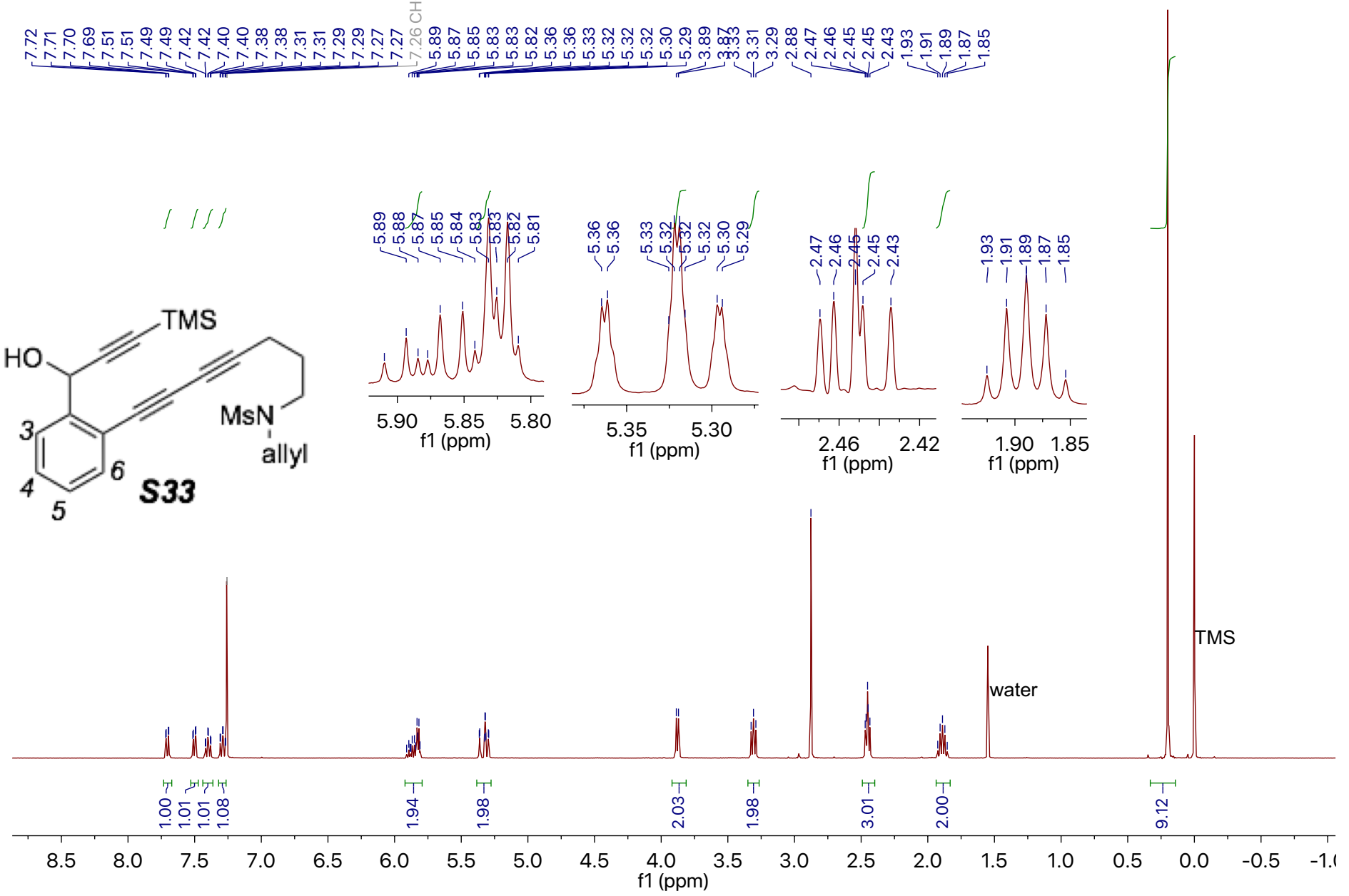
^{1}H NMR (400 MHz, chloroform-*d*)



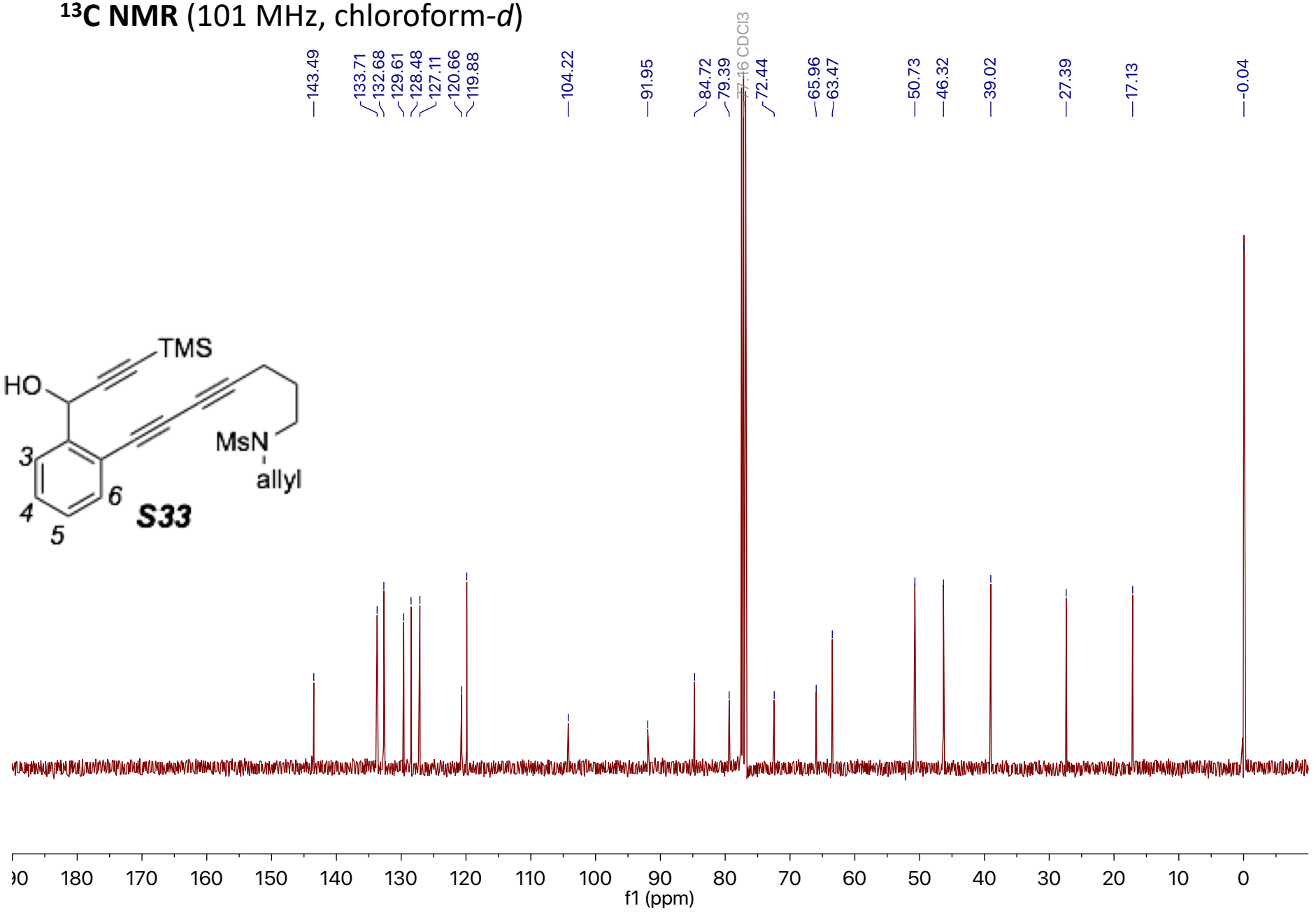
^{13}C NMR (101 MHz, chloroform-*d*)



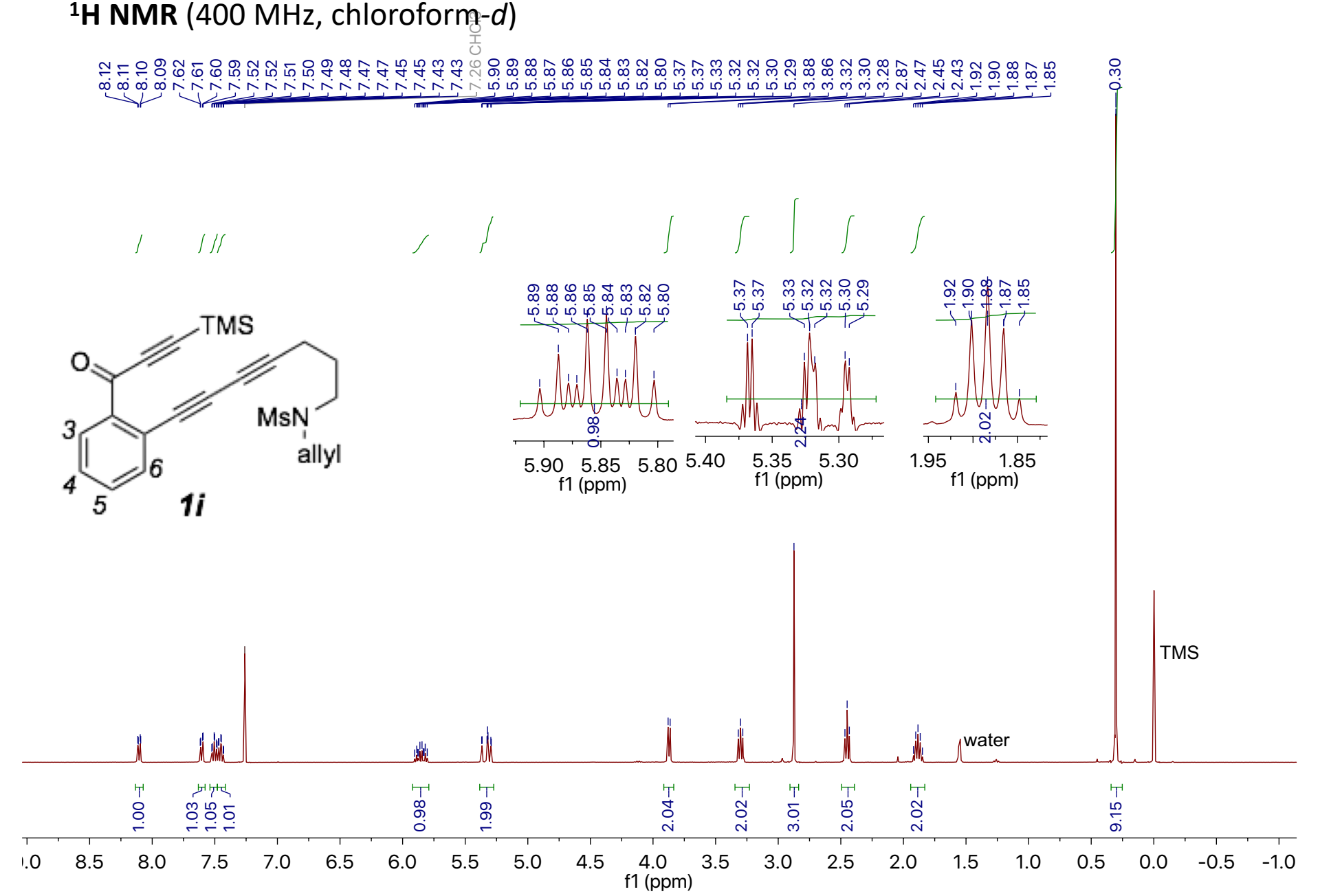
^{1}H NMR (400 MHz, chloroform-*d*)



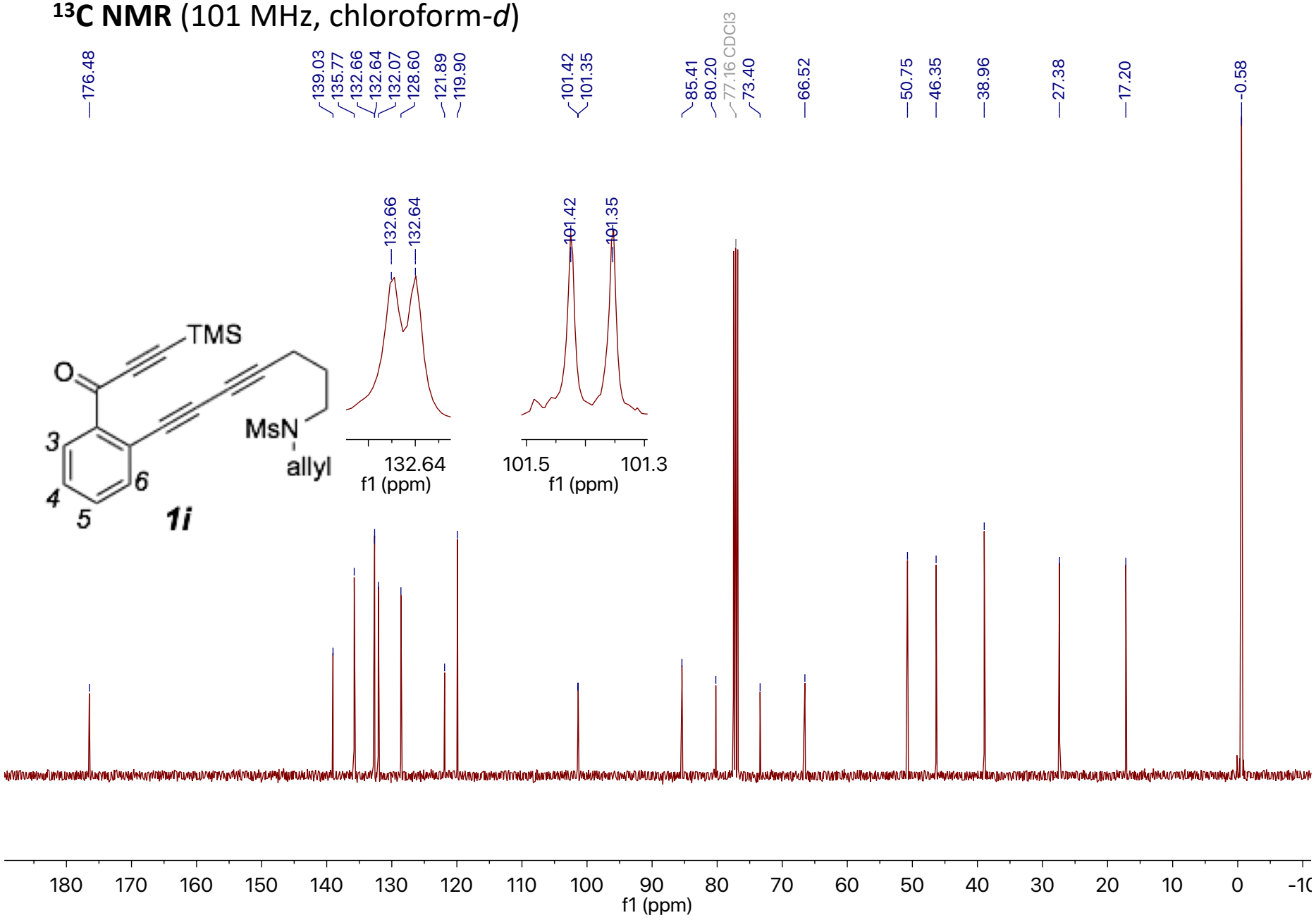
^{13}C NMR (101 MHz, chloroform-*d*)



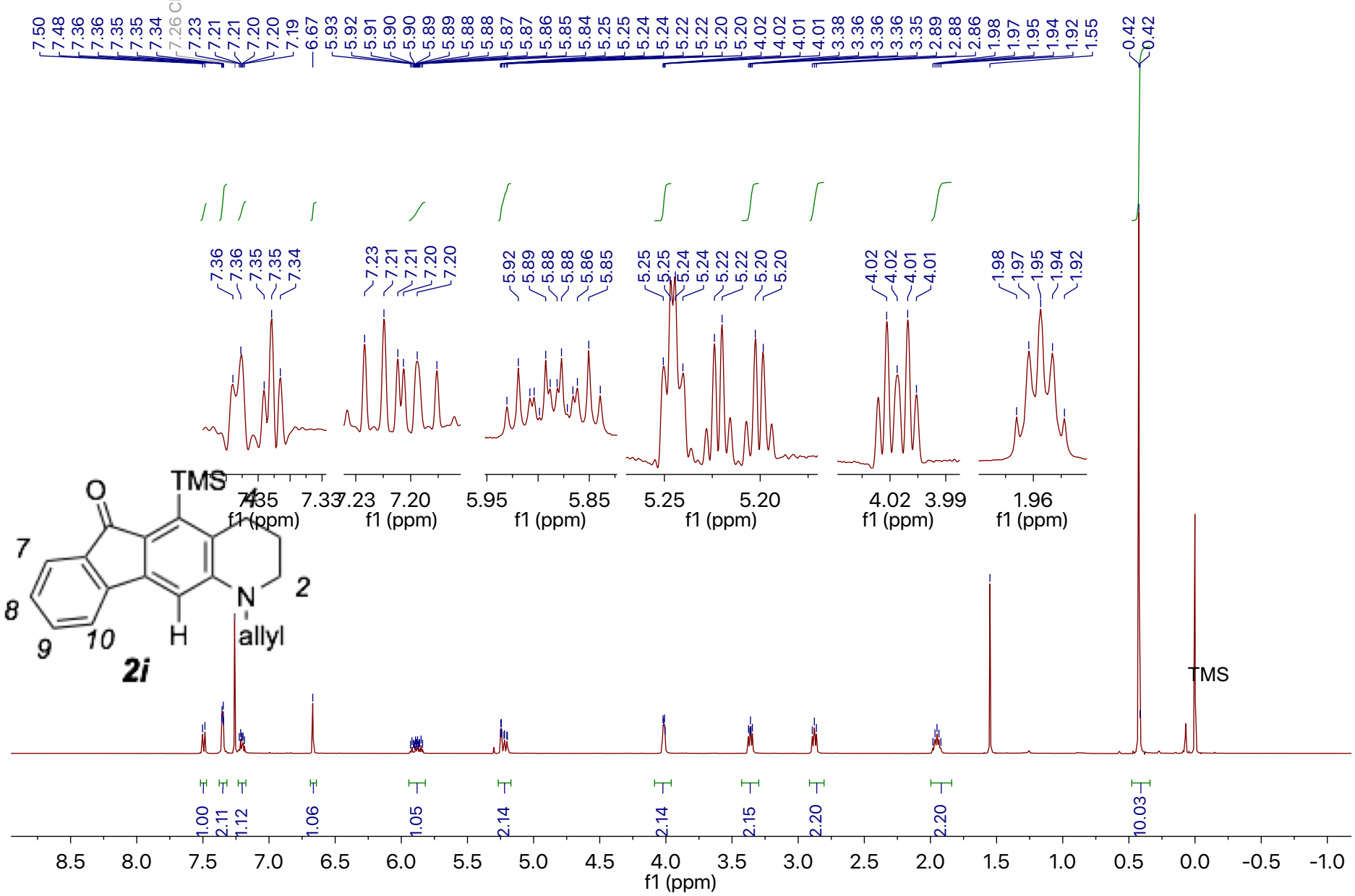
^{1}H NMR (400 MHz, chloroform-*d*)



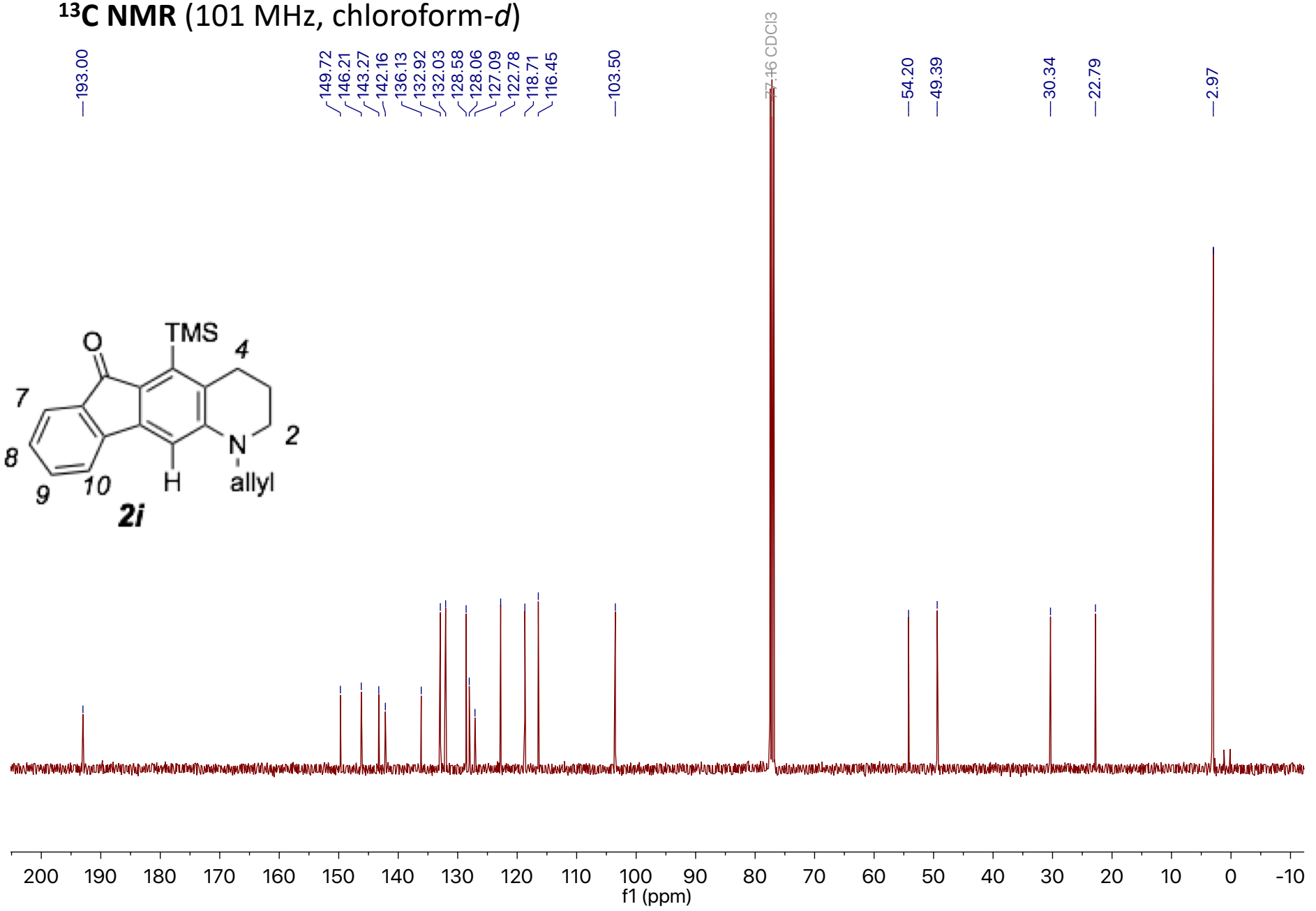
^{13}C NMR (101 MHz, chloroform-*d*)



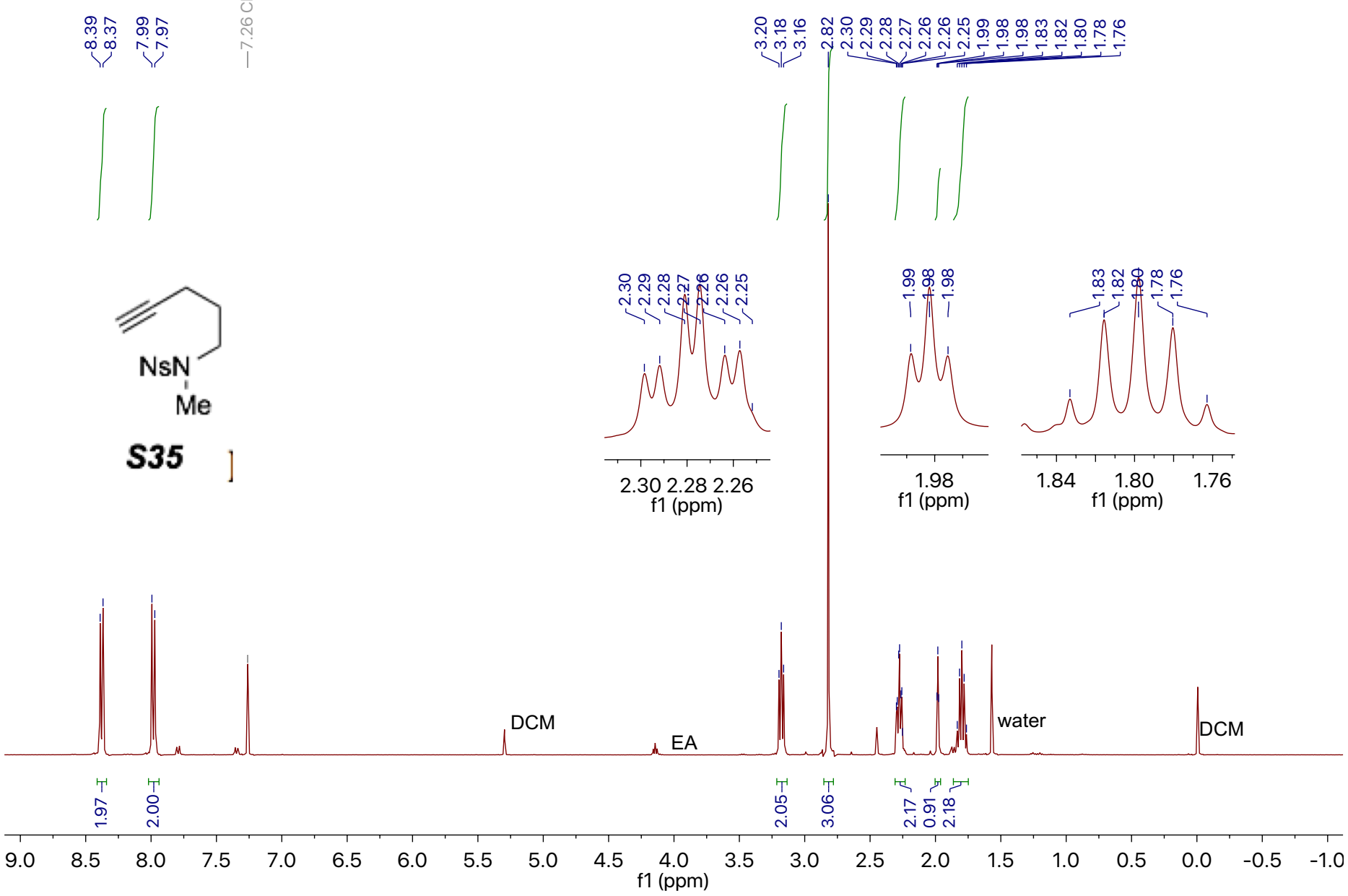
^{1}H NMR (400 MHz, chloroform-*d*)



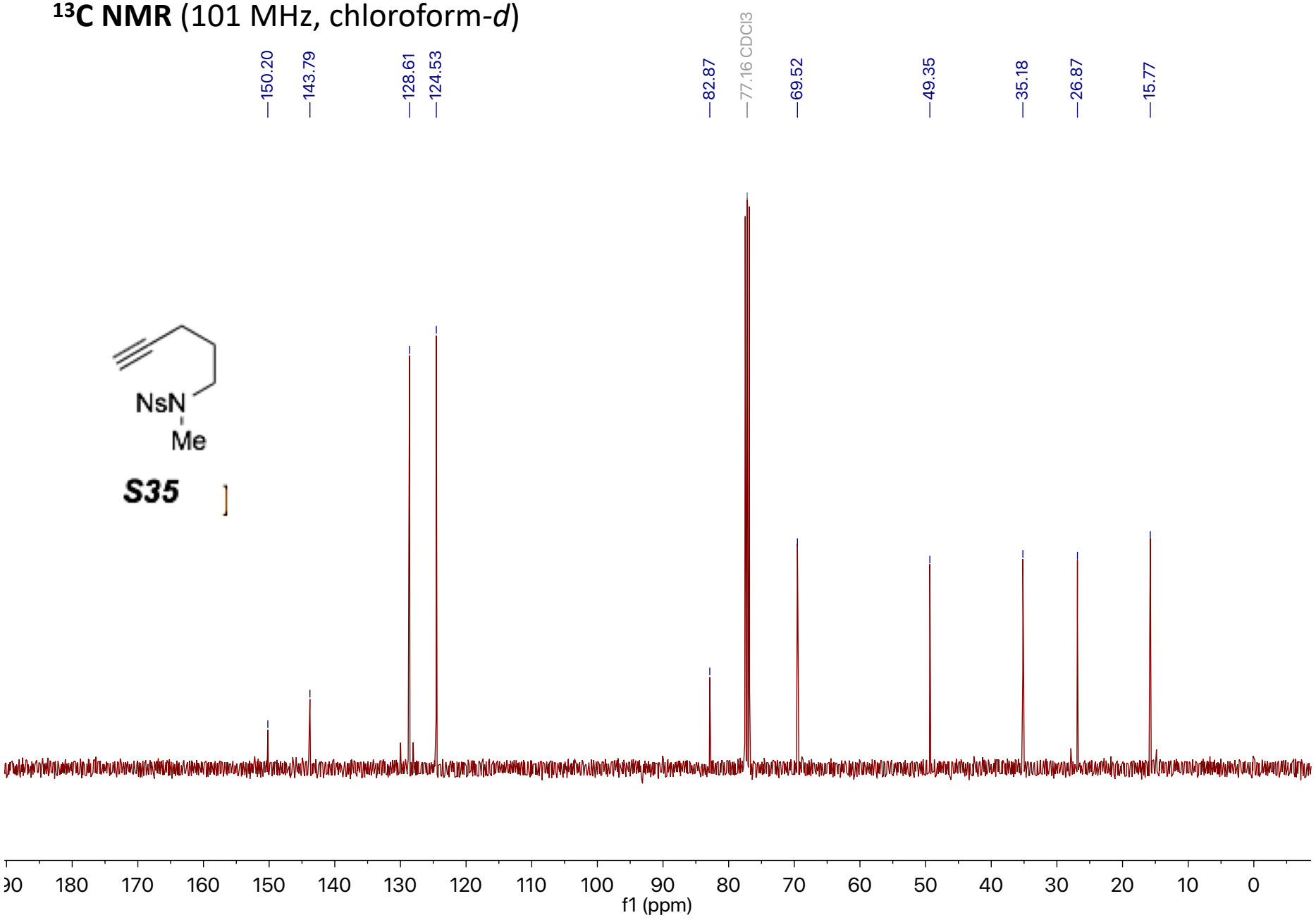
^{13}C NMR (101 MHz, chloroform-*d*)



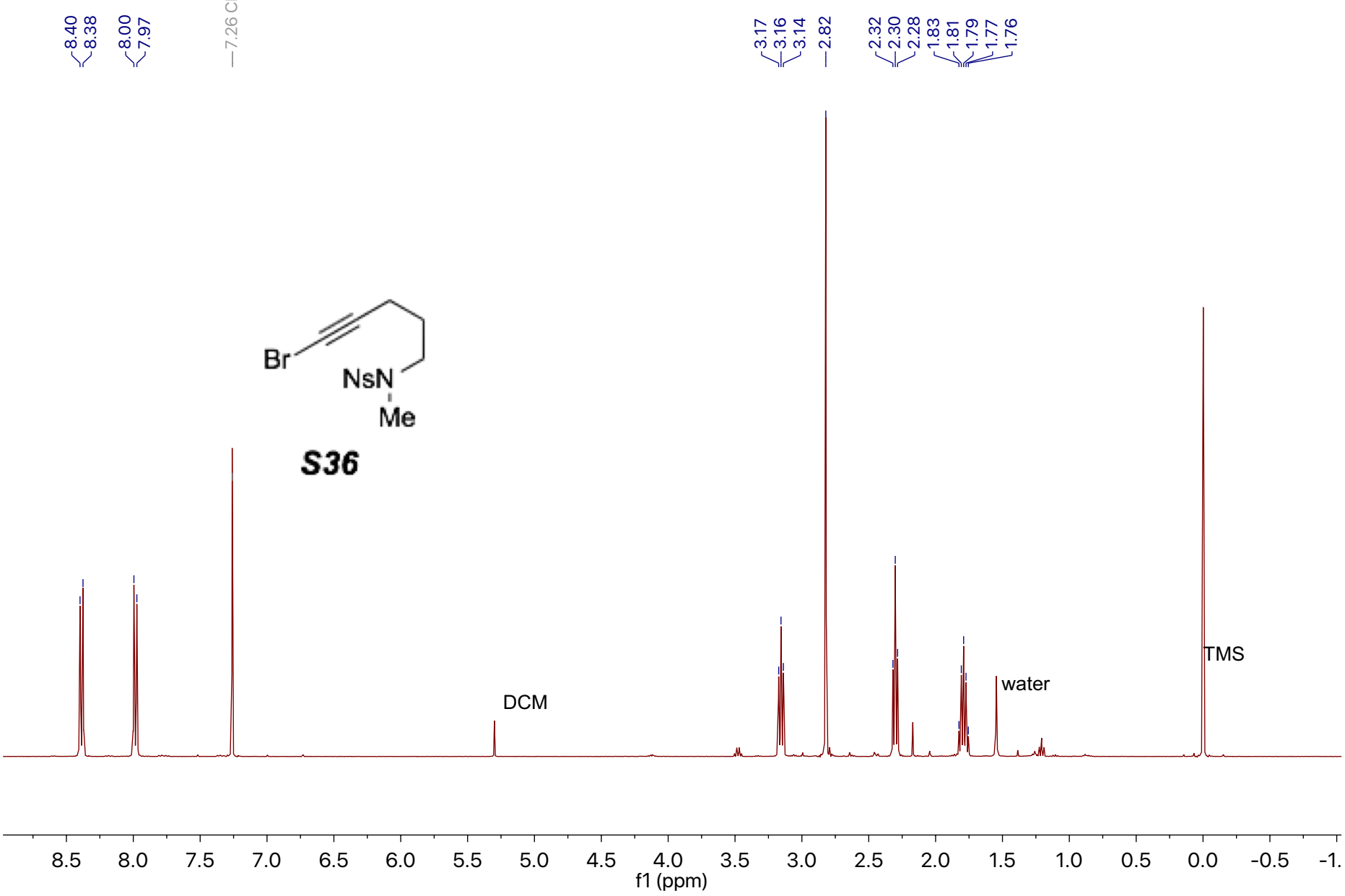
^{1}H NMR (400 MHz, chloroform-*d*)



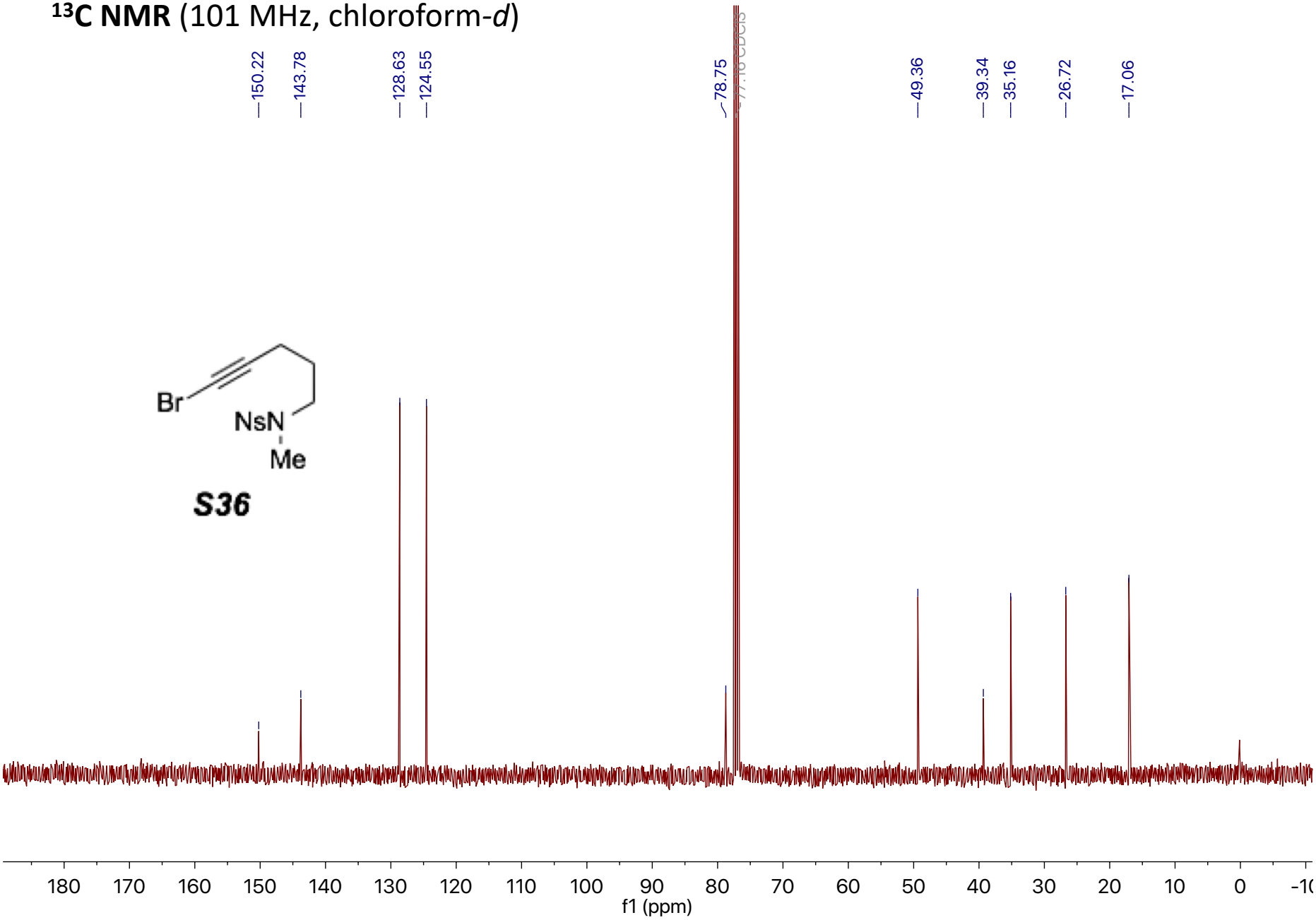
^{13}C NMR (101 MHz, chloroform-*d*)



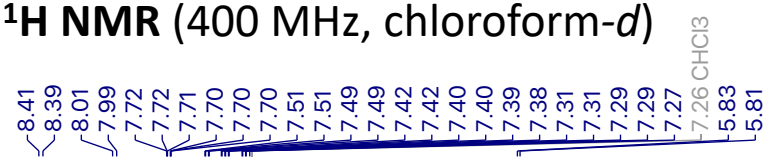
^{1}H NMR (400 MHz, chloroform-*d*)

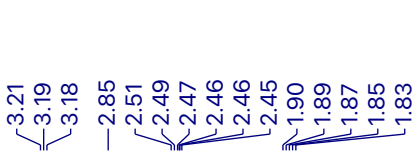


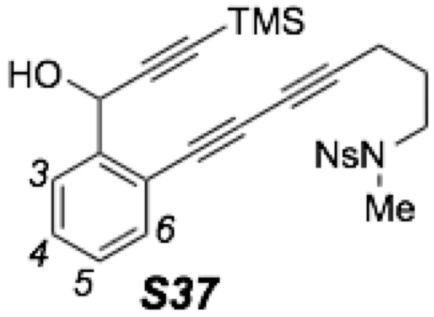
^{13}C NMR (101 MHz, chloroform-*d*)

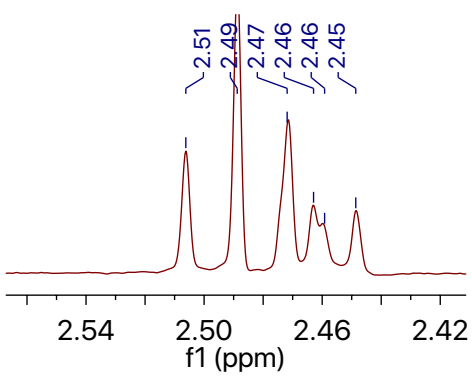


^{1}H NMR (400 MHz, chloroform-*d*)

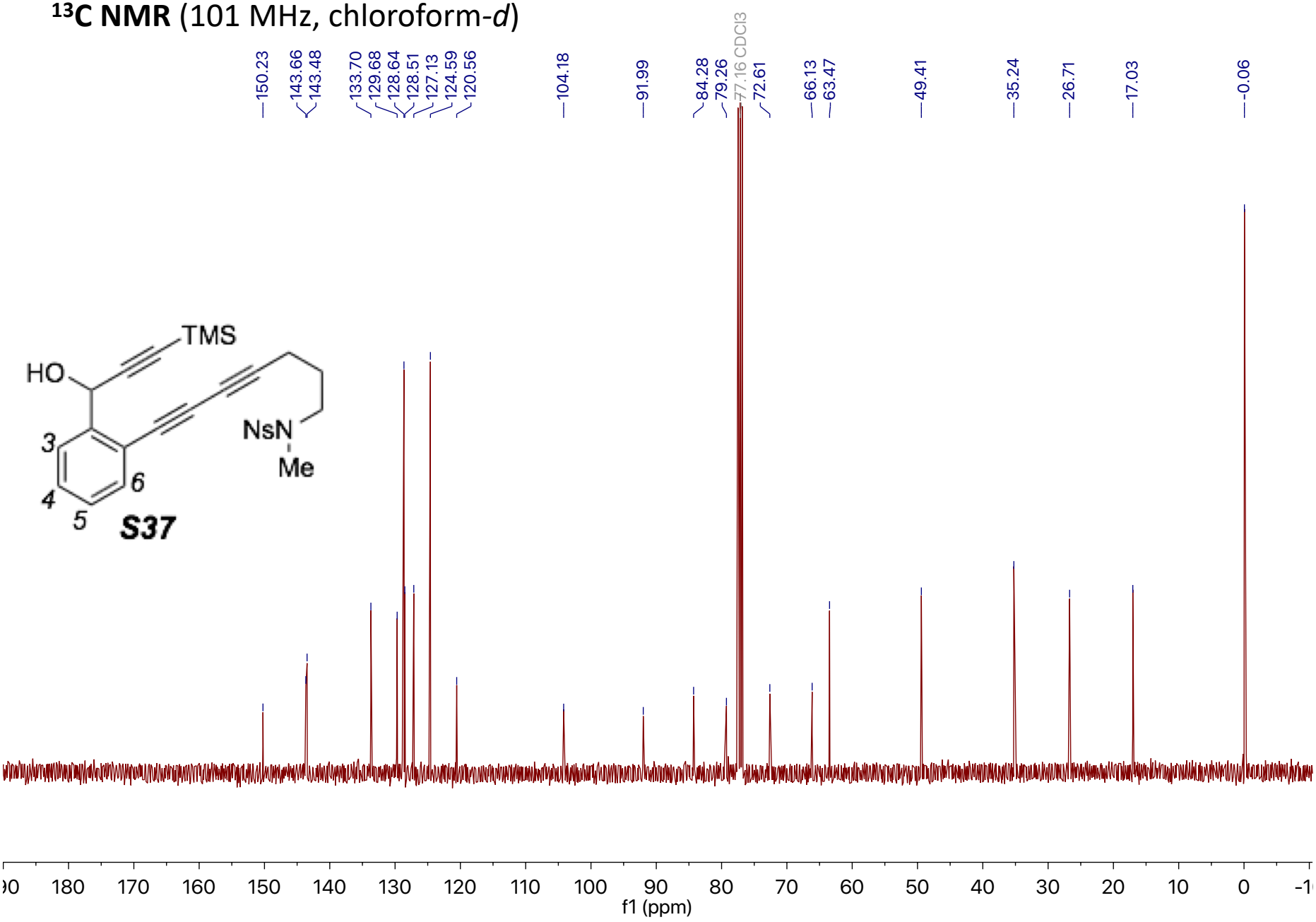




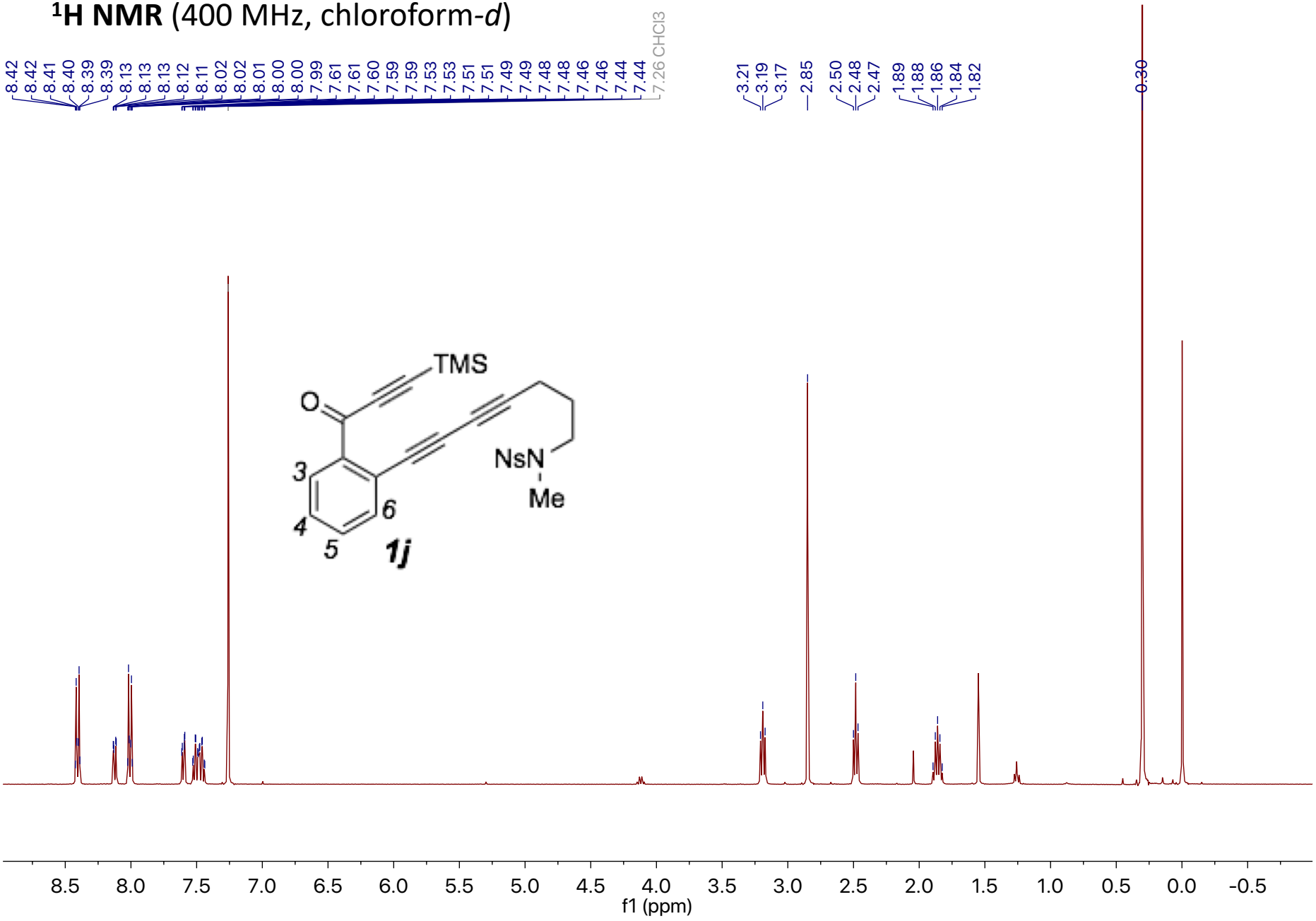




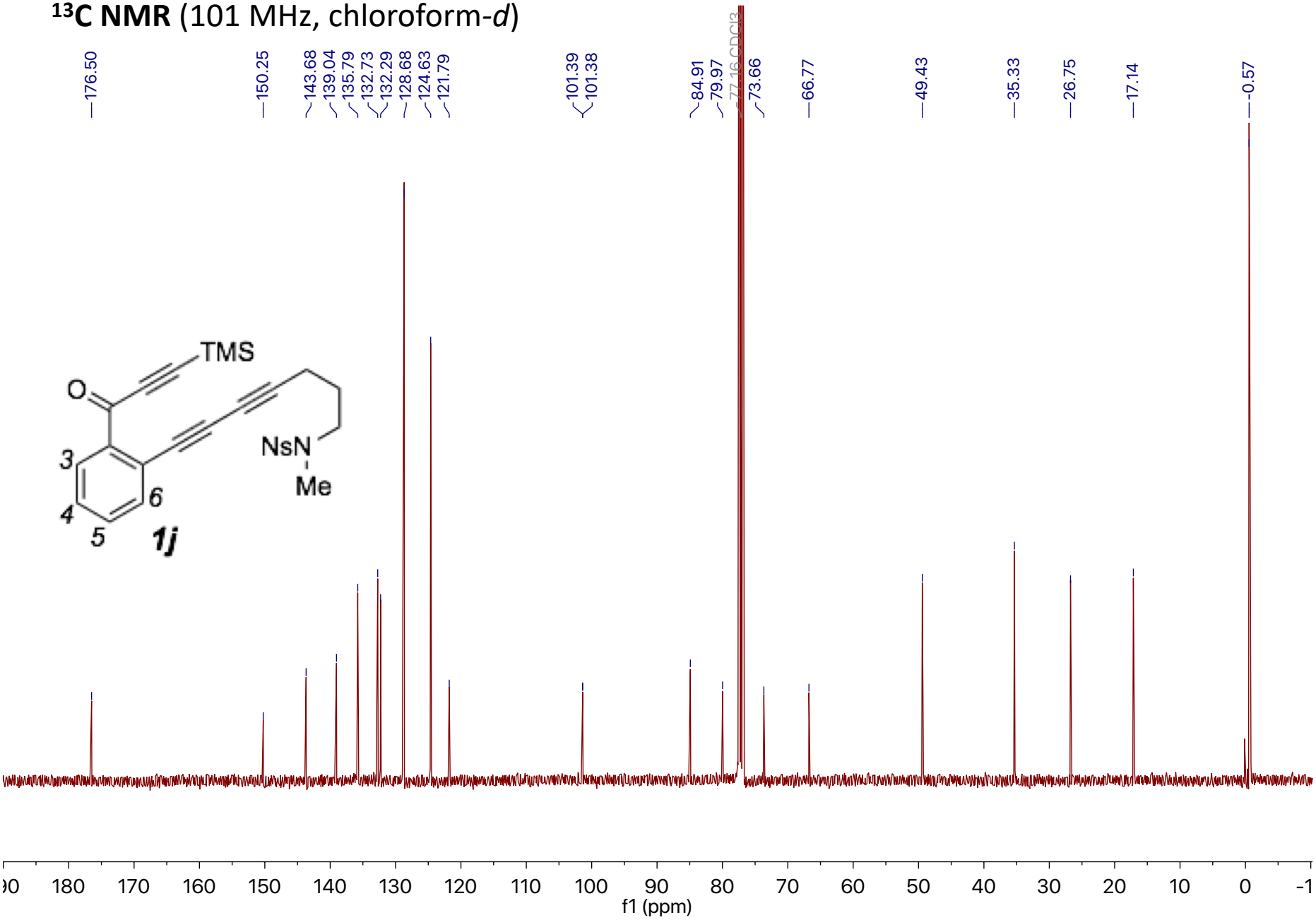
^{13}C NMR (101 MHz, chloroform-*d*)



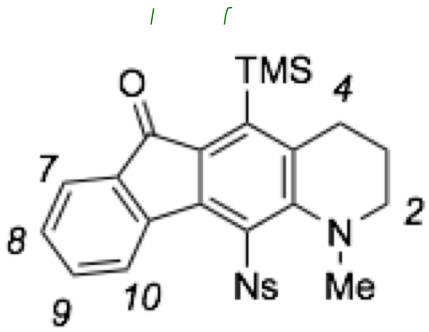
^{1}H NMR (400 MHz, chloroform-*d*)



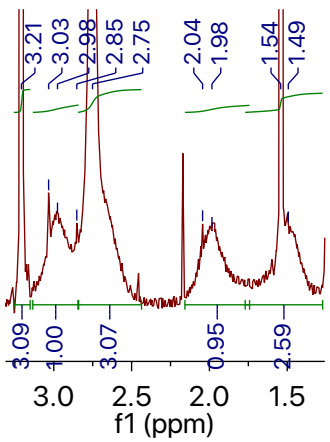
^{13}C NMR (101 MHz, chloroform-*d*)



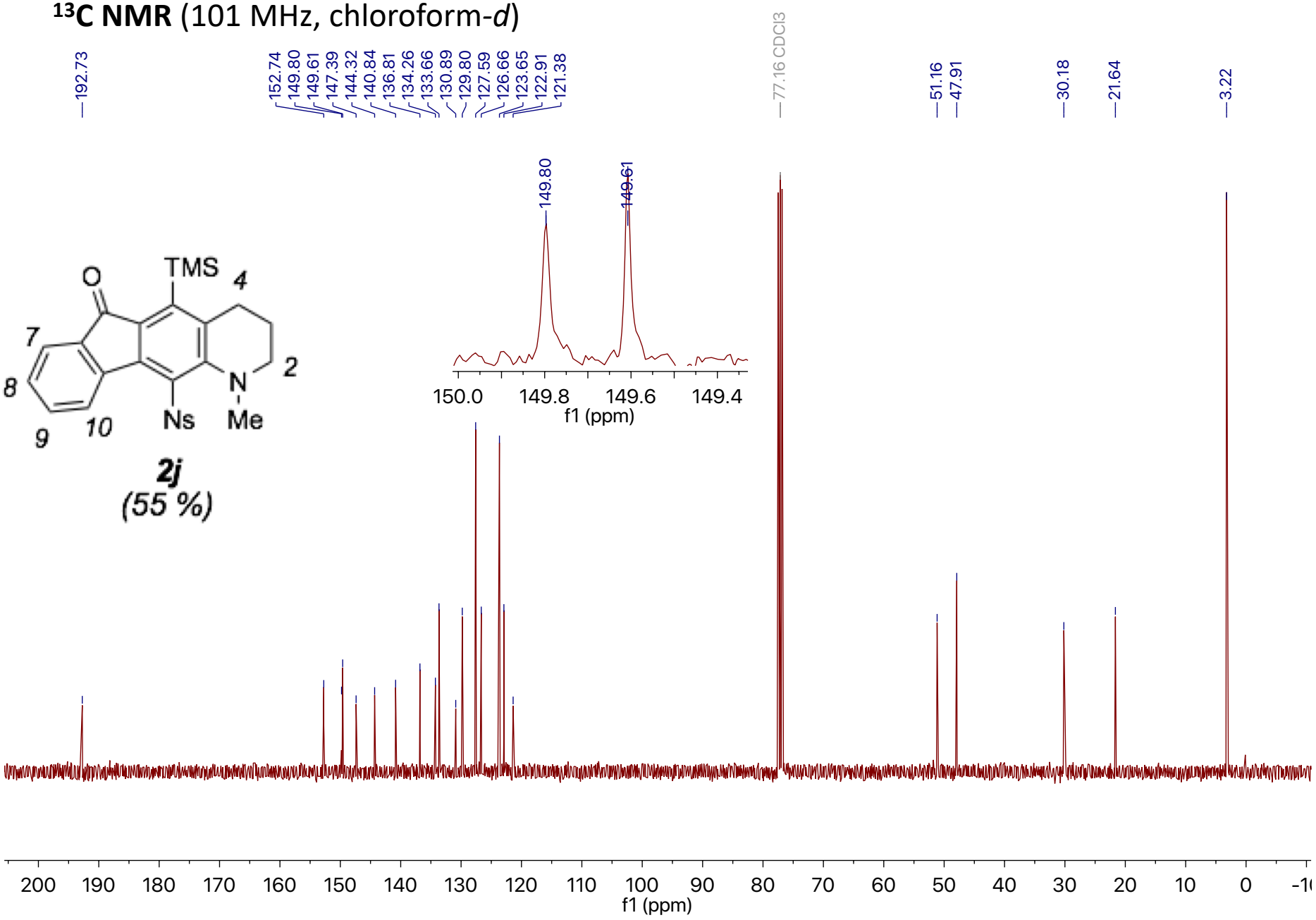
^{1}H NMR (400 MHz, chloroform-*d*)



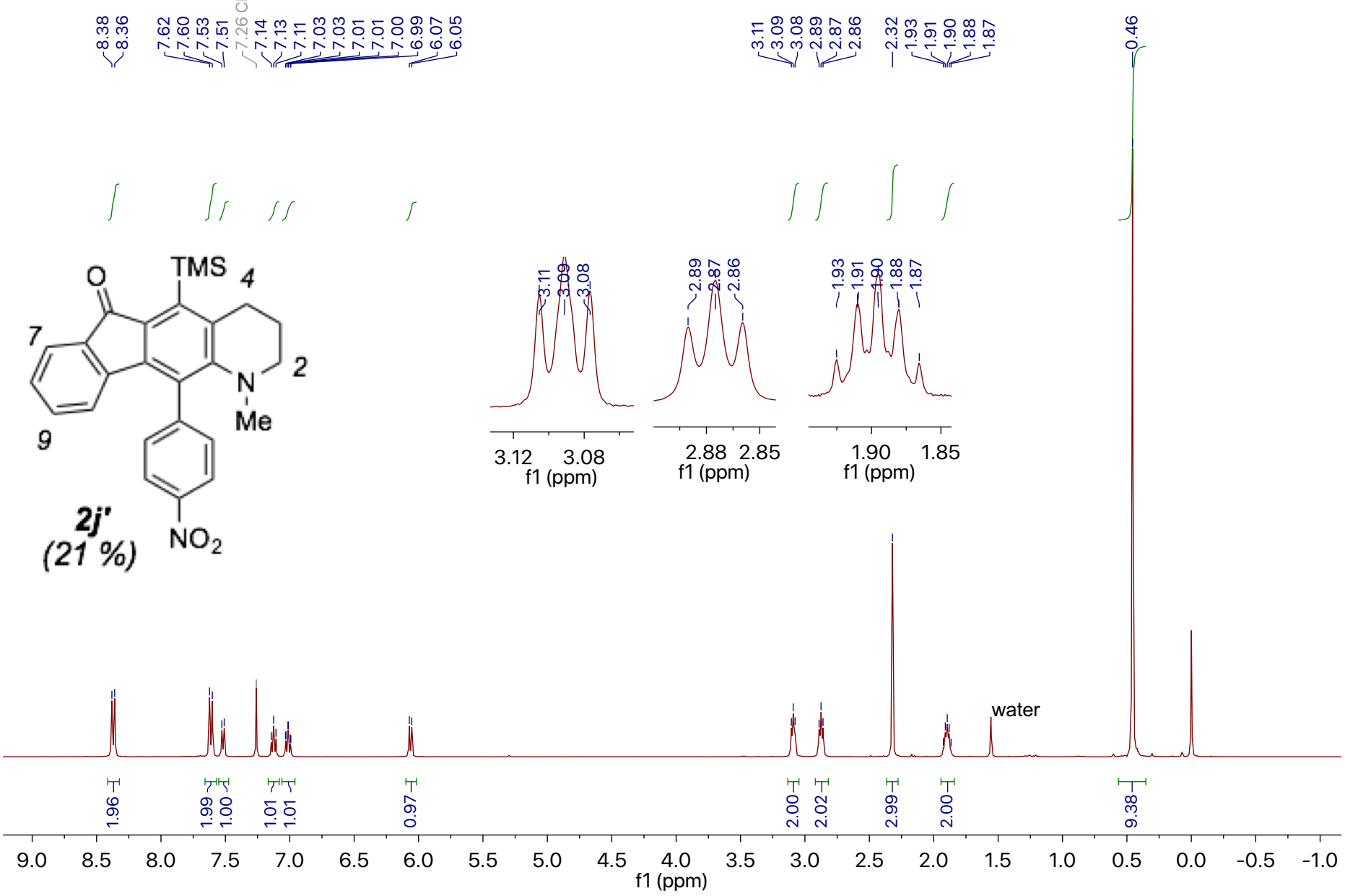
2j
(55 %)



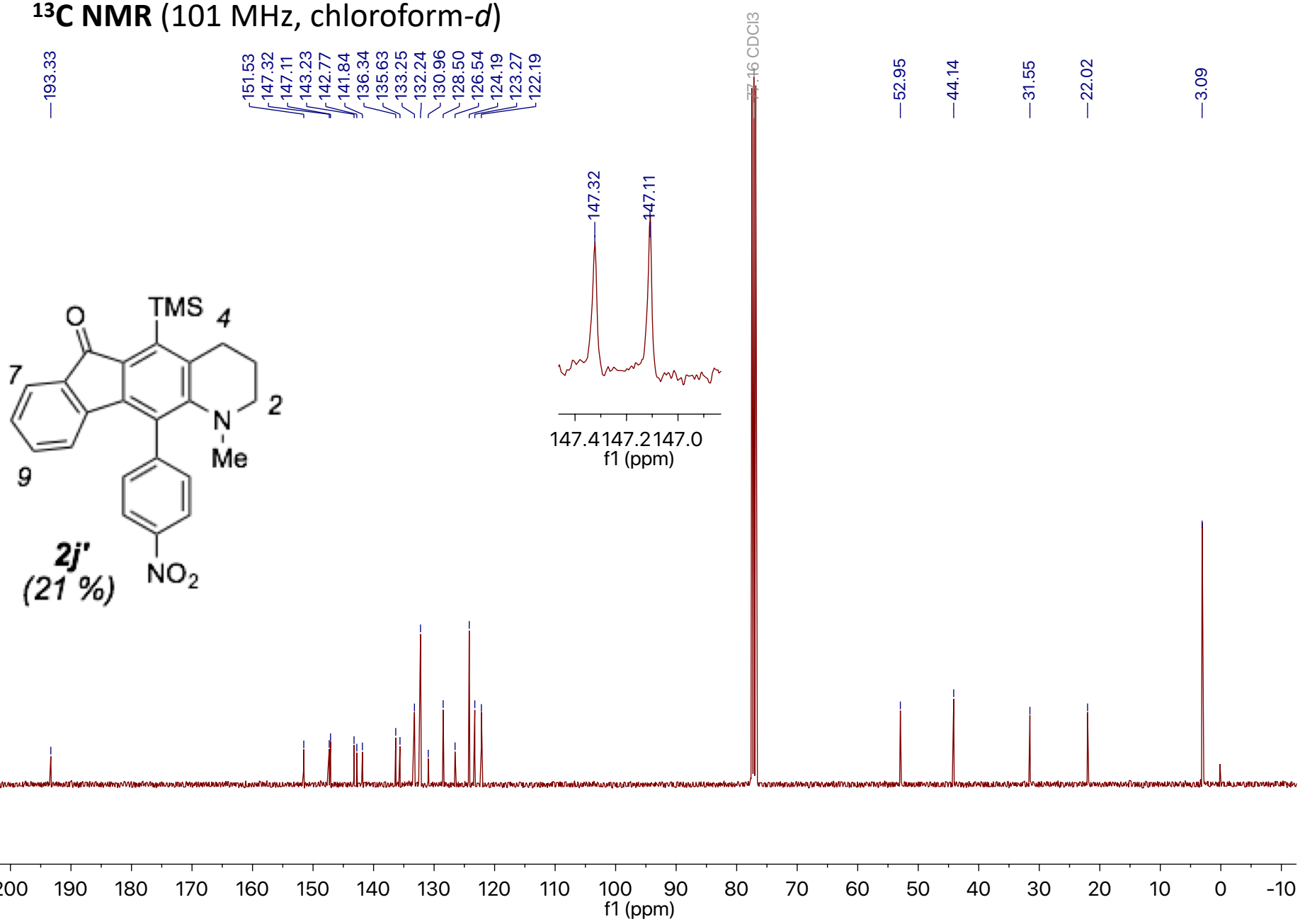
^{13}C NMR (101 MHz, chloroform-*d*)



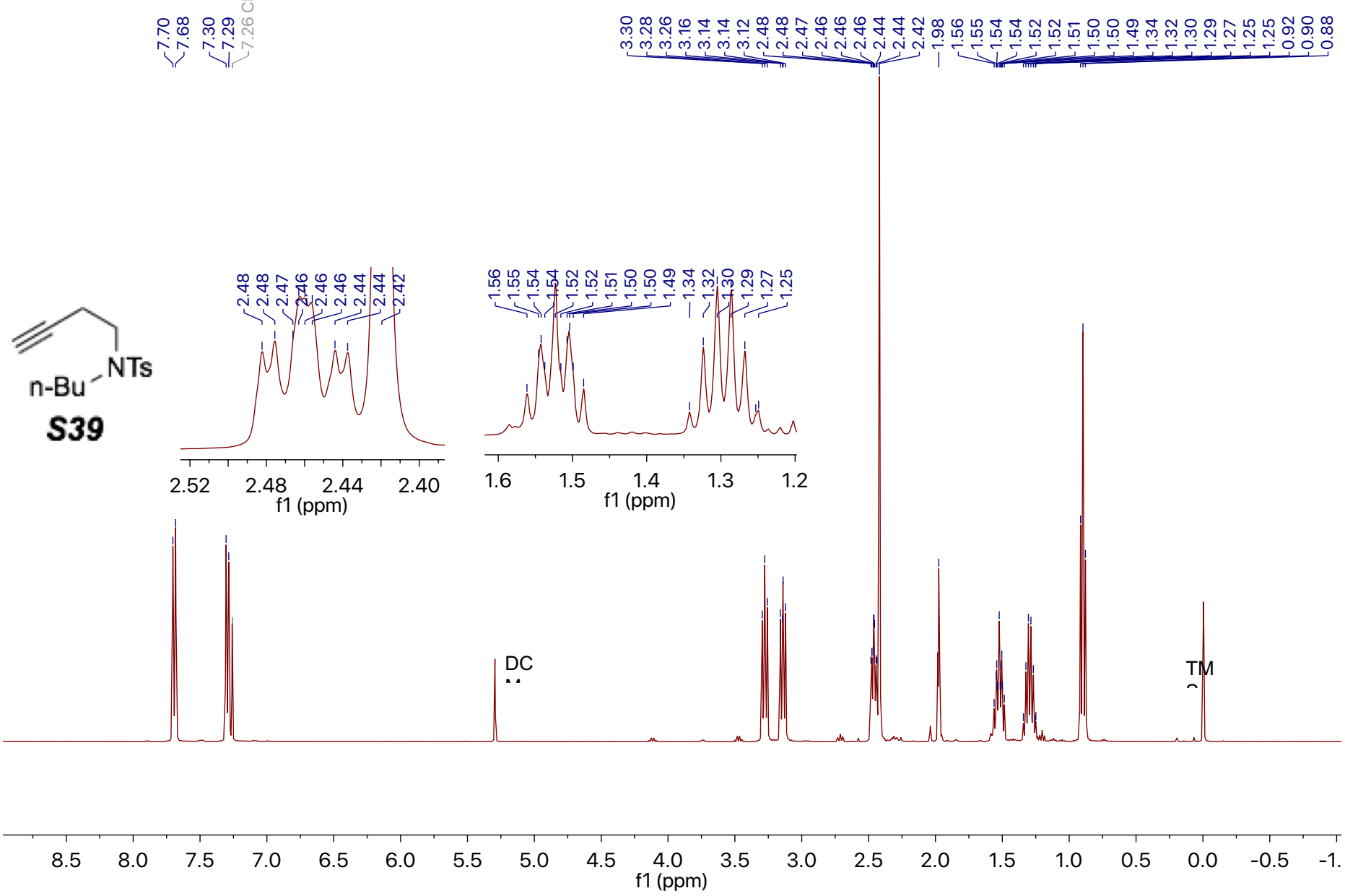
^{1}H NMR (400 MHz, chloroform-*d*)



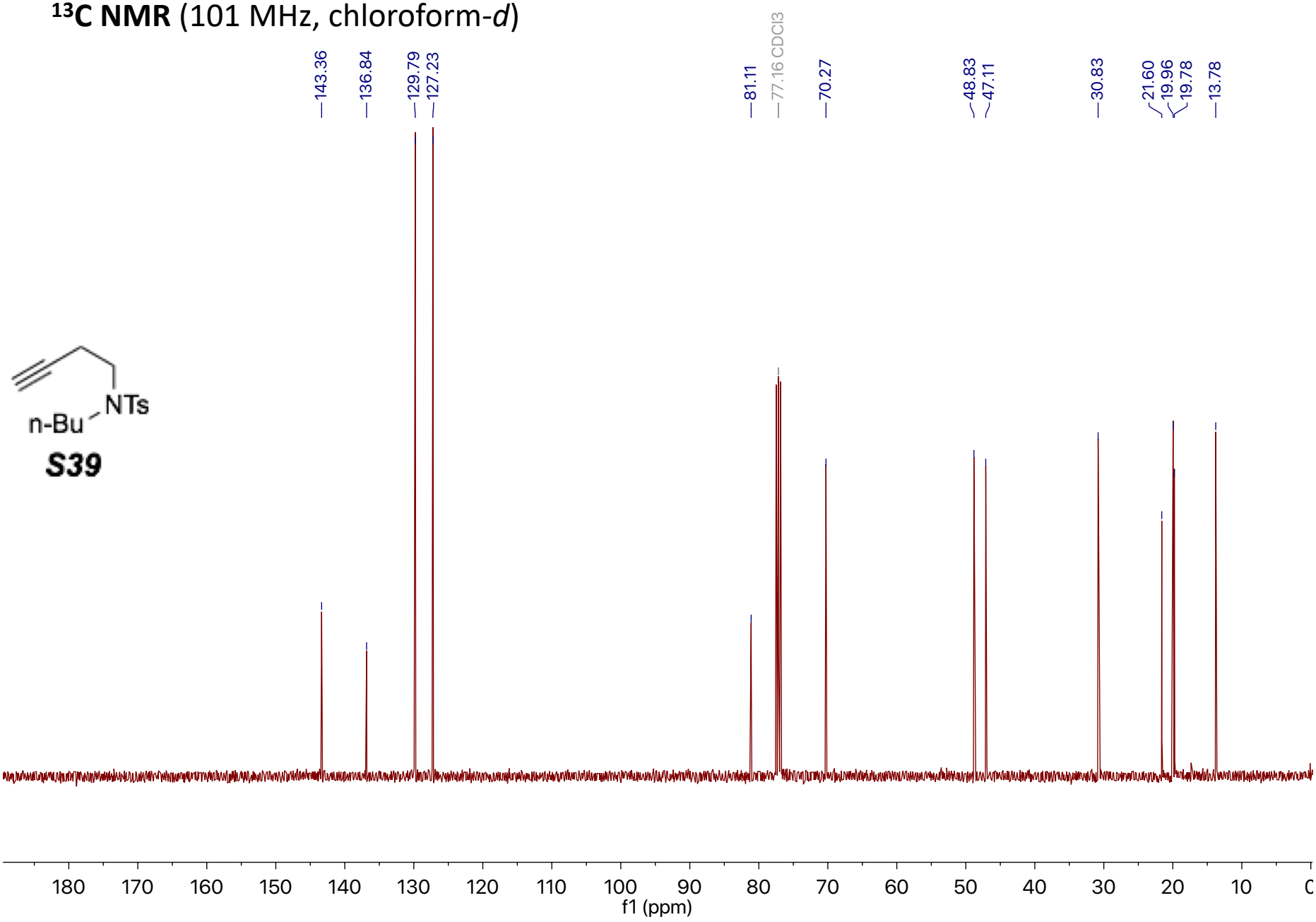
^{13}C NMR (101 MHz, chloroform-*d*)



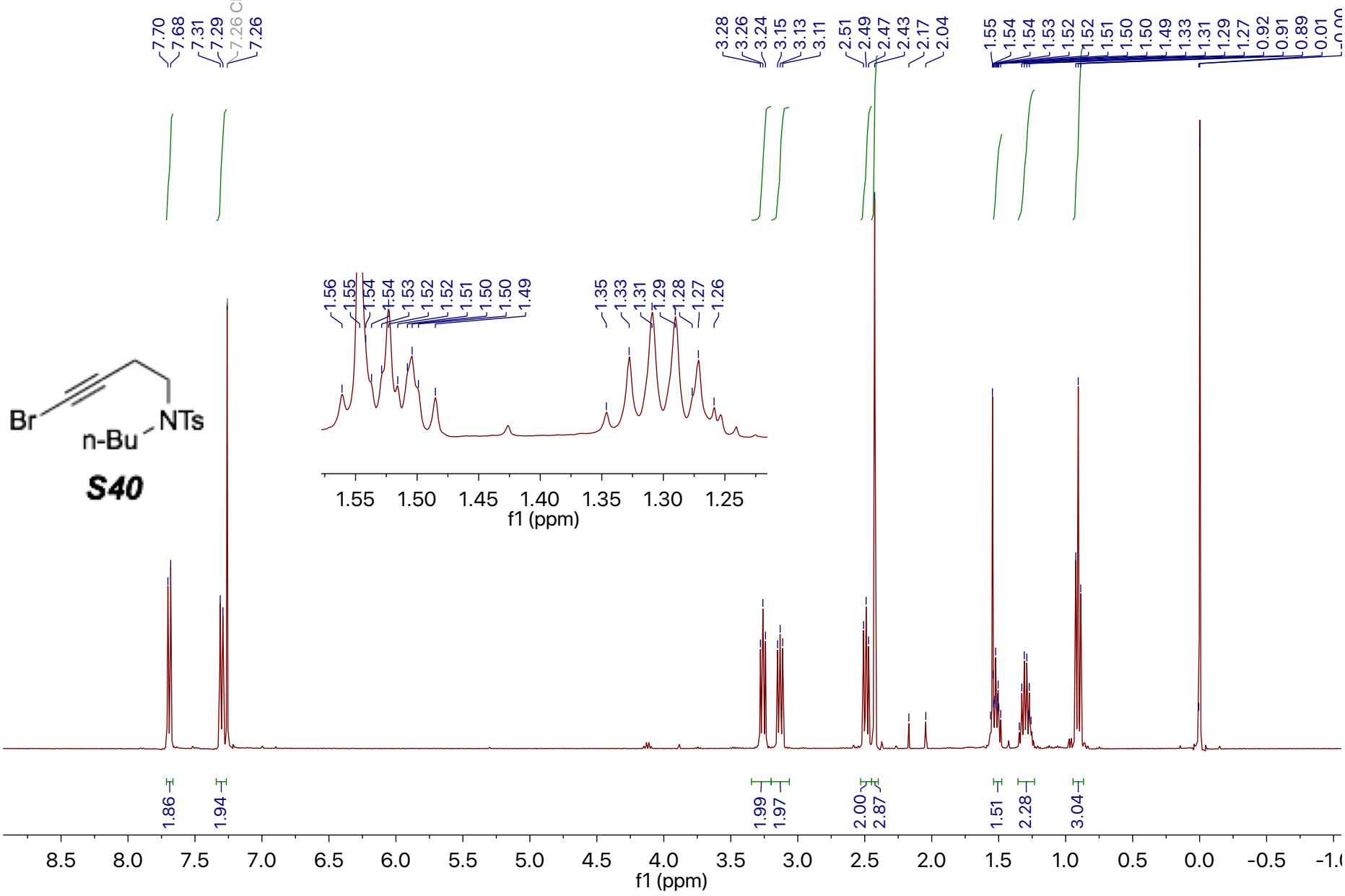
^{1}H NMR (400 MHz, chloroform-*d*)



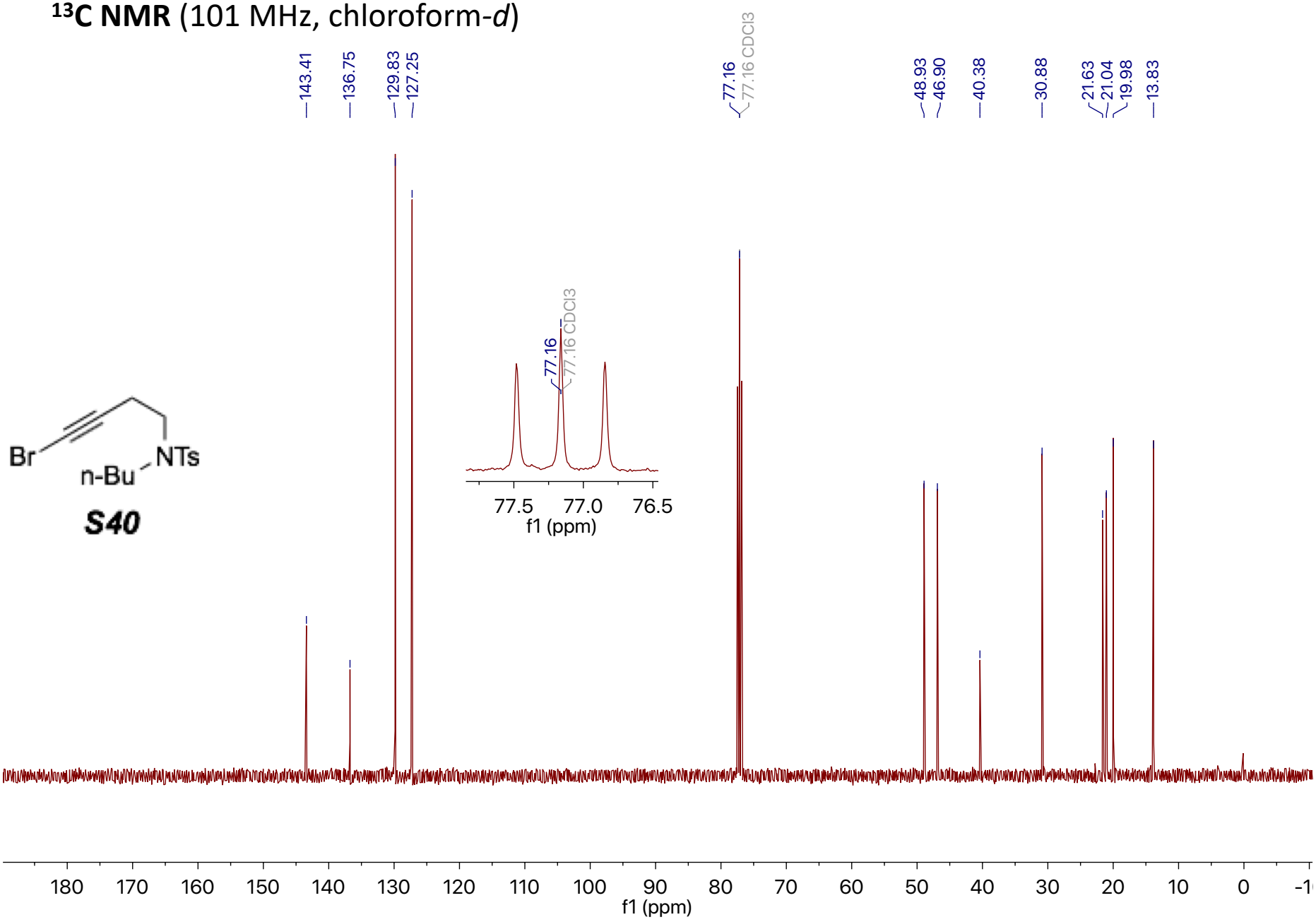
^{13}C NMR (101 MHz, chloroform-*d*)



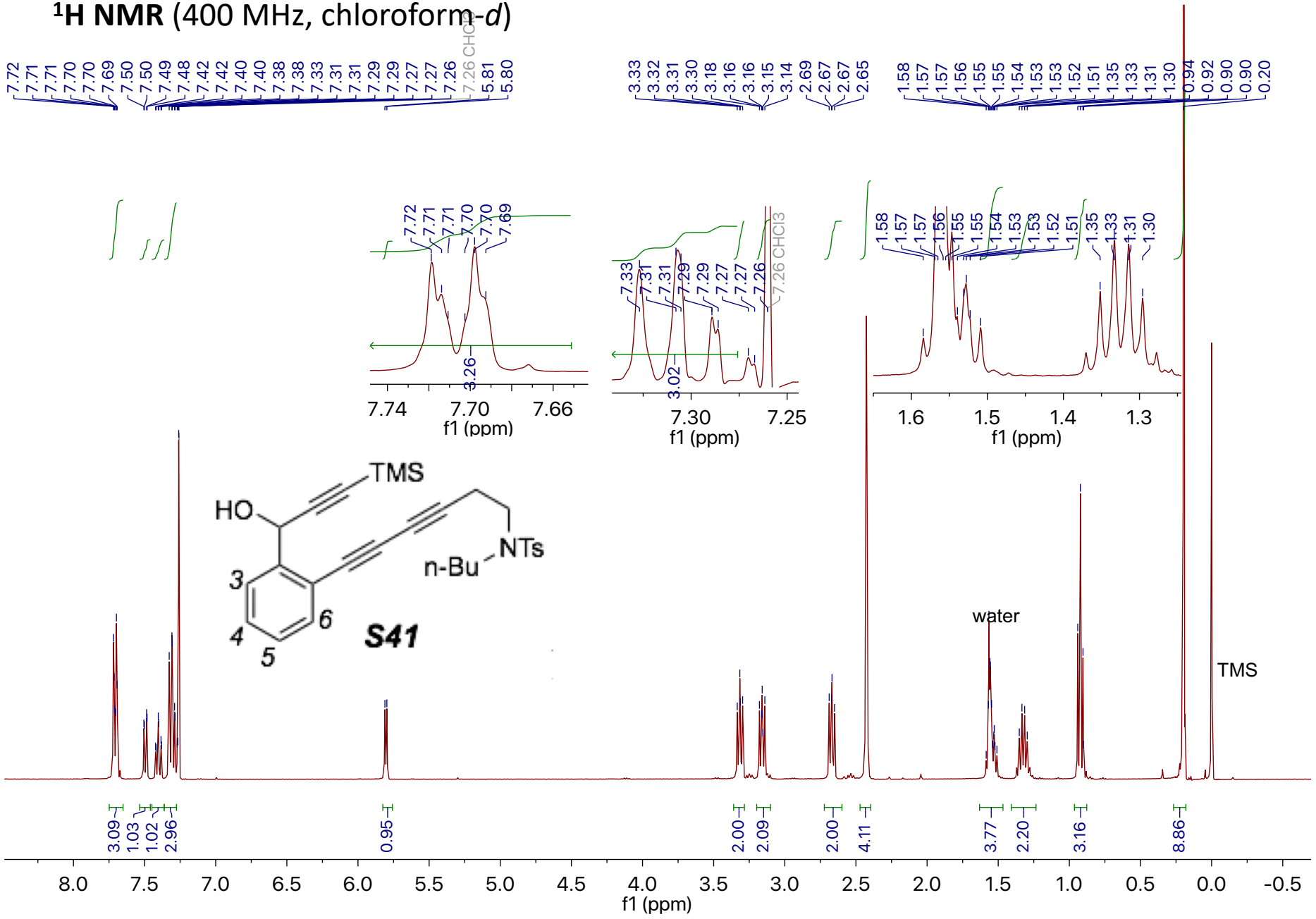
^{1}H NMR (400 MHz, chloroform-*d*)



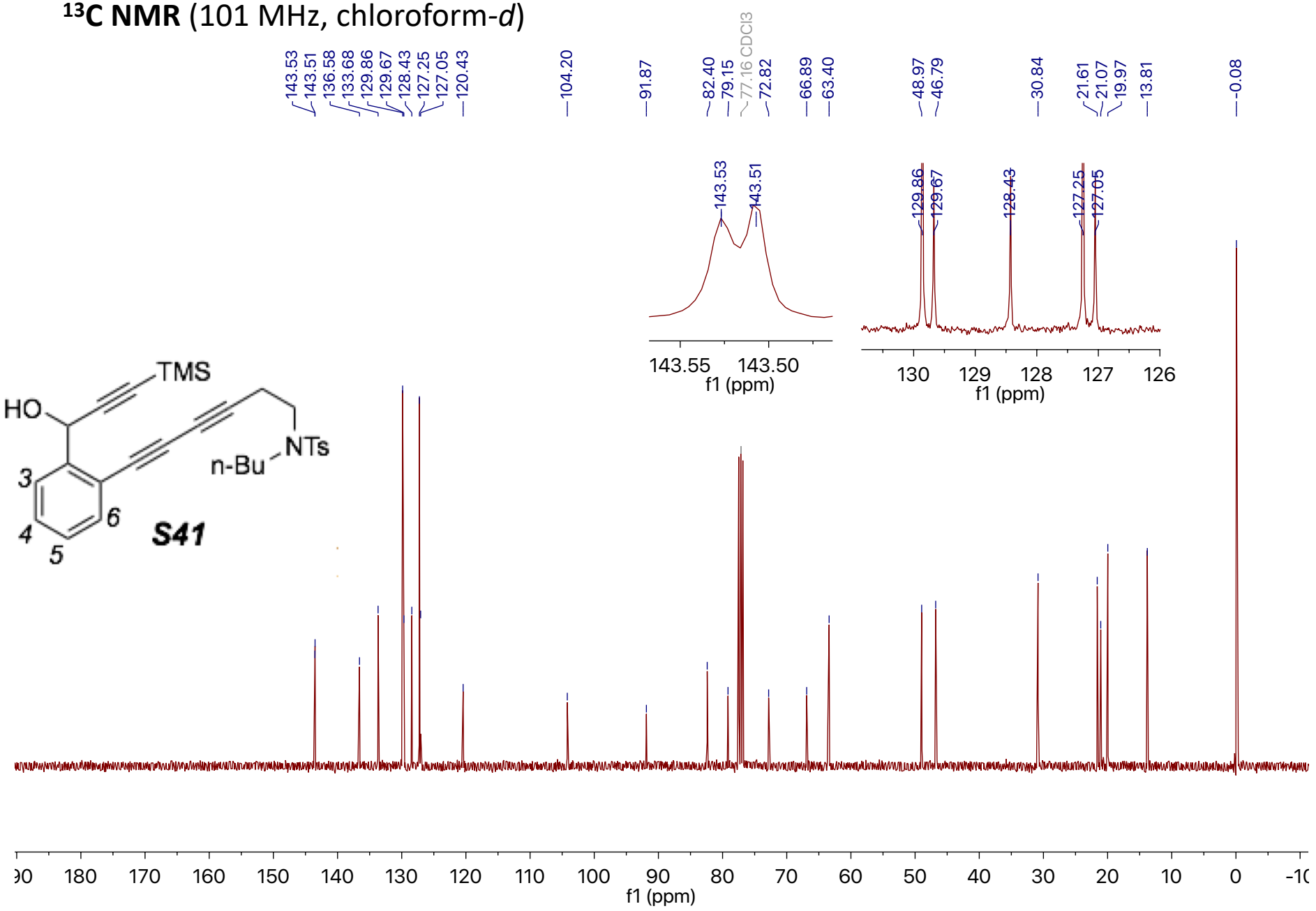
^{13}C NMR (101 MHz, chloroform-*d*)



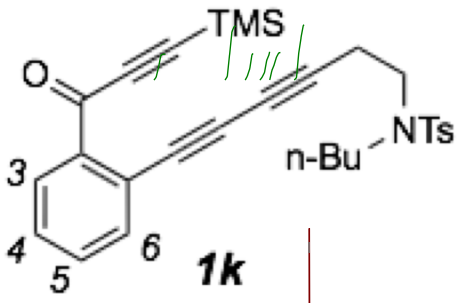
^{1}H NMR (400 MHz, chloroform-*d*)



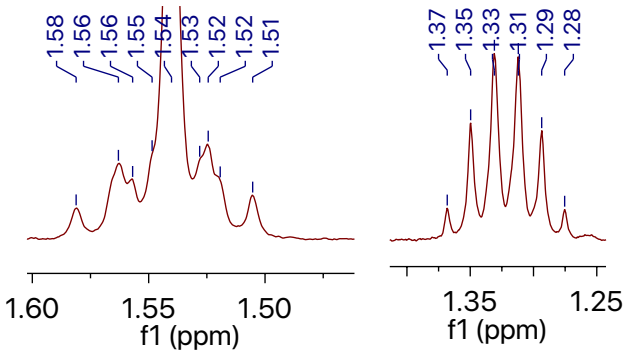
^{13}C NMR (101 MHz, chloroform-*d*)



^{1}H NMR (400 MHz, chloroform-*d*)



1k

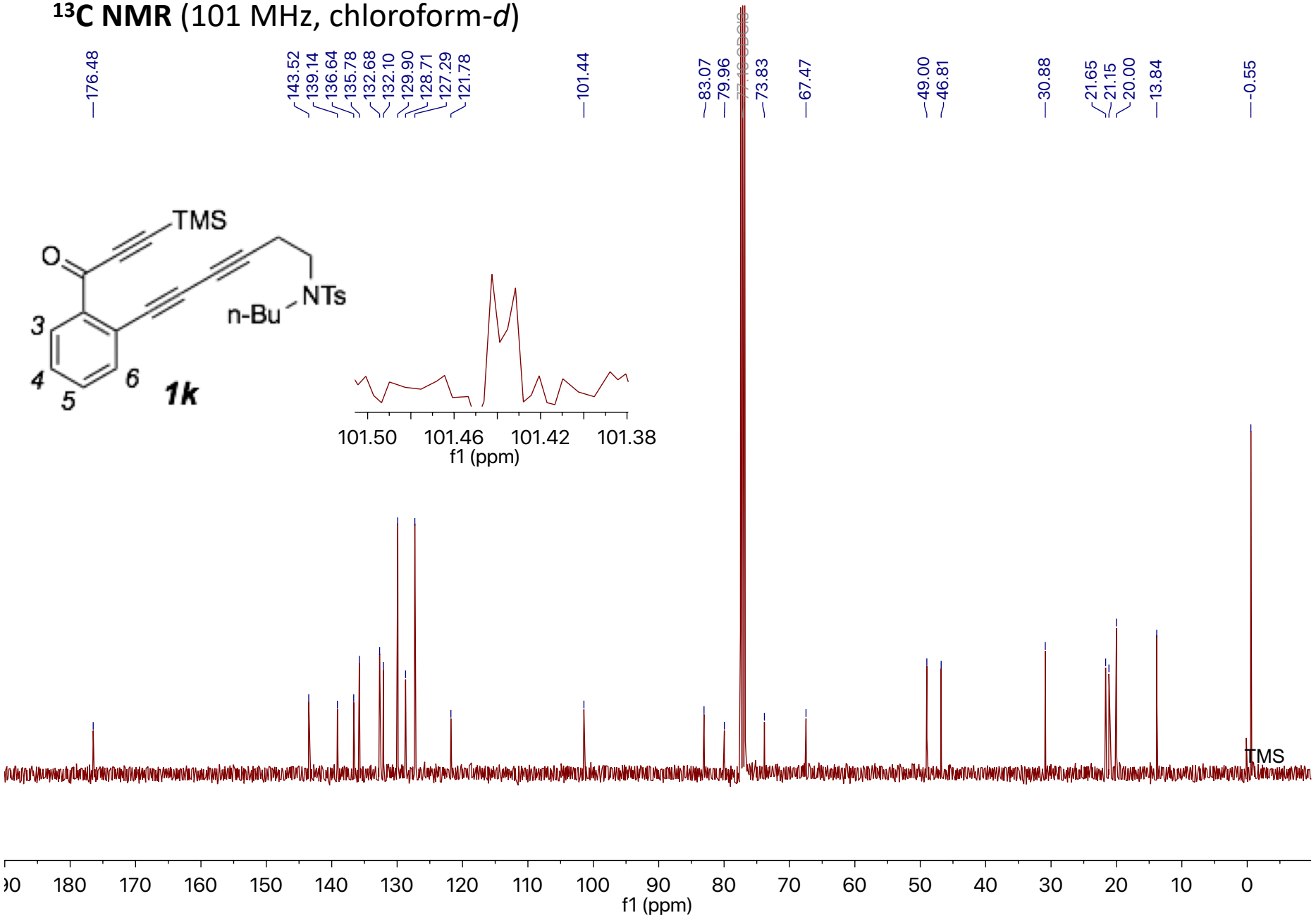


water

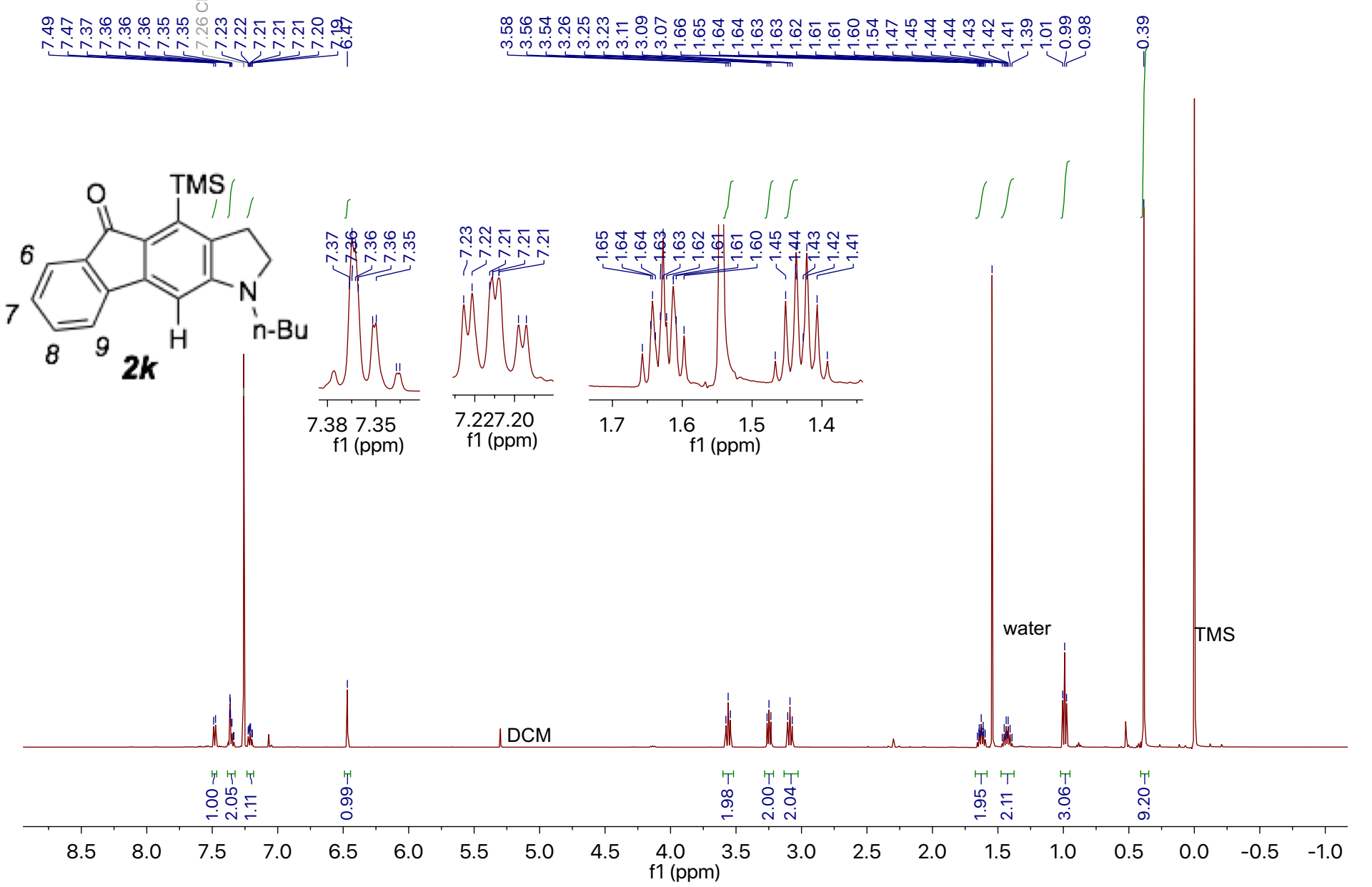
TMS

f1 (ppm)

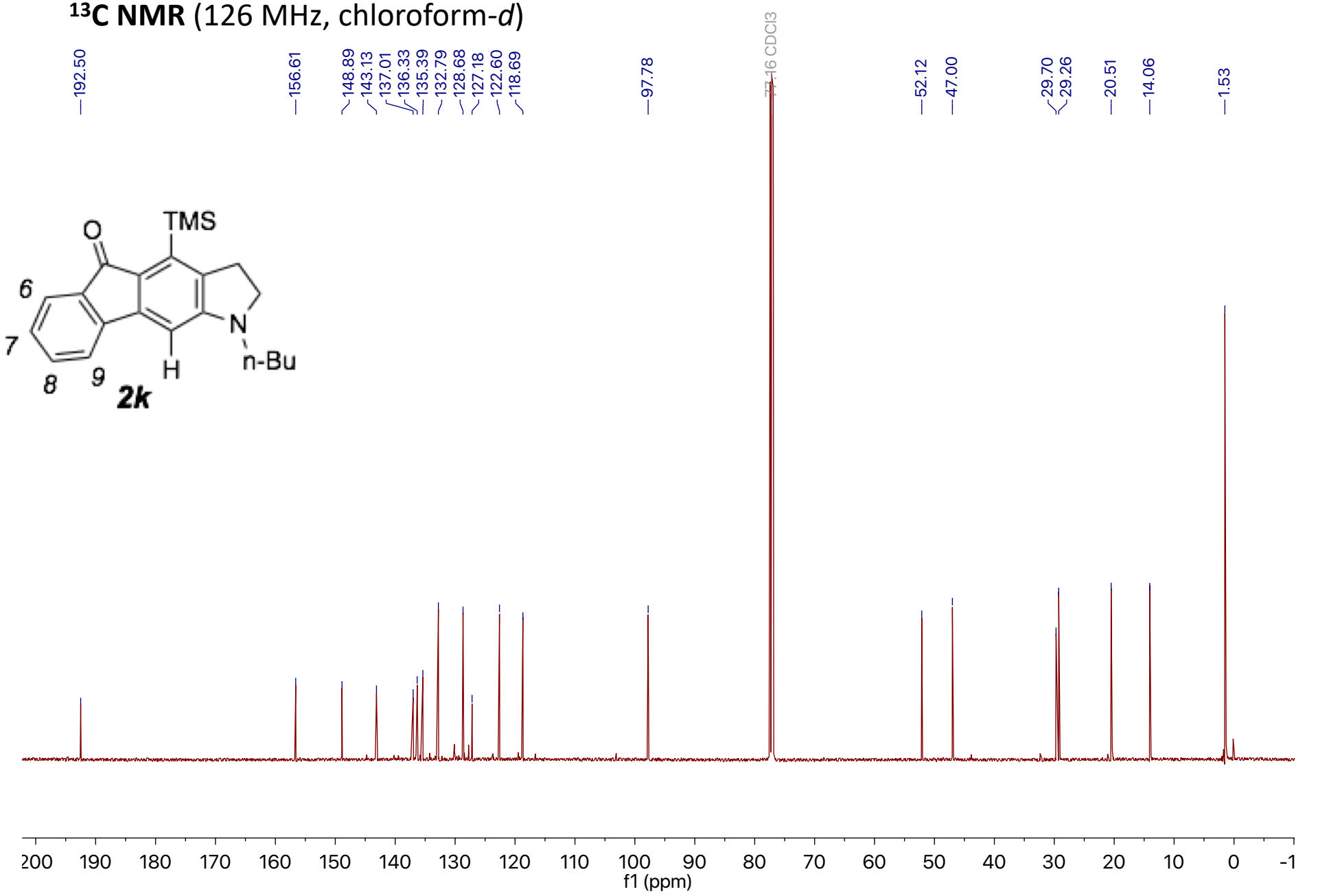
^{13}C NMR (101 MHz, chloroform-*d*)



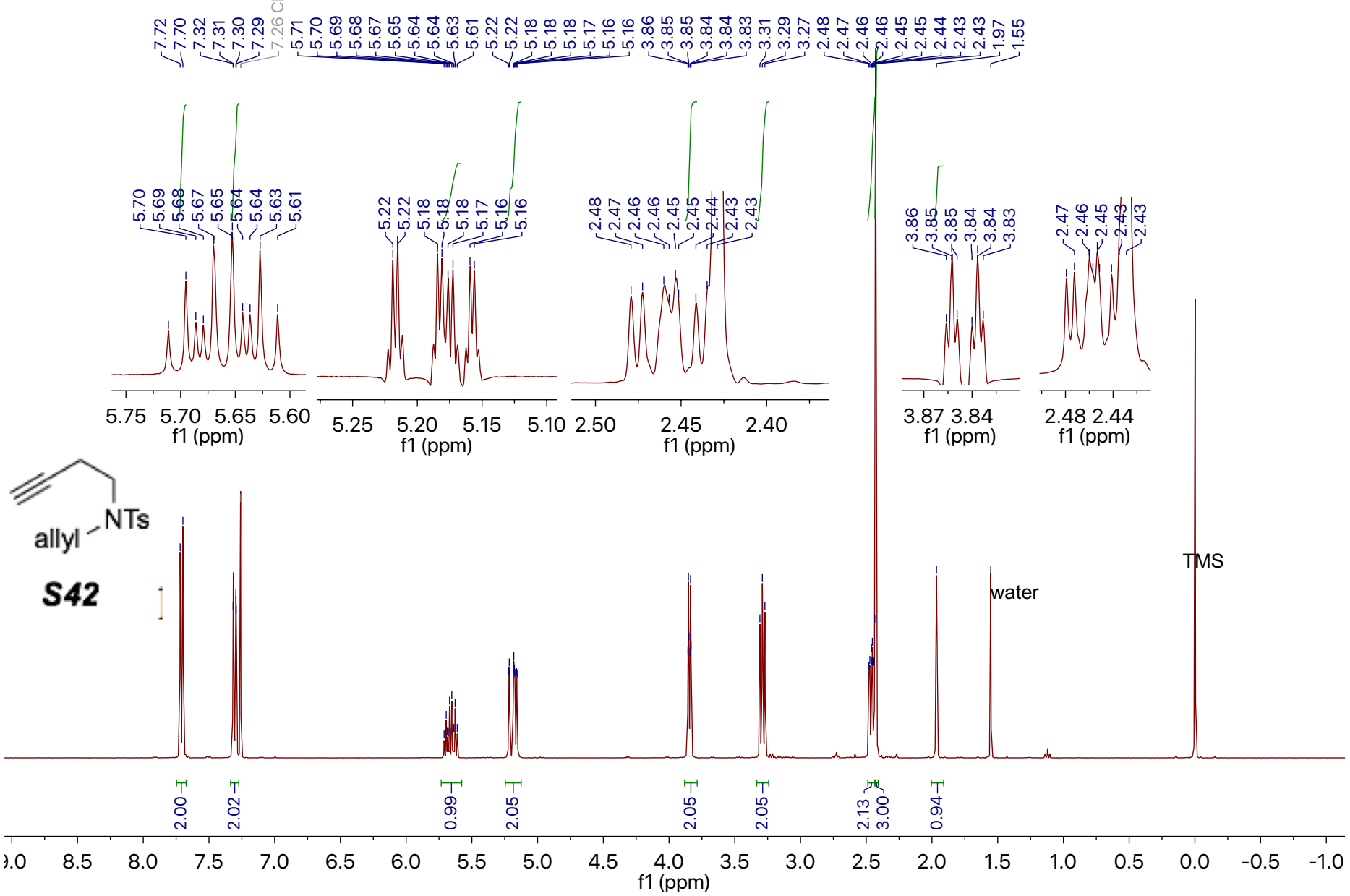
^{1}H NMR (500 MHz, chloroform-*d*)



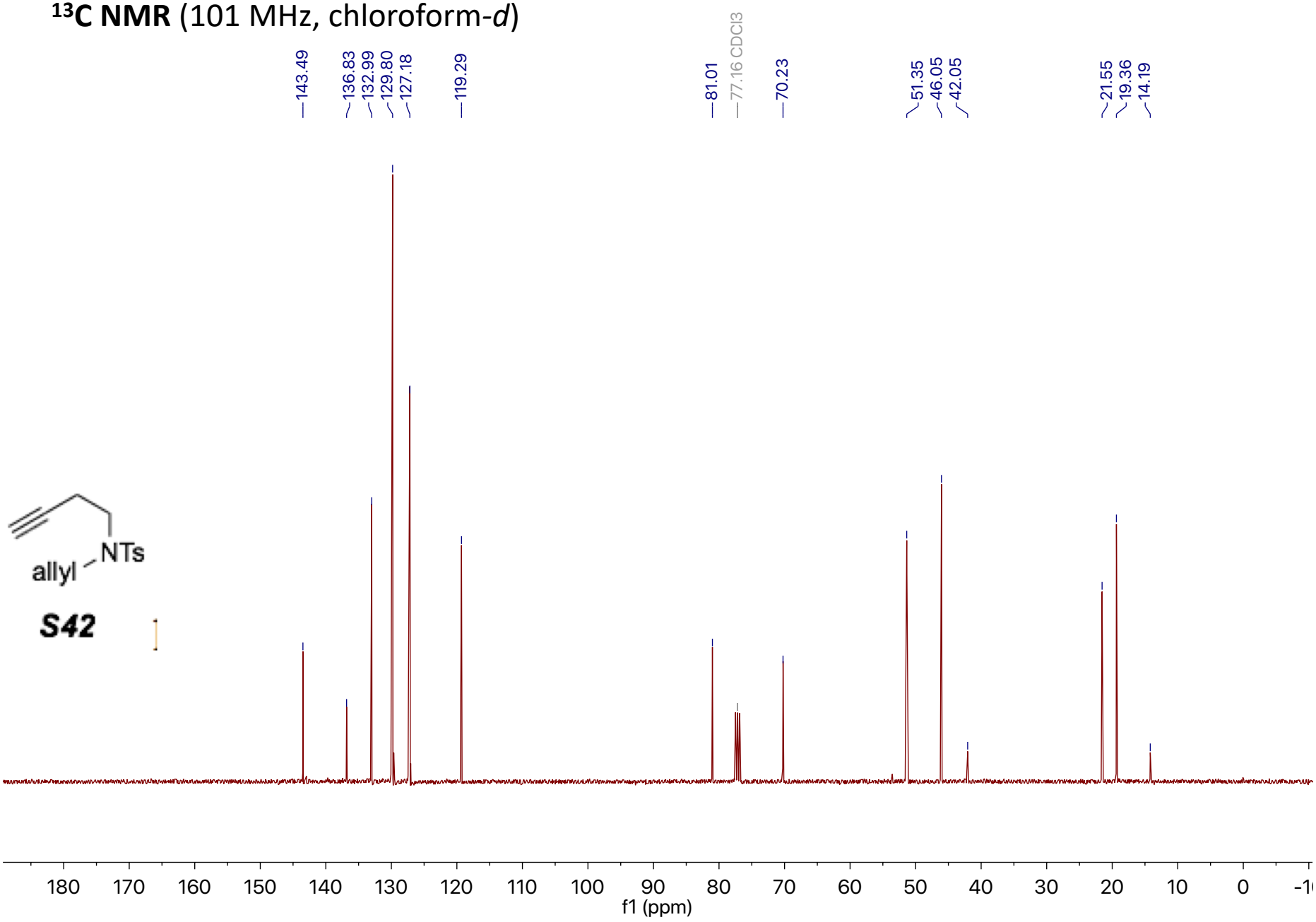
^{13}C NMR (126 MHz, chloroform-*d*)



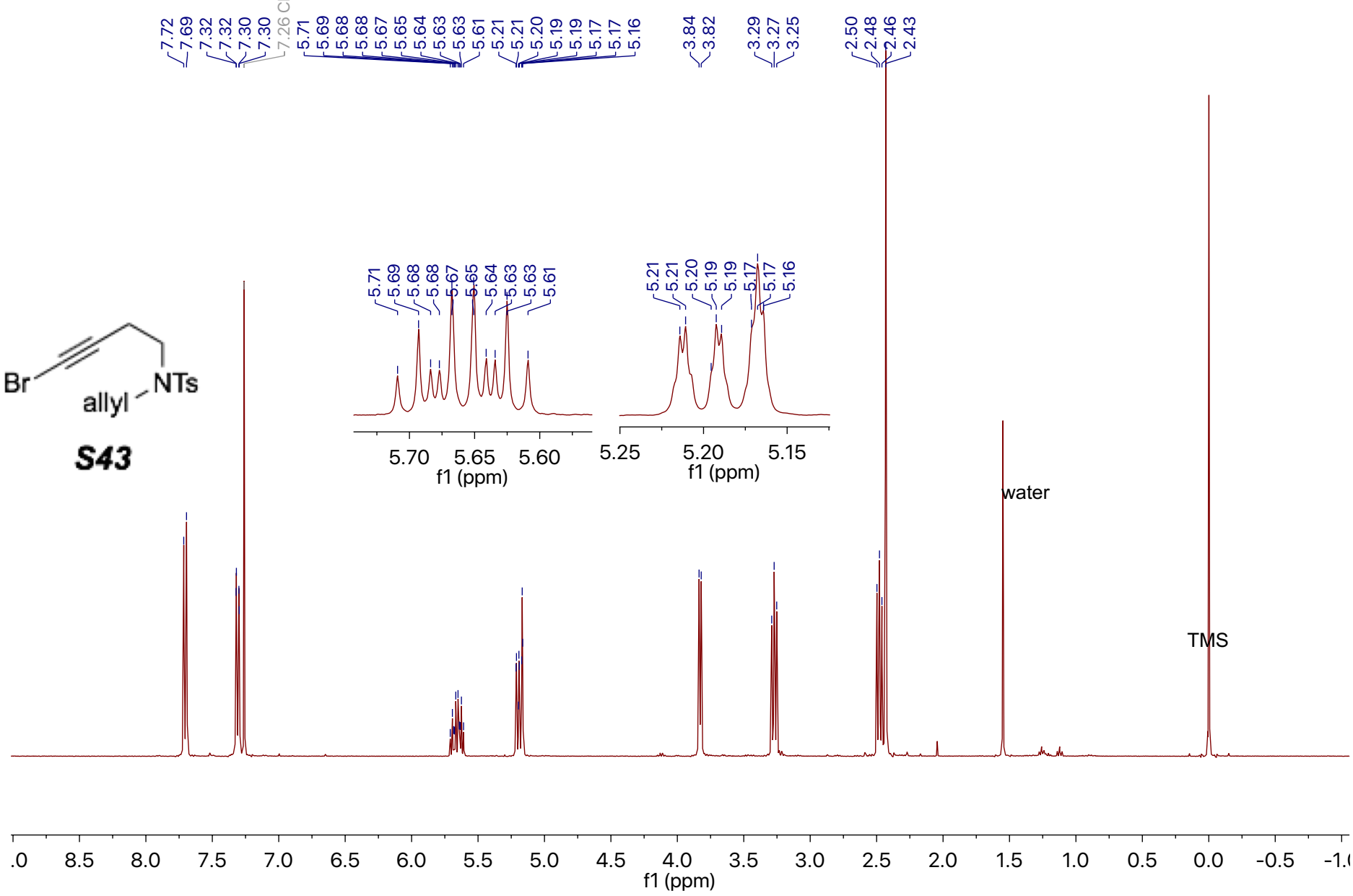
^{1}H NMR (400 MHz, chloroform-*d*)



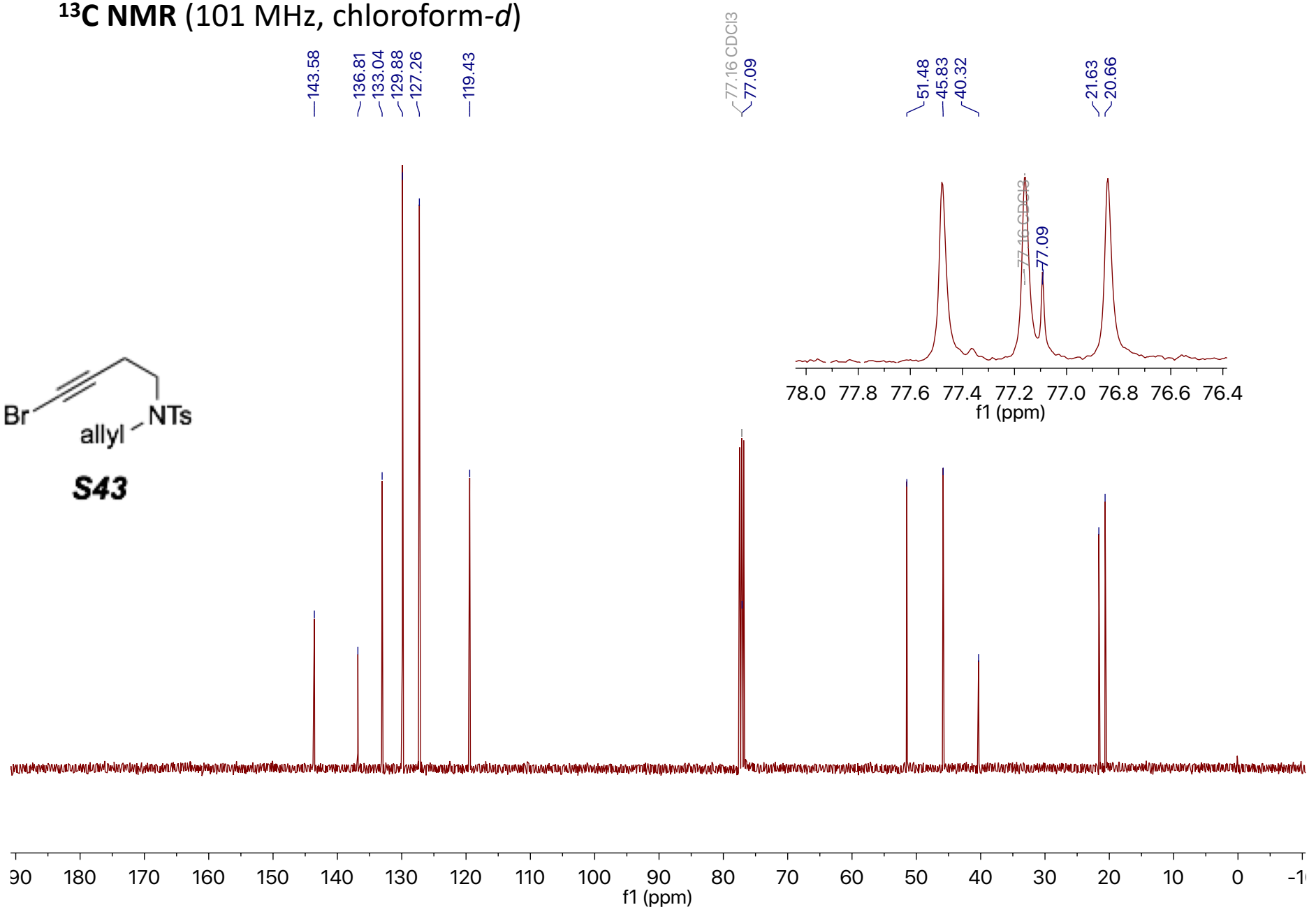
^{13}C NMR (101 MHz, chloroform-*d*)



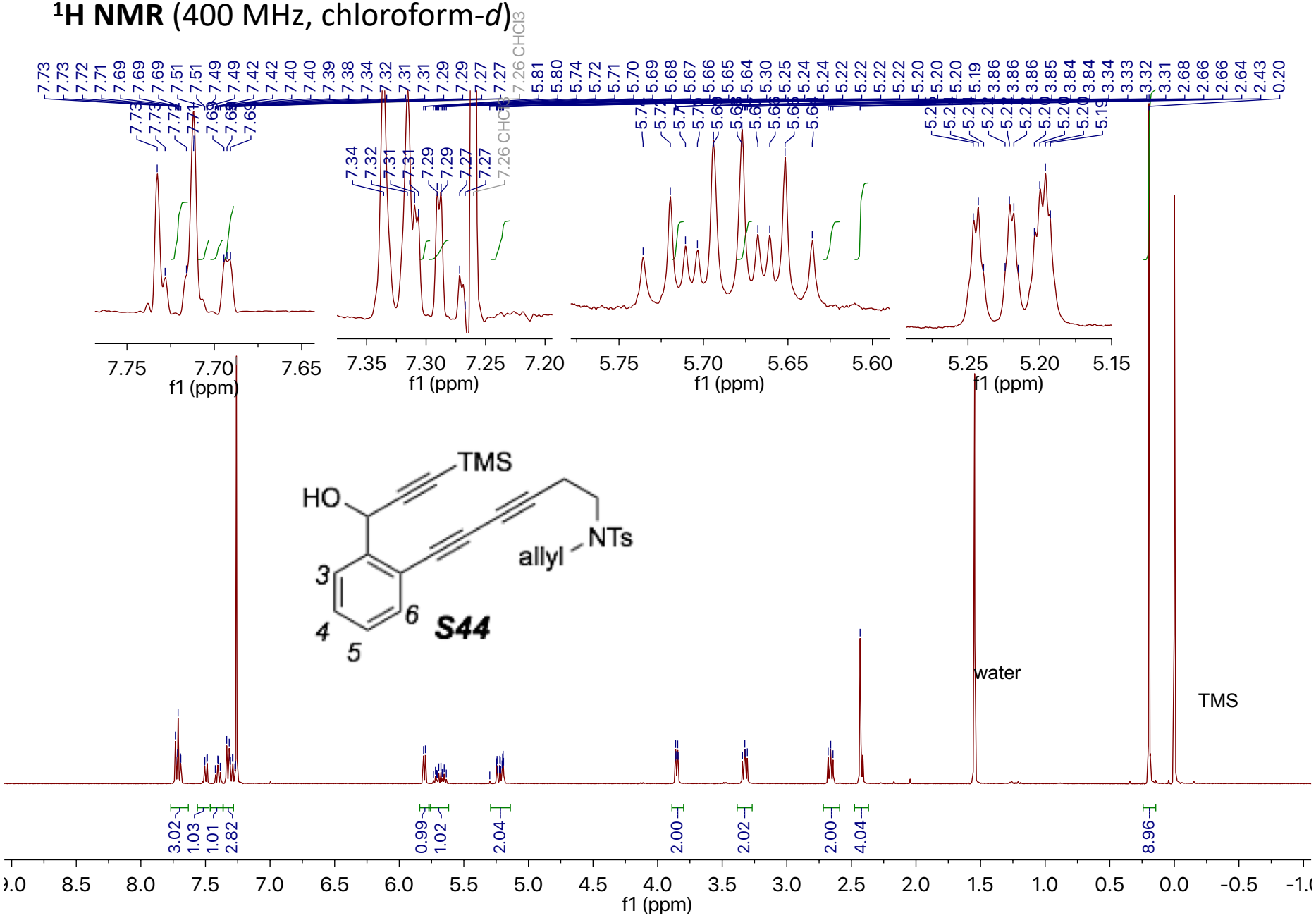
^{1}H NMR (400 MHz, chloroform-*d*)



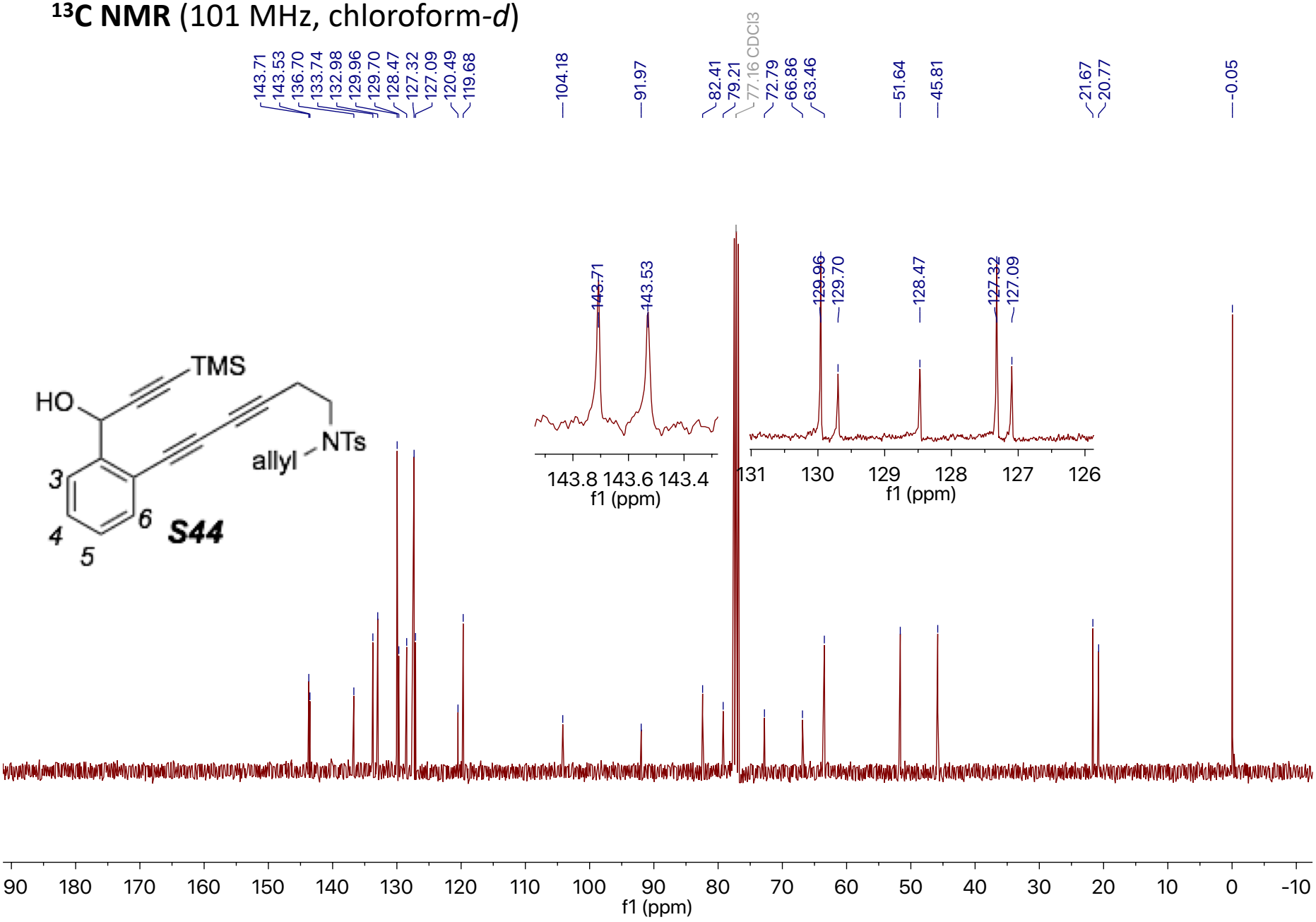
^{13}C NMR (101 MHz, chloroform-*d*)



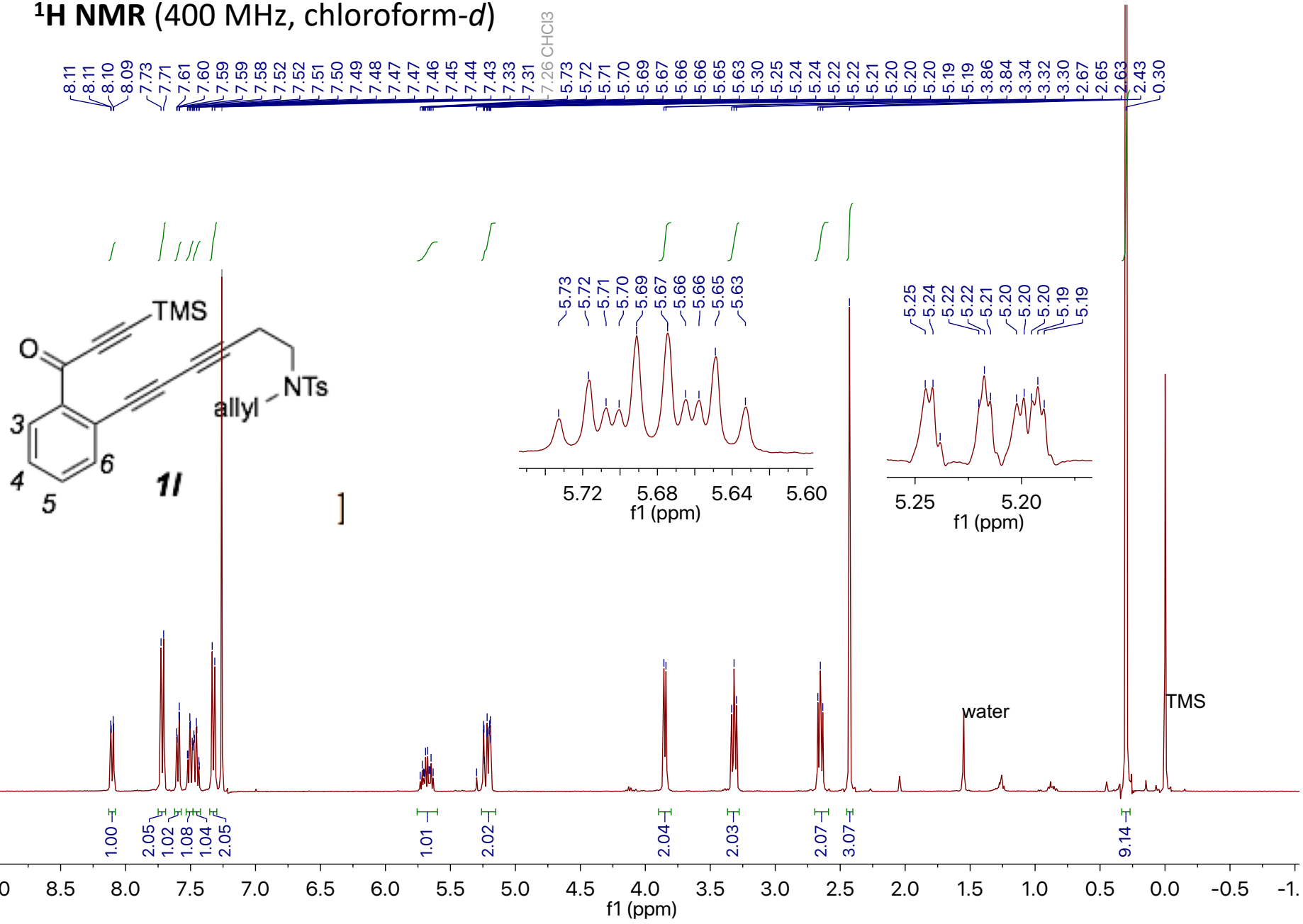
^{1}H NMR (400 MHz, chloroform-*d*)



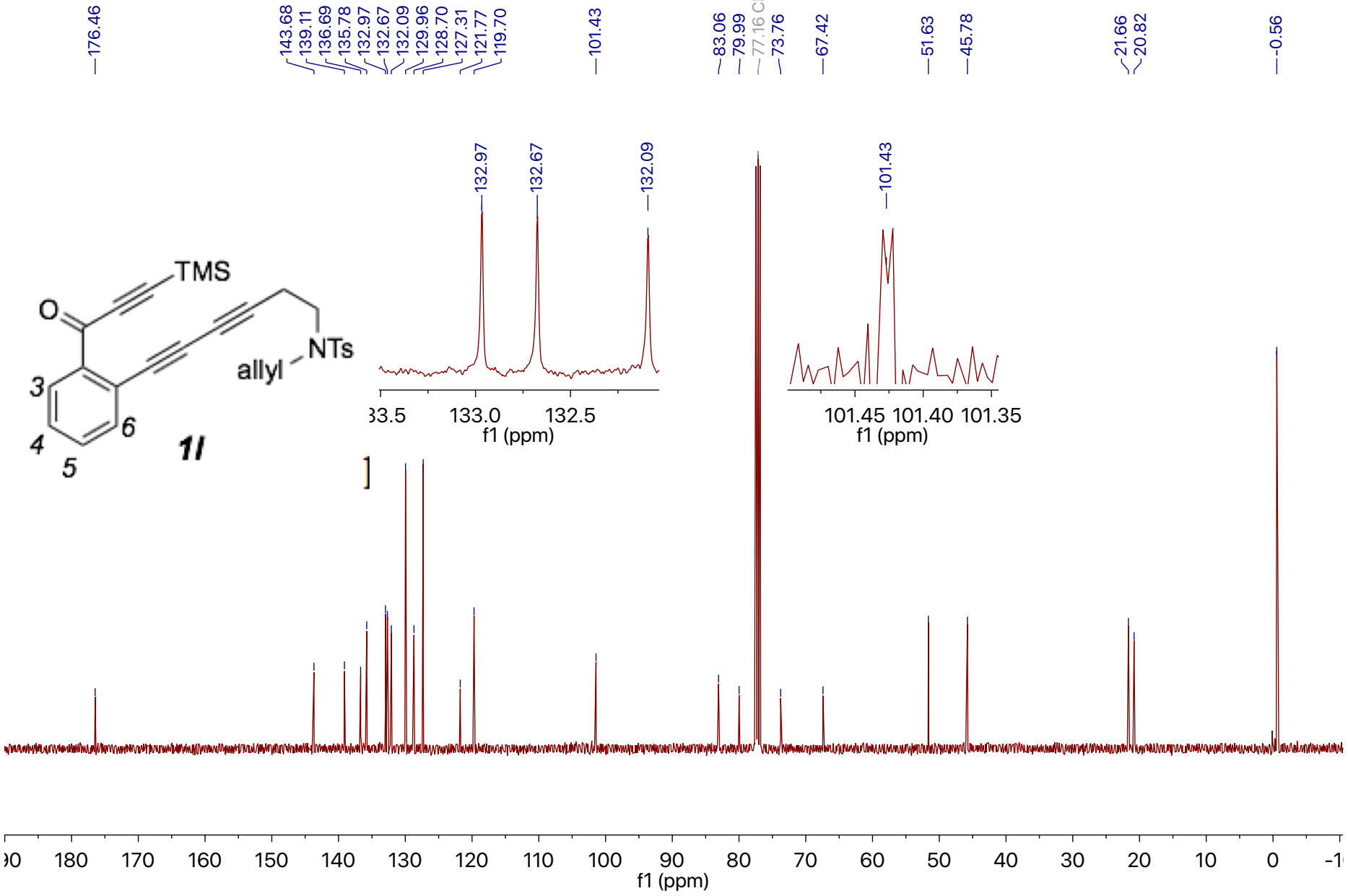
^{13}C NMR (101 MHz, chloroform-*d*)



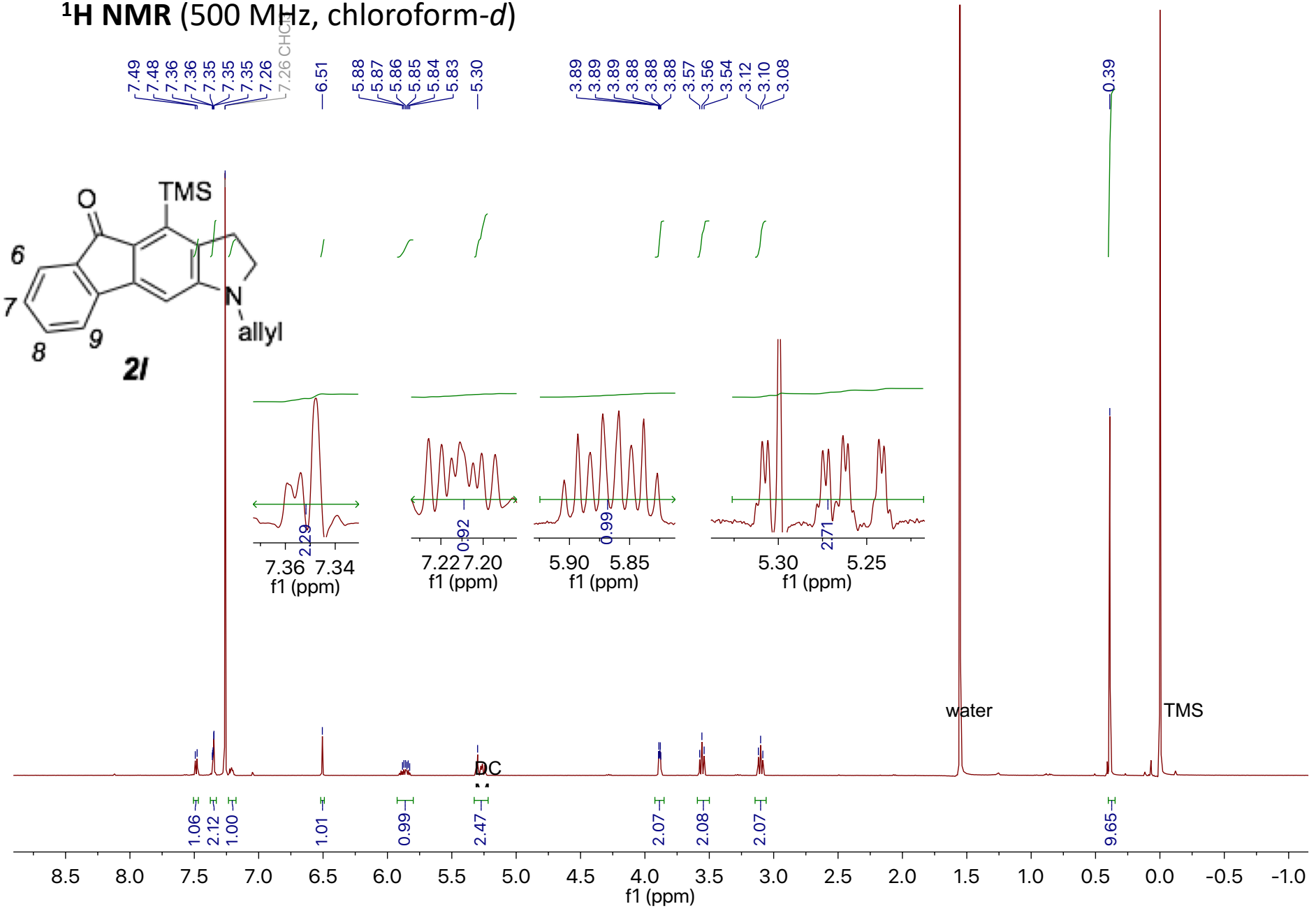
^{1}H NMR (400 MHz, chloroform-*d*)



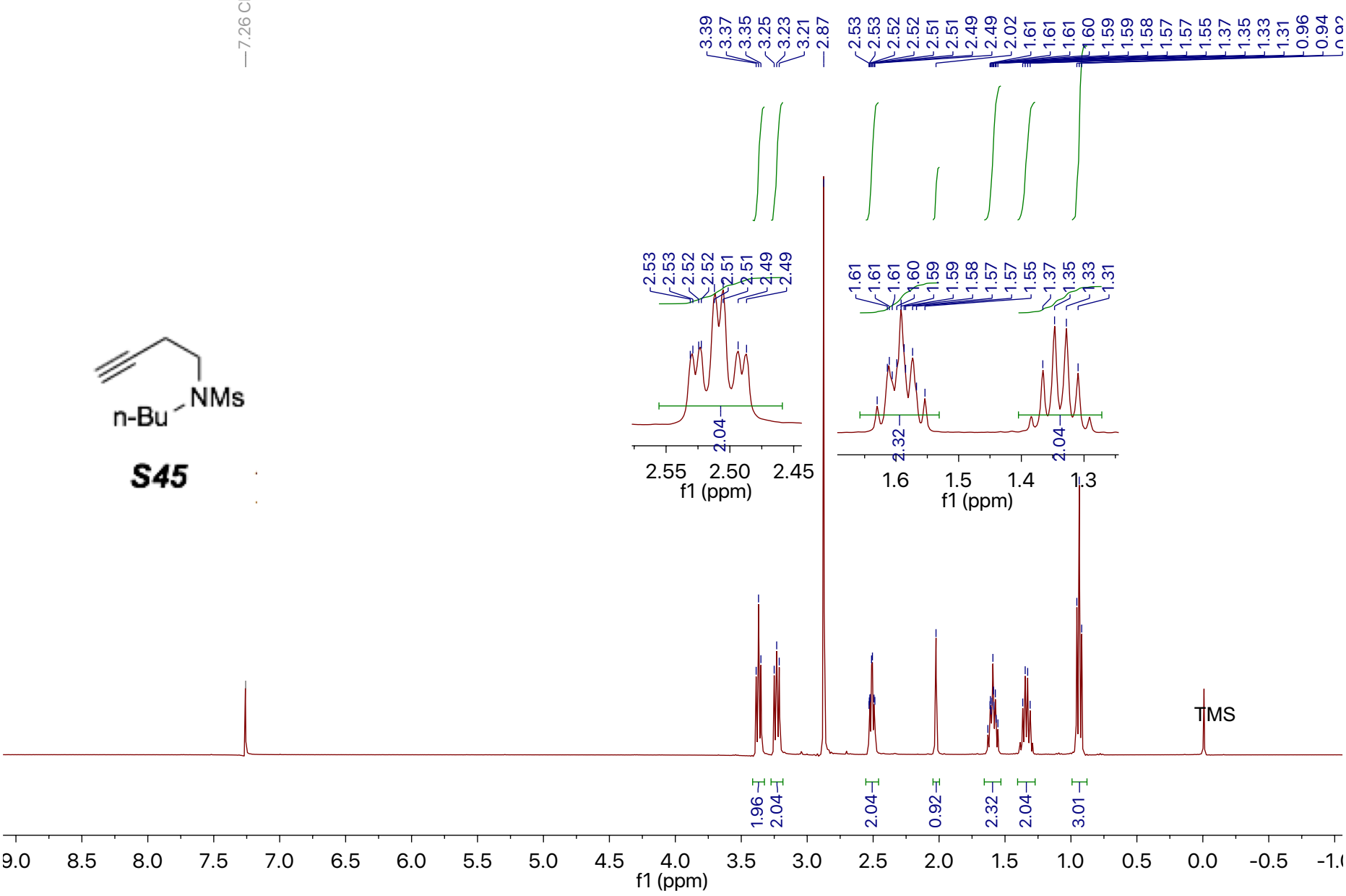
^{13}C NMR (101 MHz, chloroform-*d*)



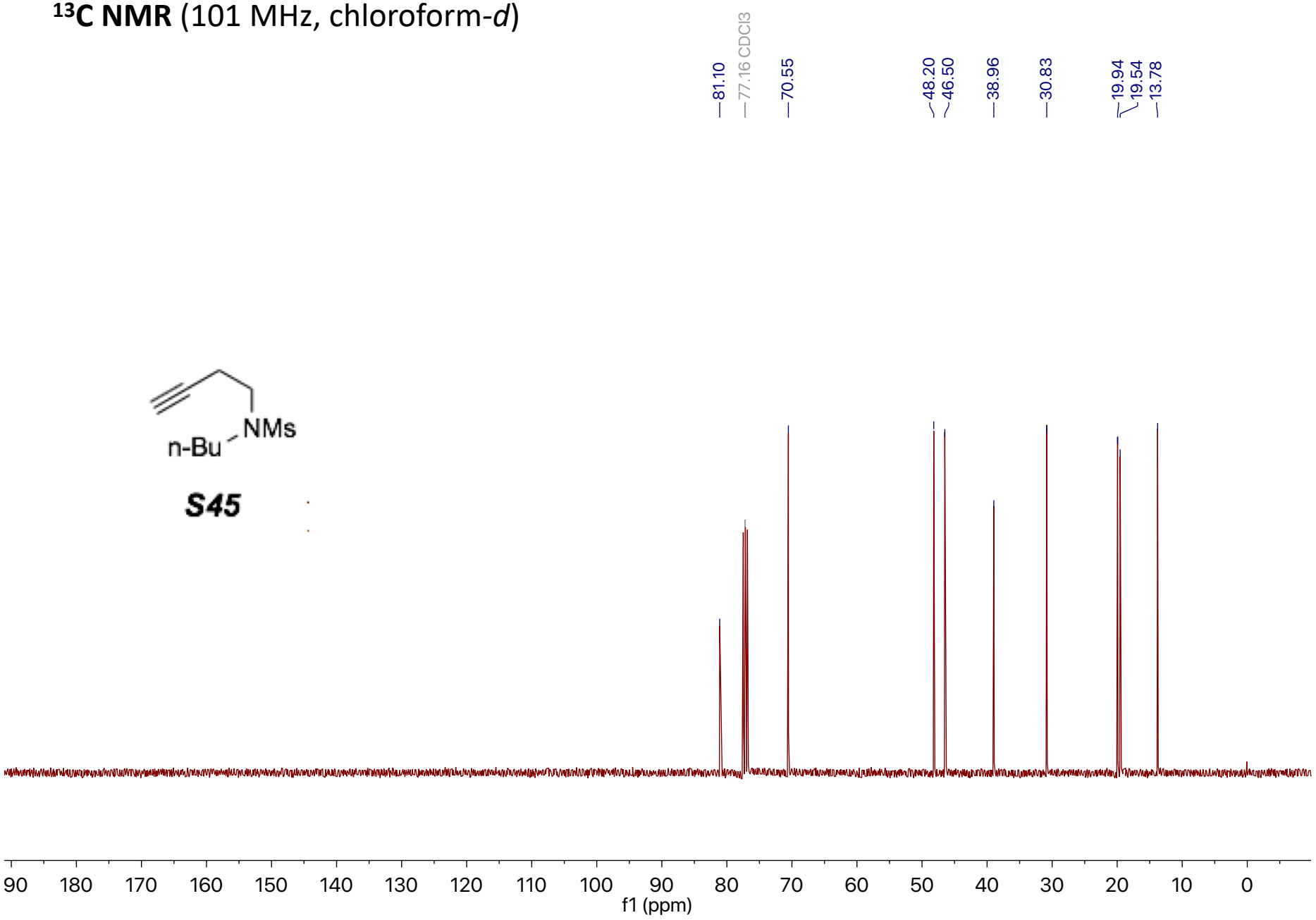
^{1}H NMR (500 MHz, chloroform-*d*)



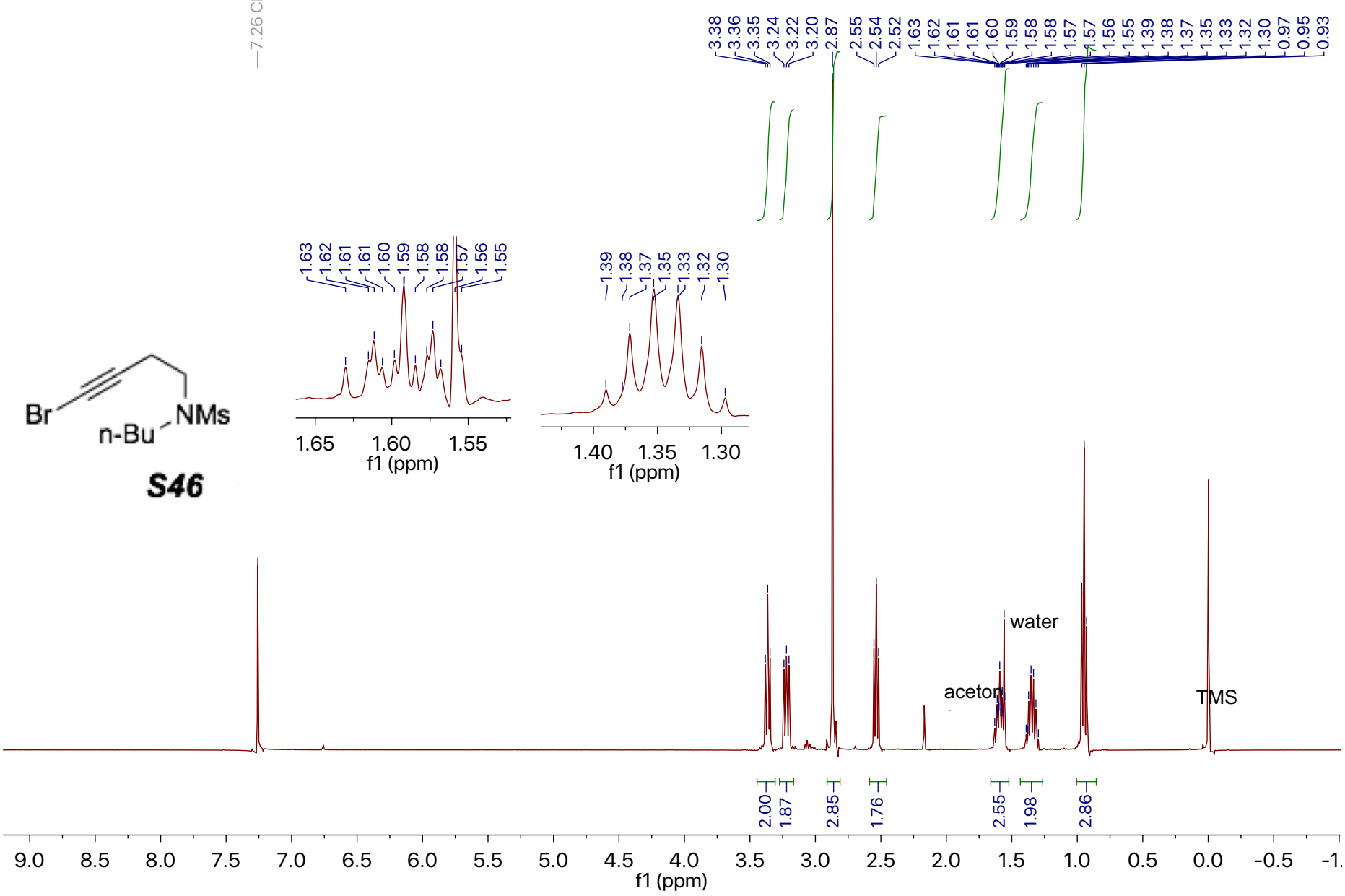
^{1}H NMR (400 MHz, chloroform-*d*)



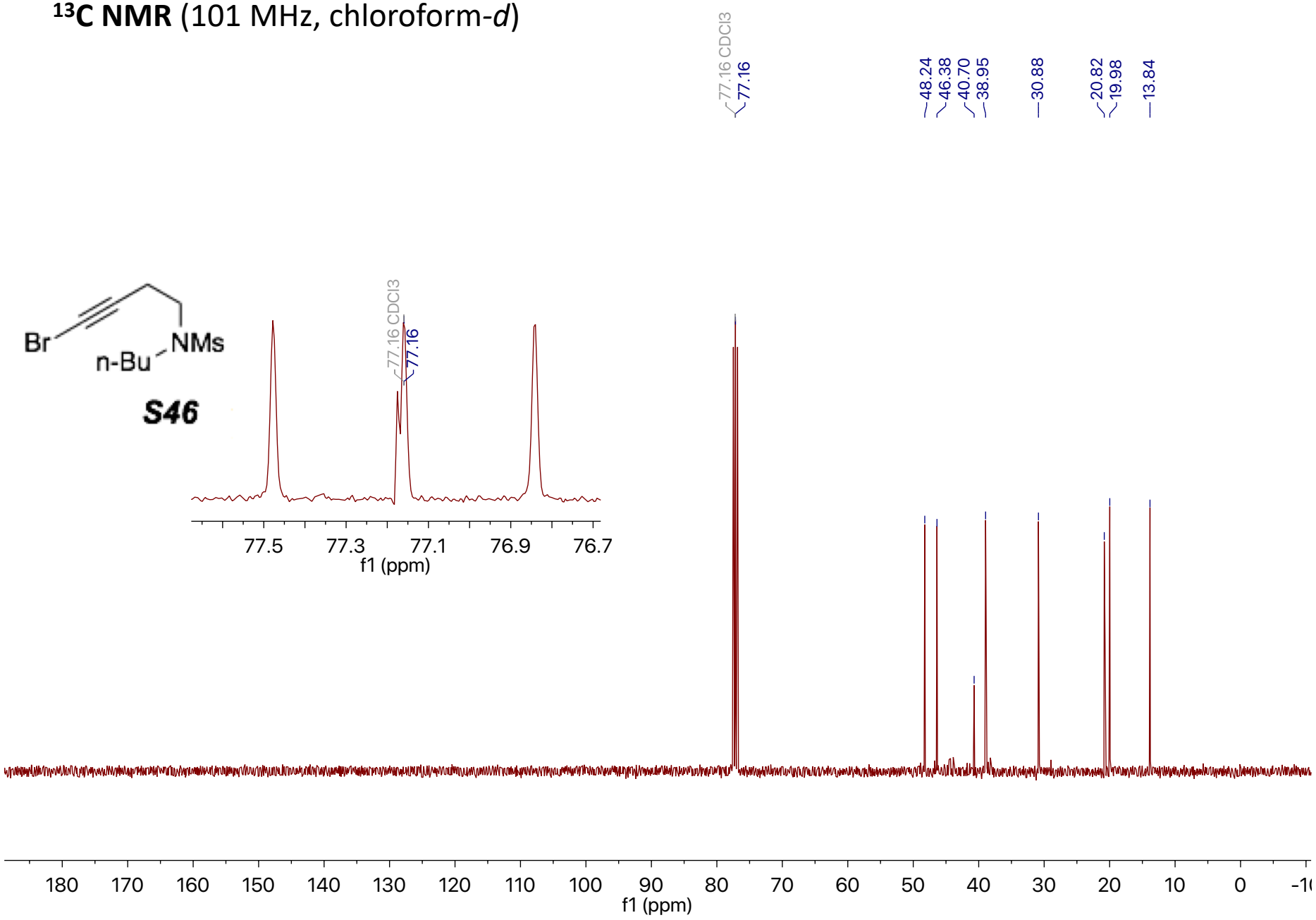
^{13}C NMR (101 MHz, chloroform-*d*)



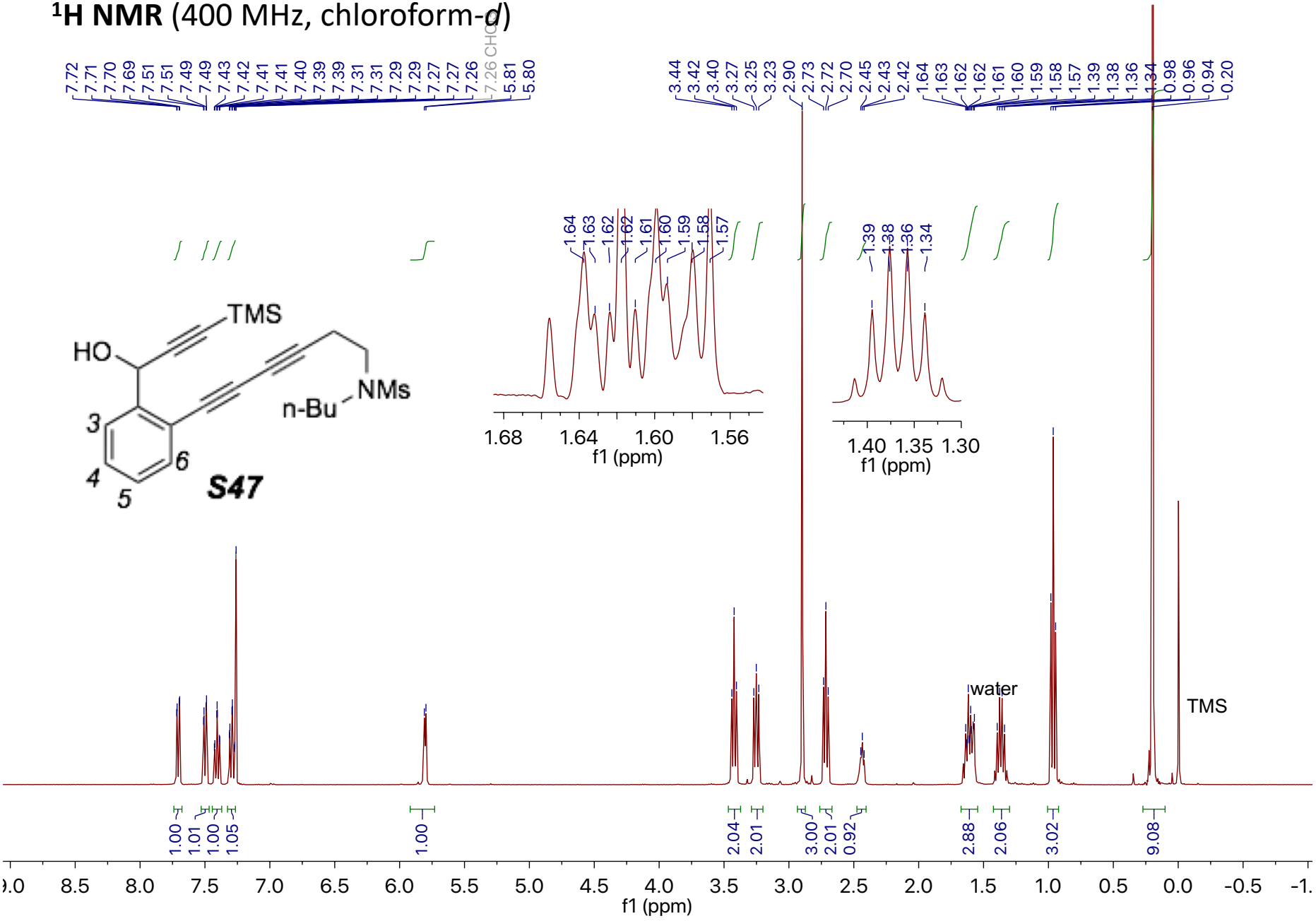
^{1}H NMR (400 MHz, chloroform-*d*)



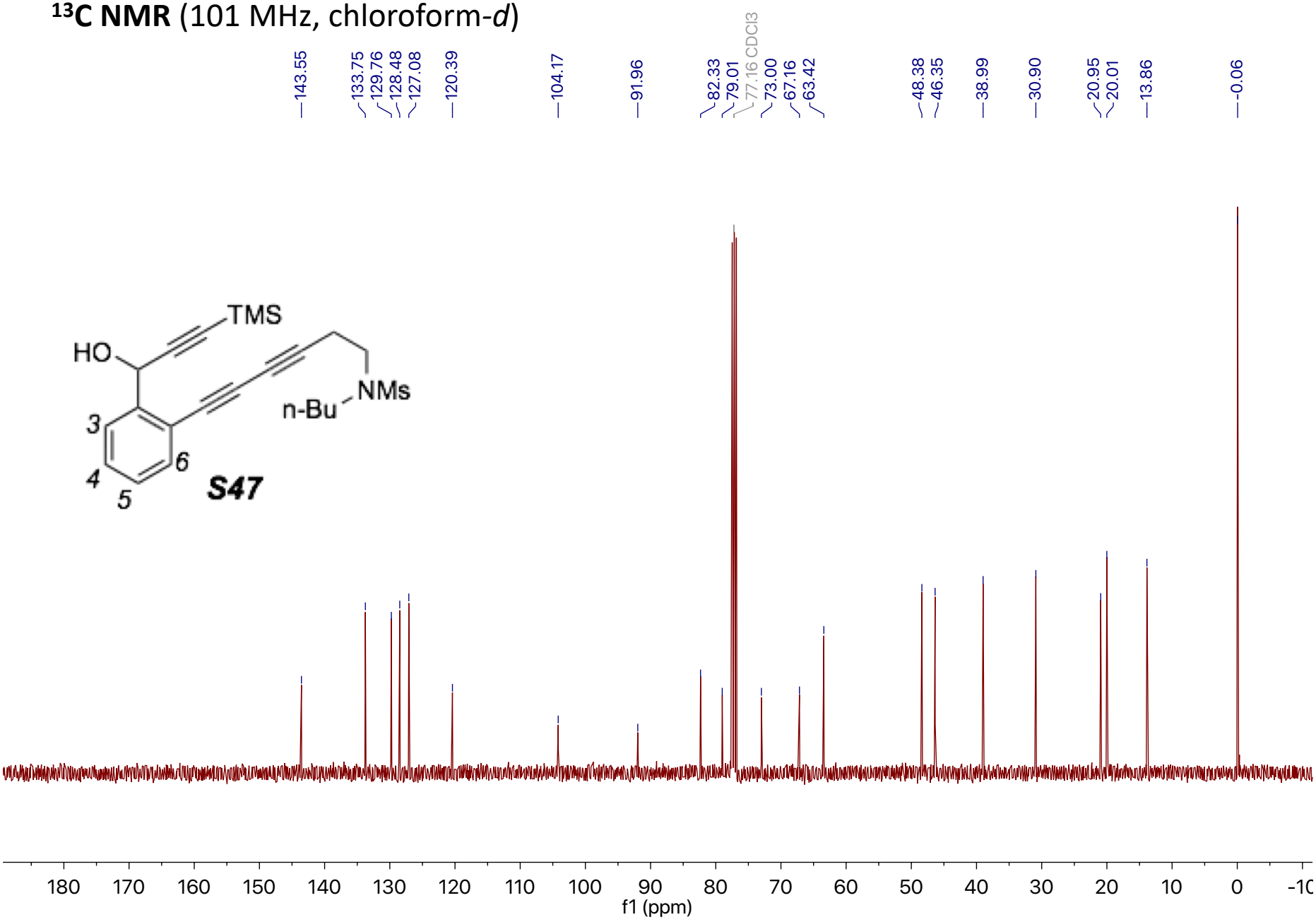
^{13}C NMR (101 MHz, chloroform-*d*)



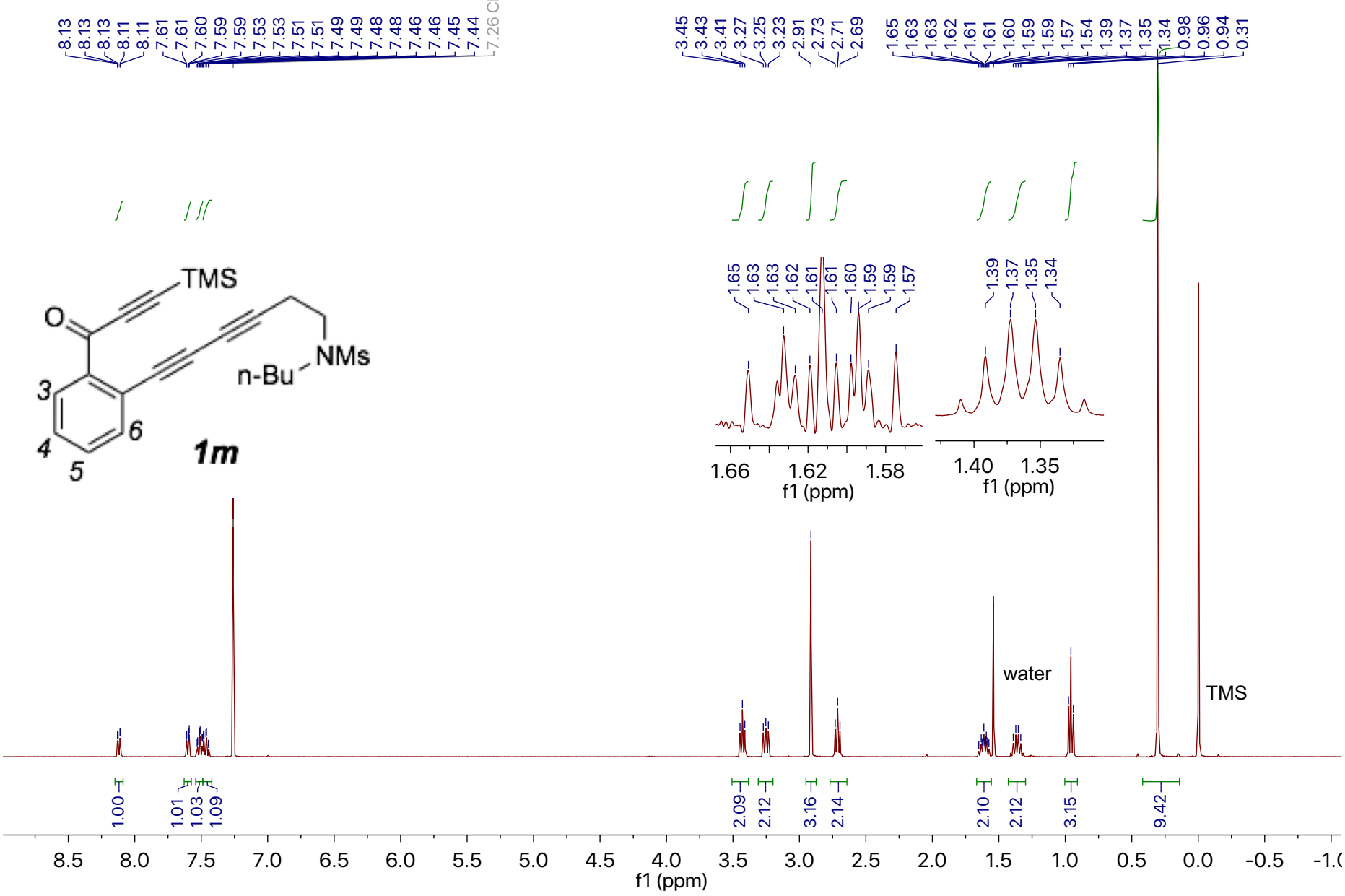
^{1}H NMR (400 MHz, chloroform-*d*)



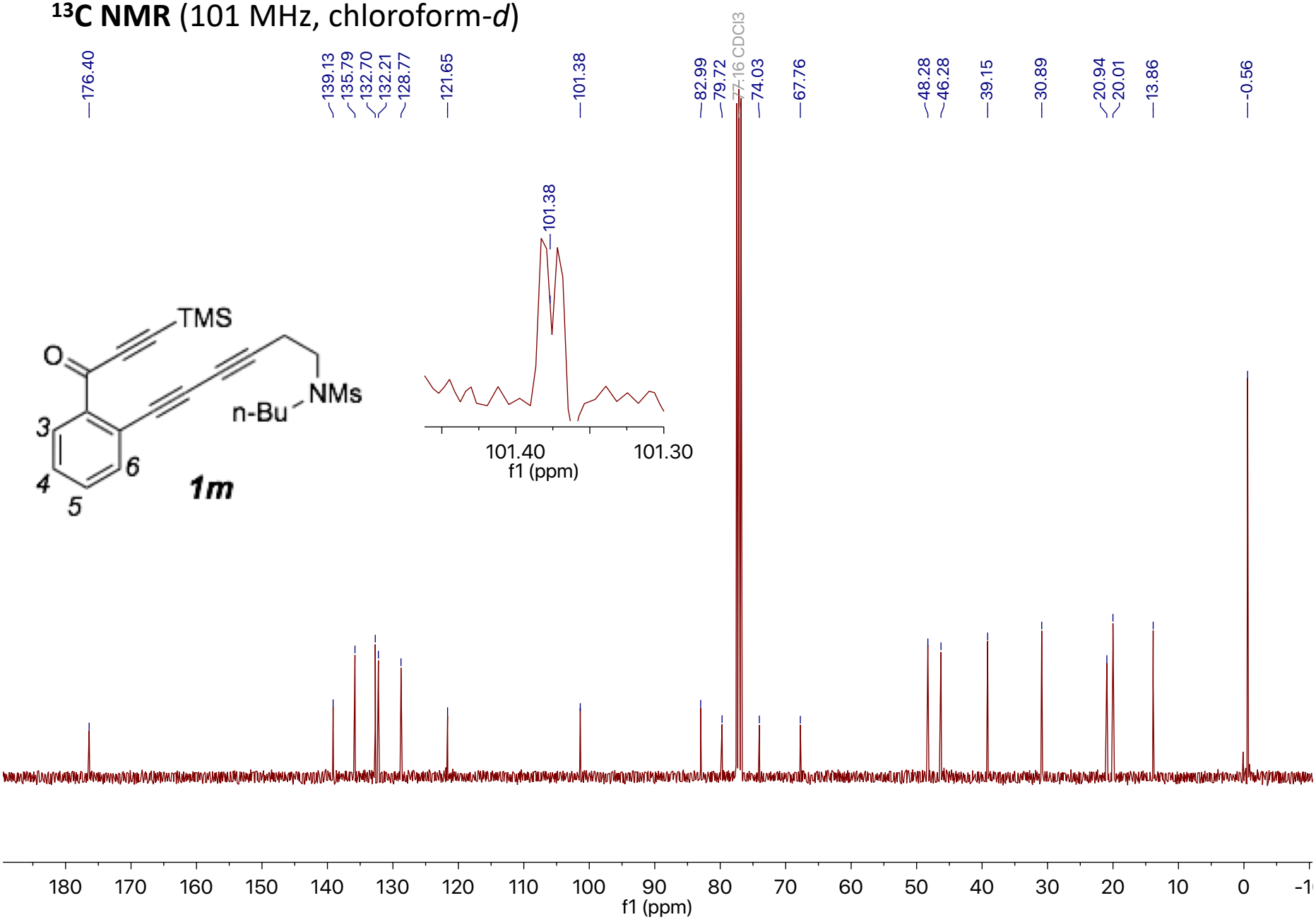
^{13}C NMR (101 MHz, chloroform-*d*)



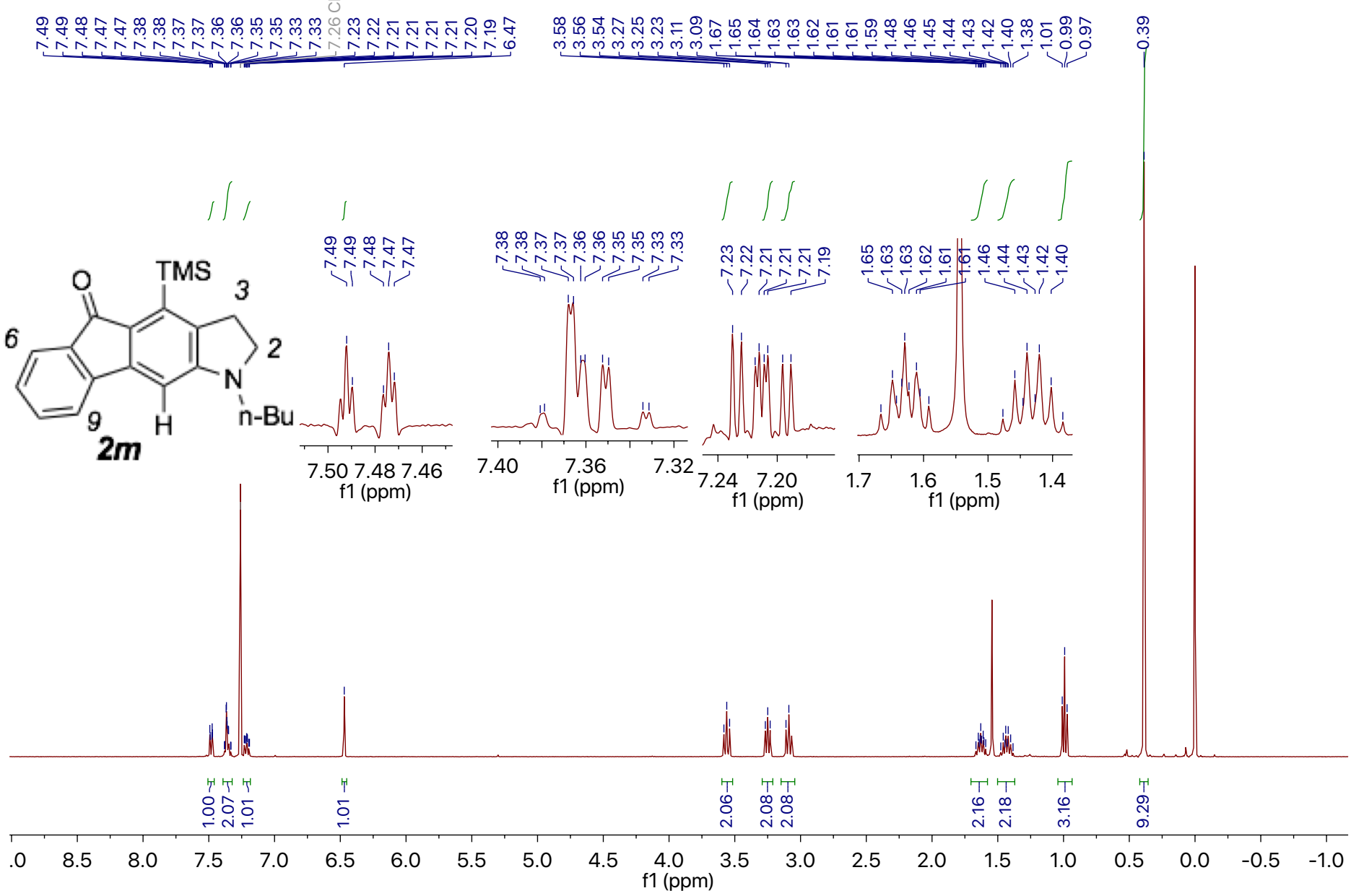
^{1}H NMR (400 MHz, chloroform-*d*)



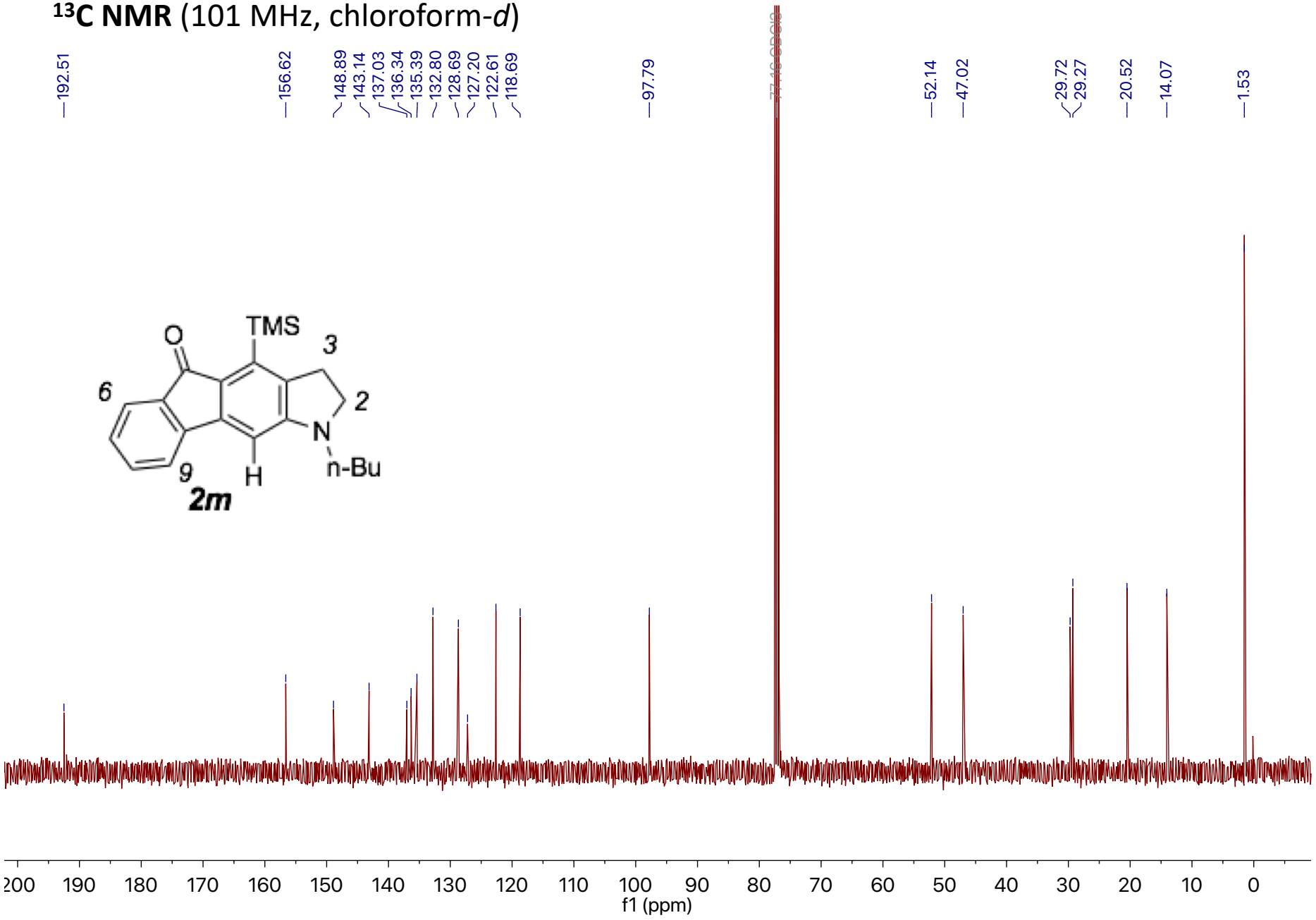
^{13}C NMR (101 MHz, chloroform-*d*)



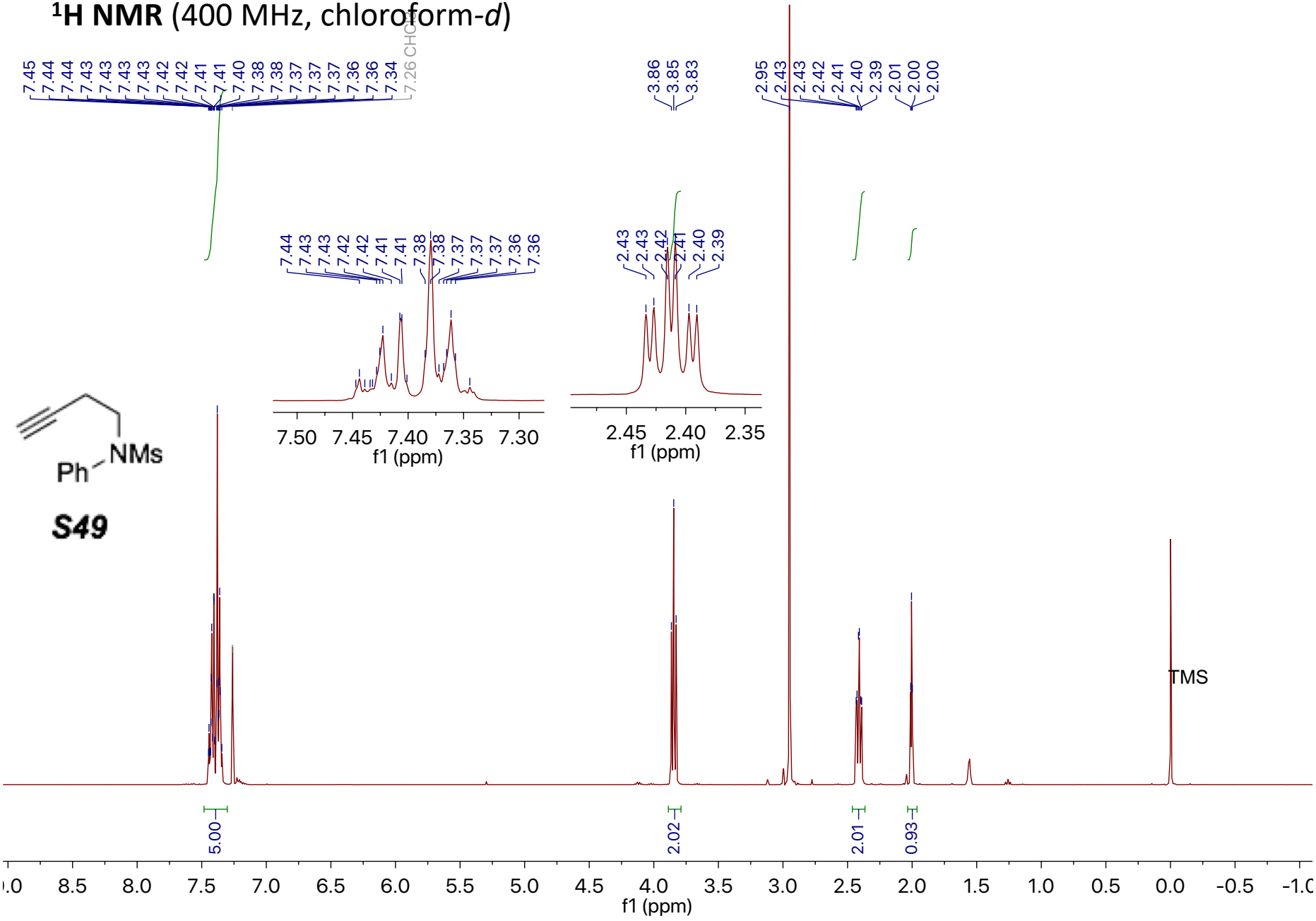
^{1}H NMR (400 MHz, chloroform-*d*)



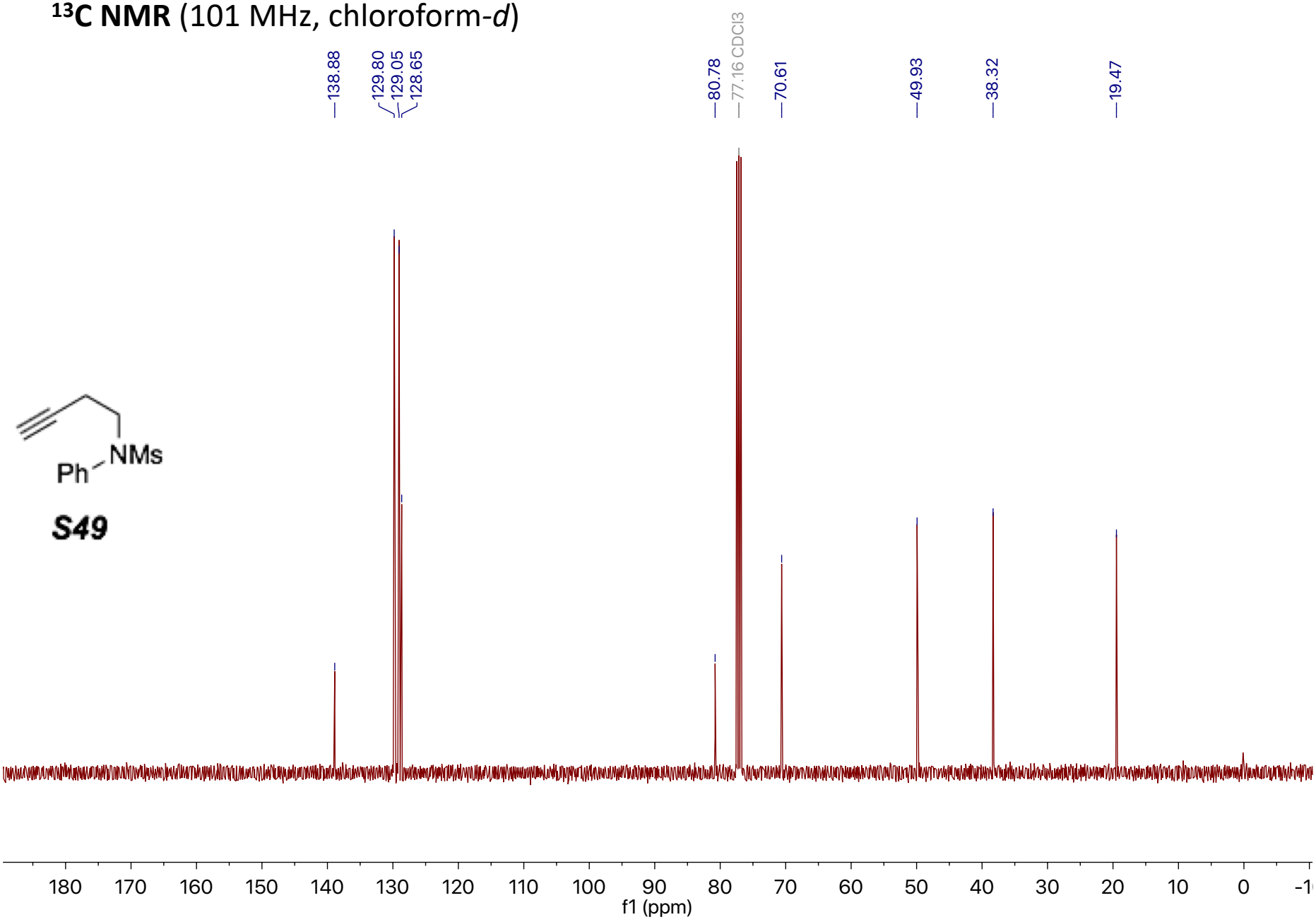
^{13}C NMR (101 MHz, chloroform-*d*)



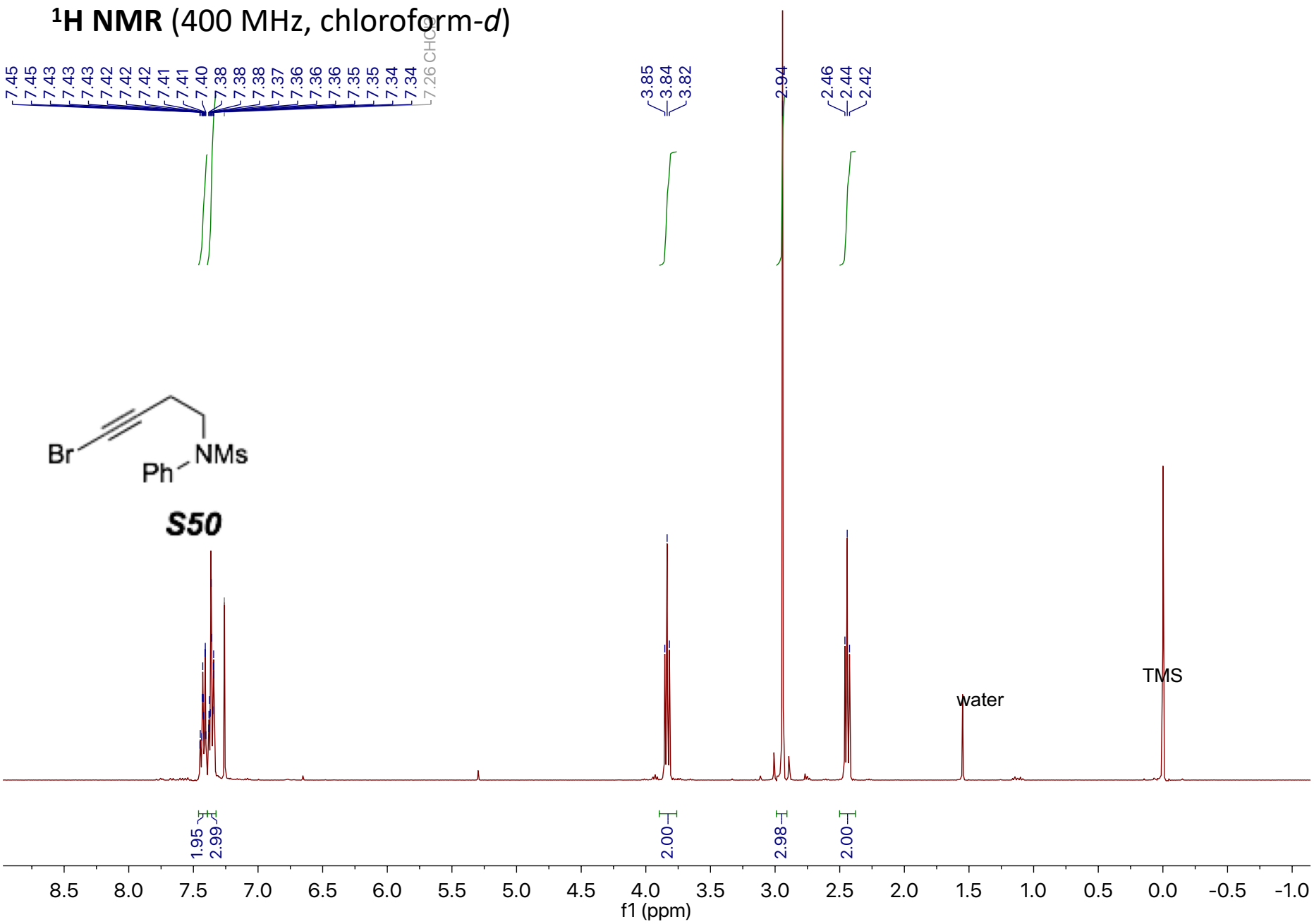
^{1}H NMR (400 MHz, chloroform-*d*)



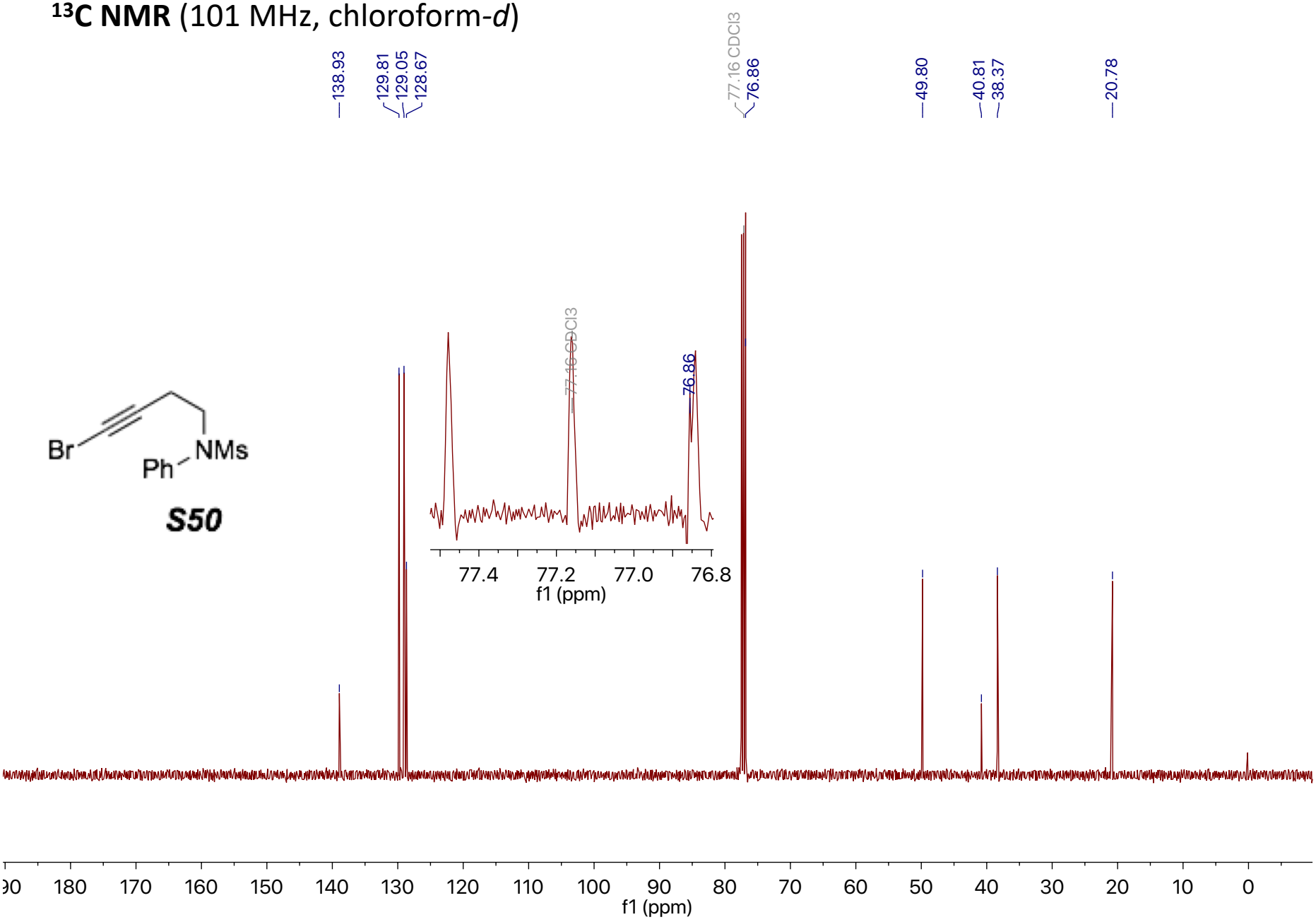
^{13}C NMR (101 MHz, chloroform-*d*)



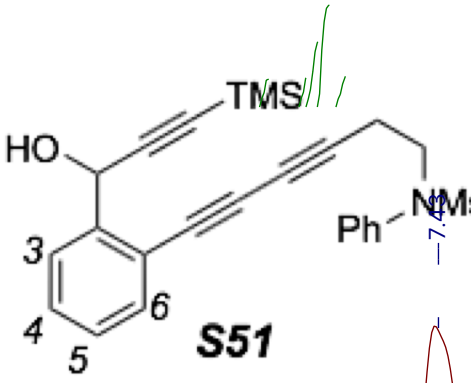
^{1}H NMR (400 MHz, chloroform-*d*)



^{13}C NMR (101 MHz, chloroform-*d*)

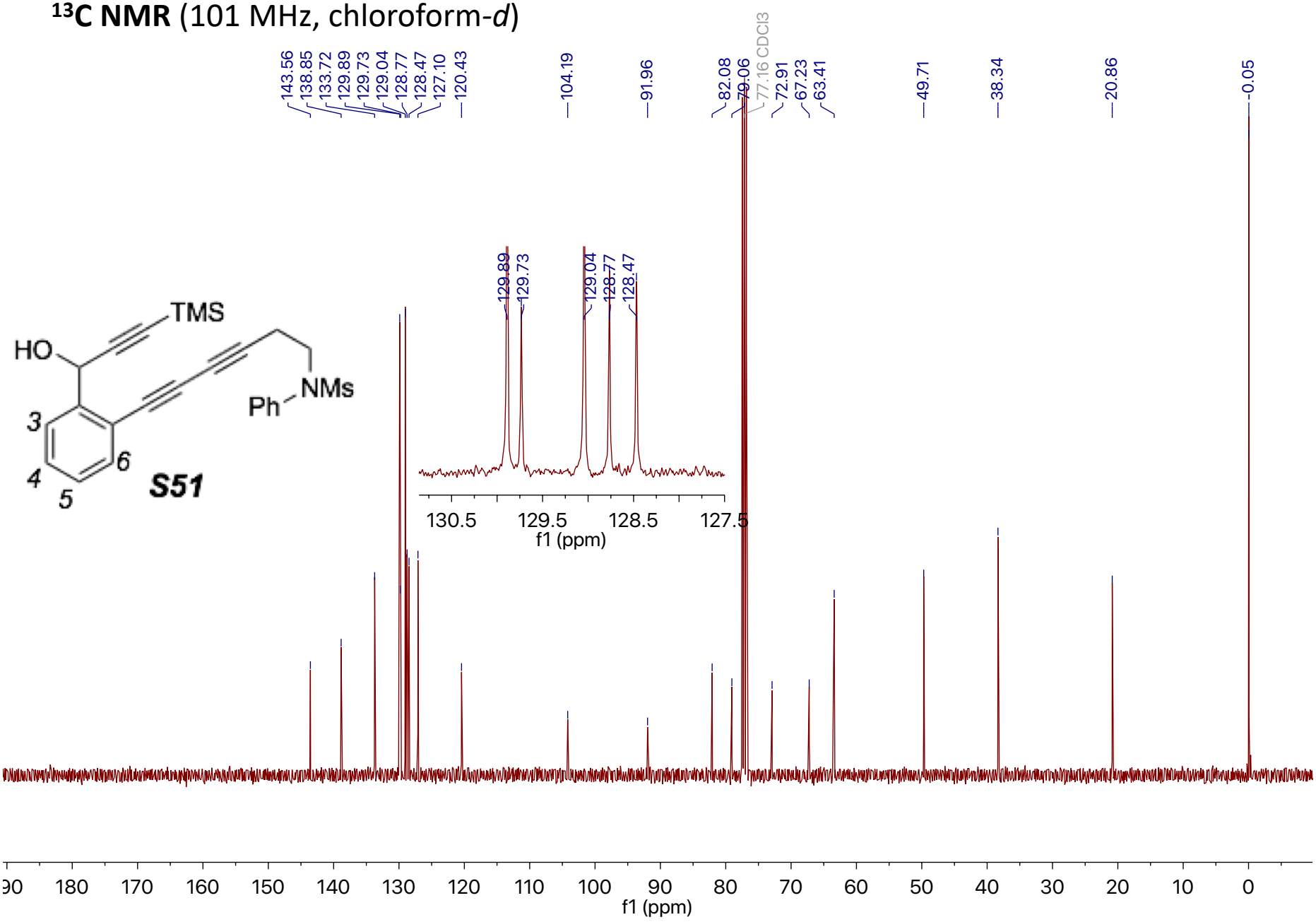


^{1}H NMR (400 MHz, chloroform-*d*)

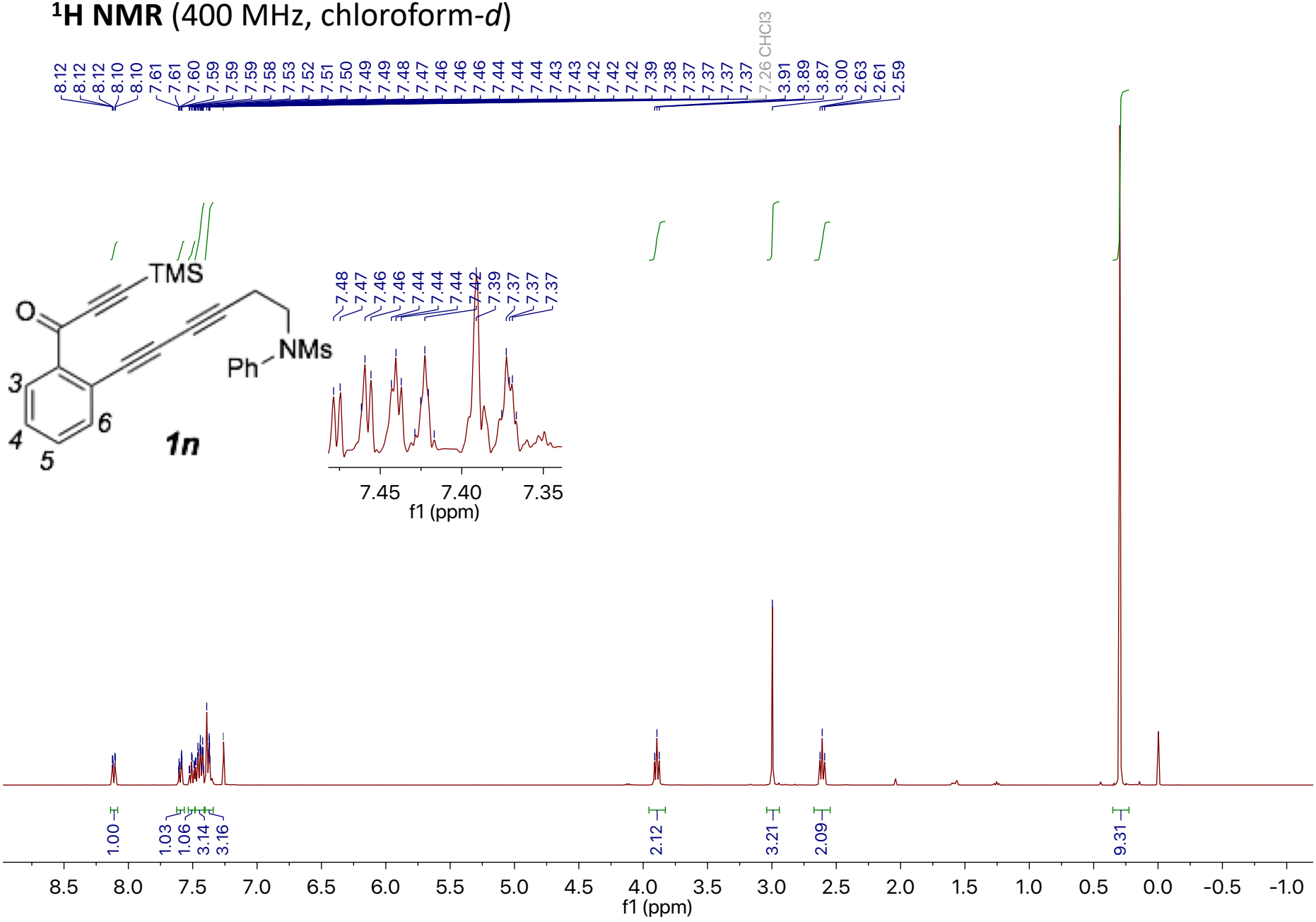


S51

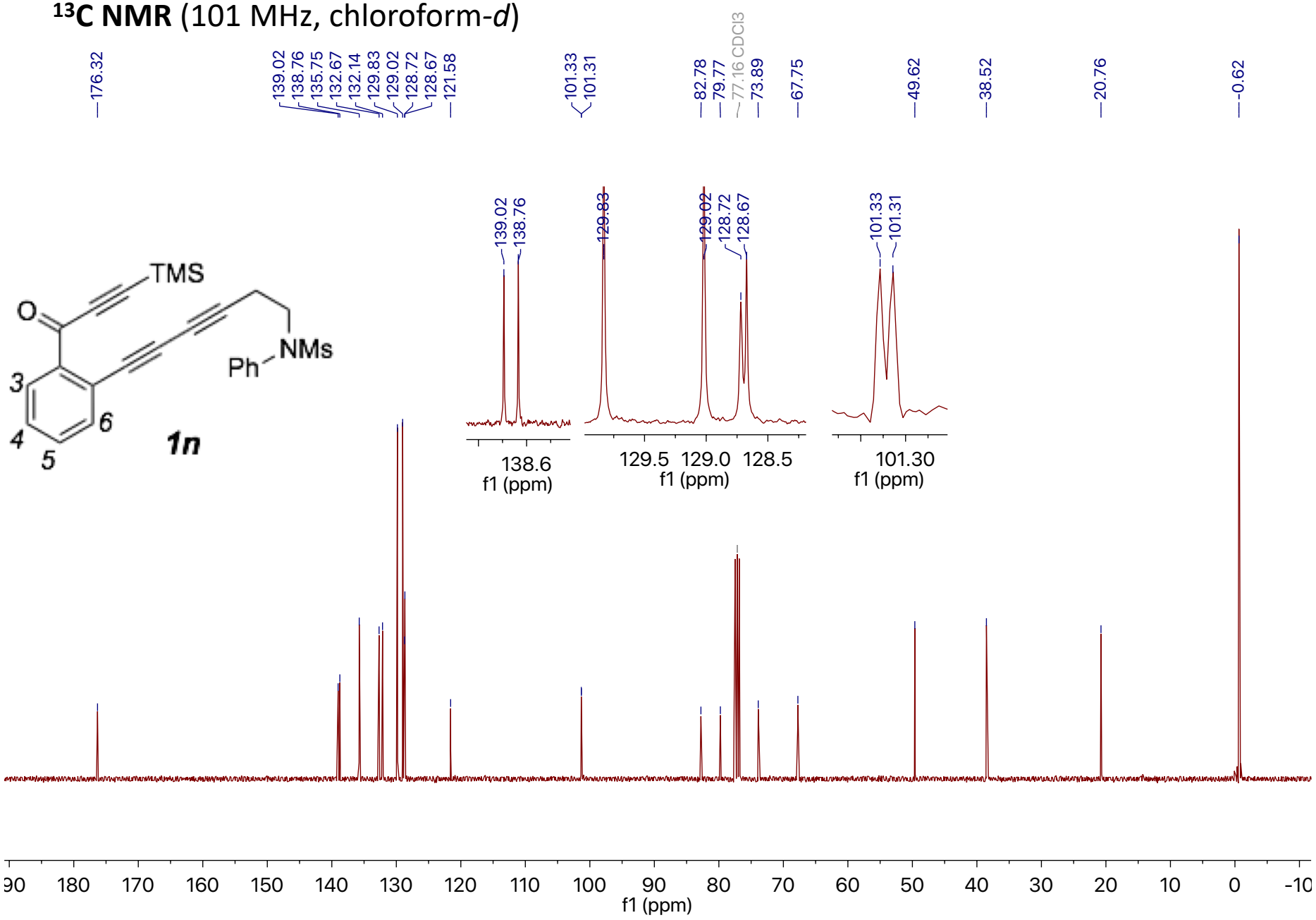
^{13}C NMR (101 MHz, chloroform-*d*)



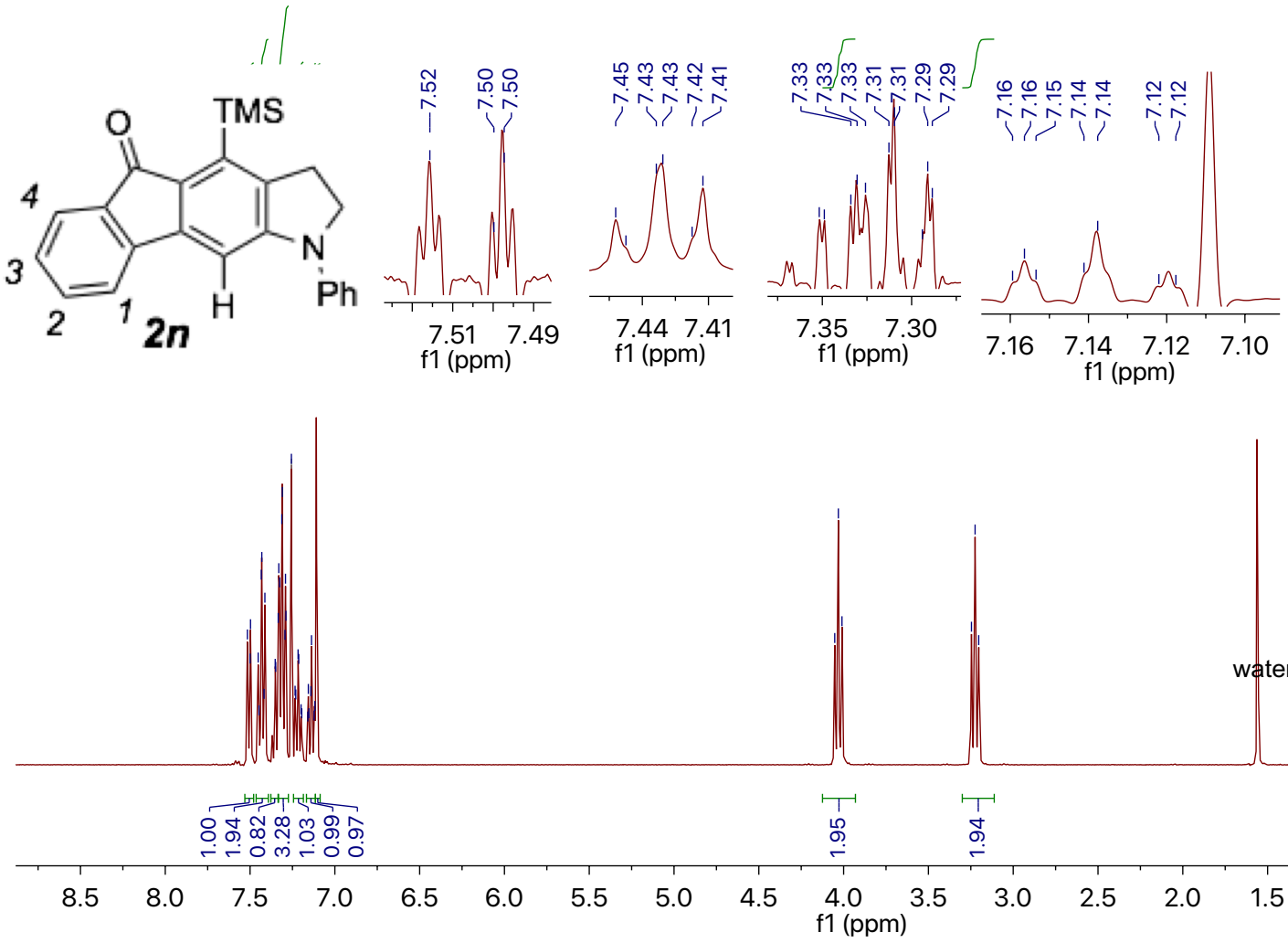
^{1}H NMR (400 MHz, chloroform-*d*)



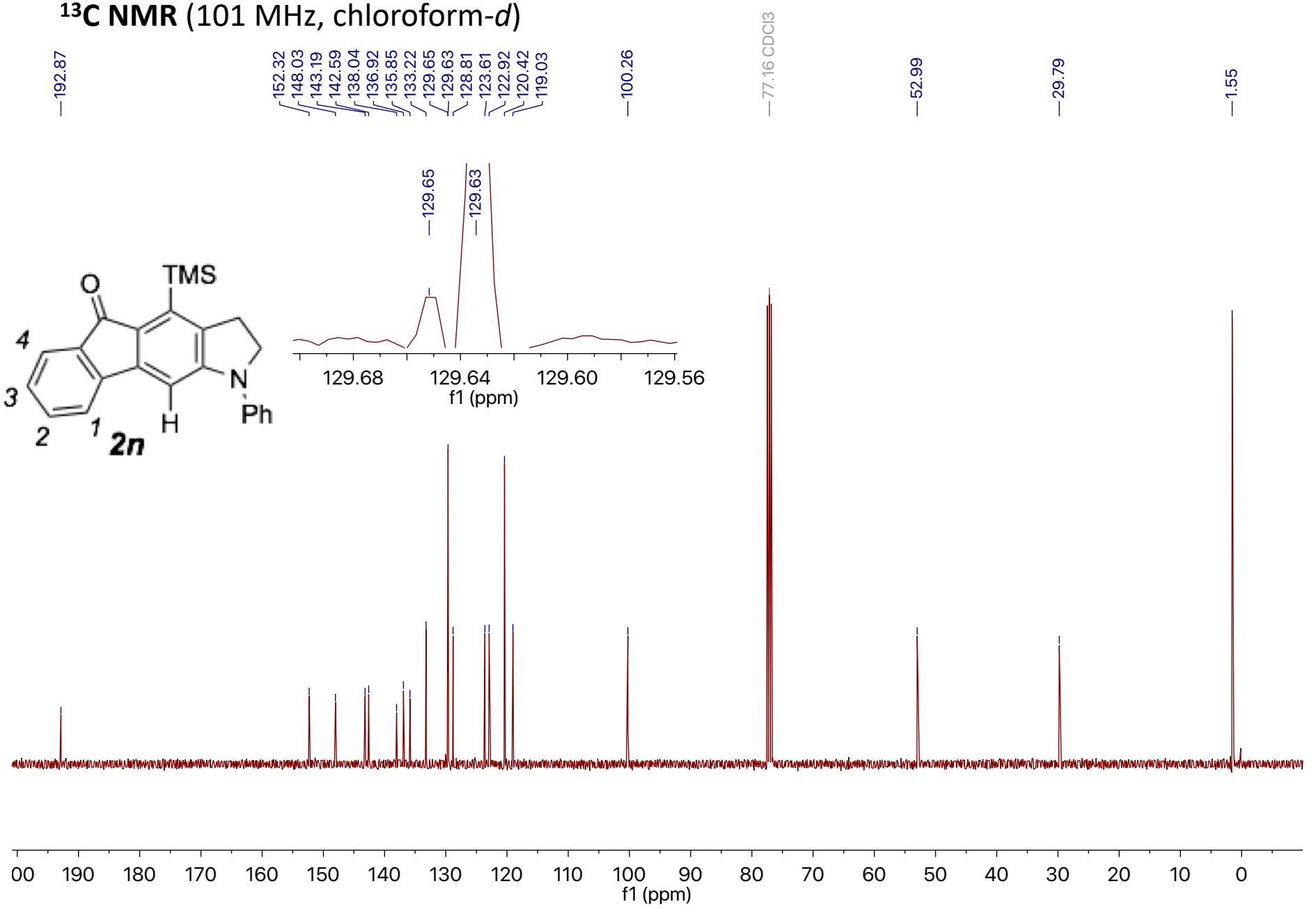
^{13}C NMR (101 MHz, chloroform-*d*)



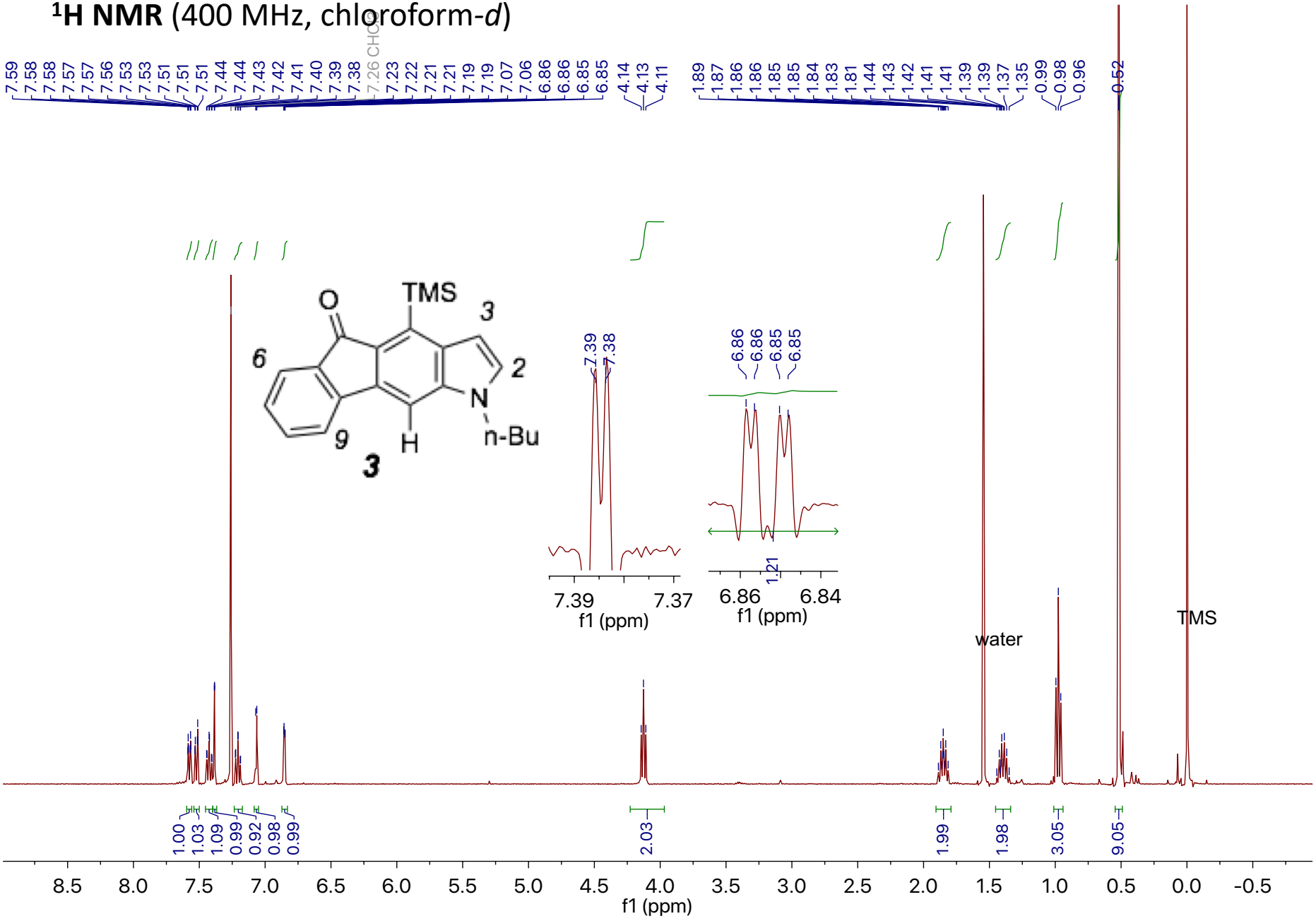
^{1}H NMR (400 MHz, chloroform-*d*)



^{13}C NMR (101 MHz, chloroform-*d*)



^{1}H NMR (400 MHz, chloroform-*d*)



^{13}C NMR (101 MHz, chloroform-*d*)