

Supporting Information for

**Bifunctional Biphenyl-2-ylphosphine Ligand Enables
Tandem Gold-Catalyzed Propargylation of Aldehyde
and Unexpected Cycloisomerization**

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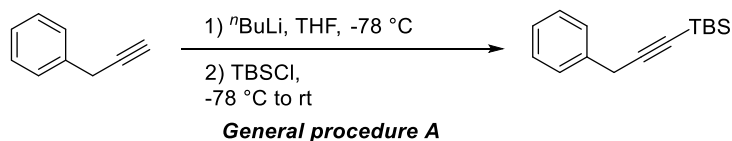
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1. General Information

Ethyl acetate (ACS grade), hexanes (ACS grade), dichloromethane (ACS grade) were purchased from Fisher Scientific and used without further purification. ACS grade 1,2-dichloroethane were purchased from Acros Organics and used directly. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Silicycle precoated silica gel plates. Flash column chromatography was performed over Silicycle silica gel (230-400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz, 500 MHz and 600 MHz spectrometers using residue solvent peaks as internal standards (CHCl_3 , ^1H : 7.26 ppm; ^{13}C : 77.00 ppm). ^{19}F NMR spectra were recorded on Varian 400 MHz calibrated by PhF or PhCF_3 (PhF , ^{19}F : -113.15 ppm. PhCF_3 , ^{19}F : -63.72 ppm). Mass spectra were recorded with Waters micromass ZQ detector using electrospray method.

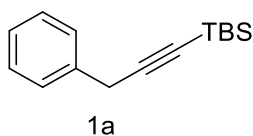
2. Preparation of Silylated Alkynes

General Procedure A:



Taking substrate **1a** for example: To a solution of prop-2-yn-1-ylbenzene (1 equiv.) in anhydrous THF was added *n*BuLi (2.5 M, 1.1 equiv.) dropwise under nitrogen at -78 °C. After 30 min, anhydrous TBSCl (1.1 equiv.) in THF solution was added dropwise at -78 °C. The reaction mixture was stirred at -78 °C for 30 min before allowed to warm up to room temperature. Stirring was continued for 1 h. The reaction mixture was diluted with ether and washed with water and brine. The organic phase was dried over anhydrous MgSO₄, filtered and concentrated under vacuum. The residue was purified by flash column chromatography to give the target silylated alkyne.

tert-butyldimethyl(3-phenylprop-1-yn-1-yl)silane (**1a**)



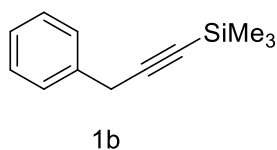
This compound was prepared from prop-2-yn-1-ylbenzene and TBSCl according to the general procedure **A** as colorless oil in 74% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.29 (m, 4H), 7.25 (t, *J* = 7.7 Hz, 1H), 3.69 (s, 2H), 0.97 (s, 9H), 0.14 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 136.45, 128.41, 127.80, 126.49, 104.69, 85.05, 26.16, 26.10, 16.56, -4.48.

HR-MS (EI-TOF) *m/z* calcd for C₁₅H₂₂Si [*M*]⁺: 230.1491, found: 230.1496.

trimethyl(3-phenylprop-1-yn-1-yl)silane (**1b**)

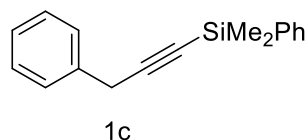


The known compound was prepared from phenylacetylene and TMSCl according to the

general procedure **A** as colorless oil in 84% yield.

This compound is known. Its spectroscopic data are in accordance with the literature data^[1].

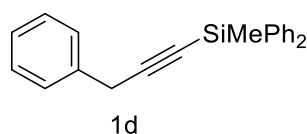
dimethyl(phenyl)(3-phenylprop-1-yn-1-yl)silane (**1c**)



This compound was prepared from prop-2-yn-1-ylbenzene and PhMe₂SiCl according to the general procedure **A** as colorless oil in 90% yield.

This compound is known. Its spectroscopic data are in accordance with the literature data^[2].

methyldiphenyl(3-phenylprop-1-yn-1-yl)silane (**1d**)



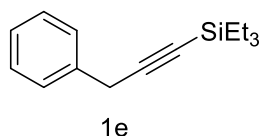
This compound was prepared from prop-2-yn-1-ylbenzene and Ph₂MeSiCl according to the general procedure **A** as colorless oil in 86% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.84 – 7.78 (m, 4H), 7.54 – 7.47 (m, 8H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 3.89 (s, 2H), 0.86 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 136.17, 135.77, 134.65, 129.75, 128.69, 128.07, 126.83, 108.07, 83.47, 26.57, -1.68.

HR-MS (EI-TOF) *m/z* calcd for C₂₁H₁₇Si [M-CH₃]⁺: 297.1100, found: 297.1097.

triethyl(3-phenylprop-1-yn-1-yl)silane (**1e**)



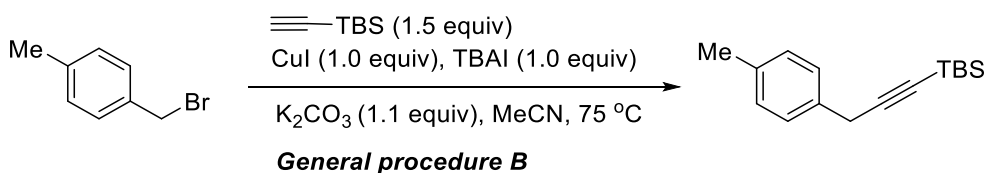
This compound was prepared from prop-2-yn-1-ylbenzene and Et₃SiCl according to the general procedure **A** as colorless oil in 85% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.29 (m, 4H), 7.25 (t, *J* = 6.5 Hz, 1H), 3.70 (s, 2H), 1.03 (dd, *J* = 9.8, 6.0 Hz, 9H), 0.64 (q, *J* = 7.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 136.51, 128.41, 127.80, 126.48, 105.20, 84.18, 26.20, 7.49, 4.49.

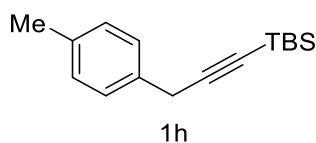
HR-MS (EI-TOF) *m/z* calcd for C₁₅H₂₂Si [M]⁺: 230.1491, found: 230.1483.

General Procedure B:



Taking substrate **1h** for example:^[3] To a solution of 1-(bromomethyl)-4-methylbenzene (2.0 mmol), copper(I) iodide (1.0 equiv), K₂CO₃ (1.1 equiv), and tetrabutylammonium iodide (1.0 equiv) in dry acetonitrile, *tert*-butyl(ethynyl)dimethylsilane (1.5 equiv) was added. The mixture was stirred at 75 °C for 24 h. The reaction mixture was quenched with saturated NH₄Cl solution and extracted with EtOAc. The crude organic layers were washed with brine, dried using MgSO₄ and filtered. The filtrate was concentrated in vacuo and purified the residue by column chromatography on silica gel to give the target silylated alkyne.

tert-butyldimethyl(3-(*p*-tolyl)prop-1-yn-1-yl)silane (**1h**)



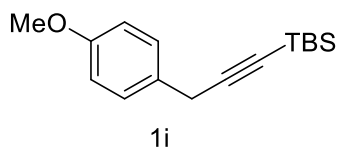
This compound was prepared from 1-(bromomethyl)-4-methylbenzene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 81% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 6.8 Hz, 1H), 7.28 – 7.08 (m, 3H), 3.61 (s, 2H), 2.34 (s, 3H), 0.99 (s, 9H), 0.16 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 135.88, 134.70, 129.94, 128.11, 126.76, 126.13, 104.45, 85.24, 26.13, 24.41, 19.27, 16.60, -4.44.

HR-MS (EI-TOF) m/z calcd for $C_{16}H_{24}Si$ $[M]^+$: 244.1647, found: 244.1655.

tert-butyl(3-(4-methoxyphenyl)prop-1-yn-1-yl)dimethylsilane (**1i**)



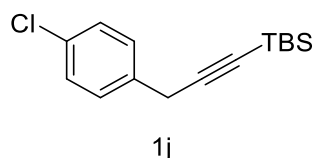
This compound was prepared from 1-(bromomethyl)-4-methoxybenzene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 84% yield.

1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 3.80 (s, 3H), 3.61 (s, 2H), 0.95 (s, 9H), 0.12 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.21, 128.74, 128.46, 113.80, 105.20, 84.69, 55.27, 26.10, 25.29, 16.57, -4.47.

HR-MS (EI-TOF) m/z calcd for $C_{26}H_{24}OSi$ $[M]^+$: 260.1596, found: 260.1596.

tert-butyl(3-(4-chlorophenyl)prop-1-yn-1-yl)dimethylsilane (**1j**)



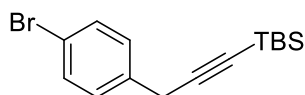
This compound was prepared from 1-(chloromethyl)-4-chlorobenzene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 85% yield.

1H NMR (500 MHz, $CDCl_3$) δ 7.29 (s, 4H), 3.63 (s, 2H), 0.95 (s, 9H), 0.13 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.99, 132.34, 129.17, 128.55, 104.07, 85.59, 26.10, 25.64, 16.56, -4.49.

HR-MS (EI-TOF) m/z calcd for $C_{15}H_{21}ClSi$ $[M]^+$: 264.1101, found: 264.1094.

(3-(4-bromophenyl)prop-1-yn-1-yl)(*tert*-butyl)dimethylsilane (**1k**)



1k

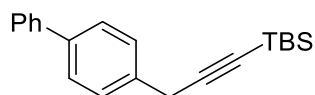
This compound was prepared from 1-bromo-4-(bromomethyl)benzene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 77% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.61 (s, 2H), 0.95 (s, 9H), 0.12 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 135.49, 131.47, 129.54, 120.33, 103.92, 85.60, 26.06, 25.69, 16.53, -4.53.

HR-MS (EI-TOF) *m/z* calcd for C₁₅H₂₁BrSi [M]⁺: 308.0596, found: 308.0582.

(3-([1,1'-biphenyl]-4-yl)prop-1-yn-1-yl)(*tert*-butyl)dimethylsilane (**1l**)



1l

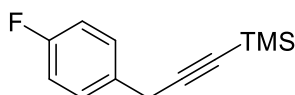
This compound was prepared from 4-(bromomethyl)-1,1'-biphenyl and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 66% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.55 (m, 4H), 7.47 (dd, *J* = 10.0, 4.8 Hz, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 3.75 (s, 2H), 1.01 (s, 9H), 0.18 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 140.87, 139.52, 135.56, 128.74, 128.25, 127.20, 127.17, 127.03, 104.63, 85.19, 26.15, 16.62, -4.43.

HR-MS (EI-TOF) *m/z* calcd for C₂₁H₂₆Si [M]⁺: 306.1804, found: 306.1806.

(3-(4-fluorophenyl)prop-1-yn-1-yl)trimethylsilane (**1m**)



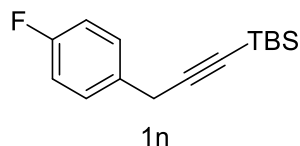
1m

This compound was prepared from 1-(bromomethyl)-4-fluorobenzene and ethynyltrimethylsilane according to the general procedure **B** as colorless oil in 78%

yield.

This compound is known. Its spectroscopic data are in accordance with the literature data^[4].

tert-butyl(3-(4-fluorophenyl)prop-1-yn-1-yl)dimethylsilane (**1n**)



This compound was prepared from 1-(bromomethyl)-4-fluorobenzene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 76% yield.

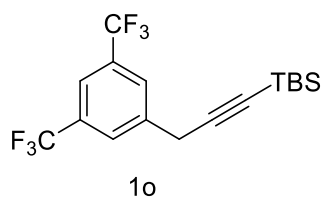
¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.28 (m, 2H), 7.05– 7.01 (m, 2H), 3.64 (s, 2H), 0.96 (s, 9H), 0.13 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 161.66 (d, *J* = 244.5 Hz), 132.12 (d, *J* = 3.1 Hz), 129.24 (d, *J* = 7.9 Hz), 115.22 (d, *J* = 21.4 Hz), 104.51, 85.33, 26.10, 25.45, 16.56, -4.48.

¹⁹F NMR (376 MHz, CDCl₃) δ -118.64.

HR-MS (EI-TOF) *m/z* calcd for C₁₅H₂₁FSi [M]⁺: 248.1397, found: 248.1392.

(3-(3,5-bis(trifluoromethyl)phenyl)prop-1-yn-1-yl)(*tert*-butyl)dimethylsilane (**1o**)



This compound was prepared from 1-(bromomethyl)-3,5-bis(trifluoromethyl)benzene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 88% yield.

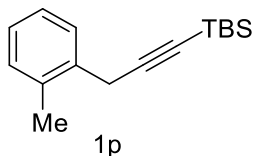
¹H NMR (500 MHz, CDCl₃) δ 7.85 (s, 2H), 7.77 (s, 1H), 3.79 (s, 2H), 0.96 (s, 9H), 0.15 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 139.08, 131.73 (q, *J* = 33.2 Hz), 128.12 (d, *J* = 3.7 Hz), 123.29 (q, *J* = 272.7 Hz), 120.77, 121.00 (m), 102.06, 87.68, 16.47, -4.66.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.03.

HR-MS (EI-TOF) m/z calcd for $C_{17}H_{20}F_6Si$ $[M]^+$: 366.1238, found: 366.1239.

tert-butyldimethyl(3-(*o*-tolyl)prop-1-yn-1-yl)silane (**1p**)



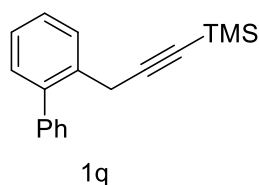
This compound was prepared from 1-(bromomethyl)-2-methylbenzene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 55% yield.

1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 6.8 Hz, 1H), 7.28 – 7.08 (m, 3H), 3.61 (s, 2H), 2.34 (s, 3H), 0.99 (s, 9H), 0.16 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.88, 134.70, 129.94, 128.11, 126.76, 126.13, 104.45, 85.24, 26.13, 24.41, 19.27, 16.60, -4.44.

HR-MS (EI-TOF) m/z calcd for $C_{16}H_{24}Si$ $[M]^+$: 244.1647, found: 244.1640.

(3-([1,1'-biphenyl]-2-yl)prop-1-yn-1-yl)trimethylsilane (**1q**)



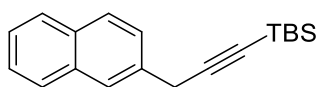
This compound was prepared from 2-(bromomethyl)-1,1'-biphenyl and ethynyltrimethylsilane according to the general procedure **B** as colorless oil in 66% yield.

1H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 1H), 7.48 – 7.27 (m, 7H), 7.23 (dd, J = 7.5, 1.4 Hz, 1H), 3.54 (s, 2H), 0.16 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.44, 140.96, 133.94, 129.86, 129.14, 128.85, 128.19, 127.67, 127.10, 126.69, 104.95, 86.73, 24.63, 0.07.

HR-MS (EI-TOF) m/z calcd for $C_{18}H_{20}Si$ $[M]^+$: 264.1334, found: 264.1336.

tert-butyldimethyl(3-(naphthalen-2-yl)prop-1-yn-1-yl)silane (**1s**)

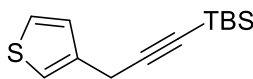


1s

This compound was prepared from 2-(bromomethyl)naphthalene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 82% yield.

This compound is known. Its spectroscopic data are in accordance with the literature data^[5].

tert-butyldimethyl(3-(thiophen-3-yl)prop-1-yn-1-yl)silane (**1t**)



1t

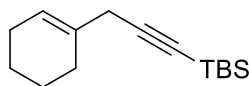
This compound was prepared from 3-(bromomethyl)thiophene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 74% yield.

¹H NMR (500 MHz, CDCl₃) δ 7.27 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.16 (dd, *J* = 2.8, 1.4 Hz, 1H), 7.03 – 6.99 (m, 1H), 3.63 (d, *J* = 0.9 Hz, 2H), 0.96 (s, 9H), 0.13 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 136.78, 127.55, 125.78, 121.16, 104.51, 84.46, 26.12, 21.41, 16.56, -4.47.

HR-MS (EI-TOF) *m/z* calcd for C₁₃H₂₀SSi [M]⁺: 236.1055, found: 236.1057.

tert-butyl(3-(cyclohex-1-en-1-yl)prop-1-yn-1-yl)dimethylsilane (**1v**)



1v

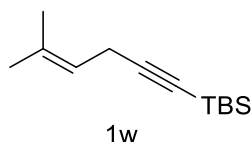
This compound was prepared from 1-(chloromethyl)cyclohex-1-ene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 52% yield.

¹H NMR (400 MHz, CDCl₃) δ 6.11 – 5.55 (m, 1H), 2.89 (d, *J* = 0.6 Hz, 2H), 2.03 – 1.81 (m, 4H), 1.75 – 1.60 (m, 2H), 1.60 – 1.53 (m, 2H), 0.94 (s, 9H), 0.10 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 132.47, 122.46, 104.89, 84.60, 28.42, 28.21, 26.08, 25.17, 22.78, 22.28, 16.52, -4.45.

HR-MS (EI-TOF) *m/z* calcd for C₁₅H₂₆Si [M]⁺: 234.1804, found: 234.1803.

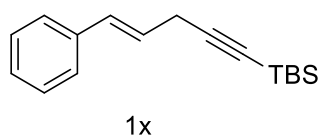
tert-butyldimethyl(5-methylhex-4-en-1-yn-1-yl)silane (**1w**)



This compound was prepared from 1-chloro-3-methylbut-2-ene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 44% yield.

This compound is known. Its spectroscopic data are in accordance with the literature data^[6].

(*E*)-*tert*-butyldimethyl(5-phenylpent-4-en-1-yn-1-yl)silane (**1x**)



This compound was prepared from (*E*)-(3-chloroprop-1-en-1-yl)benzene and *tert*-butyl(ethynyl)dimethylsilane according to the general procedure **B** as colorless oil in 66% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.18 (m, 5H), 6.70 (d, *J* = 15.7 Hz, 1H), 6.17 (dt, *J* = 15.7, 5.4 Hz, 1H), 3.20 (d, *J* = 5.4, 1.7 Hz, 2H), 0.98 (s, 9H), 0.14 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 137.10, 131.33, 128.49, 127.27, 126.21, 124.02, 109.98, 103.99, 26.10, 23.39, 16.52, -4.46.

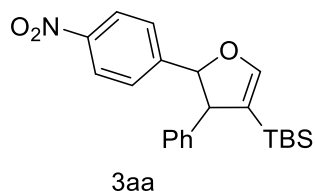
HR-MS (EI-TOF) *m/z* calcd for C₁₇H₂₄Si [M]⁺: 256.1647, found: 256.1641.

3. Synthesis of the Dihydrofuran

General procedure **C**: To a 3-dram vial were added sequentially 0.2 mmol silylated alkyne, 0.01 mmol indicated **L1**AuCl (5 mol%), 0.04 mmol NaBARF (20 mol%) and

2 mL anhydrous DCE as solvent. The reaction was then stirred at the indicated temperature monitored by TLC. Upon completion, the reaction was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to obtain pure product.

tert-butyldimethyl(5-(4-nitrophenyl)-4-phenyl-4,5-dihydrofuran-3-yl)silane (**3aa**)



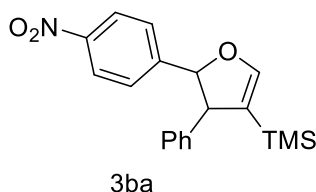
Compound **3aa** was obtained as colorless oil in a ratio of 3/1 in 78% combined yield according to general procedure **C**. The reaction was heated at 90 °C for 18 h. NMR spectra of the compound *cis*-**3aa** was reported.

¹H NMR (600 MHz, CDCl₃) δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 1H), 6.99 (t, *J* = 7.1 Hz, 2H), 6.96 – 6.92 (m, 1H), 6.80 (d, *J* = 7.1 Hz, 2H), 6.71 (d, *J* = 1.2 Hz, 2H), 5.77 (d, *J* = 9.4 Hz, 1H), 4.28 (dd, *J* = 9.4, 1.2 Hz, 1H), 0.88 (s, 6H), 0.01 (s, 3H), -0.42 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 152.54, 146.52, 145.67, 138.19, 128.87, 127.82, 127.02, 126.87, 122.73, 112.70, 86.90, 57.40, 26.61, 17.02, -5.35.

HR-MS (EI-TOF) *m/z* calcd for C₂₂H₂₇NO₃Si [*M*]⁺: 381.1760, found: 381.1753.

trimethyl(5-(4-nitrophenyl)-4-phenyl-4,5-dihydrofuran-3-yl)silane (**3ba**)



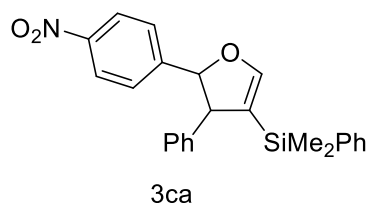
Compound **3ba** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 3 h. NMR spectra of the compound *cis*-**3ba** was reported.

¹H NMR (500 MHz, CDCl₃) δ 8.00 – 7.87 (m, 2H), 7.23 – 7.20 (m, 2H), 7.07 – 6.92 (m, 3H), 6.89 – 6.76 (m, 2H), 6.67 (d, *J* = 9.8, 1.4 Hz, 1H), 5.81 (d, *J* = 9.8 Hz, 1H), 4.32 (dd, *J* = 9.8, 1.4 Hz, 1H), -0.08 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 151.40, 146.53, 145.90, 138.28, 128.93, 127.82, 127.04, 126.89, 122.76, 86.88, 56.62, -0.98.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{Si}$ $[\text{M}]^+$: 339.1291, found: 339.1296.

dimethyl(5-(4-nitrophenyl)-4-phenyl-4,5-dihydrofuran-3-yl)(phenyl)silane (**3ca**)



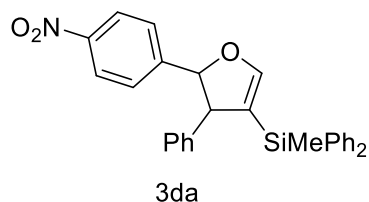
Compound **3ca** was obtained as white solid according to general procedure **C**. The reaction was heated at 90 °C for 8 h. NMR spectra of the compound *cis*-**3ca** was reported.

^1H NMR (400 MHz, CDCl_3) δ 7.89 (dd, J = 16.5, 8.8 Hz, 2H), 7.46 (dt, J = 9.1, 4.4 Hz, 2H), 7.40 – 7.31 (m, 3H), 7.19 (d, J = 8.7 Hz, 2H), 7.01 – 6.94 (m, 3H), 6.84 – 6.74 (m, 2H), 6.67 (d, J = 1.2 Hz, 1H), 5.84 (d, J = 9.7, 1H), 4.27 (dd, J = 9.7, 1.2 Hz, 1H), 0.20 (d, J = 3.3 Hz, 3H), 0.05 (d, J = 3.3 Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 152.84, 146.51, 145.68, 138.07, 137.80, 133.69, 129.10, 128.92, 127.81, 127.77, 126.98, 126.90, 122.75, 113.50, 87.06, 56.47, -2.50, -2.55.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_3\text{Si}$ $[\text{M}]^+$: 401.1447, found: 401.1448.

methyl(5-(4-nitrophenyl)-4-phenyl-4,5-dihydrofuran-3-yl)diphenylsilane (**3da**)



Compound **3da** was obtained as white solid according to general procedure **C**. The reaction was heated at 90 °C for 16 h. NMR spectra of the compound *cis*-**3da** was reported.

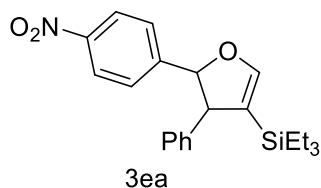
^1H NMR (600 MHz, CDCl_3) δ 7.95 – 7.87 (m, 2H), 7.51 – 7.45 (m, 4H), 7.41 – 7.36 (m, 2H), 7.36 – 7.31 (m, 4H), 7.21 (d, J = 8.6 Hz, 2H), 7.00 – 6.83 (m, 3H), 6.83 – 6.70

(m, 2H), 6.66 (d, $J = 1.3$ Hz, 1H), 5.90 (d, $J = 9.6$ Hz, 1H), 4.32 (dd, $J = 9.6, 1.3$ Hz, 1H), 0.21 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 155.06, 146.60, 145.47, 137.93, 135.83, 135.62, 134.74, 129.41, 129.38, 128.96, 127.84, 127.83, 127.82, 127.03, 126.94, 122.77, 111.96, 87.48, 56.56, -3.69.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{29}\text{H}_{25}\text{NO}_3\text{Si}$ $[\text{M}]^+$: 463.1604, found: 463.1596.

triethyl(5-(4-nitrophenyl)-4-phenyl-4,5-dihydrofuran-3-yl)silane (**3ea**)



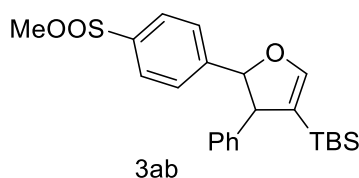
Compound **3ea** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 12 h. NMR spectra of the compound *cis*-**3ea** was reported.

^1H NMR (600 MHz, CDCl_3) δ 7.91 (d, $J = 8.8$ Hz, 2H), 7.21 (d, $J = 8.8$ Hz, 2H), 7.03 – 6.92 (m, 2H), 6.83 – 6.78 (m, 2H), 6.68 (d, $J = 1.2$ Hz, 1H), 5.78 (d, $J = 9.6$ Hz, 1H), 4.26 (dd, $J = 9.6, 1.2$ Hz, 1H), 1.03 – 0.82 (m, 9H), 0.51 – 0.33 (m, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 152.11, 146.55, 145.84, 138.34, 128.84, 127.78, 127.05, 126.91, 122.74, 111.86, 86.80, 56.77, 7.20, 3.44.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_3\text{Si}$ $[\text{M}]^+$: 381.1760, found: 381.1753.

tert-butyldimethyl(5-(4-(methylsulfonyl)phenyl)-4-phenyl-4,5-dihydrofuran-3-yl)silane (**3ab**)



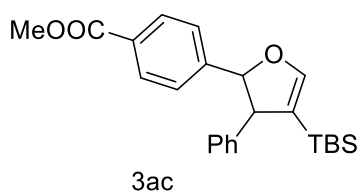
Compound **3ab** was obtained as white solid according to general procedure **C**. The reaction was heated at 90 °C for 22 h. NMR spectra of the compound *cis*-**3ab** was reported.

¹H NMR (600 MHz, CDCl₃) δ 7.64 – 7.58 (m, 2H), 7.26 – 7.20 (m, 2H), 7.01 – 6.89 (m, 3H), 6.78 (d, *J* = 7.0 Hz, 2H), 6.71 (d, *J* = 1.1 Hz, 1H), 5.76 (d, *J* = 9.4 Hz, 1H), 4.27 (dd, *J* = 9.4, 1.1 Hz, 1H), 2.87 (s, 3H), 0.87 (s, 9H), 0.01 (s, 3H), -0.42 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 152.66, 144.56, 138.27, 128.96, 127.76, 127.20, 126.78, 126.57, 112.55, 87.07, 57.43, 44.53, 26.64, 17.04, -5.31, -5.61.

HR-MS (EI-TOF) *m/z* calcd for C₂₃H₃₀SO₃Si [M]⁺: 414.1685, found: 414.1688.

methyl 4-(4-(*tert*-butyldimethylsilyl)-3-phenyl-2,3-dihydrofuran-2-yl)benzoate (**3ac**)



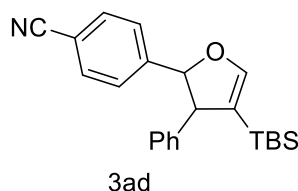
Compound **3ac** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 16 h. NMR spectra of the compound *cis*-**3ac** was reported.

¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.98 (t, *J* = 7.7 Hz, 2H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 7.0 Hz, 2H), 6.73 (d, *J* = 1.1 Hz, 1H), 5.75 (d, *J* = 9.3 Hz, 1H), 4.25 (dd, *J* = 9.3, 1.1 Hz, 1H), 3.83 (s, 3H), 1.00 – 0.71 (m, 9H), 0.02 (s, 3H), -0.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.89, 152.75, 143.18, 138.57, 129.00, 128.79, 128.34, 127.59, 126.54, 126.23, 112.52, 87.55, 57.27, 51.87, 26.63, 17.02, -5.35, -5.64.

HR-MS (EI-TOF) *m/z* calcd for C₂₄H₃₀O₃Si [M]⁺: 394.1964, found: 394.1968.

4-(4-(*tert*-butyldimethylsilyl)-3-phenyl-2,3-dihydrofuran-2-yl)benzonitrile (**3ad**)



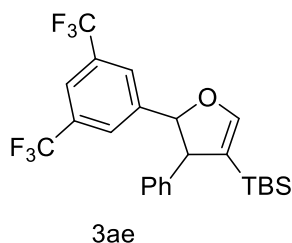
Compound **3ad** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 24 h. NMR spectra of the compound *cis*-**3ad** was reported.

¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.02 – 6.95 (m, 3H), 6.83 – 6.76 (m, 2H), 6.71 (d, *J* = 1.3 Hz, 1H), 5.74 (d, *J* = 9.4 Hz, 1H), 4.26 (dd, *J* = 9.4, 1.3 Hz, 1H), 0.88 (s, 9H), 0.02 (s, 3H), -0.41 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 152.63, 143.57, 138.29, 131.32, 128.94, 127.78, 126.95, 126.82, 118.86, 112.58, 110.38, 87.08, 57.37, 26.64, 17.04, -5.32, -5.61.

HR-MS (EI-TOF) *m/z* calcd for C₂₃H₂₇NOSi [M]⁺: 361.1862, found: 361.1855.

(5-(3,5-bis(trifluoromethyl)phenyl)-4-phenyl-4,5-dihydrofuran-3-yl)(*tert*-butyl)dimethylsilane (**3ae**)



Compound **3ae** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 18 h. NMR spectra of the compound *cis*-**3ae** was reported.

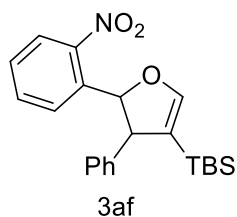
¹H NMR (500 MHz, CDCl₃) δ 7.49 (s, 1H), 7.46 (s, 2H), 6.98 (dq, *J* = 13.0, 6.9 Hz, 3H), 6.78 (d, *J* = 6.9 Hz, 2H), 6.74 (d, *J* = 1.1 Hz, 1H), 5.80 (d, *J* = 9.4 Hz, 2H), 4.31 (dd, *J* = 9.4, 1.1 Hz, 2H), 0.90 (s, 9H), 0.04 (s, 3H), -0.39 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 152.64, 140.77, 137.93, 130.60 (d, *J* = 33.3 Hz), 128.79, 127.95, 126.95, 126.56, 123.18 (d, *J* = 272.6 Hz), 120.47 (m), 112.30, 86.50, 57.49, 26.63, 17.04, -5.31, -5.58.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.00.

HR-MS (EI-TOF) *m/z* calcd for C₂₄H₂₆F₆OSi [M]⁺: 472.1657, found: 472.1655.

tert-butyldimethyl(5-(2-nitrophenyl)-4-phenyl-4,5-dihydrofuran-3-yl)silane (**3af**)



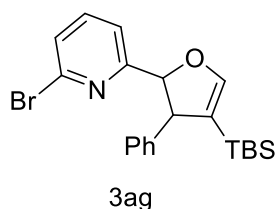
Compound **3af** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 16 h. NMR spectra of the compound *cis*-**3af** was reported.

¹H NMR (600 MHz, CDCl₃) δ 7.85 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.36 (td, *J* = 8.0, 1.1 Hz, 1H), 7.21 – 7.11 (m, 1H), 6.93 (dq, *J* = 12.9, 7.0 Hz, 3H), 6.85 – 6.78 (m, 2H), 6.72 (d, *J* = 1.4 Hz, 1H), 6.33 (d, *J* = 9.5 Hz, 1H), 4.73 (dd, *J* = 9.5, 1.4 Hz, 1H), 0.89 (s, 9H), 0.01 (s, 3H), -0.43 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 151.93, 146.50, 138.99, 135.39, 132.96, 128.93, 128.89, 127.58, 127.54, 126.48, 124.28, 109.99, 84.81, 55.84, 26.64, 17.05, -5.29, -5.61.

HR-MS (EI-TOF) *m/z* calcd for C₂₂H₂₇NO₃Si [*M*]⁺: 381.1760, found: 381.1753.

2-bromo-6-(4-(*tert*-butyldimethylsilyl)-3-phenyl-2,3-dihydrofuran-2-yl)pyridine (**3ag**)



Compound **3ag** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 3 h. NMR spectra of the compound *cis*-**3ag** was reported.

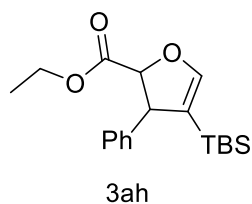
¹H NMR (500 MHz, CDCl₃) δ 7.53 (t, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.27 – 7.20 (m, 3H), 7.17 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.07 – 7.00 (m, 4H), 6.96 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.91 – 6.87 (m, 2H), 6.70 (d, *J* = 1.3 Hz, 1H), 6.61 (d, *J* = 1.6 Hz, 1H), 5.74 (d, *J* = 9.3 Hz, 1H), 5.35 (d, *J* = 4.1 Hz, 1H), 4.46 (dd, *J* = 9.3, 1.3 Hz, 1H), 4.18 (dd, *J* = 4.1, 1.6 Hz, 1H), 0.88 (s, 9H), 0.75 (s, 9H), 0.03 (s, 3H), -0.01 (s, 3H), -0.42 (s, 3H), -0.44 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 163.16, 159.84, 152.51, 151.87, 143.92, 141.75, 140.42,

138.86, 138.42, 137.93, 128.97, 128.53, 127.94, 127.52, 126.89, 126.84, 126.48, 125.73, 119.66, 118.16, 112.57, 110.43, 104.99, 90.34, 87.74, 59.84, 56.36, 26.60, 26.58, 17.17, 17.00, -5.35, -5.51, -5.64.

HR-MS (EI-TOF) m/z calcd for $C_{21}H_{26}BrNOSi$ $[M]^+$: 415.0967, found: 415.0961.

ethyl-4-(*tert*-butyldimethylsilyl)-3-phenyl-2,3-dihydrofuran-2-carboxylate (**3ah**)



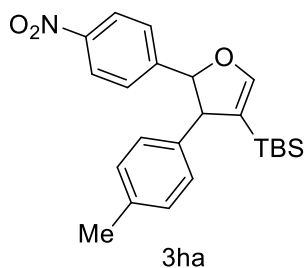
Compound **3ah** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 3 h. NMR spectra of the compound *cis*-**3ah** was reported.

¹H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.15 (m, 3H), 7.15 – 7.09 (m, 2H), 6.55 (d, J = 1.5 Hz, 1H), 5.17 (d, J = 10.3 Hz, 1H), 4.34 (dd, J = 10.3, 1.5 Hz, 1H), 3.77 (dq, J = 10.7, 7.1 Hz, 1H), 3.69 – 3.60 (m, 1H), 0.83 (s, 9H), 0.82 (t, J = 7.2 Hz, 3H), -0.03 (s, 1H), -0.45 (s, 1H).

¹³C NMR (126 MHz, $CDCl_3$) δ 168.95, 152.23, 138.74, 128.92, 127.95, 127.38, 111.35, 84.18, 60.75, 55.53, 26.59, 17.00, 13.62, -5.42, -5.62.

HR-MS (EI-TOF) m/z calcd for $C_{19}H_{28}O_3Si$ $[M]^+$: 332.1808, found: 332.1806.

tert-butyldimethyl(5-(4-nitrophenyl)-4-(*p*-tolyl)-4,5-dihydrofuran-3-yl)silane (**3ha**)



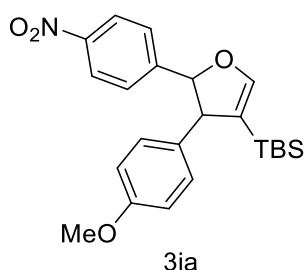
Compound **3ha** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 12 h. NMR spectra of the compound *cis*-**3ha** was reported.

¹H NMR (600 MHz, CDCl₃) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 7.7 Hz, 2H), 6.70 (dd, *J* = 9.6, 4.4 Hz, 3H), 5.75 (d, *J* = 9.4 Hz, 1H), 4.26 (dd, *J* = 9.4, 1.2 Hz, 1H), 0.89 (s, 9H), 0.02 (s, 3H), -0.41 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 152.36, 146.53, 145.88, 136.33, 128.76, 128.54, 127.08, 122.76, 112.86, 86.93, 57.05, 26.65, 20.97, 17.04, -5.30, -5.58.

HR-MS (EI-TOF) *m/z* calcd for C₂₃H₂₉NO₃Si [M]⁺: 395.1917, found: 395.1906.

tert-butyl(4-(4-methoxyphenyl)-5-(4-nitrophenyl)-4,5-dihydrofuran-3-yl)dimethyl silane (**3ia**)



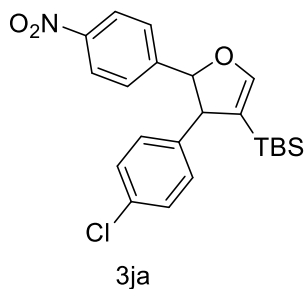
Compound **3ia** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 8 h. NMR spectra of the compound *cis*-**3ia** was reported.

¹H NMR (600 MHz, CDCl₃) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 1.2 Hz, 1H), 6.54 (d, *J* = 8.6 Hz, 2H), 5.73 (d, *J* = 9.3 Hz, 1H), 4.25 (dd, *J* = 9.3, 1.2 Hz, 1H), 3.65 (s, 3H), 0.89 (s, 9H), 0.02 (s, 3H), -0.40 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) 158.30, 152.23, 150.18, 145.86, 129.83, 127.02, 122.77, 114.12, 113.14, 112.92, 86.89, 56.62, 54.96, 26.62, 17.01, -5.33, -5.60.

HR-MS (EI-TOF) *m/z* calcd for C₂₃H₂₉NO₄Si [M]⁺: 411.1866, found: 411.1847.

tert-butyl(4-(4-chlorophenyl)-5-(4-nitrophenyl)-4,5-dihydrofuran-3-yl)dimethyl silane (**3ja**)



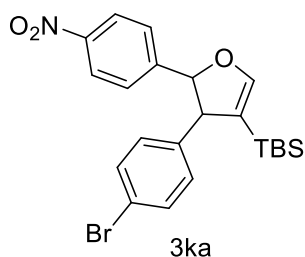
Compound **3ja** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 16 h. NMR spectra of the compound *cis*-**3ja** was reported.

¹H NMR (600 MHz, CDCl₃) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 1.2 Hz, 1H), 5.77 (d, *J* = 9.4 Hz, 1H), 4.26 (dd, *J* = 9.4, 1.2 Hz, 1H), 0.89 (s, 9H), 0.02 (s, 3H), -0.40 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 152.88, 146.73, 145.23, 136.98, 132.67, 130.13, 128.10, 126.96, 122.98, 112.81, 86.76, 56.71, 26.61, 26.57, 17.03, -5.32, -5.52.

HR-MS (EI-TOF) *m/z* calcd for C₂₂H₂₆ClNO₃Si [M]⁺: 415.1370, found: 415.1378.

(4-(4-bromophenyl)-5-(4-nitrophenyl)-4,5-dihydrofuran-3-yl)(*tert*-butyl)dimethylsilane (**3ka**)



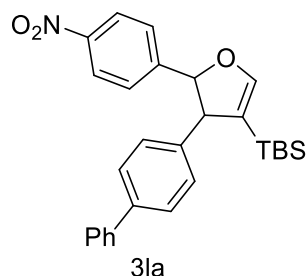
Compound **3ka** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 16 h. NMR spectra of the compound *cis*-**3ka** was reported.

¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 1.0 Hz, 1H), 6.70 (br, 2H), 5.77 (d, *J* = 9.3 Hz, 1H), 4.25 (dd, *J* = 9.3, 1.0 Hz, 1H), 0.89 (s, 6H), 0.02 (s, 3H), -0.40 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 152.91, 146.74, 145.19, 137.51, 131.05, 130.50, 126.96, 123.01, 120.82, 112.78, 86.70, 56.76, 26.62, 17.03, -5.31, -5.51.

HR-MS (EI-TOF) m/z calcd for $C_{22}H_{26}NO_3BrSi$ $[M]^+$: 459.0865, found: 459.0866.

(4-([1,1'-biphenyl]-4-yl)-5-(4-nitrophenyl)-4,5-dihydrofuran-3-yl)(tert-butyl)Dimethylsilane (**3la**)



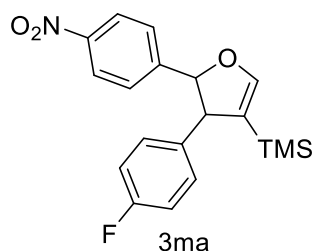
Compound **3la** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 18 h. NMR spectra of the compound *cis*-**3la** was reported.

1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 2H), 7.46 (dd, J = 5.7, 3.0 Hz, 3H), 7.37 (t, J = 7.6 Hz, 2H), 7.27 (dd, J = 8.0, 2.3 Hz, 4H), 6.90 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 1.0 Hz, 1H), 5.81 (d, J = 9.3 Hz, 1H), 4.34 (dd, J = 9.4, 1.0 Hz, 1H), 0.91 (s, 9H), 0.05 (s, 3H), -0.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.98, 146.85, 132.46, 126.99, 125.64, 124.66, 123.81, 122.97, 111.44, 86.03, 49.43, 26.73, 18.00, -5.07, -5.52.

HR-MS (EI-TOF) m/z calcd for $C_{28}H_{31}NO_3Si$ $[M]^+$: 457.2073, found: 457.2068.

(4-(4-fluorophenyl)-5-(4-nitrophenyl)-4,5-dihydrofuran-3-yl)trimethylsilane (**3ma**)



Compound **3ma** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 12 h.

NMR spectra for the compound *cis*-**3ma**:

1H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 6.82 – 6.76 (m, 2H), 6.75 – 6.69 (m, 2H), 6.67 (d, J = 1.3 Hz, 1H), 5.79 (d, J = 9.7 Hz, 1H),

4.31 (dd, $J = 9.7, 1.3$ Hz, 1H), -0.07 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 161.62 (d, $J = 245.8$ Hz), 151.53, 146.65, 145.64, 134.17 (d, $J = 3.2$ Hz), 130.30 (d, $J = 8.0$ Hz), 126.97, 122.90, 115.02, 114.77 (d, $J = 21.3$ Hz), 86.76, 55.78, -0.98.

^{19}F NMR (376 MHz, CDCl_3) δ -118.58.

NMR spectra for the compound *trans*-**3ma**:

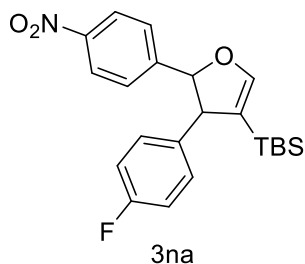
^1H NMR (600 MHz, CDCl_3) δ 7.95 (d, $J = 8.8$ Hz, 2H), 7.21 (d, $J = 8.8$ Hz, 2H), 6.82 – 6.76 (m, 2H), 6.75 – 6.69 (m, 2H), 6.67 (d, $J = 1.3$ Hz, 1H), 5.79 (d, $J = 9.7$ Hz, 1H), 4.31 (dd, $J = 9.7, 1.3$ Hz, 1H), -0.07 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 162.10 (d, $J = 245.8$ Hz), 151.09, 149.67, 147.50, 139.11 (d, $J = 3.1$ Hz), 129.39 (d, $J = 8.0$ Hz), 125.59, 124.00, 115.73 (d, $J = 21.4$ Hz), 112.68, 90.48, 61.12, -1.08.

^{19}F NMR (376 MHz, CDCl_3) δ -118.64.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{FNO}_3\text{Si}$ $[\text{M}]^+$: 357.1196, found: 37.1191.

tert-butyl(4-(4-fluorophenyl)-5-(4-nitrophenyl)-4,5-dihydrofuran-3-yl)dimethyl silane (**3na**)



Compound **3na** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 8 h.

NMR spectra for the compound *cis*-**3na**:

^1H NMR (600 MHz, CDCl_3) δ 7.95 (d, $J = 8.8$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 6.97 – 6.75 (m, 2H), 6.75 – 6.64 (m, 3H), 5.77 (d, $J = 9.4$ Hz, 1H), 4.28 (dd, $J = 9.4, 1.2$ Hz, 1H), 0.89 (s, 9H), 0.03 (s, 3H), -0.40 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 161.63 (d, $J = 245.8$ Hz), 152.69, 146.68, 145.44, 134.12 (d, $J = 3.2$ Hz), 130.28 (d, $J = 8.0$ Hz), 126.98, 122.90, 114.79 (d, $J = 21.3$ Hz),

112.90, 86.79, 56.60, 26.62, 17.03, -5.33, -5.58.

¹⁹F NMR (376 MHz, CDCl₃) δ -118.56.

HR-MS (EI-TOF) m/z calcd for C₂₂H₂₆NO₃Si [M]⁺: 399.1666, found: 399.1661.

NMR spectra for the compound *trans*-**3na**:

¹H NMR (500 MHz, CDCl₃) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.08 – 7.01 (m, 2H), 6.66 (d, *J* = 1.7 Hz, 1H), 5.34 (d, *J* = 5.6 Hz, 1H), 3.89 (dd, *J* = 5.6, 1.7 Hz, 1H), 0.76 (s, 9H), -0.01 (s, 3H), -0.44 (s, 3H).

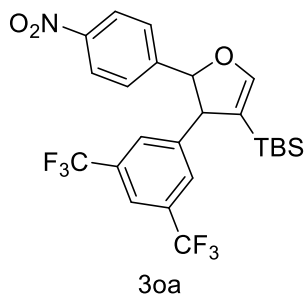
¹³C NMR (126 MHz, CDCl₃) δ 162.09 (d, *J* = 245.8 Hz), 152.47, 149.82, 147.53, 139.45 (d, *J* = 3.2 Hz), 129.29 (d, *J* = 8.0 Hz), 125.44, 124.05 115.71 (d, *J* = 21.4 Hz), 110.07, 90.30, 90.30, 61.88, 26.61, 17.18, -5.35.

¹⁹F NMR (376 MHz, CDCl₃) δ -118.15.

HR-MS (EI-TOF) m/z calcd for C₂₂H₂₆NO₃Si [M]⁺: 399.1666, found: 399.1661.

(4-(3,5-bis(trifluoromethyl)phenyl)-5-(4-nitrophenyl)-4,5-dihydrofuran-3-yl)

(*tert*-butyl)dimethylsilane (**3oa**)



Compound **3oa** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 24 h. NMR spectra of the compound *cis*-**3oa** was reported.

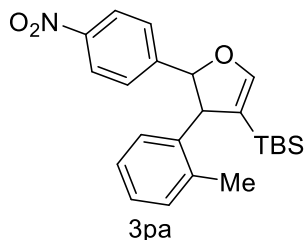
¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.93 (m, 2H), 7.52 (s, 1H), 7.26 (br, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 1.2 Hz, 1H), 5.88 (d, *J* = 9.4 Hz, 1H), 4.44 (dd, *J* = 9.4, 1.2 Hz, 1H), 0.89 (s, 9H), 0.05 (s, 3H), -0.40 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 154.12, 146.94, 144.35, 141.54, 131.15 (d, *J* = 33.3 Hz), 128.92 (m), 126.68, 123.14, 124.34 (d, *J* = 33.3 Hz), 120.76 (m), 111.78, 86.57, 56.89, 26.50, 16.96, -5.41.

^{19}F NMR (376 MHz, CDCl_3) δ -63.00.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{24}\text{H}_{25}\text{F}_6\text{NO}_3\text{Si}$ $[\text{M}]^+$: 517.1508, found: 517.1507.

tert-butyldimethyl(5-(4-nitrophenyl)-4-(*o*-tolyl)-4,5-dihydrofuran-3-yl)silane (**3pa**)



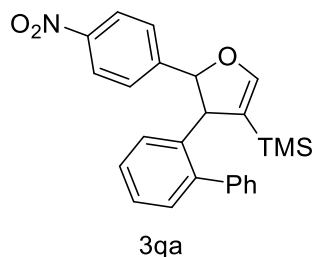
Compound **3pa** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 24 h. NMR spectra of the compound *cis*-**3pa** was reported.

^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 6.98 – 6.91 (m, 2H), 6.90 – 6.84 (m, 1H), 6.80 (d, J = 7.7 Hz, 1H), 6.74 (d, J = 1.4 Hz, 1H), 5.78 (d, J = 9.5 Hz, 1H), 4.61 (dd, J = 9.5, 1.4 Hz, 1H), 2.10 (s, 3H), 0.89 (s, 9H), 0.03 (s, 3H), -0.41 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 152.67, 145.58, 136.14, 134.44, 129.88, 129.52, 127.23, 126.77, 125.53, 124.05, 122.56, 112.60, 86.74, 51.70, 26.60, 19.99, 16.95, -5.21, -5.79.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_3\text{Si}$ $[\text{M}]^+$: 395.1917, found: 395.1929.

(4-([1,1'-biphenyl]-2-yl)-5-(4-nitrophenyl)-4,5-dihydrofuran-3-yl)trimethyl
Silane (**3qa**)



Compound **3qa** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 24 h. NMR spectra of the compound *cis*-**3qa** was reported.

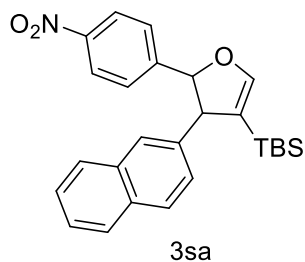
^1H NMR (500 MHz, CDCl_3) δ 8.14 – 8.04 (m, 2H), 8.02 – 7.87 (m, 2H), 7.48 – 6.86

(m, 22H), 6.67 (d, $J = 1.5$ Hz, 1H), 6.56 (d, $J = 1.8$ Hz, 1H), 5.52 (d, $J = 9.8$ Hz, 1H), 5.34 (d, $J = 6.0$ Hz, 1H), 4.67 (dd, $J = 9.8, 1.5$ Hz, 1H), 4.22 (dd, $J = 6.0, 1.8$ Hz, 1H), -0.03 (s, 9H), -0.16 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 151.76, 151.15, 149.03, 145.75, 141.28, 140.77, 140.37, 135.18, 129.99, 129.81, 129.71, 129.54, 129.42, 128.66, 128.19, 128.17, 127.97, 127.58, 127.09, 126.93, 126.74, 126.67, 126.39, 123.61, 122.53, 115.44, 113.34, 91.08, 87.05, 56.07, 51.15, -0.80, -0.97.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_3\text{Si}$ $[\text{M}]^+$: 415.1604, found: 415.1609.

tert-butyldimethyl((naphthalen-2-yl)-5-(4-nitrophenyl)-4,5-dihydrofuran-3-yl) silane (**3sa**)



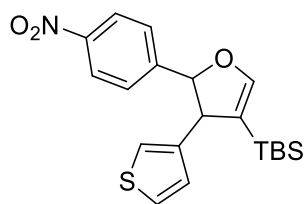
Compound **3sa** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 24 h. NMR spectra of the compound *cis*-**3sa** was reported.

^1H NMR (500 MHz, CDCl_3) δ 7.91 – 7.76 (m, 2H), 7.73 – 7.59 (m, 2H), 7.47 (d, $J = 8.5$ Hz, 1H), 7.44 – 7.32 (m, 3H), 7.27 (d, $J = 8.6$ Hz, 2H), 6.92 (d, $J = 8.3$ Hz, 1H), 6.79 (d, $J = 1.1$ Hz, 1H), 5.85 (d, $J = 8.8$ Hz, 1H), 4.48 (dd, $J = 8.8, 1.1$ Hz, 1H), 0.90 (s, 9H), 0.03 (s, 3H), -0.46 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 152.69, 146.53, 145.53, 135.98, 132.87, 132.35, 127.64, 127.60, 127.53, 127.51, 127.26, 127.02, 125.88, 125.60, 122.79, 112.88, 86.97, 57.47, 26.67, 17.07, -5.28, -5.54.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_3\text{Si}$ $[\text{M}]^+$: 431.1917, found: 431.1911.

tert-butyldimethyl(5-(4-nitrophenyl)-4-(thiophen-3-yl)-4,5-dihydrofuran-3-yl) silane (**3ta**)



3ta

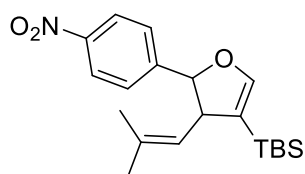
Compound **3ta** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 24 h. NMR spectra of the compound *cis*-**3ta** was reported.

¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 6.91 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.70 (dd, *J* = 3.0, 1.2 Hz, 1H), 6.67 (d, *J* = 1.2 Hz, 1H), 6.44 (dd, *J* = 5.0, 1.2 Hz, 1H), 5.68 (d, *J* = 9.1 Hz, 1H), 4.40 (dd, *J* = 9.1, 1.2 Hz, 1H), 0.89 (s, 9H), 0.04 (s, 3H), -0.32 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 152.47, 146.74, 145.64, 139.75, 127.91, 126.91, 125.28, 122.81, 122.44, 112.52, 86.56, 52.42, 26.62, 17.04, -5.35, -5.83.

HR-MS (EI-TOF) *m/z* calcd for C₂₀H₂₅NO₃SSi [M]⁺: 387.1324, found: 387.1323.

tert-butyldimethyl(4-(2-methylprop-1-en-1-yl)-5-(4-nitrophenyl)-4,5-dihydrofuran-3-yl)silane (**3wa**)



3wa

Compound **3wa** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 12 h. NMR spectra of the compound *cis*-**3wa** was reported.

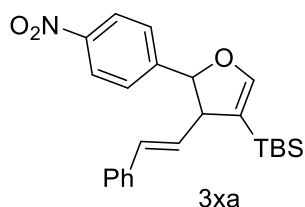
¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 1.4 Hz, 1H), 5.55 (d, *J* = 9.4 Hz, 1H), 4.48 – 4.38 (m, 1H), 4.01 (ddd, *J* = 11.0, 9.5, 1.5 Hz, 1H), 1.47 (d, *J* = 1.3 Hz, 3H), 1.36 (d, *J* = 1.2 Hz, 3H), 0.90 (s, 9H), 0.05 (s, 3H), -0.04 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 151.98, 146.86, 132.46, 126.99, 125.64, 124.65, 123.81,

122.97, 111.44, 86.03, 49.43, 26.73, 25.30, 18.00, 16.93, -5.07, -5.51.

HR-MS (EI-TOF) m/z calcd for $C_{20}H_{29}NO_3Si$ $[M]^+$: 359.1917, found: 359.1916.

tert-butyldimethyl(5-(4-nitrophenyl)-4-((*E*)-styryl)-4,5-dihydrofuran-3-yl)
silane (**3xa**)



Compound **3xa** was obtained as colorless oil according to general procedure **C**. The reaction was heated at 90 °C for 18 h. NMR spectra of the compound *trans*-**3xa** was reported.

¹H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, J = 8.7 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.35 (dt, J = 15.1, 7.4 Hz, 4H), 7.30 – 7.24 (m, 1H), 6.51 (d, J = 1.8 Hz, 1H), 6.34 (d, J = 15.7 Hz, 1H), 6.18 (dd, J = 15.7, 9.5 Hz, 1H), 5.28 (d, J = 7.1 Hz, 1H), 3.74 – 3.56 (m, 1H), 0.84 (s, 9H), 0.07 (s, 3H), 0.02 (s, 3H).

¹³C NMR (126 MHz, $CDCl_3$) δ 152.43, 149.38, 136.65, 131.37, 131.34, 128.69, 127.73, 126.31, 125.76, 123.92, 109.00, 87.42, 60.75, 26.78, 17.11, -4.47, -5.47.

HR-MS (EI-TOF) m/z calcd for $C_{24}H_{29}NO_3Si$ $[M]^+$: 407.1917, found: 407.1909.

4.X-ray of Compound 3ma

The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

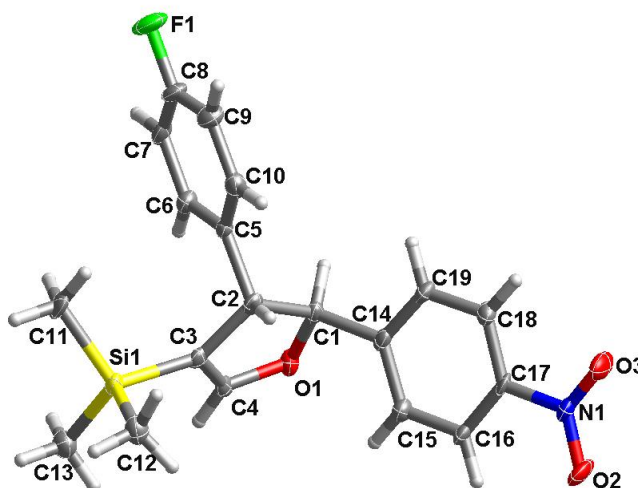


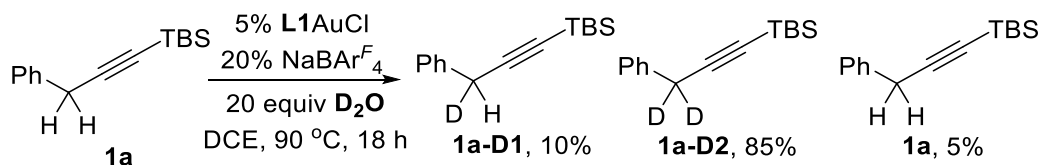
Figure S1. Ortep drawing of compound *trans*-**3ma**.

Table S1: Crystallographic Details for *trans*-**3ma**

Complex.	<i>Trans</i> - 3ma
empirical formula	C ₁₉ H ₂₀ F N O ₃ Si
formula weight	357.45
temperature, K	103(2)
radiation (Mo K α), Å	0.71073
crystal system	triclinic
space group	P
a, Å	6.84(3)
b, Å	7.717(19)
c, Å	18.32(4)
α , °	81.71(9)
β , °	85.48(10)
γ , °	72.46(7)
V , Å ³	911(4)
Z	2
$F(000)$	376

crystal size, mm	0.20 x 0.10 x 0.10
θ range, °	2.5 to 24.2
indep reflns	13551 / 2613 [R(int) = 0.1266]
data-restraints-params	2613/ 0 / 199
GOF on F^2	0.636
final R ($I > 2\sigma(I)$)	$R_1 = 0.0590$, $wR_2 = 0.1623$
R indices (all data)	$R_1 = 0.1454$, $wR_2 = 0.2243$
peak and hole, e.Å ⁻³	0.184 and -0.288

5. Mechanism Studies



To a 3-dram vial were added sequentially 0.2 mmol silylated alkyne **1a**, 0.01 mmol indicated **L1AuCl** (5 mol%), 0.04 mmol NaBARF (20 mol%), 4.0 mmol D₂O (20 equiv) and 2 mL anhydrous DCE as solvent. The reaction was then stirred at the 90 °C for 18 h. The reaction was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to obtain the compound **1a-D**.

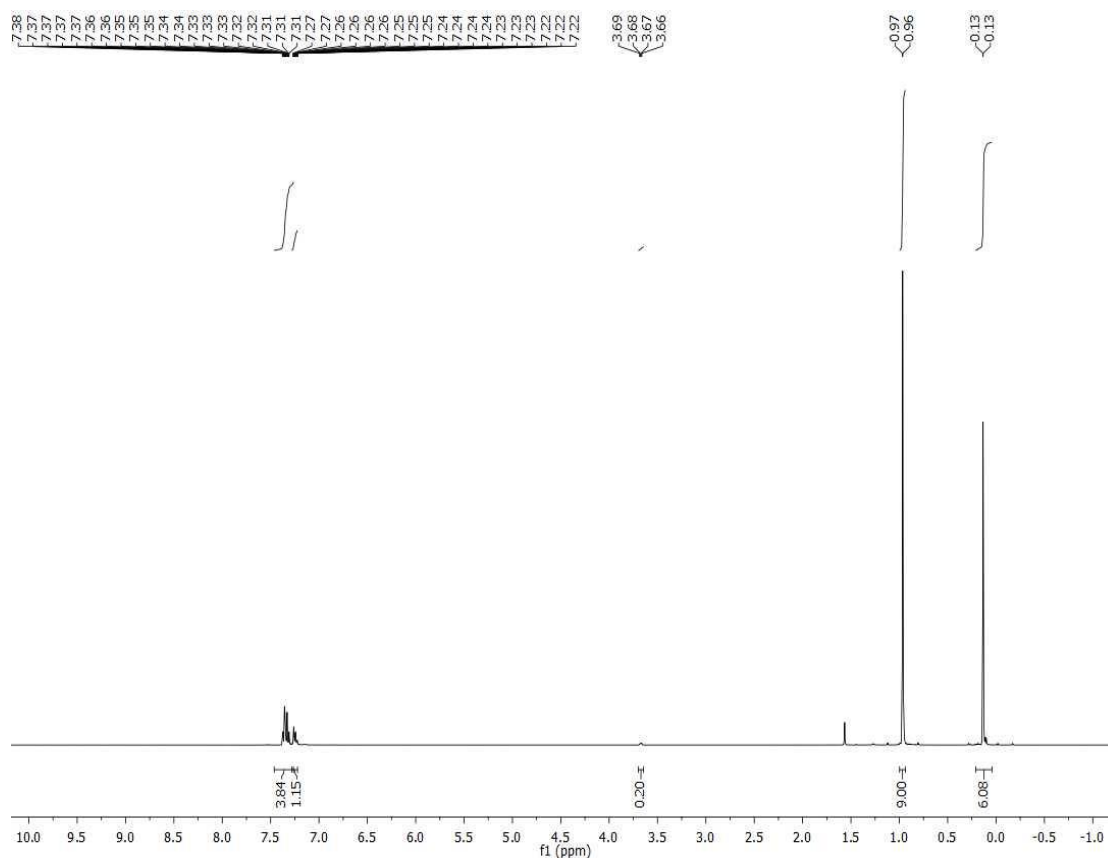
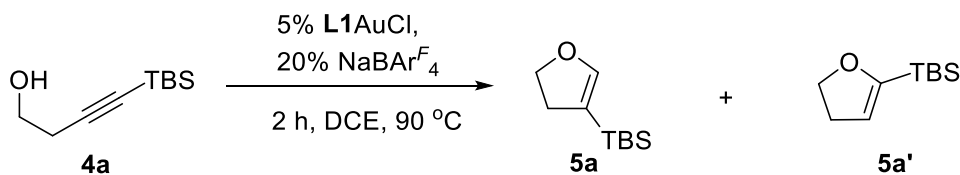


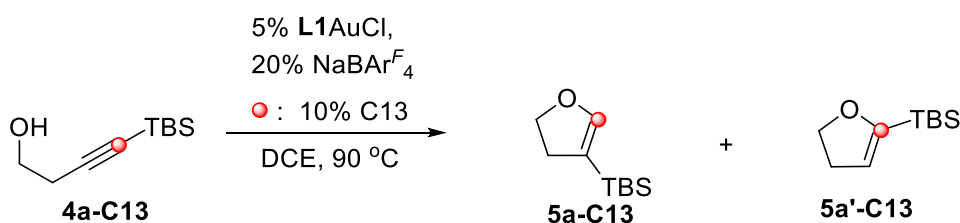
Figure S2: ¹H NMR spectra for **1a-D**



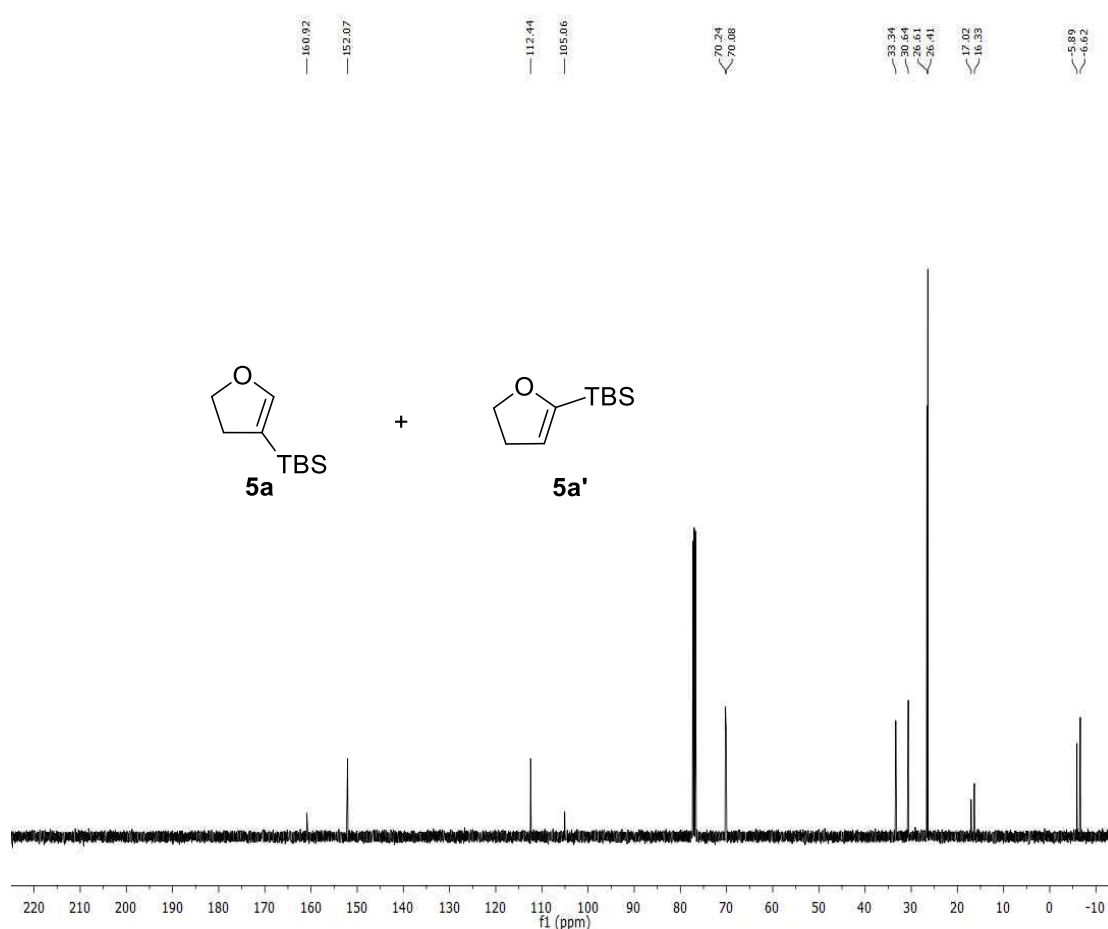
92% isolated yield, **5a/5a'** = 0.6/1

Compound **4a** was synthesized following the literature report.^[7] To a vial were added

sequentially 0.2 mmol silylated alkyne **4a**, 0.01 mmol indicated **L1AuCl** (5 mol%), 0.04 mmol NaBARF (20 mol%), and 2 mL anhydrous DCE as solvent. The reaction was then stirred at the 90 °C for 2 h. The reaction was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to obtain the compound **5a** and **5a'** in a ratio of 0.6/1 in 92% yield.



Compound **4a-C13** was synthesized following the literature report.^[8] To a NMR tube were added sequentially 0.1 mmol silylated alkyne **4a-C13**, 0.005 mmol indicated **L1AuCl** (5 mol%), 0.02 mmol NaBARF (20 mol%), and 1 mL anhydrous DCE as solvent. The reaction was then stirred at 90 °C for 2 h. The reaction was concentrated under reduced pressure. The NMR of the residue was collected.



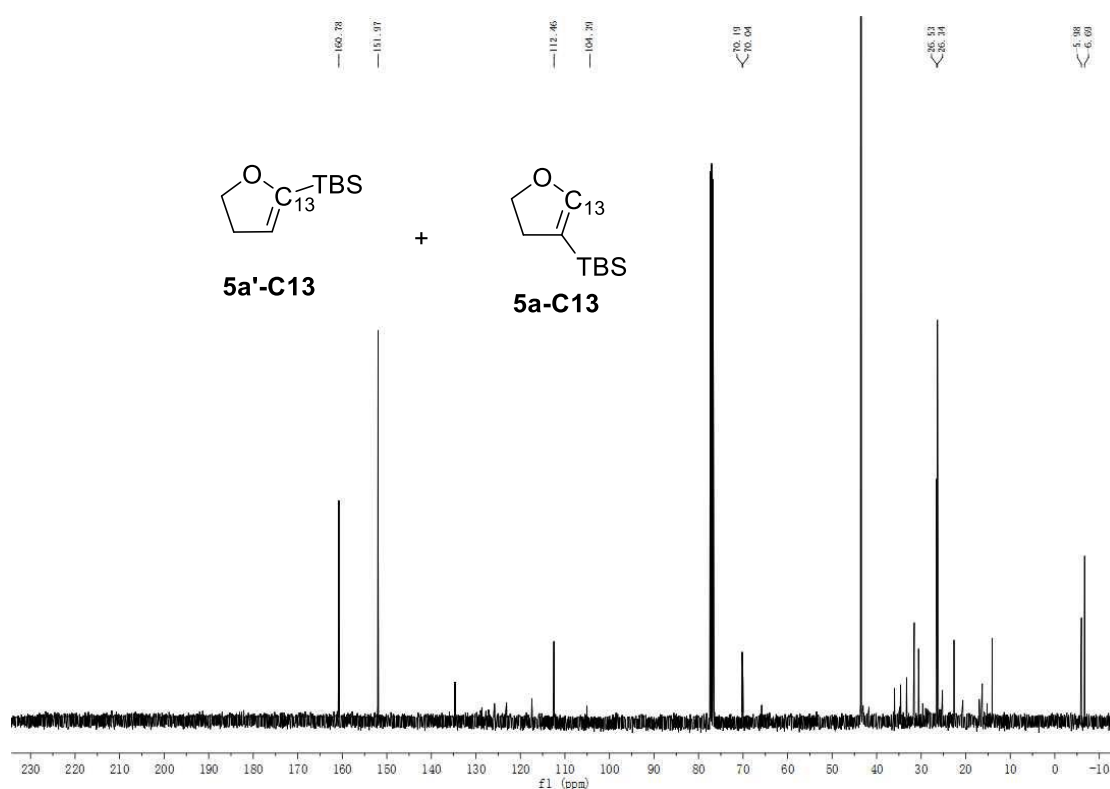
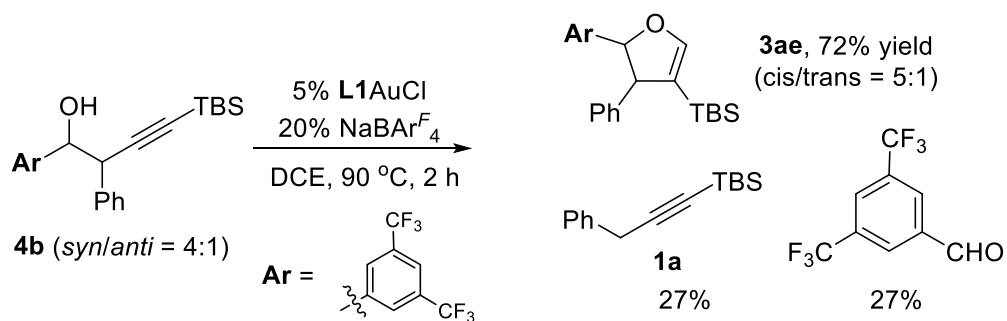
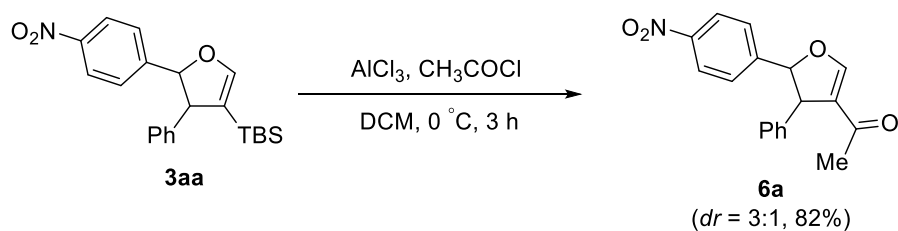


Figure S3: C^{13} NMR spectra for **5a** and **5a-C13**



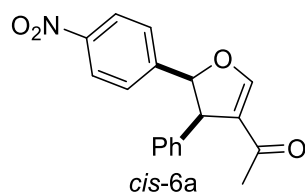
To a NMR tube were added sequentially 0.1 mmol silylated alkyne **4b**, 0.005 mmol indicated **L1AuCl** (5 mol%), 0.02 mmol NaBARF (20 mol%), and 1 mL anhydrous DCE as solvent. The reaction was then stirred at the 90 °C for 2 h. The reaction was concentrated under reduced pressure. The NMR of the residue was then collected.

6. Transformation of the Product 3aa



A 10 mL over-dried flask was charged with a stir bar and AlCl_3 (0.40 mmol). The flask was capped with a septum and DCM (1 mL) was added via syringe under N_2 . A solution of **3aa** (0.20 mmol) and acetyl chloride (0.40 mmol) in DCM (2 mL) was added to the aluminum chloride suspension at 0 °C. After 3 h, the reaction was finished. The solvent was removed and the remaining oil was purified by flash chromatography to afford **6a** as colorless oil.

1-(5-(4-nitrophenyl)-4-phenyl-4,5-dihydrofuran-3-yl)ethan-1-one (*cis*-**6a**)

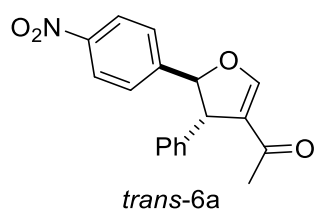


$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, J = 8.8 Hz, 2H), 7.73 (s, 1H), 7.19 (d, J = 8.6 Hz, 2H), 7.09 – 6.94 (m, 3H), 6.83 (dd, J = 7.8, 1.4 Hz, 2H), 6.08 (d, J = 9.8 Hz, 1H), 4.64 (d, J = 9.8 Hz, 1H), 2.26 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 192.16, 157.28, 147.00, 143.38, 136.41, 128.20, 128.17, 127.28, 127.07, 124.83, 122.91, 89.71, 51.37, 27.06.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_4$ $[\text{M}]^+$: 309.1001, found: 309.0990.

1-(5-(4-nitrophenyl)-4-phenyl-4,5-dihydrofuran-3-yl)ethan-1-one (*trans*-**6a**)

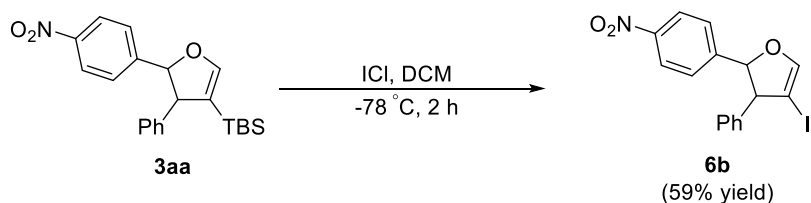


$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.26 (d, J = 8.8 Hz, 1H), 7.65 (d, J = 1.3 Hz, 1H), 7.45 (d, J = 8.8 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.31 (d, J = 7.2 Hz, 1H), 7.27 – 7.20 (m,

2H), 5.66 (d, $J = 6.1$ Hz, 1H), 4.47 – 4.13 (m, 1H), 2.22 (s, 3H).

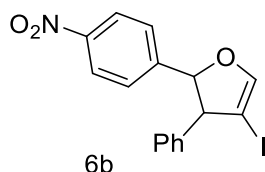
^{13}C NMR (101 MHz, CDCl_3) δ 192.09, 156.83, 147.82, 147.28, 141.50, 129.10, 127.58, 127.18, 125.77, 124.15, 123.33, 109.99, 93.22, 55.65, 27.16.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_4$ $[\text{M}]^+$: 309.1001, found: 309.0990.



To a DCM solution of **3aa** (0.20 mmol) at $-78\text{ }^\circ\text{C}$ was added ICl (0.22 mmol). The mixture was left stirring at $-78\text{ }^\circ\text{C}$ for 2 h and was monitored by TLC. The reaction mixture was then poured into 10% aq. $\text{Na}_2\text{S}_2\text{O}_3$ solution and extracted with hexanes. The combined organic phases were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the product **6b** as colorless oil.

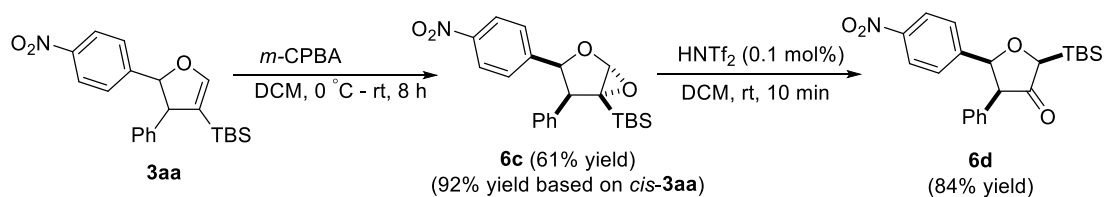
cis-4-iodo-2-(4-nitrophenyl)-3-phenyl-2,3-dihydrofuran (**6b**)



^1H NMR (400 MHz, CDCl_3) δ 8.23 – 7.78 (m, 2H), 7.19 (dd, $J = 8.9, 2.6$ Hz, 2H), 7.07 (dd, $J = 5.7, 1.3$ Hz, 3H), 6.93 – 6.74 (m, 3H), 5.99 (d, $J = 10.1$ Hz, 1H), 4.36 (dd, $J = 10.0, 1.3$ Hz, 1H).

^{13}C NMR (101 MHz, cdcl_3) δ 150.27, 146.56, 144.41, 135.28, 128.82, 128.62, 128.25, 127.63, 127.19, 127.08, 122.86, 122.73, 86.08, 65.55, 59.98.

HR-MS (EI-TOF) m/z calcd for $\text{C}_{16}\text{H}_{12}\text{INO}_3$ $[\text{M}]^+$: 392.9862, found: 392.9865.

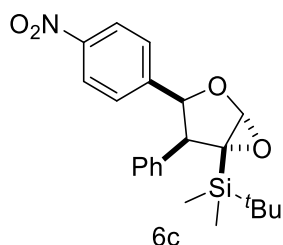


To a DCM solution of **3aa** (0.20 mmol) at $0\text{ }^\circ\text{C}$ was added 3-chloroperbenzoic acid

(74.4%, 0.22 mmol). The mixture was left stirring at room temperature. After 8 h, the reaction was finished. The solvent was removed and the remaining oil was purified by flash chromatography to afford **6c** as white solid.

To a DCM solution of **3aa** (0.20 mmol) at room temperature was added HNTf₂ solution in dichloromethane (0.2 mg/mL, 0.1 mol%). The mixture was left stirring at room temperature. After 10 min, the reaction was finished. The solvent was removed and the remaining oil was purified by flash chromatography to afford **6d** as colorless oil.

tert-butyldimethyl(3-(4-nitrophenyl)-4-phenyl-2,6-dioxabicyclo[3.1.0]hexan-5-yl) silane (**6c**)

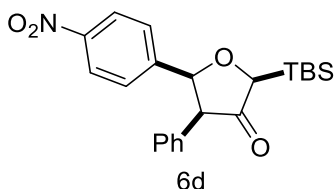


¹H NMR (500 MHz, CDCl₃) δ 7.26 – 7.15 (m, 3H), 7.15 – 7.09 (m, 2H), 6.55 (d, *J* = 1.5 Hz, 1H), 5.17 (d, *J* = 10.3 Hz, 1H), 4.34 (dd, *J* = 10.3, 1.5 Hz, 1H), 3.77 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.69 – 3.60 (m, 1H), 0.83 (s, 9H), 0.82 (t, *J* = 7.2 Hz, 3H), -0.03 (s, 1H), -0.45 (s, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 168.95, 152.23, 138.74, 128.92, 127.95, 127.38, 111.35, 84.18, 60.75, 55.53, 26.59, 17.00, 13.62, -5.42, -5.62.

HR-MS (EI-TOF) *m/z* calcd for C₂₂H₂₇NO₄Si [*M*]⁺: 397.1709, found: 397.1704.

2-(*tert*-butyldimethylsilyl)-5-(4-nitrophenyl)-4-phenyldihydrofuran-3(2*H*)-one (**6d**)



¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.08 (t, *J* = 5.9 Hz, 3H), 6.97 (dd, *J* = 7.5, 1.8 Hz, 2H), 5.61 (d, *J* = 6.6 Hz, 1H), 4.23 (s, 1H), 3.96 (d, *J* = 6.67 Hz, 1H), 1.08 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H).

¹³C NMR (101 MHz, cdcl₃) δ 214.24, 146.66, 145.43, 133.44, 129.07, 128.42, 127.23,

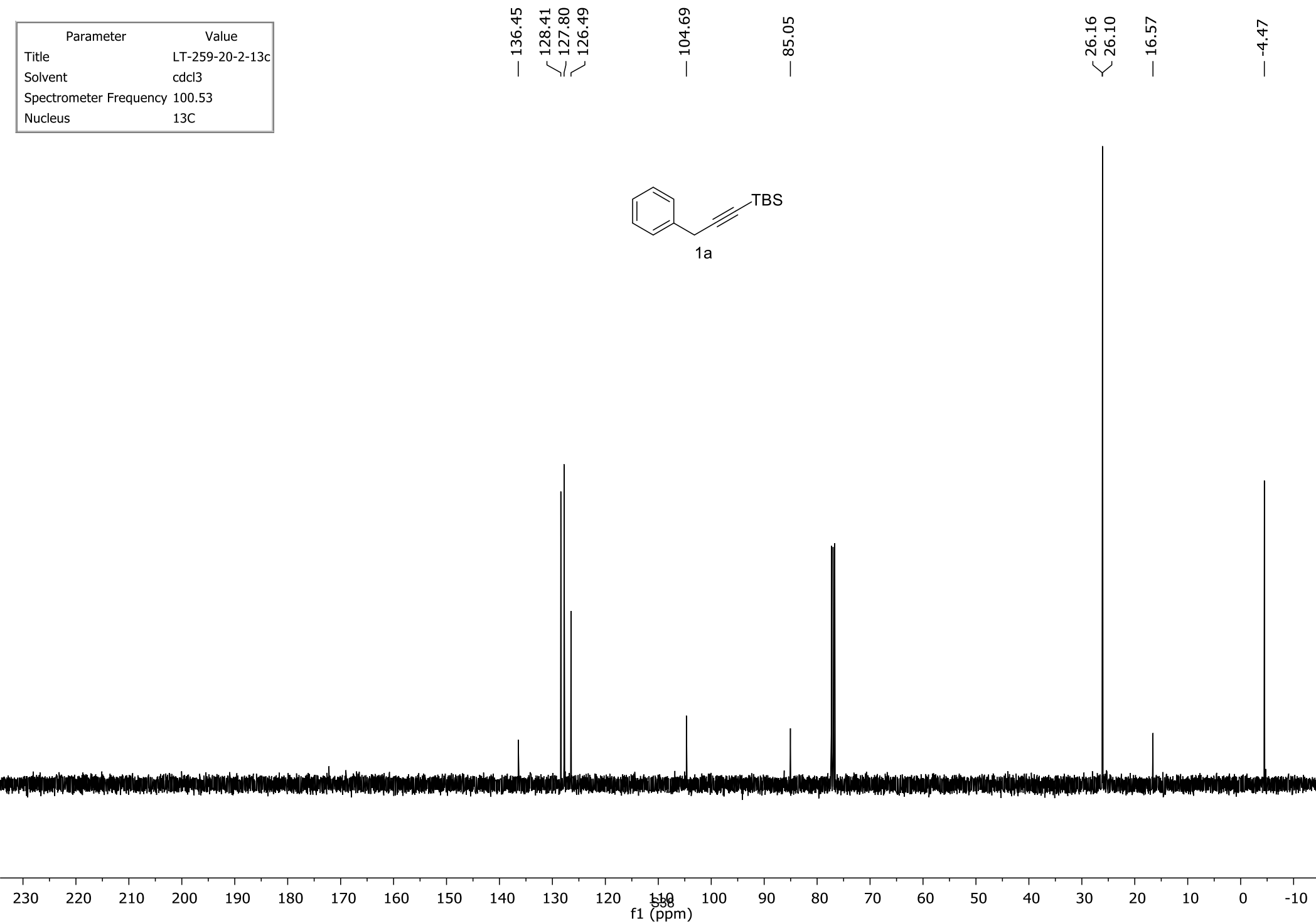
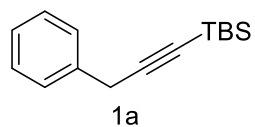
126.85, 123.21, 83.86, 58.26, 26.48, 16.97, -7.15, -7.42.

HR-MS (EI-TOF) m/z calcd for C₂₂H₂₇NO₄Si [M]⁺: 397.1709, found: 397.1704.

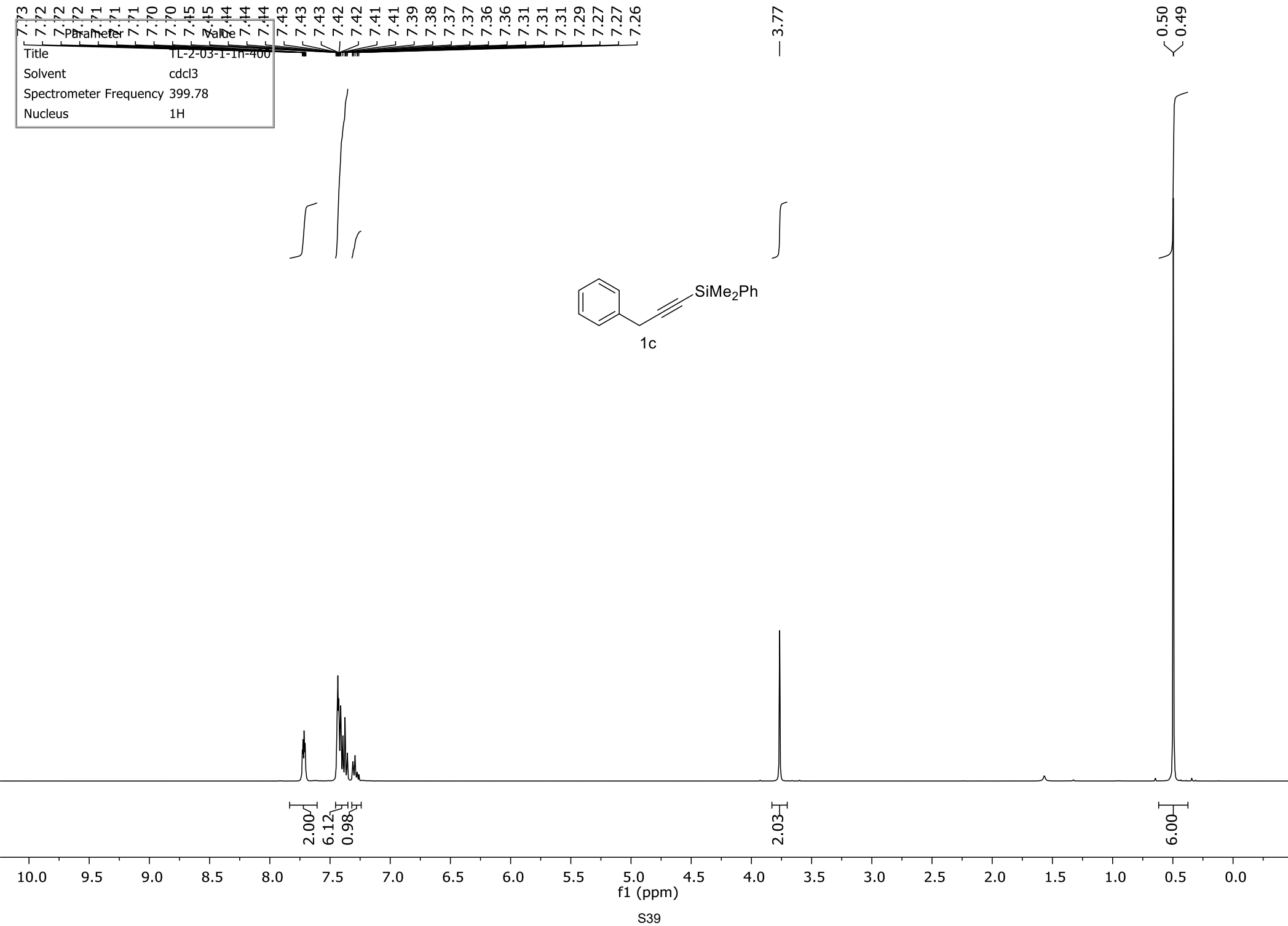
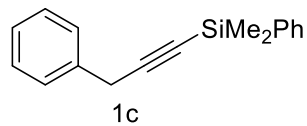
References:

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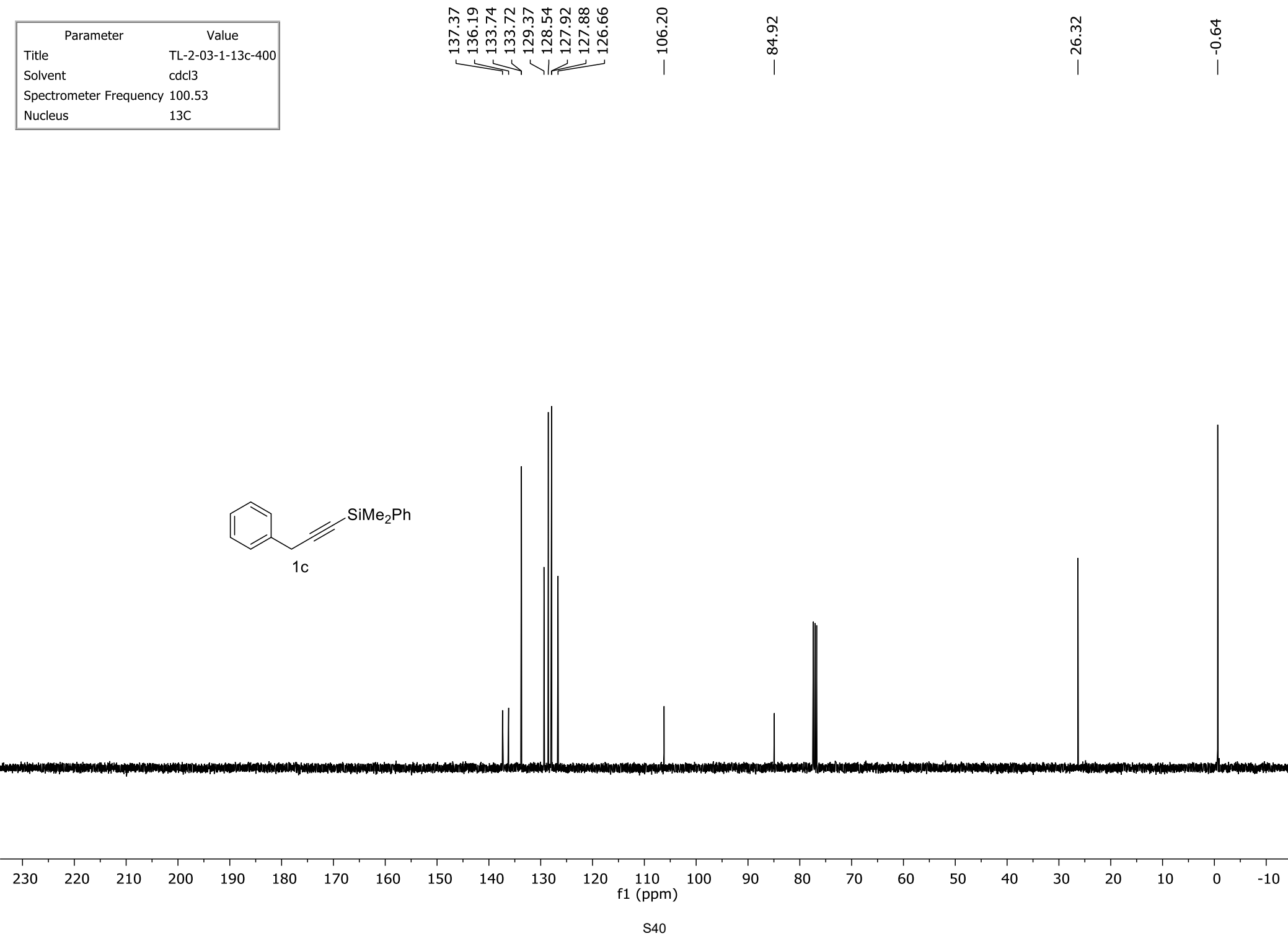
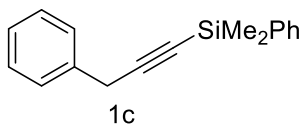
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Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C



Title	1L-2-03-1-1n-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H



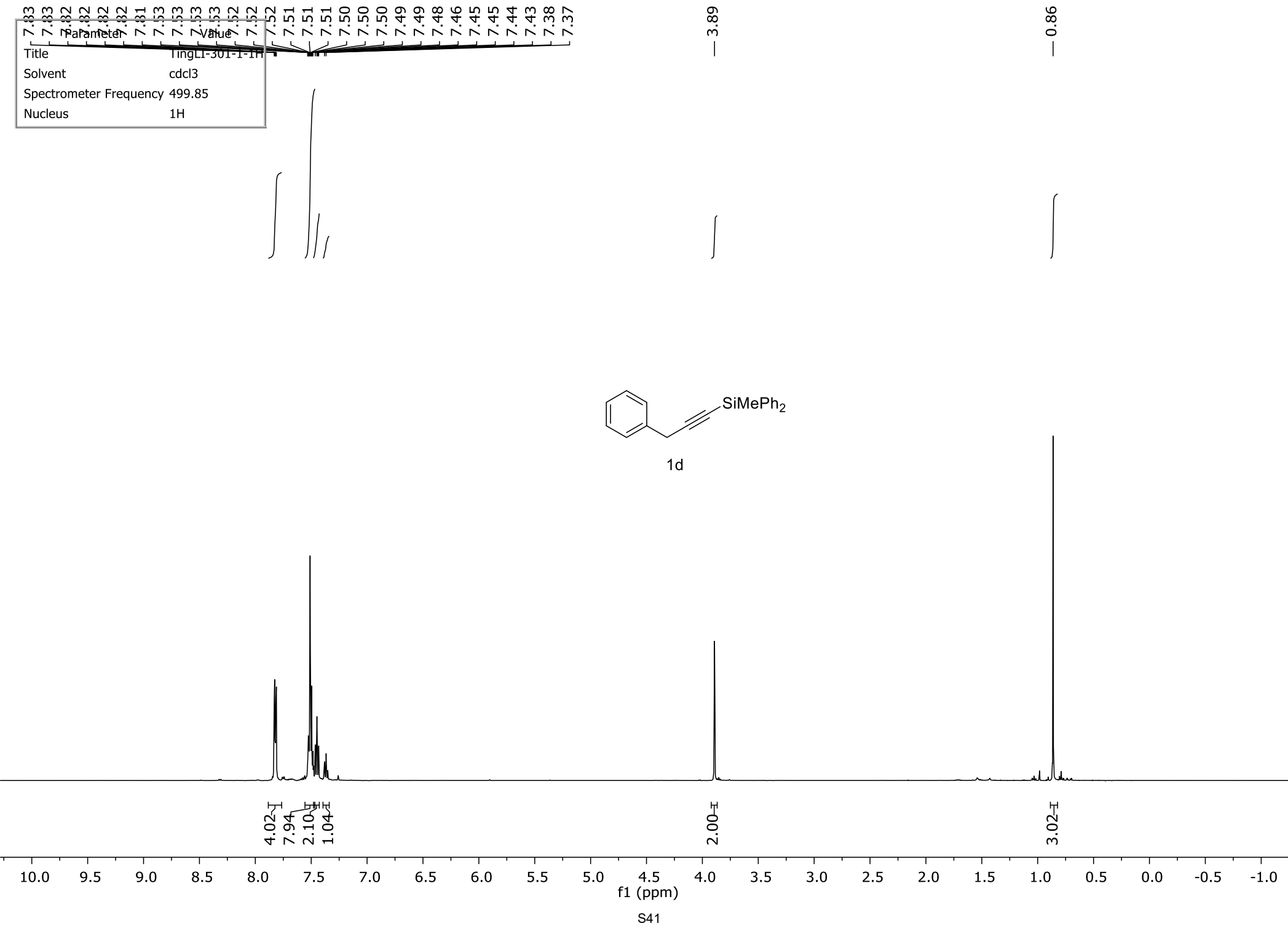
Parameter	Value
Title	TL-2-03-1-13c-400
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C



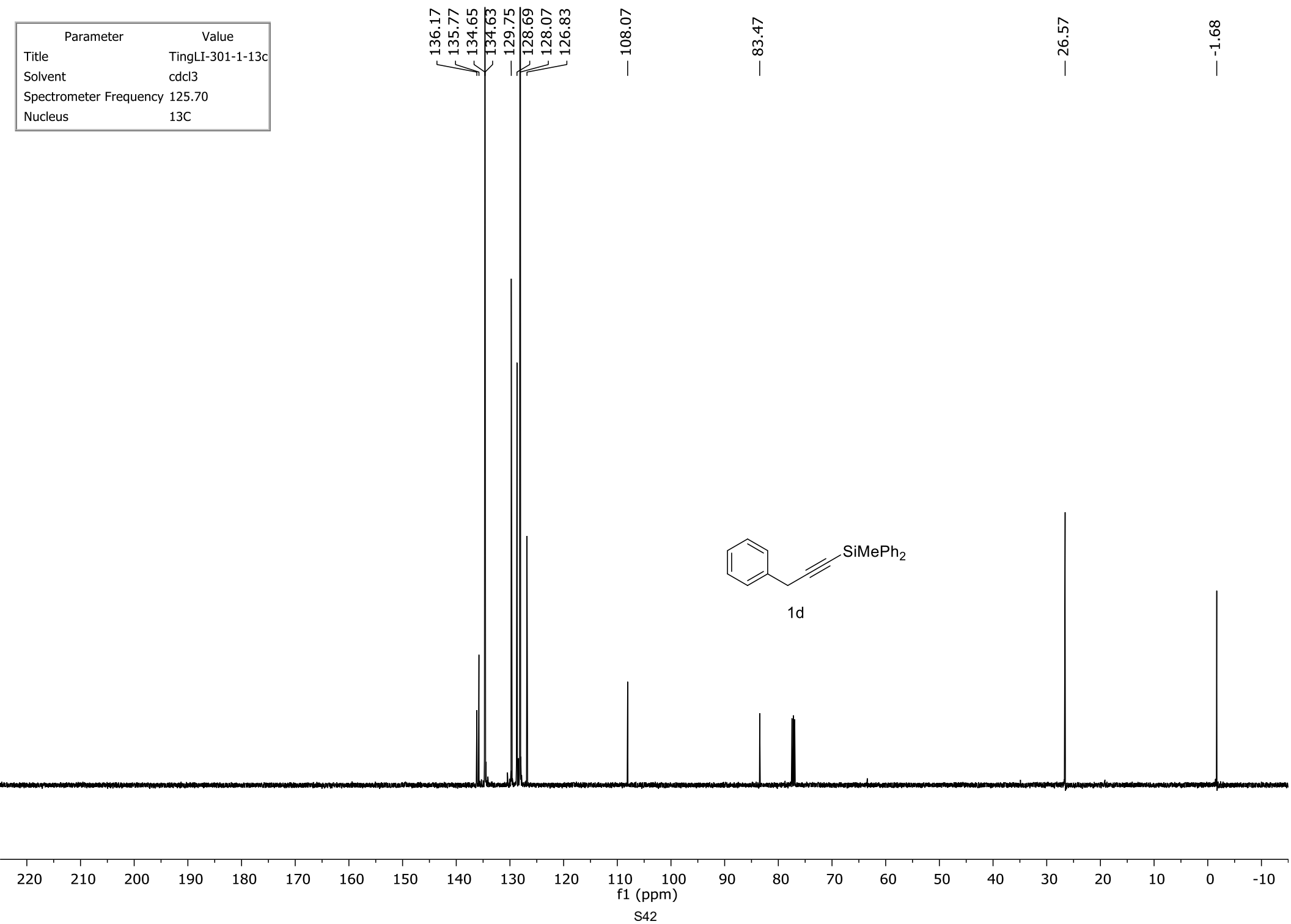
Parameter	Value
Title	lingli-301-1-1h
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	1H



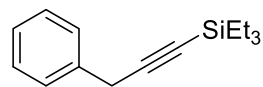
1d



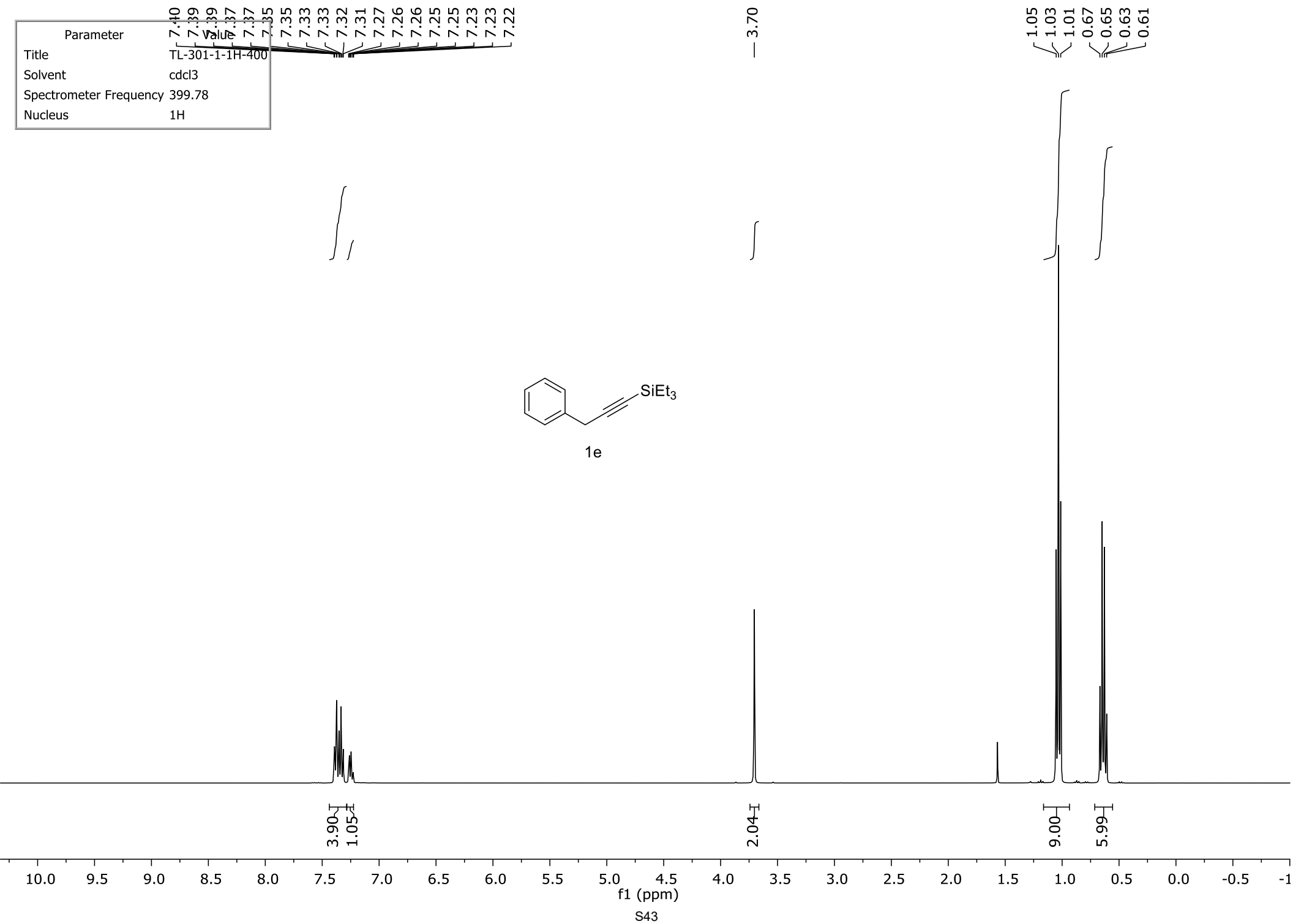
Parameter	Value
Title	TingLI-301-1-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	¹³ C



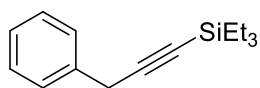
Parameter	Value
Title	TL-301-1-1H-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	¹ H



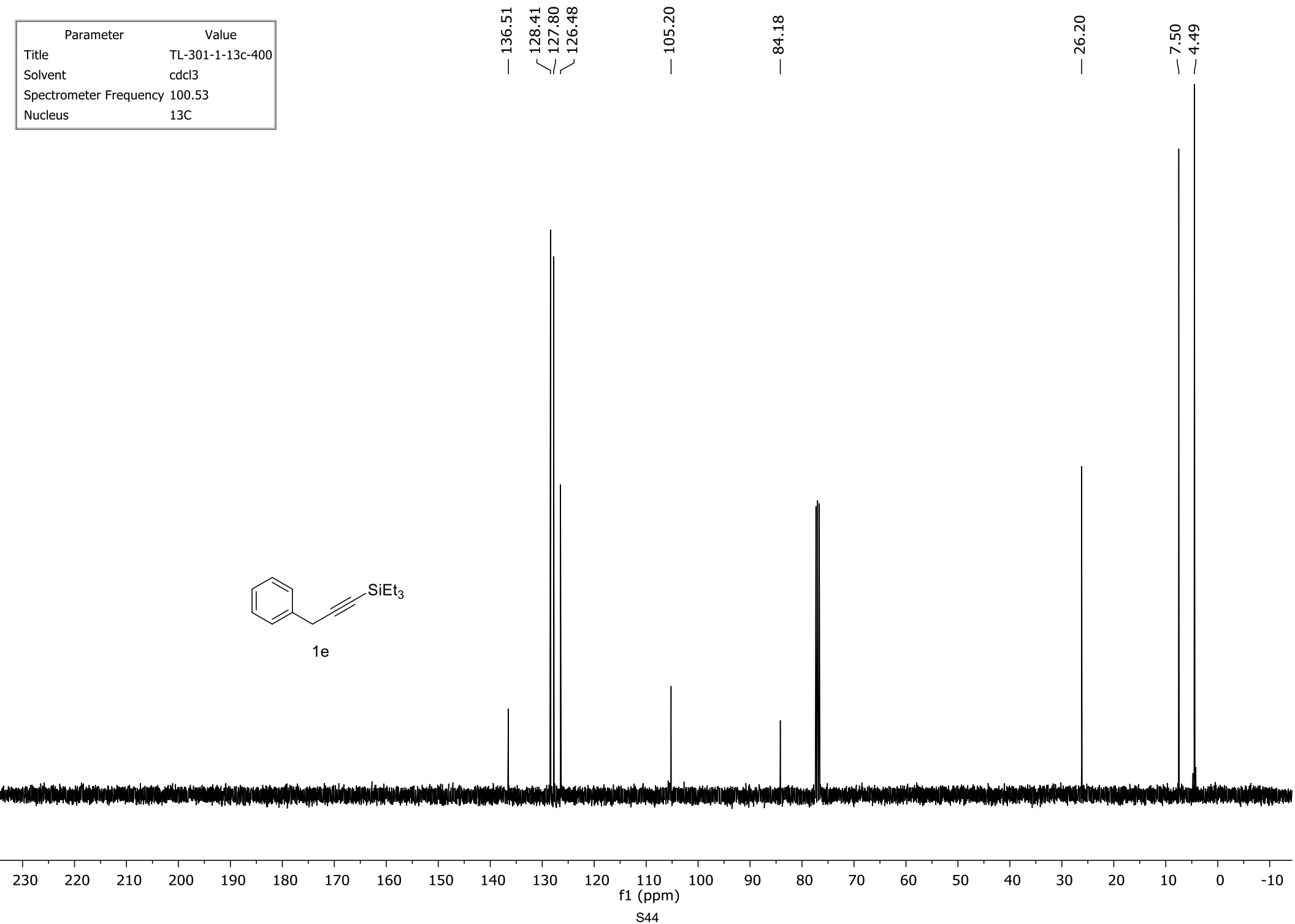
1e



Parameter	Value
Title	TL-301-1-13c-400
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C



1e



Parameter	Value
Title	TL-2-4-1H-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H

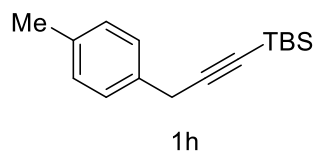
7.26
7.24
7.15
7.13

3.64

2.35

0.97

0.14



2.06

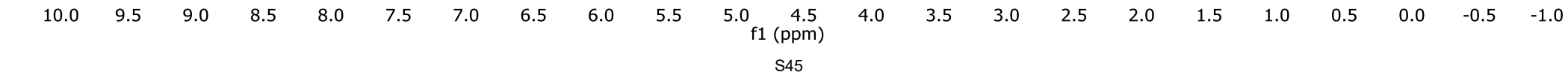
1.94

1.95

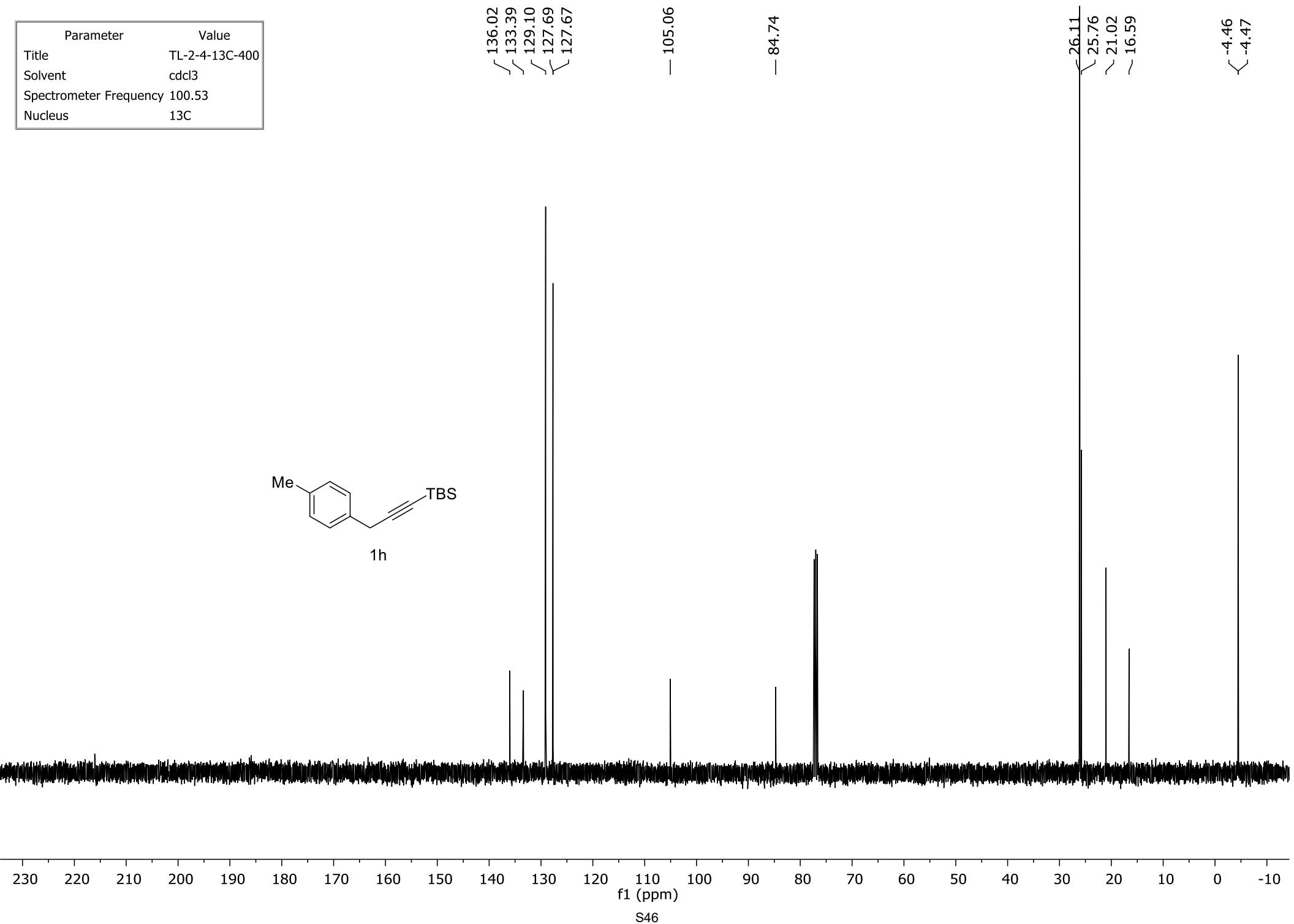
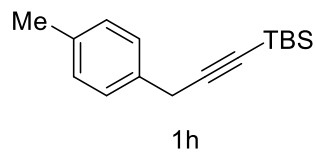
2.94

9.00

6.01



Parameter	Value
Title	TL-2-4-13C-400
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	13C



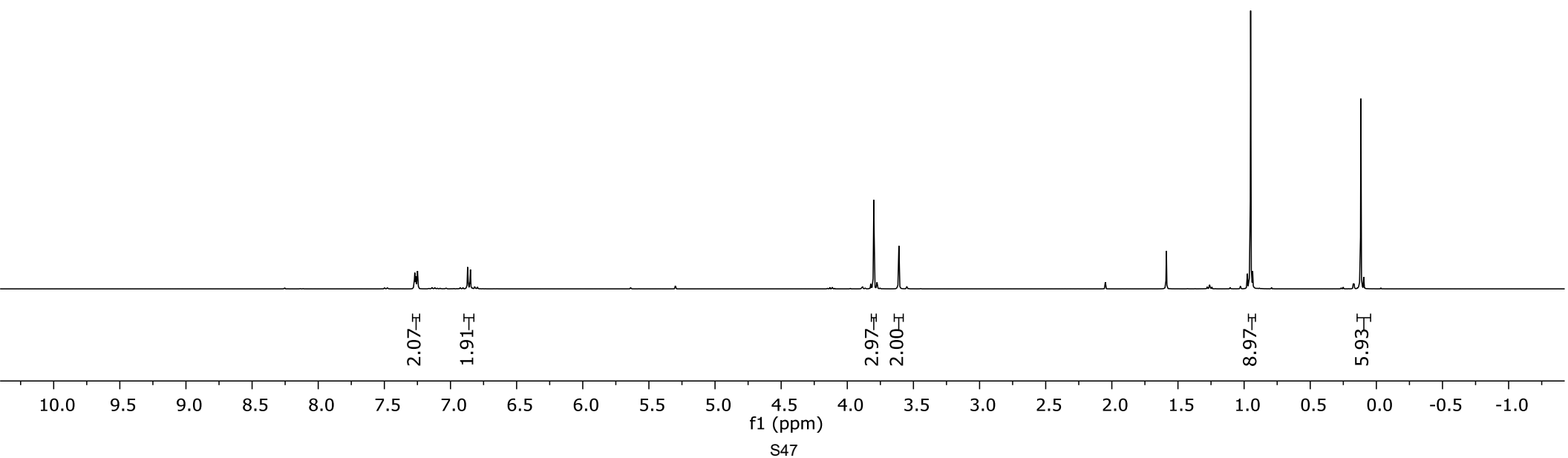
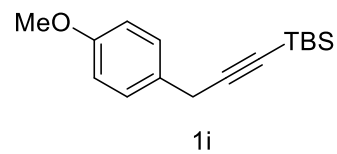
Parameter	Value
Title	TL-302-1-1H-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H

7.27
7.27
7.26
7.25
7.25
7.25
6.87
6.85

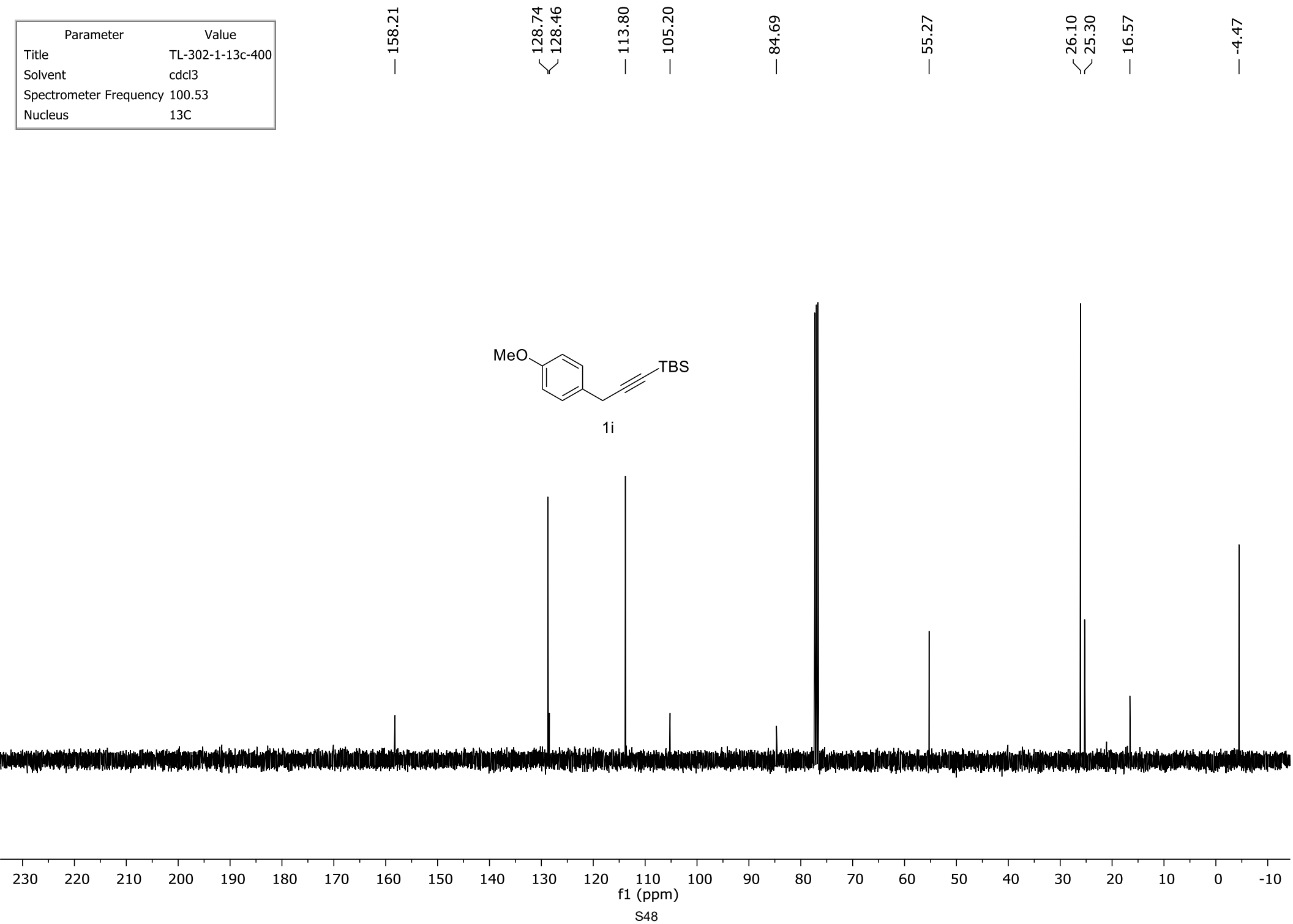
3.80
3.80
3.61
3.61

0.95
0.95

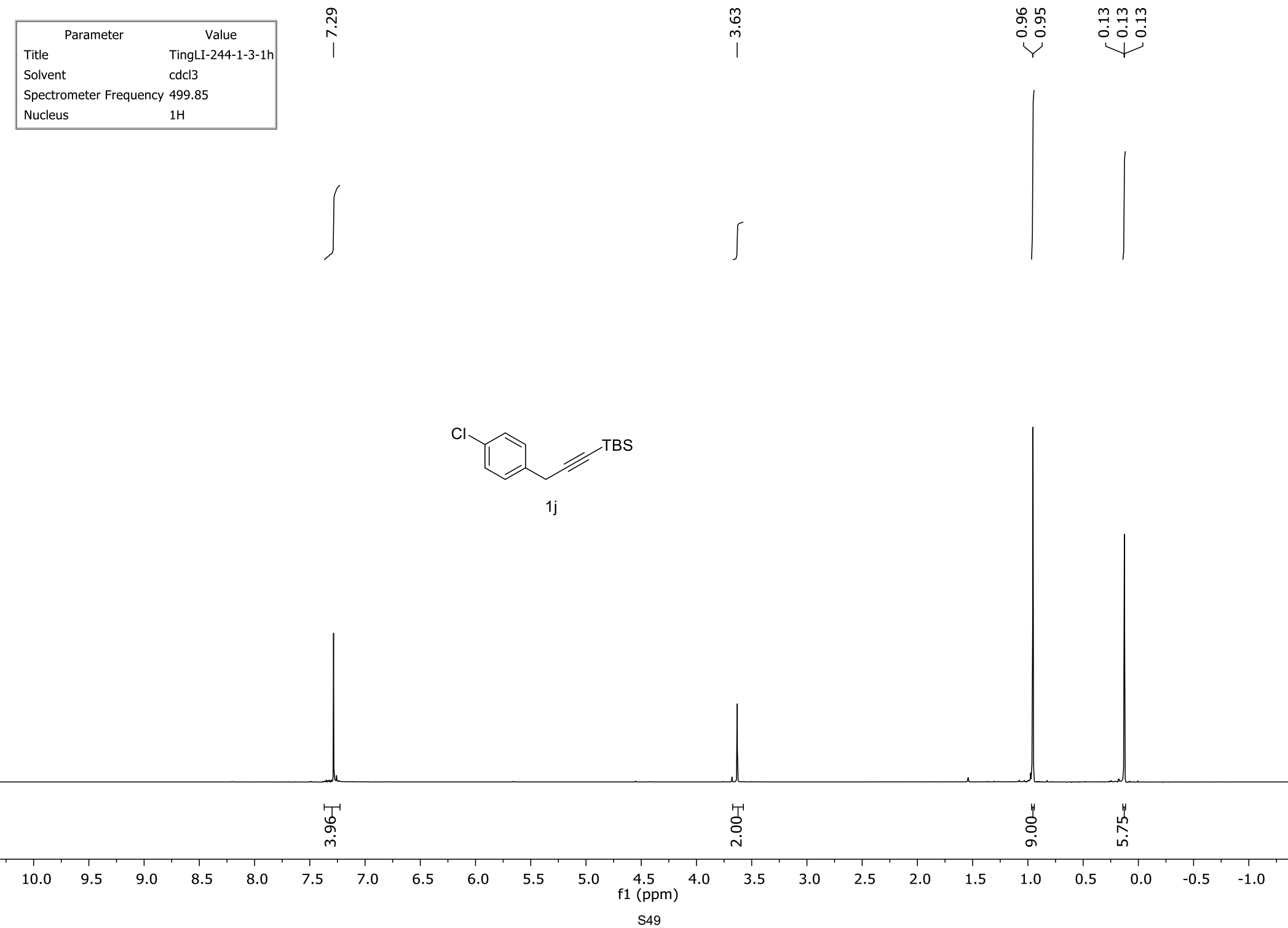
0.12
0.12



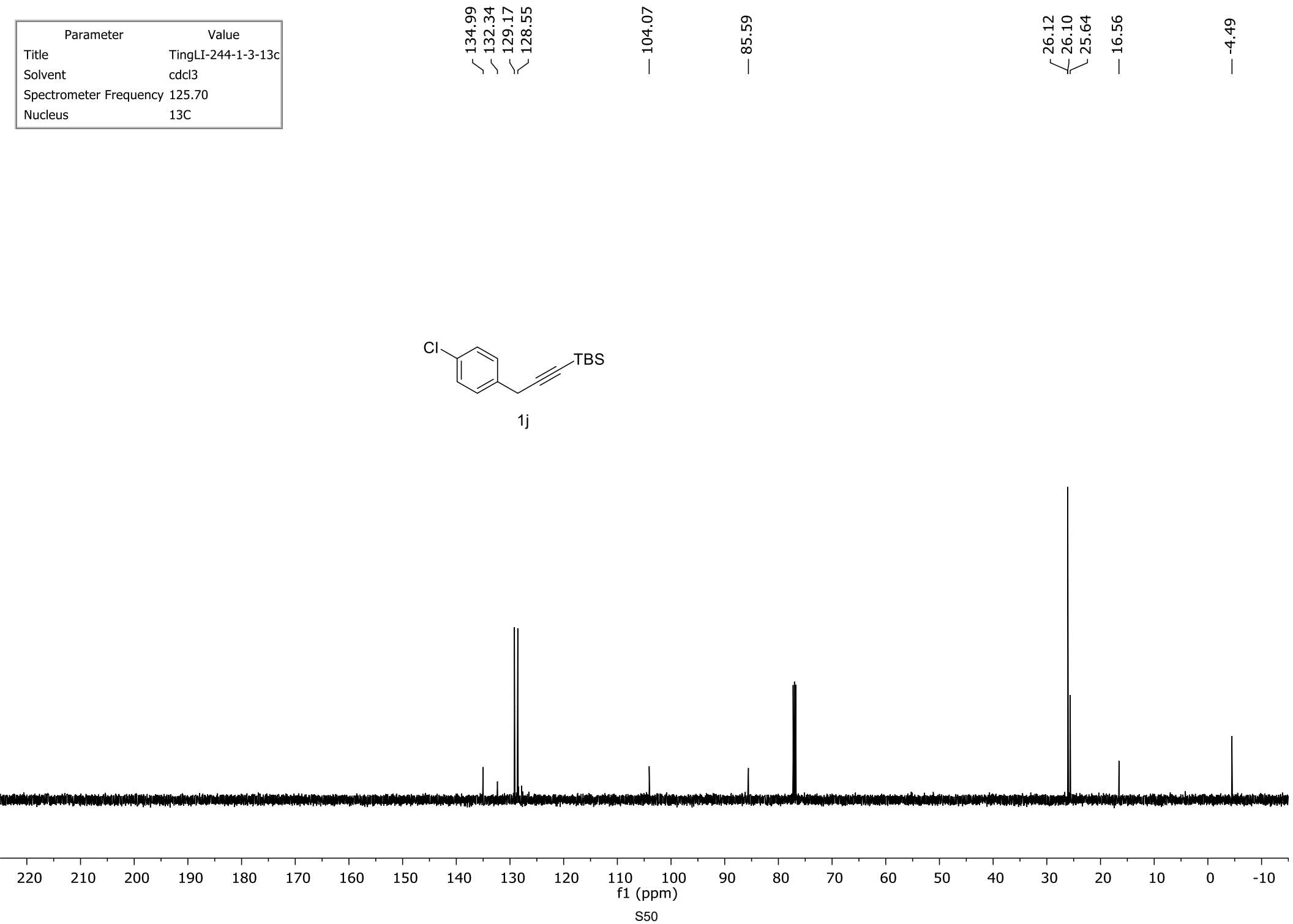
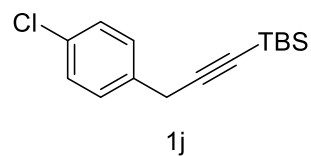
Parameter	Value
Title	TL-302-1-13c-400
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	13C



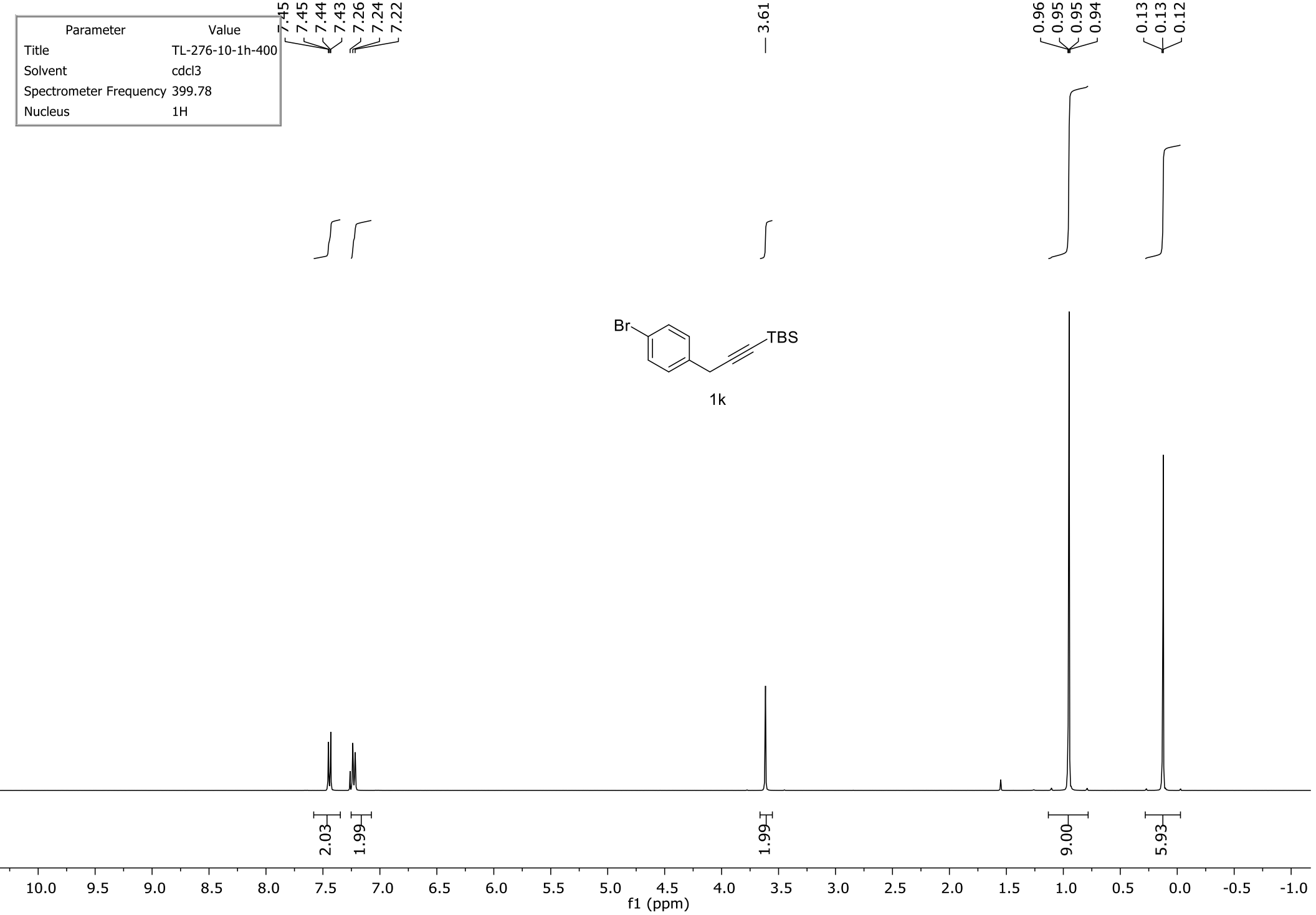
Parameter	Value
Title	TingLI-244-1-3-1h
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	¹ H



Parameter	Value
Title	TingLI-244-1-3-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	¹³ C

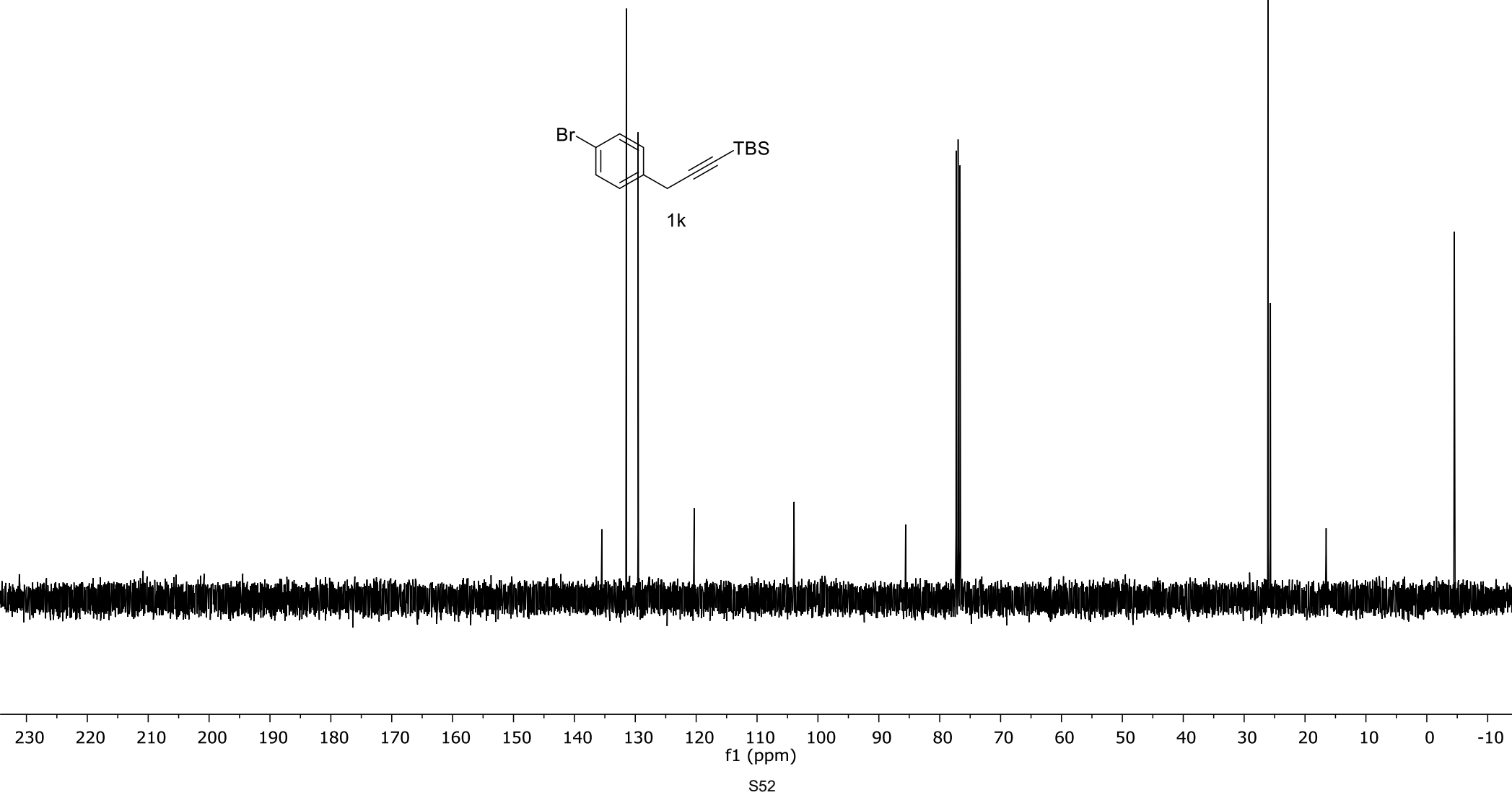
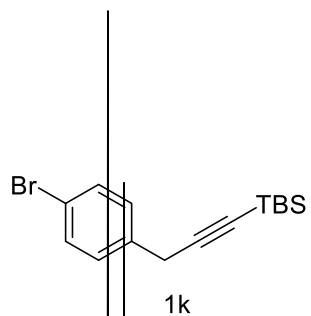


Parameter	Value
Title	TL-276-10-1h-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	¹ H

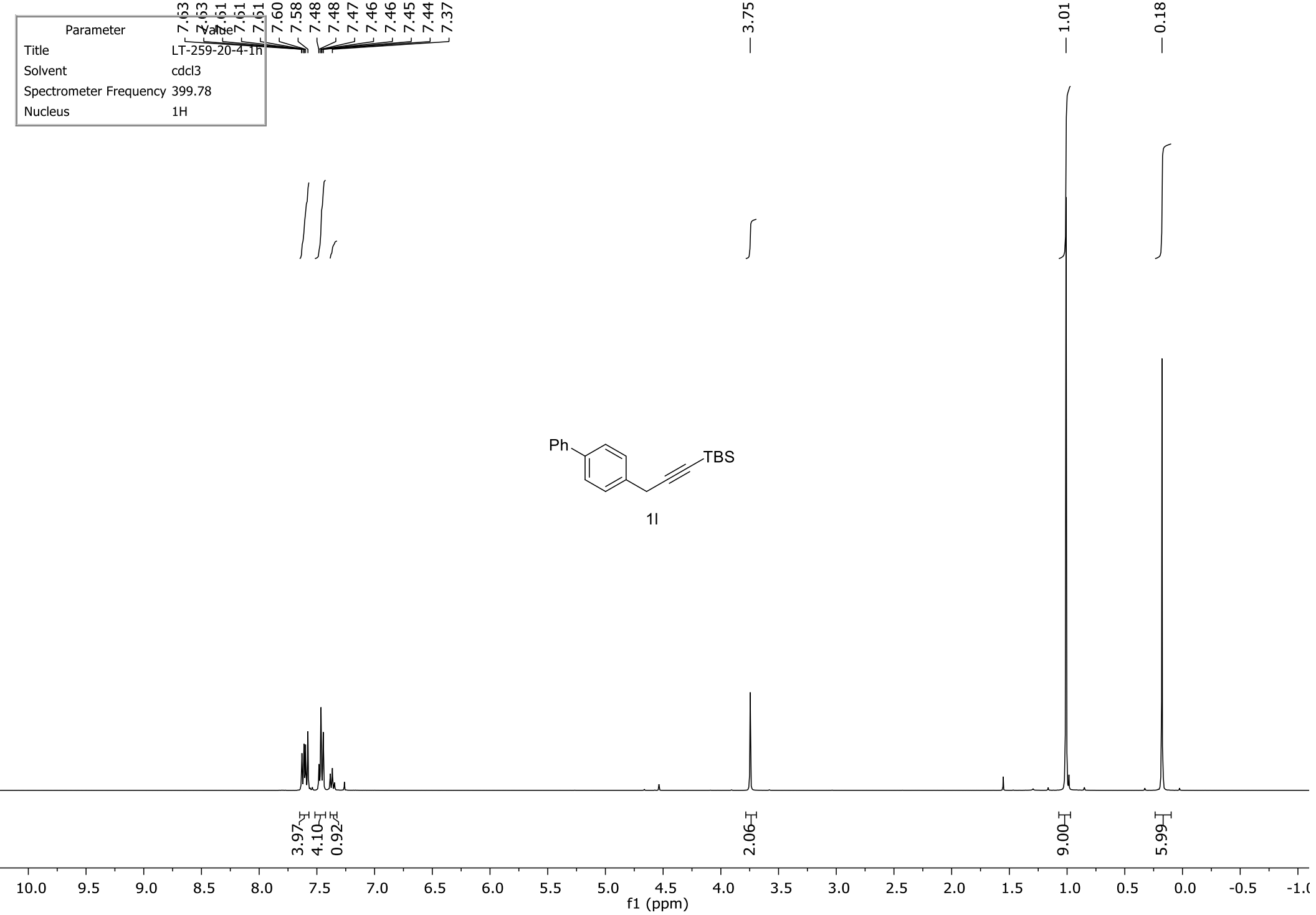


Parameter	Value
Title	TL-276-10-13c-400
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C

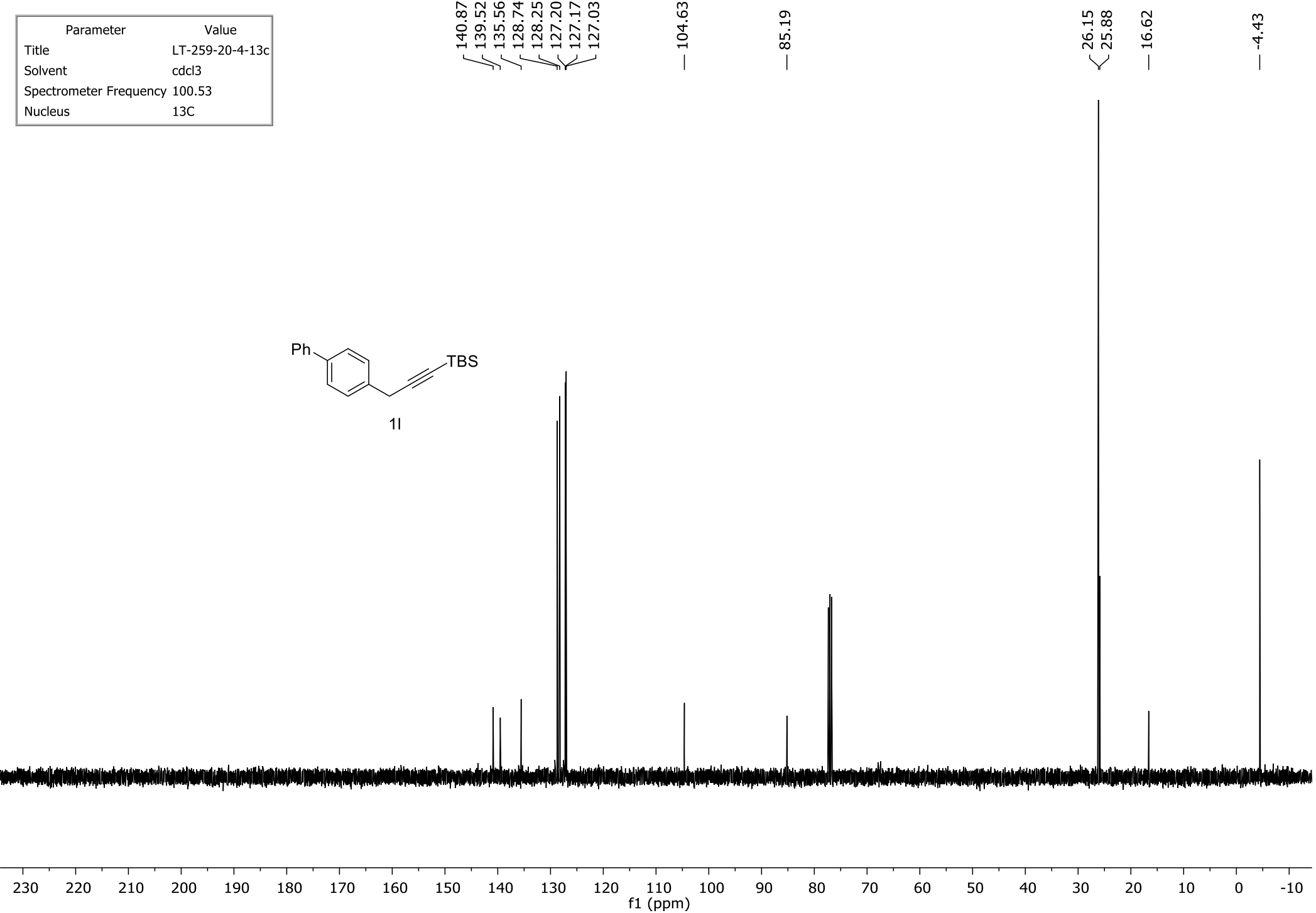
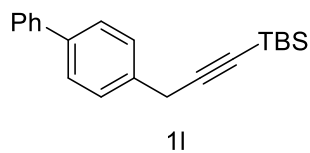
¹³C NMR chemical shifts (ppm):
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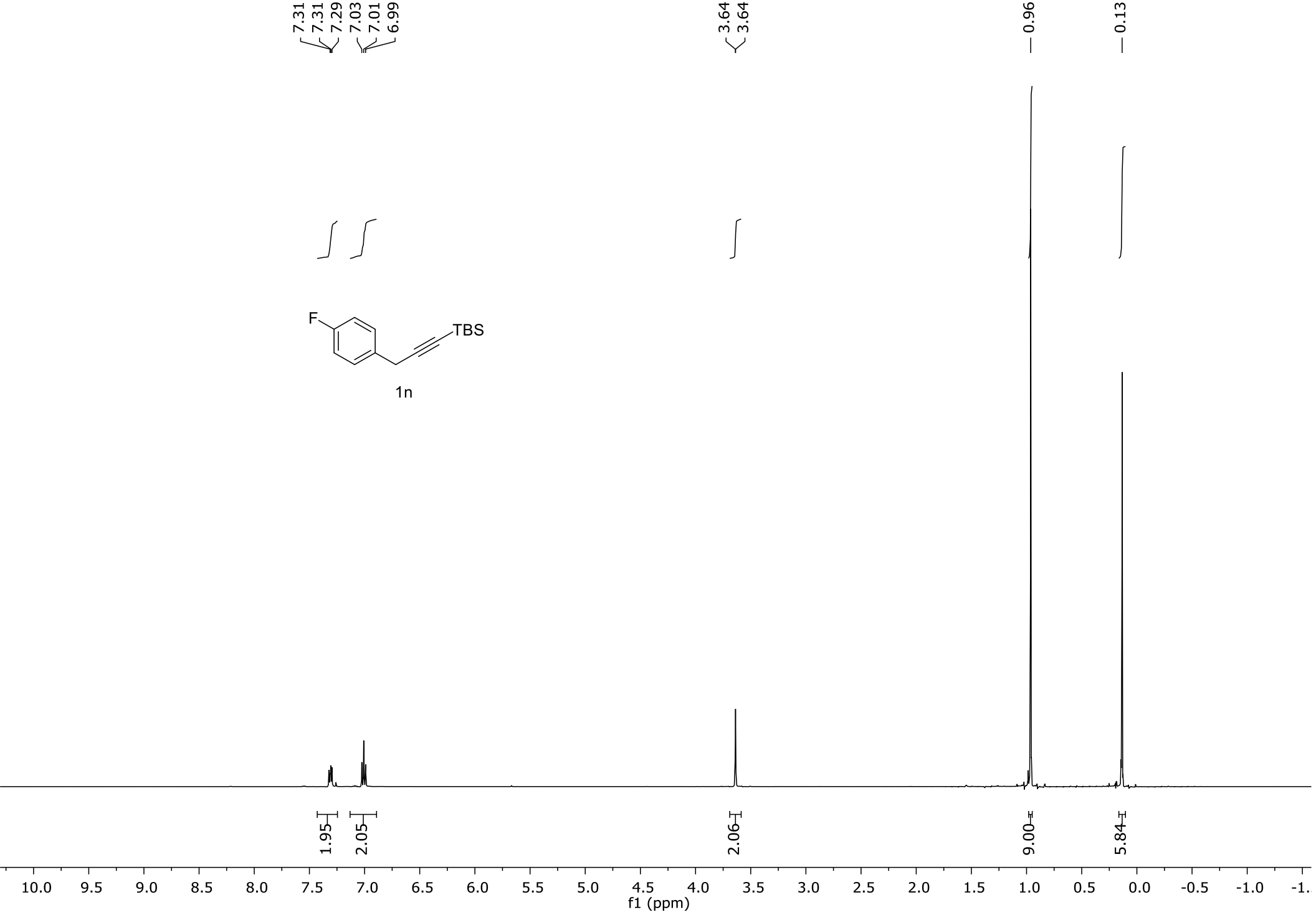


Parameter	Value
Title	LT-259-20-4-1h
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	¹ H

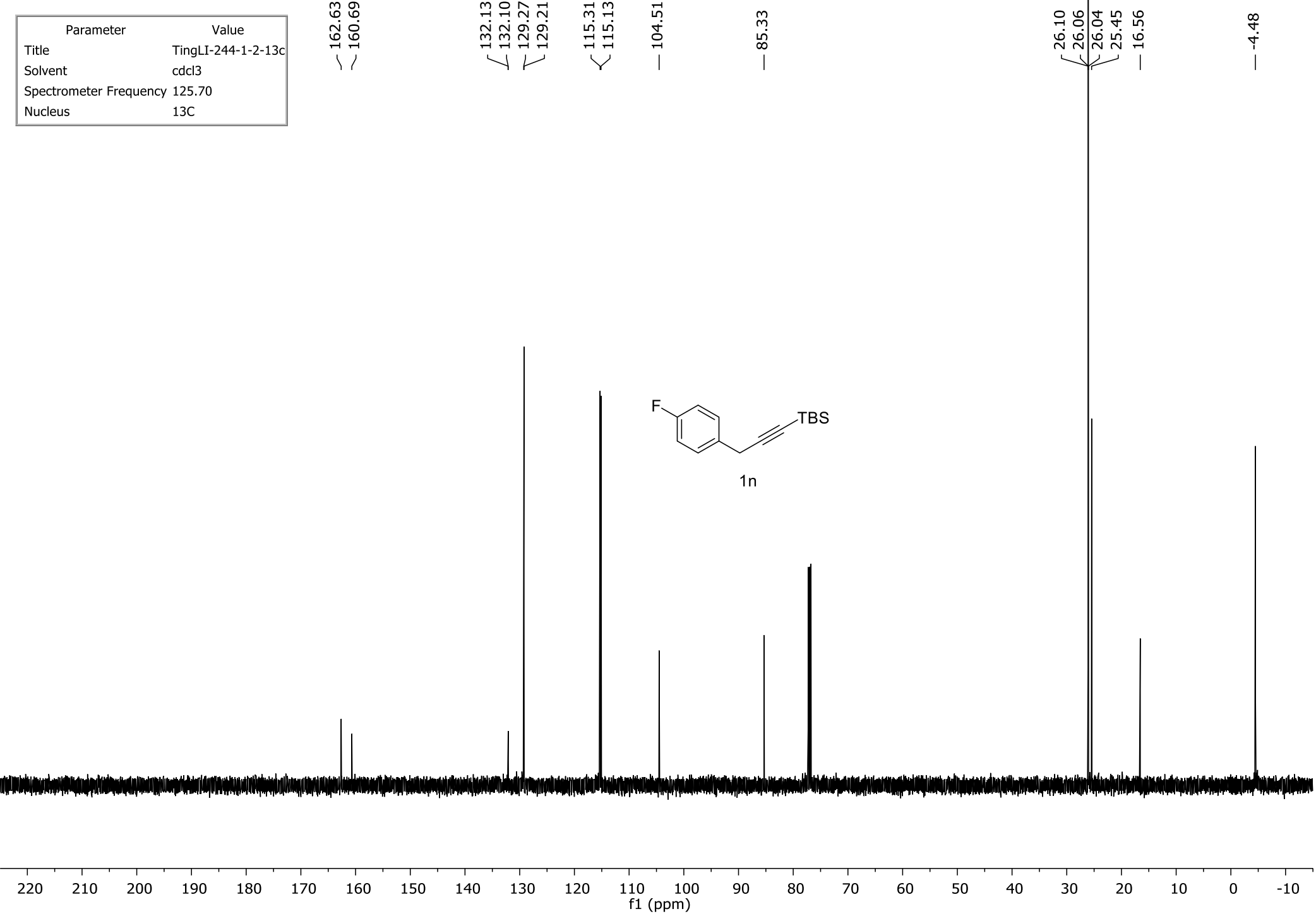


Parameter	Value
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Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C

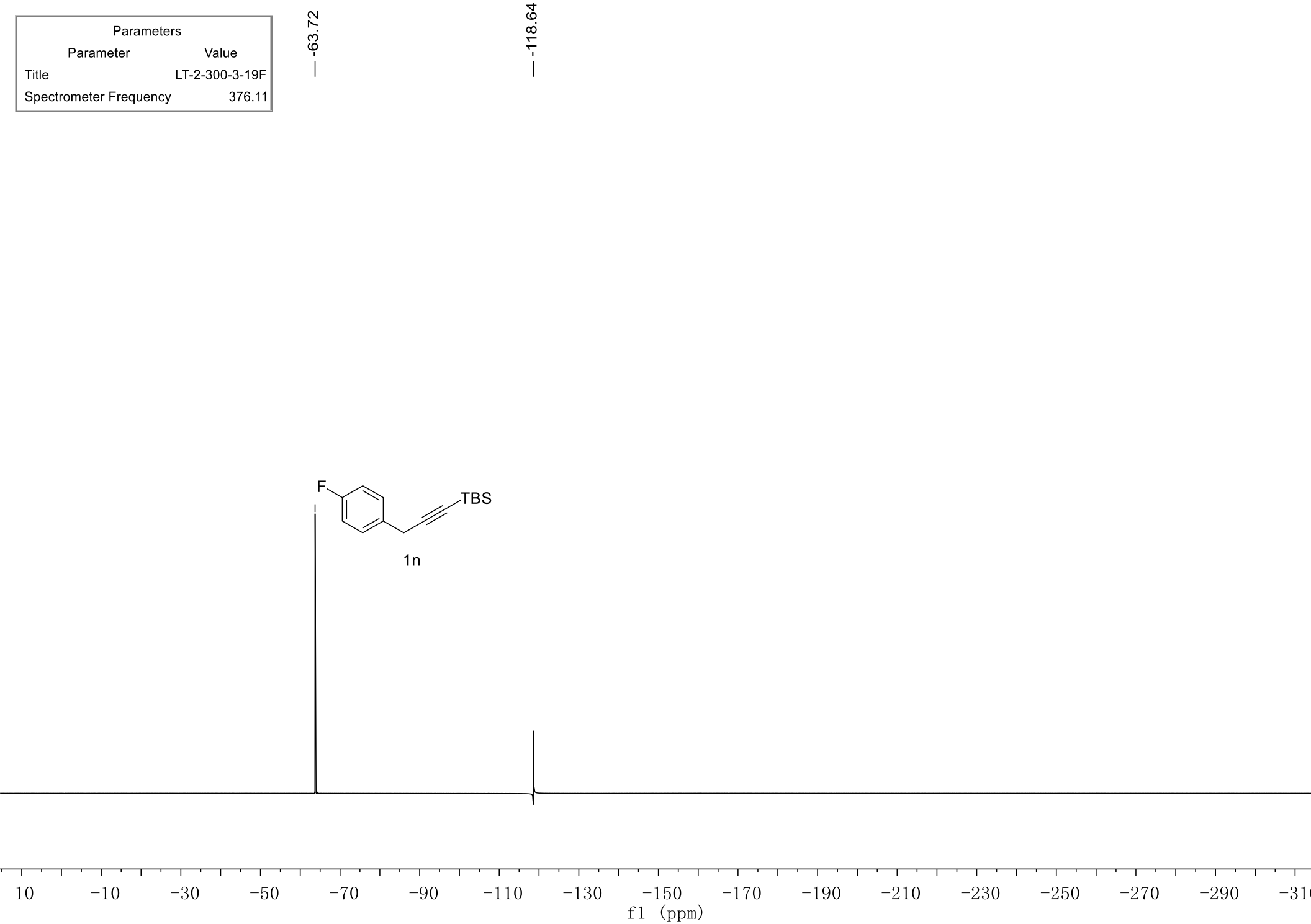




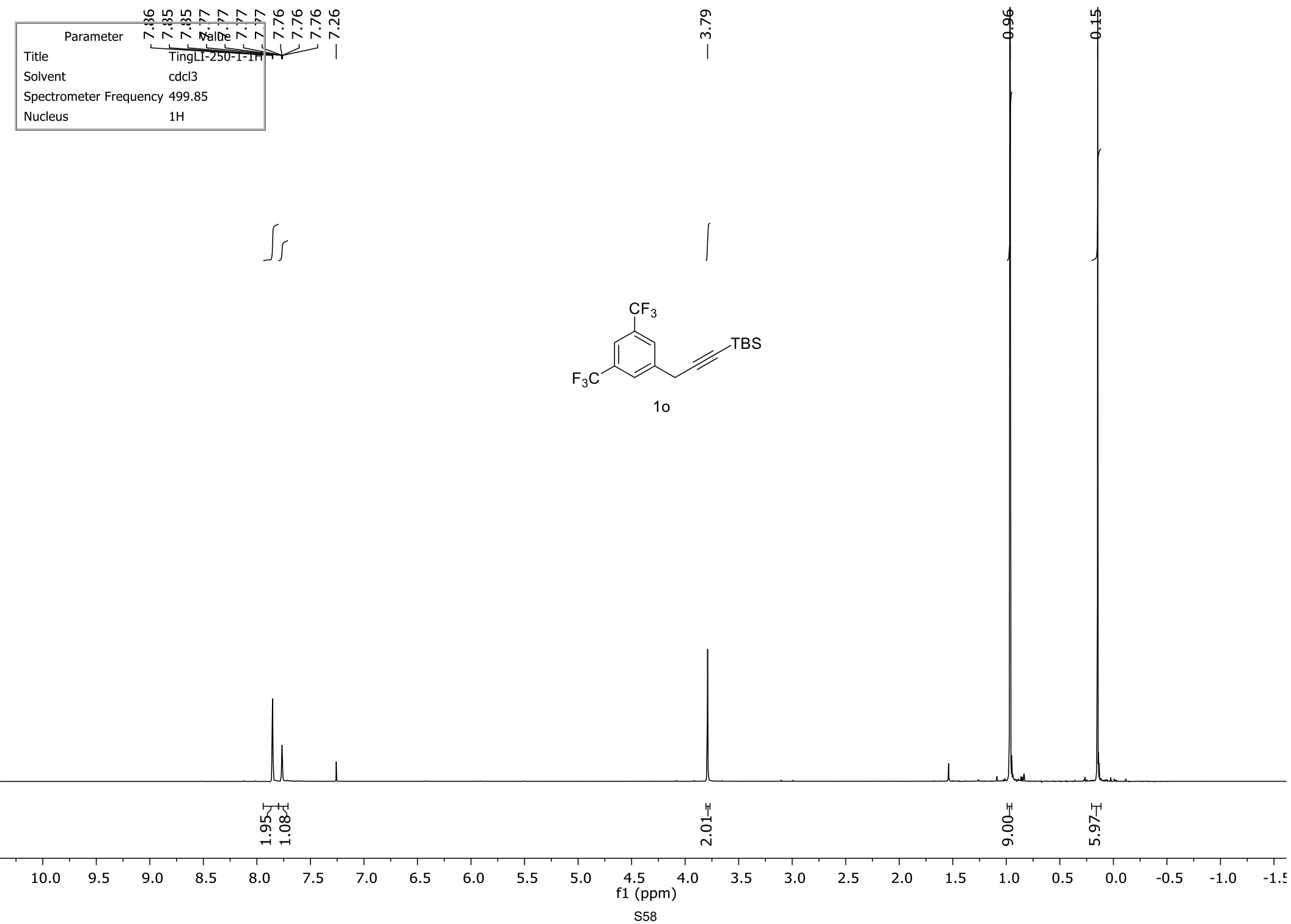
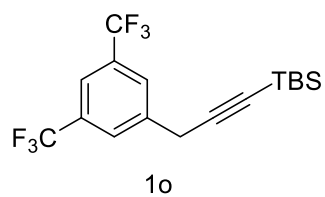
Parameter	Value
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Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	¹³ C



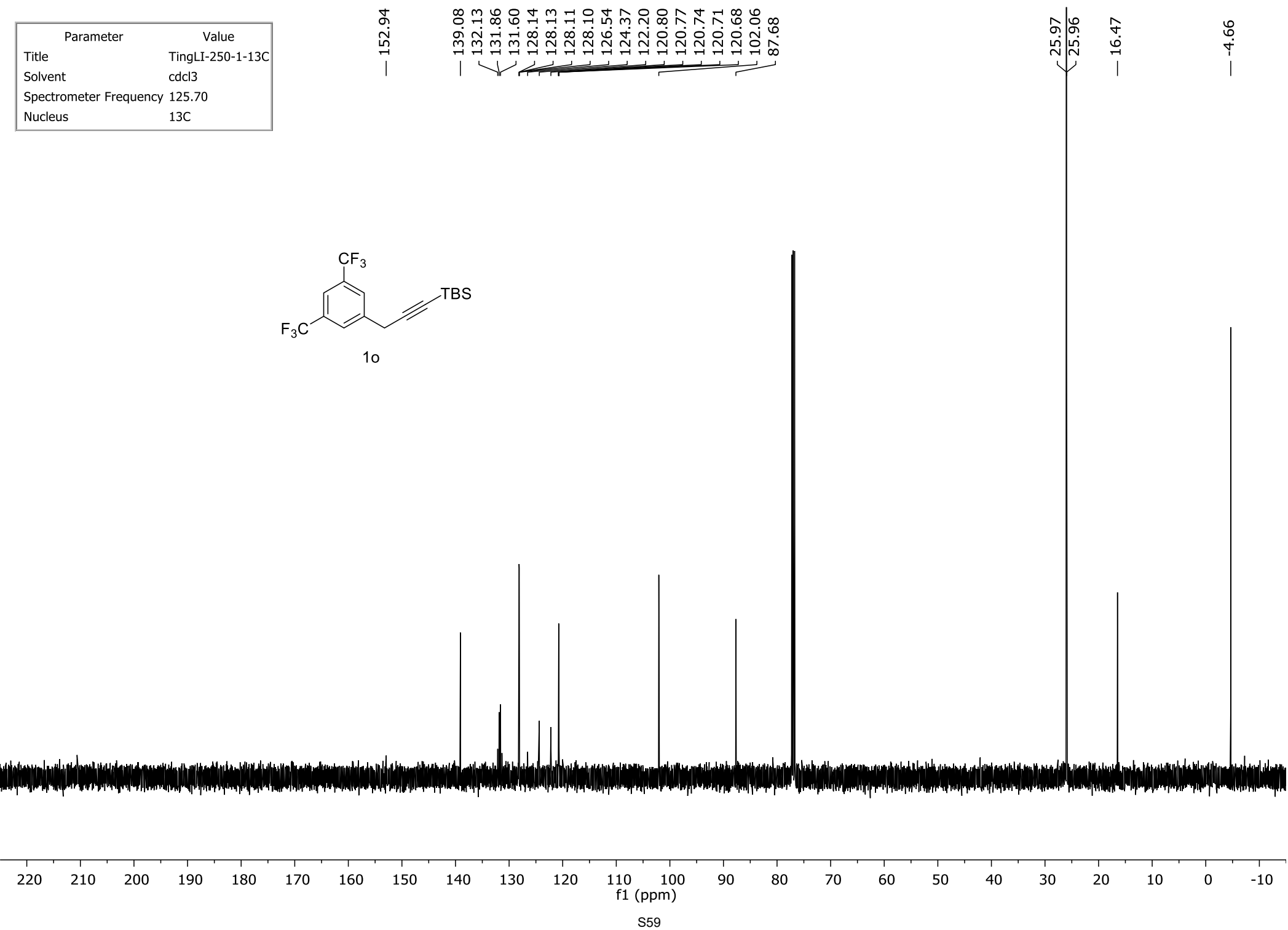
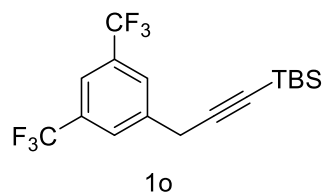
Parameters		
Parameter	Value	
Title	LT-2-300-3-19F	
Spectrometer Frequency	376.11	



Parameter	Value
Title	TingLI-250-1-1H
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	¹ H



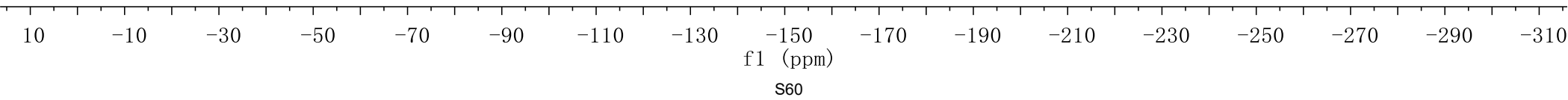
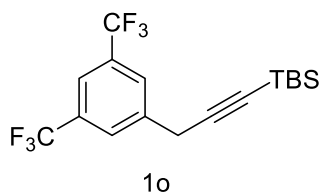
Parameter	Value
Title	TingLI-250-1-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C



Parameters	
Parameter	Value
Title	LT-2-300-6-19F
Spectrometer Frequency	376.11

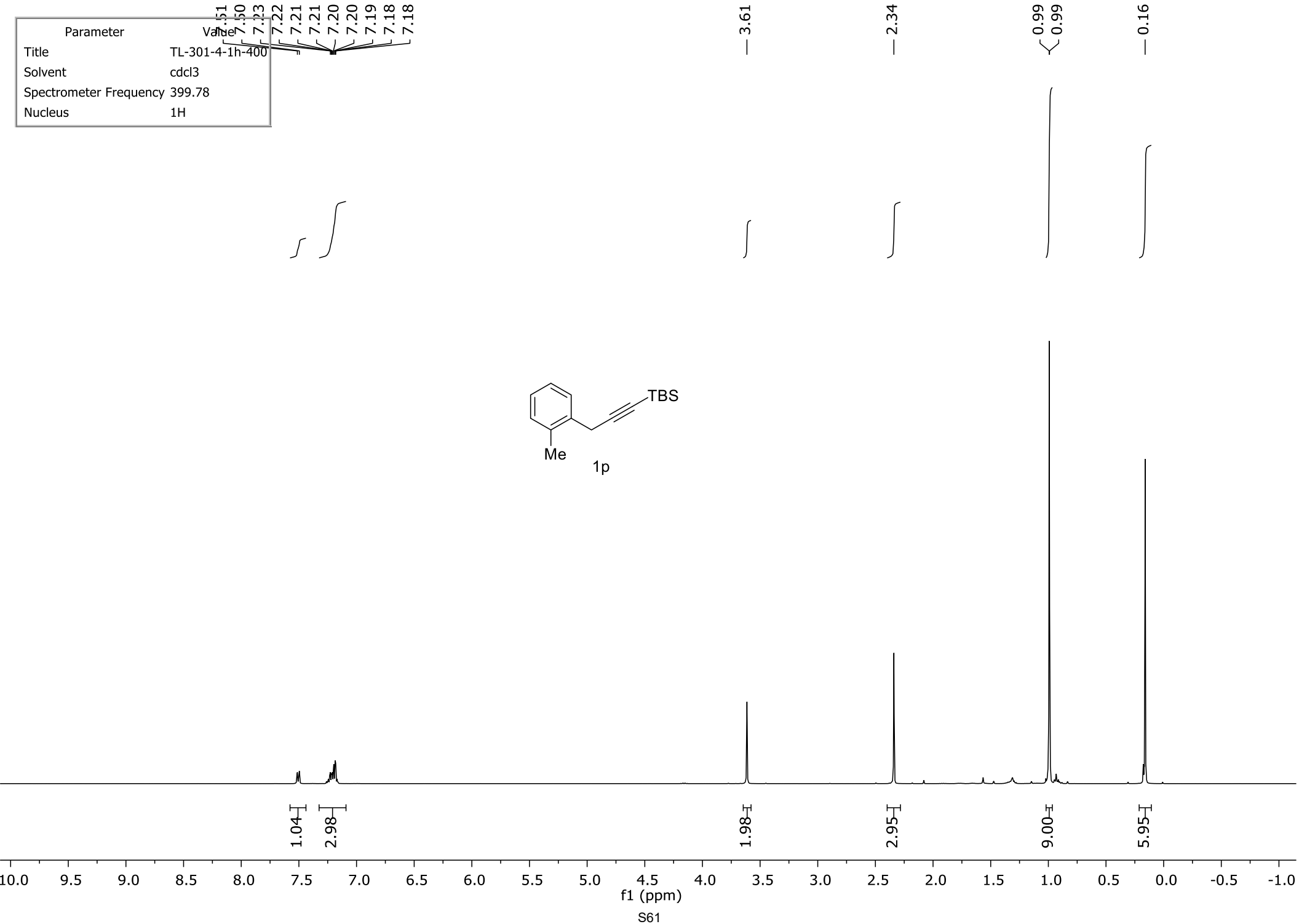
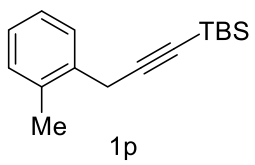
— -63.03

— -113.15

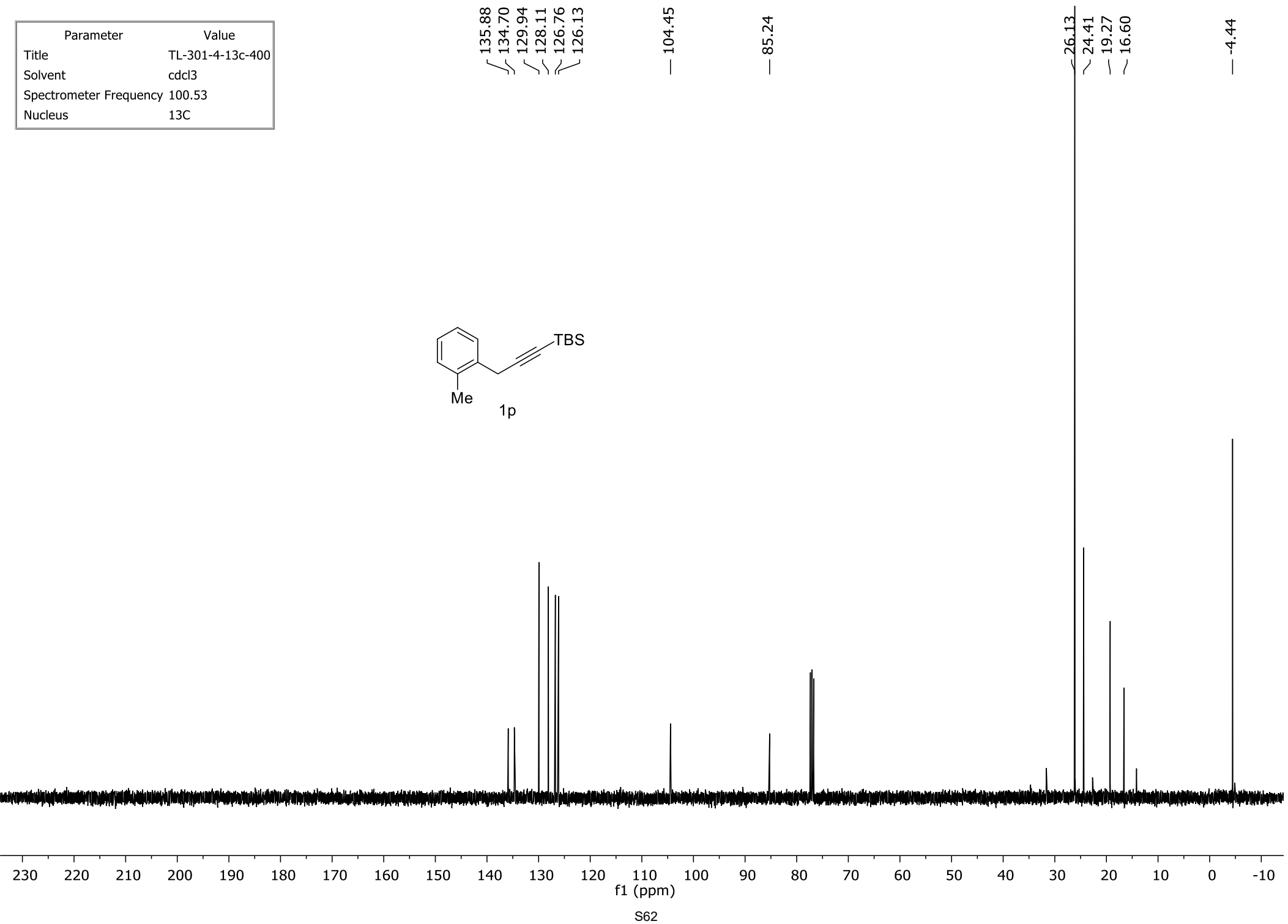
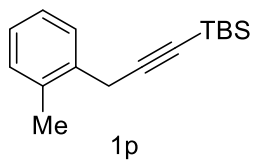


Parameter	Value
Title	TL-301-4-1h-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H

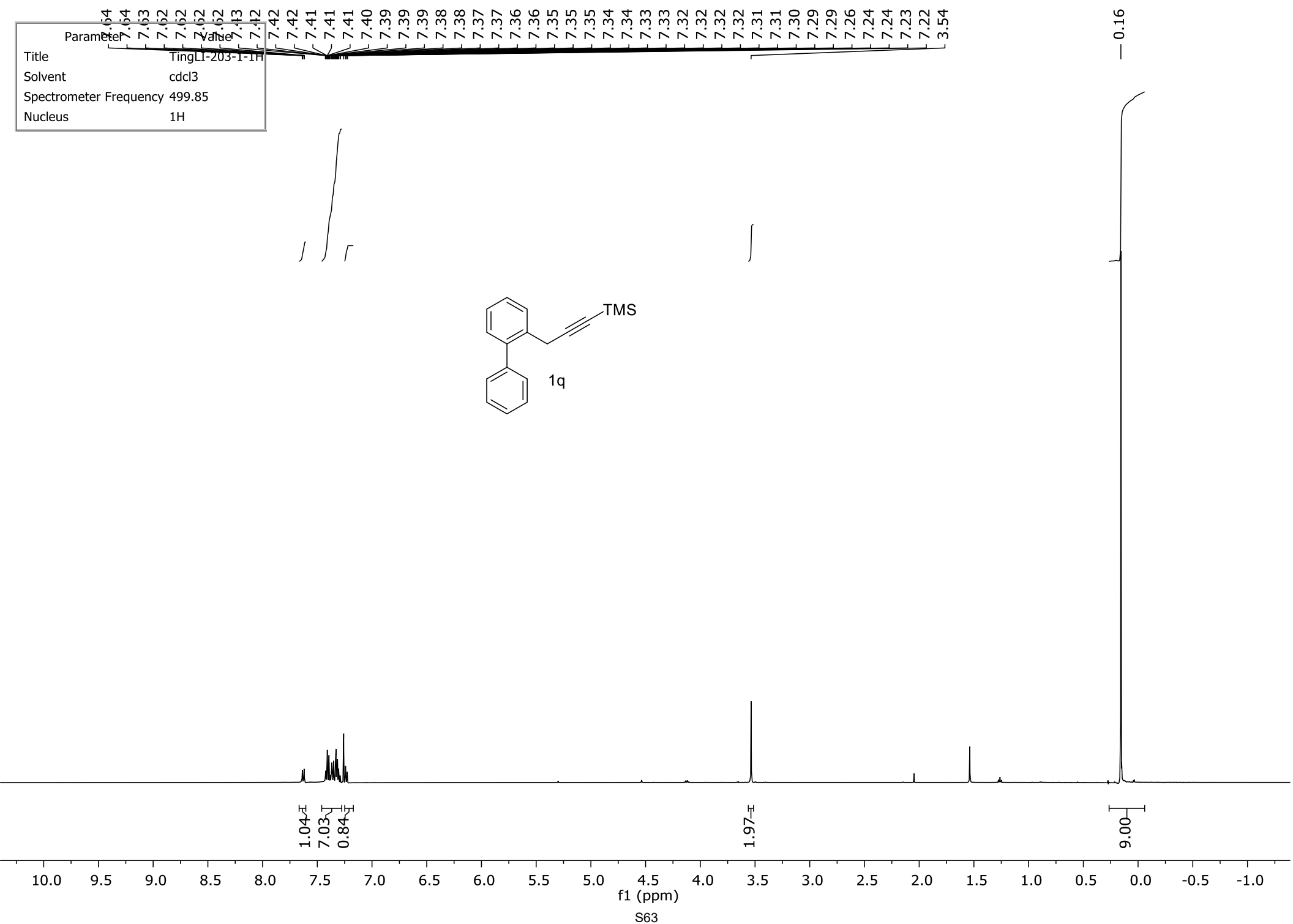
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7.50
7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.18



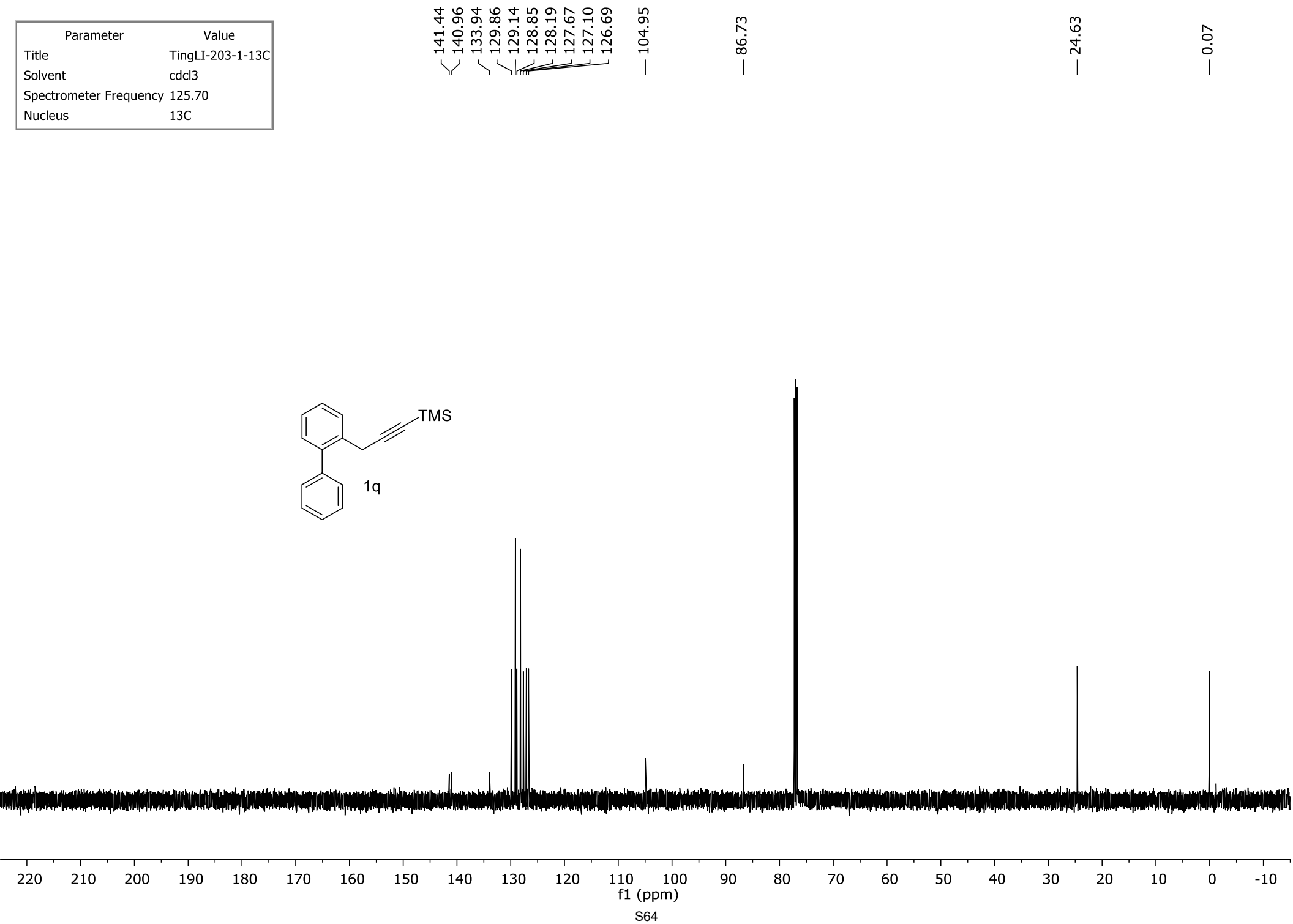
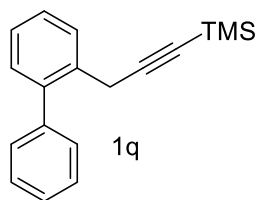
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Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	13C



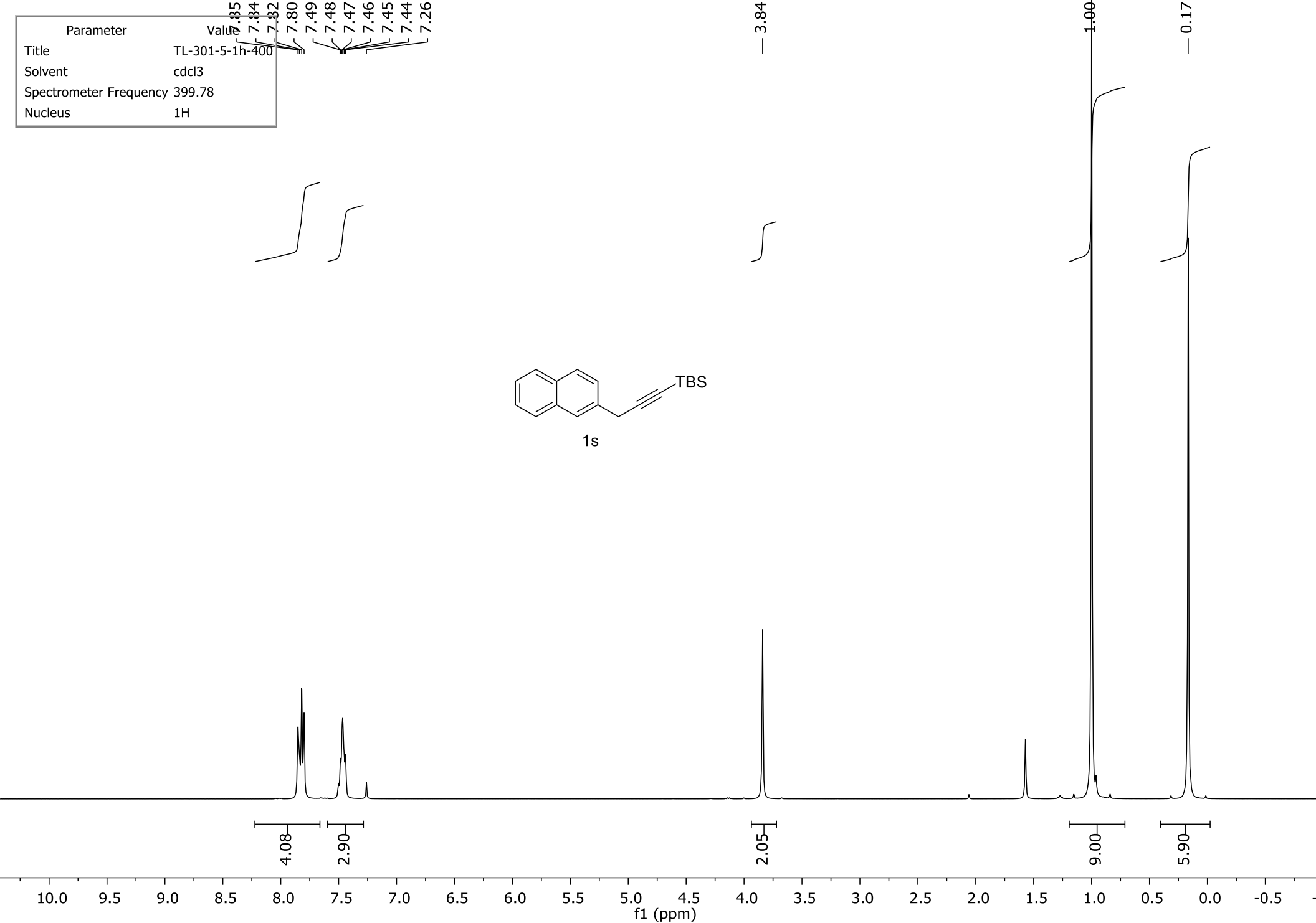
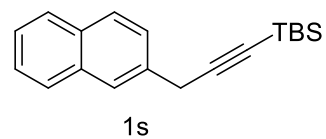
Parameter	Value
Title	TingLI-203-1-1H
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	¹ H



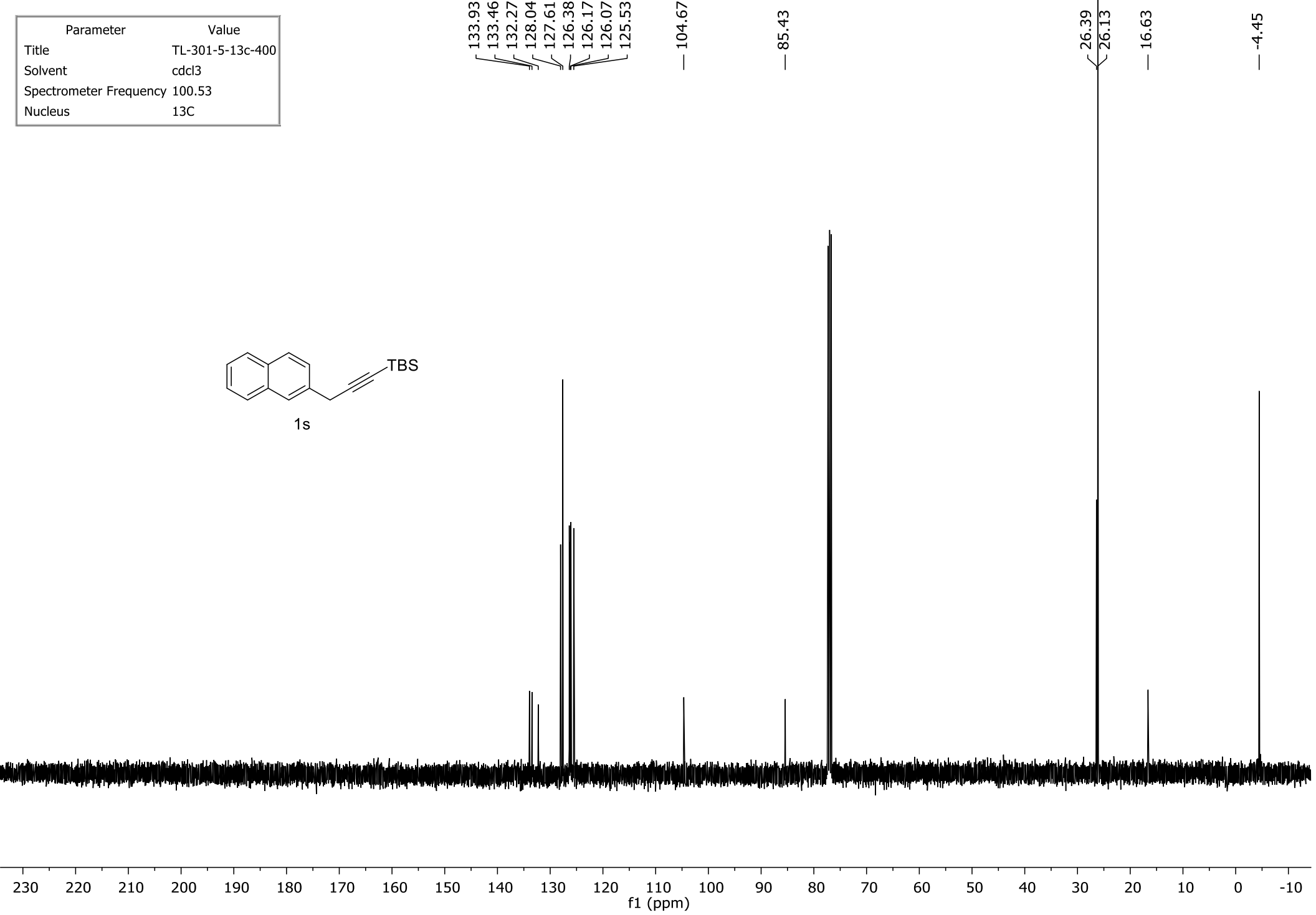
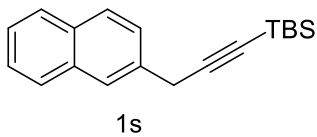
Parameter	Value
Title	TingLI-203-1-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C



Parameter	Value
Title	TL-301-5-1h-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H

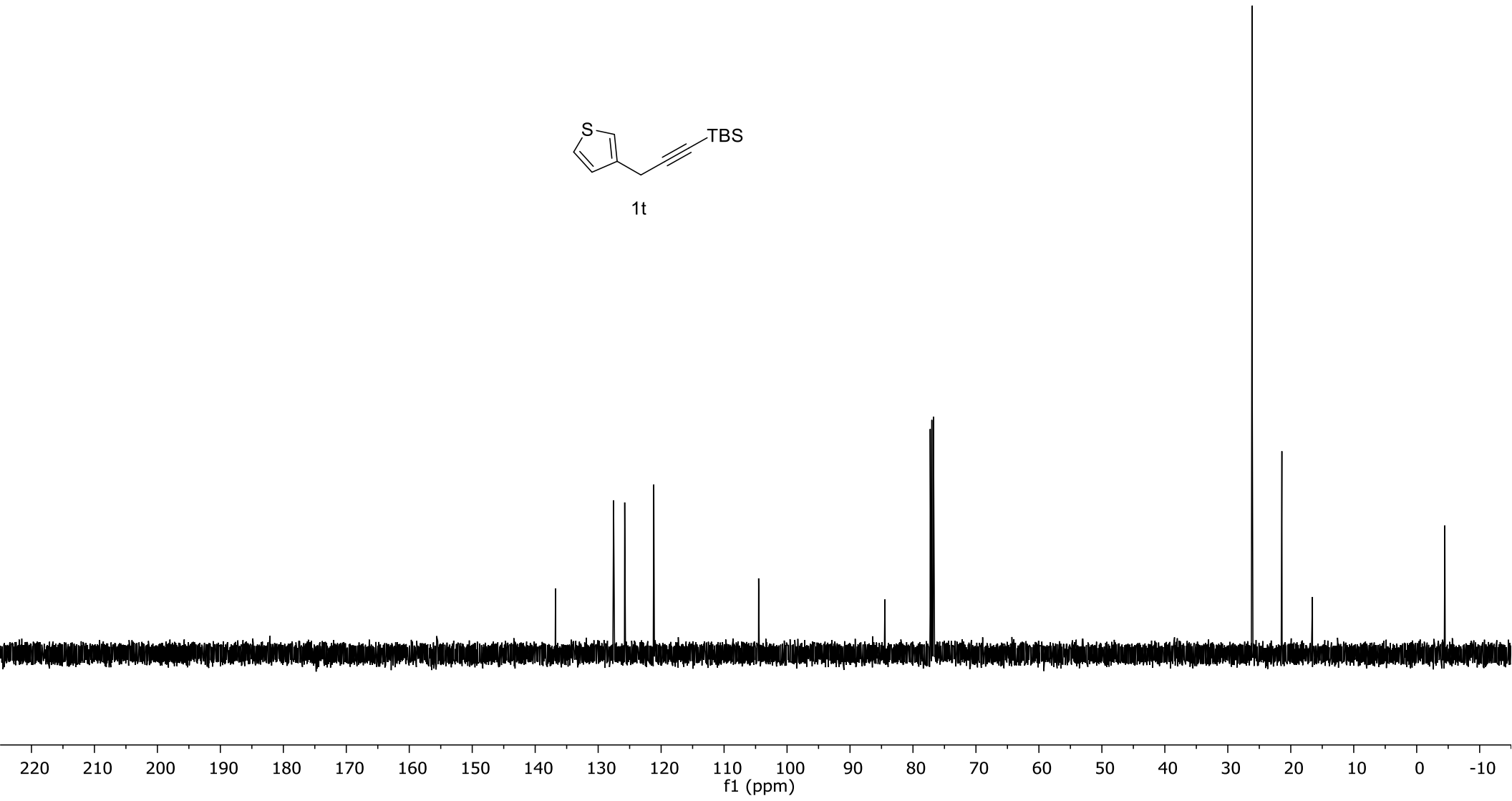
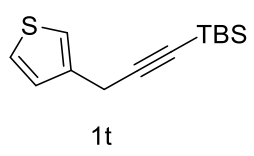


Parameter	Value
Title	TL-301-5-13c-400
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	13C

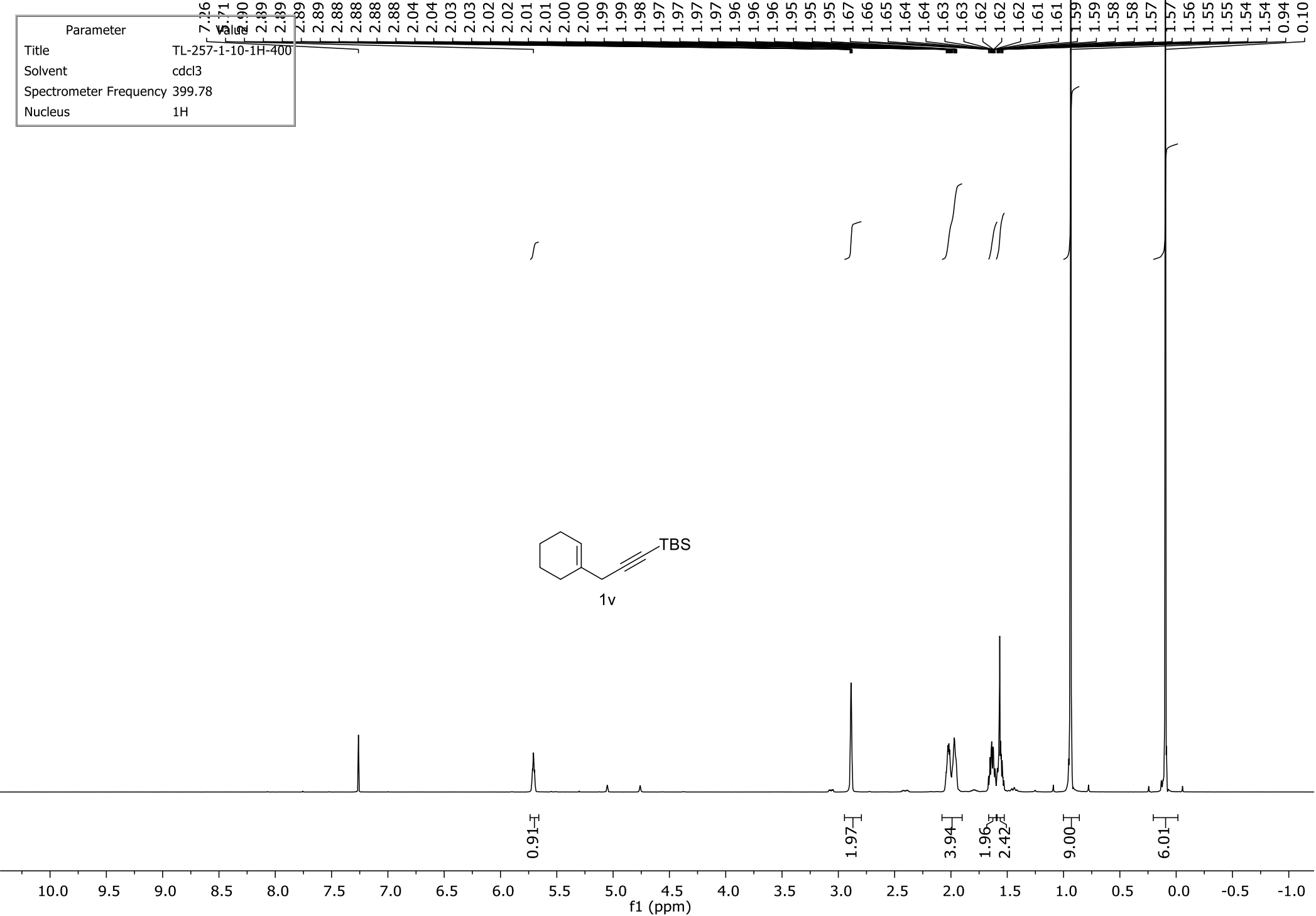


Parameter	Value
Title	TingLI-234-1-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C

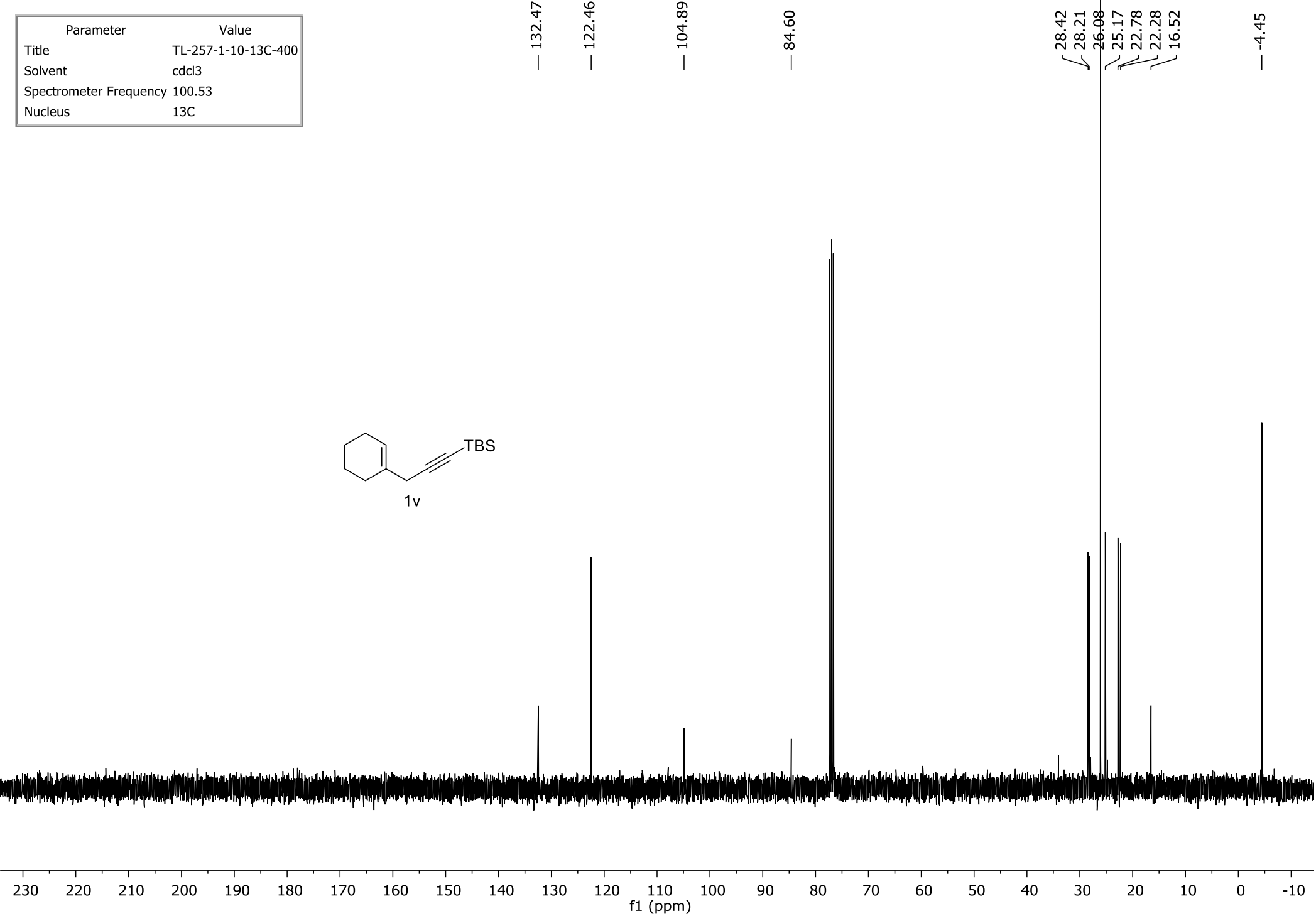
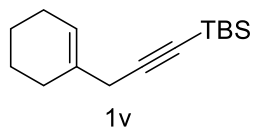
136.78 127.55 125.78 121.16 104.51 84.46 26.12 21.41 16.56 -4.47



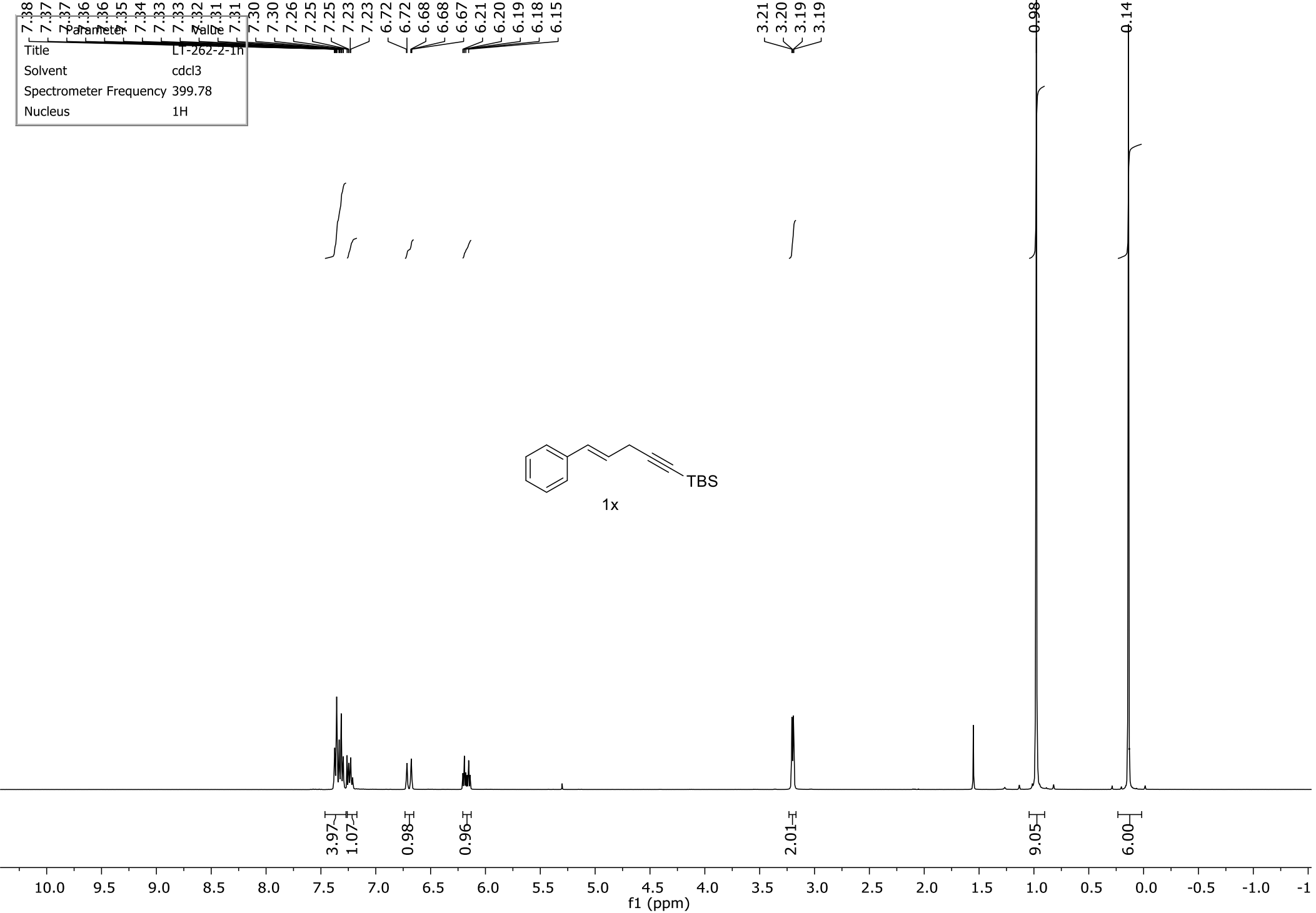
Parameter	Value
Title	TL-257-1-10-1H-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H



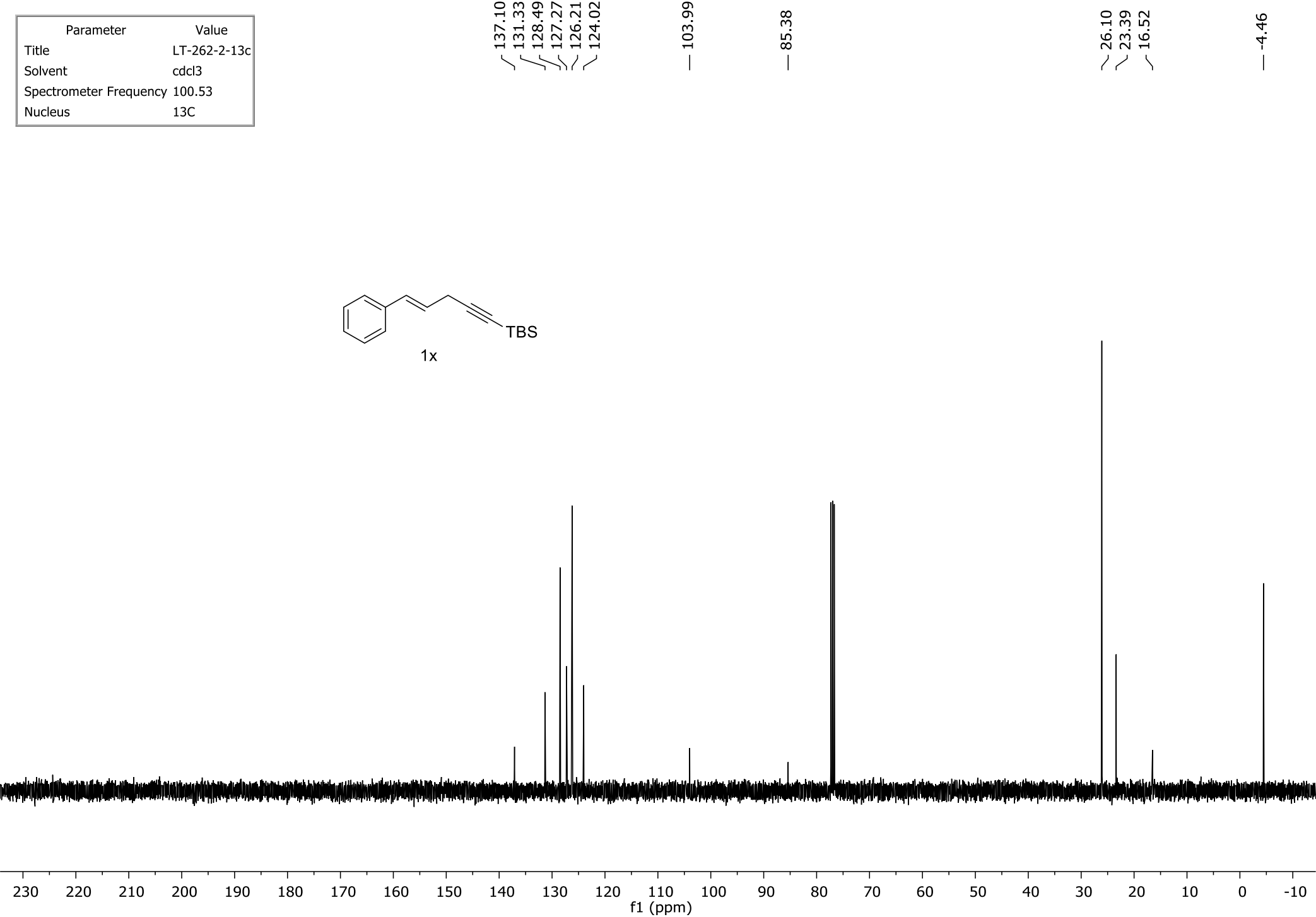
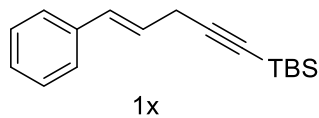
Parameter	Value
Title	TL-257-1-10-13C-400
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C



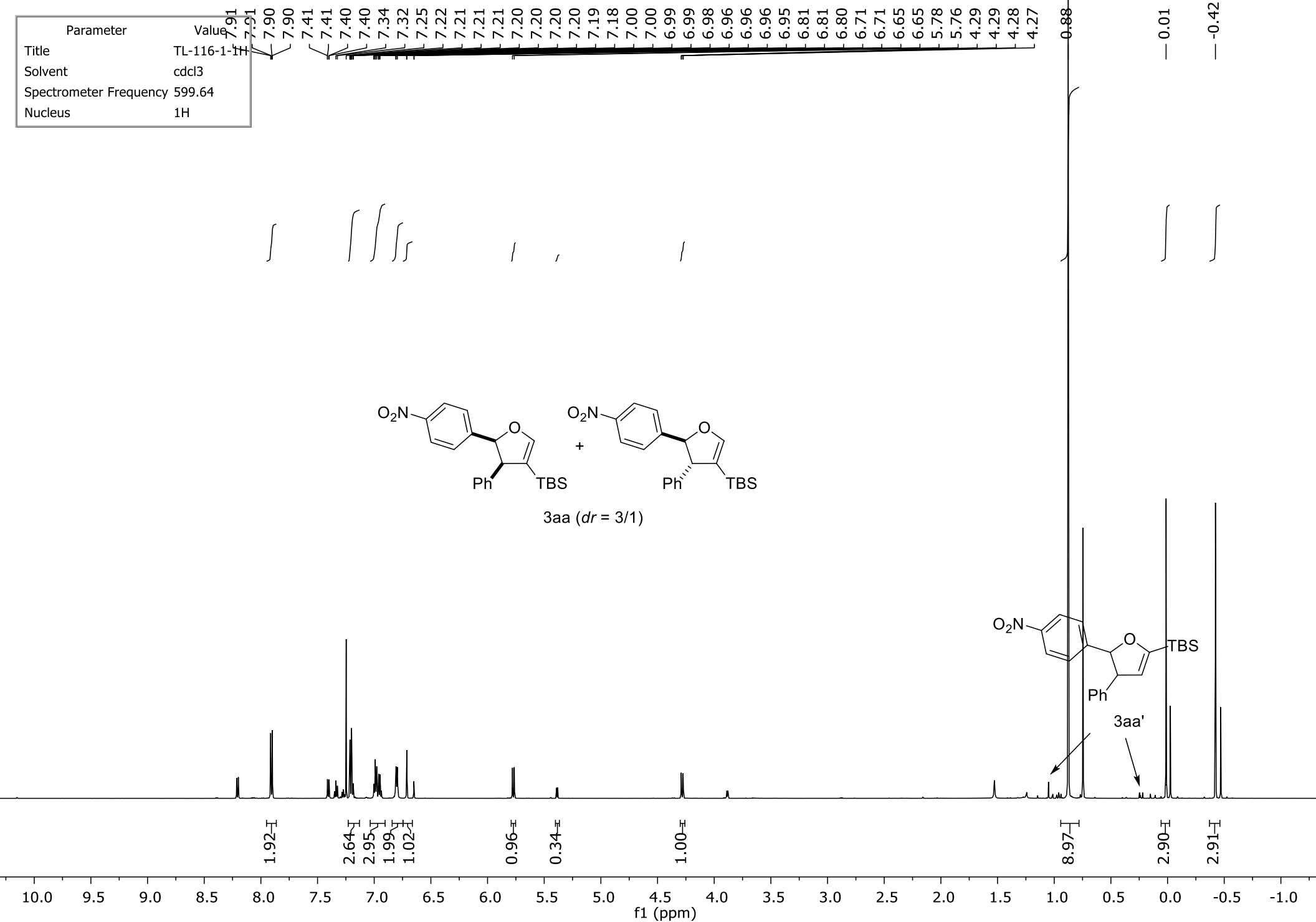
Parameter	Value
Title	LI-262-2-1h
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H



Parameter	Value
Title	LT-262-2-13c
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C

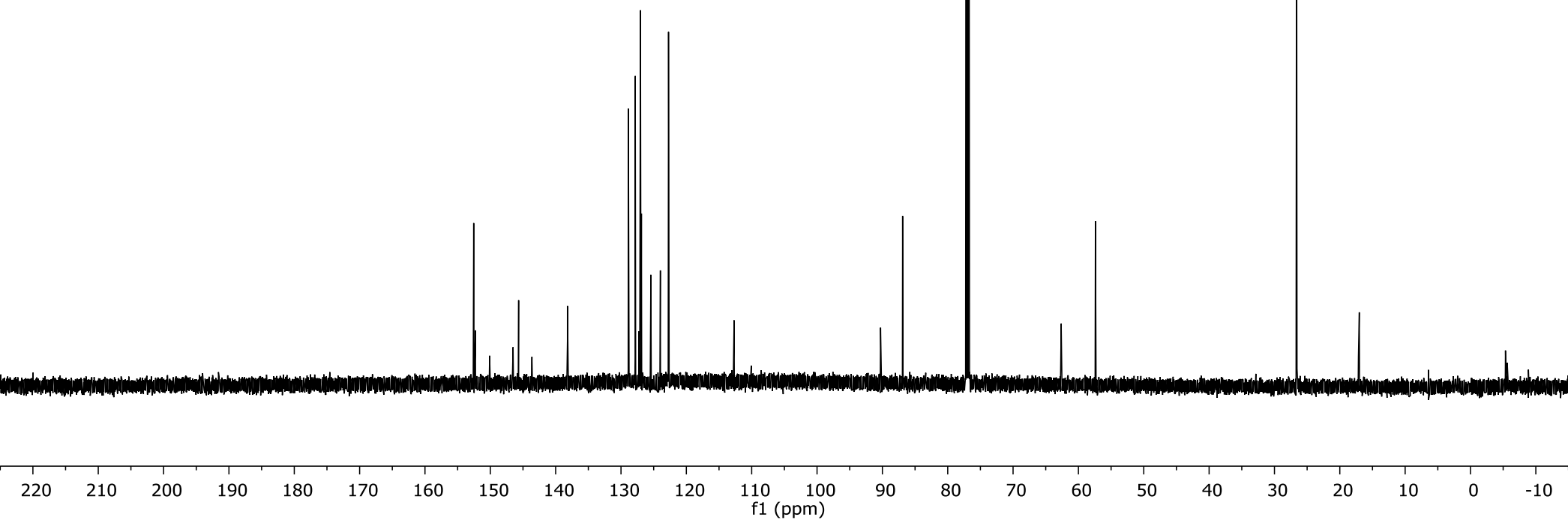
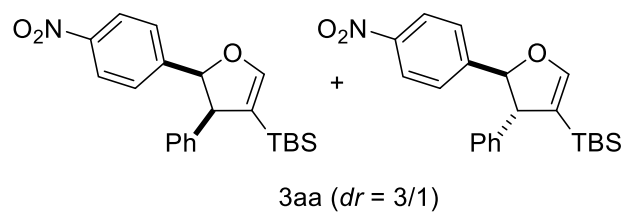


Parameter	Value
Title	TL-116-1-1H
Solvent	cdcl3
Spectrometer Frequency	599.64
Nucleus	1H

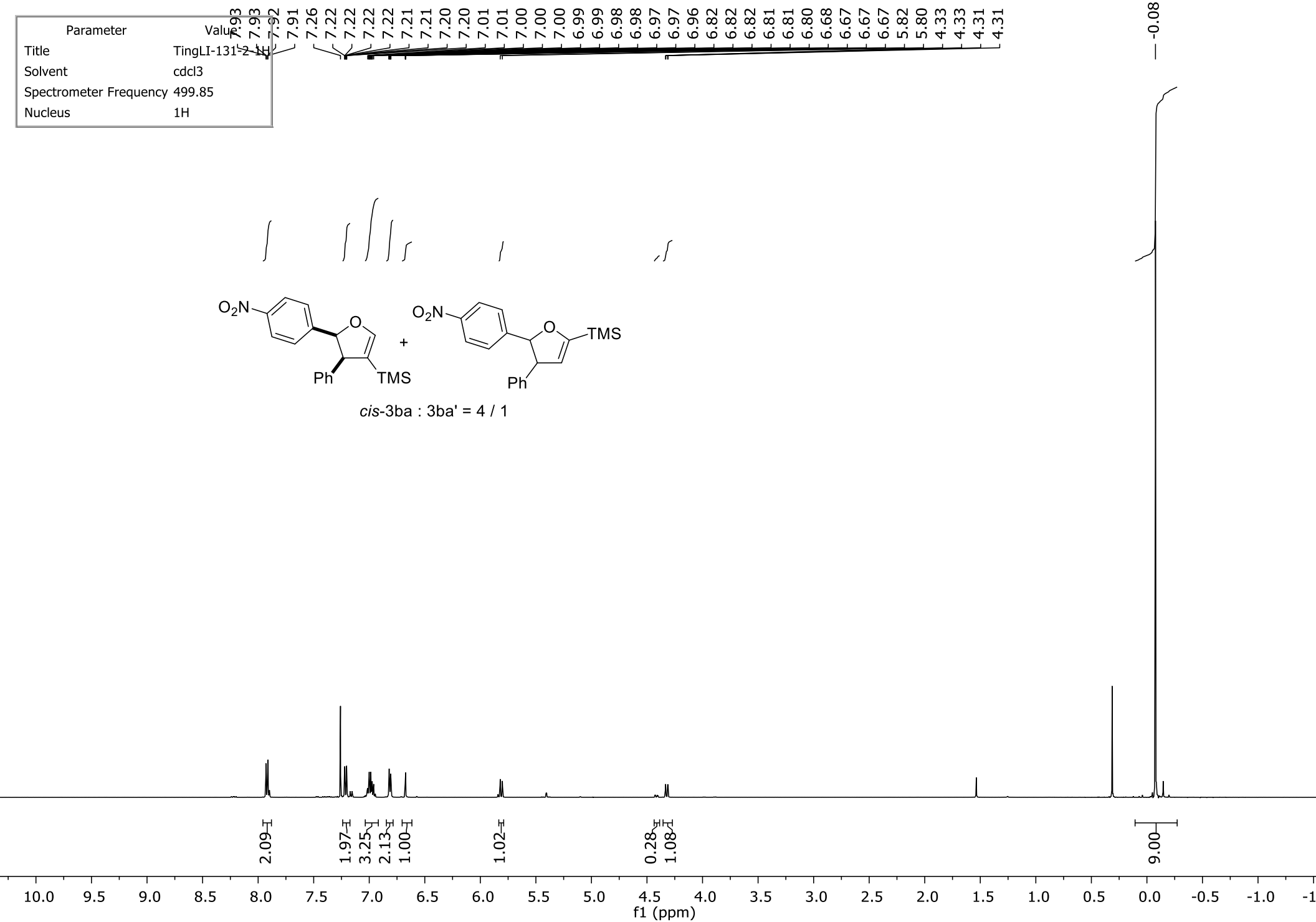
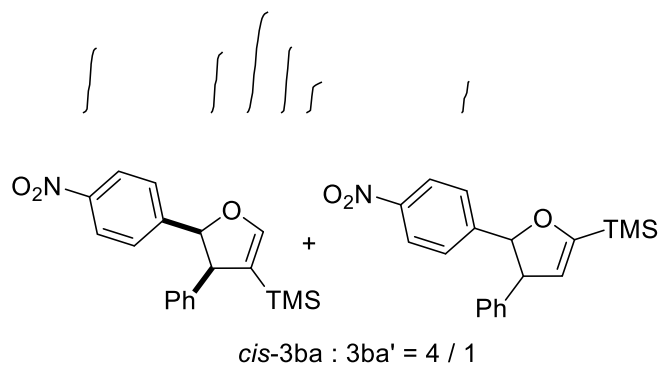


Parameter	Value
Title	TL-116-1-1-13c
Solvent	cdcl3
Spectrometer Frequency	150.79
Nucleus	¹³ C

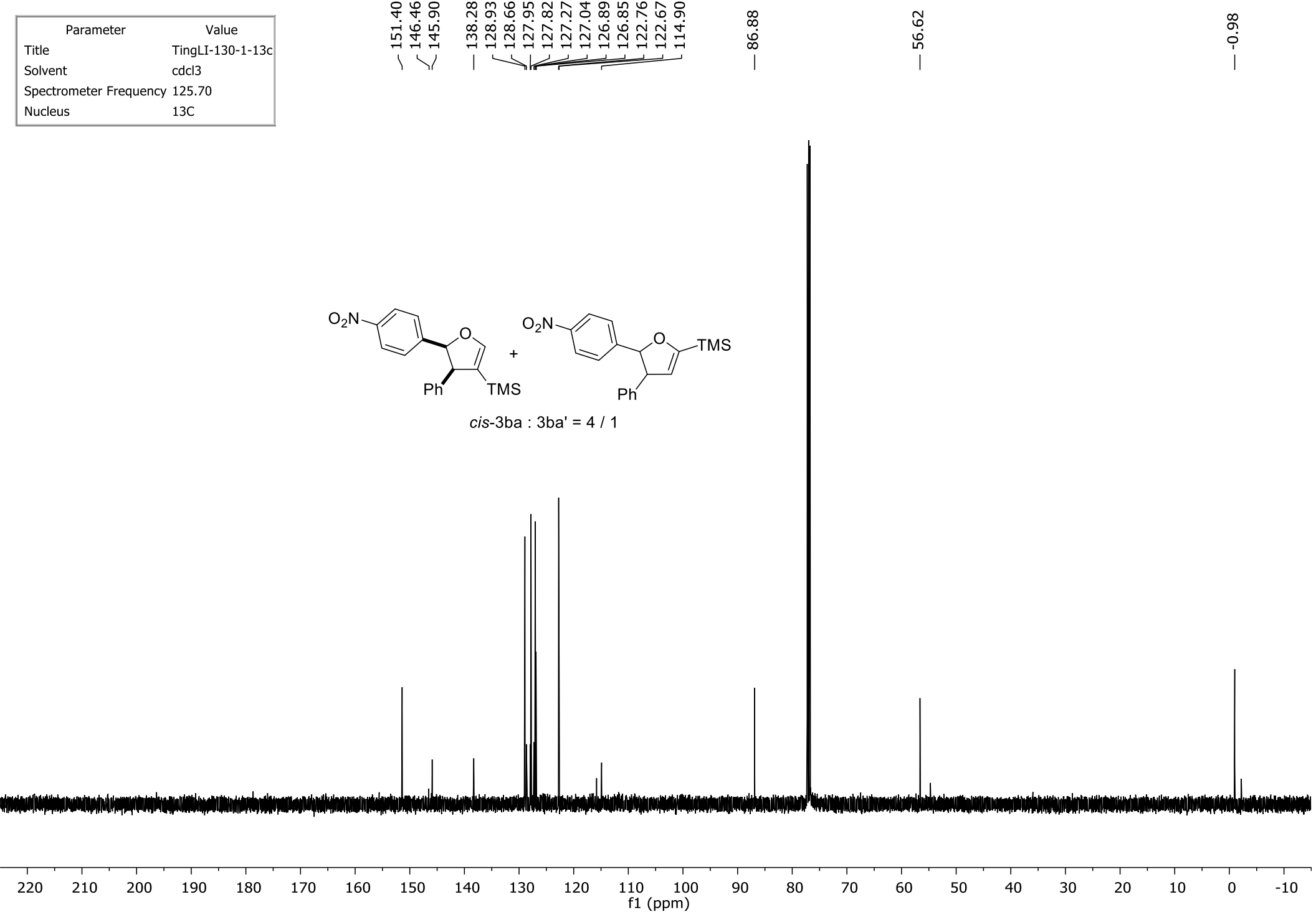
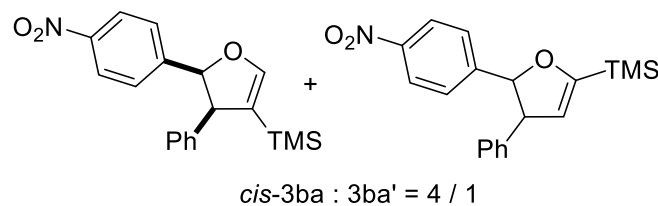
¹³C NMR chemical shifts (ppm): 152.54, 150.10, 145.67, 138.19, 128.87, 128.81, 127.83, 127.82, 127.27, 127.02, 126.87, 125.43, 123.98, 122.73, 112.70, 86.90, 57.40, 26.61, 17.02, -5.36, -5.62, -5.68.



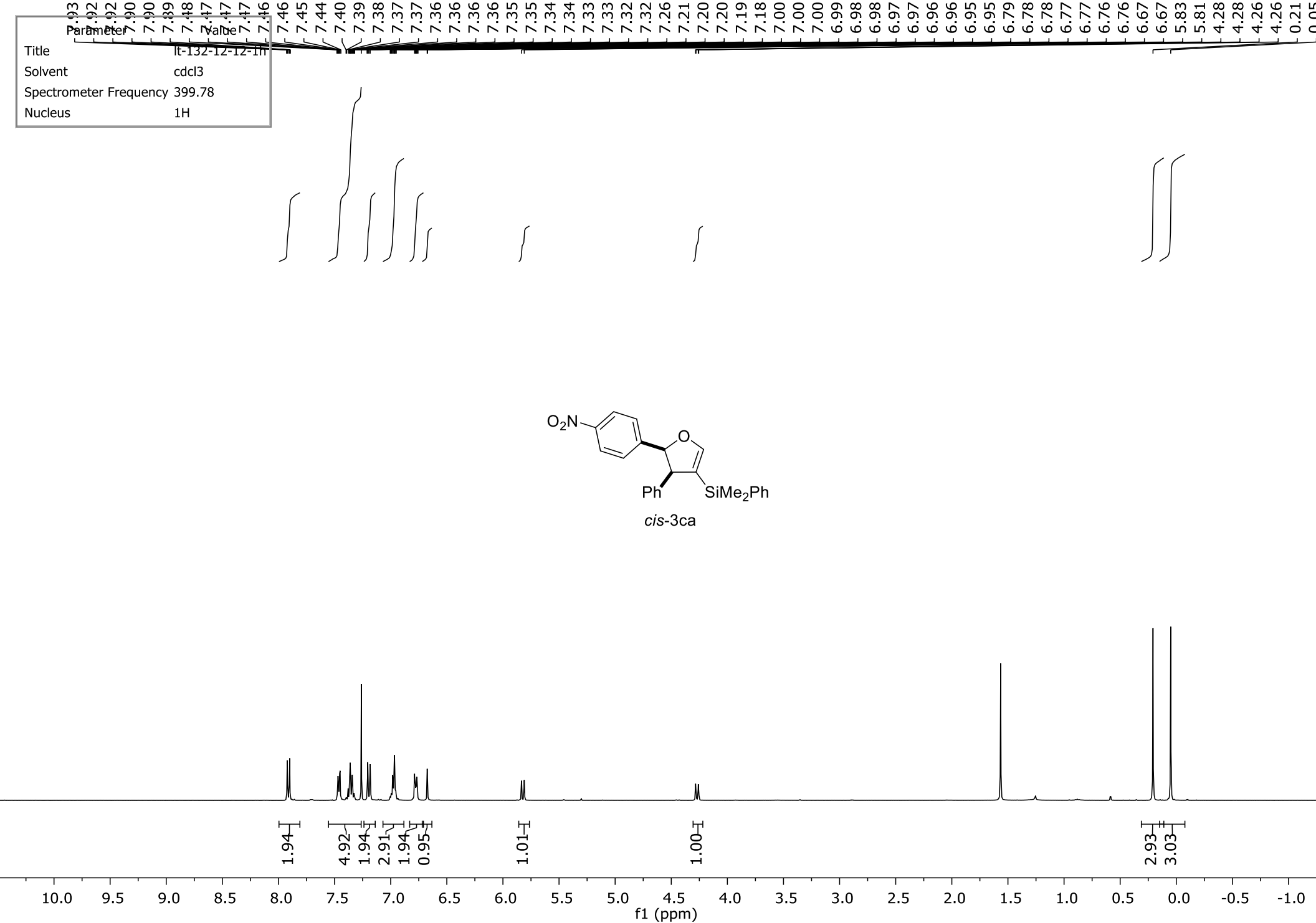
Parameter	Value
Title	TingLI-131-2-1H
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	¹ H



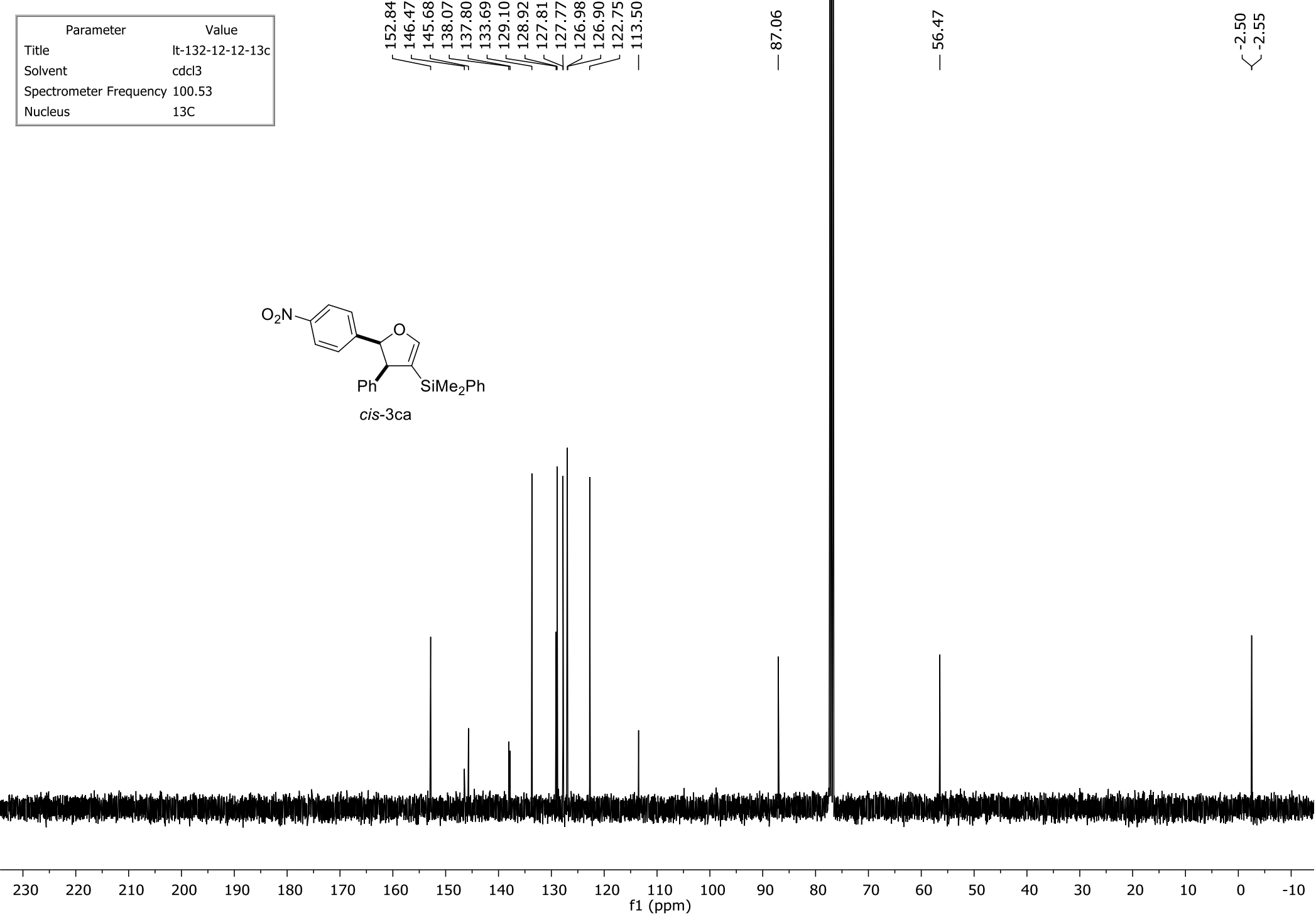
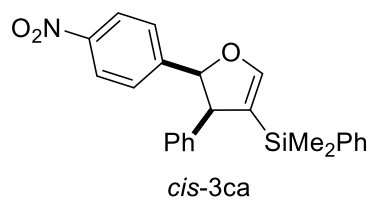
Parameter	Value
Title	TingLI-130-1-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	¹³ C

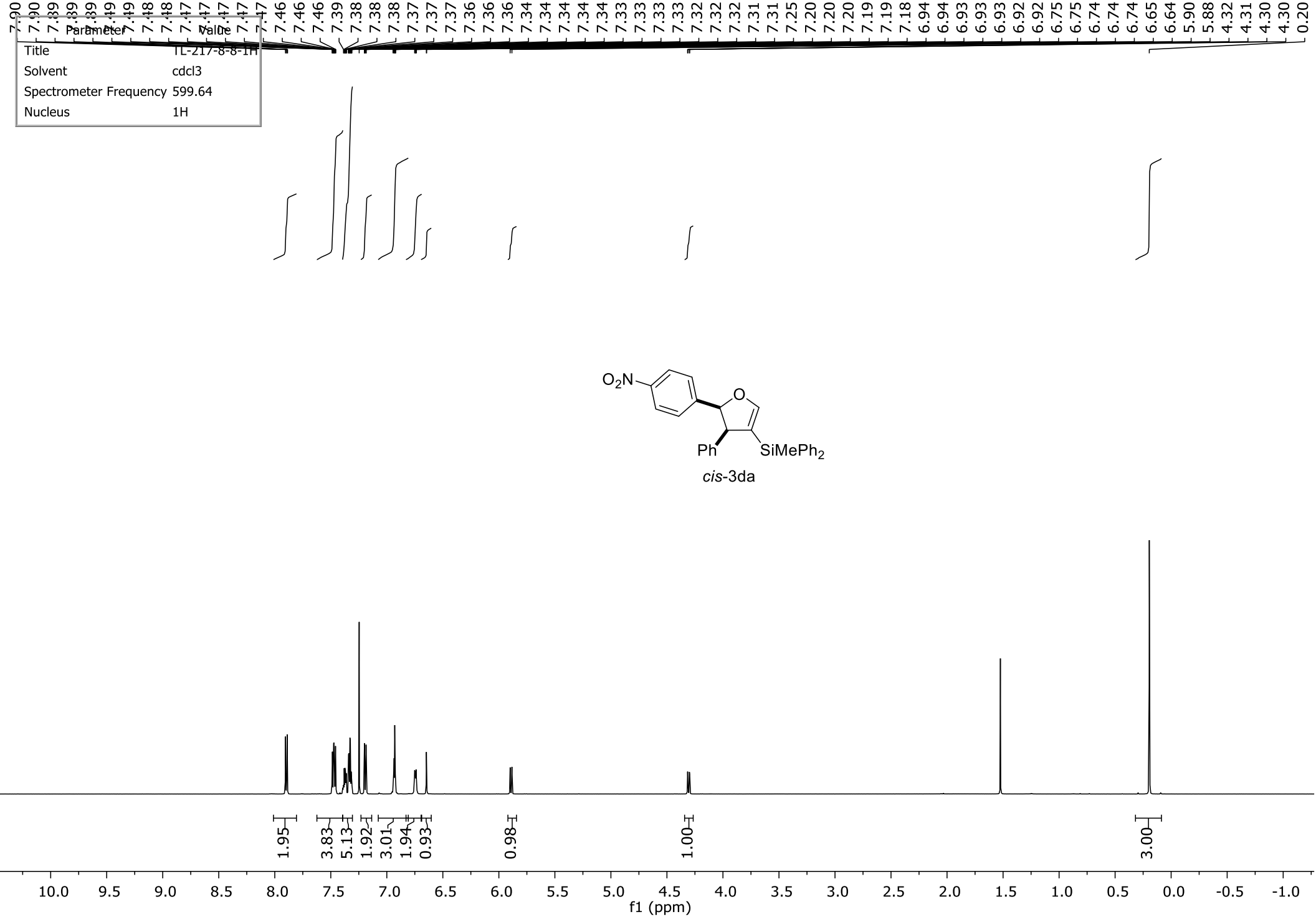


Title	lt-132-12-12-1h
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H

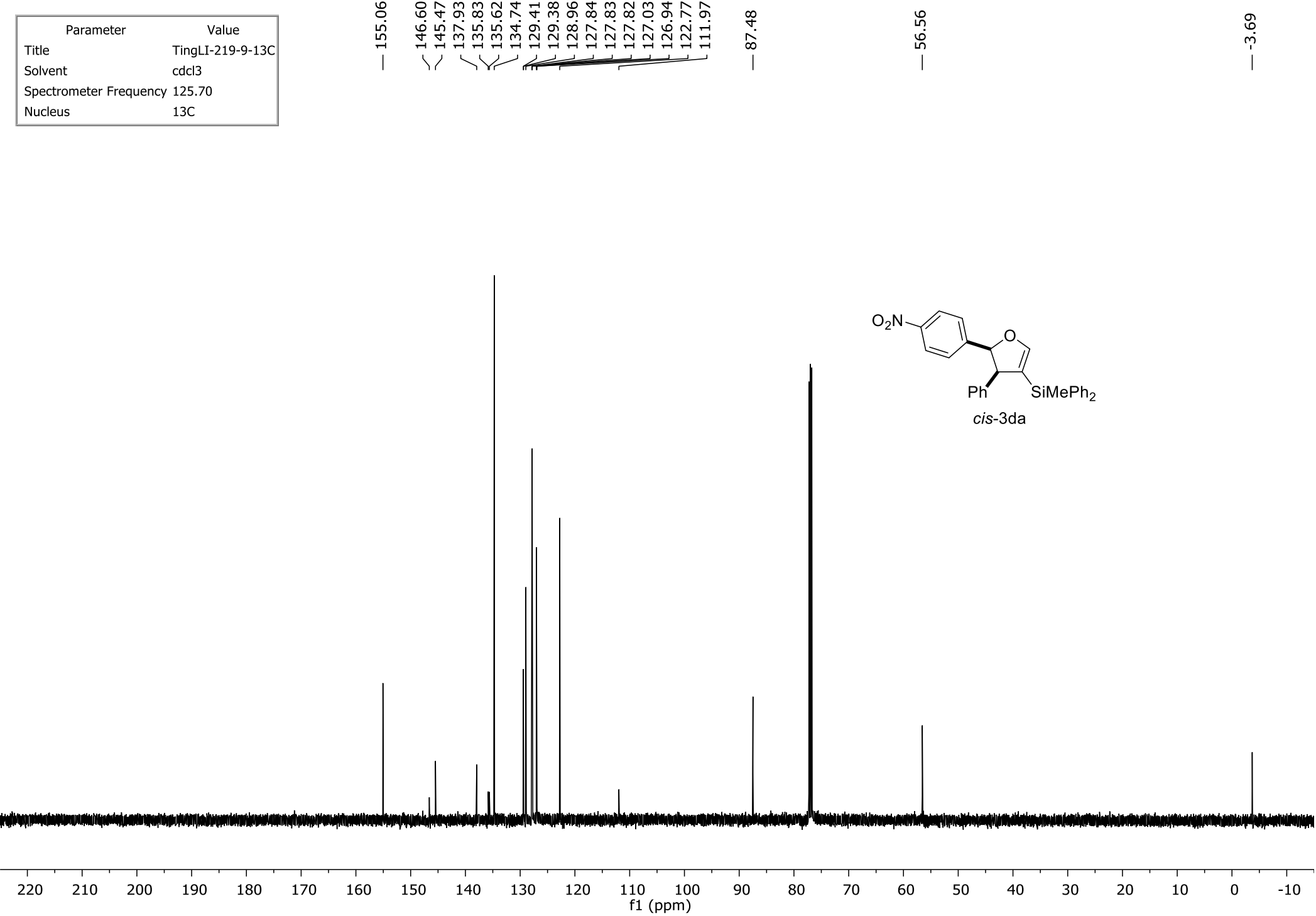


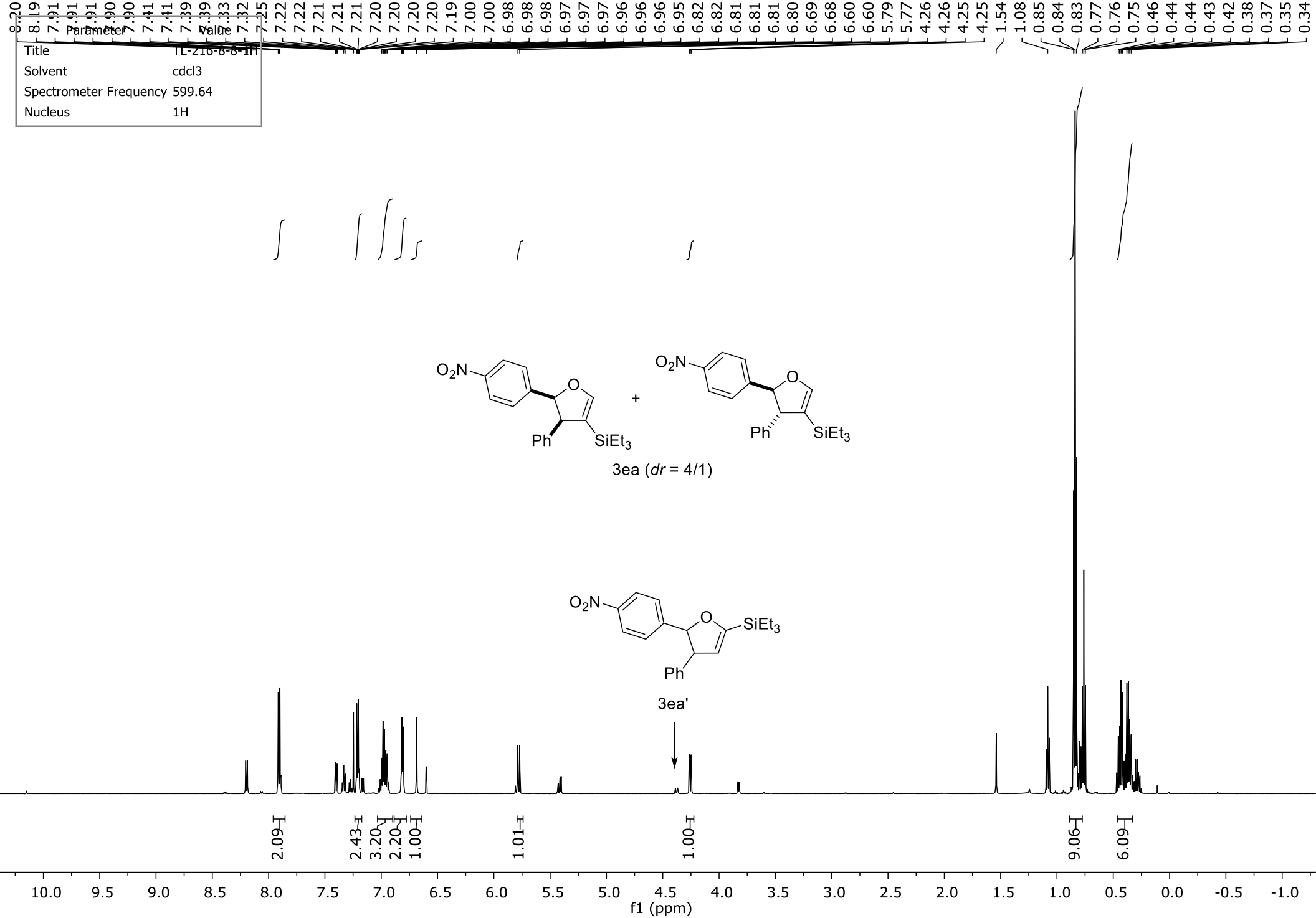
Parameter	Value
Title	lt-132-12-12-13c
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C





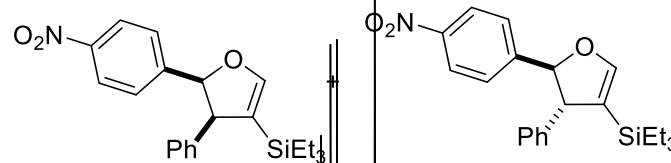
Parameter	Value
Title	TingLI-219-9-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C



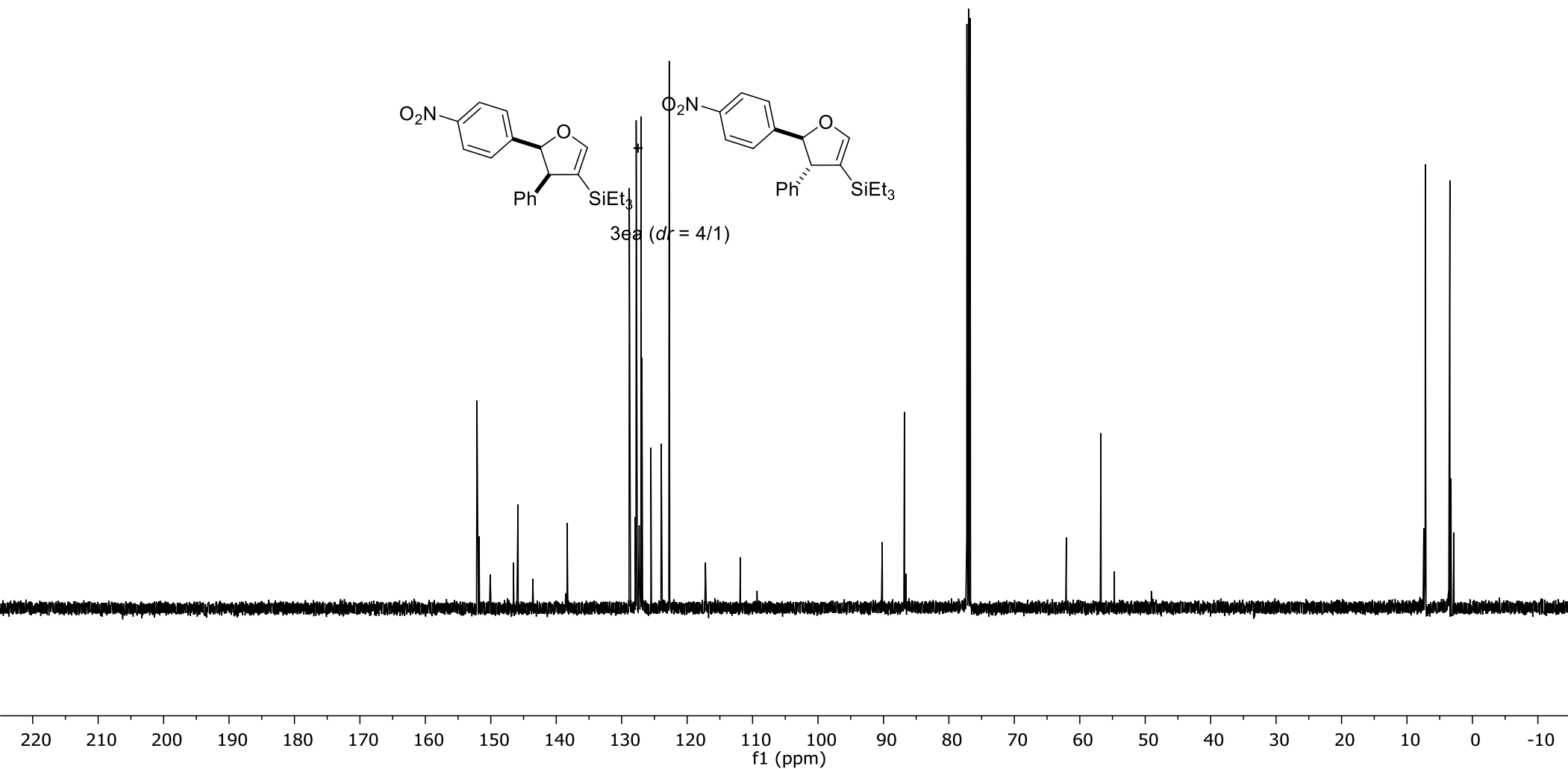


Parameter	Value
Title	TingLI-216-8-1-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C

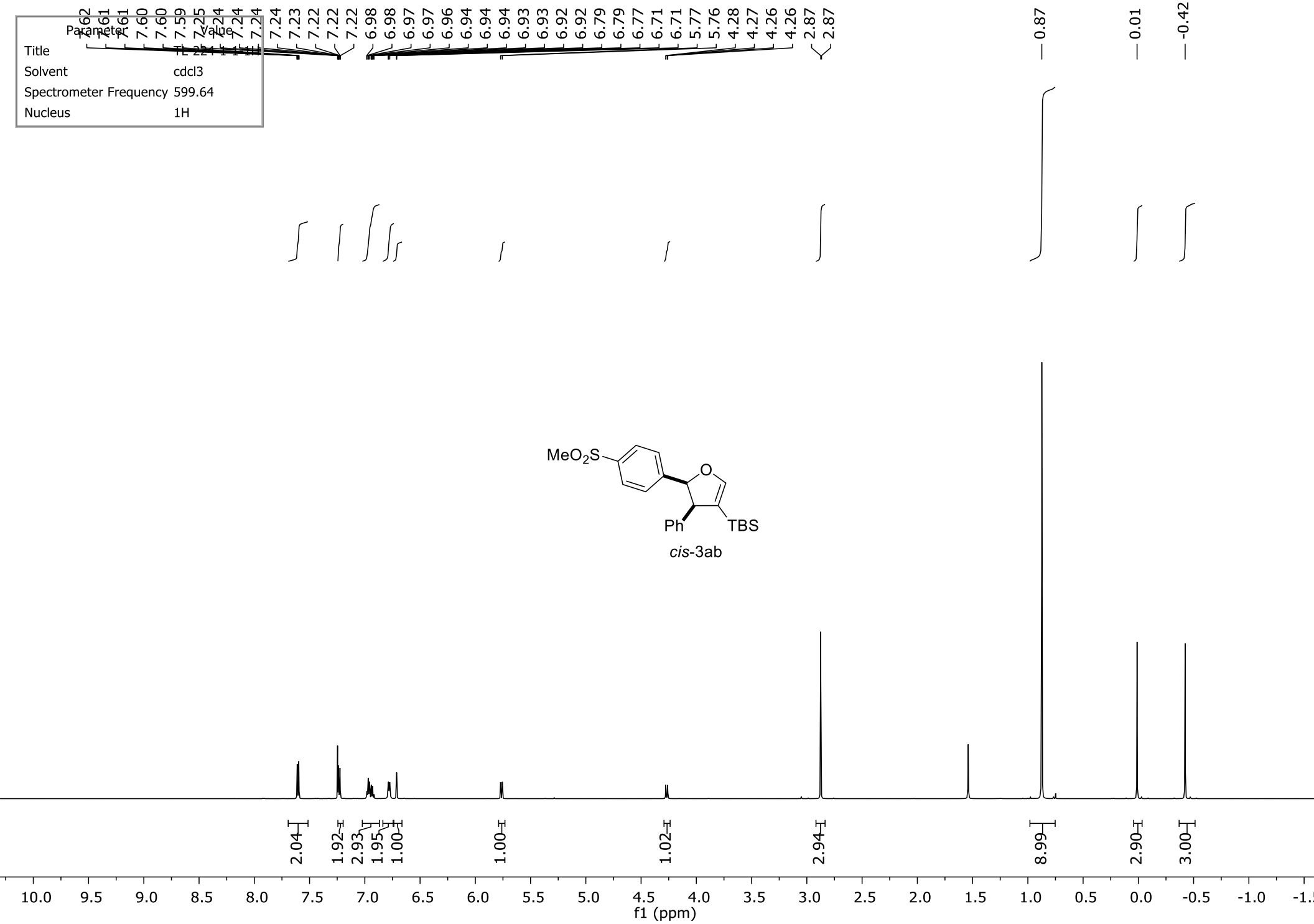
152.11	128.84	128.79	128.68	127.94	127.78	127.77	127.32	127.29	127.05	126.91	125.54	123.96	122.74	122.67	111.86	86.80	56.77	7.20	3.44
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—



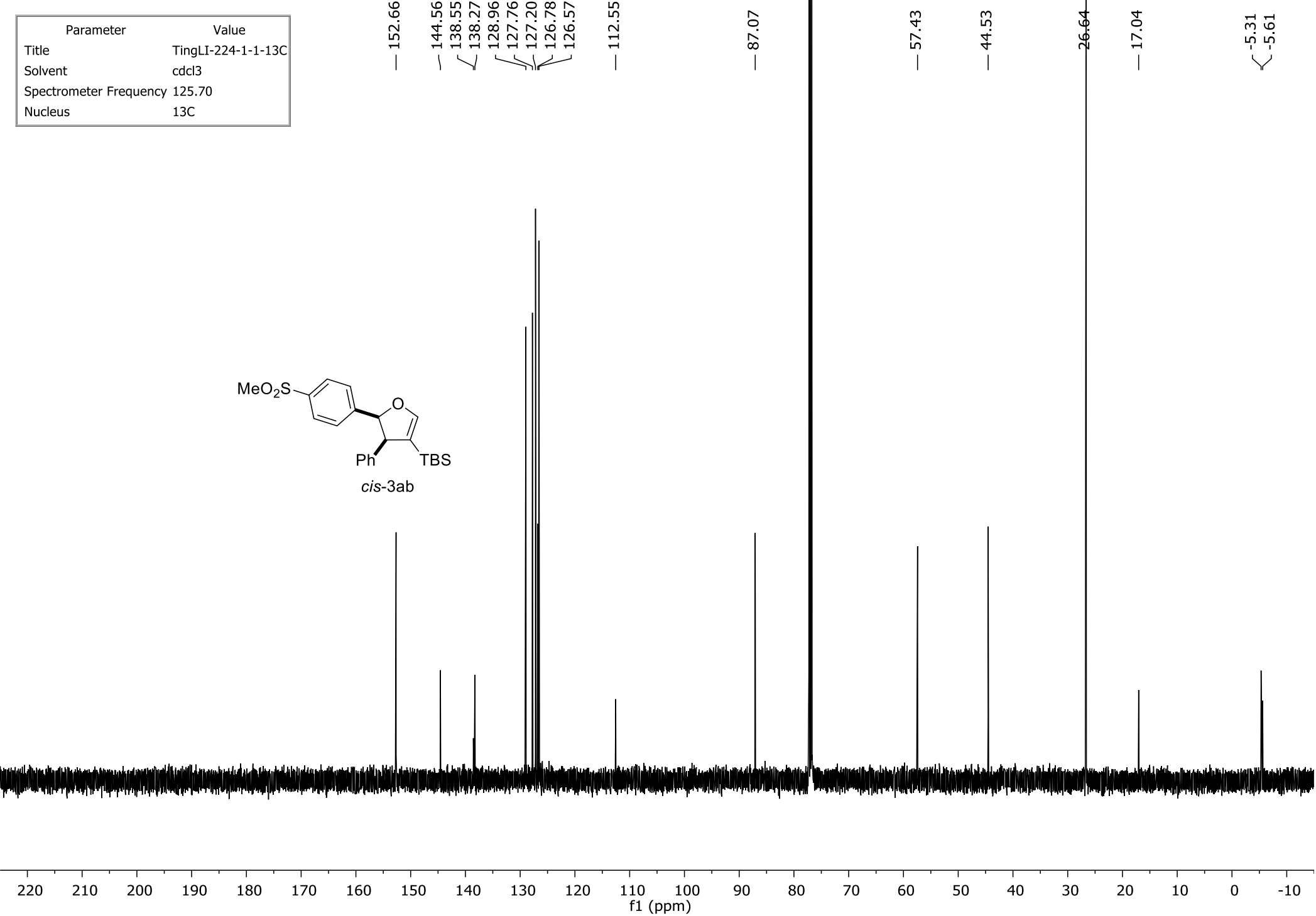
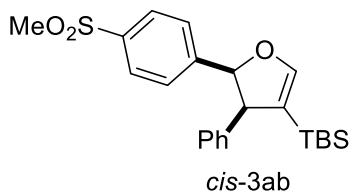
3e2 (dr = 4/1)



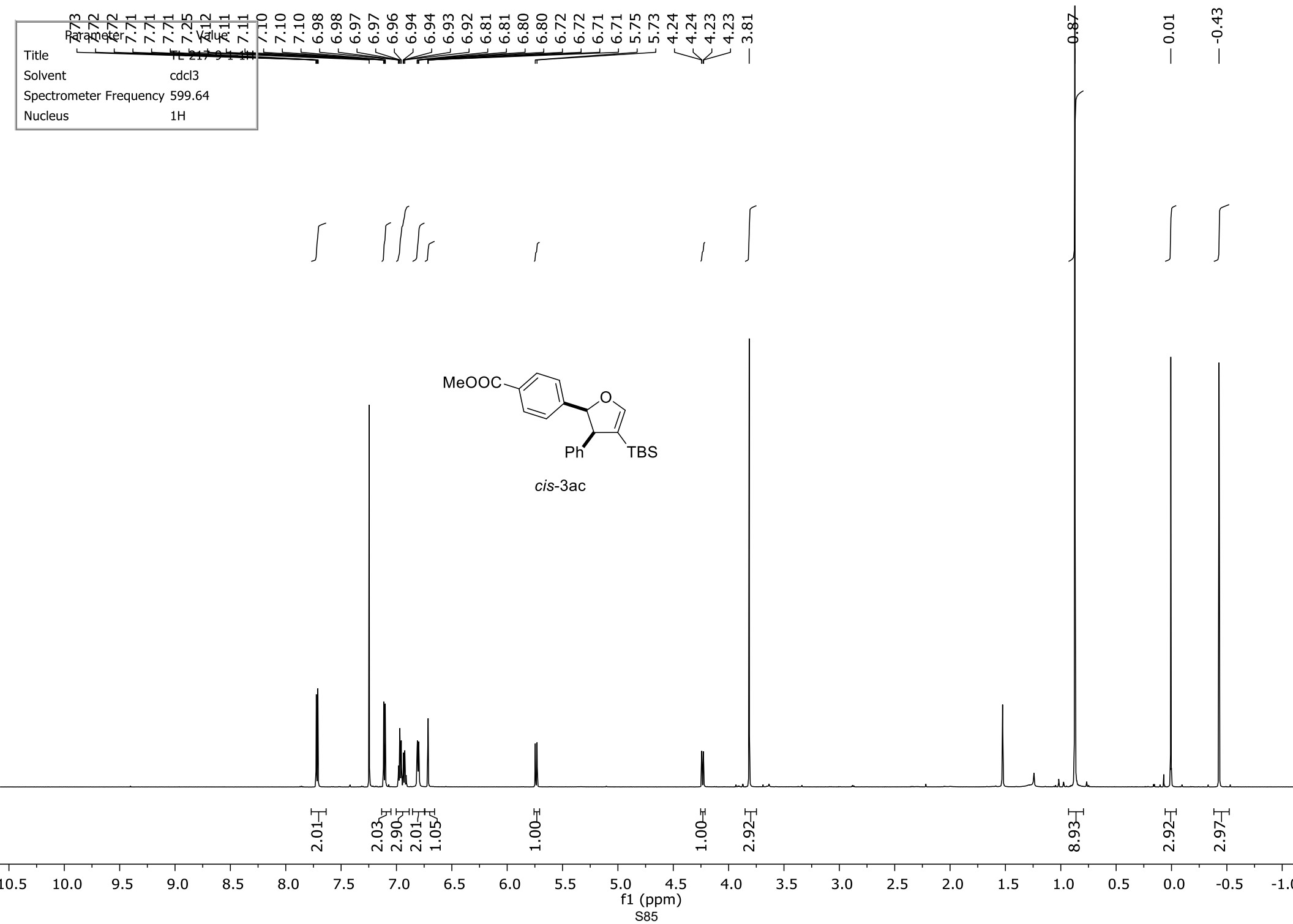
Title	Parameter
Solvent	cdcl3
Spectrometer Frequency	599.64
Nucleus	1H



Parameter	Value
Title	TingLI-224-1-1-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C

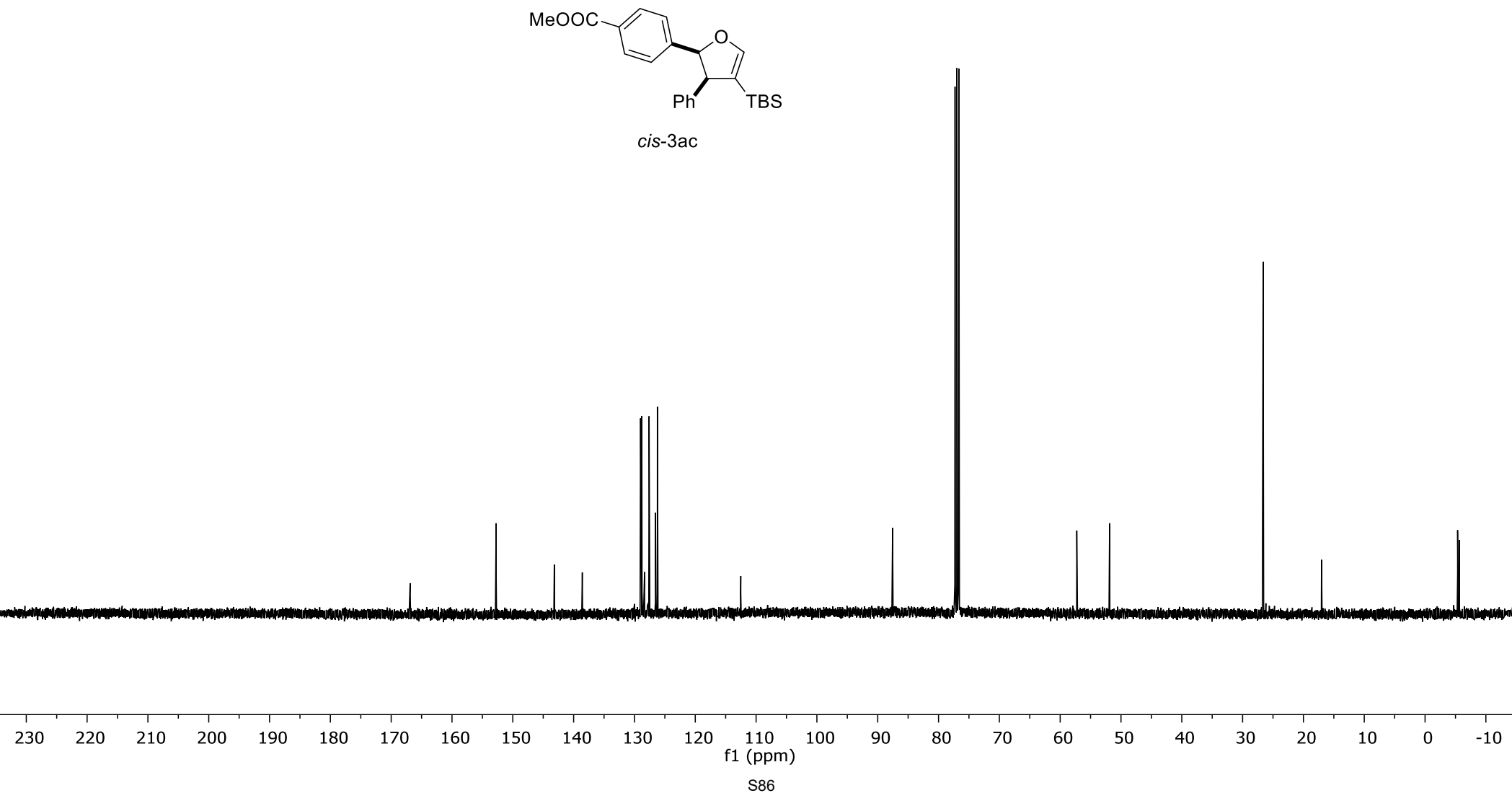
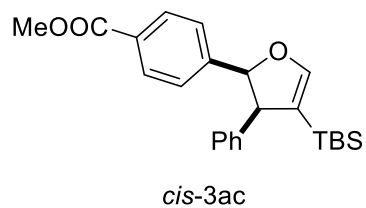


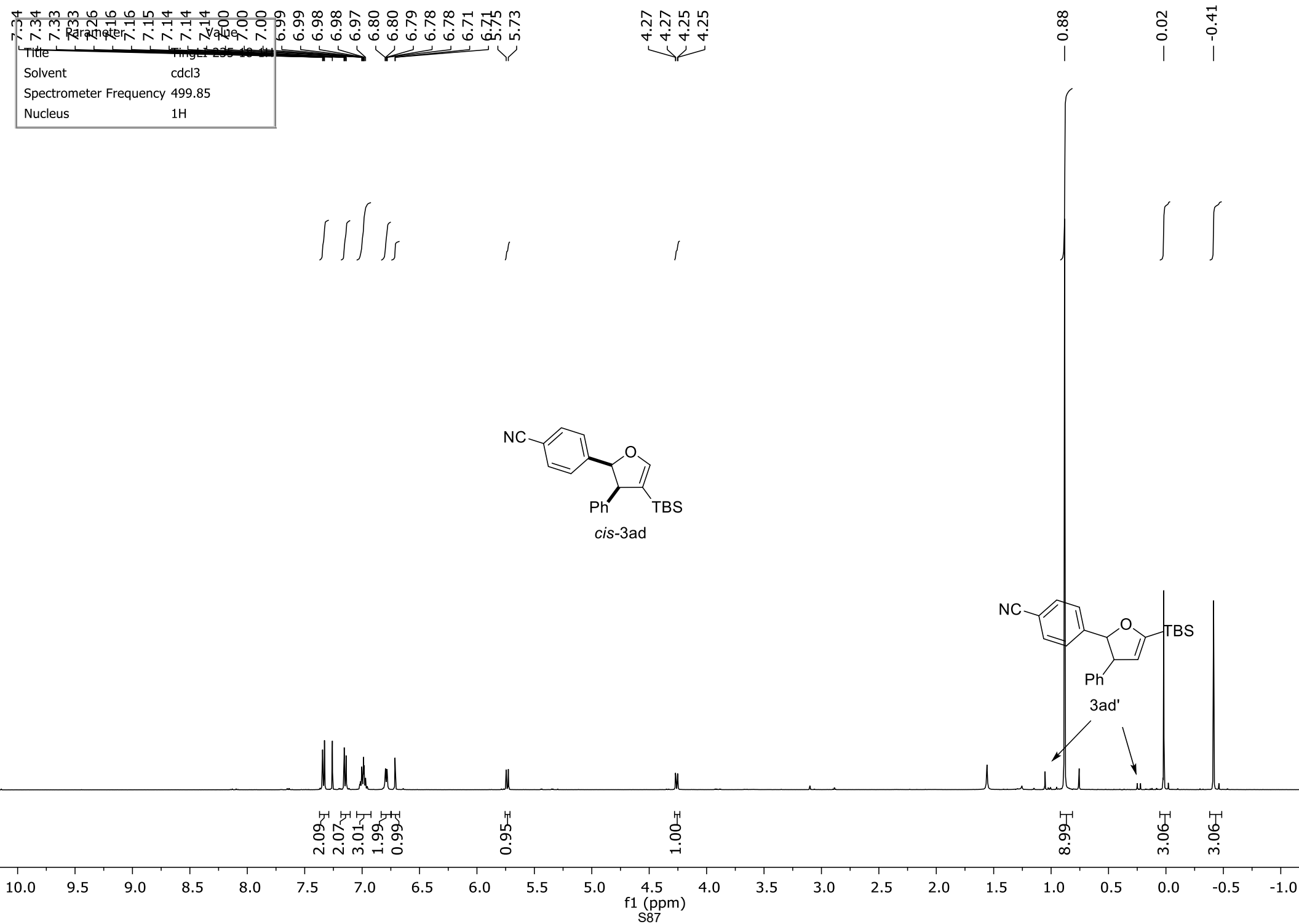
Title	Parameter
Solvent	cdcl3
Spectrometer Frequency	599.64
Nucleus	¹ H



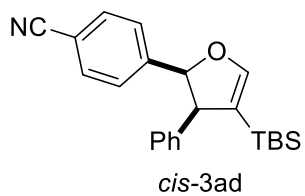
Parameter	Value
Title	TL-217-2-2-13c
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C

— 166.89
 — 152.75
 143.18
 138.57
 129.00
 128.79
 128.75
 128.34
 127.59
 126.54
 126.49
 126.23
 — 112.52
 — 87.55
 — 57.27
 — 51.87
 — 26.63
 — 17.02
 —5.35
 —5.64





Parameter	Value
Title	TingLI-235-18-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	¹³ C



152.63
143.57
138.29
132.53
131.32
128.94
128.69
127.78
126.95
126.82
118.86
112.58
110.38

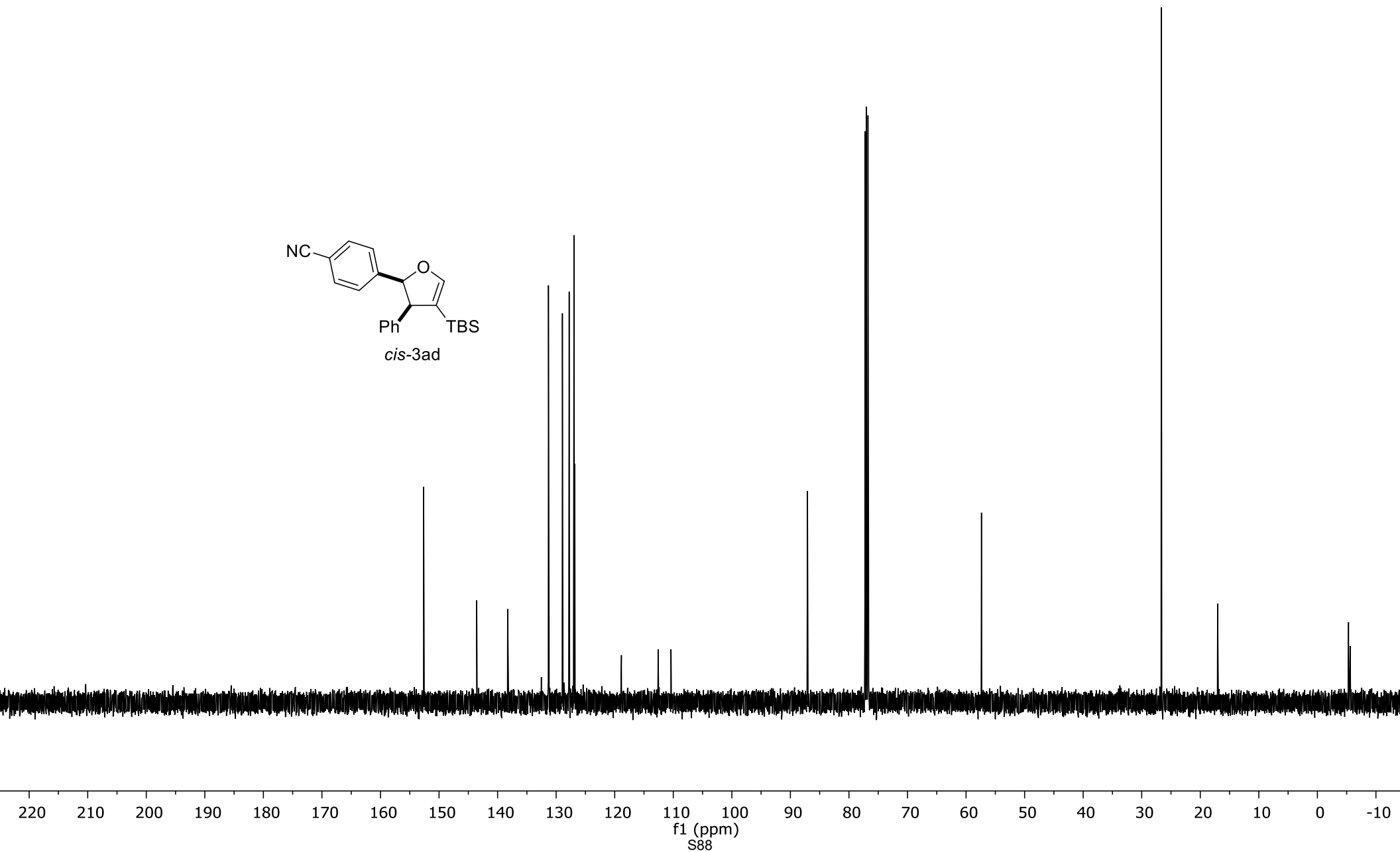
— 87.08

— 57.37

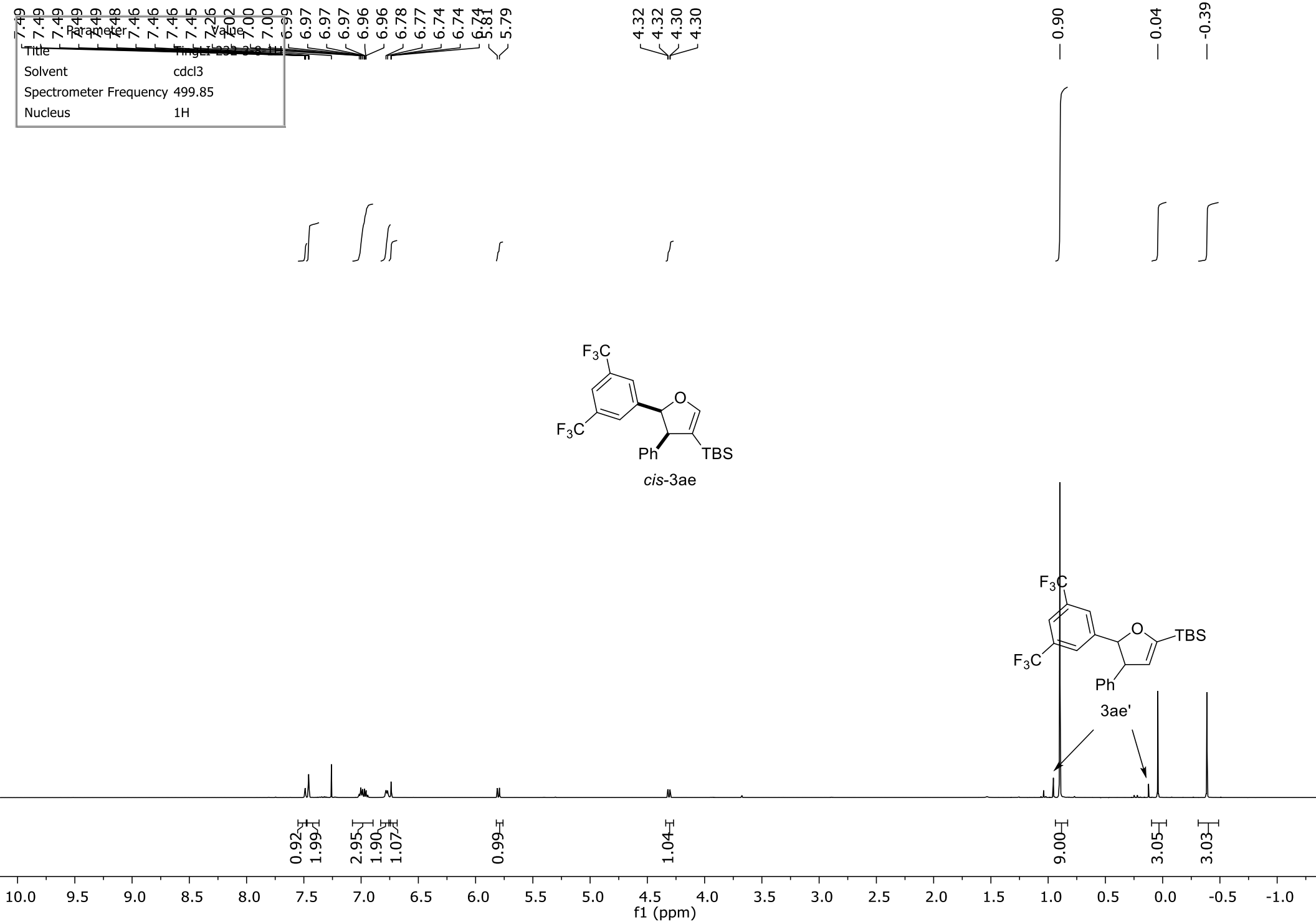
26.64
26.59

— 17.04

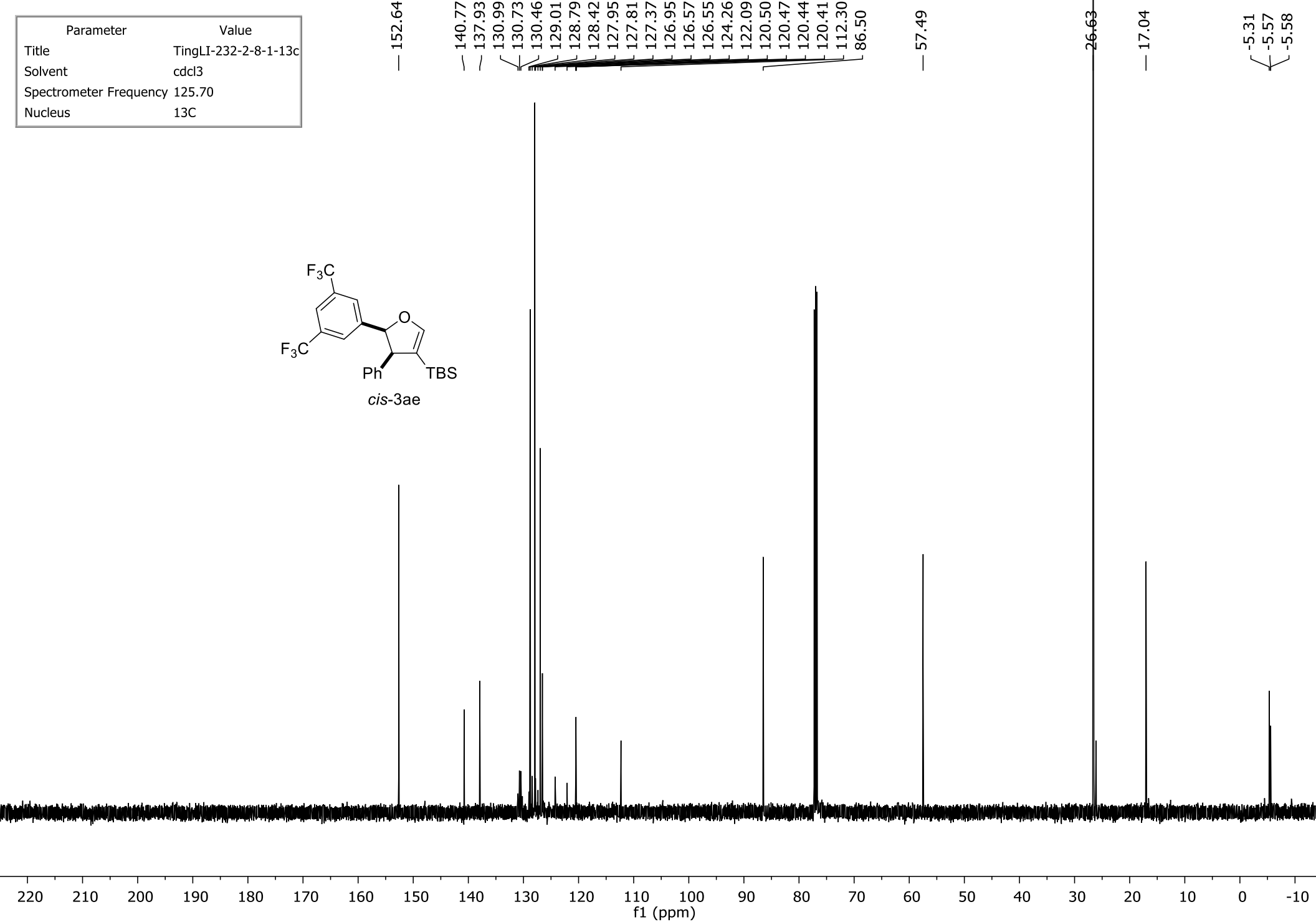
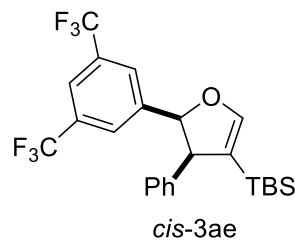
-5.32
-5.61



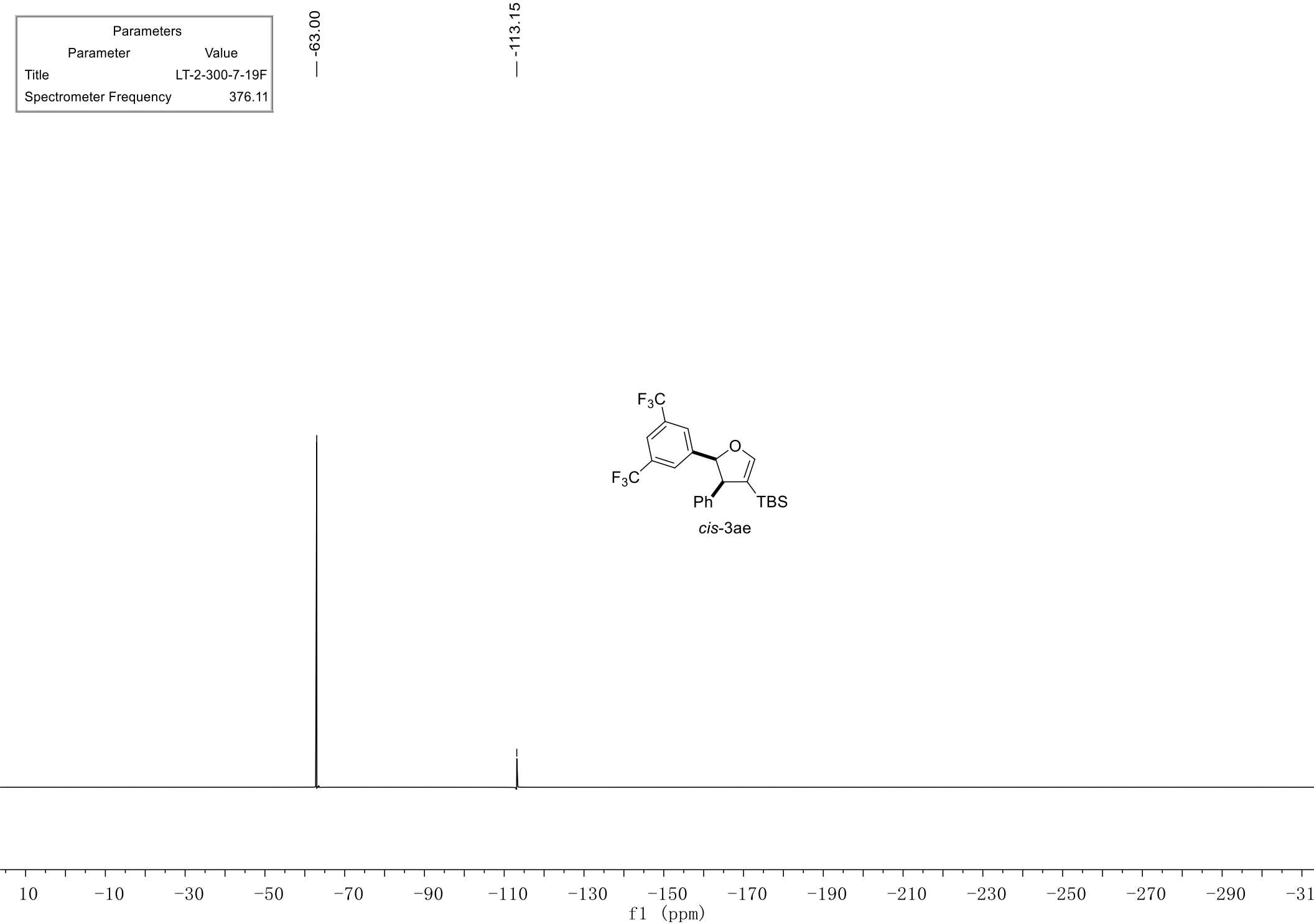
Title	1235-318-11
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	1H



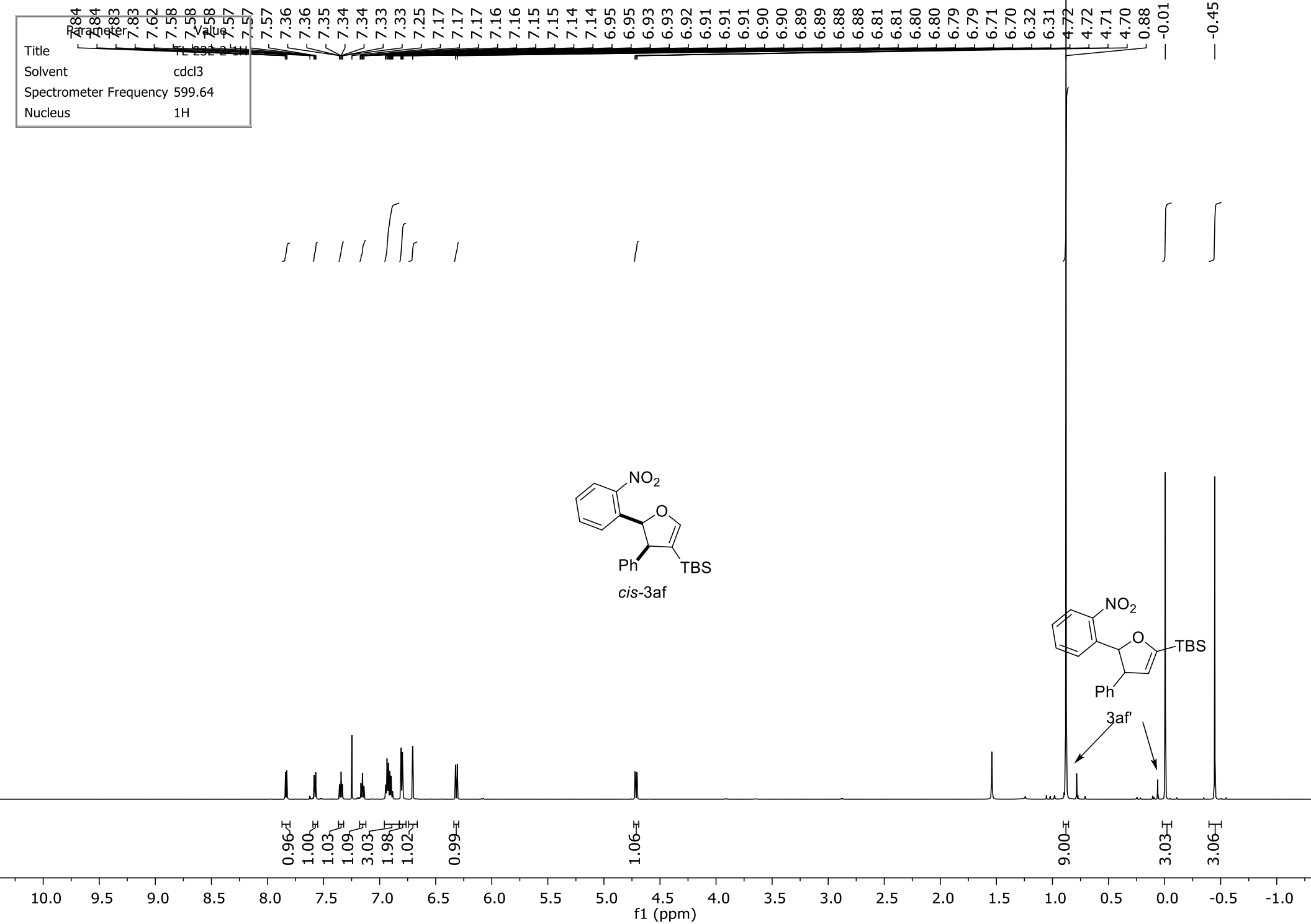
Parameter	Value
Title	TingLI-232-2-8-1-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	¹³ C



Parameters		
Parameter	Value	
Title	LT-2-300-7-19F	
Spectrometer Frequency	376.11	

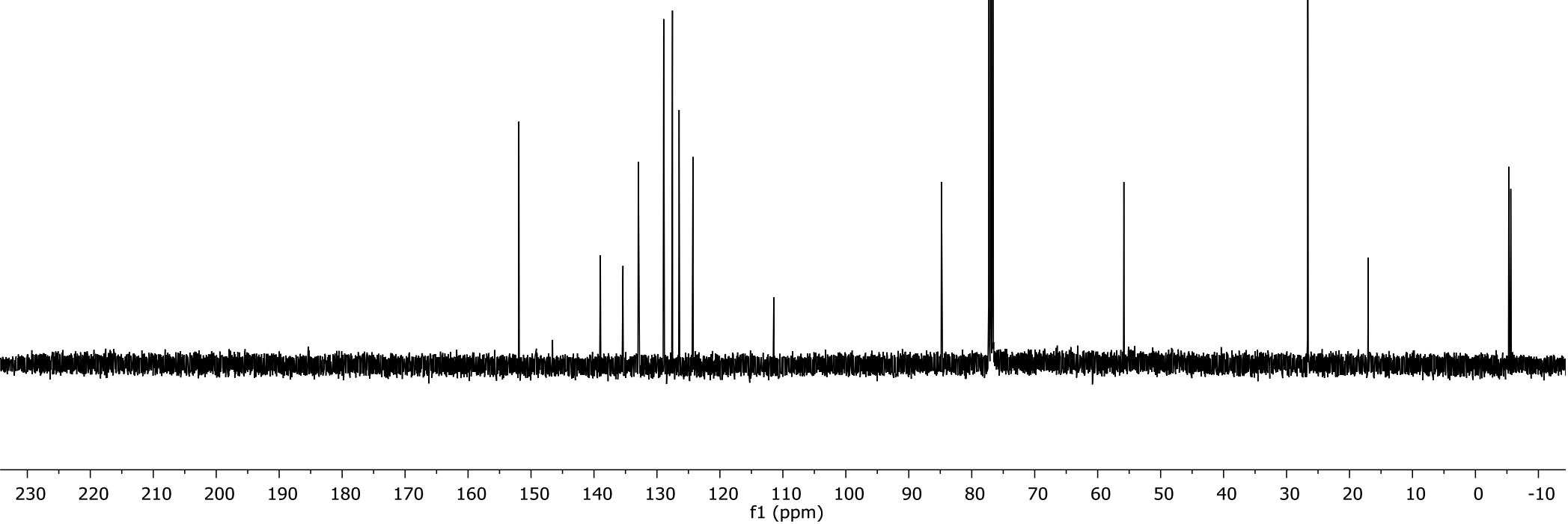
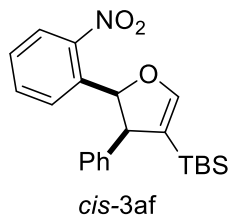


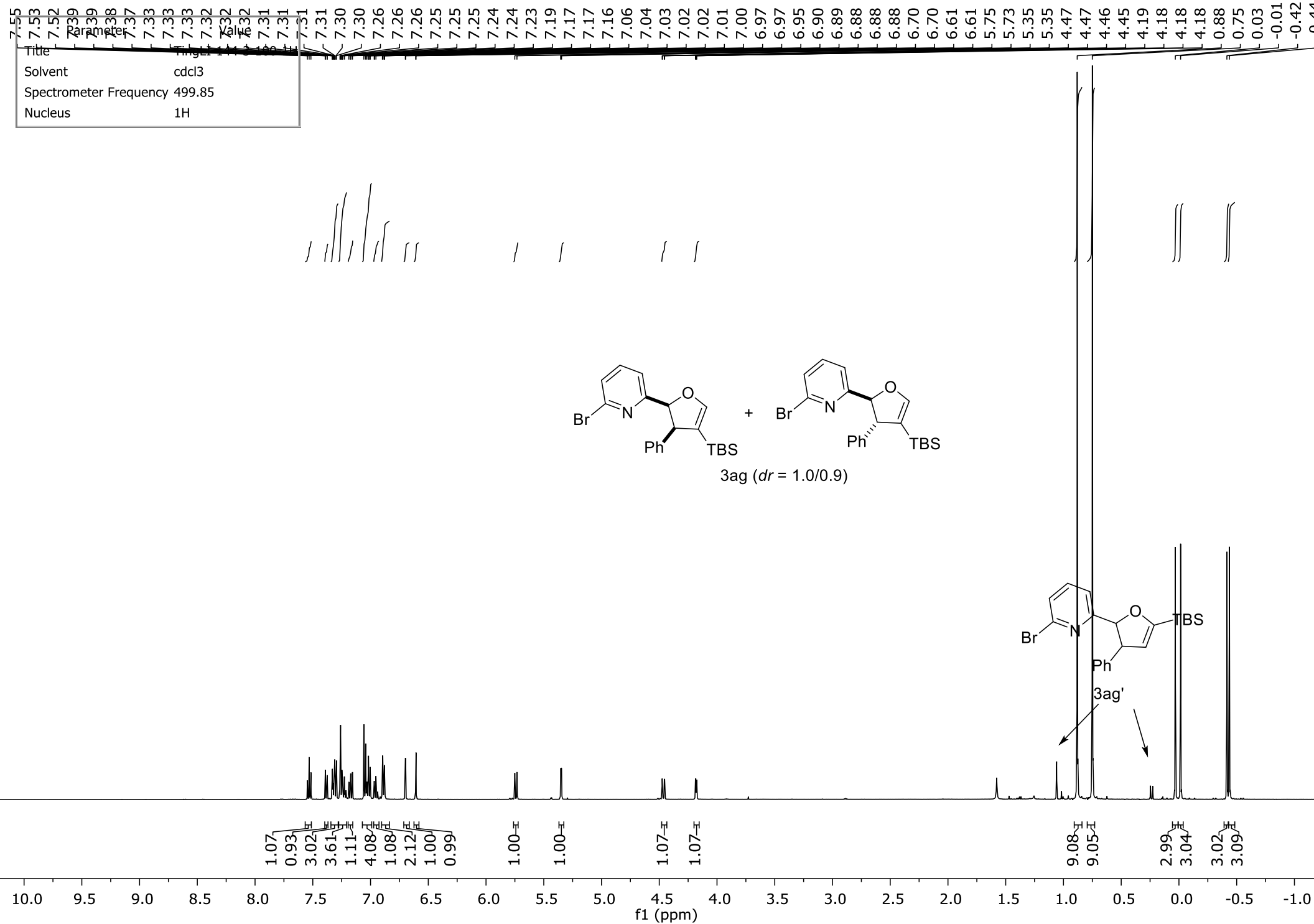
Title	FL 232-2-11
Solvent	cdcl3
Spectrometer Frequency	599.64
Nucleus	1H



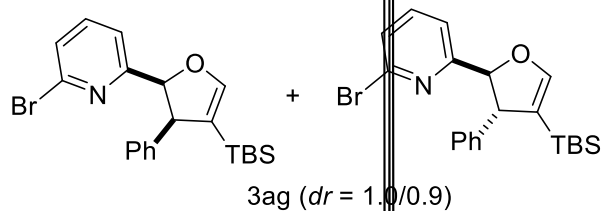
Parameter	Value
Title	LT-231-2-13c
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C

— 151.93 — 146.58 — 138.99 — 135.39 — 132.96 — 128.93 — 128.89 — 127.59 — 127.54 — 126.48 — 124.28 — 111.44 —
 — 84.81 — 55.84 — 26.64 — 17.05 — -5.29 — -5.61





Parameter	Value
Title	TingLI-144-3-100-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C

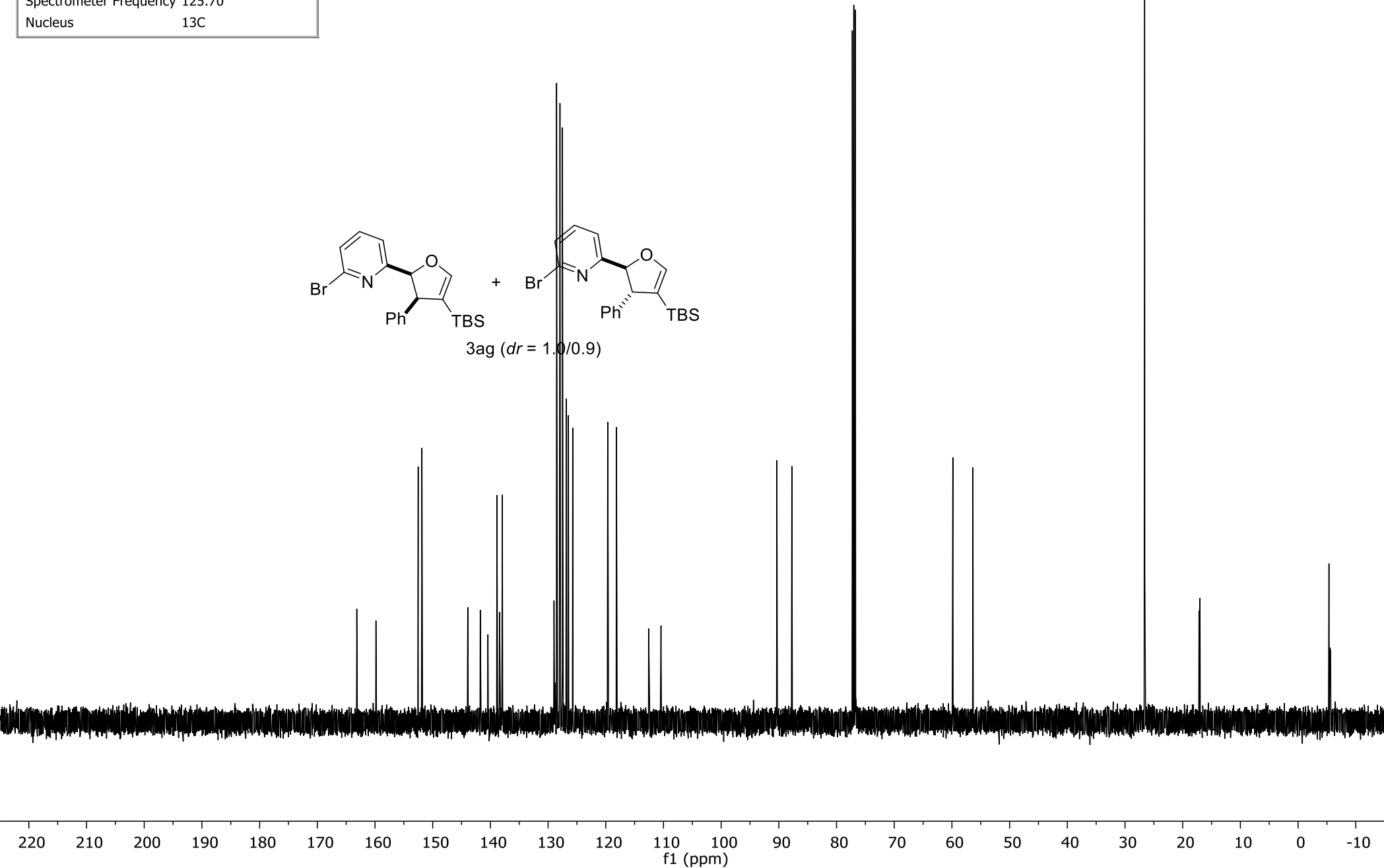


163.16
 159.84
 152.51
 151.87
 143.92
 141.75
 140.42
 138.87
 138.42
 137.93
 128.97
 128.53
 127.94
 127.52
 126.89
 126.84
 126.48
 125.73
 119.66
 118.16
 112.57
 110.43
 90.34
 87.74

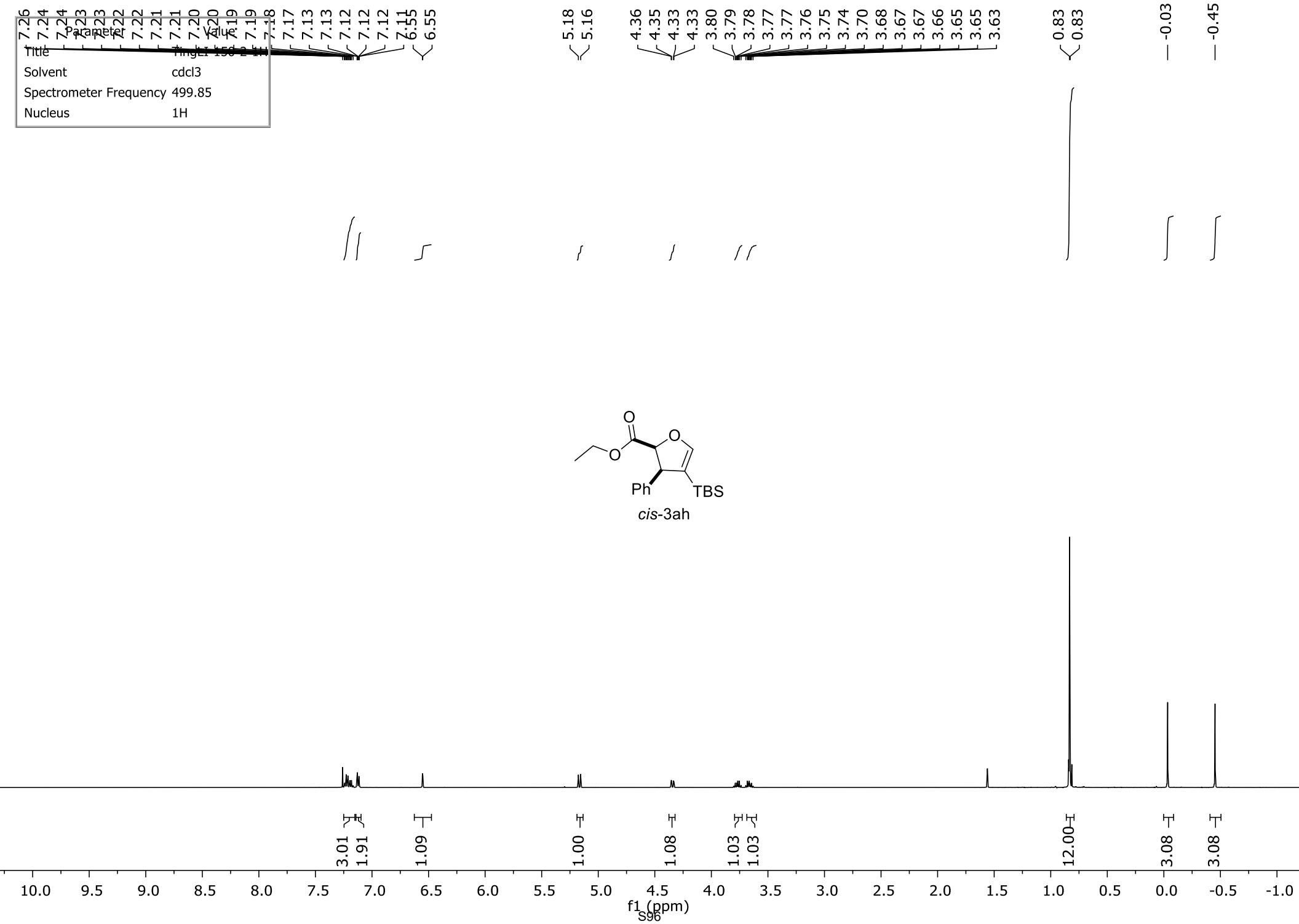
59.84
 56.36

26.60
 26.58
 17.17
 17.00

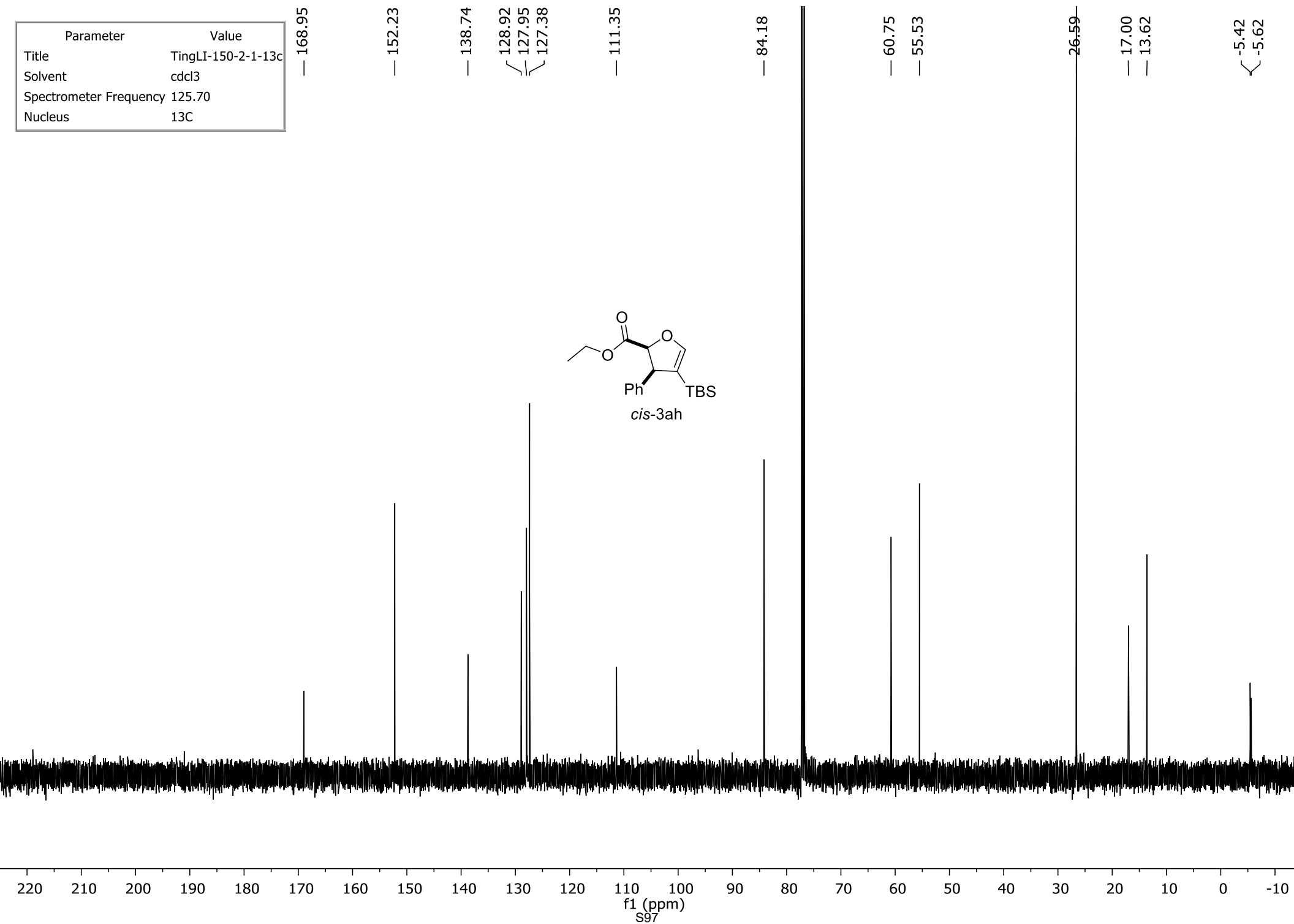
-5.35
 -5.51
 -5.64



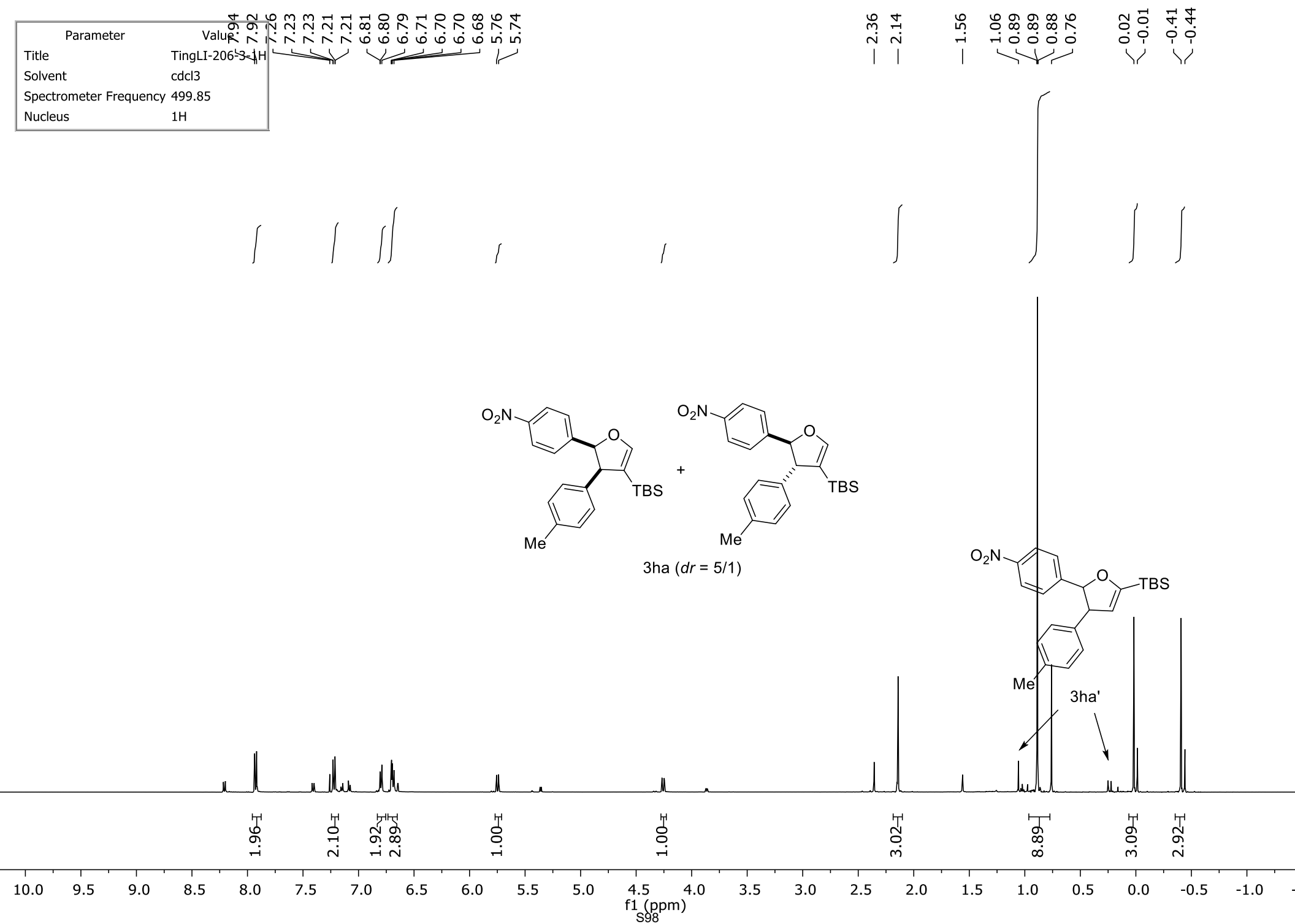
Title	AngLi 158-2-11
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	1H



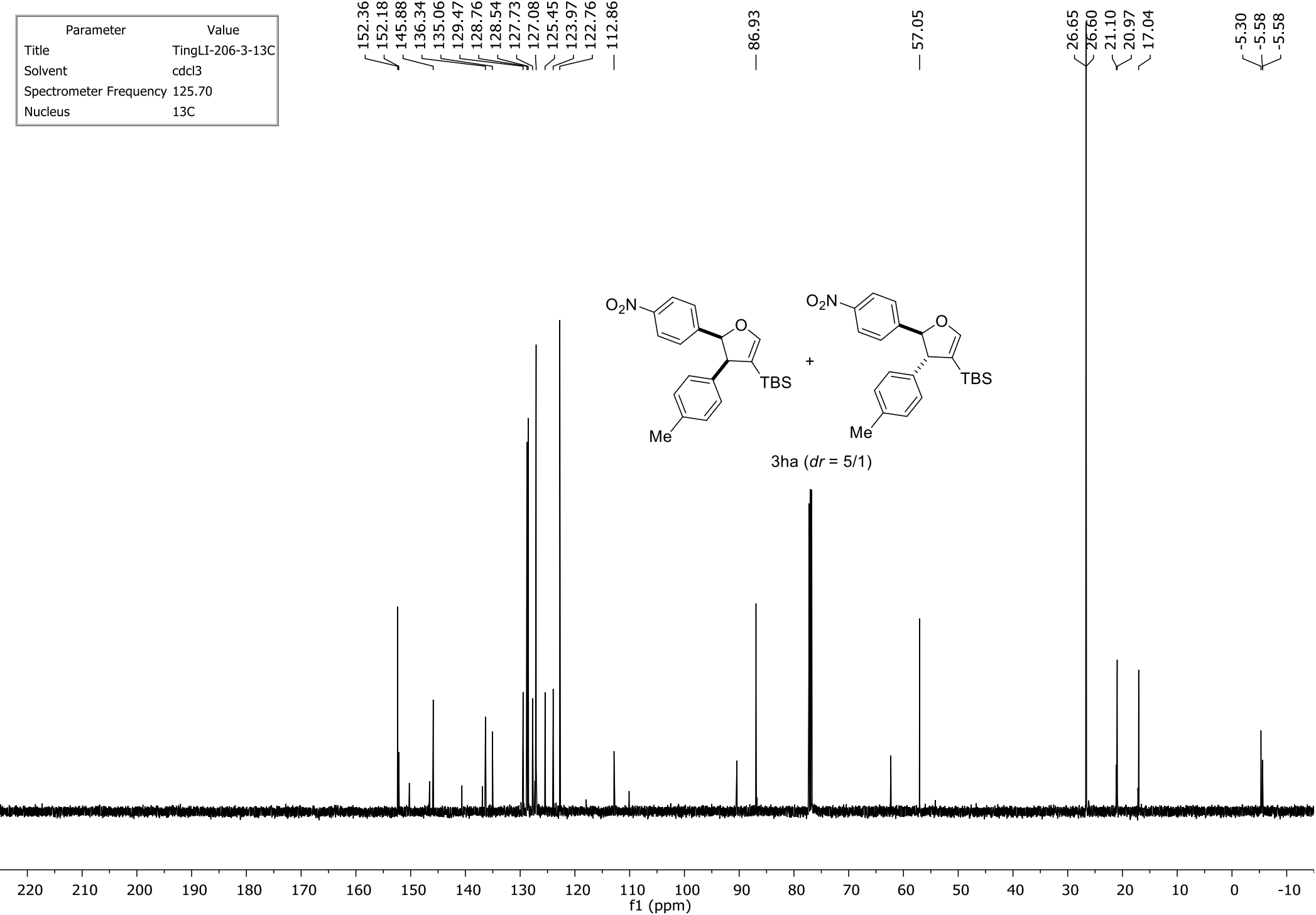
Parameter	Value
Title	TingLI-150-2-1-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C



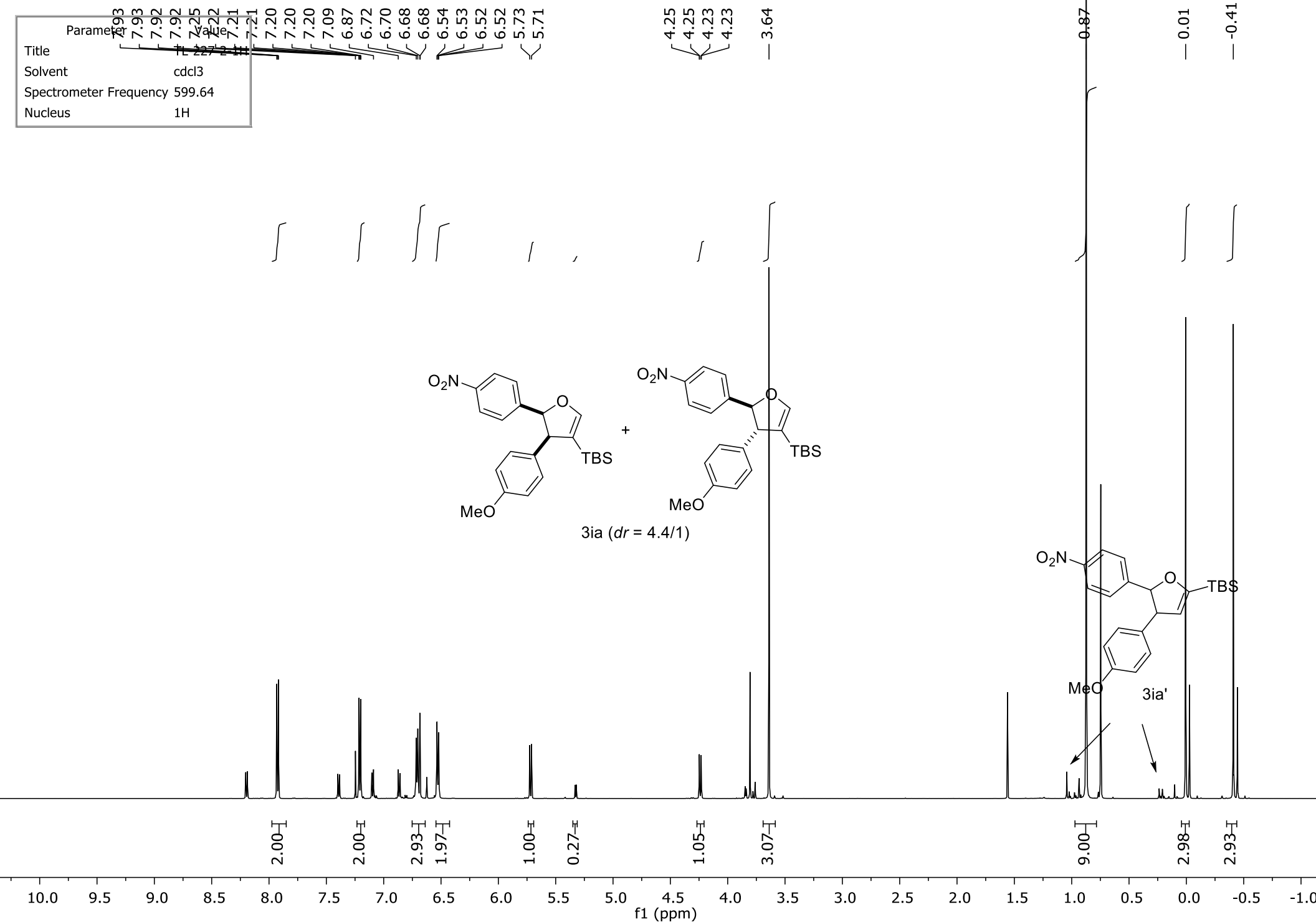
Parameter	Value
Title	TingLI-2063-1H
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	¹ H



Parameter	Value
Title	TingLI-206-3-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C

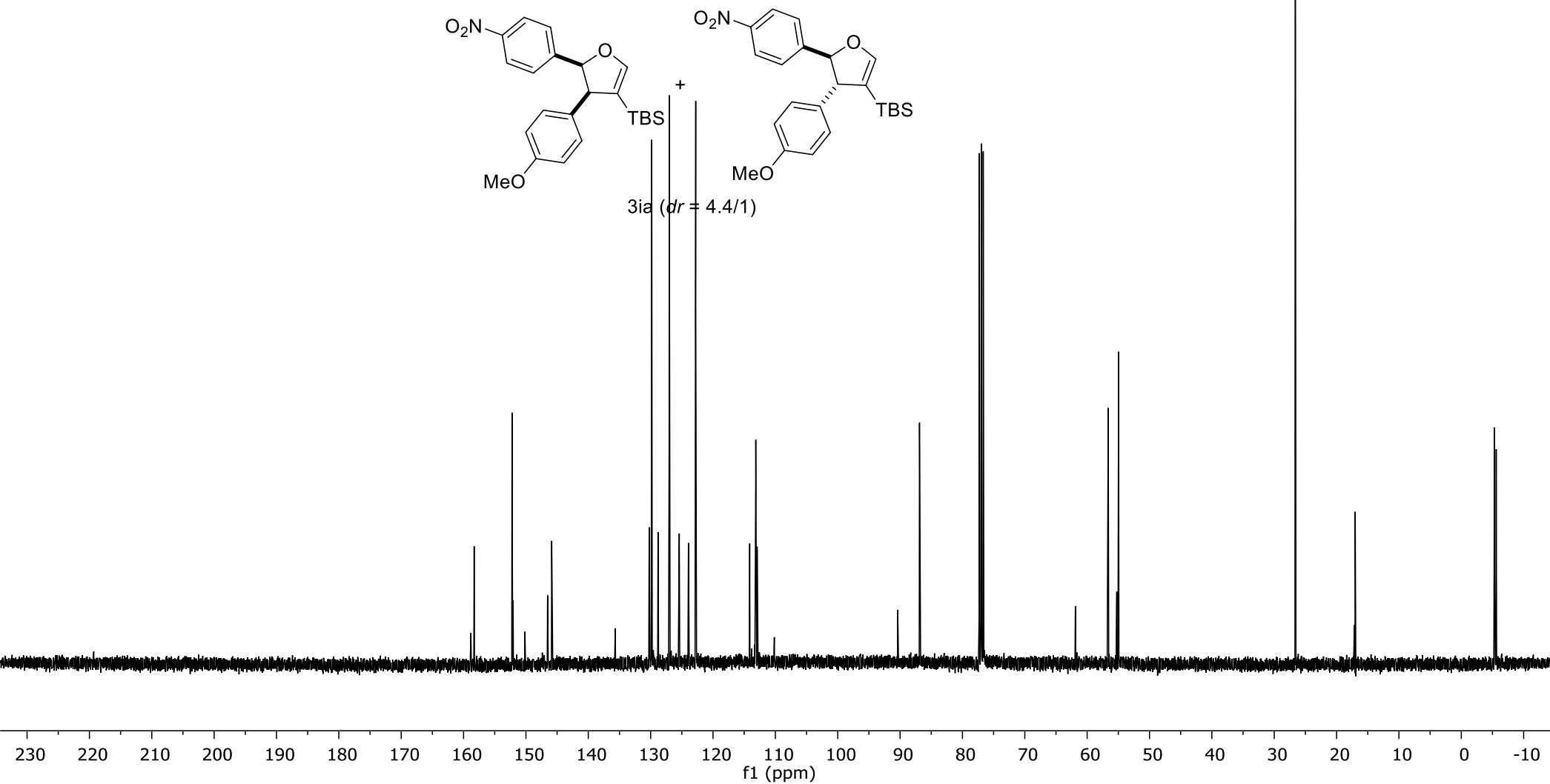
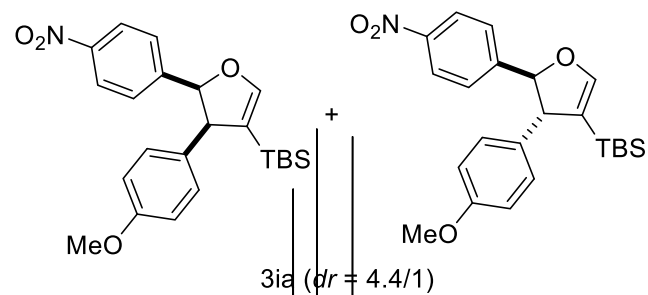


Parameter	Value
Title	FL 227 2-1H
Solvent	cdcl3
Spectrometer Frequency	599.64
Nucleus	1H

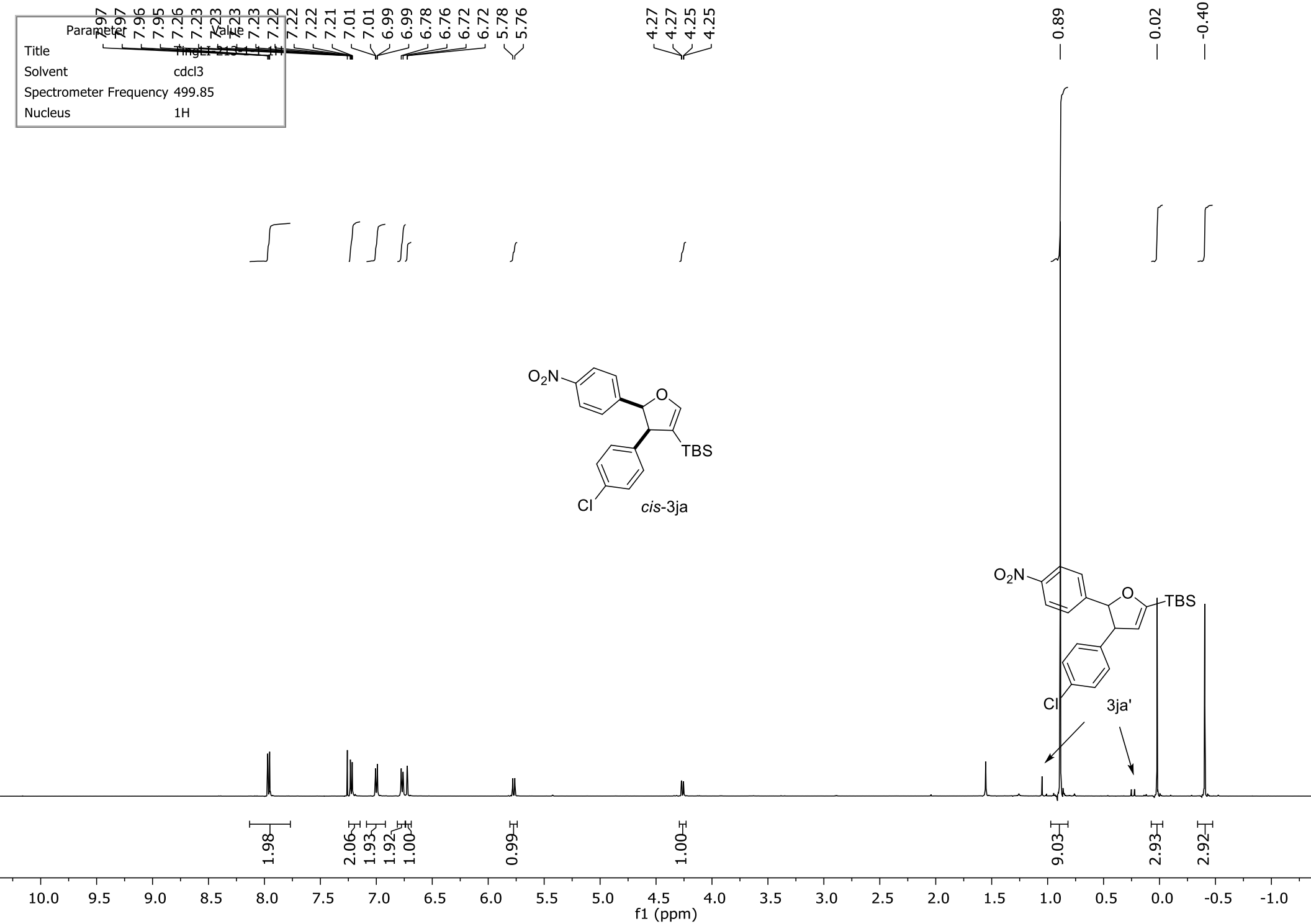


Parameter	Value
Title	LT227-2-1-1-400NMR-13c
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	13C

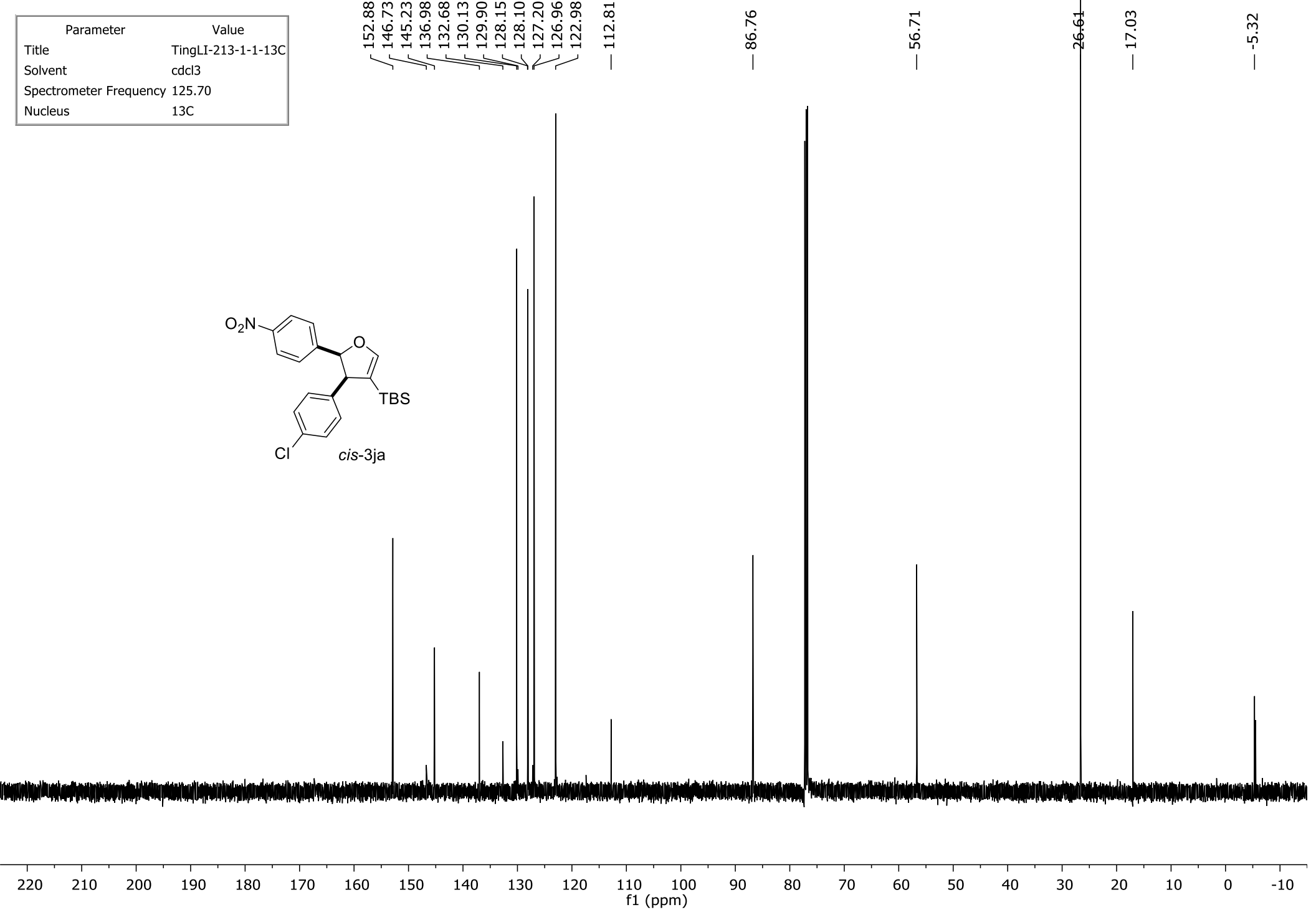
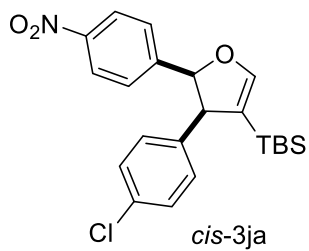
158.30
 152.23
 152.06
 146.53
 145.87
 130.23
 129.83
 128.81
 127.02
 125.41
 123.94
 122.77
 114.12
 113.14
 112.92
 — 86.89
 56.62
 54.96
 26.62
 — 17.01
 -5.33
 -5.60



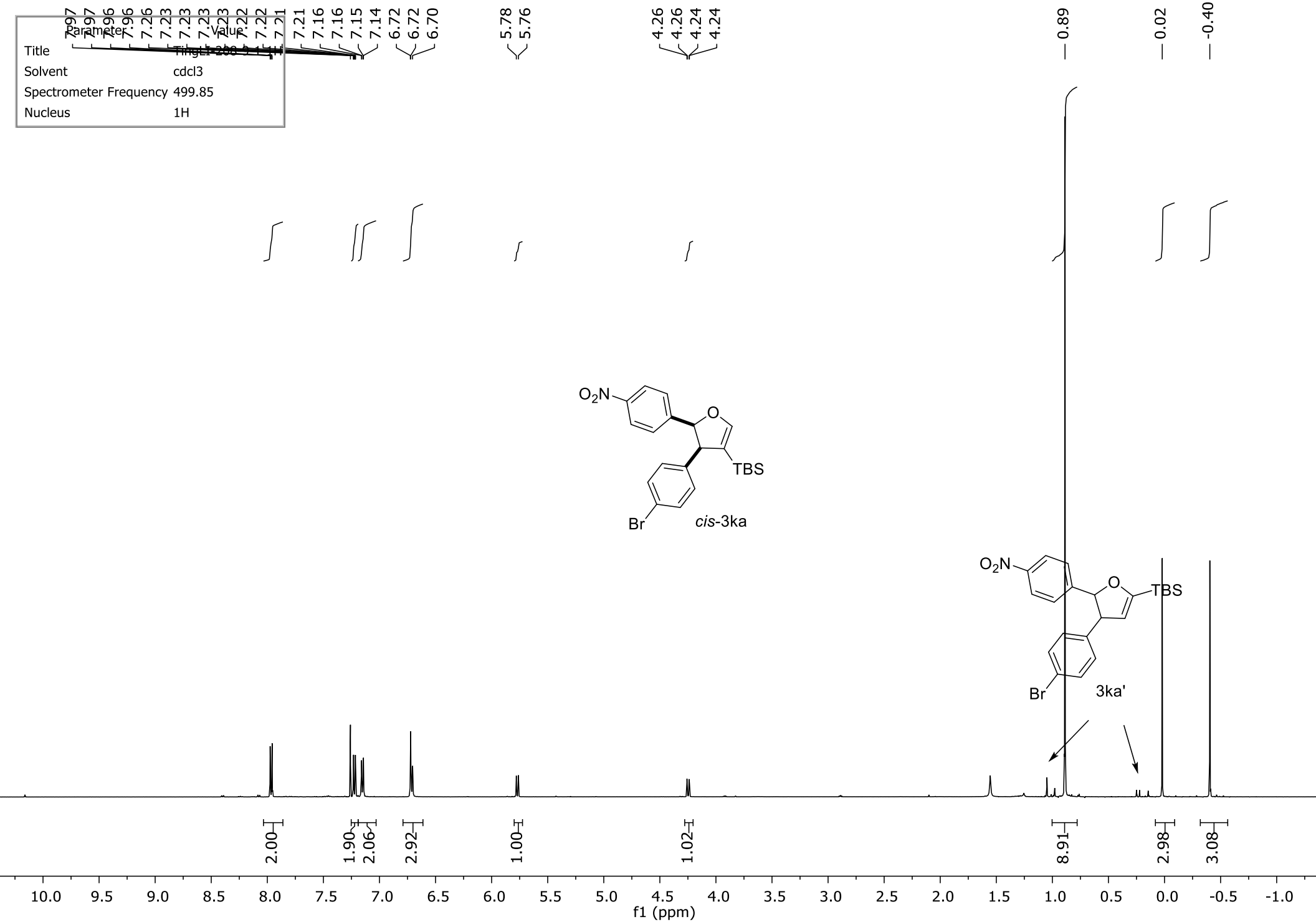
Parameter	Value
Title	1
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	¹ H



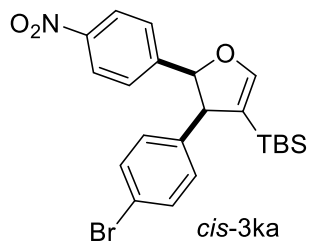
Parameter	Value
Title	TingLI-213-1-1-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C



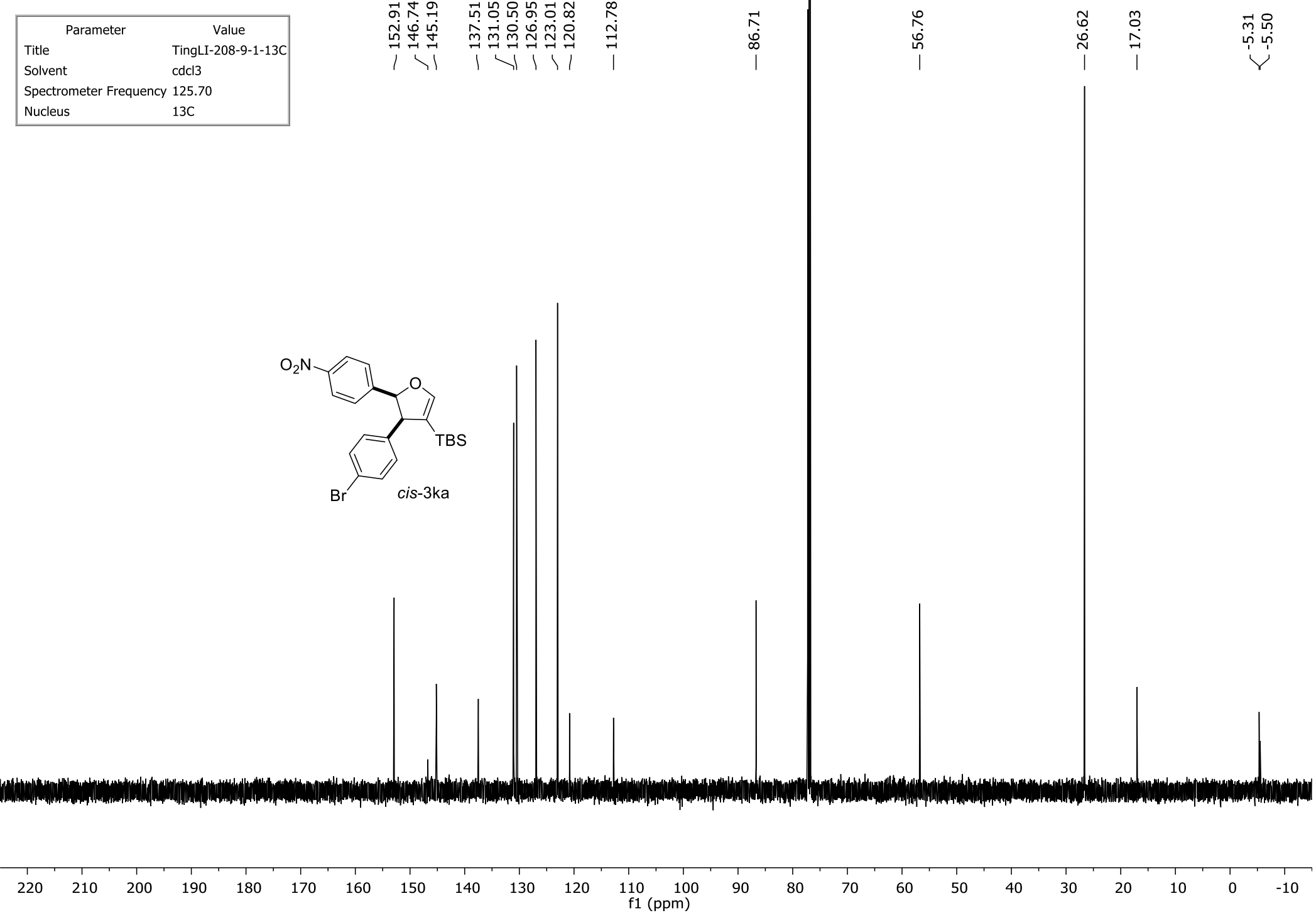
Title	Sample 1
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	¹ H

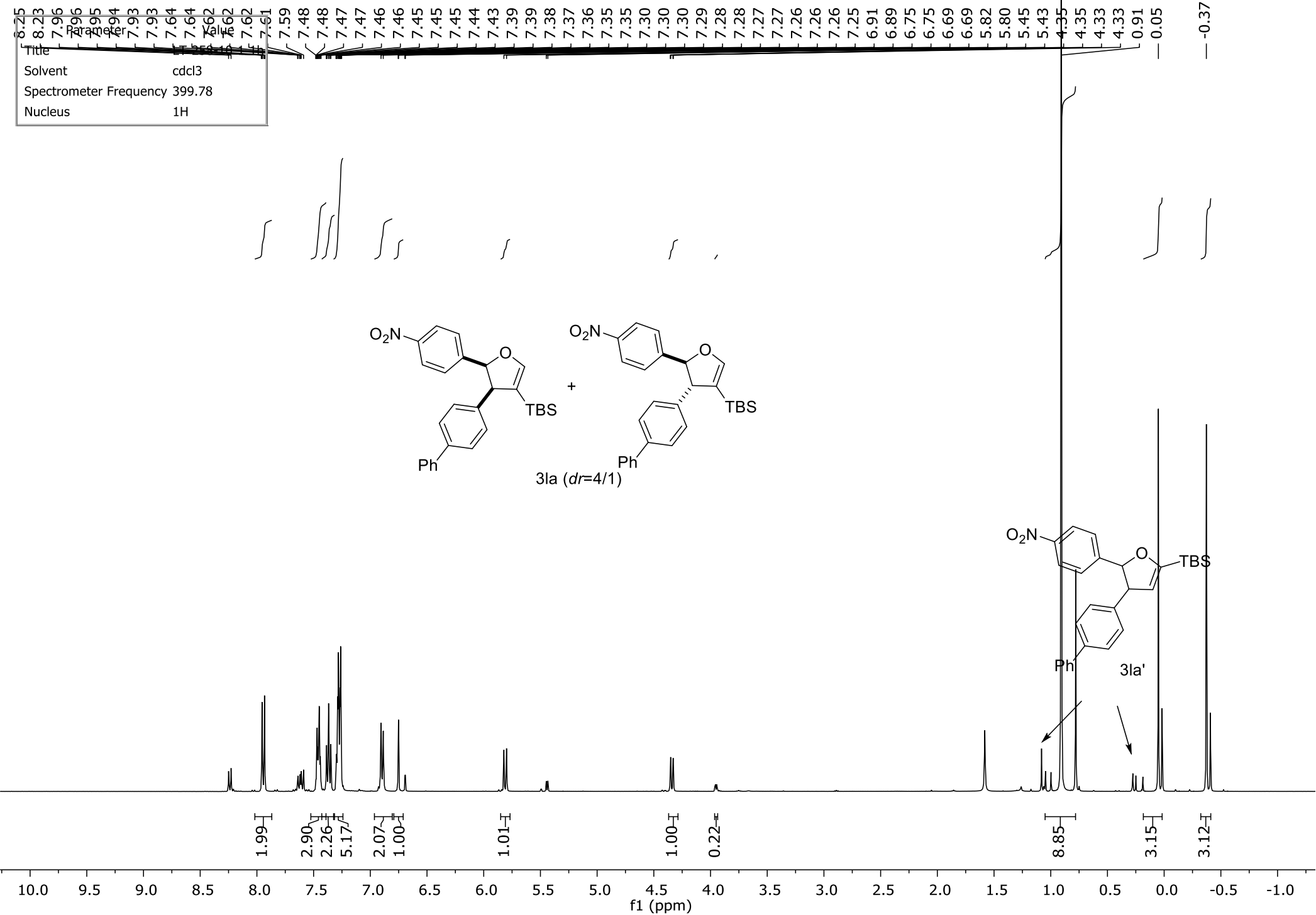


Parameter	Value
Title	TingLI-208-9-1-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	¹³ C

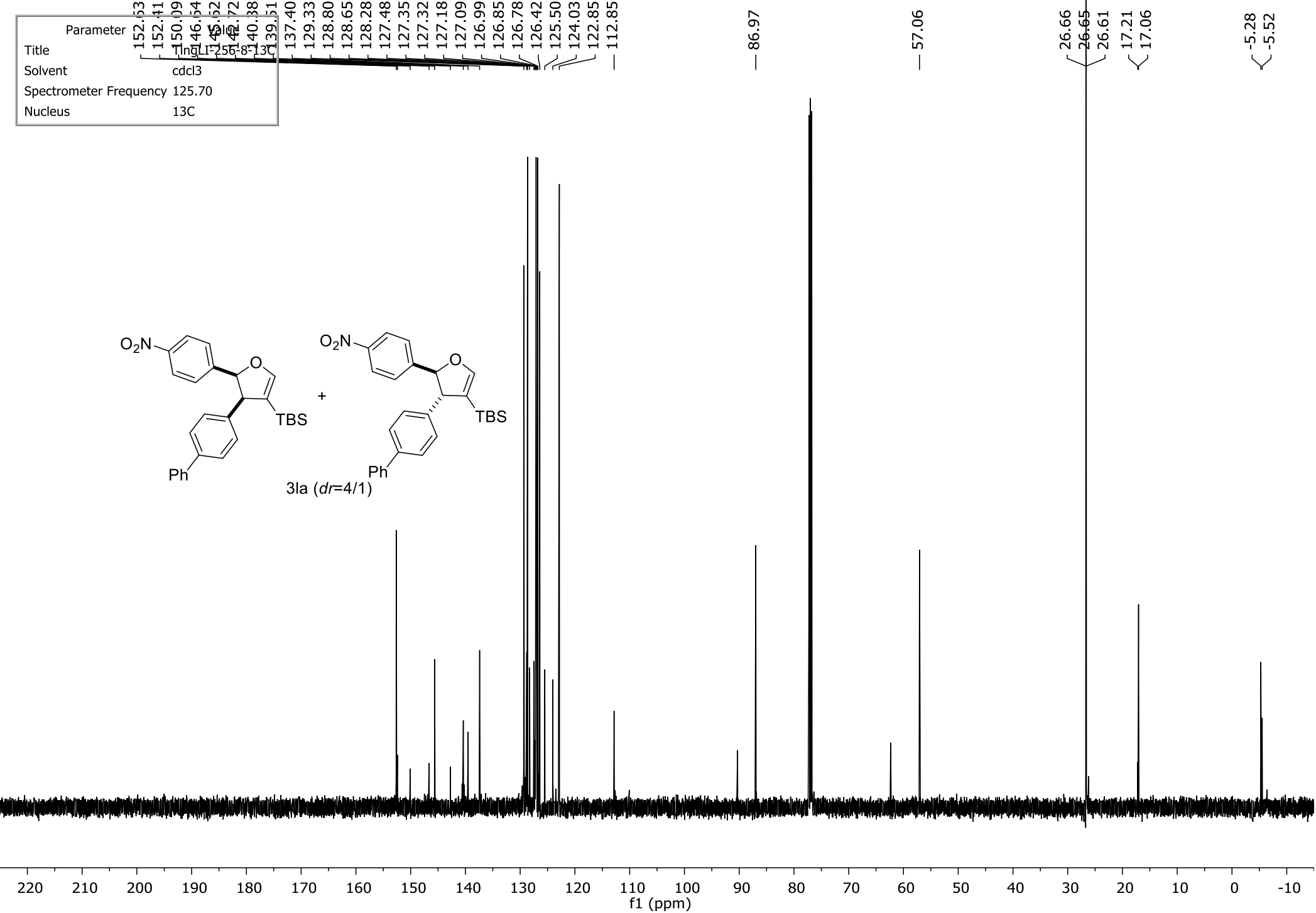
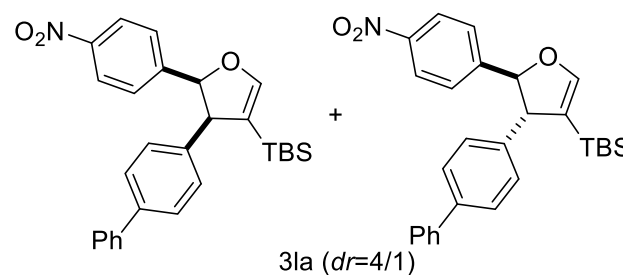


152.91	146.74	145.19	137.51	131.05	130.50	126.95	123.01	120.82	112.78	86.71	56.76	26.62	17.03	-5.31	-5.50
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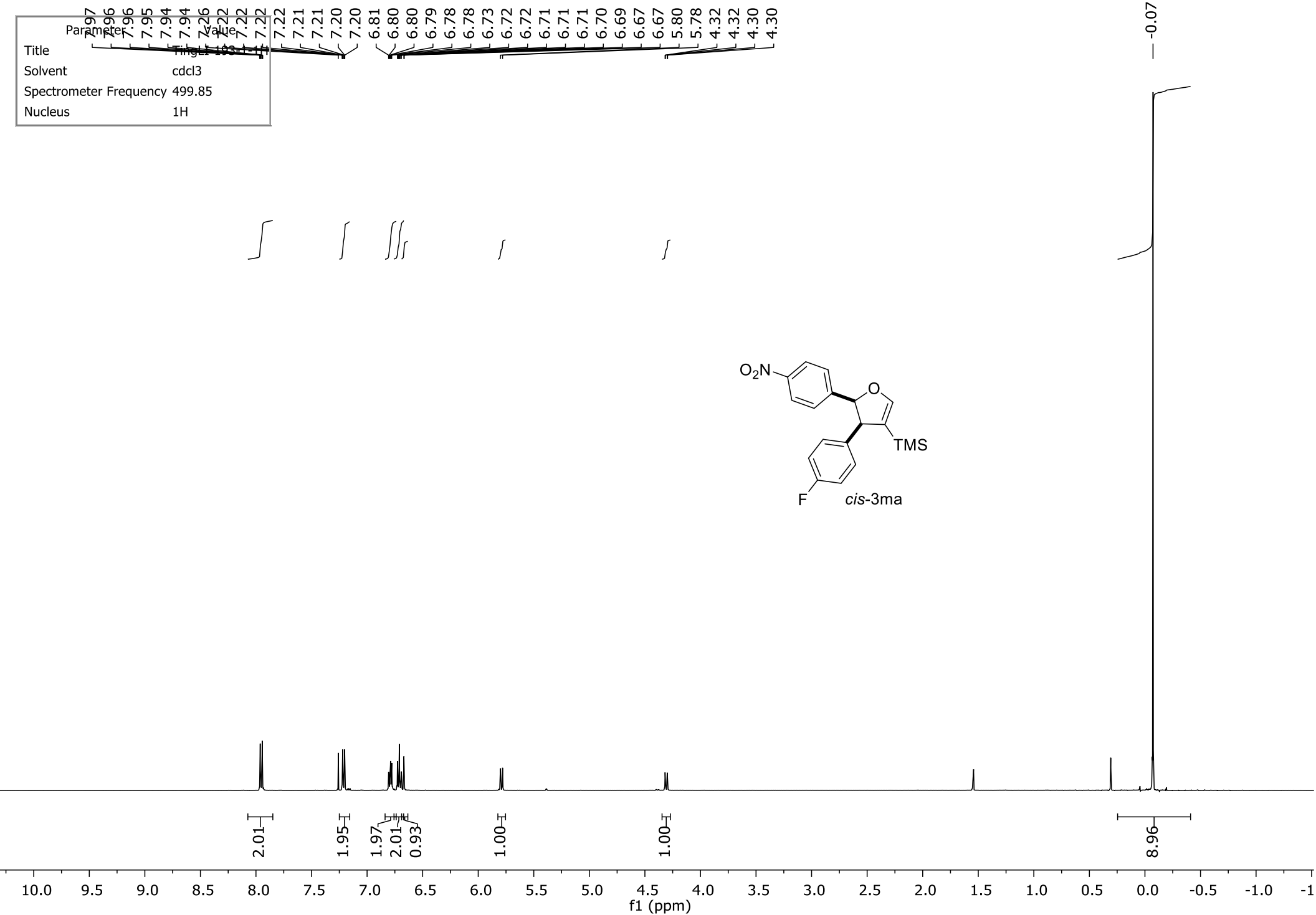




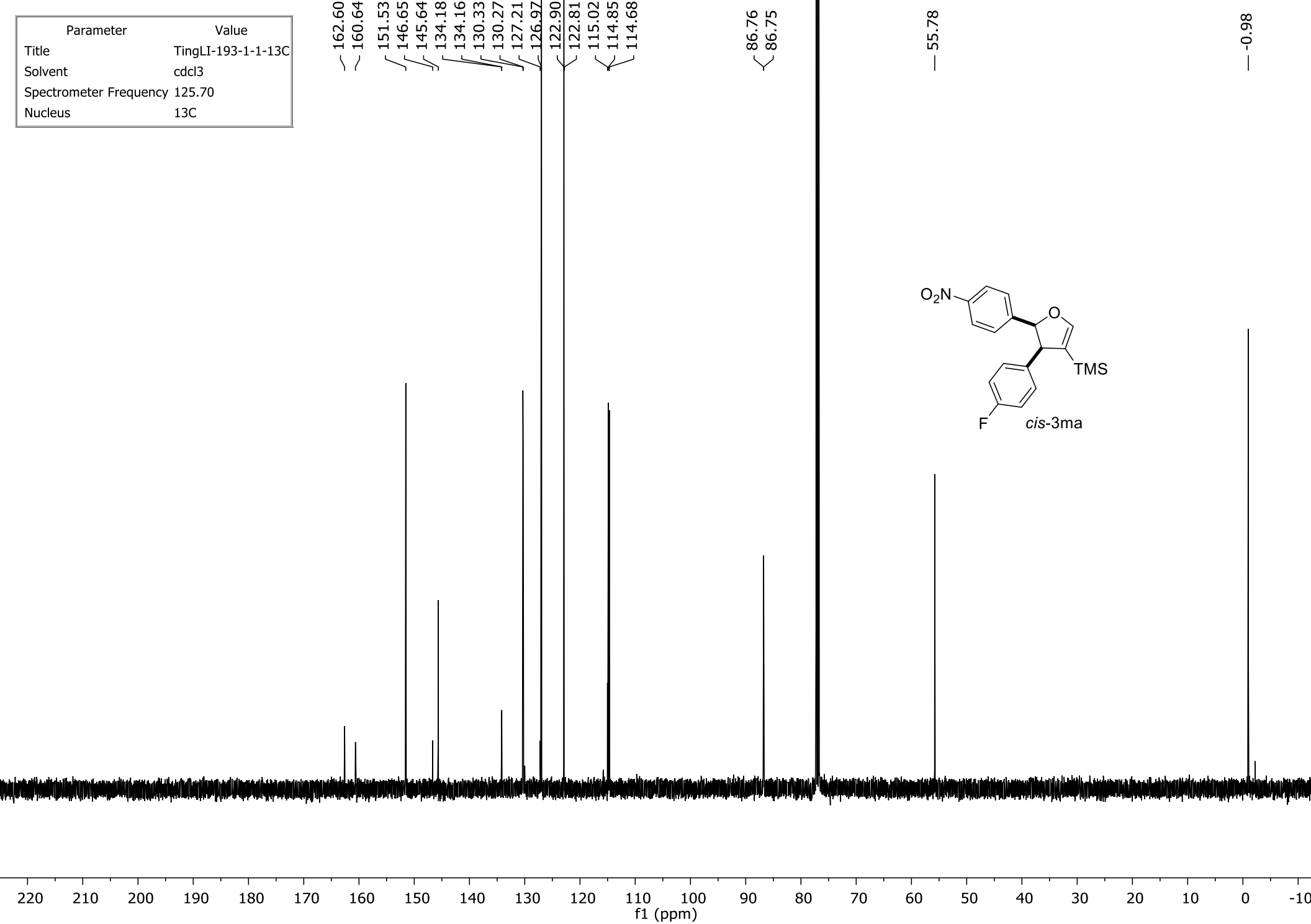
Parameter	
Title	152.63
Solvent	152.41
Spectrometer Frequency	150.09
Nucleus	146.64



Title	
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	1H



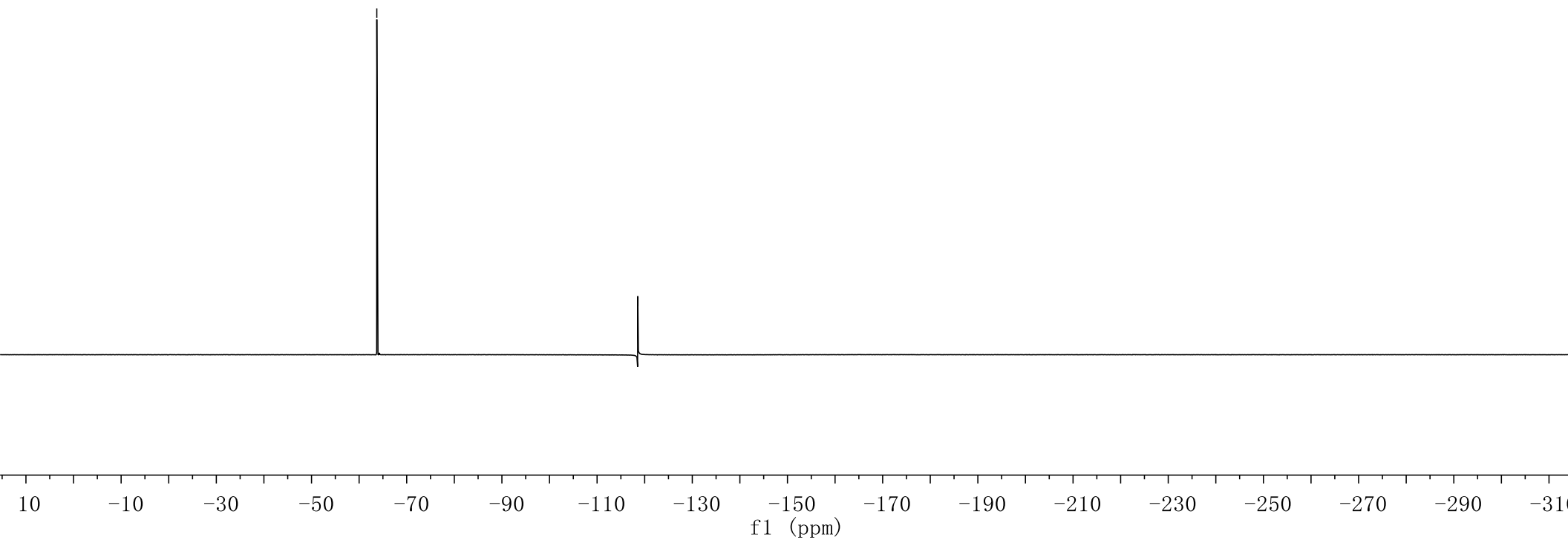
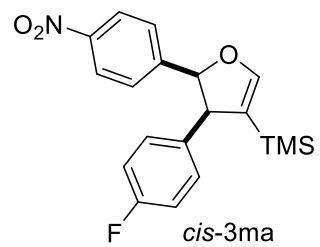
Parameter	Value
Title	TingLI-193-1-1-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C

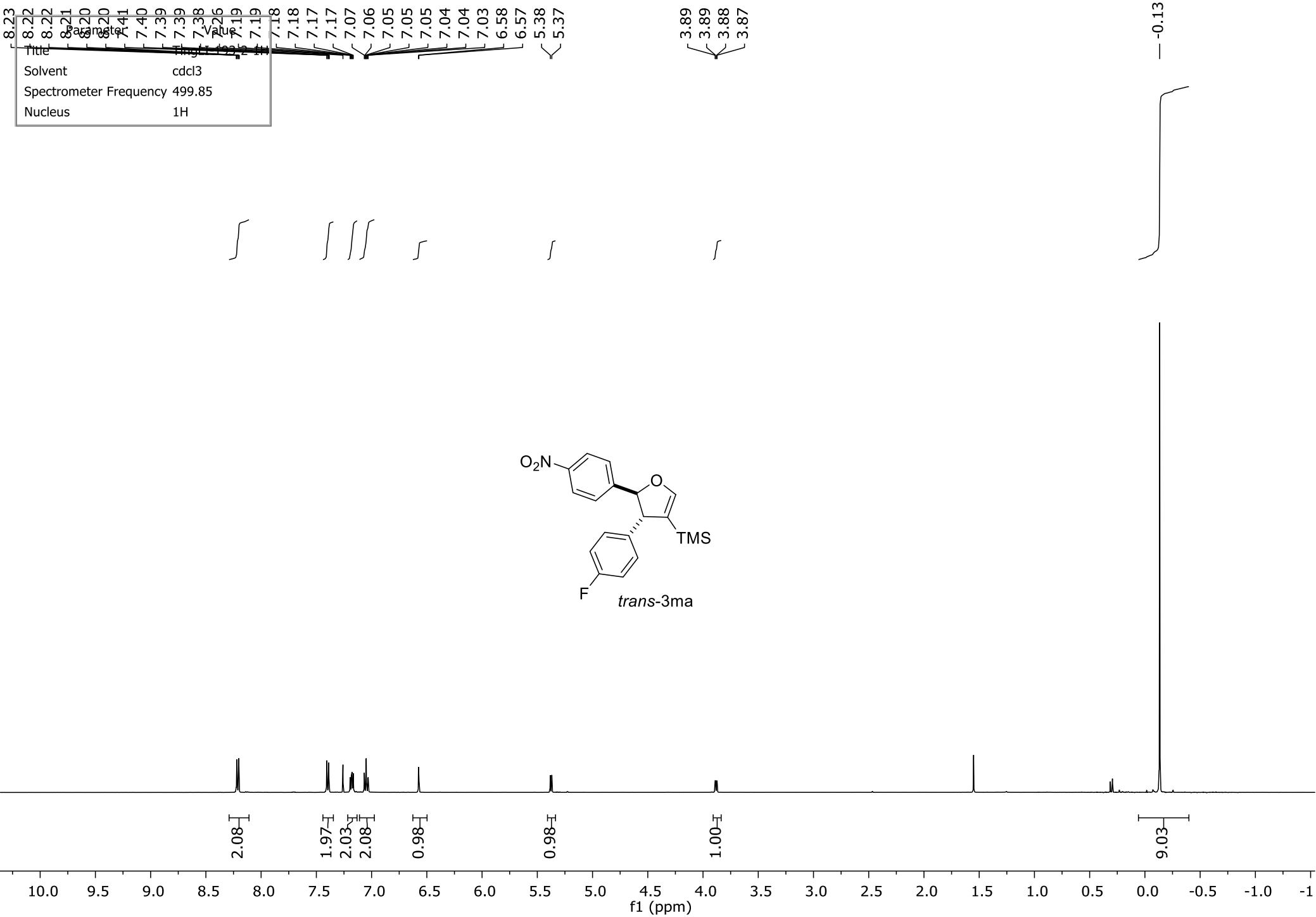


Parameters		
Parameter	Value	
Title	LT-2-300-2-19F	
Spectrometer Frequency	376.11	

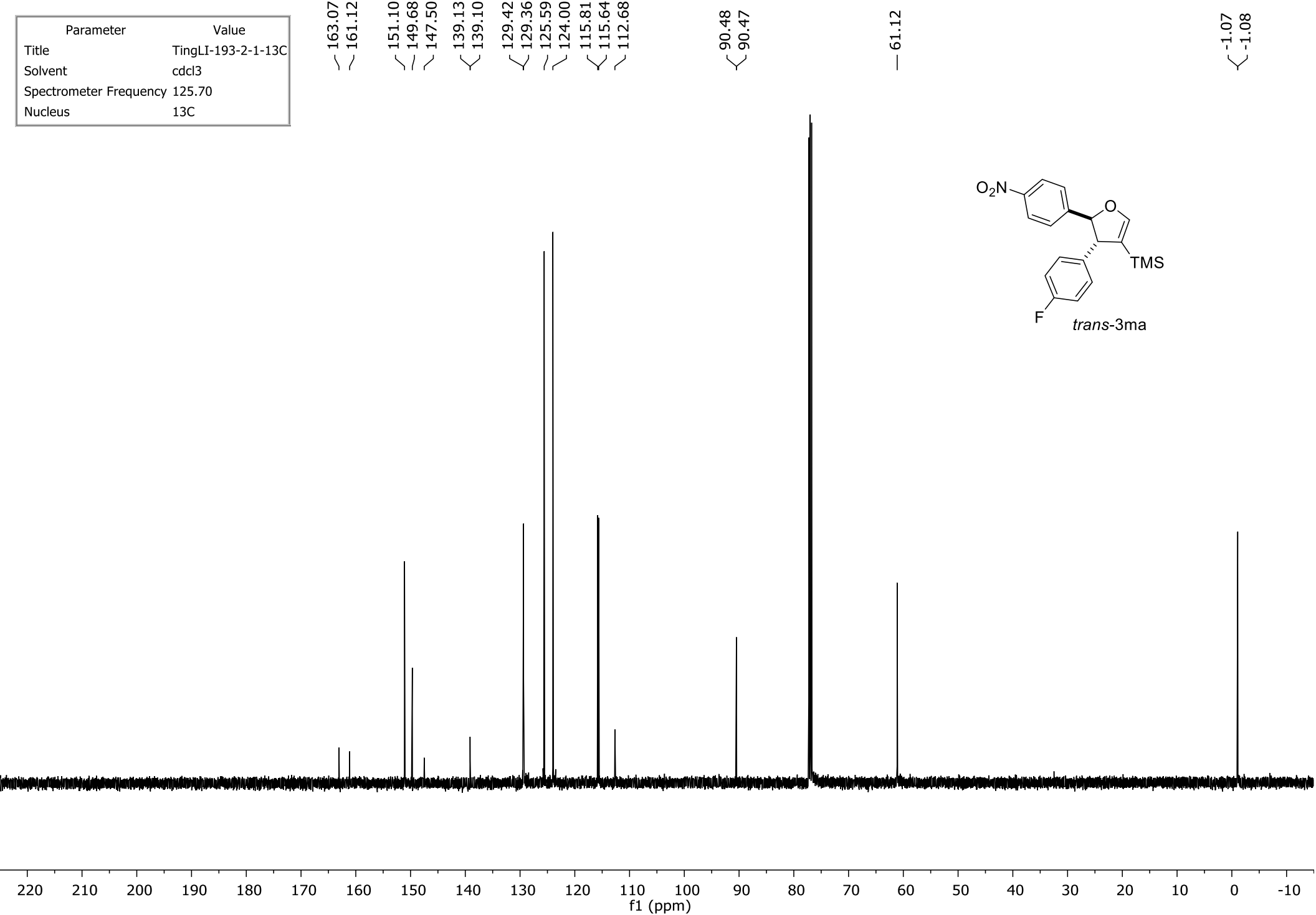
— -63.72

— -118.58





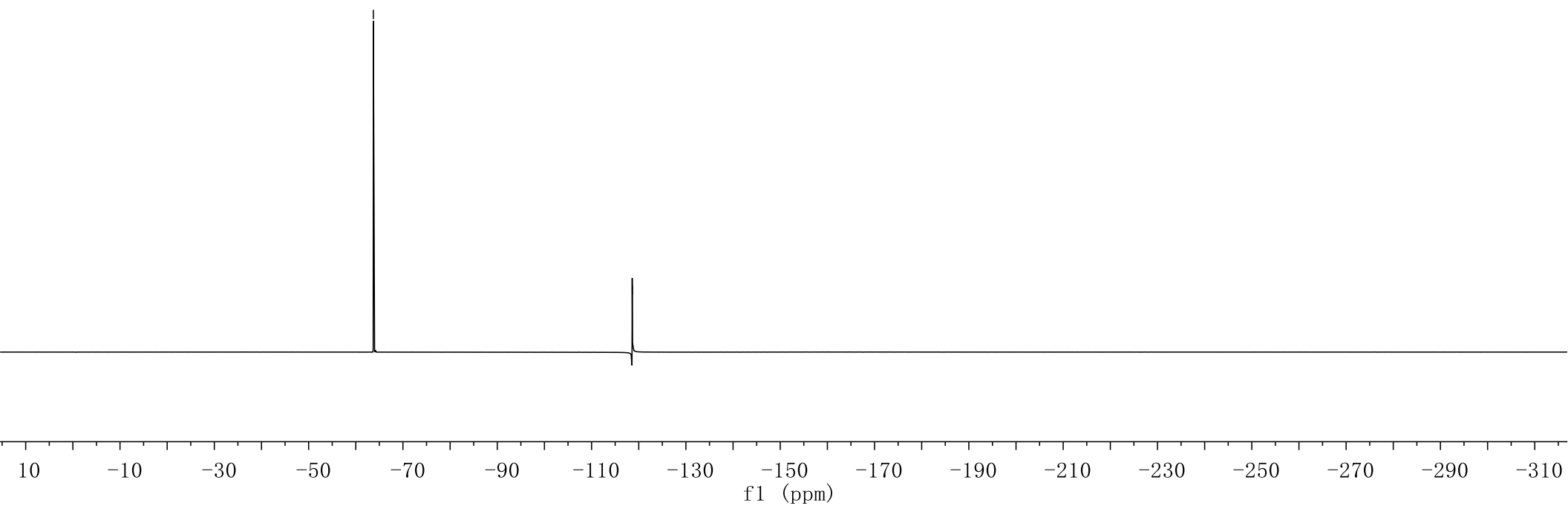
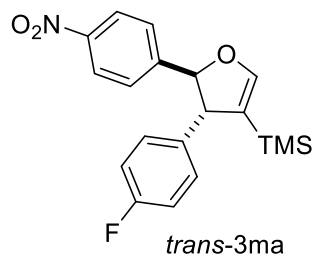
Parameter	Value
Title	TingLI-193-2-1-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C



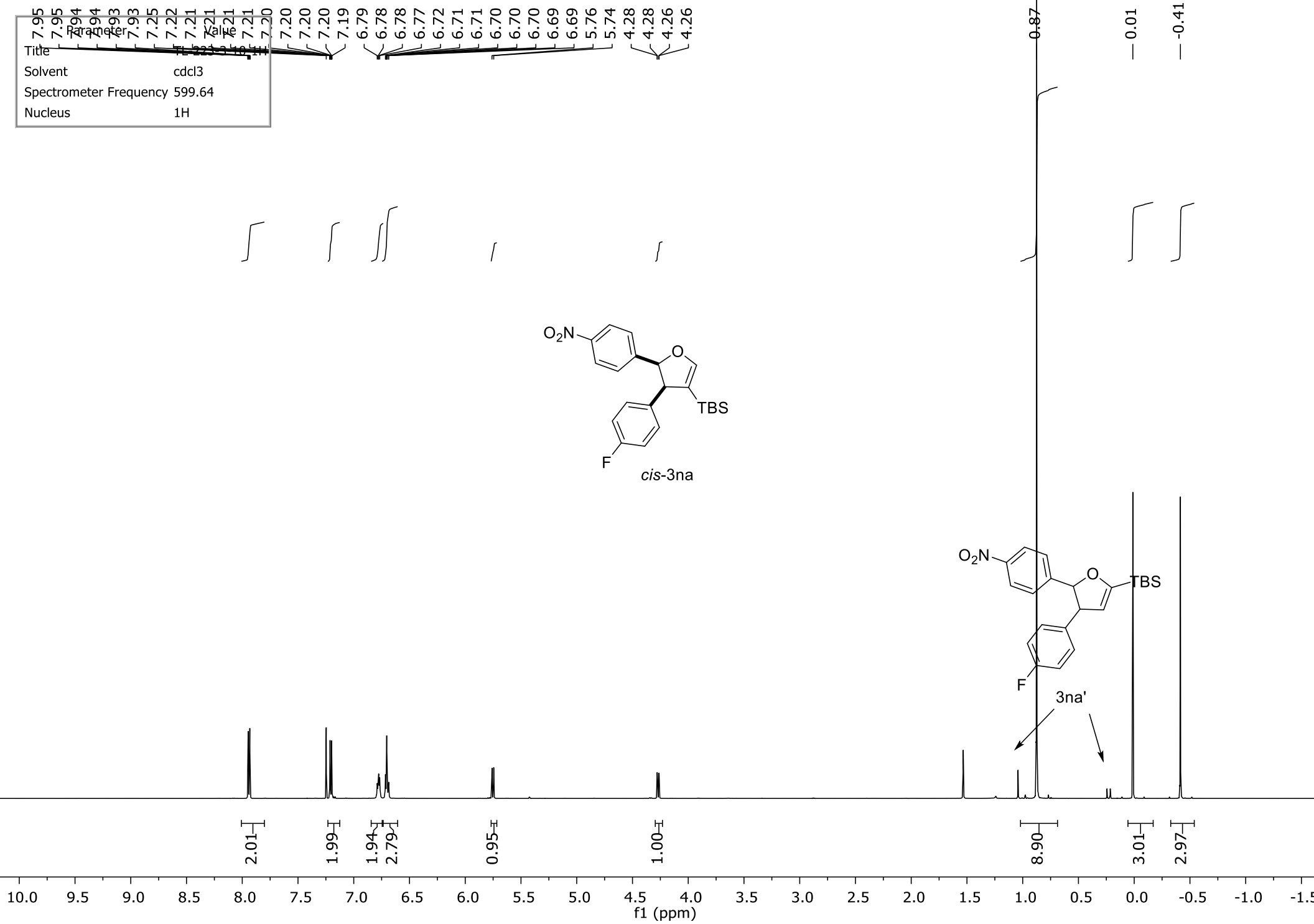
Parameters		
Parameter	Value	
Title	LT-2-300-3-19F	
Spectrometer Frequency	376.11	

— -63.72

— -118.64

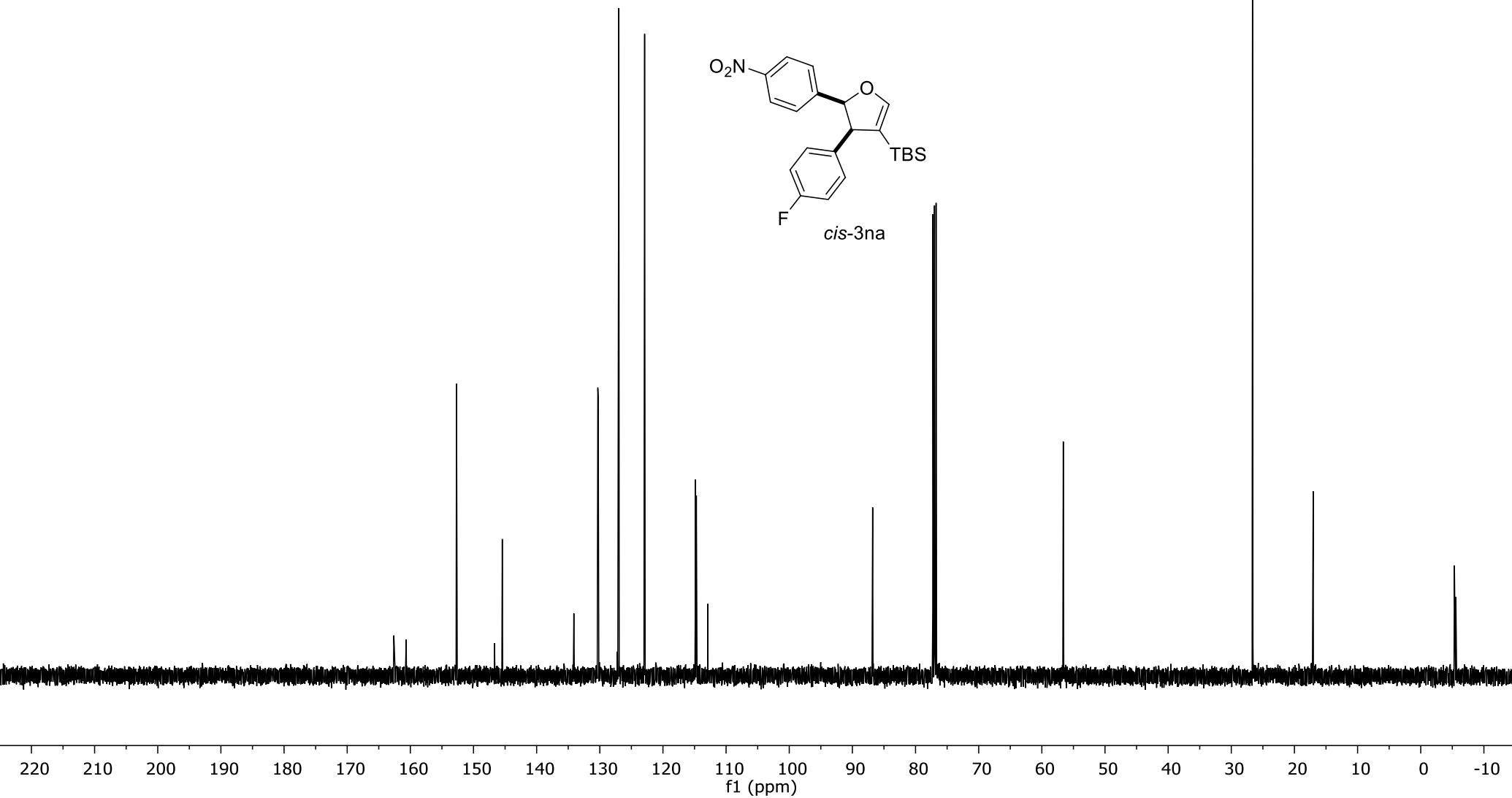
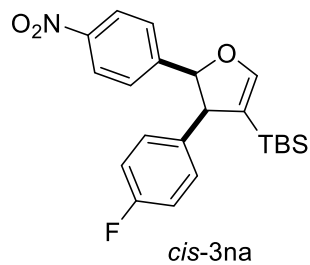


Title	FL 223-348-111
Solvent	cdcl3
Spectrometer Frequency	599.64
Nucleus	1H



Parameter	Value
Title	TingLI-223-2-1-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	¹³ C

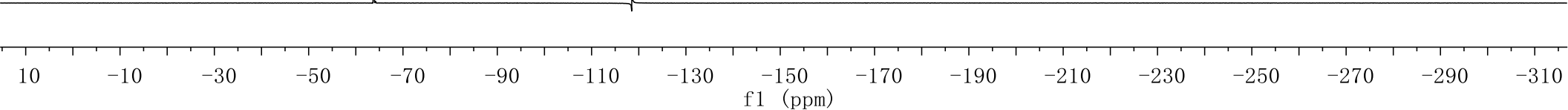
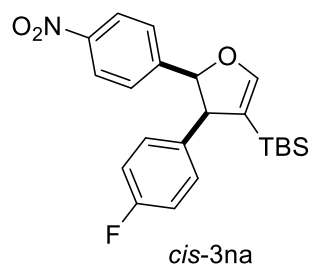
¹³C NMR chemical shifts (ppm):
 162.61, 160.66, 152.69, 146.68, 145.44, 134.13, 134.11, 130.31, 130.25, 127.22, 126.98, 122.90, 114.88, 114.71, 112.90, 86.80, 86.79, 56.60, 26.62, 26.57, 17.03, -5.33, -5.56



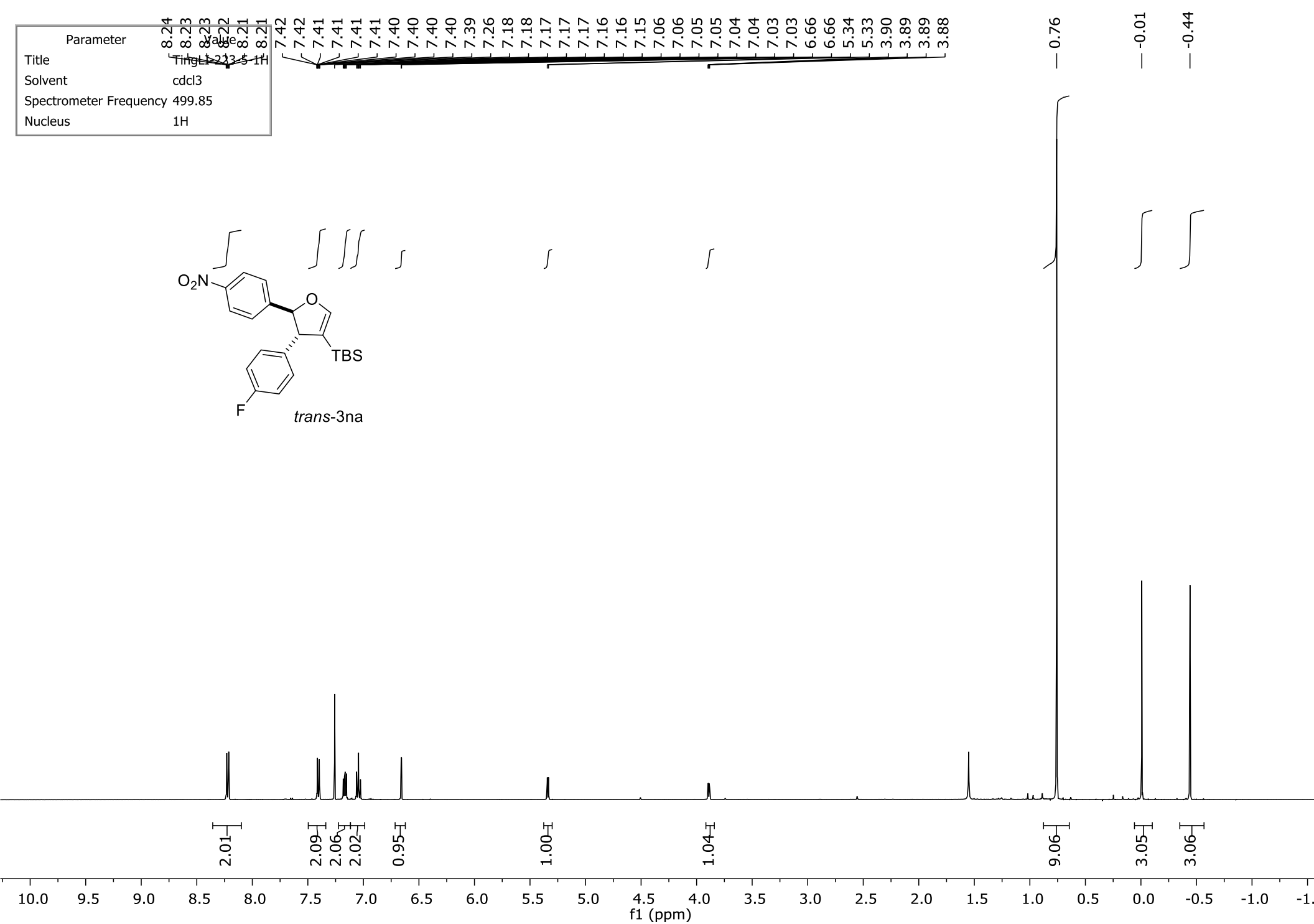
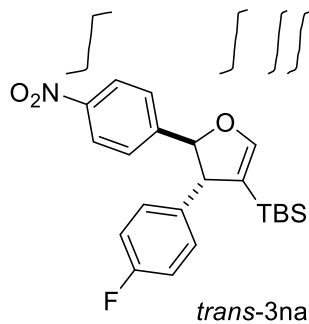
Parameter	Value
Title	LT-2-300-1-19F
Spectrometer Frequency	376.11

— -63.72

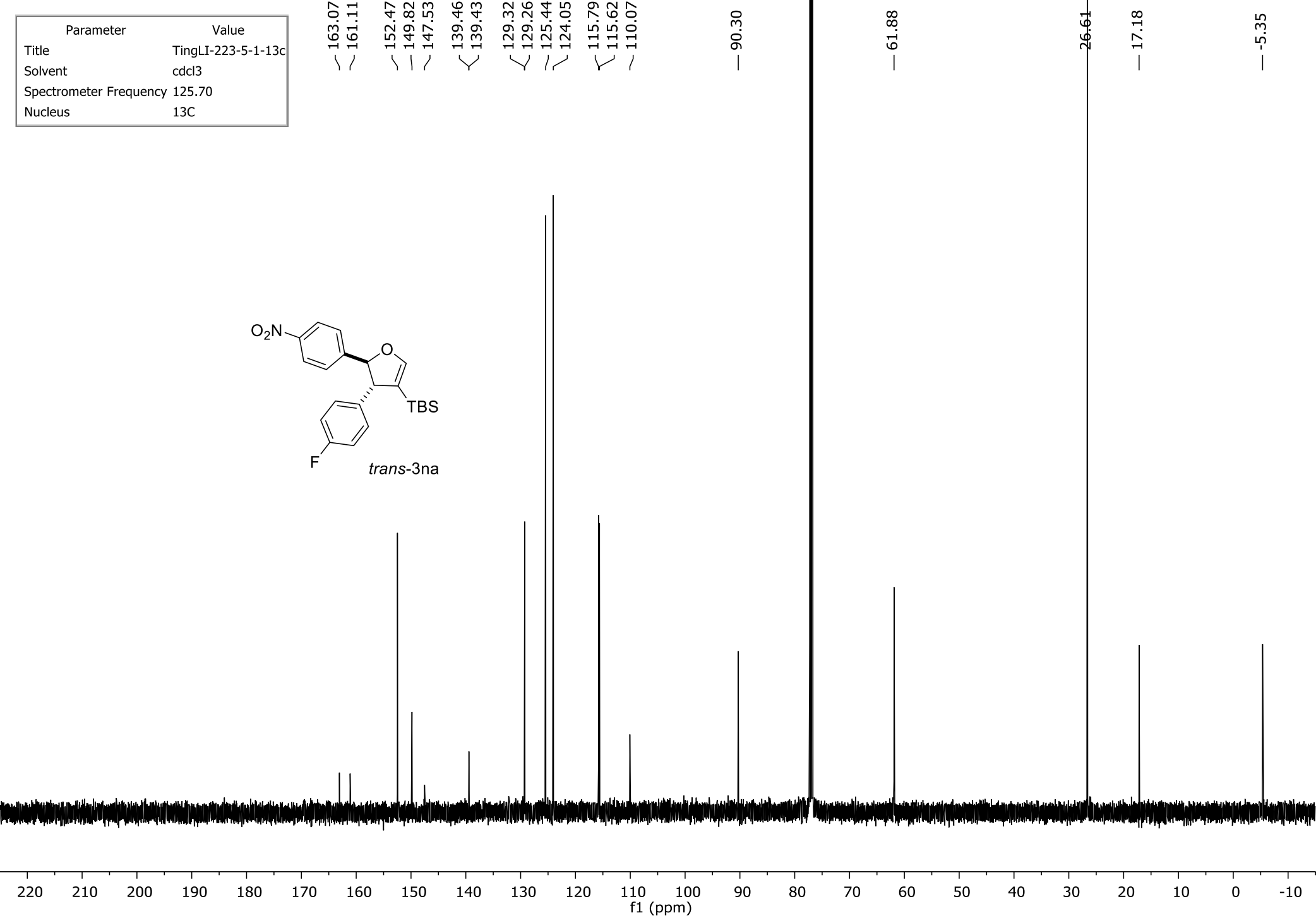
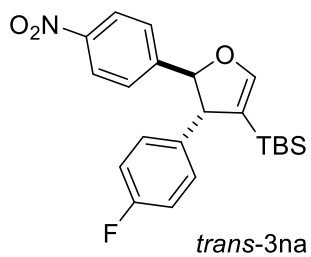
— -118.56



Parameter	
Title	11-213-5-1H
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	1H



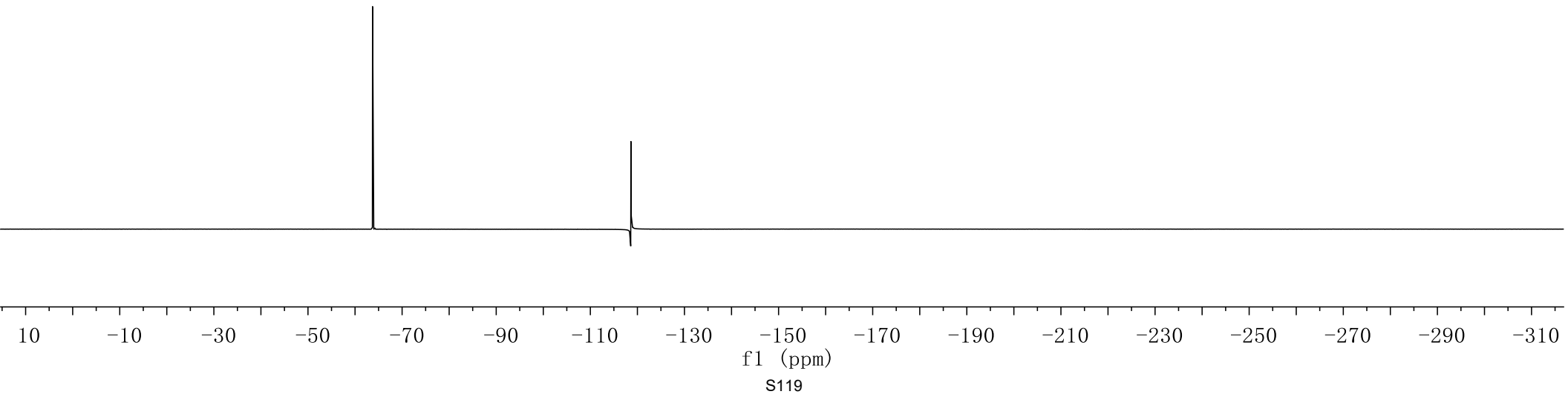
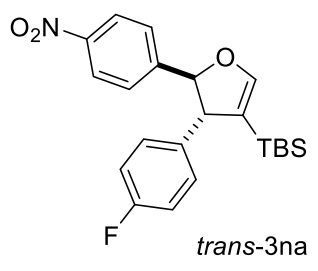
Parameter	Value
Title	TingLI-223-5-1-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C



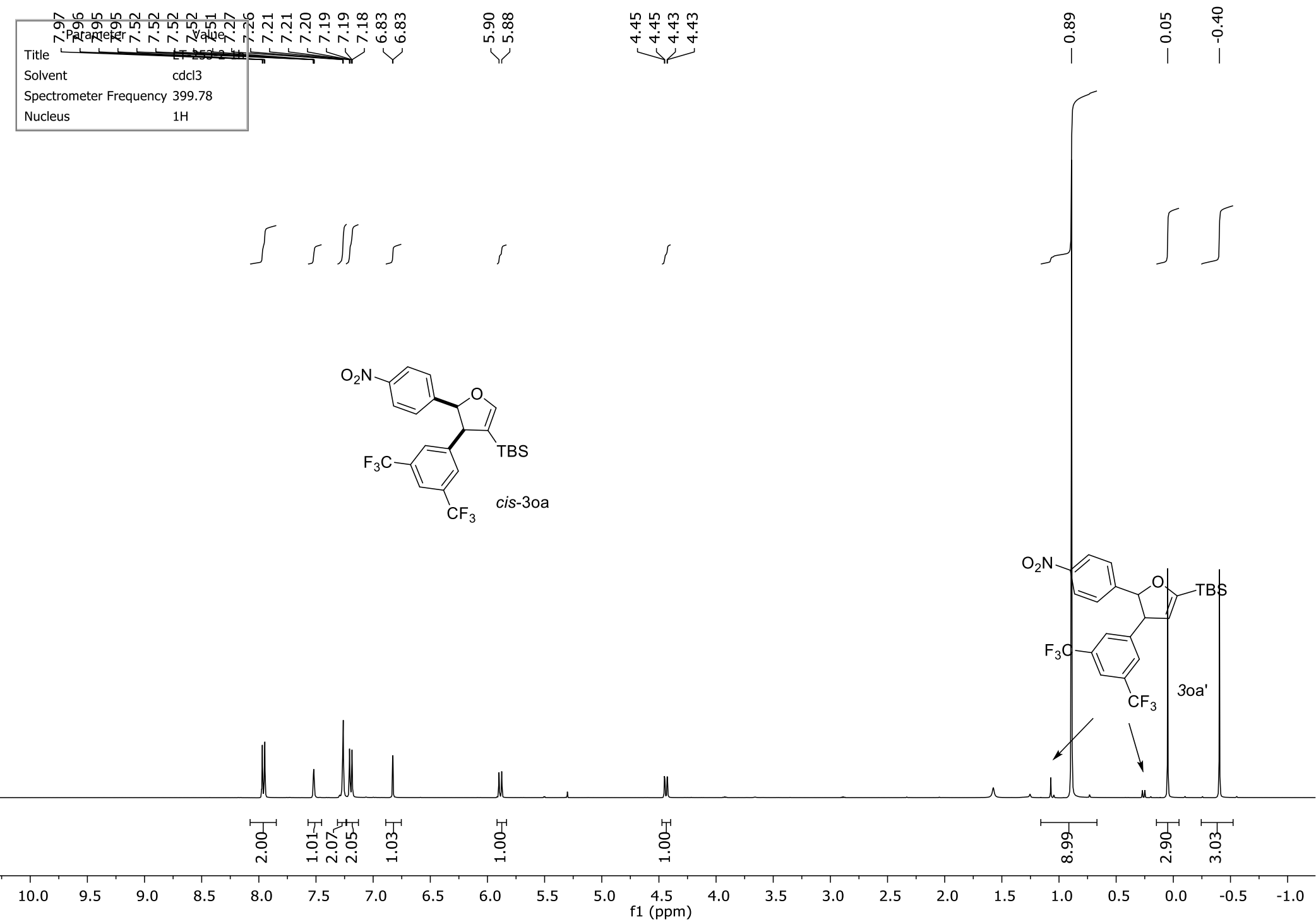
Parameters	
Parameter	Value
Title	LT-2-300-4-19F
Spectrometer Frequency	376.11

— -63.72

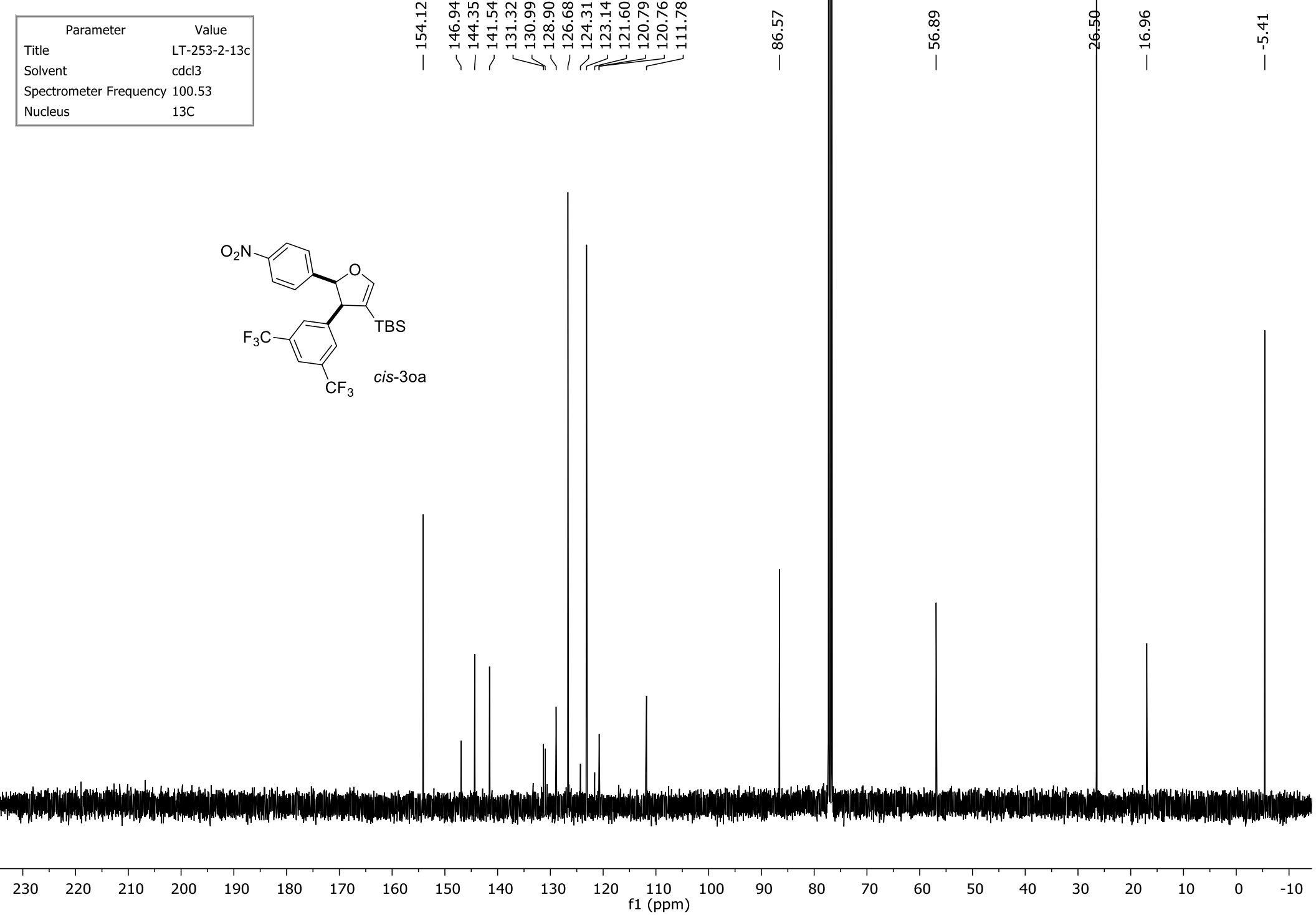
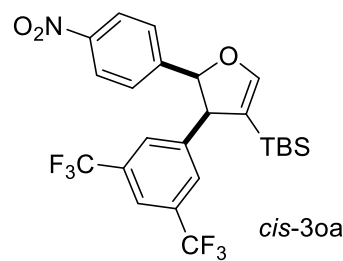
— -118.15



Title	
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H



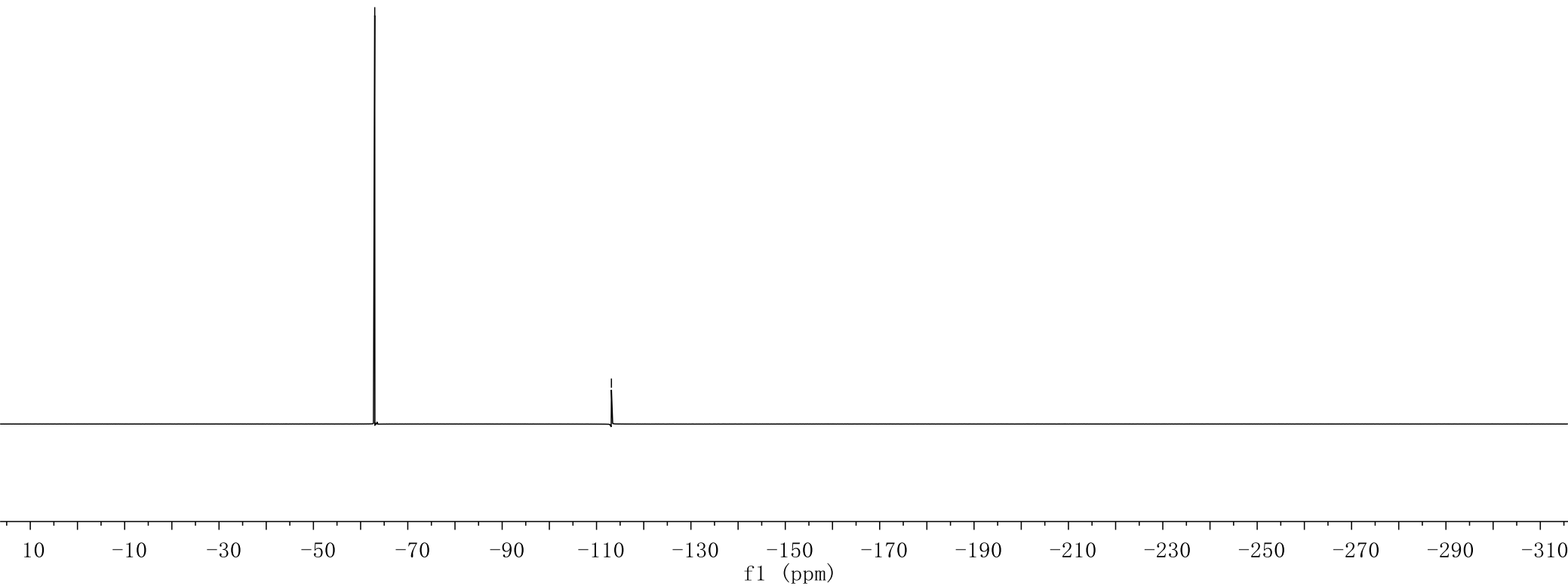
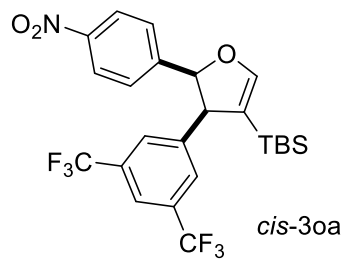
Parameter	Value
Title	LT-253-2-13c
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	13C



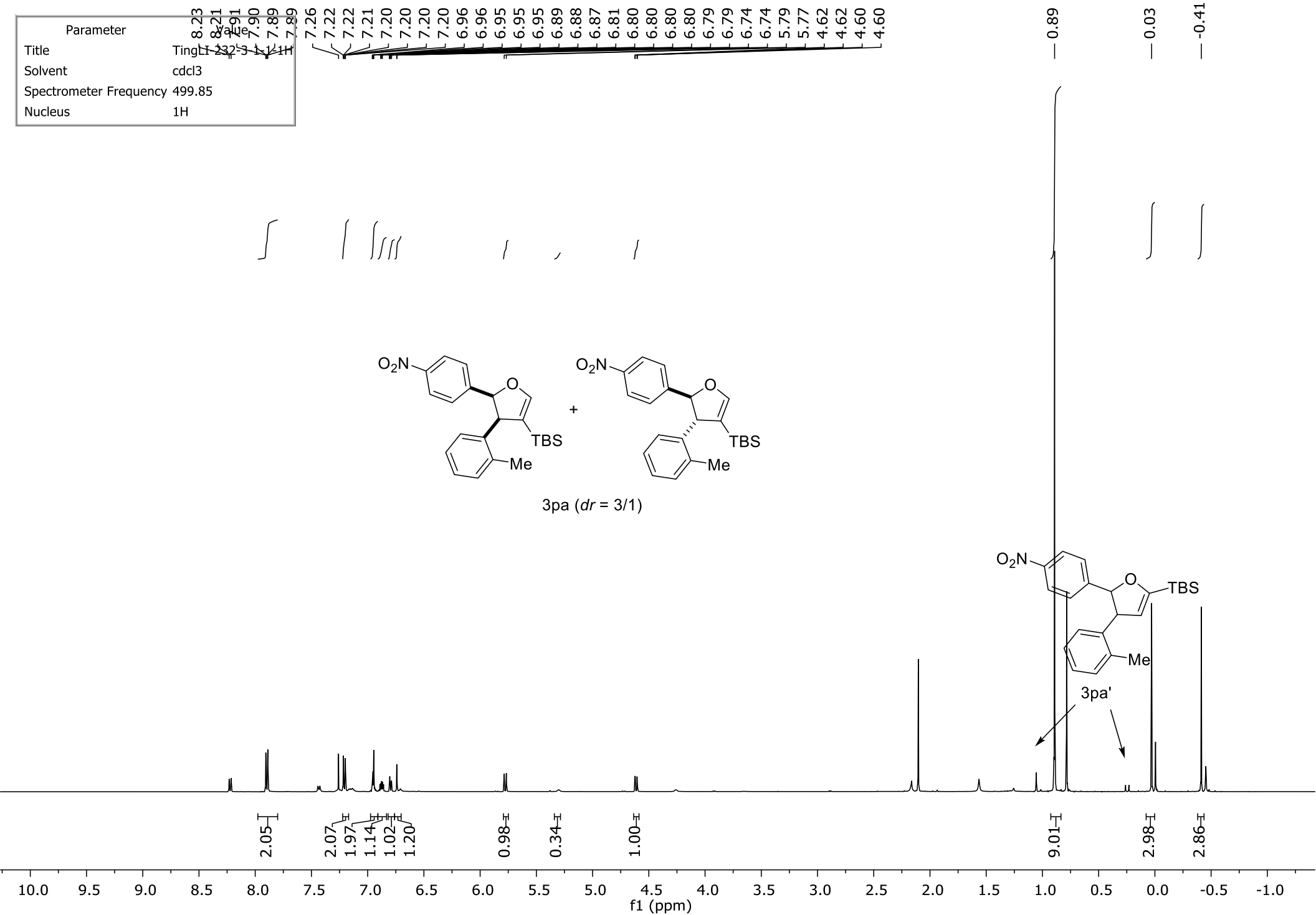
Parameters		
Parameter	Value	
Title	LT-2-300-7-19F	
Spectrometer Frequency	376.11	

— -63.00

— -113.15

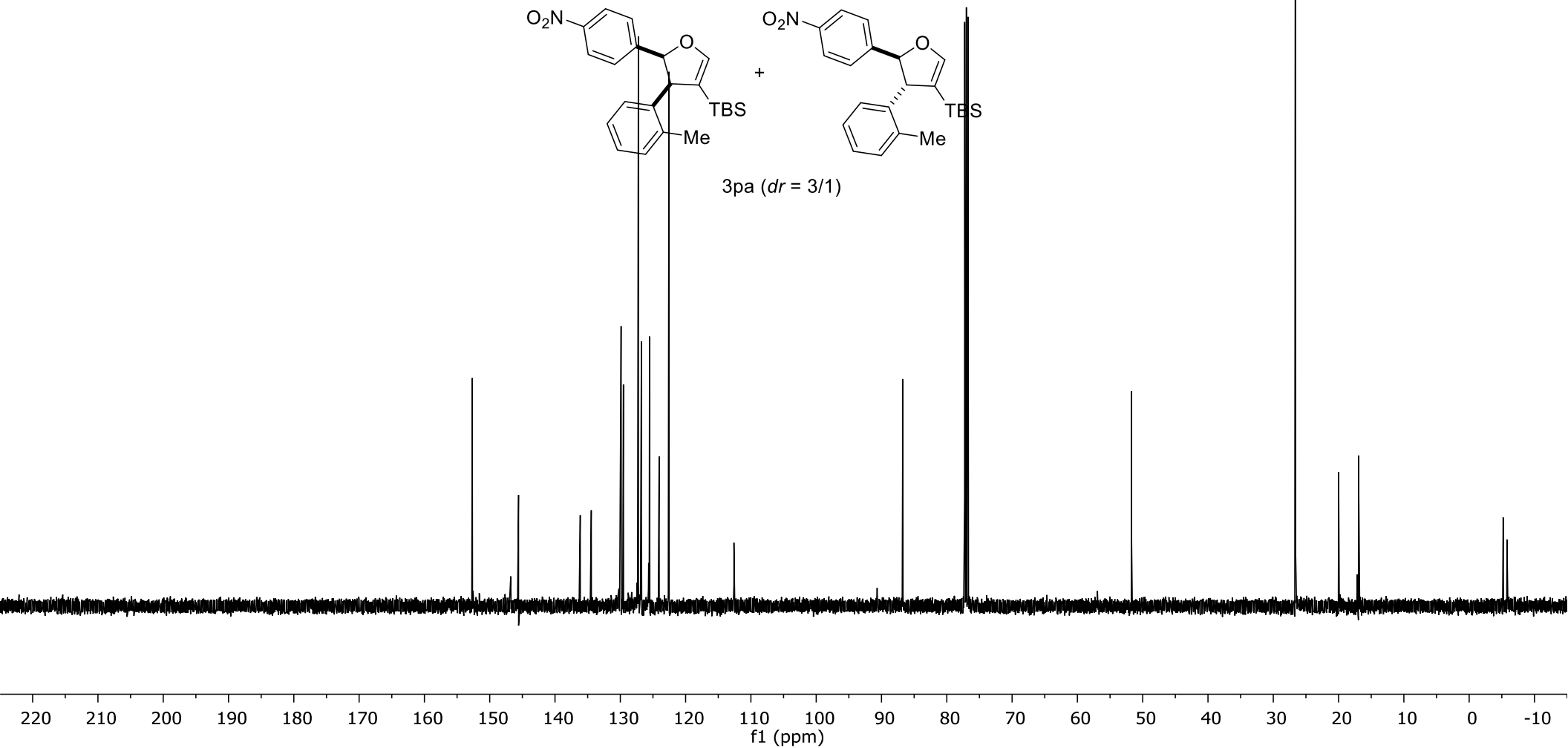
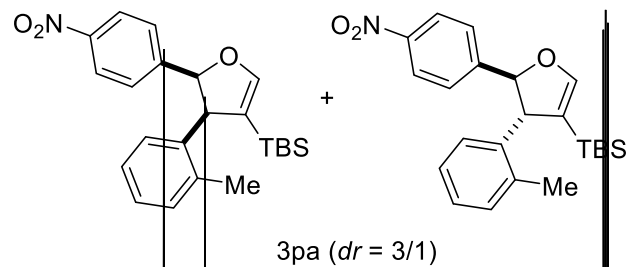


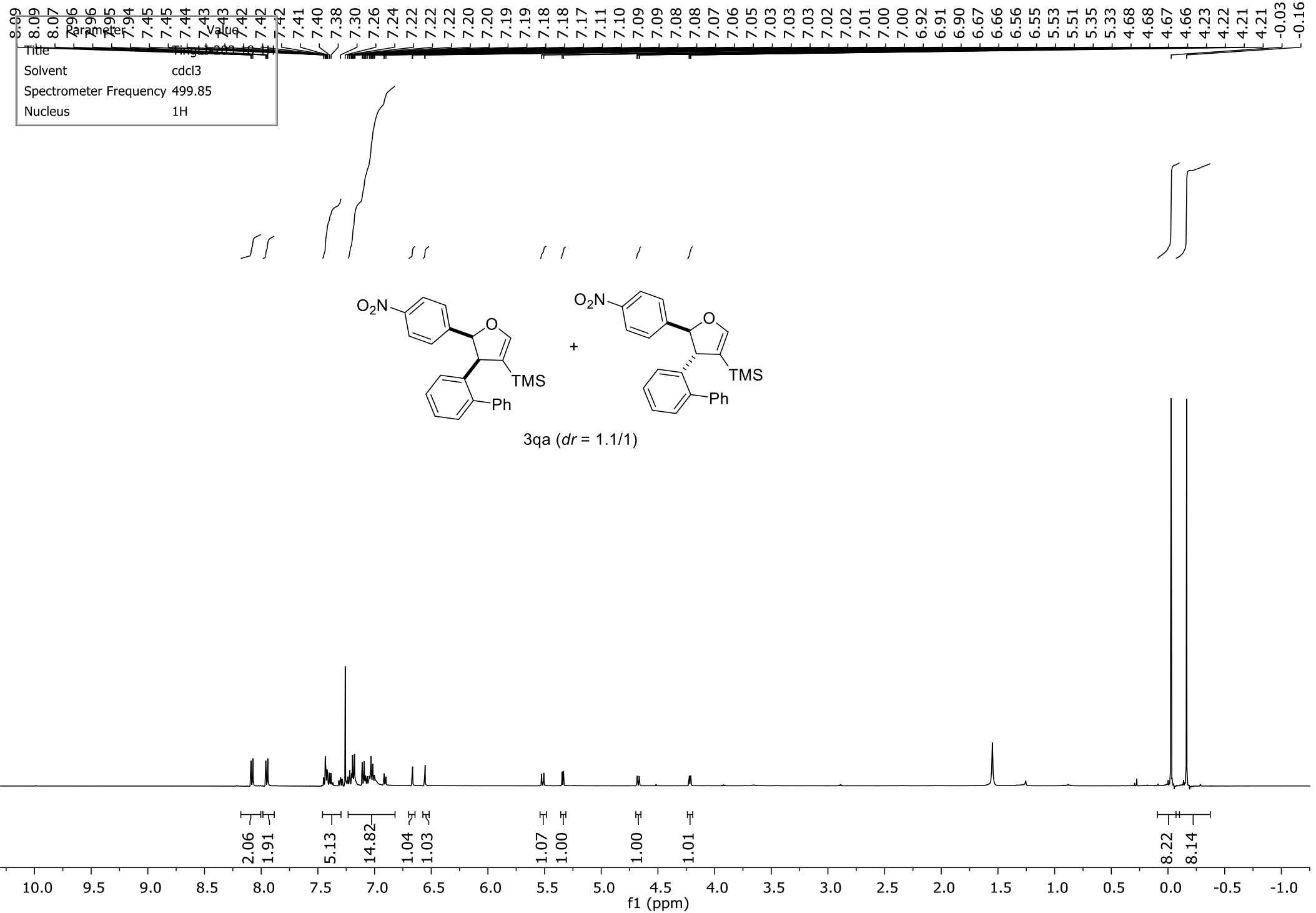
Parameter	
Title	Tingli-232-3-1-1-1H
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	1H



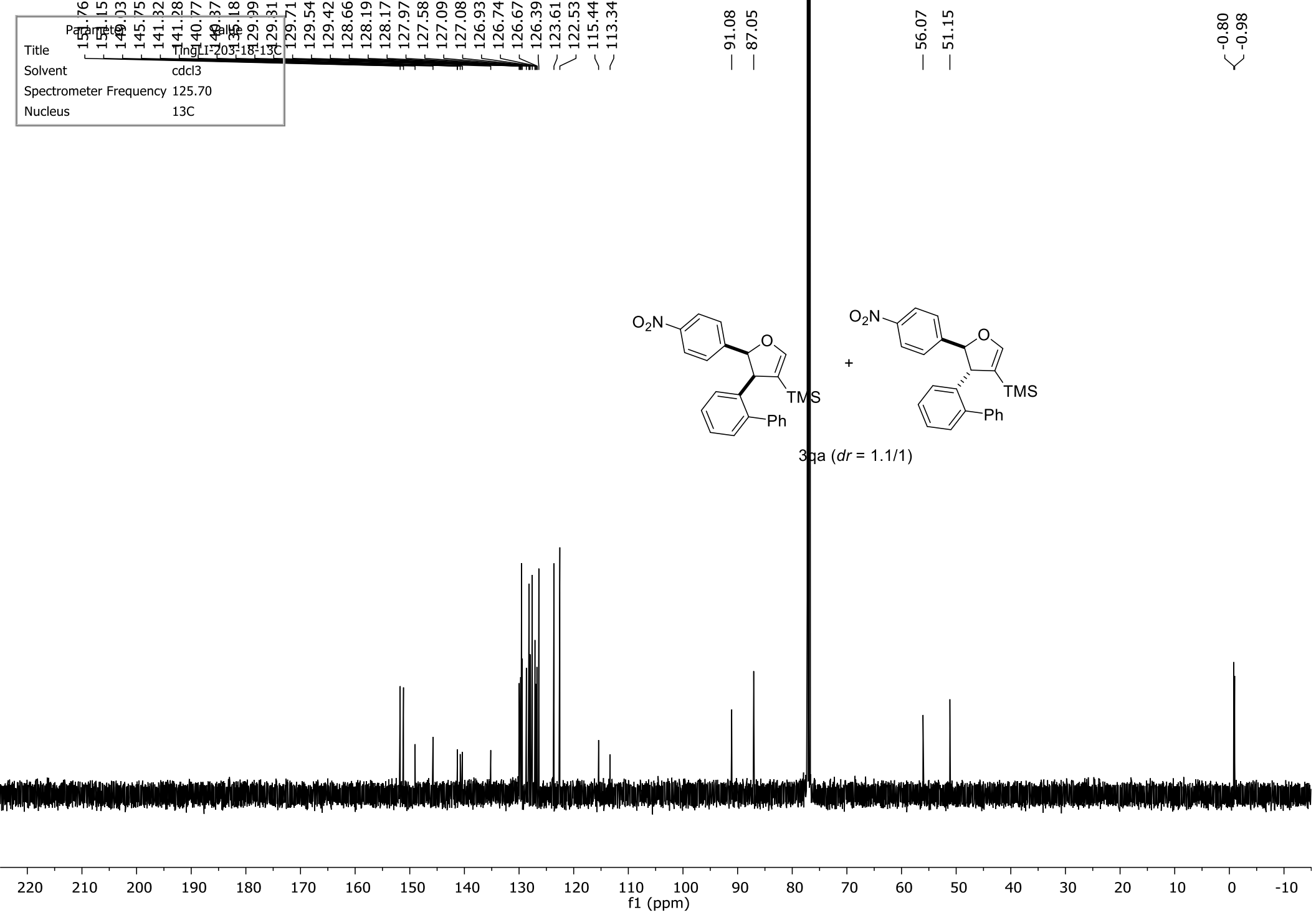
Parameter	Value
Title	TingLI-232-3-1-1-1-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C

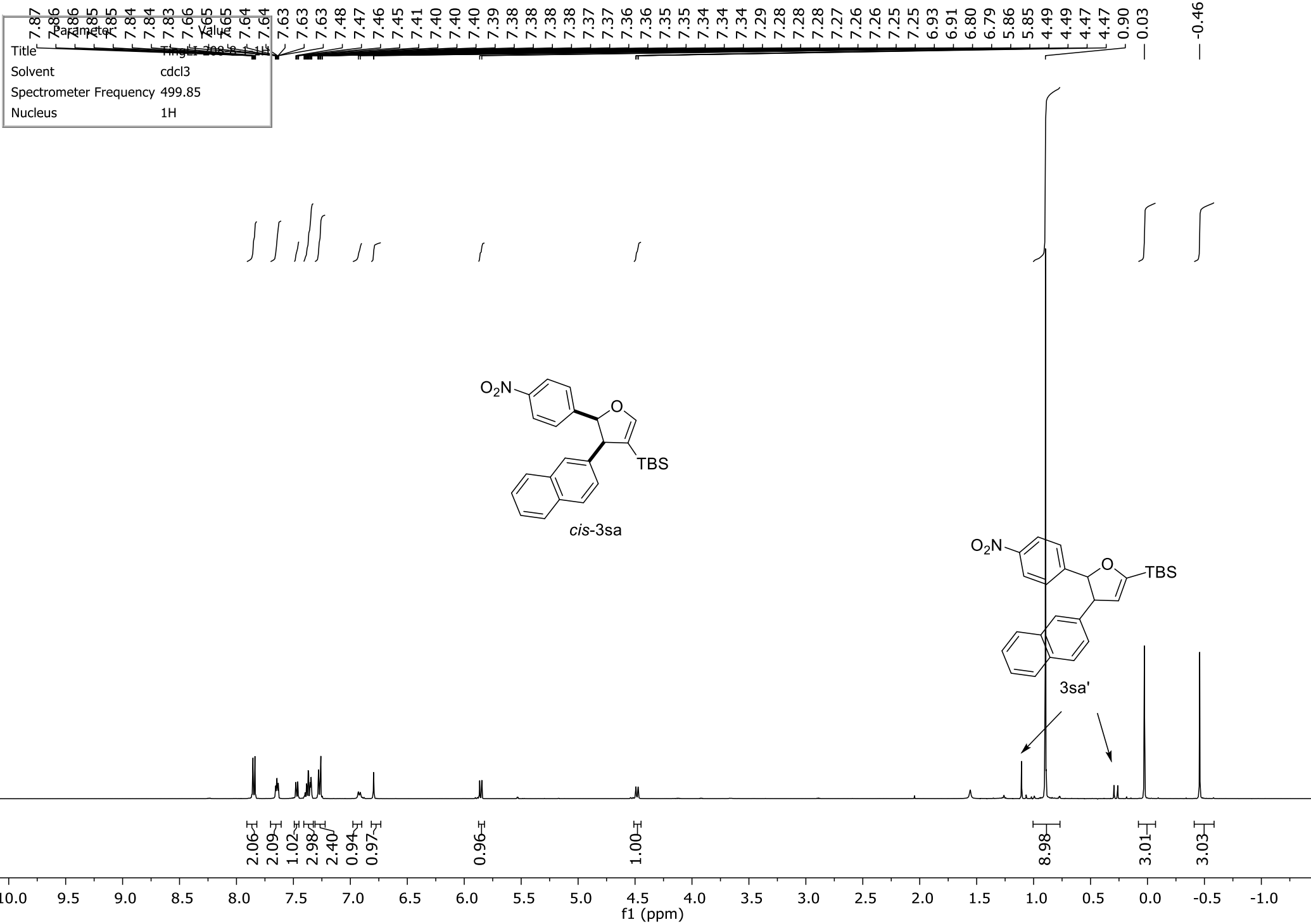
152.67
 146.78
 145.58
 136.14
 134.44
 129.88
 129.52
 127.23
 126.77
 125.66
 125.53
 124.06
 122.56
 — 112.60
 — 86.74
 — 51.70
 26.60
 19.99
 16.95
 -5.21
 -5.80



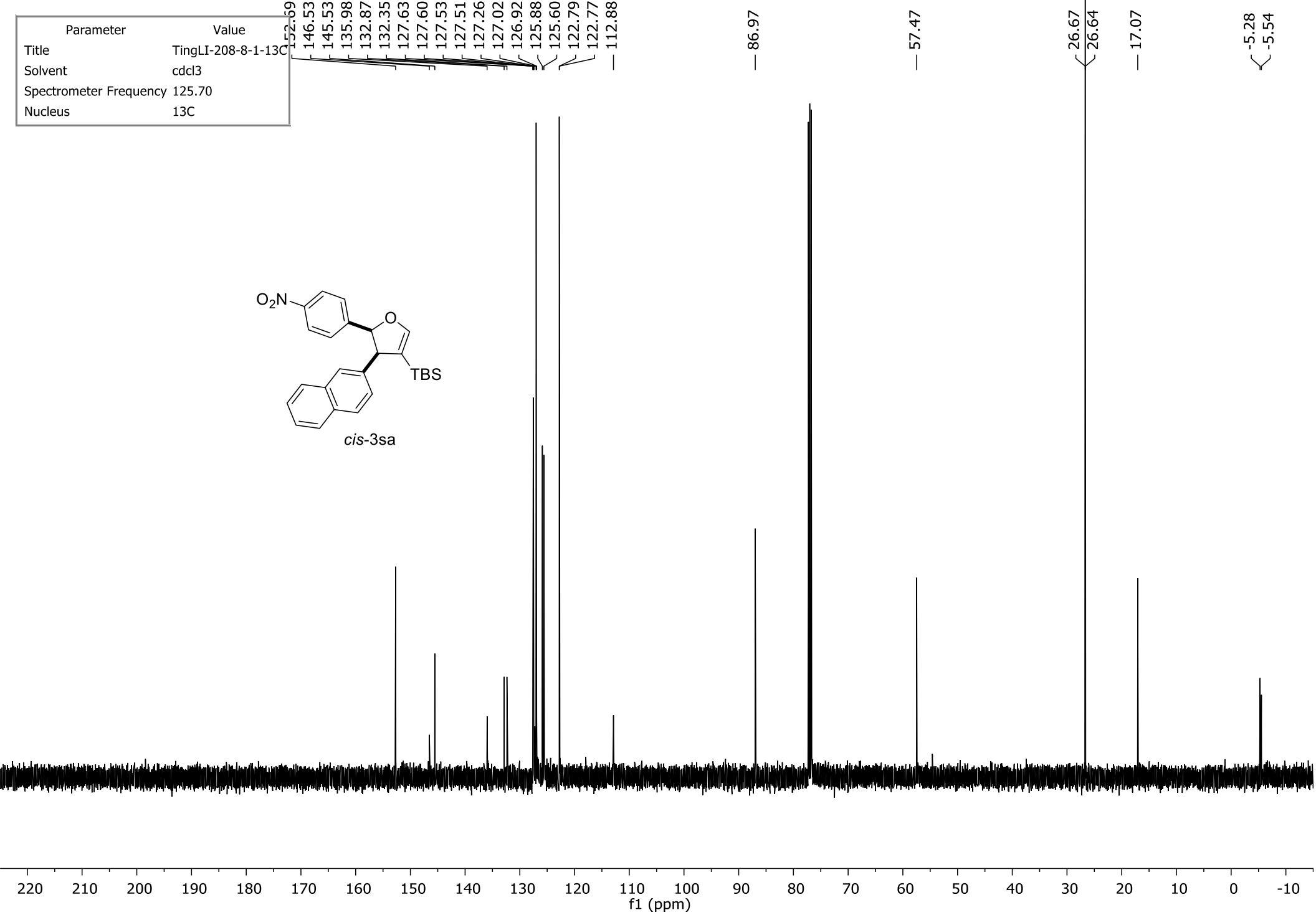
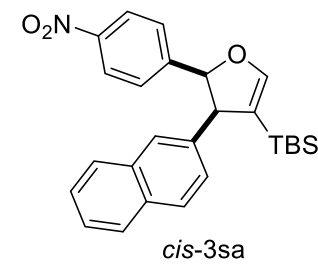


Title	Part 1
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C

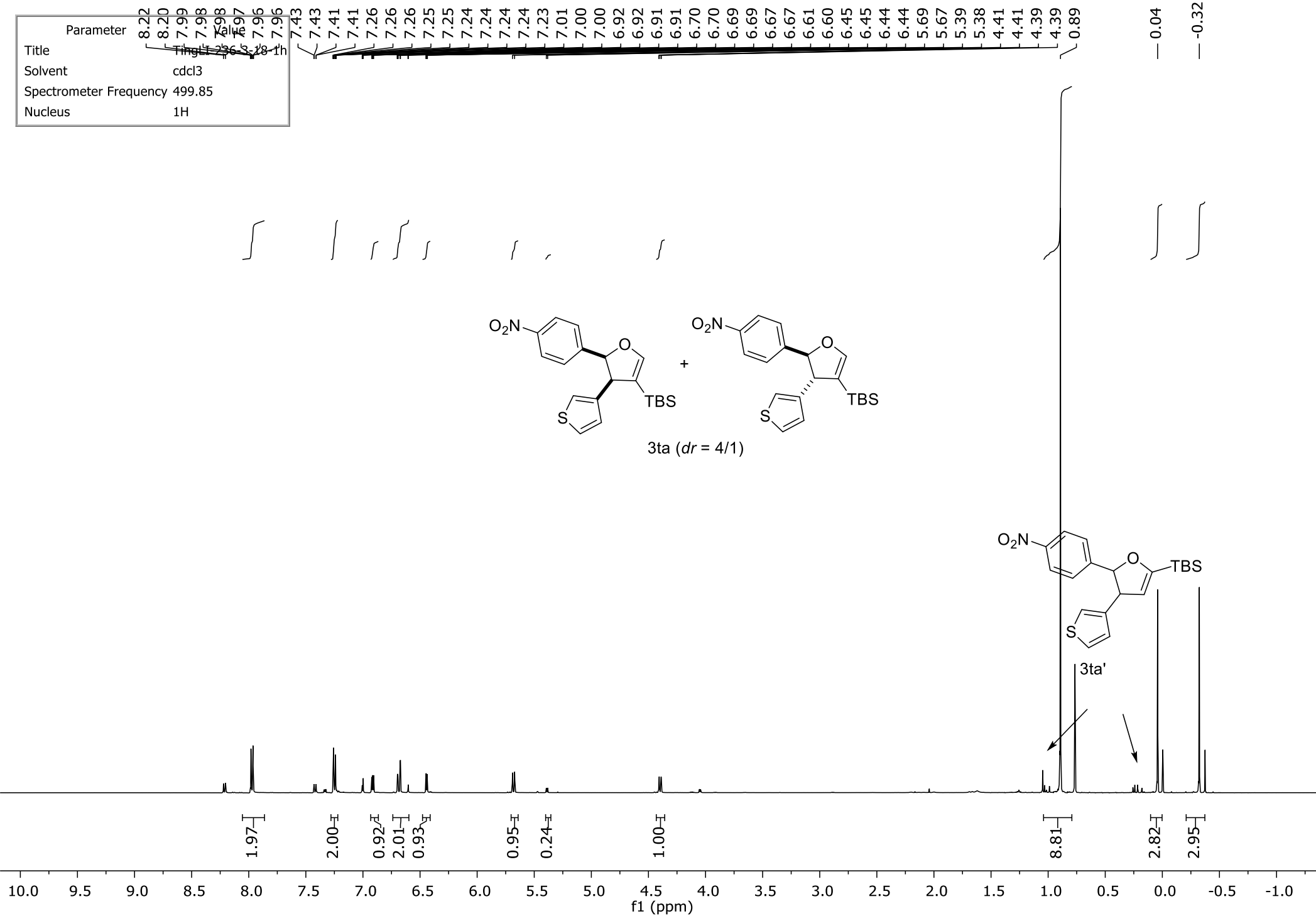




Parameter	Value
Title	TingLI-208-8-1-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C

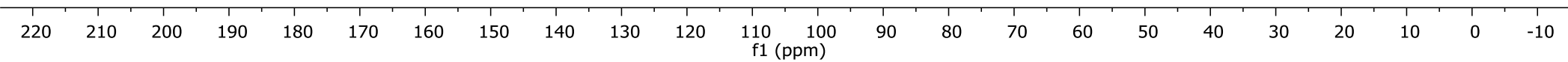
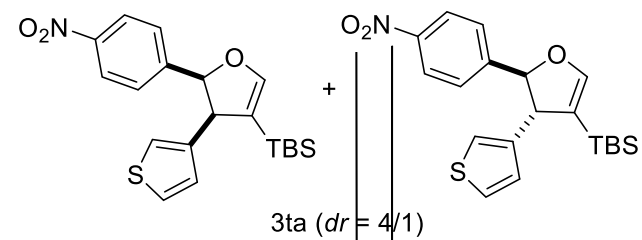


Parameter	
Title	Final 236 3.28 1h
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	1H

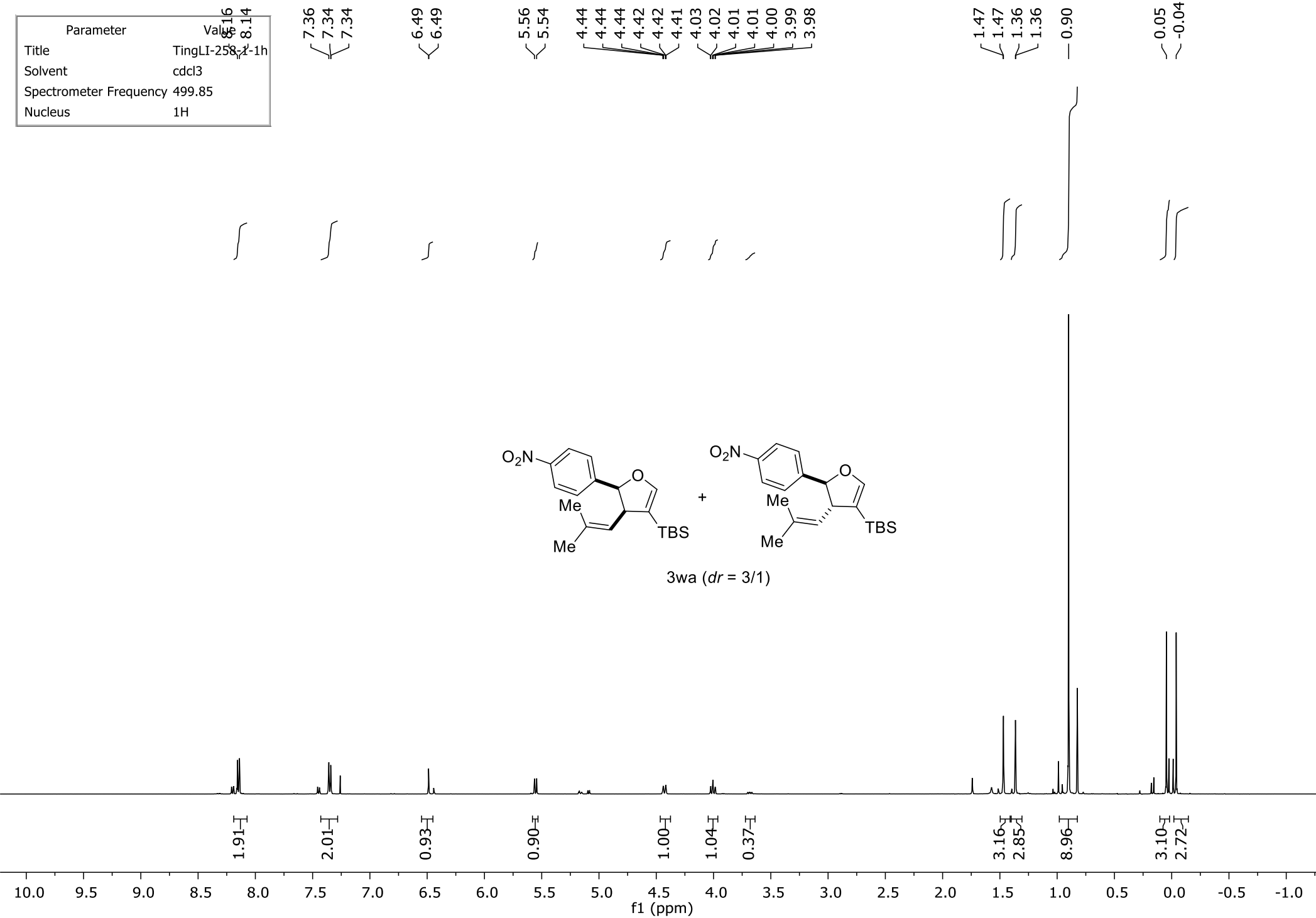


Parameter	Value
Title	TingLI-236-3-18-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C

152.47
 149.82
 145.64
 139.75
 127.91
 126.98
 126.91
 126.67
 125.53
 125.28
 123.97
 122.81
 122.76
 122.45
 121.31
 112.52
 —
 86.56
 —
 52.42
 —
 26.62
 26.59
 —
 17.04
 —
 -5.35
 -5.82
 -5.83



Parameter	Value
Title	TingLI-258-1-1h
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	¹ H



Parameter	Value
Title	TingLI-258-1-1-13c
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	¹³ C

151.98
151.93
146.85

132.46
126.99
125.64
124.66
123.81
122.97

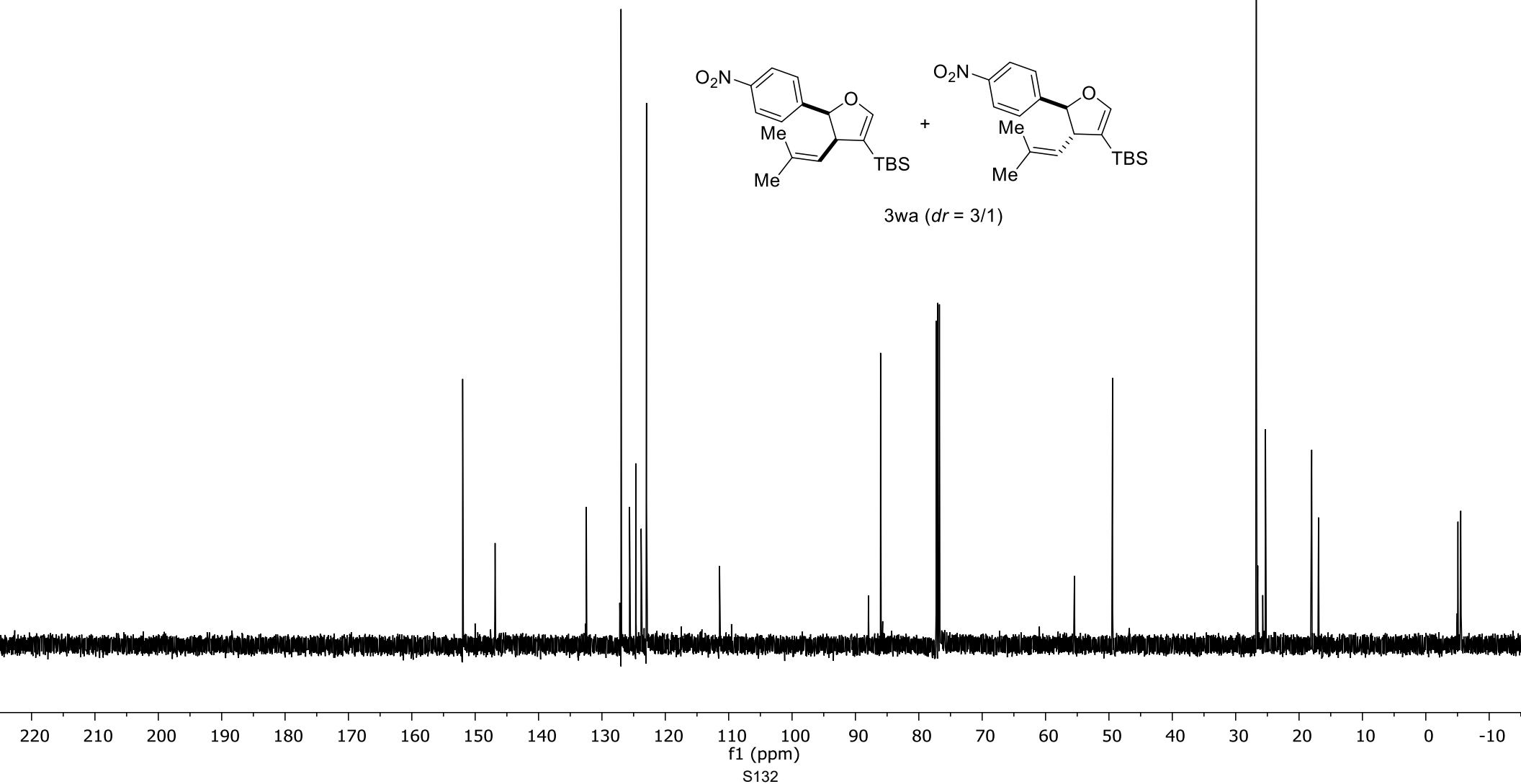
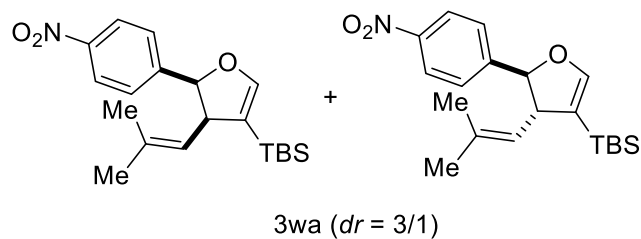
111.44

86.03

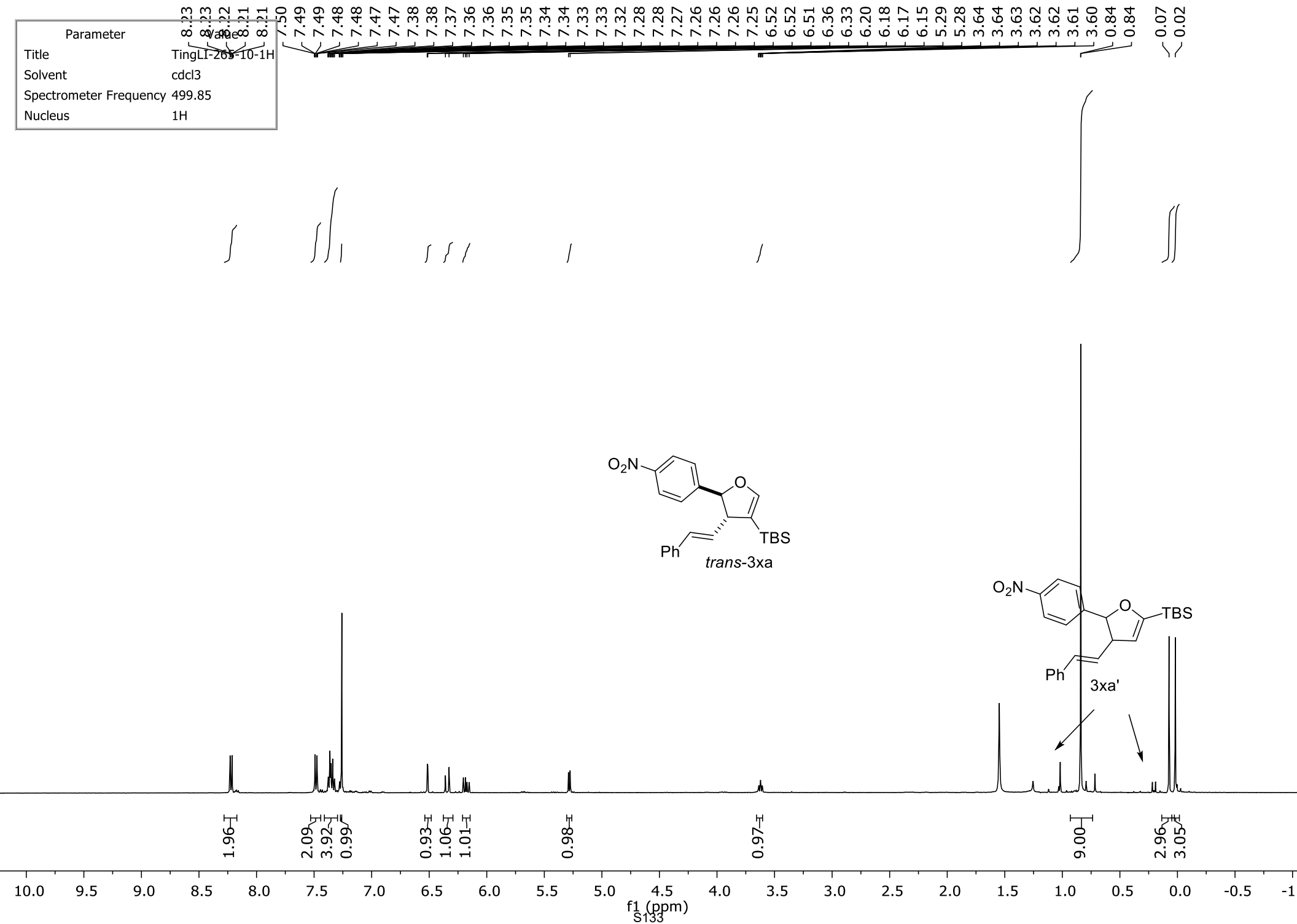
49.43

26.73
26.71
25.30
18.00

-5.07
-5.51

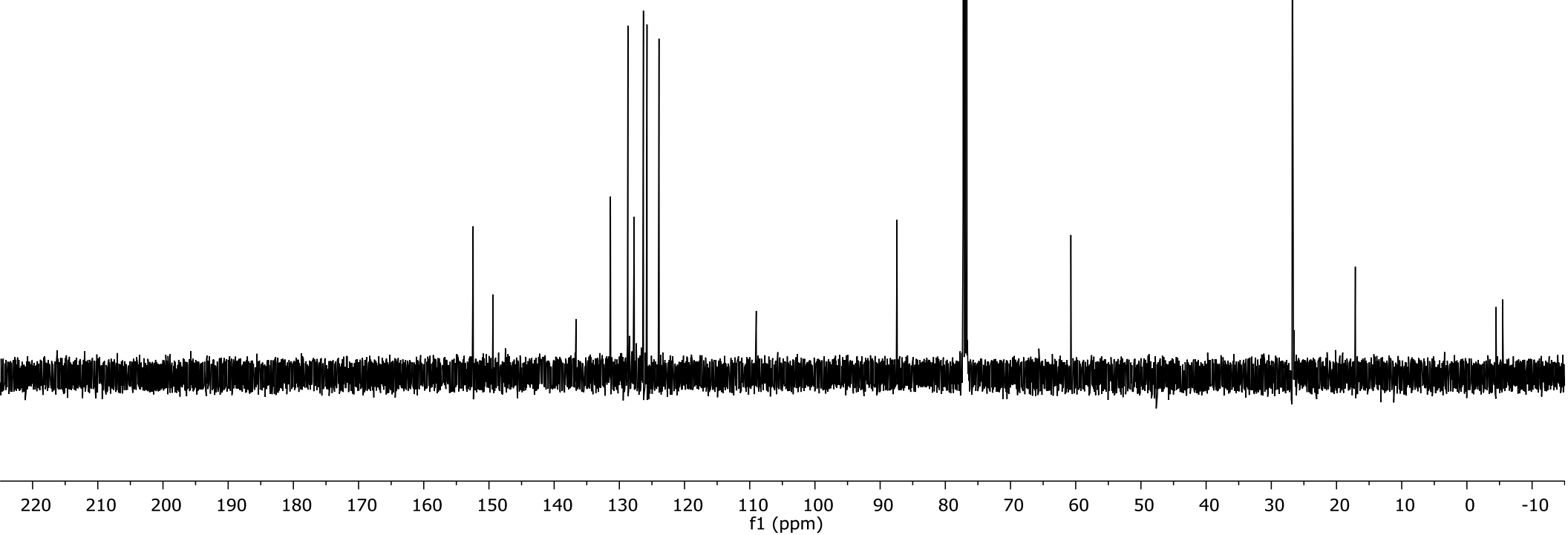
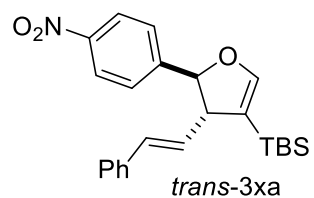


Parameter	
Title	TingLI-2019-10-1H
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	¹ H

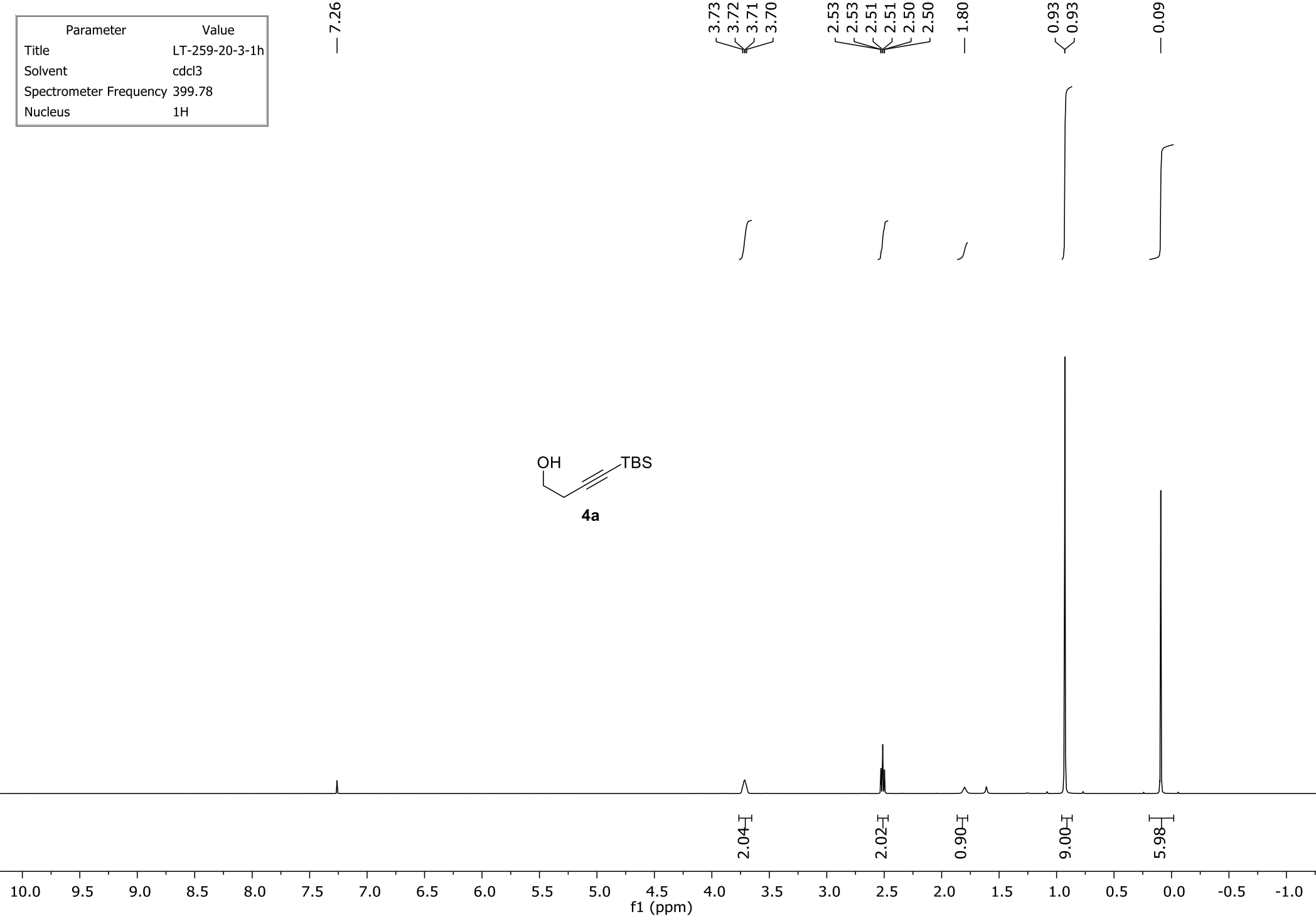


Parameter	Value
Title	TingLI-265-10-13C
Solvent	cdcl3
Spectrometer Frequency	125.70
Nucleus	13C

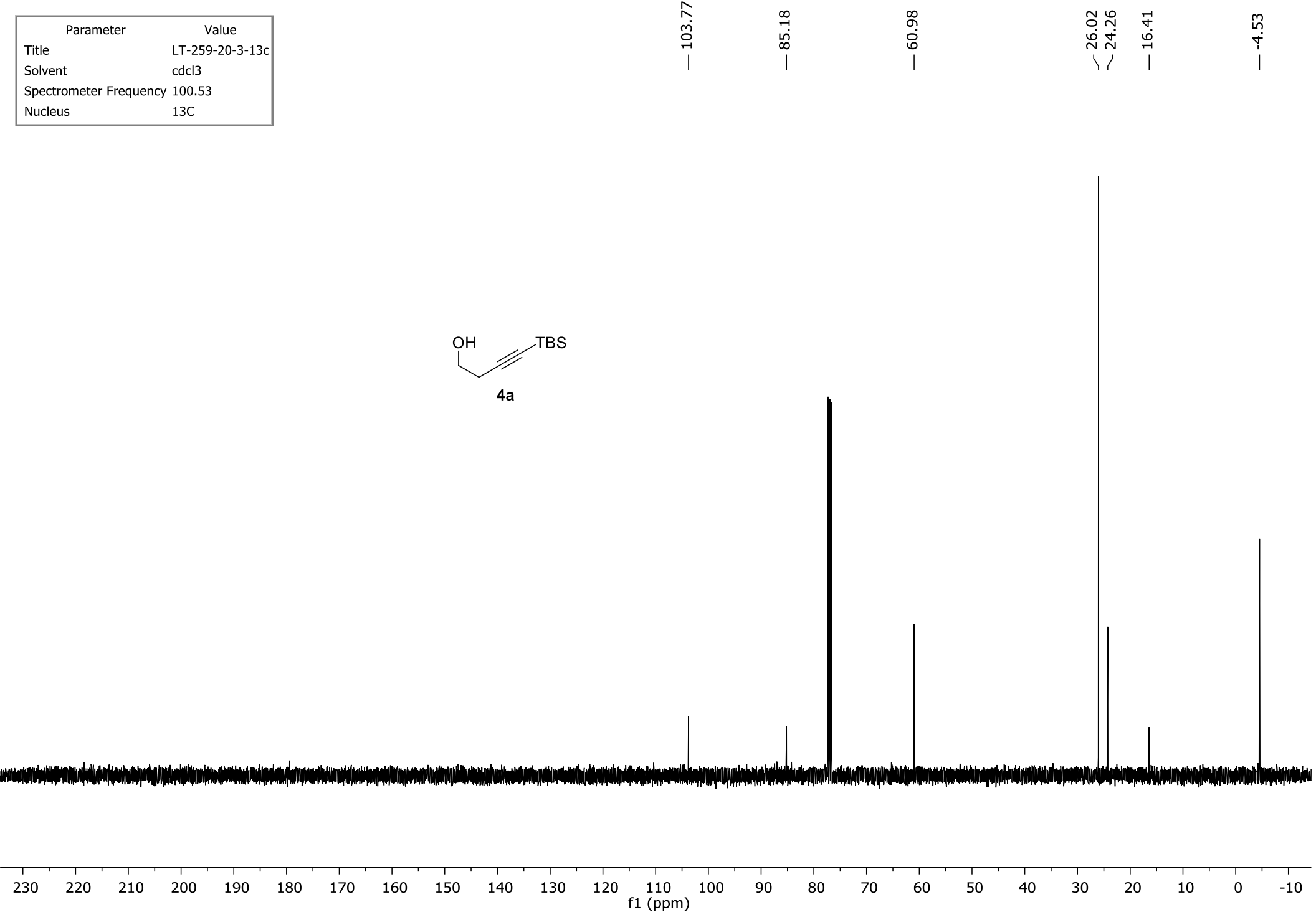
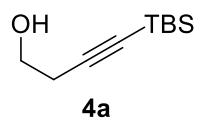
152.43
 149.38
 136.65
 131.37
 131.34
 128.69
 128.46
 127.73
 126.31
 125.76
 123.92
 109.00
 87.42
 60.75
 26.78
 26.52
 17.11
 -4.47
 -5.47



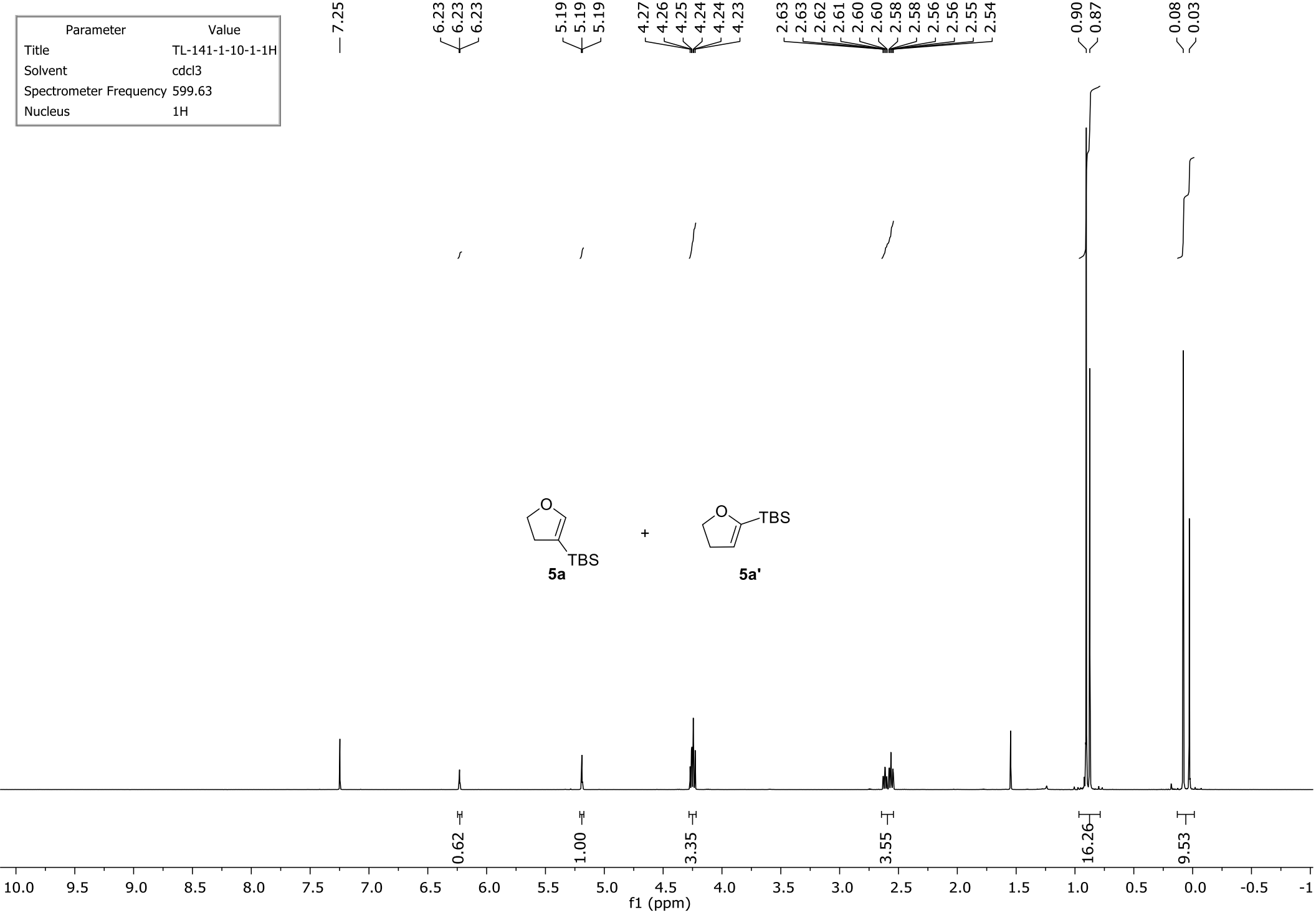
Parameter	Value
Title	LT-259-20-3-1h
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	¹ H



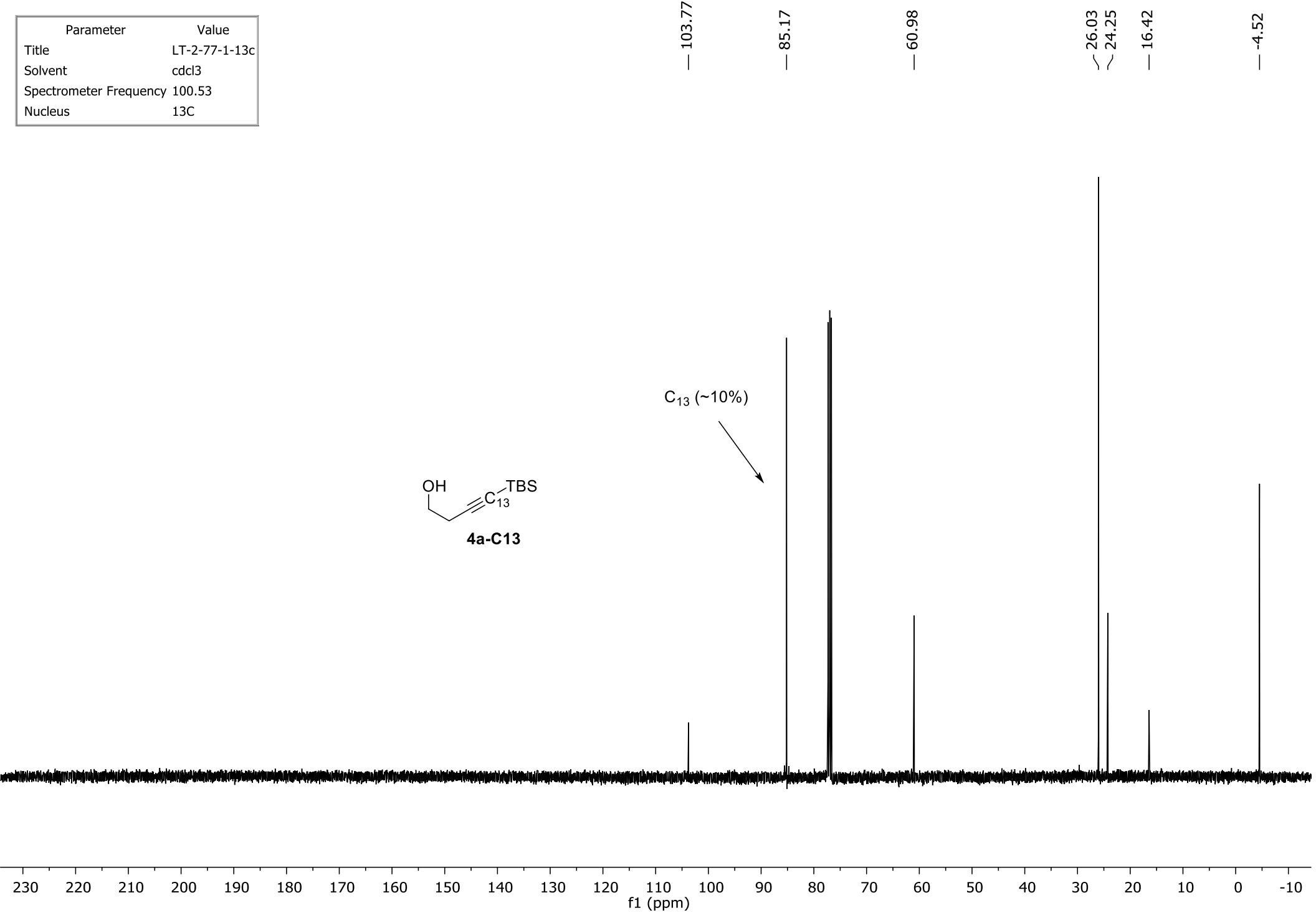
Parameter	Value
Title	LT-259-20-3-13c
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C



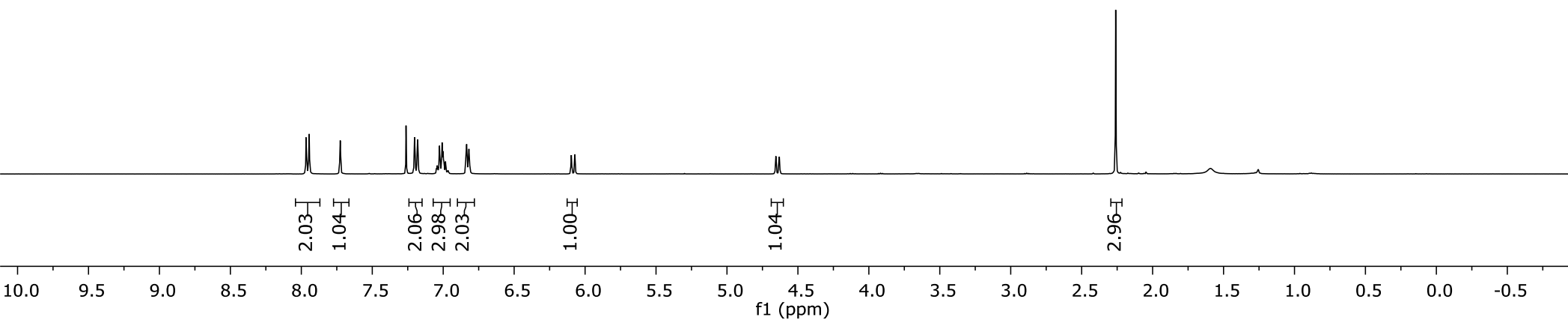
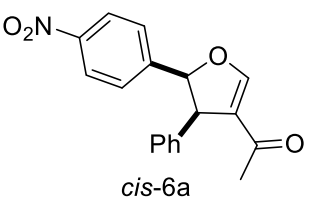
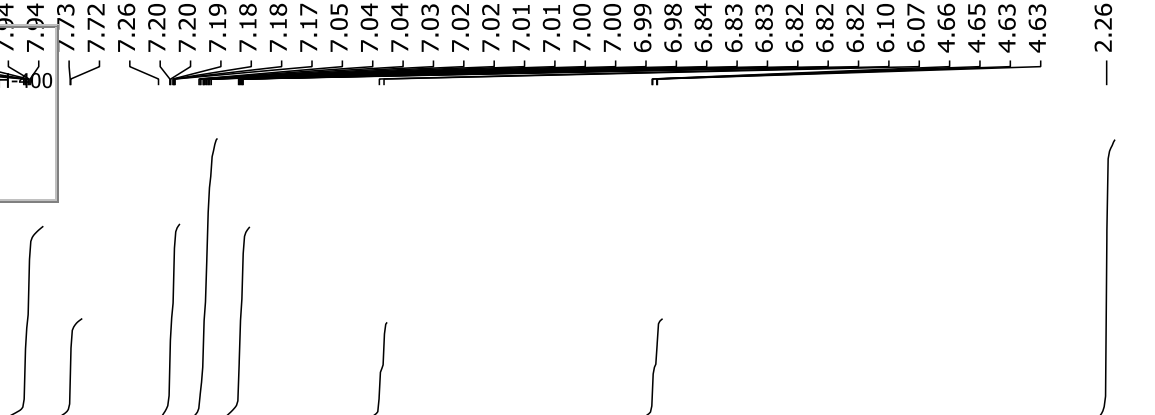
Parameter	Value
Title	TL-141-1-10-1-1H
Solvent	cdcl3
Spectrometer Frequency	599.63
Nucleus	¹ H



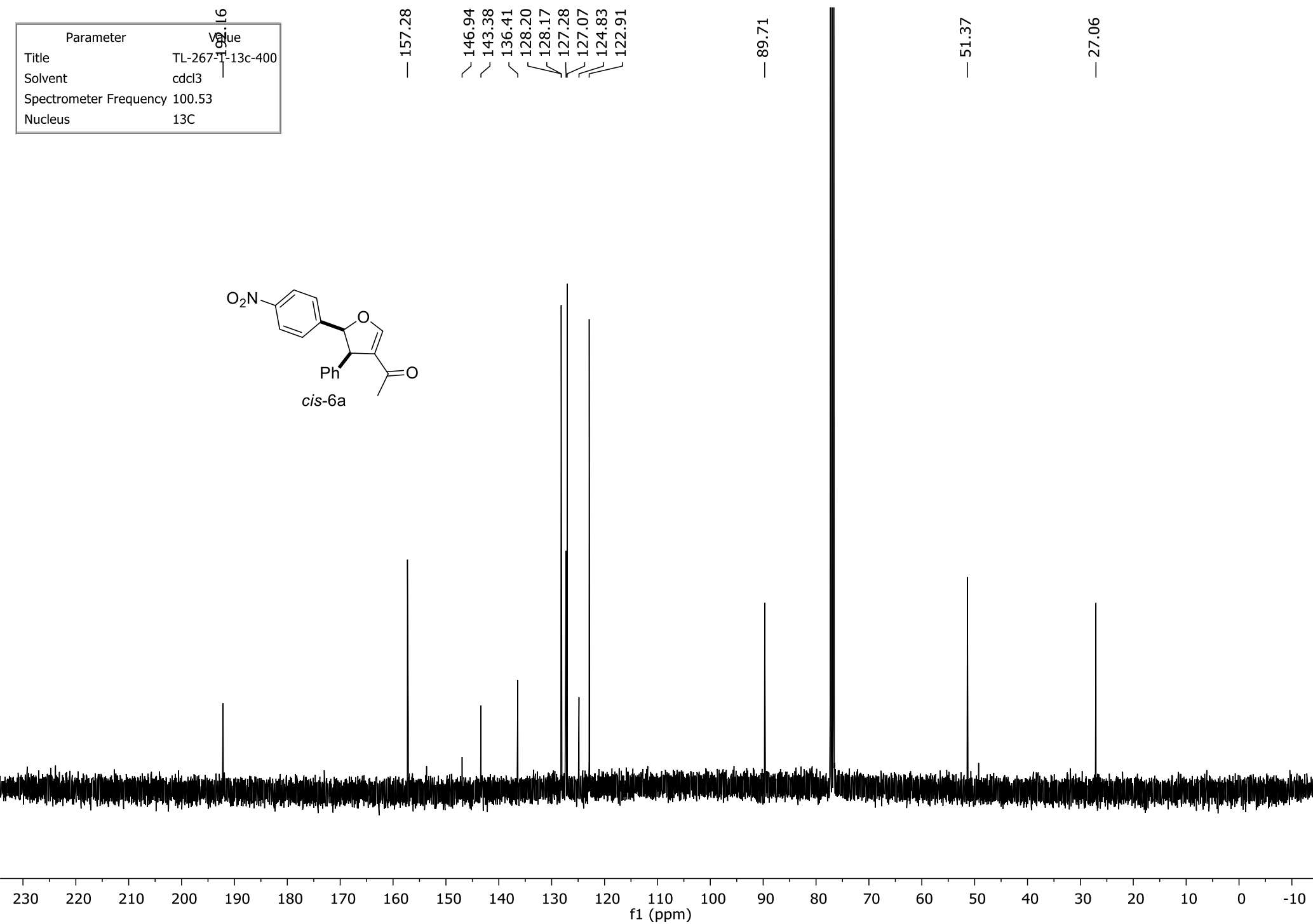
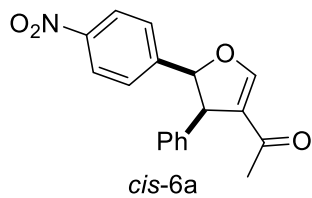
Parameter	Value
Title	LT-2-77-1-13c
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C



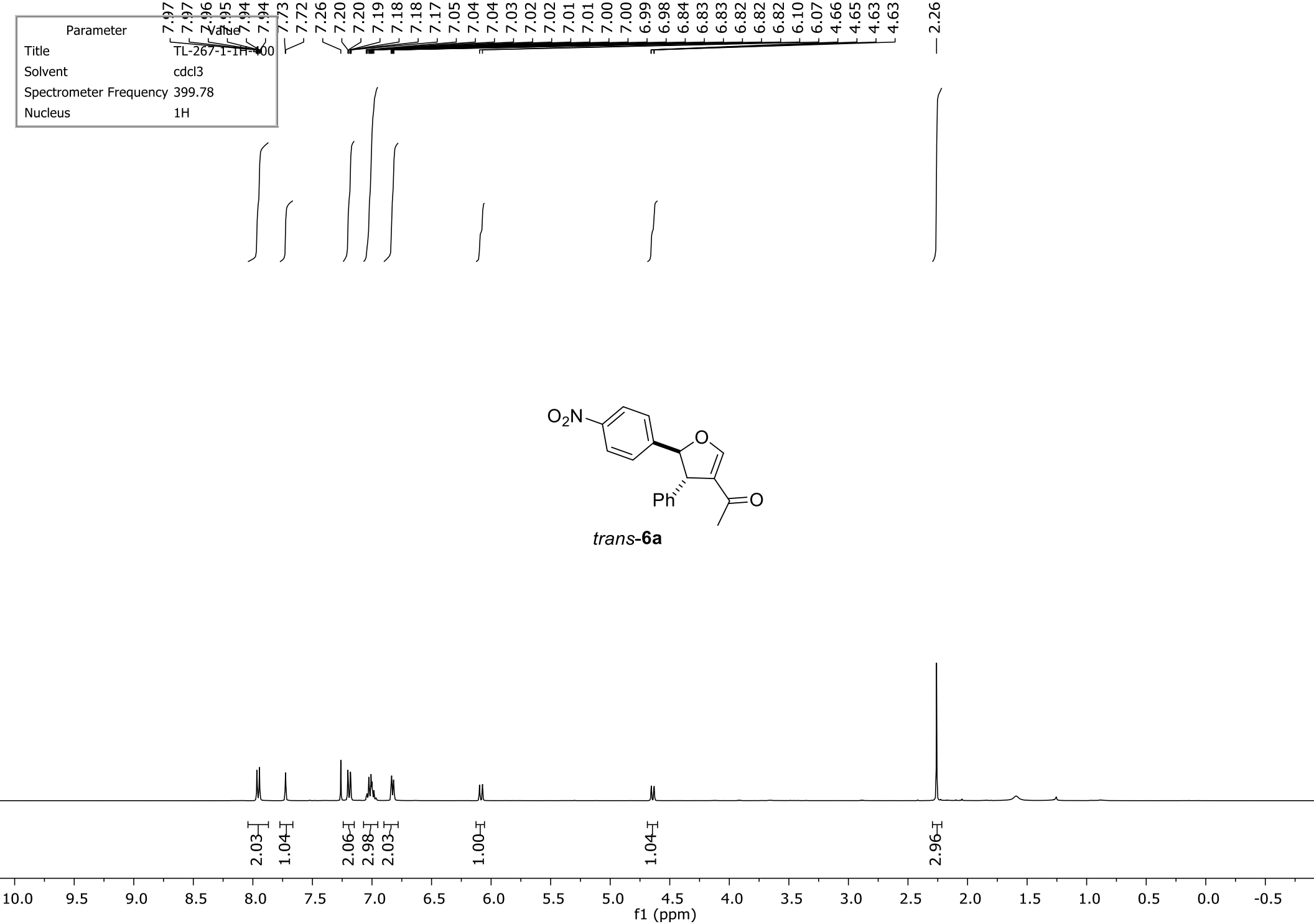
Parameter	Value
Title	TL-267-1-1H-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H



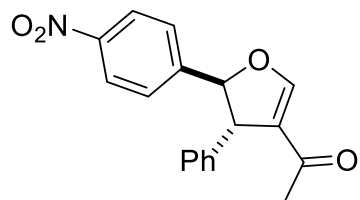
Parameter	Value
Title	TL-267-T-13c-400
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C



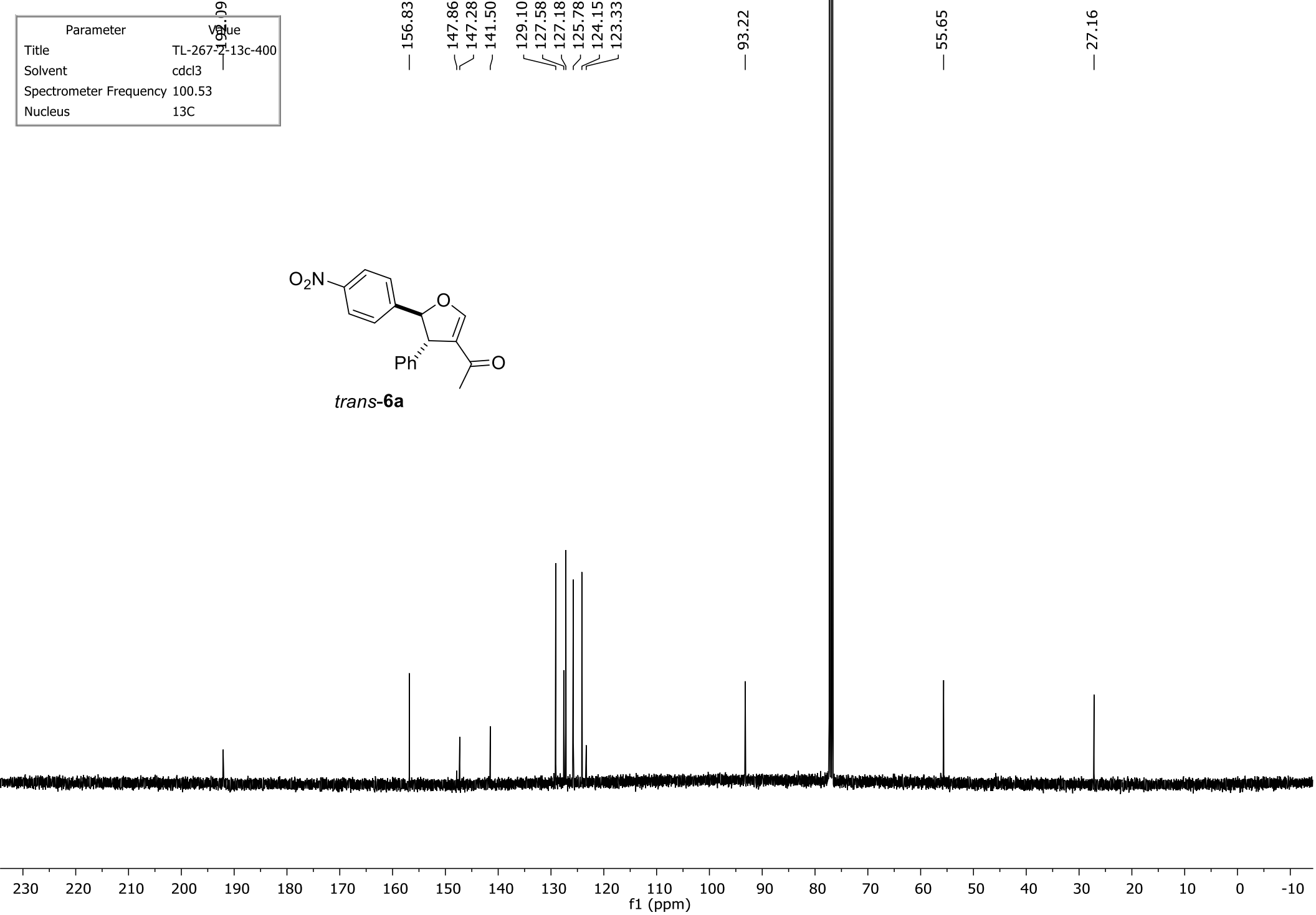
Parameter	Value
Title	TL-267-1-1H-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H



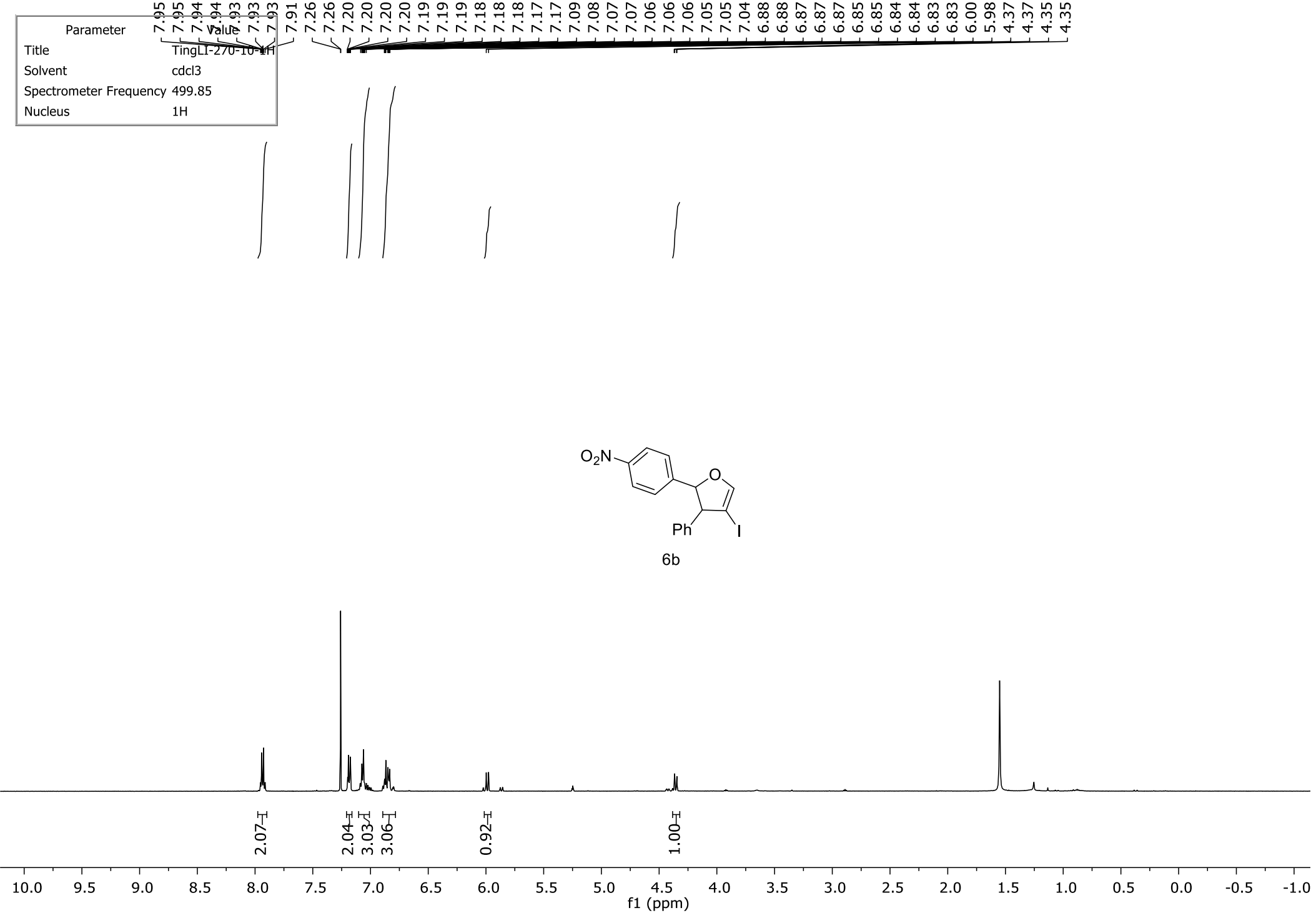
Parameter	Value
Title	TL-267-2-13c-400
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	13C



trans-6a



Parameter	Value
Title	TingLI-270-10-11
Solvent	cdcl3
Spectrometer Frequency	499.85
Nucleus	1H



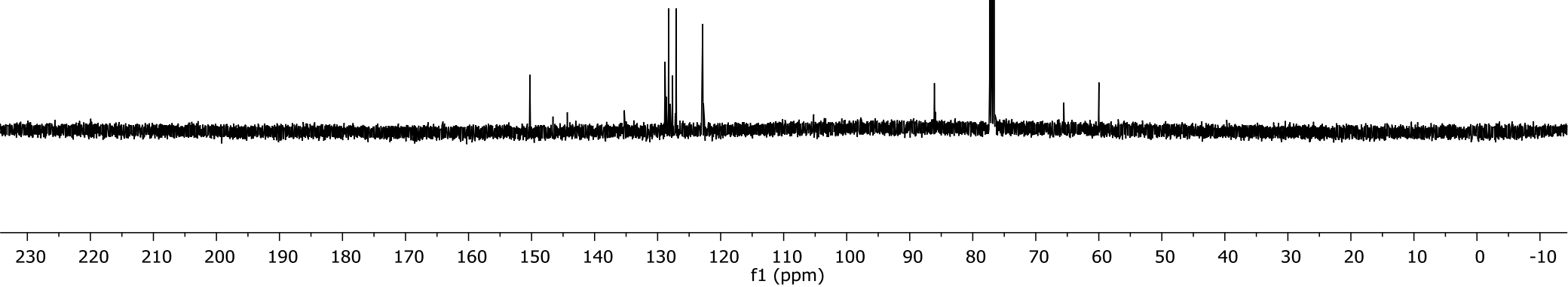
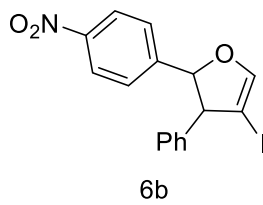
Parameter	Value
Title	LT-270-1-13c
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C

^{150.27}
^{146.60}
^{144.33}
^{128.82}
^{128.62}
^{128.25}
^{127.63}
^{127.08}
^{122.86}

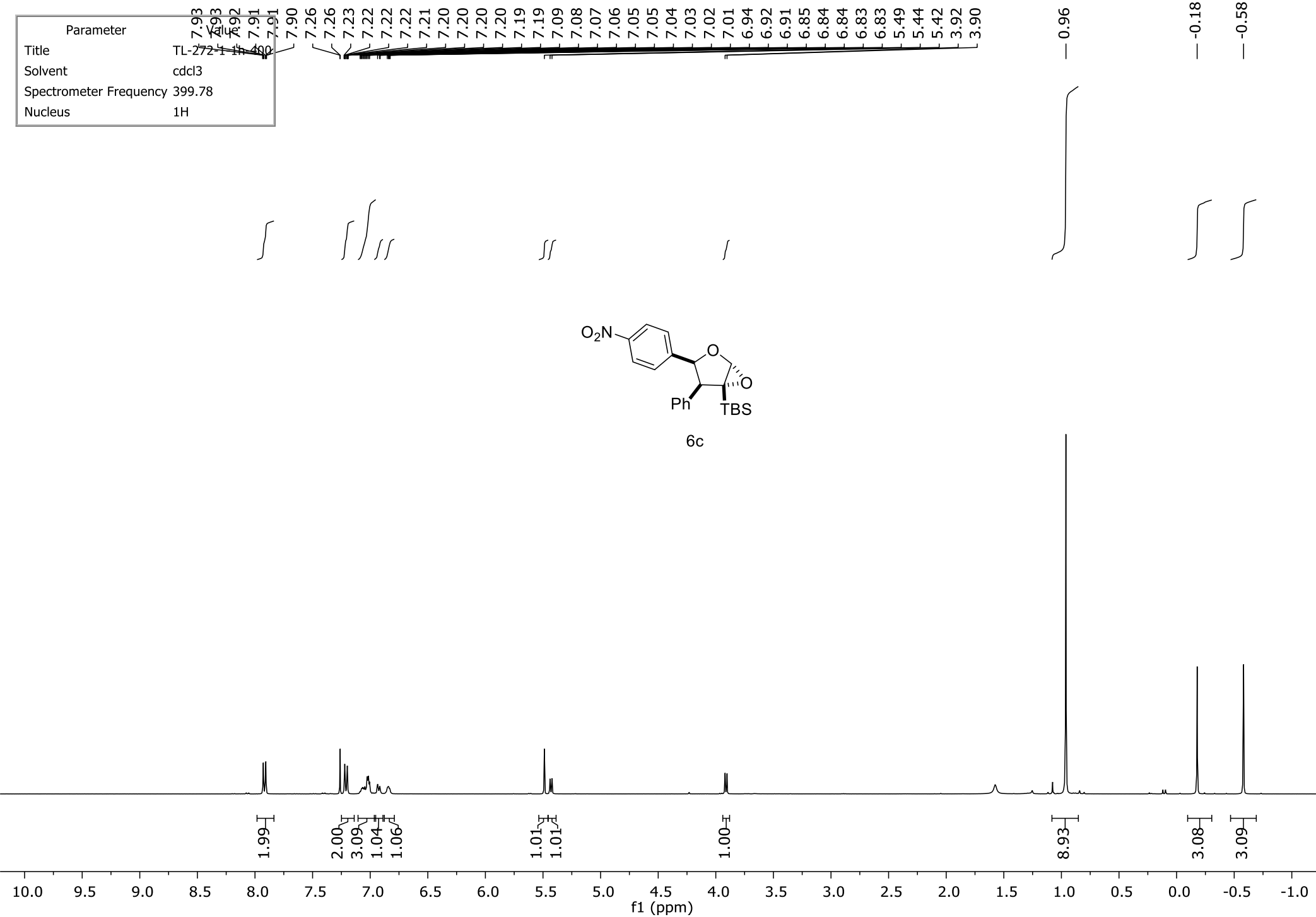
— ^{86.08} —

— ^{65.55} —

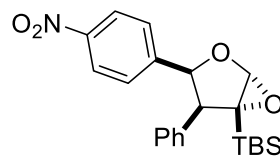
— ^{59.98} —



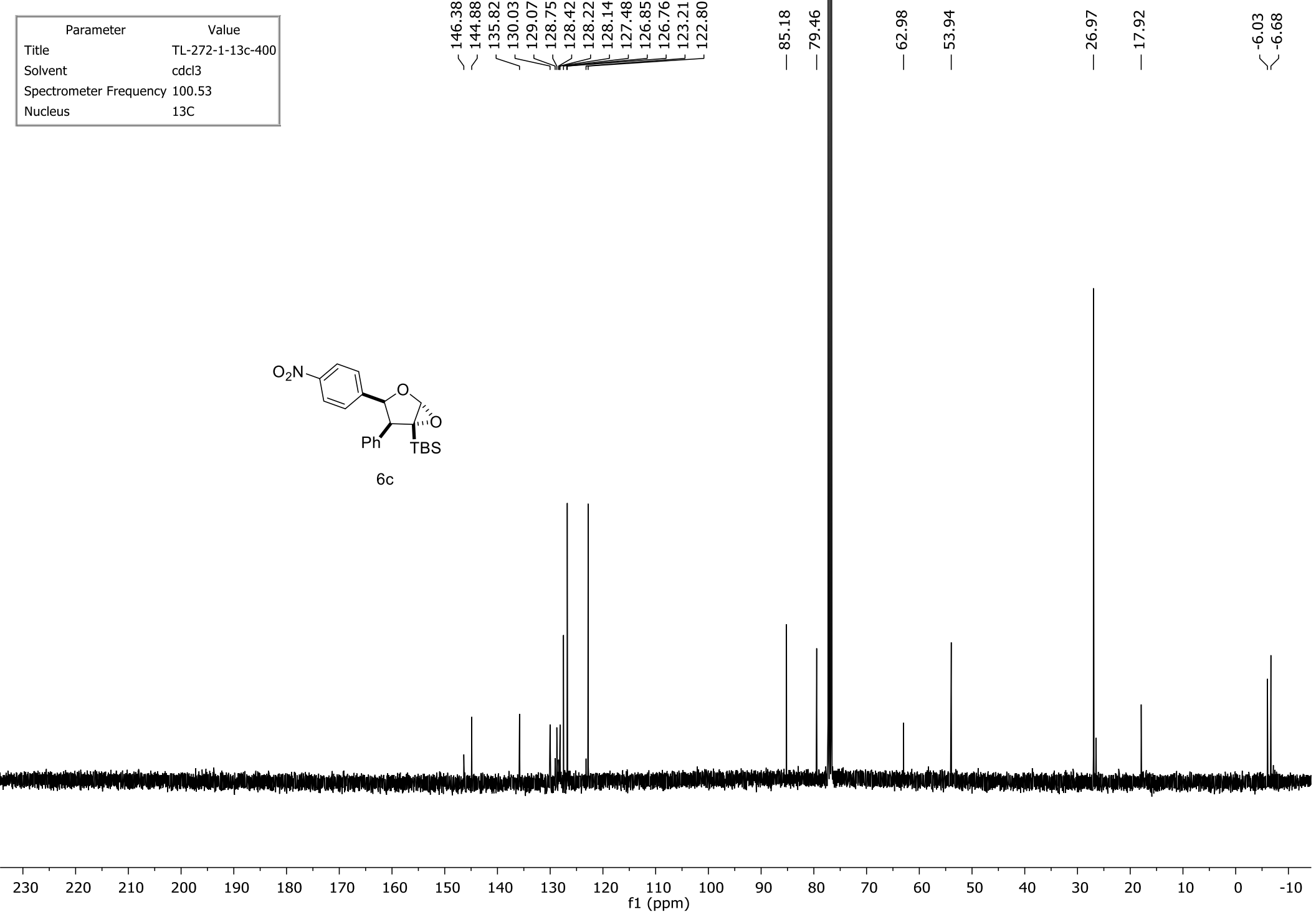
Parameter	
Title	TL-272-1-1-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H



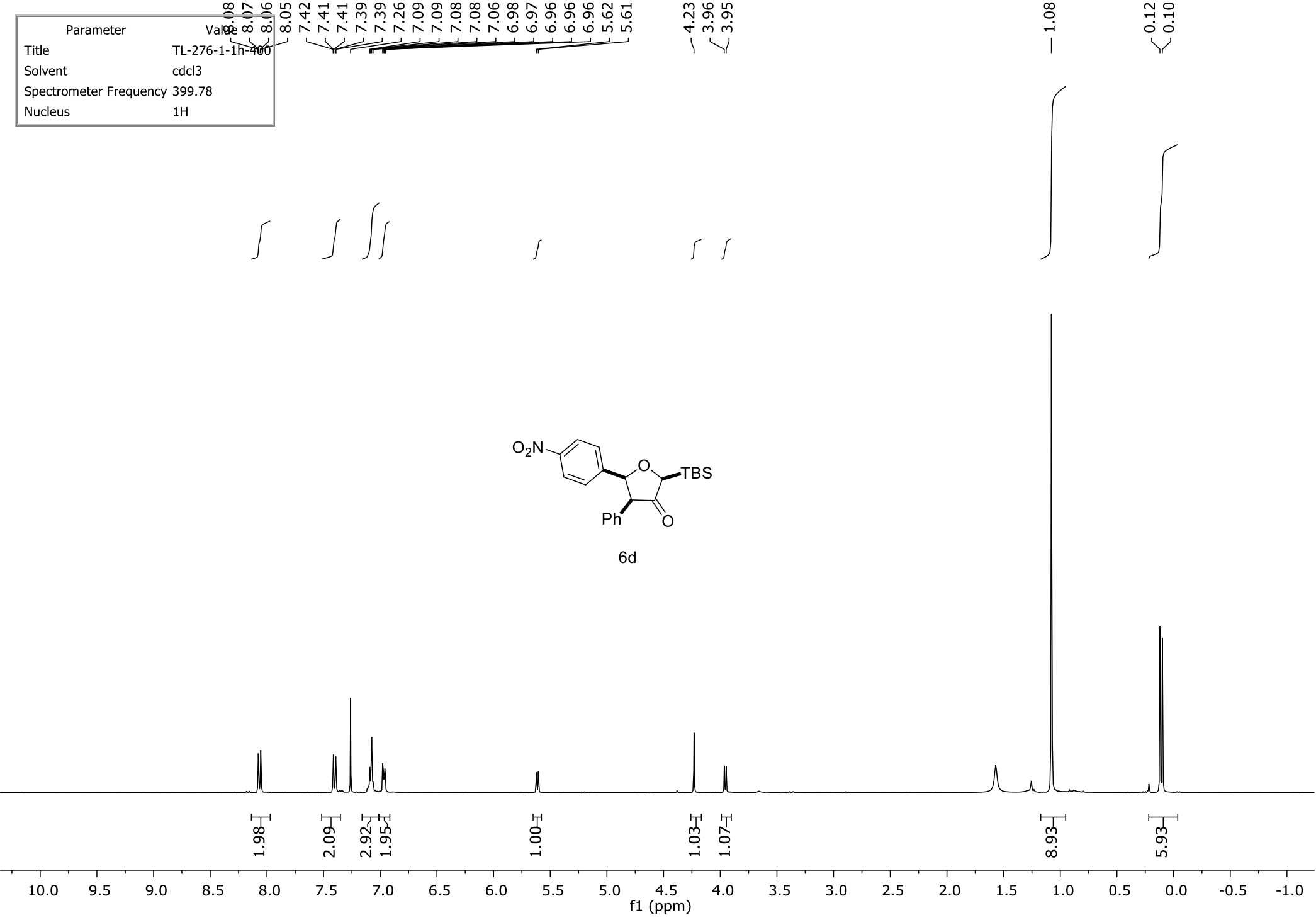
Parameter	Value
Title	TL-272-1-13c-400
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	13C



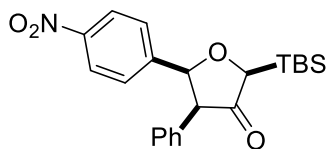
6c



Parameter	Value
Title	TL-276-1-1h-400
Solvent	cdcl3
Spectrometer Frequency	399.78
Nucleus	1H



Parameter	Value
Title	TL-276-1-13c-400
Solvent	cdcl3
Spectrometer Frequency	100.53
Nucleus	¹³ C



6d

