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I. General Experimental Protocols

"^{13}C and ^{1}H NMR spectra were measured on Bruker Avance 500 (500 MHz) spectrometers. ^{1}H NMR chemical shifts in $CDCl_3$ are referenced to TMS (δ = 0.00 ppm). Non-first order multiplets are referred to by the acronym "nfom". Non-first order doublets, often seen for 1,4-disubstituted benzene derivatives, are identified as "nfod". ^{13}C NMR chemical shifts for spectra collected in $CDCl_3$ are referenced to the carbon chemical shift in $CDCl_3$ (δ = 77.16 ppm). ^{19}F NMR spectra are referenced to $CFCl_3$ (δ = 0.00 ppm, as an external reference). The following format is used to report resonances in the ^{1}H spectra: chemical shift in ppm [multiplicity, coupling constant(s) (*J*) in Hz, integration to the nearest whole number of protons, and assignment]. ^{1}H NMR assignments are given by the substructure environment, e.g., OCH_aH_b. Complex structures are often numbered in the graphic in order to simplify the proton assignment identification. Coupling constant analysis was guided by methods we have described elsewhere.[1,2]"

Infrared spectra were measured as thin films with a Midac Corporation Prospect 4000 FT-IR spectrometer in the ATR mode (germanium window). Only particularly diagnostic and/or intense peaks are given.

High-resolution mass spectrometry (HRMS) measurements were determined on a Bruker BioTOF II (ESI-TOF) instrument in the electrospray ionization (ESI) mode. PPG or PEG was added to the sample as an internal calibrant/standard. Samples were dissolved in MeOH or DCM/MeOH. One low resolution measurement was made with a Expression CMS instrument using APCI.

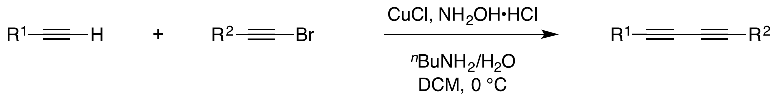
UV-Vis absorption spectra were recorded in THF at a concentration of 10^{-5} M on a Varian Cary 50 Bio UV-Visible Spectrophotometer. Fluorescence data were obtained in THF at a concentration of 10^{-7} M using a Varian Cary Eclipse Fluorescence Spectrophotometer.

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

Reactions performed under anhydrous conditions were done under an atmosphere of nitrogen in flame-dried glassware. Anhydrous methylene chloride was collected immediately prior to use after being freshly passed through a column containing activated alumina. Chloroform (amylene-stabilized) was passed through activated alumina before use. The reaction temperatures reported are the temperature of an external heating bath of the air surrounding the reaction tube. Reactions carried out at temperatures higher than the boiling point of the reaction solvent were performed in a screw-capped vial culture tube or vial, sealed with an inert, Teflon®-lined screw cap.

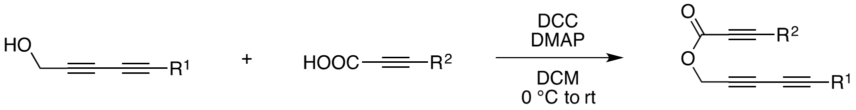
II. Procedures for preparation of and characterization data for all new compounds

A. General procedure for the Cadiot–Chodkiewicz alkyne/alkyne cross-coupling reaction



CuCl (0.10 equiv relative to the terminal alkyne substrate) was dissolved in a 30:70 (v:v) mixture of $nBuNH_2$:H_2O (5.0 mL/mmol relative to the terminal alkyne substrate). An excess of NH_2OH•HCl (ca. 10 mg per mmol of the terminal alkyne substrate) was added with stirring. The color of this solution changed from deep blue to colorless immediately, indicating full conversion of any Cu(II) to Cu(I). The headspace of the reaction vessel was flushed with N_2. The flask was closed with a septum, a balloon of nitrogen gas was attached, and the flask was cooled in an ice water bath. The terminal alkyne (1.0 equiv) in CH_2Cl_2 (ca. 2.5 mL/mmol) was injected into the flask, resulting in a yellow, orange, or red suspension, indicative of formation of an alkynyl copper species. After ca. 5 min, a solution of the 1-bromoalkyne (1.2–1.5 equiv) in CH_2Cl_2 (ca. 2.5 mL/mmol) was injected dropwise over ca. 15 min using a syringe pump. This reaction mixture was stirred at the indicated temperature (0 ºC or rt). The suspension of the alkynyl copper would typically turn to a clear, two layer mixture over the course of 10–100 min, indicating consumption of the alkynyl copper species. The reaction mixture was quenched by the addition of satd. aq. NH_4Cl and then extracted with CH_2Cl_2. The combined extracts were dried, filtered, and concentrated. The residue was purified by flash chromatography on silica gel.

B. General procedure for esterification of propargylic alcohols with propiolic acids using DCC.



The propargylic alcohol (1.0 equiv), 4-dimethylaminopyridine (DMAP, 10 mol%), and propiolic acid (1.5 equiv) were dissolved in anhydrous DCM (10 mL/mmol with respect to the propargyl alcohol) and stirred at 0 ºC. *N*,*N*'-Dicyclohexylcarbodiimide (DCC*, 1.1–1.2 equiv) was added to the solution, after which the headspace of the reaction flask was purged with N_2. The resulted brown suspension was warmed to room temperature and stirred for, typically, 16 h. The crude reaction mixture was filtered by passing through a short silica plug, concentrated, and purified by flash chromatography or MPLC.

*CAUTION: DCC is an irritant and can induce sensitization. Avoid any direct contact with the skin and inhalation.

C. General procedure for the HDDA-dimerization reaction

The poly-yne precursor(s) was added to an oven-dried, threaded glass vial. Chloroform (the source was amylene-stabilized rather than ethanol-stabilized, because ethanol is known to react with HDDA-benzynes[3]) was added to arrive at a poly-yne concentration of 0.050 M. The headspace of the vial was purged with a gentle flow of N_2 gas, and the vial was sealed with a Teflon-lined cap. The reaction solution was stirred in a heated oil bath held at the indicated temperature. After the poly-yne had been consumed (TLC), the vial was cooled to room temperature. The solution was concentrated *in vacuo*, and the residue was directly subjected to MPLC for purification, using the indicated elution solvent.

• Experimental details and characterization data for each of the poly-yne substrates

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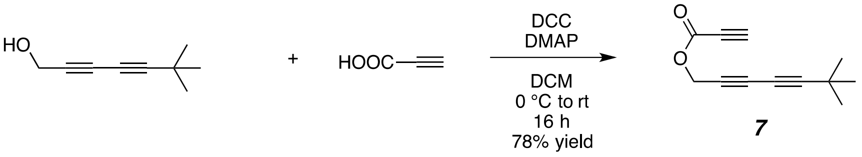
6,6-Dimethylhepta-2,4-diyn-1-yl propiolate (7)



Following general procedure B, 6,6-dimethylhepta-2,4-diyn-1-ol[4] (0.14 g, 1.0 mmol), propiolic acid (93 μL, 1.5 mmol), DMAP (12 mg, 0.10 mmol), DCC (0.25 g, 1.2 mmol), and DCM (10 mL) were used to prepare triyne **7**. Purification of the crude material by flash chromatography (hexanes:EtOAc 20:1) provided triyne **7** (0.15 g, 0.78 mmol, 78%) as a pale yellow oil.

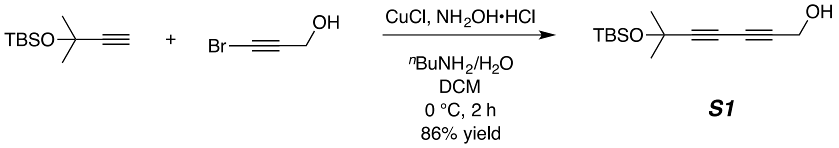
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.83 (s, 2H, $C\mathit{H}_2O$), 2.94 (s, 1H, $\equiv C\mathit{H}$), and 1.25 [s, 9H, $C(C\mathit{H}_3)_3$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 151.9, 90.3, 76.1, 74.0, 72.7, 69.0, 63.0, 54.2, 30.4, and 28.2.

IR (neat): 3288, 2973, 2932, 2869, 2124, 1722, 1366, 1289, 1178, 968, 840, and 780 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{12}H_{12}NaO_2^+$ [M+Na$^+$] requires 211.0730; found 211.0735.

6-((*tert*-Butyldimethylsilyl)oxy)-6-methylhepta-2,4-diyn-1-ol (S1)



Following general procedure A, *tert*-butyldimethyl((2-methylbut-3-yn-2-yl)oxy)silane[5] (0.79 g, 4 mmol), 3-bromoprop-2-yn-1-ol (0.68 g, 5 mmol), CuCl (40 mg, 0.4 mmol), *n*-butylamine/H_2O (v:v, 30:70, 20 mL), and DCM (20 mL) were used to prepare diyne **S1**. Purification of the crude material by flash chromatography (hexanes:EtOAc 6:1) provided diyne **S1** (0.86 g, 3.4 mmol, 86%) as a pale yellow oil.

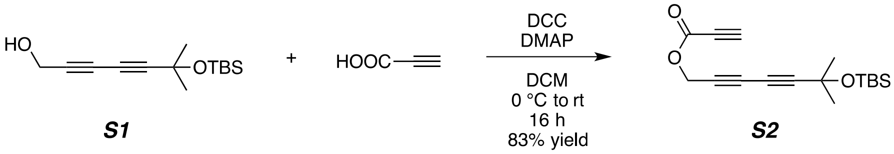
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.35 (s, 2H, $C\mathit{H}_2OH$), 1.75 (br s, 1H, $CH_2O\mathit{H}$), 1.47 [s, 6H, $C(C\mathit{H}_3)_2$], 0.86 [s, 9H, $SiC(C\mathit{H}_3)_3$], and 0.17 [s, 6H, $Si(C\mathit{H}_3)_2$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 84.9, 77.4, 70.2, 67.0, 66.7, 51.7, 32.7, 25.8, 18.0, and -3.0.

IR (neat): 3320, 2984, 2956, 2930, 2857, 2156, 1462, 1360, 1254, 1167, 1150, 1037, 838, and 776 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{14}H_{24}NaO_2Si^+$ [M+Na$^+$] requires 275.1438; found 275.1437.

6-((*tert*-Butyldimethylsilyl)oxy)-6-methylhepta-2,4-diyn-1-yl propiolate (S2)



Following general procedure B, propargyl alcohol **S1** (0.38 g, 1.5 mmol), propiolic acid (0.14 mL, 2.2 mmol), DMAP (18 mg, 0.15 mmol), DCC (0.34 g, 1.6 mmol), and DCM (15 mL) were used to prepare triyne **S2**. Purification of the crude material by flash chromatography (hexanes:EtOAc 20:1) provided triyne **S2** (0.38 g, 1.2 mmol, 83%) as a pale yellow oil.

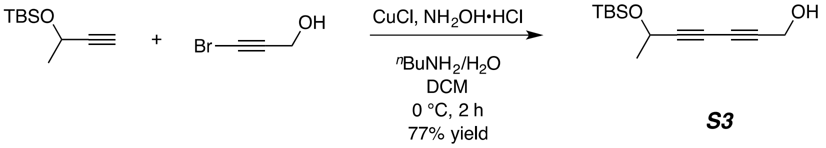
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.86 (s, 2H, CH_2O), 2.96 (s, 1H, ≡C*H*), 1.47 [s, 6H, $C(CH_3)_2$], 0.86 [s, 9H, $SiC(CH_3)_3$], and 0.16 [s, 6H, $Si(CH_3)_2$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 151.8, 85.7, 76.2, 73.9, 72.0, 71.5, 66.73, 66.71, 54.1, 32.6, 25.8, 18.0, and -2.9.

IR (neat): 3291, 2984, 2955, 2931, 2857, 2124, 1725, 1361, 1252, 1156, 1039, 971, 838, and 777 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{17}H_{24}NaO_3Si^+$ [M+Na$^+$] requires 327.1387; found 327.1387.

6-((*tert*-Butyldimethylsilyl)oxy)hepta-2,4-diyn-1-ol (S3)



Following general procedure A, (but-3-yn-2-yloxy)(*tert*-butyl)dimethylsilane[6] (0.55 g, 3 mmol), 3-bromoprop-2-yn-1-ol (0.61 g, 4.5 mmol), CuCl (30 mg, 0.3 mmol), *n*-butylamine/H_2O (v:v, 30:70, 15 mL), and DCM (15 mL) were used to prepare diyne **S3**. Purification of the crude material by flash chromatography (hexanes:EtOAc 6:1) provided diyne **S3** (0.55 g, 2.3 mmol, 77%) as a pale yellow oil.

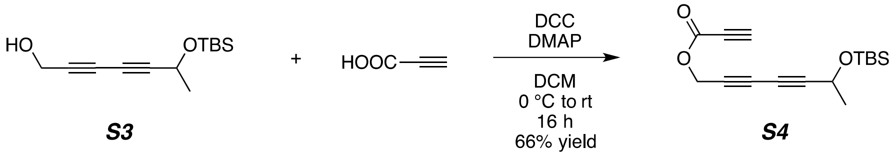
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.57 [q, *J* = 6.6 Hz, 1H, $CH(CH_3)$], 4.34 (s, 2H, CH_2OH), 1.75 (br s, 1H, CH_2OH), 1.42 [d, *J* = 6.6 Hz, 3H, $HC(CH_3)$], 0.90 [s, 9H, $SiC(CH_3)_3$], 0.13 [s, 3H, $Si(CH_3)_a$], and 0.11 [s, 3H, $Si(CH_3)_b$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 82.2, 77.1, 70.2, 67.5, 59.4, 51.6, 25.9, 25.1, 18.3, -4.5, and -4.9.

IR (neat): 3341, 2983, 2955, 2931, 2858, 2160, 1471, 1338, 1253, 1101, 1050, 1019, 966, 837, and 778 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{13}H_{22}NaO_2Si^+$ [M+Na$^+$] requires 261.1281; found 261.1275.

6-((*tert*-Butyldimethylsilyl)oxy)hepta-2,4-diyn-1-yl propiolate (S4)



Following general procedure B, propargyl alcohol **S3** (0.47 g, 2.0 mmol), propiolic acid (0.19 mL, 3.0 mmol), DMAP (24 mg, 0.20 mmol), DCC (0.49 g, 2.4 mmol), and DCM (20 mL) were used to prepare triyne **S4**. Purification of the crude material by flash chromatography (hexanes:EtOAc 20:1) provided triyne **S4** (0.38 g, 1.3 mmol, 66%) as a pale yellow oil.

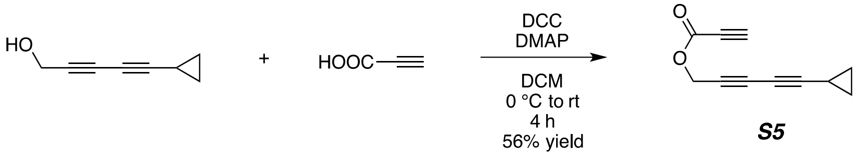
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.85 (s, 2H, $\mathrm{C}H_2\mathrm{O}$), 4.56 [q, *J* = 6.6 Hz, 1H, $\mathrm{C}H(\mathrm{CH}_3)$], 2.96 (s, 1H, ≡C*H*), 1.43 [d, *J* = 6.6 Hz, 3H, $\mathrm{HC}(\mathrm{C}H_3)$], 0.90 [s, 9H, $\mathrm{SiC}(\mathrm{C}H_3)_3$], 0.13 [s, 3H, $\mathrm{Si}(\mathrm{C}H_3)_a$], and 0.11 [s, 3H, $\mathrm{Si}(\mathrm{C}H_3)_b$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 151.8, 83.1, 76.2, 73.9, 72.0, 71.2, 67.1, 59.4, 54.1, 25.9, 25.0, 18.3, -4.5, and -4.9.

IR (neat): 3289, 2954, 2931, 2858, 2124, 1725, 1471, 1368, 1252, 1102, 1051, 975, 836, and 779 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{16}H_{22}NaO_3Si^+$ [$M+Na^+$] requires 313.1230; found 313.1235.

5-Cyclopropylpenta-2,4-diyn-1-yl propiolate (S5)



Following general procedure B, 5-cyclopropylpenta-2,4-diyn-1-ol[7] (0.12 g, 1.0 mmol), propiolic acid (93 *u*L, 1.5 mmol), DMAP (12 mg, 0.10 mmol), DCC (0.25 g, 1.2 mmol), and DCM (10 mL) were used to prepare triyne **S5**. Purification of the crude material by flash chromatography (hexanes:EtOAc 20:1) provided triyne **S5** (97 mg, 0.56 mmol, 56%) as a light brown oil.

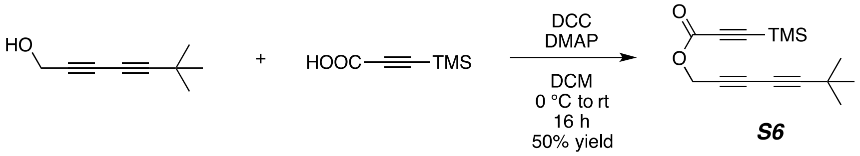
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.82 (s, 2H, $\mathrm{C}H_2\mathrm{O}$), 2.94 (s, 1H, ≡C*H*), 1.36–1.30 (nfom, 1H, ≡CC*H*), 0.88–0.83 (nfom, 2H, $\mathrm{C}H_a\mathrm{C}H_a$), and 0.82–0.78 (nfom, 2H, $\mathrm{C}H_b\mathrm{C}H_b$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 151.9, 86.0, 76.1, 74.0, 73.1, 67.2, 59.6, 54.3, 9.1, and 0.2.

IR (neat): 3281, 3016, 2945, 2122, 1720, 1429, 1377, 1356, 1090, 1031, 970, 938, and 829 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{11}H_8NaO_2^+$ [$M+Na^+$] requires 195.0417; found 195.0413.

6,6-Dimethylhepta-2,4-diyn-1-yl 3-(trimethylsilyl)propiolate (S6)



Following general procedure B, 6,6-dimethylhepta-2,4-diyn-1-ol[4] (0.14 g, 1.0 mmol), 3-(trimethylsilyl)propiolic acid (0.21 g, 1.5 mmol), DMAP (12 mg, 0.10 mmol), DCC (0.25 g, 1.2 mmol), and DCM (10 mL) were used to prepare triyne **S6**. Purification of the crude material by MPLC (hexanes:EtOAc 50:1) provided triyne **S6** (0.13 g, 0.50 mmol, 50%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.80 (s, 2H, CH_2O), 1.24 [s, 9H, $C(CH_3)_3$], and 0.25 [s, 9H, $Si(CH_3)_3$].

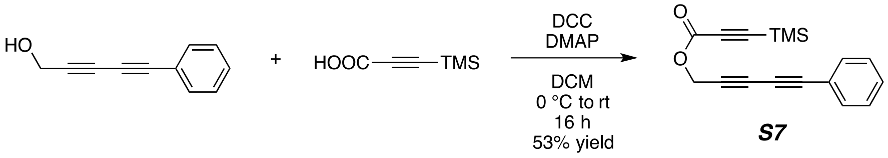
^{13}C NMR (126 MHz, $CDCl_3$): δ 152.0, 95.8, 93.7, 90.1, 72.4, 69.3, 63.0, 53.8, 30.4, 28.1, and -0.8.

IR (neat): 2970, 2933, 2869, 2174, 2118, 1719, 1365, 1253, 1179, 847, and 782 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{15}H_{20}NaO_2Si^+$ [M+Na$^+$] requires 283.1125; found 283.1134.

Mp: 31–33 ºC.

5-Phenylpenta-2,4-diyn-1-yl 3-(trimethylsilyl)propiolate (S7)



Following general procedure B, 5-phenylpenta-2,4-diyn-1-ol[4] (0.16 g, 1.0 mmol), 3-(trimethylsilyl)propiolic acid (0.21 g, 1.5 mmol), DMAP (12 mg, 0.10 mmol), DCC (0.25 g, 1.2 mmol), and DCM (10 mL) were used to prepare triyne **S7**. Purification of the crude material by MPLC (hexanes:EtOAc 50:1) provided triyne **S7** (0.15 g, 0.53 mmol, 53%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (nfod, J = 7.0 Hz, 2H, PhH_o), 7.38 (tt, J = 7.5, 1.4 Hz, 1H, PhH_p), 7.33 (nfodd, J = 7.5, 7.0 Hz, 2H, PhH_m), 4.90 (s, 2H, CH_2O), and 0.26 [s, 9H, $Si(CH_3)_3$].

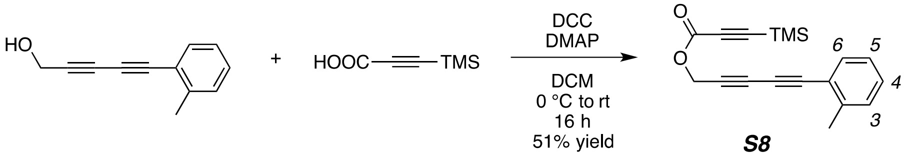
^{13}C NMR (126 MHz, $CDCl_3$): δ 152.1, 132.8, 129.7, 128.6, 121.2, 96.2, 93.6, 79.4, 75.0, 73.0, 72.2, 53.9, and -0.8.

IR (neat): 2963, 2904, 2174, 1719, 1652, 1558, 1368, 1254, 1110, 1025, 977, 865, and 826 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{17}H_{16}NaO_2Si^+$ [M+Na$^+$] requires 303.0812; found 303.0799.

Mp: 60–62 ºC.

5-(*o*-Tolyl)penta-2,4-diyn-1-yl 3-(trimethylsilyl)propiolate (S8)



Following general procedure B, 5-(*o*-tolyl)penta-2,4-diyn-1-ol[8] (0.17 g, 1.0 mmol), 3-(trimethylsilyl)propiolic acid (0.21 g, 1.5 mmol), DMAP (12 mg, 0.10 mmol), DCC (0.25 g, 1.2 mmol), and DCM (10 mL) were used to prepare triyne **S8**. Purification of the crude material by MPLC (hexanes:EtOAc 50:1) provided triyne **S8** (0.15 g, 0.51 mmol, 51%) as a pale yellow oil.

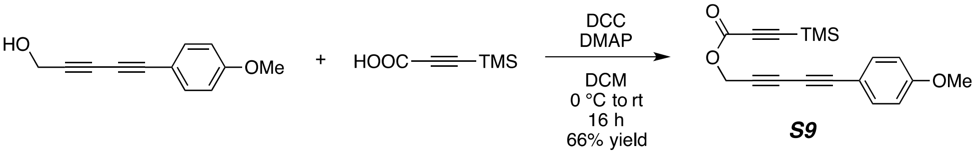
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 7.8, 0.9 Hz, 1H, *H6*), 7.27 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H, *H4*), 7.20 (d, *J* = 7.8 Hz, 1H, *H3*), 7.20 (dd, *J* = 7.4, 7.4 Hz, 1H, *H5*), 4.91 (s, 2H, CH_2O), 2.44 (s, 3H, $ArCH_3$), and 0.26 [s, 9H, $Si(CH_3)_3$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.1, 142.2, 133.3, 129.74, 129.66, 125.8, 121.0, 96.2, 93.7, 78.4, 76.5, 75.5, 72.3, 54.0, 20.8, and -0.8.

IR (neat): 2963, 2903, 2174, 2126, 1719, 1599, 1430, 1368, 1253, 1161, 1091, 978, 848, and 757 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{18}H_{18}NaO_2Si^+$ [M+Na$^+$] requires 317.0968; found 317.0965.

5-(4-Methoxyphenyl)penta-2,4-diyn-1-yl 3-(trimethylsilyl)propiolate (S9)



Following general procedure B, 5-(4-methoxyphenyl)penta-2,4-diyn-1-ol[8] (0.21 g, 1.0 mmol), 3-(trimethylsilyl)propiolic acid (0.21 g, 1.5 mmol), DMAP (12 mg, 0.10 mmol), DCC (0.25 g, 1.2 mmol), and DCM (10 mL) were used to prepare triyne **S9**. Purification of the crude material by MPLC (hexanes:EtOAc 20:1) provided triyne **S9** (0.21 g, 0.66 mmol, 66%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (nfod, *J* = 8.7 Hz, 2H, *H2*), 6.84 (nfod, *J* = 8.8 Hz, 2H, *H3*), 4.89 (s, 2H, CH_2O), 3.81 (s, 3H, OCH_3), and 0.25 [s, 9H, $Si(CH_3)_3$].

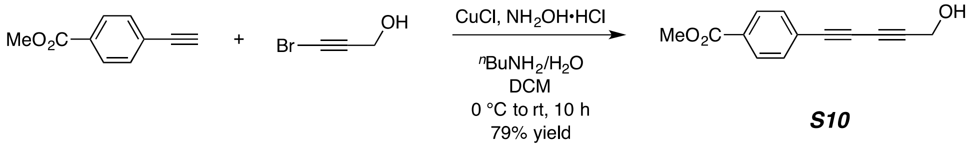
^{13}C NMR (126 MHz, $CDCl_3$): δ 160.8, 152.1, 134.5, 114.3, 113.1, 96.0, 93.7, 79.7, 74.5, 72.5, 72.0, 55.5, 54.0, and -0.8.

IR (neat): 3011, 2963, 2902, 2843, 2176, 1717, 1603, 1510, 1369, 1252, 1175, 1029, 865, 822, and 755 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{18}H_{18}NaO_3Si^+$ [M+Na$^+$] requires 333.0917; found 333.0926.

Mp: 59–62 °C.

Methyl 4-(5-Hydroxypenta-1,3-diyn-1-yl)benzoate (S10)



Following general procedure A, methyl 4-ethynylbenzoate (0.32 g, 2 mmol), 3-bromoprop-2-yn-1-ol (0.34 g, 2.5 mmol), CuCl (20 mg, 0.2 mmol), *n*-butylamine/H_2O (v:v, 30:70, 10 mL), and DCM (10 mL) were used to prepare diyne **S10**. Purification of the crude material by flash chromatography (hexanes:EtOAc 2:1) provided **S10** (0.34 g, 1.6 mmol, 79%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (nfod, *J* = 8.5 Hz, 2H, *H2*), 7.55 (nfod, *J* = 8.5 Hz, 2H, *H3*), 4.44 (s, 2H, CH_2OH), 3.92 (s, 3H, OCH_3), and 1.77 (br s, 1H, O*H*).

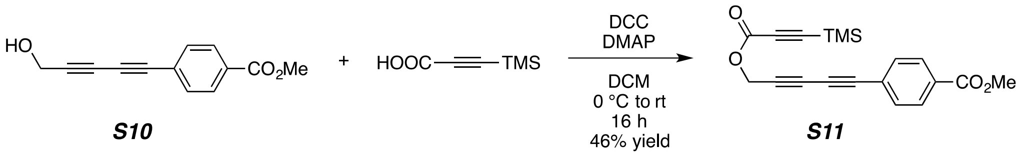
^{13}C NMR (126 MHz, $CDCl_3$): δ 166.4, 132.6, 130.6, 129.7, 126.2, 82.0, 77.6, 76.0, 70.3, 52.5, and 51.8.

IR (neat): 3503, 3006, 2957, 2127, 1694, 1607, 1438, 1403, 1310, 1278, 1109, 1022, 960, 850, and 763 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{13}H_{10}NaO_3^+$ [M+Na$^+$] requires 237.0522; found 237.0525.

Mp: 126–130 °C.

Methyl 4-(5-((3-(Trimethylsilyl)propioloyl)oxy)penta-1,3-diyn-1-yl)benzoate (S11)



Following general procedure B, propargyl alcohol **S10** (0.21 g, 1.0 mmol), 3-(trimethylsilyl)propiolic acid (0.21 g, 1.5 mmol), DMAP (12 mg, 0.10 mmol), DCC (0.25 g, 1.2 mmol), and DCM (10 mL) were used to prepare triyne **S11**. Purification of the crude material by MPLC (hexanes:EtOAc 9:1) provided **S11** (0.16 g, 0.46 mmol, 46%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (nfod, *J* = 8.6 Hz, 2H, *H2*), 7.55 (nfod, *J* = 8.5 Hz, 2H, *H3*), 4.91 (s, 2H, CH_2O), 3.92 (s, 3H, OCH_3), and 0.26 [s, 9H, $Si(CH_3)_3$].

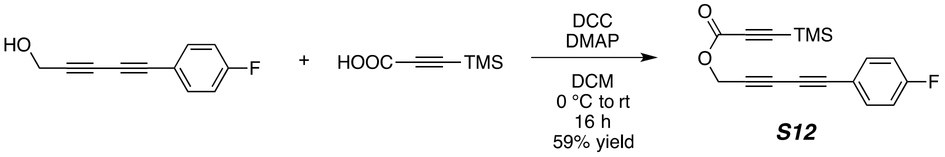
^{13}C NMR (126 MHz, $CDCl_3$): δ 166.3, 152.0, 132.7, 130.8, 129.7, 125.8, 96.3, 93.6, 78.2, 76.5, 75.7, 71.8, 53.8, 52.5, and -0.8.

IR (neat): 3011, 2959, 2902, 2855, 2176, 1720, 1695, 1438, 1402, 1276, 1255, 1212, 1119, 1018, 908, and 824 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{18}NaO_4Si^+$ [M+Na$^+$] requires 361.0867; found 361.0871.

Mp: 82–84 °C.

5-(4-Fluorophenyl)penta-2,4-diyn-1-yl 3-(trimethylsilyl)propiolate (S12)



Following general procedure B, 5-(4-fluorophenyl)penta-2,4-diyn-1-ol[8] (0.21 g, 1.2 mmol), 3-(trimethylsilyl)propiolic acid (0.20 g, 1.4 mmol), DMAP (15 mg, 0.12 mmol), DCC (0.30 g, 1.4 mmol), and DCM (12 mL) were used to prepare triyne **S12**. Purification of the crude material by MPLC (hexanes:EtOAc 20:1) provided triyne **S12** (0.21 g, 0.71 mmol, 59%) as a white solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.52–7.44 (m, 2H, *H3*), 7.06–6.99 (m, 2H, *H2*), 4.89 (s, 2H, C*H*$_2$O), and 0.25 [s, 9H, Si(C*H*$_3$)$_3$].

^{13}C NMR (126 MHz, CDCl$_3$): δ 163.4 (d, *J* = 252 Hz), 152.1, 134.9 (d, *J* = 8.8 Hz), 117.3 (d, *J* = 2.5 Hz), 116.1 (d, *J* = 23 Hz), 96.2, 93.6, 78.3, 75.1, 72.9, 72.0, 53.8, and -0.8.

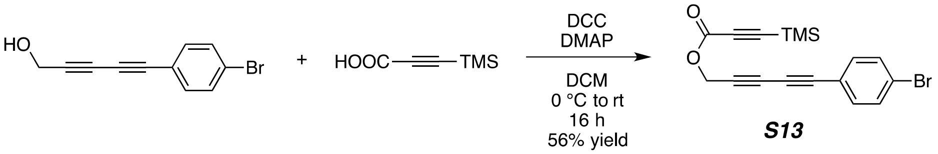
^{19}F NMR (470 MHz, CDCl$_3$): δ -107.9.

IR (neat): 3011, 2963, 2903, 2175, 1721, 1600, 1507, 1370, 1251, 1156, 1110, 978, 866, 821, and 789 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{17}H_{15}FNaO_2Si^+$ [M+Na$^+$] requires 321.0718; found 321.0707.

Mp: 38–39 °C.

5-(4-Bromophenyl)penta-2,4-diyn-1-yl 3-(trimethylsilyl)propiolate (S13)



Following general procedure B, 5-(4-bromophenyl)penta-2,4-diyn-1-ol[9] (0.24 g, 1.0 mmol), 3-(trimethylsilyl)propiolic acid (0.17 g, 1.2 mmol), DMAP (12 mg, 0.10 mmol), DCC (0.25 g, 1.2 mmol), and DCM (10 mL) were used to prepare triyne **S13**. Purification of the crude material by MPLC (hexanes:EtOAc 20:1) provided triyne **S13** (0.20 g, 0.56 mmol, 56%) as a white solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.47 (nfod, *J* = 8.6 Hz, 2H, *H2*), 7.35 (nfod, *J* = 8.6 Hz, 2H, *H3*), 4.89 (s, 2H, C*H*$_2$O), and 0.26 [s, 9H, Si(C*H*$_3$)$_3$].

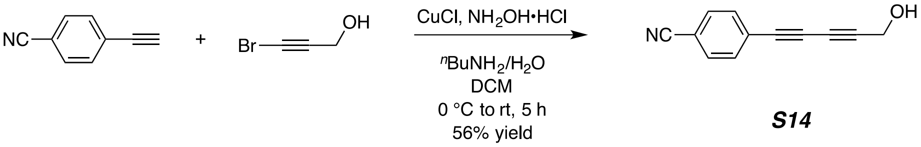
^{13}C NMR (126 MHz, CDCl$_3$): δ 152.0, 134.2, 132.0, 124.3, 120.2, 96.3, 93.6, 78.2, 75.7, 74.2, 72.0, 53.8, and -0.8.

IR (neat): 2998, 2962, 2903, 2174, 2123, 1720, 1585, 1486, 1368, 1252, 1110, 1069, 1010, 866, and 815 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{17}H_{15}{}^{79}BrNaO_2Si^+$ [M+Na$^+$] requires 380.9917; found 380.9934.

Mp: 79–81 °C.

4-(5-Hydroxypenta-1,3-diyn-1-yl)benzonitrile (S14)



Following general procedure A, 4-ethynylbenzonitrile (0.32 g, 2 mmol), 3-bromoprop-2-yn-1-ol (0.34 g, 2.5 mmol), CuCl (20 mg, 0.2 mmol), *n*-butylamine/H_2O (v:v, 30:70, 10 mL), and DCM (10 mL) were used to prepare diyne **S14**. Purification of the crude material by flash chromatography (hexanes:EA 2:1) provided **S14** (0.20 g, 1.1 mmol, 56%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (nfod, *J* = 8.6 Hz, 2H, *H2*), 7.57 (nfod, *J* = 8.7 Hz, 2H, *H3*), 4.44 (s, 2H, C*H2*OH), and 1.69 (br s, 1H, O*H*).

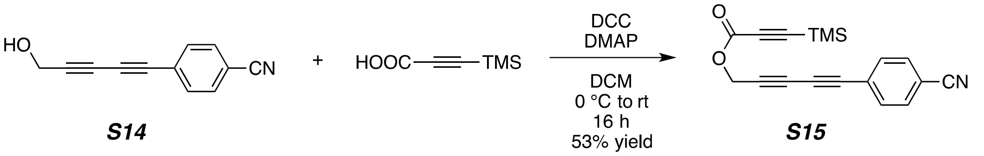
^{13}C NMR (126 MHz, $CDCl_3$): δ 133.2, 132.2, 126.5, 118.3, 112.8, 83.0, 76.5, 70.0, and 51.8 (one alkyne resonance was not observed in this sparingly $CDCl_3$-soluble analyte).

IR (neat): 3267, 2998, 2933, 2233, 1602, 1501, 1446, 1309, 1269, 1240, 1096, 1016, 828, and 769 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{12}H_7NNaO^+$ [M+Na$^+$] requires 204.0420; found 204.0421.

Mp: 151–154 ºC.

5-(4-Cyanophenyl)penta-2,4-diyn-1-yl 3-(trimethylsilyl)propiolate (S15)



Following general procedure B, propargyl alcohol **S14** (0.18 g, 1.0 mmol), 3-(trimethylsilyl)propiolic acid (0.17 g, 1.2 mmol), DMAP (12 mg, 0.10 mmol), DCC (0.25 g, 1.2 mmol), and DCM (10 mL) were used to prepare triyne **S15**. Purification of the crude material by MPLC (hexanes:EtOAc 9:1) provided triyne **S15** (0.16 g, 0.53 mmol, 53%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (nfod, *J* = 8.5 Hz, 2H, *H3*), 7.57 (nfod, *J* = 8.5 Hz, 2H, *H2*), 4.91 (s, 2H, C*H2*O), and 0.26 [s, 9H, Si(C*H3*)3].

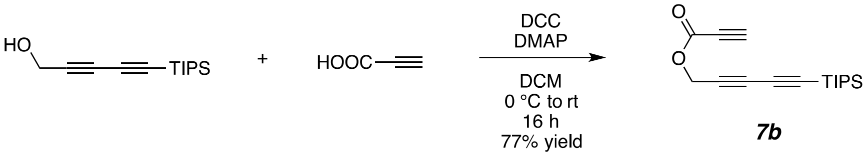
^{13}C NMR (126 MHz, $CDCl_3$): δ 152.0, 133.2, 132.2, 126.2, 118.2, 113.0, 96.5, 93.5, 77.4, 77.1, 77.0, 71.4, 53.6, and -0.8.

IR (neat): 2998, 2964, 2905, 2229, 2175, 1713, 1604, 1502, 1431, 1371, 1252, 1110, 1019, 981, 942, 865, and 823 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{18}H_{15}NNaO_2Si^+$ [M+Na$^+$] requires 328.0764; found 328.0779.

Mp: 91–93 ºC.

5-(Triisopropylsilyl)penta-2,4-diyn-1-yl propiolate (7b)



Following general procedure B, 5-(triisopropylsilyl)penta-2,4-diyn-1-ol[10] (0.24 g, 1.0 mmol), propiolic acid (93 *u*L, 1.5 mmol), DMAP (12 mg, 0.10 mmol), DCC (0.25 g, 1.2 mmol), and DCM (10 mL) were used to prepare triyne **7b**. Purification of the crude material by flash chromatography (hexanes:EtOAc 20:1) provided triyne **7b** (0.22 g, 0.76 mmol, 77%) as a pale yellow oil.

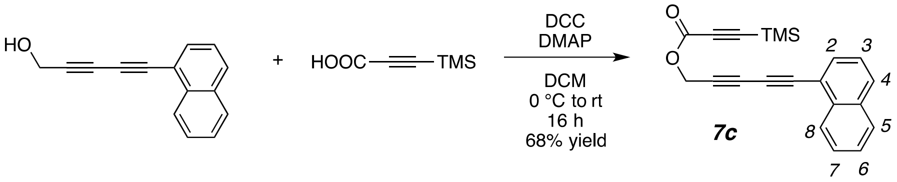
^{1}H NMR (500 MHz, CDCl$_3$): δ 4.85 (s, 2H, C*H*$_2$O), 2.96 (s, 1H, ≡C*H*), and 1.08 [m, 21H, C*H*(C*H*$_3$)$_2$].

^{13}C NMR (126 MHz, CDCl$_3$): δ 151.8, 88.5, 86.5, 76.3, 73.9, 73.0, 68.8, 54.0, 18.6, and 11.3.

IR (neat): 3296, 2945, 2867, 2124, 2111, 1725, 1462, 1366, 1206, 996, 966, 882, and 804 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{17}H_{24}NaO_2Si^+$ [M+Na$^+$] requires 311.1438; found 311.1453.

5-(Naphthalen-1-yl)penta-2,4-diyn-1-yl 3-(trimethylsilyl)propiolate (7c)



Following general procedure B, 5-(naphthalen-1-yl)penta-2,4-diyn-1-ol[11] (0.21 g, 1.0 mmol), 3-(trimethylsilyl)propiolic acid (0.17 g, 1.2 mmol), DMAP (12 mg, 0.10 mmol), DCC (0.25 g, 1.2 mmol), and DCM (10 mL) were used to prepare triyne **7c**. Purification of the crude material by MPLC (hexanes:EtOAc 20:1) provided triyne **7c** (0.23 g, 0.68 mmol, 68%) as a pale yellow solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.28 (d, *J* = 8.3 Hz, 1H, *H8*), 7.87 (d, *J* = 8.9 Hz, 1H, *H4* or H5), 7.85 (d, *J* = 8.9 Hz, 1H, *H5* or H4), 7.74 (d, *J* = 7.2 Hz, 1H, *H2*), 7.58 (ddd, *J* = 8.3, 7.9, 0.9 Hz, 1H, *H7*), 7.53 (ddd, *J* = 7.9, 7.9, 0.9 Hz, 1H, *H6*), 7.41 (dd, *J* = 7.3, 7.3 Hz, 1H, *H3*), 4.95 (s, 2H, C*H*$_2$O), and 0.26 [s, 9H, Si(C*H*$_3$)$_3$].

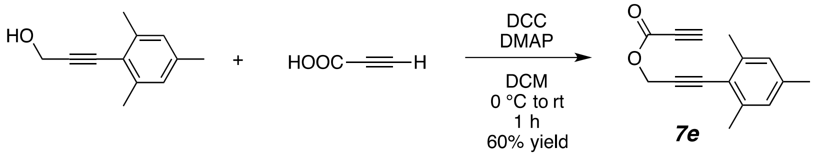
^{13}C NMR (126 MHz, CDCl$_3$): δ 152.1, 134.0, 133.1, 132.5, 130.2, 128.6, 127.5, 126.9, 126.0, 125.2, 118.8, 96.2, 93.7, 77.8, 77.6, 76.1, 72.3, 54.0, and -0.8.

IR (neat): 3060, 2963, 2902, 2175, 1713, 1585, 1505, 1428, 1365, 1253, 1068, 1012, 874, 826, and 795 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{21}H_{18}NaO_2Si^+$ [M+Na$^+$] requires 353.0968; found 353.0985.

Mp: 25–28 ºC.

3-Mesitylprop-2-yn-1-yl propiolate (7e)



Following general procedure B, 3-mesitylprop-2-yn-1-ol[12] (0.10 g, 0.6 mmol), propiolic acid (70 mg, 1.0 mmol), DMAP (7.3 mg, 0.060 mmol), DCC (0.21 g, 1.0 mmol), and DCM (10 mL) were used to prepare diyne **7e**. Purification of the crude material by MPLC (hexanes:EtOAc 30:1) provided diyne **7e** (82 mg, 0.36 mmol, 60%) as a clear oil.

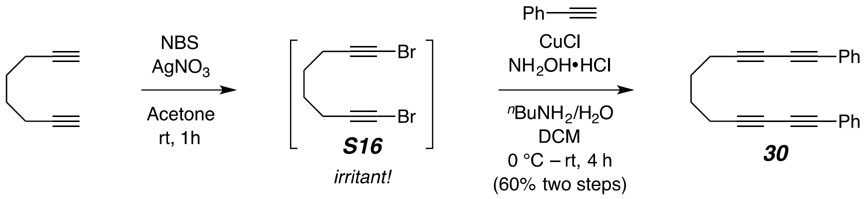
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.85 (s, 2H, Ar*H*), 5.08 (s, 2H, CH_2O), 2.93 (s, 1H, ≡C*H*), 2.37 (s, 6H, Ar$_{ortho}$CH_3), and 2.27 (s, 3H, Ar$_{para}$CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.2, 140.9, 138.6, 127.8, 118.7, 89.0, 85.6, 75.6, 74.3, 54.9, 21.5, and 21.0.

IR (neat): 3291, 2922, 2857, 2233, 2120, 1720, 1610, 1478, 1436, 1366, 1209, 1019, 990, 938, and 827 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{15}H_{14}NaO_2^+$ [M+Na$^+$] requires 249.0886; found 249.0891.

1,12-Diphenyldodeca-1,3,9,11-tetrayne (30)



To a stirred solution of 1,7-octadiyne (133 *u*L, 1.0 mmol) in acetone (10 mL) was added *N*-bromosuccinimide (0.43 g, 2.4 mmol) and silver nitrate (34 mg, 0.20 mmol). The solution quickly turned into a suspension, which was stirred at room temperature for 1 hour. The reaction mixture was then quenched by addition of hexanes (20 mL), and the suspension was passed through Celite®. The filtrate was concentrated to afford the dibromodiyne **S19**, which was used immediately in the subsequent step.

CAUTION: Dibromodiyne **S16** is a strong skin irritant! Avoid contact.

Following general procedure A, the crude dibromodiyne **S16** (ca. 1.0 mmol), phenyl acetylene (0.33 mL, 3.0 mmol), CuCl (20 mg, 0.20 mmol), *n*-butylamine/H_2O (v:v, 30:70, 5 mL), and DCM (5 mL) were used to prepare tetrayne **30**. Purification of the crude material by direct recrystallization (hexanes) provided tetrayne **30** (0.18 g, 0.60 mmol, 60%, two steps) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51–7.46 (nfom, 4H, PhH_o), 7.36–7.28 (m, 6H, PhH_{m+p}), 2.45–2.39 (nfom, 4H, ≡CCH_2), and 1.77–1.71 (nfom, 4H, CH_2CH_2).

^{13}C NMR (126 MHz, $CDCl_3$): δ 132.7, 129.0, 128.5, 122.2, 84.0, 75.1, 74.4, 65.8, 27.4, and 19.3.

IR (neat): 2955, 2934, 2901, 2866, 2242, 2175, 2157, 1592, 1489, 1441, 1333, 1295, 906, and 753 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{24}H_{18}Ag^+$ [M+Ag$^+$] requires 413.0454; found 413.0458 (measurement done using a DCM/MeOH solution of **30** that had been doped with a crystal of $AgNO_3$).

Mp: 101–104 °C.

• Experimental details and characterization data for the cyclobutadiene-derived products

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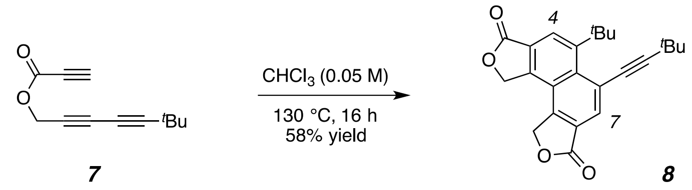
5-(*tert*-Butyl)-6-(3,3-dimethylbut-1-yn-1-yl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (8 ≡ 13a)



Following general procedure C, the naphthalene derivative **8** was prepared from triyne **7** (94 mg, 0.50 mmol) in $CHCl_3$ (10 mL). The crude product was purified by MPLC (hexanes:EtOAc 3:1) to yield **8** (55 mg, 0.29 mmol, 58%) as a white solid. Single crystal suitable for X-ray diffraction analysis was obtained by vapor diffusion method, in which *n*-pentane was slowly vaporized and diffused into a DCM solution of **8** at ca. -20 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (s, 1H, *H4*), 8.30 (s, 1H, *H7*), 5.63 (s, 2H, C*H*$_2$O), 5.60 (s, 2H, C*H*$_2$O), 1.82 [s, 9H, ArC(C*H*$_3$)$_3$], and 1.39 [s, 9H, ≡CC(C*H*$_3$)$_3$].

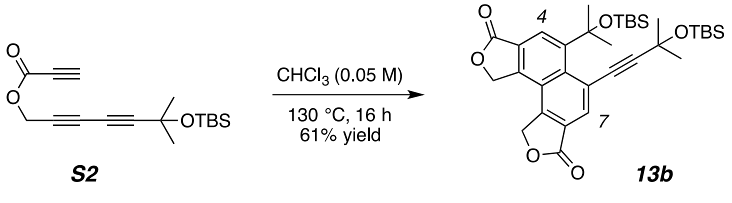
^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 169.7, 152.3, 145.2, 144.1, 137.9, 134.3, 125.2, 124.7, 124.1, 123.3, 123.2, 107.9, 83.7, 69.8, 69.5, 38.0, 34.5, 30.5, and 28.8.

IR (neat): 3020, 2968, 2930, 2870, 2204, 1762, 1459, 1411, 1365, 1239, 1120, 1119, 979, 909, and 764 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{24}H_{24}NaO_4^+$ [M+Na$^+$] requires 399.1567; found 399.1555.

Mp: 234–242 °C (with decomposition > ca. 220 °C).

5-(3-((*tert*-Butyldimethylsilyl)oxy)-3-methylbut-1-yn-1-yl)-6-(2-((*tert*-butyldimethylsilyl)oxy)propan-2-yl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13b)



Following general procedure C, naphthalene **13b** was prepared from triyne **S2** (100 mg, 0.33 mmol) in $CHCl_3$ (6.6 mL). The crude product was purified by MPLC (hexanes:EtOAc 3:1) to obtain the naphthalene derivative **13b** (61 mg, 0.10 mmol, 61%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.93 (s, 1H, *H4*), 8.34 (s, 1H, *H7*), 5.66 (s, 2H, C*H*$_2$O), 5.62 (s, 2H, C*H*$_2$O), 2.19 [s, 6H, C(C*H*$_3$)$_2$], 1.65 [s, 6H, C(C*H*$_3$)$_2$], 1.00 [s, 9H, SiC(C*H*$_3$)$_3$], 0.90 [s, 9H, SiC(C*H*$_3$)$_3$], 0.19 [s, 6H, Si(C*H*$_3$)$_2$], and 0.16 [s, 6H, Si(C*H*$_3$)$_2$].

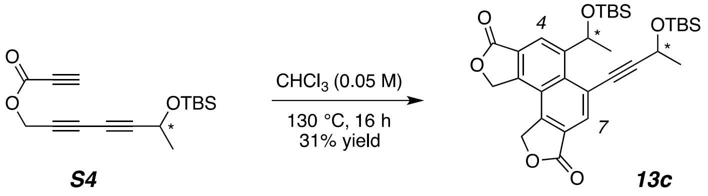
^{13}C NMR (126 MHz, CDCl$_3$): δ 170.0, 169.3, 152.0, 145.9, 144.4, 135.5, 133.7, 124.4, 124.3, 124.2, 123.3, 123.2, 103.5, 85.2, 77.4, 69.6, 69.2, 67.3, 34.0, 32.3, 26.1, 25.6, 18.5, 17.9, -1.7, and -2.7.

IR (neat): 2960, 2932, 2893, 2202, 1770, 1473, 1462, 1410, 1367, 1255, 1218, 1159, 1117, 1024, 1005, 836, and 774 cm^{-1}.

HRMS (ESI-TOF): Calcd for $\mathrm{C_{34}H_{48}NaO_6Si_2^+}$ [M+Na$^+$] requires 631.2887; found 631.2869.

Mp: 207–209 °C.

(±)-5-(3-((*tert*-Butyldimethylsilyl)oxy)but-1-yn-1-yl)-6-(1-((*tert*-butyldimethylsilyl)oxy)ethyl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13c, a 1:1 mixture of *like* and *unlike* diastereomers**)**



Following general procedure C, naphthalene **13c** was prepared from triyne **S4** (100 mg, 0.34 mmol) in CHCl$_3$ (6.8 mL). The crude product was purified by MPLC (hexanes:EtOAc 3:1) to yield the naphthalene derivative **13c** (31 mg, 0.053 mmol, 31%) as a pale yellow solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.70 (s, 0.5H, *H4*), 8.69 (s, 0.5H, *H4*), 8.29 (s, 0.5H, *H7*), 8.28 (s, 0.5H, *H7*), 6.98 (q, *J* = 6.0 Hz, 0.5H, ArC*H*), 6.94 (q, *J* = 6.0 Hz, 0.5H, ArC*H*), 5.66 (s, 2H, C*H*$_2$O), 5.64 (s, 2H, C*H*$_2$O), 4.88$^+$ (q, *J* = 6.5 Hz, 0.5H, ≡CC*H*), 4.88$^-$ (q, *J* = 6.5 Hz, 0.5H, ≡CC*H*), 1.61 (d, *J* = 6.5 Hz, 1.5H, ArCHC*H*$_3$), 1.60 (d, *J* = 6.5 Hz, 1.5H, ArCHC*H*$_3$), 1.57 (d, *J* = 6.0 Hz, 3H, ≡CCHC*H*$_3$), 0.95 [s, 4.5H, SiC(C*H*$_3$)$_3$], 0.94 [s, 4.5H, SiC(C*H*$_3$)$_3$], 0.92$^+$ [s, 4.5H, SiC(C*H*$_3$)$_3$], 0.92$^-$ [s, 4.5H, SiC(C*H*$_3$)$_3$], 0.184 [s, 1.5H, Si(C*H*$_3$)$_2$], 0.182 [s, 1.5H, Si(C*H*$_3$)$_2$], 0.179 [s, 3H, Si(C*H*$_3$)$_2$], 0.13 [s, 1.5H, Si(C*H*$_3$)$_2$], 0.12 [s, 1.5H, Si(C*H*$_3$)$_2$], -0.00 [s, 1.5H, Si(C*H*$_3$)$_2$], and -0.01 [s, 1.5H, Si(C*H*$_3$)$_2$].

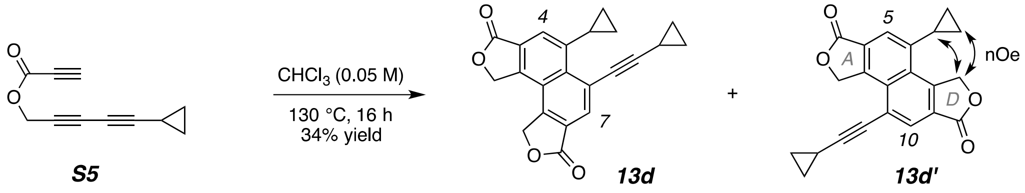
^{13}C NMR (126 MHz, CDCl$_3$): δ 170.0, 169.3, 150.1$^+$, 150.1$^-$, 145.6, 145.5, 143.9$^+$, 143.9$^-$, 134.5$^+$, 134.5$^-$, 132.5, 132.2, 125.0, 123.7$^+$, 123.7$^-$, 123.0, 122.9$^+$, 122.9$^-$, 122.8, 122.4, 99.8, 99.7, 83.3$^+$, 83.3$^-$, 69.5, 69.2, 67.1, 66.9, 59.6, 29.0, 28.9, 25.9, 25.8, 25.2, 25.1, 18.23, 18.19, 18.18, -4.47, -4.49, -4.54, -4.7, -4.8, and -4.9.

IR (neat): 2955, 2931, 2890, 2208, 1767, 1471, 1463, 1417, 1367, 1255, 1116, 1093, 1021, 836, and 778 cm^{-1}.

HRMS (ESI-TOF): Calcd for $\mathrm{C_{32}H_{44}NaO_6Si_2^+}$ [M+Na$^+$] requires 603.2574; found 603.2549.

Mp: 70–78 °C (mixture of diastereomers).

5-Cyclopropyl-6-(cyclopropylethynyl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13d) and 4-Cyclopropyl-9-(cyclopropylethynyl)-3,8-dihydronaphtho[1,2-c:5,6-c']difuran-1,6-dione (13d')



Following general procedure C, naphthalenes **13d** and **13d'** were prepared from triyne **S5** (34 mg, 0.20 mmol) in $CHCl_3$ (4.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 4:1) to obtain a mixture of coeluting naphthalene derivatives **13d** and **13d**' (12 mg, 0.035 mmol, 34%, 8:1 mixture) as a white solid.

Data for 13d (from the mixture)

^{1}**H NMR** (500 MHz, $CDCl_3$): δ 8.20 (s, 1H, *H4*), 7.86 (s, 1H, *H7*), 5.59 (s, 2H, CH_2O), 5.57 (s, 2H, CH_2O), 3.17 (tt, *J* = 8.2, 5.7 Hz, 1H, ArC*H*), 1.55 (tt, *J* = 8.4, 4.9 Hz, 1H, ≡CC*H*), 1.19 [nfom, 2H, ArCH(CH_{cis}H$_{\mathrm{trans}}$–CH_{cis}H$_{\mathrm{trans}}$)], 0.98 [nfom, 2H, ≡CCH(CH_{cis}H$_{\mathrm{trans}}$–CH_{cis}H$_{\mathrm{trans}}$)], 0.92 [nfom, 2H, ArCH(CH$_{\mathrm{cis}}$$H_{trans}$–CH$_{\mathrm{cis}}$$H_{trans}$)], and 0.85 [nfom, 2H, ≡CCH(CH$_{\mathrm{cis}}$$H_{trans}$–CH$_{\mathrm{cis}}$$H_{trans}$)].

^{13}**C NMR** (126 MHz, $CDCl_3$): δ 170.3, 169.6, 145.3, 144.2, 143.6, 139.1, 131.8, 125.3, 124.6, 124.0, 123.2, 123.1, 102.6, 76.8, 69.5, 69.4, 18.1, 10.4, 8.7, and 1.0.

Data for 13d' (from the mixture)

^{1}**H NMR** (500 MHz, $CDCl_3$): δ 8.09 (s, 1H, *H5*), 7.85 (s, 1H, *H10*), 6.09 (s, 2H, C$H_{2\text{-}ringD}$O), 5.99 (s, 2H, C$H_{2\text{-}ringA}$O), 2.27 (tt, *J* = 8.0, 5.6 Hz, 1H, ArC*H*), 1.63 (tt, *J* = 8.4, 5.0 Hz, 1H, ≡CC*H*), 1.23 [nfom, 2H, ArCH(CH_{cis}H$_{\mathrm{trans}}$–CH_{cis}H$_{\mathrm{trans}}$)], 1.05 [nfom, 2H, ≡CCH(CH_{cis}H$_{\mathrm{trans}}$–CH_{cis}H$_{\mathrm{trans}}$)], 1.02 [nfom, 2H, ArCH(CH$_{\mathrm{cis}}$$H_{trans}$–CH$_{\mathrm{cis}}$$H_{trans}$)], and 1.00–0.95 [overlapped, 2H, ≡CCH(CH$_{\mathrm{cis}}$$H_{trans}$–CH$_{\mathrm{cis}}$$H_{trans}$)].

nOe: The interactions indicated on structure **13d'** for pairs of resonances of the minor isomer led to the assignment of regiochemical orientation for each of the two constitutional isomers.

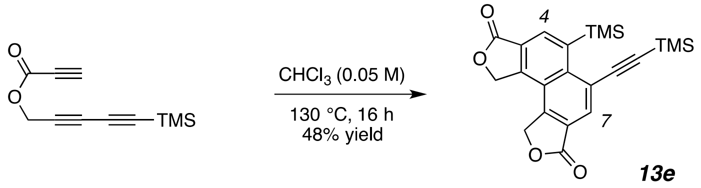
^{13}**C NMR** (126 MHz, $CDCl_3$): δ 170.9, 170.2, 145.8, 145.4, 142.8, 133.0, 132.2, 128.0, 126.3, 126.1, 124.1, 122.6, 101.7, 74.8, 72.2, 71.7, 16.1, 8.8, 8.6, and 0.6.

IR (neat): 2998, 2943, 2213, 1759, 1424, 1372, 1345, 1214, 1123, 1106, 1016, 977, 844, and 763 cm^{-1} (obtained from the mixture).

HRMS (ESI-TOF): Calcd for $C_{22}H_{16}NaO_4^+$ [M+Na$^+$] requires 367.0941; found 367.0923 (from the mixture).

Mp: 238–248 °C (mixture of constitutional isomers).

5-(Trimethylsilyl)-6-((trimethylsilyl)ethynyl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13e)



Following general procedure C, naphthalene **13e** was prepared from 5-(trimethylsilyl)penta-2,4-diyn-1-yl propiolate[13] (31 mg, 0.15 mmol) in $CHCl_3$ (3.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 4:1) to obtain the naphthalene derivative **13e** (15 mg, 0.037 mmol, 48%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47 (s, 1H, *H4* or H7), 8.41 (s, 1H, *H7* or H4), 5.65 (s, 2H, CH_2O), 5.62 (s, 2H, CH_2O), 0.62 [s, 9H, ArSi(CH_3)$_3$], and 0.33 [s, 9H, ≡CSi(CH_3)$_3$].

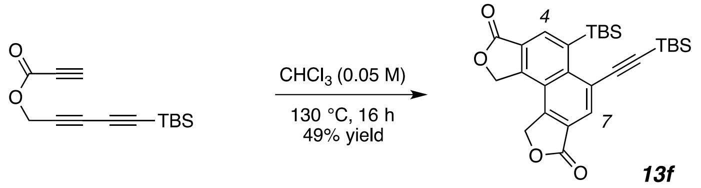
^{13}C NMR (126 MHz, $CDCl_3$): δ 170.2, 169.5, 146.8, 145.8, 144.3, 142.8, 133.9, 133.7, 126.2, 123.9, 123.8, 122.9, 107.5, 106.2, 69.6, 69.3, 4.2, and -0.2.

IR (neat): 2958, 2899, 2145, 1764, 1607, 1461, 1406, 1362, 1249, 1224, 1108, 1017, 942, 845, and 757 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{22}H_{24}NaO_4Si_2^+$ [M+Na$^+$] requires 431.1105; found 431.1085.

Mp: 254–258 ºC (with decomposition > ca. 220 ºC).

5-(*tert*-Butyldimethylsilyl)-6-((*tert*-butyldimethylsilyl)ethynyl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13f)



Following general procedure C, the naphthalene derivative **13f** was prepared from 5-(*tert*-butyldimethylsilyl)penta-2,4-diyn-1-yl propiolate[13] (37 mg, 0.15 mmol) in $CHCl_3$ (3.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 4:1) to obtain **13f** (18 mg, 0.037 mmol, 49%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.56 (s, 1H, *H4*), 8.36 (s, 1H, *H7*), 5.64 (s, 2H, CH_2O), 5.62 (s, 2H, CH_2O), 1.10 [s, 9H, SiC(CH_3)$_3$], 1.06 [s, 9H, SiC(CH_3)$_3$], 0.64 [s, 6H, ArSi(CH_3)$_2$], and 0.25 [s, 6H, ≡CSi(CH_3)$_2$].

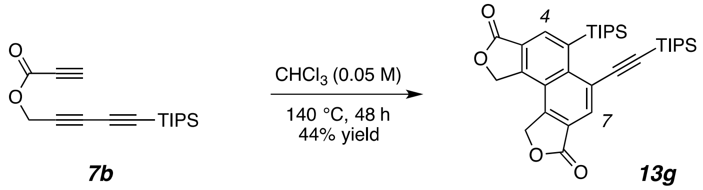
^{13}C NMR (126 MHz, CDCl$_3$): δ 170.1, 169.5, 146.6, 145.9, 143.1, 142.8, 134.0, 133.9, 126.5, 123.8, 123.3, 123.2, 107.4, 106.5, 69.6, 69.3, 28.5, 26.5, 19.4, 17.4, 0.9, and -4.7.

IR (neat): 2953, 2931, 2885, 2858, 2141, 1765, 1606, 1462, 1404, 1361, 1251, 1220, 1108, 1024, 1019, 910, 823, and 776 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{28}H_{36}NaO_4Si_2^+$ [M+Na$^+$] requires 515.2044; found 515.2048.

Mp: 242–248 °C.

5-(Triisopropylsilyl)-6-((triisopropylsilyl)ethynyl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13g)



Following general procedure C, the naphthalene derivative **13g** was prepared from triyne **7b** (43 mg, 0.15 mmol) in CHCl$_3$ (3.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 4:1) to obtain **13g** (19 mg, 0.033 mmol, 44%) as an amorphous yellow solid.

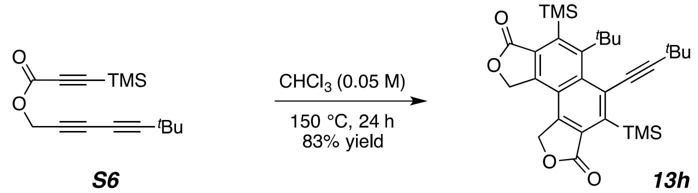
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.53 (s, 1H, *H4*), 8.39 (s, 1H, *H7*), 5.64 (s, 2H, C*H$_2$*O), 5.63 (s, 2H, C*H$_2$*O), 2.21 {sep, *J* = 7.5 Hz, 3H, ArSi[(C*H*)(CH$_3$)$_2$]$_3$}, 1.21 {sep, *J* = 6.0 Hz, 3H, ≡CSi[(C*H*)(CH$_3$)$_2$]$_3$}, 1.17 {d, *J* = 6.0 Hz, 18H, ≡CSi[CH(C*H$_3$*)$_2$]$_3$}, and 1.13 {d, *J* = 7.5 Hz, 18H, ArSi[CH(C*H$_3$*)$_2$]$_3$}.

^{13}C NMR (126 MHz, CDCl$_3$): δ 170.2, 169.5, 146.6, 145.9, 143.1, 140.8, 134.8, 134.2, 126.7, 123.7, 123.5, 123.2, 108.7, 105.4, 69.6, 69.3, 20.0, 18.8, 14.6, and 11.8.

IR (neat): 2944, 2890, 2866, 2132, 1766, 1607, 1460, 1360, 1248, 1219, 1108, 1019, 980, 909, 880, and 759 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{34}H_{48}NaO_4Si_2^+$ [M+Na$^+$] requires 599.2983; found 599.2970.

(±)-5-(*tert*-Butyl)-6-(3,3-dimethylbut-1-yn-1-yl)-4,7-bis(trimethylsilyl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13h)



Following general procedure C, the naphthalene derivative **13h** was prepared from triyne **S6** (26 mg, 0.10 mmol) in $CHCl_3$ (2.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 4:1) to obtain **13h** (22 mg, 0.042 mmol, 83%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.50 (d, *J* = 14.5 Hz, 1H, CH_aH_bO), 5.47 (d, *J* = 14.5 Hz, 1H, $CH_{a'}H_{b'}O$), 5.45 (d, *J* = 14.4 Hz, 1H, CH_bH_aO), 5.40 (d, *J* = 14.4 Hz, 1H, $CH_{b'}H_{a'}O$), 1.56 [s, 9H, $ArC(CH_3)_3$], 1.29 [s, 9H, $\equiv CC(CH_3)_3$], 0.58 [s, 9H, $Si(CH_3)_3$], and 0.54 [s, 9H, $Si(CH_3)_3$].

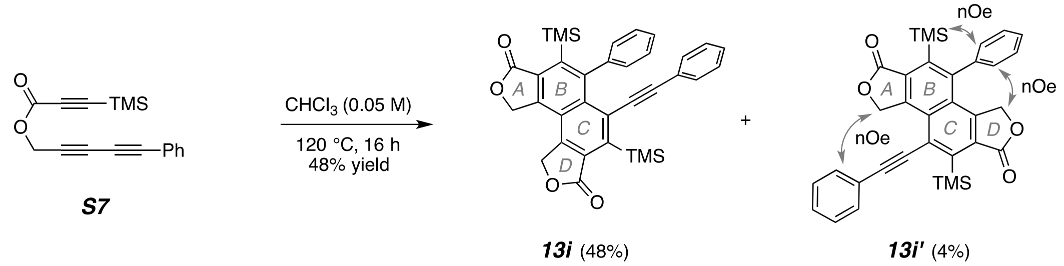
^{13}C NMR (126 MHz, $CDCl_3$): δ 171.1, 170.5, 163.2, 144.2, 143.0, 142.3, 141.3, 139.0, 132.2, 128.9, 127.3, 121.2, 115.5, 84.8, 68.6, 68.2, 42.8, 36.6, 30.2, 29.0, 4.6, and 1.5.

IR (neat): 2968, 2900, 2871, 2201, 1759, 1462, 1352, 1249, 1183, 1106, 1036, 998, 912, 841, and 765 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{30}H_{40}NaO_4Si_2^+$ [$M+Na^+$] requires 543.2357; found 543.2365.

Mp: 265–269 °C.

5-Phenyl-6-(phenylethynyl)-4,7-bis(trimethylsilyl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13i) and 4-Phenyl-9-(phenylethynyl)-5,10-bis(trimethylsilyl)-3,8-dihydronaphtho[1,2-c:5,6-c']difuran-1,6-dione (13i')



Following general procedure C, the naphthalene derivatives **13i** and **13i'** were prepared from triyne **S7** (26 mg, 0.093 mmol) in $CHCl_3$ (2.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 4:1) to yield, in the order of elution, **13i'** (1.0 mg, 1.8 *u*mol, 4%) and **13i** (13 mg, 0.022 mmol, 48%), each as a light orange solid.

Data for 13i

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (nfod, *J* = 7.3 Hz, 2H, $ArPhH_{ortho}$), 7.33 (dd, *J* = 7.4, 7.4 Hz, 2H, $ArPhH_{meta}$), 7.27–7.20 (m, 4H, $ArPhH_{para}$ and $\equiv CPhH_{meta+para}$), 7.04 (nfod, *J* = 7.7 Hz, 2H, $\equiv CPhH_{ortho}$), 5.63 (s, 2H, CH_2O), 5.61 (s, 2H, CH_2O), 0.48 [s, 9H, Ar_{ringC}-$Si(CH_3)_3$], and -0.01 [s, 9H, Ar_{ringB}-$Si(CH_3)_3$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.9, 170.2, 150.4, 147.2, 143.8, 143.3, 142.4, 141.4, 137.0, 133.0, 132.1, 131.0, 129.8, 129.0, 128.9, 128.6, 128.4, 128.1, 123.5, 122.8, 108.6, 90.6, 68.8, 68.7, 1.6, and 1.5.

IR (neat): 2951, 2897, 2189, 1760, 1490, 1400, 1357, 1192, 1112, 1034, 1000, 909, 842, and 758 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{34}H_{32}NaO_4Si_2^+$ [M+Na$^+$] requires 583.1731; found 583.1739.

Mp: 164–170 °C.

Data for 13i'

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65–7.62 (nfom, 2H, ≡CPhH_{ortho}), 7.60 (tt, *J* = 7.5, 1.3 Hz, 1H, ArPhH_{para}), 7.51 (dd, *J* = 7.8, 7.8 Hz, 2H, ArPhH_{meta}), 7.51–7.46 (m, 3H, ≡CPh$H_{meta+para}$), 7.34 (dd, *J* = 7.9, 1.2 Hz, 2H, ArPhH_{ortho}), 6.24 (s, 2H, C$H_{2\text{-}ringA}$O), 4.33 (s, 2H, C$H_{2\text{-}ringD}$O), 0.57 [s, 9H, Ar$_{ringC}$-Si(CH_3)$_3$], and 0.02 [s, 9H, Ar$_{ringB}$-Si(CH_3)$_3$].

nOe: The interactions indicated on structure **15** for pairs of resonances of the minor isomer led to the assignment of regiochemical orientation for each of the two constitutional isomers.

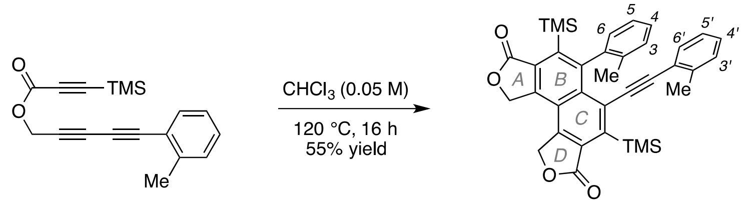
^{13}C NMR (126 MHz, $CDCl_3$): δ 171.2, 170.6, 148.4, 146.7, 146.4, 143.7, 141.3, 132.1, 131.6, 131.5, 131.4, 131.3, 131.1, 130.6, 129.9, 129.8, 129.2, 128.8, 128.7, 122.3, 100.1, 91.1, 71.6, 69.7, 2.2, and 1.6.

IR (neat): 3060, 2951, 2896, 2203, 1764, 1492, 1443, 1379, 1347, 1247, 1176, 1111, 1041, 1000, 950, 843, and 757 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{34}H_{32}NaO_4Si_2^+$ [M+Na$^+$] requires 583.1731; found 583.1747.

Mp: 235–240 °C.

(±)-5-(*o*-Tolyl)-6-(*o*-tolylethynyl)-4,7-bis(trimethylsilyl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13j)



S8 ***13j***

Following general procedure C, the naphthalene derivative **13j** was prepared from triyne **S8** (20 mg, 0.067 mmol) in $CHCl_3$ (1.3 mL). The crude product was purified by MPLC (hexanes:EtOAc 4:1) to yield **13j** (11 mg, 0.019 mmol, 55%) as a pale yellow solid. A small amount of the minor regioisomer (see **13i'**, above, for characterization of an analogous minor isomer) was observed by analysis of the ^{1}H NMR spectrum of the crude product mixture (rr = 10:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H, *H5*), 7.15 (dd, *J* = 7.5, 1.2 Hz, 1H, *H3*), 7.10 (d, *J* = 7.6 Hz, 1H, *H6*), 7.07 (dd, *J* = 7.7, 7.7 Hz, 1H, *H4*), 7.04 (d, *J* = 7.5 Hz, 1H, *H6'*), 6.99 (dd, *J* = 7.5, 7.5, 1.2 Hz, 1H, *H4'*), 6.95 (dd, *J* = 7.5, 1.2 Hz, 1H, *H3'*), 6.94 (ddd, *J* =

7.4, 7.4, 1.4 Hz, 1H, *H5'*), 5.66 (d, *J* = 15.4 Hz, 1H, CH_aH$_b$O), 5.64 (d, *J* = 15.7 Hz, 1H, C$H_{a'}$H$_{b'}$O), 5.63 (d, *J* = 15.5 Hz, 1H, CH$_a$$H_b$O), 5.62 (d, *J* = 15.9 Hz, 1H, CH$_{a'}$$H_{b'}$O), 2.12 (s, 3H, ≡CPhC$H_3$), 1.97 (s, 3H, ArPhC$H_3$), 0.41 [s, 9H, Ar$_{ringC}$-Si(C$H_3$)$_3$], and -0.04 [s, 9H, Ar$_{ringB}$-Si(C$H_3$)$_3$].

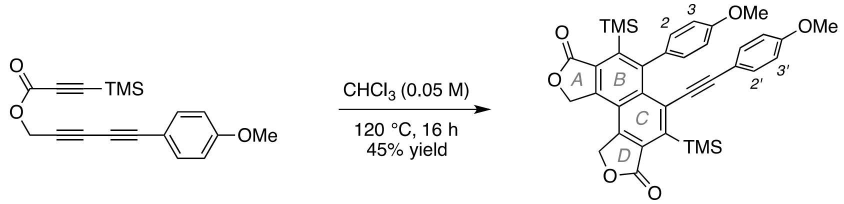
^{13}C NMR (126 MHz, CDCl$_3$): δ 170.8, 170.2, 149.4, 147.4, 144.4, 143.7, 141.7, 141.2, 139.2, 138.3, 136.1, 132.4, 132.3, 131.4, 130.0, 129.7, 129.5, 129.4, 129.0, 128.3, 125.8, 125.1, 123.7, 122.7, 106.3, 92.7, 68.79, 68.76, 20.8, 20.6, 1.6, and 1.4.

IR (neat): 2950, 2899, 2871, 2194, 1760, 1486, 1457, 1397, 1357, 1247, 1189, 1111, 1036, 1000, 909, 842, and 758 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{36}H_{36}NaO_4Si_2^+$ [M+Na$^+$] requires 611.2044; found 611.2027.

Mp: 118–122 °C.

5-(4-Methoxyphenyl)-6-((4-methoxyphenyl)ethynyl)-4,7-bis(trimethylsilyl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13k)



S9 **13k**

Following general procedure C, the naphthalene derivative **13k** was prepared from triyne **S9** (47 mg, 0.15 mmol) in CHCl$_3$ (3.0 mL). The crude product was purified by MPLC (hexanes: EtOAc 4:1) to yield **13k** (22 mg, 0.033 mmol, 47%, contained 3 wt% EtOAc based on analysis of the ^{1}H NMR spectrum, 45% corrected yield) as a yellow amorphous solid. A small amount of the minor regioisomer (see **13i'**, above, for characterization of an analogous minor isomer) was observed by analysis of the ^{1}H NMR spectrum of the crude product mixture (rr = 9:1).

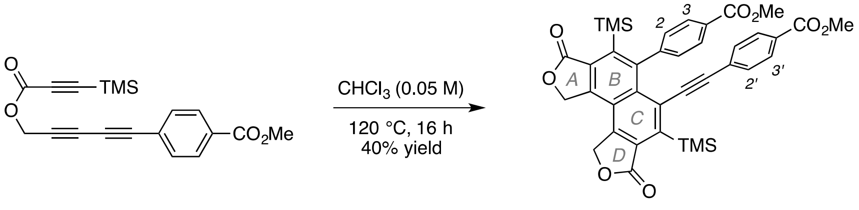
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.28 (nfod, *J* = 8.6 Hz, 2H, *H2*), 7.00 (nfod, *J* = 8.8 Hz, 2H, *H2'*), 6.83 (nfod, *J* = 8.6 Hz, 2H, *H3*), 6.78 (nfod, *J* = 8.8 Hz, 2H, *H3'*), 5.62 (s, 2H, CH_2O), 5.60 (s, 2H, CH_2O), 3.81 (s, 3H, ArOCH_3), 3.65 (s, 3H, ArOCH_3), 0.47 [s, 9H, Ar$_{ringC}$-Si(CH_3)$_3$], and 0.02 [s, 9H, Ar$_{ringB}$-Si(CH_3)$_3$].

^{13}C NMR (126 MHz, CDCl$_3$): δ 171.0, 170.3, 160.0, 159.6, 150.1, 146.9, 143.8, 143.1, 141.2, 137.4, 135.2, 133.3, 133.2, 132.3, 129.6, 128.8, 122.8, 116.1, 114.0, 113.8, 108.4, 89.4, 68.8, 68.7, 55.4, 55.2, 1.7, and 1.5.

IR (neat): 2997, 2952, 2899, 2837, 2184, 1759, 1605, 1510, 1462, 1400, 1358, 1289, 1174, 1112, 1033, 1000, 909, 842, and 766 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{36}H_{36}NaO_6Si_2^+$ [M+Na$^+$] requires 643.1943; found 643.1946.

Methyl 4-((6-(4-(Methoxycarbonyl)phenyl)-3,8-dioxo-4,7-bis(trimethylsilyl)-1,3,8,10-tetrahydronaphtho[1,2-c:7,8-c']difuran-5-yl)ethynyl)benzoate (13l)



S11 ***13l***

Following general procedure C, the naphthalene derivative **13l** was prepared from triyne **S11** (34 mg, 0.10 mmol) in $CHCl_3$ (2.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 4:1) to yield **13l** (14 mg, 0.021 mmol, 41%, contained 2 wt% EtOAc based on ^{1}H NMR spectrum, 40% corrected yield) as a pale yellow amorphous solid. A small amount of the minor regioisomer (see **13i'**, above, for characterization of an analogous minor isomer) was observed by analysis of the ^{1}H NMR spectrum of the crude product mixture (rr = 11:1).

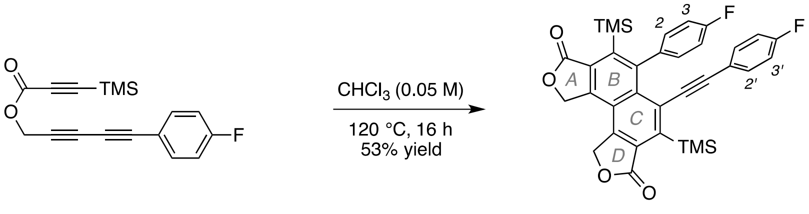
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (nfod, *J* = 8.4 Hz, 2H, *H3*), 7.88 (nfod, *J* = 8.6 Hz, 2H, *H3'*), 7.50 (nfod, *J* = 8.4 Hz, 2H, *H2*), 7.04 (nfod, *J* = 8.6 Hz, 2H, *H2'*), 5.66 (s, 2H, CH_2O), 5.63 (s, 2H, CH_2O), 3.93 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 0.47 [s, 9H, Ar$_{ringC}$-Si(CH_3)$_3$], and -0.01 [s, 9H, Ar$_{ringB}$-Si(CH_3)$_3$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 169.9, 166.5, 166.4, 149.0, 148.2, 146.9, 144.4, 144.0, 142.0, 136.4, 132.2, 131.3, 130.6, 130.5, 129.8, 129.7, 129.6, 129.4, 129.2, 127.9, 122.9, 106.3, 93.1, 68.8, 68.7, 52.4, 52.2, 1.70, and 1.66.

IR (neat): 2990, 2952, 2899, 2202, 1762, 1720, 1605, 1436, 1403, 1358, 1277, 1248, 1110, 1036, 1000, 843, and 767 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{38}H_{36}NaO_8Si_2^+$ [M+Na$^+$] requires 699.1841; found 699.1865.

5-(4-Fluorophenyl)-6-((4-fluorophenyl)ethynyl)-4,7-bis(trimethylsilyl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13m)



S12 ***13m***

Following general procedure C, the naphthalene derivative **13m** was prepared from triyne **S12** (45 mg, 0.15 mmol) in $CHCl_3$ (3.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 4:1) to yield **13m** (24 mg, 0.040 mmol, 53%) as a yellow solid. A small amount of the minor regioisomer (see **13i'**, above, for characterization of an analogous minor isomer) was observed by analysis of the ^{1}H NMR spectrum of the crude product mixture (rr = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (nfodd, *J* = 8.5, 5.5 Hz, 2H, *H2*), 7.04 (nfodd, *J* = 8.9, 5.4 Hz, 2H, *H2'*), 6.99 (nfodd, *J* = 8.6, 4.9 Hz, 2H, *H3*), 6.98 (nfodd, *J* = 8.8, 5.1 Hz, 2H, *H3'*), 5.64 (s, 2H, CH_2O), 5.62 (s, 2H, CH_2O), 0.47 [s, 9H, Ar$_{ringC}$-Si(CH_3)$_3$], and 0.02 [s, 9H, Ar$_{ringB}$-Si(CH_3)$_3$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.8, 170.1, 163.2 (d, *J* = 248 Hz), 162.6 (d, *J* = 250 Hz), 149.0, 147.7, 144.1, 143.6, 141.7, 138.7 (d, *J* = 3.4 Hz), 137.1, 133.8 (d, *J* = 8.8 Hz), 132.6 (d, *J* = 8.8 Hz), 132.3, 129.7, 129.1, 122.9, 119.5 (d, *J* = 3.5 Hz), 115.8 (d, *J* = 18 Hz), 115.6 (d, *J* = 16 Hz), 107.0, 89.9 (d, *J* = 1.7 Hz), 68.8, 68.6, 1.7, and 1.5.

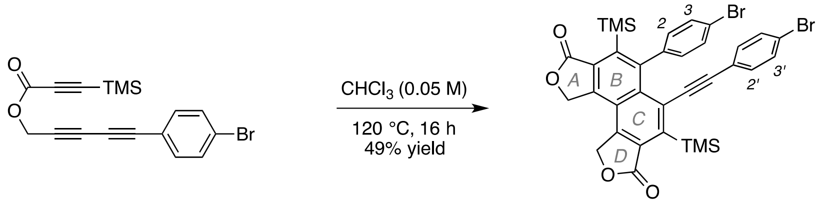
^{19}F NMR (470 MHz, $CDCl_3$): δ -110.3, and -113.1.

IR (neat): 2950, 2899, 2192, 1760, 1600, 1507, 1400, 1358, 1247, 1230, 1156, 1112, 1036, 1000, 841, and 767 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{34}H_{30}F_2NaO_4Si_2^+$ [M+Na$^+$] requires 619.1543; found 619.1534.

Mp: 131–136 °C.

5-(4-Bromophenyl)-6-((4-bromophenyl)ethynyl)-4,7-bis(trimethylsilyl)naphtho[1,2-c:7,8-c']difuran-3,8(1H,10H)-dione (13n)



S13 ***13n***

Following general procedure C, the naphthalene derivative **13n** was prepared from triyne **S13** (54 mg, 0.15 mmol) in $CHCl_3$ (3.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 4:1) to yield **13n** (26 mg, 0.037 mmol, 49%) as a yellow solid. A small amount of the minor regioisomer (see **13i'**, above, for characterization of an analogous minor isomer) was observed by analysis of the ^{1}H NMR spectrum of the crude product mixture (rr = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (nfod, *J* = 8.4 Hz, 2H, *H3*), 7.43 (nfod, *J* = 8.4 Hz, 2H, *H3'*), 7.26 (nfod, *J* = 8.3 Hz, 2H, *H2*), 6.92 (nfod, *J* = 8.5 Hz, 2H, *H2'*), 5.64 (s, 2H, CH_2O), 5.62 (s, 2H, CH_2O), 0.46 [s, 9H, Ar$_{ringC}$-Si(CH_3)$_3$], and 0.02 [s, 9H, Ar$_{ringB}$-Si(CH_3)$_3$].

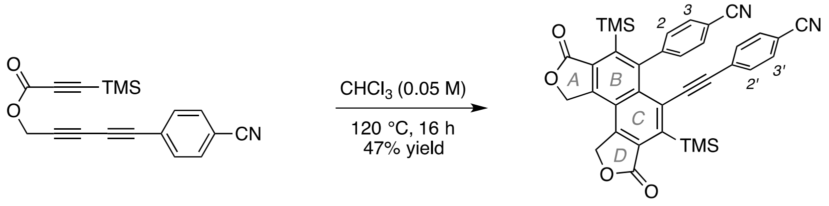
^{13}C NMR (126 MHz, $CDCl_3$): δ 170.7, 170.0, 148.8, 148.0, 144.2, 143.8, 141.8, 141.5, 136.7, 133.7, 132.2, 131.81, 131.78, 131.7, 129.8, 129.2, 123.7, 122.9, 122.9, 122.1, 106.8, 91.2, 68.8, 68.6, 1.7, and 1.5.

IR (neat): 2949, 2899, 2194, 1760, 1486, 1401, 1357, 1248, 1191, 1112, 1036, 1010, 1000, 841, and 766 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{34}H_{30}{}^{79}Br_2NaO_4Si_2^+$ [M+Na$^+$] requires 738.9942; found 738.9918.

Mp: 182–186 °C.

4-((6-(4-Cyanophenyl)-3,8-dioxo-4,7-bis(trimethylsilyl)-1,3,8,10-tetrahydronaphtho[1,2-c:7,8-c']difuran-5-yl)ethynyl)benzonitrile (13o)



S15 ***13o***

Following general procedure C, the naphthalene derivative **13o** was prepared from triyne **S15** (46 mg, 0.15 mmol) in $CHCl_3$ (3.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 4:1) to yield **13o** (22 mg, 0.036 mmol, 47%) as a pale yellow solid. A small amount of the minor regioisomer (see **13i'**, above, for characterization of an analogous minor isomer) was observed by analysis of the ^{1}H NMR spectrum of the crude product mixture (rr = 8:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (nfod, *J* = 8.3 Hz, 2H, *H3'*), 7.57 (nfod, *J* = 8.5 Hz, 2H, *H3*), 7.55 (nfod, *J* = 8.5 Hz, 2H, *H2*), 7.12 (nfod, *J* = 8.4 Hz, 2H, *H2'*), 5.66 (s, 2H, CH_2O), 5.64 (s, 2H, CH_2O), 0.47 [s, 9H, Ar_{ringC}-Si(CH_3)$_3$], and 0.01 [s, 9H, Ar_{ringB}-Si(CH_3)$_3$].

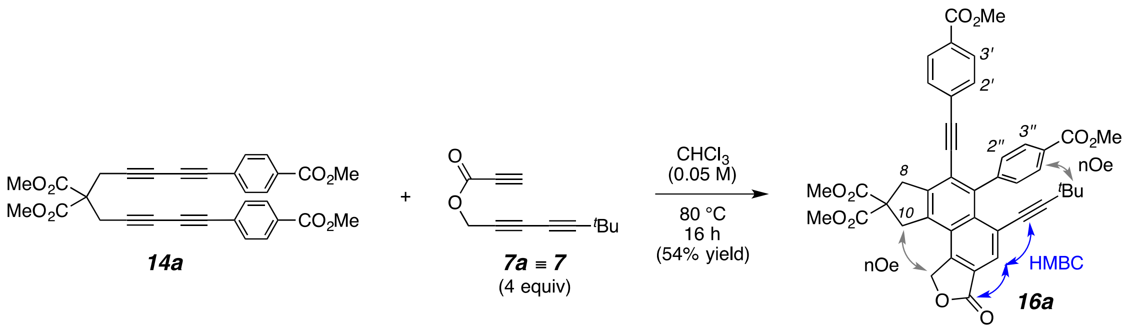
^{13}C NMR (126 MHz, $CDCl_3$): δ 170.4, 169.7, 148.8, 147.7, 147.3, 144.7, 144.4, 142.3, 136.3, 132.9, 132.4, 132.1, 130.8, 130.4, 130.0, 129.4, 127.5, 123.0, 118.23, 118.18, 113.0, 112.5, 105.2, 94.1, 68.8, 68.6, 1.7, and 1.6.

IR (neat): 2954, 2933, 2228, 1758, 1456, 1400, 1361, 1249, 1108, 1032, 1000, and 841 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{36}H_{30}N_2NaO_4Si_2^+$ [M+Na$^+$] requires 633.1636; found 633.1647.

Mp: 345–348 °C (with no obvious discoloration).

Dimethyl 5-(3,3-Dimethylbut-1-yn-1-yl)-6-(4-(methoxycarbonyl)phenyl)-7-((4-(methoxycarbonyl)phenyl)ethynyl)-3-oxo-1,3,8,10-tetrahydro-9H-cyclopenta[7,8]naphtho[1,2-c]furan-9,9-dicarboxylate (16a)



Following general procedure C, the naphthalene derivative **16a** was prepared from a mixture of the tetrayne **14a**[14] (26 mg, 0.050 mmol) and triyne **7a** (38 mg, 0.20 mmol) in $CHCl_3$ (1.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 1.5:1) to yield the heterodimer **16a** (19 mg, 0.027 mmol, 54%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (nfod, *J* = 8.3 Hz, 2H, *H3''*), 7.98 (s, 1H, Naph–*H*), 7.93 (nfod, *J* = 8.4 Hz, 2H, *H3'*), 7.48 (nfod, *J* = 8.4 Hz, 2H, *H2''*), 7.18 (nfod, *J* = 8.4 Hz, 2H, *H2'*), 5.83 (s, 2H, CH_2O), 4.08 (s, 2H, *H10*), 4.00 (s, 3H, OCH_3), 3.97 (s, 2H, *H8*), 3.92 (s, 3H, OCH_3), 3.84 (s, 6H, malonyl-CH_3), and 0.92 [s, 9H, C(CH_3)$_3$].

nOe & HMBC: The interaction indicated on structure **16a** supported the assignment of regiochemical orientation for this product.

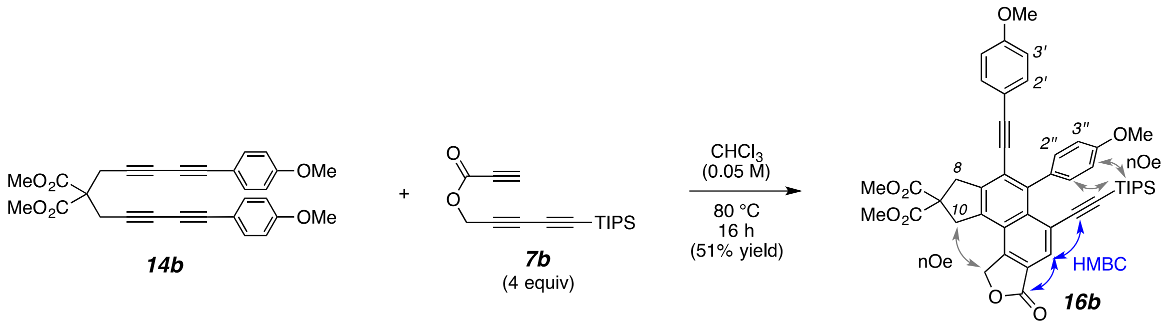
^{13}C NMR (126 MHz, $CDCl_3$): δ 171.6, 170.6, 167.2, 166.5, 145.5, 144.3, 143.1, 140.7, 135.5, 133.0, 131.6, 131.4, 130.2, 130.1, 129.7, 129.6, 129.0, 127.1, 125.5, 125.4, 123.9, 122.5, 111.1, 99.1, 89.4, 78.9, 70.9, 59.3, 53.6, 52.4, 41.9, 41.2, 30.4, and 28.1 (one methoxy carbon was not discernible).

IR (neat): 2957, 2928, 2860, 2118, 1769, 1731, 1719, 1652, 1435, 1273, 1107, and 830 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{43}H_{36}NaO_{10}^+$ [M+Na$^+$] requires 735.2201; found 735.2173.

Mp: 294–297 °C.

Dimethyl 6-(4-Methoxyphenyl)-7-((4-methoxyphenyl)ethynyl)-3-oxo-5-((triisopropylsilyl)ethynyl)-1,3,8,10-tetrahydro-9H-cyclopenta[7,8]naphtho[1,2-c]furan-9,9-dicarboxylate (16b)



Following general procedure C, the naphthalene derivative **16b** was prepared from a mixture of the tetrayne **14b**[14] (23 mg, 0.049 mmol) and triyne **7b** (57 mg, 0.20 mmol) in $CHCl_3$ (1.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 2:1) to yield the heterodimer **16b** (19 mg, 0.025 mmol, 51%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (s, 1H, Naph–*H*), 7.29 (nfod, *J* = 8.6 Hz, 2H, *H2''*), 7.18 (nfod, *J* = 8.8 Hz, 2H, *H2'*), 6.93 (nfod, *J* = 8.7 Hz, 2H, *H3''*), 6.81 (nfod, *J* = 8.8 Hz, 2H, *H3'*), 5.81 (s, 2H, CH_2O), 4.05 (s, 2H, *H10*), 3.96 (s, 2H, *H8*), 3.87 (s, 3H, Ar–ArOCH_3), 3.83 (s, 6H, malonyl-CH_3), 3.81 (s, 3H, ≡CArOCH_3), 1.00 {d, *J* = 6.8 Hz, 18H, Si[CH(CH_3)$_2$]$_3$}, and 0.96–0.89 [m, 3H, Si(CH)$_3$].

nOe & HMBC: The interaction indicated on structure **16b** supported the assignment of regiochemical orientation for this product.

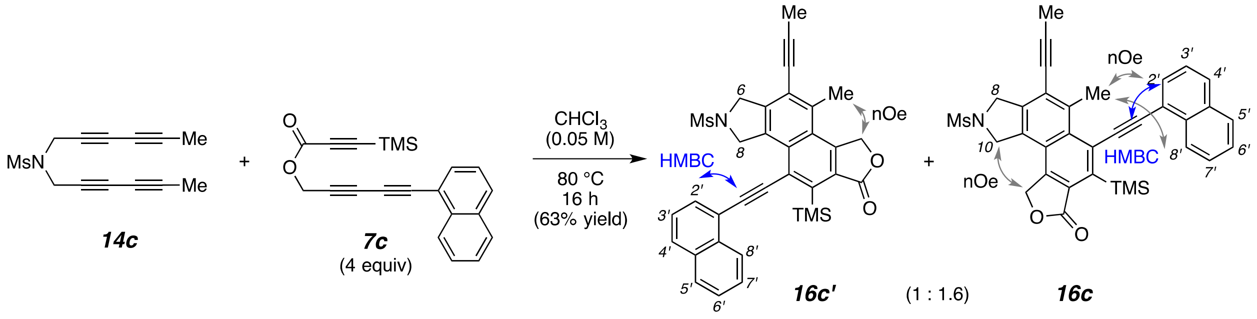
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 170.7, 160.2, 159.3, 145.2, 143.1, 140.8, 134.3, 134.0, 133.4, 132.7, 132.3, 130.8, 125.0, 124.8, 124.2, 123.2, 115.0, 114.1, 113.2, 105.7, 103.7, 100.1, 86.3, 70.8, 59.4, 55.5, 55.0, 53.6, 41.9, 41.3, 18.9, and 11.7.

IR (neat): 2953, 2864, 2197, 2130, 1772, 1735, 1601, 1509, 1457, 1400, 1285, 1248, 1170, 1028, and 826 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{46}H_{48}NaO_8Si^+$ [M+Na$^+$] requires 779.3011; found 779.3000.

Mp: 240–243 °C.

4-Methyl-7-(methylsulfonyl)-9-(naphthalen-1-ylethynyl)-5-(prop-1-yn-1-yl)-10-(trimethylsilyl)-3,6,7,8-tetrahydro-1H-isobenzofuro[5,4-e]isoindol-1-one (18c') and 6-Methyl-9-(methylsulfonyl)-5-(naphthalen-1-ylethynyl)-7-(prop-1-yn-1-yl)-4-(trimethylsilyl)-1,8,9,10-tetrahydro-3H-isobenzofuro[4,5-e]isoindol-3-one (16c)



Following general procedure C, the naphthalene derivatives **16c** and **16c'** were prepared from a mixture of tetrayne **14c**[15] (20 mg, 0.081 mmol) and triyne **7c** (106 mg, 0.32 mmol) in $CHCl_3$ (1.6 mL). The crude product mixture was purified by MPLC (hexanes:EtOAc 2.5:1) to yield, in the order of elution, the heterodimers **16c'** (11 mg, 0.019 mmol, 24%) and **16c** (18 mg, 0.031 mmol, 39%), each as a white solid.

Data for **16c'**

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.32 (d, *J* = 8.1 Hz, 1H, *H8'*), 7.93 (two d's, *J* = 7.6 Hz, 2H, overlapped *H2'* and *H5'*), 7.91 (dd, *J* = 7.5, 1.3 Hz, 1H, *H4'*), 7.61–7.53 (m, 3H, *H3'*, *H6'*, and *H7'*), 5.84 (s, 2H, C*H*$_2$O), 5.75 (s, 2H, *H8*), 4.86 (s, 2H, *H6*), 2.89 (s, 3H, ArC*H*$_3$), 2.74 (s, 3H, O$_2$S-C*H*$_3$), 2.19 (s, 3H, ≡CC*H*$_3$), and 0.57 [s, 9H, Si(C*H*$_3$)$_3$].

nOe & HMBC: The interaction indicated on structure **16c'** for a pair of resonances in the minor isomer supported the assignment of regiochemical orientation for each of the two constitutional isomers.

^{13}C NMR (126 MHz, CDCl$_3$) δ 170.9, 146.5, 143.1, 140.9, 137.9, 133.5, 133.3, 132.2, 131.2, 130.7, 129.9, 129.0, 128.9, 128.8, 128.6, 127.3, 126.8, 125.9, 125.8, 120.4, 120.1, 98.9, 97.5, 95.8, 75.7, 71.5, 57.8, 54.6, 35.1, 19.8, 5.0, and 2.2.

IR (neat): 2957, 2930, 2216, 1762, 1652, 1401, 1334, 1247, 1217, 1154, 1096, 1043, 827, and 803 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{34}H_{31}NNaO_4SSi^+$ [M+Na$^+$] requires 600.1635; found 600.1648.

Mp: 268–272 ºC.

Data for **16c**

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.27–8.23 (nfom, 1H, *H8'*), 7.90 (d, *J* = 7.2 Hz, 1H, *H4'*), 7.90–7.88 (nfom, 1H, *H5'*), 7.77 (dd, *J* = 7.1, 1.0 Hz, 1H, *H2'*), 7.56–7.49 (m, 3H, *H3'*, *H6'*, and *H7'*), 5.62 (s, 2H, C*H*$_2$O), 5.11 (s, 2H, *H10*), 4.90 (s, 2H, *H8*), 3.29 (s, 3H, ArC*H*$_3$), 2.98 (s, 3H, O$_2$S-C*H*$_3$), 2.17 (s, 3H, ≡CC*H*$_3$), and 0.59 [s, 9H, Si(C*H*$_3$)$_3$].

nOe & HMBC: The interactions indicated on structure **16c** for pairs of resonances of the major isomer supported the assignment of regiochemical orientation for each of the two constitutional isomers.

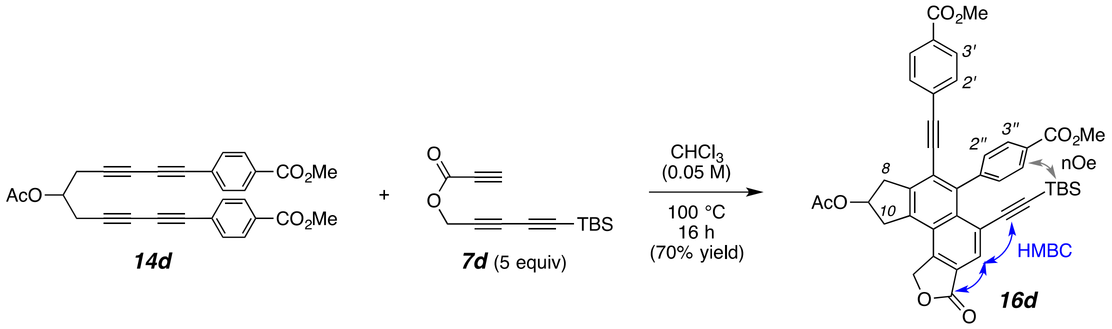
^{13}C NMR (126 MHz, CDCl$_3$) δ 170.7, 144.7, 143.8, 140.2, 138.2, 136.2, 133.5, 133.3, 130.0, 129.9, 129.5, 128.7, 128.7, 128.1, 127.1, 126.8, 126.1, 125.5, 123.0, 122.6, 121.1, 102.7, 98.5, 96.7, 76.4, 69.2, 55.3, 54.8, 35.8, 23.2, 5.0, and 2.2.

IR (neat): 3055, 2944, 2896, 2218, 1759, 1404, 1346, 1323, 1241, 1154, 1098, 1023, 826, 796, and 763 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{34}H_{31}NNaO_4SSi^+$ [M+Na$^+$] requires 600.1635; found 600.1657.

Mp: decomposition > ca. 250 ºC.

Methyl 4-((9-Acetoxy-5-((*tert*-butyldimethylsilyl)ethynyl)-6-(4-(methoxycarbonyl)phenyl)-3-oxo-3,8,9,10-tetrahydro-1H-cyclopenta[7,8]naphtho[1,2-c]furan-7-yl)ethynyl)benzoate (16d)



Following general procedure C, the anthracene derivative **16d** was prepared from a mixture of tetrayne **14d**[14] (28 mg, 0.060 mmol) and 5-(*tert*-butyldimethylsilyl)penta-2,4-diyn-1-yl propiolate[13] (74 mg, 0.30 mmol) in $CHCl_3$ (1.2 mL). The crude product was purified by MPLC (hexanes:EtOAc 1.7:1) to yield the heterodimer **16d** (30 mg, 0.042 mmol, 70%) as a yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15–8.14 (nfom, 1H, *H3’’*$_a$), 8.14–8.12 (nfom, 1H, *H3’’*$_b$), 8.05 (s, 1H, Ar*H*), 7.92 (nfod, *J* = 8.3 Hz, 2H, *H3’*), 7.53–7.50 (nfom, 1H, *H2’’*$_a$), 7.50–7.47 (nfom, 1H, *H2’’*$_b$), 7.16 (nfod, *J* = 8.3 Hz, 2H, *H2’*), 5.82 (d, *J* = 16.1 Hz, 1H, C*H*$_a$H$_b$O), 5.77 (dddd, *J* = 6.8, 6.8, 2.5, 2.5 Hz, 1H, AcOC*H*), 5.75 (d, *J* = 16.1 Hz, 1H, CH$_a$*H*$_b$O), 4.00 (s, 3H, OC*H*$_3$), 3.91 (s, 3H, OC*H*$_3$), 3.85 (dd, *J* = 17.0, 6.8 Hz, 1H, *H10*$_a$), 3.69 (dd, *J* = 18.1, 6.8 Hz, 1H, *H8*$_a$), 3.47 (dd, *J* = 17.1, 2.2 Hz, 1H, *H10*$_b$), 3.42 (dd, *J* = 18.0, 2.4 Hz, 1H, *H8*$_b$), 2.10 (s, 3H, O=CC*H*$_3$), 0.85 [s, 9H, SiC(C*H*$_3$)$_3$], and -0.12 [s, 6H, Si(C*H*$_3$)$_2$].

nOe & HMBC: The interaction indicated on structure **16d** supported the assignment of regiochemical orientation for this product.

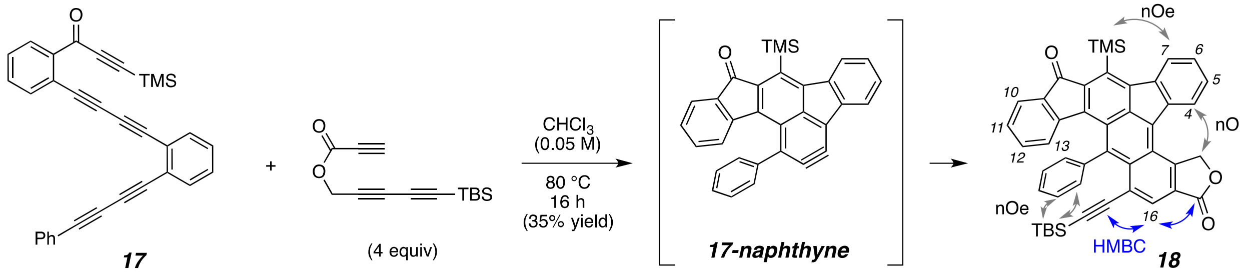
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 170.4, 167.2, 166.4, 145.5, 145.2, 142.8, 141.8, 136.2, 133.0, 131.55, 131.54, 131.52, 130.9, 130.2, 129.9, 129.6, 129.06, 129.04, 127.0, 125.6, 124.4, 123.8, 123.1, 105.5, 103.6, 99.1, 89.5, 73.7, 70.8, 52.4, 52.4, 41.4, 40.5, 26.3, 21.4, 17.1, and -4.9. (each two carbons at both 2’’ and 3’’ positions are diastereotopic)

IR (neat): 2968, 2930, 2864, 2137, 1772, 1732, 1720, 1652, 1455, 1373, 1275, 1237, 1105, 1028, and 827 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{43}H_{40}NaO_8Si^+$ [M+Na$^+$] requires 735.2385; found 735.2409

Mp: decomposition > ca. 250 ºC.

15-((*tert*-Butyldimethylsilyl)ethynyl)-14-phenyl-8-(trimethylsilyl)-1H-benzo[1,2]indeno[2',1':4,5]aceanthryleno[9,10-c]furan-1,9(3H)-dione (18)



Following general procedure C, the anthracene derivative **18** was prepared from a mixture of pentayne **17**[16] (22 mg, 0.049 mmol) and 5-(*tert*-butyldimethylsilyl)penta-2,4-diyn-1-yl propiolate[13] (49 mg, 0.20 mmol) in $CHCl_3$ (1.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 9:1) to yield the heterodimer **18** (12 mg, 0.017 mmol, 35%, via the naphthyne **17-naphthyne**) as a dark red, amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (nfod, *J* = 7.7 Hz, 1H, *H4*), 8.01 (s, 1H, *H16*), 7.98 (nfod, *J* = 7.6 Hz, 1H, *H7*), 7.65 (nfod, *J* = 7.5 Hz, 2H, PhH_o), 7.56 (dd, *J* = 7.5, 7.5 Hz, 1H, *H6*), 7.47 (d, *J* = 7.1 Hz, 1H, *H10*), 7.46–7.38 (m, 4H, PhH_{m+p} and *H5*), 6.99 (dd, *J* = 7.3, 7.3 Hz, 1H, *H11*), 6.72 (ddd, *J* = 7.6, 7.6, 0.9 Hz, 1H, *H12*), 6.14 (s, 2H, CH_2O), 5.35 (d, *J* = 7.7 Hz, 1H, *H13*), 0.80 [s, 9H, SiC(CH_3)$_3$], 0.56 [s, 9H, Si(CH_3)$_3$], and -0.10 [s, 6H, Si(CH_3)$_2$].

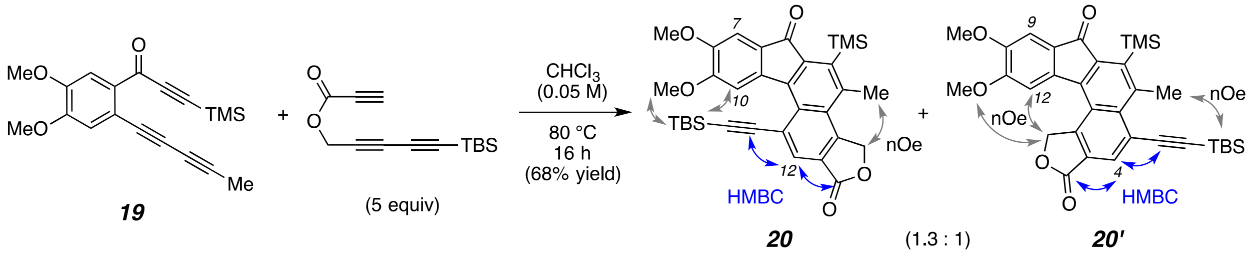
nOe & HMBC: The interaction indicated on structure **18** supported the assignment of regiochemical orientation for this product.

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.5, 170.6, 147.9, 146.5, 145.5, 144.6, 142.5, 141.0, 140.8, 139.7, 139.5, 136.8, 136.7, 134.7, 134.6, 133.9, 133.8, 132.5, 130.0, 129.5, 129.0, 128.4, 127.9, 127.5, 127.2, 127.0, 126.9, 125.2, 125.1, 124.9, 123.4, 122.9, 106.0, 103.5, 73.5, 26.4, 17.0, 1.8, and -4.3.

IR (neat): 2952, 2928, 2855, 2133, 1771, 1708, 1461, 1397, 1351, 1249, 1197, 1023, 813, and 757 cm^{-1}.

LRMS (APCI$^+$): Calcd for $C_{46}H_{41}O_3Si_2^+$ [M+H$^+$] requires 697.2589; found 697.3 (no ESI signal could be observed).

11-((*tert*-Butyldimethylsilyl)ethynyl)-8,9-dimethoxy-4-methyl-5-(trimethylsilyl)-1H-indeno[1',2':5,6]naphtho[1,2-c]furan-1,6(3H)-dione (20) and 5-((*tert*-Butyldimethylsilyl)ethynyl)-10,11-dimethoxy-6-methyl-7-(trimethylsilyl)-1H-indeno[2',1':7,8]naphtho[1,2-c]furan-3,8-dione (20’)



Following general procedure C, the anthracene derivatives **20** and **20’** were prepared from a mixture of triyne **19**[17] (16 mg, 0.049 mmol) and 5-(*tert*-butyldimethylsilyl)penta-2,4-diyn-1-yl propiolate[13] (62 mg, 0.25 mmol) in $CHCl_3$ (1.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 5:1) to yield, in the order of elution, the heterodimers **20** (11 mg, 0.019 mmol, 39%) as a cherry-red amorphous solid and **20’** (8.0 mg, 0.014 mmol, 29%) as an orange crystalline solid.

Data for **20**

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (s, 1H, *H12*), 7.72 (s, 1H, *H10*), 7.13 (s, 1H, *H7*), 5.83 (s, 2H, CH_2O), 4.02 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 2.77 (s, 3H, $ArCH_3$), 0.87 [s, 9H, $SiC(CH_3)_3$], 0.47 [s, 9H, $Si(CH_3)_3$], and 0.06 [s, 6H, $Si(CH_3)_2$].

nOe & HMBC: The interaction indicated on structure **20** supported the assignment of regiochemical orientation for this product.

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 170.4, 152.7, 149.3, 147.0, 143.7, 141.7, 140.5, 139.8, 139.2, 132.3, 131.7, 130.0, 125.6, 125.1, 122.2, 112.1, 106.9, 106.2, 104.9, 72.7, 56.6, 56.4, 26.2, 24.3, 16.9, 2.4, and -4.9.

IR (neat): 2951, 2930, 2855, 2143, 1768, 1707, 1590, 1484, 1381, 1294, 1248, 1216, 1105, 1026, 889, 840, and 776 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{33}H_{38}NaO_5Si_2^+$ [M+Na$^+$] requires 593.2150; found 593.2145

Data for **20’**

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (s, 1H, *H4*), 7.22 (s, 1H, *H9*), 7.07 (s, 1H, *H12*), 5.85 (s, 2H, CH_2O), 4.05 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 3.16 (s, 3H, $ArCH_3$), 1.03 [s, 9H, $SiC(CH_3)_3$], 0.46 [s, 9H, $Si(CH_3)_3$], and 0.24 [s, 6H, $Si(CH_3)_2$].

nOe & HMBC: The interaction indicated on structure **20’** supported the assignment of regiochemical orientation for this product.

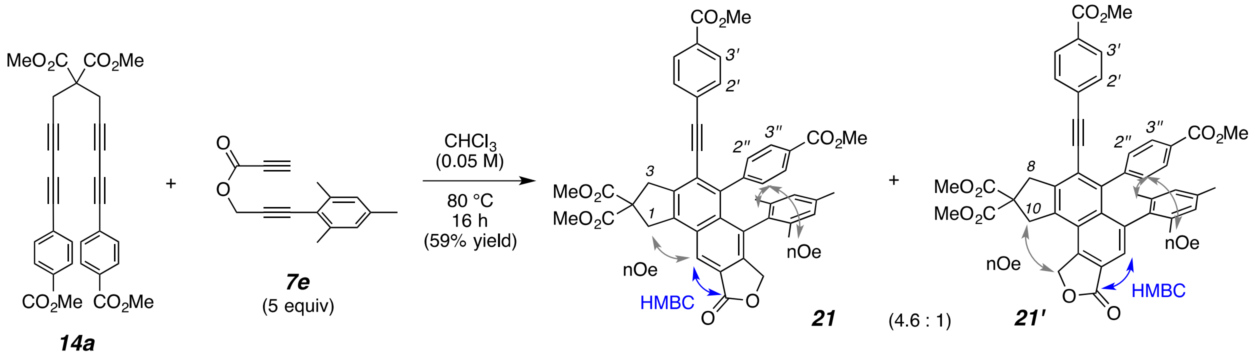
^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 170.0, 154.0, 149.8, 147.1, 144.3, 142.1, 141.0, 139.7, 139.04, 139.00, 131.5, 126.9, 124.4, 124.0, 123.8, 108.2, 107.2, 106.5, 103.3, 72.3, 56.8, 56.4, 28.6, 26.4, 17.1, 2.5, and -4.7.

IR (neat): 2952, 2856, 2114, 1769, 1701, 1591, 1494, 1459, 1371, 1313, 1244, 1086, 1021, 865, and 824 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{33}H_{38}NaO_5Si_2^+$ [M+Na$^+$] requires 593.2150; found 593.2134

Mp: 265–270 °C.

Dimethyl 6-Mesityl-5-(4-(methoxycarbonyl)phenyl)-4-((4-(methoxycarbonyl)phenyl)ethynyl)-9-oxo-1,3,7,9-tetrahydro-2H-cyclopenta[5,6]naphtho[2,3-c]furan-2,2-dicarboxylate (21) and Dimethyl 5-Mesityl-6-(4-(methoxycarbonyl)phenyl)-7-((4-(methoxycarbonyl)phenyl)ethynyl)-3-oxo-1,3,8,10-tetrahydro-9H-cyclopenta[7,8]naphtho[1,2-c]furan-9,9-dicarboxylate (21)



Following general procedure C, the naphthalene derivatives **21** and **21’** were prepared from a mixture of tetrayne **14a**[14] (26 mg, 0.050 mmol) and diyne **7e** (56 mg, 0.25 mmol) in CHCl$_3$ (1.0 mL). The crude product mixture was purified by MPLC (hexanes:EtOAc 2:1) to yield, in the order of elution, the heterodimers **21** (18 mg, 0.024 mmol, 48%) and **21’** (4.0 mg, 5.3 μmol, 11%), each as a white solid.

Data for **21**

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.50 (s, 1H, Ar*H*), 7.85 (d, *J* = 7.9 Hz, 2H, *H3’’*), 7.66 (d, *J* = 7.7 Hz, 2H, *H3’*), 7.05 (nfod, *J* = 7.8 Hz, 2H, *H2’*), 6.99 (d, *J* = 7.9 Hz, 2H, *H2’’*), 6.49 (s, 2H, mesityl-*H*), 4.74 (s, 2H, CH_2O), 4.22 (s, 2H, *H10*), 4.01 (s, 2H, *H8*), 3.94 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.86 (s, 6H, malonyl-CH_3), 2.09 (s, 3H, $\mathrm{Ar}_{para}\mathrm{C}H_3$), 1.70 (s, 6H, $\mathrm{Ar}_{ortho}\mathrm{C}H_3$).

nOe & HMBC: The interaction indicated on structure **21** supported the assignment of regiochemical orientation for this product.

^{13}C NMR (126 MHz, CDCl$_3$) δ 172.0, 171.1, 167.1, 166.5, 144.5, 142.4, 141.2, 138.63, 138.59, 138.2, 134.9, 134.6, 133.6, 132.5, 131.5, 131.3, 129.9, 129.5, 129.0, 128.6, 128.4, 128.0, 127.1, 124.0, 122.9, 122.6, 99.2, 89.6, 70.1, 59.0, 53.5, 52.4, 52.2, 42.1, 41.0, 20.8, 20.6, and 0.1.

IR (neat): 2998, 2951, 2851, 2206, 1769, 1722, 1605, 1435, 1273, 1248, 1173, 1107, 1017, 855, and 766 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{46}H_{38}NaO_{10}^+$ [M+Na$^+$] requires 773.2357; found 773.2361.

Mp: 268–273 ºC.

Data for **21’**

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (nfod, *J* = 8.4 Hz, 2H, *H3'*), 7.66 (nfod, *J* = 8.2 Hz, 2H, *H3''*), 7.50 (s, 1H, Ar*H*), 7.00 (nfod, *J* = 8.3 Hz, 2H, *H2'*), 6.97 (nfod, *J* = 8.2 Hz, 2H, *H2''*), 6.43 (s, 2H, mesityl-*H*), 5.91 (s, 2H, CH_2O), 4.16 (s, 2H, *H10*), 3.98 (s, 2H, *H8*), 3.95 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.86 (s, 6H, malonyl-CH_3), 2.08 (s, 3H, $Ar_{para}CH_3$), 1.71 (s, 6H, $Ar_{ortho}CH_3$).

nOe & HMBC: The interaction indicated on structure **21'** supported the assignment of regiochemical orientation for this product.

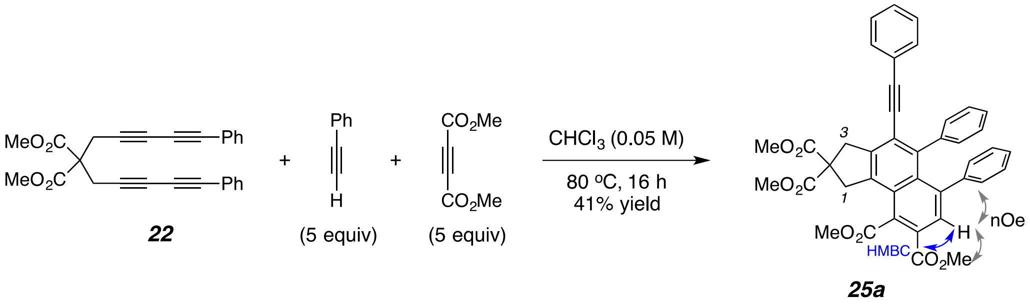
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 171.1, 167.1, 166.5, 144.8, 144.7, 142.5, 140.3, 138.2, 137.6, 135.8, 135.5, 133.7, 131.5, 130.0, 129.6, 128.7, 128.3, 128.2, 128.1, 127.0, 125.9, 124.7, 124.2, 122.8, 99.3, 89.4, 71.0, 59.2, 53.7, 52.4, 52.2, 42.2, 41.3, 21.2, 20.8, and 0.2 (one sp^2 carbon was not discernible).

IR (neat): 2952, 2920, 2852, 2206, 1769, 1760, 1721, 1604, 1435, 1274, 1247, 1107, 1020, and 768 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{46}H_{38}NaO_{10}^{+}$ [$M+Na^{+}$] requires 773.2357; found 773.2342.

Mp: 276–278 °C.

Tetramethyl 5,6-Diphenyl-4-(phenylethynyl)-1,3-dihydro-2H-cyclopenta[a]naphthalene-2,2,8,9-tetracarboxylate (25a)

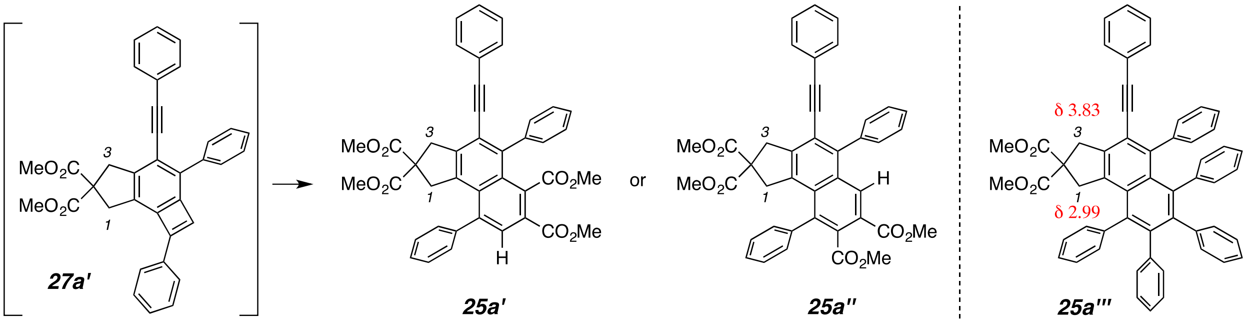


Following general procedure C, the naphthalene derivative **25a** was prepared from a mixture of tetrayne **22**[18] (40 mg, 0.098 mmol), phenylacetylene (55 *u*L, 0.50 mmol), and dimethyl but-2-ynedioate (62 *u*L, 0.50 mmol) in $CHCl_3$ (2.0 mL). The crude product mixture was purified by MPLC (hexanes:EtOAc 4:1) to yield the three-component product **25a** (26 mg, 0.040 mmol, 41%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 1H, NaphC7–*H*), 7.27–7.20 (m, 3H, ≡CPhH_{m+p}), 7.14 (br d, *J* = 7.3 Hz, 2H, ≡CPhH_o), 7.00–6.91 (m, 8H, C5-PhH_5 and C6-PhH_{m+p}), 6.89–6.83 (nfom, 2H, C6-PhH_o), 4.15 (s, 3H, C9–CO_2CH_3), 4.08 (s, 2H, *H1*), 3.96 (s, 2H, *H3*), 3.92 (s, 3H, C8–CO_2CH_3), and 3.82 (s, 6H, malonyl-CH_3).

nOe & HMBC: The interactions for the indicated pairs of resonances on structure **25a** supported the assignment of constitution for this product.

Isomers **25a’** and **25a’’**, which could be derived from the isomeric BCB intermediate **27a’** and which would have similar NOESY interactions, were ruled out by comparing the ^{1}H NMR chemical shifts of C1*H*$_2$ and C3*H*$_2$ of **25a** with the spectral data of a previously reported compound **25a’’’**.[19] Namely, C1*H*$_2$ and C3*H*$_2$ are quite differentially shielded in **25a’’’** and would be expected to be so in either **25a’** or **25a’’** as well.



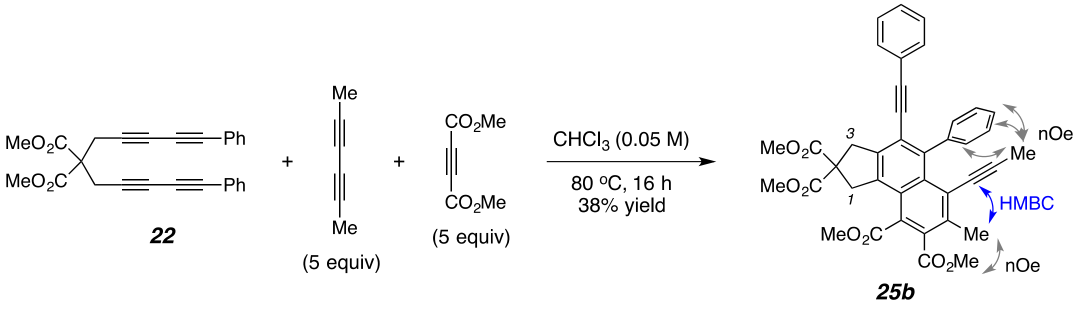
^{13}C NMR (126 MHz, CDCl$_3$) δ 172.0, 170.9, 166.1, 143.8, 143.5, 143.0, 141.2, 140.6, 134.7, 133.6, 132.1, 131.7, 131.6, 129.9, 129.6, 128.7, 128.3, 127.9, 127.4, 127.1, 126.7, 126.4, 125.1, 122.99, 122.96, 98.9, 87.4, 59.3, 53.4, 53.1, 52.8, 41.3, and 41.2.

IR (neat): 3024, 2952, 2205, 1734, 1493, 1436, 1261, 1239, 1202, 1139, 1075, and 755 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{41}H_{32}NaO_8^+$ [M+Na$^+$] requires 675.1989; found 675.1956.

Mp: 233–235 °C.

Tetramethyl 7-Methyl-5-phenyl-4-(phenylethynyl)-6-(prop-1-yn-1-yl)-1,3-dihydro-2H-cyclopenta[a]naphthalene-2,2,8,9-tetracarboxylate (25b)



Following general procedure C, the naphthalene derivative **25b** was prepared from a mixture of tetrayne **22**[18] (40 mg, 0.098 mmol), 2,4-hexadiyne (39 mg, 0.50 mmol), and dimethyl but-2-ynedioate (62 *u*L, 0.50 mmol) in CHCl$_3$ (2.0 mL). The crude product mixture was purified by MPLC (hexanes:EtOAc 4:1) to yield the three-component product **25b** (23 mg, 0.037 mmol, 38%) as a pale yellow solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.47 (br dd, *J* = 7.4, 7.4 Hz, 2H, Ar-Ph*H$_m$*), 7.39 (br d, *J* = 7.4 Hz, 2H, Ar-Ph*H$_o$*), 7.36 (br dd, *J* = 7.2, 7.2 Hz, 1H, Ar-Ph*H$_p$*), 7.26–7.23 (m, 3H, ≡CPh*H$_{m+p}$*), 7.16–7.12 (nfom, 2H, ≡CPh*H$_o$*), 4.01 (s, 3H, C9–CO$_2$C*H$_3$*), 3.93 (s, 3H, C8–CO$_2$C*H$_3$*), 3.90 (s, 2H, *H3*), 3.85 (s, 2H, *H1*), 3.77 (s, 6H, malonyl-C*H*$_3$), 2.43 (s, 3H, ArC*H*$_3$), and 1.59 (s, 3H, ≡CC*H*$_3$).

nOe & HMBC: The interactions for the indicated pairs of resonances on structure **22b** supported the assignment of constitution for this product.

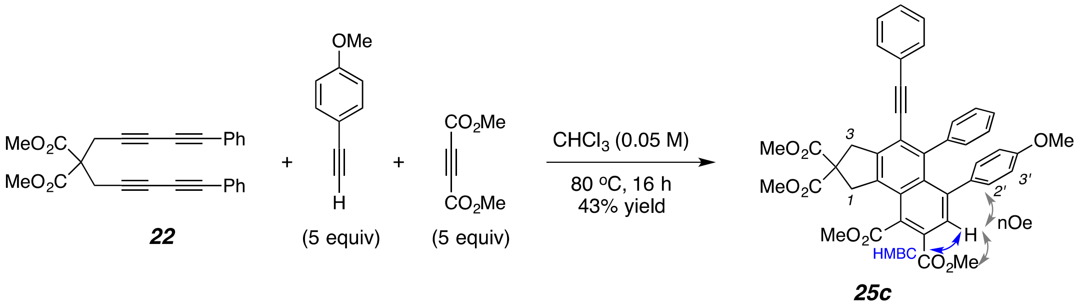
^{13}C NMR (126 MHz, CDCl$_3$) δ 171.9, 169.7, 168.9, 143.0, 141.8, 140.4, 136.8, 134.2, 132.3, 132.1, 131.7, 131.1, 128.6, 128.3, 127.6, 127.5, 127.4, 125.2, 124.9, 123.2, 122.1, 105.4, 99.0, 87.6, 78.4, 59.6, 53.3, 53.1, 52.9, 41.6, 41.2, 19.40, and 5.39.

IR (neat): 2953, 2922, 2851, 2214, 1735, 1491, 1435, 1248, 1201, 1161, 1070, 1050, and 755 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{39}H_{32}NaO_8^+$ [M+Na$^+$] requires 651.1989; found 651.1969.

Mp: 91–95 °C.

Tetramethyl 6-(4-methoxyphenyl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-cyclopenta[a]naphthalene-2,2,8,9-tetracarboxylate (25c)



Following general procedure C, the naphthalene derivative **25c** was prepared from a mixture of tetrayne **22**[18] (20 mg, 0.049 mmol), 4-methoxyphenylacetylene (33 mg, 0.25 mmol), and dimethyl but-2-ynedioate (36 mg, 0.25 mmol) in CHCl$_3$ (1.0 mL). The crude product mixture was purified by MPLC (hexanes:EtOAc 3:1) to yield the three-component product **25c** (15 mg, 0.021 mmol, 43%) as an amorphous solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.80 (s, 1H, NaphC7–*H*), 7.26–7.20 (m, 3H, ≡CPh*H*$_{m+p}$), 7.16–7.12 (m, 2H, ≡CPh*H*$_o$), 7.02–6.98 (m, 3H, C5-Ph*H*$_{m+p}$), 6.93–6.90 (m, 2H, C5-Ph*H*$_o$), 6.77 (nfod, *J* = 8.8 Hz, 2H, *H2'*), 6.49 (nfod, *J* = 8.6 Hz, 2H, *H3'*), 4.15 (s, 3H, C9–CO$_2$C*H*$_3$), 4.07 (s, 2H, *H1*), 3.95 (s, 2H, *H3*), 3.92 (s, 3H, C8–CO$_2$C*H*$_3$), 3.82 (s, 6H, malonyl-C*H*$_3$), and 3.72 (s, 3H, ArOC*H*$_3$).

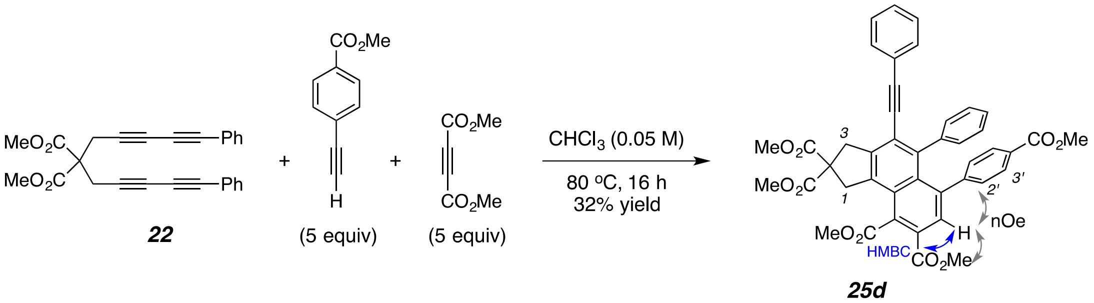
nOe & HMBC: Interactions for the indicated pairs of resonances on structure **25c** supported the assignment of constitution for this product.

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 170.9, 166.2, 158.1, 143.6, 143.5, 141.2, 140.8, 135.7, 134.6, 133.8, 131.8, 131.6, 131.4, 131.0, 129.5, 128.7, 128.3, 127.9, 127.1, 126.6, 125.1, 123.0, 122.9, 113.1, 98.8, 87.5, 59.3, 55.5, 53.4, 53.1, 52.8, 41.3, and 41.2.

IR (neat): 3000, 2952, 2837, 2205, 1735, 1511, 1437, 1245, 1203, 1174, 1138, and 757 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{42}H_{34}NaO_9^+$ [M+Na$^+$] requires 705.2095; found 705.2086.

Tetramethyl 6-(4-(methoxycarbonyl)phenyl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2H-cyclopenta[a]naphthalene-2,2,8,9-tetracarboxylate (25d)



Following general procedure C, the naphthalene derivative **25c** was prepared from a mixture of tetrayne **22**[18] (20 mg, 0.049 mmol), 4-methoxycarbonylphenylacetylene (40 mg, 0.25 mmol), and dimethyl but-2-ynedioate (36 mg, 0.25 mmol) in $CHCl_3$ (1.0 mL). The crude product mixture was purified by MPLC (hexanes:EtOAc 2.5:1) to yield the three-component product **25c** (11 mg, 0.015 mmol, 32%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (s, 1H, NaphC7–*H*), 7.62 (nfod, *J* = 8.4 Hz, 2H, *H3'*), 7.25–7.20 (m, 3H, ≡CPhH_{m+p}), 7.15–7.12 (m, 2H, ≡CPhH_o), 6.98–6.95 (m, 3H, C5-PhH_{m+p}), 6.95–6.91 (m, 4H, C5-PhH_o and *H2'*), 4.15 (s, 3H, C9–CO_2CH_3), 4.08 (s, 2H, *H1*), 3.96 (s, 2H, *H3*), 3.93 (s, 3H, C8–CO_2CH_3), 3.90 (s, 3H, C4'–CO_2CH_3), and 3.82 (s, 6H, malonyl-CH_3).

nOe & HMBC: Interactions for the indicated pairs of resonances on structure **25c** supported the assignment of constitution for this product.

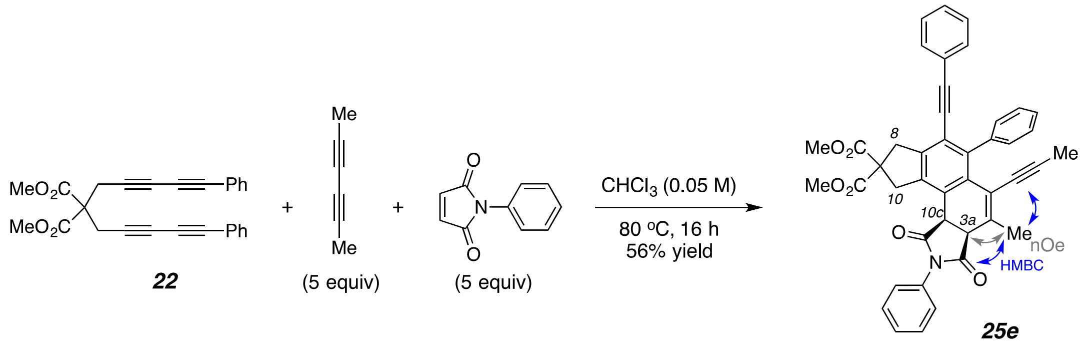
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 170.7, 167.0, 165.9, 147.7, 143.1, 142.6, 141.6, 140.3, 134.9, 133.4, 132.7, 131.71, 131.68, 129.8, 129.4, 128.8, 128.7, 128.4, 128.4, 127.8, 127.3, 127.1, 125.1, 123.2, 122.9, 99.2, 87.2, 59.3, 53.4, 53.2, 52.9, 52.2, 41.3, and 41.2.

IR (neat): 3000, 2952, 2844, 2206, 1728, 1726, 1436, 1268, 1239, 1203, 1113, and 758 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{43}H_{34}NaO_{10}^+$ [M+Na$^+$] requires 733.2044; found 733.2017.

Mp: 227–232 °C.

(±)-Dimethyl (3aS,10cR)-4-methyl-1,3-dioxo-2,6-diphenyl-7-(phenylethynyl)-5-(prop-1-yn-1-yl)-2,3,3a,8,10,10c-hexahydroindeno[4,5-e]isoindole-9,9(1H)-dicarboxylate (25e)



Following general procedure C, the dihydronaphthalene derivative **25e** was prepared from a mixture of tetrayne **22**[18] (20 mg, 0.049 mmol), 2,4-hexadiyne (20 mg, 0.25 mmol), and 1-phenyl-1H-pyrrole-2,5-dione (43 mg, 0.25 mmol) in $CHCl_3$ (1.0 mL). The crude product mixture was purified by MPLC (hexanes:EtOAc 3:1) to yield the three-component product **25e** (18 mg, 0.027 mmol, 56%) as an amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (br d, *J* = 7.6 Hz, 1H, C6-Ph$H_{o\text{-}a}$), 7.48–7.36 (m, 5H, ≡CPhH_o and C6–PhH_{m+p}), 7.33–7.28 (m, 3H, ≡CPhH_{m+p}), 7.25–7.21 (m, 3H, *N*–PhH_{m+p}), 7.17 (br d, *J* = 7.5 Hz, 1H, C6–Ph$H_{o\text{-}b}$), 7.13–7.10 (m, 2H, *N*–PhH_o), 4.44 (d, *J* = 9.3 Hz, 1H, *H10c*), 4.00 (br d, *J* = 9.5 Hz, 1H, *H3a*), 3.96 (d, *J* = 17.7 Hz, 1H, $H8_a$), 3.94 (d, *J* = 16.4 Hz, 1H, $H10_a$), 3.81 (d, *J* = 16.5 Hz, 1H, $H10_b$), 3.80 (s, 3H, malonyl-C$H_{3\text{-}a}$), 3.77 (s, 3H, malonyl-C$H_{3\text{-}b}$), 3.76 (d, *J* = 17.5 Hz, 1H, $H8_b$), 2.16 [d, *J* = 1.4 Hz, 3H, =CCH_3], and 1.45 [s, 3H, ≡CCH_3].

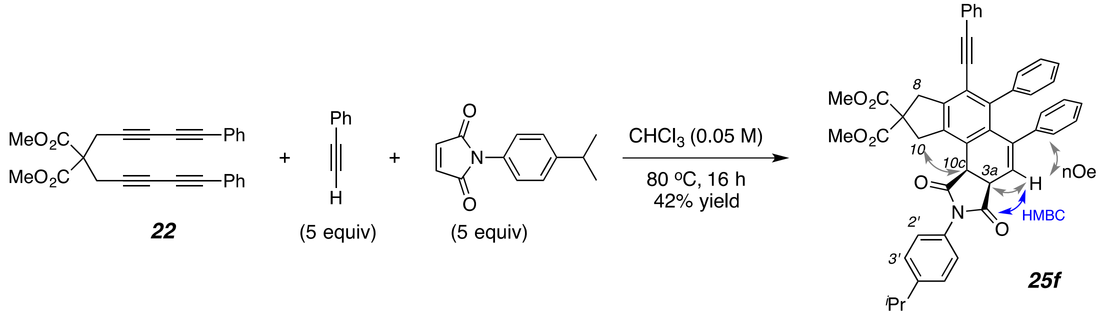
nOe & HMBC: Interactions for the indicated pairs of resonances on structure **25e** supported the assignment of constitution for this product.

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 174.7, 172.3, 171.6, 142.3, 141.6, 141.1, 139.5, 135.4, 131.9, 131.6, 131.6, 131.3, 130.8, 129.3, 128.8, 128.6, 128.3, 127.4, 127.2, 127.0, 126.4, 123.4, 123.4, 121.6, 119.5, 98.0, 97.6, 87.2, 77.4, 59.6, 53.33, 53.28, 47.0, 43.5, 41.3, 40.3, 20.2, and 4.8. The slow rotation of the C6-phenyl ring renders the two pairs of the carbon signals inequivalent (diastereotopic). This is also evident in the ^{1}H NMR spectrum.

IR (neat): 3056, 2953, 2914, 2191, 1734, 1719, 1492, 1376, 1250, 1199, 1167, and 756 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{43}H_{33}NNaO_6^+$ [M+Na$^+$] requires 682.2200; found 682.2219.

(±)-Dimethyl (3aR,10cR)-2-(4-isopropylphenyl)-1,3-dioxo-5,6-diphenyl-7-(phenylethynyl)-2,3,3a,8,10,10c-hexahydroindeno[4,5-e]isoindole-9,9(1H)-dicarboxylate (25f)



Following general procedure C, the dihydronaphthalene derivative **25f** was prepared from a mixture of tetrayne **22**[18] (20 mg, 0.049 mmol), phenylacetylene (26 mg, 0.25 mmol), and 1-(4-isopropylphenyl)-1H-pyrrole-2,5-dione (54 mg, 0.25 mmol) in $CHCl_3$ (1.0 mL). The crude product mixture was purified by MPLC (hexanes:EtOAc 3:1) to yield the three-component product **25f** (15 mg, 0.021 mmol, 42%) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (nfod, *J* = 8.4 Hz, 2H, *H3'*), 7.23–7.20 (m, 3H, ≡CPhH_{m+p}), 7.18 (nfod, *J* = 8.5 Hz, 2H, *H2'*), 7.13–7.10 (m, 2H, ≡CPhH_{o}), 7.07 (br d, *J* = 7.6 Hz, 1H, C6-Ph$H_{o\text{-}a}$), 7.01 (br ddd, *J* = 7.5, 7.5, 1.3 Hz, 1H, C6-Ph$H_{m\text{-}a}$), 6.95 (br dddd, *J* = 7.5, 7.5, 1.3, 1.3 Hz, 1H, C6-PhH_{p}), 6.91 (br ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, C6-Ph$H_{m\text{-}b}$), 6.89–6.85 (m, 3H, C5-PhH_{m+p}), 6.80–6.76 (m, 3H, C5-PhH_{o} and C6-Ph$H_{o\text{-}b}$), 5.72 (d, *J* = 2.1 Hz, 1H, alkene-*H*), 4.46 (d, *J* = 9.2 Hz, 1H, *H10c*), 4.16 (dd, *J* = 9.2, 2.2 Hz, 1H, *H3a*), 4.05 (d, *J* = 16.8 Hz, 1H, $H10_{a}$), 4.03 (d, *J* = 17.6 Hz, 1H, $H8_{a}$), 3.89 (d, *J* = 16.8 Hz, 1H, $H10_{b}$), 3.83 (s, 3H, malonyl-C$H_{3\text{-}a}$), 3.79 (s, 3H, malonyl-C$H_{3\text{-}b}$), 3.78 (d, *J* = 17.8 Hz, 1H, $H8_{b}$), 2.91 [sep, *J* = 6.8 Hz, 1H, C*H*$(CH_3)_2$], 1.229 [d, *J* = 6.9 Hz, 3H, CH$(CH_3)_a(CH_3)_b$], and 1.227 [d, *J* = 7.0 Hz, 3H, CH$(CH_3)_b(CH_3)_a$].

nOe & HMBC: The interactions for the indicated pairs of resonances on structure **25f** supported the assignment of constitution for this product.

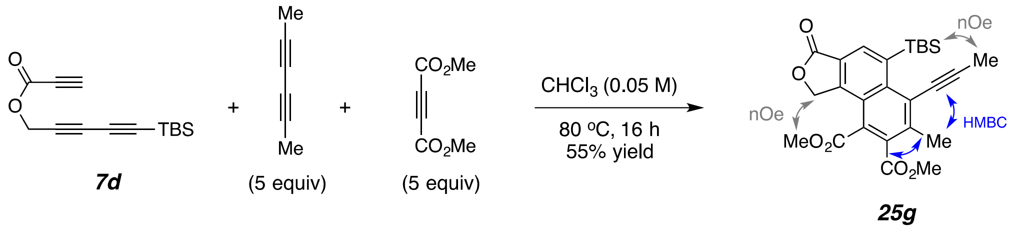
^{13}C NMR (126 MHz, $CDCl_3$) δ 177.0, 175.1, 172.3, 171.7, 149.6, 143.43, 143.41, 142.2, 141.7, 140.0, 139.9, 131.8, 131.5, 131.4, 130.8, 129.4, 128.34, 128.28, 127.9, 127.5, 127.4, 127.2, 126.7, 126.7, 126.4, 126.3, 126.2, 123.8, 123.4, 121.4, 97.2, 86.9, 59.6, 53.37, 53.35, 43.5, 43.1, 41.5, 40.4, 34.1, and 24.0 (br). The slow rotation of the C6-phenyl ring renders the two pairs of the carbon signals inequivalent (diastereotopic). This is also evident in the ^{1}H NMR spectrum.

IR (neat): 3055, 2957, 2929, 2208, 1736, 1718, 1515, 1492, 1380, 1277, 1166, 1072, 756, and 695 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{48}H_{39}NNaO_6^+$ [M+Na$^+$] requires 748.2670; found 748.2668.

Mp: 163–168 °C.

Dimethyl 5-(*tert*-butyldimethylsilyl)-7-methyl-3-oxo-6-(prop-1-yn-1-yl)-1,3-dihydronaphtho[1,2-c]furan-8,9-dicarboxylate (25g)



Following general procedure C, the naphthalene derivative **25g** was prepared from a mixture of triyne **7d** (25 mg, 0.10 mmol), 2,4-hexadiyne (39 mg, 0.50 mmol), and dimethyl but-2-ynedioate (72 mg, 0.50

mmol) in $CHCl_3$ (2.0 mL). The crude product mixture was purified by MPLC (hexanes:EtOAc 4:1) to yield the three-component product **25g** (26 mg, 0.056 mmol, 55%) as an amorphous white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (s, 1H, Ar-*H*), 5.43 (s, 2H, C*H*$_2$O), 4.00 (s, 3H, C9-CO_2CH_3), 3.96 (s, 3H, C8-CO_2CH_3), 2.64 (s, 3H, ArC*H*$_3$), 2.25 (s, 3H, ≡CC*H*$_3$), 1.05 [s, 9H, SiC(C*H*$_3$)$_3$], and 0.51 [s, 6H, Si(C*H*$_3$)$_2$].

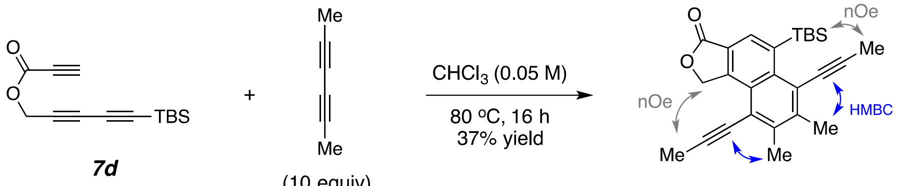
nOe & HMBC: Interactions for the indicated pairs of resonances on structure **25g** supported the assignment of constitution for this product.

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 168.9, 168.0, 146.6, 142.0, 141.3, 140.5, 132.9, 132.1, 128.4, 127.5, 123.2, 123.2, 104.6, 81.3, 70.0, 53.5, 53.1, 28.6, 20.2, 19.6, 6.4, and 0.0.

IR (neat): 2953, 2886, 2858, 2220, 1772, 1735, 1437, 1368, 1260, 1220, 1070, 822, and 761 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{26}H_{30}NaO_6Si^+$ [M+Na$^+$] requires 489.1704; found 489.1709.

5-(*tert*-Butyldimethylsilyl)-7,8-dimethyl-6,9-di(prop-1-yn-1-yl)naphtho[1,2-c]furan-3(1H)-one (25h)



7d

25h

Following general procedure C, the naphthalene derivative **25h** was prepared from a mixture of triyne **7d** (25 mg, 0.10 mmol) and 2,4-hexadiyne (78 mg, 1.0 mmol) in $CHCl_3$ (2.0 mL). The crude product mixture was purified by MPLC (hexanes:EtOAc 10:1) to yield the three-component product **25h** (15 mg, 0.037 mmol, 37%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (s, 1H, Ar-*H*), 5.95 (s, 2H, C*H*$_2$O), 2.61 (s, 3H, C7-C*H*$_3$), 2.59 (s, 3H, C8-C*H*$_3$), 2.25 (s, 3H, C9-C≡CC*H*$_3$), 2.22 (s, 3H, C6-C≡CC*H*$_3$), 1.03 [s, 9H, SiC(C*H*$_3$)$_3$], and 0.51 [s, 6H, Si(C*H*$_3$)$_2$].

nOe & HMBC: Interactions for the indicated pairs of resonances on structure **25h** supported the assignment of constitution for this product.

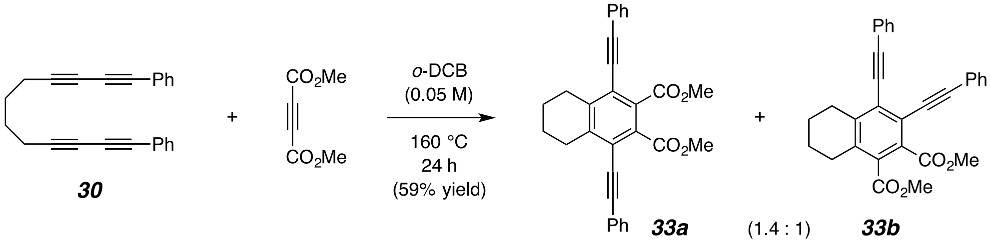
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 147.9, 143.5, 140.0, 139.93, 139.88, 131.0, 128.0, 123.4, 121.9, 119.9, 101.3, 97.3, 82.6, 79.6, 71.8, 28.6, 19.9, 19.6, 19.1, 6.4, 5.1, and 0.1.

IR (neat): 2931, 2913, 2858, 2221, 1762, 1471, 1339, 1249, 1096, 1046, 818, and 763 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{26}H_{30}NaO_2Si^+$ [M+Na$^+$] requires 425.1907; found 425.1923.

Mp: 172–176 °C.

Dimethyl 1,4-Bis(phenylethynyl)-5,6,7,8-tetrahydronaphthalene-2,3-dicarboxylate (33a) and Dimethyl 3,4-Bis(phenylethynyl)-5,6,7,8-tetrahydronaphthalene-1,2-dicarboxylate (33b)



Following general procedure C, the dialkynylbenzene derivatives **33a** and **33b** were prepared from tetrayne **30** (30 mg, 0.098 mmol) and dimethyl but-2-ynedioate (61 *u*L, 0.50 mmol) in *o*-DCB (2.0 mL). The crude product was purified by MPLC (hexanes:EtOAc 2:1) to give a 1.4:1 coeluting mixture of the benzene derivatives **33a** and **33b** (26 mg, 0.058 mmol, 59%) as a pale yellow solid. A portion of the major regioisomer **33a** was obtained as a white solid by recrystallization (hexanes/DCM).

Data for **33a**

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55–7.50 (nfom, 4H, PhH_o), 7.39–7.33 (m, 6H, PhH_{m+p}), 3.94 (s, 6H, CO_2CH_3), 3.04–2.99 (nfom, 4H, ArCH_2), and 1.89–1.84 (nfom, 4H, CH_2CH_2).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 142.4, 132.3, 131.8, 129.0, 128.6, 123.1, 121.6, 100.6, 85.4, 52.7, 29.1, and 22.4.

IR (neat): 2939, 2858, 2209, 1730, 1492, 1441, 1348, 1282, 1244, 1163, 1071, 1022, 966, and 755 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{30}H_{24}NaO_4^+$ [M+Na$^+$] requires 471.1567; found 471.1562.

Mp: 208–211 °C.

Data for **33b** (deduced from the spectra mixture)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58–7.55 (nfom, 2H, PhH_o), 7.55–7.52 (m, 2H, PhH_o), 7.38–7.31 (m, 6H, PhH_{m+p}), 3.94 (s, 3H, C2-CO_2CH_3), 3.89 (s, 3H, C1-CO_2CH_3), 3.03 (t, J = 6.3 Hz, 2H, C5-H_2), 2.82 (t, J = 6.3 Hz, 2H, C8-H_2), 1.88–1.83 (m, 2H, CH_2CH_2), and 1.82–1.76 (nfom, 2H, CH_2CH_2).

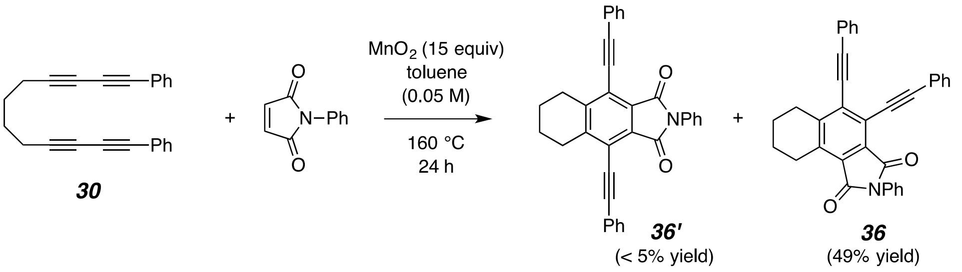
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 167.4, 142.8, 135.8, 132.3, 131.8, 131.7, 131.3, 128.9, 128.8, 128.6, 128.5, 128.4, 123.3, 123.2, 122.2, 100.8, 97.5, 86.4, 86.4, 52.7, 52.6, 29.3, 27.6, 22.3, and 22.2.

IR (neat): 2946, 2863, 2207, 1733, 1491, 1440, 1347, 1331, 1273, 1223, 1160, 1069, 1025, 912, and 755 cm^{-1} (obtained from the mixture).

HRMS (ESI-TOF): Calcd for $C_{30}H_{24}NaO_4^+$ [M+Na$^+$] requires 471.1567; found 471.1559 (obtained from the mixture).

Mp: 120–128 °C (obtained from the mixture).

2-Phenyl-4,5-bis(phenylethynyl)-6,7,8,9-tetrahydro-1H-benzo[e]isoindole-1,3(2H)-dione (36) and 2-Phenyl-4,9-bis(phenylethynyl)-5,6,7,8-tetrahydro-1H-benzo[f]isoindole-1,3(2H)-dione (36')



Following general procedure C, the dialkynylbenzene derivatives **36'** and **36** were prepared from tetrayne **30** (31 mg, 0.10 mmol), 1-phenyl-1H-pyrrole-2,5-dione (86 mg, 0.50 mmol), and manganese dioxide (150 mg, ca. 1.5 mmol) in toluene (2.0 mL). The reaction mixture was magnetically stirred. The suspension was filtered by passing through a pad of silica gel, the filtrate was concentrated, and the residue was subsequently purified by MPLC (hexanes:EtOAc 7:1) to yield, in the order of elution, the benzene derivatives **36'** (8 mg) and **36** (24 mg, 0.050 mmol, 49%), the latter as a pale yellow solid. The sample of **36'** was a coeluting mixture of **36'**, **36** (ca. 1:2) and an unidentifiable byproduct as a third component. The ratio of **36** and **36'** was ca. 5:1, as judged from analysis of the ^{1}H NMR spectrum of the crude mixture.

Data for **36**

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.70–7.66 (nfom, 2H, ≡CPhH_o), 7.65–7.62 (nfom, 2H, ≡CPhH_o), 7.50 (br t, J = 7.5 Hz, 2H, N–PhH_m), 7.45 (br d, J = 7.5 Hz, 2H, N–PhH_o), 7.42–7.37 (m, 4H, PhH_m and 2 PhH_p), 7.37–7.32 (m, 3H, PhH_m and PhH_p), 3.31 (t, J = 6.2 Hz, 2H, C6–H_2), 3.13 (t, J = 6.2 Hz, 2H, C9–H_2), 1.98–1.90 (nfom, 2H, CH$_2$CH_2), and 1.90–1.83 (nfom, 2H, CH$_2$CH_2).

^{13}C NMR (126 MHz, CDCl$_3$) δ 167.4, 166.0, 147.2, 138.0, 132.3, 132.0, 131.9, 131.7, 129.4, 129.22, 129.21, 128.8, 128.7, 128.5, 128.2, 127.3, 127.0, 123.0, 122.9, 120.2, 103.1, 100.1, 86.3, 84.6, 29.8, 26.2, 22.4, and 21.8.

IR (neat): 3060, 2936, 2868, 2204, 1713, 1597, 1492, 1405, 1374, 1359, 1116, 765, 698, and 624 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{34}H_{23}NNaO_2^+$ [M+Na$^+$] requires 500.1621; found 500.1612.

Mp: 252–255 °C.

^{1}H NMR data for **36'** (deduced from the mixture described above)

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.70–7.66 (m, 4H, ≡CPhH_o), 7.52–7.47 (m, 4H, ≡CPhH_m), 7.44–7.36 (m, 7H, N–PhH_5 and ≡CPhH_p), 3.16–3.10 (m, 4H, ArCH_2), and 1.97–1.90 (m, 4H, CH$_2$CH_2).

III. Computational methods and results

The DFT calculations were performed using Gaussian 09.[20] The geometry of each structure (including the transition structures) was optimized at the B3LYP[21]/6-31G(d) level of theory in the gas phase. The nature of the optimized structure was verified by frequency calculation (298K, at the same level of theory). Single point calculations were then performed at the B3LYP-D3BJ[22,23]/6-311+G(d,p) level of theory with SMD[24](chloroform) solvation model for each of the previously optimized geometries.

Energetics given in Figure 4 in the manuscript (and, in expanded form, in Figure S1 below)

For the benzocyclobutadiene (BCB) **10**, an initial Monte Carlo conformational search was performed using MacroModel (version 11.0, MMFF forcefield) and Maestro (version 10.4.017), implemented in the Schrödinger software suite. Each generated conformer was then subjected to a DFT geometry optimization, frequency calculation, and single point calculation sequence using the method described in the above paragraph. The free energy of each conformer was then used to determine the Boltzmann averaged free energy of BCB **10**. Averages due to rotameric populations in **7**, **TS1**, **S17**, and **TS2** (i.e., the species leading to **10**) were assumed to be sufficiently similar that they could be ignored.

Unrestricted (broken-symmetry) calculations were carried out for transition states, and intermediates along the reaction coordinate having diradical character. Energies on the singlet potential energy surface were corrected by spin purification of the mixed-spin-state energies.[25]

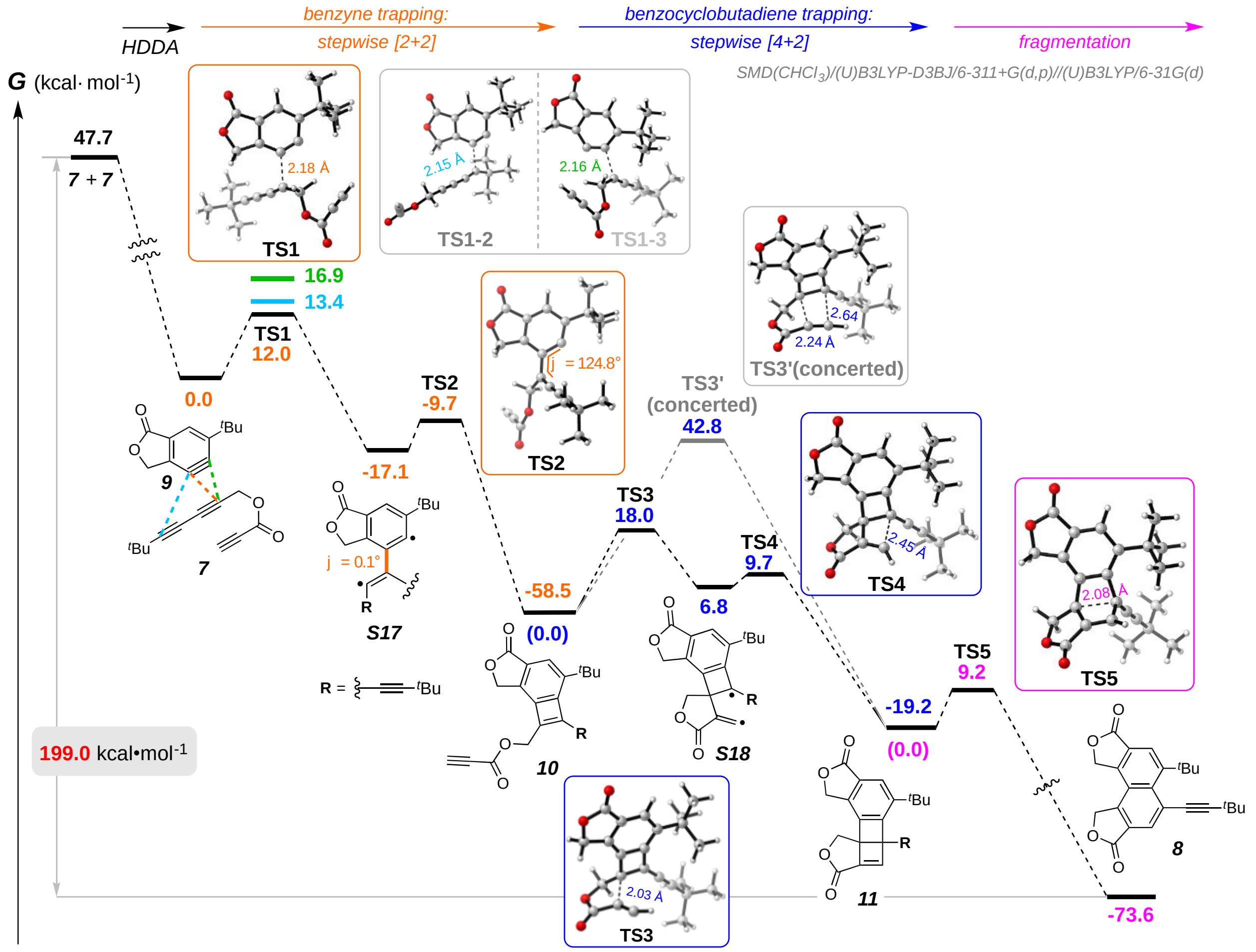


Figure S1. Calculated energy profile for the dimerization of 7 to 8.

Listed on the S46–S65 are the zero-point correction, thermal correction to Gibbs free energy, the sum of the electronic and thermal free energies, the Cartesian coordinates at B3LYP/6-31G(d), and electronic energy at SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p) for each intermediate and transition structure shown in Figure S1. For transition structures, the imaginary frequency values are included. The $<S^2>$ values and the corrected singlet energies ^1E for all of the open-shell calculations are also provided. Three dimensional views of all the transition structures were prepared using CYLview.[26]

7

Zero-point correction= 0.204648 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.157856
Sum of electronic and thermal Free Energies= -614.593669
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -614.9891592

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.283089	-0.345852	-0.001514
2	6	0	0.926645	-0.461455	-0.002045
3	6	0	-1.643111	-0.217463	-0.000678
4	6	0	-2.854628	-0.101905	0.000224
5	6	0	-4.317578	0.043624	0.000715
6	6	0	-4.884714	-0.495773	1.335988
7	1	0	-5.975956	-0.390629	1.345110
8	1	0	-4.639360	-1.554586	1.467969
9	1	0	-4.477501	0.058408	2.187785
10	6	0	-4.911310	-0.758636	-1.182252
11	1	0	-4.522065	-0.394283	-2.138429
12	1	0	-4.668156	-1.822767	-1.097160
13	1	0	-6.002626	-0.653591	-1.190754
14	6	0	-4.676358	1.541824	-0.151874
15	1	0	-5.766015	1.662738	-0.152561
16	1	0	-4.263966	2.130473	0.673832
17	1	0	-4.283424	1.946394	-1.090114
18	6	0	2.367685	-0.642028	-0.002541
19	1	0	2.690001	-1.204073	0.882658
20	1	0	2.689668	-1.202424	-0.888918
21	8	0	3.001341	0.663826	-0.001523
22	6	0	4.352092	0.750911	0.000293
23	8	0	4.896768	1.828805	0.000886
24	6	0	5.098425	-0.498528	0.001503
25	6	0	5.768834	-1.503950	0.002543
26	1	0	6.377169	-2.381328	0.003501

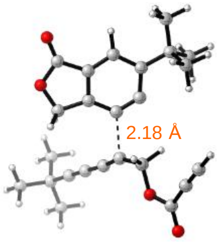
9

Zero-point correction= 0.210168 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.170825
Sum of electronic and thermal Free Energies= -614.672155
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -615.0781908

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.522604	-1.973863	0.000203
2	6	0	0.641608	-1.514846	0.000164
3	6	0	1.139201	-0.210987	0.000001
4	6	0	0.038819	0.680768	-0.000013
5	6	0	-1.285925	0.213879	0.000129
6	6	0	-1.633535	-1.145058	0.000138
7	6	0	-3.129624	-1.261731	-0.000066
8	1	0	-3.524579	-1.767049	-0.889272
9	1	0	-3.524881	-1.766995	0.889034
10	6	0	-2.545474	0.996500	0.000391
11	8	0	-3.594727	0.100286	-0.000185
12	8	0	-2.716815	2.188915	-0.000491
13	6	0	2.612870	0.171496	-0.000004
14	6	0	2.812260	1.696581	-0.000228

15	1	0	3.882334	1.930439	-0.000228
16	1	0	2.371449	2.163400	-0.888353
17	1	0	2.371395	2.163669	0.887729
18	6	0	3.273771	-0.433027	-1.260396
19	1	0	4.348636	-0.218094	-1.267318
20	1	0	3.143491	-1.520901	-1.287895
21	1	0	2.836071	-0.017676	-2.175036
22	6	0	3.273682	-0.432642	1.260622
23	1	0	4.348544	-0.217697	1.267563
24	1	0	2.835907	-0.017018	2.175102
25	1	0	3.143410	-1.520509	1.288440
26	1	0	0.210269	1.752410	-0.000010

TS1

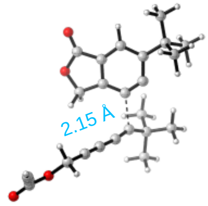


Imaginary frequency= -167.93 cm^{-1}
$\langle S^2 \rangle$=0.0000
Zero-point correction= 0.414787 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.348141
Sum of electronic and thermal Free Energies= -1229.243521
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.067694
E^1[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.067694

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.752523	1.078733	0.037958
2	6	0	-0.580917	1.408484	-0.178570
3	6	0	0.700573	-0.356549	-0.083437
4	6	0	1.830706	-0.248644	0.493334
5	6	0	0.236774	-1.481444	-0.736099
6	6	0	2.825539	-1.244742	0.540808
7	6	0	1.167635	-2.524916	-0.722814
8	6	0	-0.982775	-1.928867	-1.488203
9	6	0	2.426782	-2.430583	-0.109302
10	6	0	4.169234	-1.037562	1.237514
11	6	0	0.571879	-3.666022	-1.456287
12	1	0	-1.891102	-1.939100	-0.876002
13	1	0	-1.179804	-1.331633	-2.386054
14	8	0	-0.681166	-3.278461	-1.888276
15	1	0	3.081159	-3.295942	-0.140967
16	6	0	5.063709	-2.287786	1.169465
17	6	0	3.904750	-0.681502	2.717952
18	6	0	4.895723	0.143844	0.554534
19	8	0	1.019154	-4.761659	-1.684110
20	1	0	6.013583	-2.093308	1.679606
21	1	0	4.595225	-3.148724	1.659943
22	1	0	5.295014	-2.567352	0.135234
23	1	0	4.847331	-0.467003	3.235724
24	1	0	3.260226	0.200790	2.796507
25	1	0	3.409150	-1.508184	3.239673
26	1	0	5.841477	0.360451	1.065692

27	1	0	5.118688	-0.083225	-0.494526
28	1	0	4.276074	1.047359	0.580951
29	6	0	-2.985273	0.576756	0.285662
30	6	0	-4.101510	0.131070	0.505975
31	6	0	-5.446140	-0.387437	0.784208
32	6	0	-5.337507	-1.561425	1.788939
33	1	0	-6.339187	-1.947966	2.008901
34	1	0	-4.736353	-2.378918	1.378102
35	1	0	-4.878954	-1.235360	2.727786
36	6	0	-6.093787	-0.878663	-0.532981
37	1	0	-6.178049	-0.063080	-1.258177
38	1	0	-5.504750	-1.682342	-0.986511
39	1	0	-7.099213	-1.263308	-0.327448
40	6	0	-6.301007	0.749514	1.398910
41	1	0	-7.307573	0.372989	1.614104
42	1	0	-5.860508	1.112808	2.332614
43	1	0	-6.388677	1.594035	0.708224
44	6	0	0.455853	2.417168	-0.443262
45	1	0	1.233668	2.345350	0.325769
46	1	0	0.933479	2.232619	-1.412746
47	8	0	-0.163843	3.719387	-0.432191
48	6	0	0.598569	4.826996	-0.609104
49	8	0	0.091623	5.922547	-0.606477
50	6	0	2.025929	4.624249	-0.797748
51	6	0	3.217871	4.509236	-0.959745
52	1	0	4.272432	4.425092	-1.104223

TS1-2



Imaginary frequency= -577.18 cm^{-1}

<S^2>=0.0000

Zero-point correction= 0.413794 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.347213

Sum of electronic and thermal Free Energies= -1229.238523

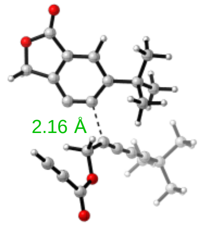
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.064515

E^1[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.064515

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.060459	1.119165	-0.424538
2	6	0	-3.104125	0.557467	-0.713015
3	6	0	1.362871	0.357515	0.186461
4	6	0	2.301814	0.196035	-0.664689
5	6	0	1.008975	-0.549971	1.166639
6	6	0	3.184577	-0.901642	-0.703760
7	6	0	1.830816	-1.680283	1.176771
8	6	0	-0.005015	-0.679498	2.266296
9	6	0	2.890369	-1.870899	0.276631
10	6	0	4.310501	-1.019178	-1.731214
11	6	0	1.365587	-2.564633	2.270376
12	1	0	0.075546	0.107597	3.025064
13	1	0	-1.038259	-0.702667	1.902301

14	8	0	0.294004	-1.945264	2.882628
15	1	0	3.464737	-2.789347	0.343869
16	6	0	5.090365	-2.339251	-1.597536
17	6	0	5.284750	0.164100	-1.530433
18	6	0	3.695755	-0.933978	-3.146420
19	8	0	1.779332	-3.637670	2.630908
20	1	0	5.884393	-2.379557	-2.351513
21	1	0	5.563961	-2.434781	-0.613682
22	1	0	4.443372	-3.210360	-1.751857
23	1	0	6.081544	0.136412	-2.283384
24	1	0	4.760252	1.121501	-1.623311
25	1	0	5.751108	0.128341	-0.539058
26	1	0	4.483869	-0.950512	-3.908860
27	1	0	3.021251	-1.777259	-3.334672
28	1	0	3.120389	-0.009471	-3.264380
29	6	0	-0.909085	1.752260	-0.097662
30	6	0	0.217739	2.175227	0.208007
31	6	0	1.119907	3.331607	0.520161
32	6	0	1.987752	3.646802	-0.718514
33	1	0	2.664166	4.477797	-0.487437
34	1	0	2.586209	2.778496	-1.009698
35	1	0	1.363125	3.935288	-1.570494
36	6	0	2.020876	3.045993	1.740290
37	1	0	1.424039	2.784519	2.621171
38	1	0	2.719904	2.230449	1.541299
39	1	0	2.599830	3.944841	1.979579
40	6	0	0.204673	4.540869	0.834290
41	1	0	0.820709	5.423370	1.042501
42	1	0	-0.450035	4.768178	-0.012571
43	1	0	-0.421855	4.343296	1.710132
44	6	0	-4.329608	-0.123261	-1.091202
45	1	0	-4.679241	0.228487	-2.070039
46	1	0	-4.159594	-1.204686	-1.168420
47	8	0	-5.336459	0.145692	-0.086677
48	6	0	-6.563983	-0.423434	-0.199967
49	8	0	-7.416631	-0.197173	0.622986
50	6	0	-6.784101	-1.298274	-1.339934
51	6	0	-7.019928	-2.033892	-2.269210
52	1	0	-7.247517	-2.687694	-3.082276

TS1-3



Imaginary frequency= -521.17 cm^{-1}
<S^2>=0.0000
Zero-point correction= 0.414510 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.349612
Sum of electronic and thermal Free Energies= -1229.232937
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.061401
E^1[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.061401

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-1.758584	0.528612	-0.276721
2	6	0	-0.674583	1.112340	-0.129930
3	6	0	1.588224	-0.127816	-1.261482
4	6	0	1.008566	-0.241151	-0.120946
5	6	0	2.800936	-0.753827	-1.503226
6	6	0	1.396401	-0.968594	1.025457
7	6	0	3.293448	-1.511206	-0.440344
8	6	0	3.763014	-0.865370	-2.652377
9	6	0	2.626872	-1.622010	0.784602
10	6	0	0.655425	-1.106309	2.364439
11	6	0	4.574285	-2.123402	-0.866368
12	1	0	3.321204	-1.330106	-3.541579
13	1	0	4.203354	0.094513	-2.946949
14	8	0	4.815186	-1.719748	-2.162895
15	1	0	3.083328	-2.226831	1.558878
16	6	0	1.511871	-1.845134	3.414375
17	6	0	-0.639352	-1.925431	2.148847
18	6	0	0.309408	0.283983	2.944379
19	8	0	5.330159	-2.844108	-0.264178
20	1	0	0.958549	-1.894022	4.358386
21	1	0	1.736553	-2.874546	3.115490
22	1	0	2.458056	-1.328087	3.609815
23	1	0	-1.175089	-2.036758	3.099598
24	1	0	-1.313139	-1.445901	1.435922
25	1	0	-0.405036	-2.927709	1.772538
26	1	0	-0.166733	0.168893	3.924985
27	1	0	1.213303	0.889521	3.080981
28	1	0	-0.386114	0.832226	2.305196
29	6	0	-2.875574	-0.216556	-0.430444
30	6	0	-3.892824	-0.878361	-0.577495
31	6	0	-5.120153	-1.662392	-0.757017
32	6	0	-5.150688	-2.248986	-2.189307
33	1	0	-6.067689	-2.832954	-2.328866
34	1	0	-5.130843	-1.453061	-2.940475
35	1	0	-4.293014	-2.906516	-2.363479
36	6	0	-6.342977	-0.735364	-0.541936
37	1	0	-6.339970	-0.306699	0.465134
38	1	0	-6.346386	0.086323	-1.264989
39	1	0	-7.265876	-1.312678	-0.670150
40	6	0	-5.144926	-2.810332	0.282527
41	1	0	-6.061132	-3.398295	0.155884

42	1	0	-4.286617	-3.477395	0.153490
43	1	0	-5.124990	-2.417295	1.303929
44	6	0	0.073025	2.382657	-0.115677
45	1	0	0.716184	2.451714	0.768020
46	1	0	0.715238	2.426561	-1.003292
47	8	0	-0.879209	3.467332	-0.124819
48	6	0	-0.441127	4.748711	-0.063288
49	8	0	-1.228564	5.663891	-0.076399
50	6	0	0.996219	4.954104	0.017301
51	6	0	2.181536	5.179374	0.083795
52	1	0	3.225623	5.394926	0.142886

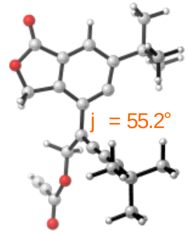
S17

<S^{2}>= 1.0410
Zero-point correction= 0.416278 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.349889
Sum of electronic and thermal Free Energies= -1229.293470
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.115290
E^{1}[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.115857

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	1.509882	-0.326835	0.002546
2	6	0	0.366933	0.349132	0.004701
3	6	0	-0.956360	-0.299200	0.003094
4	6	0	-2.144373	0.414993	0.003688
5	6	0	-1.161784	-1.697504	0.000518
6	6	0	-3.460009	-0.031515	0.002050
7	6	0	-2.446563	-2.218191	-0.000919
8	6	0	-0.193055	-2.850024	-0.000694
9	6	0	-3.600464	-1.429014	-0.000267
10	6	0	-4.630754	0.962439	0.002756
11	6	0	-2.355771	-3.696903	-0.003122
12	1	0	0.450898	-2.872229	-0.887013
13	1	0	0.449766	-2.874804	0.886382
14	8	0	-1.020810	-4.029265	-0.002932
15	1	0	-4.572959	-1.909998	-0.001557
16	6	0	-5.993083	0.248681	0.000855
17	6	0	-4.526370	1.852877	-1.256490
18	6	0	-4.528029	1.849367	1.264607
19	8	0	-3.233913	-4.522964	-0.004854
20	1	0	-6.798221	0.991861	0.001321
21	1	0	-6.123351	-0.379032	-0.887930
22	1	0	-6.124559	-0.381450	0.887747
23	1	0	-5.334128	2.594377	-1.267616
24	1	0	-3.570711	2.388430	-1.281930
25	1	0	-4.601230	1.254083	-2.171205
26	1	0	-5.335935	2.590689	1.276859
27	1	0	-4.603860	1.248003	2.177548
28	1	0	-3.572542	2.385085	1.292736
29	6	0	2.810711	-0.576498	0.001007
30	6	0	4.005962	-0.906072	-0.000060
31	6	0	5.445480	-1.188228	-0.005723
32	6	0	5.722902	-2.453770	-0.855085
33	1	0	6.799104	-2.662433	-0.864425
34	1	0	5.206619	-3.326811	-0.442673
35	1	0	5.390347	-2.314496	-1.888786
36	6	0	5.923084	-1.421715	1.449266
37	1	0	5.740073	-0.538079	2.068653

38	1	0	5.405126	-2.273213	1.902409
39	1	0	6.999227	-1.630359	1.453662
40	6	0	6.195340	0.024594	-0.613932
41	1	0	7.274159	-0.171529	-0.613731
42	1	0	5.877018	0.204560	-1.645614
43	1	0	6.006213	0.933847	-0.035216
44	6	0	0.330325	1.869890	0.006528
45	1	0	-0.194541	2.232547	-0.886280
46	1	0	-0.221485	2.229300	0.884348
47	8	0	1.672558	2.370005	0.028541
48	6	0	1.907864	3.701161	0.016835
49	8	0	3.039489	4.123568	0.039584
50	6	0	0.748444	4.579053	-0.023970
51	6	0	-0.174557	5.358336	-0.057169
52	1	0	-0.978159	6.060583	-0.086505

TS2



Imaginary frequency= -8.13 cm^{-1}
<S^2>= 1.0319
Zero-point correction= 0.416306 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.352609
Sum of electronic and thermal Free Energies= -1229.280728
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.106378
E^1[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.106727

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.566029	0.125173	0.043047
2	6	0	-0.492259	0.868566	-0.135079
3	6	0	0.887545	0.299858	0.024006
4	6	0	1.310214	-0.811161	-0.678675
5	6	0	1.869881	0.809750	0.898815
6	6	0	2.530526	-1.477202	-0.650315
7	6	0	3.110073	0.188907	0.992132
8	6	0	1.854481	1.946742	1.892901
9	6	0	3.467889	-0.934170	0.243348
10	6	0	2.779815	-2.702642	-1.540347
11	6	0	3.918804	0.891844	2.012978
12	1	0	1.732217	2.935166	1.434677
13	1	0	1.083358	1.827646	2.663218
14	8	0	3.145479	1.912550	2.523312
15	1	0	4.455360	-1.365207	0.373218
16	6	0	4.185644	-3.290345	-1.331482
17	6	0	2.622668	-2.279235	-3.018778
18	6	0	1.724767	-3.780972	-1.203513
19	8	0	5.042810	0.678637	2.391136
20	1	0	4.320145	-4.162004	-1.981425
21	1	0	4.971540	-2.568272	-1.580961
22	1	0	4.339876	-3.621389	-0.298123
23	1	0	2.767785	-3.141814	-3.680082

24	1	0	1.624077	-1.869528	-3.206699
25	1	0	3.359014	-1.514423	-3.291033
26	1	0	1.856268	-4.657730	-1.848826
27	1	0	1.814202	-4.108554	-0.161503
28	1	0	0.709325	-3.396922	-1.350157
29	6	0	-2.533383	-0.737733	0.286285
30	6	0	-3.462164	-1.529287	0.511005
31	6	0	-4.589685	-2.431410	0.771366
32	6	0	-4.637253	-2.759662	2.284515
33	1	0	-5.478457	-3.432206	2.489465
34	1	0	-3.714807	-3.251587	2.609558
35	1	0	-4.769616	-1.850562	2.879755
36	6	0	-4.400233	-3.737820	-0.039190
37	1	0	-5.240637	-4.415717	0.150743
38	1	0	-4.360630	-3.531044	-1.113536
39	1	0	-3.474357	-4.247222	0.246869
40	6	0	-5.911395	-1.742111	0.346227
41	1	0	-6.067781	-0.814685	0.906026
42	1	0	-5.901361	-1.499190	-0.721066
43	1	0	-6.757784	-2.411640	0.540768
44	6	0	-0.565426	2.314248	-0.590041
45	1	0	0.033400	2.965973	0.057649
46	1	0	-0.158580	2.405104	-1.606001
47	8	0	-1.935480	2.736779	-0.568611
48	6	0	-2.272607	3.982208	-0.977440
49	8	0	-3.425939	4.339797	-0.966139
50	6	0	-1.191105	4.849890	-1.418676
51	6	0	-0.335023	5.616192	-1.793391
52	1	0	0.408012	6.305935	-2.128292

10-confomer1

Zero-point correction= 0.420271 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.357918
Sum of electronic and thermal Free Energies= -1229.363240
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.189851
Boltzmann%= 31.6%

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.026095	-0.966685	-0.110637
2	6	0	1.148179	-0.187971	-0.296709
3	6	0	2.378706	-0.769464	-0.302776
4	6	0	2.391348	-2.176491	-0.118944
5	6	0	1.254942	-2.938768	0.053504
6	6	0	-0.048561	-2.334873	0.063254
7	1	0	1.371495	-4.008197	0.187151
8	6	0	-0.844898	0.346764	-0.200037
9	6	0	0.307376	1.060392	-0.382332
10	6	0	-2.202006	0.691206	-0.132913
11	6	0	-3.382805	0.982107	-0.070497
12	6	0	-4.806648	1.345158	0.008688
13	6	0	-5.240466	1.376061	1.494900
14	1	0	-6.300929	1.645047	1.565846
15	1	0	-5.101000	0.397603	1.965781
16	1	0	-4.659587	2.113067	2.058770
17	6	0	-5.013460	2.741633	-0.624571
18	1	0	-4.710916	2.744970	-1.676791
19	1	0	-6.071904	3.021181	-0.569831
20	1	0	-4.429199	3.503042	-0.097615

```
    21          6           0       -5.645195    0.293666   -0.757099
    22          1           0       -5.355813    0.252637   -1.812193
    23          1           0       -5.512586   -0.704184   -0.326687
    24          1           0       -6.708343    0.555048   -0.701162
    25          6           0        3.804213   -0.309188   -0.439475
    26          1           0        4.022625    0.149766   -1.410830
    27          1           0        4.108043    0.389997    0.347784
    28          8           0        4.592936   -1.510486   -0.320279
    29          6           0        3.800061   -2.625606   -0.135584
    30          8           0        4.264848   -3.732236   -0.016621
    31          6           0        0.614808    2.486334   -0.632234
    32          1           0        0.851145    2.678728   -1.687161
    33          1           0       -0.222314    3.135139   -0.356923
    34          8           0        1.783902    2.819641    0.161291
    35          6           0        2.260292    4.070791   -0.023224
    36          8           0        1.769289    4.891250   -0.767469
    37          6           0        3.439397    4.295561    0.786991
    38          6           0        4.427003    4.525175    1.441931
    39          1           0        5.300141    4.730629    2.020828
    40          6           0       -1.339414   -3.146012    0.253997
    41          6           0       -1.059407   -4.653288    0.406524
    42          1           0       -0.559109   -5.068353   -0.475758
    43          1           0       -0.439911   -4.869158    1.284363
    44          1           0       -2.006474   -5.189766    0.531766
    45          6           0       -2.066804   -2.652721    1.526887
    46          1           0       -1.437074   -2.783527    2.414330
    47          1           0       -2.335009   -1.594256    1.453021
    48          1           0       -2.990585   -3.224327    1.680234
    49          6           0       -2.255291   -2.942170   -0.975526
    50          1           0       -2.527046   -1.890173   -1.106103
    51          1           0       -1.762804   -3.283470   -1.893261
    52          1           0       -3.182299   -3.516449   -0.855653
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```

10-confomer2

Zero-point correction= 0.420797 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.359874
Sum of electronic and thermal Free Energies= -1229.363185
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.191283
Boltzmann%= 21.0%

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0        1.999484    3.618064    0.112757
      2          8           0        0.667214    3.460116    0.014761
      3          6           0        2.336385    4.524007    1.190302
      4          8           0        2.820971    3.081287   -0.604245
      5          6           0        0.203060    2.582063   -1.059619
      6          6           0        0.173075    1.156380   -0.651294
      7          6           0       -0.863183    0.317214   -0.343061
      8          6           0       -2.254158    0.481580   -0.284805
      9          6           0       -3.462954    0.618588   -0.229707
     10          6           0       -4.921312    0.801239   -0.160986
     11          6           0       -5.264646    1.674390    1.071004
     12          6           0       -5.406112    1.506734   -1.450785
     13          6           0       -5.607009   -0.579121   -0.030150
     14          6           0        2.670068    5.271584    2.077247
     15          6           0        0.125066   -0.848990   -0.122027
     16          6           0        1.184128    0.045274   -0.442351
     17          6           0        2.477224   -0.388469   -0.454918
```

18	6	0	2.663092	-1.757315	-0.124228
19	6	0	1.639083	-2.624855	0.190476
20	6	0	0.274163	-2.181979	0.199366
21	6	0	4.110722	-2.054500	-0.195062
22	8	0	4.756892	-0.897258	-0.561015
23	6	0	3.834051	0.200025	-0.738578
24	6	0	-0.901100	-3.115514	0.527628
25	6	0	-0.430518	-4.544894	0.857948
26	6	0	-1.667850	-2.561333	1.751208
27	6	0	-1.850028	-3.186324	-0.691824
28	8	0	4.698494	-3.088779	0.010212
29	1	0	-0.809391	2.932855	-1.265800
30	1	0	0.843291	2.740963	-1.931397
31	1	0	-6.349721	1.819185	1.130573
32	1	0	-4.929135	1.196602	1.997063
33	1	0	-4.788494	2.657768	1.001531
34	1	0	-6.492009	1.650921	-1.408733
35	1	0	-4.933211	2.487755	-1.564029
36	1	0	-5.172382	0.908793	-2.337615
37	1	0	-6.694237	-0.449770	0.022922
38	1	0	-5.377655	-1.215531	-0.890961
39	1	0	-5.276911	-1.097274	0.875961
40	1	0	2.965700	5.932038	2.862064
41	1	0	1.892912	-3.651782	0.426978
42	1	0	4.111535	1.005242	-0.053257
43	1	0	3.938278	0.578319	-1.760753
44	1	0	-1.300325	-5.171730	1.083998
45	1	0	0.099046	-5.007062	0.017205
46	1	0	0.229596	-4.567931	1.732412
47	1	0	-2.507976	-3.220965	2.001785
48	1	0	-1.013621	-2.499503	2.628386
49	1	0	-2.071187	-1.562753	1.557499
50	1	0	-2.695199	-3.851767	-0.476102
51	1	0	-2.254408	-2.202018	-0.946769
52	1	0	-1.327443	-3.578389	-1.571900

10-confomer3

Zero-point correction= 0.420440 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.357948
Sum of electronic and thermal Free Energies= -1229.362687
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.190068
Boltzmann%= 36.6%

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.911867	-3.845899	0.531780
2	8	0	-1.215669	-3.276777	-0.660241
3	6	0	-2.076186	-4.504248	1.087476
4	8	0	0.176700	-3.817257	1.059955
5	6	0	-0.144295	-2.528127	-1.297395
6	6	0	-0.141676	-1.122051	-0.824392
7	6	0	0.825511	-0.223338	-0.466536
8	6	0	2.222336	-0.282295	-0.373955
9	6	0	3.435794	-0.329307	-0.285632
10	6	0	4.899868	-0.412627	-0.167642
11	6	0	5.258881	-1.057496	1.194049
12	6	0	5.455163	-1.284363	-1.319501
13	6	0	5.504662	1.009011	-0.247999
14	6	0	-3.020764	-5.061376	1.592078

15	6	0	-0.258513	0.856888	-0.219817
16	6	0	-1.233762	-0.108184	-0.590552
17	6	0	-2.560040	0.197281	-0.575451
18	6	0	-2.879188	1.521303	-0.176347
19	6	0	-1.937019	2.464475	0.177210
20	6	0	-0.534674	2.151736	0.167163
21	6	0	-4.350713	1.662948	-0.203303
22	8	0	-4.880854	0.452215	-0.602890
23	6	0	-3.849908	-0.522378	-0.860938
24	6	0	0.546813	3.170353	0.559416
25	6	0	1.333538	2.632484	1.777738
26	6	0	1.512833	3.371842	-0.631668
27	6	0	-0.054654	4.538224	0.933988
28	8	0	-5.045719	2.613381	0.058456
29	1	0	0.816912	-3.010427	-1.107394
30	1	0	-0.385608	-2.592762	-2.364049
31	1	0	6.348325	-1.131889	1.292295
32	1	0	4.877514	-0.456415	2.025688
33	1	0	4.834511	-2.063033	1.277133
34	1	0	6.545588	-1.359299	-1.235549
35	1	0	5.037198	-2.295663	-1.283290
36	1	0	5.214292	-0.848287	-2.294587
37	1	0	6.595424	0.953854	-0.154304
38	1	0	5.264923	1.485214	-1.204321
39	1	0	5.121551	1.644898	0.556578
40	1	0	-3.853805	-5.554789	2.041735
41	1	0	-2.282885	3.449312	0.469402
42	1	0	-4.013887	-1.387765	-0.208693
43	1	0	-3.943346	-0.854258	-1.901543
44	1	0	2.109942	3.349210	2.072966
45	1	0	0.670202	2.479781	2.636709
46	1	0	1.822884	1.679903	1.553028
47	1	0	2.289091	4.101260	-0.369665
48	1	0	2.010973	2.437896	-0.909759
49	1	0	0.978483	3.748401	-1.511462
50	1	0	0.751144	5.231105	1.200568
51	1	0	-0.610710	4.983730	0.101267
52	1	0	-0.727233	4.468403	1.796378

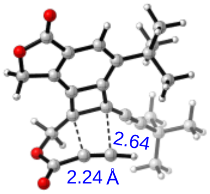
10-confomer4

Zero-point correction= 0.420194 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.358126
Sum of electronic and thermal Free Energies= -1229.360700
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.188685
Boltzmann%= 10.8%

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.001530	-3.369237	-0.000100
2	8	0	2.180411	-2.298646	-0.000039
3	6	0	4.389730	-2.953595	-0.000420
4	8	0	2.630518	-4.522753	0.000097
5	6	0	0.774888	-2.605044	0.000259
6	6	0	0.013914	-1.333846	0.000156
7	6	0	0.320662	-0.000858	0.000092
8	6	0	1.513289	0.735037	0.000118
9	6	0	2.543431	1.382656	0.000155
10	6	0	3.826430	2.102136	0.000198
11	6	0	4.624951	1.701402	1.264979

12	6	0	4.625326	1.700846	-1.264168
13	6	0	3.573451	3.627329	-0.000170
14	6	0	5.561870	-2.664135	-0.000681
15	6	0	-1.186238	0.353588	0.000001
16	6	0	-1.468184	-1.040260	0.000074
17	6	0	-2.753164	-1.492502	0.000103
18	6	0	-3.755513	-0.486319	0.000017
19	6	0	-3.486868	0.865951	-0.000076
20	6	0	-2.136021	1.353569	-0.000086
21	6	0	-5.074374	-1.152395	0.000015
22	8	0	-4.854599	-2.516508	0.000086
23	6	0	-3.448646	-2.828745	0.000170
24	6	0	-1.792804	2.851585	-0.000176
25	6	0	-3.055339	3.734432	-0.000375
26	6	0	-0.965154	3.184276	1.263626
27	6	0	-0.964921	3.184084	-1.263879
28	8	0	-6.184605	-0.681847	-0.000045
29	1	0	0.533274	-3.218350	-0.879175
30	1	0	0.533592	-3.218022	0.880014
31	1	0	5.591897	2.218522	1.272481
32	1	0	4.081657	1.974055	2.175576
33	1	0	4.806954	0.622020	1.284862
34	1	0	5.592306	2.217905	-1.271579
35	1	0	4.807261	0.621443	-1.283559
36	1	0	4.082332	1.973165	-2.175044
37	1	0	4.529768	4.163332	-0.000145
38	1	0	3.008538	3.932311	-0.887196
39	1	0	3.008276	3.932694	0.886557
40	1	0	6.601140	-2.420186	-0.000909
41	1	0	-4.324819	1.553436	-0.000146
42	1	0	-3.230614	-3.432794	0.889015
43	1	0	-3.230533	-3.432931	-0.888561
44	1	0	-2.762294	4.790113	-0.000455
45	1	0	-3.674542	3.564090	-0.888371
46	1	0	-3.674700	3.564275	0.887546
47	1	0	-0.714384	4.252154	1.280506
48	1	0	-1.530855	2.955562	2.174181
49	1	0	-0.028580	2.619254	1.292954
50	1	0	-0.714151	4.251961	-1.280869
51	1	0	-0.028338	2.619067	-1.292962
52	1	0	-1.530457	2.955237	-2.174501

TS3-concerted



Imaginary frequency= -317.17 cm^{-1}

Zero-point correction= 0.418109 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.358838

Sum of electronic and thermal Free Energies= -1229.285602

E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.122314

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.396489	-0.547126	-0.108744

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      2          6           0        1.276420    0.586559   -0.501378
      3          6           0        2.680968    0.387010   -0.579753
      4          6           0        3.115319   -0.876057   -0.305924
      5          6           0        2.269544   -1.991573    0.065735
      6          6           0        0.907698   -1.874658    0.183212
      7          1           0        2.774444   -2.932306    0.251545
      8          6           0       -0.741911    0.236792   -0.190237
      9          6           0        0.235079    1.481558   -0.578105
     10          6           0       -0.077522    2.484444    1.397200
     11          6           0       -0.773614    1.687470    2.018081
     12          6           0        0.627275    3.694958    0.974957
     13          8           0        1.136117    4.489282    1.727697
     14          8           0        0.684086    3.863163   -0.371588
     15          6           0        0.017392    2.836973   -1.156643
     16          1           0        0.442069    2.953677   -2.158691
     17          1           0       -1.054834    3.057417   -1.203729
     18          1           0       -1.396598    1.075898    2.631890
     19          6           0       -2.122496    0.092664   -0.272194
     20          6           0       -3.339210    0.031873   -0.367156
     21          6           0       -4.802059   -0.058510   -0.494811
     22          6           0       -5.444886    1.247409    0.031504
     23          1           0       -6.535810    1.189796   -0.059873
     24          1           0       -5.196178    1.411428    1.085103
     25          1           0       -5.097833    2.114557   -0.539958
     26          6           0       -5.312610   -1.262476    0.332723
     27          1           0       -6.402152   -1.341132    0.241613
     28          1           0       -4.869050   -2.198799   -0.021190
     29          1           0       -5.063908   -1.145265    1.392592
     30          6           0       -5.175754   -0.257183   -1.985017
     31          1           0       -4.821743    0.581514   -2.593299
     32          1           0       -4.733790   -1.177162   -2.380939
     33          1           0       -6.265131   -0.323574   -2.090507
     34          6           0       -0.013354   -3.033132    0.572624
     35          6           0        0.775596   -4.315970    0.893279
     36          1           0        0.077761   -5.112187    1.174751
     37          1           0        1.348264   -4.670625    0.029145
     38          1           0        1.469096   -4.171158    1.729263
     39          6           0       -0.833100   -2.639893    1.825146
     40          1           0       -0.172408   -2.427680    2.673627
     41          1           0       -1.455533   -1.758930    1.644187
     42          1           0       -1.495753   -3.465421    2.110730
     43          6           0       -0.974523   -3.331549   -0.603958
     44          1           0       -0.414924   -3.625818   -1.499157
     45          1           0       -1.644229   -4.158015   -0.336722
     46          1           0       -1.592910   -2.465313   -0.855939
     47          6           0        4.588539   -0.900970   -0.445557
     48          6           0        3.864449    1.251135   -0.903826
     49          1           0        3.834876    1.663057   -1.919932
     50          1           0        3.996030    2.082813   -0.201206
     51          8           0        4.994386    0.370357   -0.797879
     52          8           0        5.361394   -1.814709   -0.297013
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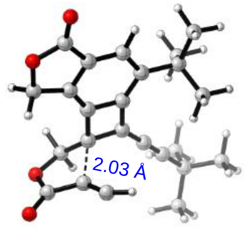
TS3



Imaginary frequency= -722.46 cm^{-1}
<S^2>= 0.4801
Zero-point correction= 0.417976 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.357844
Sum of electronic and thermal Free Energies= -1229.324080
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.155231
E^1[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.160849

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	0.411924	-0.622501	-0.108599
2	6	0	1.282221	0.477296	-0.328036
3	6	0	2.638139	0.309007	-0.368432
4	6	0	3.089554	-1.013762	-0.176170
5	6	0	2.249666	-2.098392	0.040434
6	6	0	0.838831	-1.941178	0.082163
7	1	0	2.706307	-3.071684	0.178701
8	6	0	-0.763655	0.293263	-0.227089
9	6	0	0.095981	1.431928	-0.378678
10	6	0	0.337990	2.661594	1.217767
11	6	0	0.272067	2.274664	2.403454
12	6	0	0.699572	3.888703	0.458586
13	8	0	1.154081	4.890210	0.948976
14	8	0	0.504673	3.782314	-0.877076
15	6	0	-0.169815	2.586724	-1.298901
16	1	0	0.198422	2.380897	-2.309809
17	1	0	-1.247608	2.780585	-1.347907
18	1	0	0.089603	1.577620	3.195896
19	6	0	-2.147728	0.172039	-0.217321
20	6	0	-3.367725	0.088909	-0.211587
21	6	0	-4.835437	-0.007040	-0.212130
22	6	0	-5.430746	1.294530	0.377005
23	1	0	-6.525206	1.234473	0.376331
24	1	0	-5.094920	1.450005	1.407318
25	1	0	-5.133822	2.166402	-0.214928
26	6	0	-5.271324	-1.218968	0.645647
27	1	0	-6.364480	-1.299163	0.645861
28	1	0	-4.857825	-2.151309	0.247718
29	1	0	-4.934329	-1.109116	1.681468
30	6	0	-5.330931	-0.194063	-1.668161
31	1	0	-5.034727	0.652301	-2.296284
32	1	0	-4.921280	-1.108628	-2.108955
33	1	0	-6.424787	-0.265525	-1.679741
34	6	0	-0.124068	-3.114785	0.305796
35	6	0	0.623946	-4.445685	0.511659
36	1	0	-0.101397	-5.250198	0.675409
37	1	0	1.225770	-4.717699	-0.362756
38	1	0	1.284152	-4.413750	1.385742
39	6	0	-0.980288	-2.838751	1.564577
40	1	0	-0.347199	-2.738900	2.453831

41	1	0	-1.571086	-1.923621	1.461013
42	1	0	-1.675680	-3.669210	1.737058
43	6	0	-1.046604	-3.261071	-0.927948
44	1	0	-0.461242	-3.458456	-1.833253
45	1	0	-1.738257	-4.100121	-0.783313
46	1	0	-1.643432	-2.359831	-1.097498
47	6	0	4.567356	-1.008797	-0.241764
48	6	0	3.846048	1.187779	-0.555629
49	1	0	3.877539	1.685970	-1.531238
50	1	0	3.948225	1.950768	0.224662
51	8	0	4.970583	0.290602	-0.467864
52	8	0	5.350343	-1.919435	-0.132185

S18

<S^2>= 1.0377

Zero-point correction= 0.420623 (Hartree/Particle)

Thermal correction to Gibbs Free Energy= 0.360407

Sum of electronic and thermal Free Energies= -1229.349358

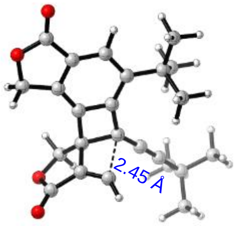
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.181210

E^1[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.181302

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.462327	-0.591819	-0.068532
2	6	0	1.302256	0.549303	-0.143521
3	6	0	2.670734	0.434438	-0.123466
4	6	0	3.163376	-0.874044	-0.035414
5	6	0	2.352176	-2.014735	0.032752
6	6	0	0.952690	-1.923707	0.019477
7	1	0	2.848903	-2.976124	0.098612
8	6	0	-0.732421	0.225444	-0.119581
9	6	0	0.112239	1.516438	-0.213144
10	6	0	0.024860	2.595259	0.868258
11	6	0	-0.276265	2.473399	2.138761
12	6	0	0.364111	3.904561	0.203139
13	8	0	0.588866	4.974771	0.700680
14	8	0	0.410912	3.695995	-1.149686
15	6	0	-0.047799	2.375046	-1.484552
16	1	0	0.546897	2.011791	-2.325129
17	1	0	-1.101899	2.431120	-1.780162
18	1	0	-0.559519	1.689555	2.827858
19	6	0	-2.101132	0.060306	-0.103057
20	6	0	-3.324838	-0.031186	-0.091905
21	6	0	-4.790256	-0.154831	-0.075487
22	6	0	-5.422060	1.257669	-0.090994
23	1	0	-6.514888	1.174696	-0.077380
24	1	0	-5.110034	1.838661	0.782897
25	1	0	-5.130600	1.809725	-0.990491
26	6	0	-5.224676	-0.908037	1.206224
27	1	0	-6.316095	-1.008651	1.224514
28	1	0	-4.785773	-1.910422	1.241014
29	1	0	-4.914148	-0.365996	2.105265
30	6	0	-5.250195	-0.947638	-1.324153
31	1	0	-4.957059	-0.434892	-2.245945
32	1	0	-4.812421	-1.951071	-1.335855
33	1	0	-6.341833	-1.047577	-1.317765
34	6	0	0.032855	-3.147303	0.096097
35	6	0	0.827570	-4.464238	0.177612
36	1	0	0.130459	-5.307775	0.228346

37	1	0	1.463331	-4.614528	-0.702174
38	1	0	1.461592	-4.506361	1.070396
39	6	0	-0.857427	-3.038212	1.357563
40	1	0	-0.245787	-3.010507	2.266606
41	1	0	-1.483190	-2.141186	1.338456
42	1	0	-1.521083	-3.908859	1.423592
43	6	0	-0.859717	-3.195729	-1.167426
44	1	0	-0.249950	-3.285333	-2.073703
45	1	0	-1.526513	-4.065348	-1.121821
46	1	0	-1.482555	-2.301422	-1.261397
47	6	0	4.640733	-0.812230	-0.026584
48	6	0	3.846397	1.373862	-0.167138
49	1	0	3.898784	1.963251	-1.089617
50	1	0	3.878928	2.063534	0.684043
51	8	0	5.002181	0.516816	-0.106650
52	8	0	5.451945	-1.702377	0.035690

TS4



Imaginary frequency= -393.81 cm^{-1}
<S^{2}>= 0.5324
Zero-point correction= 0.420596 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.363541
Sum of electronic and thermal Free Energies= -1229.336660
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.172887
E^{1}[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.179901

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.498478	-0.521455	0.056696
2	6	0	1.300129	0.610385	-0.230105
3	6	0	2.665681	0.490428	-0.391705
4	6	0	3.175402	-0.801905	-0.265503
5	6	0	2.396182	-1.932250	0.025089
6	6	0	1.011069	-1.838586	0.207762
7	1	0	2.908897	-2.883962	0.105931
8	6	0	-0.717561	0.280289	0.097025
9	6	0	0.129919	1.576201	-0.164891
10	6	0	-0.032408	2.383865	1.091497
11	6	0	-0.609481	1.725902	2.077052
12	6	0	0.226088	3.817036	0.765450
13	8	0	0.392598	4.773871	1.474222
14	8	0	0.239010	3.903858	-0.611195
15	6	0	-0.120781	2.644310	-1.236020
16	1	0	0.491206	2.538676	-2.134028
17	1	0	-1.179030	2.681105	-1.519074
18	1	0	-1.021672	1.959823	3.052478
19	6	0	-2.075698	0.055953	-0.097552
20	6	0	-3.274366	-0.096146	-0.284120
21	6	0	-4.717758	-0.276578	-0.502679
22	6	0	-5.497124	0.704040	0.407509

23	1	0	-6.574609	0.580658	0.247461
24	1	0	-5.281923	0.514936	1.464112
25	1	0	-5.232711	1.742845	0.184968
26	6	0	-5.110169	-1.733230	-0.159041
27	1	0	-6.185313	-1.874543	-0.318566
28	1	0	-4.571642	-2.445924	-0.792071
29	1	0	-4.884165	-1.964820	0.886813
30	6	0	-5.049085	0.016817	-1.987003
31	1	0	-4.778395	1.043203	-2.255428
32	1	0	-4.510982	-0.665509	-2.652971
33	1	0	-6.124296	-0.111082	-2.157646
34	6	0	0.125652	-3.048623	0.526451
35	6	0	0.954852	-4.326707	0.755861
36	1	0	0.282927	-5.156383	1.001343
37	1	0	1.520379	-4.616521	-0.136794
38	1	0	1.659494	-4.213369	1.587463
39	6	0	-0.692232	-2.765866	1.808680
40	1	0	-0.030034	-2.603893	2.666779
41	1	0	-1.331097	-1.884819	1.703026
42	1	0	-1.336829	-3.623260	2.035889
43	6	0	-0.833812	-3.298987	-0.662478
44	1	0	-0.272500	-3.517880	-1.578100
45	1	0	-1.478531	-4.159781	-0.447095
46	1	0	-1.477526	-2.435647	-0.854019
47	6	0	4.639550	-0.745336	-0.479353
48	6	0	3.811833	1.420947	-0.684685
49	1	0	3.724015	1.930552	-1.651170
50	1	0	3.961223	2.179644	0.092152
51	8	0	4.972733	0.570429	-0.723109
52	8	0	5.457778	-1.630291	-0.461802

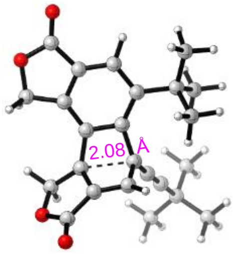
11

Zero-point correction= 0.424415 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.366904
Sum of electronic and thermal Free Energies= -1229.389147
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.229237

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.512929	-0.406324	0.300365
2	6	0	1.212227	0.677595	-0.246707
3	6	0	2.520394	0.527246	-0.674065
4	6	0	3.062549	-0.748635	-0.524413
5	6	0	2.376242	-1.828589	0.034717
6	6	0	1.049349	-1.691647	0.488435
7	1	0	2.901117	-2.774410	0.109231
8	6	0	-0.755053	0.439247	0.560689
9	6	0	0.093881	1.674462	-0.038711
10	6	0	-0.068616	2.275282	1.342224
11	6	0	-0.760039	1.262118	1.882414
12	6	0	0.092808	3.743473	1.277035
13	8	0	0.243933	4.584250	2.123239
14	8	0	0.010009	4.043054	-0.069898
15	6	0	-0.292851	2.872004	-0.893984
16	1	0	0.282562	2.978825	-1.815710
17	1	0	-1.363110	2.878733	-1.128290
18	1	0	-1.250340	1.087512	2.833743
19	6	0	-2.042718	0.091500	0.011844
20	6	0	-3.138828	-0.160409	-0.442940

21	6	0	-4.468329	-0.469871	-1.000127
22	6	0	-5.118292	-1.603942	-0.172417
23	1	0	-6.108223	-1.842071	-0.578878
24	1	0	-4.507264	-2.512053	-0.201772
25	1	0	-5.238858	-1.306754	0.874505
26	6	0	-4.314617	-0.920409	-2.471929
27	1	0	-5.298599	-1.151282	-2.896459
28	1	0	-3.855093	-0.132726	-3.078098
29	1	0	-3.689304	-1.816168	-2.546125
30	6	0	-5.354775	0.796426	-0.932519
31	1	0	-5.476071	1.137221	0.100888
32	1	0	-4.916440	1.615094	-1.512938
33	1	0	-6.347909	0.578415	-1.342341
34	6	0	0.257079	-2.868707	1.077306
35	6	0	1.185065	-4.015953	1.524981
36	1	0	0.587729	-4.804498	1.995618
37	1	0	1.716054	-4.472547	0.683032
38	1	0	1.928235	-3.676068	2.255334
39	6	0	-0.560092	-2.405186	2.304183
40	1	0	0.088920	-1.971570	3.073889
41	1	0	-1.319865	-1.666187	2.033377
42	1	0	-1.082875	-3.260414	2.748011
43	6	0	-0.707895	-3.408129	-0.006924
44	1	0	-0.152639	-3.761692	-0.883116
45	1	0	-1.287552	-4.250906	0.389650
46	1	0	-1.409258	-2.634895	-0.335614
47	6	0	4.451954	-0.725863	-1.040344
48	6	0	3.568129	1.412191	-1.293779
49	1	0	3.274909	1.817221	-2.269470
50	1	0	3.865692	2.248045	-0.649745
51	8	0	4.708231	0.554568	-1.483841
52	8	0	5.269724	-1.608634	-1.100842

TS5



Imaginary frequency= -728.26 cm^{-1}
<S^2>= 0.0000
Zero-point correction= 0.421313 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.363305
Sum of electronic and thermal Free Energies= -1229.372004
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.210948
E^1[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.210948

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.531054	-0.405123	0.453683
2	6	0	1.019103	0.769499	-0.156840
3	6	0	2.268622	0.727994	-0.773812
4	6	0	2.997347	-0.451437	-0.657327
5	6	0	2.548718	-1.577625	0.032197

6	6	0	1.274224	-1.583975	0.629481
7	1	0	3.195300	-2.446249	0.068818
8	6	0	-0.845800	0.092070	0.812611
9	6	0	0.020572	1.835353	0.068037
10	6	0	-0.493452	2.132884	1.403431
11	6	0	-0.904527	0.997175	2.012623
12	6	0	-0.593668	3.604315	1.561358
13	8	0	-0.832064	4.284075	2.525543
14	8	0	-0.388128	4.139298	0.306211
15	6	0	-0.159291	3.117460	-0.700488
16	1	0	0.725780	3.410500	-1.276605
17	1	0	-1.023531	3.111564	-1.378025
18	1	0	-1.050193	0.736348	3.053580
19	6	0	-1.986376	-0.175007	0.040047
20	6	0	-2.997273	-0.481118	-0.570500
21	6	0	-4.220869	-0.823319	-1.311412
22	6	0	-5.338831	-1.200531	-0.309210
23	1	0	-6.258133	-1.447389	-0.853035
24	1	0	-5.051231	-2.069393	0.291777
25	1	0	-5.553413	-0.370024	0.371042
26	6	0	-3.936085	-2.015808	-2.254473
27	1	0	-4.843191	-2.271822	-2.814064
28	1	0	-3.146452	-1.769800	-2.971789
29	1	0	-3.621075	-2.898887	-1.688910
30	6	0	-4.663994	0.406060	-2.144182
31	1	0	-4.868312	1.265845	-1.498088
32	1	0	-3.890370	0.692377	-2.864057
33	1	0	-5.578737	0.165963	-2.698656
34	6	0	0.707594	-2.828697	1.333324
35	6	0	1.820487	-3.828811	1.707382
36	1	0	1.387231	-4.663998	2.268676
37	1	0	2.310953	-4.253277	0.825135
38	1	0	2.588983	-3.364797	2.336025
39	6	0	-0.025827	-2.427047	2.631753
40	1	0	0.638870	-1.886665	3.315200
41	1	0	-0.900204	-1.798685	2.430937
42	1	0	-0.387878	-3.322671	3.149411
43	6	0	-0.288754	-3.533362	0.380032
44	1	0	0.209722	-3.844567	-0.544804
45	1	0	-0.701406	-4.428884	0.860787
46	1	0	-1.122409	-2.876739	0.111153
47	6	0	4.288111	-0.275584	-1.363498
48	6	0	3.091250	1.706186	-1.570821
49	1	0	2.615994	2.012852	-2.510555
50	1	0	3.356335	2.609504	-1.007834
51	8	0	4.302342	0.999028	-1.889767
52	8	0	5.204520	-1.044954	-1.504049

8

Zero-point correction= 0.426969 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.369270
Sum of electronic and thermal Free Energies= -1229.503122
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -1230.348900

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.860826	-0.220260	0.083210
2	6	0	-1.659616	0.525144	-0.003041
3	6	0	-0.371239	-0.177737	-0.048162

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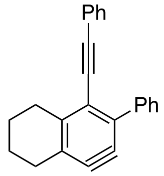
    4     6      0    -0.390910   -1.647193   -0.085040
    5     6      0    -1.617019   -2.286412    0.015758
    6     6      0    -1.703315    1.939526   -0.041062
    7     6      0     0.815959    0.681542   -0.049511
    8     1      0    -1.686975   -3.364116    0.008668
    9     6      0     0.695693    2.072846   -0.087687
   10     6      0    -0.555323    2.682520   -0.097033
   11     1      0     1.591735    2.682807   -0.095415
   12     6      0    -4.311649    0.195787    0.169799
   13     1      0    -4.544120    0.786026    1.063946
   14     1      0    -4.663003    0.748032   -0.709712
   15     8      0    -5.048098   -1.033297    0.245989
   16     6      0    -2.821534   -1.582347    0.111021
   17     6      0    -4.196690   -2.117565    0.212037
   18     8      0    -4.586072   -3.255889    0.259963
   19     6      0    -0.893426    4.122574   -0.130600
   20     6      0    -2.864931    2.907555   -0.035867
   21     1      0    -3.527570    2.797726   -0.902330
   22     1      0    -3.474039    2.855273    0.874132
   23     8      0    -2.268368    4.211248   -0.095664
   24     8      0    -0.176593    5.088190   -0.178455
   25     6      0     2.197116    0.298532    0.024076
   26     6      0     3.409349    0.251128    0.097728
   27     6      0     0.841529   -2.580750   -0.255898
   28     6      0     0.441773   -4.069032   -0.440263
   29     1      0    -0.048233   -4.492765    0.442308
   30     1      0    -0.204936   -4.225919   -1.310028
   31     1      0     1.356944   -4.648062   -0.605280
   32     6      0     1.604283   -2.234465   -1.562161
   33     1      0     2.524481   -2.827576   -1.621293
   34     1      0     0.981677   -2.498609   -2.425256
   35     1      0     1.883351   -1.188703   -1.659600
   36     6      0     1.707811   -2.566038    1.031538
   37     1      0     1.160204   -3.061506    1.841802
   38     1      0     2.635918   -3.126671    0.863942
   39     1      0     1.977817   -1.569579    1.371864
   40     6      0     4.875965    0.145943    0.196652
   41     6      0     5.380178   -1.007684   -0.702083
   42     1      0     4.950598   -1.965556   -0.391347
   43     1      0     5.112380   -0.836641   -1.749850
   44     1      0     6.471775   -1.082313   -0.634050
   45     6      0     5.268826   -0.130367    1.668341
   46     1      0     6.359683   -0.197089    1.755750
   47     1      0     4.919731    0.672723    2.325545
   48     1      0     4.837348   -1.072713    2.021280
   49     6      0     5.508619    1.479931   -0.267237
   50     1      0     6.601055    1.418931   -0.198395
   51     1      0     5.242052    1.701587   -1.305912
   52     1      0     5.171442    2.313620    0.357479
 ---------------------------------------------------------------------
```

Comparison of benzyne 30-benz and the isomeric cyclobutadiene 32

The zero-point correction, thermal correction to Gibbs free energy, the sum of the electronic and thermal free energies, the Cartesian coordinates at B3LYP/6-31G(d), and electronic energy at SMD(chloroform)/ B3LYP-D3BJ/6-311+G(d,p) for each of **30-benz** and **32** is given on pages S66 and S67, respectively.

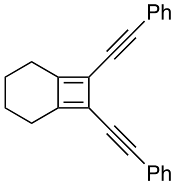
30-benz



Zero-point correction= 0.341211 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.290975
Sum of electronic and thermal Free Energies= -924.947785
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -925.5899531

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	3.596920	-0.311910	-0.025593
2	6	0	3.598329	1.076209	-0.049038
3	6	0	2.631828	1.862153	-0.047866
4	6	0	1.279960	1.550301	0.029376
5	6	0	1.133927	0.114334	0.025089
6	6	0	2.258255	-0.783002	-0.002162
7	6	0	2.002347	-2.284141	0.017784
8	1	0	1.661906	-2.570183	1.024499
9	1	0	1.165620	-2.516429	-0.650077
10	6	0	3.227403	-3.125712	-0.364674
11	1	0	3.022796	-4.181332	-0.149668
12	1	0	3.401337	-3.052862	-1.447590
13	6	0	4.479059	-2.650945	0.378467
14	1	0	5.333941	-3.303620	0.166013
15	1	0	4.301750	-2.701547	1.461823
16	6	0	4.811598	-1.209463	-0.025138
17	1	0	5.573293	-0.782108	0.638343
18	1	0	5.254459	-1.204326	-1.032679
19	6	0	0.203565	2.561947	0.071897
20	6	0	0.408339	3.782107	-0.597719
21	6	0	-0.990683	2.391024	0.792707
22	6	0	-0.555776	4.785965	-0.573095
23	1	0	1.335321	3.928994	-1.145898
24	6	0	-1.952624	3.400610	0.822094
25	1	0	-1.157510	1.476453	1.348759
26	6	0	-1.744933	4.597778	0.135015
27	1	0	-0.378375	5.716305	-1.106182
28	1	0	-2.864045	3.253118	1.395781
29	1	0	-2.498293	5.380656	0.158282
30	6	0	-0.169565	-0.460515	0.006880
31	6	0	-1.270761	-0.979181	-0.029392
32	6	0	-2.585566	-1.526473	-0.065376
33	6	0	-2.803527	-2.903444	0.141731
34	6	0	-3.695233	-0.690189	-0.306628
35	6	0	-4.093986	-3.424503	0.109767
36	1	0	-1.952745	-3.551682	0.328492
37	6	0	-4.981861	-1.220756	-0.335451
38	1	0	-3.529995	0.370435	-0.469857
39	6	0	-5.187049	-2.587296	-0.128054
40	1	0	-4.247936	-4.488048	0.271414
41	1	0	-5.828488	-0.565592	-0.522534
42	1	0	-6.192841	-2.997606	-0.152647

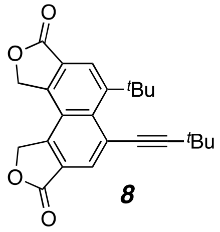
32



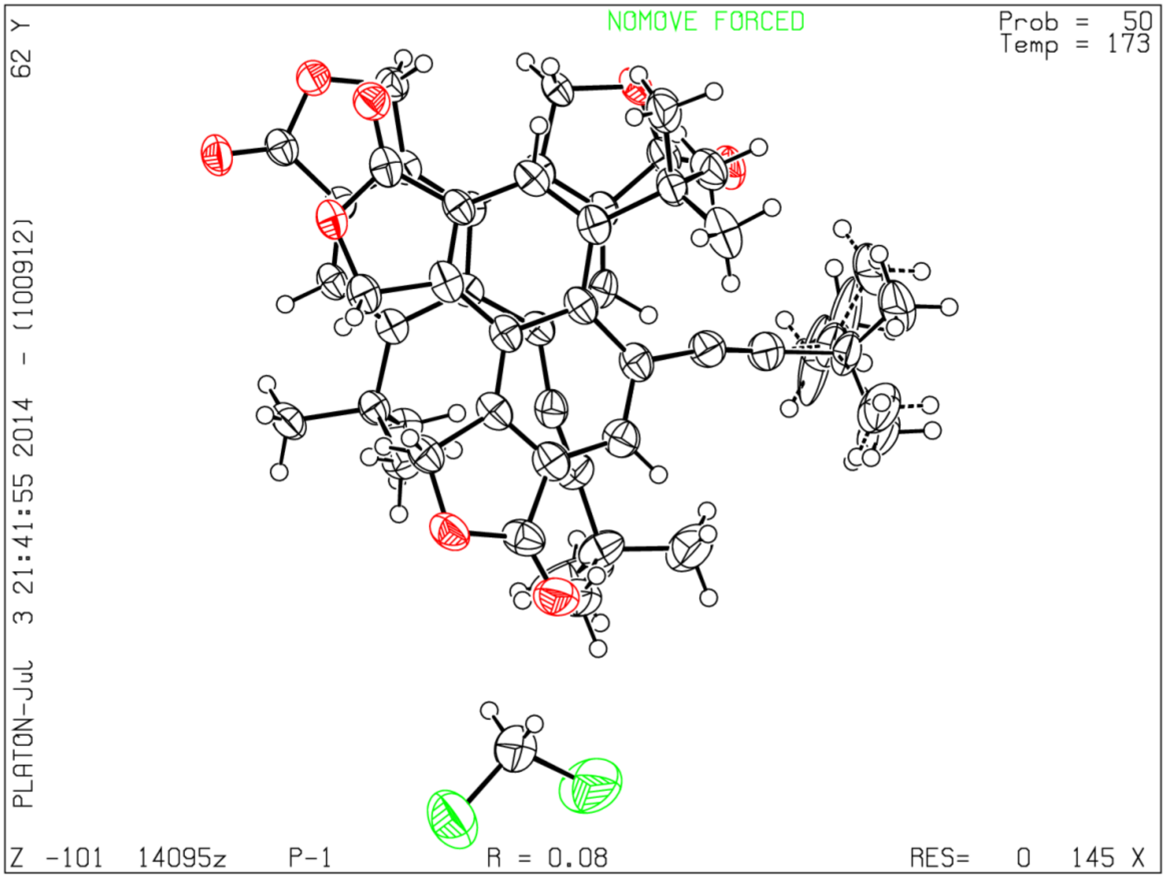
Zero-point correction= 0.338524 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.285058
Sum of electronic and thermal Free Energies= -924.904752
E[SMD(chloroform)/B3LYP-D3BJ/6-311+G(d,p)]= -925.5353682

```
---------------------------------------------------------------------
 Center   Atomic    Atomic              Coordinates (Angstroms)
 Number   Number     Type          X              Y              Z
---------------------------------------------------------------------
    1        6        0       0.751822    2.864114   -0.002795
    2        6        0       0.815601    1.503636   -0.011786
    3        6        0      -0.749411    2.865270   -0.010016
    4        6        0      -0.815320    1.504862   -0.008575
    5        6        0       1.578907    4.099599    0.059715
    6        1        0       1.940403    4.247732    1.090312
    7        1        0       2.474775    4.034948   -0.570658
    8        6        0       0.690560    5.306745   -0.339441
    9        1        0       1.219659    6.238138   -0.107074
   10        1        0       0.534295    5.297722   -1.427351
   11        6        0      -1.779520    0.514495   -0.011854
   12        6        0      -2.596823   -0.397679   -0.010340
   13        6        0      -0.683764    5.300551    0.367401
   14        1        0      -0.528119    5.268209    1.454959
   15        1        0      -1.211192    6.237510    0.154391
   16        6        0      -1.573417    4.103303   -0.057598
   17        1        0      -1.926994    4.270308   -1.088124
   18        1        0      -2.473627    4.030569    0.565534
   19        6        0      -3.561853   -1.435328   -0.007685
   20        6        0      -4.942292   -1.134893   -0.006147
   21        6        0      -3.163968   -2.790658   -0.005374
   22        6        0      -5.885830   -2.156848   -0.001911
   23        1        0      -5.255245   -0.095301   -0.008071
   24        6        0      -4.116697   -3.804261   -0.001409
   25        1        0      -2.104758   -3.028641   -0.006508
   26        6        0      -5.479818   -3.494447    0.000517
   27        1        0      -6.944182   -1.909714   -0.000502
   28        1        0      -3.795097   -4.842405    0.000484
   29        1        0      -6.220217   -4.289583    0.003965
   30        6        0       1.779083    0.512606   -0.007598
   31        6        0       2.600671   -0.395660   -0.010054
   32        6        0       3.562180   -1.436513   -0.001054
   33        6        0       4.943614   -1.140829    0.000898
   34        6        0       3.159563   -2.790451    0.005653
   35        6        0       5.883686   -2.165946    0.009426
   36        1        0       5.260128   -0.102323   -0.004346
   37        6        0       4.108856   -3.807236    0.014566
   38        1        0       2.099539   -3.024741    0.004014
   39        6        0       5.473052   -3.502095    0.016344
   40        1        0       6.942875   -1.922433    0.010756
   41        1        0       3.783743   -4.844270    0.019942
   42        1        0       6.210709   -4.299755    0.022977
---------------------------------------------------------------------
```

IV. X-ray data for 8 (CCDC deposition number: 1818955)



8



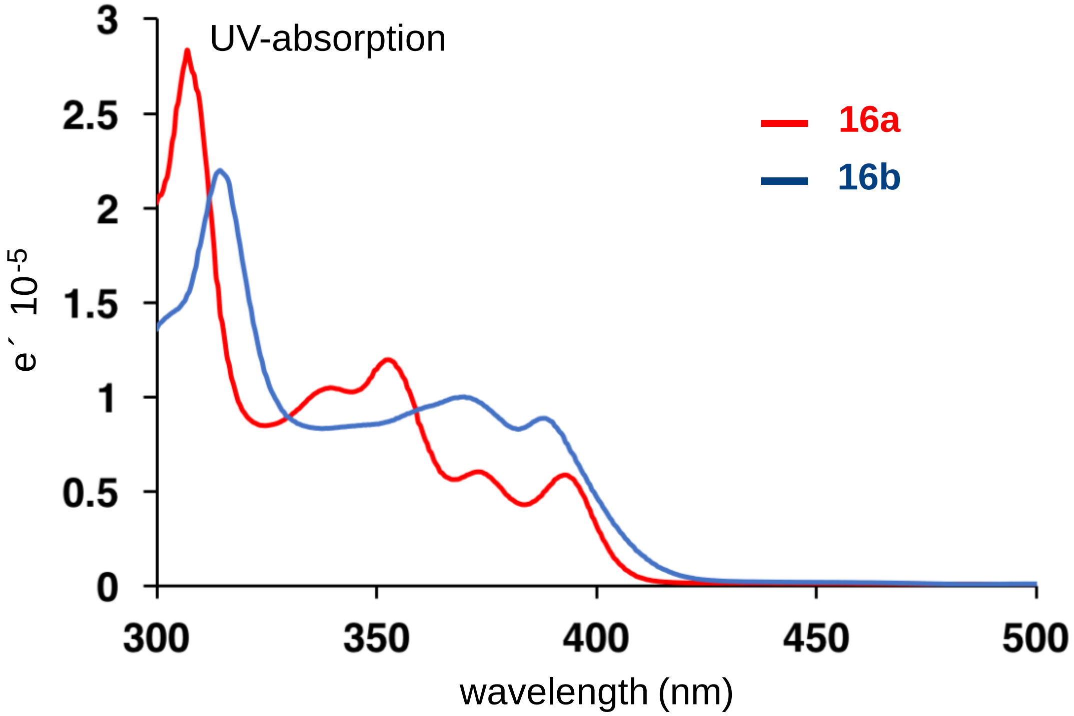
Structure description

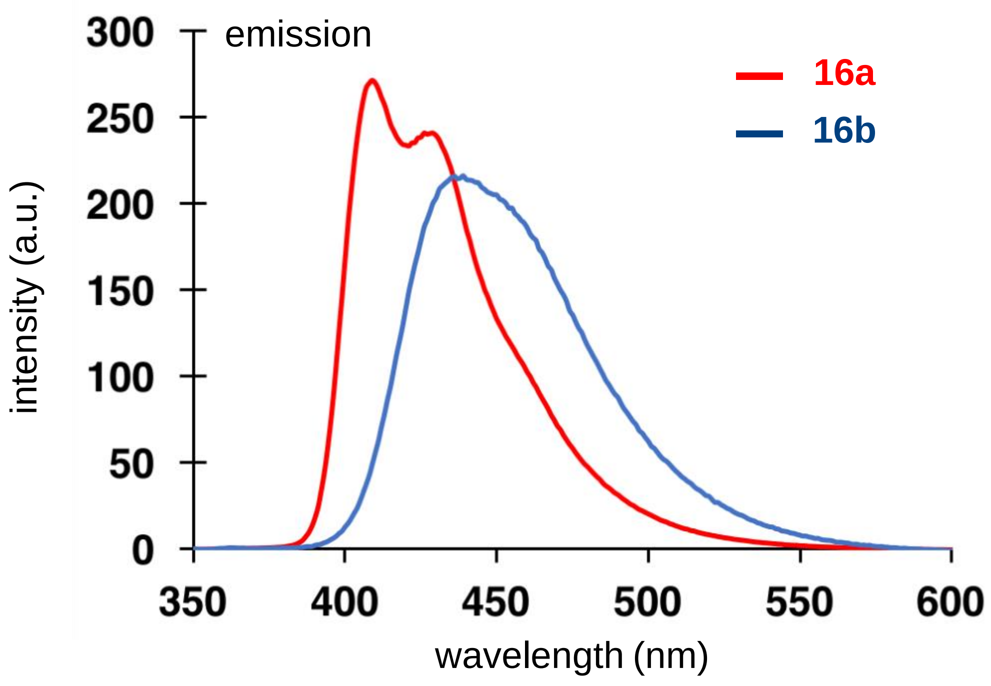
There are two unique molecules in the asymmetric unit, one of which required disorder modeling of the t-butyl group. The t-butyl group was found to be in a 63:37 ratio and was modeled using SAME restraints.

Empirical formula	$C_{49} H_{50} Cl_2 O_8$
Formula weight	837.79
Temperature	173(2) K
Wavelength	1.54178 Å

Crystal system	TRICLINIC	
Space group	P-1	
Unit cell dimensions	a = 10.1822(3) Å	α = 86.262(2)°
	b = 11.4248(4) Å	β = 88.850(2)°
	c = 20.2749(7) Å	γ = 65.461(2)°
Volume	2140.91(12) $Å^3$	
Z	2	
Density (calculated)	1.300 Mg/m^3	
Absorption coefficient	1.808 mm^{-1}	
F(000)	884	
Crystal color, morphology	COLORLESS, PLATE	
Crystal size	0.13 x 0.05 x 0.03 mm^3	
Theta range for data collection	4.26 to 67.04°	
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 10$, $-24 \le l \le 24$	
Reflections collected	24076	
Independent reflections	7514 [R(int) = 0.0820]	
Observed reflections	4050	
Completeness to theta = 67.04°	98.4%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9478 and 0.8003	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7514 / 18 / 560	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	$R1$ = 0.0812, $wR2$ = 0.1991	
R indices (all data)	$R1$ = 0.1503, $wR2$ = 0.2384	
Largest diff. peak and hole	0.794 and -0.735 e.$Å^{-3}$	

V. UV and FL spectral data for 16a and 16b





VI. References for Supporting Information

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[1] T.R. Hoye, P. R. Hanson, J. R. Vyvyan, *J. Org. Chem.* **1994**, *59*, 4096.

[2] T.R. Hoye, H. Zhao, *J. Org. Chem.* **2002**, *67*, 4014.

[3] P. H. Willoughby, D. W. Niu, T. Wang, M. K. Haj, C. J. Cramer, T. R. Hoye, *J. Am. Chem. Soc.* **2014**, *136*, 13657.

[4] N. P. Bowling, N. J. Burrmann, R. J. Halter, J. A. Hodges, R. J. McMahon, *J. Org. Chem.* **2010**, *75*, 6382.

[5] M. S. Shepard, E. M. Carreira, *Tetrahedron* **1997**, *53*, 16253.

[6] L. H. Andrade, T. Barcellos, *Org. Lett.* **2009**, *11*, 3052.

[7] B. M. Trost, J. L. Gunzner, O. Dirat, Y. H. Rhee, *J. Am. Chem. Soc.* **2002**, *124*, 10396.

[8] R. Karmakar, S. Y. Yun, J. J. Chen, Y. Z. Xia, D. Lee, *Angew. Chem. Int. Ed.* **2015**, *54*, 6582.

[9] W. Y. Yin, C. He, M. Chen, H. Zhang, A. W. Lei, *Org. Lett.* **2009**, *11*, 709.

[10] J. Cho, Y. M. Lee, D. Kim, S. Kim, *J. Org. Chem.* **2009**, *74*, 3900.

[11] R. Balamurugan, N. Naveen, S. Manojveer, M. V. Nama, *Aust. J. Chem.* **2011**, *64*, 567.

[12] P. Wessig, G. Muller, R. Herre, A. Kuhn, *Helv. Chim. Acta.* **2006**, 89, 2694.

[13] D. J. Marell, L. R. Furan, B. P. Woods, X. Y. Lei, A. J. Bendelsmith, C. J. Cramer, T. R. Hoye, K. T, Kuwata, *J. Org. Chem.* **2015**, *80*, 11744.

[14] F. Xu, X. Xiao, T. R. Hoye, *J. Am. Chem. Soc.* **2017**, *139*, 8400.

[15] J. H. Chen, V. Palani, T. R. Hoye, *J. Am. Chem. Soc.* **2016**, *138*, 4318.

[16] X. Xiao, T. R. Hoye, *Nature Chem.* **2018**, accepted, DOI:10.1038/s41557-018-0075-y.

[17] J. T. Zhang, D. W. Niu, V. A. Brinker, T. R. Hoye, *Org. Lett.* **2016**, *18*, 5596.

[18] F. Xu, X. Xiao, T. R. Hoye, *Org. Lett.* **2016**, *18*, 5636.

[19] F. Xu, K. W. Hershey, R. J. Holmes, T. R. Hoye, *J. Am. Chem. Soc.* **2016**, *138*, 12739.

[20] M. J. Frisch, *et. al.*, Gaussian 09, Revision E.01, Gaussian Inc. Wallingford CT, **2013**.

[21] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

[22] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

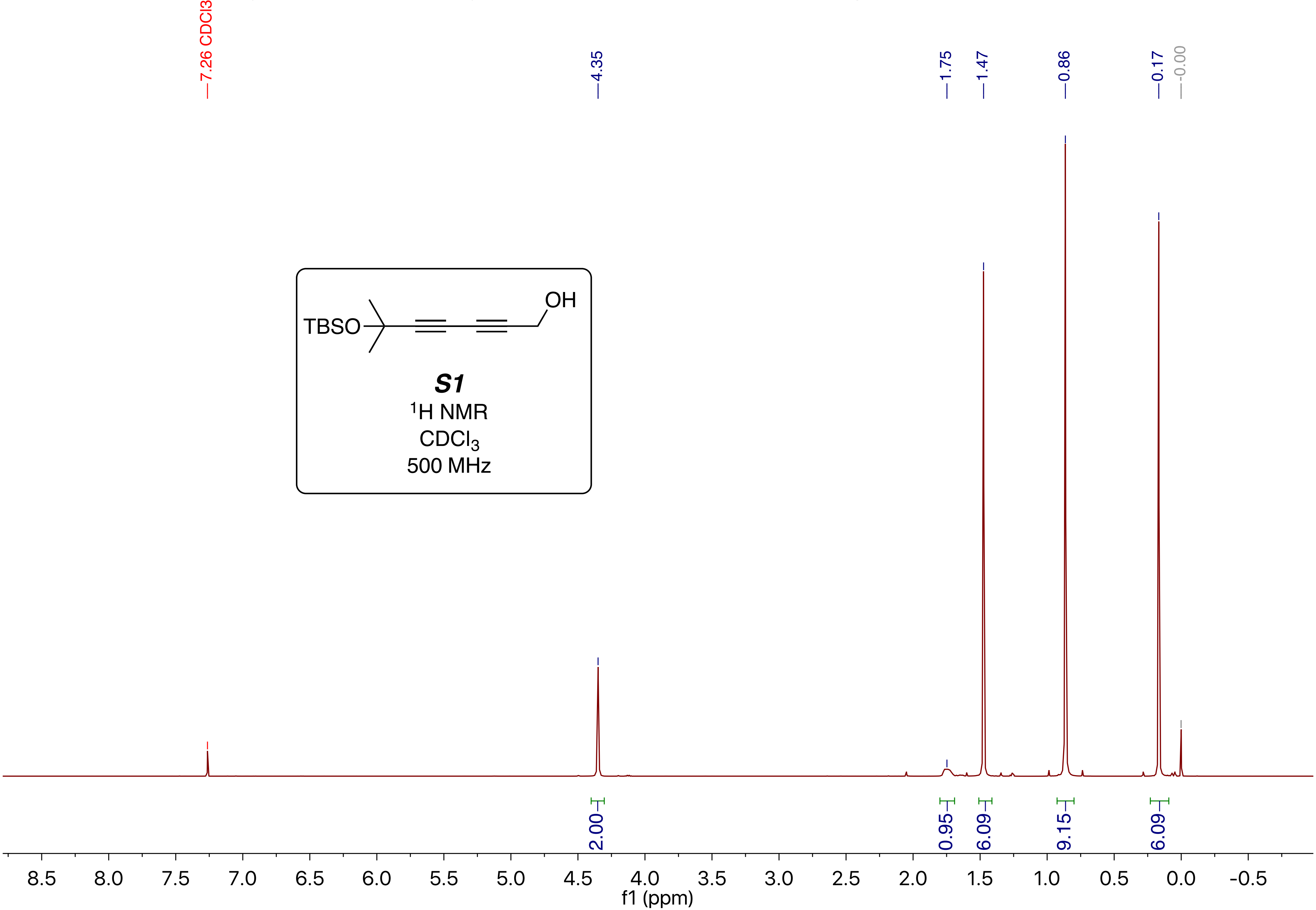
[23] E. R. Johnson, A. D. Becke, *J. Chem. Phys.* **2006**, *124*, 174104.

[24] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B*, **2009**, *113*, 6378.

[25] K. Yamaguchi, F. Jensen, A. Dorigo, K. N. Houk, *Chem. Phys. Lett.* **1988**, *149*, 537.

[26] CYLview, 1.0b; C. Y. Legault, Université de Sherbrooke, **2009** (http://www.cylview.org)

VII. Copies of ^{1}H, and ^{13}C NMR spectra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4.35
1.75
1.47
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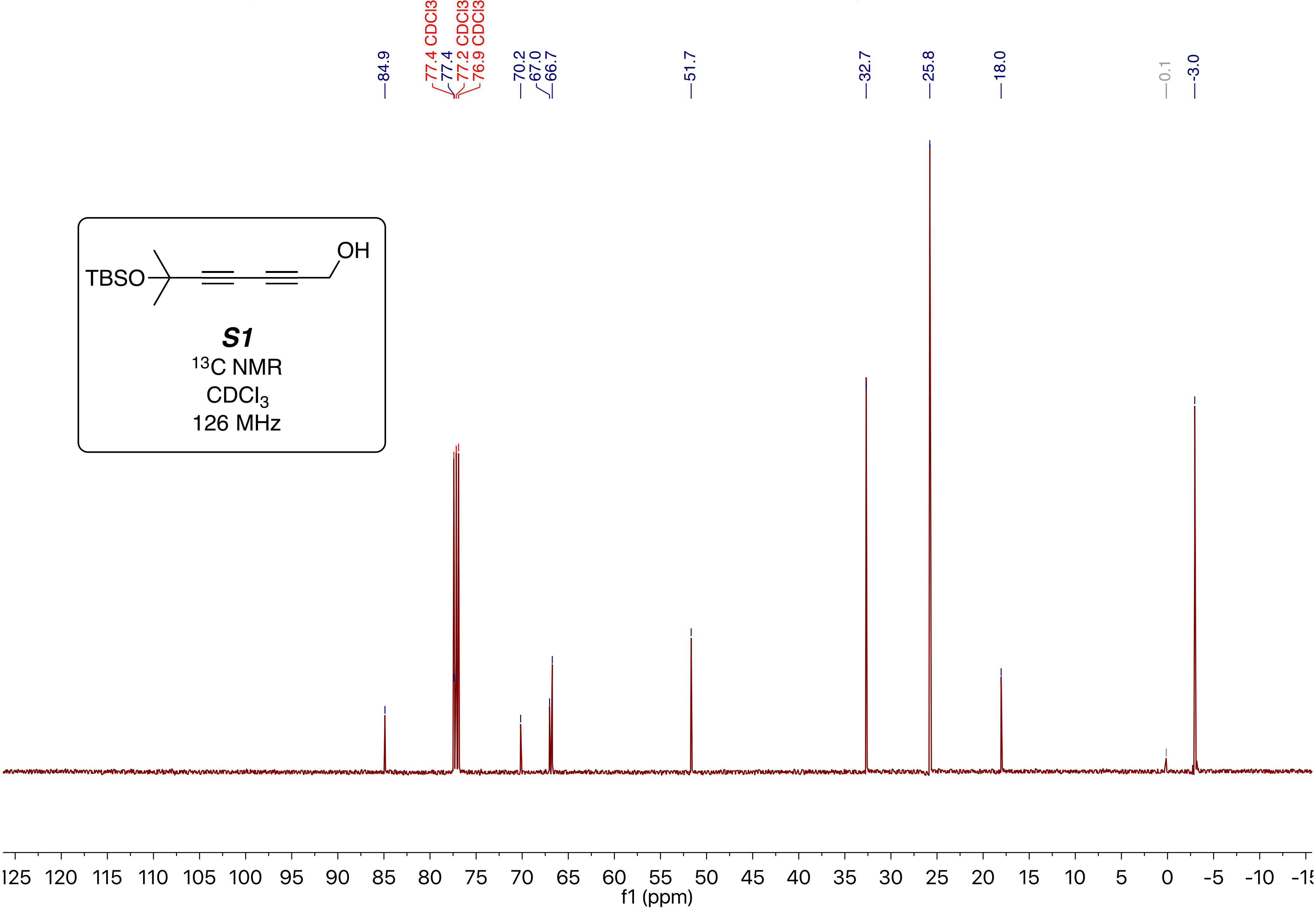
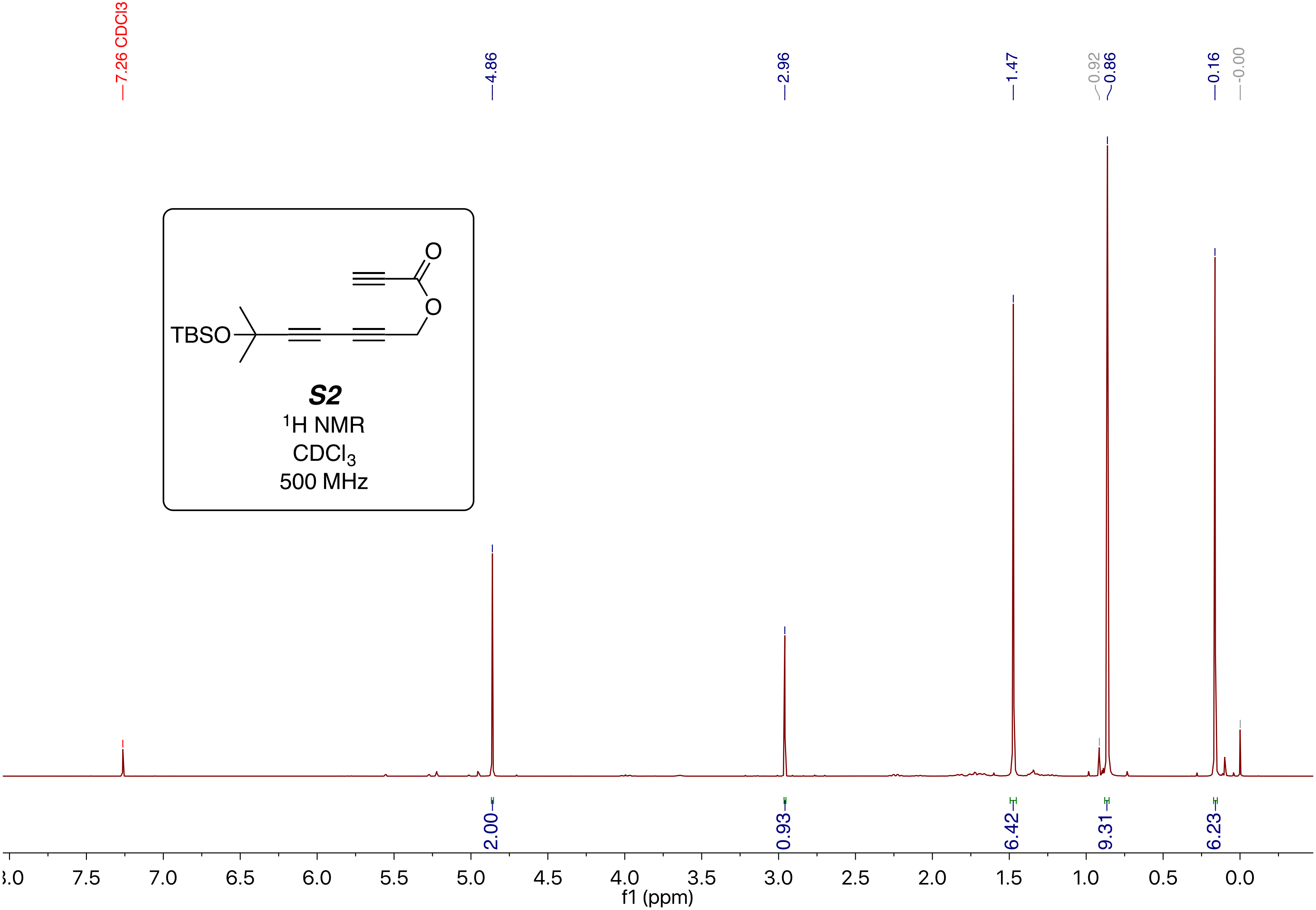
TBSO
OH
S1
1H NMR
CDCl3
500 MHz
2.00
0.95
6.09
9.15
6.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


84.9
77.4 CDCl3
77.4
77.2 CDCl3
76.9 CDCl3
70.2
67.0
66.7
51.7
32.7
25.8
18.0
0.1
-3.0
TBSO
OH
S1
13C NMR
CDCl3
126 MHz
125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)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4.86
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1.47
0.92
0.86
0.16
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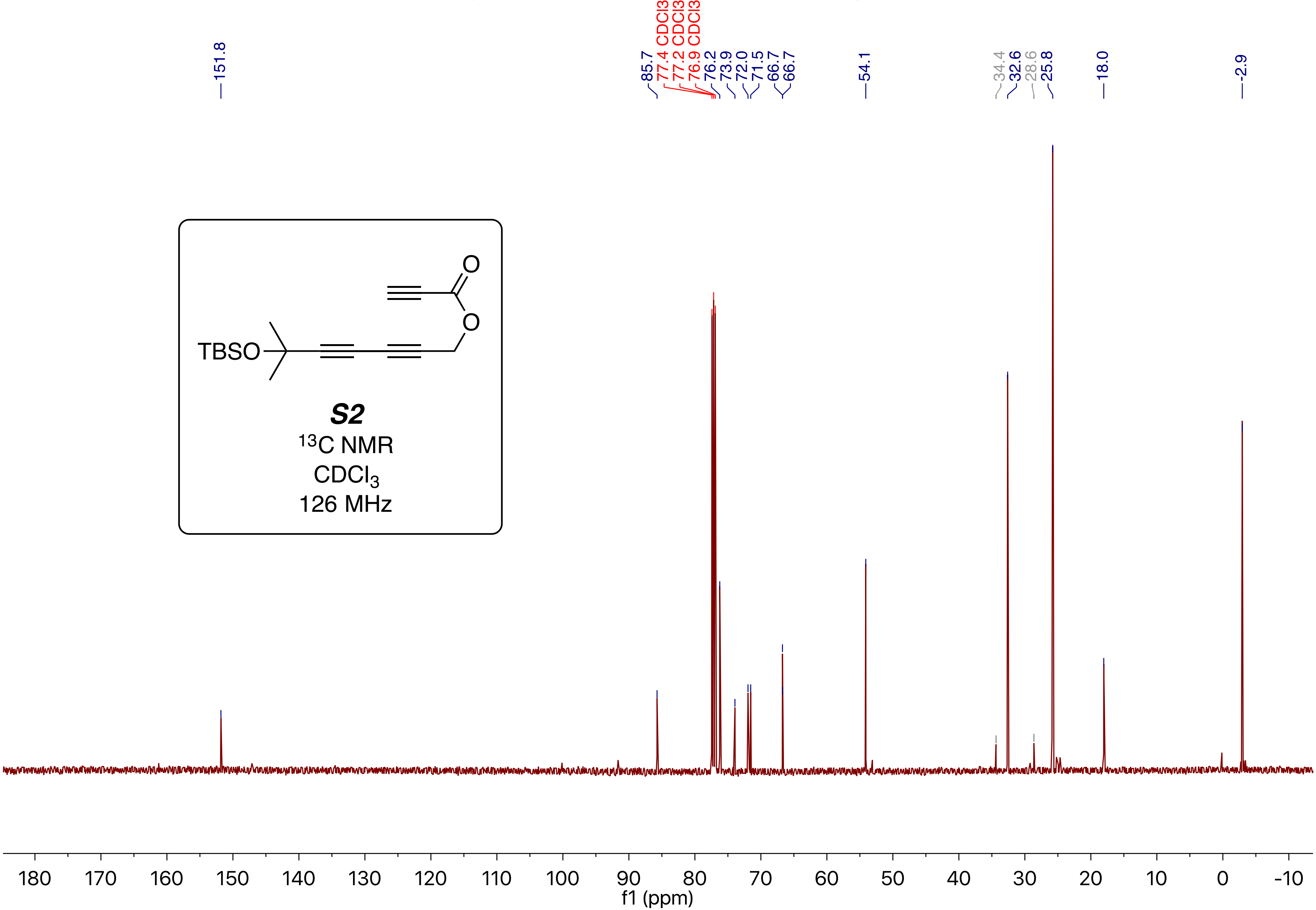
O
O
S2
^{1}H NMR
$CDCl_3$
500 MHz
2.00
0.93
6.42
9.31
6.23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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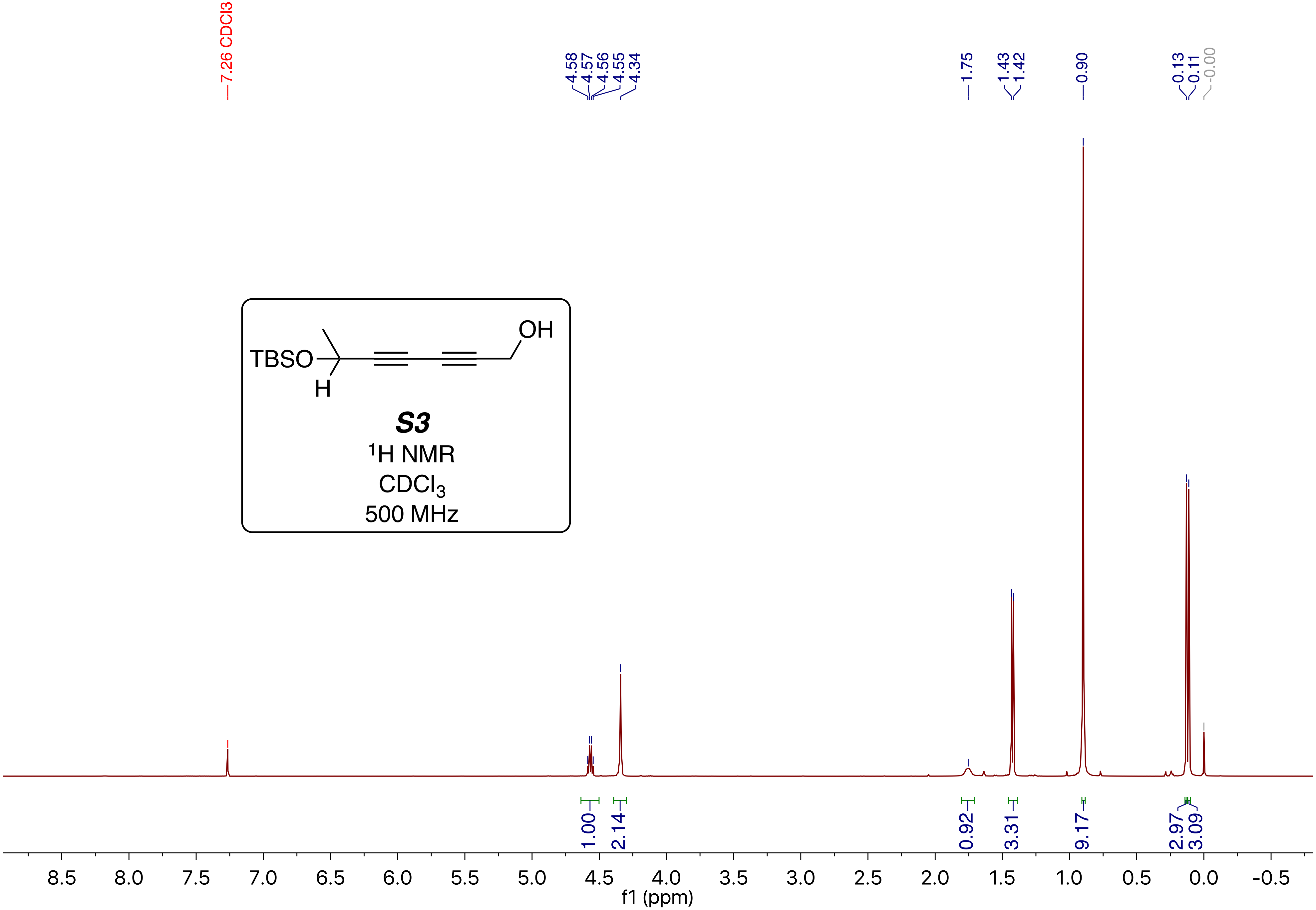
85.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.2
73.9
72.0
71.5
66.7
66.7
54.1
34.4
32.6
28.6
25.8
18.0
-2.9
O
O
TBSO
S2
^{13}C NMR
$CDCl_3$
126 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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4.57
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1.75
1.43
1.42
0.90
0.13
0.11
-0.00
TBSO
H
OH
S3
^{1}H NMR
$CDCl_3$
500 MHz
1.00
2.14
0.92
3.31
9.17
2.97
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
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0.5
0.0
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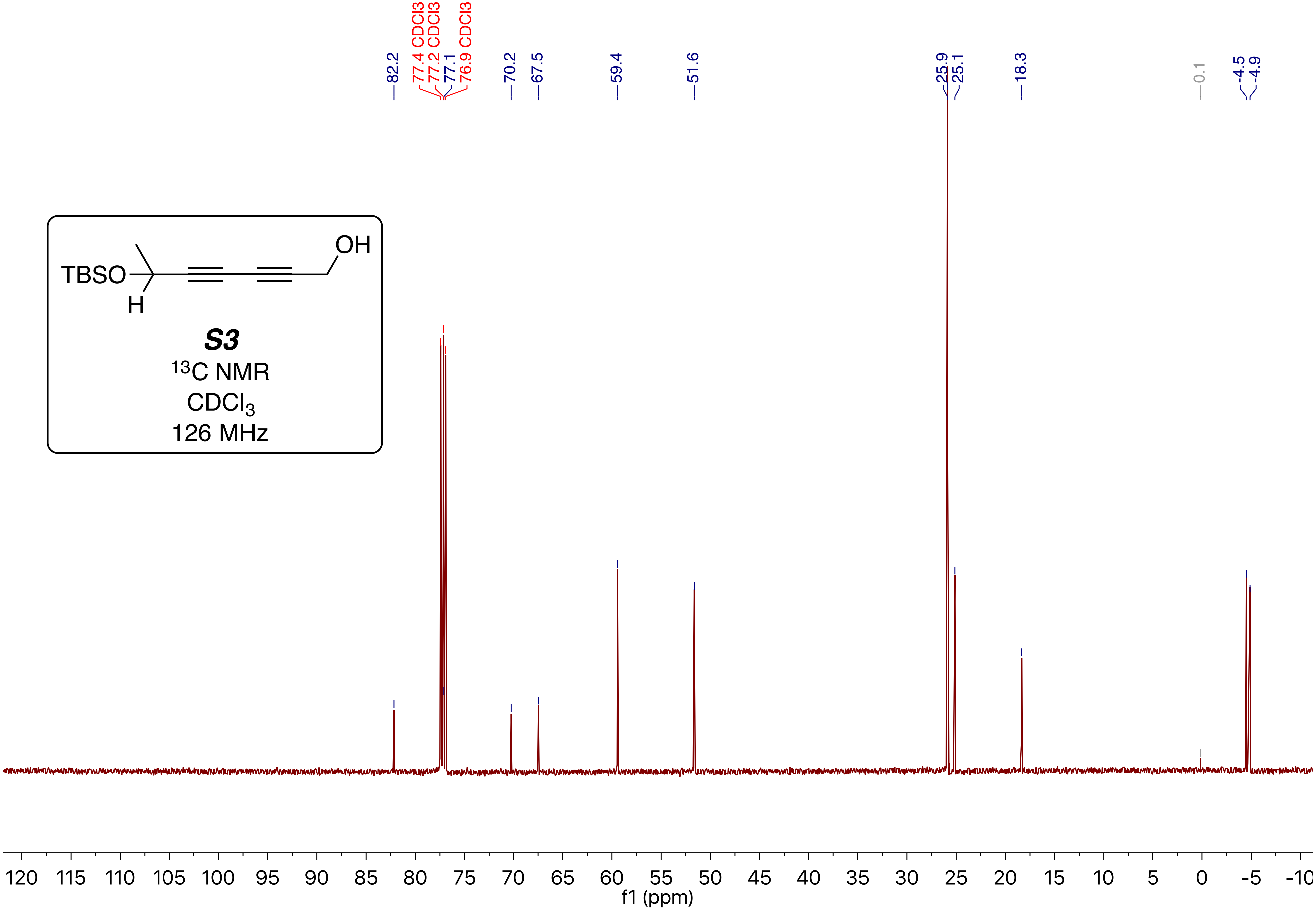
f1 (ppm)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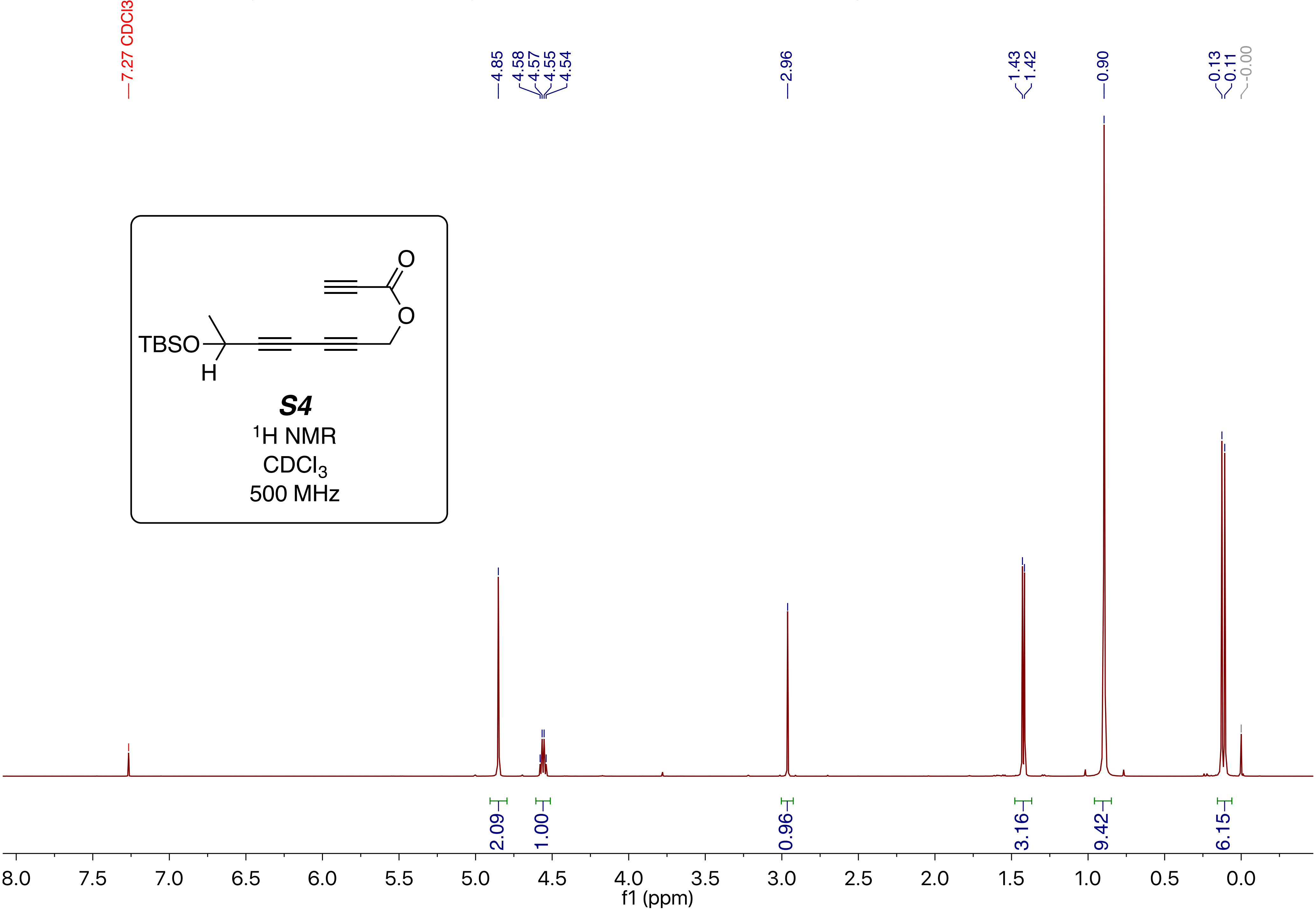
77.2 CDCl3
77.1
76.9 CDCl3
70.2
67.5
59.4
51.6
25.9
25.1
18.3
0.1
-4.5
-4.9
TBSO
H
OH
S3
^{13}C NMR
CDCl$_3$
126 MHz
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (ppm)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4.85
4.58
4.57
4.55
4.54
2.96
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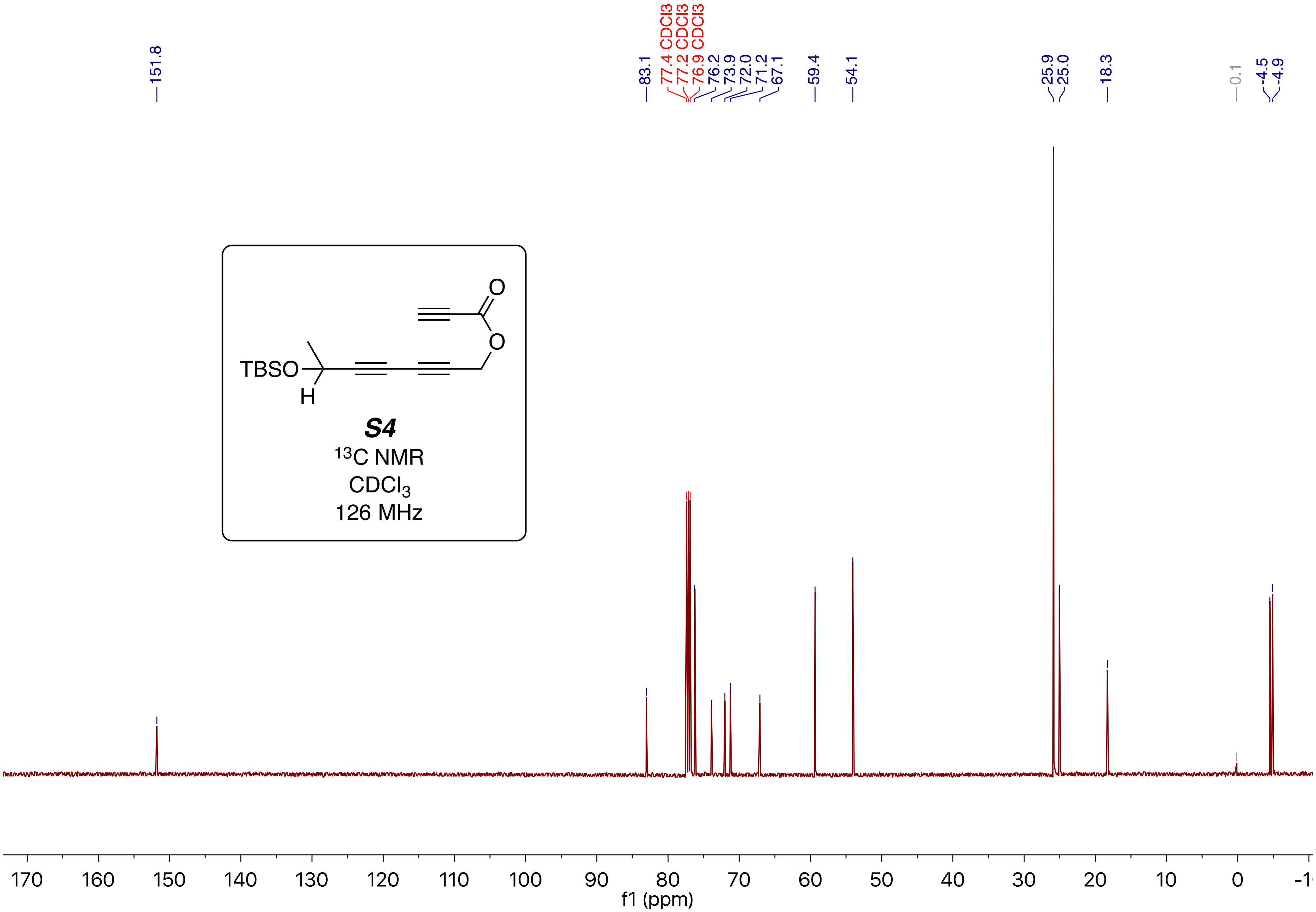
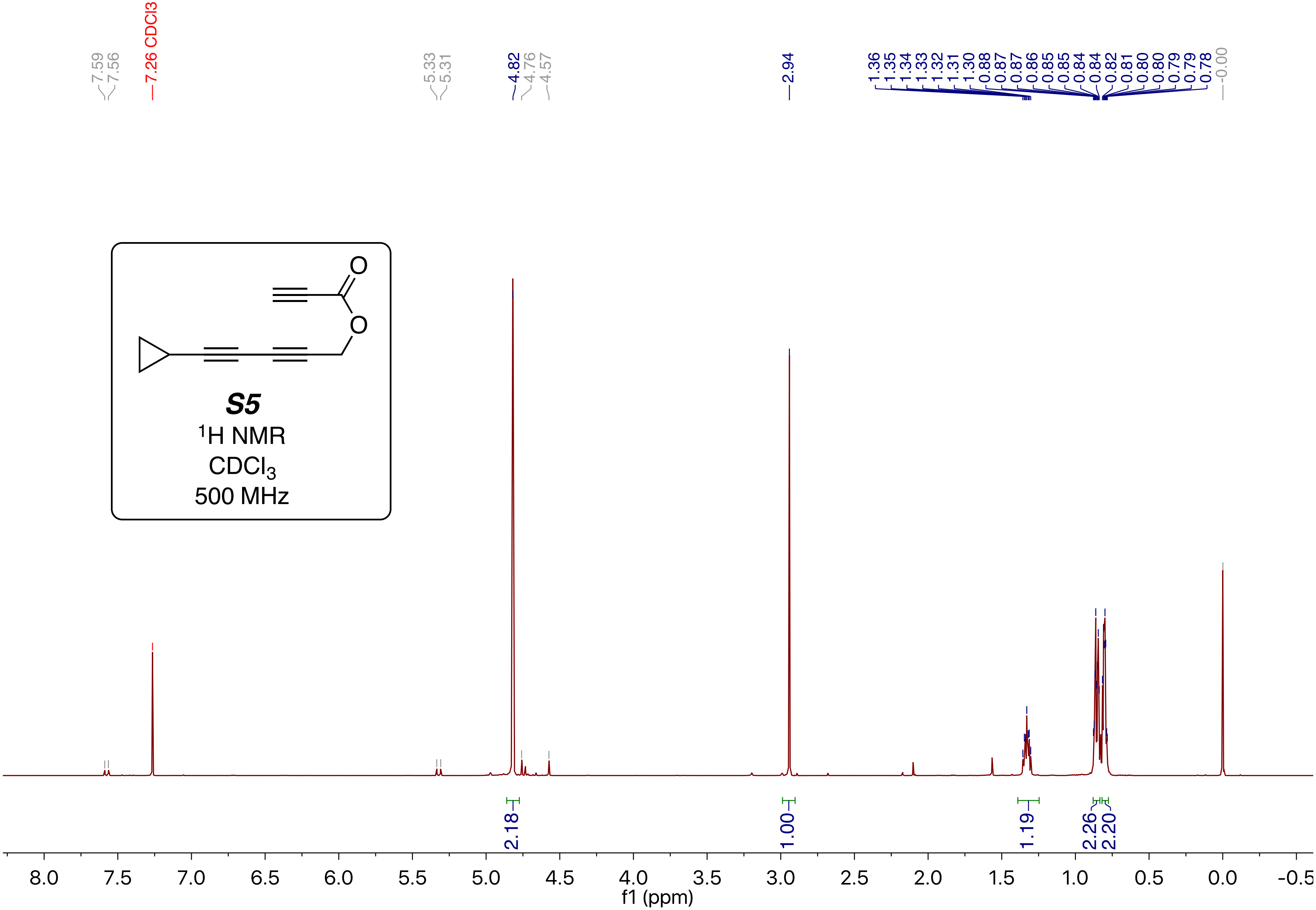
0.90
0.13
0.11
-0.00
TBSO
H
O
O
S4
^{1}H NMR
CDCl$_3$
500 MHz
2.09
1.00
0.96
3.16
9.42
6.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


151.8
83.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.2
73.9
72.0
71.2
67.1
59.4
54.1
25.9
25.0
18.3
0.1
-4.5
-4.9
TBSO
H
O
O
S4
^{13}C NMR
$CDCl_3$
126 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.56
7.26 CDCl3
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4.57
2.94
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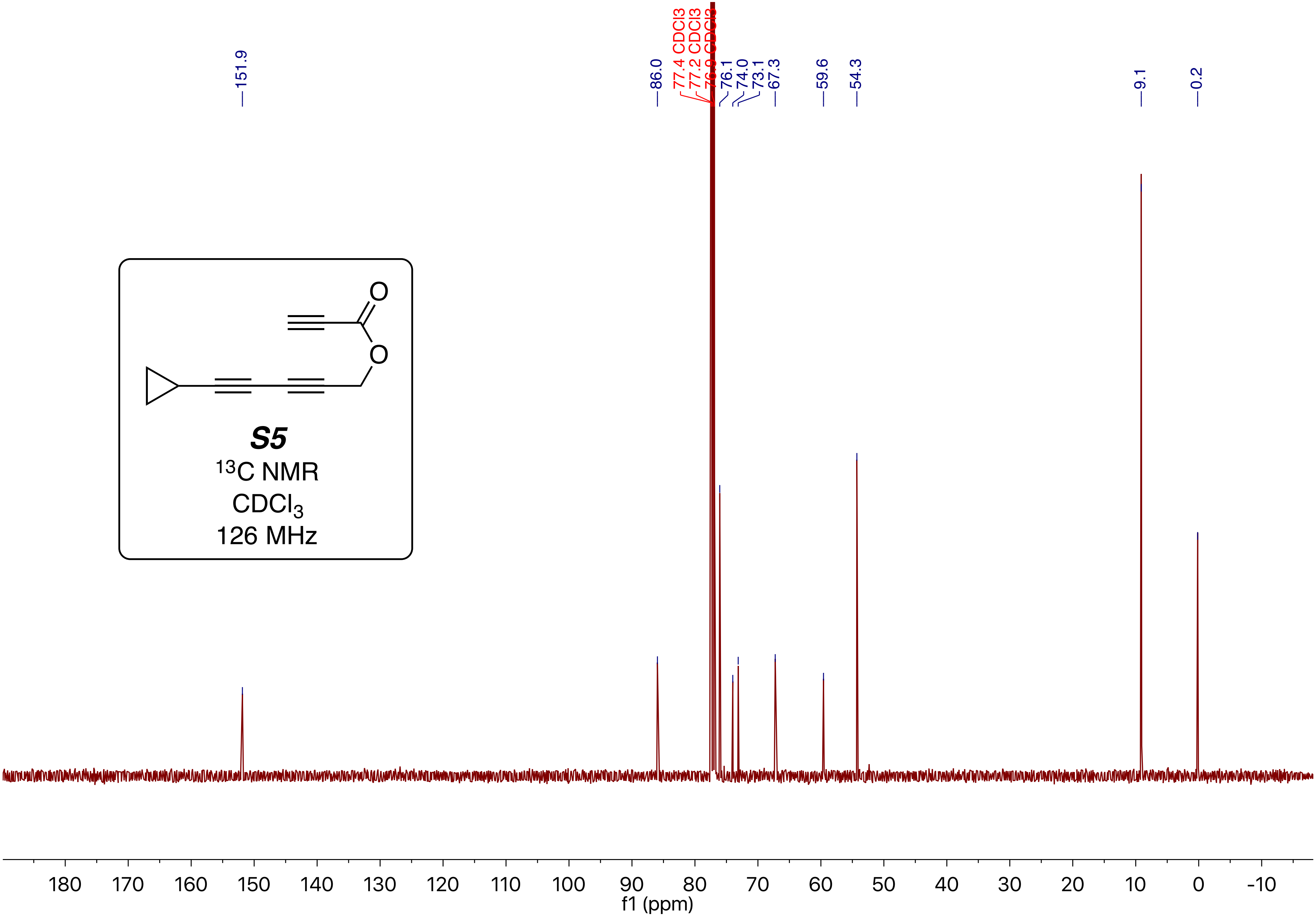
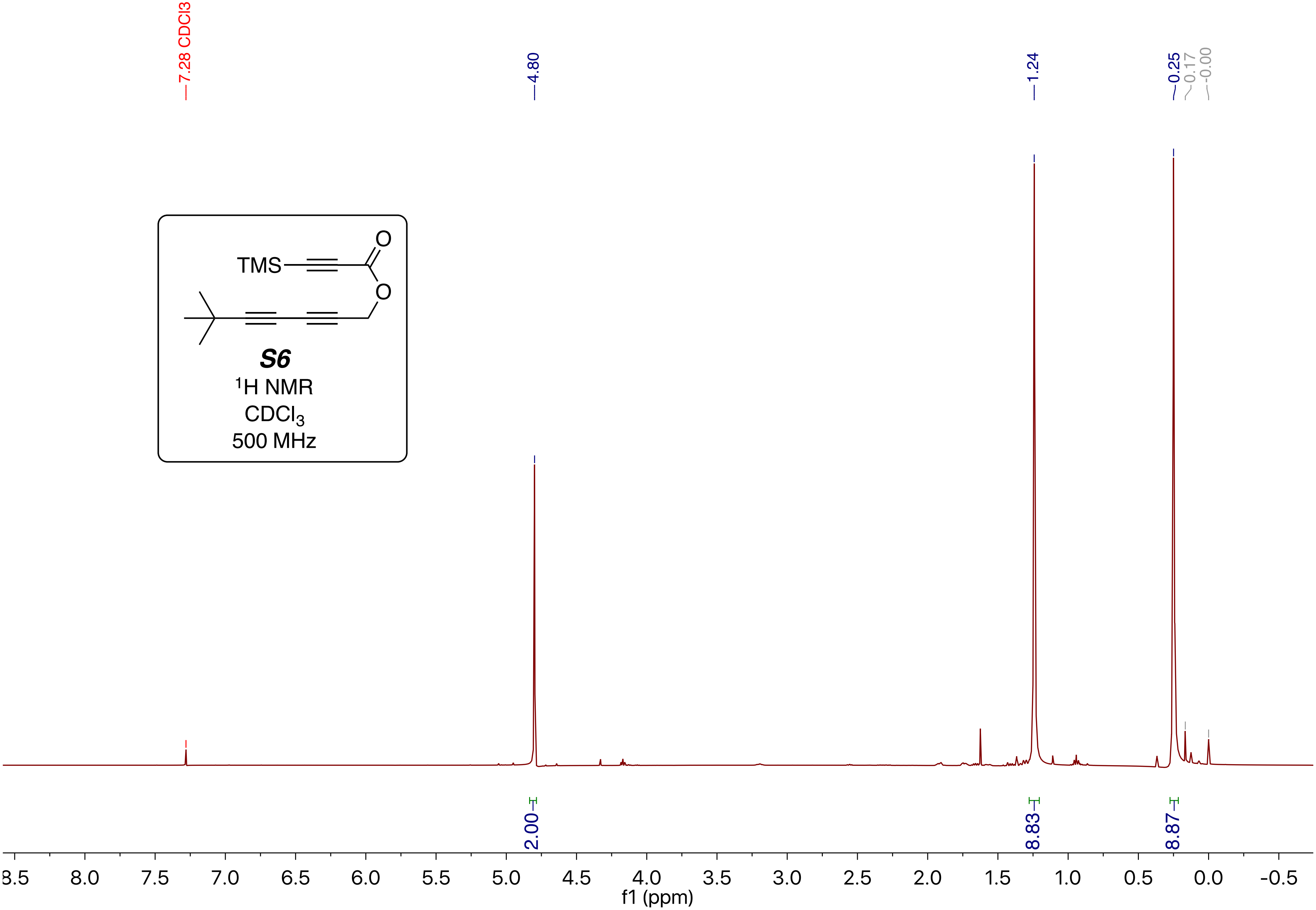
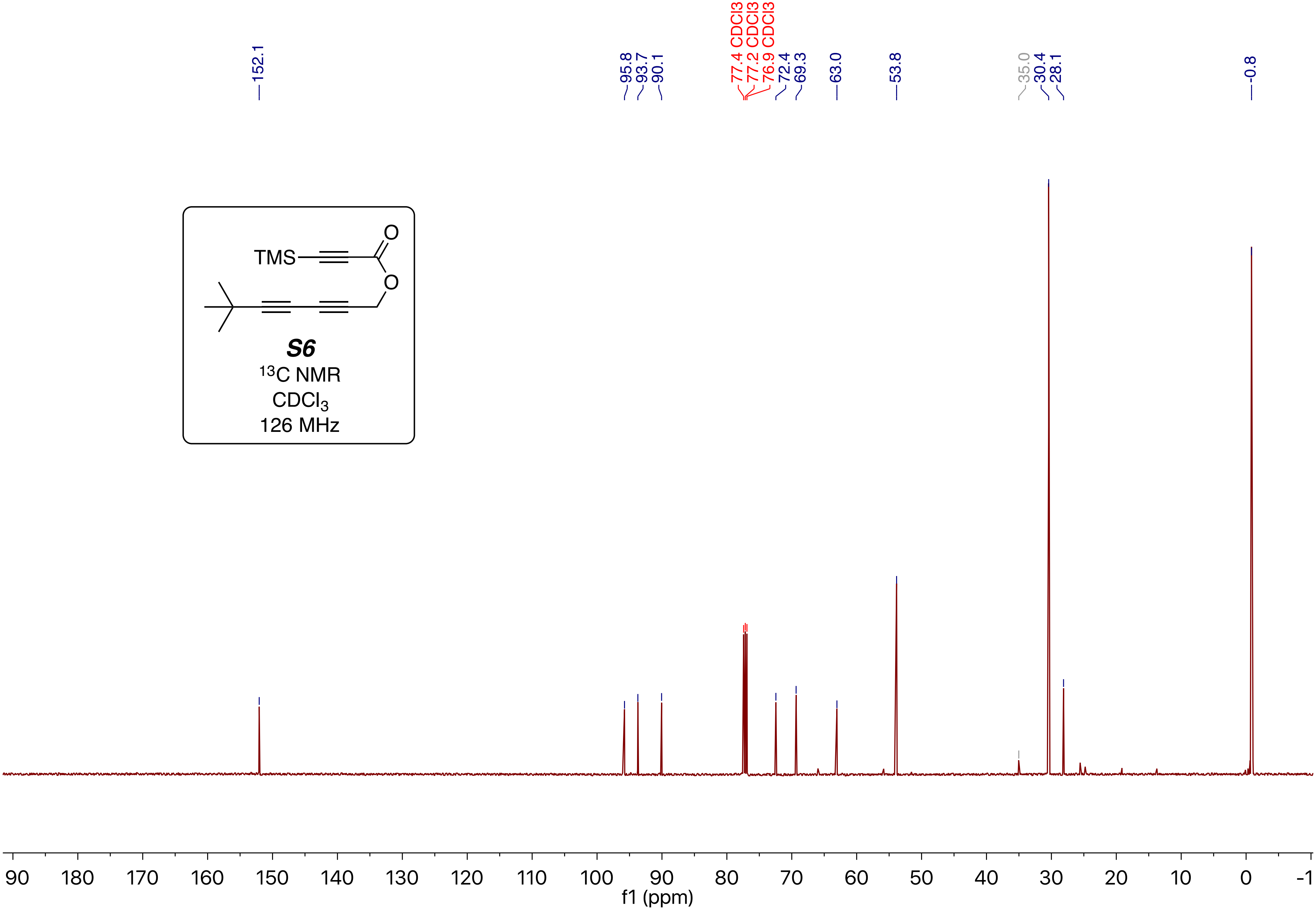
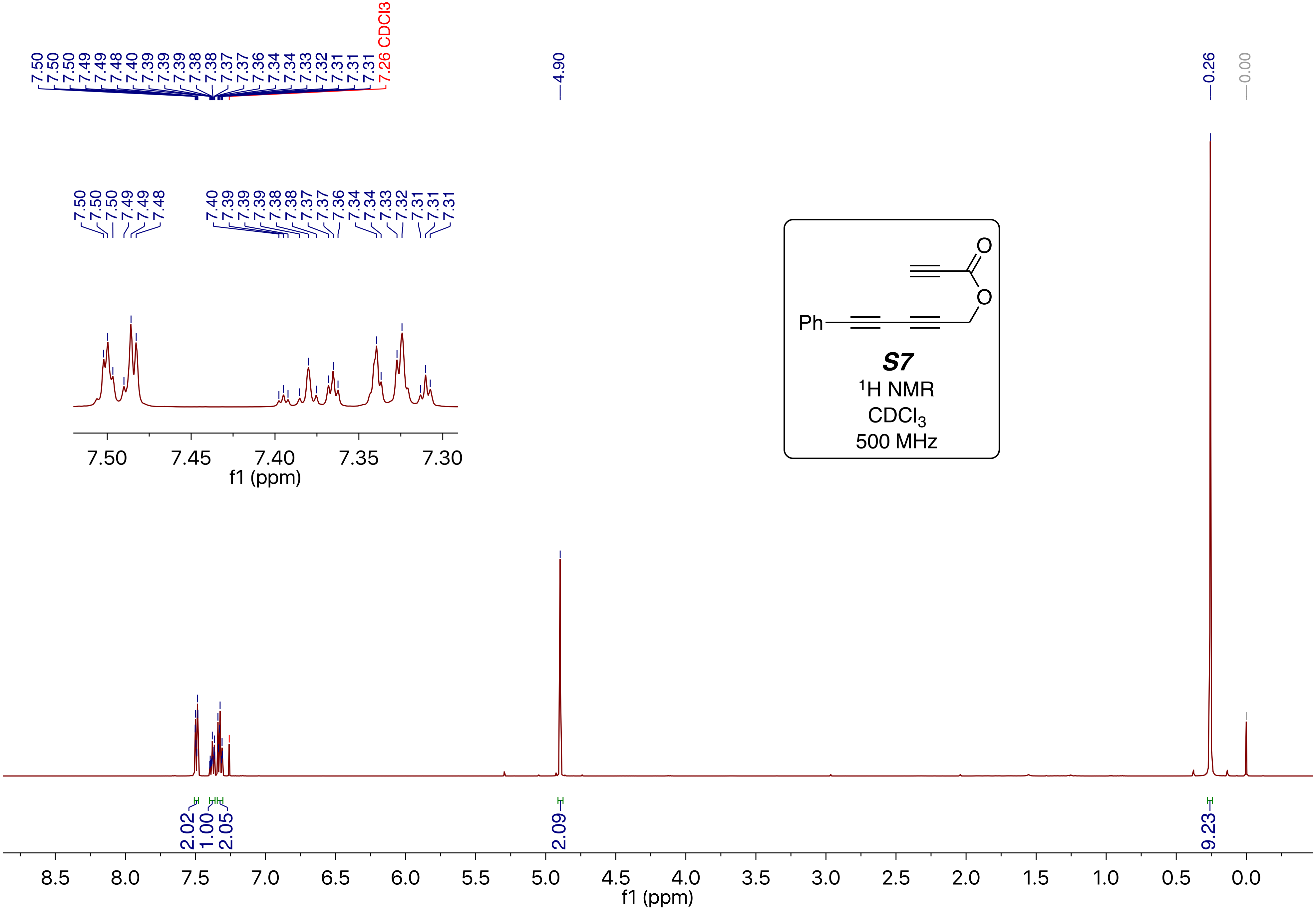
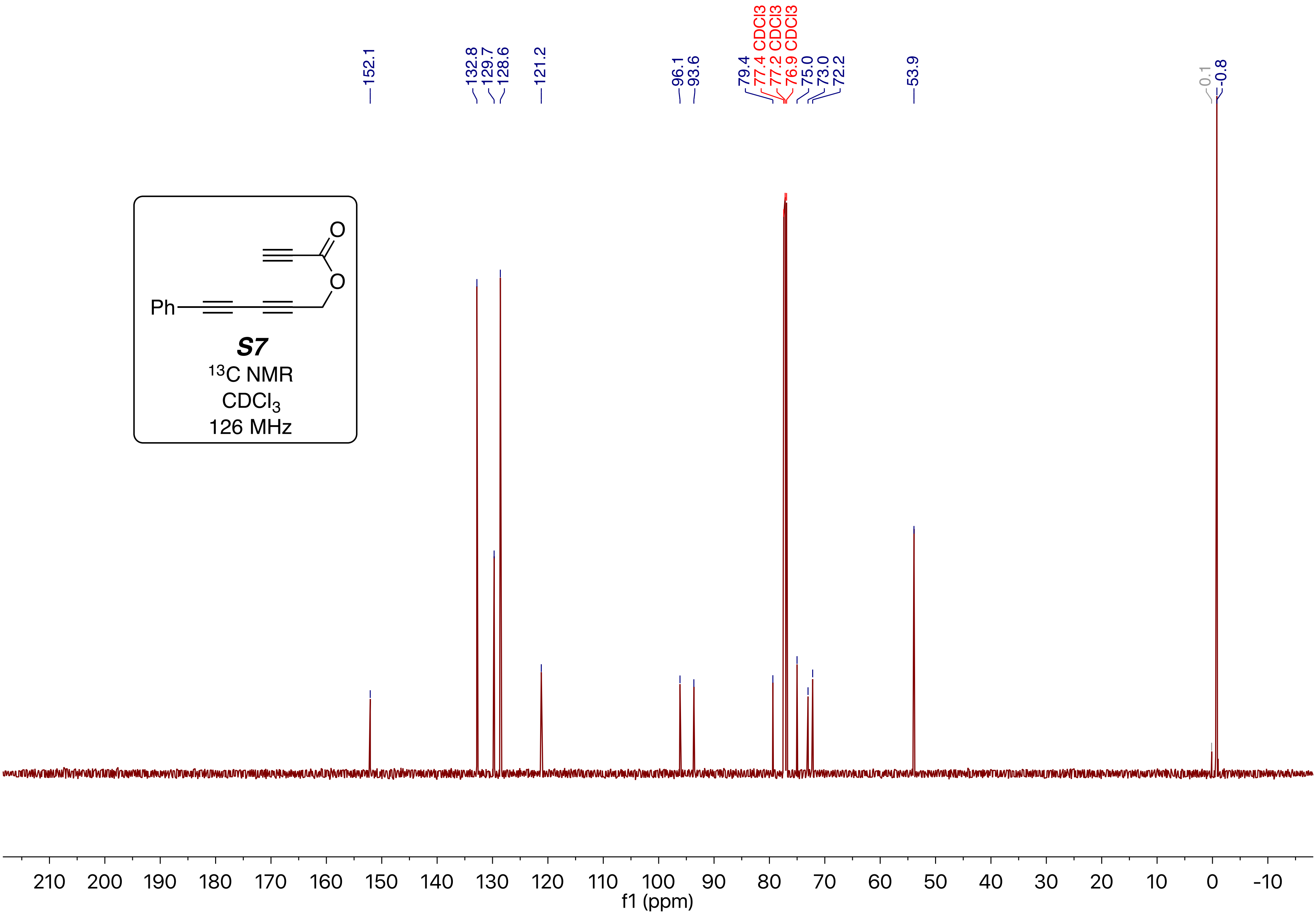
1.35
1.34
1.33
1.32
1.31
1.30
0.88
0.87
0.87
0.86
0.85
0.85
0.84
0.84
0.82
0.81
0.80
0.80
0.79
0.79
0.78
-0.00
O
O
S5
^{1}H NMR
CDCl$_3$
500 MHz
2.18
1.00
1.19
2.26
2.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

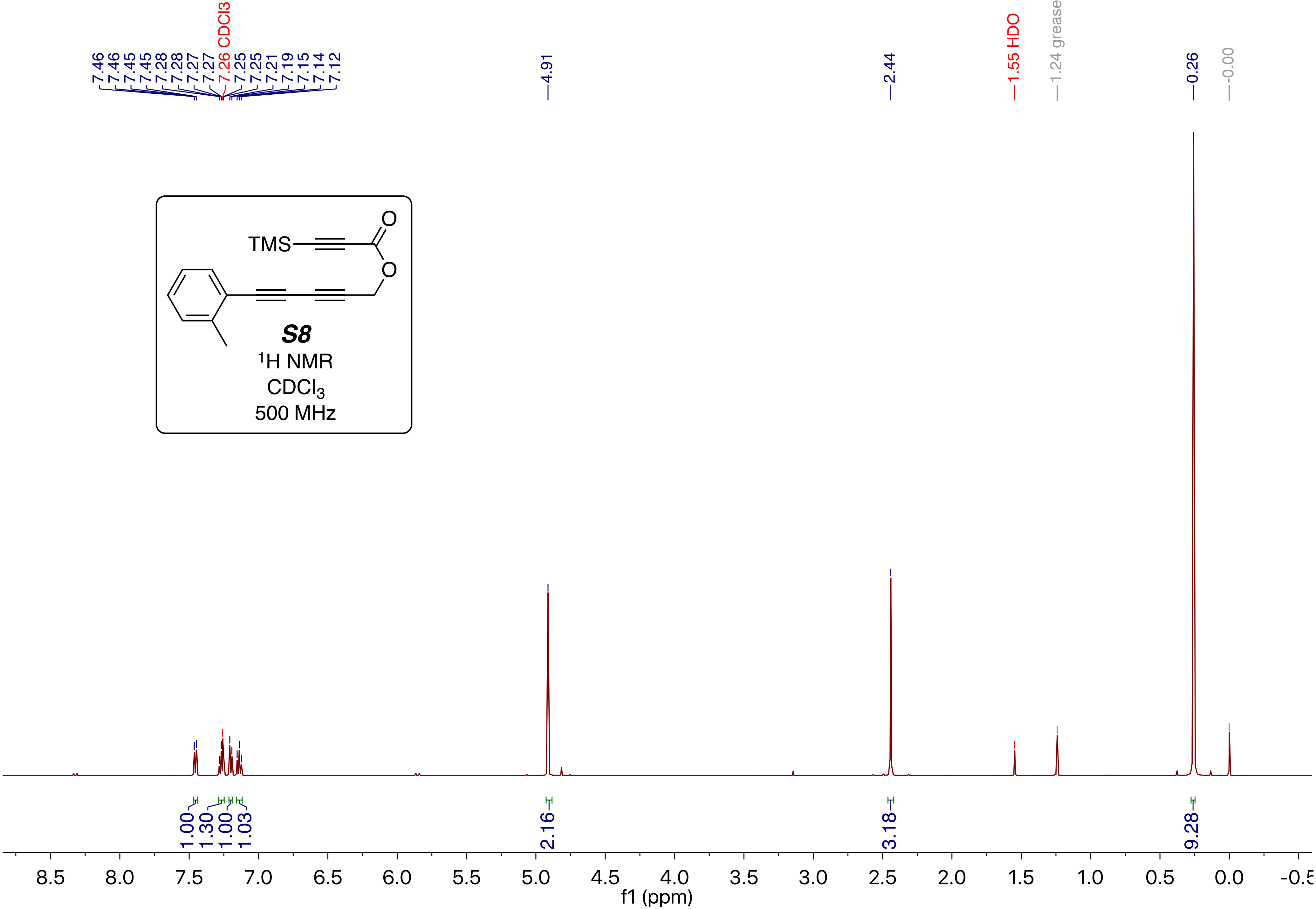

151.9
86.0
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.1
74.0
73.1
67.3
59.6
54.3
9.1
0.2
O
O
S5
^{13}C NMR
CDCl$_3$
126 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

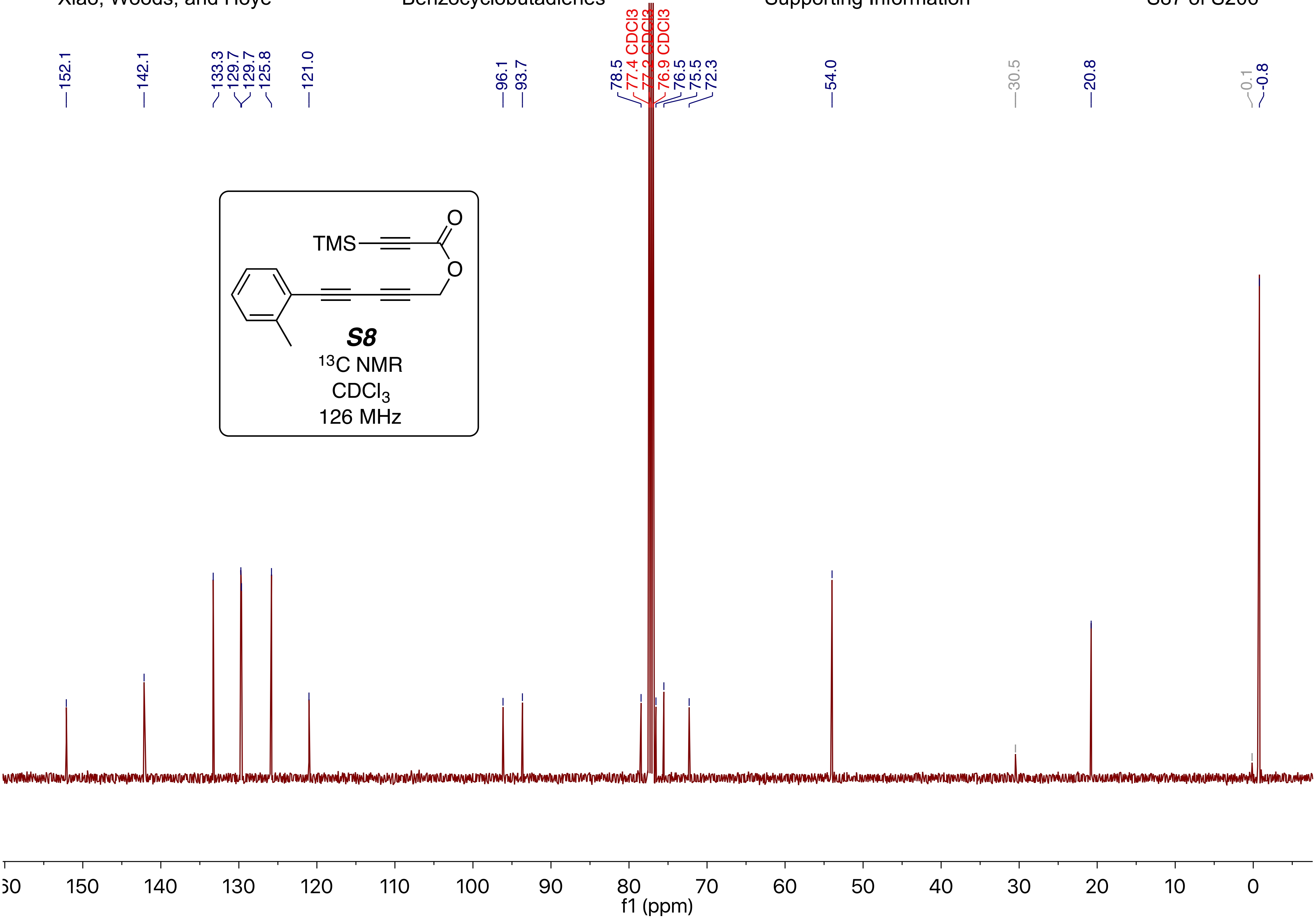

7.28 CDCl3
4.80
1.24
0.25
0.17
-0.00
TMS
O
O
S6
^{1}H NMR
$CDCl_3$
500 MHz
2.00
8.83
8.87
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

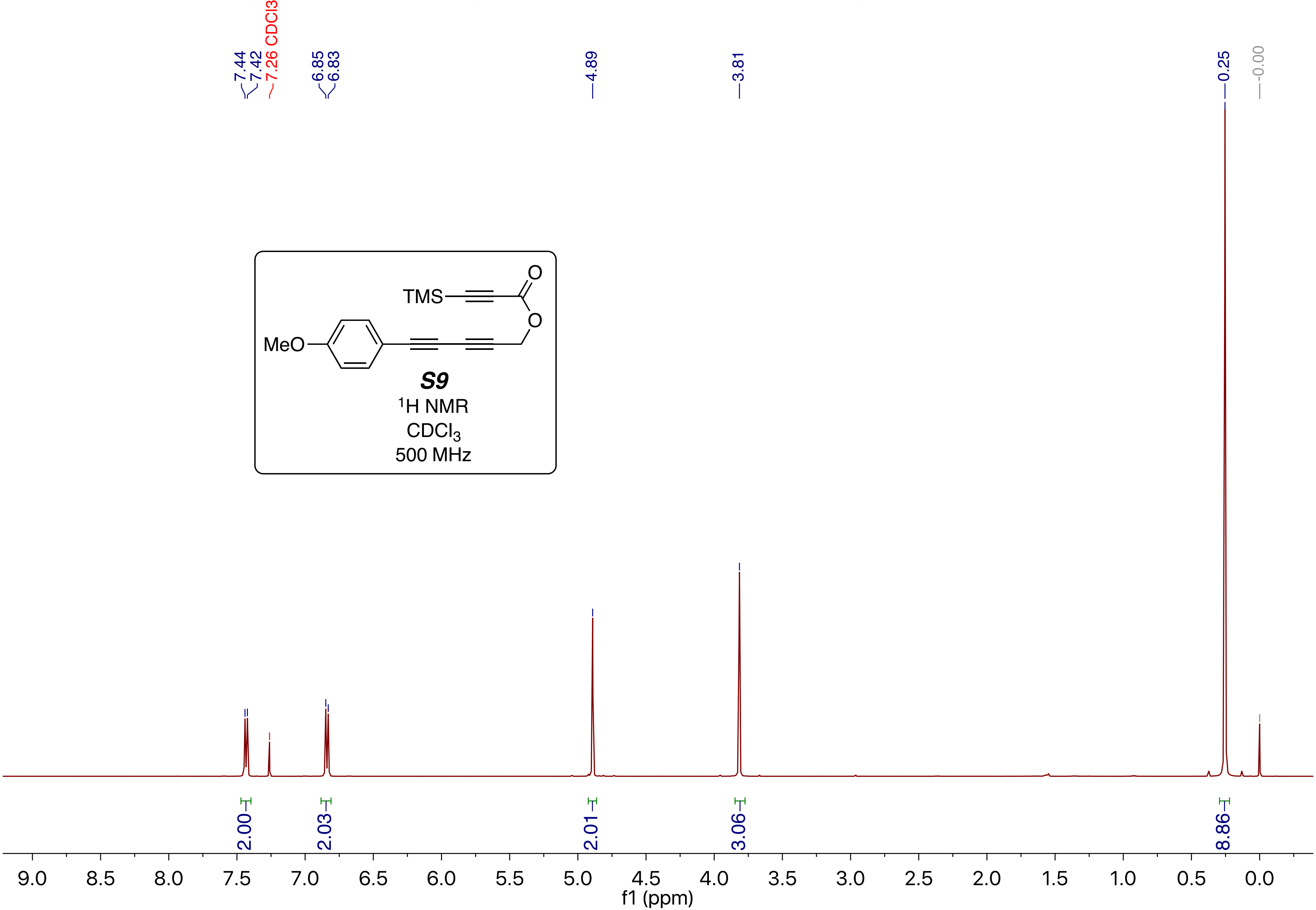

152.1
95.8
93.7
90.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.4
69.3
63.0
53.8
35.0
30.4
28.1
-0.8
TMS
O
O
S6
^{13}C NMR
$CDCl_3$
126 MHz
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

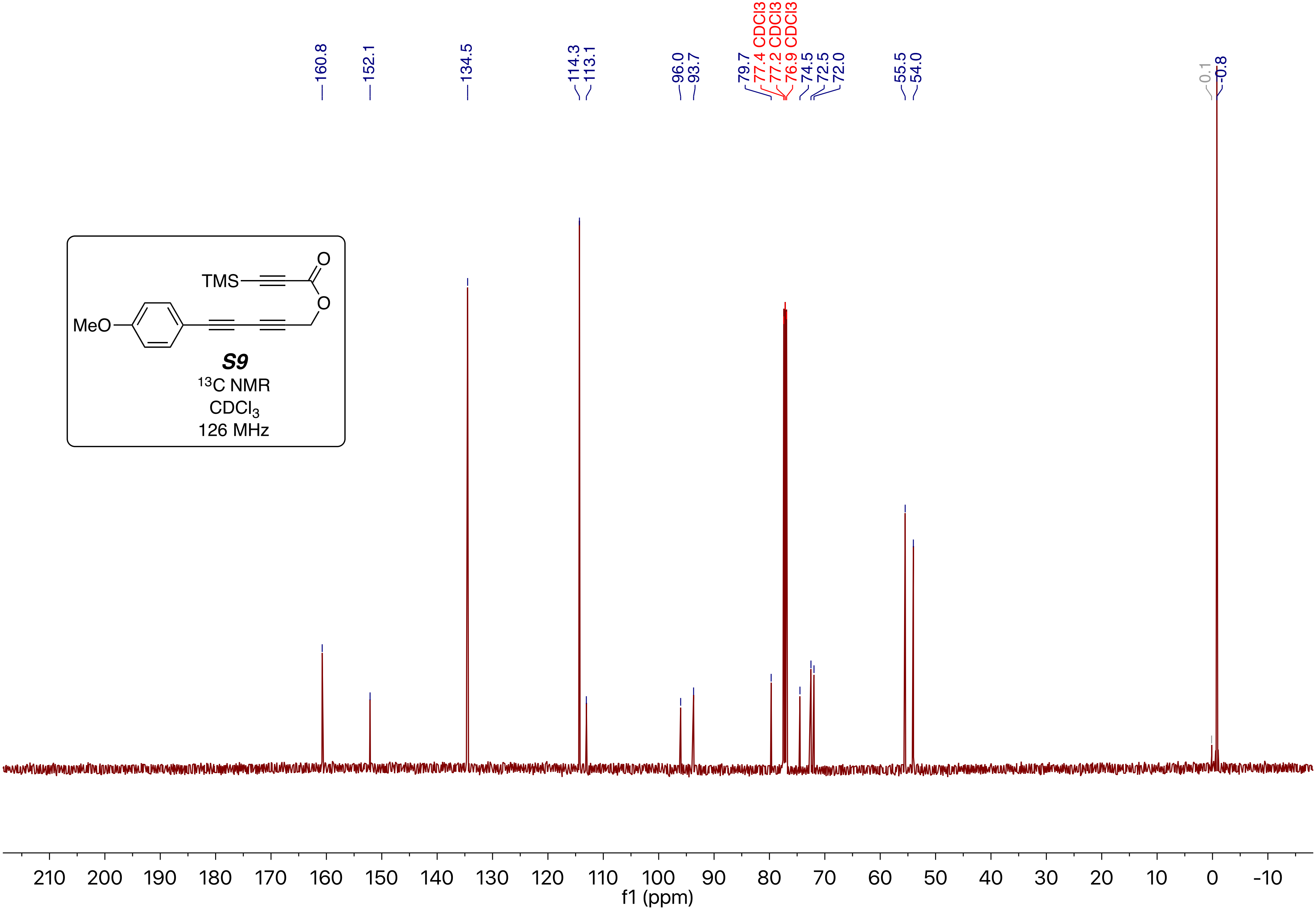

7.50
7.50
7.50
7.49
7.49
7.48
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.34
7.34
7.33
7.32
7.31
7.31
7.31
7.26 CDCl3
4.90
0.26
0.00
7.50
7.45
7.40
7.35
7.30
f1 (ppm)
Ph
O
O
S7
1H NMR
CDCl3
500 MHz
2.02
1.00
2.05
2.09
9.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

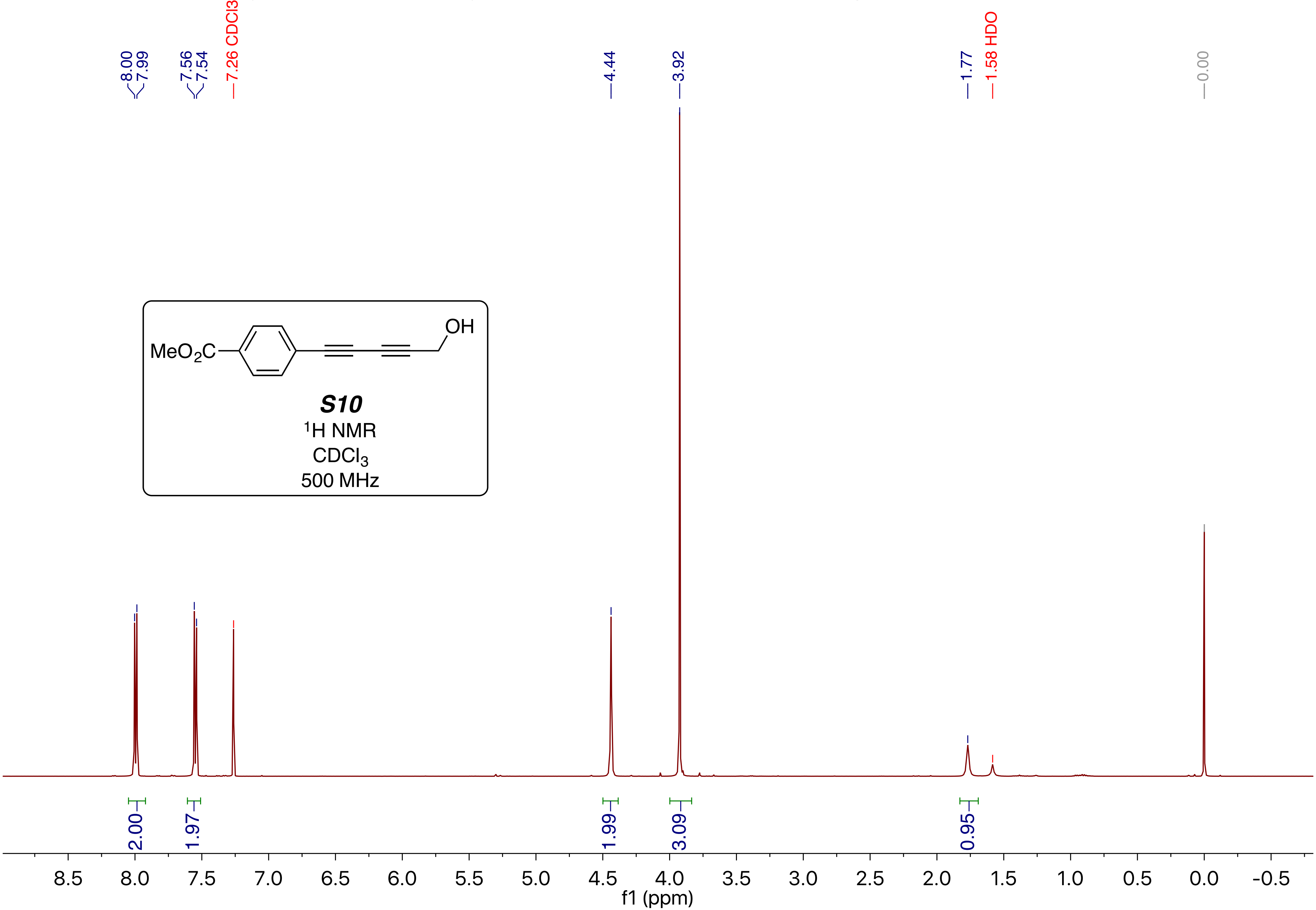

152.1
132.8
129.7
128.6
121.2
96.1
93.6
79.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
75.0
73.0
72.2
53.9
0.1
-0.8
O
O
Ph
S7
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

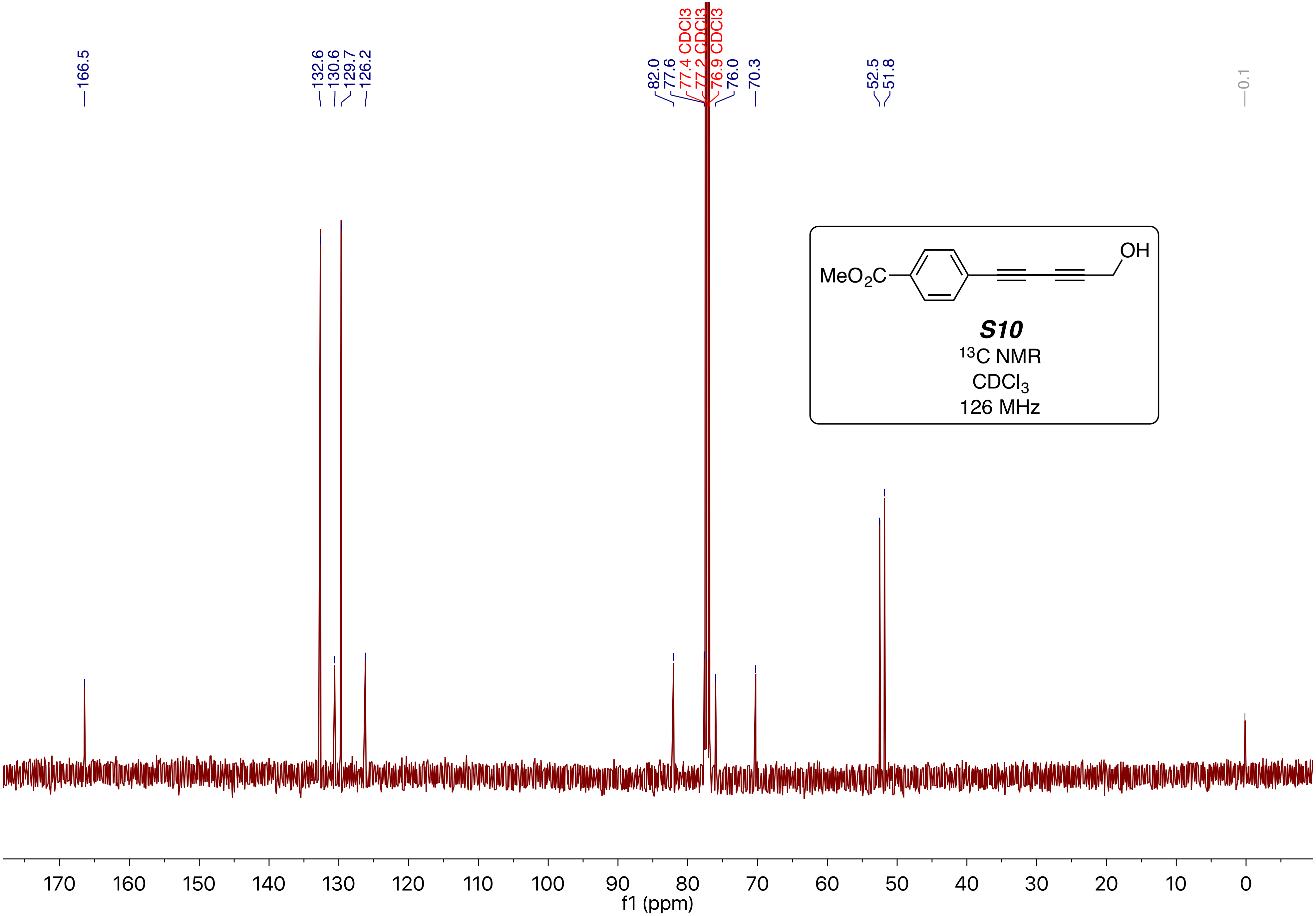

7.46
7.46
7.45
7.45
7.28
7.28
7.27
7.27
7.26 CDCl3
7.25
7.25
7.21
7.19
7.15
7.14
7.12
4.91
2.44
1.55 HDO
1.24 grease
0.26
-0.00
TMS
O
O
S8
^{1}H NMR
CDCl$_3$
500 MHz
1.00
1.30
1.00
1.03
2.16
3.18
9.28
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


152.1
142.1
133.3
129.7
129.7
125.8
121.0
96.1
93.7
78.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.5
75.5
72.3
54.0
30.5
20.8
0.1
-0.8
TMS
O
O
S8
^{13}C NMR
$CDCl_3$
126 MHz
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.44
7.42
7.26 CDCl3
6.85
6.83
4.89
3.81
0.25
-0.00
TMS
O
O
MeO
S9
^{1}H NMR
$CDCl_3$
500 MHz
2.00
2.03
2.01
3.06
8.86
9.0 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
f1 (ppm)


160.8
152.1
134.5
114.3
113.1
96.0
93.7
79.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
74.5
72.5
72.0
55.5
54.0
0.1
-0.8
TMS
O
O
MeO
S9
^{13}C NMR
CDCl$_3$
126 MHz
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)


8.00
7.99
7.56
7.54
7.26 CDCl3
4.44
3.92
1.77
1.58 HDO
0.00
MeO2C
OH
S10
1H NMR
CDCl3
500 MHz
2.00
1.97
1.99
3.09
0.95
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)

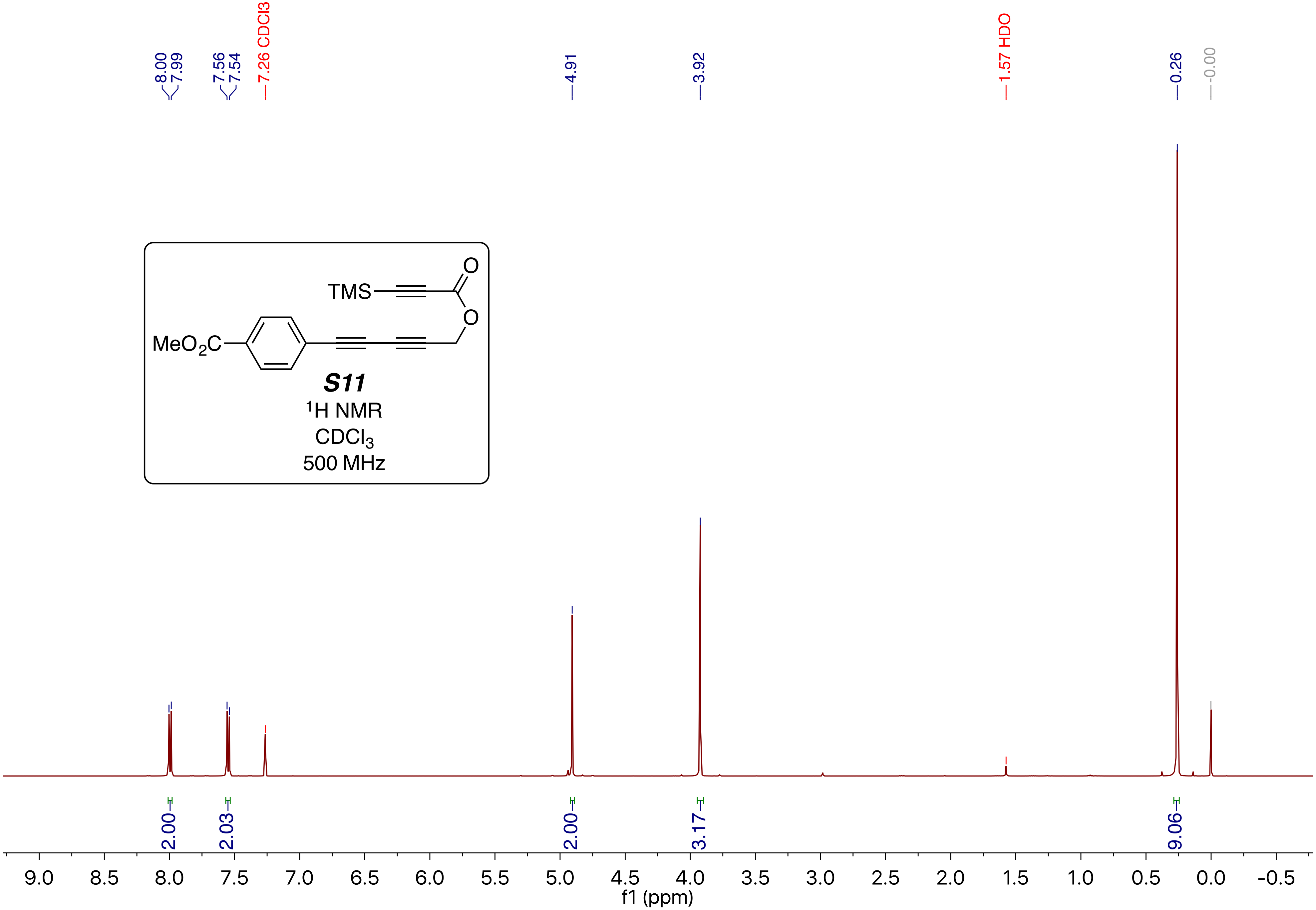


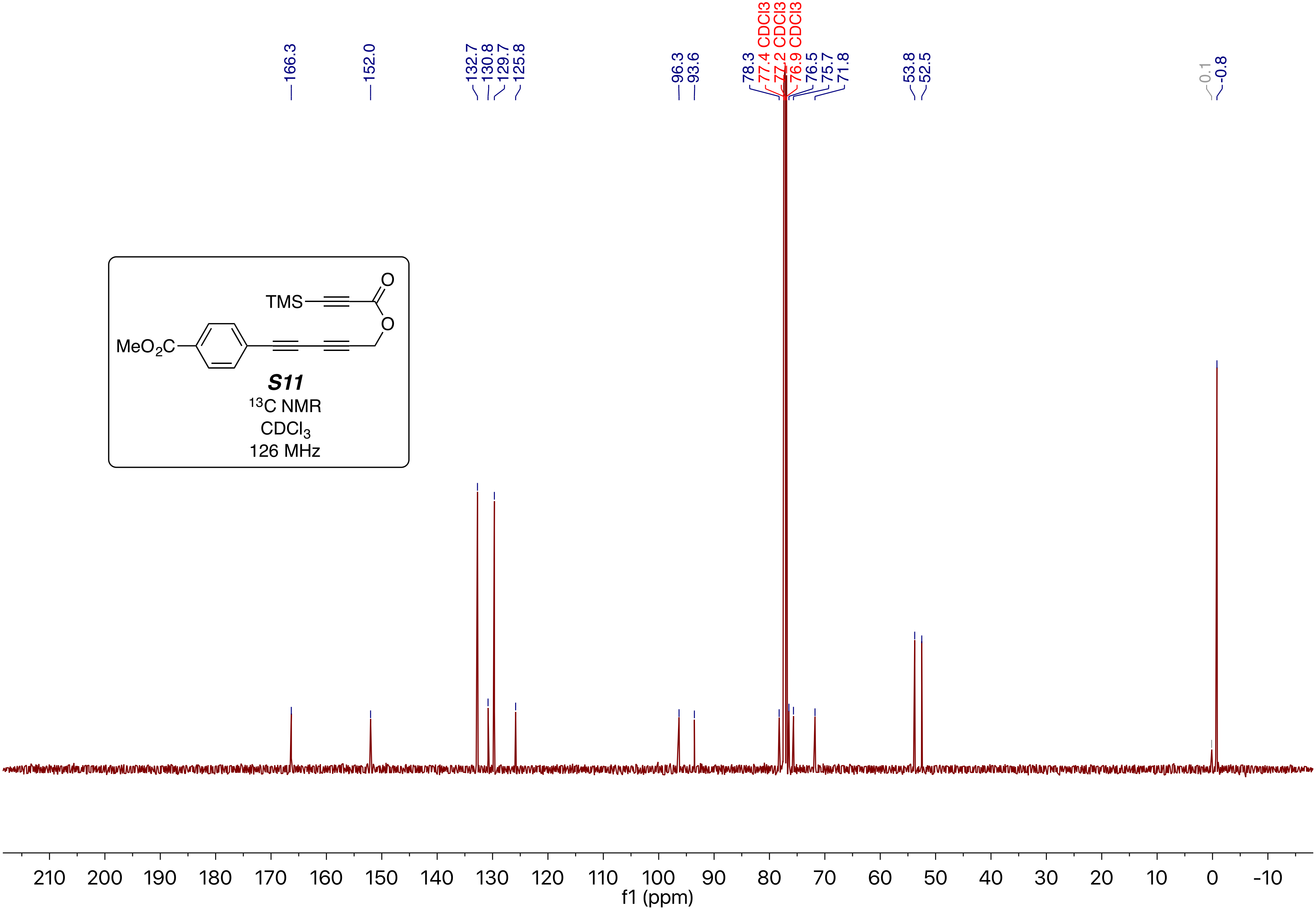
S10

^{13}C NMR

$CDCl_3$

126 MHz


8.00
7.99
7.56
7.54
7.26 CDCl3
4.91
3.92
1.57 HDO
0.26
-0.00
TMS
O
O
MeO_2C
S11
^1H NMR
$CDCl_3$
500 MHz
2.00
2.03
2.00
3.17
9.06
9.0
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
f1 (ppm)

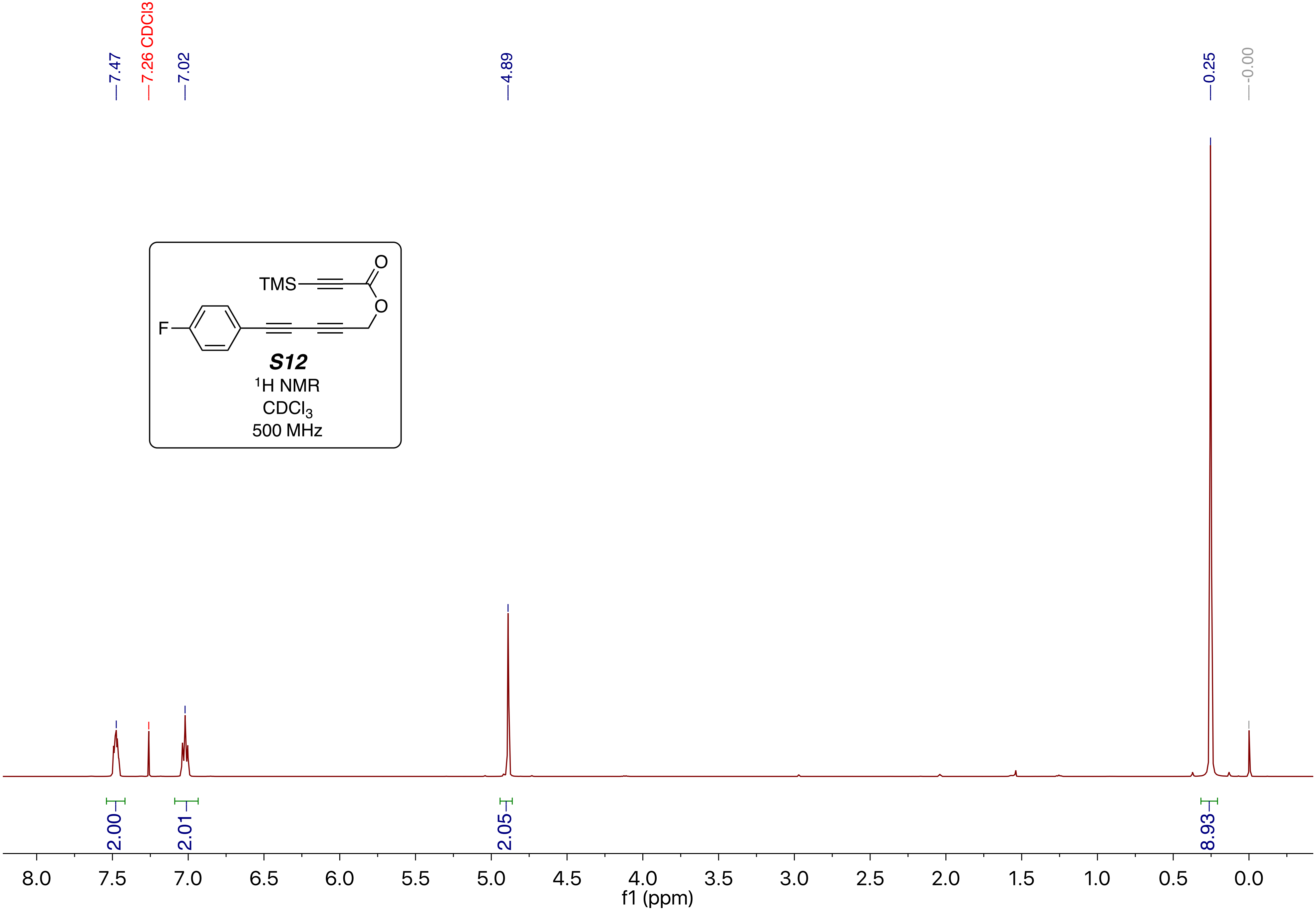


S11

^{13}C NMR

$CDCl_3$

126 MHz

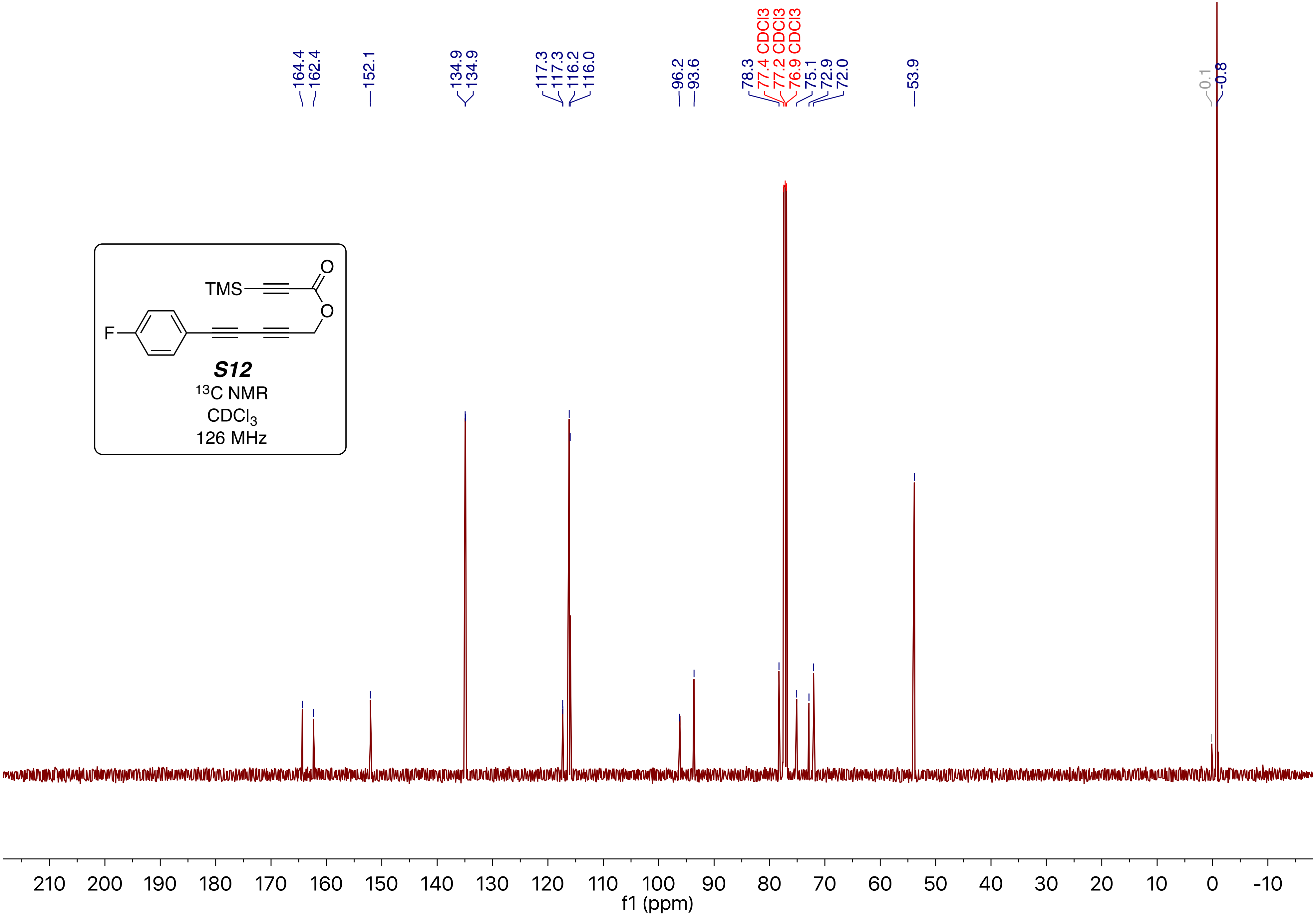


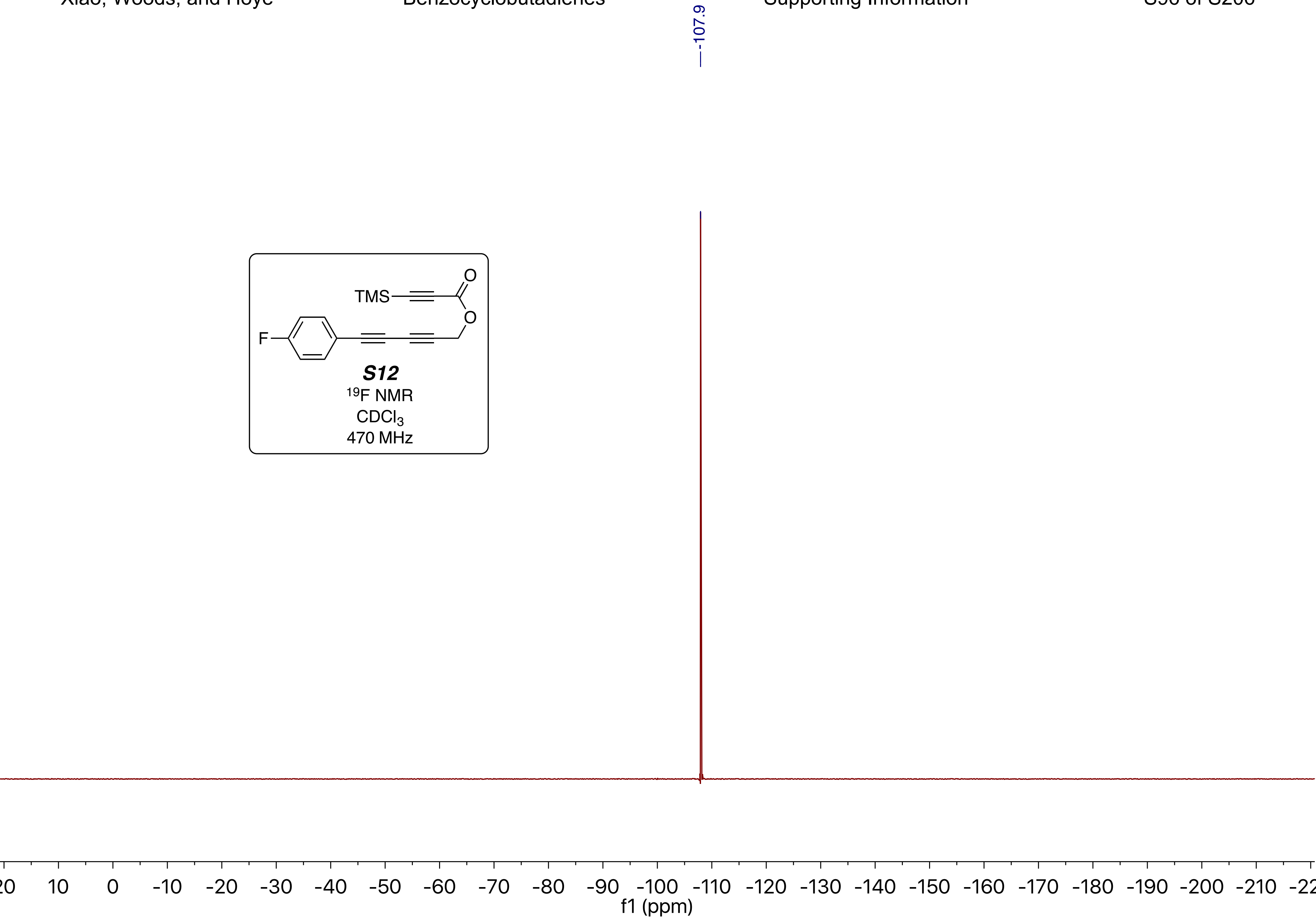
S12

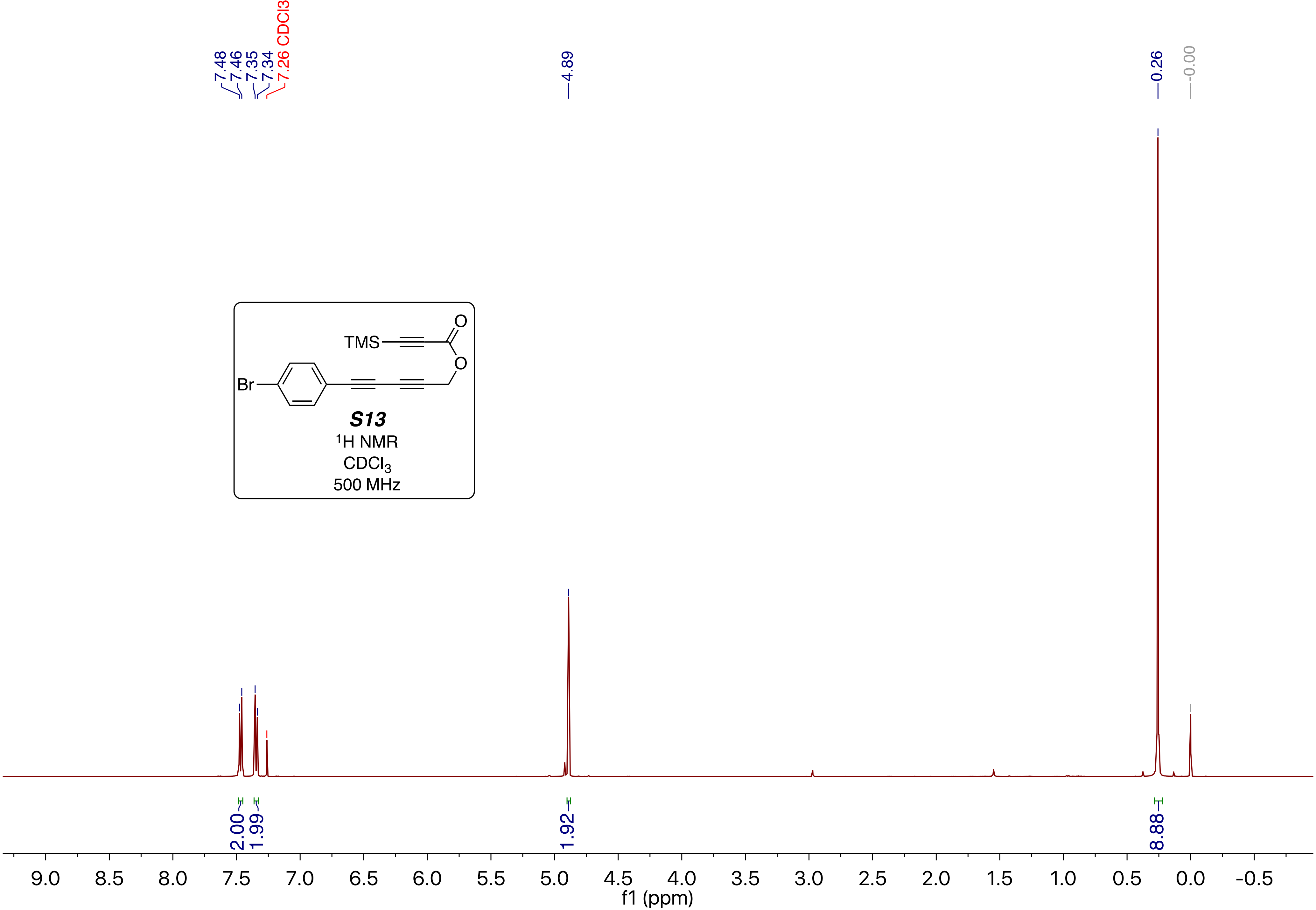
^{1}H NMR

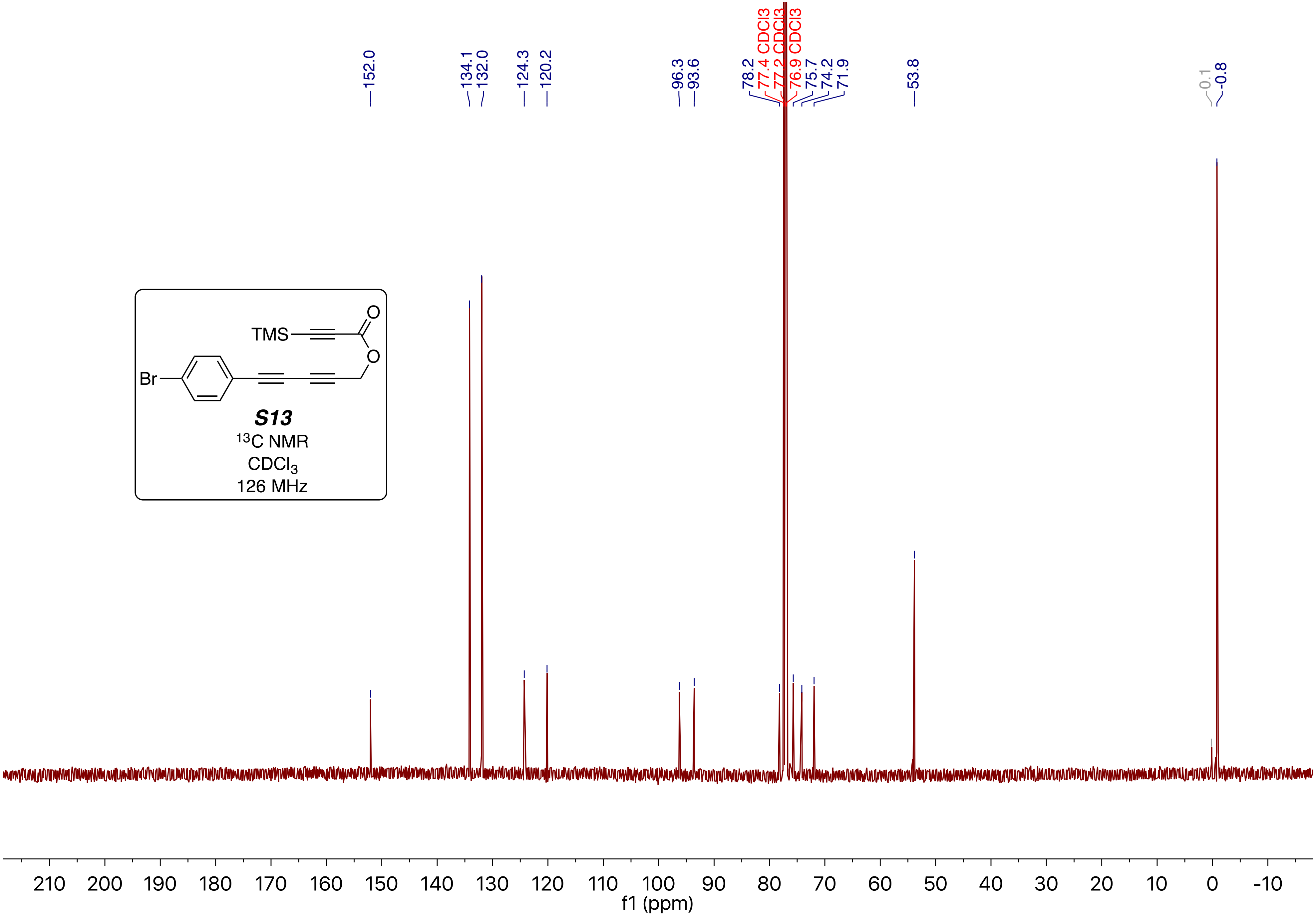
$CDCl_3$

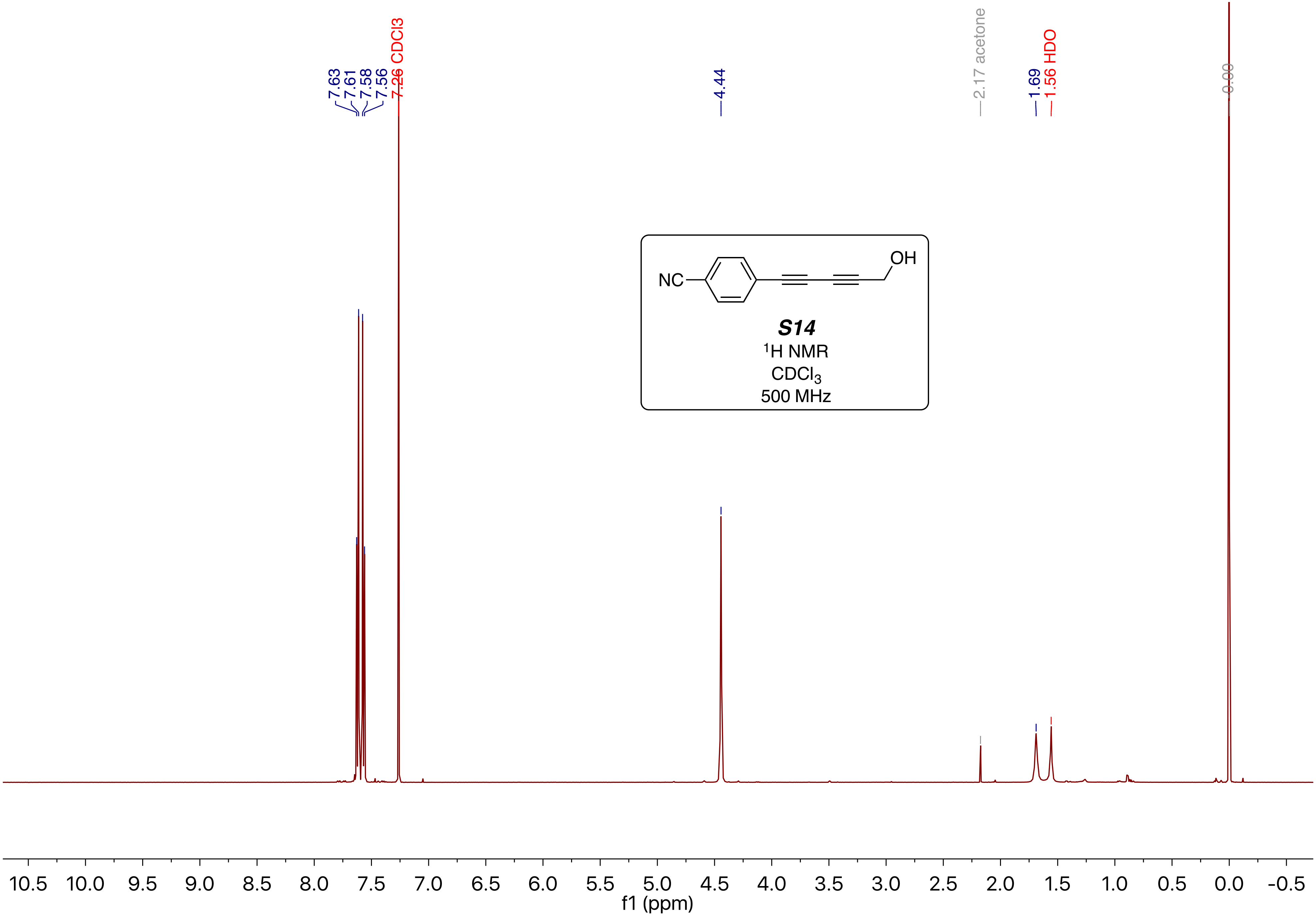
500 MHz

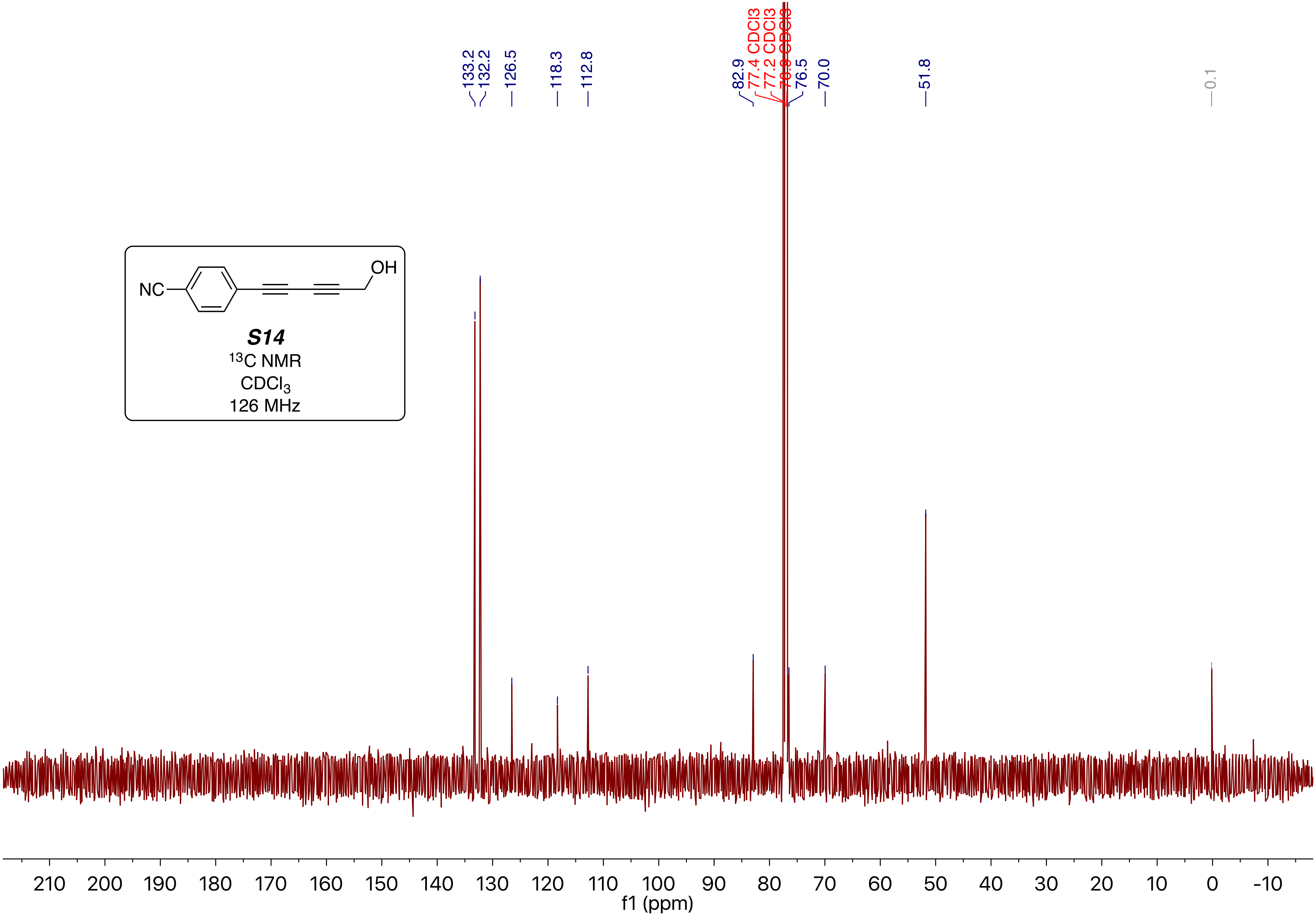

164.4
162.4
152.1
134.9
134.9
117.3
117.3
116.2
116.0
96.2
93.6
78.3
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
75.1
72.9
72.0
53.9
0.1
-0.8
TMS
O
O
F
S12
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

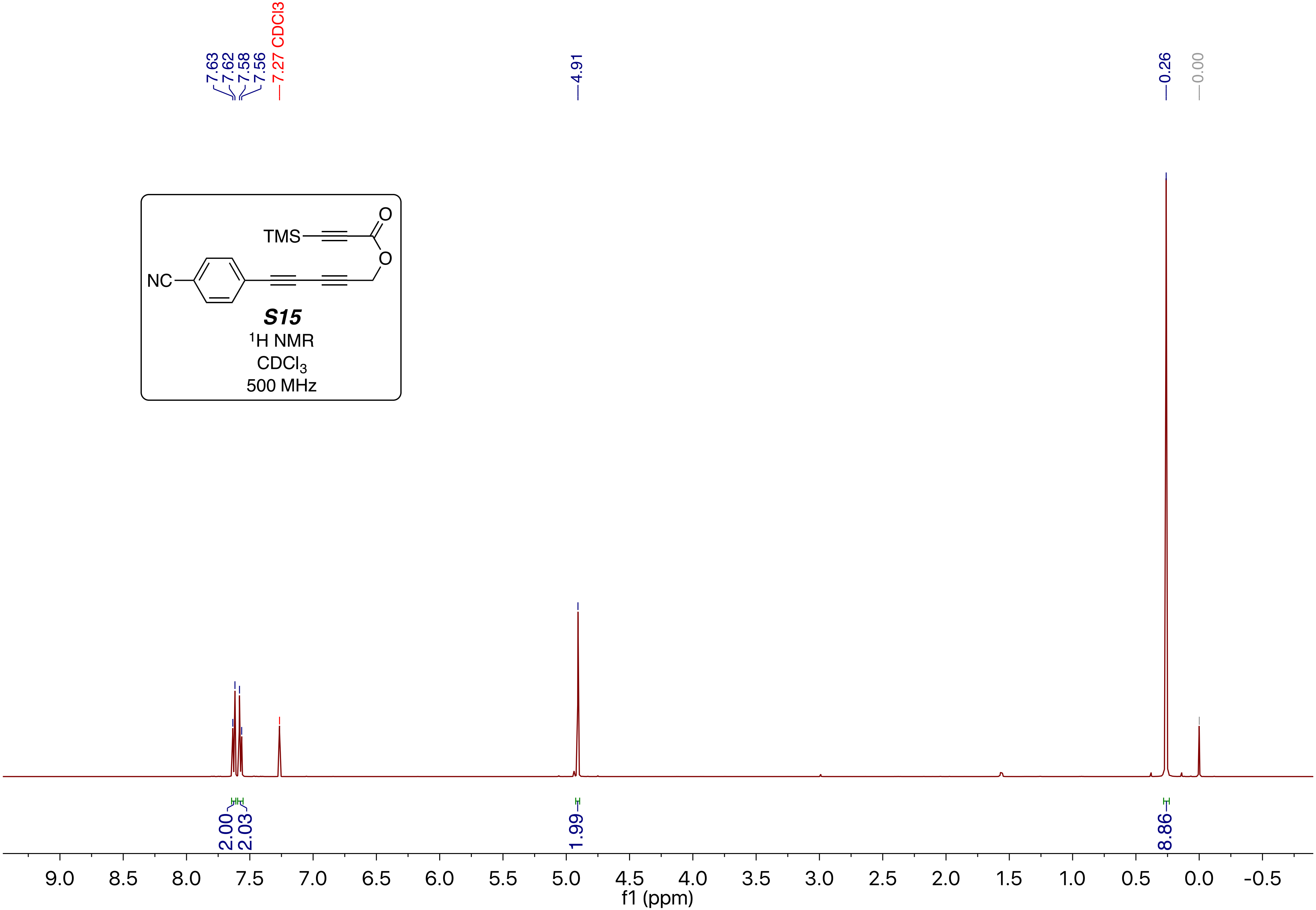

-107.9
TMS
O
O
F
S12
^{19}F NMR
CDCl$_3$
470 MHz
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

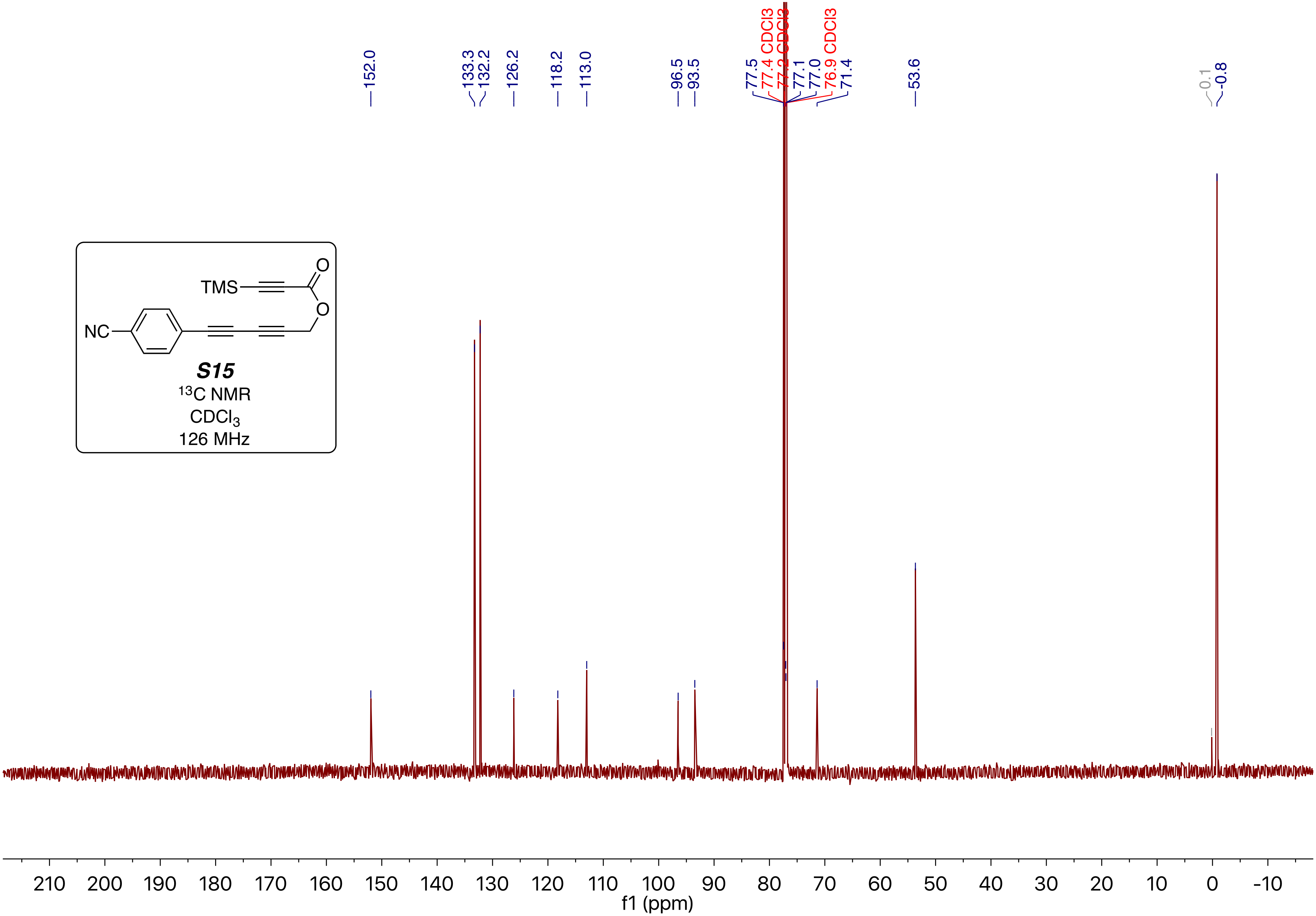

7.48
7.46
7.35
7.34
7.26 CDCl3
4.89
0.26
-0.00
TMS
O
O
Br
S13
^{1}H NMR
$CDCl_3$
500 MHz
2.00
1.99
1.92
8.88
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

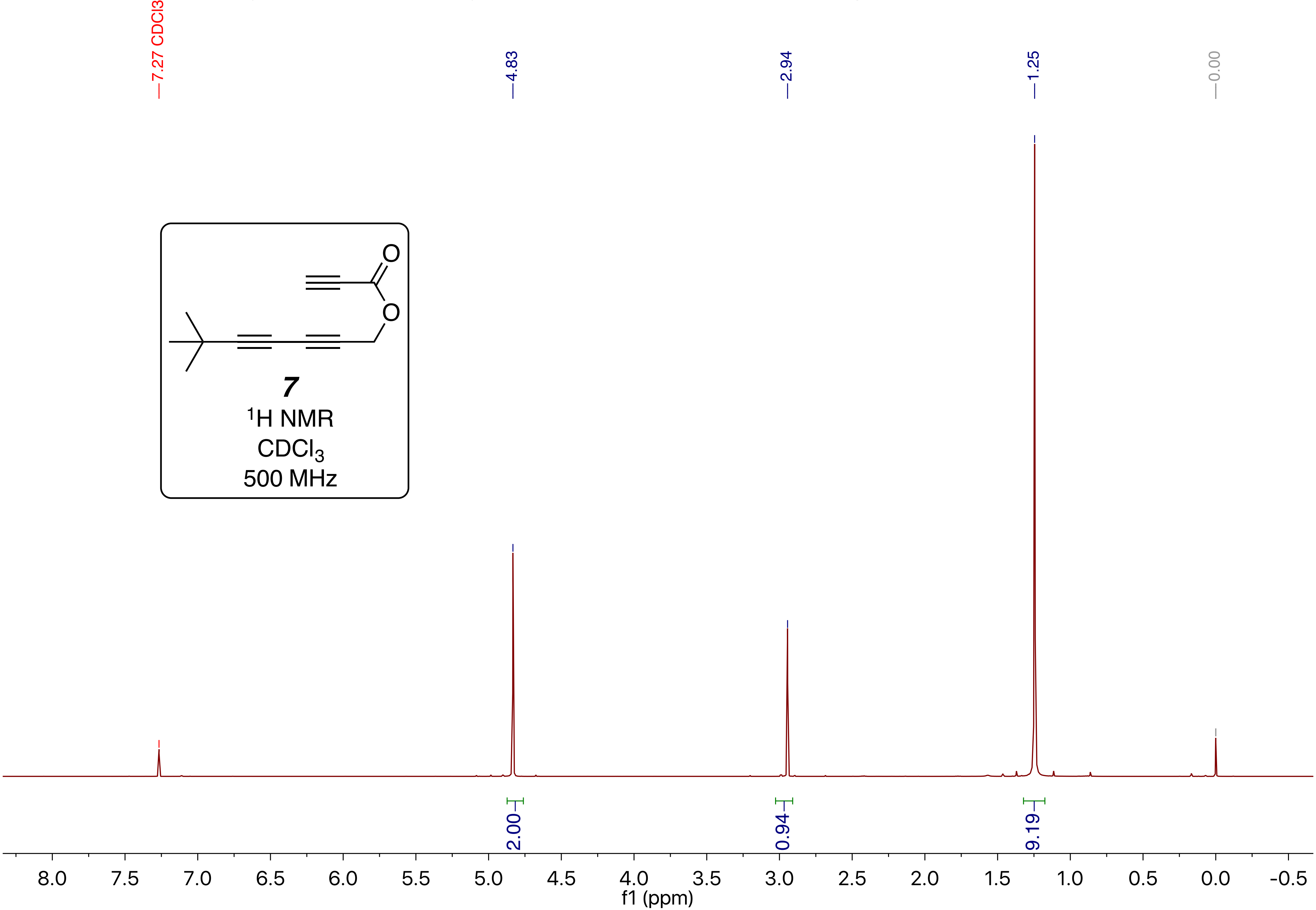

152.0
134.1
132.0
124.3
120.2
96.3
93.6
78.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
75.7
74.2
71.9
53.8
0.1
-0.8
TMS
O
O
Br
S13
^{13}C NMR
$CDCl_3$
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

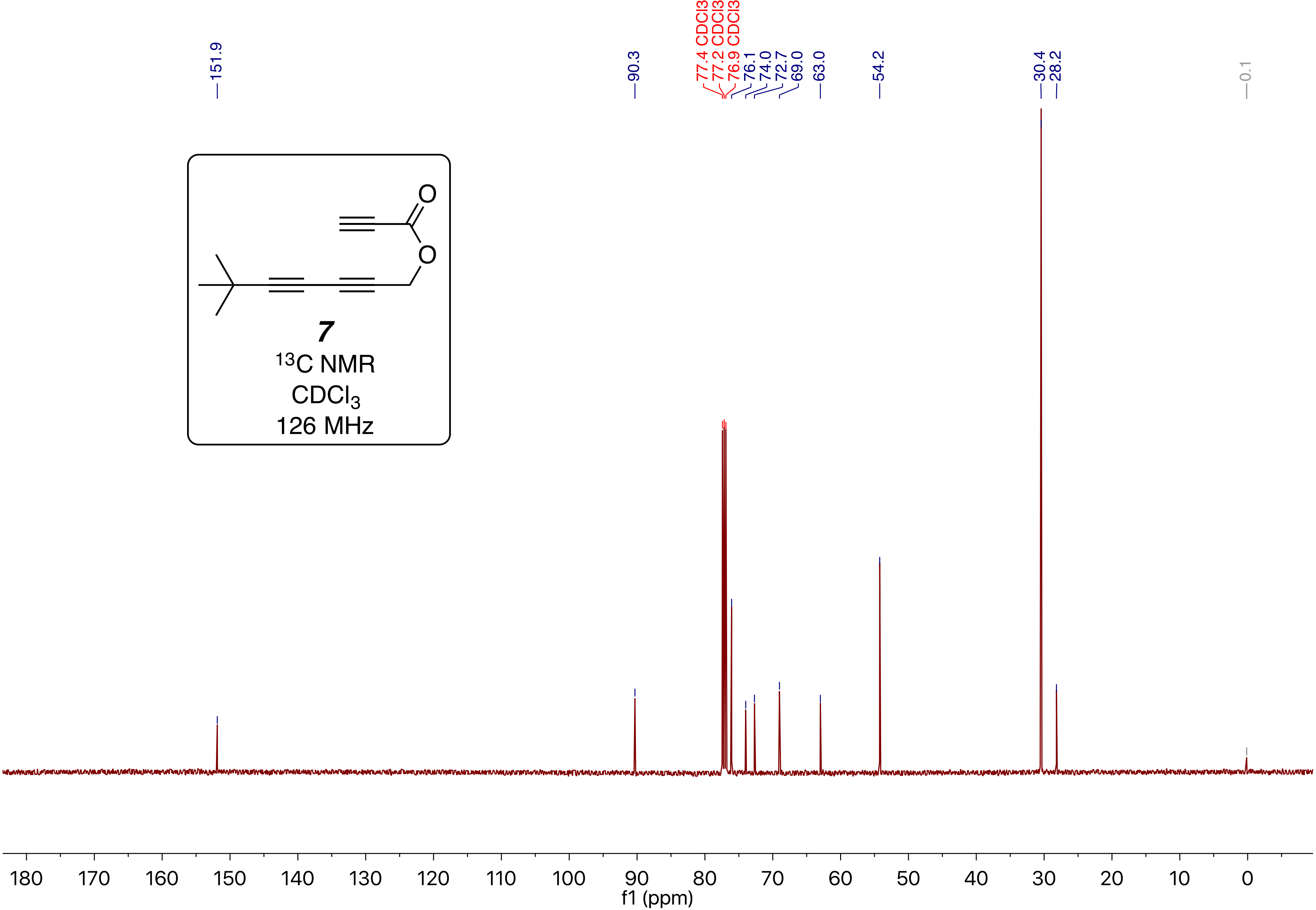

7.63
7.61
7.58
7.56
7.26 CDCl3
4.44
2.17 acetone
1.69
1.56 HDO
0.00
NC
OH
S14
^{1}H NMR
CDCl$_3$
500 MHz
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

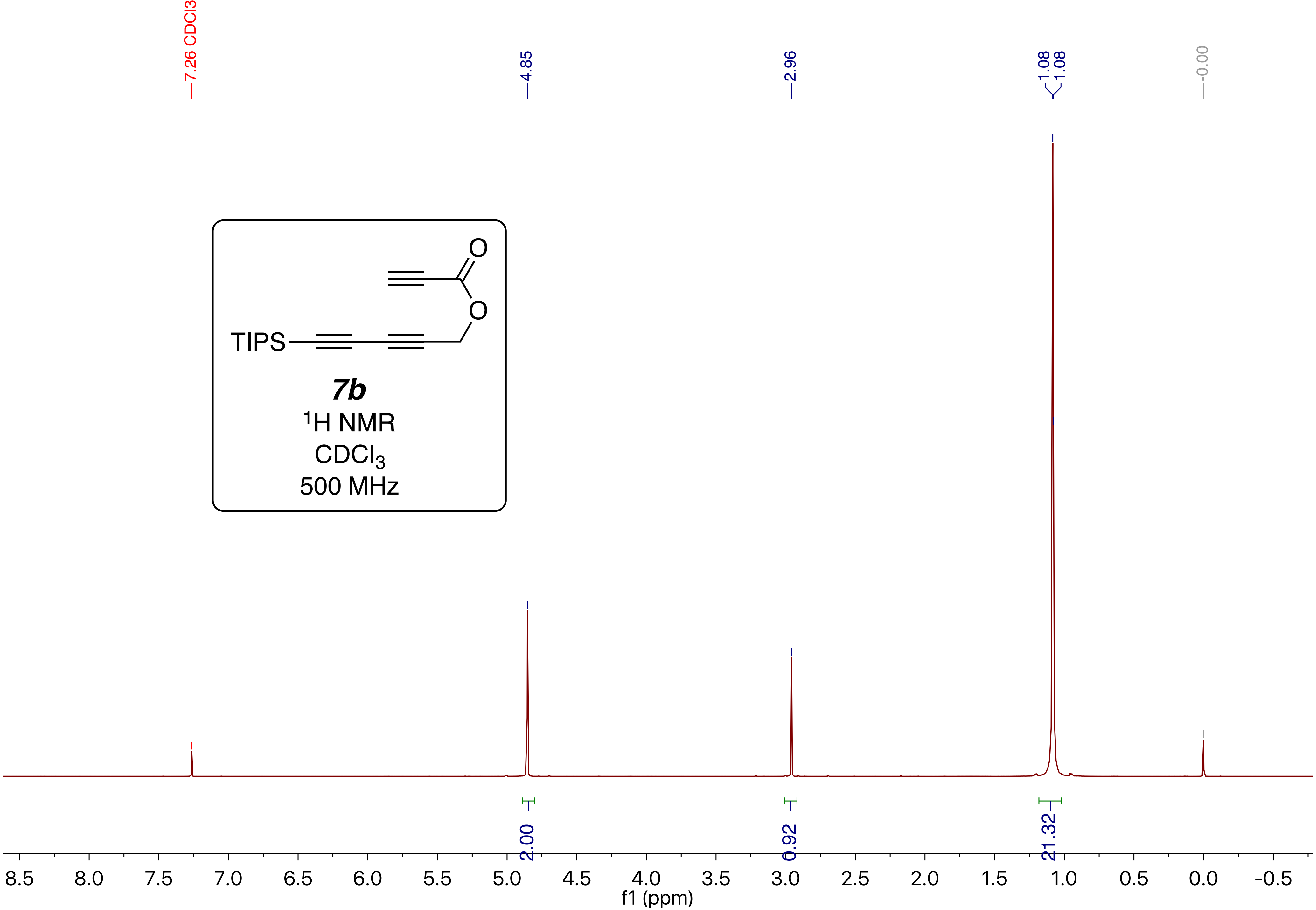

133.2
132.2
126.5
118.3
112.8
82.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.5
70.0
51.8
0.1
NC
OH
S14
^{13}C NMR
$CDCl_3$
126 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.63
7.62
7.58
7.56
7.27 CDCl3
4.91
0.26
0.00
TMS
O
O
NC
S15
^{1}H NMR
CDCl$_3$
500 MHz
2.00
2.03
1.99
8.86
9.0
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
f1 (ppm)


152.0
133.3
132.2
126.2
118.2
113.0
96.5
93.5
77.5
77.4 CDCl3
77.2 CDCl3
77.1
77.0
76.9 CDCl3
71.4
53.6
0.1
-0.8
TMS
O
O
NC
S15
^{13}C NMR
$CDCl_3$
126 MHz
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
4.83
2.94
1.25
0.00
O
O
7
^{1}H NMR
$CDCl_3$
500 MHz
2.00
0.94
9.19
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)


151.9
90.3
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.1
74.0
72.7
69.0
63.0
54.2
30.4
28.2
0.1
O
O
7
^{13}C NMR
$CDCl_3$
126 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

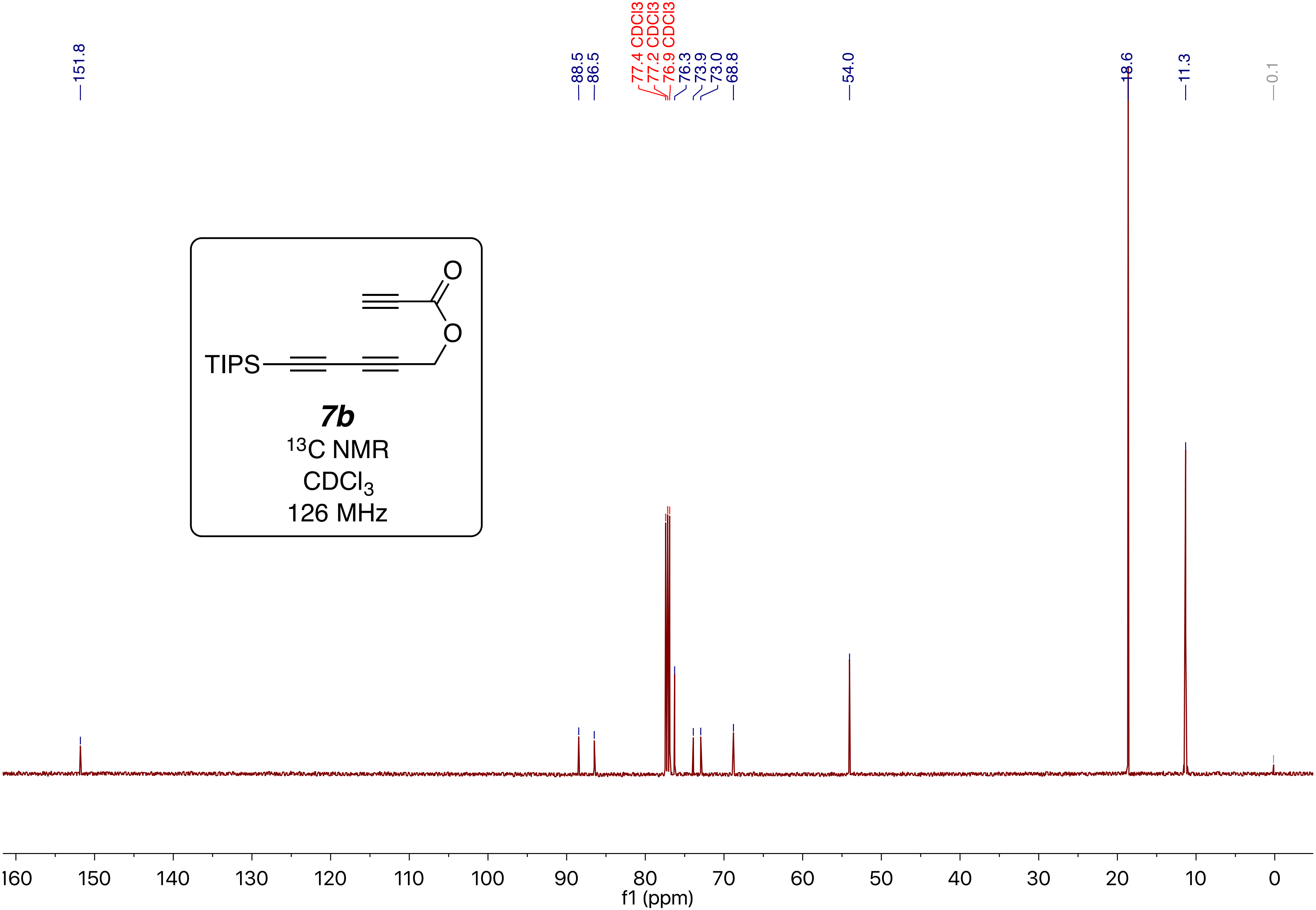


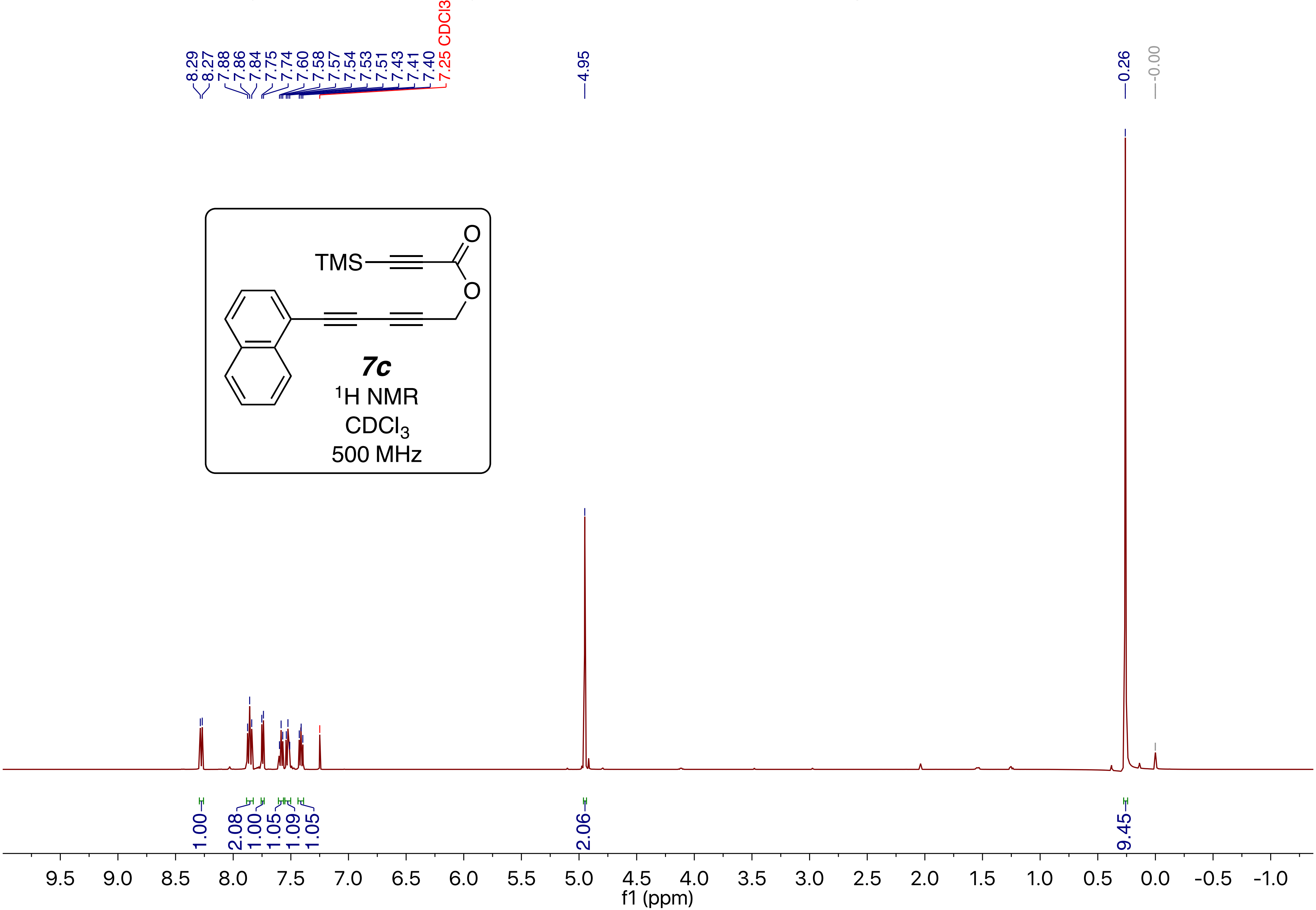
7b

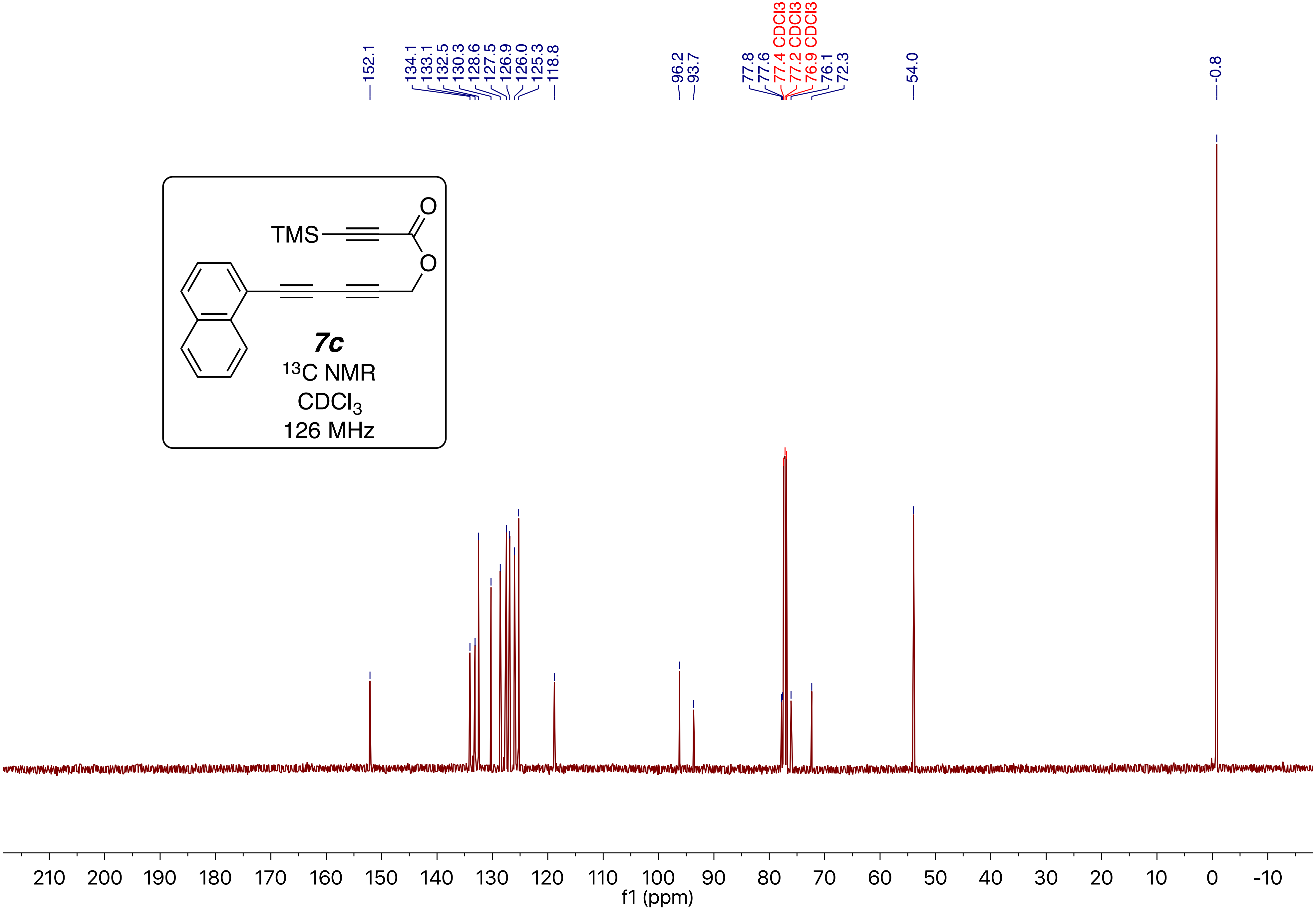
^{1}H NMR

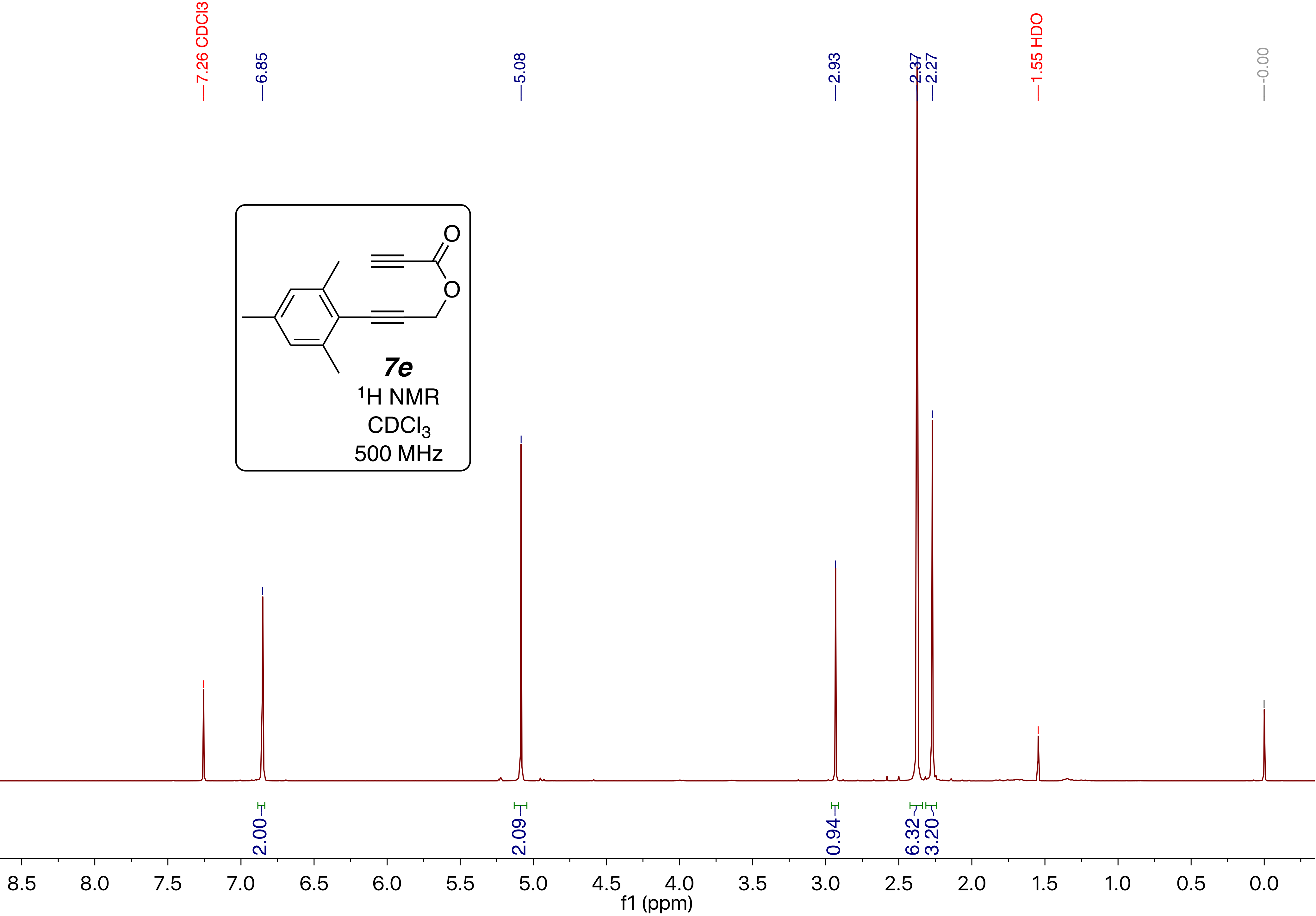
CDCl$_3$

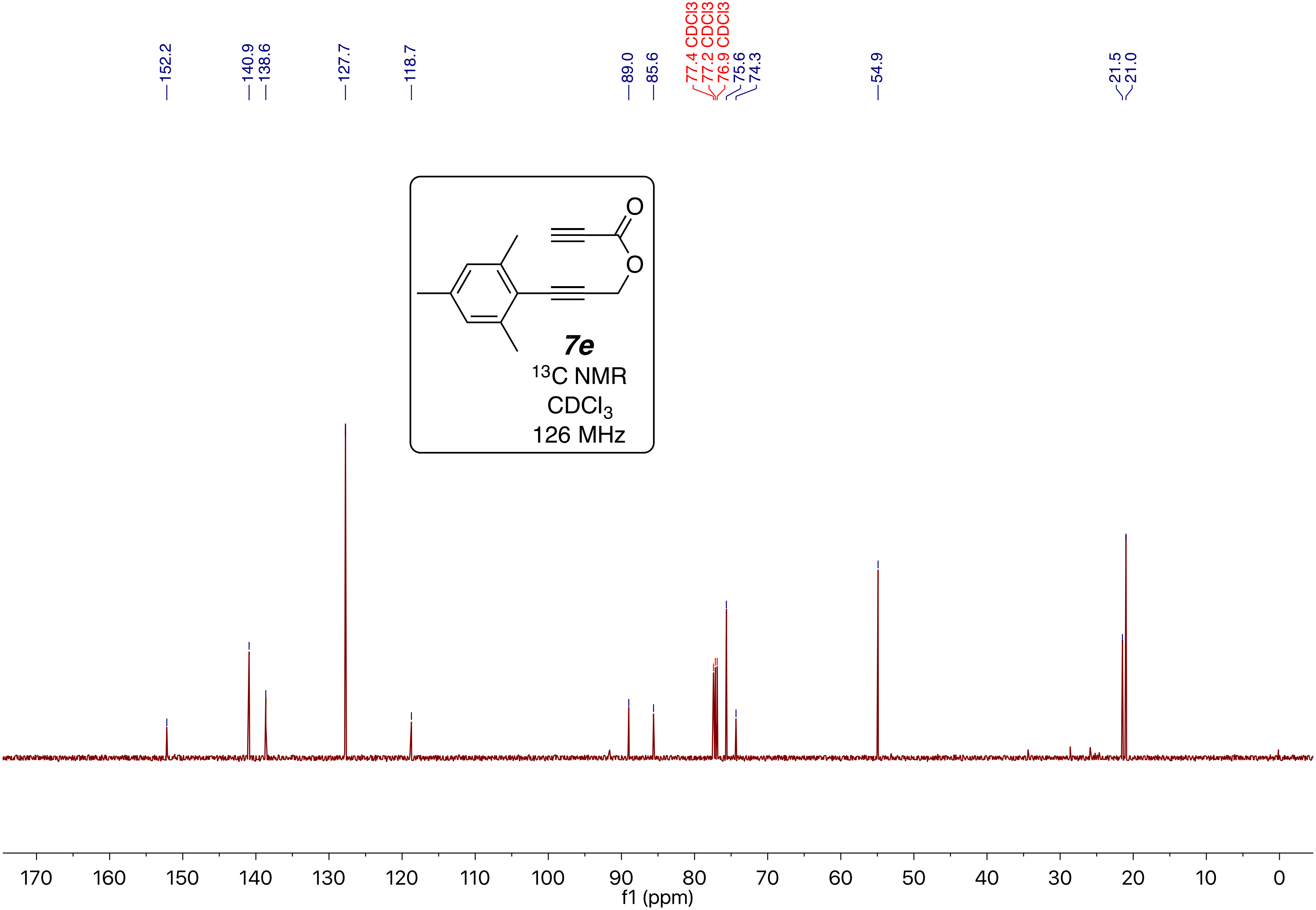
500 MHz

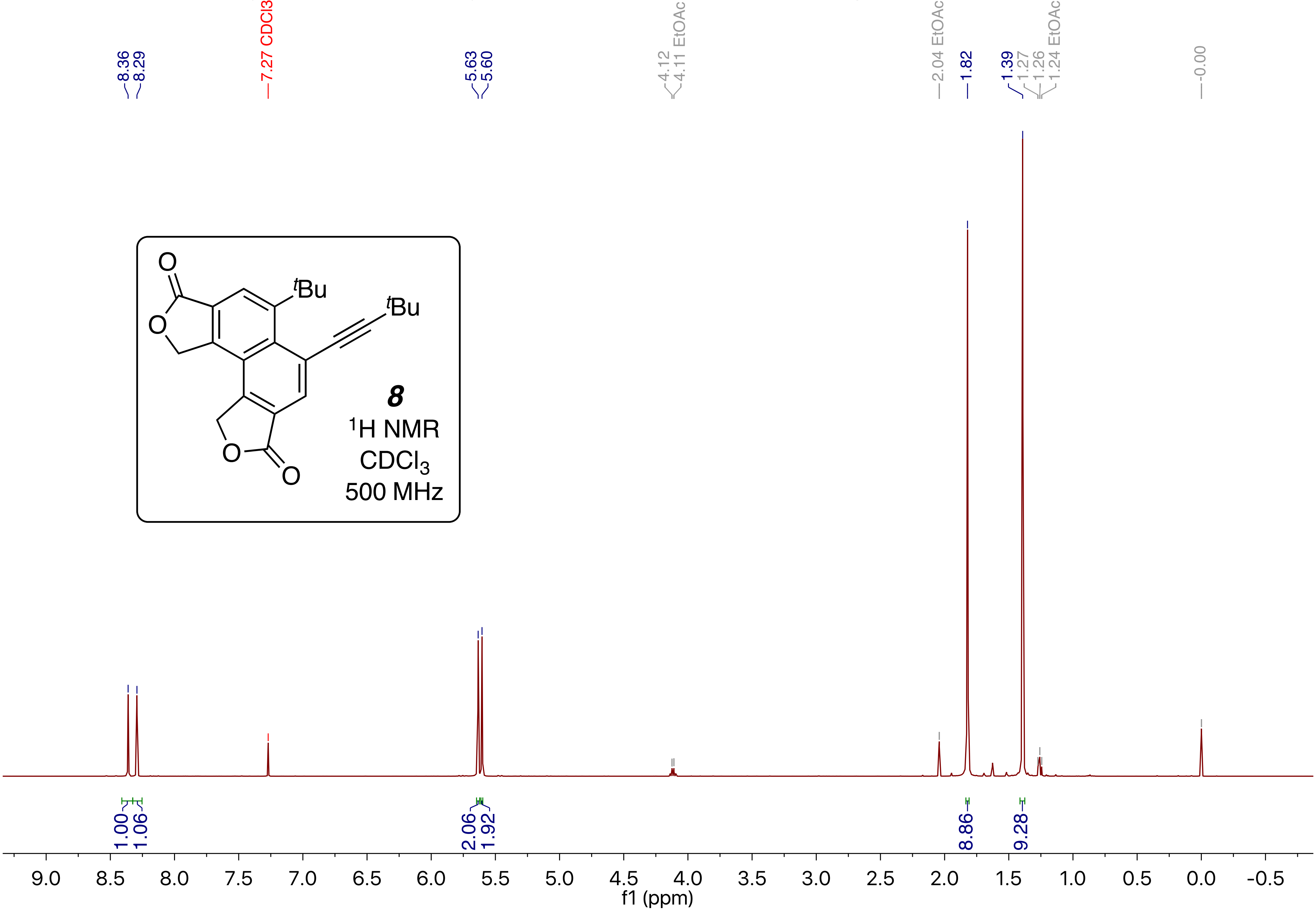

151.8
88.5
86.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.3
73.9
73.0
68.8
54.0
18.6
11.3
-0.1
TIPS
O
O
7b
^{13}C NMR
$CDCl_3$
126 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

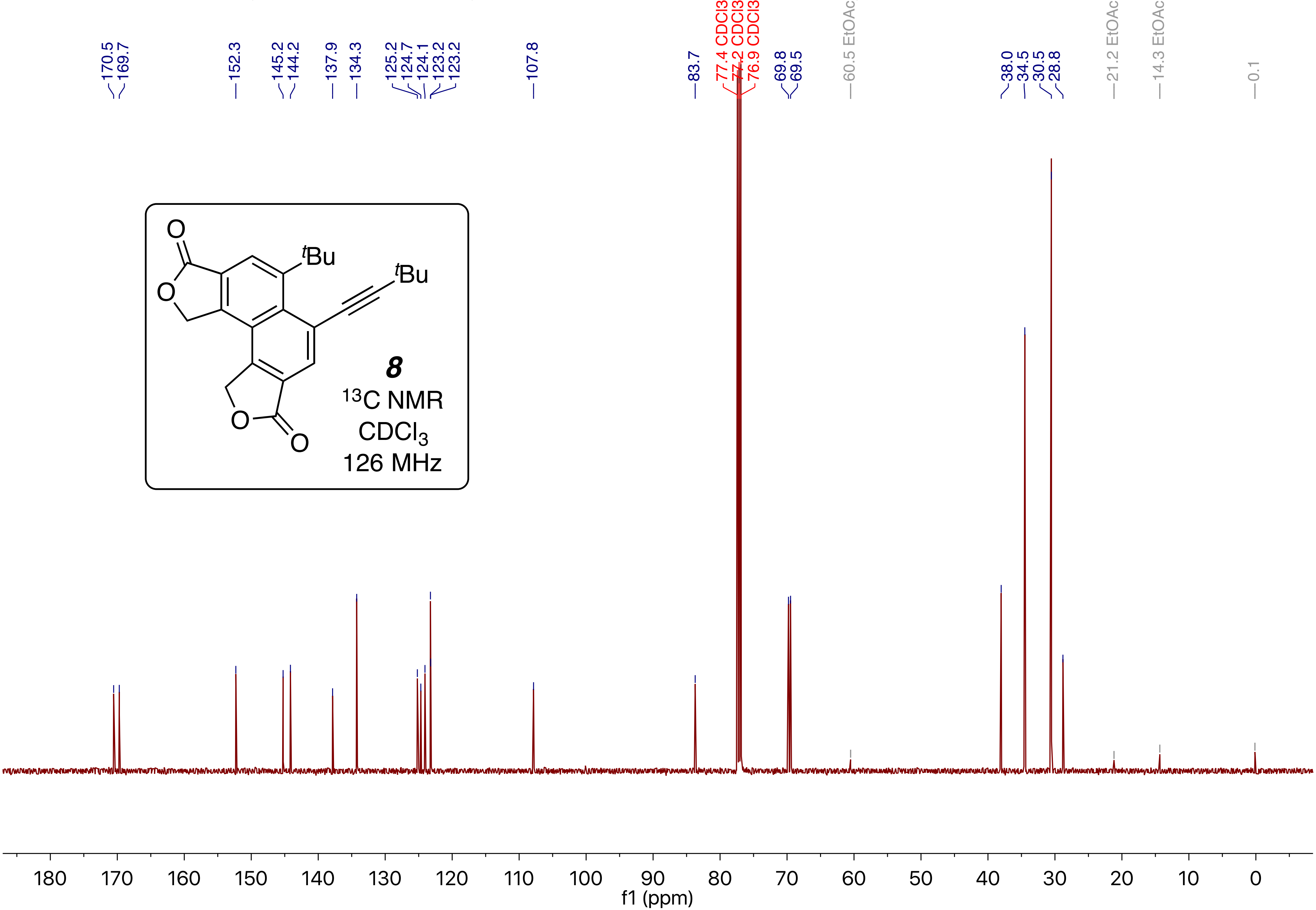

8.29
8.27
7.88
7.86
7.84
7.75
7.74
7.60
7.58
7.57
7.54
7.53
7.51
7.43
7.41
7.40
7.25 CDCl3
4.95
0.26
-0.00
TMS
O
O
7c
^{1}H NMR
CDCl$_3$
500 MHz
1.00
2.08
1.00
1.05
1.09
1.05
2.06
9.45
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

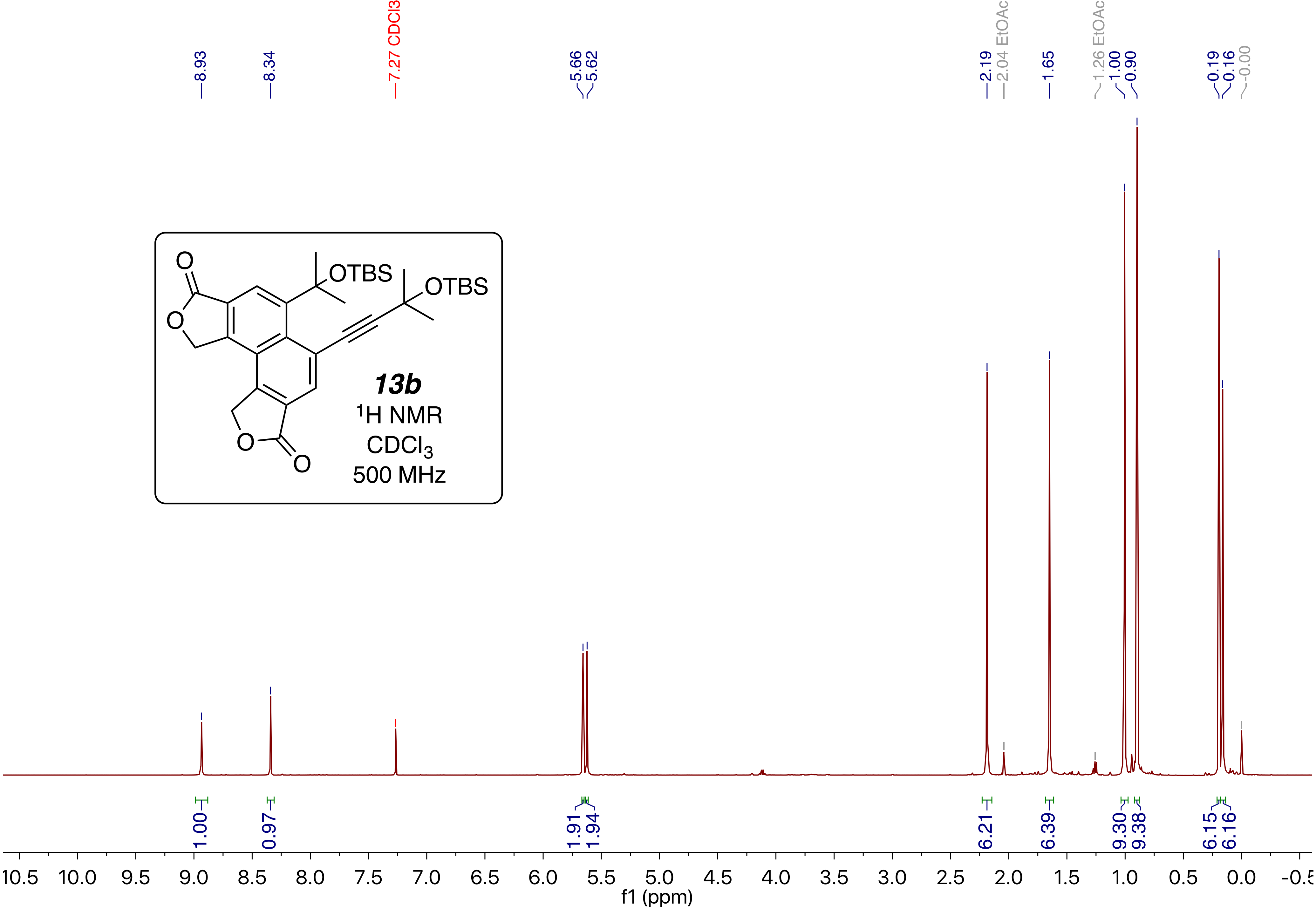

152.1
134.1
133.1
132.5
130.3
128.6
127.5
126.9
126.0
125.3
118.8
96.2
93.7
77.8
77.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.1
72.3
54.0
-0.8
TMS
O
O
7c
^{13}C NMR
$CDCl_3$
126 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26 CDCl3
6.85
5.08
2.93
2.37
2.27
1.55 HDO
-0.00
7e
^{1}H NMR
CDCl$_3$
500 MHz
2.00
2.09
0.94
6.32
3.20
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
f1 (ppm)


152.2
140.9
138.6
127.7
118.7
89.0
85.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
75.6
74.3
54.9
21.5
21.0
O
O
7e
^{13}C NMR
$CDCl_3$
126 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.36
8.29
7.27 CDCl3
5.63
5.60
4.12
4.11 EtOAc
2.04 EtOAc
1.82
1.39
1.27
1.26
1.24 EtOAc
-0.00
O
O
O
O
tBu
tBu
8
¹H NMR
CDCl3
500 MHz
1.00
1.06
2.06
1.92
8.86
9.28
9.0
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
f1 (ppm)


170.5
169.7
152.3
145.2
144.2
137.9
134.3
125.2
124.7
124.1
123.2
123.2
107.8
83.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
69.8
69.5
60.5 EtOAc
38.0
34.5
30.5
28.8
21.2 EtOAc
14.3 EtOAc
0.1
O
O
tBu
tBu
O
O
8
13C NMR
CDCl3
126 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

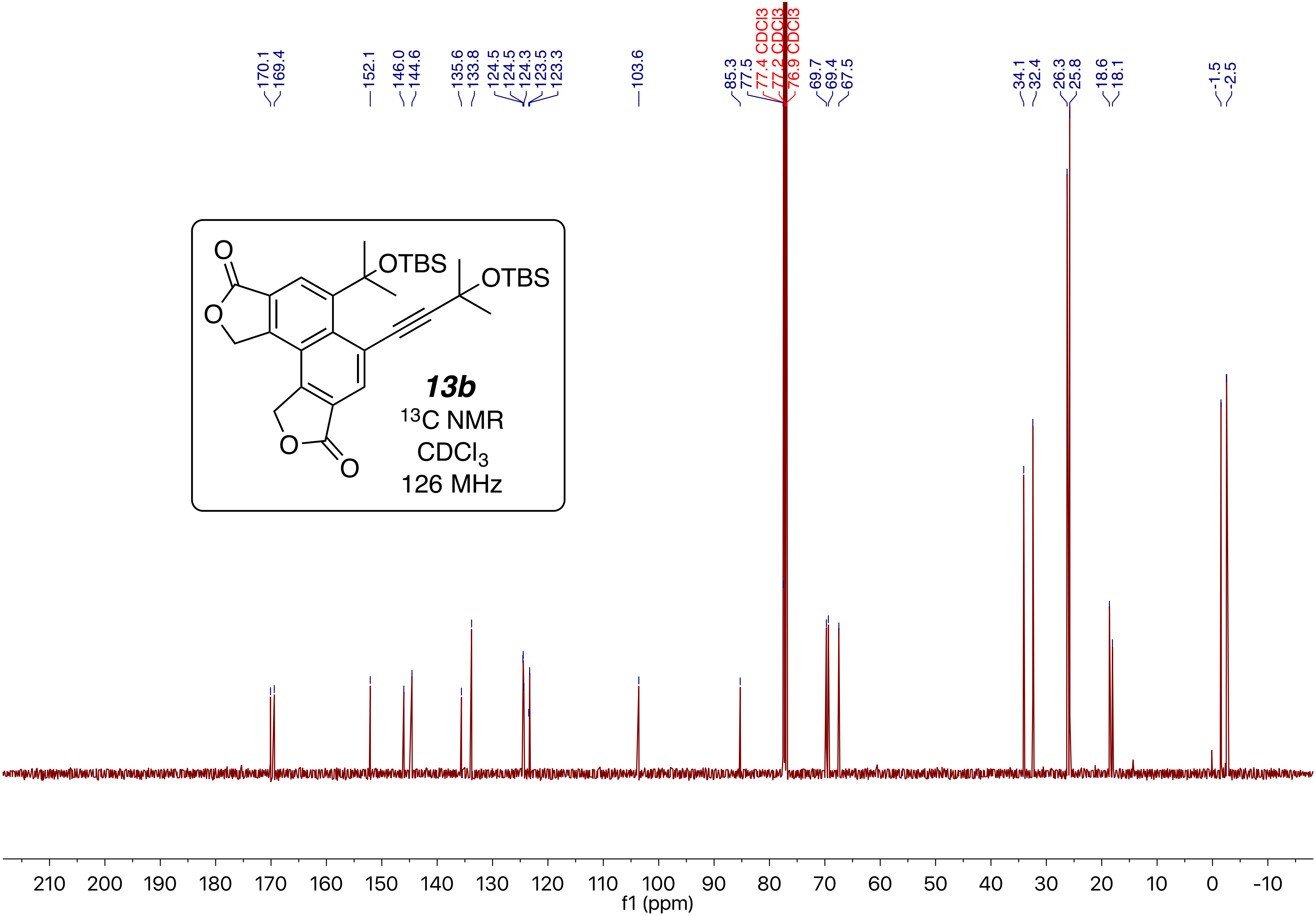


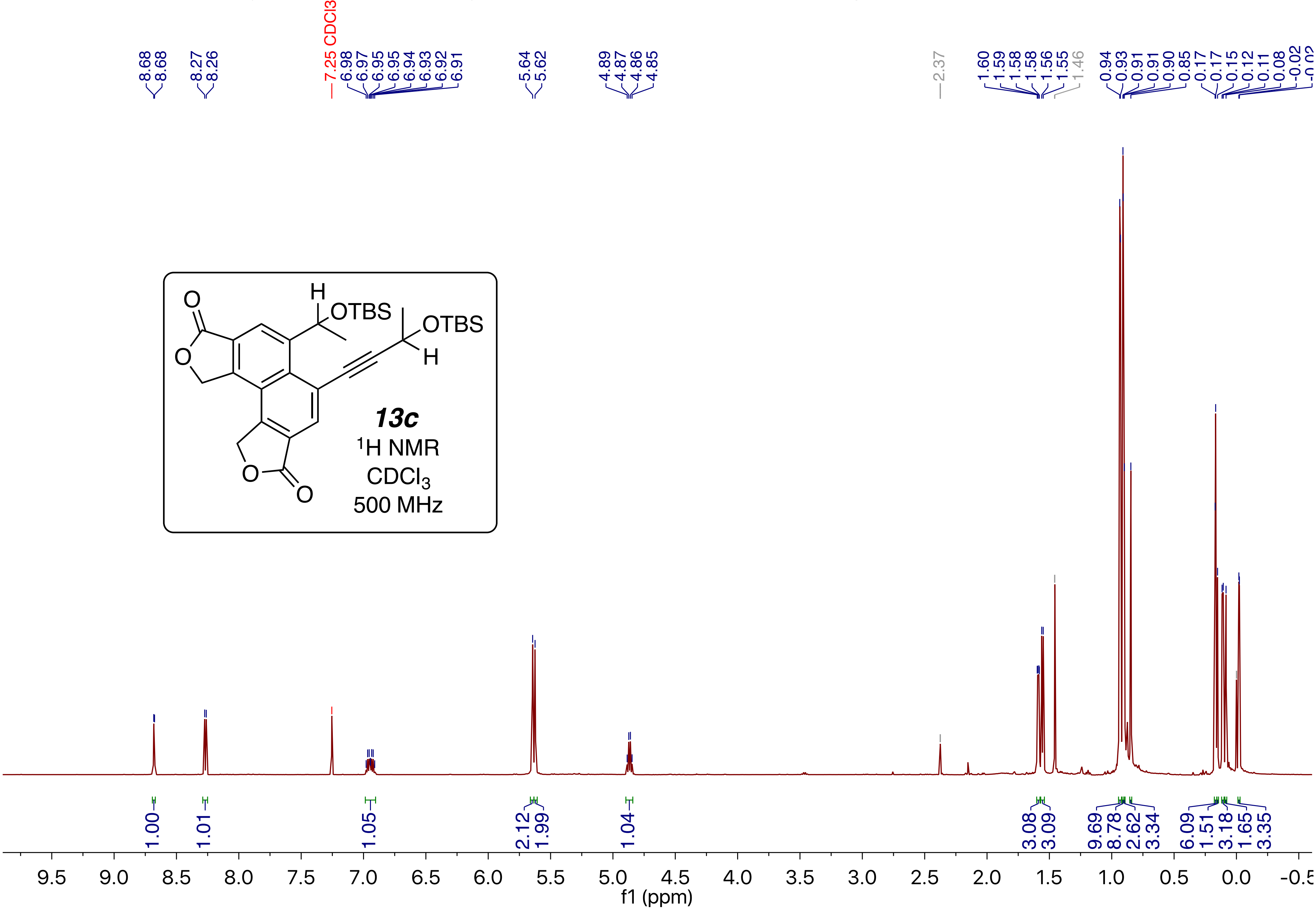
13b

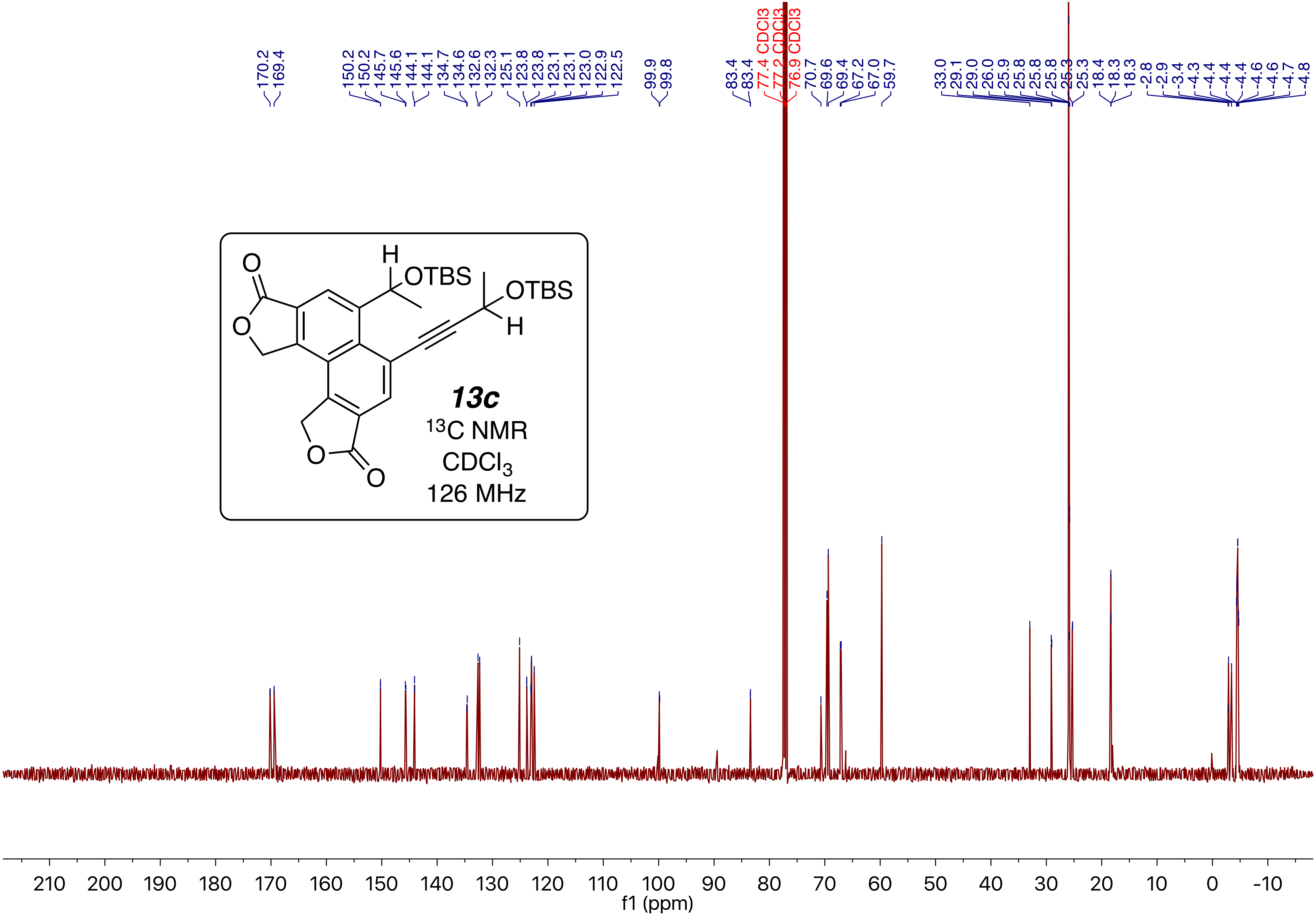
^{1}H NMR

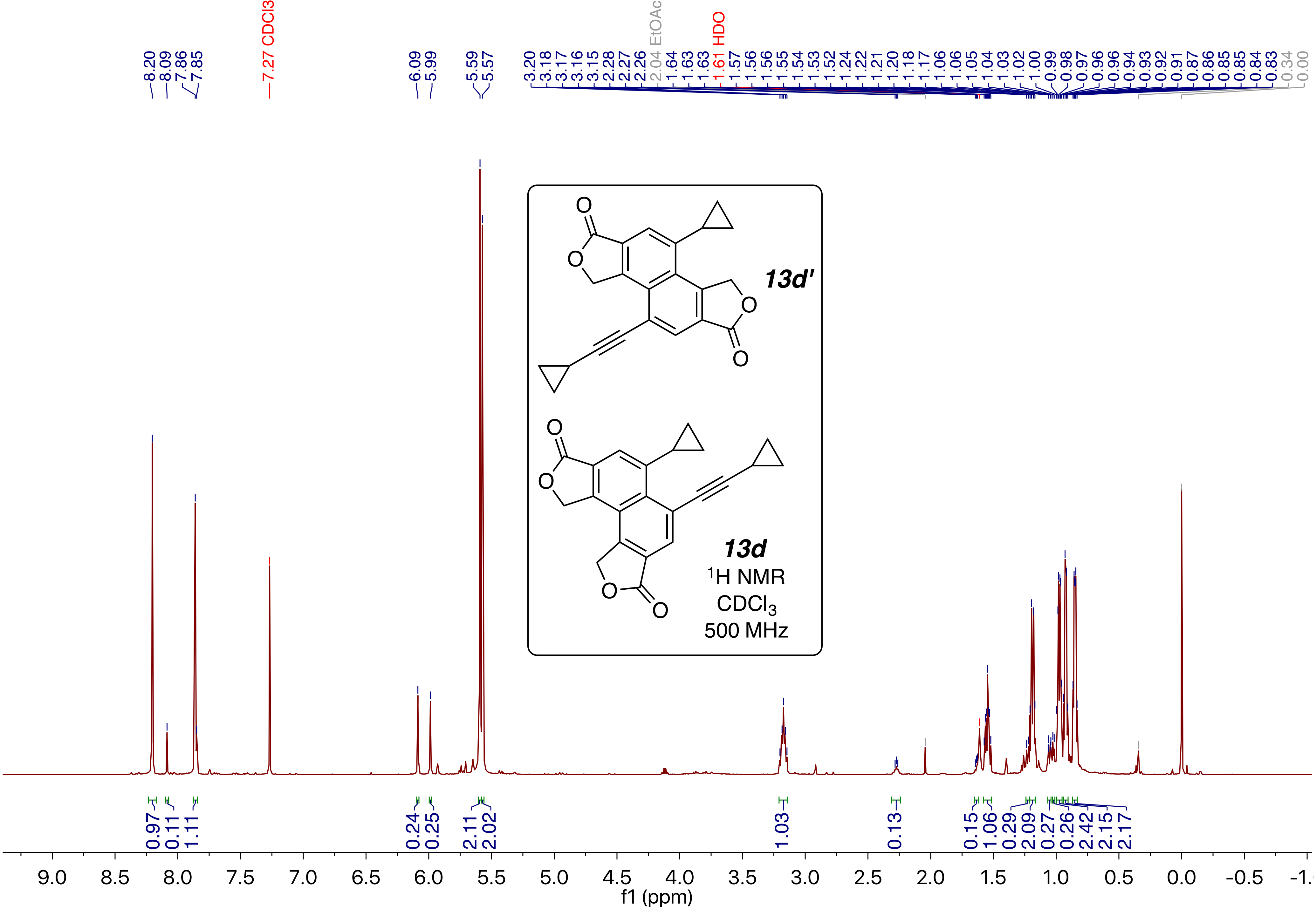
$CDCl_3$

500 MHz


170.1
169.4
152.1
146.0
144.6
135.6
133.8
124.5
124.5
124.3
123.5
123.3
103.6
85.3
77.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
69.7
69.4
67.5
34.1
32.4
26.3
25.8
18.6
18.1
-1.5
-2.5
O
O
OTBS
OTBS
O
O
13b
^{13}C NMR
$CDCl_3$
126 MHz
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)


7.25 CDCl3
8.68
8.68
8.27
8.26
6.98
6.97
6.95
6.95
6.94
6.93
6.92
6.91
5.64
5.62
4.89
4.87
4.86
4.85
2.37
1.60
1.59
1.58
1.58
1.56
1.55
1.46
0.94
0.93
0.91
0.91
0.90
0.85
0.17
0.17
0.15
0.12
0.11
0.08
-0.02
O
O
H
OTBS
OTBS
H
O
O
13c
1H NMR
CDCl3
500 MHz
1.00
1.01
1.05
2.12
1.99
1.04
3.08
3.09
9.69
8.78
2.62
3.34
6.09
1.51
3.18
1.65
3.35
9.5
9.0
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
f1 (ppm)


170.2
169.4
150.2
150.2
145.7
145.6
144.1
144.1
134.7
134.6
132.6
132.3
125.1
123.8
123.8
123.1
123.1
123.0
122.9
122.5
99.9
99.8
83.4
83.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
70.7
69.6
69.4
67.2
67.0
59.7
33.0
29.1
29.0
26.0
25.9
25.8
25.8
25.8
25.3
25.3
18.4
18.3
18.3
-2.8
-2.9
-3.4
-4.3
-4.4
-4.4
-4.4
-4.6
-4.6
-4.7
-4.8
O
O
H
OTBS
OTBS
H
O
O
13c
^{13}C NMR
$CDCl_3$
126 MHz
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)



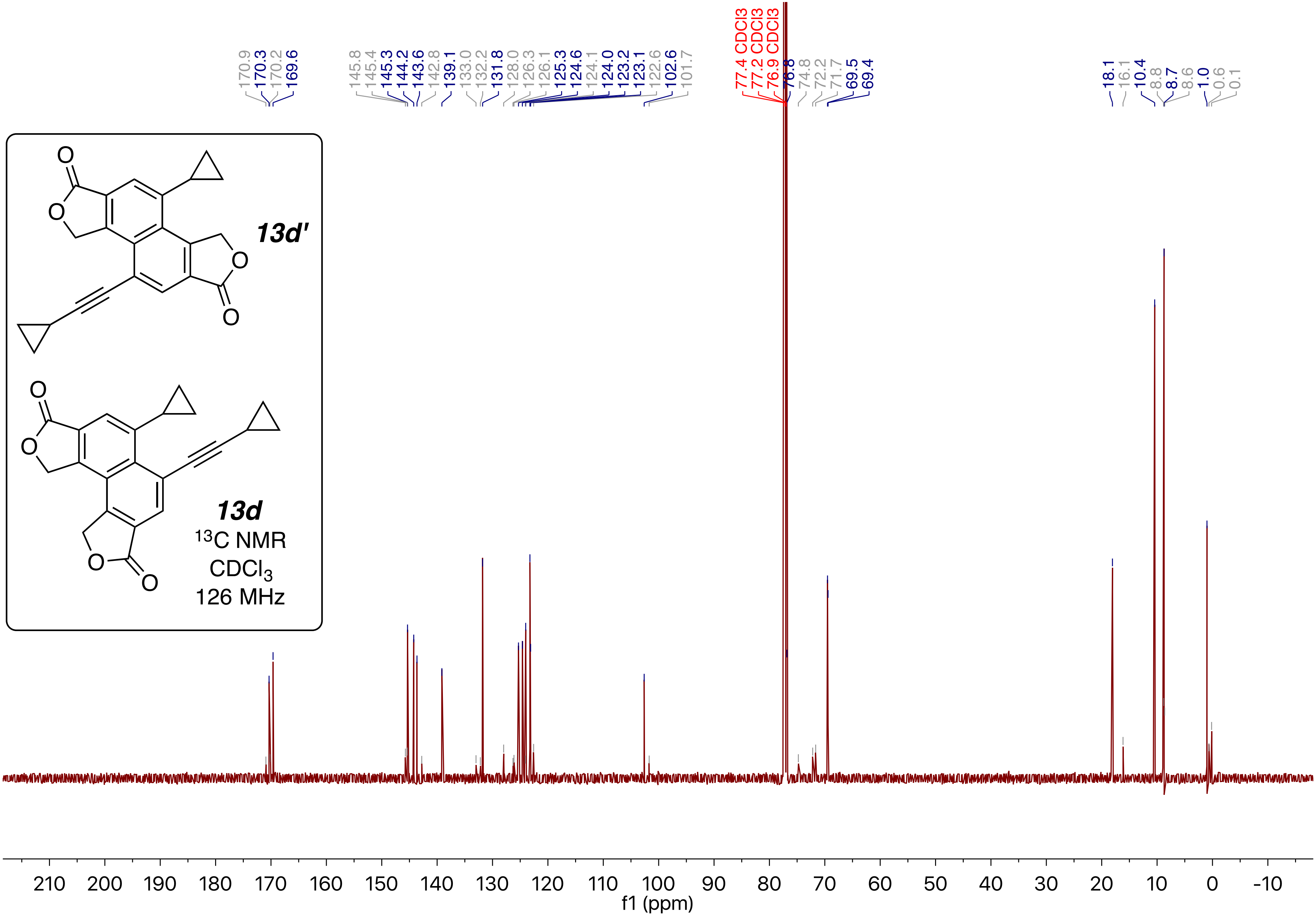
13d'

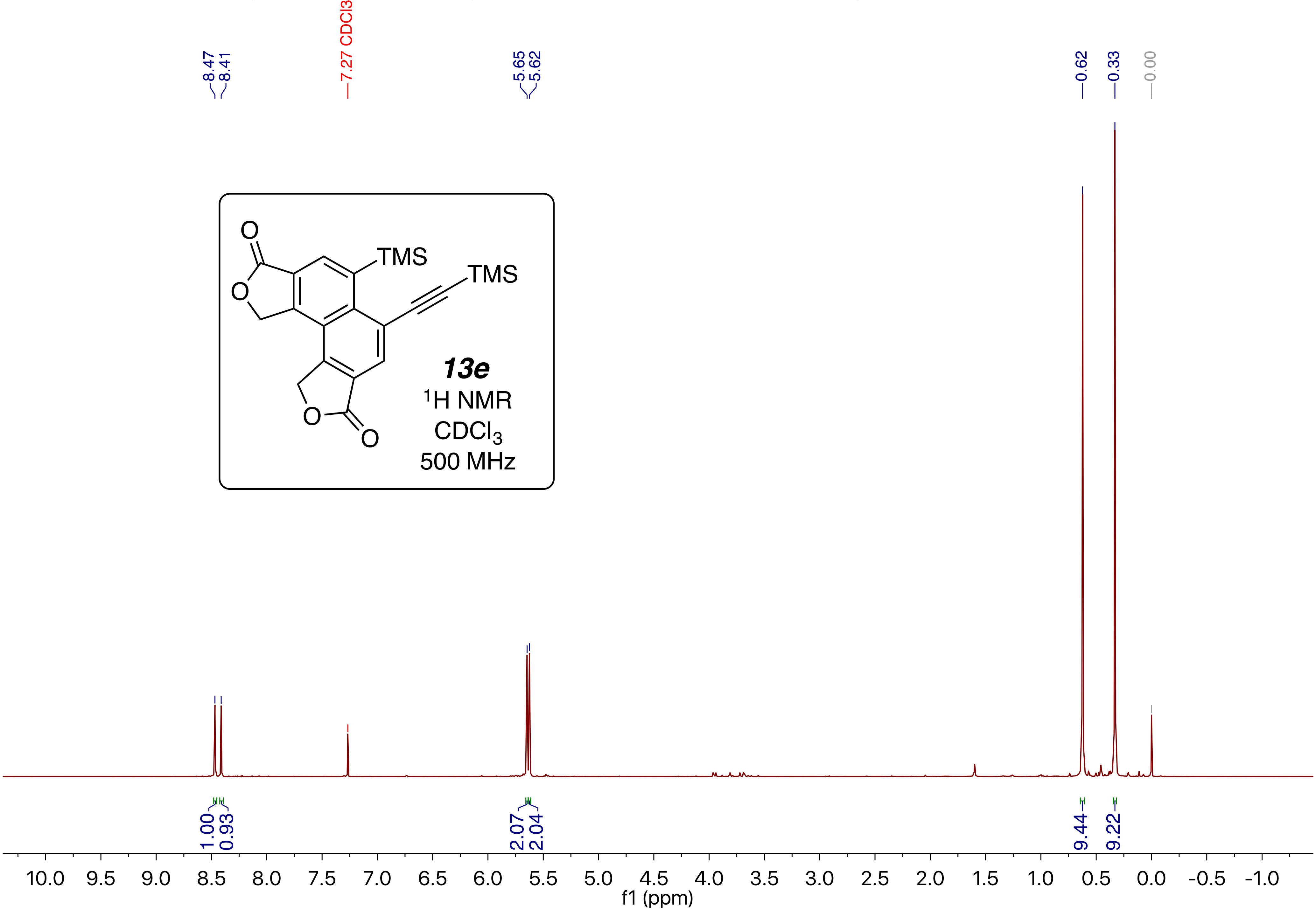
13d

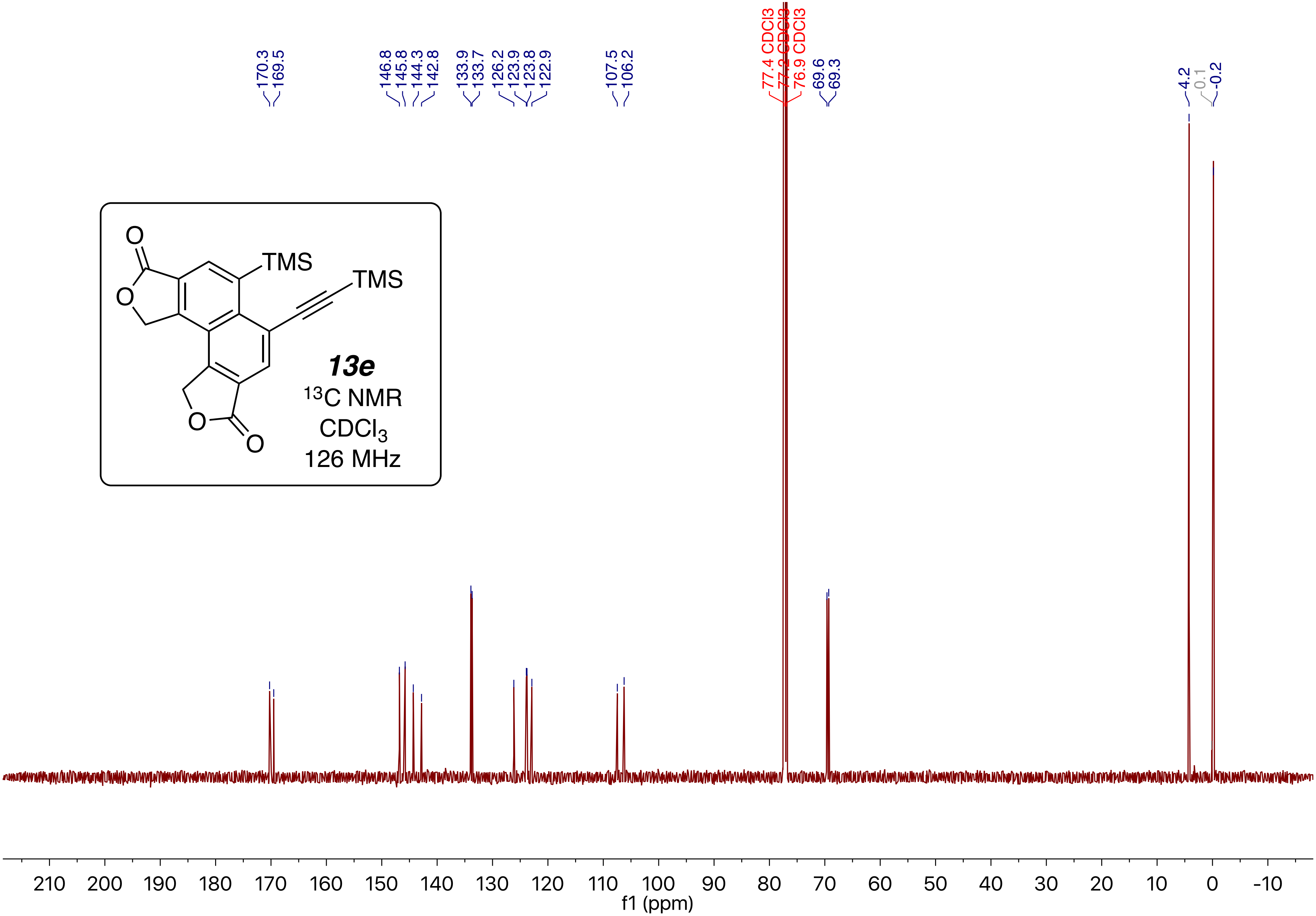
^{1}H NMR

$CDCl_3$

500 MHz


170.9
170.3
170.2
169.6
145.8
145.4
145.3
144.2
143.6
142.8
139.1
133.0
132.2
131.8
128.0
126.3
126.1
125.3
124.6
124.1
124.0
123.2
123.1
122.6
102.6
101.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.8
74.8
72.2
71.7
69.5
69.4
18.1
16.1
10.4
8.8
8.7
8.6
1.0
0.6
0.1
O
O
O
O
13d'
O
O
O
O
13d
^{13}C NMR
$CDCl_3$
126 MHz
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)


8.47
8.41
7.27 CDCl3
5.65
5.62
0.62
0.33
0.00
TMS
TMS
O
O
O
O
13e
^{1}H NMR
$CDCl_3$
500 MHz
1.00
0.93
2.07
2.04
9.44
9.22
10.0 9.5 9.0 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)

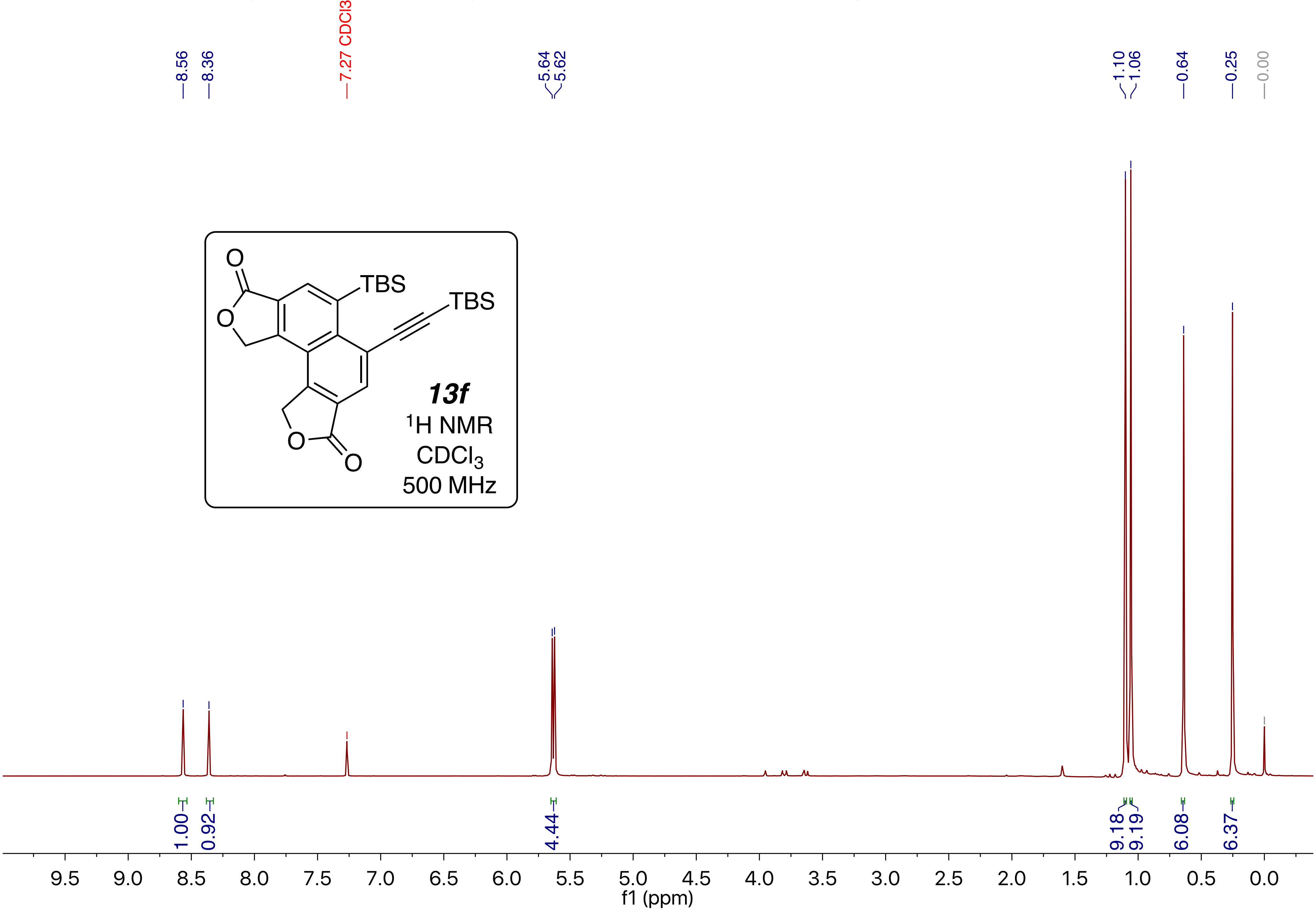


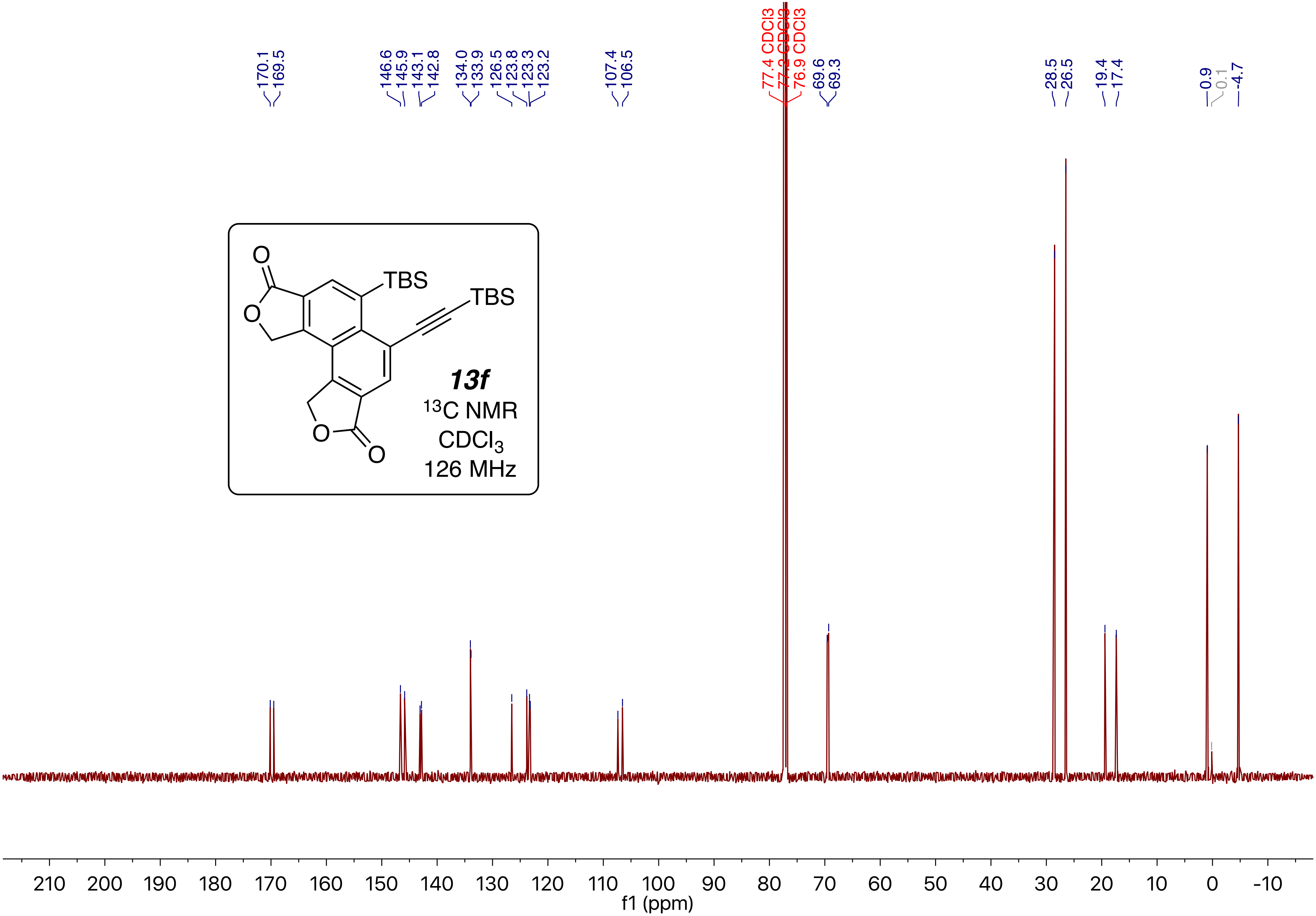
13e

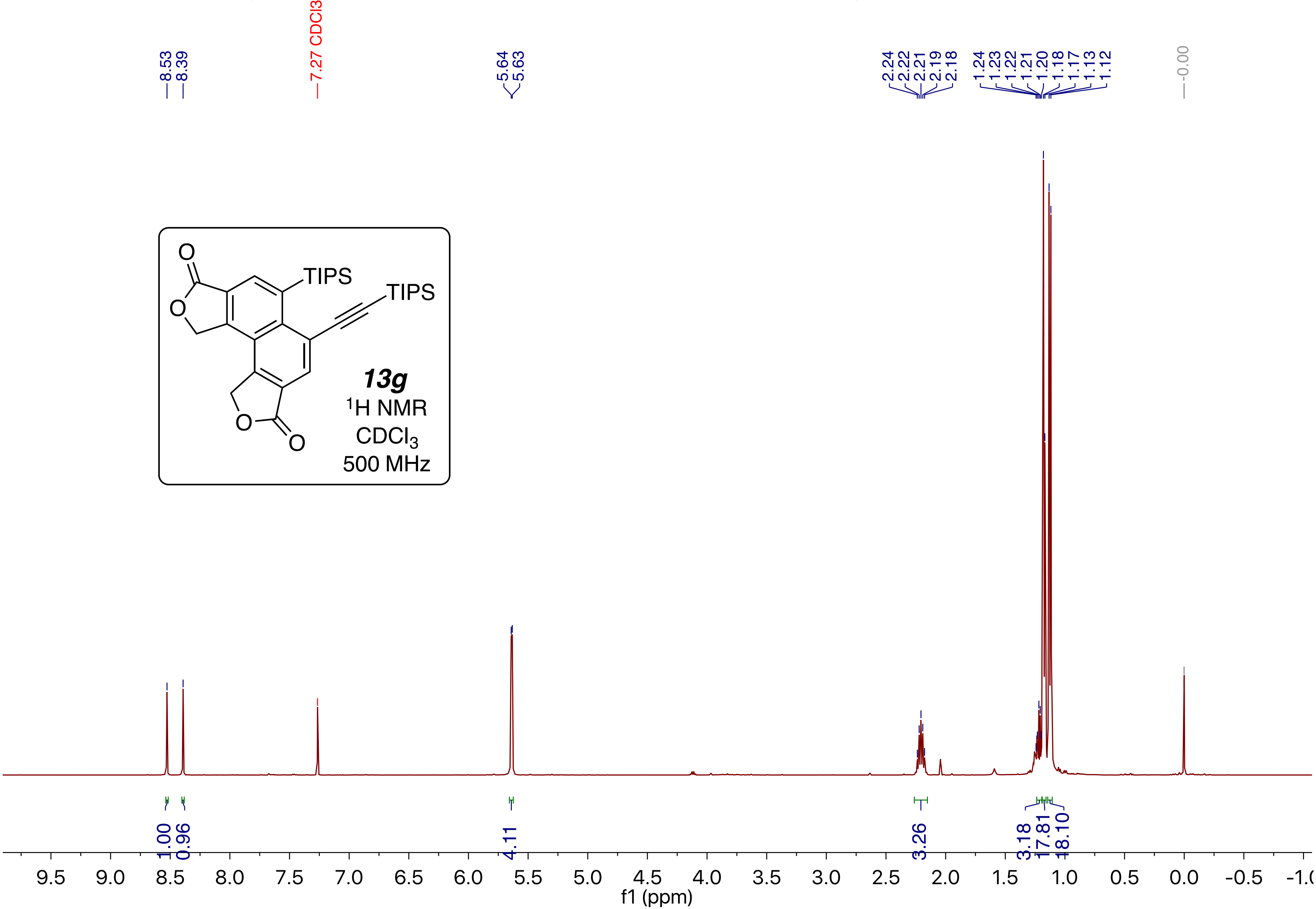
^{13}C NMR

$CDCl_3$

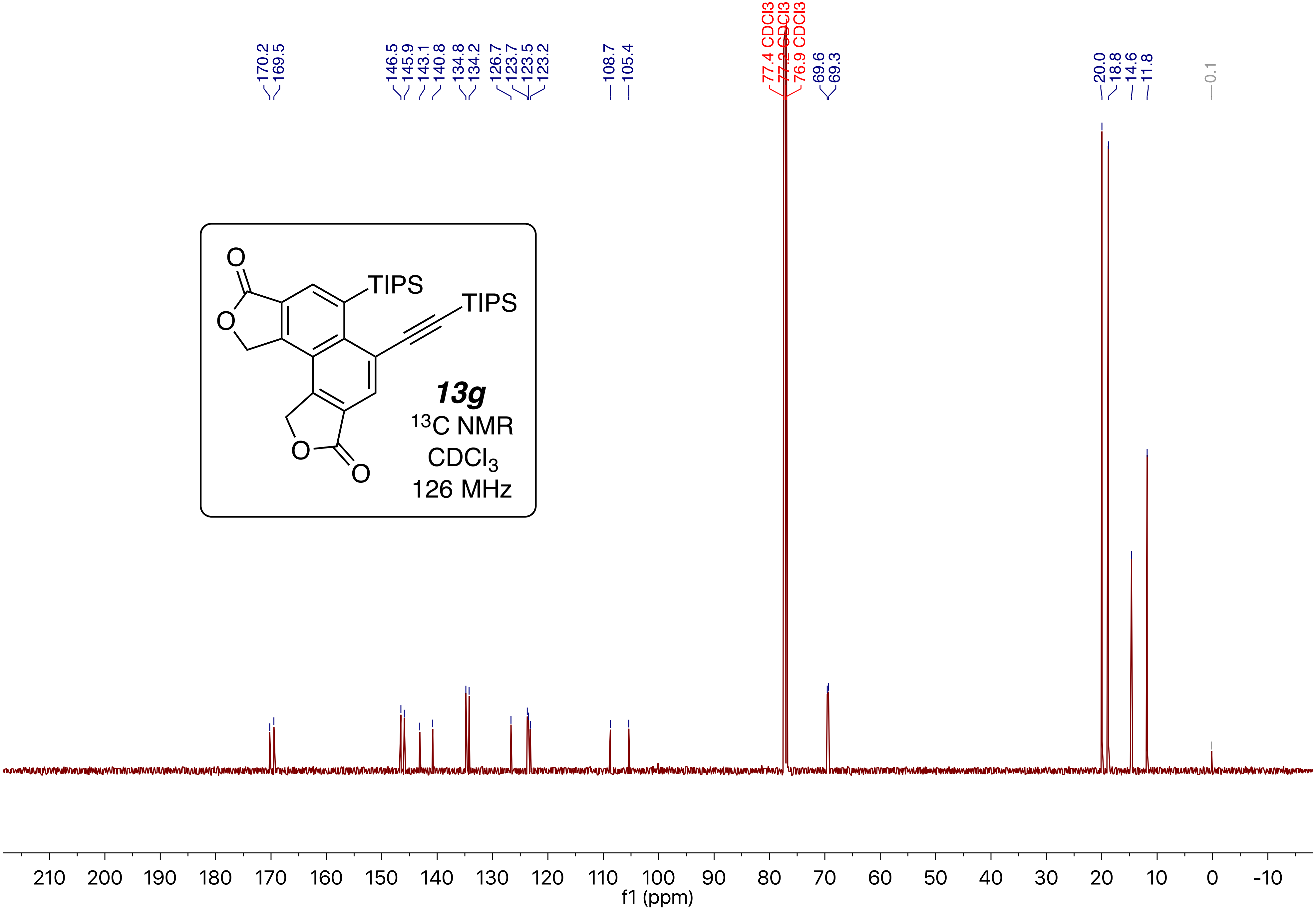
126 MHz

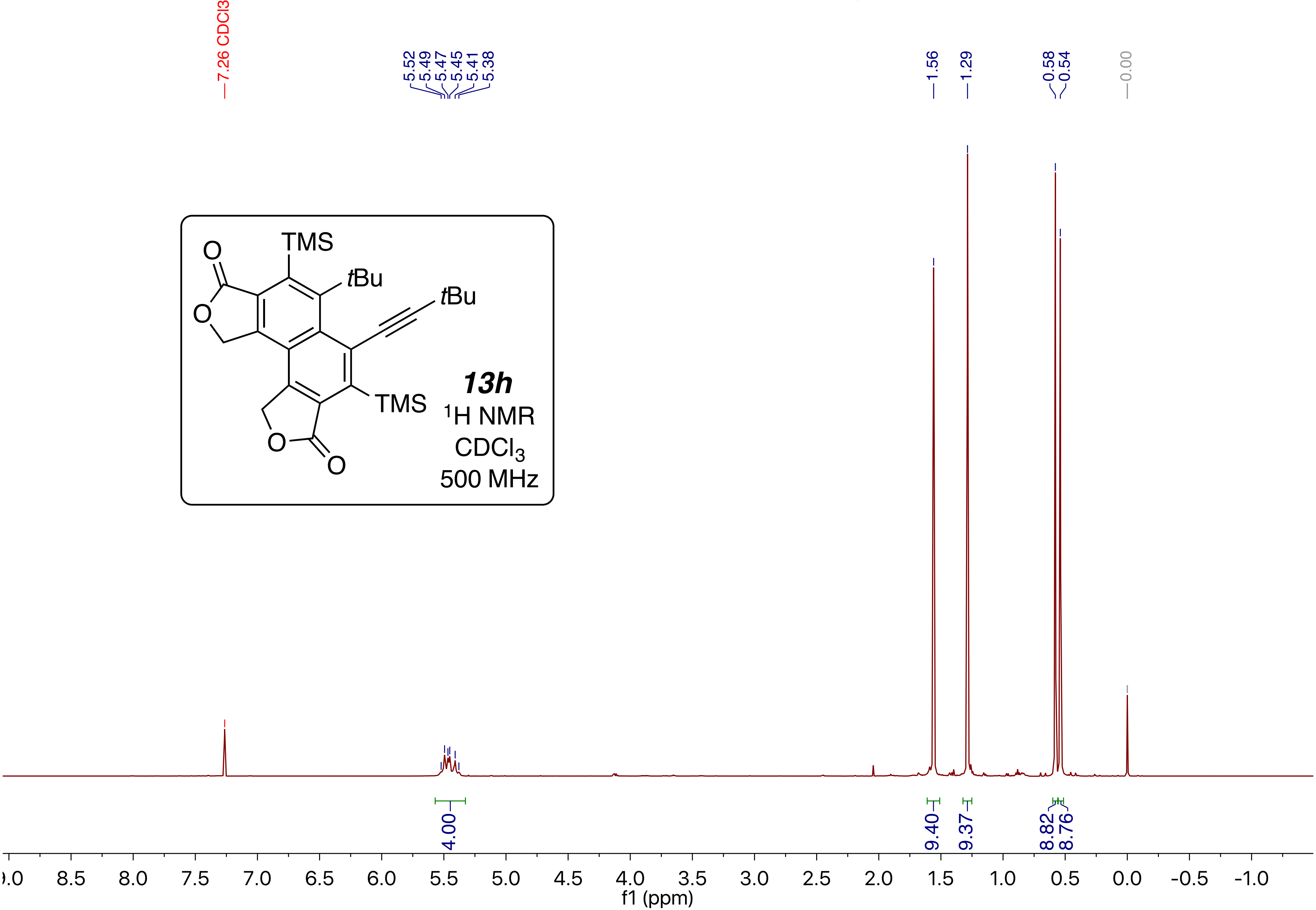

8.56
8.36
7.27 CDCl3
5.64
5.62
1.10
1.06
0.64
0.25
0.00
O
O
O
O
TBS
TBS
13f
^{1}H NMR
$CDCl_3$
500 MHz
1.00
0.92
4.44
9.18
9.19
6.08
6.37
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

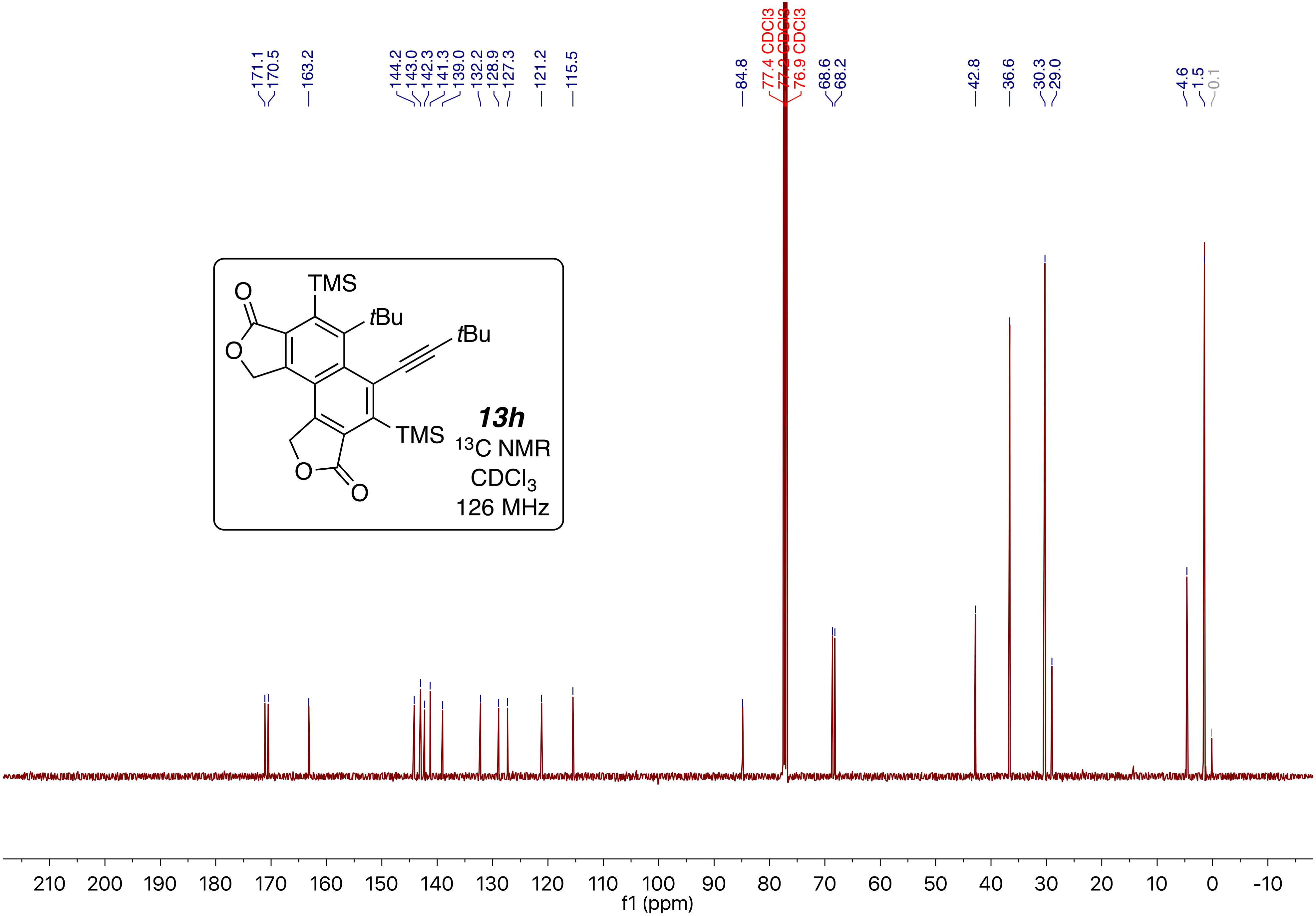

170.1
169.5
146.6
145.9
143.1
142.8
134.0
133.9
126.5
123.8
123.3
123.2
107.4
106.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
69.6
69.3
28.5
26.5
19.4
17.4
0.9
0.1
-4.7
O
O
TBS
TBS
O
O
13f
^{13}C NMR
$CDCl_3$
126 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

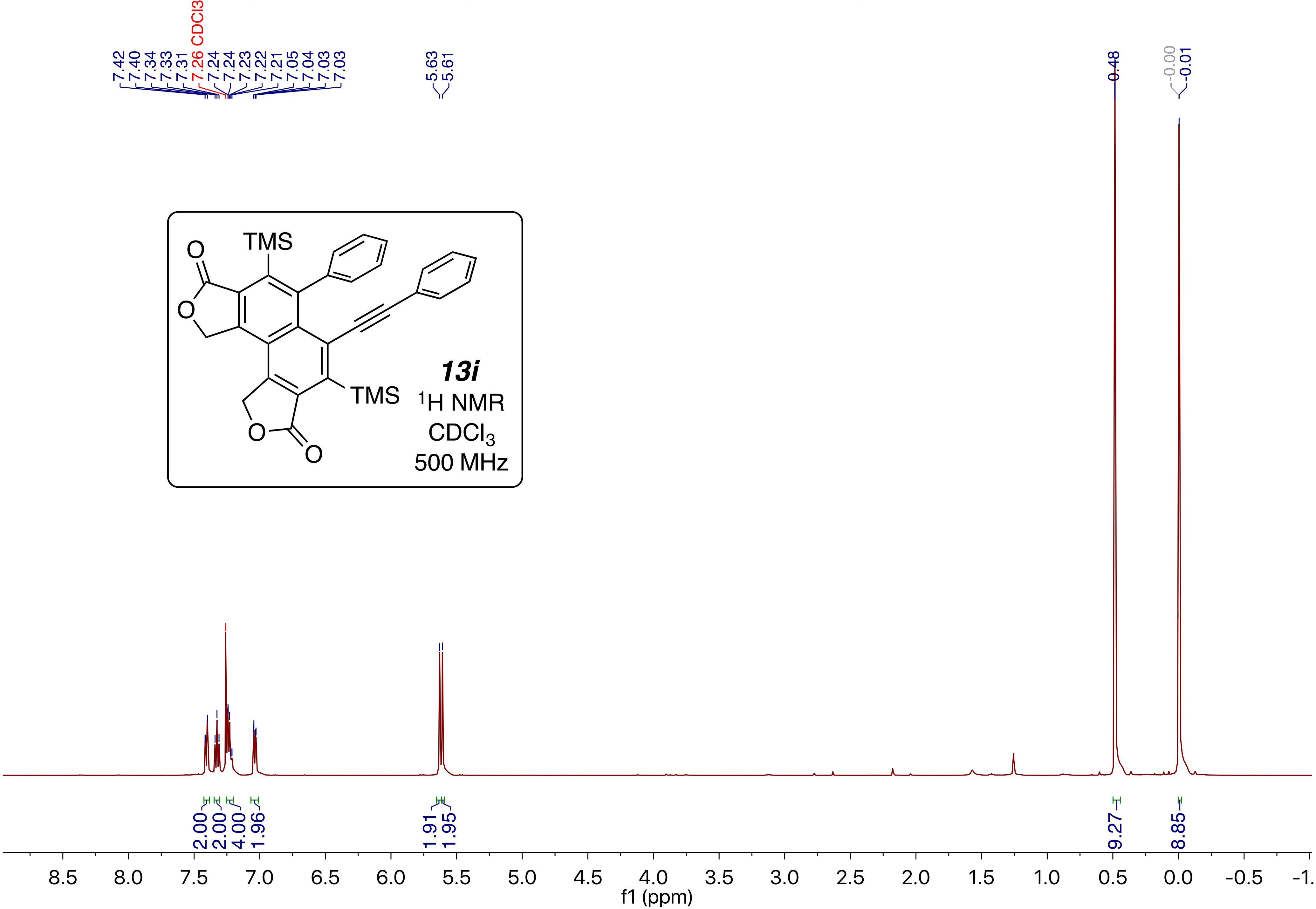


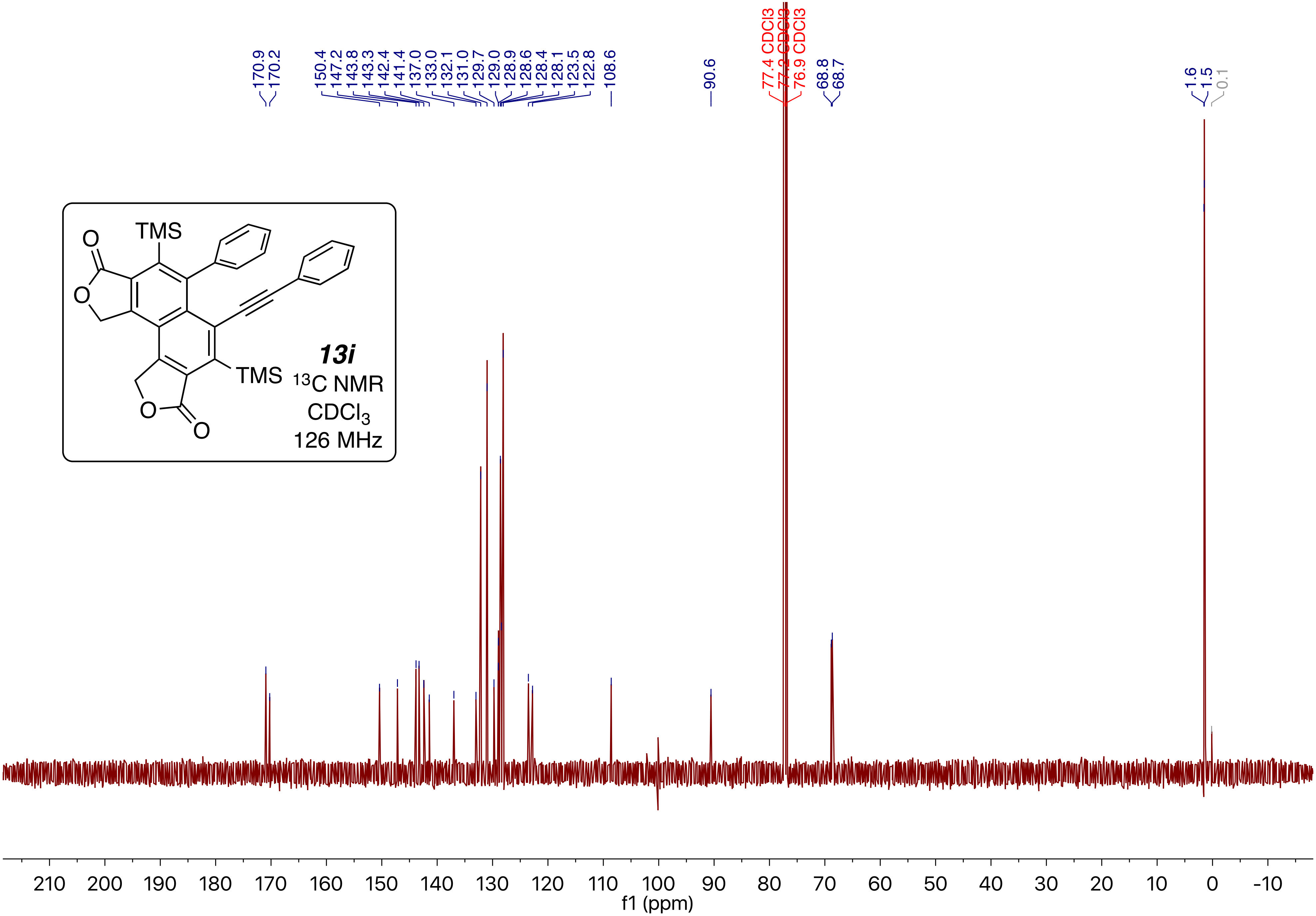
13g
^{1}H NMR
$CDCl_3$
500 MHz

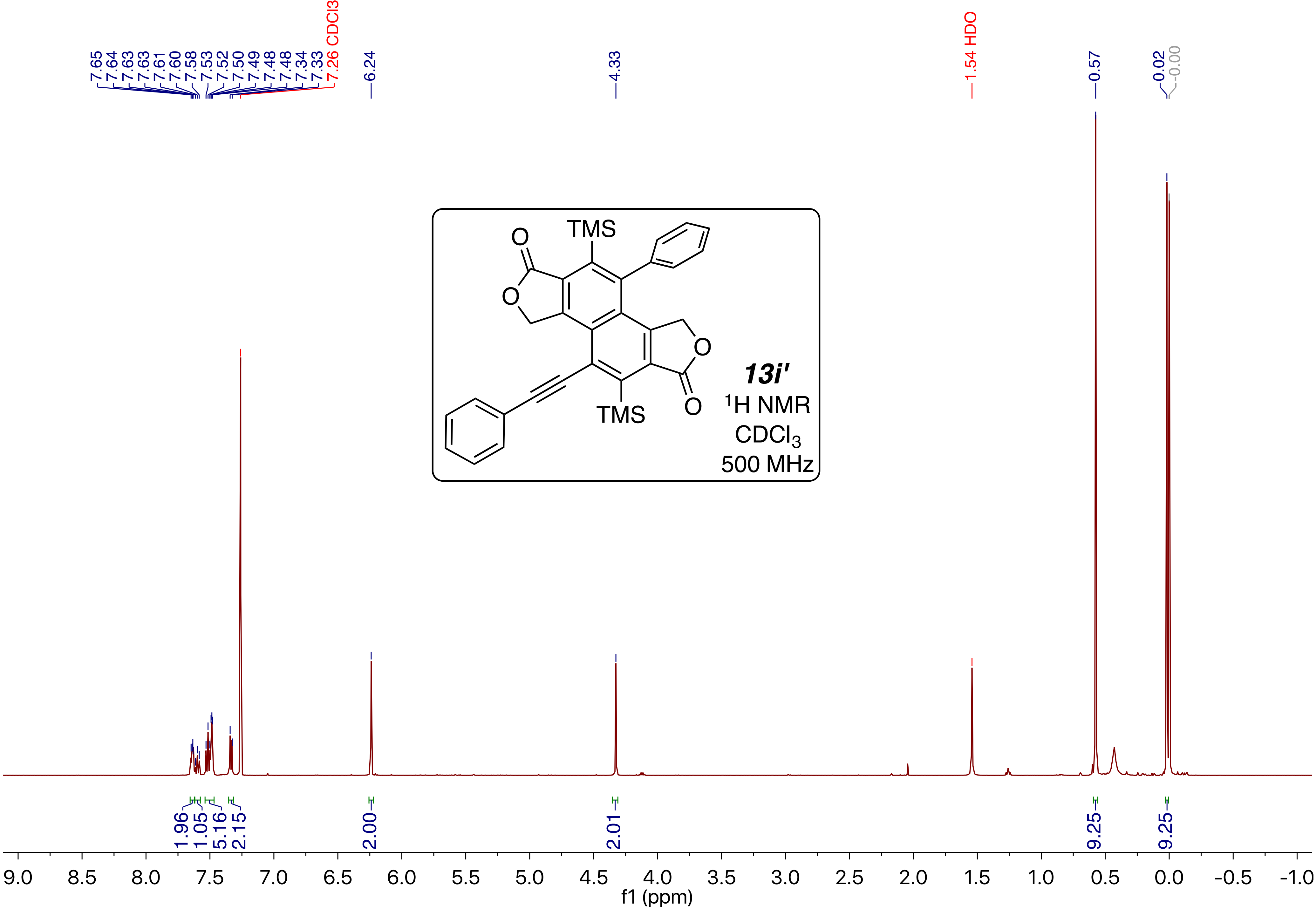

170.2
169.5
146.5
145.9
143.1
140.8
134.8
134.2
126.7
123.7
123.5
123.2
108.7
105.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
69.6
69.3
20.0
18.8
14.6
11.8
0.1
O
O
O
O
TIPS
TIPS
13g
^{13}C NMR
CDCl$_3$
126 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

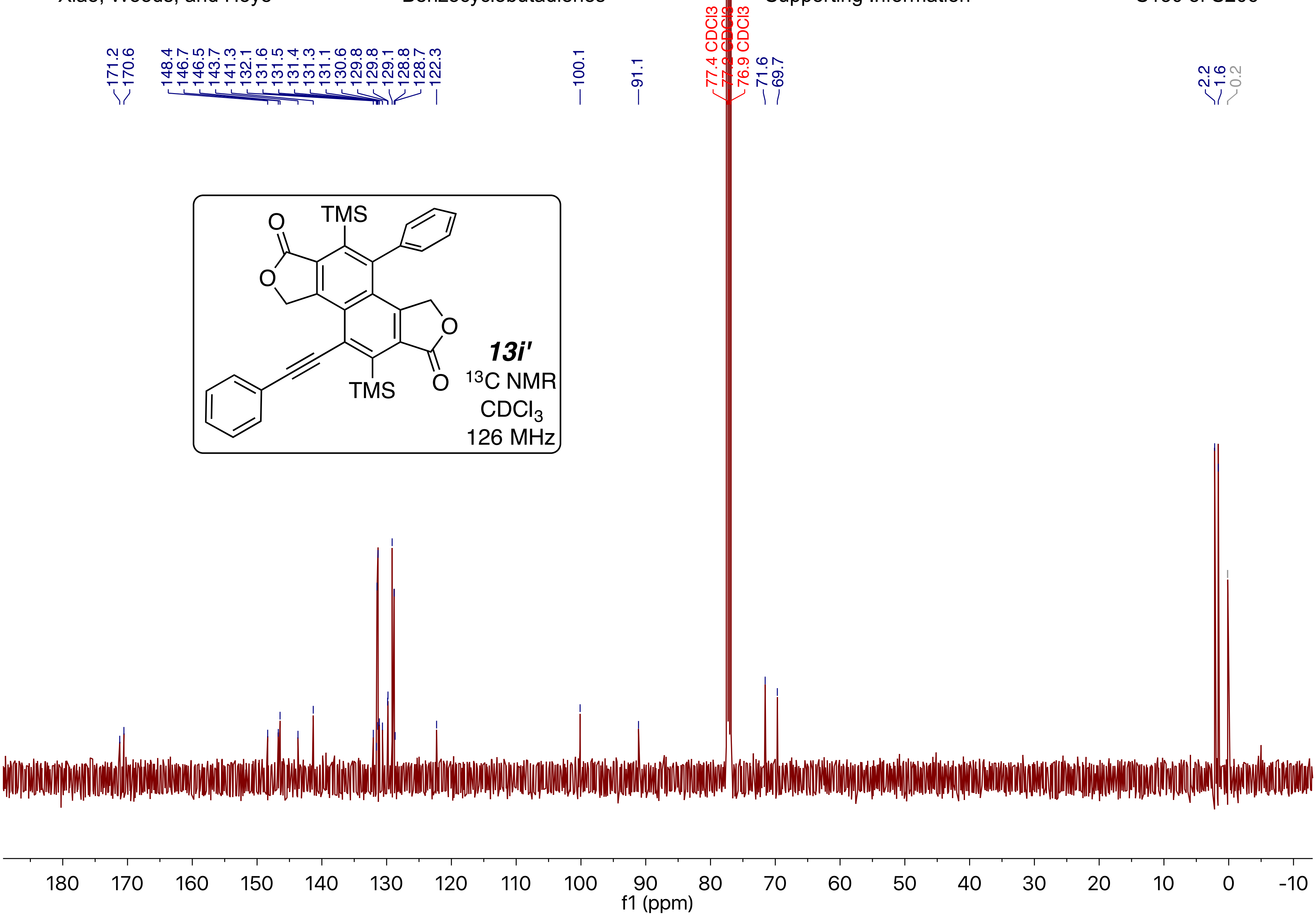

7.26 CDCl3
5.52
5.49
5.47
5.45
5.41
5.38
1.56
1.29
0.58
0.54
0.00
O
TMS
tBu
tBu
O
TMS
O
O
13h
^{1}H NMR
$CDCl_3$
500 MHz
4.00
9.40
9.37
8.82
8.76
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

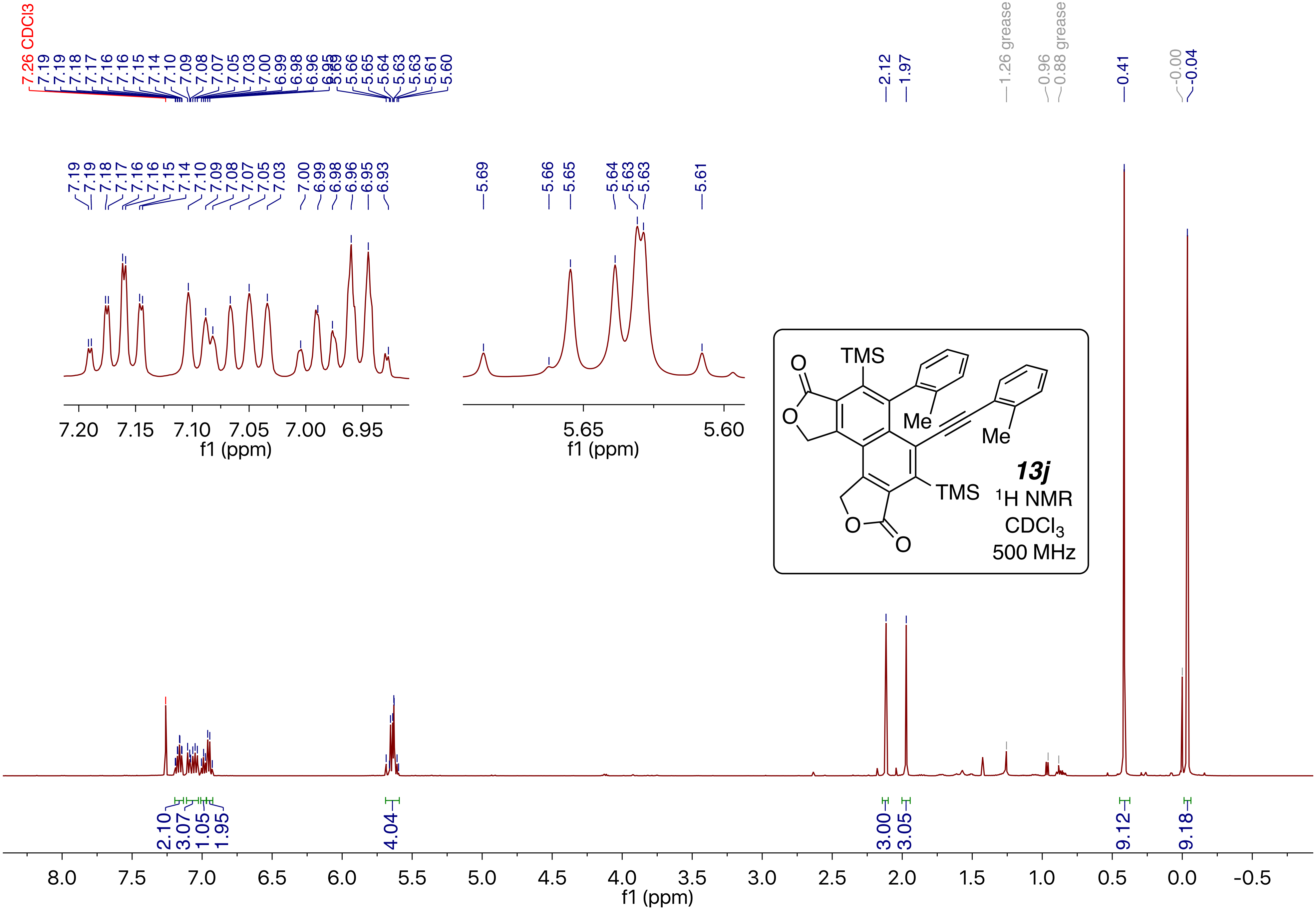

171.1
170.5
163.2
144.2
143.0
142.3
141.3
139.0
132.2
128.9
127.3
121.2
115.5
84.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
68.6
68.2
42.8
36.6
30.3
29.0
4.6
1.5
0.1
TMS
tBu
tBu
TMS
O
O
O
O
13h
^{13}C NMR
$CDCl_3$
126 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

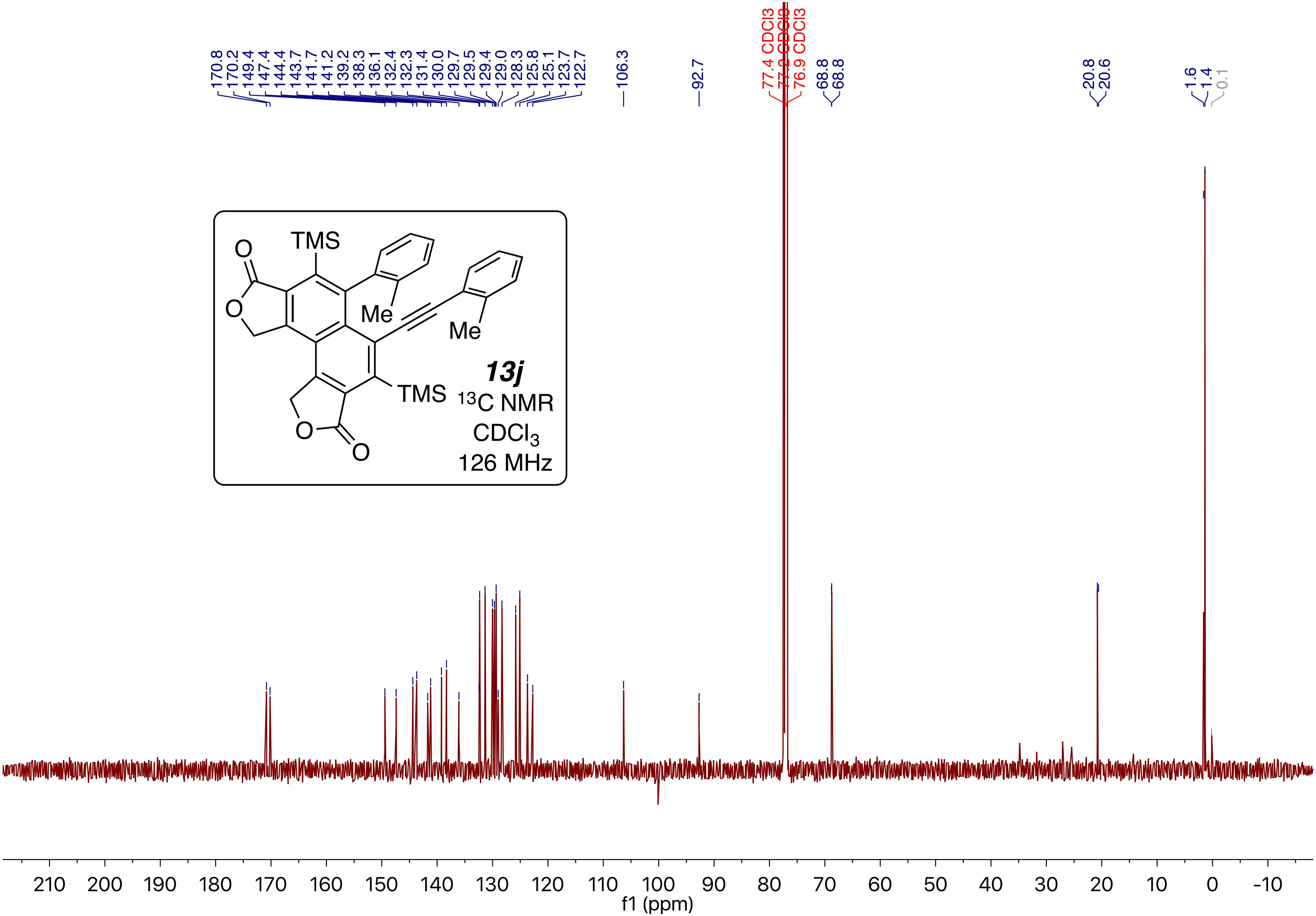

7.42
7.40
7.34
7.33
7.31
7.26 CDCl3
7.24
7.24
7.23
7.22
7.21
7.05
7.04
7.03
7.03
5.63
5.61
0.48
-0.00
-0.01
O
TMS
O
O
TMS
O
O
13i
^{1}H NMR
$CDCl_3$
500 MHz
2.00
2.00
4.00
1.96
1.91
1.95
9.27
8.85
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)


170.9
170.2
150.4
147.2
143.8
143.3
142.4
141.4
137.0
133.0
132.1
131.0
129.7
129.0
128.9
128.6
128.4
128.1
123.5
122.8
108.6
90.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
68.8
68.7
1.6
1.5
0.1
TMS
O
O
TMS
O
O
13i
13C NMR
CDCl3
126 MHz
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)


7.65
7.64
7.63
7.63
7.61
7.60
7.58
7.53
7.52
7.50
7.49
7.48
7.48
7.34
7.33
7.26 CDCl3
6.24
4.33
1.54 HDO
0.57
0.02
-0.00
TMS
O
O
O
O
TMS
13i'
^{1}H NMR
$CDCl_3$
500 MHz
1.96
1.05
5.16
2.15
2.00
2.01
9.25
9.25
9.0
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)


171.2
170.6
148.4
146.7
146.5
143.7
141.3
132.1
131.6
131.5
131.4
131.3
131.1
130.6
129.8
129.8
129.1
128.8
128.7
122.3
100.1
91.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
71.6
69.7
2.2
1.6
0.2
TMS
O
O
TMS
O
O
13i'
^{13}C NMR
$CDCl_3$
126 MHz
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
7.19 7.19 7.18 7.17 7.16 7.16 7.15 7.14 7.10 7.09 7.08 7.07 7.05 7.03 7.00 6.99 6.98 6.96 6.95 6.93
5.69 5.66 5.65 5.64 5.63 5.63 5.61 5.60
2.12 1.97
1.26 grease
0.96 0.88 grease
0.41
-0.00 -0.04
2.10 3.07 1.05 1.95
4.04
3.00 3.05
9.12
9.18
7.20 7.15 7.10 7.05 7.00 6.95
f1 (ppm)
5.65 5.60
f1 (ppm)
TMS
Me
Me
O
O
O
O
TMS
13j
^{1}H NMR
$CDCl_3$
500 MHz
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)

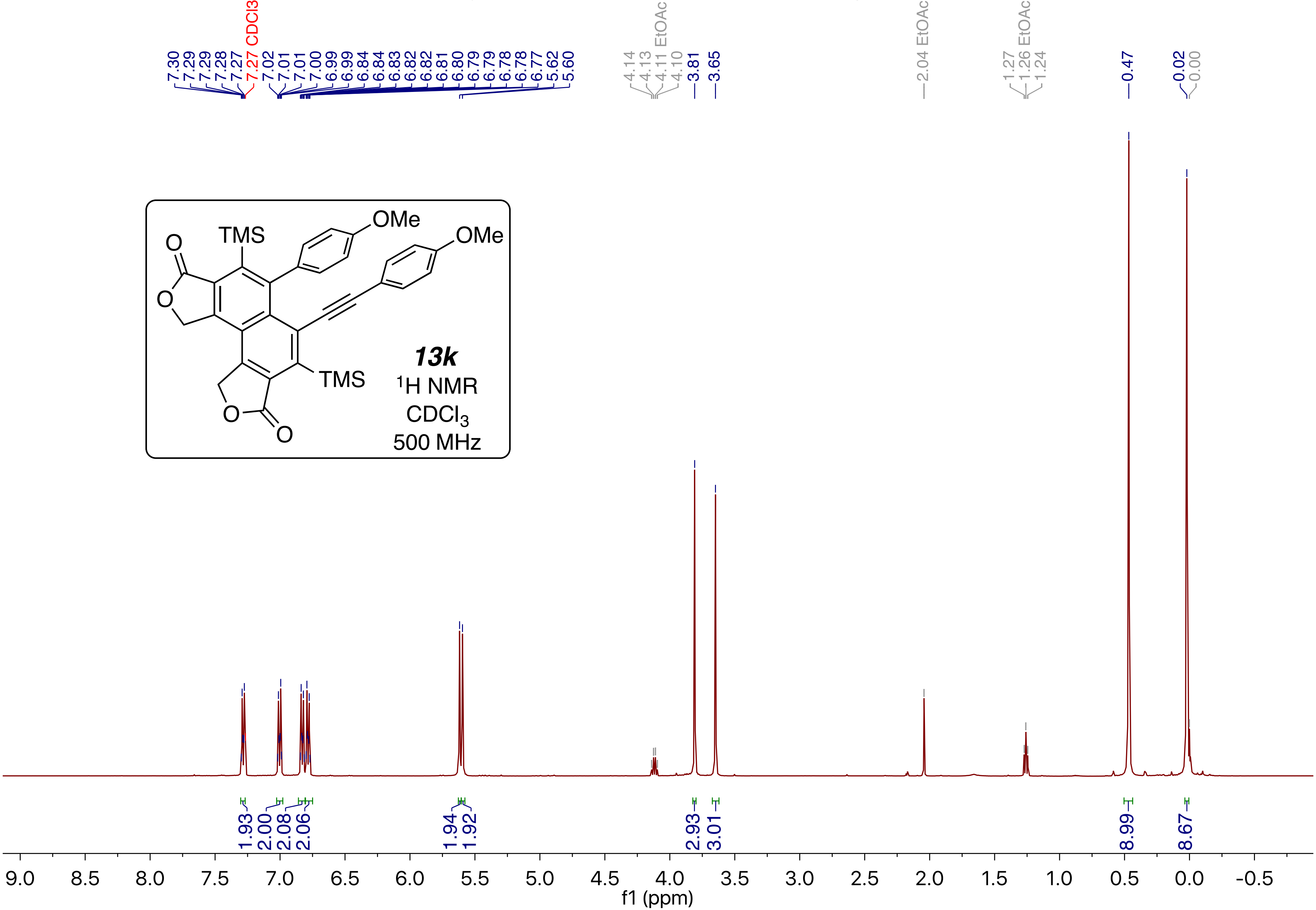


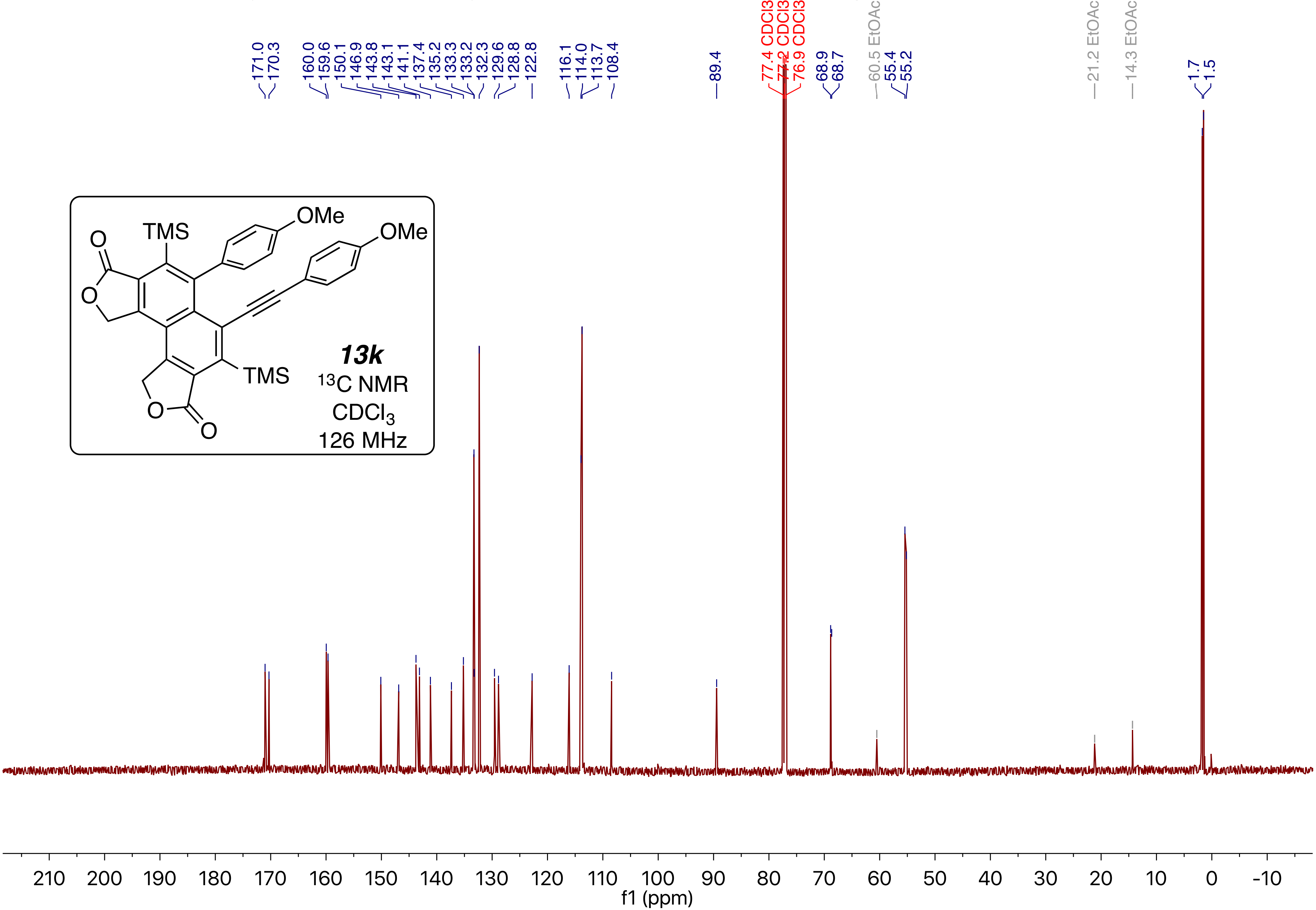
13j

^{13}C NMR

$CDCl_3$

126 MHz


7.30
7.29
7.29
7.28
7.27
7.27 CDCl3
7.02
7.01
7.01
7.00
6.99
6.99
6.84
6.84
6.83
6.82
6.82
6.81
6.80
6.79
6.79
6.78
6.78
6.77
5.62
5.60
4.14
4.13
4.11 EtOAc
4.10
3.81
3.65
2.04 EtOAc
1.27
1.26 EtOAc
1.24
0.47
0.02
0.00
TMS
OMe
OMe
O
O
TMS
O
O
13k
^{1}H NMR
CDCl$_3$
500 MHz
1.93
2.00
2.08
2.06
1.94
1.92
2.93
3.01
8.99
8.67
9.0
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
f1 (ppm)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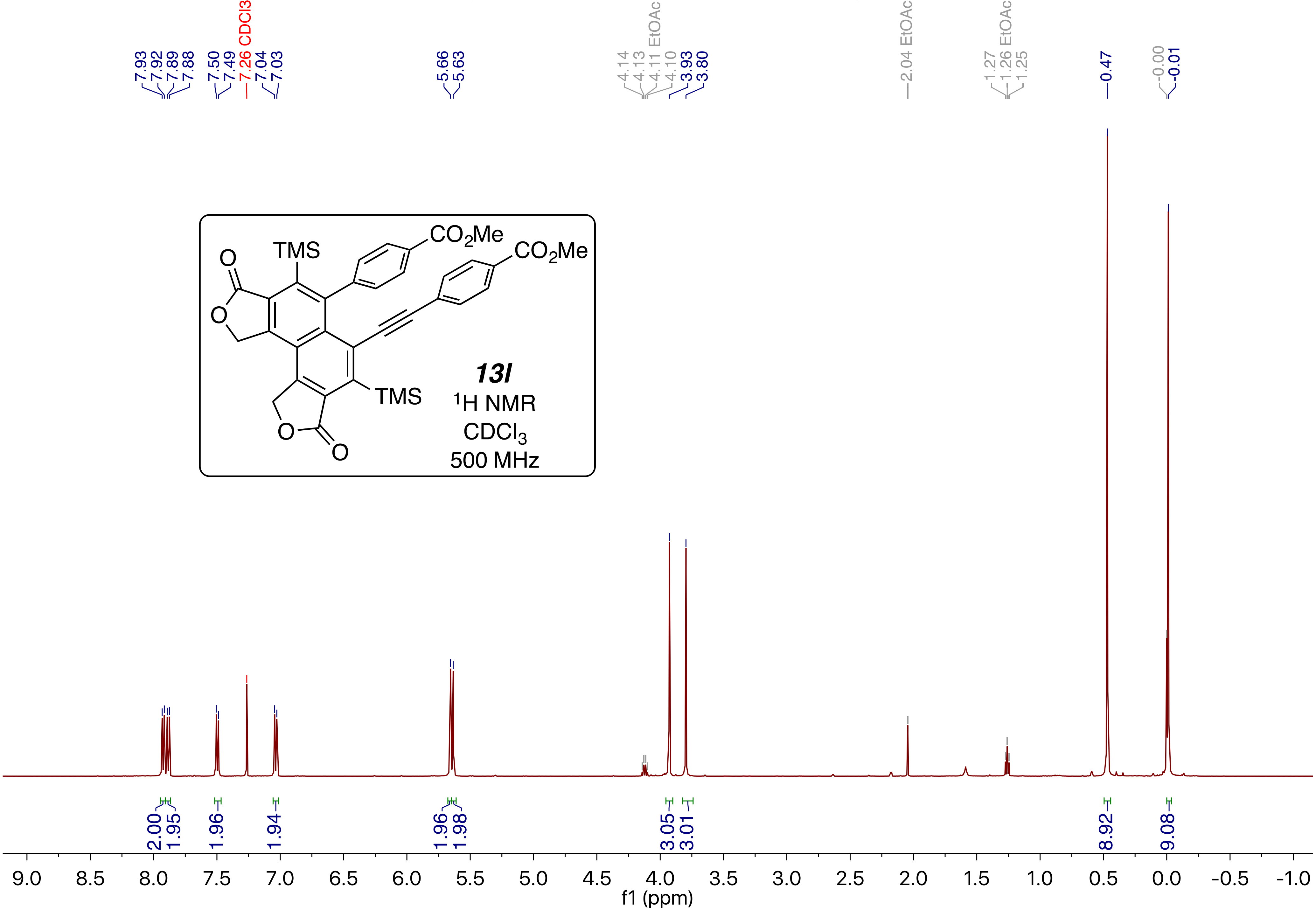
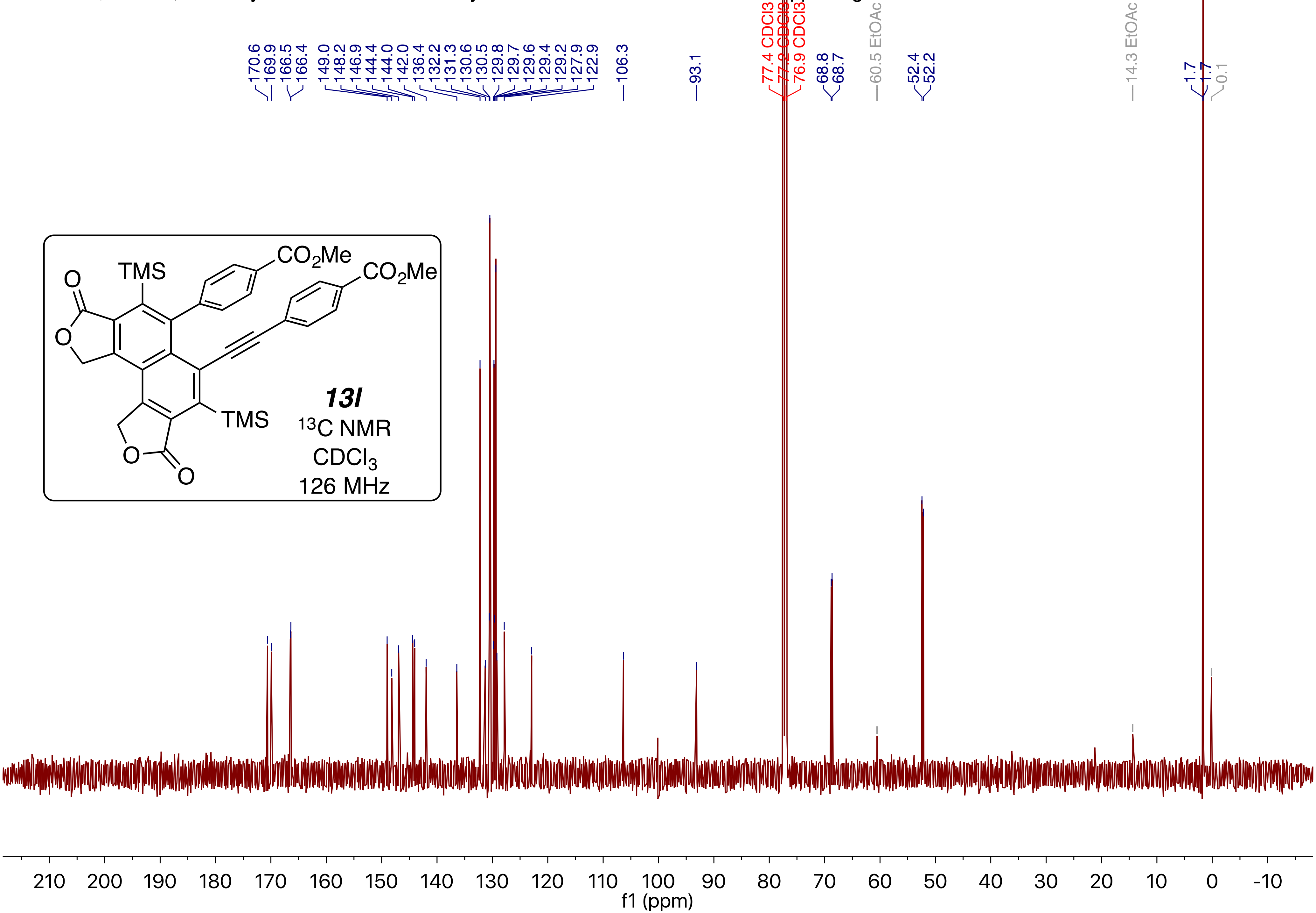
170.3
160.0
159.6
150.1
146.9
143.8
143.1
141.1
137.4
135.2
133.3
133.2
132.3
129.6
128.8
122.8
116.1
114.0
113.7
108.4
89.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
68.9
68.7
60.5 EtOAc
55.4
55.2
21.2 EtOAc
14.3 EtOAc
1.7
1.5
TMS
OMe
OMe
O
O
O
O
TMS
13k
^{13}C NMR
$CDCl_3$
126 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.93
7.92
7.89
7.88
7.50
7.49
7.26 CDCl3
7.04
7.03
5.66
5.63
4.14
4.13
4.11 EtOAc
4.10
3.93
3.80
2.04 EtOAc
1.27
1.26 EtOAc
1.25
0.47
-0.00
-0.01
TMS
CO2Me
CO2Me
O
O
O
O
TMS
13l
1H NMR
CDCl3
500 MHz
2.00
1.95
1.96
1.94
1.96
1.98
3.05
3.01
8.92
9.08
9.0
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)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169.9
166.5
166.4
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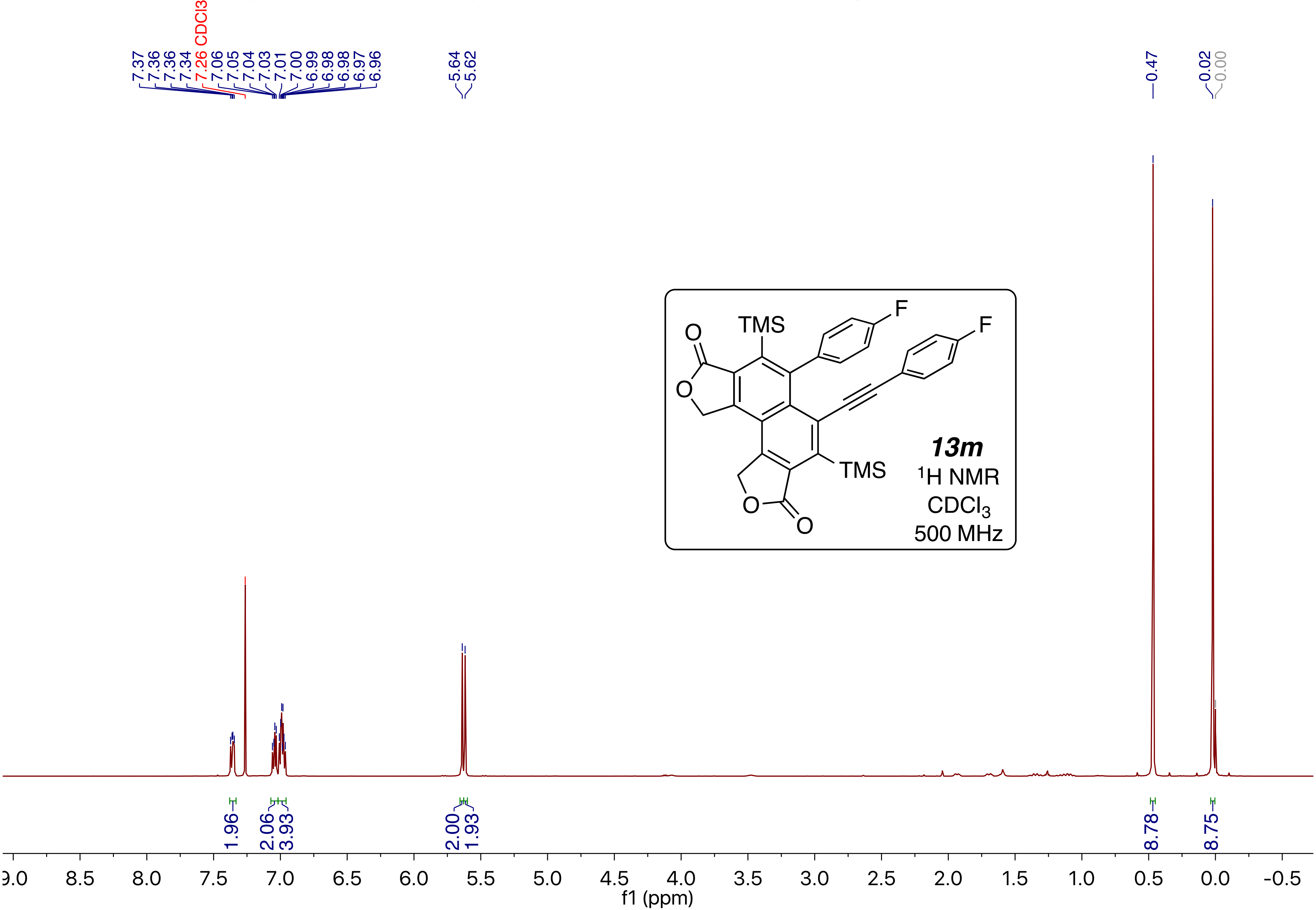
148.2
146.9
144.4
144.0
142.0
136.4
132.2
131.3
130.6
130.5
129.8
129.7
129.6
129.4
129.2
127.9
122.9
106.3
93.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
68.8
68.7
60.5 EtOAc
52.4
52.2
14.3 EtOAc
1.7
1.7
0.1
TMS
CO_2Me
CO_2Me
O
O
TMS
O
O
13l
^{13}C NMR
$CDCl_3$
126 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

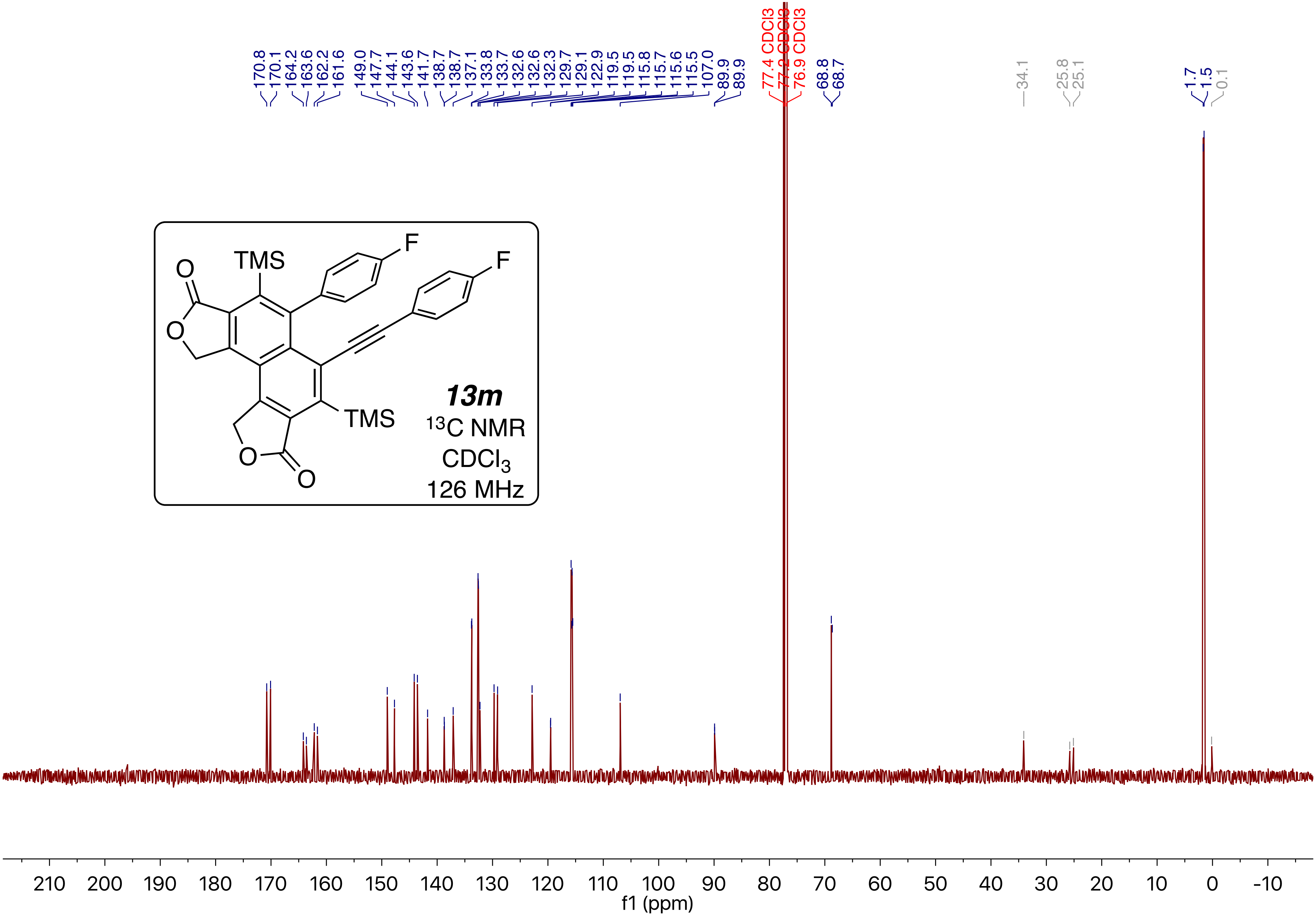


13m

^{1}H NMR

$CDCl_3$

500 MHz

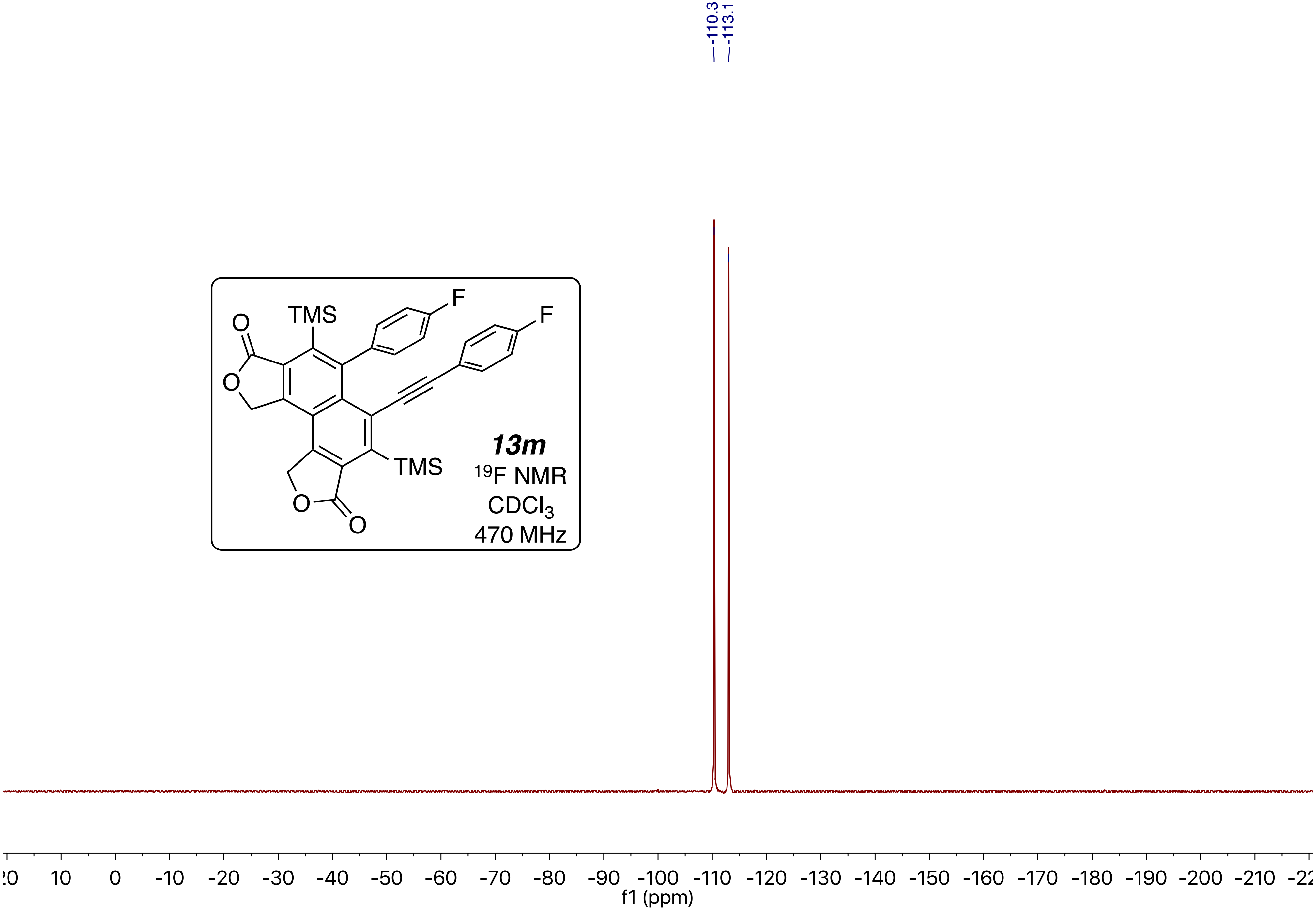


13m

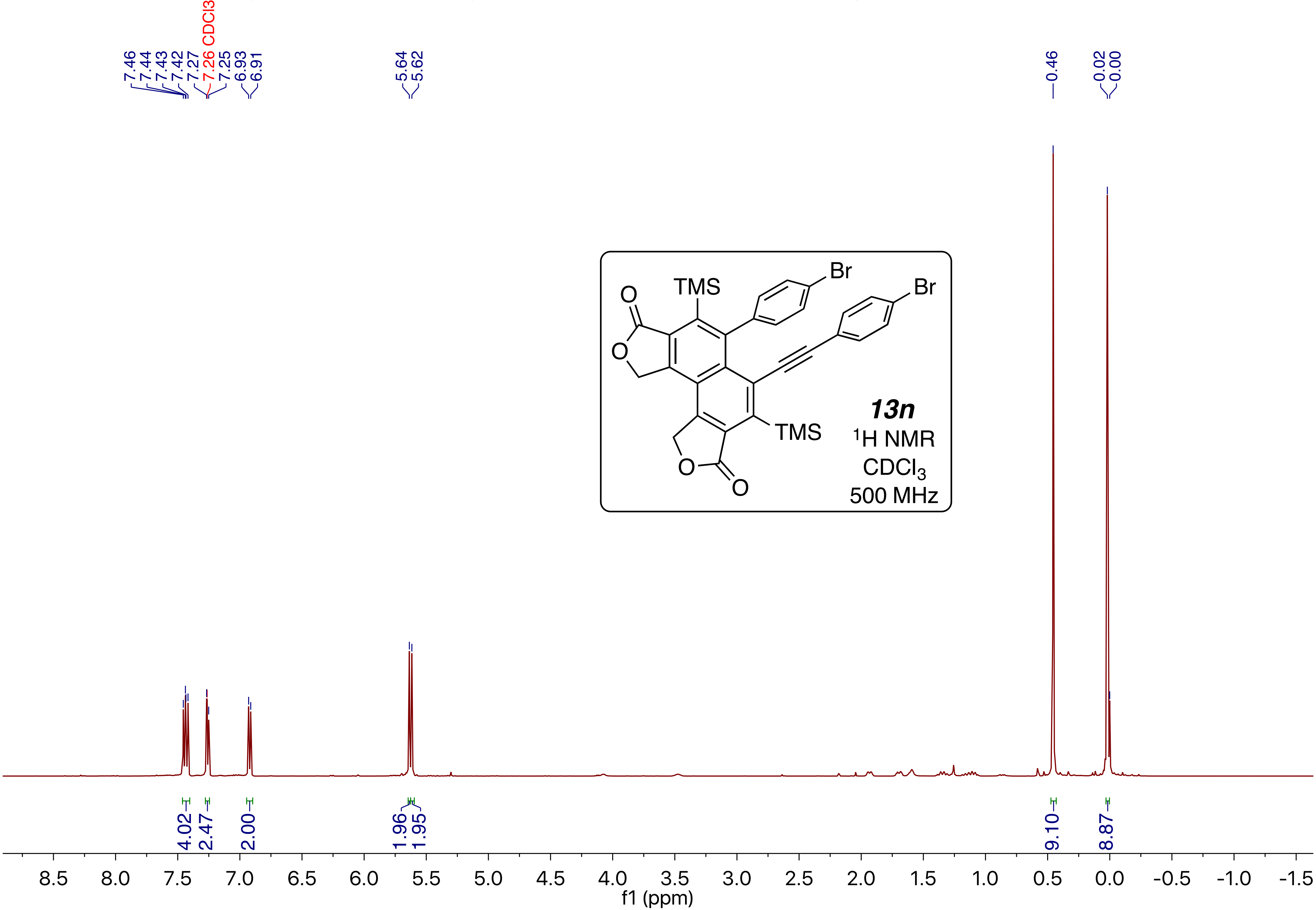
^{13}C NMR

$CDCl_3$

126 MHz


-110.3
-113.1
TMS
TMS
F
F
O
O
O
O
19F NMR
CDCl3
470 MHz
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

13m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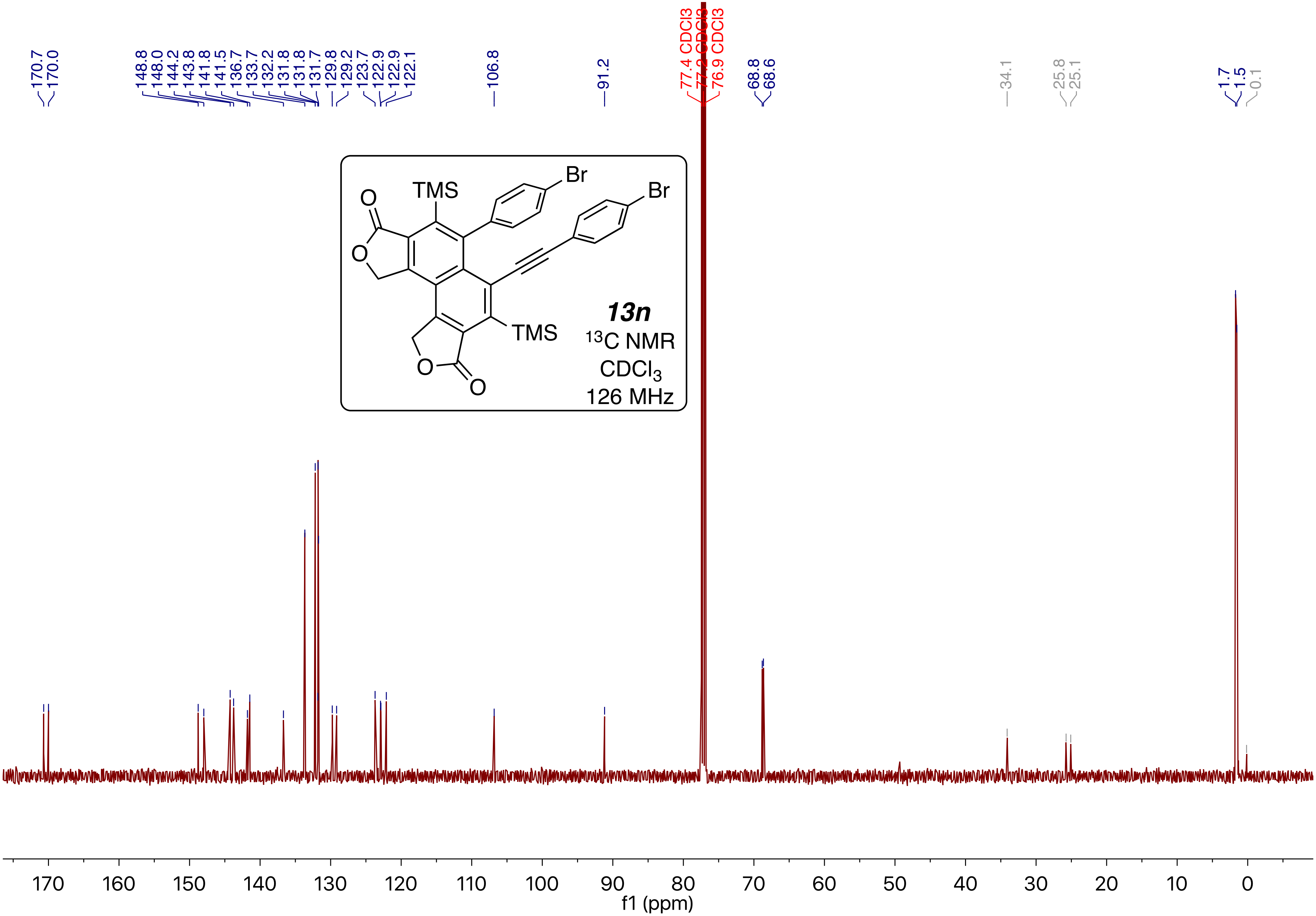
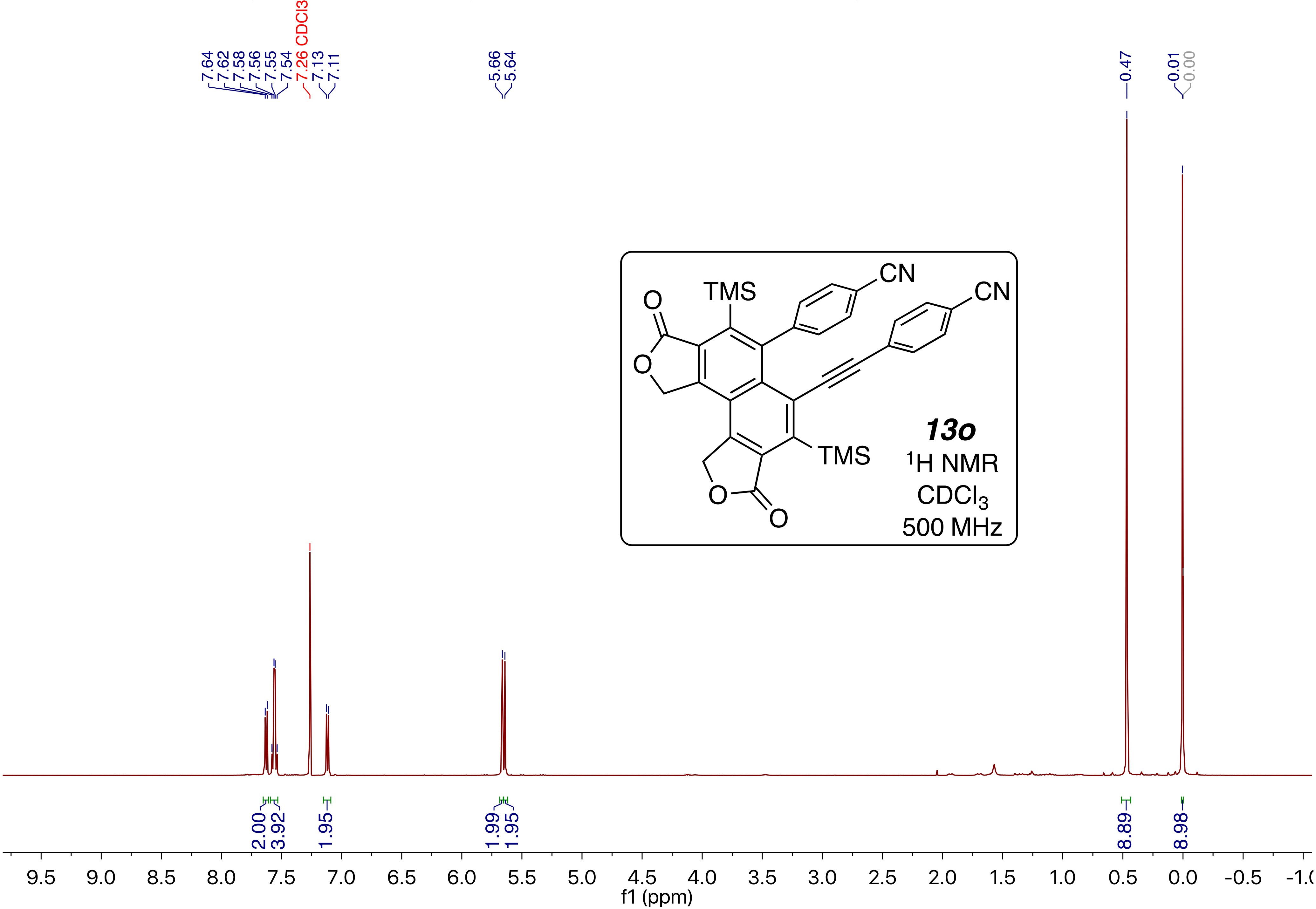
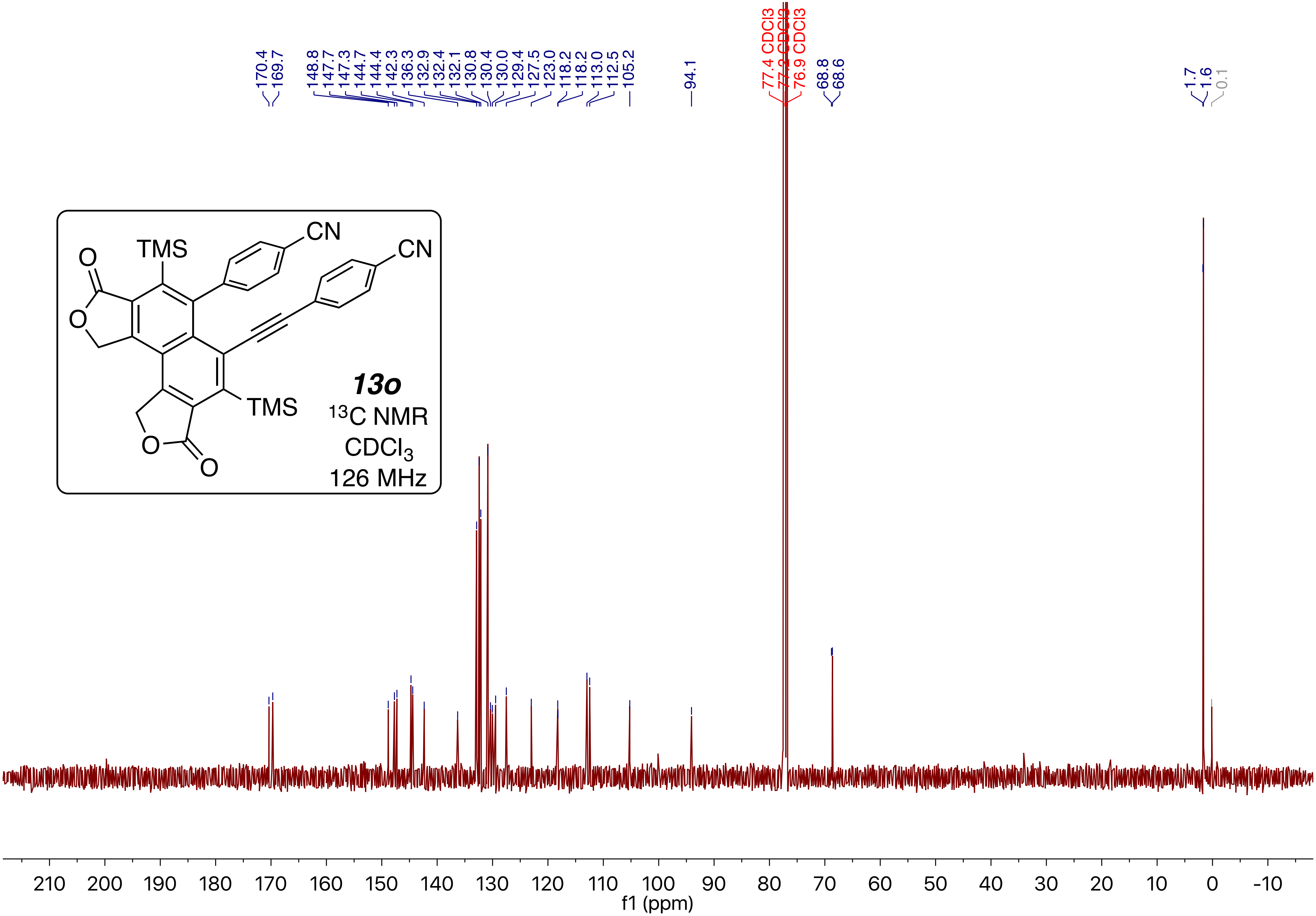
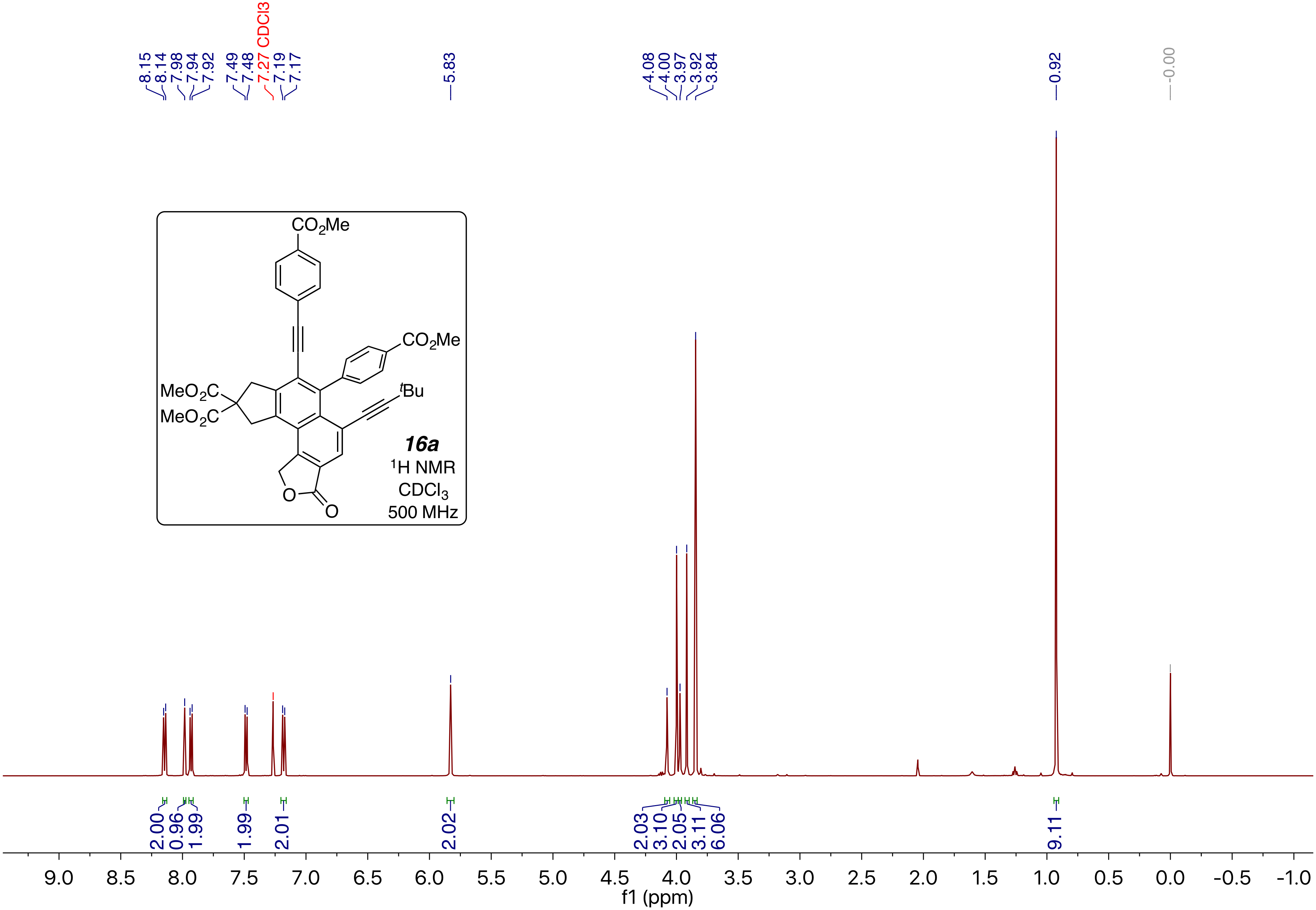
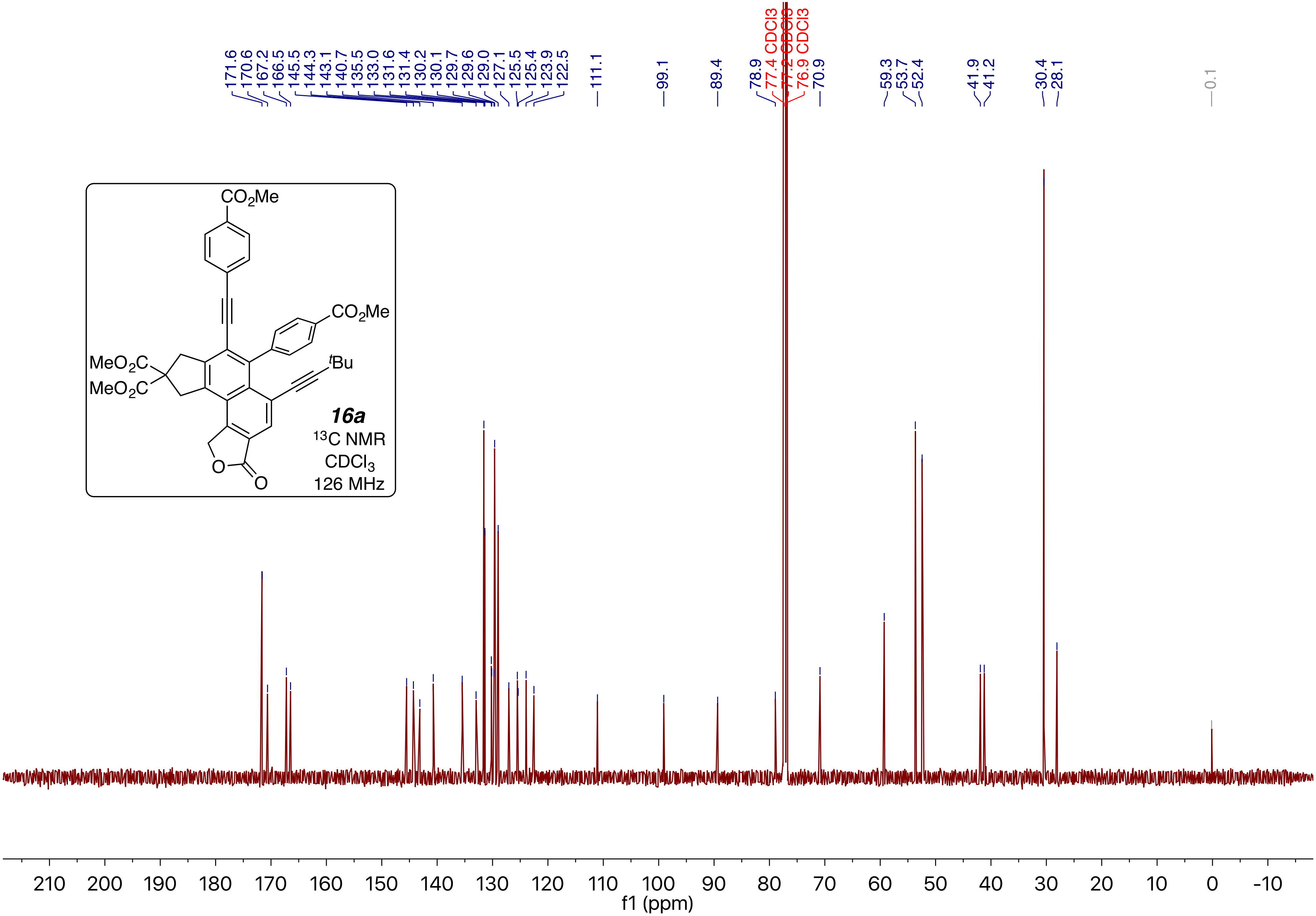
7.44
7.43
7.42
7.27
7.26 CDCl3
7.25
6.93
6.91
5.64
5.62
0.46
0.02
0.00
TMS
Br
Br
O
O
TMS
O
O
13n
^{1}H NMR
$CDCl_3$
500 MHz
4.02
2.47
2.00
1.96
1.95
9.10
8.87
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

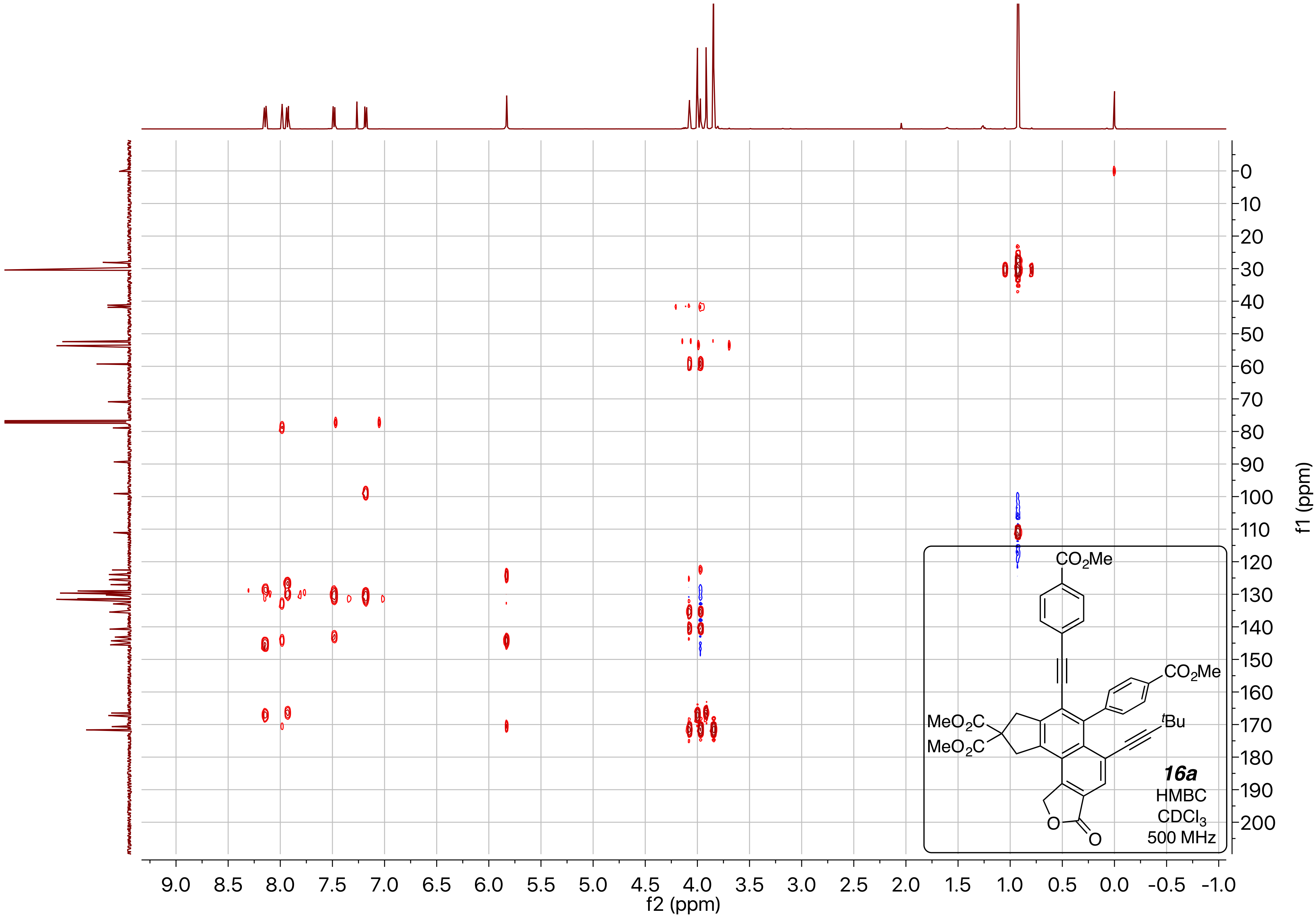

170.7
170.0
148.8
148.0
144.2
143.8
141.8
141.5
136.7
133.7
132.2
131.8
131.8
131.7
129.8
129.2
123.7
122.9
122.9
122.1
106.8
91.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
68.8
68.6
34.1
25.8
25.1
1.7
1.5
0.1
TMS
Br
O
O
Br
O
TMS
O
O
13n
^{13}C NMR
CDCl$_3$
126 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

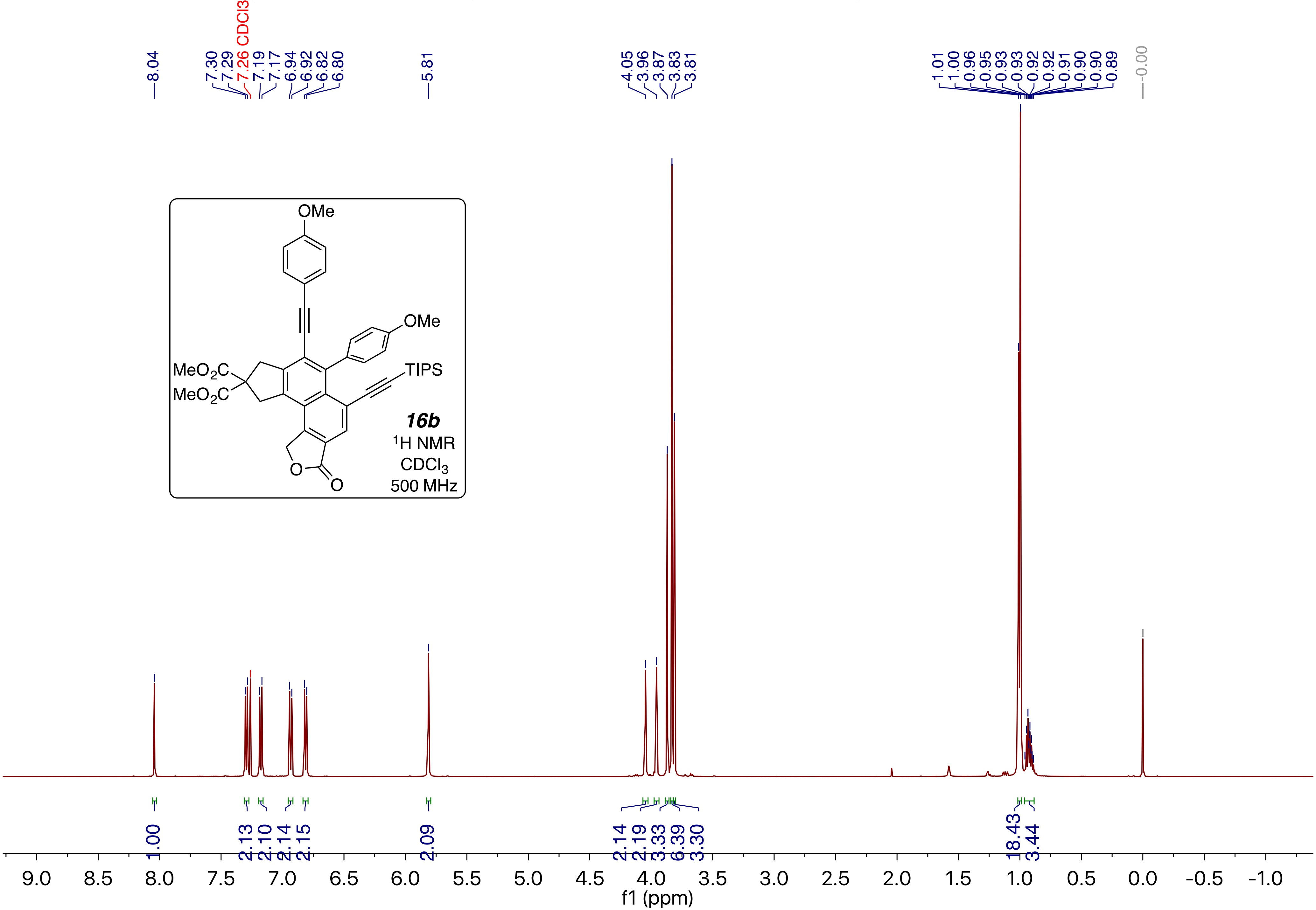

7.64
7.62
7.58
7.56
7.55
7.54
7.26 CDCl3
7.13
7.11
5.66
5.64
0.47
0.01
0.00
2.00
3.92
1.95
1.99
1.95
8.89
8.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
TMS
CN
CN
O
O
O
O
TMS
13o
¹H NMR
CDCl₃
500 MHz

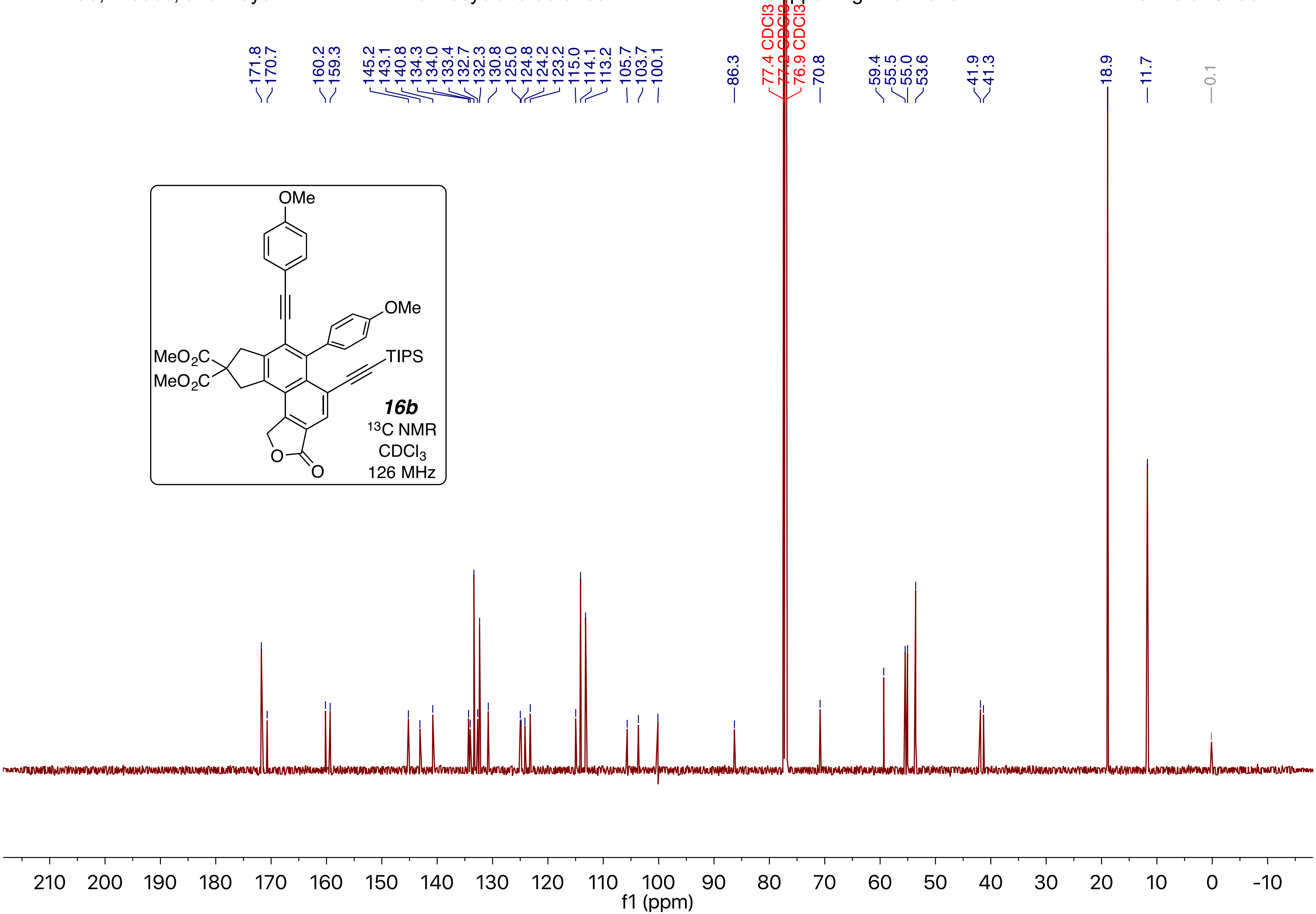

170.4
169.7
148.8
147.7
147.3
144.7
144.4
142.3
136.3
132.9
132.4
132.1
130.8
130.4
130.0
129.4
127.5
123.0
118.2
118.2
113.0
112.5
105.2
94.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
68.8
68.6
1.7
1.6
0.1
TMS
CN
CN
O
O
O
O
TMS
13o
^{13}C NMR
$CDCl_3$
126 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.15
8.14
7.98
7.94
7.92
7.49
7.48
7.27 CDCl3
7.19
7.17
5.83
4.08
4.00
3.97
3.92
3.84
0.92
-0.00
CO2Me
CO2Me
tBu
MeO2C
MeO2C
O
O
16a
1H NMR
CDCl3
500 MHz
2.00
0.96
1.99
1.99
2.01
2.02
2.03
3.10
2.05
3.11
6.06
9.11
9.0
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)


171.6
170.6
167.2
166.5
145.5
144.3
143.1
140.7
135.5
133.0
131.6
131.4
130.2
130.1
129.7
129.6
129.0
127.1
125.5
125.4
123.9
122.5
111.1
99.1
89.4
78.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
70.9
59.3
53.7
52.4
41.9
41.2
30.4
28.1
0.1
CO2Me
CO2Me
MeO2C
MeO2C
tBu
O
O
16a
13C NMR
CDCl3
126 MHz
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)


CO2Me
CO2Me
tBu
MeO2C
MeO2C
O
O
16a
HMBC
CDCl3
500 MHz
f2 (ppm)
f1 (ppm)
9.0 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
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200


8.04
7.30
7.29
7.26 CDCl3
7.19
7.17
6.94
6.92
6.82
6.80
5.81
4.05
3.96
3.87
3.83
3.81
1.01
1.00
0.96
0.95
0.93
0.93
0.92
0.92
0.91
0.90
0.90
0.89
-0.00
OMe
OMe
TIPS
MeO2C
MeO2C
O
O
16b
1H NMR
CDCl3
500 MHz
1.00
2.13
2.10
2.14
2.15
2.09
2.14
2.19
3.33
6.39
3.30
18.43
3.44
9.0
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)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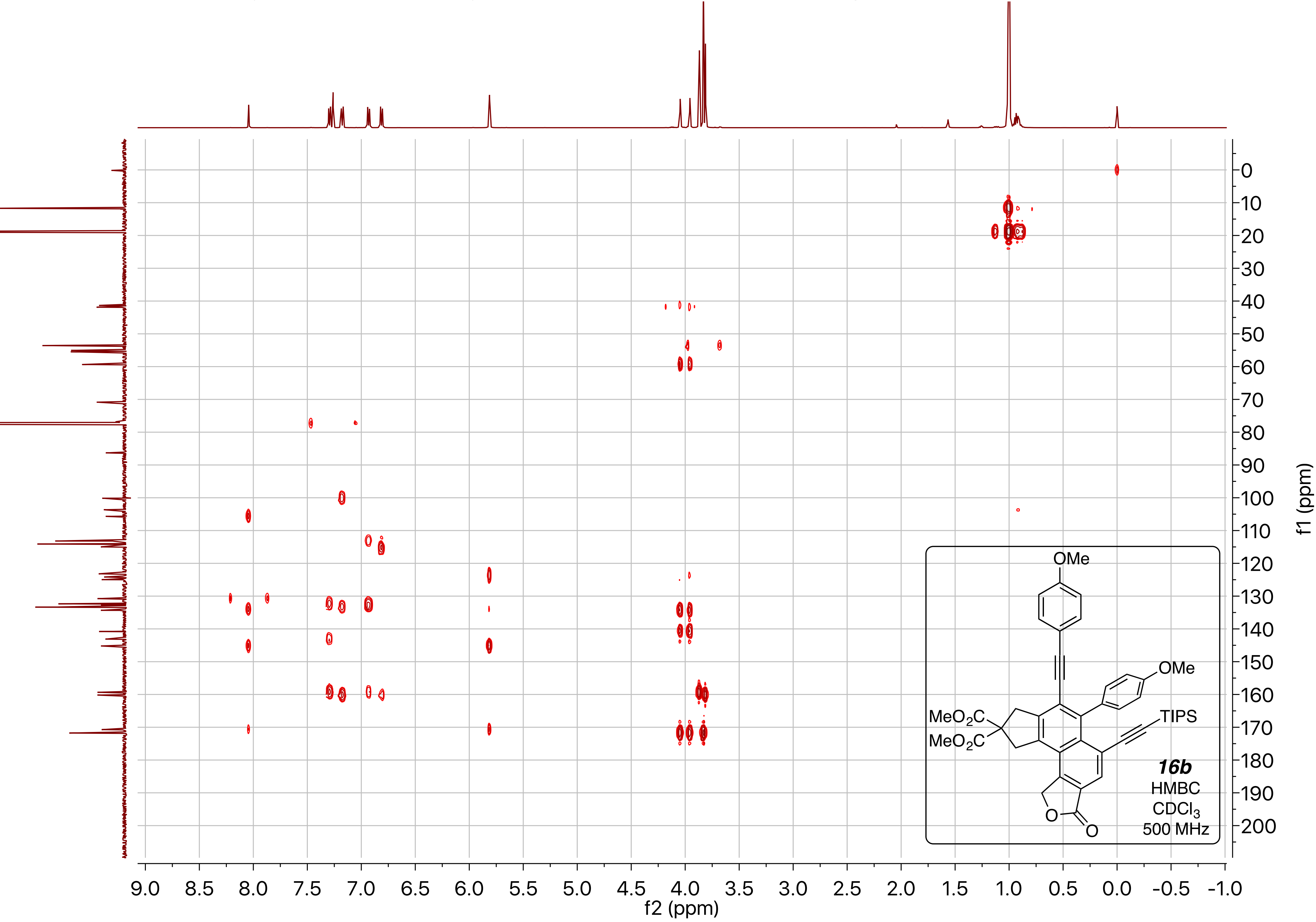
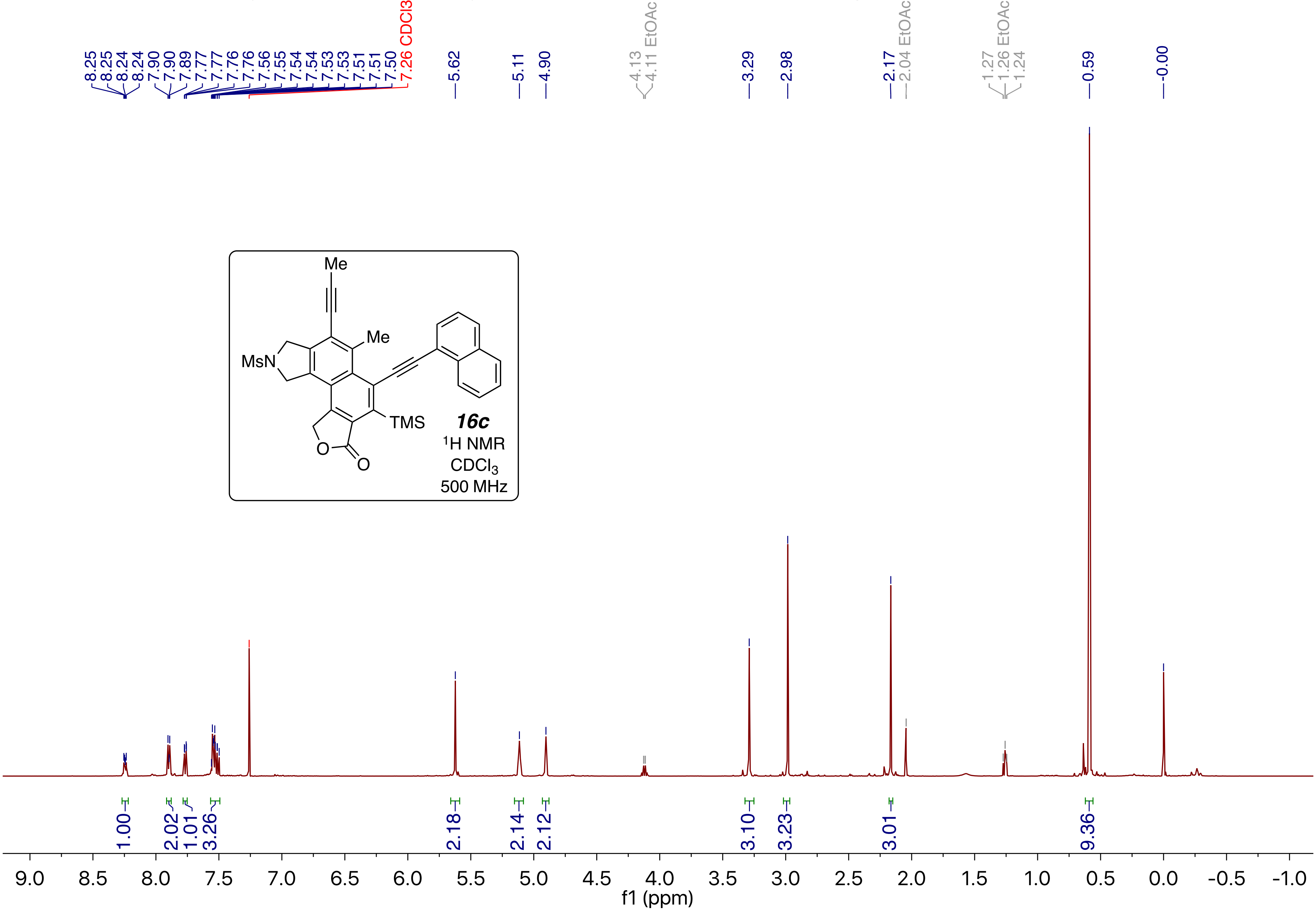
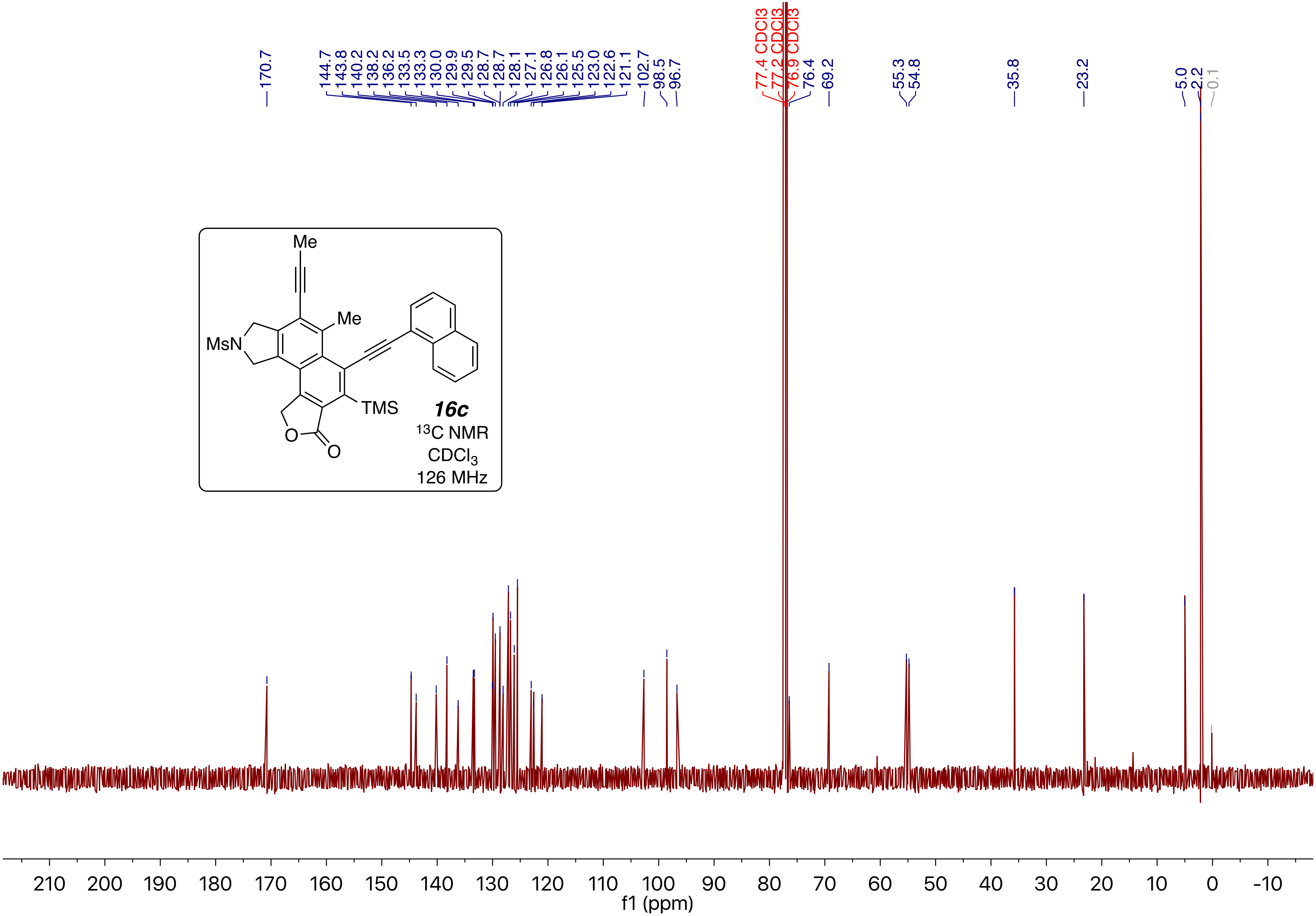
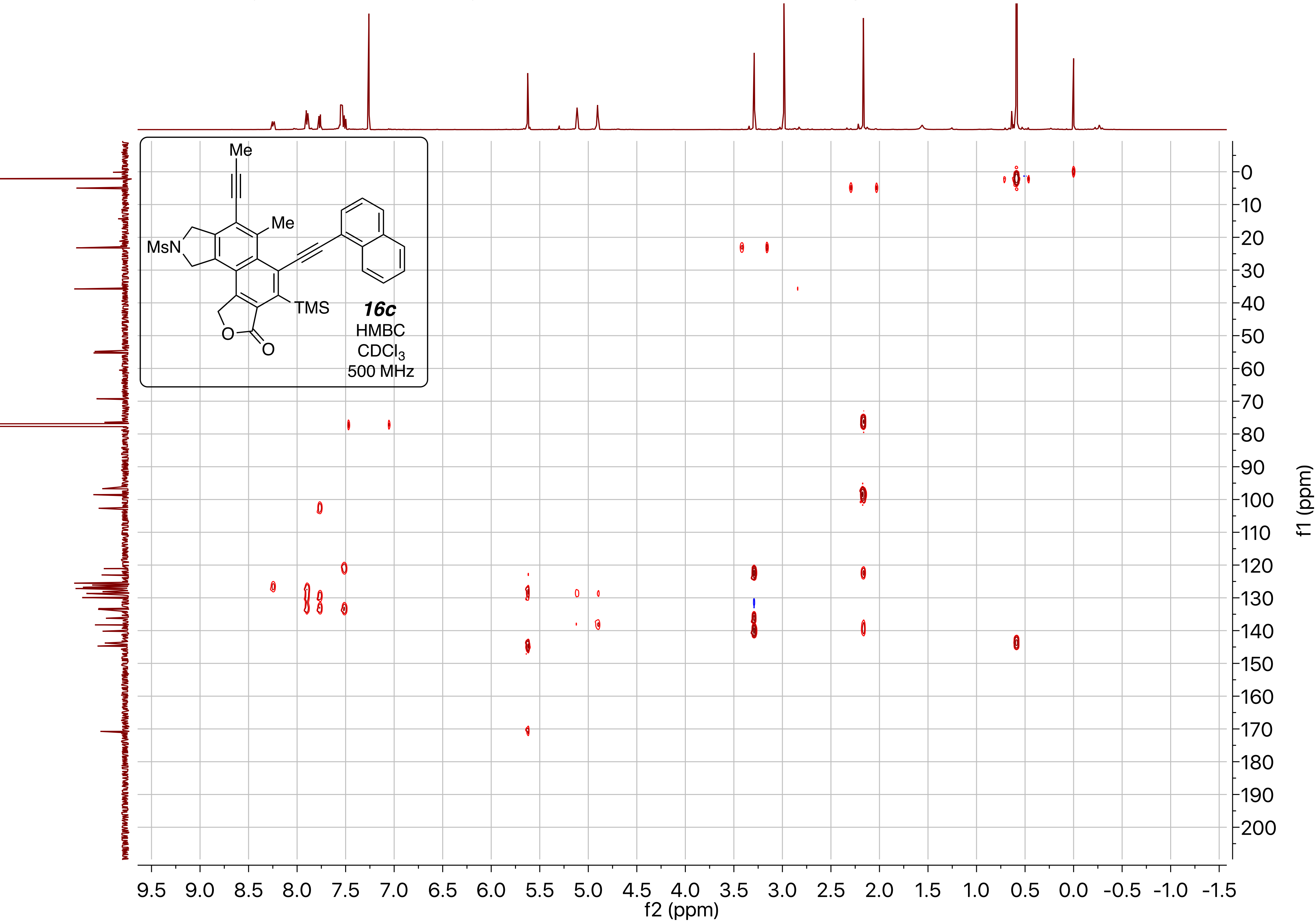
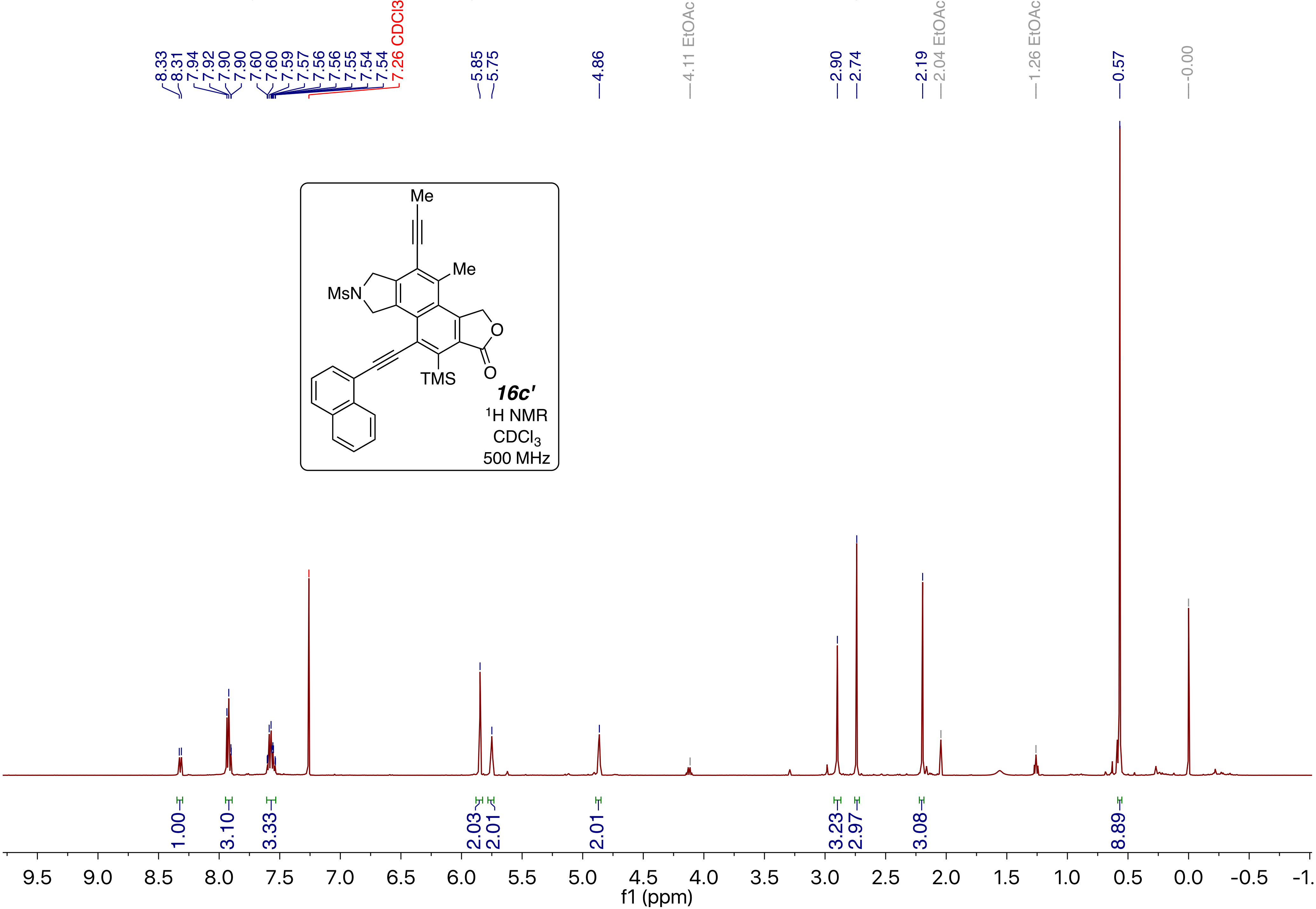
170.7
160.2
159.3
145.2
143.1
140.8
134.3
134.0
133.4
132.7
132.3
130.8
125.0
124.8
124.2
123.2
115.0
114.1
113.2
105.7
103.7
100.1
86.3
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
70.8
59.4
55.5
55.0
53.6
41.9
41.3
18.9
11.7
0.1
OMe
OMe
MeO$_2$C
MeO$_2$C
TIPS
O
O
16b
^{13}C NMR
CDCl$_3$
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

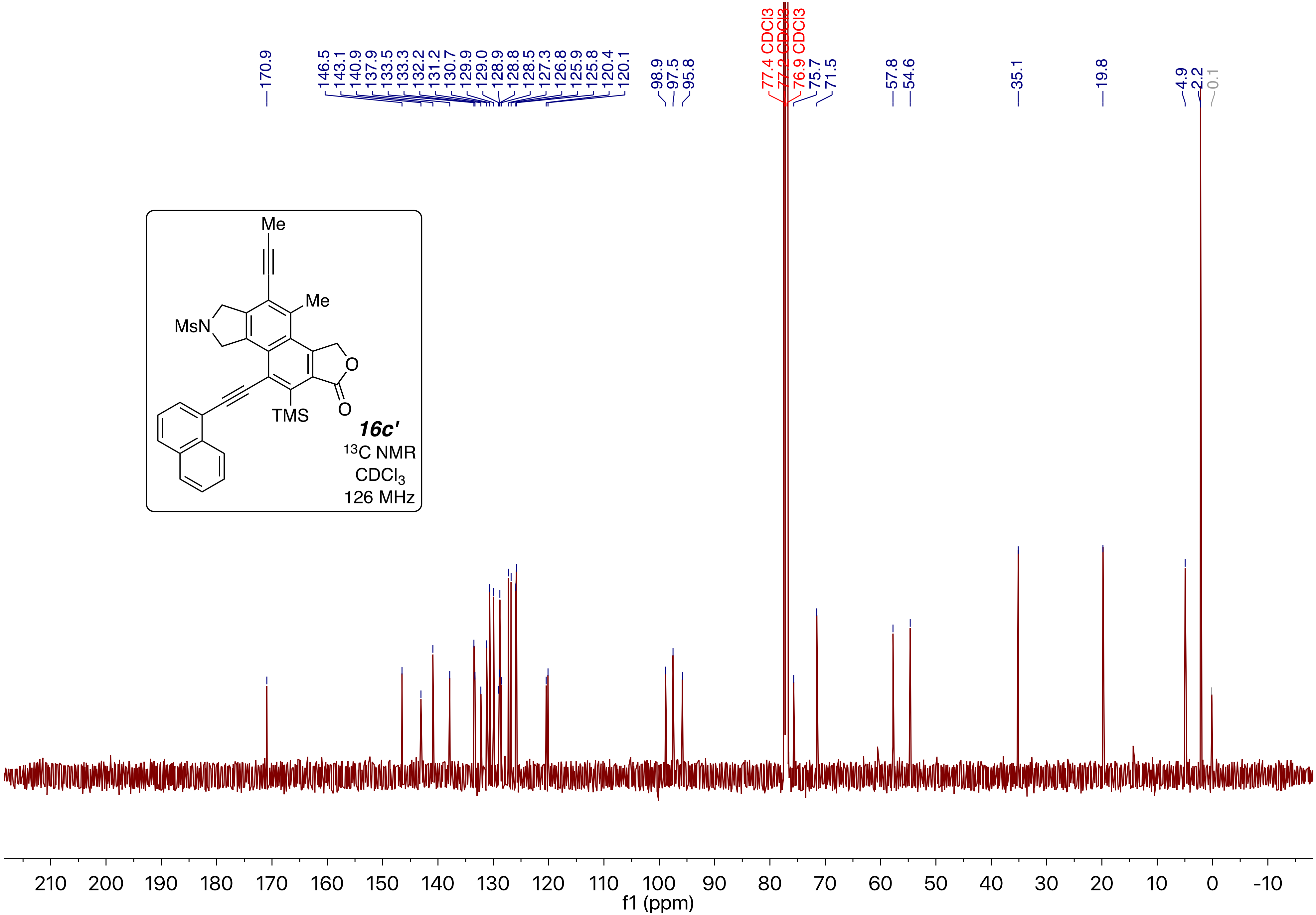

OMe
OMe
TIPS
MeO$_2$C
MeO$_2$C
O
O
16b
HMBC
CDCl$_3$
500 MHz
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
f1 (ppm)

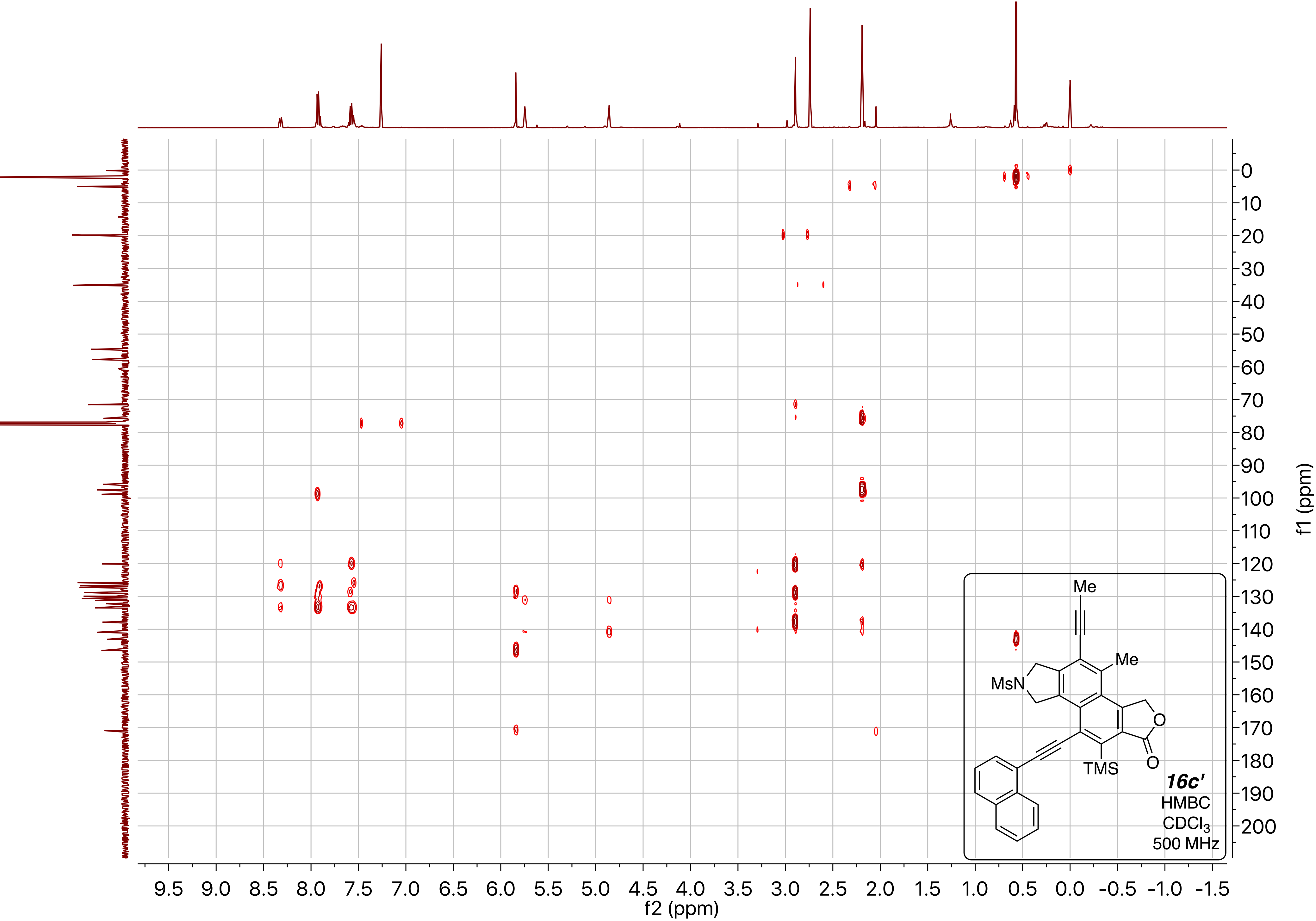

8.25
8.25
8.24
8.24
7.90
7.90
7.89
7.77
7.77
7.76
7.76
7.56
7.55
7.54
7.54
7.53
7.53
7.51
7.51
7.50
7.26 CDCl3
5.62
5.11
4.90
4.13
4.11 EtOAc
3.29
2.98
2.17
2.04 EtOAc
1.27
1.26 EtOAc
1.24
0.59
-0.00
Me
Me
MsN
TMS
O
O
16c
^{1}H NMR
$CDCl_3$
500 MHz
1.00
2.02
1.01
3.26
2.18
2.14
2.12
3.10
3.23
3.01
9.36
9.0
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)


170.7
144.7
143.8
140.2
138.2
136.2
133.5
133.3
130.0
129.9
129.5
128.7
128.7
128.1
127.1
126.8
126.1
125.5
123.0
122.6
121.1
102.7
98.5
96.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.4
69.2
55.3
54.8
35.8
23.2
5.0
2.2
0.1
Me
Me
MsN
TMS
O
O
16c
13C NMR
CDCl3
126 MHz
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)

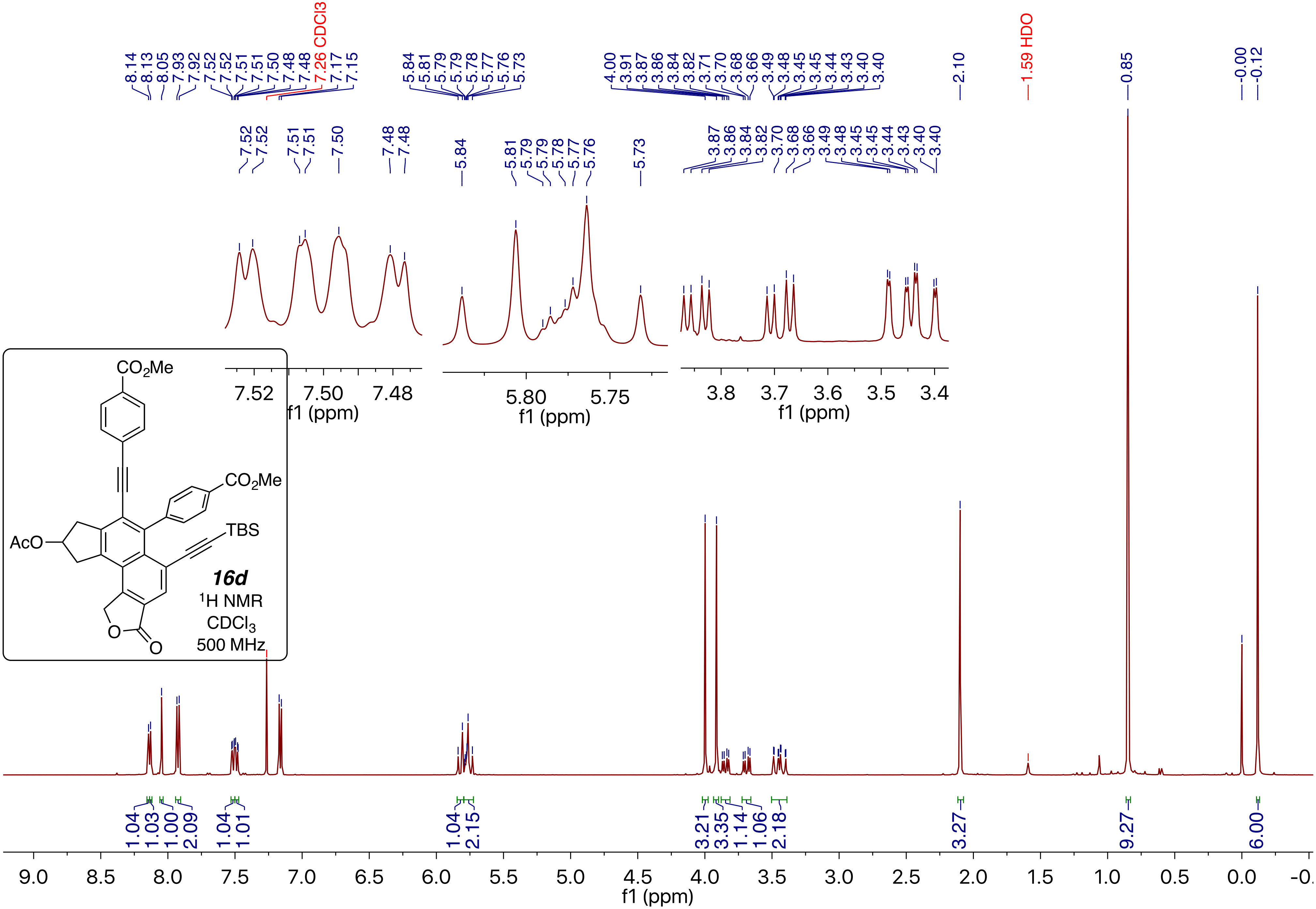

Me
Me
MsN
TMS
O
O
16c
HMBC
CDCl$_3$
500 MHz
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f2 (ppm)


8.33
8.31
7.94
7.92
7.90
7.90
7.60
7.60
7.59
7.57
7.56
7.56
7.55
7.54
7.54
7.26 CDCl3
5.85
5.75
4.86
4.11 EtOAc
2.90
2.74
2.19
2.04 EtOAc
1.26 EtOAc
0.57
-0.00
Me
Me
MsN
O
O
TMS
16c'
^{1}H NMR
$CDCl_3$
500 MHz
1.00
3.10
3.33
2.03
2.01
2.01
3.23
2.97
3.08
8.89
9.5
9.0
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.
f1 (ppm)

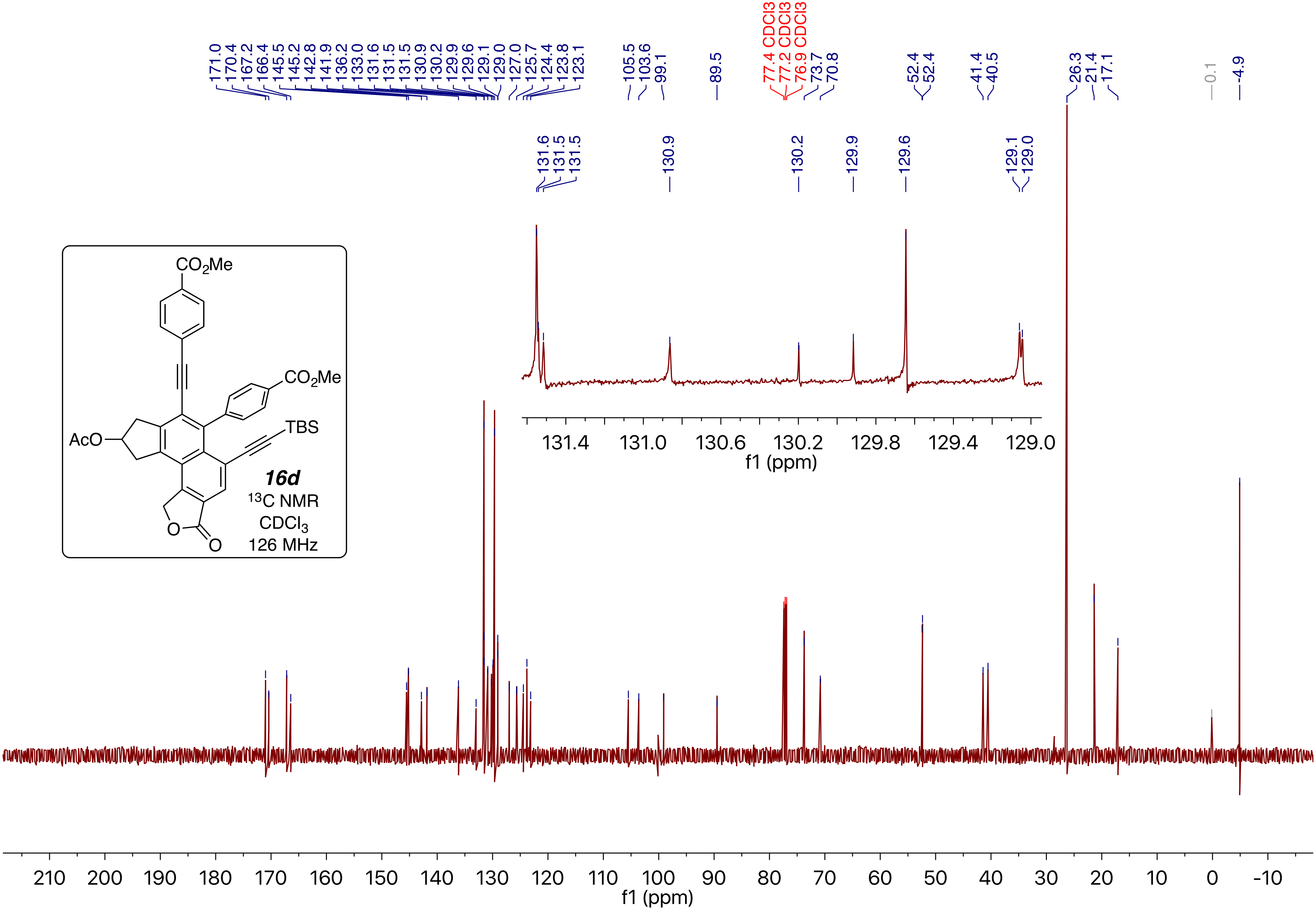

170.9
146.5
143.1
140.9
137.9
133.5
133.3
132.2
131.2
130.7
129.9
129.0
128.9
128.8
128.5
127.3
126.8
125.9
125.8
120.4
120.1
98.9
97.5
95.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
75.7
71.5
57.8
54.6
35.1
19.8
4.9
2.2
0.1
Me
Me
MsN
O
O
TMS
16c'
13C NMR
CDCl3
126 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

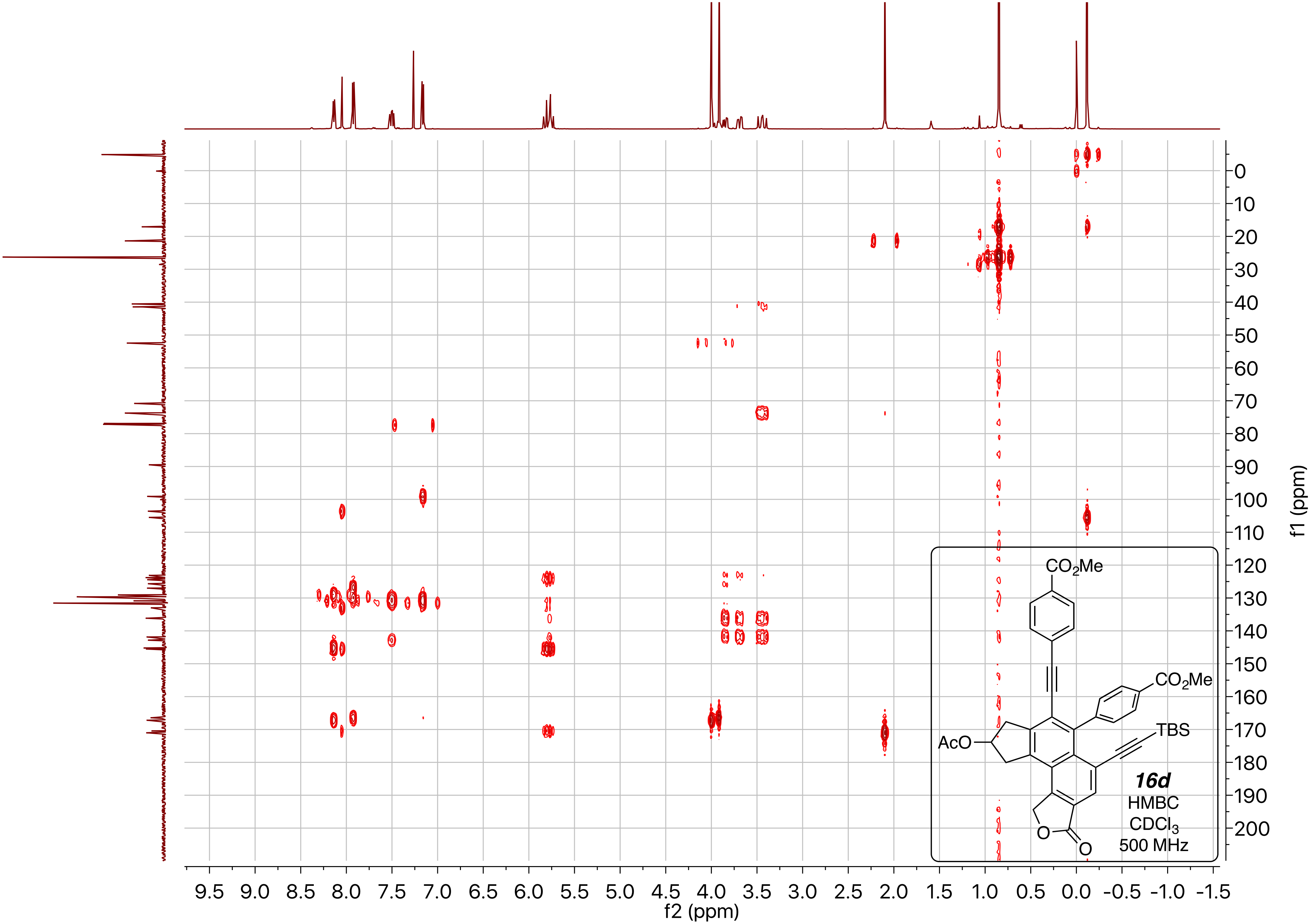


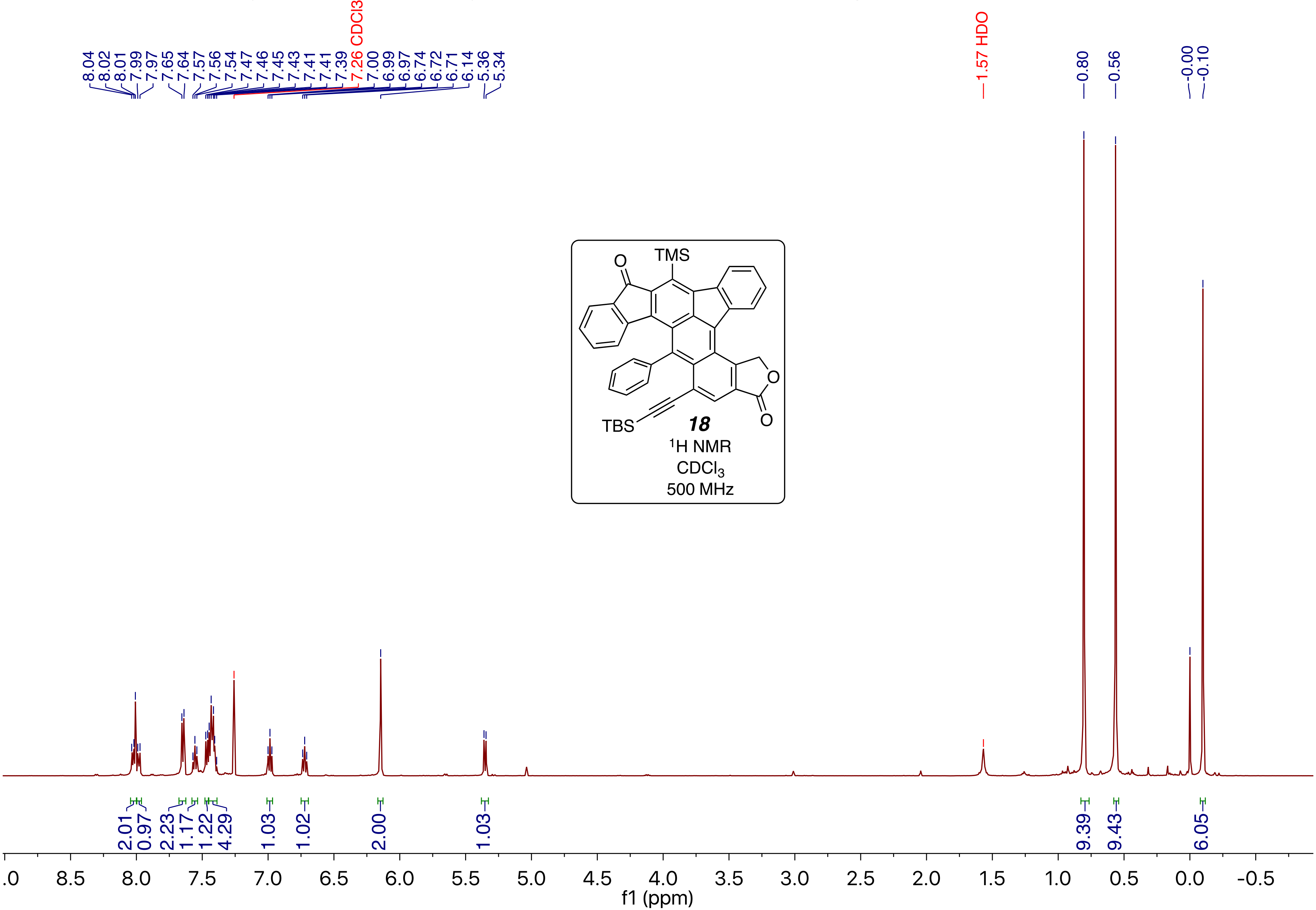
16c'
HMBC
$CDCl_3$
500 MHz

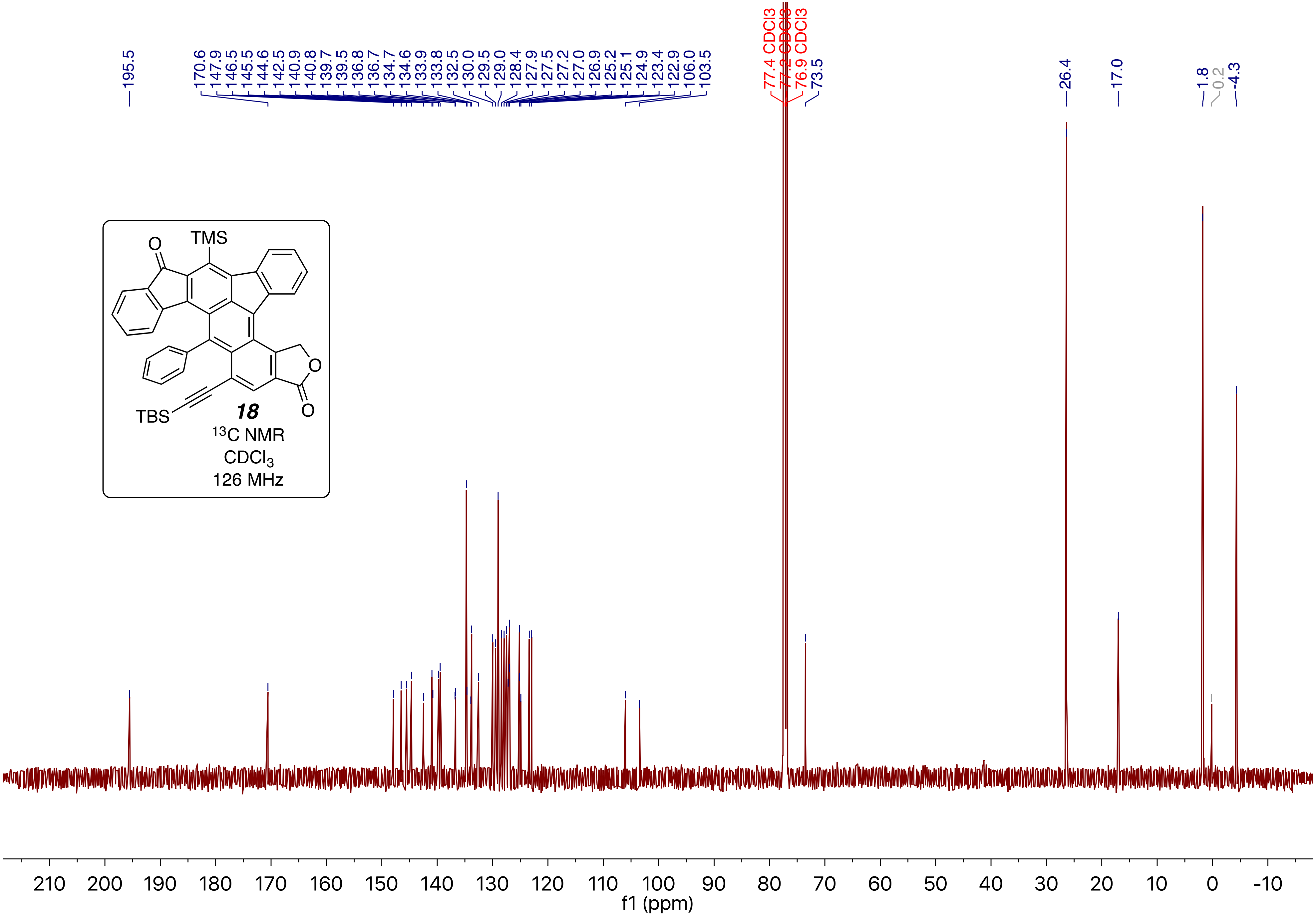


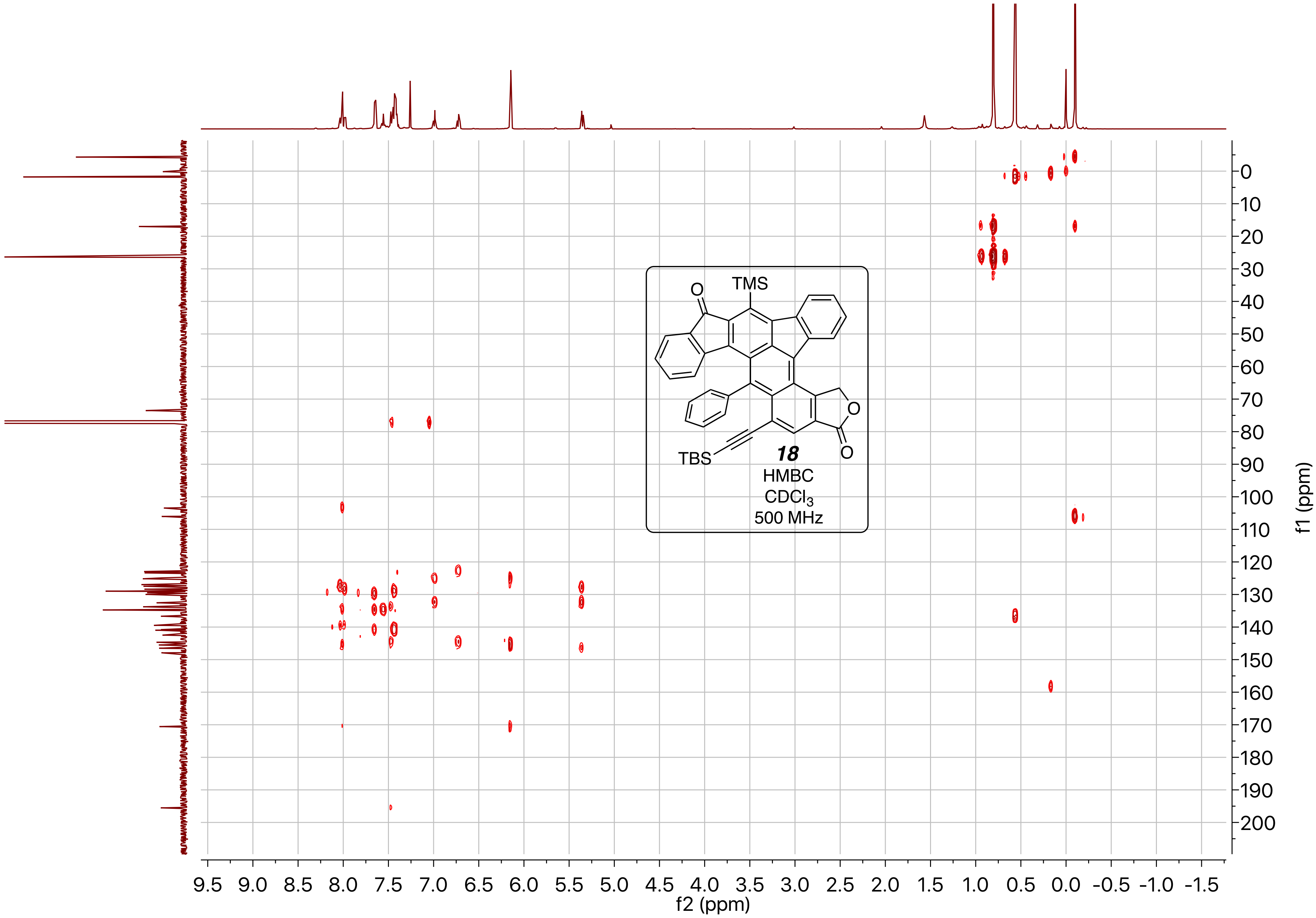
16d
^{1}H NMR
$CDCl_3$
500 MHz

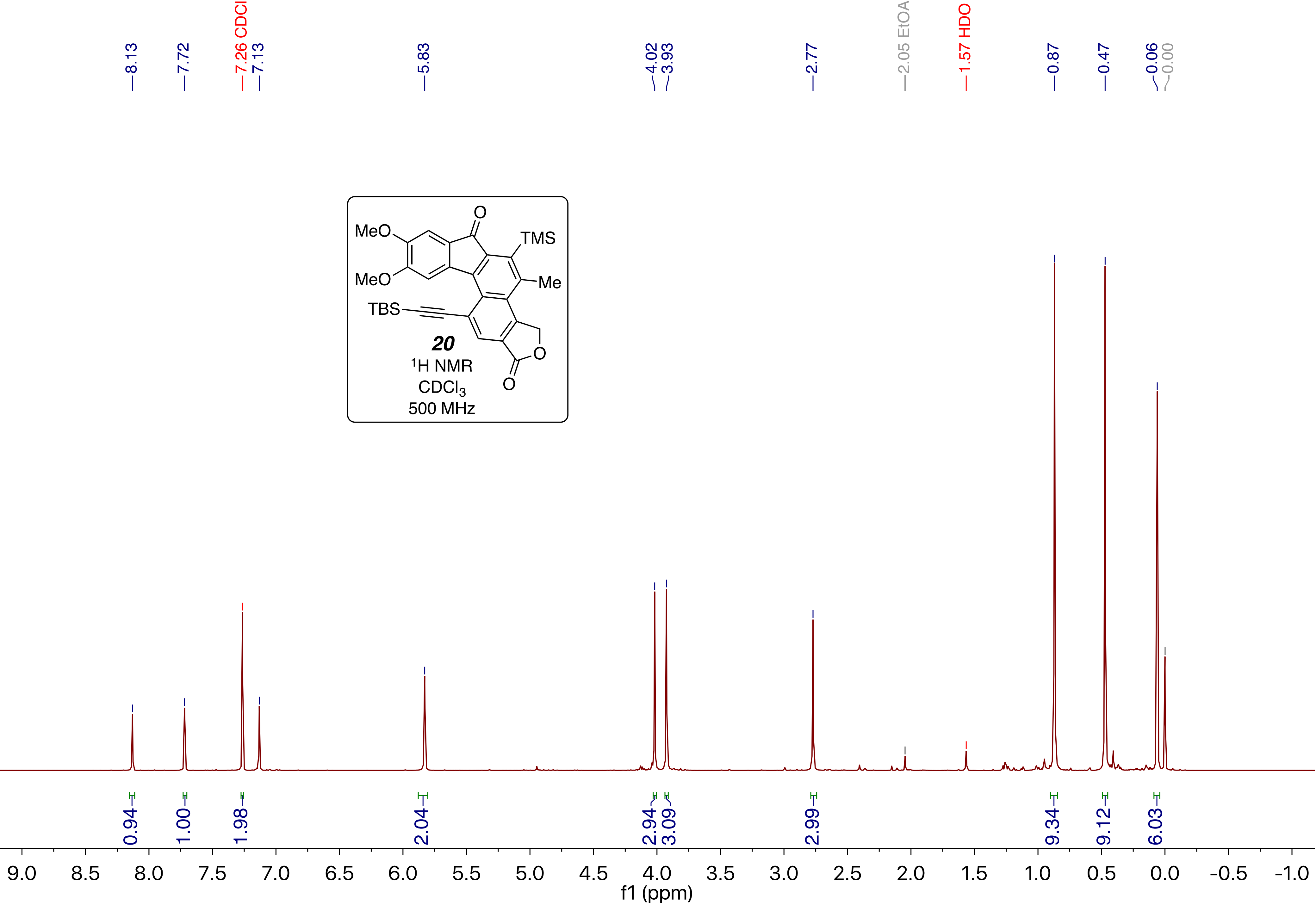

171.0
170.4
167.2
166.4
145.5
145.2
142.8
141.9
136.2
133.0
131.6
131.5
131.5
130.9
130.2
129.9
129.6
129.1
129.0
127.0
125.7
124.4
123.8
123.1
105.5
103.6
99.1
89.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
73.7
70.8
52.4
52.4
41.4
40.5
26.3
21.4
17.1
0.1
-4.9
131.6
131.5
131.5
130.9
130.2
129.9
129.6
129.1
129.0
131.4
131.0
130.6
130.2
129.8
129.4
129.0
f1 (ppm)
CO2Me
CO2Me
TBS
AcO
O
O
16d
13C NMR
CDCl3
126 MHz
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)

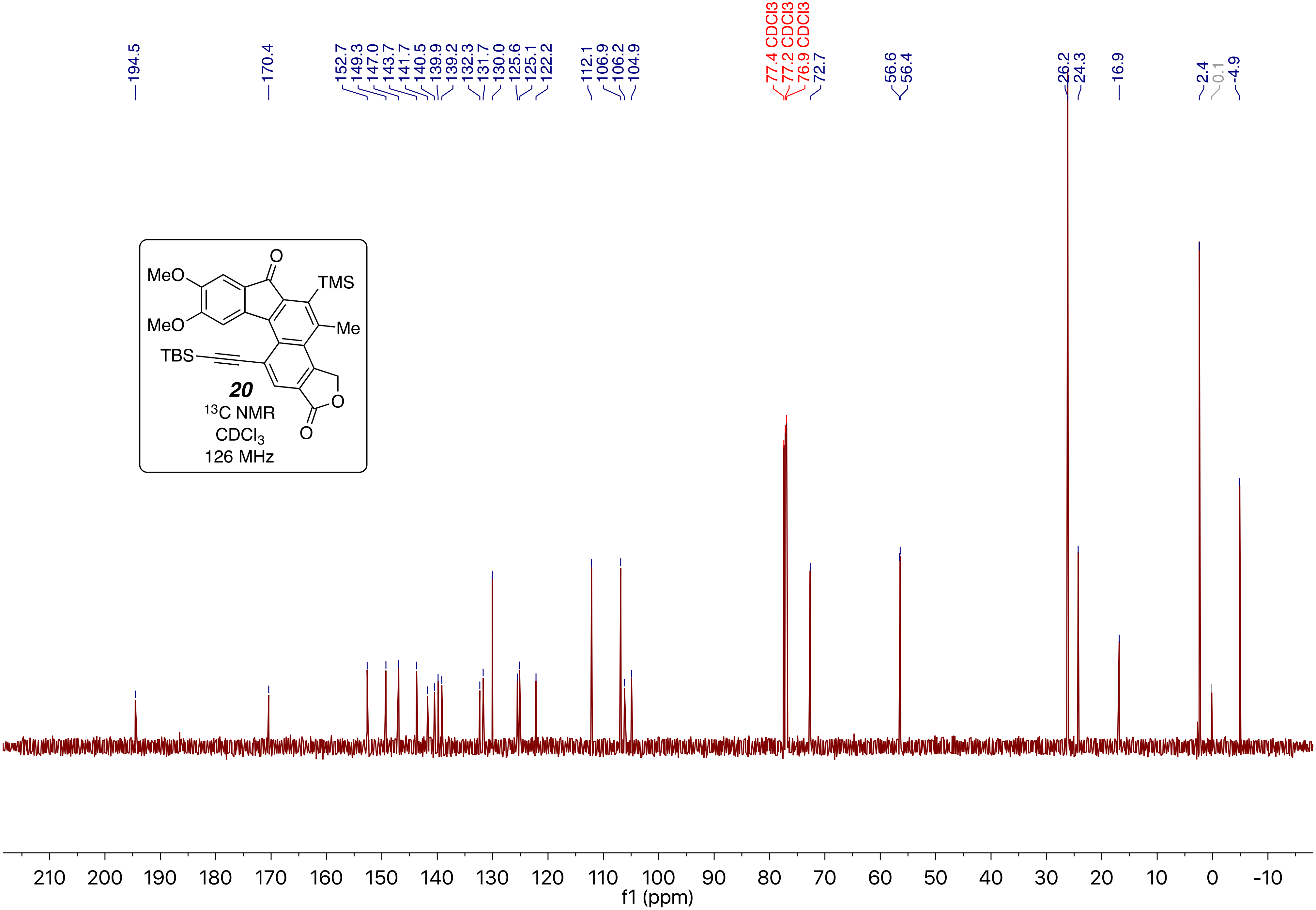

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)
CO_2Me
CO_2Me
TBS
AcO
O
O
16d
HMBC
$CDCl_3$
500 MHz

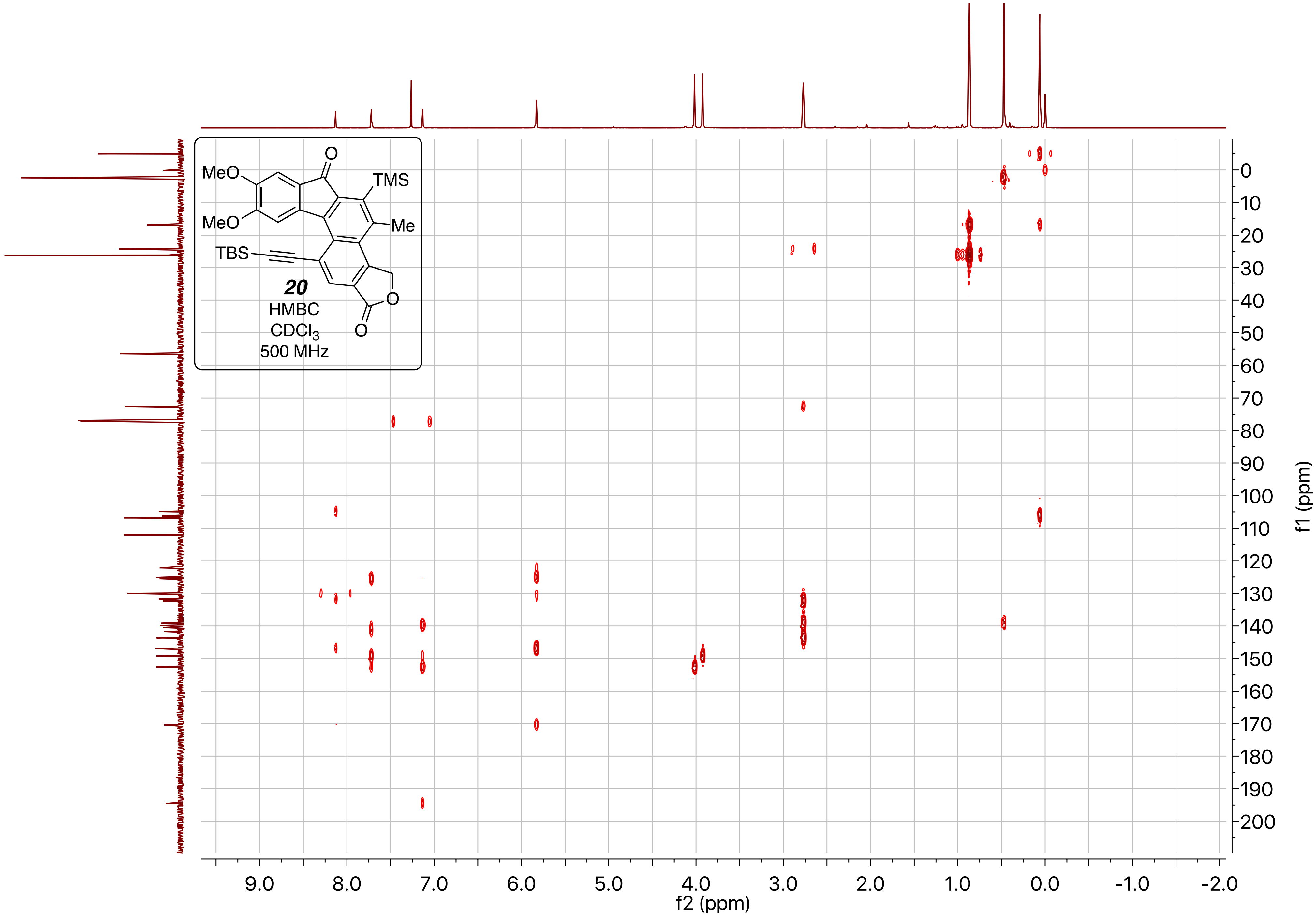

8.04
8.02
8.01
7.99
7.97
7.65
7.64
7.57
7.56
7.54
7.47
7.46
7.45
7.43
7.41
7.41
7.39
7.26 CDCl3
7.00
6.99
6.97
6.74
6.72
6.71
6.14
5.36
5.34
1.57 HDO
0.80
0.56
-0.00
-0.10
TMS
O
O
O
O
TBS
18
^{1}H NMR
$CDCl_3$
500 MHz
2.01
0.97
2.23
1.17
1.22
4.29
1.03
1.02
2.00
1.03
9.39
9.43
6.05
.0
8.5
8.0
7.5
7.0
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
f1 (ppm)

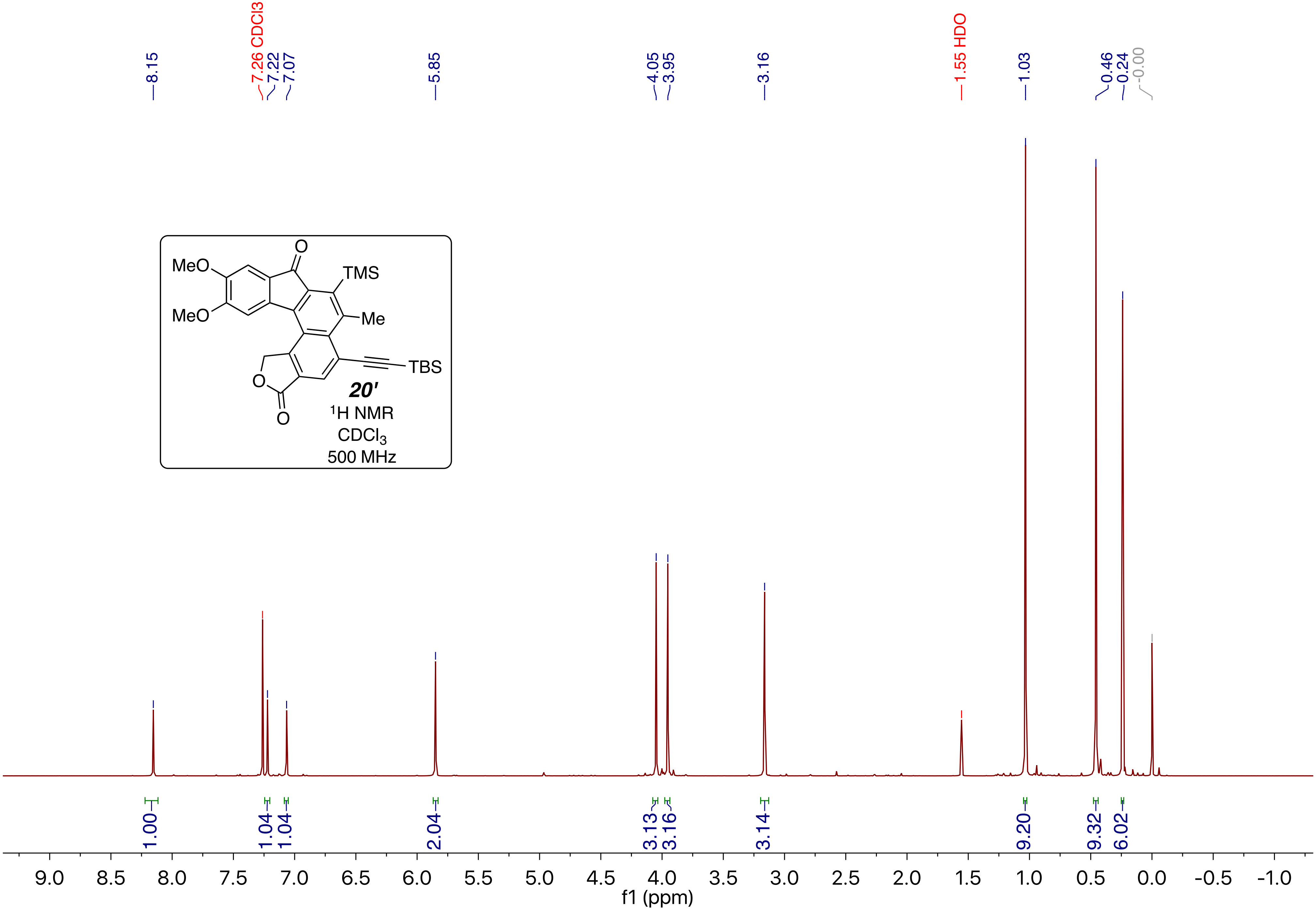

195.5
170.6
147.9
146.5
145.5
144.6
142.5
140.9
140.8
139.7
139.5
136.8
136.7
134.7
134.6
133.9
133.8
132.5
130.0
129.5
129.0
128.4
127.9
127.5
127.2
127.0
126.9
125.2
125.1
124.9
123.4
122.9
106.0
103.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
73.5
26.4
17.0
1.8
0.2
-4.3
O
TMS
O
O
TBS
18
^{13}C NMR
$CDCl_3$
126 MHz
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)


TMS
O
O
O
TBS
18
HMBC
CDCl3
500 MHz
f2 (ppm)
f1 (ppm)
9.5 9.0 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 -1.5
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200


8.13
7.72
7.26 CDCl3
7.13
5.83
4.02
3.93
2.77
2.05 EtOAc
1.57 HDO
0.87
0.47
0.06
0.00
MeO
MeO
O
TMS
Me
TBS
O
O
20
1H NMR
CDCl3
500 MHz
0.94
1.00
1.98
2.04
2.94
3.09
2.99
9.34
9.12
6.03
9.0
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)


194.5
170.4
152.7
149.3
147.0
143.7
141.7
140.5
139.9
139.2
132.3
131.7
130.0
125.6
125.1
122.2
112.1
106.9
106.2
104.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.7
56.6
56.4
26.2
24.3
16.9
2.4
0.1
-4.9
MeO
MeO
O
TMS
Me
TBS
O
O
20
^{13}C NMR
$CDCl_3$
126 MHz
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)


MeO
MeO
O
TMS
Me
TBS
O
O
20
HMBC
$CDCl_3$
500 MHz
f1 (ppm)
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0

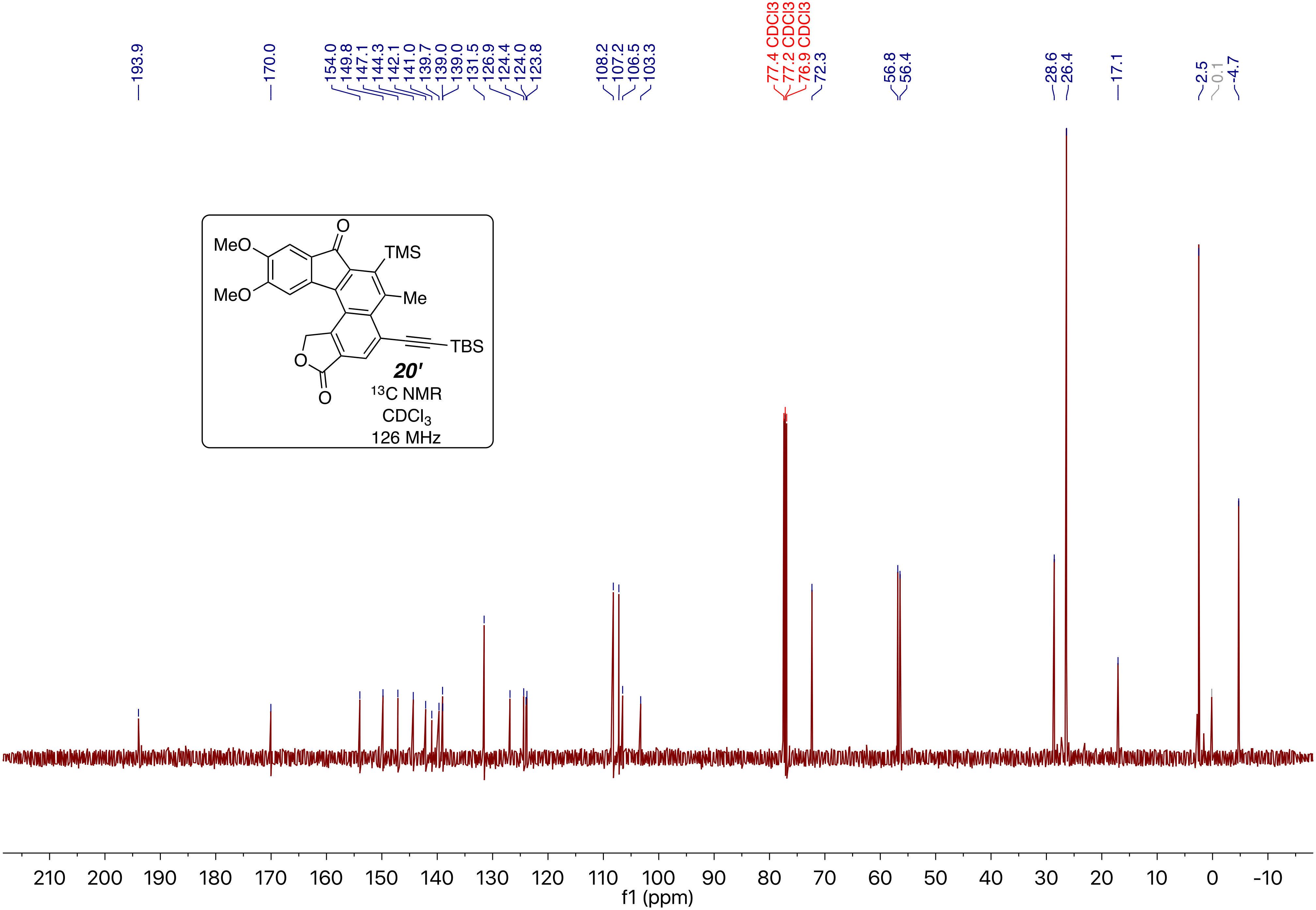


20′

^{1}H NMR

$CDCl_3$

500 MHz

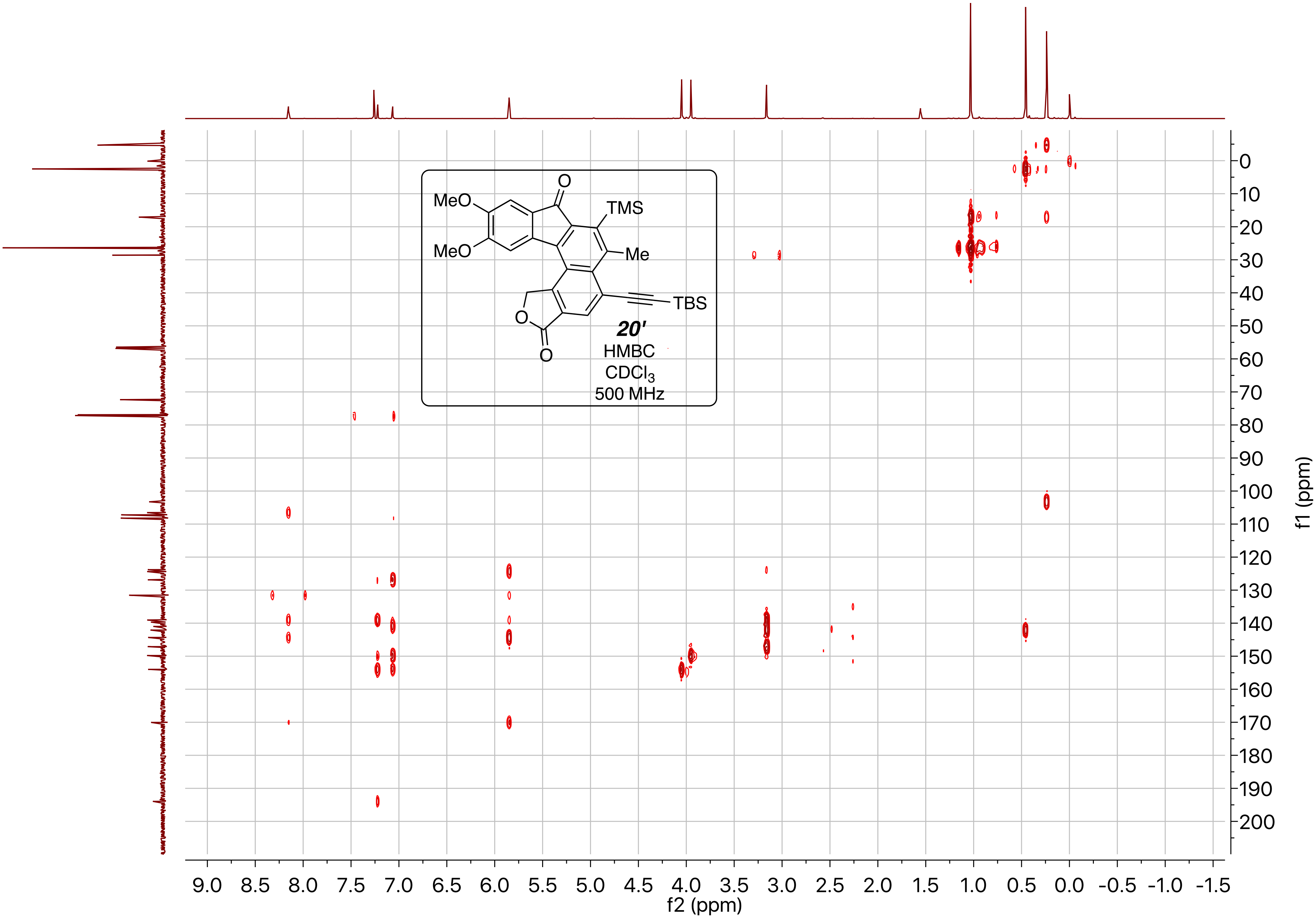


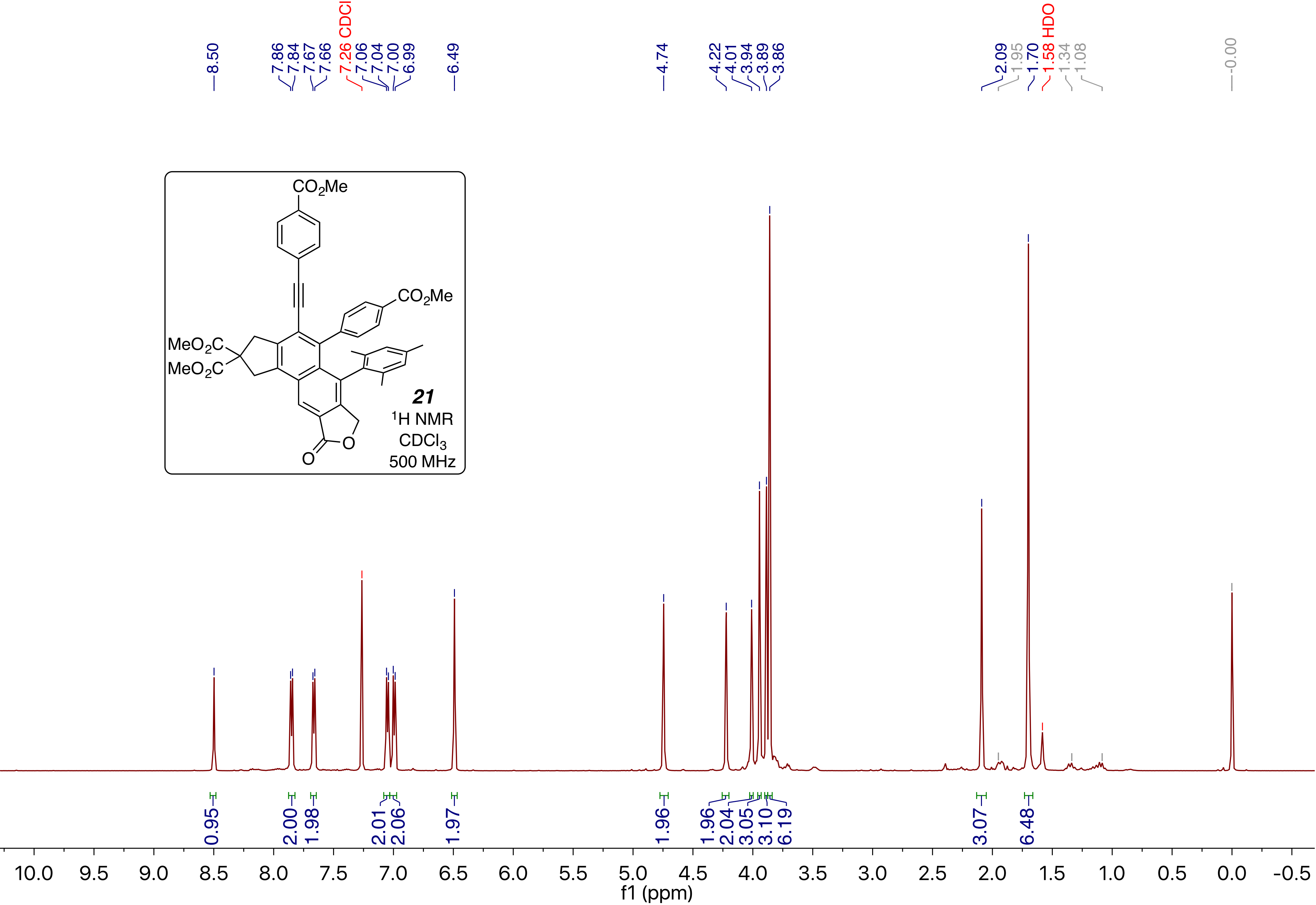
20′

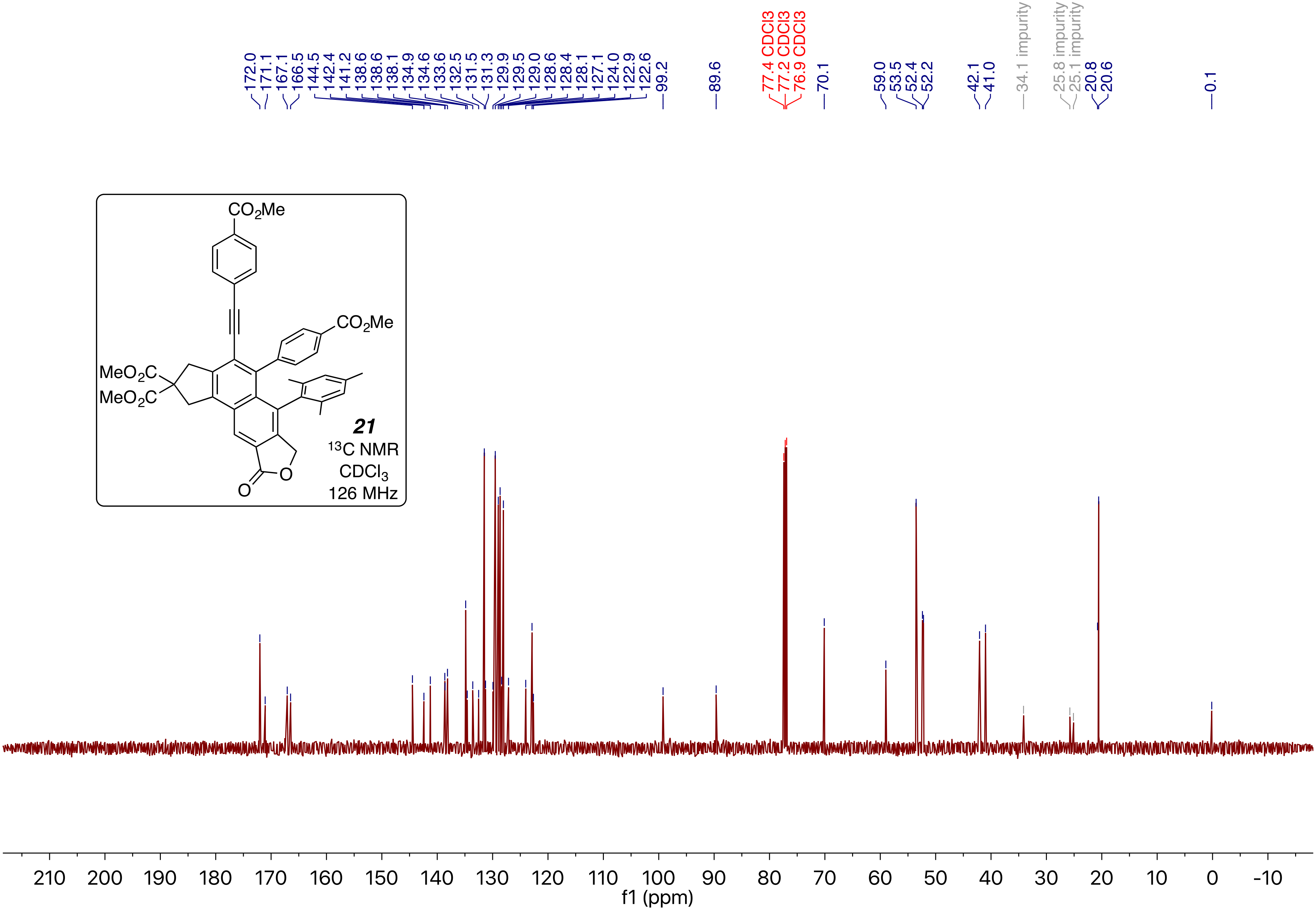
^{13}C NMR

$CDCl_3$

126 MHz


MeO
MeO
O
TMS
Me
TBS
O
O
20′
HMBC
CDCl3
500 MHz
9.0 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 -1.5
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
f1 (ppm)


8.50
7.86
7.84
7.67
7.66
7.26 CDCl3
7.06
7.04
7.00
6.99
6.49
4.74
4.22
4.01
3.94
3.89
3.86
2.09
1.95
1.70
1.58 HDO
1.34
1.08
-0.00
CO$_2$Me
CO$_2$Me
MeO$_2$C
MeO$_2$C
O
O
21
^{1}H NMR
CDCl$_3$
500 MHz
0.95
2.00
1.98
2.01
2.06
1.97
1.96
1.96
2.04
3.05
3.10
6.19
3.07
6.48
10.0
9.5
9.0
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
f1 (ppm)

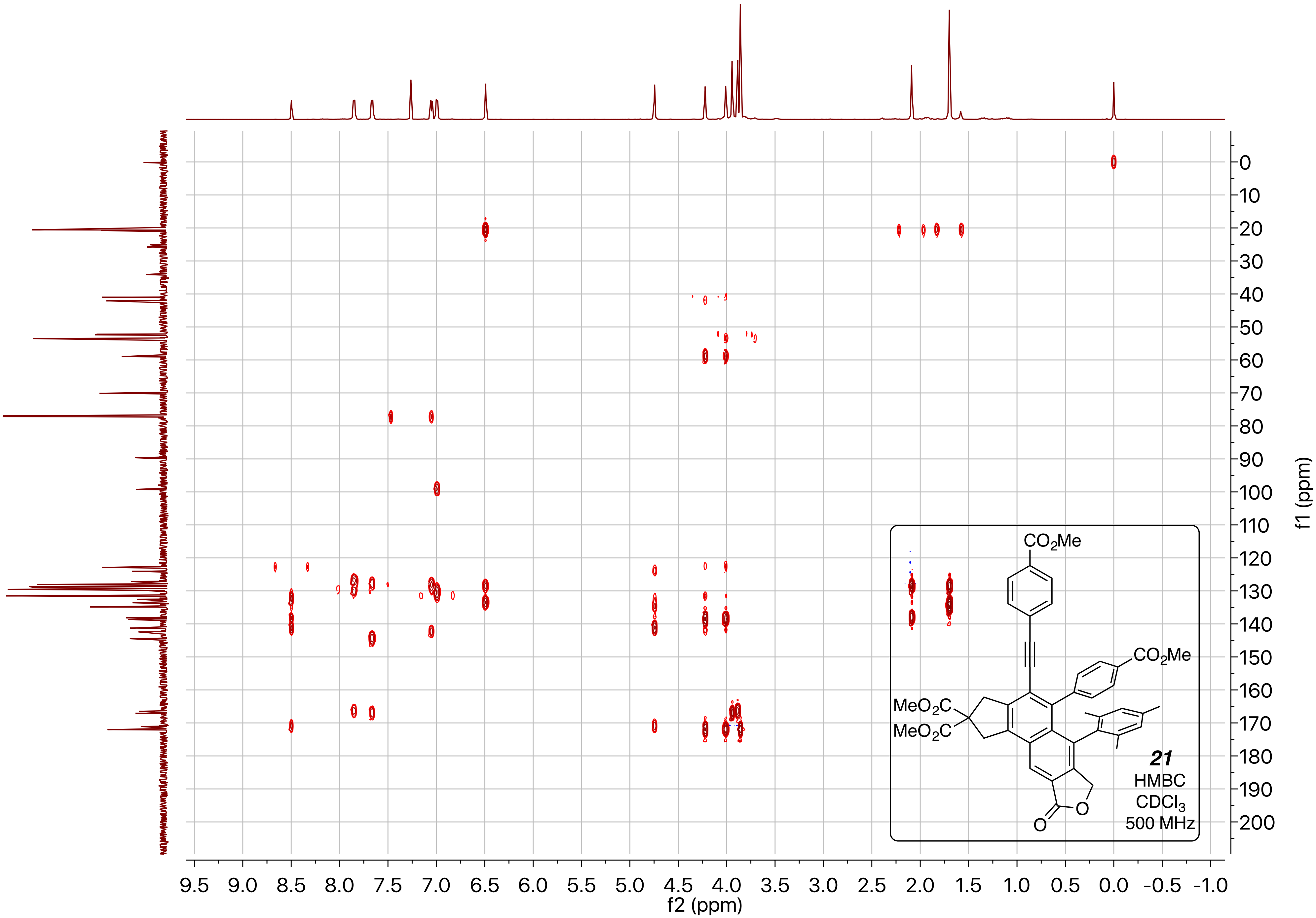


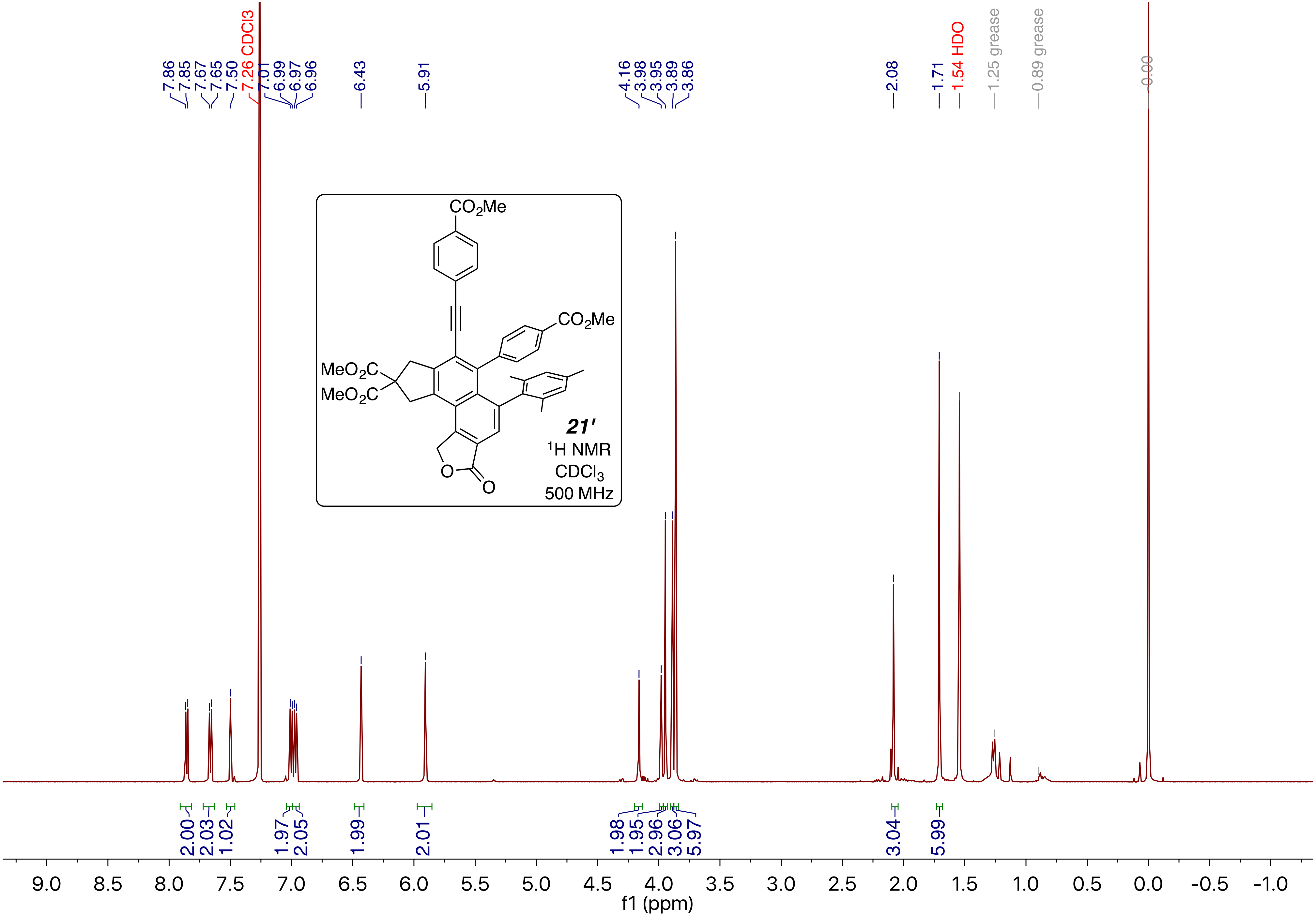
21

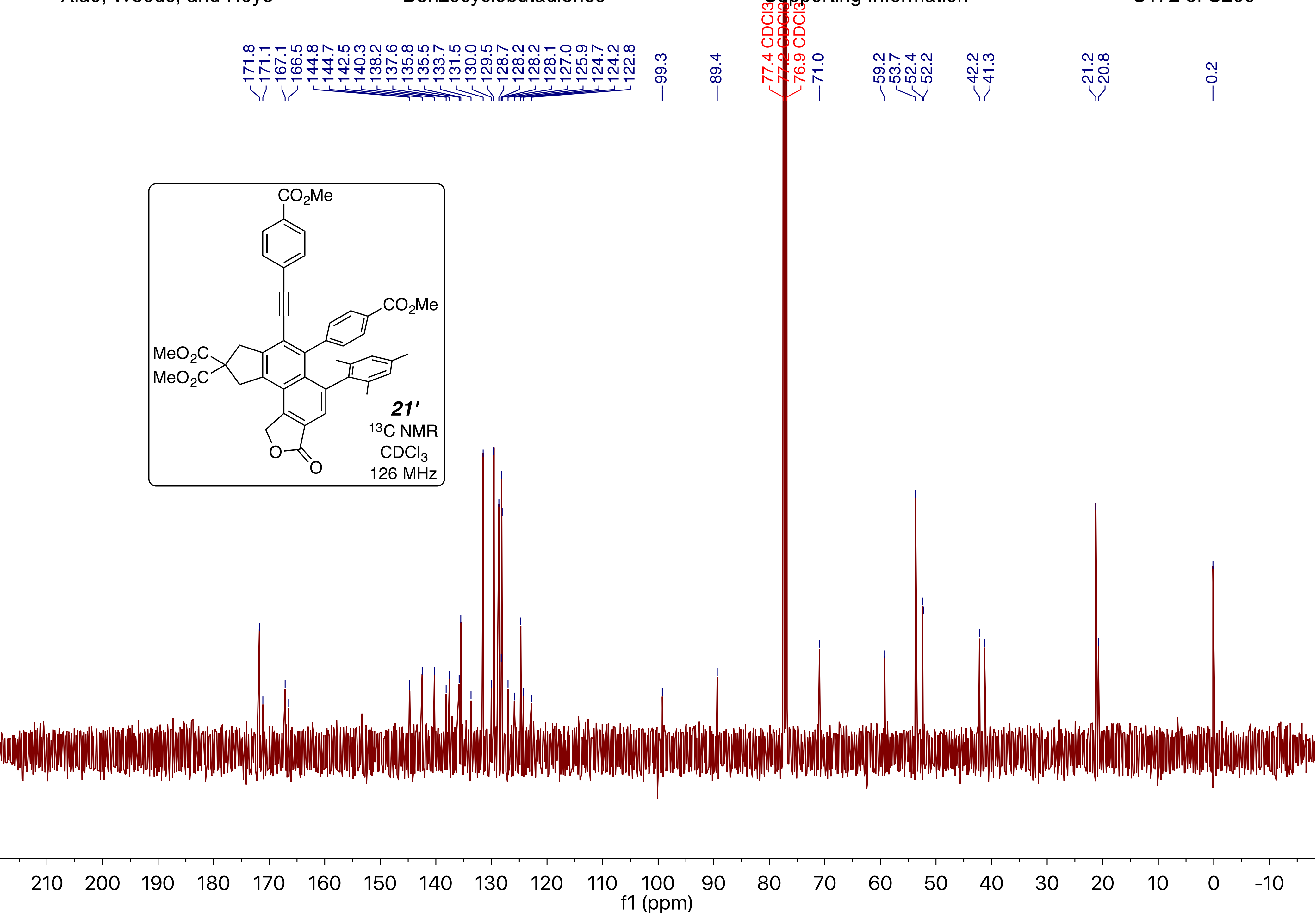
^{13}C NMR

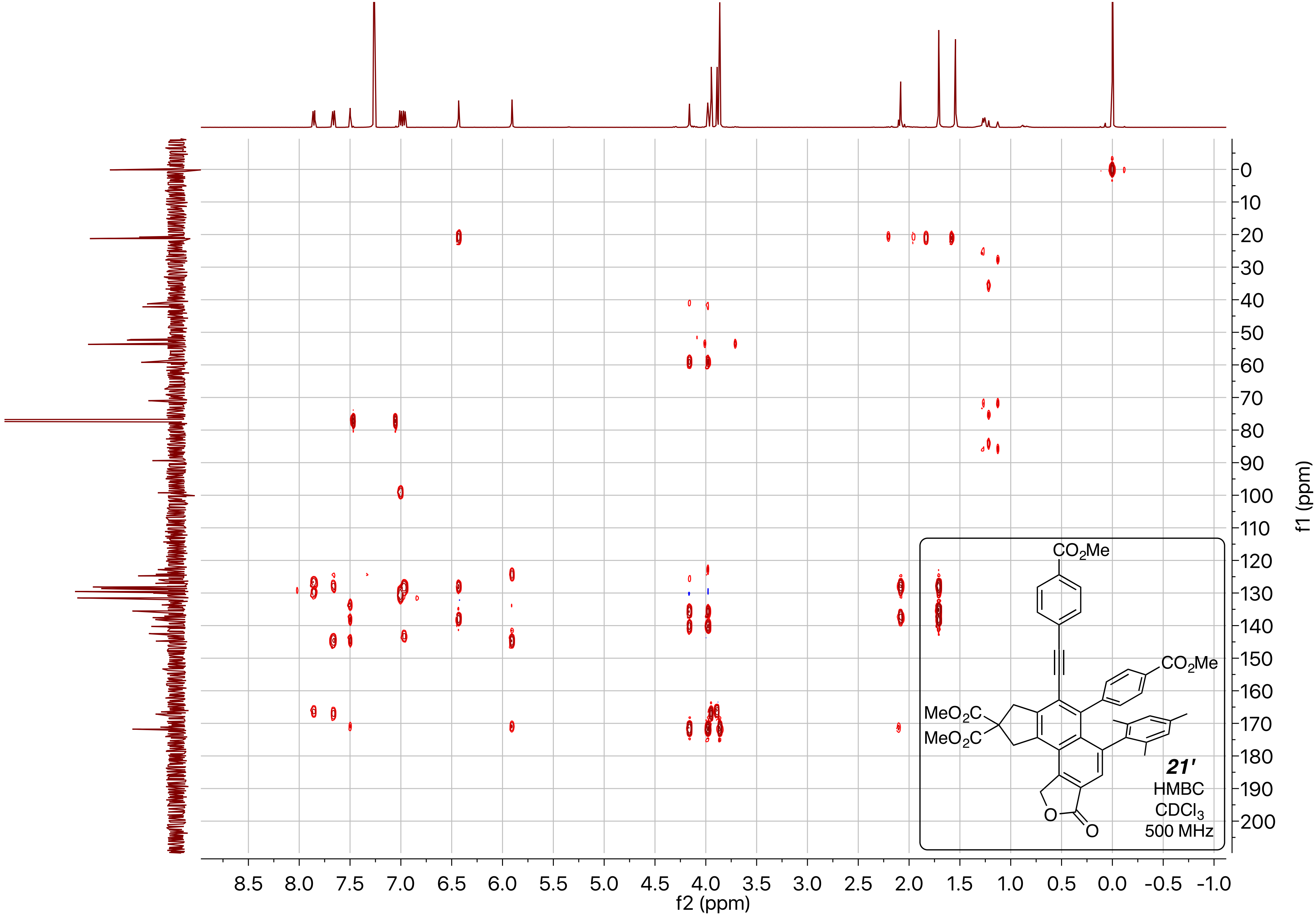
CDCl$_3$

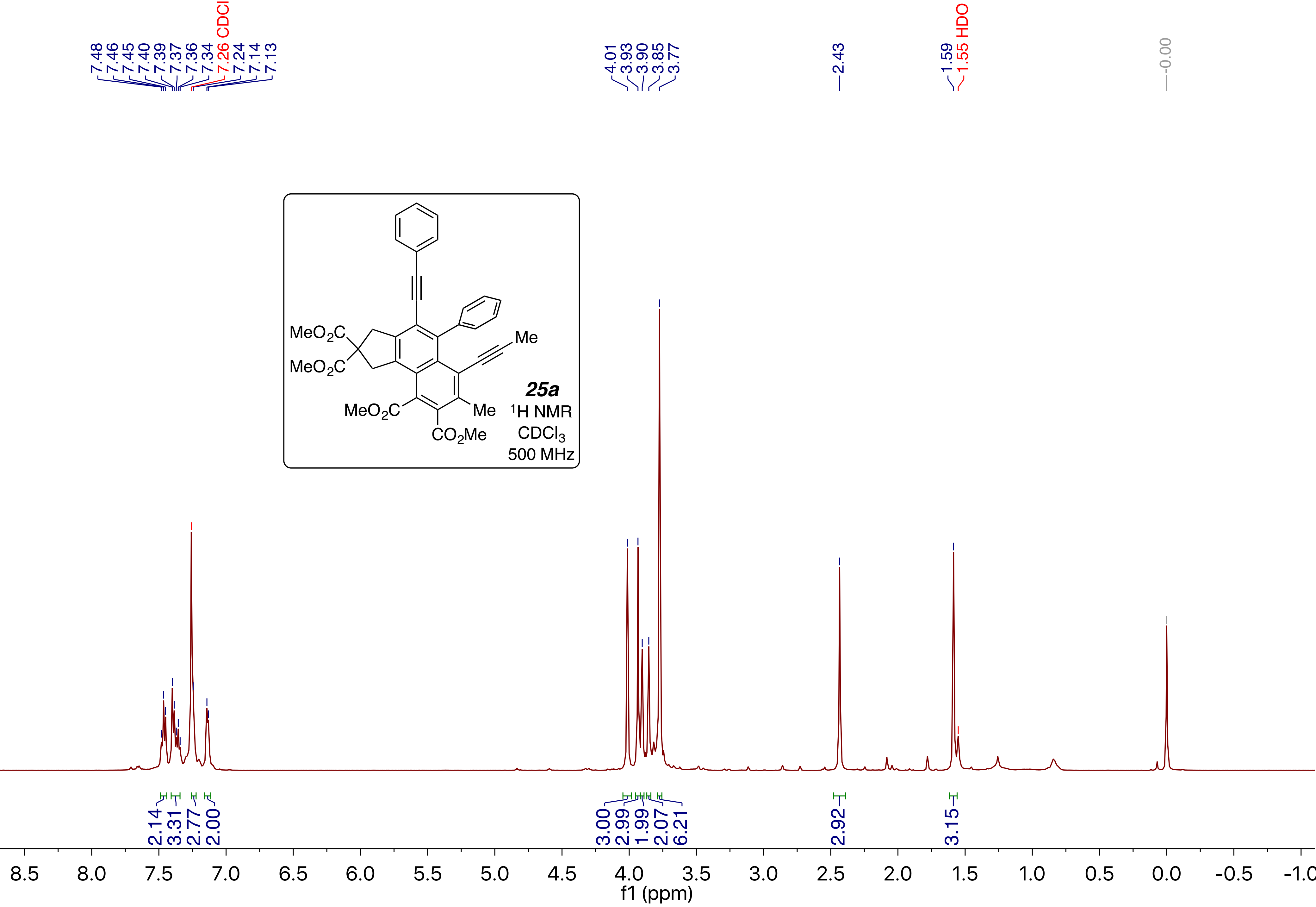
126 MHz

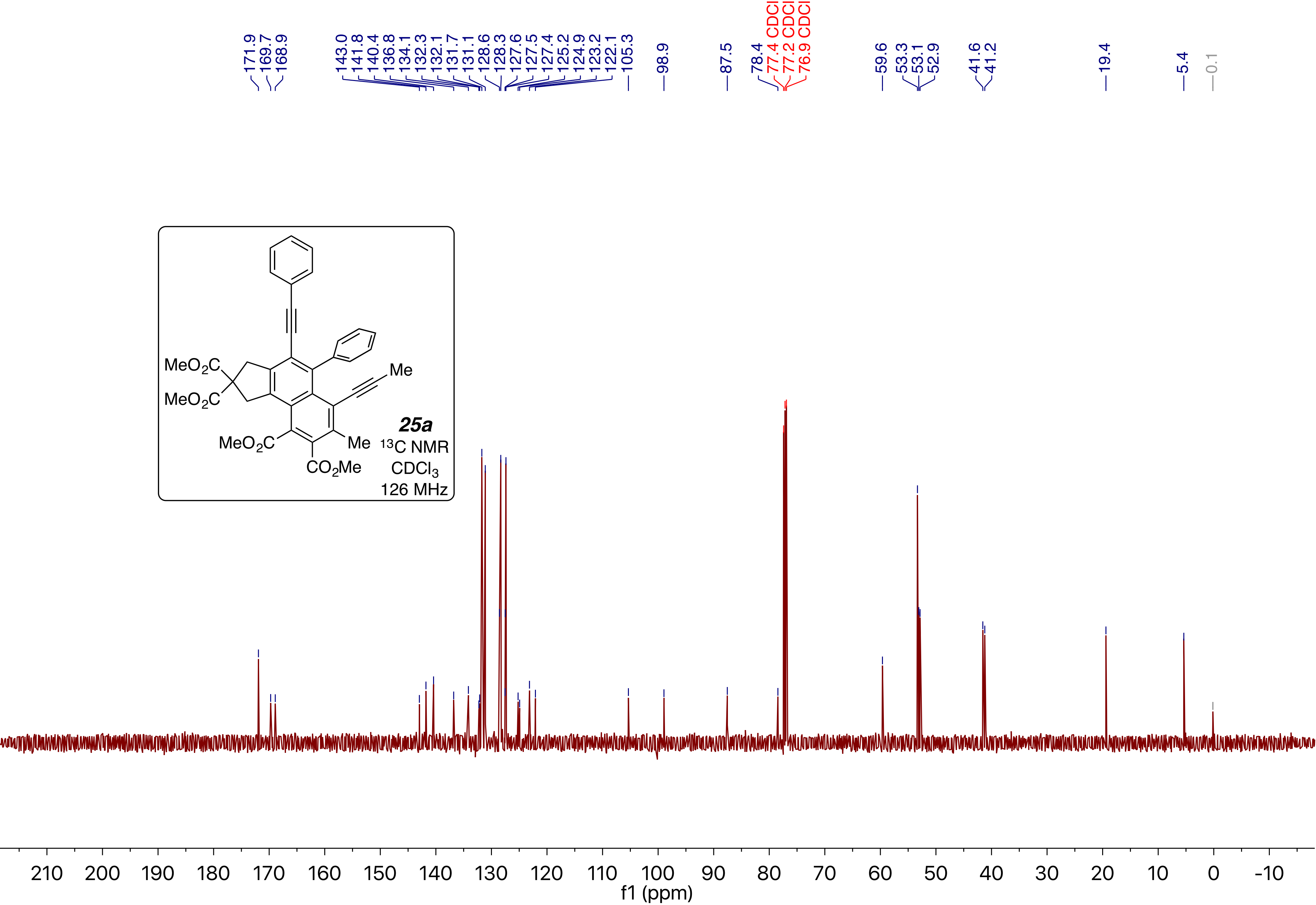

CO2Me
CO2Me
MeO2C
MeO2C
O
O
21
HMBC
CDCl3
500 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
f1 (ppm)

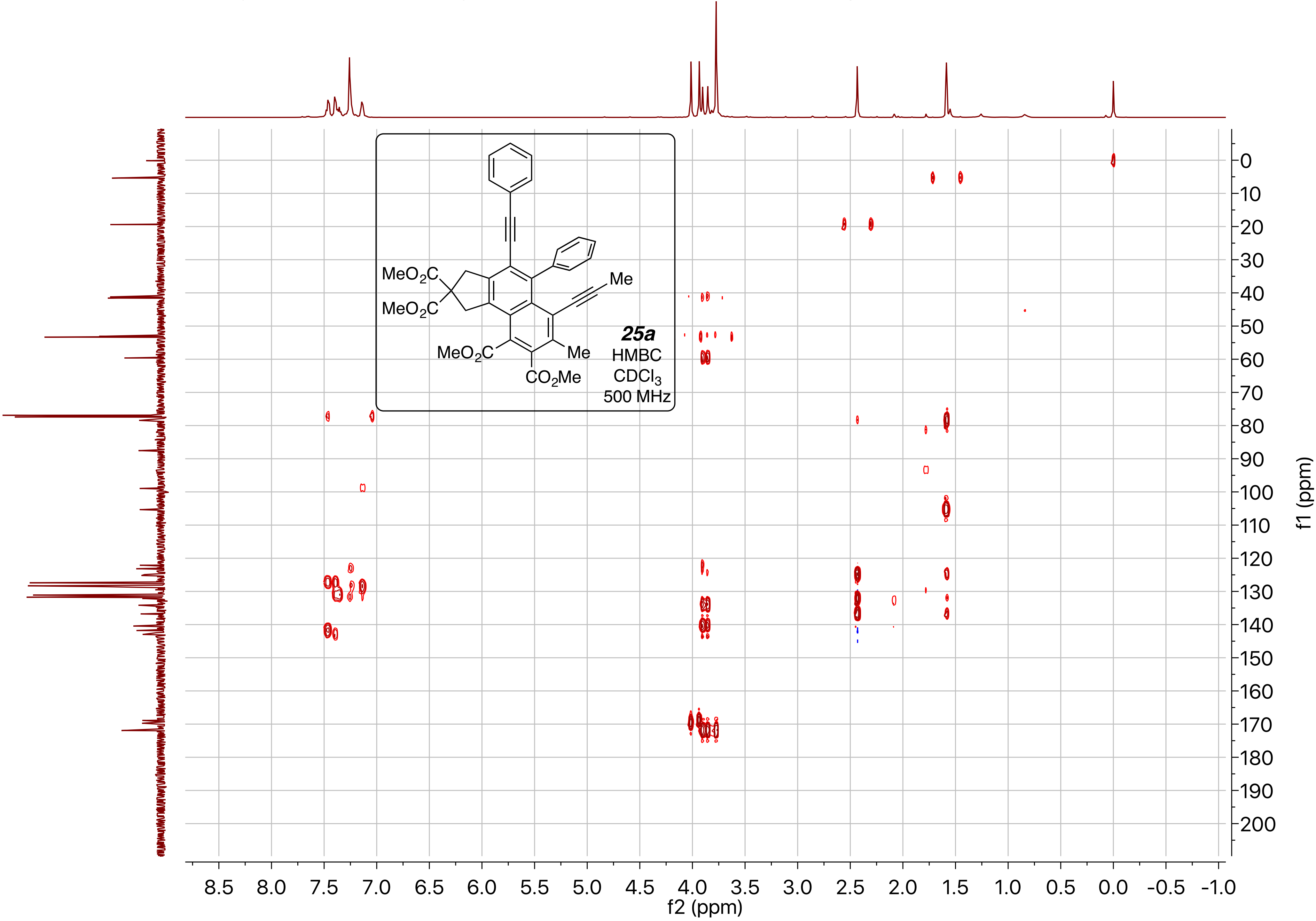

7.86
7.85
7.67
7.65
7.50
7.26 CDCl3
7.01
6.99
6.97
6.96
6.43
5.91
4.16
3.98
3.95
3.89
3.86
2.08
1.71
1.54 HDO
1.25 grease
0.89 grease
0.00
CO2Me
CO2Me
MeO2C
MeO2C
O
O
21′
1H NMR
CDCl3
500 MHz
2.00
2.03
1.02
1.97
2.05
1.99
2.01
1.98
1.95
2.96
3.06
5.97
3.04
5.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

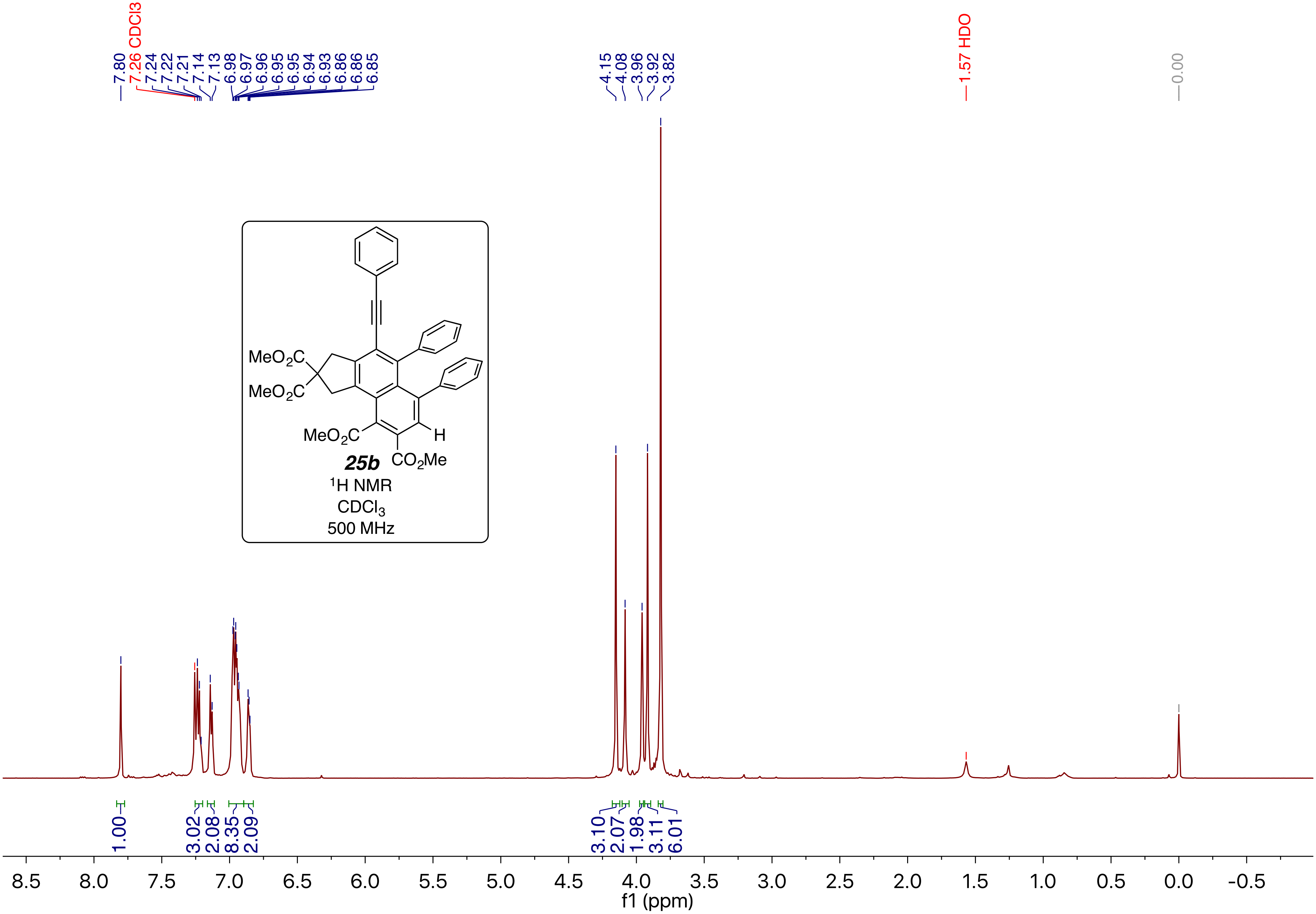

171.8
171.1
167.1
166.5
144.8
144.7
142.5
140.3
138.2
137.6
135.8
135.5
133.7
131.5
130.0
129.5
128.7
128.2
128.2
128.1
127.0
125.9
124.7
124.2
122.8
99.3
89.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
71.0
59.2
53.7
52.4
52.2
42.2
41.3
21.2
20.8
0.2
CO2Me
CO2Me
MeO2C
MeO2C
O
O
21′
13C NMR
CDCl3
126 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

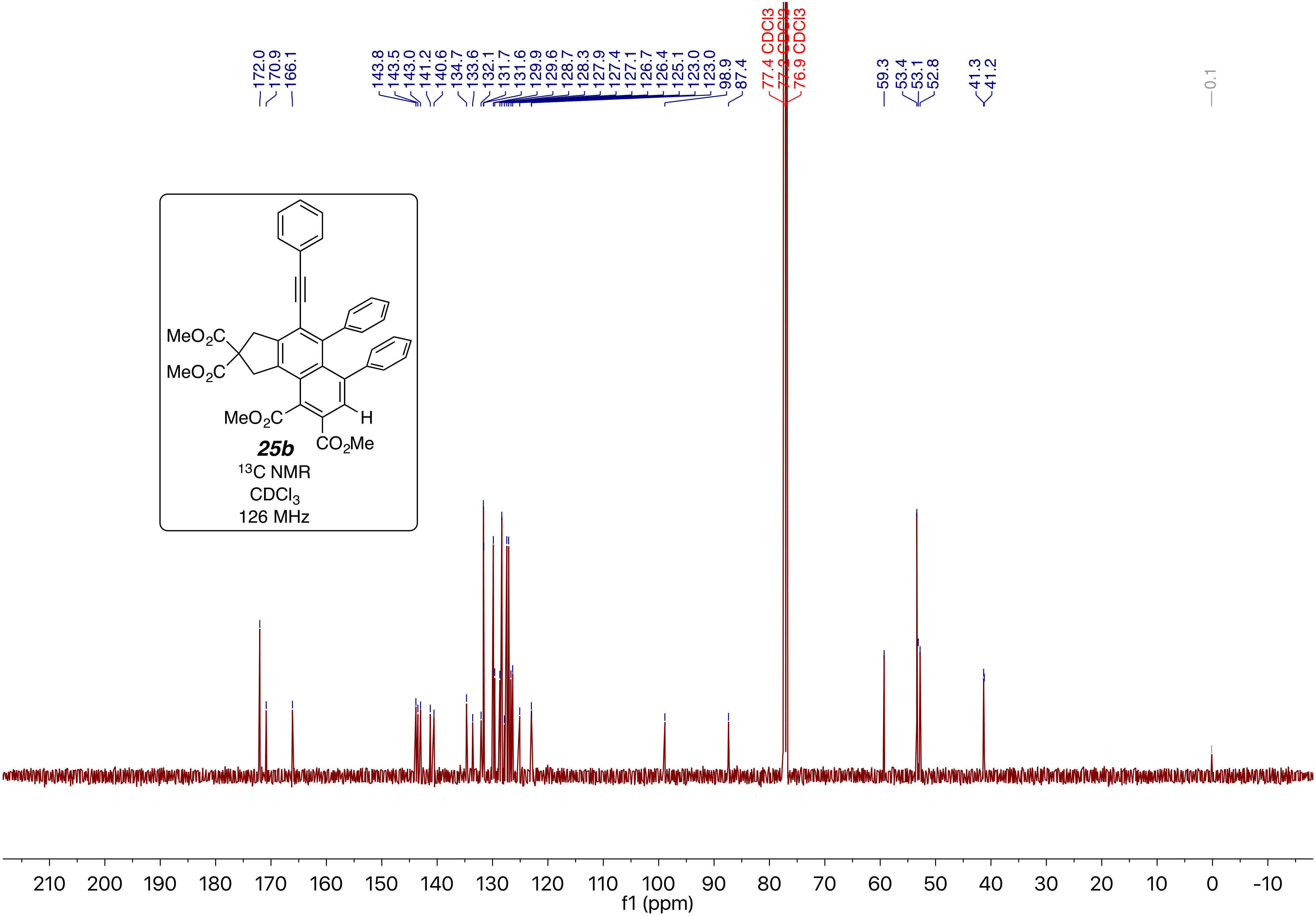

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
CO2Me
CO2Me
MeO2C
MeO2C
O
O
21′
HMBC
CDCl3
500 MHz


7.48
7.46
7.45
7.40
7.39
7.37
7.36
7.34
7.26 CDCl3
7.24
7.14
7.13
4.01
3.93
3.90
3.85
3.77
2.43
1.59
1.55 HDO
-0.00
MeO$_2$C
MeO$_2$C
MeO$_2$C
CO$_2$Me
Me
Me
25a
^{1}H NMR
CDCl$_3$
500 MHz
2.14
3.31
2.77
2.00
3.00
2.99
1.99
2.07
6.21
2.92
3.15
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)


171.9
169.7
168.9
143.0
141.8
140.4
136.8
134.1
132.3
132.1
131.7
131.1
128.6
128.3
127.6
127.5
127.4
125.2
124.9
123.2
122.1
105.3
98.9
87.5
78.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
59.6
53.3
53.1
52.9
41.6
41.2
19.4
5.4
0.1
MeO2C
MeO2C
MeO2C
CO2Me
Me
Me
25a
13C NMR
CDCl3
126 MHz
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)


MeO$_2$C
MeO$_2$C
MeO$_2$C
CO$_2$Me
Me
Me
25a
HMBC
CDCl$_3$
500 MHz
f2 (ppm)
f1 (ppm)
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
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200


7.80
7.26 CDCl3
7.24
7.22
7.21
7.14
7.13
6.98
6.97
6.96
6.95
6.95
6.94
6.93
6.86
6.86
6.85
4.15
4.08
3.96
3.92
3.82
1.57 HDO
0.00
MeO$_2$C
MeO$_2$C
MeO$_2$C
H
CO$_2$Me
25b
^{1}H NMR
CDCl$_3$
500 MHz
1.00
3.02
2.08
8.35
2.09
3.10
2.07
1.98
3.11
6.01
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)

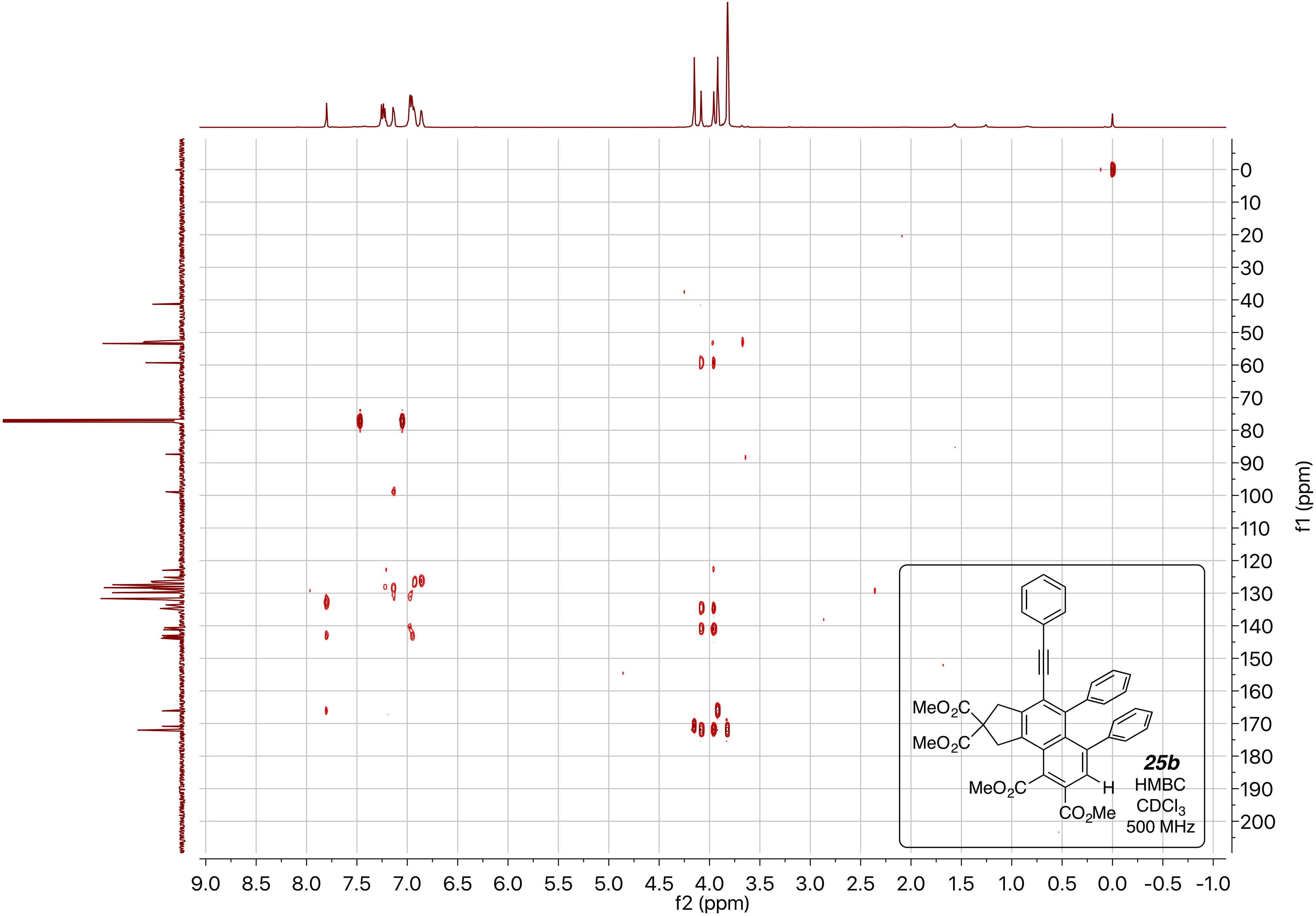


25b

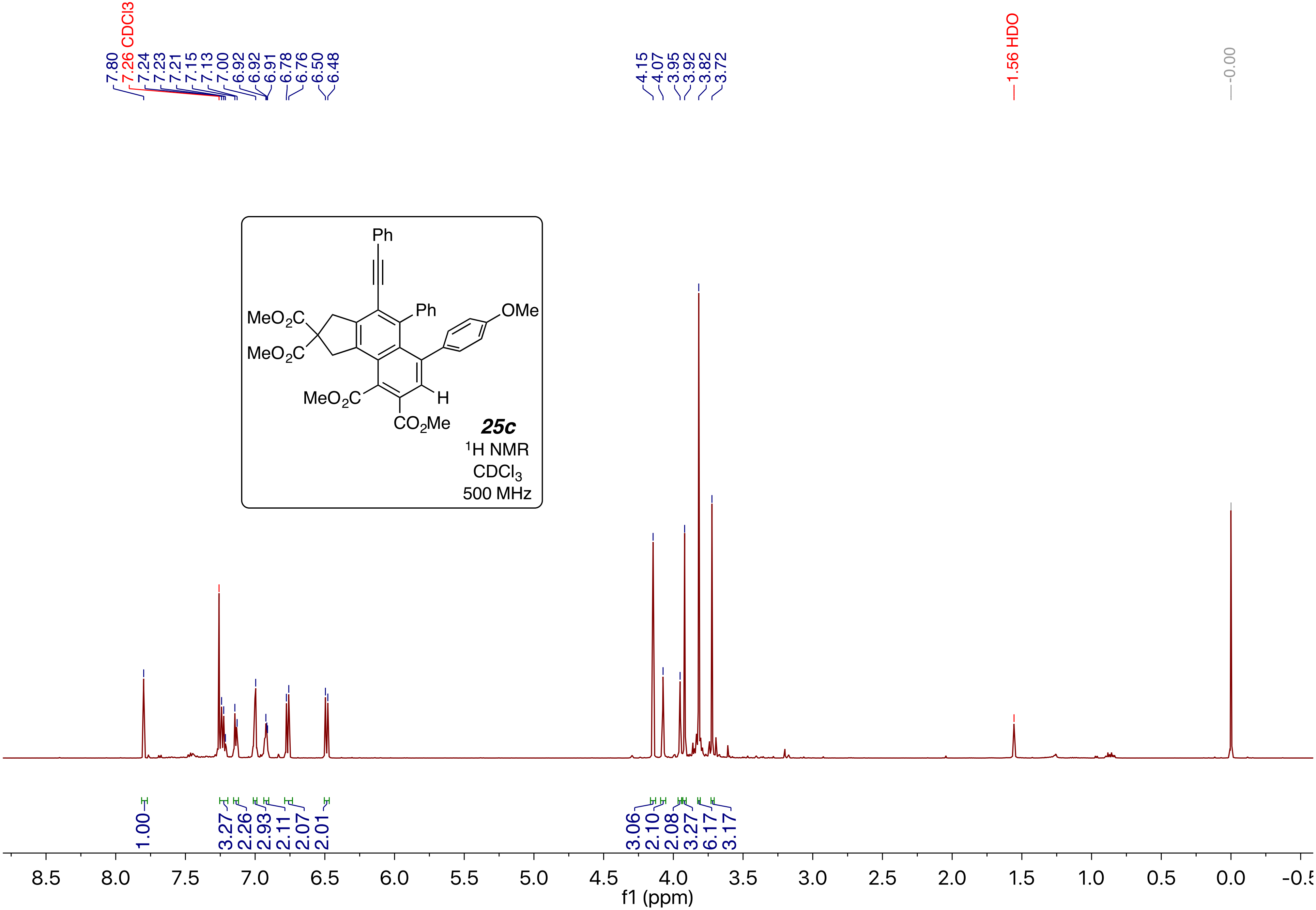
^{13}C NMR

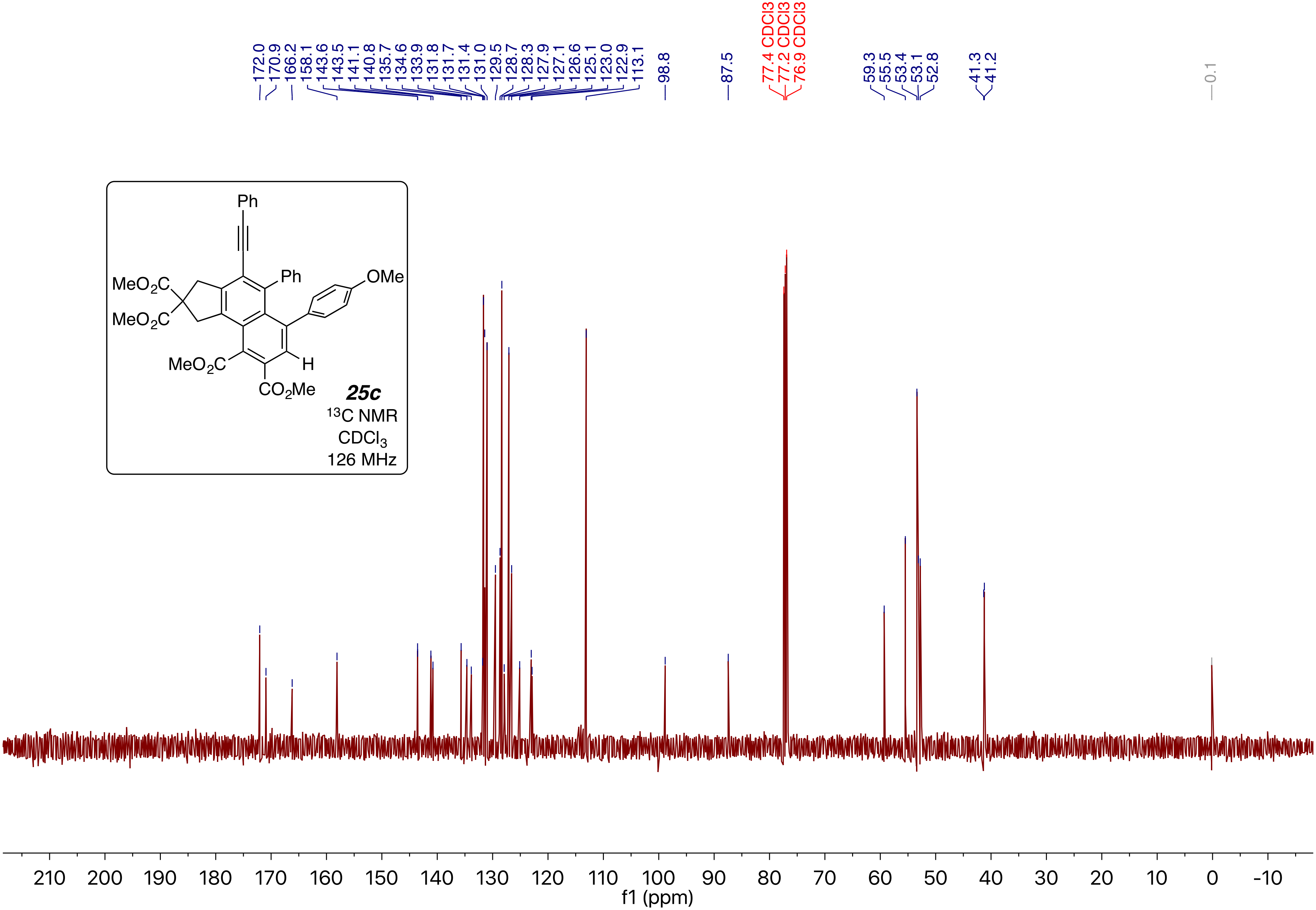
$CDCl_3$

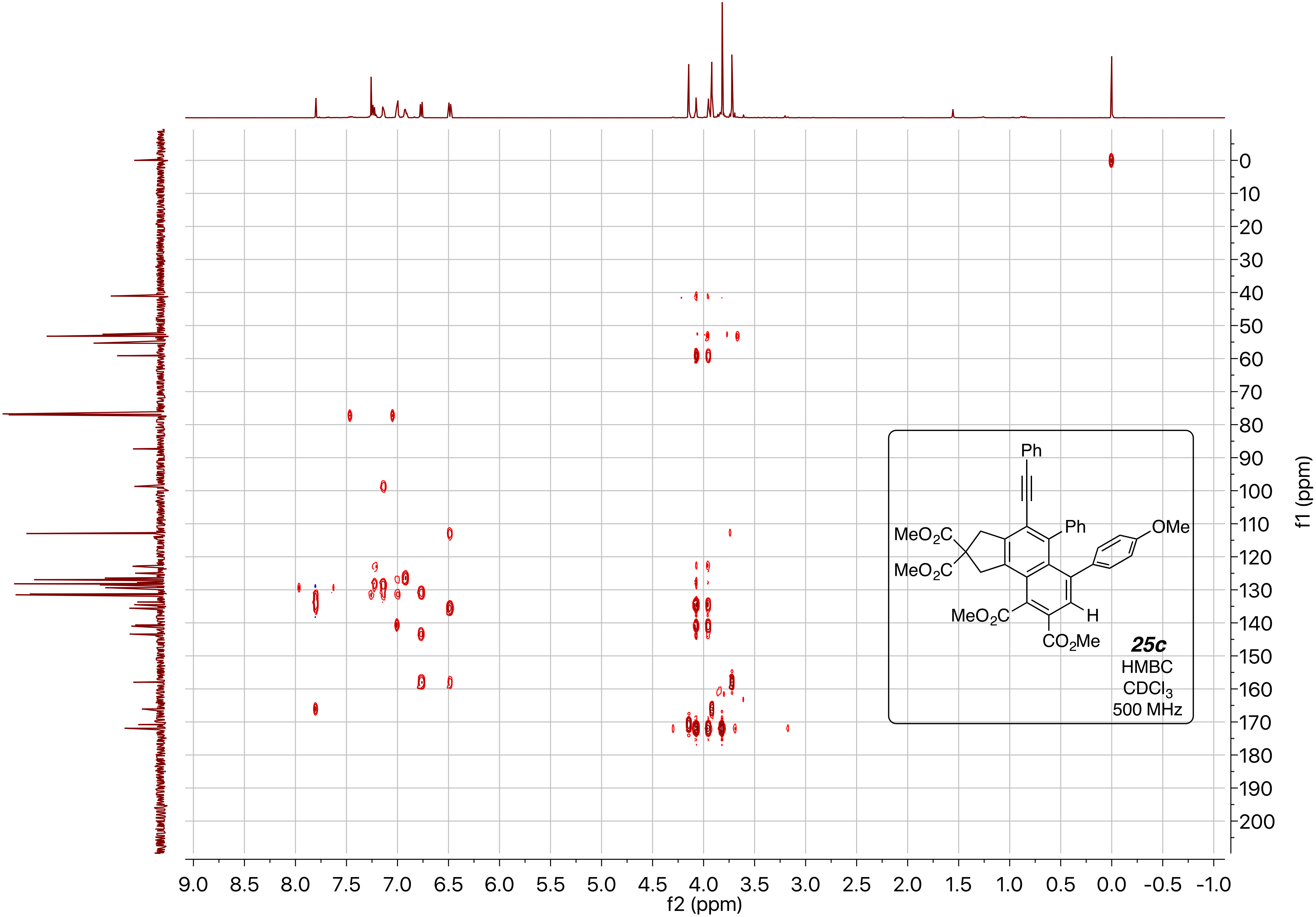
126 MHz

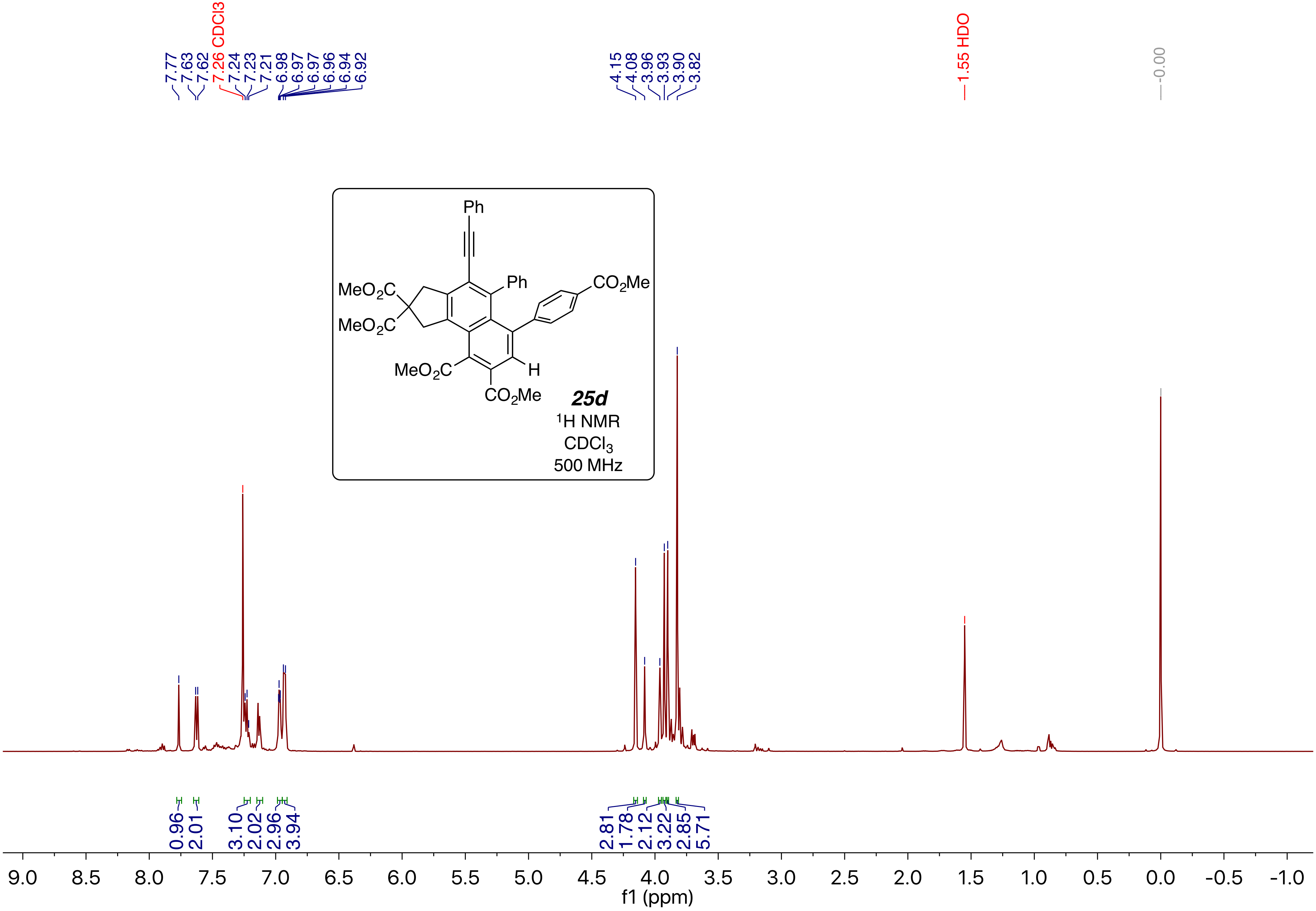


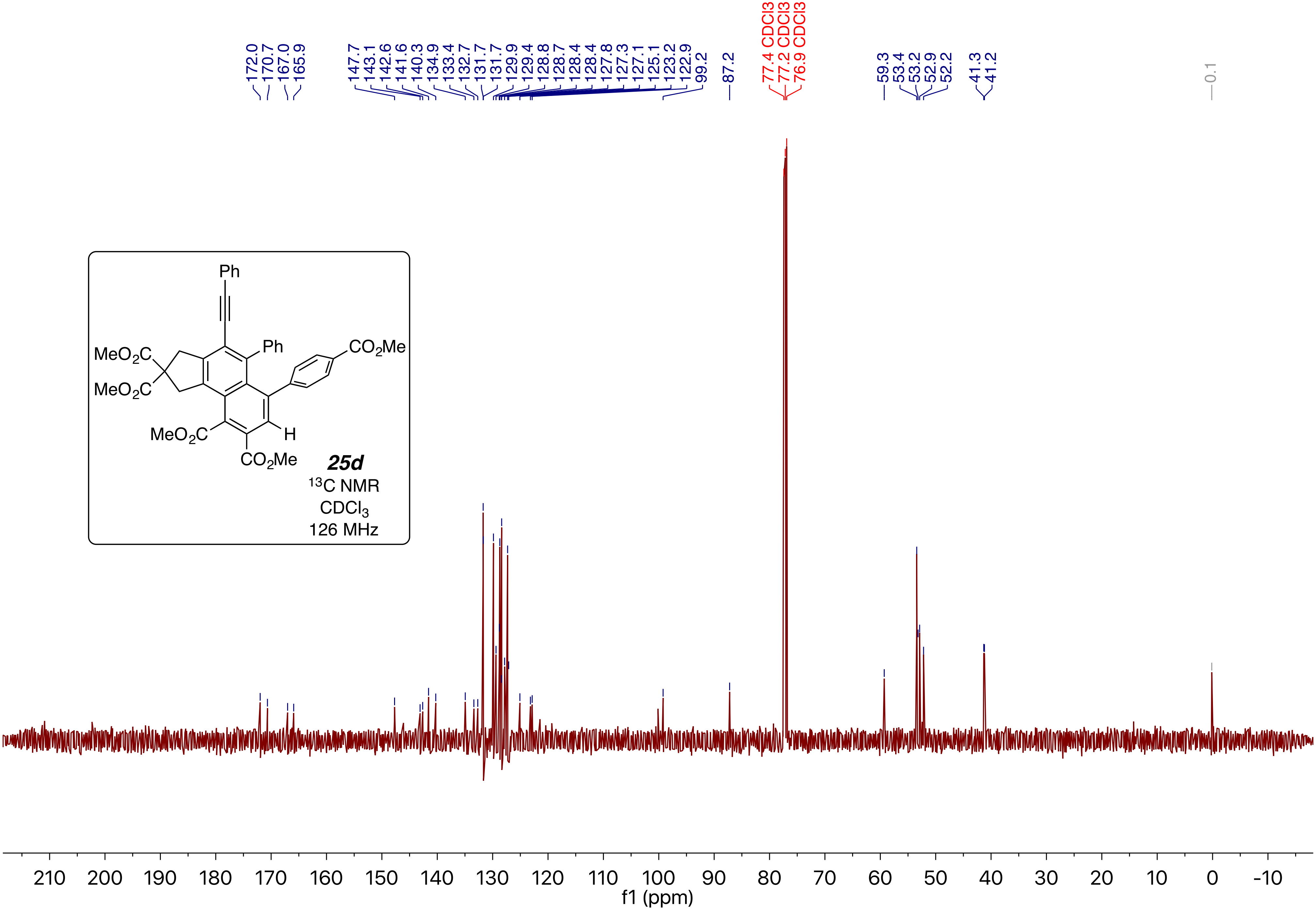
25b
HMBC
$CDCl_3$
500 MHz

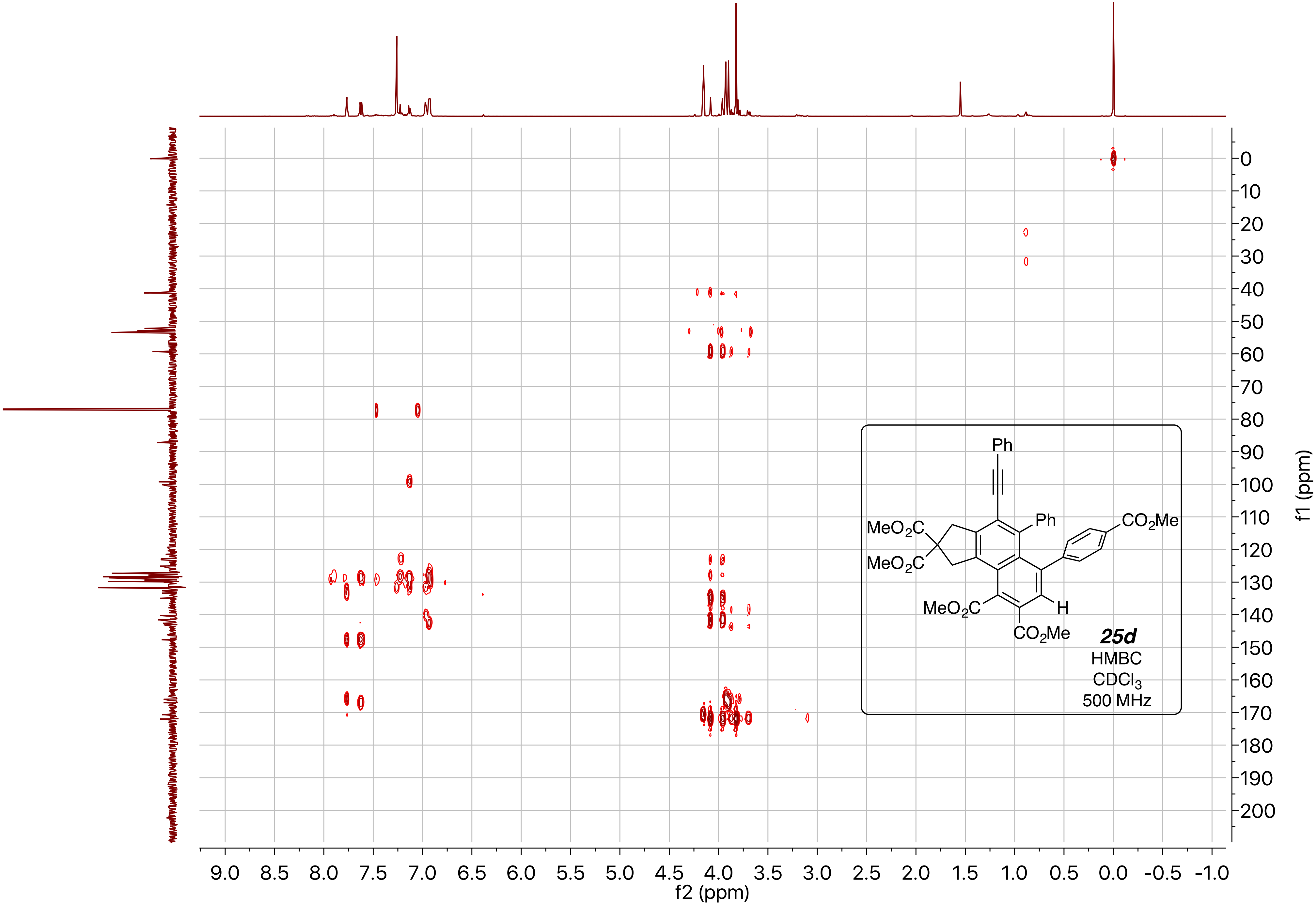

7.80
7.26 CDCl3
7.24
7.23
7.21
7.15
7.13
7.00
6.92
6.92
6.91
6.78
6.76
6.50
6.48
4.15
4.07
3.95
3.92
3.82
3.72
1.56 HDO
-0.00
Ph
Ph
OMe
MeO_2C
MeO_2C
MeO_2C
H
CO_2Me
25c
^{1}H NMR
$CDCl_3$
500 MHz
1.00
3.27
2.26
2.93
2.11
2.07
2.01
3.06
2.10
2.08
3.27
6.17
3.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

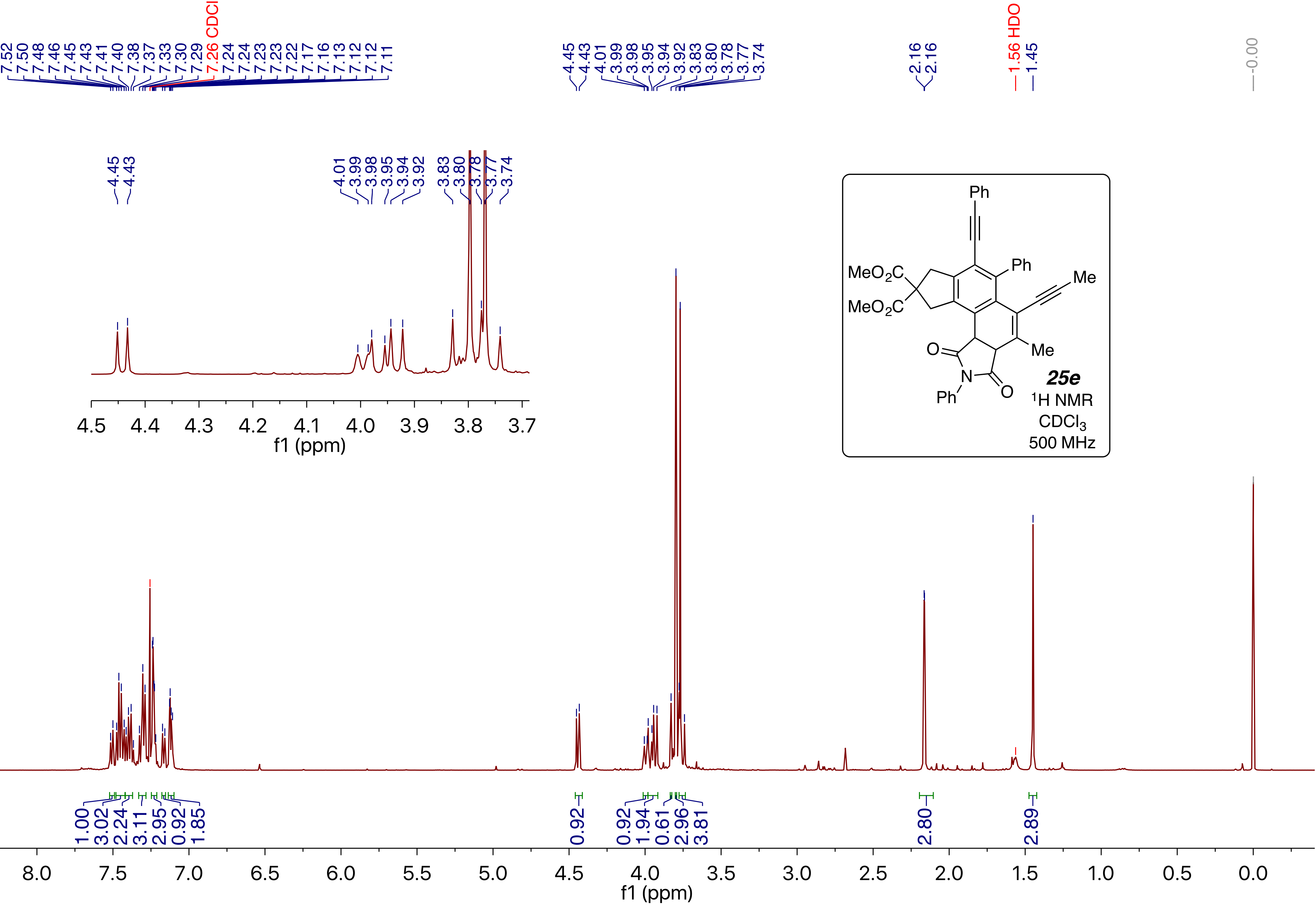

172.0
170.9
166.2
158.1
143.6
143.5
141.1
140.8
135.7
134.6
133.9
131.8
131.7
131.4
131.0
129.5
128.7
128.3
127.9
127.1
126.6
125.1
123.0
122.9
113.1
98.8
87.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
59.3
55.5
53.4
53.1
52.8
41.3
41.2
0.1
Ph
Ph
OMe
MeO2C
MeO2C
MeO2C
CO2Me
H
25c
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

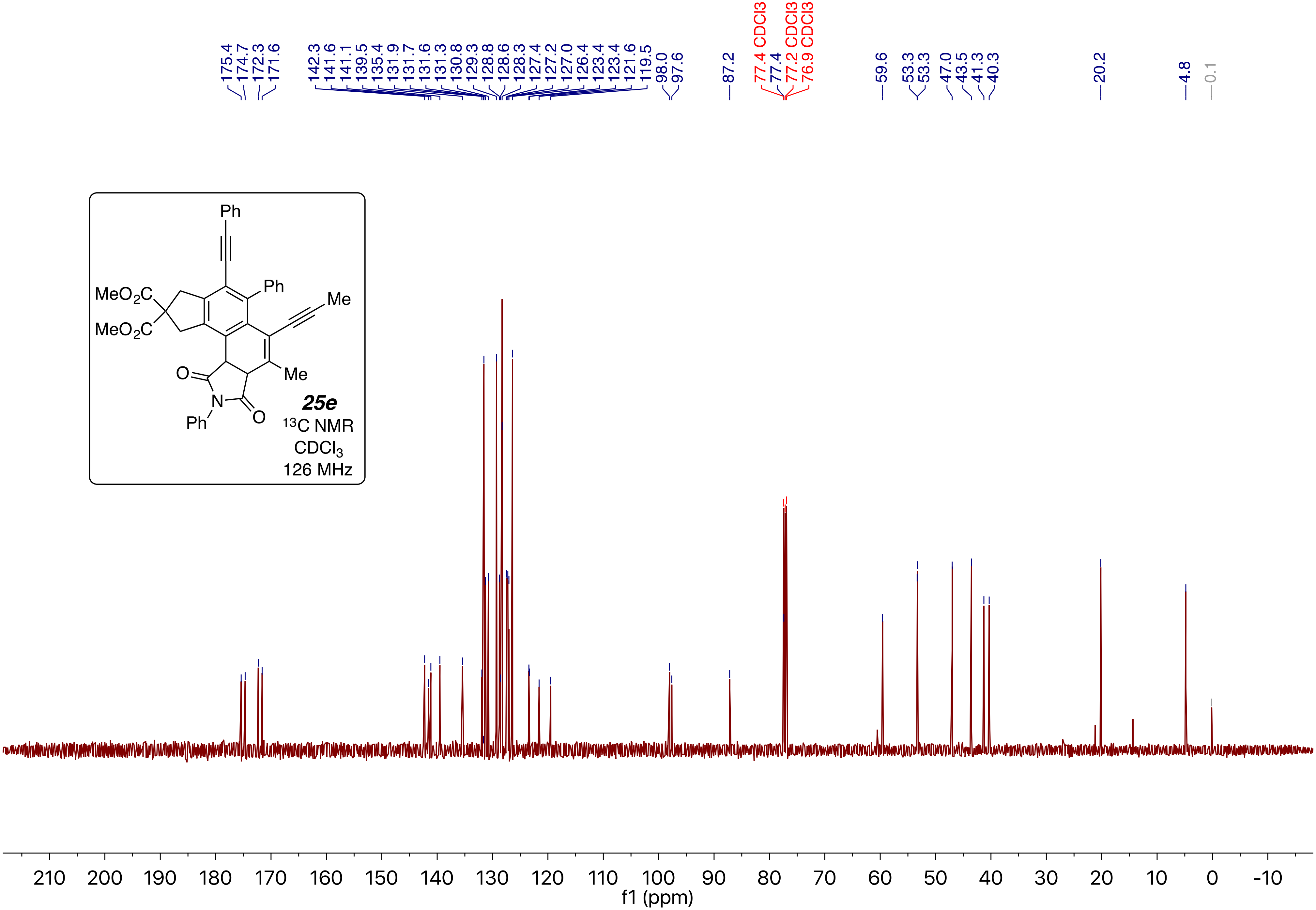

Ph
Ph
OMe
MeO₂C
MeO₂C
MeO₂C
H
CO₂Me
25c
HMBC
CDCl₃
500 MHz
f1 (ppm)
f2 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200


7.77
7.63
7.62
7.26 CDCl3
7.24
7.23
7.21
6.98
6.97
6.97
6.96
6.94
6.92
4.15
4.08
3.96
3.93
3.90
3.82
1.55 HDO
-0.00
Ph
MeO$_2$C
MeO$_2$C
Ph
CO$_2$Me
MeO$_2$C
H
CO$_2$Me
25d
^{1}H NMR
CDCl$_3$
500 MHz
0.96
2.01
3.10
2.02
2.96
3.94
2.81
1.78
2.12
3.22
2.85
5.71
9.0
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)


172.0
170.7
167.0
165.9
147.7
143.1
142.6
141.6
140.3
134.9
133.4
132.7
131.7
131.7
129.9
129.4
128.8
128.7
128.4
128.4
127.8
127.3
127.1
125.1
123.2
122.9
99.2
87.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
59.3
53.4
53.2
52.9
52.2
41.3
41.2
0.1
Ph
Ph
CO2Me
MeO2C
MeO2C
MeO2C
H
CO2Me
25d
13C NMR
CDCl3
126 MHz
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)


Ph
Ph
CO_2Me
MeO_2C
MeO_2C
MeO_2C
H
CO_2Me
25d
HMBC
$CDCl_3$
500 MHz
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
9.0
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
f2 (ppm)


7.52
7.50
7.48
7.46
7.45
7.43
7.41
7.40
7.38
7.37
7.33
7.30
7.29
7.26 CDCl3
7.24
7.24
7.23
7.23
7.22
7.17
7.16
7.13
7.12
7.12
7.11
4.45
4.43
4.01
3.99
3.98
3.95
3.94
3.92
3.83
3.80
3.78
3.77
3.74
2.16
2.16
1.56 HDO
1.45
0.00
1.00
3.02
2.24
3.11
2.95
0.92
1.85
0.92
0.92
1.94
0.61
2.96
3.81
2.80
2.89
f1 (ppm)
MeO2C
MeO2C
Ph
Ph
Me
Me
O
O
N
Ph
25e
1H NMR
CDCl3
500 MHz

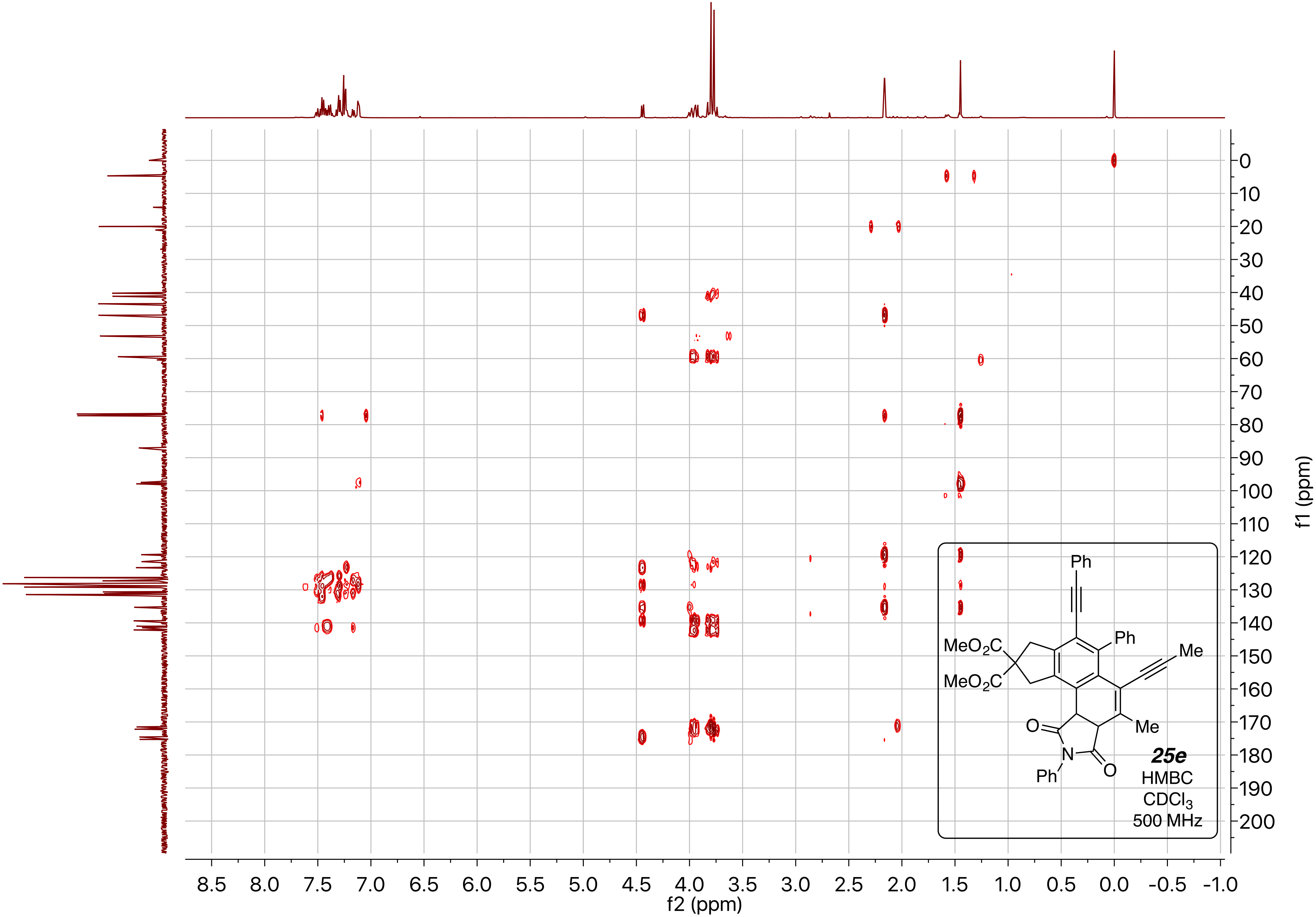


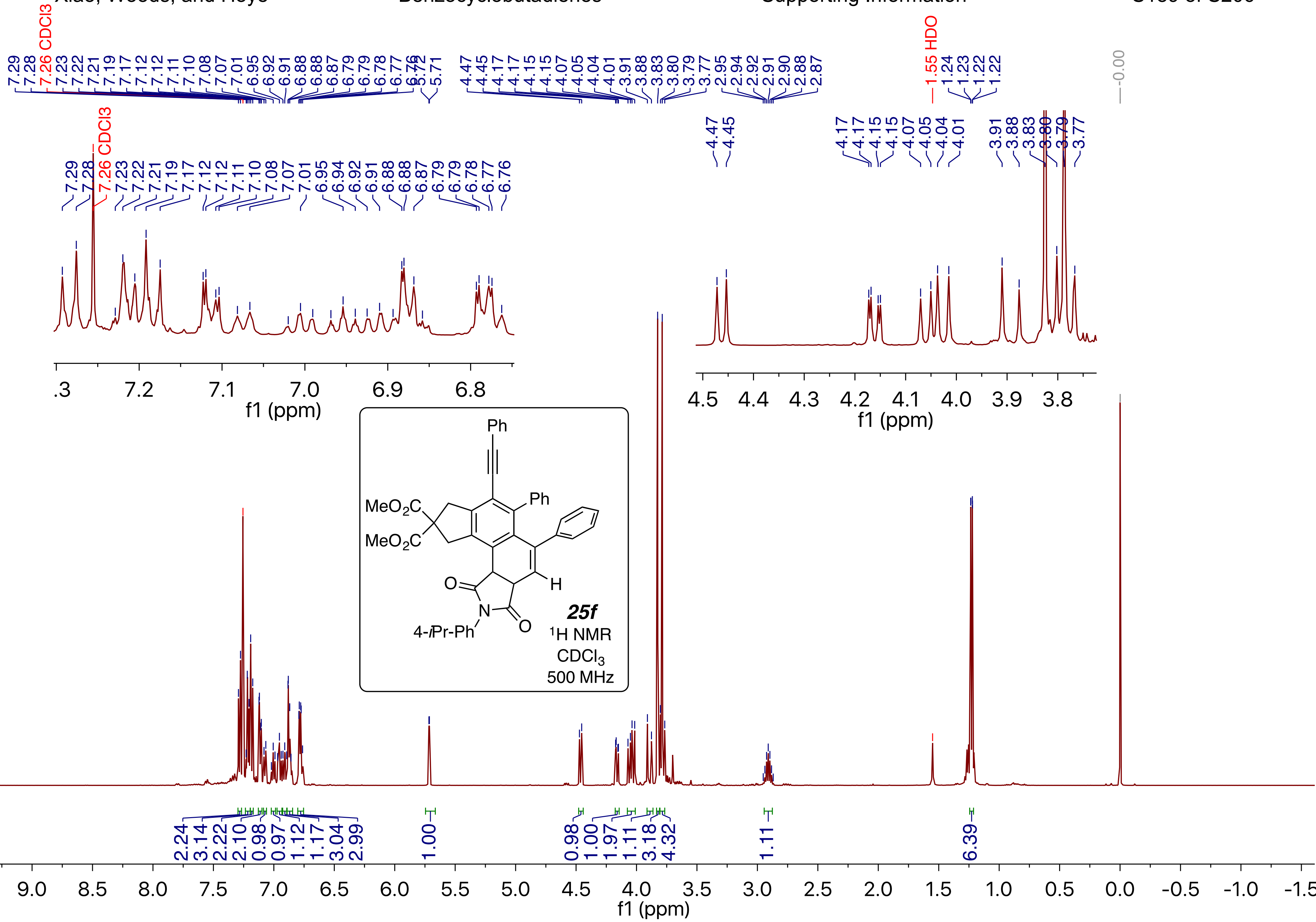
25e

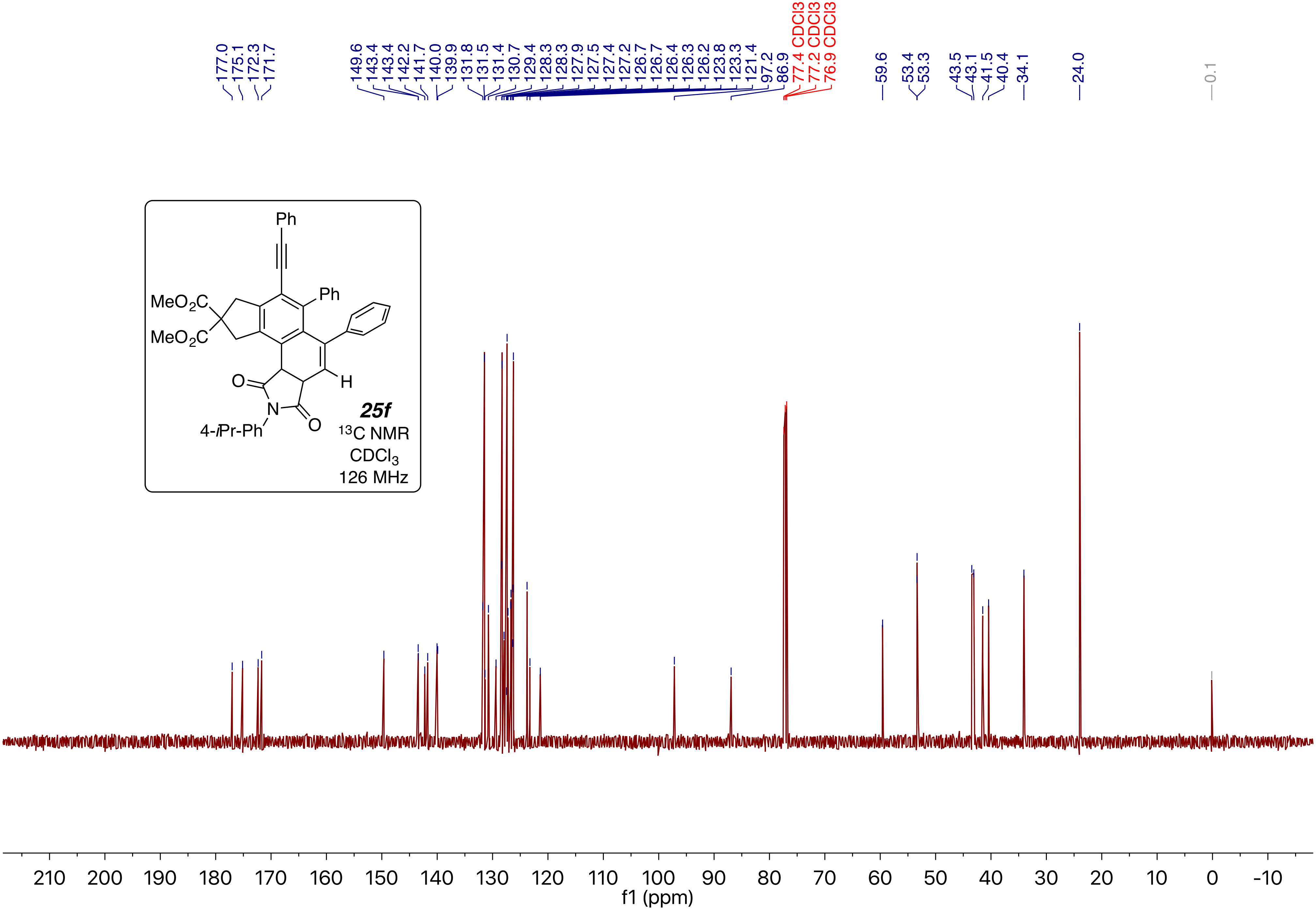
^{13}C NMR

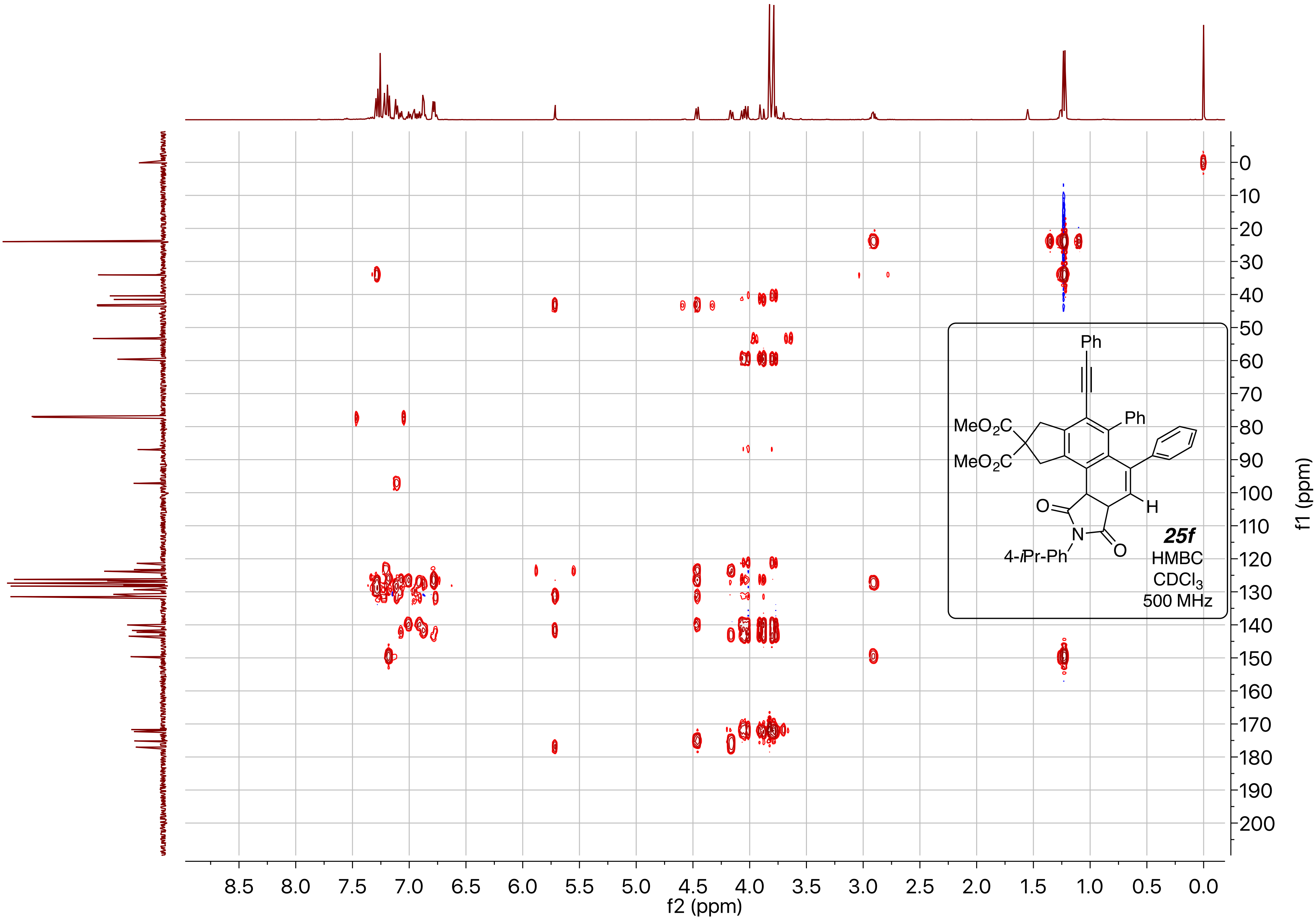
$CDCl_3$

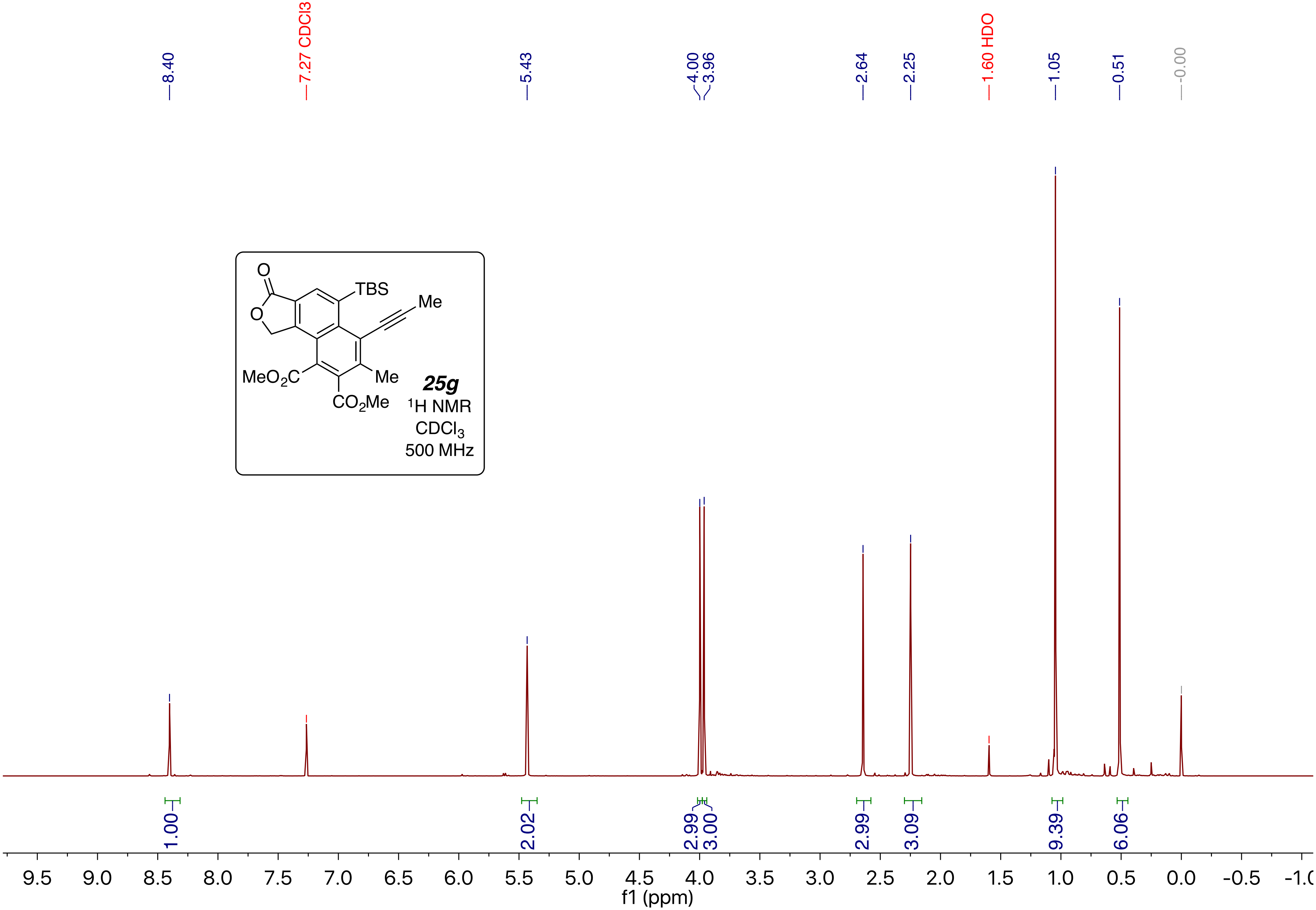
126 MHz


25e
HMBC
CDCl$_3$
500 MHz
MeO$_2$C
MeO$_2$C
Ph
Ph
Me
Me
O
N
O
Ph
f2 (ppm)
f1 (ppm)
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
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

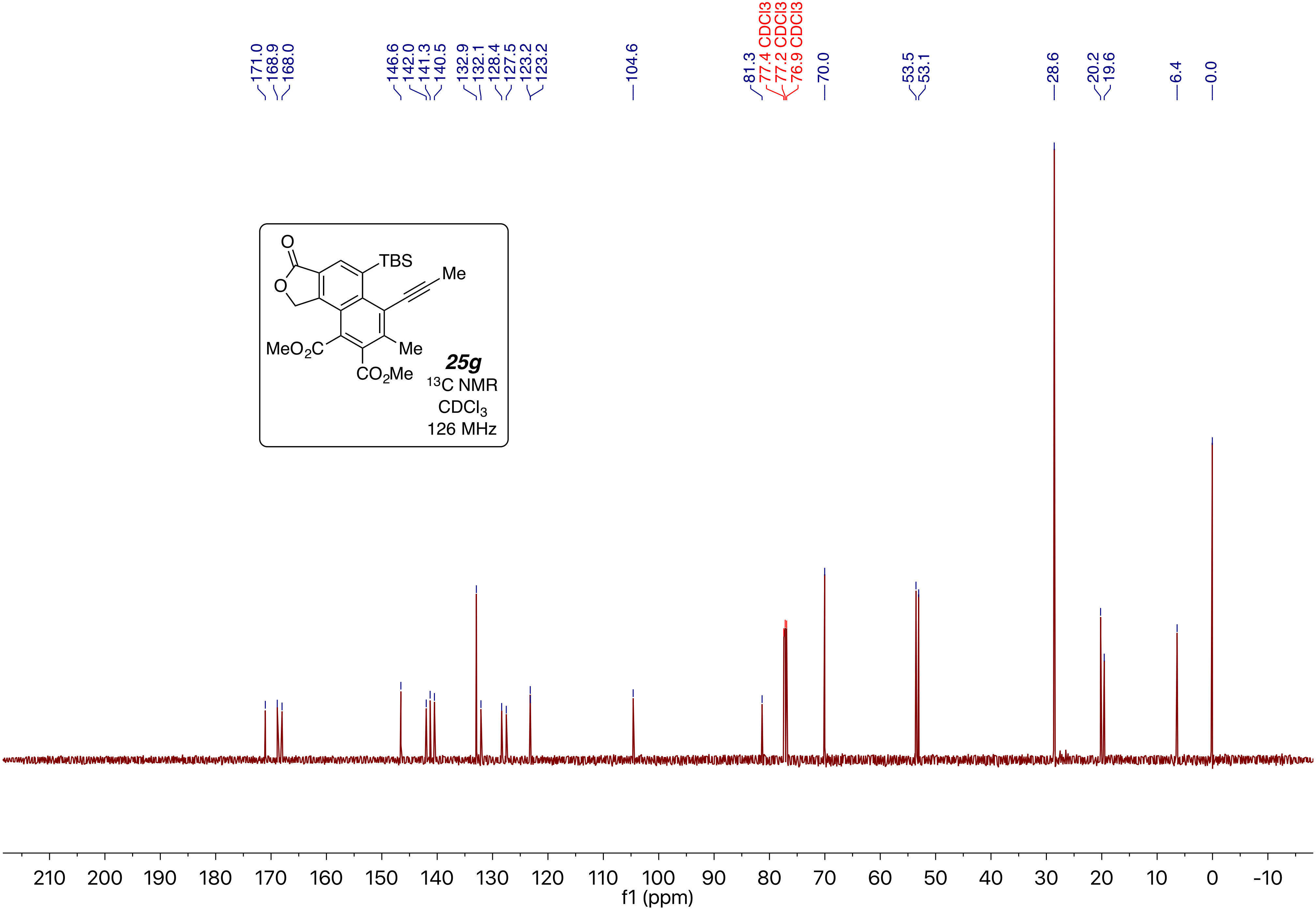

7.26 CDCl3
7.29 7.28 7.23 7.22 7.21 7.19 7.17 7.12 7.12 7.11 7.10 7.08 7.07 7.01 6.95 6.92 6.91 6.88 6.88 6.87 6.79 6.79 6.78 6.77 6.76 5.72 5.71
4.47 4.45 4.17 4.17 4.15 4.15 4.07 4.05 4.04 4.01 3.91 3.88 3.83 3.80 3.79 3.77 2.95 2.94 2.92 2.91 2.90 2.88 2.87
1.55 HDO
1.24 1.23 1.22 1.22
-0.00
7.29 7.28 7.26 CDCl3 7.23 7.22 7.21 7.19 7.17 7.12 7.12 7.11 7.10 7.08 7.07 7.01 6.95 6.94 6.92 6.91 6.88 6.88 6.87 6.79 6.79 6.78 6.77 6.76
.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
4.47 4.45 4.17 4.17 4.15 4.15 4.07 4.05 4.04 4.01 3.91 3.88 3.83 3.80 3.79 3.77
4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8
f1 (ppm)
Ph
Ph
MeO$_2$C
MeO$_2$C
O
N
O
H
4-iPr-Ph
25f
^{1}H NMR
CDCl$_3$
500 MHz
2.24 3.14 2.22 2.10 0.98 0.97 1.12 1.17 3.04 2.99
1.00
0.98 1.00 1.97 1.11 3.18 4.32
1.11
6.39
9.0 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 -1.5
f1 (ppm)

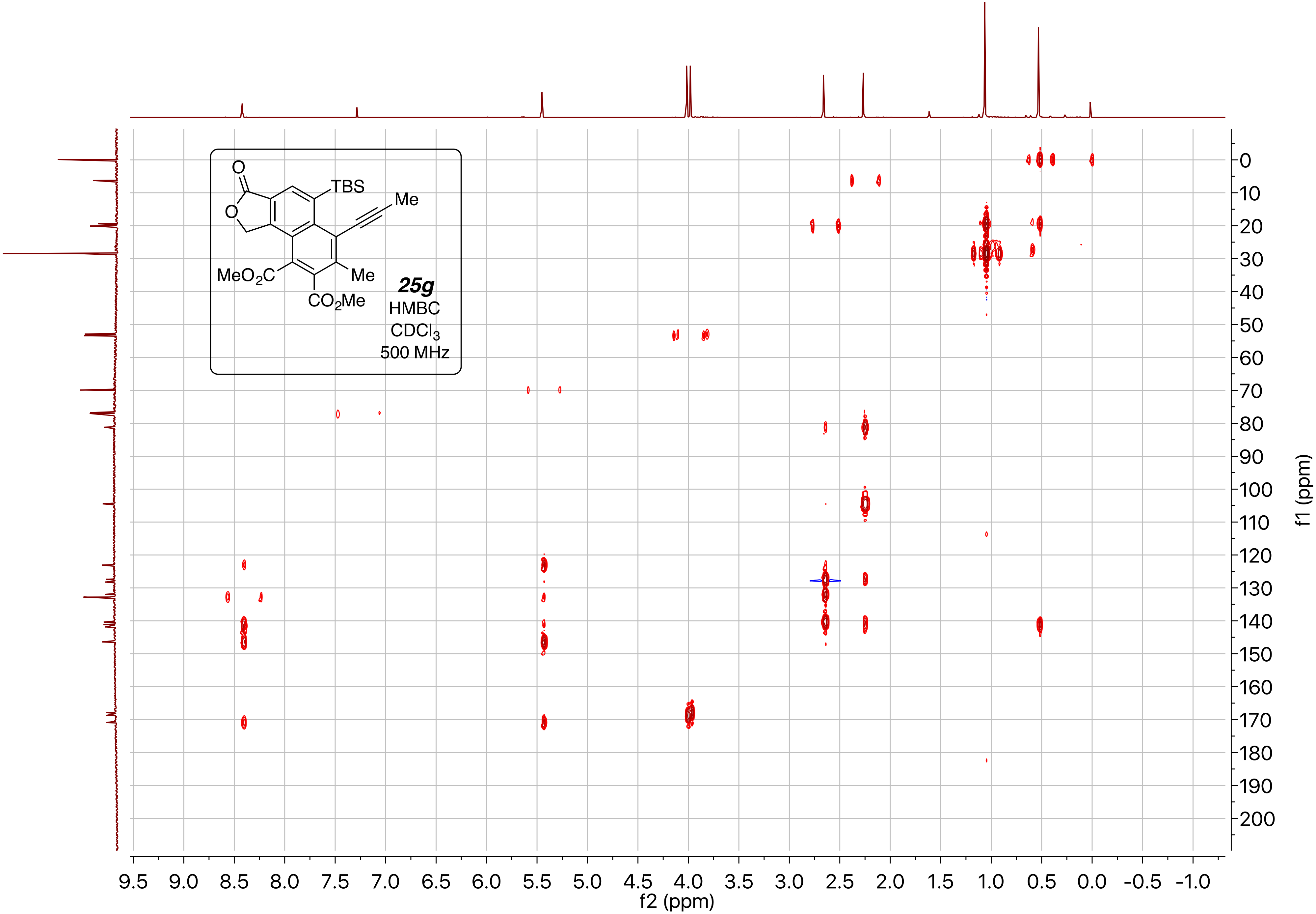

177.0
175.1
172.3
171.7
149.6
143.4
143.4
142.2
141.7
140.0
139.9
131.8
131.5
131.4
130.7
129.4
128.3
128.3
127.9
127.5
127.4
127.2
126.7
126.7
126.4
126.3
126.2
123.8
123.3
121.4
97.2
86.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
59.6
53.4
53.3
43.5
43.1
41.5
40.4
34.1
24.0
0.1
Ph
Ph
MeO_2C
MeO_2C
O
H
N
O
4-*i*Pr-Ph
25f
^{13}C NMR
$CDCl_3$
126 MHz
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)

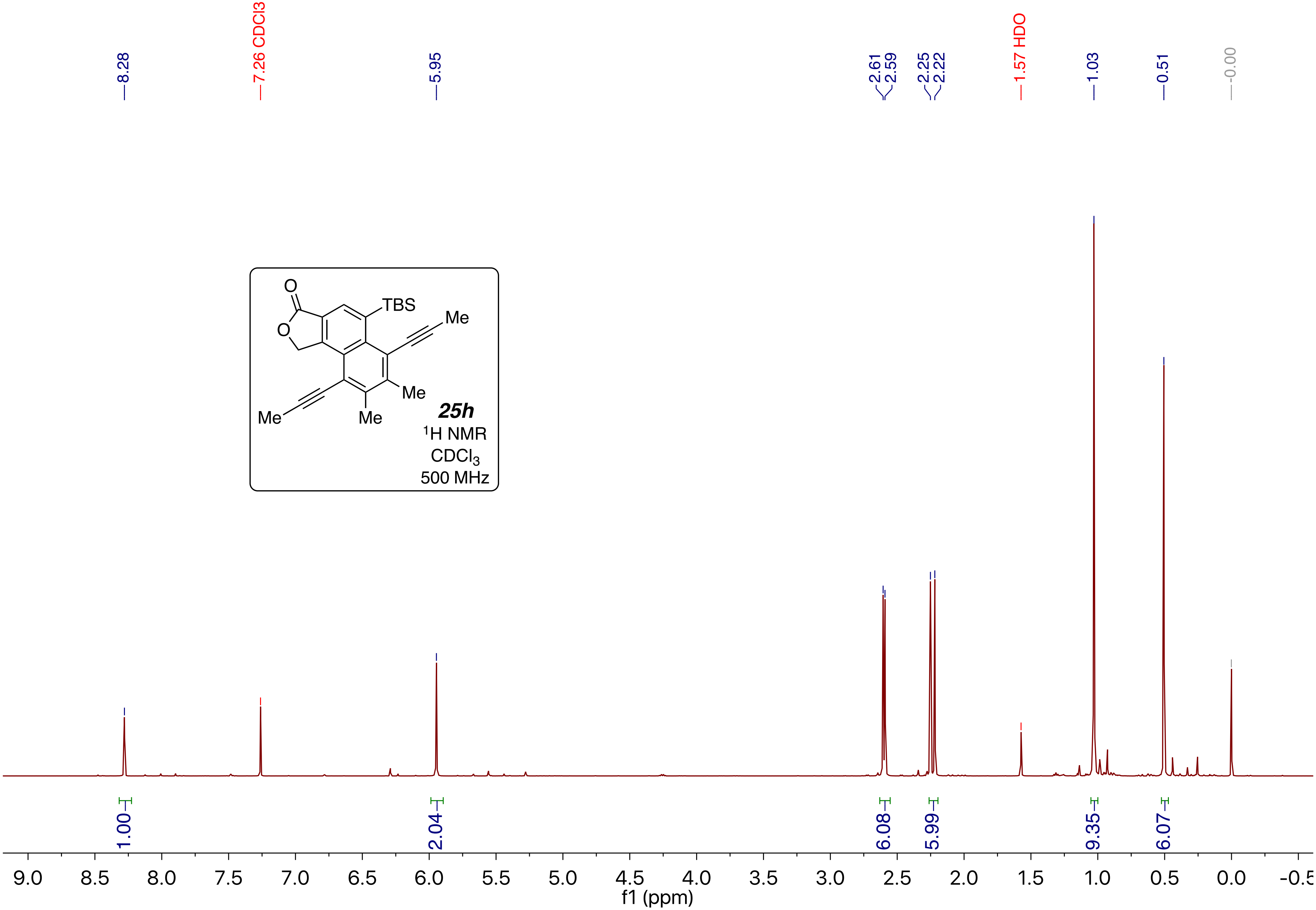

Ph
Ph
MeO2C
MeO2C
O
N
O
H
4-iPr-Ph
25f
HMBC
CDCl3
500 MHz
f2 (ppm)
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200



25g
^{1}H NMR
$CDCl_3$
500 MHz


171.0
168.9
168.0
146.6
142.0
141.3
140.5
132.9
132.1
128.4
127.5
123.2
123.2
104.6
81.3
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
70.0
53.5
53.1
28.6
20.2
19.6
6.4
0.0
O
O
TBS
Me
MeO$_2$C
Me
CO$_2$Me
25g
^{13}C NMR
CDCl$_3$
126 MHz
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)


TBS
Me
O
O
MeO$_2$C
Me
CO$_2$Me
25g
HMBC
CDCl$_3$
500 MHz
f2 (ppm)
f1 (ppm)
9.5 9.0 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
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

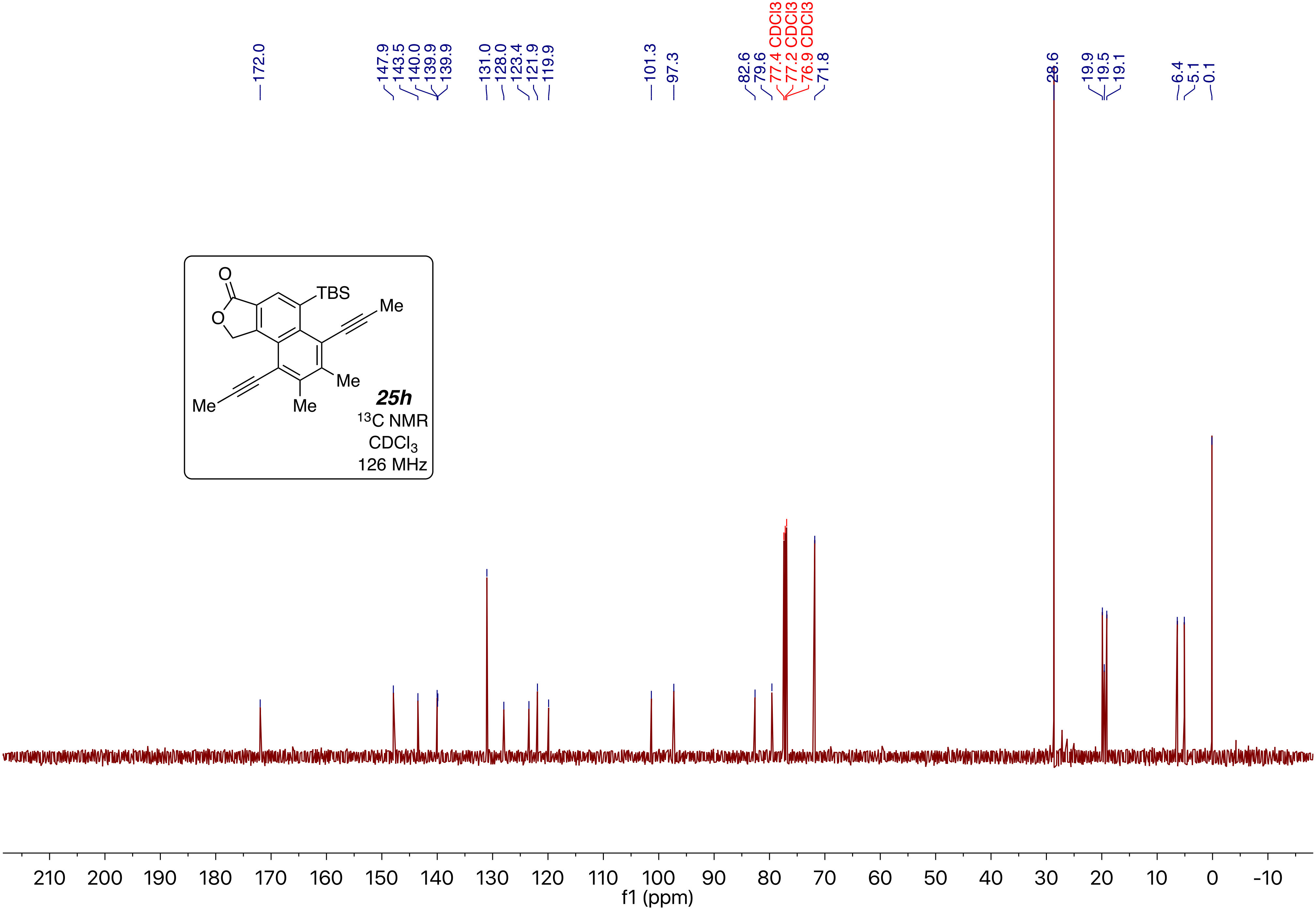


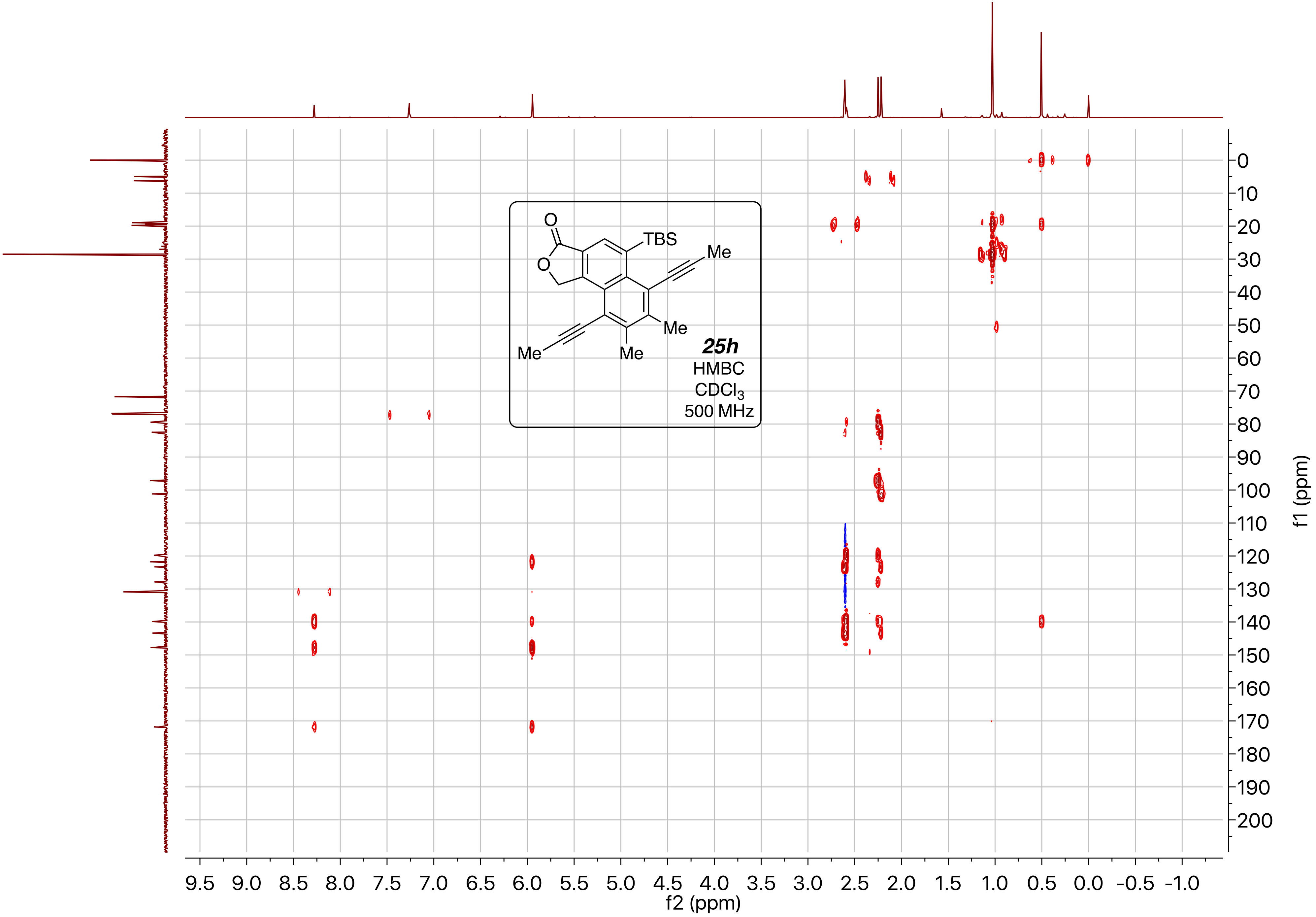
25h

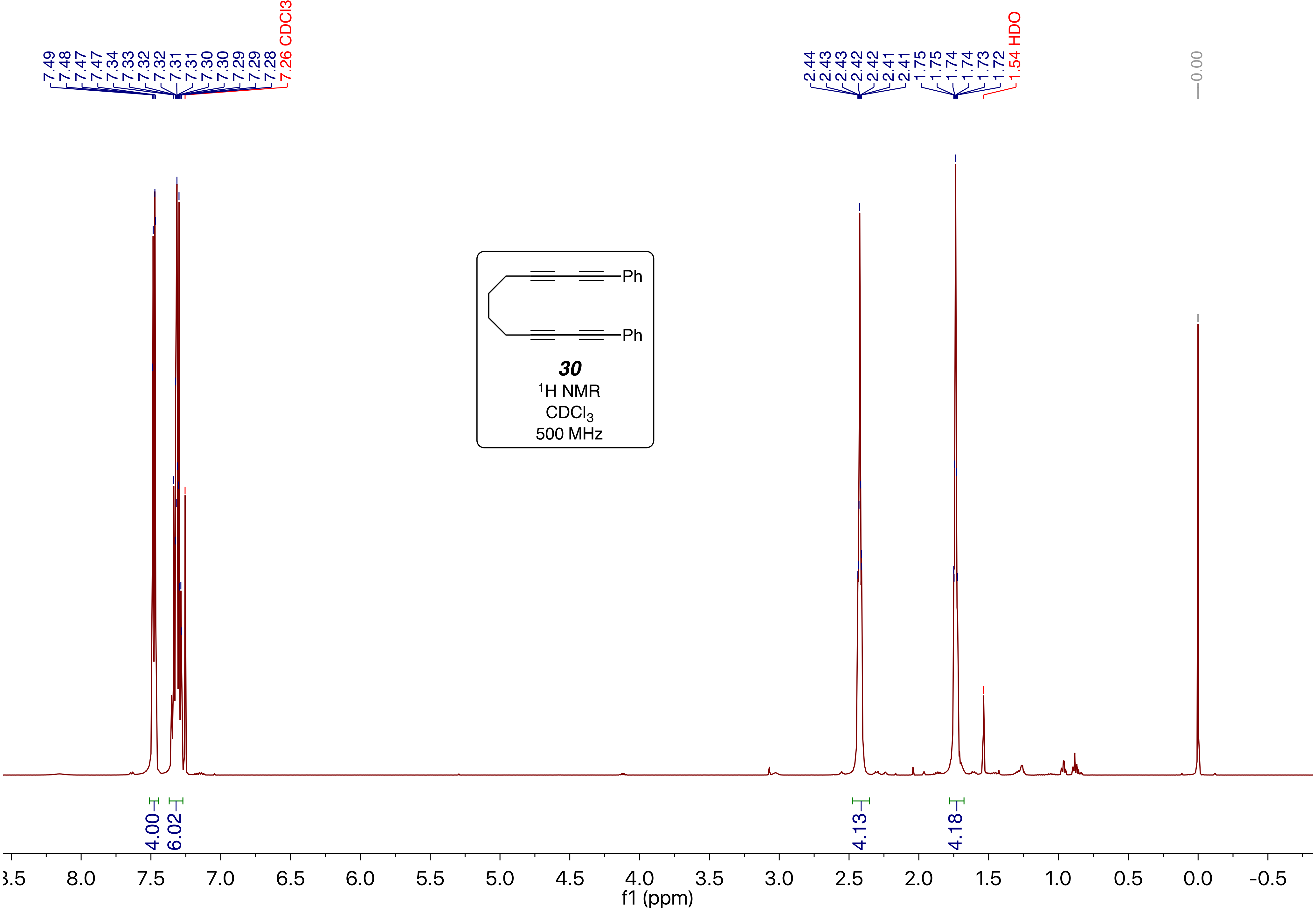
^{1}H NMR

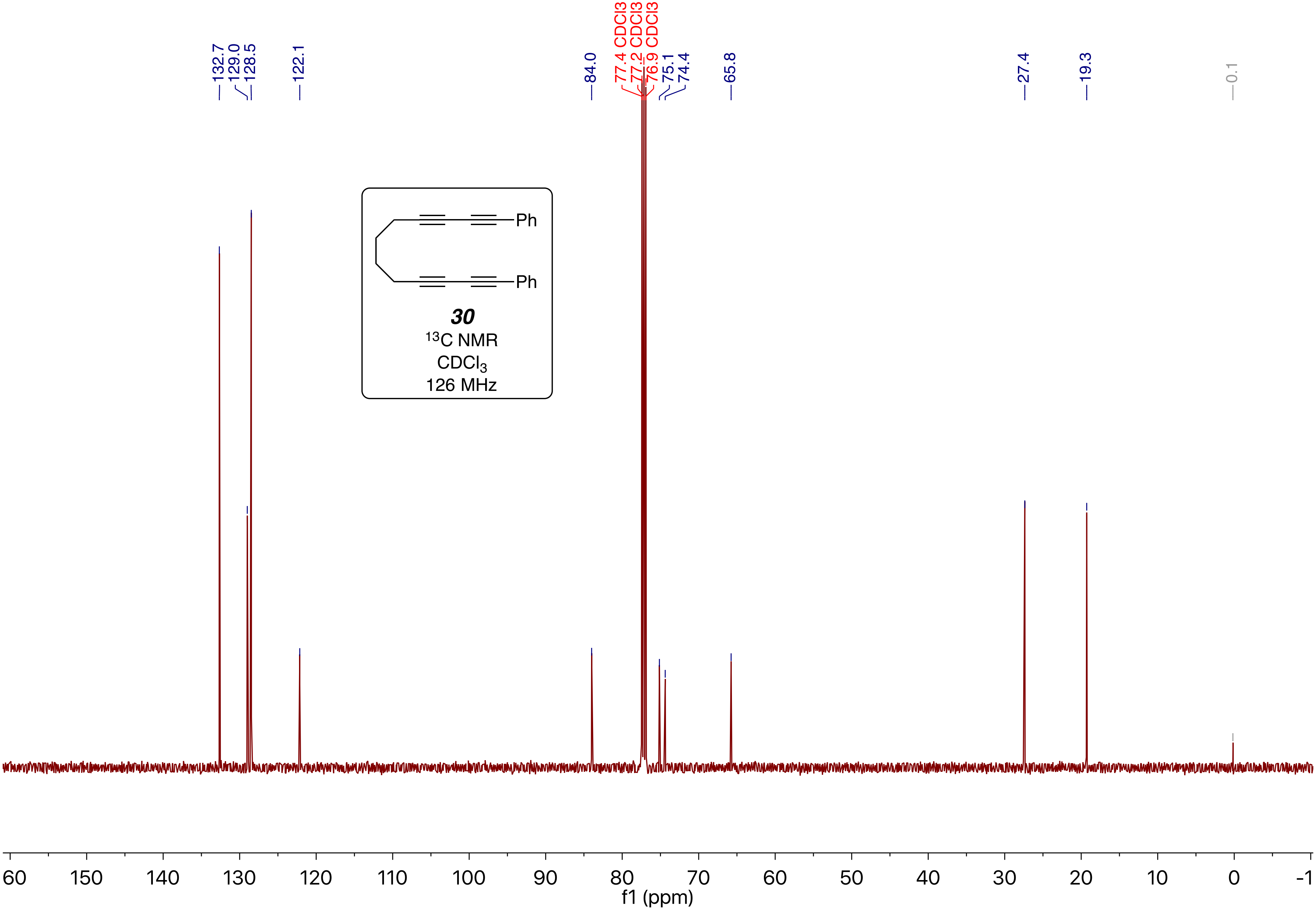
$CDCl_3$

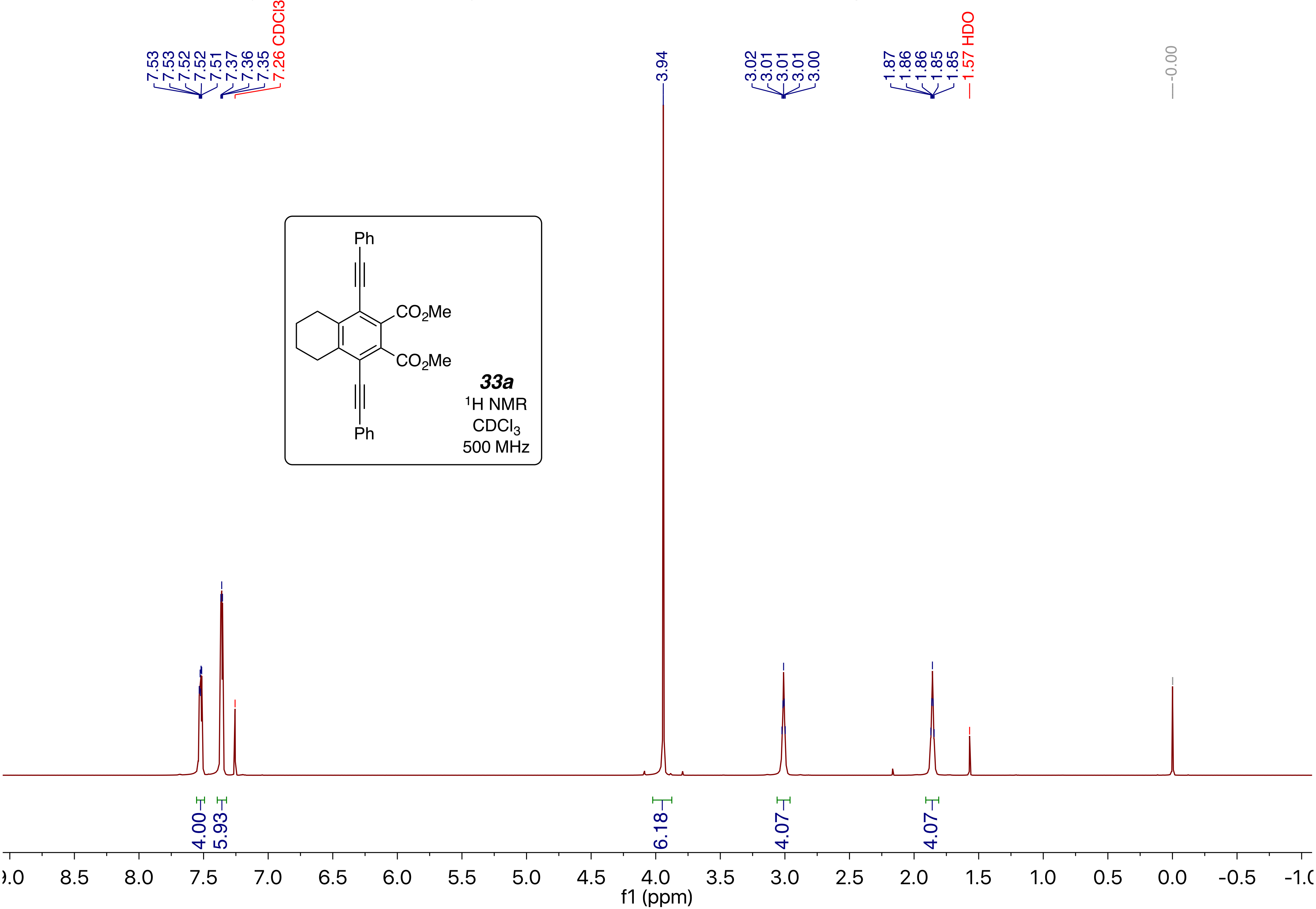
500 MHz

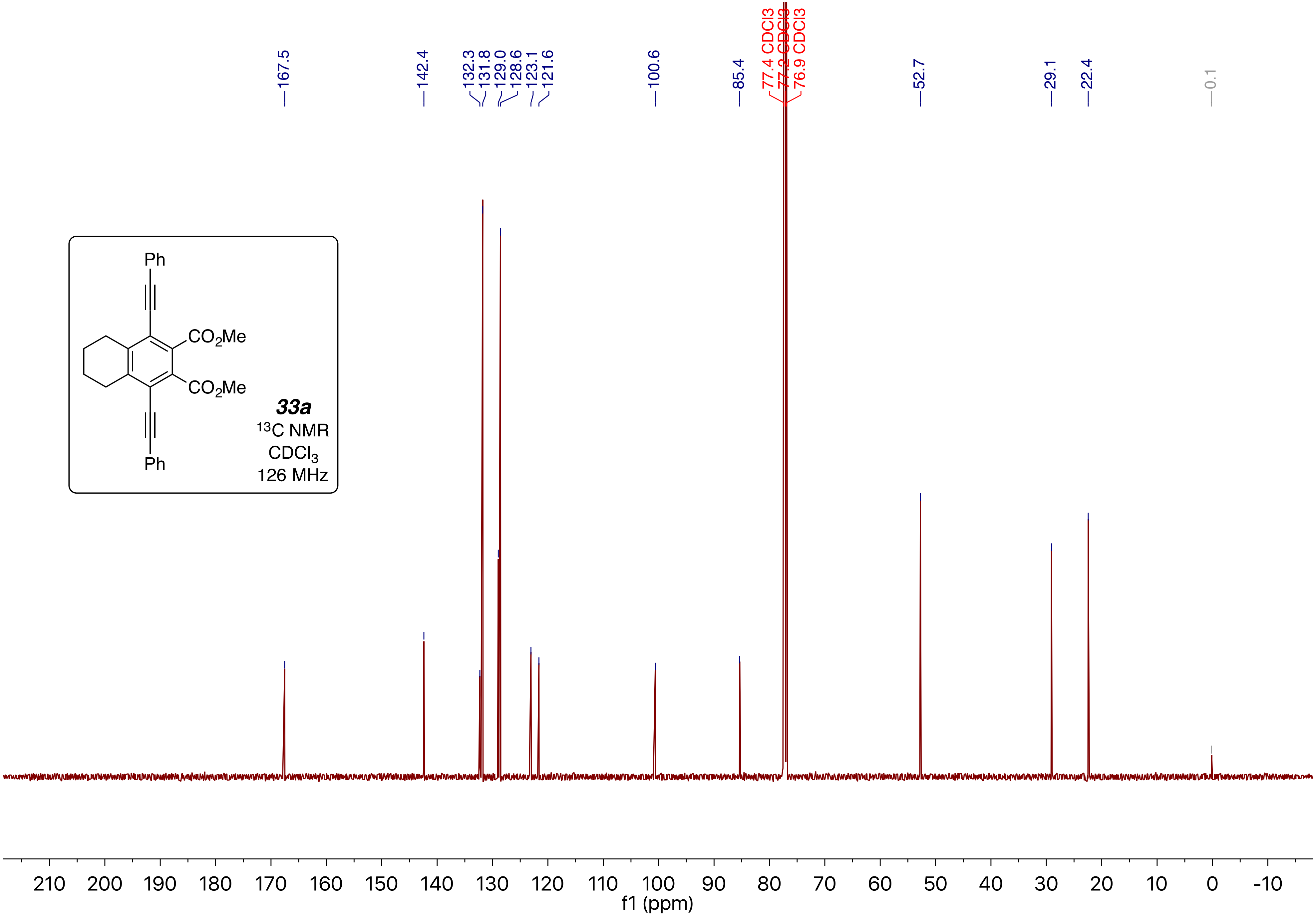

172.0
147.9
143.5
140.0
139.9
139.9
131.0
128.0
123.4
121.9
119.9
101.3
97.3
82.6
79.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
71.8
28.6
19.9
19.5
19.1
6.4
5.1
0.1
O
O
TBS
Me
Me
Me
Me
25h
^{13}C NMR
CDCl$_3$
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
TBS
Me
Me
Me
Me
25h
HMBC
$CDCl_3$
500 MHz
f1 (ppm)
f2 (ppm)
9.5 9.0 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
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200


7.49
7.48
7.47
7.47
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.26 CDCl3
2.44
2.43
2.43
2.42
2.42
2.41
2.41
1.75
1.75
1.74
1.74
1.73
1.72
1.54 HDO
0.00
Ph
Ph
30
^{1}H NMR
$CDCl_3$
500 MHz
4.00
6.02
4.13
4.18
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)


132.7
129.0
128.5
122.1
84.0
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
75.1
74.4
65.8
27.4
19.3
0.1
Ph
Ph
30
^{13}C NMR
$CDCl_3$
126 MHz
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.53
7.53
7.52
7.52
7.51
7.37
7.36
7.35
7.26 CDCl3
3.94
3.02
3.01
3.01
3.01
3.00
1.87
1.86
1.86
1.85
1.85
1.57 HDO
-0.00
Ph
CO$_2$Me
CO$_2$Me
Ph
33a
^{1}H NMR
CDCl$_3$
500 MHz
4.00
5.93
6.18
4.07
4.07
.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.
f1 (ppm)

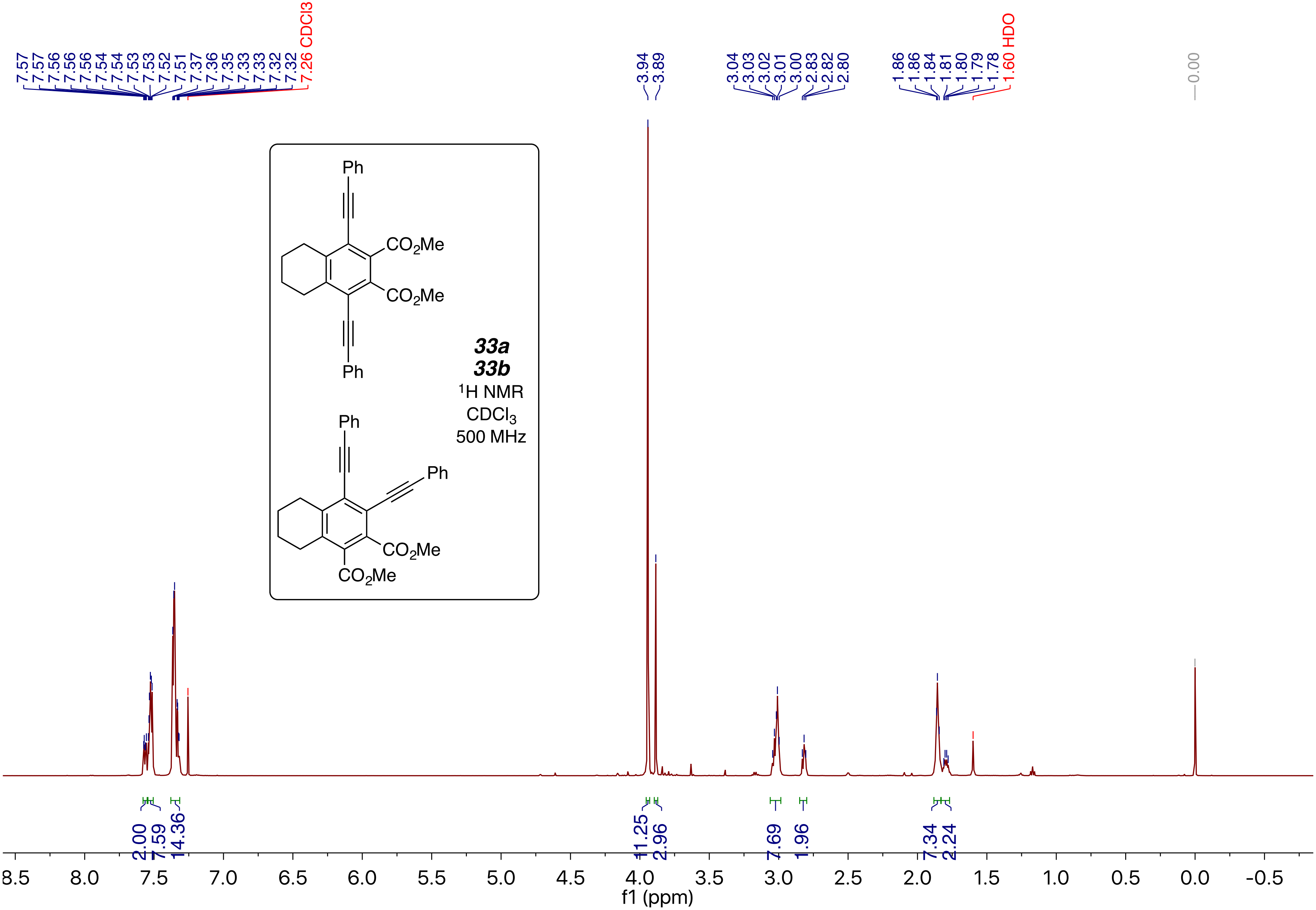


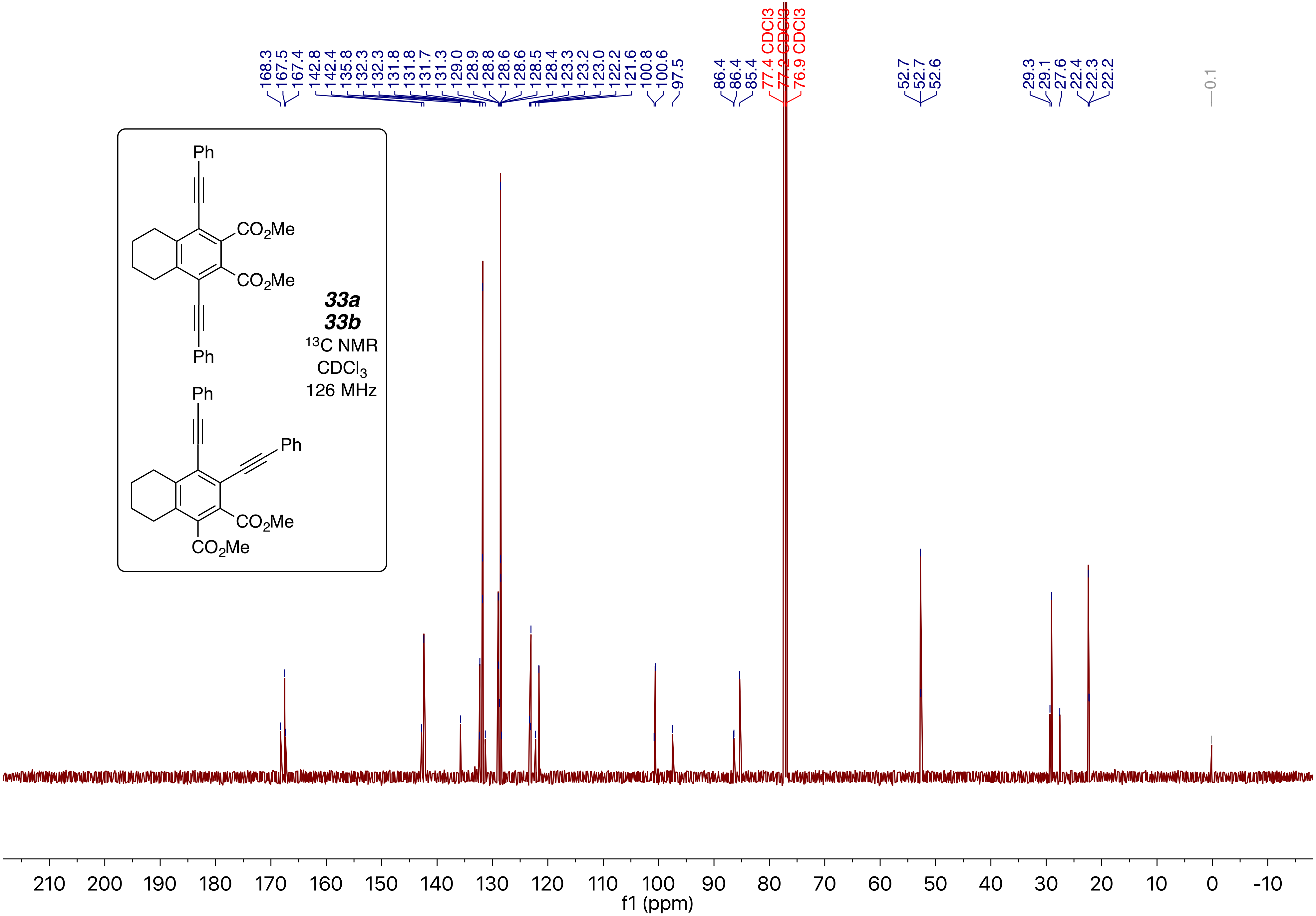
33a

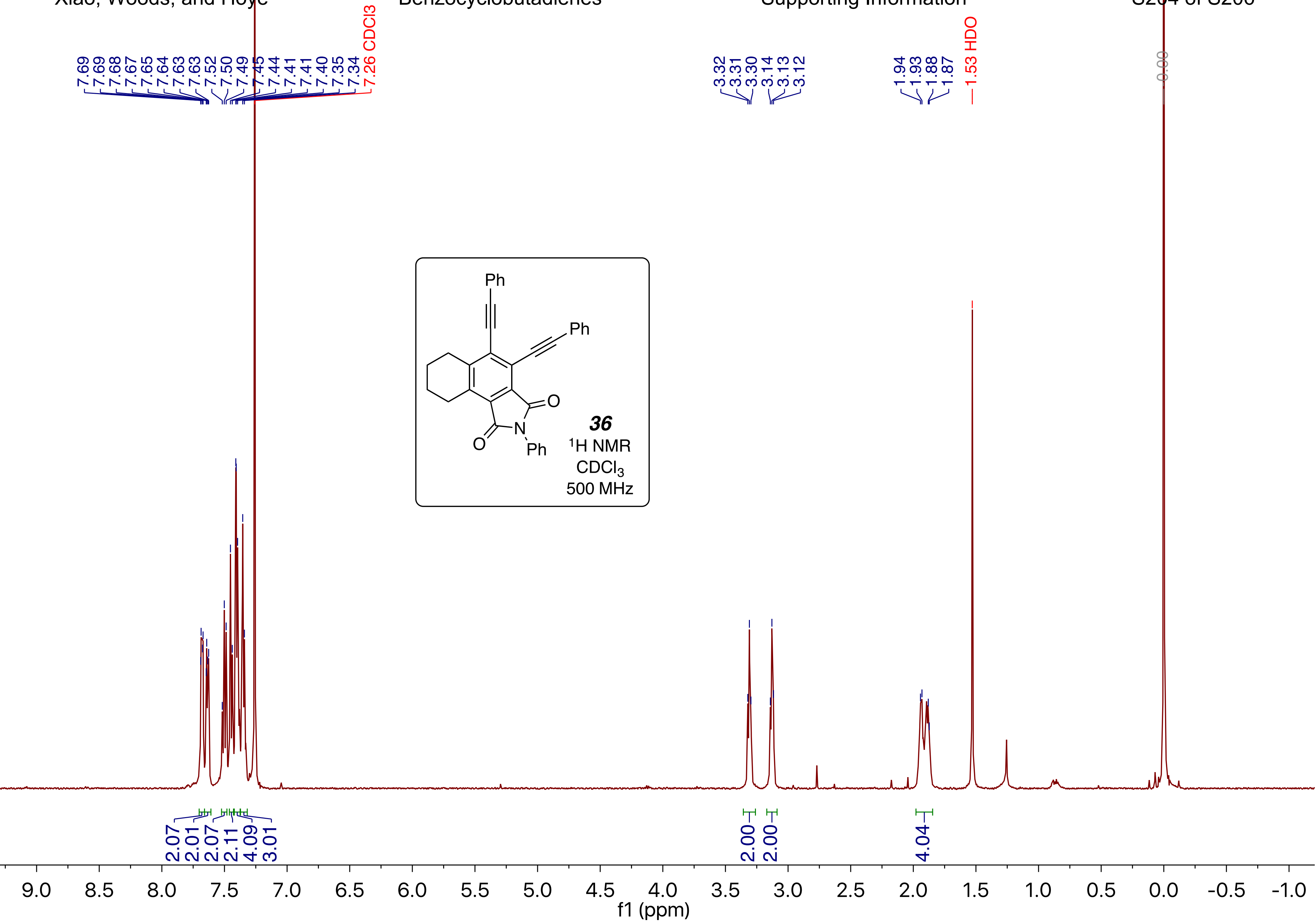
^{13}C NMR

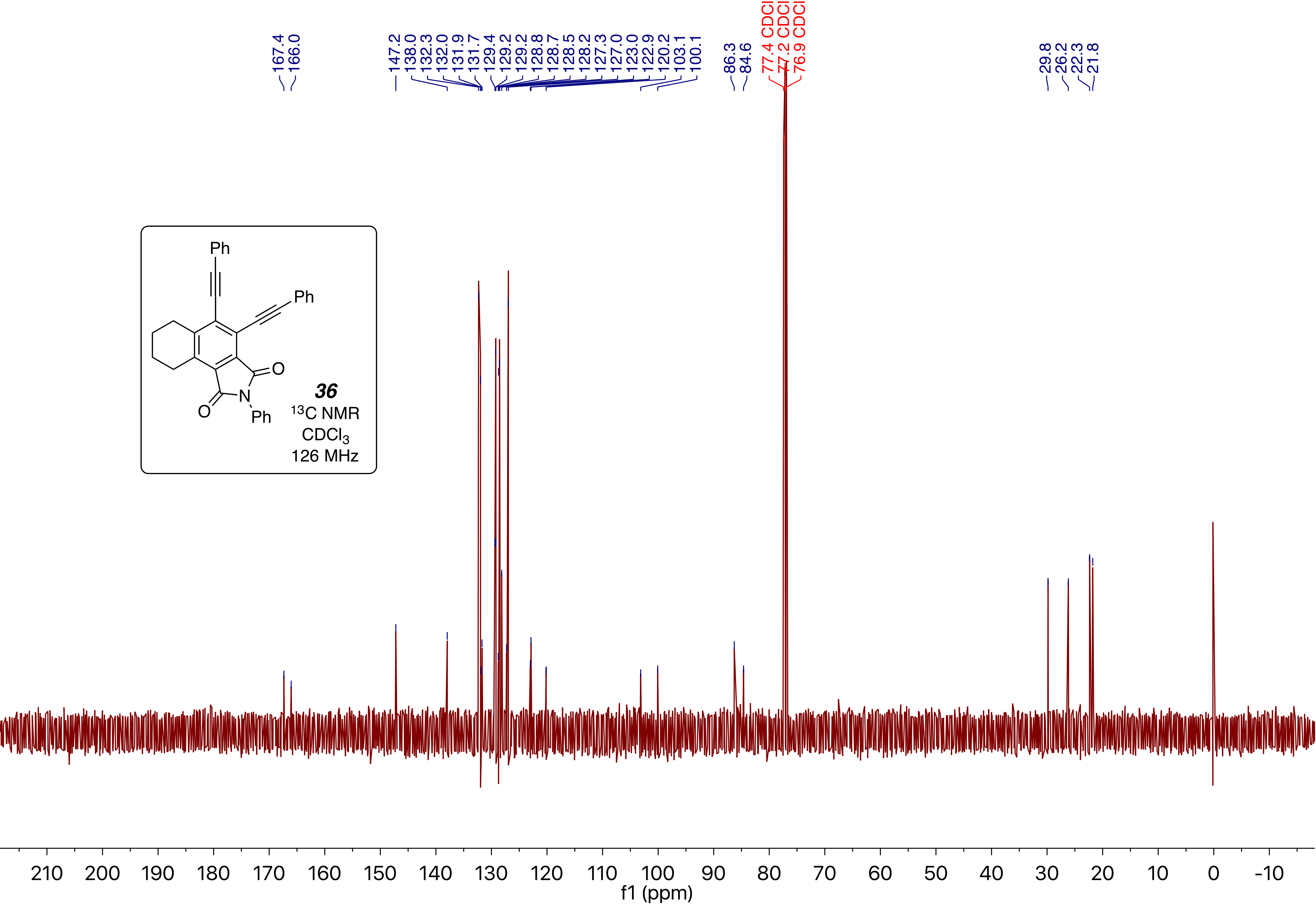
$CDCl_3$

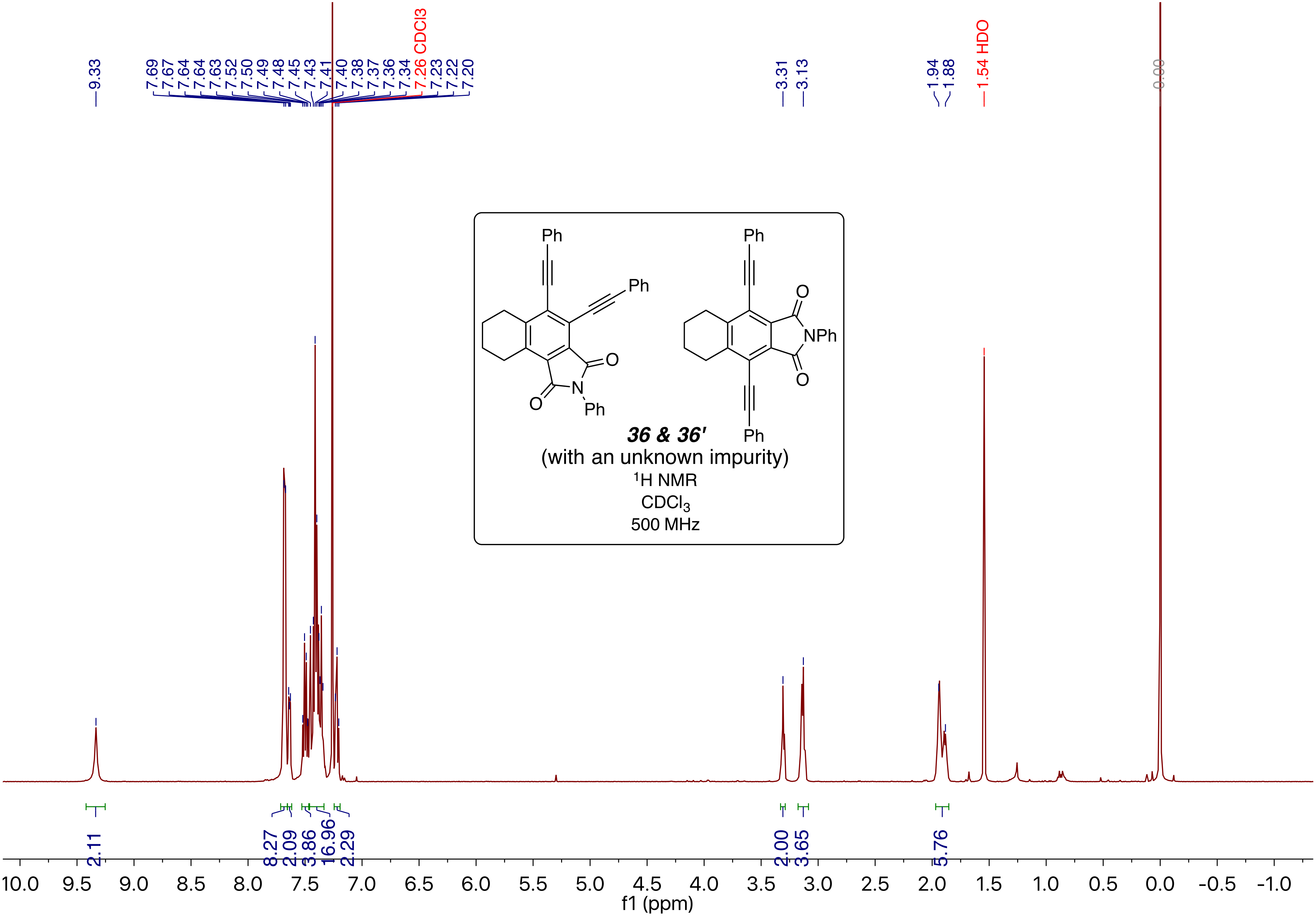
126 MHz


7.57
7.57
7.56
7.56
7.56
7.54
7.54
7.53
7.53
7.52
7.51
7.37
7.36
7.35
7.33
7.33
7.32
7.32
7.26 CDCl3
3.94
3.89
3.04
3.03
3.02
3.01
3.00
2.83
2.82
2.80
1.86
1.86
1.84
1.81
1.80
1.79
1.78
1.60 HDO
0.00
Ph
CO_2Me
CO_2Me
Ph
Ph
Ph
CO_2Me
CO_2Me
33a
33b
^{1}H NMR
$CDCl_3$
500 MHz
2.00
7.59
14.36
11.25
2.96
7.69
1.96
7.34
2.24
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)


33a
33b
^{13}C NMR
$CDCl_3$
126 MHz


7.69
7.69
7.68
7.67
7.65
7.64
7.63
7.63
7.52
7.50
7.49
7.45
7.44
7.41
7.41
7.40
7.35
7.34
7.26 CDCl3
3.32
3.31
3.30
3.14
3.13
3.12
1.94
1.93
1.88
1.87
1.53 HDO
0.00
Ph
Ph
O
N
Ph
O
36
1H NMR
CDCl3
500 MHz
2.07
2.01
2.07
2.11
4.09
3.01
2.00
2.00
4.04
9.0
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)


167.4
166.0
147.2
138.0
132.3
132.0
131.9
131.7
129.4
129.2
129.2
128.8
128.7
128.5
128.2
127.3
127.0
123.0
122.9
120.2
103.1
100.1
86.3
84.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
29.8
26.2
22.3
21.8
Ph
Ph
O
N
Ph
O
36
^{13}C NMR
$CDCl_3$
126 MHz
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)



36 & 36′
(with an unknown impurity)
^{1}H NMR
$CDCl_3$
500 MHz