Supplementary Information:

Alkane Desaturation via Concerted Double Hydrogen Atom Transfer to Benzyne

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Contents of Supplementary Information

I. General Experimental Protocols

^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 500 (500 MHz), Varian Inova 300 (300 MHz), Varian VXR 300 (300 MHz), and Bruker Avance 500 (500 MHz) spectrometers. ^{1}H NMR chemical shifts in $CDCl_3$ are referenced to TMS (δ 0.00 ppm). Non-first order multiplets are identified as "nfom". ^{13}C NMR chemical shifts in $CDCl_3$ are referenced to chloroform (δ 77.16 ppm). A spurious spike at *ca.* 5 ppm is sometimes present in the copies of the ^{1}H NMR spectra that were processed using iNMR software. TMS is present in some ^{13}C NMR samples (δ ca. 0.0 ppm). The following format is used to report resonances: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^{1}H NMR assignments are indicated by structure environment, e.g., CH_aH_b. Some complex structures are numbered in order to simplify proton assignment numbering and naming. Coupling constant analysis was guided by methods we have described elsewhere.[1,2] Quantitative ^{1}H NMR (i.e. qNMR) spectra were obtained on a Bruker Avance 500 (500 MHz) spectrometer. Acquisition parameters were modified as described by Paul *et al.*[3] (e.g., 256 transients and d1 delay time of 13.0 seconds).

Infrared spectra were recorded on a Midac Corporation Prospect 4000 FT-IR spectrometer. The most intense and/or diagnostic peaks are reported, and all spectra were collected in attenuated total reflectance (ATR) mode as thin films on a germanium window.

High-resolution mass spectrometry (HRMS) measurements were made on one of two instruments. Chemical ionization mass spectrometry was performed on a Finnigan MAT 95 (CIMS) mass spectrometer. Samples were introduced via capillary gas chromatography using an oven temperature profile of 25-320 ºC ramped at 50 ºC/min. Electrospray ionization (ESI) mass spectrometry was performed on a Bruker BioTOF II (ESI-TOF) instrument using PEG or PPG as an internal standard/calibrant. Samples were introduced as solutions in methanol or acetonitrile.

MPLC refers to medium pressure liquid chromatography (25-200 psi) using hand-packed columns of Silasorb silica gel (18-32 µm, 60 Å pore size), a Waters HPLC pump, a Waters R401 differential refractive index detector, and a Gilson 116 UV detector. Flash chromatography was performed using E. Merck silica gel (230-400 mesh). Thin layer chromatography was performed on glass or plastic backed plates of silica gel and visualized by UV detection and/or a solution of ceric ammonium molybdate, anisaldehyde, potassium permanganate, or phosphomolybdic acid.

Reactions requiring anhydrous conditions were performed under an atmosphere of nitrogen or argon in flame or oven dried glassware. Piperidine, diisopropylamine and triethylamine for cross-coupling reactions were deaerated by a freeze-pump-thaw cycle and then stored in a Schlenk flask or by direct purging with N_2 gas immediately prior to use. Anhydrous THF, diethyl ether, toluene, and methylene chloride were taken immediately prior to use after being passed through a column of activated alumina. Reported (external) reaction temperatures are the temperature of the heating bath. HDDA reactions, including those that were carried out at temperatures above the boiling point of the solvent, were typically performed in a screw-capped vial or culture tube fitted with an inert, teflon-lined cap. Those carried out in deuterated solvents were often performed directly in a capped 5 mm NMR sample tube.

General Procedure A: Alkyne Bromination

Powdered $AgNO_3$ (0.1 equiv) was added to a stirred solution of alkyne (1.0 equiv) and *N*-bromosuccinimide (NBS, 1.1 equiv) in acetone (0.1 M) at rt. After 1 h the slurry was either i) filtered through Celite® (acetone eluent) and concentrated or ii) partitioned between Et_2O and water, further extracted with Et_2O, washed with brine, dried ($MgSO_4$), and concentrated. The crude material was typically purified by flash chromatography on silica gel.

General Procedure B: Cadiot–Chodkiewicz Alkyne Cross-Coupling

CuCl (0.05 equiv) was added to a stirred solution of alkyne (partner A, 1.0 equiv) and 1-bromoalkyne (partner B, 1.5 equiv) in freshly deaerated piperidine (0.3 M) at 0 ºC and under an inert atmosphere. After 1 h the reaction mixture was diluted with satd. aq. NH_4Cl and extracted with EtOAc or Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. The crude material was typically purified by flash chromatography on silica gel.

General Procedure C: Tandem HDDA/Alkane Double Hydrogen Atom Transfer

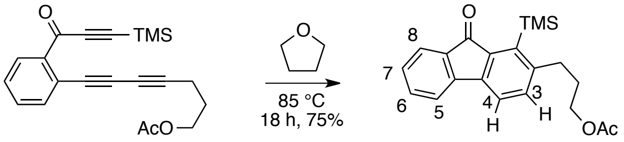
A solution of HDDA triyne or tetrayne precursor in cyclooctane (ca. 0.01 M) was heated at the indicated temperature in a culture tube fitted with an inert, Teflon®-lined cap. After 12-48 h (as specified) the reaction mixture was loaded onto a bed of silica gel and washed sequentially with hexanes, to remove the excess cyclooctane, and ethyl acetate. The ethyl acetate fraction was concentrated to provide the crude product mixture. This material was typically purified by flash chromatography on silica gel.

Tabular Inset Notes (a-f) for Fig. 3a

[a]Isolated yields from experiments carried out in neat 2H-donor solvent ($[\mathbf{12}]_o = 0.01$ M). [b]We have observed that norbornene[4] and 2,3-dihydrofuran adduct with HDDA-generated benzynes. [c]By qNMR[3] analysis of experiments performed in $CDCl_3$ containing 20 molar equiv each of cyclopentane and the second donor. [d]From 2H *vs.* 2D-incorporation using a 1:10 molar ratio of cyclopentane and THF-d_8. [e]$\Delta G^{\ddagger}$ values (kcal mol^{-1}) were determined using M06-2X/6-311+G(d,p). [f]For the TS leading to 2,3-dihydrofuran.

II. Preparation procedures and characterization data for all new compounds

3-(9-Oxo-1-(trimethylsilyl)-9*H*-fluoren-2-yl)propyl acetate (10-h$_2$)



8 **10-h$_2$**

A solution of known acetate **8**[4] (20 mg, 0.057 mmol) in THF (6 mL) was heated to 85 °C for 18 h. The resulting solution was concentrated and purified using flash column chromatography (hexanes:EtOAc 15:1) to yield **10-h$_2$** (15 mg, 0.043 mmol, 75%) as a golden oil.

^{1}H NMR (500 MHz, CD$_3$Cl): δ 7.57 (d, *J* = 7.3 Hz, 1H, *H8*), 7.42-7.46 (m, 3H, *H4/H5/H6*), 7.24-7.26 (nfom, 1H, *H7*), 7.22 (d, *J* = 7.6 Hz, 1H, *H3*), 4.11 (t, *J* = 6.5 Hz, 2H, C*H*$_2$O), 2.85 (d, *J* = 8.0 Hz, 2H, ArC*H*$_2$), 2.07 (s, 3H, C*H*$_3$CO), 1.86 (nfom, 2H, C*H*$_2$CH$_2$O), 0.45 [s, 9H, Si(C*H*$_3$)$_3$].

^{1}H NMR (500 MHz, CD$_3$OD): δ 7.59 (ddd, *J* = 7.4, 1.0, 1.0 Hz, 1H, *H8*), 7.58 (d, *J* = 7.6 Hz, 1H, *H4*), 7.53 (ddd, *J* = 7.3, 1.0, 1.0 Hz, 1H, *H5*), 7.51 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H, *H6*), 7.33 (d, *J* = 7.7 Hz, 1H, *H3*), 7.29 (ddd, *J* = 7.4, 7.4, 1.1 Hz, *H7*), 4.11 (t, *J* = 6.4 Hz, 2H, C*H*$_2$O), 2.89 (br t, *J* = 8.0 Hz, 2H, ArC*H*$_2$), 2.04 (s, 3H, C*H*$_3$CO), 1.87 (nfom that includes *J* = 8.1 and 6.2 Hz, 2H, C*H*$_2$CH$_2$O), and 0.43 [s, 9H, Si(C*H*$_3$)$_3$].

^{13}C NMR (125 MHz, CDCl$_3$): δ 195.5, 171.3, 149.2, 144.1, 143.6, 141.2, 140.6, 135.4, 134.7, 134.0, 128.9, 124.1, 121.1, 119.7, 63.9, 33.2, 32.5, 21.2, and 2.6 ppm.

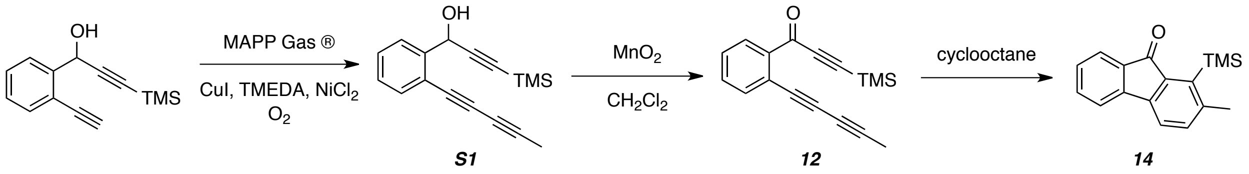
IR (neat): 2950, 2848, 1739, 1713, 1606, 1586, 1467, 1438, 1386, 1365, 1245, 1183, 1043, 862, and 847 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{21}H_{24}NaO_3Si^+$ $[M+Na]^+$ requires 375.1387; found 375.1386.

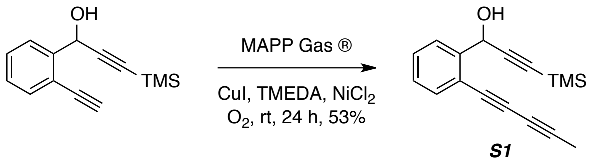
An analogous experiment using THF-*d$_8$* gave **10-d$_2$**. The ^{1}H NMR spectrum is provided in section **V** (page 52).

An analogous experiment using a 6:1 molar ratio of THF-*d$_8$* and THF-*h$_8$* gave an ca. 1:1 mixture of **10-d$_2$** (page and **10-h$_2$**. The ^{1}H NMR spectrum is provided in section **V** (page 53).

Synthesis of indenone 14 from 12 (Fig. 3A of manuscript)



1-(2-(Penta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S1)



MAPP Gas® was bubbled through THF (50 mL) for 1 h at 0 °C to give a 1.4 M solution of propyne in THF as determined by integrations (solvent vs. $CH_3C{\equiv}CH$, propene, allene, and propane were also present) of the No-D ^{1}H NMR spectrum[5]. 1-(2-Ethynylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol[6] (433 mg, 1.90 mmol), TMEDA (70 µL, 0.47 mmol), $NiCl_2$ (32 mg, 0.25 mmol), and CuI (41 mg, 0.22 mmol) were added to the propyne/THF solution (14 mL). An oxygen balloon was introduced through a septum and the reaction mixture was allowed to warm to room temperature with stirring. After 24 h the reaction mixture was diluted in satd. aq. NH_4Cl and extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexanes:EtOAc 6:1) gave triyne **S1** as an orange-yellow oil (266 mg, 1.00 mmol, 53%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 7.8, 1.5 Hz, 1H, *H6*), 7.50 (dd, *J* = 7.7, 1.5 Hz, 1, *H3*), 7.39 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H4or5*), 7.28 (ddd, *J* = 7.6, 7.6, 1.4, Hz, 1H, *H4or5*), 5.82 (d, *J* = 5.7 Hz, 1H, ArC*H*OH), 2.45 (d, J = 5.7 Hz, 1H, O*H*), 2.04 (s, 3H, CCH_3), and 0.20 [s, 9H, Si(CH_3)$_3$].

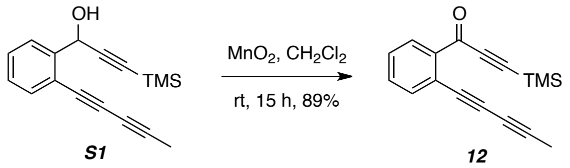
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.5, 133.7, 129.5, 128.4, 127.1, 120.8, 104.2, 91.9, 82.1, 79.9, 71.3, 64.4, 63.5, 4.8, and -0.1.

IR (neat): 3406, 2960, 2242, 2173, 1482, 1449, 1250, 1037, 983, 846, and 761 cm^{-1}.

HR ESI-MS: $C_{17}H_{18}NaOSi^+$ [M+Na$^+$] requires 289.1019; found 289.1013.

TLC: R_f 0.5 (4:1 Hex/EtOAc).

1-(2-(Penta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (12)



MnO_2 (2.21 g, 25 mmol) was added to a stirred solution of triyne **S1** (247 mg, 0.93 mmol) in CH_2Cl_2 (2.5 mL) at room temperature. After 15 h the reaction mixture filtered through a small column of SiO_2

(EtOAc eluent). The crude reaction mixture was sufficiently pure to give triynone **12** (220 mg, 0.83 mmol, 89%) as a brown oil.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.08 (dd, *J* = 7.8, 1.6 Hz,1H, *H6*), 7.60 (dd, *J* = 7.7, 1.5 Hz, 1H, *H3*), 7.49 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H, *H4*), 7.44 (ddd, *J* = 7.6, 7.6, 1.5, Hz, 1H, *H5*), 2.04 (s, 3H, C*H$_3$*), and 0.31 [s, 9H, Si(C*H$_3$*)$_3$].

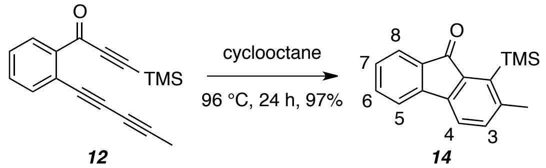
^{13}C NMR (125 MHz, CDCl$_3$): δ = 176.6, 139.2, 135.7, 132.6, 131.8, 128.5, 122.2, 101.6, 101.5, 82.9, 80.9, 72.3, 65.0, 4.9, and -0.5.

IR (neat): 2961, 2246, 2152, 1648, 1480, 1235, 1014, 850, and 757 cm^{-1}.

HR ESI-MS: $C_{17}H_{16}NaOSi^+$ [M+Na$^+$] requires 287.0863; found 287.0866.

TLC: R$_f$ 0.4 (9:1 Hex/EtOAc).

2-Methyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (14)



Fluorenone **14** was prepared following general procedure C (96 ºC, 24 h) from triyne **12** (38 mg, 0.144 mmol) and cyclooctane (14 mL). The crude material was purified by flash chromatography (hexanes:EtOAc 19:1) to give fluorenone **14** (37 mg, 0.139 mmol, 97%) as a yellow solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.57 (ddd, *J* = 7.3, 1.1, 1.0 Hz, 1H, *H8*), 7.44 (m, 2H, *H5* and *H6*), 7.39 (d, *J* = 7.6 Hz, 1H, *H4*), 7.24 (nfom, 1H, *H7*), 7.19 (ddd, *J* = 7.6, 1.5, 0.8 Hz, 1H, *H3*), 2.47 (s, 3H, C*H$_3$*), and 0.42 [s, 9H, Si(C*H$_3$*)$_3$].

^{13}C NMR (125 MHz, CDCl$_3$): δ 195.6, 145.3, 144.2, 143.0, 141.4, 140.3, 135.7, 134.6, 134.0, 128.6, 124.0, 120.8, 119.5, 25.3, and 2.6.

IR (neat): 2946, 1714, 1606, 1249, 862, 843, and 763 cm^{-1}.

HR ESI-MS: $C_{17}H_{18}NaOSi^+$ [M+Na$^+$] requires 289.1019; found 289.1047.

TLC: R$_f$ 0.5 (9:1 Hex/EtOAc).

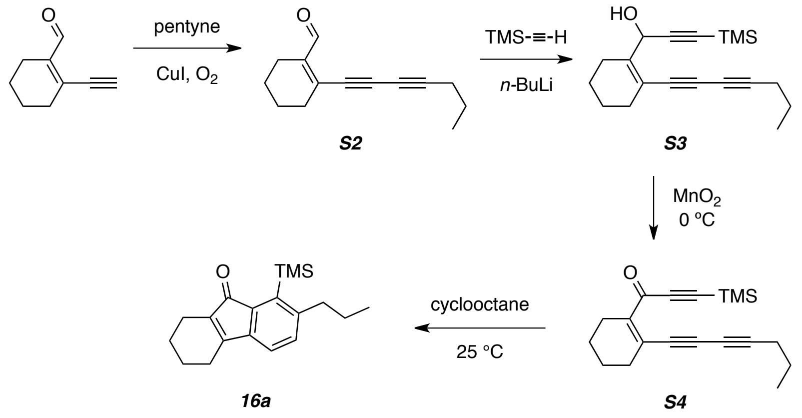
MP: 65–69 ºC.

A similar procedure to that on the previous page was used to obtain the yields of transfer dehydrogenation included in Figure 3A. The specific volume of 2H-donor, masses for the starting triyne **12** and isolated fluorenone **14**, and yields are shown in Table S1.

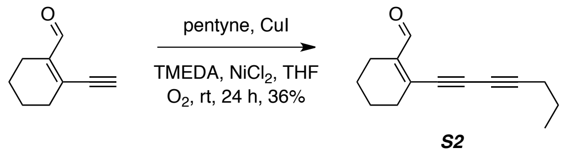
Table S1. Experimental quantities for preparative (i.e., instances when the product was purified by column chromatography) double hydrogen atom transfer to the benzyne **13** (from **12**) from a variety of 2H-donors.

2H-donor (solvent)	Solvent Volume (mL)	Conc. of triyne **12** (M)	Mass (mg) **12**	Mass (mg) **14**	**% yield**
cyclooctane	14	0.01	38	37	97%
cycloheptane	8	0.009	19	18	94%
cyclopentane	12	0.009	27	23	84%
norbornane	12	0.01	33	22	66%
cyclohexane	5	0.009	12	2	20%
THF	13	0.009	30	18	60%
1,4-dioxane	2	0.009	5	0	0%
n-heptane	3.5	0.01	9	3	30%

Synthesis of indenone 16a (Figure 3D of manuscript)



2-(Hepta-1,3-diyn-1-yl)cyclohex-1-enecarbaldehyde (S2)



CuI (5 mg, 0.03 mmol) was added to a stirred solution of 2-ethynylcyclohex-1-enecarbaldehyde[7] (82 mg, 0.61 mmol), pentyne (1.0 mL, 10 mmol), TMEDA (20 µL, 0.13 mmol), and $NiCl_2$ (5 mg, 0.04 mmol) in THF solution (2 mL) at room temperature. An oxygen balloon was attached through a septum. After 24 h the reaction mixture was diluted in satd. aq. NH_4Cl and extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by MPLC (hexanes:EtOAc 19:1) gave the sample of diyne **S2** as a clear brown oil (43 mg, 0.22 mmol, 36%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.13 (s, 1H, C*H*O), 2.40 (m, 2H, =C-CH_2), 2.35 (t, *J* = 7.0 Hz, 2H, ≡CCH_2), 2.27 (m, 2H, =C-CH_2), 1.60-1.70 [m, 4H, $CH_2(C\mathit{H}_2)_2CH_2$], 1.61 (sext, *J* = 7.3 Hz, 2H, ≡CCH_2CH_2), and 1.02 [t, *J* = 7.4 Hz, 3H, CH_3].

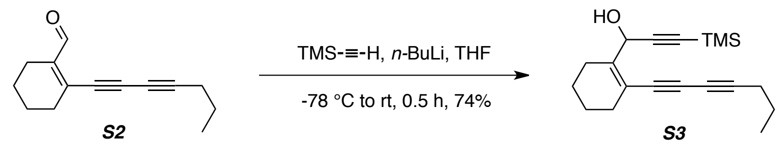
^{13}C NMR (125 MHz, $CDCl_3$): δ 192.4, 146.1, 139.0, 88.7, 83.7, 71.5, 64.9, 32.3, 22.3, 22.0, 21.83, 21.79, 21.1, and 13.7.

IR (neat): 2933, 2869, 2229, 1742 w, 1677, and 1221 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{14}H_{16}NaO^+$ [M+Na$^+$] requires 223.1093; found 223.1102.

TLC: R_f 0.4 (19:1 Hex/EtOAc).

1-(2-(Hepta-1,3-diyn-1-yl)cyclohex-1-en-1-yl)-3-(trimethylsilyl)prop-2-yn-1-ol (S3)



n-BuLi (130 µL, 2.5 M in hexanes, 0.33 mmol) was added to a stirred solution of ethynyltrimethylsilane (54 µL, 0.38 mmol) in THF (380 µL) at -78 ºC. After 1 h a solution of aldehyde **S2** (38 mg, 0.19 mmol) in THF (200 µL) was added and the reaction mixture was allowed to warm to rt.

After 30 min satd. aq. NH_4Cl was added and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. The crude product triynol **S3** (43 mg, 0.14 mmol, 74%) was a clear red oil and used directly in the next reaction.

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.59 (s, 1H, C*H*OH), 2.32 (t, *J* = 7.0 Hz, 2H, ≡CC*H*$_2$), 2.33 (m, 2H, =C-C*H*$_2$), 2.19 (m, 2H, =C-C*H*$_2$), 1.94 (br s, 1H, O*H*), 1.55-1.75 (m, 4H, $CH_2(CH_2)_2CH_2$), 1.58 (sext, *J* = 7.2 Hz, 2H, ≡CH_2CH_2), 1.01 [t, *J* = 7.4 Hz, 3H, C*H*$_3$], and 0.18 [s, 6H, $Si(CH_3)_2C$].

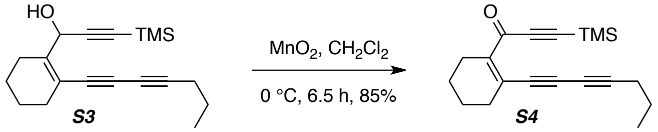
^{13}C NMR (125 MHz, $CDCl_3$): δ 146.3, 118.0, 104.1, 90.7, 85.7, 78.4, 73.4, 65.3, 64.7, 30.1, 23.7, 22.2, 22.0, 21.9, 21.7, 13.7, and 0.0.

IR (neat): 3440, 2934, 2235, 2170, 1250, 1028, and 845 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{26}NaOSi^+$ [M+Na$^+$] requires 321.1645; found: 321.1658.

TLC: R_f 0.4 (6:1 Hex/EtOAc).

1-(2-(Hepta-1,3-diyn-1-yl)cyclohex-1-en-1-yl)-3-(trimethylsilyl)prop-2-yn-1-one (S4)



MnO_2 (160 mg, 1.84 mmol) was added to a stirred solution of alcohol **S3** (20 mg, 0.067 mmol) in CH_2Cl_2 (0.8 mL) at 0 ºC. After 6.5 h the reaction mixture was rapidly filtered through Celite® (Et_2O eluent) and concentrated (0 ºC bath) to give ketone **S4** (17 mg, 0.057 mmol, 85%) as a clear red oil. Because of the high reactivity of this ketone at ambient temperature this sample was characterized without further purification.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.41 [m, 4H, =C-(C*H*$_2$)$_2$], 2.34 (t, *J* = 7.0 Hz, 2H, ≡CC*H*$_2$), 1.63 (m, 4H, $CH_2(CH_2)_2CH_2$), 1.58 (sext, *J* = 7.2 Hz, 2H, ≡CH_2CH_2), 1.00 [t, *J* = 7.4 Hz, 3H, C*H*$_3$], and 0.28 [s, 6H, $Si(CH_3)_2C$].

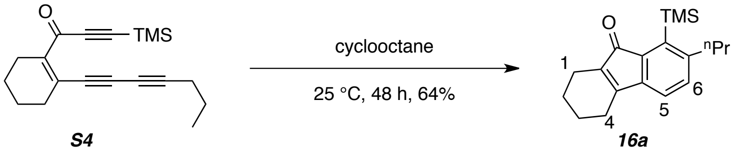
^{13}C NMR (125 MHz, $CDCl_3$): δ 177.4, 144.2, 131.9, 102.5, 101.4, 89.2, 85.7, 73.9, 66.1, 33.5, 25.6, 21.9, 21.8 (2x), 21.6, 13.7, and -0.5.

IR (neat): 2936, 2225, 2149, 1610, 1591, 1249, 861, and 846 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{24}NaOSi^+$ [M+Na$^+$] requires 319.1489; found 319.1474.

TLC: R_f 0.4 (9:1 Hex/EtOAc).

7-Propyl-8-(trimethylsilyl)-1,2,3,4-tetrahydro-fluoren-9-one (16a)



Indenone **16a** was prepared following general procedure C (25 ºC, 48 h) from ketone **S4** (17 mg, 0.057 mmol) and cyclooctane (6 mL). The crude material was purified by MPLC (hexanes:EtOAc 39:1) to give the indenone **16a** (11 mg, 0.037 mmol, 64%) as a clear amber oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02 (d, *J* = 7.3 Hz, 1H, *H5*), 6.83 (d, *J* = 7.3 Hz, 1H, *H6*), 2.66 (br t, *J* = 8.0 Hz, 2H, ArC*H*$_2$), 2.38 (tt, *J* = 6.0, 2.7 Hz, 2H, *H1*$_2$), 2.19 (tt, *J* = 6.1, 2.7 Hz, 2H, *H4*$_2$), 1.79

(nfom, 2H, $CH_2(CH_2)_2CH_2$), 1.71 (nfom, 2H, $CH_2(CH_2)_2CH_2$), 1.49 (br sext, J = 7 Hz, 2H, CH_2CH_3), 0.94 (t, J = 7.3 Hz, 3H,CH_3), and 0.38 [s, 9H, $Si(CH_3)_3$].

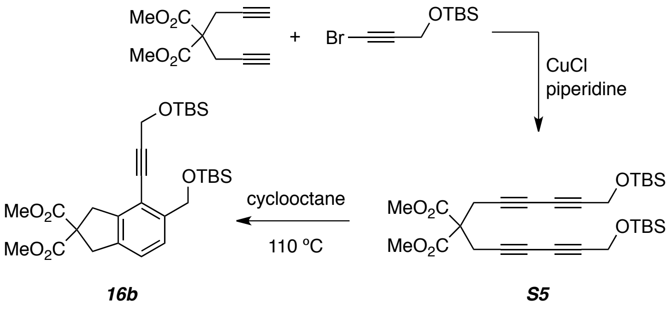
^{13}C NMR (125 MHz, $CDCl_3$): δ 199.2, 157.0, 149.2, 143.4, 138.6, 138.4, 133.1, 132.7, 118.7, 39.0, 27.1, 22.6, 22.21, 22.20, 19.7, 13.9, and 2.5.

IR (neat): 2953, 2874, 1714, 1607, 1248, 968, 862, 849, and 769 cm^{-1}.

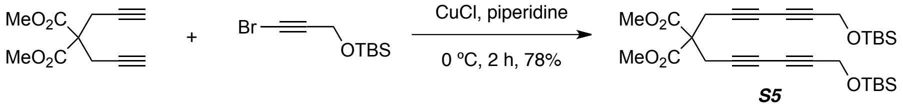
HRMS (ESI-TOF): Calcd for $C_{19}H_{26}NaOSi^+$ [$M+Na^+$] requires 321.1645; found: 321.1677.

TLC: R_f 0.5 (9:1 Hex/EtOAc).

Synthesis of indane 16b (Figure 3D of manuscript)



Dimethyl 2,2-bis(6-((tert-butyldimethylsilyl)oxy)hexa-2,4-diyn-1-yl)malonate (S5)



Tetrayne **S5** was prepared following general procedure B from dimethyl 2,2-di(prop-2-yn-1-yl)malonate[8] (166 mg, 0.8 mmol), ((3-bromoprop-2-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane[9] (620 mg, 2.5 mmol), CuCl (30 mg, 0.30 mmol), and piperidine (3.0 mL). Purification by flash chromatography (hexanes:EtOAc 3:1) gave the tetrayne **S5** (340 mg, 0.63 mmol, 78%) as a clear amber oil.

^{1}H NMR (500 MHz, CDCl$_3$): δ 4.35 (s, 4H, CH_2OSi), 3.77 (s, 6H, CO$_2$CH_3), 3.08 (s, 4H, CH$_2$CC), 0.90 [s, 18H, SiC(CH_3)$_3$], and 0.11 [s, 12H, Si(CH_3)$_2$].

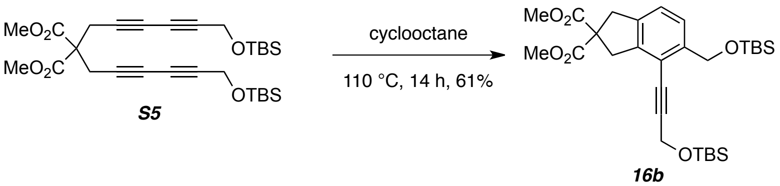
^{13}C NMR (125 MHz, CDCl$_3$): δ 168.7, 75.8, 74.2, 69.4, 68.1, 56.8, 53.5, 52.2, 25.9, 24.0, 18.4, and -5.1.

IR (neat): 2955, 2930, 2857, 1746, 1254, 1212, 1089, 837, and 780 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{29}H_{44}NaO_6Si_2^+$ [M+Na$^+$] requires 567.2569; found 567.2543.

TLC: R$_f$ 0.4 (3:1 hex:EtOAc).

Dimethyl 5-(((tert-butyldimethylsilyl)oxy)methyl)-4-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-1*H*-indene-2,2(3*H*)-dicarboxylate (16b)



Indane **16b** was prepared following general procedure C (110 ºC, 14 h) from tetrayne **S5** (28 mg, 0.05 mmol) and cyclooctane (5 mL). The crude material was purified by MPLC (hexanes:EtOAc 3:1) to give the indane **16b** (17 mg, 0.03 mmol, 61%) as a clear amber oil.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.36 (d, J = 7.8 Hz, 1H, $H7$), 7.15 (d, J = 7.8 Hz, 1H, $H6$), 4.83 (s, 2H, ArCH_2O), 4.59 (s, 2H, C≡CCH_2O), 3.75 (s, 6H, CO$_2$CH_3), 3.66 (s, 2H, $H3_2$), 3.59 (s, 2H, $H1_2$), 0.95 [s, 9H, SiC(CH_3)$_3$], 0.94 [s, 9H, SiC(CH_3)$_3$], 0.17 [s, 6H, Si(CH_3)$_2$], and 0.10 [s, 6H, Si(CH_3)$_2$].

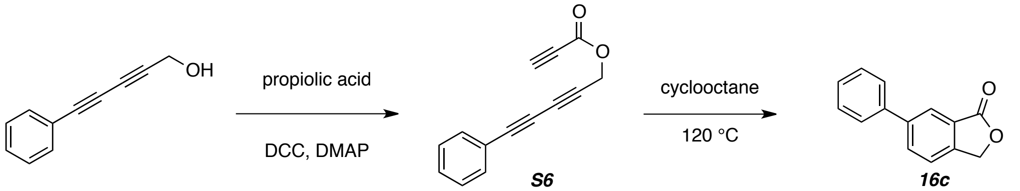
^{13}C NMR (125 MHz, $CDCl_3$): δ 172.2, 142.7, 142.2, 138.2, 125.0, 124.2, 116.0, 96.4, 80.2, 63.4, 59.9, 53.1, 52.5, 40.8, 40.6, 26.1, 26.0, 18.6, 18.5, -4.9, and -5.1.

IR (neat): 2952, 2923, 2857, 1739, 1249, 1105, 1084, 838, and 780 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{29}H_{46}NaO_6Si_2^+$ [M+Na$^+$] requires 569.2725; found 569.2704.

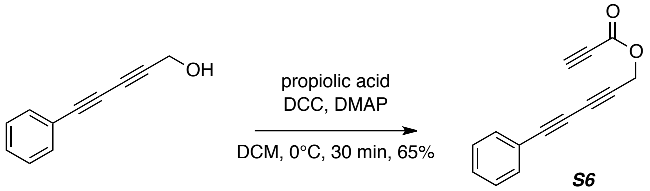
TLC: R_f 0.3 (6:1 hex:EtOAc).

Synthesis of phthalide 16c (Figure 3D of manuscript)



S6 **16c**

5-Phenylpenta-2,4-diyn-1-yl propiolate (S6)



S6

To a solution of 5-phenylpenta-2,4-diyn-1-ol[10] (312 mg, 2.0 mmol) and propiolic acid (154 mg, 2.2 mmol) in dichloromethane cooled at 0 °C was added DCC (494 mg, 2.4 mmol) and DMAP (12 mg, 0.1 mmol). The reaction mixture was stirred for an additional 30 min at this temperature. The resulting slurry was filtered through Celite®, concentrated, and purified with column chromatography (hexanes:EtOAc 12:1) to give ester **S6** (270 mg, 1.3 mmol, 65%) as a dark yellow oil.

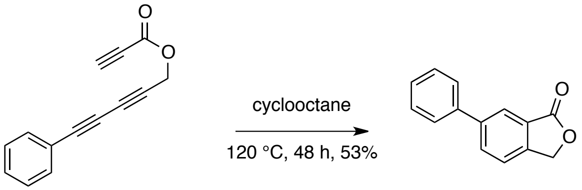
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.50 (br d, *J* = 7.4 Hz, 2H, ArH_o), 7.38 (tt, *J* = 7.5, 1.4 Hz, 1H, ArH_p), 7.33 (br dd, *J* = 7.3, 7.3 Hz, ArH_m), 4.93 (s, 2H, CH_2O), and 2.97 (s, 1H, C≡C*H*).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 151.9, 132.9, 129.8, 128.7, 121.2, 79.6, 76.3, 74.7, 74.0, 73.0, 72.5, and 54.3 ppm.

IR: 3283, 2932, 2856, 2250, 2121, 1722, 1649, 1596, 1491, 1441, 1368, 1209, 963, 755, and 689 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{14}H_8AgO_2^+$ [M+Ag$^+$] requires 314.9570; found 314.9587.

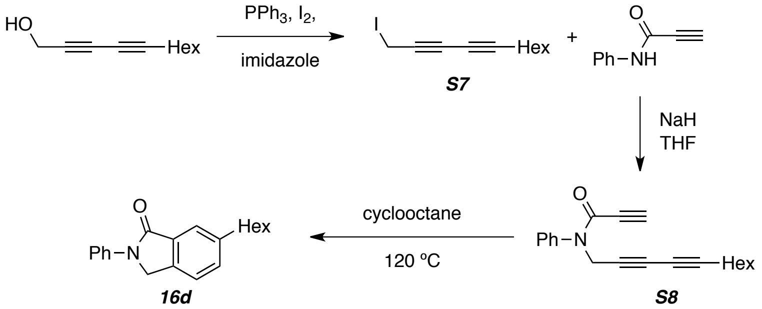
6-Phenylisobenzofuran-1(3*H*)-one (16c)



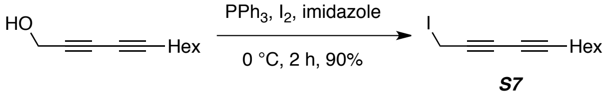
S6 **16c**

Phthalide **16c** was prepared following general procedure C (120 ºC, 48 h) from ester **S6** (21 mg, 0.10 mmol) and cyclooctane (10 mL). The crude material was purified by flash column chromatography (hexanes:EtOAc 3:1) to yield phthalide **16c** (11 mg, 0.053 mmol, 53%). The ^{1}H NMR spectrum is consistent with the reported data[11].

Synthesis of isoindolinone 16d (Figure 3D of manuscript)



1-Iodoundeca-2,4-diyne (S7)



PPh_3 (1.15 g, 4.4 mmol), I_2 (1.2 g, 4.8 mmol), and imidazole (0.56 g, 8 mmol) were sequentially added to a stirred solution of undeca-2,4-diyn-1-ol[12] (678 mg, 4.1 mmol) in CH_2Cl_2 (20 mL) at 0 °C. After 2 h the reaction mixture was diluted with CH_2Cl_2 and washed with satd. aq. $Na_2S_2O_3$. The organic extract was washed with brine, dried (Na_2SO_4), and concentrated. Purification by flash chromatography (hexanes:EtOAc 12:1) gave the iodide **S7** (1.0 g, 3.7 mmol, 90%) as a pale yellow oil. This compound was stored in a refrigerator as a precaution toward decomposition.

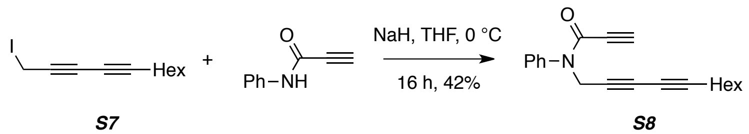
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.75 (t, J = 1.2 Hz, 2H, CH_2I), 2.27 (tt, J = 7.0, 1.1 Hz, 2H, $C{\equiv}CCH_2CH_2$), 1.53 (tt, J = 7.3, 7.3 Hz, 2H, $C{\equiv}CCH_2CH_2$), 1.41-1.34 (m, 2H), 1.33-1.23 (m, 4H), and 0.89 (t, J = 7.2 Hz, 3H, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ 83.2, 72.2, 70.6, 65.0, 31.5, 28.7, 28.3, 22.7, 19.6, 14.3 and -18.1 ppm.

IR (neat): 2953, 2929, 2857, 2248, 1460, 1378, 1255, and 1143 cm^{-1}.

GC-MS: Retention time 8.39 min; electron impact (70 eV), *m/z* (ion, rel int): 274 (M+, 4), 203 (M+-C5H11, 5), 147 (M+-I, 7), 127 (I+, 18), 119 (C_9H_{11}+, 51), 105 (C_8H_9+, 100), 91 (C_7H_7+, 95), and 77 (C_6H_5+, 66).

N-Phenyl-*N*-(undeca-2,4-diyn-1-yl)propiolamide (S8)



NaH (60% dispersion in mineral oil, 44 mg, 1.1 mmol) was added to a stirred solution of *N*-phenylpropiolamide[13] (145 mg, 1 mmol) in THF (6 mL) pre-cooled at 0 °C. The resulting mixture was kept at this temperature for 30 min, after which iodide **S7** (345 mg, 1.2 mmol) in THF (1.2 mL) was added dropwise. The reaction mixture was stirred for an additional 3 h and quenched by addition of satd. aq. NH_4Cl. The resulting mixture was separated and the aqueous layer washed with EtOAc. The combined organic layers were washed with brine, dried, and concentrated. The residue was purified by flash chromatography (hexanes:EtOAc 5:1) to give the amide **S8** (122 mg, 0.42 mmol, 42%) as a pale yellow oil.

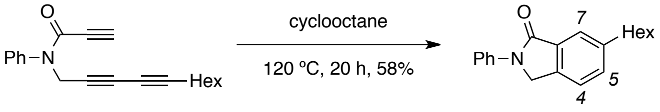
^{1}H NMR (500 MHz, CDCl$_3$, as a 6:1 mixture of rotamers): major rotamer: δ 7.45-7.40 (m, 3H, Ar*H$_m$H$_p$*), 7.35 (d, *J* = 7.5 Hz, 2H, Ar*H$_o$*), 4.58 (s, 2H, NC*H$_2$*), 2.82 (s, 1H, C≡C*H*), 2.45 (t, *J* = 7.0 Hz, 2H, C≡CC*H$_2$*CH$_2$), 1.51 (tt, *J* = 7.6, 7.6 Hz, 2H, C≡CCH$_2$C*H$_2$*), 1.37 (tt, *J* = 7.8, 7.8 Hz, 2H, C≡CCH$_2$CH$_2$C*H$_2$*), 1.33-1.23 (m, 4H), and 0.89 (t, *J* = 7.1 Hz, 3H, C*H$_3$*). Minor rotamer: δ 4.75 (s, NC*H$_2$*), 3.28 (s, C≡C*H*).

^{13}C NMR (125 MHz, CDCl$_3$): δ 152.7, 140.6, 129.6, 129.1, 128.5, 81.0, 80.5, 76.0, 69.9, 69.8, 64.8, 38.9, 31.4, 28.7, 28.3, 22.7, 19.4, and 14.2 ppm.

IR (neat): 2954, 2930, 2858, 2257, 2110, 1646, 1595, 1494, 1456, 1383, 1275, 1220, and 697 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{20}H_{21}NNaO^+$ [M+Na]$^+$ requires 314.1515; found 314.1509.

6-Hexyl-2-phenylisoindolin-1-one (16d)



S8 *16d*

Isoindolinone **16d** was prepared following general procedure C (120 ºC, 20 h) from amide **S8** (15 mg, 0.052 mmol) and cyclooctane (5 mL). The crude material was purified by flash column chromatography (hexanes:EtOAc 3:1) to yield the isoindolinone **16d** (9 mg, 0.03 mmol, 58%) as a colorless solid.

^{1}H NMR (500 MHz, CDCl$_3$): 7.87 (dd, *J* = 8.6, 1.0 Hz, 2H, Ph*H$_o$*), 7.74 (s, 1H, *H7*), 7.42 (dd, *J* = 8.6, 7.5 Hz, 2H, Ph*H$_m$*), 7.43-7.39 (m, 2H, *H4H5*), 7.17 (tt, *J* = 7.4, 1.1 Hz, 1H, Ph*H$_p$*), 4.82 (s, 2H, C*H$_2$*N), 2.72 (br t, *J* = 7.8 Hz, 2H, ArC*H$_2$*CH$_2$), 1.69-1.62 (m, 2H, ArCH$_2$C*H$_2$*), 1.36-1.25 (m, 6H), and 0.88 (br t, *J* = 7.0 Hz, C*H$_3$*).

^{1}H NMR (500 MHz, CD$_3$CN): 7.90 (dd, *J* = 8.8, 1.1 Hz, 2H, Ph*H$_o$*), 7.61 (dd, *J* = 1.6, 0.8 Hz, 1H, *H7*), 7.50 (ddt, *J* = 7.7, 0.8, 0.8 Hz, 1H, *H4*), 7.48 (dd, *J* =7.7, 1.6 Hz, 1H, *H5*), 7.44 (dd, *J* = 8.8, 7.4 Hz, 2H, Ph*H$_m$*), 7.18 (tt, *J* = 7.4, 1.8 Hz, 1H, Ph*H$_p$*), 4.86 (d, *J* = 0.8 Hz, 2H, NC*H$_2$*), 2.73 (br t, *J* = 7.7 Hz, 2H, ArC*H$_2$*), 1.65 (br tt, *J* = 7.5, 7.5 Hz, 2H, ArCH$_2$C*H$_2$*), 1.38-1.26 (m, 6H), and 0.89 (br t, *J* = 7.0 Hz, C*H$_3$*).

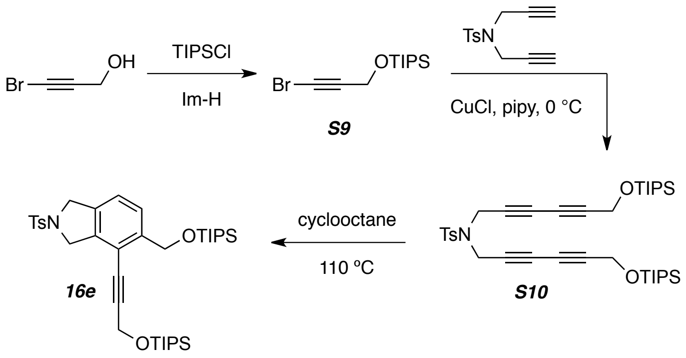
^{13}C NMR (125 MHz, CDCl$_3$): δ 168.0, 143.8, 139.9, 137.8, 133.5, 132.8, 129.3, 124.6, 123.9, 122.5, 119.7, 50.8, 36.0, 31.9, 31.7, 29.1, 22.8, and 14.3 ppm.

IR (neat): 2954, 2924, 2855, 1682, 1598, 1500, 1463, 1382, 1307, 1171, 1142, and 908 cm^{-1}.

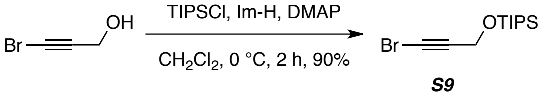
HRMS (ESI-TOF): Calcd for $C_{20}H_{23}NNaO^+$ [M+Na]$^+$ requires 316.1672; found 316.1667.

Mp: 121-123 °C.

Synthesis of isoindole 16e (Figure 3D of manuscript)



((3-Bromoprop-2-yn-1-yl)oxy)triisopropylsilane (S9)



TIPSCl (1.27 g, 6.6 mmol) was added to a solution of imidazole (449 mg, 6.6 mmol), DMAP (81 mg, 0.66 mmol), and 3-bromo-2-propyn-1-ol[14] (804 mg, 6.0 mmol) in DCM (20 mL) at 0 °C with stirring. After 2 h the reaction mixture was diluted with water (30 mL) and extracted with CH_2Cl_2 (2x20 mL). The combined organic extracts were washed with brine (20 mL), dried ($MgSO_4$), and concentrated. Purification by flash chromatography (hexanes:EtOAc 19:1) gave the silylether **S9** (1.57 g, 5.4 mmol, 90%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.40 (2H, s, CH_2OTIPS), 1.17-1.05 (3H, m, *J* = 5.5 Hz, Si(C*H*(CH_3)$_2$)$_3$), and 1.08 [18H, d, *J* = 5.5 Hz, Si(CH(C*H*$_3$)$_2$)$_3$].

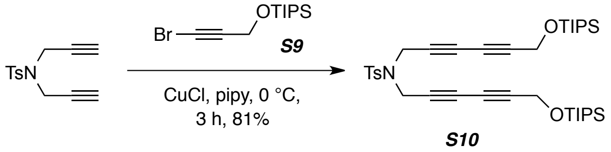
^{13}C NMR (125 MHz, $CDCl_3$): δ 78.7 (*C*-CH_2OTIPS), 52.9 (*C*H_2OTIPS), 44.4 (C-Br), 17.9 (SiCH(*C*H_3)$_2$), and 12.0 (Si*C*H(CH_3)$_2$.

IR (neat): 2943, 2866, 2220, 1463, 1368, 1260, 1102, 1093, 1070, 1014, 997, 919, 882, 748, 688, 671, and 648 cm^{-1}.

GC-MS: Retention time 7.05 min; electron impact (70 eV), *m/z* (ion, rel int): 290/292 (M+, 2), 247/249 (30), and 205/207 (100).

TLC: R_f 0.6 (19:1 Hex/EtOAc).

4-Methyl-*N*,*N*-bis(6-((triisopropylsilyl)oxy)hexa-2,4-diyn-1-yl)benzenesulfonamide (S10)



CuCl (40 mg, 0.4 mmol) was added to a solution of 4-methyl-*N*,*N*-di(prop-2-yn-1-yl)benzenesulfonamide[15] (494 mg, 2.0 mmol) and 3-bromo-1-triisopropylsilyloxy-2-propyne **S9** (1.28 g, 4.4 mmol) in freshly deaerated piperidine (8 mL, 0.4 M) at 0 °C. After 3 h the reaction mixture was partitioned between EtOAc (20 mL) and satd. aq. NH_4Cl (20 mL). The aqueous phase was extracted twice with EtOAc (2x15 mL) and the combined organic extracts were washed with brine (10 mL), dried over

$MgSO_4$, and concentrated. Purification by flash column (hexanes:EtOAc 19:1) gave tetrayne **S10** (1.08 g, 1.62 mmol, 81%). On some occasions following nominally this same procedure resulted in considerably reduced yields. There likely is an important unidentified variable that is important to control.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (2H, d, *J* = 8.0 Hz, Ar-H), 7.31 (2H, d, *J* = 8.0 Hz, Ar-H), 4.41 (4H, s, CH_2OTIPS), 4.20 (4H, s, N-CH_2), 2.43 (3H, s, Ar-CH_3), 1.16-1.04 (6H, m, *J* = 5.5 Hz, OSi[C*H*$(CH_3)_2]_3$), and 1.07 (36H, d, *J* = 5.5 Hz, OSi[CH(C*H*$_3)_2]_3$).

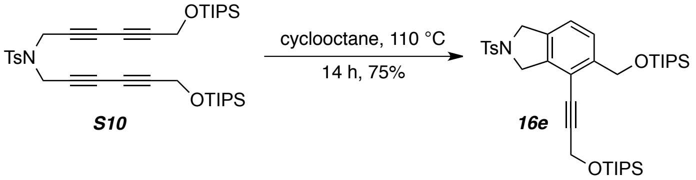
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 134.6, 129.8, 127.8, 77.6, 71.3, 70.3, 68.3, 52.2, 37.3, 21.6, 17.9, and 11.9.

IR (neat): 2943, 2866, 1463, 1356, 1165, 1093, 1069, 996, 884, 748, and 685 cm^{-1}.

HR ESI-MS: $[C_{37}H_{57}NNaO_4SSi_2]^+$ requires 690.3439; found 692.3446.

TLC: R_f 0.35 (9:1 Hex/EtOAc).

2-Tosyl-5-(((triisopropylsilyl)oxy)methyl)-4-(3-((triisopropylsilyl)oxy)prop-1-yn-1-yl) isoindoline (16e)



Isoindole **16e** was prepared following general procedure C (110 ºC, 14 h) from tetrayne **S10** (20 mg, 0.03 mmol) and cyclooctane (1 mL). The crude material was purified by MPLC (hexanes:EtOAc 19:1) to give the bicyclic-isoindole **16e** (15 mg, 0.022 mmol, 75%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (2H, d, *J* = 8.0 Hz, Ar-H), 7.51 (1H, d, *J* = 8.0 Hz, Ar-H), 7.31 (2H, d, *J* = 8.0 Hz, Ar-H), 7.13 (1H, d, *J* = 8.0 Hz, Ar-H), 4.89 (2H, br s, Ar-CH_2OTIPS), 4.64 (2H, br s, -CH_2OTIPS or N-CH_2), 4.63 (4H, br s, -CH_2OTIPS or N-CH_2), 2.41 (3H, s, Ar-CH_3), 1.25-1.00 (6H, m, *J* = 5.5 Hz, Si[C*H*$(CH_3)_2]_3$), 1.11 (18H, d, *J* = 5.5 Hz, Ar-CH_2OSi[CH(C*H*$_3)_2]_3$), and 1.07 (18H, d, *J* = 5.5 Hz, CH_2OSi[CH(C*H*$_3)_2]_3$).

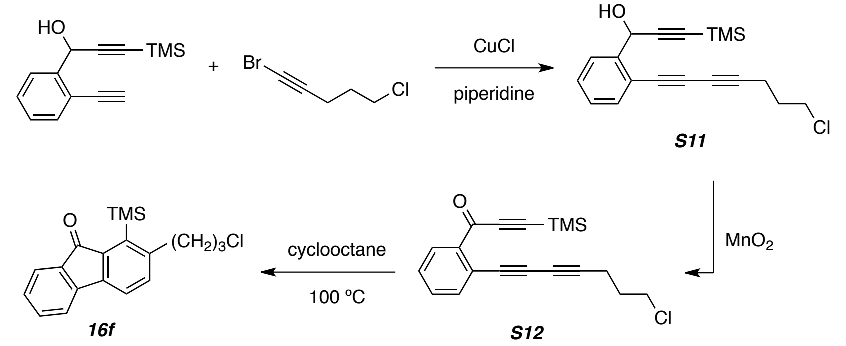
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.8, 143.3, 138.9, 134.3, 133.9, 130.0, 127.7, 125.3, 122.4, 114.5, 97.6, 78.6, 63.2, 54.2, 54.0, 52.6, 21.6, 18.2, 18.1, 12.2, and 12.1.

IR (neat): 2942, 2865, 1463, 1351, 1273, 1165, 1098, 1068, 996, 882, 815, 765, and 684 cm^{-1}.

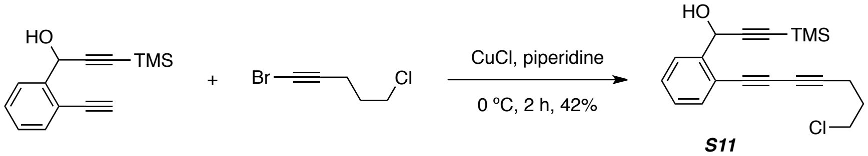
HR ESI-MS: $[C_{37}H_{59}NNaO_4SSi_2]^+$ requires 692.3596; found 692.3589.

TLC: R_f 0.25 (9:1 Hex/EtOAc).

Synthesis of fluorenone 16f (Figure 3D of manuscript)



1-(2-(7-Chlorohepta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S11)



Triyne **S11** was prepared following general procedure B from 1-(2-ethynylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol[6] (228 mg, 1.00 mmol), 1-bromo-5-chloropent-1-yne (from 5-chloro-1-pentyne using general procedure A) (216 mg, 1.20 mmol), CuCl (30 mg, 0.30 mmol), and piperidine (2.7 mL). Purification by flash chromatography (hexanes:EtOAc 6:1) gave the triyne **S11** (139 mg, 0.42 mmol, 42%) as a clear amber oil.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.67 (dd, *J* = 7.8, 1.6 Hz, 1H, *H6*), 7.50 (dd, *J* = 7.7, 1.5 Hz, 1H, *H3*), 7.40 (ddd, *J* = 7.7, 7.6, 1.5 Hz, 1H, *H4*), 7.29 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H5*), 5.82 (bs, 1H, ArC*H*OH), 3.68 (t, *J* = 6.3 Hz, 2H, CH_2Cl), 2.59 (t, *J* = 6.8 Hz, 2H, C≡CCH_2), 2.49, (bs, 1H, CH$_2$O*H*), 2.04 (p, *J* = 6.5 Hz, 2H, CH_2CH$_2$Cl), and 0.20 [s, 9H, Si(CH$_3$)$_3$].

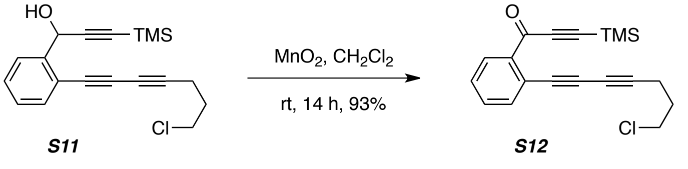
^{13}C NMR (125 MHz, CDCl$_3$): δ 143.5, 133.8, 129.6, 128.5, 127.1, 120.6, 104.2, 91.9, 84.2, 79.4, 72.4, 66.1, 63.5, 43.5, 31.1, 17.2, and 0.1.

IR (neat): 3427, 2960, 2901, 2239, 2173, 1446, 1250, 1037, 846, and 761 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{21}NaClOSi^+$ [M+Na$^+$] requires 351.0942; found 351.0935.

TLC: R$_f$ 0.2 (6:1 hex:EtOAc)

1-(2-(7-Chlorohepta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (S12)



MnO$_2$ (750 mg, 8.65 mmol) was added to a stirred solution of alcohol **S11** (268 mg, 0.82 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature. After 14 h the reaction mixture was filtered through a small column of SiO_2 (EtOAc eluent) and purified by MPLC (hexanes:EtOAc 6:1) to give the triyne **S12** (247 mg, 0.76 mmol, 93%) as an amber oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (dd, *J* = 7.7, 1.6 Hz, 1H, *H6*), 7.60 (dd, *J* = 7.6, 1.5 Hz, 1H, *H3*), 7.51 (ddd, *J* = 7.6, 7.5, 1.5, 1H, *H4*), 7.45 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H, *H5*), 3.68 (t, *J* = 6.3 Hz, 2H, CH_2Cl), 2.59 (t, *J* = 6.8 Hz, 2H, $ArCH_2$), 2.03 (p, *J* = 6.5 Hz, 2H, $CH_2CH_2CH_2Cl$), and 0.31[s, 9H, $Si(CH_3)_3$].

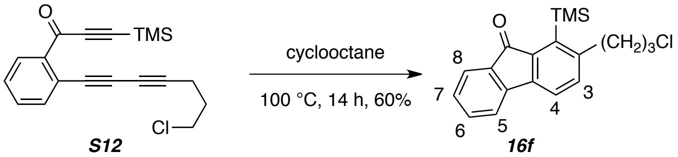
^{13}C NMR (125 MHz, $CDCl_3$): δ 176.6, 139.1, 135.8, 132.6, 132.0, 128.6, 121.9, 101.50, 101.49, 84.9, 80.3, 73.3, 66.6, 43.6, 31.1, 17.3, and -0.6.

IR (neat): 2964, 2243, 2152, 1641, 1560, 1481, 1296, 1250, 1232, 1012, 846, and 758 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{19}NaClOSi^+$ [M+Na$^+$] requires 349.0786; found 349.0780.

TLC: R_f 0.3 (6:1 hex:EtOAc)

2-(3-Chloropropyl)-1-(trimethylsilyl)-9*H*-fluoren-9-one (16f)



Fluorenone **16f** was prepared following general procedure C (100 ºC, 14 h) from triynone **S12** (10 mg, 0.03 mmol) and cyclooctane (3 mL). The crude material was purified by MPLC (hexanes:EtOAc 6:1) to give fluorenone **16f** (6 mg, 0.02 mmol, 60%) as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (ddd, *J* = 7.3, 0.9, 0.9 Hz, 1H, *H8*), 7.43-7.46 (m, 2H, *H6/H5*), 7.45 (d, *J* = 7.6 Hz, 1H, *H4*), 7.24-7.27 (nfom, 1H, *H7*), 7.25 (d, *J* = 7.6 Hz, 1H, *H3*), 3.55 (t, *J* = 6.5 Hz, 2H, CH_2Cl), 2.95 (br t, *J* = 7.6 Hz, 2H, $ArCH_2$), 1.97-2.03 (br p, *J* = 7.1 Hz, 2H, $ArCH_2CH_2$), and 0.44 [s, 9H, $Si(CH_3)_3$].

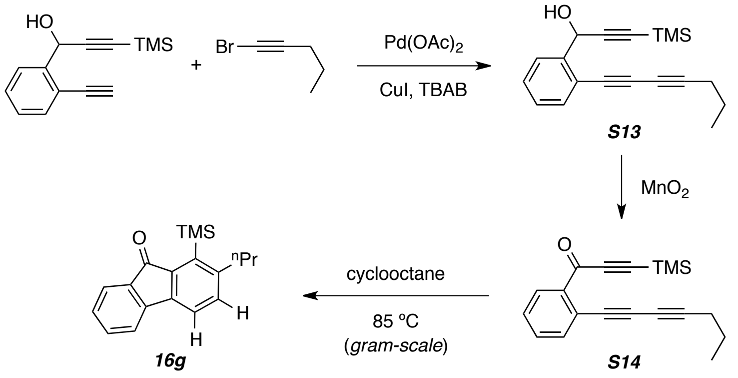
^{13}C NMR (125 MHz, $CDCl_3$): δ 195.4, 148.5, 144.0, 143.6, 141.2, 140.7, 135.4, 134.7, 133.9, 128.8, 124.1, 121.0, 119.6, 44.1, 36.0, 33.7, and 2.6.

IR (neat): 2950, 2898, 1711, 1606, 1438, 1247, 1182, 861, 846, and 745 cm^{-1}.

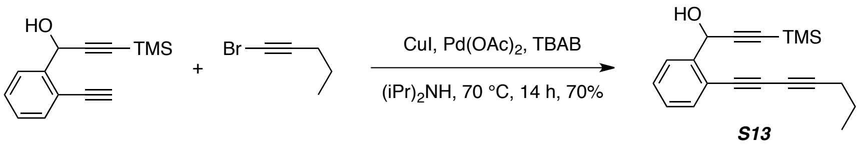
HRMS (ESI-TOF): Calcd for $C_{19}H_{21}NaClOSi^+$ [M+Na$^+$] requires 351.0942; found 351.0918.

TLC: R_f 0.2 (6:1 hex:EtOAc)

Gram-scale reaction of S14 to fluorenone 16g



1-(2-(Hepta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (S13)



CuI (5 mg, 0.03 mmol) was added to a solution of 1-(2-ethynylphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol[6] (1.52 g, 6.67 mmol), 1-bromopent-1-yne[16] (1.35 g, 9.35 mmol), tetrabutylammonium bromide (13 mg, 40 mmol), and diisopropylamine (67 mL) at 70 ºC under an inert atmostphere. $Pd(OAc)_2$ (2 mg, 0.009 mmol) was added after five minutes. After 14 h the reaction mixture was diluted in 2 M HCl and extracted with EtOAc. Purification by MPLC (hexanes:EtOAc 6:1) gave the triyne **S13** (1.38 g, 4.69 mmol, 70%) as a clear yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (ddd, *J* = 7.8, 1.4, 0.5 Hz, 1H, *H6*), 7.50 (ddd, *J* = 7.7, 1.5, 0.5 Hz, 1H, *H3*), 7.39 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H4*), 7.28 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, *H5*), 5.83 (d, *J* = 5.7 Hz, 1H, C*H*OH), 2.48 (d, *J* = 5.7, 1H O*H*), 2.36 (t, *J* = 7.0 Hz, 2H, $CH_2CH_2CH_3$), 1.62 (sext, *J* = 7.3 Hz, 2H, CH_2CH_3), 1.04 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), and 0.20 (s, 9H, $SiCH_3$).

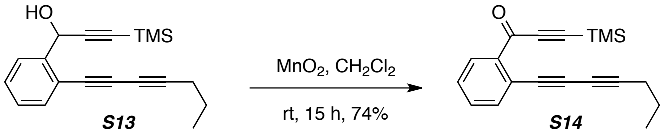
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.4, 133.7, 129.4, 128.4, 127.1, 120.9, 104.2, 91.9, 86.5, 79.9, 71.8, 65.2, 63.6, 21.9, 21.8, 13.7, and 0.0.

IR (neat): 3439, 2963, 2239, 2173, 1701, 1250, 1038, 985, 844, and 761 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{22}NaOSi^+$ [$M+Na^+$] requires 317.1332; found 317.1318.

TLC: R_f 0.3 (9:1 Hex/EtOAc).

1-(2-(Hepta-1,3-diyn-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (S14)



MnO_2 (1.79 g, 20.6 mmol) was added to a solution of alcohol **S13** (611 mg, 2.08 mmol) in CH_2Cl_2 (10 mL) and the resulting suspension was vigorously stirred for 15 h. The reaction mixture was filtered through a plug of Celite® (EtOAc eluent) and concentrated to give the ketone **S14** (450 mg, 1.54 mmol, 74%) as a clear amber oil.

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.07 (dd, *J* = 7.8, 1.5 Hz, 1H, *H6*), 7.61 (dd, *J* = 7.7, 1.5 Hz, 1H, *H3*), 7.49 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H, *H4*), 7.43 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H, *H5*), 2.36 (t, *J* = 7.0 Hz, 2H, CH_2CH$_2$CH$_3$), 1.61 (sext, *J* = 7.2 Hz, 2H, CH_2CH$_3$), 1.03 (t, *J* = 7.4 Hz, 3H, CH$_2$CH_3), and 0.31 (s, 9H, SiCH_3).

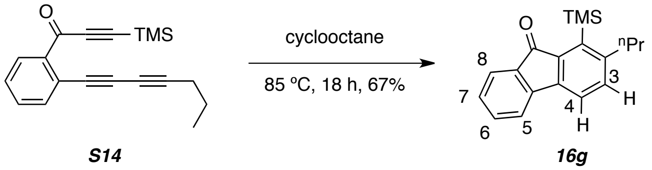
^{13}C NMR (125 MHz, CDCl$_3$): δ 176.7, 139.1, 135.7, 132.6, 131.8, 128.4, 122.3, 101.6, 101.5, 87.2, 80.9, 72.8, 65.8, 21.8 (likely 2x), 13.7, and -0.6.

IR (neat): 2965, 2242, 2152, 1648, 1234, 1014, 847, and 756 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{20}NaOSi^+$ [M+Na$^+$] requires 315.1176; found 315.1192.

TLC: R$_f$ 0.4 (9:1 Hex/EtOAc).

2-Propyl-1-(trimethylsilyl)-9*H*-fluoren-9-one (16g, gram-scale reaction)



A solution of triynone **S14** (1.21 g, 4.14 mol) in cyclooctane (410 mL) was heated at 85 °C in a 1000 mL round bottom flask with stirring and under inert atmosphere. After 18 h the reaction mixture was loaded onto a bed of silica gel and washed sequentially with hexanes, to remove the excess cyclooctane, and ethyl acetate. The ethyl acetate fraction was concentrated to provide the crude product mixture. The crude material was purified by flash chromatography (hexanes:EtOAc 19:1) to give fluorenone **16g** (820 mg, 2.79 mmol, 67%) as an orange oil.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.56 (ddd, *J* = 7.3, 1.0, 1.0 Hz, 1H, *H8*), 7.43 (m, 2H, *H5* and *H6*), 7.42 (d, *J* = 7.6 Hz, 1H, *H4*), 7.23 (nfom, 1H, *H7*), 7.21 (d, *J* = 7.6 Hz, 1H, *H3*), 2.73 (br t, *J* = 8.0 Hz, 2H, CH_2CH$_2$CH$_3$), 1.54 (br sext, *J* = 7 Hz, 2H, CH_2CH$_3$), 0.97 (t, *J* = 7.3 Hz, CH$_2$CH_3), and 0.43 (s, 9H, SiCH_3).

^{13}C NMR (125 MHz, CDCl$_3$): δ 195.6, 150.7, 144.2, 143.2, 141.0, 140.4, 135.4, 134.5, 134.0, 128.6, 124.0, 120.8, 119.5, 39.0, 27.1, 14.0, and 2.5.

IR (neat): 2955, 2935, 2875, 1713, 1606, 1248, 968, 861, and 846 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{22}NaOSi^+$ [M+Na$^+$] requires 317.1332; found 317.1358.

TLC: R$_f$ 0.5 (9:1 Hex/EtOAc).

III. Computational details for double hydrogen atom transfer reactions

DFT calculations were carried out in Gaussian 09[17] using the M06-2X/6-311+G(d,p) functional[18]/basis set for geometry optimizations and frequency calculations. To identify starting geometries for the DFT calculations of the cyclic hydrocarbon donors, Monte Carlo conformational searches were carried out in MacroModel version 9.9[19]. Each of the identified conformers was subjected to geometry optimization using the above DFT method. The optimized reactant and product geometries were found to have no imaginary frequencies and the optimized transition structure geometries were found to have only one imaginary frequency. The values for the "Sum of electronic and thermal Free Energies=" were used to determine the free energy (G) of each of the two reactants (G_{Benzyne} and $G_{\text{2H-Donor}}$) and of the transition structure (G_{TS}) for each bimolecular double hydrogen atom transfer reaction. The $\Delta G^{\ddagger}$ value for the double hydrogen atom transfer between the benzyne and each 2H-donor were determined using the following equation:

$$\Delta G^{\ddagger} = G_{\text{TS}} - (G_{\text{Benzyne}} + G_{\text{2H-Donor}})$$

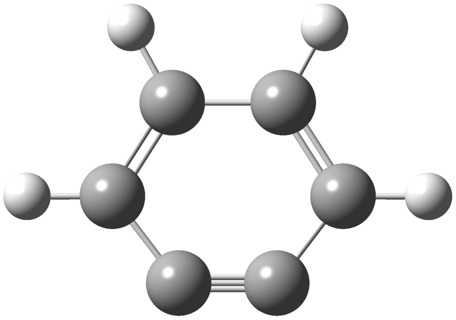
where the G values were those of the lowest energy conformer of the 2H-donor, the *o*-benzyne, and the transition structure.

Table S2. Computed free energies for all reactant, product, and transition structures used for determining the $\Delta G^{\ddagger}$ (cf. Figure 3A and 4C in the manuscript) and ΔG_{RXN} (i.e. for double hydrogen atom transfer between *o*-benzyne and cyclopentane) values. In cases where multiple conformers of a given reactant or transition structure were found, only the lowest energy structure is presented. For comparison we calculated the $\Delta G^{\ddagger}$ for the double hydrogen atom transfer reaction between aryne **13** (from the manuscript) and cyclopentane and found it to be (reassuringly) similar to the corresponding $\Delta G^{\ddagger}$ for the parent benzyne.

	Entry	Structure	Computed Free Energy G (kcal•mol^{-1})	$G_{TS} - G_{Reactants}$	$\Delta G^{\ddagger}$
Reactant and Product Structures	1	*o*-Benzyne	-144840.7		
	2	Cyclooctane	-197170.8		
	3	Cycloheptane	-172528.2		
	4	Cyclopentane	-123236.7		
	5	Norbornane	-171784.6		
	6	Cyclohexane	-147887.9		
	7	THF	-145781.0		
	8	1,4-Dioxane	-192972.9		
	9	Benzene	-145660.4		
	10	Cyclopentene	-122482.5		
	11	Fluorynone (**13** in manuscript)	-641139.1		
Transition Structures	12	1 + Cyclooctane	-341993.9	$G_{12} - (G_1 + G_2)$	17.6
	13	1 + Cycloheptane	-317351.2	$G_{13} - (G_1 + G_3)$	17.7
	14	1 + Cyclopentane	-268058.6	$G_{14} - (G_1 + G_4)$	18.7
	15	1 + Norbornane	-316606.7	$G_{15} - (G_1 + G_5)$	18.5
	16	1 + Cyclohexane	-292704.5	$G_{16} - (G_1 + G_6)$	24.1
	17	1 + THF	-290602.5	$G_{17} - (G_1 + G_7)$	19.2
	18	1 + 1,4-Dioxane	-337786.5	$G_{18} - (G_1 + G_8)$	27.1
	19	12 + Cyclopentane	-764356.3	$G_{19} - (G_4 + G_{11})$	19.4

Energies and geometries for all of the entries in Table S2 (Pages 23 – 46)

Computed energy and geometry of *o*-benzyne



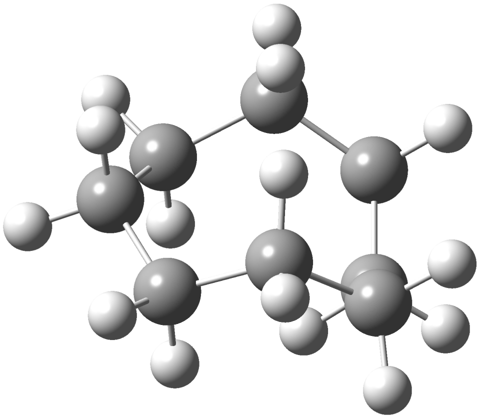
`Sum of electronic and thermal Free Energies`[a] `= -230.818447 A.U.`[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-1.459052	-0.132412	0.000018
C	-0.619665	-1.230665	-0.000010
C	0.619772	-1.230671	-0.000012
C	1.459048	-0.132316	0.000019
C	0.702178	1.051807	-0.000005
C	-0.702256	1.051763	-0.000003
H	-2.540326	-0.134912	0.000002
H	2.540323	-0.134729	0.000002
H	1.224618	2.002344	-0.000019
H	-1.224760	2.002265	-0.000024

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry of the lowest energy conformation of cyclooctane



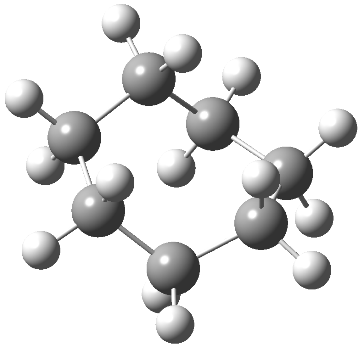
`Sum of electronic and thermal Free Energies`[a] `= -314.211943 A.U.`[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.386062	1.302498	0.075459
C	1.555205	0.000013	-0.708312
C	1.386085	-1.302476	0.075458
C	-0.011757	-1.594145	0.645066
C	-1.181610	-1.318856	-0.319334
C	-1.932003	-0.000017	-0.088097
C	-1.181635	1.318835	-0.319336
C	-0.011786	1.594147	0.645064
H	2.116816	1.330163	0.891727
H	1.651515	2.125159	-0.597901
H	0.872340	0.000008	-1.563660
H	2.560936	0.000022	-1.140582
H	1.651548	-2.125132	-0.597905
H	2.116842	-1.330131	0.891723
H	-0.027389	-2.649099	0.932882
H	-0.170345	-1.039328	1.572997
H	-0.833023	-1.373252	-1.357020
H	-1.917232	-2.121427	-0.214552
H	-2.818322	-0.000026	-0.731086
H	-2.306930	-0.000020	0.943276
H	-0.833049	1.373237	-1.357022
H	-1.917272	2.121392	-0.214553
H	-0.027435	2.649103	0.932874
H	-0.170367	1.039333	1.572998

[a] Used for the $\Delta G^{\ddagger}_{\mathrm{M06\text{-}2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry of the lowest energy conformation of cycloheptane



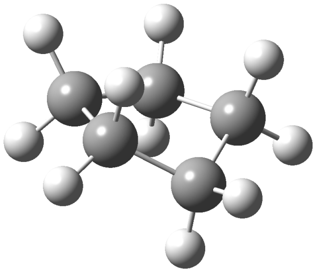
`Sum of electronic and thermal Free Energies`[a] `= -274.941457 A.U.`[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-0.302164	-1.501933	-0.412011
C	-1.540652	-0.758057	0.103147
C	-1.540629	0.758091	-0.103154
C	-0.302128	1.501937	0.412016
C	0.957234	1.228415	-0.423200
C	1.775429	-0.000027	-0.000010
C	0.957196	-1.228429	0.423215
H	-0.517731	-2.573709	-0.383694
H	-0.121706	-1.254041	-1.465273
H	-2.433889	-1.169259	-0.377531
H	-1.642722	-0.973246	1.173961
H	-1.642680	0.973282	-1.173970
H	-2.433859	1.169320	0.377513
H	-0.517671	2.573718	0.383692
H	-0.121687	1.254047	1.465280
H	0.652717	1.122283	-1.470333
H	1.616574	2.100311	-0.393454
H	2.433845	-0.274850	-0.830377
H	2.433899	0.274763	0.830324
H	1.616513	-2.100345	0.393505
H	0.652673	-1.122254	1.470341

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry of the lowest energy conformation of cyclopentane



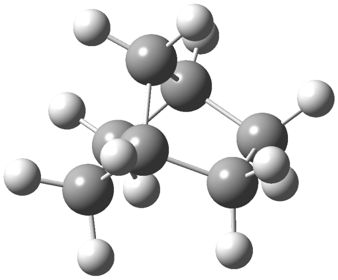
Sum of electronic and thermal Free Energies[a] = -196.390277 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	0.385818	1.231221	-0.105059
C	1.258905	0.011173	0.235529
C	0.429546	-1.170900	-0.272733
C	-0.987219	-0.803866	0.182930
C	-1.080434	0.722828	-0.039973
H	0.567075	2.070685	0.567847
H	0.617753	1.576142	-1.115782
H	1.380797	-0.074487	1.320421
H	2.255624	0.066707	-0.205884
H	0.473479	-1.208453	-1.366795
H	0.767610	-2.135947	0.109375
H	-1.766379	-1.355194	-0.346028
H	-1.090109	-1.033565	1.247707
H	-1.601467	0.943684	-0.973666
H	-1.644074	1.207694	0.758645

[a] Used for the $\Delta G^{\ddagger}_{\mathrm{M06\text{-}2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry of the lowest energy conformation of norbornane

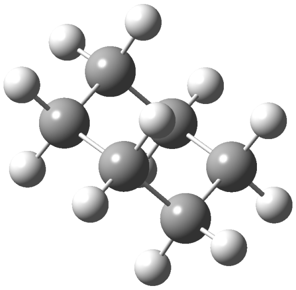


Sum of electronic and thermal Free Energies[a] = -273.756351 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	0.000002	-1.129721	0.339789
C	1.248387	-0.779489	-0.492222
C	1.248383	0.779492	-0.492223
C	-0.000002	1.129721	0.339790
C	-1.248387	0.779489	-0.492222
C	-1.248384	-0.779492	-0.492223
H	1.196535	-1.200976	-1.498320
H	2.151392	-1.170004	-0.017696
H	2.151388	1.170013	-0.017701
H	1.196527	1.200977	-1.498322
H	-2.151392	1.170005	-0.017696
H	-1.196534	1.200976	-1.498320
H	-1.196528	-1.200977	-1.498322
H	-2.151388	-1.170013	-0.017700
C	0.000000	0.000000	1.384438
H	-0.000003	2.147370	0.730337
H	0.000003	-2.147371	0.730336
H	0.891968	0.000001	2.016324
H	-0.891968	-0.000002	2.016324

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.
[b] Atomic Units = Hartrees

Computed energy and geometry of the lowest energy conformation of cyclohexane



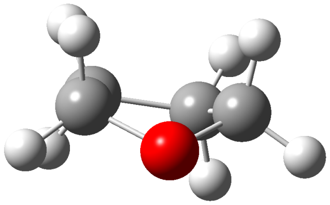
Sum of electronic and thermal Free Energies[a] = -235.674605 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.211373	0.811084	-0.233837
C	-0.097080	1.454448	0.233650
C	-1.308099	0.643098	-0.233836
C	-1.211372	-0.811078	0.233847
C	0.097074	-1.454448	-0.233651
C	1.308100	-0.643103	0.233827
H	-2.234114	1.097326	0.129326
H	-0.100726	1.503293	1.329698
H	-0.166880	2.483590	-0.129270
H	1.252818	0.838955	-1.329834
H	2.067958	1.384997	0.130436
H	-1.252793	-0.838932	1.329846
H	-2.067962	-1.385004	-0.130393
H	0.166880	-2.483590	0.129272
H	0.100713	-1.503296	-1.329698
H	1.352108	-0.664365	1.329875
H	2.234109	-1.097319	-0.129368
H	-1.352089	0.664347	-1.329887

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry of the lowest energy conformation of tetrahydrofuran



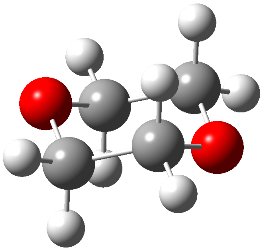
Sum of electronic and thermal Free Energies[a] = -232.317059 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-0.727053	1.048685	0.001155
C	0.814257	0.971705	-0.102986
C	-1.151828	-0.431331	0.118007
H	-1.051389	1.620296	0.871252
H	-1.157310	1.516745	-0.883978
H	1.321852	1.642671	0.590240
H	1.142241	1.214535	-1.114335
H	-1.402299	-0.679166	1.157989
H	-1.993612	-0.700530	-0.518644
O	-0.032045	-1.195054	-0.293715
C	1.100281	-0.503504	0.196032
H	1.199749	-0.668713	1.278647
H	1.983193	-0.898732	-0.304702

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry of the lowest energy conformation of 1,4-dioxane



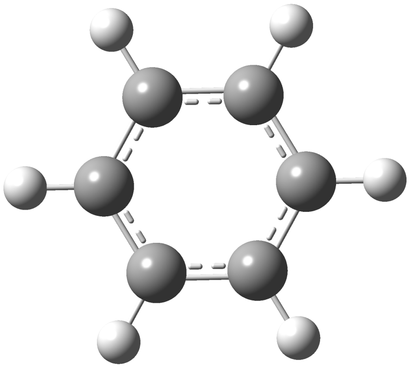
Sum of electronic and thermal Free Energies[a] = -307.522164 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.197526	-0.179741	-0.682838
C	-0.140416	-0.670677	-1.209619
O	-1.189925	0.151375	-0.732743
C	-1.197526	0.179741	0.682838
C	0.140416	0.670677	1.209619
O	1.189925	-0.151375	0.732743
H	1.398345	0.828230	-1.072404
H	2.006123	-0.846886	-0.984057
H	-0.305174	-1.707625	-0.884566
H	-0.172068	-0.628468	-2.299057
H	-2.006123	0.846886	0.984057
H	-1.398345	-0.828230	1.072404
H	0.305174	1.707625	0.884566
H	0.172068	0.628468	2.299057

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry of benzene



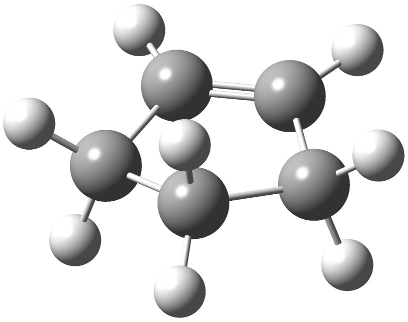
Sum of electronic and thermal Free Energies[a] = -232.124771 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-1.391337	-0.031931	0.000000
C	-0.667949	-1.220979	0.000009
C	0.723285	-1.188838	0.000001
C	1.391335	0.031992	0.000002
C	0.668002	1.220950	0.000001
C	-0.723336	1.188808	-0.000005
H	-2.474672	-0.056246	-0.000007
H	-1.188429	-2.171454	-0.000018
H	1.286545	-2.114684	-0.000021
H	2.474673	0.056165	-0.000012
H	1.188364	2.171490	0.000009
H	-1.286478	2.114725	0.000000

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry of cyclopentene



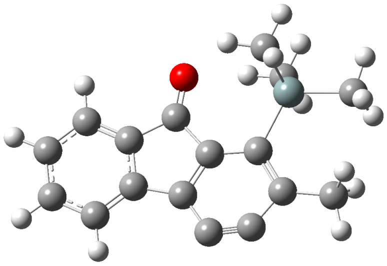
Sum of electronic and thermal Free Energies[a] = −195.188423 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-0.303216	-1.189786	0.000000
C	0.078190	-0.333163	1.226730
C	0.078190	1.069551	0.665108
C	0.078190	1.069551	-0.665108
C	0.078190	-0.333163	-1.226730
H	-1.384460	-1.346354	0.000000
H	1.075923	-0.586623	1.604461
H	-0.618163	-0.460452	2.058666
H	0.118614	1.956325	1.286629
H	0.118614	1.956325	-1.286629
H	1.075923	-0.586623	-1.604461
H	-0.618163	-0.460452	-2.058666
H	0.174438	-2.170083	0.000000

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry of fluorynone **13-comp**



Sum of electronic and thermal Free Energies[a] = –1021.720925 A.U.[b]

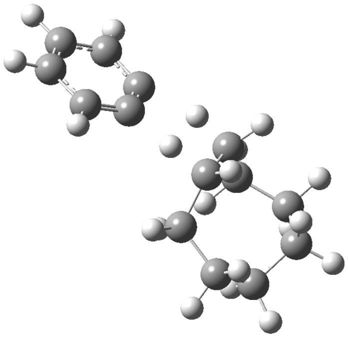
Atom Type	Cartesian Coordinates (x,y,z)		
C	-3.376586	-1.568926	0.000097
C	-4.662063	-1.019773	-0.000056
C	-4.840752	0.361839	-0.000211
C	-3.749231	1.236231	-0.000224
H	-3.214349	-2.640635	0.000236
H	-5.527599	-1.670916	-0.000050
H	-5.845969	0.766727	-0.000320
H	-3.892029	2.310480	-0.000332
C	-0.837833	-1.008104	0.000234
C	-2.304416	-0.699238	0.000066
C	-2.479968	0.686666	-0.000093
C	-0.121849	0.323846	-0.000073
C	-1.146687	1.312595	-0.000082
C	-0.655318	2.601049	-0.000016
C	0.575819	2.780441	0.000059
C	1.688362	1.973070	0.000020
C	1.261215	0.600346	-0.000126
C	3.100969	2.487509	0.000205
O	-0.355483	-2.113049	0.000702
C	2.288681	-1.856895	-1.587161
C	4.322963	-0.374847	-0.000942
C	2.289512	-1.855642	1.587784
H	3.647751	2.152402	0.881594
H	3.647737	2.152968	-0.881414
H	3.089526	3.576133	0.000552
H	2.976890	-2.707580	-1.581617
H	1.279030	-2.238808	-1.723083
H	2.548916	-1.228829	-2.443826
H	4.880949	-1.317754	-0.001166

H	4.632825	0.178075	-0.888607
H	4.633637	0.178116	0.886409
H	2.980000	-2.704485	1.584085
H	2.547035	-1.225858	2.444011
H	1.280667	-2.239973	1.722936
Si	2.504424	-0.879762	-0.000135

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry for the benzyne + cyclooctane TS



Sum of electronic and thermal Free Energies[a] = -545.002382 A.U.[b]

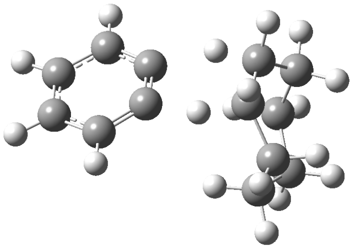
Atom Type	Cartesian Coordinates (x,y,z)		
C	-3.040245	-1.361495	0.316047
C	-4.247015	-0.809740	-0.125296
C	-4.358290	0.553455	-0.435982
C	-3.270941	1.425609	-0.318634
H	-2.948716	-2.412130	0.563610
H	-5.116561	-1.449755	-0.226857
H	-5.313941	0.938303	-0.776410
H	-3.371011	2.477901	-0.557925
C	-2.022376	-0.425539	0.395875
C	-2.096565	0.821113	0.116074
C	0.648616	0.928510	0.668793
C	0.572092	-0.538036	0.789480
C	1.038190	-1.460510	-0.332431
C	2.520558	-1.856095	-0.299352
C	3.544466	-0.765138	-0.628164
C	3.646551	0.368932	0.409650
C	2.988222	1.680815	-0.022369
C	1.514578	1.561013	-0.418629
H	0.454851	-2.384777	-0.264959
H	0.786471	-1.022880	-1.303738
H	2.751328	-2.267060	0.691415
H	2.656187	-2.678187	-1.009562
H	4.518670	-1.253071	-0.721337
H	3.326379	-0.346024	-1.617992
H	3.211565	0.034442	1.358402
H	4.698776	0.576569	0.622436
H	3.076402	2.406565	0.793908

H	3.546280	2.096839	-0.869052
H	1.131924	2.561941	-0.638484
H	1.419092	0.995813	-1.349229
H	0.830106	1.403597	1.637048
H	0.821655	-0.926838	1.778954
H	-0.454704	1.251789	0.410361
H	-0.651807	-0.740403	0.789043

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry for the benzyne + cycloheptane TS



Sum of electronic and thermal Free Energies[a] = –505.731727 A.U.[b]

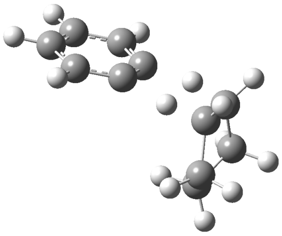
Atom Type	Cartesian Coordinates (x,y,z)		
C	2.358479	1.403046	0.060657
C	3.495967	0.752452	-0.427241
C	3.562531	-0.646397	-0.503637
C	2.496928	-1.455265	-0.095208
H	2.302392	2.483378	0.122838
H	4.346361	1.341932	-0.752210
H	4.464594	-1.109434	-0.889494
H	2.559396	-2.535682	-0.157045
C	1.354614	0.526931	0.440710
C	1.395998	-0.752587	0.379849
C	-1.984284	-1.251629	-1.004763
C	-2.529686	0.077388	-1.526323
C	-1.832764	1.322139	-0.978831
C	-1.992488	1.536455	0.531186
C	-1.097727	0.683237	1.420838
C	-1.176370	-0.780696	1.405238
C	-2.186496	-1.480841	0.497562
H	-2.481615	-2.060879	-1.548054
H	-0.915618	-1.328306	-1.239294
H	-2.450688	0.085597	-2.617895
H	-3.600512	0.138262	-1.292977
H	-0.765380	1.285451	-1.227790
H	-2.241525	2.197627	-1.492333
H	-1.784253	2.585329	0.760822
H	-3.041388	1.364091	0.810118
H	-2.115162	-2.553337	0.699332
H	-3.206159	-1.183397	0.776341
H	-1.010072	1.095076	2.426728

H	-1.193987	-1.195366	2.414445
H	0.052756	0.920203	0.996440
H	-0.107359	-1.135943	1.009797

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry for the benzyne + cyclopentane TS



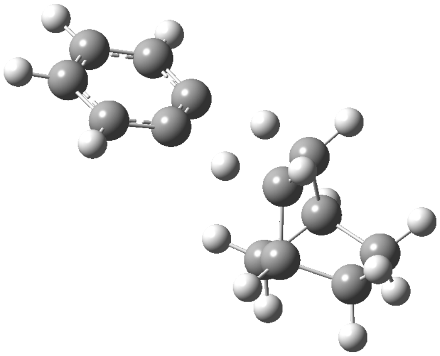
Sum of electronic and thermal Free Energies[a] = -427.178882 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.936071	1.419798	-0.070021
C	3.115873	0.758905	0.285953
C	3.188398	-0.641143	0.322237
C	2.086226	-1.442008	0.005123
H	1.877126	2.501027	-0.103869
H	3.995206	1.341273	0.538809
H	4.124348	-1.112727	0.602504
H	2.153516	-2.523320	0.032028
C	0.943597	-0.727851	-0.334072
C	0.895947	0.552441	-0.363669
C	-2.371611	0.035678	1.246519
C	-2.545284	-1.169909	0.313210
C	-1.739723	-0.763853	-0.928924
C	-1.674332	0.702123	-0.946129
C	-2.413744	1.230038	0.283738
H	-3.128781	0.089219	2.029962
H	-1.388913	-0.012579	1.725594
H	-3.601729	-1.289493	0.049659
H	-2.202332	-2.106892	0.755942
H	-3.451493	1.457333	0.014063
H	-1.971928	2.138038	0.699109
H	-1.840205	1.211877	-1.892960
H	-2.003653	-1.252317	-1.865291
H	-0.475229	0.951560	-0.736132
H	-0.614443	-1.118306	-0.733204

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry for the benzyne + norbornane TS



Sum of electronic and thermal Free Energies[a] = -504.545282 A.U.[b]

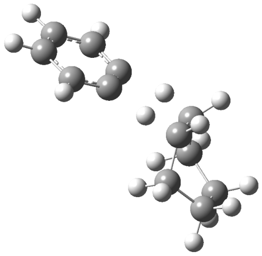
Atom Type	Cartesian Coordinates (x,y,z)		
C	2.719658	1.430940	-0.014251
C	3.848384	0.646372	0.243223
C	3.788447	-0.754443	0.226184
C	2.596051	-1.430207	-0.050577
H	2.774227	2.513244	0.000175
H	4.794312	1.131091	0.460305
H	4.687618	-1.324789	0.432268
H	2.547979	-2.512544	-0.065152
C	1.568809	0.700687	-0.280430
C	1.526190	-0.582597	-0.294306
C	-1.051181	-0.695977	-0.871667
C	-1.084265	0.771529	-0.864241
C	-1.914618	-1.124874	0.315531
C	-1.618703	0.008129	1.313436
C	-1.981254	1.131378	0.327073
C	-3.426935	0.742384	-0.059008
C	-3.381399	-0.814204	-0.069336
H	-1.746482	-2.142857	0.665394
H	-2.273815	-0.016736	2.187519
H	-0.575866	0.037794	1.635717
H	-1.869742	2.152263	0.690584
H	-4.134618	1.108662	0.688380
H	-3.716244	1.162826	-1.024082
H	-3.646084	-1.239757	-1.039259
H	-4.064838	-1.231953	0.673671
H	-1.201901	-1.213194	-1.818054
H	-1.296611	1.271064	-1.808927

H	0.050370	1.112787	-0.607556
H	0.136599	-0.982596	-0.600762

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry for the benzyne + cyclohexane TS



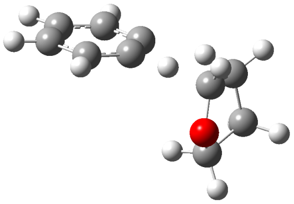
Sum of electronic and thermal Free Energies[a] = –466.454652 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	2.558048	-1.432210	-0.021464
C	3.677709	-0.656503	-0.339859
C	3.625160	0.745027	-0.340818
C	2.449767	1.432749	-0.022447
H	2.606004	-2.514784	-0.020985
H	4.610784	-1.149338	-0.591249
H	4.517502	1.307386	-0.593581
H	2.408576	2.515366	-0.020765
C	1.426086	-0.687701	0.282230
C	1.388866	0.592931	0.279567
C	-1.200384	0.705021	0.847346
C	-1.969783	1.359873	-0.290983
C	-3.397440	0.793354	-0.351894
C	-3.410445	-0.755278	-0.420161
C	-1.998506	-1.356843	-0.331628
C	-1.227653	-0.761596	0.840415
H	-1.456406	1.166837	-1.238606
H	-1.995669	2.444117	-0.163426
H	-3.937019	1.129170	0.538222
H	-3.921522	1.219624	-1.210683
H	-4.011180	-1.155360	0.401264
H	-3.887032	-1.092232	-1.344007
H	-2.055122	-2.443726	-0.240404
H	-1.453144	-1.150661	-1.258306
H	-1.479741	-1.207150	1.803753
H	-1.381706	1.159386	1.822023
H	-0.015245	0.991593	0.651721
H	-0.077625	-1.093173	0.683206

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry for the benzyne + tetrahydrofuran TS



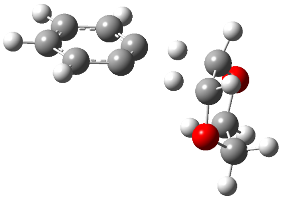
`Sum of electronic and thermal Free Energies`[a] `= -463.104873 A.U.`[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	1.785857	-1.368935	-0.146323
C	3.017036	-0.851078	0.258615
C	3.220388	0.532563	0.356529
C	2.206252	1.443669	0.052873
H	1.608090	-2.434081	-0.230493
H	3.826792	-1.530131	0.500390
H	4.189881	0.899580	0.677842
H	2.389003	2.509880	0.133376
C	0.849913	-0.383946	-0.422008
C	0.980790	0.900737	-0.341891
C	-2.323308	-0.198769	1.211650
O	-2.193127	-1.238526	0.231388
C	-1.667861	-0.661355	-0.897495
C	-1.850454	0.800291	-0.887791
C	-2.656201	1.050157	0.396175
H	-3.094836	-0.508101	1.914434
H	-1.368500	-0.086622	1.735561
H	-3.726387	1.091928	0.182023
H	-2.362042	1.965315	0.909579
H	-1.844114	-1.260206	-1.787280
H	-2.275433	1.204697	-1.803738
H	-0.368824	-0.787448	-0.796966
H	-0.803076	1.263404	-0.767843

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry for the benzyne + 1,4-dioxane TS



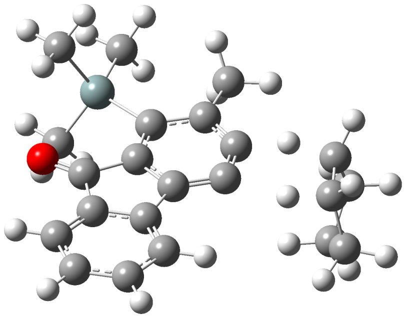
Sum of electronic and thermal Free Energies[a] = -538.297484 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-2.018263	1.405022	0.046566
C	-3.269890	0.945620	-0.366027
C	-3.551915	-0.426345	-0.425090
C	-2.598541	-1.384806	-0.074682
H	-1.783838	2.461259	0.100855
H	-4.034507	1.661554	-0.645636
H	-4.535858	-0.747012	-0.751723
H	-2.838694	-2.441114	-0.124974
C	-1.355478	-0.896124	0.329851
C	-1.139680	0.380427	0.367537
C	1.340084	0.425284	1.126588
O	2.091019	1.342197	0.440495
C	2.430906	0.939037	-0.882781
C	2.973410	-0.472256	-0.852815
O	1.958984	-1.353024	-0.419304
C	1.421400	-1.013726	0.837652
H	1.536303	0.978851	-1.515285
H	3.167775	1.658484	-1.238271
H	3.269067	-0.798024	-1.850162
H	3.844015	-0.521637	-0.184469
H	1.298249	0.688767	2.180728
H	1.890609	-1.576306	1.651363
H	0.083095	0.683424	0.776074
H	0.311562	-1.374423	0.791167

[a] Used for the $\Delta G^{\ddagger}_{M06\text{-}2X}$ calculation.

[b] Atomic Units = Hartrees

Computed energy and geometry for the fluorynone **13-comp** + cyclopentane TS



Sum of electronic and thermal Free Energies[a] = –1218.080249 A.U.[b]

Atom Type	Cartesian Coordinates (x,y,z)		
C	-0.362336	3.686943	0.258095
C	0.370684	4.868713	0.111076
C	1.745371	4.845722	-0.116549
C	2.427895	3.629507	-0.203637
H	-1.431241	3.708248	0.437063
H	-0.139373	5.822980	0.176810
H	2.284941	5.778634	-0.225556
H	3.496797	3.587032	-0.379268
C	0.317876	2.485456	0.170220
C	1.695595	2.467757	-0.058036
C	2.158774	1.044103	-0.102145
C	-0.154523	1.088687	0.279565
C	0.928534	0.194351	0.112867
C	0.812697	-1.208560	0.171475
C	-0.486838	-1.735938	0.428616
C	-0.835710	-3.194959	0.566234
O	3.296998	0.679082	-0.265888
C	3.045916	-1.973642	-1.839435
C	3.606383	-2.003784	1.277877
C	2.059289	-4.155060	-0.086679
H	-0.280362	-3.665874	1.378368
H	-1.899496	-3.297848	0.786039
H	-0.624516	-3.751715	-0.347205
C	-1.460393	-0.757142	0.563625
C	-1.400302	0.532781	0.507435
C	-4.436356	-0.435864	-1.476031
C	-4.844517	0.757355	-0.601142

C	-4.191039	0.436154	0.752781
C	-4.021815	-1.019043	0.806064
C	-4.511498	-1.622552	-0.506002
H	-3.404166	-0.305700	-1.814516
H	-5.933806	0.788973	-0.495135
H	-4.517551	1.714808	-1.010414
H	-4.638557	0.895263	1.632770
H	-4.240315	-1.545471	1.732634
H	-5.552526	-1.942633	-0.380522
H	-3.934442	-2.491566	-0.829580
H	3.969778	-2.543307	-1.978809
H	2.325378	-2.328403	-2.581989
H	3.263810	-0.925073	-2.031539
H	3.034937	-4.618060	-0.271851
H	1.701125	-4.536823	0.870208
H	1.389116	-4.498896	-0.876255
H	4.516017	-2.579540	1.081426
H	3.884775	-0.957483	1.387768
H	3.187040	-2.361117	2.222735
H	-5.068363	-0.562713	-2.355671
H	-3.094770	0.871344	0.714339
H	-2.753492	-1.174082	0.766998
Si	2.378655	-2.292823	-0.112813

[a] Used for the $\Delta G^{\ddagger}_{\text{M06-2X}}$ calculation.

[b] Atomic Units = Hartrees

IV. References for the Supplementary Information

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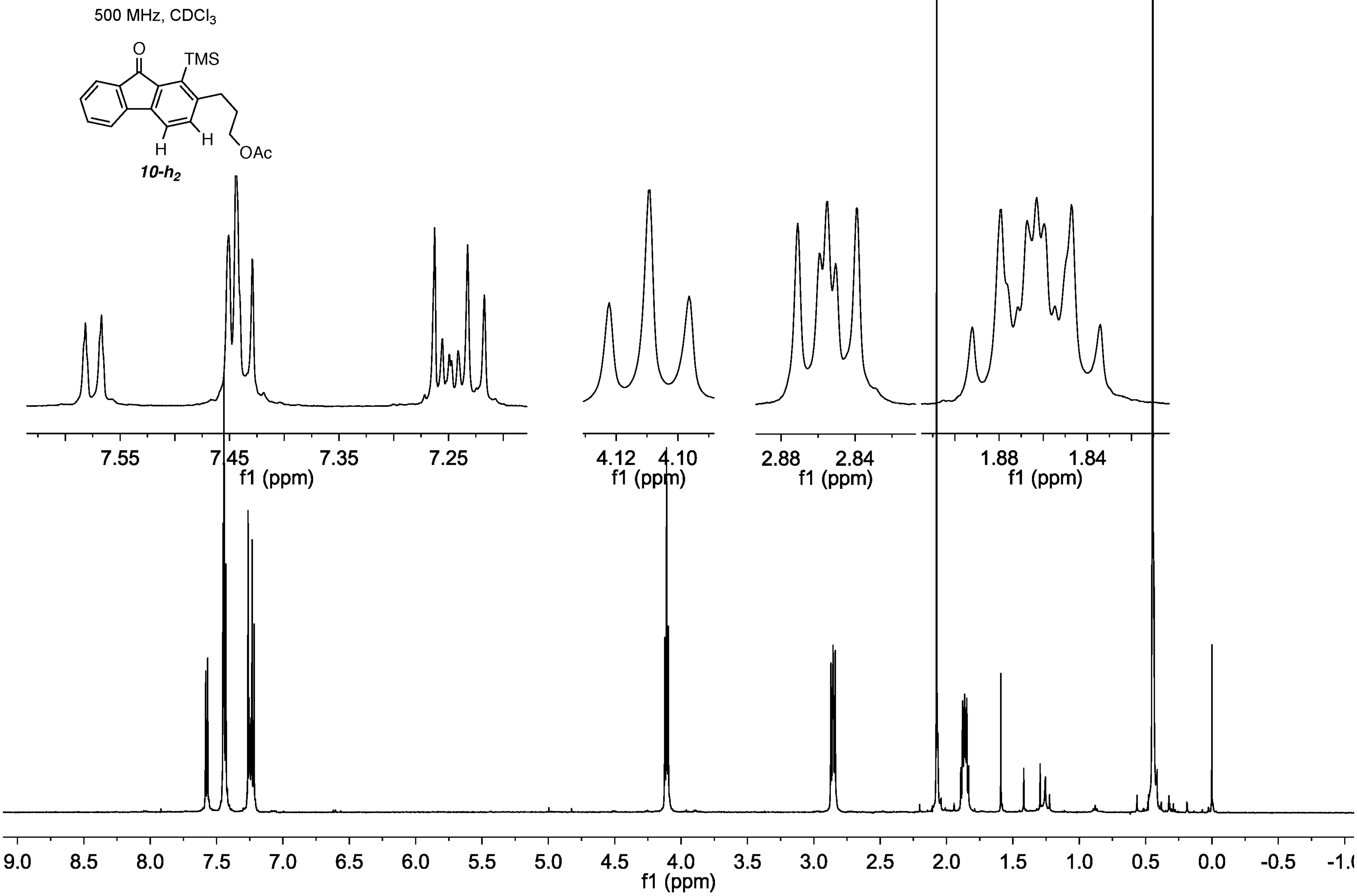
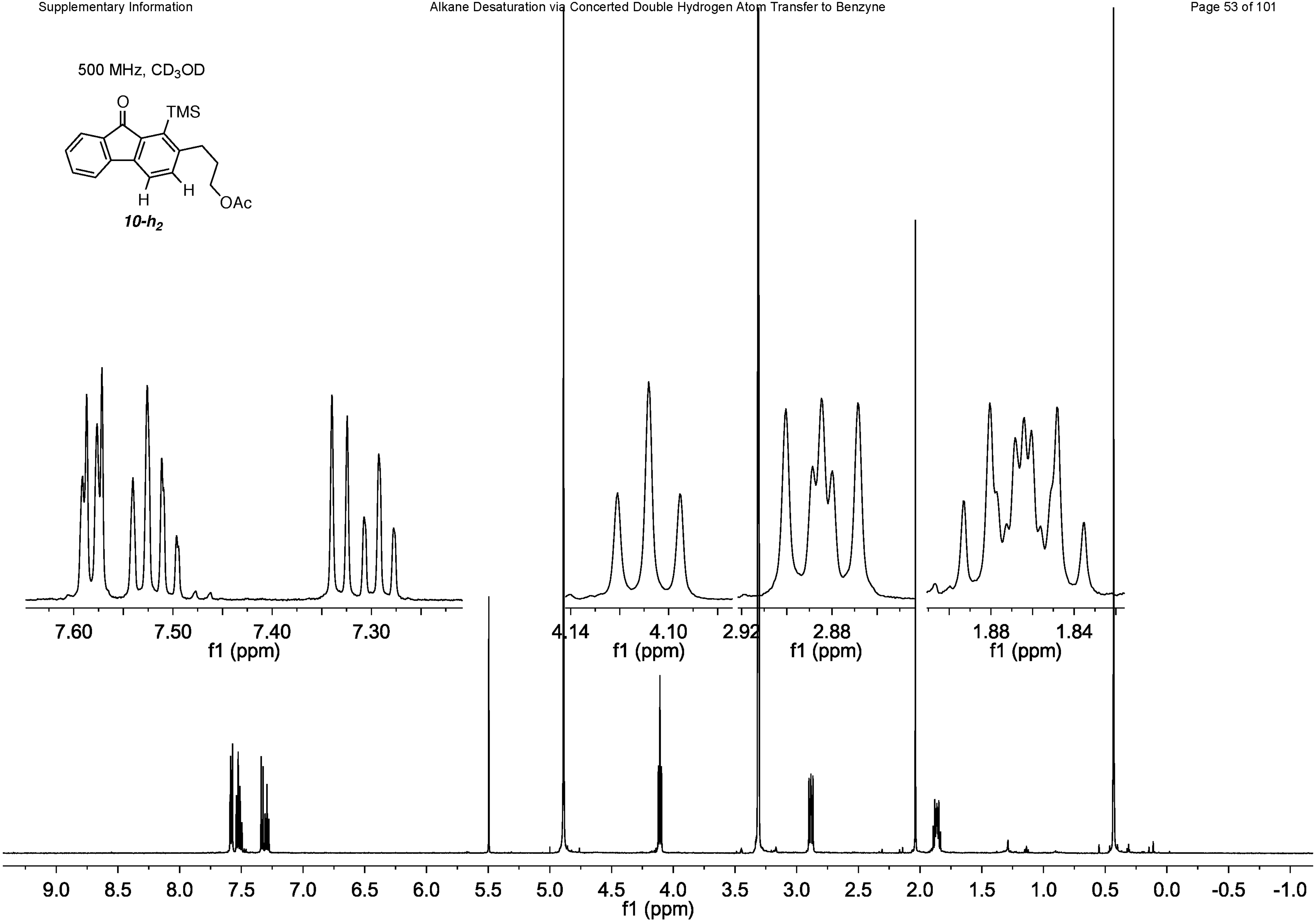
V. Copies of ^{1}H and ^{13}C NMR spectra of all new compounds



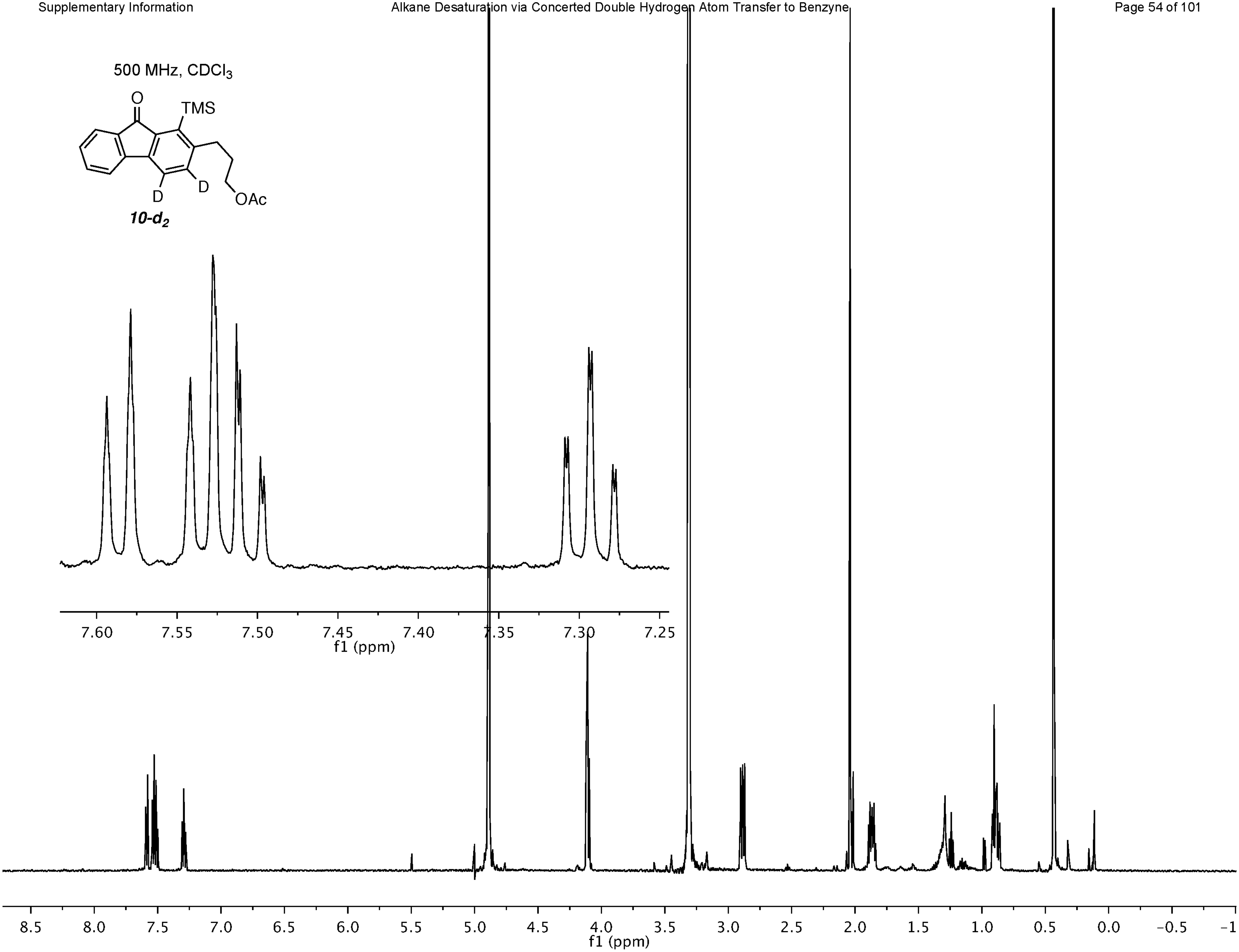
10-h$_2$

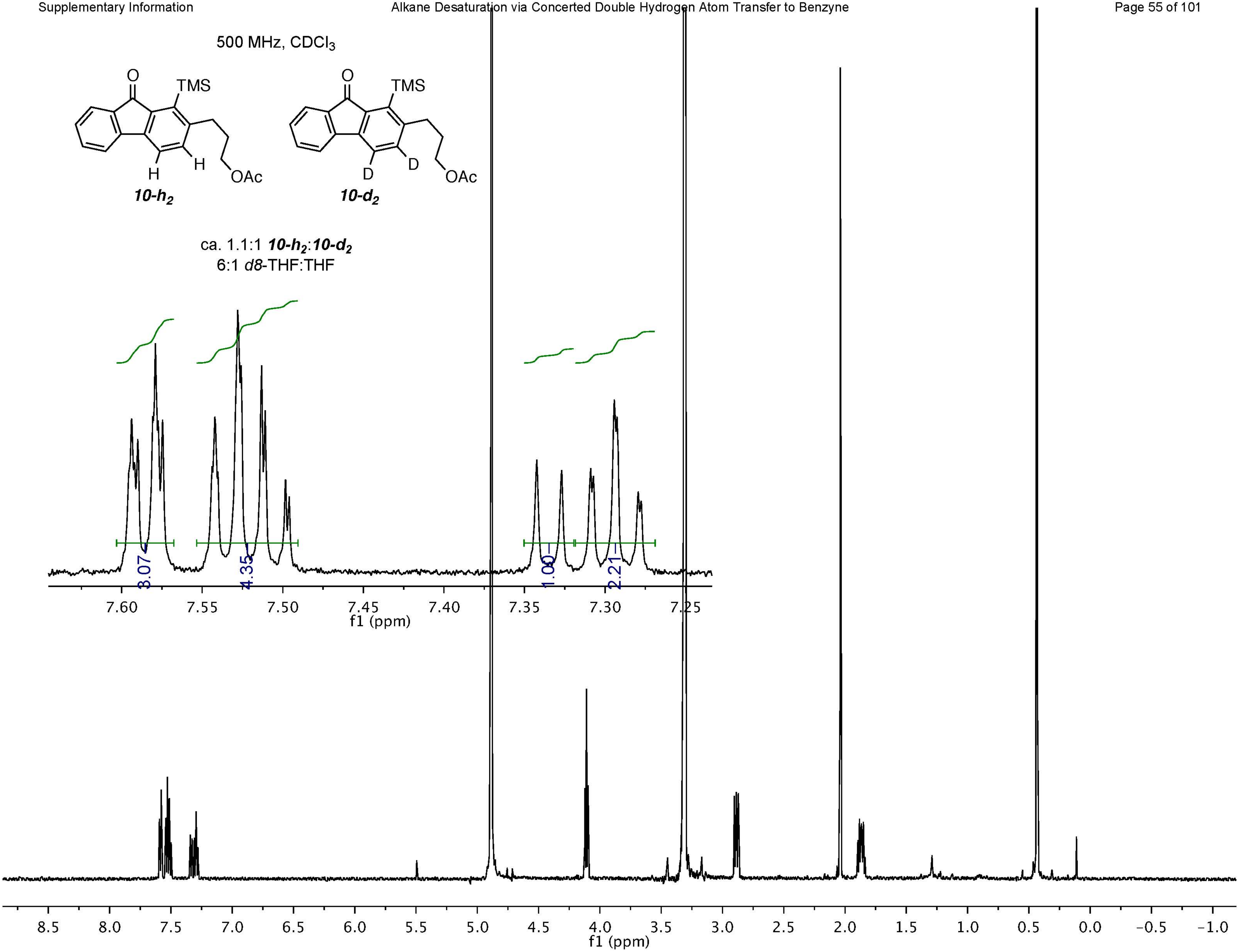
500 MHz, CDCl3
O
TMS
H
H
OAc
7.55
7.45
7.35
7.25
f1 (ppm)
4.12
4.10
f1 (ppm)
2.88
2.84
f1 (ppm)
1.88
1.84
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



500 MHz, CD_3OD

10-h$_2$


500 MHz, $CDCl_3$
O
TMS
D
D
OAc
10-*d*$_2$
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)



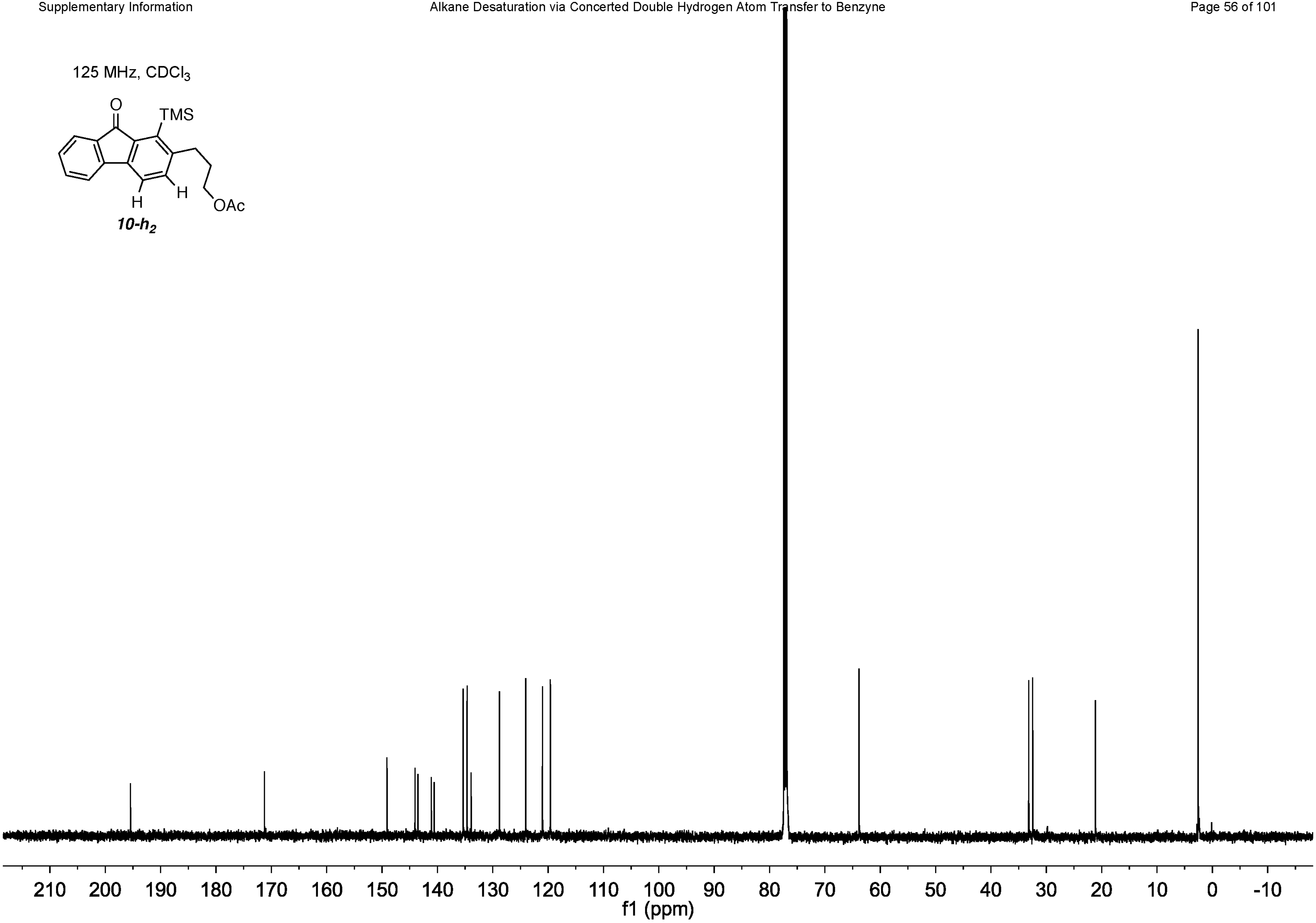
500 MHz, $CDCl_3$

10-h_2

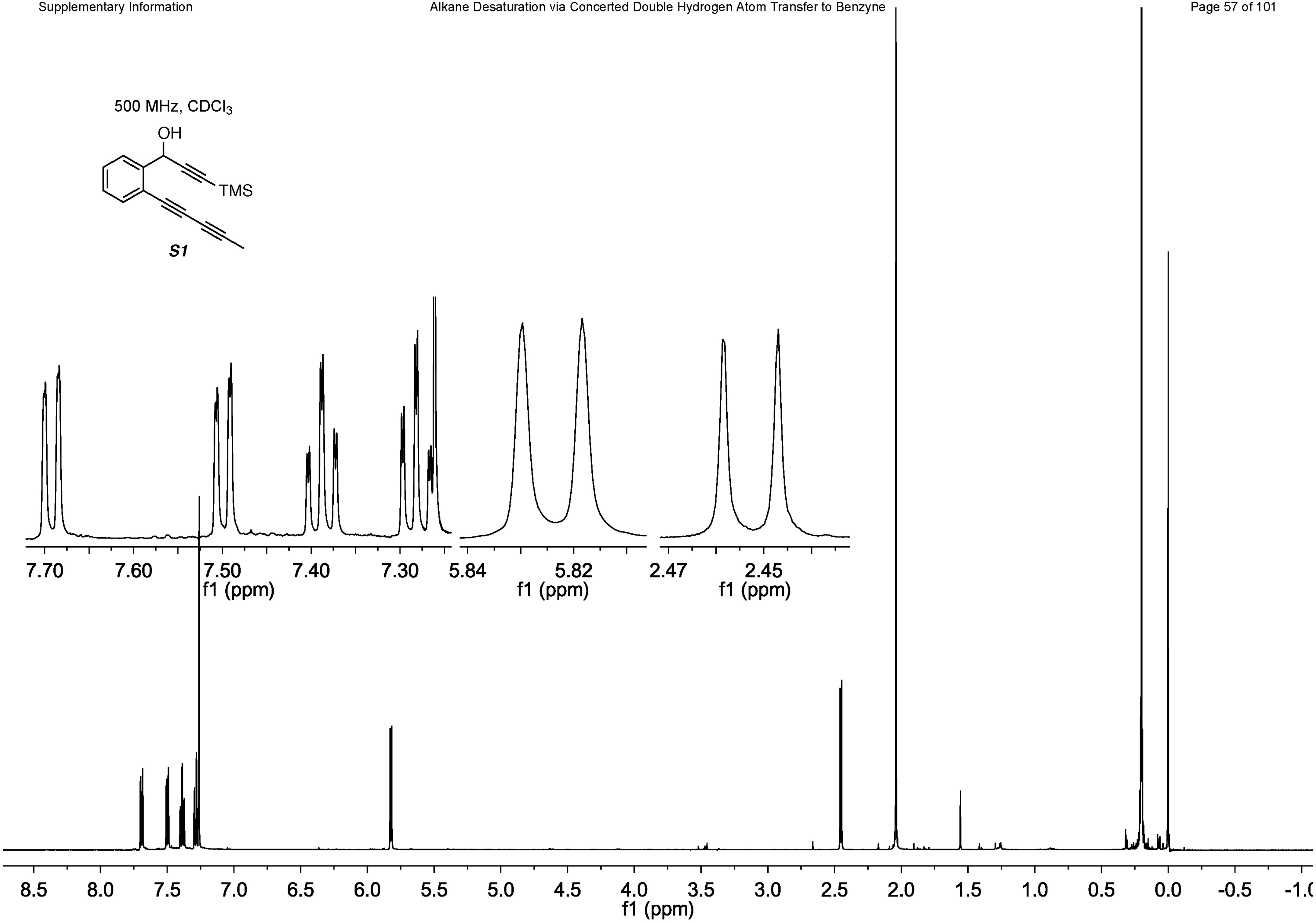
10-d_2

ca. 1.1:1 **10-h_2**:**10-d_2**

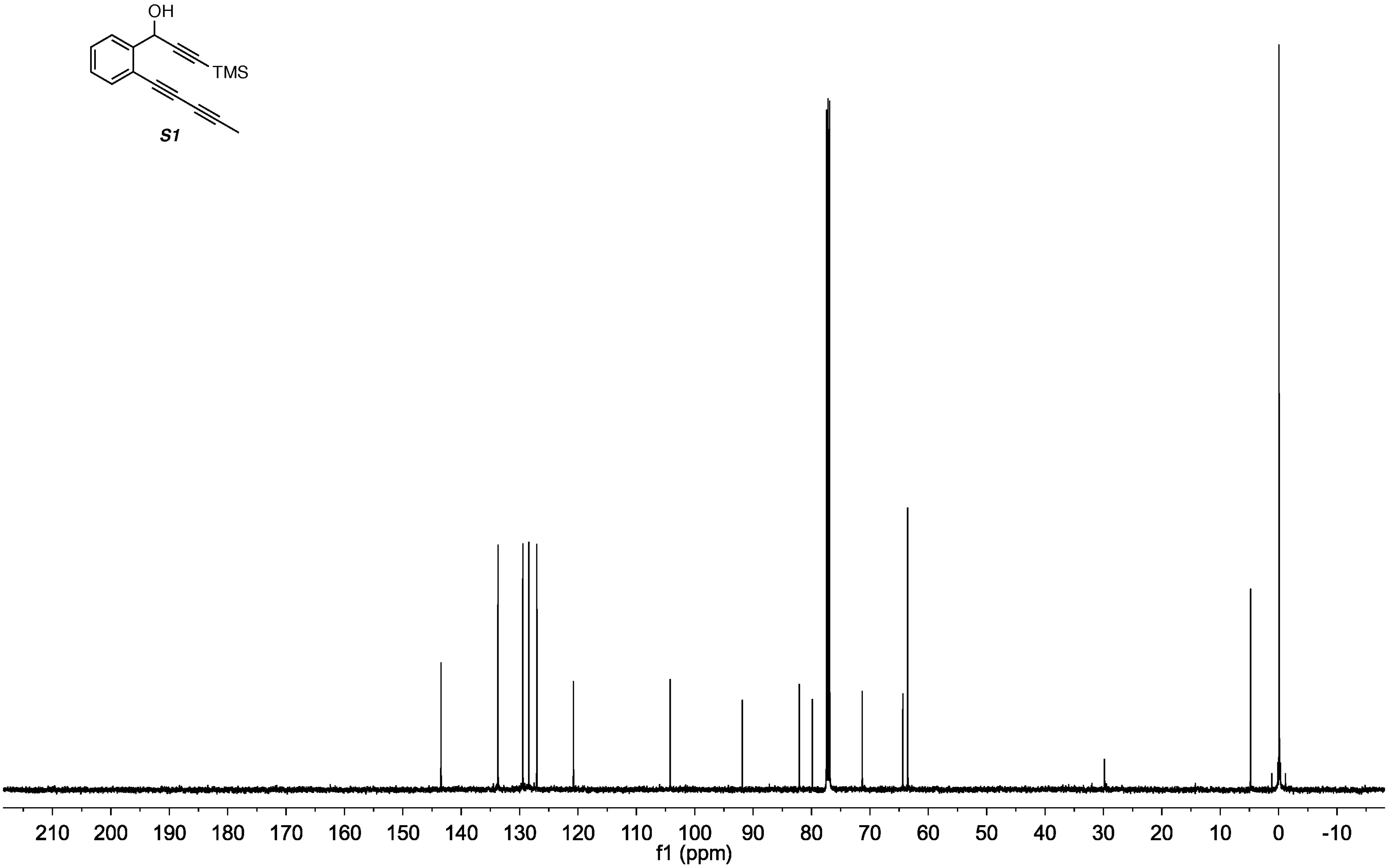
6:1 *d8*-THF:THF


125 MHz, $CDCl_3$
O
TMS
H
H
OAc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

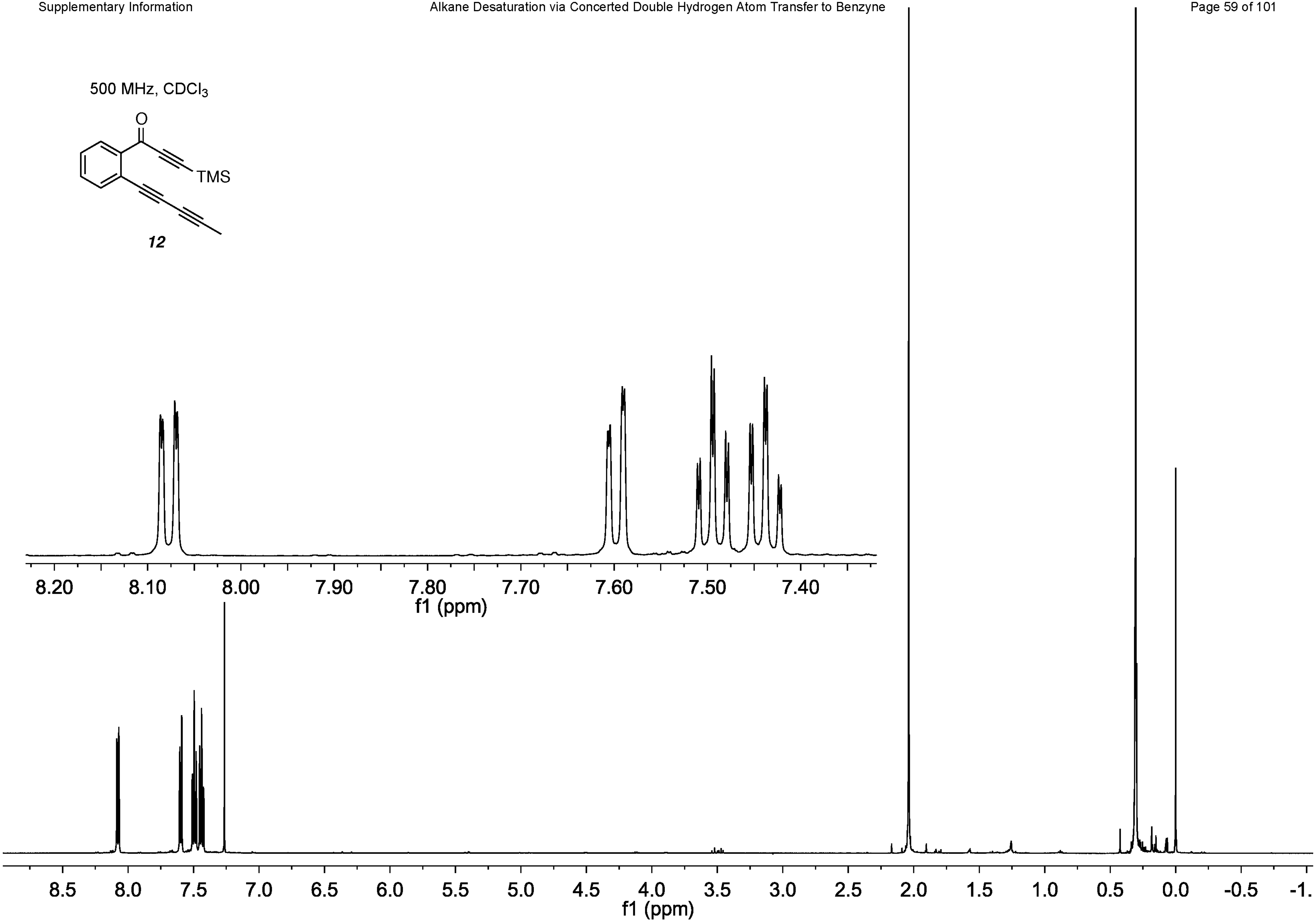
10-h₂


500 MHz, CDCl3
OH
TMS
S1
7.70
7.60
7.50
7.40
7.30
f1 (ppm)
5.84
5.82
f1 (ppm)
2.47
2.45
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

125 MHz, $CDCl_3$

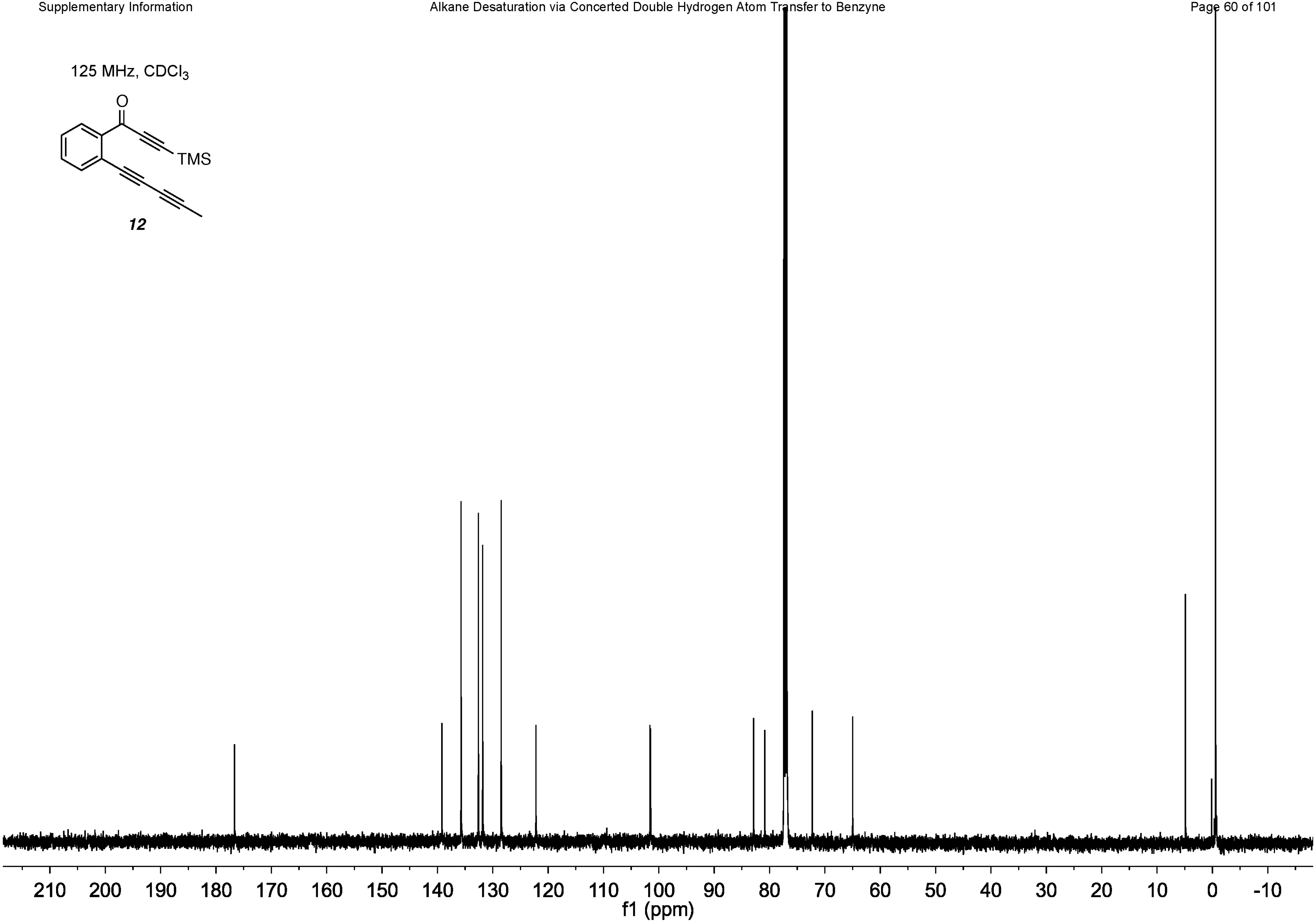


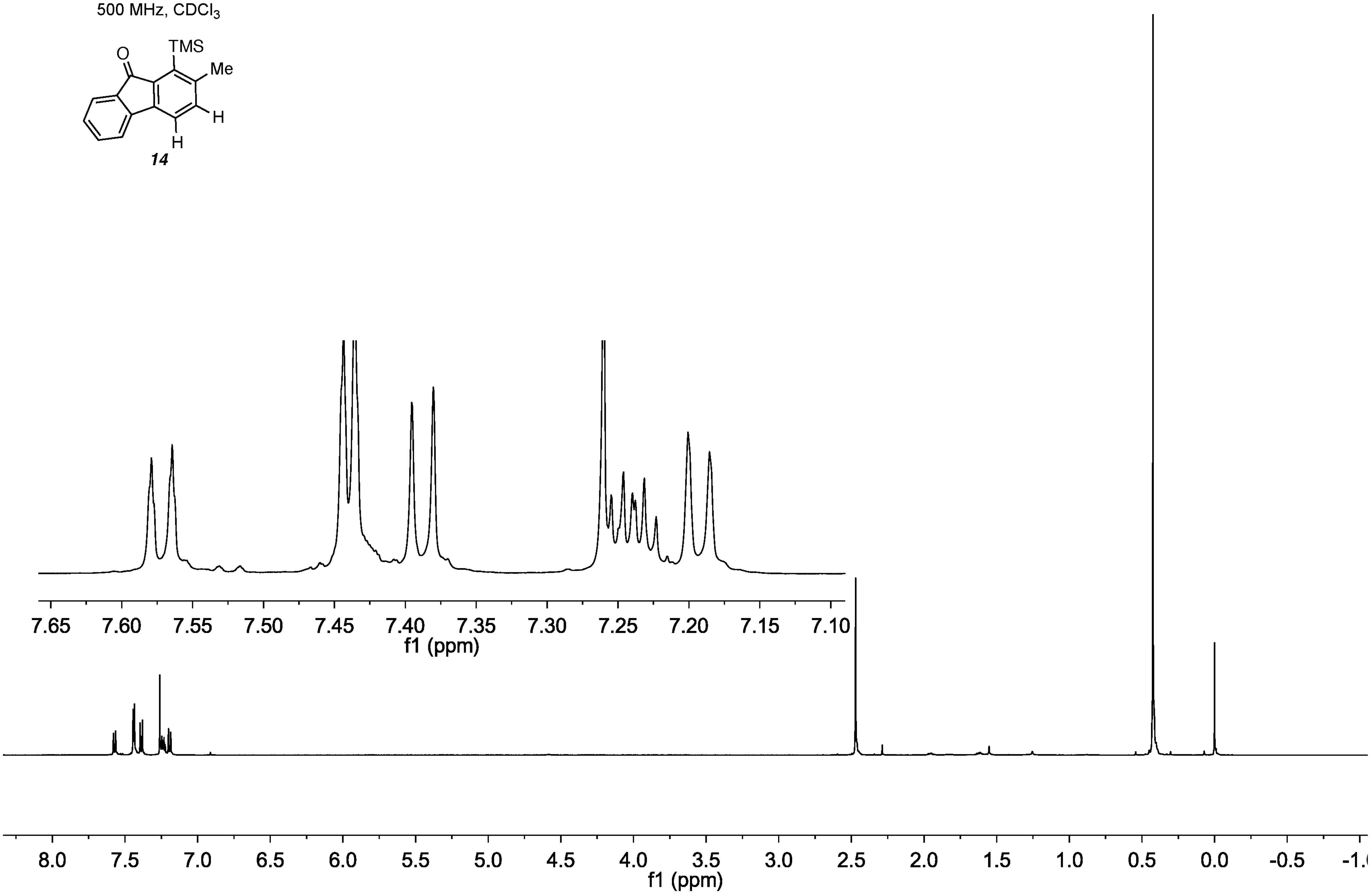
S1


500 MHz, CDCl$_3$
O
TMS
12
8.20
8.10
8.00
7.90
7.80
7.70
7.60
7.50
7.40
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

125 MHz, $CDCl_3$

12

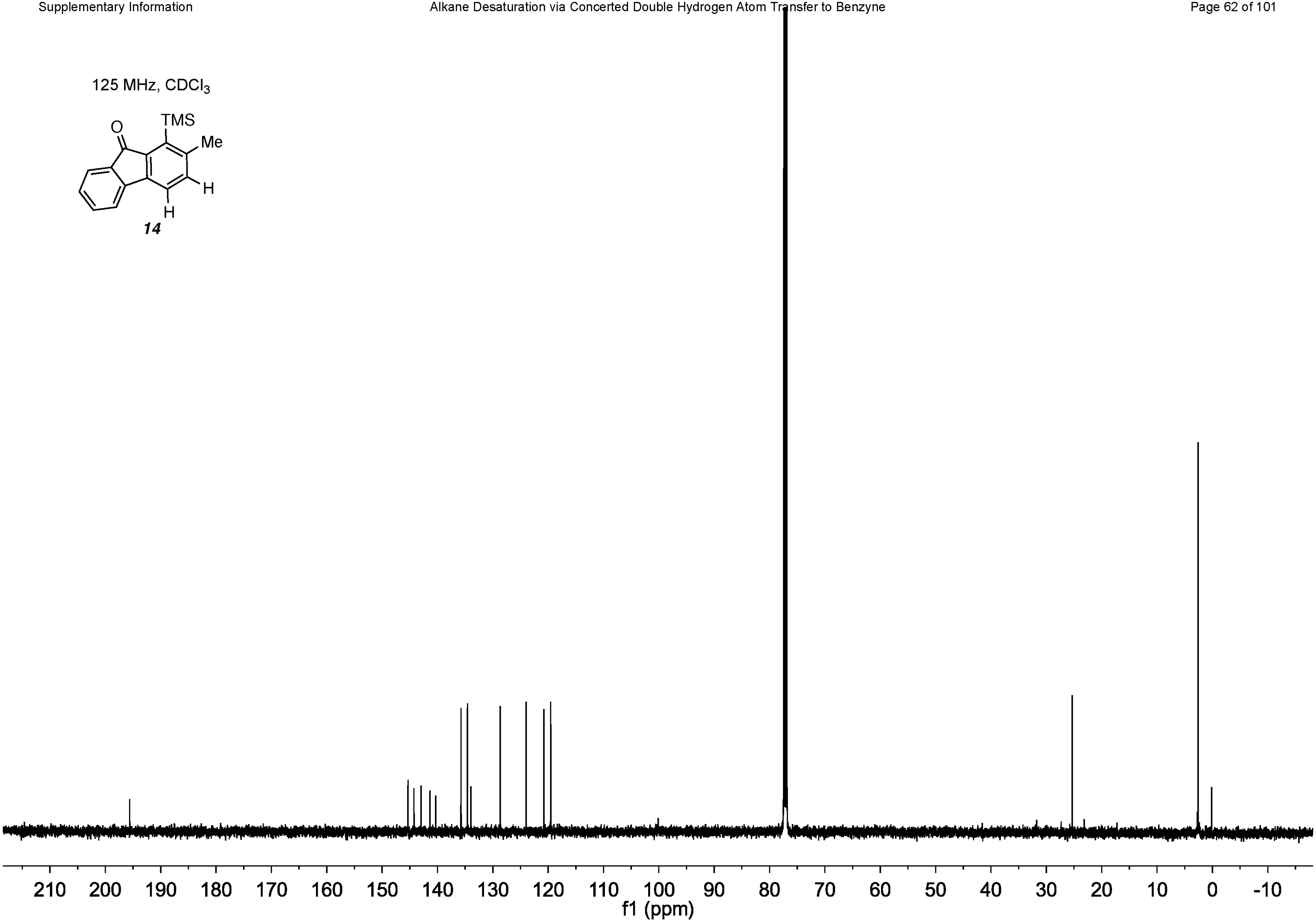



500 MHz, $CDCl_3$
O
TMS
Me
H
H
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

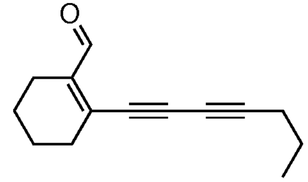
14

125 MHz, $CDCl_3$

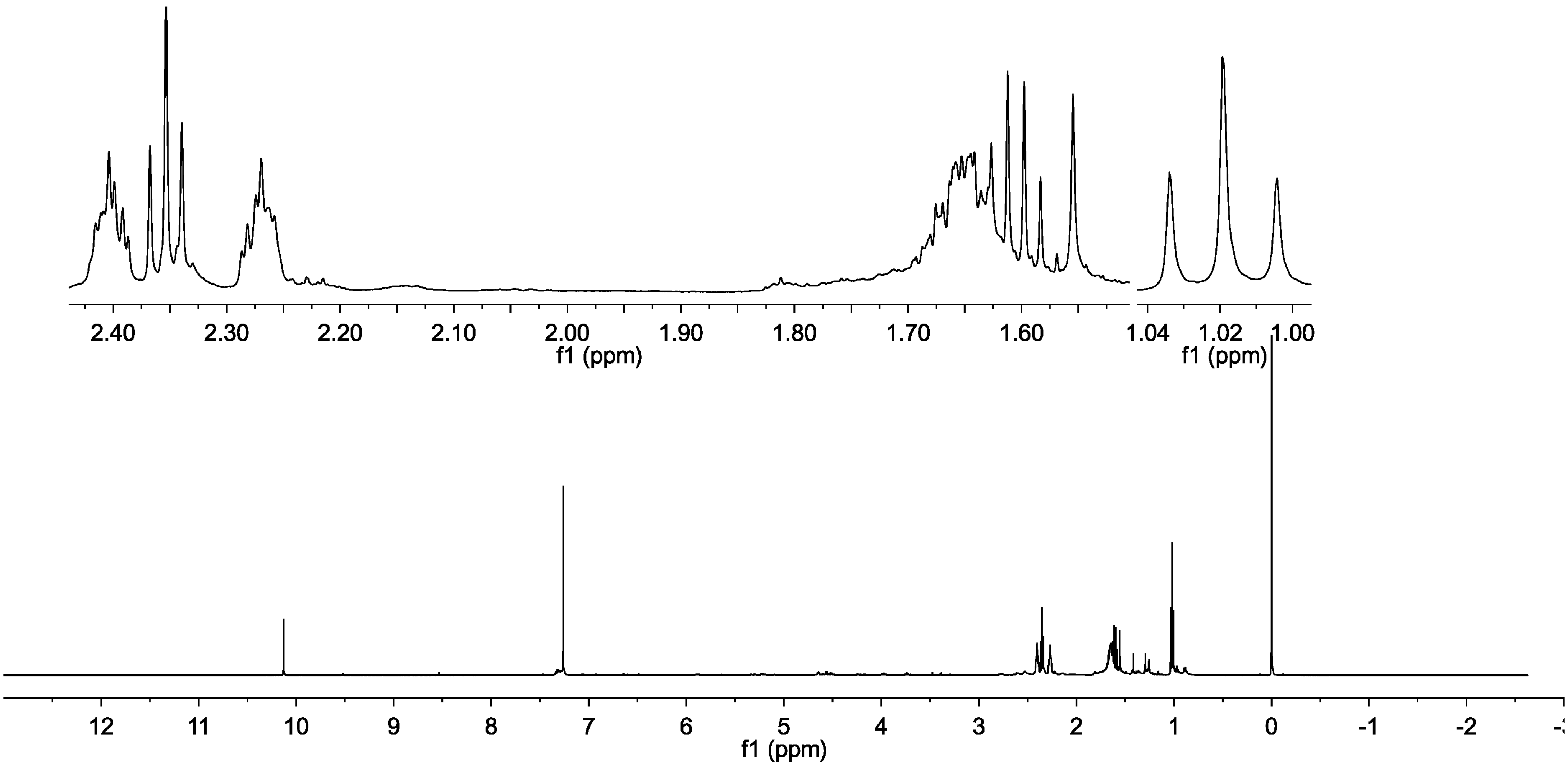
14



500 MHz, $CDCl_3$

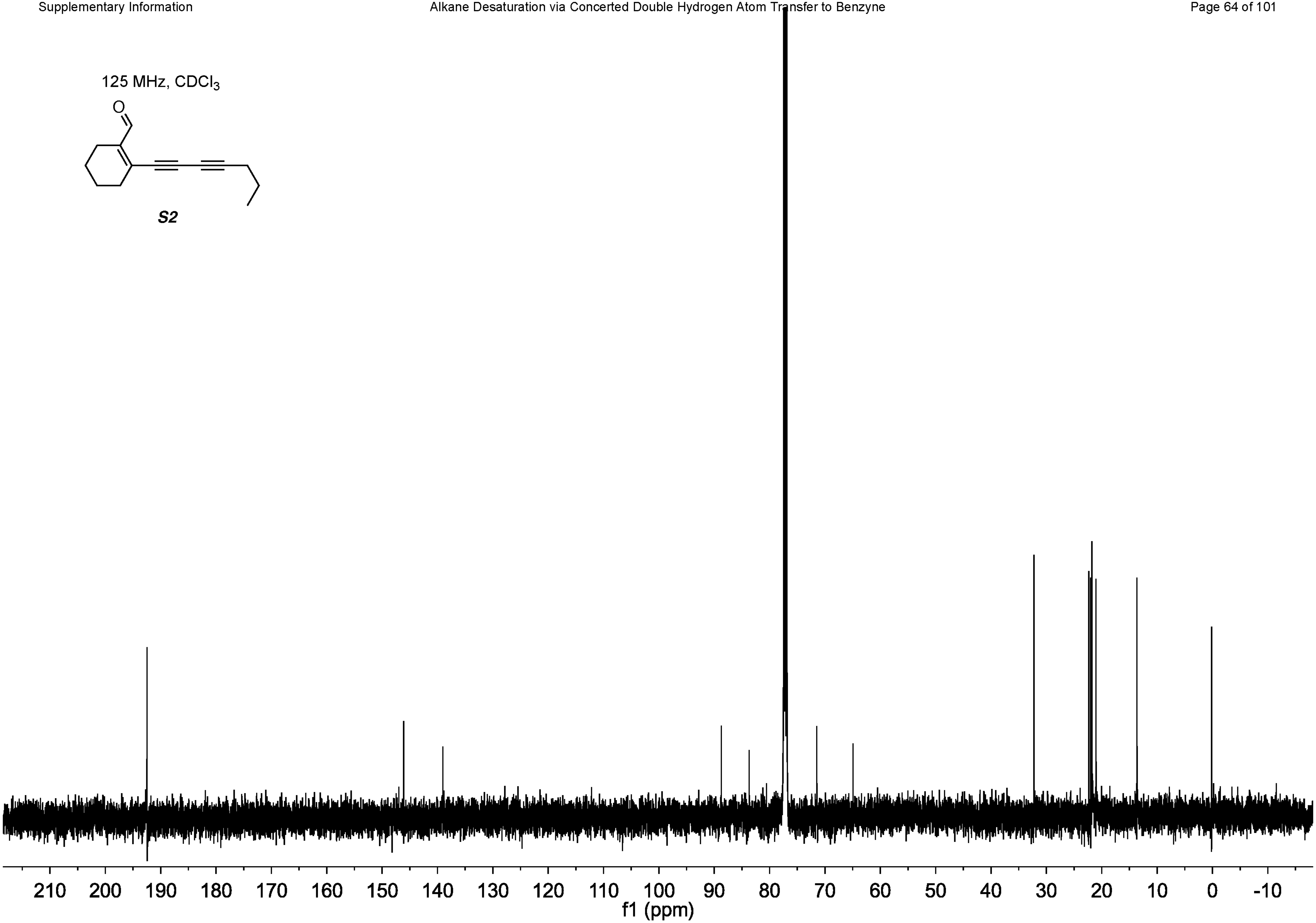


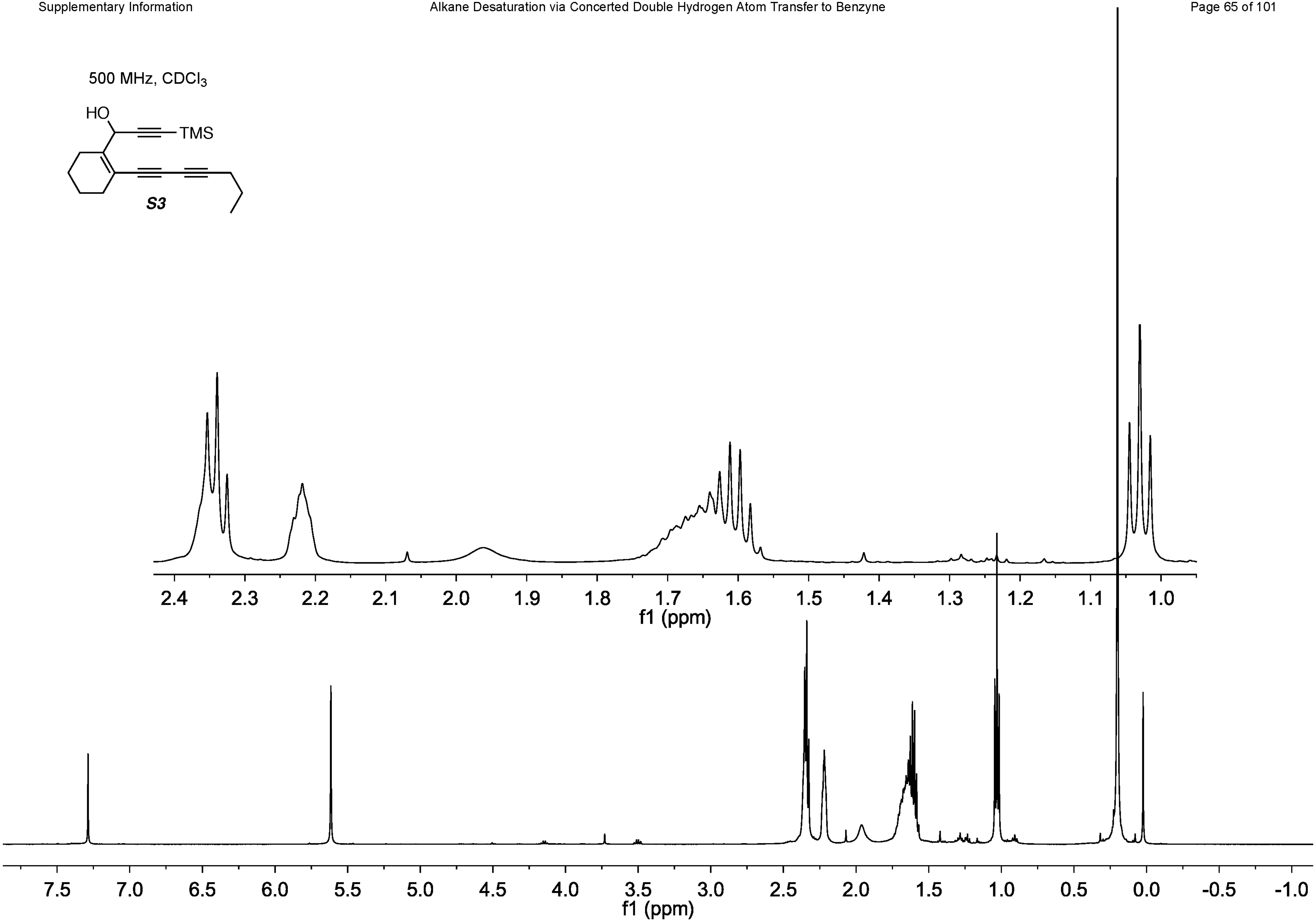
S2

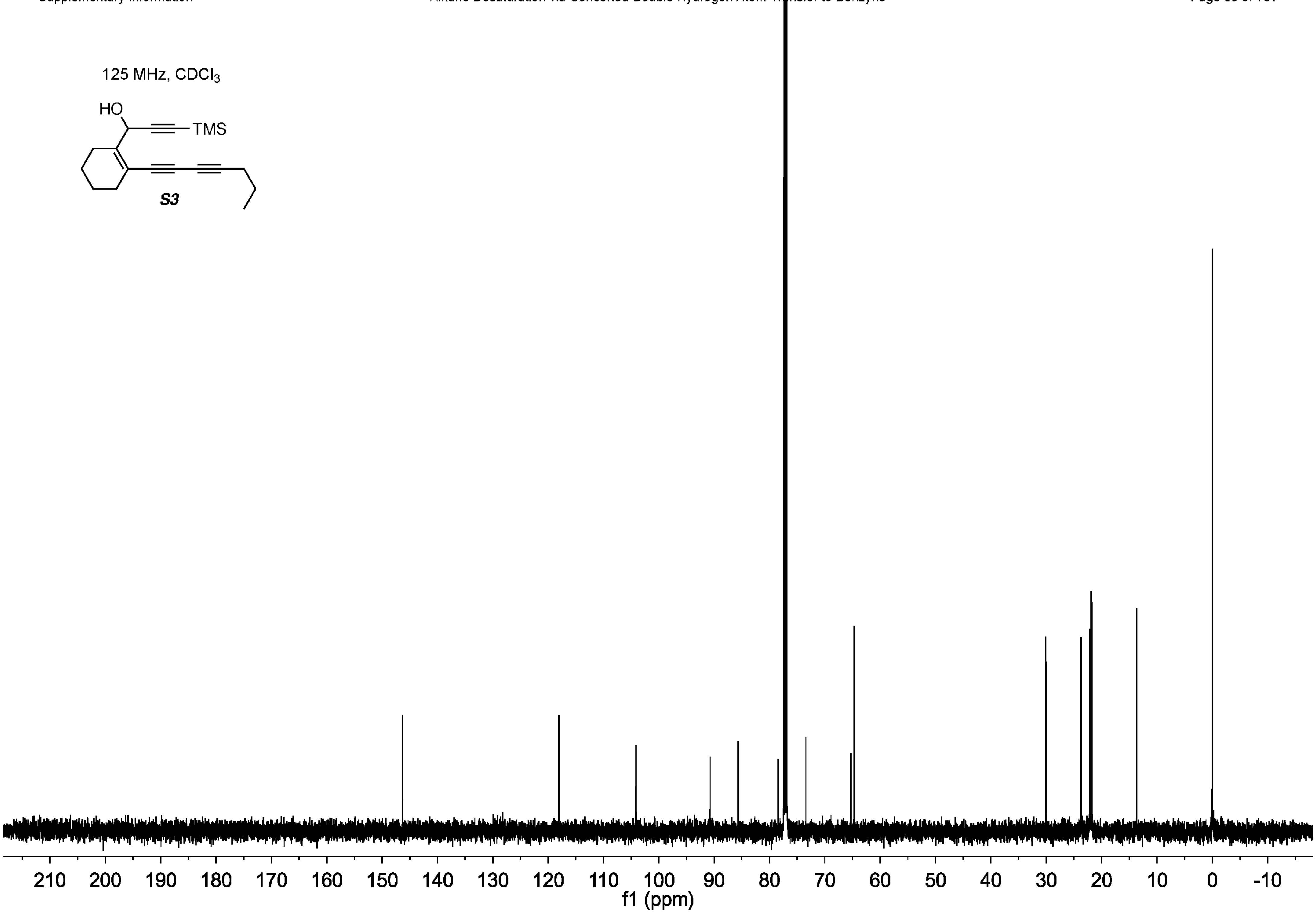


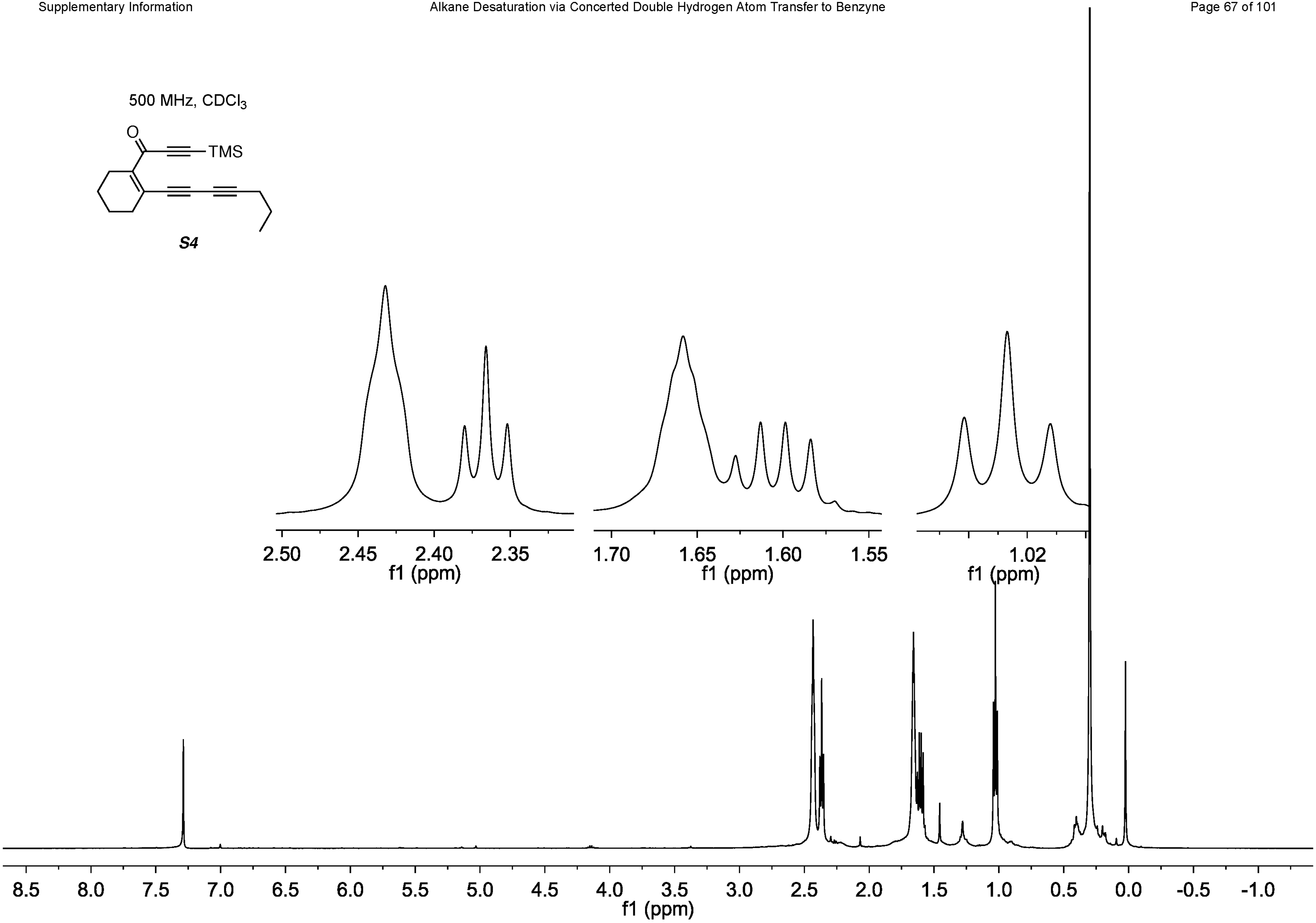
125 MHz, $CDCl_3$

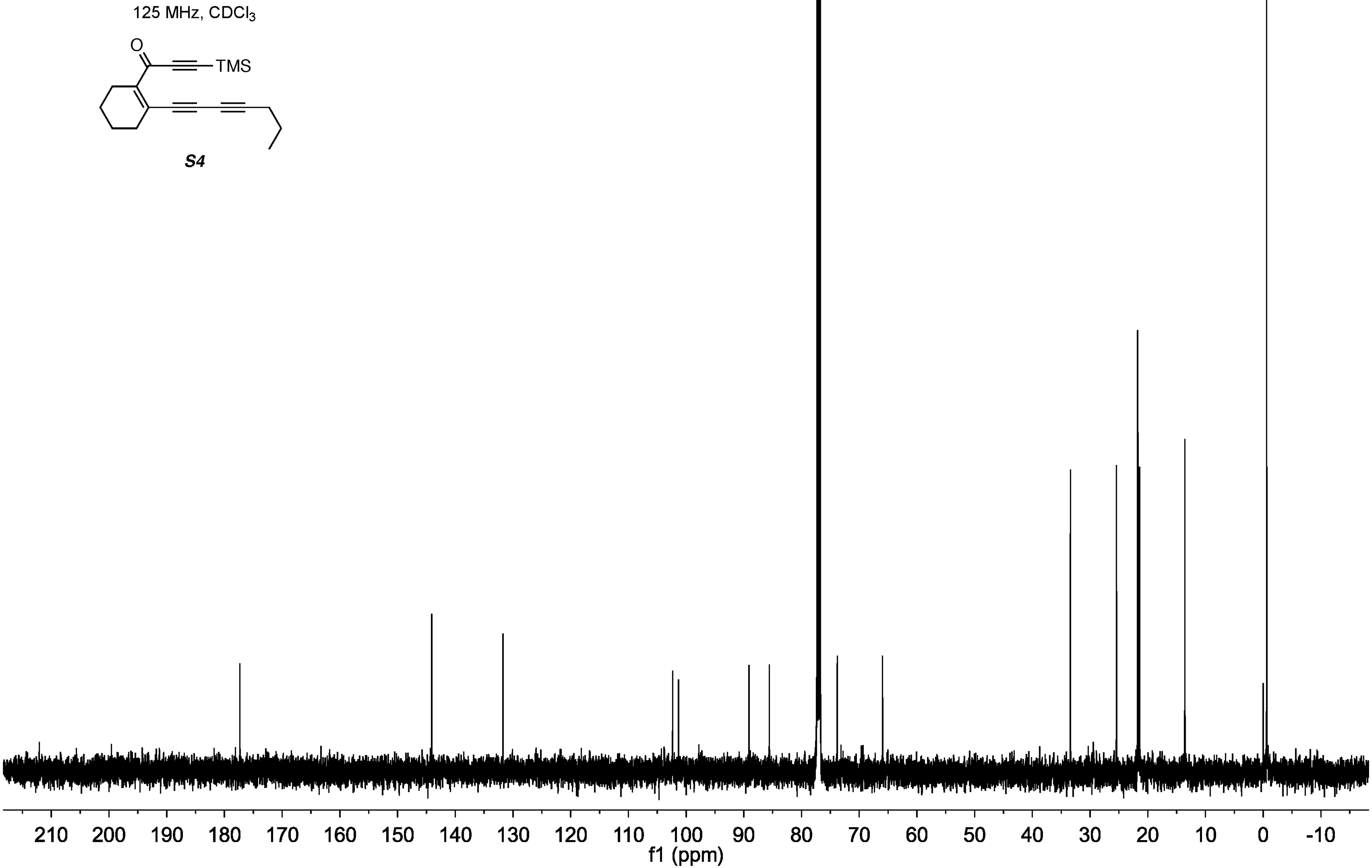
S2



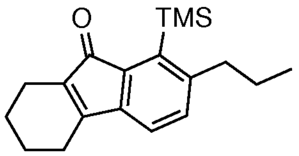

500 MHz, $CDCl_3$
HO
TMS
S3
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


125 MHz, $CDCl_3$
HO
TMS
S3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

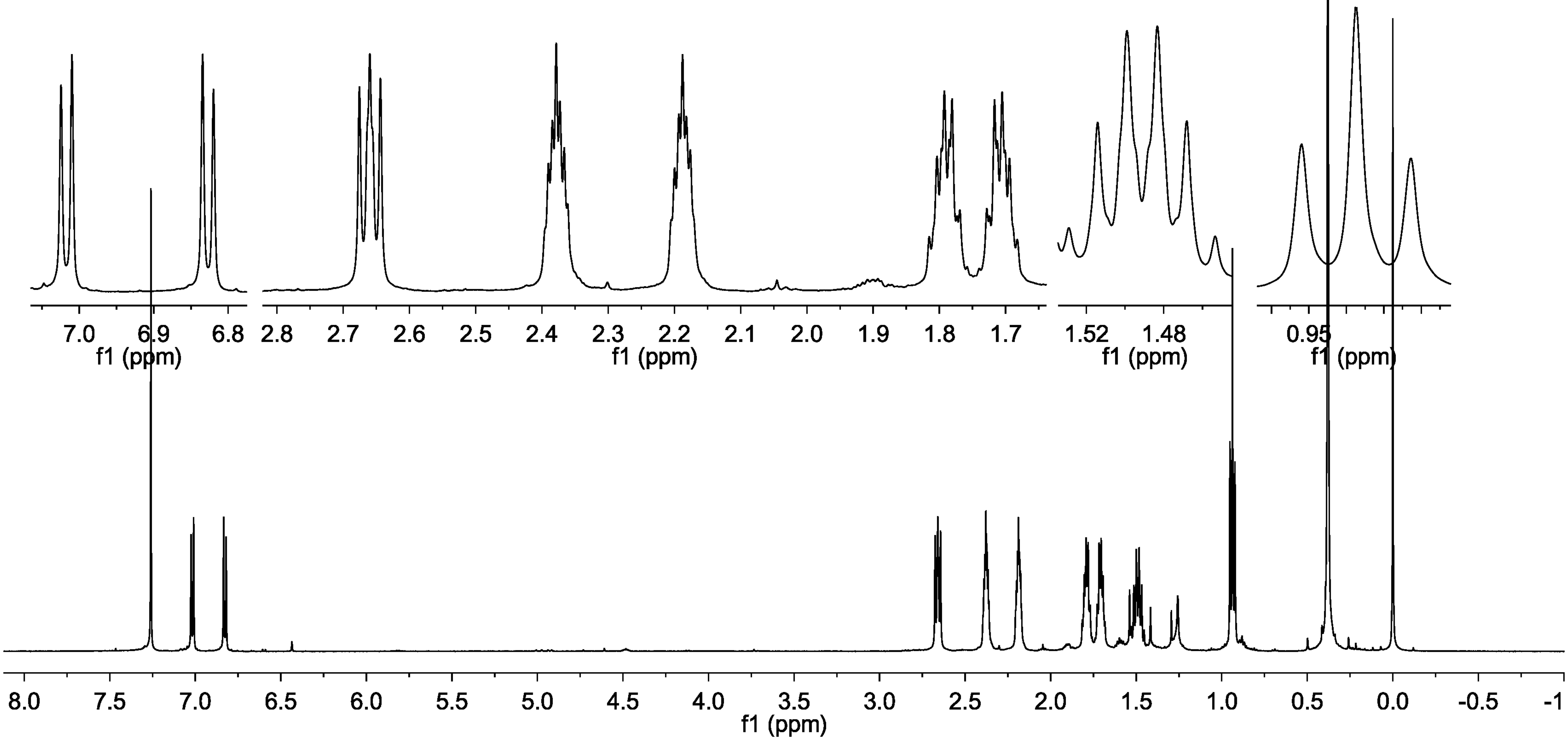

500 MHz, $CDCl_3$
O
TMS
S4
2.50
2.45
2.40
2.35
f1 (ppm)
1.70
1.65
1.60
1.55
f1 (ppm)
1.02
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


125 MHz, CDCl3
O
TMS
S4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

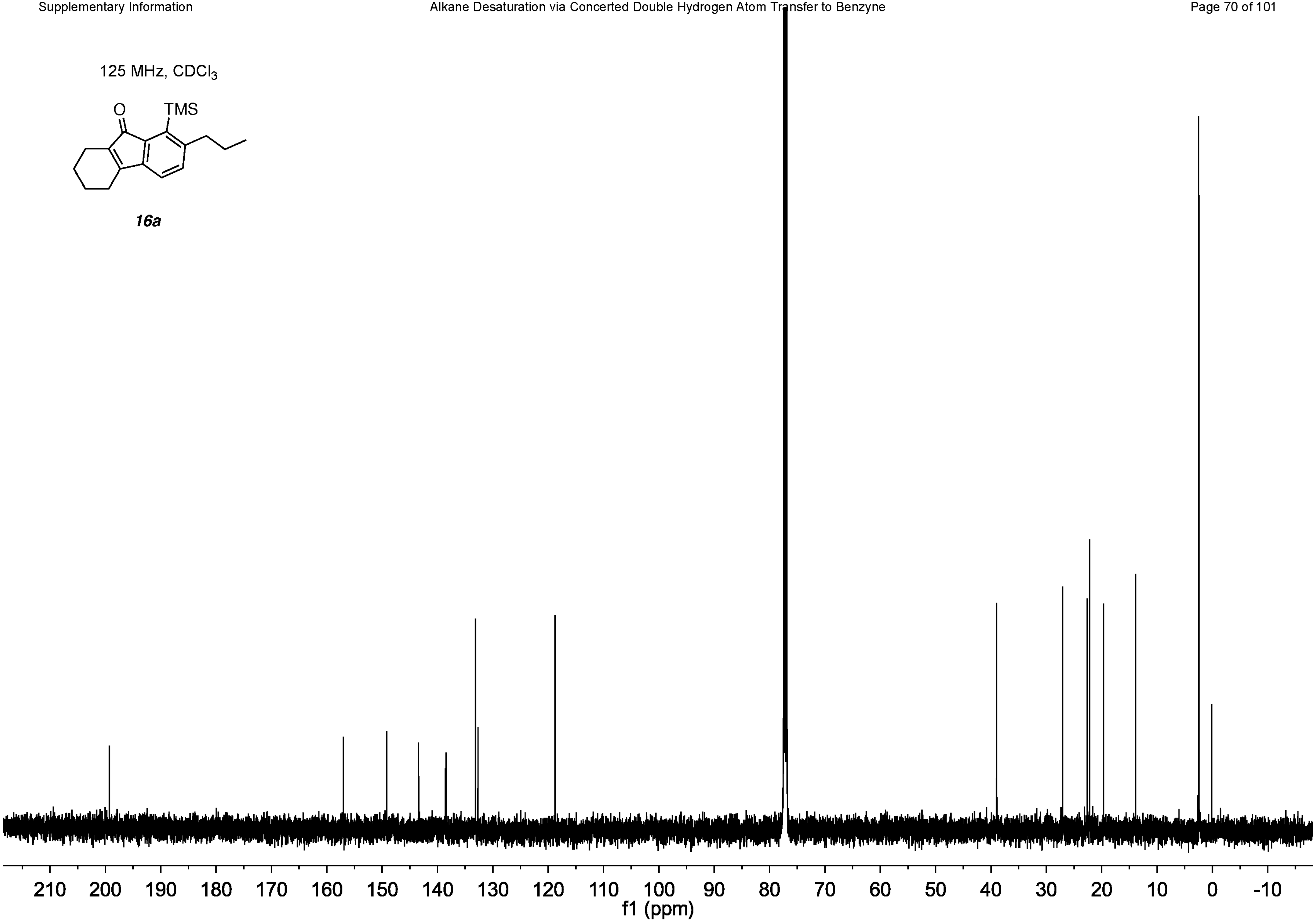
500 MHz, $CDCl_3$



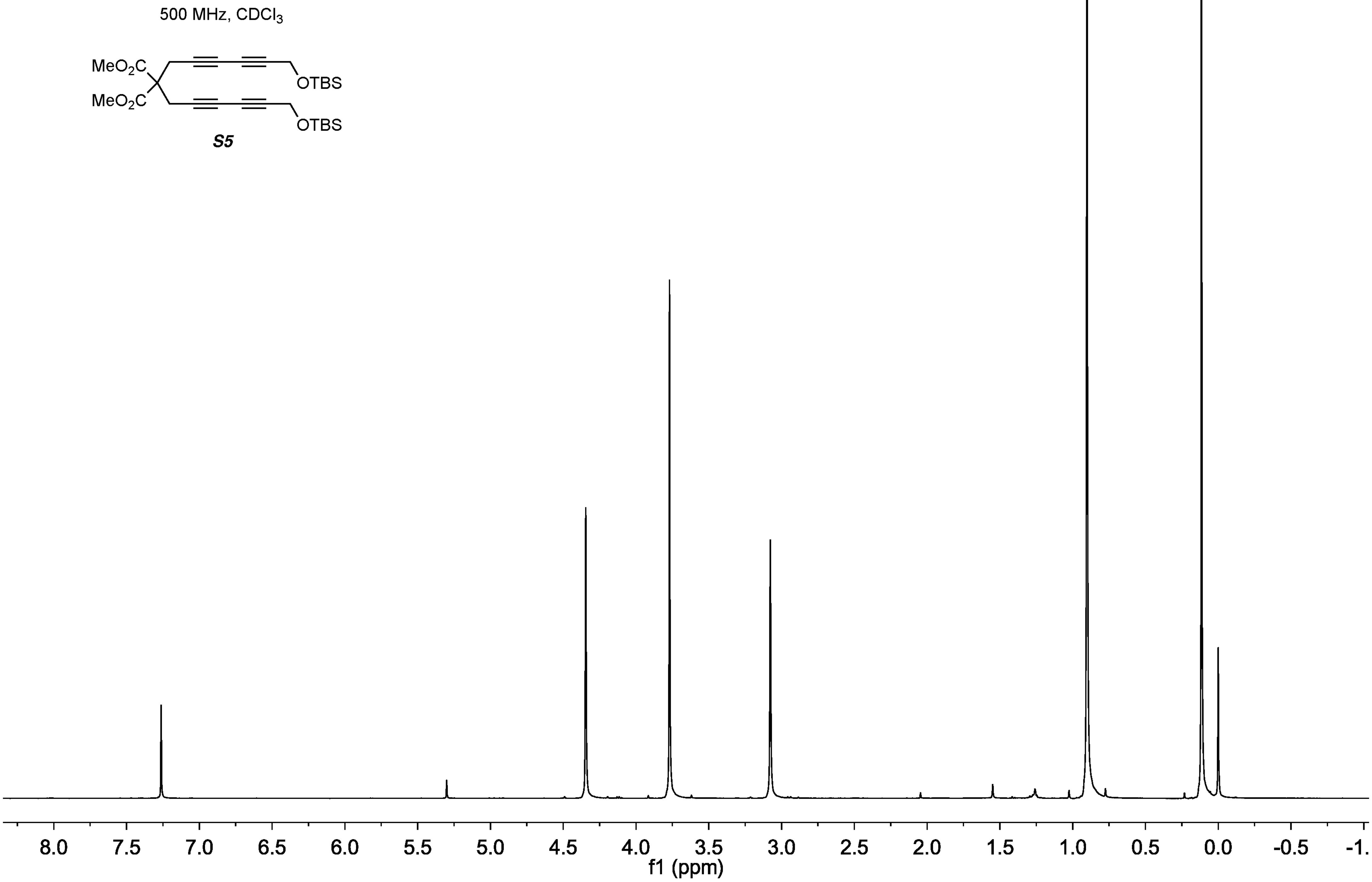
16a



125 MHz, $CDCl_3$

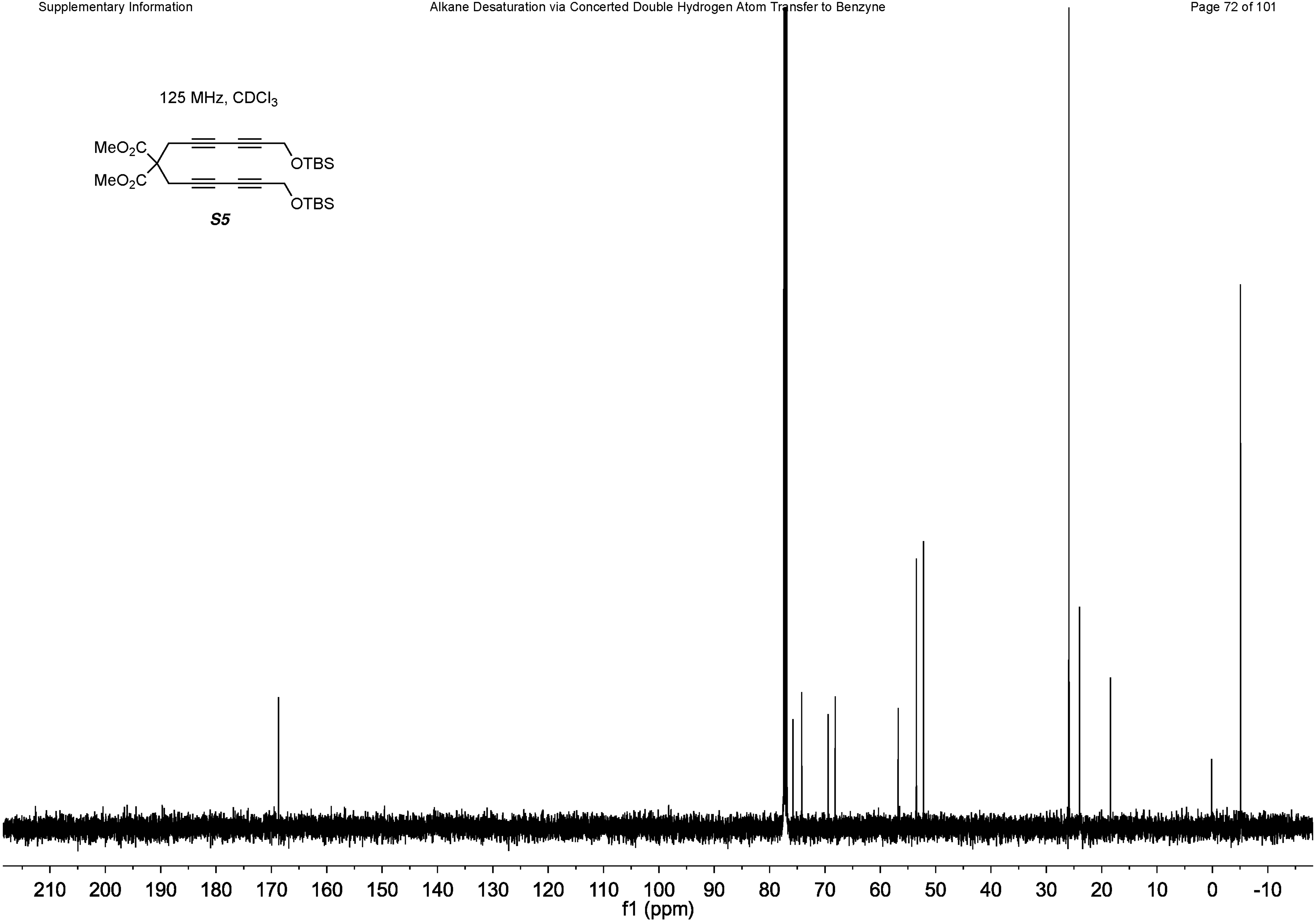


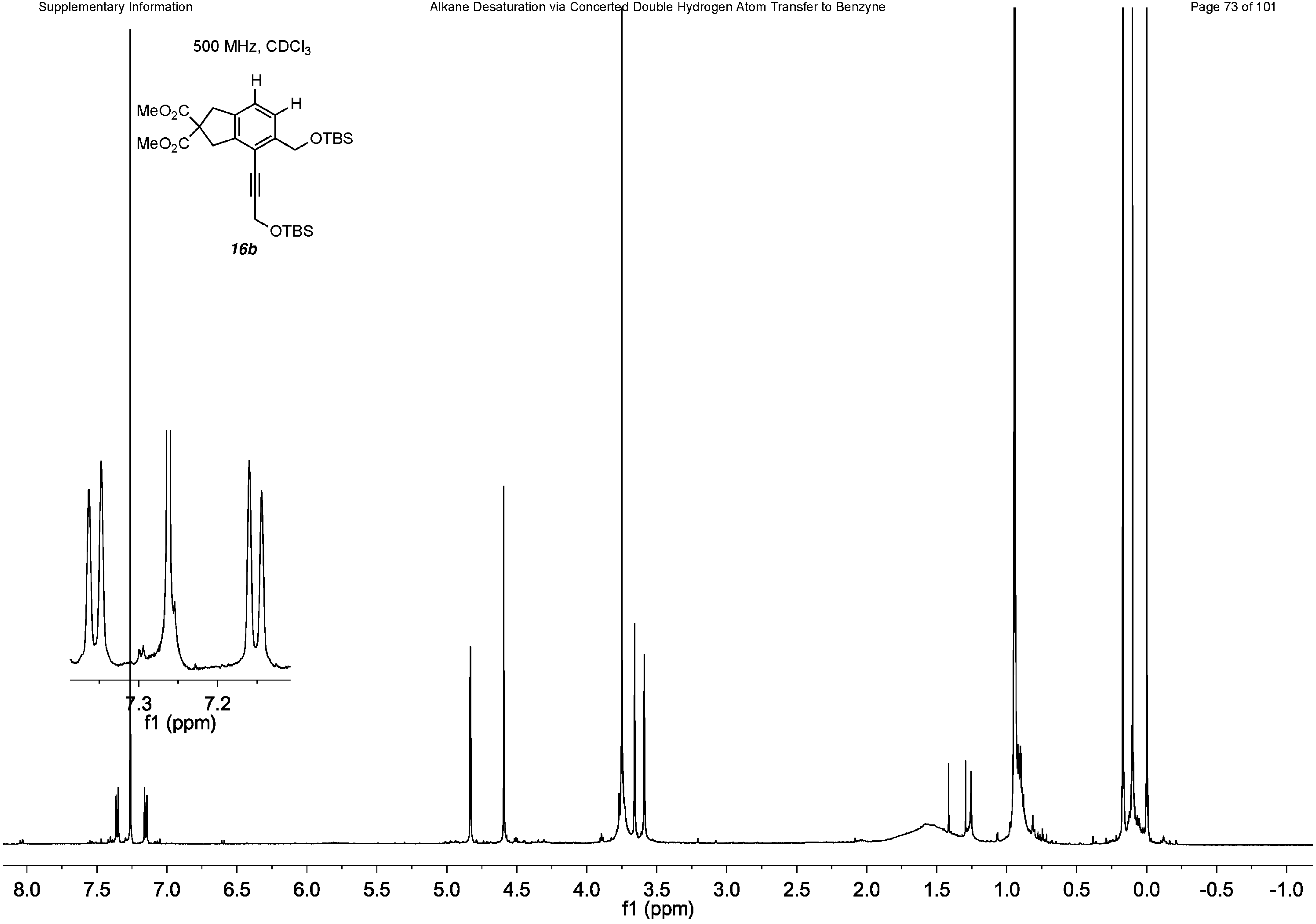
16a



S5

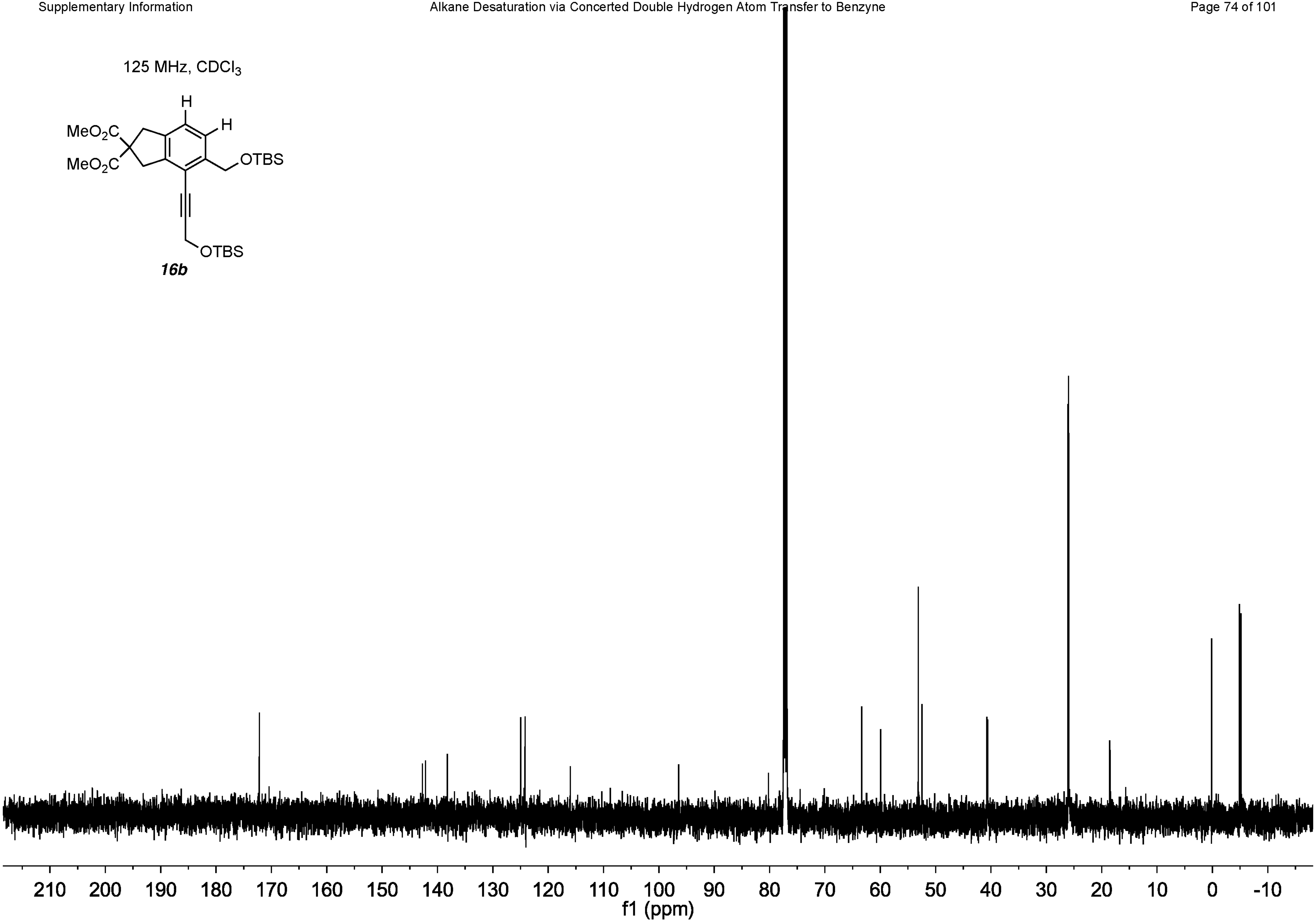
500 MHz, $CDCl_3$
MeO_2C
MeO_2C
OTBS
OTBS
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)


125 MHz, CDCl$_3$
MeO$_2$C
MeO$_2$C
OTBS
OTBS
S5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



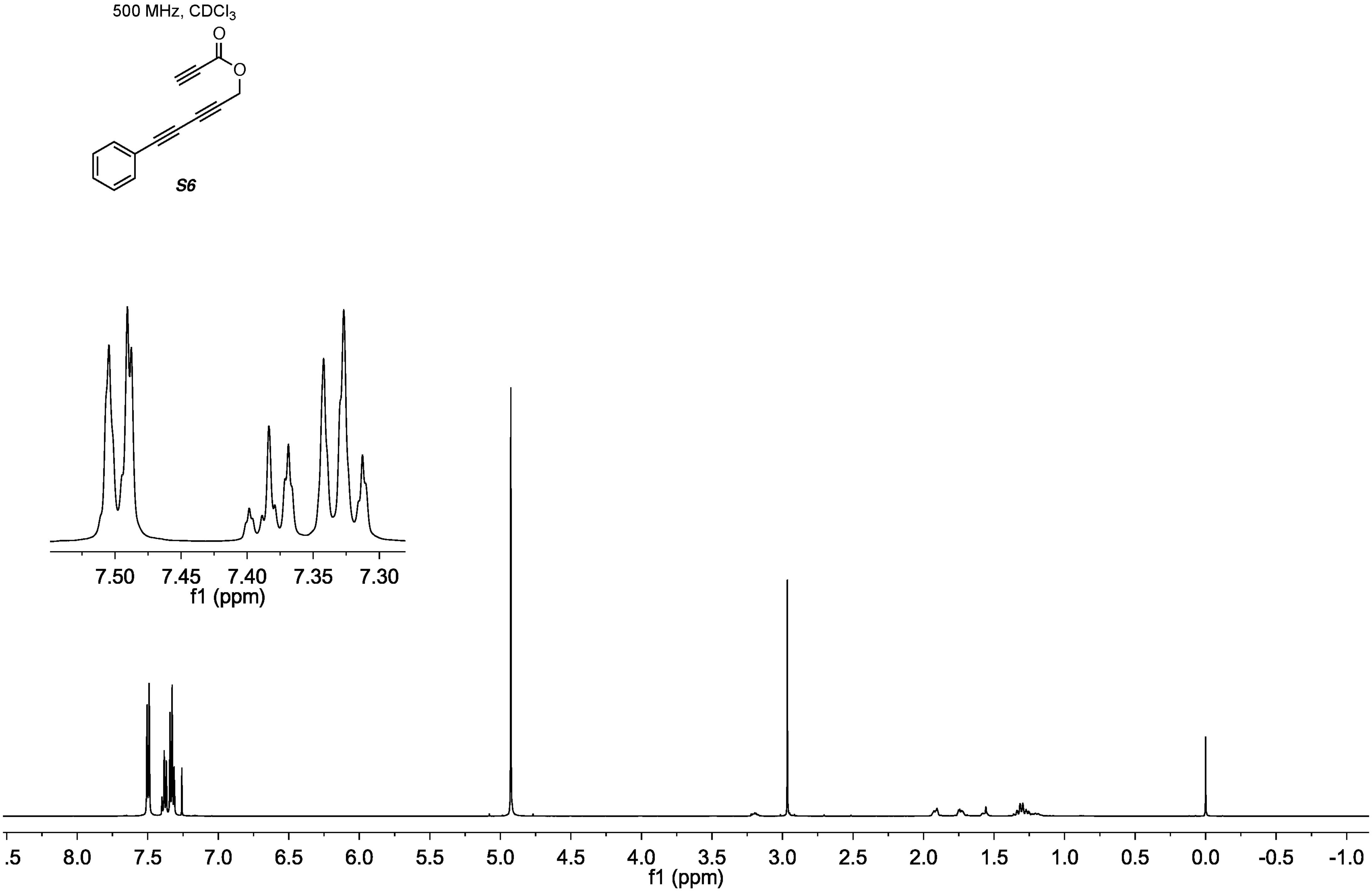
16b

500 MHz, $CDCl_3$
H
H
MeO_2C
MeO_2C
OTBS
OTBS
7.3
7.2
f1 (ppm)
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)

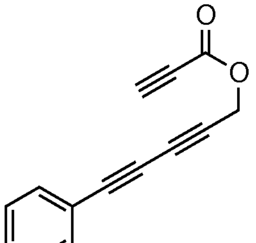


125 MHz, $CDCl_3$

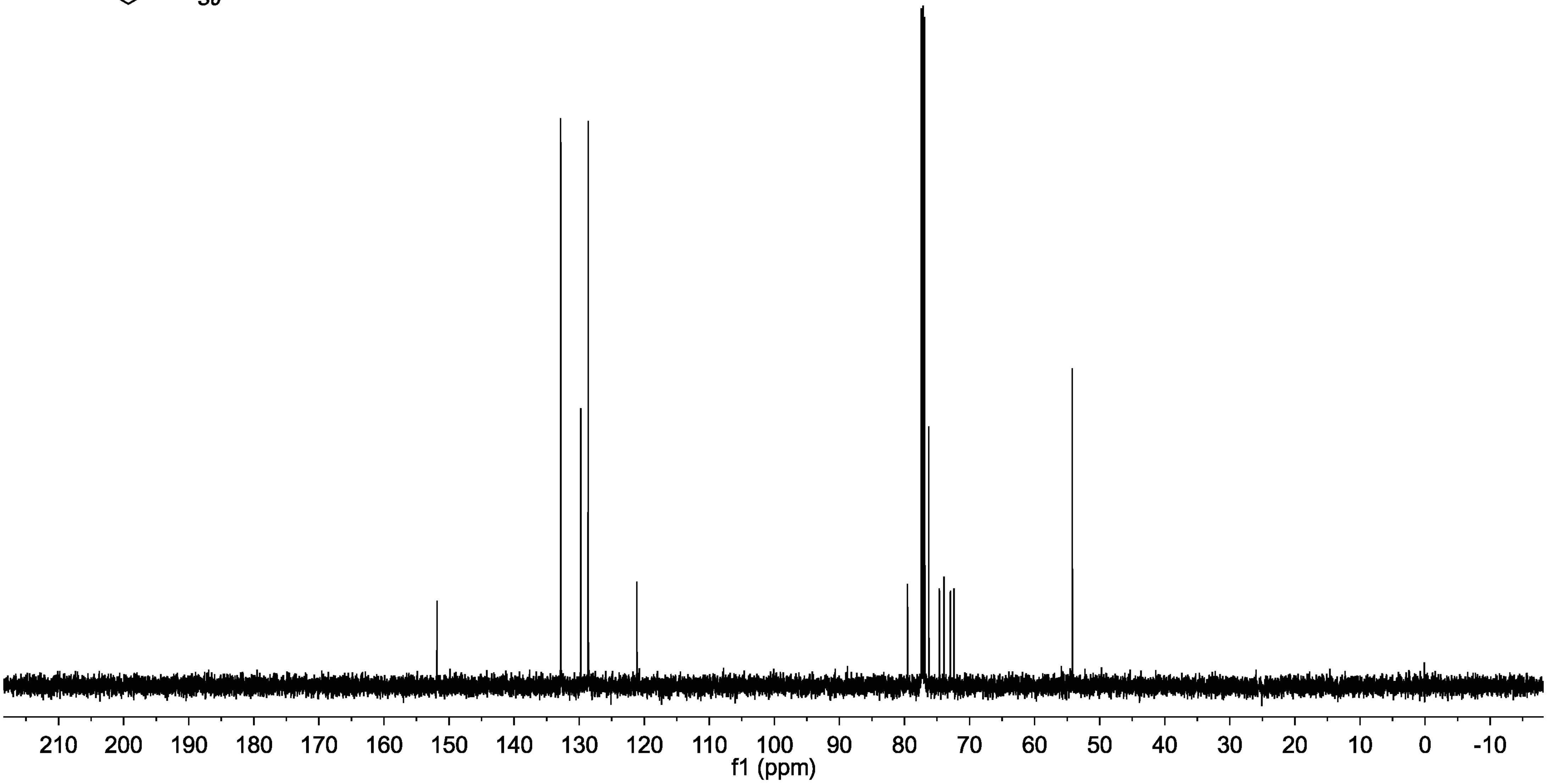
16b

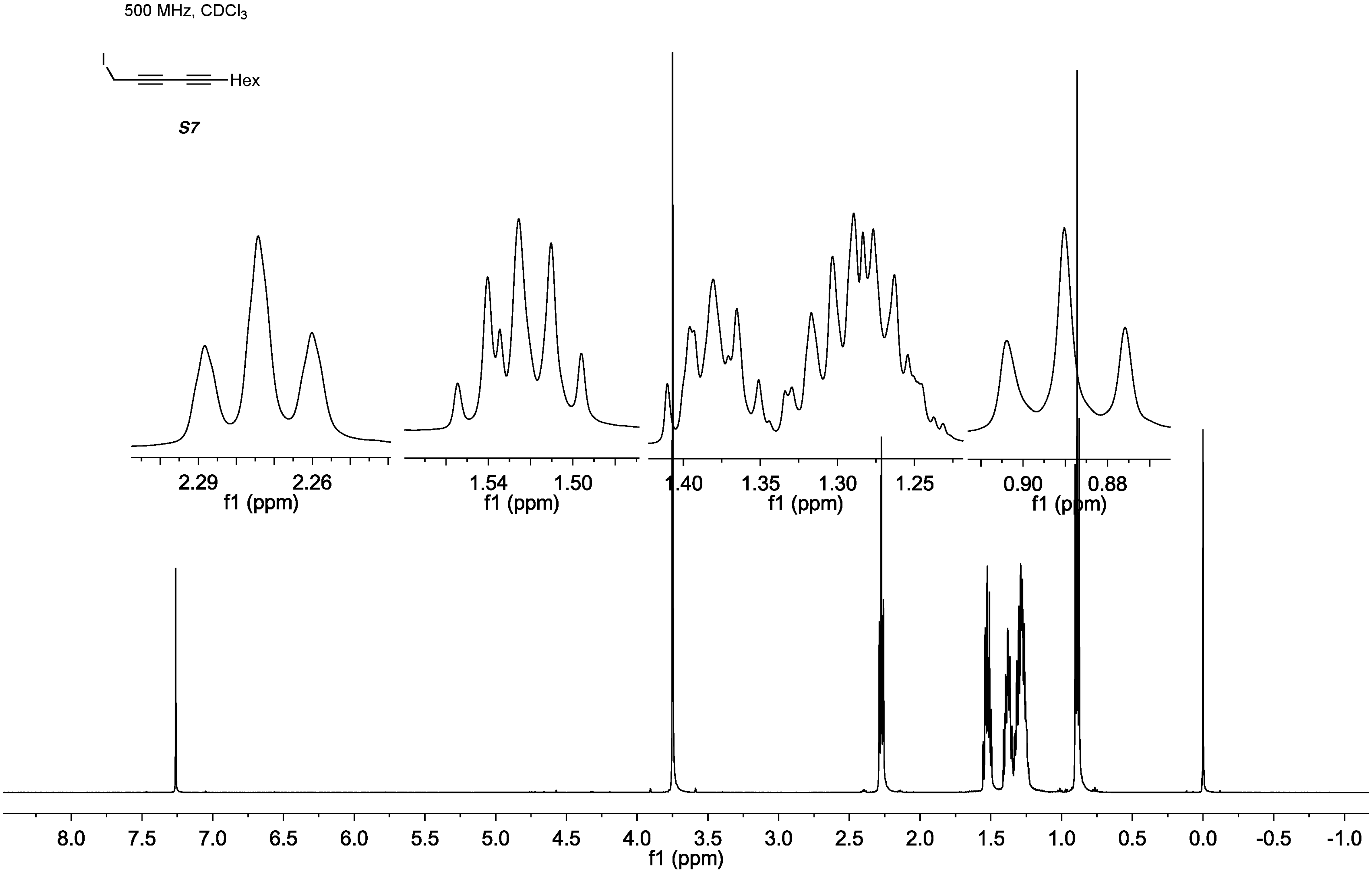

500 MHz, CDCl$_3$
O
O
S6
7.50
7.45
7.40
7.35
7.30
f1 (ppm)
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

125 MHz, $CDCl_3$

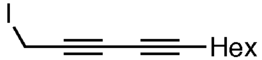


S6

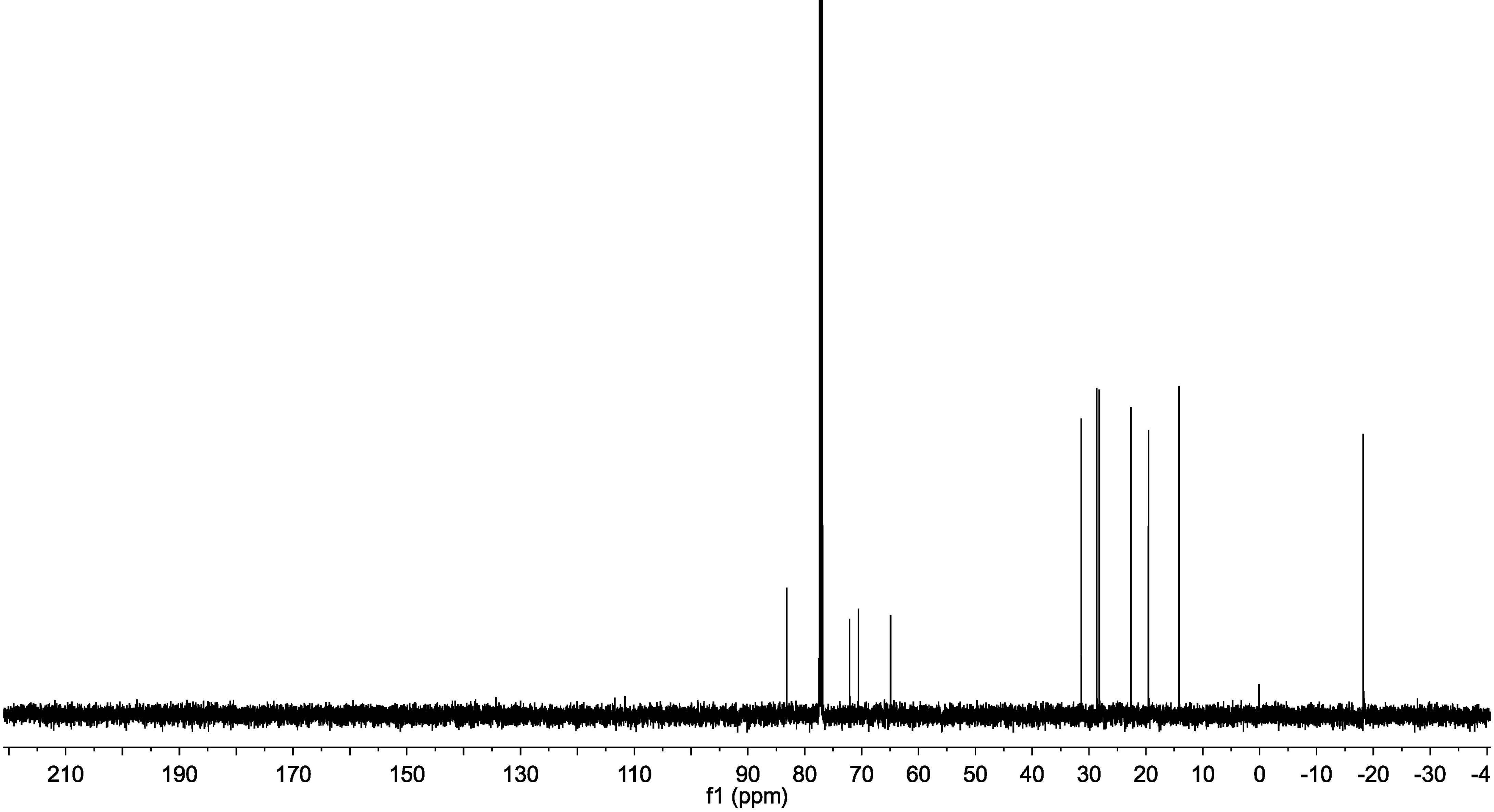



500 MHz, $CDCl_3$
I
Hex
S7
2.29
2.26
f1 (ppm)
1.54
1.50
f1 (ppm)
1.40
1.35
1.30
1.25
f1 (ppm)
0.90
0.88
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

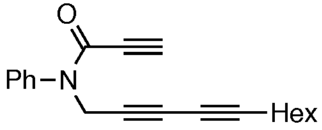
125 MHz, $CDCl_3$



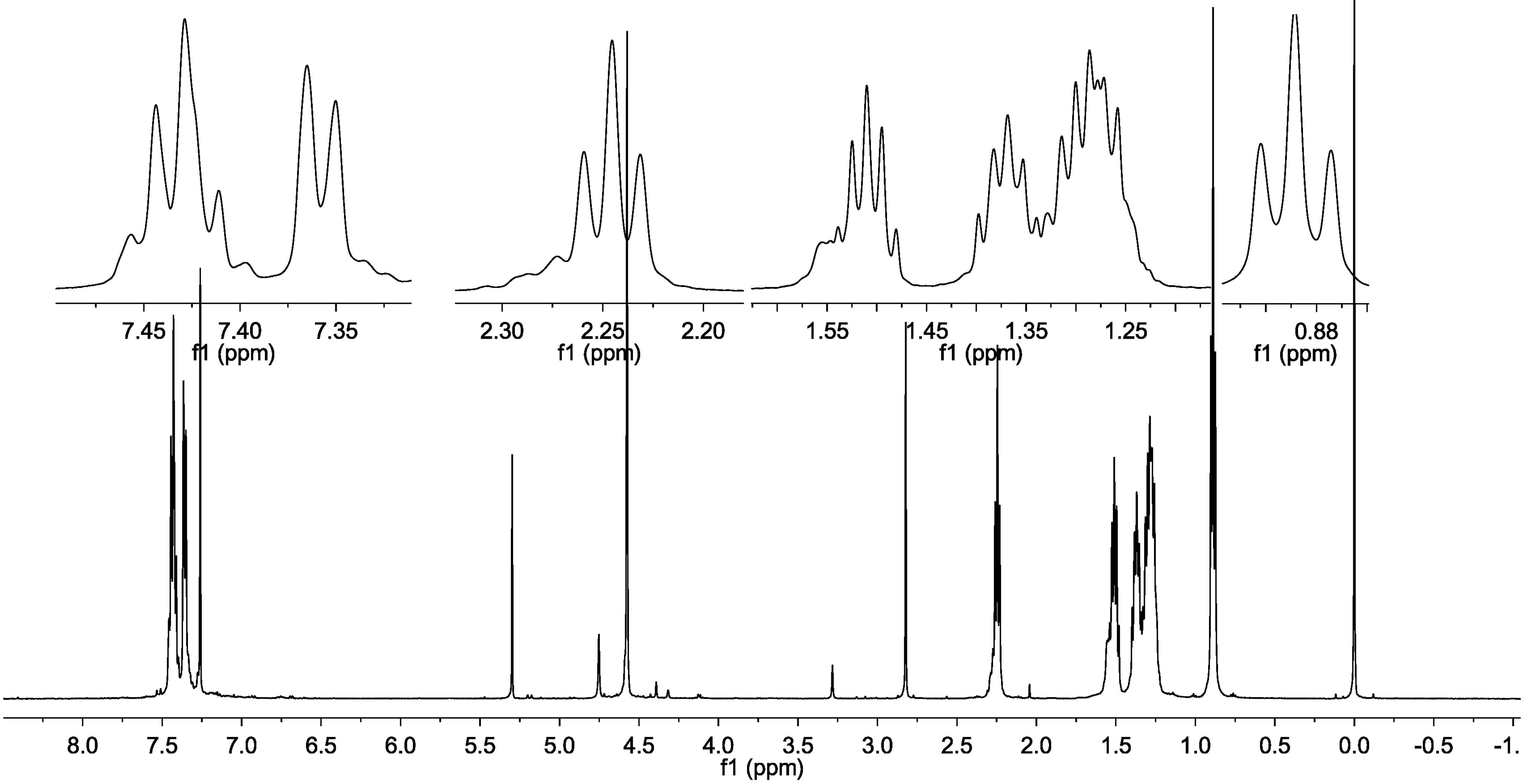
S7

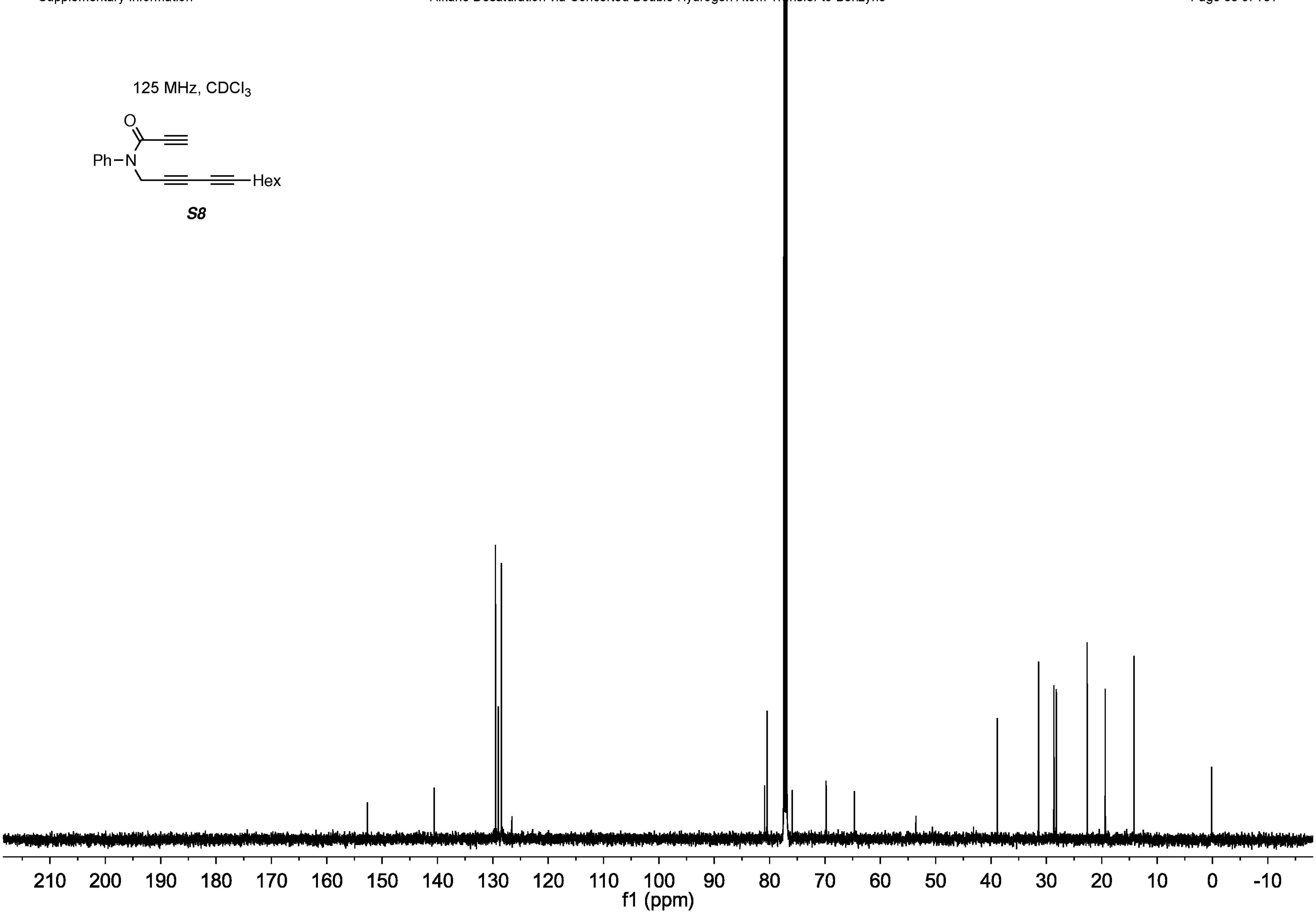


500 MHz, $CDCl_3$

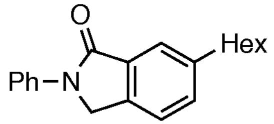


S8

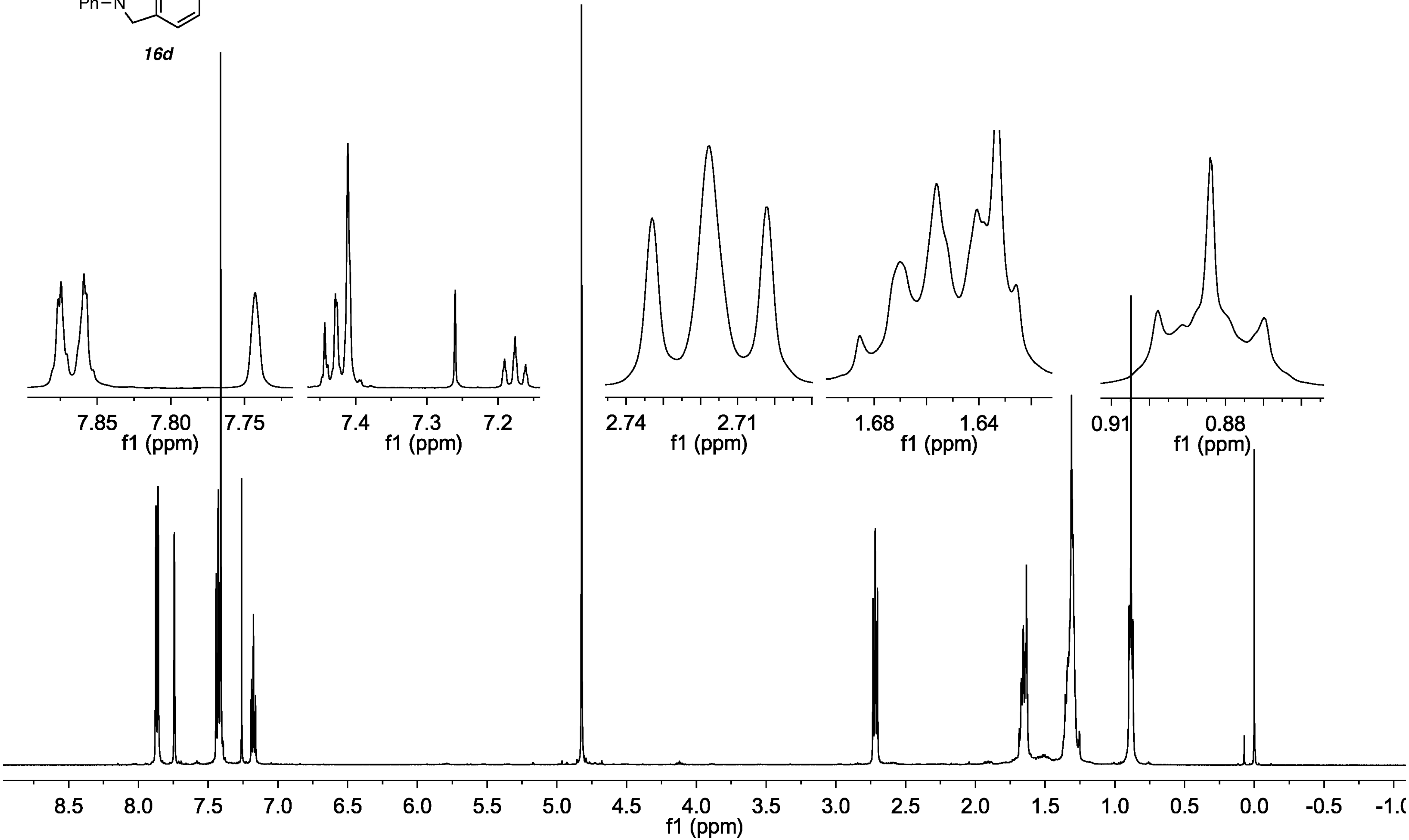


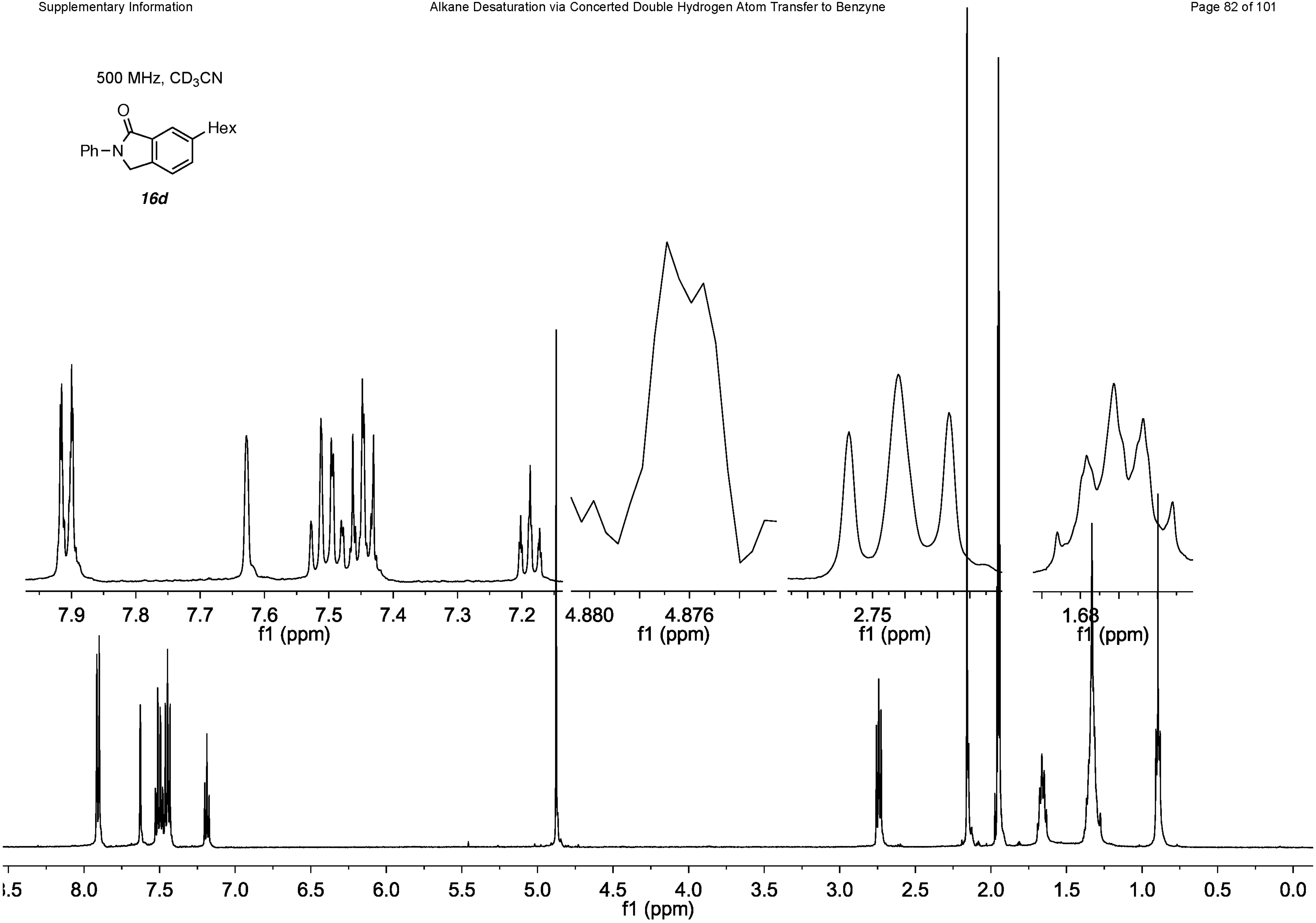

125 MHz, $CDCl_3$
O
Ph−N
Hex
S8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

500 MHz, $CDCl_3$

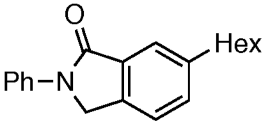


16d

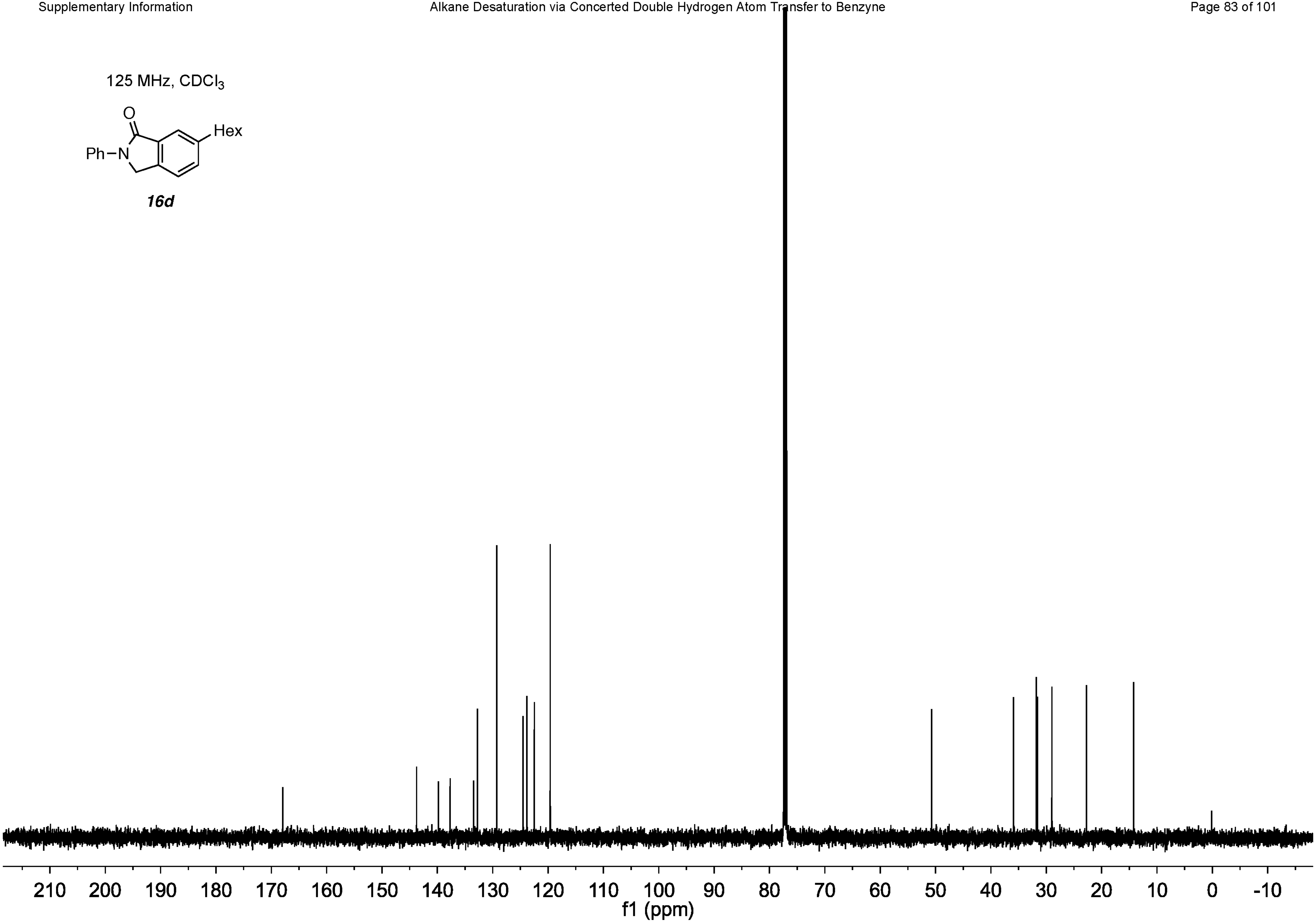


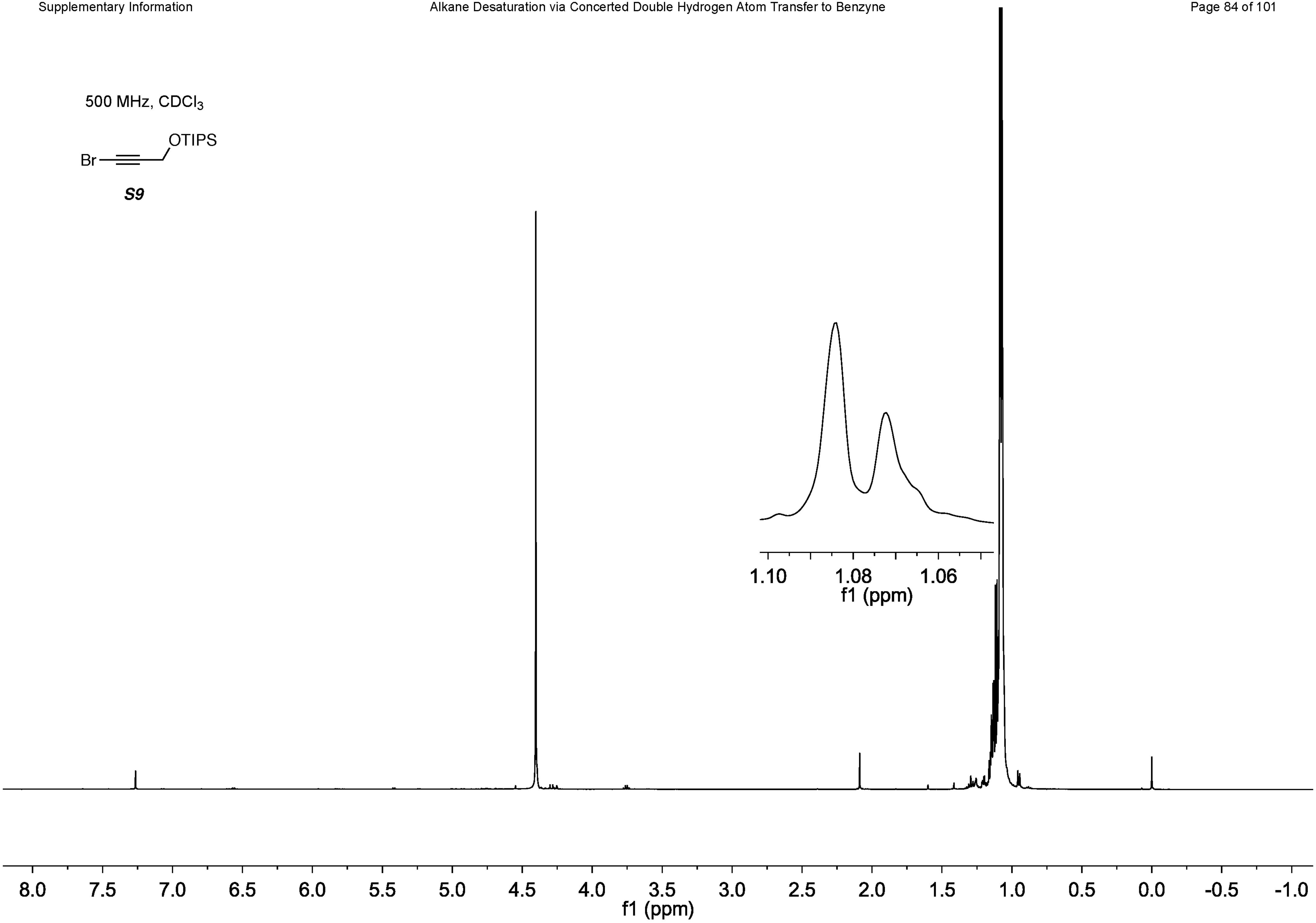

500 MHz, CD_3CN
O
Hex
Ph–N
16d
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
4.880
4.876
f1 (ppm)
2.75
f1 (ppm)
1.68
f1 (ppm)
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

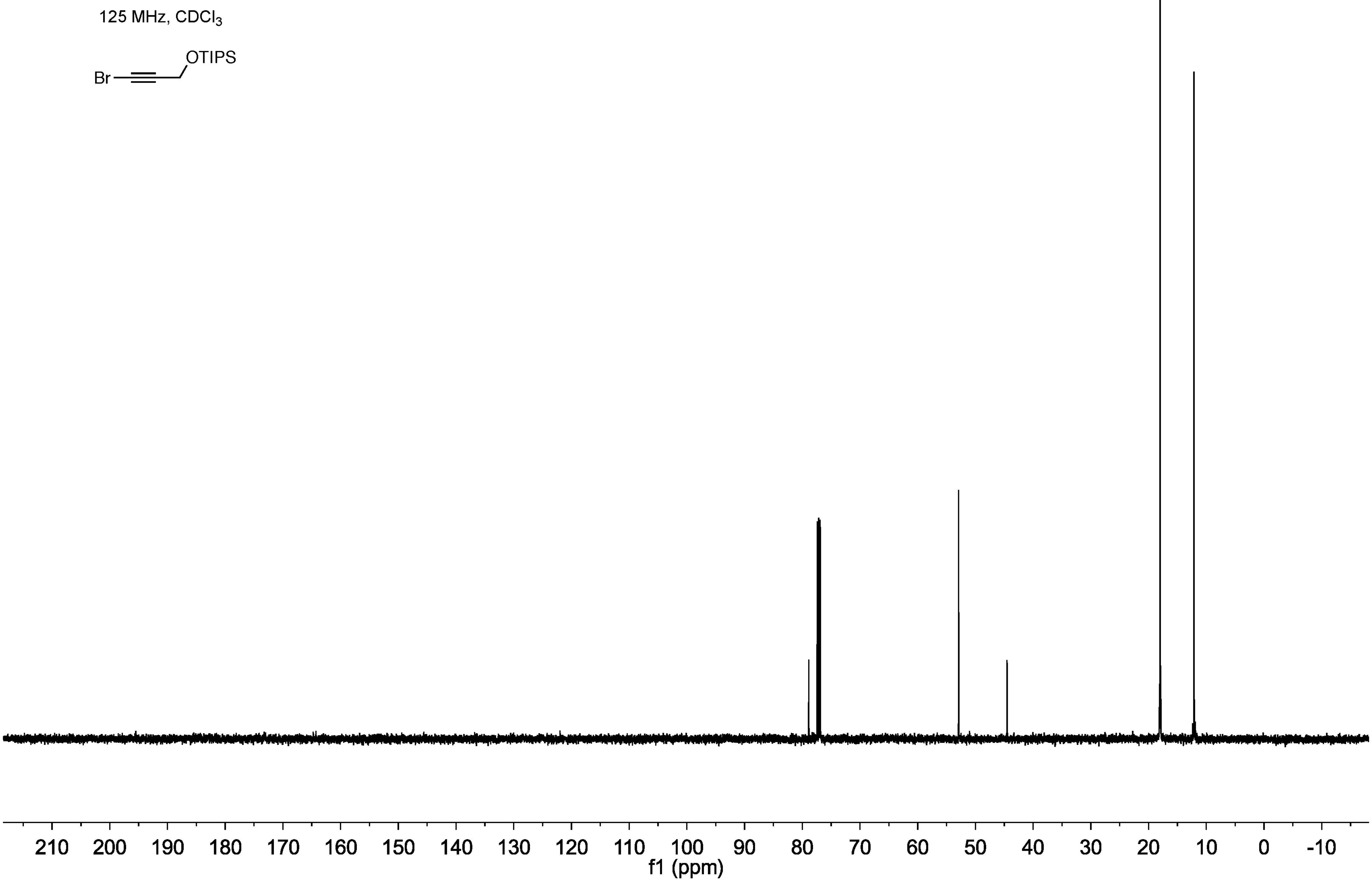
125 MHz, $CDCl_3$

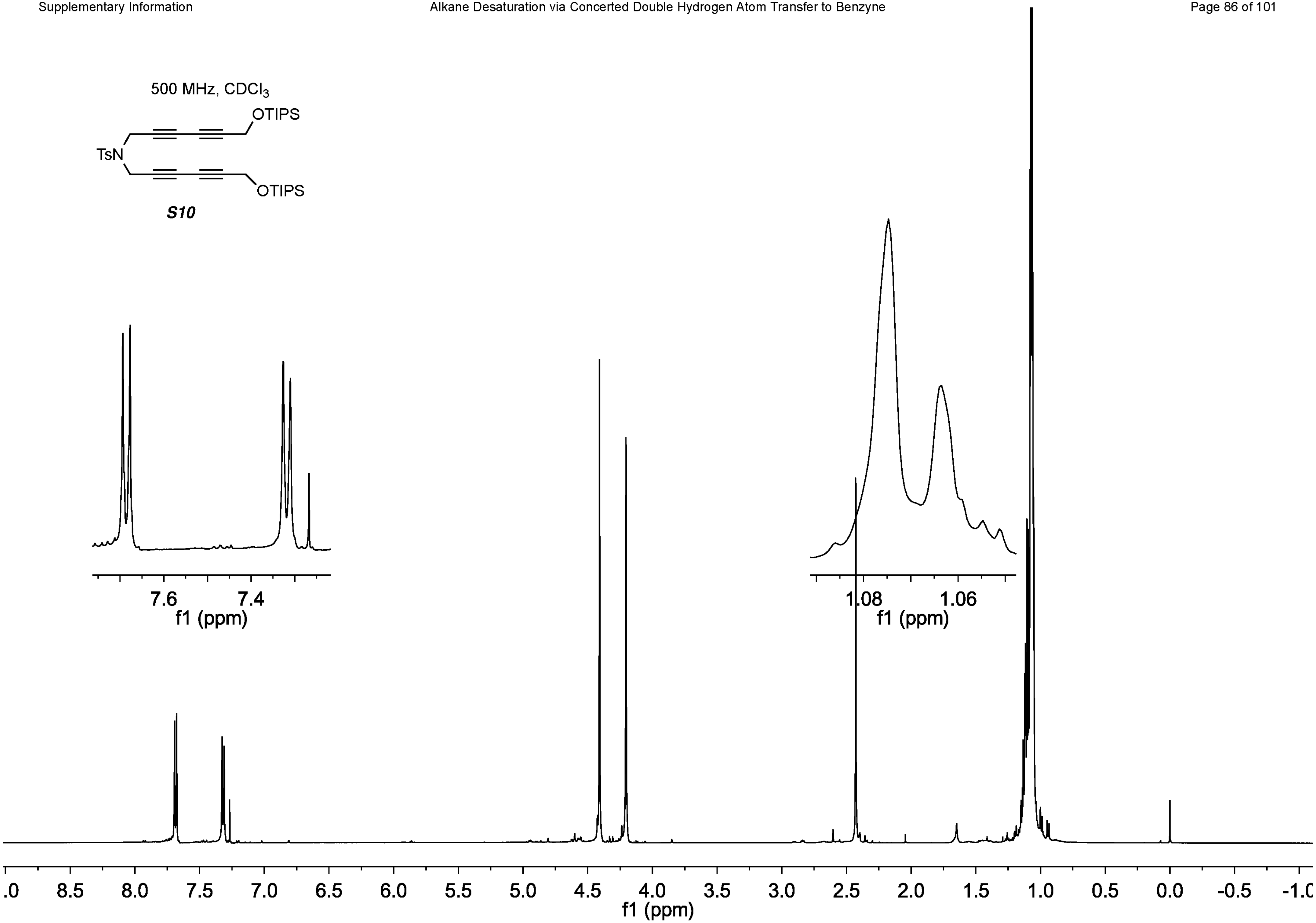


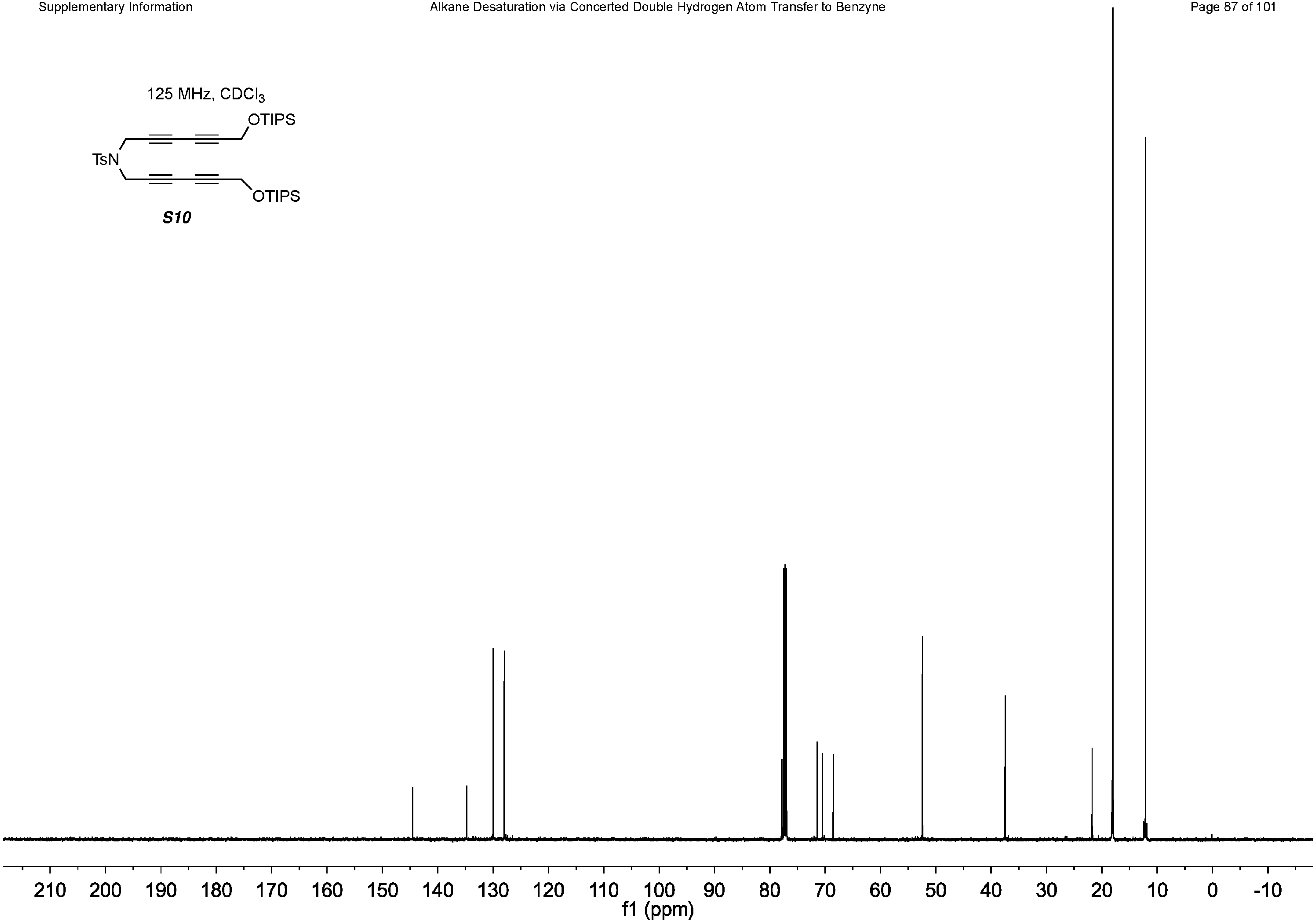
16d

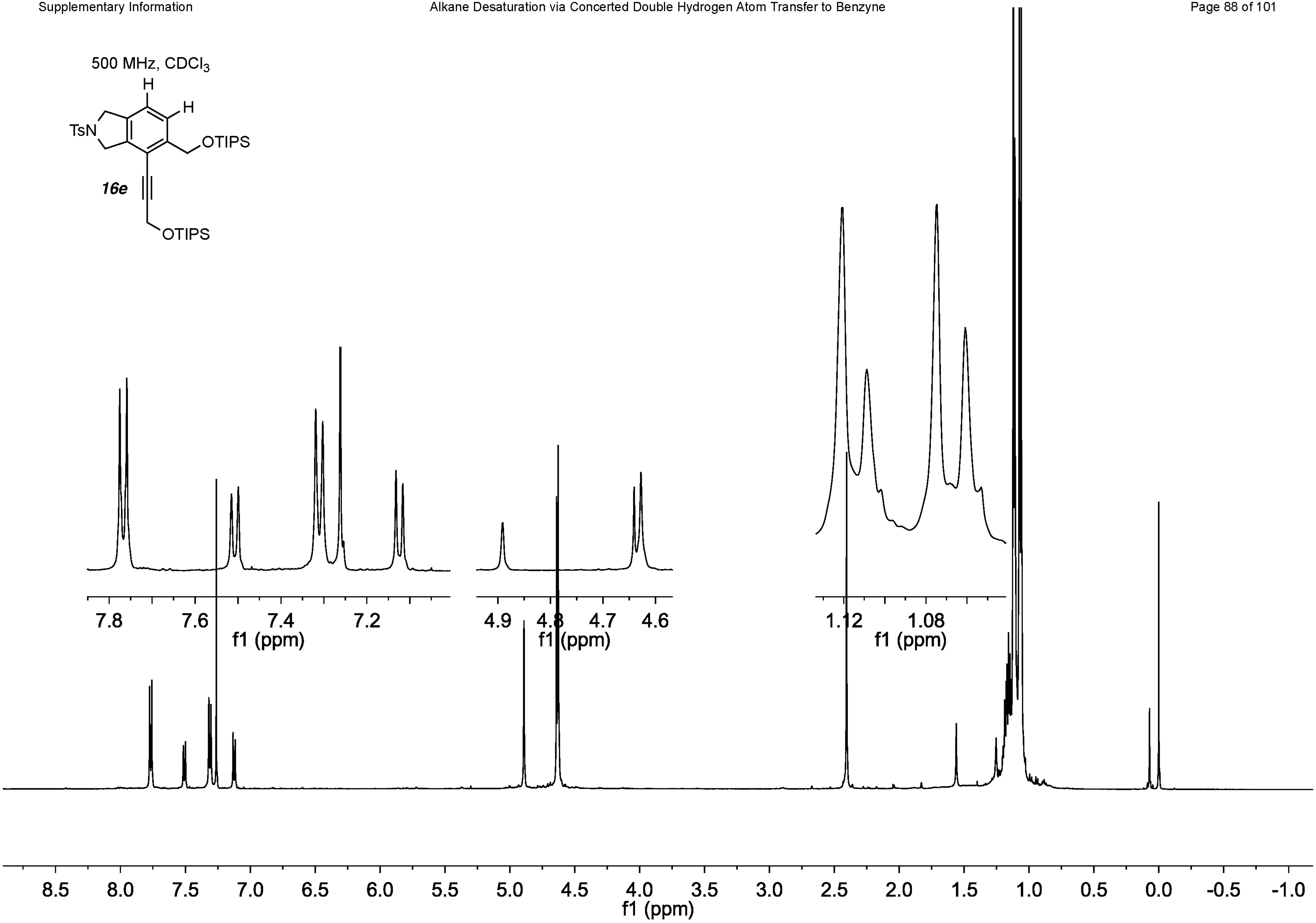


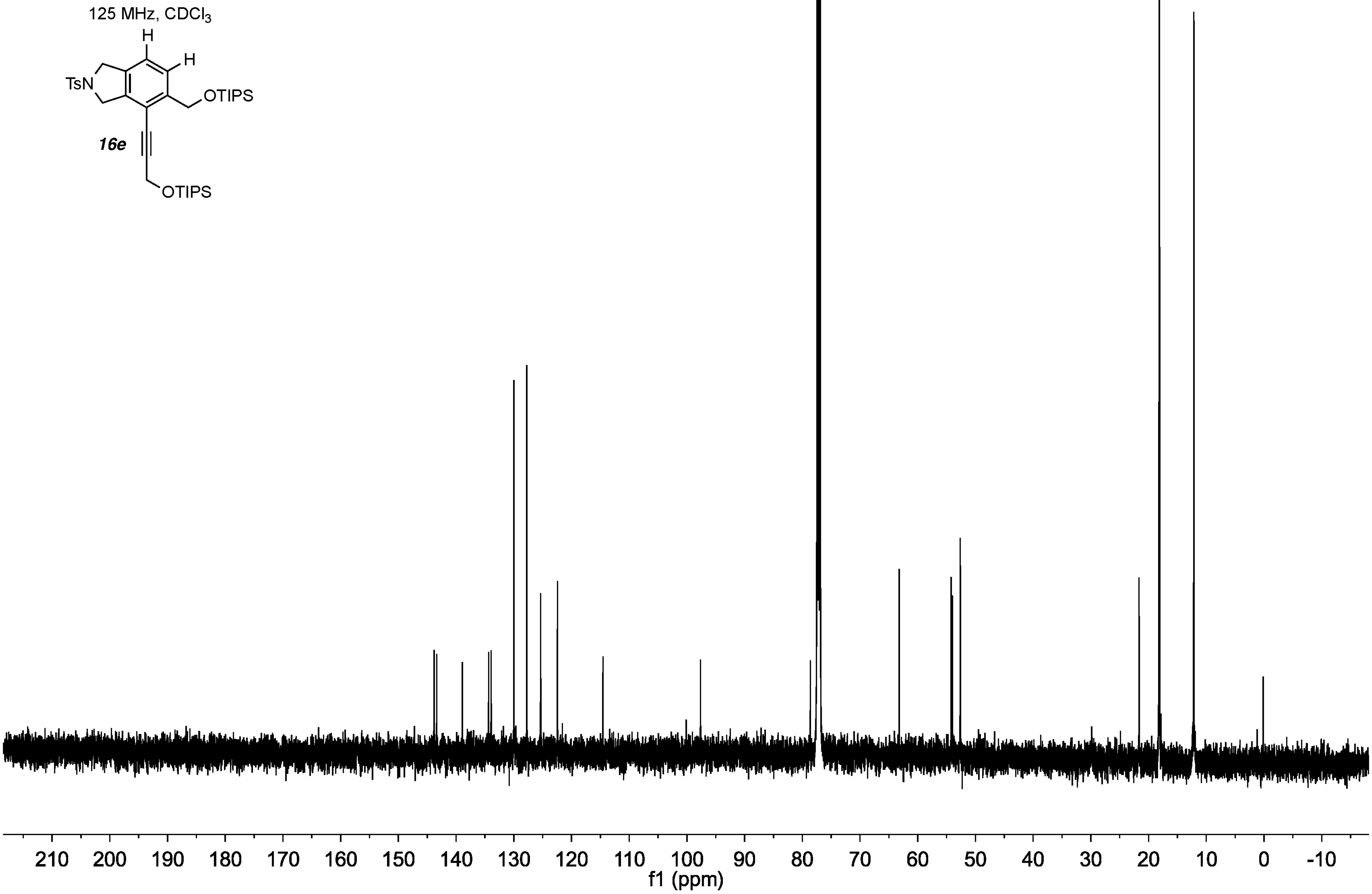

500 MHz, CDCl$_3$
OTIPS
Br
S9
1.10
1.08
1.06
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


125 MHz, $CDCl_3$
OTIPS
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


500 MHz, CDCl3
OTIPS
TsN
OTIPS
S10
7.6
7.4
f1 (ppm)
1.08
1.06
f1 (ppm)
.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)

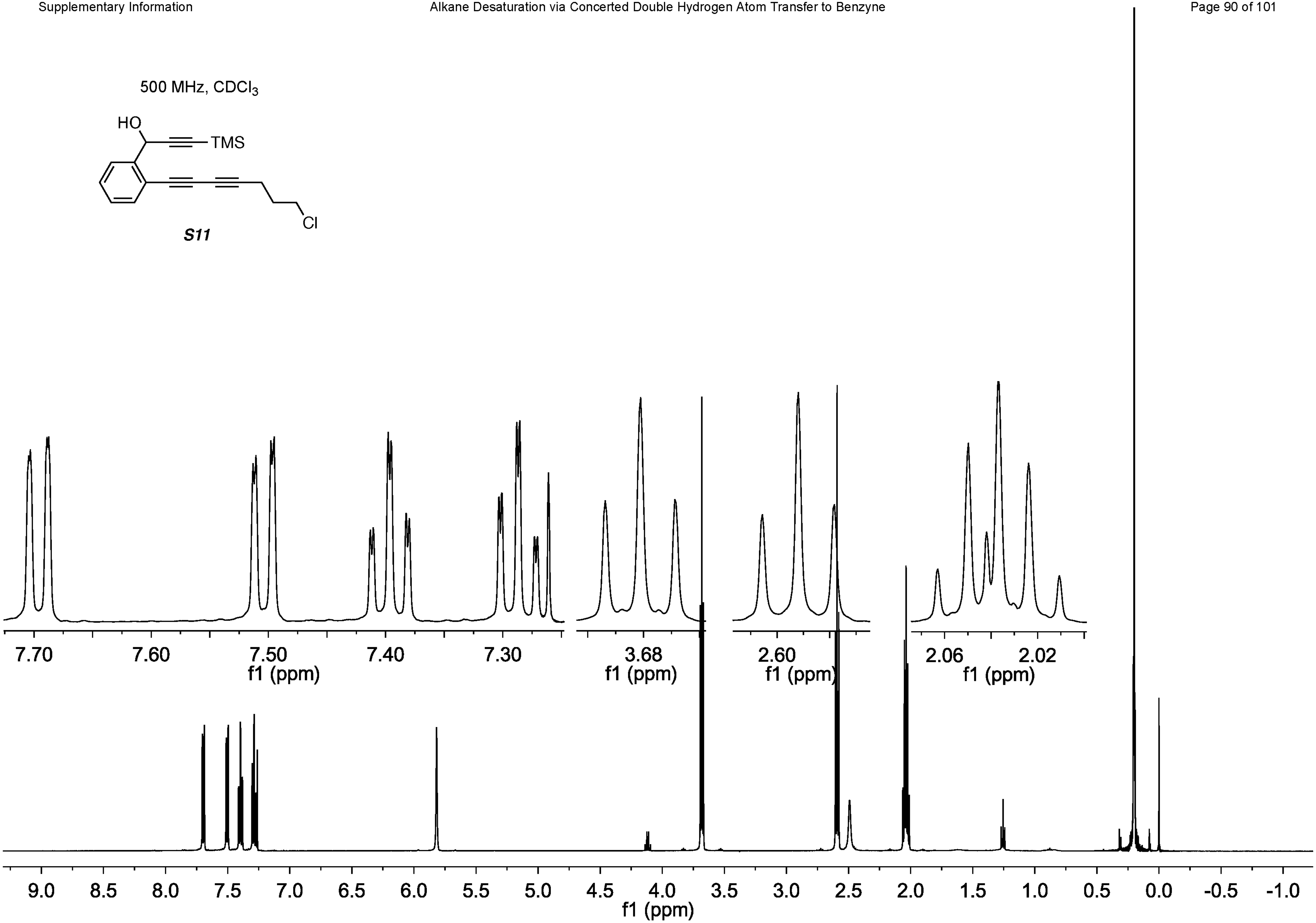

125 MHz, $CDCl_3$
OTIPS
TsN
OTIPS
S10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


500 MHz, CDCl3
H
H
TsN
OTIPS
16e
OTIPS
7.8
7.6
7.4
7.2
f1 (ppm)
4.9
4.8
4.7
4.6
f1 (ppm)
1.12
1.08
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

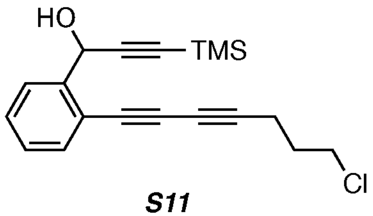

125 MHz, CDCl3
H
H
TsN
OTIPS
16e
OTIPS
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

500 MHz, $CDCl_3$

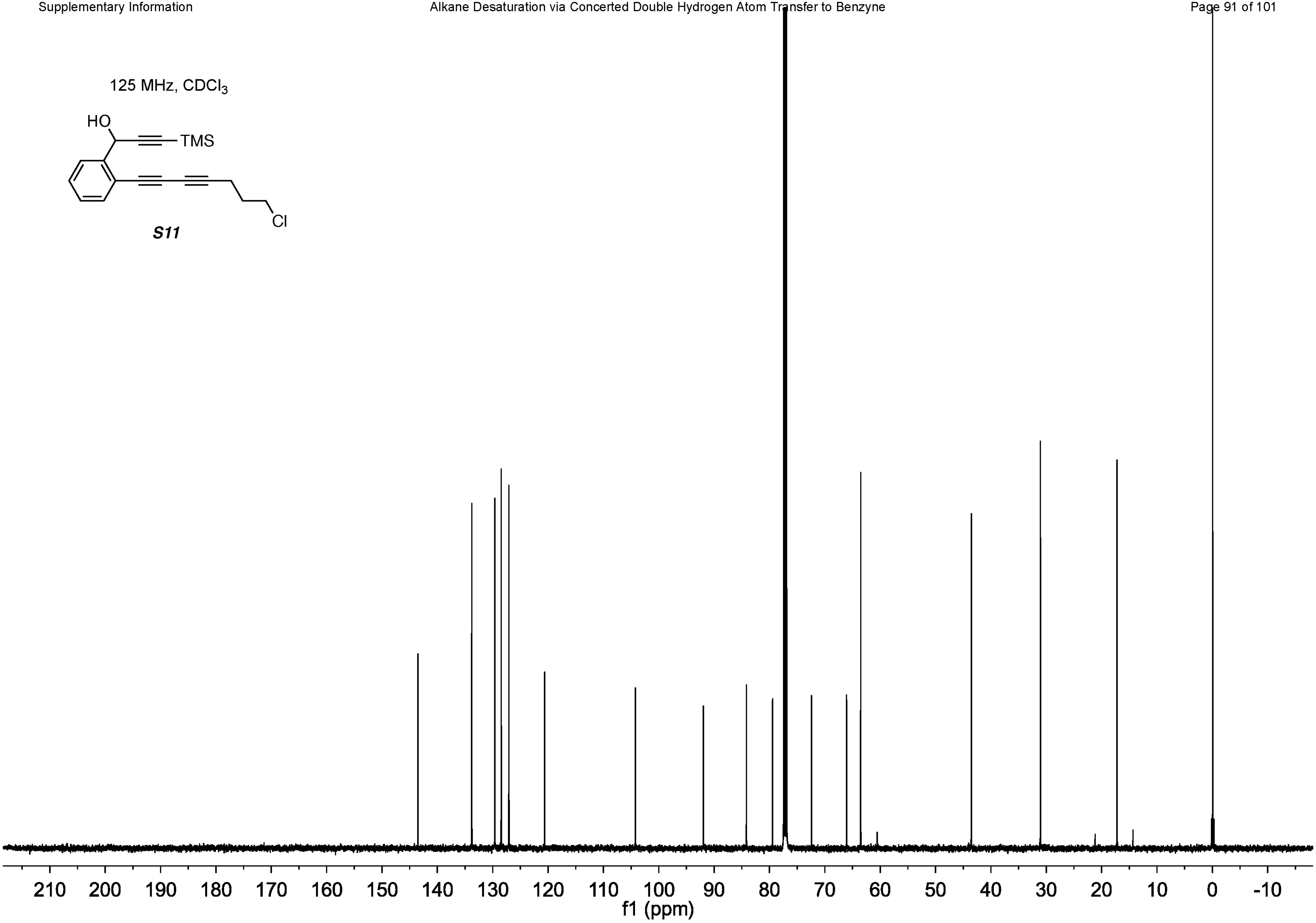
S11



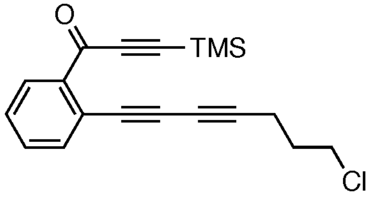
125 MHz, $CDCl_3$



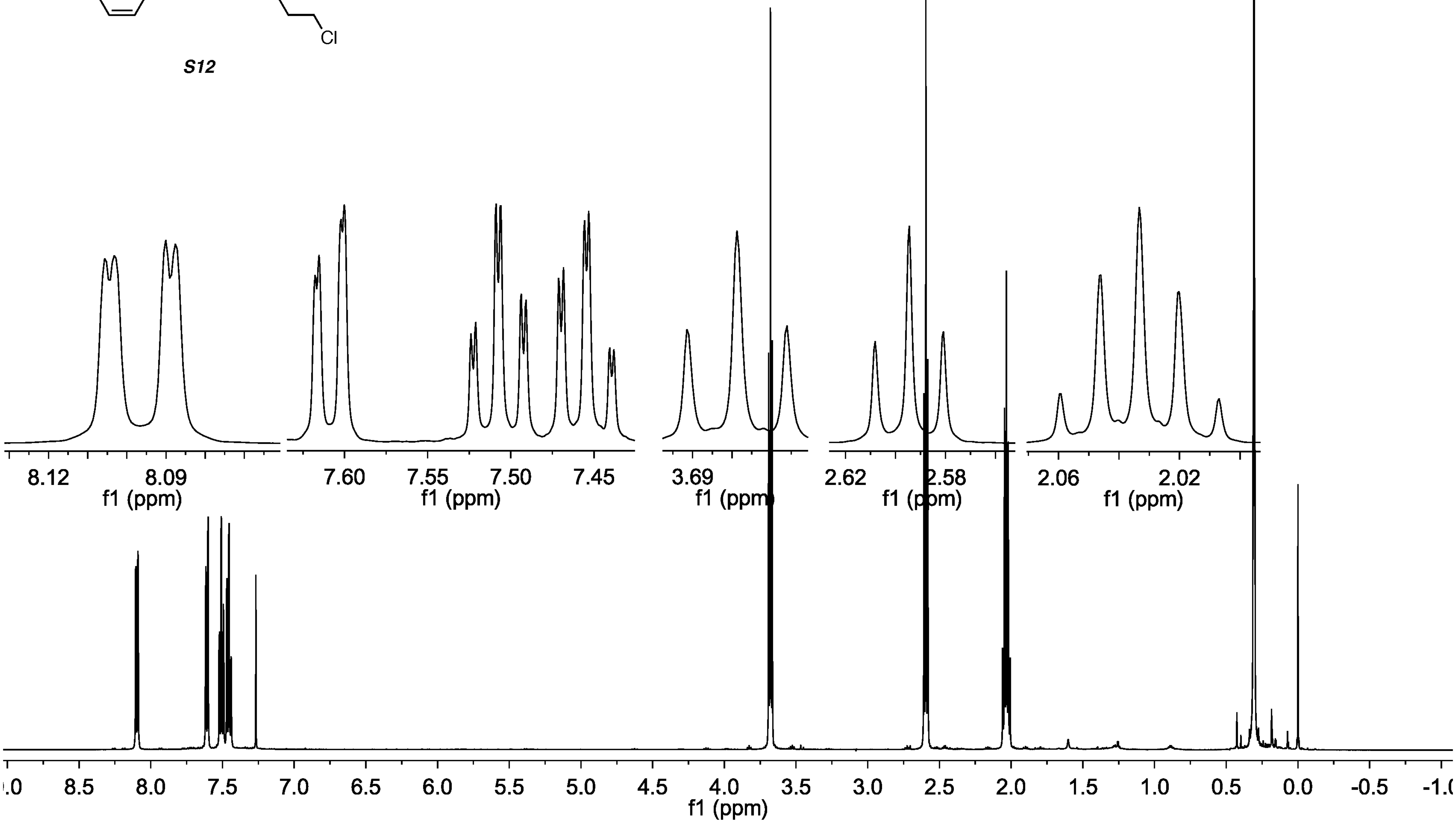
S11

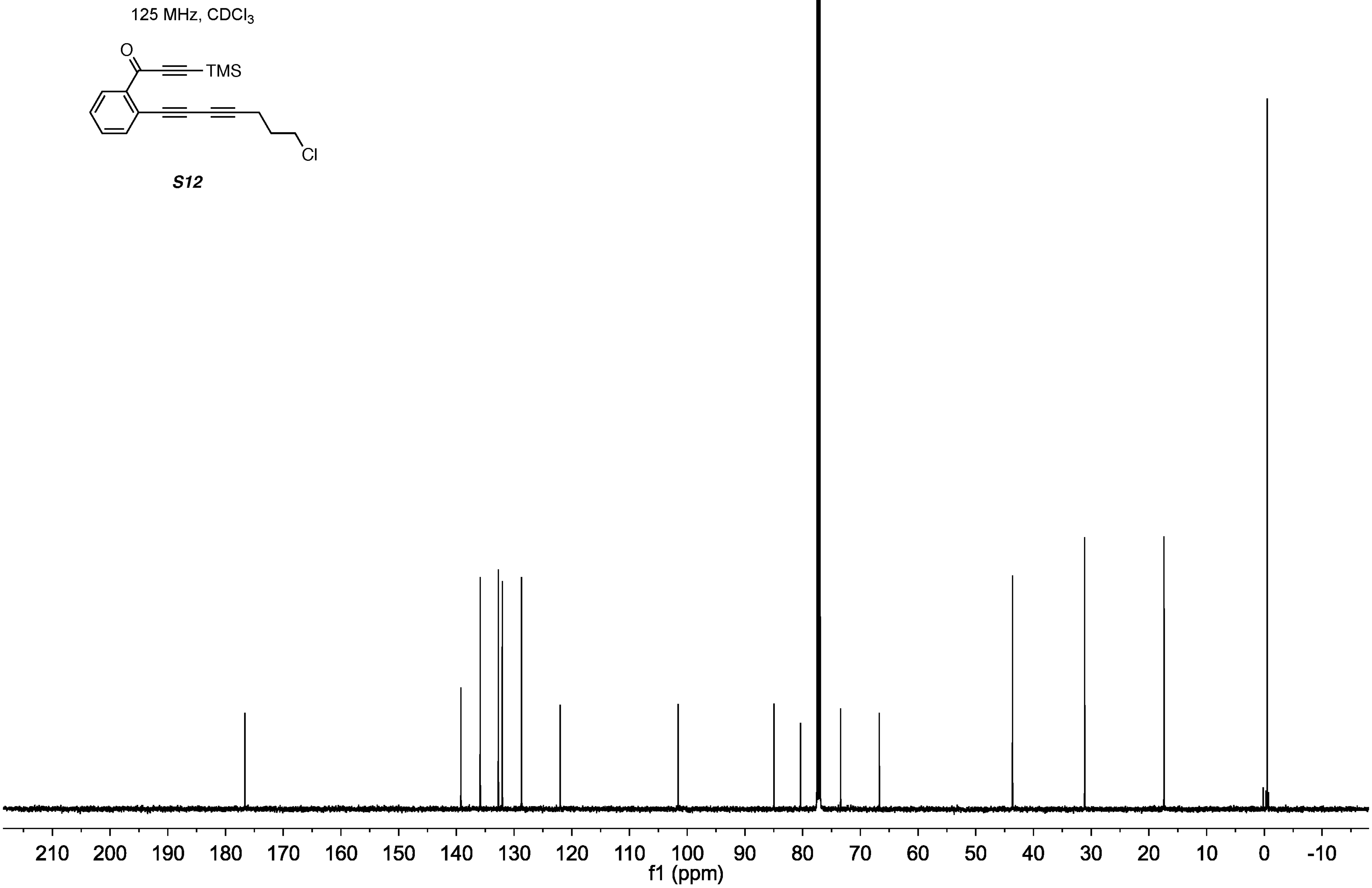


500 MHz, $CDCl_3$

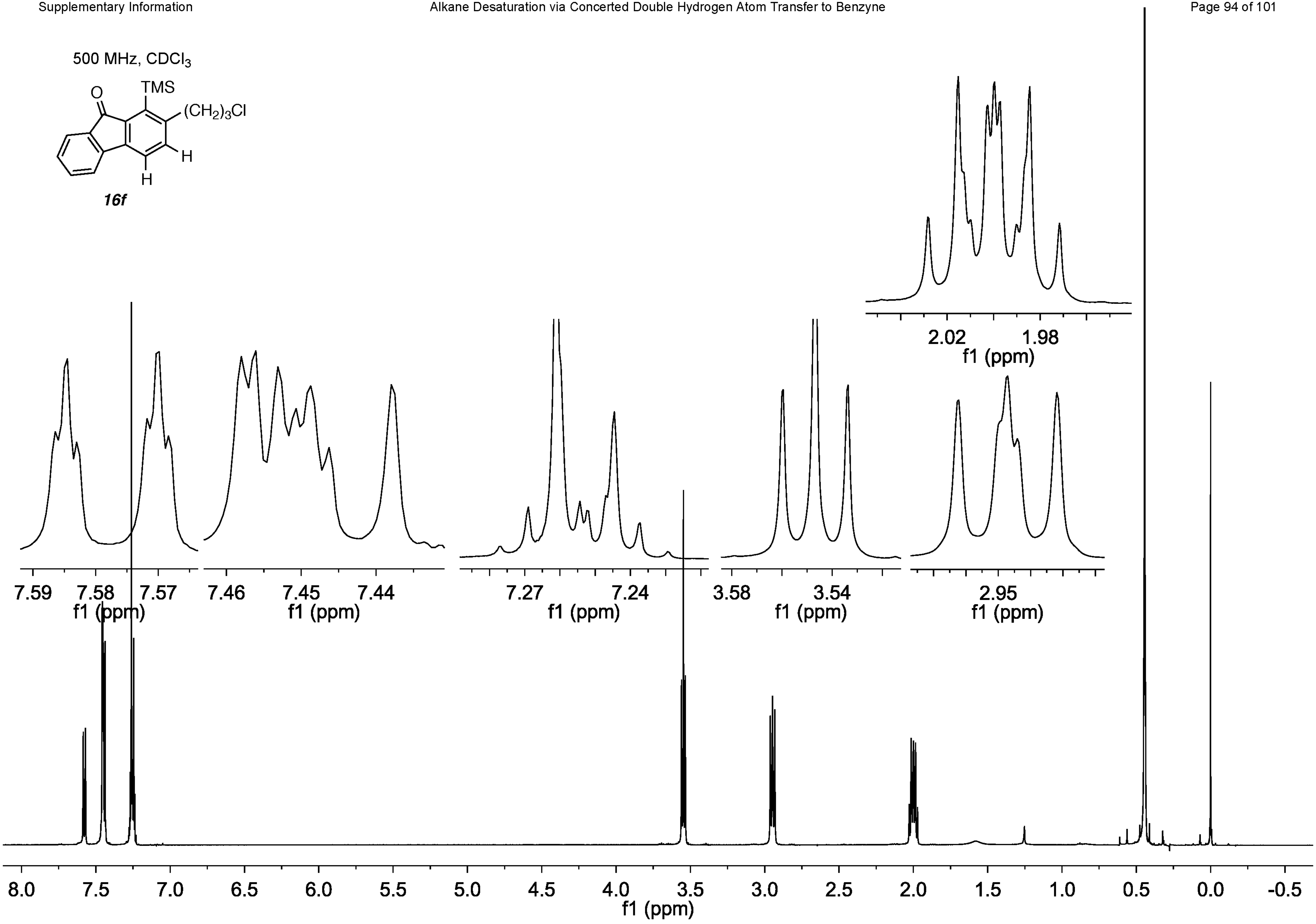


S12



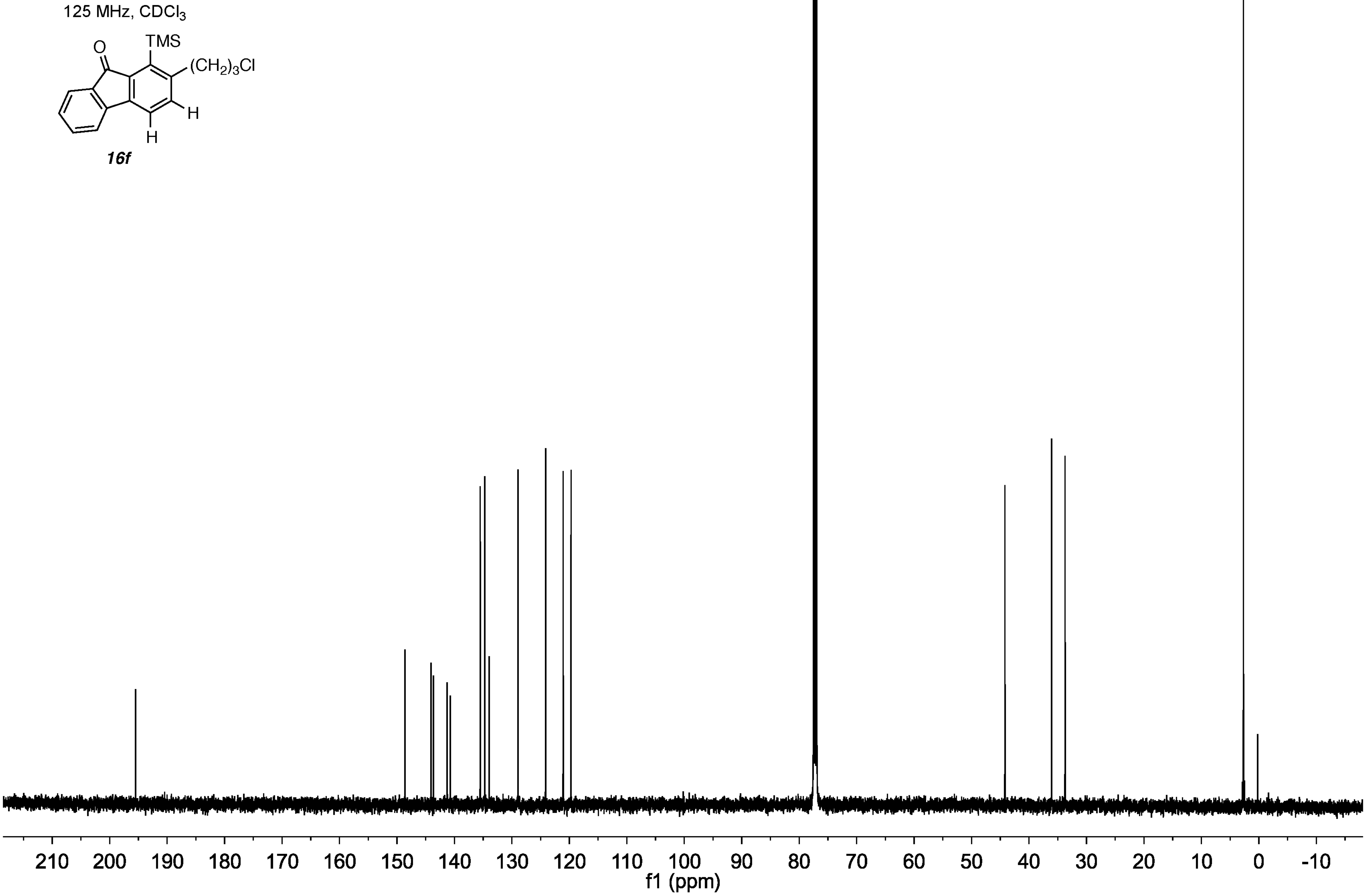

125 MHz, $CDCl_3$
O
TMS
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

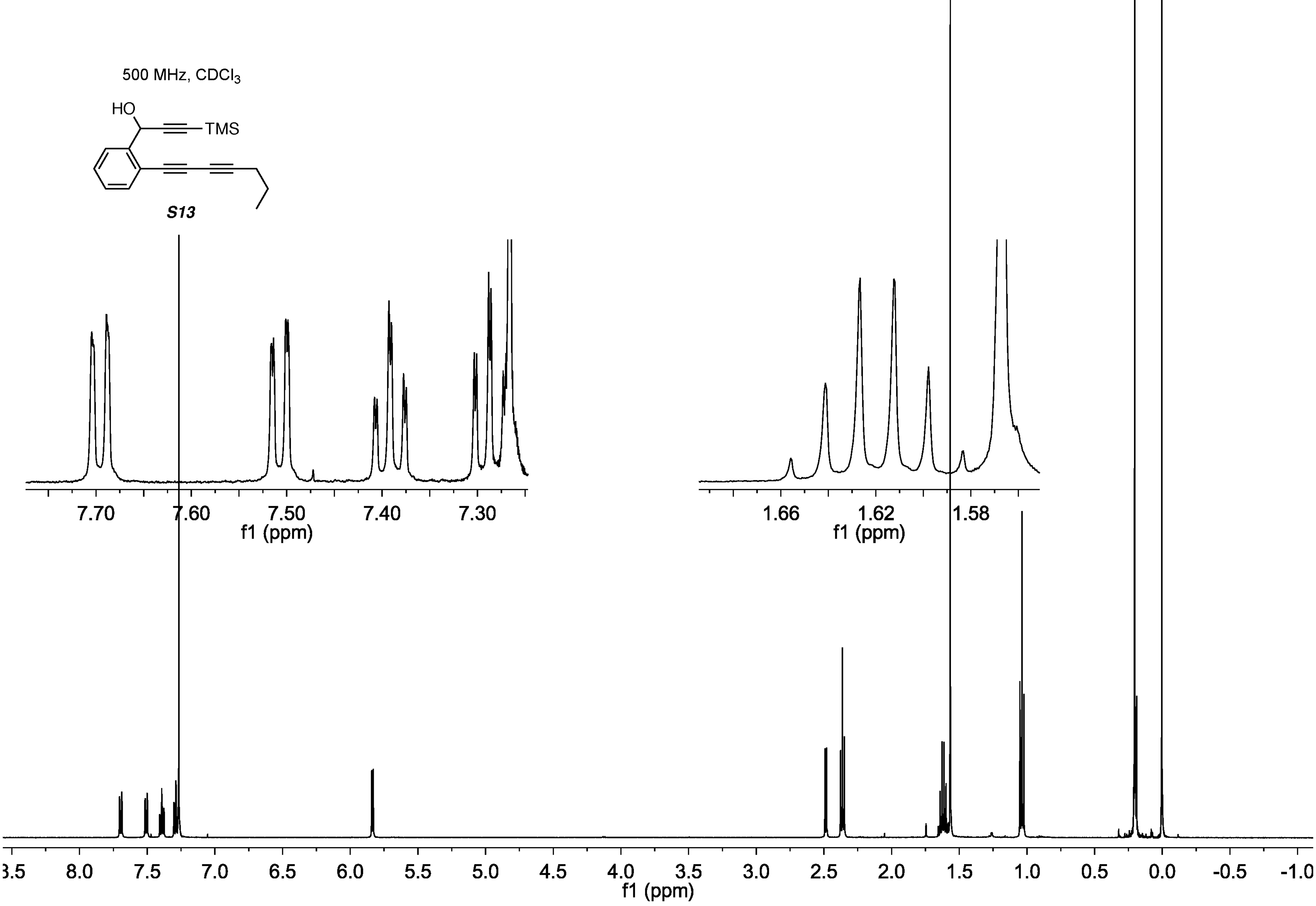
S12

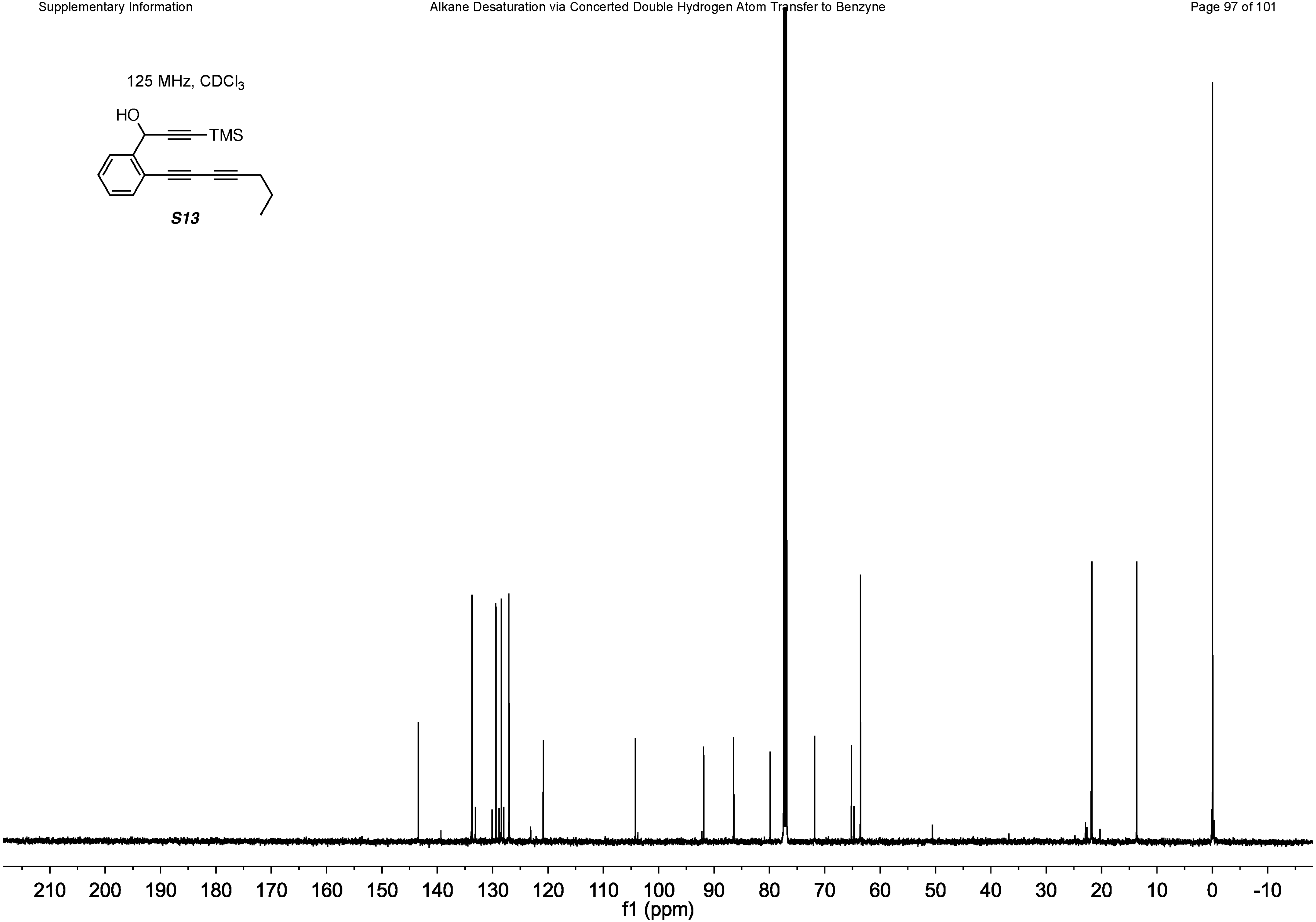


500 MHz, $CDCl_3$

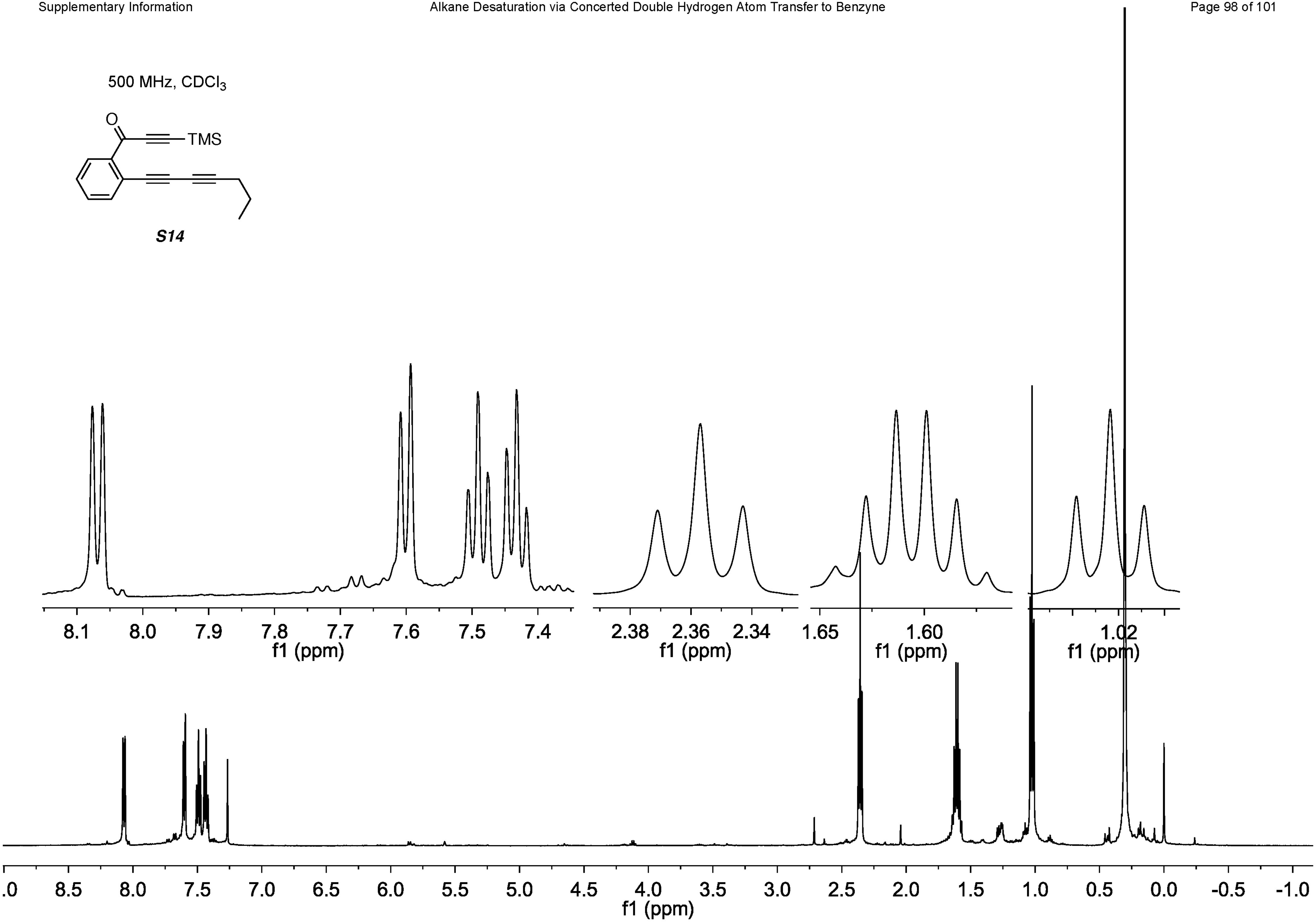
16f


125 MHz, $CDCl_3$
O
TMS
$(CH_2)_3Cl$
H
H
16f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

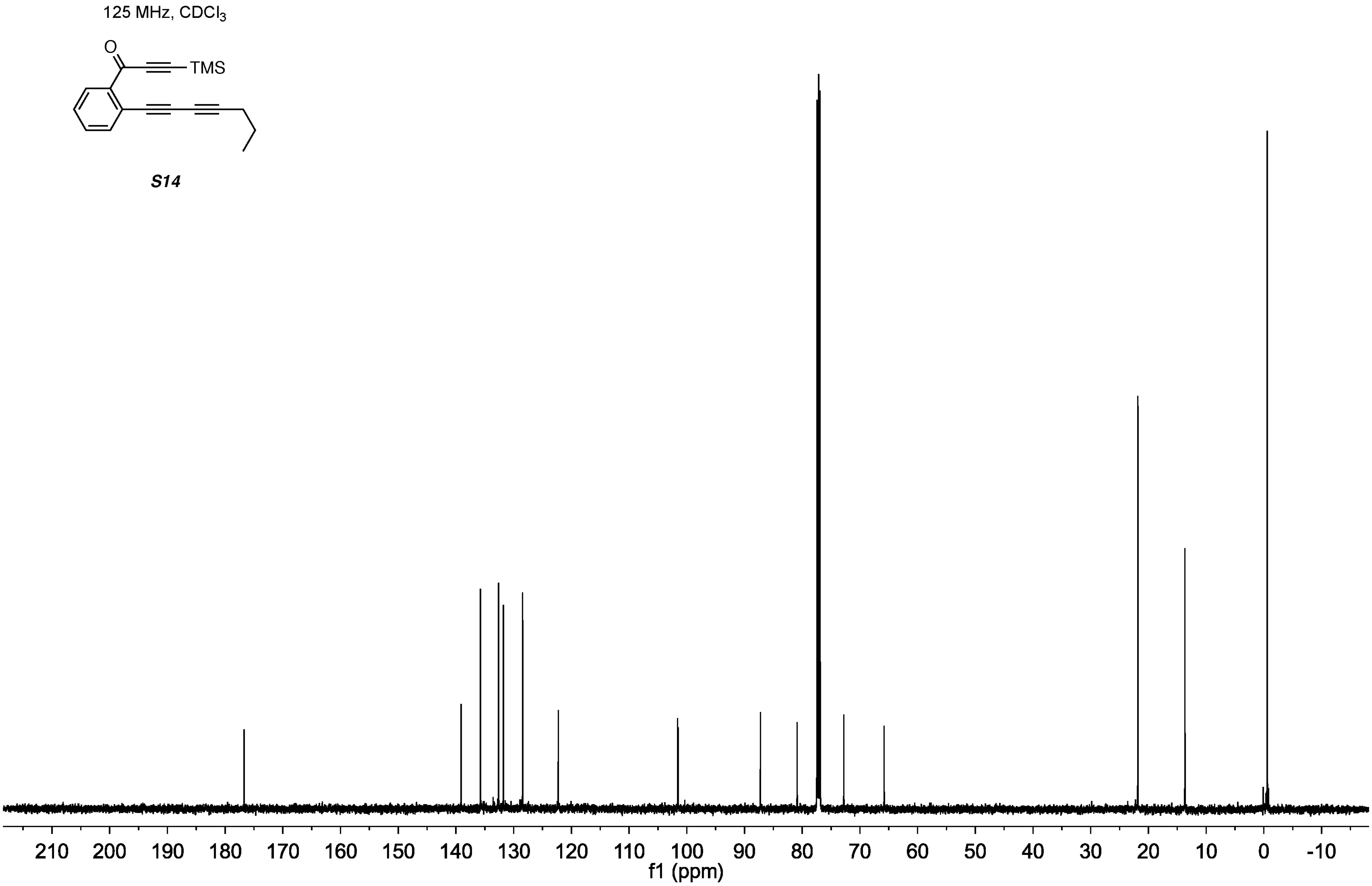

500 MHz, CDCl3
HO
TMS
S13
7.70
7.60
7.50
7.40
7.30
f1 (ppm)
1.66
1.62
1.58
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

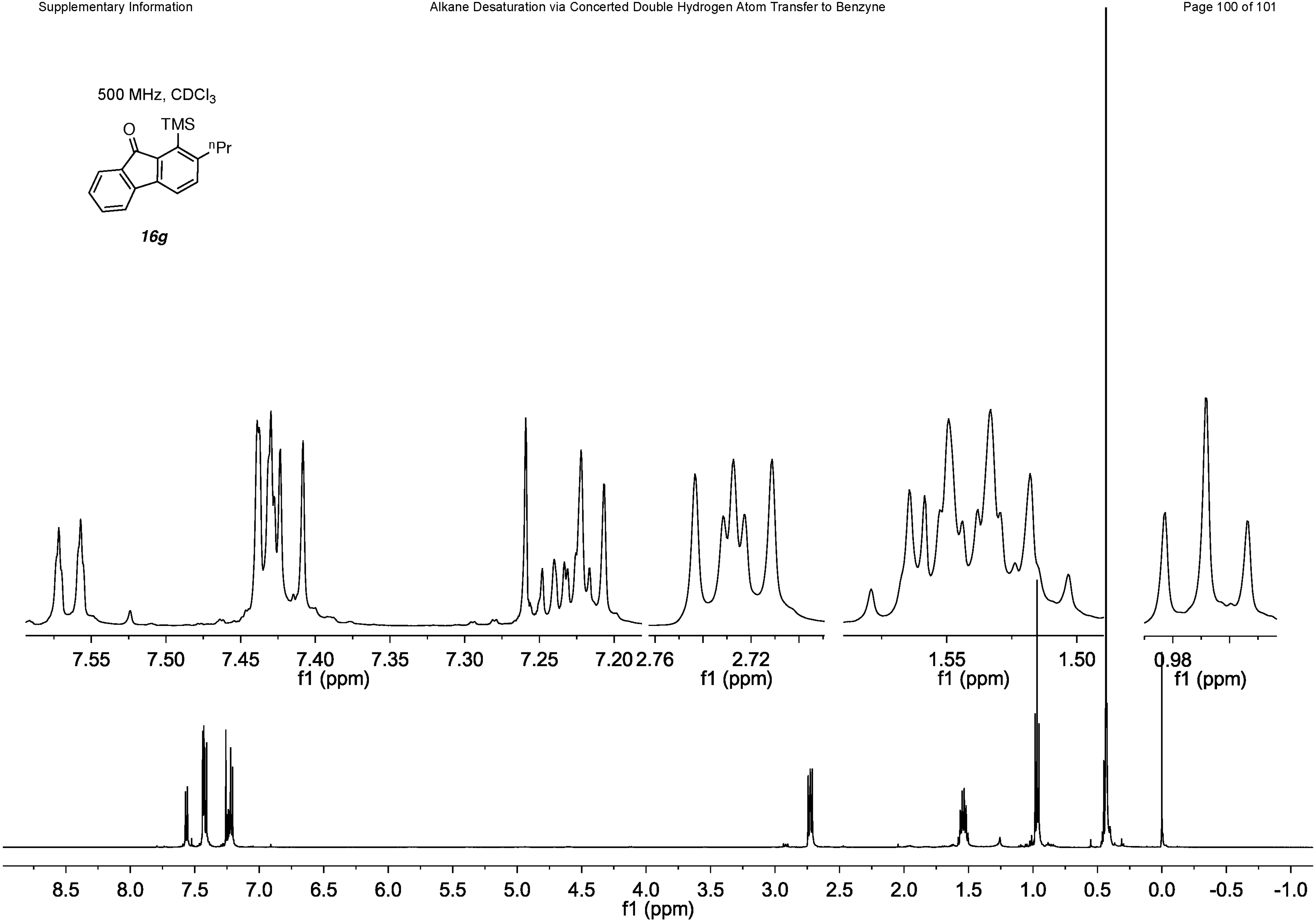

125 MHz, $CDCl_3$
HO
TMS
S13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

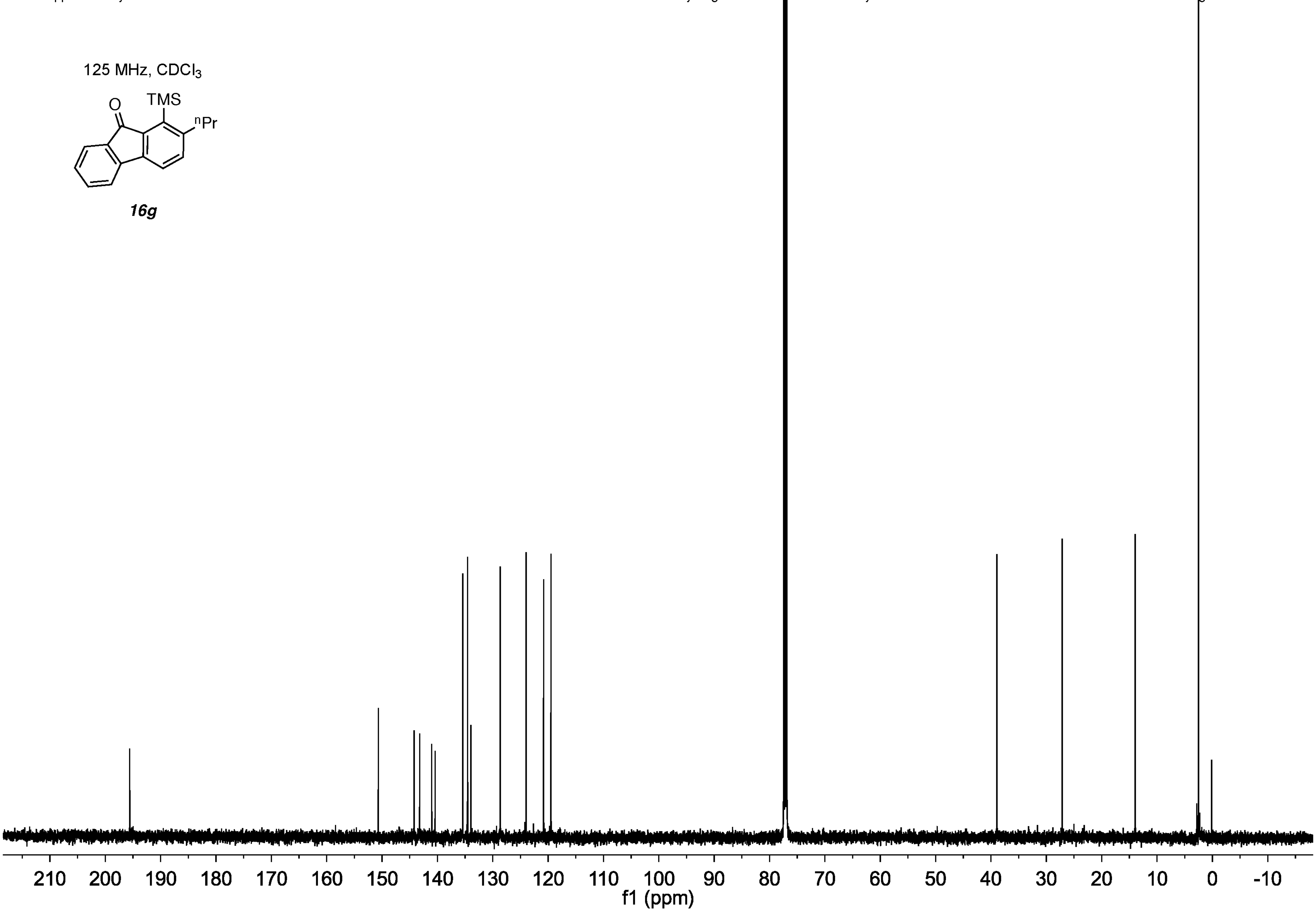
500 MHz, $CDCl_3$



S14


125 MHz, CDCl3
O
TMS
S14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


500 MHz, CDCl3
O
TMS
nPr
16g
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)
2.76
2.72
f1 (ppm)
1.55
1.50
f1 (ppm)
0.98
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


125 MHz, $CDCl_3$
O
TMS
^{n}Pr
16g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)