Supporting Information for

A One-pot, Three-Aryne Cascade Strategy for Naphthalene Formation from 1,3-Diynes and 1,2-Benzdiyne Equivalents

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I. General Experimental Protocols

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

Infrared spectra were measured for thin films (oils) or solids with a Bruker Alpha II FT-IR spectrometer in the ATR mode (diamond window).

Most of the high-resolution mass spectrometry (HRMS) measurements were made on a Bruker BioTOF II (ESI-TOF) instrument in electrospray ionization (ESI) mode. PEG was added to the sample to serve as an internal calibrant/standard. Samples were dissolved in MeOH. A few HRMS were collected on a Thermo Orbitrap Velos (with mass accuracy < 3 ppm) in the positive APCI mode against an external standard (Pierce™ LTQ). Samples were injected directly as dilute methanolic solutions (concentration less than 10^{-6} M). The one low resolution measurement was made with an Advion Expression CMS instrument using APCI.

MPLC refers to medium pressure liquid chromatography, performed at ca. 50–100 psi, using columns packed with RediSep Rf Gold® Normal-Phase Silica (20–40 μm, 60 Å pore size, Teledyne/ISCO). Elution solvent was delivered with a Waters HPLC pump; a differential refractive index detector (Waters R401) was used to detect the eluted solutes. Flash chromatography was performed with columns packed with Agela silica gel (40–63 μm). Thin layer chromatography was carried out on plastic-backed silica gel plates; TLC visualization was done by potassium permanganate or ceric ammonium molybdate staining and/or by UV detection.

Anhydrous reaction conditions were achieved under an atmosphere of nitrogen in flame-dried or oven-dried glassware. Commercial chlorobenzene was dried over CaH_2, distilled under reduced pressure, and stored over 4Å molecular sieves. Commercial 18-crown-6 was recrystallized in anhydrous acetonitrile, dried *in vacuo*, and stored under inert atmosphere.[3] The reaction temperatures reported are the temperature of the silicone oil of an external heating bath. Reactions 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 sealed with an inert, Teflon®-lined screw cap.

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

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

"CuCl (0.10 equiv relative to the terminal alkyne substrate) was dissolved in a 30:70 (v:v) mixture of $^{n}BuNH_2$:H_2O (5.0 mL/mmol relative to the terminal alkyne substrate). An excess of NH_2OH•HCl (ca. 10 mg per mmol of the terminal alkyne substrate) was added with stirring. The color of this solution changed from deep blue to colorless immediately, indicating full conversion of any Cu(II) to Cu(I). The headspace of the reaction vessel was flushed with N_2. The flask was closed with a septum, a balloon of nitrogen gas was attached, and the flask was cooled in an ice water bath. The terminal alkyne (1.0 equiv) in CH_2Cl_2 (ca. 2.5 mL/mmol) was injected into the flask, resulting in a yellow, orange, or red suspension, indicative of formation of an alkynyl copper species. After ca. 5 min, a solution of the 1-bromoalkyne (1.2–1.5 equiv) in CH_2Cl_2 (ca. 2.5 mL/mmol) was injected dropwise over ca. 15 min using a syringe pump. This reaction mixture was stirred at the indicated temperature (0 ºC or rt). The suspension of the alkynyl copper would typically turn to a clear, two-layer mixture over the course of 10–100 min, indicating consumption of the alkynyl copper species. The reaction mixture was quenched by the addition of satd. aq. NH_4Cl and then extracted with CH_2Cl_2. The combined extracts were dried, filtered, and concentrated. The residue was purified by flash chromatography on silica gel."[4]

B. General procedure for bromination of terminal or TMS-alkyne

"To a stirred solution of terminal alkyne or TMS-protected terminal alkyne (1.0 equiv) and *N*-bromosuccinimide (NBS, 1.1 equiv) in acetone (0.10 M), powdered $AgNO_3$ (0.10 equiv) was added. After being stirred at room temperature for 1–2 hours (TLC monitoring), an equal volume of hexanes was added to the suspension, and the solid succinimide was removed by filtration through Celite®. Following solvent removal from the filtrate, the crude material was purified by flash chromatography."[4]

C. General procedure for aryne reactions using precursor 4-Ts.

Anhydrous potassium carbonate, 18-crown-6, Kobayashi benzyne precursor **4-Ts**, and the diyne trapping agent were added to an oven-dried, threaded glass vial. The indicated anhydrous solvent (chlorobenzene in most cases) was added to achieve an initial poly-yne concentration of 0.020 M. The headspace of the vial was purged with a gentle flow of N_2 gas, and the vial was sealed with a Teflon-lined cap. The reaction solution was stirred in a heated oil bath held at the indicated temperature. After the poly-yne or benzyne precursor **4-Ts** had been consumed (TLC and direct MS analysis, typically ca. 5 hours), the vial was cooled to room temperature. The suspension was filtered through a short pad of silica (washing with hexanes/EtOAc), and the filtrate was concentrated *in vacuo*. The residue was directly subjected to MPLC for purification, using the indicated elution solvent.

D. General procedure for aryne reactions using precursor 4-Tf.

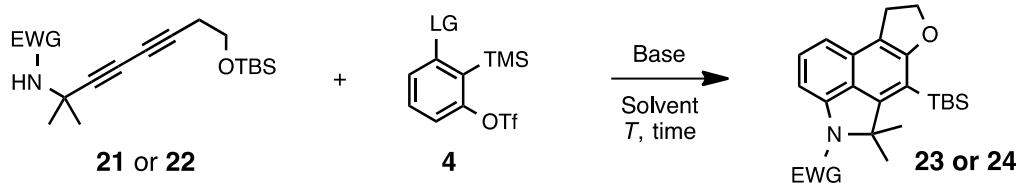
Anhydrous potassium carbonate, 18-crown-6, and the poly-yne trapping agent were added to an oven-dried, threaded glass vial. The indicated anhydrous solvent (chlorobenzene in most cases) was added to achieve an initial poly-yne concentration of 0.020 M. The headspace of the vial was purged with a gentle flow of N_2 gas, and the vial was sealed with a Teflon-lined cap. The reaction solution was stirred in a heated oil bath held at the indicated temperature for 10–15 min. The Kobayashi benzyne precursor **4-Tf** was then added to the solution. After the poly-yne or benzyne precursor **4-Tf** had been consumed (TLC and direct MS analysis, typically ca. 2 hours), the vial was cooled to room temperature. The suspension was filtered through a short pad of silica (washing with hexanes/EtOAc), and the filtrate was concentrated *in vacuo*. The residue was directly subjected to MPLC for purification, using the indicated elution solvent.

• Reaction optimization

For experimental details, see general procedures C and D. Reactions in the Table S1 were quenched when one of **21/22** or **4** was fully consumed, as indicated by direct mass spec analysis of aliquots.

We also examined CsF with substrates lacking a silyl ether. However, under the best of circumstances, the cascade reaction still only proceeded with lower efficiency (analysis of the crude NMR spectra suggested, at best, yields of ≤30–40%). Similar observations have been reported by Li *et al.* (ref 5e in the manuscript). We also examined CsF at lower temperatures (even at rt) with the substrate TsNHCH2C≡CC≡CCH$_2$CH$_2$CH$_2$Ph and observed its decomposition even under conditions where the 1,2-benzdiyne synthon was largely intact.

Table S1. Optimization



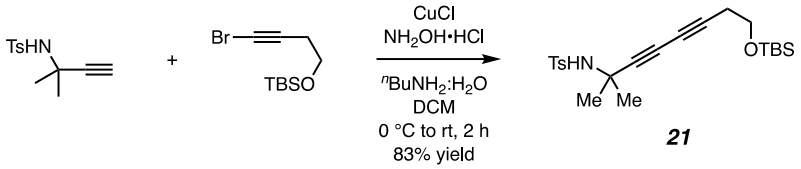
21 or **22** **4** **23 or 24**

EWG	LG	Base	Solvent	*T* (°C)	NMR Yield[a] of **23/24**	Conv. of **21/22**
Ts	OTs	K_2CO_3 + 18-c-6	PhCl	130, 5 h	50%	100%
Ts	OTs	Cs_2CO_3 + 18-c-6	PhCl	130, 5 h	37%	100%
Ts	OTs	CsF + Cs_2CO_3	MeCN	80, 15 h	20%[b]	100%
Ts	OTs	K_2CO_3 + 18-c-6	PhCl	80, 24 h	29%	100%
Ts	OTs	K_2CO_3 + 18-c-6	MeCN	100, 5 h	42%	100%
Ts	OTs	K_2CO_3 + 18-c-6	PhMe	100, 15 h	40%	100%
Ts	**OTf**	K_2CO_3 + 18-c-6	PhCl	130, 2 h	**27%**[c]	**32%**[c]
Tf	OTs	K_2CO_3 + 18-c-6	PhCl	130, 5 h	**76%**[c]	100%
Tf	**OTf**	K_2CO_3 + 18-c-6	PhCl	130, 2 h	**72%**[c]	100%

Reaction conditions: **21/22** (0.050 mmol), **4** (0.10 mmol), Base (0.40 mmol), 18-c-6 (0.10 mmol), and solvent (2.5 mL). [a] Yields were determined by crude ^{1}H NMR analysis using *p*-nitrotoluene as an internal standard unless otherwise noted. [b] Yield of desilylated analog of **23**. [c] Isolated yields after column chromatography on silica gel.

• Experimental details and characterization data

N-(8-((*tert*-Butyldimethylsilyl)oxy)-2-methylocta-3,5-diyn-2-yl)-4-methylbenzenesulfonamide (21)



Following general procedure A, 4-methyl-*N*-(2-methylbut-3-yn-2-yl)benzenesulfonamide[5] (0.24 g, 1.0 mmol), [(4-bromobut-3-yn-1-yl)oxy](*tert*-butyl)dimethylsilane[6] (0.31 g, 1.2 mmol), CuCl (5.0 mg), $^{n}BuNH_2$:H_2O (5.0 mL), and DCM (5.0 mL) were used to prepare diyne **21**. Purification of the crude material by flash chromatography (hexanes:EtOAc, 6:1) provided diyne **21** (0.35 g, 0.83 mmol, 83%) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (nfod, *J* = 7.8 Hz, 2H, SO_2ArH_o), 7.30 (nfod, *J* = 8.0 Hz, 2H, SO_2ArH_m), 4.77 (br s, 1H, N*H*), 3.70 (t, *J* = 7.2 Hz, 2H, OCH_2), 2.45 (t, *J* = 7.2 Hz, 2H, $\equiv CCH_2$), 2.42 (s, 3H, $ArCH_3$), 1.53 [s, 6H, $C(CH_3)_2$], 0.90 [s, 9H, $SiC(CH_3)_3$], and 0.07 [s, 6H, $Si(CH_3)_2$].

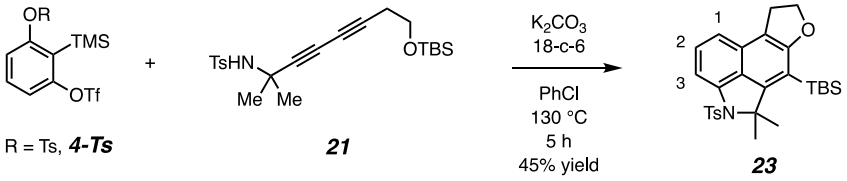
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.5, 138.3, 129.6, 127.8, 78.6, 76.9, 68.4, 65.4, 61.5, 50.5, 30.7, 26.0, 23.8, 21.7, 18.4, and -5.2.

IR (neat): 3259, 2929, 2857, 2251, 1599, 1383, 1327, 1366, 1145, 1093, 995, 837, and 812 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{22}H_{33}NNaO_3SSi^+$ [M+Na^+] requires 442.1843; found 442.1843.

m.p. 76–78 °C.

6-(*tert*-Butyldimethylsilyl)-5,5-dimethyl-4-tosyl-4,5,8,9-tetrahydrobenzofuro[6,5,4-cd]indole (23)



Following general procedure C, diyne **21** (21 mg, 0.050 mmol), benzyne precursor **4-Ts**[7] (47 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare naphthalene **23**. Purification of the crude material by MPLC (hexanes:EtOAc, 15:1) provided the naphthalene derivative **23** (11 mg, 0.022 mmol, 45%) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (nfod, *J* = 8.3 Hz, 2H, SO_2ArH_o), 7.40 (dd, *J* = 8.0, 8.0 Hz, 1H, *H2*), 7.21 (nfod, *J* = 8.1 Hz, 2H, SO_2ArH_m), 7.20 (d, *J* = 7.8 Hz, 1H, *H3*), 7.02 (d, *J* = 8.2 Hz, 1H, *H1*), 4.60 (t, *J* = 8.9 Hz, 2H, OCH_2), 3.31 (t, *J* = 9.0 Hz, 2H, $ArCH_2$), 2.35 (s, 3H, $ArCH_3$), 1.98 [s, 6H, $C(CH_3)_2$], 0.90 [s, 9H, $SiC(CH_3)_3$], and 0.50 [s, 6H, $Si(CH_3)_2$].

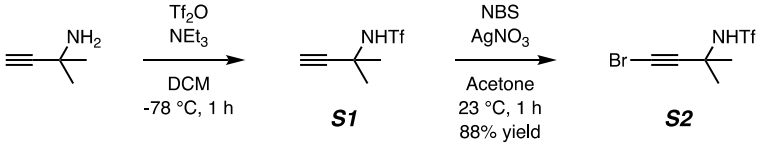
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 154.2, 143.8, 142.0, 139.1, 130.4, 129.64, 129.63, 127.0, 122.6, 115.3, 113.4, 112.0, 103.4, 76.8, 70.6, 30.0, 28.7, 27.8, 21.6, 18.8, and 1.2.

IR (neat): 2953, 2886, 2856, 1624, 1600, 1555, 1353, 1258, 1165, 1121, 1091, 983, 839, and 810 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{28}H_{35}NNaO_3SSi^+$ [M+Na^+] requires 516.1999; found 516.1987.

m.p. 198–202 °C.

***N*-(4-Bromo-2-methylbut-3-yn-2-yl)-1,1,1-trifluoromethanesulfonamide (S2)**



To a stirred solution of 2-methylbut-3-yn-2-amine (0.42 g, 5.0 mmol) and triethylamine (0.7 mL, 5.0 mmol) in DCM (20 mL) was added triflic anhydride (0.89 mL, 5.3 mmol) slowly at –78 °C under inert atmosphere. After 1 hour, the crude reaction mixture was quenched with water and extracted with EtOAc. The combined organic phase was dried and concentrated in an ambient temperature water bath under reduced pressure. The residue was directly used in further transformations without additional purification. This crude sample of sulfonamide **S1** was an 80 wt% mixture with EtOAc, as determined by ^{1}H NMR analysis.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.02 (br s, 1H, N*H*), 2.51 (s, 1H, ≡C*H*), and 1.71 [s, 6H, $C(CH_3)_2$].

Bromoalkyne **S2** was synthesized from sulfonamide **S1** (1.3 g, 80 wt% solution, 5.0 mmol), *N*-bromo succinimide (0.98 g, 5.5 mmol), silver nitrate (85 mg, 0.5 mmol), and acetone (50 mL) following general procedure B. Purification of the crude material using flash column chromatography (6:1 hexanes/EtOAc) afforded bromoalkyne **S2** (1.34 g, 4.5 mmol, 91%, containing 3 wt% EtOAc as indicated by ^{1}H NMR analysis, 88% corrected yield) as a pale-yellow oil, which crystallizes upon freezing.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (br s, 1H, N*H*) and 1.69 [s, 6H, $C(CH_3)_2$].

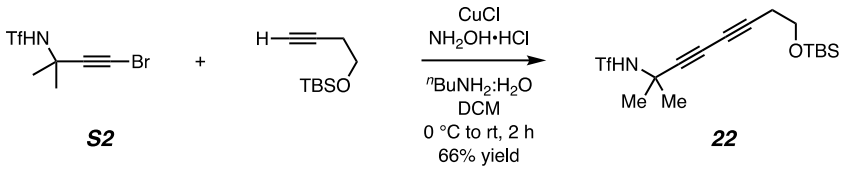
^{13}C NMR (126 MHz, $CDCl_3$) δ 119.2 (q, *J* = 322 Hz), 80.7, 54.0, 45.4, and 30.7.

IR (neat): 3288, 2992, 2225, 1710, 1429, 1361, 1189, 1134, 996, 878, and 792 cm^{-1}.

HRMS measurements of **S2** were not successful. HRMS using ESI or APCI conditions gave only unidentifiable fragments. The thermal instability of this compound renders it unstable to GC-

HRMS conditions. We suggest that all of the products of its subsequent derivatization serve as a means of further characterization of this relatively simple compound.

_N_-(8-((*tert*-Butyldimethylsilyl)oxy)-2-methylocta-3,5-diyn-2-yl)-1,1,1-trifluoromethanesulfonamide (22)



S2 ***22***

Following general procedure A, bromoalkyne **S2** (1.5 g, 5.0 mmol), (but-3-yn-1-yloxy)(*tert*-butyl)dimethylsilane (0.74 g, 4.0 mmol), CuCl (40 mg), ^{n}BuNH$_2$:H$_2$O (20 mL), and DCM (20 mL) were used to prepare diyne **22**. Purification of the crude material by flash chromatography (hexanes:EtOAc, 9:1) provided diyne **22** (1.0 g, 2.5 mmol, 66%) as a clear oil.

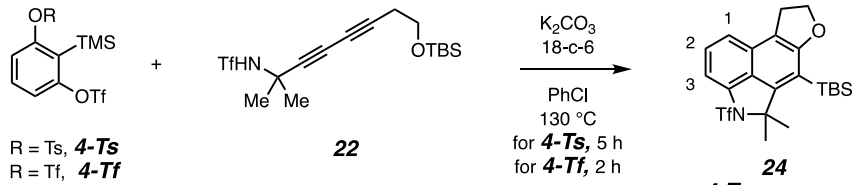
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.74 (t, *J* = 7.0 Hz, 2H, OC*H*$_2$), 2.50 (t, *J* = 7.0 Hz, 2H, ≡CC*H*$_2$), 1.69 [s, 6H, C(C*H*$_3$)$_2$], 0.90 [s, 9H, SiC(C*H*$_3$)$_3$], and 0.07 [s, 6H, Si(C*H*$_3$)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 119.2 (q, *J* = 321 Hz), 80.0, 75.9, 69.0, 65.1, 61.3, 53.6, 30.7, 26.0, 23.8, 18.4, and -5.2.

IR (neat): 3287, 2931, 2859, 2259, 1472, 1429, 1364, 1230, 1195, 1137, 1055, 998, 836, and 778 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{16}H_{26}F_3NNaO_3SSi^+$ [M+Na$^+$] requires 420.1247; found 420.1260.

(±)-6-(*tert*-Butyldimethylsilyl)-5,5-dimethyl-4-((trifluoromethyl)sulfonyl)-4,5,8,9-tetrahydrobenzofuro[6,5,4-cd]indole (24)



R = Ts, ***4-Ts***
R = Tf, ***4-Tf***

22

for ***4-Ts,*** 5 h
for ***4-Tf,*** 2 h

24
4-Ts, 76% yield
4-Tf, 72% yield

Following general procedure C, diyne **22** (20 mg, 0.050 mmol), benzyne precursor **4-Ts**[7] (47 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare the naphthalene derivative **24**. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) gave **24** (18 mg, 0.038 mmol, 76%) as a white crystalline solid.

Alternatively, naphthalene **24** was synthesized from sulfonamide **22** (20 mg, 0.050 mmol), benzyne precursor **4-Tf**[8] (47 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) following general procedure D. Purification of the

crude material using flash column chromatography (hexanes/EtOAc, 20:1) afforded naphthalene **24** (17 mg, 0.036 mmol, 72%) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.9, 7.9 Hz, 1H, *H2*), 7.17 (d, *J* = 8.2 Hz, 1H, *H1*), 7.13 (d, *J* = 7.7 Hz, 1H, *H3*), 4.66 (dt, *J* = 9.9, 8.7 Hz, 1H, OCH_aH$_b$), 4.64 (dt, *J* = 9.9, 8.6 Hz, 1H, OCH$_a$$H_b$), 3.37 (dt, *J* = 15.0, 8.5 Hz, 1H, ArCH_aH$_b$), 3.36 (dt, *J* = 15.0, 8.3 Hz, 1H, ArCH$_a$$H_b$), 2.05 [q, *J* = 1.0 Hz, 3H, C(CH_3)$_a$], 2.03 [s, 3H, C(CH_3)$_b$], 0.93 [s, 9H, SiC(CH_3)$_3$], 0.54 [s, 3H, Si(CH_3)$_a$], and 0.50 [s, 3H, Si(CH_3)$_b$].

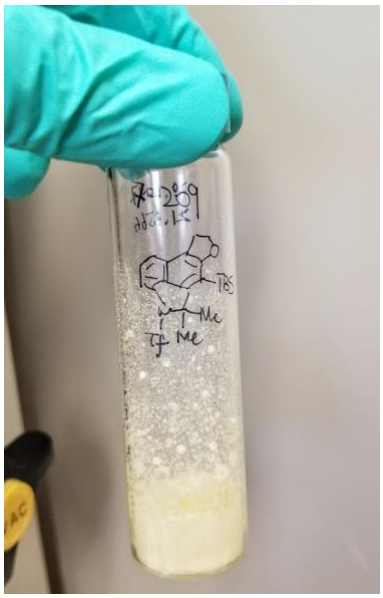
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 152.4, 139.5, 130.0, 129.6, 122.1, 120.2 (q, *J* = 326 Hz), 115.9, 115.6, 113.2, 104.9 (q, *J* = 1.3 Hz, C3), 79.8, 70.7, 31.8, 28.6, 27.8, 27.7 (q, *J* = 2.7 Hz), 18.8, 1.6, and 0.8.

IR (neat): 2932, 2897, 2858, 1627, 1600, 1399, 1382, 1258, 1223, 1141, 987, 839, and 810 cm^{-1}.

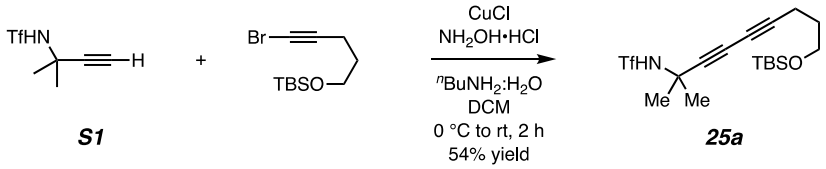
HRMS (ESI-TOF): Calcd for $C_{22}H_{28}F_3NNaO_3SSi^+$ [M+Na$^+$] requires 494.1403; found 494.1417.

m.p. 153–156 °C.

This reaction was also performed on a larger scale: Namely, benzyne precursor **4-Ts** (1.8 g, 3.8 mmol), potassium carbonate (2.1 g, 15 mmol), and 18-crown-6 (0.98 g, 3.8 mmol) were added into an oven-dried, 55 mL threaded culture tube. The headspace of the vessel was gently flushed with N_2 gas while diyne **22** (1.0 g, 2.5 mmol) in 50 mL of chlorobenzene was added. The culture tube was sealed with a Teflon-lined screw-cap and heated for 5 h at 130 °C in an oil bath. Both **4-Ts** and **22** were fully consumed after 5 h, as indicated by TLC and MS analysis. The reaction mixture was filtered through a short pad of silica gel, the filtrate was concentrated *in vacuo*, and the residue was directly subjected to flash column chromatography (hexanes:EtOAc, 40:1) to afford naphthalene derivative **24** (0.79 g, 1.7 mmol, 67%) as a pale-yellow crystalline solid (see photo at right).



***N*-(9-((*tert*-Butyldimethylsilyl)oxy)-2-methylnona-3,5-diyn-2-yl)-1,1,1-trifluoromethanesulfonamide (25a)**



S1 ***25a***

Following general procedure A, alkyne **S1** (0.13 g, 80 wt% solution, 0.48 mmol), [(5-bromopent-4-yn-1-yl)oxy](*tert*-butyl)dimethylsilane[9] (0.17 g, 0.61 mmol), CuCl (5.0 mg), ^{n}BuNH$_2$:H$_2$O (2.5

mL), and DCM (2.5 mL) were used to prepare diyne **25a**. Purification of the crude material by flash chromatography (hexanes:EtOAc, 10:1) provided diyne **25a** (0.11 g, 0.27 mmol, 54%) as a pale-yellow oil.

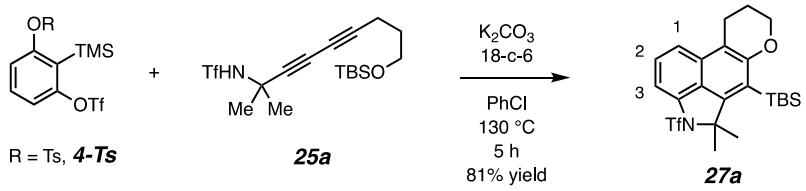
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.01 (br s, 1H, N*H*), 3.68 (t, *J* = 6.0 Hz, 2H, OCH_2), 2.38 (t, *J* = 7.1 Hz, 2H, ≡CCH_2), 1.73 (tt, *J* = 7.0, 6.0 Hz, 2H, $CH_2CH_2CH_2$), 1.70 [s, 6H, C(CH_3)$_2$], 0.89 [s, 9H, SiC(CH_3)$_3$], and 0.06 [s, 6H, Si(CH_3)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 119.2 (q, *J* = 323 Hz), 82.8, 75.6, 69.2, 64.1, 61.4, 53.7, 31.2, 30.7, 26.9, 18.4, 15.9, and -5.2.

IR (neat): 3288, 2930, 2858, 2257, 1428, 1387, 1364, 1229, 1193, 1136, 997, 834, and 776 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{17}H_{28}F_3NNaO_3SSi^+$ [M+Na$^+$] requires 434.1403; found 434.1419.

(±)-6-(*tert*-Butyldimethylsilyl)-5,5-dimethyl-4-((trifluoromethyl)sulfonyl)-5,8,9,10-tetrahydro-4H-chromeno[7,6,5-cd]indole (27a)



Following general procedure C, diyne **25a** (21 mg, 0.051 mmol), benzyne precursor **4-Ts**[7] (47 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare naphthalene **27a**. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) provided naphthalene **27a** (20 mg, 0.041 mmol, 81%) as a pale-yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.0, 8.0 Hz, 1H, *H2*), 7.33 (dd, *J* = 8.2 Hz, 1H, *H1*), 7.19 (d, *J* = 7.7 Hz, 1H, *H3*), 4.21 (dt, *J* = 10.6, 5.0 Hz, 1H, OCH_aH$_b$), 4.17 (dt, *J* = 10.7, 5.0 Hz, 1H, OCH$_a$$H_b$), 3.01 (dt, *J* = 16.8, 6.6 Hz, 1H, ArCH_aH$_b$), 3.00 (dt, *J* = 16.8, 6.6 Hz, 1H, ArCH$_a$$H_b$), 2.11 (tt, *J* = 6.3, 5.1 Hz, 2H, $CH_2CH_2CH_2$), 2.06 [q, *J* = 1.0 Hz, 3H, C(CH_3)$_a$], 2.04 [s, 3H, C(CH_3)$_b$], 0.95 [s, 9H, SiC(CH_3)$_3$], 0.51 [s, 3H, Si(CH_3)$_a$], and 0.46 [s, 3H, Si(CH_3)$_b$].

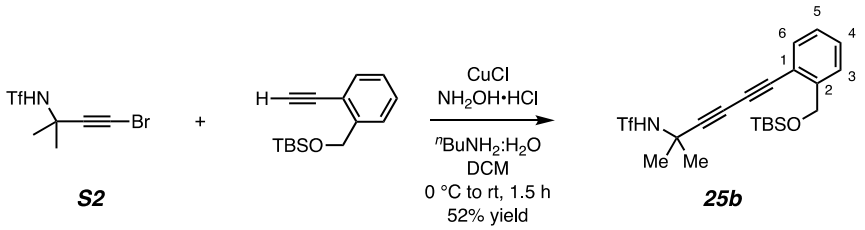
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 151.2, 139.2, 132.4, 129.6, 121.3, 120.5, 120.2 (q, *J* = 326 Hz), 115.0, 111.3, 105.6 (q, *J* = 1.4 Hz), 79.8, 65.7, 31.7, 29.3, 27.6 (q, *J* = 2.7 Hz), 21.6, 21.4, 18.8, 3.2, and 2.3.

IR (neat): 2998, 2934, 2853, 1604, 1556, 1400, 1309, 1254, 1199, 1143, 1100, 1000, and 809 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{23}H_{30}F_3NNaO_3SSi^+$ [M+Na$^+$] requires 508.1560; found 508.1554.

m.p. 154–160 °C.

_N_-(6-(2-(((*tert*-Butyldimethylsilyl)oxy)methyl)phenyl)-2-methylhexa-3,5-diyn-2-yl)-1,1,1-trifluoromethanesulfonamide (**25b**)



Following general procedure A, bromoalkyne **S2** (74 mg, 0.25 mmol), *tert*-butyl((2-ethynylbenzyl)oxy)dimethylsilane[10] (0.10 g, 0.30 mmol), CuCl (3.0 mg), ^{n}BuNH$_2$:H$_2$O (1.5 mL), and DCM (1.5 mL) were used to prepare diyne **25b**. Purification of the crude material by flash chromatography (hexanes:EtOAc, 8:1) provided diyne **25b** (60 mg, 0.13 mmol, 52%) as a pale-yellow oil.

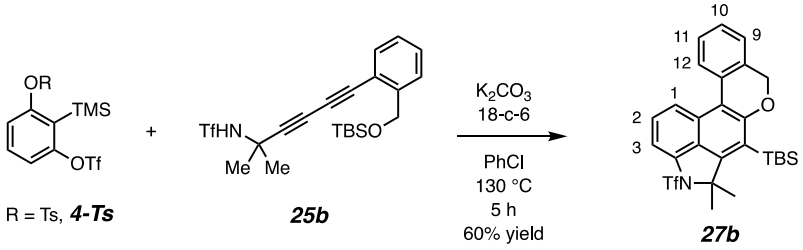
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.9 Hz, 1H, Ar*H6* or ArH3), 7.46 (dd, *J* = 7.9, 1.1 Hz, 1H, Ar*H3* or ArH6), 7.39 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H, Ar*H4* or ArH5), 7.21 (dd, *J* = 7.6, 7.6 Hz, 1H, Ar*H5* or ArH4), 5.10 (br s, 1H, N*H*), 4.86 (s, 2H, OC*H*$_2$), 1.77 [s, 6H, C(C*H*$_3$)$_2$], 0.96 [s, 9H, SiC(C*H*$_3$)$_3$], and 0.13 [s, 6H, Si(C*H*$_3$)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 145.2, 133.2, 129.9, 126.8, 126.3, 119.2 (q, *J* = 321 Hz), 118.1, 83.3, 77.4, 77.2, 68.7, 63.2, 53.8, 30.6, 26.1, 18.5, and -5.2.

IR (neat): 3288, 2955, 2931, 2858, 2240, 1429, 1365, 1256, 1198, 1139, 1084, 1000, 839, and 778 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{21}H_{28}F_3NNaO_3SSi^+$ [M+Na$^+$] requires 482.1403; found 482.1411.

(±)-6-(*tert*-Butyldimethylsilyl)-5,5-dimethyl-4-((trifluoromethyl)sulfonyl)-5,8-dihydro-4H-benzo[3,4]chromeno[7,6,5-cd]indole (27b)



Following general procedure C, diyne **25b** (20 mg, 0.044 mmol), benzyne precursor **4-Ts**[7] (47 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare the naphthalene derivative **27b**. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) provided **27b** (14 mg, 0.026 mmol, 60%) as a pale-yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 1H, *H1*), 8.03 (br d, *J* = 7.6 Hz, 1H, *H12*), 7.53 (dd, *J* = 7.9, 7.9 Hz, 1H, *H2*), 7.46 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, *H11*), 7.36 (ddd, *J* = 7.5, 7.5, 0.9 Hz, 1H, *H10*), 7.32 (d, *J* = 7.5, 1.0 Hz, 1H, *H9*), 7.29 (d, *J* = 7.7 Hz, 1H, *H3*), 4.98 (d, *J* = 12.2 Hz, 1H, OCH_aH_b), 4.94 (d, *J* = 12.2 Hz, 1H, OCH_aH_b), 2.11 [q, *J* = 1.0 Hz, 3H, $C(CH_3)_a$], 2.08 [s, 3H, $C(CH_3)_b$], 1.00 [s, 9H, $SiC(CH_3)_3$], 0.55 [s, 3H, $Si(CH_3)_a$], and 0.44 [s, 3H, $Si(CH_3)_b$].

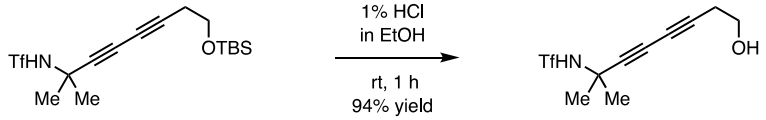
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0, 153.2, 139.5, 132.9, 130.3, 130.2, 129.4, 128.4, 127.4, 126.1, 124.9, 123.0, 120.2, 120.1 (q, *J* = 326 Hz), 117.6, 115.2, 106.4 (q, *J* = 1.3 Hz), 79.4, 68.9, 31.8, 29.4, 27.6 (q, *J* = 2.5 Hz), 18.8, 3.2, and 2.1.

IR (neat): 2996, 2933, 2857, 1621, 1577, 1462, 1401, 1382, 1255, 1225, 1203, 1144, 1022, 976, and 815 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{27}H_{31}F_3NO_3SSi^+$ [$M+H^+$] requires 534.1741; found 534.1751.

m.p. 192–196 °C.

1,1,1-Trifluoro-*N*-(8-hydroxy-2-methylocta-3,5-diyn-2-yl)methanesulfonamide (25c)



22 ***25c***

Diyne **22** (0.15 g, 0.38 mmol) was added to 4 mL of 1% aq HCl (37%) in EtOH and stirred at room temperature for 1 hour. The reaction was quenched with aqueous sodium bicarbonate solution and extracted with EtOAc. The combined organic phase was dried and concentrated. The residue was subjected to flash column chromatography (2:1 hexanes/EtOAc) to obtain alcohol **25c** (0.10 g, 0.35 mmol, 94%) as a clear oil.

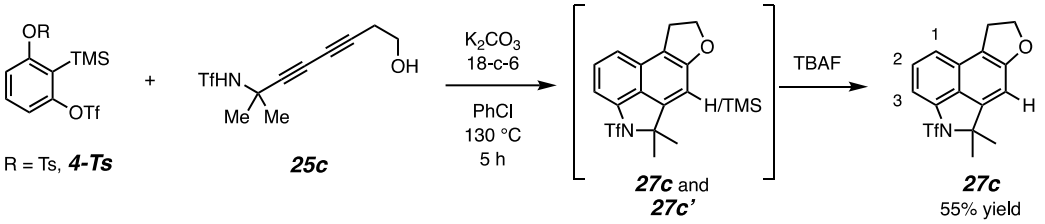
^{1}H NMR (500 MHz, $CDCl_3$): δ 3.77 (t, *J* = 6.2 Hz, 2H, OCH_2), 2.58 (t, *J* = 6.2 Hz, 2H, $\equiv CCH_2$), and 1.69 [s, 6H, $C(CH_3)_2$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 119.2 (q, *J* = 321 Hz), 79.2, 76.5, 68.6, 65.8, 60.7, 53.3, 30.6, and 23.7.

IR (neat): 3554, 3291, 2897, 2259, 1432, 1364, 1274, 1229, 1192, 1137, 1040, 1000, 845, and 633 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{10}H_{12}F_3NNaO_3S^+$ [$M+Na^+$] requires 306.0382; found 306.0388.

(±)-5,5-Dimethyl-4-((trifluoromethyl)sulfonyl)-4,5,8,9-tetrahydrobenzofuro[6,5,4-cd]indole (27c)



Preparation of the naphthalene derivative **27c** began with general procedure C from diyne **25c** (20 mg, 0.070 mmol), benzyne precursor **4-Ts**[7] (63 mg, 0.14 mmol), K_2CO_3 (75 mg, 0.54 mmol), 18-crown-6 (36 mg, 0.14 mmol), and chlorobenzene (3.0 mL). A mixture of **27c** and **27c'** was obtained as suggested by TLC and MS analysis. The crude reaction mixture was directly treated with TBAF (1M in THF, 0.1 mL) and stirred at ambient temperature for 5 min, which was quenched with addition of water. After extraction with EtOAc, the combined organic phase was dried and passed through a pad of silica gel. The filtrate was concentrated *in vacuo* and subjected to MPLC to provide **27c** (14 mg, 0.038 mmol, 55%) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.0, 8.0 Hz, 1H, *H2*), 7.24 (d, *J* = 8.3 Hz, 1H, *H1*), 7.14 (d, *J* = 7.6 Hz, 1H, *H3*), 6.78 (s, 1H, Ar*H*), 4.79 (t, *J* = 8.9 Hz, 2H, OCH_2), 3.43 (dt, *J* = 15.1, 9.0 Hz, 1H, ArCH_aH$_b$), 3.42 (dt, *J* = 15.4, 9.1 Hz, 1H, ArCH$_a$$H_b$), and 1.91 [br s, 6H, C(CH_3)$_2$].

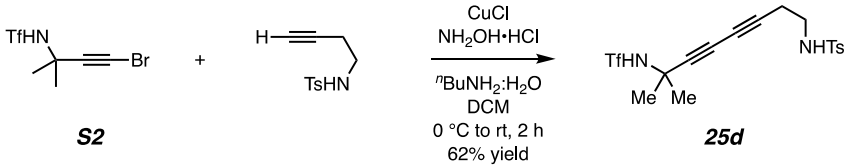
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 145.8, 140.0, 130.0, 128.9, 121.8, 120.1 (q, *J* = 326 Hz), 117.1, 116.3, 105.5 (q, *J* = 1.2 Hz), 102.3, 78.3, 72.6, 31.5, 28.0, and 27.1 (q, *J* = 2.7 Hz).

IR (neat): 3003, 2978, 2907, 1632, 1594, 1402, 1378, 1221, 1198, 1153, 1122, 994, and 762 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{16}H_{14}F_3NNaO_3S^+$ [M+Na$^+$] requires 380.0539; found 380.0552.

m.p. 126–128 °C.

4-Methyl-*N*-(7-methyl-7-((trifluoromethyl)sulfonamido)octa-3,5-diyn-1-yl)benzenesulfonamide (25d)



Following general procedure A, bromoalkyne **S2** (74 mg, 0.25 mmol), *N*-(but-3-yn-1-yl)-4-methylbenzenesulfonamide[11] (67 mg, 0.30 mmol), CuCl (3.0 mg), ^{n}BuNH$_2$:H$_2$O (1.5 mL), and DCM (1.5 mL) were used to prepare diyne **25d**. Purification of the crude material by flash chromatography (hexanes:EtOAc, 3:1) provided diyne **25d** (73 mg, 0.17 mmol, 67%, containing 2wt% EtOAc and 6 wt% hexanes as indicated by the ^{1}H NMR spectrum, 62% corrected yield) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (nfod, *J* = 8.2 Hz, 2H, SO_2ArH_o), 7.33 (nfod, *J* = 8.2 Hz, 2H, SO_2ArH_m), 5.24 (br s, 1H, TfN*H*), 5.24 (t, *J* = 6.5 Hz, 1H, TsN*H*), 3.13 (dt, *J* = 6.5, 6.5 Hz, 2H, TsNHCH_2), 2.47 (t, *J* = 6.6 Hz, 2H, ≡CCH_2), 2.44 (s, 3H, ArCH_3), and 1.70 [s, 6H, C(CH_3)$_2$].

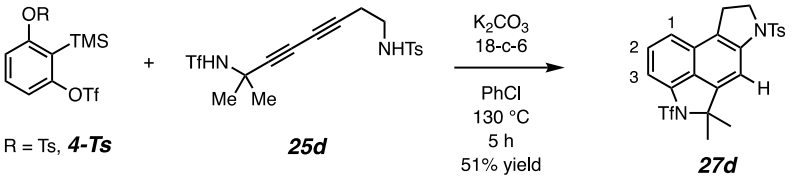
^{13}C NMR (126 MHz, $CDCl_3$): δ 144.0, 136.9, 130.0, 127.2, 119.2 (q, *J* = 320 Hz), 78.3, 77.0, 68.4, 66.5, 53.4, 41.4, 30.6, 21.7, and 21.1.

IR (neat): 3253, 2988, 2934, 2880, 2257, 1728, 1598, 1435, 1364, 1192, 1138, 1090, 998, and 814 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{17}H_{19}F_3N_2NaO_4S_2^+$ [M+Na^+] requires 459.0631; found 459.0630.

m.p. 119–120 °C.

(±)-5,5-Dimethyl-7-tosyl-4-((trifluoromethyl)sulfonyl)-5,7,8,9-tetrahydro-4H-indolo[6,5,4-cd]indole (27d)



Following general procedure C, diyne **25d** (20 mg, 0.046 mmol), benzyne precursor **4-Ts**[7] (47 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare the naphthalene derivative **27d**. Purification of the crude material by MPLC (hexanes:EtOAc, 6:1) provided **27d** (12 mg, 0.024 mmol, 51%) as a pale-yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H, Ar*H*), 7.64 (nfod, *J* = 8.4 Hz, 2H, SO_2ArH_o), 7.45 (dd, *J* = 7.9, 7.9 Hz, 1H, *H2*), 7.21 (nfod, *J* = 8.3 Hz, 2H, SO_2ArH_m), 7.20 (d, *J* = 7.5 Hz, 1H, *H3*), 7.18 (d, *J* = 8.2 Hz, 1H, *H1*), 4.133 (dt, *J* = 10.7, 8.9 Hz, 1H, TsNCH_aH$_b$), 4.129 (dt, *J* = 10.8, 8.8 Hz, 1H, TsNCH$_a$$H_b$), 3.12 (dt, *J* = 16.0, 8.6 Hz, 1H, ArCH_aH$_b$), 3.11 (dt, *J* = 16.0, 8.6 Hz, 1H, ArCH$_a$$H_b$), 2.35 (s, 3H, ArC$H_3$), 1.973 [q, *J* = 1.0 Hz, 3H, C(CH_3)$_a$], and 1.968 [s, 3H, C(CH_3)$_b$].

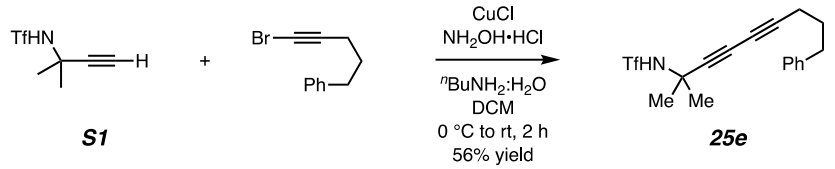
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 144.6, 142.7, 140.0, 133.8, 130.2, 129.9, 128.3, 127.4, 124.1, 123.5, 120.0 (q, *J* = 325 Hz), 116.6, 107.1 (q, *J* = 1.3 Hz), 106.2, 78.7, 51.0, 31.5, 27.1 (q, *J* = 2.4 Hz), 26.0, and 21.7.

IR (neat): 3006, 2933, 2861, 1735, 1632, 1596, 1402, 1354, 1292, 1199, 1165, 1139, 1015, 814, and 763 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{23}H_{21}F_3N_2NaO_4S_2^+$ [M+Na^+] requires 533.0787; found 533.0789.

m.p. 183–188 °C.

1,1,1-Trifluoro-*N*-(2-methyl-9-phenylnona-3,5-diyn-2-yl)methanesulfonamide (**25e**)



S1 ***25e***

Following general procedure A, alkyne **S1** (0.13 g, 80 wt% solution, 0.48 mmol), (5-bromopent-4-yn-1-yl)benzene[12] (0.16 g, 0.72 mmol), CuCl (5.0 mg), ^{n}BuNH$_2$:H$_2$O (2.5 mL), and DCM (2.5 mL) were used to prepare diyne **25e**. Purification of the crude material by flash chromatography (hexanes:EtOAc, 20:1) provided diyne **25e** (0.10 g, 0.28 mmol, 56%) as a pale-yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31–7.26 (nfom, 2H, Ph*H*$_o$), 7.22–7.16 (m, 3H, Ph*H*$_{m+p}$), 5.12 (br s, 1H, N*H*), 2.72 (t, *J* = 7.5 Hz, 2H, PhC*H*$_2$), 2.29 (t, *J* = 7.1 Hz, 2H, ≡CC*H*$_2$), 1.86 (tt, *J* = 7.2, 7.2 Hz, 2H, CH$_2$C*H*$_2$CH$_2$), and 1.70 [s, 6H, C(C*H*$_3$)$_2$].

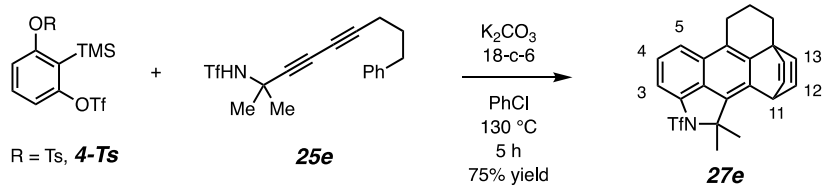
^{13}C NMR (126 MHz, $CDCl_3$): δ 141.2, 128.6, 128.6, 126.2, 119.2 (q, *J* = 321 Hz), 82.5, 75.8, 69.1, 64.6, 53.6, 34.8, 30.7, 29.7, and 18.8.

IR (neat): 3291, 2998, 2944, 2859, 2256, 1426, 1363, 1192, 1133, 994, 943, 871, and 732 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{17}H_{18}F_3NNaO_2S^+$ [M+Na$^+$] requires 380.0903; found 380.0916.

m.p. 43–45 °C.

(±)-1,1-Dimethyl-2-((trifluoromethyl)sulfonyl)-2,7,8,11-tetrahydro-1H,6H-8a,11-ethenophenaleno[1,2,3-cd]indole (27e)



R = Ts, ***4-Ts*** ***25e*** ***27e***

Following general procedure C, diyne **25e** (20 mg, 0.056 mmol), benzyne precursor **4-Ts**[7] (52 mg, 0.11 mmol), K_2CO_3 (62 mg, 0.45 mmol), 18-crown-6 (29 mg, 0.11 mmol), and chlorobenzene (2.5 mL) were used to prepare the naphthalene derivative **27e**. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) provided **27e** (18 mg, 0.042 mmol, 75%) as a pale-yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.3, 1.1 Hz, 1H, *H5*), 7.39 (dd, *J* = 8.2, 8.2 Hz, 1H, *H4*), 7.26 (d, *J* = 7.7 Hz, 1H, *H3*), 6.84 (dd, *J* = 8.7, 6.3 Hz, 1H, *H12*$_a$), 6.83 (dd, *J* = 8.7, 6.3 Hz, 1H, *H12*$_b$), 6.67 (dd, *J* = 6.8, 1.3 Hz, 1H, *H13*$_a$), 6.66 (dd, *J* = 7.0, 1.2 Hz, 1H, *H13*$_b$), 5.14 (dddd, *J* = 6.0, 6.0, 1.5, 1.5 Hz, 1H, *H11*), 2.98 (dt, *J* = 16.6, 6.0 Hz, 1H, ArC*H*$_a$H$_b$), 2.96 (dt, *J* = 16.4, 6.0 Hz, 1H, ArCH$_a$*H*$_b$), 2.54 (dt, *J* = 13.5, 5.4 Hz, 1H, CC*H*$_a$H$_b$), 2.53 (dt, *J* = 13.5, 5.3 Hz, 1H,

CCH_aH_b), 2.08 [q, J = 1.0 Hz, 3H, $C(CH_3)_a$], 2.07–2.01 (m, 2H, $CH_2CH_2CH_2$), and 2.04 [s, 3H, $C(CH_3)_b$].

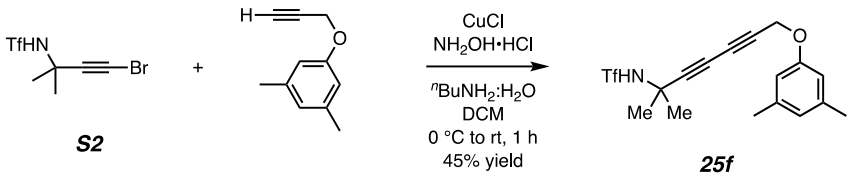
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4 (x2), 144.4, 139.0, 138.40, 138.38, 135.4, 132.2, 128.1, 127.7, 127.1, 123.2, 120.1 (q, J = 328 Hz), 116.8, 108.2 (q, J = 1.3 Hz), 78.3, 51.3, 43.9, 31.7, 30.6, 26.5 (q, J = 2.6 Hz), 24.5, and 21.1.

IR (neat): 3000, 2932, 2860, 1609, 1502, 1444, 1402, 1255, 1220, 1144, 978, 957, and 849 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{23}H_{20}F_3NNaO_2S^+$ [M+Na$^+$] requires 454.1059; found 454.1045.

m.p. 186–190 °C.

N-(7-(3,5-Dimethylphenoxy)-2-methylhepta-3,5-diyn-2-yl)-1,1,1-trifluoromethanesulfonamide (25f)



Following general procedure A, bromoalkyne **S2** (0.78 g, 2.6 mmol), 1-ethynyl-2-methoxynaphthalene[13] (0.60 g, 3.8 mmol), CuCl (10 mg), ^{n}BuNH$_2$:H$_2$O (15 mL), and DCM (15 mL) were used to prepare diyne **25f**. Purification of the crude material by flash chromatography (hexanes:EtOAc, 6:1 to 3:1) provided diyne **25f** (0.44 g, 1.2 mmol, 45%) as a light brown oil.

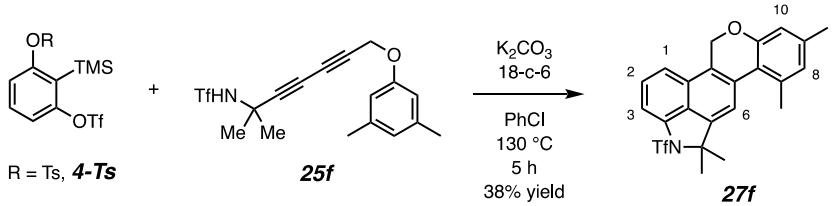
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.66 (s, 1H, ArH_p), 6.57 (s, 2H, ArH_o), 4.95 (br s, 1H, TfNH), 4.72 (s, 2H, OCH_2), 2.30 (s, 6H, ArCH_3), and 1.70 [s, 6H, $C(CH_3)_2$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 157.6, 139.5, 123.7, 119.2 (q, J = 321 Hz), 112.7, 79.6, 70.5, 68.1, 56.2, 53.4, 30.5, and 21.6.

IR (neat): 3299, 2992, 2918, 2859, 2256, 1614, 1594, 1430, 1362, 1293, 1197, 1150, 1062, 998, and 828 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{17}H_{18}F_3NNaO_3S^+$ [M+Na$^+$] requires 396.0852; found 396.0862.

(±)-5,5,7,9-Tetramethyl-4-((trifluoromethyl)sulfonyl)-5,12-dihydro-4H-benzo[3,4]isochromeno[6,7,8-cd]indole (27f)



Following general procedure C, diyne **25f** (19 mg, 0.051 mmol), benzyne precursor **4-Ts**[7] (47 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare the naphthalene derivative **27f**. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) provided **27f** (8.6 mg, 0.019 mmol, 38%) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.52 (m, 2H, *H1* and *H2*), 7.54 (s, 1H, *H6*), 7.35–7.30 (nfom, 1H, *H3*), 6.84 (s, 1H, *H8* or H10), 6.81 (s, 1H, H8 or *H10*), 5.35 (d, *J* = 13.0 Hz, 1H, OC*H*$_a$H$_b$), 5.30 (d, *J* = 13.0 Hz, 1H, OCH$_a$*H*$_b$), 2.69 (s, 3H, C7C*H*$_3$), 2.35 (s, 3H, C9C*H*$_3$), 1.98 [q, *J* = 1.0 Hz, 3H, C(C*H*$_3$)$_a$], and 1.97 [s, 3H, C(C*H*$_3$)$_b$].

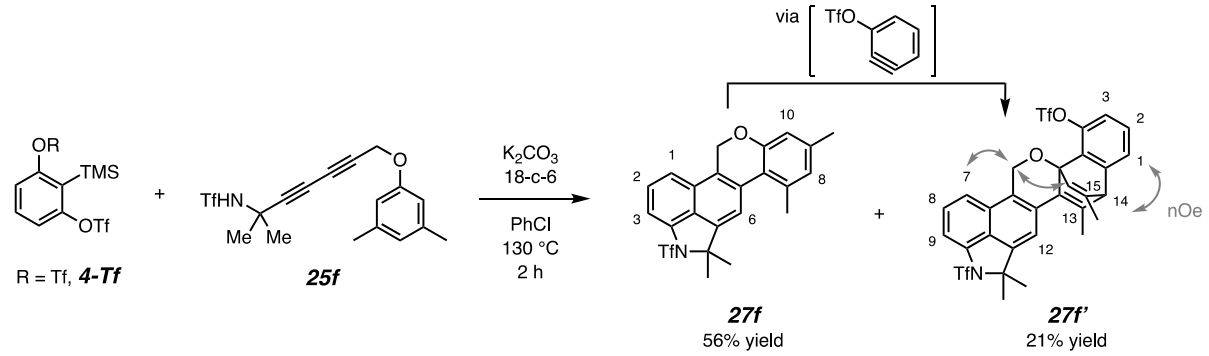
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 143.8, 139.8, 139.7, 135.0, 131.6, 129.8, 127.6, 127.0, 126.8, 124.8, 121.5, 120.1 (q, *J* = 325 Hz), 116.5, 115.5, 114.3, 108.1 (q, *J* = 1.2 Hz), 78.9, 64.9, 31.6, 27.2 (q, *J* = 2.5 Hz), 22.7, and 21.4.

IR (neat): 2976, 2926, 2853, 1614, 1453, 1386, 1223, 1200, 1141, 1029, and 843 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{23}H_{20}F_3NNaO_3S^+$ [M+Na$^+$] requires 470.1008; found 470.1015.

m.p. 199–203 °C.

27f and (±)-11,11,13,15-Tetramethyl-10-((trifluoromethyl)sulfonyl)-6,10,11,14-tetrahydro-4b,14-ethenonaphtho[1',2':3,4]isochromeno[6,7,8-cd]indol-4-yl Trifluoromethanesulfonate (27f')



Alternatively, naphthalene derivatives **27f** and **27f'** were prepared from benzyne precursor **4-Tf**[8] (45 mg, 0.10 mmol), diyne **25f** (18 mg, 0.048 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) following general procedure D. Purification of the crude material by MPLC (hexanes:EtOAc, 30:1 to 10:1) afforded, in the order of elution, **27f** (12.0 mg, 0.027 mmol, 56%) as a white crystalline solid and the naphthalene derivative **27f'** (6.7 mg, 0.010 mmol, 21%) as a yellow crystalline solid.

Data for 27f'

The regiochemistry is assigned primarily by the nOe correlation as indicated on the structure. This compound exists as a 1:1 pair of diastereoisomers in the NMR time scale because of slow

inversion of the nitrogen center. This is reflected in the four resonances of very similar intensity in the ^{19}F spectrum as well as the C6-methylene protons in the ^{1}H spectrum.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.4 Hz, 1H, *H7*), 7.53 (dd, *J* = 8.5, 7.4 Hz, 1H, *H8*), 7.31 (d, *J* = 7.4 Hz, 1H, *H9*), 7.23 (d, *J* = 7.2 Hz, 1H, *H1*), 7.11 (s, 1H, *H12*), 7.01 (dd, *J* = 8.2, 7.2 Hz, 1H, *H2*), 6.81 (d, *J* = 8.3 Hz, 1H, *H3*), 6.53 (dq, *J* = 1.8, 1.8 Hz, 1H, alkenyl-*H*), 5.40 (d, *J* = 14.4 Hz, 0.5H, diastereomer A, OCH_aH$_b$), 5.39 (d, *J* = 14.4 Hz, 0.5H, diastereomer B, OCH_aH$_b$), 5.33 (d, *J* = 14.4 Hz, 0.5H, diastereomer A, OCH$_a$$H_b$), 5.31 (d, *J* = 14.4 Hz, 0.5H, diastereomer B, OCH$_a$$H_b$), 4.36 (d, *J* = 1.8 Hz, 1H, *H14*), 2.38 (s, 3H, C13-CH_3), 1.98 (d, *J* = 1.7 Hz, 3H, C15-CH_3), 1.92 [q, *J* = 1.0 Hz, 3H, C(CH_3)$_a$], and 1.88 [s, 3H, C(CH_3)$_b$].

^{13}C NMR (126 MHz, $CDCl_3$) δ [148.95 (diastereomer A), 148.90 (diastereomer B)], 148.88, 143.5, [143.16 (A), 143.14 (B)], 139.7, [138.13 (A), 138.08 (B)], 134.1, 131.3, 130.3, 129.7, 129.4, 127.9, 126.0, 124.4, 121.6, 120.1 (q, *J* = 325 Hz), 119.0 (q, *J* = 319 Hz), 118.6, 117.7, 116.7, 114.2, 108.3, 87.9, 78.7, 62.8, [61.75 (A), 61.73 (B)], [31.7 (A), 31.5 (B)], [27.2 (q, *J* = 2.5 Hz, A), 27.1 (q, *J* = 2.6 Hz, B)], [20.10 (A), 20.07 (B)], and 19.6.

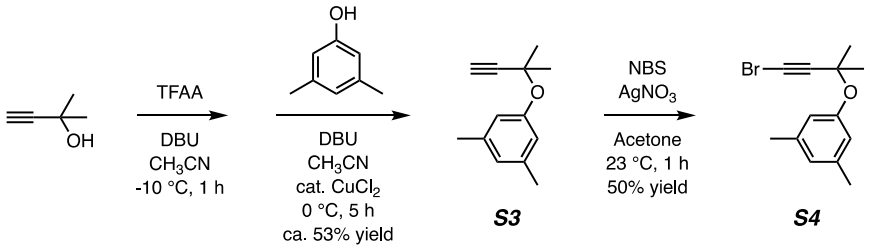
^{19}F NMR (471 MHz, $CDCl_3$) δ [-73.81 (A), -73.83 (B)], and [-74.29 (A), -74.30 (B)].

IR (neat): 2977, 2943, 2933, 1759, 1611, 1424, 1404, 1384, 1246, 1229, 1203, 1143, 1061, and 852 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{30}H_{23}F_6NNaO_6S_2^+$ [M+Na^+] requires 694.0763; found 694.0765.

m.p. 136–140 °C.

1-((4-Bromo-2-methylbut-3-yn-2-yl)oxy)-3,5-dimethylbenzene (S4)



Alkyne **S3** was synthesized following a reported procedure[14]: To a solution of 2-methylbut-3-yn-2-ol (1.3 g, 16 mmol) in anhydrous acetonitrile (25 mL) under nitrogen at ca. -10 °C was added DBU (2.9 mL, 20 mmol). Trifluoroacetic anhydride (2.1 mL, 15 mmol) was added over 15 min while carefully keeping the temperature below -10 °C. The resulting solution was stirred at 0 °C for 45 min before the addition of the trifluoroacetate ester to the solution of 3,5,-dimethylphenol as described below.

3,5-Dimethylphenol (1.6 g, 13 mmol) was dissolved in anhydrous acetonitrile (25 mL) under nitrogen and cooled to below -10 °C. DBU (2.9 mL, 20 mmol) and $CuCl_2$ (15 mg) were added. The above described trifluoroacetate solution was added to the 3,5-dimethylphenol solution over 20 min, while maintaining the temperature below 0 °C. After being stirred for 5 h at 0 °C, the

mixture was poured into 30 mL of saturated NH_4Cl aqueous solution. The mixture was extracted with EtOAc, dried, and concentrated. The residue was redissolved in hexanes/EtOAc (40:1) and passed through a short silica plug, eluting with additional hexanes/EtOAc (40:1). The filtrate was concentrated and the crude material (1.3 g, ca. 6.9 mmol, 53%) was used for the next step without further purification.

Bromoalkyne **S4** was prepared from crude **S3** (0.94 g, ca. 5.0 mmol), NBS (1.0 g, 5.5 mmol), $AgNO_3$ (70 mg, 0.5 mmol), and acetone (50 mL) following general procedure B. Purification of the crude mixture by flash column chromatography (hexanes:EtOAc, 50:1) afforded bromoalkyne **S4** (0.67 g, 2.5 mmol, 50%) as a clear oil.

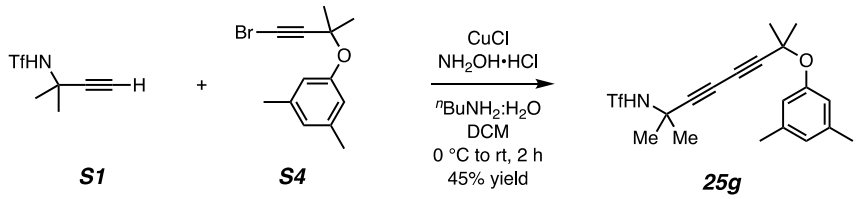
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (s, 2H, ArH_o), 6.71 (s, 1H, ArH_p), 2.29 (s, 6H, ArCH_3), and 1.60 [s, 6H, C(CH_3)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4, 138.7, 124.9, 119.5, 82.7, 73.4, 46.0, 29.6, and 21.5.

IR (neat): 2984, 2935, 2226, 1758, 1610, 1594, 1467, 1380, 1300, 1240, 1135, 1048, and 850 cm^{-1}.

LRMS (GCMS-EI, t_R = 6.95 min): Calcd for $C_{13}H_{15}{}^{79}BrO^+$ [M^+] requires 266.0301; found 266.1, and Calcd for $C_{13}H_{15}{}^{81}BrO^+$ [M^+] requires 268.0280, found 268.0. **HRMS** measurements were not successful.

N-(7-(3,5-Dimethylphenoxy)-2,7-dimethylocta-3,5-diyn-2-yl)-1,1,1-trifluoromethanesulfonamide (25g)



S1 ***S4*** ***25g***

Following general procedure A, alkyne **S1** (0.54 g, 80 wt% solution, 2.0 mmol), bromoalkyne **S4** (0.67 g, 2.5 mmol), CuCl (20 mg), ^{n}BuNH$_2$:H$_2$O (10 mL), and DCM (10 mL) were used to prepare diyne **25g**. Purification of the crude material by flash chromatography (hexanes:EtOAc, 10:1) provided the diyne **25g** (0.37 g, 0.92 mmol, 46%, containing 2 wt% EtOAc as suggested by its ^{1}H NMR spectrum, 45% corrected yield) as a yellowish oil.

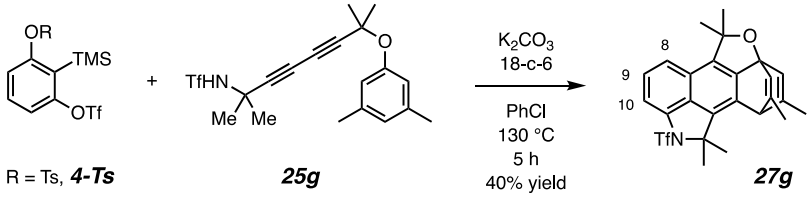
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78 (s, 2H, ArH_o), 6.72 (s, 1H, ArH_p), 5.10 (br s, 1H, TfN*H*), 2.29 (s, 6H, ArCH_3), 1.70 [s, 6H, C(CH_3)$_2$], and 1.62 [s, 6H, C(CH_3)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 155.2, 138.8, 125.1, 119.4, 119.2 (q, J = 321 Hz), 83.0, 80.0, 72.7, 69.2, 68.1, 53.5, 30.6, 29.4, and 21.5.

IR (neat): 3287, 2989, 2923, 2870, 2250, 1610, 1592, 1430, 1364, 1191, 1133, 995, and 860 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{22}F_3NNaO_3S^+$ [M+Na$^+$] requires 424.1165; found 424.1161.

(±)-1,1,4,6,6,11-Hexamethyl-7-((trifluoromethyl)sulfonyl)-6,7-dihydro-1H,5H-2a,5-ethenofuro[4',3',2':4,5]naphtho[1,2,3-cd]indole (27g)



Following general procedure C, diyne **25g** (23 mg, 0.057 mmol), benzyne precursor **4-Ts**[7] (54 mg, 0.12 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare the naphthalene derivative **27g**. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) provided **27g** (11 mg, 0.023 mmol, 40%) as a yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.1, 8.1 Hz, 1H, *H9*), 7.32 (d, *J* = 8.2 Hz, 1H, *H8*), 7.28 (d, *J* = 7.7 Hz, 1H, *H10*), 6.54 (dq, *J* = 1.5, 1.5 Hz, 2H, alkenyl-*H*), 4.42 (t, *J* = 1.6 Hz, 1H, bridgehead-*H*), 2.06 [br s, 3H, C(CH_3)$_a$], 2.03 [s, 3H, C(CH_3)$_b$], 1.91 [d, *J* = 1.6 Hz, 6H, alkenyl-CH_3], and 1.81 [br s, 6H, C(CH_3)$_2$].

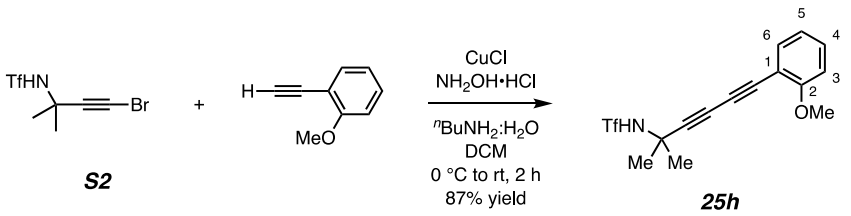
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 144.49, 144.46, 140.3, 137.60, 137.55, 135.9, 129.0, 128.3, 127.7, 125.9, 124.4, 120.1 (q, *J* = 326 Hz), 116.3, 108.0 (q, *J* = 1.4 Hz), 93.7, 92.8, 76.5, 55.5, 31.5, 29.27, 29.25, 27.2 (q, *J* = 2.5 Hz), 19.32, and 19.28 (all diastereotopic carbon signals are resolved).

IR (neat): 2971, 2931, 2857, 1758, 1605, 1461, 1408, 1384, 1252, 1201, 1148, 1056, and 967 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{25}H_{24}F_3NNaO_3S^+$ [M+Na^+] requires 498.1321; found 498.1325.

m.p. 88–92 °C.

1,1,1-Trifluoro-*N*-(6-(2-methoxyphenyl)-2-methylhexa-3,5-diyn-2-yl)methanesulfonamide (25h)



Following general procedure A, bromoalkyne **S2** (0.15 g, 0.50 mmol), 1-ethynyl-2-methoxybenzene (0.10 g, 0.76 mmol), CuCl (5.0 mg), ^{n}BuNH$_2$:H$_2$O (2.5 mL), and DCM (2.5 mL)

were used to prepare diyne **25h**. Purification of the crude material by flash chromatography (hexanes:EtOAc, 6:1) provided diyne **25h** (0.15 g, 0.44 mmol, 87%) as a yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 7.6, 1.7 Hz, 1H, *H6*), 7.34 (ddd, *J* = 8.4, 7.6, 1.7 Hz, 1H, *H4*), 6.91 (ddd, *J* = 7.6, 7.6, 0.9 Hz, 1H, *H5*), 6.88 (d, *J* = 8.5 Hz, 1H, *H3*), 5.14 (br s, 1H, TfN*H*), 3.89 (s, 3H, OCH_3), and 1.75 [s, 6H, C(CH_3)$_2$].

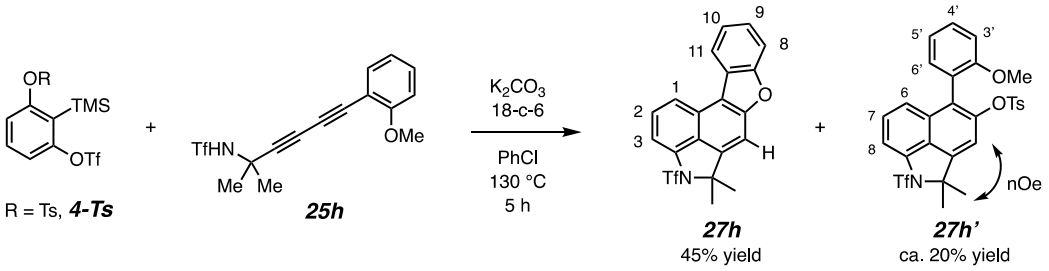
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.7, 134.7, 131.2, 120.7, 119.2 (q, *J* = 321 Hz), 110.8, 110.5, 82.9, 76.49 (q, *J* = 2.4 Hz), 76.45 (q, *J* = 1.3 Hz), 69.0, 56.0, 53.9, and 30.6.

IR (neat): 3290, 2992, 2943, 2840, 2239, 1595, 1493, 1434, 1364, 1279, 1198, 1138, 997, and 753 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{15}H_{14}F_3NNaO_3S^+$ [M+Na^+] requires 368.0539; found 368.0527.

m.p. 68–71 °C.

(±)-5,5-Dimethyl-4-((trifluoromethyl)sulfonyl)-4,5-dihydrobenzo[2,3]benzofuro[6,5,4-cd]indole (27h)



Following general procedure C, diyne **25h** (17 mg, 0.049 mmol), benzyne precursor **4-Ts**[7] (47 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare the naphthalene derivative **27h**. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1 to 6:1) provided, in the order of elution, **27h** (9.0 mg, 0.022 mmol, 45%) as a pale-yellow crystalline solid and **27h'** (5.8 mg, 20% yield) as a yellow amorphous solid.

Data for 27h

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 7.2, 1.7 Hz, 1H, *H11*), 8.12 (d, *J* = 8.3 Hz, 1H, *H1*), 7.72 (dd, *J* = 7.9, 7.9 Hz, 1H, *H2*), 7.69 (dd, *J* = 7.4, 1.2 Hz, 1H, *H8*), 7.52 (ddd, *J* = 7.3, 7.3, 1.5 Hz, 1H, *H9*), 7.48 (ddd, *J* = 7.3, 7.3, 1.2 Hz, 1H, *H10*), 7.46 (s, 1H, Ar*H*), 7.43 (d, *J* = 7.6 Hz, 1H, *H3*), 2.03 [q, *J* = 1.0 Hz, 3H, C(CH_3)$_a$], and 2.02 [s, 3H, C(CH_3)$_b$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 156.2, 145.0, 140.2, 130.6, 126.8, 126.4, 124.5, 123.6, 122.8, 121.8, 120.1 (q, *J* = 326 Hz), 117.4, 116.5, 112.0, 107.6 (q, *J* = 1.3 Hz), 103.2, 78.1, 31.8, and 27.3 (q, *J* = 2.6 Hz).

IR (neat): 3067, 3000, 2932, 1631, 1603, 1459, 1406, 1383, 1346, 1242, 1141, 1021, 998, and 744 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{20}H_{14}F_3NNaO_3S^+$ [M+Na^+] requires 428.0539; found 428.0538.

m.p. 147–150 °C.

(±)-5-(2-Methoxyphenyl)-2,2-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydrobenzo[cd]indol-4-yl 4-methylbenzenesulfonate (27h')

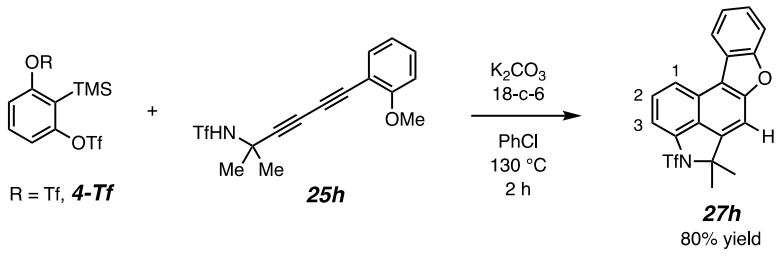
The assignment of constitution was made on the basis of nOe correlations as shown in the above scheme.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (nfod, *J* = 8.3 Hz, 2H, $SO_2Ar\mathit{H}_o$), 7.397 (dd, *J* = 7.5, 1.6 Hz, 1H, *H6'*), 7.393 (d, *J* = 7.9 Hz, 1H, *H8*), 7.34 (ddd, *J* = 8.6, 7.7, 1.5 Hz, 1H, *H4'*), 7.27 (nfod, *J* = 8.3 Hz, 2H, $SO_2Ar\mathit{H}_m$), 7.23 (dd, *J* = 8.2, 8.2 Hz, 1H, *H7*), 7.14 (d, *J* = 8.2 Hz, 1H, *H6*), 6.96 (dd, *J* = 7.5, 7.5 Hz, 1H, *H5'*), 6.90 (d, *J* = 8.5 Hz, 1H, *H3'*), 6.67 (s, 1H, Ar*H*), 3.89 (s, 3H, $OC\mathit{H}_3$), 2.39 (s, 3H, $ArC\mathit{H}_3$), 1.99 [br s, 3H, $C(C\mathit{H}_3)_a$], and 1.88 [s, 3H, $C(C\mathit{H}_3)_b$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 148.3, 146.2, 142.0, 132.9, 132.2, 130.8, 130.5, 129.8, 128.9, 120.7, 119.9 (q, *J* = 326 Hz), 119.8, 118.9, 113.3 (q, *J* = 1.3 Hz), 112.5, 110.8, 104.2, 98.5, 90.1, 76.8, 55.7, 27.1, 22.9 (q, *J* = 2.4 Hz), and 21.77 (one aromatic carbon resonance was not discernable).

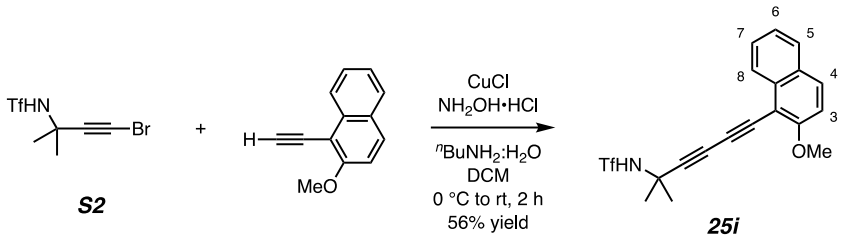
IR (neat): 3058, 2941, 2840, 1596, 1492, 1403, 1385, 1274, 1219, 1179, 1140, 1024, 837, and 776 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{28}H_{24}F_3NNaO_6S_2^+$ [M+Na^+] requires 614.0889; found 614.0902.



Alternatively, the naphthalene derivative **27h** was prepared from benzyne precursor **4-Tf**[8] (45 mg, 0.10 mmol), diyne **25h** (17 mg, 0.049 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) following general procedure D. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) afforded naphthalene **27h** (16 mg, 0.040 mmol, 80%) as a pale-yellow crystalline solid.

1,1,1-Trifluoro-*N*-(6-(2-methoxynaphthalen-1-yl)-2-methylhexa-3,5-diyn-2-yl)methanesulfonamide (25i)



Following general procedure A, bromoalkyne **S2** (0.15 g, 0.50 mmol), 1-ethynyl-2-methoxynaphthalene[15] (0.14 g, 0.75 mmol), CuCl (5.0 mg), $^{n}BuNH_2$:H_2O (2.5 mL), and DCM (2.5 mL) were used to prepare diyne **25i**. Purification of the crude material by flash chromatography (hexanes:EtOAc, 4:1) provided **25i** (0.11 g, 0.28 mmol, 56%) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (dd, *J* = 8.4, 1.1 Hz, 1H, *H8*), 7.86 (d, *J* = 9.1 Hz, 1H, *H4*), 7.78 (d, *J* = 8.2 Hz, 1H, *H5*), 7.56 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H, *H6* or H7), 7.39 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H, *H7* or H6), 7.23 (d, *J* = 9.1 Hz, 1H, *H3*), 5.12 (br s, 1H, TfN*H*), 4.03 (s, 3H, OCH_3), and 1.79 [s, 6H, C(CH_3)$_2$].

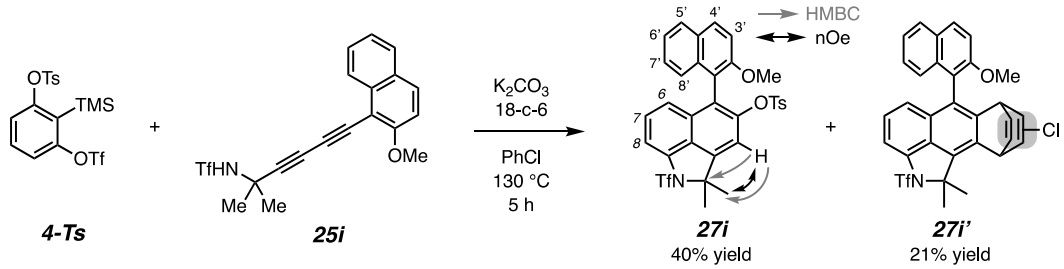
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.6, 135.4, 131.7, 128.5, 128.4, 128.1, 125.1, 124.7, 119.2 (q, *J* = 322 Hz), 112.4, 104.2, 84.1, 81.7, 75.0, 69.3, 56.7, 54.1, and 30.6.

IR (neat): 3291, 3065, 2990, 2944, 2844, 2229, 1621, 1590, 1510, 1431, 1363, 1271, 1196, 1068, 995, and 809 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{19}H_{16}F_3NNaO_3S^+$ [M+Na^+] requires 418.0695; found 418.0702.

m.p. 152–154 °C.

(±)-5-(2-Methoxynaphthalen-1-yl)-2,2-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2-dihydrobenzo[cd]indol-4-yl 4-methylbenzenesulfonate (27i)



Following general procedure C, diyne **25i** (20 mg, 0.051 mmol), benzyne precursor **4-Ts**[7] (47 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare binaphthol derivative **27i**. Purification of the crude material by MPLC (hexanes:EtOAc, 6:1) provided, in the order of elution, **27i'** (6.1 mg, a coeluting mixture

of regioisomers and diastereomeric atropisomers and NTf invertomers, 0.010 mmol, 21% yield) as a white amorphous solid and binaphthol derivative **27i** (13 mg, 0.021 mmol, 40%) as a yellow crystalline solid.

Data for 27i

The constitution was determined by nOe and HMBC correlations as shown in structure **27i**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.5, 1.2 Hz, 1H, *H8'*), 7.86 (d, *J* = 9.1 Hz, 1H, *H4'*), 7.81 (d, *J* = 8.1 Hz, 1H, *H5'*), 7.73 (nfod, *J* = 8.4 Hz, 2H, SO_2ArH_o), 7.61 (ddd, *J* =8.1, 6.7, 1.3 Hz, 1H, *H7'*), 7.424 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H, *H6'*), 7.418 (d, *J* = 8.2 Hz, 1H, *H8*), 7.29 (nfod, *J* = 8.2 Hz, 2H, SO_2ArH_m), 7.264 (d, *J* = 9.2 Hz, 1H, *H3'*), 7.258 (dd, *J* = 8.2, 8.2 Hz, 1H, *H7*), 7.19 (dd, *J* = 8.3, 0.8 Hz, 1H, *H6*), 6.79 (s, 1H, Ar*H*), 4.02 (s, 3H, OCH_3), 2.37 (s, 3H, $TsCH_3$), 2.08 [s, 3H, $C(CH_3)_a$], and 1.96 [s, 3H, $C(CH_3)_b$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 147.8, 146.2, 146.1, 142.0, 134.2, 132.3, 131.0, 130.8, 129.9, 128.9, 128.6, 128.4, 127.8, 125.2, 124.6, 119.9 (q, *J* = 326 Hz), 119.9, 119.1, 113.3 (q, *J* = 1.4 Hz), 112.4, 106.3, 104.2, 97.0, 95.4, 76.9, 56.4, 27.2, 22.9 (q, *J* = 2.4 Hz), and 21.8.

IR (neat): 2974, 2931, 2853, 1597, 1563, 1512, 1459, 1378, 1341, 1269, 1193, 1068, 1007, 880 and 775 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{32}H_{26}F_3NNaO_6S_2^+$ [M+Na^+] requires 664.1046; found 664.1029.

m.p. 242–244 °C.

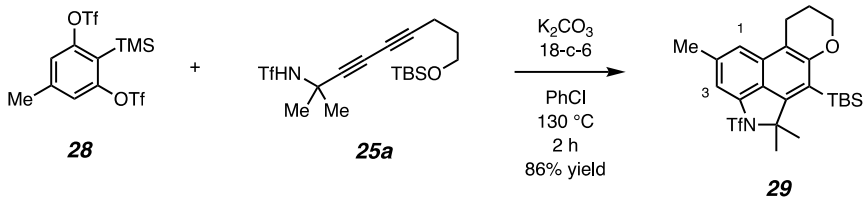
Data for 27i' (mixture of multiple regioisomers and atropisomers)

Due to the complexity of the spectral data, only partial characterization and peak assignments are listed.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06–8.01 (m, 1H, Ar*H*), 7.93–7.88 (m, 1H, Ar*H*), 7.51–7.45 (m, 1H, Ar*H*), 7.39–7.33 (m, 1H, Ar*H*), 7.31–7.26 (m, 1H, Ar*H*), 7.25–7.21 (m, 1H, Ar*H*), 7.21–7.13 (m, 1H, Ar*H*), 7.10–6.56 (m, 5H, Ar*H* and alkene-*H*), 6.39 (ddd, *J* = 2.3, 6.3, 6.3 Hz, 0.4H, alkene-*H*), 5.22 (m, 0.2H, bridgehead-*H*), 5.09 (ddd, *J* = 1.5, 2.3, 6.0 Hz, 0.4H, bridgehead-*H*), 4.51–4.45 (m, 0.8H, bridgehead-*Hs*), 4.40 (tt, *J* = 2.4, 2.4, 5.6 Hz, 0.3H, bridgehead-*H*), 3.81, 3.79, 3.78, 3.75 (four singlets, ca. 0.35H each, OCH_3), 3.80, 3.77 (two singlets, 0.6H each, OCH_3), 2.51 (q, *J* = 0.9 Hz, 0.45H, $CMeCH_3$), 2.50 (q, *J* = 0.9 Hz, 0.45H, $CMeCH_3$), 2.48 (s, 0.45H, $CMeCH_3$), 2.47 (s, 0.45H, $CMeCH_3$), 2.26 (q, *J* = 0.8 Hz, 0.8H, $CMeCH_3$), 2.24 (s, 0.8H, $CMeCH_3$), 2.19 (q, *J* = 0.9 Hz, 0.4H, $CMeCH_3$), 2.17 (q, *J* = 0.9 Hz, 0.3H, $CMeCH_3$), 2.16 (s, 0.5H, $CMeCH_3$), 2.15 (q, *J* = 0.9 Hz, 0.5H, $CMeCH_3$), 2.14 (s, 0.5H, $CMeCH_3$), and 2.13 (s, 1.0H, $CMeCH_3$).

LRMS (APCI$^+$): Calcd for $C_{32}H_{28}{}^{35}ClF_3NO_3S^+$ [M+H^+] requires 598.1425; found 598.1.

6-(*tert*-Butyldimethylsilyl)-2,5,5-trimethyl-4-((trifluoromethyl)sulfonyl)-5,8,9,10-tetrahydro-4H-chromeno[7,6,5-cd]indole (29)



Naphthalene derivative **29** was prepared from benzyne precursor **28**[8] (46 mg, 0.10 mmol), diyne **25a** (20 mg, 0.049 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) following general procedure D. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) afforded naphthalene **29** (21 mg, 0.042 mmol, 86%) as a pale-yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (s, 1H, *H1*), 7.04 (s, 1H, *H3*), 4.19 (dt, *J* = 10.5, 5.0 Hz, 1H, OC*H*$_a$H$_b$), 4.15 (dt, *J* = 10.5, 5.0 Hz, 1H, OCH$_a$*H*$_b$), 2.97 (ddd, *J* = 16.6, 6.5, 6.5 Hz, 1H, ArC*H*$_a$H$_b$), 2.96 (dd, *J* = 16.6, 6.5, 6.5 Hz, 1H, ArCH$_a$*H*$_b$), 2.51 (s, 3H, ArC*H*$_3$), 2.10 (br app pent, *J* = 6 Hz, 2H, CH$_2$C*H*$_2$CH$_2$), 2.05 [s, 3H, C(C*H*$_3$)$_a$], 2.02 [s, 3H, C(C*H*$_3$)$_b$], 0.94 [s, 9H, SiC(C*H*$_3$)$_3$], 0.50 [s, 3H, Si(C*H*$_3$)$_a$], and 0.44 [s, 3H, Si(C*H*$_3$)$_b$].

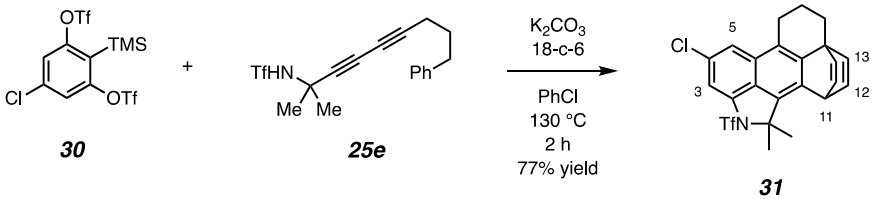
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 150.9, 140.3, 139.2, 132.3, 120.2 (q, *J* = 328 Hz), 119.9, 119.0, 114.4, 110.8, 107.5 (q, *J* = 1.4 Hz), 80.2, 65.7, 31.7, 29.3, 27.6 (q, *J* = 2.5 Hz), 23.1, 21.7, 21.4, 18.8, 3.2, and 2.3.

IR (neat): 2934, 2894, 2858, 1758, 1626, 1607, 1558, 1400, 1370, 1249, 1199, 1141, 1071, 1017, and 823 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{24}H_{32}F_3NNaO_3SSi^+$ [M+Na$^+$] requires 522.1716; found 522.1722.

m.p. 180–182 °C.

4-Chloro-1,1-dimethyl-2-((trifluoromethyl)sulfonyl)-2,7,8,11-tetrahydro-1H,6H-8a,11-ethenophenaleno[1,2,3-cd]indole (31)



Naphthalene derivatives **31** was prepared from benzyne precursor **30**[8] (48 mg, 0.10 mmol), diyne **25e** (18 mg, 0.050 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) following general procedure D. Purification of the crude material by

MPLC (hexanes:EtOAc, 20:1) afforded **31** (18 mg, 0.039 mmol, 77%) as a pale-yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 1.2 Hz, 1H, *H5*), 7.26 (s, 1H, *H3*), 6.84 (dd, *J* = 6.5, 6.5 Hz, 1H, *H12$_a$*), 6.82 (dd, *J* = 6.5, 6.5 Hz, 1H, *H12$_b$*), 6.66 (dd, *J* = 6.6, 1.2 Hz, 1H, *H13$_a$*), 6.65 (dd, *J* = 6.6, 1.2 Hz, 1H, *H13$_b$*), 5.12 (tt, *J* = 6.0, 1.5 Hz, 1H, *H11*), 2.91 (ddd, *J* = 16.4, 5.9, 5.9 Hz, 1H, ArC*H$_a$*H$_b$), 2.89 (ddd, *J* = 16.4, 6.0, 6.0 Hz, 1H, ArCH$_a$*H$_b$*), 2.54 (ddd, *J* = 13.5, 5.3, 5.3 Hz, 1H, CC*H$_a$*H$_b$), 2.52 (ddd, *J* = 13.6, 5.3, 5.3 Hz, 1H, CCH$_a$*H$_b$*), 2.07 [q, *J* = 1.1 Hz, 3H, C(C*H$_3$*)$_a$], 2.03 (br app pent, *J* = 6 Hz, 2H, $CH_2CH_2CH_2$), and 2.02 [s, 3H, C(C*H$_3$*)$_b$].

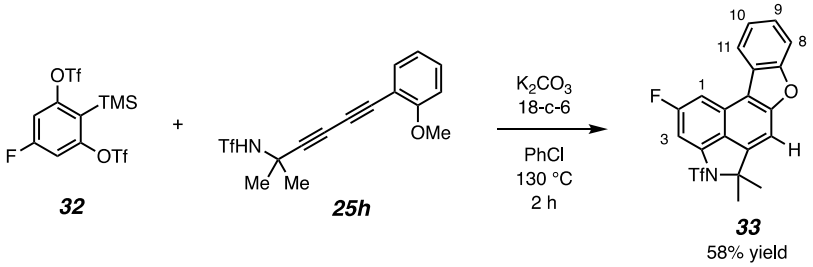
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.8, 145.4, 145.3, 140.0, 138.39, 138.37, 135.8, 134.0, 131.9, 127.8, 126.6, 121.8, 120.0 (q, *J* = 326 Hz), 116.4, 109.4 (q, *J* = 1.2 Hz), 79.1, 51.3, 43.8, 31.5, 30.6, 26.4 (q, *J* = 2.6 Hz), 24.4, and 21.0.

IR (neat): 3067, 2998, 2934, 2860, 1739, 1606, 1496, 1405, 1384, 1223, 1201, 1145, 1090, 964, and 892 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{23}H_{19}{}^{35}ClF_3NNaO_2S^+$ [M+Na^+] requires 488.0669; found 488.0672.

m.p. 198–202 °C.

(±)-2-Fluoro-5,5-dimethyl-4-((trifluoromethyl)sulfonyl)-4,5-dihydrobenzo[2,3]benzofuro[6,5,4-cd]indole (33)



Naphthalene derivative **33** was prepared from benzyne precursor **32**[8] (46 mg, 0.10 mmol), diyne **25h** (17 mg, 0.049 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) following general procedure D. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) afforded **33** (12 mg, 0.028 mmol, 58%) as a pale-yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.2, 1.3 Hz, 1H, *H11*), 7.71 (dd, *J* = 10.1, 1.6 Hz, 1H, *H1*), 7.68 (dd, *J* = 7.7, 0.8 Hz, 1H, *H8*), 7.52 (ddd, *J* = 7.4, 7.4, 1.3 Hz, 1H, *H9*), 7.49 (ddd, *J* = 7.2, 7.2, 1.0 Hz, 1H, *H10*), 7.40 (s, 1H, Ar*H*), 7.21 (dd, *J* = 9.8, 1.3 Hz, 1H, *H3*), 2.03 [s, 3H, C(C*H$_3$*)$_a$], and 2.01 [s, 3H, C(C*H$_3$*)$_b$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7 (q, *J* = 248 Hz), 157.3, 156.2, 144.8 (d, *J* = 1.8 Hz), 141.8 (d, *J* = 15 Hz), 126.6, 126.5, 124.1, 123.8, 121.5, 120.0 (q, *J* = 325 Hz), 119.7, 116.4 (d, *J* = 5.5

Hz), 112.1, 102.4 (d, *J* = 2.7 Hz), 102.2 (d, *J* = 25 Hz), 99.2 (dq, *J* = 34, 1.5 Hz), 79.2, 31.7, and 27.2 (q, *J* = 2.7 Hz).

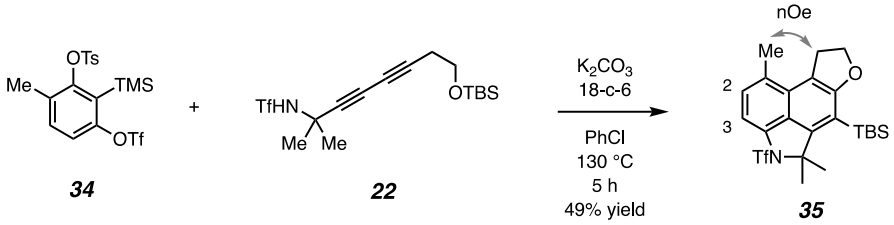
^{19}F NMR (471 MHz, $CDCl_3$) δ -74.2, and -105.7 (dd, *J* = 10.0, 10.0 Hz).

IR (neat): 3070, 2981, 2940, 1737, 1637, 1608, 1404, 1386, 1354, 1296, 1198, 1134, 1089, 1051, 985, and 840 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{20}H_{13}F_4NNaO_3S^+$ [M+Na^+] requires 446.0444; found 446.0460.

m.p. 160–164 °C.

(±)-6-(*tert*-Butyldimethylsilyl)-1,5,5-trimethyl-4-((trifluoromethyl)sulfonyl)-4,5,8,9-tetrahydrobenzofuro[6,5,4-cd]indole (35)



Following general procedure C, diyne **22** (20 mg, 0.050 mmol), benzyne precursor **34**[7] (48 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare naphthalene **35**. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) provided **35** (12 mg, 0.025 mmol, 49%) as a white amorphous solid.

The constitution is assigned on the basis of the nOe correlation indicated in structure **35.**

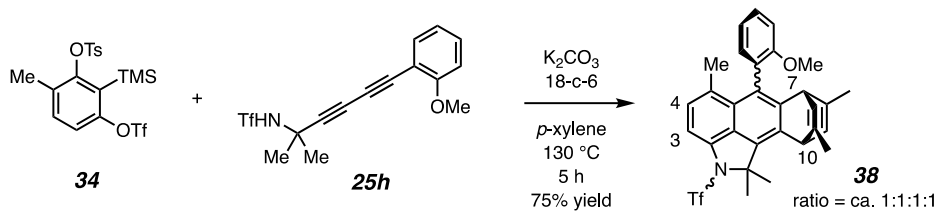
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.7 Hz, 1H, *H2*), 6.99 (d, *J* = 7.8 Hz, 1H, *H3*), 4.59 (ddd, *J* = 9.3, 8.5, 8.5 Hz, 1H, OCH_aH$_b$), 4.57 (ddd, *J* = 9.6, 9.6, 8.5 Hz, 1H, OCH$_a$$H_b$), 3.71 (ddd, *J* = 14.9, 8.4, 8.4 Hz, 1H, ArCH_aH$_b$), 3.70 (ddd, *J* = 14.9, 9.2, 8.5 Hz, 1H, ArCH$_a$$H_b$), 2.66 (s, 3H, ArC$H_3$), 2.02 [s, 3H, C(C$H_3$)$_a$], 2.00 [s, 3H, C(C$H_3$)$_b$], 0.93 [s, 9H, SiC(C$H_3$)$_3$], 0.53 [s, 3H, Si(C$H_3$)$_a$], and 0.49 [s, 3H, Si(C$H_3$)$_b$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 137.7, 130.5 (x2), 129.9, 125.9, 122.8, 120.2 (q, *J* = 327 Hz), 115.9, 113.1, 104.8 (q, *J* = 1.5 Hz), 78.9, 70.2, 31.9, 30.9, 28.8, 27.8 (q, *J* = 2.6 Hz), 20.8, 18.8, 1.9, and 1.1.

IR (neat): 2956, 2933, 2895, 2858, 1742, 1620, 1553, 1399, 1315, 1259, 1136, 988, and 821 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{23}H_{30}F_3NNaO_3SSi^+$ [M+Na^+] requires 508.1560; found 508.1546.

(±)-(7S)-6-((S)-2-Methoxyphenyl)-1,1,5,8,11-pentamethyl-2-((trifluoromethyl)sulfonyl)-1,2,7,10-tetrahydro-7,10-ethenonaphtho[1,2,3-cd]indole (38)



Following general procedure C, diyne **25h** (18 mg, 0.052 mmol), benzyne precursor **34**[7] (48 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and *para*-xylene (2.5 mL) were used to prepare naphthalene **38**. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) provided **38** (21 mg, 0.039 mmol, 75%) as a pale-yellow amorphous solid.

NMR data for this compound indicate that it exists as an ca. 1:1:1:1 mixture of slowly interconverting atropisomeric (biaryl) invertomers (NTf) on the NMR time scale.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.43 (m, 1H, Ar*H*), 7.13–7.09 (m, 1H, Ar*H*), 7.09–7.00 (m, 4H, Ar*H*), 6.32–6.25 (four overlapping br d, 1H, alkenyl-H), 6.23–6.17 (four overlapping br d, 1H, alkenyl-H), 4.76 (dd, *J* = 6.0, 1.9 Hz, 0.5H, bridgehead-*H10*), 4.75 (dd, *J* = 6.0, 1.9 Hz, 0.5H, bridgehead-*H10'*), 4.07 (dd, *J* = 6.5, 1.7 Hz, 0.5H, bridgehead-*H7*), 4.06 (dd, *J* = 6.3, 1.8 Hz, 0.5H, bridgehead-*H7'*), 3.78 (s, 0.75H, **A**-OC*H*$_3$), 3.771 (s, 0.75H, **B**-OC*H*$_3$), 3.766 (s, 0.75H, **C**-OC*H*$_3$), 3.75 (s, 0.75H, **D**-OC*H*$_3$), 2.15 [q, *J* = 1 Hz, 0.75H, **A**-C(C*H*$_3$)], 2.14 [q, *J* = 1 Hz, 0.75H, **B**-C(C*H*$_3$)], 2.13 [s, 0.75H, **A**-C(C*H*$_3$)], 2.11 [br s, 1.5H, **B**-C(C*H*$_3$), **C**-C(C*H*$_3$)], 2.082 [q, *J* = 1 Hz, 0.75H, **D**-C(C*H*$_3$)], 2.075 [s, 0.75H, **C**-C(C*H*$_3$)], 2.04 [s, 0.75H, **D**-C(C*H*$_3$)], 1.931 (br s, 0.75H, **A**-ArC*H*$_3$), 1.927 (br s, 0.75H, **B**-ArC*H*$_3$), 1.924 (br s, 0.75H, **C**-ArC*H*$_3$), 1.921 (br s, 0.75H, **D**-ArC*H*$_3$), 1.83 (br s, 1.5H, alkenyl-C*H*$_3$), 1.81 (br s, 1.5H, alkenyl-C*H*$_3$), 1.754 (d, *J* = 1.8 Hz, 0.75H, alkenyl-C*H*$_3$), 1.746 (d, *J* = 1.8 Hz, 0.75H, alkenyl-C*H*$_3$), 1.696 (d, *J* = 1.8 Hz, 0.75H, alkenyl-C*H*$_3$), and 1.695 (d, *J* = 1.7 Hz, 0.75H, alkenyl-C*H*$_3$).

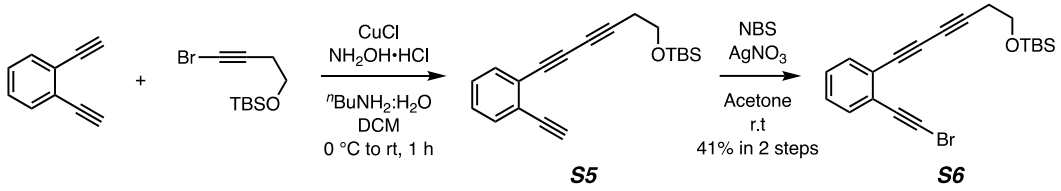
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.89, 157.87, 157.82, 157.78, 150.73, 150.71, 150.68, 150.64, 148.40 (2x), 148.19, 148.14, 148.06, 148.00, 147.76 (2x), 137.42 (2x), 137.40, 137.39, 135.23, 135.21, 135.05, 135.03, 134.53, 133.28, 133.26, 132.51, 132.40, 132.26, 132.14, 131.70, 131.69, 131.66, 131.64, 130.76, 130.28, 130.26, 130.22, 130.19, 129.88, 129.86, 129.73, 129.67, 129.65 (2x), 129.61, 129.35, 129.33, 129.31, 129.30, 129.29 (4x), 126.99, 126.97, 126.93, 126.89, 126.60, 126.58, 126.57, 126.55, 124.43, 124.35, 124.28, 124.22, 120.38, 120.31, 120.22, 120.2 (four nearly identical chemical shift q, *J* = ca. 326 Hz), 120.18, 110.73, 110.72, 110.24 (2x), 107.81 (br m, 4x, C3), 77.45, 77.43, 77.40 (and perhaps hidden by a $CDCl_3$ line), 55.63, 55.57, 55.32, 55.23, 51.64, 51.61, 51.61, 51.59, 49.10, 49.05, 48.96, 48.91, 31.21, 31.05, 30.65, 30.50, 27.1 (q, *J* = 2.6 Hz), 26.9 (q, *J* = 2.5 Hz), 26.5 (q, *J* = 2.6 Hz), 26.3 (q, *J* = 2.6 Hz), 21.55, 21.52, 21.35, 21.31, 19.21, 19.17, 19.16, 19.15 (2x), 19.13, 19.09, and 19.07.

^{19}F NMR (471 MHz, $CDCl_3$) δ -73.9, -73.98, -74.05, -74.2.

IR (neat): 2991, 2964, 2932, 2852, 1769, 1612, 1487, 1462, 1401, 1384, 1201, 1138, and 973 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{30}H_{28}F_3NNaO_3S^+$ [M+Na^+] requires 562.1634; found 562.1609.

((6-(2-(Bromoethynyl)phenyl)hexa-3,5-diyn-1-yl)oxy)(tert-butyl)dimethylsilane (S6)



Following general procedure A, (but-3-yn-1-yloxy)(*tert*-butyl)dimethylsilane[5] (0.40 g, 1.5 mmol), 1,2-diethynyl-benzene (0.19 g, 1.5 mmol), CuCl (7.5 mg), ^{n}BuNH$_2$:H$_2$O (7.5 mL), and DCM (7.5 mL) were used to prepare crude triyne **S5**. The crude material was passed through a short pad of silica gel (hexanes:EtOAc, 10:1), and the filtrate was collected and concentrated. The residue (0.27 g, ca. 0.88 mmol) was used directly in the following step without further purification. Following general procedure B, the above crude triyne **S5** (0.27 g, ca. 0.88 mmol), NBS (0.18 g, 1.0 mmol), silver nitrate (17 mg, 0.10 mmol), and acetone (10 mL) were used to prepare bromoalkyne **S6**. Purification of the crude mixture by MPLC (hexanes:EtOAc, 50:1) afforded **S6** (0.24 g, 0.62 mmol, 41% over two steps) as a yellowish oil.

Data for S6

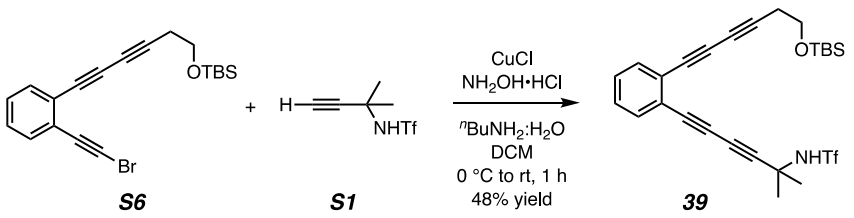
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47–7.44 (nfom, 1H, ArH_o), 7.44–7.42 (nfom, 1H, Ar$H_{o'}$), 7.29–7.26 (m, 2H, ArH_m), 3.80 (t, J = 7.0 Hz, 2H, OCH_2), 2.60 (t, J = 7.0 Hz, 2H, ≡CCH_2), 0.92 [s, 9H, SiC(CH_3)$_3$], and 0.10 [s, 6H, Si(CH_3)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 133.2, 132.7, 128.6, 128.4, 126.3, 125.3, 83.2, 78.5, 78.2, 73.1, 66.4, 61.5, 54.4, 26.0, 24.3, 18.5, and -5.1.

IR (neat): 3063, 2953, 2928, 2855, 2240, 2198, 1471, 1442, 1384, 1253, 1103, 907, 835, 777, and 756 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{20}H_{23}{}^{79}BrNaOSi^+$ [M+Na^+] requires 409.0594; found 409.0592.

***N*-(6-(2-(6-((*tert*-Butyldimethylsilyl)oxy)hexa-1,3-diyn-1-yl)phenyl)-2-methylhexa-3,5-diyn-2-yl)-1,1,1-trifluoromethanesulfonamide (39)**



Following general procedure A, alkyne **S1** (0.10 g, 80 wt%, 0.39 mmol), bromotriyne **S6** (0.10 g, 0.26 mmol), CuCl (2.6 mg), ^{n}BuNH$_2$:H$_2$O (2.0 mL), and DCM (2.0 mL) were used to prepare

tetrayne **39**. Purification of the crude mixture by MPLC (hexanes:EtOAc, 9:1) afforded **39** (65 mg, 0.12 mmol, 48%) as a yellow-brown oil.

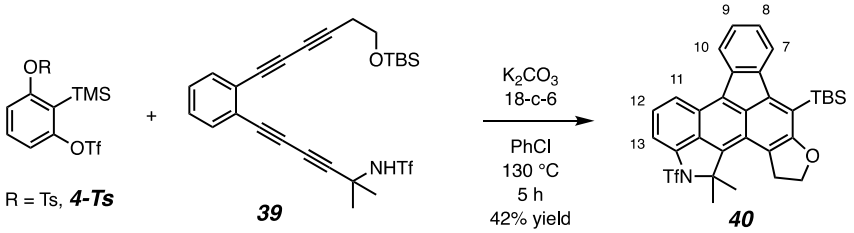
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49–7.48 (nfom, 1H, Ar*H*$_o$), 7.48–7.46 (nfom, 1H, Ar*H*$_o$*'*), 7.33–7.27 (m, 2H, Ar*H*$_m$), 5.10 (br s, 1H, TfN*H*), 3.80 (t, *J* = 7.1 Hz, 2H, OC*H*$_2$), 2.61 (t, *J* = 7.0 Hz, 2H, ≡CC*H*$_2$), 1.77 [s, 6H, C(C*H*$_3$)$_2$], 0.91 [s, 9H, SiC(C*H*$_3$)$_3$], and 0.10 [s, 6H, Si(C*H*$_3$)$_2$].

^{13}C NMR (126 MHz, $CDCl_3$): δ 133.45, 133.44, 129.2, 128.7, 125.9, 124.8, 119.2 (q, *J* = 323 Hz), 83.65, 83.57, 78.7, 77.8, 76.5, 72.8, 68.9, 66.3, 61.5, 53.8, 30.6, 26.0, 24.3, 18.5, and -5.2.

IR (neat): 3288, 2954, 2930, 2857, 2241, 1427, 1363, 1193, 1136, 994, 909, 834, and 756 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{26}H_{30}F_3NNaO_3SSi^+$ [M+Na$^+$] requires 544.1560; found 544.1554.

(±)-6-(*tert*-Butyldimethylsilyl)-2,2-dimethyl-1-((trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydrofuro[3',2':4,5]fluoranthe no[3,2,1-cd]indole (40)



Following general procedure C, tetrayne **39** (25 mg, 0.048 mmol), benzyne precursor **4-Ts**[7] (47 mg, 0.10 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare anthracene **40**. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) provided **40** (12 mg, 0.020 mmol, 42%) as an orange crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.6 Hz, 1H, *H10*), 8.23 (d, *J* = 8.6 Hz, 1H, *H11*), 8.17 (d, *J* = 7.8 Hz, 1H, *H7*), 7.55 (dd, *J* = 8.3, 7.5 Hz, 1H, *H12*), 7.42 (dd, *J* = 7.5, 7.5 Hz, 1H, *H8* or *H9*), 7.31 (dd, *J* = 7.7, 7.7 Hz, 1H, *H8* or *H9*), 7.30 (d, *J* = 7.5 Hz, 1H, *H13*), 4.76 (ddd, *J* = 10.6, 9.3, 7.7 Hz, 1H, OC*H*$_a$H$_b$), 4.68 (ddd, *J* = 10.6, 9.1, 9.1 Hz, 1H, OCH$_a$*H*$_b$), 3.79 (ddd, *J* = 14.7, 9.3, 9.3 Hz, 1H, ArC*H*$_a$H$_b$), 3.74 (ddd, *J* = 14.7, 9.6, 7.3 Hz, 1H, ArCH$_a$*H*$_b$), 2.28 [s, 3H, C(C*H*$_3$)$_a$], 2.27 [br s, 3H, C(C*H*$_3$)$_b$], 1.19 [s, 9H, SiC(C*H*$_3$)$_3$], and 0.54 [s, 6H, Si(C*H*$_3$)$_2$].

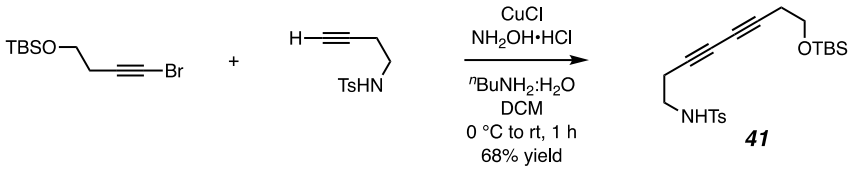
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 148.4, 140.7, 140.0, 139.0, 137.7, 131.18, 131.16, 128.8, 128.5, 128.1, 125.9, 125.6, 125.3, 124.0, 123.2, 120.9, 120.2 (q, *J* = 326 Hz), 117.8, 112.1, 106.4 (q, *J* = 1.4 Hz), 79.6, 70.2, 34.5, 31.4, 28.3, 27.5 (q, *J* = 2.7 Hz), 19.8, and 0.2.

IR (neat): 2954, 2928, 2856, 1568, 1466, 1403, 1383, 1264, 1199, 1142, 992, and 755 cm^{-1}.

HRMS (APCI$^+$): Calcd for $C_{31}H_{34}NOSi^+$ [M–Tf+2H]$^+$ requires 464.2404; found 464.2400. The major ion observed represents the protonated molecular ion followed by loss of TfOH.

m.p. 154–157 °C.

N-(8-((*tert*-Butyldimethylsilyl)oxy)octa-3,5-diyn-1-yl)-4-methylbenzenesulfonamide (41)



Following general procedure A, ((4-bromobut-3-yn-1-yl)oxy)(tert-butyl)dimethylsilane[5] (0.26 g, 1.0 mmol), *N*-(but-3-yn-1-yl)-4-methylbenzenesulfonamide[11] (0.18 g, 0.80 mmol), CuCl (8.0 mg), ^{n}BuNH$_2$:H$_2$O (5.0 mL), and DCM (5.0 mL) were used to prepare diyne **41**. Purification of the crude material by flash chromatography (hexanes:EtOAc, 4:1) provided diyne **41** (0.22 g, 0.54 mmol, 68% yield) as a low-melting, pale-yellow crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (nfod, *J* = 8.3 Hz, 2H, $SO_2Ar\mathit{H}_o$), 7.32 (nfod, *J* = 8.2 Hz, 2H, $SO_2Ar\mathit{H}_m$), 4.73 (br t, *J* = 6.8 Hz, 1H, TsN*H*), 3.73 (t, *J* = 7.0 Hz, 2H, $OC\mathit{H}_2$), 3.11 (dt, *J* = 6.8, 6.8 Hz, 2H, $TsNHC\mathit{H}_2$), 2.47 (t, *J* = 7.0 Hz, 2H, $C\mathit{H}_2CH_2O$), 2.44 (s, 3H, $SO_2ArC\mathit{H}_3$), 2.41 (t, *J* = 6.6 Hz, 2H, $C\mathit{H}_2CH_2N$), 0.90 [s, 9H, $SiC(C\mathit{H}_3)_3$], and 0.07 [s, 6H, $Si(C\mathit{H}_3)_2$].

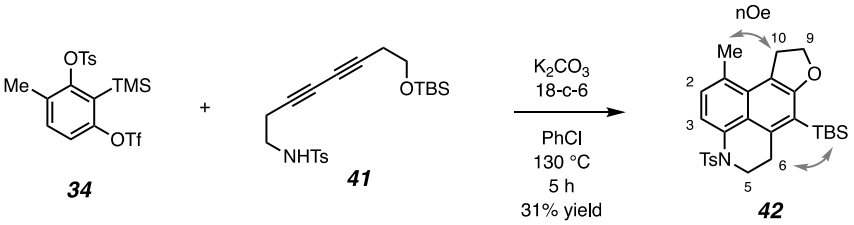
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.8, 137.0, 130.0, 127.2, 76.0, 73.1, 67.8, 65.9, 61.5, 41.7, 26.0, 23.7, 21.7, 20.8, 18.4, and -5.2.

IR (neat): 3283, 2953, 2929, 2857, 2253, 1728, 1599, 1471, 1415, 1328, 1255, 1159, 1094, 1007, 911, and 837 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{21}H_{31}NNaO_3SSi^+$ [M+Na$^+$] requires 428.1686; found 428.1695.

m.p. 26–29 °C.

7-(*tert*-Butyldimethylsilyl)-1-methyl-4-tosyl-5,6,9,10-tetrahydro-4H-benzofuro[6,5,4-de]quinoline (42)



Following general procedure C, diyne **41** (20 mg, 0.050 mmol), benzyne precursor **34**[7] (72 mg, 0.15 mmol), K_2CO_3 (55 mg, 0.40 mmol), 18-crown-6 (26 mg, 0.10 mmol), and chlorobenzene (2.5 mL) were used to prepare naphthalene **42**. Purification of the crude material by MPLC (hexanes:EtOAc, 20:1) provided **42** (7.7 mg, 0.016 mmol, 31%) as a pale yellow amorphous foam.

Naphthalene **42** slowly decomposed when held in solution under ambient light and air, which resulted in an increase of a few resonances from unidentified species in the ^{1}H NMR spectrum.

The constitution of **42** was assigned on the basis of the nOe correlations indicated in structure **42.**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 1H, *H3*), 7.43 (nfod, *J* = 8.3 Hz, 2H, SO_2Ar*H*$_o$), 7.16 (d, *J* = 7.8 Hz, 1H, *H2*), 7.08 (nfod, *J* = 8.3 Hz, 2H, SO_2Ar*H*$_m$), 4.48 (t, *J* = 9.3, 8.9 Hz, 2H, *H9*), 3.96 (t, *J* = 6.2 Hz, 2H, *H5*), 3.78 (t, *J* = 8.9 Hz, 2H, *H10*), 2.79 (t, *J* = 6.1 Hz, 2H, *H6*), 2.74 (s, 3H, ArC*H*$_3$), 2.30 (s, 3H, SO_2ArC*H*$_3$), 0.81 [s, 9H, $SiC(C$*H*$_3)_3$], and 0.25 [s, 6H, $Si(C$*H*$_3)_2$].

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 140.1, 132.9, 130.8, 130.0, 129.7, 128.8, 128.7, 128.5, 127.2, 121.5, 120.8, 118.8, 116.0, 69.7, 45.4, 32.9, 31.0, 27.2, 23.4, 21.6, 18.8, and -0.5.

IR (neat): 2953, 2927, 2855, 1598, 1551, 1471, 1352, 1336, 1290, 1258, 1194, 1091, 1014, 961, 909, and 807 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{28}H_{35}NNaO_3SSi^+$ [M+Na^+] requires 516.1999; found 516.1983.

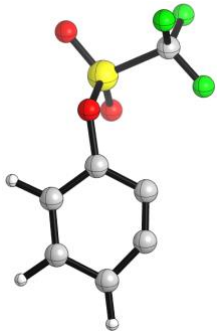
III. Computational methods and results

The DFT calculations were performed using Gaussian 09.[16] The geometry of each structure was optimized at the SMD(chlorobenzene)/B3LYP/6-31G(d,p) level of theory in the gas phase. The nature of the optimized structure was verified by frequency calculation (298K, at the same level of theory). For data presented in Figure S1 (Page S42), a single point calculation at SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p) level of theory was also performed on each optimized geometry to obtain more accurate energies.

Listed are the sum of the electronic and thermal free energies (in Hartree), the Cartesian coordinates at SMD(chlorobenzene)/B3LYP/ 6-31G(d,p) for each structure shown in Figure 4. The sum of the electronic and thermal free energies (in Hartree), the Cartesian coordinates at SMD(chlorobenzene)/B3LYP/ 6-31G(d,p), as well as the electronic energy at SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p) for each structure shown in Figure S1 are also presented. Three dimensional views were prepared using CYLview.[17]

Data in Figure 4:

5-Tf



Sum of electronic and thermal Free Energies= -1191.670983

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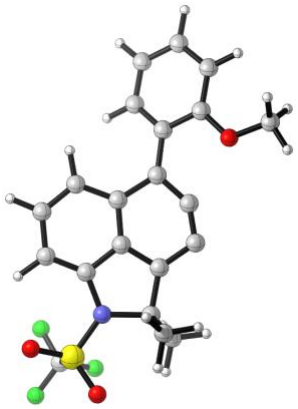
1	6	0	1.409473	-0.167664	-0.374474
2	6	0	1.658495	1.139167	0.014584
3	6	0	2.856180	1.415273	0.272001
4	6	0	4.057774	0.759727	0.259755
5	6	0	3.805577	-0.573821	-0.144778
6	6	0	2.514762	-1.032807	-0.450228
7	16	0	-1.074256	-0.829693	0.285667
8	8	0	-1.856719	-1.967804	-0.164372
9	8	0	-0.596847	-0.692194	1.652720
10	6	0	-2.058757	0.706737	-0.141156
11	9	0	-2.346973	0.701993	-1.437936

12	9	0	-3.181274	0.682533	0.573643
13	9	0	-1.354126	1.792846	0.163518
14	1	0	5.041041	1.137818	0.506659
15	1	0	4.644412	-1.261261	-0.212572
16	1	0	2.361908	-2.063077	-0.755147
17	8	0	0.156197	-0.666802	-0.790454

26h

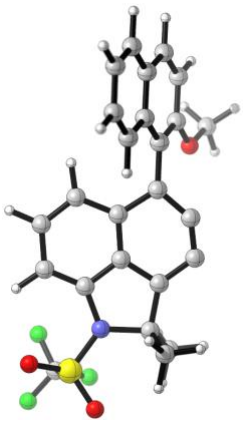


Sum of electronic and thermal Free Energies= -1787.571837

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.186793	-0.647500	-0.573950
2	6	0	0.064366	-0.067999	-0.266210
3	6	0	1.295894	-0.790533	-0.301110
4	6	0	1.186909	-2.147581	-0.728085
5	6	0	-0.048125	-2.689569	-1.034034
6	6	0	-1.268635	-1.967707	-0.954501
7	6	0	-0.080379	1.305341	0.034821
8	6	0	1.108520	1.969005	0.290119
9	6	0	2.141275	1.236671	0.253763
10	6	0	2.520298	-0.060807	0.050824
11	7	0	-2.173438	0.377090	-0.414582
12	6	0	-1.536891	1.733050	-0.038232
13	6	0	-2.035761	2.248839	1.316218
14	6	0	-1.745214	2.761842	-1.158808
15	16	0	-3.792412	0.124291	-0.613910
16	8	0	-4.480879	1.411684	-0.606550
17	8	0	-4.017408	-0.863091	-1.667161
18	6	0	-4.341058	-0.741815	0.962316
19	9	0	-4.127714	0.039421	2.022176
20	9	0	-5.645285	-1.003053	0.863338

21	9	0	-3.669136	-1.885391	1.115474
22	6	0	3.894008	-0.563877	0.168258
23	6	0	4.957295	0.374869	0.072111
24	6	0	6.287661	-0.038056	0.176206
25	6	0	6.580362	-1.384205	0.406140
26	6	0	5.552420	-2.314258	0.549166
27	6	0	4.225373	-1.901086	0.435605
28	8	0	4.579737	1.668633	-0.112810
29	6	0	5.574884	2.693703	-0.142518
30	1	0	2.070225	-2.758362	-0.855451
31	1	0	-0.092810	-3.722782	-1.366128
32	1	0	-2.203928	-2.446828	-1.209480
33	1	0	-1.449431	3.133180	1.583063
34	1	0	-3.088005	2.537001	1.272276
35	1	0	-1.897761	1.498728	2.098378
36	1	0	-1.120489	3.635491	-0.949053
37	1	0	-1.443221	2.349304	-2.125353
38	1	0	-2.786665	3.081933	-1.215394
39	1	0	7.092685	0.681151	0.085104
40	1	0	7.617577	-1.695514	0.487505
41	1	0	5.776635	-3.355216	0.758927
42	1	0	3.434879	-2.622842	0.595865
43	1	0	5.029259	3.630992	-0.258668
44	1	0	6.149299	2.717818	0.790065
45	1	0	6.253564	2.561112	-0.992333

26i



Sum of electronic and thermal Free Energies= -1941.174211

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	1.571133	-0.687210	-0.264966
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3	6	0	-0.870186	-0.170292	-0.184245
4	6	0	-1.017559	-0.996297	-1.337469
5	6	0	0.085793	-1.619153	-1.888491
6	6	0	1.405501	-1.489467	-1.371100
7	6	0	0.850260	0.742620	1.423861
8	6	0	-0.213705	1.397182	2.002741
9	6	0	-1.372540	1.246939	1.523314
10	6	0	-1.946864	0.544584	0.499070
11	7	0	2.719060	-0.303604	0.501228
12	6	0	2.342459	0.627798	1.677550
13	6	0	3.034862	1.991643	1.576146
14	6	0	2.613618	-0.056887	3.025188
15	16	0	4.253387	-0.810276	0.162609
16	8	0	5.129801	-0.460397	1.276512
17	8	0	4.216546	-2.159703	-0.395920
18	6	0	4.811658	0.272267	-1.269940
19	9	0	4.906293	1.544805	-0.882118
20	9	0	6.008187	-0.153956	-1.676470
21	9	0	3.940668	0.182056	-2.277941
22	6	0	-3.373347	0.508227	0.088268
23	6	0	-3.963241	1.673220	-0.408032
24	6	0	-5.320150	1.678929	-0.822366
25	6	0	-6.073565	0.532475	-0.732117
26	6	0	-5.529107	-0.669992	-0.217083
27	6	0	-4.157883	-0.683266	0.208136
28	8	0	-3.167506	2.774076	-0.477446
29	6	0	-3.713094	3.998534	-0.967513
30	1	0	-1.996682	-1.133313	-1.781471
31	1	0	-0.051361	-2.243983	-2.766381
32	1	0	2.227673	-2.007965	-1.845412
33	1	0	2.626915	2.642529	2.355241
34	1	0	4.111633	1.904788	1.733962
35	1	0	2.846541	2.459664	0.607162
36	1	0	2.163954	0.547021	3.819298
37	1	0	2.161130	-1.051820	3.053166
38	1	0	3.684020	-0.144647	3.215783
39	1	0	-5.764965	2.584429	-1.216133
40	1	0	-7.110791	0.542482	-1.055934
41	1	0	-2.898434	4.722890	-0.918935
42	1	0	-4.047958	3.905299	-2.007052
43	1	0	-4.543394	4.350175	-0.344534
44	6	0	-6.311641	-1.851270	-0.102578
45	6	0	-3.644104	-1.893113	0.759369
46	6	0	-4.431240	-3.018645	0.860435

47	6	0	-5.777677	-3.005800	0.421149
48	1	0	-6.383331	-3.903125	0.505517
49	1	0	-4.014973	-3.927135	1.286457
50	1	0	-7.346102	-1.820317	-0.434914
51	1	0	-2.618830	-1.922165	1.110232

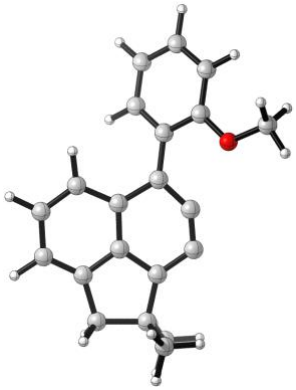
A

Sum of electronic and thermal Free Energies= -1442.080983

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.700534	0.739842	-0.362583
2	6	0	-1.929070	0.139112	-0.013652
3	6	0	-3.138412	0.870044	0.150963
4	6	0	-3.048530	2.277696	-0.056150
5	6	0	-1.836618	2.846309	-0.397129
6	6	0	-0.633525	2.100799	-0.560708
7	6	0	-1.785084	-1.260310	0.136855
8	6	0	-2.972239	-1.868280	0.472346
9	6	0	-4.027304	-1.187215	0.613777
10	6	0	-4.333519	0.137309	0.505601
11	7	0	0.271080	-0.310215	-0.423732
12	6	0	-0.357106	-1.695553	-0.139469
13	6	0	0.269991	-2.369555	1.085787
14	6	0	-0.294561	-2.590006	-1.386313
15	16	0	1.867455	-0.059003	-0.765464
16	8	0	2.510410	-1.344531	-1.020296
17	8	0	2.002520	1.067804	-1.685193
18	6	0	2.612411	0.560579	0.846395
19	9	0	2.571828	-0.395177	1.775533
20	9	0	3.881874	0.898332	0.617571
21	9	0	1.938529	1.627963	1.281363
22	1	0	-3.933939	2.896042	0.052857
23	1	0	-1.786853	3.919996	-0.553951
24	1	0	0.282950	2.605666	-0.834553

25	1	0	-0.300539	-3.275634	1.310583
26	1	0	1.305459	-2.657589	0.894641
27	1	0	0.230584	-1.715031	1.959505
28	1	0	-0.906869	-3.479302	-1.208076
29	1	0	-0.693772	-2.067795	-2.259983
30	1	0	0.728490	-2.905723	-1.594588
31	1	0	-5.291271	0.624057	0.646493

B

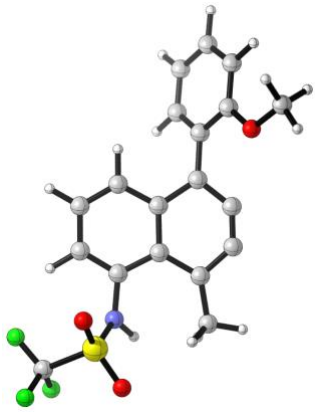


Sum of electronic and thermal Free Energies= -885.952070

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.819121	1.288357	-0.271680
2	6	0	1.686345	0.475094	-0.031112
3	6	0	0.336755	0.950208	-0.095445
4	6	0	0.198287	2.315063	-0.486090
5	6	0	1.311281	3.100806	-0.732639
6	6	0	2.637865	2.609076	-0.616274
7	6	0	2.081038	-0.867005	0.245552
8	6	0	0.990653	-1.694347	0.438262
9	6	0	-0.175638	-1.214378	0.385467
10	6	0	-0.756015	0.009322	0.184155
11	6	0	3.594212	-1.015149	0.221485
12	6	0	4.123992	-1.499921	1.584343
13	6	0	4.023995	-1.998887	-0.884390
14	6	0	-2.195708	0.312311	0.243544
15	6	0	-3.137341	-0.685388	-0.128609
16	6	0	-4.509900	-0.423814	-0.068887
17	6	0	-4.966970	0.817943	0.378777
18	6	0	-4.061863	1.797594	0.780501
19	6	0	-2.692836	1.537358	0.714429

20	8	0	-2.615264	-1.875940	-0.529896
21	6	0	-3.501514	-2.939503	-0.874588
22	1	0	-0.786763	2.743639	-0.622653
23	1	0	1.161058	4.133442	-1.036582
24	1	0	3.478971	3.267476	-0.816258
25	1	0	3.725296	-2.491211	1.825860
26	1	0	5.217752	-1.568562	1.570647
27	1	0	3.836003	-0.815474	2.389150
28	1	0	3.614468	-2.997423	-0.696655
29	1	0	3.671695	-1.669447	-1.867489
30	1	0	5.116124	-2.081990	-0.923503
31	1	0	-5.224482	-1.181827	-0.365976
32	1	0	-6.035813	1.006358	0.421188
33	1	0	-4.413266	2.754421	1.153642
34	1	0	-1.994206	2.287343	1.066358
35	1	0	-2.862213	-3.783916	-1.136495
36	1	0	-4.142641	-3.218424	-0.030347
37	1	0	-4.124874	-2.677182	-1.737214
38	6	0	4.075975	0.454475	-0.098497
39	1	0	4.698275	0.478018	-1.000424
40	1	0	4.696329	0.847004	0.716085

C



Sum of electronic and thermal Free Energies= -1710.178196

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.284440	-0.395055	0.425930
2	6	0	-0.072590	0.371370	0.578427
3	6	0	1.175340	-0.347860	0.289585
4	6	0	1.111677	-1.681358	-0.199594
5	6	0	-0.079331	-2.349931	-0.342652

6	6	0	-1.278740	-1.709576	0.004871
7	6	0	-0.054461	1.779412	0.989191
8	6	0	1.241194	2.217573	0.990960
9	6	0	2.301442	1.593357	0.755620
10	6	0	2.492217	0.279990	0.437738
11	7	0	-2.575469	0.179764	0.685500
12	6	0	-1.209032	2.662392	1.396744
13	16	0	-3.682449	0.545032	-0.495386
14	8	0	-4.295028	1.837974	-0.187298
15	8	0	-3.146472	0.222900	-1.813224
16	6	0	-5.045912	-0.693107	-0.166025
17	9	0	-5.447807	-0.586057	1.102339
18	9	0	-6.068373	-0.431108	-0.980727
19	9	0	-4.616117	-1.938290	-0.388371
20	6	0	3.800538	-0.396202	0.299119
21	6	0	4.854217	0.238281	-0.409869
22	6	0	6.108863	-0.375271	-0.505056
23	6	0	6.334415	-1.608684	0.109576
24	6	0	5.318901	-2.236864	0.827347
25	6	0	4.067645	-1.626571	0.917781
26	8	0	4.560233	1.440824	-0.971479
27	6	0	5.582740	2.138550	-1.680642
28	1	0	2.034526	-2.172243	-0.480466
29	1	0	-0.097634	-3.367820	-0.718456
30	1	0	-2.221577	-2.237143	-0.073913
31	1	0	6.911139	0.102563	-1.053828
32	1	0	7.314306	-2.070051	0.027200
33	1	0	5.496574	-3.187002	1.321022
34	1	0	3.283026	-2.099959	1.498935
35	1	0	5.125190	3.069782	-2.018162
36	1	0	6.437076	2.369319	-1.033626
37	1	0	5.926979	1.569694	-2.552274
38	1	0	-2.715137	0.733337	1.523487
39	1	0	-1.702722	2.304492	2.308775
40	1	0	-0.821001	3.658049	1.620572
41	1	0	-1.970581	2.770956	0.620932

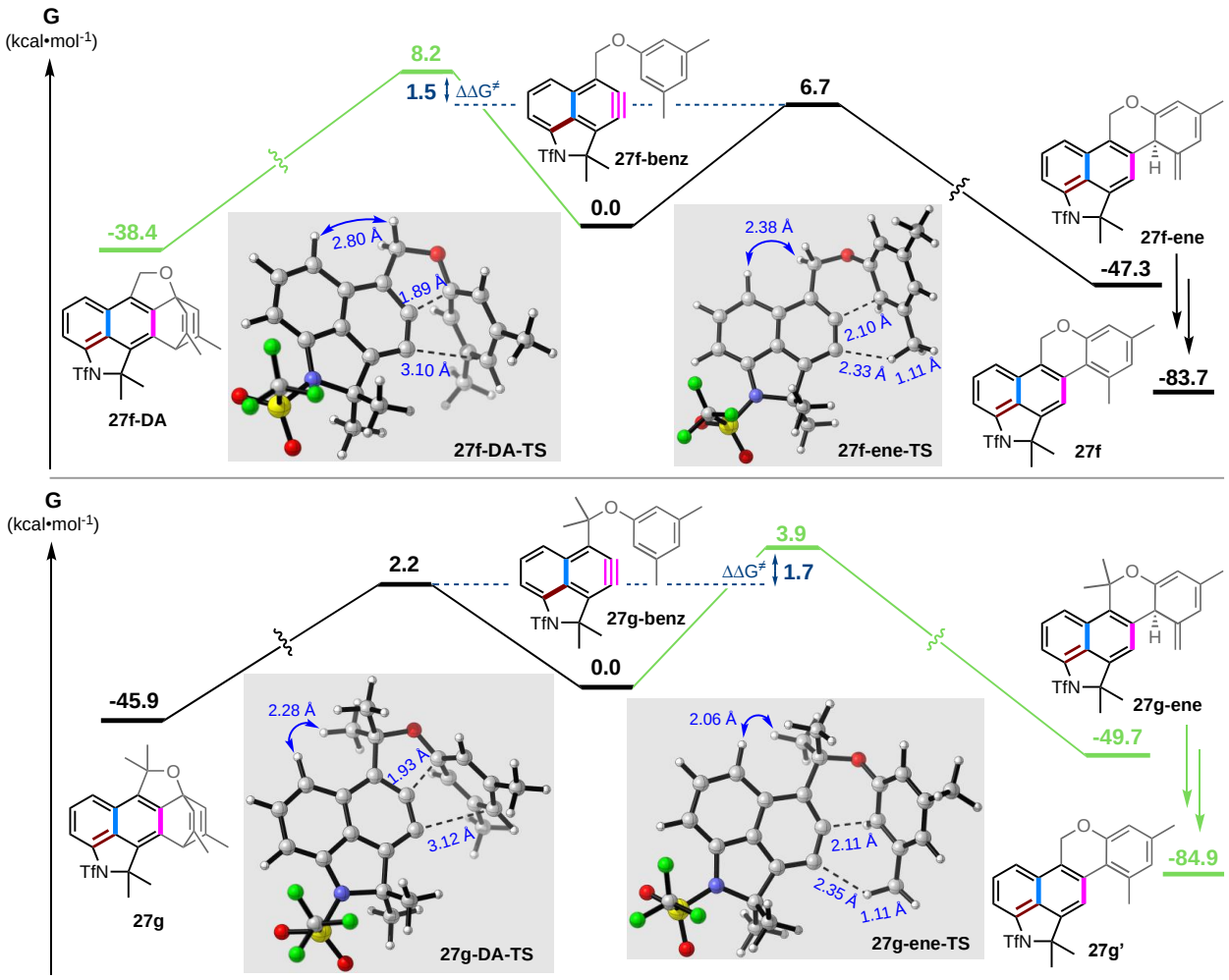


Figure S1. DFT-Calculated energy profiles of reactions leading to **27f** (the ene product for the CH_2 linker) and **27g** (the Diels-Alder product for the CMe_2 linker). Full conformational analyses were not performed for the benzyne intermediates **27f-benz** and **27g-benz**.

Data for Figure S1:

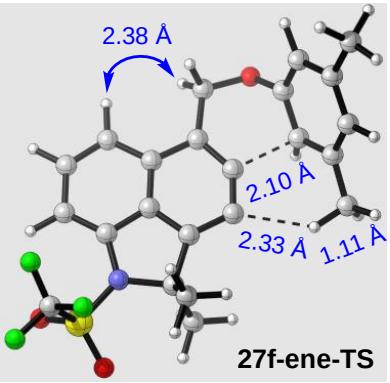
27f-benz

Thermal correction to Gibbs Free Energy= 0.320925
Sum of electronic and thermal Free Energies= -1866.164850
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1867.00993708

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.975729	2.781193	-0.613851
2	6	0	-2.213780	2.080233	-0.631657
3	6	0	-2.165271	0.709335	-0.506540
4	6	0	-0.921559	0.055916	-0.373022
5	6	0	0.324099	0.742643	-0.351305

6	6	0	0.252416	2.161425	-0.479397
7	6	0	-1.095993	-1.345601	-0.271255
8	6	0	0.105790	-1.997492	-0.140177
9	6	0	1.196993	-1.361887	-0.118111
10	6	0	1.537206	-0.042233	-0.204108
11	7	0	-3.174068	-0.305404	-0.469200
12	6	0	-2.563388	-1.723453	-0.358000
13	6	0	-3.028828	-2.458892	0.903783
14	6	0	-2.844707	-2.532564	-1.632715
15	16	0	-4.793383	0.015309	-0.530714
16	8	0	-5.031859	1.190151	-1.365561
17	8	0	-5.520598	-1.234290	-0.731929
18	6	0	-5.234617	0.579826	1.207992
19	9	0	-6.510638	0.966565	1.212961
20	9	0	-5.073550	-0.419548	2.075994
21	9	0	-4.456453	1.604206	1.565871
22	6	0	2.911704	0.556296	-0.158162
23	8	0	3.834771	-0.511921	0.012931
24	6	0	5.169658	-0.213687	0.086896
25	6	0	5.694772	1.076328	0.009557
26	6	0	7.085660	1.270344	0.097817
27	6	0	7.919673	0.165103	0.262693
28	6	0	7.397778	-1.139322	0.341692
29	6	0	6.019896	-1.318586	0.252400
30	6	0	8.322750	-2.319431	0.522464
31	6	0	7.651136	2.668266	0.006871
32	1	0	-1.008222	3.862287	-0.713439
33	1	0	-3.142424	2.622873	-0.744591
34	1	0	1.159117	2.757187	-0.475797
35	1	0	-2.459994	-3.389795	0.986119
36	1	0	-2.841810	-1.864007	1.800699
37	1	0	-4.089582	-2.711150	0.849733
38	1	0	-2.251518	-3.451700	-1.602243
39	1	0	-3.899939	-2.800205	-1.704709
40	1	0	-2.556263	-1.967321	-2.523018
41	1	0	5.047663	1.936861	-0.118092
42	1	0	8.994783	0.313504	0.331098
43	1	0	5.579713	-2.309575	0.309355
44	1	0	8.890193	-2.238516	1.457177
45	1	0	7.770424	-3.262749	0.545545
46	1	0	9.055434	-2.377064	-0.290973
47	1	0	7.214784	3.325654	0.767964
48	1	0	8.735954	2.669367	0.143463
49	1	0	7.435422	3.121747	-0.968106
50	1	0	2.989011	1.273554	0.672050
51	1	0	3.123187	1.106853	-1.086569

27f-ene-TS

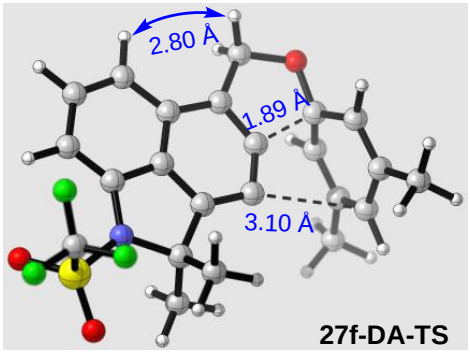


One imaginary frequency: -182.85 cm^{-1}
Thermal correction to Gibbs Free Energy= 0.326623
Sum of electronic and thermal Free Energies= -1866.148841
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1867.00501394

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.764973	1.101528	-0.364203
2	6	0	-0.377262	0.863060	-0.448398
3	6	0	-2.236491	2.381246	-0.173322
4	7	0	-2.407815	-0.170356	-0.498777
5	6	0	0.596299	1.885891	-0.344256
6	6	0	-0.086411	-0.499856	-0.641946
7	6	0	-1.268615	3.420566	-0.064706
8	1	0	-3.291109	2.613018	-0.108221
9	6	0	-1.379328	-1.307687	-0.717926
10	16	0	-4.041137	-0.378330	-0.432882
11	6	0	0.094756	3.206745	-0.141075
12	6	0	1.977430	1.484010	-0.451037
13	6	0	1.243213	-0.863459	-0.742640
14	1	0	-1.632628	4.432996	0.085612
15	6	0	-1.549518	-1.930137	-2.110003
16	6	0	-1.446541	-2.359261	0.393393
17	8	0	-4.716143	0.789502	-0.996010
18	8	0	-4.372177	-1.735919	-0.857223
19	6	0	-4.462781	-0.316816	1.397903
20	1	0	0.774597	4.047101	-0.046582
21	6	0	2.103550	0.124133	-0.636120
22	6	0	3.082571	2.499752	-0.313675
23	1	0	-0.691532	-2.581639	-2.302599
24	1	0	-2.463195	-2.522950	-2.176098
25	1	0	-1.568763	-1.155348	-2.881726
26	1	0	-0.608050	-3.049290	0.259681

27	1	0	-1.351664	-1.897083	1.378916
28	1	0	-2.374319	-2.933802	0.350771
29	9	0	-4.057886	0.842665	1.922562
30	9	0	-5.786266	-0.424714	1.529004
31	9	0	-3.874245	-1.322130	2.048213
32	8	0	4.372409	2.023265	-0.753432
33	1	0	3.161026	2.831612	0.732001
34	1	0	2.879603	3.381001	-0.927729
35	6	0	4.670249	0.773403	-0.283326
36	6	0	4.126150	-0.325440	-1.000678
37	6	0	5.394604	0.592519	0.880576
38	6	0	4.386395	-1.646579	-0.529661
39	1	0	3.880541	-0.174844	-2.047582
40	6	0	5.636566	-0.711012	1.354664
41	1	0	5.770114	1.458172	1.418031
42	6	0	5.108545	-1.805675	0.652500
43	6	0	3.760258	-2.788135	-1.246788
44	6	0	6.440414	-0.914270	2.611556
45	1	0	5.286921	-2.808836	1.030304
46	1	0	4.061520	-3.757860	-0.843553
47	1	0	2.659816	-2.665679	-1.135891
48	1	0	3.960413	-2.763225	-2.323290
49	1	0	5.977275	-0.398091	3.460548
50	1	0	6.530956	-1.973297	2.864597
51	1	0	7.449739	-0.500520	2.500671

27f-DA-TS



One imaginary frequency: -210.03 cm^{-1}
Thermal correction to Gibbs Free Energy= 0.324869
Sum of electronic and thermal Free Energies= -1866.143613
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1867.00076976

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-1.626770	1.152157	-0.396204
2	6	0	-0.232373	1.068918	-0.212951
3	6	0	0.592405	2.209193	-0.044254
4	6	0	-0.062268	3.474578	-0.061812
5	6	0	-1.431921	3.533285	-0.241342
6	6	0	-2.251044	2.381177	-0.414933
7	6	0	0.232496	-0.264869	-0.239990
8	6	0	1.585301	-0.504556	-0.090469
9	6	0	2.309564	0.598249	0.087617
10	6	0	1.986455	1.932386	0.119396
11	7	0	-2.104408	-0.191328	-0.529104
12	6	0	-0.942245	-1.214342	-0.476227
13	6	0	-0.797577	-1.933385	-1.823947
14	6	0	-1.101288	-2.202064	0.683516
15	16	0	-3.694078	-0.580874	-0.707349
16	8	0	-4.382105	0.461494	-1.467119
17	8	0	-3.808877	-1.992470	-1.064456
18	6	0	-4.423939	-0.448065	1.020008
19	9	0	-4.216150	0.776154	1.512128
20	9	0	-5.736316	-0.677439	0.942923
21	9	0	-3.869150	-1.348045	1.834006
22	6	0	3.125829	2.888926	0.287218
23	8	0	4.301339	2.102080	0.588457
24	6	0	4.172950	0.736744	0.352402
25	6	0	4.305758	-0.120644	1.496983
26	6	0	4.314039	-1.486483	1.315166
27	6	0	4.310419	-1.971033	-0.014724
28	6	0	4.560172	-1.145942	-1.135273
29	6	0	4.550919	0.219255	-0.936613
30	6	0	4.751521	-1.754148	-2.501357
31	6	0	4.257974	-2.448943	2.473794
32	1	0	0.510145	4.388800	0.062068
33	1	0	-1.919787	4.503818	-0.255083
34	1	0	-3.317410	2.492314	-0.558965
35	1	0	0.144441	-2.490505	-1.816313
36	1	0	-1.618139	-2.631533	-1.998556
37	1	0	-0.760145	-1.213017	-2.646112
38	1	0	-0.183756	-2.794352	0.750284
39	1	0	-1.236088	-1.678445	1.633063
40	1	0	-1.940095	-2.882865	0.523874
41	1	0	4.249237	0.329233	2.482993
42	1	0	4.248773	-3.046078	-0.170454
43	1	0	4.678186	0.917805	-1.758021
44	1	0	5.490002	-2.562400	-2.482204
45	1	0	3.809094	-2.181612	-2.864881
46	1	0	5.081328	-1.005559	-3.226467

47	1	0	5.033180	-3.218497	2.394585
48	1	0	4.386130	-1.929942	3.427210
49	1	0	3.289627	-2.963154	2.497497
50	1	0	2.981937	3.591300	1.116628
51	1	0	3.302870	3.480750	-0.622426

27f-ene

Thermal correction to Gibbs Free Energy= 0.332044
Sum of electronic and thermal Free Energies= -1866.233065
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1867.09638085

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.824031	1.116542	0.252450
2	6	0	0.438011	0.865912	0.244841
3	6	0	-0.533554	1.849234	-0.027968
4	6	0	-0.035316	3.152761	-0.316030
5	6	0	1.328527	3.384214	-0.311407
6	6	0	2.295833	2.381043	-0.026832
7	6	0	0.140954	-0.464428	0.571841
8	6	0	-1.172992	-0.863711	0.604892
9	6	0	-2.195806	0.082860	0.290391
10	6	0	-1.895567	1.414019	0.019659
11	7	0	2.464060	-0.118806	0.576528
12	6	0	1.425431	-1.232953	0.858901
13	6	0	1.495323	-1.660721	2.332020
14	6	0	1.594005	-2.423191	-0.091424
15	16	0	4.101088	-0.314334	0.629038
16	8	0	4.732818	0.920425	1.088498
17	8	0	4.410346	-1.607771	1.231698
18	6	0	4.625735	-0.463154	-1.170434
19	9	0	4.238127	0.618857	-1.850322
20	9	0	5.954898	-0.563426	-1.214037
21	9	0	4.084187	-1.548767	-1.725315
22	6	0	-3.020538	2.397260	-0.180829
23	8	0	-4.210196	2.021720	0.538887
24	6	0	-4.649299	0.760669	0.269657
25	6	0	-3.641561	-0.377103	0.329821
26	6	0	-4.062374	-1.491629	-0.637546
27	6	0	-5.497257	-1.792554	-0.581806
28	6	0	-6.407202	-0.854565	-0.214693
29	6	0	-5.958011	0.503837	0.092818
30	6	0	-7.887397	-1.125765	-0.209322

31	6	0	-3.228849	-2.174553	-1.440466
32	1	0	-0.713792	3.967143	-0.546461
33	1	0	1.691512	4.383504	-0.533719
34	1	0	3.349672	2.623971	-0.029207
35	1	0	-1.454114	-1.880279	0.860689
36	1	0	0.652725	-2.325449	2.546755
37	1	0	2.422008	-2.196153	2.544580
38	1	0	1.423762	-0.792587	2.992855
39	1	0	0.769806	-3.122241	0.079420
40	1	0	1.559684	-2.102803	-1.135155
41	1	0	2.530123	-2.953570	0.093681
42	1	0	-5.828888	-2.765192	-0.937722
43	1	0	-6.680875	1.312897	0.141971
44	1	0	-8.414320	-0.443375	-0.888510
45	1	0	-8.111275	-2.151888	-0.513248
46	1	0	-8.313567	-0.962978	0.788935
47	1	0	-3.603674	-2.996640	-2.044977
48	1	0	-2.174634	-1.941378	-1.530972
49	1	0	-2.754015	3.381174	0.210349
50	1	0	-3.270738	2.514408	-1.245386
51	1	0	-3.796642	-0.826691	1.328992

27f

Thermal correction to Gibbs Free Energy= 0.331793
Sum of electronic and thermal Free Energies= -1866.295931
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1867.15414149

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.826129	1.097686	0.286628
2	6	0	0.442774	0.871771	0.147116
3	6	0	-0.499746	1.893005	-0.091225
4	6	0	0.032278	3.211942	-0.208066
5	6	0	1.392726	3.418385	-0.077543
6	6	0	2.328573	2.375693	0.176165
7	6	0	0.106939	-0.476838	0.311932
8	6	0	-1.208430	-0.863266	0.215083
9	6	0	-2.207174	0.119367	-0.078427
10	6	0	-1.856870	1.473483	-0.189518
11	7	0	2.426234	-0.175430	0.532357
12	6	0	1.357418	-1.293304	0.618276
13	6	0	1.302615	-1.868540	2.040940
14	6	0	1.592851	-2.382431	-0.433765
15	16	0	4.048251	-0.400935	0.724421

16	8	0	4.639369	0.764862	1.377426
17	8	0	4.289974	-1.758232	1.205777
18	6	0	4.745766	-0.361733	-1.020765
19	9	0	4.472104	0.811484	-1.596332
20	9	0	6.067623	-0.523684	-0.948234
21	9	0	4.221569	-1.344755	-1.754781
22	6	0	-2.982852	2.449068	-0.394919
23	8	0	-4.116616	2.080837	0.407078
24	6	0	-4.560672	0.809464	0.166481
25	6	0	-3.648964	-0.220620	-0.171962
26	6	0	-4.196838	-1.482008	-0.521234
27	6	0	-5.579539	-1.677414	-0.413971
28	6	0	-6.456729	-0.678526	0.024247
29	6	0	-5.928348	0.584883	0.296893
30	6	0	-7.932529	-0.950115	0.178558
31	6	0	-3.377087	-2.636488	-1.058201
32	1	0	-0.618613	4.057304	-0.403358
33	1	0	1.780217	4.429055	-0.168174
34	1	0	3.380790	2.602727	0.280943
35	1	0	-1.494152	-1.891861	0.386489
36	1	0	0.433544	-2.528708	2.121443
37	1	0	2.199376	-2.446141	2.270295
38	1	0	1.193182	-1.068612	2.778248
39	1	0	0.753759	-3.083869	-0.400703
40	1	0	1.642661	-1.955919	-1.438269
41	1	0	2.508709	-2.941680	-0.232476
42	1	0	-5.985927	-2.646723	-0.692059
43	1	0	-6.566584	1.414854	0.584842
44	1	0	-8.532973	-0.078957	-0.101940
45	1	0	-8.249823	-1.797987	-0.435578
46	1	0	-8.179651	-1.189946	1.220793
47	1	0	-4.006174	-3.274731	-1.685444
48	1	0	-2.530856	-2.301359	-1.663086
49	1	0	-2.980273	-3.273425	-0.258153
50	1	0	-2.717819	3.457201	-0.074227
51	1	0	-3.292271	2.493827	-1.451274

27f-DA

Thermal correction to Gibbs Free Energy= 0.332166
Sum of electronic and thermal Free Energies= -1866.217687
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1867.08232050

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-1.409650	1.223298	-0.424295
2	6	0	-0.016138	1.152342	-0.235634
3	6	0	0.784301	2.319673	-0.076086
4	6	0	0.113453	3.569362	-0.114850
5	6	0	-1.257058	3.609841	-0.305015
6	6	0	-2.052007	2.445591	-0.465226
7	6	0	0.440656	-0.196230	-0.237080
8	6	0	1.790235	-0.417295	-0.066346
9	6	0	2.556025	0.748498	0.095130
10	6	0	2.175266	2.051475	0.103048
11	7	0	-1.891469	-0.119323	-0.534982
12	6	0	-0.734601	-1.141941	-0.461982
13	6	0	-0.600086	-1.881514	-1.802103
14	6	0	-0.911787	-2.113584	0.711382
15	16	0	-3.484335	-0.509633	-0.706299
16	8	0	-4.166907	0.515471	-1.492653
17	8	0	-3.600443	-1.928899	-1.031031
18	6	0	-4.216349	-0.337349	1.017391
19	9	0	-4.010828	0.897218	1.482118
20	9	0	-5.527427	-0.571012	0.942140
21	9	0	-3.660135	-1.218804	1.850248
22	6	0	3.428672	2.875367	0.310012
23	8	0	4.519120	1.912302	0.419477
24	6	0	4.027266	0.578838	0.285828
25	6	0	4.156447	-0.345615	1.502848
26	6	0	3.482005	-1.495396	1.365800
27	6	0	2.749590	-1.623983	0.000642
28	6	0	3.815396	-1.369492	-1.101983
29	6	0	4.486498	-0.221282	-0.939399
30	6	0	3.993891	-2.368533	-2.203579
31	6	0	3.373594	-2.600919	2.370560
32	1	0	0.676507	4.490224	0.001804
33	1	0	-1.758571	4.572779	-0.336574
34	1	0	-3.118774	2.535247	-0.617792
35	1	0	0.304039	-2.497051	-1.778468
36	1	0	-1.456467	-2.533124	-1.981868
37	1	0	-0.510761	-1.171865	-2.629089
38	1	0	-0.020780	-2.744189	0.777440
39	1	0	-1.021231	-1.576055	1.656082
40	1	0	-1.775600	-2.764474	0.563672
41	1	0	4.718457	-0.040002	2.379461
42	1	0	2.255408	-2.589233	-0.115622
43	1	0	5.256984	0.162864	-1.600008
44	1	0	4.264127	-3.355539	-1.806000
45	1	0	3.064377	-2.502812	-2.772482
46	1	0	4.776354	-2.057212	-2.901641

47	1	0	3.751388	-3.547841	1.963242
48	1	0	3.938449	-2.371848	3.278862
49	1	0	2.327799	-2.776673	2.655428
50	1	0	3.397786	3.478997	1.227032
51	1	0	3.637791	3.552669	-0.529074

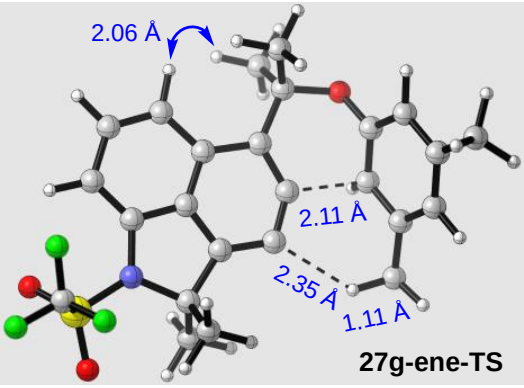
27g-benz

Thermal correction to Gibbs Free Energy= 0.373764
Sum of electronic and thermal Free Energies= -1944.742571
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1945.67167129

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.413787	2.848769	-0.745691
2	6	0	-2.588029	2.047998	-0.725157
3	6	0	-0.137387	2.344517	-0.585194
4	1	0	-1.535018	3.917357	-0.898364
5	6	0	-2.419191	0.696106	-0.530105
6	1	0	-3.559203	2.503094	-0.863633
7	6	0	0.067598	0.944368	-0.385054
8	1	0	0.702632	3.027092	-0.614377
9	6	0	-1.124091	0.156298	-0.364516
10	7	0	-3.341805	-0.394804	-0.441353
11	6	0	1.337825	0.251357	-0.206442
12	6	0	-1.185955	-1.246461	-0.189956
13	6	0	-2.618127	-1.747117	-0.254667
14	16	0	-4.980544	-0.215961	-0.536136
15	6	0	1.063302	-1.073899	-0.050681
16	6	0	2.745249	0.827231	-0.196878
17	6	0	0.051499	-1.831812	-0.025825
18	6	0	-3.025071	-2.448045	1.046207
19	6	0	-2.823714	-2.647677	-1.481593
20	8	0	-5.307753	0.885823	-1.438092
21	8	0	-5.597611	-1.531980	-0.672264
22	6	0	-5.494394	0.401343	1.164187
23	6	0	2.950740	1.811177	0.962304
24	8	0	3.540311	-0.385464	0.019282
25	6	0	3.102888	1.461057	-1.547761
26	1	0	-2.379548	-3.321063	1.180500
27	1	0	-2.893161	-1.790166	1.908340
28	1	0	-4.060508	-2.791927	1.007803
29	1	0	-2.149588	-3.505925	-1.401009
30	1	0	-3.850174	-3.013049	-1.536929

31	1	0	-2.584366	-2.109453	-2.402808
32	9	0	-6.806851	0.637164	1.145632
33	9	0	-5.224981	-0.516895	2.093160
34	9	0	-4.843651	1.529505	1.458211
35	1	0	3.989073	2.152008	0.992037
36	1	0	2.313577	2.690329	0.843450
37	1	0	2.706264	1.337696	1.916870
38	6	0	4.917678	-0.316626	0.123446
39	1	0	4.139003	1.809636	-1.542955
40	1	0	2.976222	0.736445	-2.356533
41	1	0	2.461299	2.320381	-1.755049
42	6	0	5.710803	-0.473575	-1.015973
43	6	0	5.509377	-0.210770	1.386867
44	6	0	7.107769	-0.498965	-0.906063
45	1	0	5.232587	-0.588030	-1.983760
46	6	0	6.902026	-0.239094	1.519006
47	1	0	4.873981	-0.122757	2.262526
48	6	0	7.684481	-0.376286	0.363683
49	6	0	7.967251	-0.642058	-2.139951
50	6	0	7.546235	-0.163051	2.883124
51	1	0	8.767831	-0.398478	0.457546
52	1	0	7.982121	0.287124	-2.723348
53	1	0	9.001495	-0.884854	-1.880213
54	1	0	7.588956	-1.428852	-2.801386
55	1	0	8.547011	0.276101	2.828912
56	1	0	6.947452	0.434769	3.577071
57	1	0	7.653334	-1.162182	3.324613

27g-ene-TS

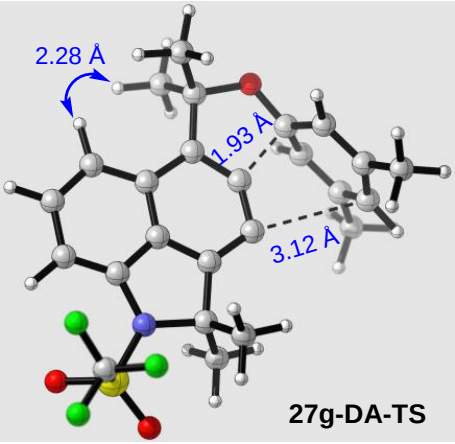


One imaginary frequency: -155.84 cm^{-1}
Thermal correction to Gibbs Free Energy= 0.378926
Sum of electronic and thermal Free Energies= -1944.732231
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1945.67063229

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.904350	1.044037	-0.298631
2	6	0	-0.524350	0.758707	-0.406043
3	6	0	-2.333490	2.322233	-0.028058
4	7	0	-2.601584	-0.188801	-0.505296
5	6	0	0.500085	1.731002	-0.249681
6	6	0	-0.302062	-0.602220	-0.681765
7	6	0	-1.325990	3.310981	0.136711
8	1	0	-3.378744	2.586254	0.057532
9	6	0	-1.626412	-1.348314	-0.806578
10	16	0	-4.242350	-0.331979	-0.446936
11	6	0	0.027333	3.051995	0.036309
12	6	0	1.874428	1.270968	-0.391552
13	6	0	1.005216	-1.024865	-0.800298
14	1	0	-1.644689	4.326592	0.353549
15	6	0	-1.823650	-1.866175	-2.237803
16	6	0	-1.733221	-2.471885	0.228863
17	8	0	-4.871263	0.895736	-0.930385
18	8	0	-4.629365	-1.644449	-0.957196
19	6	0	-4.657285	-0.373864	1.385998
20	1	0	0.714007	3.874404	0.181909
21	6	0	1.911570	-0.087079	-0.644545
22	6	0	3.069807	2.219123	-0.251812
23	1	0	2.242113	-2.926805	-1.413256
24	1	0	-0.994154	-2.538273	-2.478269
25	1	0	-2.761555	-2.414265	-2.340138
26	1	0	-1.811756	-1.040343	-2.954810
27	1	0	-0.921859	-3.182078	0.044030
28	1	0	-1.620138	-2.083973	1.244048
29	1	0	-2.682544	-3.005833	0.148867
30	9	0	-4.210478	0.733599	1.983975
31	9	0	-5.983518	-0.443576	1.515742
32	9	0	-4.103097	-1.439836	1.966194
33	6	0	3.891490	-0.739304	-0.998272
34	8	0	4.345193	1.532158	-0.530601
35	6	0	3.185231	2.780276	1.173768
36	6	0	3.069045	3.322509	-1.316963
37	6	0	3.331409	-3.124720	-1.508882
38	6	0	4.473634	0.234195	-0.151749
39	6	0	4.015985	-2.118696	-0.653289
40	1	0	3.704002	-0.467485	-2.032434
41	1	0	4.073906	3.414615	1.241727
42	1	0	2.313331	3.375805	1.450110
43	1	0	3.276536	1.966540	1.898443

44	1	0	3.020571	2.880997	-2.315879
45	1	0	2.230472	4.009540	-1.202196
46	1	0	3.997278	3.895517	-1.235075
47	1	0	3.541965	-4.152721	-1.204180
48	1	0	3.573294	-3.003046	-2.570158
49	6	0	5.128199	-0.125322	1.020359
50	6	0	4.662467	-2.454523	0.530871
51	6	0	5.239499	-1.479851	1.367073
52	1	0	5.555809	0.647099	1.651086
53	1	0	4.746076	-3.502027	0.809175
54	6	0	5.932214	-1.888002	2.640582
55	1	0	5.202531	-2.028492	3.448588
56	1	0	6.463161	-2.836900	2.518302
57	1	0	6.645568	-1.128325	2.971657

27g-DA-TS



One imaginary frequency: -185.52 cm^{-1}
Thermal correction to Gibbs Free Energy= 0.377509
Sum of electronic and thermal Free Energies= -1944.733085
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1945.67194673

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.745939	1.068081	-0.444702
2	6	0	-0.359892	0.864441	-0.283225
3	6	0	0.572091	1.927143	-0.149370
4	6	0	0.021472	3.243351	-0.187671
5	6	0	-1.340031	3.420251	-0.348573
6	6	0	-2.262137	2.344734	-0.482000
7	6	0	-0.025003	-0.507372	-0.281426
8	6	0	1.299940	-0.867454	-0.135107

9	6	0	2.121598	0.165953	-0.009383
10	6	0	1.946068	1.527353	0.003983
11	7	0	-2.346624	-0.228955	-0.535718
12	6	0	-1.283186	-1.351165	-0.478371
13	6	0	-1.225025	-2.105846	-1.813324
14	6	0	-1.509081	-2.298356	0.703732
15	16	0	-3.967108	-0.477945	-0.686623
16	8	0	-4.570290	0.602984	-1.464291
17	8	0	-4.211590	-1.881964	-1.006512
18	6	0	-4.661807	-0.243277	1.044480
19	9	0	-4.377841	0.982180	1.493296
20	9	0	-5.986311	-0.398717	0.990585
21	9	0	-4.148985	-1.147370	1.881472
22	6	0	3.174646	2.396260	0.169837
23	8	0	4.310428	1.465654	0.273315
24	6	0	4.034162	0.110726	0.212360
25	6	0	4.046123	-0.634028	1.438860
26	6	0	3.901521	-2.006379	1.400972
27	6	0	3.858937	-2.626462	0.132065
28	6	0	4.191579	-1.952020	-1.064455
29	6	0	4.334370	-0.580188	-1.008801
30	6	0	3.453024	3.283922	-1.048549
31	6	0	3.163593	3.213441	1.467493
32	6	0	4.315245	-2.715258	-2.358807
33	6	0	3.727906	-2.824628	2.655229
34	1	0	0.664403	4.111443	-0.096431
35	1	0	-1.736704	4.431166	-0.378095
36	1	0	-3.316963	2.545557	-0.612111
37	1	0	-0.337450	-2.746145	-1.807457
38	1	0	-2.108603	-2.728839	-1.962371
39	1	0	-1.135018	-1.407224	-2.650084
40	1	0	-0.644472	-2.965446	0.770683
41	1	0	-1.584934	-1.745963	1.643419
42	1	0	-2.405584	-2.907478	0.569492
43	1	0	4.042620	-0.084718	2.374899
44	1	0	3.686838	-3.699981	0.088063
45	1	0	4.542276	0.009246	-1.896021
46	1	0	2.678351	4.046514	-1.165974
47	1	0	4.416438	3.788194	-0.924962
48	1	0	3.486445	2.685699	-1.963197
49	1	0	2.383134	3.978874	1.445650
50	1	0	2.985265	2.566130	2.330548
51	1	0	4.129595	3.711127	1.597348
52	1	0	4.976351	-3.581875	-2.253101
53	1	0	3.334996	-3.090039	-2.677480
54	1	0	4.706885	-2.080649	-3.157938

55	1	0	4.395786	-3.692443	2.665295
56	1	0	3.928252	-2.227862	3.548881
57	1	0	2.700993	-3.203050	2.727197

27g

Thermal correction to Gibbs Free Energy= 0.383965
Sum of electronic and thermal Free Energies= -1944.809803
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1945.75499427

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.505617	1.166329	-0.454256
2	6	0	-0.129680	0.925192	-0.274788
3	6	0	0.816939	1.984014	-0.158260
4	6	0	0.303527	3.306188	-0.226924
5	6	0	-1.053317	3.514625	-0.404342
6	6	0	-1.991103	2.457209	-0.523940
7	6	0	0.149913	-0.469792	-0.238401
8	6	0	1.460805	-0.856631	-0.071460
9	6	0	2.375166	0.204036	0.040114
10	6	0	2.168656	1.545569	0.011995
11	7	0	-2.154831	-0.106885	-0.524122
12	6	0	-1.136650	-1.265660	-0.428367
13	6	0	-1.105638	-2.052015	-1.748172
14	6	0	-1.428670	-2.172951	0.772722
15	16	0	-3.783760	-0.297431	-0.694199
16	8	0	-4.330536	0.780280	-1.515606
17	8	0	-4.077291	-1.700442	-0.975187
18	6	0	-4.495076	0.015938	1.018310
19	9	0	-4.181256	1.245837	1.431921
20	9	0	-5.822007	-0.103238	0.947498
21	9	0	-4.020693	-0.875973	1.890111
22	6	0	3.526484	2.228709	0.179279
23	8	0	4.479611	1.099345	0.294088
24	6	0	3.813592	-0.155125	0.218881
25	6	0	3.836886	-1.045513	1.468949
26	6	0	3.012656	-2.098406	1.384695
27	6	0	2.248998	-2.177242	0.033342
28	6	0	3.321155	-2.111276	-1.088759
29	6	0	4.140962	-1.057456	-0.978800
30	6	0	3.940156	3.051935	-1.044069
31	6	0	3.634236	3.046791	1.469543
32	6	0	3.347974	-3.167373	-2.150552
33	6	0	2.774314	-3.143650	2.430923

34	1	0	0.975013	4.154436	-0.145232
35	1	0	-1.428439	4.532560	-0.458279
36	1	0	-3.040116	2.675296	-0.669330
37	1	0	-0.279513	-2.768543	-1.715440
38	1	0	-2.034785	-2.602368	-1.903190
39	1	0	-0.942370	-1.379798	-2.594930
40	1	0	-0.634114	-2.920579	0.848970
41	1	0	-1.450333	-1.600135	1.702646
42	1	0	-2.376487	-2.701046	0.651729
43	1	0	4.449869	-0.786130	2.326153
44	1	0	1.625962	-3.069345	-0.038788
45	1	0	4.946517	-0.806254	-1.661243
46	1	0	3.283916	3.918960	-1.170248
47	1	0	4.966360	3.413288	-0.923524
48	1	0	3.889101	2.445840	-1.952890
49	1	0	2.969403	3.916067	1.440250
50	1	0	3.365733	2.437389	2.337086
51	1	0	4.660205	3.405208	1.600735
52	1	0	3.487500	-4.165677	-1.715440
53	1	0	2.401350	-3.196672	-2.706244
54	1	0	4.155629	-2.993291	-2.867479
55	1	0	3.020522	-4.145677	2.055767
56	1	0	3.375828	-2.958365	3.325595
57	1	0	1.718528	-3.171871	2.731259

27g-ene

Thermal correction to Gibbs Free Energy= 0.383944
Sum of electronic and thermal Free Energies= -1944.815639
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1945.76098303

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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4	6	0	0.018005	2.946137	-0.427395
5	6	0	1.370670	3.220548	-0.511621
6	6	0	2.386037	2.284787	-0.182606
7	6	0	0.372881	-0.591980	0.676597
8	6	0	-0.914040	-1.058928	0.727238
9	6	0	-1.993722	-0.176872	0.416962
10	6	0	-1.790825	1.180193	0.155890
11	7	0	2.671811	-0.153930	0.577135
12	6	0	1.695699	-1.288223	0.964197

13	6	0	1.827784	-1.616693	2.459120
14	6	0	1.884334	-2.529726	0.086015
15	16	0	4.316745	-0.275074	0.596232
16	8	0	4.906446	1.008747	0.968674
17	8	0	4.697430	-1.518417	1.260521
18	6	0	4.802456	-0.507408	-1.205227
19	9	0	4.370843	0.524895	-1.933795
20	9	0	6.132636	-0.576049	-1.275735
21	9	0	4.277463	-1.635414	-1.686629
22	6	0	-2.997826	2.127383	0.083519
23	8	0	-4.172629	1.505474	0.702181
24	6	0	-4.486303	0.239249	0.337655
25	6	0	-3.380981	-0.789071	0.408278
26	6	0	-3.649550	-1.908509	-0.609301
27	6	0	-5.050002	-2.347216	-0.625263
28	6	0	-6.061449	-1.509669	-0.281294
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30	6	0	-2.838141	3.373008	0.967719
31	6	0	-3.366435	2.489638	-1.361424
32	6	0	-7.507645	-1.918693	-0.355995
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36	1	0	3.429281	2.559784	-0.254499
37	1	0	-1.138757	-2.087415	0.990831
38	1	0	1.018824	-2.296276	2.744391
39	1	0	2.780932	-2.101865	2.675258
40	1	0	1.742208	-0.709983	3.064210
41	1	0	1.098519	-3.250592	0.330619
42	1	0	1.800952	-2.279698	-0.974151
43	1	0	2.848839	-3.006783	0.269874
44	1	0	-5.270155	-3.336491	-1.019599
45	1	0	-6.554735	0.608642	0.133470
46	1	0	-2.116307	4.085062	0.572272
47	1	0	-3.808557	3.873214	1.030371
48	1	0	-2.531415	3.088466	1.977904
49	1	0	-2.535984	2.991239	-1.865217
50	1	0	-3.612584	1.589533	-1.932686
51	1	0	-4.233858	3.157132	-1.370926
52	1	0	-8.064759	-1.267872	-1.042070
53	1	0	-7.618991	-2.951362	-0.697555
54	1	0	-7.993770	-1.827194	0.623851
55	1	0	-3.001439	-3.308308	-2.049607
56	1	0	-1.696233	-2.147834	-1.443140
57	1	0	-3.520448	-1.282408	1.389035

27g'

Thermal correction to Gibbs Free Energy= 0.383740
Sum of electronic and thermal Free Energies= -1944.876426
E[SMD(chlorobenzene)/B3LYP-D3BJ/6-311+G(d,p)] = -1945.81696758

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.989664	1.017152	-0.312067
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3	6	0	0.391465	1.721675	-0.029456
4	6	0	-0.114908	3.041857	0.189351
5	6	0	-1.472680	3.293722	0.141467
6	6	0	-2.452031	2.299596	-0.124556
7	6	0	-0.343131	-0.616642	-0.442324
8	6	0	0.949594	-1.061697	-0.354625
9	6	0	2.002294	-0.131747	-0.084379
10	6	0	1.749271	1.253618	-0.020366
11	7	0	-2.649205	-0.225587	-0.563992
12	6	0	-1.631475	-1.377220	-0.725996
13	6	0	-1.651560	-1.906868	-2.167576
14	6	0	-1.864182	-2.493237	0.298335
15	16	0	-4.285883	-0.387669	-0.679804
16	8	0	-4.866856	0.821855	-1.258098
17	8	0	-4.600457	-1.715958	-1.198539
18	6	0	-4.894519	-0.391003	1.099085
19	9	0	-4.507138	0.727431	1.717256
20	9	0	-6.226773	-0.454195	1.087494
21	9	0	-4.409940	-1.446076	1.756014
22	6	0	2.964603	2.190286	0.072795
23	8	0	4.082000	1.565320	-0.634482
24	6	0	4.407567	0.289744	-0.290033
25	6	0	3.392847	-0.622643	0.061135
26	6	0	3.796997	-1.906633	0.511591
27	6	0	5.157936	-2.238785	0.473812
28	6	0	6.144925	-1.355214	0.021252
29	6	0	5.753257	-0.064968	-0.341762
30	6	0	2.842104	3.515304	-0.695513
31	6	0	3.369200	2.445975	1.532795
32	6	0	7.592184	-1.774505	-0.052663
33	6	0	2.856068	-2.940629	1.095680
34	1	0	0.548508	3.861260	0.421442
35	1	0	-1.818750	4.308049	0.318370
36	1	0	-3.500999	2.559213	-0.164767
37	1	0	1.187293	-2.103458	-0.517237
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39	1	0	-2.578902	-2.441169	-2.380195
40	1	0	-1.538250	-1.087727	-2.882896
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45	1	0	6.479009	0.682951	-0.646698
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47	1	0	3.855958	3.878454	-0.883300
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50	1	0	3.591895	1.511389	2.054711
51	1	0	4.254844	3.088641	1.573244
52	1	0	8.262966	-0.948495	0.204158
53	1	0	7.802253	-2.609599	0.622030
54	1	0	7.855200	-2.099301	-1.067661
55	1	0	3.402548	-3.578125	1.796720
56	1	0	2.020873	-2.487876	1.635708
57	1	0	2.433537	-3.603986	0.330966

IV. References for Supporting Information

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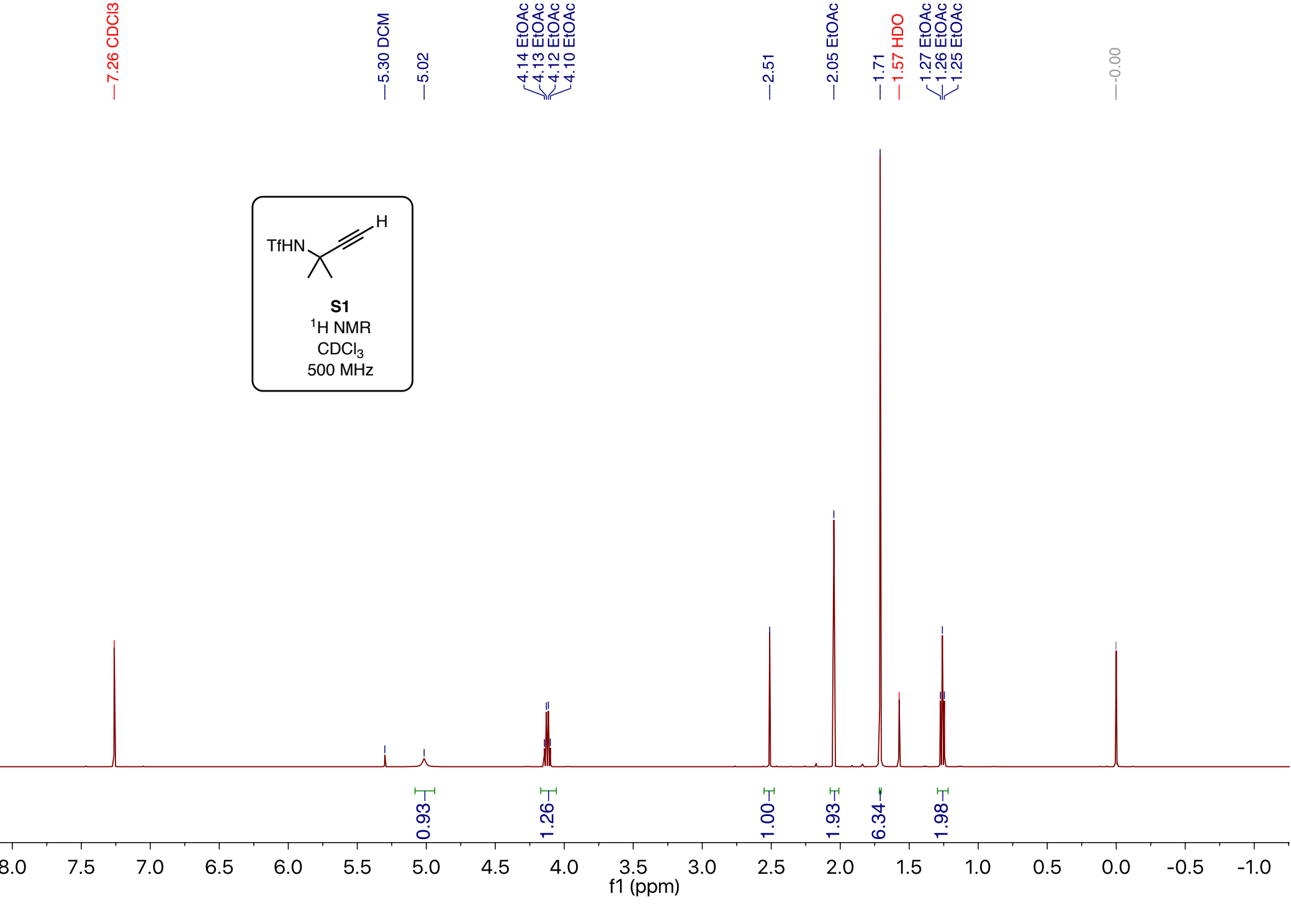
V. Copies of ^{1}H, and ^{13}C NMR spectra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1.71
1.57 HDO
1.27 EtOAc
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0.00
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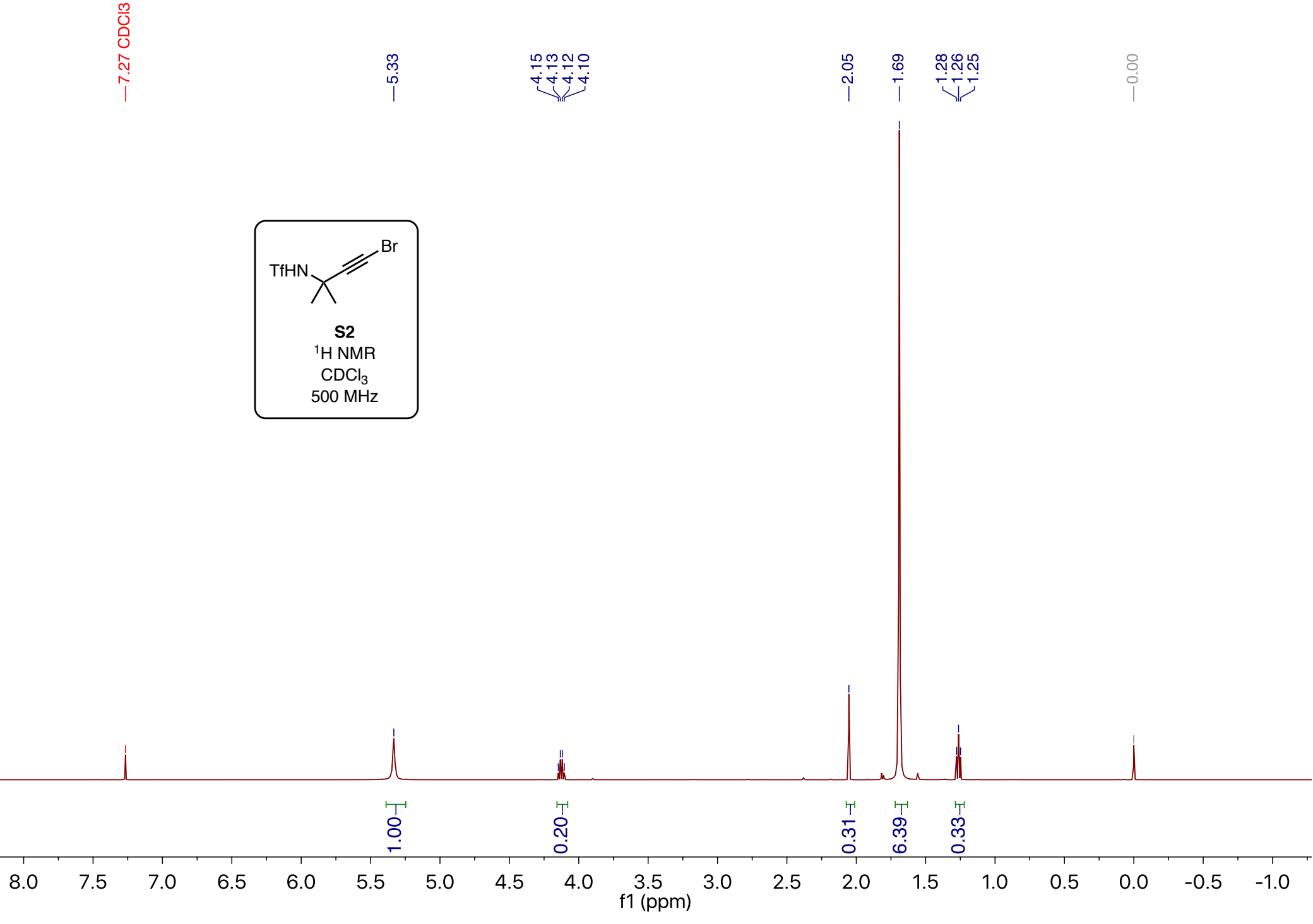
f1 (ppm)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0.33
8.0
7.5
7.0
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6.0
5.5
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4.5
4.0
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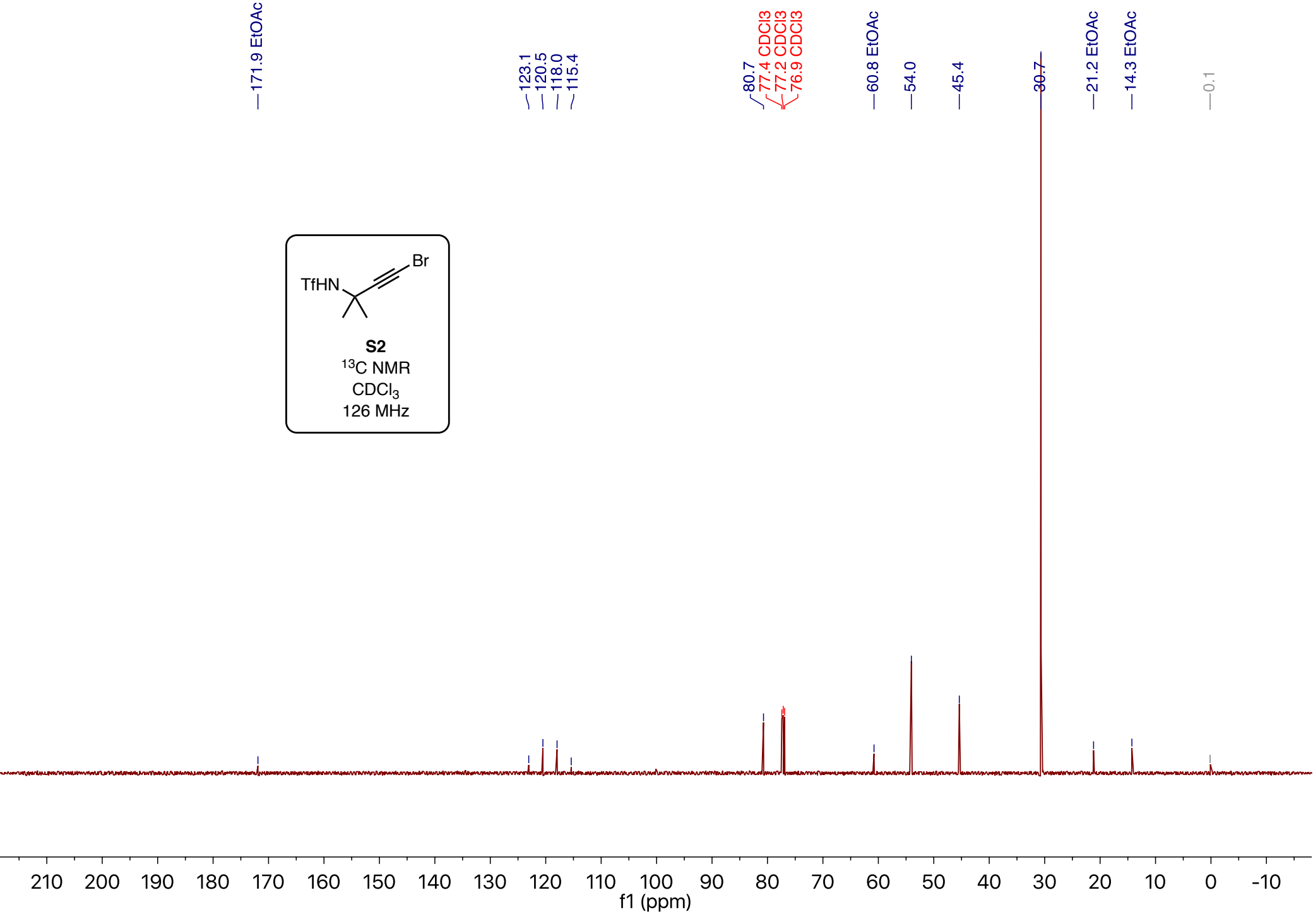
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45.4
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0.1
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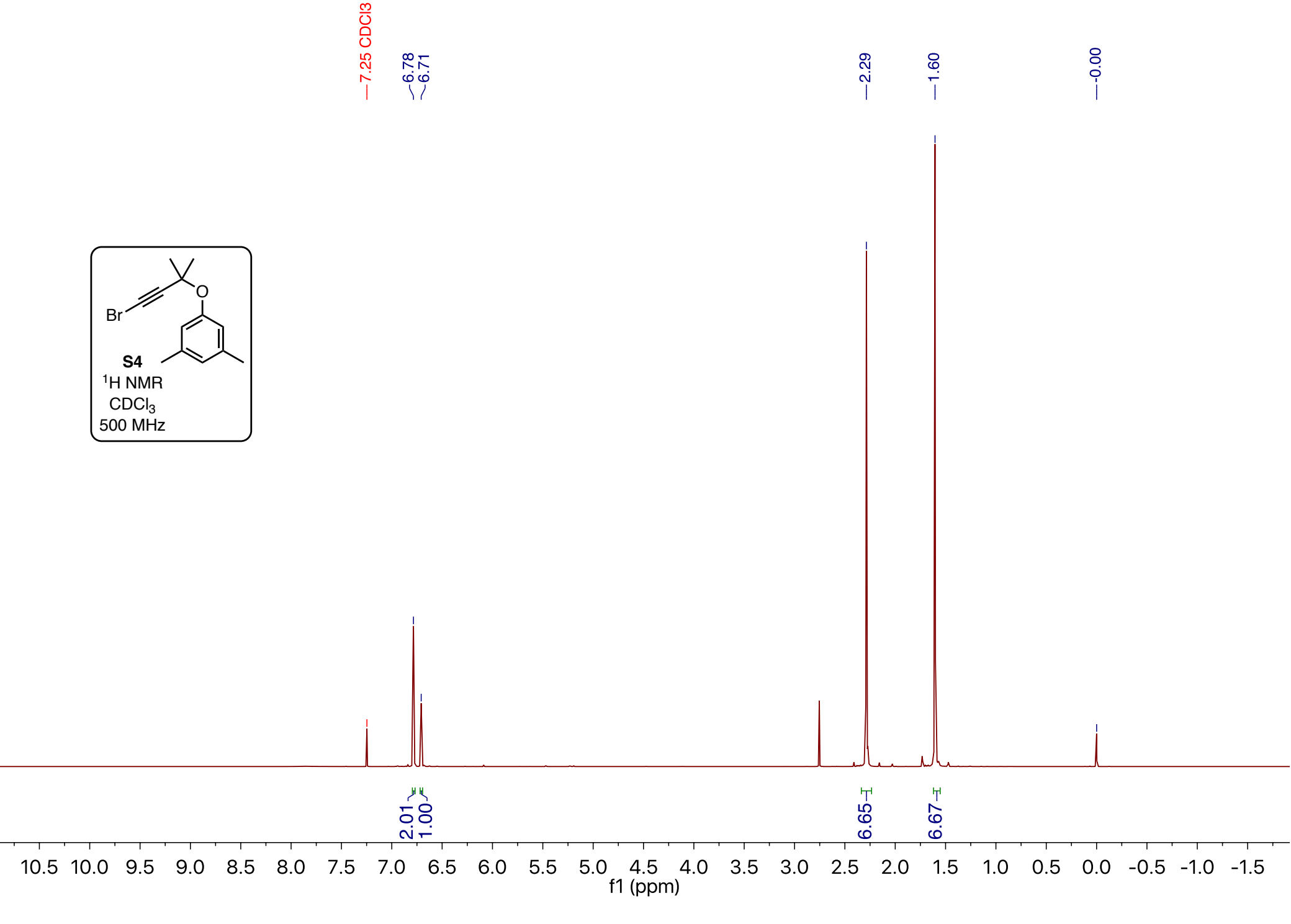
f1 (ppm)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1.00
6.65
6.67
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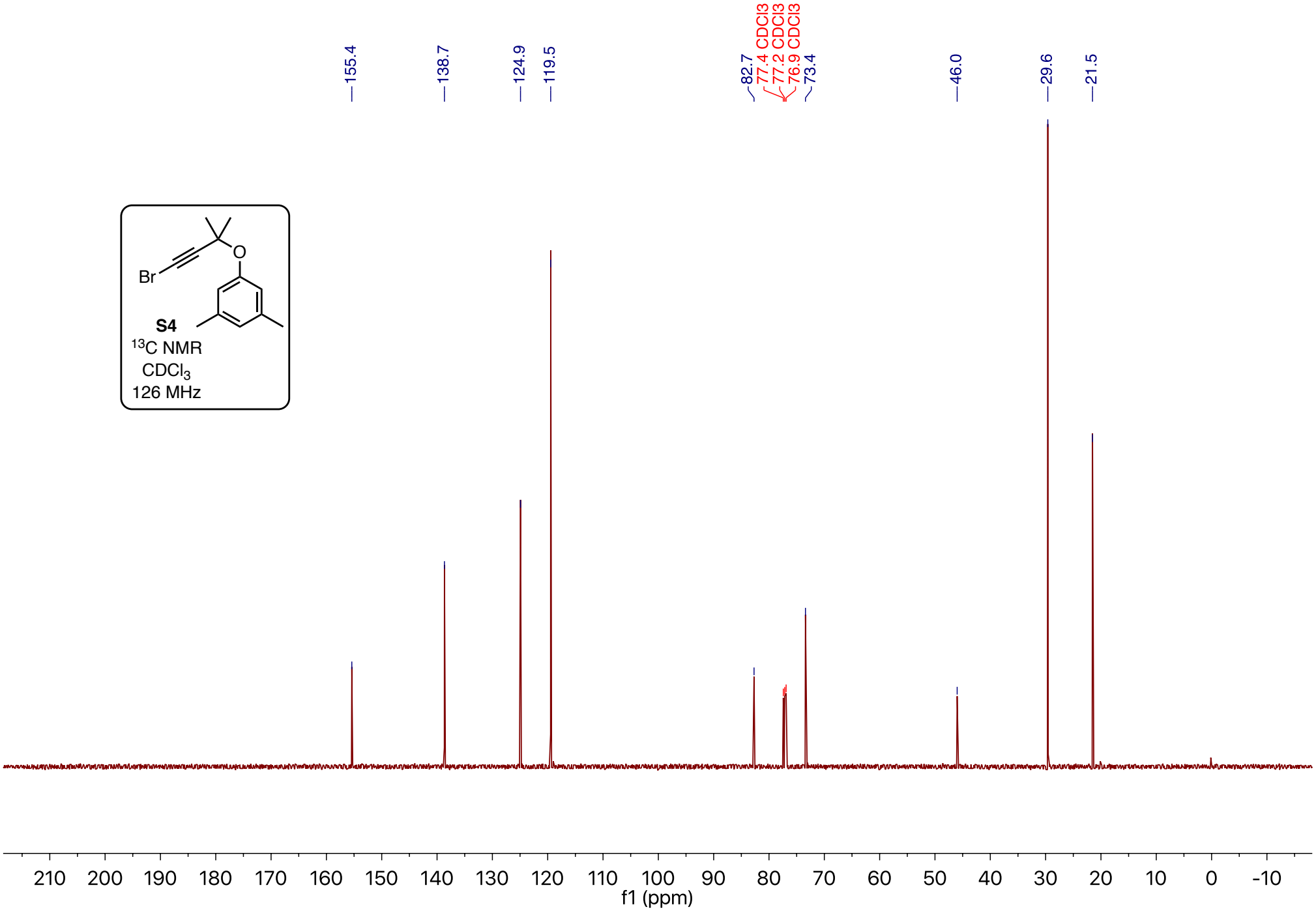
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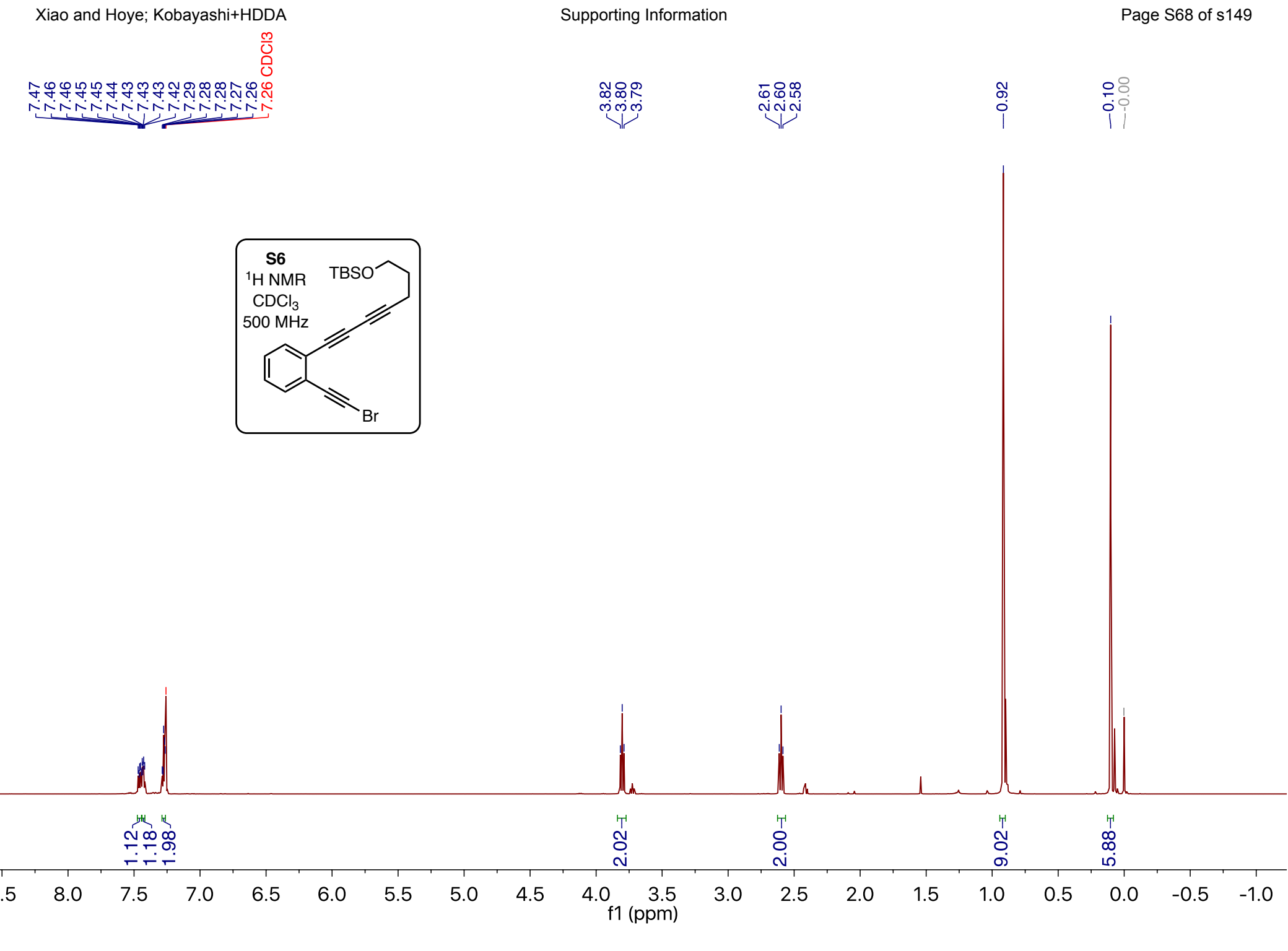
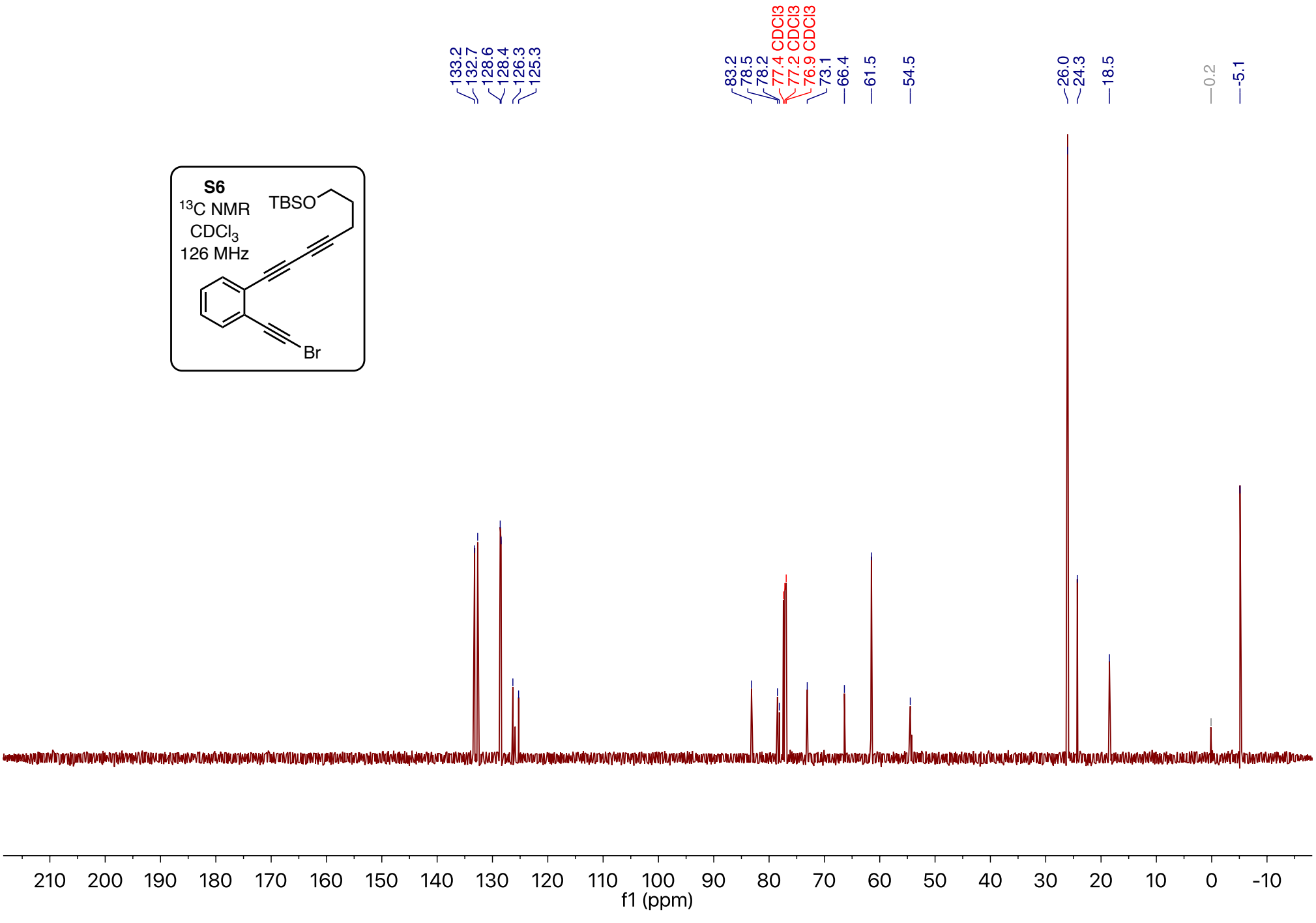
76.9 CDCl3
73.4
46.0
29.6
21.5
Br
O
S4
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.43
7.42
7.29
7.28
7.28
7.27
7.26
7.26 CDCl3
3.82
3.80
3.79
2.61
2.60
2.58
0.92
0.10
-0.00
S6
1H NMR
CDCl3
500 MHz
TBSO
Br
1.12
1.18
1.98
2.02
2.00
9.02
5.88
f1 (ppm)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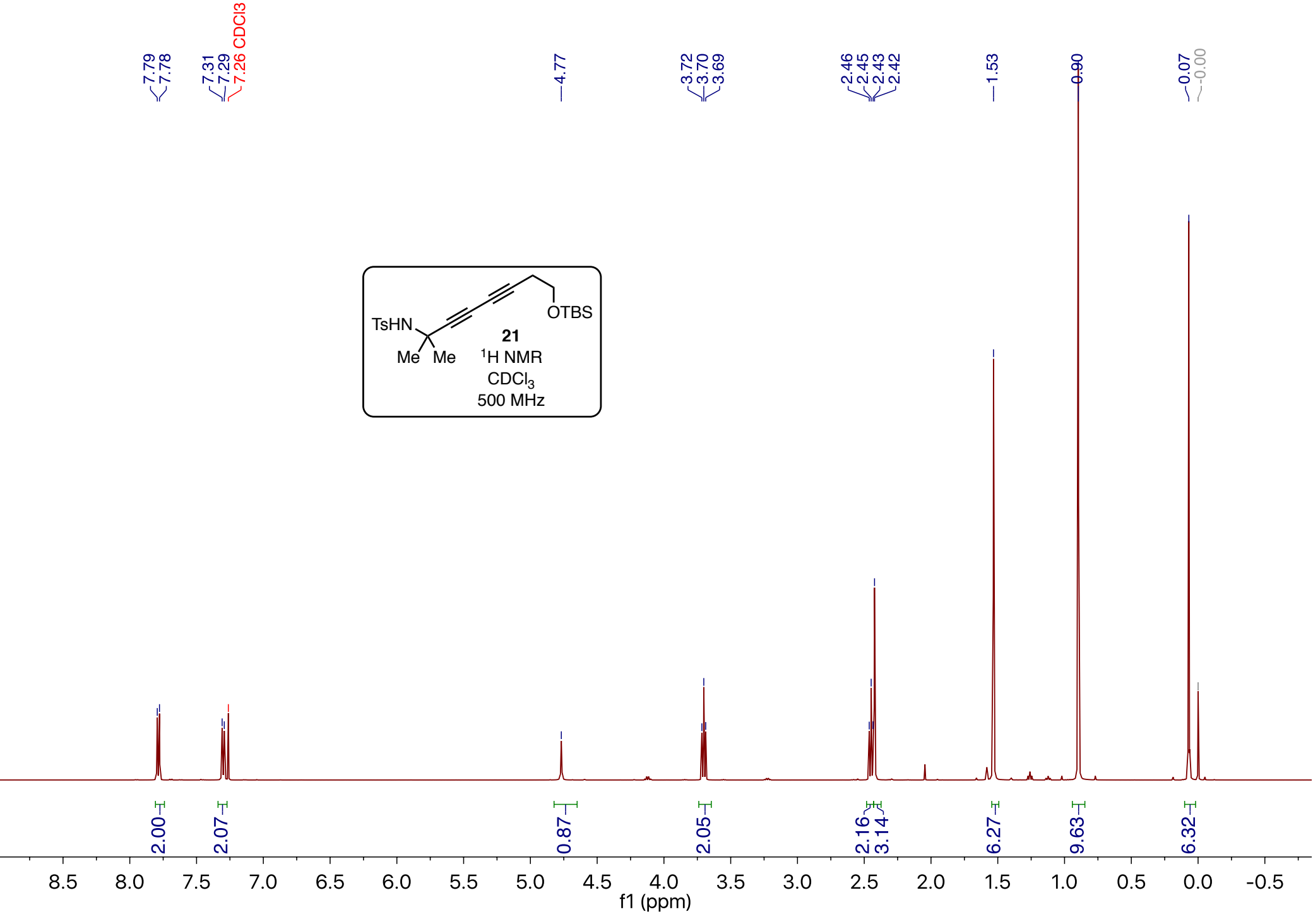
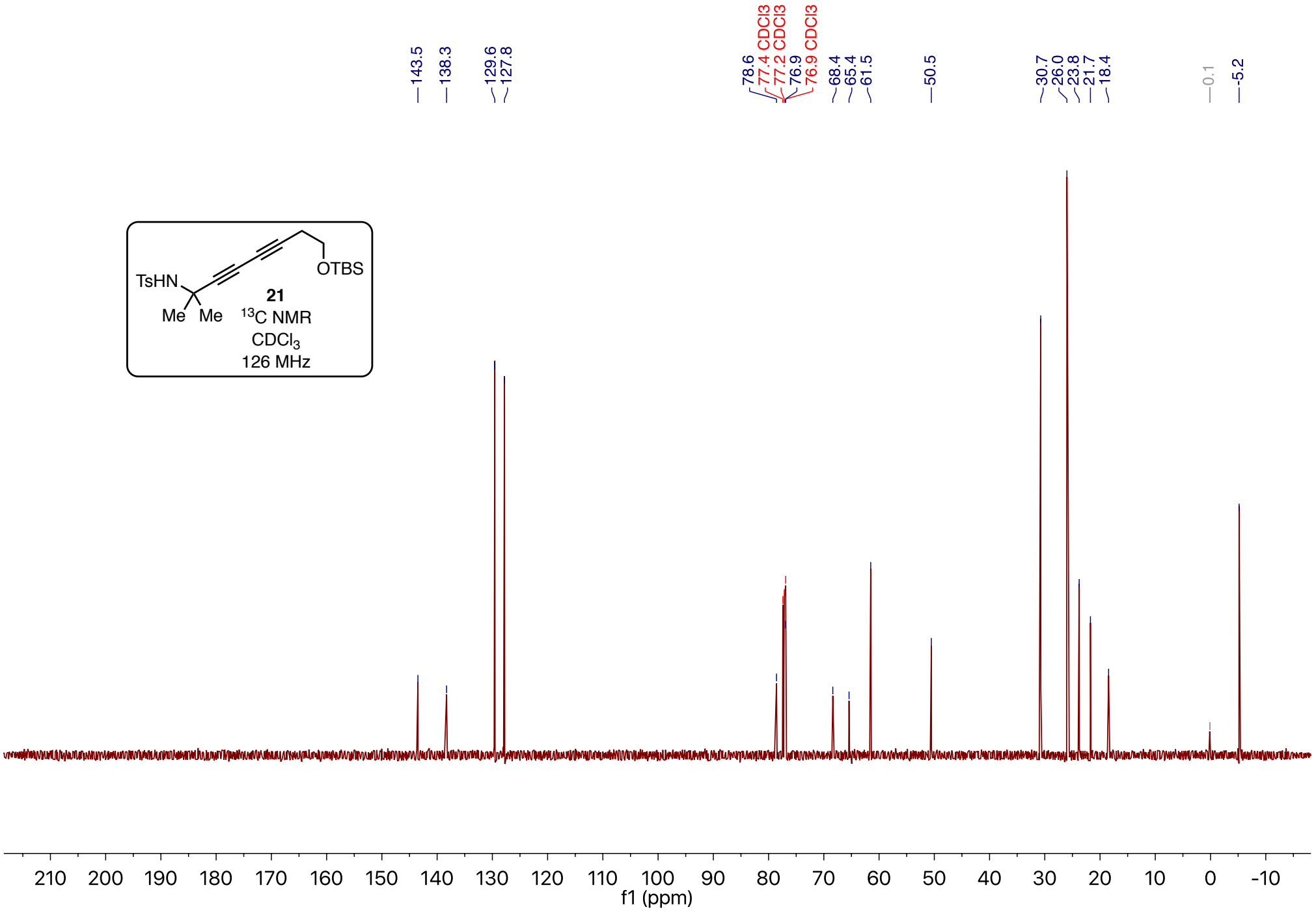
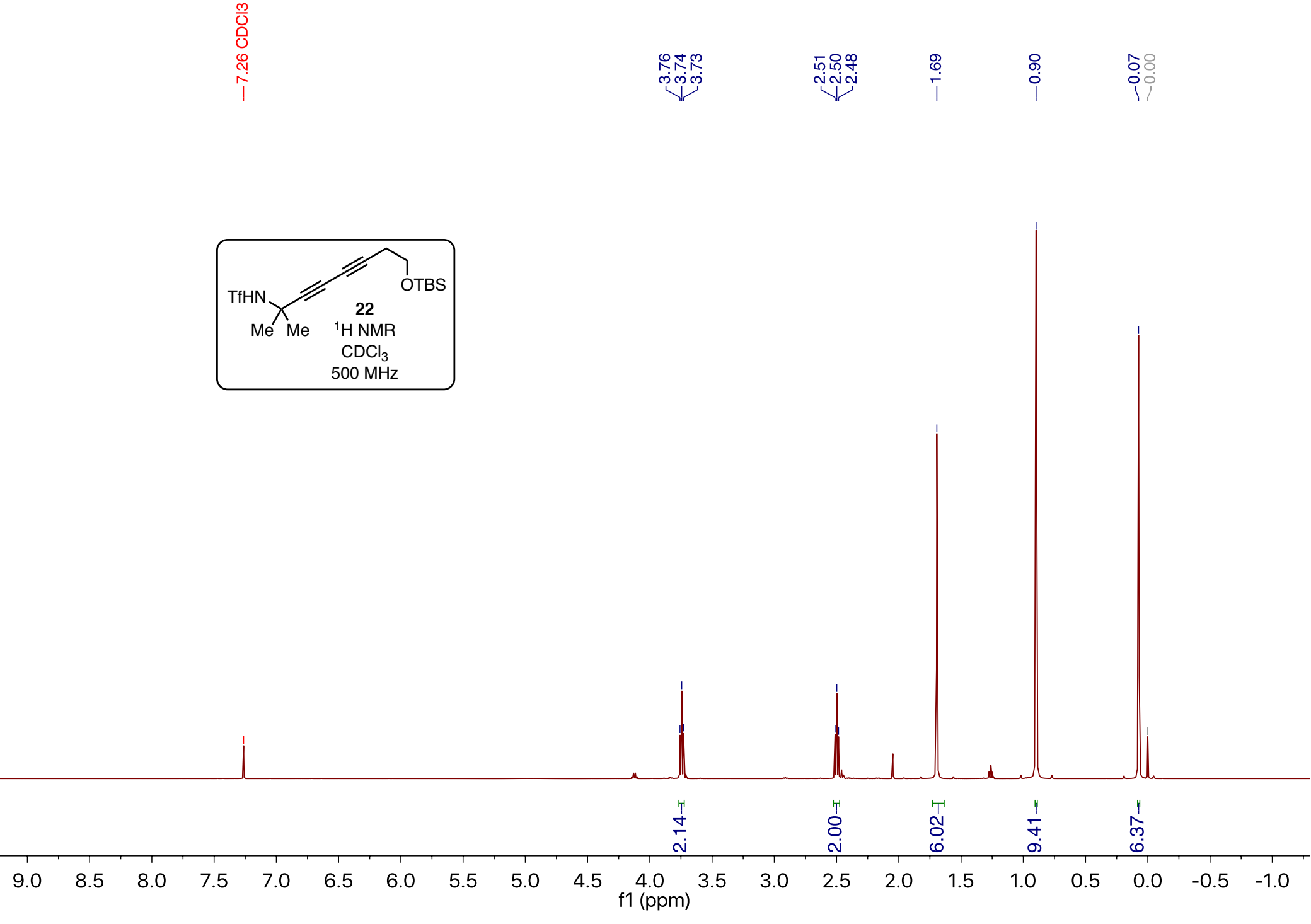
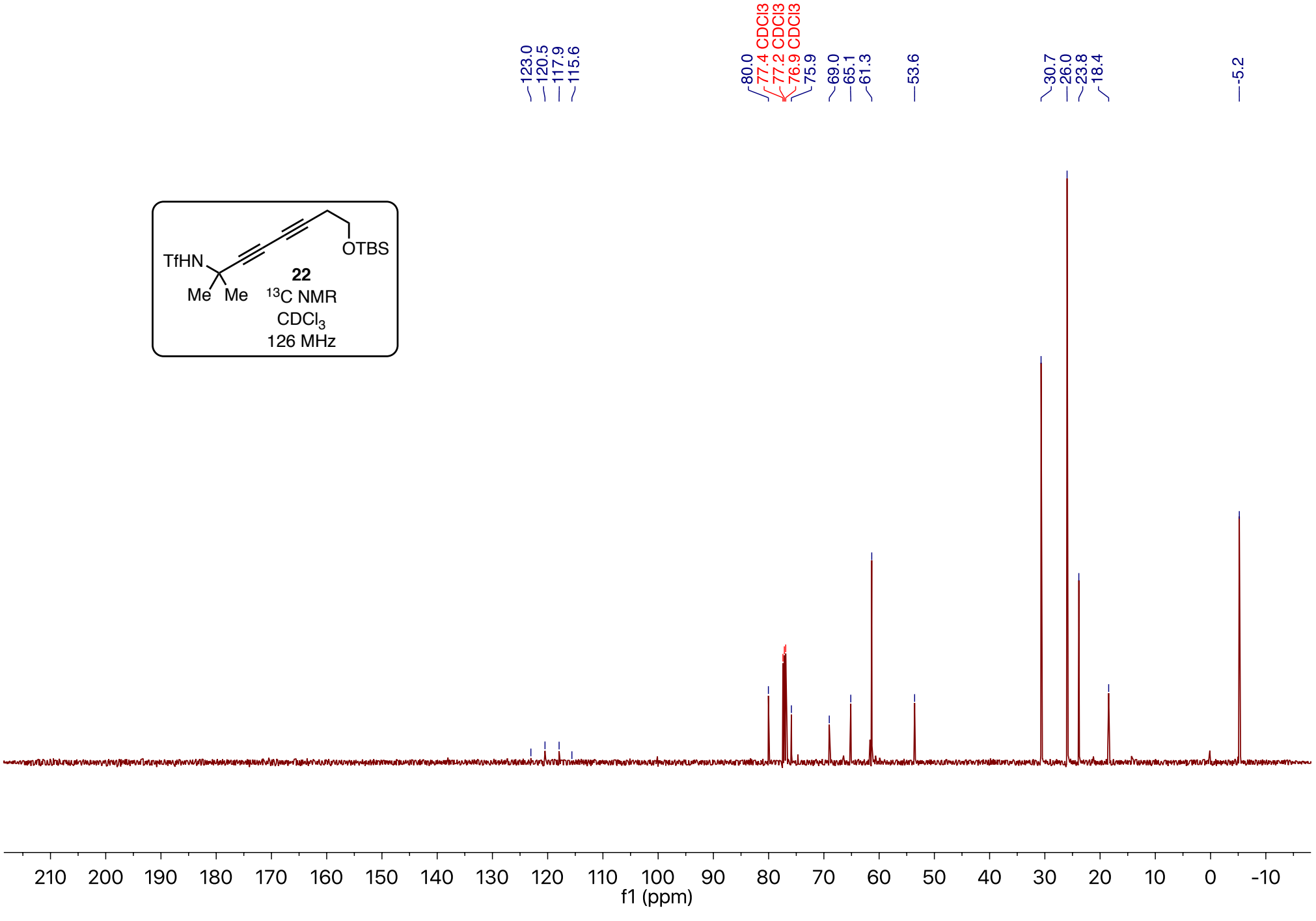
132.7
128.6
128.4
126.3
125.3
83.2
78.5
78.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
73.1
66.4
61.5
54.5
26.0
24.3
18.5
0.2
-5.1
S6
13C NMR
CDCl3
126 MHz
TBSO
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.79
7.78
7.31
7.29
7.26 CDCl3
4.77
3.72
3.70
3.69
2.46
2.45
2.43
2.42
1.53
0.90
0.07
-0.00
TsHN
Me Me
OTBS
21
1H NMR
CDCl3
500 MHz
2.00
2.07
0.87
2.05
2.16
3.14
6.27
9.63
6.32
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


143.5
138.3
129.6
127.8
78.6
77.4 CDCl3
77.2 CDCl3
76.9
76.9 CDCl3
68.4
65.4
61.5
50.5
30.7
26.0
23.8
21.7
18.4
0.1
-5.2
TsHN
OTBS
Me Me
21
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26 CDCl3
3.76
3.74
3.73
2.51
2.50
2.48
1.69
0.90
0.07
0.00
TfHN
OTBS
Me Me
22
1H NMR
CDCl3
500 MHz
2.14
2.00
6.02
9.41
6.37
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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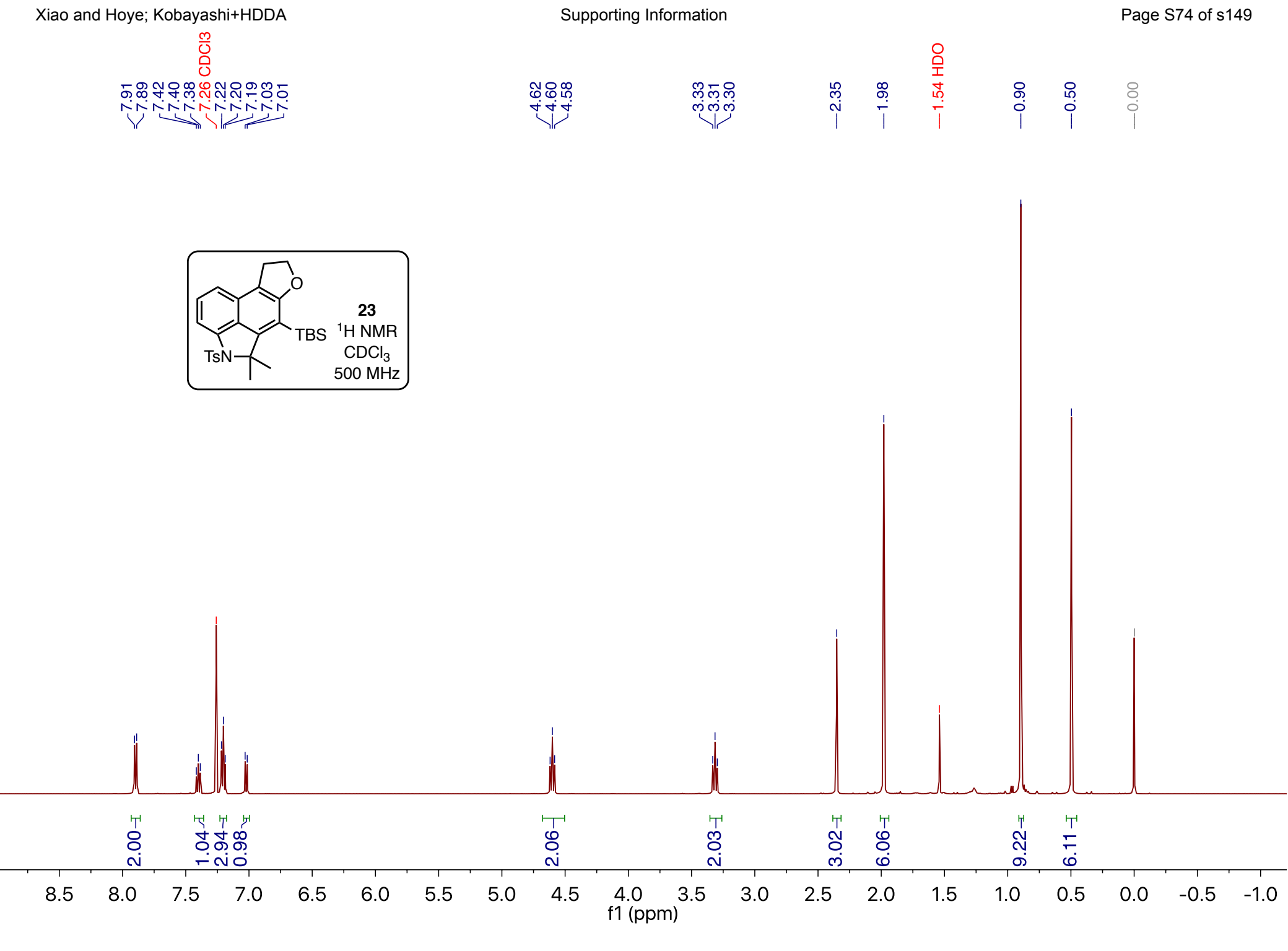
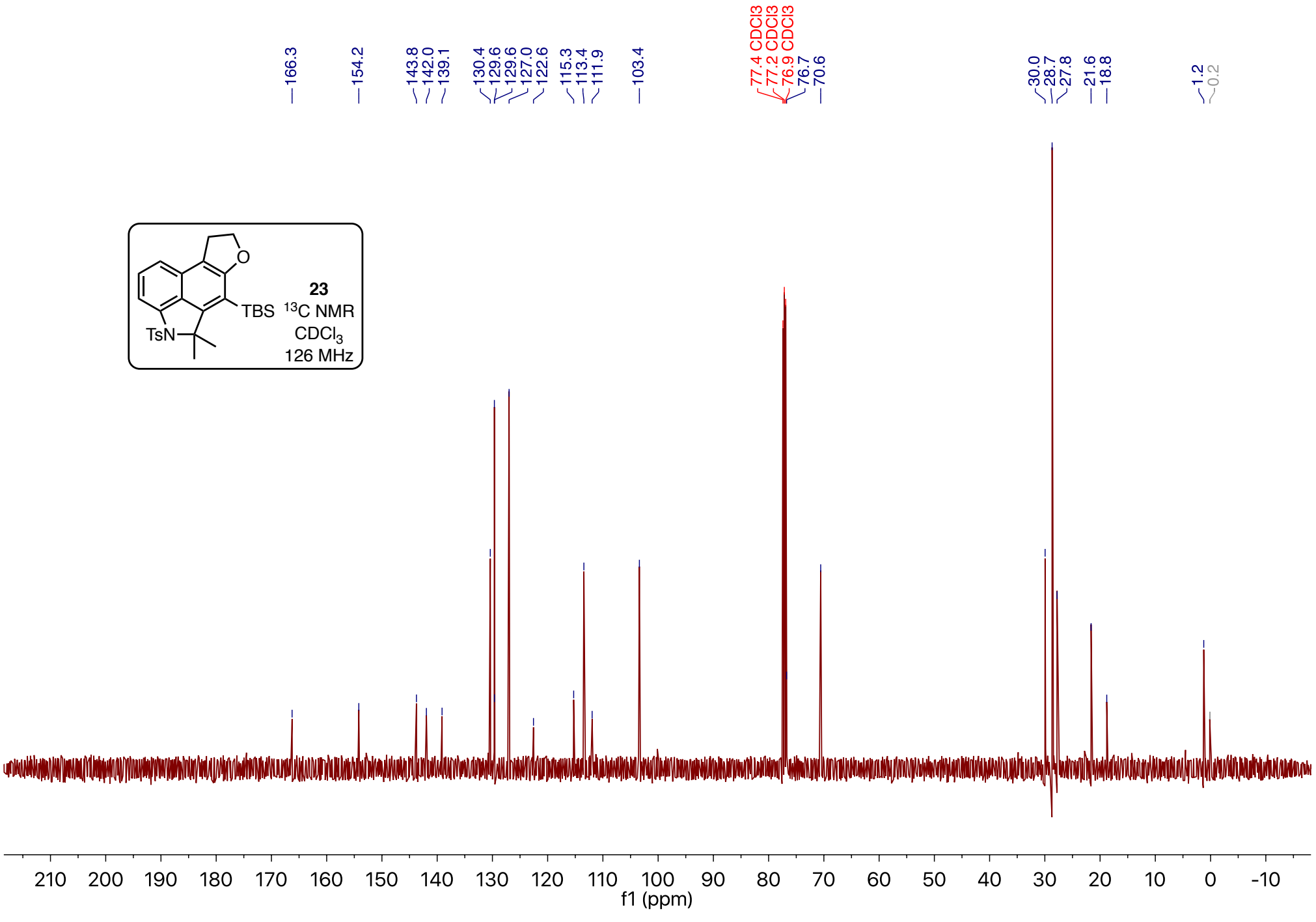
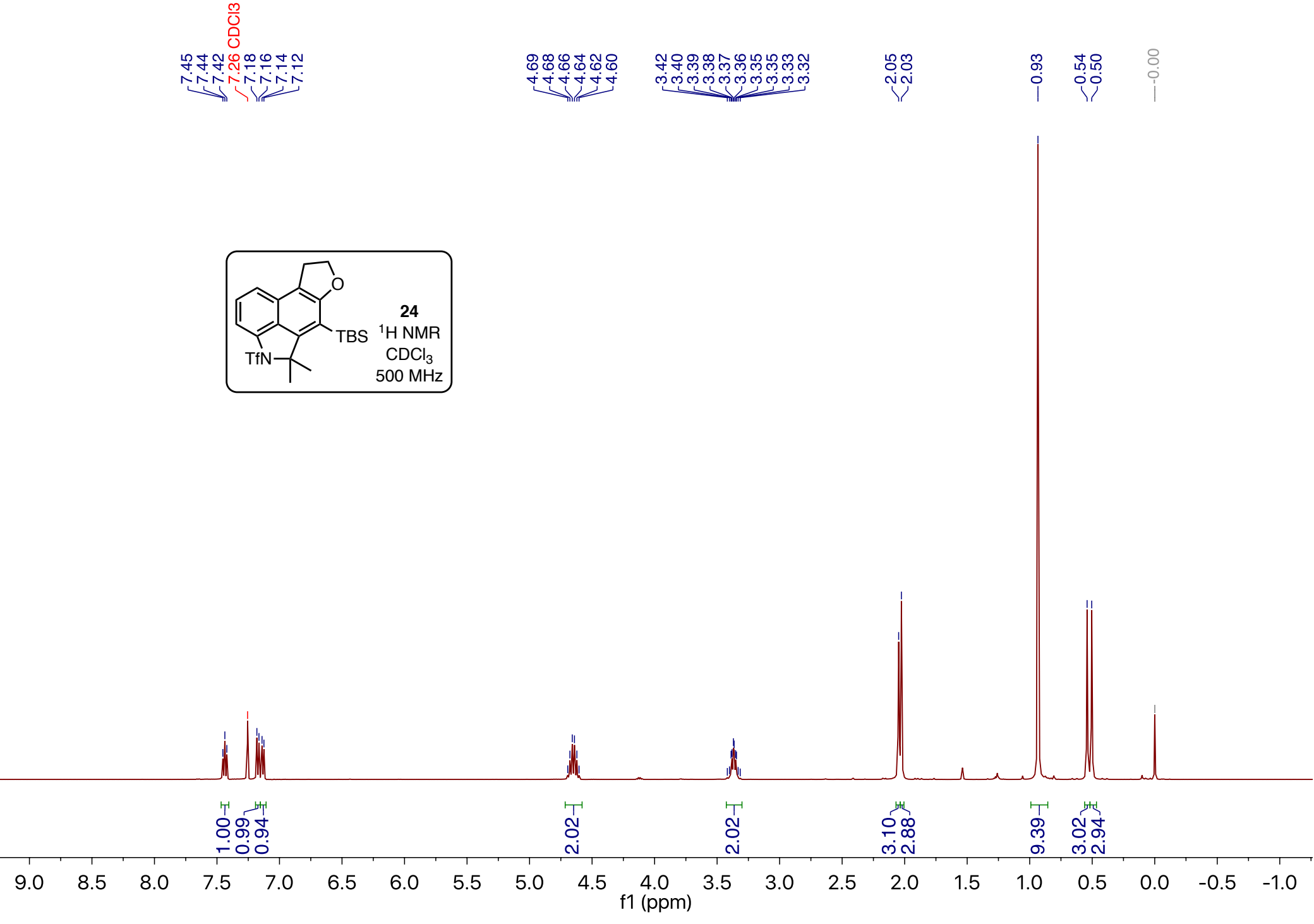
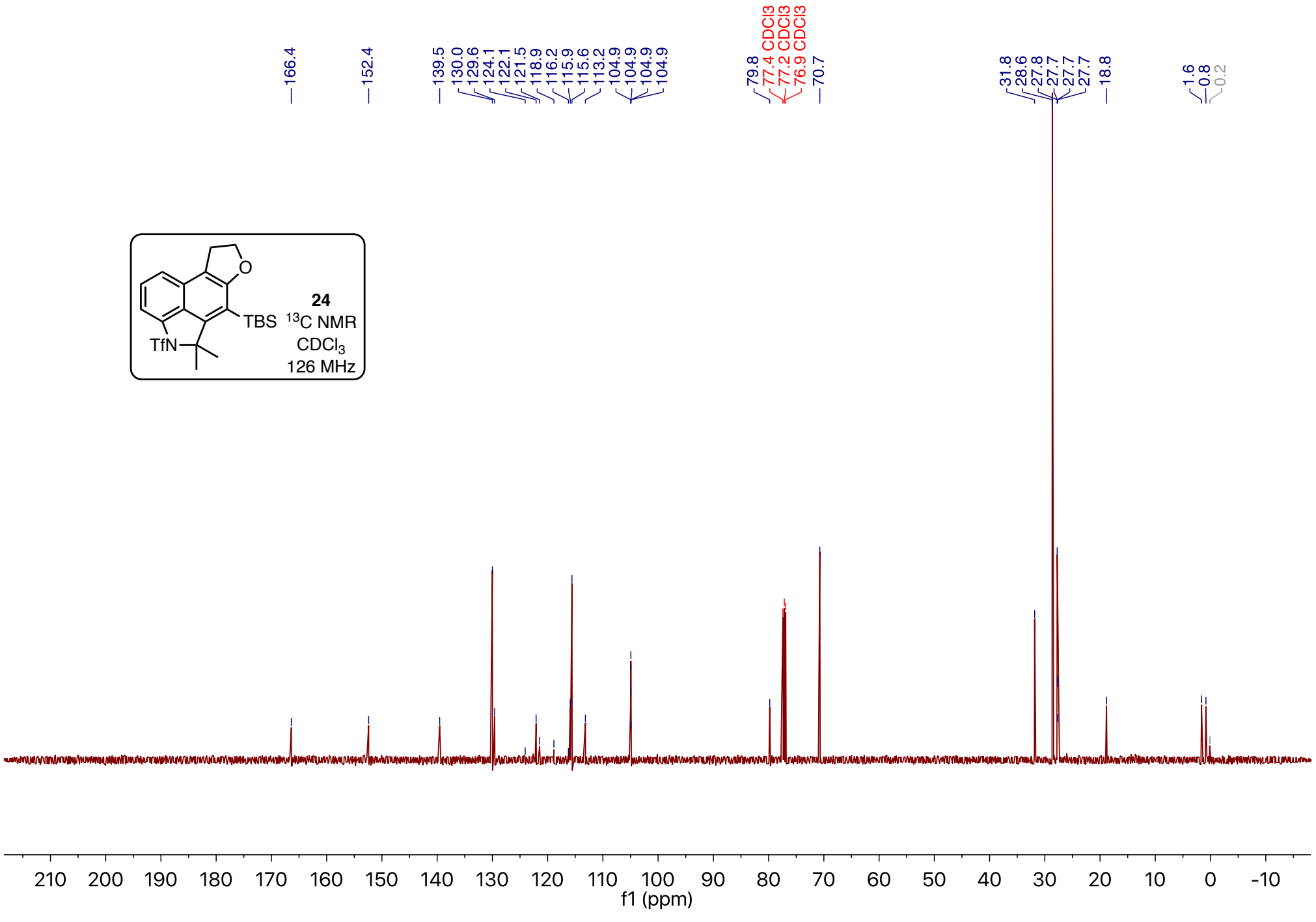
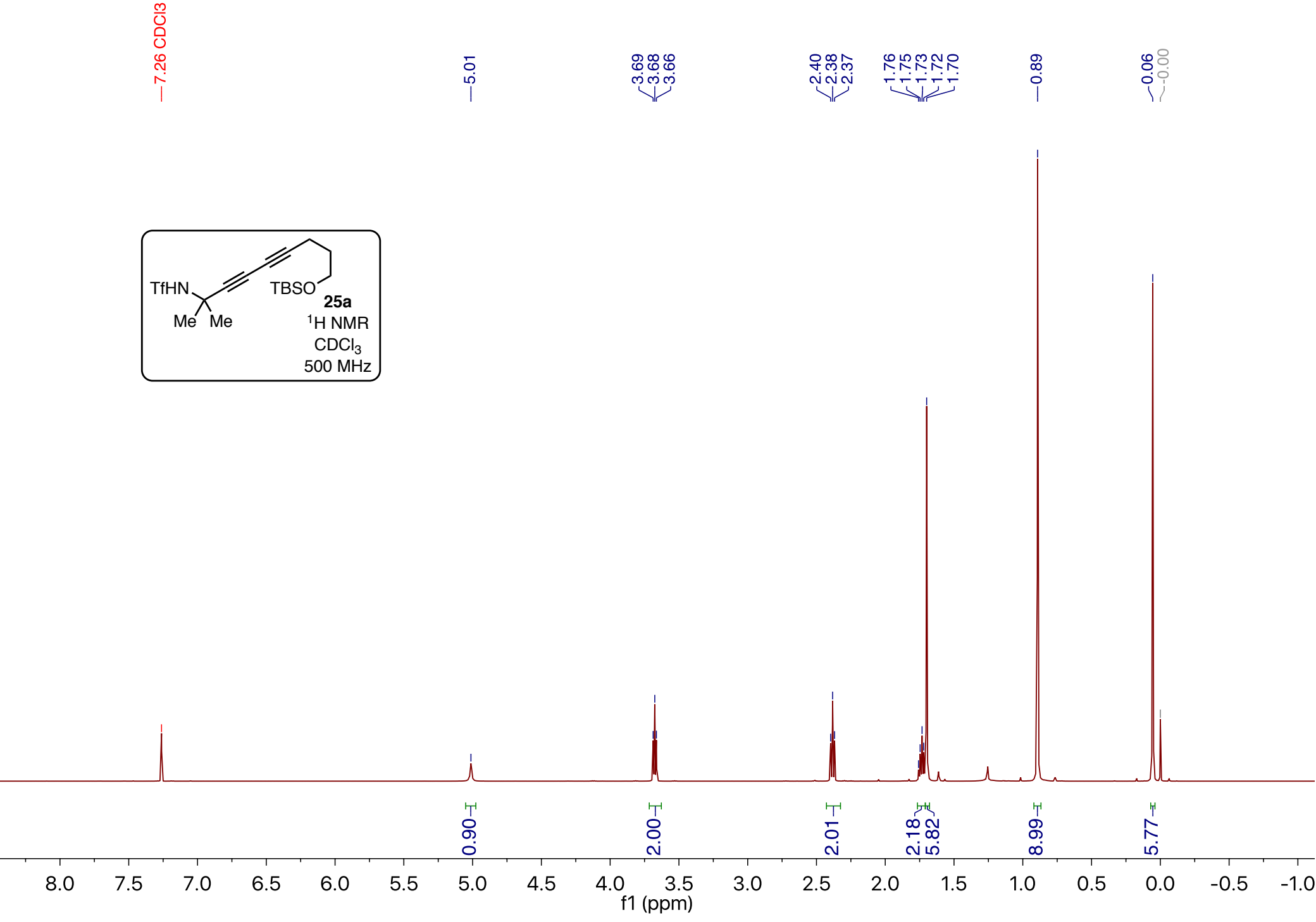
120.5
117.9
115.6
80.0
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
75.9
69.0
65.1
61.3
53.6
30.7
26.0
23.8
18.4
-5.2
TfHN
OTBS
Me Me
22
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

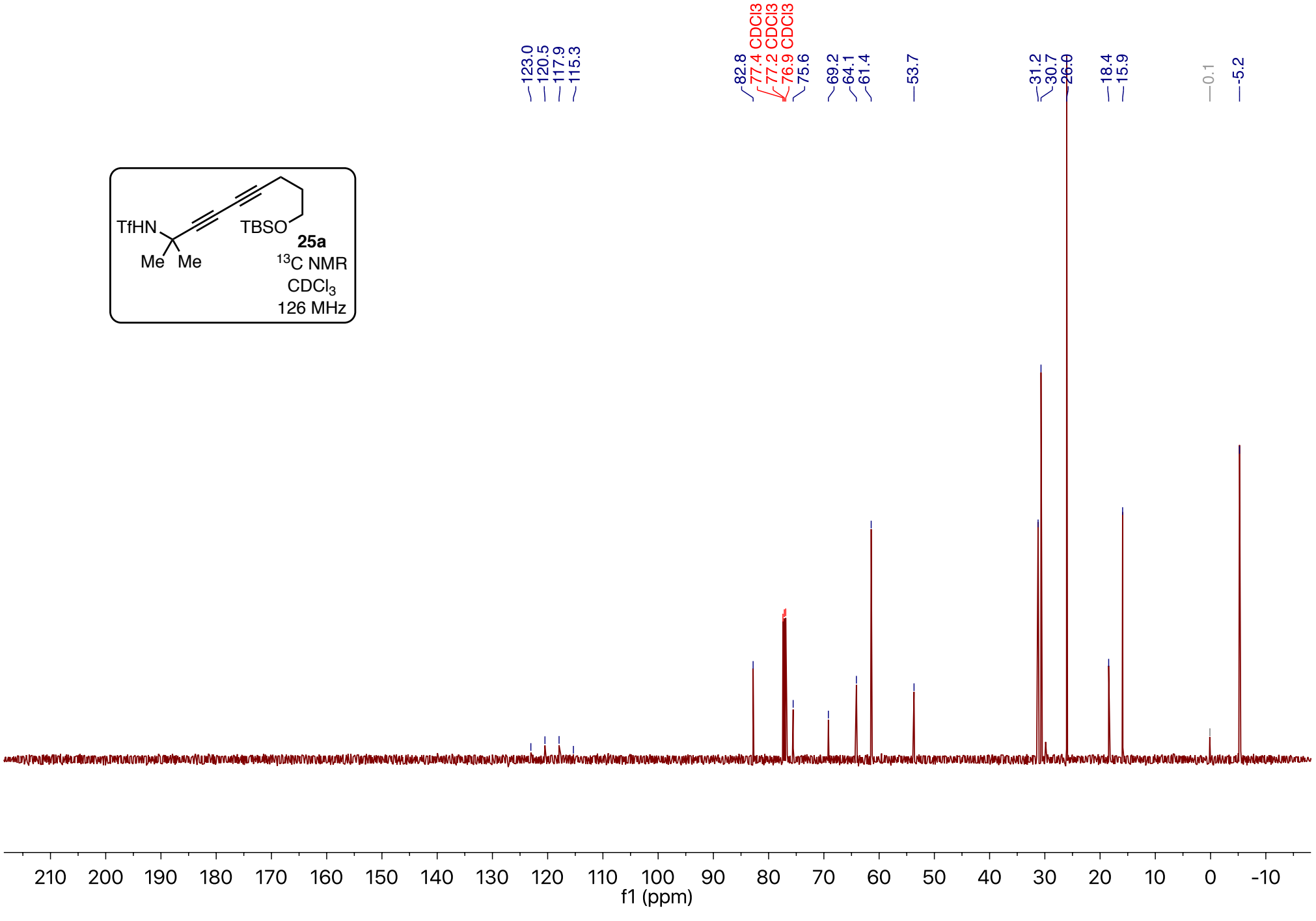

7.91
7.89
7.42
7.40
7.38
7.26 CDCl3
7.22
7.20
7.19
7.03
7.01
4.62
4.60
4.58
3.33
3.31
3.30
2.35
1.98
1.54 HDO
0.90
0.50
0.00
TBS
TsN
O
23
1H NMR
CDCl3
500 MHz
2.00
1.04
2.94
0.98
2.06
2.03
3.02
6.06
9.22
6.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

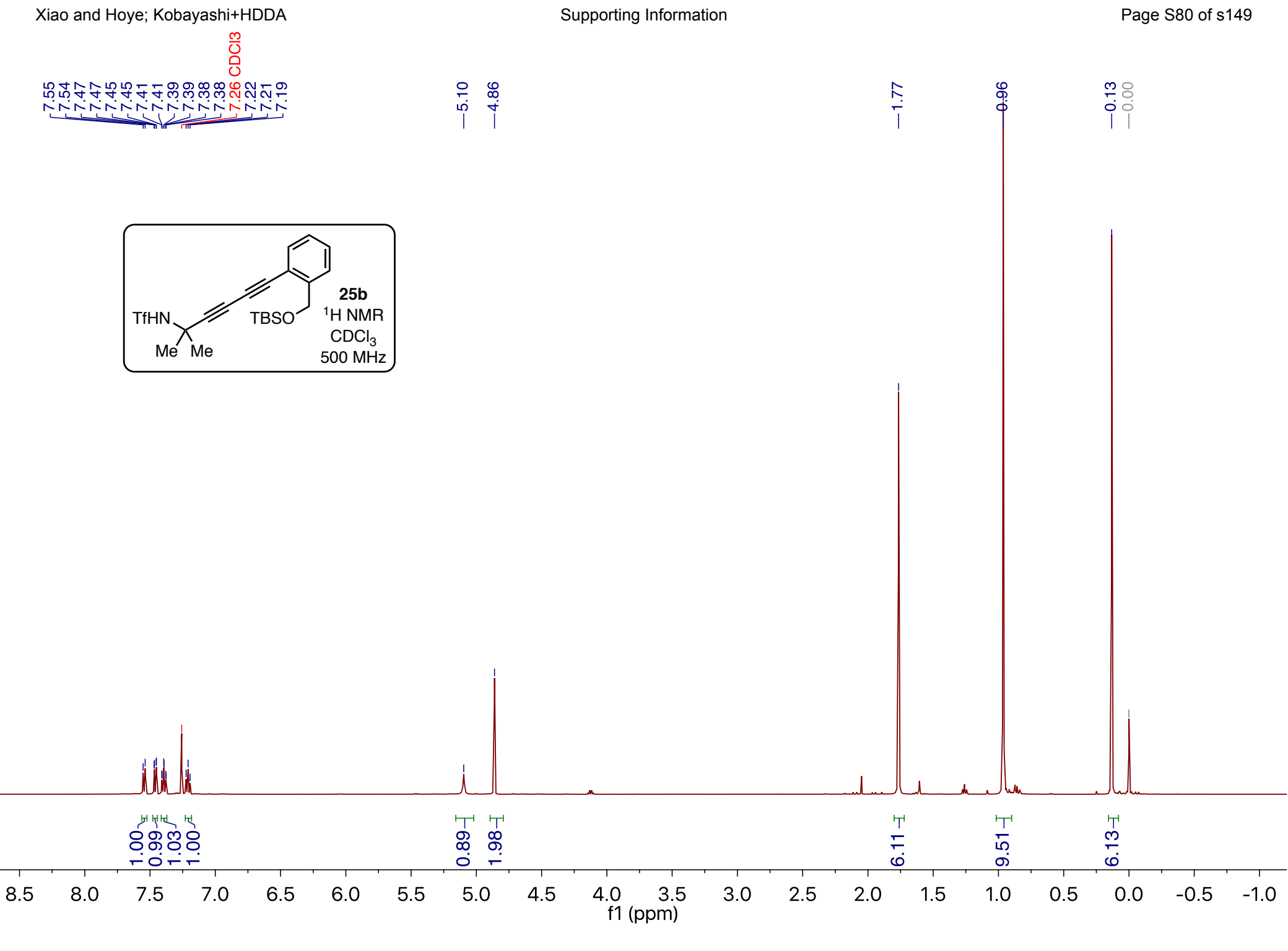

166.3
154.2
143.8
142.0
139.1
130.4
129.6
129.6
127.0
122.6
115.3
113.4
111.9
103.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.7
70.6
30.0
28.7
27.8
21.6
18.8
1.2
0.2
O
TBS
TsN
23
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

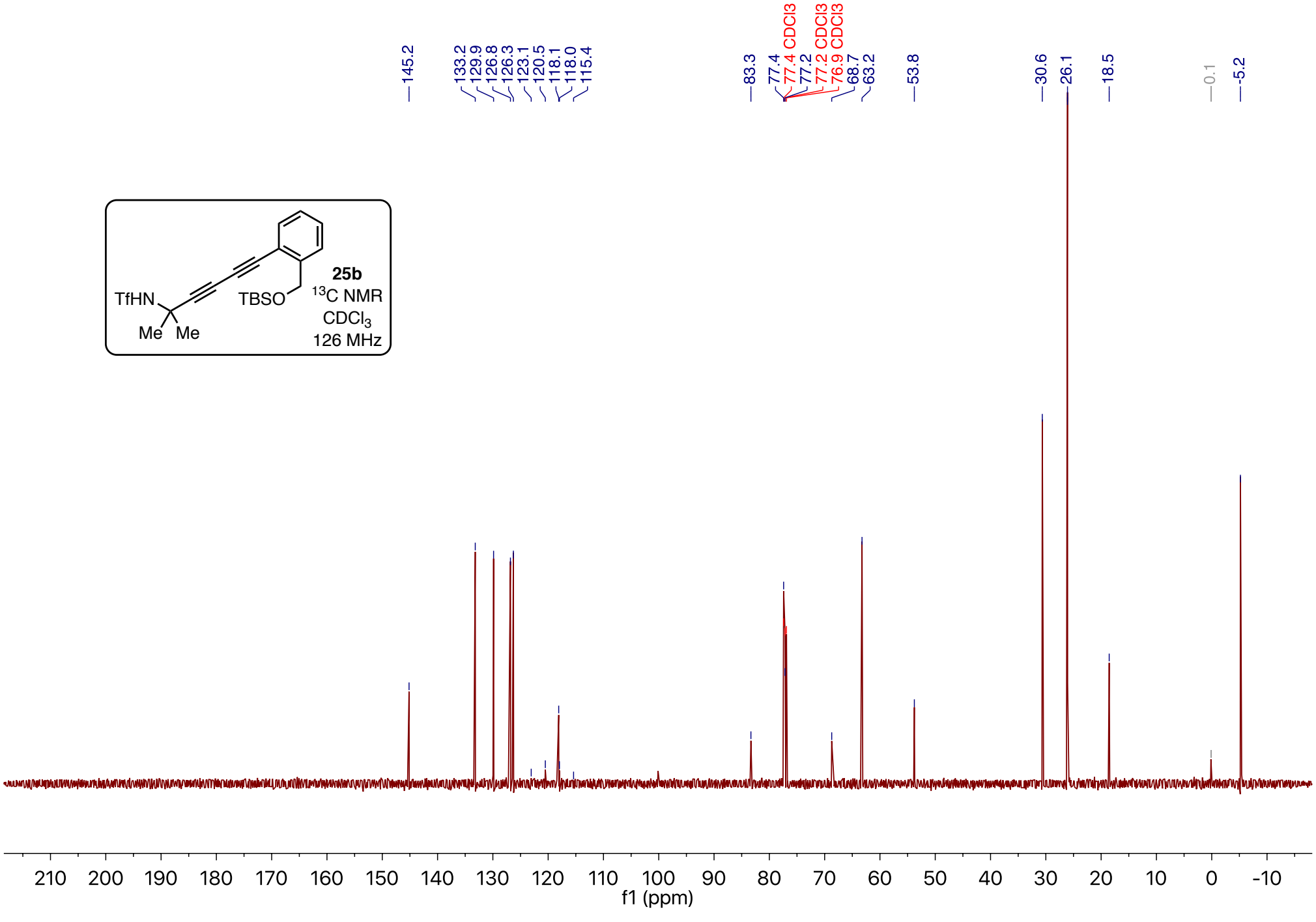

7.45
7.44
7.42
7.26 CDCl3
7.18
7.16
7.14
7.12
4.69
4.68
4.66
4.64
4.62
4.60
3.42
3.40
3.39
3.38
3.37
3.36
3.35
3.35
3.33
3.32
2.05
2.03
0.93
0.54
0.50
-0.00
O
TBS
TfN
24
1H NMR
CDCl3
500 MHz
1.00
0.99
0.94
2.02
2.02
3.10
2.88
9.39
3.02
2.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

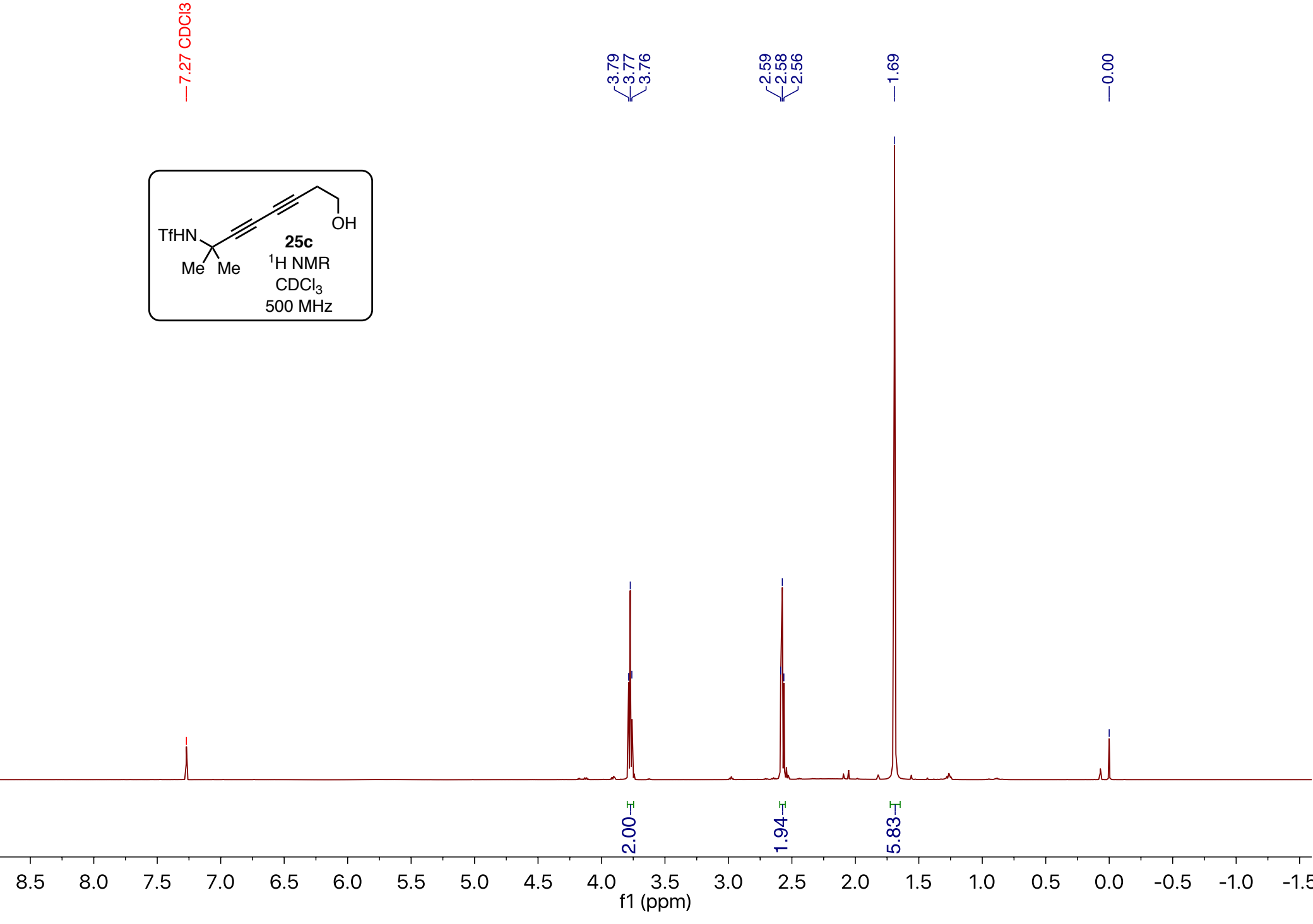

166.4
152.4
139.5
130.0
129.6
124.1
122.1
121.5
118.9
116.2
115.9
115.6
113.2
104.9
104.9
104.9
104.9
79.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
70.7
31.8
28.6
27.8
27.7
27.7
27.7
18.8
1.6
0.8
0.2
O
TBS
TfN
24
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

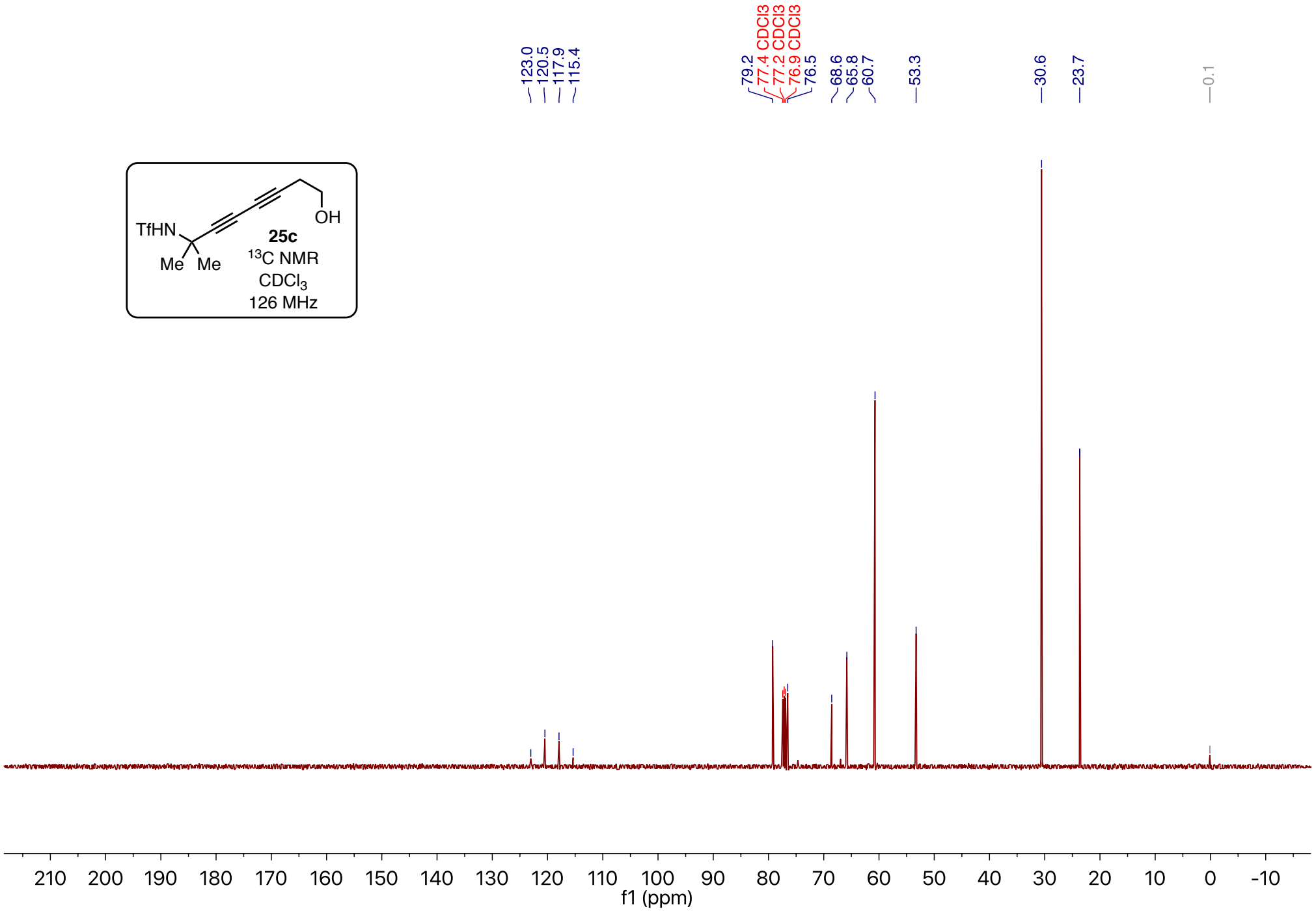

7.26 CDCl3
5.01
3.69
3.68
3.66
2.40
2.38
2.37
1.76
1.75
1.73
1.72
1.70
0.89
0.06
-0.00
TfHN
TBSO
Me Me
25a
1H NMR
CDCl3
500 MHz
0.90
2.00
2.01
2.18
5.82
8.99
5.77
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

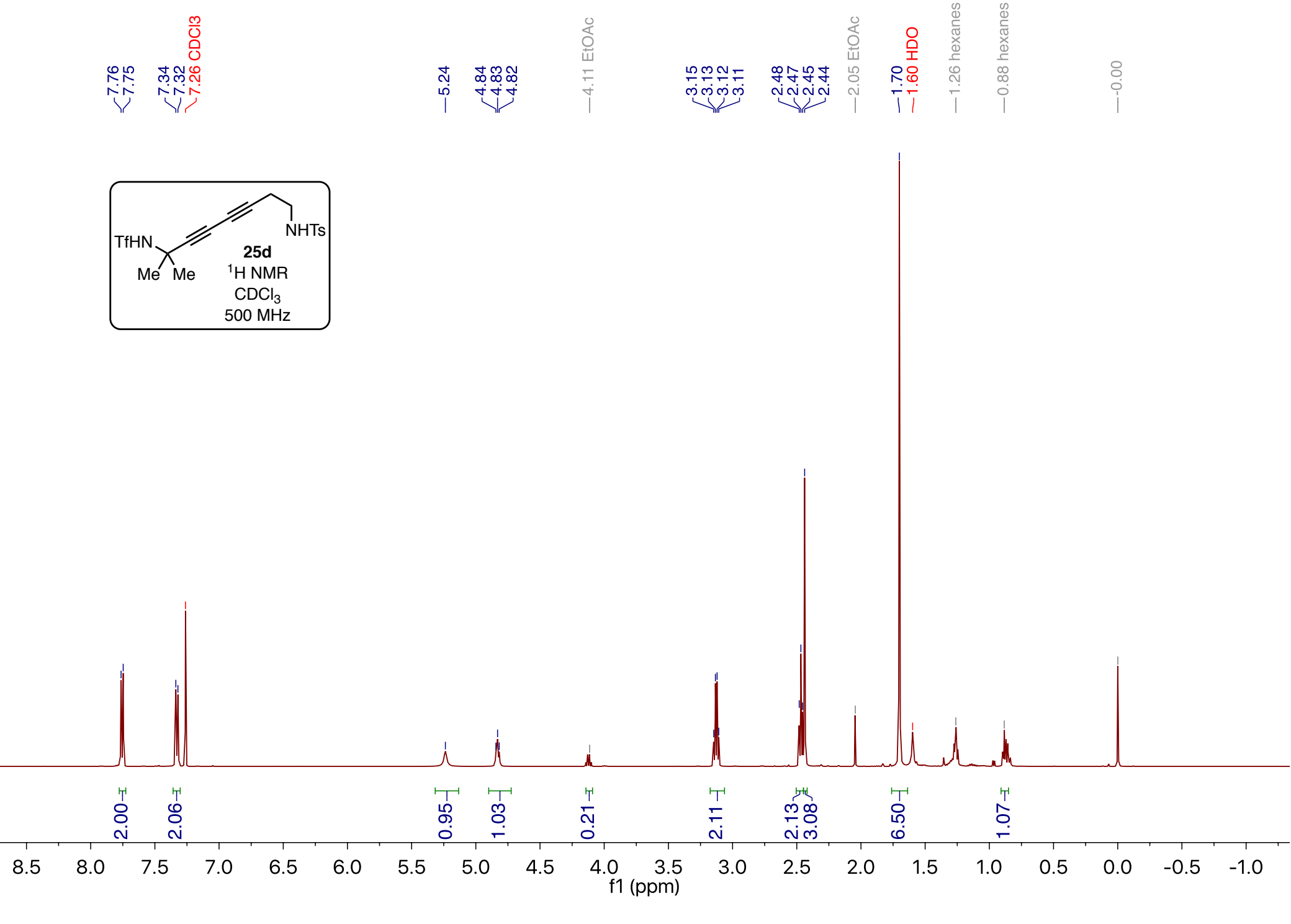

123.0
120.5
117.9
115.3
82.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
75.6
69.2
64.1
61.4
53.7
31.2
30.7
26.0
18.4
15.9
0.1
-5.2
TfHN
TBSO
Me Me
25a
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

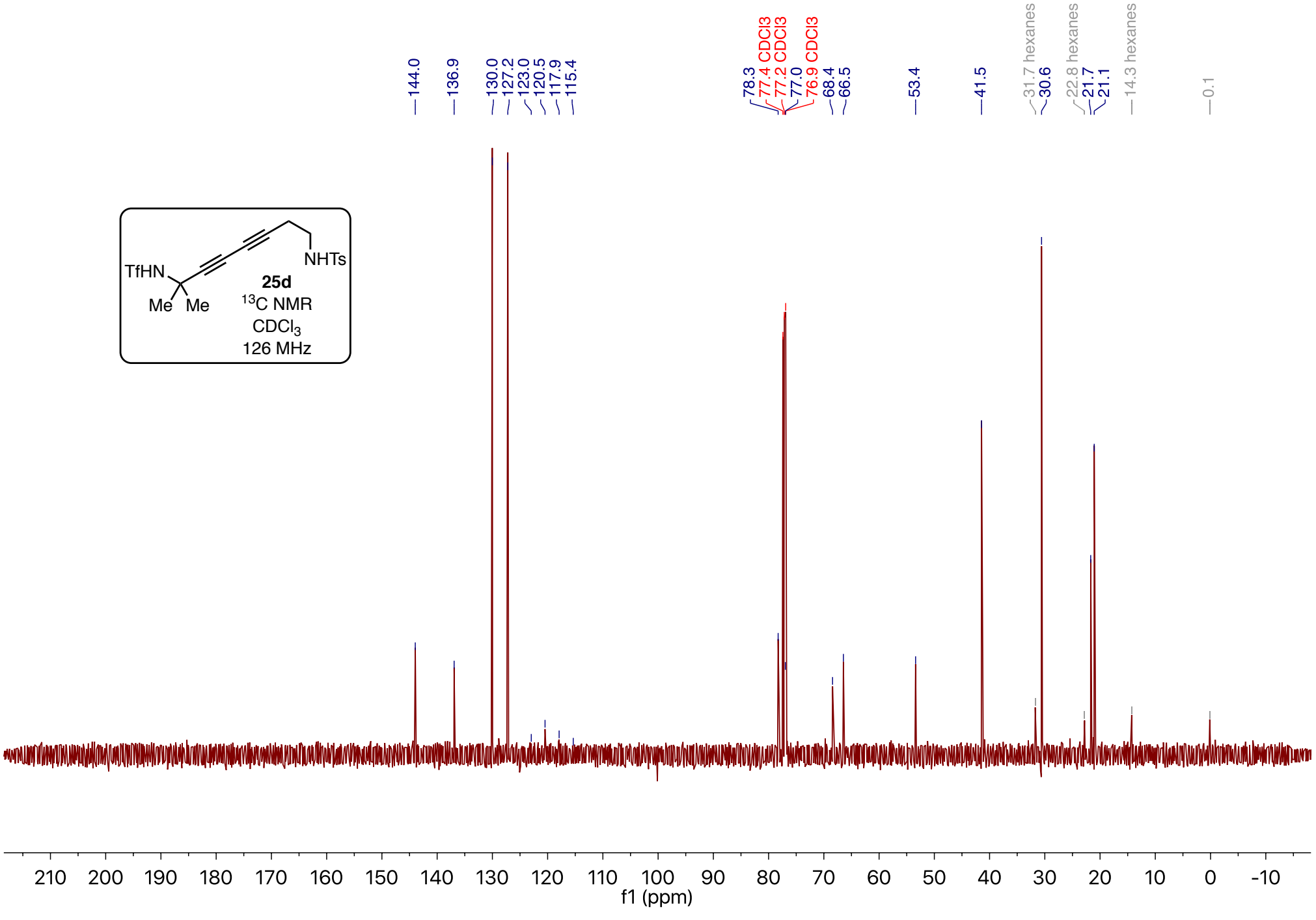

7.55
7.54
7.47
7.47
7.45
7.45
7.41
7.41
7.39
7.39
7.38
7.38
7.26 CDCl3
7.22
7.21
7.19
5.10
4.86
1.77
0.96
0.13
0.00
TfHN
TBSO
Me Me
25b
1H NMR
CDCl3
500 MHz
1.00
0.99
1.03
1.00
0.89
1.98
6.11
9.51
6.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

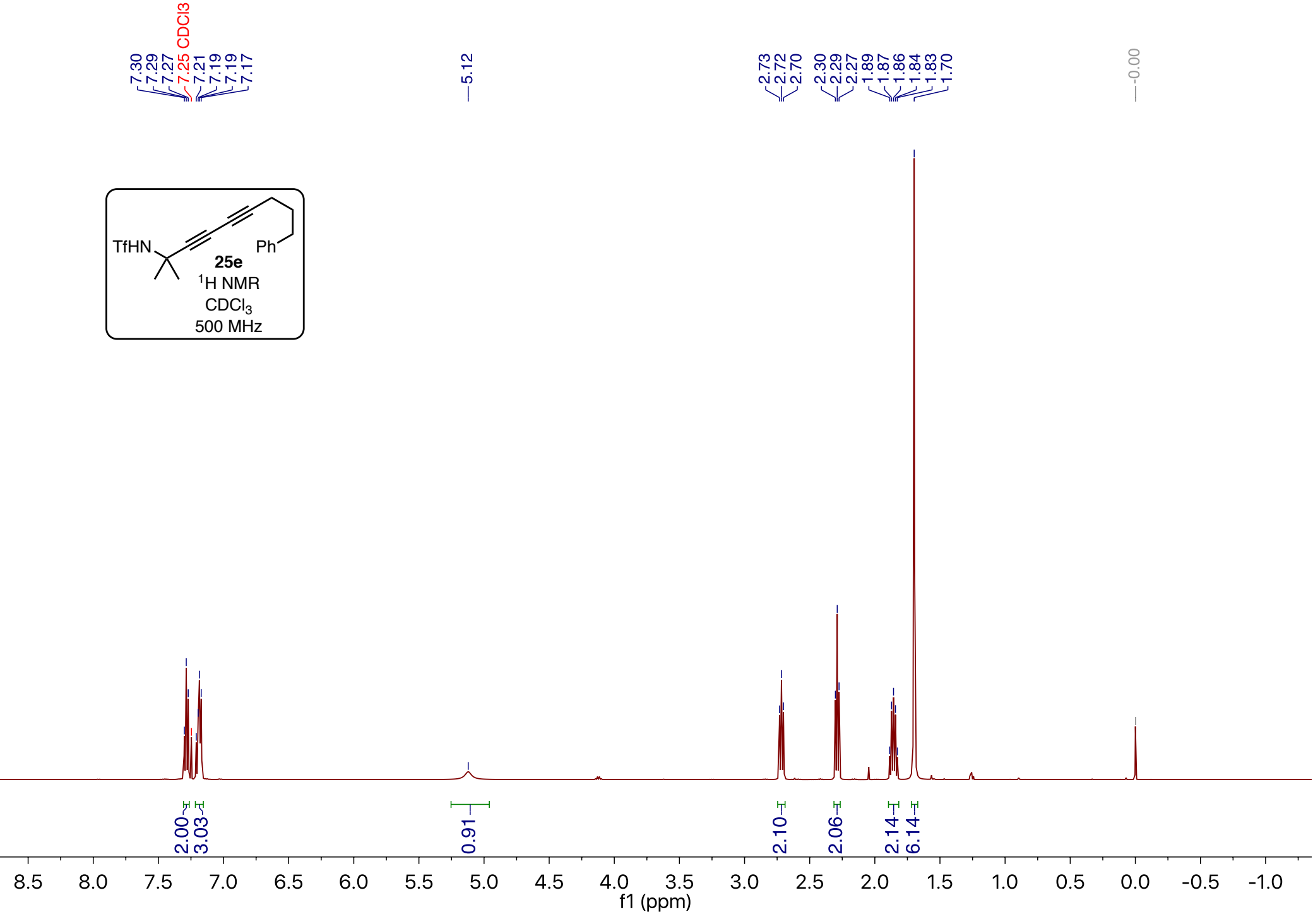

145.2
133.2
129.9
126.8
126.3
123.1
120.5
118.1
118.0
115.4
83.3
77.4
77.4 CDCl3
77.2
77.2 CDCl3
76.9 CDCl3
68.7
63.2
53.8
30.6
26.1
18.5
0.1
-5.2
TfHN
TBSO
Me Me
25b
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

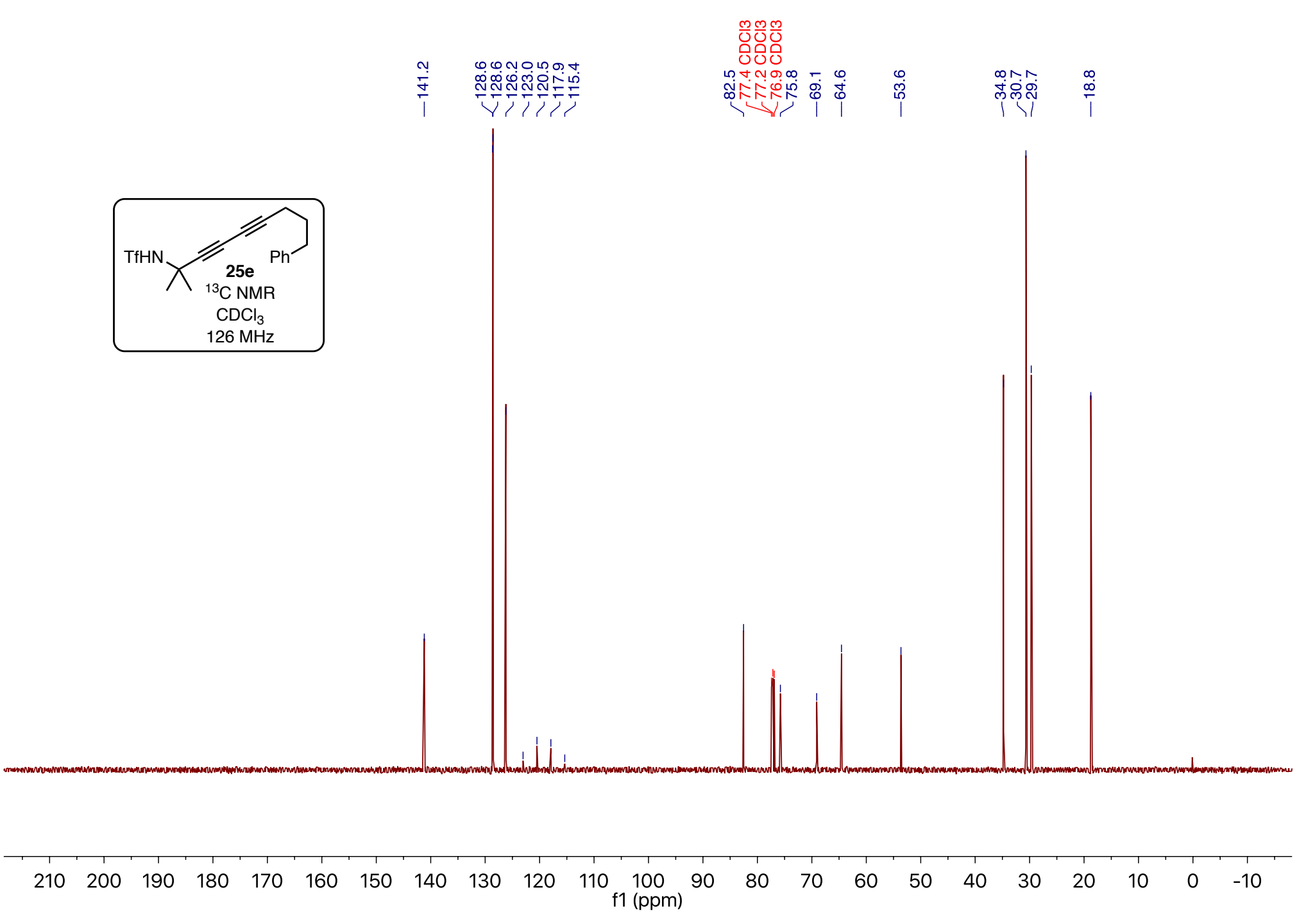

7.27 CDCl3
3.79
3.77
3.76
2.59
2.58
2.56
1.69
0.00
TfHN
Me
Me
OH
25c
1H NMR
CDCl3
500 MHz
2.00
1.94
5.83
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

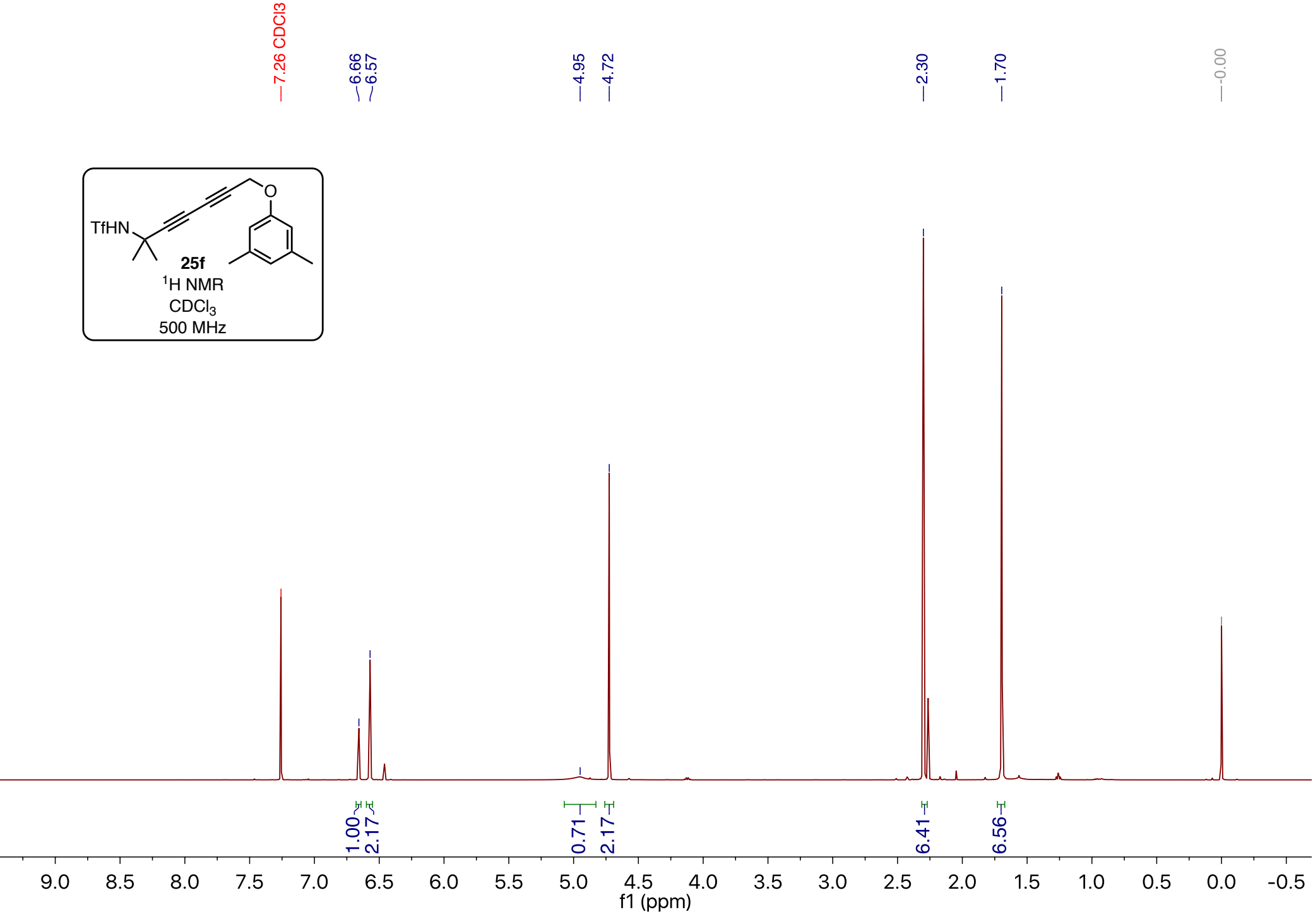

123.0
120.5
117.9
115.4
79.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.5
68.6
65.8
60.7
53.3
30.6
23.7
0.1
TfHN
Me Me
OH
25c
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

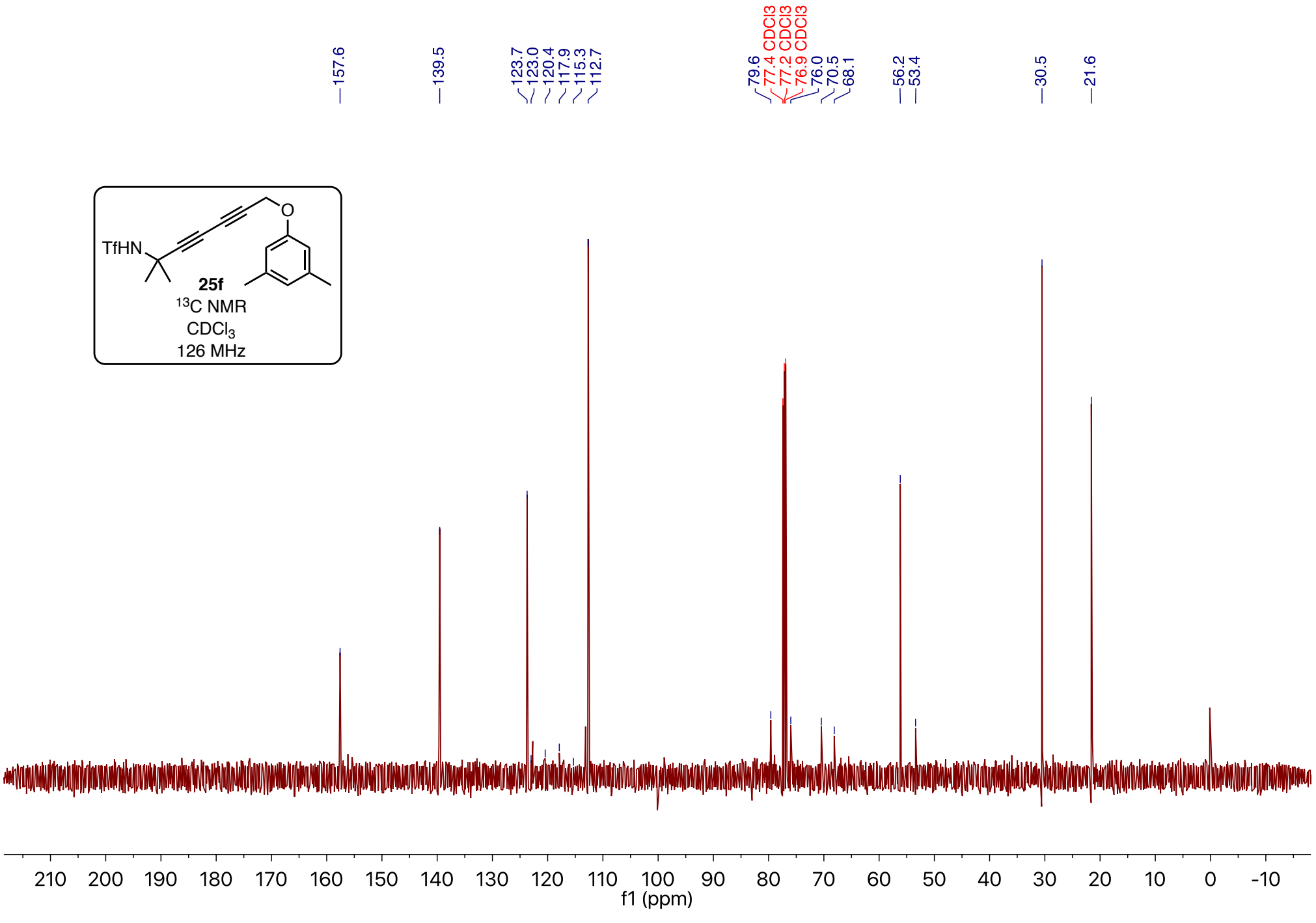

7.76
7.75
7.34
7.32
7.26 CDCl3
5.24
4.84
4.83
4.82
4.11 EtOAc
3.15
3.13
3.12
3.11
2.48
2.47
2.45
2.44
2.05 EtOAc
1.70
1.60 HDO
1.26 hexanes
0.88 hexanes
0.00
TfHN
NHTs
Me Me
25d
1H NMR
CDCl3
500 MHz
2.00
2.06
0.95
1.03
0.21
2.11
2.13
3.08
6.50
1.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

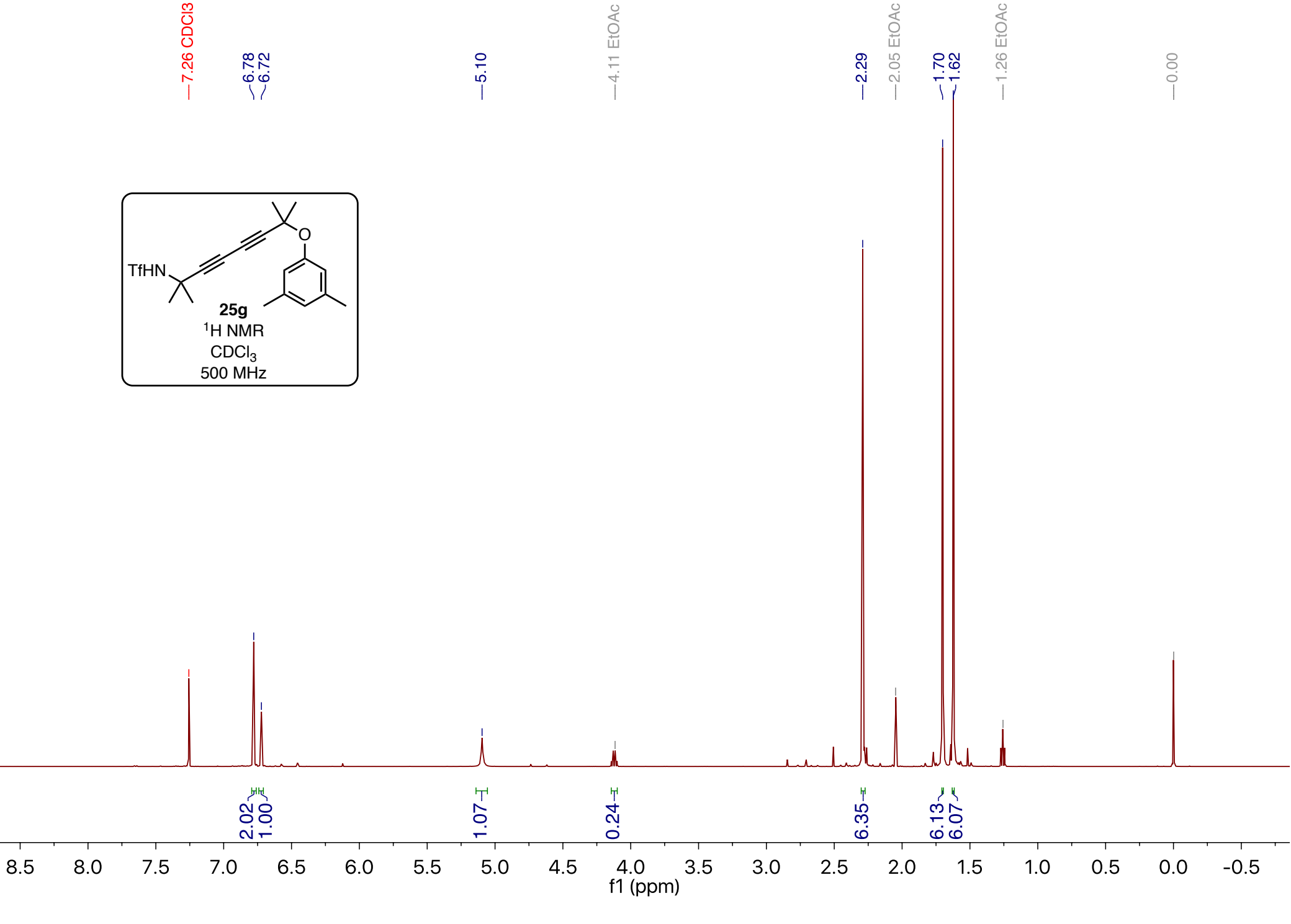

144.0
136.9
130.0
127.2
123.0
120.5
117.9
115.4
78.3
77.4 CDCl3
77.2 CDCl3
77.0
76.9 CDCl3
68.4
66.5
53.4
41.5
31.7 hexanes
30.6
22.8 hexanes
21.7
21.1
14.3 hexanes
0.1
TfHN
NHTs
Me
Me
25d
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

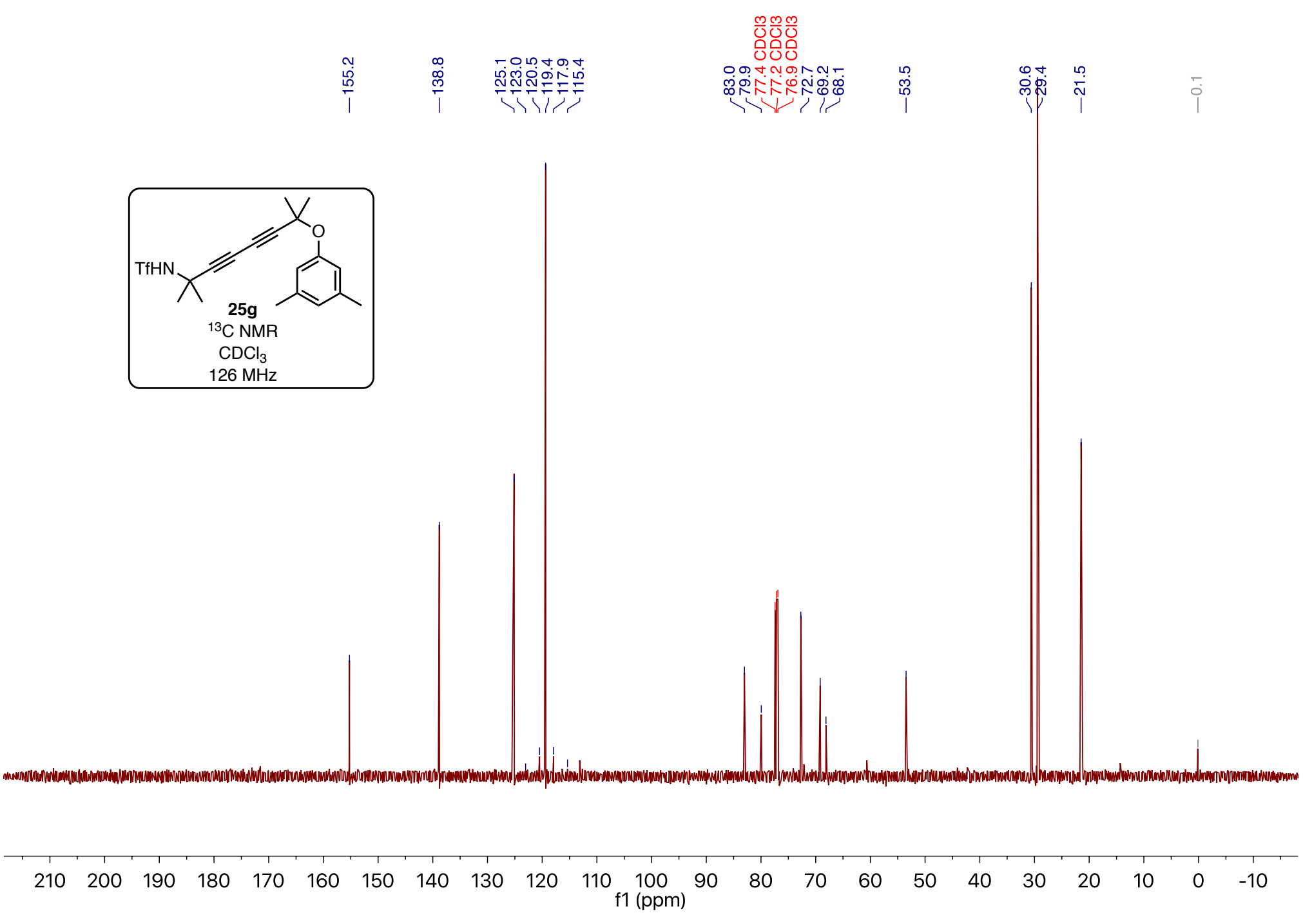

7.30
7.29
7.27
7.25 CDCl3
7.21
7.19
7.19
7.17
5.12
2.73
2.72
2.70
2.30
2.29
2.27
1.89
1.87
1.86
1.84
1.83
1.70
0.00
TfHN
Ph
25e
1H NMR
CDCl3
500 MHz
2.00
3.03
0.91
2.10
2.06
2.14
6.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


141.2
128.6
128.6
126.2
123.0
120.5
117.9
115.4
82.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
75.8
69.1
64.6
53.6
34.8
30.7
29.7
18.8
TfHN
Ph
25e
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26 CDCl3
6.66
6.57
4.95
4.72
2.30
1.70
0.00
TfHN
O
25f
1H NMR
CDCl3
500 MHz
1.00
2.17
0.71
2.17
6.41
6.56
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)


157.6
139.5
123.7
123.0
120.4
117.9
115.3
112.7
79.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.0
70.5
68.1
56.2
53.4
30.5
21.6
TfHN
O
25f
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26 CDCl3
6.78
6.72
5.10
4.11 EtOAc
2.29
2.05 EtOAc
1.70
1.62
1.26 EtOAc
0.00
TfHN
O
25g
1H NMR
CDCl3
500 MHz
2.02
1.00
1.07
0.24
6.35
6.13
6.07
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)


155.2
138.8
125.1
123.0
120.5
119.4
117.9
115.4
83.0
79.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.7
69.2
68.1
53.5
30.6
29.4
21.5
0.1
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13C NMR
CDCl3
126 MHz
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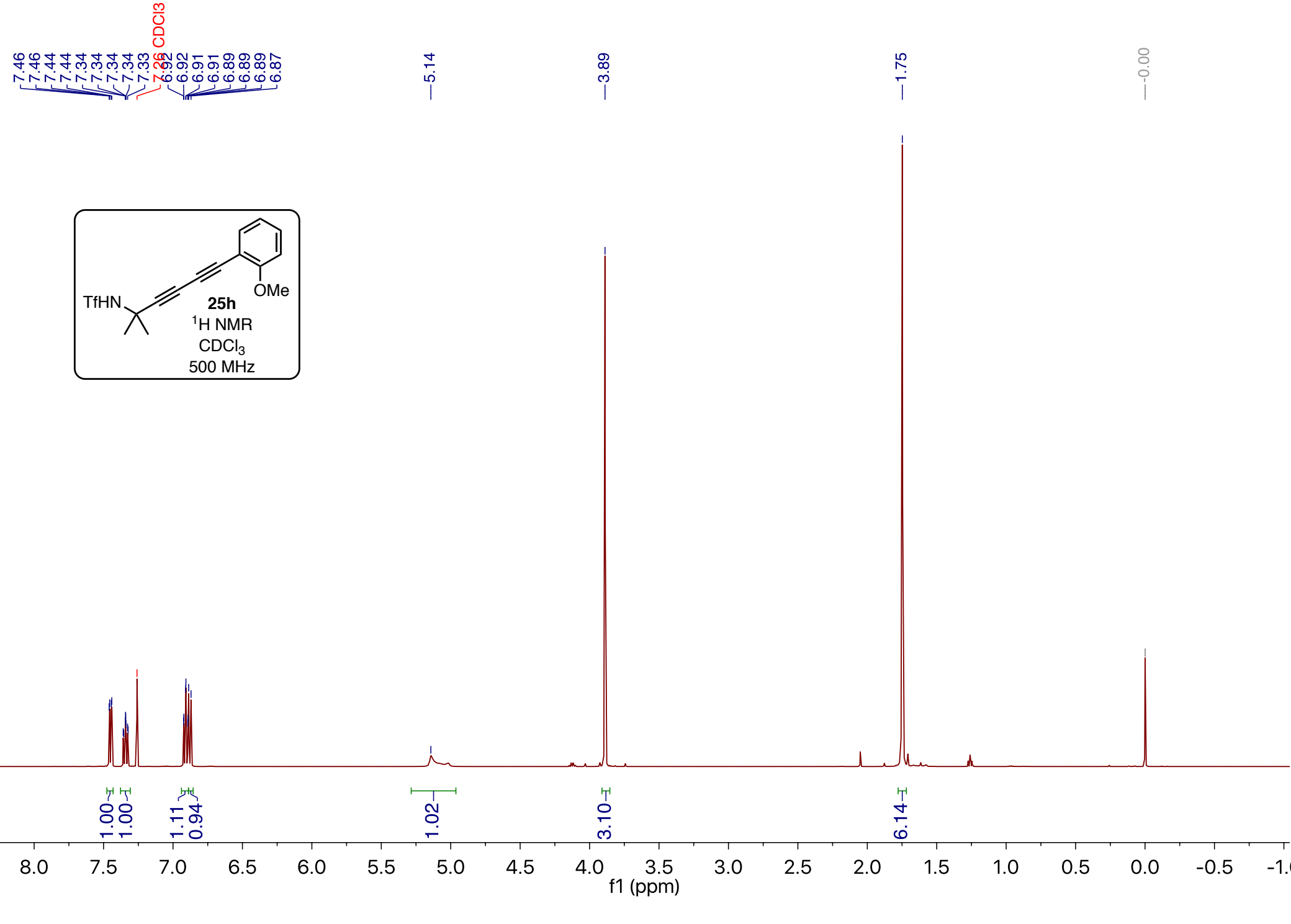
f1 (ppm)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6.92
6.91
6.91
6.89
6.89
6.89
6.87
5.14
3.89
1.75
0.00
TfHN
OMe
25h
1H NMR
CDCl3
500 MHz
1.00
1.00
1.11
0.94
1.02
3.10
6.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
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1.0
0.5
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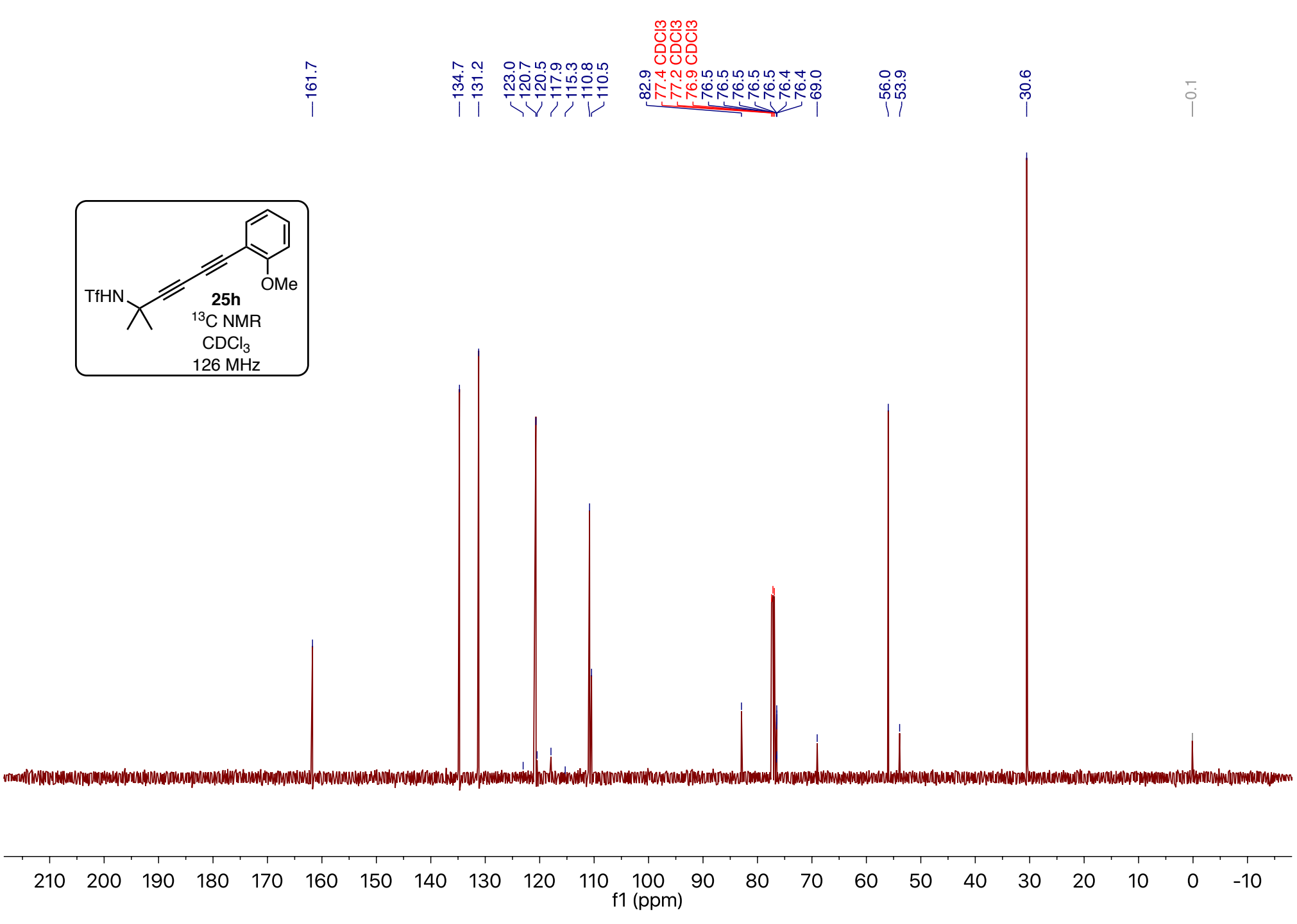
f1 (ppm)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131.2
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117.9
115.3
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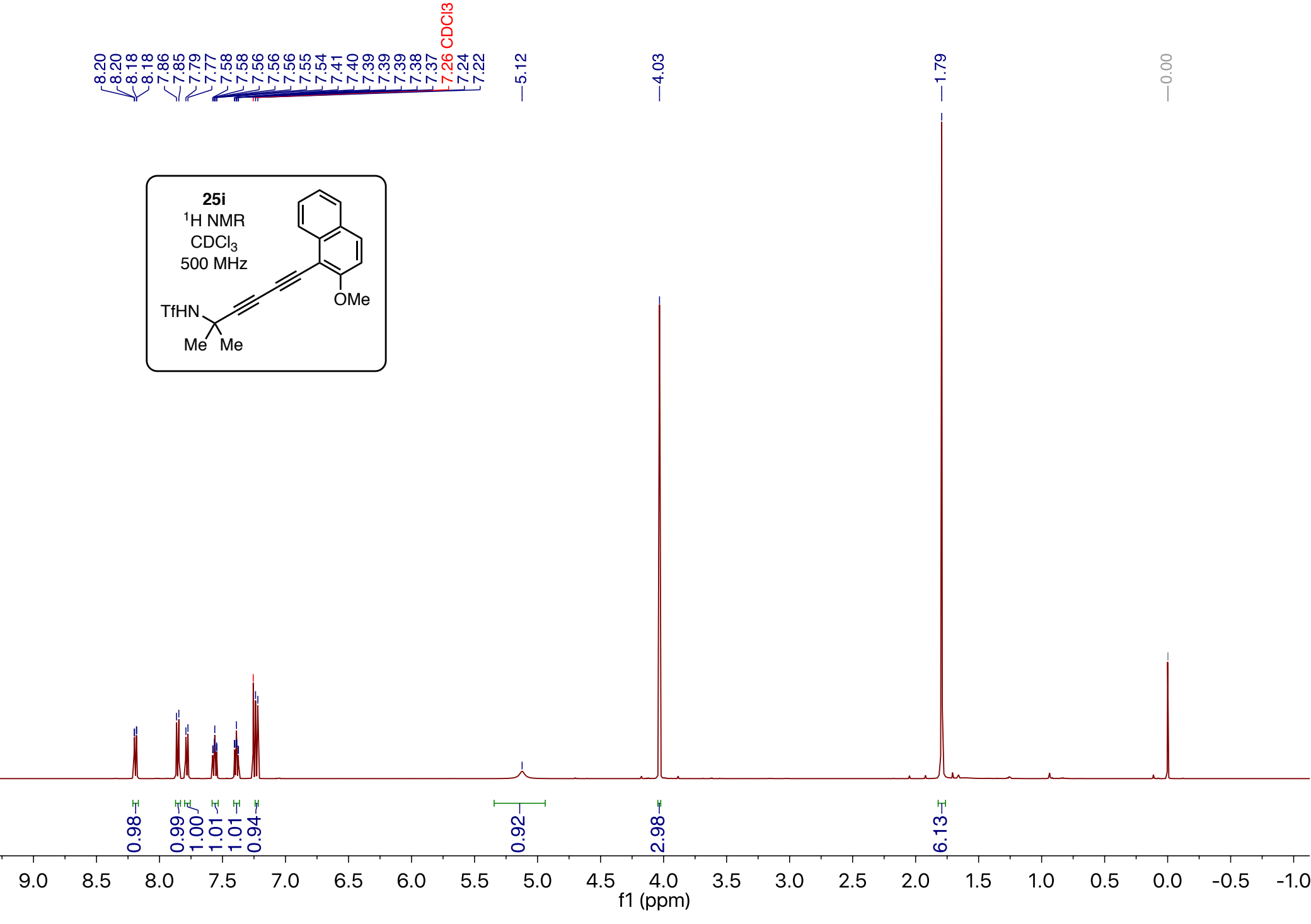
110.5
82.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.5
76.5
76.5
76.5
76.4
76.4
69.0
56.0
53.9
30.6
0.1
TfHN
OMe
25h
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.18
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7.77
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7.58
7.56
7.56
7.56
7.55
7.54
7.41
7.40
7.39
7.39
7.39
7.38
7.37
7.26 CDCl3
7.24
7.22
5.12
4.03
1.79
0.00
25i
1H NMR
CDCl3
500 MHz
TfHN
OMe
Me
Me
0.98
0.99
1.00
1.01
1.01
0.94
0.92
2.98
6.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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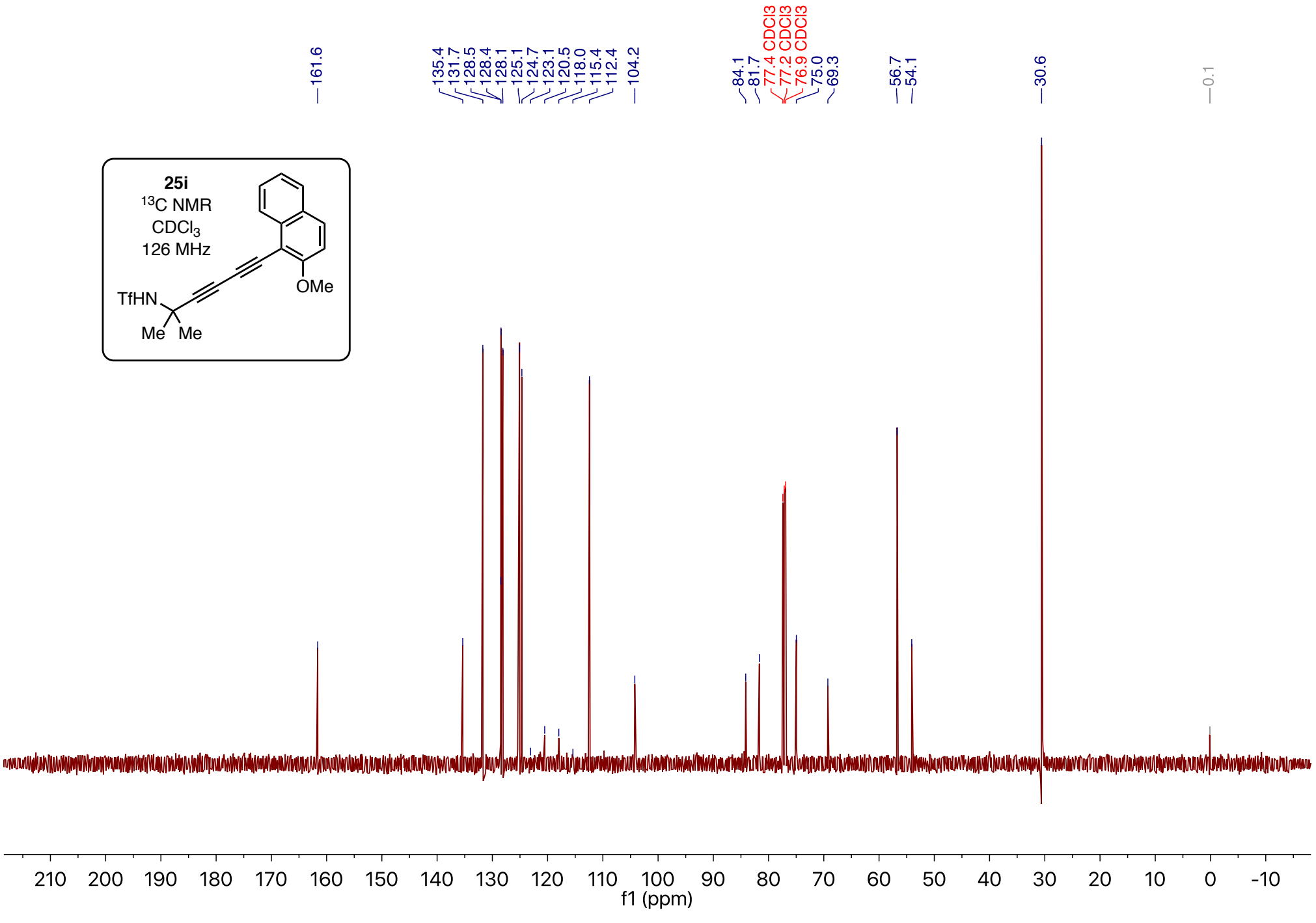
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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135.4
131.7
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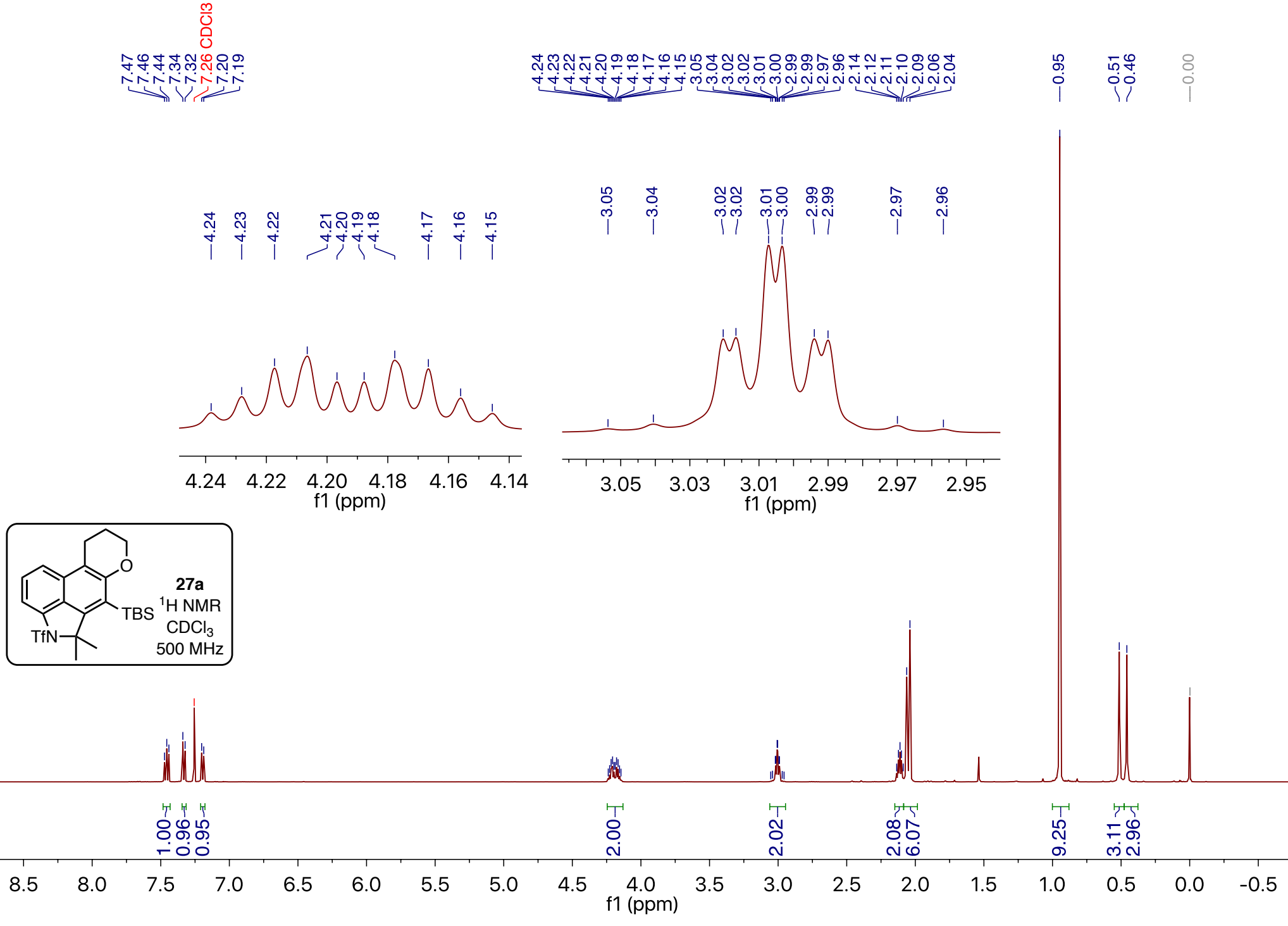
128.1
125.1
124.7
123.1
120.5
118.0
115.4
112.4
104.2
84.1
81.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
75.0
69.3
56.7
54.1
30.6
0.1
25i
13C NMR
CDCl3
126 MHz
TfHN
OMe
Me Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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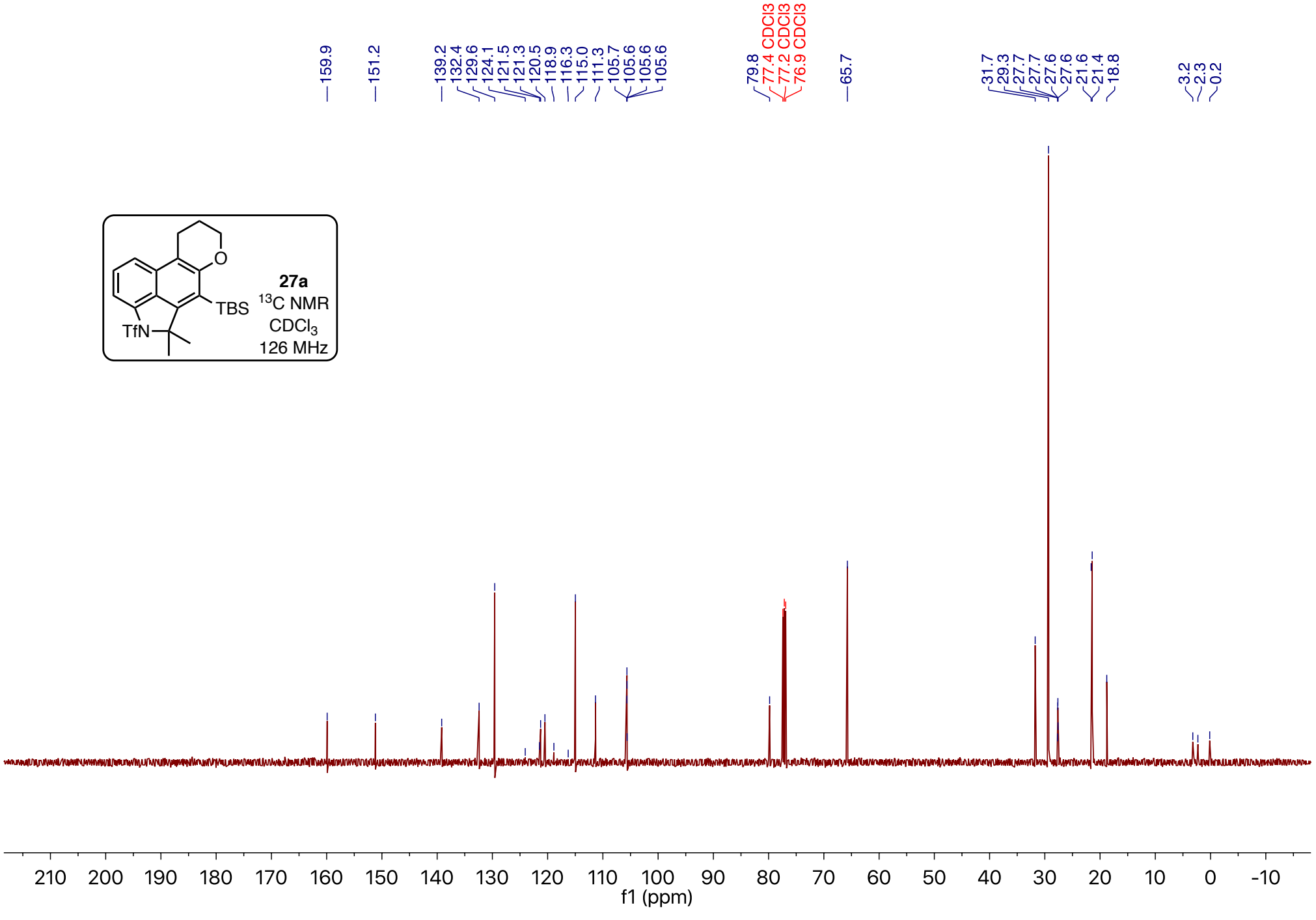
7.46
7.44
7.34
7.32
7.26 CDCl3
7.20
7.19
4.24
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
3.05
3.04
3.02
3.02
3.01
3.00
2.99
2.99
2.97
2.96
2.14
2.12
2.11
2.10
2.09
2.06
2.04
0.95
0.51
0.46
0.00
4.24 4.22 4.20 4.18 4.16 4.14
f1 (ppm)
3.05 3.03 3.01 2.99 2.97 2.95
f1 (ppm)
O
TBS
TfN
27a
1H NMR
CDCl3
500 MHz
1.00
0.96
0.95
2.00
2.02
2.08
6.07
9.25
3.11
2.96
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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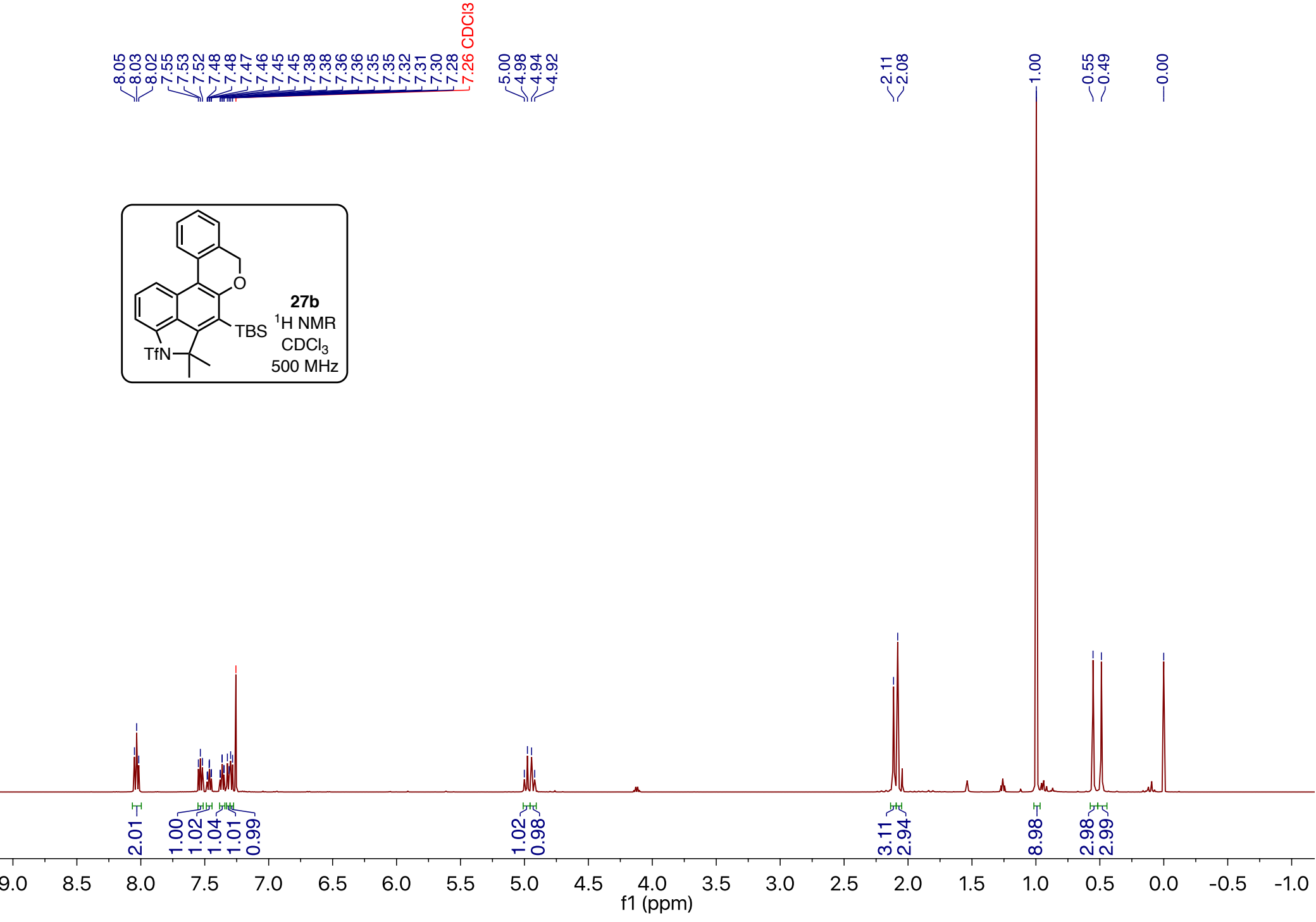
139.2
132.4
129.6
124.1
121.5
121.3
120.5
118.9
116.3
115.0
111.3
105.7
105.6
105.6
105.6
79.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
65.7
31.7
29.3
27.7
27.7
27.6
27.6
21.6
21.4
18.8
3.2
2.3
0.2
O
TBS
TfN
27a
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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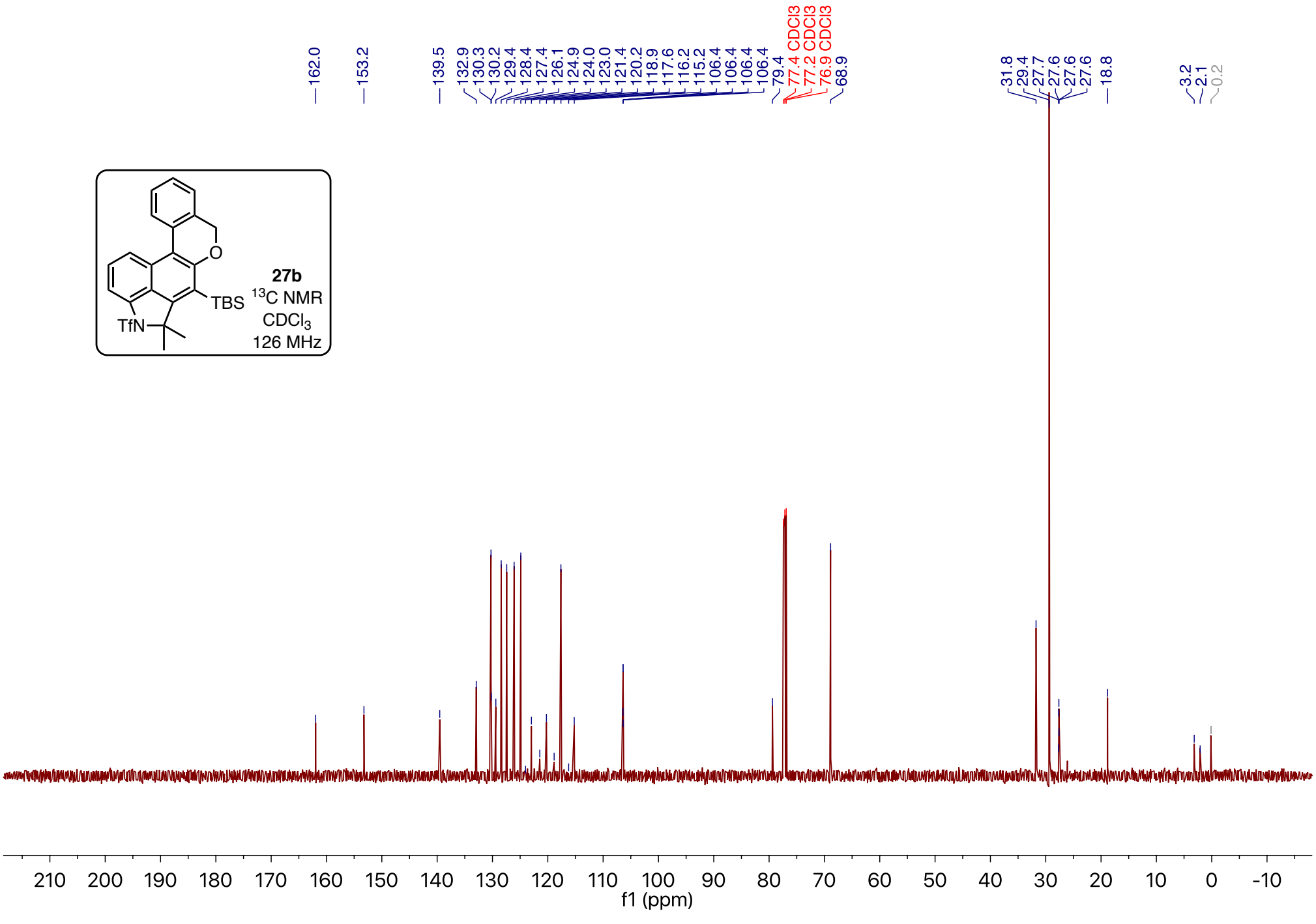
8.03
8.02
7.55
7.53
7.52
7.48
7.48
7.47
7.46
7.45
7.45
7.38
7.38
7.36
7.36
7.35
7.35
7.32
7.31
7.30
7.28
7.26 CDCl3
5.00
4.98
4.94
4.92
2.11
2.08
1.00
0.55
0.49
0.00
O
TBS
TfN
27b
1H NMR
CDCl3
500 MHz
2.01
1.00
1.02
1.04
1.01
0.99
1.02
0.98
3.11
2.94
8.98
2.98
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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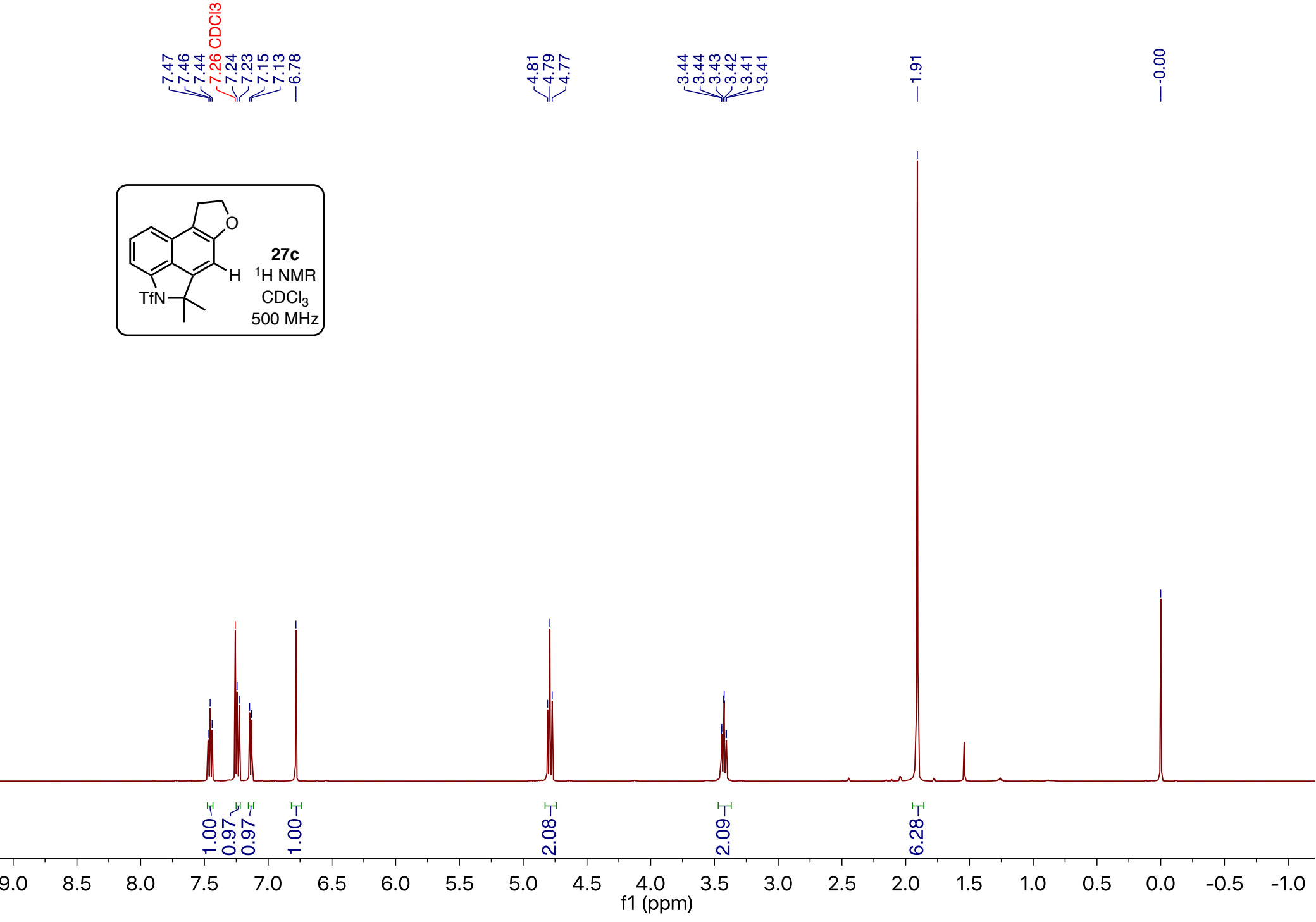
153.2
139.5
132.9
130.3
130.2
129.4
128.4
127.4
126.1
124.9
124.0
123.0
121.4
120.2
118.9
117.6
116.2
115.2
106.4
106.4
106.4
79.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
68.9
31.8
29.4
27.7
27.6
27.6
27.6
18.8
3.2
2.1
0.2
O
TBS
TfN
27b
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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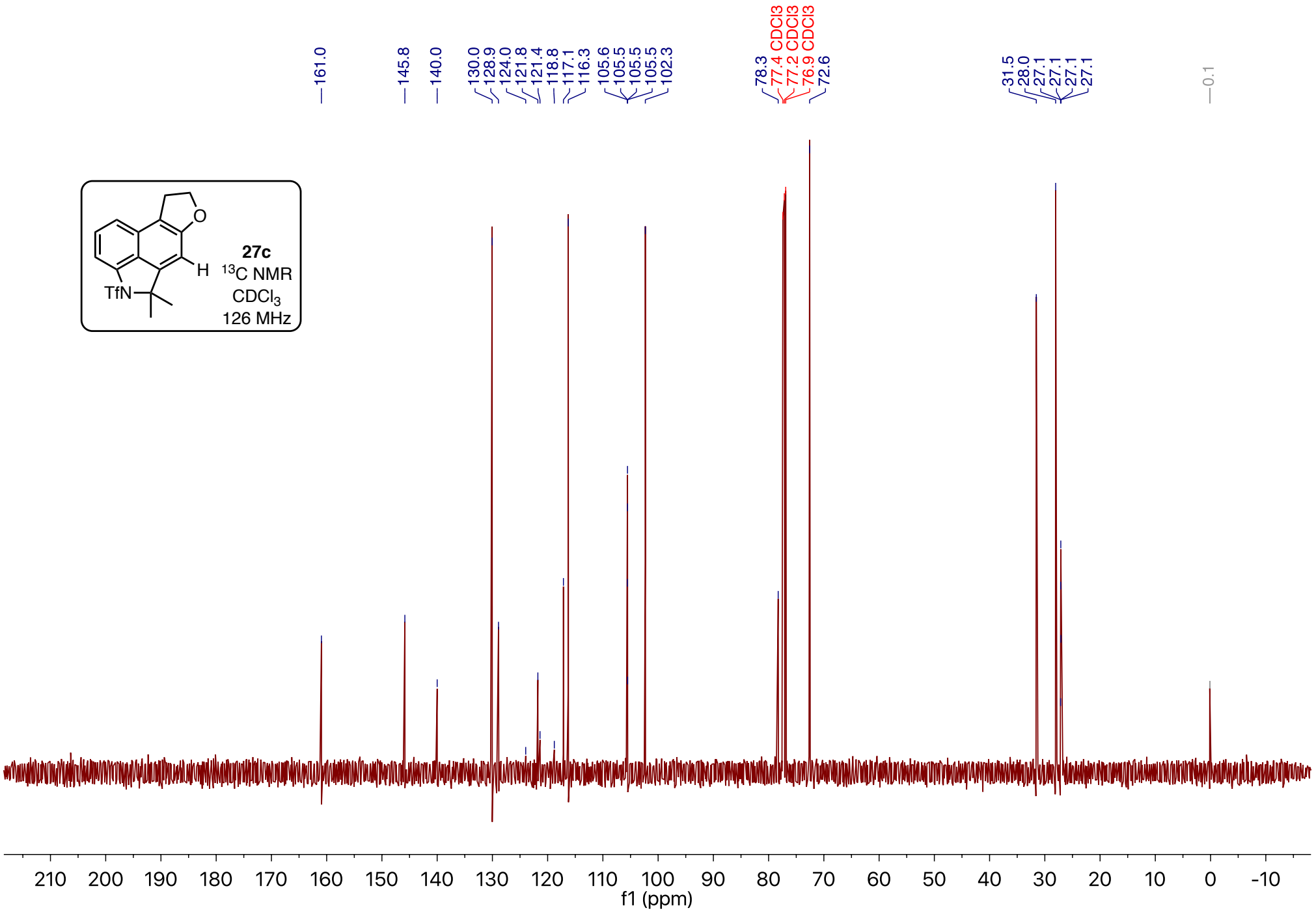
7.46
7.44
7.26 CDCl3
7.24
7.23
7.15
7.13
6.78
4.81
4.79
4.77
3.44
3.44
3.43
3.42
3.41
3.41
1.91
-0.00
O
H
TfN
27c
1H NMR
CDCl3
500 MHz
1.00
0.97
0.97
1.00
2.08
2.09
6.28
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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145.8
140.0
130.0
128.9
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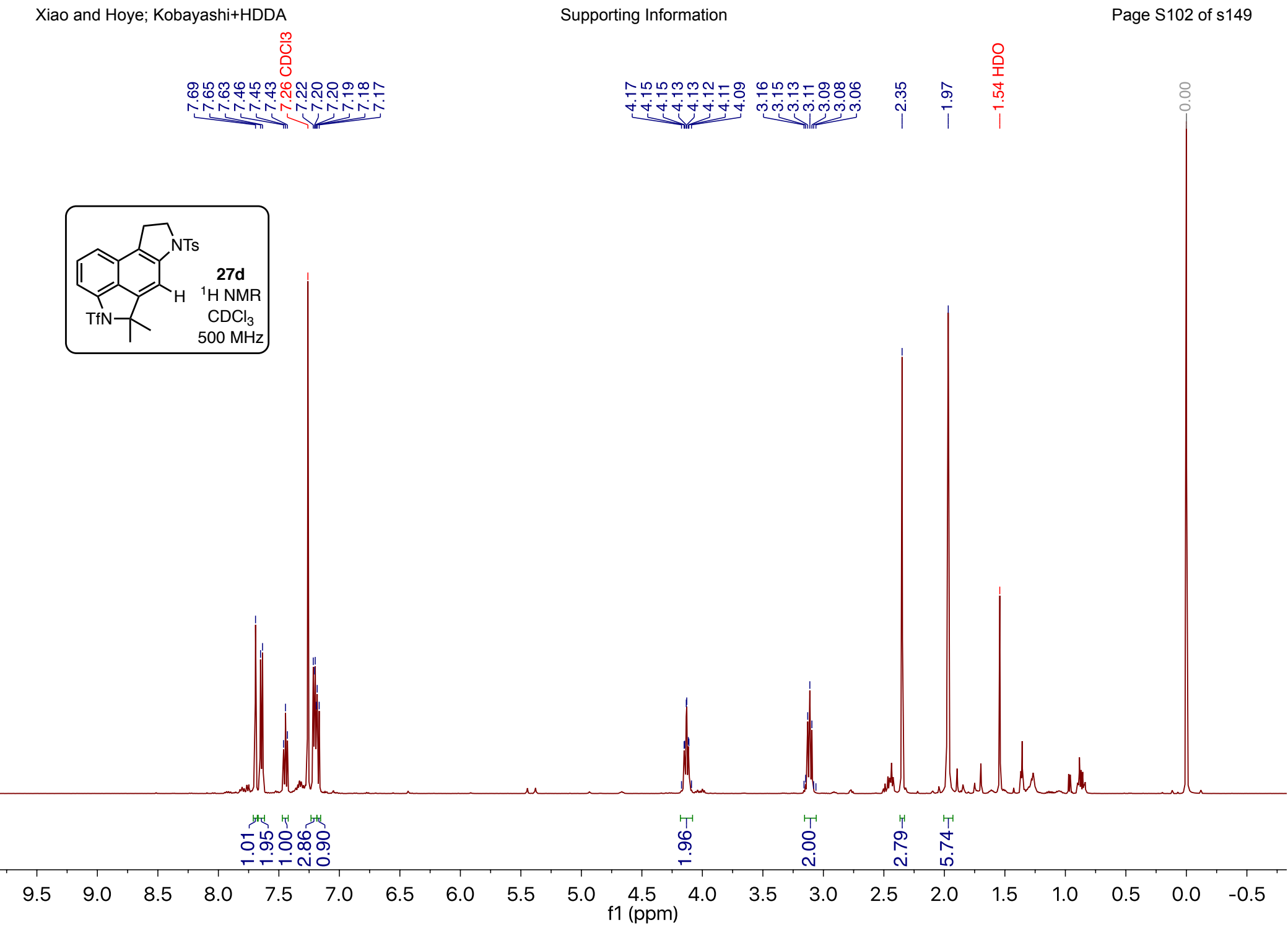
121.8
121.4
118.8
117.1
116.3
105.6
105.5
105.5
105.5
102.3
78.3
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
72.6
31.5
28.0
27.1
27.1
27.1
27.1
0.1
O
H
TfN
27c
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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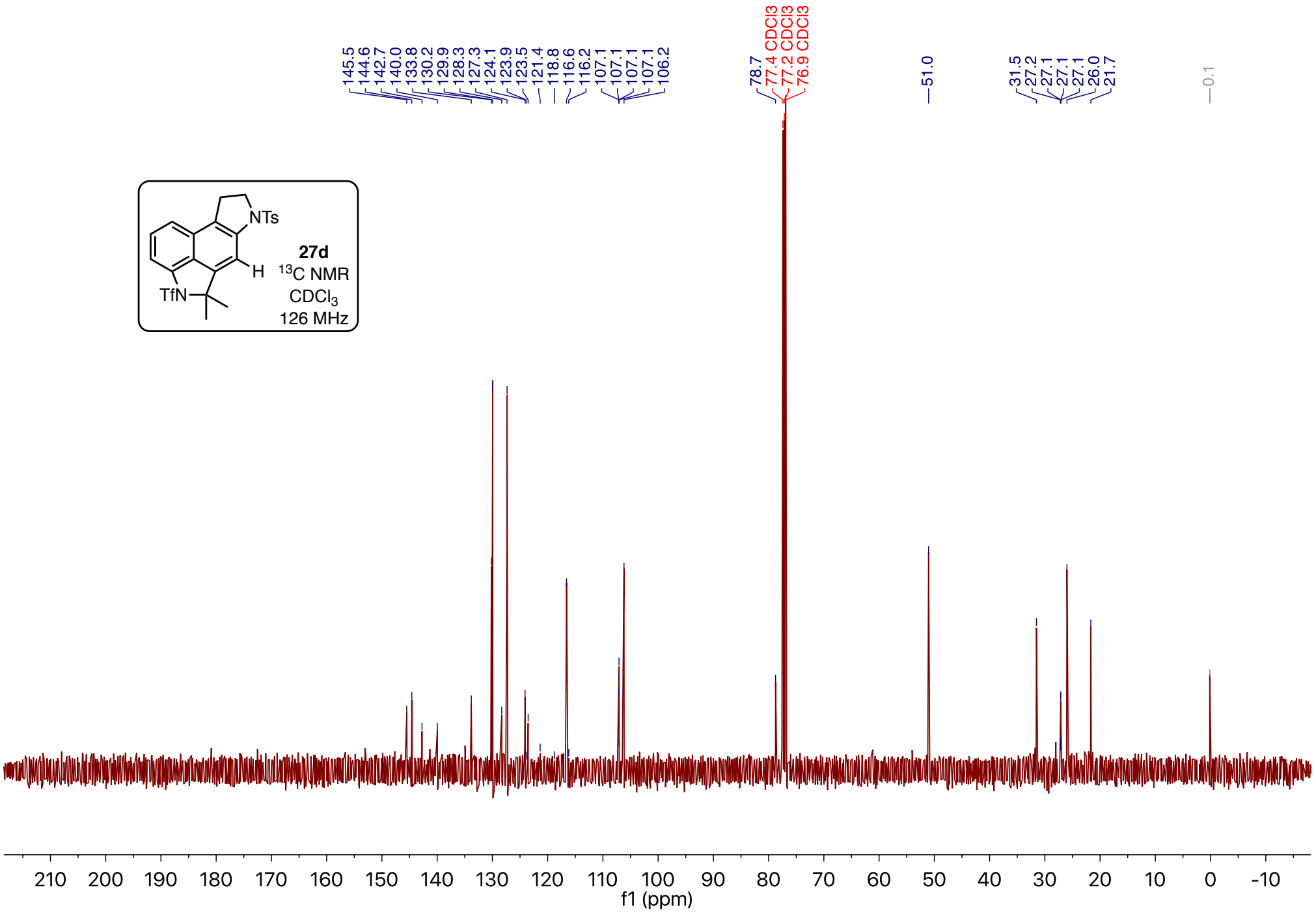
7.65
7.63
7.46
7.45
7.43
7.26 CDCl3
7.22
7.20
7.20
7.19
7.18
7.17
4.17
4.15
4.15
4.13
4.13
4.12
4.11
4.09
3.16
3.15
3.13
3.11
3.09
3.08
3.06
2.35
1.97
1.54 HDO
0.00
NTs
H
TfN
27d
1H NMR
CDCl3
500 MHz
1.01
1.95
1.00
2.86
0.90
1.96
2.00
2.79
5.74
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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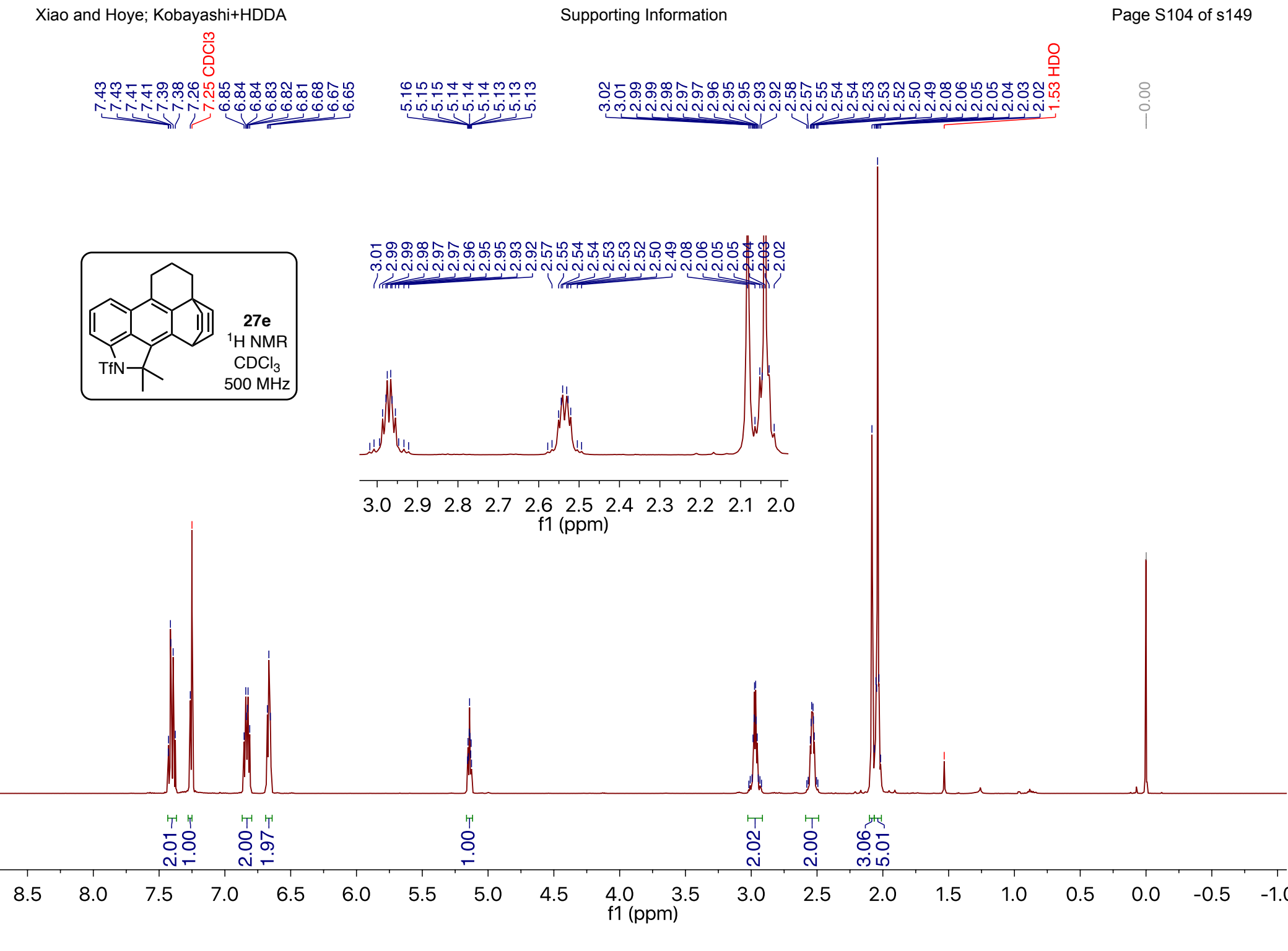
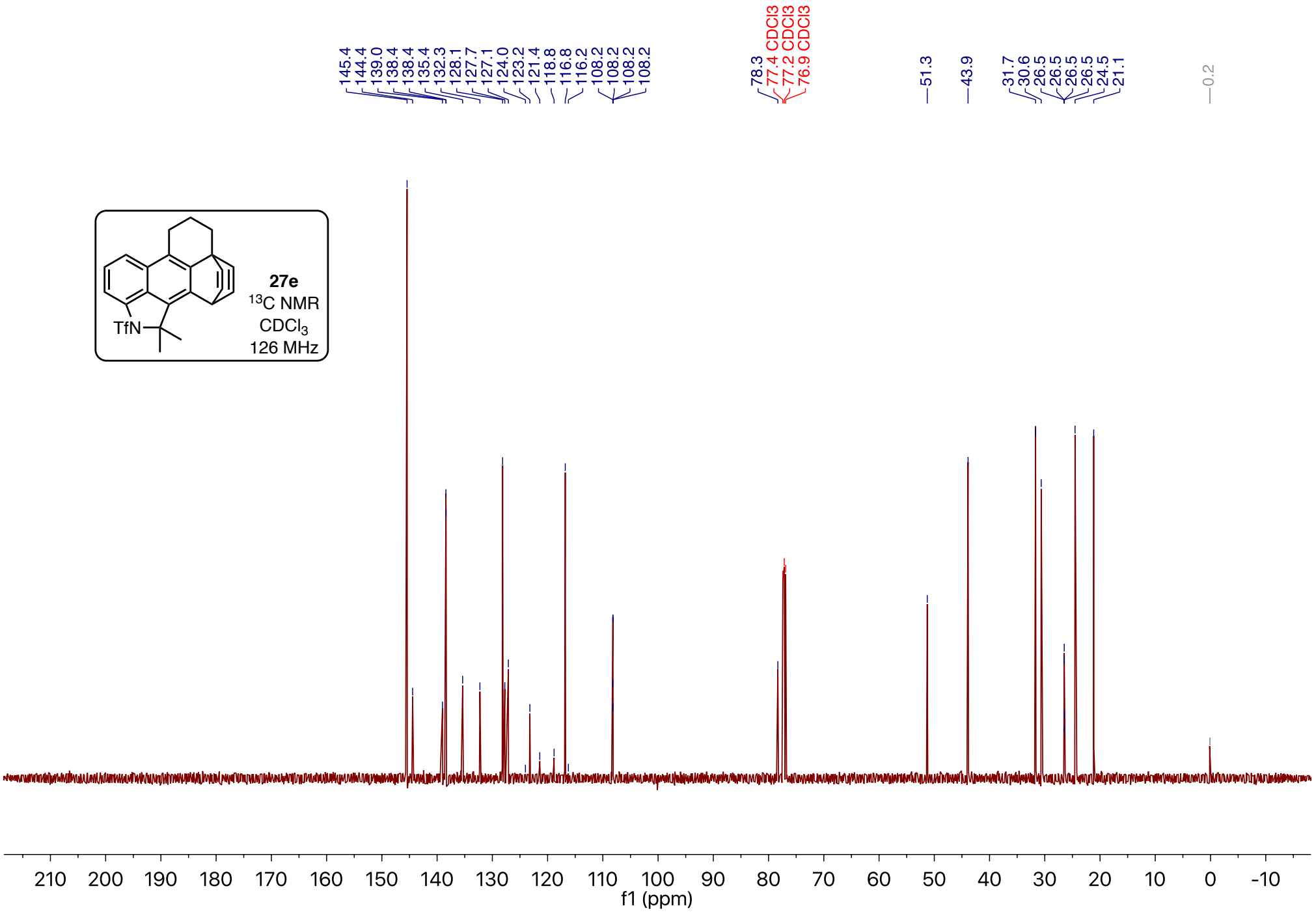
144.6
142.7
140.0
133.8
130.2
129.9
128.3
127.3
124.1
123.9
123.5
121.4
118.8
116.6
116.2
107.1
107.1
107.1
107.1
106.2
78.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
51.0
31.5
27.2
27.1
27.1
27.1
26.0
21.7
0.1
NTs
H
TfN
27d
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.43 7.43 7.41 7.41 7.39 7.38 7.26 7.25 CDCl3 6.85 6.84 6.84 6.83 6.82 6.81 6.68 6.67 6.65
5.16 5.15 5.15 5.14 5.14 5.14 5.13 5.13 5.13
3.02 3.01 2.99 2.99 2.98 2.97 2.97 2.96 2.95 2.95 2.93 2.92 2.58 2.57 2.55 2.54 2.54 2.53 2.53 2.52 2.50 2.49 2.08 2.06 2.05 2.04 2.03 2.02 1.53 HDO
0.00
TfN
27e
1H NMR
CDCl3
500 MHz
3.01 2.99 2.99 2.98 2.97 2.97 2.96 2.95 2.95 2.93 2.92 2.57 2.55 2.54 2.54 2.53 2.53 2.52 2.50 2.49 2.08 2.06 2.05 2.04 2.03 2.02
3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0
f1 (ppm)
2.01 1.00 2.00 1.97 1.00 2.02 2.00 3.06 5.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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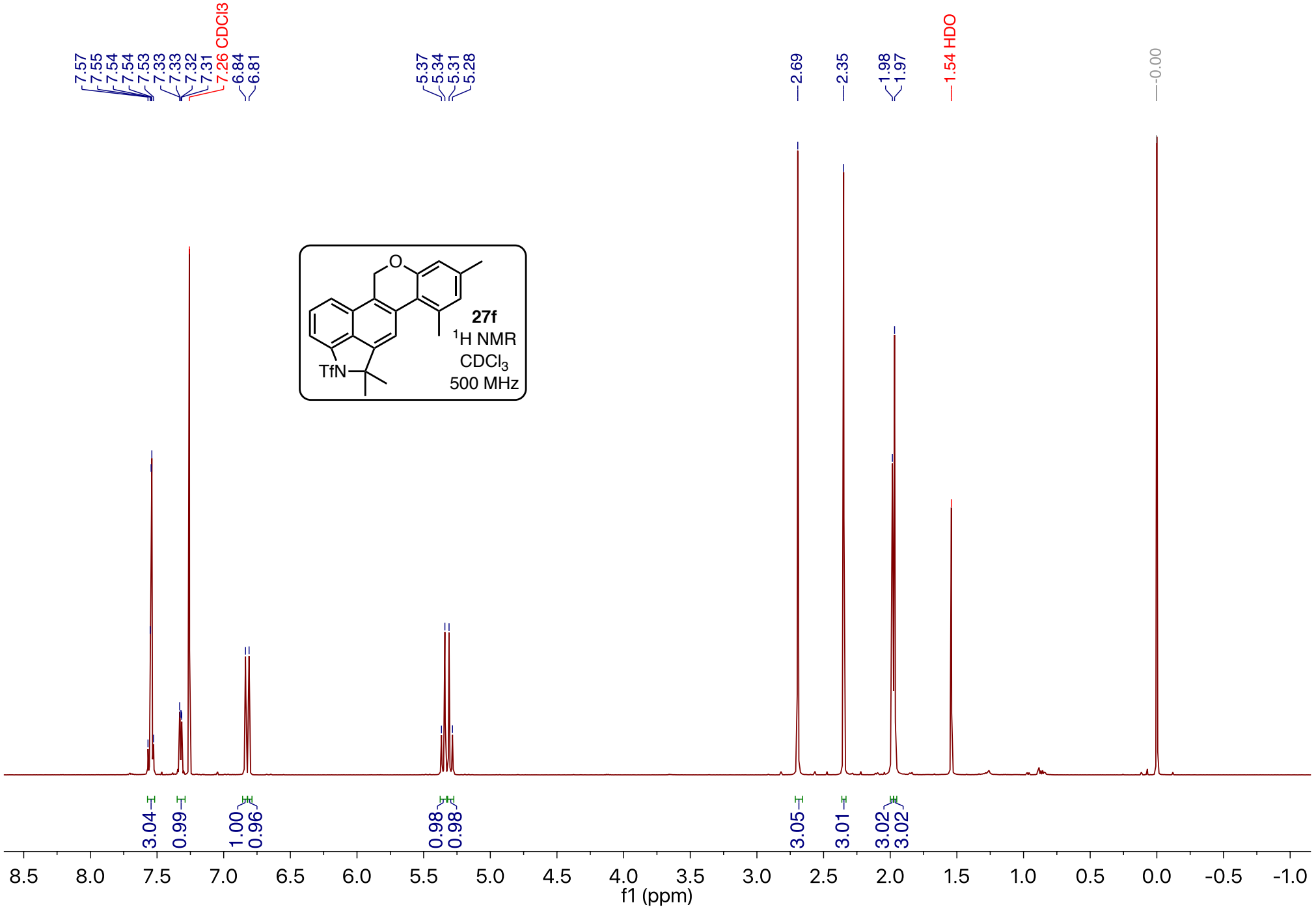
139.0
138.4
138.4
135.4
132.3
128.1
127.7
127.1
124.0
123.2
121.4
118.8
116.2
116.2
108.2
108.2
108.2
108.2
78.3
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
51.3
43.9
31.7
30.6
26.5
26.5
26.5
24.5
21.1
0.2
TfN
27e
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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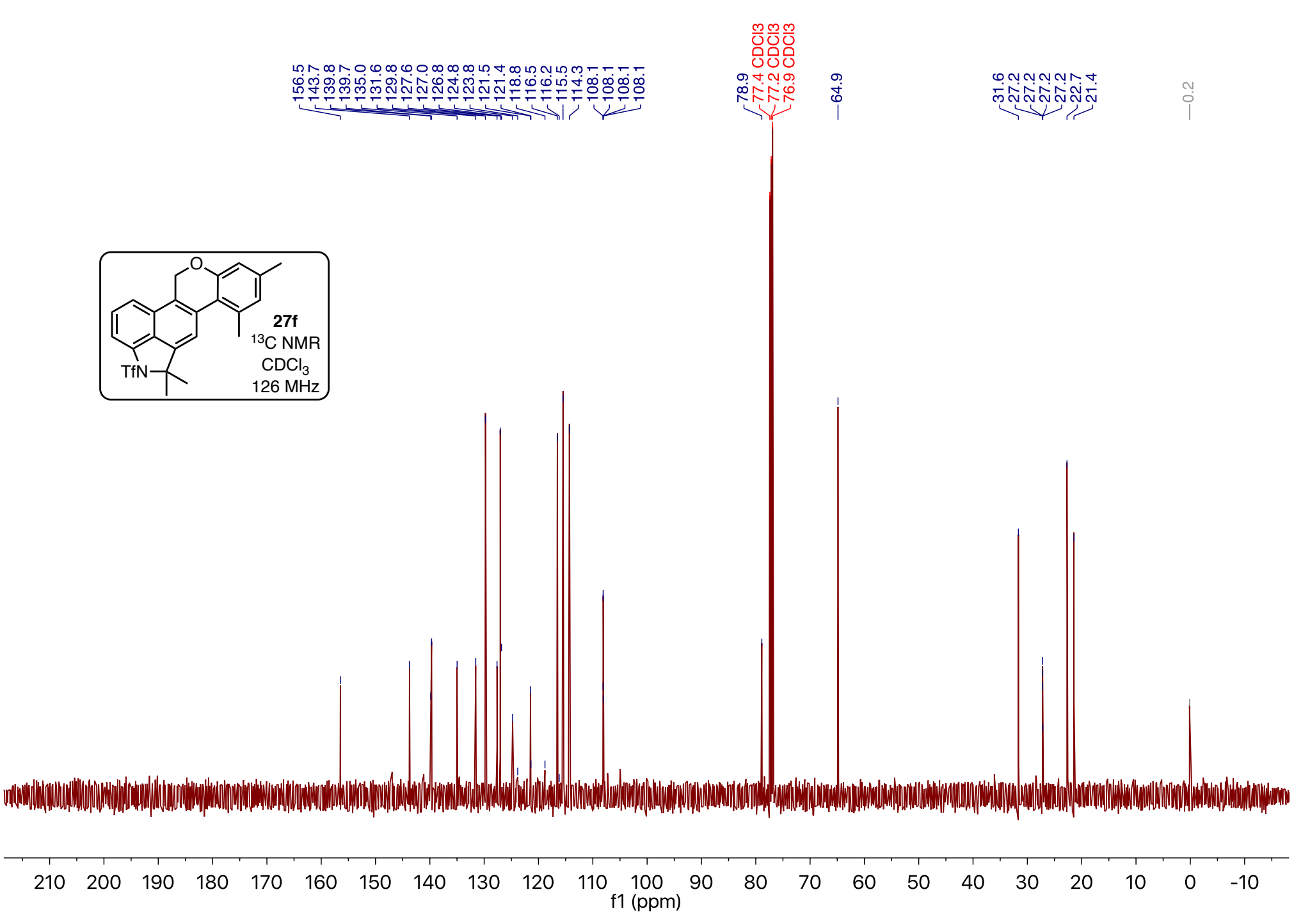
7.55
7.54
7.54
7.53
7.33
7.33
7.32
7.31
7.26 CDCl3
6.84
6.81
5.37
5.34
5.31
5.28
2.69
2.35
1.98
1.97
1.54 HDO
0.00
O
TfN
27f
1H NMR
CDCl3
500 MHz
3.04
0.99
1.00
0.96
0.98
0.98
3.05
3.01
3.02
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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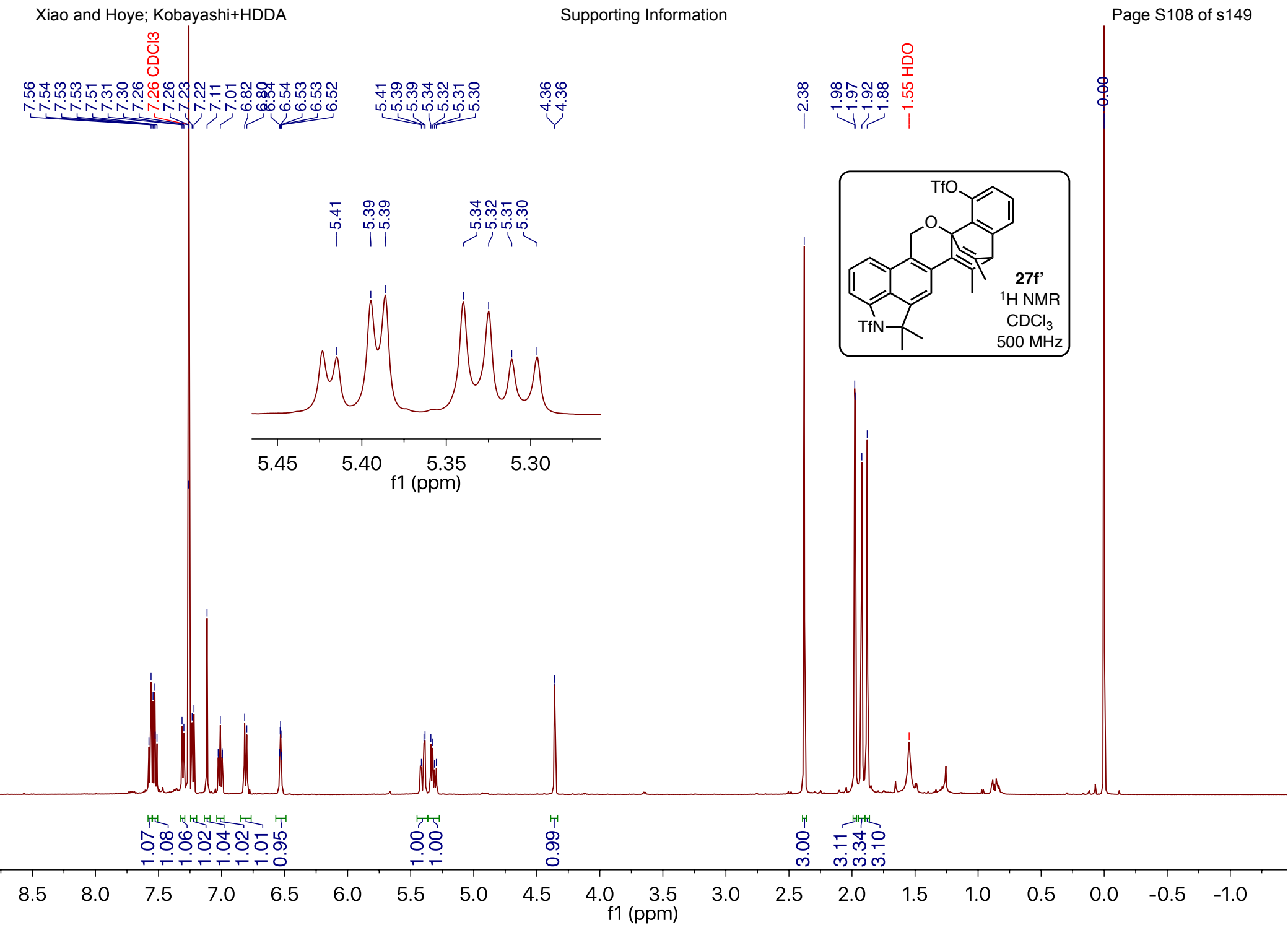
143.7
139.8
139.7
135.0
131.6
129.8
127.6
127.0
126.8
124.8
123.8
121.5
121.4
118.8
116.5
116.2
115.5
114.3
108.1
108.1
108.1
108.1
78.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
64.9
31.6
27.2
27.2
27.2
27.2
22.7
21.4
0.2
O
TfN
27f
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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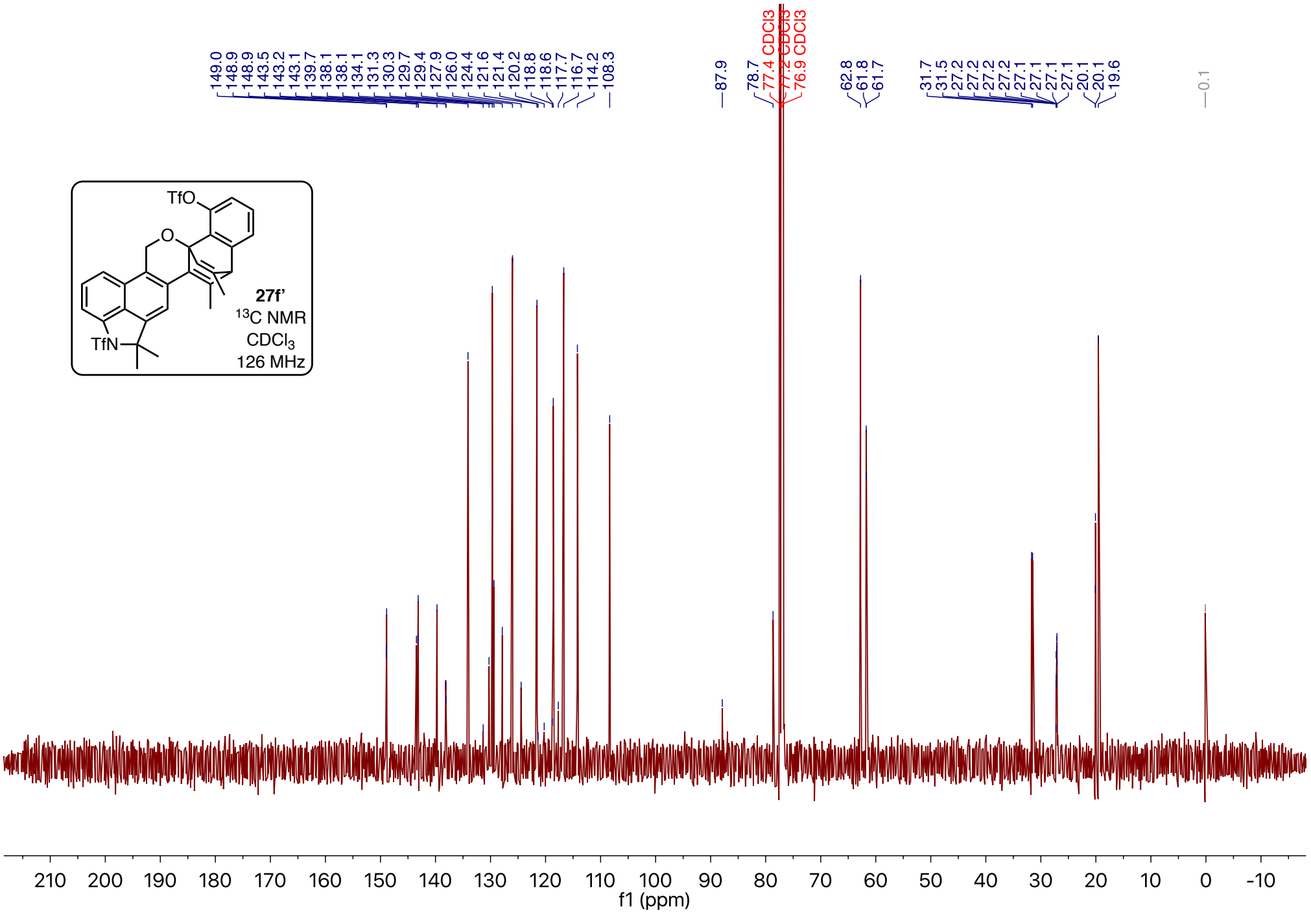
7.51
7.31
7.30
7.26
7.26 CDCl3
7.26
7.23
7.22
7.11
7.01
6.82
6.80
6.54
6.54
6.53
6.53
6.52
5.41
5.39
5.39
5.34
5.32
5.31
5.30
4.36
4.36
2.38
1.98
1.97
1.92
1.88
1.55 HDO
0.00
5.41
5.39
5.39
5.34
5.32
5.31
5.30
5.45
5.40
5.35
5.30
f1 (ppm)
TfO
O
TfN
27f'
1H NMR
CDCl3
500 MHz
1.07
1.08
1.06
1.02
1.04
1.02
1.01
0.95
1.00
1.00
0.99
3.00
3.11
3.34
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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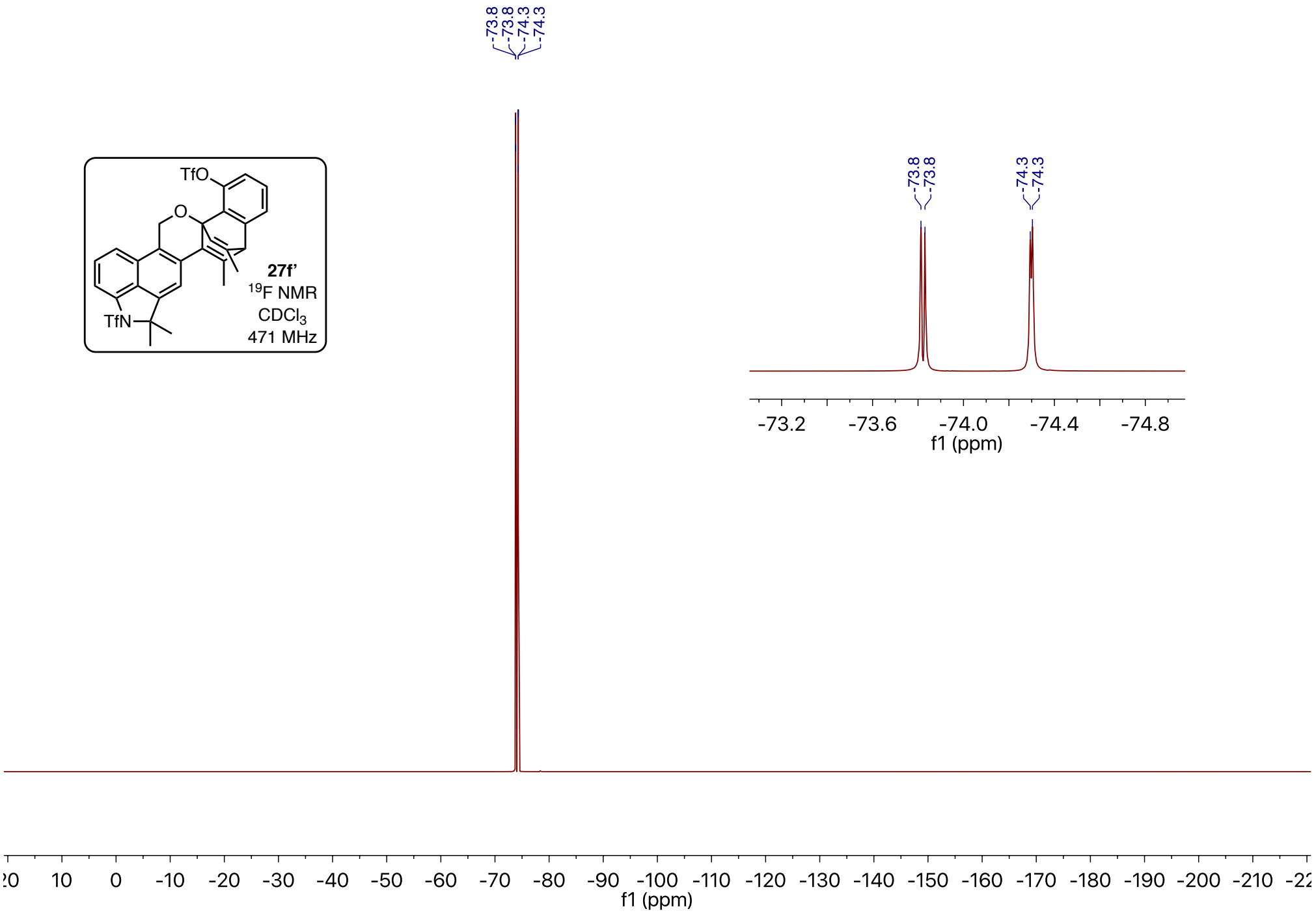
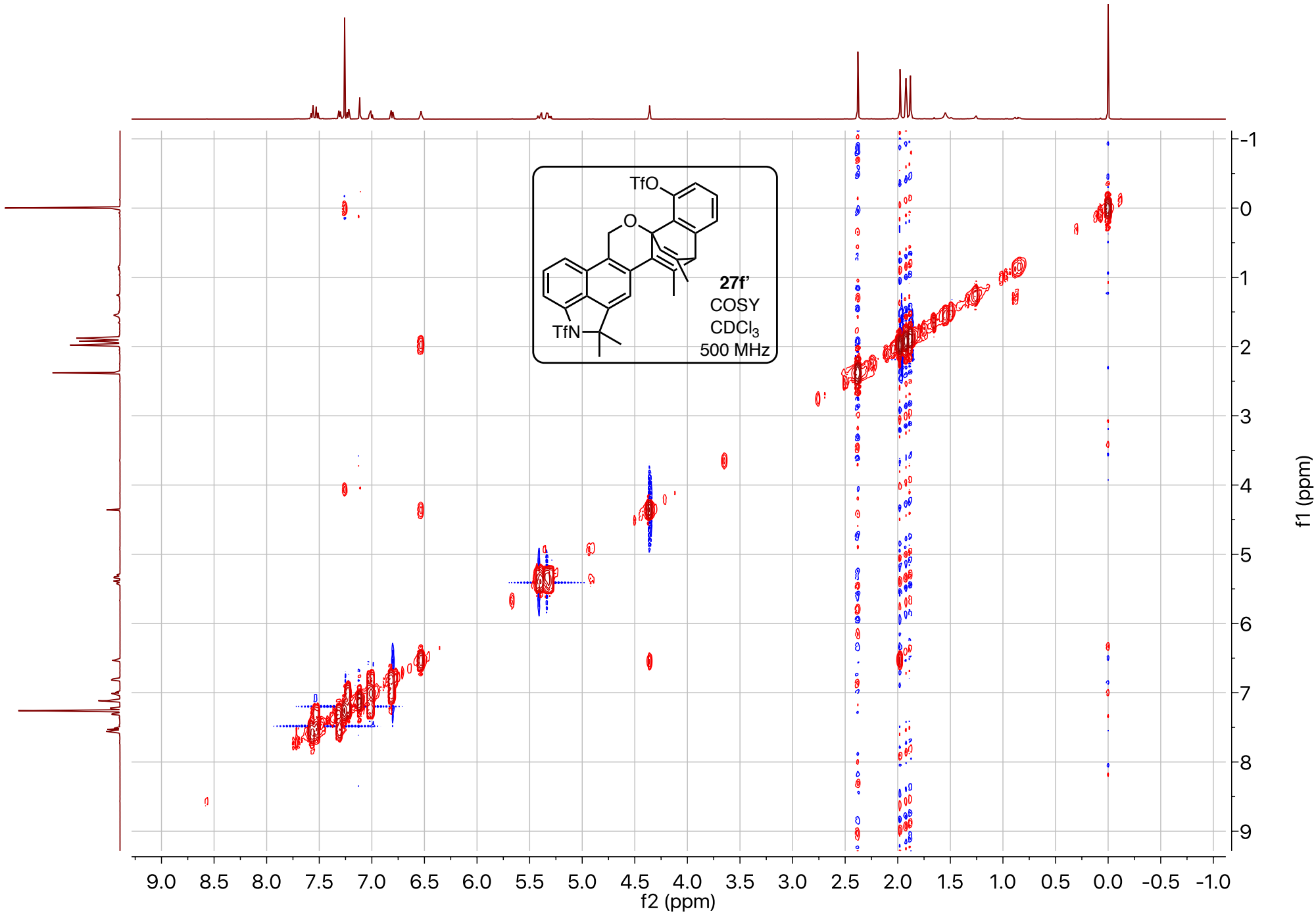
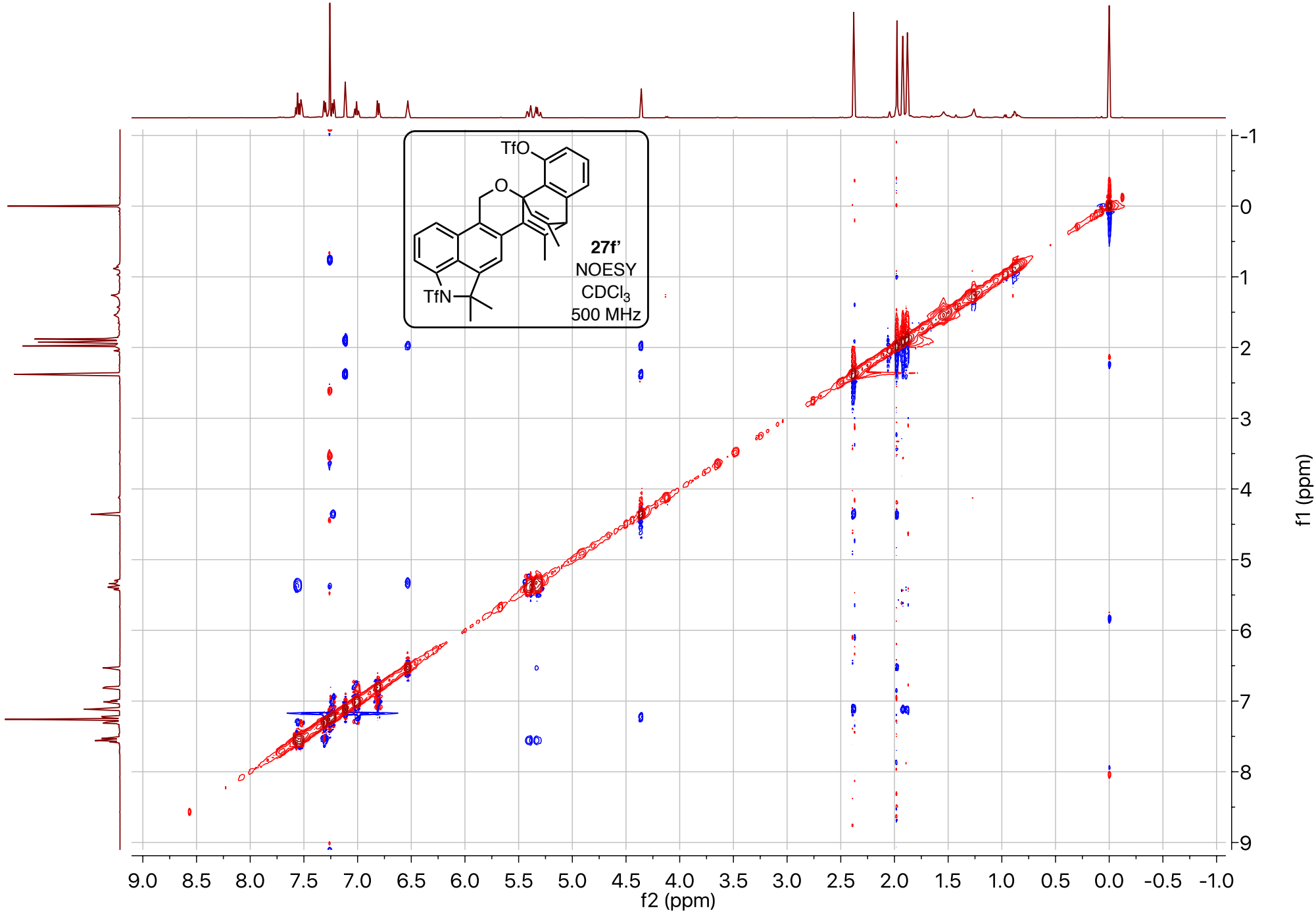
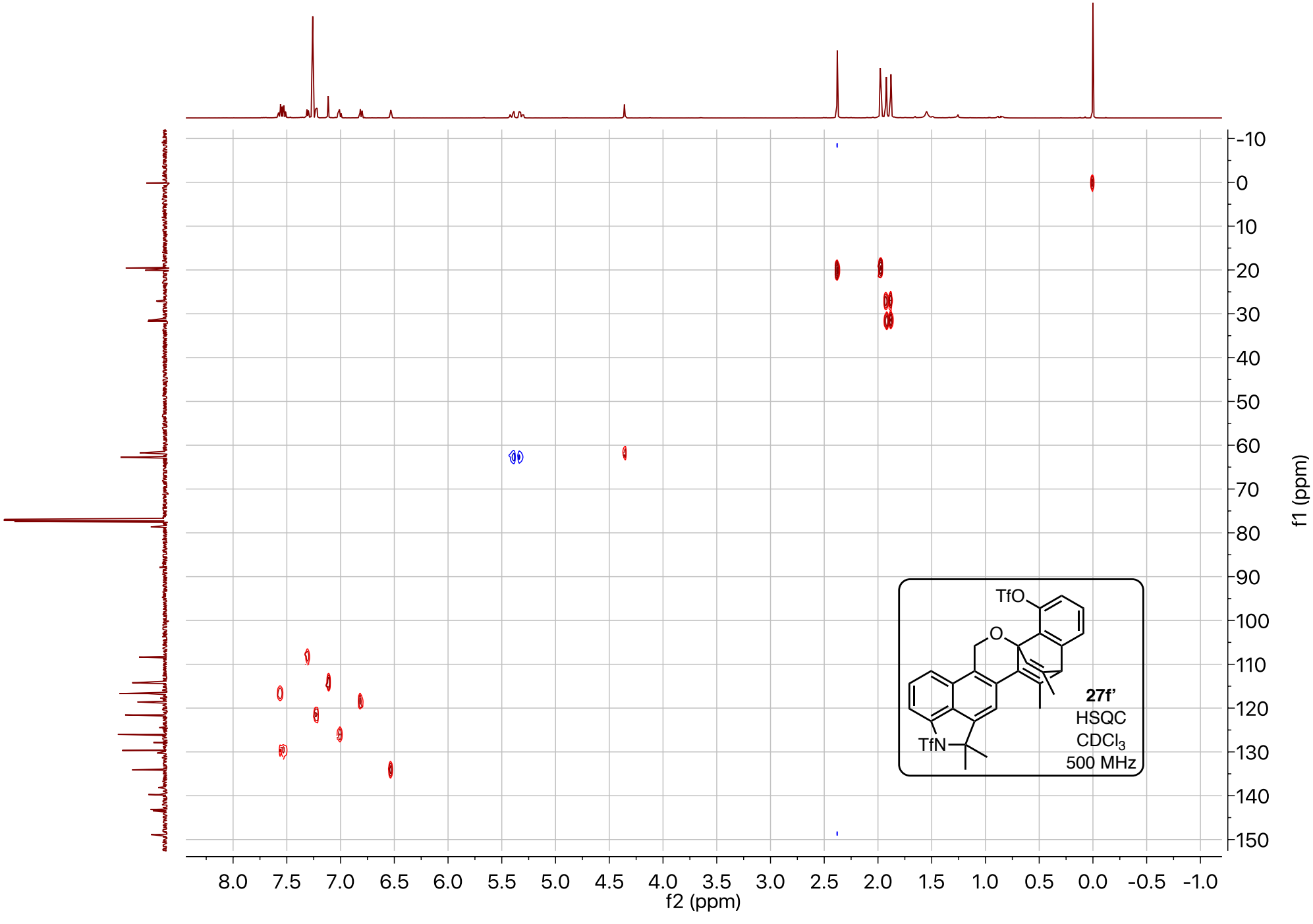
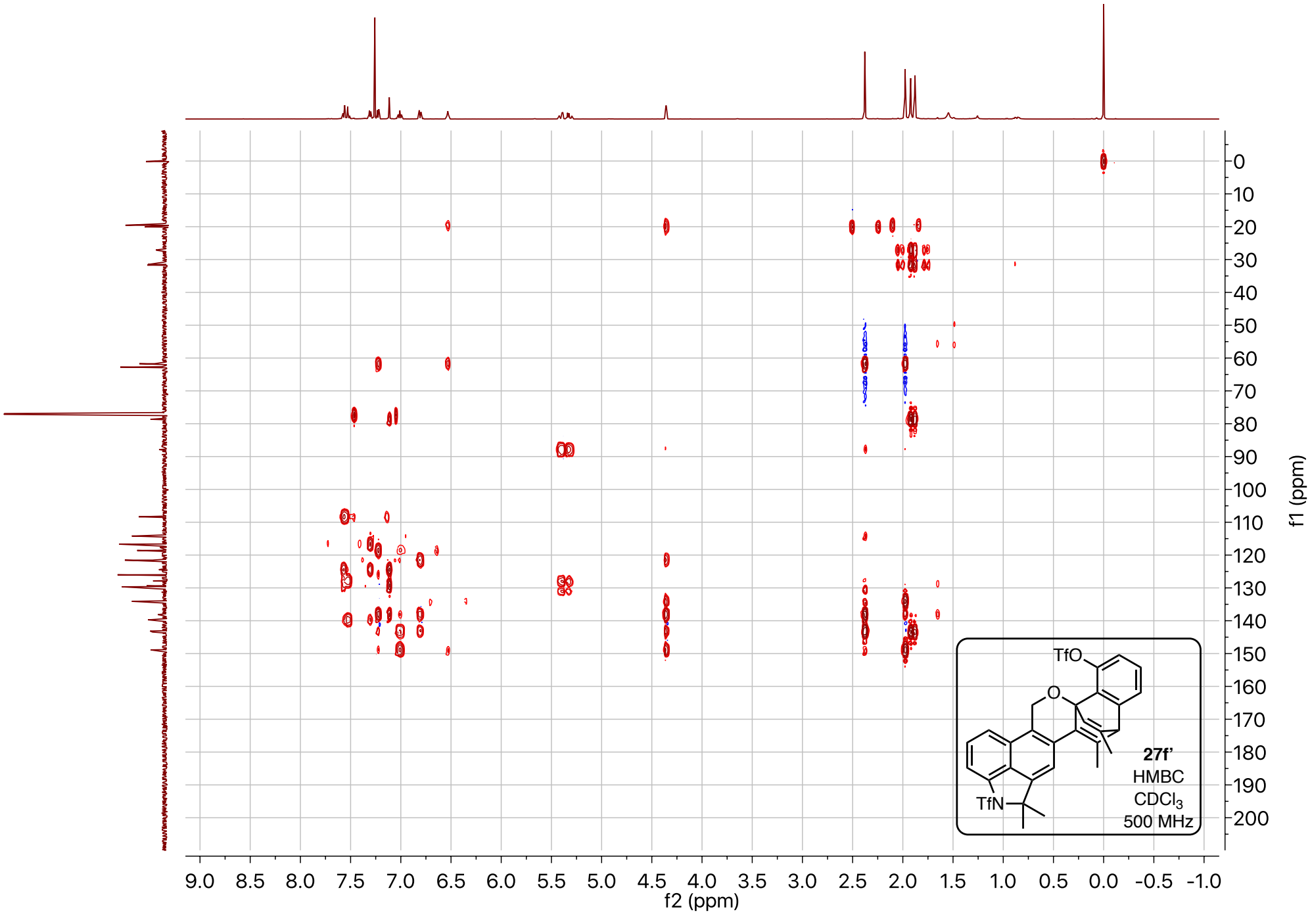
138.1
138.1
134.1
131.3
130.3
129.7
129.4
127.9
126.0
124.4
121.6
121.4
120.2
118.8
118.6
117.7
116.7
114.2
108.3
87.9
78.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
62.8
61.8
61.7
31.7
31.5
27.2
27.2
27.2
27.2
27.1
27.1
27.1
27.1
20.1
20.1
19.6
0.1
TfO
O
TfN
27f'
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

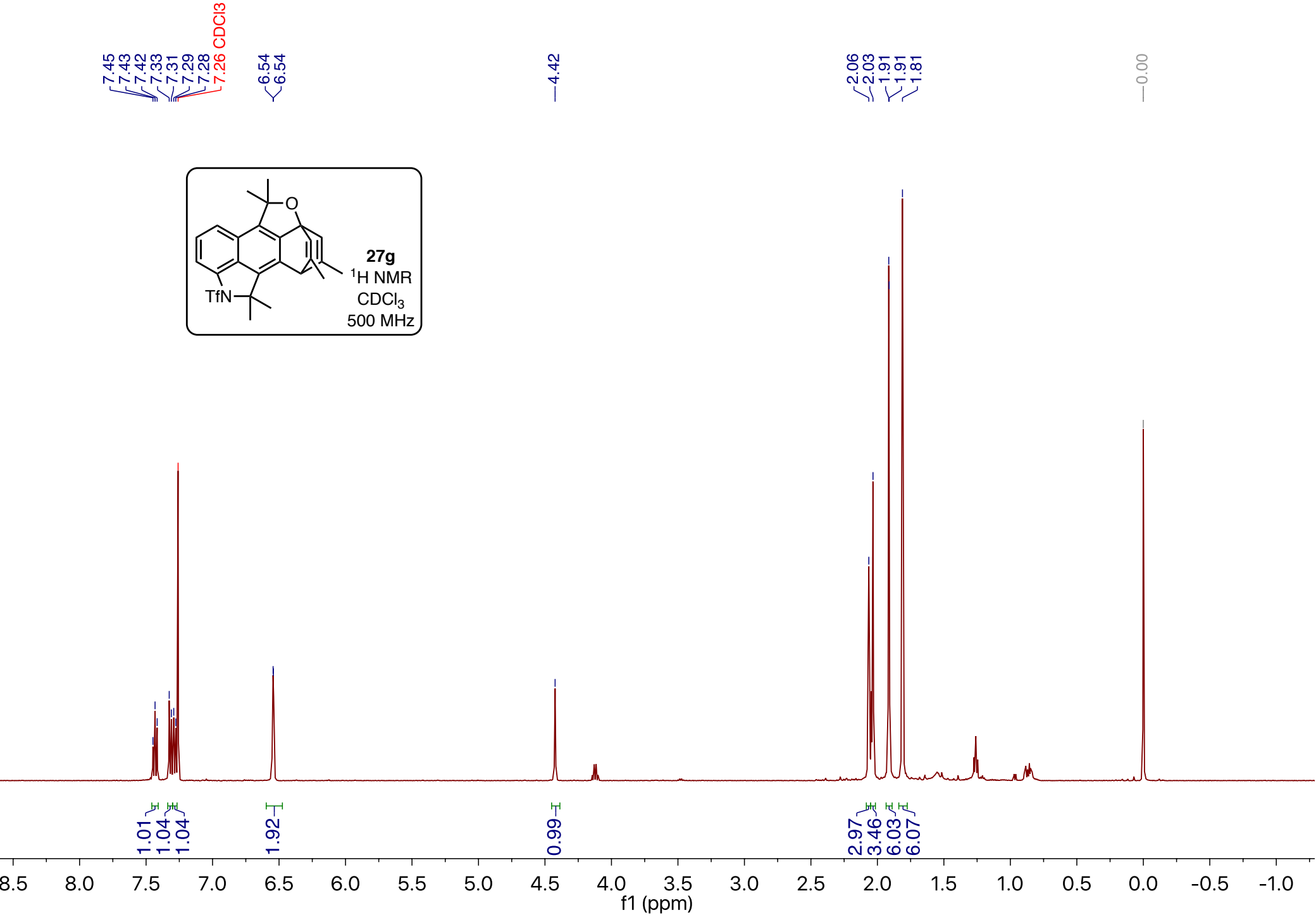

-73.8
-73.8
-74.3
-74.3
TfO
O
TfN
27f'
19F NMR
CDCl3
471 MHz
-73.8
-73.8
-74.3
-74.3
-73.2
-73.6
-74.0
-74.4
-74.8
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

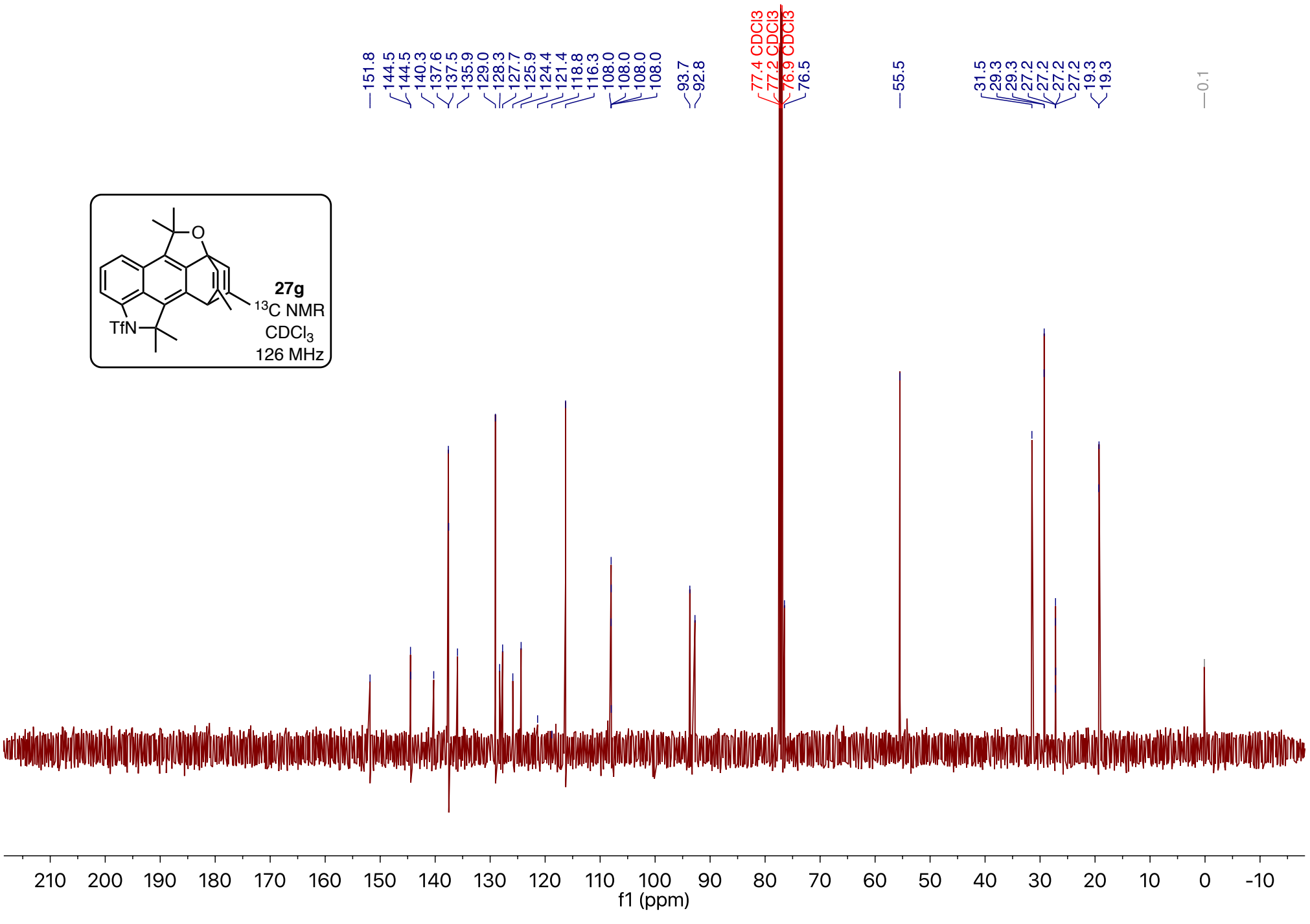

TfO
O
TfN
27f'
COSY
CDCl3
500 MHz
f2 (ppm)
f1 (ppm)


TfO
O
TfN
27f'
NOESY
CDCl3
500 MHz
f2 (ppm)
f1 (ppm)


TfO
O
TfN
27f'
HSQC
CDCl3
500 MHz
f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)
TfO
O
TfN
27f'
HMBC
CDCl3
500 MHz


7.45
7.43
7.42
7.33
7.31
7.29
7.28
7.26 CDCl3
6.54
6.54
4.42
2.06
2.03
1.91
1.91
1.81
0.00
O
TfN
27g
1H NMR
CDCl3
500 MHz
1.01
1.04
1.04
1.92
0.99
2.97
3.46
6.03
6.07
f1 (ppm)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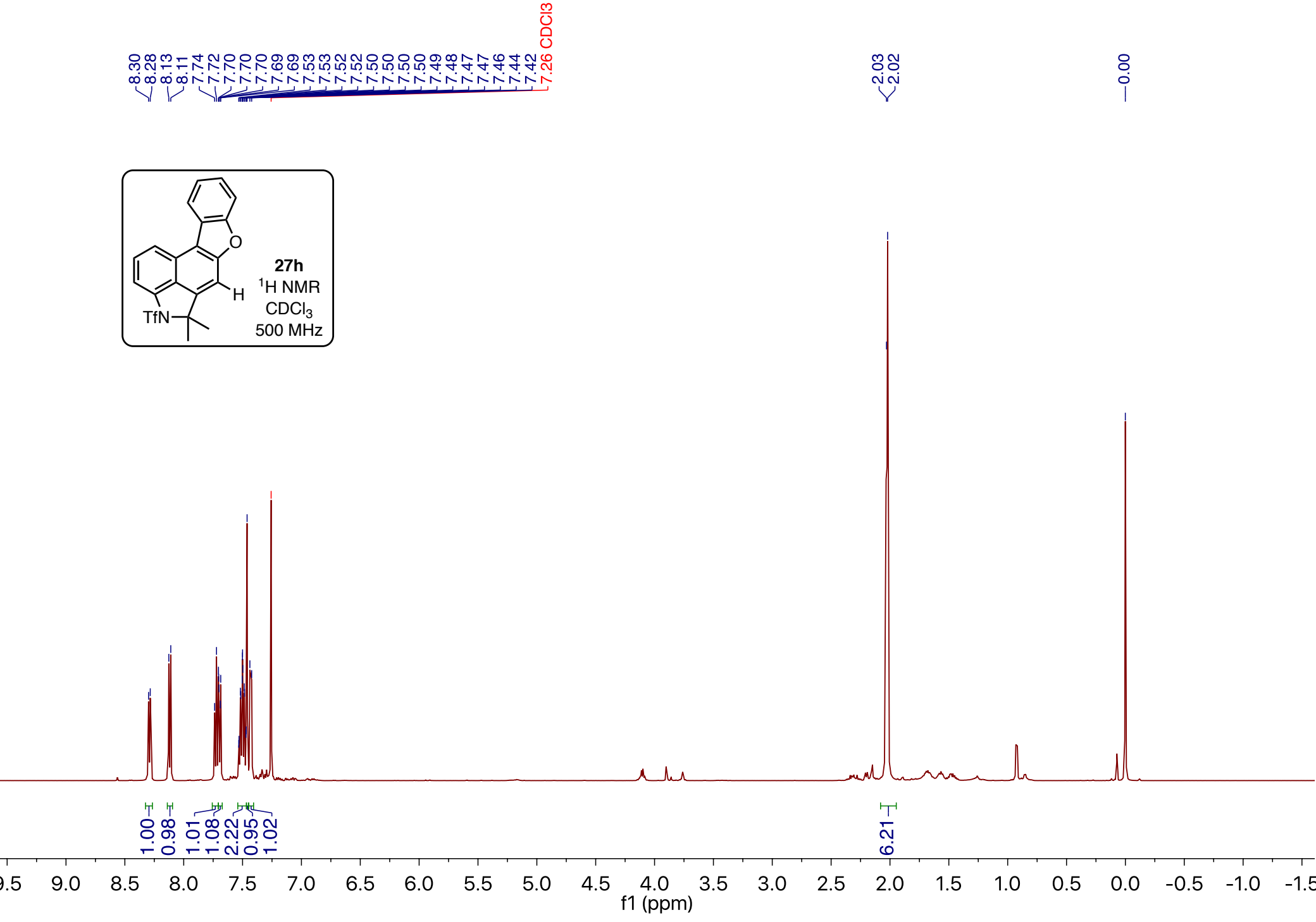
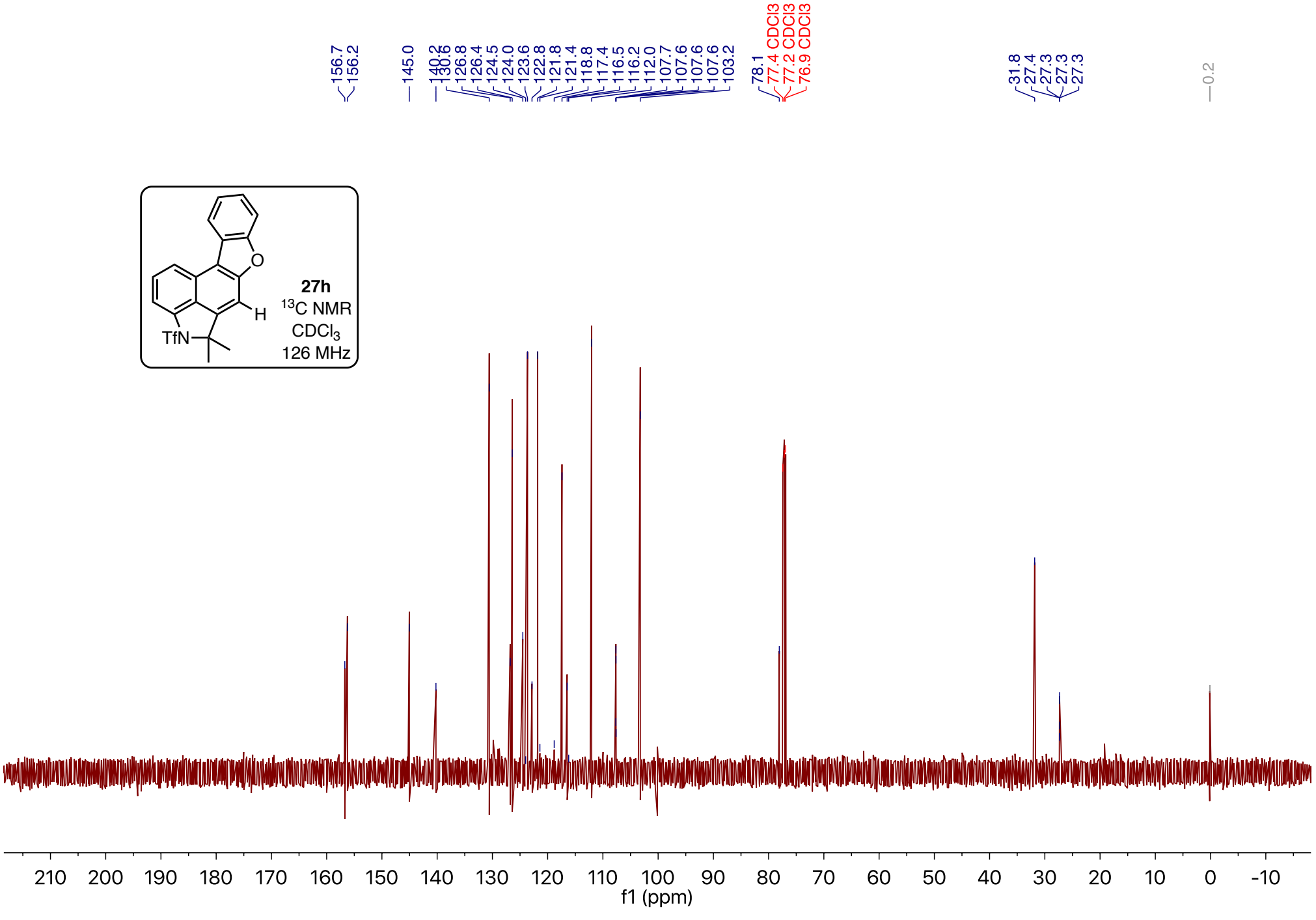
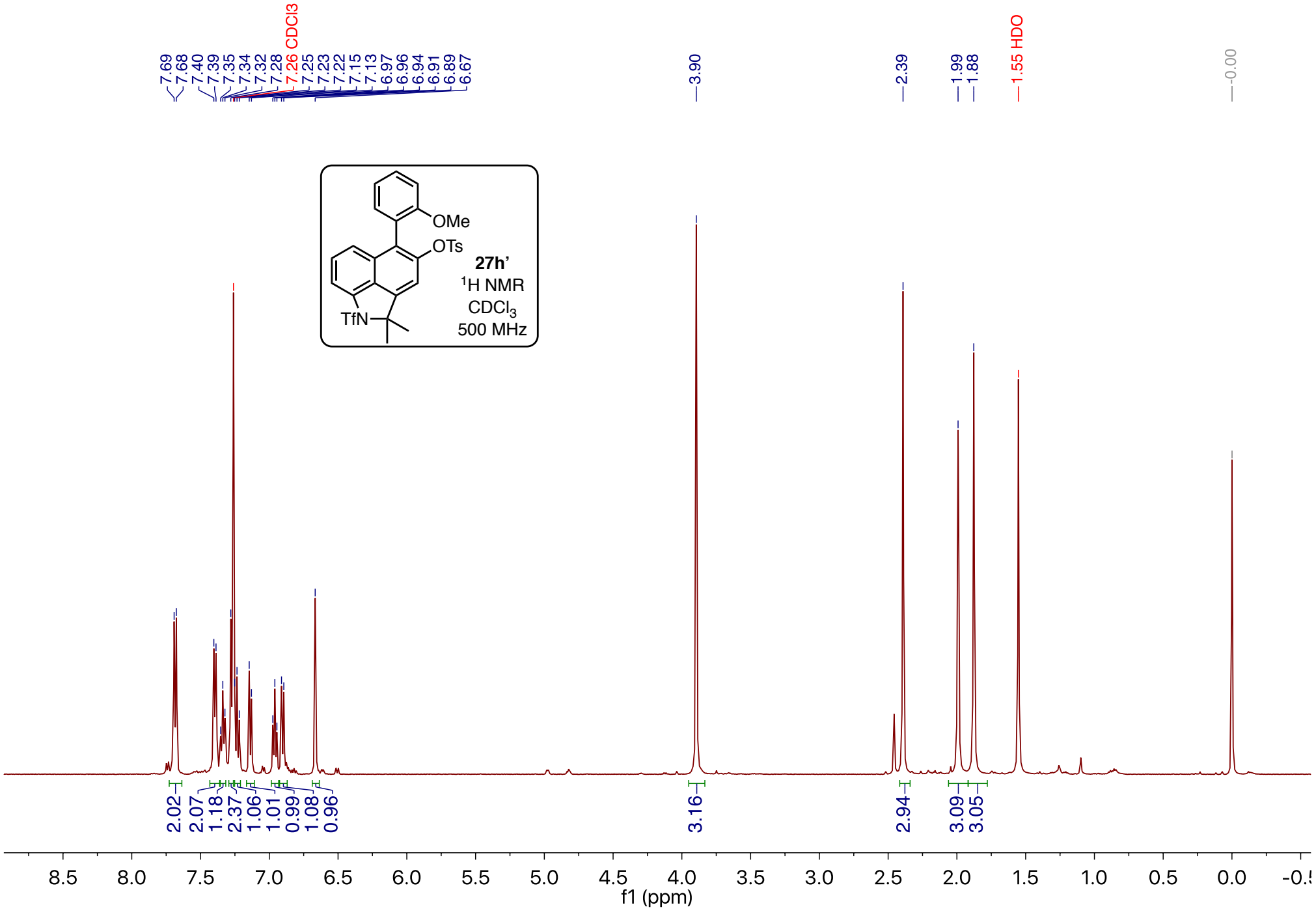
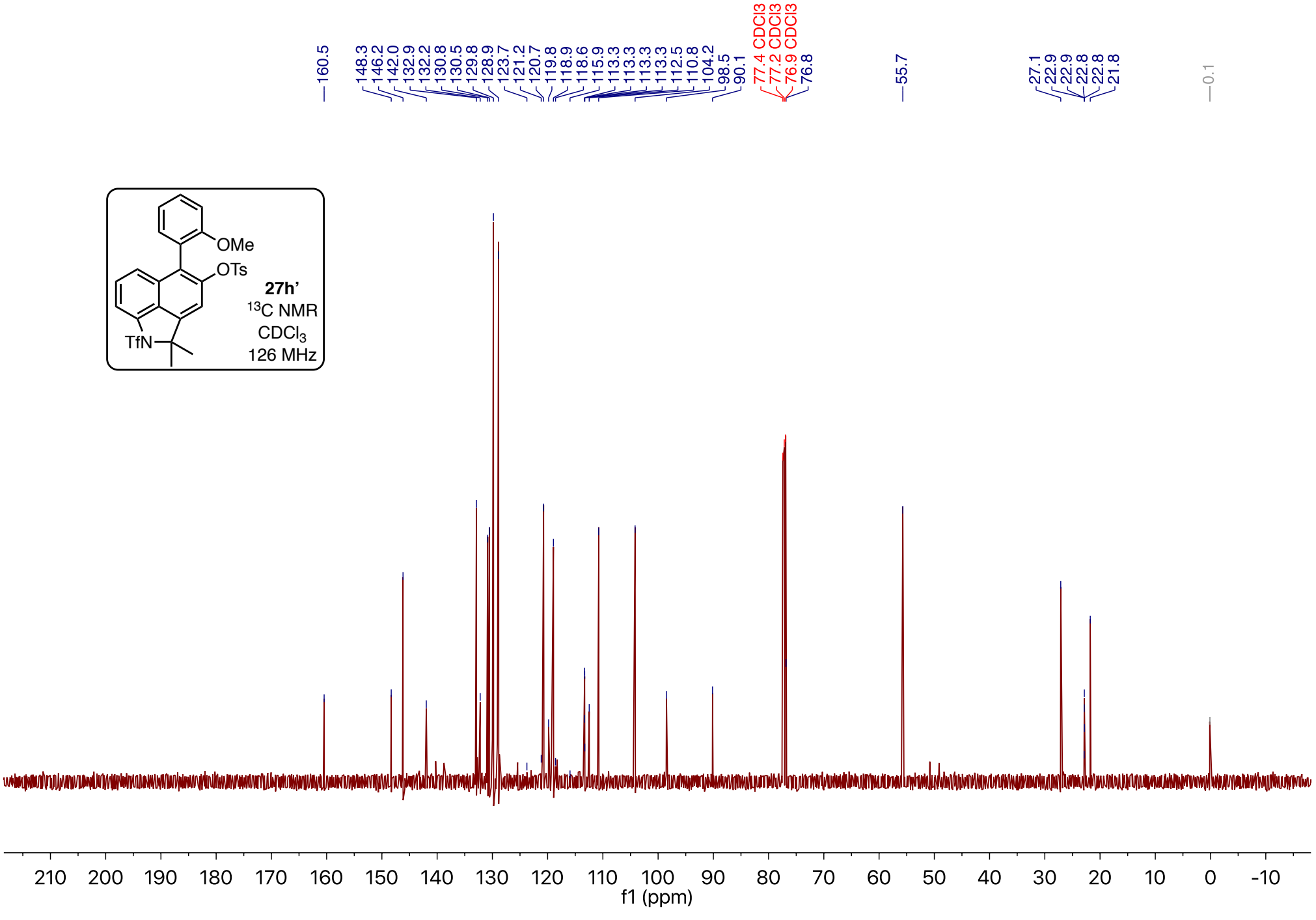
144.5
144.5
140.3
137.6
137.5
135.9
129.0
128.3
127.7
125.9
124.4
121.4
118.8
116.3
108.0
108.0
108.0
108.0
93.7
92.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.5
55.5
31.5
29.3
29.3
27.2
27.2
27.2
27.2
19.3
19.3
0.1
O
TfN
27g
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.30
8.28
8.13
8.11
7.74
7.72
7.70
7.70
7.70
7.69
7.69
7.53
7.53
7.52
7.52
7.50
7.50
7.50
7.50
7.49
7.48
7.47
7.47
7.46
7.44
7.42
7.26 CDCl3
2.03
2.02
0.00
O
H
TfN
27h
1H NMR
CDCl3
500 MHz
1.00
0.98
1.01
1.08
2.22
0.95
1.02
6.21
f1 (ppm)


156.7
156.2
145.0
140.2
130.6
126.8
126.4
124.5
124.0
123.6
122.8
121.8
121.4
118.8
117.4
116.5
116.2
112.0
107.7
107.6
107.6
107.6
103.2
78.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
31.8
27.4
27.3
27.3
27.3
0.2
O
H
TfN
27h
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.69
7.68
7.40
7.39
7.35
7.34
7.32
7.28
7.26 CDCl3
7.25
7.23
7.22
7.15
7.13
6.97
6.96
6.94
6.91
6.89
6.67
3.90
2.39
1.99
1.88
1.55 HDO
0.00
OMe
OTs
TfN
27h'
1H NMR
CDCl3
500 MHz
2.02
2.07
1.18
2.37
1.06
1.01
0.99
1.08
0.96
3.16
2.94
3.09
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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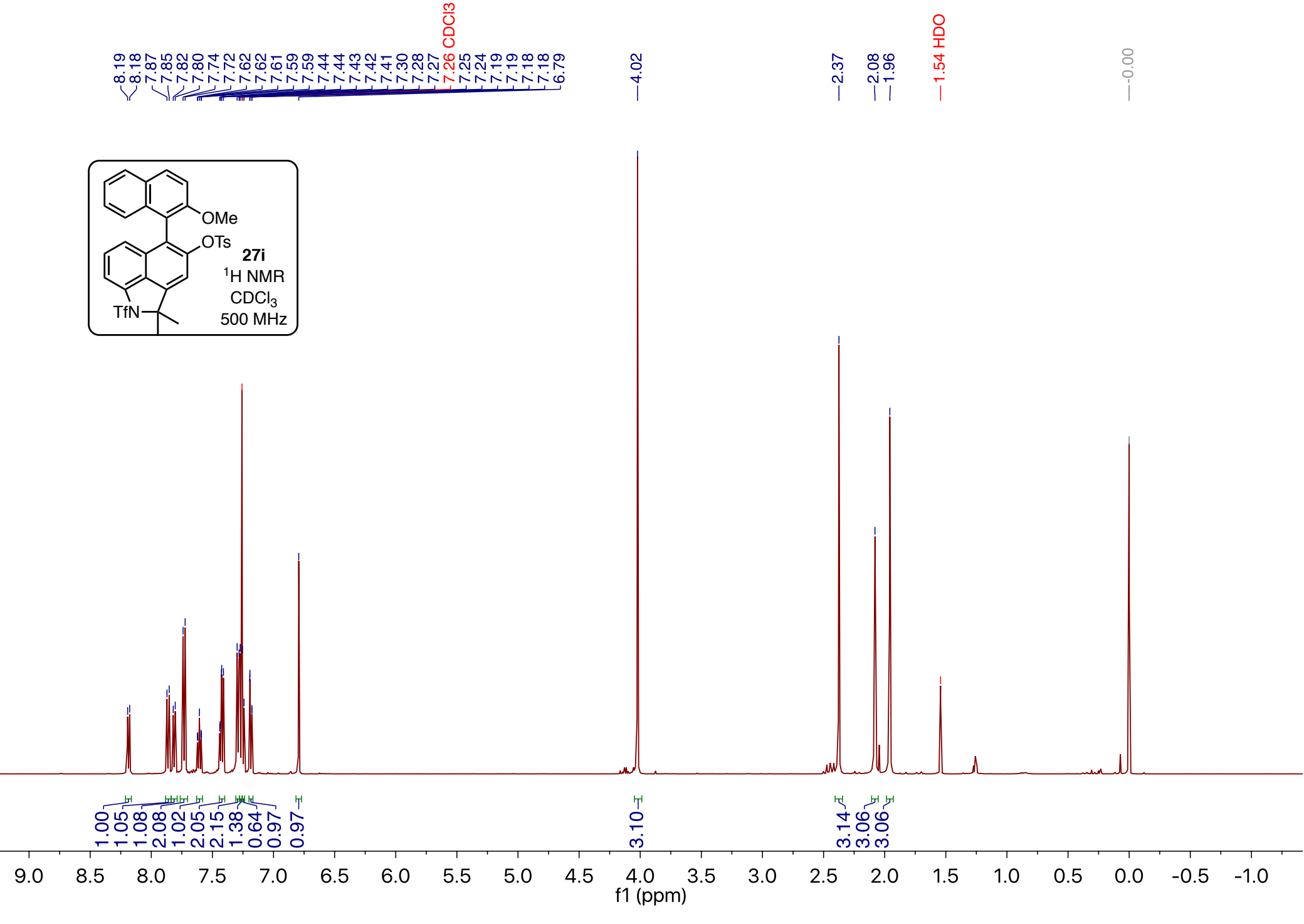
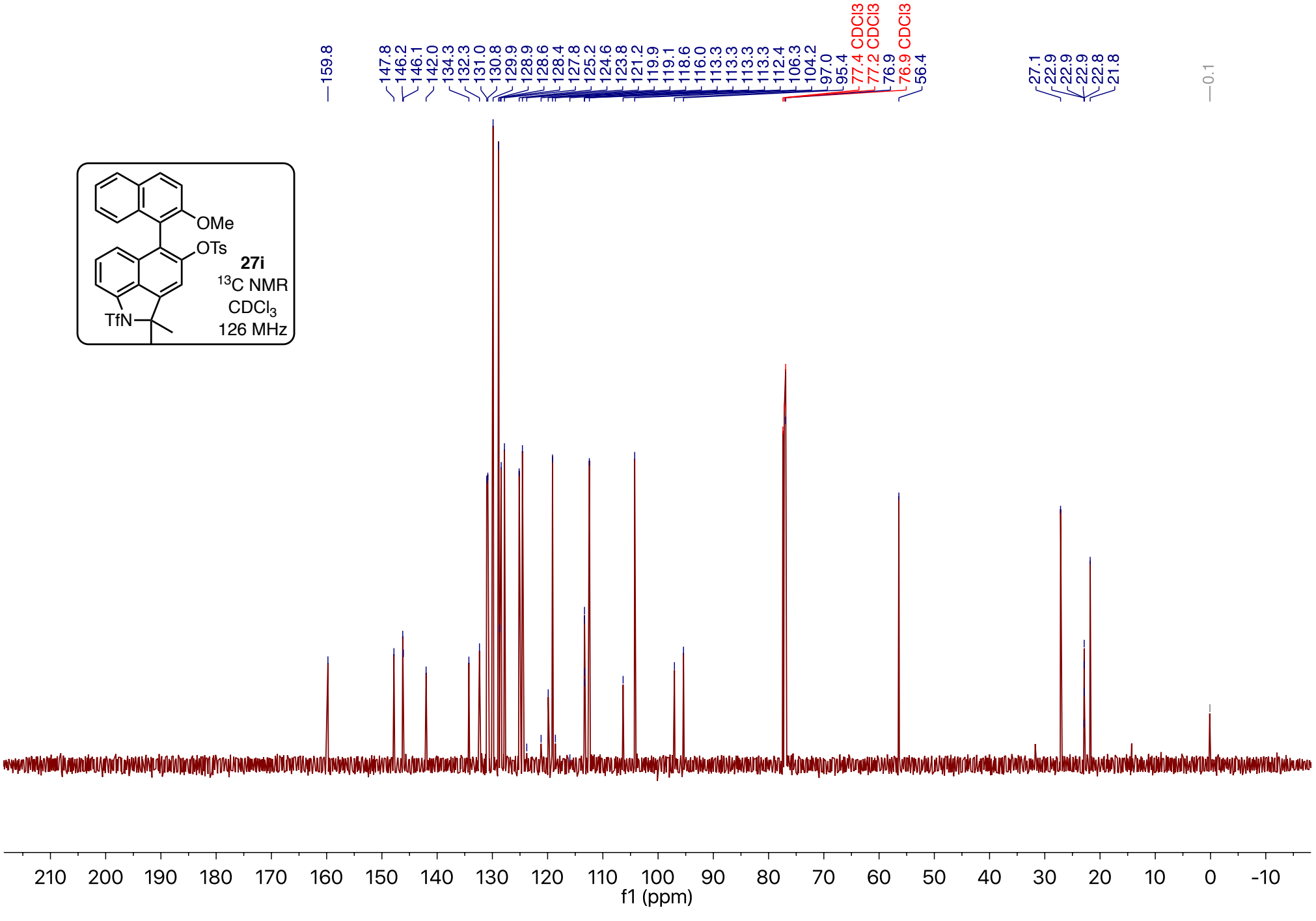
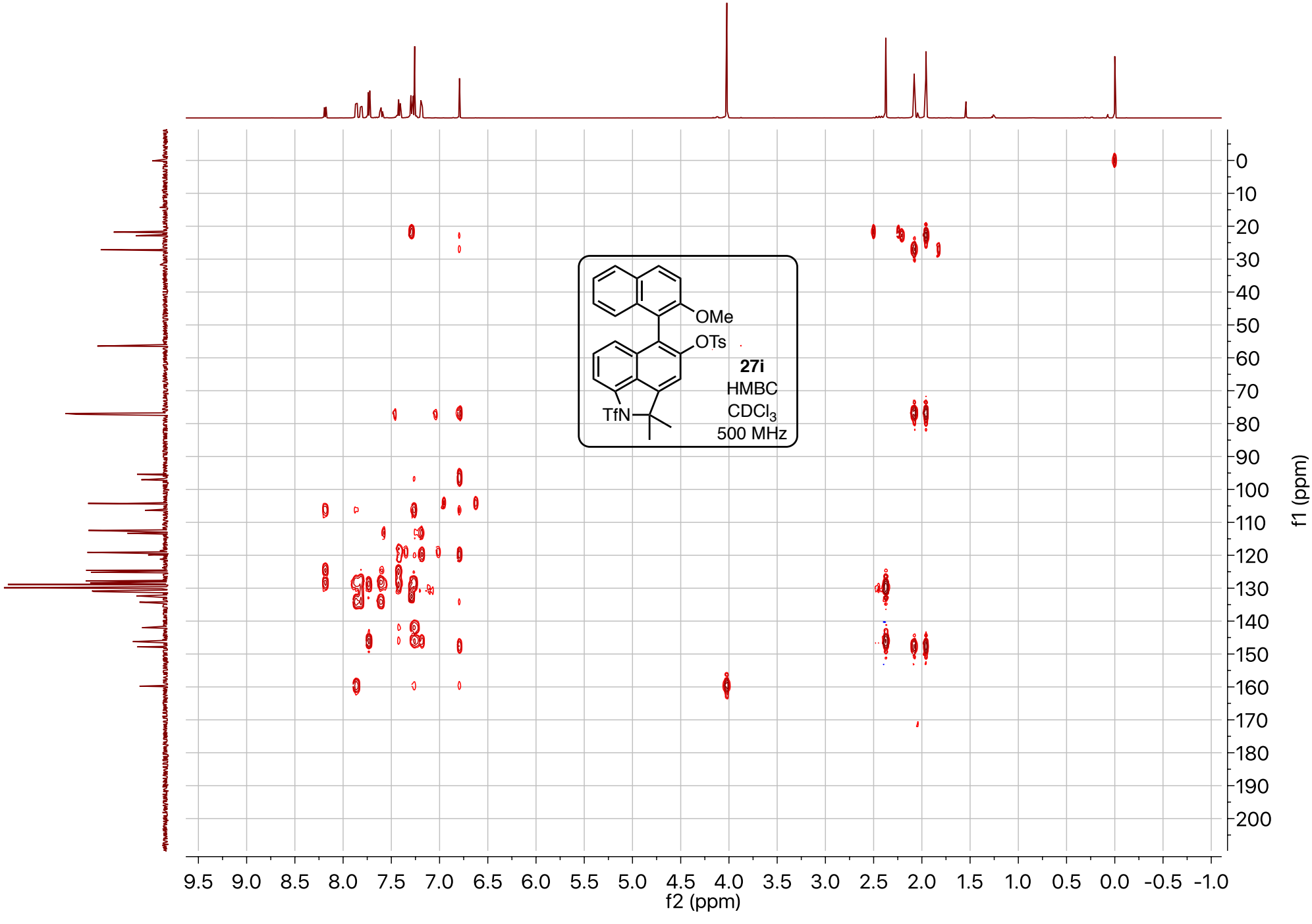
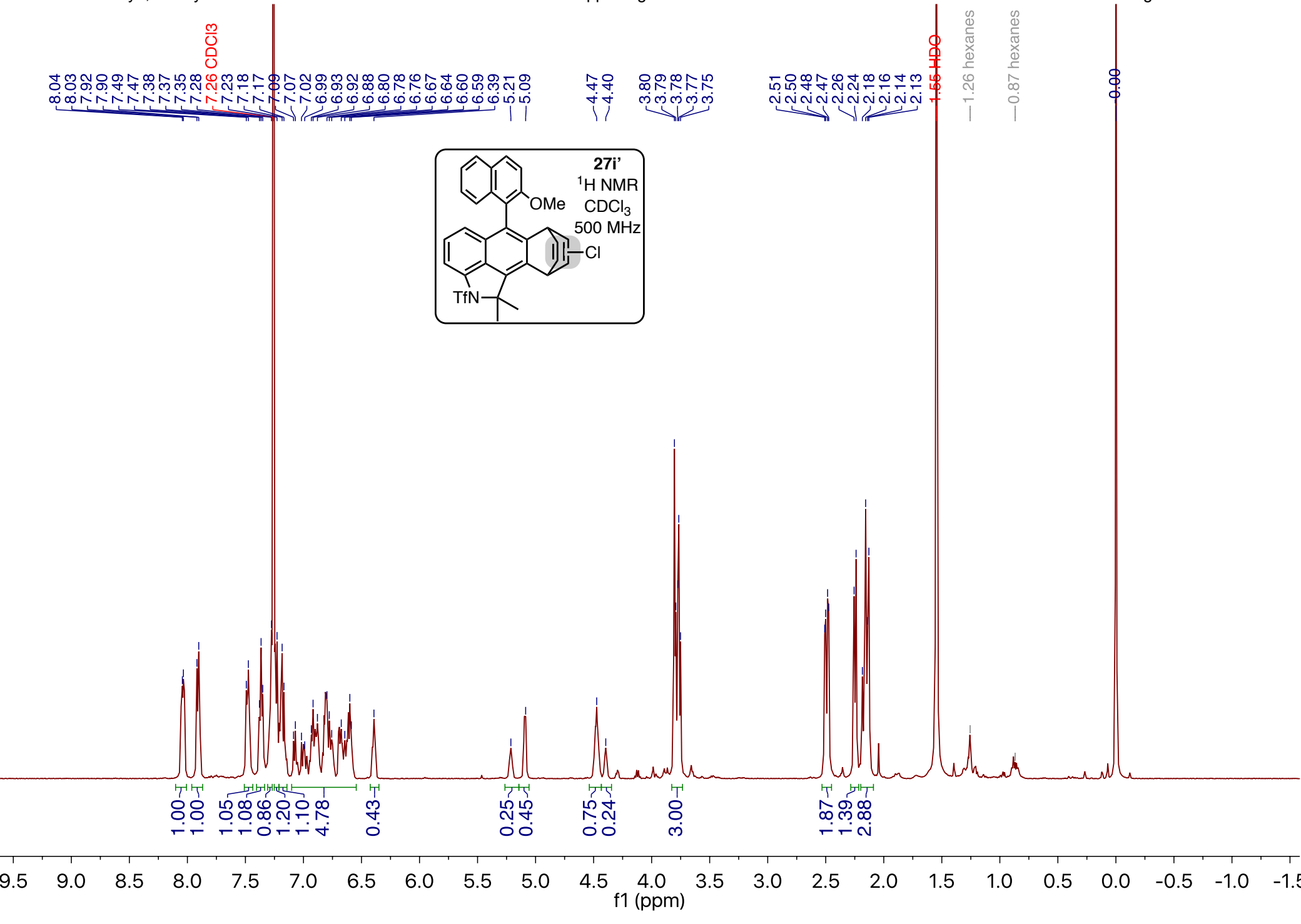
148.3
146.2
142.0
132.9
132.2
130.8
130.5
129.8
128.9
123.7
121.2
120.7
119.8
118.9
118.6
115.9
113.3
113.3
113.3
113.3
112.5
110.8
104.2
98.5
90.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.8
55.7
27.1
22.9
22.9
22.8
22.8
21.8
0.1
OMe
OTs
TfN
27h'
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

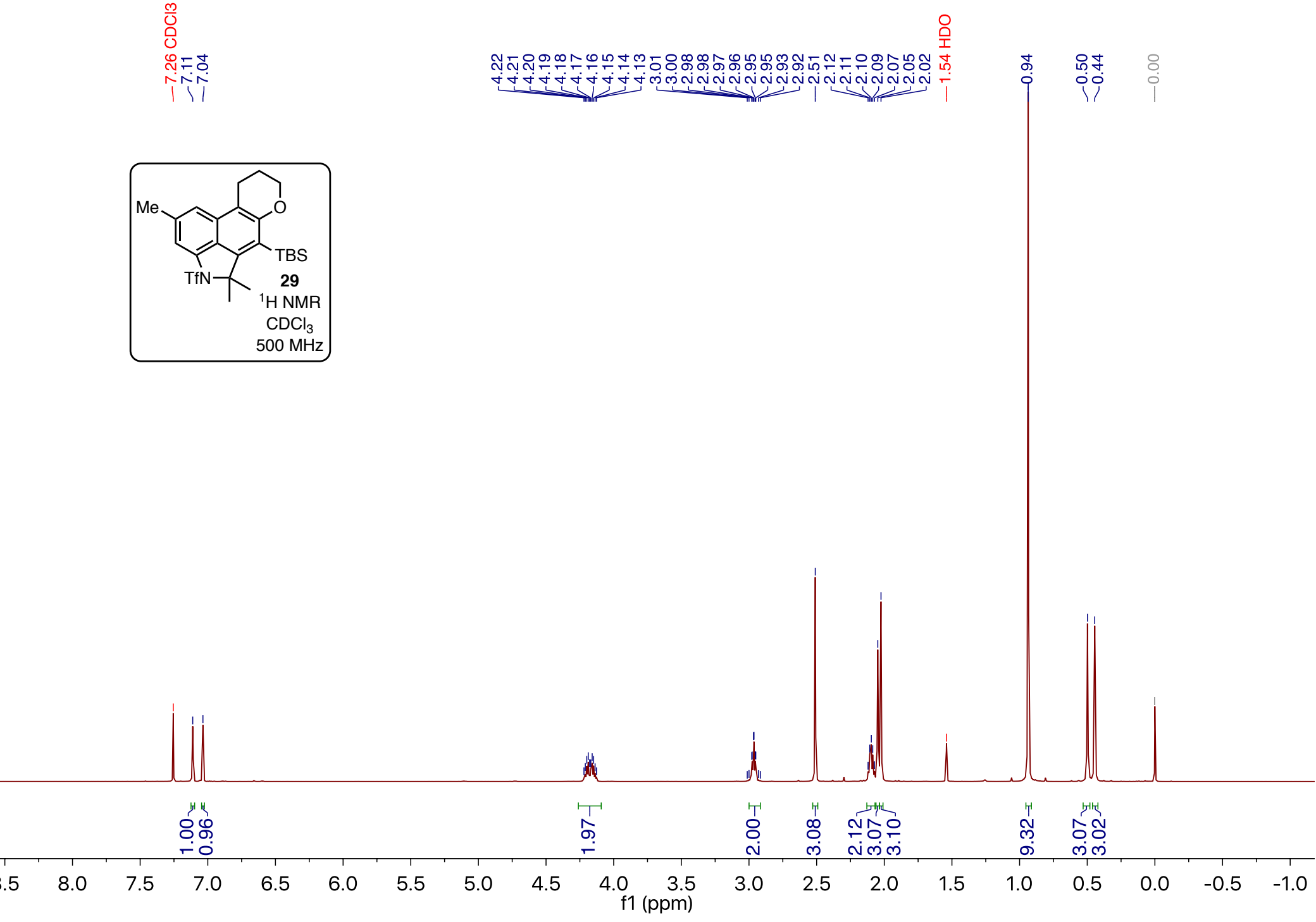

8.19
8.18
7.87
7.85
7.82
7.80
7.74
7.72
7.62
7.62
7.61
7.59
7.59
7.44
7.44
7.43
7.42
7.41
7.30
7.28
7.27
7.26 CDCl3
7.25
7.24
7.19
7.19
7.18
7.18
6.79
4.02
2.37
2.08
1.96
1.54 HDO
0.00
OMe
OTs
TfN
27i
1H NMR
CDCl3
500 MHz
1.00
1.05
1.08
2.08
1.02
2.05
2.15
1.38
0.64
0.97
0.97
3.10
3.14
3.06
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


159.8
147.8
146.2
146.1
142.0
134.3
132.3
131.0
130.8
129.9
128.9
128.6
128.4
127.8
125.2
124.6
123.8
121.2
119.9
119.1
118.6
116.0
113.3
113.3
113.3
113.3
112.4
106.3
104.2
97.0
95.4
77.4 CDCl3
77.2 CDCl3
76.9
76.9 CDCl3
56.4
27.1
22.9
22.9
22.9
22.8
21.8
0.1
OMe
OTs
TfN
27i
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OMe
OTs
TfN
27i
HSQC
CDCl3
500 MHz
f2 (ppm)
f1 (ppm)


OMe
OTs
TfN
27i
HMBC
CDCl3
500 MHz
f2 (ppm)
f1 (ppm)


8.04
8.03
7.92
7.90
7.49
7.47
7.38
7.37
7.35
7.28
7.26 CDCl3
7.23
7.18
7.17
7.09
7.07
7.02
6.99
6.93
6.92
6.88
6.80
6.78
6.76
6.67
6.64
6.60
6.59
6.39
5.21
5.09
4.47
4.40
3.80
3.79
3.78
3.77
3.75
2.51
2.50
2.48
2.47
2.26
2.24
2.18
2.16
2.14
2.13
1.55 HDO
1.26 hexanes
0.87 hexanes
0.00
27i'
1H NMR
CDCl3
500 MHz
OMe
Cl
TfN
1.00
1.00
1.05
1.08
0.86
1.20
1.10
4.78
0.43
0.25
0.45
0.75
0.24
3.00
1.87
1.39
2.88
f1 (ppm)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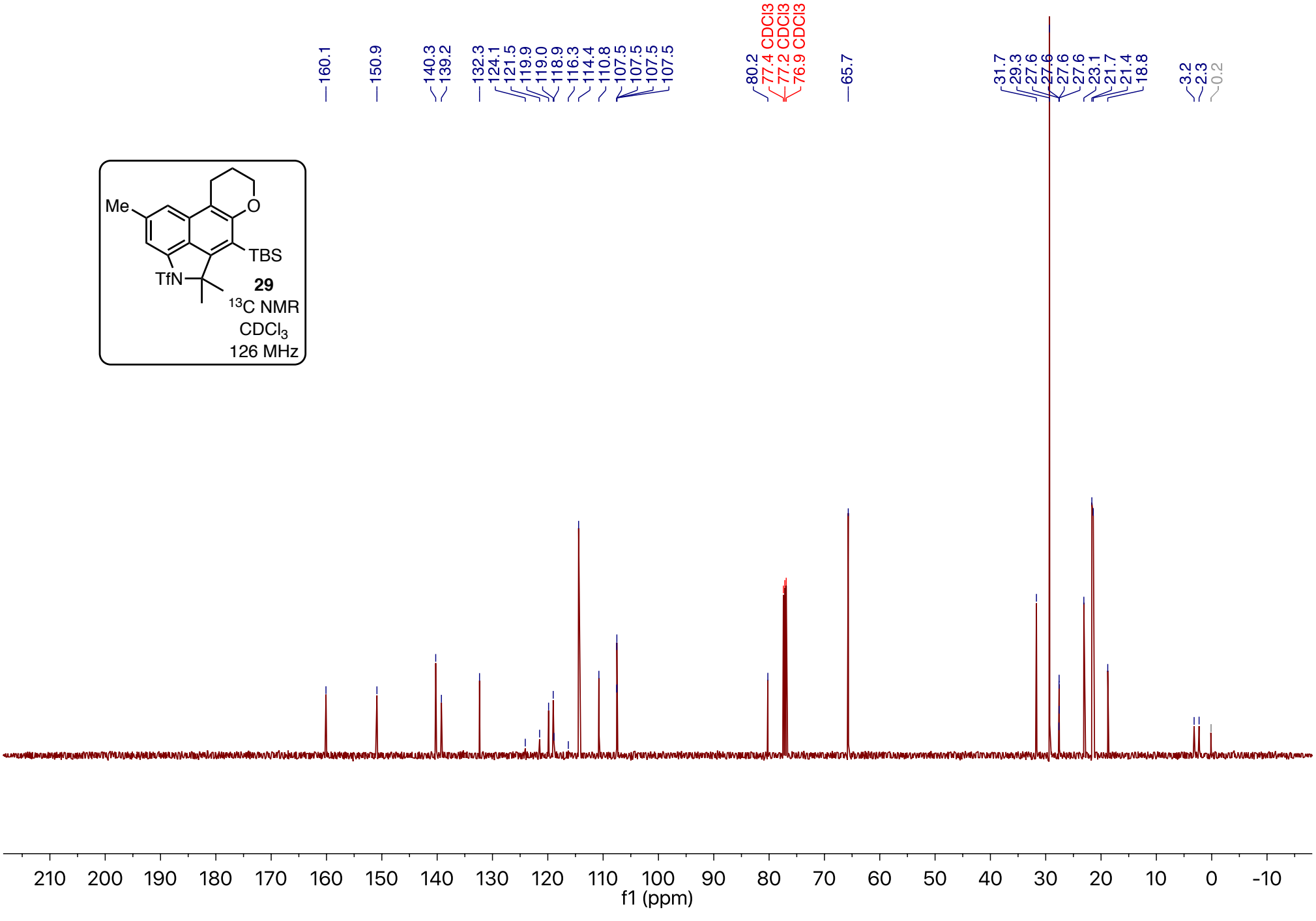
7.11
7.04
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
3.01
3.00
2.98
2.98
2.97
2.96
2.95
2.95
2.93
2.92
2.51
2.12
2.11
2.10
2.09
2.07
2.05
2.02
1.54 HDO
0.94
0.50
0.44
0.00
Me
O
TBS
TfN
29
1H NMR
CDCl3
500 MHz
1.00
0.96
1.97
2.00
3.08
2.12
3.07
3.10
9.32
3.07
3.02
f1 (ppm)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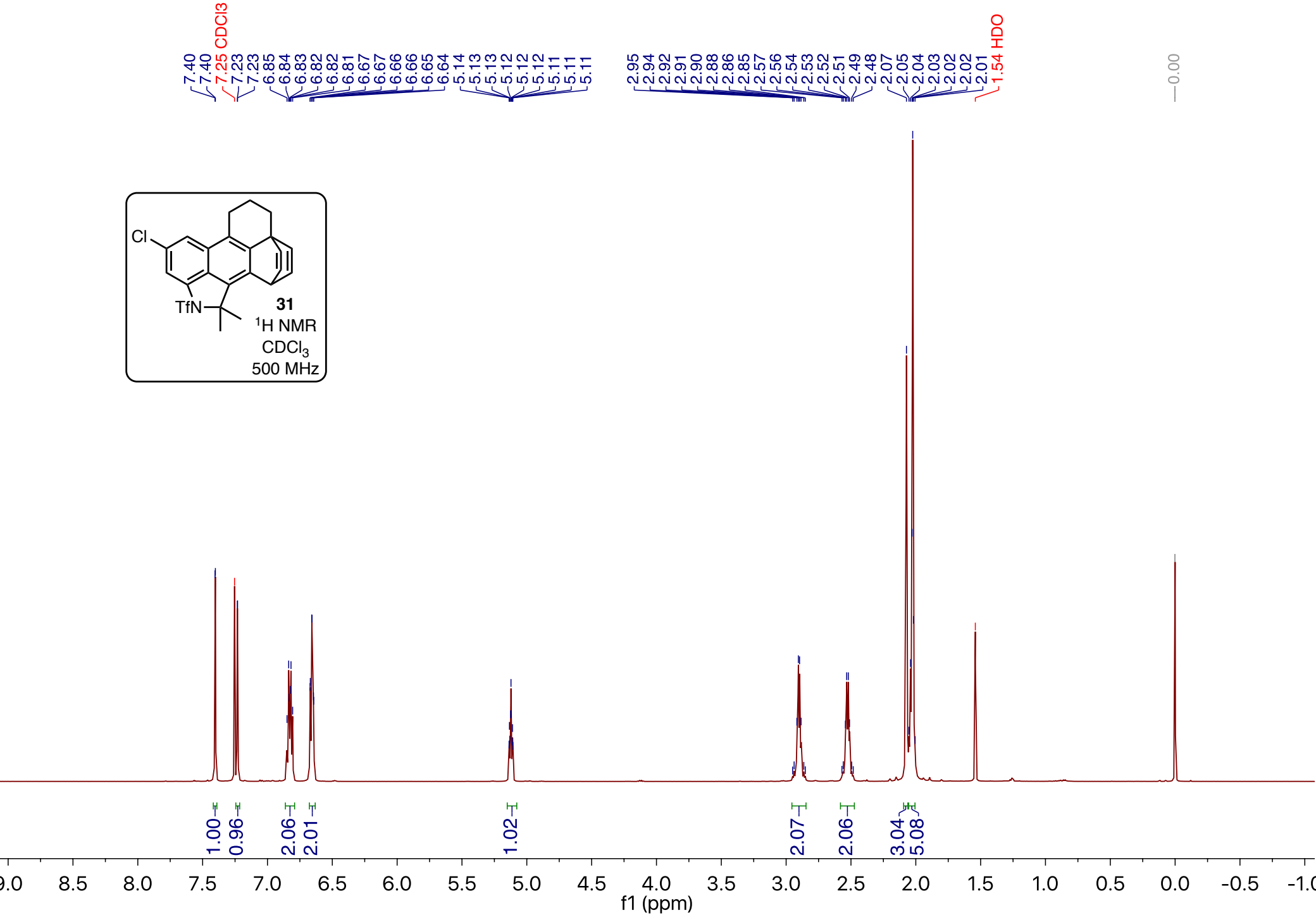
150.9
140.3
139.2
132.3
124.1
121.5
119.9
119.0
118.9
116.3
114.4
110.8
107.5
107.5
107.5
107.5
80.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
65.7
31.7
29.3
27.6
27.6
27.6
27.6
23.1
21.7
21.4
18.8
3.2
2.3
0.2
Me
O
TBS
TfN
29
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.40
7.40
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7.23
7.23
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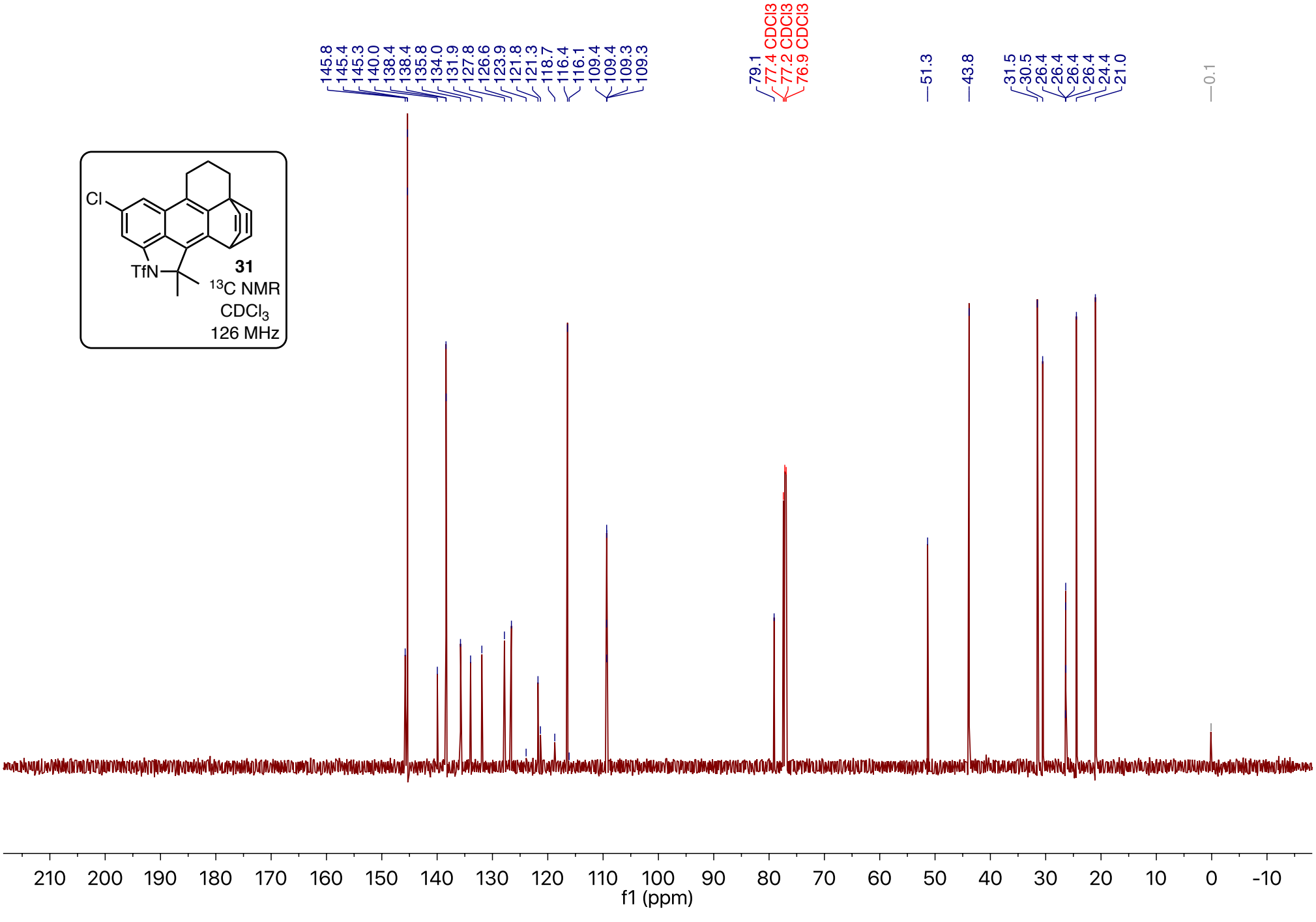
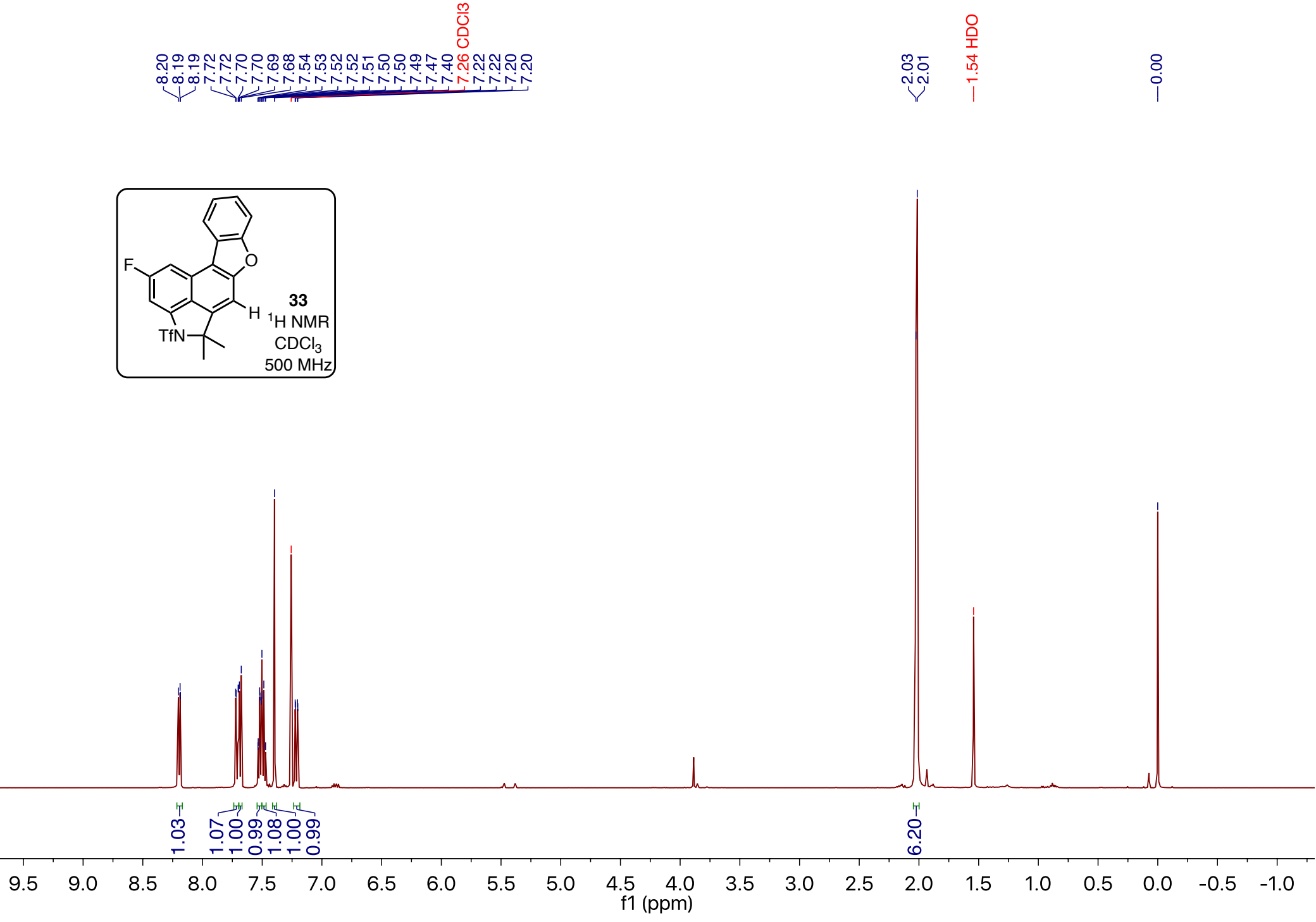
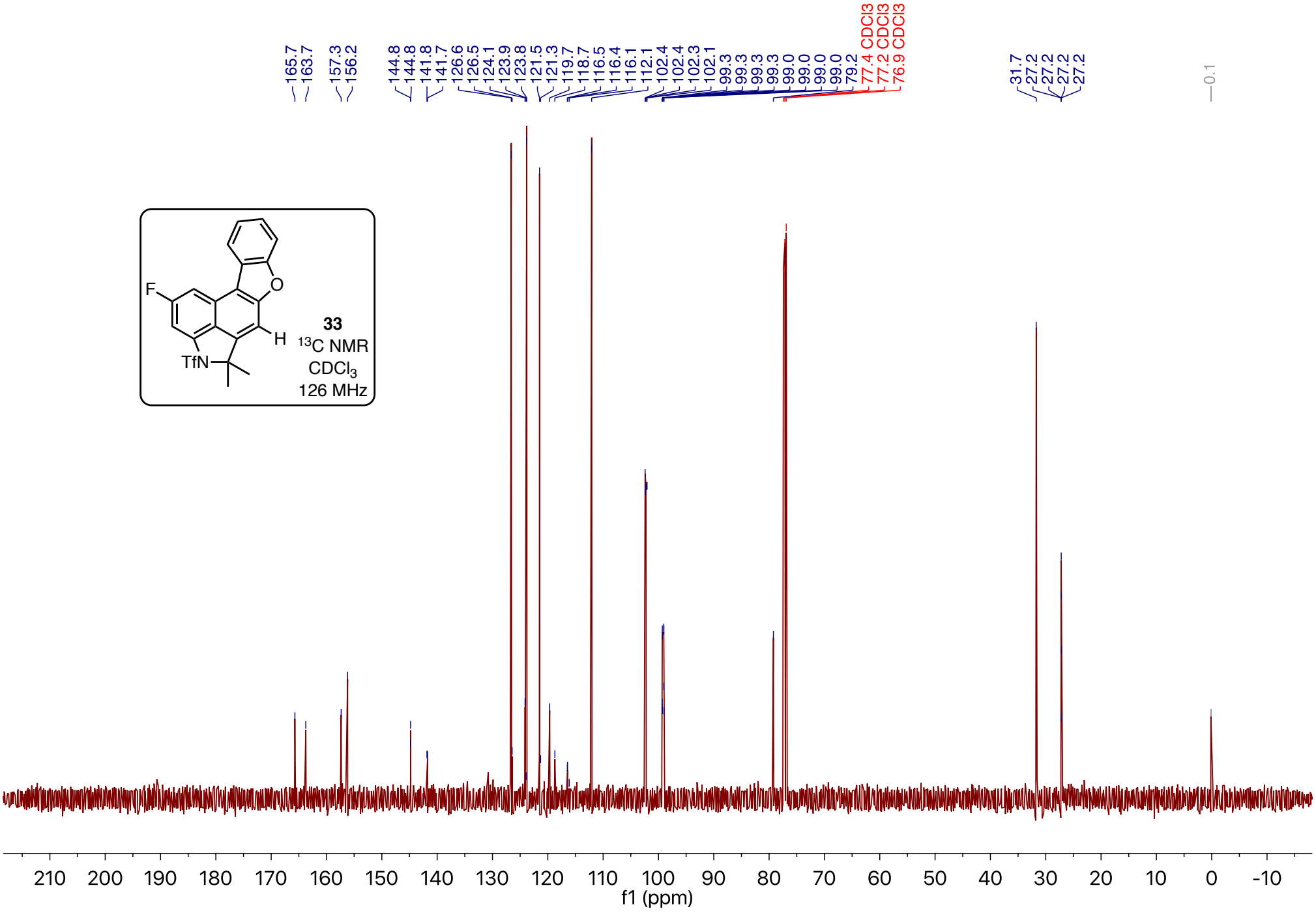
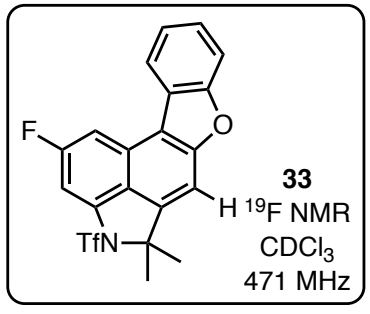
6.84
6.83
6.82
6.82
6.81
6.67
6.67
6.66
6.65
6.64
5.14
5.13
5.13
5.12
5.12
5.12
5.11
5.11
5.11
2.95
2.94
2.92
2.91
2.90
2.88
2.86
2.85
2.57
2.56
2.54
2.53
2.52
2.51
2.49
2.48
2.07
2.05
2.04
2.03
2.02
2.02
2.01
1.54 HDO
0.00
Cl
TfN
31
1H NMR
CDCl3
500 MHz
1.00
0.96
2.06
2.01
1.02
2.07
2.06
3.04
5.08
f1 (ppm)

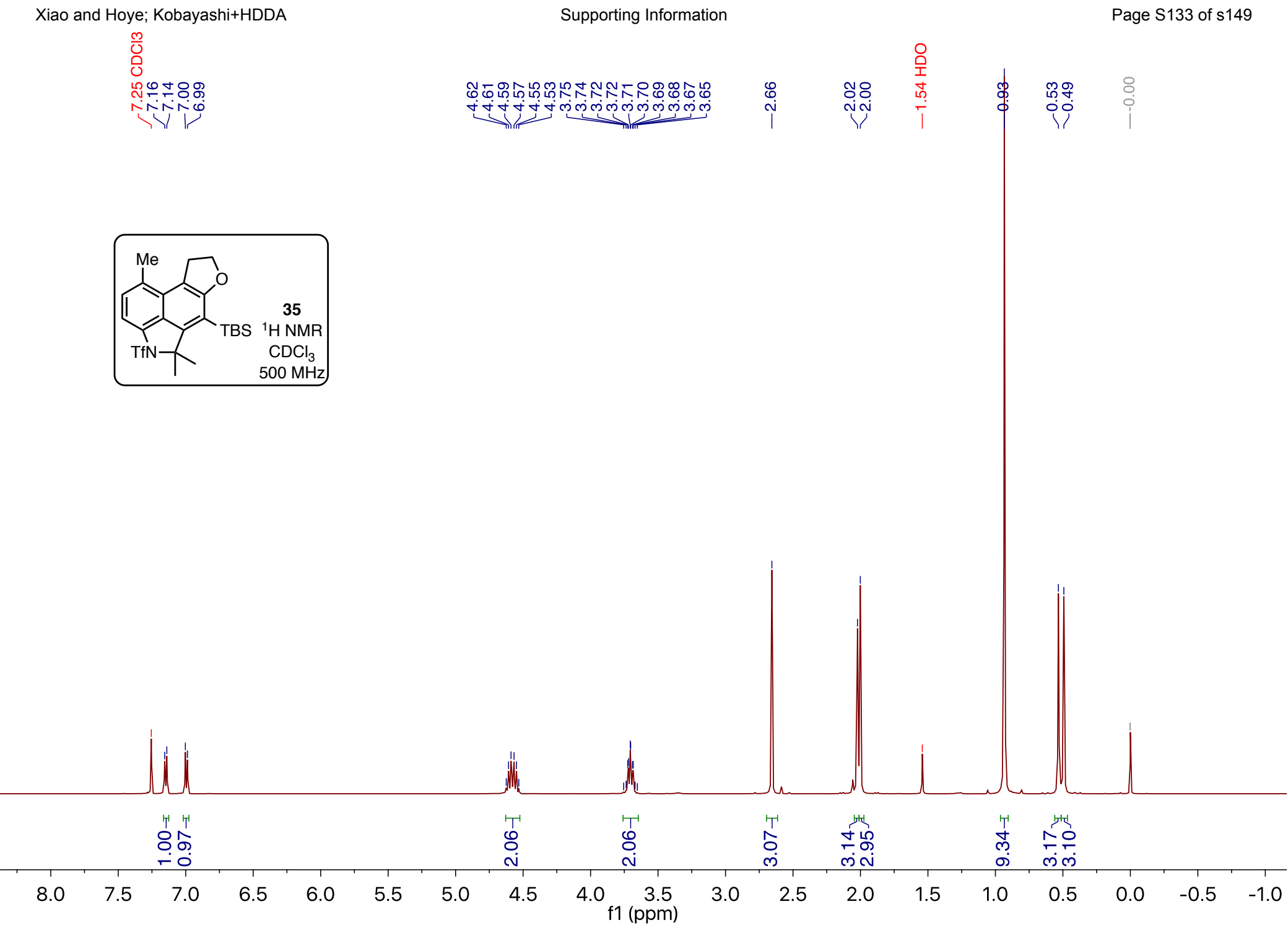

145.8
145.4
145.3
140.0
138.4
138.4
135.8
134.0
131.9
127.8
126.6
123.9
121.8
121.3
118.7
116.4
116.1
109.4
109.4
109.3
109.3
79.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
51.3
43.8
31.5
30.5
26.4
26.4
26.4
26.4
24.4
21.0
0.1
Cl
TfN
31
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

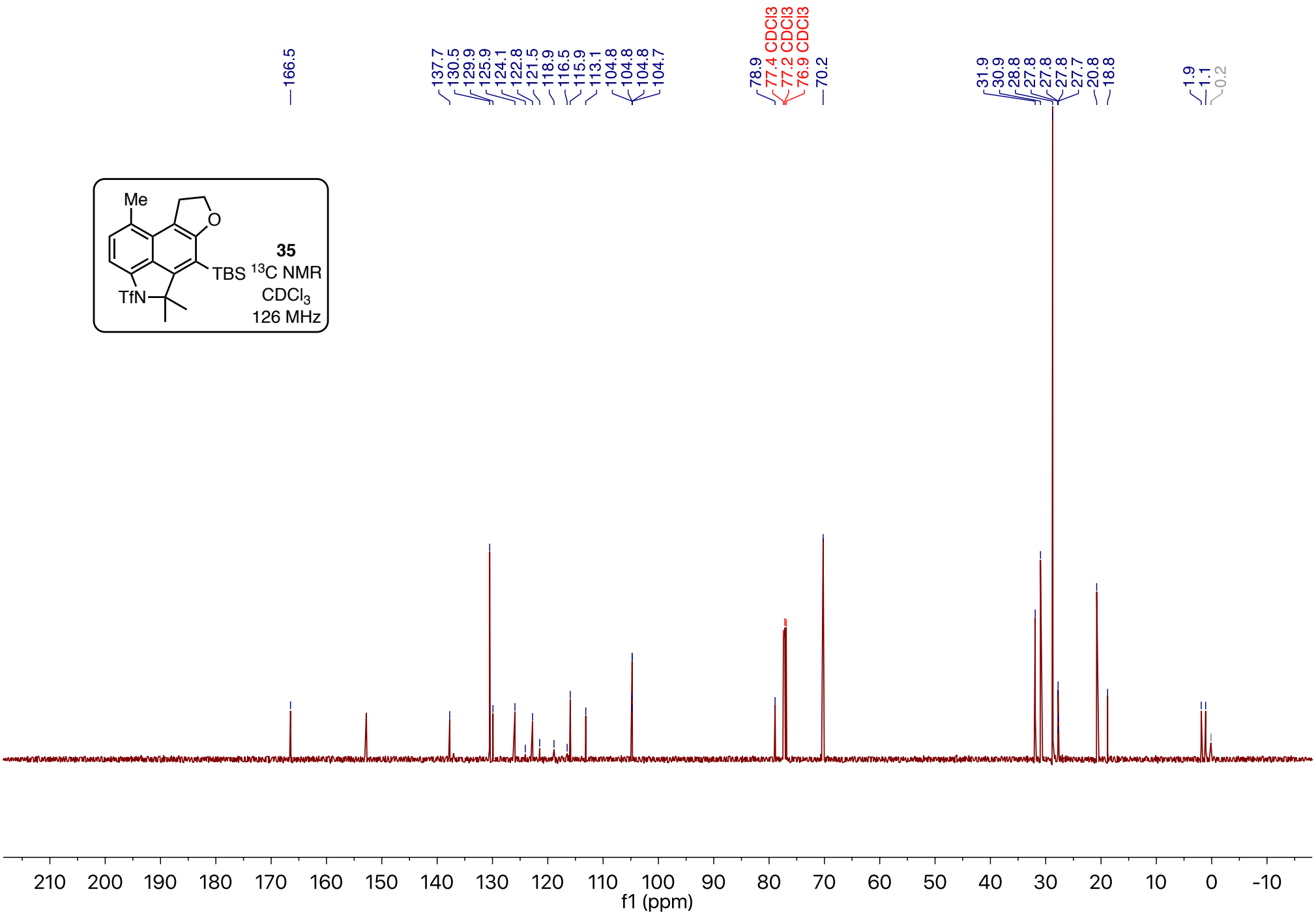

8.20
8.19
8.19
7.72
7.72
7.70
7.70
7.69
7.68
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.47
7.40
7.26 CDCl3
7.22
7.22
7.20
7.20
2.03
2.01
1.54 HDO
0.00
F
O
H
TfN
33
1H NMR
CDCl3
500 MHz
1.03
1.07
1.00
0.99
1.08
1.00
0.99
6.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

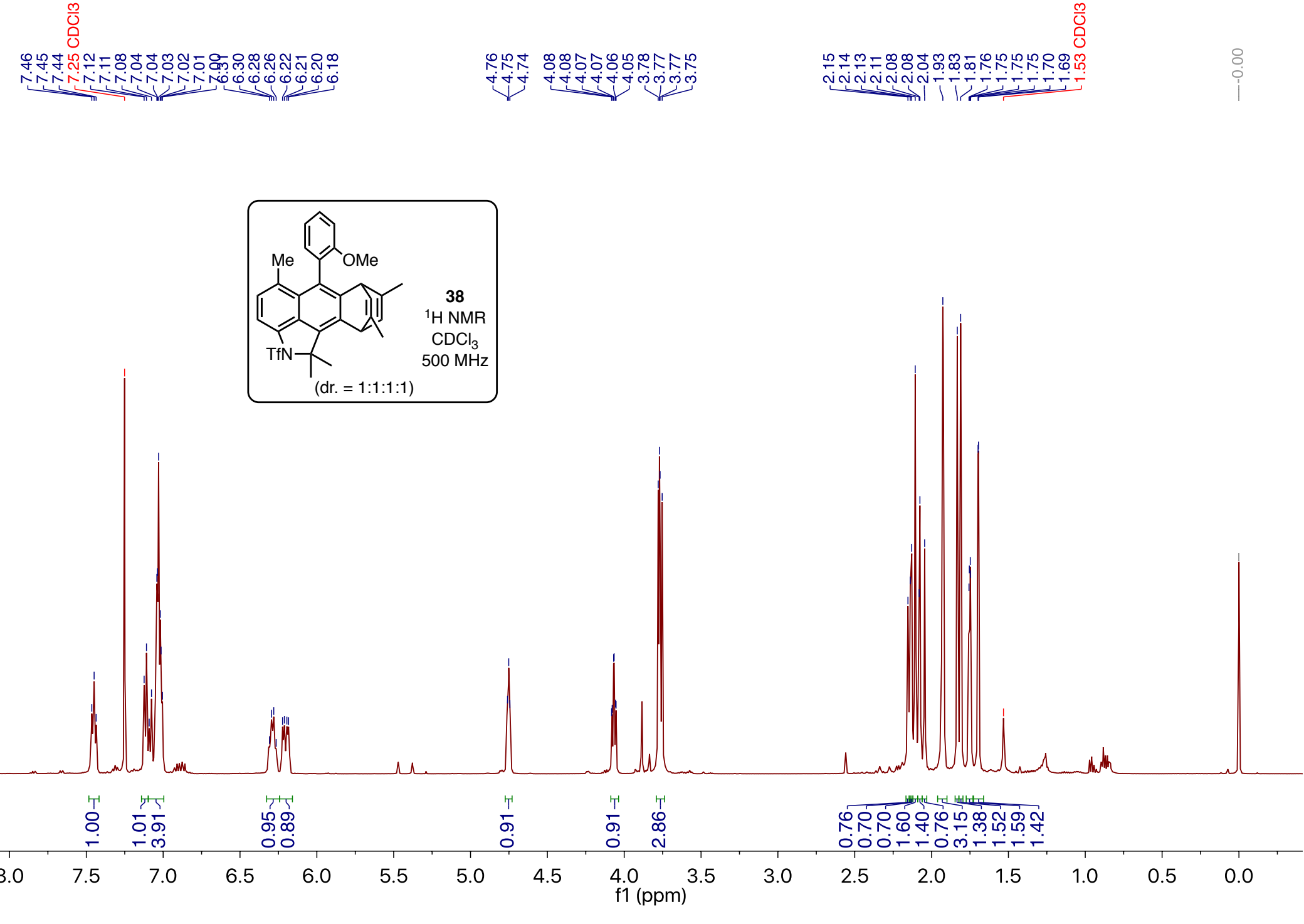

165.7
163.7
157.3
156.2
144.8
144.8
141.8
141.7
126.6
126.5
124.1
123.9
123.8
121.5
121.3
119.7
118.7
116.5
116.4
116.1
112.1
102.4
102.4
102.3
102.1
99.3
99.3
99.3
99.3
99.0
99.0
99.0
99.0
79.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
31.7
27.2
27.2
27.2
27.2
0.1
F
O
H
TfN
33
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

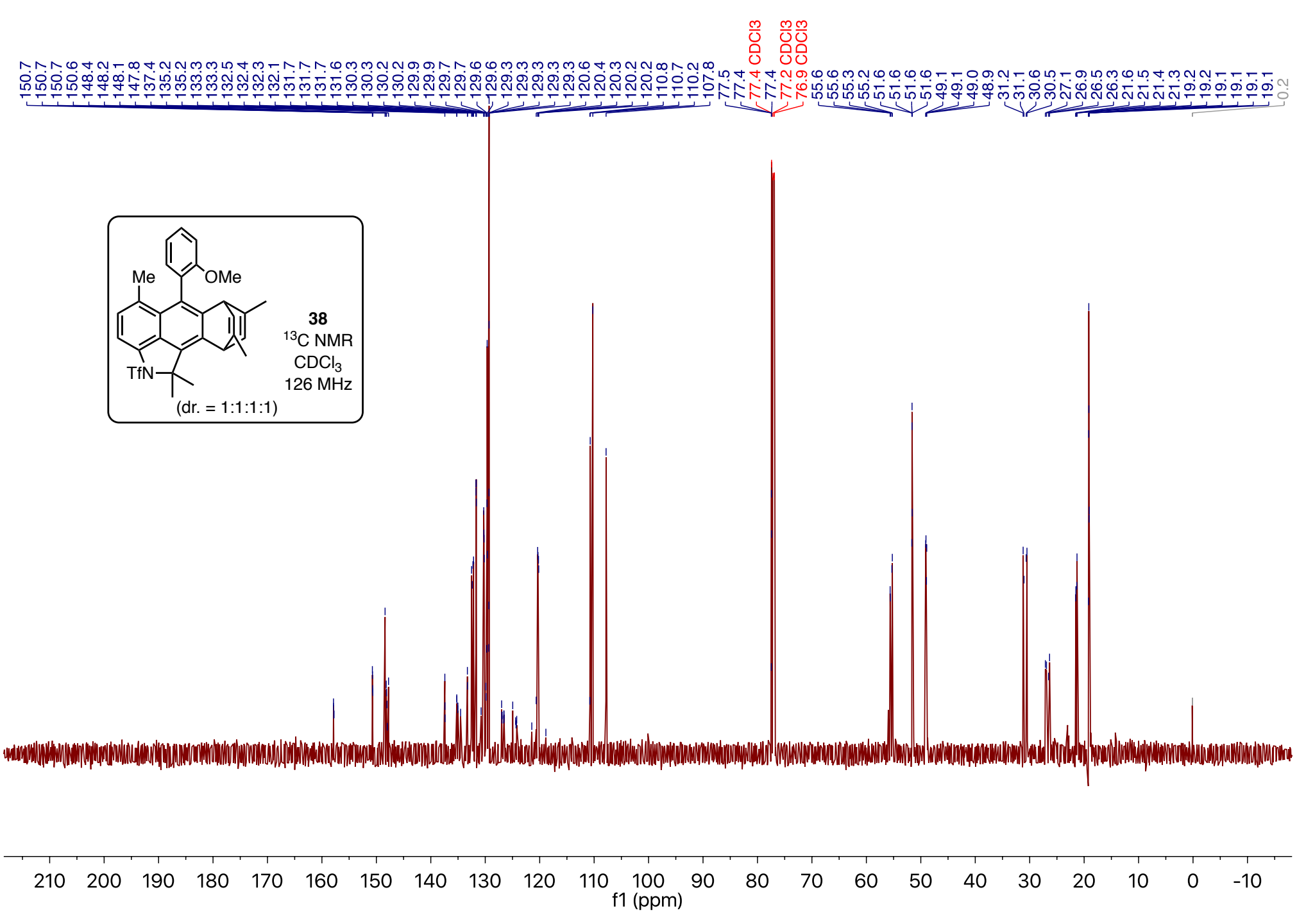

F
O
H
TfN
33
^{19}F NMR
$CDCl_3$
471 MHz

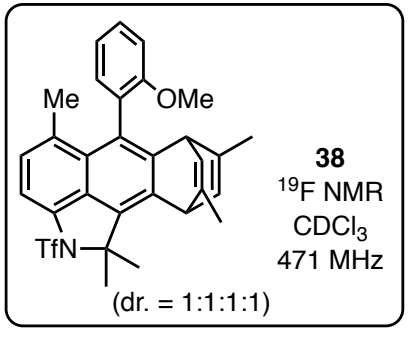
-74.2
-105.6
-105.7
-105.7
-105.6
-105.7
-105.7
-105.60
-105.70
-105.80
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.25 CDCl3
7.16
7.14
7.00
6.99
4.62
4.61
4.59
4.57
4.55
4.53
3.75
3.74
3.72
3.72
3.71
3.70
3.69
3.68
3.67
3.65
2.66
2.02
2.00
1.54 HDO
0.93
0.53
0.49
-0.00
Me
O
TBS
TfN
35
1H NMR
CDCl3
500 MHz
1.00
0.97
2.06
2.06
3.07
3.14
2.95
9.34
3.17
3.10
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)


166.5
137.7
130.5
129.9
125.9
124.1
122.8
121.5
118.9
116.5
115.9
113.1
104.8
104.8
104.8
104.7
78.9
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
70.2
31.9
30.9
28.8
27.8
27.8
27.8
27.7
20.8
18.8
1.9
1.1
0.2
Me
O
TBS
TfN
35
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.46
7.45
7.44
7.25 CDCl3
7.12
7.11
7.08
7.04
7.04
7.03
7.02
7.01
7.00
6.31
6.30
6.28
6.26
6.22
6.21
6.20
6.18
4.76
4.75
4.74
4.08
4.08
4.07
4.07
4.06
4.05
3.78
3.77
3.77
3.75
2.15
2.14
2.13
2.11
2.08
2.08
2.04
1.93
1.83
1.81
1.76
1.75
1.75
1.75
1.70
1.69
1.53 CDCl3
0.00
Me
OMe
TfN
38
1H NMR
CDCl3
500 MHz
(dr. = 1:1:1:1)
1.00
1.01
3.91
0.95
0.89
0.91
0.91
2.86
0.76
0.70
0.70
1.60
1.40
0.76
3.15
1.38
1.52
1.59
1.42
f1 (ppm)


150.7 150.7 150.7 150.6 148.4 148.2 148.1 147.8 137.4 135.2 135.2 133.3 133.3 132.5 132.4 132.3 132.1 131.7 131.7 131.7 131.6 130.3 130.3 130.2 130.2 129.9 129.9 129.7 129.7 129.6 129.6 129.3 129.3 129.3 129.3 129.3 120.6 120.4 120.3 120.2 120.2 110.8 110.7 110.2 107.8
77.5 77.4 77.4 CDCl3 77.4 77.2 CDCl3 76.9 CDCl3
55.6 55.6 55.3 55.2 51.6 51.6 51.6 51.6 49.1 49.1 49.0 48.9 31.2 31.1 30.6 30.5 27.1 26.9 26.5 26.3 21.6 21.5 21.4 21.3 19.2 19.2 19.1 19.1 19.1 19.1 0.2
Me
OMe
TfN
38
13C NMR
CDCl3
126 MHz
(dr. = 1:1:1:1)
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)



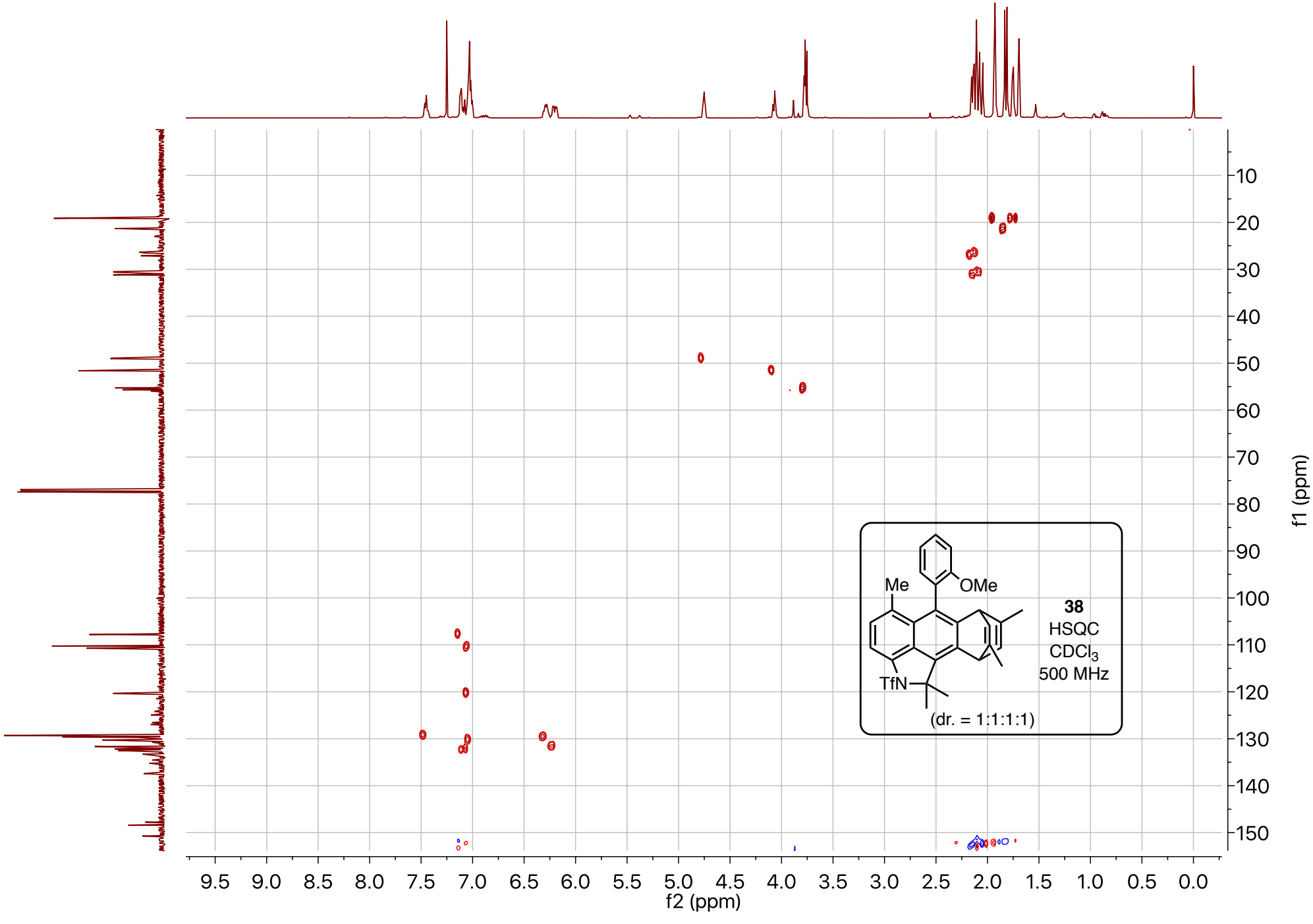
38
^{19}F NMR
$CDCl_3$
471 MHz
(dr. = 1:1:1:1)

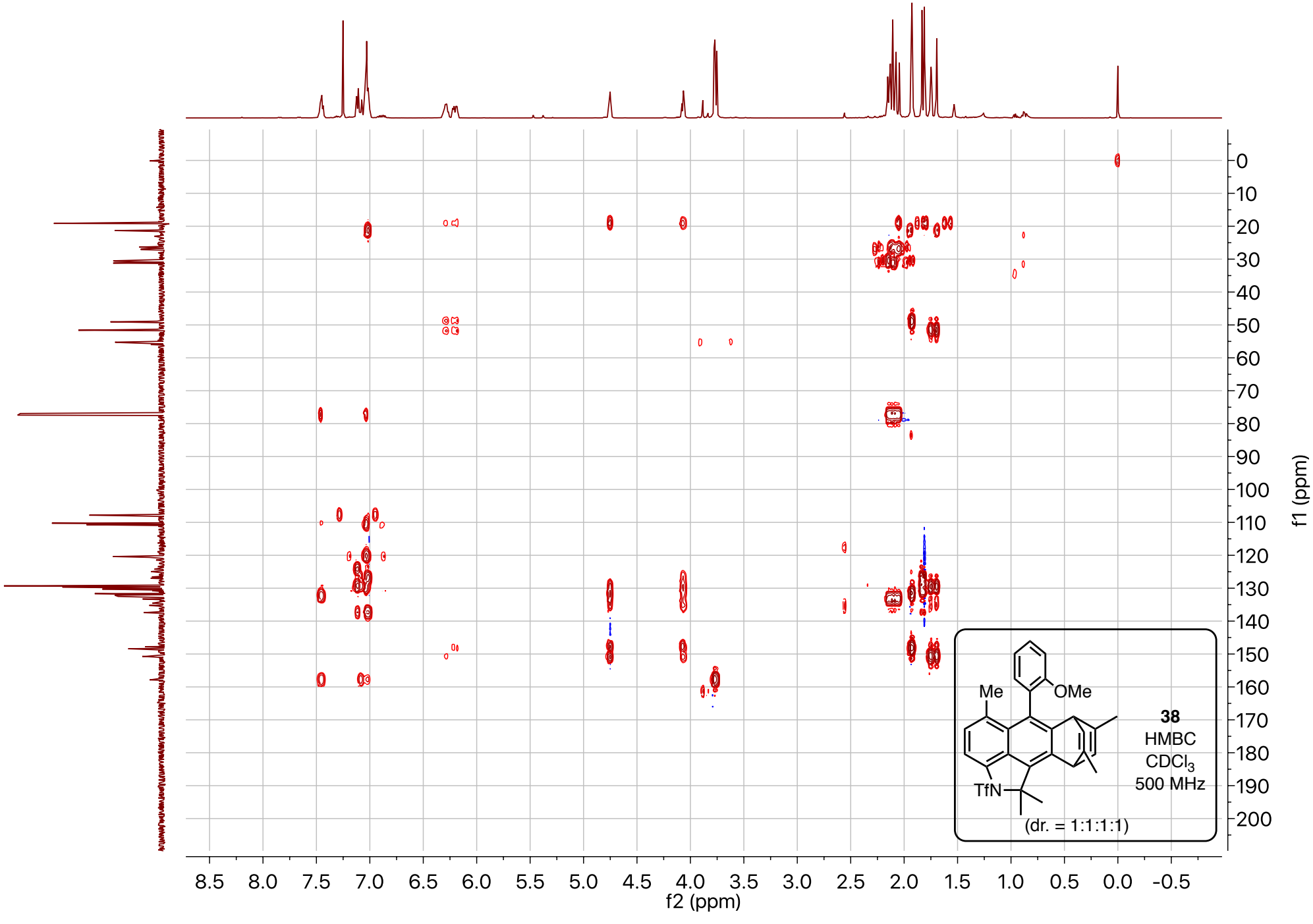
-73.9
-74.0
-74.1
-74.2

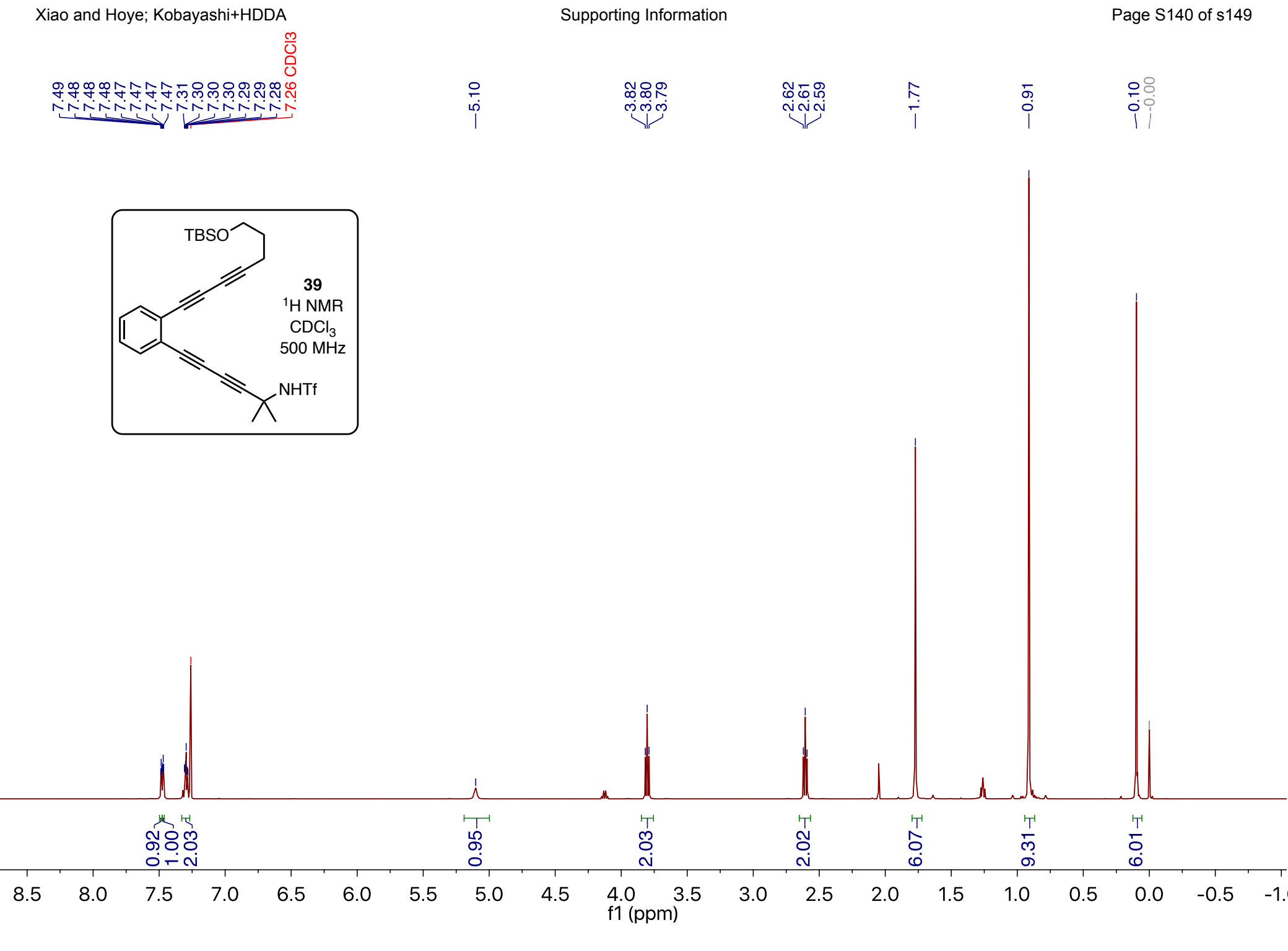
-73.88
-73.98
-74.05
-74.16

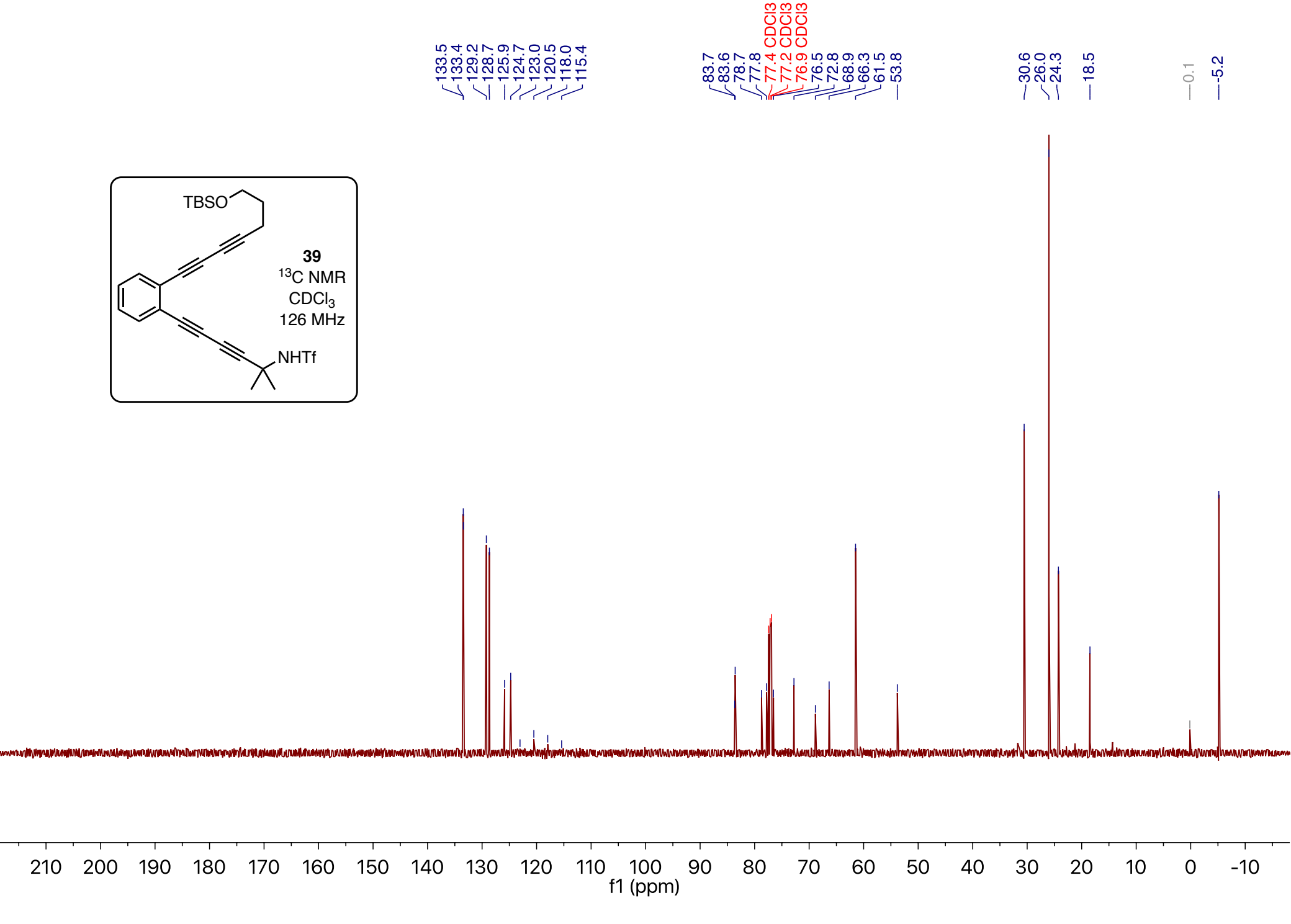
-72.5 -73.0 -73.5 -74.0 -74.5 -75.0 -75.5
f1 (ppm)

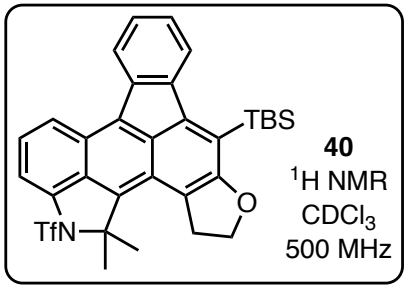
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)


Me
OMe
TfN
38
HSQC
CDCl3
500 MHz
(dr. = 1:1:1:1)
f2 (ppm)
f1 (ppm)

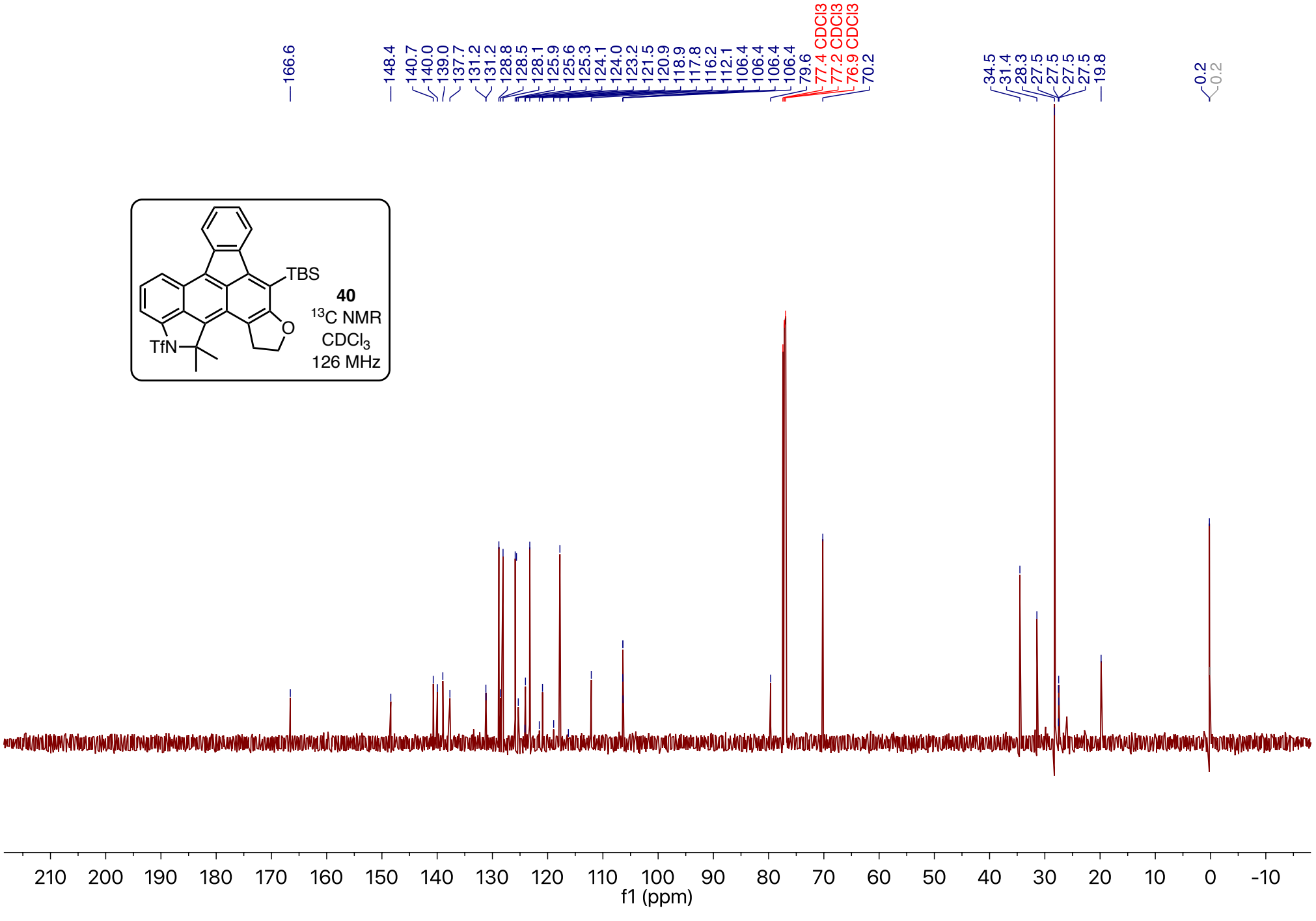

f2 (ppm)
f1 (ppm)
Me
OMe
TfN
(dr. = 1:1:1:1)
38
HMBC
CDCl3
500 MHz

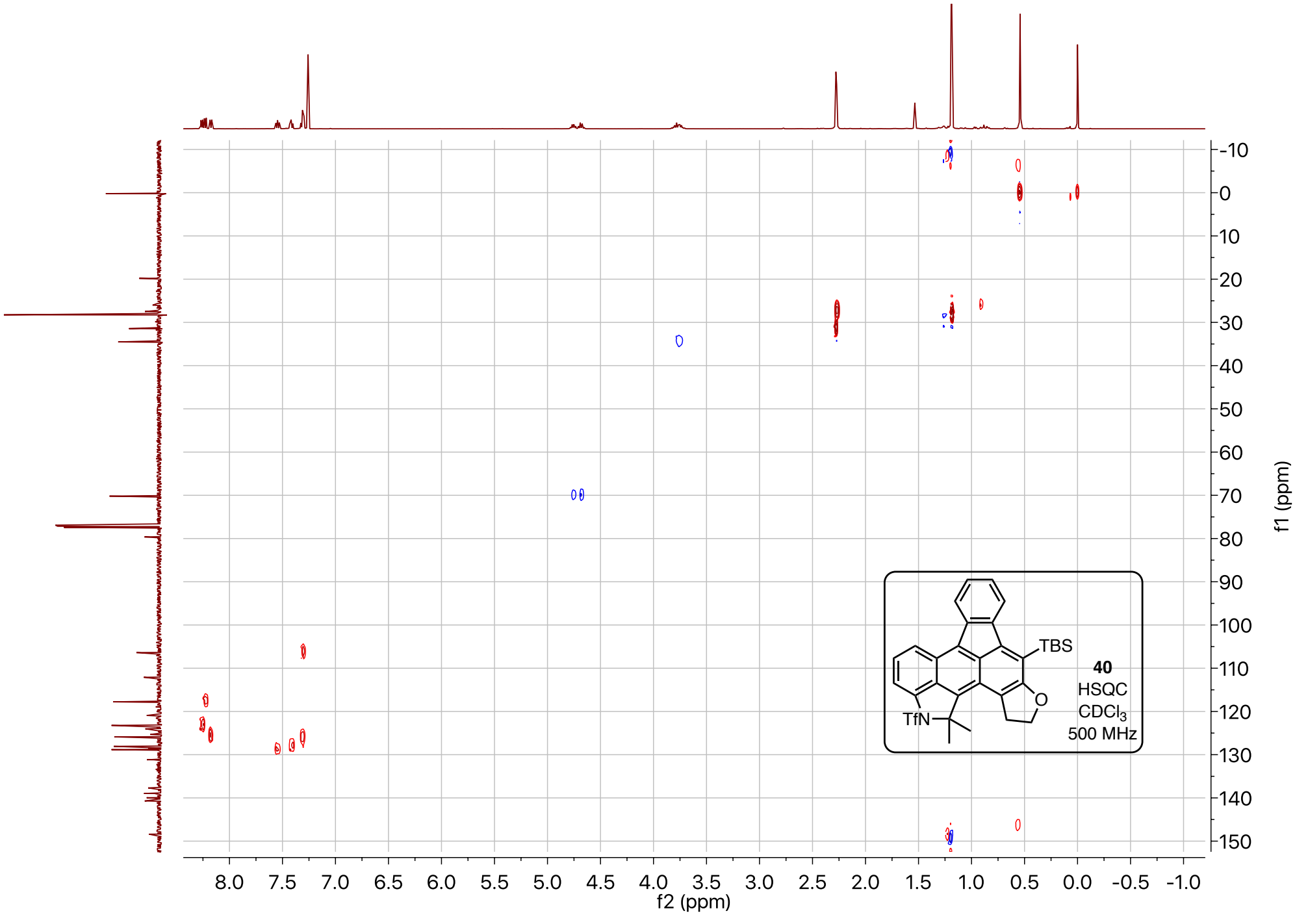

7.49
7.48
7.48
7.48
7.47
7.47
7.47
7.47
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.26 CDCl3
5.10
3.82
3.80
3.79
2.62
2.61
2.59
1.77
0.91
0.10
0.00
TBSO
NHTf
39
1H NMR
CDCl3
500 MHz
0.92
1.00
2.03
0.95
2.03
2.02
6.07
9.31
6.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

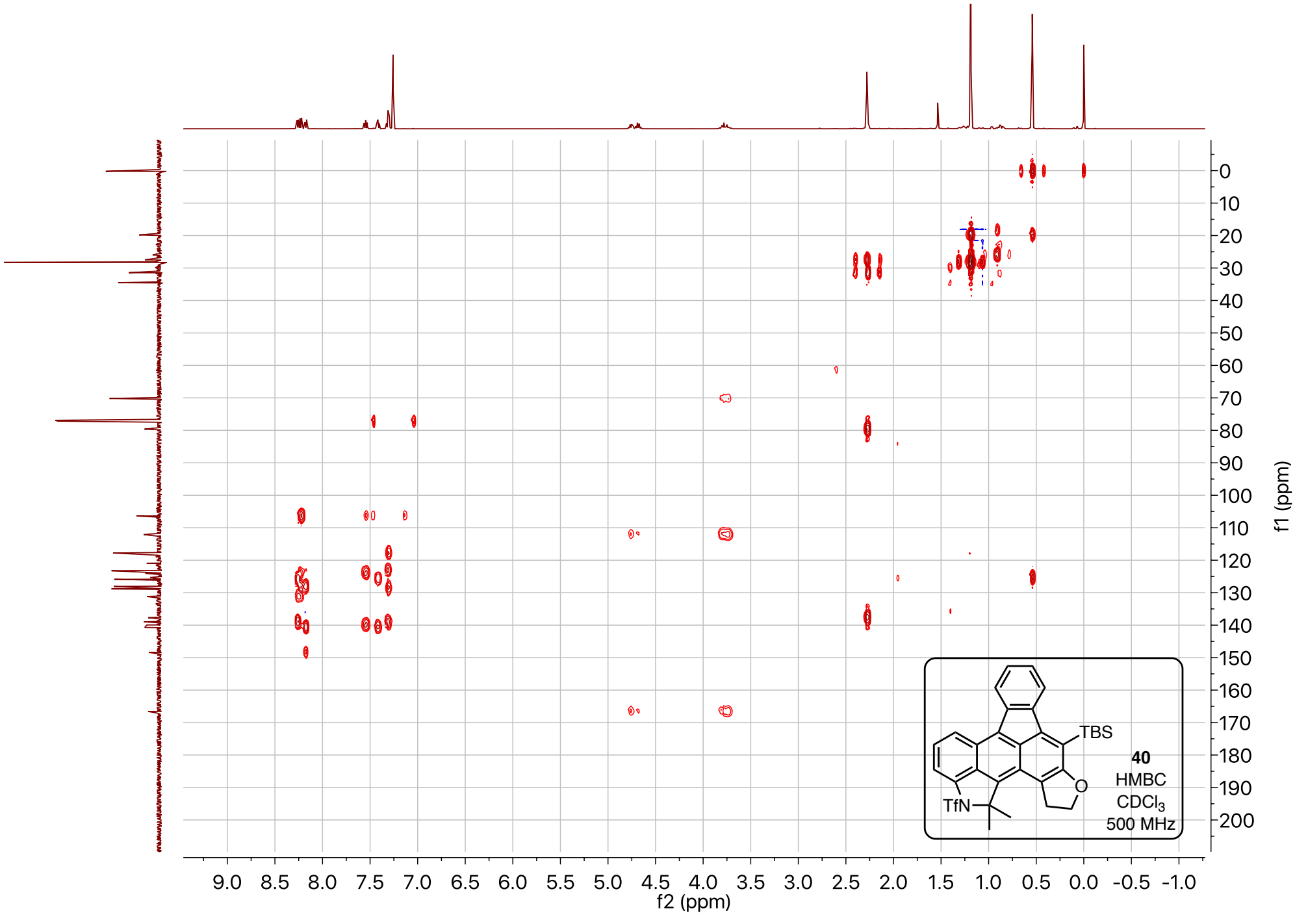

133.5
133.4
129.2
128.7
125.9
124.7
123.0
120.5
118.0
115.4
83.7
83.6
78.7
77.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.5
72.8
68.9
66.3
61.5
53.8
30.6
26.0
24.3
18.5
0.1
-5.2
TBSO
NHTf
39
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

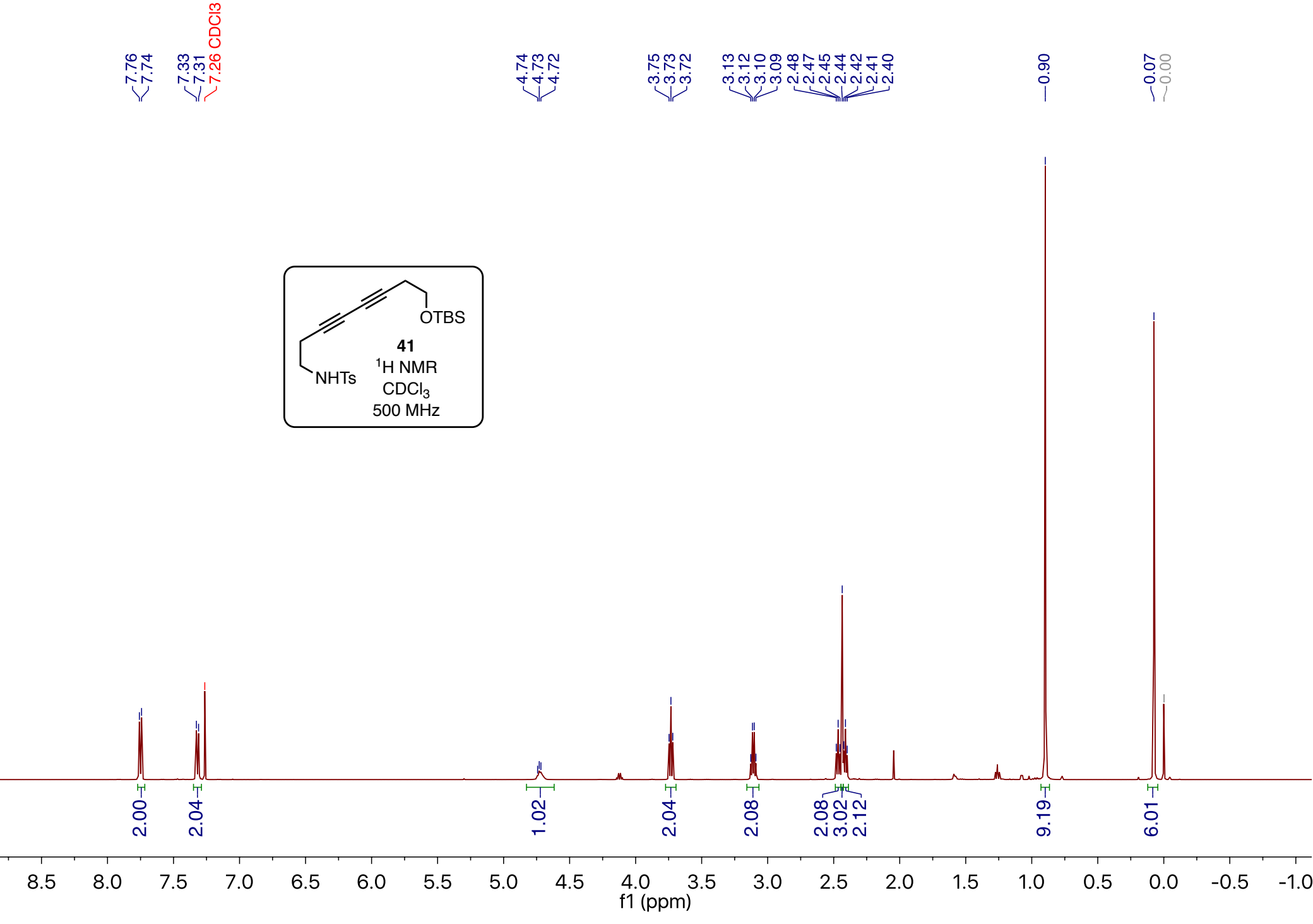


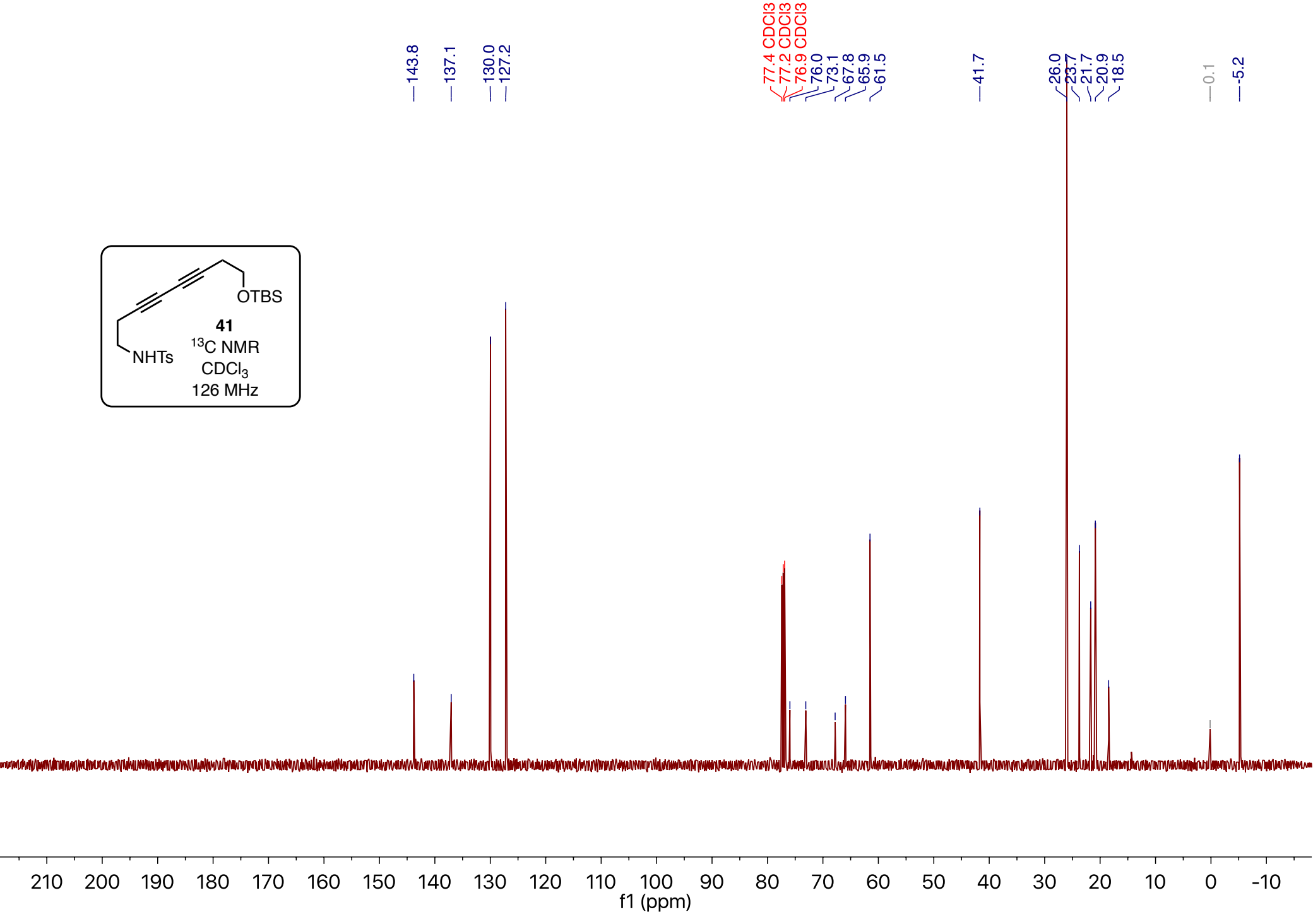
40
^{1}H NMR
$CDCl_3$
500 MHz

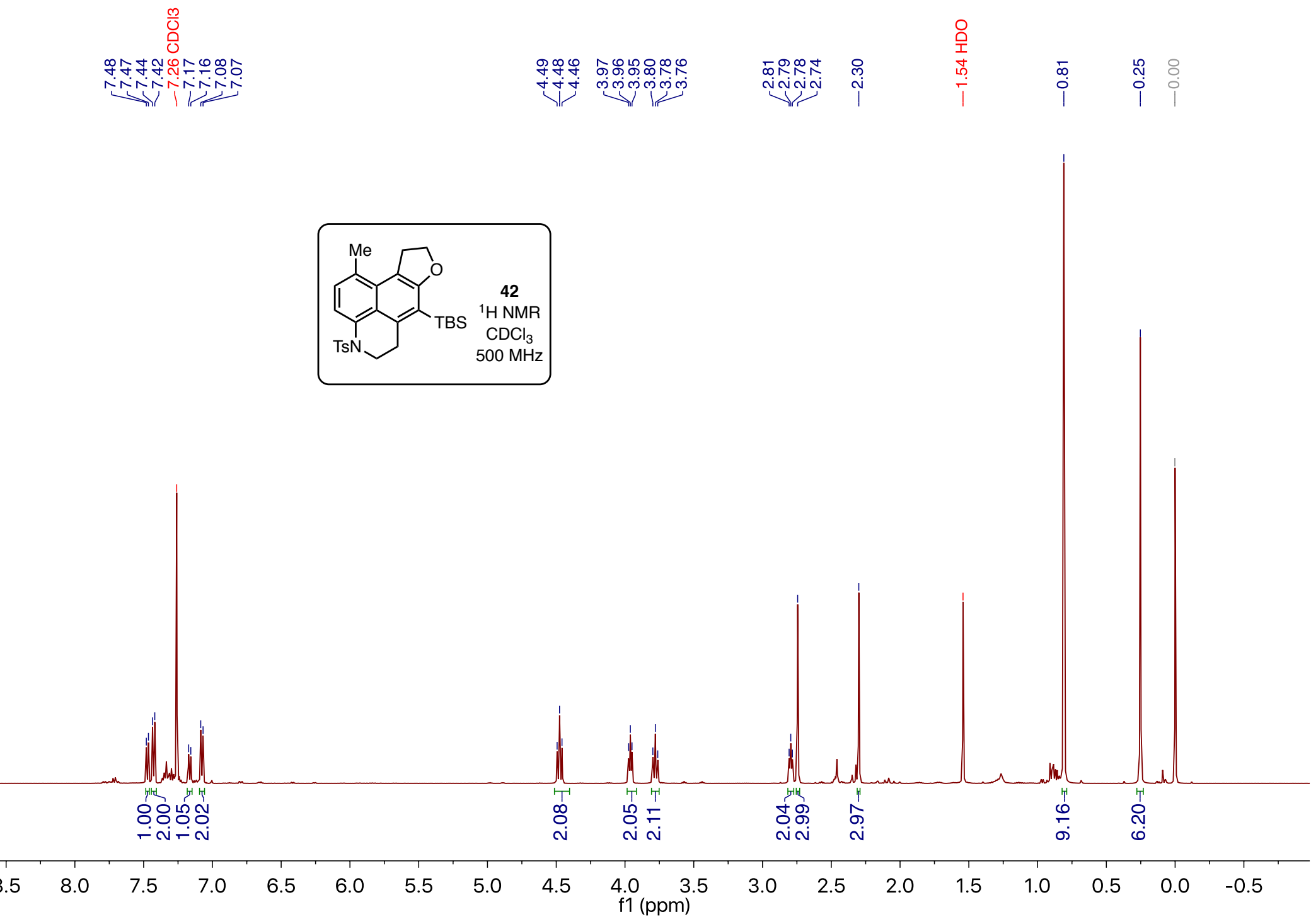

166.6
148.4
140.7
140.0
139.0
137.7
131.2
131.2
128.8
128.5
128.1
125.9
125.6
125.3
124.1
124.0
123.2
121.5
120.9
118.9
117.8
116.2
112.1
106.4
106.4
106.4
106.4
79.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
70.2
34.5
31.4
28.3
27.5
27.5
27.5
19.8
0.2
0.2
TBS
TfN
O
40
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

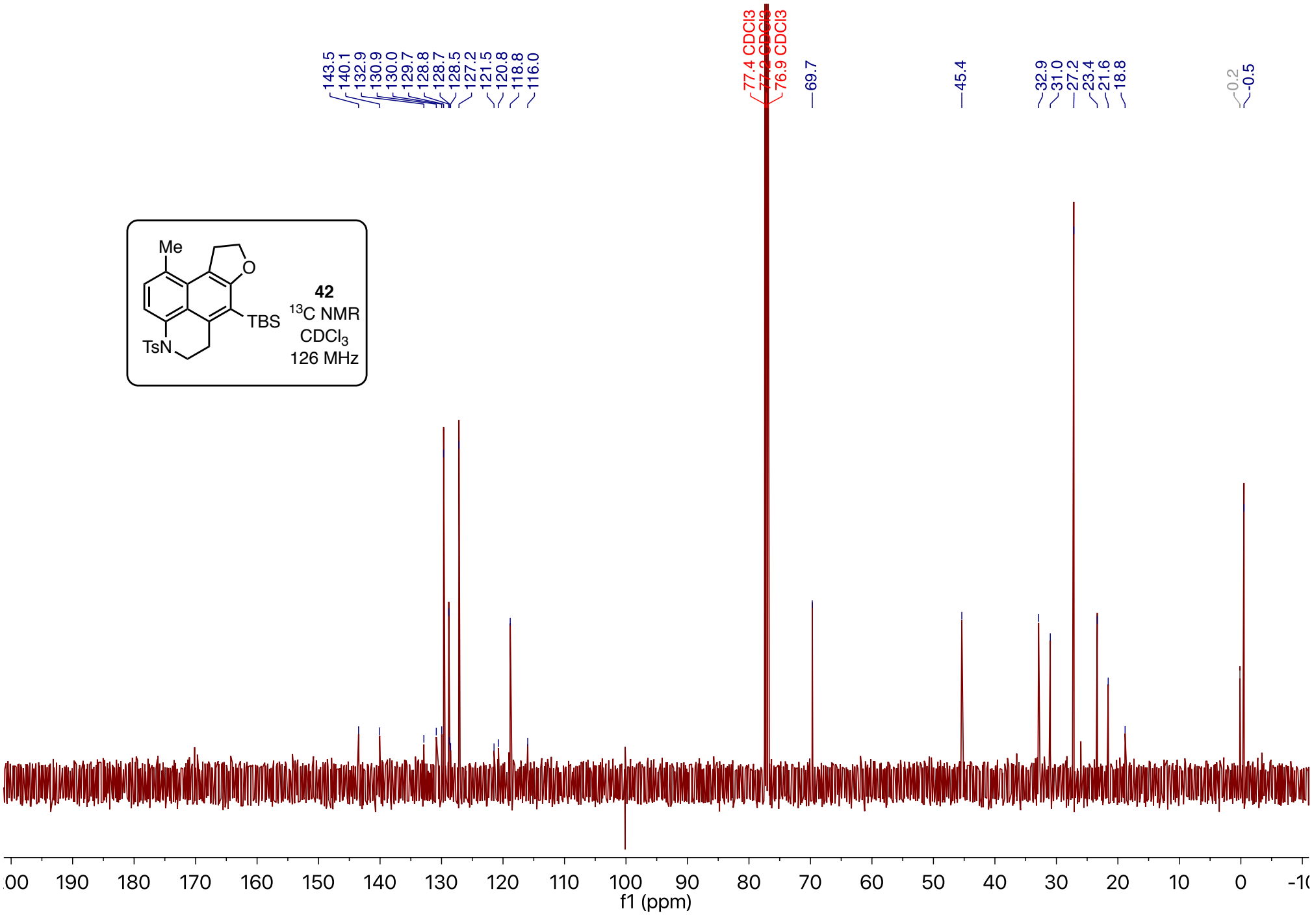

TBS
TfN
O
40
HSQC
CDCl3
500 MHz
f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)
TBS
TfN
O
40
HMBC
CDCl3
500 MHz


7.76
7.74
7.33
7.31
7.26 CDCl3
4.74
4.73
4.72
3.75
3.73
3.72
3.13
3.12
3.10
3.09
2.48
2.47
2.45
2.44
2.42
2.41
2.40
0.90
0.07
0.00
OTBS
NHTs
41
1H NMR
CDCl3
500 MHz
2.00
2.04
1.02
2.04
2.08
2.08
3.02
2.12
9.19
6.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


143.8
137.1
130.0
127.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
76.0
73.1
67.8
65.9
61.5
41.7
26.0
23.7
21.7
20.9
18.5
0.1
-5.2
OTBS
NHTs
41
13C NMR
CDCl3
126 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.48
7.47
7.44
7.42
7.26 CDCl3
7.17
7.16
7.08
7.07
4.49
4.48
4.46
3.97
3.96
3.95
3.80
3.78
3.76
2.81
2.79
2.78
2.74
2.30
1.54 HDO
0.81
0.25
0.00
Me
O
TBS
TsN
42
1H NMR
CDCl3
500 MHz
1.00
2.00
1.05
2.02
2.08
2.05
2.11
2.04
2.99
2.97
9.16
6.20
f1 (ppm)


143.5
140.1
132.9
130.9
130.0
129.7
128.8
128.7
128.5
127.2
121.5
120.8
118.8
116.0
77.4 CDCl3
77.0 CDCl3
76.9 CDCl3
69.7
45.4
32.9
31.0
27.2
23.4
21.6
18.8
0.2
-0.5
Me
O
TBS
TsN
42
13C NMR
CDCl3
126 MHz
f1 (ppm)