Supporting Information for

Reactions of Diaziridines with Benzynes Give N-Arylhydrazones

Sahil Arora, Vignesh Palani, and Thomas R. Hoye*

Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455

E-mail: hoye@umn.edu

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I. General Experimental Protocols

^{13}C and ^{1}H NMR spectra were recorded on an HD-500 or AV-500 (500 MHz) spectrometer. ^{1}H chemical shifts are referenced to TMS (δ 0.00 ppm) in $CDCl_3$ and to the residual CHD_5 resonances (δ 7.15 ppm) in benzene-d_6. Where encountered, a non-first order multiplet in a ^{1}H NMR spectrum is designated as 'nfom'. Data are reported in the following format: chemical shift (ppm) [multiplicity, coupling constant(s) (in Hz), integral (to the nearest whole integer), and assignment of the substructural unit within the overall structure]. This is indicated by, e.g., R^{1}C*Ha*Hb for diastereotopic geminal protons; arbitrarily, the more downfield resonance is labeled as H_a. Coupling constants have been analyzed using protocols previously described.[1,2] The ^{13}C NMR shifts are deciphered from the "1D" spectra.

Infrared spectra were recorded using a Midac Corporation (Prospect 4000) FT-IR spectrometer. Neat or thin films of samples were deposited on a NaCl plate.

High-resolution **mass spectrometry** (HRMS) measurements were made on either a Bruker BioTOF II (ESI-TOF) or Thermo Orbitrap Velos (mass accuracy < 3 ppm) instrument, both in the electrospray ionization mode (ESI). On the Bruker instrument poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG) was added to the sample as the standard/calibrant. Samples were infused as methanol solutions. HRMS data were collected as approximately 6–7 separate data sets and then averaged to obtain the reported "found" value. On the Velos instrument samples were introduced as a dilute solution in acetonitrile; an external standard/calibrant was used (Pierce™ LTQ).

Medium pressure liquid chromatography (MPLC) was performed on hand-packed columns of silica gel (20-40 μm, 60 Å pore size, Teledyne RediSep Rf Gold® normal-phase) operated at 25-200 psi. The device comprised a Waters HPLC pump (M6000), a Waters (R401) differential refractive index detector, and a Gilson (112 UV) detector. Agela silica gel (230-400 mesh) was used to pack flash chromatography columns. Thin layer chromatography (TLC) was performed on silica gel glass- or plastic-backed plates. These were visualized initially by UV then by dipping into a solution of potassium permanganate or ceric ammonium molybdate (CAM) and heating.

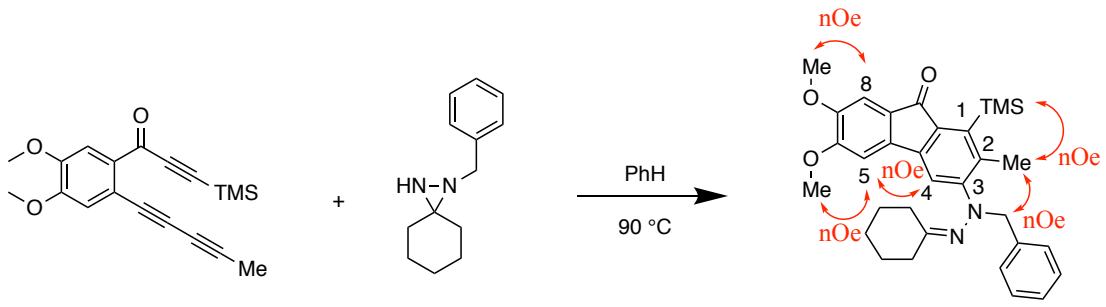
Some compounds were purified by HPLC to achieve mg quantities of samples of high purity, from which the full characterization data set were then collected. This was done in a 10 mm diameter x 250 mm long column of silica gel (Alltech, Econosil, 10 μm).

Unless otherwise noted, the indicated reaction temperature refers to the temperature of the external cooling or heating bath. HDDA reactions, including those carried out at temperatures higher than the boiling point of the reaction solvent, were performed in a screw-capped vial or culture tube that was fitted with an inert, Teflon®-lined screw cap.

For an experiment performed on a 1 mmol scale of limiting reactant, see page S12 to give products **7ce1** and **7ce2**.

II. Preparation and Characterization Data for Hydrazones:

3-(1-Benzyl-2-cyclohexylidenehydrazinyl)-6,7-dimethoxy-2-methyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (7aa):



6a ***2a*** ***7aa, 88%***

Triynone **6a** (40 mg, 0.123 mmol) and 1-benzyl-1,2-diazaspiro[2.5]octane (**2a**, 50 mg, 0.246 mmol, 2 equiv) were combined in a culture tube, dissolved in benzene (8 mL, 0.02 M), and sealed with a Teflon-lined cap. The solution was heated overnight (18–19 h) in an oil bath at 90 °C and cooled to room temperature. The residue was purified by MPLC (2:1 Hex:EtOAc) to give **7aa** (0.108 mmol, 88%) as a bright orange oil.

The assignment of the structure of **7aa** was based upon the indicated nOe interactions. The preference for formation of this isomer is consistent with what is predicted on the basis of distortion analysis[3] of the computed (DFT) geometry.

Data for 7aa:

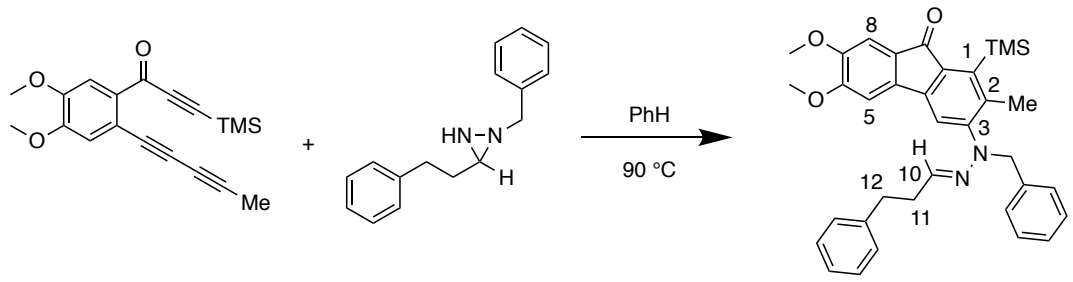
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.4 Hz, 2H, ArH_o), 7.34 (s, 1H, Ar*H4*), 7.33 (dd, *J* = 7.4, 7.4 Hz , 2H, ArH_m), 7.25 (d, *J* = 7 Hz, 1H, ArH_p), 7.11 (s, 1H, Ar*H8*), 6.90 (s, 1H, Ar*H5*), 4.32 (s, 2H, benzylic CH_2), 3.97 (s, 3H, OC6H_3), 3.90 (s, 3H, OC7H_3), 2.55 (s, 3H, ArCH_3), 2.34 (t, *J* = 6.7 Hz, 2H, N=CCH_2), 2.21 (t, *J* = 6.7 Hz, 2H, N=CCH_2), 1.62 (quin, *J* = 6.6 Hz, 2H, CH_2), 1.49 (quin, *J* = 6.2 Hz, 2H, CH_2), 1.33 (quin, *J* = 6.2 Hz, 2H, CH_2), and 0.44 [s, 9H, $Si(CH_3)_3$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 193.9, 174.3, 157.3, 154.1, 149.4, 143.62, 143.57, 138.7, 135.8, 135.7, 128.9, 128.6, 128.2, 127.2, 127.0, 113.2, 106.7, 102.7, 62.9, 56.4, 56.2, 42.0, 35.7, 30.3, 27.2, 27.0, 25.8, 25.7, 20.1, and 2.8.

IR (CH_2Cl_2): 2939, 2857, 1703, 1588, 1464, 1380, 1352, 1245, 1216, 1092, 1019, 993, and 863 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{32}H_{39}N_2O_3Si^+$ [M+H$^+$] requires 527.2724; found 527.2714

1-Benzyl-2-(3-phenylpropylidene)hydrazinyl)-6,7-dimethoxy-2-methyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (7ab)



6a ***2b*** ***7ab, 85.4%***

Triynone **6a** (25 mg, 0.077 mmol) and 1-benzyl-3-phenethyldiaziridine (**2b**, 37 mg, 0.246 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (4 mL, 0.02 M). The tube was sealed with a Teflon-lined cap. The solution was heated overnight (18-19 h) in an oil bath at 90 °C and cooled to room temperature. The residue was purified by MPLC (3:1 Hex:EtOAc) to give **7ab** (0.066 mmol, 85%) as a bright orange oil. This sample was then separately repurified by HPLC (3:1 Hex:EtOAc) to give a sample of **7ab** of higher purity that was used for collection of spectral data.

Data for 7ab:

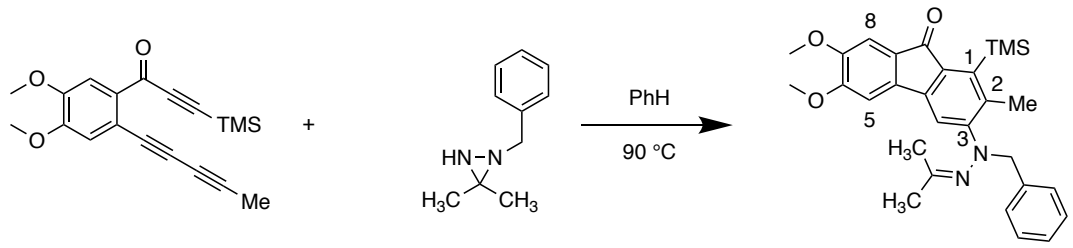
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.26 (m, 5H, Ph*H*), 7.23 (dd, *J* = 7.3, 7.3 Hz, 1H, NCH_2Ar*H*$_m$), 7.16 (br t, *J* = 7 Hz, 1H, NCH_2Ar*H*$_p$), 7.12 (s, 1H, Ar*H8*), 7.10 (s, 1H, Ar*H5*), 7.09 (d, *J* = 7 Hz, 2H, NCH_2Ar*H*$_o$), 6.86 (s, 1H, Ar*H4*), 6.58 (t, *J* = 5.8 Hz, 1H, *H*C=N), 4.70 (s, 2H, ArNC*H*$_2$), 4.00 (s, 3H, OC*H*$_3$), 3.91 (s, 3H, OC*H*$_3$), 2.76 (t, *J* = 7.7 Hz, 2H, C*12*H_2), 2.57 (td, *J* = 7.7, 5.8 Hz, 2H, C*11*H_2), 2.23 (s, 3H, $ArCH_3$), and 0.40 [s, 9H, $Si(CH_3)_3$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 193.9, 154.2, 151.9, 149.5, 143.9, 143.5, 141.2, 139.1, 138.6, 138.5, 137.5, 137.2, 128.5, 128.5, 128.3, 127.4, 127.1, 127.1, 125.9, 116.2, 106.7, 102.8, 58.0, 56.4, 56.2, 34.6, 33.8, 20.7, and 2.7.

IR (CH_2Cl_2): 3061, 3027, 2939, 2838, 1703, 1588, 1551, 1495, 1454, 1417, 1383, 1316, 1245, 1217, 1150, 1090, 1076, 1045, 1019, 996, 976, 862, 798, 736, and 700 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{35}H_{39}N_2O_3Si^+$ [$M+H^+$] requires 563.2724; found 563.2719.

3-(1-Benzyl-2-(propan-2-ylidene)hydrazinyl)-6,7-dimethoxy-2-methyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (7ac)



6a ***2c*** ***7ac, 99%***

Triynone **6a** (25 mg, 0.077 mmol) and 1-benzyl-3,3-dimethyldiaziridine **2c** (25 mg, 0.154 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (4 mL, 0.02 M). The tube was sealed with a Teflon-lined cap. The solution was heated overnight (18-19 h) in an oil bath at 90 °C and cooled to room temperature. The residue was purified by MPLC (1:1 Hex:EtOAc) to give **7ac** (0.076 mmol, 99 %) as a bright orange oil.

Data for 7ac:

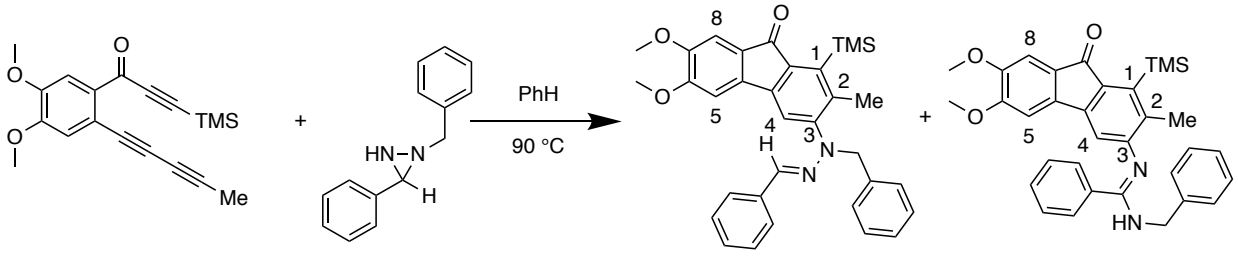
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.24 (m, 6H, Ph*H* and *H4*), 7.12 (s, 1H, Ar*H8*), 6.90 (s, 1H, *H5*), 4.32 (s, 2H, ArNCH_2), 3.98 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 2.55 (s, 3H, ArCH_3), 2.01 (s, 3H, CH_3–C=N), 1.70 (s, 3H, CH_3–C=N), and 0.44 [s, 9H, Si$(CH_3)_3$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 193.9, 168.4, 156.7, 154.1, 149.4, 143.6, 143.6, 138.7, 138.6, 136.5, 136.1, 128.5, 128.2, 127.1, 127.0, 113.4, 106.7, 102.8, 63.3, 56.4, 56.2, 25.3, 20.3, 19.8, and 2.8.

HRMS (ESI-TOF): Calcd for $C_{29}H_{35}N_2O_3Si^+$ [M+H$^+$] requires 487.2411; found 487.2409.

IR (CH_2Cl_2): 2951, 2839, 1702, 1636, 1587, 1495, 1315, 1244, 1216, 1091, 1077, 1019, 862, and 797 cm^{-1}.

3-(1-Benzyl-2-benzylidenehydrazinyl)-6,7-dimethoxy-2-methyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (7ad) and *N*-benzyl-*N*'-(6,7-dimethoxy-2-methyl-9-oxo-1-(trimethylsilyl)-9*H*-fluoren-3-yl)benzimidamide (12ad):



6a ***2d*** ***7ad, 31%*** ***12ad, 45%***

Triynone **6a** (25 mg, 0.077 mmol) and 1-benzyl-3-phenyldiaziridine (**2d**, 25 mg, 0.154 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (4 mL, 0.02 M). The tube was sealed with a Teflon-lined cap. The solution was heated overnight (18-19 h) in an oil bath at 90 °C and cooled to room temperature. The residue was purified by MPLC (3:1 Hex:EtOAc) to give, in order of elution, the tertiary amine-trapped adduct **7ad** (11.0 mg, 31%) as a yellow oil and the secondary amine-trapped product **10ad** (16.0 mg, 45%) also as a yellow oil. A small portion of **10ad** was repurified by normal-phase HPLC (3:1 Hex:EtOAc + 1% NEt_3) to give as a yellow oil, which was used for collection of spectral data.

Data for faster eluting tertiary amine-trapped, hydrazone 7ad:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.5 Hz, 2H, Ph*H*), 7.36 (s, 1H, Ar*H4*), 7.25 (s, 1H, Ar*H8*), 7.38–7.22 (m, 8H, PhH_m and PhH_p), 7.19 (s, 1H, Ar*H5*), 7.13 (d, *J* = 7.1 Hz, 1H, PhH_o), 7.12 (s, 1H, Ar*H5*), 6.84 (s, 1H, *H*C=N), 4.89 (s, 2H, ArNCH_2), 3.96 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 2.30 (s, 3H, $ArCH_3$), and 0.43 [s, 9H, $Si(CH_3)_3$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 194.6, 155.2, 151.2, 150.4, 144.7, 144.2, 140.2, 139.2, 139.0, 137.8, 137.1, 135.9, 129.4, 129.3, 128.7, 128.6, 128.1, 127.8, 126.7, 118.2, 107.5, 103.6, 59.5, 57.2, 57.0, 21.3, and 3.5.

IR (CH_2Cl_2): 2840, 2685, 1704, 1588, 1495, 1455, 1383, 1317, 1217, 1150, 1098, 1048, 1075, 1019, 997, and 860 cm^{-1}

HRMS (ESI-TOF): Calcd for $C_{33}H_{35}N_2O_3Si^+$ [$M+H^+$] requires 535.2411, found 535.2400.

Data for slower eluting secondary amine-trapped, amidine 12ad:

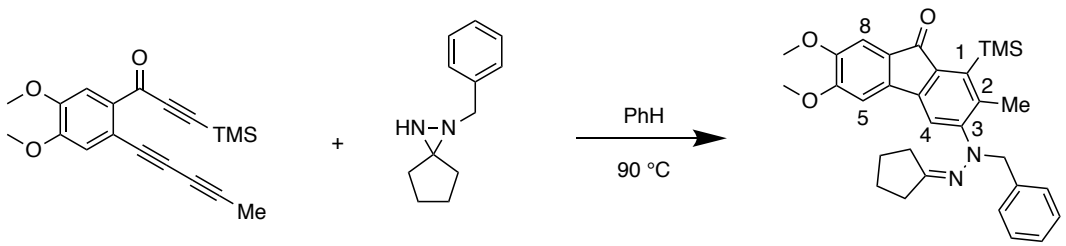
^{1}H NMR (500 MHz, $CDCl_3$): 7.42–7.31 (m, 10H, PhH), 7.06 (s, 1H, Ar*H8*), 6.69 (s, 1H, Ar*H5*), 6.47 (br s, 1H, Ar*H4*), 4.99 [br t, *J* = 5.3 Hz, 1H, (C=N)N*H*)], 4.67 [br d, *J* = 4.6 Hz, 2H, Ar(CH_2)N], 3.92 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 2.24 (s, 3H, $ArCH_3$), and 0.37 [s, 9H, $Si(CH_3)_3$].

^{13}C NMR (125 MHz, $CDCl_3$): 193.9, 156.2 (br, HMBC from CH_2N), 153.6, 149.2, 143.4, 142.2, 138.9, 138.5, 135.0, 134.7, 134.2, 129.9, 128.7, 128.6, 127.8 (2x), 127.6, 127.5, 114.1, 106.5, 102.5, 56.3, 56.2, 46.4 (br, HSQC from CH_2N), 19.4, and 2.7 (one aromatic carbon was not observed).

HRMS (ESI-TOF): Calcd for $C_{33}H_{35}N_2O_3Si^+$ [$M+H^+$] requires 535.2411, found 535.2421.

IR (CH_2Cl_2): 3380, 2948, 1695, 1627, 1576, 1493, 1469, 1423, 1382, 1311, 1243, 1216, 1185, 1156, 1134, 1090, 1076, 1052, 1019, 873 848, 749, and 699 cm^{-1}.

3-(1-Benzyl-2-cyclopentylidenehydrazinyl)-6,7-dimethoxy-2-methyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (7ae):



6a ***2e*** ***7ae, 99%***

Triynone **6a** (20 mg, 0.062 mmol) and 1-benzyl-1,2-diazaspiro[2.4]heptane **2e** (25 mg, 0.129 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (4 mL, 0.02 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated overnight (18-19 h) in an oil bath held at 90 °C and then allowed to cool to room temperature. The residue was purified by MPLC (1:1 Hex:EtOAc) to give **7ae** (31 mg, 0.061 mmol, 99%) as a bright orange oil.

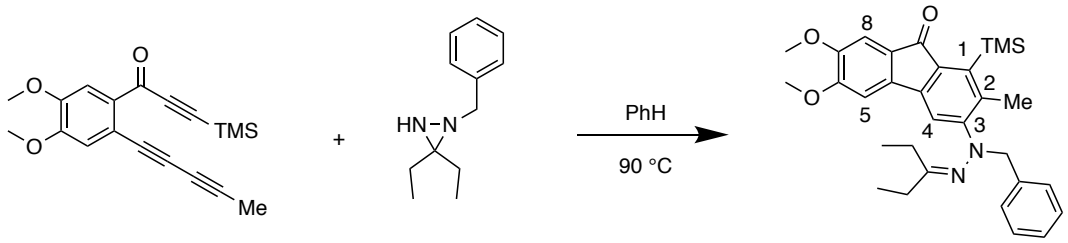
Data for 7ae:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.30 (m, 6H, Ph*H* and *H4*), 7.12 (s, 1H, Ar*H8*), 6.91 (s, 1H, Ar*H5*), 4.31 (s, 2H, benzylic CH_2), 3.98 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 2.52 (s, 3H, ArCH_3), 2.41 [t, J = 7.6 Hz, 2H, N=C(CH_2)'], 2.05 [t, J = 7.6 Hz, 2H, N=C(CH_2)], 1.65 (m, 4H, N=C$(CH_2)_2$$(CH_2)_2$, and 0.43 [s, 9H, Si$(CH_3)_3$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 193.9, 180.2, 156.5, 154.2, 149.4, 143.6, 143.5, 138.7, 137.2, 136.3, 128.6, 128.5 (from HMBC), 128.2, 127.1, 127.0, 113.9, 106.7, 102.8, 63.5, 56.4, 56.2, 33.6, 31.2, 24.6, 24.5, 19.6, and 2.6.

HRMS (ESI-TOF): Calcd for $C_{31}H_{37}N_2O_3Si^+$ [$M+H^+$] requires 513.2568; found 513.2566.
IR (CH_2Cl_2): 2956, 1703, 1644, 1587, 1494, 1454, 1379, 1316, 1245, 1216, 1147, 1091, 1020, 993, 862, 797, 733, and 669 cm^{-1}.

3-(1-Benzyl-2-(pentan-3-ylidene)hydrazinyl)-6,7-dimethoxy-2-methyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (7af):



6a ***2f*** ***7af, 94%***

Triynone **6a** (25 mg, 0.077 mmol) and 1-benzyl-3,3-diethyldiaziridine **2f** (30 mg, 0.154 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (4 mL, 0.02 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated overnight (18-19 h) in an oil bath held at 95 °C and then cooled to room temperature. The residue was purified by MPLC (3:1 Hex:EtOAc) to give **7af** (0.072 mmol, 94%) as a bright orange oil.

Data for 7af:

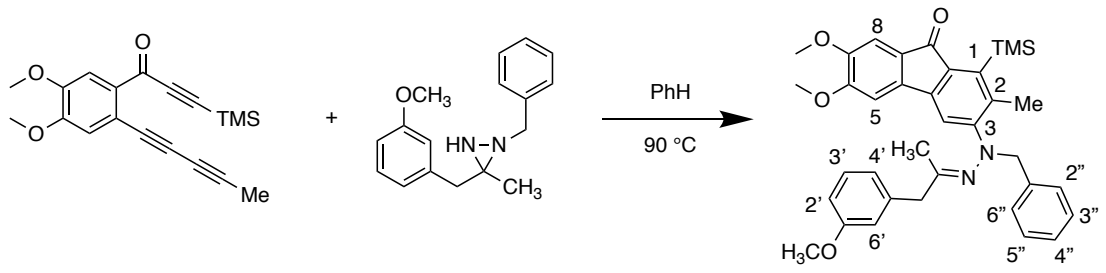
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.24 (m, 6H, Ph*H* and *H4*), 7.11 (s, 1H, Ar*H8*), 6.88 (s, 1H, Ar*H5*), 4.28 (s, 2H, benzylic CH_2), 3.97 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 2.58 (s, 3H, $ArCH_3$), 2.30 [q, *J* = 7.6 Hz, 2H, (N=C)C$H_2$$CH_2$], 2.12 [q, *J* = 7.6 Hz, 2H, (N=C)C$H_2$$CH_2$], 1.07 [t, *J* = 7.6 Hz, 2H, (N=C)CH_2CH_2], 0.77 [t, *J* = 7.6 Hz, 2H, (N=C)CH_2CH_2], and 0.45 [s, 9H, $Si(CH_3)_3$].

^{13}C NMR (125 MHz, $CDCl_3$): 193.9, 177.3, 157.5, 154.1, 149.4, 143.5, 138.7, 138.5, 136.1, 135.8, 129.0, 128.6, 128.1, 127.2, 127.0, 113.3, 106.7, 102.6, 63.3, 56.3, 56.2, 28.9, 24.7, 19.9, 11.5, 9.9, and 2.8.

IR (CH_2Cl_2): 3061, 2928, 2851, 1702, 1588, 1495, 1464, 1420, 1383, 1354, 1216, 1245, 1216, 1150, 1092, 1077, 1048, 1019, 997, 861, 793, and 737 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{31}H_{39}N_2O_3Si^+$ [$M+H^+$] requires 515.2724; found 515.2724.

3-(1-Benzyl-2-(1-(3-methoxyphenyl)propan-2-ylidene)hydrazinyl)-6,7-dimethoxy-2-methyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (7ag):



6a ***2g*** ***7ag, 69%***

Triynone **6a** (40 mg, 0.123 mmol) and 1-benzyl-3-(3-methoxybenzyl)-3-methyldiaziridine **2g** (66 mg, 0.246 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (4mL, 0.02 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated overnight (18-19 h) in an oil bath held at 90 °C and then cooled to room temperature. The residue was purified by MPLC (3:1 Hex:EtOAc) to give **7ag** (0.084 mmol, 68% yield) as a yellow oil.

Data for 7ag [the sample contains ca. 6% of what was judged to be the isomeric (and co-eluting) *Z*-hydrazone]:

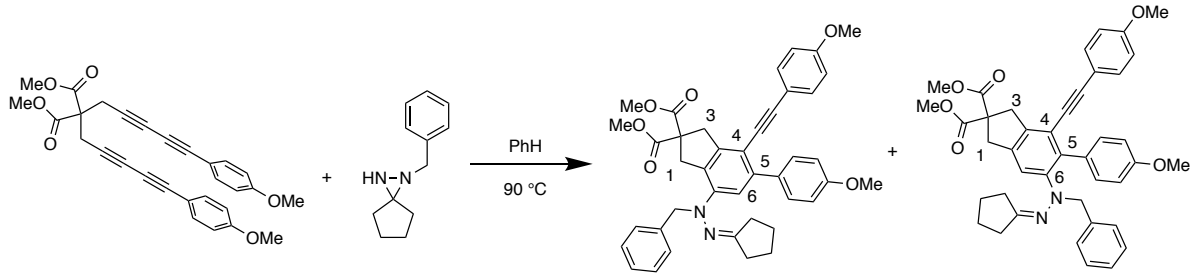
^{1}H NMR (500 MHz, $CDCl_3$): 7.40 (d, *J* = 7.2 Hz, 2H, *H2"* and *H6"*), 7.34 (t, *J* = 7.4 Hz, 2H, *H5"* and *H3"*), 7.31 (s, 1H, *H4*), 7.28 (t, *J* = 7.3 Hz, 1H, *H4"*), 7.12 (s, 1H, *H8*), 7.10 (dd, 1H, *J* = 7.7, 7.7 Hz, *H3'*), 6.88 (s, 1H, *H5*), 6.71 (dd, *J* = 8.2, 2.5 Hz, 1H, *H2'*), 6.65 (s, 1H, *H6'*), 6.60 (d, *J* = 7.6 Hz, 1H, *H4'*), 4.40 (s, 2H, NC*H*$_2$Ph), 4.00 (s, 3H, OC*H*$_3$), 3.91 (s, 3H, OC*H*$_3$), 3.66 (s, 3H, OC*H*$_3$), 3.56 [s, 2H, C*H*$_2$(C=N)CH$_3$], 2.54 (s, 3H, NArC*H*$_3$), 1.61 [s, 3H, CH$_2$(C=N)C*H*$_3$], and 0.43 [s, 9H, Si(CH$_3$)$_3$]. [Minor resonances consistent with the presence of the *Z*-hydrazone were observed at 1.86 (s, CH$_3$C=N), 2.62 (ArCH$_3$), 3.54 (CH$_2$C=N), and 4.35 (NC*H*$_2$Ph).]

^{13}C NMR (125 MHz, $CDCl_3$): δ 193.9, 168.8, 159.7, 156.4, 154.2, 149.5, 143.7, 143.6, 138.8, 138.5, 136.6, 136.2, 129.5, 128.5, 128.3, 127.1, 127.0, 121.3, 114.9, 113.6, 111.8, 106.7, 102.8, 63.3, 56.4, 56.2, 55.1, 45.5, 19.7, 18.6, and 2.8. (resonance for one aromatic carbon atom not observed).

HRMS (ESI-TOF): Calcd for $C_{36}H_{41}N_2O_4Si^+$ [M+H$^+$] requires 593.2830; found 593.2820.

IR (CH_2Cl_2): 2838, 2685, 2410, 1702, 1640, 1600, 1495, 1422, 1315, 1216, 1149, 1091, and 862 cm^{-1}.

Dimethyl 7-(1-benzyl-2-cyclopentylidenehydrazineyl)-5-(4-methoxyphenyl)-4-((4-methoxyphenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (7be1) and dimethyl 6-(1-benzyl-2-cyclopentylidenehydrazineyl)-5-(4-methoxyphenyl)-4-((4-methoxyphenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (7be2)



6b ***2e*** ***7be1 (63%)*** ***7be2 (14.2%)***

Tetrayne **6b** (20 mg, 0.043 mmol) and 1-benzyl-1,2-diazaspiro[2.4]heptane **2e** (16 mg, 0.085 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (4 mL, 0.01 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated overnight (18–19 h) in an oil bath at 90 °C and cooled to room temperature. The residue was purified by MPLC (2:1 Hex:EtOAc) to give, in order of elution, **7be1** (63.4%) and **7be2** (14.2%), each as a transparent oil. The assignment of the structure of each of these was based upon observed (difference) nOe interactions between the aromatic proton and the adjacent aromatic proton (PhH_m to OMe group) or methylene protons, respectively.

Data for faster eluting, major isomer 7be1:

^{1}H NMR (500 MHz, $CDCl_3$): 7.52 [d, J = 8.4 Hz, 2H, ArH_m (to OMe)], 7.36 (d, 2H, J = 7.5 Hz, 2H, PhH_o), 7.33–7.24 [m, 5H, Ar'H_m (to OMe), PhH_m and PhH_p], 7.01 (s, 1H, Ar*H6*), 6.94 [d, J = 7.6 Hz, 2H, Ar'H_o (to OMe)], 6.83 [d, J = 7.9 Hz, 2H, Ar'H_o (to OMe)], 4.48 (s, 2H, NCH_2Ph), 3.85 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.81 (s, 2H, C1H_2 or C3H_2), 3.77 (s, 6H, CO_2CH_3), 3.57 (s, 2H, C1H_2 or C3H_2), 2.39 [t, J = 7.1 Hz, 2H, N=C*(CH$_2$)*(CH_2)], 2.01 [t, J = 7.1 Hz, 2H, N=C*(C'H$_2$)*(CH_2)], and 1.61 [m, 4H, N=C$(CH_2)_2$*(CH$_2$)$_2$*].

^{13}C NMR (125 MHz, $CDCl_3$): δ 178.4, 172.1, 159.4, 159.0, 148.2, 144.6, 143.2, 138.9, 132.9, 132.7, 131.6, 130.4, 128.5, 128.2, 126.9, 121.0, 115.9, 113.9, 113.2, 113.1, 95.2, 86.2, 62.9, 59.8, 55.3, 53.0 (2x), 41.2, 39.8, 33.5, 31.0, 24.8, and 24.4.

HRMS (ESI-TOF): Calcd for $C_{41}H_{41}N_2O_6^+$ [M+H$^+$] requires 657.2959; found 657.2947.

IR (CH_2Cl_2): 2957, 2859, 2350, 1733, 1644, 1607, 1511, 1664, 1436, 1248, 1203, 1176, 1107, 1032, 960, and 834 cm^{-1}.

Data for slower eluting, minor isomer 7be2:

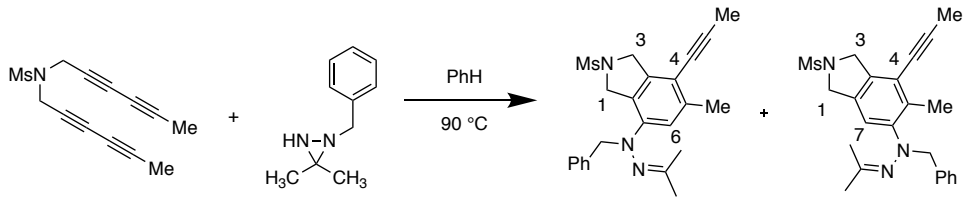
^{1}H NMR (500 MHz, $CDCl_3$): 7.40 [d, J = 8.1 Hz, 2H, ArH_m (to OMe)], 7.21 (s, 1H, Ar*H7*), 7.14 [d, J = 8.4 Hz, 2H, Ar'H_m (to OMe)], 7.12–7.09 (m, 3H, Ph*H*), 7.00 [d, J = 8.2 Hz, 2H, ArH_o (to OMe)], 6.78 [d, J = 8.3 Hz, 2H, Ar'H_o (to OMe)], 6.76 (nfom, 2H, Ph*H*), 4.09 (s, 2H, N-CH_2-Ph), 3.87 (s, 3H, OCH_3), 3.78 (s, 9H, OCH_3), 3.75 (s, 2H, C1H_2 or C3H_2), 3.62 (s, 2H, C1H_2 or C3H_2), 2.32 [t, J = 7.0 Hz, 2H, N=C*(CH$_2$)*(CH_2)], 1.98 [t, J = 7.4 Hz, 2H, N=C*(C'H$_2$)*(CH_2)], and 1.62–1.50 [m, 4H, N=C$(CH_2)_2$*(CH$_2$)$_2$*].

^{13}C NMR (125 MHz, $CDCl_3$): 179.7, 172.2, 159.5, 158.7, 150.8, 139.4, 138.9, 137.4, 136.5, 132.9, 131.9, 131.6, 129.0, 127.6, 126.6, 121.0, 116.6, 115.6, 113.8, 113.4, 96.3, 86.1, 63.6, 59.6, 55.5, 55.3, 53.1, 41.1, 40.7, 33.4, 31.5, 24.7, and 24.3.

HRMS (ESI-TOF): Calcd for $C_{41}H_{41}N_2O_6^+$ [M+H$^+$] requires 657.2959; found 657.2945.

IR (CH_2Cl_2): 2955, 2837, 2360, 2206, 1735, 1606, 1511, 1436, 1247, 1200, 1173, 1106, 1071, 1031, and 833 cm^{-1}.

7-(1-Benzyl-2-(propan-2-ylidene)hydrazinyl)-5-methyl-2-(methylsulfonyl)-4-(prop-1-yn-1-yl)isoindoline (7cc1) and 6-(1-benzyl-2-(propan-2-ylidene)hydrazinyl)-5-methyl-2-(methylsulfonyl)-4-(prop-1-yn-1-yl)isoindoline (7cc2):



6c ***2c*** ***7cc1*** ***7cc2***

93%** overall **(7cc1: 7cc2= 1: 1.8)

Tetrayne **6c** (50 mg, 0.202 mmol) and 1-benzyl-3,3-dimethyldiaziridine (**2c**, 65.6 mg, 0.404 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (10 mL, 0.02 M). The tube was sealed with a Teflon-lined cap. The solution was heated overnight (18-19 h) in an oil bath at 90 °C and cooled to room temperature. The residue was purified by MPLC (1:1 Hex:EtOAc) to give, in order of elution, **7cc1** as a yellow oil and **7cc2** also as a yellow oil, which solidified upon storage at -10 °C (93% combined yield, 0.158 mmol). The assignment of the structure of each of these was based upon observed nOe interactions between the aromatic proton and the adjacent benzylic methyl or methylene protons, respectively.

Data for faster eluting, minor isomer 7cc1:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.23 (m, 5H, PhH), 6.85 (s, 1H, Ar*H6*), 4.66 (s, 2H, ArNCH_2), 4.53 (s, 2H, MsNC1H_2 or MsNC3H_2), 4.37 [s, 2H, N(Ms)C1H_2 or N(Ms)C3H_2], 2.80 (s, 3H, C$H_3$$SO_2$N), 2.33 (s, 3H, NArC$H_3$), 2.09 (s, 3H, C≡CC$H_3$), 1.99 (s, 3H, [(C$H_3$)$_2$C=N], and 1.70 (s, 3H, [(CH_3)$_2$C=N].

^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 146.4, 141.1, 140.4, 137.9, 128.5, 128.3, 127.2, 125.3, 120.1, 113.2, 93.3, 75.4, 62.0, 54.3, 54.1, 34.5, 25.0, 20.4, 19.7, and 4.6.

IR (CH_2Cl_2): 2919, 2854, 2685, 2231, 1606, 1496, 1422, 1339, 1157, 1080, and 960 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{23}H_{28}N_3O_2S^+$ [M+H$^+$] requires 410.1897; found 410.1893

Data for slower eluting, major isomer 7cc2::

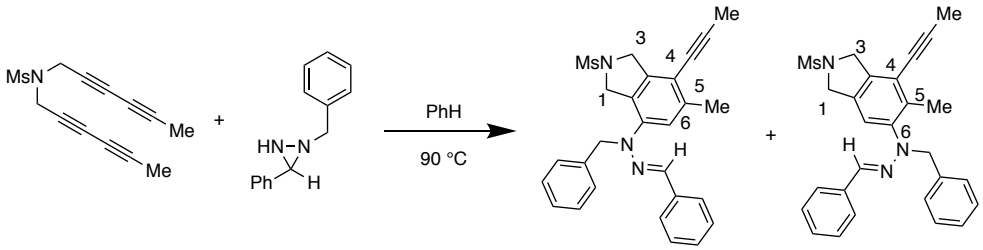
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34- 7.06 (m, 5H, PhH), 7.06 (s, 1H, Ar*H7*), 4.68 (s, 2H, N-CH_2-Ph), 4.62 [s, 2H, N(Ms)C1H_2], 4.22 [s, 2H, N(Ms)C3H_2], 2.86 (s, 3H, C$H_3$$SO_2$N), 2.50 (s, 3H, NArC$H_3$), 2.12 (s, 3H, C≡CC$H_3$), 1.93 (s, 3H, [(C$H_3$)$_2$C=N], and 1.63 (s, 3H, [(CH_3)$_2$C=N].

^{13}C NMR (125 MHz, $CDCl_3$): δ 166.8, 152.5, 138.9, 134.4, 133.8, 133.8, 128.5, 128.1, 126.9, 120.1, 115.6, 94.8, 75.7, 63.5, 54.3, 54.2, 34.7, 25.2, 19.9, 16.0, and 4.6.

HRMS (ESI-TOF): Calcd for $C_{23}H_{28}N_3O_2S^+$ [M+H$^+$] requires 410.1897; found 410.1892.

IR (CH_2Cl_2): 2986, 2920, 2855, 2685, 2232, 1590, 1496, 1455, 1422, 1339, 1156, 1078, 960, and 824 cm^{-1}.

7-(1-Benzyl-2-benzylidenehydrazinyl)-5-methyl-2-(methylsulfonyl)-4-(prop-1-yn-1-yl)isoindoline (7cd1) and 6-(1-benzyl-2-benzylidenehydrazinyl)-5-methyl-2-(methylsulfonyl)-4-(prop-1-yn-1-yl)isoindoline (7cd2):



6c ***2d*** ***7cd1 (14%)*** ***7cd2 (38%)***

Tetrayne **6c** (60 mg, 0.243 mmol) and 1-benzyl-3-phenyldiaziridine (**2d**, 102 mg, 0.486 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (12 mL, 0.02 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated overnight (18-19 h) in an oil bath held at 90 °C and then allowed to cool to room temperature. The residue was purified by MPLC (3:1 Hex:EtOAc) to give, in order of elution, **7cd1** (14%, 0.033 mmol) as a flaky white powder and **7cd2** (38%, 0.092 mmol) as a transparent oil, which solidified to a white material upon storage at -10 °C. A small portion of **7cd1** was repurified by normal-phase HPLC (3:1 Hex:EtOAc) to give **7cd1** as a white amorphous powder, which was used for collection of spectral data. The assignment of the structure of each of these was based upon observed nOe interactions (difference nOe) between the aromatic proton and the adjacent benzylic methyl or methylene protons, respectively, for **7cd1** or **7cd2**.

Data for faster eluting minor isomer 7cd1:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.3 Hz, 2H, PhH_o), 7.38–7.30 (m, 7H, PhH_m, PhH_p, Ph'H_m, Ph'H_p, and Ph*H*C=N), 7.22 (d, *J* = 7.2 Hz, 2H, Ph'H_o), 6.60 (s, 1H, *H6*), 5.21 (s, 2H, N(Ms)*C1H*$_2$ or N(Ms)*C3H*$_2$), 5.18 (s, 2H, N(Ms)*C1H*$_2$ or N(Ms)*C3H*$_2$), 4.74 (s, 2H, N-CH_2-Ph), 2.89 (s, 3H, CH_3SO_2N), 2.33 (s, 3H, NArCH_3), and 2.11 (s, 3H, NArC≡CCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): 142.4, 141.4, 141.0, 135.7, 134.8, 134.5, 129.2, 128.8, 128.3, 127.5, 126.3, 125.9, 121.2, 114.7, 111.5, 93.1, 75.4, 57.2, 54.1, 51.3, 34.4, 20.5, and 4.6.

HRMS (ESI-TOF): Calcd for $C_{27}H_{28}N_3O_2S^+$ [M+H$^+$] requires 458.1897; found 458.1892.

IR (CH_2Cl_2): 2916, 2849, 1606, 1588, 1564, 1496, 1465, 1415, 1327, 1183, 1152, 1123, 1071, 962, and 825 cm^{-1} (alkyne stretching frequency was not observed).

Data for slower eluting major isomer 7cd2:

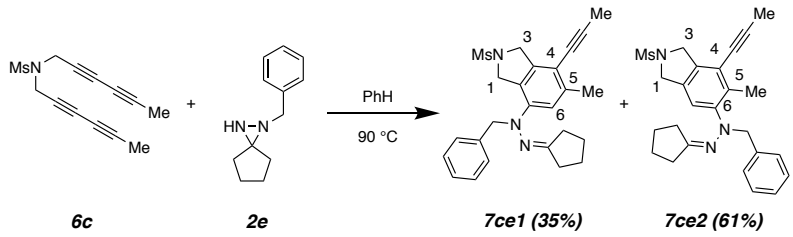
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.4 Hz, 2H, PhH_o), 7.32–7.26 (m, 7H, PhH), 7.21 (br t, *J* = 7.4 Hz, 1H, PhH_p), 6.95 (s, 1H, Ph-C*H*=N), 6.88 (s, 1H, Ar*H7*), 4.84 (s, 2H, N-CH_2-Ph), 4.72 (s, 2H, N(Ms)C3H_2), 4.63 (s, 2H, N(Ms)*C1H*$_2$), 2.88 (s, 3H, CH_3SO_2N), 2.28 (s, 3H, NArCH_3), and 2.12 (s, 3H, NArC≡CCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ 145.2, 137.4, 137.3, 137.2, 136.3, 134.2, 134.0, 128.5, 128.5, 128.0, 127.7, 127.3, 125.8, 120.6, 119.9, 95.5, 75.4, 59.8, 54.2 (2x), 34.9, 16.4, and 4.6.

HRMS (ESI-TOF): Calcd for $C_{27}H_{28}N_3O_2S^+$ [M+H$^+$] requires 458.1897; found 458.1892.

IR (CH_2Cl_2): 2920, 2854, 2231, 1641, 1588, 1562, 1495, 1454, 1422, 1340, 1156, 1075, 1001, 960, and 825 cm^{-1}.

7-(1-Benzyl-2-cyclopentylidenehydrazinyl)-5-methyl-2-(methylsulfonyl)-4-(prop-1-yn-1-yl)isoindoline (7ce1) and 6-(1-benzyl-2-cyclopentylidenehydrazinyl)-5-methyl-2-(methylsulfonyl)-4-(prop-1-yn-1-yl)isoindoline (7ce2):



Tetrayne **6c** (40 mg, 0.162 mmol) and 1-benzyl-1,2-diazaspiro[2.4]heptane (**2e**, 60.9 mg, 0.323 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (8 mL, 0.02 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated overnight (18–19 h) in an oil bath at 90 °C and cooled to room temperature. The residue was purified by MPLC (2:1 Hex:EtOAc) to give, in order of elution, **7ce1** (35%) and **7ce2** (61%), each as a transparent oil. The assignment of the structure of each of these was based upon observed nOe interactions (difference nOe) between the aromatic proton and the adjacent benzylic methyl or methylene protons, respectively.

This reaction was also performed on a 1 mmol scale. Namely, a mixture of tetrayne **6c** (247 mg, 1 mmol, 1 equiv) and 1-benzyl-1,2-diazaspiro[2.4]heptane (**2e**, 377 mg, 2 mmol, 2 equiv) was dissolved in benzene in a 55 mL threaded culture tube, sealed with a Teflon-lined screw-cap, and heated overnight at 90 °C. The products **7ce1** (159 mg, 0.37 mmol, 37%) and **7ce2** (225 mg, 0.50 mmol, 50%) were isolated using the purification conditions described above.

Data for faster eluting, minor isomer 7ce1:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.24 (m, 5H, Ar*H*), 6.89 (s, 1H, NAr*H*), 4.65 (s, 2H, NCH_2Ph), 4.47 (s, 2H, N(Ms)C1H_2 or N(Ms)C3H_2), 4.41 (s, 2H, N(Ms)*C1*H_2 or N(Ms)*C3*H_2), 2.78 (s, 3H, C$H_3$$SO_2$N), 2.41 [t, *J* = 7.7 Hz, 2H, N=C*(*CH_2*)*(CH_2)], 2.33 (s, 3H, ArCH_3), 2.09 (s, 3H, ≡CCH_3), 2.00 [t, *J* = 7.7 Hz, 2H, N=C*(C'*H_2*)*(CH_2)] and 1.71-1.60 (m, 4H, N=C(CH_2)$_2$*(*CH_2*)*$_2$).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.0, 146.3, 141.1, 140.2, 138.0, 128.5, 128.3, 127.2, 126.0, 120.8, 113.5, 93.5, 75.3, 62.6, 54.3, 54.1, 34.5, 33.6, 31.0, 24.7, 24.4, 20.4, and 4.6.

HRMS (ESI-TOF): Calcd for $C_{25}H_{30}N_3O_2S^+$ [M+H$^+$] requires 436.2053; found 436.2047.

IR (CH_2Cl_2): 2966, 2685, 1604, 1495, 1479, 1453, 1422, 1139, 1157, 1081, and 960 cm^{-1}.

Data for slower eluting, major isomer 7ce2:

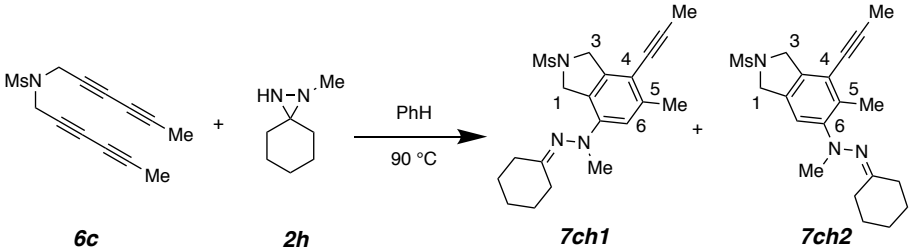
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.22 (m, 5H, Ar*H*), 7.09 (s, 1H, NAr*H*), 4.68 (s, 2H, NCH_2Ph), 4.63 (s, 2H, N(Ms)C1H_2 or N(Ms)C3H_2), 4.24 (s, 2H, N(Ms)*C1*H_2 or N(Ms)*C3*H_2), 2.88 (s, 3H, C$H_3$$SO_2$N), 2.46 [t, *J* = 7.7 Hz, 2H, N=C*(*CH_2*)*(CH_2)], 2.34 (s, 3H, ArCH_3), 2.12 (s, 3H, C≡CH_3), 1.91 [t, *J* = 7.7 Hz, 2H, N=C*(C'*H_2*)*(CH_2)]. and 1.61 (m, 4H, N=C(CH_2)$_2$*(*CH_2*)*$_2$).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.8, 152.3, 138.9, 134.7, 134.5, 133.9, 128.5, 128.1, 126.9, 120.0, 116.3, 94.8, 75.7, 63.8, 54.3, 54.2, 34.9, 33.5, 30.9, 24.7, 24.4, 15.8, and 4.6.

HRMS (ESI-TOF): Calcd for $C_{25}H_{30}N_3O_2S^+$ [M+H$^+$] requires 436.2053; found 436.2044.

IR (CH_2Cl_2): 2967, 1603, 1495, 1480, 1453, 1422, 1338, 1207, 1157, 1080 and 960 cm^{-1}.

7-(2-Cyclohexylidene-1-methylhydrazineyl)-5-methyl-2-(methylsulfonyl)-4-(prop-1-yn-1-yl)isoindoline (7ch1) and 6-(2-cyclohexylidene-1-methylhydrazineyl)-5-methyl-2-(methylsulfonyl)-4-(prop-1-yn-1-yl)isoindoline (7ch2):



6c ***2h*** ***7ch1*** ***7ch2***

91% *(overall)*
regiomeric ratio 7ch1: 7ch2= 1:2.7 (NMR)

Tetrayne **6c** (50 mg, 0.202 mmol) and 1-methyl-1,2-diazaspiro[2.5]octane (**2h**, 65.6 mg, 0.404 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (10 mL, 0.02 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated overnight (18–19 h) in an oil bath held at 90 °C and allowed to cool to room temperature. The residue was purified by MPLC (1:1 Hex:EtOAc) to give a mixture of coeluting regioisomers in ratio of 1:2.7 (NMR) ratio (91% combined yield, 0.166 mmol). A small portion of this mixture was further separated using HPLC (1:1 Hex:EtOAc) to give, in order of elution, **7ch1** as a transparent oil and **7ch2** also as a transparent oil, corresponding to the minor and major isomers, respectively. Both of the products solidified upon storage at -10 °C. The assignment of the structure of each of these was based upon observed (difference) nOe interactions between the aromatic proton and the adjacent benzylic methyl or methylene protons, respectively.

Data for faster eluting, minor isomer 7ch1:

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.69 (s, 1H, Ar*H6*), 4.65 (s, 2H, MsNC1H_2 or MsNC3H_2), 4.61 [s, 2H, N(Ms)C1H_2 or N(Ms)C3H_2], 2.87 (s, 3H, NCH_3), 2.82 (s, 3H, CH_3SO$_2$N), 2.52 (t, J = 6.2 Hz, 2H, N=CCH_2), 2.38 (t, J = 6.2 Hz, 2H, N=CC'H_2), 2.38 (s, 3H, NArCH_3), 2.09 (s, 3H, C≡CCH_3), 1.79 (quin, J = 7.0 Hz, 2H, NCH$_2$CH_2], and 1.69–1.64 [m, 4H, NC'H$_2$(CH_2)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.9, 146.5, 140.9, 140.5, 123.4, 115.8, 111.5, 92.6, 75.6, 55.0, 54.2, 41.9, 35.5, 34.2, 29.3, 27.2, 26.1, 25.7, 20.5, and 4.6.

HRMS (ESI-TOF): Calcd for $C_{20}H_{28}N_3O_2S^+$ [M+H$^+$] requires 374.1902; found 374.1894.

IR (CH_2Cl_2): 2927, 2856, 1705, 1604, 1445, 1332, 1225, 1151, 1077, 1034, 962, 826, 755, 734, 702, and 621 cm^{-1}.

Data for slower eluting, major isomer 7ch2:

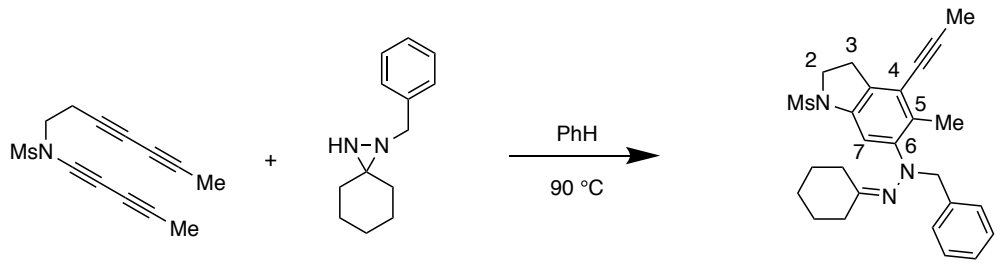
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (s, 1H, Ar*H7*), 4.67 (s, 2H, MsNC3H_2), 4.64 (s, 2H, MsNC1H_2), 2.85 (s, 3H, CH_3SO$_2$N), 2.83 (s, 3H, NCH_3), 2.39 (s, 3H, NArCH_3), 2.32 (t, J = 6.3 Hz, 2H, N=CCH_2), 2.12 (s, 3H, C≡CCH_3), 1.71 (quin, J = 6.3 Hz, 2H, NCH$_2$CH_2], 1.57 (quin, J = 5.3 Hz, 2H, NC'H$_2$CH_2), and 1.51 (quin, J = 5.3 Hz, 2H, NCH$_2$CH$_2$CH_2).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 153.8, 134.0, 133.697, 133.688, 120.1, 114.3, 94.5, 75.8, 54.4, 54.2, 46.1, 35.6, 34.6, 29.6, 27.2, 25.8, 25.7, 16.1, and 4.6.

HRMS (ESI-TOF): Calcd for $C_{20}H_{28}N_3O_2S^+$ [M+H$^+$] requires 374.1902; found 374.1890.

IR (CH_2Cl_2): 2929, 2856, 1705, 1632, 1591, 1448, 1333, 1296, 1269, 1151, 1076, 1029, 960, 878, and 824.

6-(1-Benzyl-2-cyclohexylidenehydrazinyl)-5-methyl-1-(methylsulfonyl)-4-(prop-1-yn-1-yl)indoline (7da)



6d ***2a*** ***7da, 71%***

Tetrayne **6d** (30 mg, 0.121 mmol) and 1-benzyl-1,2-diazaspiro[2.5]octane (**2a,** 50 mg, 0.242 mmol, 2 equiv) were combined in a culture tube, dissolved in benzene (6 mL, 0.02 M), and sealed with a Teflon-lined cap. The solution was heated overnight (18-19 h) in an oil bath at 90 °C and cooled to room temperature. The residue was purified by MPLC (2:1 Hex:EtOAc) to give **7da** (0.158 mmol, 72%) as a faint yellow oil.

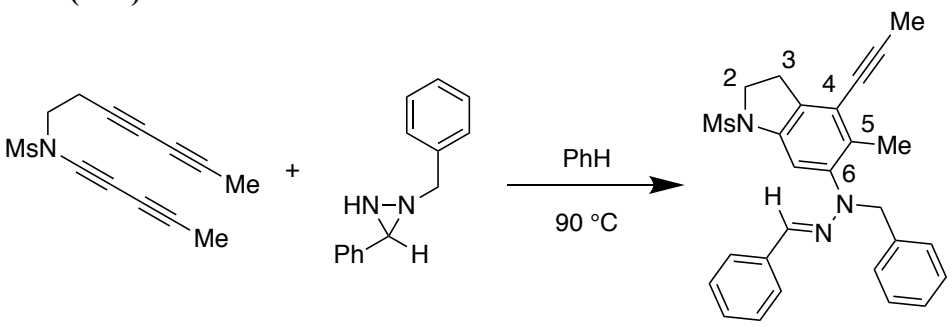
Data for 7da (has 6% of the other regioisomer as well, inseparable through MPLC):
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.5 Hz, 2H, ArH_o), 7.29-7.26 (dd, *J* = 7.2, 7.2 Hz, 2H, ArH_m), 7.20 (d, *J* = 7.3 Hz, 1H ArH_p), 7.18 (s, 1H, *H7*), 3.91 (t, *J* = 8.3 Hz, 2H, MsNCH_2), 3.10 (t, *J* = 8.3 Hz, 2H, MsNCH$_2$CH_2), 2.70 (s, 3H, CH_3SO$_2$N), 2.42 (s, 3H, NArCH_3), 2.27 (t, *J* = 6.7 Hz, 2H, N=CCH_2), 2.13 (s, 3H, NArC≡CH_3), 2.13 (t, *J* = 6.7 Hz, 2H, N=CCH_2), 1.63 (quin, *J* = 6.6 Hz, 2H, CH_2), 1.48 (quin, *J* = 6.2 Hz, 2H, CH_2), and 1.33 (quin, *J* = 6.2 Hz, 2H, CH_2).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 152.3, 139.9, 139.0, 129.1, 128.8, 128.6, 128.0, 126.7, 122.0, 107.6, 94.0, 76.3, 62.4, 50.4, 35.6, 34.2, 30.1, 28.0, 27.1, 25.7, 25.6, 16.0, and 4.6.

IR (CH_2Cl_2): 2929, 2856, 2230, 1633, 1591, 1495, 1452, 1348, 1266, 1161, 1102, 967, 736, and 699 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{26}H_{32}N_3O_2S^+$ [M+H$^+$] requires 450.2210; found 450.2203.

6-(1-Benzyl-2-benzylidenehydrazinyl)-5-methyl-1-(methylsulfonyl)-4-(prop-1-yn-1-yl)indoline (7dd):



6d ***2d*** ***7dd, 31% (regiomeric ratio= 5:1)***

Tetrayne **6d** (22 mg, 0.089 mmol) and 1-benzyl-3-phenyldiaziridine **2d** (25 mg, 0.116 mmol, 1.3 equiv) were combined in a culture tube and dissolved in benzene (4 mL, 0.02 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated overnight (18–19 h) in an oil bath at 90 °C and cooled to room temperature. The residue was purified by MPLC (3:1 Hex:EtOAc) to give **7dd** [0.228 mmol, 31% yield, corrected for the presence of the other regioisomer (~20%)] as a yellow oil.

Data for 7dd [contains co-eluting other regioisomer (~20%)]:

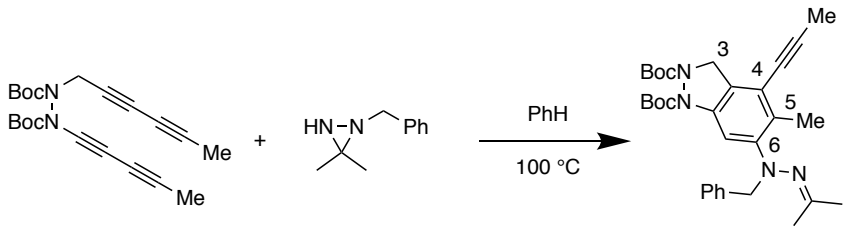
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.4 Hz, 2H, PhH_o), 7.34 (d, *J* = 7.8 Hz, 2H, Ph'H_o), 7.30–7.25 (m, 4H, PhH_m and Ph'H_m), 7.24–7.18 (m, 2H, PhH_o and Ph'H_o), 7.04 [s, 1H, *H7* or *H*(C=N)Ph], 6.93 [s, 1H, *H7* or *H*(C=N)Ph], 4.87 (s, 2H, N–CH_2Ph), 3.95 (t, *J* = 8.3 Hz, 2H, MsNCH_2), 3.16 (t, *J* = 8.3 Hz, 2H, MsNCH$_2$CH_2), 2.65 (s, 3H, CH_3SO$_2$N), 2.21 (s, 3H, NArCH_3), and 2.12 (s, 3H, NArC≡CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ 143.4, 140.3, 137.7, 136.4, 133.8, 133.4, 132.6, 128.44, 128.43, 128.39, 127.6, 127.2, 122.5, 125.8, 111.6, 94.8, 75.9, 60.1, 50.4, 34.1, 28.1, 16.0, and 4.6.

HRMS (ESI-TOF): Calcd for $C_{27}H_{28}N_3O_2S^+$ [M+H$^+$] requires 458.1897; found 458.1891.

IR (CH_2Cl_2): 2921, 2851, 2685, 1641, 1589, 1454, 1422, 1350, 1162, 1070, and 738 cm^{-1}.

di-*tert*-Butyl 6-(1-benzyl-2-(propan-2-ylidene)hydrazinyl)-5-methyl-4-(prop-1-yn-1-yl)-1*H*-indazole-1,2(3*H*)-dicarboxylate (7ec):



6e ***2c*** ***7ec, 60%***

Tetrayne **6e** (20 mg, 0.054 mmol) and 1-benzyl-3,3-dimethyldiaziridine (**2c**, 17.52 mg, 0.108 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (4 mL, 0.01 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated for 48 h in an oil bath held at 100 °C and then cooled to room temperature. The residue was purified by MPLC (6:1 Hex:EtOAc) to give **7ec** as a transparent oil (64% yield, 0.035 mmol).

Data for 7ec:

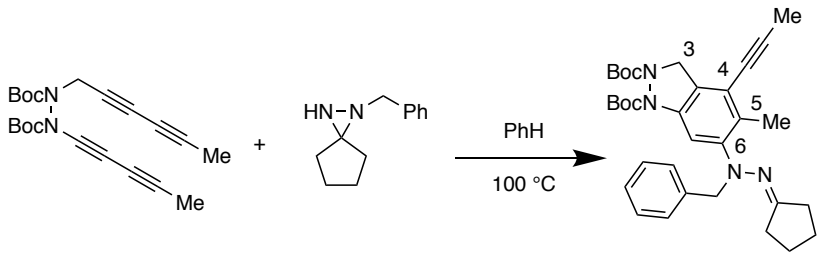
^{1}H NMR (500 MHz, $CDCl_3$): 7.36 (m, 3H, Ar*H7* and PhH_o), 7.32 (dd, J = 7.3, 6.7 Hz, 2H, PhH_m), 7.25 (tt, J = 7.2, 1.5 Hz, 1H, Ph*Hp*), 5.07 [br d, J = 14.6 Hz, 1H, ArCH_aH$_b$N(C=O)], 4.62 (br d, J = 14.6 Hz, 1H, ArCH$_a$$H_b$N(C=O), 4.27 (s, 2H, ArNCH_2), 2.46 (s, 3H, NArCH_3), 2.15 (s, 3H, C≡CCH_3), 1.94 (s, 3H, [(CH_3)$_2$C=N], 1.65 (s, 3H, [(CH_3)$_2$C=N], 1.57 (s, 9H, (CH$_3$)$_3$CO(C=O)NAr), and 1.54 (s, 9H, (CH$_3$)$_3$CO(C=O)NAr).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.9, 156.2, 152.5, 152.1, 139.2, 138.4, 129.9, 128.5, 128.1, 126.7, 126.4, 119.0, 110.3, 94.2, 82.5, 82.0, 75.6, 63.6, 51.8, 28.24, 28.19, 25.3, 19.9, 15.7, and 4.6.

HRMS (ESI-TOF): Calcd for $C_{31}H_{41}N_4O_4^+$ [M+H$^+$] requires 533.3122; found 533.3116.

IR (CH_2Cl_2): 2982, 2920, 2874, 2230, 1708, 1640, 1597, 1496, 1454, 1369, 1212, 1149, 1077, 1043, 1027, 1004, 978, 942, 896, and 858 cm^{-1}.

di-*tert*-Butyl 6-(2-cyclopentylidene-1-methylhydrazinyl)-5-methyl-4-(prop-1-yn-1-yl)-1*H*-indazole-1,2(3*H*)-dicarboxylate (7ee):



6e ***2e*** ***7ee, 59.7%***

Tetrayne **6e** (20 mg, 0.054 mmol) and 1-benzyl-1,2-diazaspiro[2.4]heptane **2e** (20.3 mg, 0.108 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (4 mL, 0.01 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated for 48 h in an oil bath held at 100 °C and allowed to cool to room temperature. The residue was purified by MPLC (6:1 Hex:EtOAc) to give **7ee** as a transparent oil (59.7% yield, 0.032 mmol).

Data for 7ee:

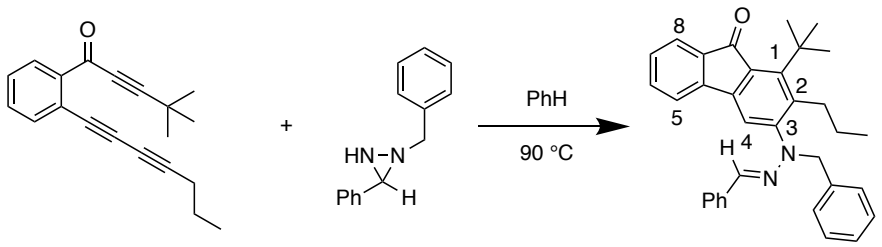
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (s, 1H, NArH), 7.33 (dd, J = 7, 1 Hz, 2H, PhH_o), 7.29 (dd, J = 7.2, 7.2 Hz, 2H, PhH_m), 7.22 (tt, J = 7.1, 1.5 Hz, 1H, PhHp), 5.04 (br d, J = 14.6 Hz, 1H, ArCH_aH$_b$N(C=O), 4.60 (br d, J = 14.6 Hz, 1H, ArCH$_a$$H_b$N(C=O), 4.29 (d, J = 13.4 Hz, 1H, PhNCH_aH$_b$), 4.28 (d, J = 13.2 Hz, 1H, PhNCH$_a$$H_b$), 2.38 (s, 3H, ArC$H_3$), 2.34 [t, J = 6.4 Hz, 2H, N=C(CH_2)(CH$_2$)], 2.12 (s, 3H, C≡CCH_3), 1.91 2.34 [t, J = 6.5 Hz, 2H, N=C$(C'H_2)$(CH$_2$)], 1.64–1.59 (m, 4H, N=C(CH$_2$)$_2$(CH_2)$_2$), 1.54 (s, 9H, (CH$_3$)$_3$CO(C=O)NAr), and 1.52 (s, 9H, (CH$_3$)$_3$CO(C=O)NAr).

^{13}C NMR (126 MHz, $CDCl_3$): δ 176.3, 152.5, 151.7, 139.1, 138.4, 130.9, 128.4, 128.1, 126.8, 126.7, 118.9, 111.1, 94.2, 82.5, 82.0, 75.6, 63.9, 51.8, 33.6, 30.9, 28.3, 28.2, 24.8, 24.5, 15.6, and 4.6. (one carbon atom not observed)

HRMS (ESI-TOF): Calcd for $C_{33}H_{43}N_4O_4^+$ [M+H$^+$] requires 559.3279; found 559.3268.

IR (CH_2Cl_2): 2982, 2874, 1708, 1598, 1495, 1454, 1423, 1393, 1369, 1211, 1150, 1027, and 857 cm^{-1}.

(1-Benzyl-2-benzylidenehydrazineyl)-1-(*tert*-butyl)-2-propyl-9*H*-fluoren-9-one (7fd):



6f ***2d*** ***7fd, 38%***

Triynone **6f** (30 mg, 0.108 mmol) and 1-benzyl-3-phenyldiaziridine **2d** (46 mg, 0.216 mmol, 2 equiv) were combined in a culture tube and dissolved in benzene (6 mL, 0.02 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated overnight (18-19 h) in an oil bath held at 90 °C and then cooled to room temperature. The residue was purified by MPLC (19:1 Hex:EtOAc) to give **7fd** (0.041 mmol, 38%) as a bright yellow oil, which turned into a flaky amorphous solid after being subjected to high vacuum. A small portion of this product was repurified by HPLC to give a pure sample of **7fd**, that was used for collection of spectral data.

Data for 7fd: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.3 Hz, 1H, *H8*), 7.54 (br d, *J* = 7 Hz, 2H, PhH_o), 7.39–7.29 (m, 8H, Ar*H*), 7.25–7.21 (m, 3H, Ar*H*), 7.15 (s, 1H, Ar*H4* or PhC(*H*)=N), 7.04 (s, 1H, Ar*H4* or PhC(*H*)=N), 4.88 (s, 2H, ArNCH_2), 2.91 (br t, *J* = 8.1 Hz, 2H, ArCH_2), 1.62 [(s, 9H, $(CH_3)_3$], 1.41 (br sextet, *J* = 7.5 Hz, 2H, $ArCH_2CH_2CH_2CH_2$), and 0.82 (t, *J* = 7.4 Hz, 3H, $ArCH_2CH_2CH_3$).

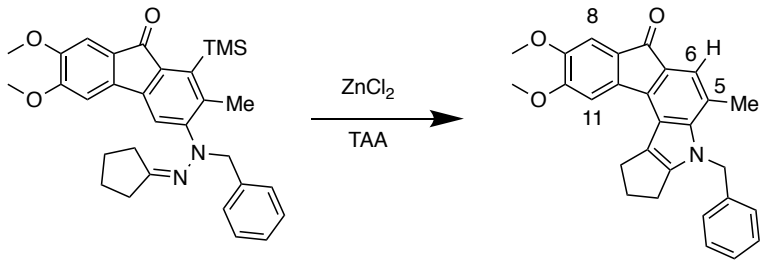
^{13}C NMR (125 MHz, $CDCl_3$): δ 194.2, 156.1, 152.1, 144.9, 142.5, 141.2, 137.2, 136.3, 135.2, 134.2, 134.1, 132.6, 128.8, 128.5, 128.5, 128.1, 127.9, 127.4, 126.0, 123.9, 119.0, 115.9, 60.2, 38.8, 32.8, 32.5, 25.7, and 14.2.

IR (CH_2Cl_2): 3028, 2957, 2869, 1705, 1606, 1589, 1564, 1542, 1495, 1472, 1453, 1398, 1364, 1348, 1297, 1264, 1202, 1180, 1124, 1088, 1072, 1049, 1028, 972, 924, and 886 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{34}H_{35}N_2O^+$ [$M+H^+$] requires 487.2744; found 487.2741.

III. Preparation and Characterization Data for Fischer Indole Products

4-Benzyl-9,10-dimethoxy-5-methyl-1,2,3,4-tetrahydro-7*H*-cyclopenta[*b*]indeno[1,2-*e*]indol-7-one (9ae):



7ae ***9ae, 43 %***

Hydrazone **7ae** (30 mg, 0.059 mmol) and $ZnCl_2$ (10 mg, 0.071 mmol) were combined in a culture tube and dissolved in tertiary amyl alcohol (2 mL, 0.03 M). The tube was sealed with a Teflon-lined screw cap. The solution was heated in an oil bath at 130 °C until the reaction was judged to be complete by crude mass spectrometric analysis of an aliquot (~ 8h). The reaction mixture was cooled to room temperature, filtered through a plug of silica gel (EtOAc), and concentrated. The residue was purified by MPLC (2:1 Hex:EtOAc) to give **9ae** (0.025 mmol, 43%) as an amorphous red powder.

Data for 9ae:

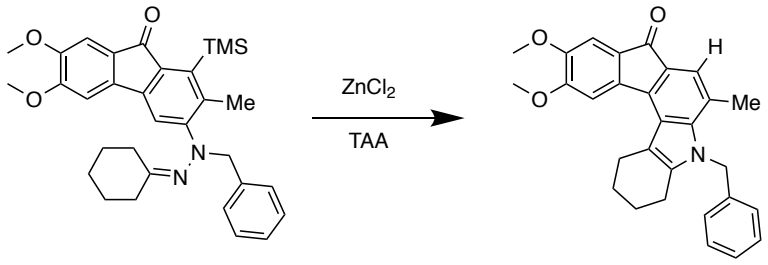
^{1}H NMR (500 MHz, $CDCl_3$): 7.33–7.23 (m, 3H, PhH_m and PhH_p), 7.28 (s, 1H, *H11*) 7.14 (s, 1H, *H6* or *H8*), 7.04 (s, 1H, *H6* or *H8*), 6.90 (d, J = 7.5 Hz, 2H, PhH_o), 5.43 (s, 2H, NCH_2), 3.98 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.25 (t, J =7.0 Hz, 2H, NC=CCH_2), 2.76 (t, J =7.0 Hz, 2H, NC=CCH_2), 2.57 (pent, 2H, J =7.7 Hz, NC=CCH$_2$CH_2), and 2.42 (s, 3H, ArCH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ 194.4, 153.4, 151.1, 148.4, 145.3, 140.0, 138.9, 135.2, 129.0, 127.9, 127.4, 126.7, 125.1, 120.1, 119.94, 119.88, 117.0, 107.2, 105.5, 56.2, 56.2, 50.3, 28.5, 27.8, 25.1, and 19.4.

HRMS (ESI-TOF): Calcd for $C_{28}H_{26}NO_3^+$ [M+H$^+$] requires 424.1907; found 424.1907.

IR (CH_2Cl_2): 3052, 2927, 2846, 1696, 1601, 1581, 1496, 1475, 1440, 1386, 1366, 1302, 1279, 1265, 1213, 1199, 1154, 1093, 1022, 874, 843, and 802 cm^{-1}.

5-Benzyl-10,11-dimethoxy-6-methyl-2,3,4,5-tetrahydroindeno[2,1-*c*]carbazol-8(1*H*)-one (9aa):



7aa ***9aa, 48 %***

Hydrazone, **S1** (30 mg, 0.057 mmol) and $ZnCl_2$ (9 mg, 0.063 mmol) were combined in a culture tube and dissolved in tertiary amyl alcohol (1 mL, 0.06 M), and the tube was sealed with a Teflon-lined cap. The solution was heated in an oil bath at 130 °C until the reaction was judged to be complete by thin layer chromatography (~ 8h). The reaction mixture was cooled to room temperature, filtered through a plug of silica gel (EtOAc), and concentrated. The residue was purified by MPLC (2:1 Hex:EtOAc) to give **9aa** (0.027 mmol, 48%) as a bright orange amorphous powder.

Data for 9aa:

^{1}H NMR (500 MHz, $CDCl_3$): 7.53 (s, 1H, 7*H*), 7.30-7.22 (m, 3H, PhH_m and PhH_p), 7.17 (s, 1H, 9*H*), 7.11 (s, 1H, 12*H*), 6.86 (d, 1H, PhH_o), 5.48 (s, 2H, NCH_2), 3.98 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.23 (brs, 2H, NC=CCH_2), 2.58 (brs, 2H, NC(CH_2)=C, 2.47 (s, 3H, ArCH_3), and 1.90 [m, 4H, NC=C$(CH_2)_2$*$(CH_2)_2$*].

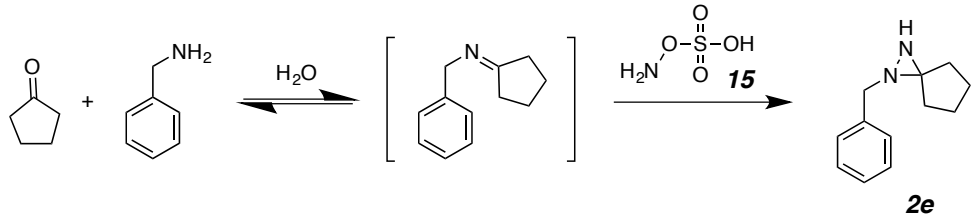
^{13}C NMR (125 MHz, $CDCl_3$): δ 194.4, 153.1, 148.3, 141.2, 139.9, 138.9, 136.4, 129.0, 128.4, 127.3, 127.2, 124.9, 123.9, 120.7, 119.3, 109.9, 107.7, 107.3, 56.3, 56.2, 47.8, 26.3, 23.8, 22.6, 22.2, and 20.1 (one aromatic carbon resonance not observed).

IR (CH_2Cl_2): 3026, 2930, 2838, 1689, 1597, 1582, 1496, 1474, 1460, 1420, 1408, 1394, 1378, 1363, 1305, 1282, 1213, 1195, 1153, 1177, 1106, 1074, 1044, 1013, 997, 909, 889, 869 and 850 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{29}H_{28}NO_3$ [M+H^+] requires 438.2064; found 438.2057.

IV. Preparation and Characterization Data for New Diaziridines

1-Benzyl-1,2-diazaspiro[2.4]heptane (2e):



In a round-bottomed flask at 0 °C, cyclopentanone (0.44 mL, 5.0 mmol, 1.0 equiv) and benzylamine (1.64 mL, 15 mmol, 3.0 equiv) were dissolved in 5 mL of H_2O. This reaction mixture was stirred for two hours. Hydroxylamine-*O*-sulfonic acid (**15**, 0.556 g, 5 mmol, 1 equiv) was added portion wise to this reaction mixture at 0 °C, and the mixture was allowed to warm to room temperature until complete conversion had occurred as judged by ^{1}H NMR analysis of an aliquot (~ 4 h). This mixture was diluted with H_2O (20 mL) and extracted with diethyl ether (3 × 20 mL). The organic layers were dried with $MgSO_4$, filtered, and concentrated by rotary evaporation. This crude product was passed through a plug of silica gel (3:1, Hex:EtOAc), and the resulting residue was purified by MPLC (6:1 Hex:EtOAc) to give **2e** (3.4 mmol, 68% yield) as a yellow oil, which solidified to a yellow solid upon storage at -10 °C. This product returned to an oily state upon being allowed to warm to ambient temperature.

Data for 2e:

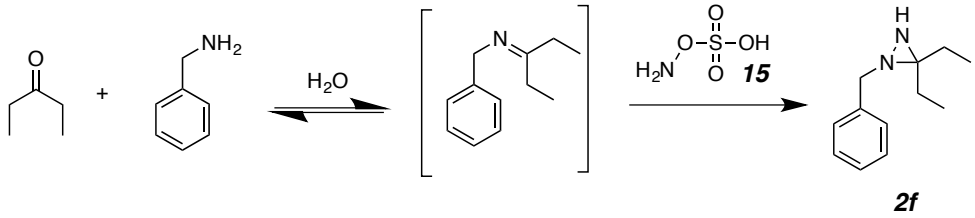
^{1}H NMR (500 MHz, $CDCl_3$): 7.39 (d, J =7.3 Hz, 2H, PhH_o), 7.34 (dd, J =7.2, 7.2 Hz, 2H, PhH_m), 7.26 (t, J = 7 Hz, 1H, PhH_p), 3.67 (d, J = 13.7 Hz, 1H, PhCH_aCH$_b$), 3.52 (d, J = 13.7 Hz, 1H, PhCH$_a$CH_b), 2.11 (br s, 1H, *NH*), and 2.08–1.65 [m, 8H, C(CH_2)$_4$].

^{13}C NMR (125 MHz, $CDCl_3$): 138.7, 128.4, 128.2, 127.0, 69.2, 59.5, 36.7, 27.3, 25.6, and 24.5.

HRMS (ESI-TOF): Calcd for $C_{12}H_{17}N_2^+$ [M+H$^+$] requires 189.1386; found 189.1381.

IR (neat): 3390, 3204, 3087, 3062, 3029, 2959, 2870, 1496, 1453, 1437, 1377, 1323, 1270, 1209, 1164, 1029, 954, 734, and 698 cm^{-1}.

1-Benzyl-3,3-diethyldiaziridine (2f):



In a round-bottomed flask at 0 °C, pentan-3-one (0.53 mL, 5.0 mmol, 1.0 equiv) and benzylamine (1.64 mL, 15 mmol, 3.0 equiv) were dissolved in 5 mL of H_2O. This reaction mixture was stirred for two hours. Hydroxylamine-*O*-sulfonic acid (**15**, 0.556 g, 4.9 mmol, 1 equiv) was added portion wise to this reaction mixture at 0 °C, and this mixture was allowed to warm to room temperature until complete conversion had occurred, as judged by ^{1}H NMR spectroscopy of an aliquot (~ 4 h). This mixture was diluted with H_2O (20 mL) and extracted with diethyl ether (3 × 20 mL). Organic layers were dried with $MgSO_4$, filtered, and concentrated by rotary evaporation to afford the crude product. This material was passed through a plug of silica gel (3:1, Hex:EtOAc), and the residue was purified by MPLC (6:1 Hex:EtOAc) to give **2f** (2.64 mmol, 53% yield) as a transparent oil.

Data for 2f:

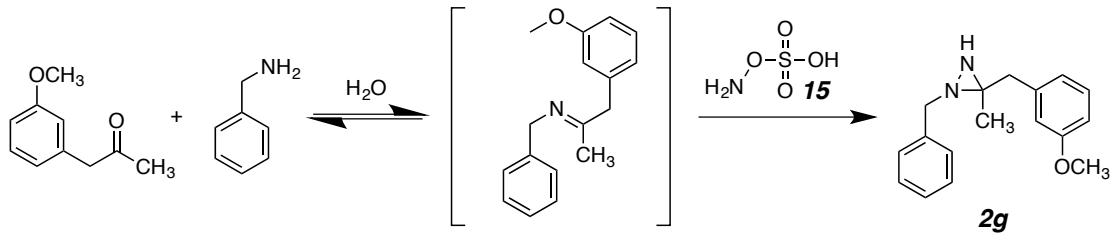
^{1}H NMR (500 MHz, $CDCl_3$): 7.39 (d, J =7.7 Hz, 2H, PhH_o), 7.33 (dd, J =7.5, 7.5 Hz, 2H, PhH_m), 7.27–7.24 (t, J = 7.3 Hz, 1H, PhH_p), 3.78 (d, J = 13.7 Hz, 1H, PhCH_aCH$_b$), 3.70 (d, J = 13.7 Hz, 1H, PhCH$_a$CH_b), 2.02 (br s, 1H, *NH*), 1.81–1.67 [m, 3H, CH_2CH$_3$ and CH$_a$$H_bCH_3$), 1.53 (dq, J = 14.3, 7.4 Hz, 1H, CH_aH$_b$CH$_3$'), 1.06 (t, J =7.5 Hz, 3H, CH_3), and 0.93 (t, J =7.5 Hz, 3H, CH_3').

^{13}C NMR (125 MHz, $CDCl_3$): 139.1, 128.4, 128.3, 127.0, 64.1, 56.8, 30.4, 21.2, 9.9, and 8.9.

HRMS (ESI-TOF): Calcd for $C_{12}H_{19}N_2^+$ [M+H$^+$] requires 191.1543; found 191.1535.

IR (neat): 3387, 3313, 2969, 3063, 3030, 2937, 2979, 1496, 1455, 1379, 1350, 1300, 1235, 1211, 1096, 1060, 982, 935, 732, and 698 cm^{-1}.

1-Benzyl-3-(3-methoxybenzyl)-3-methyldiaziridine (2g):



In a round-bottomed flask at 0 °C, 1-(3-methoxyphenyl)propan-2-one (0.43 mL, 5.0 mmol, 1.0 equiv) and benzylamine (1.64 mL, 15 mmol, 3.0 equiv) were dissolved in 5 mL of H_2O. This reaction mixture was stirred for two hours. Hydroxylamine-*O*-sulfonic acid (**15**, 0.556 g, 5.0 mmol, 1.0 equiv) was added portion wise at 0 °C. The mixture was allowed to warm to room temperature until complete conversion had occurred as judged by ^{1}H NMR analysis of an aliquot (~ 6 h). This mixture was diluted with H_2O (20 mL) and extracted with diethyl ether (3 × 20 mL). The organic layers were dried with $MgSO_4$, filtered, and concentrated by rotary evaporation. This crude product was passed through a plug of silica gel (1:1, Hex:EtOAc), and the residue was purified by MPLC (6:1 Hex:EtOAc + 1% NEt_3) to give **2g** (2.5 mmol, 50% yield) as a transparent oil.

Data for 2g [an ca. 9:1 mixture of interconverting *N*-invertomers[4]]:

^{1}H NMR (500 MHz, $CDCl_3$): 7.38 (d, J = 7.7 Hz, 2H, PhH_o), 7.33 (dd, J = 7.4, 7.4 Hz, 2H, PhH_m), 7.27 (t, J = 7.4 Hz, 1H, PhH_p), 7.19 [dd, J = 7.6, 7.6 Hz, 1H, *meta* to OMe], 6.79–6.77 [m, 3H, *ortho* and *para* to OMe], 3.75 (s, 3H, OMe), 3.72 [d, J = 13.4 Hz, 1H, PhCH_aCH$_b$)], 3.67 [d, J = 13.6 Hz, PhCH_aCH$_b$)], 2.93 [d, J = 13.8 Hz, 1H, ArCH_aCH$_b$)], 2.76 [d, J = 13.8 Hz, 1H, ArCH$_a$CH_b)], 2.15 (s, 1H, *NH*), and 1.38 [s, 3H, CH$_2$(C)CH_3].

^{13}C NMR (125 MHz, $CDCl_3$): major isomer: 159.5, 138.8, 138.2, 129.3, 128.5, 128.4, 127.1, 122.0, 115.3, 112.3, 60.2, 57.5, 55.1, 47.7, and 15.7. [minor isomer includes: 139.4, 139.0, 129.4, 128.5, 128.3, 127.1, 122.0, 115.3, 60.6, and 16.2.]

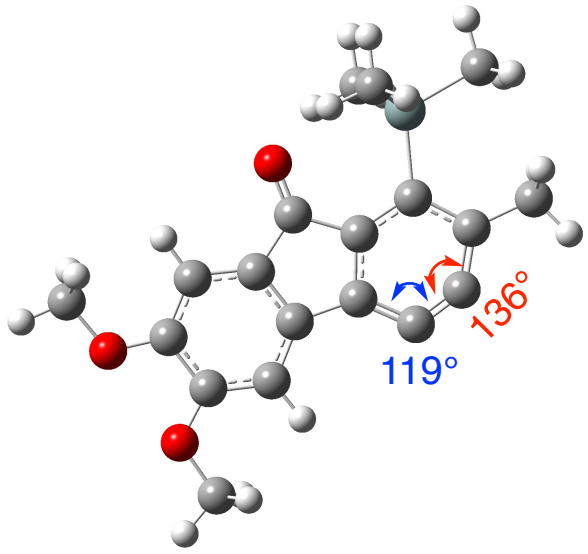
HRMS (ESI-TOF): Calcd for $C_{17}H_{20}N_2ONa^+$ [M+Na$^+$] requires 291.1468; found 291.1468.

IR (CH_2Cl_2): 3423, 3004, 2938, 2836, 1601, 1584, 1490, 1466, 1454, 1436, 1392, 1190, 1153, 1074, 1050, and 781 cm^{-1}.

V. Discussion of Computational Results

DFT computations were performed with the Gaussian 09 software package.[5] The geometries were optimized with the M06-2X functional;[6] the basis set was double-ζ split-valence 6-311+G(d, p). The SMD continuum solvation model[7] with benzene as solvent was applied during geometry optimization. Harmonic vibrational frequency calculations were performed at 298 K and used for the thermal correction of enthalpies. The value for the "Sum of electronic and thermal Free Energies=" was used as the free energy (G) of the reactants and products.

Optimized Geometry of Benzyne 8a [Note the angle difference between two carbons (red vs blue)]:

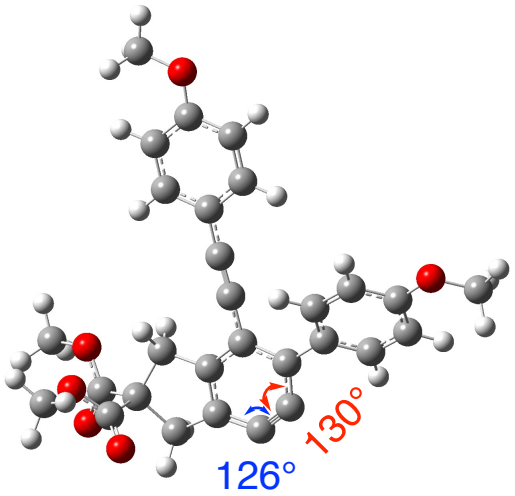


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.028192	1.409079	-0.009421
2	6	0	0.564696	2.680886	-0.015190
3	6	0	1.810209	2.808598	-0.029424
4	6	0	2.893301	1.961494	-0.041855
5	6	0	2.408676	0.603440	-0.024423
6	6	0	1.016849	0.380198	-0.017238
7	6	0	0.242696	-0.922052	-0.038428
8	6	0	-1.326248	0.826417	-0.005122
9	6	0	-1.202441	-0.556574	-0.022272
10	6	0	-2.314451	-1.394224	-0.024846
11	6	0	-2.578188	1.431694	0.012383
12	6	0	-3.576689	-0.808343	-0.006823
13	6	0	-3.707027	0.609106	0.012542
14	8	0	0.688675	-2.051426	-0.073444
15	8	0	-4.745649	-1.490299	-0.005086
16	8	0	-4.977318	1.061424	0.030081
17	6	0	-4.670201	-2.904899	-0.032597
18	1	0	-4.162018	-3.252942	-0.939011
19	1	0	-4.148012	-3.287292	0.851745
20	1	0	-5.699760	-3.259086	-0.031159
21	6	0	-5.179436	2.464562	0.060326
22	1	0	-6.258463	2.608632	0.075053

23	1	0	-4.736749	2.904505	0.960704
24	1	0	-4.756578	2.940604	-0.831120
25	14	0	3.596243	-0.920706	0.030160
26	6	0	5.434993	-0.492002	0.121404
27	1	0	5.820244	0.011930	-0.768258
28	1	0	5.711016	0.087835	1.005583
29	1	0	5.949645	-1.458405	0.195204
30	6	0	3.267257	-1.875290	1.617687
31	1	0	2.224003	-2.169058	1.733697
32	1	0	3.881904	-2.782594	1.625186
33	1	0	3.564145	-1.266062	2.478219
34	6	0	3.412870	-1.912350	-1.556588
35	1	0	2.392171	-2.257746	-1.722631
36	1	0	3.727629	-1.304145	-2.411445
37	1	0	4.071156	-2.787363	-1.510545
38	6	0	4.326875	2.414453	-0.078049
39	1	0	4.862285	2.127445	0.829796
40	1	0	4.858245	1.988165	-0.931268
41	1	0	4.362363	3.501052	-0.163087
42	1	0	-2.180812	-2.469924	-0.039650
43	1	0	-2.667072	2.511583	0.025938

Optimized Geometry of Benzyne 8b [Note the angle difference between two carbons (red vs blue)]:

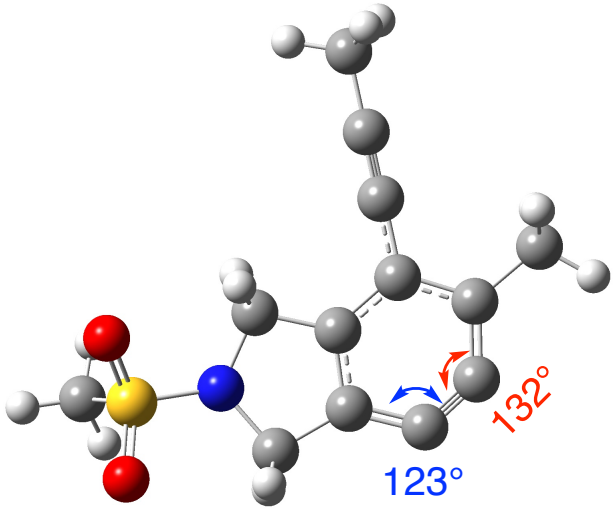


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.218597	-2.558096	-0.495104
2	6	0	-1.355656	-3.638023	-0.465494
3	6	0	-0.119594	-3.582350	-0.337168
4	6	0	0.707966	-2.478848	-0.178286
5	6	0	-0.096457	-1.291701	-0.223416
6	6	0	-1.502914	-1.357204	-0.365559
7	6	0	2.173130	-2.536310	-0.029635
8	6	0	2.908181	-1.609689	0.727204
9	6	0	2.866415	-3.588109	-0.633105
10	6	0	4.282049	-1.725686	0.848527
11	1	0	2.397015	-0.804723	1.242718
12	6	0	4.247603	-3.714423	-0.524816
13	1	0	2.309119	-4.322365	-1.209334
14	6	0	4.964194	-2.772967	0.217104
15	1	0	4.855417	-1.021200	1.442416
16	1	0	4.746202	-4.540326	-1.017638
17	6	0	0.494626	0.008893	-0.177212
18	6	0	0.960899	1.128451	-0.160785
19	6	0	1.577649	2.416851	-0.127769
20	6	0	0.812081	3.586966	-0.119990
21	6	0	2.980167	2.526012	-0.099132
22	6	0	1.415368	4.840171	-0.083292
23	1	0	-0.270649	3.512568	-0.143019
24	6	0	3.586943	3.766526	-0.061985
25	1	0	3.581802	1.622008	-0.109311

26	6	0	2.809161	4.932822	-0.053163
27	1	0	0.794396	5.727925	-0.078727
28	1	0	4.666900	3.867083	-0.039831
29	6	0	2.756660	7.302083	0.000341
30	1	0	3.489725	8.107365	0.035682
31	1	0	2.146518	7.402408	-0.904684
32	1	0	2.110067	7.357258	0.883617
33	8	0	3.498842	6.098228	-0.014706
34	8	0	6.309062	-2.793846	0.390606
35	6	0	7.030862	-3.848928	-0.213287
36	1	0	6.918926	-3.832864	-1.303634
37	1	0	8.076575	-3.686416	0.046190
38	1	0	6.705536	-4.822591	0.170861
39	6	0	-2.452349	-0.187327	-0.448155
40	1	0	-2.243279	0.601894	0.279201
41	1	0	-2.412799	0.275470	-1.440840
42	6	0	-3.693393	-2.325967	-0.654979
43	1	0	-3.999998	-2.447530	-1.700251
44	6	0	-3.842453	-0.850145	-0.217159
45	1	0	-4.305056	-2.989875	-0.042498
46	6	0	-4.146636	-0.805875	1.285220
47	6	0	-5.005977	-0.169154	-0.922027
48	8	0	-4.103640	-1.749220	2.031897
49	8	0	-6.060980	-0.718321	-1.130706
50	8	0	-4.744243	1.095384	-1.257189
51	8	0	-4.448599	0.439796	1.671636
52	6	0	-4.724179	0.592924	3.068053
53	1	0	-4.947270	1.648557	3.210028
54	1	0	-5.578066	-0.024606	3.352424
55	1	0	-3.853524	0.299360	3.657249
56	6	0	-5.834004	1.798760	-1.861109
57	1	0	-6.686727	1.824020	-1.179922
58	1	0	-5.464319	2.803666	-2.055390
59	1	0	-6.130524	1.308805	-2.790544

Optimized Geometry of Benzyne 8c [Note the angle difference between two carbons (red vs blue)]:

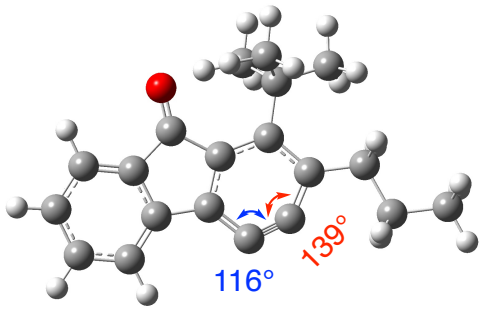


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.121153	-1.760666	-0.040651
2	6	0	1.078365	-2.758246	-0.029091
3	6	0	2.304144	-2.532204	-0.018936
4	6	0	3.017868	-1.350970	-0.010453
5	6	0	2.090861	-0.264086	-0.019284
6	6	0	0.698711	-0.484812	-0.034871
7	6	0	-0.373750	0.569207	-0.028138
8	1	0	-0.382644	1.144296	0.904681
9	1	0	-0.268755	1.274512	-0.861188
10	6	0	-1.378776	-1.697608	-0.037233
11	1	0	-1.825489	-2.243078	-0.875400
12	1	0	-1.808237	-2.085133	0.892622
13	6	0	2.588121	1.080018	-0.012052
14	6	0	3.005298	2.215557	-0.003786
15	6	0	3.509432	3.587699	0.010468
16	1	0	2.698842	4.299941	-0.165557
17	1	0	3.965059	3.822777	0.976734
18	1	0	4.265820	3.731648	-0.766166
19	6	0	4.502335	-1.144587	0.004203
20	1	0	4.823393	-0.592313	-0.884749
21	1	0	4.799742	-0.554019	0.876281
22	1	0	5.024085	-2.101757	0.031502

23	7	0	-1.597086	-0.244605	-0.175965
24	16	0	-3.068749	0.405997	0.178983
25	6	0	-3.730782	0.855113	-1.413853
26	1	0	-4.713486	1.300856	-1.250644
27	1	0	-3.055463	1.576358	-1.876166
28	1	0	-3.812337	-0.048602	-2.018759
29	8	0	-2.855615	1.638390	0.927522
30	8	0	-3.897987	-0.662854	0.720840

Optimized Geometry of Benzyne 8f [Note the angle difference between two carbons (red vs blue)]:



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.172525	-1.785959	-0.177442
2	6	0	1.907714	-0.628713	-0.088981
3	6	0	0.986957	0.484695	-0.074618
4	6	0	-0.415904	0.206532	-0.058709
5	6	0	-0.956643	-1.112345	-0.130278
6	6	0	-0.024265	-2.131915	-0.207781
7	6	0	-1.637438	1.108140	0.111521
8	6	0	-2.838756	0.215249	0.073635
9	6	0	-4.173778	0.560986	0.171198
10	6	0	-5.116866	-0.470495	0.114509
11	6	0	-4.708836	-1.797090	-0.030966
12	6	0	-3.353765	-2.135499	-0.124122
13	6	0	-2.427465	-1.107482	-0.070585
14	1	0	-4.468264	1.599761	0.287124
15	1	0	-6.175137	-0.240489	0.184830
16	1	0	-5.457643	-2.582339	-0.072492
17	1	0	-3.038390	-3.168788	-0.234430
18	8	0	-1.714573	2.305581	0.285678
19	6	0	1.472419	1.958749	-0.082667
20	6	0	2.980851	2.165861	-0.301460
21	1	0	3.153359	3.245007	-0.366562
22	1	0	3.594193	1.795959	0.520824
23	1	0	3.327056	1.727148	-1.241097
24	6	0	1.142102	2.607626	1.273801
25	1	0	1.447025	3.660227	1.256464
26	1	0	0.080816	2.568054	1.510681
27	1	0	1.703233	2.106366	2.070445
28	6	0	0.817332	2.699455	-1.267863
29	1	0	1.165927	2.264311	-2.210866
30	1	0	-0.267715	2.679049	-1.251456
31	1	0	1.129839	3.749392	-1.246588
32	6	0	3.415918	-0.698987	0.049127
33	1	0	3.918172	-0.192560	-0.778991
34	1	0	3.728839	-0.186144	0.964840
35	6	0	3.906580	-2.146861	0.107645
36	1	0	3.594789	-2.669706	-0.805457
37	1	0	3.418379	-2.661152	0.944636
38	6	0	5.422092	-2.226287	0.260806
39	1	0	5.761792	-3.264593	0.302723
40	1	0	5.927265	-1.740245	-0.580361
41	1	0	5.748411	-1.727858	1.179677

VI. Anecdotal Account of TRH's 1972 Preparation ^{15}N-Labeled Hydroxylamine-*O*-sulfonic acid—an Exemplary Tribute to Harold W. Heine

I (TRH, the corresponding author of this manuscript) share the following anecdote, which captures, in small part at least, some of the essence of Harold Heine's (HWH's) approach to teaching and mentoring. During our studies that culminated in the results described in ref 1[8] in the manuscript, I was asked by HWH to prepare a sample of ^{15}N-labeled hydroxylamine-*O*-sulfonic acid (HASA, NH_2OSO_3H) for the (eventually incisive) mass spectrometry experiment. He suggested that before ordering the requisite $^{15}NH_2OH$•HCl (ca. $600/0.5 g in 1972), I first convince us that I could prepare HASA with unlabeled material, which involved treating hydroxylamine with fuming sulfuric acid, filtering the precipitated solid, and washing it with ether. I did so with ease in January 1972. HWH ordered the labeled sample, which arrived several months later. He handed over the precious $^{15}NH_2OH$•HCl with the suggestion that I practice repeating the preparation of $^{14}NH_2OSO_3H$ once more, just to ensure that I had the details fresh in mind. Being an overly brash "senior investigator" (BS, Bucknell, 1972), I ignored that advice and proceeded to mix the $^{15}NH_2OH$•HCl with oleum, just as I had done six months earlier. All was well until the white crystalline ^{15}N-HASA substance, captured on the vacuum filtration funnel, turned to a soupy liquid in a matter of seconds and disappeared through the frit into the filtrate in irretrievable form. I had demonstrated that the highly hygroscopic HASA, a zwitterionic inner salt, was incompatible with the stifling humidity levels in the non-air-conditioned Bucknell laboratory in June of 1972. I reported to HWH the error of my ways, having ignored his advice, expecting a rather severe scolding ($600 was an entire student summer stipend at the time!). Instead of a tongue lashing, I received from him, after only a few seconds of his consideration of my confessional, "If I buy another sample for us, will you do it right this time?" What a (giant relief to me and) remarkable and formative example of the right way to react to a young researcher's indiscretion. The take home lesson? Be tolerant of any mistake (at least the first time!) by a research student and, more broadly, by people in all walks of engagement. As for the eventual scientific bottom line here? See Figure S1 below [graphics extracted from ref 8 (= ref 1 in the manuscript)].

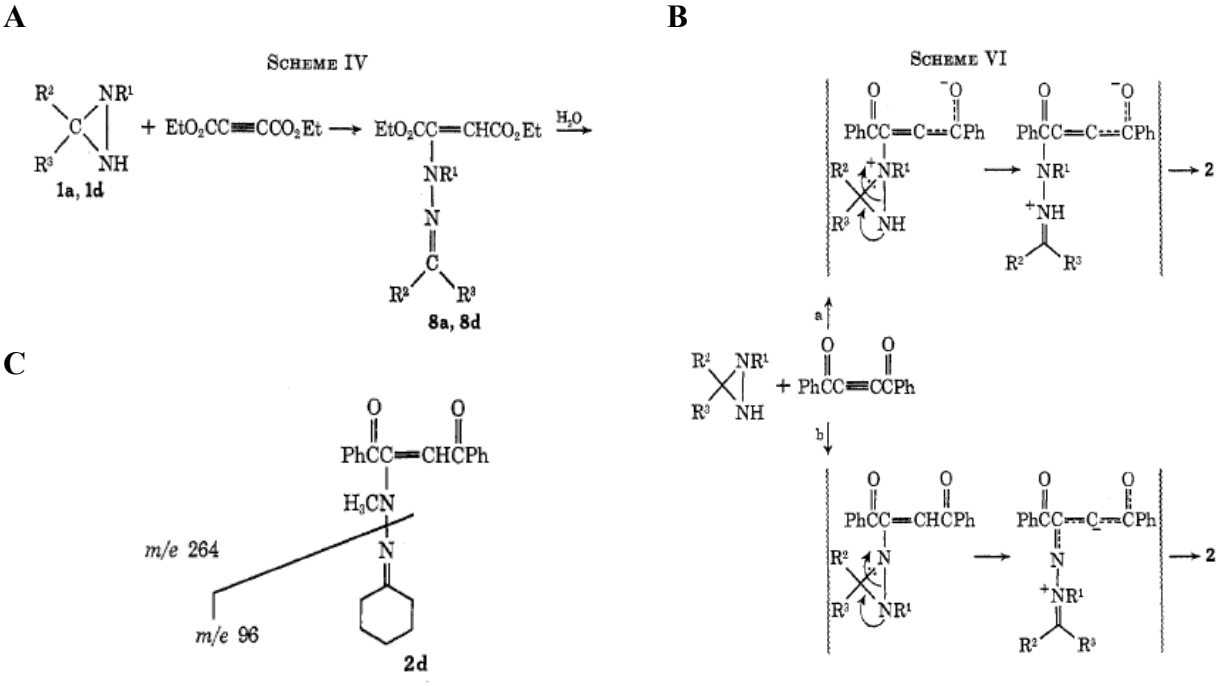


Figure S1. A) The reaction of 1,3,3-trisubstituted diaziridines with diethyl acetylenedicarboxylate. **B**) The two possible mechanisms (path a vs. b), differing in which nitrogen atom initiates attack on the alkyne. **C**) The mass spectral fragmentation event that allowed identification of path a as the operative mechanism when the ^{15}N-labeled isotopolog of the diaziridine was used to prepare **2d**. (Graphics reprinted from Ref. 8, with permission. Copyright 1973, American Chemical Society.)

VII. References for the Supporting Information

[1] Hoye, T. R., Hanson, P. R. & Vyvyan, J. R. A practical guide to first-order multiplet analysis in ^{1}H NMR spectroscopy. *J. Org. Chem*. **59**, 4096-4103 (1994).

[2] Hoye, T. R. & Zhao, H. A method for easily determining coupling constant values: an addendum to "a practical guide to first-order multiplet analysis in ^{1}H NMR spectroscopy". *J. Org. Chem*. **67**, 4014–4016 (2002).

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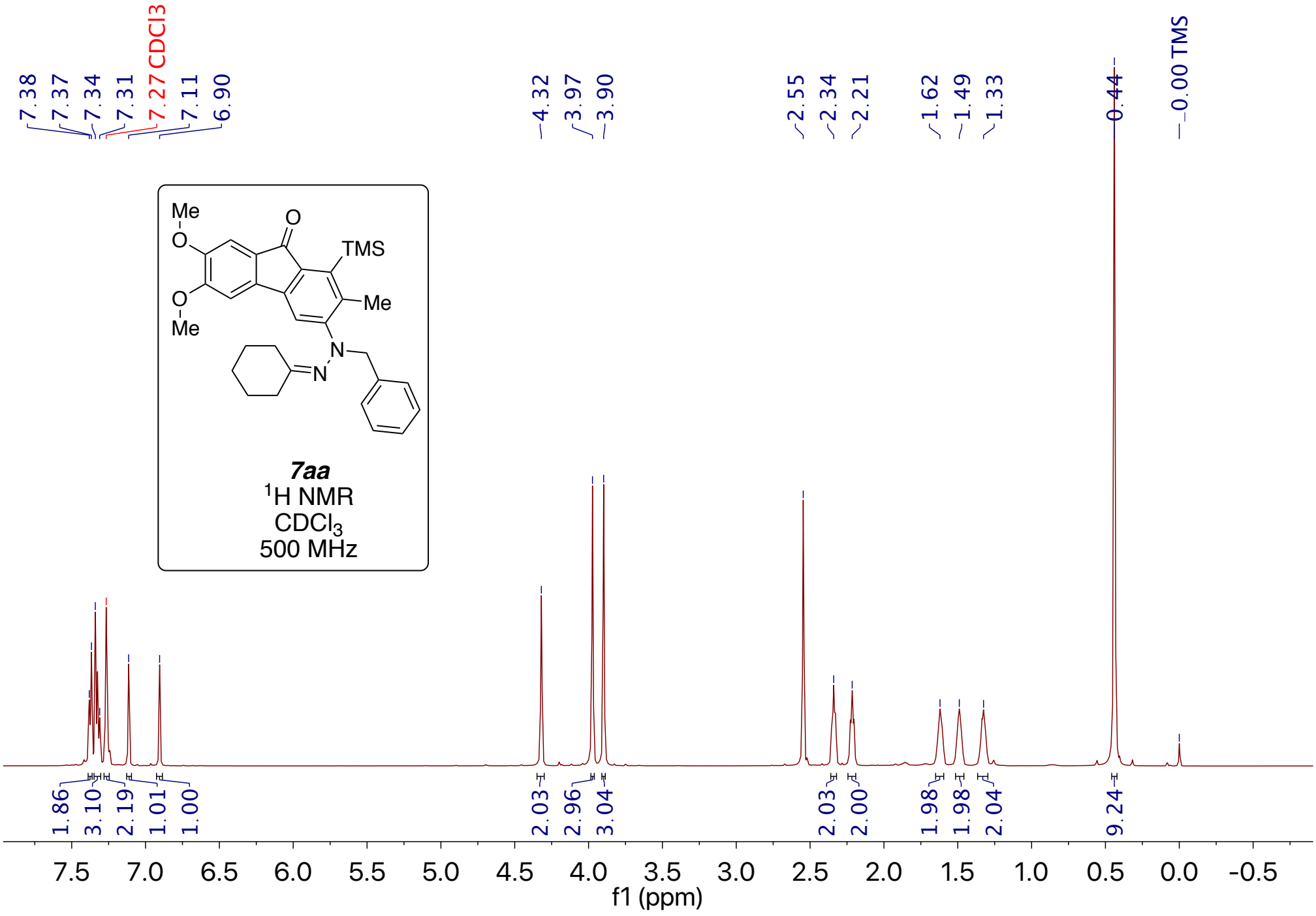
VIII. Copies of NMR spectra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2.21
1.62
1.49
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0.44
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O
Me
O
TMS
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N
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CDCl3
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3.10
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1.01
1.00
2.03
2.96
3.04
2.03
2.00
1.98
1.98
2.04
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6.0
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5.0
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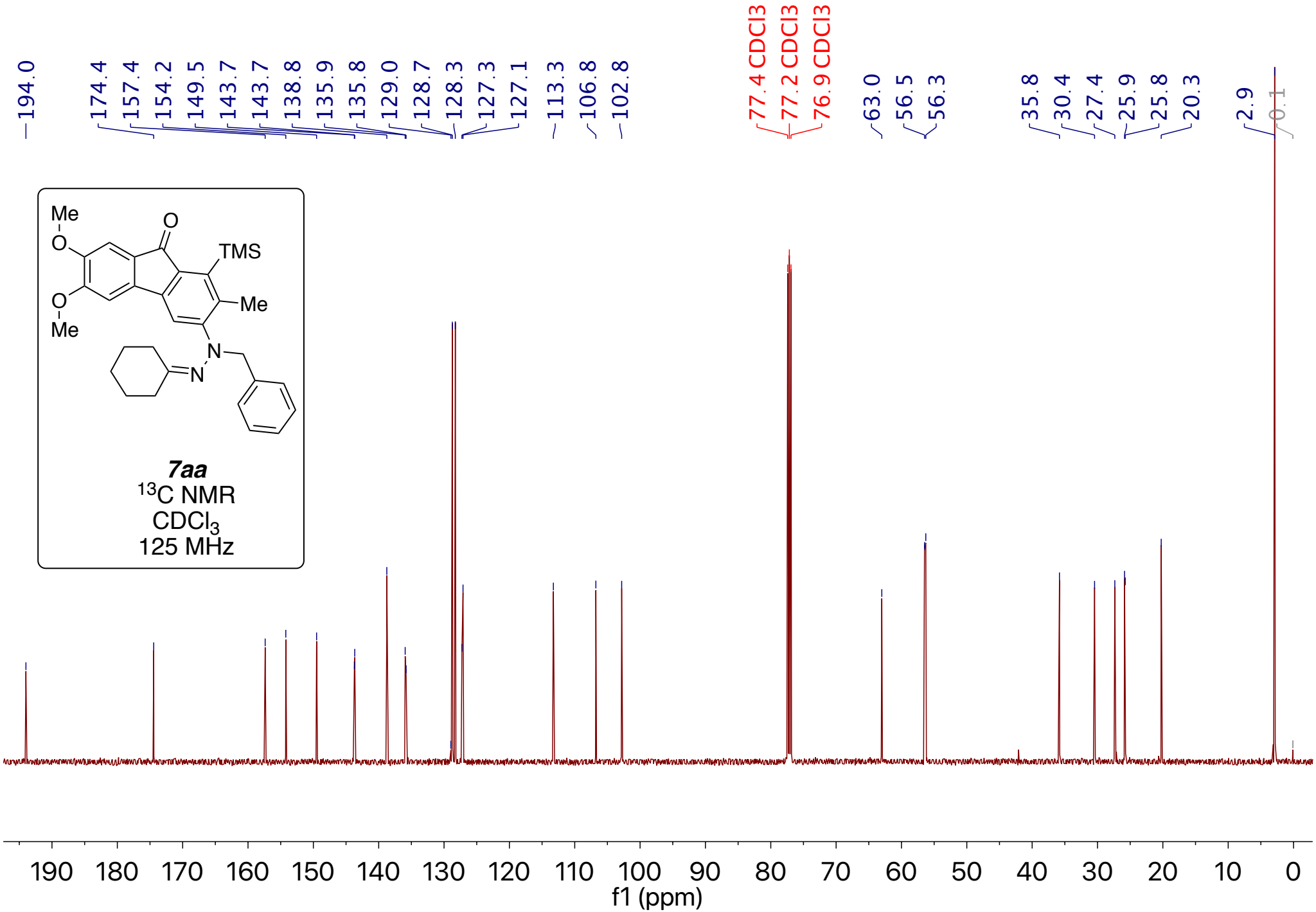
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128.3
127.3
127.1
113.3
106.8
102.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
63.0
56.5
56.3
35.8
30.4
27.4
25.9
25.8
20.3
2.9
0.1
Me
O
O
Me
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CDCl3
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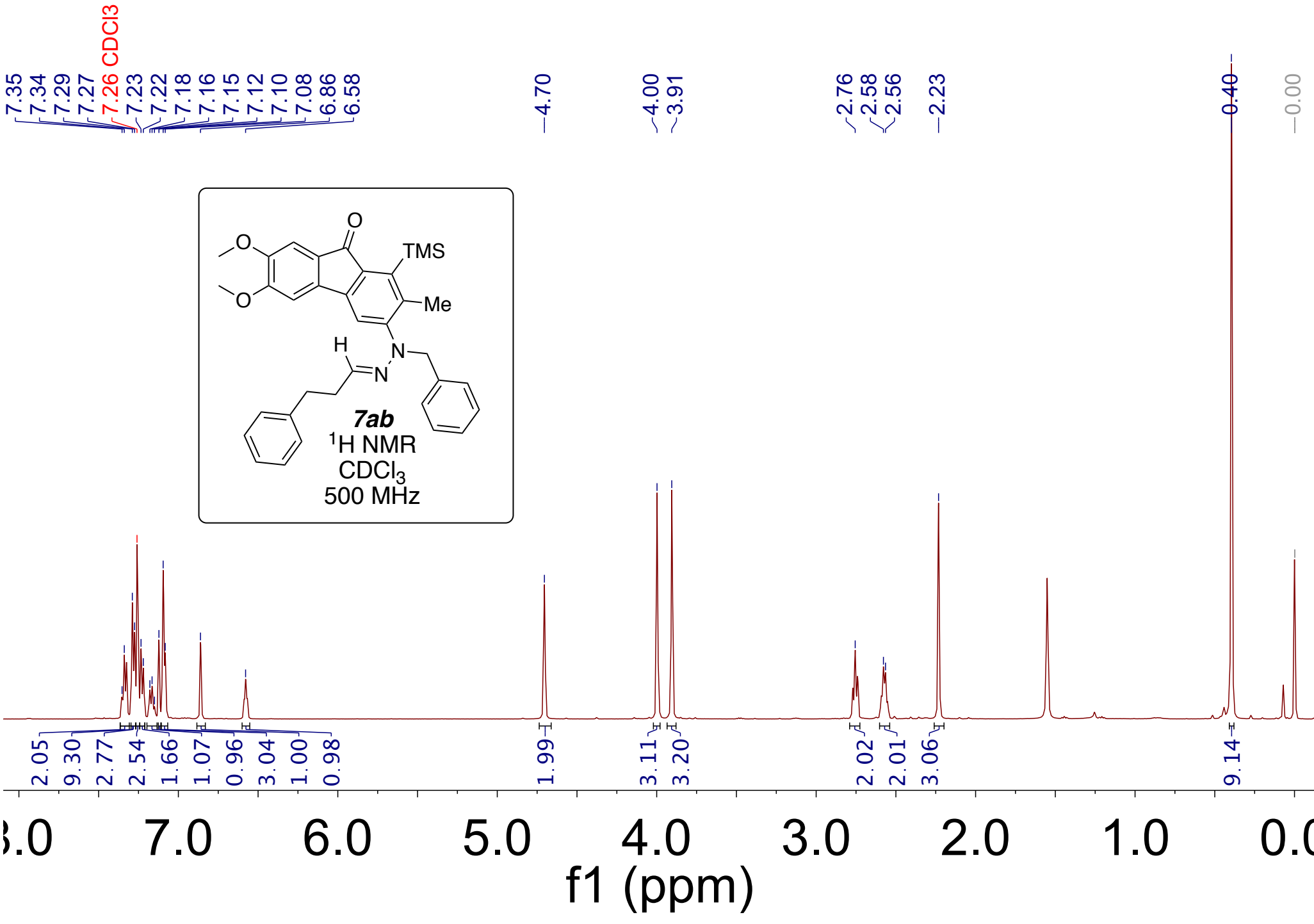
f1 (ppm)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2.56
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0.00
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O
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TMS
Me
H
N
N
7ab
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9.30
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1.07
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3.04
1.00
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1.99
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2.02
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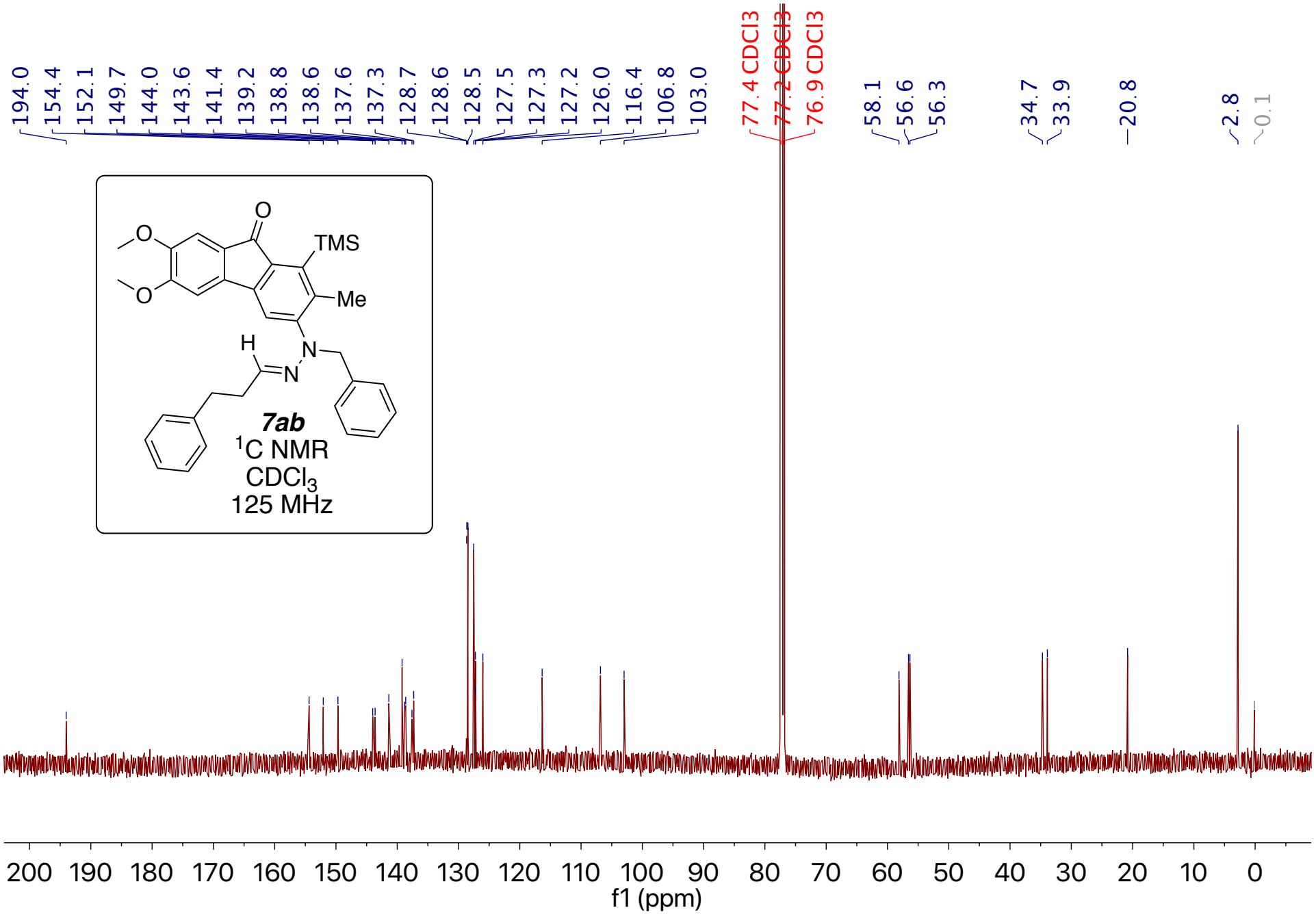
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127.5
127.3
127.2
126.0
116.4
106.8
103.0
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
58.1
56.6
56.3
34.7
33.9
20.8
2.8
0.1
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O
O
TMS
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CDCl3
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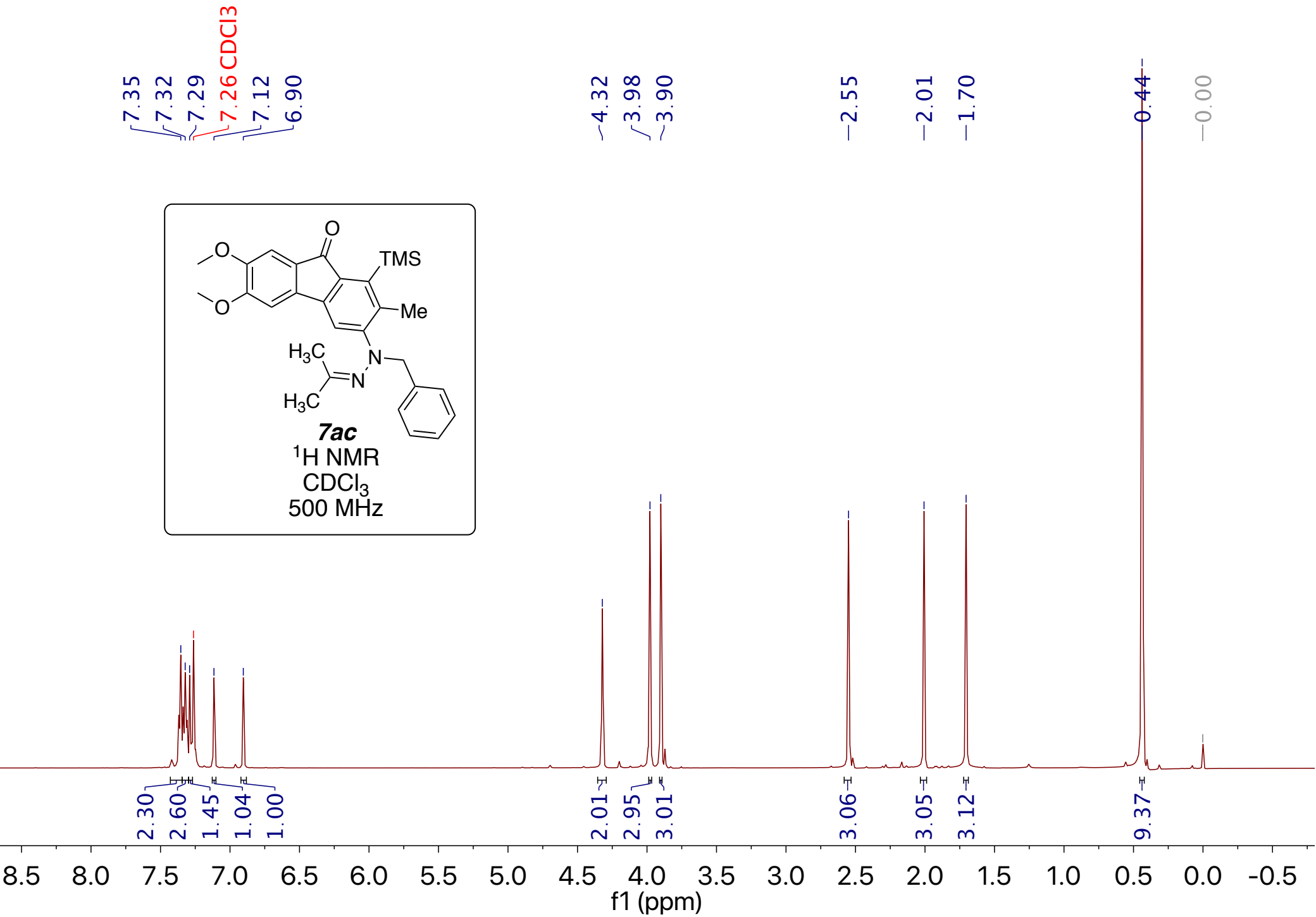
f1 (ppm)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2.01
1.70
0.44
0.00
TMS
Me
O
O
O
N
N
H3C
H3C
7ac
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CDCl3
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2.60
1.45
1.04
1.00
2.01
2.95
3.01
3.06
3.05
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9.37
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
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2.0
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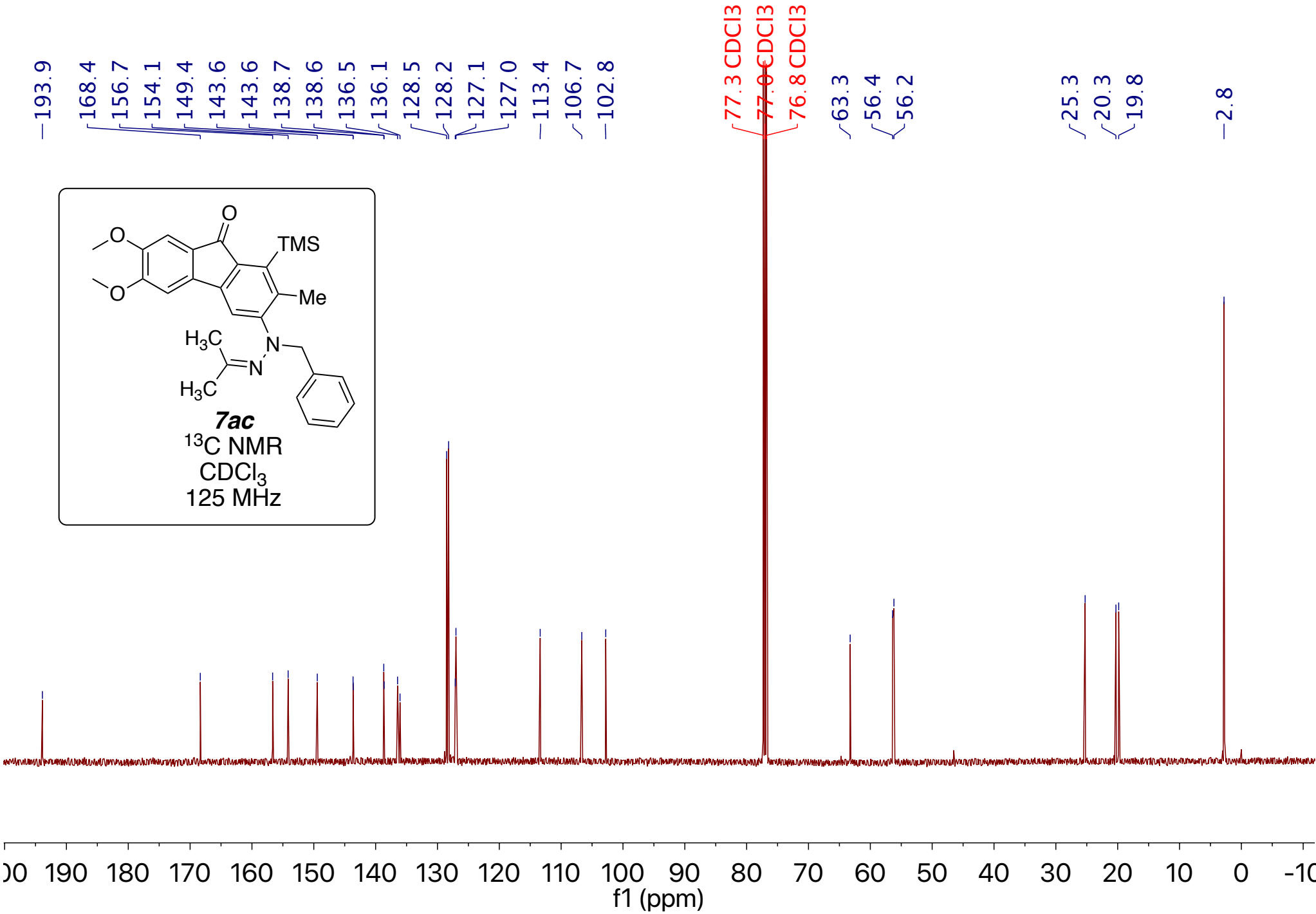
f1 (ppm)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127.1
127.0
113.4
106.7
102.8
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
63.3
56.4
56.2
25.3
20.3
19.8
2.8
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TMS
Me
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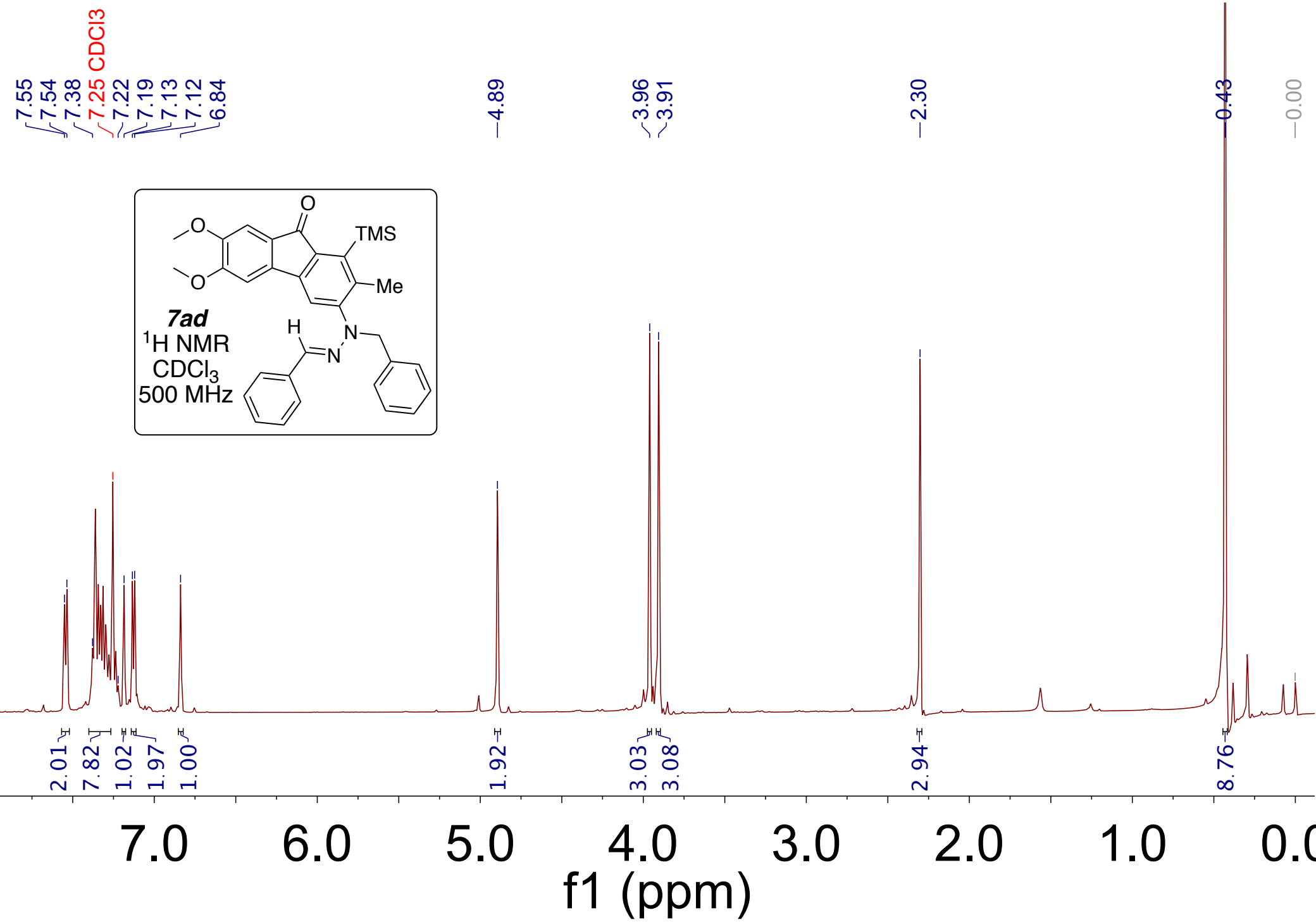
H3C
7ac
13C NMR
CDCl3
125 MHz
f1 (ppm)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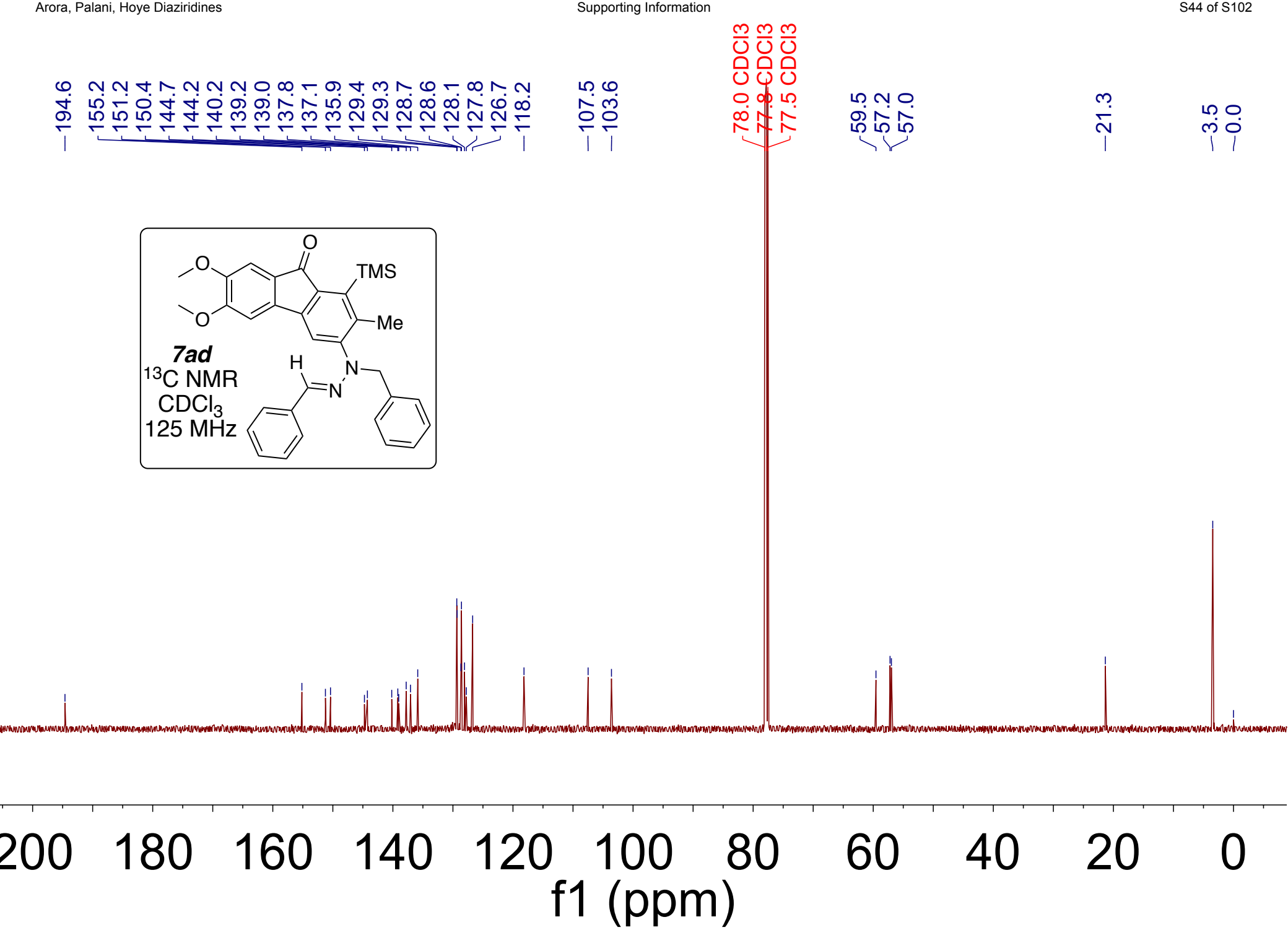
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128.1
127.8
126.7
118.2
107.5
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57.2
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O
O
TMS
Me
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H
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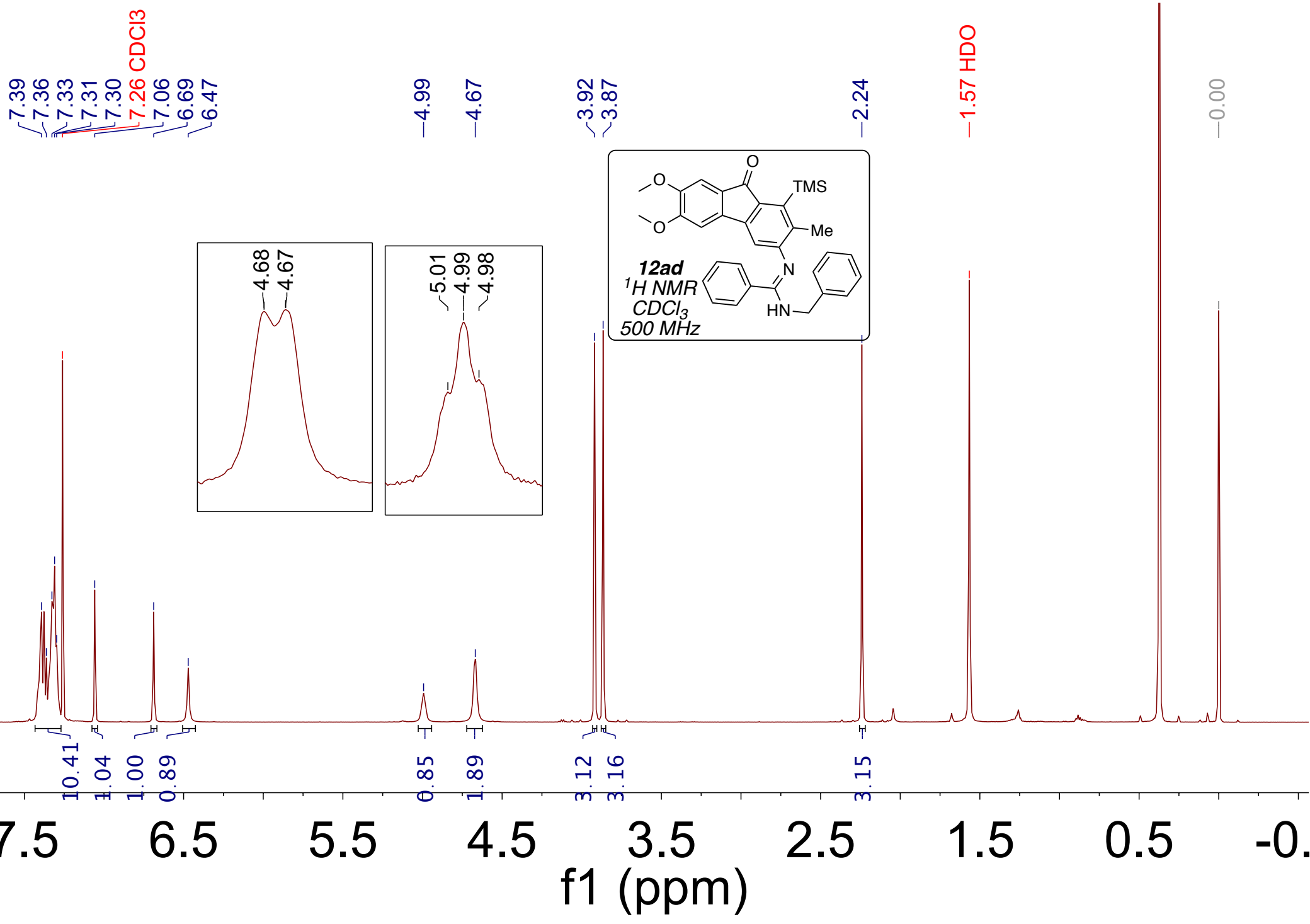
f1 (ppm)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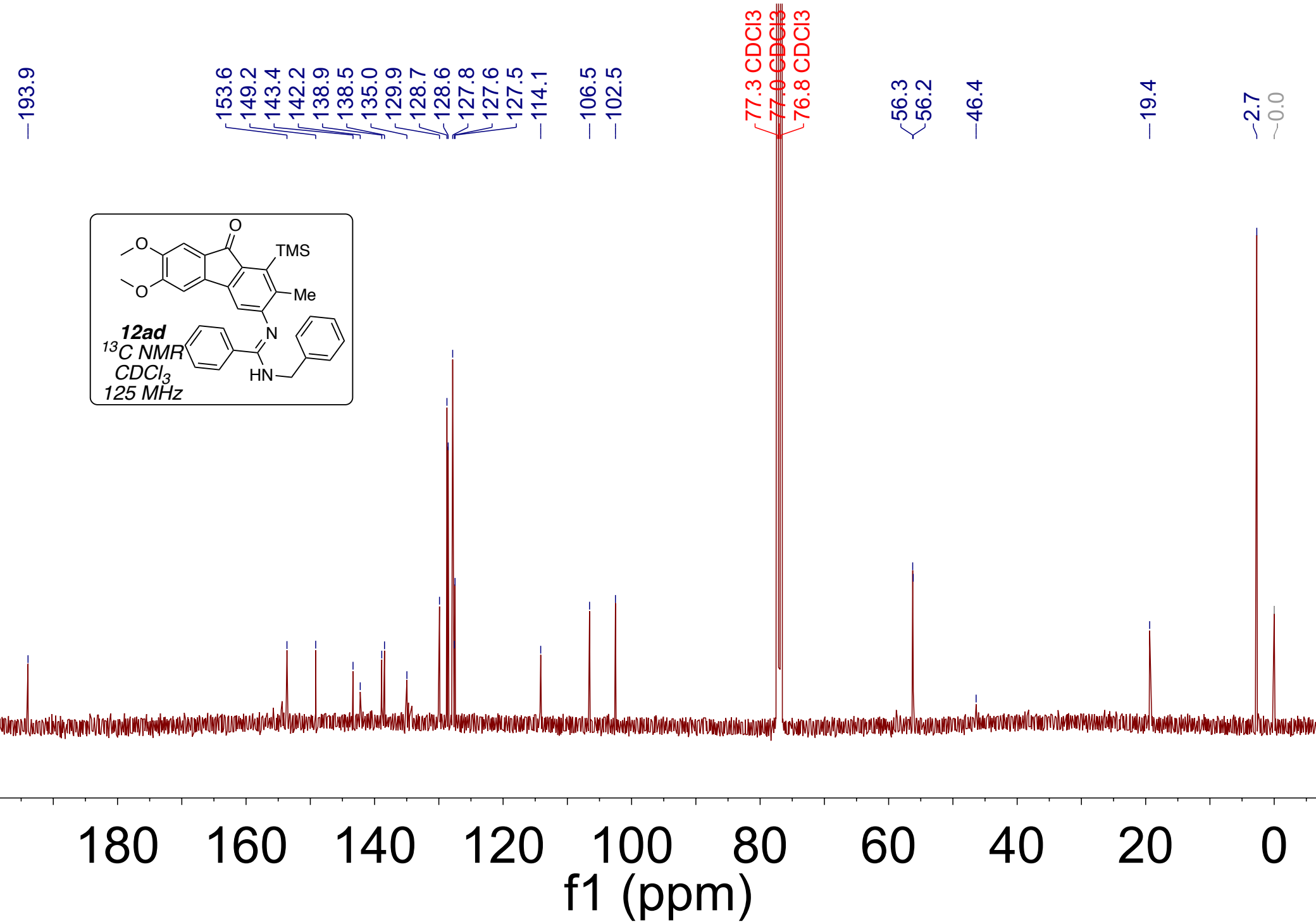
f1 (ppm)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77.0 CDCl3
76.8 CDCl3
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56.2
46.4
19.4
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O
O
TMS
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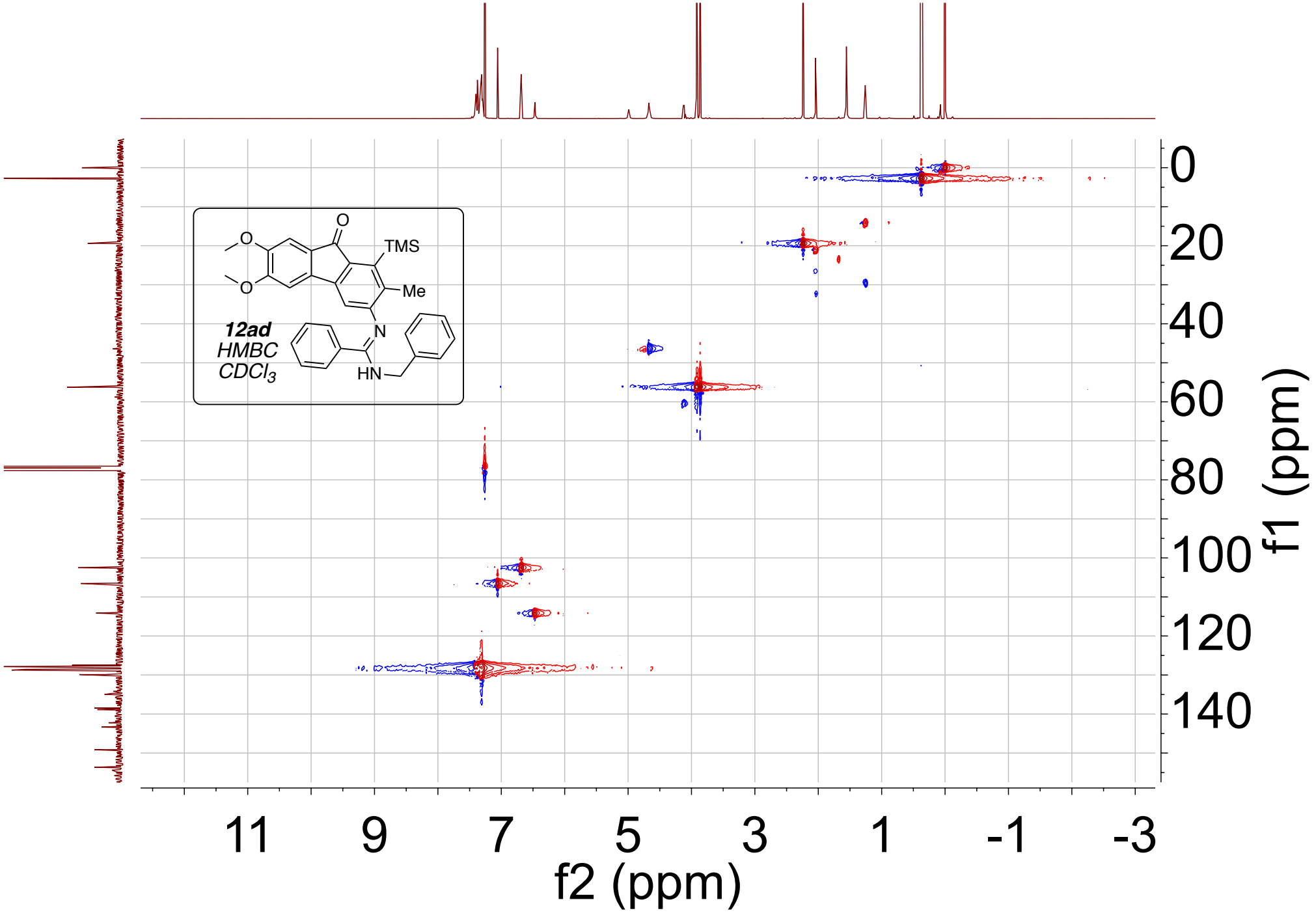
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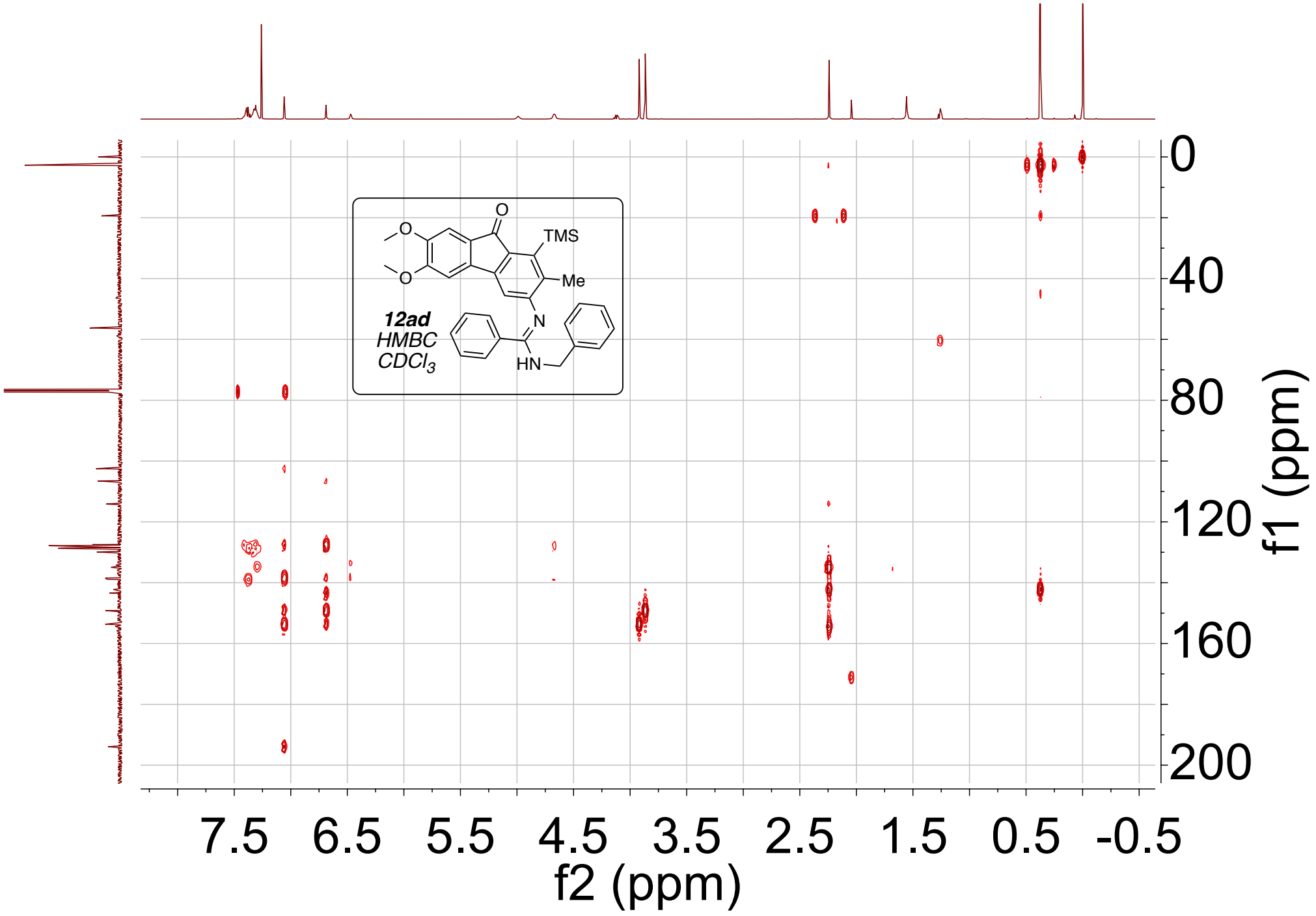
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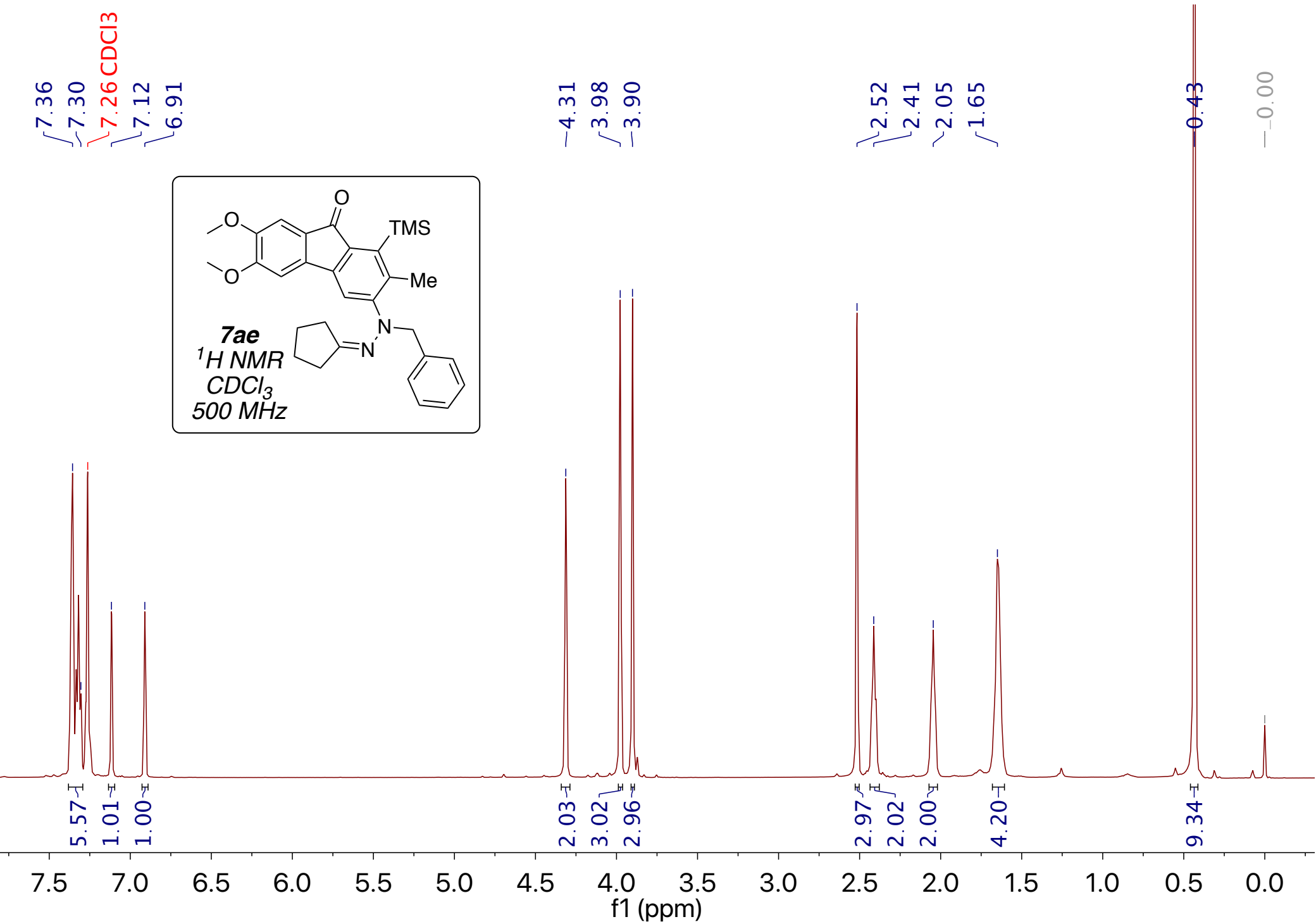
f2 (ppm)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O
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O
TMS
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7ae
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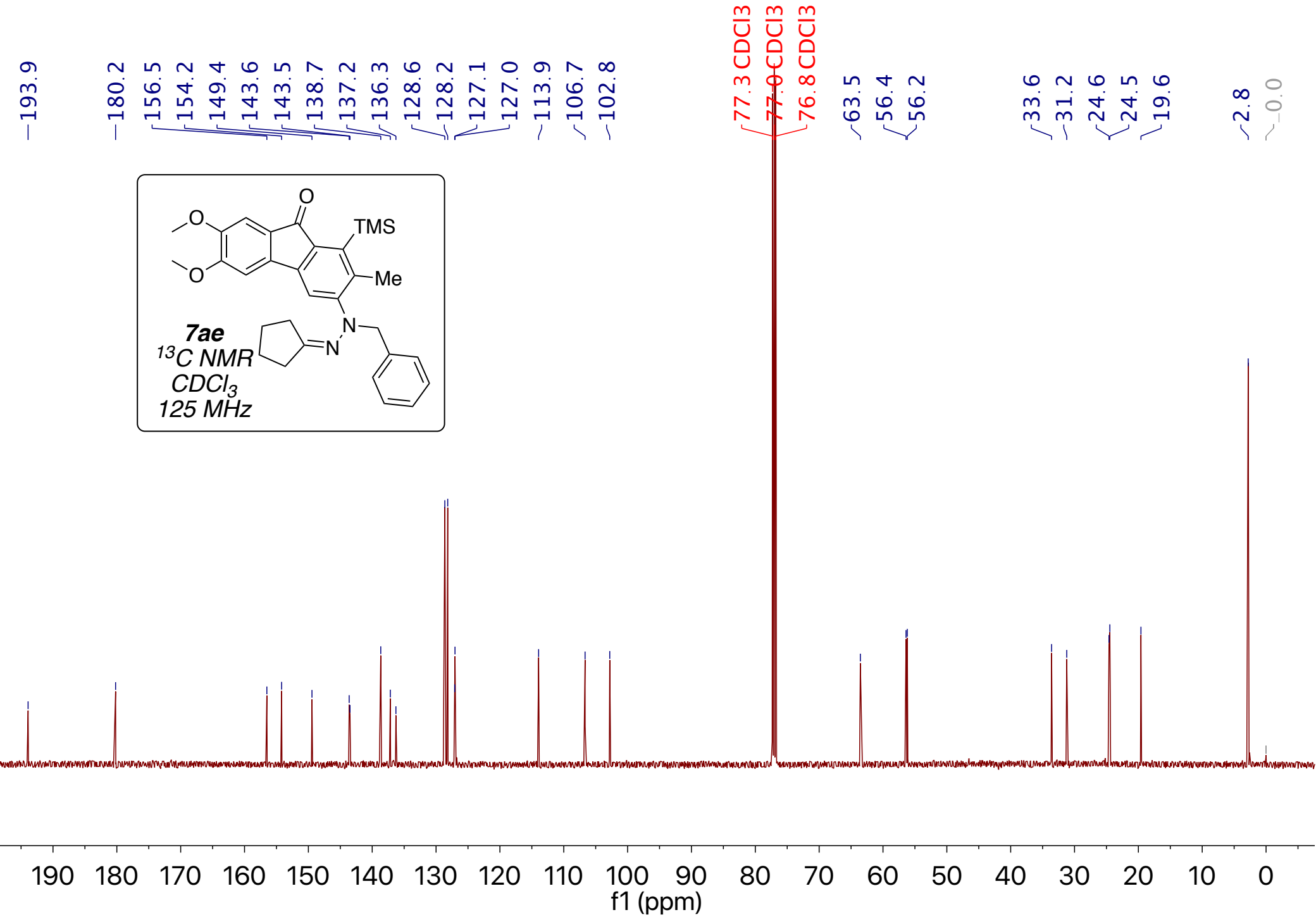
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106.7
102.8
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77.0 CDCl3
76.8 CDCl3
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31.2
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24.5
19.6
2.8
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O
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7ae
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CDCl3
125 MHz
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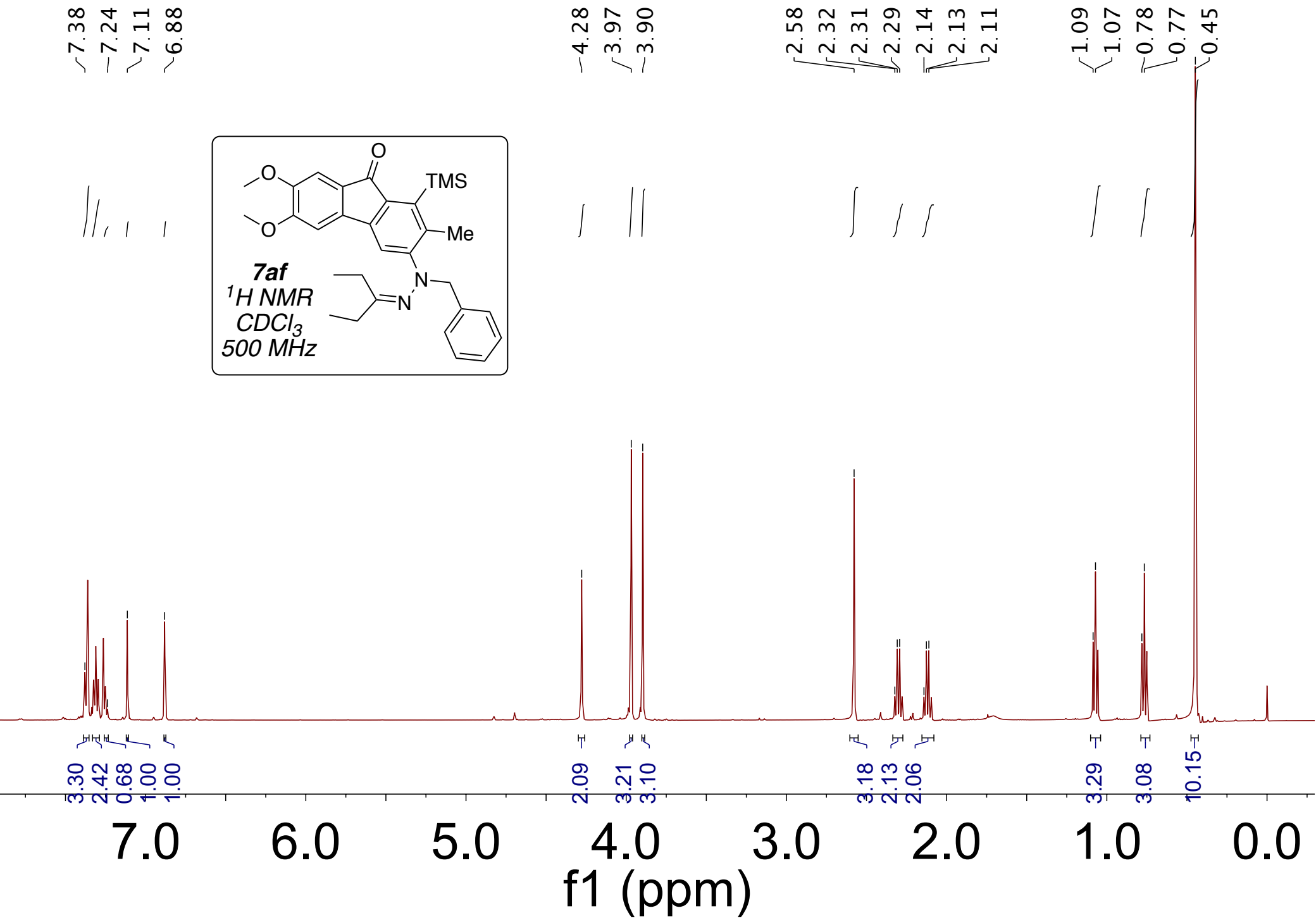
f1 (ppm)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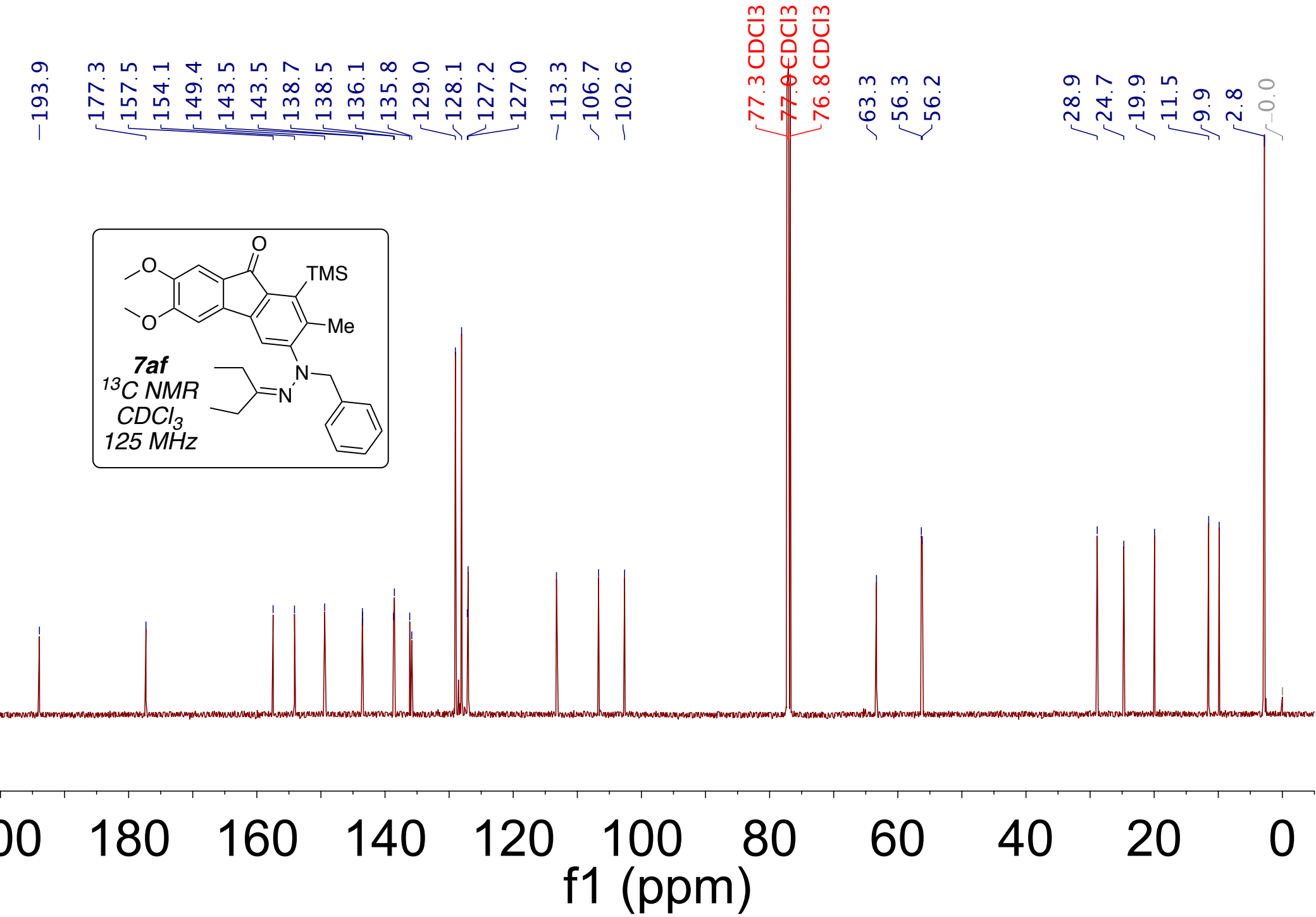
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106.7
102.6
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
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56.2
28.9
24.7
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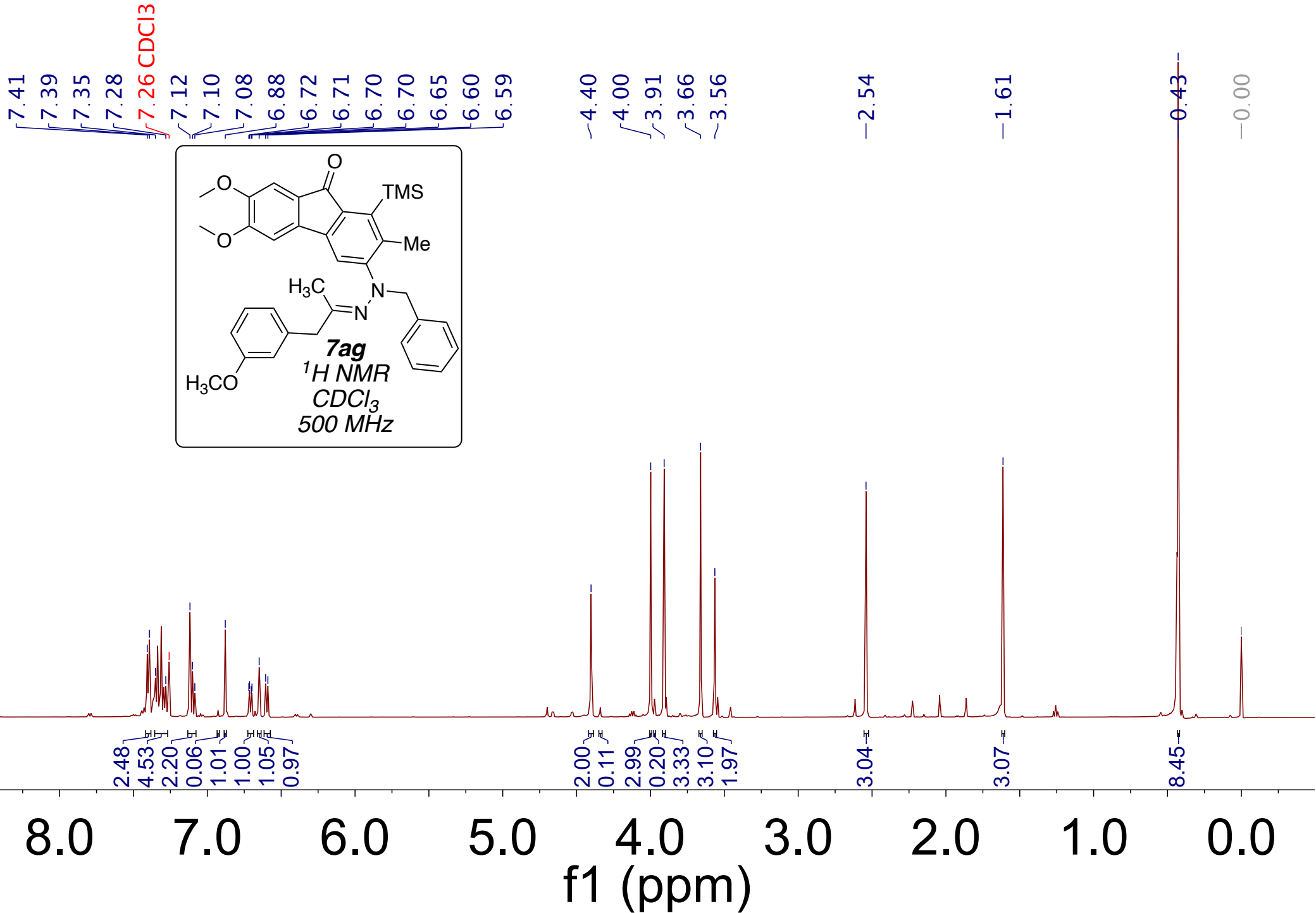
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O
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500 MHz
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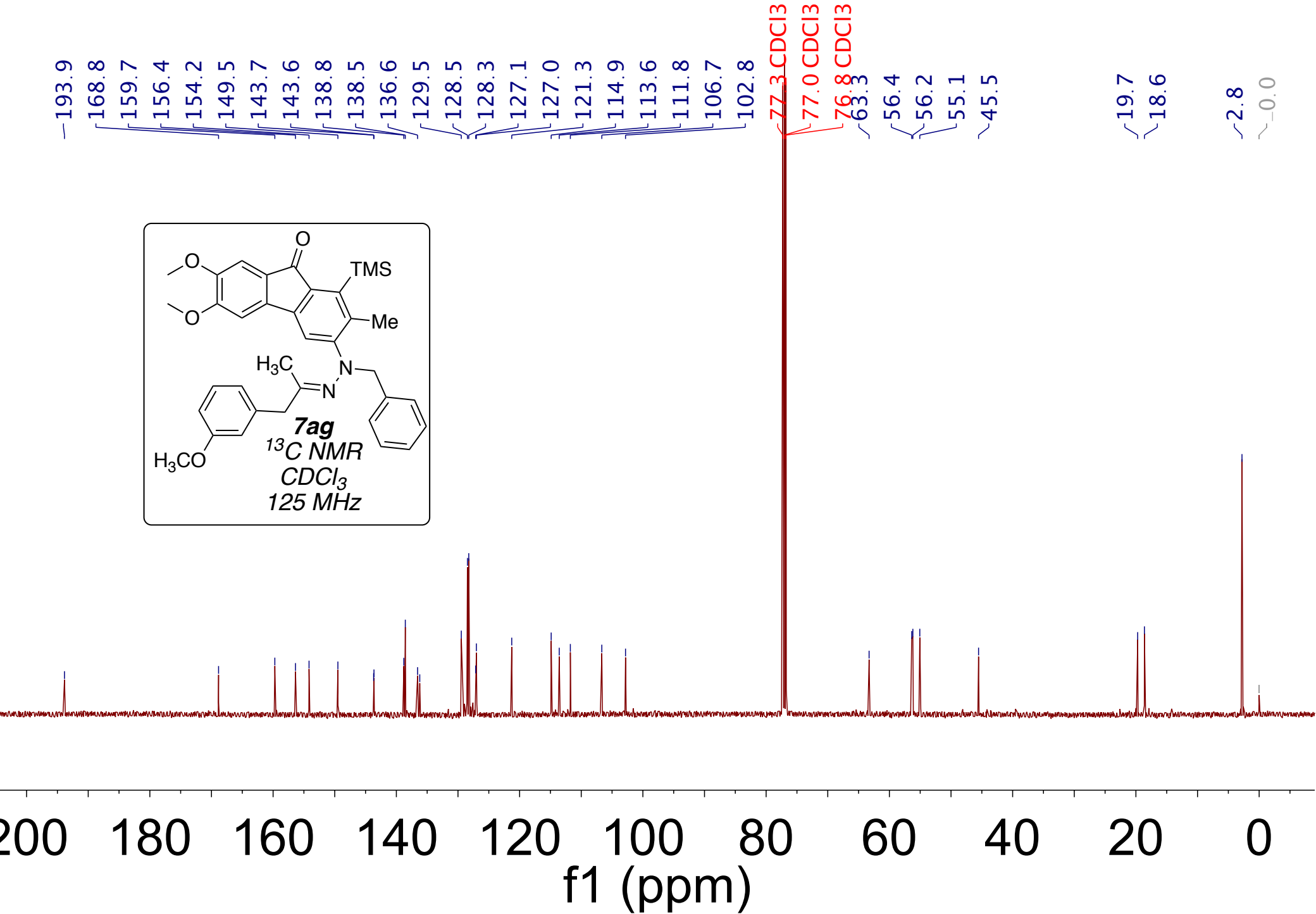
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114.9
113.6
111.8
106.7
102.8
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
63.3
56.4
56.2
55.1
45.5
19.7
18.6
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TMS
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H3C
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N
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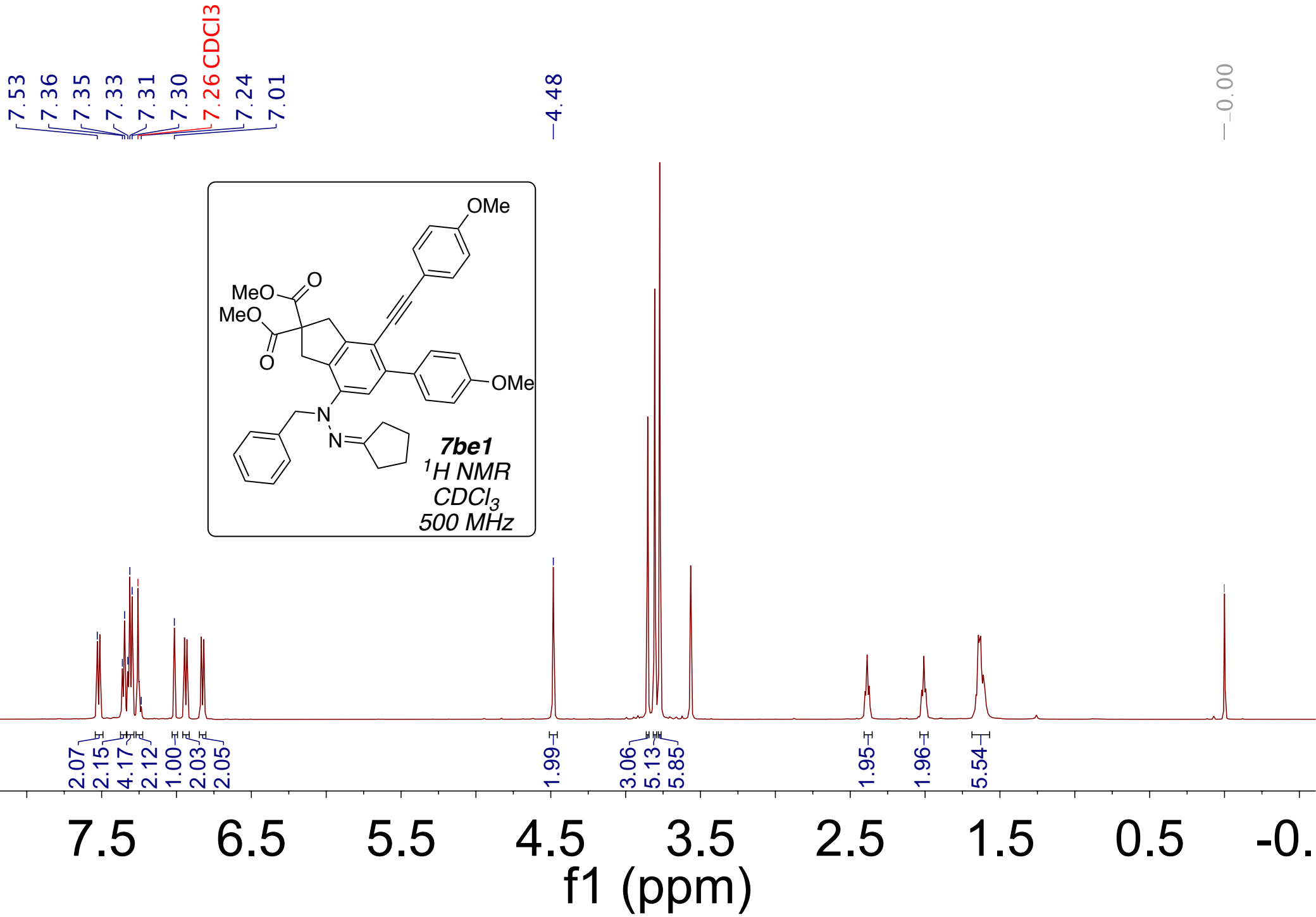
f1 (ppm)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7be1
1H NMR
CDCl3
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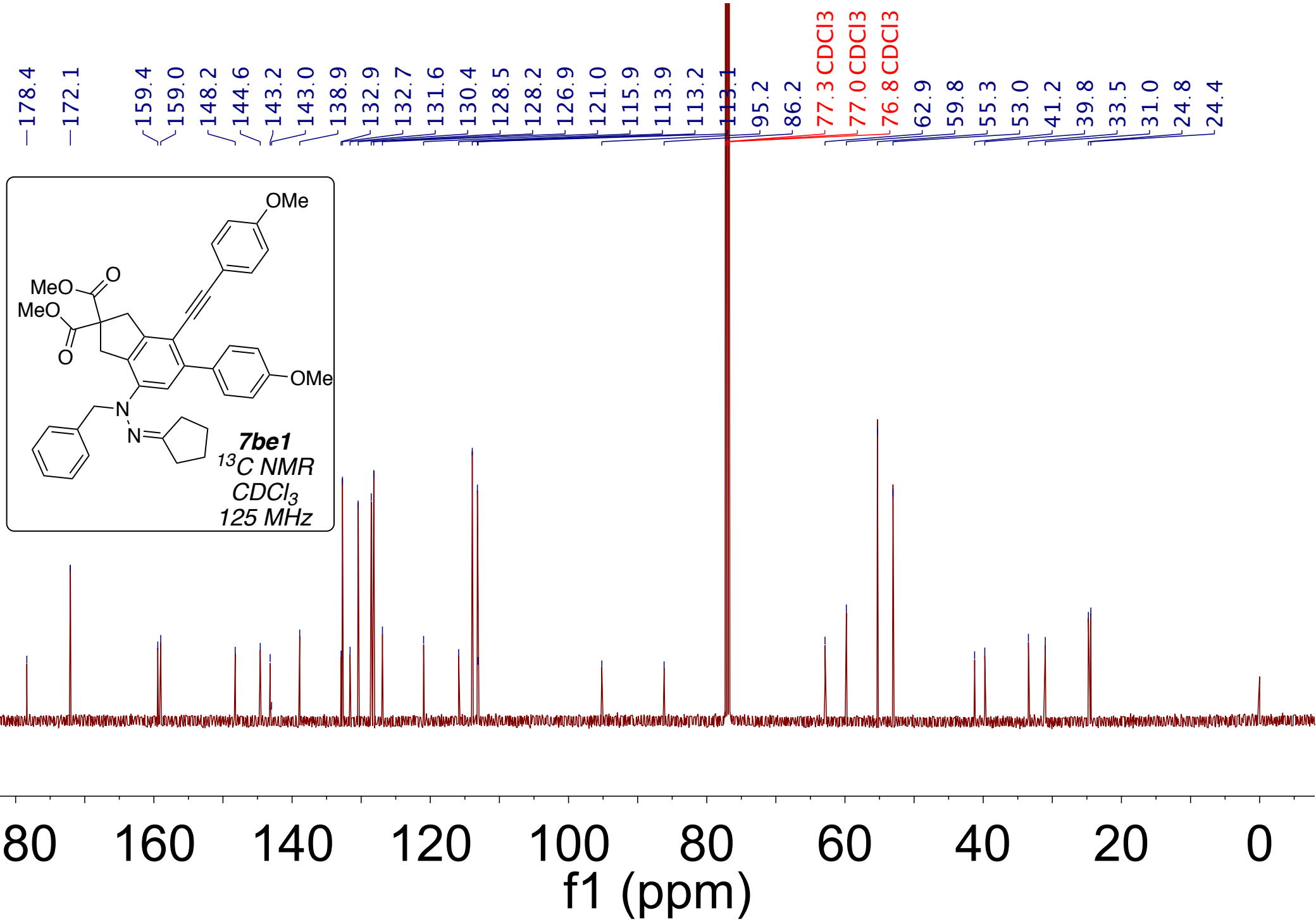
1.00
2.03
2.05
1.99
3.06
5.13
5.85
1.95
1.96
5.54
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.
f1 (ppm)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172.1
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144.6
143.2
143.0
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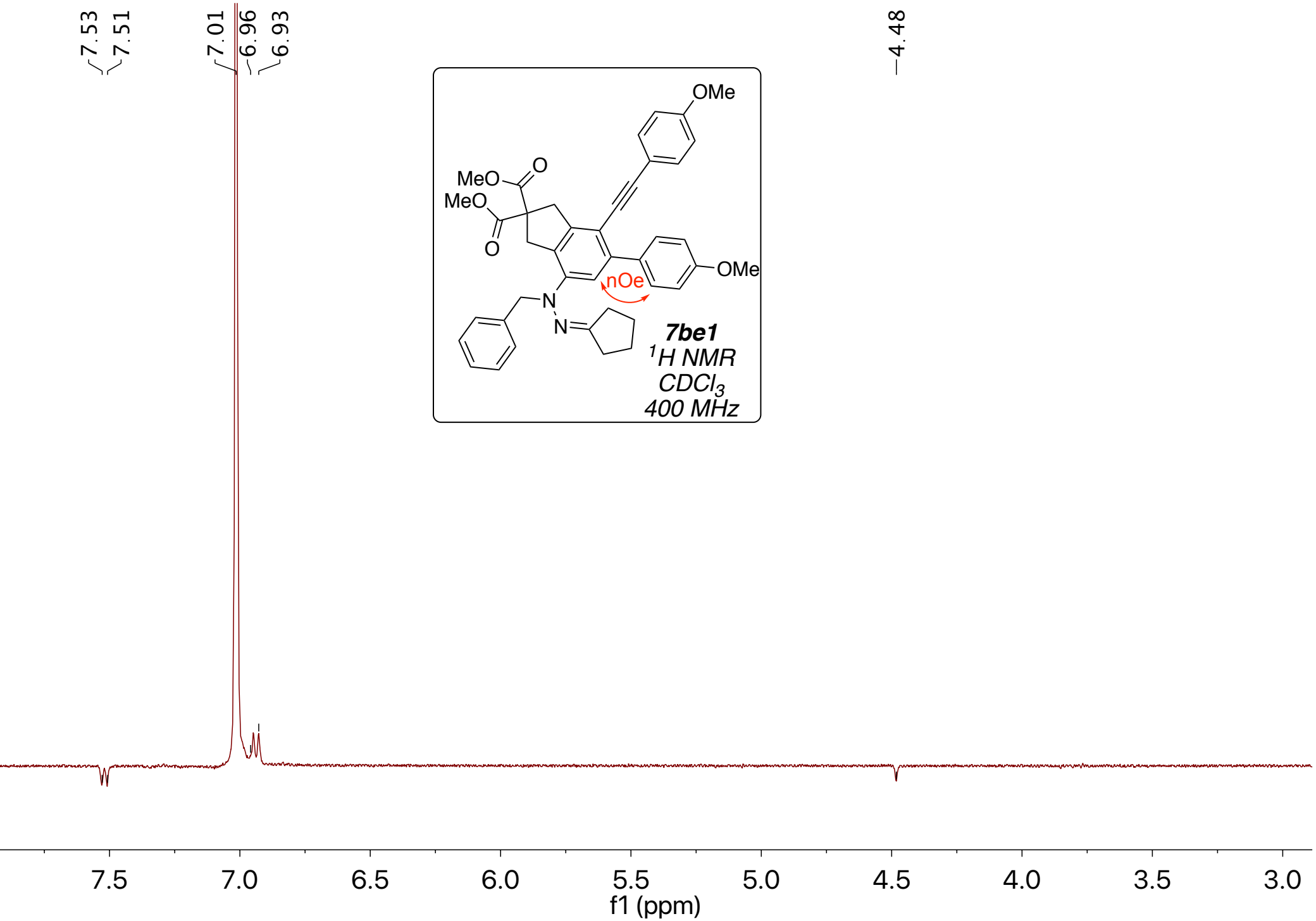
132.9
132.7
131.6
130.4
128.5
128.2
126.9
121.0
115.9
113.9
113.2
113.1
95.2
86.2
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
62.9
59.8
55.3
53.0
41.2
39.8
33.5
31.0
24.8
24.4
OMe
MeO
MeO
O
O
OMe
N
N
7be1
13C NMR
CDCl3
125 MHz
80
160
140
120
100
80
60
40
20
0
f1 (ppm)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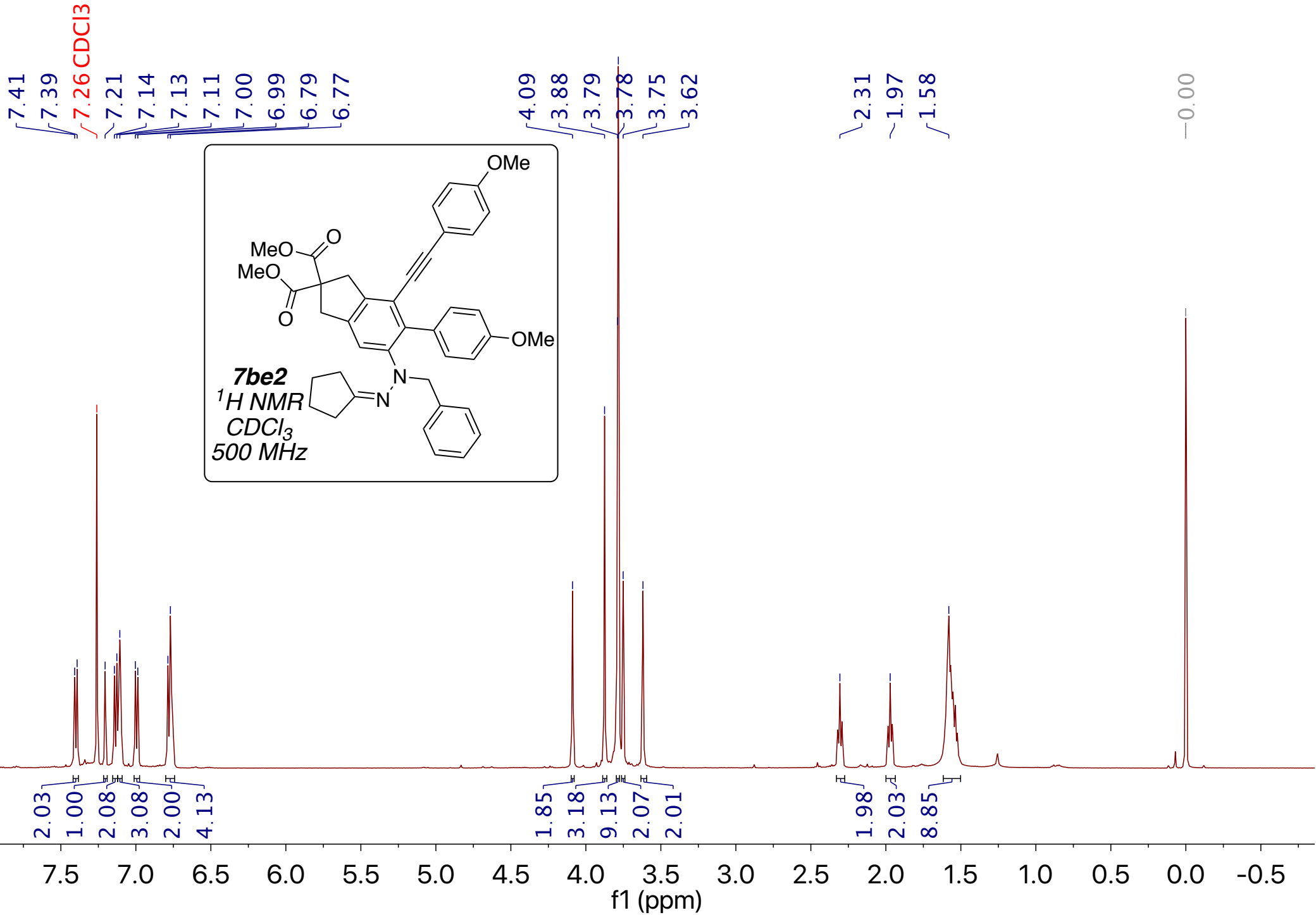
7.51
7.01
6.96
6.93
4.48
OMe
MeO
MeO
O
O
OMe
nOe
N
N
7be1
1H NMR
CDCl3
400 MHz
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f1 (ppm)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7.26 CDCl3
7.21
7.14
7.13
7.11
7.00
6.99
6.79
6.77
4.09
3.88
3.79
3.78
3.75
3.62
2.31
1.97
1.58
0.00
OMe
MeO
MeO
O
O
OMe
N
N
7be2
1H NMR
CDCl3
500 MHz
2.03
1.00
2.08
3.08
2.00
4.13
1.85
3.18
9.13
2.07
2.01
1.98
2.03
8.85
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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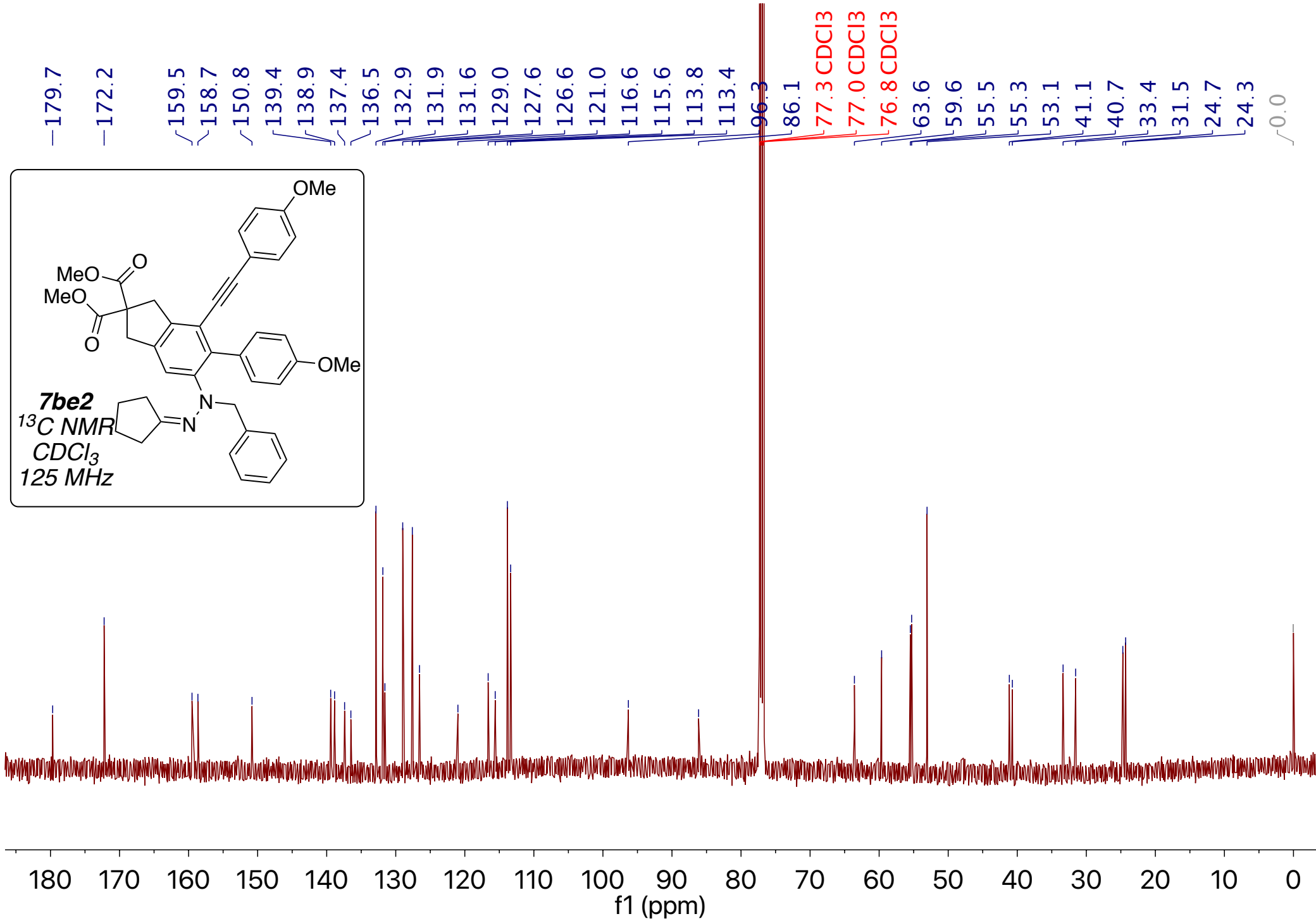
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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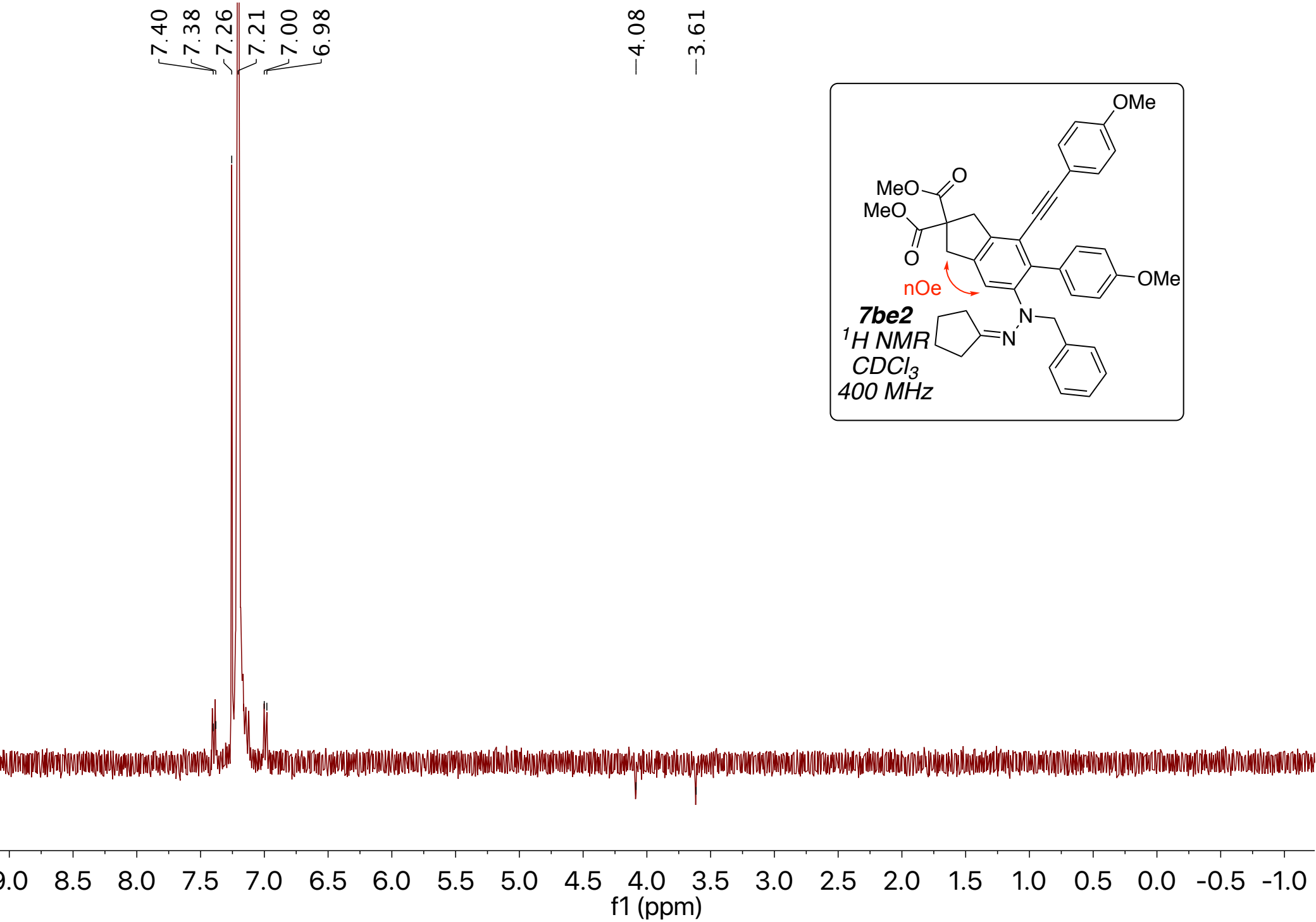
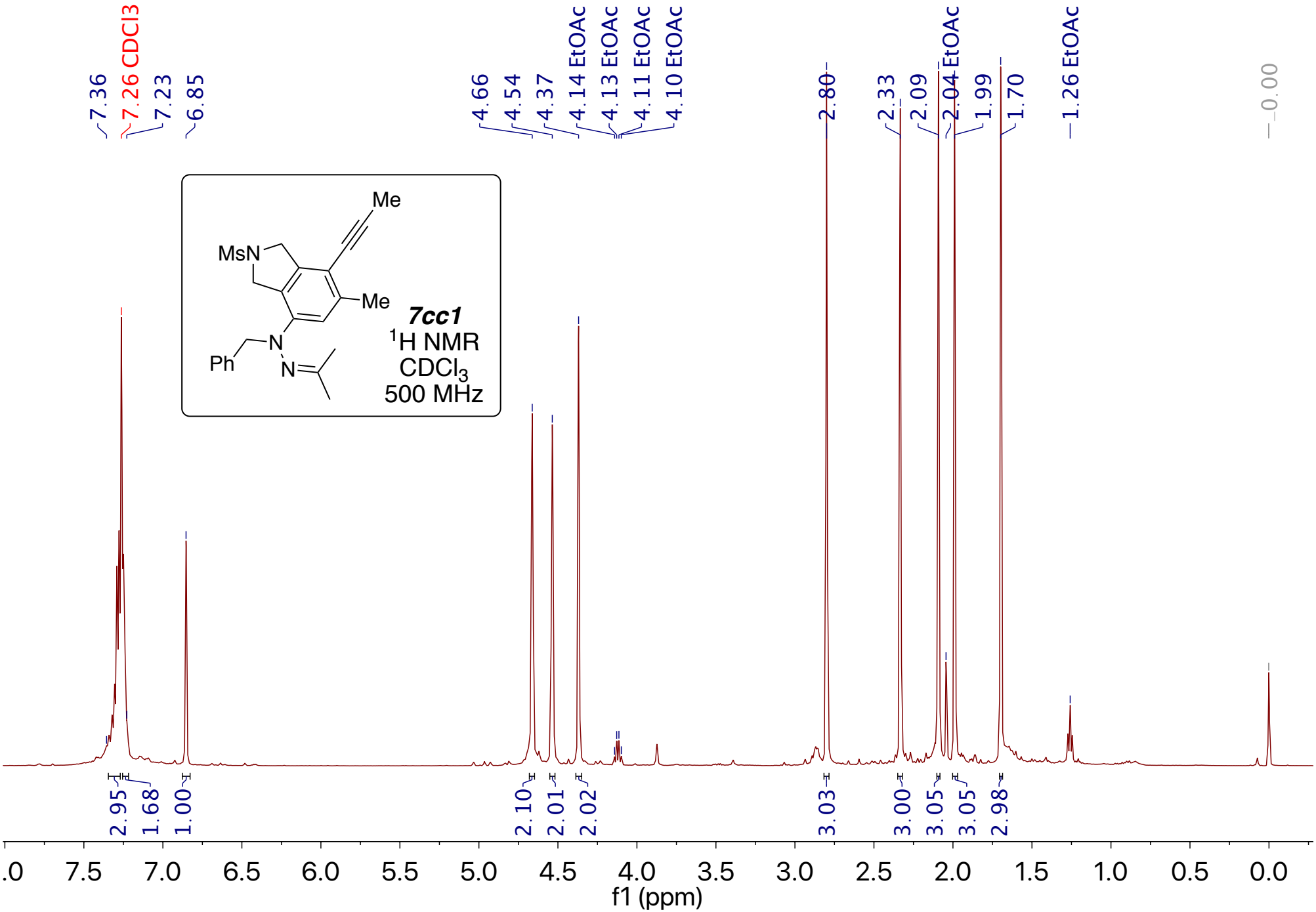
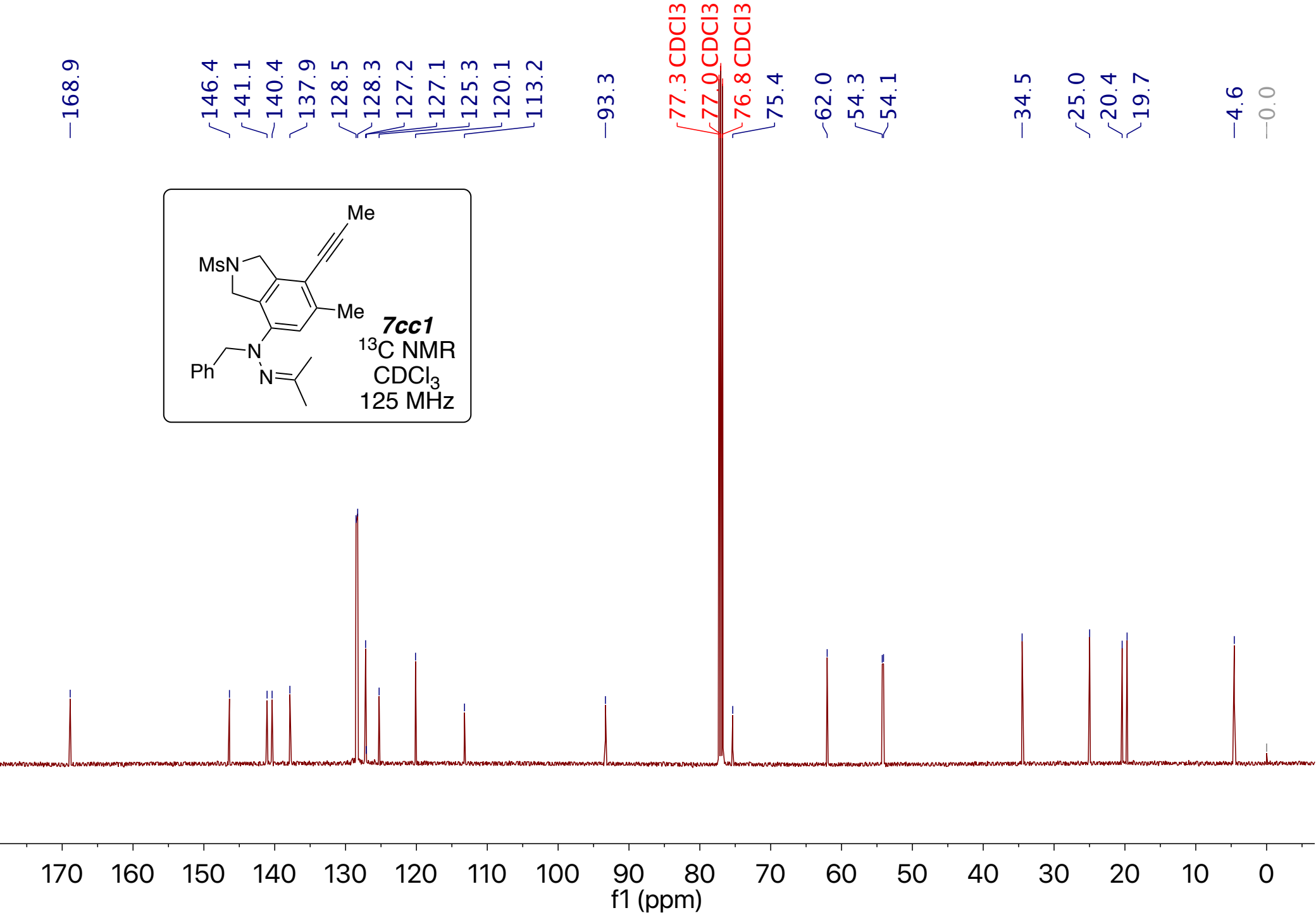
172.2
159.5
158.7
150.8
139.4
138.9
137.4
136.5
132.9
131.9
131.6
129.0
127.6
126.6
121.0
116.6
115.6
113.8
113.4
96.3
86.1
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
63.6
59.6
55.5
55.3
53.1
41.1
40.7
33.4
31.5
24.7
24.3
0.0
OMe
MeO
MeO
O
O
OMe
N
N
7be2
13C NMR
CDCl3
125 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.40
7.38
7.26
7.21
7.00
6.98
4.08
3.61
OMe
MeO
MeO
O
O
nOe
OMe
N
N
7be2
1H NMR
CDCl3
400 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
f1 (ppm)


7.36
7.26 CDCl3
7.23
6.85
4.66
4.54
4.37
4.14 EtOAc
4.13 EtOAc
4.11 EtOAc
4.10 EtOAc
2.80
2.33
2.09
2.04 EtOAc
1.99
1.70
1.26 EtOAc
0.00
Me
MsN
Me
N
Ph
N
7cc1
1H NMR
CDCl3
500 MHz
2.95
1.68
1.00
2.10
2.01
2.02
3.03
3.00
3.05
3.05
2.98
f1 (ppm)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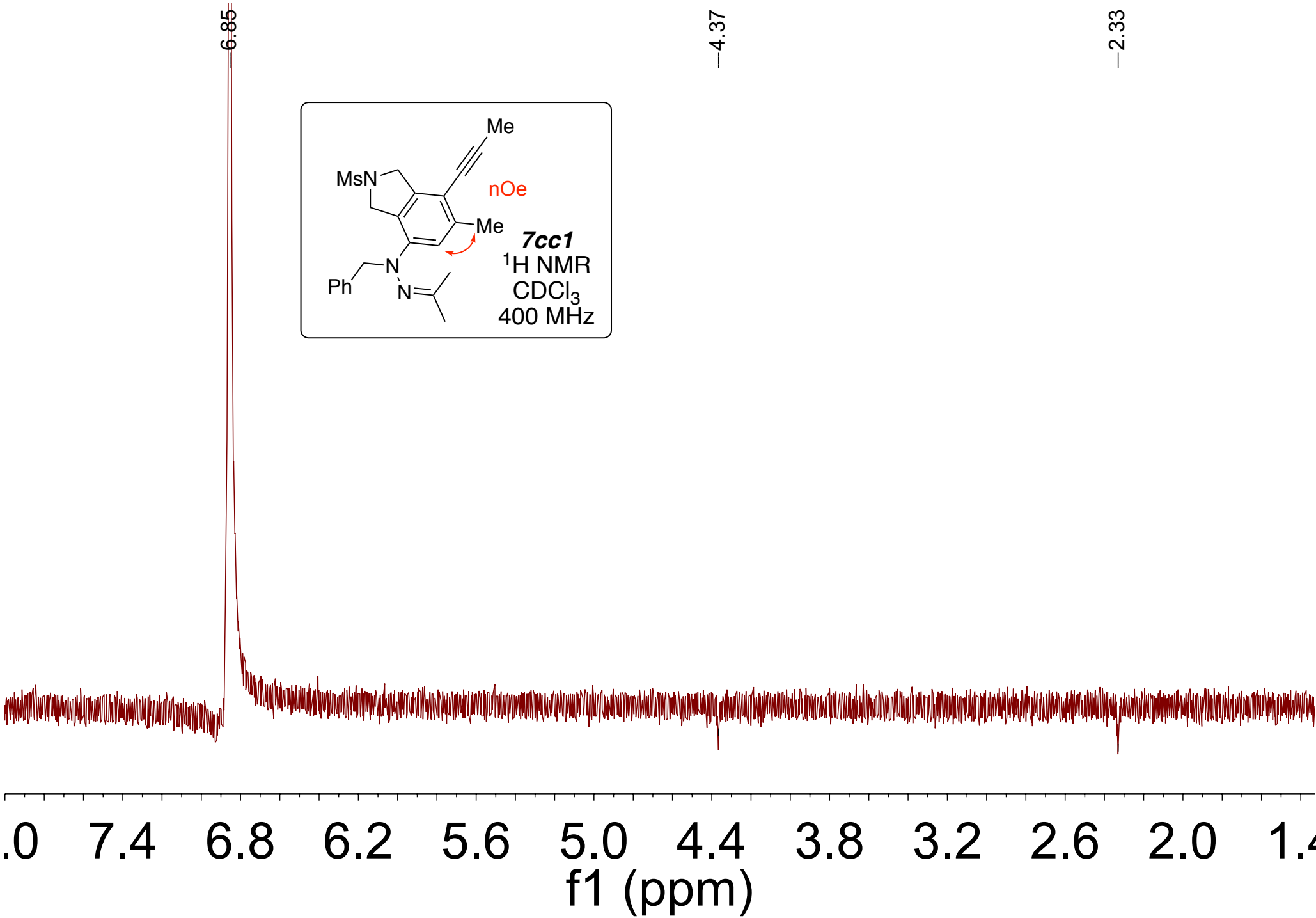
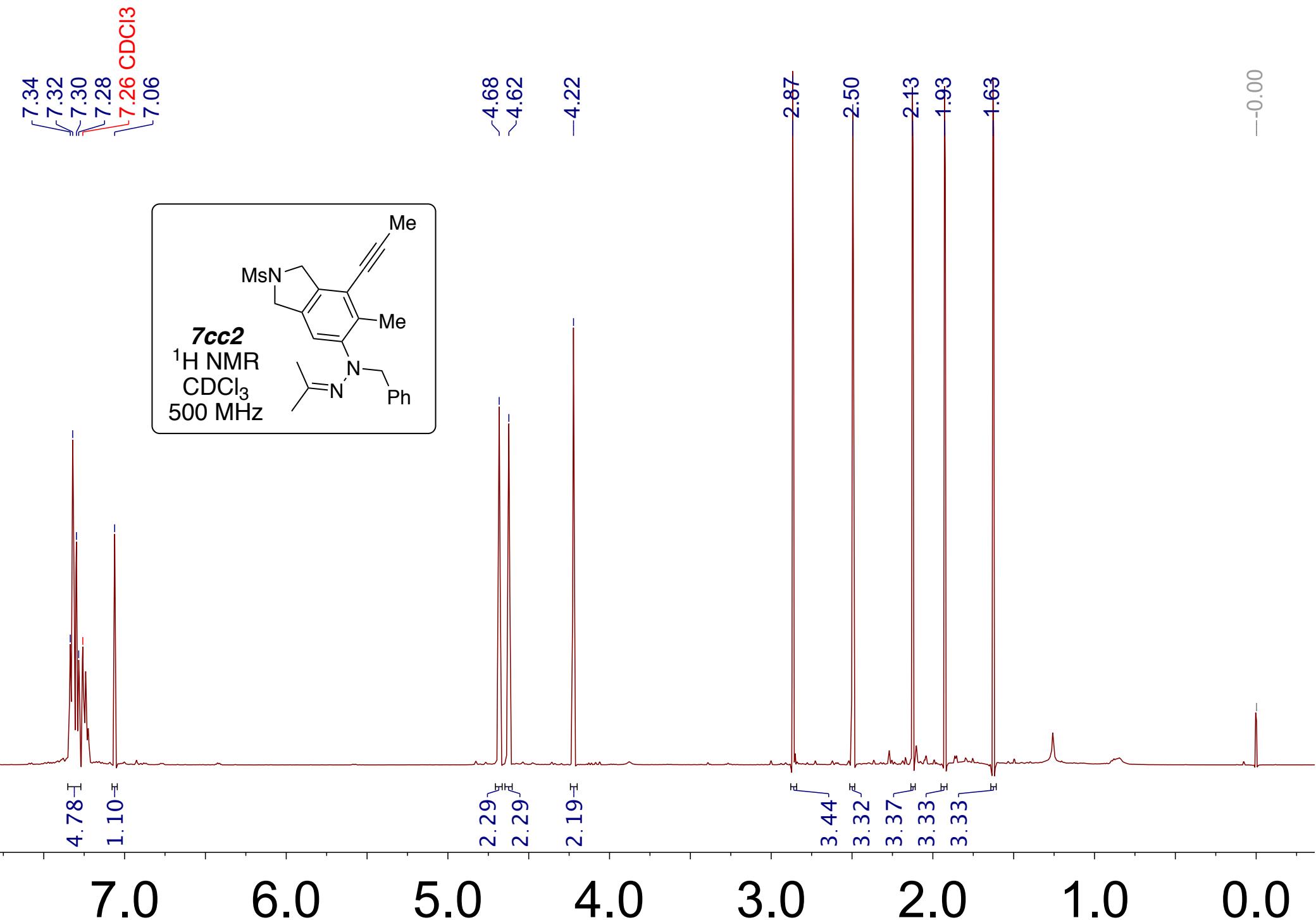
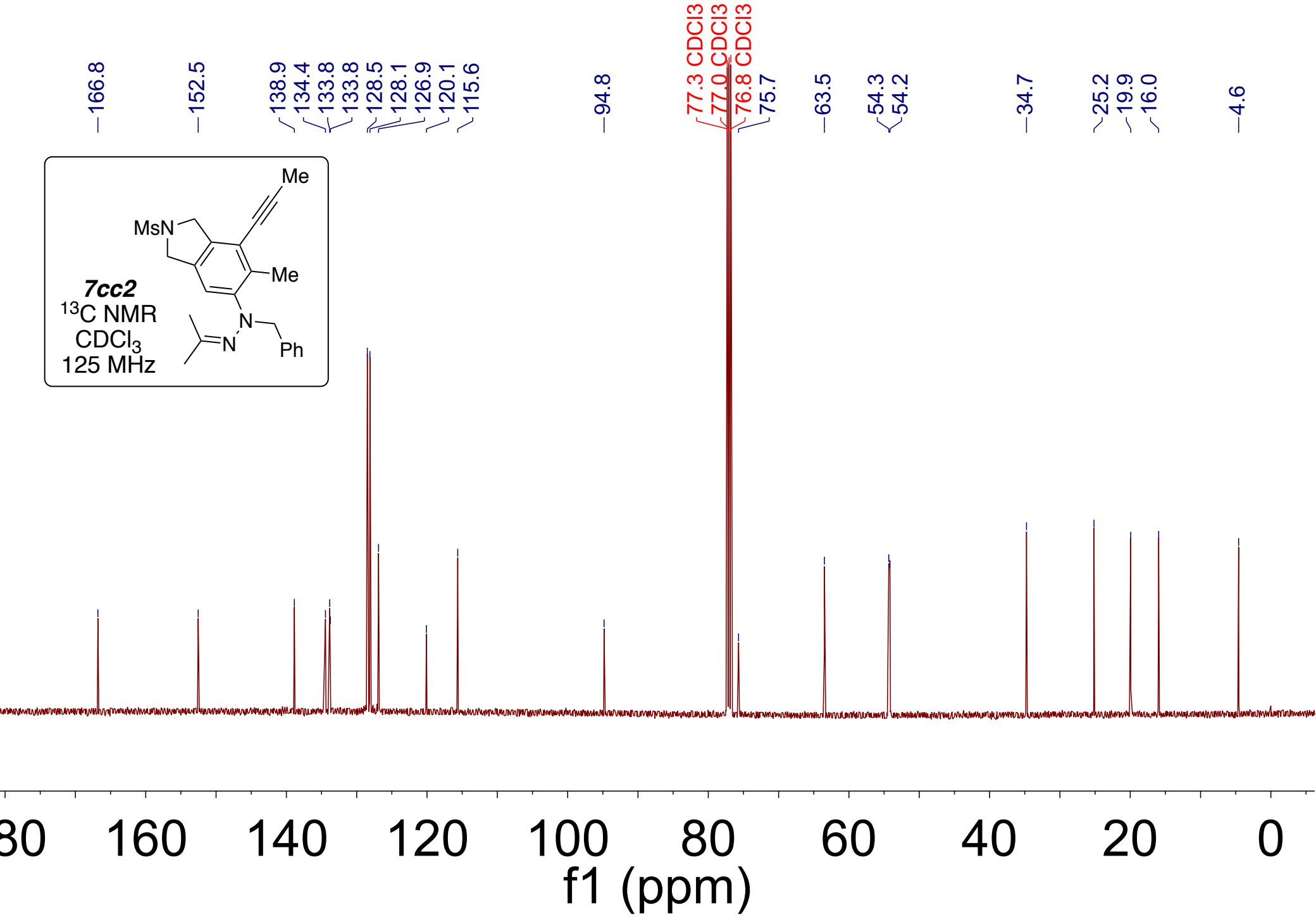
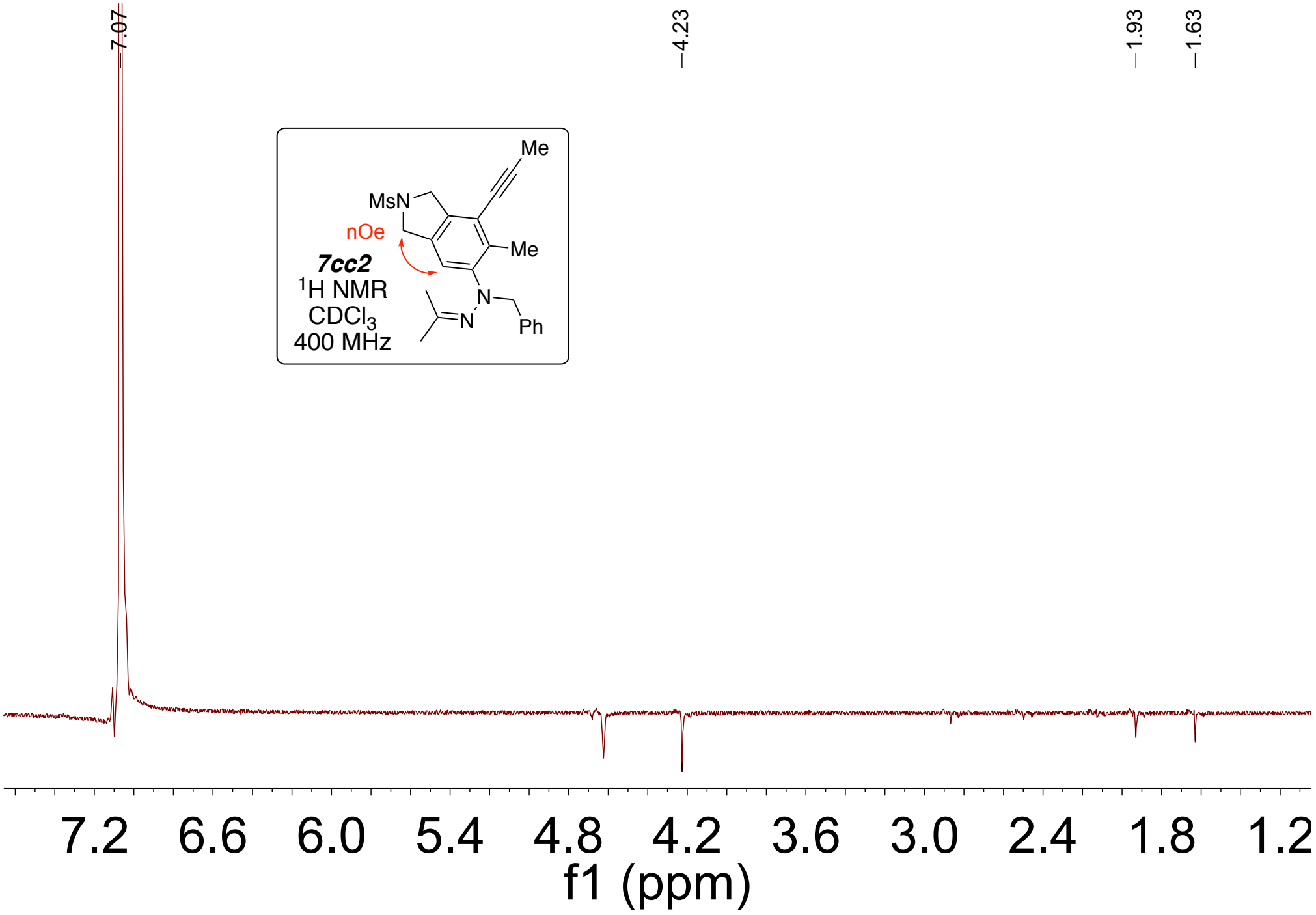
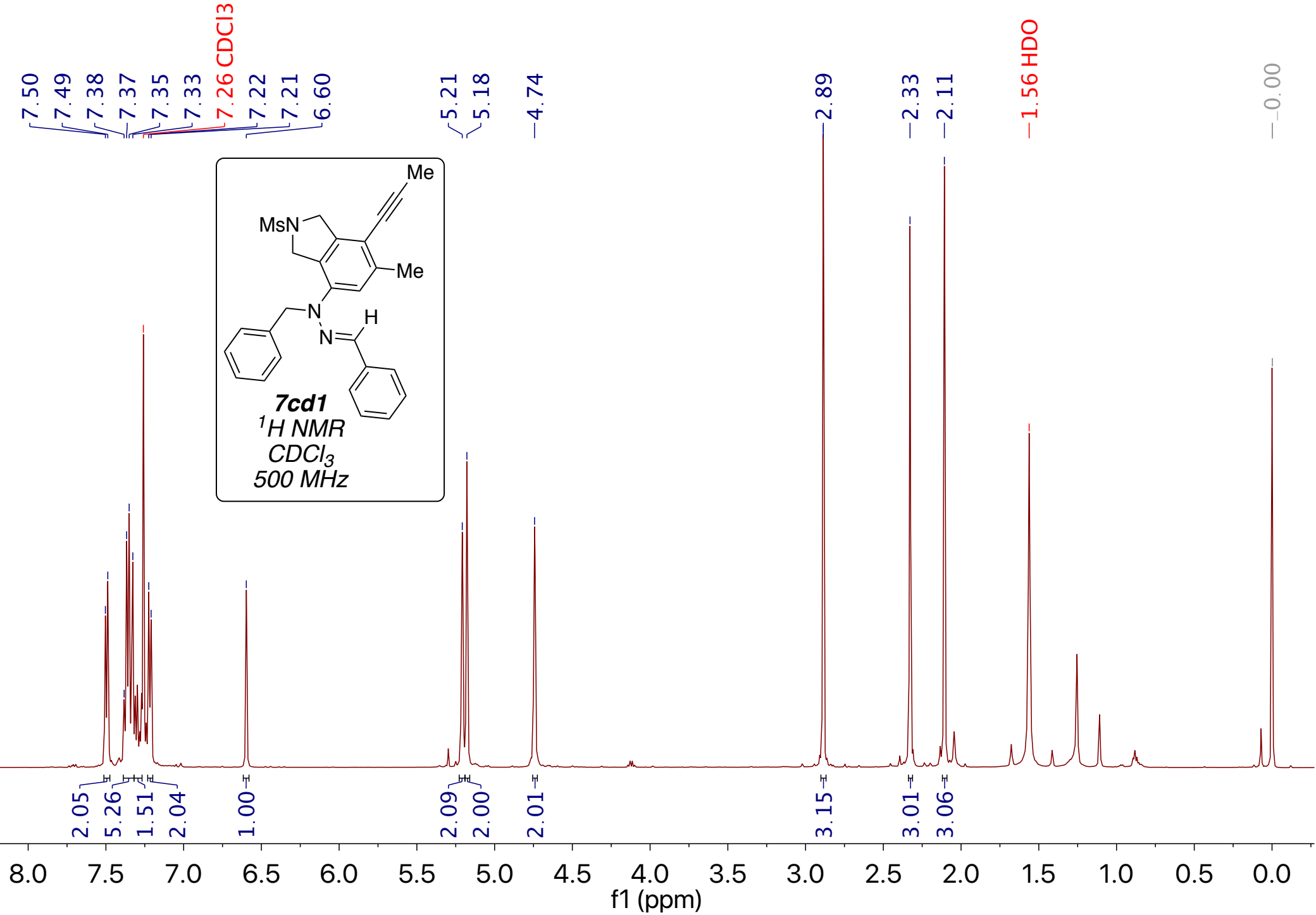
146.4
141.1
140.4
137.9
128.5
128.3
127.2
127.1
125.3
120.1
113.2
93.3
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
75.4
62.0
54.3
54.1
34.5
25.0
20.4
19.7
4.6
0.0
Me
MsN
Me
N
Ph
N
7cc1
13C NMR
CDCl3
125 MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

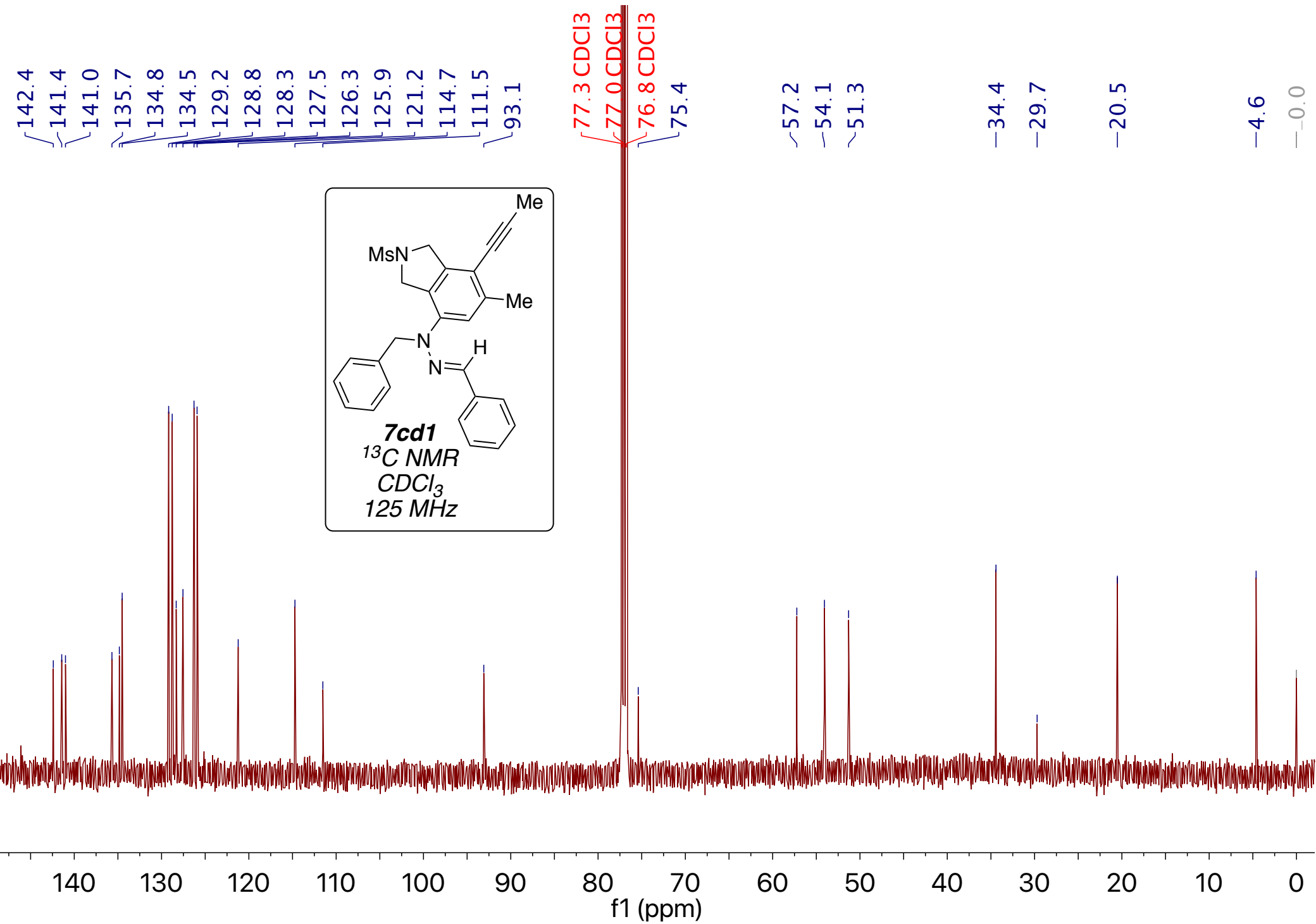

6.85
4.37
2.33
Me
MsN
nOe
Me
N
Ph
N
7cc1
1H NMR
CDCl3
400 MHz
.0 7.4 6.8 6.2 5.6 5.0 4.4 3.8 3.2 2.6 2.0 1.4
f1 (ppm)


7.34
7.32
7.30
7.28
7.26 CDCl3
7.06
4.68
4.62
4.22
2.87
2.50
2.13
1.93
1.63
0.00
Me
MsN
Me
N
N
Ph
7cc2
1H NMR
CDCl3
500 MHz
4.78
1.10
2.29
2.29
2.19
3.44
3.32
3.37
3.33
3.33
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


166.8
152.5
138.9
134.4
133.8
133.8
128.5
128.1
126.9
120.1
115.6
94.8
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
75.7
63.5
54.3
54.2
34.7
25.2
19.9
16.0
4.6
Me
MsN
Me
N
N
Ph
7cc2
13C NMR
CDCl3
125 MHz
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.07
4.23
1.93
1.63
Me
MsN
nOe
Me
7cc2
1H NMR
CDCl3
400 MHz
N
N
Ph
7.2
6.6
6.0
5.4
4.8
4.2
3.6
3.0
2.4
1.8
1.2
f1 (ppm)


7.50
7.49
7.38
7.37
7.35
7.33
7.26 CDCl3
7.22
7.21
6.60
5.21
5.18
4.74
2.89
2.33
2.11
1.56 HDO
0.00
Me
MsN
Me
N
N
H
7cd1
1H NMR
CDCl3
500 MHz
2.05
5.26
1.51
2.04
1.00
2.09
2.00
2.01
3.15
3.01
3.06
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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141.4
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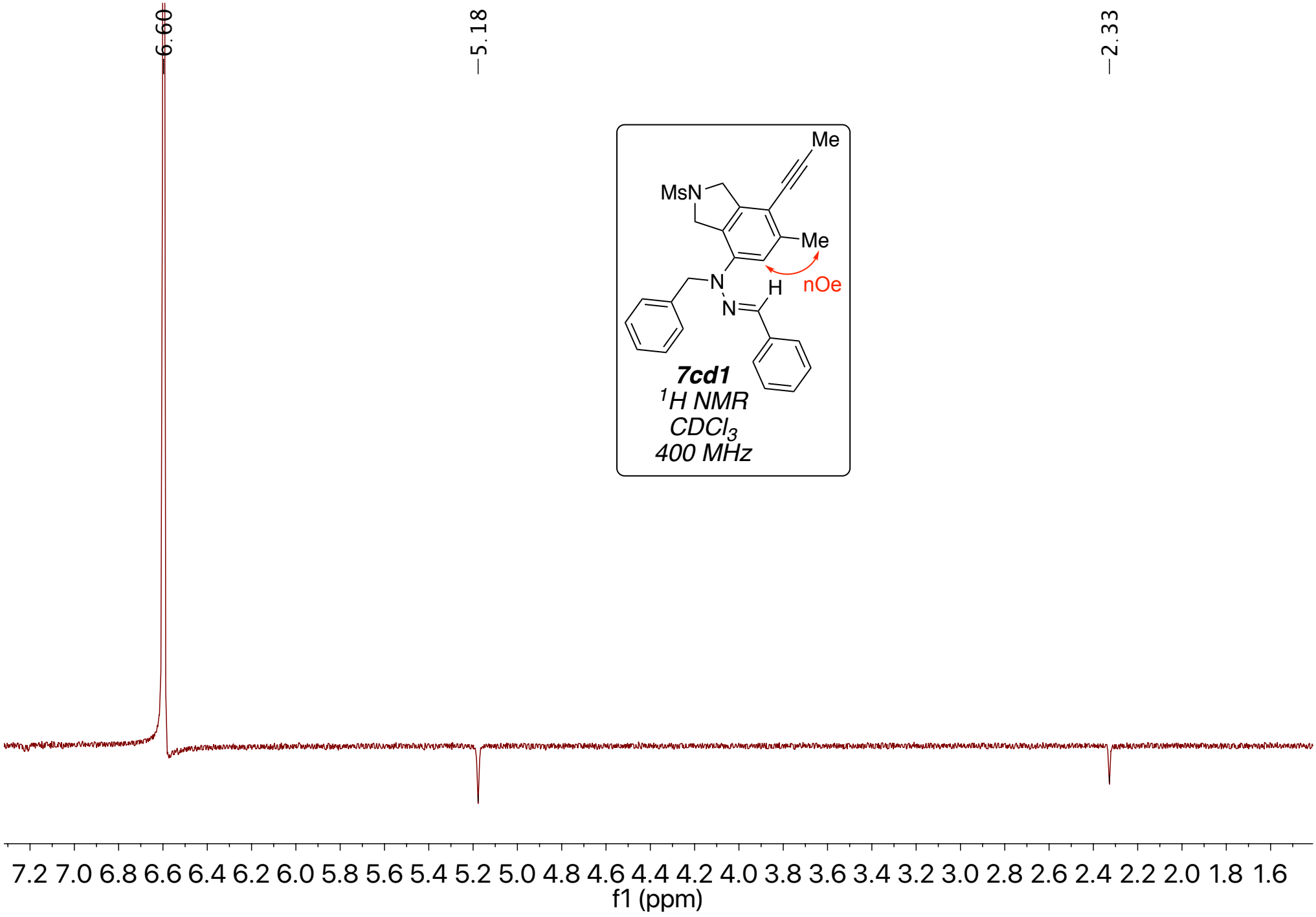
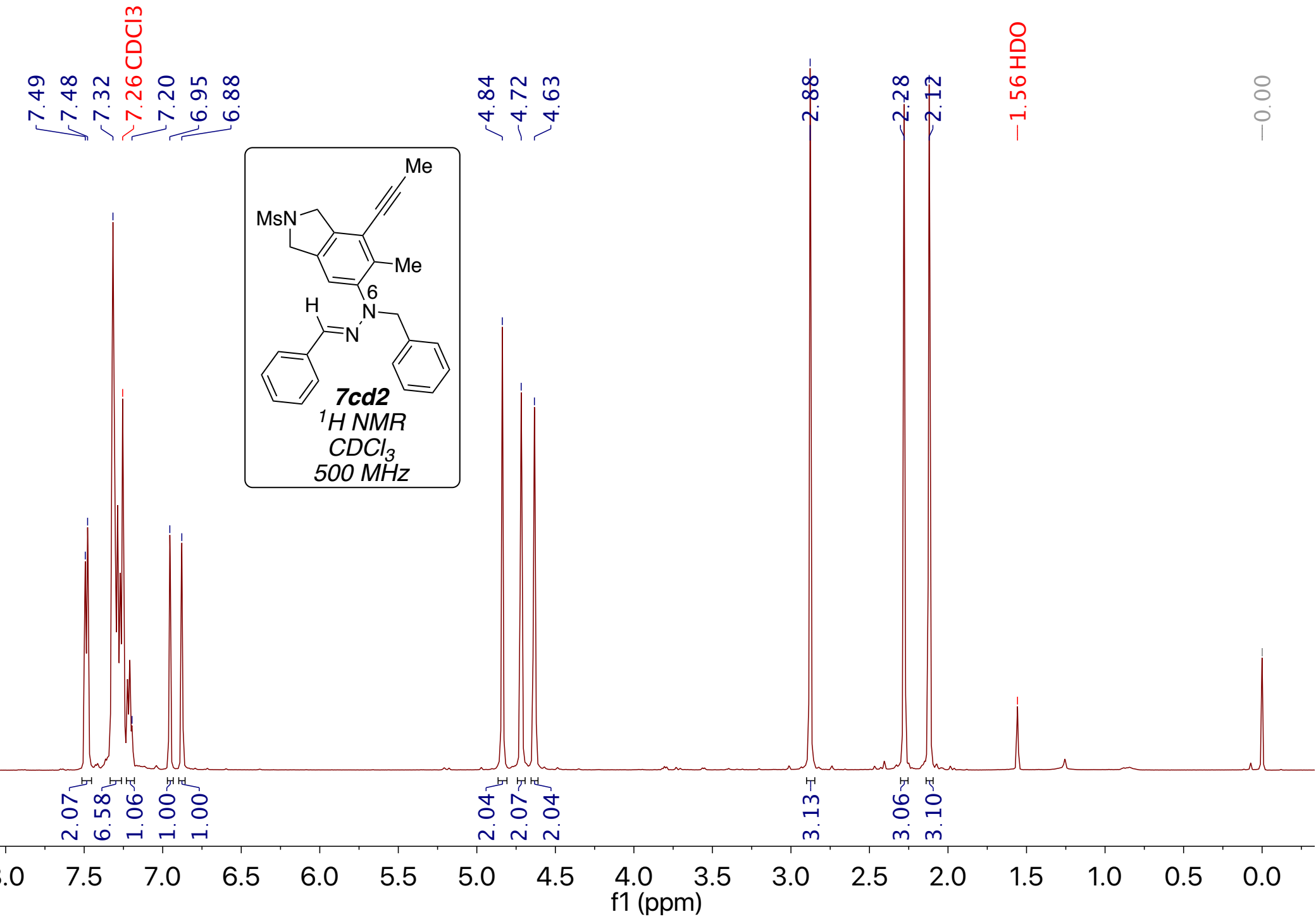
134.5
129.2
128.8
128.3
127.5
126.3
125.9
121.2
114.7
111.5
93.1
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
75.4
57.2
54.1
51.3
34.4
29.7
20.5
4.6
0.0
Me
MsN
Me
N
N
H
7cd1
13C NMR
CDCl3
125 MHz
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.60
5.18
2.33
Me
MsN
Me
N
H
nOe
N
7cd1
1H NMR
CDCl3
400 MHz
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)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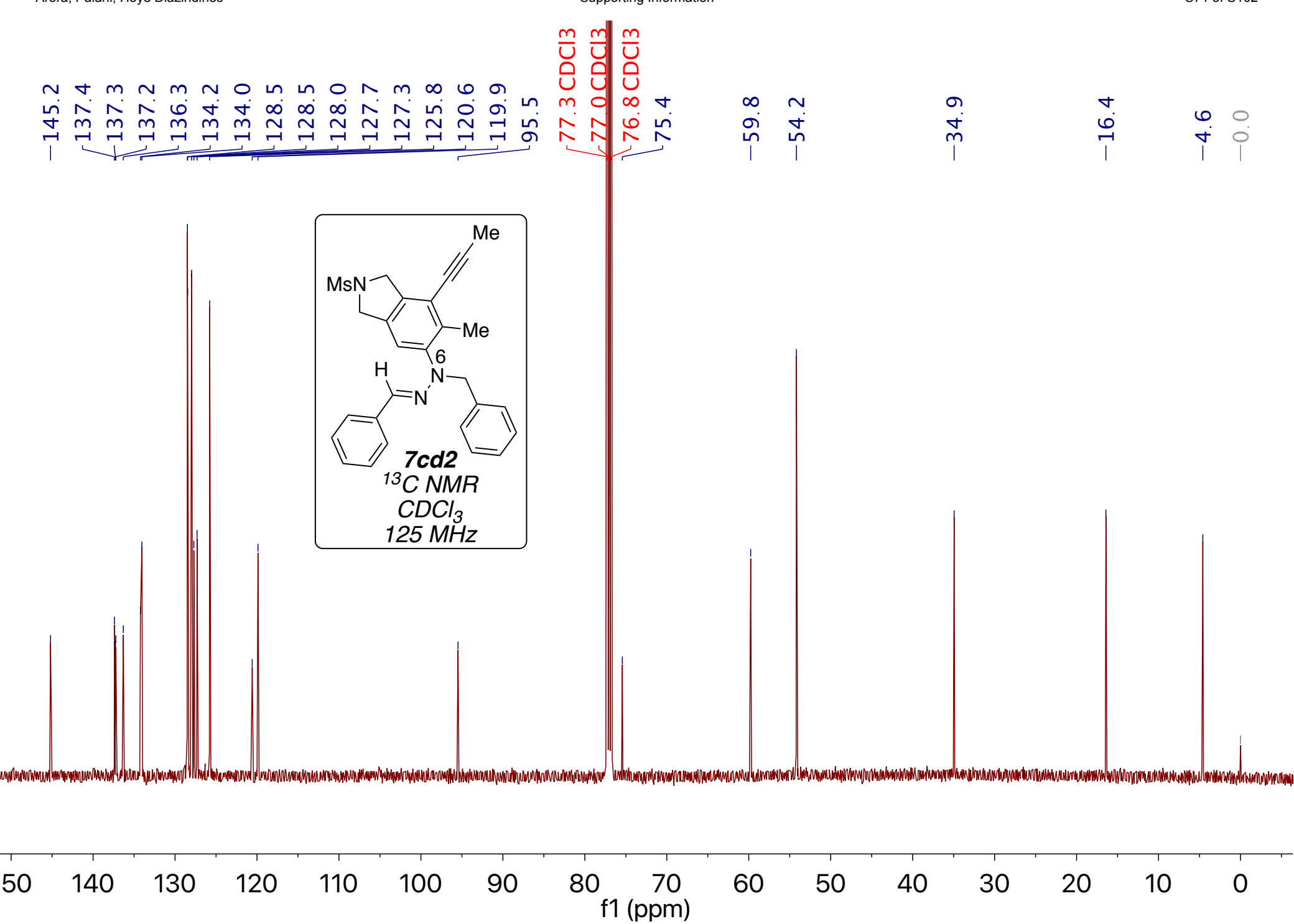
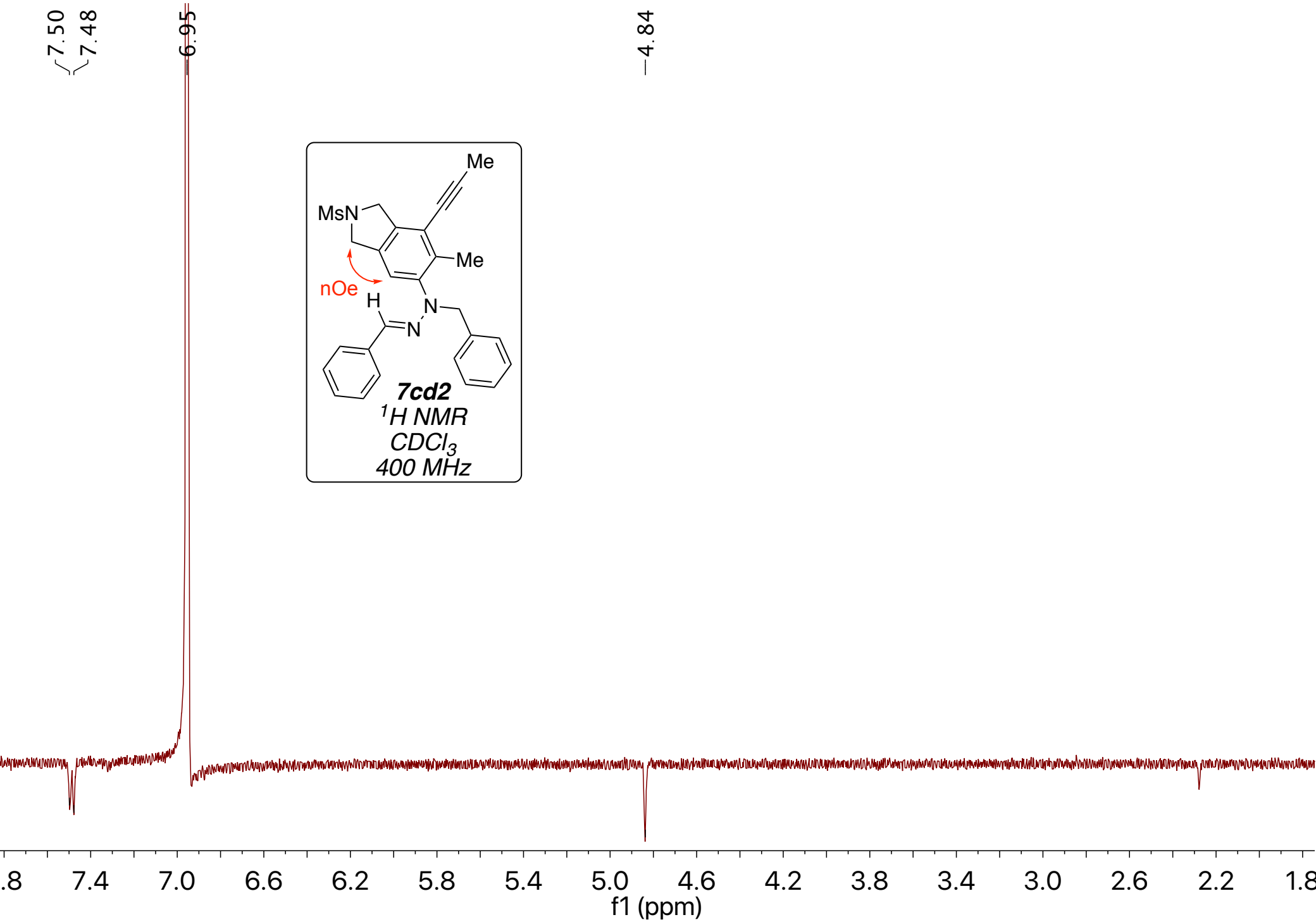
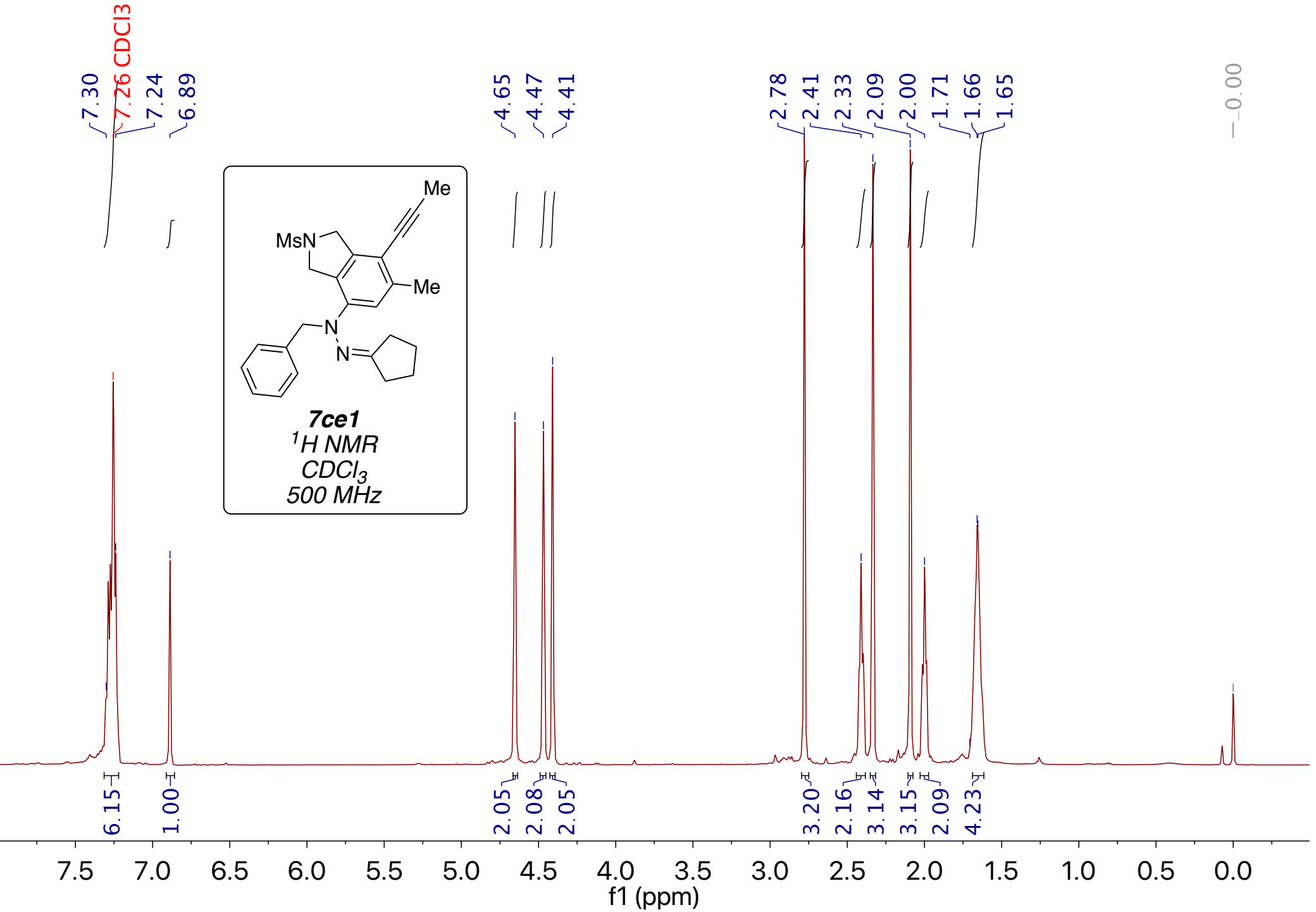
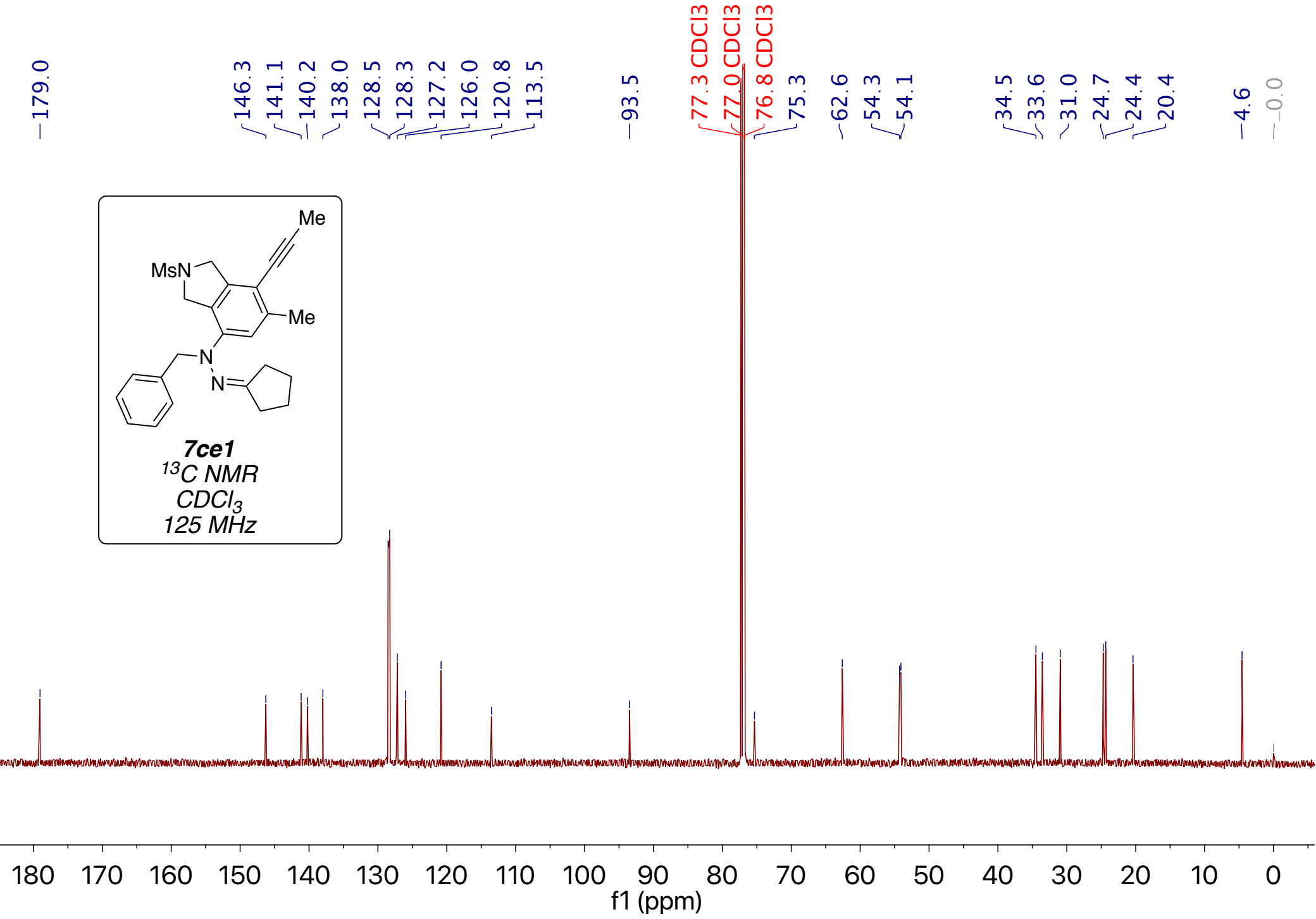
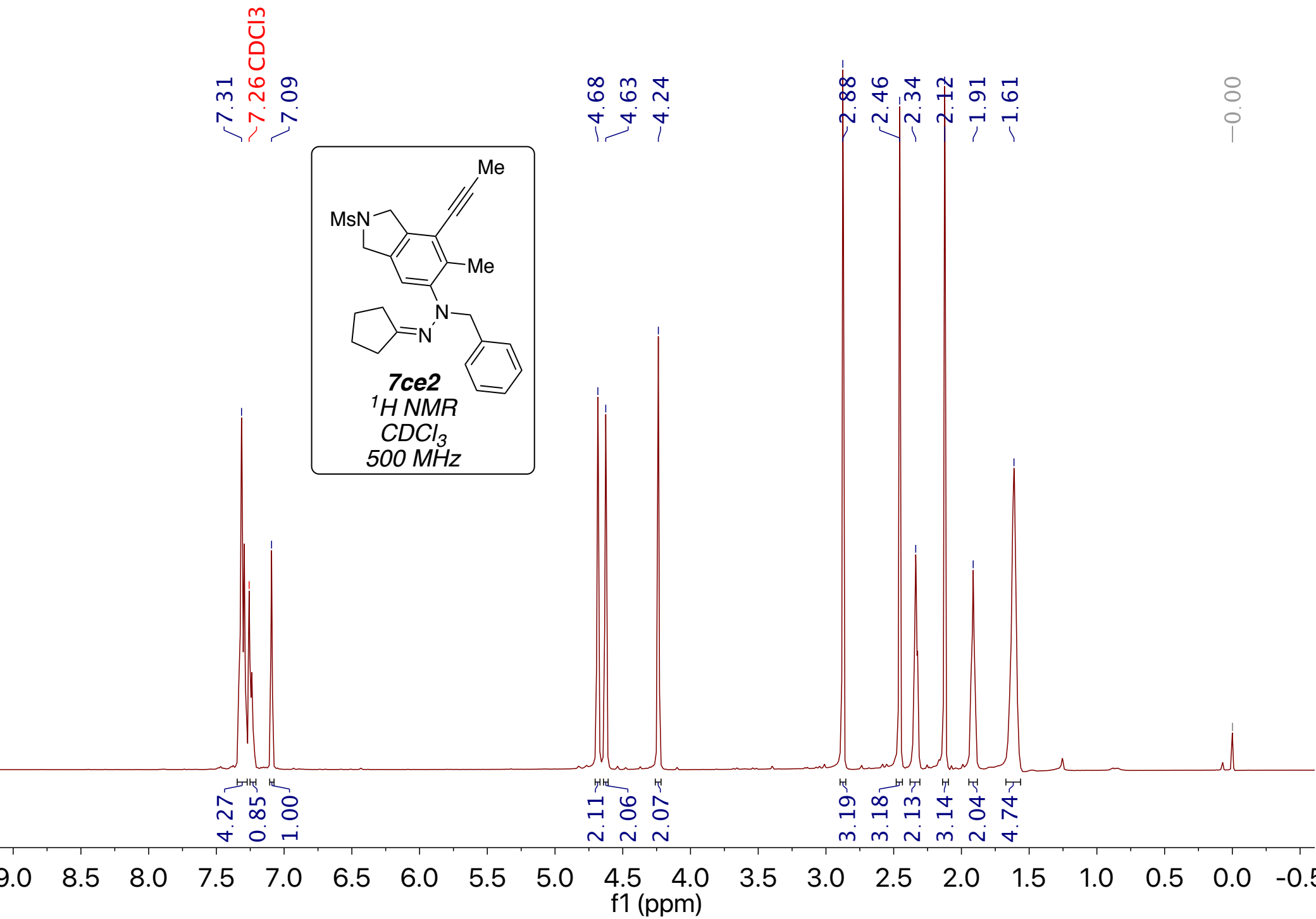
7.48
7.32
7.26 CDCl3
7.20
6.95
6.88
4.84
4.72
4.63
2.88
2.28
2.12
1.56 HDO
0.00
Me
MsN
Me
6
H
N
N
7cd2
1H NMR
CDCl3
500 MHz
2.07
6.58
1.06
1.00
1.00
2.04
2.07
2.04
3.13
3.06
3.10
f1 (ppm)

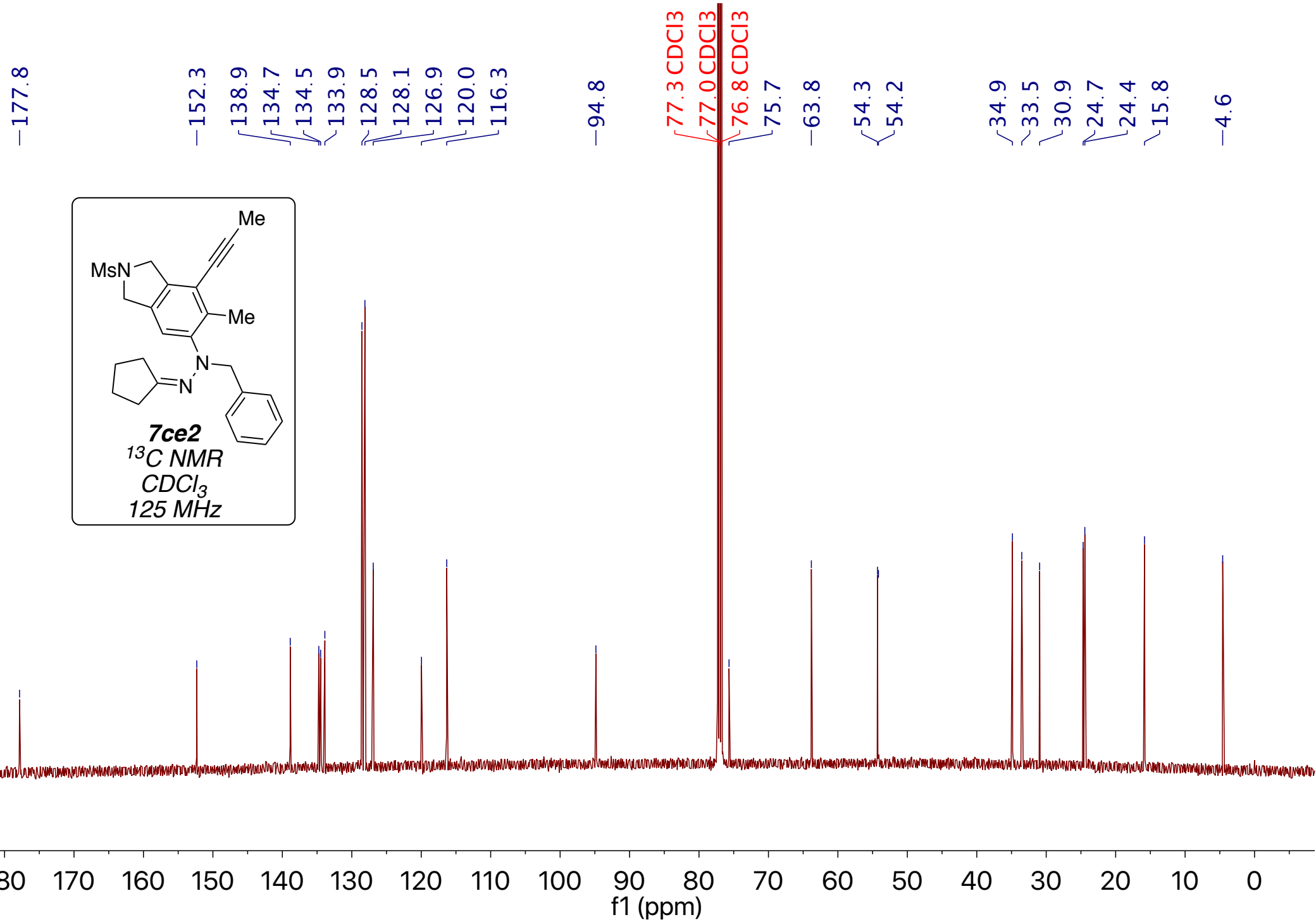

145.2
137.4
137.3
137.2
136.3
134.2
134.0
128.5
128.5
128.0
127.7
127.3
125.8
120.6
119.9
95.5
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
75.4
59.8
54.2
34.9
16.4
4.6
0.0
Me
MsN
Me
6
H
N
N
7cd2
13C NMR
CDCl3
125 MHz
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

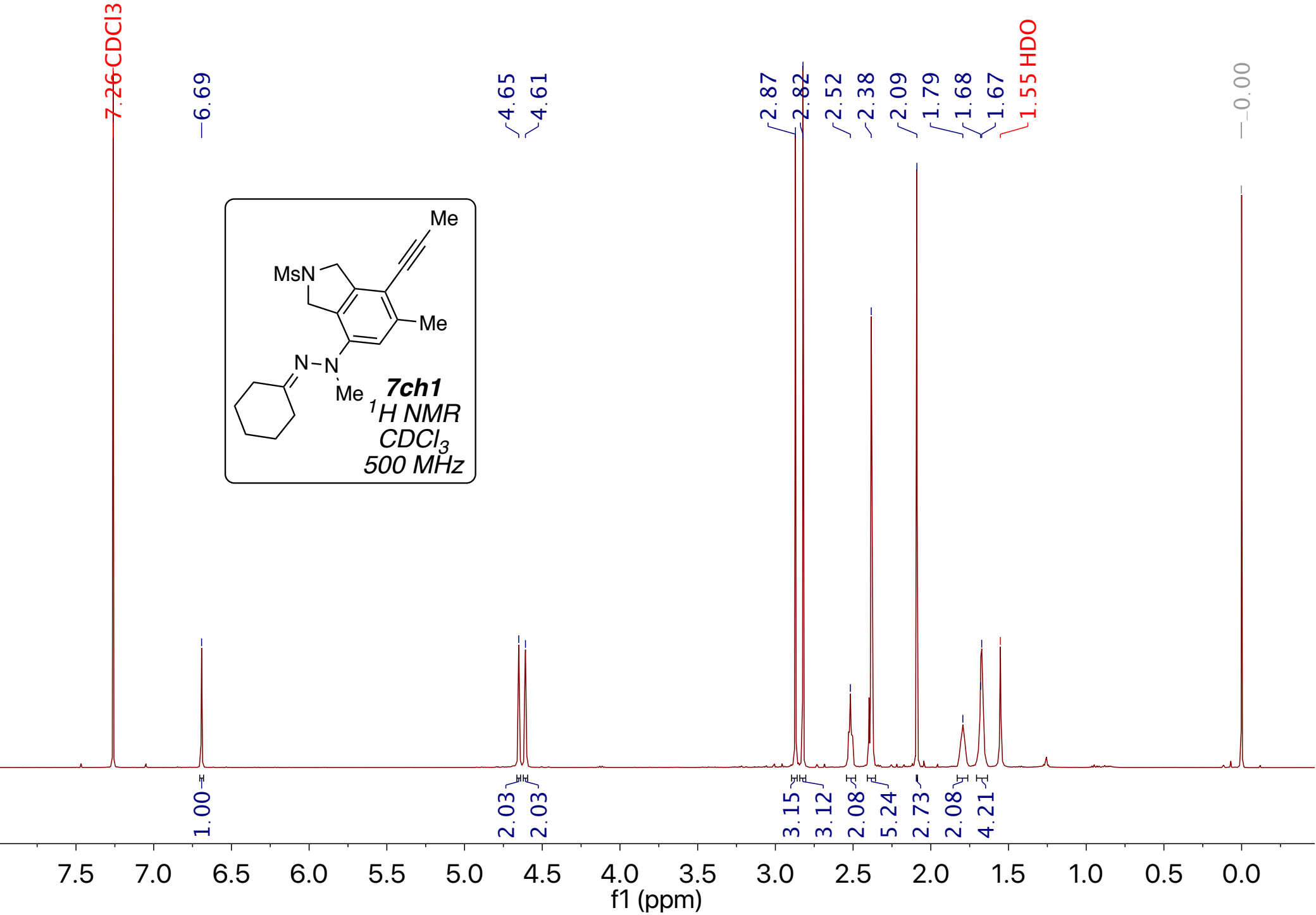

7.50
7.48
6.95
4.84
Me
MsN
Me
nOe
H
N
N
7cd2
1H NMR
CDCl3
400 MHz
.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
f1 (ppm)

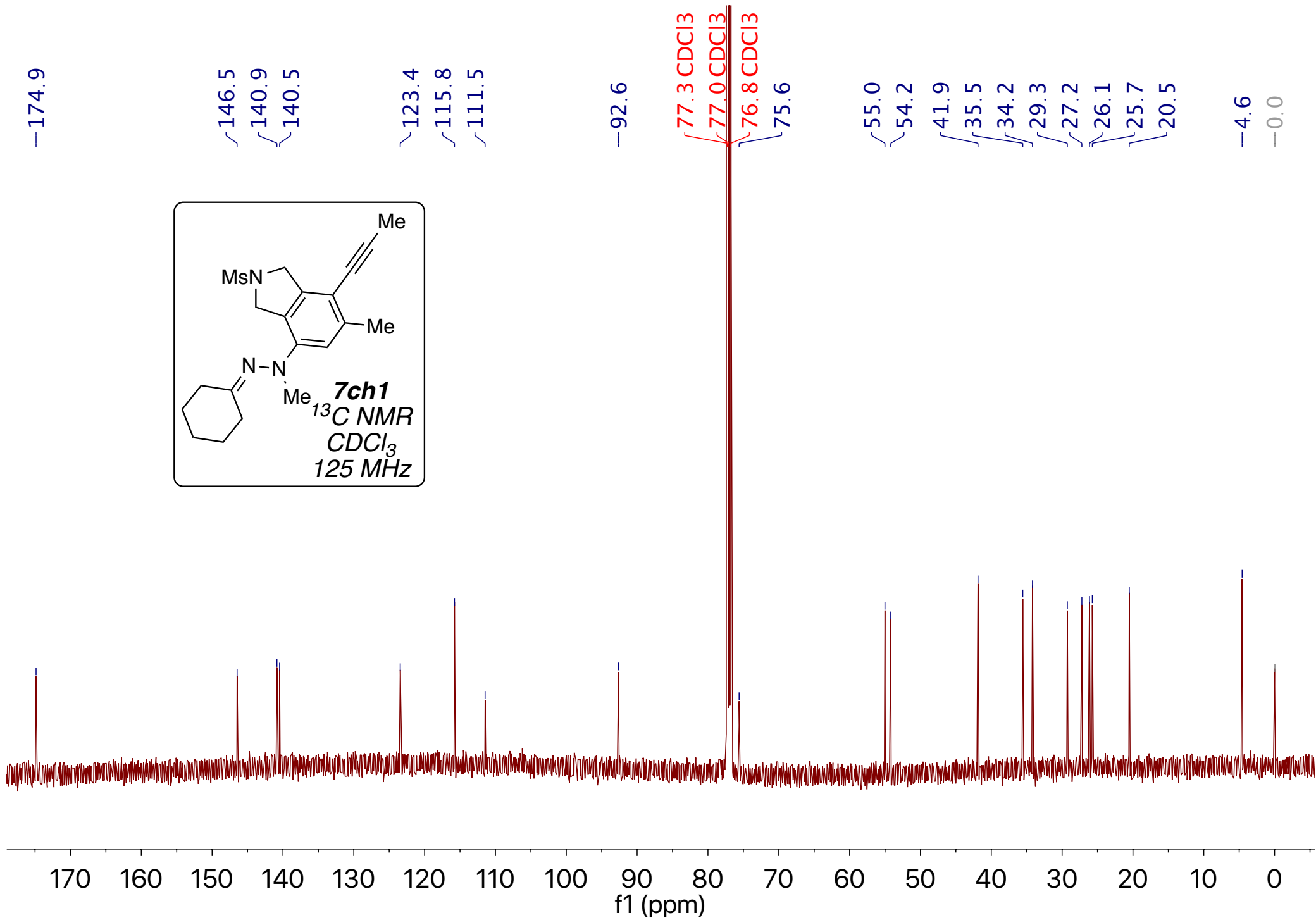

7.30
7.26 CDCl3
7.24
6.89
4.65
4.47
4.41
2.78
2.41
2.33
2.09
2.00
1.71
1.66
1.65
0.00
Me
MsN
Me
N
N
7ce1
1H NMR
CDCl3
500 MHz
6.15
1.00
2.05
2.08
2.05
3.20
2.16
3.14
3.15
2.09
4.23
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

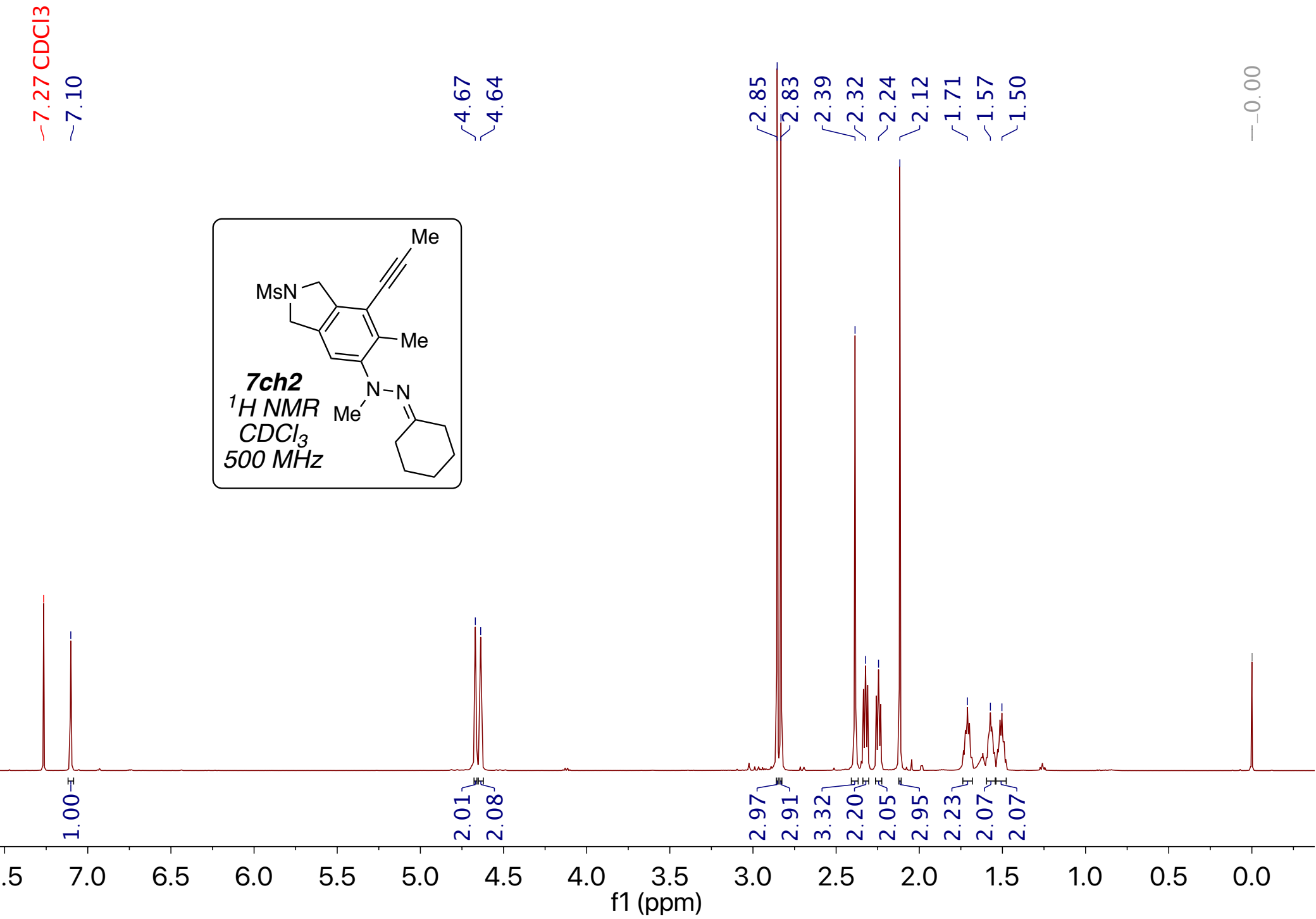

179.0
146.3
141.1
140.2
138.0
128.5
128.3
127.2
126.0
120.8
113.5
93.5
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
75.3
62.6
54.3
54.1
34.5
33.6
31.0
24.7
24.4
20.4
4.6
0.0
Me
MsN
Me
N
N
7ce1
13C NMR
CDCl3
125 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

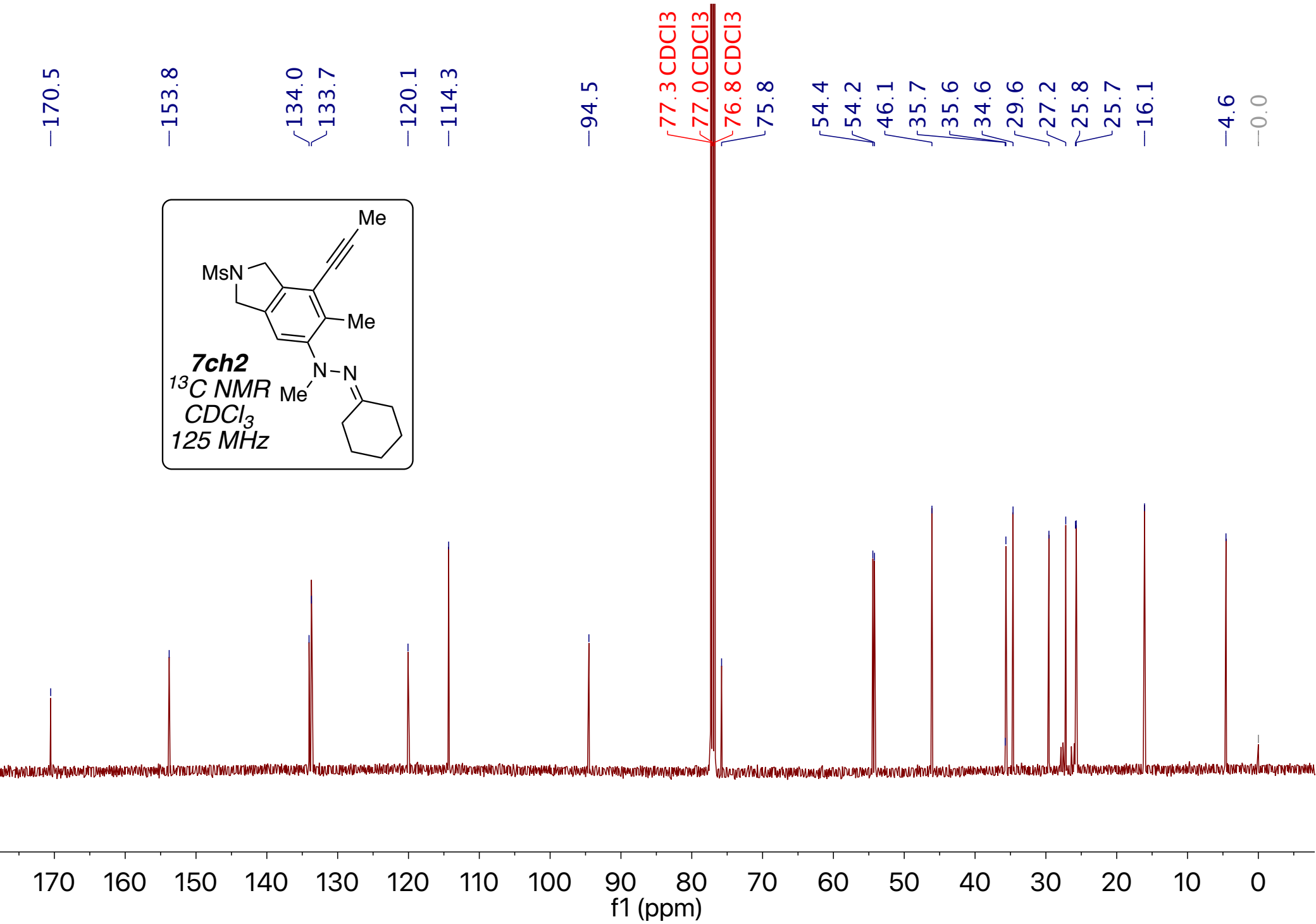

7.31
7.26 CDCl3
7.09
4.68
4.63
4.24
2.88
2.46
2.34
2.12
1.91
1.61
0.00
Me
MsN
Me
N
N
7ce2
1H NMR
CDCl3
500 MHz
4.27
0.85
1.00
2.11
2.06
2.07
3.19
3.18
2.13
3.14
2.04
4.74
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

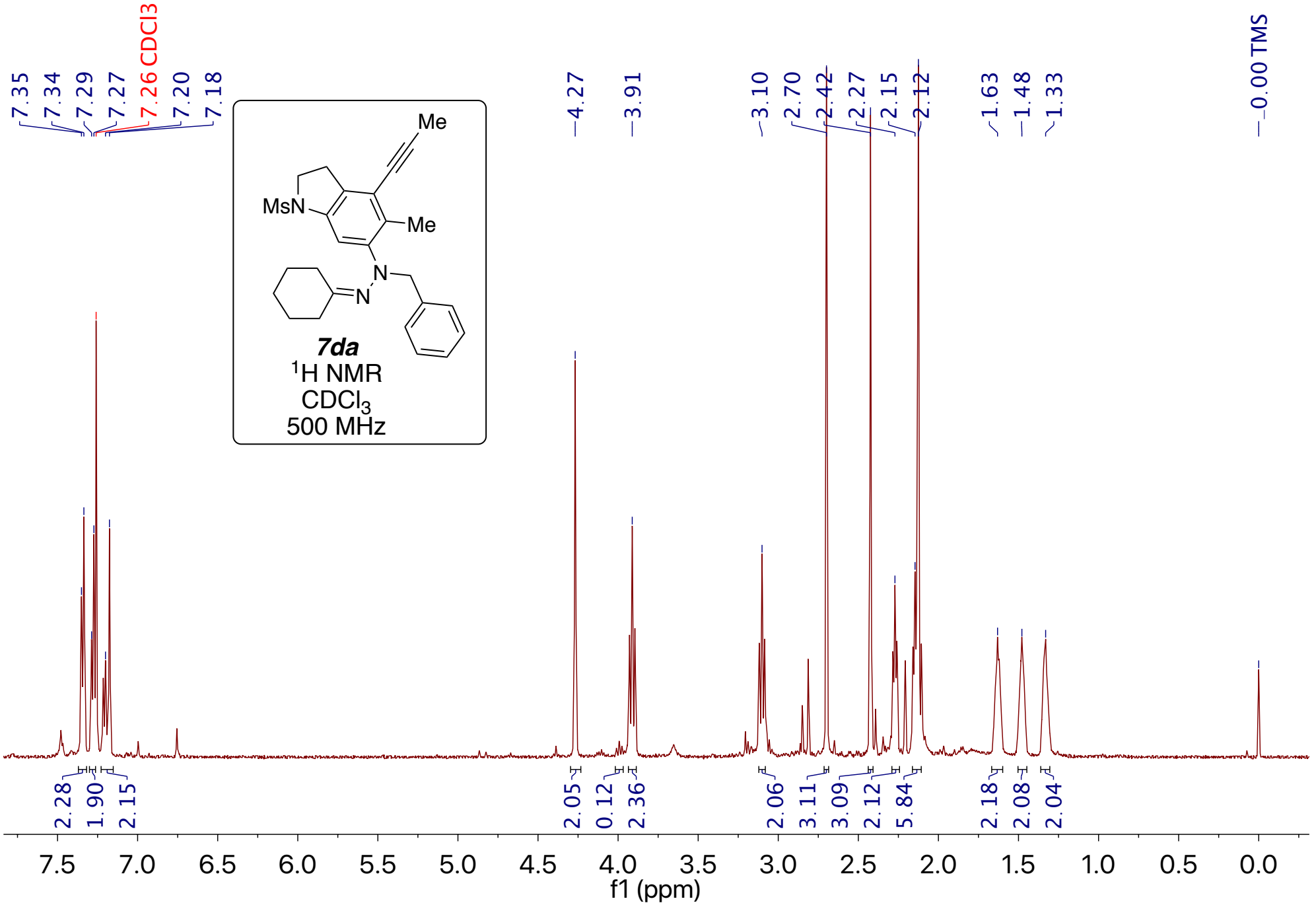

177.8
152.3
138.9
134.7
134.5
133.9
128.5
128.1
126.9
120.0
116.3
94.8
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
75.7
63.8
54.3
54.2
34.9
33.5
30.9
24.7
24.4
15.8
4.6
Me
MsN
Me
N
N
7ce2
13C NMR
CDCl3
125 MHz
f1 (ppm)


7.26 CDCl3
6.69
4.65
4.61
2.87
2.82
2.52
2.38
2.09
1.79
1.68
1.67
1.55 HDO
0.00
Me
MsN
Me
N–N
Me
7ch1
1H NMR
CDCl3
500 MHz
1.00
2.03
2.03
3.15
3.12
2.08
5.24
2.73
2.08
4.21
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)


174.9
146.5
140.9
140.5
123.4
115.8
111.5
92.6
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
75.6
55.0
54.2
41.9
35.5
34.2
29.3
27.2
26.1
25.7
20.5
4.6
0.0
Me
MsN
Me
N–N
Me
7ch1
13C NMR
CDCl3
125 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.27 CDCl3
7.10
4.67
4.64
2.85
2.83
2.39
2.32
2.24
2.12
1.71
1.57
1.50
0.00
Me
MsN
Me
N–N
Me
7ch2
1H NMR
CDCl3
500 MHz
1.00
2.01
2.08
2.97
2.91
3.32
2.20
2.05
2.95
2.23
2.07
2.07
f1 (ppm)


170.5
153.8
134.0
133.7
120.1
114.3
94.5
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
75.8
54.4
54.2
46.1
35.7
35.6
34.6
29.6
27.2
25.8
25.7
16.1
4.6
0.0
Me
MsN
Me
N–N
Me
7ch2
13C NMR
CDCl3
125 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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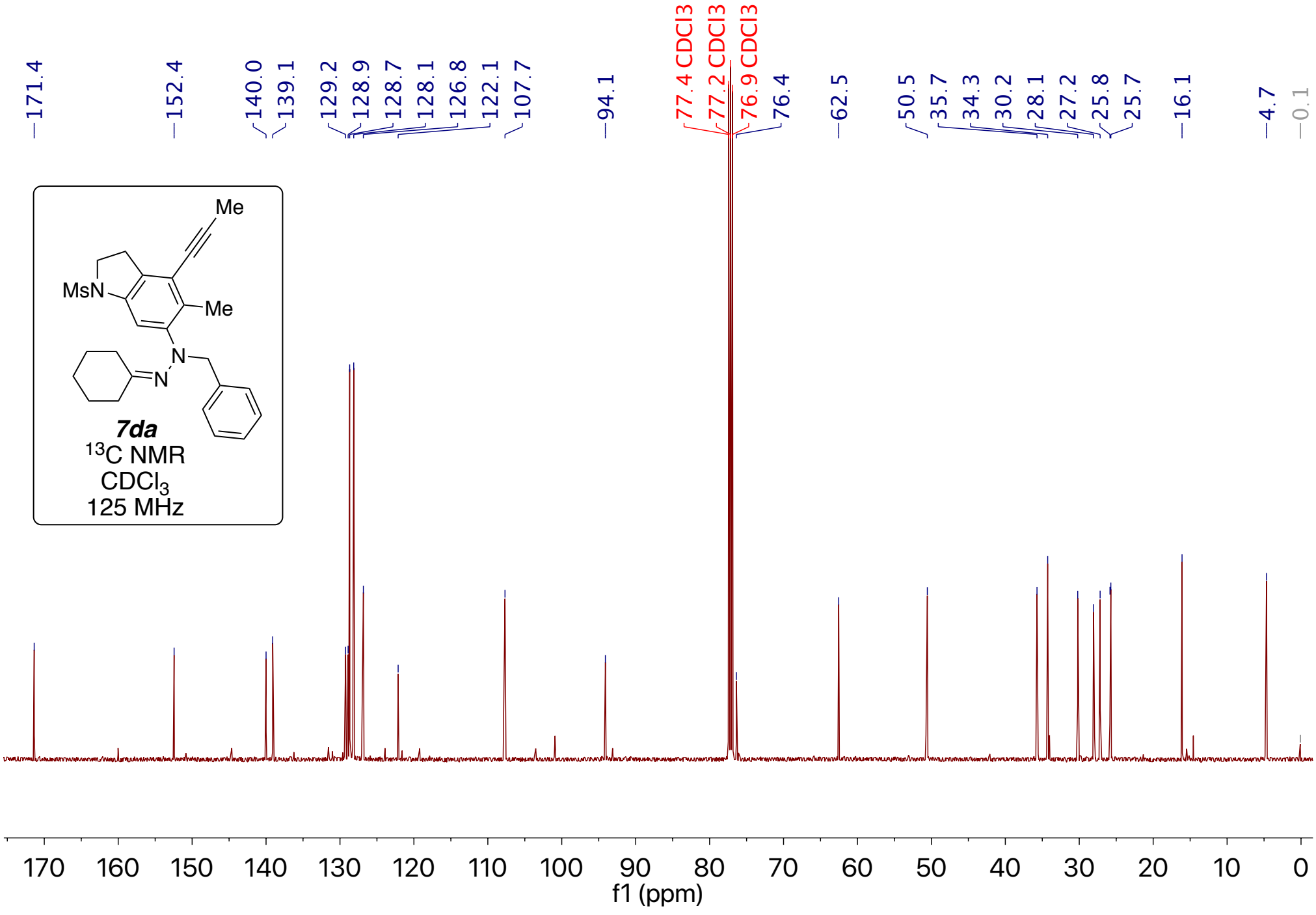
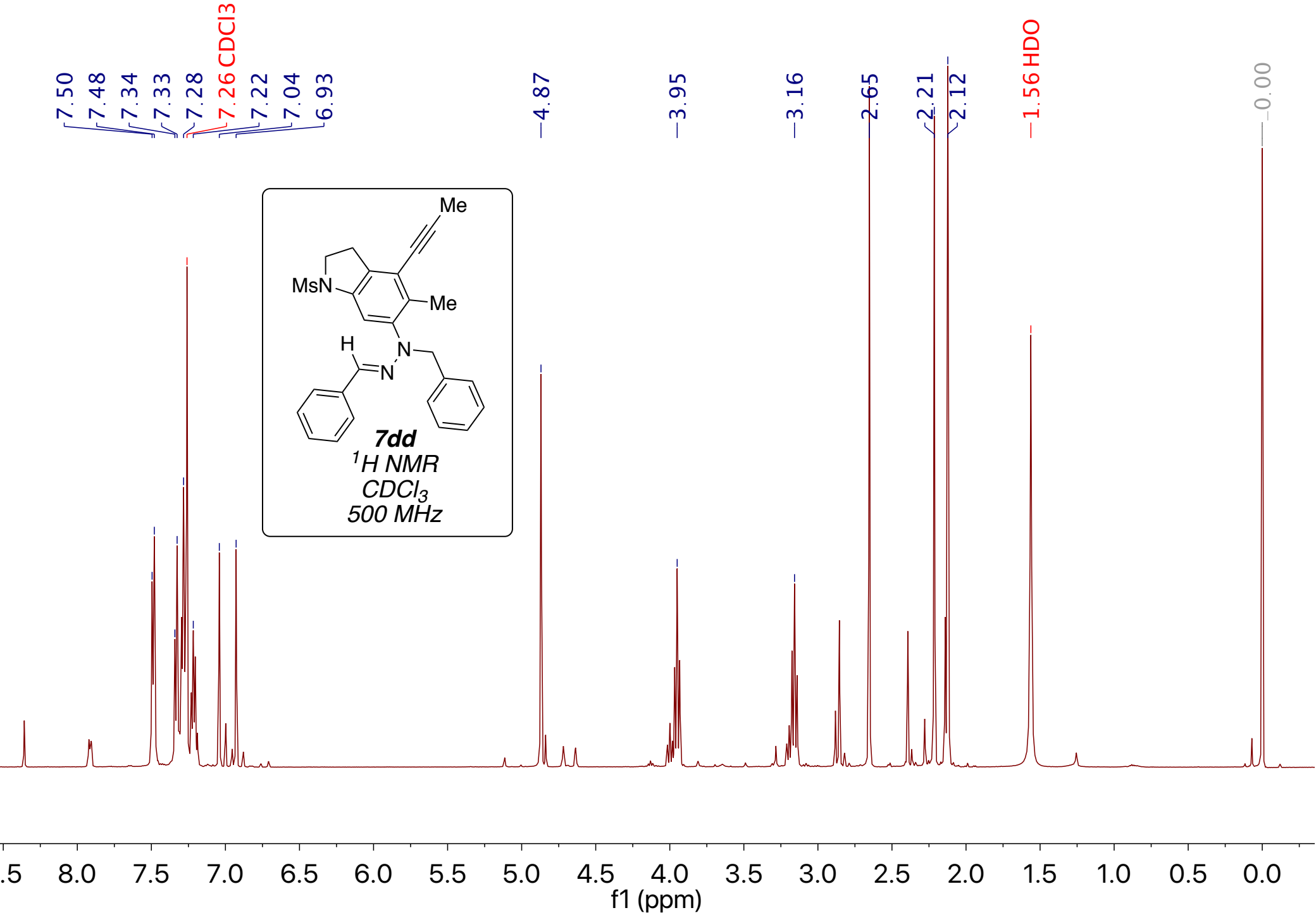
7.34
7.29
7.27
7.26 CDCl3
7.20
7.18
4.27
3.91
3.10
2.70
2.42
2.27
2.15
2.12
1.63
1.48
1.33
0.00 TMS
Me
MsN
Me
N
N
7da
1H NMR
CDCl3
500 MHz
2.28
1.90
2.15
2.05
0.12
2.36
2.06
3.11
3.09
2.12
5.84
2.18
2.08
2.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


171.4
152.4
140.0
139.1
129.2
128.9
128.7
128.1
126.8
122.1
107.7
94.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.4
62.5
50.5
35.7
34.3
30.2
28.1
27.2
25.8
25.7
16.1
4.7
0.1
Me
MsN
Me
N
N
7da
13C NMR
CDCl3
125 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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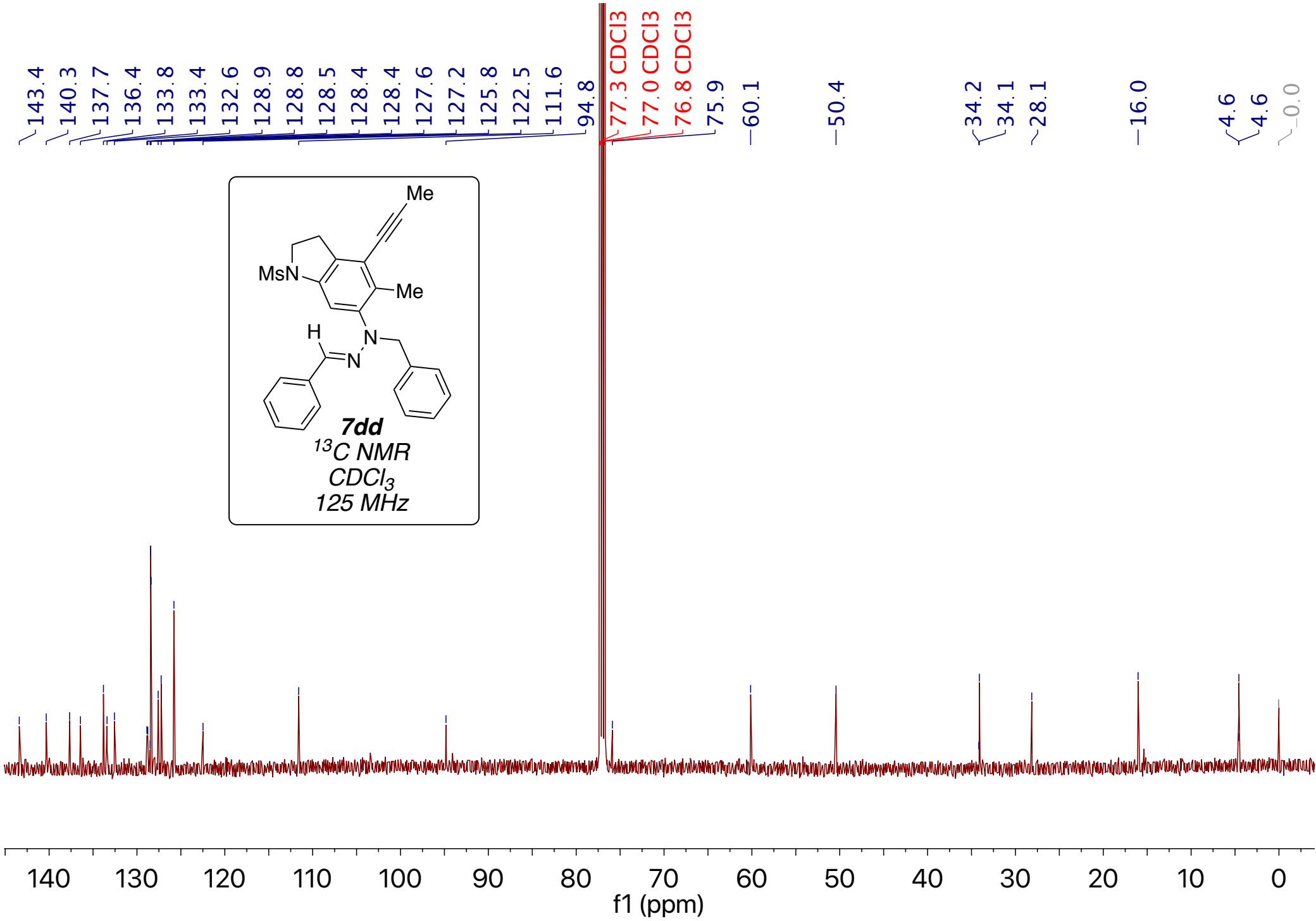
7.48
7.34
7.33
7.28
7.26 CDCl3
7.22
7.04
6.93
4.87
3.95
3.16
2.65
2.21
2.12
1.56 HDO
0.00
Me
MsN
Me
H
N
N
7dd
1H NMR
CDCl3
500 MHz
f1 (ppm)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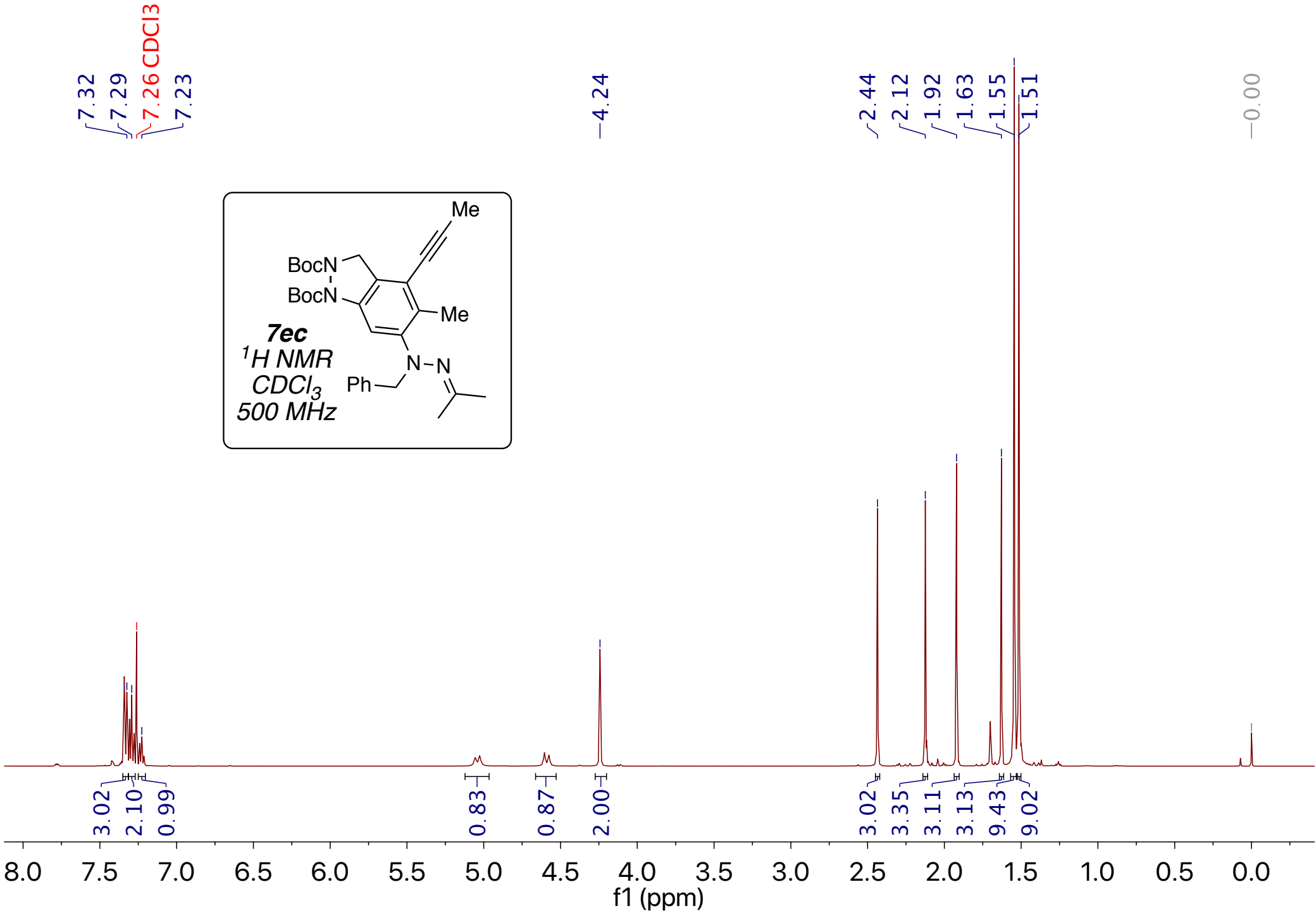
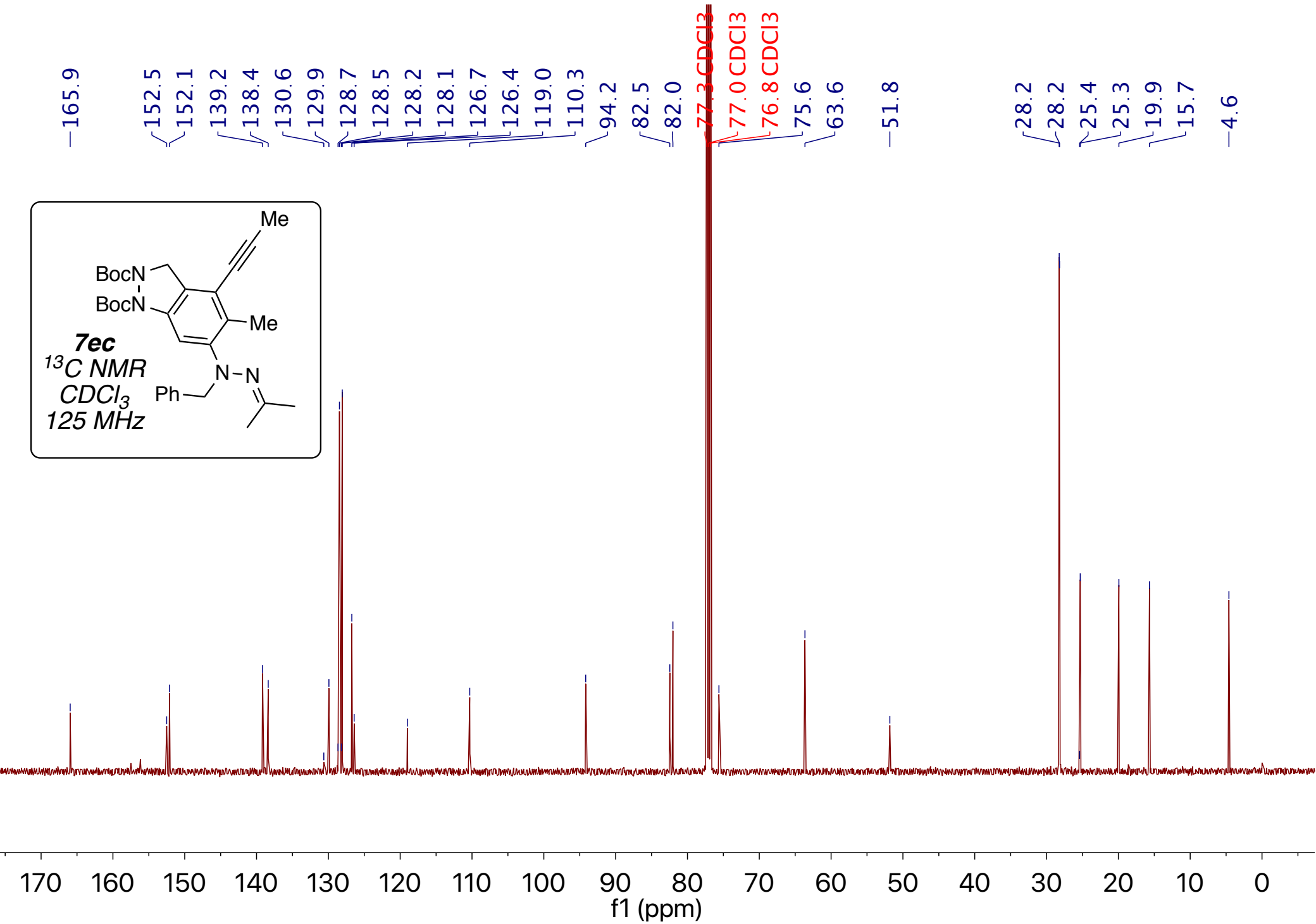
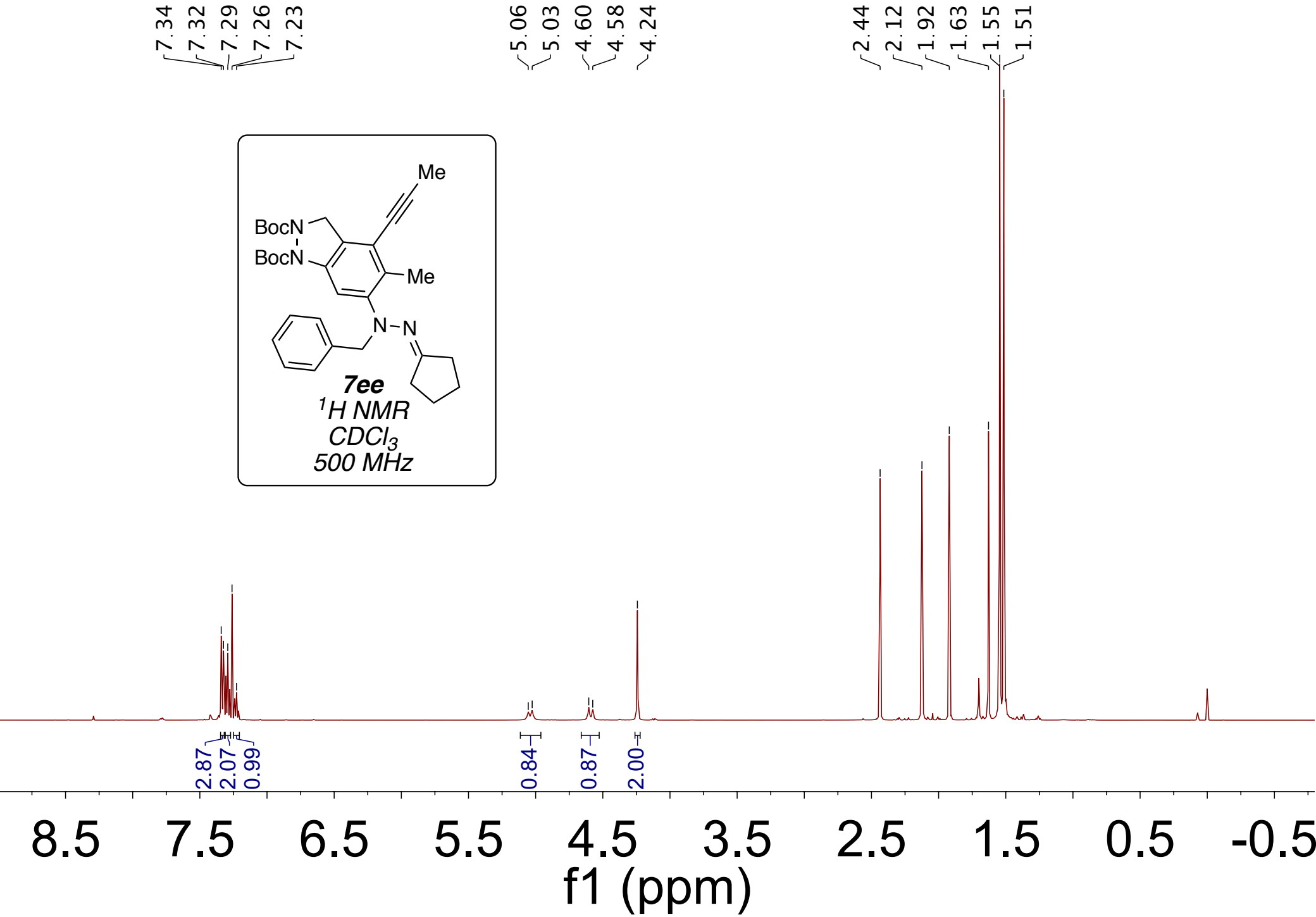
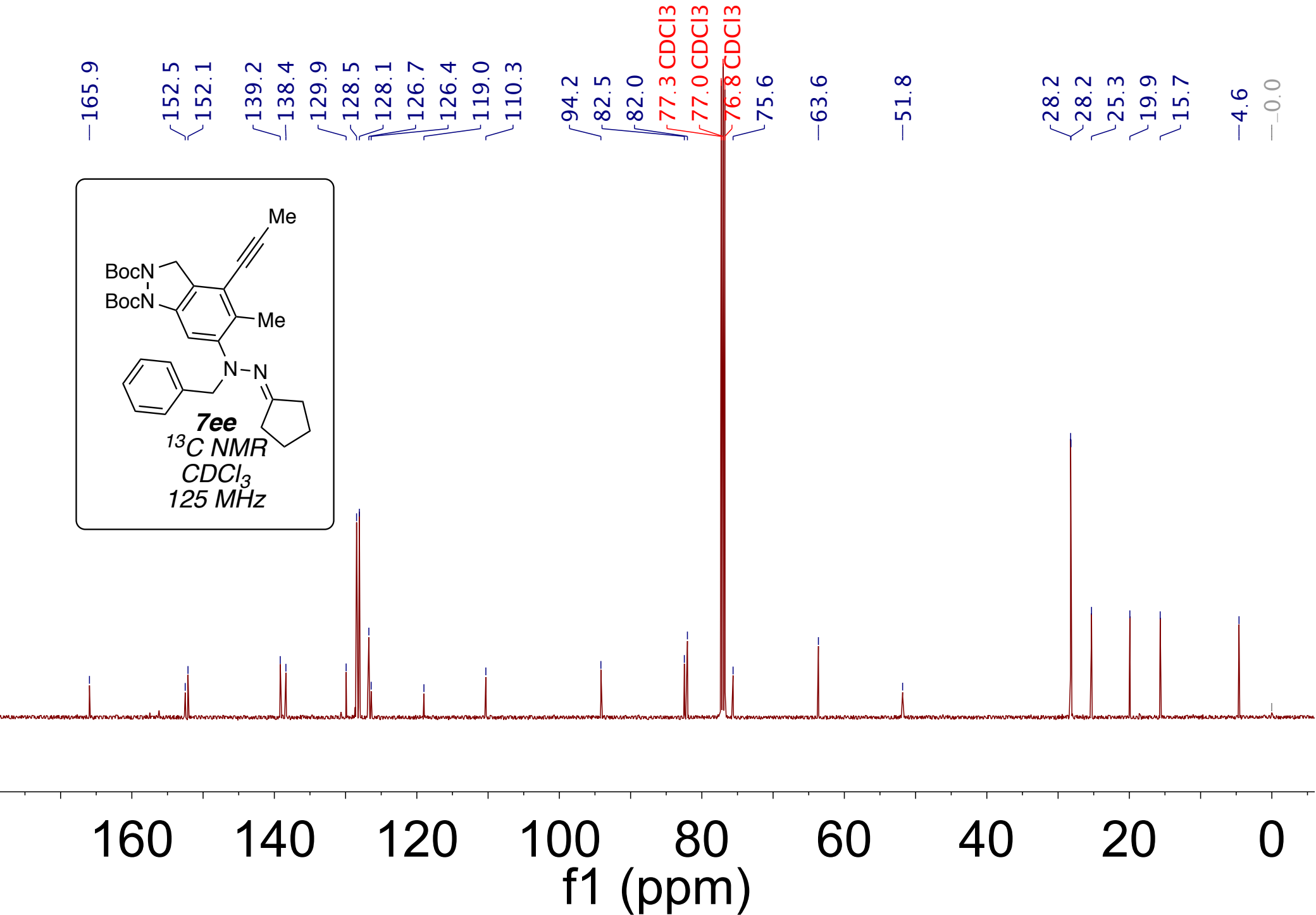
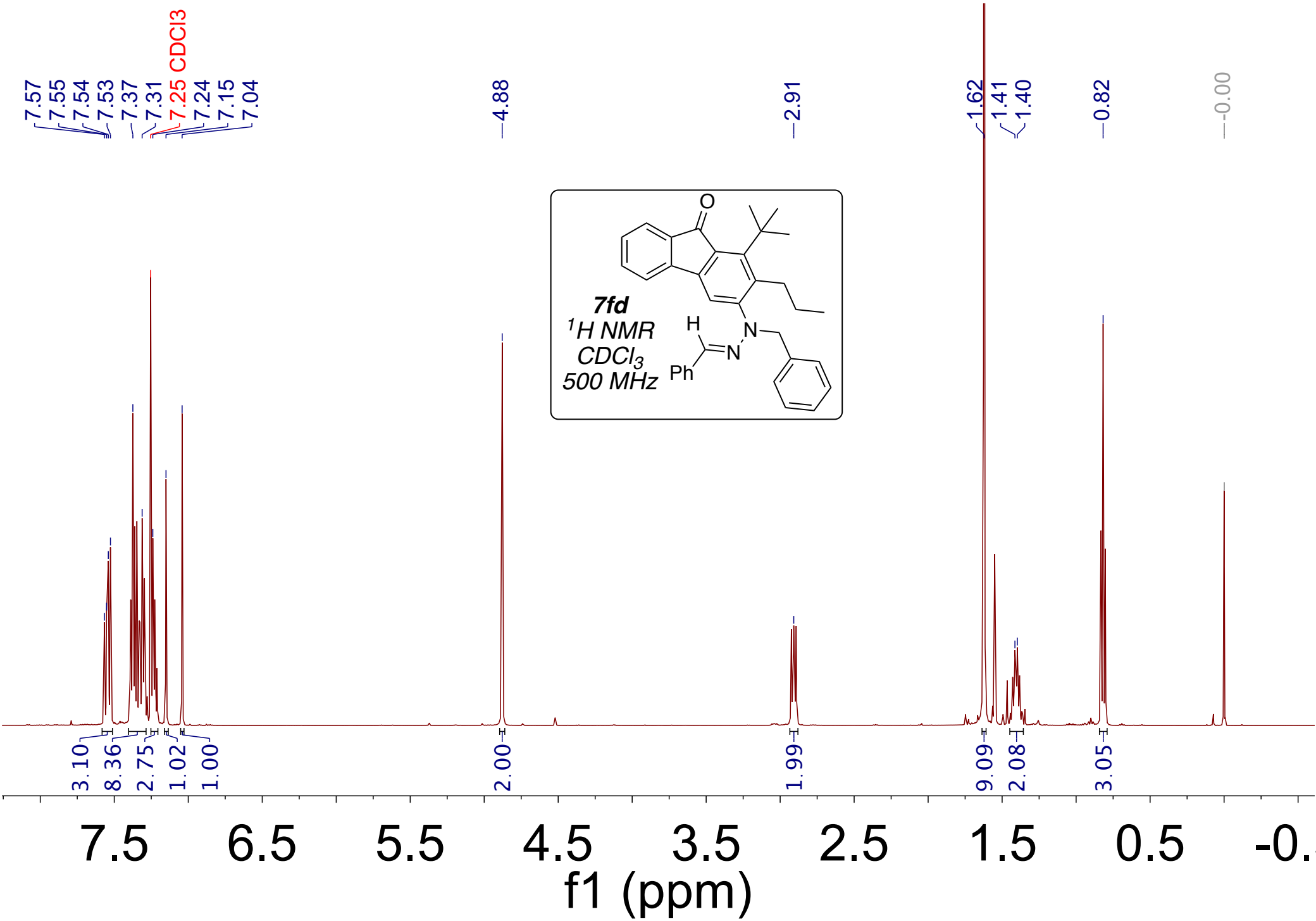
140.3
137.7
136.4
133.8
133.4
132.6
128.9
128.8
128.5
128.4
128.4
127.6
127.2
125.8
122.5
111.6
94.8
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
75.9
60.1
50.4
34.2
34.1
28.1
16.0
4.6
4.6
0.0
Me
MsN
Me
H
N
N
7dd
13C NMR
CDCl3
125 MHz
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

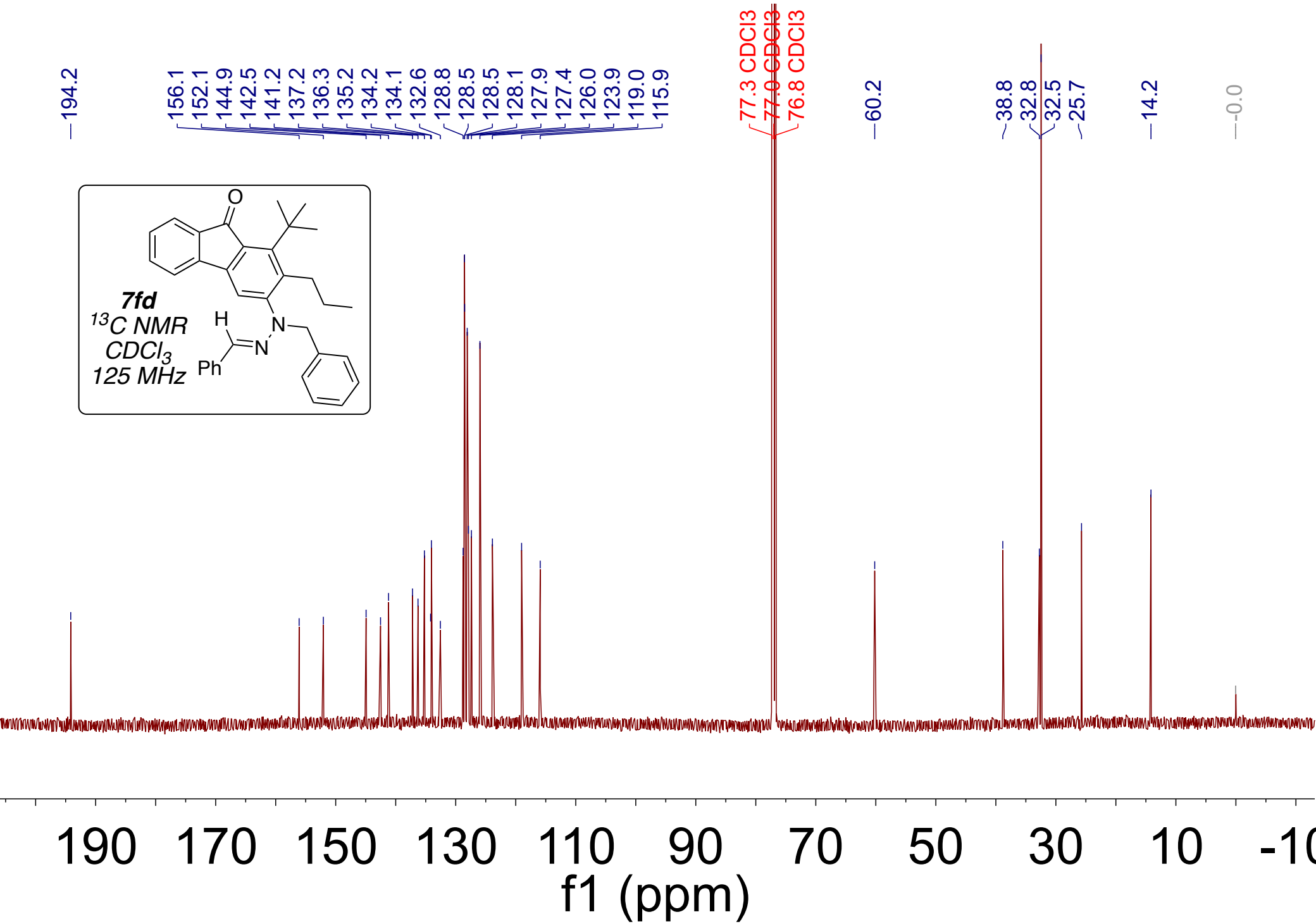

7.32
7.29
7.26 CDCl3
7.23
4.24
2.44
2.12
1.92
1.63
1.55
1.51
0.00
Me
BocN
BocN
Me
N–N
Ph
7ec
1H NMR
CDCl3
500 MHz
3.02
2.10
0.99
0.83
0.87
2.00
3.02
3.35
3.11
3.13
9.43
9.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

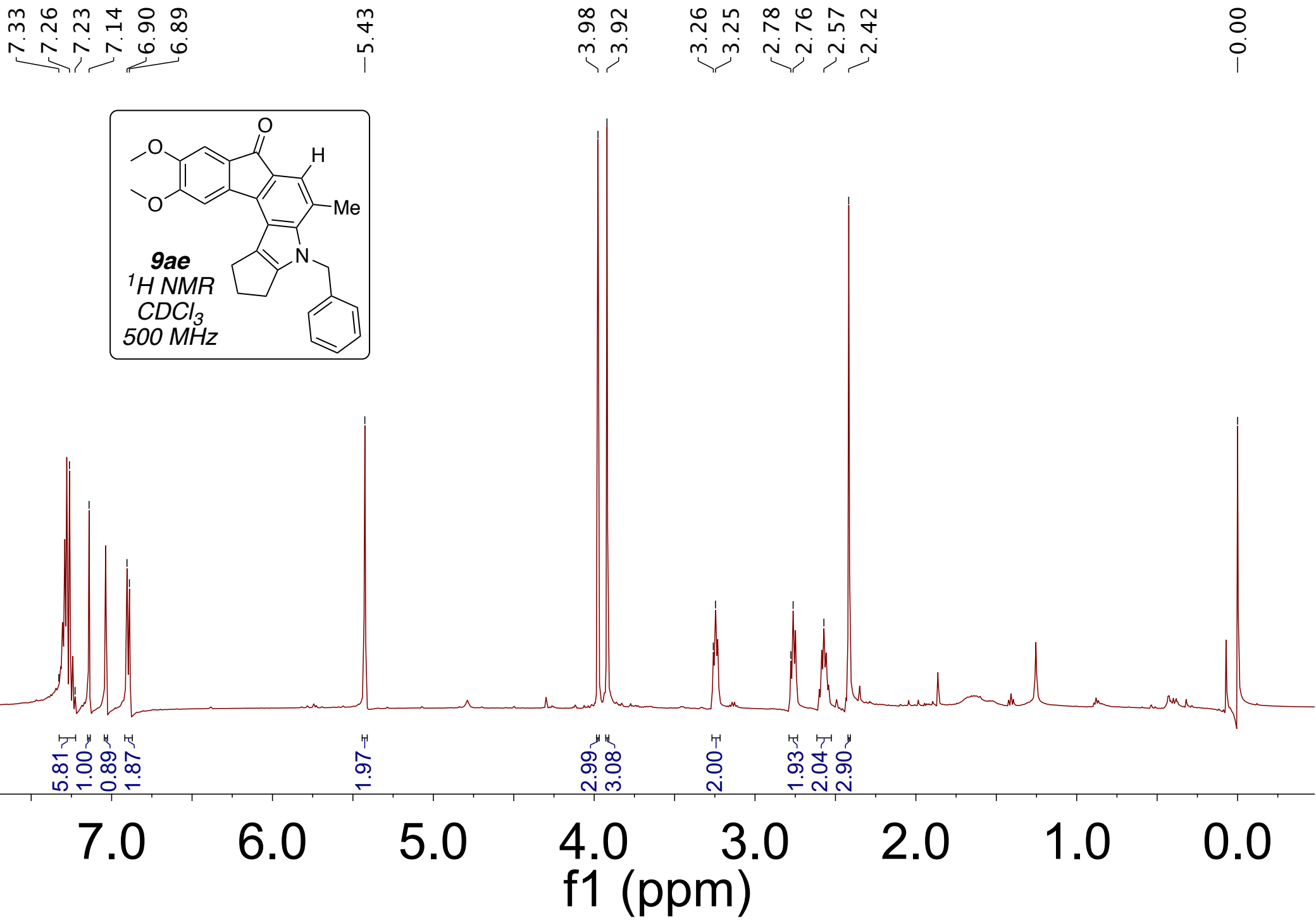

165.9
152.5
152.1
139.2
138.4
130.6
129.9
128.7
128.5
128.2
128.1
126.7
126.4
119.0
110.3
94.2
82.5
82.0
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
75.6
63.6
51.8
28.2
28.2
25.4
25.3
19.9
15.7
4.6
Me
BocN
BocN
Me
N–N
Ph
7ec
13C NMR
CDCl3
125 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

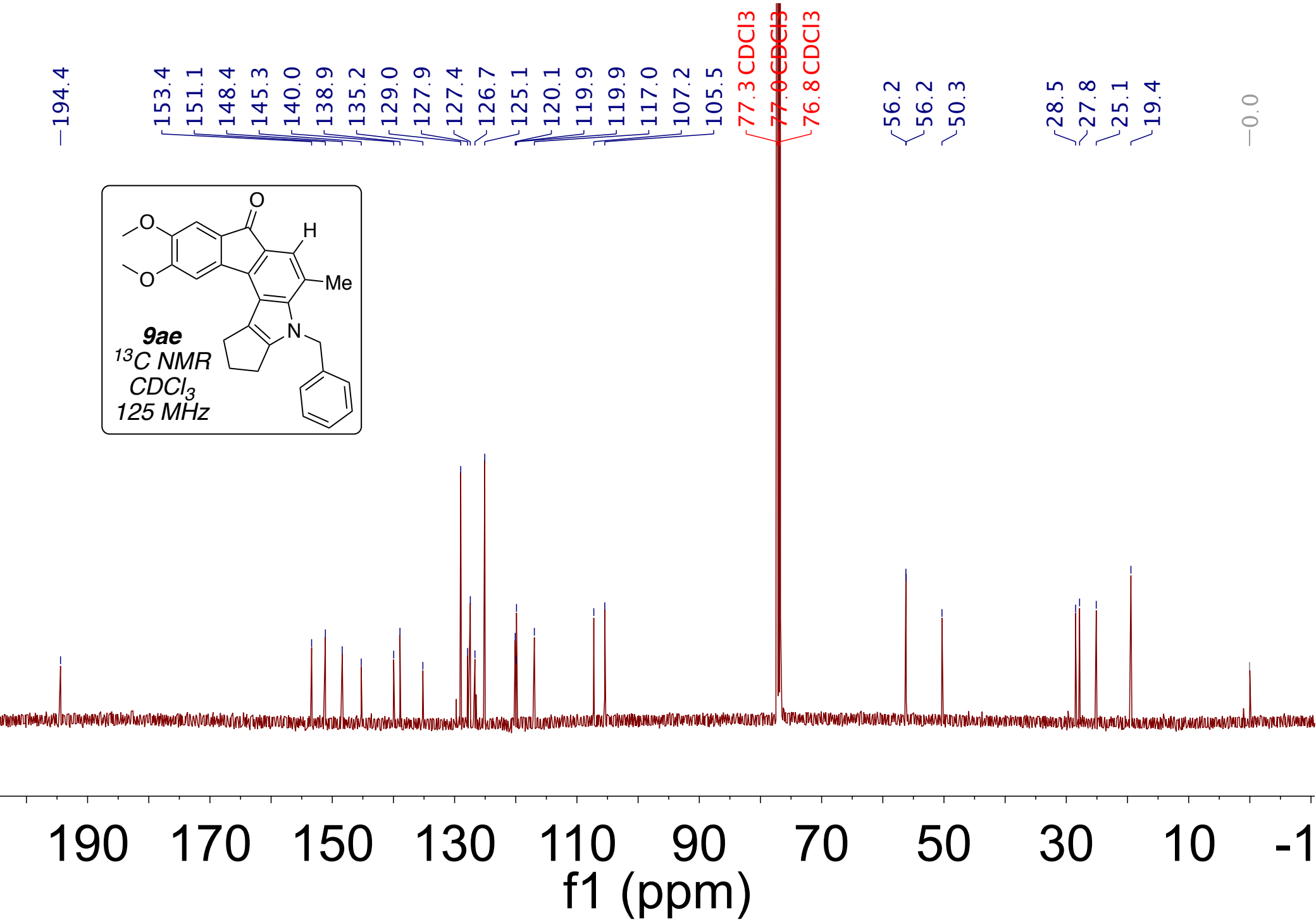

7.34
7.32
7.29
7.26
7.23
5.06
5.03
4.60
4.58
4.24
2.44
2.12
1.92
1.63
1.55
1.51
Me
BocN
BocN
Me
N–N
7ee
1H NMR
CDCl3
500 MHz
2.87
2.07
0.99
0.84
0.87
2.00
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

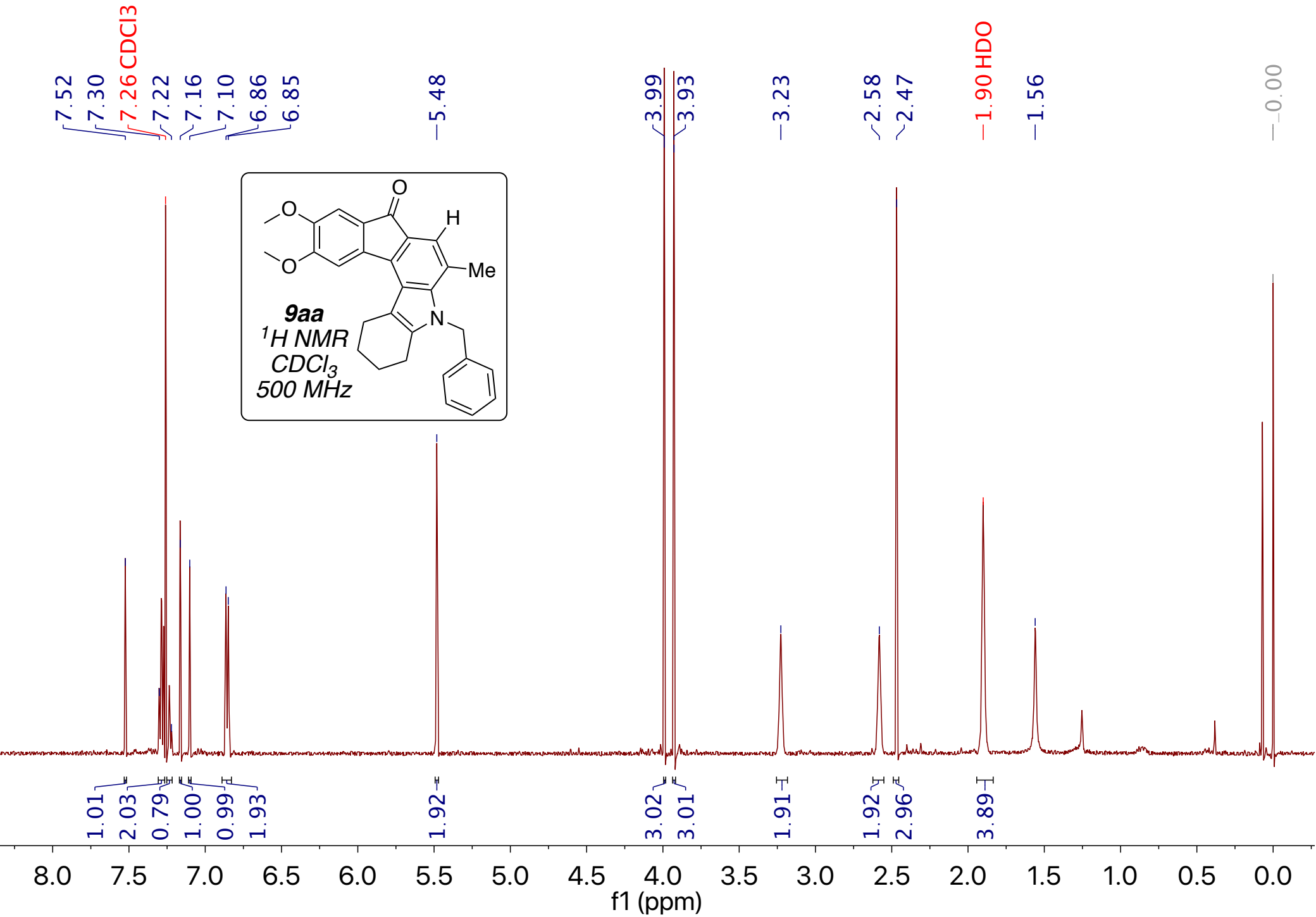

165.9
152.5
152.1
139.2
138.4
129.9
128.5
128.1
126.7
126.4
119.0
110.3
94.2
82.5
82.0
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
75.6
63.6
51.8
28.2
28.2
25.3
19.9
15.7
4.6
0.0
Me
BocN
BocN
Me
N–N
7ee
13C NMR
CDCl3
125 MHz
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.57
7.55
7.54
7.53
7.37
7.31
7.25 CDCl3
7.24
7.15
7.04
4.88
2.91
1.62
1.41
1.40
0.82
0.00
7fd
1H NMR
CDCl3
500 MHz
O
H
N
N
Ph
3.10
8.36
2.75
1.02
1.00
2.00
1.99
9.09
2.08
3.05
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


194.2
156.1
152.1
144.9
142.5
141.2
137.2
136.3
135.2
134.2
134.1
132.6
128.8
128.5
128.5
128.1
127.9
127.4
126.0
123.9
119.0
115.9
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
60.2
38.8
32.8
32.5
25.7
14.2
0.0
O
H
N
N
Ph
7fd
13C NMR
CDCl3
125 MHz
190
170
150
130
110
90
70
50
30
10
-10
f1 (ppm)


7.33
7.26
7.23
7.14
6.90
6.89
5.43
3.98
3.92
3.26
3.25
2.78
2.76
2.57
2.42
0.00
O
O
O
H
Me
N
9ae
1H NMR
CDCl3
500 MHz
5.81
1.00
0.89
1.87
1.97
2.99
3.08
2.00
1.93
2.04
2.90
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


194.4
153.4
151.1
148.4
145.3
140.0
138.9
135.2
129.0
127.9
127.4
126.7
125.1
120.1
119.9
119.9
117.0
107.2
105.5
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
56.2
56.2
50.3
28.5
27.8
25.1
19.4
0.0
O
O
O
H
Me
N
9ae
13C NMR
CDCl3
125 MHz
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)


7.52
7.30
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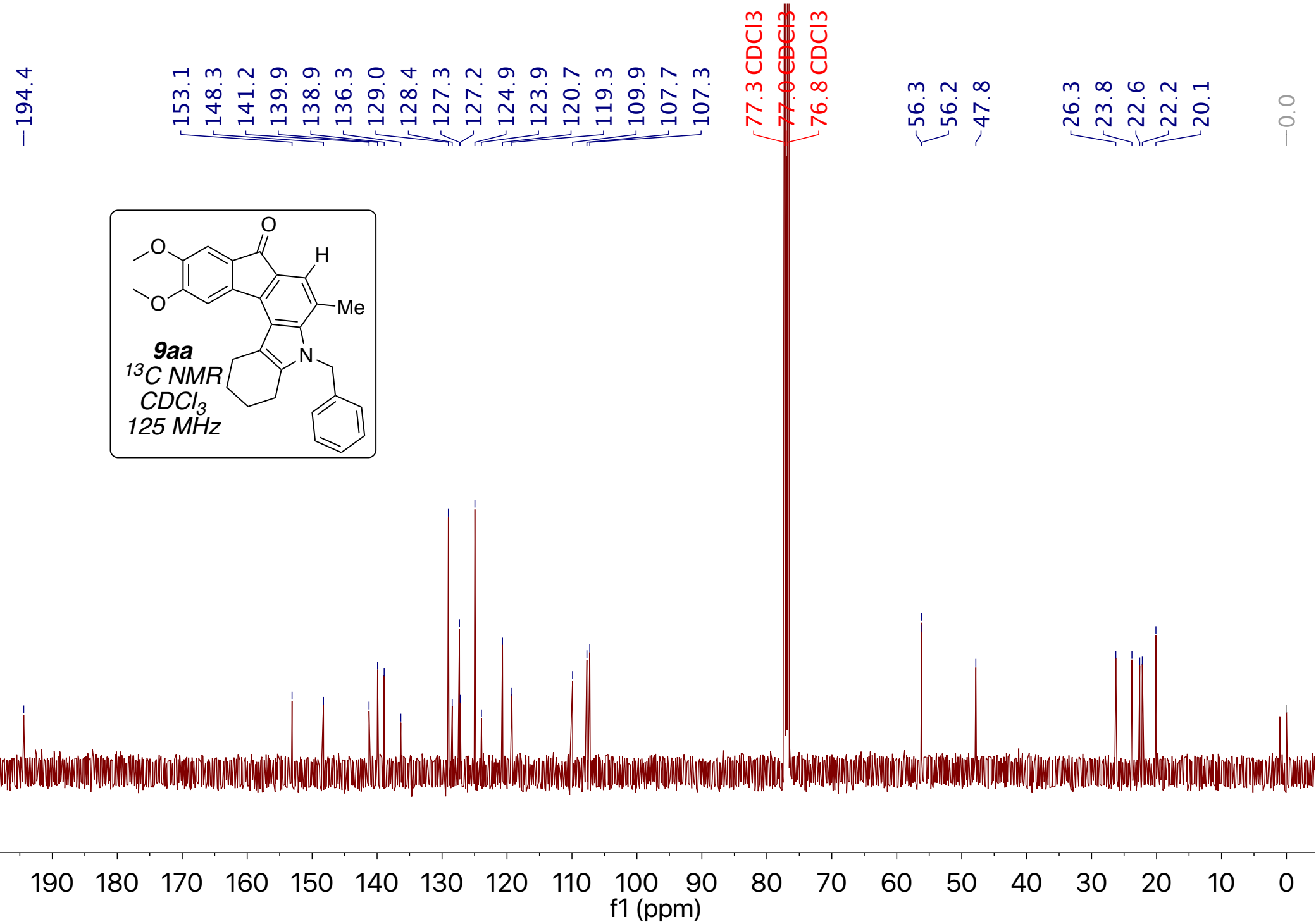
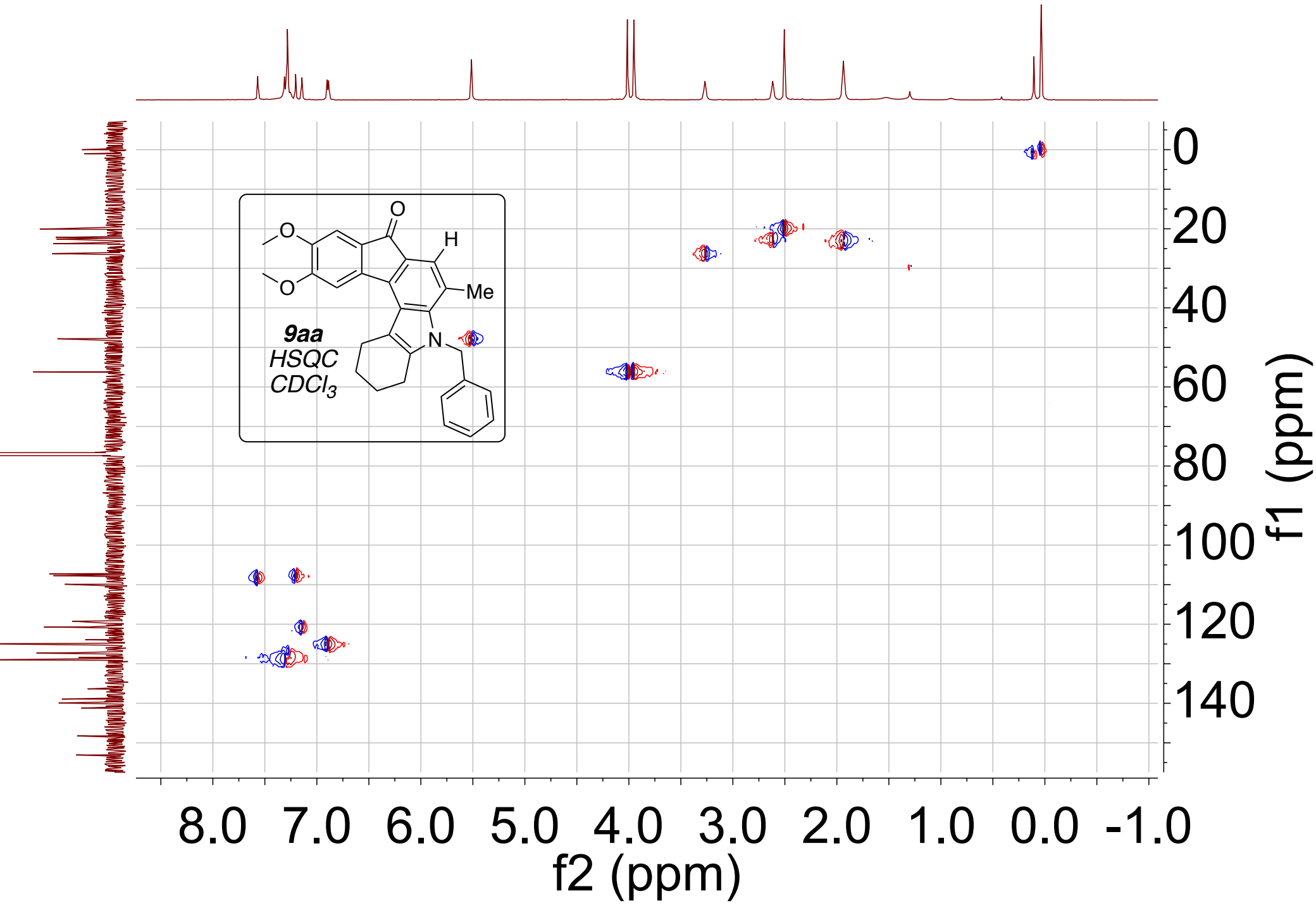
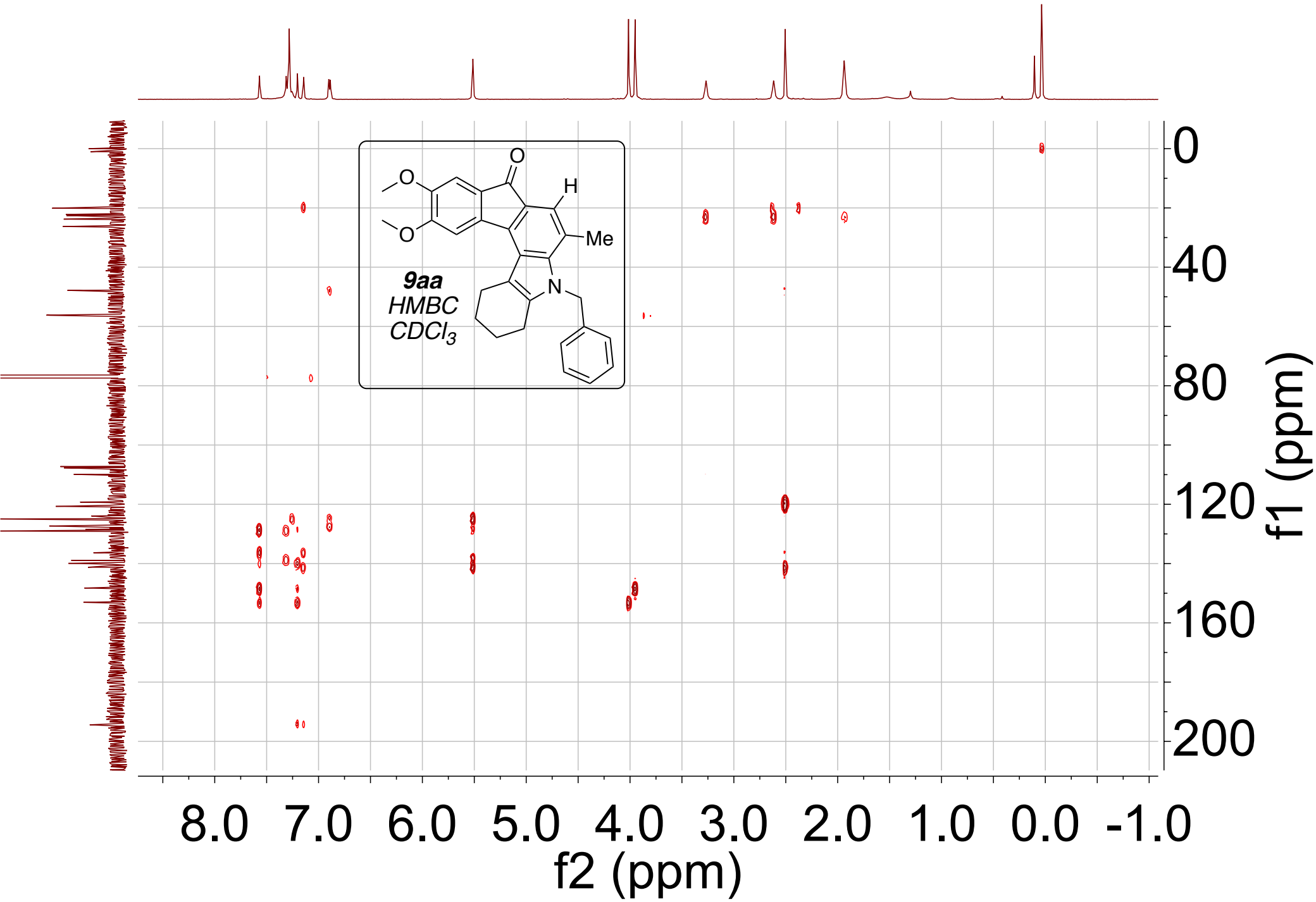
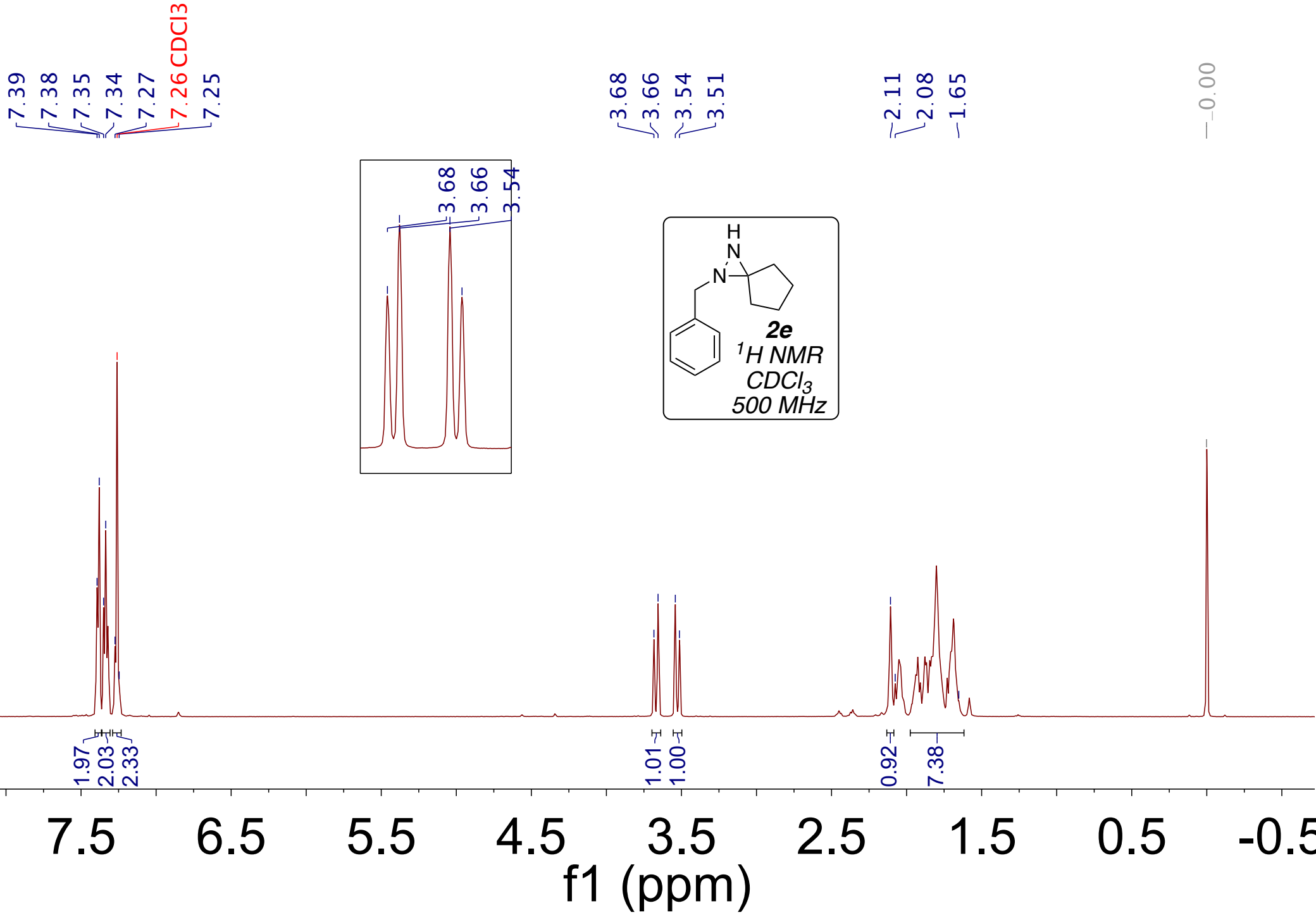
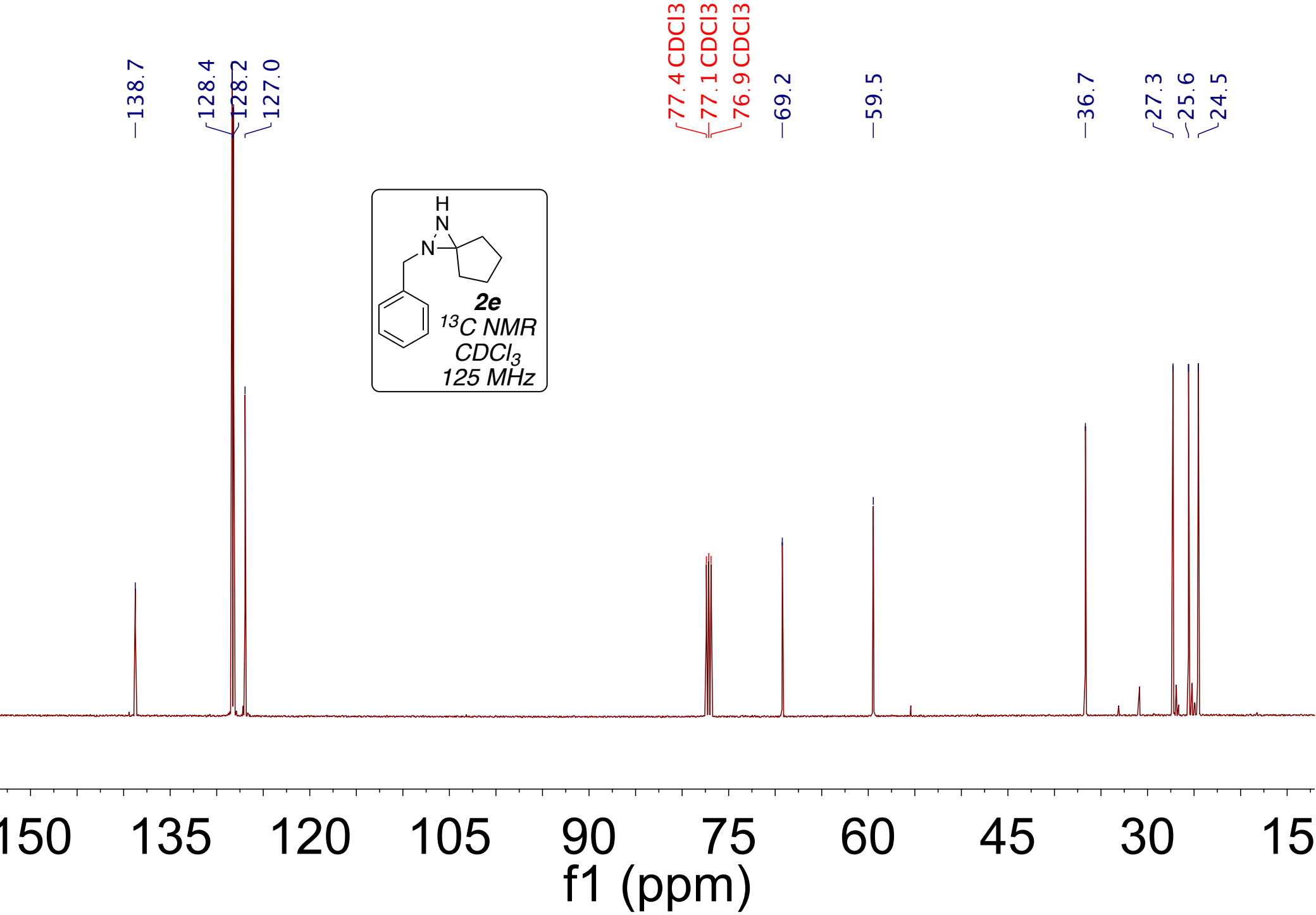
7.22
7.16
7.10
6.86
6.85
5.48
3.99
3.93
3.23
2.58
2.47
1.90 HDO
1.56
0.00
O
O
O
H
Me
N
9aa
1H NMR
CDCl3
500 MHz
1.01
2.03
0.79
1.00
0.99
1.93
1.92
3.02
3.01
1.91
1.92
2.96
3.89
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

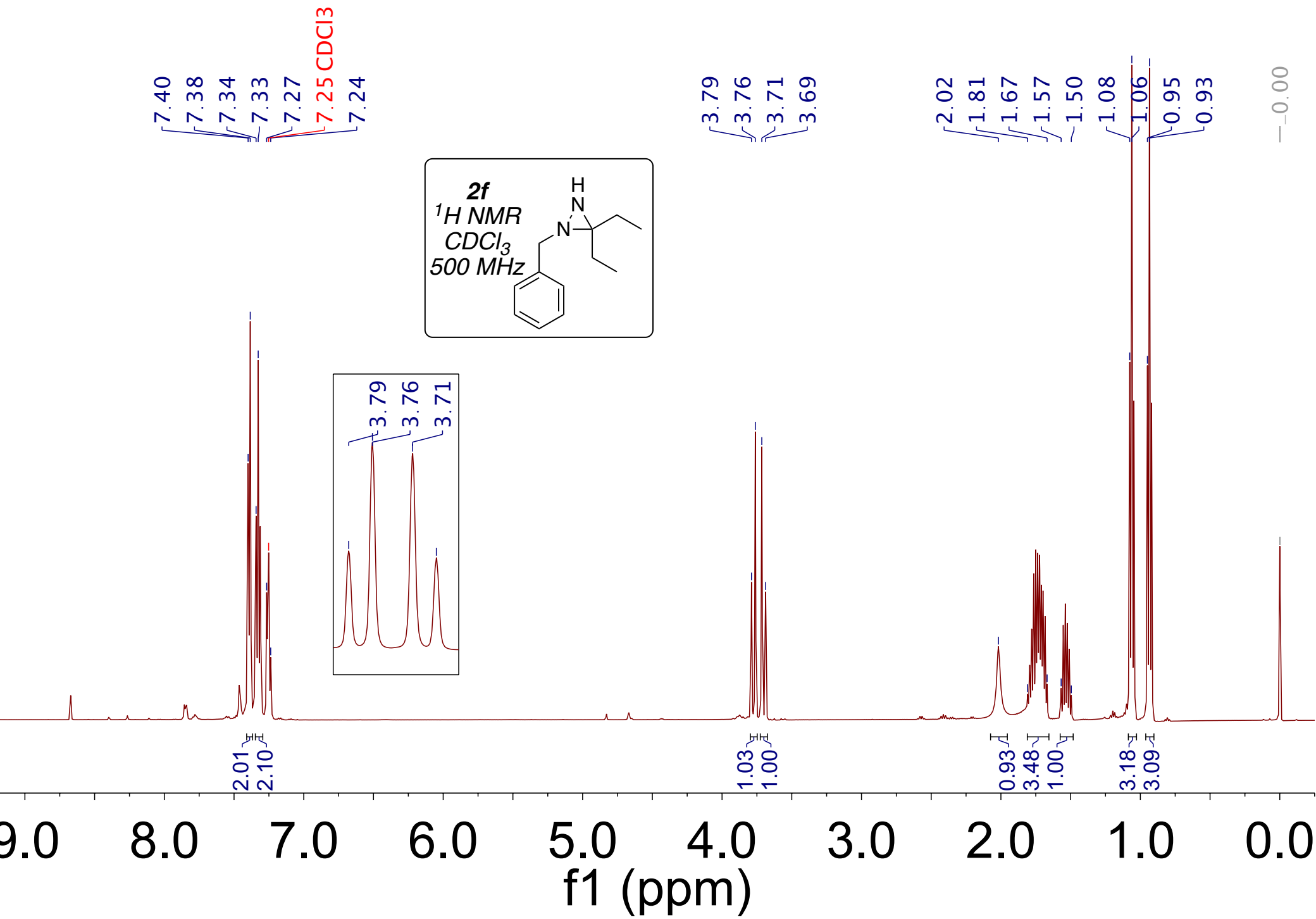

194.4
153.1
148.3
141.2
139.9
138.9
136.3
129.0
128.4
127.3
127.2
124.9
123.9
120.7
119.3
109.9
107.7
107.3
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
56.3
56.2
47.8
26.3
23.8
22.6
22.2
20.1
0.0
O
O
O
H
Me
N
9aa
13C NMR
CDCl3
125 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

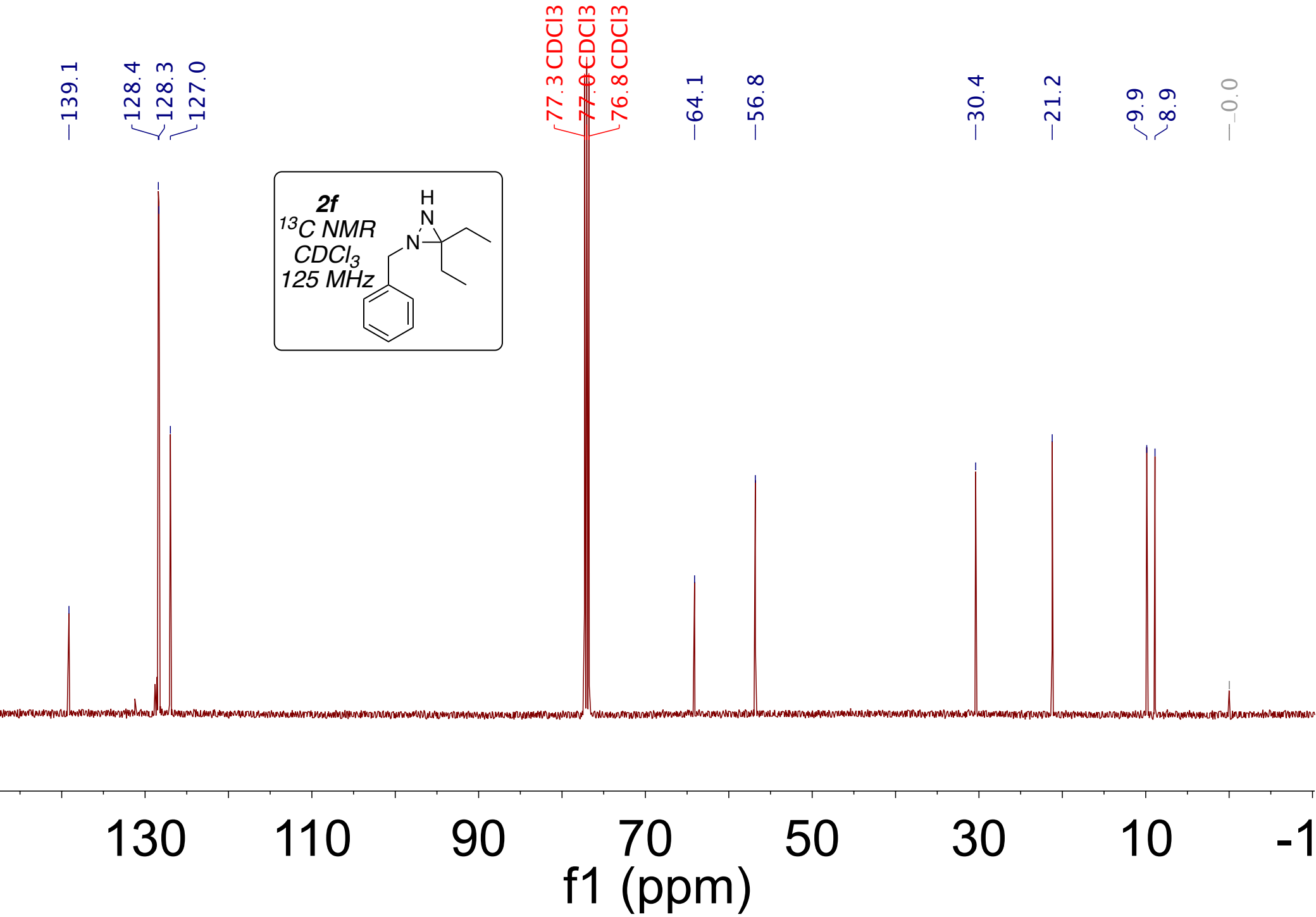

O
O
O
H
Me
N
9aa
HSQC
CDCl3
0
20
40
60
80
100
120
140
f1 (ppm)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f2 (ppm)

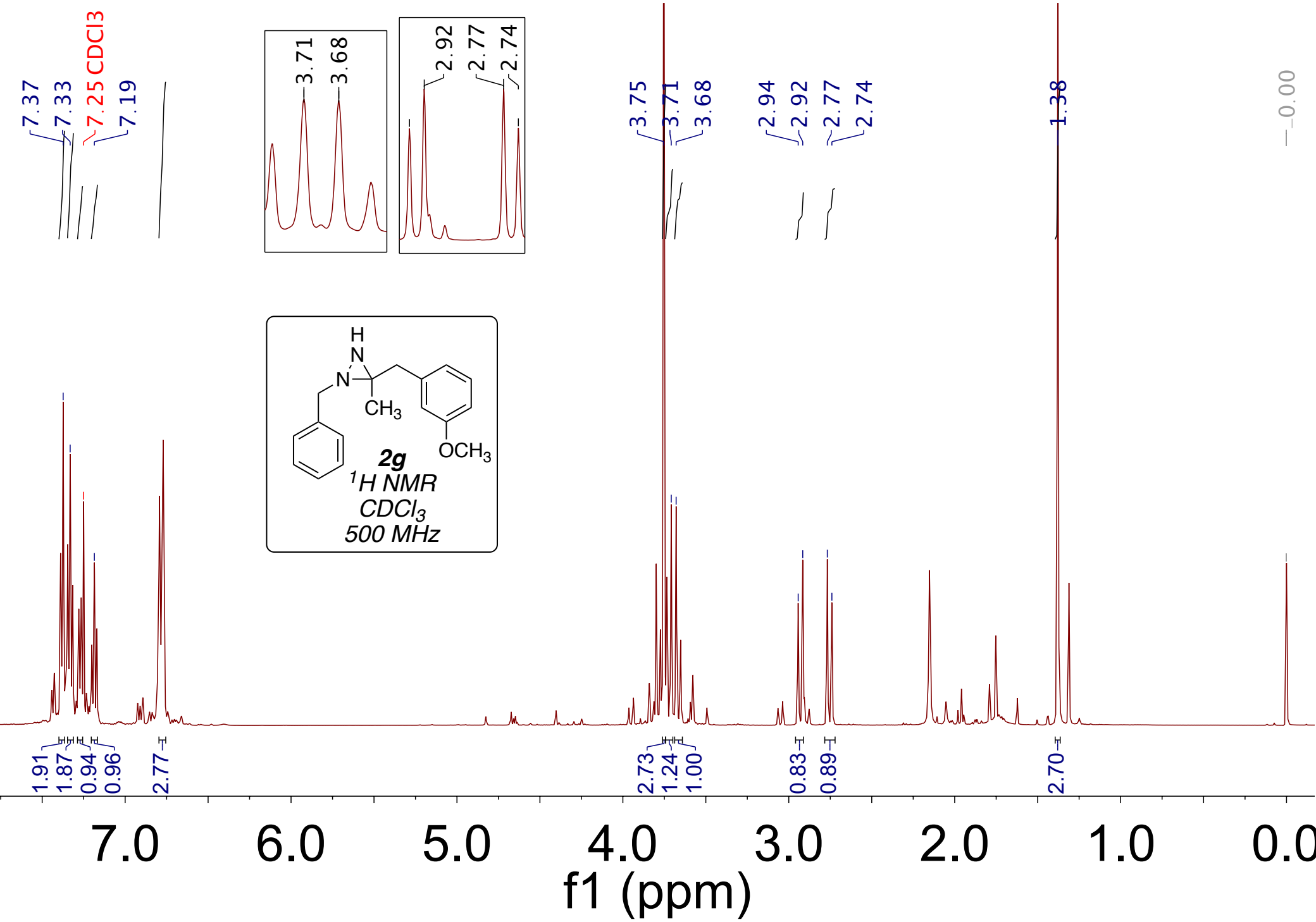

O
O
O
H
Me
N
9aa
HMBC
CDCl3
0
40
80
120
160
200
f1 (ppm)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f2 (ppm)

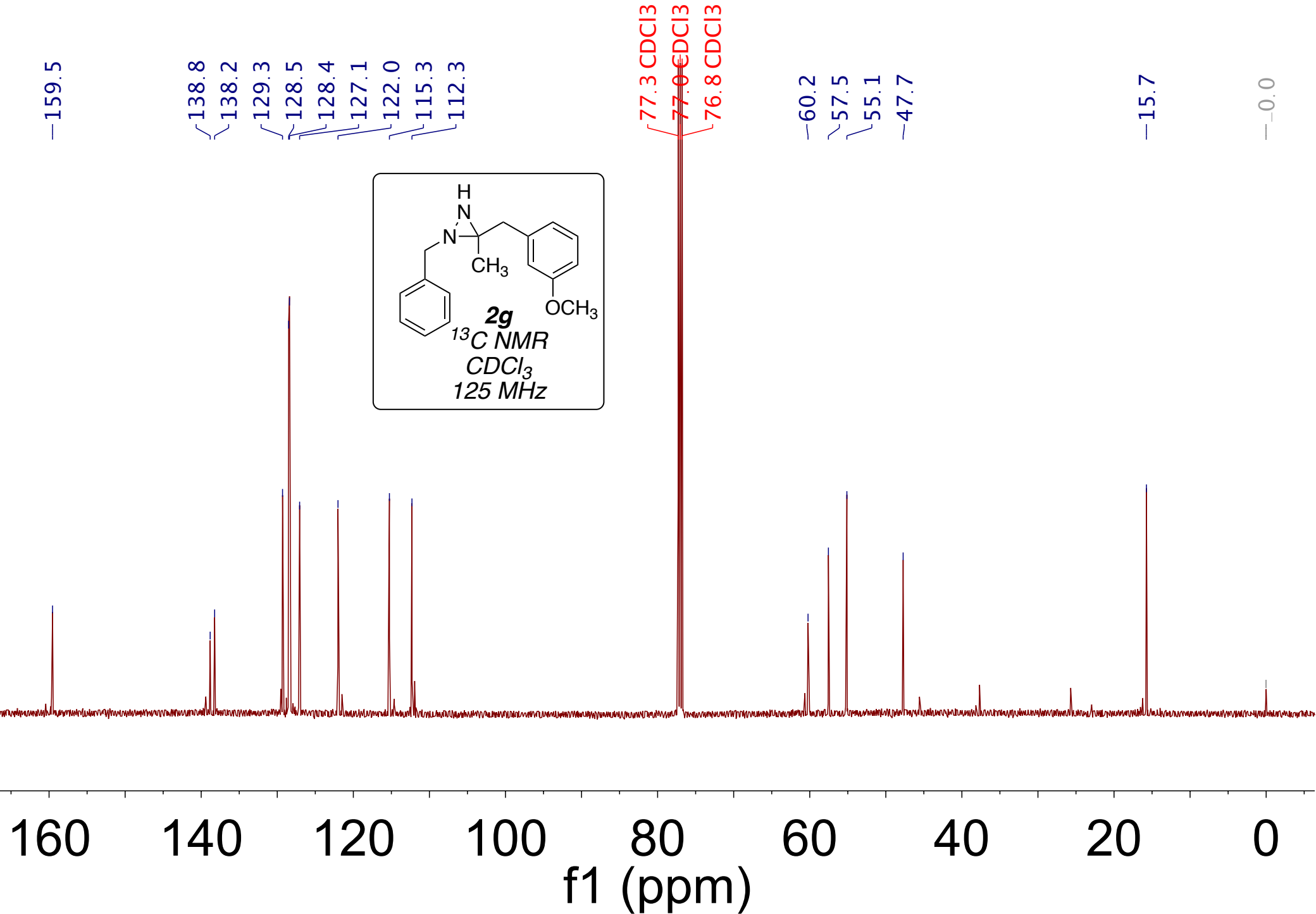

7.39
7.38
7.35
7.34
7.27
7.26 CDCl3
7.25
3.68
3.66
3.54
3.51
2.11
2.08
1.65
0.00
3.68
3.66
3.54
H
N
N
2e
1H NMR
CDCl3
500 MHz
1.97
2.03
2.33
1.01
1.00
0.92
7.38
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


138.7
128.4
128.2
127.0
77.4 CDCl3
77.1 CDCl3
76.9 CDCl3
69.2
59.5
36.7
27.3
25.6
24.5
H
N
N
2e
13C NMR
CDCl3
125 MHz
150
135
120
105
90
75
60
45
30
15
f1 (ppm)


7.40
7.38
7.34
7.33
7.27
7.25 CDCl3
7.24
3.79
3.76
3.71
3.69
2.02
1.81
1.67
1.57
1.50
1.08
1.06
0.95
0.93
0.00
2f
1H NMR
CDCl3
500 MHz
H
N
N
2.01
2.10
1.03
1.00
0.93
3.48
1.00
3.18
3.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


139.1
128.4
128.3
127.0
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
64.1
56.8
30.4
21.2
9.9
8.9
0.0
2f
13C NMR
CDCl3
125 MHz
H
N
N
130
110
90
70
50
30
10
-1
f1 (ppm)


7.37
7.33
7.25 CDCl3
7.19
3.71
3.68
2.92
2.77
2.74
3.75
3.71
3.68
2.94
2.92
2.77
2.74
1.38
0.00
H
N
N
CH3
OCH3
2g
1H NMR
CDCl3
500 MHz
1.91
1.87
0.94
0.96
2.77
2.73
1.24
1.00
0.83
0.89
2.70
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


159.5
138.8
138.2
129.3
128.5
128.4
127.1
122.0
115.3
112.3
77.3 CDCl3
77.0 CDCl3
76.8 CDCl3
60.2
57.5
55.1
47.7
15.7
0.0
H
N
N
CH3
OCH3
2g
13C NMR
CDCl3
125 MHz
160
140
120
100
80
60
40
20
0
f1 (ppm)