Supporting Information for

BF_3-Promoted, Carbene-like, C–H Insertion Reactions of Benzynes

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I. General Experimental Protocols

^{1}H and ^{13}C NMR spectral data were recorded on Bruker Avance 400 and 500 (400 and 500 MHz) spectrometers. Proton NMR chemical shifts in $CDCl_3$ are referenced to TMS (δ = 0.00 ppm) and in C_6D_6 to residual C_6HD_5 (δ = 7.16 ppm). Non-first order multiplets are identified as "nfom". Carbon NMR chemical shifts for spectra collected in $CDCl_3$ are referenced to δ = 77.16 ppm, the shift of the carbon in $CDCl_3$. Carbon NMR chemical shifts for spectra recorded in C_6D_6 are referenced to δ = 128.06 ppm, the shift of the carbon in C_6D_6. Proton resonances are reported using the following format: chemical shift in ppm [multiplicity, coupling constant(s) (*J*) in Hz, integration (to the nearest whole number of protons), and assignment]. Proton NMR assignments are indicated by the substructure environment, e.g., =CHCH_aH$_b$. The proton-bearing carbons in some of the more complex structures are numbered in order to simplify the correlation with the proton assignment in the line listings. Coupling constant analysis was guided by previously reported methods.[1]

Infrared spectra were obtained using a Prospect 4000 FT-IR spectrometer (Midac Corporation). The most intense and/or diagnostic peaks are reported. Spectra were collected in attenuated total reflectance (ATR) mode on a germanium window, and the samples were drop-cast, neat thin-films.

High-resolution mass spectrometry (HRMS) was performed on (i) a Thermo Orbitrap Velos in the positive electrospray (ESI) or atmospheric pressure chemical ionization (APCI) mode using an external standard (Pierce™ LTQ); the mass accuracy of the instrument is 3 ppm; or (ii) in electrospray ionization mode (ESI) on a Bruker BioTOF II (ESI-TOF) instrument using PEG as an added internal standard/calibrant. Samples were injected directly as dilute solutions (concentration less than 10^{-5} M) in methanol.

“MPLC refers to medium pressure liquid chromatography (ca. 50-100 psi) using columns hand-packed with RediSep Rf Gold® Normal-Phase Silica (20–40 μm, 60 Å pore size, Teledyne/ISCO). Eluent was pumped with a Waters HPLC pump; detection was done with a differential refractive index detector (Waters R401) and a UV detector (Gilson 111). Flash chromatography was done with columns packed with E. Merck silica gel (230-400 mesh). Thin layer chromatography was performed on plastic-backed plates of silica gel; tlc visualization was done by UV detection and/or a ceric ammonium molybdate staining.”[2]

Reactions requiring anhydrous conditions were performed under an atmosphere of nitrogen inside flame- or oven-dried glassware. Triethylamine and *n*-butylamine were distilled from CaH_2 and stored over molecular sieves (3 Å). Anhydrous toluene, Et_2O, and THF were collected immediately prior to use upon being passed through a column packed with activated alumina. Reported reaction temperatures are the temperature of the external heating bath. Reactions carried out at a temperature higher than the boiling point of the solvent were carried out in a screw-capped vial or culture tube that was closed with an inert, Teflon®-lined screw cap.

II. Preparation procedures and characterization data for all new compounds

General Procedure A: Cadiot–Chodkiewicz Alkyne Cross-Coupling

CuCl (0.1 equiv) was dissolved in a solution of *n*-butylamine in water (4:10 vol:vol) at 0 °C under an inert atmosphere with stirring. Solid hydroxylamine hydrochloride was added in portions until the solution was colorless. A solution of alkyne (1.0 equiv) in dichloromethane (1~2 M) was added with stirring. The volume ratio of the aqueous butylamine and CH_2Cl_2 solutions was ca. 2-1.5:1. A yellow precipitate appeared. A solution of 1-bromoalkyne (1.2 equiv) in CH_2Cl_2 (0.3 M) was slowly added dropwise over ca. 20 min to the yellow suspension with robust stirring. After 1 h the reaction mixture was diluted with satd. aq. NH_4Cl and extracted with EtOAc. The organic extracts were combined, washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel using hexanes:EtOAc as the eluant.

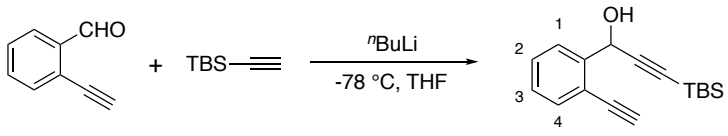
General Procedure B: Oxidation of Alcohol Using MnO_2

Manganese dioxide (ca. 15 molar equiv; "activated MnO_2" from Aldrich-Millipore) was added to a stirred solution of the propargylic alcohol (1.0 equiv) in CH_2Cl_2 (0.5 M) at room temperature. After 1 h the reaction mixture was filtered through a small column of silica gel using CH_2Cl_2 as the eluant. The filtrate was concentrated to give the desired ketone that was typically used without further purification.

General Procedure C: Tandem HDDA Reaction/C-H Insertion Reaction

Boron trifluoride diethyl etherate (1~1.3 equiv) was added to a solution of HDDA triyne or tetrayne precursor in dry toluene (ca. 0.05 M) in a culture tube fitted with an inert, Teflon®-lined cap. The vessel was firmly sealed and heated at in an oil bath that had been pre-equilibrated to the indicated temperature. After, typically, 4-6 h (as specified), the reaction mixture was quenched by addition of satd. aq. $NaHCO_3$, and the mixture was then extracted with ethyl acetate. The combined ethyl acetate layers were concentrated under reduced pressure to provide the crude product mixture which was typically purified by medium pressure liquid chromatography (MPLC).

3-(*tert*-Butyldimethylsilyl)-1-(2-ethynylphenyl)prop-2-yn-1-ol (S1)



S1

A 100 mL three-neck round-bottom flask fitted with a magnetic stir bar and a pressure equalizing dropping funnel was loaded with a solution of (*tert*-butyldimethylsilyl)acetylene (2.8 mL, 15 mmol) in THF (30 mL) under an atmosphere of N_2. The solution was stirred in a dry ice-acetone

bath while a solution of *n*-butyllithium (6 mL, 2.5 M in hexanes, 15 mmol) was added dropwise through a dropping funnel. The resulting solution was stirred at –78 °C for 30 min, and a solution of 2-ethynylbenzaldehyde (1.43 g, 11 mmol) in 20 mL of THF was added dropwise via a second dropping funnel. After 4 h the mixture was quenched with satd. NH_4Cl (30 mL). The organic layer was separated. The aqueous layer was extracted with Et_2O (3x15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo, and the crude product was purified by flash chromatography on silica gel to give **S1** as a yellow oil (2.55 g, 86%).

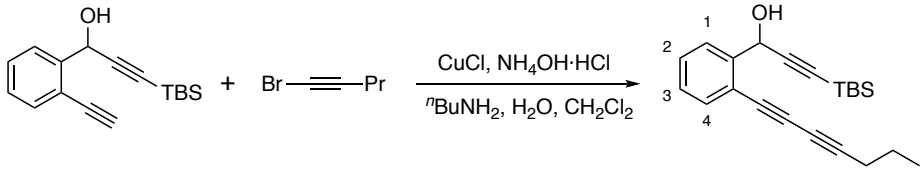
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73 (d, *J* = 7.8 Hz, 1H, H1), 7.52 (d, *J* = 7.7 Hz, 1H, H4), 7.40 (dd, *J* = 7.6, 7.6 Hz, 1H, H2), 7.30 (dd, *J* = 7.5, 7.5 Hz, 1H, H3), 5.88 (d, *J* = 5.9 Hz, 1H, *CH*OH), 3.37 (s, 1H, C≡CH), 2.55 (d, *J* = 5.9 Hz, 1H, CH*OH*), 0.94 [s, 9H, $SiC(CH_3)_3$], 0.14 [s, 3H, $Si(CH_3)$], and 0.13 [s, 3H, $Si(CH_3)$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 133.3, 129.5, 128.4, 127.0, 120.7, 104.9, 90.3, 82.8, 81.2, 63.6, 26.2, 16.7, and -4.6.

IR (neat) 3550, 3301, 2953, 2928, 2885, 2856, 2172, 1462, 1448, 1362, 1250, 1036, 980, 836, 828, 811, 774, and 758 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $[(C_{17}H_{23}OSi)^+]$ $[(M+H)^+]$ 271.1513; found: 271.1514.

3-(*tert*-Butyldimethylsilyl)-1-(2-(hepta-1,3-diyn-1-yl)phenyl)prop-2-yn-1-ol (S2)



S1 ***S2***

S2 was prepared following general procedure A from diyne **S1** (270 mg, 1.0 mmol) and 1-bromopent-1-yne (175 mg, 1.2 mmol). The crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give **S2** (255 mg, 76%) as a yellow oil.

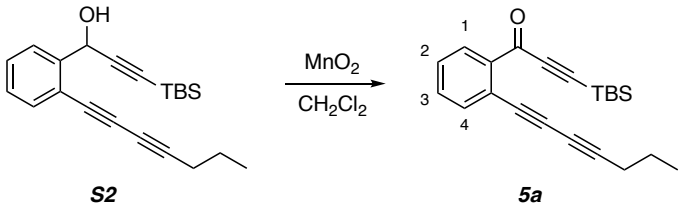
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (d, *J* = 7.8 Hz, 1H, H1), 7.50 (d, *J* = 7.6 Hz, 1H, H4), 7.38 (dd, *J* = 7.6, 7.6 Hz, 1H, H2), 7.27 (dd, *J* = 7.6, 7.6 Hz, 1H, H3), 5.83 (d, *J* = 5.5 Hz, 1H, *CH*OH), 2.48 (d, *J* = 5.7 Hz, 1H, CHO*H*), 2.35 (t, *J* = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 1.61 (qt, *J* = 7.3, 7.3 Hz, 2H, $CH_2CH_2CH_3$), 1.03 (t, *J* = 7.3 Hz, 3H, $CH_2CH_2CH_3$), 0.94 [s, 9H, $SiC(CH_3)_3$], and 0.13 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 133.7, 129.4, 128.4, 126.9, 120.8, 105.0, 90.2, 86.5, 79.8, 71.9, 65.2, 63.6, 26.2, 21.9, 21.8, 16.7, 13.7 and -4.6.

IR (neat) 3561, 2956, 2930, 2856, 2237, 2172, 1470, 1462, 1249, 1036, 981, 812, 773, and 758 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $[(C_{22}H_{29}OSi)^+]$ $[(M+H)^+]$ 337.1982; found: 337.1981.

3-(*tert*-Butyldimethylsilyl)-1-(2-(hepta-1,3-diyn-1-yl)phenyl)prop-2-yn-1-one (5a)



S2 ***5a***

5a was prepared following general procedure B from alcohol **S2** (269 mg, 0.8 mmol) to give **5a** (254 mg, 95%) as a yellow oil.

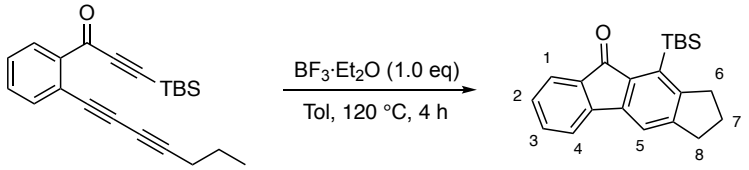
^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, *J* = 7.8 Hz, 1H, H1), 7.60 (d, *J* = 7.6 Hz, 1H, H4), 7.49 (dd, *J* = 7.5, 7.5 Hz, 1H, H3), 7.43 (dd, *J* = 7.6, 7.6 Hz, 1H, H2), 2.35 (t, *J* = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 1.61 (qt, *J* = 7.3, 7.3 Hz, 2H, $CH_2CH_2CH_3$), 1.02 (t, *J* = 7.3 Hz, 3H, $CH_2CH_2CH_3$), 1.01 [s, 9H, $SiC(CH_3)_3$], and 0.24 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 139.2, 135.8, 132.6, 132.0, 128.4, 122.2, 102.3, 100.0, 87.2, 80.7, 72.9, 65.8, 26.2, 21.9 (2x, confirmed by HSQC to $CH_2CH_2CH_3$ and $CH_2CH_2CH_3$), 16.8, 13.7, and -4.9.

IR (neat) 2955, 2930, 2857, 2240, 2149, 1649, 1589, 1560, 1478, 1462, 1233, 1015, 814, 778, and 758 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $[(C_{22}H_{27}OSi)^+]$ $[(M+H)^+]$ 335.1826; found: 335.1824.

10-(*tert*-Butyldimethylsilyl)-2,3-dihydrocyclopenta[b]fluoren-9(1H)-one (7a)



5a ***7a***

7a was prepared following general procedure C from triyne **5a** (33 mg, 0.1 mmol) at 120 °C for 4 h. The crude material was purified by MPLC (hexanes:EtOAc 80:1) to give the fluorenone **7a** (27 mg, 82%) as a yellow crystalline solid.

^{1}H NMR (Benzene-d_6, 500 MHz) δ 7.57 (d, *J* = 7.2 Hz, 1H, H1), 7.08 (d, *J* = 7.4 Hz, 1H, H4), 7.04 (s, 1H, H5), 7.01 (dd, *J* = 7.5, 7.5 Hz, 1H, H3), 6.81 (dd, *J* = 7.3, 7.3 Hz, 1H, H2), 2.84 (t, *J* = 7.3 Hz, 2H, H6), 2.55 (t, *J* = 7.5 Hz, 2H, H8), 1.73 (tt, *J* = 7.4, 7.4 Hz, 2H, H7), 1.16 [s, 9H, $SiC(CH_3)_3$], and 0.57 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, Benzene-d_6) δ 194.0, 152.8, 150.2, 145.0, 144.2, 139.7, 135.6, 135.0, 134.0, 128.7, 124.1, 119.2, 117.8, 36.5, 33.2, 28.2, 25.8, 20.1, and 0.2.

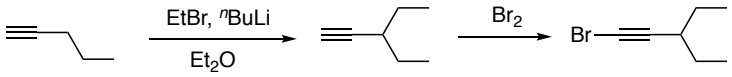
IR (neat) 2951, 2927, 2891, 2853, 1713, 1605, 1585, 1469, 1462, 1420, 1293, 1247, 1219, 1179,

979, 901, 858, 835, 800, 779, and 765 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $[(C_{21}H_{23}OSi)^+]$ $[(M+H–CH_4)^+]$ 319.1513; found: 319.1514.

m.p. 135–138 °C.

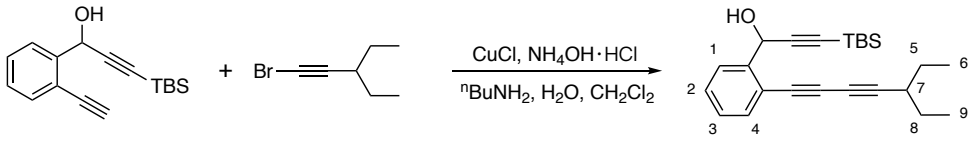
1-Bromo-3-ethylpent-1-yne (S3)



S3

S3 was synthesized according to the reported procedure for synthesis of an analog.[3] *n*-BuLi (0.88 mL, 2.5 M in hexane, 2.2 mmol) at -78 °C was added dropwise to a solution of 1-pentyne (0.20 mL, 2.0 mmol) in dry Et_2O (2 mL). After stirring at 0 °C for 5 h, *n*-EtBr (0.15 mL, 2.0 mmol) was added to the mixture, which was then stirred at room temperature overnight. The resulting solution was recooled to -78 °C and neat bromine (0.10 mL, 2.0 mmol) was added dropwise. After 30 minutes, brine and Et_2O were poured into the mixture with vigorous stirring. The layers were separated and the aqueous layer was extracted with Et_2O. The combined extracts were dried ($MgSO_4$) and concentrated at room temperature to give material that, in view of its volatility, was directly used in the next step rather than subject it to chromatographic purification. The concentration of the bromopentyne **S3** was determined by combining known amounts of this crude bromoalkyne and of *n*-butylamine as an internal standard in $CDCl_3$ and integrating the appropriate resonances. The yield of **S3** was estimated to be 122 mg (35%).

3-(*tert*-Butyldimethylsilyl)-1-(2-(5-ethylhepta-1,3-diyn-1-yl)phenyl)prop-2-yn-1-ol (S4)



S1 ***S3*** ***S4***

S4 was prepared following general procedure A from diyne **S1** (135 mg, 0.5 mmol) and 1-bromo-3-ethylpent-1-yne (**S3,** 104 mg, 0.6 mmol). The crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give **S4** (78 mg, 43%) as a yellow oil.

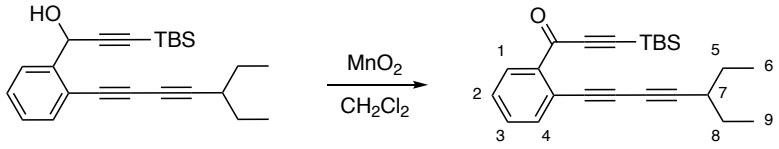
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (d, *J* = 7.7 Hz, 1H, *H*1), 7.51 (dd, *J* = 7.6, 1.3 Hz, 1H, *H*4), 7.38 (ddd, *J* = 7.7, 7.7, 1.3 Hz, 1H, *H*2), 7.27 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, *H*3), 5.84 (d, *J* = 5.5 Hz, 1H, *CH*OH), 2.47 (d, *J* = 5.7 Hz, 1H, CHO*H*), 2.38 (tt, *J* = 8.4, 5.5 Hz, 1H, *H*7), 1.60–1.48 (m, 4H, *H*5 and *H*8), 1.04 (t, *J* = 7.4 Hz, 6H, *H*6 and *H*9), 0.94 [s, 9H, SiC(CH_3)$_3$], 0.133 (s, 3H, SiCH_3), and 0.132 (s, 3H, SiCH_3).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 133.8, 129.3, 128.4, 126.9, 120.9, 105.0, 90.2, 89.7, 79.9, 72.1, 66.2, 63.6, 36.2, 27.5, 26.2, 16.7, 12.0, and -4.5.

IR (neat) 3426, 2961, 2929, 2857, 2236, 2172, 1470, 1460, 1380, 1361, 1352, 1249, 1036, 982, 838, 827, 811, 775, and 758 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $[(C_{24}H_{31}Si)^+]$ $[(M+H–H_2O)^+]$ 347.2189; found: 347.2188.

3-(*tert*-Butyldimethylsilyl)-1-(2-(5-ethylhepta-1,3-diyn-1-yl)phenyl)prop-2-yn-1-one (5b)



S4 ***5b***

5b was prepared following general procedure B from alcohol **S4** (109 mg, 0.3 mmol) to give **5b** (101 mg, 93%) as a yellow oil.

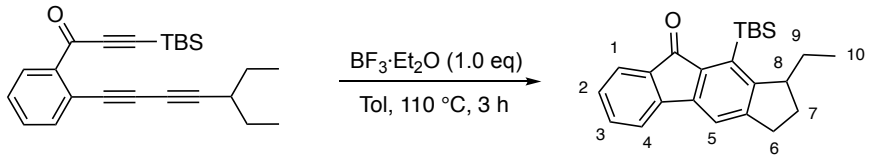
^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, *J* = 7.8 Hz, 1H, H1), 7.62 (d, *J* = 7.7 Hz, 1H, H4), 7.49 (dd, *J* = 7.6, 7.6 Hz, 1H, H3), 7.43 (dd, *J* = 7.6, 7.6 Hz, 1H, H2), 2.38 (nfom, 1H, H7), 1.54 (ddq, *J* = 14, 7, 7 Hz, 2H, H5b and H8b), 1.04 (t, *J* = 7.5 Hz, 6H, H6 and H9), 1.01 [s, 9H, $SiC(CH_3)_3$], and 0.24 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 139.1, 135.8, 132.6, 132.0, 128.3, 122.3, 102.3, 100.0, 90.5, 80.8, 73.2, 66.8, 36.3, 27.5, 26.2, 16.8, 12.0, and -4.9.

IR (neat) 2962, 2930, 2861, 2233, 2150, 1650, 1590, 1560, 1479, 1462, 1352, 1272, 1250, 1233, 1129, 1015, 838, 828, 814, 779, and 754 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{24}H_{31}OSi)^+$ $[(M+H)^+]$ 363.2139; found: 363.2141.

10-(*tert*-Butyldimethylsilyl)-1-ethyl-2,3-dihydrocyclopenta[*b*]fluoren-9(1*H*)-one (7b)



5b ***7b***

7b was prepared following general procedure C from triyne **5b** (36 mg, 0.1 mmol) at 110 °C for 3 h. The crude material was purified by MPLC (hexanes:EtOAc 80:1) to give the fluorenone **7b** (21 mg, 58%) as a yellow crystalline solid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54 (d, *J* = 7.4 Hz, 1H, H1), 7.43–7.40 (m, 2H, H4 and H3), 7.38 (s, 1H, H5), 7.24–7.19 (nfom, 1H, H2), 3.26–3.22 (m, 1H, H8), 2.98 (ddd, *J* = 18, 9, 9 Hz, 1H, H6a), 2.77 (nfod, *J* = 17.2 Hz, 1H, H6b), 2.10–1.99 (m, 2H, H7), 1.51–1.41 (m, 1H, H9a), 1.38–1.27 (m, 1H, H9b), 1.01 (t, *J* = 7.3 Hz, 3H, H10), 0.97 [s, 9H, $SiC(CH_3)_3$], 0.51 (s, 3H, $SiCH_3$), and 0.42 (s, 3H, $SiCH_3$).

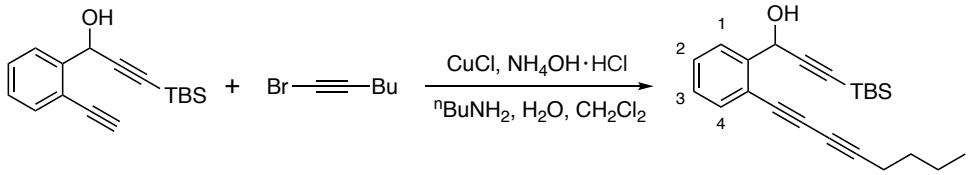
^{13}C NMR (125 MHz, $CDCl_3$) δ 194.8, 150.0, 144.9, 144.0, 139.6, 134.5, 134.3, 128.6, 123.8, 119.2, 117.9, 47.0 (br), 30.6, 28.8 (br), 28.77, 28.5, 18.9 (br), 12.6, and 0.80 (br). (two aromatic carbons not observed; several broad aliphatic resonances suggest slowed rotation that interconvert two diastereomeric rotamers from Ar—Si bond rotation)

IR (neat) 2952, 2926, 2854, 1714, 1605, 1585, 1469, 1462, 1418, 1289, 1248, 1179, 966, 901, 881, 846, 837, 799, 780, and 765 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $(C_{23}H_{27}OSi)^+$ [$(M+H–CH_4)^+$] 347.1826; found: 347.1825.

m.p. 110–113 °C.

3-(*tert*-Butyldimethylsilyl)-1-(2-(octa-1,3-diyn-1-yl)phenyl)prop-2-yn-1-ol (S5)



S1 ***S5***

S5 was prepared following general procedure A from diyne **S1** (135 mg, 0.5 mmol) and 1-bromohex-1-yne (97 mg, 0.6 mmol). The crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give **S5** (138 mg, 79%) as a yellow oil.

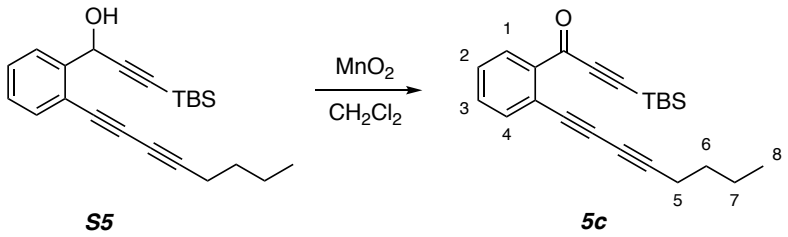
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (d, J = 7.8 Hz, 1H, H1), 7.50 (d, J = 7.6 Hz, 1H, H4), 7.38 (dd, J = 7.6, 7.6 Hz, 1H, H2), 7.28 (dd, J = 7.6, 7.6 Hz, 1H, H3), 5.84 (d, J = 4.0 Hz, 1H, *CH*OH), 2.45 (d, J = 5.4 Hz, 1H, CHO*H*), 2.38 (t, J = 6.9 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.57 (tt, J = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.46 (qt, J = 7.5, 7.5 Hz, 2H, $CH_2CH_2CH_2CH_3$), 0.94 (t, J = 7.3 Hz, 3H, $CH_2CH_2CH_2CH_3$), 0.94 [s, 9H, $SiC(CH_3)_3$], and 0.13 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 133.7, 129.4, 128.4, 127.0, 120.9, 104.9, 90.2, 86.6, 79.9, 71.8, 65.1, 63.6, 30.4, 26.2, 22.1, 19.5, 16.7, 13.7 and -4.6.

IR (neat) 3426, 2955, 2929, 2856, 2238, 2172, 1469, 1462, 1362, 1249, 1036, 982, 827, 811, 774, and 756 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for [$(C_{23}H_{29}Si)^+$] [$(M+H–H_2O)^+$] 333.2033; found: 333.2034.

3-(*tert*-Butyldimethylsilyl)-1-(2-(octa-1,3-diyn-1-yl)phenyl)prop-2-yn-1-one (5c)



S5 ***5c***

5c was prepared following general procedure B from alcohol **S5** (105 mg, 0.3 mmol) to give **5c** (101 mg, 96%) as a yellow oil.

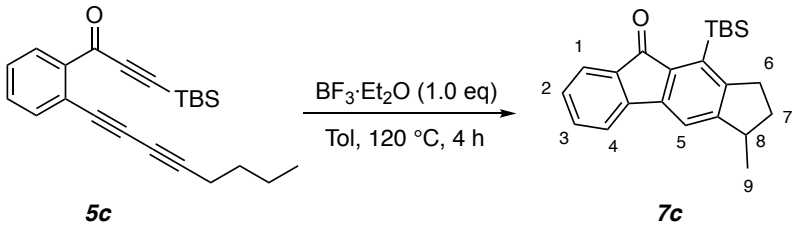
^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.10 (dd, *J* = 7.8, 1.4 Hz, 1H, H1), 7.60 (dd, *J* = 7.6, 1.3 Hz, 1H, H4), 7.49 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H, H3), 7.43 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, H2), 2.38 (t, *J* = 7.0 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.56 (tt, *J* = 7.3, 7.3 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.61 (qt, *J* = 7.3, 7.3 Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.01 [s, 9H, $SiC(CH_3)_3$], 0.93 (t, *J* = 7.3 Hz, 3H, $CH_2CH_2CH_3$), and 0.24 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 139.2, 135.8, 132.6, 132.0, 128.4, 122.2, 102.3, 100.0, 87.4, 80.7, 72.9, 65.7, 30.4, 26.2, 22.1, 19.6, 16.8, 13.7, and -4.9.

IR (neat) 2955, 2930, 2858, 2238, 2149, 1649, 1589, 1560, 1478, 1233, 1015, 814, 778, and 753 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for [$(C_{23}H_{29}OSi)^+$] [$(M+H)^+$] 349.1982; found: 349.1980.

10-(*tert*-Butyldimethylsilyl)-3-methyl-2,3-dihydrocyclopenta[b]fluoren-9(1H)-one (7c)



5c ***7c***

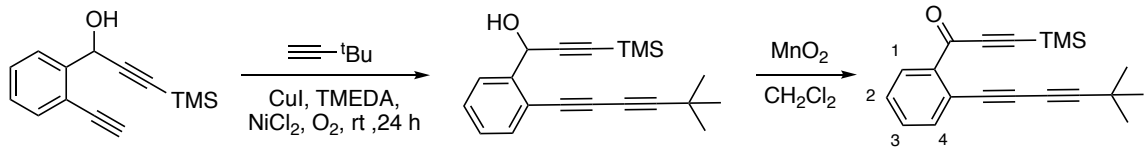
7c was prepared following general procedure C from triyne **5c** (35 mg, 0.1 mmol) at 120 ^oC for 4 h. The crude material was purified by MPLC (hexanes:EtOAc 80:1) to give the fluorenone **7c** (25 mg, 72%) as a yellow crystalline solid.

^{1}H NMR (Benzene-d_6, 500 MHz) δ 7.56 (d, *J* = 7.2 Hz, 1H, H1), 7.12 (s, 1H, H5), 7.05 (d, *J* = 7.3 Hz, 1H, H4), 7.00 (ddd, *J* = 7.4, 7.4, 0.9 Hz, 1H, H3), 6.80 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H, H2), 2.97 (ddd, *J* = 15.7, 8.2, 3.8 Hz, 1H, H6a), 2.82 (qdd, *J* = 7.4, 7.4, 7.4 Hz, 1H, H8), 2.76 (ddd, *J* = 16.1, 8.4, 8.4 Hz, 1H, H6b), 2.02 (dddd, *J* = 11.6, 7.7, 7.7, 3.8 Hz, 1H, H7a), 1.37 (dddd, *J* = 12.1, 8.5, 8.5, 8.5 Hz, 1H, H7b), 1.16 [s, 9H, $SiC(CH_3)_3$], 1.13 (d, *J* = 6.8 Hz, 3H, H9), 0.64 [s, 3H, $Si(CH_3)_2$], and 0.51 [s, 3H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 194.4, 155.0, 152.8, 144.9, 143.9, 139.2, 136.0, 134.5, 134.3, 128.6, 123.8, 119.2, 116.4, 39.2, 34.82, 34.77, 28.0, 20.0, 19.4, 0.23 and -0.3.

IR (neat) 2952, 2926, 2854, 1714, 1605, 1585, 1469, 1462, 1418, 1289, 1248, 1179, 966, 901, 881, 846, 837, 799, 780, and 765 cm^{-1}.
HRMS (APCI-Orbitrap): Calcd for $[(C_{22}H_{25}OSi)^+]$ $[(M+H–CH_4)^+]$ 333.1669; found: 333.1671.

1-(2-(5,5-Dimethylhexa-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (5d)



S6 ***5d***

Triyne **S6** was prepared by a reported oxidative cross-coupling method.[4] TMEDA (37 μL, 0.25 mmol), $NiCl_2$ (17 mg, 0.13 mmol), and CuI (21 mg, 0.11 mmol) were added to a THF solution (7 mL) of 1-(2-ethynylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol[5] (228 mg, 1.0 mmol). An oxygen balloon was introduced through a septum and the headspace of the reaction mixture was flushed with the gas. The mixture was stirred and allowed to warm to room temperature. After 24 h the reaction mixture was diluted with satd. aq. NH_4Cl and extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to provide the crude product that was passed through a small column of SiO_2 (hexanes:EtOAc 10:1eluent) and directly used in the next step.

Manganese dioxide (435 mg, 5 mmol) was added to a stirred solution of alcohol **S6** in CH_2Cl_2 (1 mL) at room temperature. After 1 h the reaction mixture was filtered through a small column of silica gel using CH_2Cl_2 as the eluent. Purification by MPLC (hexanes:EtOAc 80:1) gave triyne **5d** as an yellow oil (91 mg, 30% yield for two steps).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.05 (d, *J* = 7.7 Hz, 1H, H1), 7.60 (d, *J* = 7.5 Hz, 1H, H4), 7.49 (dd, *J* = 7.5, 7.5 Hz, 1H, H3), 7.43 (dd, *J* = 7.6, 7.6 Hz, 1H, H2), 1.29 [s, 9H, $C(CH_3)_3$], and 0.31 [s, 9H, $Si(CH_3)_3$].

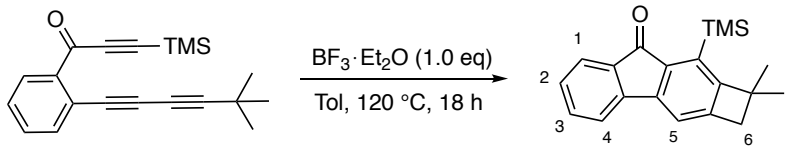
^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 139.1, 135.7, 132.6, 131.7, 128.5, 122.4, 101.6, 94.6, 80.7, 74.0, 64.5, 30.6, 28.6, and -0.5. (one alkyne carbon not observed.)

^{13}C NMR (125 MHz, benzene-d_6) δ 176.2, 139.7, 135.8, 132.3, 131.5, 128.2,* 122.6, 102.6, 100.3, 94.5, 81.8, 74.8, 65.7, 30.4, 28.5, and -0.8. (* this resonance is obscured by that from the deuterobenzene solvent, but its presence was established by an HSQC experiment.)

IR (neat) 2970, 2930, 2900, 2868, 2232, 2153, 1651, 1589, 1561, 1481, 1455, 1363, 1324, 1294, 1276, 1251, 1330, 1015, 847, and 756 cm^{-1}.

HRMS (ESI-TOF): Calcd for $[(C_{20}H_{22}OSiNa)^+]$ $[(M+Na)^+]$ 329.1332; found: 329.1340.

1,1-Dimethyl-9-(trimethylsilyl)-1,2-dihydro-8*H*-cyclobuta[*b*]fluoren-8-one (7d)



5d ***7d***

Fluorenone **7d** was prepared following general procedure C from triyne **5d** (21 mg, 0.07 mmol) at 120 °C for 18 h. The crude material was purified by MPLC (hexanes:EtOAc 100:1) to give the cyclobutanofluorenone **7d** (13 mg, 62%) as a yellow crystalline solid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (d, *J* = 7.2 Hz, 1H, H1), 7.42–7.40 (m, 2H, H4 and H3), 7.23-7.20 (nfom, 1H, H2), 2.82 (s, 2H, H6), 1.51 [s, 6H, $C(CH_3)_2$], and 0.40 [s, 9H, $C(CH_3)_3$]. (the singlet for H5 was not observed.)

^{1}H NMR (benzene-d_6, 500 MHz) δ 7.54 (d, *J* = 7.2 Hz, 1H, H1), 7.02 (d, *J* = 7.2 Hz, 1H, H4), 6.98 (dd, *J* = 7.3, 7.3 Hz, 1H, H3), 6.87 (s, 1H, H5), 6.78 (dd, *J* = 7.1, 7.1 Hz, 1H, H2), 2.58 (s, 2H, H6), 1.38 [s, 6H, $C(CH_3)_2$], and 0.59 [s, 9H, $C(CH_3)_3$].

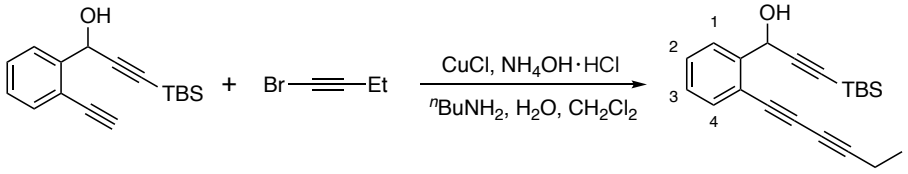
^{13}C NMR (125 MHz, $CDCl_3$) δ 195.5, 161.0, 149.1, 145.3, 144.8, 138.3, 136.8, 134.4, 133.8, 128.6, 123.7, 119.4, 116.7, 47.1, 44.2, 27.3, and 1.1.

IR (neat) 2982, 2954, 2919, 1708, 1606, 1568, 1464, 1420, 1274, 1245, 1201, 1131, 925, 861, 843, 825, and 744 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $[(C_{19}H_{19}OSi)^+]$ $[(M+H–CH_4)^+]$ 291.1200; found: 291.1200.

m.p. 155–159 °C.

3-(*tert*-Butyldimethylsilyl)-1-(2-(hexa-1,3-diyn-1-yl)phenyl)prop-2-yn-1-ol (S7)



S1 ***S7***

S7 was prepared following general procedure A from diyne **S1** (81 mg, 0.3 mmol) and 1-bromobut-1-yne (48 mg, 0.36 mmol). The crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give **S7** (80 mg, 83%) as a yellow oil.

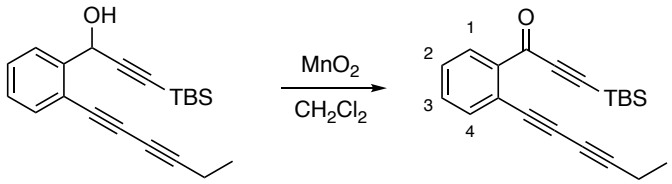
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (d, *J* = 7.8 Hz, 1H, H1), 7.50 (d, *J* = 7.6 Hz, 1H, H4), 7.38 (dd, *J* = 7.7, 7.7 Hz, 1H, H2), 7.28 (dd, *J* = 7.6, 7.6 Hz, 1H, H3), 5.83 (d, *J* = 2.7 Hz, 1H, C*H*OH), 2.45 (d, *J* = 3.4 Hz, 1H, CHO*H*), 2.39 (q, *J* = 7.4 Hz, 2H, CH_2CH_3), 1.22 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 0.94 [s, 9H, $SiC(CH_3)_3$], and 0.13 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 133.7, 129.4, 128.4, 127.0, 120.8, 104.9, 90.3, 87.6, 79.8, 72.0, 64.5, 63.6, 26.2, 16.7, 13.5, 13.4, and -4.5.

IR (neat) 3417, 2953, 2928, 2884, 2856, 2236, 2172, 1470, 1461, 1449, 1362, 1328, 1295, 1250, 1036, 982, 812, 774, and 757 cm^{-1}.

HRMS (ESI-TOF): Calcd for $(C_{21}H_{26}OSiNa)^+$ [$(M+Na)^+$] 345.1645; found: 345.1653.

3-(*tert*-Butyldimethylsilyl)-1-(2-(hexa-1,3-diyn-1-yl)phenyl)prop-2-yn-1-one (5e)



S7 ***5e***

5e was prepared following general procedure B from alcohol **S7** (65 mg, 0.2 mmol) to give **5e** (62 mg, 97%) as a yellow oil.

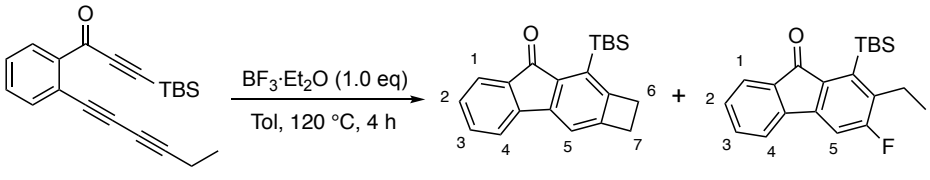
^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, *J* = 7.8 Hz, 1H, H1), 7.60 (d, *J* = 7.6 Hz, 1H, H4), 7.49 (dd, *J* = 7.5, 7.5 Hz, 1H, H3), 7.44 (dd, *J* = 7.6, 7.6 Hz, 1H, H2), 2.39 (q, *J* = 7.5 Hz, 2H, CH_2CH_3), 1.21 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 1.01 [s, 9H, $SiC(CH_3)_3$], and 0.24 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 139.2, 135.8, 132.6, 132.0, 128.4, 122.2, 102.4, 100.0, 88.4, 80.6, 73.0, 65.1, 26.2, 16.8, 13.6, 13.4 and -4.9.

IR (neat) 2951, 2930, 2883, 2857, 2239, 2149, 1649, 1589, 1560, 1479, 1462, 1250, 1233, 1014, 810, 778, and 754 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for [$(C_{21}H_{25}OSi)^+$] [$(M+H)^+$] 321.1669; found: 321.1668.

9-(*tert*-Butyldimethylsilyl)-1,2-dihydro-*8H*-cyclobuta[b]fluoren-8-one (7e) and 1-(*tert*-Butyldimethylsilyl)-2-ethyl-3-fluoro-*9H*-fluoren-9-one (7e')



5e ***7e*** ***7e'***

Triyne **5e** (32 mg, 0.1 mmol) was treated following general procedure C at 120 °C for 4 h. The crude material was purified by MPLC (hexanes:EtOAc 100:1) to give, in order of elution, the fluoroarene **7e'** (6.5 mg, 20%) followed by the fluorenone **7e** (10.6 mg, 33%), each as a crystalline yellow solid.

Data for 7e

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54 (d, *J* = 7.3 Hz, 1H, H1), 7.42–7.40 (m, 2H, H3 and H4), 7.23 (s, 1H, H5), 7.22–7.20 (nfom, 1H, H2), 3.24 (br t, *J* = 4.4 Hz, 2H, H6), 3.06 (br t, *J* = 4.4 Hz, 2H, H7), 0.93 [s, 9H, $SiC(CH_3)_3$], and 0.41 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 195.1, 154.6, 151.8, 145.2, 144.8, 138.5, 134.4, 134.1, 133.7, 128.6, 123.8, 119.3, 115.6, 33.1, 28.4, 27.4, 19.4, and -2.7.

IR (neat) 2951, 2930, 2882, 2855, 1718, 1605, 1587, 1467, 1386, 1360, 1295, 1261, 1242, 1204, 1178, 1165, 1119, 1021, 1002, 946, 901, 849, 834, 813, 804, 775, and 763 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $[(C_{20}H_{21}OSi)^+]$ $[(M+H–CH_4)^+]$ 305.1356; found: 305.1355.

m.p. 126–129 °C.

Data for 7e'

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56 (d, *J* = 7.3 Hz, 1H, H1), 7.45 (dd, *J* = 7.4, 7.4 Hz, 1H, H3), 7.40 (d, *J* = 7.4 Hz, 1H, H4), 7.28 (dd, *J* = 7.3, 7.3 Hz, 1H, H2), 7.18 (d, *J* = 9.5 Hz, 1H, H5), 2.82 (qd, *J* = 7.4, 2.5 Hz, 2H, CH_2CH_3), 1.21 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 1.06 [s, 9H, $SiC(CH_3)_3$], and 0.43 [s, 6H, $Si(CH_3)_2$].

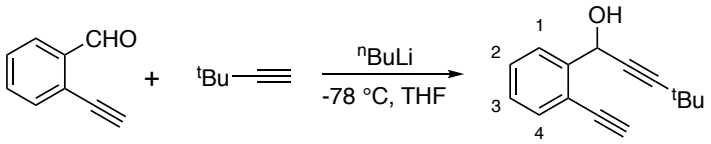
^{13}C NMR (125 MHz, $CDCl_3$) δ 193.2, 165.4 (d, *J* = 256.4 Hz), 146.3 (d, *J* = 10.2 Hz), 143.5 (d, *J* = 3.0 Hz), 142.4 (d, *J* = 2.3 Hz), 139.2 (d, *J* = 13.3 Hz), 136.9 (d, *J* = 3.2 Hz), 134.5, 134.3, 129.3, 123.9, 119.5, 108.9 (d, *J* = 26.3 Hz), 28.5, 24.3 (d, *J* = 4.3 Hz), 19.5, 15.2 (d, *J* = 3.7 Hz), and 1.39.

IR (neat) 2949, 2925, 2891, 2853, 1711, 1605, 1563, 1463, 1421, 1268, 1246, 1214, 1196, 976, 933, 893, 852, 839, 822, 816, 805, 773, and 755 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $(C_{20}H_{22}FOSi)^+$ $[(M+H–CH_4)^+]$ 325.1418; found: 325.1419.

m.p. 107–110 °C.

1-(2-Ethynylphenyl)-4,4-dimethylpent-2-yn-1-ol (S8)



S8

A three-neck round-bottom flask fitted with a magnetic stir bar was loaded with a solution of 3,3-dimethyl-1-butyne (0.92 mL, 7.5 mmol) in THF (15 mL) under an atmosphere of N_2. The solution was stirred in a dry ice-acetone bath while a solution of *n*-butyllithium (3 mL, 2.5 M in hexanes, 7.5 mmol) was added dropwise via a syringe. The resulting solution was stirred at –78 ^oC for 30 min, and a solution of 2-ethynylbenzaldehyde (0.65 g, 5 mmol) in 8 mL of THF was added dropwise via a syringe. After 2.5 h the mixture was quenched with satd. NH_4Cl (15 mL). The organic layer was collected. The aqueous layer was further extracted with Et_2O (3x8 mL).

The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give a yellow oil (0.95 g, 90%).

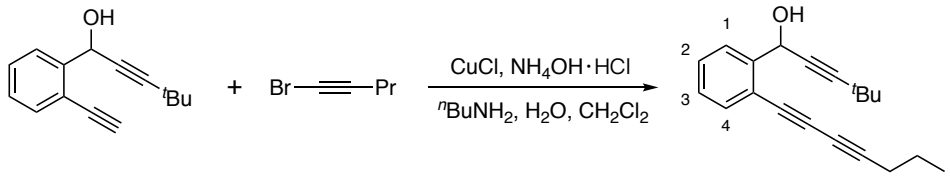
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (d, *J* = 7.7 Hz, 1H, H1), 7.51 (d, *J* = 7.6 Hz, 1H, H4), 7.40 (dd, *J* = 7.6, 7.6 Hz, 1H, H2), 7.28 (dd, *J* = 7.5, 7.5 Hz, 1H, H3), 5.87 (d, *J* = 5.5 Hz, 1H, *CH*OH), 3.36 (s, 1H, C≡CH), 2.48 (d, *J* = 5.3 Hz, 1H, CH*OH*), and 1.26 [s, 9H, $C(CH_3)_3$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 133.3, 129.5, 128.2, 127.0, 120.7, 96.1, 82.6, 81.3, 77.7, 63.2, 31.0, and 27.7.

IR (neat) 3550 (br), 3292, 2968, 2928, 2901, 2866, 2234, 1476, 1447, 1362, 1261, 1203, 1063, 982, 952, 850, and 758 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $[(C_{15}H_{17}O)^+]$ $[(M+H)^+]$ 213.1274; found: 213.1277.

1-(2-(Hepta-1,3-diyn-1-yl)phenyl)-4,4-dimethylpent-2-yn-1-ol (S9)



S8 ***S9***

S9 was prepared following general procedure A from diyne **S8** (64 mg, 0.3 mmol) and 1-bromopent-1-yne (53 mg, 0.36 mmol). The crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give **S9** (71 mg, 85%) as a yellow oil.

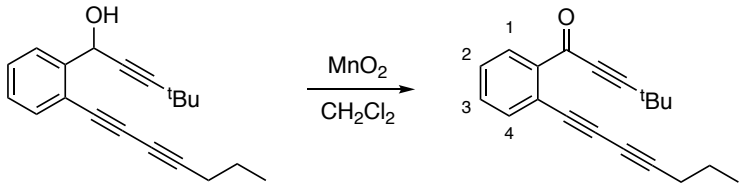
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.67 (d, *J* = 7.7 Hz, 1H, H1), 7.49 (d, *J* = 7.6 Hz, 1H, H4), 7.37 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H, H2), 7.26 (ddd, *J* = 7.7, 7.7, 0.7 Hz, 1H, H3), 5.80 (s, 1H, *CH*OH), 2.47 (br s, 1H, CHO*H*), 2.35 (t, *J* = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 1.61 (qt, *J* = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_3$), 1.25 [s, 9H, $C(CH_3)_3$], and 1.03 (t, *J* = 7.4 Hz, 3H, $CH_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.4, 133.7, 129.3, 128.2, 126.9, 120.7, 96.0, 86.3, 79.7, 77.8, 72.0, 65.2, 63.3, 31.0, 27.6, 21.9, 21.7, and 13.7.

IR (neat) 3397 (br), 2967, 2932, 2901, 2870, 2237, 1476, 1455, 1449, 1424, 1380, 1362, 1340, 1299, 1263, 1203, 1184, 1088, 1064, 984, 951, 848, 807, and 757 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{20}H_{21})^+$ $[(M+H-H_2O)^+]$ 261.1637; found: 261.1636.

1-(2-(Hepta-1,3-diyn-1-yl)phenyl)-4,4-dimethylpent-2-yn-1-one (5f)



S9 *5f*

5f was prepared following general procedure B from alcohol **S9** (56 mg, 0.2 mmol) to give **5f** (53 mg, 96%) as a yellow oil.

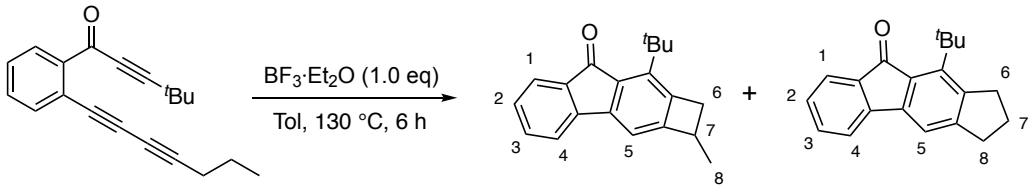
^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.00 (dd, *J* = 7.8, 1.4 Hz, 1H, H1), 7.59 (dd, *J* = 7.7, 1.3 Hz, 1H, H4), 7.47 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H, H3), 7.41 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, H2), 2.36 (t, *J* = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 1.60 (qt, *J* = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_3$), 1.36 [s, 9H, $C(CH_3)_3$], and 1.02 (t, *J* = 7.4 Hz, 3H, $CH_2CH_2CH_3$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 140.0, 135.7, 132.2, 131.3, 128.4, 122.1, 104.8, 87.1, 80.6, 79.4, 72.9, 65.9, 30.2, 28.2, 21.9, 21.8, and 13.7.

IR (neat) 2968, 2932, 2870, 2209, 1649, 1589, 1560, 1478, 1456, 1441, 1363, 1340, 1286, 1264, 1227, 1049, 1038, 880, 786, and 753 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{20}H_{21}O)^+$ [$(M+H)^+$] 277.1587; found: 277.1585.

9-(*tert*-Butyl)-2-methyl-1,2-dihydro-8*H*-cyclobuta[b]fluoren-8-one (7f) and 10-(*tert*-Butyl)-2,3-dihydrocyclopenta[b]fluoren-9(1*H*)-one (7f')



5f *7f* *7f'*

Triyne **5f** (28 mg, 0.1 mmol) was treated following general procedure C at 130 °C for 6 h. The crude material was purified by MPLC (hexanes:EtOAc 100:1) to give, in order of elution, the cyclobutanofluorenone **7f** (16.4 mg, 59%) followed by the cyclopentanofluorenone **7f'** (9.0 mg, 32%), each as a yellow crystalline solid.

Data for 7f

^{1}H NMR (Benzene-d_6, 500 MHz) δ 7.57 (d, *J* = 7.3 Hz, 1H, H1), 7.03 (d, *J* = 7.3 Hz, 1H, H4), 6.98 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 1H, H3), 6.80 (ddd, *J* = 7.3, 7.3, 1.1 Hz, 1H, H2), 6.79 (s, 1H, H5), 3.26 (dd, *J* = 14.0, 5.5 Hz, 1H, H6a), 3.02 (qdd, *J* = 7.0, 5.3, 2.4 Hz, 1H, H7), 2.65 (dd, *J* = 14.0, 2.6 Hz, 1H, H6b), 1.62 [s, 9H, $C(CH_3)_3$], and 1.14 [d, *J* = 7.1 Hz, 3H, H8].

^{13}C NMR (125 MHz, $CDCl_3$) δ 194.5, 159.4, 148.9, 147.6, 144.1, 142.3, 134.1, 133.9, 130.5, 128.6, 123.9, 119.0, 112.4, 42.0, 36.8, 36.2, 29.9 and 18.9.

IR (neat) 2955, 2921, 2865, 1702, 1604, 1576, 1463, 1451, 1423, 1390, 1360, 1295, 1268, 1224, 1216, 1193, 1165, 1136, 1098, 1027, 959, 885, 867, and 765 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $(C_{20}H_{21}O)^+$ $[(M+H)^+]$ 277.1587; found: 277.1586.

m.p. 84–88 °C.

Data for 7f'

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54 (d, J = 7.3 Hz, 1H, H1), 7.40-7.38 (m, 2H, H4 and H3), 7.27 (s, 1H, H5), 7.24-7.19 (nfom, 1H, H2), 3.20 (t, J = 7.3 Hz, 2H, H6), 2.85 (t, J = 7.6 Hz, 2H, H8), 2.00 (tt, J = 7.5, 7.5 Hz, 2H, H7), and 1.56 [s, 9H, $C(CH_3)_3$].

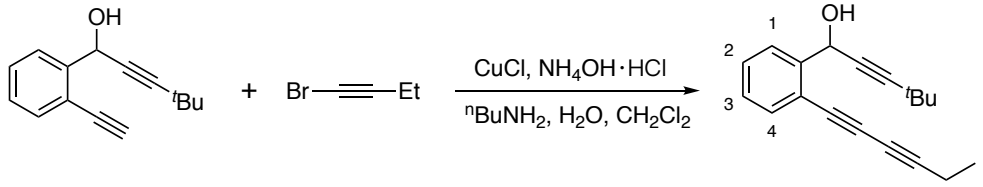
^{13}C NMR (125 MHz, $CDCl_3$) δ 194.5, 153.9, 151.0, 146.7, 143.2, 143.1, 134.8, 134.0, 131.5, 128.6, 123.9, 118.8, 115.1, 38.1, 35.9, 33.3, 31.8, and 25.6.

IR (neat) 2951, 2917, 2867, 1700, 1604, 1592, 1463, 1431, 1420, 1393, 1361, 1295, 1259, 1218, 1209, 1182, 1144, 1104, 1030, 977, 910, 883, 868, and 766 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $(C_{20}H_{21}O)^+$ $[(M+H)^+]$ 277.1587; found: 277.1585.

m.p. 115–118 °C.

1-(2-(Hepta-1,3-diyn-1-yl)phenyl)-4,4-dimethylpent-2-yn-1-ol (S10)



S8 ***S10***

S10 was prepared following general procedure A from diyne **S8** (64 mg, 0.3 mmol) and 1-bromobut-1-yne (48 mg, 0.36 mmol). The crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give **S10** (69 mg, 87%) as a yellow oil.

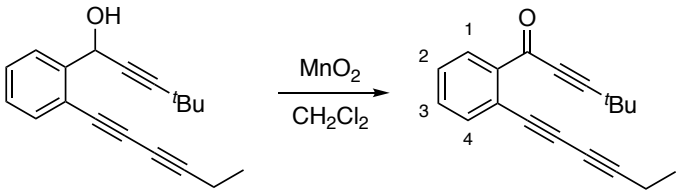
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.67 (dd, J = 7.8, 1.2 Hz, 1H, H1), 7.49 (dd, J = 7.6, 1.3 Hz, 1H, H4), 7.37 (ddd, J = 7.6, 7.6, 1.4 Hz, 1H, H2), 7.26 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H, H3), 5.81 (d, J = 5.5 Hz, 1H, *CH*OH), 2.40 (d, J = 5.5 Hz, 1H, CHO*H*), 2.39 (q, J = 7.5 Hz, 2H, CH_2CH_3), 1.25 [s, 9H, $C(CH_3)_3$], and 1.22 (t, J = 7.5 Hz, 3H, CH_2CH_3).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 133.7, 129.3, 128.2, 126.9, 120.7, 96.0, 87.5, 79.6, 77.8, 72.2, 64.6, 63.3, 31.0, 27.6, 13.5, and 13.4.

IR (neat) 3377, 2969, 2903, 2871, 2235, 1476, 1455, 1362, 1327, 1294, 1262, 1203, 1184, 1063, 986, 951, 850, and 757 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{19}H_{19})^+$ $[(M+H–H_2O)^+]$ 247.1481; found: 247.1480.

1-(2-(Hexa-1,3-diyn-1-yl)phenyl)-4,4-dimethylpent-2-yn-1-one (5g)



S10 ***5g***

5g was prepared following general procedure B from alcohol **S10** (53 mg, 0.2 mmol) to give **5g** (50 mg, 95%) as a yellow oil.

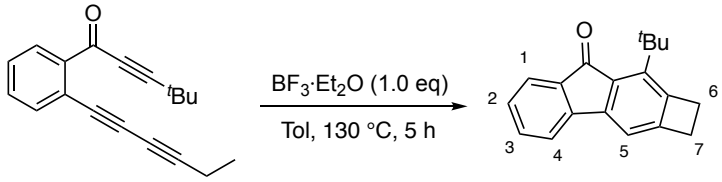
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (dd, *J* = 7.5, 1.5 Hz, 1H, H1), 7.59 (dd, *J* = 7.7, 1.2 Hz, 1H, H4), 7.47 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H, H3), 7.41 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H, H2), 2.39 (q, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 1.36 [s, 9H, C(CH$_3$)$_3$], and 1.21 (t, *J* = 7.5 Hz, 3H, CH$_2$C*H*$_3$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 140.0, 135.6, 132.2, 131.3, 128.4, 122.0, 104.8, 88.3, 80.5, 79.4, 73.1, 65.2, 30.2, 28.2, 13.6, and 13.4.

IR (neat) 2972, 2937, 2870, 2209, 1649, 1589, 1560, 1478, 1456, 1441, 1363, 1330, 1286, 1264, 1227, 1048, 882, 785, and 754 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{19}H_{19}O)^+$ [$(M+H)^+$] 263.1430; found: 263.1427.

9-(*tert*-Butyl)-1,2-dihydro-8*H*-cyclobuta[b]fluoren-8-one (7g)



5g ***7g***

7g was prepared following general procedure C from triyne **5g** (26 mg, 0.1 mmol) at 130 °C for 5 h. The crude material was purified by MPLC (hexanes:EtOAc 80:1) to give the four-membered fluorenone **7g** (17 mg, 65%) as a yellow crystalline solid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.53 (ddd, *J* = 7.4, 1.0, 1.0 Hz, 1H, H1), 7.39-7.38 (m, 2H, H4 and H3), 7.21 (nfom, 1H, H2), 7.11 (s, 1H, H5), 3.39 (br t, *J* = 4.4 Hz, 2H, H6), 3.00 (br t, *J* = 4.5 Hz, 2H, H7), and 1.49 [s, 9H, C(CH$_3$)$_3$].

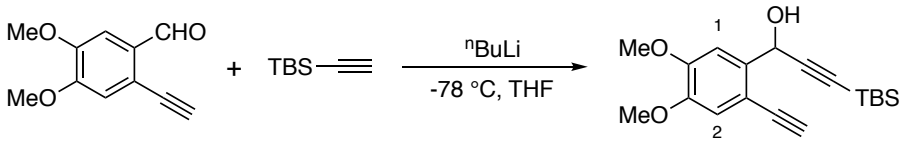
^{13}C NMR (125 MHz, $CDCl_3$) δ 194.5, 154.5, 148.2, 147.5, 144.5, 144.1, 134.1, 133.9, 130.1, 128.6, 123.8, 119.0, 113.6, 36.7, 33.9, 29.9 and 28.3.

IR (neat) 2947, 2926, 2866, 1693, 1603, 1583, 1464, 1424, 1411, 1391, 1361, 1272, 1217, 1193, 1137, 1096, 1028, 984, 947, 896, 866, and 759 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $(C_{19}H_{19}O)^+$ [$(M+H)^+$] 263.1430; found: 263.1430.

m.p. 175–177 °C.

3-(*tert*-Butyldimethylsilyl)-1-(2-ethynyl-4,5-dimethoxyphenyl)prop-2-yn-1-ol (S11)



S11

To a solution of TBS acetylene (0.6 mL, 3 mmol) in 8 mL of dry THF, under a nitrogen atmosphere, was added dropwise *n*-BuLi (1.2 mL, 2.5 M in hexanes, 3 mmol) at -78 ^{o}C. The mixture was stirred at 0 °C for 0.5 h then a solution of 2-ethynyl-4,5-dimethoxybenzaldehyde (475 mg, 2.5 mmol) in 2 mL of tetrahydrofuran was added dropwise at -78 °C. After stirring for 3 h, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride solution. The organic phase was separated and the aqueous phase was extracted with ethyl acetate. The organic phases were combined and the solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography (hexanes:EtOAc 5:1) to give diyne **S11** (643 mg, 78%) as a yellow crystalline solid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.29 (s, 1H, H1), 6.98 (s, 1H, H2), 5.88 (d, *J* = 4.7 Hz, 1H, C*H*OH), 3.92 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.29 (s, 1H, C≡CH), 2.44 (d, *J* = 4.9 Hz, 1H, CH*OH*), 0.95 [s, 9H, $SiC(CH_3)_3$], 0.15 [s, 3H, $Si(CH_3)$], and 0.14 [s, 3H, $Si(CH_3)$].

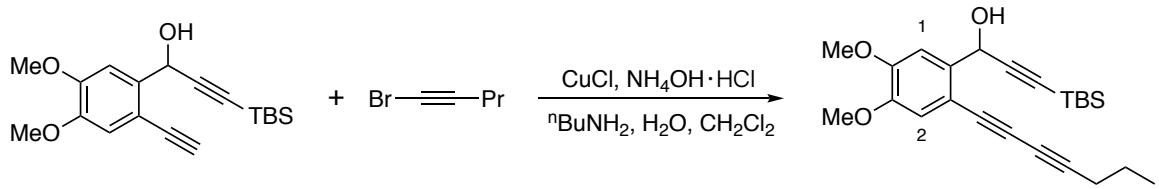
^{13}C NMR (125 MHz, $CDCl_3$) δ 150.1, 148.7, 136.5, 115.1, 112.8, 110.0, 105.2, 90.1, 81.21, 81.16, 63.3, 56.2, 56.0, 26.2, 16.7, -4.5 and -4.6.

IR (neat) 3501, 3283, 2953, 2931, 2855, 2172, 2102, 1603, 1510, 1462, 1398, 1344, 1302, 1259, 1210, 1095, 1035, 1005, 967, 839, 827, 812, and 775 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $[(C_{19}H_{27}O_3Si)^+]$ $[(M+H)^+]$ 331.1724; found: 331.1723.

m.p. 103–106 °C.

3-(*tert*-Butyldimethylsilyl)-1-(2-(hepta-1,3-diyn-1-yl)-4,5-dimethoxyphenyl)prop-2-yn-1-ol (S12)



S11 ***S12***

S12 was prepared following general procedure A from diyne **S11** (330 mg, 1.0 mmol) and 1-bromopent-1-yne (180 mg, 1.2 mmol). The crude material was purified by flash chromatography (hexanes:EtOAc 5:1) to give **S12** (293 mg, 74%) as a yellow oil.

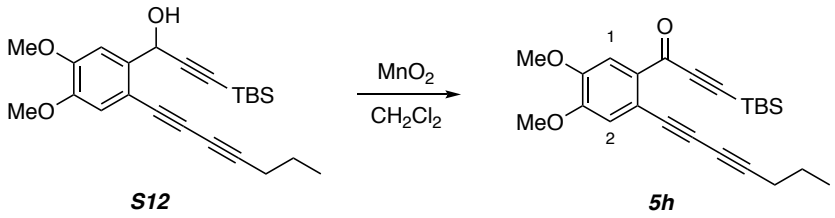
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (s, 1H, H1), 6.96 (s, 1H, H2), 5.84 (s, 1H, *CH*OH), 3.91 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 2.41 (br s, 1H, CHO*H*), 2.35 (t, *J* = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 1.61 (qt, *J* = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_3$), 1.03 (t, *J* = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 0.95 [s, 9H, $SiC(CH_3)_3$], 0.14 [s, 3H, $Si(CH_3)$], and 0.13 [s, 3H, $Si(CH_3)$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 148.7, 137.4, 115.4, 112.8, 110.0, 105.3, 90.1, 85.9, 78.3, 72.0, 65.3, 63.3, 56.2, 56.0, 26.2, 21.9, 21.7, 16.7, 13.7, -4.5, and -4.6.

IR (neat) 3500, 2956, 2932, 2855, 2170, 1601, 1510, 1462, 1348, 1246, 1208, 1150, 1079, 1034, 1005, 965, 861, 838, 826, 812, and 775 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $[(C_{24}H_{31}O_2Si)^+]$ $[(M+H-H_2O)^+]$ 379.2087; found: 379.2089.

3-(*tert*-Butyldimethylsilyl)-1-(2-(hepta-1,3-diyn-1-yl)-4,5-dimethoxyphenyl)prop-2-yn-1-one (5h)



S12 ***5h***

5h was prepared following general procedure B from alcohol **S12** (119 mg, 0.3 mmol) to give **5h** (112 mg, 95%) as a yellow crystalline solid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.63 (s, 1H, H1), 7.04 (s, 1H, H2), 3.94 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 2.36 (t, *J* = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 1.60 (qt, *J* = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_3$), 1.03 (t, *J* = 7.3 Hz, 3H, $CH_2CH_2CH_3$), 1.01 [s, 9H, $SiC(CH_3)_3$], and 0.24 [s, 6H, $Si(CH_3)_2$].

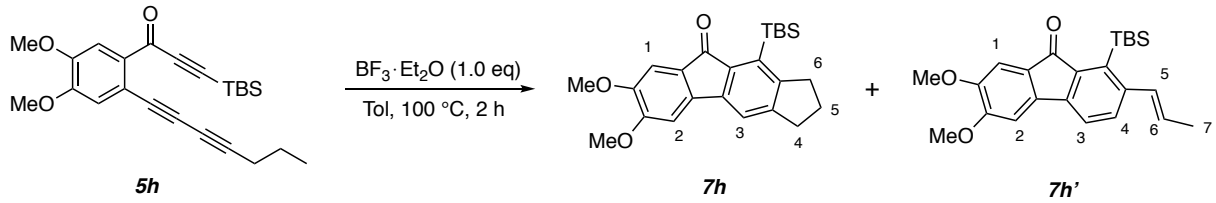
^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 152.5, 149.0, 132.7, 117.4, 116.3, 114.0, 102.6, 99.5, 86.9, 79.7, 73.2, 65.9, 56.4, 56.1, 26.2, 21.90, 21.87, 16.8, 13.7, and -4.9.

IR (neat) 2956, 2932, 2856, 2232, 2149, 1644, 1587, 1555, 1515, 1462, 1395, 1354, 1252, 1201, 1169, 1098, 1026, 964, 870, 838, 829, 814, 779, and 762 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $[(C_{24}H_{31}O_3Si)^+]$ $[(M+H)^+]$ 395.2037; found: 395.2034.

m.p. 94–96 °C.

10-(*tert*-Butyldimethylsilyl)-6,7-dimethoxy-2,3-dihydrocyclopenta[b]fluoren-9(1*H*)-one (7h) and (*E*)-1-(*tert*-Butyldimethylsilyl)-6,7-dimethoxy-2-(prop-1-en-1-yl)-9*H*-fluoren-9-one (7h')



5h *7h* *7h'*

Fluorenones **7h** and **7h'** was prepared following general procedure C from triyne **5h** (27 mg, 0.07 mmol) at 100 °C for 2 h. The crude material was purified by MPLC (hexanes:EtOAc 10:1) to give, in order of elution, **7h** (17 mg, 63%) followed by **7h'** (3 mg, 11%), each as a yellow crystalline solid.

Data for 7h

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.12 (s, 1H, H1), 6.92 (s, 1H, H2), 3.99 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 2.97 (t, J = 7.3 Hz, 2H, H6), 2.85 (t, J = 7.5 Hz, 2H, H4), 2.02 (tt, J = 7.3, 7.3 Hz, 2H, H5), 1.01 [s, 9H, $SiC(CH_3)_3$], and 0.42 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 154.3, 151.6, 149.9, 149.5, 144.1, 139.7, 138.7, 135.4, 127.2, 116.6, 106.9, 102.5, 56.4, 56.3, 36.2, 33.2, 28.0, 25.7, 19.9, and 0.03.

IR (neat) 2952, 2891, 2853, 2252, 1704, 1598, 1588, 1496, 1469, 1423, 1372, 1318, 1297, 1243, 1215, 1156, 1134, 1069, 1004, 914, 870, 840, 805, and 793 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $[(C_{23}H_{27}O_3Si)^+]$ $[(M+H–CH_4)^+]$ 379.1724; found: 379.1721.

m.p. 163–166 °C.

Data for 7h'

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38 (d, J = 7.7 Hz, 1H, H4), 7.31 (d, J = 7.7 Hz, 1H, H3), 7.13 (s, 1H, H1), 6.94 (s, 1H, H2), 6.72 (d, J = 15.5 Hz, 1H, H5), 5.89 (dq, J = 15.3, 6.7 Hz, 2H, H6), 4.00 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 1.87 (d, J = 6.6 Hz, 3H, H7), 1.08 [s, 9H, $SiC(CH_3)_3$], and 0.36 [s, 6H, $Si(CH_3)_2$].

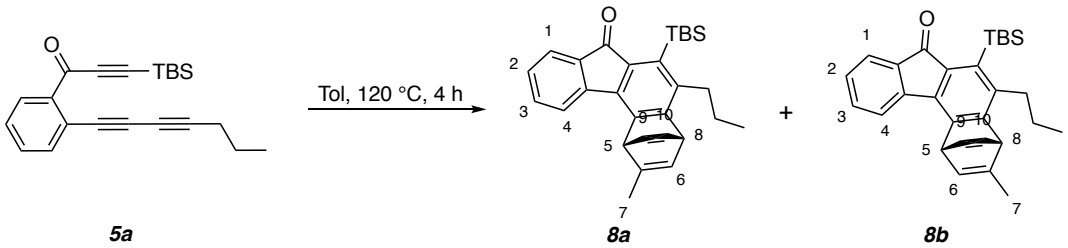
^{13}C NMR (125 MHz, $CDCl_3$) δ 193.9, 154.6, 149.7, 146.8, 143.3, 141.8, 138.6, 138.3, 135.4, 132.1, 126.9, 126.7, 119.9, 107.0, 102.7, 56.5, 56.4, 28.6, 19.9, 18.6, and 1.2.

IR (neat) 2949, 2926, 2853, 1705, 1598, 1582, 1496, 1470, 1352, 1323, 1290, 1244, 1233, 1215, 1145, 1109, 1029, 1047, 1011, 971, 862, 840, 826, and 793 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $[(C_{23}H_{27}O_3Si)^+]$ $[(M+H–CH_4)^+]$ 379.1724; found: 379.1727.

m.p. 144–147 °C.

(1R,4S)-6-(*tert*-Butyldimethylsilyl)-3-methyl-5-propyl-1,4-dihydro-7*H*-1,4-ethenobenzo[*c*]fluoren-7-one (8a) and
(1R,4S)-6-(*tert*-Butyldimethylsilyl)-2-methyl-5-propyl-1,4-dihydro-7*H*-1,4-ethenobenzo[*c*]fluoren-7-one (8b)



5a ***8a*** ***8b***

Control experiment: The triyne **5a** (33 mg, 0.1 mmol) was dissolved in toluene (2 mL) and the solution was heated at 120 °C in a culture tube fitted with an inert, Teflon®-lined cap. After 3 h, the reaction mixture was quenched by the addition of satd. aq. $NaHCO_3$, and this mixture was extracted with ethyl acetate. The ethyl acetate fraction was concentrated to provide the crude product mixture, which was purified by MPLC (hexanes:EtOAc 80:1) to give the co-eluting mixture of two products (19 mg, 1.5:1, 45%) as a yellow oil.

Data for 8a The 2-methyl isomer (major isomer)

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.90 (d, *J* = 7.6 Hz, 1H, H4), 7.59 (d, *J* = 7.1 Hz, 1H, H1), 7.47 (ddd, *J* = 7.4, 7.4, 1.3 Hz, 1H, H3), 7.22 (dd, *J* = 7.4, 7.4 Hz, 1H, H2), 6.93–6.89 (m, 2H, H9 and H10), 6.31 (ddd, *J* = 5.9, 1.8, 1.8 Hz, 1H, H6), 5.35 (ddd, *J* = 5.9, 1.8, 1.8 Hz, 1H, H5), 5.03 (ddd, *J* = 5.9, 5.9, 1.7 Hz, 1H, H8), 2.84 (t, 2H, *J* = 7.8 Hz, $CH_2CH_2CH_3$), 1.99 (d, *J* = 1.7 Hz, 1H, H7), 1.57–1.46 (m, 2H, $CH_2CH_2CH_3$), 1.10 (t, *J* = 8.2 Hz, 3H, $CH_2CH_2CH_3$), 1.08 [s, 9H, $SiC(CH_3)_3$], and 0.34 [s, 6H, $Si(CH_3)_2$].

Data for 8b The 3-methyl isomer (the minor isomer)

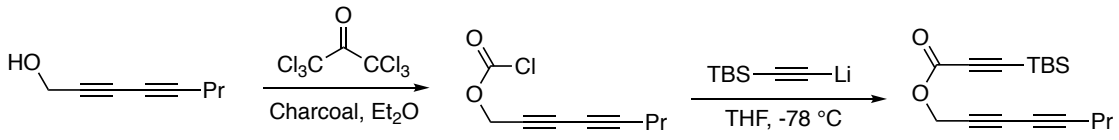
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.89 (d, *J* = 7.6 Hz, 1H, H4), 7.58 (d, *J* = 7.4 Hz, 1H, H1), 7.45 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H, H3), 7.22 (dd, *J* = 7.3, 7.3 Hz, 1H, H2), 6.88–6.85 (m, 2H, H9 and H10), 6.41 (ddd, *J* = 6.0, 1.8, 1.8 Hz, 1H, H6), 5.55 (ddd, *J* = 5.8, 5.8, 1.9 Hz, 1H, H5), 4.86 (ddd, *J* = 5.7, 1.9, 1.9 Hz, 1H, H8), 2.85 (t, 2H, *J* = 7.2 Hz, $CH_2CH_2CH_3$), 1.97 (d, *J* = 1.7 Hz, 1H, H7), 1.57–1.46 (m, 2H, $CH_2CH_2CH_3$), 1.10 (t, *J* = 8.2 Hz, 3H, $CH_2CH_2CH_3$), 1.08 [s, 9H, $SiC(CH_3)_3$], and 0.34 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 193.9, 193.8, 152.8, 152.0, 149.5, 149.1, 144.3, 144.2, 143.5, 143.2, 142.8, 142.7, 139.4, 139.2, 138.6, 138.5, 138.3, 138.1, 137.7, 137.4, 135.3, 135.2, 135.1, 134.8, 134.04, 134.00, 131.2, 130.8, 127.93, 127.91, 124.0, 123.9, 122.1, 121.8, 51.8, 50.5, 46.1, 44.7, 36.7, 36.6, 29.0, 28.9, 26.2, 25.7, 20.0, 19.7, 19.59, 19.57, 14.6, 14.5, 2.0, and 1.9. (likely overlap of three $SiCH_3$ resonances)

IR (neat) 2955, 2928, 2854, 1709, 1606, 1586, 1466, 1389, 1303, 1258, 1215, 1086, 998, 909, 846, 824, 810, 785, and 754 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for $(C_{28}H_{31}OSi)^+$ $[(M+H–CH_4)^+]$ 411.2139; found: 411.2131.

Octa-2,4-diyn-1-yl 3-(*tert*-butyldimethylsilyl)propiolate (10a)



10a

10a was synthesized according to the reported procedure for synthesis of the methylated (in place of propyl) analog.[6] Activated charcoal (20 mg) was added to an anhydrous ether solution (10 mL) of triphosgene (742 mg, 2.5 mmol), and this suspension was stirred for 1 h at room temperature. Octa-2,4-diyn-1-ol (610 mg, 5 mmol) in ether (3 mL) was added dropwise, and the resulting mixture was stirred overnight at room temperature. The slurry was filtered through Celite^{TM} (eluting with anhydrous ether), and the filtrate was concentrated to give crude octa-2,4-diyn-1-yl carbonochloridate. TBS-acetylene (1.0 mL, 5.5 mmol) was added to a 25 mL round bottom flask, placed under nitrogen, dissolved in THF (10 mL), and cooled to 0 °C. *n*-BuLi (2.5 M in hexanes, 2.2 mL, 5.4 mmol) was added dropwise over 15 min, and the solution was stirred at 0 °C for 0.5 h. The mixture was cooled to -78 °C, and a solution of octa-2,4-diyn-1-yl carbonochloridate in THF (5 mL) was added dropwise. After being stirred at -78 °C for 3 h, the reaction mixture was quenched by the addition of acetic acid (1 mL). The mixture was transferred to a separatory funnel with additional ether (50 mL) and washed with $NaHCO_3$ (25 mL x 3) and brine (25 mL). The ether layer was dried ($MgSO_4$), filtered, concentrated, and passed through a plug of silica (10:1 Hex:EtOAc). The resulting residue was purified by MPLC (50:1 Hex:EtOAc) to give the propiolate ester **10a** (690 mg, 48%) as a colorless oil.

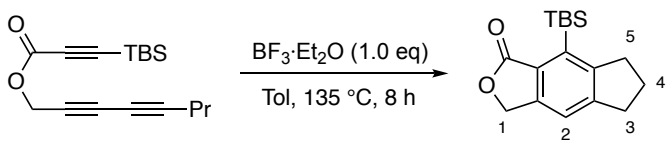
^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.80 (s, 2H, OC*H*$_2$), 2.26 (t, *J* = 7.0 Hz, 2H, C*H*$_2$CH$_2$CH$_3$), 1.57 (qt, *J* = 7.2, 7.2 Hz, 2H, CH$_2$C*H*$_2$CH$_3$), 0.99 (t, *J* = 7.3 Hz, 3H, CH$_2$CH$_2$C*H*$_3$), 0.97 [s, 9H, SiC(CH$_3$)$_3$], and 0.18 [s, 6H, Si(CH$_3$)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 94.6, 94.5, 82.6, 72.6, 68.2, 64.5, 53.9, 26.1, 21.7, 21.3, 16.7, 13.6 and -5.1.

IR (neat) 2955, 2932, 2859, 2258, 2173, 1719, 1470, 1463, 1429, 1364, 1252, 1203, 1007, 983, 859, 840, 826, 812, and 779 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{17}H_{25}O_2Si)^+$ [$(M+H)^+$] 289.1618; found: 289.1620.

8-(*tert*-Butyldimethylsilyl)-3,5,6,7-tetrahydro-1*H*-indeno[5,6-c]furan-1-one (11a)



10a ***11a***

The indanofuranone derivative **11a** was prepared following general procedure C from triyne **10a** (29 mg, 0.1 mmol) at 135 °C for 8 h. The crude material was purified by MPLC (hexanes:EtOAc 30:1) to give the **11a** (12 mg, 41%) as a crystalline white solid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28 (s, 1H, H2), 5.17 (s, 2H, H1), 3.07 (t, *J* = 7.3 Hz, 2H, *H*3 or *H*5), 2.93 (t, *J* = 7.5 Hz, 2H, *H*3 or *H*5), 2.06 (tt, *J* = 7.4, 7.4 Hz, 2H, H4), 0.98 [s, 9H, $SiC(CH_3)_3$], and 0.47 [s, 6H, $Si(CH_3)_2$].

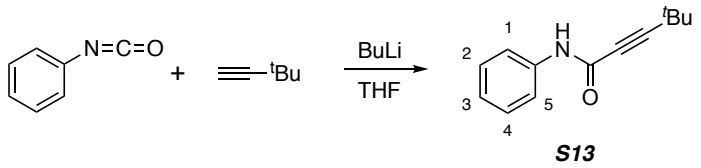
^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 153.8, 150.7, 146.6, 135.2, 129.3, 118.6, 68.2, 36.1, 33.0, 27.7, 26.1, 19.6, and -0.1.

IR (neat) 2956, 2928, 2878, 2854, 1755, 1469, 1460, 1352, 1248, 1213, 1177, 1092, 1032, 1020, 883, 841, 819, 808, 785, and 765 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{16}H_{21}O_2Si)^+$ $[(M+H–CH_4)^+]$ 273.1305; found: 273.1306.

m.p. 146–150 °C.

4,4-Dimethyl-*N*-phenylpent-2-ynamide (S13)



S13

S13 was synthesized according to the reported procedure[7]: To a solution of *tert*-butyl acetylene (0.68 mL, 5.5 mmol) in 10 mL of dry THF, under a nitrogen atmosphere, was added dropwise *n*-butyllithium (2.2 mL, 2.5 M in hexanes, 5.5 mmol) at -78 °C. The mixture was stirred at 0 °C for 0.5 h and a solution of phenyl isocyanate (0.54 mL, 5 mmol) in 3 mL of THF was added dropwise at -78 °C. After being stirred at 0 °C for 4 h, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride solution. The organic phase was separated and the aqueous phase was washed with methylene chloride. The organic phases were combined and the solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography (hexanes:EtOAc 5:1) to give amide **S13** (0.84 g, 84%) as a crystalline light yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (brs, 1H, CON*H*), 7.52 (d, *J* = 7.9 Hz, 2H, H1 and H5), 7.32 (dd, *J* = 7.8, 7.8 Hz, 2H, H2 and H4), 7.14 (t, *J* = 7.5 Hz, 1H, H3), and 0.99 [s, 9H, $C(CH_3)_3$].

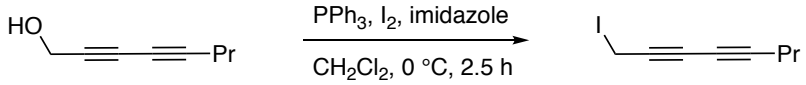
^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 137.6, 129.2, 124.8, 120.0, 95.8, 74.8, 30.3, and 27.6.

IR (neat) 3250, 3130, 3060, 2972, 2929, 2900, 2866, 2219, 1641, 1597, 1542, 1499, 1441, 1321, 1268, 1031, 905, 874, 837, and 754 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{13}H_{16}NO)^+$ $[(M+H)^+]$ 202.1226; found: 202.1227.

m.p. 180–184 °C.

1-Iodoocta-2,4-diyne (S14)



S14

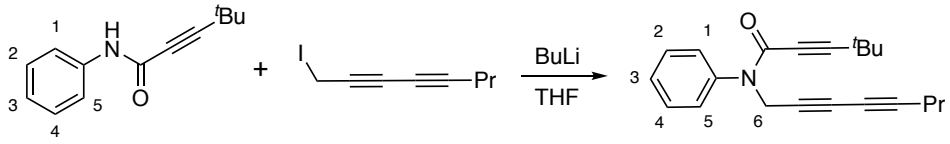
S14 was synthesized according to the reported procedure for an analog[8]: PPh_3 (577 mg, 2.2 mmol), I_2 (610 mg, 2.4 mmol), and imidazole (272 mg, 4.0 mmol) were sequentially added to a stirred solution of octa-2,4-diyn-1-ol[9] (prepared from coupling of propargyl alcohol with 1-bromopentyne) in CH_2Cl_2 (20 mL) at 0 °C. After 2.5 h the reaction mixture was diluted with CH_2Cl_2 and washed with satd. aq. $Na_2S_2O_3$. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexanes:EtOAc 50:1) gave the iodide **S14** (348 mg, 75%) as a light yellow oil. This compound was stored in a refrigerator and in the dark as a precaution toward decomposition.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.75 (t, J = 1.2 Hz, 2H, CH_2I), 2.26 (tt, J = 7.0, 1.2 Hz, 2H, $CH_2CH_2CH_3$), 1.56 (tq, J = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_2CH_3$), and 0.99 (t, J = 7.4 Hz, 3H, $CH_2CH_2CH_3$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 83.0, 72.1, 70.6, 65.1, 21.8, 21.5, 13.6, and -18.3.

IR (neat) 2963, 2933, 2901, 2872, 2248, 2199, 1683, 1530, 1462, 1422, 1380, 1338, 1252, 1143, 1094, and 972 cm^{-1}.

4,4-Dimethyl-*N*-(octa-2,4-diyn-1-yl)-*N*-phenylpent-2-ynamide (10b)



S13 ***S14*** ***10b***

To a solution of **S13** (201 mg, 1 mmol) in THF (7 mL) at -78 °C was added *n*-BuLi (0.44 mL, 2.5 M in hexanes, 1.1 mmol) dropwise, and the solution was stirred for 1 h. 1-Iodoocta-2,4-diyne **S14** (278 mg, 1.2 mmol) was added and the solution was allowed to warm to room temperature overnight. The reaction mixture was quenched by addition of satd. aqueous NH_4Cl and extracted with Et_2O. The combined extracts were washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The crude material was purified by flash chromatography (hexanes:EtOAc 10:1) to give amide **10b** (214 mg, 70%) as a yellow oil.

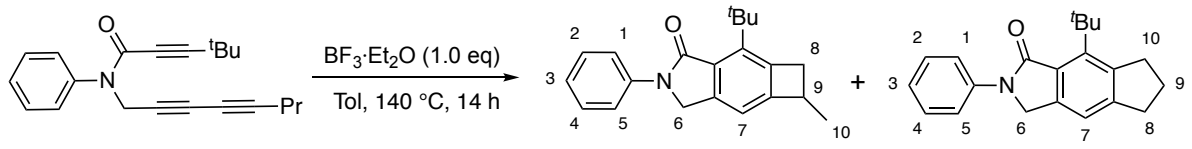
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.43-7.37 (m, 3H, H2–H4), 7.35-7.32 (m, 2H, H1 and H5), 4.57 (s, 2H, H6), 2.22 (t, J = 7.1 Hz, 2H, $CH_2CH_2CH_3$), 1.54 (qt, J = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_3$), 0.98 (t, J = 7.4 Hz, 3H, $CH_2CH_2CH_3$), and 0.94 [s, 9H, $C(CH_3)_3$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 141.6, 129.2, 128.6, 128.5, 102.2, 80.4, 73.3, 70.5, 69.3, 64.9, 38.5, 29.7, 27.5, 21.8, 21.3, and 13.6.

IR (neat) 2967, 2932, 2901, 2870, 2232, 1643, 1595, 1493, 1454, 1414, 1377, 1279, 1219, 1017, 924, 772, and 758 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{21}H_{24}NO)^+$ [$(M+H)^+$] 306.1852; found: 306.1851.

7-(*tert*-Butyl)-5-methyl-2-phenyl-2,3,5,6-tetrahydro-1*H*-cyclobuta[*f*]isoindol-1-one (11b) and 8-(*tert*-Butyl)-2-phenyl-3,5,6,7-tetrahydrocyclopenta[*f*]isoindol-1(2*H*)-one (11b')



10b *11b* *11b'*

Triyne **10b** (30 mg, 0.1 mmol) was treated following general procedure C at 140 °C for 14 h. The crude material was purified by MPLC (hexanes:EtOAc 15:1) to give, in order of elution, the benzocyclobutene derivative **11b** (18 mg, 60%) followed by the benzocyclopentene derivative **11b'** (9 mg, 30%), each as a white crystalline solid.

Data for 11b

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (d, *J* = 7.8 Hz, 2H, H1 and H5), 7.40 (dd, *J* = 7.5, 7.5 Hz, 2H, H2 and H4), 7.14 (t, *J* = 7.4 Hz, 1H, H3), 7.02 (s, 1H, H7), 4.72 (s, 2H, H6), 3.65 (dd, *J* = 14.0, 5.4 Hz, 1H, H8a), 3.42 (br qd, *J* = 7.1, 5.8 Hz, 1H, H9), 2.98 (d, *J* = 14.0 Hz, 1H, H8b), 1.59 [s, 9H, $C(CH_3)_3$], and 1.39 (d, *J* = 7.0 Hz, 3H, H10).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 156.4, 146.9, 143.0, 140.7, 140.0, 129.1, 128.8, 124.2, 120.0, 114.2, 50.2, 41.9, 36.9, 36.0, 30.9, and 19.1.

IR (neat) 2955, 2922, 2864, 1686, 1597, 1500, 1459, 1450, 1375, 1309, 1227, 1188, 1173, 1155, 1145, 1089, 981, 909, 859, 793, and 754 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for [$(C_{21}H_{24}NO)^+$] [$(M+H)^+$] 306.1852; found: 306.1853.

m.p. 133–136 °C.

Data for 11b'

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (d, *J* = 7.8 Hz, 2H, H1 and H5), 7.41 (dd, *J* = 7.7, 7.7 Hz, 2H, H4 and H3), 7.19 (s, 1H, H7), 7.15 (t, *J* = 7.5 Hz, 1H, H3), 4.70 (s, 2H, H6), 3.30 (t, *J* = 7.3 Hz, 2H, H10), 2.90 (t, *J* = 7.6 Hz, 2H, H8), 2.01 (tt, *J* = 7.4, 7.3 Hz, 2H, H9), and 1.68 [s, 9H, $C(CH_3)_3$].

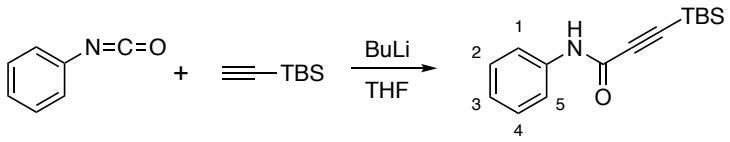
^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 151.2, 148.6, 142.5, 141.8, 140.1, 129.4, 129.1, 124.3, 120.2, 116.9, 49.4, 38.2, 35.8, 33.0, 32.7, and 25.9.

IR (neat) 2948, 2909, 2866, 1685, 1598, 1499, 1459, 1373, 1300, 1281, 1248, 1222, 1184, 1164, 1093, 941, and 792 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for [$(C_{21}H_{24}NO)^+$] [$(M+H)^+$] 306.1852; found: 306.1852.

m.p. 122–125 °C.

3-(*tert*-Butyldimethylsilyl)-*N*-phenylpropiolamide (S15)



S15

S15 was synthesized according to the procedure for an analog **S14**: To a solution of 1-TBS-acetylene (1.0 mL, 5.5 mmol) in 10 mL of dry THF under a nitrogen atmosphere was added dropwise *n*-butyllithium (2.2 mL, 2.5 M in hexanes, 5.5 mmol) at -78 ^{o}C. The mixture was stirred at 0 °C for 0.5 h, and a solution of phenyl isocyanate (0.5 mL, 5 mmol) in 3 mL of THF was added dropwise at -78 °C. After stirring at 0 °C for 4 h, the reaction mixture was quenched by the addition of saturated aqueous ammonium chloride solution. The organic phase was separated and the aqueous phase was washed with methylene chloride. The organic phases were combined and the solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography (hexanes:EtOAc 5:1) to give amide **S15** (1.03 g, 80%) as a crystalline white solid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.52 (d, *J* = 8.0 Hz, 2H, H1 and H5), 7.44 (br s, 1H, CON*H*), 7.33 (dd, *J* = 7.7, 7.7 Hz, 2H, H2 and H4), 7.14 (t, *J* = 7.5 Hz, 1H, H3), 0.99 [s, 9H, $SiC(CH_3)_3$], and 0.20 [s, 6H, $Si(CH_3)_2$].

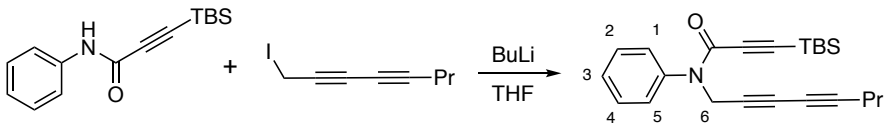
^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 137.3, 129.2, 125.1, 120.1, 98.8, 91.4, 26.2, 16.7, and -4.9.

IR (neat) 3323, 3130, 3064, 2953, 2928, 2884, 2857, 2158, 1638, 1612, 1597, 1548, 1499, 1490, 1469, 1443, 1321, 1256, 1216, 968, 839, 825, 811, 777, and 756 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{15}H_{22}NOSi)^{+}$ [$(M+H)^{+}$] 260.1465; found: 260.1464.

m.p. 116–120 °C.

3-(*tert*-Butyldimethylsilyl)-*N*-(octa-2,4-diyn-1-yl)-*N*-phenylpropiolamide (10c)



S15 ***S14*** ***10c***

To a solution of **S15** (259 mg, 1 mmol) in THF (7 mL) at -78 °C was added *n*-BuLi (0.44 mL, 2.5 M in hexanes, 1.1 mmol) dropwise, and the solution was stirred for 1 h. 1-Iodoocta-2,4-diyne **S14** (278 mg, 1.2 mmol) was added and the solution was allowed to warm to room temperature overnight. The reaction mixture was quenched with NH_4Cl and extracted with Et_2O, washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The crude material

was purified by flash chromatography (hexanes:EtOAc 10:1) to give amide **10c** (240 mg, 66%) as a yellow oil.

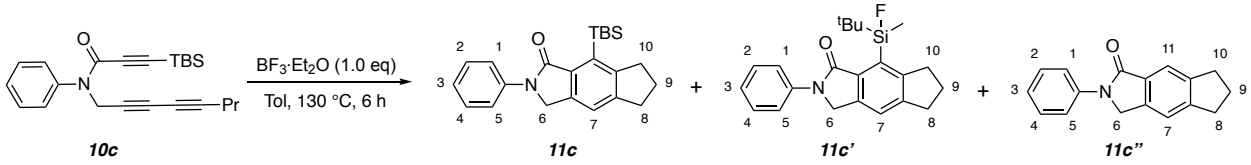
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.43-7.40 (nfom, 2H, H1 and H5), 7.38-7.34 (m, 3H, H2, H3 and H4), 4.56 (s, 2H, H6), 2.23 (t, J = 7.1 Hz, 2H, $CH_2CH_2CH_3$), 1.55 (qt, J = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_3$), 0.98 (t, J = 7.5 Hz, 3H, $CH_2CH_2CH_3$), 0.67 [s, 9H, $SiC(CH_3)_3$], and -0.06 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 141.1, 129.4, 128.8, 128.7, 98.3, 96.8, 80.5, 70.1, 69.5, 64.9, 38.7, 25.9, 21.8, 21.3, 16.4, 13.6, and -5.3.

IR (neat) 2957, 2930, 2883, 2857, 2255, 1645, 1594, 1493, 1462, 1413, 1380, 1275, 1251, 1220, 1036, 1016, 839, 827, 813, and 778 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{23}H_{30}NOSi)^+$ [$(M+H)^+$] 364.2091; found: 364.2090.

8-(*tert*-Butyldimethylsilyl)-2-phenyl-3,5,6,7-tetrahydrocyclopenta[*f*]isoindol-1(2*H*)-one (11c), 8-(*tert*-Butylfluoro(methyl)silyl)-2-phenyl-3,5,6,7-tetrahydrocyclopenta[*f*]isoindol-1(2*H*)-one (11c'), and 2-Phenyl-3,5,6,7-tetrahydrocyclopenta[*f*]isoindol-1(2*H*)-one (11c'')



Triyne **10c** (36 mg, 0.1 mmol) was treated following general procedure C at 130 °C for 6 h. The crude material was purified by MPLC (hexanes:EtOAc 15:1) to give, in order of elution, the amide product **11c** (12.8 mg, 36%), the fluorinated byproduct **11c'** (5.9 mg, 16%) and the desilylated byproduct **11c''** (5.0 mg, 20%), each as a white crystalline solid.

Data for 11c

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.80 (d, J = 8.1 Hz, 2H, H1 and H5), 7.40 (dd, J = 7.8, 7.8 Hz, 2H, H2 and H4), 7.34 (s, 1H, H7), 7.13 (t, J = 7.4 Hz, 1H, H3), 4.72 (s, 2H, H6), 3.09 (t, J = 7.3 Hz, 2H, H10), 2.94 (t, J = 7.4 Hz, 2H, H8), 2.05 (tt, J = 7.3, 7.3 Hz, 2H, H9), 1.02 [s, 9H, $SiC(CH_3)_3$], and 0.50 [s, 3H, $Si(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 152.7, 148.3, 140.2, 139.9, 137.0, 133.5, 129.2, 124.0, 119.7, 119.6, 49.8, 36.4, 33.0, 28.2, 26.1, 19.6, and 0.8.

IR (neat) 2949, 2923, 2852, 1715, 1698, 1652, 1598, 1500, 1469, 1459, 1450, 1377, 1305, 1254, 1241, 1172, 839, 821, 802, and 782 cm^{-1}.

HRMS (APCI-Orbitrap): Calcd for [$(C_{23}H_{30}NOSi)^+$] [$(M+H)^+$] 364.2091; found: 364.2092.

m.p. 202–205 °C.

Data for 11c'

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.80 (d, *J* = 8.1 Hz, 2H, H1 and H5), 7.43-7.39 (m, 2H, H2 and H4), 7.15 (t, *J* = 7.4, Hz, 1H, H3), 4.80 (d, *J* = 16.0 Hz, 1H, H6a), 4.76 (d, *J* = 16.0 Hz, 1H, H6b), 3.29 (dddd, *J* = 16.8, 8.1, 8.1, 2.9 Hz, 1H, H10a), 3.13 (dddd, *J* = 17.0, 8.8, 4.6, 4.6 Hz, 1H, H10b), 2.96 (t, *J* = 7.5 Hz, 2H, H8), 2.18–2.11 (nfom, 1H, H9a), 2.08–1.99 (nfom, 1H, H9b), 1.05 [s, 9H, $SiC(CH_3)_3$], and 0.70 (d, *J* = 9.3 Hz, 3H, $SiCH_3$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 153.0 (d, *J* = 3.0 Hz), 149.3, 139.9, 138.8, 137.0 (d, *J* = 6.3 Hz), 129.3, 129.1 (d, *J* = 16.3 Hz), 124.3, 120.3, 119.5, 50.5, 34.7 (d, *J* = 11.3 Hz), 33.0, 27.1, 25.7 (d, *J* = 6.8 Hz), 20.8 (d, *J* = 12.5 Hz), and -1.7 (d, *J* = 17.5 Hz).

IR (neat) 2958, 2929, 2892, 2856, 1693, 1598, 1500, 1471, 1460, 1449, 1381, 1304, 1250, 1246, 1225, 1171, 900, 836, 822, and 778 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $[(C_{22}H_{27}FNOSi)^+]$ $[(M+H)^+]$ 368.1840; found: 368.1839.

m.p. 147–150 °C.

Data for 11c''

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.88 (d, *J* = 8.2 Hz, 2H, H1 and H5), 7.74 (s, 1H, H11), 7.42 (dd, *J* = 7.8, 7.8 Hz, 2H, H2 and H4), 7.33 (s, 1H, H7), 7.16 (t, *J* = 7.4 Hz, 1H, H3), 4.80 (s, 2H, H6), 3.00 (t, *J* = 7.5 Hz, 4H, H8 and H10), and 2.16 (tt, *J* = 7.4, 7.4 Hz, 2H, H9).

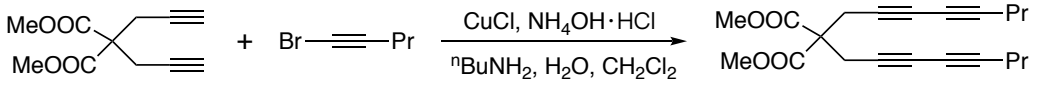
^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 149.8, 145.2, 140.0, 139.0, 131.9, 129.3, 124.3, 119.9, 119.4, 118.5, 50.6, 33.2, 32.6, and 25.9.

IR (neat) 2955, 2919, 1681, 1598, 1499, 1451, 1445, 1383, 1303, 1256, 1164, 869, and 767 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $[(C_{17}H_{16}NO)^+]$ $[(M+H)^+]$ 250.1226; found: 250.1226.

m.p. 150–153 °C.

Dimethyl 2,2-di(octa-2,4-diyn-1-yl)malonate (10d)



S16 ***10d***

Tetrayne **10d** was prepared following general procedure A from diyne **S16**[10] (104 mg, 0.5 mmol) and 1-bromopent-1-yne (176 mg, 1.2 mmol). The crude material was purified by flash chromatography (hexanes:EtOAc 10:1) to give **10d** (119 mg, 70%) as a white amorphous solid.

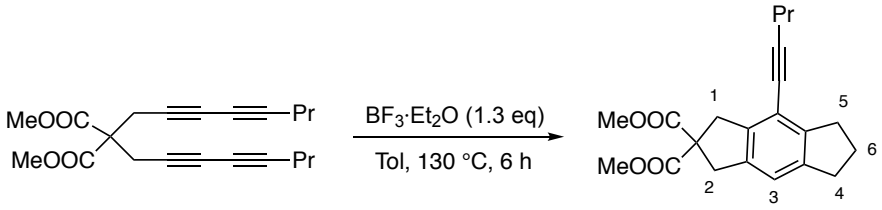
^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.77 [s, 6H, $C(COOCH_3)_2$], 3.06 [s, 4H, $C(CH_2)_2$], 2.22 [t, *J* = 7.1 Hz, 4H, $(CH_2CH_2CH_3)_2$], 1.54 [qt, *J* = 7.1, 7.1 Hz, 4H, $(CH_2CH_2CH_3)_2$], and 0.98 [t, *J* = 7.2 Hz, 6H, $(CH_2CH_2CH_3)_2$].

^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.9, 78.9, 70.6, 68.8, 65.1, 56.9, 53.4, 23.9, 21.8, 21.3, and 13.6.

IR (neat) 2963, 2935, 2874, 2257, 1742, 1453, 1434, 1320, 1290, 1248, 1208, 1184, 1071, 1055, 965, and 839 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{21}H_{25}O_4)^+$ $[(M+H)^+]$ 341.1747; found: 341.1745.

4-(Pent-1-yn-1-yl)-3,5,6,7-tetrahydro-s-indacene-2,2(1H)-dicarboxylate (11d)



10d ***11d***

The bis-indane derivative **11d** was prepared following general procedure C from tetrayne **10d** (34 mg, 0.1 mmol) at 130 °C for 6 h in the presence of 1.3 equivalents of $BF_3{\cdot}Et_2O$. The crude material was purified by MPLC (hexanes:EtOAc 10:1) to give **11d** (12 mg, 35%) as a light yellow oil.

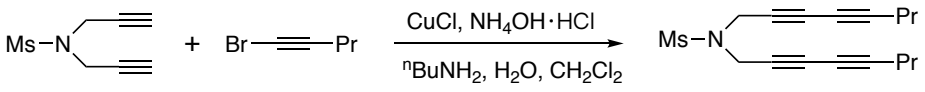
^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.95 (s, 1H, H3), 3.74 [s, 6H, $C(COOMe)_2$], 3.61 (s, 2H, H1), 3.54 (s, 2H, H2), 2.90 (t, J = 7.5 Hz, 2H, H5), 2.85 (t, J = 7.4 Hz, 2H, H4), 2.43 (t, J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 2.04 (tt, J = 7.4, 7.4 Hz, 2H, H6), 1.64 (qt, J = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_3$), and 1.06 (t, J = 7.4 Hz, 3H, $CH_2CH_2CH_3$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 145.4, 143.4, 139.8, 137.8, 119.5, 116.6, 96.6, 77.6, 60.3, 53.1, 40.8, 40.2, 33.2, 32.4, 25.3, 22.5, 21.8, and 13.6.

IR (neat) 2957, 2874, 2845, 2189, 1734, 1598, 1453, 1434, 1379, 1277, 1249, 1200, 1161, 1071, 959, and 887 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $(C_{21}H_{25}O_4)^+$ $[(M+H)^+]$ 341.1747; found: 341.1745.

***N*,*N*-Di(octa-2,4-diyn-1-yl)methanesulfonamide (10e)**



S17 ***10e***

Tetrayne **10e** was prepared following general procedure A from diyne **S17**[11] (171 mg, 1.0 mmol) and 1-bromopent-1-yne (323 mg, 2.2 mmol). The crude material was purified by flash chromatography (hexanes:EtOAc 10:1) to give **10e** (227 mg, 75%) as a light yellow solid.

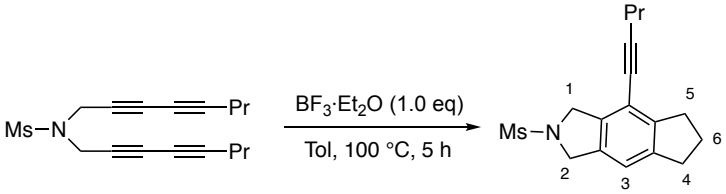
^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.23 [s, 4H, $N(CH_2)_2$], 2.98 (s, 3H, SO_2CH_3), 2.26 [t, J = 7.0 Hz, 4H, $(CH_2CH_2CH_3)_2$], 1.57 [qt, J = 7.1, 7.1 Hz, 4H, $(CH_2CH_2CH_3)_2$], and 1.00 [t, J = 7.3 Hz, 6H, $(CH_2CH_2CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$) δ 81.6, 71.6, 68.4, 64.4, 38.9, 37.6, 21.7, 21.3, and 13.6.

IR (neat) 2964, 2934, 2873, 2254, 1461, 1424, 1345, 1254, 1233, 1154, 1073, 965, 944, 896, and 780 cm^{-1}.

HRMS (ESI-Orbitrap): Calcd for $[(C_{17}H_{22}NO_2S)^+]$ $[(M+H)^+]$ 304.1366; found: 304.1367.

2-(Methylsulfonyl)-4-(pent-1-yn-1-yl)-1,2,3,5,6,7-hexahydrocyclopenta[f]isoindole (11e)



10e ***11e***

The iso-indoline derivative **11e** was prepared following general procedure C from tetrayne **10e** (30 mg, 0.1 mmol) at 100 °C for 5 h. The crude material was purified by MPLC (hexanes:EtOAc 6:1) to give the **11e** (4.6 mg, 15%) as a white crystalline solid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.99 (s, 1H, H3), 4.68 (s, 2H, H1), 4.66 (s, 2H, H2), 2.94 (t, J = 7.5 Hz, 2H, H5), 2.91 (t, J = 7.5 Hz, 2H, H4), 2.86 (s, 3H, SO_2CH_3), 2.43 (t, J = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 2.10 (tt, J = 7.5, 7.5 Hz, 2H, H6), 1.63 (qt, J = 7.2, 7.2 Hz, 2H, $CH_2CH_2CH_3$), and 1.06 (t, J = 7.3 Hz, 3H, $CH_2CH_2CH_3$).

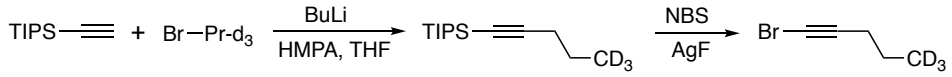
^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 144.7, 136.2, 134.1, 117.8, 115.6, 97.9, 76.4, 54.4, 53.9, 34.7, 33.2, 32.3, 25.3, 22.4, 21.7, and 13.6.

IR (neat) 2957, 2931, 2870, 1456, 1356, 1320, 1144, 1086, 966, 825, and 754.

HRMS (ESI-Orbitrap): Calcd for $[(C_{17}H_{22}NO_2S)^+]$ $[(M+H)^+]$ 304.1366; found: 304.1365.

m.p. 167–170 °C.

1-Bromopent-1-yne-5,5,5-*d*$_3$ (S18)



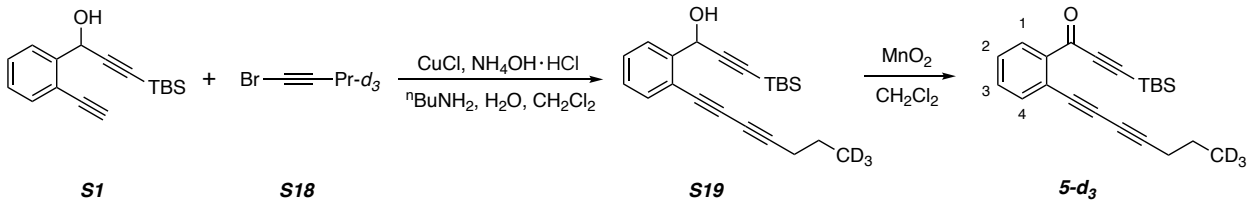
S18

S18 was synthesized according to the reported procedure for synthesis of an analog.[12] *n*-BuLi (0.88 mL, 2.5 M in hexane, 2.2 mmol) was dropwise added to the solution of (triisopropylsilyl)acetylene (0.45 mL, 2 mmol) in dry THF (6 mL) at -78 °C. The resulting mixture was warmed to 0 °C for 10 minutes and then recooled to -78 °C before HMPA (0.38 mL,

2.2 mmol) was added. After 30 minutes, 1-bromopropane-3,3,3-d_3 (0.2 mL, 2.2 mmol) was added to the solution. The reaction mixture was allowed to warm to room temperature and was stirred overnight. Upon completion, the reaction mixture was washed with water and then brine. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated to afford a crude colorless oil (408 mg, 90%).

To a solution of triisopropyl(pent-1-yn-1-yl-5,5,5-d_3)silane (408 mg, 1.8 mmol) in dry MeCN (15 mL) was added *N*-bromosuccinimide (392 mg, 2.2 mmol) and AgF (457 mg, 3.6 mmol) in the dark. The reaction mixture was stirred at room temperature for 3 h and then filtered through a pad of Celite. The filtrate was diluted with hexanes, washed with brine, dried with $MgSO_4$, and filtered. The resulting solution of bromoalkyne **S18** was used directly in the next step after determining the concentration of the deuterated bromopentyne using butylamine as internal standard (214 mg, 79%; ^{1}H NMR integration). The structure was verified by GC-MS.

3-(*tert*-Butyldimethylsilyl)-1-(2-(hepta-1,3-diyn-1-yl-7,7,7-d_3)phenyl)prop-2-yn-1-one (5-d_3)

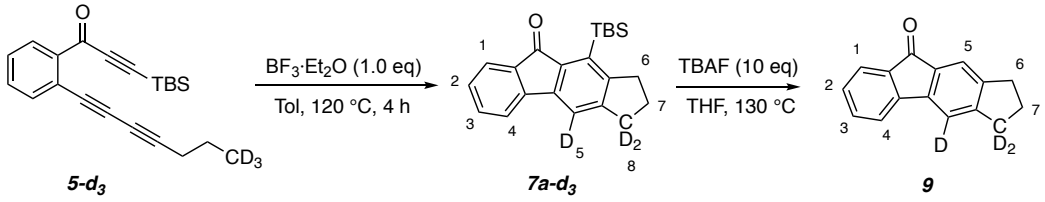


S19 was prepared following general procedure A from diyne **S1** (41 mg, 0.15 mmol) and 1-bromopent-1-yne-5,5,5-d_3 **S18** (30 mg, 0.2 mmol). The crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give **S19** (36 mg, 71%) as a yellow oil.

5-d_3 was prepared following general procedure B from alcohol **S19** (30 mg, 0.09 mmol) to give **5-d_3** (27 mg, 92%) as a yellow oil.

^{1}H NMR (Benzene-d_6, 400 MHz) δ 8.03 (dd, J = 7.3, 1.9 Hz, 1H, H1), 7.29 (dd, J = 7.2, 1.8 Hz, 1H, H4), 6.78 (ddd, J = 7.5, 7.5, 1.7 Hz, 1H, H3), 6.74 (ddd, J = 7.4, 7.4, 1.7 Hz, 1H, H2), 1.90 (t, J = 7.0 Hz, 2H, CH_2CH$_2$CD$_3$), 1.20 (t, J = 7.2 Hz, 3H, CH$_2$CH_2CD$_3$), 0.93 [s, 9H, SiC(CH$_3$)$_3$], and 0.08 [s, 6H, Si(CH$_3$)$_2$].

2,3-Dihydrocyclopenta[b]fluoren-9(*1H*)-one-3,3,4-d_3 (9)



The fluorenone **7a-d_3** was prepared following general procedure C from triyne **5-d_3** (33 mg, 0.1 mmol) at 120 °C for 4 h. The crude material was purified by MPLC (hexanes:EtOAc 80:1) to give **7a-d_3** (25 mg, 76%) as a yellow solid.

^{1}H NMR (Benzene-d_6, 400 MHz) δ 7.57 (d, J = 7.3 Hz, 1H, H1), 7.08 (d, J = 7.4 Hz, 1H, H4), 7.04 (s, ca. 0.11H, H5), 7.02 (ddd, J = 7.4, 7.4, 1.0 Hz, 1H, H3), 6.81 (ddd, J = 7.4, 7.4, 0.9 Hz, 1H, H2), 2.84 (t, J = 7.3 Hz, 2H, H6), 1.72 (t, J = 7.3 Hz, 2H, H7), 1.16 [s, 9H, $SiC(CH_3)_3$], and 0.57 [s, 6H, $Si(CH_3)_2$].

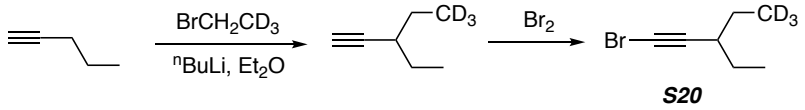
Fluorenone **7a-*d*$_3$** (6 mg, 0.017 mmol) was dissolved in THF (0.05 mL). Tetrabutylammonium fluoride (0.17 mL, 1 M in THF, 0.17 mmol) was added. The mixture was heated overnight at 130 ^{o}C in a sealed culture tube. The mixture was cooled and water (0.5 mL) was added. This mixture was extracted with EtOAc and the extract was concentrated under reduced pressure. The residue was purified by MPLC to afford **9** (2 mg, 50 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.3 Hz, 1H, H1), 7.49 (s, 1H, H5), 7.46–7.43 (m, 2H, H4 and H3), 7.36 (s, ca. 0.05H), 7.26–7.22 (nfom, 1H, H2), 2.94 (t, J = 7 Hz, ca. 0.15H, H8*), 2.90 (t, J = 7.5 Hz, 2H, H6), and 2.12 (t, J = 7.3 Hz, 2H, H7).

*The small proportion of protons observed at this position are likely introduced during the treatment with TBAF at 130 °C; notice that no intensity for the H8 protons was observed in the precursor fluorenone **7a-*d*$_3$**.

HRMS (ESI-Orbitrap): Calcd for $(C_{16}H_{10}D_3O)^+$ [$(M+H)^+$] 224.1149; found: 224.1149.

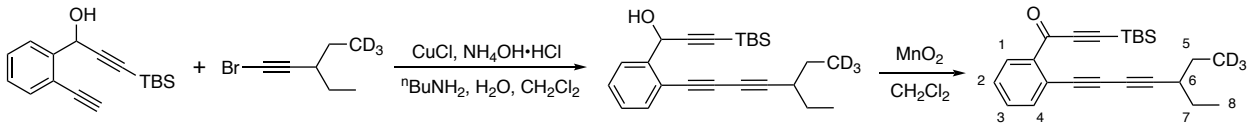
1-Bromo-3-ethylpent-1-yne-5,5,5-*d*$_3$ (S20)



S20

S20 was synthesized by the same procedure as was used for the synthesis of 1-bromo-3-ethylpent-1-yne except that 1-bromoethane was replaced by 1-bromoethane-2,2,2-d_3 (99%-d_3, per manufacturer).

3-(*tert*-Butyldimethylsilyl)-1-(2-(5-ethylhepta-1,3-diyn-1-yl-7,7,7-d3)phenyl)prop-2-yn-1-one (12)



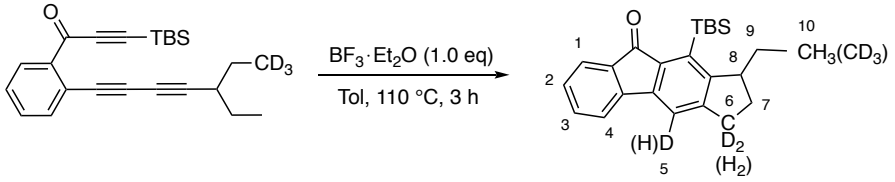
S1 ***S20*** ***S21*** ***12***

Alcohol **S21** was prepared following general procedure A from diyne **S1** (27 mg, 0.1 mmol) and 1-bromo-3-ethylpent-1-yne-5,5,5-d_3 **S20** (27 mg, 0.15 mmol). The crude material was purified by flash chromatography (hexanes:EtOAc 9:1) to give **S21** (15 mg, 40%) as a yellow oil.

Ketone **12** was prepared following general procedure B from alcohol **S21** (12 mg, 0.03 mmol) to give **12** (10 mg, 85%) as a yellow oil.

^{1}H NMR (Benzene-d_6, 400 MHz) δ 8.02 (dd, J = 6.9, 2.2 Hz, 1H, H1), 7.29 (dd, J = 7.3, 1.6 Hz, 1H, H4), 6.78–6.71 (m, 2H, H3 and H2), 2.08 (tt, J = 8.5, 5.4 Hz, 1H, H6), 1.35–1.18 (m, 4H, H5 and H7), 0.93 [s, 9H, $SiC(CH_3)_3$], 0.88 (t, J = 7.4 Hz, 3H, H8), and 0.08 [s, 6H, $Si(CH_3)_2$].

10-(*tert*-Butyldimethylsilyl)-1-ethyl-2,3-dihydrocyclopenta[*b*]fluoren-9(1*H*)-one (13)



12 ***13***

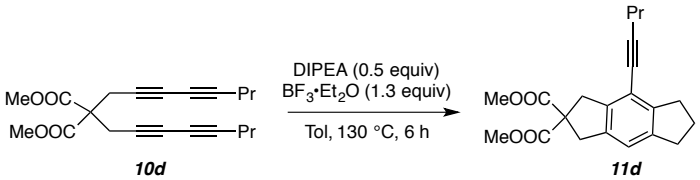
Fluorenone **13** was prepared following general procedure C from triyne **12** (8 mg, 0.02 mmol) at 110 °C for 3 h. The crude material was purified by MPLC (hexanes:EtOAc 80:1) to give **13** (4.6 mg, 58%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54 (d, J = 7.4 Hz, 1H, H1), 7.42–7.40 (m, 2H, H4 and H3), 7.39 (s, 0.39H, H5), 7.24–7.19 (nfom, 1H, H2), 3.25–3.22 (nfom, 1H, H8), 2.98 (ddd, J = 17.1, 9.1, 8.0 Hz, 0.38H, H6a), 2.78 (nfod, J = 17.0 Hz, 0.36H, H6b), 2.06–2.00 (m, 2H, H7), 1.50–1.43 (m, 1H, H9a), 1.34–1.26 (m, 1H, H9b), 1.01–0.97 [m, ca. 10.6H, CH_3/CD_3 and $SiC(CH_3)_3$], 0.51 (s, 3H, $SiCH_3$), and 0.42 (s, 3H, $SiCH_3$).

^{1}H NMR (Benzene-d_6, 500 MHz) δ 7.56 (d, J = 7.3 Hz, 1H, H1), 7.06 (dd, J = 7.3, 1.0 Hz, 1H, H4), 7.02 [s, ca. (because of partial overlap) 0.44H, H5], 7.01 (ddd, J = 7.4, 7.4, 1.1 Hz, 1H, H3), 6.80 (ddd, J = 7.3, 7.3, 1.1 Hz, 1H, H2), 3.25–3.21 (nfom, 1H, H8), 2.71 (dddd, J = 16.6, 11.1, 8.0, 1.2 Hz, 0.34H, H6a), 2.78 (dd, J = 16.6, 8.7 Hz, 0.37H, H6b), 1.86–1.75 (m, 2H, H7), 1.55–1.46 (m, 1H, H9a), 1.29–1.22 (m, 1H, H9b), 1.19 [s, 9H, $SiC(CH_3)_3$], 0.92 (t, J = 7.3 Hz, ca. 1.85H, CH_3/CD_3), 0.59 (s, 3H, $SiCH_3$), and 0.40 (s, 3H, $SiCH_3$).

HRMS (APCI-Orbitrap): Calcd for [$(C_{23}H_{24}D_3OSi)^+$] [$(M+H–CH_4)^+$ (from the TBS group] 350.2014; found: 350.2014.

Control experiment in the presence of diisopropylethylamine (DIPEA)



10d ***11d***

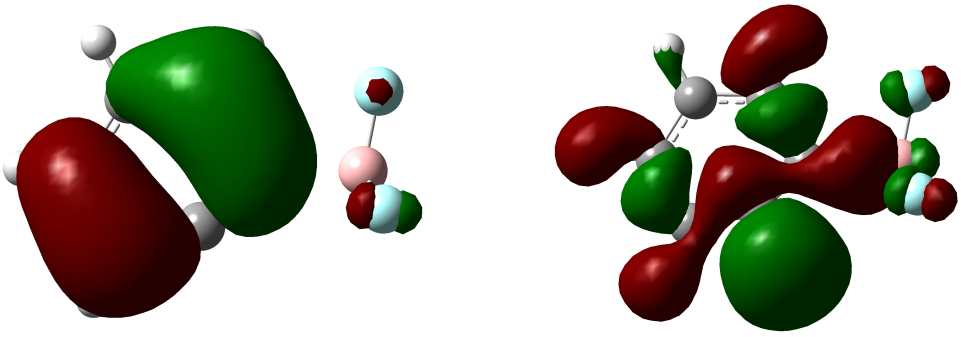
BF_3•OEt_2 (3.2 μL, 0.026 mmol) and DIPEA (2 μL, 0.010 mmol) were sequentially added to a solution of triyne **10d** (7 mg, 0.020 mmol) in toluene (ca. 0.05 M) in a culture tube fitted with an inert, Teflon®-lined cap. The vessel was firmly sealed and heated at in an oil bath that had been pre-equilibrated to 130 °C. After 6 h, the mixture was partitioned between aq. $NaHCO_3$ and EtOAc. The organic layer was concentrated and the crude product mixture was transferred to a NMR tube. The yield of **11d** was measured to be ca. 26%, using mesitylene as an internal standard.

III. Computational details

The DFT calculations were performed using Gaussian 09.[13] The geometry of each structure (including the transition structures, **1–4**, **BF_3**, **CH_4**, **$TS_{2\rightarrow3}$**, and **$TS_{3\rightarrow4}$**) was optimized at the M06-2X[14]/6-311+G(d,p) level of theory with SMD[15](toluene) solvation model. The nature of the optimized structure was verified by frequency calculation (298K, at the same level of theory). For improving the computational efficiency, the same protocol was used for structures **S22**–**S25** (Figure S1, below) using M06-2X/6-31+G(d,p) level of theory with SMD(toluene) solvation model.

Listed on pages **S35–S48** are: the zero-point correction, thermal correction to the Gibbs energy, the sum of the electronic and thermal free energies, and the Cartesian coordinates for the optimized geometries (as well as the calculated HOMO/LUMO orbitals of **2**). For transition structures, the imaginary frequency values are given. Three dimensional views of all the transition structures were prepared using CYLview.[16]

HOMO and LUMO orbitals of the BF_3-benzyne complex 2:



HOMO of **2** LUMO of **2**

Computational data for Figure 1b:

1

Zero-point correction= 0.075662 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.048326
Sum of electronic and thermal Free Energies= -230.826683

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000004	-1.230582	0.619738
2	6	0	0.000004	-1.230582	-0.619738
3	6	0	0.000004	-0.132476	-1.458893

4	6	0	-0.000006	1.051863	-0.702115
5	6	0	-0.000006	1.051863	0.702115
6	6	0	0.000004	-0.132476	1.458893
7	1	0	0.000002	-0.134761	-2.540176
8	1	0	-0.000014	2.001931	-1.225261
9	1	0	-0.000014	2.001931	1.225261
10	1	0	0.000002	-0.134761	2.540176

BF_3

Zero-point correction= 0.012191 (Hartree/Particle)
Thermal correction to Gibbs Energy= -0.013322
Sum of electronic and thermal Free Energies= -324.574263

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.000000	0.000000	-0.000451
2	9	0	0.000000	0.000000	1.313150
3	9	0	0.000000	-1.138125	-0.656450
4	9	0	0.000000	1.138125	-0.656450

CH_4

Zero-point correction= 0.045139 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.027823
Sum of electronic and thermal Free Energies= -40.468677

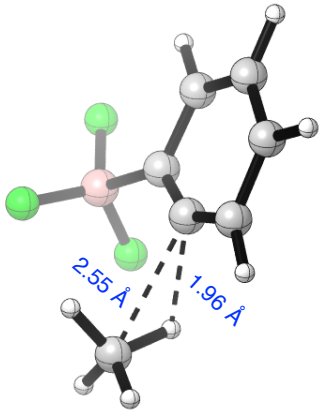
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	1	0	0.629496	0.629496	0.629496
3	1	0	-0.629496	-0.629496	0.629496
4	1	0	-0.629496	0.629496	-0.629496
5	1	0	0.629496	-0.629496	-0.629496

2

Zero-point correction= 0.088418 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.053231
Sum of electronic and thermal Free Energies= -555.395611

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.058030	-0.101855	-0.000001
2	6	0	-0.973169	-0.991640	-0.000005
3	6	0	-2.285728	-1.281092	-0.000011
4	6	0	-2.930991	-0.025838	0.000006
5	6	0	-2.185741	1.156745	-0.000003
6	6	0	-0.796297	1.137713	-0.000010
7	1	0	-2.782316	-2.238162	-0.000010
8	1	0	-4.014373	-0.014252	0.000015
9	1	0	-2.700703	2.109071	0.000002
10	1	0	-0.193102	2.039646	-0.000010
11	5	0	1.766002	-0.052675	0.000004
12	9	0	2.108007	-0.699883	-1.150961
13	9	0	2.032905	1.288972	0.000003
14	9	0	2.108001	-0.699880	1.150973

$TS_{2\rightarrow3}$



One imaginary frequency: -288.80 cm^{-1}
Zero-point correction= 0.134698 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.095846
Sum of electronic and thermal Free Energies= -595.855737

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	0.099496	-0.362917	0.028817
2	6	0	2.184426	1.063321	0.079832
3	6	0	2.965094	-0.106272	0.002968
4	6	0	2.357819	-1.361443	-0.056217
5	6	0	0.974894	-1.493932	-0.043916
6	1	0	2.573119	2.068788	0.133096
7	1	0	4.042778	0.005548	-0.004936
8	1	0	2.975057	-2.249331	-0.113060
9	1	0	0.489989	-2.463606	-0.091516
10	5	0	-1.596561	-0.473784	0.013791
11	9	0	-2.029142	0.093935	-1.178802
12	9	0	-1.909080	-1.821252	0.093070
13	9	0	-2.063834	0.238049	1.111875
14	6	0	0.898986	0.665654	0.080940
15	6	0	-0.490335	2.797836	-0.087099
16	1	0	0.112169	3.706128	-0.077255
17	1	0	-0.431236	2.317079	-1.063110
18	1	0	-0.164141	2.161860	0.757329
19	1	0	-1.538709	3.012391	0.123249

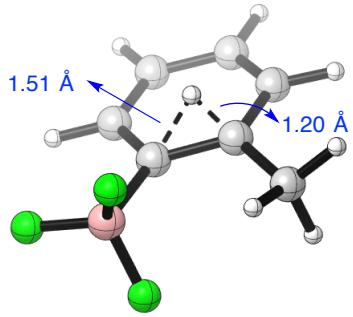
3

Zero-point correction= 0.140839 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.104341
Sum of electronic and thermal Free Energies= -595.910682

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.016150	-0.296355	-0.034948
2	6	0	0.792680	0.929590	-0.274458
3	6	0	2.257424	0.825563	-0.224525
4	6	0	2.878519	-0.366928	-0.035025
5	6	0	2.083495	-1.524337	0.155488
6	6	0	0.695735	-1.492626	0.147521
7	1	0	2.831577	1.736401	-0.367230
8	1	0	3.957914	-0.445876	-0.016947
9	1	0	2.586767	-2.474556	0.310060
10	1	0	0.132415	-2.406742	0.293540

11	5	0	-1.627358	-0.233214	-0.040056
12	9	0	-2.040265	0.608745	-1.089676
13	9	0	-2.142434	-1.522683	-0.214538
14	9	0	-2.039563	0.294736	1.195886
15	1	0	0.580031	1.057150	-1.368446
16	6	0	0.233423	2.211450	0.382216
17	1	0	0.787055	3.080235	0.023861
18	1	0	-0.819872	2.328978	0.137269
19	1	0	0.336703	2.145159	1.465511

$TS_{3\rightarrow4}$



One imaginary frequency: -453.34 cm^{-1}
Zero-point correction= 0.138896 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.103467
Sum of electronic and thermal Free Energies= -595.908959

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.035751	-0.283192	0.028761
2	6	0	0.793247	0.949812	-0.071962
3	6	0	2.237125	0.884410	-0.042151
4	6	0	2.881671	-0.316489	-0.001442
5	6	0	2.131947	-1.515133	0.054137
6	6	0	0.757516	-1.497787	0.061160
7	1	0	2.792499	1.815817	-0.062974
8	1	0	3.964020	-0.358229	0.002396
9	1	0	2.657741	-2.463299	0.087007
10	1	0	0.191003	-2.419833	0.112187
11	5	0	-1.618565	-0.261879	-0.001938
12	9	0	-2.025910	0.389165	-1.182801
13	9	0	-2.083734	-1.579295	0.016961

14	9	0	-2.077615	0.439920	1.120241
15	1	0	0.525150	0.521424	-1.157428
16	6	0	0.123362	2.292848	0.119708
17	1	0	0.677846	3.074374	-0.401264
18	1	0	-0.904595	2.279178	-0.235528
19	1	0	0.110774	2.525034	1.186422

4

Zero-point correction= 0.128455 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.097996
Sum of electronic and thermal Free Energies= -271.416204

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.192848	1.200418	-0.007854
2	6	0	0.910148	0.003098	-0.010510
3	6	0	0.196716	-1.197911	-0.007990
4	6	0	-1.193945	-1.203392	0.001960
5	6	0	-1.897662	-0.002290	0.007291
6	6	0	-1.199084	1.200462	0.001967
7	1	0	0.739679	-2.137941	-0.015539
8	1	0	-1.729343	-2.146162	0.001898
9	1	0	-2.981409	-0.004505	0.011979
10	1	0	-1.737724	2.141374	0.001842
11	6	0	2.416211	0.001000	0.008252
12	1	0	2.817368	-0.815345	-0.595611
13	1	0	2.817697	0.940484	-0.375431
14	1	0	2.790669	-0.128830	1.027931
15	1	0	0.731673	2.142619	-0.015765

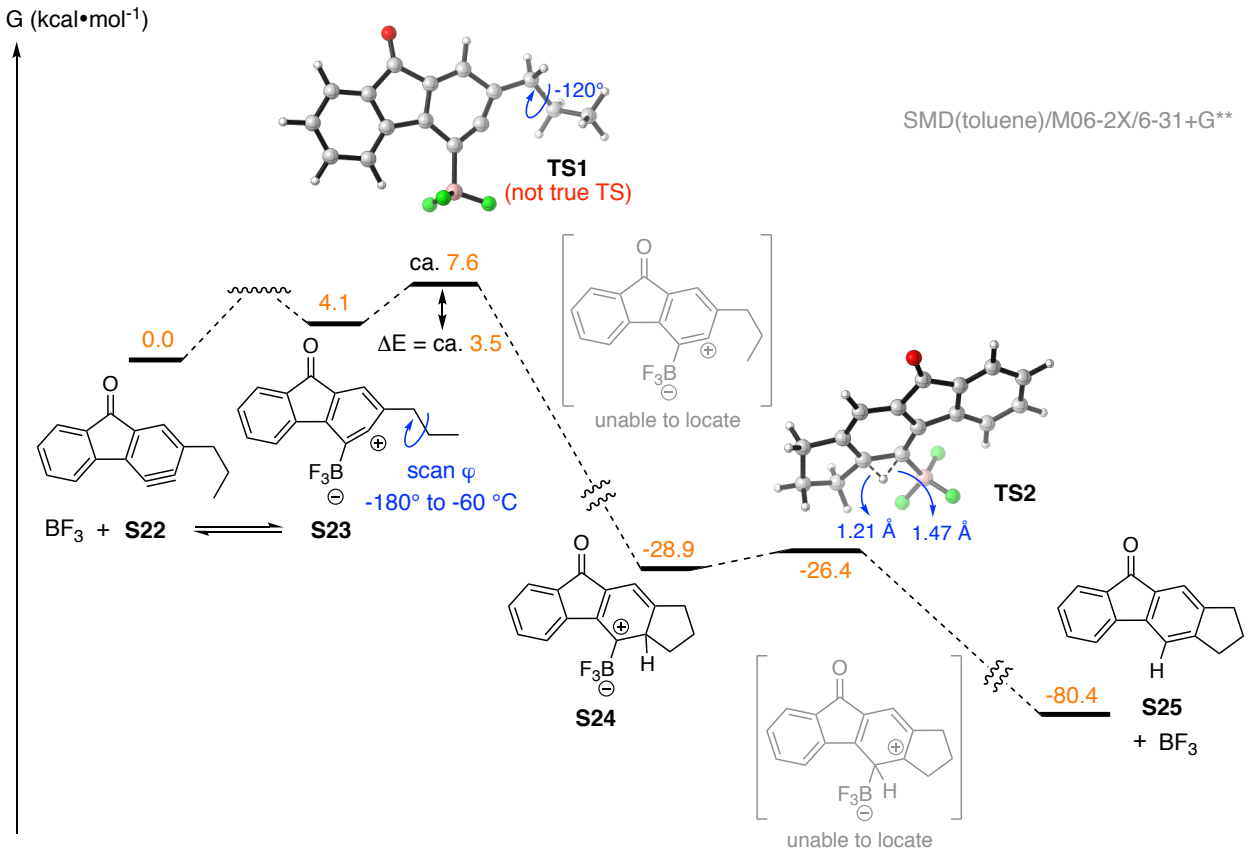


Figure S1. Computed potential energy surface for the intramolecular C–H insertion reaction of **S22** (to give **S25**).

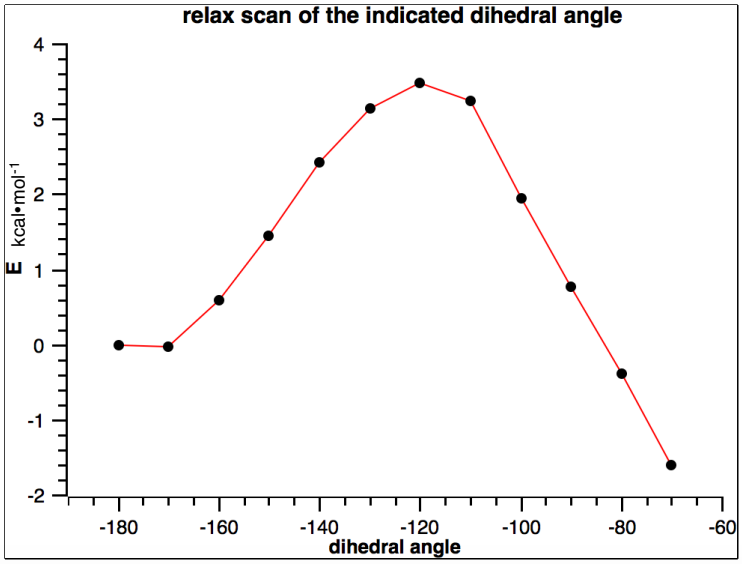


Figure S2. Relaxed scan of the indicated dihedral angle in **S23**. Geometry optimization of the intermediate having the dihedral angle = -60º directly collapsed to the energy minimum structure **S24**.

Detailed computational data for the species in Figure S1:

S22

Zero-point correction= 0.230691 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.188187
Sum of electronic and thermal Free Energies= -691.612348

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.855373	-1.819348	0.000023
2	6	0	1.988186	-0.738648	0.000022
3	6	0	2.484054	0.575833	0.000002
4	6	0	3.842252	0.839031	-0.000047
5	6	0	4.722072	-0.250743	-0.000076
6	6	0	4.232237	-1.557145	-0.000041
7	6	0	1.331141	1.537821	0.000086
8	6	0	0.092505	0.686242	0.000073
9	6	0	0.513026	-0.669780	0.000009
10	6	0	-0.566935	-1.528972	0.000083
11	6	0	-1.753026	-1.132147	0.000027
12	6	0	-2.306129	0.137078	-0.000080
13	6	0	-1.242626	1.081036	0.000172
14	8	0	1.391971	2.747814	-0.000028
15	6	0	-3.760484	0.515674	-0.000158
16	6	0	-4.693802	-0.693142	0.000033
17	6	0	-6.162993	-0.284458	-0.000026
18	1	0	2.480686	-2.838505	0.000027
19	1	0	4.206980	1.862000	-0.000057
20	1	0	5.793658	-0.079206	-0.000116
21	1	0	4.931628	-2.387746	-0.000067
22	1	0	-3.964509	1.141867	-0.878535
23	1	0	-3.964524	1.142176	0.877991
24	1	0	-4.476208	-1.311278	0.879791
25	1	0	-4.476216	-1.311541	-0.879543
26	1	0	-6.818616	-1.159769	0.000108
27	1	0	-6.405248	0.314072	0.884670
28	1	0	-6.405253	0.313803	-0.884902
29	1	0	-1.487254	2.141634	0.000245

BF_3

Zero-point correction= 0.012310 (Hartree/Particle)
Thermal correction to Gibbs Energy= -0.012173
Sum of electronic and thermal Free Energies= -324.483368

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.000000	0.000000	0.000000
2	9	0	0.000000	1.317067	0.000000
3	9	0	-1.140613	-0.658533	0.000000
4	9	0	1.140613	-0.658533	0.000000

S23

Zero-point correction= 0.243843 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.195007
Sum of electronic and thermal Free Energies= -1016.089194

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.776663	1.163068	0.000584
2	6	0	-1.992361	0.020430	0.000211
3	6	0	-2.584383	-1.255418	0.000291
4	6	0	-3.958748	-1.419057	0.000728
5	6	0	-4.754565	-0.267759	0.001116
6	6	0	-4.168175	0.997905	0.001049
7	6	0	-1.515650	-2.299448	-0.000171
8	6	0	-0.219257	-1.537547	-0.000582
9	6	0	-0.517410	-0.162022	-0.000407
10	6	0	0.522772	0.818718	-0.000793
11	6	0	1.587940	0.068378	-0.001255
12	6	0	2.191058	-1.132173	-0.001336
13	6	0	1.078348	-2.027491	-0.000971
14	8	0	-1.643314	-3.502725	-0.000317
15	6	0	3.649974	-1.491923	-0.001804
16	6	0	4.549939	-0.254335	0.002559
17	6	0	6.026748	-0.630295	0.002033
18	1	0	-2.336211	2.153639	0.000524
19	1	0	-4.396867	-2.412816	0.000772

20	1	0	-5.835876	-0.359022	0.001461
21	1	0	-4.801851	1.879190	0.001346
22	1	0	3.849401	-2.108793	-0.885589
23	1	0	3.848514	-2.114590	0.878079
24	1	0	4.318533	0.353062	0.886491
25	1	0	4.319356	0.358650	-0.877754
26	1	0	6.657239	0.262477	0.005115
27	1	0	6.282346	-1.223432	0.886148
28	1	0	6.283170	-1.217892	-0.885531
29	5	0	0.371886	2.553133	-0.000523
30	9	0	-0.324988	2.874050	1.148676
31	9	0	-0.325527	2.874414	-1.149301
32	9	0	1.660733	3.055378	-0.000752
33	1	0	1.289955	-3.095110	-0.001020

TS1 [not a true TS (see Figure S2)]

SCF Done: E(RM062X) = -1016.27864595 a.u.

C	3.1673277	1.5118081	0.0067472
C	2.4297707	0.3384551	0.0029082
C	3.0735827	-0.9122049	0.0054922
C	4.4533597	-1.0198669	0.0111222
C	5.2017107	0.1626771	0.0144722
C	4.5645737	1.4033701	0.0126212
C	2.0492807	-1.9998199	-0.0005888
C	0.7229107	-1.2910419	-0.0049178
C	0.9639997	0.0945621	-0.0060098
C	-0.1200573	1.0271561	-0.0196168
C	-1.1539313	0.2351221	-0.0225378
C	-1.7064643	-0.9907199	-0.0285618
C	-0.5535753	-1.8333629	-0.0166508
O	2.2266097	-3.1967409	-0.0022768
C	-3.1402323	-1.4385189	-0.0249938
C	-4.1301223	-0.3807209	-0.5669728
C	-5.1756733	0.0213921	0.4688762
H	2.6866287	2.4834231	0.0046462
H	4.9321797	-1.9947039	0.0123392
H	6.2859137	0.1155011	0.0184412
H	5.1621987	2.3095421	0.0152162
H	-3.3957833	-1.6938419	1.0107882

H	-3.1900743	-2.3704729	-0.5943428
H	-4.6258683	-0.7753879	-1.4582998
H	-3.5858833	0.5122791	-0.8974978
H	-5.8650743	0.7654841	0.0609142
H	-5.7664473	-0.8441079	0.7868472
H	-4.7038243	0.4535611	1.3576532
B	-0.0374583	2.7674211	-0.0282098
F	0.6676107	3.1067021	-1.1671538
F	0.6274497	3.1209971	1.1300272
F	-1.3440153	3.2208761	-0.0548998
H	-0.7206223	-2.9088169	-0.0255808

S24

Zero-point correction= 0.247163 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.202235
Sum of electronic and thermal Free Energies= -1016.141755

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.401518	1.383313	0.174947
2	6	0	1.758245	0.159982	0.042714
3	6	0	2.514898	-1.024988	-0.001168
4	6	0	3.902216	-1.023795	0.070233
5	6	0	4.545733	0.206966	0.193964
6	6	0	3.799228	1.387450	0.248201
7	6	0	1.602083	-2.181069	-0.113252
8	6	0	0.200567	-1.587028	-0.126250
9	6	0	0.304505	-0.180245	-0.044613
10	6	0	-0.826722	0.619188	-0.066436
11	6	0	-2.111117	-0.108970	-0.164104
12	6	0	-2.142636	-1.581265	-0.099216
13	6	0	-0.981703	-2.320130	-0.163470
14	8	0	1.846931	-3.364728	-0.173158
15	6	0	-3.537082	-2.059650	0.150439
16	6	0	-4.389898	-0.776897	0.156215
17	6	0	-3.408786	0.329889	0.565661
18	1	0	1.842925	2.309986	0.220624
19	1	0	4.457557	-1.956143	0.030176
20	1	0	5.628449	0.250819	0.251785
21	1	0	4.314793	2.337498	0.351532

22	1	0	-3.539856	-2.530203	1.144234
23	1	0	-3.854475	-2.827881	-0.561578
24	1	0	-5.247896	-0.851511	0.826216
25	1	0	-4.766353	-0.573669	-0.852596
26	1	0	-3.719142	1.330762	0.274999
27	1	0	-3.222063	0.319261	1.644970
28	1	0	-2.336646	0.074525	-1.250843
29	5	0	-0.797684	2.271698	-0.149657
30	9	0	0.051427	2.656018	-1.200949
31	9	0	-0.312526	2.767739	1.072465
32	9	0	-2.090755	2.756871	-0.396860
33	1	0	-0.963933	-3.406267	-0.161063

TS2

One imaginary frequency: -570.40 cm^{-1}
Zero-point correction= 0.244966 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.201086
Sum of electronic and thermal Free Energies= -1016.137810

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.404764	1.384109	-0.015480
2	6	0	-1.759801	0.155460	0.000008
3	6	0	-2.519953	-1.029029	0.009385
4	6	0	-3.904800	-1.023398	0.004880
5	6	0	-4.551828	0.215340	-0.010831
6	6	0	-3.806520	1.394068	-0.021153
7	6	0	-1.600321	-2.193209	0.021692
8	6	0	-0.208428	-1.599542	0.008433
9	6	0	-0.309451	-0.212018	0.002506
10	6	0	0.854378	0.607559	-0.015684
11	6	0	2.109040	-0.130617	0.014036
12	6	0	2.156062	-1.577846	-0.035432
13	6	0	0.994798	-2.312664	-0.012724
14	8	0	-1.858185	-3.375358	0.033163
15	6	0	3.579177	-2.039839	-0.159954
16	6	0	4.397983	-0.799919	0.242578
17	6	0	3.527248	0.398167	-0.170330
18	1	0	-1.850907	2.313308	-0.024716

19	1	0	-4.460459	-1.956331	0.013605
20	1	0	-5.636011	0.261704	-0.015922
21	1	0	-4.321743	2.349733	-0.035332
22	1	0	3.763372	-2.296298	-1.212505
23	1	0	3.790361	-2.931340	0.435846
24	1	0	5.384331	-0.778771	-0.224223
25	1	0	4.539071	-0.791058	1.328941
26	1	0	3.727605	1.304946	0.395691
27	1	0	3.652651	0.637616	-1.232974
28	1	0	1.673102	0.145616	1.110083
29	5	0	0.787664	2.273285	0.001660
30	9	0	0.075397	2.675567	1.142390
31	9	0	0.113876	2.657532	-1.164807
32	9	0	2.072861	2.817669	0.027959
33	1	0	0.989649	-3.399326	-0.033559

S25

Zero-point correction= 0.235267 (Hartree/Particle)
Thermal correction to Gibbs Energy= 0.196662
Sum of electronic and thermal Free Energies= -691.740431

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.345934	-1.843922	0.006025
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3	6	0	-2.251095	0.572497	-0.014052
4	6	0	-3.630518	0.679186	-0.044834
5	6	0	-4.381298	-0.502661	-0.049705
6	6	0	-3.743338	-1.743182	-0.024638
7	6	0	-1.211773	1.654636	-0.001566
8	6	0	0.103508	0.941322	0.033289
9	6	0	-0.134041	-0.443977	0.041866
10	6	0	0.925182	-1.342164	0.066191
11	6	0	2.218761	-0.812459	0.074545
12	6	0	2.450062	0.571249	0.065385
13	6	0	1.385175	1.472897	0.047390
14	8	0	-1.400889	2.852945	-0.016990
15	6	0	3.934922	0.852306	0.096274
16	6	0	4.546161	-0.490201	-0.355144

17	6	0	3.533427	-1.556762	0.109899
18	1	0	-1.866188	-2.818116	0.025885
19	1	0	-4.109830	1.653914	-0.064840
20	1	0	-5.465412	-0.456035	-0.073475
21	1	0	-4.341233	-2.649740	-0.028482
22	1	0	4.244561	1.095732	1.121615
23	1	0	4.224480	1.693077	-0.540106
24	1	0	5.550450	-0.655945	0.041623
25	1	0	4.607860	-0.507176	-1.448684
26	1	0	3.533244	-2.454708	-0.514387
27	1	0	3.747292	-1.873259	1.139882
28	1	0	0.760344	-2.416834	0.069925
29	1	0	1.541607	2.548789	0.036963

IV. References for Supplementary Information

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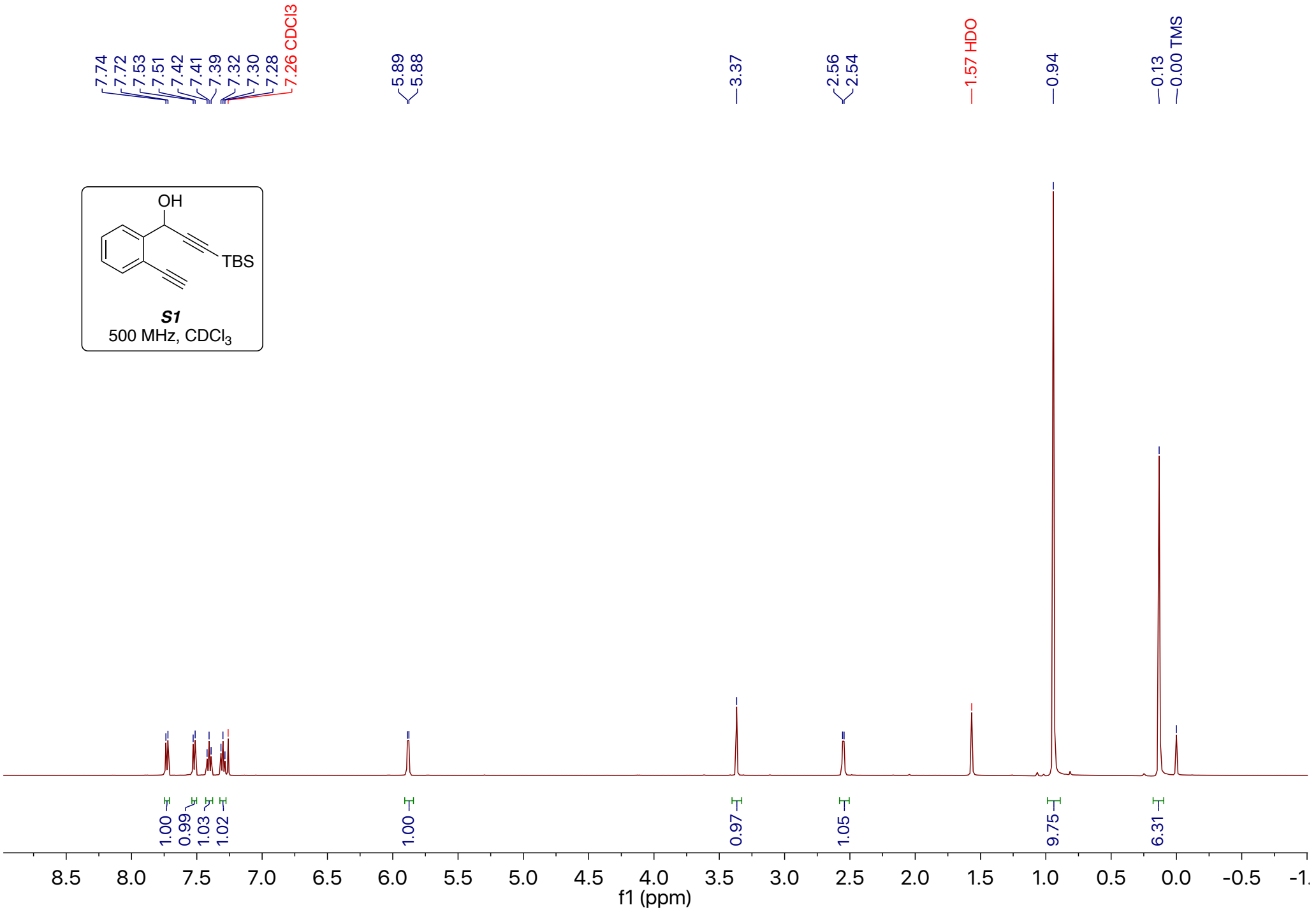
V. Copies of ^{1}H, and ^{13}C NMR spectra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5.88
3.37
2.56
2.54
1.57 HDO
0.94
0.13
0.00 TMS
OH
TBS
S1
500 MHz, CDCl3
1.00
0.99
1.03
1.02
1.00
0.97
1.05
9.75
6.31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
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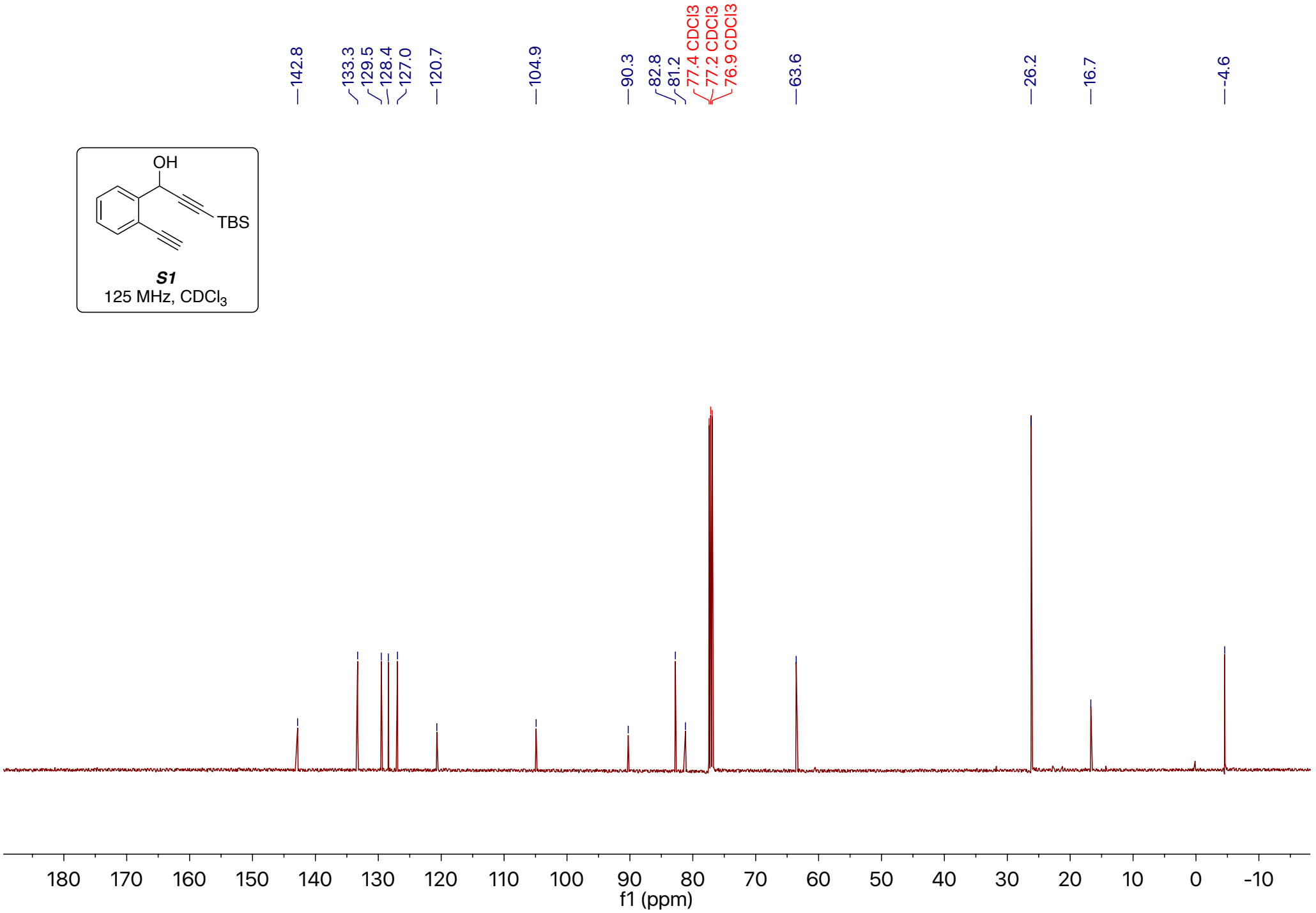
f1 (ppm)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77.2 CDCl3
76.9 CDCl3
63.6
26.2
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OH
TBS
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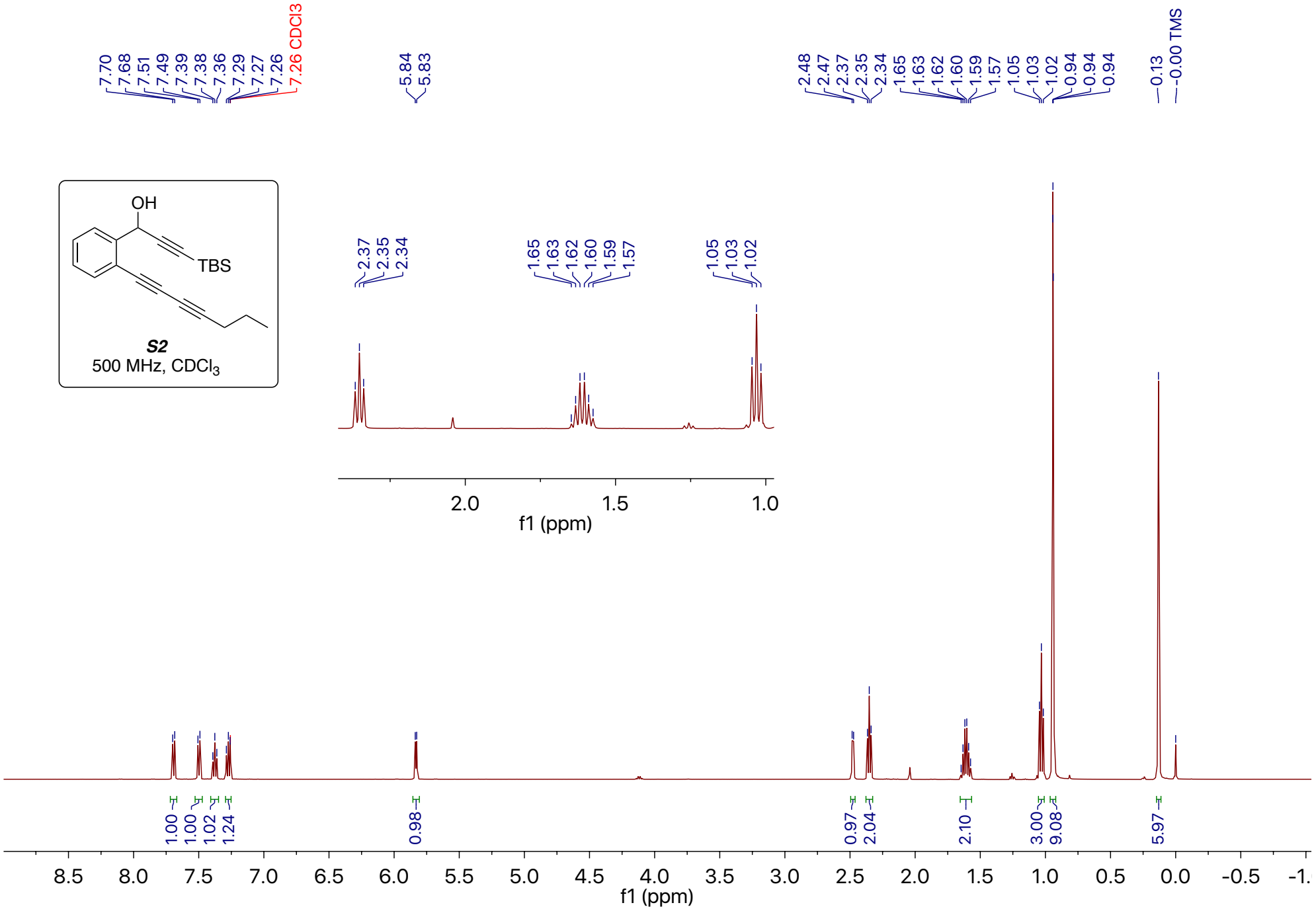
f1 (ppm)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2.35
2.34
1.65
1.63
1.62
1.60
1.59
1.57
1.05
1.03
1.02
0.94
0.94
0.94
0.13
-0.00 TMS
OH
TBS
S2
500 MHz, CDCl3
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2.34
1.65
1.63
1.62
1.60
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1.57
1.05
1.03
1.02
2.0
1.5
1.0
f1 (ppm)
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1.00
1.02
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0.97
2.04
2.10
3.00
9.08
5.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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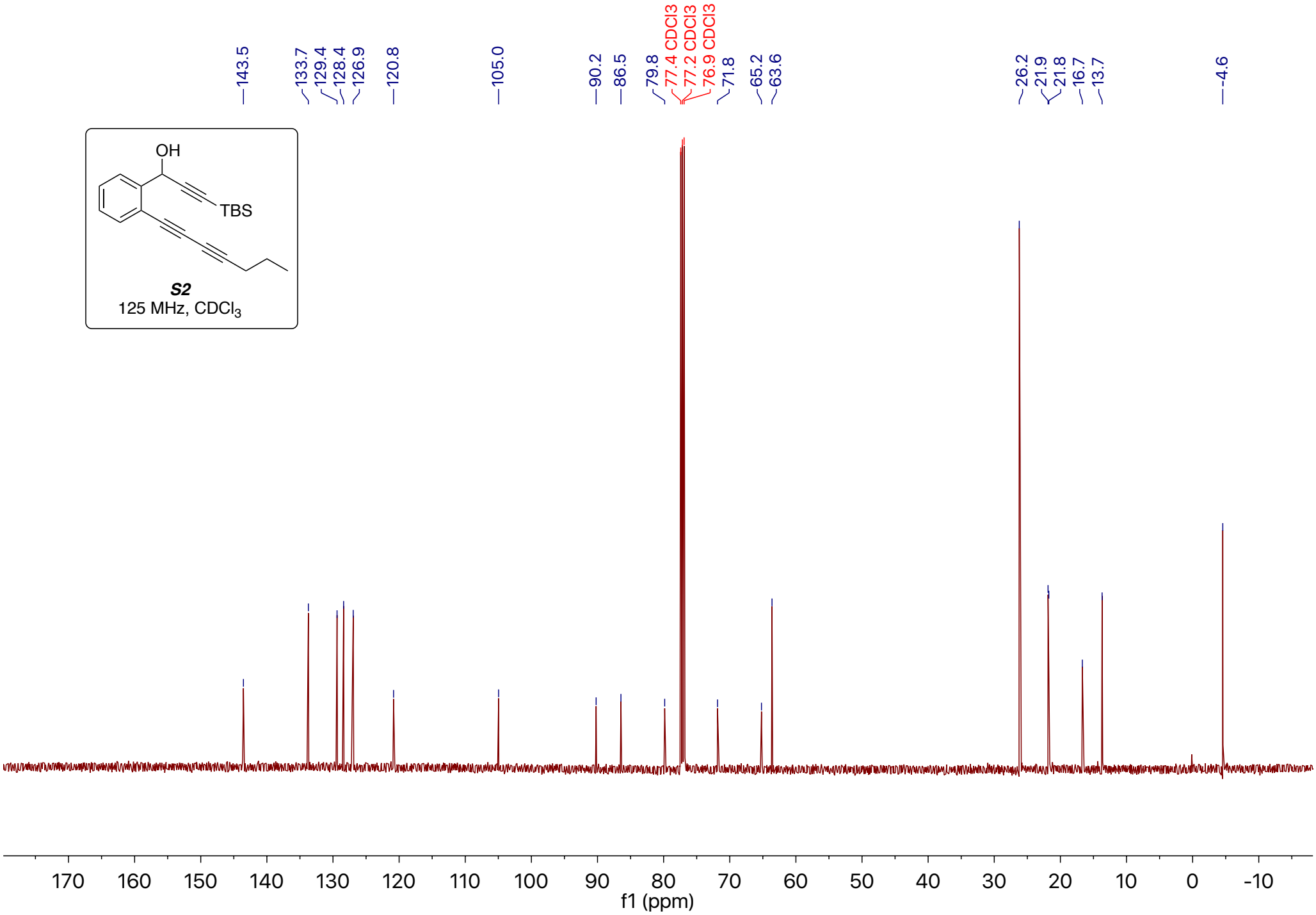
f1 (ppm)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77.2 CDCl3
76.9 CDCl3
71.8
65.2
63.6
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21.9
21.8
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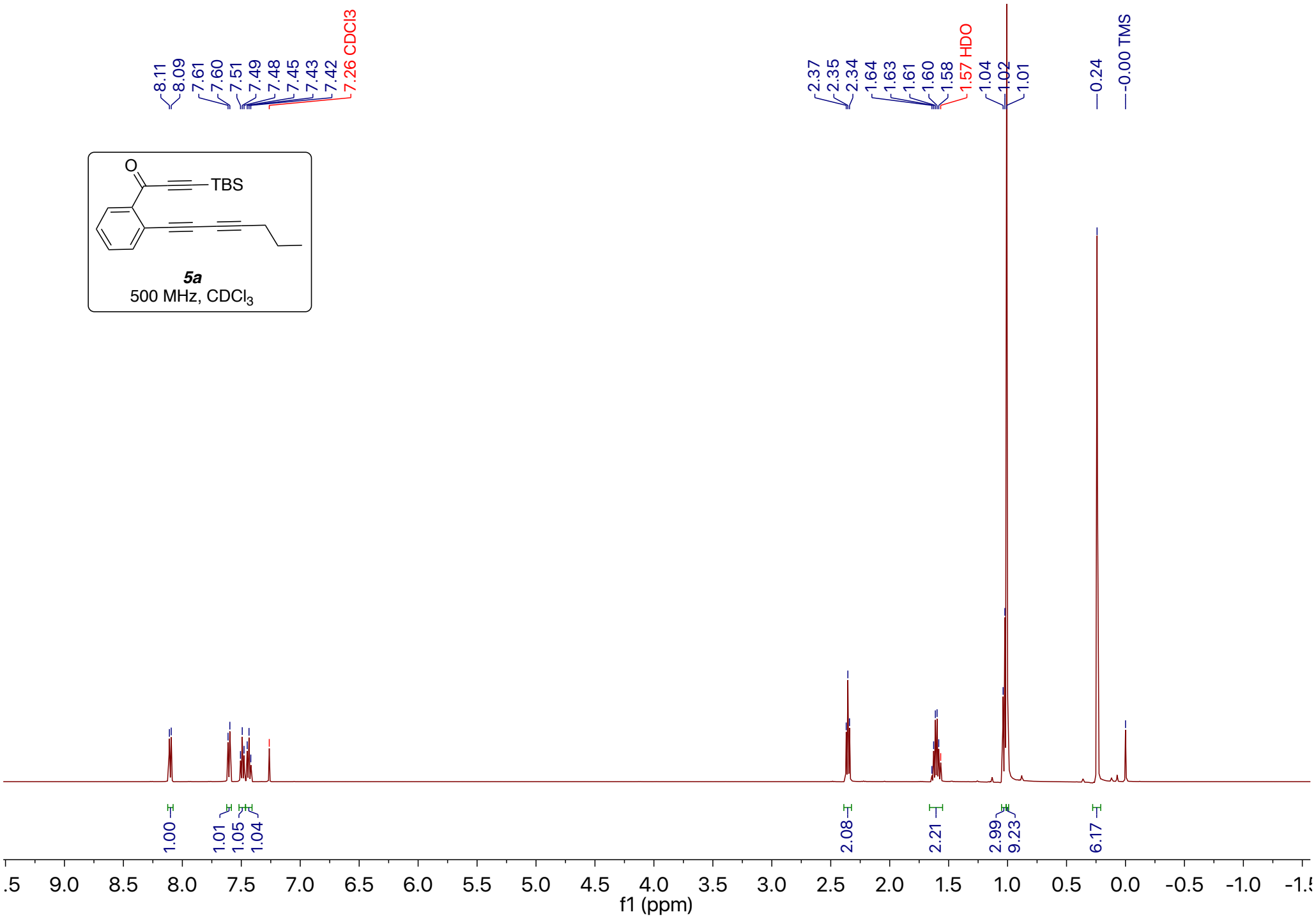
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2.34
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1.58
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1.02
1.01
0.24
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O
TBS
5a
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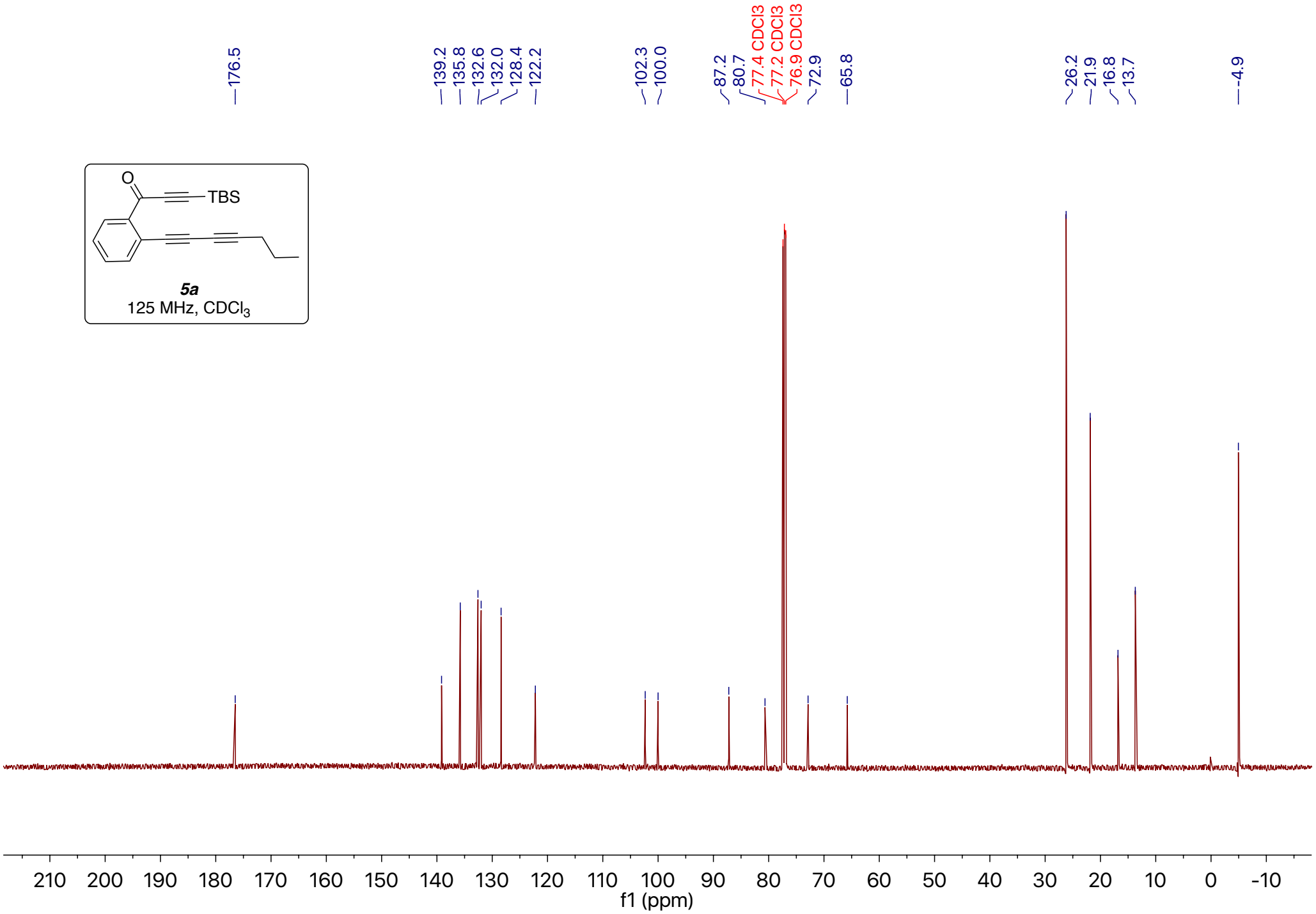
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77.2 CDCl3
76.9 CDCl3
72.9
65.8
26.2
21.9
16.8
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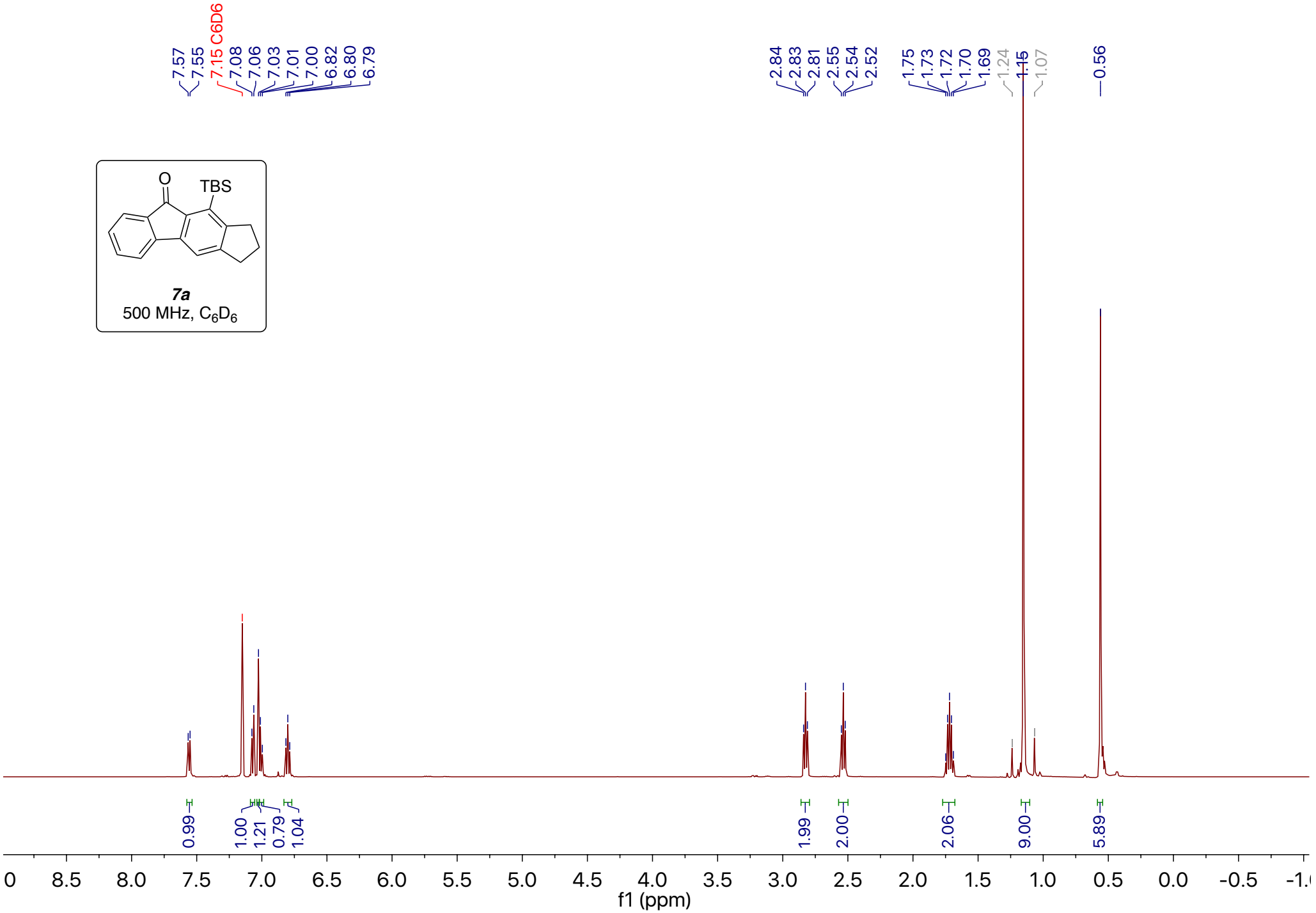
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2.54
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1.73
1.72
1.70
1.69
1.24
1.15
1.07
0.56
O
TBS
7a
500 MHz, C6D6
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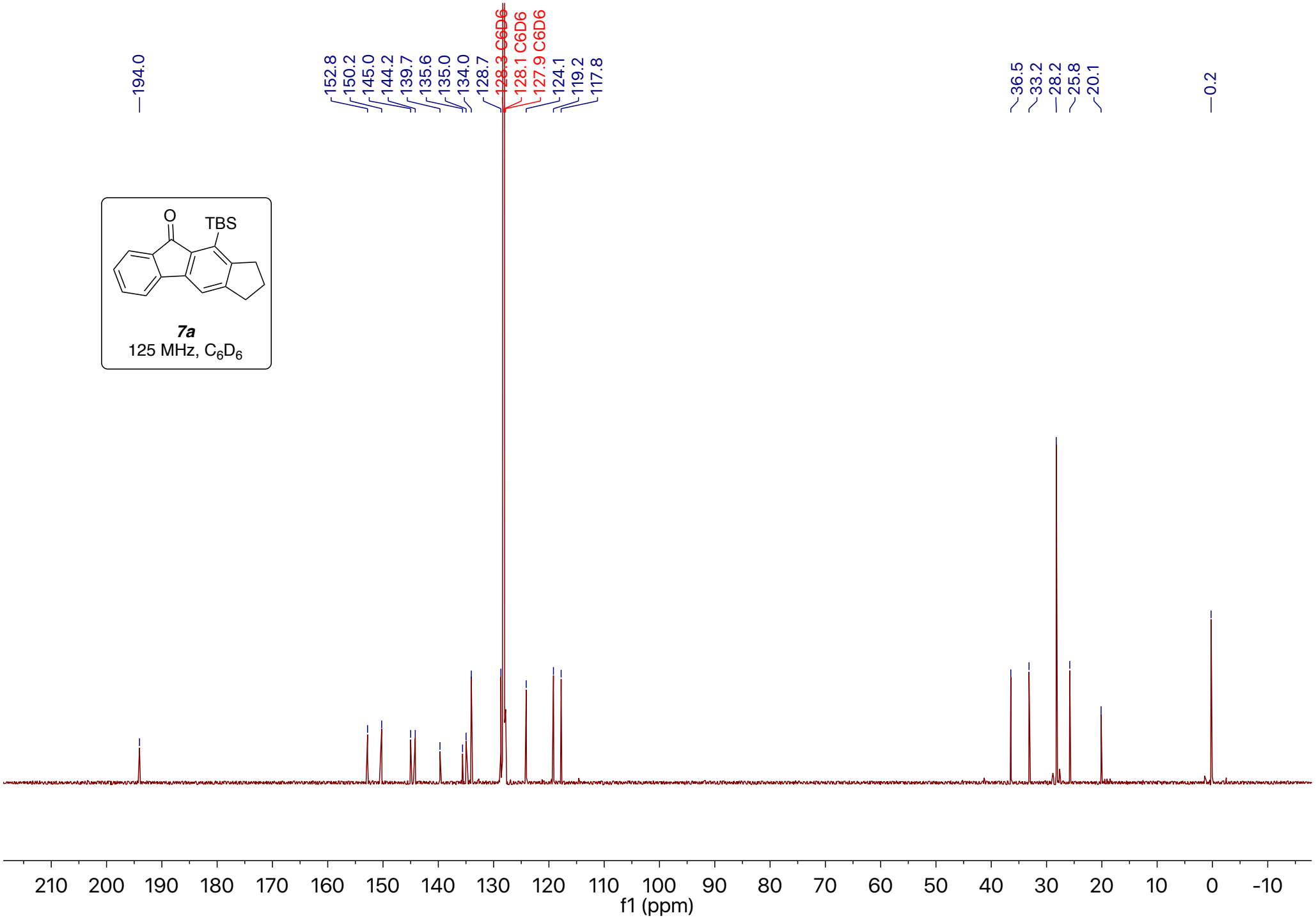
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128.1 C6D6
127.9 C6D6
124.1
119.2
117.8
36.5
33.2
28.2
25.8
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TBS
7a
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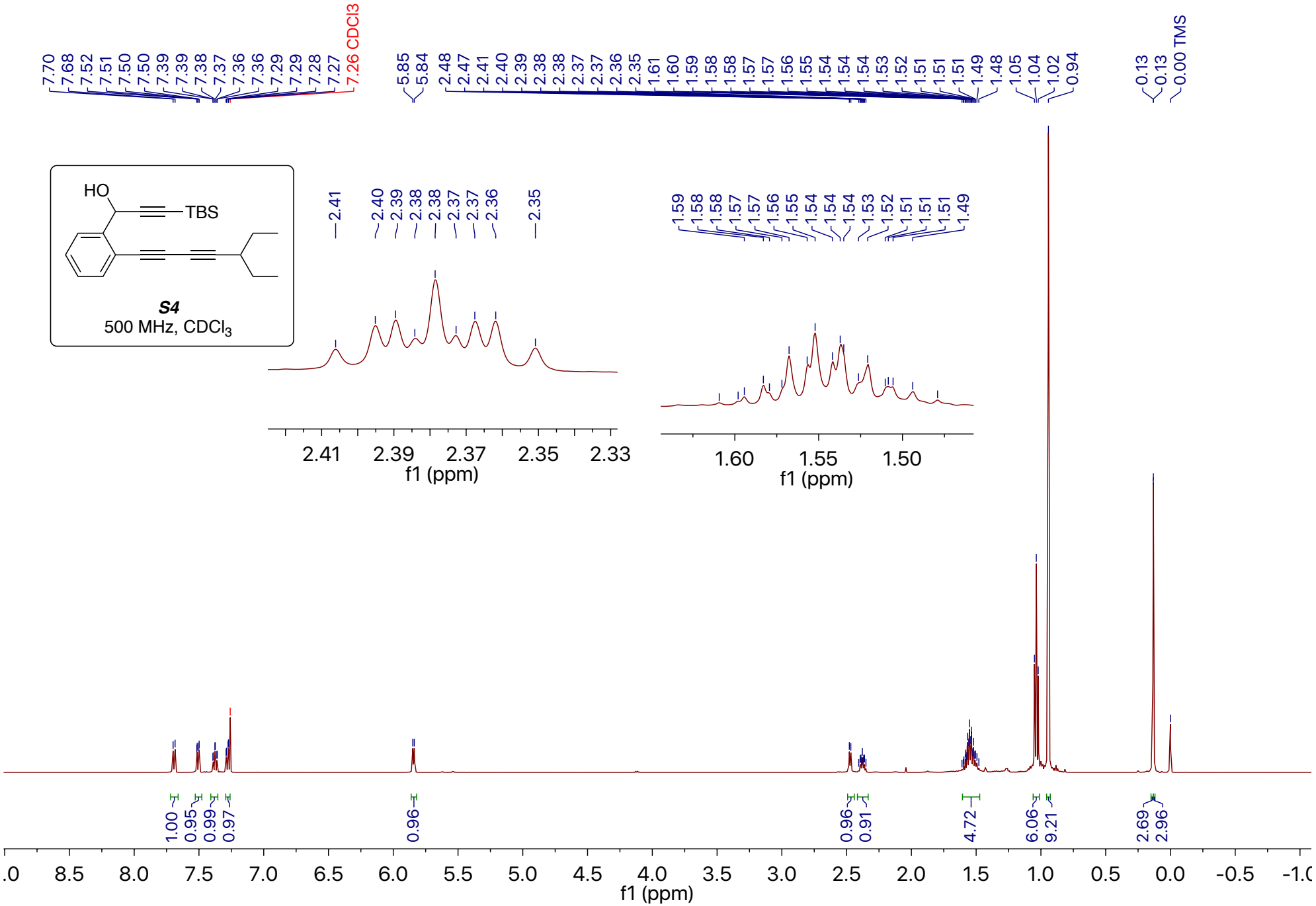
f1 (ppm)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2.38
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2.37
2.37
2.36
2.35
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1.60
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1.52
1.51
1.51
1.51
1.49
1.48
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1.04
1.02
0.94
0.13
0.13
0.00 TMS
HO
TBS
S4
500 MHz, CDCl3
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2.38
2.38
2.37
2.37
2.36
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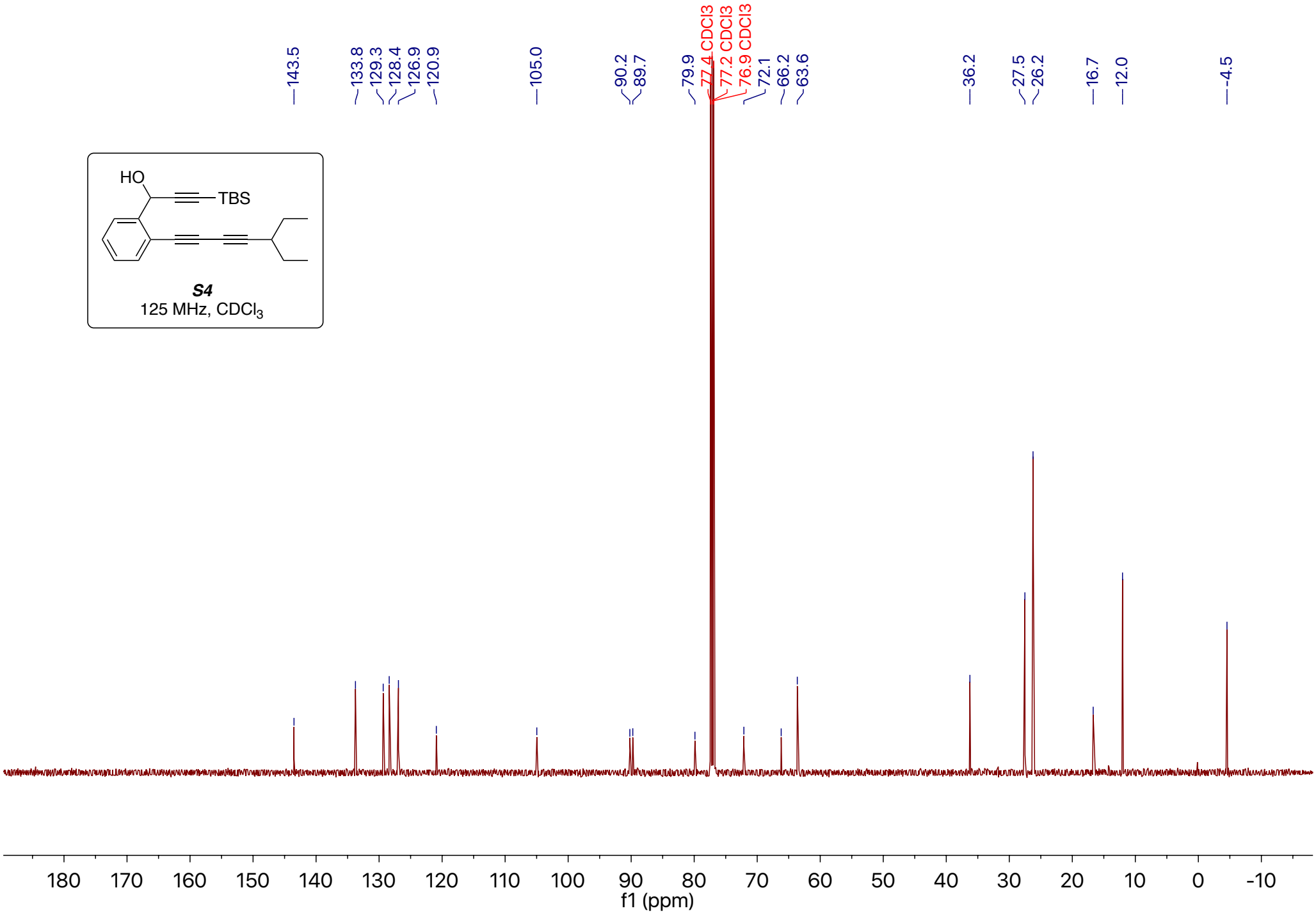
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76.9 CDCl3
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26.2
16.7
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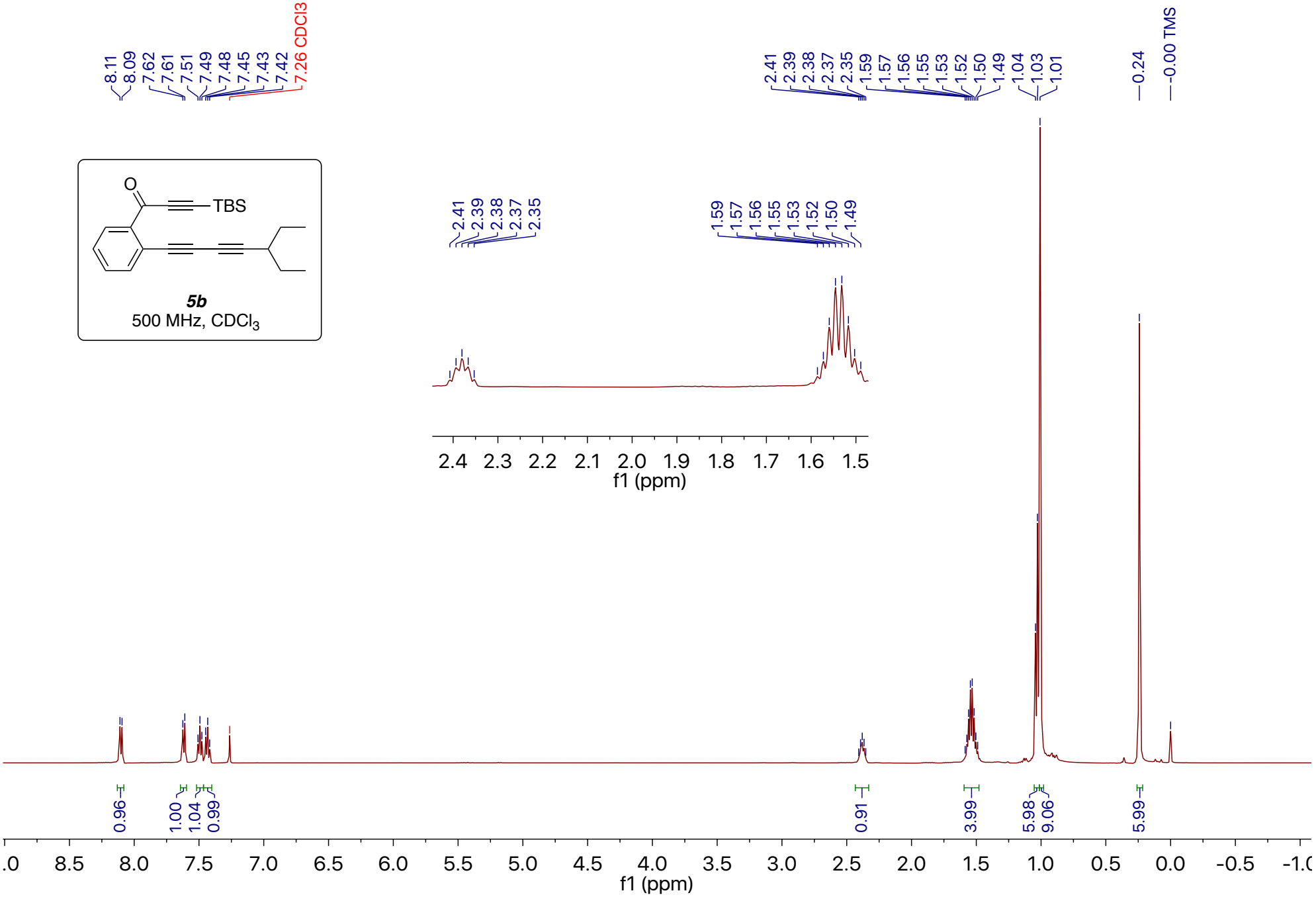
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2.35
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1.57
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1.55
1.53
1.52
1.50
1.49
1.04
1.03
1.01
0.24
-0.00 TMS
O
TBS
5b
500 MHz, CDCl3
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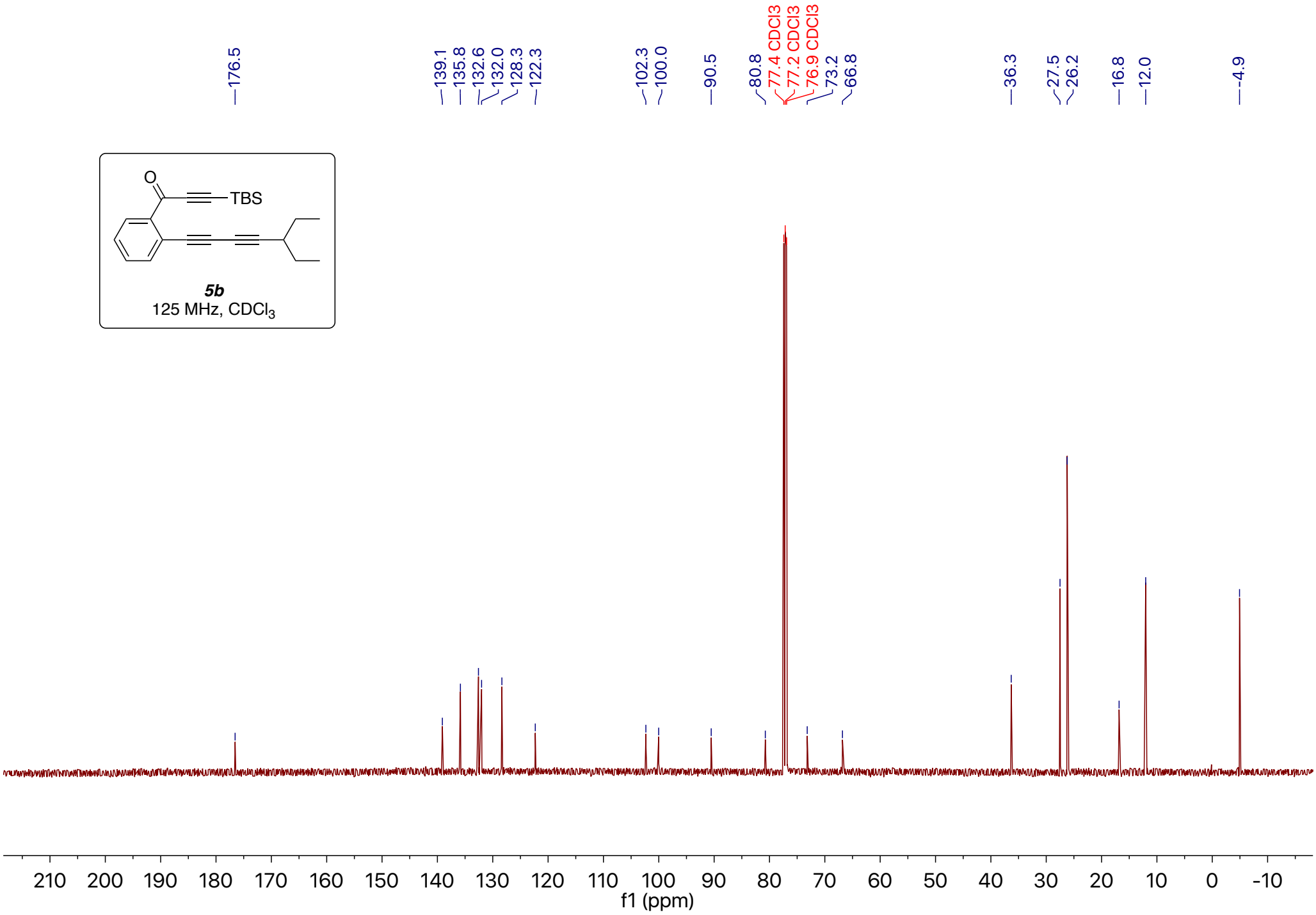
f1 (ppm)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90.5
80.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
73.2
66.8
36.3
27.5
26.2
16.8
12.0
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TBS
5b
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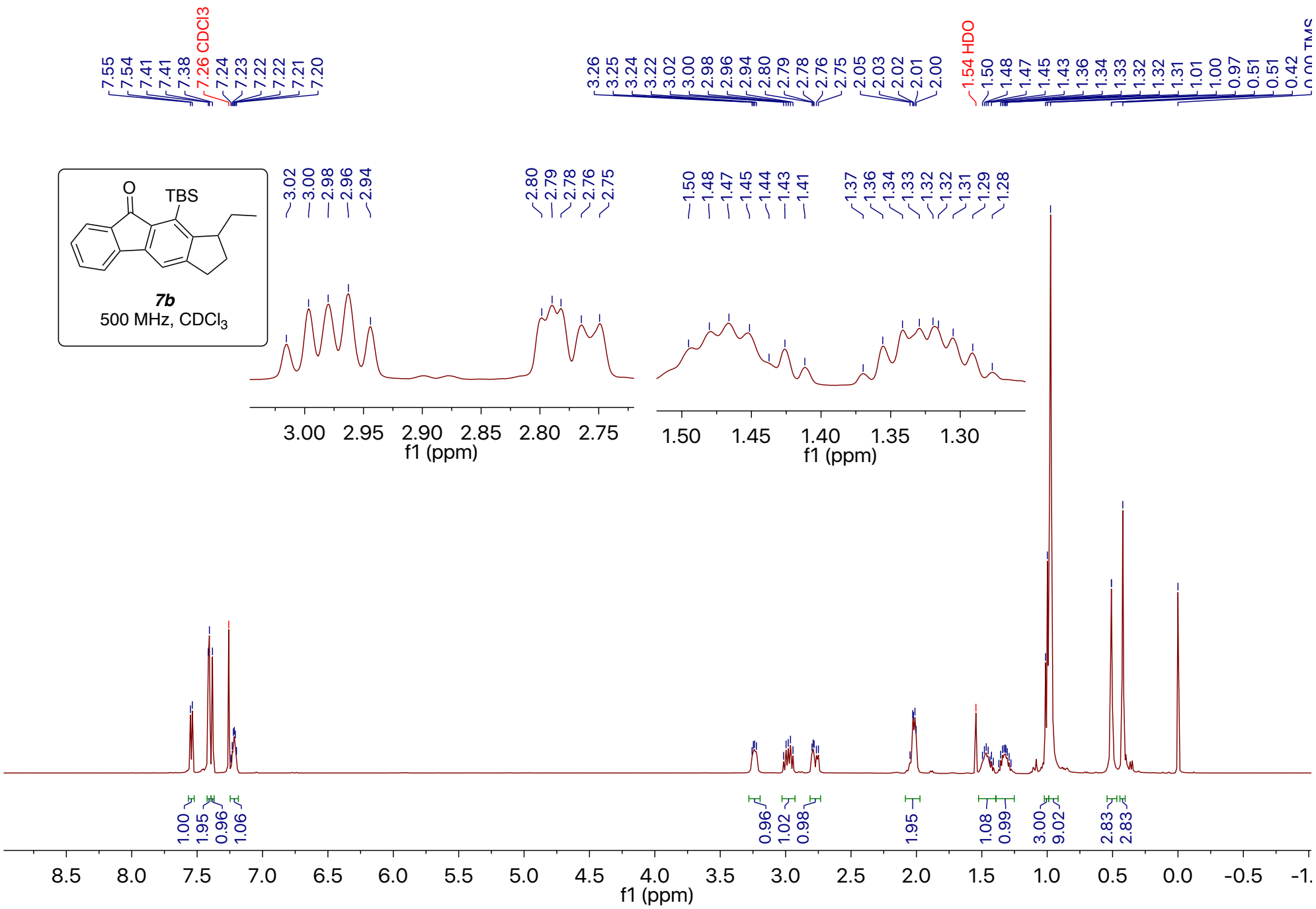
f1 (ppm)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3.25
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7b
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1.33
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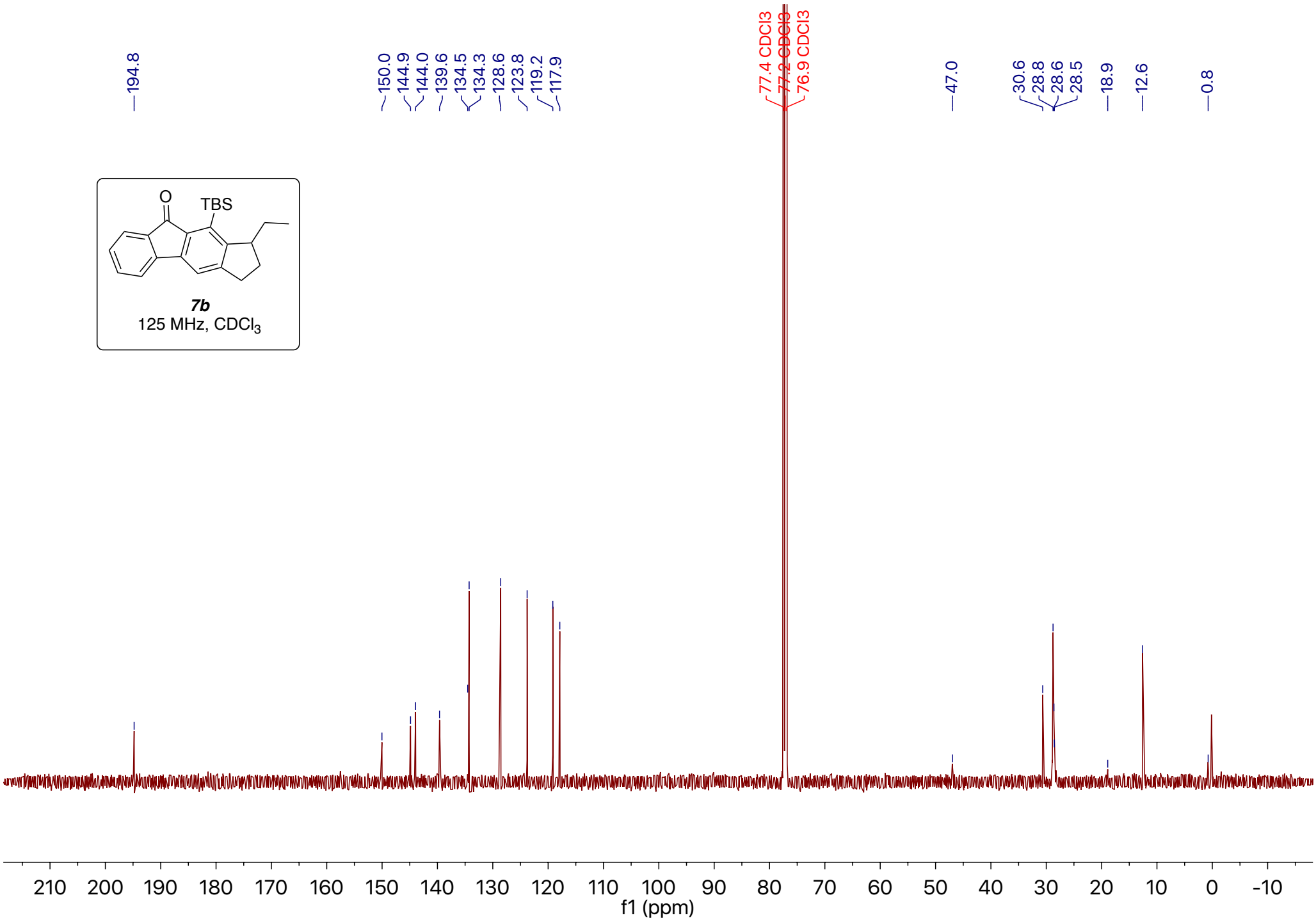
2.83
2.83
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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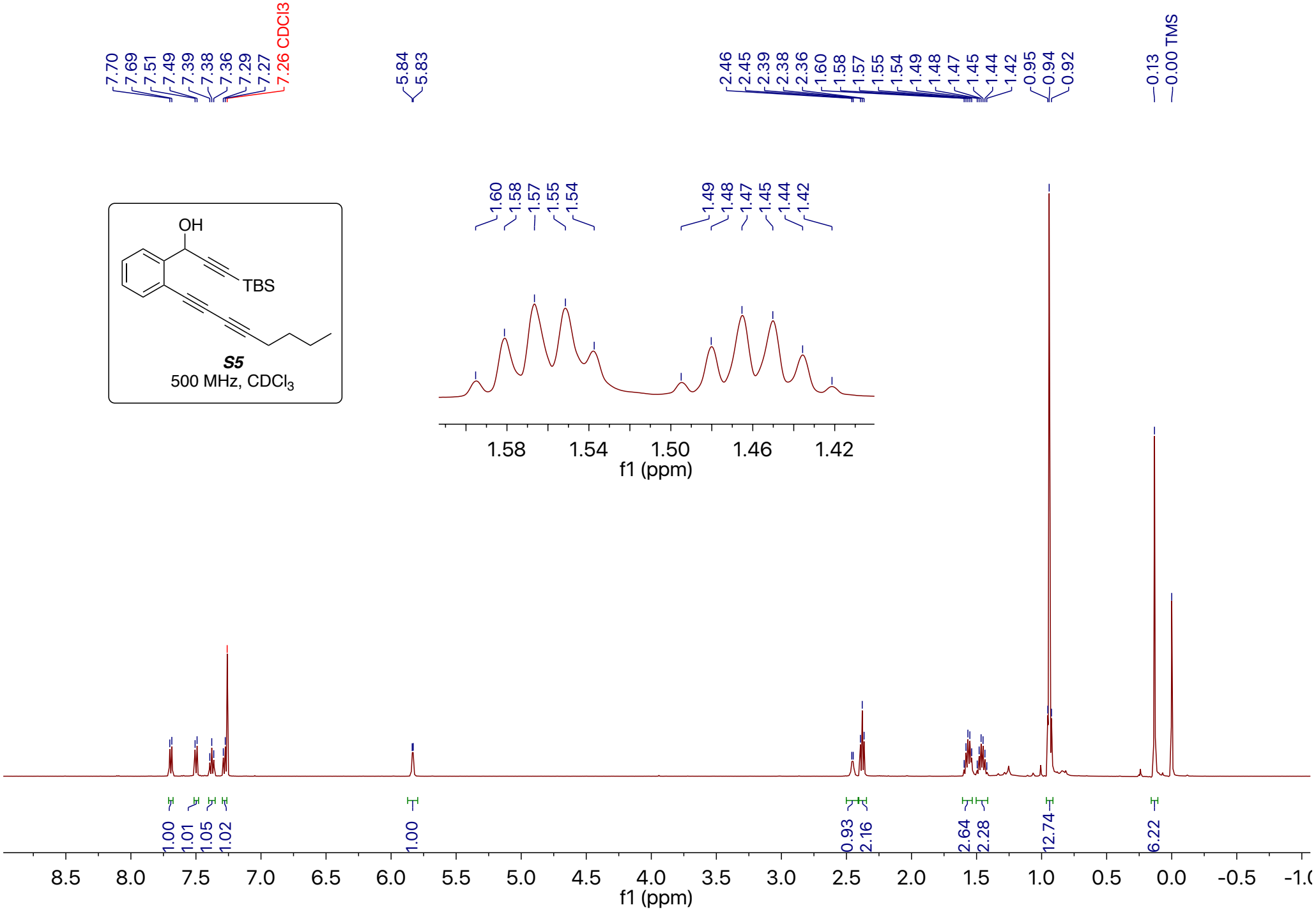
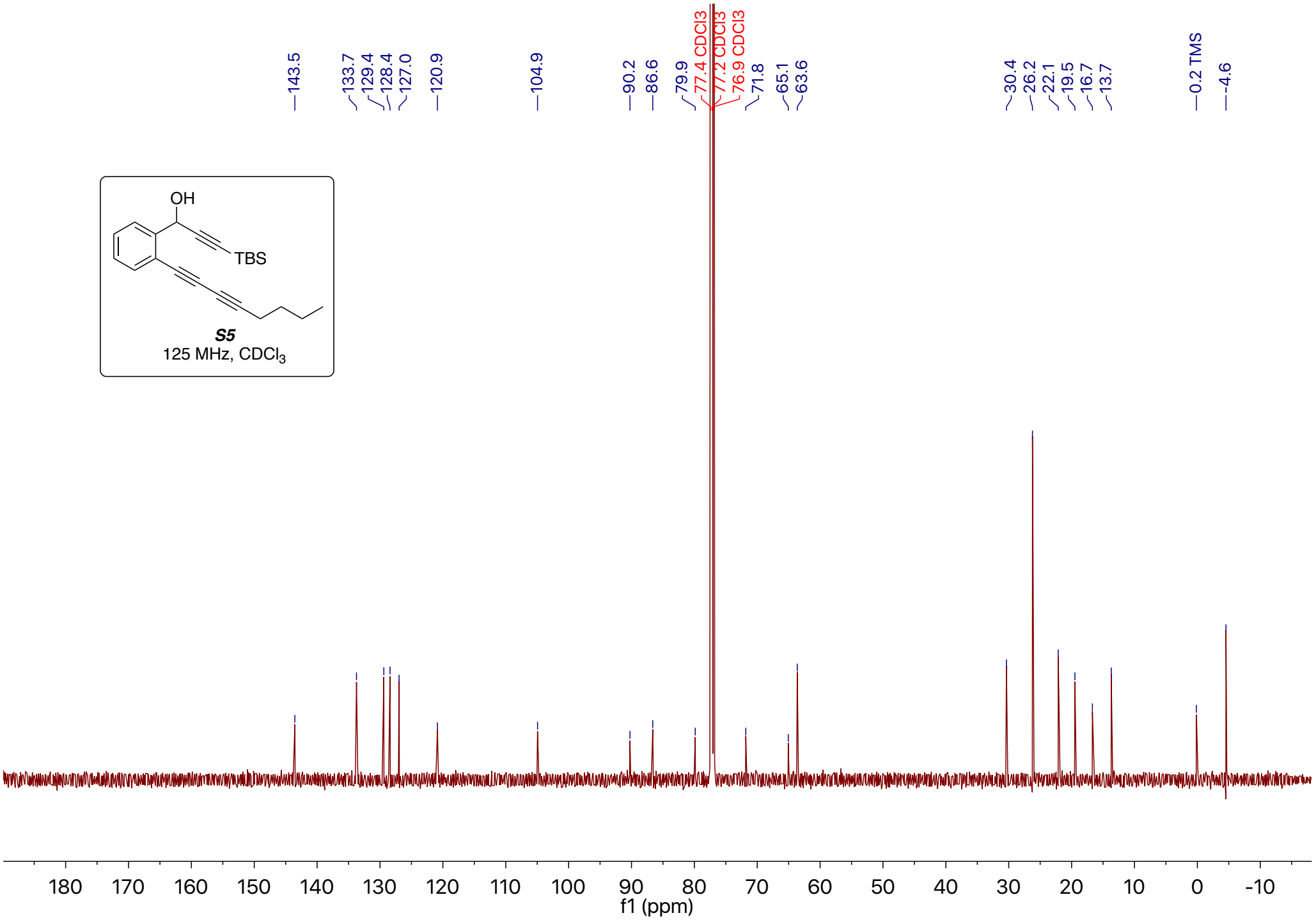
150.0
144.9
144.0
139.6
134.5
134.3
128.6
123.8
119.2
117.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
47.0
30.6
28.8
28.6
28.5
18.9
12.6
0.8
O
TBS
7b
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.70
7.69
7.51
7.49
7.39
7.38
7.36
7.29
7.27
7.26 CDCl3
5.84
5.83
2.46
2.45
2.39
2.38
2.36
1.60
1.58
1.57
1.55
1.54
1.49
1.48
1.47
1.45
1.44
1.42
0.95
0.94
0.92
0.13
0.00 TMS
OH
TBS
S5
500 MHz, CDCl3
1.60
1.58
1.57
1.55
1.54
1.49
1.48
1.47
1.45
1.44
1.42
1.58
1.54
1.50
1.46
1.42
f1 (ppm)
1.00
1.01
1.05
1.02
1.00
0.93
2.16
2.64
2.28
12.74
6.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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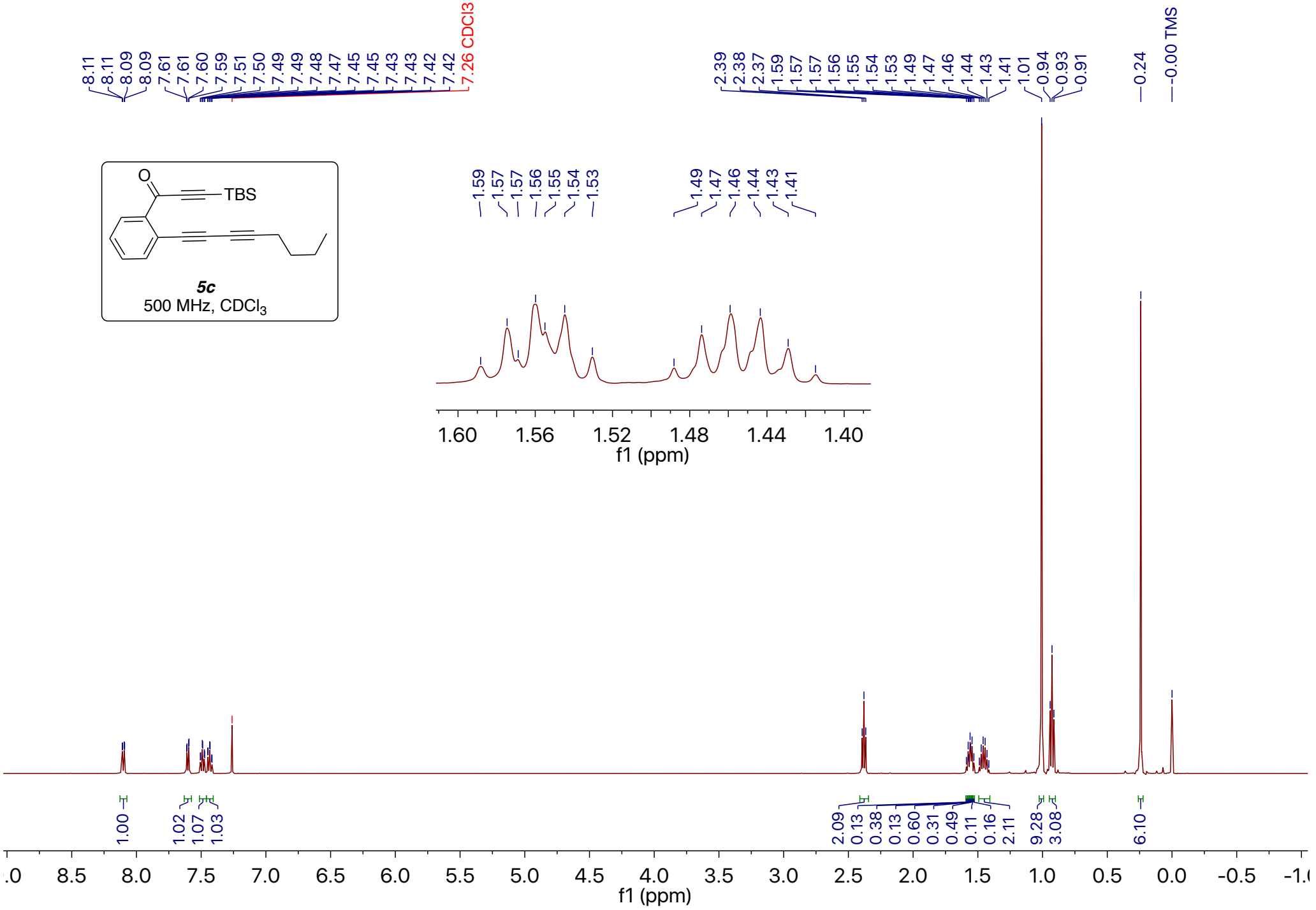
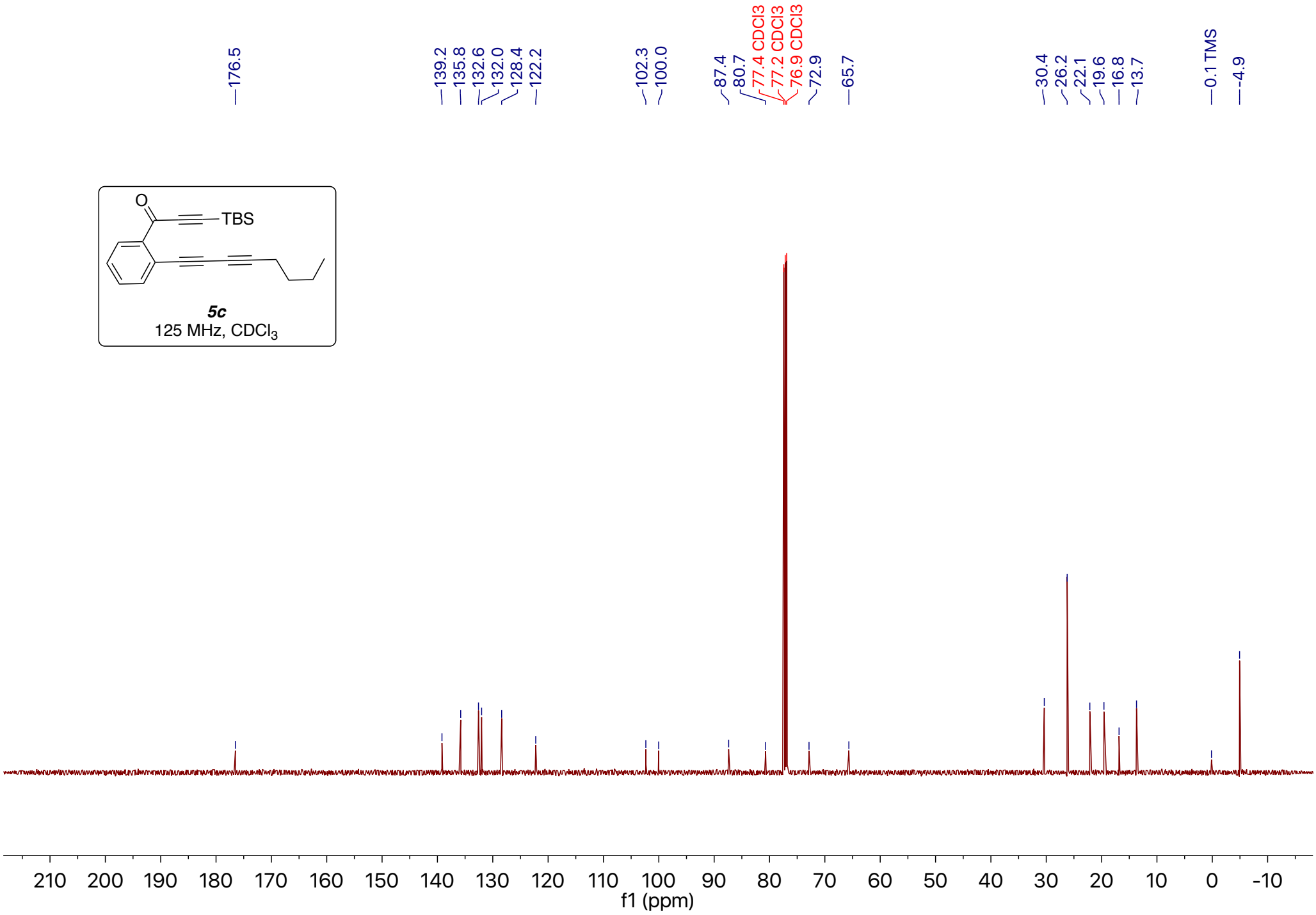
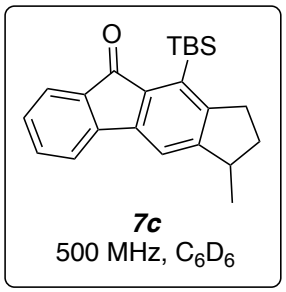
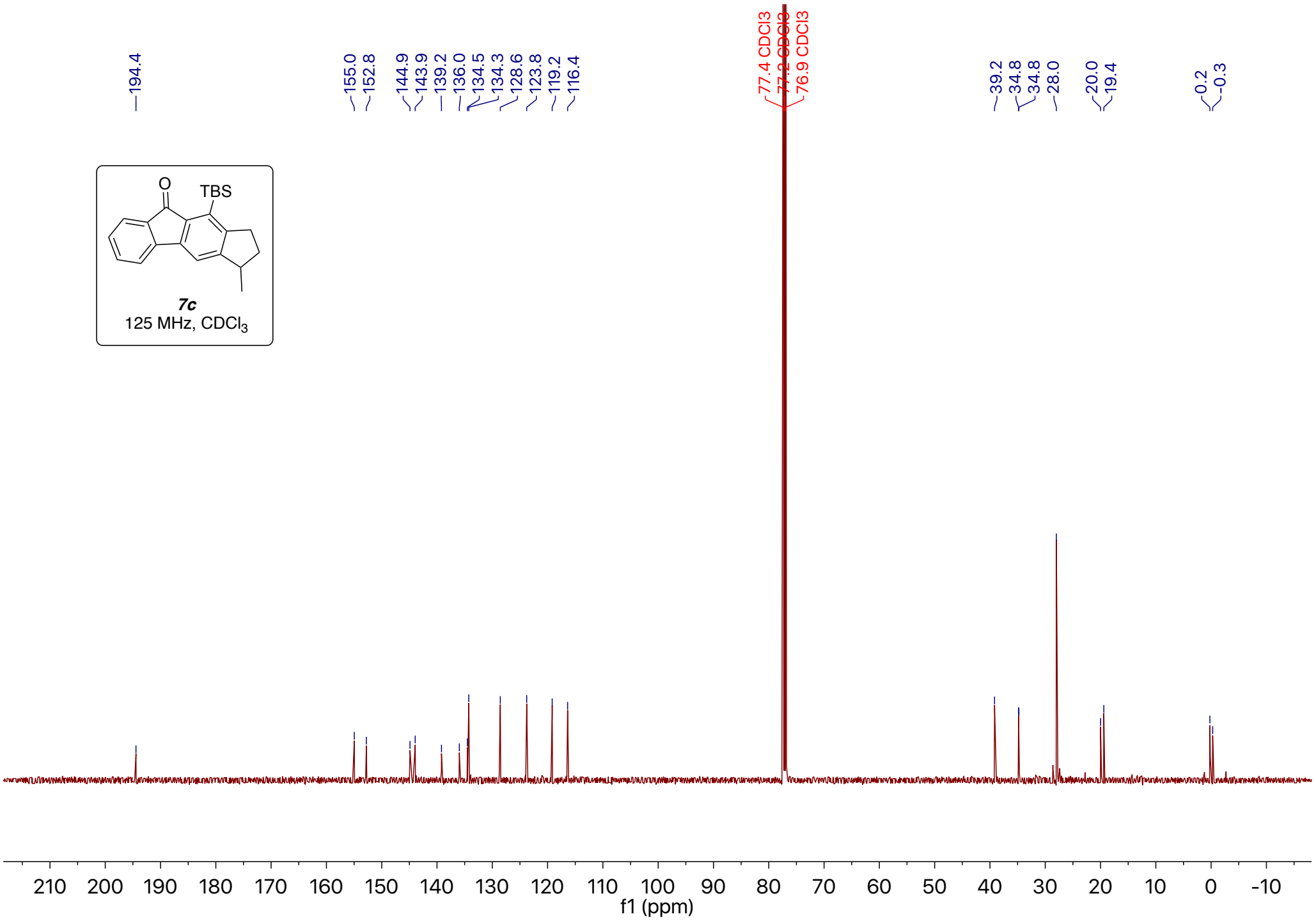
133.7
129.4
128.4
127.0
120.9
104.9
90.2
86.6
79.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
71.8
65.1
63.6
30.4
26.2
22.1
19.5
16.7
13.7
0.2 TMS
-4.6
OH
TBS
S5
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

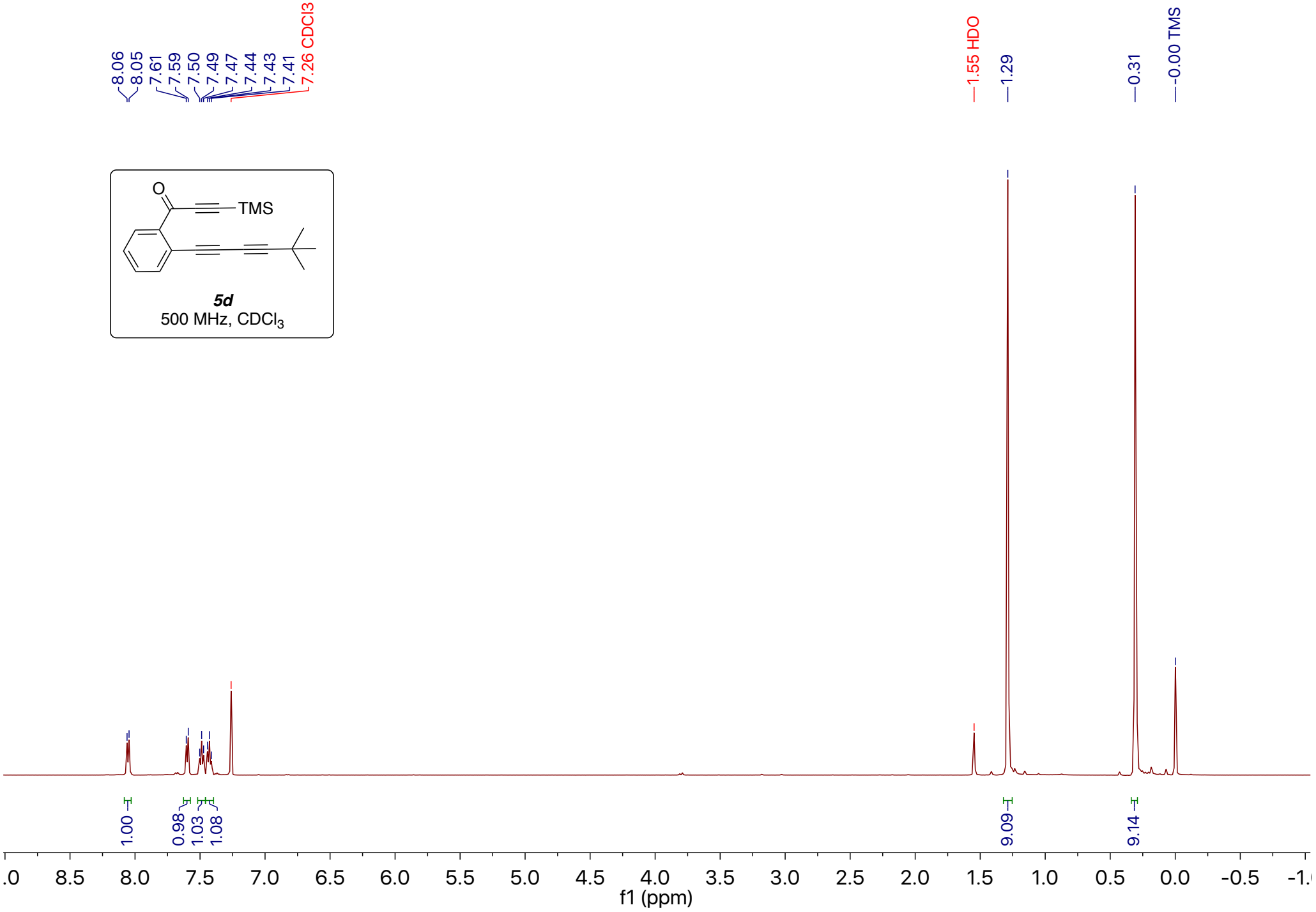

8.11
8.11
8.09
8.09
7.61
7.61
7.60
7.59
7.51
7.50
7.49
7.49
7.48
7.47
7.45
7.45
7.43
7.43
7.42
7.42
7.26 CDCl3
2.39
2.38
2.37
1.59
1.57
1.57
1.56
1.55
1.54
1.53
1.49
1.47
1.46
1.44
1.43
1.41
1.01
0.94
0.93
0.91
0.24
-0.00 TMS
O
TBS
5c
500 MHz, CDCl3
1.60
1.56
1.52
1.48
1.44
1.40
f1 (ppm)
1.00
1.02
1.07
1.03
2.09
0.13
0.38
0.13
0.60
0.31
0.49
0.11
0.16
2.11
9.28
3.08
6.10
f1 (ppm)

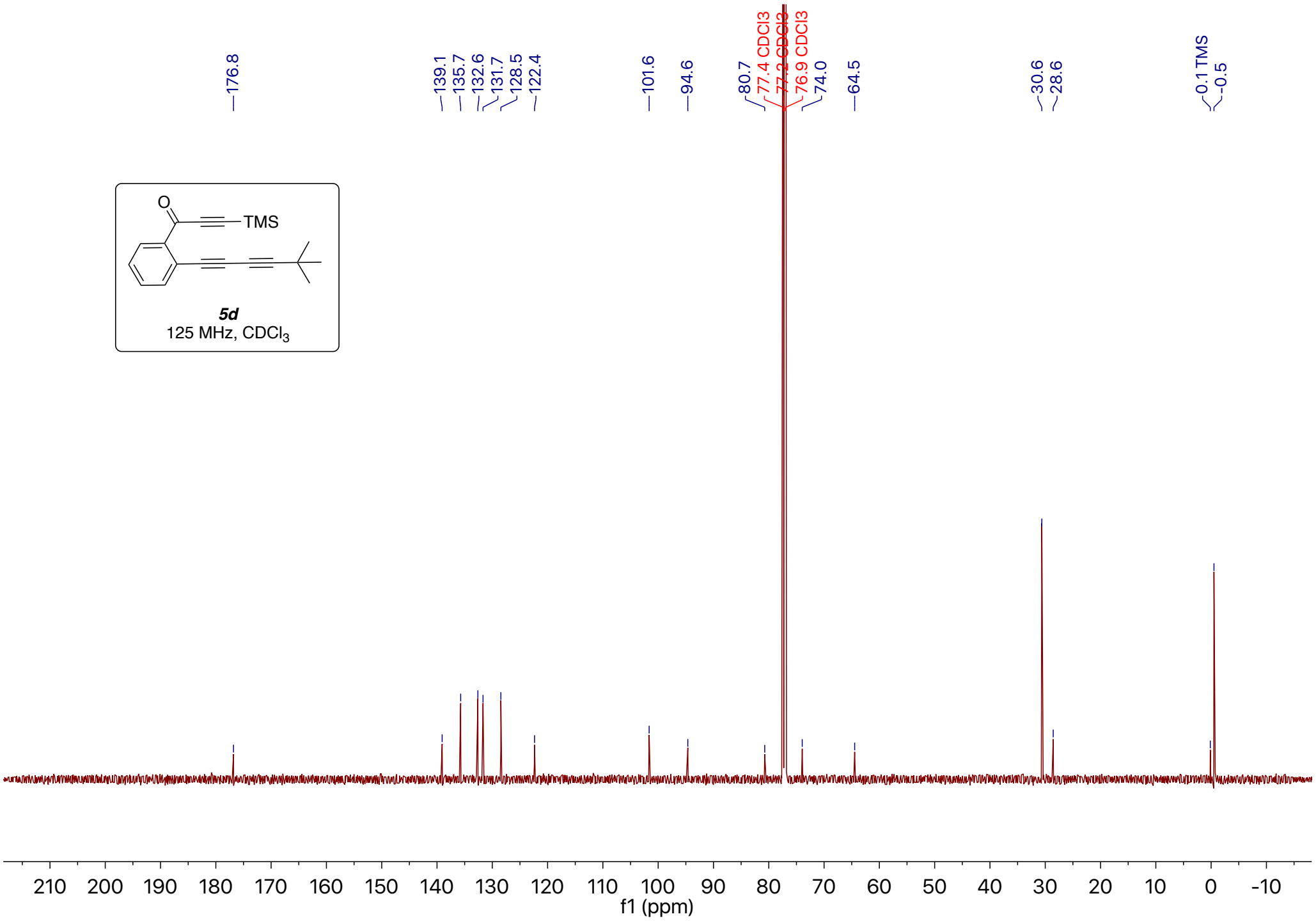

176.5
139.2
135.8
132.6
132.0
128.4
122.2
102.3
100.0
87.4
80.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.9
65.7
30.4
26.2
22.1
19.6
16.8
13.7
0.1 TMS
-4.9
O
TBS
5c
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

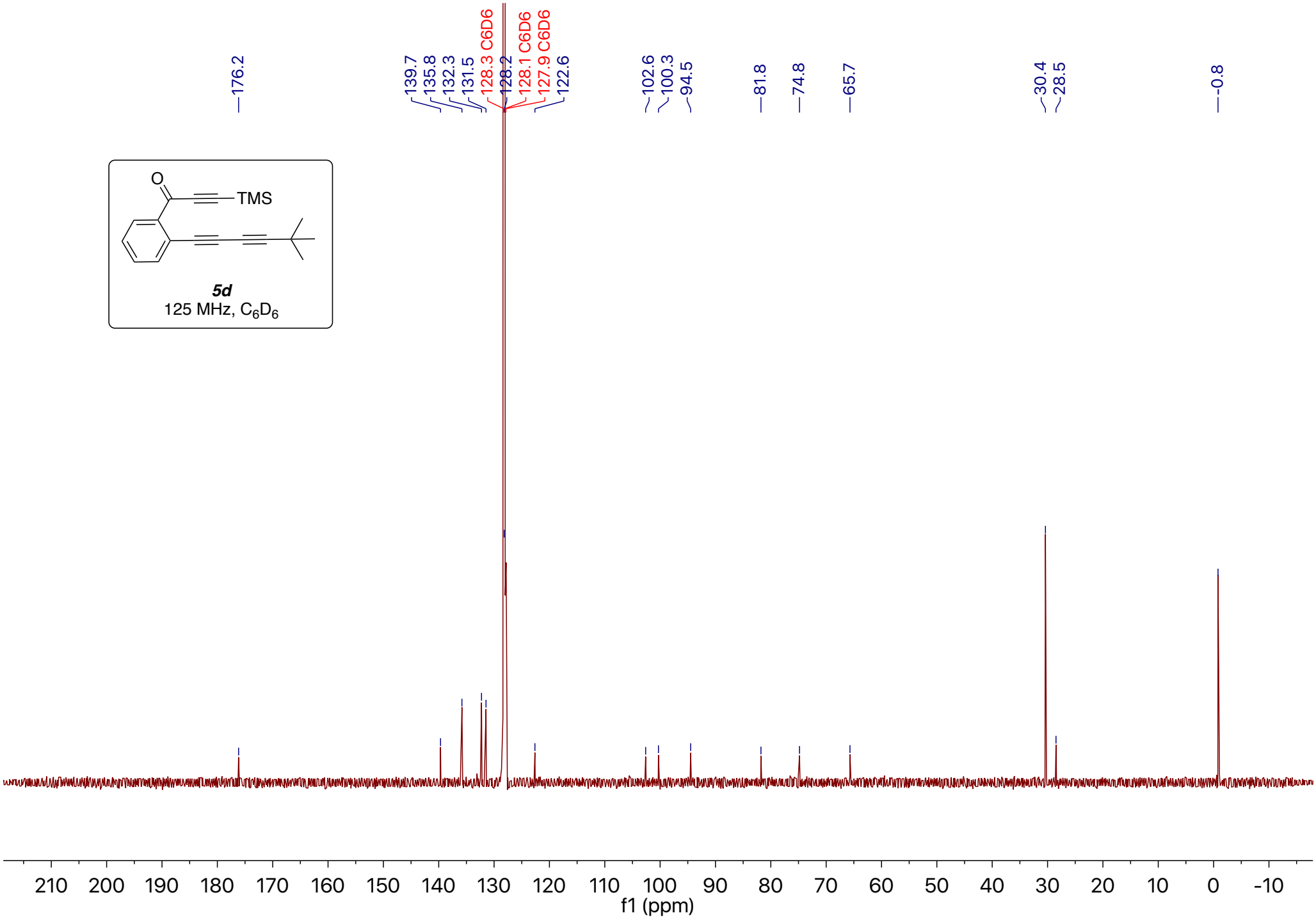


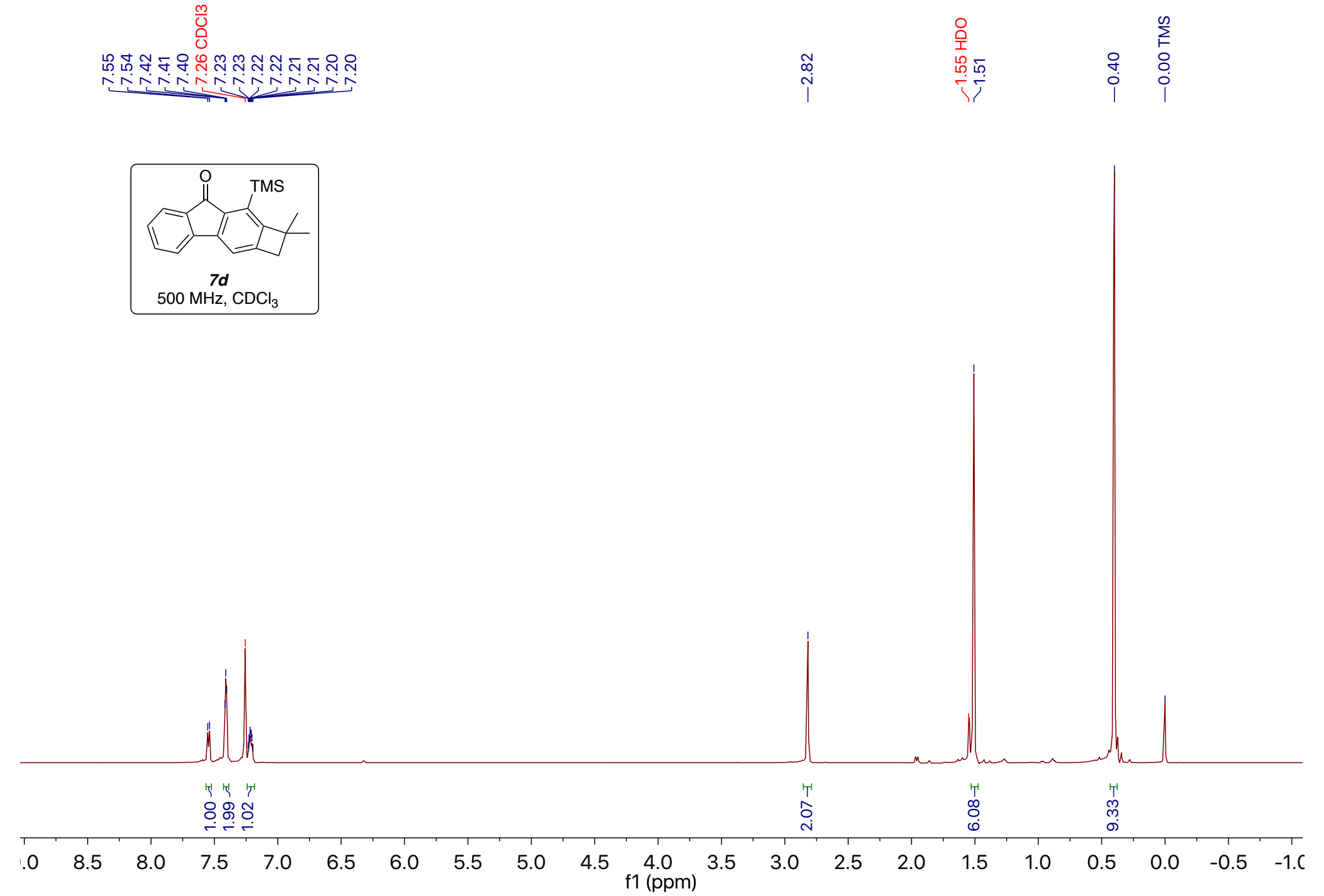
7c
500 MHz, C_6D_6

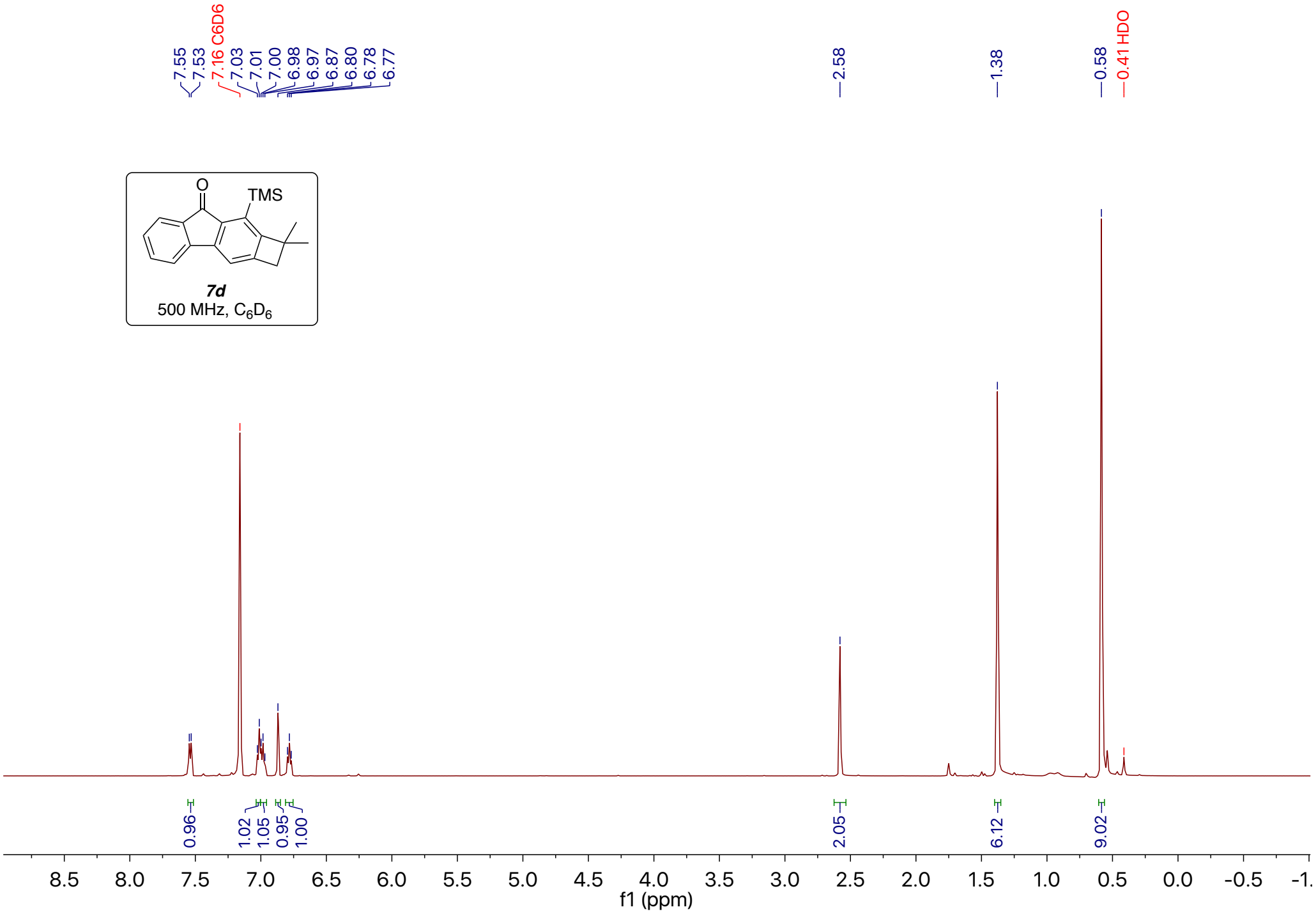

194.4
155.0
152.8
144.9
143.9
139.2
136.0
134.5
134.3
128.6
123.8
119.2
116.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
39.2
34.8
34.8
28.0
20.0
19.4
0.2
-0.3
O
TBS
7c
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

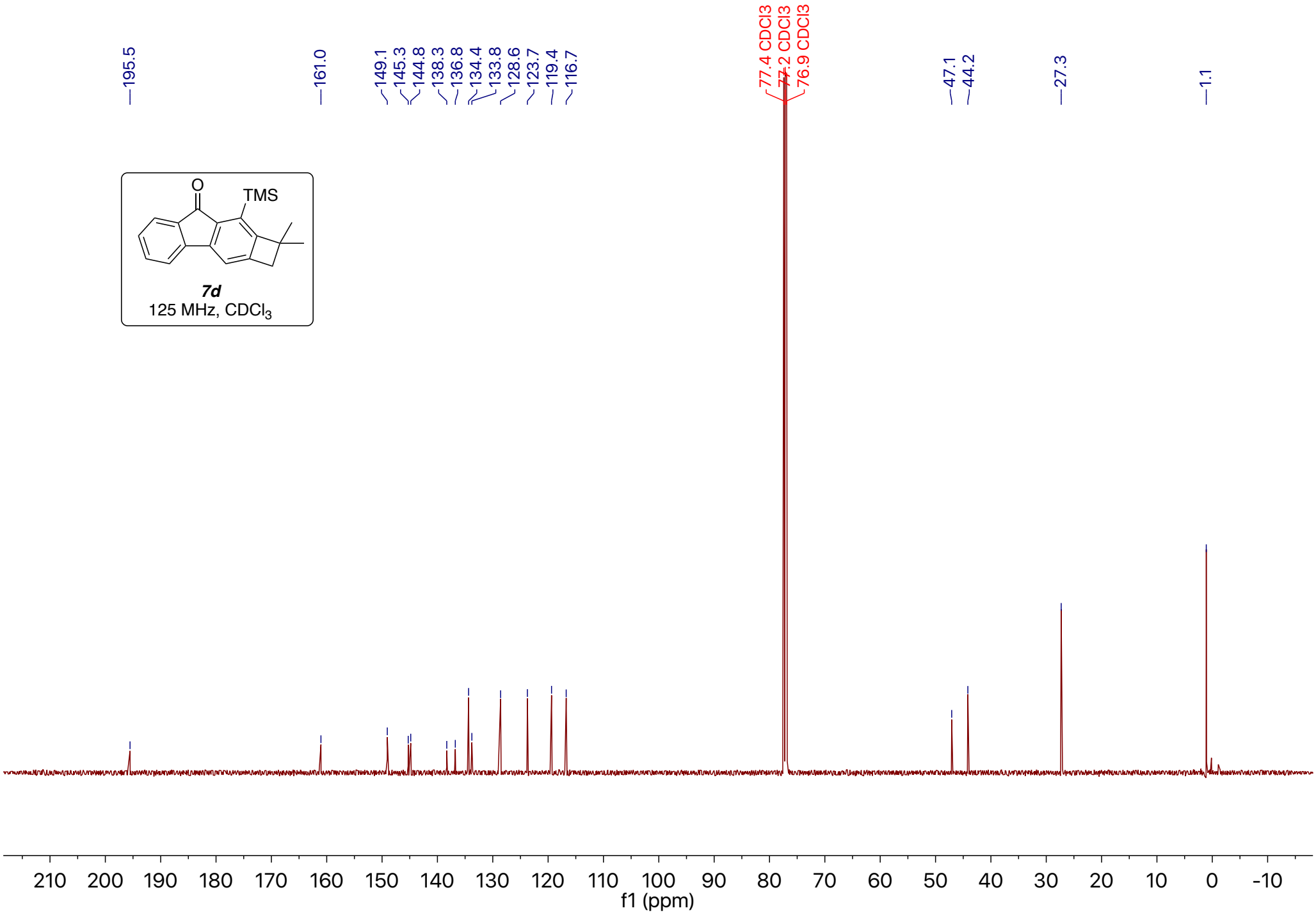

8.06
8.05
7.61
7.59
7.50
7.49
7.47
7.44
7.43
7.41
7.26 CDCl3
1.55 HDO
1.29
0.31
-0.00 TMS
O
TMS
5d
500 MHz, CDCl3
1.00
0.98
1.03
1.08
9.09
9.14
f1 (ppm)

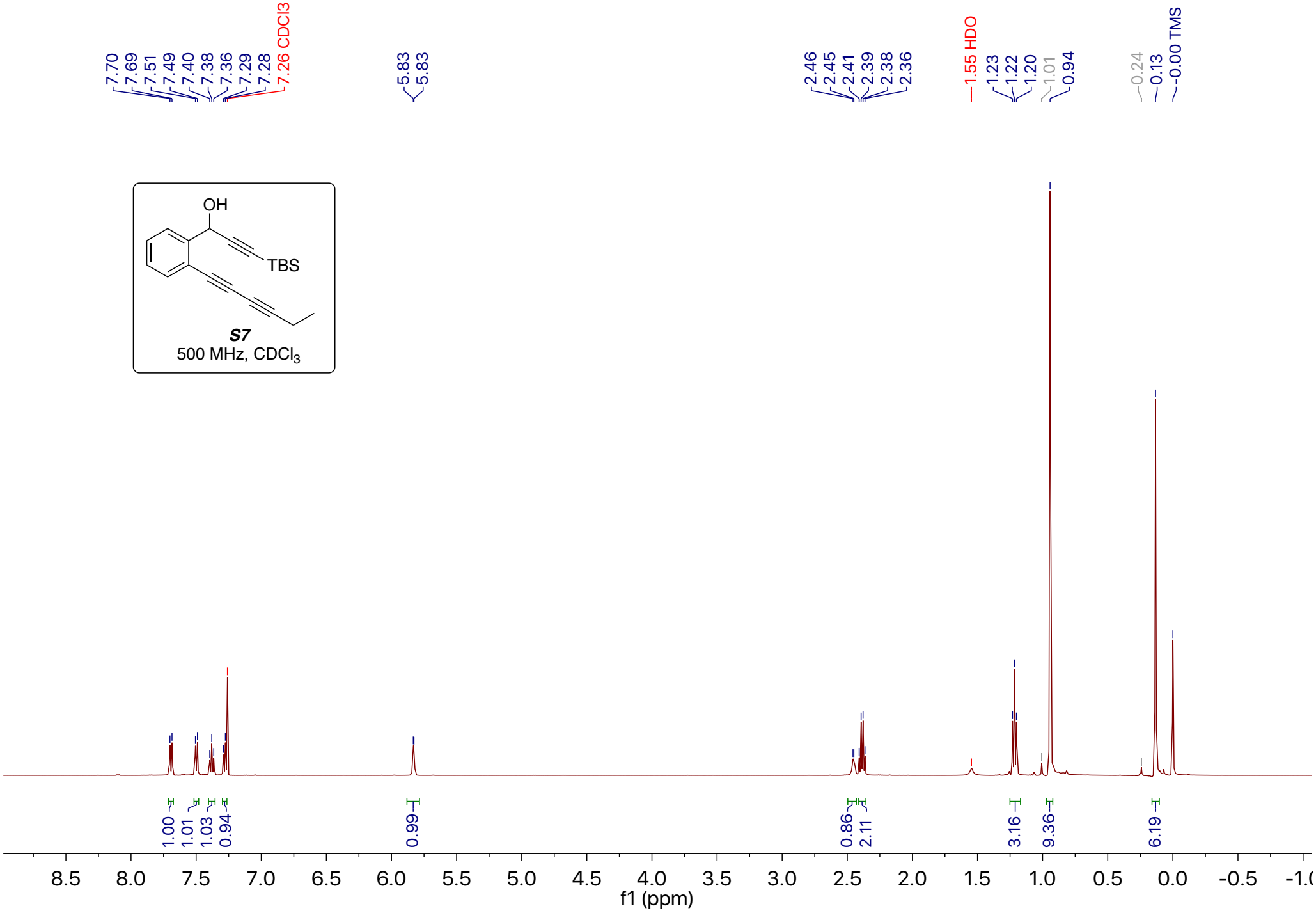

176.8
139.1
135.7
132.6
131.7
128.5
122.4
101.6
94.6
80.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
74.0
64.5
30.6
28.6
0.1 TMS
-0.5
O
TMS
5d
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

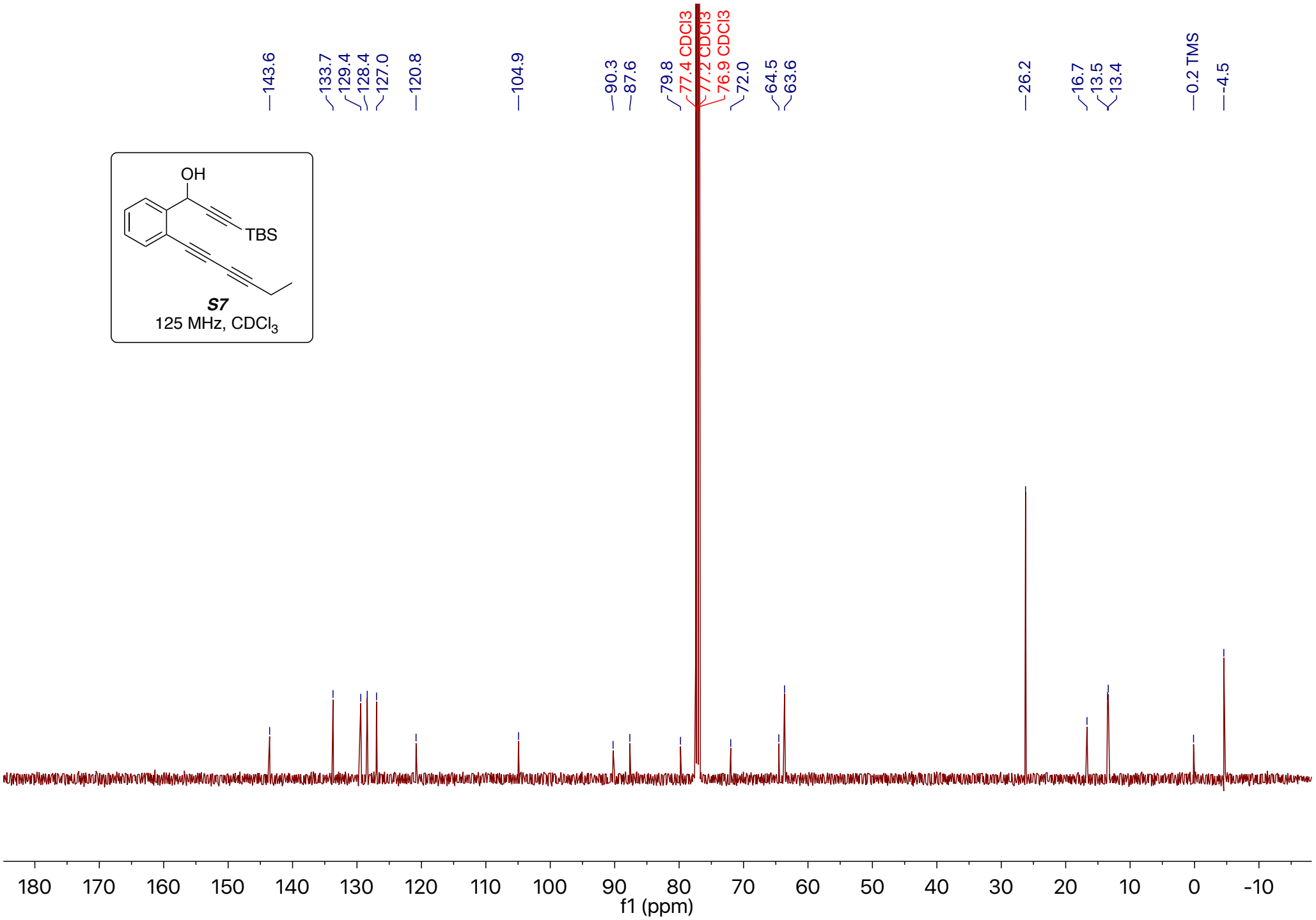

176.2
139.7
135.8
132.3
131.5
128.3 C6D6
128.2
128.1 C6D6
127.9 C6D6
122.6
102.6
100.3
94.5
81.8
74.8
65.7
30.4
28.5
-0.8
O
TMS
5d
125 MHz, C6D6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

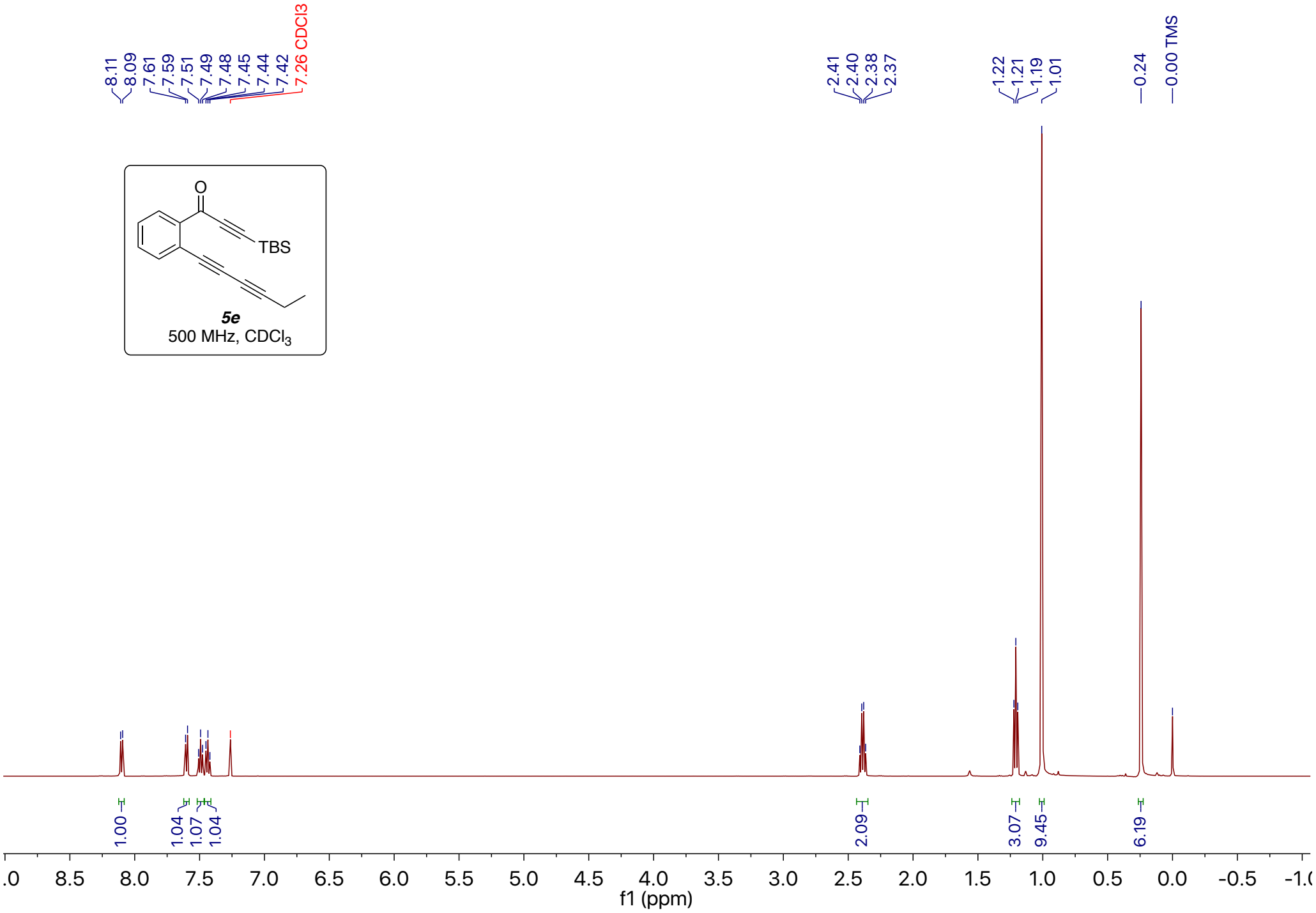

7.55
7.54
7.42
7.41
7.40
7.26 CDCl3
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.20
2.82
1.55 HDO
1.51
0.40
0.00 TMS
O
TMS
7d
500 MHz, CDCl3
1.00
1.99
1.02
2.07
6.08
9.33
f1 (ppm)

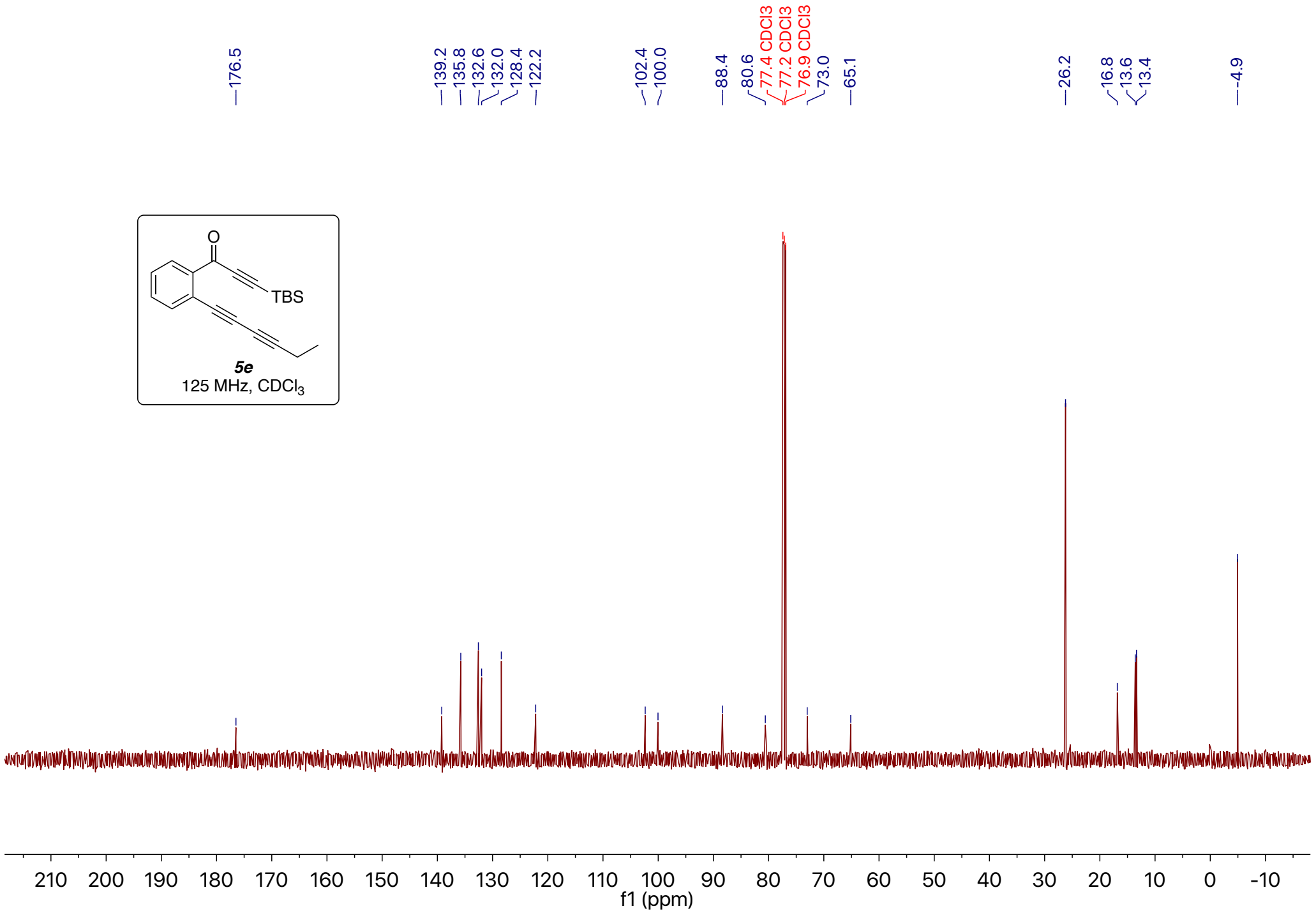

7.55
7.53
7.16 C6D6
7.03
7.01
7.00
6.98
6.97
6.87
6.80
6.78
6.77
2.58
1.38
0.58
0.41 HDO
O
TMS
7d
500 MHz, C6D6
0.96
1.02
1.05
0.95
1.00
2.05
6.12
9.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

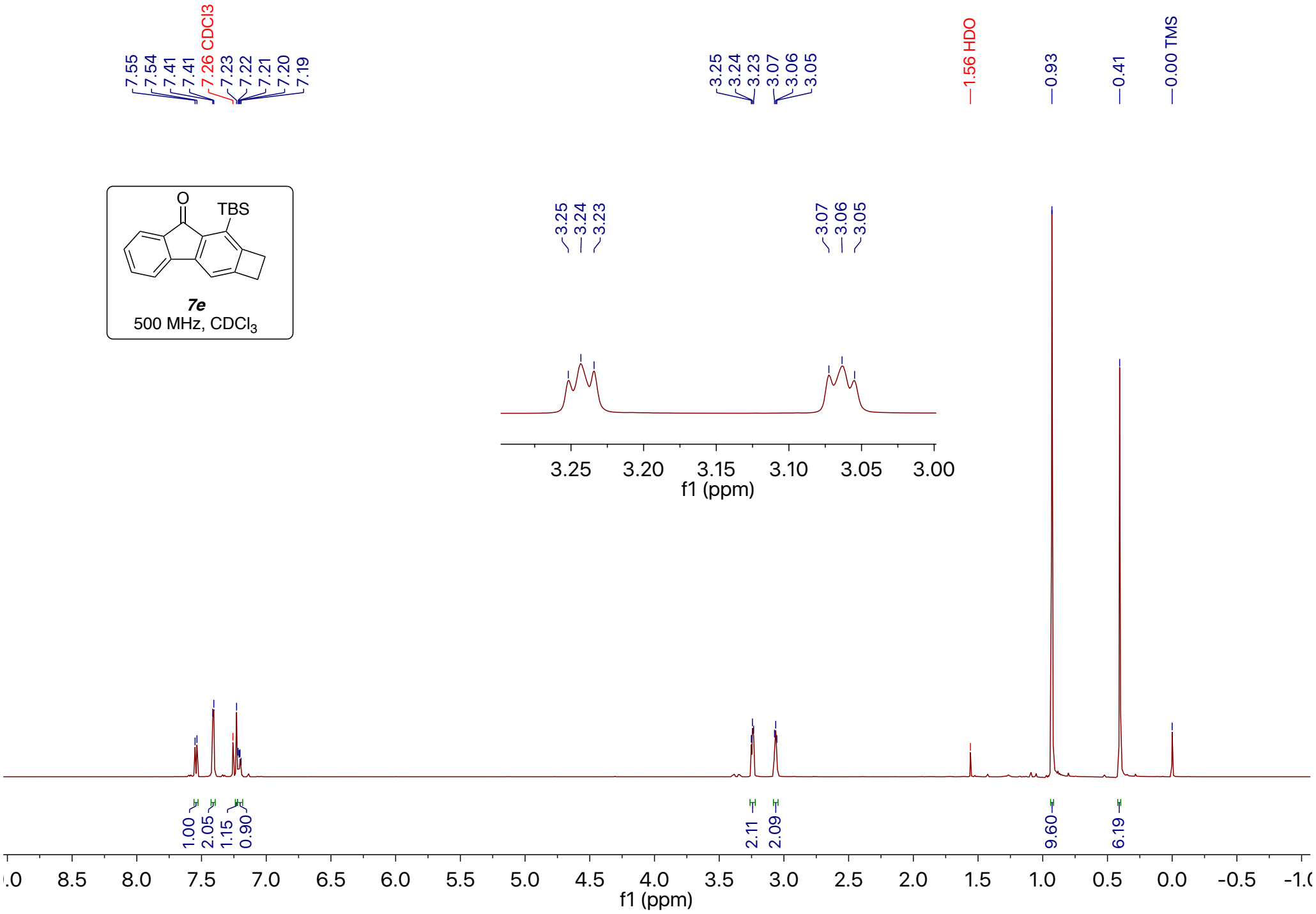

195.5
161.0
149.1
145.3
144.8
138.3
136.8
134.4
133.8
128.6
123.7
119.4
116.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
47.1
44.2
27.3
1.1
O
TMS
7d
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

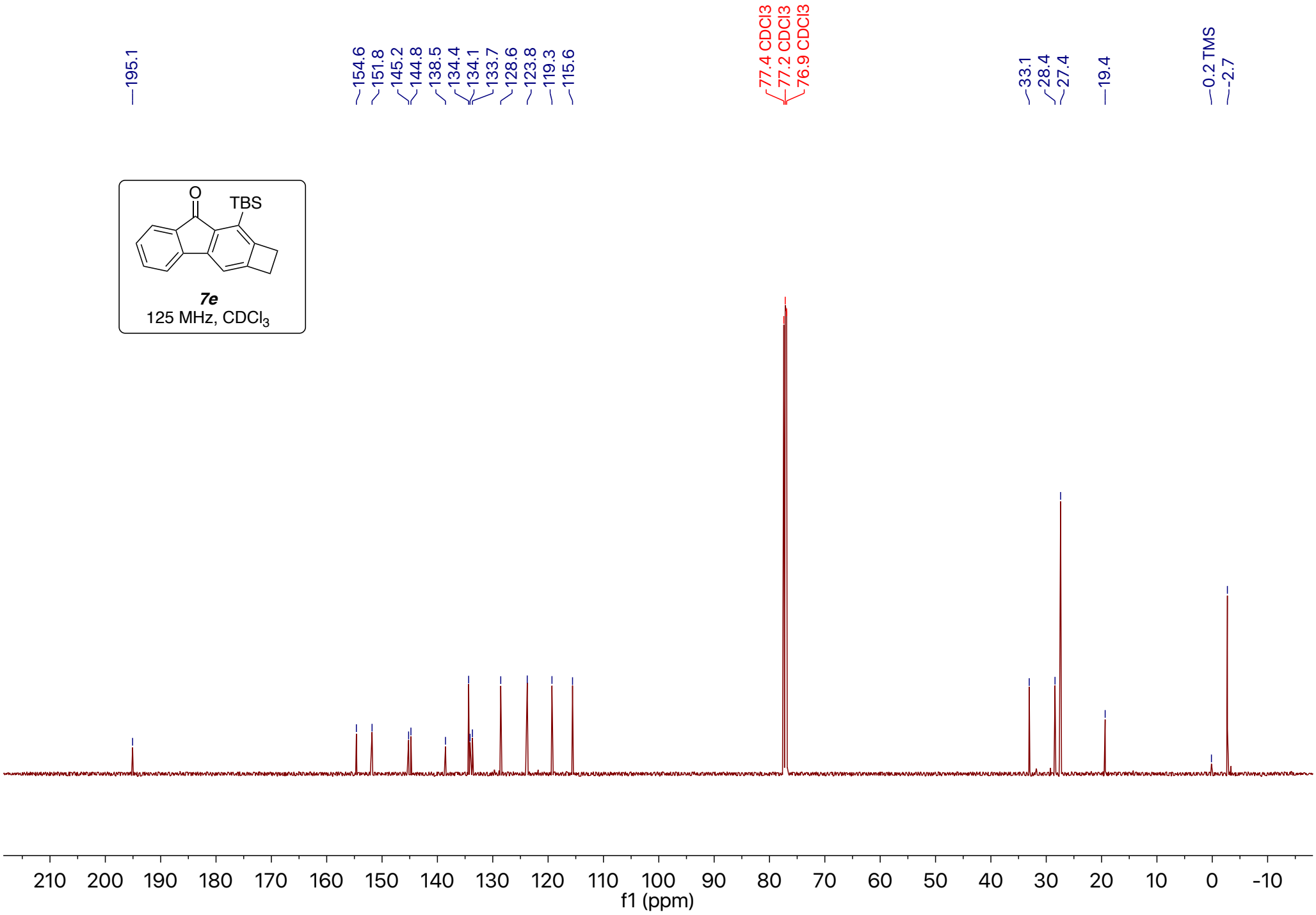

7.70
7.69
7.51
7.49
7.40
7.38
7.36
7.29
7.28
7.26 CDCl3
5.83
5.83
2.46
2.45
2.41
2.39
2.38
2.36
1.55 HDO
1.23
1.22
1.20
1.01
0.94
0.24
0.13
-0.00 TMS
OH
TBS
S7
500 MHz, CDCl3
1.00
1.01
1.03
0.94
0.99
0.86
2.11
3.16
9.36
6.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

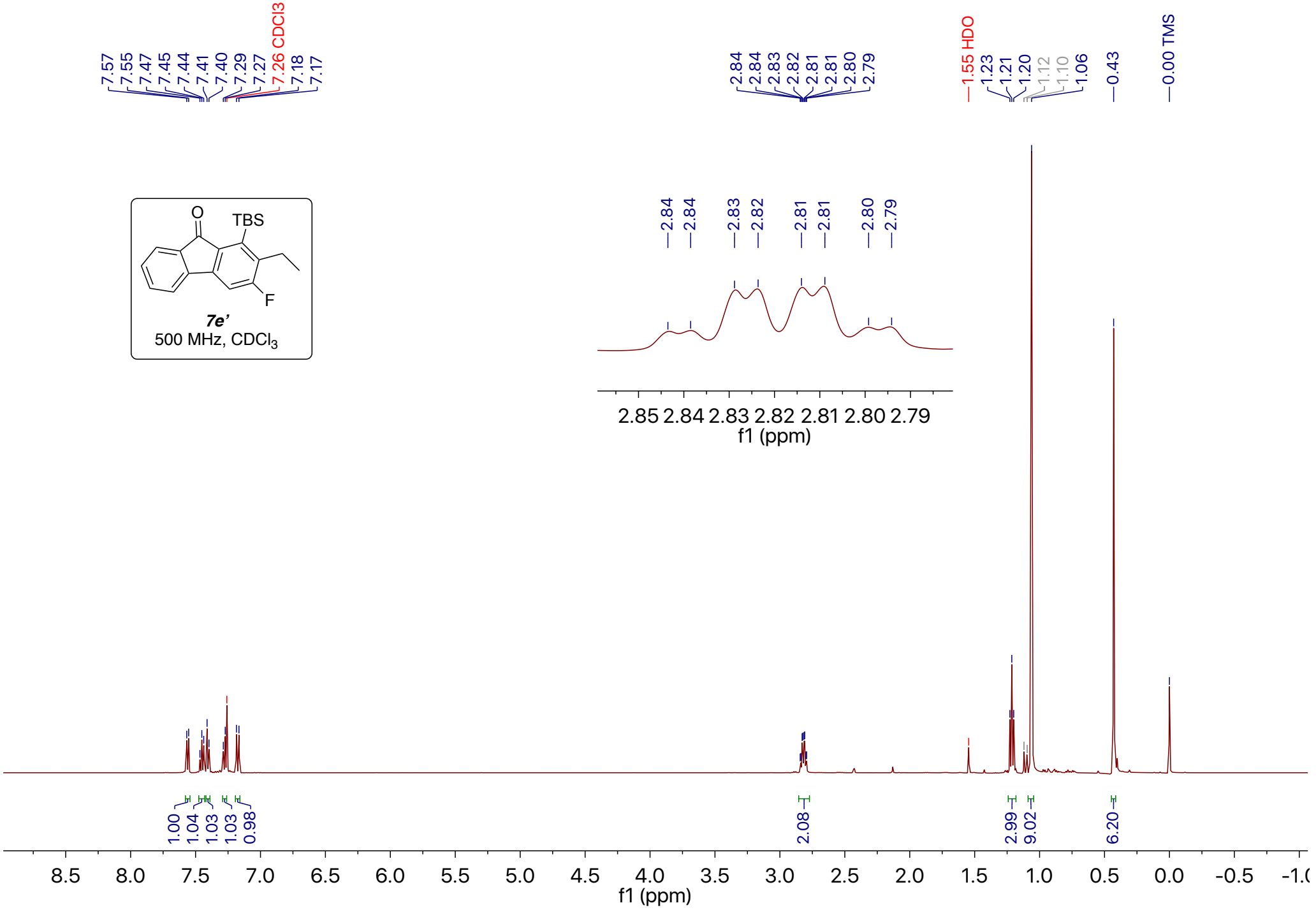

143.6
133.7
129.4
128.4
127.0
120.8
104.9
90.3
87.6
79.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.0
64.5
63.6
26.2
16.7
13.5
13.4
0.2 TMS
-4.5
OH
TBS
S7
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

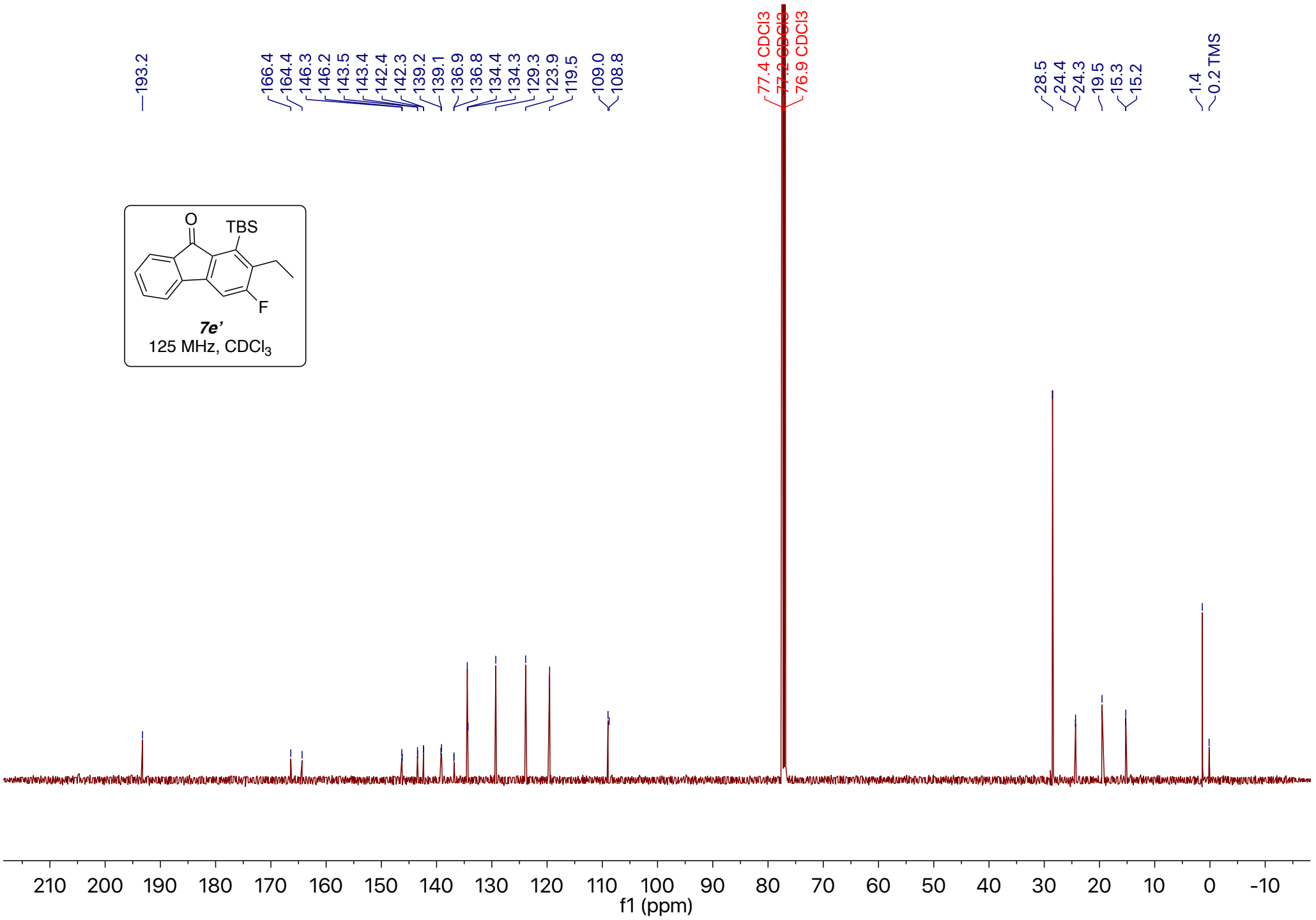

8.11
8.09
7.61
7.59
7.51
7.49
7.48
7.45
7.44
7.42
7.26 CDCl3
2.41
2.40
2.38
2.37
1.22
1.21
1.19
1.01
0.24
0.00 TMS
O
TBS
5e
500 MHz, CDCl3
1.00
1.04
1.07
1.04
2.09
3.07
9.45
6.19
f1 (ppm)

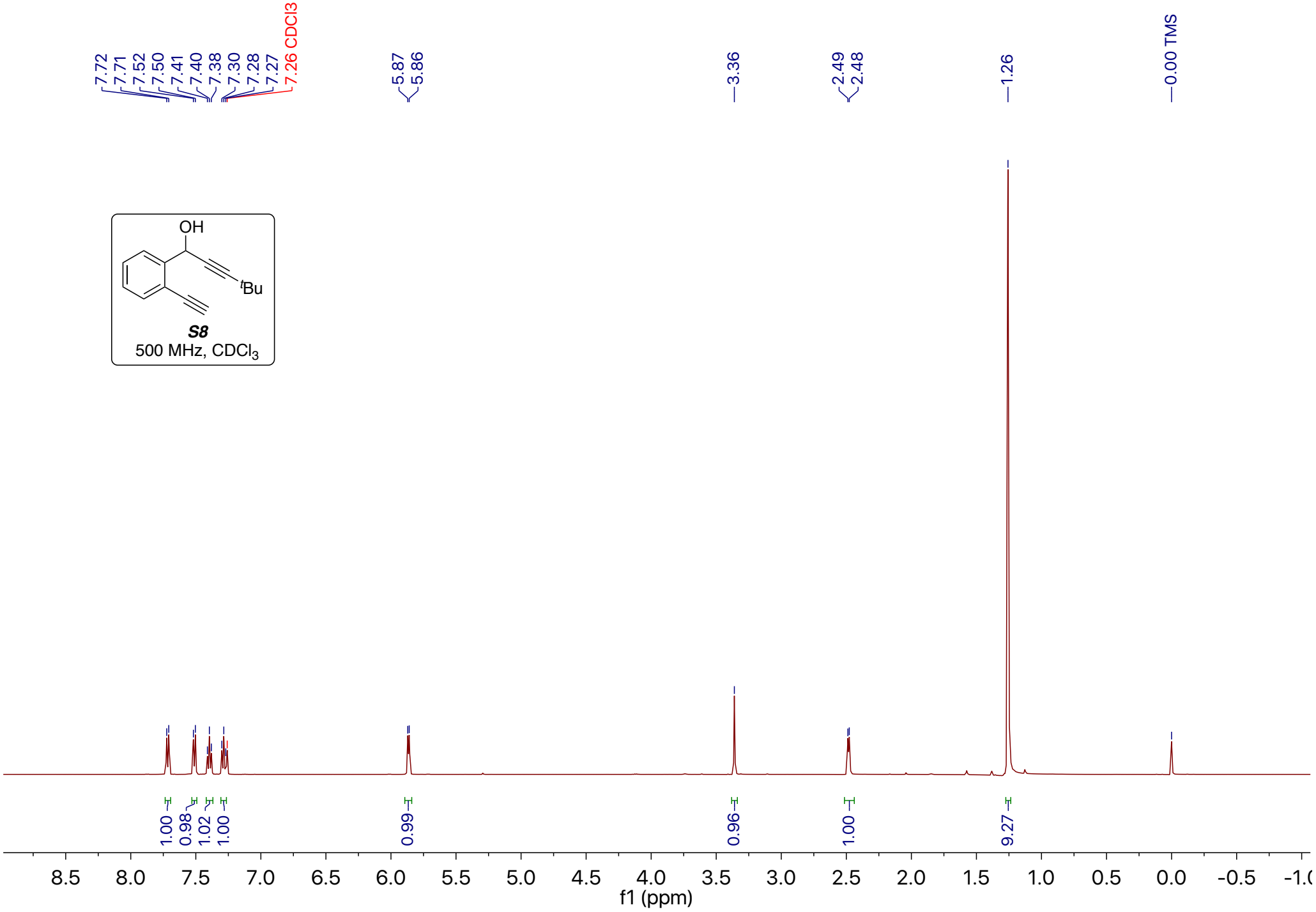

176.5
139.2
135.8
132.6
132.0
128.4
122.2
102.4
100.0
88.4
80.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
73.0
65.1
26.2
16.8
13.6
13.4
-4.9
O
TBS
5e
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

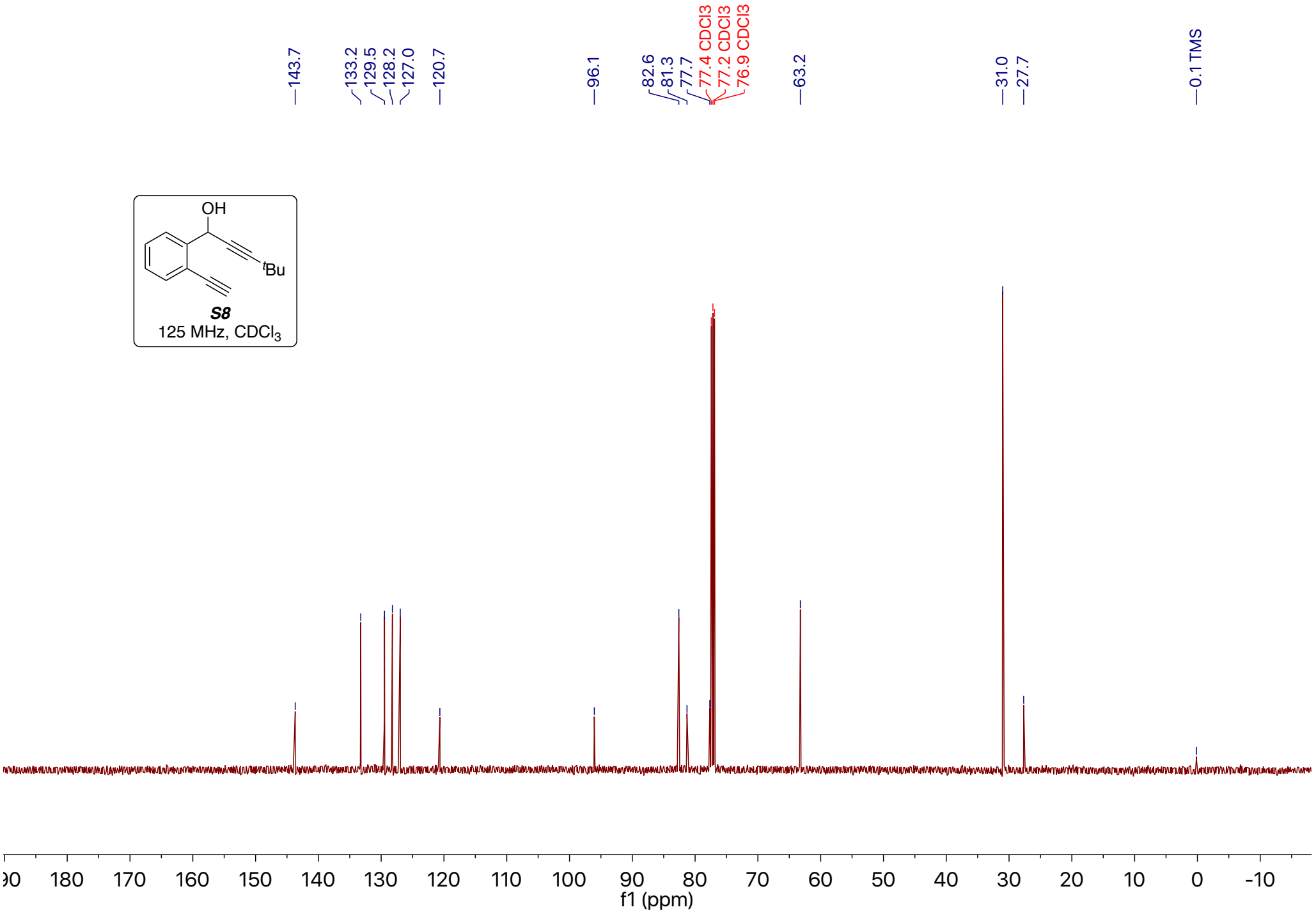

7.55
7.54
7.41
7.41
7.26 CDCl3
7.23
7.22
7.21
7.20
7.19
3.25
3.24
3.23
3.07
3.06
3.05
1.56 HDO
0.93
0.41
0.00 TMS
O
TBS
7e
500 MHz, CDCl3
3.25
3.24
3.23
3.07
3.06
3.05
3.25 3.20 3.15 3.10 3.05 3.00
f1 (ppm)
1.00
2.05
1.15
0.90
2.11
2.09
9.60
6.19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

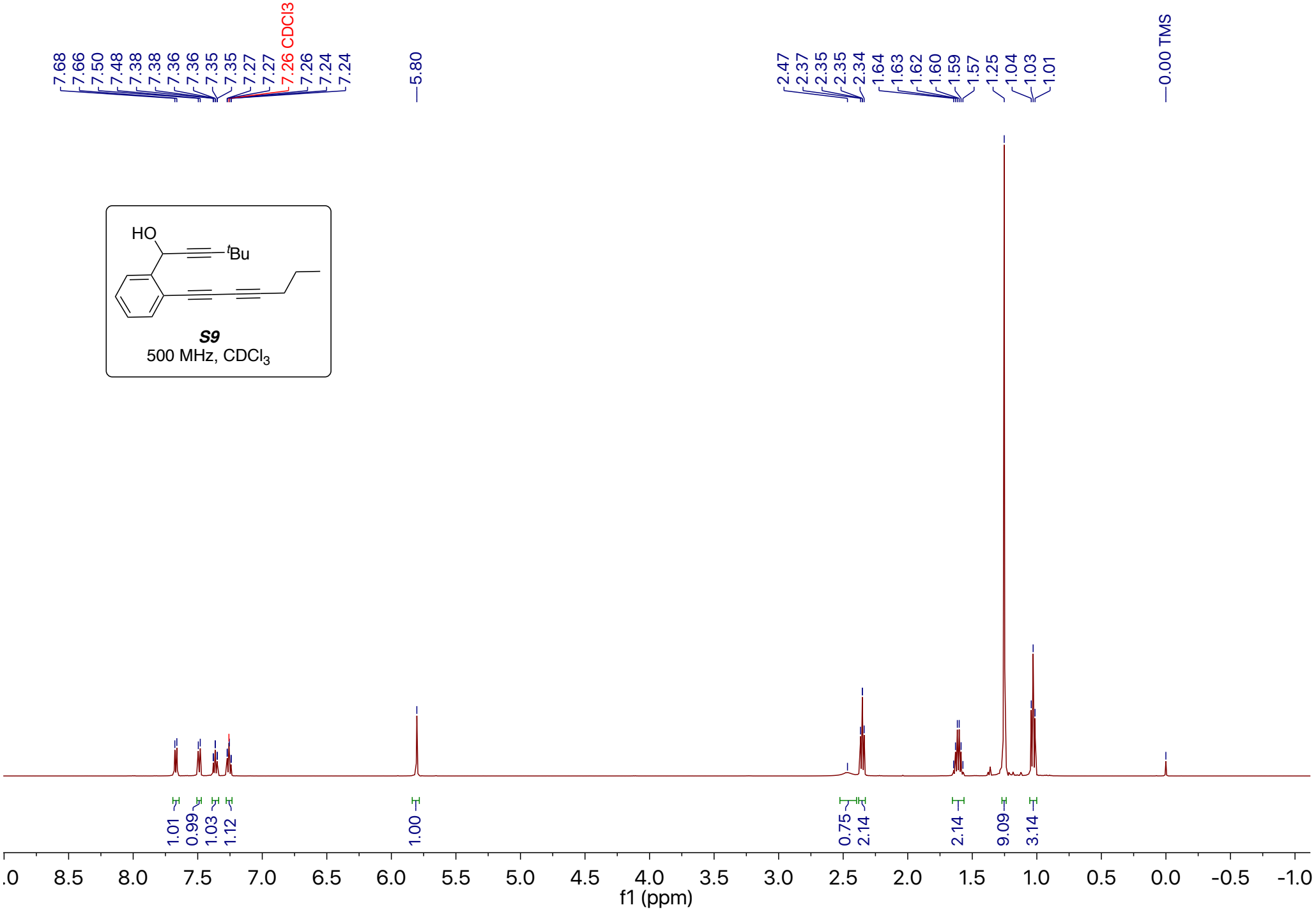

195.1
154.6
151.8
145.2
144.8
138.5
134.4
134.1
133.7
128.6
123.8
119.3
115.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
33.1
28.4
27.4
19.4
0.2 TMS
-2.7
O
TBS
7e
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

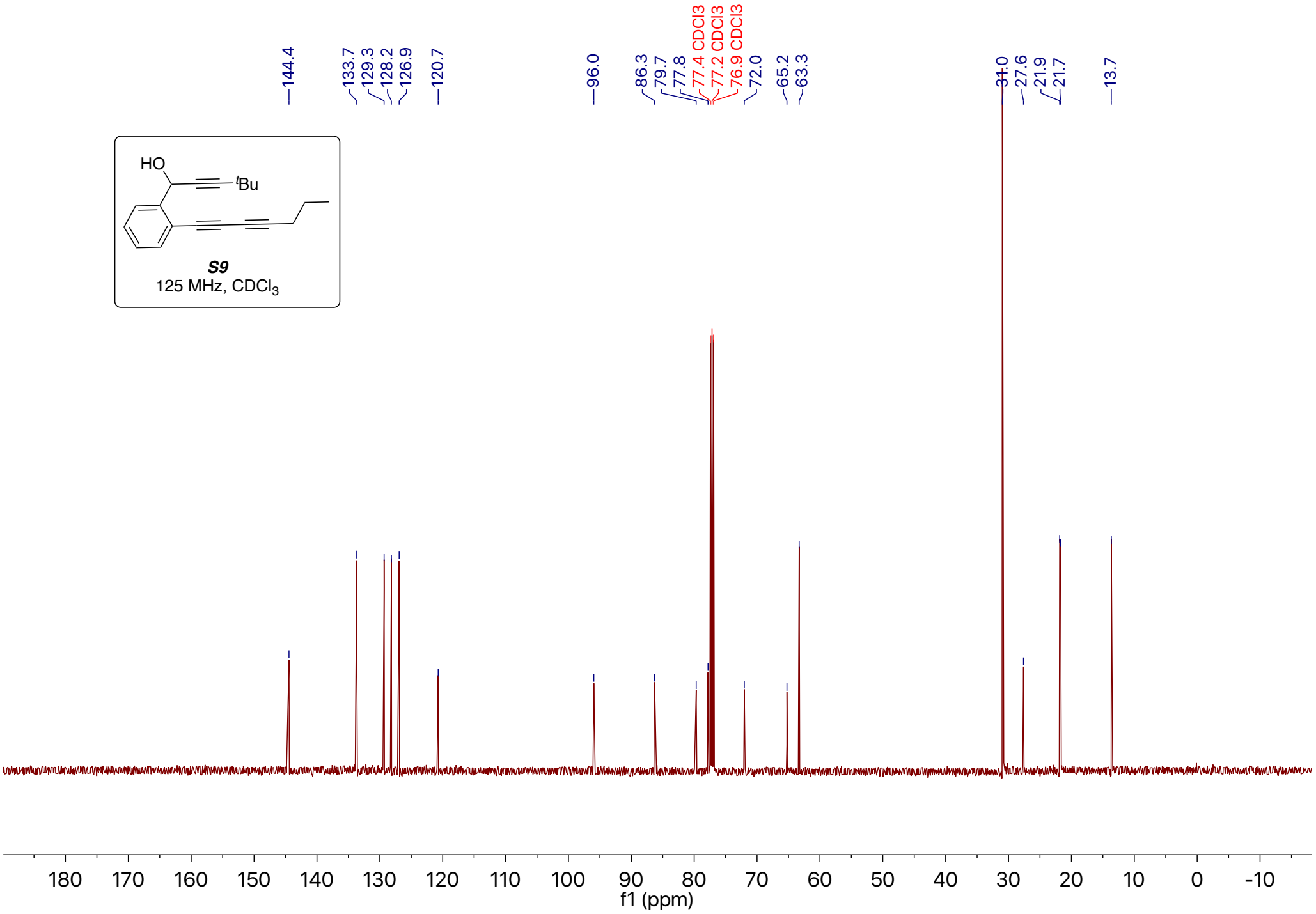

7.57
7.55
7.47
7.45
7.44
7.41
7.40
7.29
7.27
7.26 CDCl3
7.18
7.17
2.84
2.84
2.83
2.82
2.81
2.81
2.80
2.79
1.55 HDO
1.23
1.21
1.20
1.12
1.10
1.06
0.43
0.00 TMS
O
TBS
F
7e'
500 MHz, CDCl3
2.85 2.84 2.83 2.82 2.81 2.80 2.79
f1 (ppm)
1.00
1.04
1.03
1.03
0.98
2.08
2.99
9.02
6.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

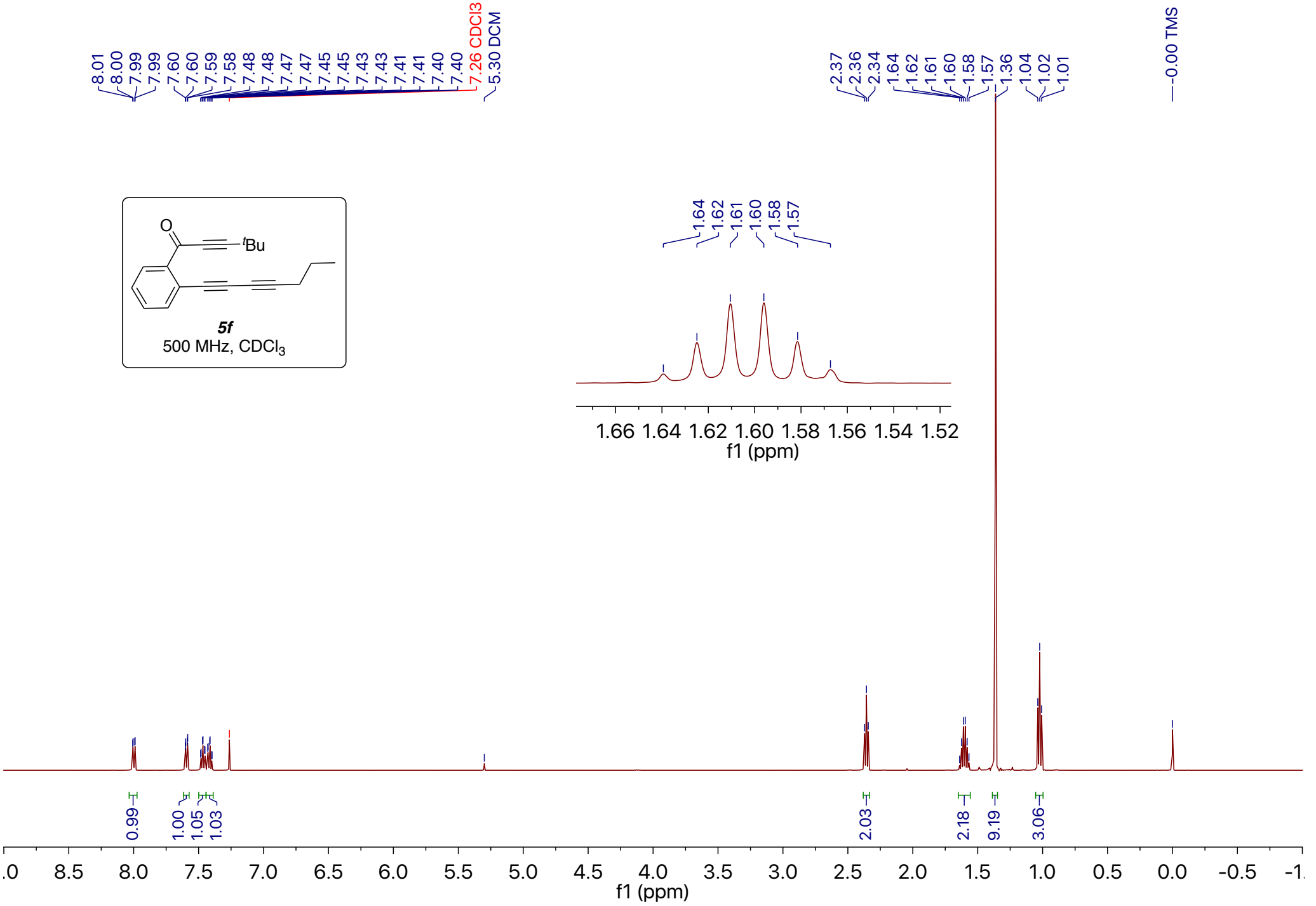

193.2
166.4
164.4
146.3
146.2
143.5
143.4
142.4
142.3
139.2
139.1
136.9
136.8
134.4
134.3
129.3
123.9
119.5
109.0
108.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
28.5
24.4
24.3
19.5
15.3
15.2
1.4
0.2 TMS
O
TBS
F
7e'
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

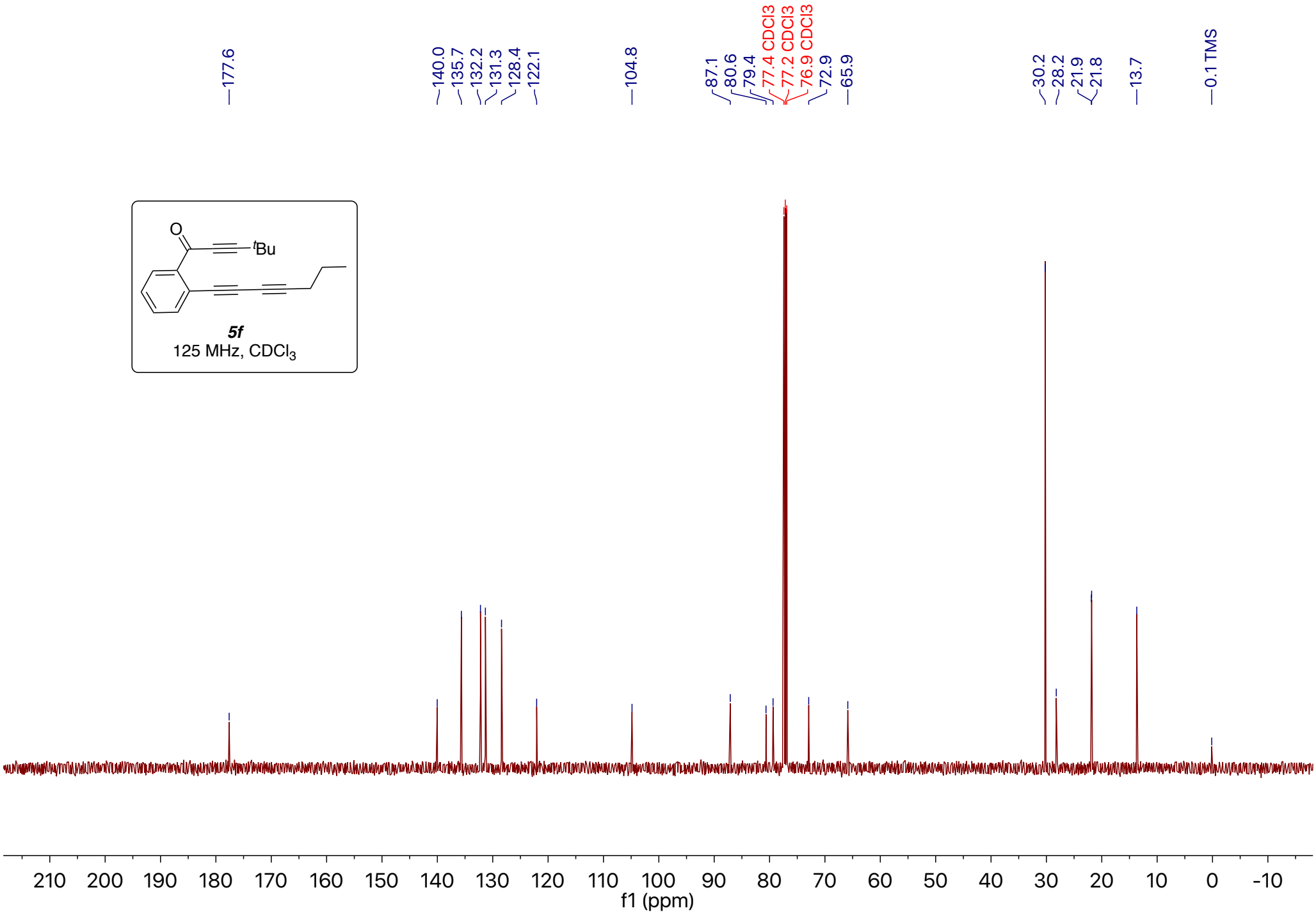

7.72
7.71
7.52
7.50
7.41
7.40
7.38
7.30
7.28
7.27
7.26 CDCl3
5.87
5.86
3.36
2.49
2.48
1.26
0.00 TMS
OH
tBu
S8
500 MHz, CDCl3
1.00
0.98
1.02
1.00
0.99
0.96
1.00
9.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

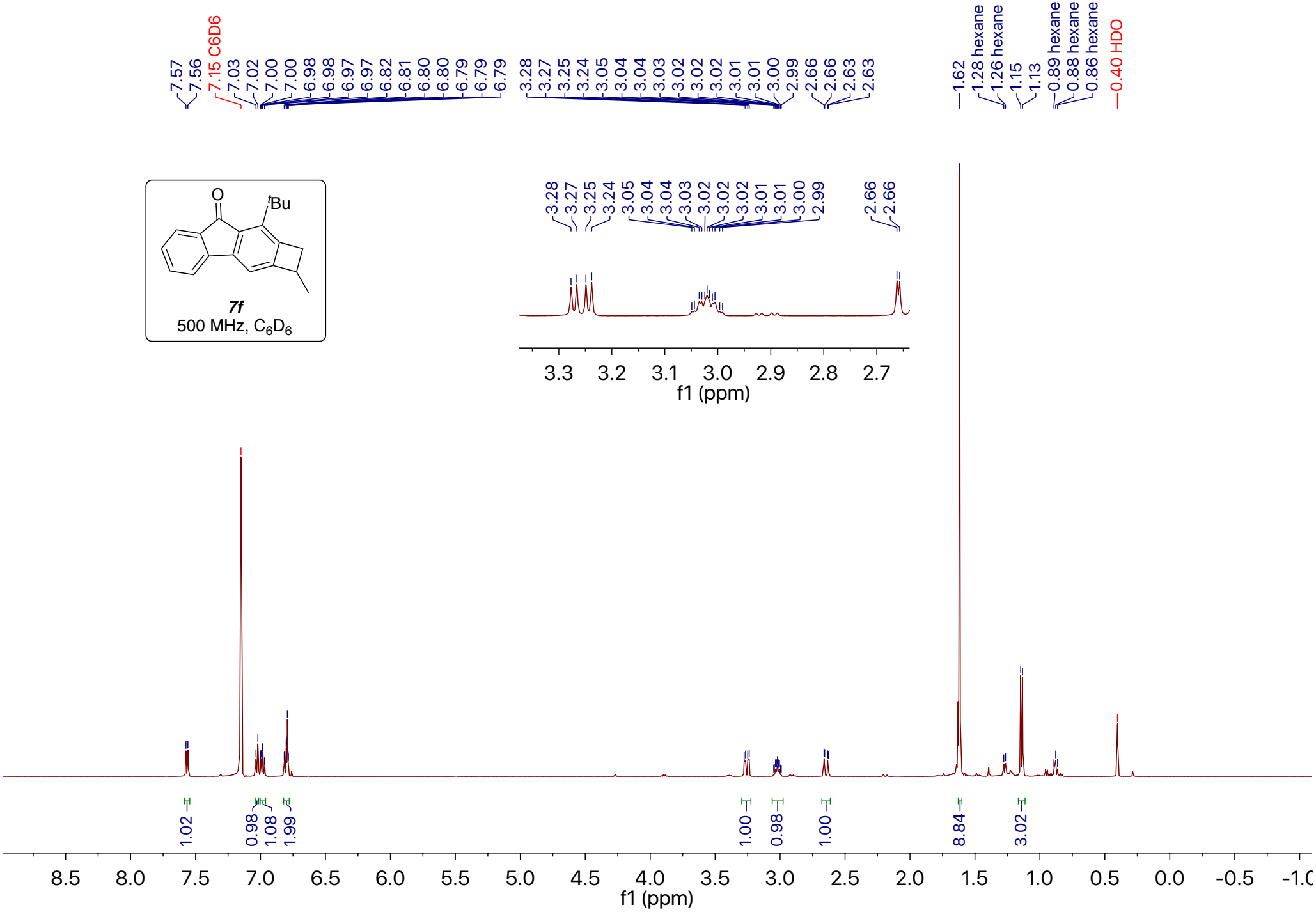

143.7
133.2
129.5
128.2
127.0
120.7
96.1
82.6
81.3
77.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
63.2
31.0
27.7
0.1 TMS
OH
tBu
S8
125 MHz, CDCl3
f1 (ppm)

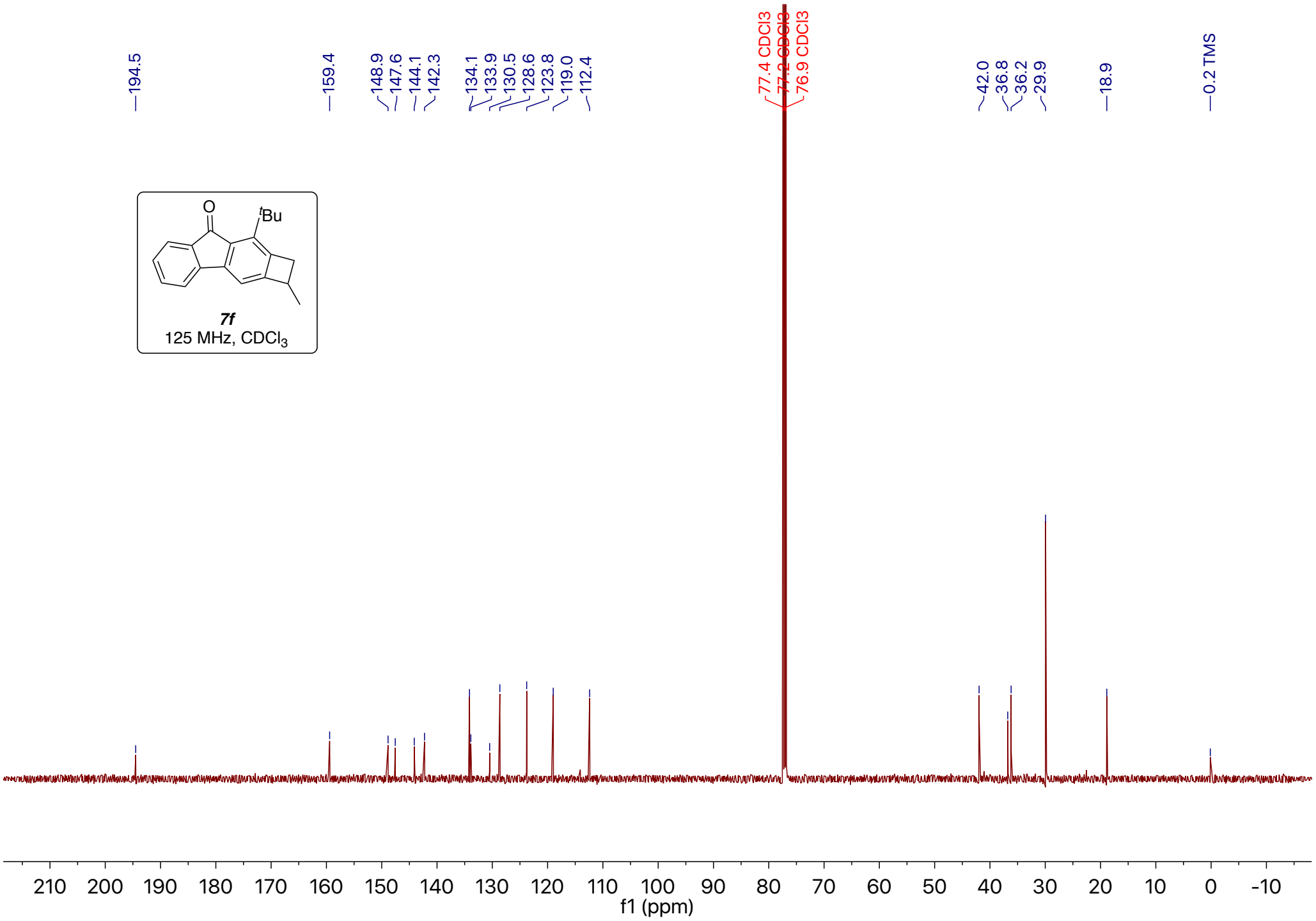

7.68
7.66
7.50
7.48
7.38
7.38
7.36
7.36
7.35
7.35
7.27
7.27
7.26 CDCl3
7.26
7.24
7.24
5.80
2.47
2.37
2.35
2.35
2.34
1.64
1.63
1.62
1.60
1.59
1.57
1.25
1.04
1.03
1.01
0.00 TMS
HO
tBu
S9
500 MHz, CDCl3
1.01
0.99
1.03
1.12
1.00
0.75
2.14
2.14
9.09
3.14
f1 (ppm)

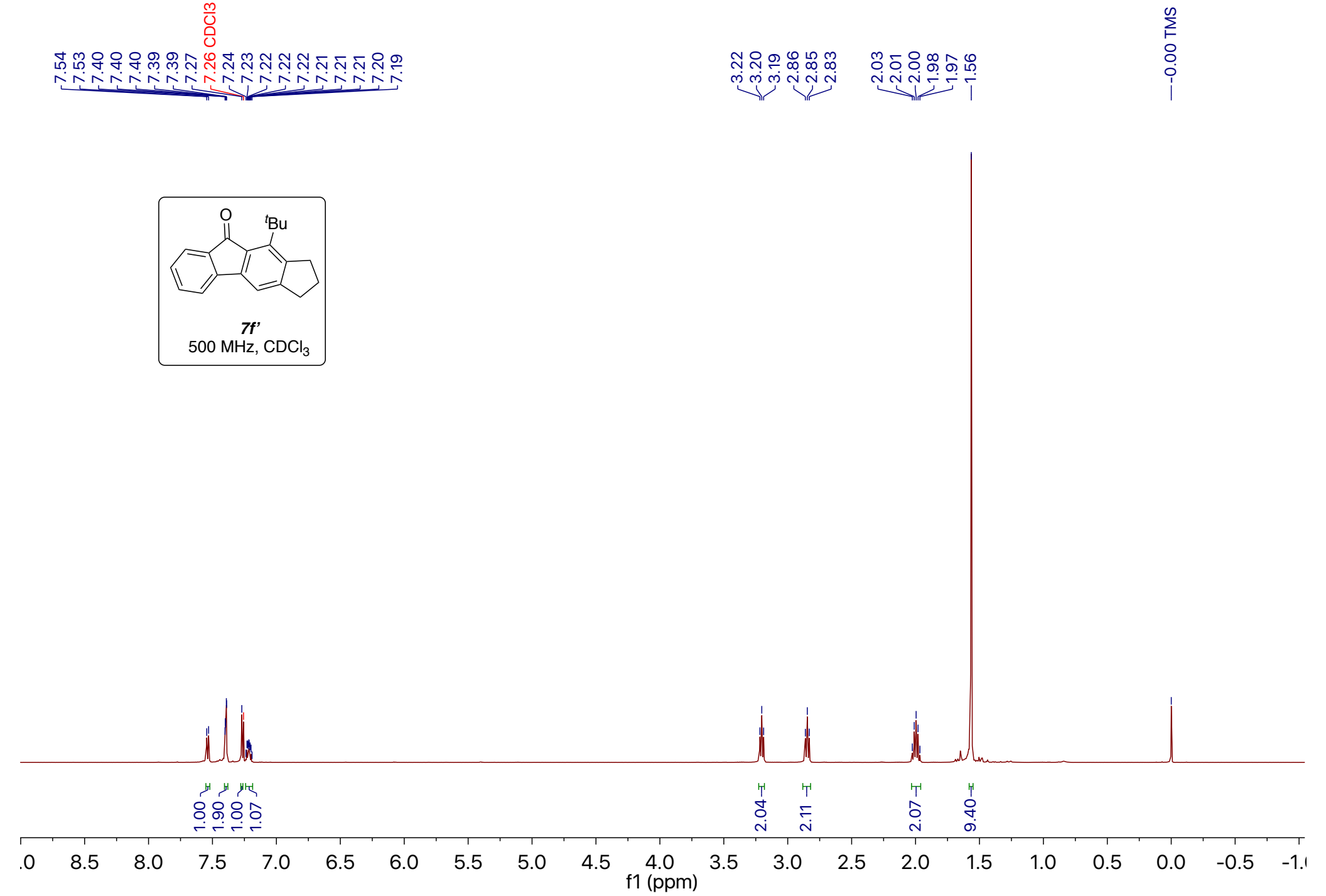

144.4
133.7
129.3
128.2
126.9
120.7
96.0
86.3
79.7
77.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.0
65.2
63.3
31.0
27.6
21.9
21.7
13.7
HO
tBu
S9
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

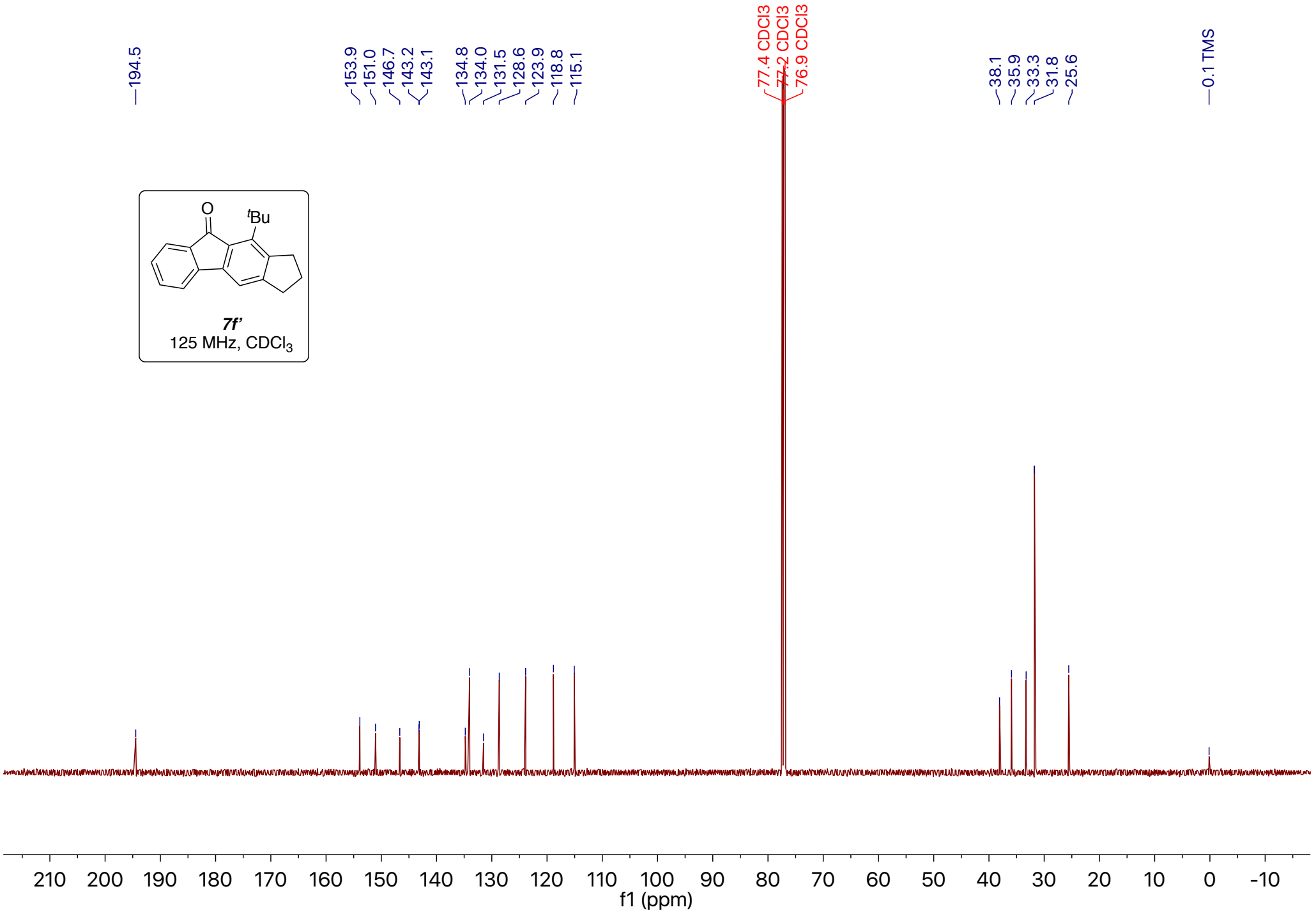

8.01
8.00
7.99
7.99
7.60
7.60
7.59
7.58
7.48
7.48
7.47
7.47
7.45
7.45
7.43
7.43
7.41
7.41
7.40
7.40
7.26 CDCl3
5.30 DCM
2.37
2.36
2.34
1.64
1.62
1.61
1.60
1.58
1.57
1.36
1.04
1.02
1.01
-0.00 TMS
O
tBu
5f
500 MHz, CDCl3
1.64
1.62
1.61
1.60
1.58
1.57
1.66 1.64 1.62 1.60 1.58 1.56 1.54 1.52
f1 (ppm)
0.99
1.00
1.05
1.03
2.03
2.18
9.19
3.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

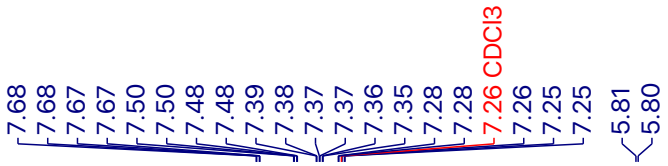

177.6
140.0
135.7
132.2
131.3
128.4
122.1
104.8
87.1
80.6
79.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.9
65.9
30.2
28.2
21.9
21.8
13.7
0.1 TMS
O
tBu
5f
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

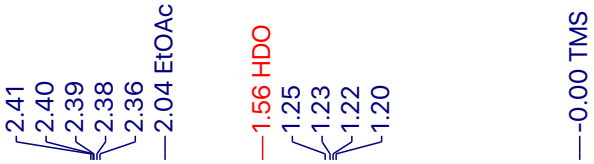

7.57
7.56
7.15 C6D6
7.03
7.02
7.00
7.00
6.98
6.98
6.97
6.97
6.82
6.81
6.80
6.80
6.79
6.79
6.79
3.28
3.27
3.25
3.24
3.05
3.04
3.04
3.03
3.02
3.02
3.02
3.01
3.01
3.00
2.99
2.66
2.66
2.63
2.63
1.62
1.28 hexane
1.26 hexane
1.15
1.13
0.89 hexane
0.88 hexane
0.86 hexane
0.40 HDO
O
tBu
7f
500 MHz, C6D6
f1 (ppm)
1.02
0.98
1.08
1.99
1.00
0.98
1.00
8.84
3.02
f1 (ppm)

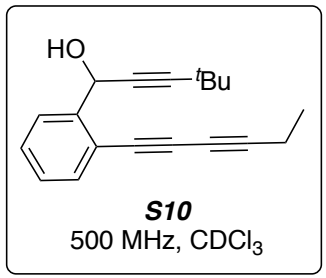

194.5
159.4
148.9
147.6
144.1
142.3
134.1
133.9
130.5
128.6
123.8
119.0
112.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
42.0
36.8
36.2
29.9
18.9
0.2 TMS
O
tBu
7f
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.54
7.53
7.40
7.40
7.40
7.39
7.39
7.27
7.26 CDCl3
7.24
7.23
7.22
7.22
7.22
7.21
7.21
7.21
7.20
7.19
3.22
3.20
3.19
2.86
2.85
2.83
2.03
2.01
2.00
1.98
1.97
1.56
0.00 TMS
O
tBu
7f'
500 MHz, CDCl3
1.00
1.90
1.00
1.07
2.04
2.11
2.07
9.40
f1 (ppm)

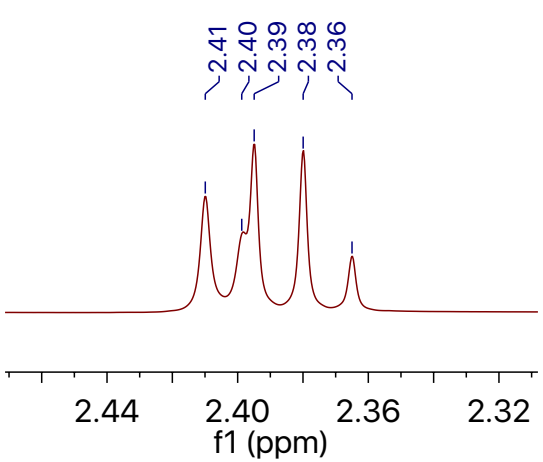

194.5
153.9
151.0
146.7
143.2
143.1
134.8
134.0
131.5
128.6
123.9
118.8
115.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
38.1
35.9
33.3
31.8
25.6
0.1 TMS
O
tBu
7f'
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

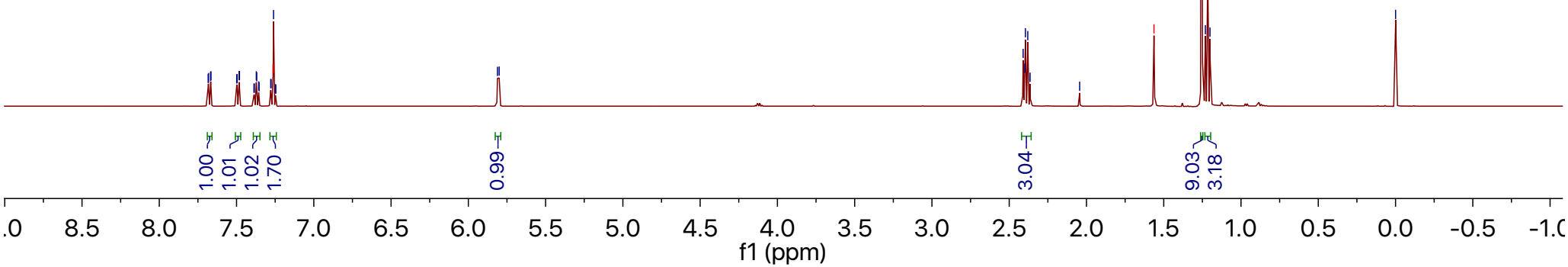


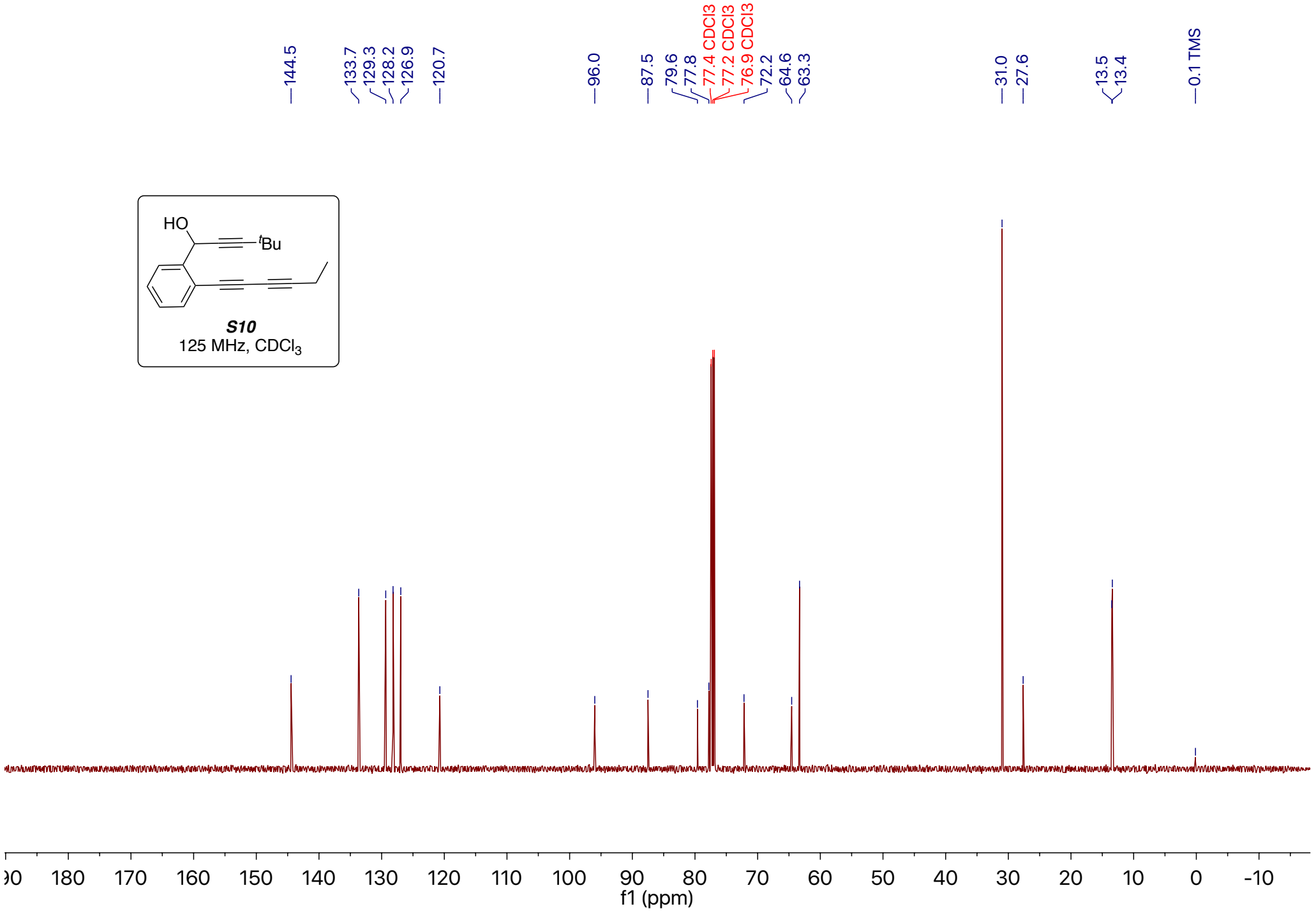


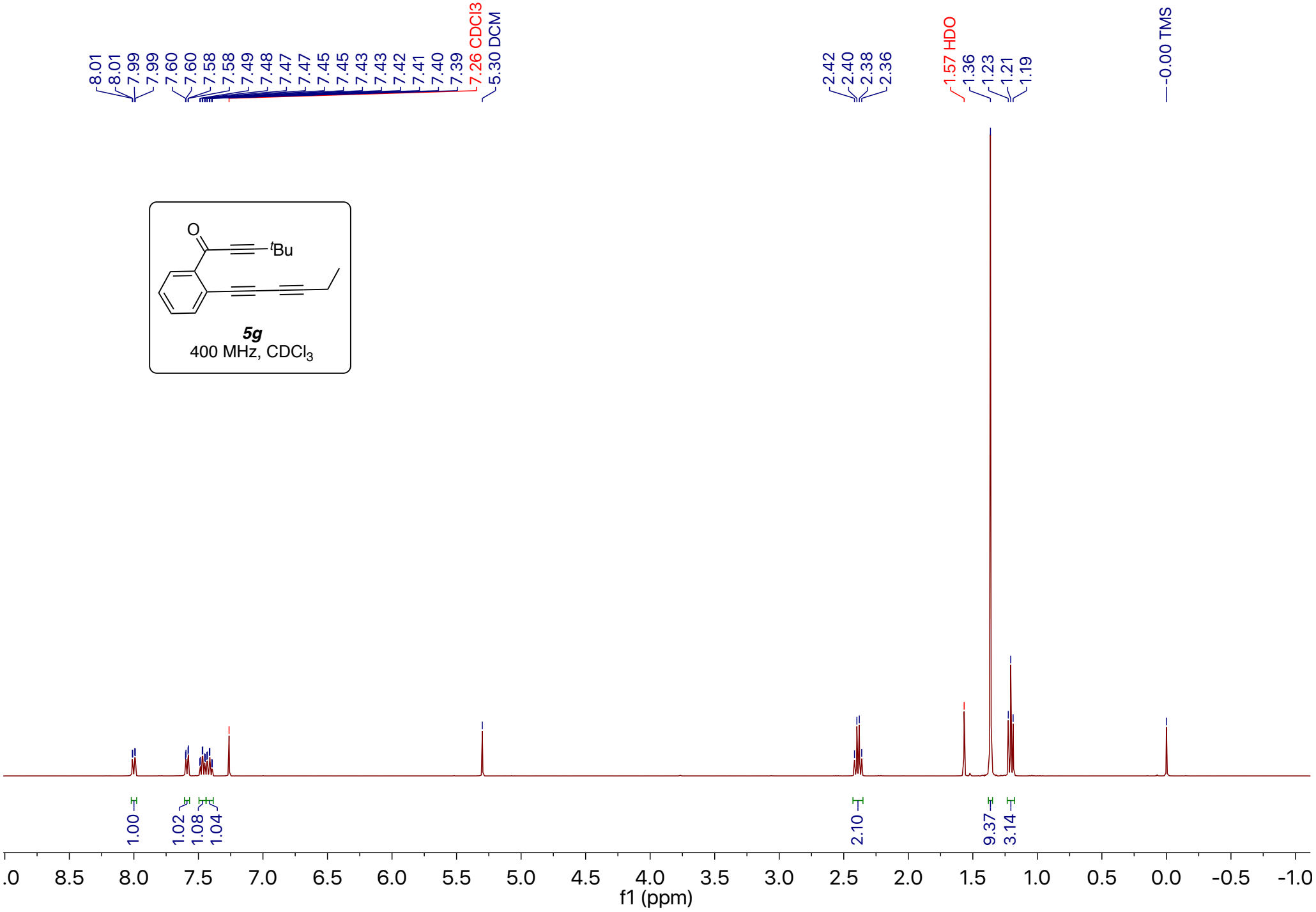


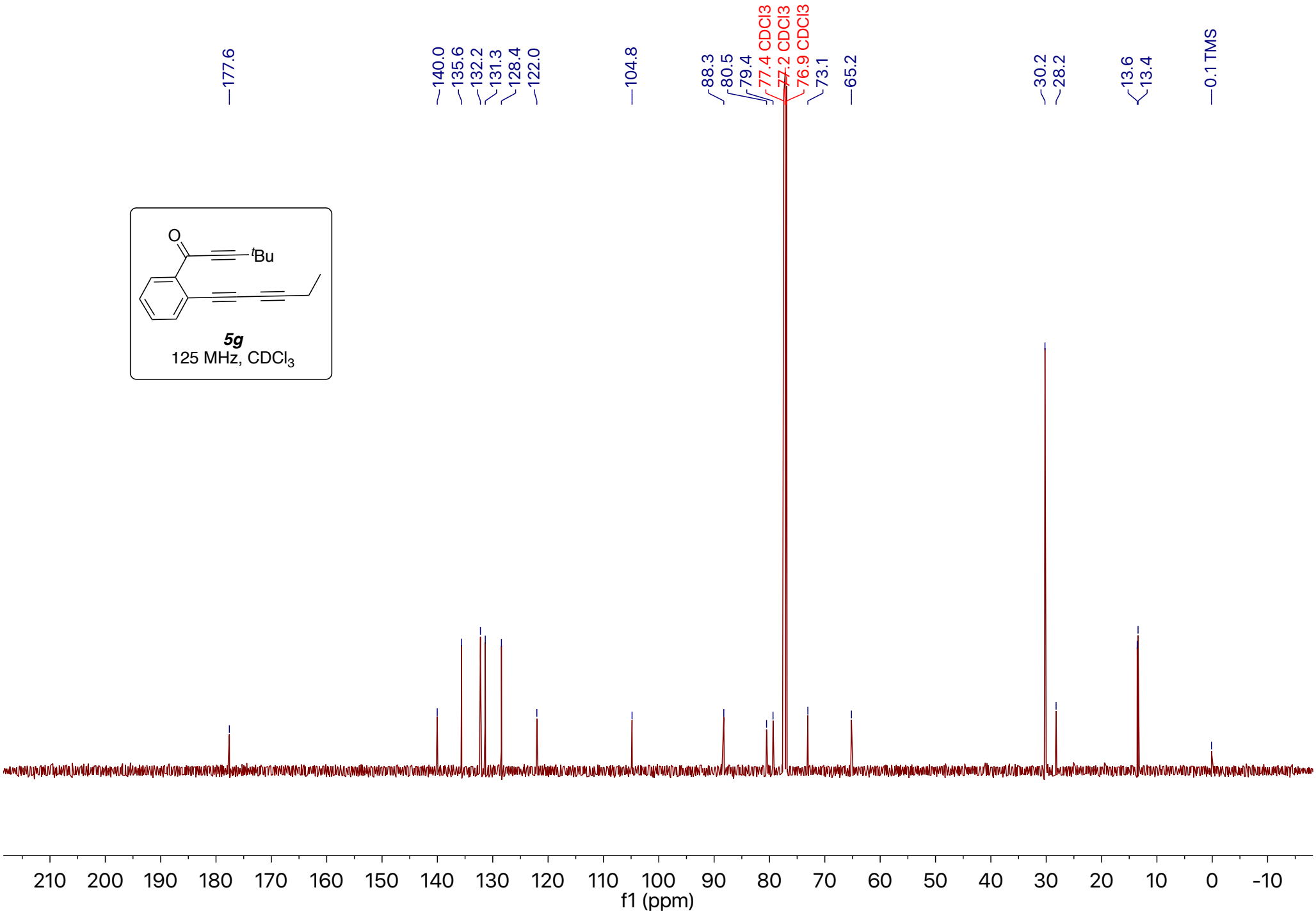
S10
500 MHz, $CDCl_3$

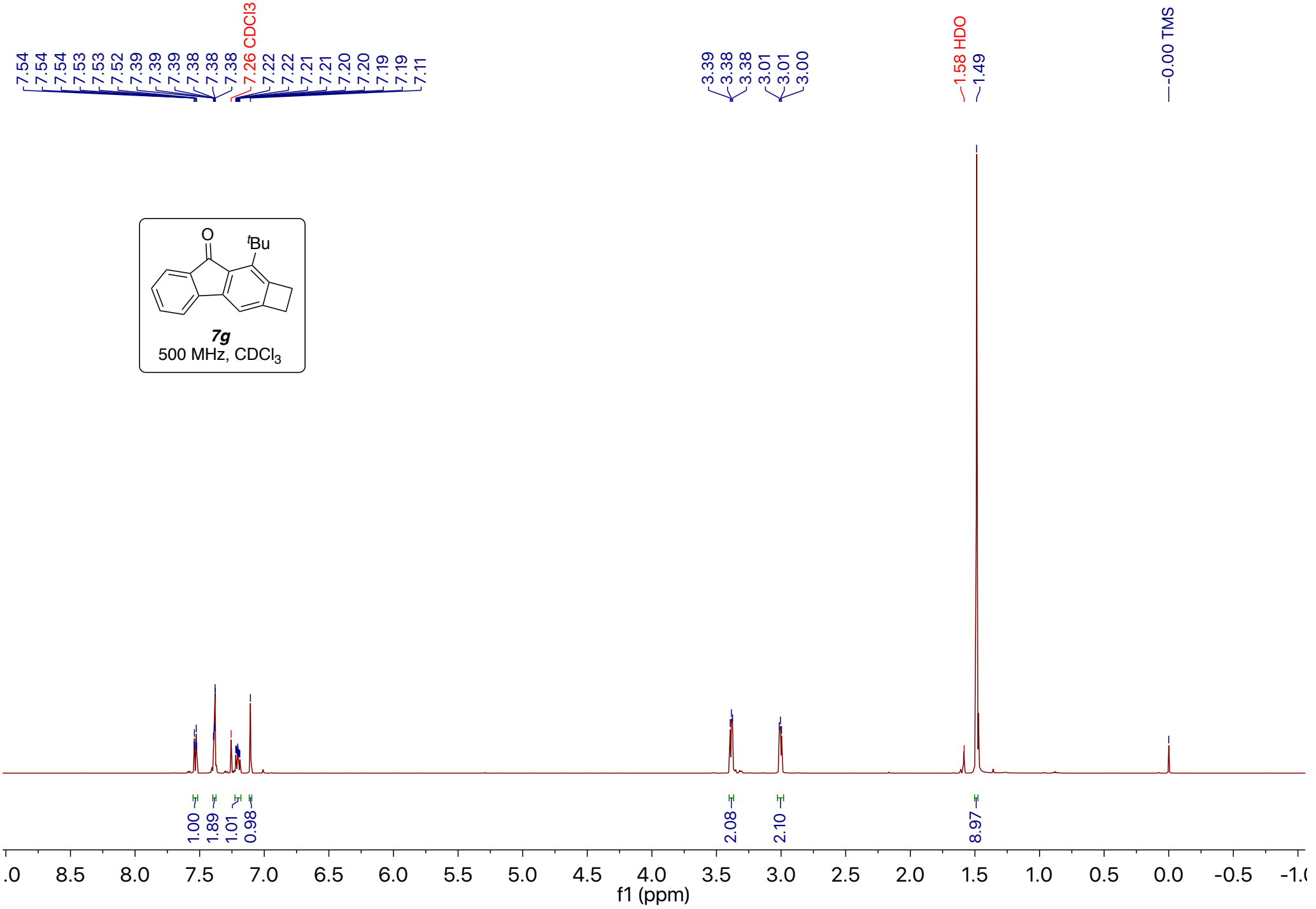


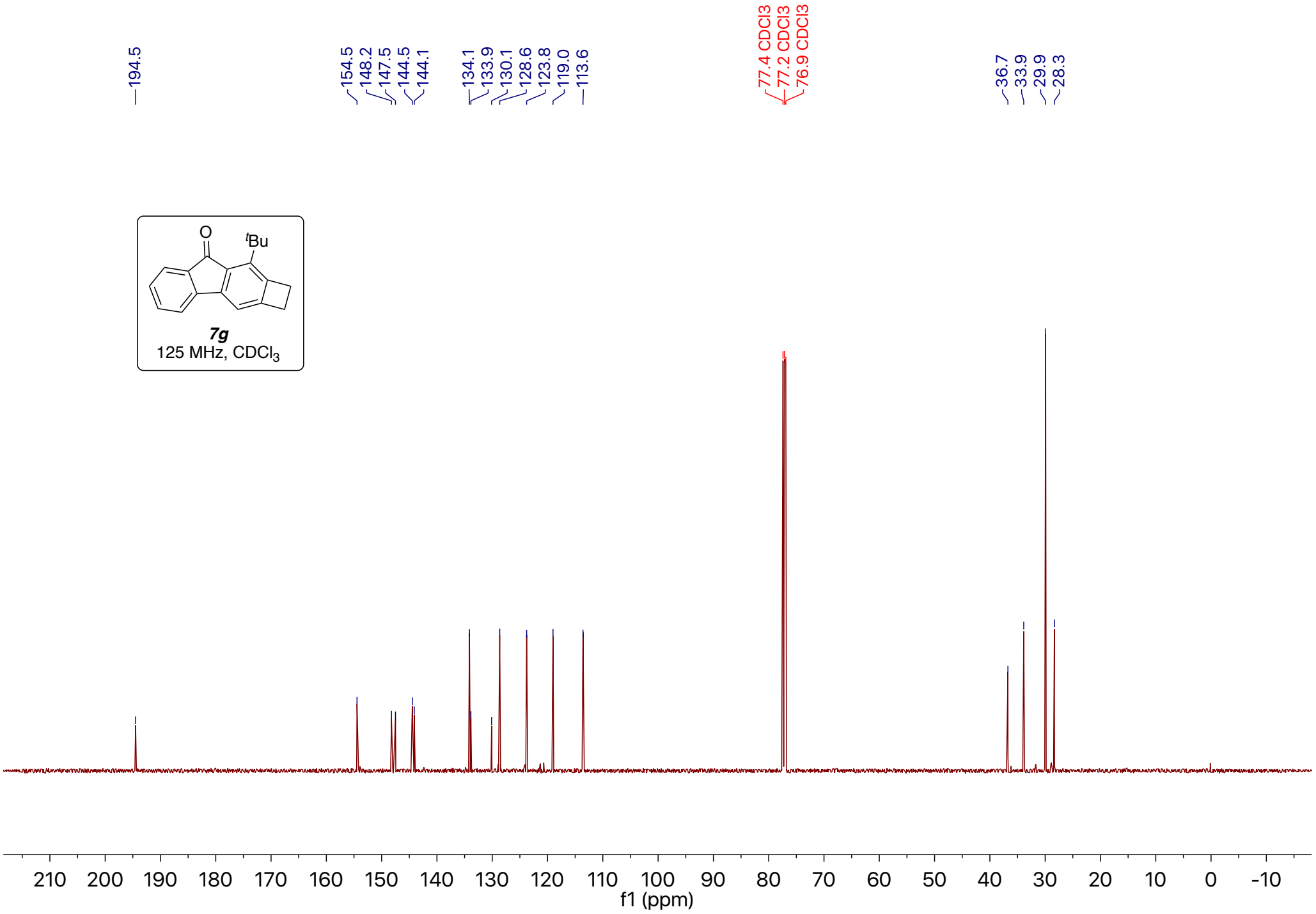


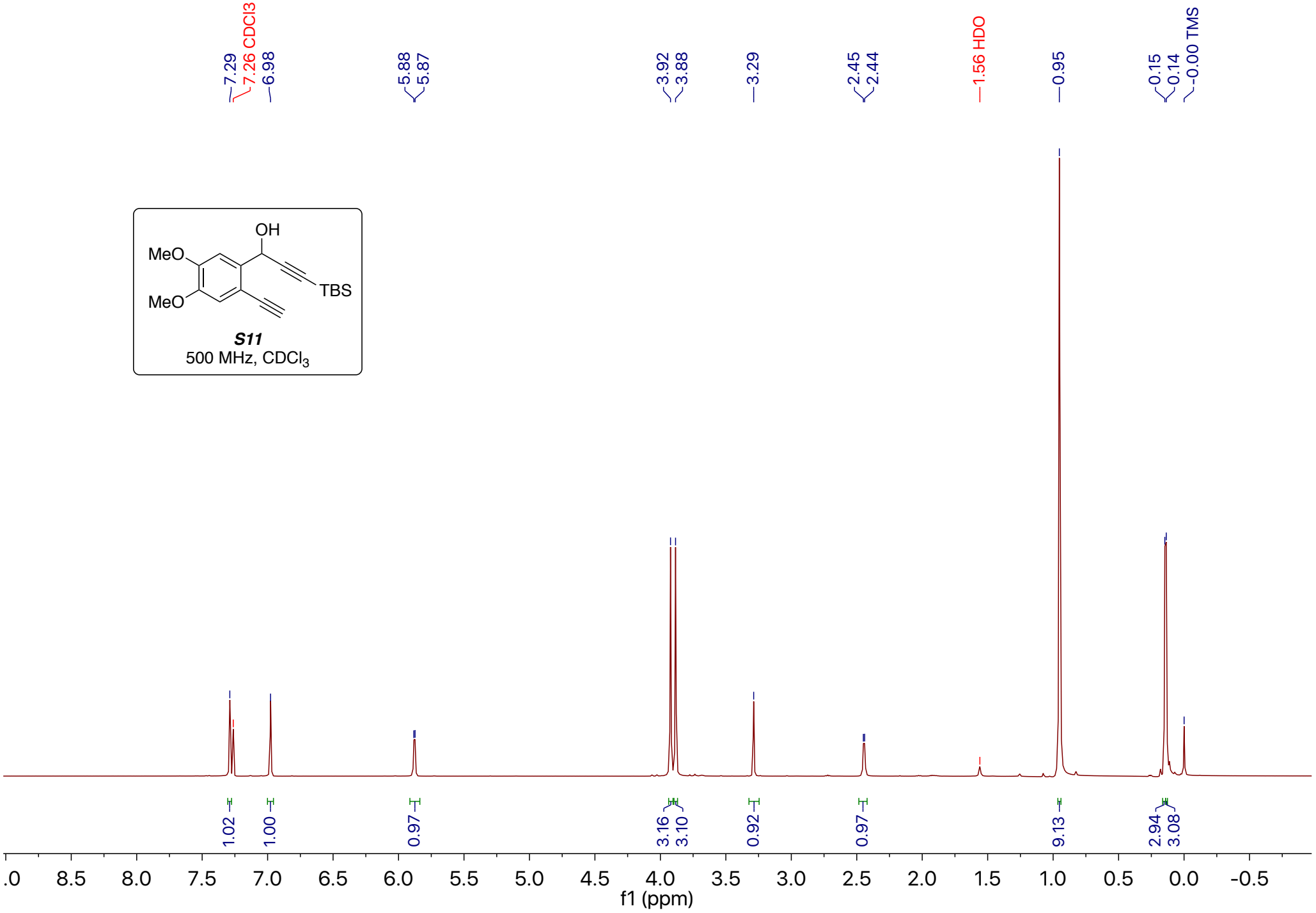

144.5
133.7
129.3
128.2
126.9
120.7
96.0
87.5
79.6
77.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.2
64.6
63.3
31.0
27.6
13.5
13.4
0.1 TMS
HO
tBu
S10
125 MHz, CDCl3
f1 (ppm)

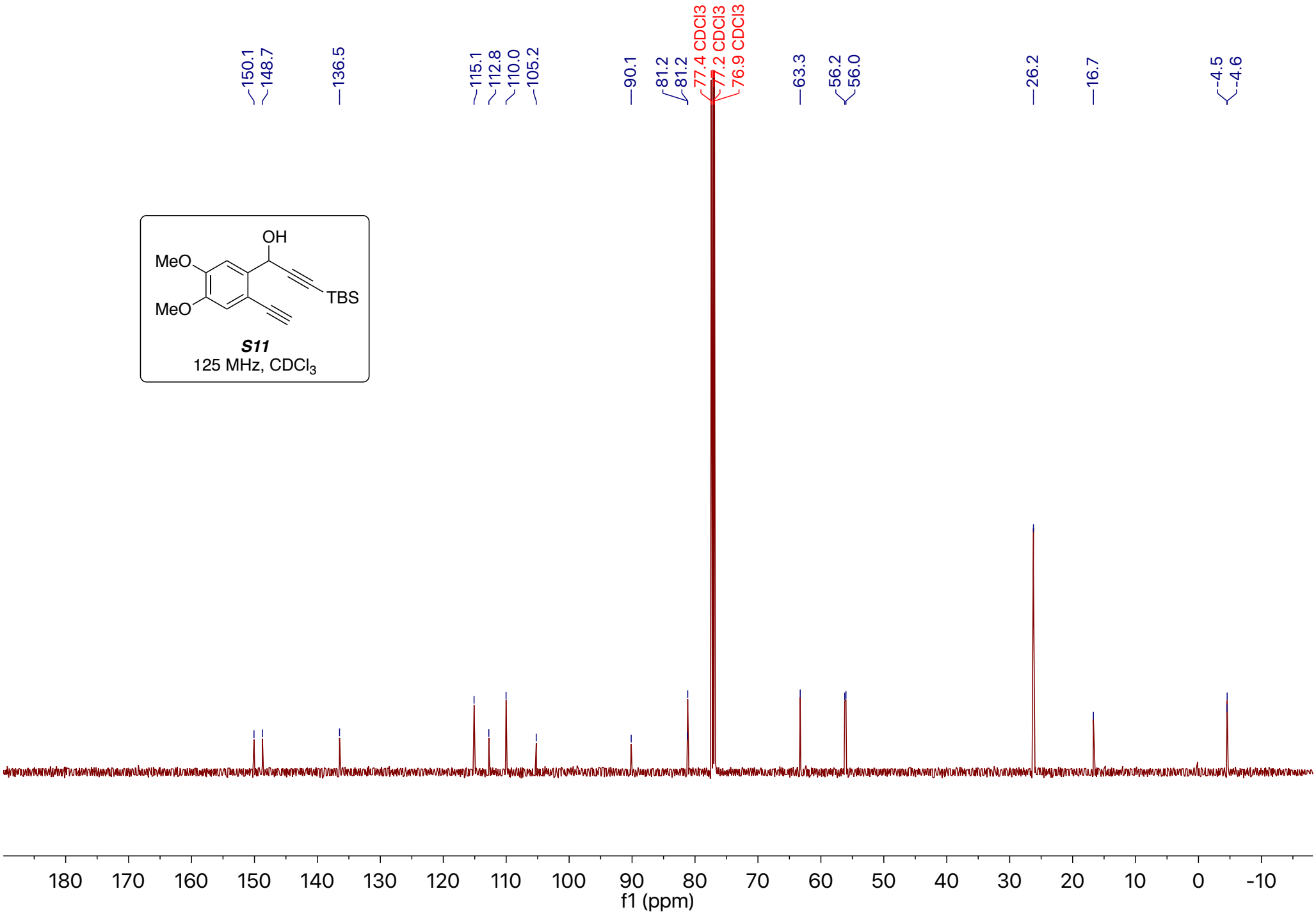

8.01
8.01
7.99
7.99
7.60
7.60
7.58
7.58
7.49
7.48
7.47
7.47
7.45
7.45
7.43
7.43
7.42
7.41
7.40
7.39
7.26 CDCl3
5.30 DCM
2.42
2.40
2.38
2.36
1.57 HDO
1.36
1.23
1.21
1.19
-0.00 TMS
O
tBu
5g
400 MHz, CDCl3
1.00
1.02
1.08
1.04
2.10
9.37
3.14
f1 (ppm)

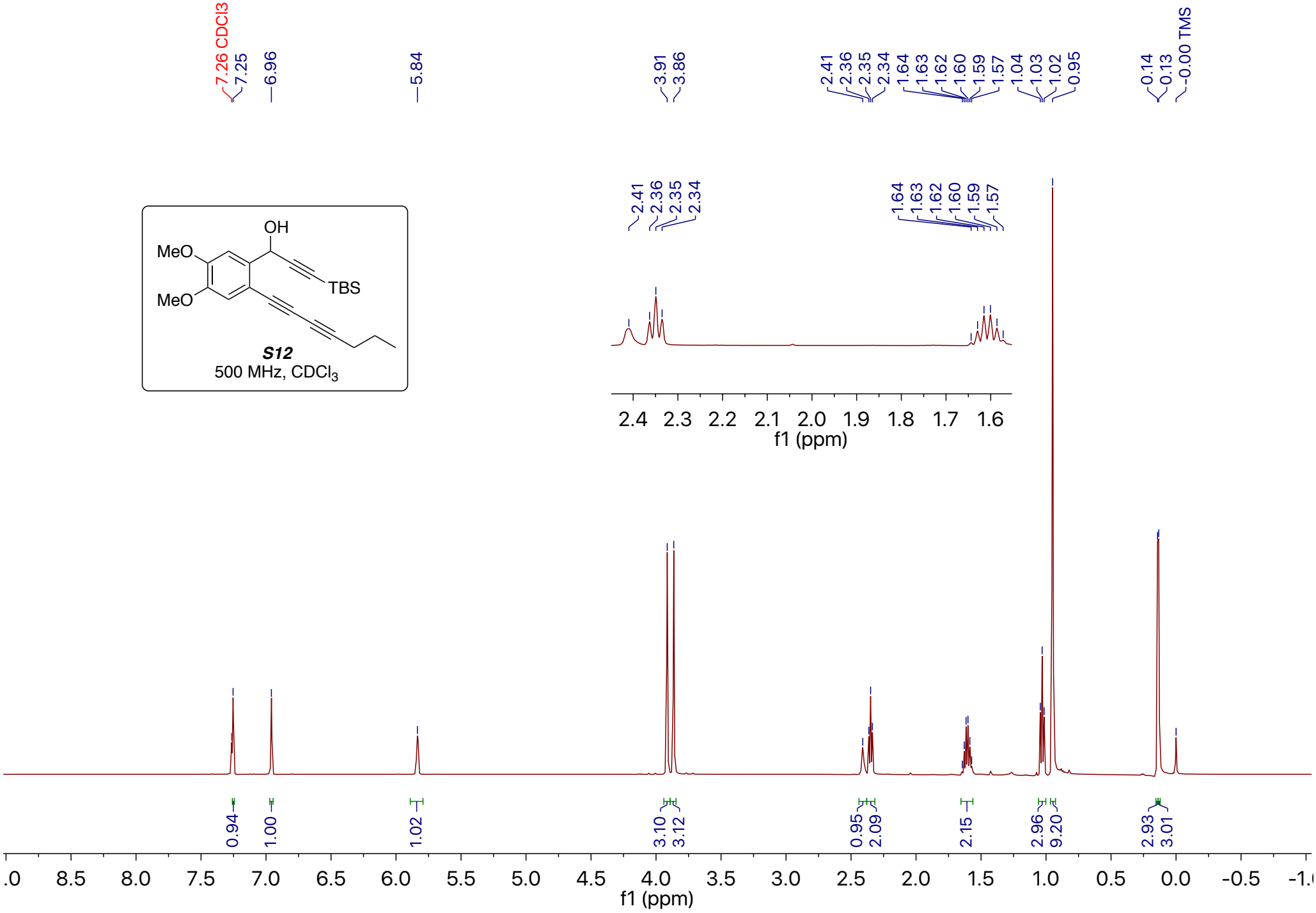

177.6
140.0
135.6
132.2
131.3
128.4
122.0
104.8
88.3
80.5
79.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
73.1
65.2
30.2
28.2
13.6
13.4
0.1 TMS
O
tBu
5g
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

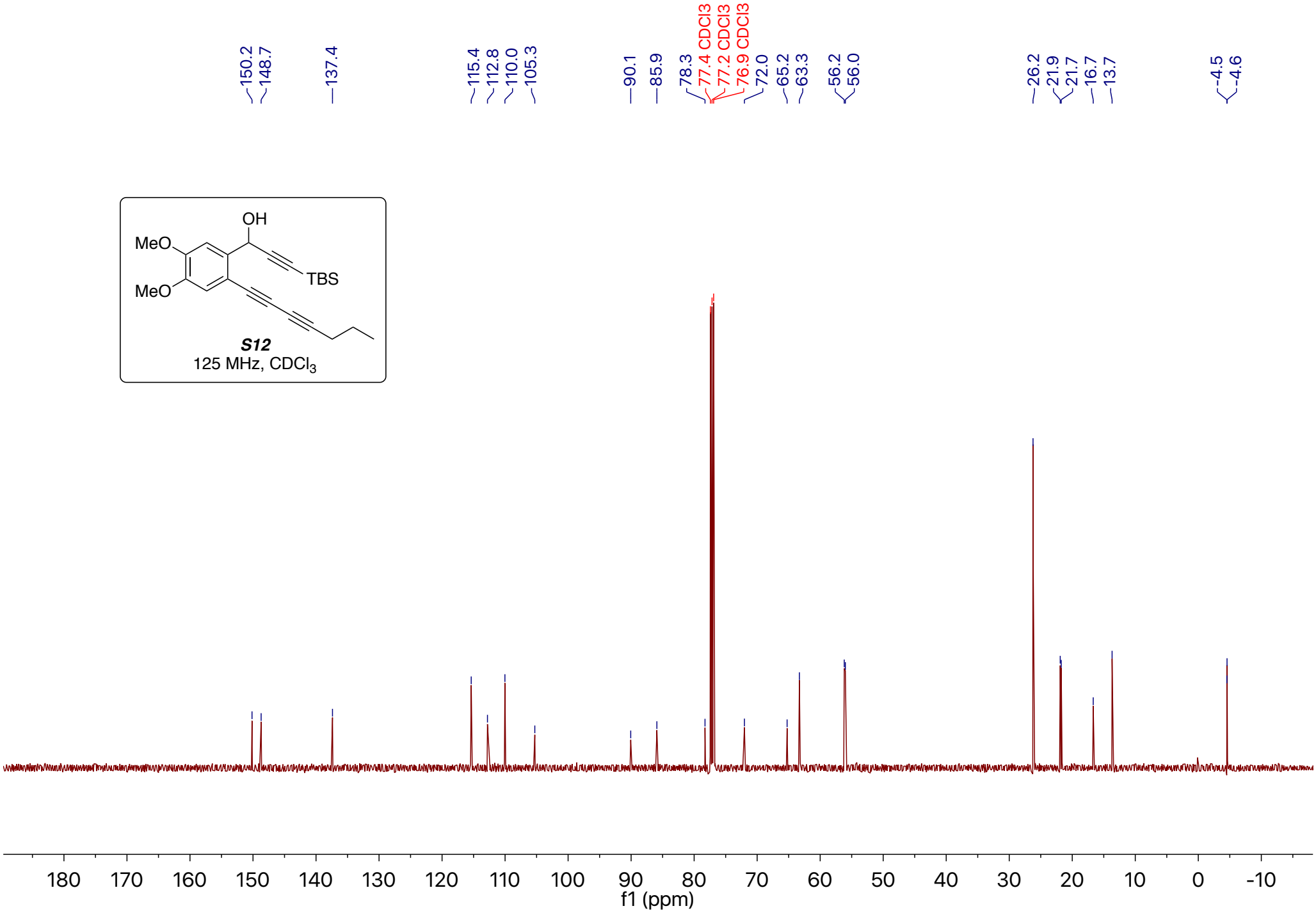

7.54
7.54
7.54
7.53
7.53
7.52
7.39
7.39
7.39
7.38
7.38
7.38
7.26 CDCl3
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.11
3.39
3.38
3.38
3.01
3.01
3.00
1.58 HDO
1.49
0.00 TMS
O
tBu
7g
500 MHz, CDCl3
1.00
1.89
1.01
0.98
2.08
2.10
8.97
f1 (ppm)

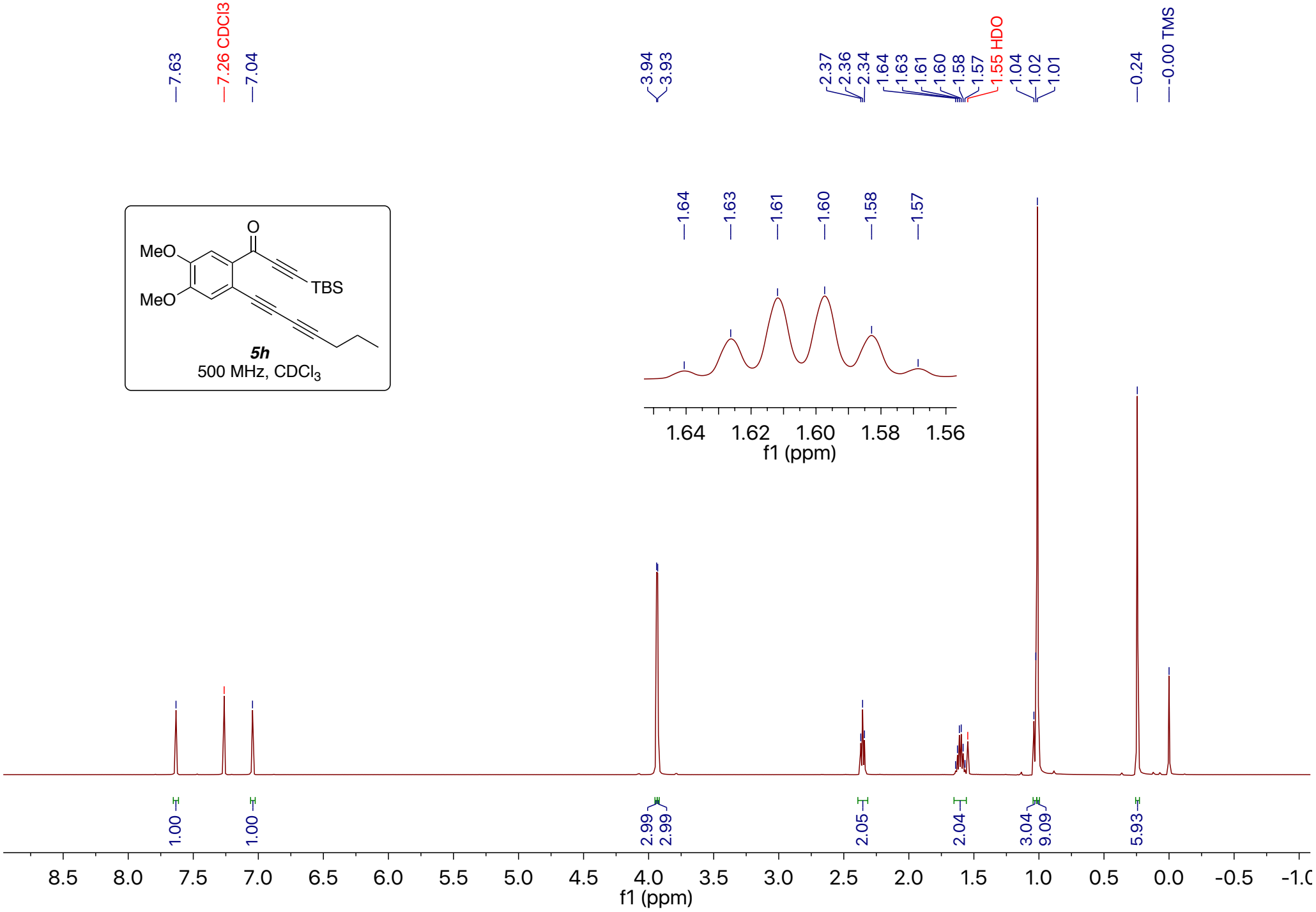

194.5
154.5
148.2
147.5
144.5
144.1
134.1
133.9
130.1
128.6
123.8
119.0
113.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
36.7
33.9
29.9
28.3
O
tBu
7g
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

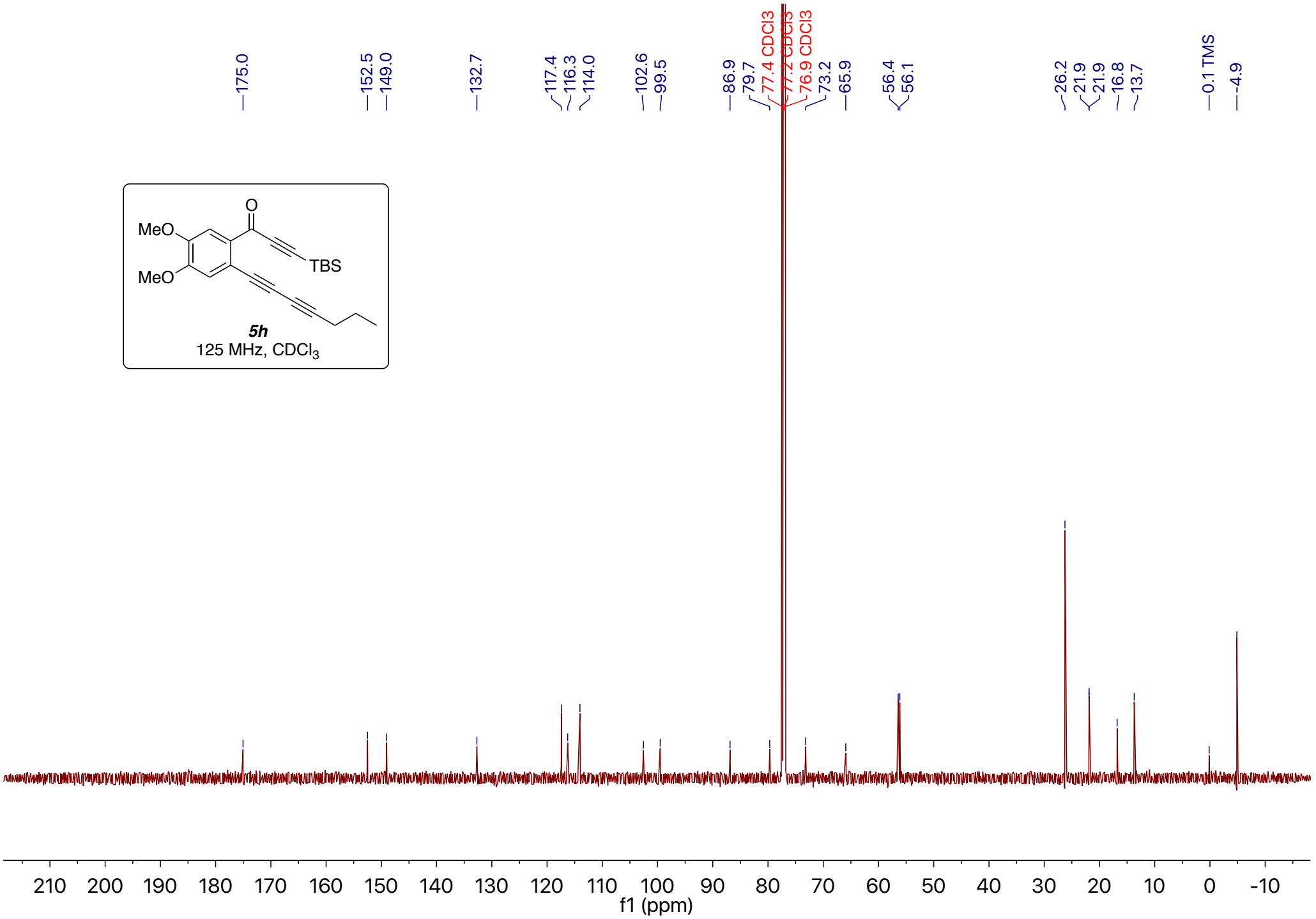

7.29
7.26 CDCl3
6.98
5.88
5.87
3.92
3.88
3.29
2.45
2.44
1.56 HDO
0.95
0.15
0.14
-0.00 TMS
OH
MeO
MeO
TBS
S11
500 MHz, CDCl3
1.02
1.00
0.97
3.16
3.10
0.92
0.97
9.13
2.94
3.08
f1 (ppm)

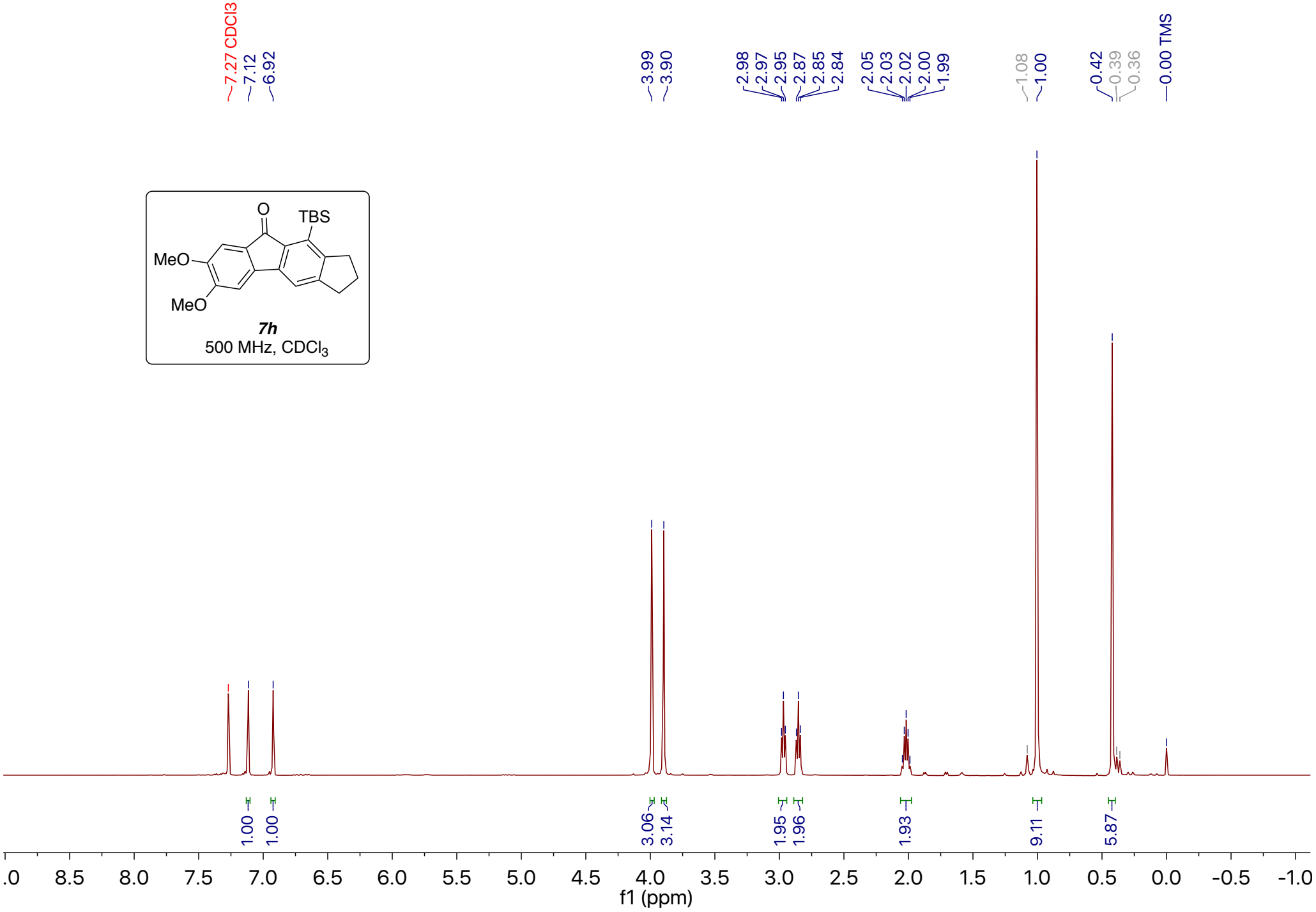

150.1
148.7
136.5
115.1
112.8
110.0
105.2
90.1
81.2
81.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
63.3
56.2
56.0
26.2
16.7
-4.5
-4.6
OH
MeO
MeO
TBS
S11
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

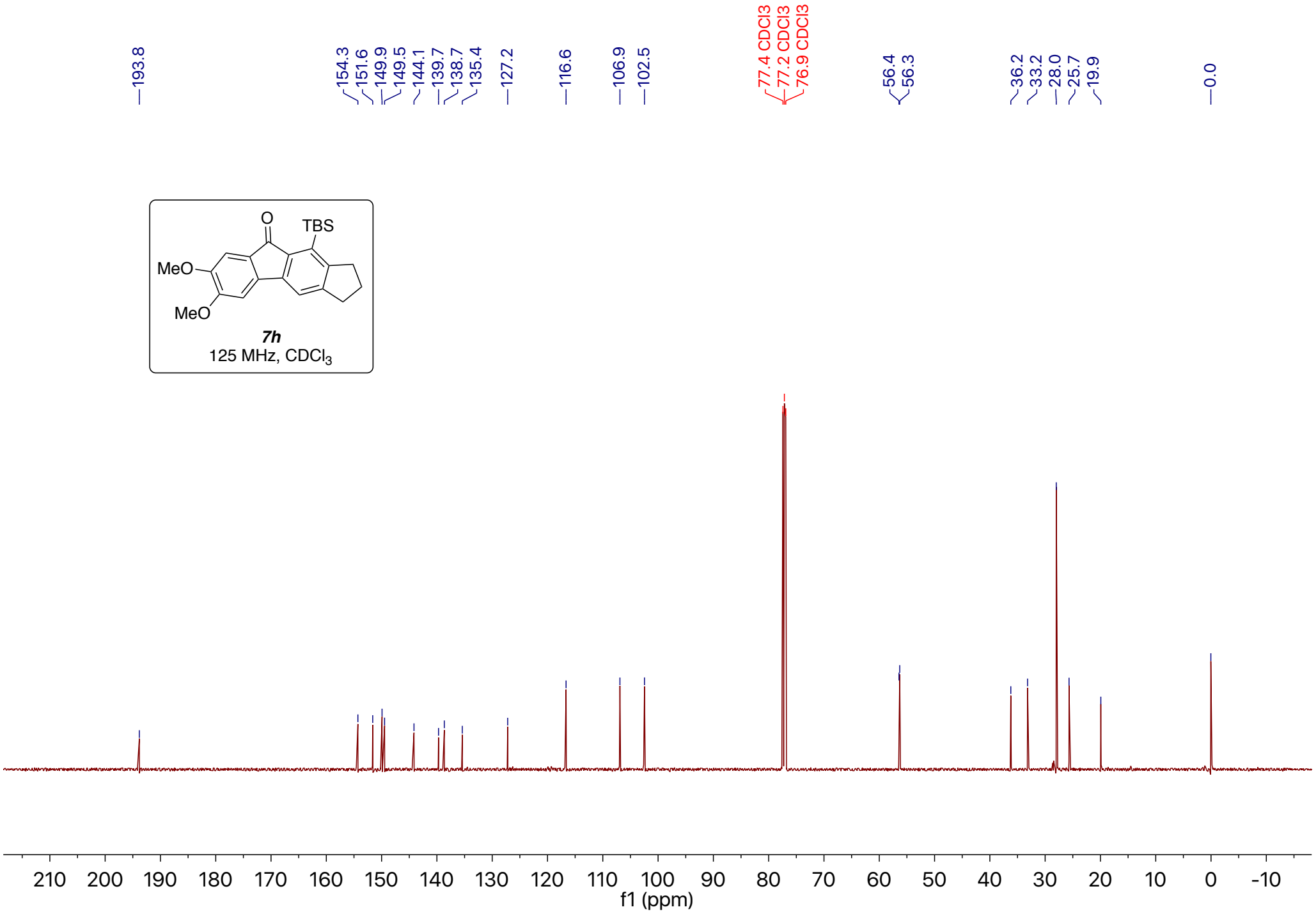

7.26 CDCl3
7.25
6.96
5.84
3.91
3.86
2.41
2.36
2.35
2.34
1.64
1.63
1.62
1.60
1.59
1.57
1.04
1.03
1.02
0.95
0.14
0.13
-0.00 TMS
OH
MeO
MeO
TBS
S12
500 MHz, CDCl3
f1 (ppm)
0.94
1.00
1.02
3.10
3.12
0.95
2.09
2.15
2.96
9.20
2.93
3.01
f1 (ppm)

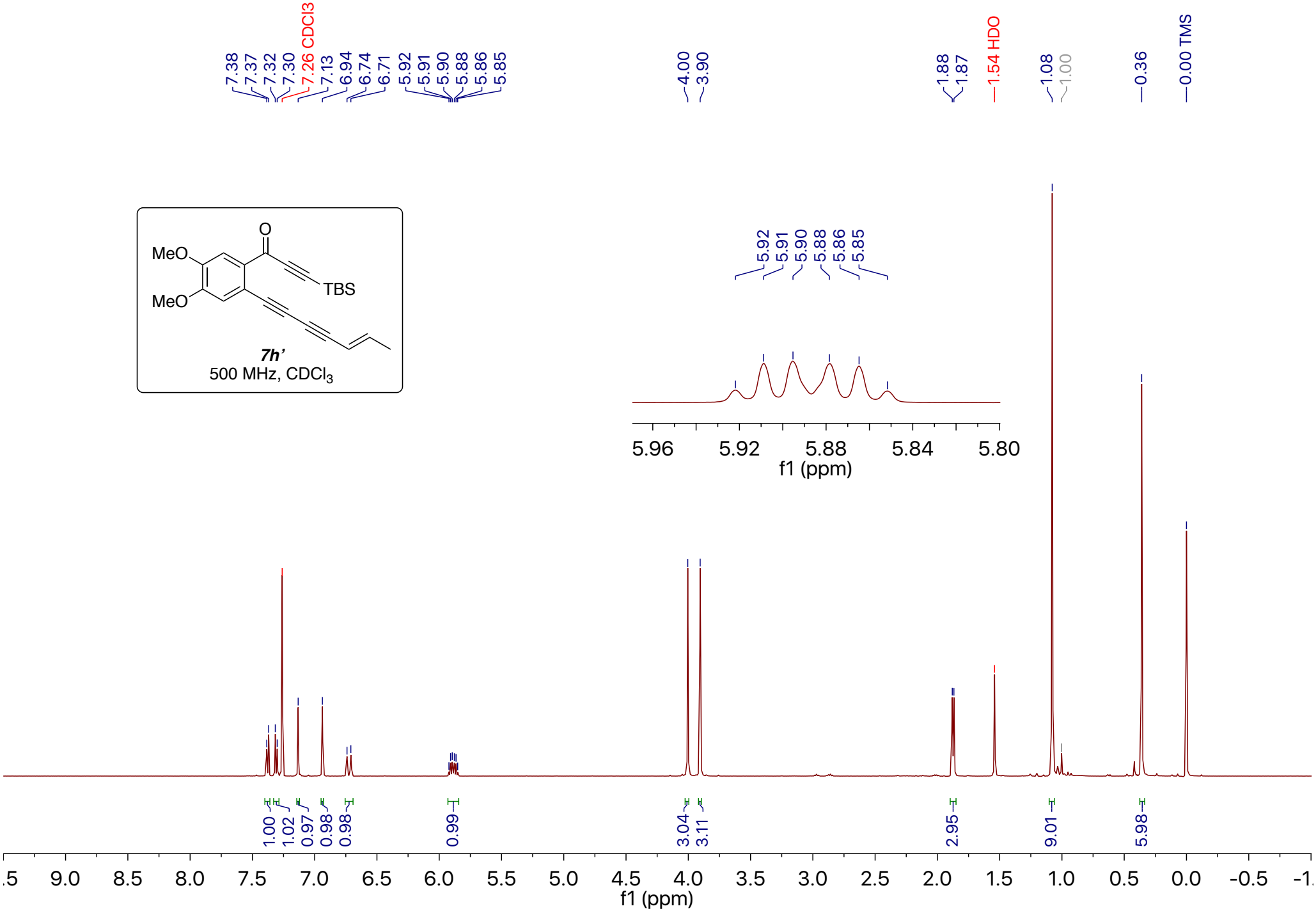

150.2
148.7
137.4
115.4
112.8
110.0
105.3
90.1
85.9
78.3
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.0
65.2
63.3
56.2
56.0
26.2
21.9
21.7
16.7
13.7
-4.5
-4.6
OH
MeO
MeO
TBS
S12
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

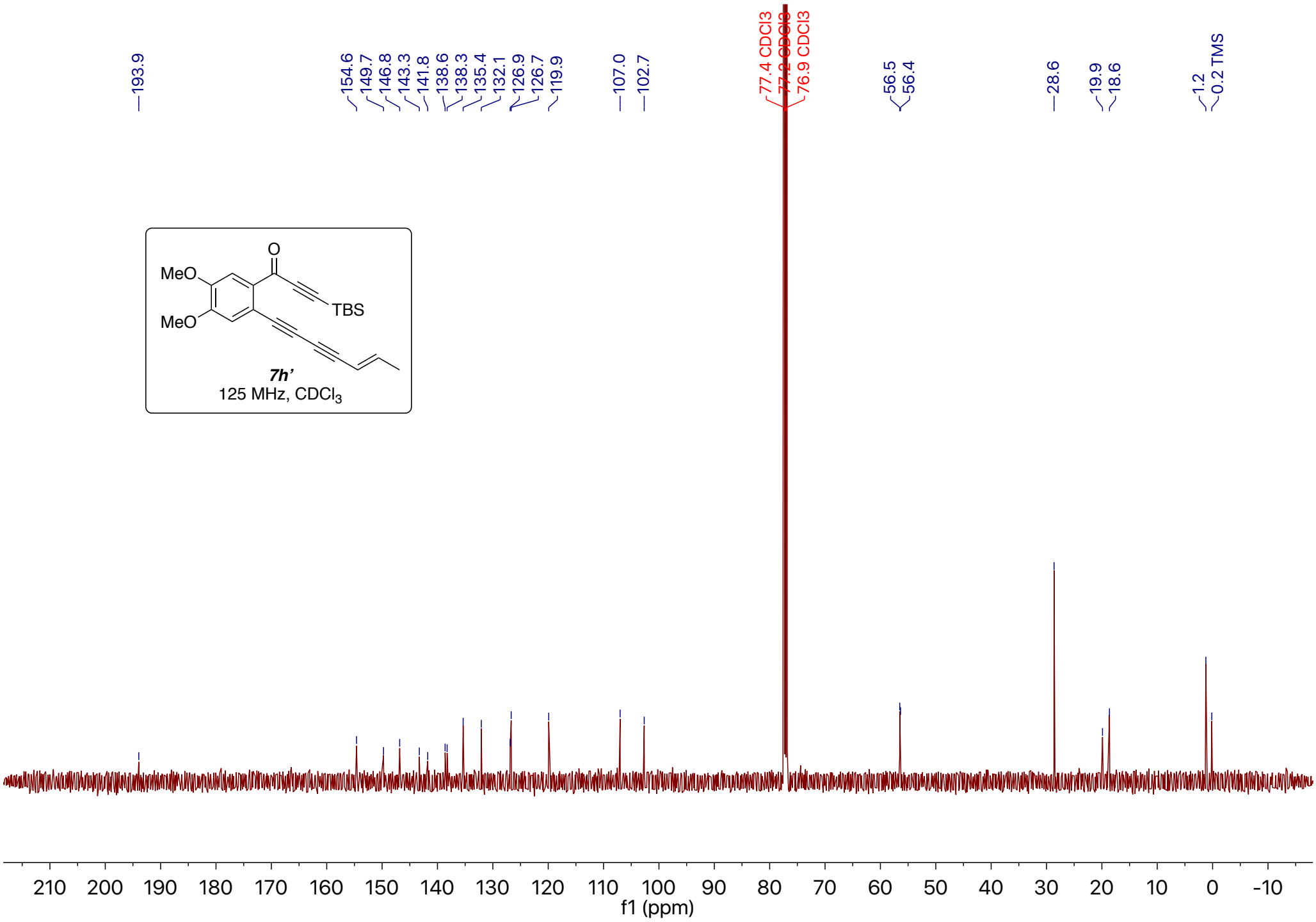

7.63
7.26 CDCl3
7.04
3.94
3.93
2.37
2.36
2.34
1.64
1.63
1.61
1.60
1.58
1.57
1.55 HDO
1.04
1.02
1.01
0.24
-0.00 TMS
MeO
MeO
O
TBS
5h
500 MHz, CDCl3
1.64 1.62 1.60 1.58 1.56
f1 (ppm)
1.00
1.00
2.99
2.99
2.05
2.04
3.04
9.09
5.93
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

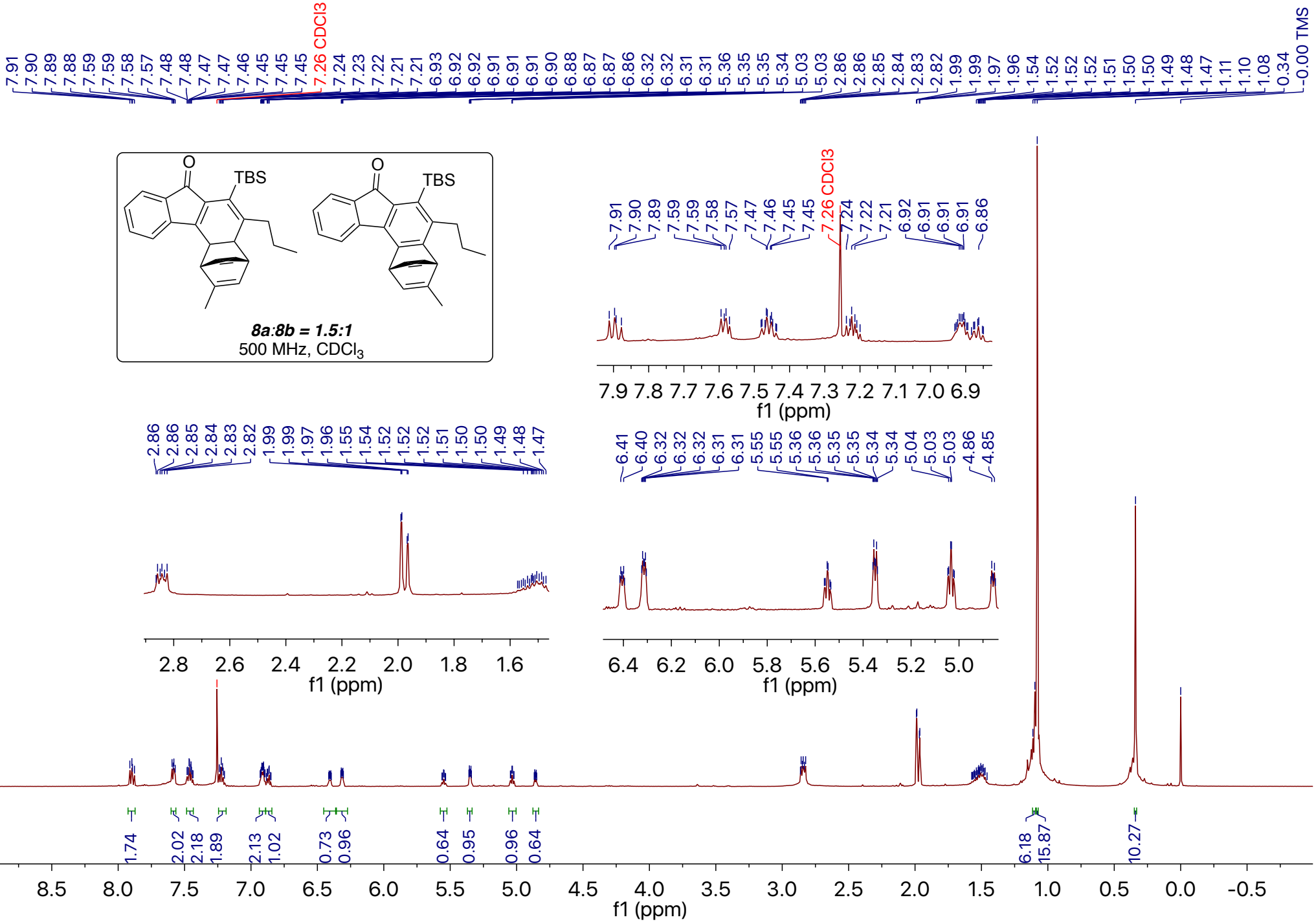

175.0
152.5
149.0
132.7
117.4
116.3
114.0
102.6
99.5
86.9
79.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
73.2
65.9
56.4
56.1
26.2
21.9
21.9
16.8
13.7
0.1 TMS
-4.9
MeO
MeO
O
TBS
5h
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

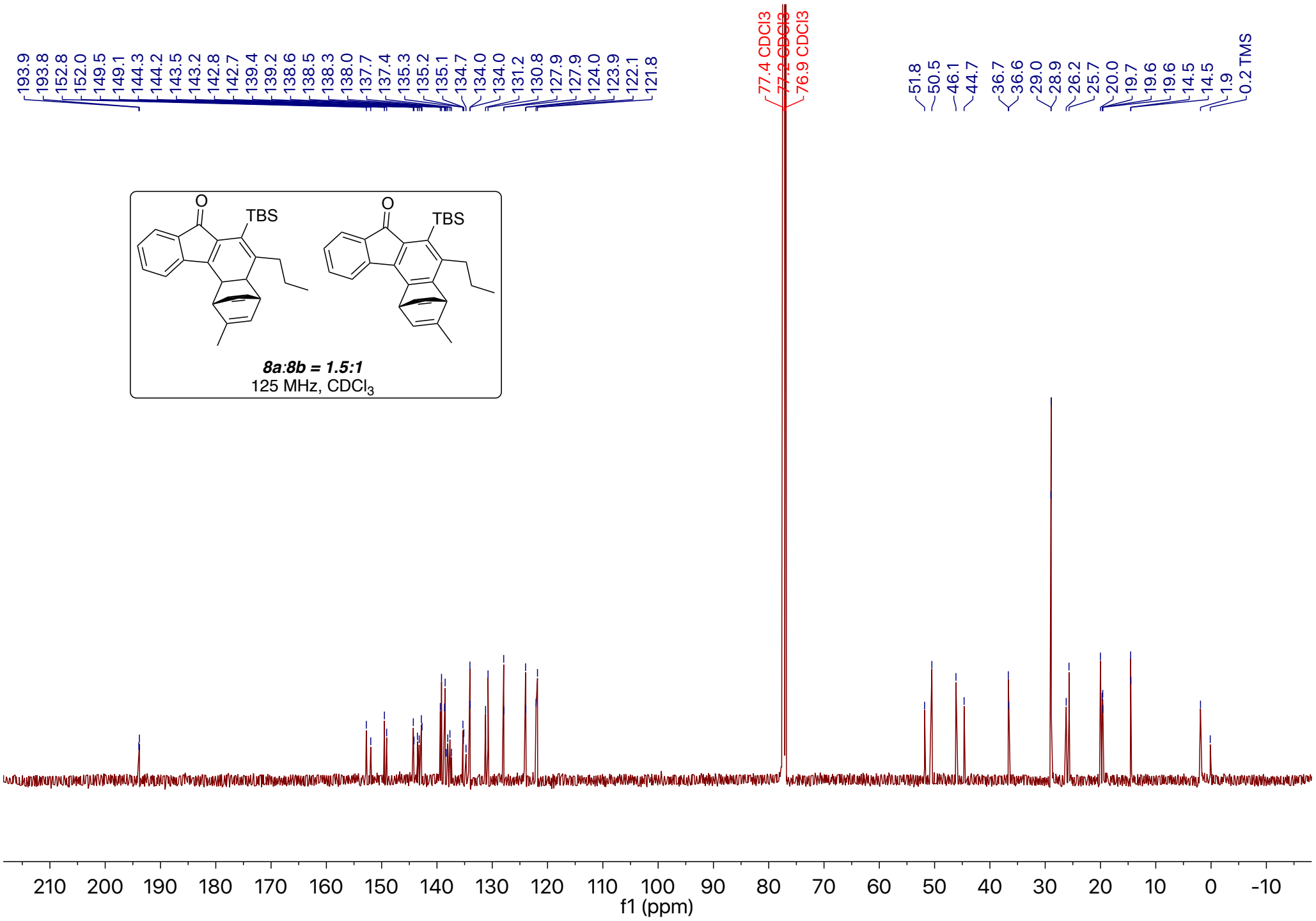

7.27 CDCl3
7.12
6.92
3.99
3.90
2.98
2.97
2.95
2.87
2.85
2.84
2.05
2.03
2.02
2.00
1.99
1.08
1.00
0.42
0.39
0.36
0.00 TMS
O
TBS
MeO
MeO
7h
500 MHz, CDCl3
1.00
1.00
3.06
3.14
1.95
1.96
1.93
9.11
5.87
f1 (ppm)

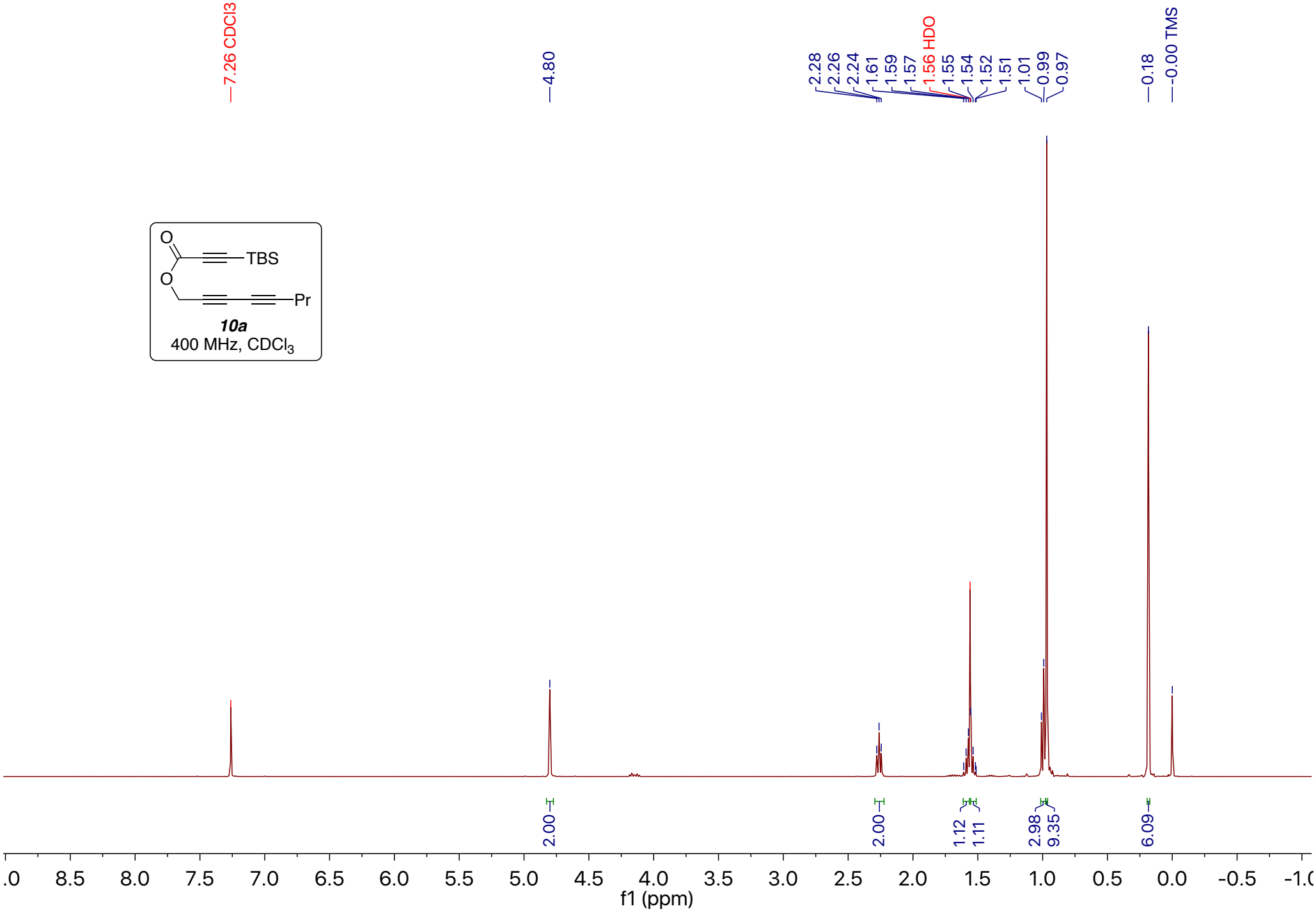

193.8
154.3
151.6
149.9
149.5
144.1
139.7
138.7
135.4
127.2
116.6
106.9
102.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
56.4
56.3
36.2
33.2
28.0
25.7
19.9
0.0
O
TBS
MeO
MeO
7h
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

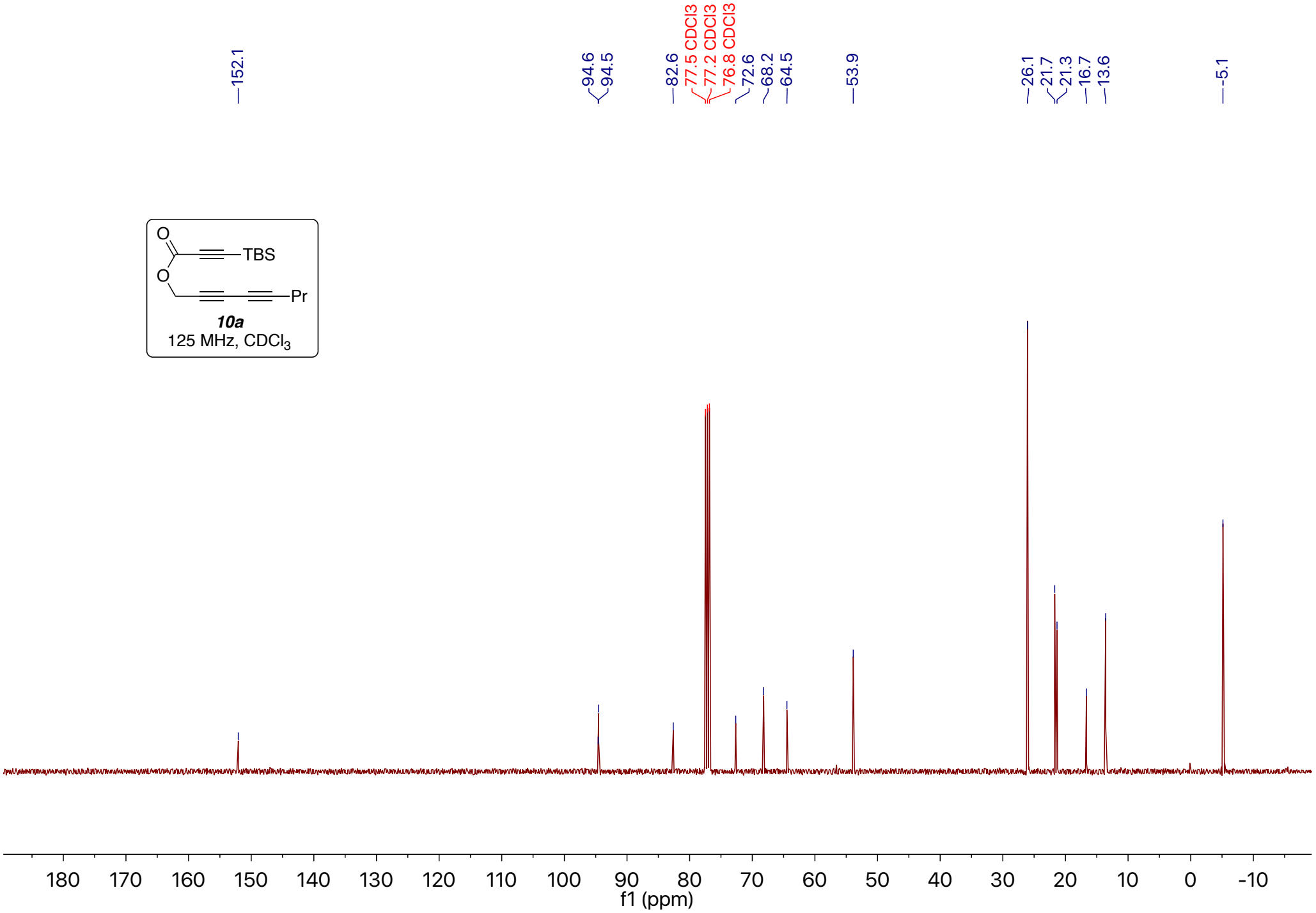

7.38
7.37
7.32
7.30
7.26 CDCl3
7.13
6.94
6.74
6.71
5.92
5.91
5.90
5.88
5.86
5.85
4.00
3.90
1.88
1.87
1.54 HDO
1.08
1.00
0.36
0.00 TMS
MeO
MeO
O
TBS
7h'
500 MHz, CDCl3
5.96
5.92
5.88
5.84
5.80
f1 (ppm)
1.00
1.02
0.97
0.98
0.98
0.99
3.04
3.11
2.95
9.01
5.98
f1 (ppm)

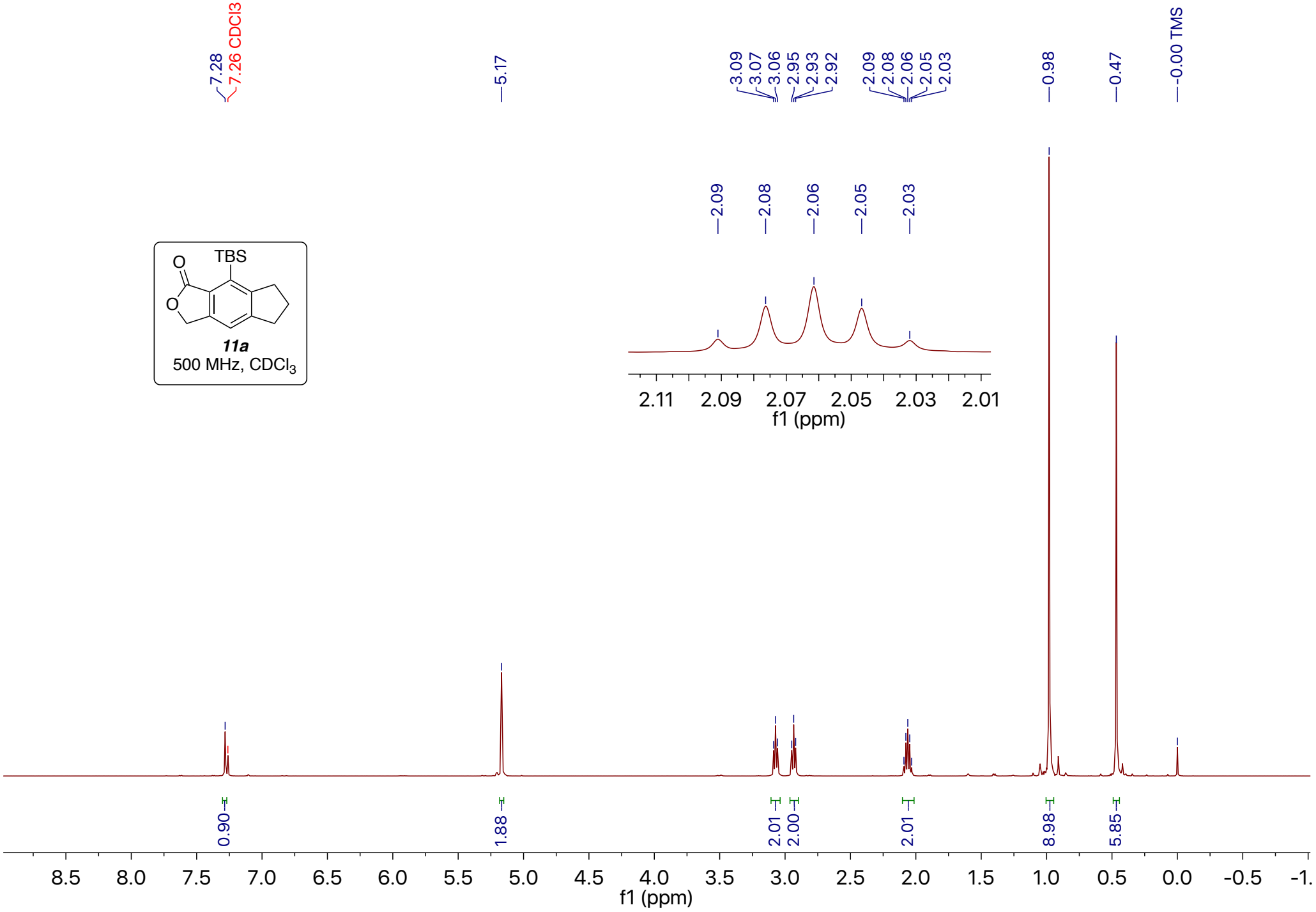

193.9
154.6
149.7
146.8
143.3
141.8
138.6
138.3
135.4
132.1
126.9
126.7
119.9
107.0
102.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
56.5
56.4
28.6
19.9
18.6
1.2
0.2 TMS
MeO
MeO
O
TBS
7h'
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

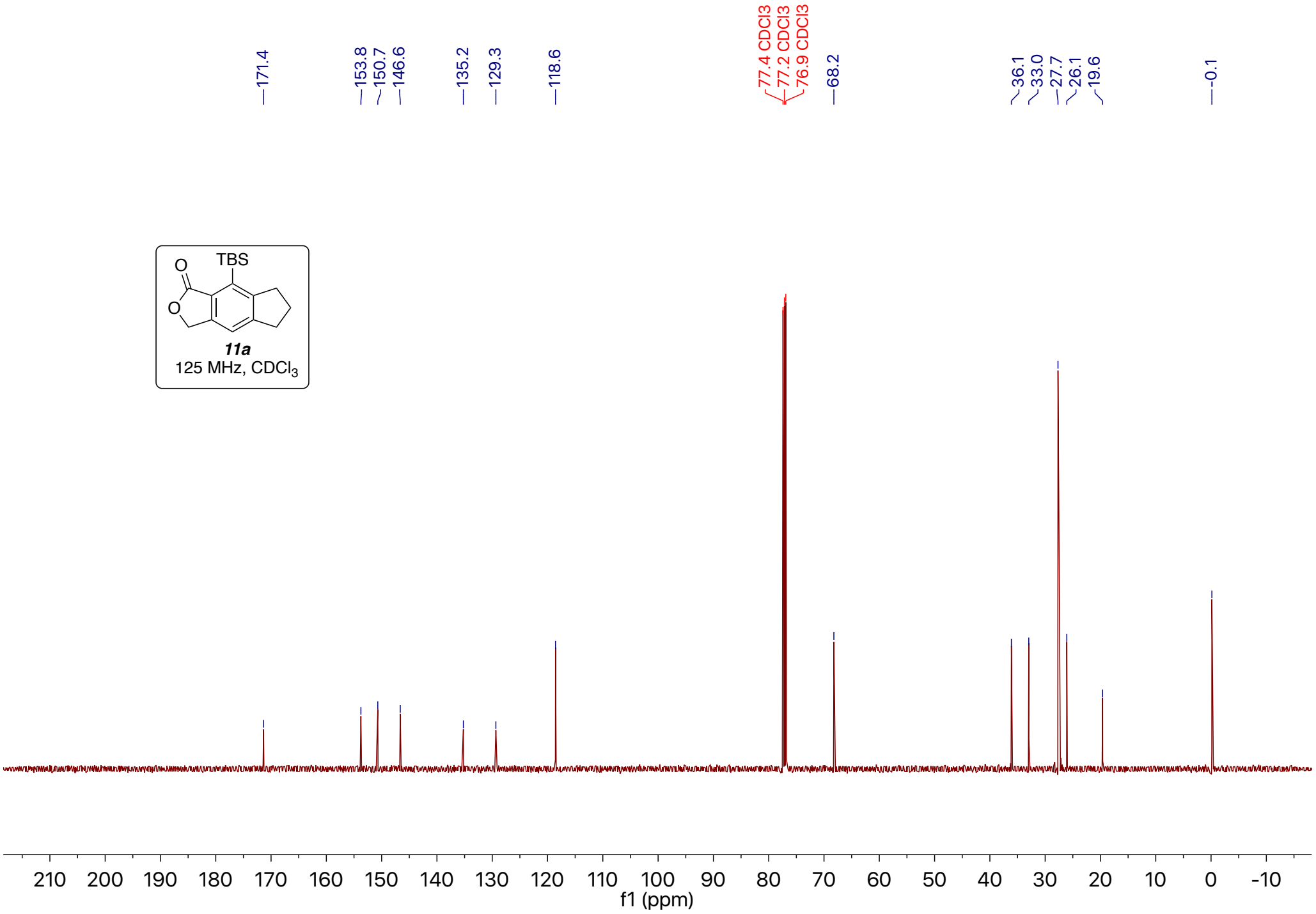

7.91 7.90 7.89 7.88 7.59 7.59 7.58 7.57 7.48 7.48 7.47 7.47 7.46 7.45 7.45 7.45 7.26 CDCl3 7.24 7.23 7.22 7.21 7.21 6.93 6.92 6.92 6.91 6.91 6.91 6.90 6.88 6.87 6.87 6.86 6.32 6.32 6.31 6.31 5.36 5.35 5.35 5.34 5.03 5.03 2.86 2.86 2.85 2.84 2.83 2.82 1.99 1.99 1.97 1.96 1.54 1.52 1.52 1.52 1.51 1.50 1.50 1.49 1.48 1.47 1.11 1.10 1.08 0.34 -0.00 TMS
O
TBS
O
TBS
8a:8b = 1.5:1
500 MHz, CDCl3
7.91 7.90 7.89 7.59 7.59 7.58 7.57 7.47 7.46 7.45 7.45 7.26 CDCl3 7.24 7.22 7.21 6.92 6.91 6.91 6.91 6.86
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
2.86 2.86 2.85 2.84 2.83 2.82 1.99 1.99 1.97 1.96 1.55 1.54 1.52 1.52 1.52 1.51 1.50 1.50 1.49 1.48 1.47
2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)
6.41 6.40 6.32 6.32 6.32 6.31 6.31 5.55 5.55 5.36 5.36 5.35 5.35 5.34 5.34 5.04 5.03 5.03 4.86 4.85
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0
f1 (ppm)
1.74 2.02 2.18 1.89 2.13 1.02 0.73 0.96 0.64 0.95 0.96 0.64 6.18 15.87 10.27
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

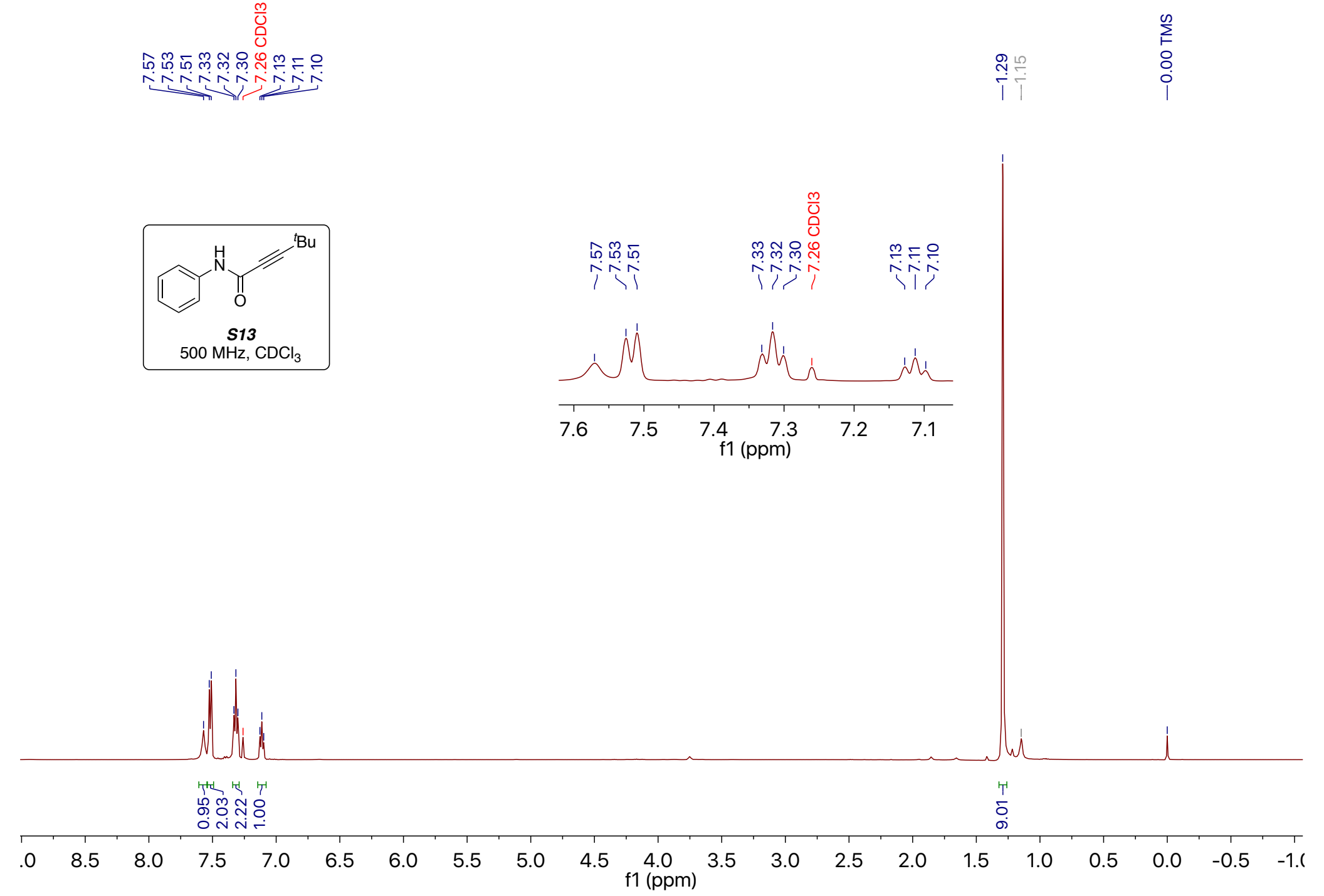

193.9
193.8
152.8
152.0
149.5
149.1
144.3
144.2
143.5
143.2
142.8
142.7
139.4
139.2
138.6
138.5
138.3
138.0
137.7
137.4
135.3
135.2
135.1
134.7
134.0
134.0
131.2
130.8
127.9
127.9
124.0
123.9
122.1
121.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
51.8
50.5
46.1
44.7
36.7
36.6
29.0
28.9
26.2
25.7
20.0
19.7
19.6
19.6
14.5
14.5
1.9
0.2 TMS
O
TBS
O
TBS
8a:8b = 1.5:1
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

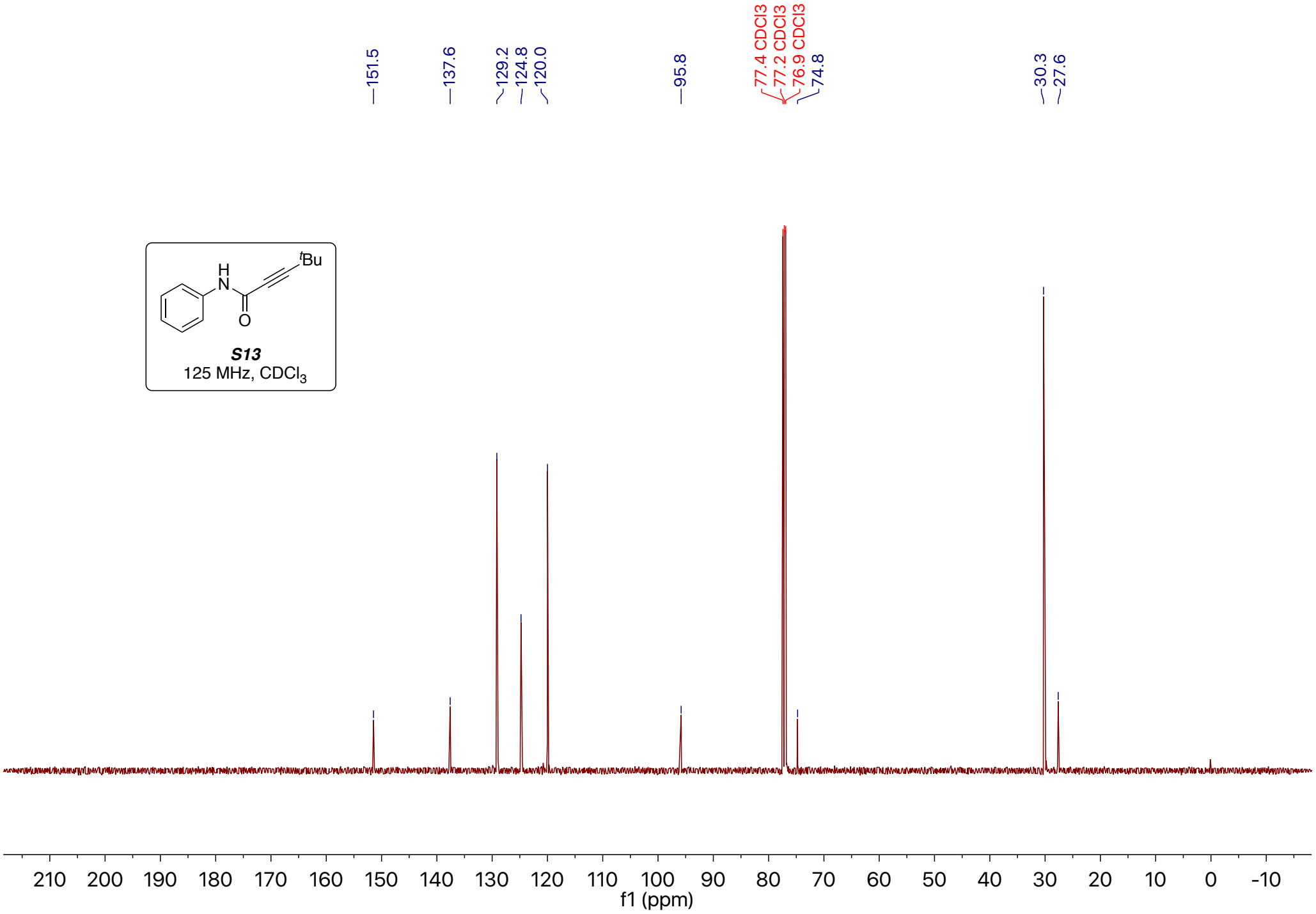

7.26 CDCl3
4.80
2.28
2.26
2.24
1.61
1.59
1.57
1.56 HDO
1.55
1.54
1.52
1.51
1.01
0.99
0.97
0.18
-0.00 TMS
TBS
Pr
10a
400 MHz, CDCl3
2.00
2.00
1.12
1.11
2.98
9.35
6.09
f1 (ppm)

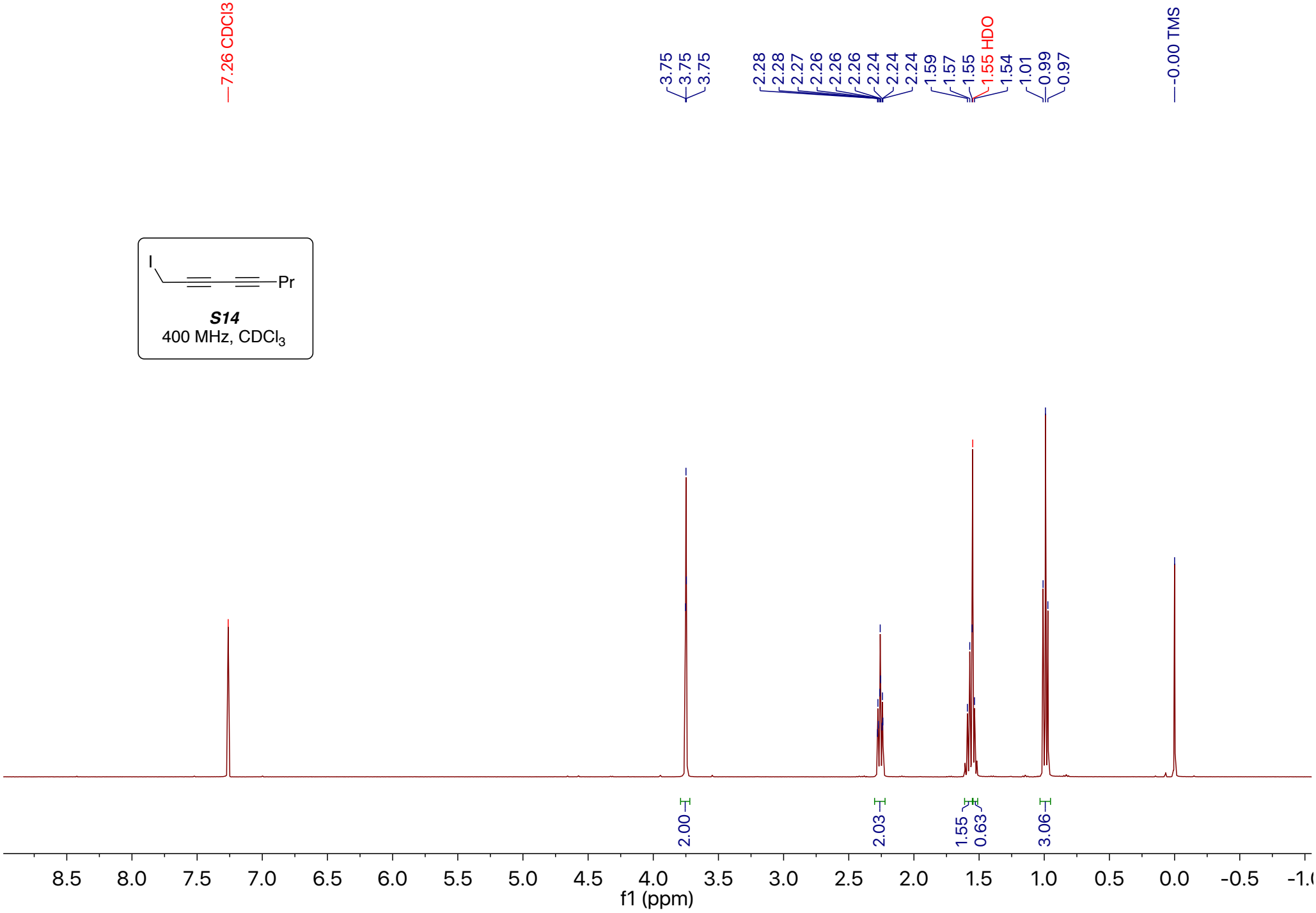

152.1
94.6
94.5
82.6
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
72.6
68.2
64.5
53.9
26.1
21.7
21.3
16.7
13.6
-5.1
O
TBS
O
Pr
10a
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

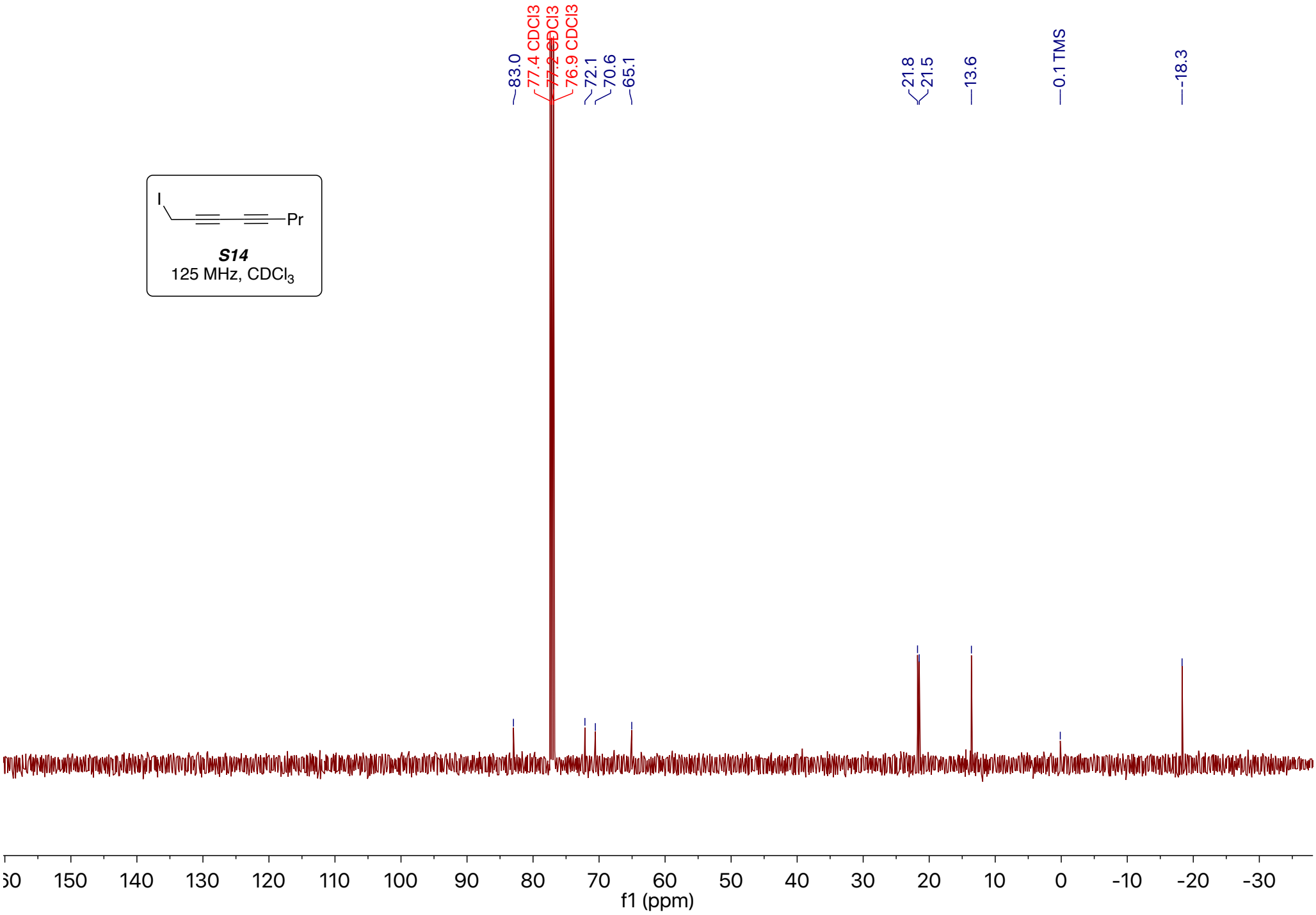

7.28
7.26 CDCl3
5.17
3.09
3.07
3.06
2.95
2.93
2.92
2.09
2.08
2.06
2.05
2.03
0.98
0.47
-0.00 TMS
TBS
O
O
11a
500 MHz, CDCl3
2.09
2.08
2.06
2.05
2.03
2.11 2.09 2.07 2.05 2.03 2.01
f1 (ppm)
0.90
1.88
2.01
2.00
2.01
8.98
5.85
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

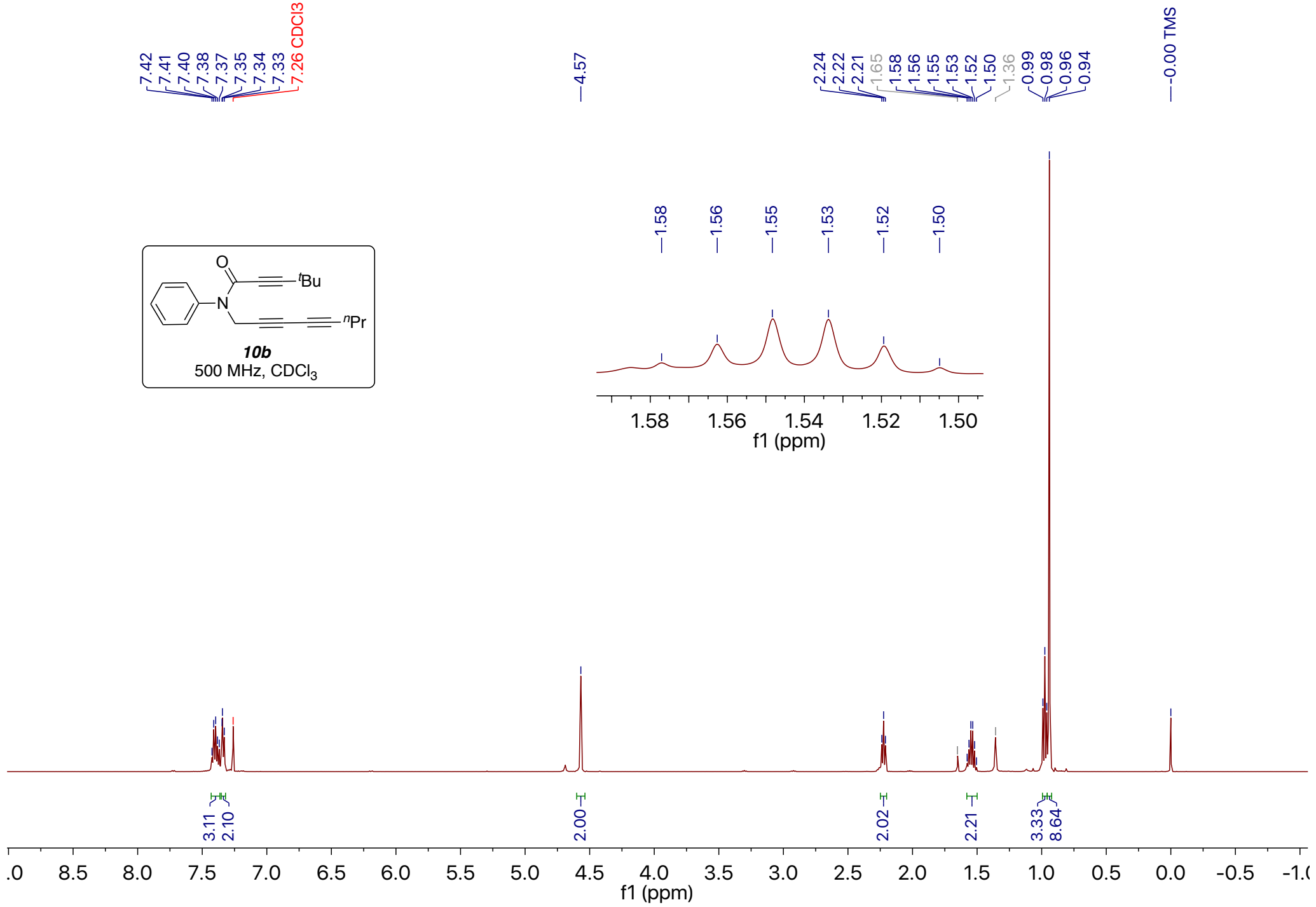

171.4
153.8
150.7
146.6
135.2
129.3
118.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
68.2
36.1
33.0
27.7
26.1
19.6
-0.1
TBS
O
O
11a
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

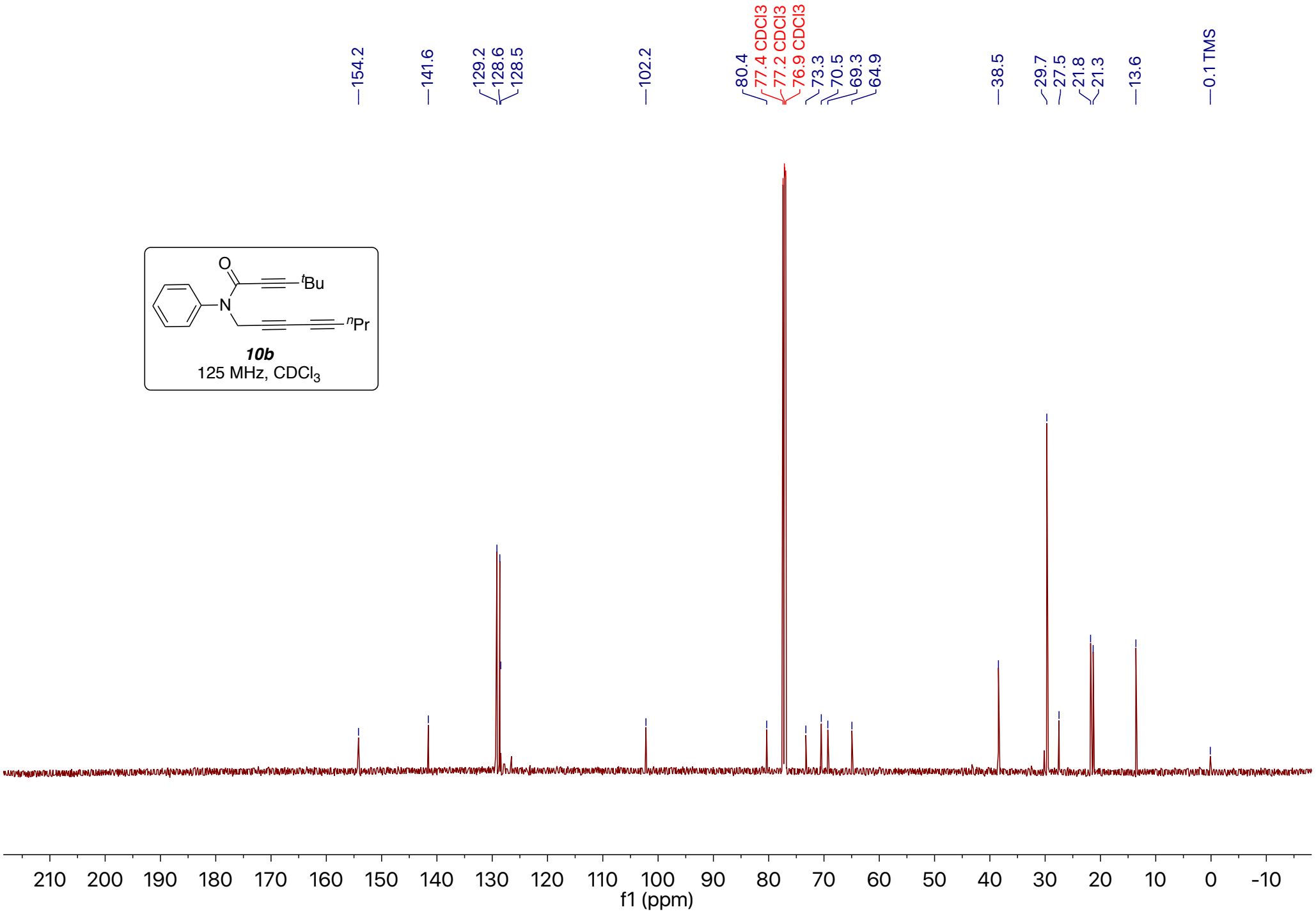

7.57
7.53
7.51
7.33
7.32
7.30
7.26 CDCl3
7.13
7.11
7.10
1.29
1.15
0.00 TMS
tBu
H
N
O
S13
500 MHz, CDCl3
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
0.95
2.03
2.22
1.00
9.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

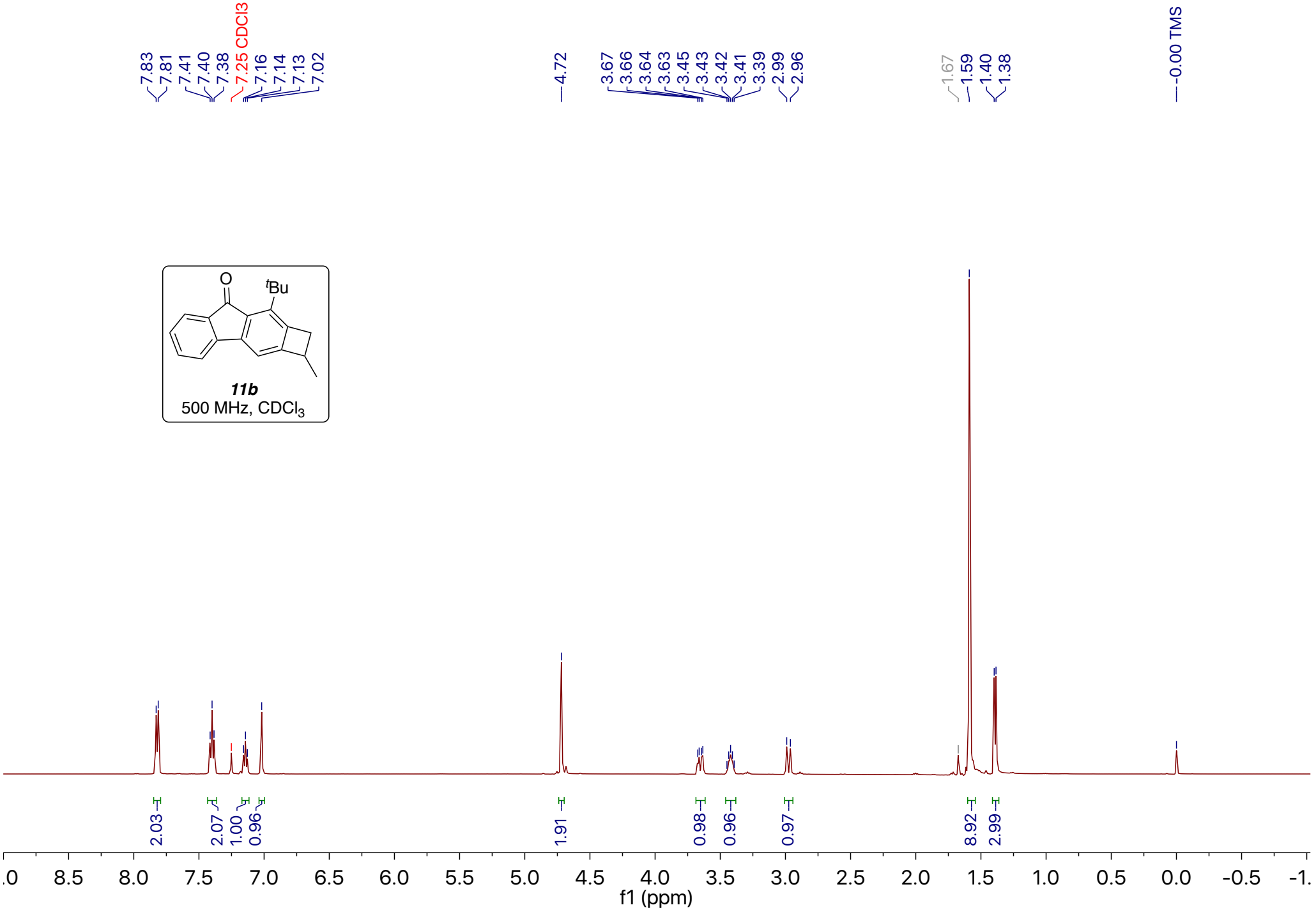

151.5
137.6
129.2
124.8
120.0
95.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
74.8
30.3
27.6
tBu
H
N
O
S13
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

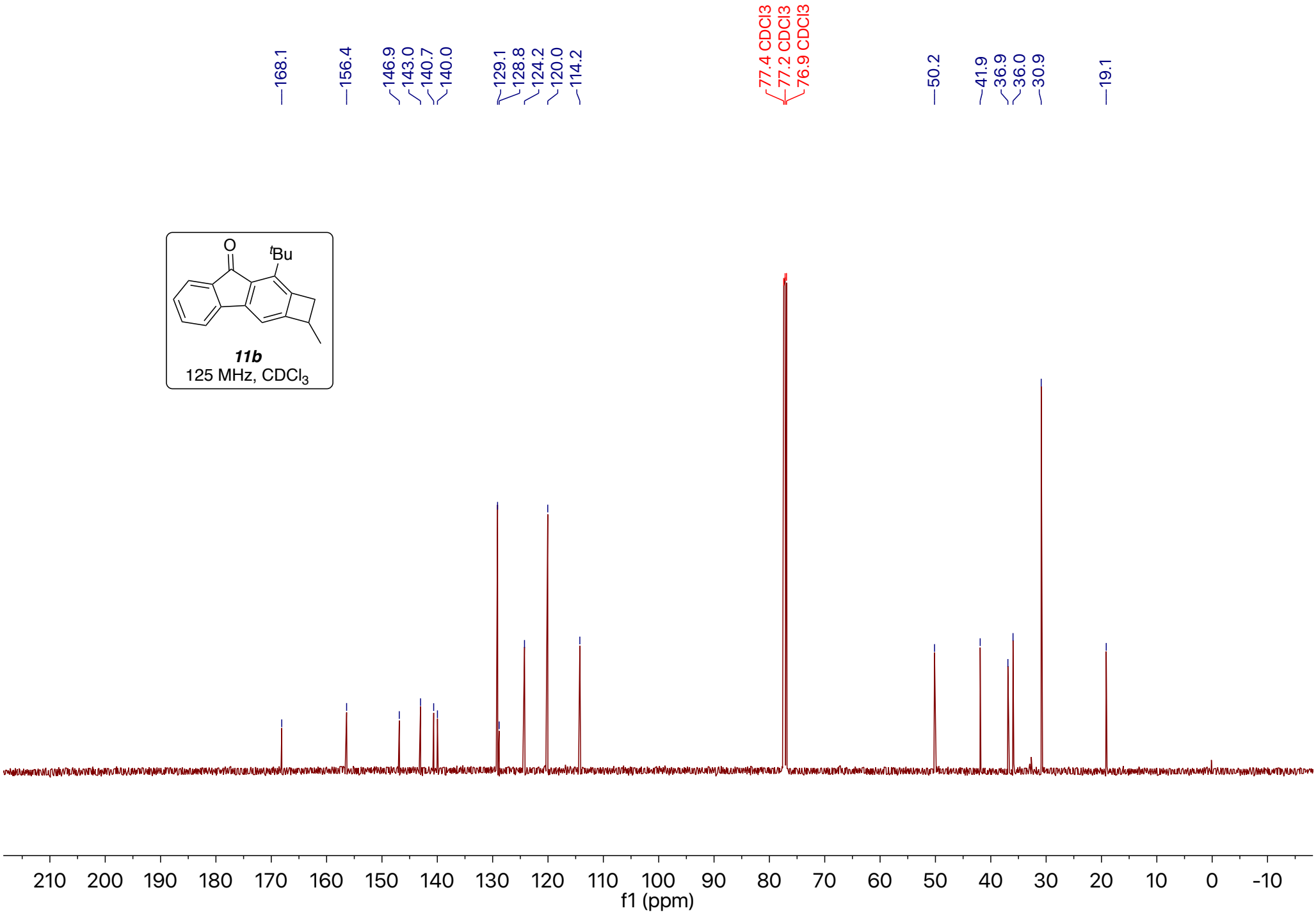

7.26 CDCl3
3.75
3.75
3.75
2.28
2.28
2.27
2.26
2.26
2.26
2.24
2.24
2.24
1.59
1.57
1.55
1.55 HDO
1.54
1.01
0.99
0.97
-0.00 TMS
I
Pr
S14
400 MHz, CDCl3
2.00
2.03
1.55
0.63
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

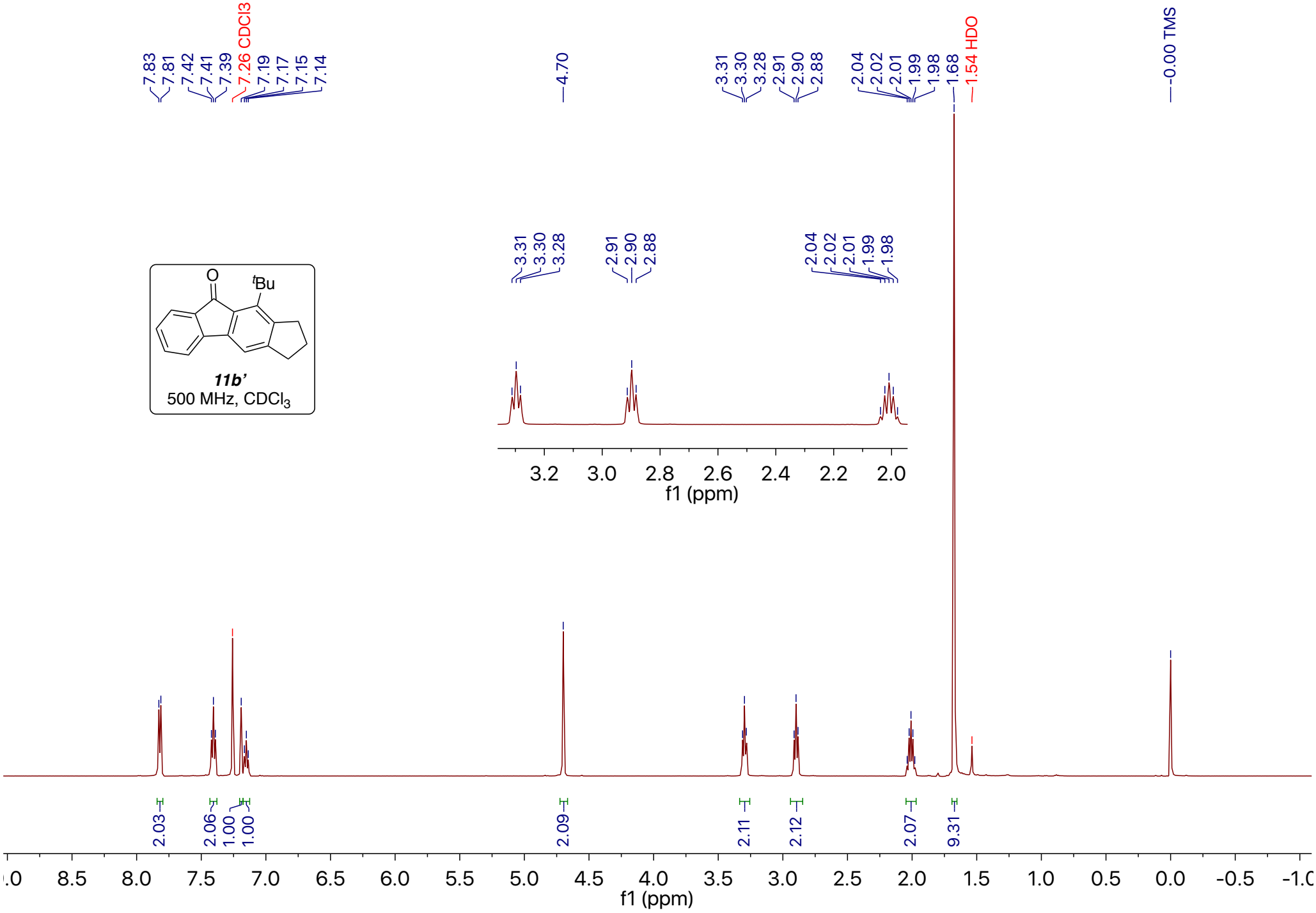

83.0
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.1
70.6
65.1
21.8
21.5
13.6
0.1 TMS
-18.3
I
Pr
S14
125 MHz, CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)

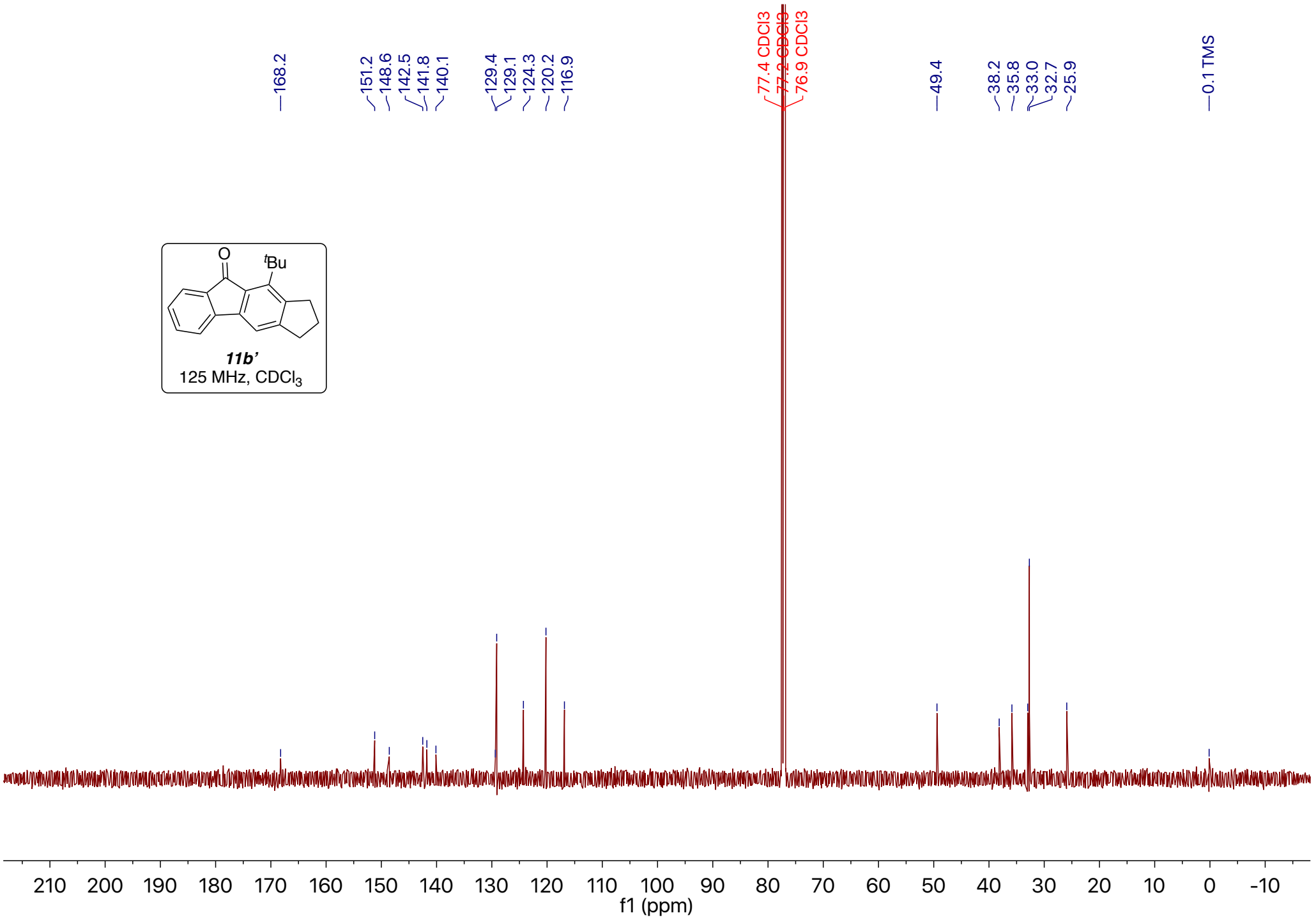

7.42
7.41
7.40
7.38
7.37
7.35
7.34
7.33
7.26 CDCl3
4.57
2.24
2.22
2.21
1.65
1.58
1.56
1.55
1.53
1.52
1.50
1.36
0.99
0.98
0.96
0.94
-0.00 TMS
O
N
tBu
nPr
10b
500 MHz, CDCl3
1.58
1.56
1.55
1.53
1.52
1.50
1.58 1.56 1.54 1.52 1.50
f1 (ppm)
3.11
2.10
2.00
2.02
2.21
3.33
8.64
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

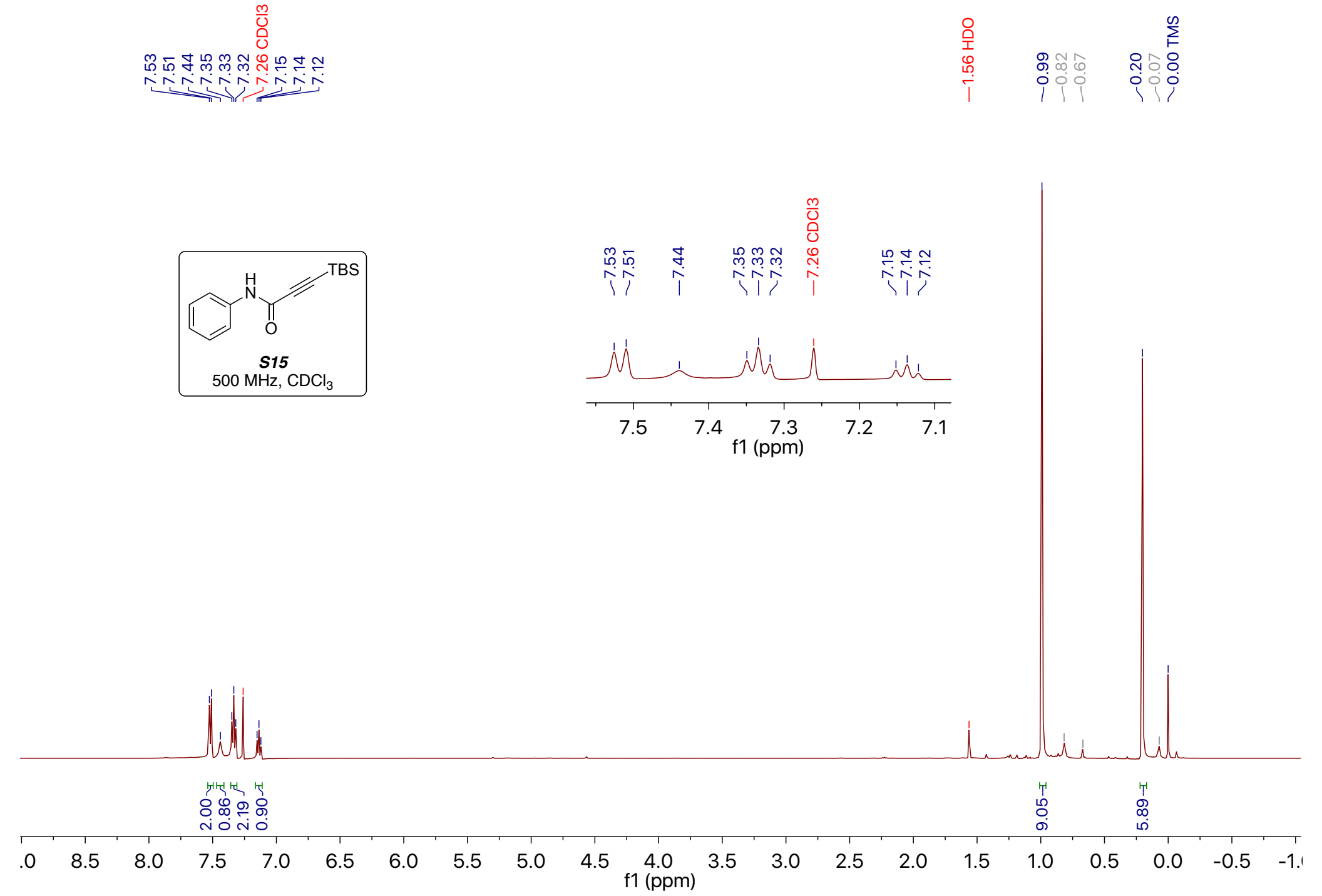

154.2
141.6
129.2
128.6
128.5
102.2
80.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
73.3
70.5
69.3
64.9
38.5
29.7
27.5
21.8
21.3
13.6
0.1 TMS
O
tBu
N
nPr
10b
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

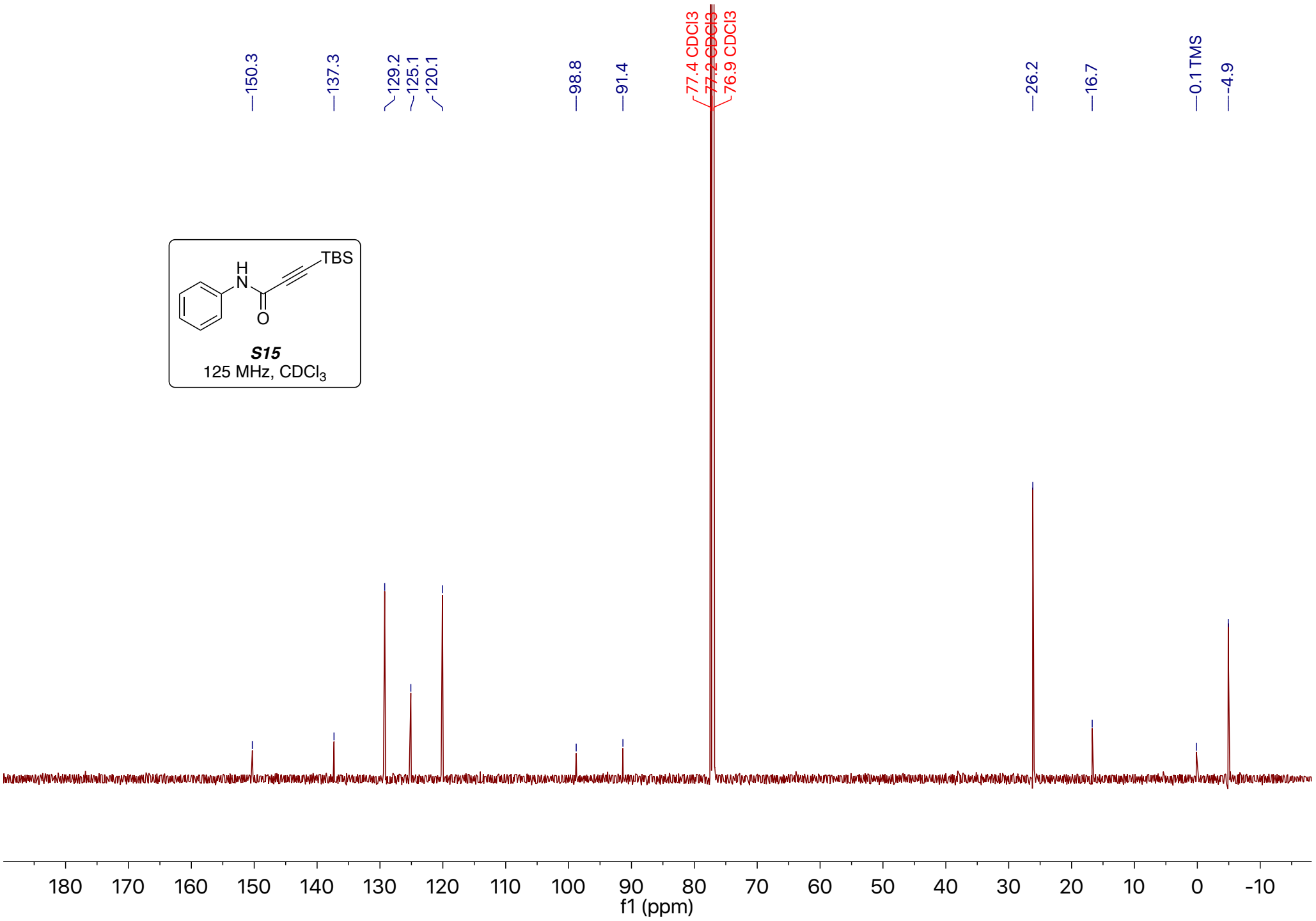

7.83
7.81
7.41
7.40
7.38
7.25 CDCl3
7.16
7.14
7.13
7.02
4.72
3.67
3.66
3.64
3.63
3.45
3.43
3.42
3.41
3.39
2.99
2.96
1.67
1.59
1.40
1.38
-0.00 TMS
O
tBu
11b
500 MHz, CDCl3
2.03
2.07
1.00
0.96
1.91
0.98
0.96
0.97
8.92
2.99
f1 (ppm)

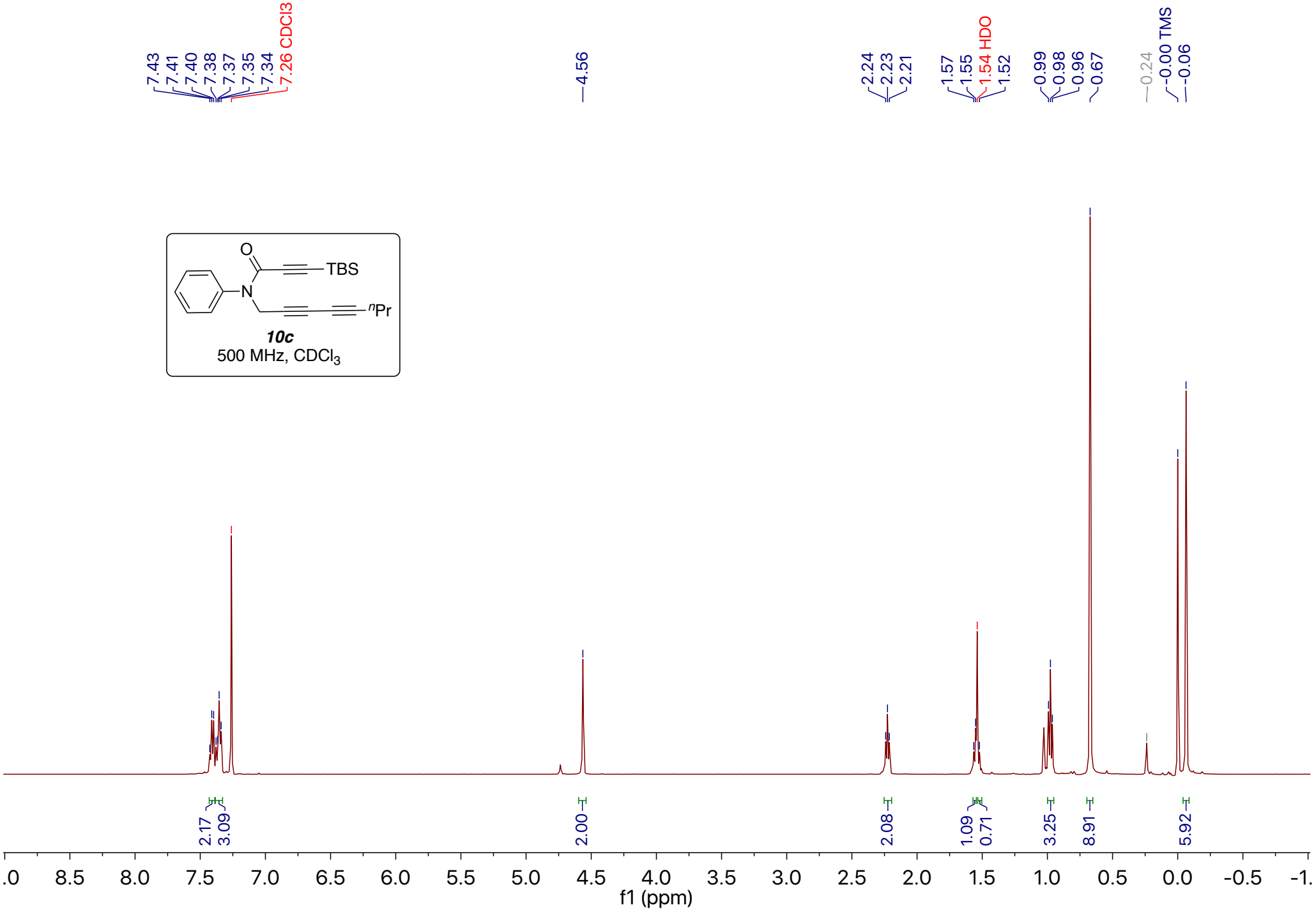

168.1
156.4
146.9
143.0
140.7
140.0
129.1
128.8
124.2
120.0
114.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
50.2
41.9
36.9
36.0
30.9
19.1
O
tBu
11b
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

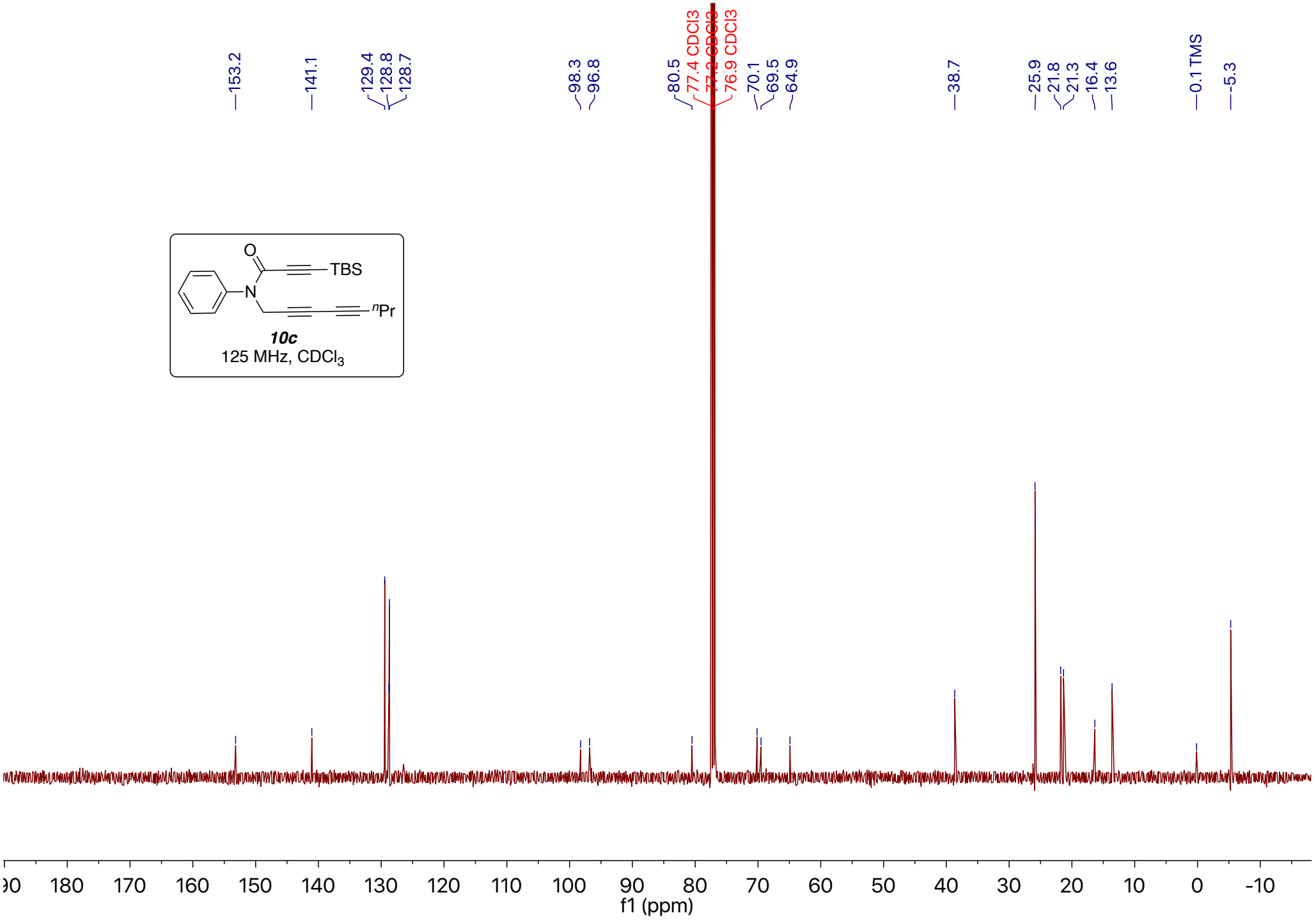

7.83
7.81
7.42
7.41
7.39
7.26 CDCl3
7.19
7.17
7.15
7.14
4.70
3.31
3.30
3.28
2.91
2.90
2.88
2.04
2.02
2.01
1.99
1.98
1.68
1.54 HDO
-0.00 TMS
O
tBu
11b'
500 MHz, CDCl3
f1 (ppm)
2.03
2.06
1.00
1.00
2.09
2.11
2.12
2.07
9.31

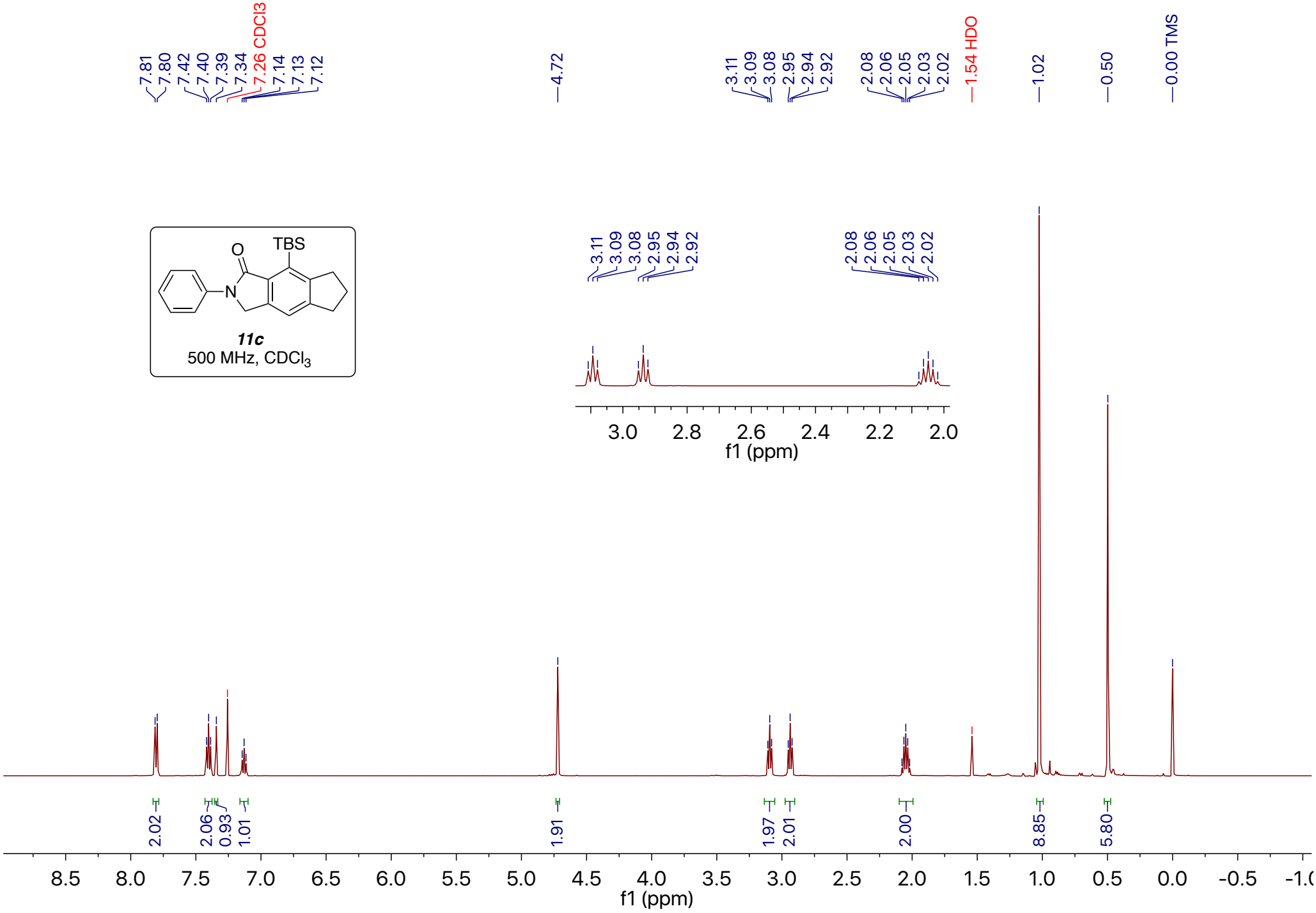

168.2
151.2
148.6
142.5
141.8
140.1
129.4
129.1
124.3
120.2
116.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
49.4
38.2
35.8
33.0
32.7
25.9
0.1 TMS
O
tBu
11b'
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

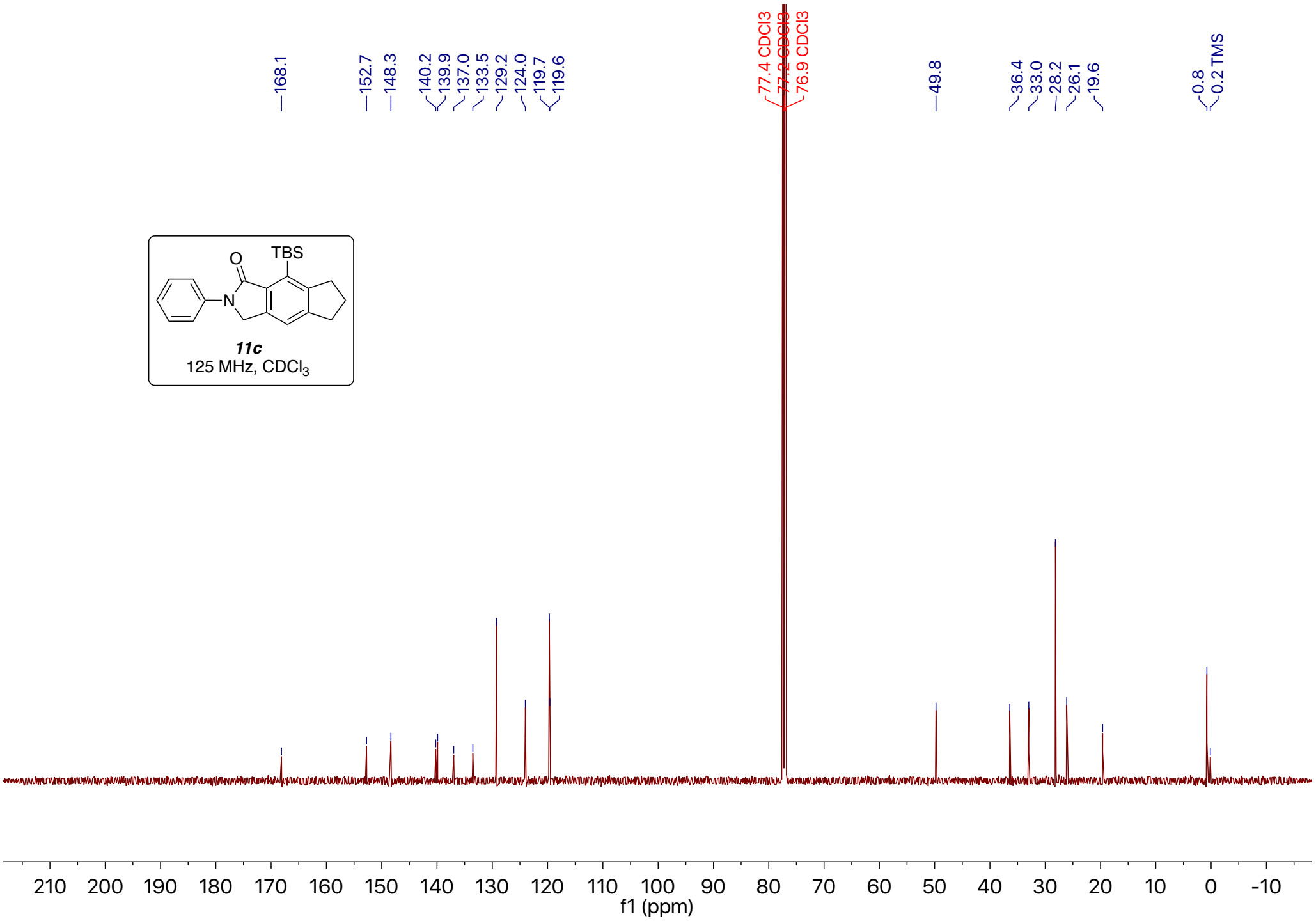

7.53
7.51
7.44
7.35
7.33
7.32
7.26 CDCl3
7.15
7.14
7.12
1.56 HDO
0.99
0.82
0.67
0.20
0.07
0.00 TMS
TBS
H
N
O
S15
500 MHz, CDCl3
f1 (ppm)
2.00
0.86
2.19
0.90
9.05
5.89
f1 (ppm)

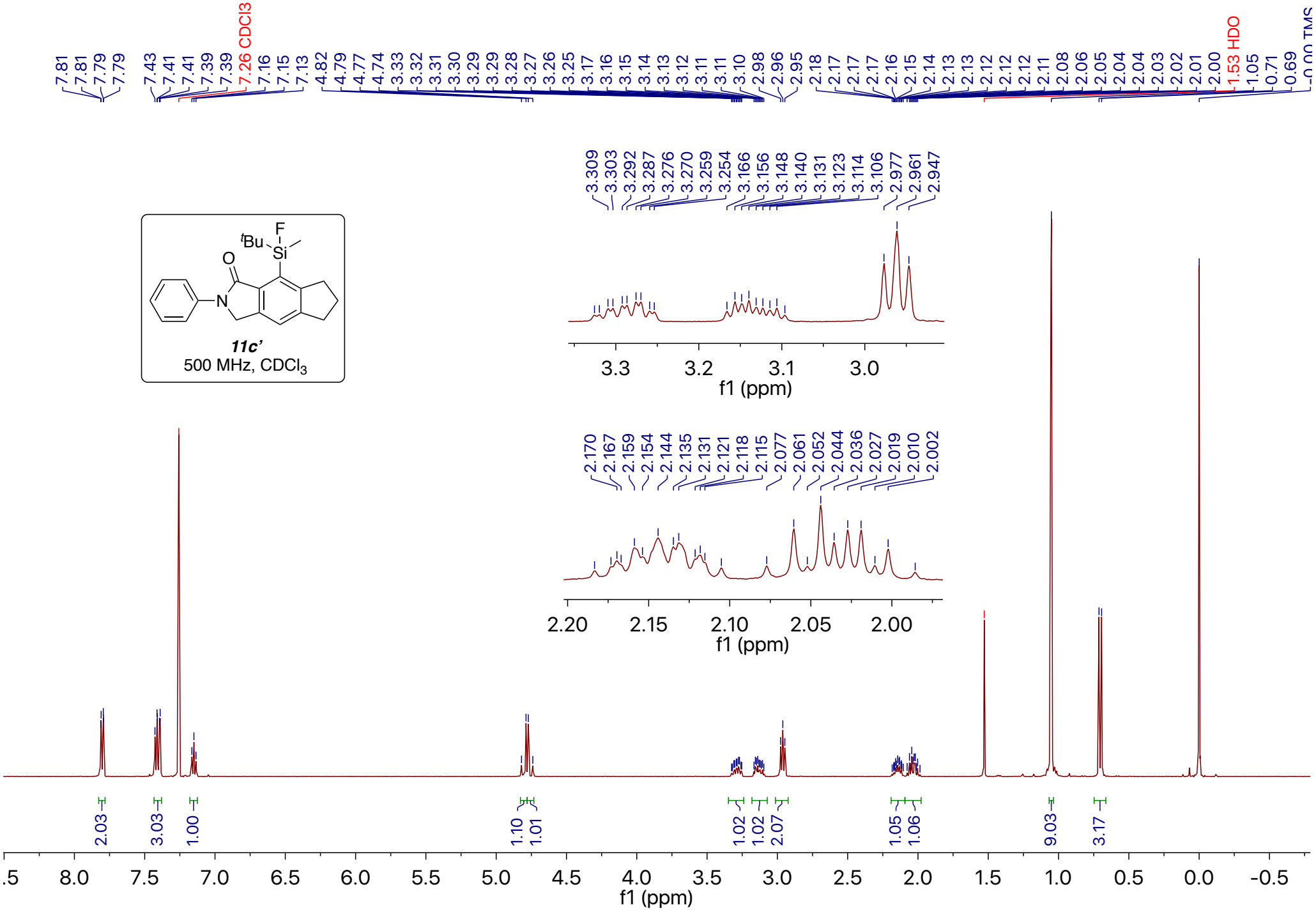

150.3
137.3
129.2
125.1
120.1
98.8
91.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
26.2
16.7
0.1 TMS
-4.9
TBS
H
N
O
S15
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

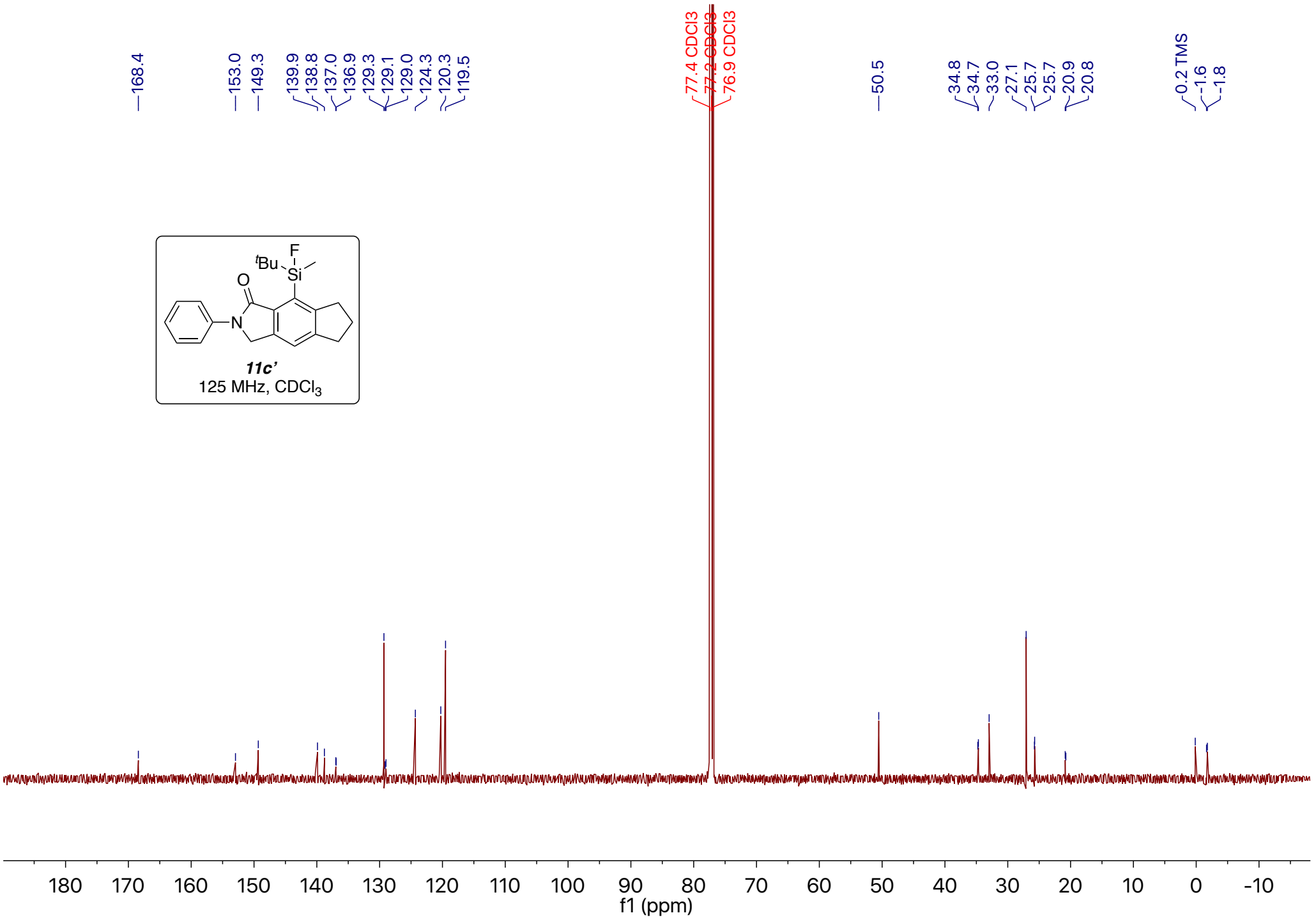

7.43
7.41
7.40
7.38
7.37
7.35
7.34
7.26 CDCl3
4.56
2.24
2.23
2.21
1.57
1.55
1.54 HDO
1.52
0.99
0.98
0.96
0.67
0.24
-0.00 TMS
-0.06
O
TBS
N
nPr
10c
500 MHz, CDCl3
2.17
3.09
2.00
2.08
1.09
0.71
3.25
8.91
5.92
f1 (ppm)

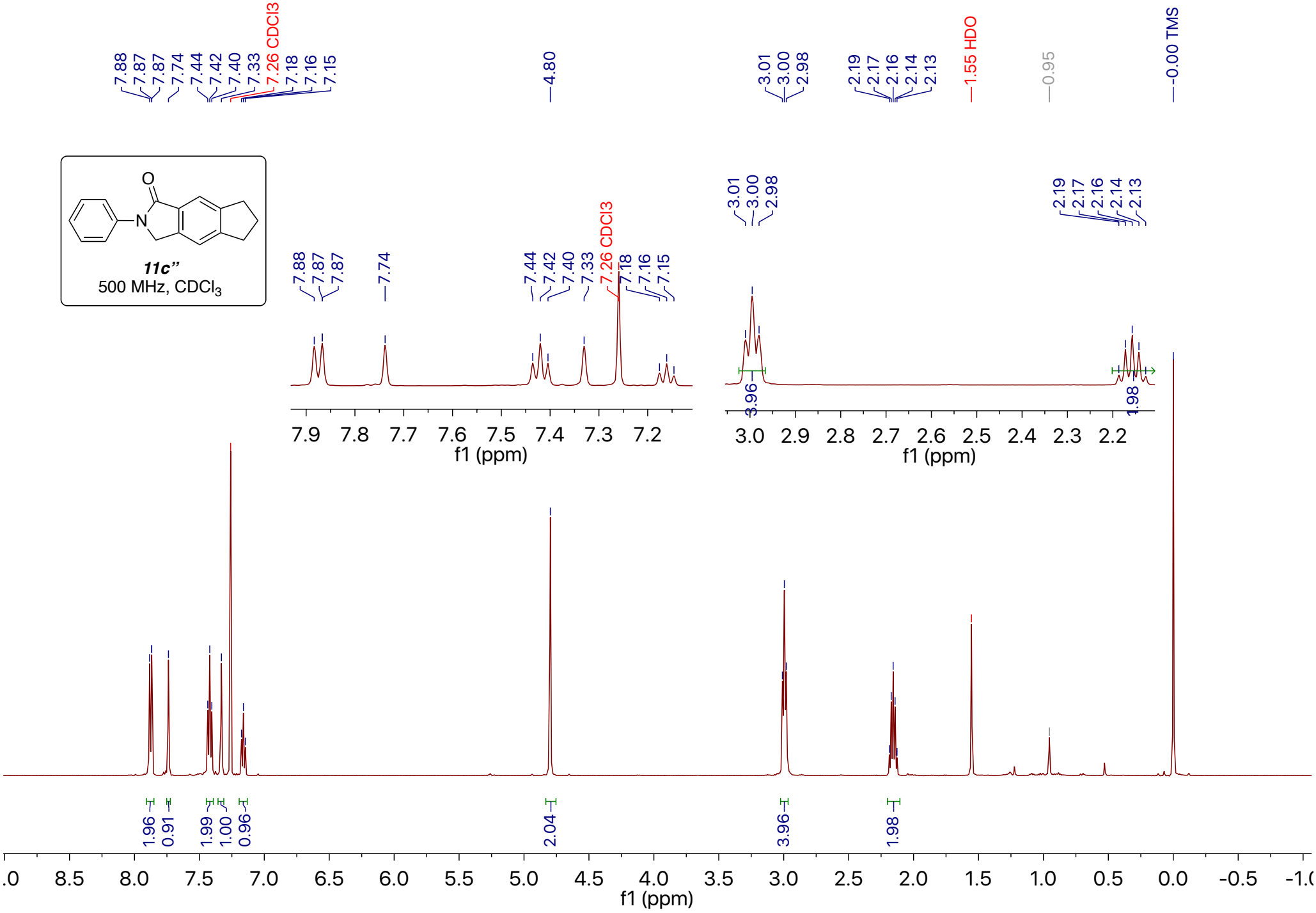

153.2
141.1
129.4
128.8
128.7
98.3
96.8
80.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
70.1
69.5
64.9
38.7
25.9
21.8
21.3
16.4
13.6
0.1 TMS
-5.3
O
TBS
N
nPr
10c
125 MHz, CDCl3
f1 (ppm)

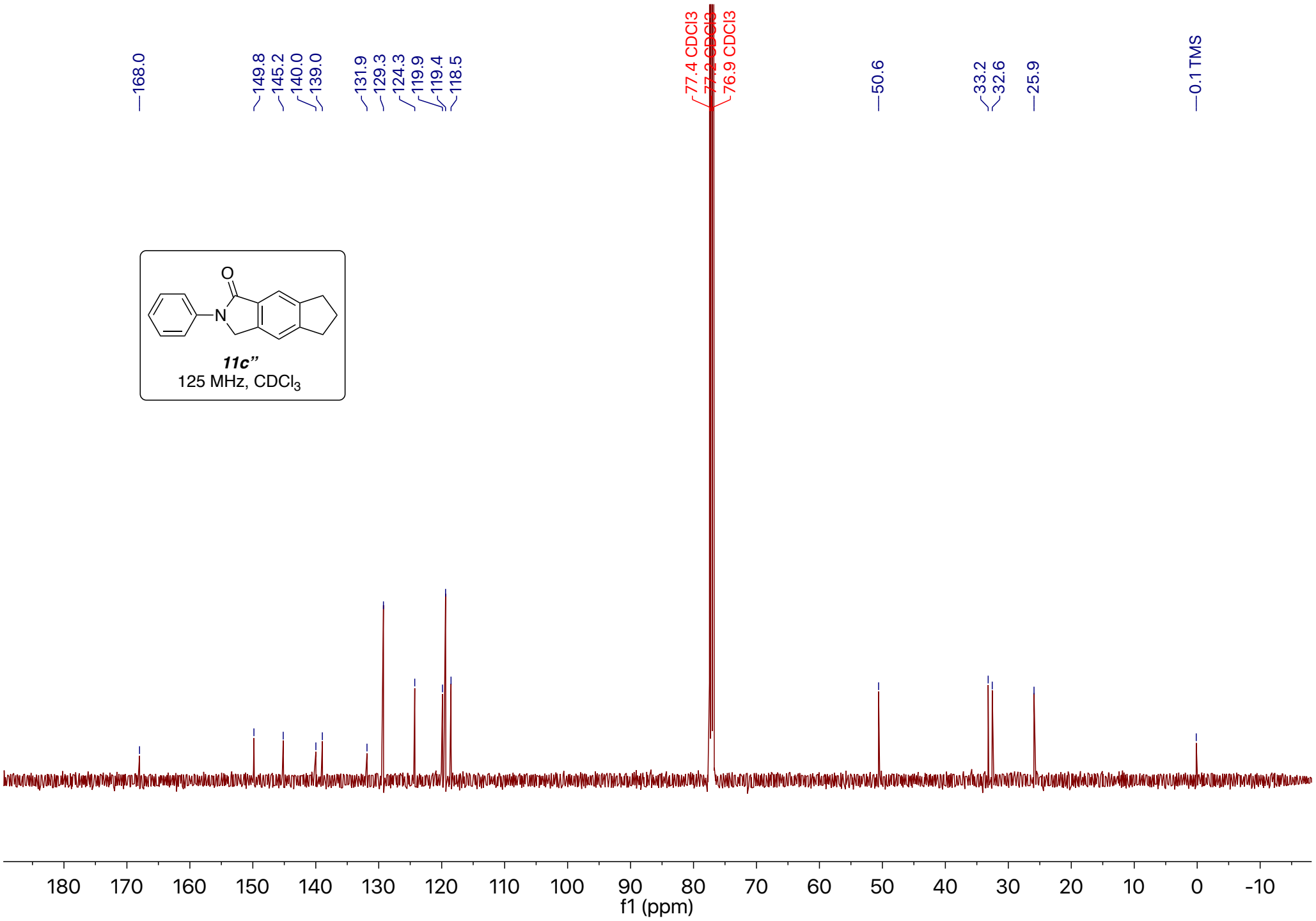

7.81
7.80
7.42
7.40
7.39
7.34
7.26 CDCl3
7.14
7.13
7.12
4.72
3.11
3.09
3.08
2.95
2.94
2.92
2.08
2.06
2.05
2.03
2.02
1.54 HDO
1.02
0.50
0.00 TMS
TBS
O
N
11c
500 MHz, CDCl3
f1 (ppm)
2.02
2.06
0.93
1.01
1.91
1.97
2.01
2.00
8.85
5.80

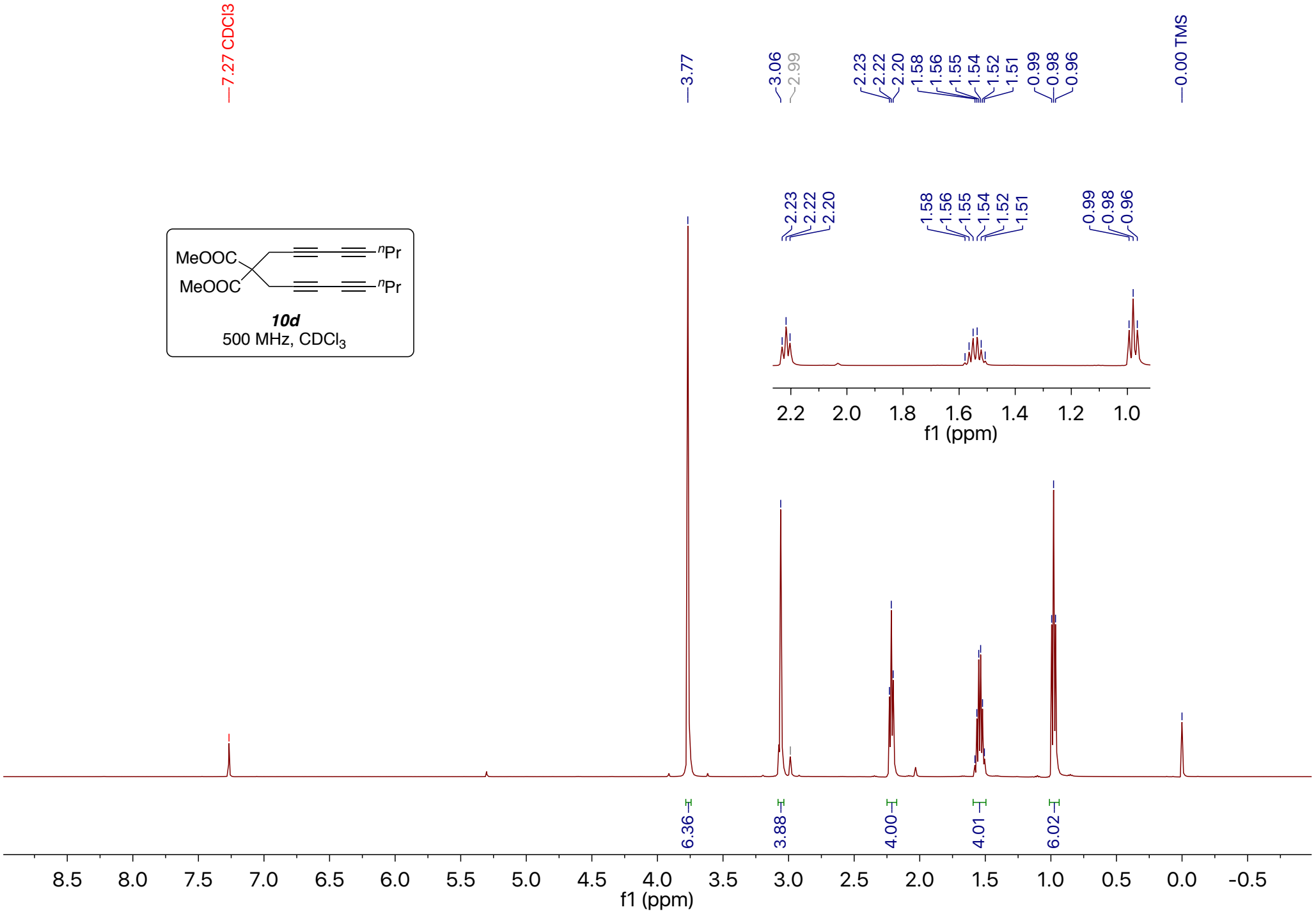

168.1
152.7
148.3
140.2
139.9
137.0
133.5
129.2
124.0
119.7
119.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
49.8
36.4
33.0
28.2
26.1
19.6
0.8
0.2 TMS
O
TBS
N
11c
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

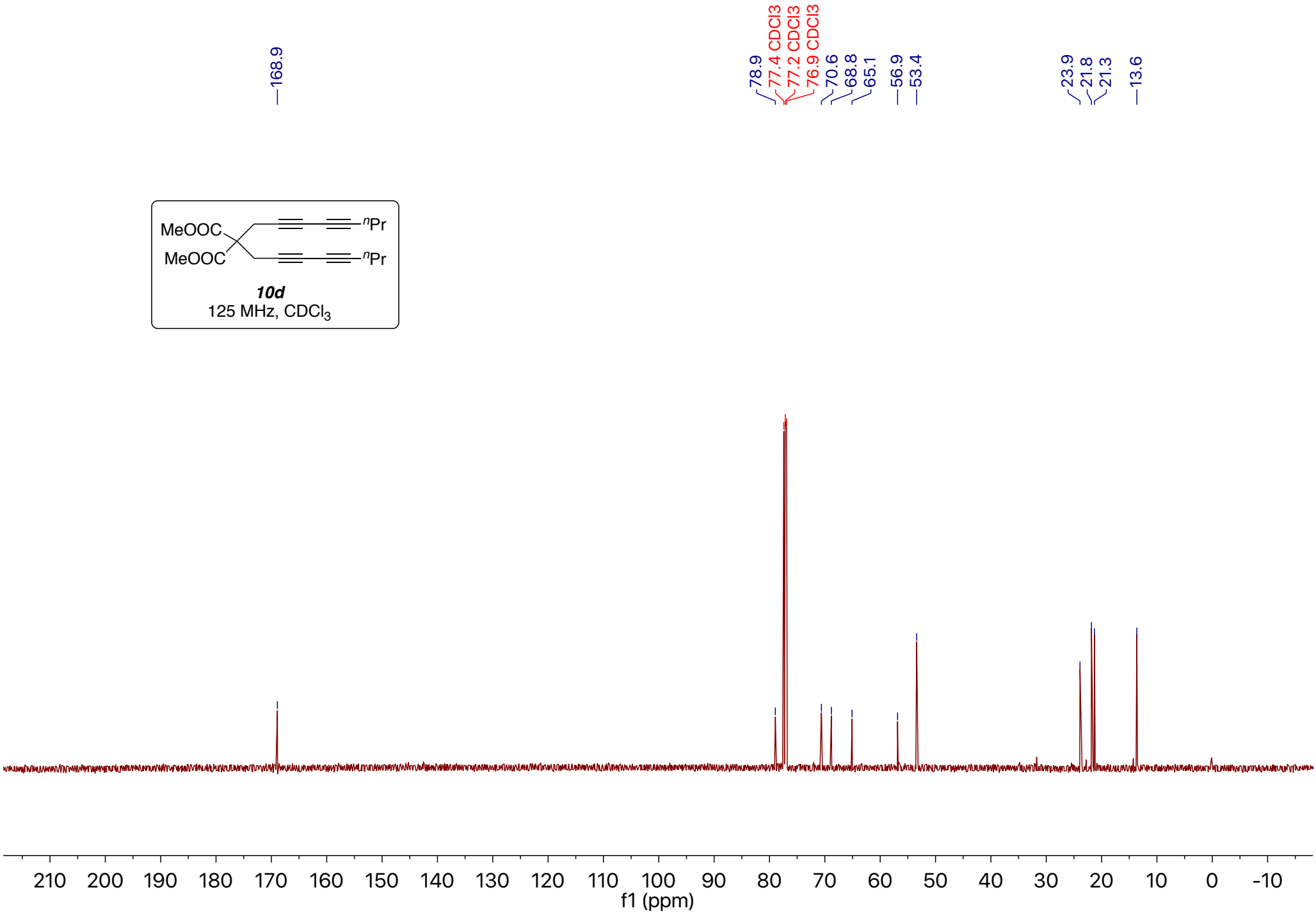

7.81 7.81 7.79 7.79 7.43 7.41 7.41 7.39 7.39 7.26 CDCl3 7.16 7.15 7.13 4.82 4.79 4.77 4.74 3.33 3.32 3.31 3.30 3.29 3.29 3.28 3.27 3.26 3.25 3.17 3.16 3.15 3.14 3.13 3.12 3.11 3.11 3.10 2.98 2.96 2.95 2.18 2.17 2.17 2.17 2.16 2.15 2.14 2.13 2.13 2.12 2.12 2.12 2.11 2.08 2.06 2.05 2.04 2.04 2.03 2.02 2.01 2.00 1.53 HDO 1.05 0.71 0.69 0.00 TMS
3.309 3.303 3.292 3.287 3.276 3.270 3.259 3.254 3.166 3.156 3.148 3.140 3.131 3.123 3.114 3.106 2.977 2.961 2.947
3.3 3.2 3.1 3.0
f1 (ppm)
2.170 2.167 2.159 2.154 2.144 2.135 2.131 2.121 2.118 2.115 2.077 2.061 2.052 2.044 2.036 2.027 2.019 2.010 2.002
2.20 2.15 2.10 2.05 2.00
f1 (ppm)
tBu F Si O N
11c'
500 MHz, CDCl3
2.03 3.03 1.00 1.10 1.01 1.02 1.02 2.07 1.05 1.06 9.03 3.17
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

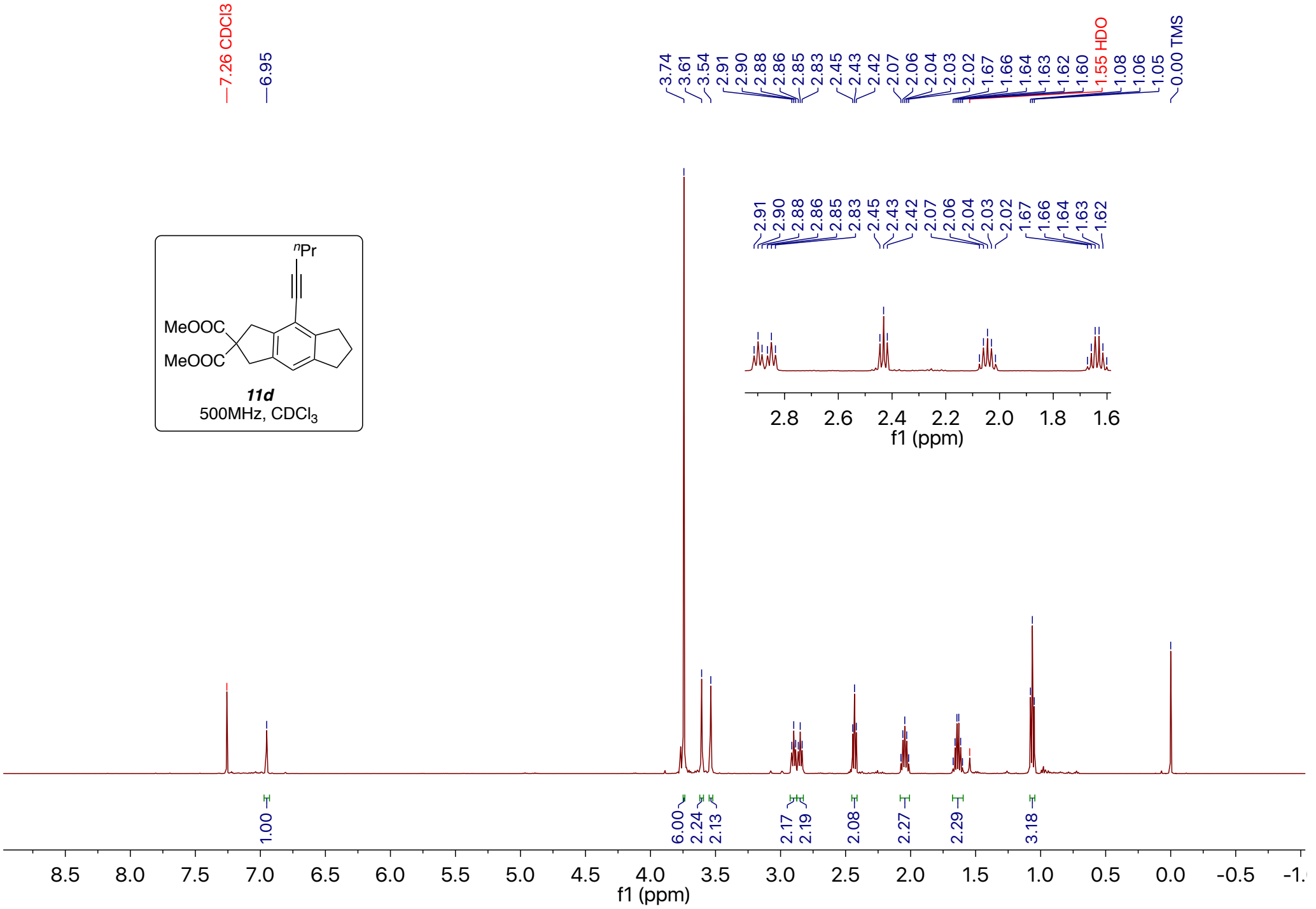

168.4
153.0
149.3
139.9
138.8
137.0
136.9
129.3
129.1
129.0
124.3
120.3
119.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
50.5
34.8
34.7
33.0
27.1
25.7
25.7
20.9
20.8
0.2 TMS
-1.6
-1.8
F
tBu
Si
O
N
11c'
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

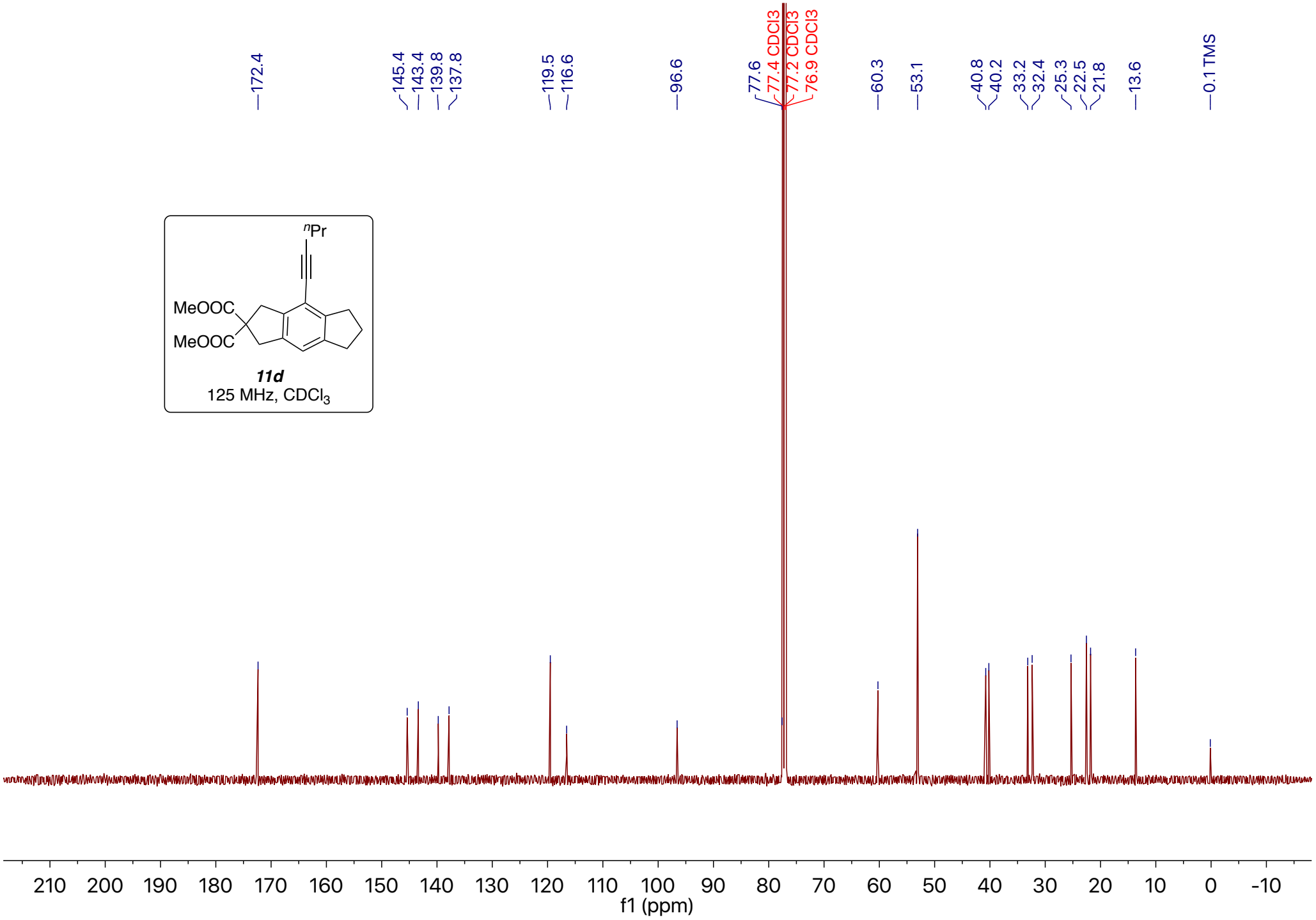

7.88
7.87
7.87
7.74
7.44
7.42
7.40
7.33
7.26 CDCl3
7.18
7.16
7.15
4.80
3.01
3.00
2.98
2.19
2.17
2.16
2.14
2.13
1.55 HDO
0.95
-0.00 TMS
O
N
11c"
500 MHz, CDCl3
f1 (ppm)
1.96
0.91
1.99
1.00
0.96
2.04
3.96
1.98

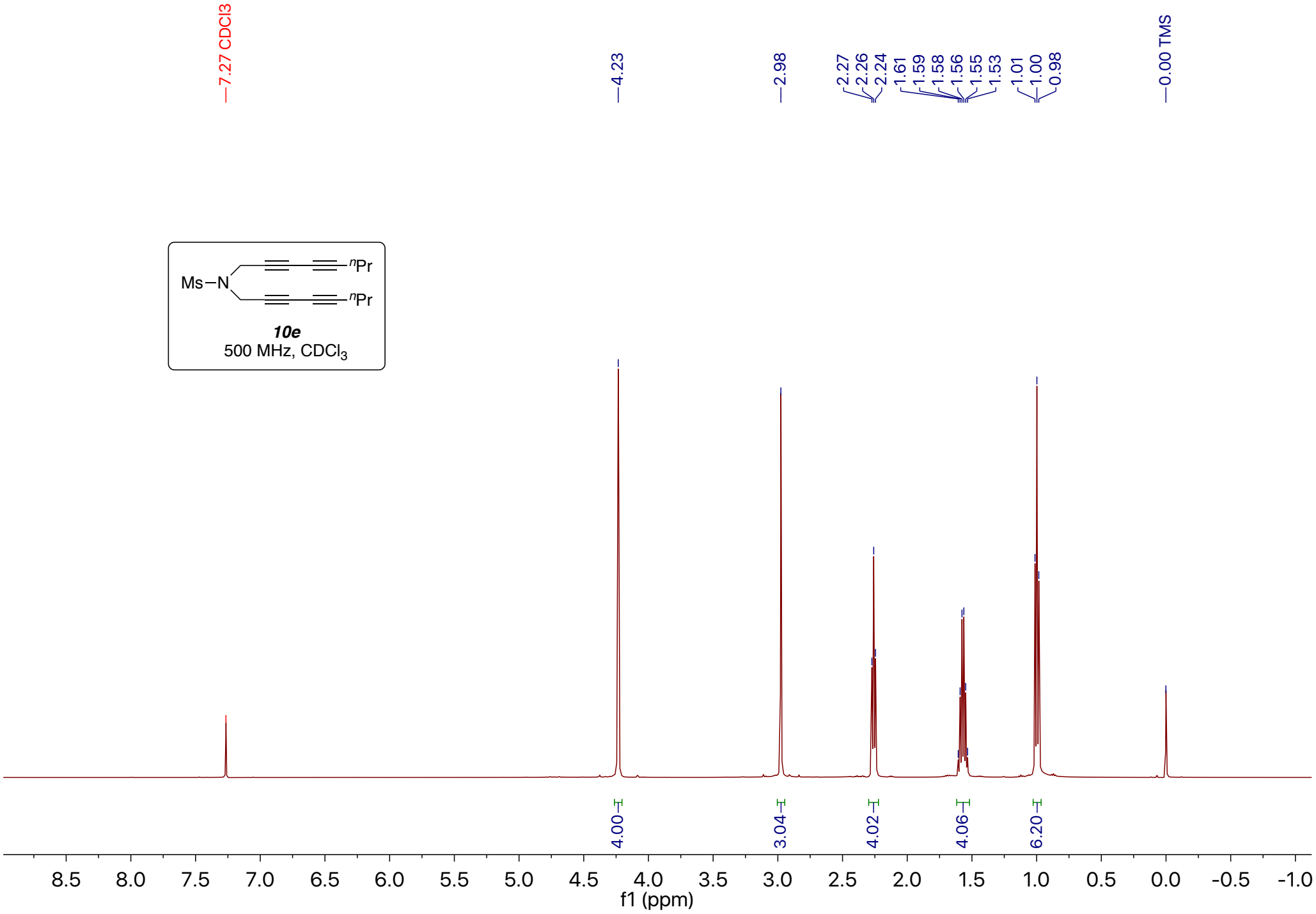

168.0
149.8
145.2
140.0
139.0
131.9
129.3
124.3
119.9
119.4
118.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
50.6
33.2
32.6
25.9
0.1 TMS
O
N
11c"
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

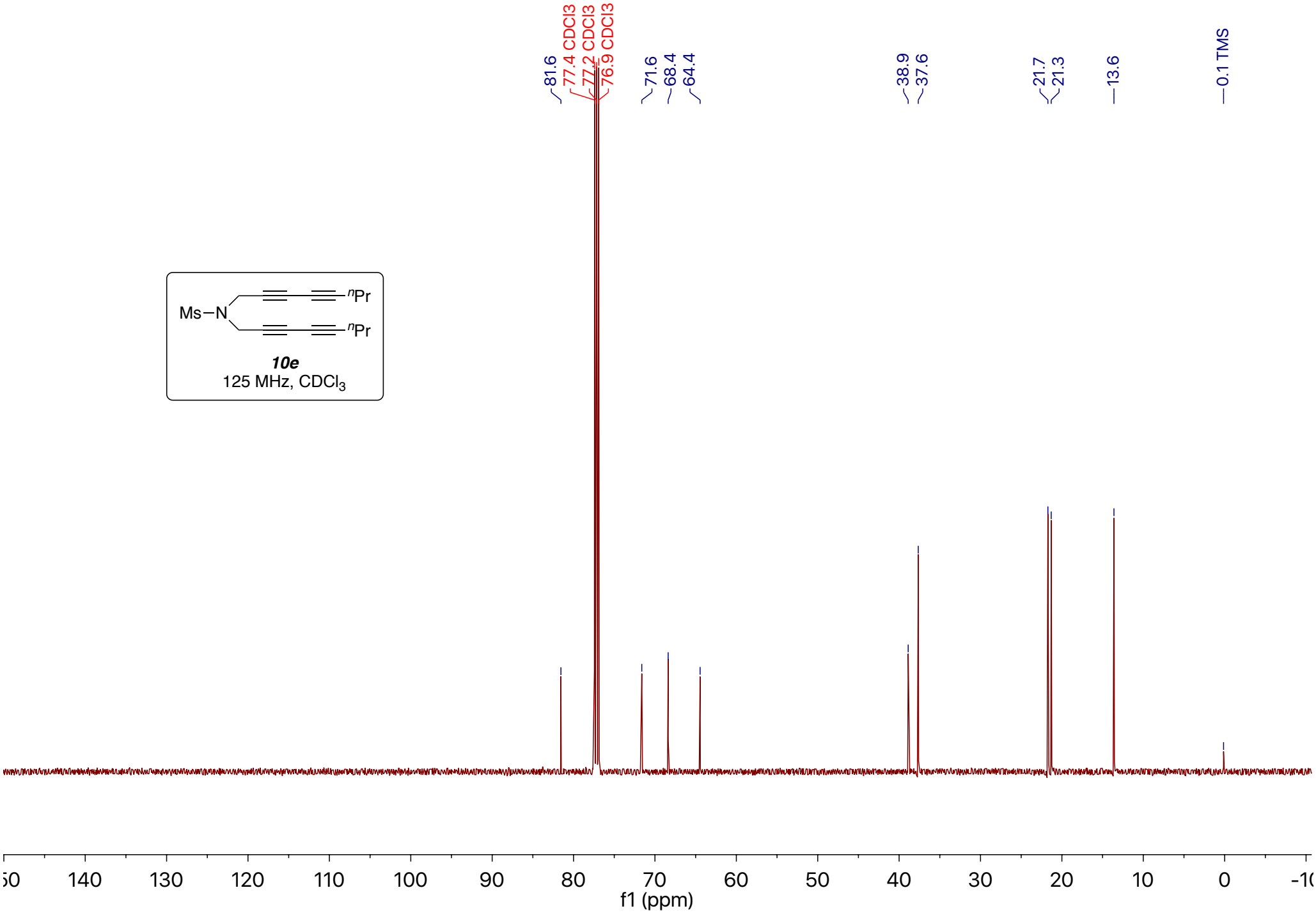

7.27 CDCl3
3.77
3.06
2.99
2.23
2.22
2.20
1.58
1.56
1.55
1.54
1.52
1.51
0.99
0.98
0.96
0.00 TMS
MeOOC
MeOOC
nPr
nPr
10d
500 MHz, CDCl3
f1 (ppm)
6.36
3.88
4.00
4.01
6.02
f1 (ppm)

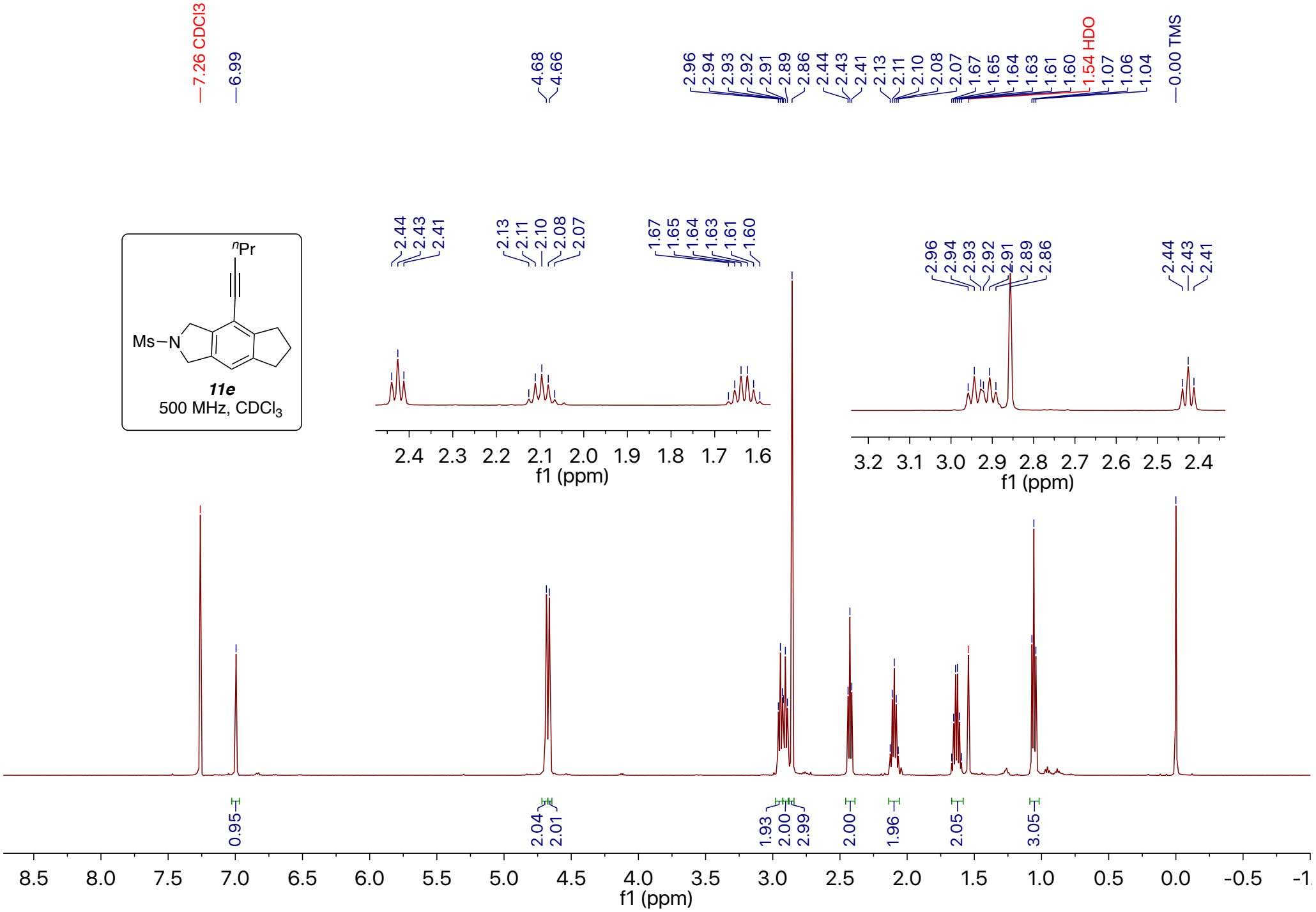

168.9
78.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
70.6
68.8
65.1
56.9
53.4
23.9
21.8
21.3
13.6
MeOOC
MeOOC
nPr
nPr
10d
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

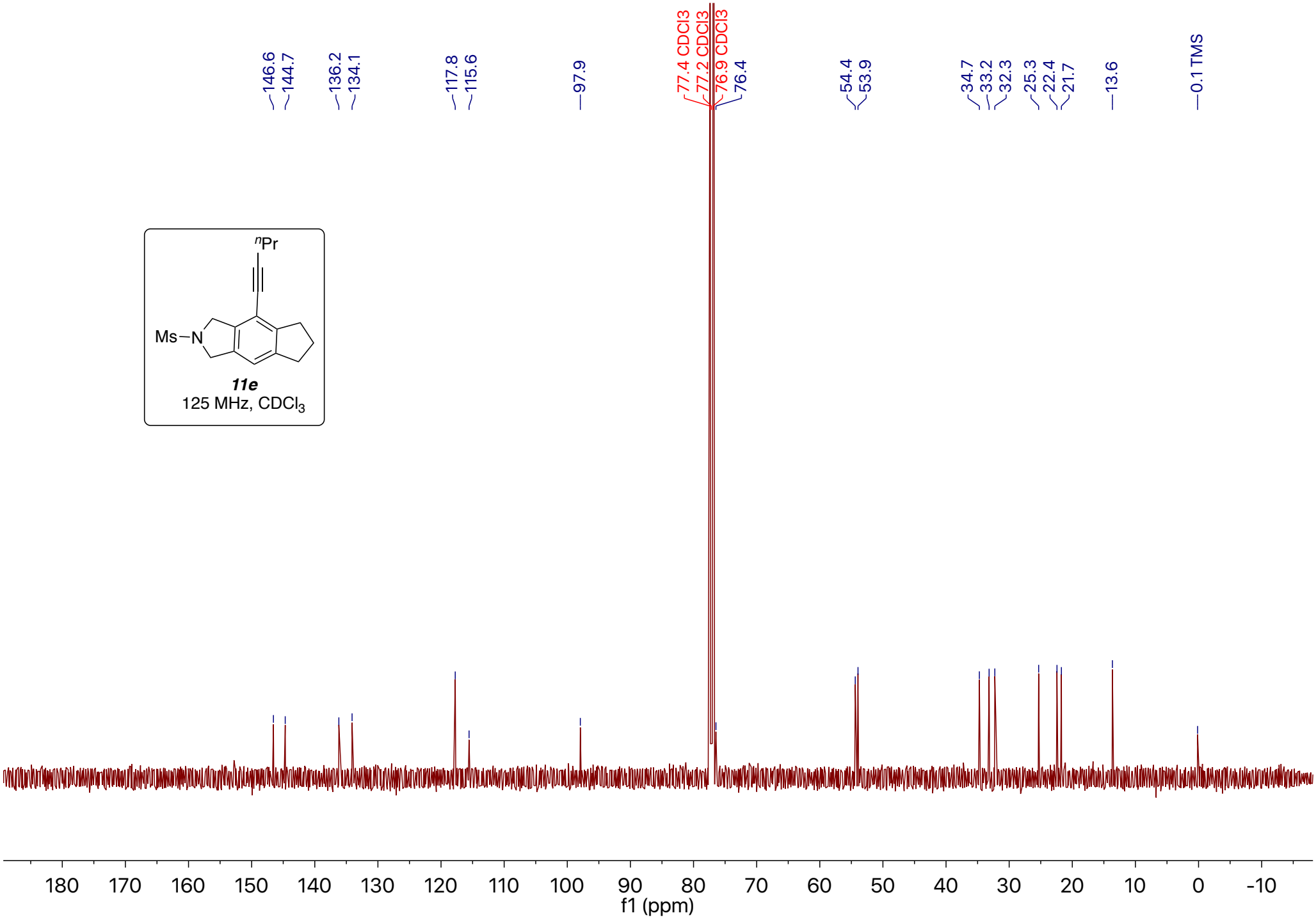

7.26 CDCl3
6.95
3.74
3.61
3.54
2.91
2.90
2.88
2.86
2.85
2.83
2.45
2.43
2.42
2.07
2.06
2.04
2.03
2.02
1.67
1.66
1.64
1.63
1.62
1.60
1.55 HDO
1.08
1.06
1.05
0.00 TMS
nPr
MeOOC
MeOOC
11d
500MHz, CDCl3
f1 (ppm)
1.00
6.00
2.24
2.13
2.17
2.19
2.08
2.27
2.29
3.18
f1 (ppm)

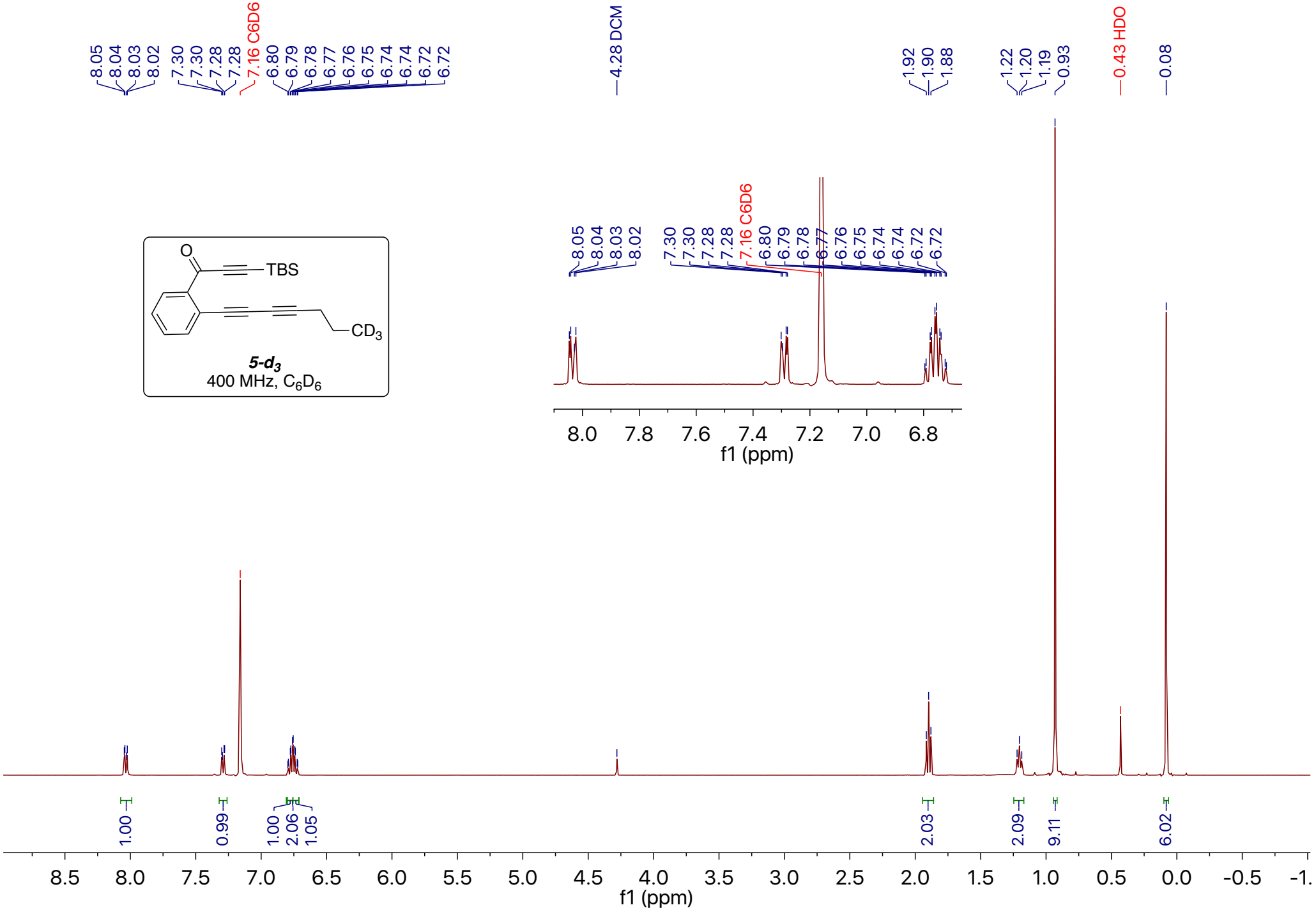

172.4
145.4
143.4
139.8
137.8
119.5
116.6
96.6
77.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
60.3
53.1
40.8
40.2
33.2
32.4
25.3
22.5
21.8
13.6
0.1 TMS
nPr
MeOOC
MeOOC
11d
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

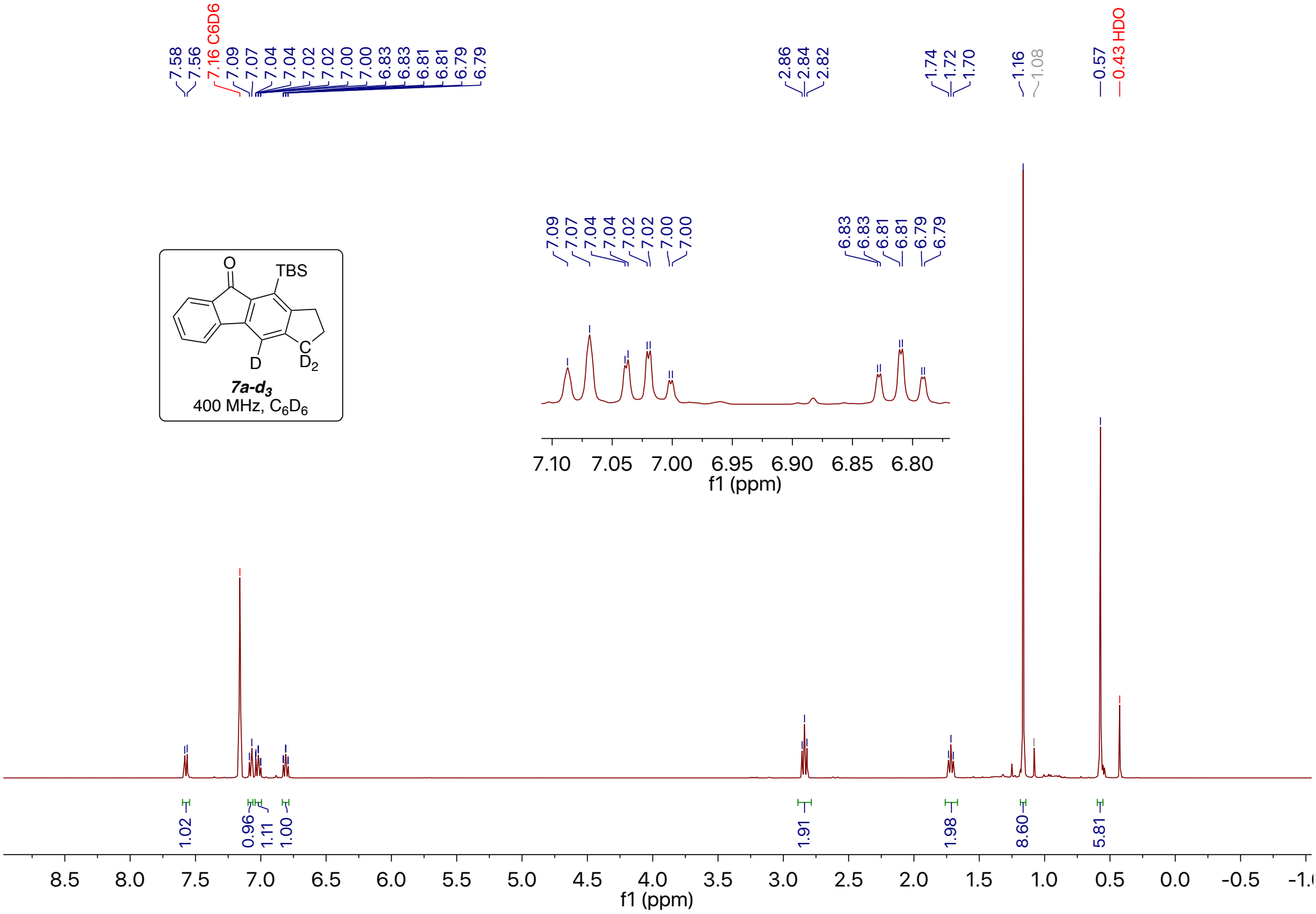

7.27 CDCl3
4.23
2.98
2.27
2.26
2.24
1.61
1.59
1.58
1.56
1.55
1.53
1.01
1.00
0.98
0.00 TMS
Ms–N
nPr
nPr
10e
500 MHz, CDCl3
4.00
3.04
4.02
4.06
6.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

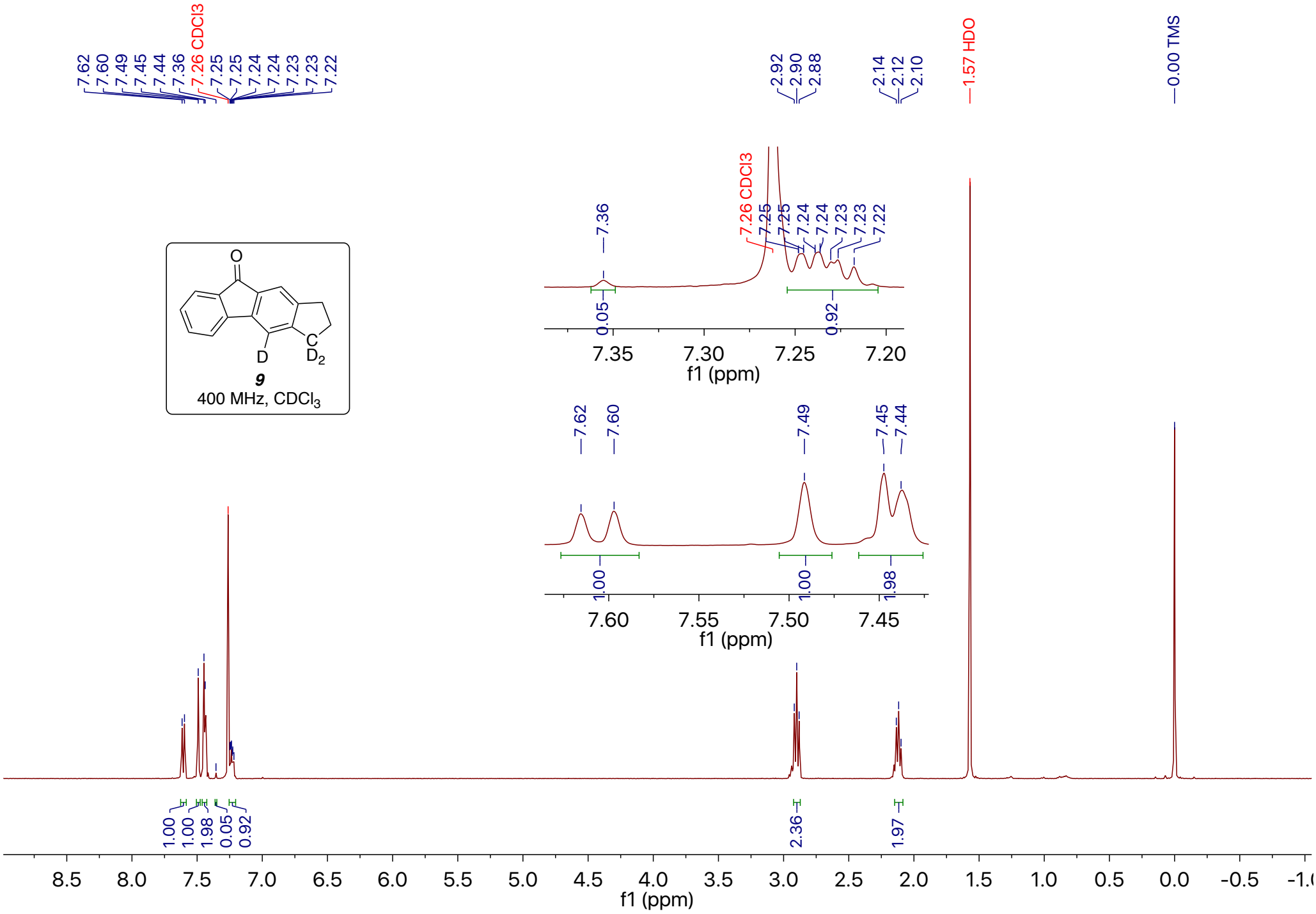

81.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
71.6
68.4
64.4
38.9
37.6
21.7
21.3
13.6
0.1 TMS
Ms–N
nPr
nPr
10e
125 MHz, CDCl3
f1 (ppm)

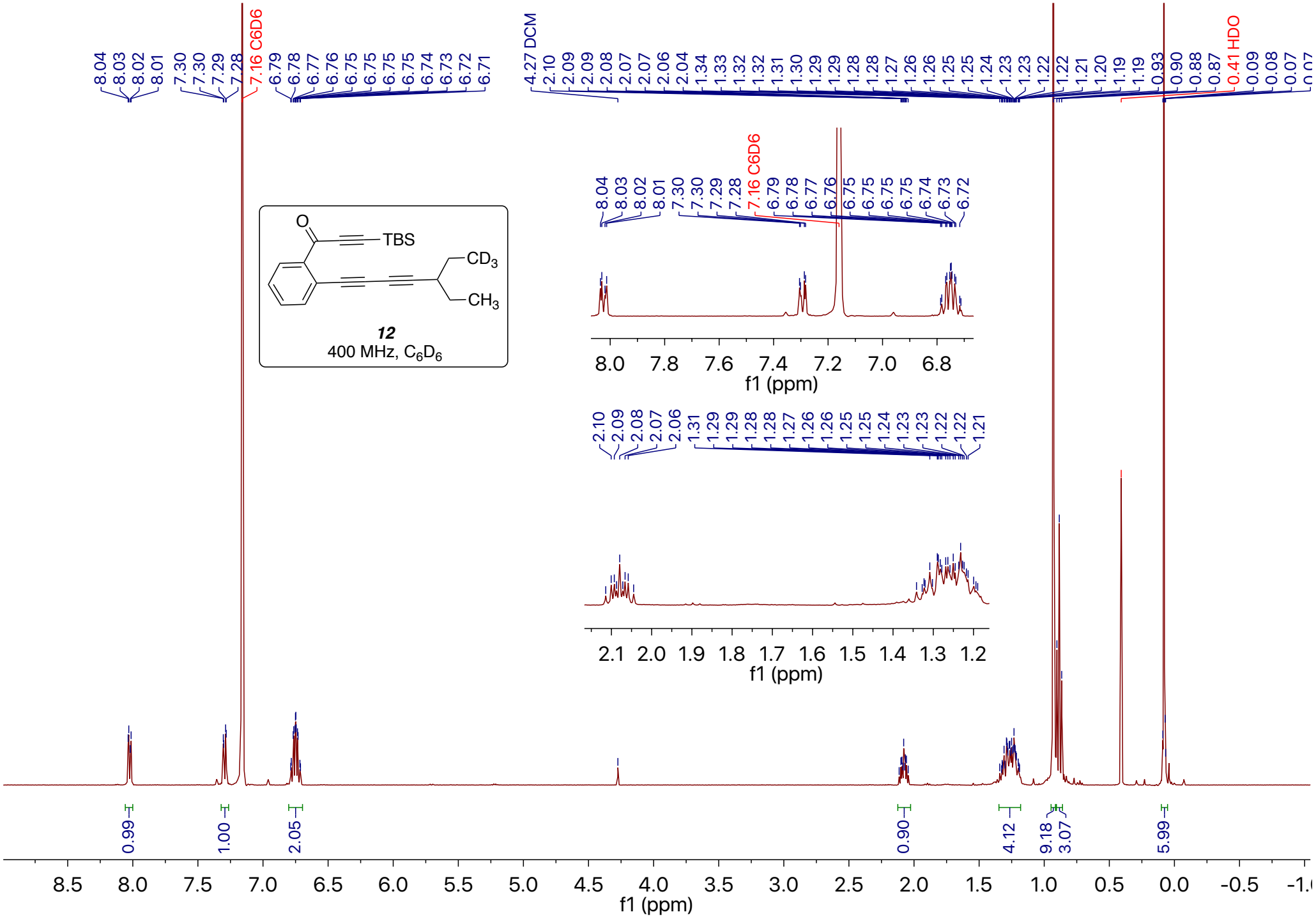

7.26 CDCl3
6.99
4.68
4.66
2.96
2.94
2.93
2.92
2.91
2.89
2.86
2.44
2.43
2.41
2.13
2.11
2.10
2.08
2.07
1.67
1.65
1.64
1.63
1.61
1.60
1.54 HDO
1.07
1.06
1.04
0.00 TMS
nPr
Ms–N
11e
500 MHz, CDCl3
f1 (ppm)
0.95
2.04
2.01
1.93
2.00
2.99
2.00
1.96
2.05
3.05

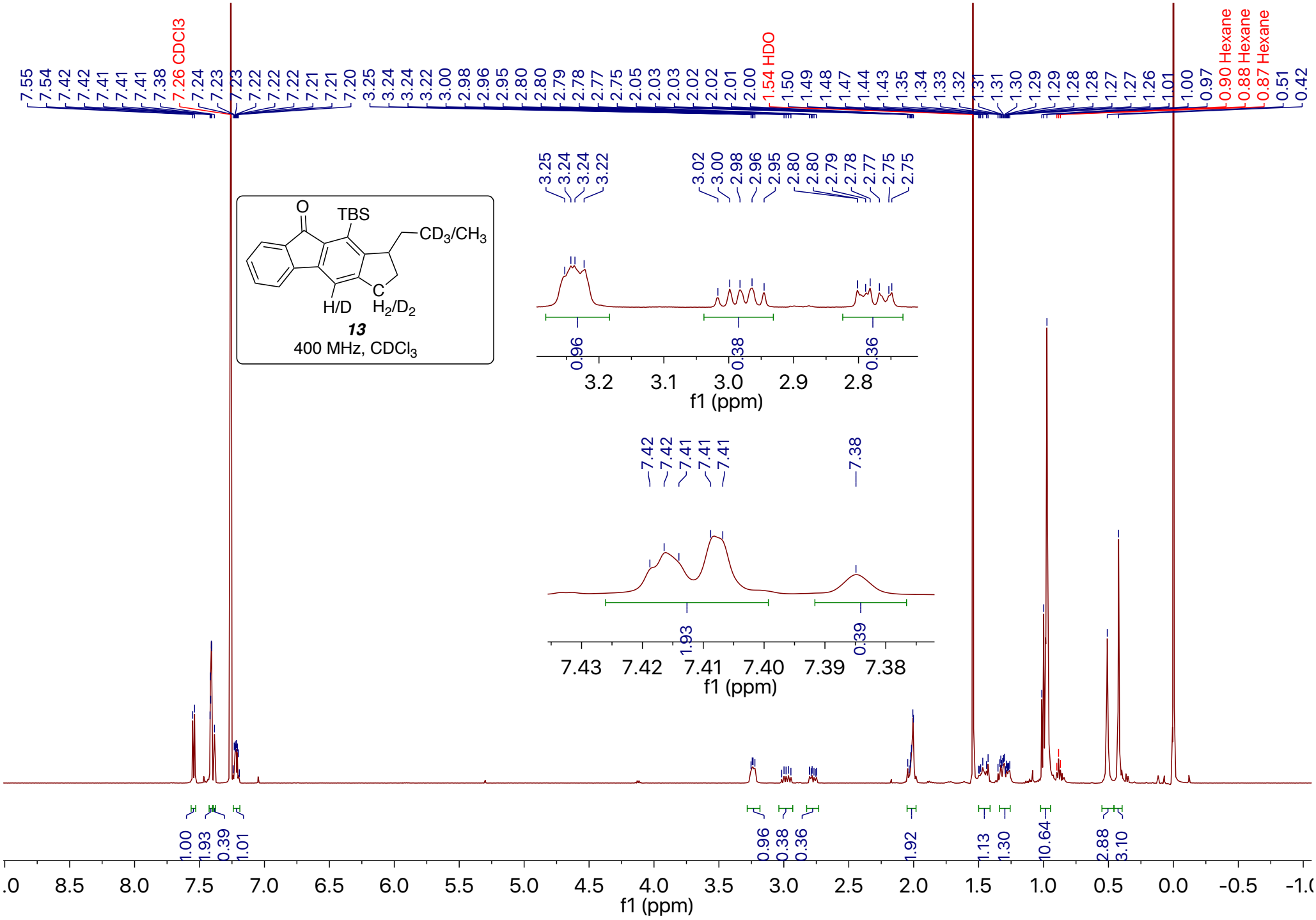

146.6
144.7
136.2
134.1
117.8
115.6
97.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.4
54.4
53.9
34.7
33.2
32.3
25.3
22.4
21.7
13.6
0.1 TMS
nPr
Ms–N
11e
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

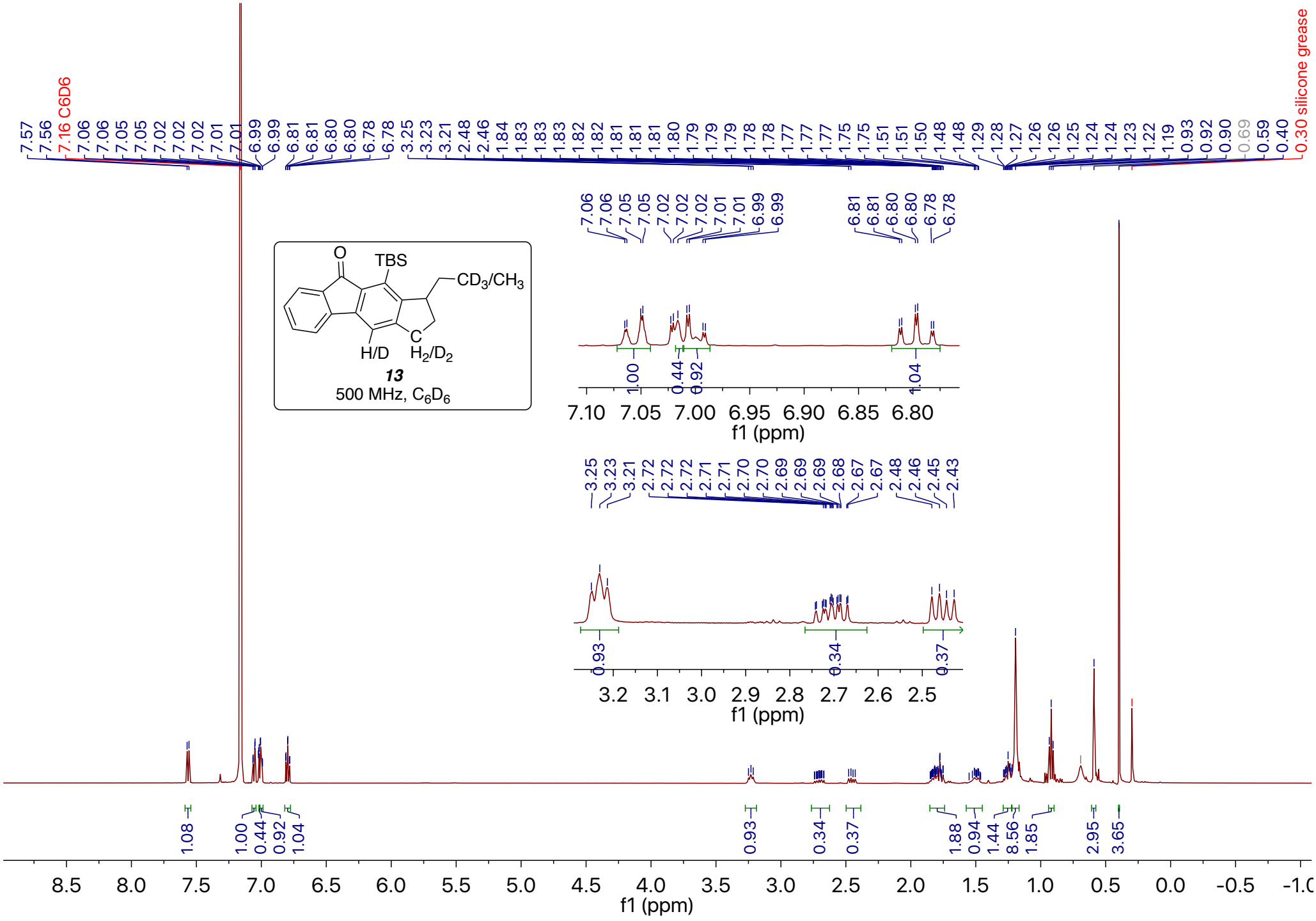

8.05
8.04
8.03
8.02
7.30
7.30
7.28
7.28
7.16 C6D6
6.80
6.79
6.78
6.77
6.76
6.75
6.74
6.74
6.72
6.72
4.28 DCM
1.92
1.90
1.88
1.22
1.20
1.19
0.93
0.43 HDO
0.08
O
TBS
CD3
5-d3
400 MHz, C6D6
f1 (ppm)
1.00
0.99
1.00
2.06
1.05
2.03
2.09
9.11
6.02


7.58
7.56
7.16 C6D6
7.09
7.07
7.04
7.04
7.02
7.02
7.00
7.00
6.83
6.83
6.81
6.81
6.79
6.79
2.86
2.84
2.82
1.74
1.72
1.70
1.16
1.08
0.57
0.43 HDO
O
TBS
D
C
D2
7a-d3
400 MHz, C6D6
7.09
7.07
7.04
7.04
7.02
7.02
7.00
7.00
6.83
6.83
6.81
6.81
6.79
6.79
7.10 7.05 7.00 6.95 6.90 6.85 6.80
f1 (ppm)
1.02
0.96
1.11
1.00
1.91
1.98
8.60
5.81
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


7.62
7.60
7.49
7.45
7.44
7.36
7.26 CDCl3
7.25
7.25
7.24
7.24
7.23
7.23
7.22
2.92
2.90
2.88
2.14
2.12
2.10
1.57 HDO
0.00 TMS
O
D
C
D2
9
400 MHz, CDCl3
7.36
7.26 CDCl3
7.25
7.25
7.24
7.24
7.23
7.23
7.22
0.05
0.92
7.35
7.30
7.25
7.20
f1 (ppm)
7.62
7.60
7.49
7.45
7.44
1.00
1.00
1.98
7.60
7.55
7.50
7.45
f1 (ppm)
1.00
1.00
1.98
0.05
0.92
2.36
1.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
TBS
CD3
CH3
12
400 MHz, C6D6
7.16 C6D6
4.27 DCM
0.41 HDO
f1 (ppm)
0.99
1.00
2.05
0.90
4.12
9.18
3.07
5.99


7.55 7.54 7.42 7.42 7.41 7.41 7.41 7.38 7.26 CDCl3 7.24 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.20
3.25 3.24 3.24 3.22 3.00 2.98 2.96 2.95 2.80 2.80 2.79 2.78 2.77 2.75 2.05 2.03 2.03 2.02 2.02 2.01 2.00
1.54 HDO
1.50 1.49 1.48 1.47 1.44 1.43 1.35 1.34 1.33 1.32 1.31 1.31 1.30 1.29 1.29 1.28 1.28 1.27 1.27 1.26 1.01 1.00 0.97
0.90 Hexane 0.88 Hexane 0.87 Hexane 0.51 0.42
O
TBS
CD3/CH3
C
H/D H2/D2
13
400 MHz, CDCl3
3.25 3.24 3.24 3.22 3.02 3.00 2.98 2.96 2.95 2.80 2.80 2.79 2.78 2.77 2.75 2.75
0.96 0.38 0.36
3.2 3.1 3.0 2.9 2.8
f1 (ppm)
7.42 7.42 7.41 7.41 7.41 7.38
1.93 0.39
7.43 7.42 7.41 7.40 7.39 7.38
f1 (ppm)
1.00 1.93 0.39 1.01 0.96 0.38 0.36 1.92 1.13 1.30 10.64 2.88 3.10
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


7.57 7.56 7.16 C6D6 7.06 7.06 7.05 7.05 7.02 7.02 7.02 7.01 7.01 6.99 6.99 6.81 6.81 6.80 6.80 6.78 6.78 3.25 3.23 3.21 2.48 2.46 1.84 1.83 1.83 1.83 1.82 1.82 1.81 1.81 1.81 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.77 1.75 1.75 1.51 1.51 1.50 1.48 1.48 1.29 1.28 1.27 1.26 1.26 1.25 1.24 1.24 1.23 1.22 1.19 0.93 0.92 0.90 0.69 0.59 0.40 0.30 silicone grease
O
TBS
CD3/CH3
C
H/D
H2/D2
13
500 MHz, C6D6
1.00 0.44 0.92 1.04
7.10 7.05 7.00 6.95 6.90 6.85 6.80
f1 (ppm)
0.93 0.34 0.37
3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5
f1 (ppm)
1.08 1.00 0.44 0.92 1.04 0.93 0.34 0.37 1.88 0.94 1.44 8.56 1.85 2.95 3.65
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)