Copper-Catalyzed Propargylic C-H Functionalization for Allene Syntheses

Dongjie Zhang, Junjie Fan†, Yaqi Shi†, Yankai Huang†, Chunling Fu, Xiaoyan Wu* and Shengming Ma*

† These authors contributed equally.

Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, Hangzhou 310027, Zhejiang, P. R. China.

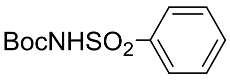
E-mail: masm@sioc.ac.cn

Supporting Information

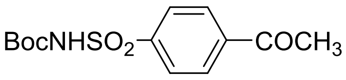
Table of Contents

General Information

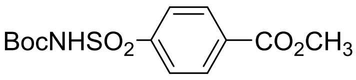
^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded using a Bruker AM 300 MHz NMR spectrometer (^{1}H at 300 MHz, 400 MHz, and 500 MHz, ^{13}C at 75 MHz, 100 MHz, and 125 MHz, ^{19}F at 282 MHz, 376 MHz, 564 MHz) unless noted otherwise: All ^{1}H NMR spectra were measured with TMS (0 ppm) in $CDCl_3$; all ^{19}F NMR spectra were measured with $CFCl_3$ (0 ppm) as the internal standard; all ^{13}C NMR spectra were recorded in relative to the signal of $CDCl_3$ (77.0 ppm). IR spectra were recorded with a Perkin–Elmer 983G instrument. Elemental analyses were conducted with a Carlo-Erba EA1110 elementary analysis instrument. Mass spectrometry was performed with an HP 5989A system. High-resolution mass spectrometry was determined with a Finnigan MAT 8430 or Bruker APEXIII instrument. $Cu(CH_3CN)_4PF_6$ was purchased from TCI, ligand **L1** was purchased from Adamas, and **L2** was purchased from Bidepharm. Acetonitrile and dichloromethane were dried over CaH_2 and distilled freshly before use. Tetrahydrofuran was dried over sodium wire with benzophenone as the indicator and distilled freshly before use. The range of boiling point of the petroleum ether used for chromatography was 60~90 °C unless noted otherwise. Boc-protected benzenesulfonamides **TsNHBoc**,[1] **Boc 1q-Boc 1x**,[1] alkynol **S1p**,[2] and ligand (*S*,*S*)-**L13***[3] were prepared according to the literature procedure. Other commercially available reagents were purchased and used as received.



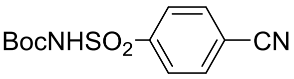
Boc-1v



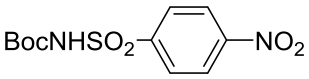
Boc-1w



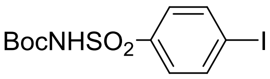
Boc-1x



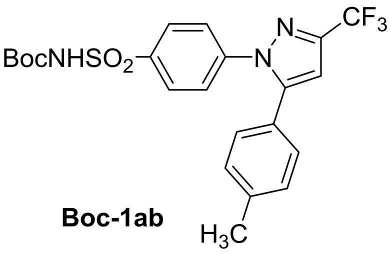
Boc-1y



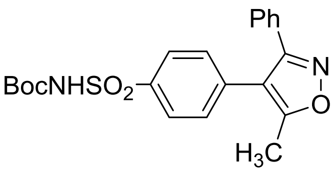
Boc-1z



Boc-1aa



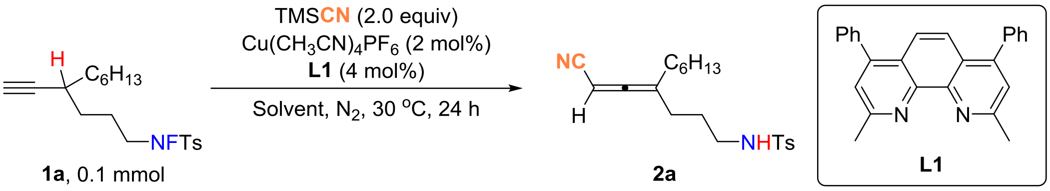
Boc-1ab



Boc-1ac

1. Optimization of Reaction Conditions

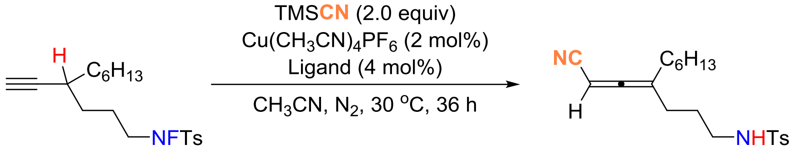
Table S1. Optimization of Solvents[a]



Entry	Solvent	Yield of **2a** (%)[b]	Recovery of **1a** (%)[b]
1	DCE	17	70
2	toluene	10	67
3	ethyl acetate	29	35
4	MTBE	13	56
5	THF	13	24
6	dioxane	38	17
7	DMF	44	-
8	CH_3CN	75	12
9[c]	CH_3CN	83	-

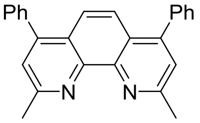
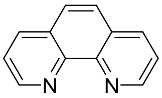
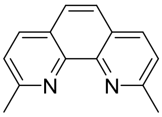
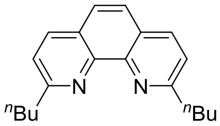
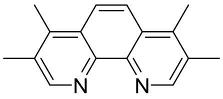
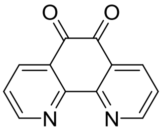
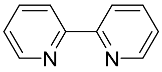
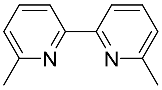
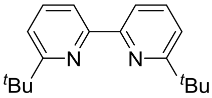
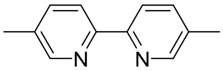
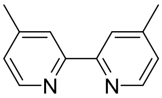
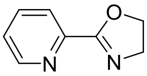
[a] All reactions were run on 0.1 mmol scale in solvent (1 mL) at 30 °C for 24 hours under a nitrogen atmosphere. [b] Yield and recovery were determined via crude ^{1}H NMR analysis with CH_3NO_2 as internal standard. [c] The reaction was run for 30 hours.

Table S2. Optimization of Ligands[a, b]



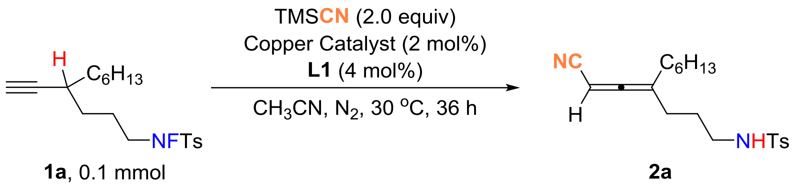
1a, 0.1 mmol

2a

 **L1** 83% yield[c]	 **L2** 49% yield 47% recovery of **1a**	 **L3** 75% yield 7% recovery of **1a**	 **L4** 71% yield 5% recovery of **1a**
 **L5** 3% yield 67% recovery of **1a**	 **L6** 78% yield 2% recovery of **1a**	 **L7** 77% yield	 **L8** 65% yield 23% recovery of **1a**
 **L9** 5% yield 91% recovery of **1a**	 **L10** 67% yield 6% recovery of **1a**	 **L11** 12% yield 73% recovery of **1a**	 **L12** 62% yield

[a] All reactions were run on 0.1 mmol scale in CH_3CN (1 mL) at 30 °C for 36 hours under a nitrogen atmosphere. [b] Yield and recovery were determined via crude ^1H NMR with CH_3NO_2 as internal standard. [c] The reaction was run for 30 hours.

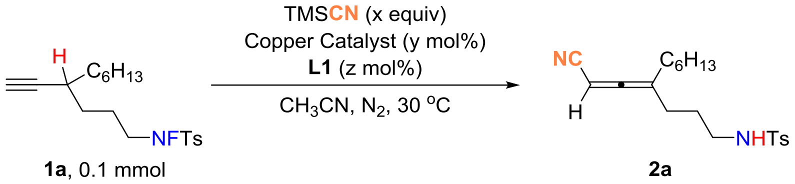
Table S3. Optimization of Copper Catalysts[a]



Entry	Copper catalyst	Yield of **2a** (%)[b]	Recovery of **1a** (%)[b]
1[c]	$Cu(CH_3CN)_4PF_6$	83	-
2	$Cu(CH_3CN)_4BF_4$	61	10
3	CuCN	69	-
4	CuTc	61	-
5	CuCl	61	-
6	CuBr	59	-
7	CuOAc	66	-
8	$Cu(OAc)_2$	72	-
9	$Cu(OTf)_2$	57	27

[a] All reactions were run on 0.1 mmol scale in CH_3CN (1 mL) at 30 °C for 36 hours under a nitrogen atmosphere. [b] Yield and recovery were determined via crude ^1H NMR with CH_3NO_2 as internal standard. [c] The reaction was run for 30 hours.

Table S4. Optimization of Other Conditions [a]



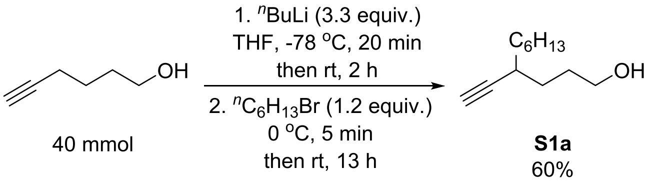
Entry	x	y	z	Time/h	Yield of **2a** (%)[b]	Recovery of **1a** (%)[b]
1	1.5	2	4	32	76	-
2	2	2	4	30	83	-
3	2.5	2	4	32	65	11
4[c]	2	1	2	36	77	-
5	2	3	6	26	80	-
6	2	2	2	36	14	83
7	2	2	3	36	80	3
8	2	2	5	24	77	-

[a] All reactions were run on 0.1 mmol scale in CH_3CN (1 mL) at 30 °C under a nitrogen atmosphere.
[b] Yield and recovery were determined via crude ^1H NMR analysis with CH_3NO_2 as internal standard.
[c] Reaction on 0.2 mmol scale.

2. Synthesis of Starting Materials

2.1. Synthesis of **1a**.

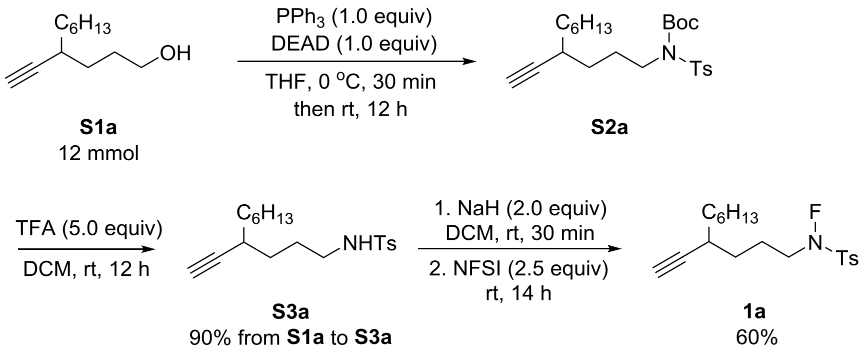
2.1.1. Synthesis of 4-hexylhex-5-ynol **S1a**. (zdj-4-002)



Typical Procedure I:[4] To a 250 mL flame-dried three-neck flask were added 5-hexynol (4.3 mL, d = 0.91 g/mL, 3.91 g, 39.8 mmol) and THF (120 mL) under a N_2 atmosphere. The resulting solution was cooled down to -78 °C and ^{n}BuLi (2.4 M in hexane, 55 mL, 132 mmol) was added dropwise at -78 °C within 20 minutes. The resulting mixture was stirred at room temperature for 2 hours, cooled down to 0 °C with an ice-water bath followed by the dropwise addition of ^{n}hexyl bromide (6.8 mL, d = 1.176 g/mL, 8.00 g, 48.4 mmol) at 0 °C within 5 minutes, stirred at room temperature for 13 hours, and quenched with a saturated aqueous solution of NH$_4$Cl slowly. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (120 mL × 2). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtrated, and concentrated in vacuo. The crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 7/1 (800 mL)] to afford **S1a** (4.3255 g, 60%) as an oil: ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.67 (t, *J* = 6.3 Hz, 2 H, OCH$_2$), 2.41-2.26 (m, 1 H, CH), 2.06 (d, *J* = 2.5 Hz, 1 H, ≡CH), 1.86-1.74 (m, 1 H, one proton of CH$_2$), 1.72-1.62 (m, 2 H, OH and one proton of CH$_2$), 1.62-1.22 (m, 12 H, CH$_2$ × 6), 0.89 (t, *J* = 7.0 Hz, 3 H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 87.8, 69.4, 62.6, 35.0, 31.7, 31.3, 31.1, 30.4, 29.1, 27.2, 22.6, 14.0; IR (neat) *ν* (cm^{-1}) 3331, 2108; MS (EI): *m/z* (%) 182 (M$^+$, 0.75), 79 (100); Anal. Calcd. for C$_{12}$H$_{22}$O (%): C, 79.06; H, 12.16; Found: C, 78.90; H, 12.01.

2.1.2. Synthesis of *N*-fluoro-*N*-(4-hexylhex-5-ynyl)-4-methylbenzenesulfonamide **1a**.

(zdj-3-033, zdj-3-037, zdj-3-040, zdj-3-017)



Typical Procedure II:[5] To a 100 mL flame-dried round-bottomed flask were added PPh_3 (3.9452 g, 15.0 mmol), TsNHBoc (4.3640 g, 16.1 mmol), and THF (15 mL). The resulting solution was cooled down to 0 °C with an ice-water bath followed by the dropwise addition of a solution of **S1a** (2.7455 g, 15.1 mmol) and DEAD (2.4 mL, d = 1.106 g/mL, 2.65 g, 15.2 mmol) in THF (9 mL) within 30 minutes. The cooling bath was removed and the reaction was stirred at room temperature for 12 hours as monitored by TLC. The resulting mixture was concentrated in vacuo followed by the slow addition of Et_2O with stirring and filtered through a short column of silica gel eluted with Et_2O. The filtrate was concentrated in vacuo and the crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 20/1 (800 mL)] to afford **S2a** (6.2625 g) as an oil, which was used for the next step without further characterization.

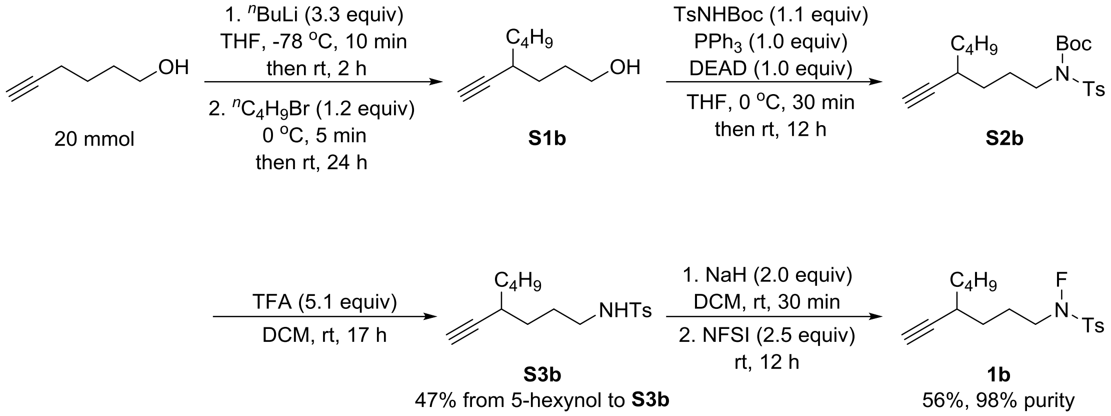
Typical Procedure III:[5] To a 100 mL round-bottomed flask were added **S2a** (6.2625 g), CH_2Cl_2 (30 mL), and TFA (5.5 mL, d = 1.489 g/mL, 8.19 g, 71.8 mmol). The resulting mixture was stirred at room temperature for 12 hours as monitored by TLC and washed subsequently with H_2O (50 mL), a saturated aqueous solution of $NaHCO_3$ (50 mL), and brine sequentially. The organic phase was dried over anhydrous Na_2SO_4, filtrated through a short column of silica gel eluted with CH_2Cl_2 (30 mL × 5), and concentrated in vacuo to afford **S3a** (4.5718 g, 90% from **S1a** to **S3a**) as a solid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2 H, ArH), 7.31 (d, J = 8.1 Hz, 2 H, ArH), 4.79 (t, J = 6.2 Hz, 1 H, NH), 2.96 (q, J = 6.6 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.33-2.14 (m, 1 H, CH), 2.01 (d, J = 2.1 Hz, 1 H, ≡CH), 1.80-1.19 (m, 14 H, CH_2 × 7), 0.88 (t, J = 6.6 Hz, 3 H, CH_3). **S3a** was used for the next step without further characterization.

Typical Procedure IV:[6] To a 250 mL flame-dried three-neck flask was added **S3a** (2.3467 g, 7.0 mmol). After degassing under vacuum and backfilling with nitrogen for three times, CH_2Cl_2 (90 mL) and NaH (0.5633 g, 60 wt% in mineral oil, 14.1 mmol) were added sequentially at room temperature under a N_2 atmosphere. The resulting mixture was stirred for 30 minutes followed by the addition of NFSI (5.5080 g, 17.5 mmol). The resulting mixture was stirred for 14 hours as monitored by TLC and quenched with H_2O slowly. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (90 mL × 2). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 80/1 (400 mL) to 60/1 (300 mL) to 40/1 (400 mL)] to afford **1a** (1.4894 g, 60%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 8.4 Hz, 2 H, ArH), 7.41 (d, J = 7.8 Hz, 2 H, ArH), 3.31 (td, J_1 = 6.9 Hz, J_2 = 1.2 Hz, 1 H, one proton of NCH_2), 3.17 (td, J_1 = 6.9 Hz, J_2 = 1.5 Hz, 1 H, one proton of NCH_2), 2.49 (s, 3 H, CH_3), 2.42-2.25 (m, 1 H, CH), 2.04 (d, J = 2.4 Hz, 1 H, ≡CH), 2.02-1.87 (m, 1 H, one proton of CH_2), 1.87-1.70 (m, 1 H, one proton of CH_2), 1.70-1.17 (m, 12 H, CH_2 × 6), 0.88 (t, J = 6.3 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 129.95, 129.93, 128.8, 87.1, 69.7, 53.5 (d, J = 11.7 Hz), 34.9, 31.70, 31.67, 31.1, 29.0, 27.1, 24.1, 22.6, 21.7, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.4; IR (neat) v (cm^{-1}) 3306, 2103, 1597, 1456, 1376, 1307; MS (ESI): m/z 392 [(M + K)$^+$], 376 [(M + Na)$^+$], 371 [(M + NH_4)$^+$]; HRMS (ESI) Calcd for $C_{19}H_{28}FNNaO_2S$ [(M

+ Na)$^+$]: 376.1717; Found: 376.1716.

2.2. Synthesis of *N*-fluoro-*N*-(4-butylhex-5-ynyl)-4-methylbenzenesulfonamide **1b**.

(zdj-3-052, zdj-3-063, zdj-3-068, zdj-3-075)



Following **Typical Procedure I**, the reaction of 5-hexynol (2.7 mL, d = 0.91 g/mL, 2.46 g, 25.1 mmol), ^{n}BuLi (2.5 M in hexane, 33 mL, 82.5 mmol), and ^{n}butyl bromide (3.3 mL, d = 1.276 g/mL, 4.21 g, 30.7 mmol) in THF (75 mL) afforded **S1b** (2.2161 g) as an oil [eluent: petroleum ether/ethyl acetate = 7/1 (1000 mL)], which was used for the next step without further characterization.

Following **Typical Procedure II**, the reaction of PPh$_3$ (3.8065 g, 14.5 mmol), TsNHBoc (4.1415 g, 15.3 mmol), DEAD (2.3 mL, d = 1.106 g/mL, 2.54 g, 14.6 mmol), and **S1b** (2.2161 g, 14.4 mmol) in THF (14 + 8 mL) afforded **S2b** (5.4365 g) as an oil [eluent: petroleum ether/ethyl acetate = 30/1 (465 mL) to 20/1 (420 mL)], which was used for the next step without further characterization.

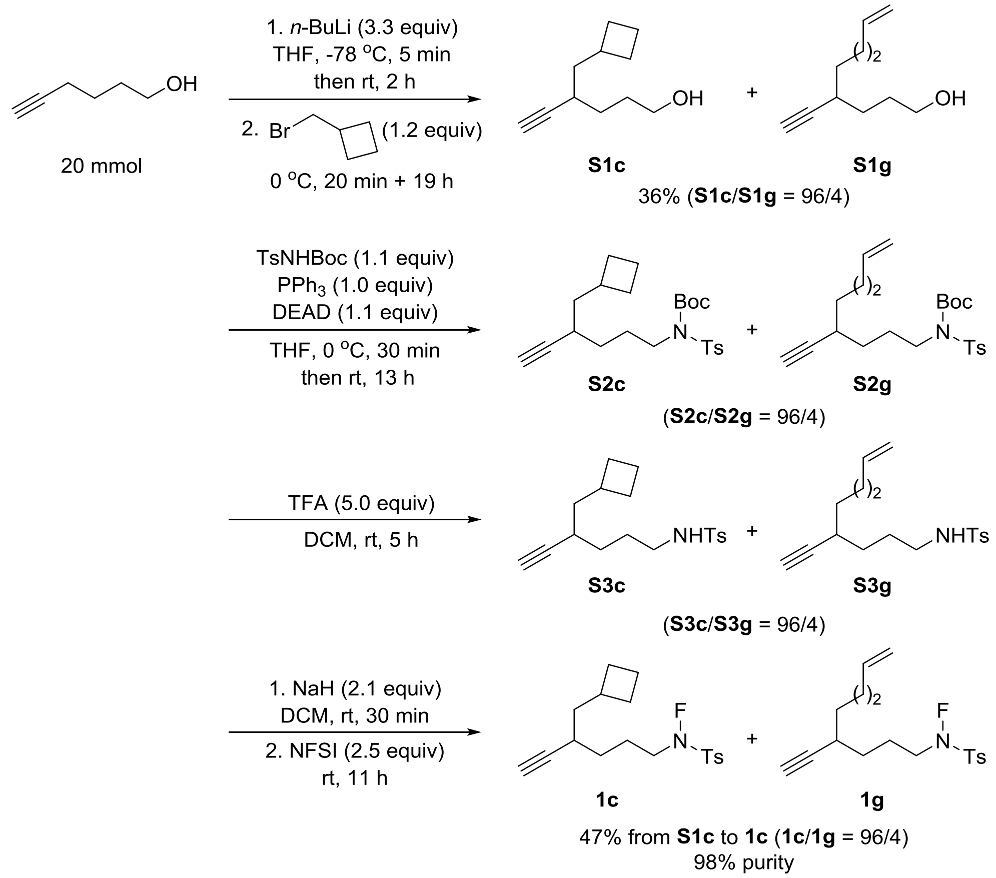
Following **Typical Procedure III**, the reaction of **S2b** (5.4365 g) and TFA (5.2 mL, d = 1.489 g/mL, 7.74 g, 67.9 mmol) in CH$_2$Cl$_2$ (30 mL) afforded **S3b** (3.5877 g, 47% from 5-hexynol to **S3b**) as an oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.1 Hz, 2

H, ArH), 7.31 (d, *J* = 8.7 Hz, 2 H, ArH), 4.62-4.43 (m, 1 H, NH), 2.97 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.33-2.13 (m, 1 H, CH), 2.01 (d, *J* = 2.4 Hz, 1 H, ≡CH), 1.77-1.18 (m, 10 H, CH_2 × 5), 0.89 (t, *J* = 7.1 Hz, 3 H, CH_3). **S3b** was used for the next step without further characterization.

To a 250 mL flame-dried three-neck flask was added NaH (0.5633 g, 60 wt% in mineral oil, 14.1 mmol). After degassing under vacuum and backfilling with nitrogen for three times, CH_2Cl_2 (75 mL) and a solution of **S3b** (2.1535 g, 7.0 mmol) in CH_2Cl_2 (15 mL) were added sequentially at room temperature under a N_2 atmosphere. The resulting mixture was stirred for 30 minutes followed by the addition of NFSI (5.5050 g, 17.5 mmol). The resulting mixture was stirred for 12 hours as monitored by TLC and quenched with H_2O slowly. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (90 mL × 2). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 20/1 (840 mL)] to afford **1b** (1.3016 g, 56%, 98% purity) as an oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2 H, ArH), 7.41 (d, *J* = 7.8 Hz, 2 H, ArH), 3.30 (td, J_1 = 6.8 Hz, J_2 = 1.7 Hz, 1 H, one proton of NCH_2), 3.17 (td, J_1 = 6.7 Hz, J_2 = 1.4 Hz, 1 H, one proton of NCH_2), 2.49 (s, 3 H, CH_3), 2.41-2.20 (m, 1 H, CH), 2.04 (d, *J* = 2.4 Hz, 1 H, ≡CH), 2.02-1.71 (m, 2 H, CH_2), 1.70-1.17 (m, 8 H, CH_2 × 4), 0.90 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 129.94, 129.92, 128.8, 87.1, 69.7, 53.5 (d, *J* = 12.6 Hz), 34.6, 31.6, 31.0, 29.3, 24.1, 22.4, 21.7, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.4; IR (neat) *v* (cm^{-1}) 3294, 2108, 1597, 1493, 1456, 1375; MS (ESI): *m/z* 364 [(M

+ K)$^+$], 348 [(M + Na)$^+$], 343 [(M + NH$_4$)$^+$], 326 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{17}H_{24}FNNaO_2S$ [(M + Na)$^+$]: 348.1404; Found: 348.1405.

2.3. Synthesis of *N*-fluoro-*N*-(4-(cyclobutyl)methylhex-5-ynyl)-4-methylbenzenesulfonamide **1c**. (zdj-4-057, zdj-4-059, zdj-4-062, zdj-4-063)



To a 250 mL flame-dried three-neck flask were added 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol) and THF (60 mL) under a N_2 atmosphere. The resulting solution was cooled down to -78 °C and ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol) was added dropwise at -78 °C within 5 minutes. The resulting mixture was stirred at room temperature for 2 hours followed by the dropwise addition of cyclobutylmethyl bromide (2.7 mL, d = 1.326 g/mL, 3.58 g, 24.0 mmol) at 0 °C within 20 minutes, stirred at 0 °C for 19 hours, and quenched with a saturated aqueous solution of NH_4Cl slowly. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (60 mL × 2). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 7/1 (800 mL)] to afford **S1c** (1.2158 g, 36%, **S1c**/**S1g** = 96/4 as determined by ^{1}H NMR analysis of the isolated product) as an oil. **S1c** was used for the next step without further characterization.

S1c: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.65 (t, J = 6.5 Hz, 2 H, OCH_2), 2.64-2.43 (m, 1 H, CH), 2.41-1.34 (m, 15 H, CH and CH_2 × 7).

The following signals are discernible for **S1g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91-5.70 (m, 0.04 H, =CH), 5.06-4.90 (m, 0.08 H, $=CH_2$).

Typical Procedure V: To a 100 mL flame-dried round-bottomed flask were added TsNHBoc (2.0662 g, 7.6 mmol), PPh_3 (1.9310 g, 7.4 mmol), and THF (10 mL). The resulting solution was cooled down to 0 °C with an ice-water bath followed by the dropwise addition of a solution of **S1c** (1.1882 g, 7.1 mmol) and DEAD (1.2 mL, d = 1.106 g/mL, 1.33 g, 7.6 mmol) in THF (6 mL) within 30 minutes. The cooling bath was removed and the resulting mixture was stirred at room temperature for 13 hours as monitored by TLC, concentrated in vacuo followed by the slow addition of Et_2O with stirring, and filtered through a short column of silica gel eluted with Et_2O. The filtrate was concentrated in vacuo and the crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 40/1 (410 mL) to 20/1 (220 mL)] to afford **S2c** (2.9074 g, **S2c**/**S2g** = 96/4 as determined by ^{1}H NMR analysis of the isolated product) as an oil, which was used for the next step without further characterization.

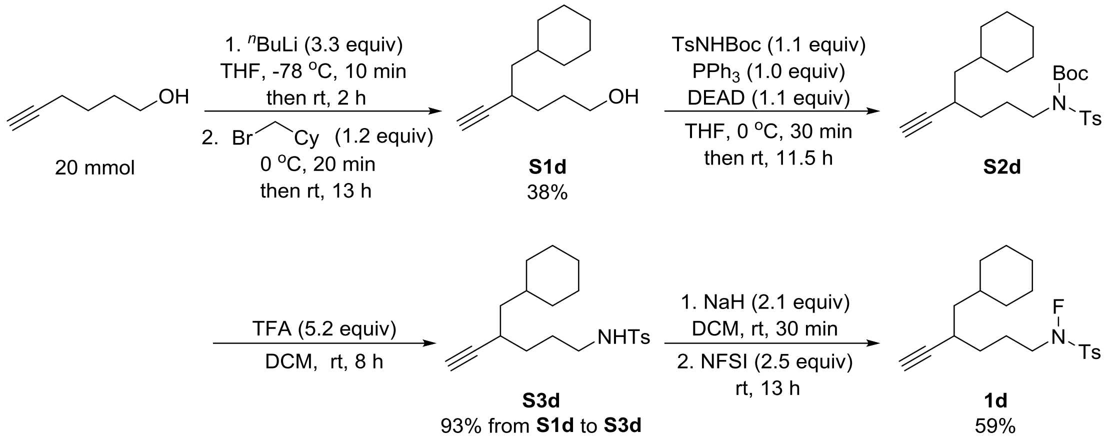
Following **Typical Procedure III**, the reaction of **S2c** (2.8651 g) and TFA (2.6 mL, d = 1.489 g/mL, 3.87 g, 33.9 mmol) in CH_2Cl_2 (15 mL) afforded **S3c** (2.1084 g, **S3c**/**S3g** = 96/4 as determined by ^1H NMR analysis of the isolated product) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3c** (2.0810 g), NaH (0.5375 g, 60 wt% in mineral oil, 13.4 mmol), and NFSI (5.1439 g, 16.3 mmol) in CH_2Cl_2 (70 mL) afforded **1c** (1.1207 g, 47% from **S1c** to **1c,** 98% purity, **1c**/**1g** = 96/4 as determined by ^1H NMR analysis of the isolated product) [eluent: petroleum ether/ethyl acetate = 50/1 (765 mL)].

1c, oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 8.5 Hz, 2 H, ArH), 7.41 (d, J = 8.0 Hz, 2 H, ArH), 3.36-3.08 (m, 2 H, NCH_2), 2.56-2.43 (m, 4 H, CH_3 and CH), 2.32-2.23 (m, 1 H, CH), 2.12-1.99 (m, 3 H, CH_2 and ≡CH), 1.99-1.73 (m, 4 H, $CH_2 \times 2$), 1.69-1.41 (m, 6 H, $CH_2 \times 3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 129.93, 129.91, 128.8, 87.1, 69.6, 53.5 (d, J = 12.6 Hz), 42.1, 34.0, 31.7, 29.2, 28.5, 28.3, 24.0, 21.7, 18.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.3; IR (neat) v (cm^{-1}) 3294, 2112, 1597, 1445, 1375, 1308; MS (ESI): m/z 376 [$(M + K)^+$]; 360 [$(M + Na)^+$], 355 [$(M + NH_4)^+$], 338 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{18}H_{24}FNNaO_2S$ [$(M + Na)^+$]: 360.1404; Found: 360.1405.

The following signals are discernible for **1g**: ^1H NMR (500 MHz, $CDCl_3$) δ 5.85-5.75 (m, 0.035 H, =CH), 5.04-4.92 (m, 0.07 H, $=CH_2$).

2.4. Synthesis of *N*-fluoro-*N*-(4-(cyclohexyl)methylhex-5-ynyl)-4-methylbenzenesulfonamide **1d**. (zdj-3-143, zdj-3-147, zdj-3-149, zdj-3-151)



Following **Typical Procedure I**, the reaction of 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and cyclohexylmethyl bromide (3.4 mL, d = 1.269 g/mL, 4.32 g, 24.4 mmol) in THF (60 mL) afforded **S1d** (1.5046 g, 38%) as an oil [eluent: petroleum ether/ethyl acetate = 8/1 (900 mL) to 6/1 (350 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (t, *J* = 6.5 Hz, 2 H, CH_2), 2.58-2.36 (m, 1 H, CH), 2.05 (d, *J* = 2.4 Hz, 1 H, ≡CH), 1.94-1.34 (m, 12 H, $CH_2 \times 5$, CH and OH), 1.34-1.04 (m, 4 H, $CH_2 \times 2$), 1.04-0.71 (m, 2 H, CH_2). **S1d** was used for the next step without further characterization.

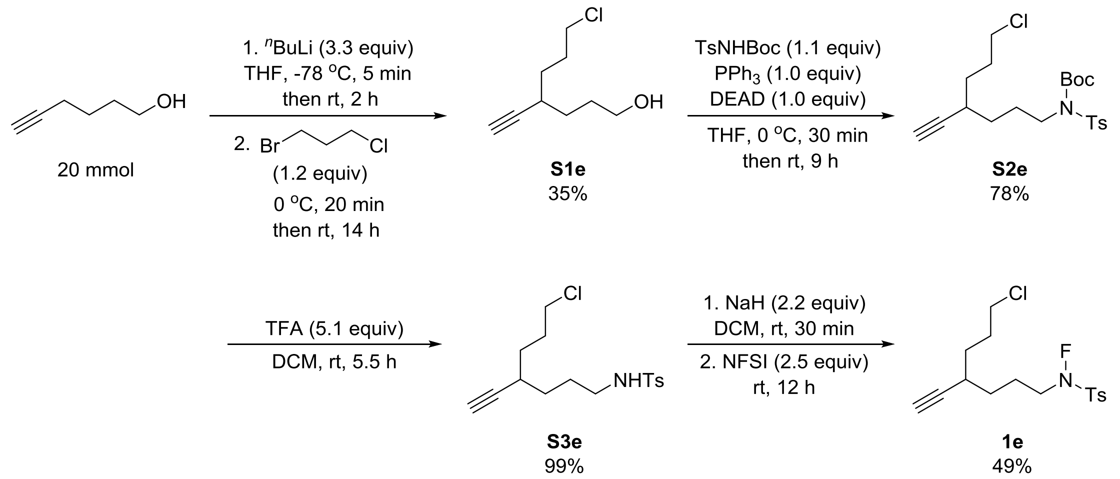
Following **Typical Procedure II**, the reaction of PPh_3 (2.0316 g, 7.7 mmol), TsNHBoc (2.2371 g, 8.2 mmol), DEAD (1.3 mL, d = 1.106 g/mL, 1.47 g, 8.4 mmol), and **S1d** (1.4820 g, 7.6 mmol) in THF (10 + 6 mL) afforded **S2d** (3.2035 g) as a solid [eluent: petroleum ether/ethyl acetate = 20/1 (600 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2d** (3.1912 g) and TFA (2.8 mL, d = 1.489 g/mL, 4.17 g, 36.6 mmol) in CH_2Cl_2 (15 mL) afforded **S3d** (2.4626 g, 93%

from **S1d** to **S3d**) as a solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2 H, ArH), 7.31 (d, *J* = 8.1 Hz, 2 H, ArH), 4.75-4.46 (m, 1 H, NH), 2.96 (q, *J* = 6.6 Hz, 2 H, NCH_2), 2.49-2.26 (m, 4 H, CH_3 and CH), 2.00 (d, *J* = 2.1 Hz, 1 H, ≡CH), 1.82-1.02 (m, 15 H, $CH_2 \times 7$ and CH), 1.02-0.64 (m, 2 H, CH_2). **S3d** was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3d** (2.4124 g, 6.9 mmol), NaH (0.5871 g, 60 wt% in mineral oil, 14.7 mmol), and NFSI (5.5029 g, 17.5 mmol) in CH_2Cl_2 (90 mL) afforded **1d** (1.4977 g, 59%) as an oil [eluent: petroleum ether/ethyl acetate = 35/1 (700 mL)]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2 H, ArH), 7.41 (d, *J* = 8.0 Hz, 2 H, ArH), 3.36-3.12 (m, 2 H, NCH_2), 2.55-2.39 (m, 4 H, CH_3 and CH), 2.03 (d, *J* = 2.4 Hz, 1 H, ≡CH), 2.01-1.89 (m, 1 H, and one proton of CH_2), 1.88-1.34 (m, 10 H, one proton of CH_2, $CH_2 \times 4$ and CH), 1.33-1.06 (m, 4 H, $CH_2 \times 2$), 0.98-0.72 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 129.94, 129.91, 128.8, 87.2, 69.6, 53.5 (d, *J* = 12.6 Hz), 42.7, 35.2, 33.8, 32.5, 32.1, 28.2, 26.5, 26.2, 26.1, 24.0, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.3; IR (neat) *v* (cm^{-1}) 3293, 2108, 1597, 1449, 1376; MS (ESI): *m/z* 404 [$(M + K)^+$], 388 [$(M + Na)^+$], 383 [$(M + NH_4)^+$], 366 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{20}H_{28}FNNaO_2S$ [$(M + Na)^+$]: 388.1717; Found: 388.1720.

2.5. Synthesis of *N*-fluoro-*N*-(4-(3-chloropropyl)hex-5-ynyl)-4-methylbenzenesulfonamide **1e**. (zdj-4-051, zdj-4-055, zdj-4-060, zdj-4-061)



Following **Typical Procedure I**, the reaction of 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and 3-chloropropyl bromide (2.4 mL, d = 1.592 g/mL, 3.82 g, 24.3 mmol) in THF (60 mL) afforded crude **S1e** as an oil [eluent: petroleum ether/ethyl acetate = 4/1 (1000 mL)], which was evacuated at 45 °C/153.3 Pa to afford **S1e** (1.2455 g, 35%) as an oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.69 (t, J = 6.2 Hz, 2 H, OCH$_2$), 3.58 (t, J = 6.5 Hz, 2 H, ClCH$_2$), 2.50-2.32 (m, 1 H, CH), 2.14-1.40 (m, 10 H, ≡CH, CH$_2$ × 4 and OH). **S1e** was used for the next step without further characterization.

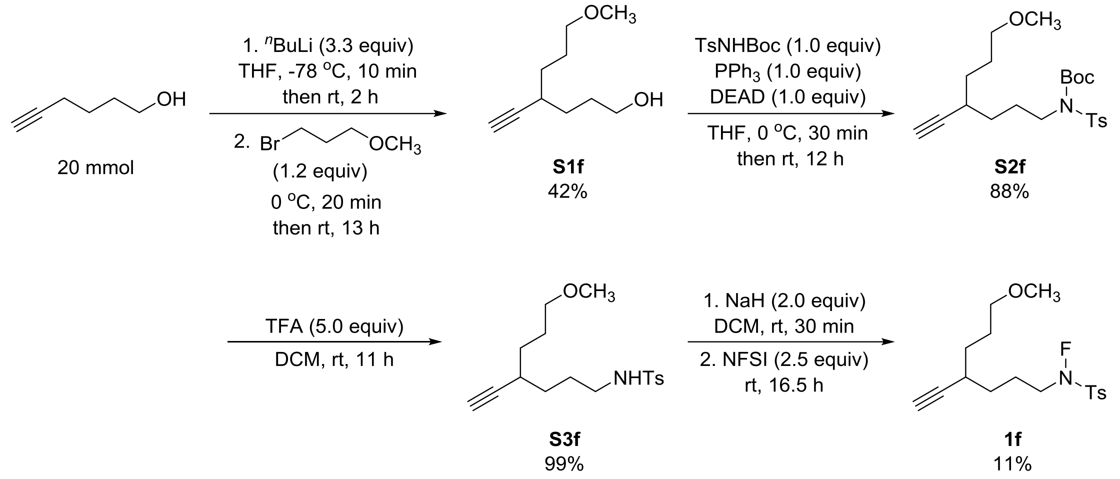
Following **Typical Procedure V**, the reaction of TsNHBoc (2.0215 g, 7.5 mmol), PPh$_3$ (1.8711 g, 7.1 mmol), DEAD (1.1 mL, d = 1.106 g/mL, 1.22 g, 7.0 mmol), and **S1e** (1.2290 g, 7.0 mmol) in THF (10 + 6 mL) afforded **S2e** (2.3539 g, 78%) as an oil [eluent: petroleum ether/ethyl acetate = 18/1 (570 mL) to 9/1 (200 mL)]: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.79 (d, J = 8.1 Hz, 2 H, ArH), 7.31 (d, J = 8.1 Hz, 2 H, ArH), 3.85 (t, J = 7.4 Hz, 2 H, NCH$_2$), 3.58 (t, J = 6.6 Hz, 2 H, ClCH$_2$), 2.52-2.36 (m, 4 H, CH$_3$ and CH), 2.11 (d, J = 1.8 Hz, 1 H, ≡CH), 2.08-1.75 (m, 4 H, CH$_2$ × 2), 1.75-1.45 (m, 4 H, CH$_2$ × 2), 1.34 (s, 9 H, CH$_3$ × 3). **S2e** was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2e** (2.3205 g, 5.4 mmol) and TFA (2.1 mL, d = 1.489 g/mL, 3.13 g, 27.5 mmol) in CH_2Cl_2 (10 mL) afforded **S3e** (1.7541 g, 99%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2 H, ArH), 7.32 (d, *J* = 8.1 Hz, 2 H, ArH), 4.72-4.57 (m, 1 H, NH), 3.54 (t, *J* = 6.5 Hz, 2 H, $ClCH_2$), 2.97 (q, *J* = 6.6 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.36-2.23 (m, 1 H, CH), 2.04 (d, J = 2.1 Hz, 1 H, ≡CH), 2.02-1.34 (m, 8 H, CH_2 × 4). **S3e** was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3e** (1.7271 g, 5.3 mmol), NaH (0.4679 g, 60 wt% in mineral oil, 11.7 mmol), and NFSI (4.2051 g, 13.3 mmol) in CH_2Cl_2 (60 mL) afforded **1e** (0.8928 g, 49%) as an oil [eluent: petroleum ether/ethyl acetate = 17/1 (720 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2 H, ArH), 7.41 (d, *J* = 8.0 Hz, 2 H, ArH), 3.56 (t, *J* = 6.5 Hz, 2 H, $ClCH_2$), 3.35-3.14 (m, 2 H, NCH_2), 2.49 (s, 3 H, CH_3), 2.42-2.34 (m, 1 H, CH), 2.08 (d, *J* = 2.5 Hz, 1 H, ≡CH), 2.06-1.76 (m, 4 H, CH_2 × 2), 1.71-1.48 (m, 4 H, CH_2 × 2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 129.9, 128.7, 86.0, 70.5, 53.4 (d, *J* = 11.5 Hz), 44.7, 32.0, 31.7, 30.5, 30.1, 24.0, 21.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.3; IR (neat) *ν* (cm^{-1}) 3296, 2108, 1596, 1453, 1375; MS (ESI): *m/z* 370 ([M(^{37}Cl) + Na]$^+$), 368 ([M(^{35}Cl) + Na]$^+$), 365 ([M(^{37}Cl) + NH_4]$^+$), 363 ([M(^{35}Cl) + NH_4]$^+$), 348 ([M(^{37}Cl) + H]$^+$), 346 ([M(^{35}Cl) + H]$^+$); HRMS (ESI) Calcd for $C_{16}H_{21}{}^{35}ClFNNaO_2S$ ([M(^{35}Cl) + Na]$^+$): 368.0858; Found: 368.0860.

2.6. Synthesis of *N*-fluoro-*N*-(4-(3-methoxpropyl)hex-5-ynyl)-4-

methylbenzenesulfonamide **1f**. (zdj-3-194, zdj-3-196, zdj-3-197, zdj-3-199)



Following **Typical Procedure I**, the reaction of 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and 3-methoxylpropyl bromide (2.7 mL, d = 1.36 g/mL, 3.67 g, 24.0 mmol) in THF (60 mL) afforded **S1f** (1.4479 g, 42%) as an oil [eluent: petroleum ether/ethyl acetate = 3/1 (800 mL) to 2/1 (450 mL)]: ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.67 (t, *J* = 6.5 Hz, 2 H, OCH$_2$), 3.41 (t, *J* = 6.3 Hz, 2 H, OCH$_2$), 3.34 (s, 3 H, OCH$_3$), 2.48-2.30 (m, 1 H, CH), 2.08 (d, *J* = 2.4 Hz, 1 H, ≡CH), 1.95-1.35 (m, 9 H, CH$_2$ × 4 and OH). **S1f** was used for the next step without further characterization.

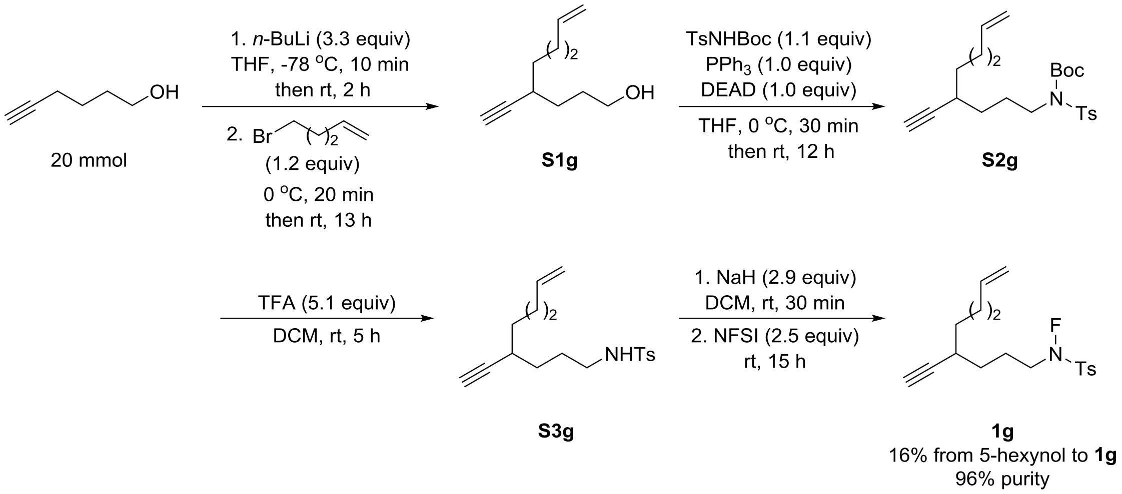
Following **Typical Procedure II**, the reaction of PPh$_3$ (2.2155 g, 8.4 mmol), TsNHBoc (2.3967 g, 8.8 mmol), DEAD (1.3 mL, d = 1.106 g/mL, 1.44 g, 8.3 mmol), and **S1f** (1.4210 g, 8.3 mmol) in THF (10 + 6 mL) afforded **S2f** (3.0946 g, 88%) as an oil [eluent: petroleum ether/ethyl acetate = 12/1 (650 mL) to 8/1 (450 mL)]: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.79 (d, *J* = 8.4 Hz, 2 H, ArH), 7.30 (d, *J* = 8.1 Hz, 2 H, ArH), 3.84 (t, *J* = 7.4 Hz, 2 H, NCH$_2$), 3.40 (t, *J* = 6.3 Hz, 2 H, OCH$_2$), 3.34 (s, 3 H, OCH$_3$), 2.50-2.31 (m, 4 H, CH$_3$ and CH), 2.13-1.92 (m, 2 H, ≡CH and one proton of CH$_2$), 1.91-

1.43 (m, 7 H, one proton of CH_2 and $CH_2 \times 3$), 1.34 (s, 9 H, $CH_3 \times 3$). **S2f** was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2f** (3.0711 g, 7.3 mmol) and TFA (2.8 mL, d = 1.489 g/mL, 4.17 g, 36.6 mmol) in CH_2Cl_2 (15 mL) afforded **S3f** (2.3222 g, 99%) as an oil [**S3f** was afforded by filtrated through a short column of silica gel eluted with ethyl acetate (30 mL × 3)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2 H, ArH), 7.31 (d, *J* = 8.1 Hz, 2 H, ArH), 4.56 (t, *J* = 6.0 Hz, 1 H, NH), 3.48-3.25 (m, 5 H, OCH_2 and OCH_3), 2.96 (q, *J* = 6.6 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.37-2.18 (m, 1 H, CH), 2.02 (d, *J* = 1.8 Hz, 1 H, ≡CH), 1.88-1.27 (m, 8 H, $CH_2 \times 4$). **S3f** was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3f** (2.2975 g, 7.1 mmol), NaH (0.5802 g, 60 wt% in mineral oil, 14.5 mmol), and NFSI (5.6451 g, 17.9 mmol) in CH_2Cl_2 (90 mL) afforded **1f** (0.2606 g, 11%) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (1100 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2 H, ArH), 7.41 (d, *J* = 8.0 Hz, 2 H, ArH), 3.44-3.35 (m, 2 H, OCH_2), 3.33 (s, 3 H, OCH_3), 3.30-3.14 (m, 2 H, NCH_2), 2.49 (s, 3 H, CH_3), 2.42-2.32 (m, 1 H, CH), 2.06 (d, *J* = 2.5 Hz, 1 H, ≡CH), 2.01-1.90 (m, 1 H, one proton of CH_2), 1.88-1.74 (m, 2 H, CH_2), 1.72-1.41 (m, 5 H, one proton of CH_2 and $CH_2 \times 2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 129.9, 128.7, 86.6, 72.3, 70.1, 58.5, 53.4 (d, *J* = 11.5 Hz), 31.7, 31.5, 30.9, 27.2, 24.0, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.3; IR (neat) *v* (cm^{-1}) 3292, 2103, 1596, 1454, 1375; MS (ESI): *m/z* 380 [$(M + K)^+$]; 364 [$(M + Na)^+$], 359 [$(M + NH_4)^+$], 342 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{17}H_{24}FNNaO_3S$ [$(M + Na)^+$]: 364.1353; Found: 364.1357.

2.7. Synthesis of *N*-fluoro-*N*-(4-(5-pentenyl)hex-5-ynyl)-4-methylbenzenesulfonamide **1g**. (zdj-4-155, zdj-4-158, zdj-4-159, zdj-4-163)



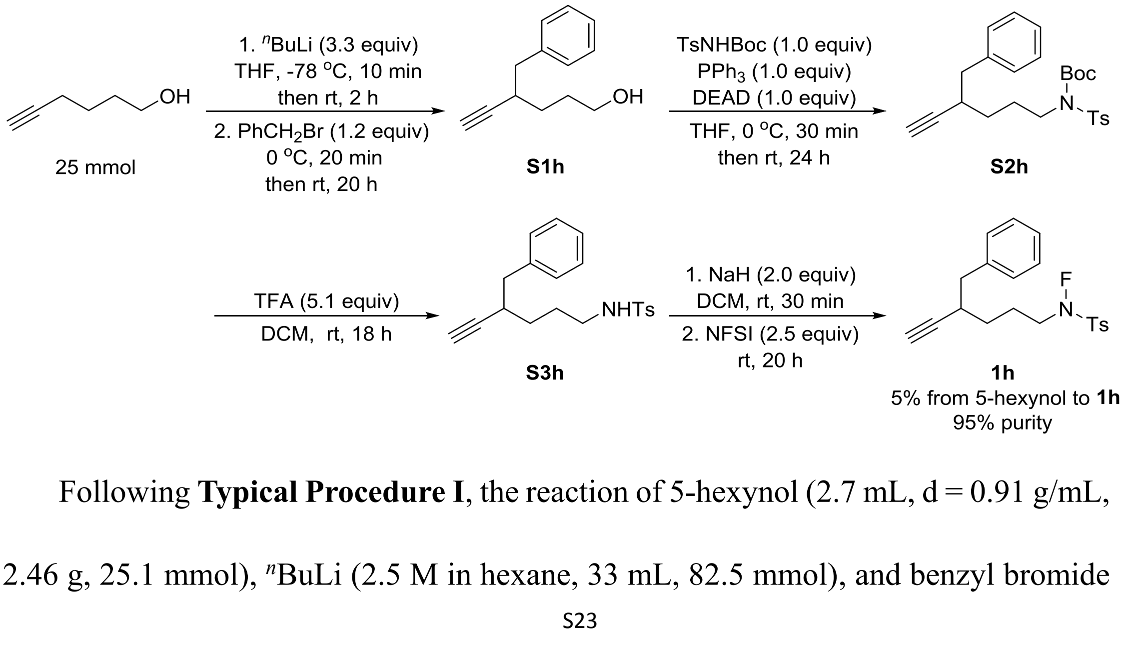
Following **Typical Procedure I**, the reaction of 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and 5-pentenyl bromide (2.8 mL, d = 1.258 g/mL, 3.52 g, 23.6 mmol) in THF (60 mL) afforded **S1g** (1.8095 g) as an oil [eluent: petroleum ether/ethyl acetate = 6/1 (700 mL)], which was used for the next step without further characterization.

Following **Typical Procedure V**, the reaction of TsNHBoc (3.0819 g, 11.4 mmol), PPh_3 (2.8352 g, 10.8 mmol), DEAD (1.7 mL, d = 1.106 g/mL, 1.88 g, 10.8 mmol), and **S1g** (1.7845 g) in THF (12 + 6 mL) afforded **S2g** (3.3827 g) as an oil [eluent: petroleum ether/ethyl acetate = 25/1 (780 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2g** (3.3315 g) and TFA (3.1 mL, d = 1.489 g/mL, 4.62 g, 40.5 mmol) in CH_2Cl_2 (20 mL) afforded **S3g** (2.2826 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3g** (2.2519 g), NaH (0.8206 g, 60 wt% in mineral oil, 20.5 mmol), and NFSI (5.5462 g, 17.6 mmol) in CH_2Cl_2 (70 mL) afforded **1g** (1.1142 g, 16% from 5-hexynol to **1g**, 96% purity) as an oil [eluent: petroleum ether/ethyl acetate = 40/1 (615 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2 H, ArH), 7.41 (d, *J* = 8.1 Hz, 2 H, ArH), 5.88-5.69 (m, 1 H, =CH), 5.08-4.87 (m, 2 H, $=CH_2$), 3.39-3.24 (m, 1 H, one proton of NCH_2), 3.23-3.07 (m, 1 H, one proton of NCH_2), 2.48 (s, 3 H, CH_3), 2.42-2.23 (m, 1 H, CH), 2.17-1.71 (m, 5 H, ≡CH and $CH_2 \times 2$), 1.70-1.35 (m, 6 H, $CH_2 \times 3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 138.5, 129.9, 128.7, 114.6, 86.8, 69.9, 53.5 (d, *J* = 12.6 Hz), 34.2, 33.4, 31.6, 30.9, 26.3, 24.0, 21.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.4; IR (neat) *v* (cm^{-1}) 3299, 2110, 1640, 1596, 1493, 1457, 1375, 1308; MS (ESI): *m/z* 376 [$(M + K)^+$], 360 [$(M + Na)^+$], 355 [$(M + NH_4)^+$], 338 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{18}H_{25}FNO_2S$ [$(M + H)^+$]: 338.1585; Found: 338.1588.

2.8. Synthesis of *N*-fluoro-*N*-(4-benzylhex-5-ynyl)-4-methylbenzenesulfonamide **1h**. (zdj-3-038, zdj-3-047, zdj-3-051, zdj-3-064)



Following **Typical Procedure I**, the reaction of 5-hexynol (2.7 mL, d = 0.91 g/mL, 2.46 g, 25.1 mmol), ^{n}BuLi (2.5 M in hexane, 33 mL, 82.5 mmol), and benzyl bromide

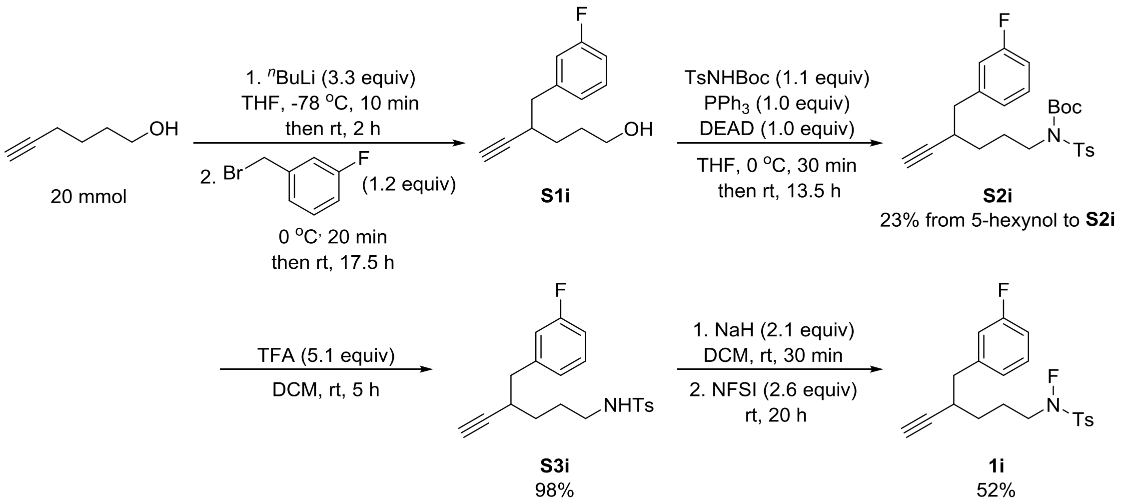
(3.6 mL, d = 1.44 g/mL, 5.18 g, 30.3 mmol) in THF (75 mL) afforded crude **S1h** as an oil [eluent: petroleum ether/ethyl acetate = 5/1 (480 mL) to 3/1 (400 mL)], which was evacuated at 40 °C/139.9 Pa to afford **S1h** (1.5443 g) as an oil. **S1h** which was used for the next step without further characterization.

Following **Typical Procedure II**, the reaction of PPh_3 (2.1620 g, 8.2 mmol), TsNHBoc (2.3404 g, 8.6 mmol), DEAD (1.3 mL, d = 1.106 g/mL, 1.47 g, 8.4 mmol), and **S1h** (1.5443 g) in THF (10 + 6 mL) afforded **S2h** (3.2708 g) as a solid [eluent: petroleum ether/ethyl acetate = 20/1 (400 mL) to 15/1 (600 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2h** (3.2708 g) and TFA (2.9 mL, d = 1.489 g/mL, 4.32 g, 37.9 mmol) in CH_2Cl_2 (15 mL) afforded **S3h** (2.4529 g) as an oil.

Following **Typical Procedure IV**, the reaction of **S3h** (2.4529 g), NaH (0.5845 g, 60 wt% in mineral oil, 14.6 mmol), and NFSI (5.7016 g, 18.1 mmol) in CH_2Cl_2 (90 mL) afforded **1h** (0.5105 g, 5% from 5-hexynol to **1h**, 95% purity) as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (1200 mL)]: ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.4 Hz, 2 H, ArH), 7.39 (d, J = 8.0 Hz, 2 H, ArH), 7.33-7.14 (m, 5 H, ArH), 3.35-3.09 (m, 2 H, NCH_2), 2.81 (dd, J_1 = 13.4 Hz, J_2 = 7.8 Hz, 1 H, one proton of CH_2), 2.73 (dd, J_1 = 13.2 Hz, J_2 = 6.4 Hz, 1 H, one proton of CH_2), 2.68-2.57 (m, 1 H, CH), 2.46 (s, 3 H, CH_3), 2.04 (dd, J_1 = 2.2 Hz, J_2 = 1.0 Hz, 1 H, ≡CH), 2.04-1.92 (m, 1 H, one proton of CH_2), 1.88-1.73 (m, 1 H, one proton of CH_2), 1.70-1.57 (m, 1 H, one proton of CH_2), 1.56-1.43 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 138.9, 129.9, 129.1, 128.7, 128.2, 126.4, 86.2, 70.8, 53.3 (d, J = 12.7 Hz), 41.1, 33.0, 30.9, 24.0, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.3; IR (neat) ν (cm^{-1}) 3292, 2108, 1596, 1495, 1454, 1374, 1307; MS (ESI): *m/z* 398 [(M + K)$^+$], 382 [(M + Na)$^+$], 377 [(M + NH_4)$^+$]; HRMS (ESI) Calcd for $C_{20}H_{22}FNNaO_2S$ [(M + Na)$^+$]: 382.1247; Found: 382.1249.

2.9. Synthesis of *N*-fluoro-*N*-(4-(3-fluorobenzyl)hex-5-ynyl)-4-methylbenzenesulfonamide **1i**. (zdj-3-148, zdj-3-152, zdj-3-153, zdj-3-155)



Following **Typical Procedure I**, the reaction of 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and 3-fluorobenzyl bromide (3.0 mL, d = 1.541 g/mL, 4.62 g, 24.5 mmol) in THF (60 mL) afforded crude **S1i** as an oil [eluent: petroleum ether/ethyl acetate = 5/1 (960 mL) to 3/1 (200 mL)], which was evacuated at 40 °C/153.3 Pa to afford **S1i** (1.3691 g) as an oil. **S1i** was used for the next step without further characterization.

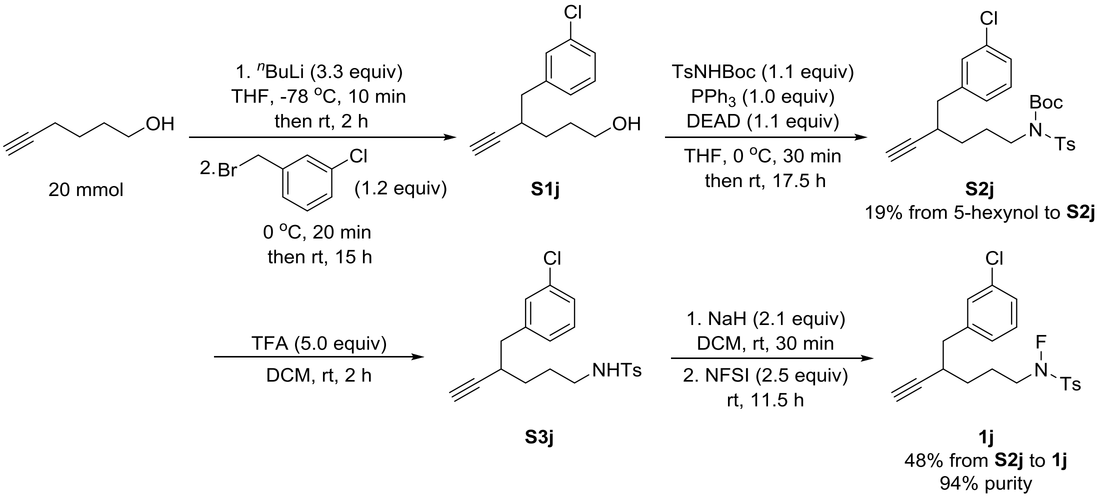
Following **Typical Procedure V**, the reaction of TsNHBoc (1.9015 g, 7.0 mmol), PPh_3 (1.7568 g, 6.7 mmol), DEAD (1.1 mL, d = 1.106 g/mL, 1.22 g, 7.0 mmol), and

S1i (1.3512 g) in THF (10 + 6 mL) afforded **S2i** (2.1461 g, 23% from 5-hexynol to **S2i**) as a solid [eluent: petroleum ether/ethyl acetate = 20/1 (1200 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2 H, ArH), 7.34-7.18 (m, 3 H, ArH), 7.05-6.84 (m, 3 H, ArH), 3.84 (t, *J* = 7.4 Hz, 2 H, NCH_2), 2.86-2.74 (m, 2 H, CH_2), 2.74-2.58 (m, 1 H, CH), 2.44 (s, 3 H, CH_3), 2.16-1.95 (m, 2 H, ≡CH and one proton of CH_2), 1.95-1.75 (m, 1 H, one proton of CH_2), 1.68-1.41 (m, 2 H, CH_2), 1.33 (s, 9 H, CH_3 × 3). **S2i** was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2i** (2.1209 g, 4.6 mmol) and TFA (1.8 mL, d = 1.489 g/mL, 2.68 g, 23.5 mmol) in CH_2Cl_2 (15 mL) afforded **S3i** (1.6211 g, 98%) as a solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2 H, ArH), 7.41-7.12 (m, 3 H, ArH), 7.06-6.78 (m, 3 H, ArH), 4.92-4.56 (m, 1 H, NH), 2.95 (q, *J* = 6.5 Hz, 2 H, NCH_2), 2.82-2.60 (m, 2 H, CH_2), 2.60-2.46 (m, 1 H, CH), 2.42 (s, 3 H, CH_3), 2.05 (d, *J* = 2.1 Hz, 1 H, ≡CH), 1.84-1.29 (m, 4 H, CH_2 × 2). **S3i** was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3i** (1.5824 g, 4.4 mmol), NaH (0.3655 g, 60 wt% in mineral oil, 9.1 mmol), and NFSI (3.5493 g, 11.3 mmol) in CH_2Cl_2 (60 mL) afforded **1i** (0.8657 g, 52%) as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (840 mL)]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2 H, ArH), 7.40 (d, *J* = 8.0 Hz, 2 H, ArH), 7.32-7.15 (m, 1 H, ArH), 7.05-6.82 (m, 3 H, ArH), 3.36-3.10 (m, 2 H, NCH_2), 2.87-2.69 (m, 2 H, CH_2), 2.69-2.56 (m, 1 H, CH), 2.48 (s, 3 H, CH_3), 2.08 (d, *J* = 2.4 Hz, 1 H, ≡CH), 2.06-1.92 (m, 1 H, one proton of CH_2), 1.90-1.74 (m, 1 H, one proton of CH_2), 1.72-1.42 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 230.2 Hz), 146.3, 141.4 (d, *J* = 7.2 Hz), 129.9, 129.6 (d, *J* = 8.1 Hz), 128.8, 124.8 (d, *J* = 2.7 Hz), 116.0 (d, *J* = 20.7 Hz), 113.3 (d, *J* = 20.8 Hz), 85.7, 71.1, 53.3 (d, *J* = 12.6 Hz), 40.8 (d, *J* = 1.8 Hz), 32.8, 31.1, 24.0, 21.7; ^{19}F NMR (376 MHz, CDCl$_3$) δ -50.2, -114.2; IR (neat) *v* (cm^{-1}) 3299, 2116, 1617, 1595, 1488, 1450, 1374; MS (ESI): *m/z* 400 [(M + Na)$^+$], 395 [(M + NH$_4$)$^+$]; HRMS (ESI) Calcd for $C_{20}H_{21}F_2NNaO_2S$ [(M + Na)$^+$]: 400.1153; Found: 400.1152.

2.10. Synthesis of *N*-fluoro-*N*-(4-(3-chlorobenzyl)hex-5-ynyl)-4-methylbenzenesulfonamide **1j**. (zdj-3-180, zdj-3-185, zdj-3-187, zdj-3-190)



Following **Typical Procedure I**, the reaction of 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and 3-chlorobenzyl bromide (3.2 mL, d = 1.565 g/mL, 5.01 g, 24.4 mmol) in THF (60 mL) afforded crude **S1j** as an oil [eluent: petroleum ether/ethyl acetate = 5/1 (960 mL) to 3/1 (300 mL)], which was evacuated at 50 °C/163.3 Pa to afford **S1j** (1.3288 g) as an oil. **S1j** was used for the next step without further characterization.

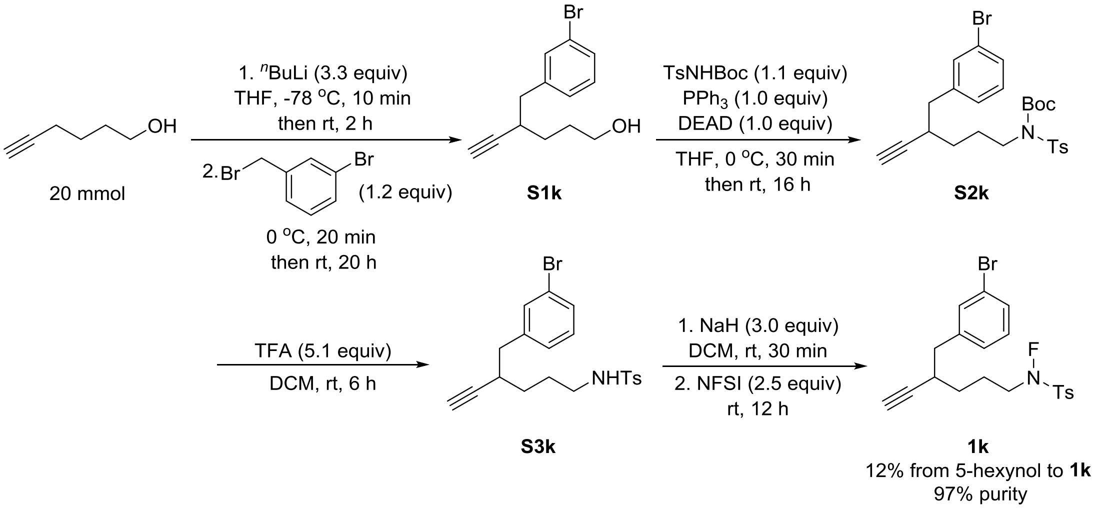
Following **Typical Procedure V**, the reaction of TsNHBoc (1.7071 g, 6.3 mmol),

PPh_3 (1.5835 g, 6.0 mmol), DEAD (1.0 mL, d = 1.106 g/mL, 1.11 g, 6.4 mmol), and **S1j** (1.3025 g) in THF (10 + 6 mL) afforded **S2j** (1.8493 g, 19% from 5-hexynol to **S2j**) as a solid [eluent: petroleum ether/ethyl acetate = 20/1 (800 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2 H, ArH), 7.34-7.06 (m, 6 H, ArH), 3.84 (t, *J* = 7.1 Hz, 2 H, NCH_2), 2.81-2.72 (m, 2 H, CH_2), 2.72-2.60 (m, 1 H, CH), 2.44 (s, 3 H, CH_3), 2.17-1.96 (m, 2 H, CH and one proton of CH_2), 1.95-1.74 (m, 1 H, one proton of CH_2), 1.66-1.38 (m, 2 H, CH_2), 1.33 (s, 9 H, CH_3 × 3). **S2j** was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2j** (1.8287 g, 3.8 mmol) and TFA (1.5 mL, d = 1.489 g/mL, 2.23 g, 19.6 mmol) in CH_2Cl_2 (10 mL) afforded **S3j** (1.4485 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3j** (1.4210 g, 3.8 mmol), NaH (0.3221 g, 60 wt% in mineral oil, 8.1 mmol), and NFSI (3.0071 g, 9.5 mmol) in CH_2Cl_2 (50 mL) afforded **1j** (0.7649 g, 48% from **S2j** to **1j**, 94% purity) as an oil [eluent: petroleum ether/ethyl acetate = 16/1 (850 mL)]: ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2 H, ArH), 7.40 (d, *J* = 8.0 Hz, 2 H, ArH), 7.28-7.16 (m, 3 H, ArH), 7.12-7.07 (m, 1 H, ArH), 3.35-3.11 (m, 2 H, NCH_2), 2.84-2.67 (m, 2 H, CH_2), 2.66-2.56 (m, 1 H, CH), 2.47 (s, 3 H, CH_3), 2.08 (d, *J* = 2.5 Hz, 1 H, ≡CH), 2.05-1.93 (m, 1 H, one proton of CH_2), 1.88-1.74 (m, 1 H, one proton of CH_2), 1.69-1.58 (m, 1 H, one proton of CH_2), 1.57-1.46 (m, 1 H, one proton of CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 141.0, 134.0, 130.02, 129.99, 129.6, 129.3, 128.8, 127.5, 126.7, 85.7, 71.3, 53.4 (d, *J* = 12.6 Hz), 40.8, 32.9, 31.2, 24.1, 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.2; IR (neat) *v* (cm^{-1}) 3298, 2112, 1597, 1574, 1477, 1430, 1374, 1306; MS (ESI): *m/z* 418 ([M(^{37}Cl) + Na]$^+$), 416 ([M(^{35}Cl) + Na]$^+$); HRMS (ESI) Calcd for $C_{20}H_{21}{}^{35}ClFNNaO_2S$ ([M(^{35}Cl) + Na]$^+$): 416.0858; Found: 416.0862.

2.11. Synthesis of *N*-fluoro-*N*-(4-(3-bromobenzyl)hex-5-ynyl)-4-methylbenzenesulfonamide **1k**. (zdj-4-025, zdj-4-041, zdj-4-045, zdj-4-050)



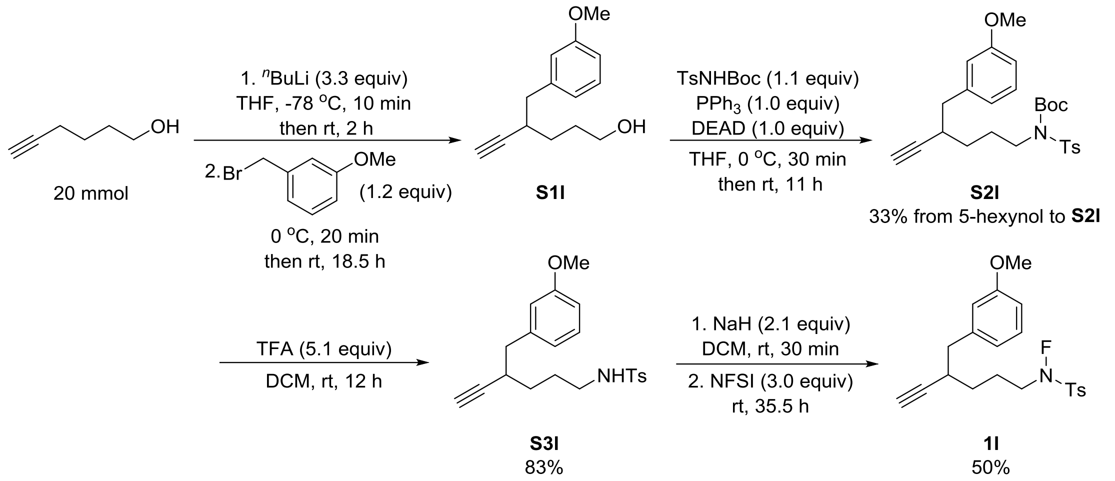
Following **Typical Procedure I**, the reaction of 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and 3-bromobenzyl bromide (6.0171 g, 24.1 mmol) in THF (60 mL) afforded crude **S1k** as an oil [eluent: petroleum ether/ethyl acetate = 4/1 (1000 mL)], which was evacuated at 50 °C/149.9 Pa to afford **S1k** (1.6670 g) as an oil. **S1k** was used for the next step without further characterization.

Following **Typical Procedure V**, the reaction of TsNHBoc (1.7789 g, 6.6 mmol), PPh_3 (1.6748 g, 6.4 mmol), DEAD (1.0 mL, d = 1.106 g/mL, 1.11 g, 6.4 mmol), and **S1k** (1.6308 g) in THF (10 + 5 mL) afforded **S2k** (2.4333 g) as an oil [eluent: petroleum ether/ethyl acetate = 18/1 (570 mL) to 7/1 (280 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2k** (2.3948 g) and TFA (1.8 mL, d = 1.489 g/mL, 2.68 g, 23.5 mmol) in CH_2Cl_2 (10 mL) afforded **S3k** (1.8905 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV,** the reaction of **S3k** (1.8729 g), NaH (0.5414 g, 60 wt% in mineral oil, 13.5 mmol), and NFSI (3.5465 g, 11.2 mmol) in CH_2Cl_2 (50 mL) afforded **1k** (1.0912 g, 12% from 5-hexynol to **1k**, 97% purity) as an oil [eluent: petroleum ether/ethyl acetate = 18/1 (760 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2 H, ArH), 7.45-7.31 (m, 4 H, ArH), 7.19-7.12 (m, 2 H, ArH), 3.33-3.13 (m, 2 H, NCH_2), 2.81-2.67 (m, 2 H, CH_2), 2.65-2.57 (m, 1 H, CH), 2.48 (s, 3 H, CH_3), 2.09 (d, *J* = 2.5 Hz, 1 H, ≡CH), 2.05-1.93 (m, 1 H, one proton of CH_2), 1.89-1.76 (m, 1 H, one proton of CH_2), 1.71-1.57 (m, 1 H, one proton of CH_2), 1.57-1.44 (m, 1 H, one proton of CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 141.2, 132.1, 129.93, 129.91, 129.8, 129.5, 128.7, 127.8, 122.2, 85.6, 71.3, 53.3 (d, *J* = 11.5 Hz), 40.7, 32.9, 31.1, 24.0, 21.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.2; IR (neat) *ν* (cm^{-1}) 3296, 2112, 1596, 1568, 1474, 1453, 1427, 1374; MS (ESI): *m/z* 462 ($[M(^{81}Br) + Na]^+$), 460 ($[M(^{79}Br) + Na]^+$), 457 ($[M(^{81}Br) + NH_4]^+$), 455 ($[M(^{79}Br) + NH_4])^+$, 440 ($[M(^{81}Br) + H]^+$), 438 ($[M(^{79}Br) + H]^+$); HRMS (ESI) Calcd for $C_{20}H_{21}{}^{79}BrFNNaO_2S$ ($[M(^{79}Br) + Na]^+$): 460.0353; Found: 460.0354.

2.12. Synthesis of *N*-fluoro-*N*-(4-(3-methoxybenzyl)hex-5-ynyl)-4-methylbenzenesulfonamide **1l**. (zdj-3-163, zdj-3-169, zdj-3-172, zdj-3-175)



Following **Typical Procedure I**, the reaction of 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and 3-methoxybenzyl bromide (4.8228 g, 24.0 mmol) in THF (60 mL) afforded crude **S1l** as an oil [eluent: petroleum ether/ethyl acetate = 4/1 (1000 mL)], which was evacuated at 50 °C/146.6 Pa to afford **S1l** (1.8203 g) as an oil. **S1l** was used for the next step without further characterization.

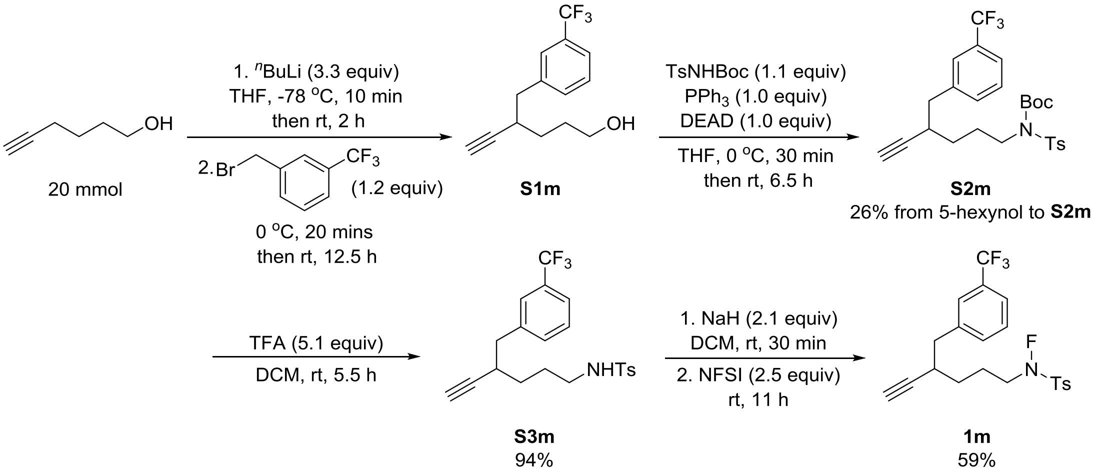
Following **Typical Procedure V**, the reaction of TsNHBoc (2.3907 g, 8.8 mmol), PPh_3 (2.1828 g, 8.3 mmol), DEAD (1.3 mL, d = 1.106 g/mL, 1.47 g, 8.4 mmol), and **S1l** (1.8001 g) in THF (10 + 6 mL) afforded **S2l** (3.1758 g, 33% from 5-hexynol to **S2l**) as a solid [eluent: petroleum ether/ethyl acetate = 15/1 (930 mL) to 12/1 (660 mL) to 10/1 (100 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2 H, ArH), 7.29 (d, *J* = 8.1 Hz, 2 H, ArH), 7.21 (t, *J* = 7.8 Hz, 1 H, ArH), 6.89-6.68 (m, 3 H, ArH), 3.94-3.67 (m, 5 H, NCH_2 and OCH_3), 2.89-2.59 (m, 3 H, CH_2 and CH), 2.44 (s, 3 H, CH_3), 2.19-1.95 (m, 2 H, ≡CH and one proton of CH_2), 1.95-1.72 (m, 1 H, one proton of CH_2), 1.69-1.40 (m, 2 H, CH_2), 1.33 (s, 9 H, CH_3 × 3). **S2l** was used for the next step without further characterization.

To a 100 mL round-bottomed flask were added **S2l** (3.1512 g, 6.7 mmol), CH_2Cl_2 (15 mL), and TFA (2.6 mL, d = 1.489 g/mL, 3.87 g, 33.9 mmol). The resulting mixture was stirred at room temperature for 12 hours as monitored by TLC, and washed subsequently with H_2O (15 mL), saturated aqueous solution of $NaHCO_3$ (15 mL), and brine (15 mL) sequentially. The organic phase was dried over anhydrous Na_2SO_4, filtrated, concentrated in vacuo. The crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 4/1 (1000 mL) to 1/1 (200 mL)] to afford **S3l** (2.0589 g, 83%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2 H, ArH), 7.30 (d, *J* = 8.1 Hz, 2 H, ArH), 7.20 (d, *J* = 7.4 Hz, 1 H, ArH), 6.85-6.64 (m, 3 H, ArH), 4.70-4.49 (m, 1 H, NH), 3.79 (s, 3 H, OCH_3), 2.93 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.84-2.47 (m, 3 H, CH_2 and CH), 2.42 (s, 3 H, CH_3), 2.04 (d, *J* = 2.1 Hz, 1 H, ≡CH), 1.84-1.18 (m, 4 H, CH_2 × 2). **S3l** was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3l** (2.0339 g, 5.5 mmol), NaH (0.4576 g, 60 wt% in mineral oil, 11.4 mmol), and NFSI (5.2241 g, 16.6 mmol) in CH_2Cl_2 (70 mL) afforded **1l** (1.0668 g, 50%) as an oil [eluent: petroleum ether/ethyl acetate = 15/1 (800 mL) to 12/1 (650 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2 H, ArH), 7.40 (d, *J* = 7.8 Hz, 2 H, ArH), 7.28-7.13 (m, 1 H, ArH), 6.84-6.70 (m, 3 H, ArH), 3.79 (s, 3 H, OCH_3), 3.39-3.04 (m, 2 H, NCH_2), 2.90-2.53 (m, 3 H, CH_2 and CH), 2.47 (s, 3 H, CH_3), 2.13-1.90 (m, 2 H, ≡CH and one proton of CH_2), 1.90-1.72 (m, 1 H, one proton of CH_2), 1.71-1.37 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 146.2, 140.5, 129.9, 129.2, 128.8, 121.5, 114.8, 111.7, 86.2, 70.8, 55.1, 53.3

(d, J = 11.8 Hz), 41.2, 32.9, 30.9, 24.0, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.2; IR (neat) ν (cm^{-1}) 3290, 2108, 1596, 1585, 1490, 1454, 1437, 1374; MS (ESI): *m/z* 428 [(M + K)$^+$], 412 [(M + Na)$^+$], 407 [(M + NH_4)$^+$], 390 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{21}H_{24}FNNaO_3S$ [(M + Na)$^+$]: 412.1353; Found: 412.1354.

2.13. Synthesis of *N*-fluoro-*N*-(4-((3-trifluoromethyl)benzyl)hex-5-ynyl)-4-methylbenzenesulfonamide **1m**. (zdj-3-198, zdj-4-007, zdj-4-014, zdj-4-017)



Following **Typical Procedure I**, the reaction of 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and 3-(trifluoromethyl)benzyl bromide (3.7 mL, d = 1.565 g/mL, 5.79 g, 24.2 mmol) in THF (60 mL) afforded crude **S1m** as an oil [eluent: petroleum ether/ethyl acetate = 4/1 (1000 mL)], which was evacuated at 45 °C/146.6 Pa to afford **S1m** (1.7983 g) as an oil. **S1m** was used for the next step without further characterization.

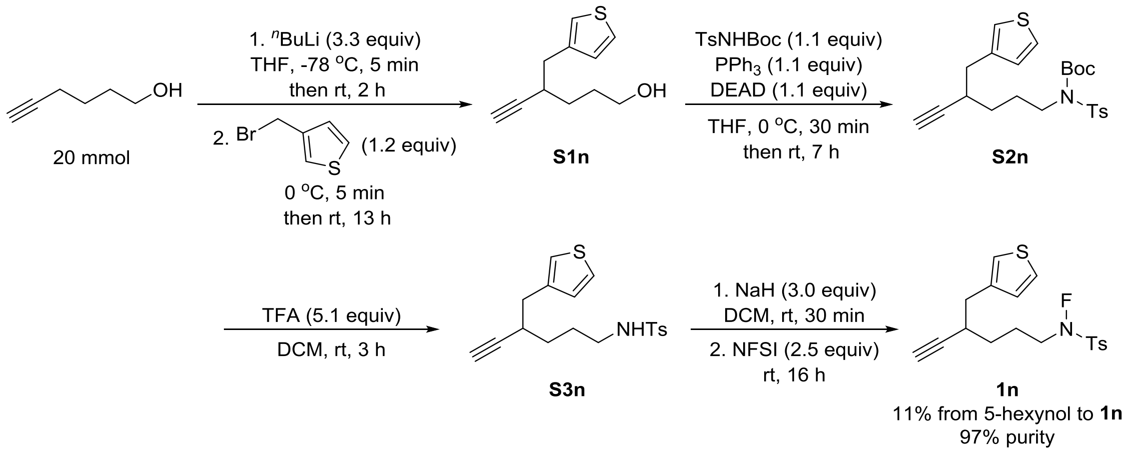
Following **Typical Procedure V**, the reaction of TsNHBoc (1.9873 g, 7.3 mmol), PPh_3 (1.8129 g, 6.9 mmol), DEAD (1.1 mL, d = 1.106 g/mL, 1.22 g, 7.0 mmol), and **S1m** (1.7631 g) in THF (10 + 6 mL) afforded **S2m** (2.6497 g, 26% from 5-hexynol to

S2m) as an oil [eluent: petroleum ether/ethyl acetate = 16/1 (850 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2 H, ArH), 7.57-7.36 (m, 4 H, ArH), 7.29 (d, *J* = 8.1 Hz, 2 H, ArH), 3.85 (t, *J* = 7.4 Hz, 2 H, NCH_2), 2.93-2.59 (m, 3 H, CH_2 and CH), 2.44 (s, 3 H, CH_3), 2.16-1.75 (m, 3 H, ≡CH and CH_2), 1.69-1.44 (m, 2 H, CH_2), 1.33 (s, 9 H, CH_3 × 3). **S2m** was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2m** (2.6150 g, 5.1 mmol) and TFA (2.0 mL, d = 1.489 g/mL, 2.98 g, 26.1 mmol) in CH_2Cl_2 (10 mL) afforded **S3m** (1.9736 g, 94%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2 H, ArH), 7.54-7.20 (m, 6 H, ArH), 4.80-4.64 (m, 1 H, NH), 2.96 (q, *J* = 6.5 Hz, 2 H, NCH_2), 2.76 (d, *J* = 7.2 Hz, 2 H, CH_2), 2.67-2.48 (m, 1 H, CH), 2.42 (s, 3 H, CH_3), 2.05 (d, *J* = 2.1 Hz, 1 H, ≡CH), 1.86-1.30 (m, 4 H, CH_2 × 2). **S3m** was used for the next step without further characterization.

Following **Typical Procedure IV** the reaction of **S3m** (1.9309 g, 4.7 mmol), NaH (0.3995 g, 60 wt% in mineral oil, 10.0 mmol), and NFSI (3.7091 g, 11.8 mmol) in CH_2Cl_2 (50 mL) afforded **1m** (1.1947 g, 59%) as an oil [eluent: petroleum ether/ethyl acetate = 18/1 (950 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2 H, ArH), 7.53-7.45 (m, 2 H, ArH), 7.44-7.34 (m, 4 H, ArH), 3.36-3.13 (m, 2 H, NCH_2), 2.82 (d, *J* = 7.0 Hz, 2 H, CH_2), 2.71-2.60 (m, 1 H, CH), 2.47 (s, 3 H, CH_3), 2.08 (d, *J* = 2.0 Hz, 1 H, ≡CH), 2.05-1.94 (m, 1 H, one proton of CH_2), 1.89-1.78 (m, 1 H, one proton of CH_2), 1.73-1.64 (m, 1 H, one proton of CH_2), 1.60-1.48 (m, 1 H, one proton of CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 139.8, 132.6, 130.4 (q, *J* = 31.8 Hz), 129.93, 129.88, 128.6, 125.9 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270.5 Hz), 123.3 (q, *J* = 3.5 Hz), 85.4, 71.4, 53.3 (d, J = 12.8 Hz), 40.8, 32.9, 31.2, 24.0, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.3, -63.0; IR (neat) ν (cm^{-1}) 3304, 2116, 1773, 1597, 1493, 1451; MS (ESI): *m/z* 466 [(M + K)$^+$], 450 [(M + Na)$^+$], 445 [(M + NH_4)$^+$], 428 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{21}H_{21}F_4NNaO_2S$ [(M + Na)$^+$]: 450.1121; Found: 450.1124.

2.14. Synthesis of *N*-fluoro-*N*-(4-(thien-3-ylmethyl)hex-5-ynyl)-4-methyl-benzenesulfonamide **1n**. (zdj-6-197, zdj-7-008, zdj-7-010, zdj-7-012)



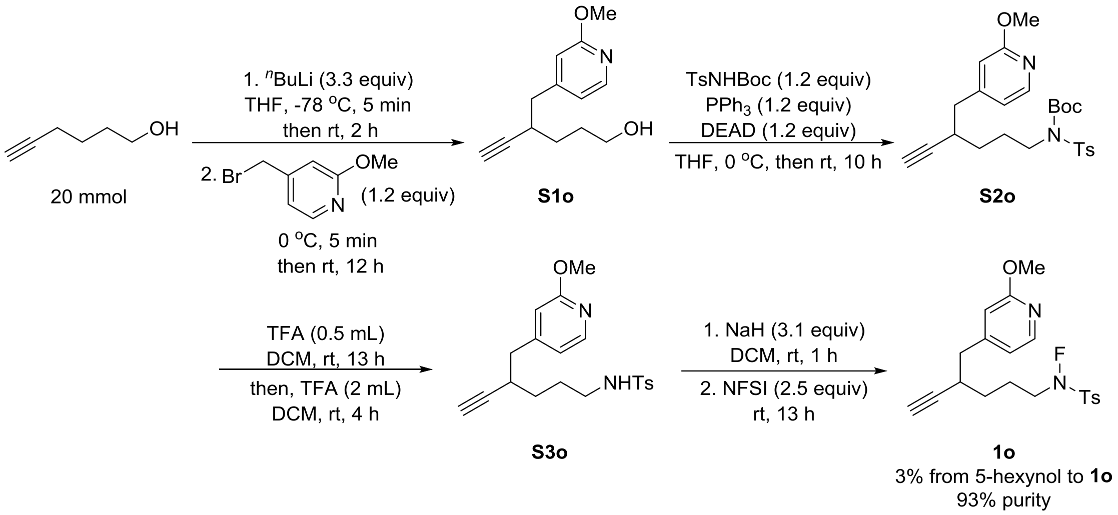
Following **Typical Procedure I**, the reaction of 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and 3-(thienyl)methyl bromide (2.6 mL, d = 1.616 g/mL, 4.20 g, 23.7 mmol) in THF (60 mL) afforded **S1n** as an oil [eluent: petroleum ether/ethyl acetate = 4/1 (750 mL)], which was evacuated at 40 °C/133.3 Pa to afford **S1n** (1.1000 g) as an oil. **S1n** was used for the next step without further characterization.

Following **Typical Procedure II**, the reaction of PPh_3 (1.5749 g, 6.0 mmol), TsNHBoc (1.6335 g, 6.0 mmol), DEAD (0.94 mL, d = 1.106 g/mL, 1.040 g, 6.0 mmol), and **S1n** (1.1000 g) in THF (10 + 5 mL) afforded **S2n** (2.2672 g) as an oil [eluent: petroleum ether/ethyl acetate = 13/1 (420 mL) to 10/1 (220 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2n** (2.2672 g) and TFA (2.0 mL, d = 1.489 g/mL, 2.98 g, 26.1 mmol) in CH_2Cl_2 (10 mL) afforded impure **S3n** (1.7587 g) as an oil, which was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 4/1 (750 mL)] to afford pure **S3n** (1.3898 g) as an oil. It was used for next steps without further characterization.

Following **Typical Procedure IV**, the reaction of **S3n** (1.3898 g), NaH (0.4800 g, 60 wt% in mineral oil, 12.0 mmol), and NFSI (3.1609 g, 10.0 mmol) in CH_2Cl_2 (40 mL) afforded **1n** (0.8812 g, 11% from 5-hexynol to **1n**, 97% purity) as an oil [eluent: petroleum ether/ethyl acetate = 15/1 (800 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2 H, ArH), 7.38 (d, J = 7.8 Hz, 2 H, ArH), 7.22 (dd, J_1 = 4.8 Hz, J_2 = 3.0 Hz, 1 H, ArH), 7.05-7.01 (m, 1 H, ArH), 6.98 (dd, J_1 = 5.1 Hz, J_2 = 1.2 Hz, 1 H, ArH), 3.36-3.21 (m, 1 H, one proton of NCH_2), 3.21-3.06 (m, 1 H, one proton of NCH_2), 2.90-2.70 (m, 2 H, CH_2), 2.69-2.55 (m, 1 H, CH), 2.46 (s, 3 H, CH_3), 2.08 (d, J = 2.1 Hz, 1 H, ≡CH), 2.06-1.89 (m, 1 H, one proton of CH_2), 1.89-1.71 (m, 1 H, one proton of CH_2), 1.71-1.56 (m, 1 H, one proton of CH_2), 1.56-1.40 (m, 1 H, one proton of CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 139.1, 129.9, 129.8, 128.44, 128.39, 125.1, 121.7, 86.3, 70.7, 53.3 (d, J = 11.9 Hz), 35.3, 32.2, 30.8, 23.9, 21.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.3; IR (neat) v (cm^{-1}) 3295, 2112, 1596, 1492, 1446, 1371; MS (ESI): *m/z* 388 [$(M + Na)^+$], 383 [$(M + NH_4)^+$], 366 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{18}H_{20}FNNaO_2S_2$ [$(M + Na)^+$]: 388.0812; Found: 388.0810.

2.15. Synthesis of *N*-fluoro-*N*-(4-((2-methoxypyridin-4-yl)methyl)hex-5-ynyl)-4-methylbenzenesulfonamide **1o**. (zdj-6-179, zdj-6-183, zdj-6-185, zdj-6-189)



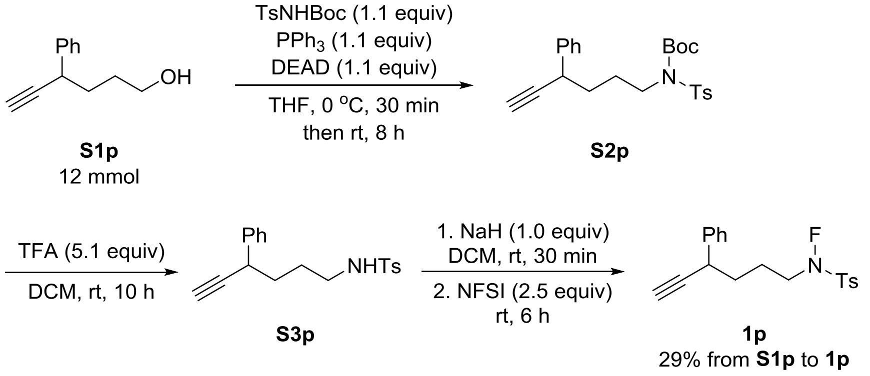
Following **Typical Procedure I**, the reaction of 5-hexynol (2.2 mL, d = 0.91 g/mL, 2.00 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and 4-(2-methoxypyridinyl)methyl bromide (4.8460 g, 24.0 mmol) in THF (60 mL) afforded **S1o** (320.7 mg) as an oil [eluent: petroleum ether/ethyl acetate = 2/1 (450 mL) to 3/2 (500 mL)], which was used for the next step without further characterization.

To a 25 mL flame-dried Schlenk tube were added PPh$_3$ (473.0 mg, 1.8 mmol), TsNHBoc (491.2 mg, 1.8 mmol), and a solution of **S1o** (320.7 mg) in THF (5 mL) sequentially. The resulting solution was cooled down to 0 °C with an ice-water bath followed by the addition of DEAD (283 μL, d = 1.106 g/mL, 313.0 mg, 1.8 mmol). The cooling bath was removed and the resulting mixture was stirred at room temperature for 10 hours as monitored by TLC. The resulting mixture was concentrated in vacuo and the crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 7/1 (480 mL) to 5/1 (400 mL)] to afford **S2o** (571.3 mg) as an oil, which was used for the next step without further characterization.

To a 50 mL round-bottomed flask were added **S2o** (571.3 mg), CH_2Cl_2 (5 mL), and TFA (0.5 mL). The resulting mixture was stirred at room temperature for 13 hours. TFA (2 mL) was added to the reaction mixture. The resulting mixture was stirred at room temperature for another 4 hours as monitored by TLC, and washed subsequently with H_2O (5 mL) and saturated aqueous solution of $NaHCO_3$ (5 mL) sequentially. The organic phase was dried over anhydrous Na_2SO_4, filtrated, concentrated in vacuo to afford **S3o** (467.6 mg) as an oil, which was used for the next step without further characterization.

To a 25 mL flame-dried Schlenk tube was added NaH (161.7 mg, 60 wt% in mineral oil, 4.0 mmol). After degassing under vacuum and backfilling with nitrogen for three times, CH_2Cl_2 (5 mL) and a solution of **S3o** (467.6 mg) in CH_2Cl_2 (5 mL) were added sequentially at room temperature under a N_2 atmosphere. The resulting mixture was stirred for 1 hour followed by the addition of NFSI (1024.1 mg, 3.3 mmol). The resulting mixture was stirred for 13 hours as monitored by TLC and quenched with H_2O (2 mL) slowly. The resulting mixture was filtrated through a short column of silica gel eluted with ethyl acetate (10 mL), concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 5/1 (480 mL) to 4/1 (450 mL)] to afford **1o** (261.6 mg, 3% from 5-hexynol to **1o**, 93% purity) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 5.1 Hz, 1 H, ArH), 7.81 (d, J = 8.1 Hz, 2 H, ArH), 7.40 (d, J = 7.8 Hz, 2 H, ArH), 6.75 (dd, J_1 = 5.4 Hz, J_2 = 1.2 Hz, 1 H, ArH), 6.61 (s, 1 H, ArH), 3.92 (s, 3 H, OCH_3), 3.39-3.24 (m, 1 H, one proton of NCH_2), 3.24-3.09 (m, 1 H, one proton of NCH_2), 2.80-2.58 (m, 3 H, CH_2 and CH), 2.48 (s, 3 H, CH_3), 2.09 (d, $J = 2.1$ Hz, 1 H, ≡CH), 2.07-1.92 (m, 1 H, one proton of CH_2), 1.92-1.74 (m, 1 H, one proton of CH_2), 1.71-1.45 (m, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 150.5, 146.5, 146.3, 129.91, 129.89, 128.8, 117.9, 111.0, 85.3, 71.3, 53.3, 53.2 (d, $J =$ 10.3 Hz), 40.3, 31.9, 31.2, 24.0, 21.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.1; IR (neat) *v* (cm^{-1}) 3293, 2112, 1613, 1561, 1450, 1399; MS (ESI): *m/z* 413 [$(M + Na)^+$], 391 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{20}H_{23}FN_2NaO_3S$ [$(M + Na)^+$]: 413.1306; Found: 413.1304.

2.16. Synthesis of *N*-fluoro-*N*-(4-phenylhex-5-ynyl)-4-methylbenzenesulfonamide **1p**. (zdj-7-002, zdj-7-003, zdj-7-007)



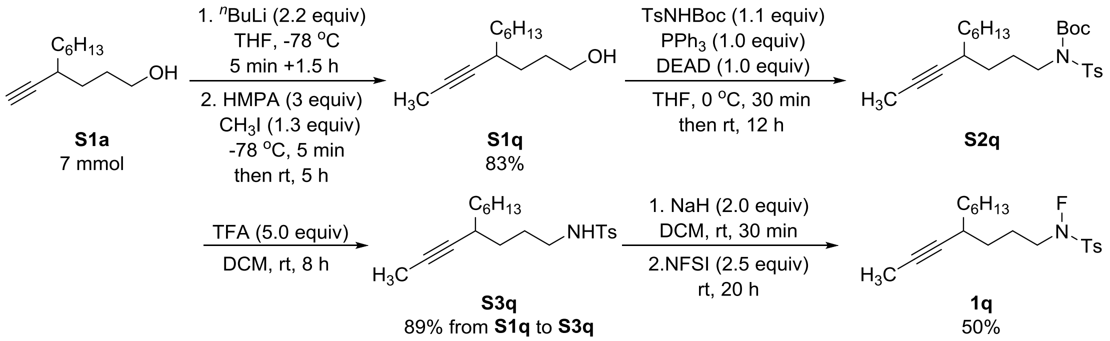
Following **Typical Procedure II**, the reaction of PPh_3 (1.7992 g, 6.8 mmol), TsNHBoc (1.8459 g, 6.8 mmol), DEAD (1.1 mL, d = 1.106 g/mL, 1.22 g, 7.0 mmol), and **S1p** (1.1354 g, 6.5 mmol) in THF (10 + 5 mL) afforded **S2p** (2.6102 g) as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (630 mL) to 10/1 (220 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2p** (2.6102 g) and TFA (2.4 mL, d = 1.489 g/mL, 3.57 g, 31.3 mmol) in CH_2Cl_2 (10 mL) afforded **S3p** (2.0338 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3p** (1.7467 g), NaH (0.2079 g, 60 wt% in mineral oil, 5.2 mmol), and NFSI (4.1352 g, 13.1 mmol) in CH_2Cl_2 (50 mL) afforded **1p** (0.5675 g, 29% from **S1p** to **1p**) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (660 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2 H, ArH), 7.42-7.18 (m, 7 H, ArH), 3.72-3.60 (m, 1 H, CH), 3.36-3.22 (m, 1 H, one proton of NCH_2), 3.21-3.08 (m, 1 H, one proton of NCH_2), 2.46 (s, 3 H, CH_3), 2.27 (d, *J* = 2.7 Hz, 1 H, ≡CH), 1.97-1.75 (m, 4 H, $CH_2 \times 2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.3, 140.7, 129.89, 129.87, 128.7, 128.5, 127.2, 126.9, 85.0, 71.6, 53.3 (d, *J* = 11.9 Hz), 36.9, 34.9, 24.0, 21.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.1; IR (neat) *v* (cm^{-1}) 3292, 2115, 1596, 1493, 1453, 1374; MS (ESI): *m/z* 368 [(M + Na)$^+$], 363 [(M + NH_4)$^+$]; HRMS (ESI) Calcd for $C_{19}H_{20}FNNaO_2S$ [(M + Na)$^+$]: 368.1091; Found: 368.1089.

2.17. Synthesis of *N*-fluoro-*N*-(4-hexylpent-5-ynyl)-4-methylbenzenesulfonamide **1q**.[7]

(zdj-4-021, zdj-4-024, zdj-4-027, zdj-4-029)



To a 100 mL flame-dried three-neck flask were added a solution of **S1a** (1.2737 g, 7.0 mmol) in THF (15 mL) under a N_2 atmosphere. The resulting solution was cooled down to -78 °C and ^{n}BuLi (2.4 M in hexane, 6.4 mL, 15.4 mmol) was added dropwise at -78 $^{\circ}$C within 5 minutes. After being stirred at -78 $^{\circ}$C for 1.5 hours, HMAP (3.7 mL, d = 1.03 g/mL, 3.81 g, 21.3 mmol) and methyl iodide (0.56 mL, d = 2.28 g/mL, 1.28 g, 9.0 mmol) sequentially dropwise. The resulting mixture was stirred at room temperature for 5 hours as monitored by TLC, quenched with a saturated aqueous solution of NH_4Cl slowly, and extracted with ethyl acetate (20 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 7/1 (400 mL) to 4/1 (100 mL)] to afford **S1q** (1.1359 g, 83%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (t, J = 6.5 Hz, 2 H, OCH_2), 2.41-2.12 (m, 1 H, CH), 1.92-1.14 (m, 18 H, OH, CH_3 and CH_2 × 7), 0.89 (t, J = 6.6 Hz, 3 H, CH_3). **S1q** was used for the next step without further characterization.

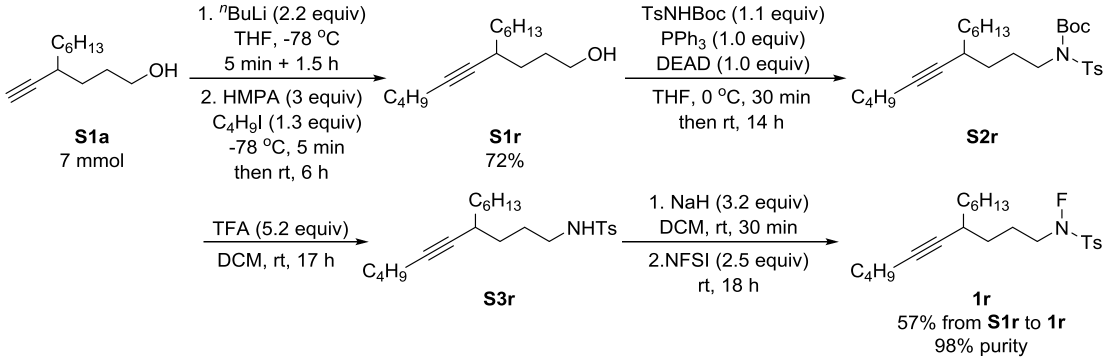
Following **Typical Procedure V**, the reaction of TsNHBoc (1.6539 g, 6.1 mmol), PPh_3 (1.5058 g, 5.7 mmol), DEAD (0.9 mL, d = 1.106 g/mL, 1.00 g, 5.7 mmol), and **S1q** (1.1141 g, 5.7 mmol) in THF (10 + 5 mL) afforded **S2q** (2.2780 g) as an oil [eluent: petroleum ether/ethyl acetate = 30/1 (480 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2q** (2.2470 g) and TFA (1.9 mL, d = 1.489 g/mL, 2.83 g, 24.8 mmol) in CH_2Cl_2 (10 mL) afforded **S3q** (1.7372 g, 89% from **S1q** to **S3q**) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2 H, ArH), 7.31 (d, J = 7.8 Hz, 2 H, ArH), 4.68-4.48 (m, 1 H, NH), 2.96 (q, J = 6.6 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.26-2.05 (m, 1 H, CH), 1.76 (d, J = 2.1 Hz, 3 H, CH_3), 1.72-1.14 (m, 14 H, CH_2 × 7), 0.88 (t, J = 6.5 Hz, 3 H, CH_3). **S3q** was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3q** (1.7109 g, 4.9 mmol), NaH (0.4015 g, 60 wt% in mineral oil, 10.0 mmol), and NFSI (3.8659 g, 12.3 mmol) in CH_2Cl_2 (50 mL) afforded **1q** (0.8920 g, 50%) as an oil [eluent: petroleum ether/ethyl acetate = 60/1 (610 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2 H, ArH), 7.41 (d, *J* = 8.5 Hz, 2 H, ArH), 3.33-3.13 (m, 2 H, NCH_2), 2.48 (s, 3 H, CH_3), 2.31-2.20 (m, 1 H, CH), 1.99-1.87 (m, 1 H, one proton of CH_2), 1.84-1.74 (m, 4 H, one proton of CH_2 and CH_3), 1.59-1.50 (m, 1 H, one proton of CH_2), 1.49-1.19 (m, 11 H, one proton of CH_2 and CH_2 × 5), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 129.94, 129.89, 128.9, 81.8, 77.05, 53.6 (d, *J* = 11.5 Hz), 35.4, 32.2, 31.8, 31.3, 29.1, 27.3, 24.3, 22.6, 21.7, 14.0, 3.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.4; IR (neat) *v* (cm^{-1}) 1597, 1456, 1376, 1307; Ramam *v* (cm^{-1}) 2242; MS (ESI): *m/z* 406 [(M + K)$^+$], 390 [(M + Na)$^+$], 385 [(M + NH_4)$^+$], 368 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{20}H_{30}FNNaO_2S$ [(M + Na)$^+$]: 390.1873; Found: 390.1875.

2.18. Synthesis of *N*-fluoro-*N*-(4-hexyldec-5-ynyl)-4-methylbenzenesulfonamide **1r**.[7]

(zdj-4-143, zdj-4-146, zdj-4-150, zdj-4-161)



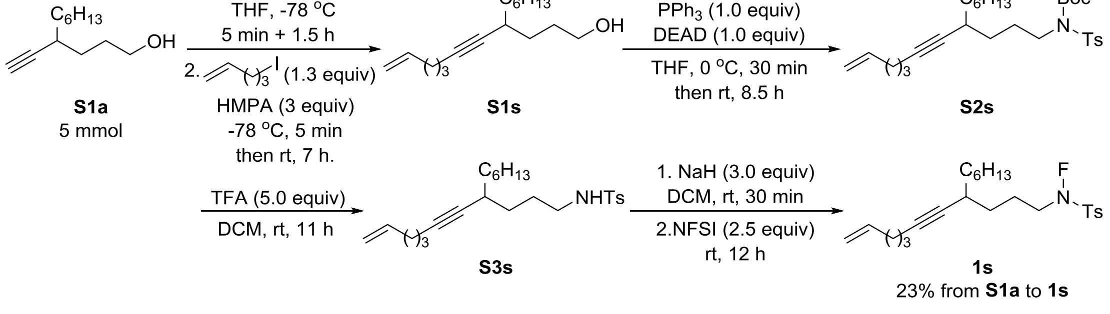
To a 100 mL flame-dried three-neck flask were added a solution of **S1a** (1.2771 g, 7.0 mmol) in THF (10 mL) under a N_2 atmosphere. The resulting solution was cooled down to -78 °C. Then ^{n}BuLi (2.4 M in hexane, 6.4 mL, 15.4 mmol) was added dropwise at -78 °C within 5 minutes. After being stirred at -78 °C for 1.5 hours, HMAP (3.6 mL, d = 1.03 g/mL, 3.71 g, 20.7 mmol) was added, which was followed by the dropwise addition of and ^{n}butyl iodide (1.05 mL, d = 1.617 g/mL, 1.70 g, 9.2 mmol) within 5 minutes. The resulting mixture was stirred at room temperature for 6 hours as monitored by TLC and quenched with a saturated aqueous solution of NH_4Cl slowly. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (15 mL × 2). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 10/1 (550 mL)] to afford **S1r** (1.2053 g, 72%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.67 (t, J = 6.8 Hz, 2 H, OCH_2), 2.38-2.23 (m, 1 H, CH), 2.16 (td, J_1 = 6.9 Hz, J_2 = 2.2 Hz, 2 H, CH_2), 1.84-1.12 (m, 19 H, OH and CH_2 × 9), 0.99-0.79 (m, 6 H, CH_3 × 2). **S1r** was used for the next step without further characterization.

Following **Typical Procedure V**, the reaction of PPh_3 (1.3129 g, 5.0 mmol), TsNHBoc (1.4510 g, 5.3 mmol), DEAD (0.8 mL, d = 1.106 g/mL, 0.88 g, 5.1 mmol), and **S1r** (1.1811 g, 5.0 mmol) in THF (10 + 5 mL) afforded **S2r** (2.2682 g) as an oil [eluent: petroleum ether/ethyl acetate = 30/1 (310 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2r** (2.2305 g) and TFA (1.8 mL, d = 1.489 g/mL, 2.68 g, 23.5 mmol) in CH_2Cl_2 (10 mL) afforded **S3r** (1.8083 g) as a solid, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3r** (1.7826 g), NaH (0.5816 g, 60 wt% in mineral oil, 14.5 mmol), and NFSI (3.5947 g, 11.4 mmol) in CH_2Cl_2 (50 mL) afforded **1r** (1.1390 g, 57% from **S1r** to **1r**, 98% purity) as an oil [eluent: petroleum ether/ethyl acetate = 70/1 (710 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2 H, ArH), 7.41 (d, *J* = 8.0 Hz, 2 H, ArH), 3.35-3.11 (m, 2 H, NCH_2), 2.48 (s, 3 H, CH_3), 2.33-2.23 (m, 1 H, CH), 2.14 (td, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 2 H, CH_2), 2.01-1.88 (m, 1 H, one proton of CH_2), 1.85-1.74 (m, 1 H, one proton of CH_2), 1.60-1.51 (m, 1 H, one proton of CH_2), 1.50-1.17 (m, 15 H, one proton of CH_2 and CH_2 × 7), 0.96-0.81 (m, 6 H, CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 129.93, 129.88, 128.9, 82.6, 81.9, 53.6 (d, *J* = 11.5 Hz), 35.5, 32.2, 31.7, 31.3, 31.2, 29.1, 27.2, 24.3, 22.6, 21.8, 21.7, 18.3, 14.0, 13.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.4; IR (neat) *v* (cm^{-1}) 1597, 1493, 1456, 1378, 1307; Ramam *v* (cm^{-1}) 2235; MS (ESI): *m/z* 448 [(M + K)$^+$], 432 [(M + Na)$^+$], 410 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{23}H_{37}FNO_2S$ [(M + H)$^+$]: 410.2524; Found: 410.2526.

2.19. Synthesis of *N*-fluoro-*N*-(4-hexylundec-10-en-5-ynyl)-4-methylbenzenesulfonamide 1s.[7] (zdj-4-185, zdj-4-186, zdj-4-190, zdj-4-191)



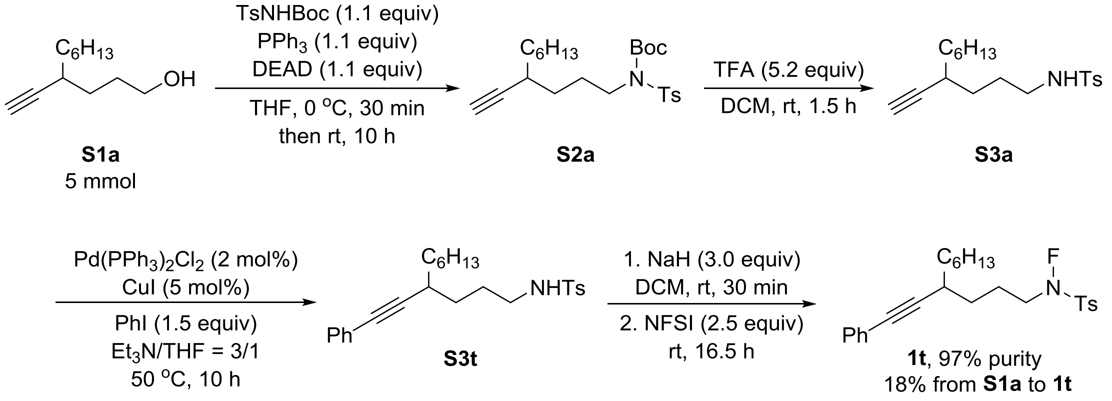
To a 100 mL flame-dried three-neck flask were added a solution of **S1a** (0.9125 g, 5.0 mmol) in THF (10 mL) under a N_2 atmosphere. The resulting solution was cooled down to -78 °C. Then ^{n}BuLi (2.4 M in hexane, 4.6 mL, 11.0 mmol) was added dropwise at -78 °C within 5 minutes. After being stirred at -78 °C for 1.5 hours, HMAP (2.6 mL, d = 1.03 g/mL, 2.68 g, 14.9 mmol) was added, followed by the dropwise addition of 5-pentenyl iodide (1.2909 g, 6.6 mmol) within 5 minutes. The resulting mixture was stirred at room temperature for 7 hours as monitored by TLC and quenched with a saturated aqueous solution of NH_4Cl slowly. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (10 mL × 2). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 9/1 (500 mL)] to afford **S1s** (1.0151 g) as an oil,[7] which was used for the next step without further characterization.

Following **Typical Procedure V**, the reaction of TsNHBoc (1.1512 g, 4.2 mmol), PPh_3 (1.0529 g, 4.0 mmol), DEAD (0.64 mL, d = 1.106 g/mL, 0.71 g, 4.1 mmol), and **S1s** (0.9901 g, 4.0 mmol) in THF (10 + 5 mL) afforded **S2s** (1.7555 g) as an oil [eluent: petroleum ether/ethyl acetate = 40/1 (205 mL) to 20/1 (210 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2s** (1.7202 g) and TFA (1.3 mL, d = 1.489 g/mL, 1.94 g, 17.0 mmol) in CH_2Cl_2 (10 mL) afforded **S3s** (1.2793 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3s** (1.2684 g), NaH (0.4015 g, 60 wt% in mineral oil, 10.0 mmol), and NFSI (2.4623 g, 7.8 mmol) in CH_2Cl_2 (30 mL) afforded **1s** (0.4560 g, 23% from **S1a** to **1s**) as an oil [eluent: petroleum ether/ethyl acetate = 60/1 (420 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2 H, ArH), 7.41 (d, *J* = 8.0 Hz, 2 H, ArH), 5.84-5.73 (m, 1 H, =CH), 5.07-4.92 (m, 2 H, $=CH_2$), 3.35-3.13 (m, 2 H, NCH_2), 2.48 (s, 3 H, CH_3), 2.33-2.25 (m, 1 H, CH), 2.22-2.09 (m, 4 H, CH_2 × 2), 2.01-1.88 (m, 1 H, one proton of CH_2), 1.86-1.73 (m, 1 H, one proton of CH_2), 1.61-1.52 (m, 3 H, one proton of CH_2 and CH_2), 1.50-1.20 (m, 11 H, one proton of CH_2 and CH_2 × 5), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 138.0, 129.93, 129.89, 128.8, 114.9, 83.0, 81.5, 53.6 (d, *J* = 12.6 Hz), 35.5, 32.7, 32.2, 31.7, 31.3, 29.1, 28.3, 27.2, 24.3, 22.6, 21.7, 18.1, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.4; IR (neat) *v* (cm^{-1}) 1641, 1597, 1456, 1378; Ramam *v* (cm^{-1}) 2232; MS (ESI): *m/z* 460 [(M + K)$^+$], 444 [(M + Na)$^+$], 439 [(M + NH_4)$^+$], 422 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{24}H_{37}FNO_2S$ [(M + H)$^+$]: 422.2524; Found: 422.2524.

2.20. Synthesis of *N*-fluoro-*N*-(4-hexyl-6-phenylhex-5-ynyl)-4-methylbenzenesulfonamide **1t**.[8] (zdj-6-169, zdj-6-170, zdj-6-171, zdj-6-173).



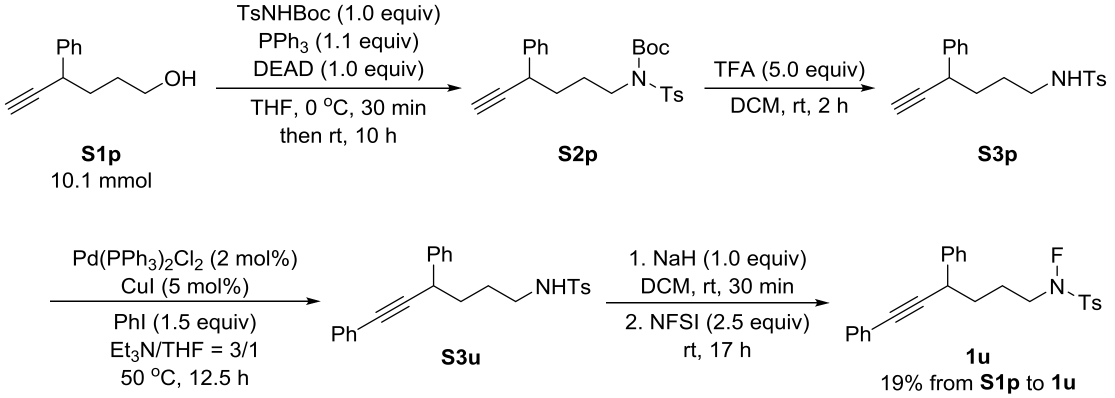
Following **Typical Procedure II**, the reaction of PPh_3 (1.3789 g, 5.3 mmol), TsNHBoc (1.4271 g, 5.3 mmol), DEAD (0.83 mL, d = 1.106 g/mL, 0.9180 g, 5.3 mmol), and **S1a** (0.9111 g, 5.0 mmol) in THF (10 + 5 mL) afforded **S2a** (2.0911 g) as an oil [eluent: petroleum ether/ethyl acetate = 30/1 (620 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2a** (2.0911 g) and TFA (1.9 mL, d = 1.489 g/mL, 2.83 g, 24.8 mmol) in CH_2Cl_2 (10 mL) afforded **S3a** (1.5476 g) as a solid, which was used for the next step without further characterization.

To a 100 mL Schlenk flask were added $Pd(PPh_3)_2Cl_2$ (64.4 mg, 0.092 mmol) and CuI (44.5 mg, 0.23 mmol). After degassing under vacuum and backfilling with nitrogen for three times, a solution of **S3a** (1.5476 g) in THF (5 mL), Et_3N (15 mL), and PhI (0.78 mL, d = 1.823 g/mL, 1.422 g, 7.0 mmol) were added sequentially. The resulting mixture was stirred at 50 ^oC for 10 hours as monitored by TLC, filtrated through a short column of silica gel eluted with ethyl acetate (20 mL), concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 7/1 (560 mL)] to afford **S3t** (1.8259 g) as a solid, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3t** (1.8259 g), NaH (0.5299 g, 60 wt% in mineral oil, 13.2 mmol), and NFSI (3.4779 g, 11.0 mmol) in CH_2Cl_2 (50 mL) afforded **1t** (0.4030 g, 18% from **S1a** to **1t**, 97% purity) as an oil [eluent: petroleum ether/ethyl acetate = 30/1 (465 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 8.4 Hz, 2 H, ArH), 7.41-7.32 (m, 4 H, ArH), 7.29-7.21 (m, 3 H, ArH), 3.43-3.28 (m, 1 H, one proton of NCH_2), 3.28-3.12 (m, 1 H, one proton of NCH_2), 2.62-2.49 (m, 1 H, CH), 2.45 (s, 3 H, CH_3), 2.10-1.79 (m, 2 H, CH_2), 1.76-1.39 (m, 6 H, $CH_2 \times 3$), 1.38-1.19 (m, 6 H, $CH_2 \times 3$), 0.89 (t, J = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 131.5, 129.9, 128.8, 128.1, 127.5, 123.8, 92.7, 82.3, 53.6 (d, J = 12.5 Hz), 35.2, 31.92, 31.88, 31.7, 29.1, 27.3, 24.3, 22.6, 21.7, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.2; IR (neat) v (cm^{-1}) 2228, 1597, 1490, 1377; MS (ESI): m/z 452 [(M + Na)$^+$], 447 [(M + NH_4)$^+$], 430 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{25}H_{32}FNNaO_2S$ [(M + Na)$^+$]: 452.2030; Found: 452.2030.

2.21. Synthesis of Synthesis of *N*-fluoro-*N*-(4,6-diphenylhex-5-yn)-4-methylbenzenesulfonamide **1u**.[8] (zdj-7-020, zdj-7-021, zdj-7-022, zdj-7-024).



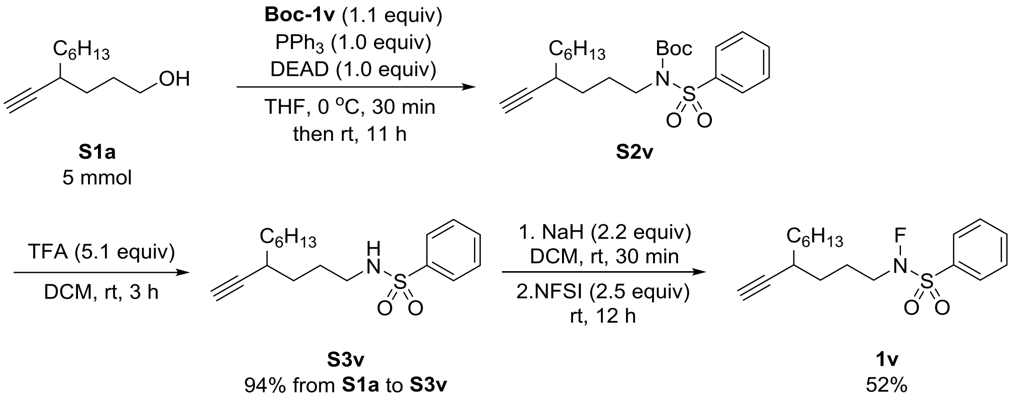
Following **Typical Procedure II**, the reaction of PPh_3 (2.7739 g, 10.6 mmol), TsNHBoc (2.8450 g, 10.4 mmol), DEAD (1.65 mL, d = 1.106 g/mL, 1.825 g, 10.5 mmol), and **S1p** (1.7632 g, 10.1 mmol) in THF (15 + 10 mL) afforded **S2p** (3.9316 g) as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (630 mL) to 10/1 (330 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2p** (3.9316 g) and TFA (3.5 mL, d = 1.489 g/mL, 5.21 g, 45.7 mmol) in CH_2Cl_2 (15 mL) afforded **S3p** (2.9714 g) as an oil, which was used for the next step without further characterization.

To a 100 mL Schlenk flask were added $Pd(PPh_3)_2Cl_2$ (122.3 mg, 0.17 mmol) and CuI (85.4 mg, 0.45 mmol). After degassing under vacuum and backfilling with nitrogen for three times, a solution of **S3p** (2.9714 g) in THF (10 mL), Et_3N (30 mL), and PhI (1.5 mL, d = 1.823 g/mL, 2.73 g, 13.4 mmol) were added sequentially. The resulting mixture was stirred at 50 ^{o}C for 12.5 hours as monitored by TLC, filtrated through a short column of silica gel eluted with ethyl acetate (20 mL), concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 9/2 (770 mL)] to afford **S3u** (3.1342 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3u** (3.1342 g), NaH (0.2985 g, 60 wt% in mineral oil, 7.5 mmol), and NFSI (6.0433 g, 19.2 mmol) in CH_2Cl_2 (80 mL) afforded **1u** (0.8093 g, 19% from **S1p** to **1u**) as an oil [eluent: petroleum ether/ethyl acetate = 18/1 (760 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2 H, ArH), 7.49-7.17 (m, 12 H, ArH), 3.94-3.80 (m, 1 H, CH), 3.41-3.22 (m, 1 H, one proton of NCH_2), 3.22-3.07 (m, 1 H, one proton of NCH_2), 2.42 (s, 3 H, CH_3), 2.07-1.78 (m, 4 H, CH_2 × 2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 141.3, 131.5, 129.87, 129.84, 128.5, 128.2, 127.8, 127.3, 126.8, 123.3, 90.5, 83.8, 53.4 (d, *J* = 12.5 Hz), 37.7, 35.2, 24.1, 21.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.2; IR (neat) *v* (cm^{-1}) 2258, 1597, 1490, 1453, 1374; MS (ESI): 444 [$(M + Na)^+$], 439 [$(M + NH_4)^+$], 422 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{25}H_{24}FNNaO_2S$ [$(M + Na)^+$]: 444.1404; Found: 444.1403.

2.22. Synthesis of *N*-fluoro-*N*-(4-hexylhex-5-ynyl)benzenesulfonamide **1v**. (zdj-4-005, zdj-4-012, zdj-4-013)



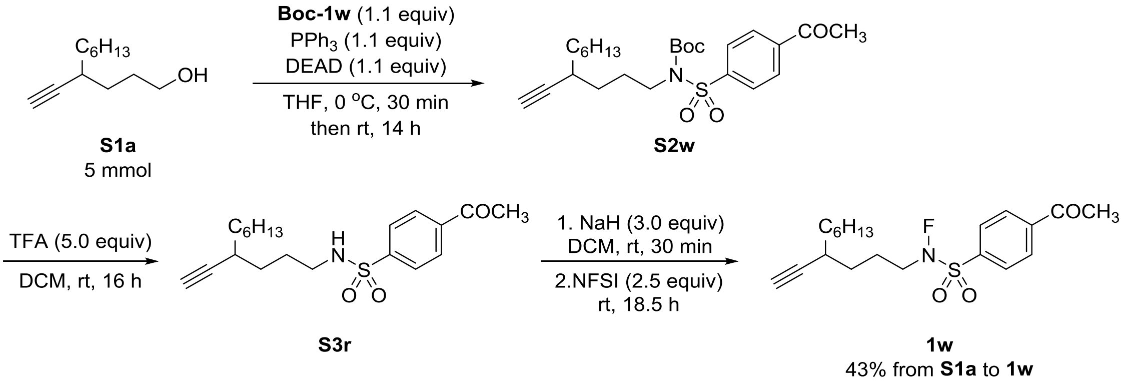
Following **Typical Procedure V**, the reaction of **Boc-1v** (1.3721 g, 5.3 mmol), PPh_3 (1.3344 g, 5.1 mmol), DEAD (0.8 mL, d = 1.106 g/mL, 0.88 g, 5.1 mmol), and **S1a** (0.9119 g, 5.0 mmol) in THF (10 + 5 mL) afforded **S2v** (1.9725 g) as an oil [eluent: petroleum ether/ethyl acetate = 30/1 (620 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2v** (1.9410 g) and TFA (1.8 mL, d = 1.489 g/mL, 2.68 g, 23.5 mmol) in CH_2Cl_2 (10 mL) afforded **S3v** (1.4805 g, 94% from **S1a** to **S3v**) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 6.6 Hz, 2 H, ArH), 7.65-7.47 (m, 3 H, ArH), 4.87-4.67 (m, 1 H, NH), 2.98 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.35-2.15 (m, 1 H, CH), 2.01 (d, *J* = 2.1 Hz, 1 H, ≡CH), 1.79-1.18 (m, 14 H, $CH_2 \times 7$), 0.88 (t, *J* = 6.5 Hz, 3 H, CH_3). **S3v** was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3v** (1.4501 g, 4.5 mmol), NaH (0.3894 g, 60 wt% in mineral oil, 9.7 mmol), and NFSI (3.5619 g, 11.3 mmol) in CH_2Cl_2 (50 mL) afforded **1v** (0.7923 g, 52%) as an oil [eluent: petroleum ether/ethyl acetate =

50/1 (700 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2 H, ArH), 7.75 (t, *J* = 7.5 Hz, 1 H, ArH), 7.62 (t, *J* = 7.8 Hz, 2 H, ArH), 3.38-3.13 (m, 2 H, NCH_2), 2.40-2.28 (m, 1 H, CH), 2.04 (d, *J* = 2.5 Hz, 1 H, ≡CH), 2.01-1.90 (m, 1 H, one proton of CH_2), 1.87-1.75 (m, 1 H, one proton of CH_2), 1.68-1.57 (m, 1 H, one proton of CH_2), 1.56-1.12 (m, 11 H, one proton of CH_2 and CH_2 × 5), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.9, 132.0, 129.9, 129.3, 87.1, 69.8, 53.4 (d, *J* = 11.5 Hz), 34.9, 31.7, 31.6, 31.0, 29.0, 27.1, 24.1, 22.6, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.5; IR (neat) *v* (cm^{-1}) 3304, 2108, 1586, 1449, 1376; MS (ESI): *m/z* 378 [(M + K)$^+$], 362 [(M + Na)$^+$], 357 [(M + NH_4)$^+$], 340 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{18}H_{26}FNNaO_2S$ [(M + Na)$^+$]: 362.1560; Found: 362.1563.

2.23. Synthesis of *N*-fluoro-*N*-(4-hexylhex-5-ynyl)-4-acetylbenzenesulfonamide **1w**. (zdj-4-101, zdj-4-103, zdj-4-108)

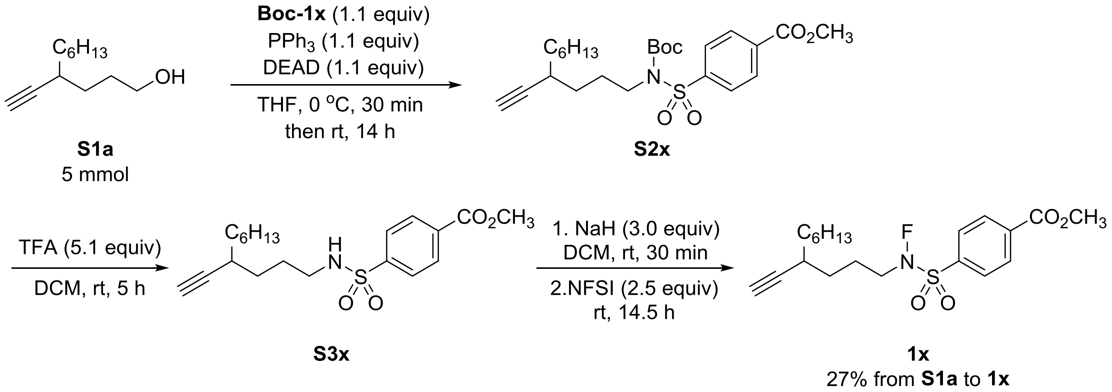


Following **Typical Procedure V**, the reaction of **Boc-1w** (1.6304 g, 5.4 mmol), PPh_3 (1.4434 g, 5.5 mmol), DEAD (0.88 mL, d = 1.106 g/mL, 0.97 g, 5.6 mmol), and **S1w** (0.9124 g, 5.0 mmol) in THF (10 + 5 mL) afforded **S2w** (1.9843 g) as an oil [eluent: petroleum ether/ethyl acetate = 8/1 (450 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2w** (1.9544 g) and TFA (1.6 mL, d = 1.489 g/mL, 2.38 g, 20.9 mmol) in CH_2Cl_2 (10 mL) afforded **S3w** (1.4952 g) as an oil, which was used for the next step without further characterization. **S3w** was afforded by filtrated through a short column of silica gel eluted with ethyl acetate (30 mL × 2)].

To a 100 mL flame-dried three-neck flask was added **S3w** (1.4716 g). After degassing under vacuum and backfilling with nitrogen for three times, CH_2Cl_2 (40 mL) and NaH (0.5019 g, 60 wt% in mineral oil, 12.5 mmol) were added sequentially at room temperature under a N_2 atmosphere. The resulting mixture was stirred for 30 minutes followed by the the addition of NFSI (3.1450 g, 10.0 mmol). The resulting mixture was stirred for 18.5 hours as monitored by TLC and quenched with H_2O slowly. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (40 mL × 2). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, concentrated in vacuo followed by the addition of petroleum ether/diethyl ether = 1/1 (20 mL) and filteration. The filtrate was concentrated in vacuo and the crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 9/1 (600 mL)] to afford **1w** (0.7884 g, 43% from **S1a** to **1w**) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.5 Hz, 2 H, ArH), 8.05 (d, J = 8.5 Hz, 2 H, ArH), 3.39-3.19 (m, 2 H, NCH_2), 2.69 (s, 3 H, CH_3), 2.40-2.28 (m, 1 H, CH), 2.05 (d, J = 2.5 Hz, 1 H, ≡CH), 2.02-1.92 (m, 1 H, one proton of CH_2), 1.90-1.76 (m, 1 H, one proton of CH_2), 1.70-1.57 (m, 1 H, one proton of CH_2), 1.56-1.20 (m, 11 H, one proton of CH_2 and $CH_2 \times 5$), 0.88 (t, J = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 141.7, 135.8, 130.3, 128.8, 87.0, 69.8, 53.3 (d, J = 12.6 Hz), 34.9, 31.7, 31.6, 31.0, 29.0, 27.1, 26.9, 24.0, 22.5, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.2; IR (neat) ν (cm^{-1}) 3293, 2111, 1697, 1573, 1457, 1428, 1400, 1381; MS (ESI): *m/z* 404 [$(M + Na)^+$], 399 [$(M + NH_4)^+$], 382 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{20}H_{29}FNO_3S$ [$(M + H)^+$]: 382.1847; Found: 382.1848.

2.24. Synthesis of *N*-fluoro-*N*-(4-hexylhex-5-ynyl)-4-methoxycarbonylbenzenesulfonamide **1x**. (zdj-4-160, zdj-4-165, zdj-4-167)



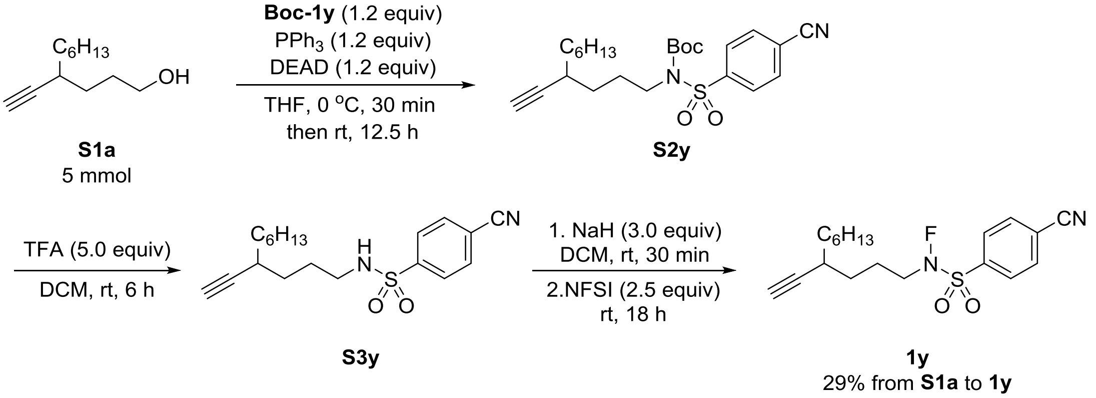
Following **Typical Procedure V**, the reaction of **Boc-1x** (1.7501 g, 5.5 mmol), PPh_3 (1.4505 g, 5.5 mmol), DEAD (0.9 mL, d = 1.106 g/mL, 1.00 g, 5.7 mmol), and **S1a** (0.9109 g, 5.0 mmol) in THF (10 + 5 mL) afforded **S2x** (2.2312 g) as a solid [eluent: petroleum ether/ethyl acetate = 12/1 (390 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2x** (2.2105 g) and TFA (1.8 mL, d = 1.489 g/mL, 2.68 g, 23.5 mmol) in CH_2Cl_2 (10 mL) afforded **S3x** (1.6859 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3x** (1.6525 g), NaH (0.5229 g, 13.1 mmol, 60 wt% in mineral oil), and NFSI (3.5019 g, 11.1 mmol) in CH_2Cl_2 (50 mL) afforded **1x** (0.5274 g, 27% from **S1a** to **1x**) as an oil [eluent: petroleum ether/ethyl acetate = 15/1 (480 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, J = 8.5 Hz, 2 H, ArH), 8.03 (d, J = 8.5 Hz, 2 H, ArH), 3.99 (s, 3 H, OCH_3), 3.40-3.18 (m, 2 H, NCH_2), 2.41-2.25 (m, 1 H, CH), 2.05 (d, J = 2.5 Hz, 1 H, ≡CH), 2.02-1.91 (m, 1 H, one proton of CH_2), 1.89-1.78 (m, 1 H, one proton of CH_2), 1.70-1.57 (m, 1 H, one proton of CH_2), 1.57-1.20 (m, 11 H, one proton of CH_2 and $CH_2 \times 5$), 0.88 (t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 135.84, 135.80, 130.3, 129.9, 86.9, 69.8, 53.4 (d, J = 12.6 Hz), 52.8, 34.9, 31.7, 31.6, 31.0, 29.0, 27.1, 24.0, 22.5, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.2; IR (neat) v (cm^{-1}) 3303, 2110, 1733, 1575, 1456, 1437, 1401, 1383; MS (ESI): m/z 420 [$(M + Na)^+$], 415 [$(M + NH_4)^+$], 398 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{20}H_{29}FNO_4S$ [$(M + H)^+$]: 398.1796; Found: 398.1795.

2.25. Synthesis of *N*-fluoro-*N*-(4-hexylhex-5-ynyl)-4-cyanobenzenesulfonamide **1y**.

(zdj-4-120, zdj-4-122, zdj-4-125)



Following **Typical Procedure V**, the reaction of **Boc-1y** (1.6837 g, 6.0 mmol),

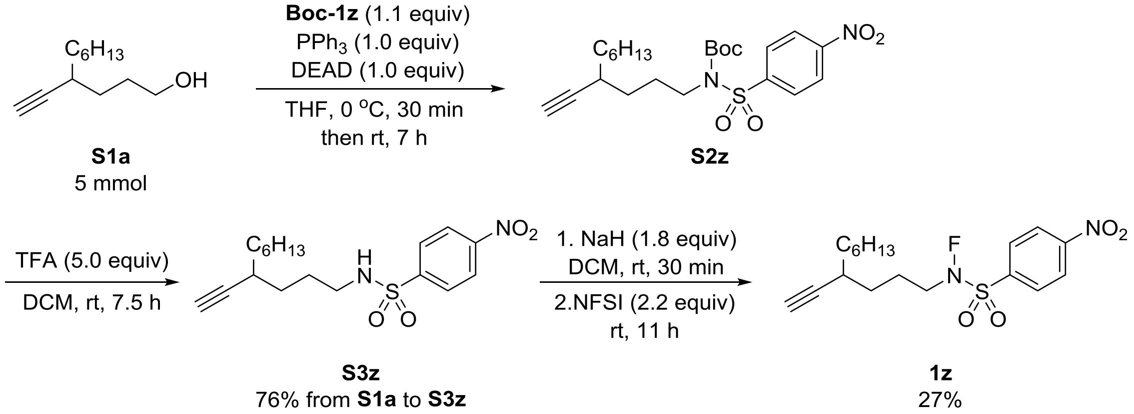
PPh_3 (1.5390 g, 5.9 mmol), DEAD (0.96 mL, d = 1.106 g/mL, 1.06 g, 6.1 mmol), and **S1a** (0.9100 g, 5.0 mmol) in THF (10 + 5 mL) afforded **S2y** (2.0047 g) as an oil [eluent: petroleum ether/ethyl acetate = 10/1 (440 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2y** (1.9875 g) and TFA (1.7 mL, d = 1.489 g/mL, 2.53 g, 22.2 mmol) in CH_2Cl_2 (10 mL) afforded **S3y** (1.5539 g) as a solid, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3y** (1.5340 g), NaH (0.5289 g, 60 wt% in mineral oil, 13.2 mmol), and NFSI (3.4550 g, 10.9 mmol) in CH_2Cl_2 (40 mL) afforded **1y** (0.5177 g, 29% from **S1a** to **1y**) as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (630 mL)]: ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 2 H, ArH), 7.93 (d, *J* = 8.5 Hz, 2 H, ArH), 3.44-3.21 (m, 2 H, NCH_2), 2.39-2.29 (m, 1 H, CH), 2.06 (d, *J* = 2.5 Hz, 1 H, ≡CH), 2.04-1.93 (m, 1 H, one proton of CH_2), 1.90-1.79 (m, 1 H, one proton of CH_2), 1.68-1.57 (m, 1 H, one proton of CH_2), 1.56-1.21 (m, 11 H, one proton of CH_2 and $CH_2 \times 5$), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.4, 132.9, 130.4, 118.6, 116.8, 86.8, 69.9, 53.1 (d, *J* = 11.5 Hz), 34.9, 31.6, 31.5, 31.0, 29.0, 27.0, 24.0, 22.5, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -49.9; IR (neat) ν (cm^{-1}) 3297, 2236, 2110, 1488, 1463, 1384; MS (ESI): *m/z* 387 [$(M + Na)^+$], 382 [$(M + NH_4)^+$], 365 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{19}H_{26}FN_2O_2S$ [$(M + H)^+$]: 365.1694; Found: 365.1697.

2.26. Synthesis of *N*-fluoro-*N*-(4-hexylhex-5-ynyl)-4-nitrobenzenesulfonamide **1z**.

(zdj-4-015, zdj-4-020, zdj-4-026)



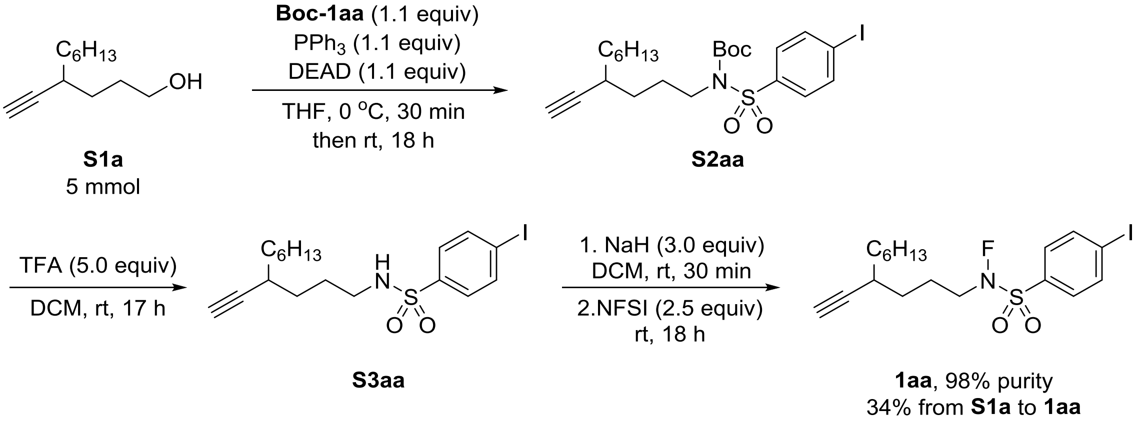
Following **Typical Procedure V**, the reaction of **Boc-1z** (1.6201 g, 5.4 mmol), PPh_3 (1.3237 g, 5.0 mmol), DEAD (0.8 mL, d = 1.106 g/mL, 0.88 g, 5.1 mmol), and **S1a** (0.9106 g, 5.0 mmol) in THF (10 + 5 mL) afforded **S2z** (1.8717 g) as an oil [eluent: petroleum ether/ethyl acetate = 20/1 (630 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2z** (1.8395 g) and TFA (1.5 mL, d = 1.489 g/mL, 2.23 g, 19.6 mmol) in CH_2Cl_2 (10 mL) afforded **S3z** (1.3884 g, 76% from **S1a** to **S3z**) as a soild: ^1H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.7 Hz, 2 H, ArH), 8.07 (d, *J* = 8.4 Hz, 2 H, ArH), 5.02-4.66 (m, 1 H, NH), 3.06 (q, *J* = 6.6 Hz, 2 H, NCH_2), 2.37-2.15 (m, 1 H, CH), 2.03 (d, *J* = 2.1 Hz, 1 H, ≡CH), 1.88-1.12 (m, 14 H, $CH_2 \times 7$), 0.88 (t, *J* = 6.9 Hz, 3 H, CH_3). **S3z** was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3z** (1.3639 g, 3.7 mmol), NaH (0.2712 g, 60 wt% in mineral oil, 6.8 mmol), and NFSI (2.5050 g, 7.9 mmol) in CH_2Cl_2 (40 mL) afforded **1z** (393.1 mg, 27%) as a solid (m.p. 38.1-38.8 °C, without recrystallization) [eluent: petroleum ether/ethyl acetate = 30/1 (620 mL)]: ^1H NMR

(500 MHz, CDCl$_3$) δ 8.46 (d, *J* = 9.0 Hz, 2 H, ArH), 8.17 (d, *J* = 8.5 Hz, 2 H, ArH), 3.45-3.25 (m, 2 H, NCH$_2$), 2.39-2.30 (m, 1 H, CH), 2.06 (d, *J* = 2.5 Hz, 1 H, ≡CH), 2.04-1.94 (m, 1 H, one proton of CH$_2$), 1.92-1.78 (m, 1 H, one proton of CH$_2$), 1.69-1.57 (m, 1 H, one proton of CH$_2$), 1.57-1.18 (m, 11 H, one proton of CH$_2$ and CH$_2$ × 5), 0.88 (t, *J* = 6.8 Hz, 3 H, CH$_3$); ^{13}C NMR (125 MHz, CDCl$_3$) δ 151.4, 138.0, 131.3, 124.4, 86.9, 69.9, 53.1 (d, *J* = 11.5 Hz), 34.9, 31.7, 31.5, 31.0, 29.0, 27.1, 24.0, 22.6, 14.0; ^{19}F NMR (376 MHz, CDCl$_3$) δ -49.9; IR (neat) *ν* (cm^{-1}) 3301, 2103, 1608, 1537, 1463, 1404, 1386; MS (EI): 365 [(M - F)$^+$, 6.25], 122 (100); Anal. Calcd. for $C_{18}H_{25}FN_2O_4S$ (%): C, 56.23; H, 6.55; N, 7.29; Found: C, 56.35; H, 6.59; N, 7.20.

2.27. Synthesis of *N*-fluoro-*N*-(4-hexylhex-5-ynyl)-4-iodobenzenesulfonamide **1aa**. (zdj-4-106, zdj-4-110, zdj-4-114)

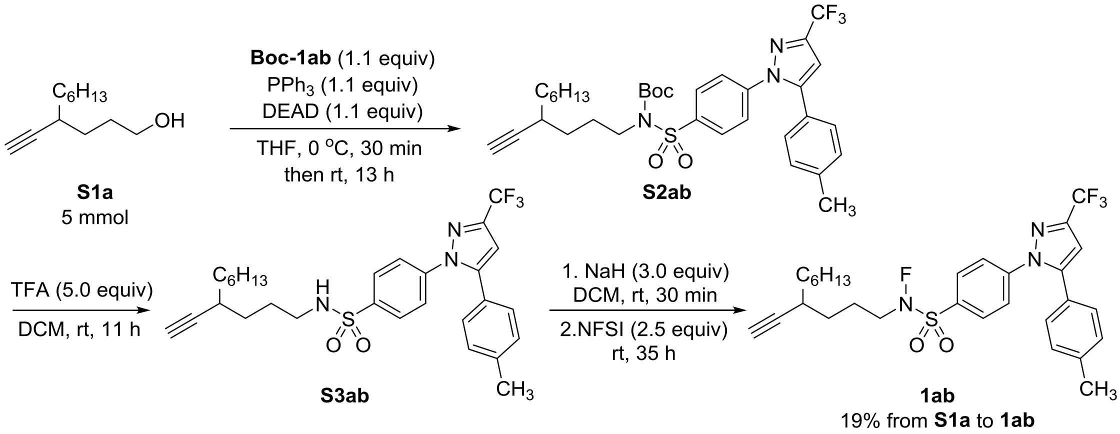


Following **Typical Procedure V**, the reaction of **Boc-1aa** (2.1430 g, 5.6 mmol), PPh$_3$ (1.4491 g, 5.5 mmol), DEAD (0.90 mL, d = 1.106 g/mL, 1.00 g, 5.7 mmol), and **S1a** (0.9127 g, 5.0 mmol) in THF (10 + 5 mL) afforded **S2aa** (2.3457 g) as an oil [eluent: petroleum ether/ethyl acetate = 30/1 (620 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2aa** (2.3198 g) and TFA (1.6 mL, d = 1.489 g/mL, 2.38 g, 20.9 mmol) in CH_2Cl_2 (10 mL) afforded **S3aa** (1.9713 g) as a solid, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3aa** (1.9529 g), NaH (0.5325 g, 60 wt% in mineral oil, 13.3 mmol), and NFSI (3.4591 g, 11.0 mmol) in CH_2Cl_2 (40 mL) afforded **1aa** (0.7988 g, 34% from **S1a** to **1aa**, 98% purity) as an oil [eluent: petroleum ether/ethyl acetate = 50/1 (510 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.5 Hz, 2 H, ArH), 7.64 (d, J = 8.5 Hz, 2 H, ArH), 3.38-3.15 (m, 2 H, NCH_2), 2.39-2.28 (m, 1 H, CH), 2.06 (d, J = 2.0 Hz, 1 H, ≡CH), 2.02-1.90 (m, 1 H, one proton of CH_2), 1.90-1.74 (m, 1 H, one proton of CH_2), 1.66-1.56 (m, 1 H, one proton of CH_2), 1.56-1.20 (m, 11 H, one proton of CH_2 and CH_2 × 5), 0.88 (t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 131.5, 130.9, 103.3, 86.9, 69.8, 53.3 (d, J = 12.6 Hz), 34.8, 31.6, 31.5, 31.0, 29.0, 27.0, 24.0, 22.5, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.1; IR (neat) ν (cm^{-1}) 3302, 2110, 1568, 1467, 1386; MS (ESI): m/z 504 [(M + K)$^+$], 488 [(M + Na)$^+$]; HRMS (ESI) Calcd for $C_{18}H_{26}FINO_2S$ [(M + H)$^+$]: 466.0707; Found: 466.0708.

2.28. Synthesis of *N*-fluoro-*N*-(4-hexylhex-5-ynyl)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazolyl)benzenesulfonamide **1ab**. (zdj-4-136, zdj-4-138, zdj-4-141)



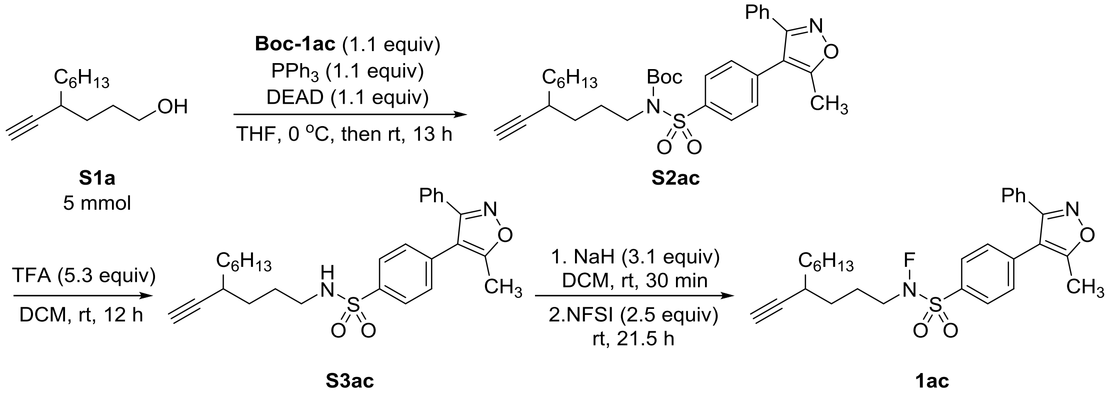
Following **Typical Procedure V**, the reaction of **Boc-1ab** (2.6500 g, 5.5 mmol), PPh_3 (1.4398 g, 5.5 mmol), DEAD (0.86 mL, d = 1.106 g/mL, 0.95 g, 5.5 mmol), and **S1a** (0.9110 g, 5.0 mmol) in THF (10 + 5 mL) afforded **S2ab** (3.1055 g) as an oil [eluent: petroleum ether/ethyl acetate = 15/1 (480 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2ab** (3.1055 g) and TFA (1.9 mL, d = 1.489 g/mL, 2.83 g, 24.8 mmol) in CH_2Cl_2 (10 mL) afforded **S3ab** (2.6429 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3ab** (2.6051 g), NaH (0.5829 g, 60 wt% in mineral oil, 14.6 mmol), and NFSI (3.7845 g, 12.0 mmol) in CH_2Cl_2 (50 mL) afforded **1ab** (0.5336 g, 19% from **S1a** to **1ab**) as an oil [eluent: petroleum ether/ethyl acetate = 40/1 (615 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 2 H, ArH), 7.58 (d, *J* = 8.5 Hz, 2 H, ArH), 7.21 (d, *J* = 8.0 Hz, 2 H, ArH), 7.13 (d, *J* = 8.0 Hz, 2 H, ArH), 6.76 (s, 1 H, ArH), 3.36-3.15 (m, 2 H, NCH_2), 2.40 (s, 3 H, CH_3), 2.37-2.29 (m, 1 H, CH), 2.05 (d, *J* = 2.5 Hz, 1 H, ≡CH), 2.02-1.90 (m, 1 H, one proton of CH_2), 1.89-1.77 (m, 1 H, one proton of CH_2), 1.66-1.56 (m, 1 H, one proton of CH_2), 1.55-1.19 (m, 11 H, one proton of CH_2 and CH_2 × 5), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 145.4, 144.5 (q, *J* = 38.7 Hz), 144.3, 140.0, 131.1, 130.9, 129.8, 128.7, 125.5, 125.3, 120.9 (q, *J* = 267.4 Hz), 106.7, 86.9, 69.8, 53.5 (d, *J* = 12.6 Hz), 34.9, 31.7, 31.6, 31.0, 29.0, 27.1, 24.0, 22.5, 21.3, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.0, -63.1; IR (neat) *v* (cm^{-1}) 3307, 2108, 1596, 1498, 1471, 1411, 1375; MS (ESI): *m/z* 586 [$(M + Na)^+$], 564 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{29}H_{34}F_4N_3O_2S$ [$(M + H)^+$]: 564.2302; Found: 564.2302.

2.29. Synthesis of *N*-fluoro-*N*-(4-hexylhex-5-ynyl)-4-(5-methyl-3-phenylisoxazol-4-yl)benzenesulfonamide **1ac**. (zdj-4-139, zdj-4-140, zdj-4-147)



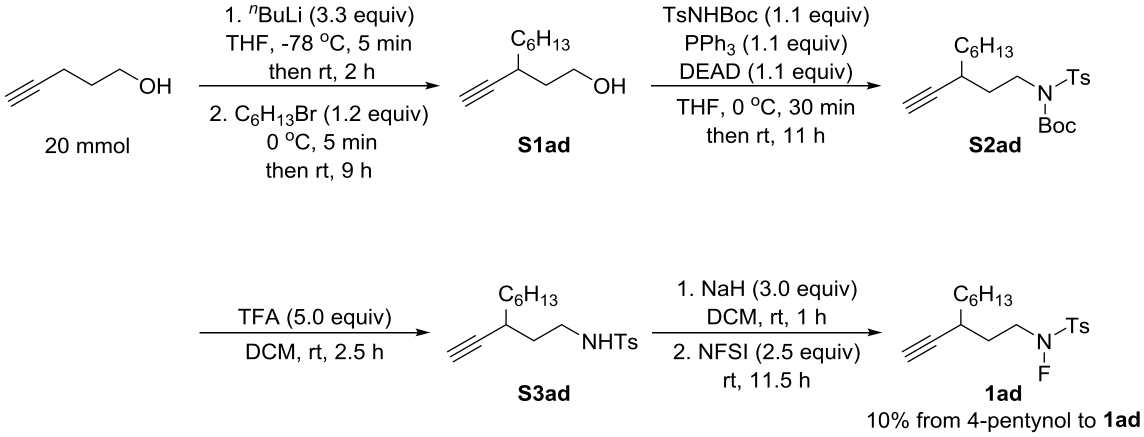
Following **Typical Procedure V**, the reaction of **Boc-1ac** (2.3015 g, 5.6 mmol), PPh_3 (1.4416 g, 5.5 mmol), DEAD (0.88 mL, d = 1.106 g/mL, 0.97 g, 5.6 mmol), and **S1a** (0.9109 g, 5.0 mmol) in THF (10 + 5 mL) afforded **S2ac** (2.4267 g) as an oil [eluent: petroleum ether/ethyl acetate = 12/1 (520 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2ac** (2.4267 g) and TFA (1.7 mL, d = 1.489 g/mL, 2.53 g, 22.2 mmol) in CH_2Cl_2 (10 mL) afforded **S3ac** (2.0288 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3ac** (1.9825 g), NaH (0.5029 g, 60 wt% in mineral oil, 12.6 mmol), and NFSI (3.2047 g, 10.2 mmol) in CH_2Cl_2 (40 mL) afforded **1ac** (0.6140 g, 25% from **S1a** to **1ac**) as an oil [eluent: petroleum ether/ethyl acetate = 15/1 (800 mL)]: ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 2 H, ArH), 7.48-7.31 (m, 7 H, ArH), 3.42-3.23 (m, 2 H, NCH_2), 2.53 (s, 3 H, CH_3), 2.41-2.31 (m, 1 H, CH), 2.05 (d, *J* = 2.0 Hz, 1 H, ≡CH), 2.04-1.94 (m, 1 H, one proton of CH_2), 1.91-1.80 (m, 1 H, one proton of CH_2), 1.67-1.59 (m, 1 H, one proton of CH_2), 1.58-1.19 (m, 11 H, one proton of CH_2 and CH_2 × 5), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 161.0, 137.5, 131.0, 130.22, 130.18, 129.8, 128.7, 128.4, 128.2, 114.1, 86.9, 69.8, 53.2 (d, *J* = 12.6 Hz), 34.8, 31.61, 31.59, 31.0, 29.0, 27.0, 24.0, 22.5, 14.0, 11.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.1; IR (neat) *v* (cm^{-1}) 3303, 2110, 1621, 1595, 1494, 1465, 1445; MS (ESI): *m/z* 519 [$(M + Na)^+$], 497 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{28}H_{34}FN_2O_3S$ [$(M + H)^+$]: 497.2269; Found: 497.2272.

2.30. Synthesis of *N*-fluoro-*N*-(5-hexylhept-6-ynyl)-4-methylbenzenesulfonamide **1ad**.

(zdj-6-191, zdj-6-199, zdj-6-200, zdj-7-001)



Following **Typical Procedure I**, the reaction of 4-pentynol (1.9 mL, d = 0.904

g/mL, 1.72 g, 20.4 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and ^{n}hexyl bromide (3.4 mL, d = 1.176 g/mL, 4.00 g, 24.2 mmol) in THF (60 mL) afforded **S1ad** (0.8511 g, 25%) as an oil [eluent: petroleum ether/ethyl acetate = 7/1 (720 mL)], which was used for the next step without further characterization.

Following **Typical Procedure II**, the reaction of PPh_3 (1.3821 g, 5.3 mmol), TsNHBoc (1.4305 g, 5.3 mmol), DEAD (0.83 mL, d = 1.106 g/mL, 0.918 g, 5.3 mmol), and **S1ad** (0.8511 g) in THF (10 + 5 mL) afforded **S2ad** (1.8934 g) as an oil [eluent: petroleum ether/ethyl acetate = 35/1 (360 mL) to 20/1 (210 mL)], which was used for the next step without further characterization.

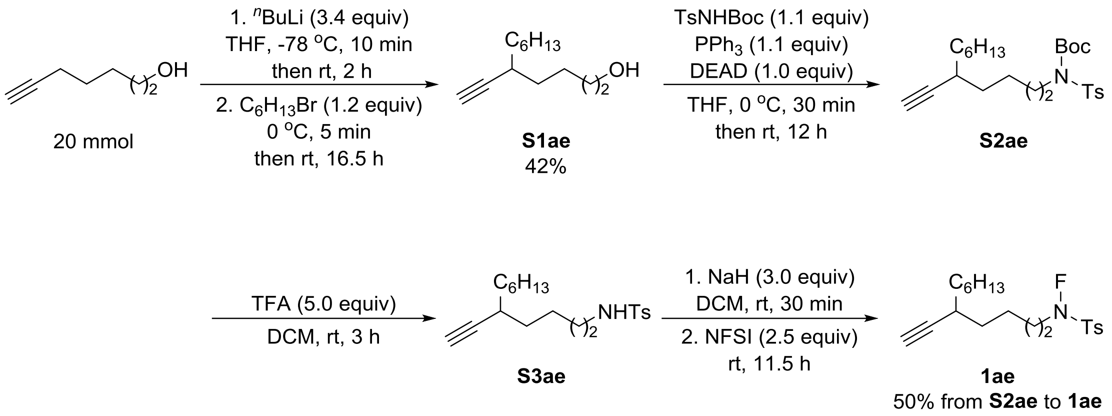
Following **Typical Procedure III**, the reaction of **S2ad** (1.8934 g) and TFA (1.7 mL, d = 1.489 g/mL, 2.53 g, 22.2 mmol) in CH_2Cl_2 (10 mL) afforded **S3ad** (1.4785 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3ad** (1.4785 g), NaH (0.5504 g, 60 wt% in mineral oil, 13.8 mmol), and NFSI (3.6450 g, 11.6 mmol) in CH_2Cl_2 (50 mL) afforded **1ad** (0.7106 g, 10% from 4-pentynol to **1ad**) as an oil [eluent: petroleum ether/ethyl acetate = 70/1 (497 mL) to 50/1 (255 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2 H, ArH), 7.41 (d, *J* = 8.1 Hz, 2 H, ArH), 3.58-3.25 (m, 2 H, NCH_2), 2.58-2.42 (m, 4 H, CH and CH_3), 2.08 (d, *J* = 2.4 Hz, 1 H, ≡CH), 1.98-1.71 (m, 2 H, CH_2), 1.57-1.17 (m, 10 H, $CH_2 \times 5$), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 129.9, 128.8, 85.9, 70.4, 51.8 (d, *J* = 12.5 Hz), 34.7, 31.6, 31.4, 28.9, 28.8, 26.9, 22.5, 21.6, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ -49.6; IR (neat) *ν* (cm^{-1}) 3306, 2113, 1597, 1456, 1378; MS (ESI): *m/z* 362 [$(M + Na)^+$], 357 [$(M + NH_4)^+$], 340

[(M + H)$^+$]; HRMS (ESI) Calcd for $C_{18}H_{26}FNNaO_2S$ [(M + Na)$^+$]: 362.1560; Found: 362.1562.

2.31. Synthesis of *N*-fluoro-*N*-(5-hexylhept-6-ynyl)-4-methylbenzenesulfonamide **1ae**.

(zdj-6-176, zdj-6-180, zdj-6-181, zdj-6-182)



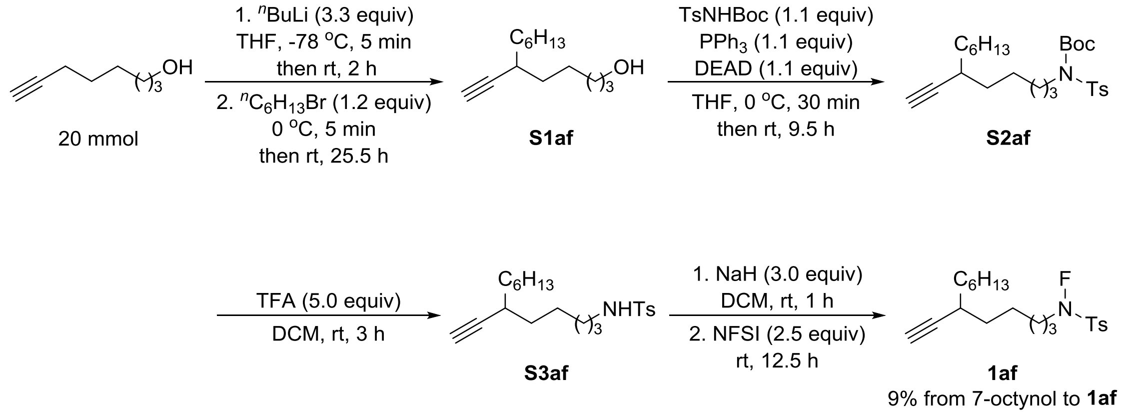
Following **Typical Procedure I**, the reaction of 6-heptynol (2.6 mL, d = 0.8469 g/mL, 2.20 g, 19.6 mmol), ^{n}BuLi (2.4 M in hexane, 27.5 mL, 66 mmol), and ^{n}hexyl bromide (3.4 mL, d = 1.176 g/mL, 4.00 g, 24.2 mmol) in THF (60 mL) afforded **S1ae** (1.6085 g, 42%) as an oil [eluent: petroleum ether/ethyl acetate = 8/1 (450 mL) to 7/1 (400 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (t, *J* = 6.5 Hz, 2 H, OCH_2), 2.41-2.25 (m, 1 H, CH), 2.05 (d, *J* = 2.4 Hz, 1 H, ≡CH), 1.68-1.18 (m, 17 H, $CH_2 \times 8$ and OH), 0.89 (t, *J* = 6.6 Hz, 3 H, CH_3). **S1ae** was used for the next step without further characterization.

Following **Typical Procedure II**, the reaction of PPh_3 (2.2795 g, 8.7 mmol), TsNHBoc (2.3390 g, 8.6 mmol), DEAD (1.34 mL, d = 1.106 g/mL, 1.482 g, 8.5 mmol), and **S1ae** (1.6085 g, 8.2 mmol) in THF (10 + 5 mL) afforded **S2ae** (3.5056 g) as an oil, [eluent: petroleum ether/ethyl acetate = 30/1 (620 mL)] which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2ae** (3.5056 g) and TFA (3.0 mL, d = 1.489 g/mL, 4.47 g, 39.2 mmol) in CH_2Cl_2 (10 mL) afforded **S3ae** (2.6053 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3ae** (2.6053 g), NaH (0.9141 g, 60 wt% in mineral oil, 22.8 mmol), and NFSI (5.9091 g, 18.7 mmol) in CH_2Cl_2 (75 mL) afforded **1ae** (1.5068 g, 50% from **S1ae** to **1ae**) as an oil [eluent: petroleum ether/ethyl acetate = 70/1 (497 mL) to 50/1 (408 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2 H, ArH), 7.41 (d, *J* = 7.8 Hz, 2 H, ArH), 3.28 (t, *J* = 6.8 Hz, 1 H, one proton of NCH_2), 3.15 (t, *J* = 6.9 Hz, 1 H, one proton of NCH_2), 2.48 (s, 3 H, CH_3), 2.38-2.23 (m, 1 H, CH), 2.03 (d, *J* = 2.4 Hz, 1 H, ≡CH), 1.82-1.16 (m, 16 H, CH_2 × 8), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 129.9, 128.8, 87.5, 69.3, 53.6 (d, *J* = 12.5 Hz), 34.8, 34.3, 31.7, 31.3, 29.0, 27.1, 26.1, 24.3, 22.5, 21.7, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.4; IR (neat) *v* (cm^{-1}) 3306, 2110, 1597, 1463, 1377; MS (ESI): *m/z* 390 [(M + Na)$^+$], 385 [(M + NH_4)$^+$]; HRMS (ESI) Calcd for $C_{20}H_{30}FNNaO_2S$ [(M + Na)$^+$]: 390.1873; Found: 390.1873.

2.32. Synthesis of *N*-fluoro-*N*-(6-hexyloct-7-ynyl)-4-methylbenzenesulfonamide **1af**. (zdj-7-025, zdj-7-027 zdj-7-029, zdj-7-030)



Following **Typical Procedure I**, the reaction of 7-octynol (2.8 mL, d = 0.889 g/mL, 2.49 g, 19.7 mmol), ^{n}BuLi (2.5 M in hexane, 26.5 mL, 66.3 mmol), and ^{n}hexyl bromide (3.4 mL, d = 1.176 g/mL, 4.00 g, 24.2 mmol) in THF (60 mL) afforded **S1af** (0.8346 g) as an oil [eluent: petroleum ether/ethyl acetate = 8/1 (900 mL)], which was used for the next step without further characterization.

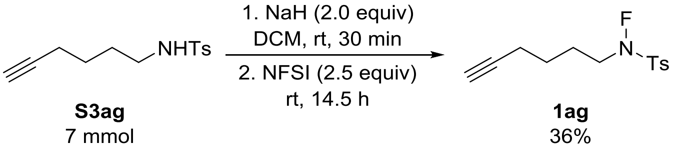
Following **Typical Procedure II**, the reaction of PPh$_3$ (1.1008 g, 4.2 mmol), TsNHBoc (1.1420 g, 4.2 mmol), DEAD (0.66 mL, d = 1.106 g/mL, 0.730 g, 4.2 mmol), and **S1af** (0.8346 g) in THF (10 + 5 mL) afforded **S2af** (1.5571 g) as an oil [eluent: petroleum ether/ethyl acetate = 30/1 (620 mL)], which was used for the next step without further characterization.

Following **Typical Procedure III**, the reaction of **S2af** (1.5571 g) and TFA (1.3 mL, d = 1.489 g/mL, 1.94 g, 17.0 mmol) in CH$_2$Cl$_2$ (10 mL) afforded **S3af** (1.1809 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3af** (1.1809 g), NaH (0.3902 g, 60 wt% in mineral oil, 9.8 mmol), and NFSI (2.5219 g, 8 mmol) in CH$_2$Cl$_2$ (30 mL) afforded **1af** (0.6795 g, 9% from 7-octynol to **1af)** as an oil [eluent: petroleum ether/ethyl acetate = 70/1 (355 mL) to 50/1 (255 mL)]: ^{1}H NMR (300 MHz, CDCl$_3$) δ

7.82 (d, *J* = 8.4 Hz, 2 H, ArH), 7.41 (d, *J* = 8.4 Hz, 2 H, ArH), 3.27 (t, *J* = 7.1 Hz, 1 H, one proton of NCH_2), 3.14 (t, *J* = 6.9 Hz, 1 H, one proton of NCH_2), 2.48 (s, 3 H, CH_3), 2.37-2.22 (m, 1 H, CH), 2.03 (d, *J* = 2.4 Hz, 1 H, ≡CH), 1.81-1.66 (m, 2 H, CH_2), 1.60-1.18 (m, 16 H, $CH_2 \times 8$), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 129.9, 128.8, 87.8, 69.1, 53.6 (d, *J* = 12.5 Hz), 34.9, 34.6, 31.7, 31.3, 29.1, 27.1, 26.7, 26.3, 26.1, 22.6, 21.7, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.5; IR (neat) *ν* (cm^{-1}) 3306, 2110, 1597, 1465, 1378; MS (ESI): *m/z* 404 [$(M + Na)^+$], 399 [$(M + NH_4)^+$]; HRMS (ESI) Calcd for $C_{21}H_{32}FNNaO_2S$ [$(M + Na)^+$]: 404.2030; Found: 404.2029.

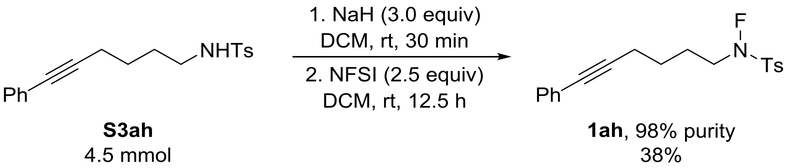
2.33. Synthesis of *N*-fluoro-*N*-(hex-5-ynyl)-4-methylbenzenesulfonamide **1ag**. (zdj-3-009)



To a 250 mL flame-dried three-neck flask was added **S3ag** (1.7572 g, 7.0 mmol). After degassing under vacuum and backfilling with nitrogen for three times, CH_2Cl_2 (90 mL) and NaH (0.5615 g, 60 wt% in mineral oil, 14.0 mmol) were added sequentially at room temperature under a N_2 atmosphere. The resulting mixture was stirred for 30 minutes followed by the addition of NFSI (5.5441 g, 17.6 mmol). The resulting mixture was stirred for 14.5 hours as monitored by TLC, quenched with a little H_2O slowly, diluted with H_2O (90 mL), and extracted with CH_2Cl_2 (90 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtrated, concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 30/1 (450 mL) to 25/1 (1000 mL) to 20/1 (200 mL)] to afford impure **1ag**, which was further purified by recrystallization from dichloromethane/petroleum ether at -20 °C to afford **1ag** (0.6859 g, 36%) as a soild (m.p. 53.5-53.7 °C, dichloromethane/petroleum ether): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2 H, ArH), 7.41 (d, *J* = 8.1 Hz, 2 H, ArH), 3.31 (t, *J* = 6.8 Hz, 1 H, one proton of NCH_2), 3.18 (t, *J* = 6.8 Hz, 1 H, one proton of NCH_2), 2.49 (s, 3 H, CH_3), 2.24 (td, J_1 = 6.9 Hz, J_2 = 2.4 Hz, 2 H, CH_2), 1.95 (t, *J* = 2.3 Hz, 1 H, ≡CH), 1.91-1.75 (m, 2 H, CH_2), 1.75-1.55 (m, 2 H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 129.9, 128.7, 83.5, 68.9, 53.1 (d, *J* = 12.7 Hz), 25.23, 25.20, 21.7, 17.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.4; IR (neat) *v* (cm^{-1}) 3295, 2116, 1596, 1493, 1457, 1429, 1374; MS (ESI): *m/z* 308 [(M + K)$^+$], 292 [(M + Na)$^+$]; Anal. Calcd. for $C_{13}H_{16}FNO_2S$ (%): C, 57.97; H, 5.99; N, 5.20; Found: C, 57.95; H, 6.00; N, 5.08.

2.34. Synthesis of *N*-fluoro-*N*-(6-phenylhex-5-ynyl)-4-methylbenzenesulfonamide **1ah**.

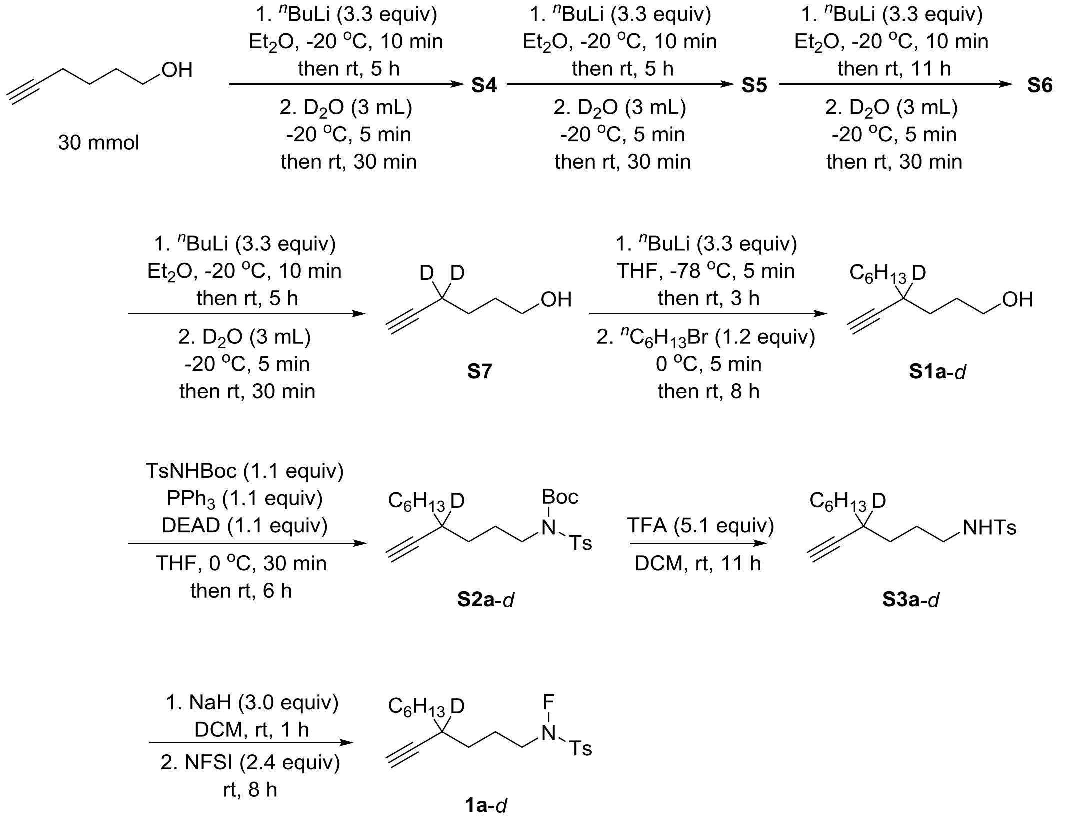
(zdj-7-054)



Following **Typical Procedure IV**, the reaction of **S3ah** (1.4798 g, 4.5 mmol), NaH (0.5425 g, 60 wt% in mineral oil, 13.6 mmol), and NFSI (3.5425 g, 11.2 mmol) in CH_2Cl_2 (50 mL) afforded **1ah** (0.6108 g, 38%, 98% purity) as an oil [eluent: petroleum ether/ethyl acetate = 18/1 (760 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2 H, ArH), 7.43-7.33 (m, 4 H, ArH), 7.32-7.22 (m, 3 H, ArH), 3.34 (t, *J* = 6.6 Hz, 1 H, one proton of NCH_2), 3.21 (t, *J* = 6.8 Hz, 1 H, one proton of NCH_2), 2.52-2.39 (m, 5 H,

CH_3 and CH_2), 1.98-1.82 (m, 2 H, CH_2), 1.80-1.65 (m, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 131.5, 129.9, 128.6, 128.1, 127.6, 123.7, 89.1, 81.2, 53.2 (d, *J* = 12.5 Hz), 25.5, 25.4, 21.7, 18.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.4; IR (neat) *v* (cm^{-1}) 2235, 1597, 1490, 1442, 1374; MS (ESI): *m/z* 368 [(M + Na)$^+$], 363 [(M + NH_4)$^+$], 346 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{19}H_{20}FNNaO_2S$ [(M + Na)$^+$]: 368.1091; Found: 368.1088.

2.35. Synthesis of *N*-fluoro-*N*-(4-hexylhex-5-ynyl-4-*d*)-4-methylbenzenesulfonamide **1a**-*d*. (zdj-7-031, zdj-7-035, zdj-7-036, zdj-7-037, zdj-7-040, zdj-7-041, zdj-7-044, zdj-7-045)



8% from 5-hexynol to **1a**-*d*, 96% D

To a 250 mL flame-dried three-neck flask were added 5-hexynol (3.2 mL, d = 0.91 g/mL, 2.91 g, 29.7 mmol) and Et_2O (90 mL) under a N_2 atmosphere. The resulting solution was cooled down to -20 °C and ^{n}BuLi (2.5 M in hexane, 40 mL, 100 mmol) was added dropwise at -20 °C within 10 minutes. The resulting mixture was stirred at room temperature for 5 hours and cooled down to -20 °C followed by the addition of D_2O (3 mL). After stirring at that temperature for 10 minutes, the cooling bath was removed. The resulting mixture was stirred at room temperature for 30 minutes, filtered through a short column of silica gel eluted with Et_2O (30 mL × 3). The filtrate was concentrated in vacuo to afford crude **S4** as an oil (2.3167 g).

To a 250 mL flame-dried three-neck flask were added crude **S4** (2.3167 g) and Et_2O (75 mL) under a N_2 atmosphere. The resulting solution was cooled down to -20 °C and ^{n}BuLi (2.5 M in hexane, 31 mL, 77.5 mmol) was added dropwise at -20 °C within 10 minutes. The resulting mixture was stirred at room temperature for 5 hours and cooled down to -20 °C followed by the addition of D_2O (3 mL). After stirring at that temperature for 5 minutes, the cooling bath was removed. The resulting mixture was stirred at room temperature for 30 minutes and diluted with 75 mL of H_2O. The organic phase was separated and the aqueous phase was extracted with Et_2O (75 mL × 2). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude residual was then filtered through a short column of silica gel eluted with Et_2O (20 mL × 3) and the filtrate was concentrated in vacuo to afford crude **S5** as an oil (1.9979 g).

To a 250 mL flame-dried three-neck flask were added crude **S5** (1.9979 g) and Et_2O (60 mL) under a N_2 atmosphere. The resulting solution was cooled down to -20 °C and ^{n}BuLi (2.5 M in hexane, 26.5 mL, 66.3 mmol) was added dropwise at -20 °C within 10 minutes. The resulting mixture was stirred at room temperature for 11 hours and cooled down to -20 °C followed by the addition of D_2O (3 mL). After stirring at that temperature for 10 minutes, the cooling bath was removed. The resulting mixture was stirred at room temperature for 30 minutes and diluted with 60 mL of H_2O. The organic phase was separated and the aqueous phase was extracted with Et_2O (60 mL × 2). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude residual was then filtered through a short column of silica gel eluted with Et_2O (20 mL × 3) and the filtrate was concentrated in vacuo to afford crude **S6** as an oil (1.7652 g).

To a 250 mL flame-dried three-neck flask were added crude **S6** (1.7652 g) and Et_2O (55 mL) under a N_2 atmosphere. The resulting solution was cooled down to -20 °C and ^{n}BuLi (2.5 M in hexane, 23.5 mL, 58.8 mmol) was added dropwise at -20 °C within 10 minutes. The resulting mixture was stirred at room temperature for 5 hours and cooled down to -20 °C followed by the addition of D_2O (3 mL). After stirring at that temperature for 5 minutes, the cooling bath was removed. The resulting mixture was stirred at room temperature for 30 minutes and diluted with 55 mL of H_2O. The organic phase was separated and the aqueous phase was extracted with Et_2O (55 mL × 2). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl ether = 2/1 (450 mL) to petroleum ether/ethyl ether = 1/1 (300 mL)] to afford **S7**, which was used for the next step without further characterization.

Following **Typical Procedure I**, the reaction of **S7** (1.2211 g), ^{n}BuLi (2.5 M in hexane, 16.0 mL, 40 mmol), and ^{n}hexyl bromide (2.0 mL, d = 1.176 g/mL, 2.35 g, 14.6 mmol) in THF (40 mL) afforded **S1a**-*d* (1.0245 g) as an oil [eluent: petroleum ether/ethyl acetate = 7/1 (800 mL)], which was used for the next step without further characterization.

Following **Typical Procedure II**, the reaction of PPh_3 (1.5559 g, 5.9 mmol), TsNHBoc (1.6015 g, 5.9 mmol), DEAD (0.93 mL, d = 1.106 g/mL, 1.029 g, 5.9 mmol), and **S1a**-*d* (1.0245 g) in THF (10 + 5 mL) afforded **S2a**-*d* (2.2229 g) as an oil [eluent: petroleum ether/ethyl acetate = 30/1 (620 mL)], which was used for the next step without further characterization.

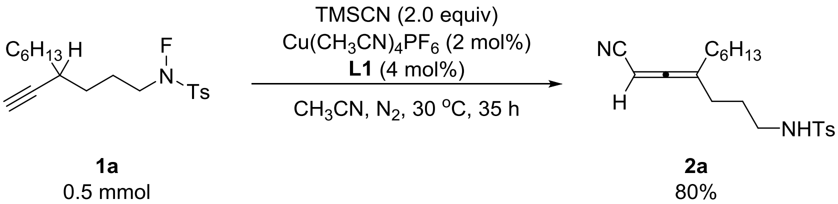
Following **Typical Procedure III**, the reaction of **S2a**-*d* (2.2229 g) and TFA (2.0 mL, d = 1.489 g/mL, 2.98 g, 26.1 mmol) in CH_2Cl_2 (10 mL) afforded **S3a**-*d* (1.7016 g) as an oil, which was used for the next step without further characterization.

Following **Typical Procedure IV**, the reaction of **S3a**-*d* (1.7016 g), NaH (0.6109 g, 60 wt% in mineral oil, 15.3 mmol), and NFSI (3.8517 g, 12.2 mmol) in CH_2Cl_2 (50 mL) afforded **1a**-*d* (0.8157 g, 8% from 5-hexynol to **1a**-*d*, 96% D) as an oil [eluent: petroleum ether/ethyl acetate = 70/1 (497 mL) to 50/1 (255 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2 H, ArH), 7.41 (d, *J* = 8.1 Hz, 2 H, ArH), 3.38-3.23 (m, 1 H, one proton of NCH_2), 3.23-3.09 (m, 1 H, one proton of NCH_2), 2.48 (s, 3 H, CH_3), 2.04 (s, 1 H, ≡CH), 2.04-1.72 (m, 2 H, CH_2), 1.68-1.17 (m, 12 H, $CH_2 \times 6$), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 129.9, 128.6, 87.0, 69.7, 53.5 (d, *J* = 12.5 Hz), 34.7, 31.6, 31.5, 30.6 (t, *J* = 19.5 Hz), 29.0, 27.0, 24.0, 22.5, 21.7, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -50.4; IR (neat) ν (cm^{-1}) 3307, 2110, 1597, 1456, 1377;

MS (ESI): *m/z* 377 [(M + Na)+], 372 [(M + NH_4)+], 355 [(M + H)+]; HRMS (ESI) Calcd for $C_{19}H_{27}DFNNaO_2S$ [(M + Na)+]: 377.1780; Found: 377.1776. The following signals are discernible for **1a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37-2.30 (m, 0.04 H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.9, 31.0.

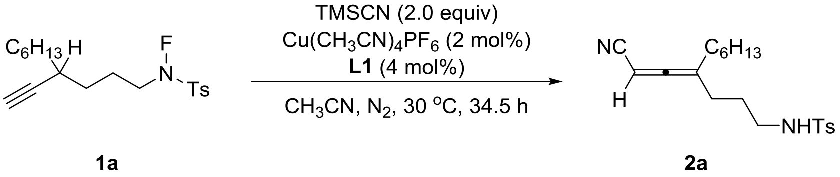
3. Copper-Catalyzed Propargylic C-H Functionalization

3.1. Synthesis of *N*-(6-cyano-4-hexylhexa-4,5-allenyl)-4-methylbenzenesulfonamide **2a**. (zdj-3-118, zdj-3-026-2)



Typical Procedure VI: To a 25 mL flame-dried Schlenk tube with a polytetrafluoroethylene plug was added **L1** (7.1 mg, 0.02 mmol). Then the Schlenk tube was taken to the glove box, $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol) and CH_3CN (2.5 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **1a** (177.0 mg, 0.5 mmol), CH_3CN (2.5 mL), and TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol). The Schlenk tube was taken out from the glove box. The resulting mixture was stirred at 30 °C for 35 hours as monitored by TLC, filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3), concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 9/2 (440 mL)] to afford **2a** (145.2 mg, 80%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2 H, ArH), 7.32 (d, *J* = 8.4 Hz, 2 H, ArH), 5.20-5.12 (m, 1 H, =CH), 5.03-4.91 (m, 1 H, NH), 2.95 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.44 (s, 3 H, CH_3), 2.13-1.94 (m, 4 H, CH_2 × 2), 1.67-1.55 (m, 2 H, CH_2), 1.47-1.18 (m, 8 H, CH_2 × 4), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 143.5, 136.8, 129.7, 127.0, 114.2, 110.7, 68.2, 42.4, 31.7, 31.4, 28.7, 28.4, 27.1, 26.8, 22.5, 21.4, 14.0; IR (neat) *v* (cm^{-1}) 3284, 2222, 1957, 1598, 1455, 1328; MS (EI): *m/z* (%) 360 (M$^+$, 34.63), 205 (100); HRMS (ESI) Calcd for $C_{20}H_{28}N_2NaO_2S$ [(M + Na)$^+$]: 383.1764; Found: 383.1765.

Gram-Scale Synthesis of **2a** (zdj-4-098)

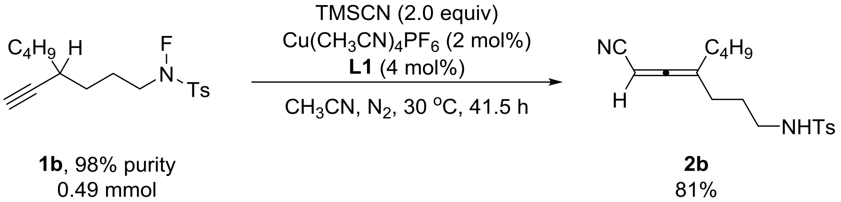


1a
4.0 mmol

2a
84%

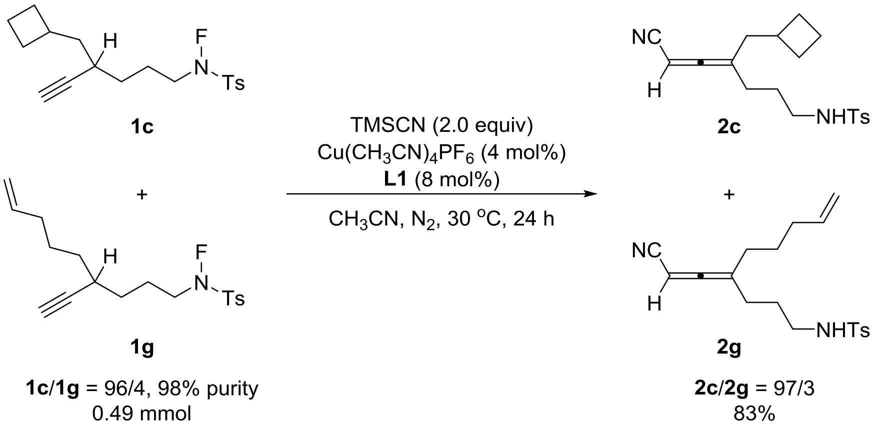
To a 100 mL flame-dried Schlenk tube with a polytetrafluoroethylene plug was added **L1** (58.4 mg, 0.16 mmol). Then the Schlenk tube was taken to the glove box, $Cu(CH_3CN)_4PF_6$ (30.1 mg, 0.08 mmol) and CH_3CN (20 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **1a** (1.4128 g, 4.0 mmol), CH_3CN (20 mL), and TMSCN (1.0 mL, d = 0.793 g/mL, 0.79 g, 8.0 mmol). The Schlenk tube was taken out from the glove box. The resulting mixture was stirred at 30 °C for 34.5 hours as monitored by TLC, filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3), concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 4/1 (450 mL)] to afford **2a** (1.2134 g, 84%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 2 H, ArH), 7.32 (d, *J* = 8.5 Hz, 2 H, ArH), 5.19-5.10 (m, 1 H, =CH), 4.85 (t, *J* = 6.3 Hz, 1 H, NH), 2.96 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.44 (s, 3 H, CH_3), 2.13-1.92 (m, 4 H, CH_2 × 2), 1.66-1.57 (m, 2 H, CH_2), 1.46-1.34 (m, 2 H, CH_2), 1.34-1.20 (m, 6 H, CH_2 × 3), 0.89 (t, *J* = 6.8 Hz, 3 H, CH_3).

3.2. Synthesis of *N*-(6-cyano-4-butylhexa-4,5-allenyl)-4-methylbenzenesulfonamide **2b**. (zdj-3-124)



Following **Typical Procedure VI**, the reaction of **1b** (162.9 mg, 98% purity, 0.49 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol), and **L1** (7.3 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2b** (131.9 mg, 81%) as an oil [eluent: petroleum ether/ethyl acetate = 4/1 (500 mL)]: ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2 H, ArH), 7.32 (d, *J* = 8.0 Hz, 2 H, ArH), 5.24-5.08 (m, 1 H, =CH), 4.99-4.82 (m, 1 H, NH), 2.95 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.44 (s, 3 H, CH_3), 2.13-1.93 (m, 4 H, CH_2 × 2), 1.68-1.54 (m, 2 H, CH_2), 1.47-1.20 (m, 4 H, CH_2 × 2), 0.90 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 143.5, 136.8, 129.7, 127.0, 114.2, 110.7, 68.2, 42.4, 31.4, 29.0, 28.4, 27.1, 22.1, 21.5, 13.7; IR (neat) *v* (cm^{-1}) 3281, 2223, 1958, 1599, 1454, 1327; MS (EI): *m/z* (%) 332 (M^+, 57.19), 177 (100); HRMS (ESI) Calcd for $C_{18}H_{24}N_2NaO_2S$ [$(M + Na)^+$]: 355.1451; Found: 355.1451.

3.3. Synthesis of *N*-(6-cyano-4-(cyclobutyl)methylhexa-4,5-allenyl)-4-methylbenzenesulfonamide **2c**. (hyk-1-199)

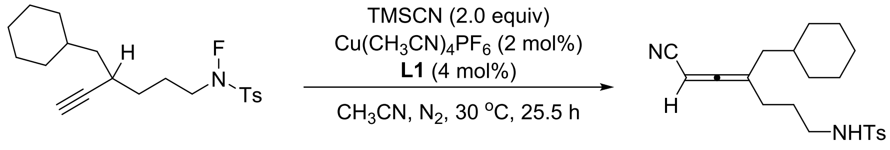


Following **Typical Procedure VI**, the reaction of **1c** (170.0 mg, **1c**/**1g** = 96/4, 98% purity, 0.49 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (7.4 mg, 0.02 mmol), and **L1** (14.3 mg, 0.04 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2c** (139.5 mg, 83%, **2c**/**2g** = 97/3 as determined by ^1H NMR analysis of the isolated product) as an oil [eluent: petroleum ether/ethyl acetate = 7/2 (540 mL)].

2c: ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2 H, ArH), 7.32 (d, *J* = 8.1 Hz, 2 H, ArH), 5.23-5.07 (m, 1 H, =CH), 5.07-4.92 (m, 1 H, NH), 2.94 (q, *J* = 6.6 Hz, 2 H, NCH_2), 2.55-2.27 (m, 4 H, CH_3 and CH), 2.18-1.74 (m, 8 H, $CH_2 \times 4$), 1.70-1.44 (m, 4 H, $CH_2 \times 2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.9, 143.5, 136.8, 129.7, 127.0, 114.1, 109.2, 68.0, 42.3, 38.9, 33.6, 28.5, 28.1, 27.1, 21.4, 18.2; IR (neat) *ν* (cm^{-1}) 3281, 2222, 1953, 1594, 1442, 1327; MS (EI): *m/z* (%) 344 (M^+, 100); HRMS (ESI) Calcd for $C_{19}H_{24}N_2NaO_2S$ [$(M + Na)^+$]: 367.1451; Found: 367.1452.

The following signals are discernible for **2g**: ^1H NMR (500 MHz, $CDCl_3$) δ 5.80-5.65 (m, 0.03 H, =CH).

3.4. Synthesis of *N*-(6-cyano-4-(cyclohexyl)methylhexa-4,5-allenyl)-4-methylbenzenesulfonamide **2d**. (zdj-3-154)

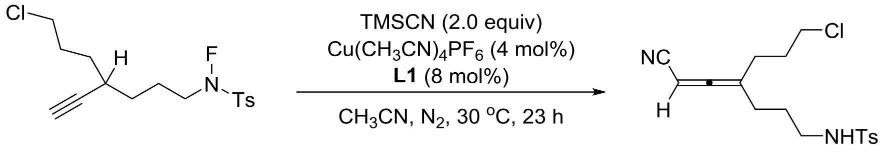


1d
0.5 mmol

2d
80%

Following **Typical Procedure VI**, the reaction of **1d** (183.0 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol), and **L1** (7.2 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2d** (149.6 mg, 80%) as an oil [eluent: petroleum ether/ethyl acetate = 9/2 (440 mL)]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2 H, ArH), 7.32 (d, J = 8.0 Hz, 2 H, ArH), 5.19-5.07 (m, 1 H, =CH), 5.05-4.89 (m, 1 H, NH), 2.95 (q, J = 6.7 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.12-1.95 (m, 2 H, CH_2), 1.89 (dd, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 2 H, CH_2), 1.75-1.53 (m, 7 H, $CH_2 \times 3$ and CH), 1.46-1.30 (m, 1 H, one proton of CH_2), 1.29-1.03 (m, 3 H, one proton CH_2 and CH_2), 0.95-0.76 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.0, 143.5, 136.8, 129.7, 127.0, 114.1, 108.8, 67.5, 42.4, 39.6, 35.5, 33.1, 33.0, 28.4, 27.1, 26.2, 25.9, 21.4; IR (neat) ν (cm^{-1}) 3279, 2223, 1957, 1599, 1449, 1327; MS (EI): *m/z* (%) 372 (M$^+$, 27.90), 289 (100); HRMS (ESI) Calcd for $C_{21}H_{28}N_2NaO_2S$ [(M + Na)$^+$]: 395.1764; Found: 395.1763.

3.5. Synthesis of *N*-(6-cyano-4-(3-chloropropyl)hexa-4,5-allenyl)-4-methylbenzenesulfonamide **2e**. (zdj-4-069)

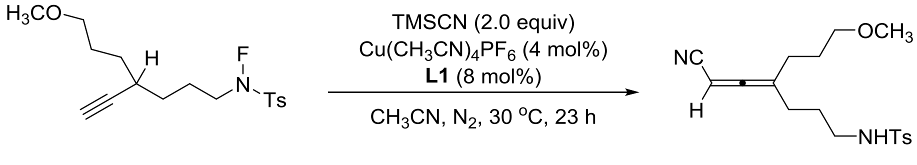


1e
0.5 mmol

2e
80%

Following **Typical Procedure VI**, the reaction of **1e** (172.9 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol), and **L1** (14.4 mg, 0.04 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2e** (140.4 mg, 80%) as an oil [eluent: petroleum ether/ethyl acetate = 5/2 (490 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2 H, ArH), 7.33 (d, *J* = 8.0 Hz, 2 H, ArH), 5.30-5.16 (m, 1 H, =CH), 5.05 (t, *J* = 6.3 Hz, 1 H, NH), 3.60-3.46 (m, 2 H, $ClCH_2$), 2.95 (q, *J* = 6.5 Hz, 2 H, NCH_2), 2.44 (s, 3 H, CH_3), 2.19 (td, J_1 = 7.3 Hz, J_2 = 3.0 Hz, 2 H, CH_2), 2.15-2.03 (m, 2 H, CH_2), 1.94-1.83 (m, 2 H, CH_2), 1.68-1.57 (m, 2 H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.3, 143.6, 136.7, 129.8, 127.0, 113.8, 109.7, 69.1, 43.8, 42.2, 29.6, 28.8, 28.5, 27.0, 21.4; IR (neat) *ν* (cm^{-1}) 3282, 2223, 1958, 1598, 1495, 1443, 1327; MS (EI): *m/z* (%) 354 [M(^{37}Cl)$^+$, 20.92], 352 [M(^{35}Cl)$^+$, 56.15], 197 (100); HRMS (ESI) Calcd for $C_{17}H_{21}{}^{35}ClN_2NaO_2S$ [(M(^{35}Cl) + Na)$^+$]: 375.0904; Found: 375.0906.

3.6. Synthesis of *N*-(6-cyano-4-(3-methoxypropyl)hexa-4,5-allenyl)-4-methylbenzenesulfonamide **2f**. (zdj-4-016)

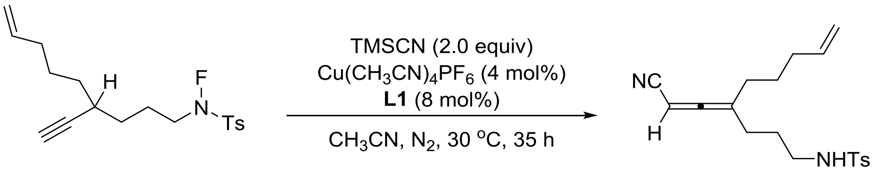


1f
0.5 mmol

2f
77%

Following **Typical Procedure VI**, the reaction of **1f** (171.9 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), Cu(CH_3CN)$_4$$PF_6$ (7.4 mg, 0.02 mmol), and **L1** (14.3 mg, 0.04 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2f** (135.5 mg, 77%) as an oil [eluent: petroleum ether/ethyl acetate = 5/2 (490 mL) to 2/1 (150 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2 H, ArH), 7.32 (d, *J* = 8.0 Hz, 2 H, ArH), 5.23-5.15 (m, 1 H, =CH), 5.05 (t, *J* = 6.3 Hz, 1 H, NH), 3.37 (t, *J* = 6.0 Hz, 2 H, OCH_2), 3.32 (s, 3 H, OCH_3), 2.95 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.16-2.00 (m, 4 H, CH_2 × 2), 1.75-1.54 (m, 4 H, CH_2 × 2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 143.5, 136.8, 129.7, 126.9, 114.0, 110.4, 71.4, 68.6, 58.5, 42.3, 28.5, 28.3, 27.0, 21.4; IR (neat) *v* (cm^{-1}) 3280, 2222, 1958, 1598, 1495, 1448, 1399, 1328; MS (EI): *m/z* (%) 348 (M$^+$, 7.38), 135 (100); HRMS (ESI) Calcd for $C_{18}H_{24}N_2NaO_3S$ [(M + Na)$^+$]: 371.1400; Found: 371.1403.

3.7. Synthesis of *N*-(6-cyano-4-(5-pentenyl)hexa-4,5-allenyl)-4-methylbenzenesulfonamide **2g**. (zdj-4-174)

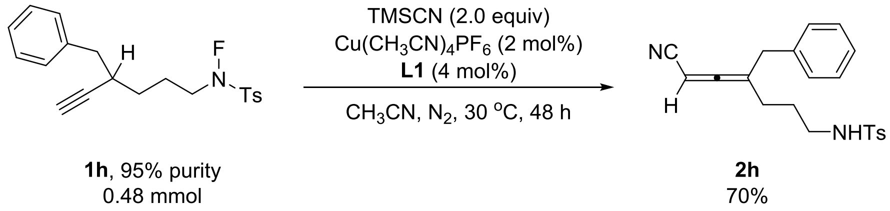


1g, 96% purity
0.5 mmol

2g
76%, 98% purity

Following **Typical Procedure VI**, the reaction of **1g** (175.3 mg, 96% purity, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), Cu(CH_3CN)$_4$$PF_6$ (7.6 mg, 0.02 mmol), and **L1** (14.5 mg, 0.04 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2g** (132.6 mg, 76%, 98% purity) as an oil [eluent: petroleum ether/ethyl acetate = 7/2 (360 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2 H, ArH), 7.32 (d, *J* = 8.1 Hz, 2 H, ArH), 5.85-5.66 (m, 1 H, =CH), 5.26-5.10 (m, 2 H, =CH and NH), 5.07-4.90 (m, 2 H, $=CH_2$), 2.94 (q, *J* = 6.6 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.17-1.93 (m, 6 H, $CH_2 \times 3$), 1.70-1.39 (m, 4 H, $CH_2 \times 2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 143.4, 137.6, 136.7, 129.7, 126.9, 115.2, 114.1, 110.4, 68.3, 42.3, 32.9, 30.9, 28.4, 26.9, 26.0, 21.4; IR (neat) *v* (cm^{-1}) 3281, 2222, 1957, 1640, 1598, 1495, 1439, 1327; MS (EI): *m/z* (%) 344 (M^+, 1.23), 91 (100); HRMS (ESI) Calcd for $C_{19}H_{24}N_2NaO_2S$ [$(M + Na)^+$]: 367.1451; Found: 367.1453.

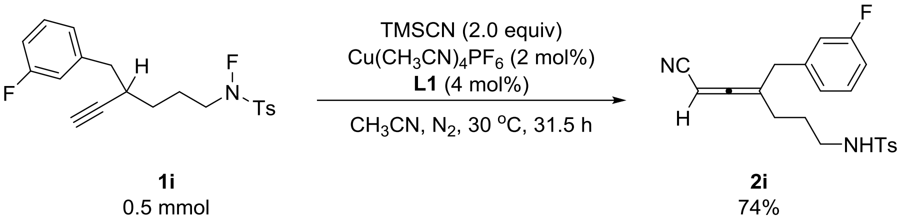
3.8. Synthesis of *N*-(6-cyano-4-benzylhexa-4,5-allenyl)-4-methylbenzenesulfonamide **2h**. (zdj-3-130)



Following **Typical Procedure VI**, the reaction of **1h** (180.2 mg, 95% purity, 0.48 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol), and **L1** (7.3 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2h** (122.8 mg, 70%) as an oil [eluent: petroleum ether/ethyl acetate = 4/1 (650 mL)]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2 H, ArH), 7.37-7.20 (m, 5 H, ArH), 7.18-7.09 (m, 2 H, ArH), 5.16-5.07 (m, 1 H, =CH), 4.70 (t, *J* = 6.2 Hz, 1 H, NH), 3.42-3.28 (m, 2 H, CH_2), 2.91 (q, *J* = 6.7 Hz, 2 H, CH_2), 2.43 (s, 3 H, CH_3), 2.05 (td, J_1 = 7.4 Hz, J_2 = 3.2 Hz, 2 H, CH_2), 1.65-1.52 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$)

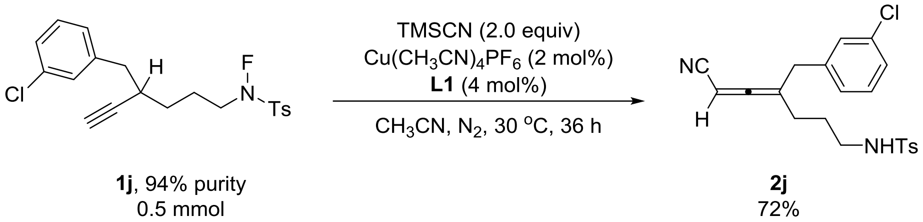
δ 213.3, 143.5, 136.8, 136.7, 129.8, 128.8, 128.6, 127.1, 127.0, 113.8, 110.4, 68.5, 42.3, 38.6, 27.8, 27.1, 21.5; IR (neat) *v* (cm^{-1}) 3281, 2223, 1960, 1599, 1495, 1454, 1326; MS (EI): *m/z* (%) 366 (M$^+$, 75.31), 91 (100); HRMS (ESI) Calcd for $C_{21}H_{22}N_2NaO_2S$ [(M + Na)$^+$]: 389.1294; Found: 389.1294.

3.9. Synthesis of *N*-(6-cyano-4-(3-fluorobenzyl)hexa-4,5-allenyl)-4-methylbenzenesulfonamide **2i**. (zdj-3-159)



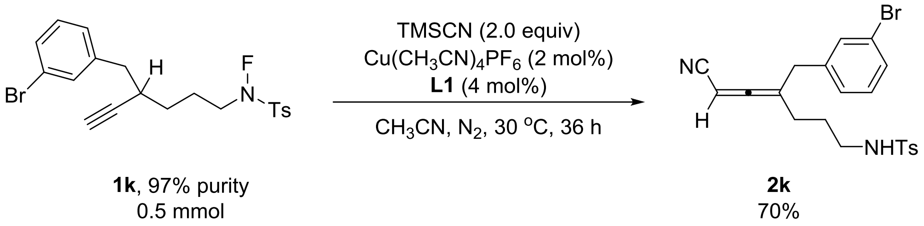
Following **Typical Procedure VI**, the reaction of **1i** (188.8 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.8 mg, 0.01 mmol), and **L1** (7.2 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2i** (142.6 mg, 74%) as an oil [eluent: petroleum ether/ethyl acetate = 5/2 (420 mL)]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2 H, ArH), 7.38-7.21 (m, 3 H, ArH), 7.01-6.88 (m, 2 H, ArH), 6.87-6.80 (m, 1 H, ArH), 5.19-5.11 (m, 1 H, =CH), 5.11-4.98 (m, 1 H, NH), 3.38-3.26 (m, 2 H, CH_2), 2.92 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.13-1.97 (m, 2 H, CH_2), 1.68-1.54 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1, 162.7 (d, *J* = 244.7 Hz), 143.5, 139.2 (d, *J* = 7.2 Hz), 136.7, 130.1 (d, *J* = 8.2 Hz), 129.7, 126.9, 124.5 (d, *J* = 3.6 Hz), 115.6 (d, *J* = 20.7 Hz), 113.9 (d, *J* = 20.8 Hz), 113.6, 110.0, 68.8, 42.2, 38.1, 27.8, 26.9, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2; IR (neat) *v* (cm^{-1}) 3279, 2224, 1961, 1616, 1590, 1488, 1449, 1327; MS (EI): *m/z* (%) 384 (M$^+$, 100); HRMS (ESI) Calcd for $C_{21}H_{21}FN_2NaO_2S$ [(M + Na)$^+$]: 407.1200; Found: 407.1198.

3.10. Synthesis of *N*-(6-cyano-4-(3-chlorobenzyl)hexa-4,5-allenyl)-4-methylbenzenesulfonamide . (zdj-4-001)



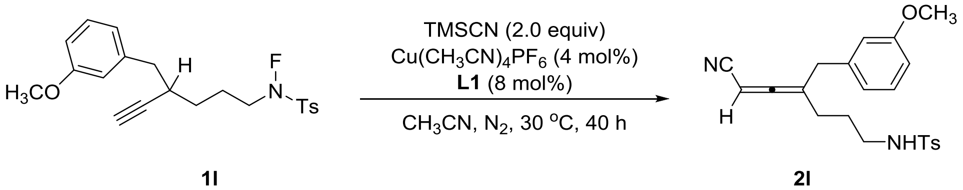
Following **Typical Procedure VI**, the reaction of **1j** (207.9 mg, 94% purity, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol), and **L1** (7.4 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2j** (143.1 mg, 72%) as an oil [eluent: petroleum ether/ethyl acetate = 3/1 (500 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2 H, ArH), 7.32 (d, *J* = 8.0 Hz, 2 H, ArH), 7.27-7.21 (m, 2 H, ArH), 7.12 (s, 1 H, ArH), 7.07-7.01 (m, 1 H, ArH), 5.18-5.12 (m, 1 H, =CH), 4.87 (t, *J* = 6.3 Hz, 1 H, NH), 3.37-3.25 (m, 2 H, CH_2), 2.93 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.11-1.99 (m, 2 H, CH_2), 1.66-1.55 (m, 2 H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.2, 143.6, 138.7, 136.7, 134.3, 129.9, 129.8, 128.9, 127.3, 127.02, 126.99, 113.6, 110.0, 68.9, 42.2, 38.1, 27.8, 27.0, 21.5; IR (neat) *ν* (cm^{-1}) 3282, 2223, 1960, 1597, 1574, 1475, 1431, 1327; MS (EI): *m/z* (%) 402 [M(^{37}Cl)$^+$, 39.40], 400 [M(^{35}Cl)$^+$, 100]; HRMS (ESI) Calcd for $C_{21}H_{21}{}^{35}ClN_2NaO_2S$ ([M(^{35}Cl) + Na]$^+$): 423.0904; Found: 423.0905.

3.11. Synthesis of *N*-(6-cyano-4-(3-bromobenzyl)hexa-4,5-allenyl)-4-methylbenzenesulfonamide **2k**. (zdj-4-053)



Following **Typical Procedure VI**, the reaction of **1k** (225.7 mg, 97% purity, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.8 mg, 0.01 mmol), and **L1** (7.4 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2k** (154.6 mg, 70%) as an oil [eluent: petroleum ether/ethyl acetate = 3/1 (400 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.5 Hz, 2 H, ArH), 7.38 (d, *J* = 8.0 Hz, 1 H, ArH), 7.34-7.25 (m, 3 H, ArH), 7.18 (t, *J* = 7.8 Hz, 1 H, ArH), 7.08 (d, *J* = 7.5 Hz, 1 H, ArH), 5.19-5.12 (m, 1 H, =CH), 4.94 (t, *J* = 6.3 Hz, 1 H, NH), 3.36-3.24 (m, 2 H, CH_2), 2.93 (q, *J* = 6.5 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.12-1.97 (m, 2 H, CH_2), 1.68-1.54 (m, 2 H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.1, 143.6, 139.0, 136.7, 131.8, 130.2, 129.8, 127.5, 127.0, 122.5, 113.5, 110.0, 68.9, 42.2, 38.1, 27.8, 27.0, 21.5; IR (neat) *v* (cm^{-1}) 3279, 2224, 1960, 1597, 1568, 1495, 1473, 1427, 1326; MS (EI): *m/z* (%) 446 [M(^{81}Br)$^+$, 100], 444 [M(^{79}Br)$^+$, 91.42]; HRMS (ESI) Calcd for $C_{21}H_{21}{}^{79}BrN_2NaO_2S$ ([M(^{79}Br) + Na]$^+$): 467.0399; Found: 467.0400.

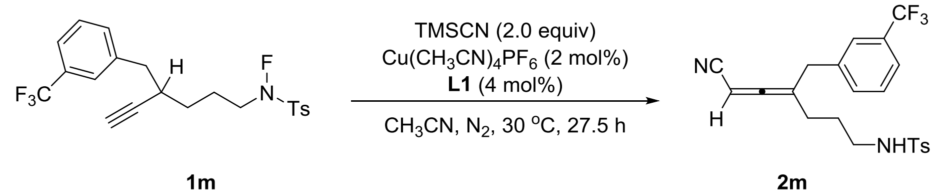
3.12. Synthesis of *N*-(6-cyano-4-(3-methoxybenzyl)hexa-4,5-allenyl)-4-methylbenzenesulfonamide **2l**. (zdj-3-195, zdj-3-182)


1l
0.5 mmol

2l
71%

Following **Typical Procedure VI**, the reaction of **1l** (194.7 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (7.3 mg, 0.02 mmol), and **L1** (14.2 mg, 0.04 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2l** (140.6 mg, 71%) as an oil [eluent: petroleum ether/ethyl acetate = 3/1 (600 mL)]: ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2 H, ArH), 7.31 (d, *J* = 8.0 Hz, 2 H, ArH), 7.21 (t, *J* = 8.0 Hz, 1 H, ArH), 6.79 (dd, J_1 = 8.3 Hz, J_2 = 2.3 Hz, 1 H, ArH), 6.72 (d, *J* = 7.5 Hz, 1 H, ArH), 6.70-6.65 (m, 1 H, ArH), 5.18-5.08 (m, 1 H, =CH), 4.76 (t, *J* = 6.3 Hz, 1 H, NH), 3.80 (s, 3 H, OCH_3), 3.36-3.26 (m, 2 H, CH_2), 2.91 (q, *J* = 6.8 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.11-1.99 (m, 2 H, CH_2), 1.66-1.53 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.2, 159.7, 143.5, 138.2, 136.7, 129.7, 129.6, 127.0, 121.1, 114.4, 113.8, 112.5, 110.2, 68.4, 55.1, 42.2, 38.5, 27.8, 27.0, 21.4; IR (neat) *v* (cm^{-1}) 3281, 2223, 1959, 1599, 1585, 1490, 1454, 1437, 1326; MS (EI): *m/z* (%) 396 (M^+, 100); HRMS (ESI) Calcd for $C_{22}H_{24}N_2NaO_3S$ [$(M + Na)^+$]: 419.1400; Found: 419.1402.

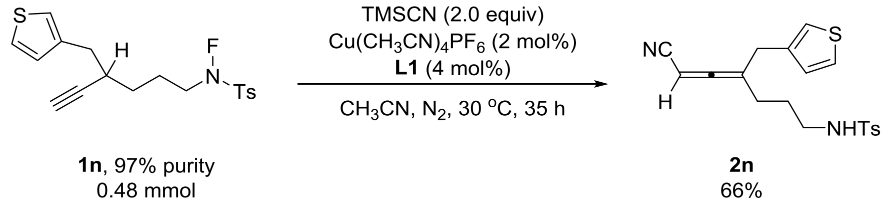
3.13. Synthesis of *N*-(6-cyano-4-(3-trifluoromethylbenzyl)hexa-4,5-allenyl)-4-methylbenzenesulfonamide **2m**. (zdj-4-023)


1m
0.5 mmol

2m
67%

Following **Typical Procedure VI**, the reaction of **1m** (213.7 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.8 mg, 0.01 mmol), and **L1** (7.3 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2m** (146.2 mg, 67%) as an oil [eluent: petroleum ether/ethyl acetate = 3/1 (600 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2 H, ArH), 7.52 (d, *J* = 8.0 Hz, 1 H, ArH), 7.44 (t, *J* = 7.8 Hz, 1 H, ArH), 7.39 (s, 1 H, ArH), 7.37-7.27 (m, 3 H, ArH), 5.16-5.10 (m, 1 H, =CH), 4.90 (t, *J* = 6.3 Hz, 1 H, NH), 3.47-3.34 (m, 2 H, CH_2), 2.94 (q, *J* = 6.5 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.16-2.03 (m, 2 H, CH_2), 1.68-1.57 (m, 2 H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.2, 143.6, 137.7, 136.7, 132.2, 130.9 (q, *J* = 31.8 Hz), 129.8, 129.1, 127.0, 125.5 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 270.8 Hz), 113.4, 110.2, 69.3, 42.2, 38.3, 28.0, 27.0, 21.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.1; IR (neat) *v* (cm^{-1}) 3280, 2225, 1961, 1598, 1495, 1451, 1333; MS (EI): *m/z* (%) 434 (M^+, 100); HRMS (ESI) Calcd for $C_{22}H_{22}F_3N_2O_2S$ [$(M + H)^+$]: 435.1349; Found: 435.1349.

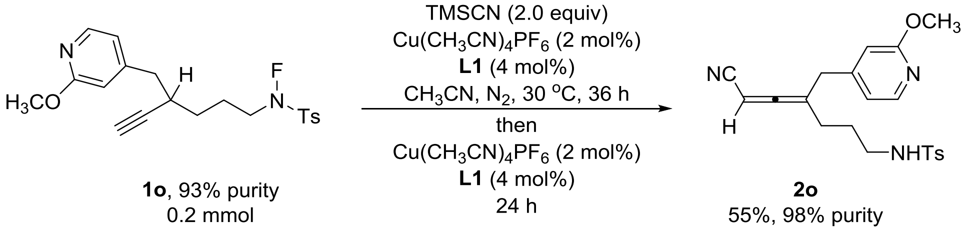
3.14. Synthesis of *N*-(6-cyano-4-(thien-3-ylmethyl)hexa-4,5-allenyl)-4-methylbenzenesulfonamide **2n**. (zdj-7-013)



Following **Typical Procedure VI**, the reaction of **1n** (181.9 mg, 97% purity, 0.48 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.8 mg, 0.01 mmol), and **L1** (7.2 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2n**

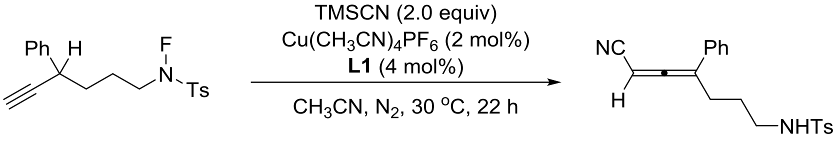
(119.2 mg, 66%) as an oil [eluent: petroleum ether/ethyl acetate = 3/1 (400 mL) to 5/2 (280 mL)]: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.74 (d, *J* = 8.4 Hz, 2 H, ArH), 7.31 (d, *J* = 8.1 Hz, 2 H, ArH), 7.27 (dd, J_1 = 5.0 Hz, J_2 = 2.9 Hz, 1 H, ArH), 7.02-6.98 (m, 1 H, ArH), 6.89 (dd, J_1 = 5.0 Hz, J_2 = 1.4 Hz, 1 H, ArH), 5.17-5.10 (m, 1 H, =CH), 4.95 (t, *J* = 6.3 Hz, 1 H, NH), 3.37 (d, *J* = 2.4 Hz, 2 H, CH$_2$), 2.92 (q, *J* = 6.7 Hz, 2 H, NCH$_2$), 2.43 (s, 3 H, CH$_3$), 2.07 (td, J_1 = 7.4 Hz, J_2 = 3.1 Hz, 2 H, CH$_2$), 1.67-1.53 (m, 2 H, CH$_2$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 213.1, 143.4, 136.8, 136.6, 129.7, 128.0, 126.9, 126.0, 122.3, 113.8, 110.0, 68.5, 42.2, 32.9, 27.8, 26.9, 21.4; IR (neat) *v* (cm^{-1}) 3281, 2223, 1960, 1598, 1433, 1326; MS (EI): *m/z* (%) 372 (M$^+$, 29.66), 97 (100); HRMS (ESI) Calcd for $C_{19}H_{20}N_2NaO_2S_2$ [(M + Na)$^+$]: 395.0858; Found: 395.0861.

3.15. Synthesis of *N*-(6-cyano-4-((2-methoxypyridin-4-yl)methyl)hexa-4,5-allenyl)-4-methylbenzenesulfonamide **2o**. (zdj-6-190)



To a 25 mL flame-dried Schlenk tube with a polytetrafluoroethylene plug was added **L1** (2.9 mg, 0.008 mmol). Then the Schlenk tube was taken into a glove box. Cu(CH$_3$CN)$_4$PF$_6$ (1.5 mg, 0.004 mmol) and CH$_3$CN (1 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **1o** (83.6 mg, 93% purity, 0.2 mmol), CH$_3$CN (1 mL), and TMSCN (50 μL, d = 0.793 g/mL, 39.7 mg, 0.4 mmol). The Schlenk tube was taken out from the glove box and resulting mixture was stirred at 30 °C. After stirring for 36 hours, the tube was taken into the glove box, $Cu(CH_3CN)_4PF_6$ (1.5 mg, 0.004 mmol) and **L1** (2.9 mg, 0.008 mmol) were added. The resulting mixture was stirred at 30 °C for 24 hours as monitored by TLC, filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3), concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 3/2 (400 mL)] to afford impure **2o** (48.1 mg) as an oil, which was further purified by chromatography on silica gel [eluent: petroleum ether/acetone = 5/2 (420 mL)] to afford **2o** (44.8 mg, 55%, 98% purity) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, J_1 = 5.1 Hz, J_2 = 0.6 Hz, 1 H, ArH), 7.77-7.68 (m, 2 H, ArH), 7.35-7.27 (m, 2 H, ArH), 6.67 (dd, J_1 = 5.3 Hz, J_2 = 1.4 Hz, 1 H, ArH), 6.54-6.50 (m, 1 H, ArH), 5.21-5.15 (m, 1 H, =CH), 4.90 (t, J = 6.3 Hz, 1 H, NH), 3.93 (s, 3 H, OCH_3), 3.36-3.20 (m, 2 H, CH_2), 2.94 (q, J = 6.6 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.07 (td, J_1 = 7.6 Hz, J_2 = 3.2 Hz, 2 H, CH_2), 1.67-1.55 (m, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.1, 164.5, 148.4, 147.1, 143.5, 136.8, 129.7, 127.0, 117.3, 113.4, 110.7, 109.0, 69.1, 53.4, 42.2, 37.6, 28.0, 27.0, 21.4; IR (neat) v (cm^{-1}) 3281, 2224, 1961, 1612, 1561, 1450, 1398; MS (EI): m/z (%) 397 (M^+, 49.92), 242 (100); HRMS (ESI) Calcd for $C_{21}H_{23}N_3NaO_3S$ [$(M + Na)^+$]: 420.1352; Found: 420.1353.

3.16. Synthesis of *N*-(6-cyano-4-phenylhexa-4,5-allenyl)-4-methylbenzenesulfonamide **2p**. (zdj-7-009)

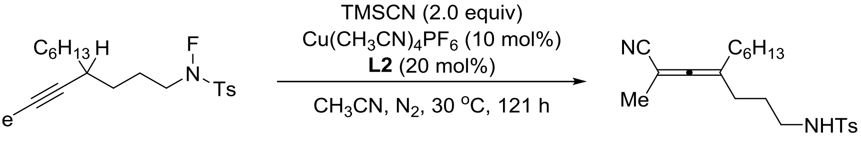


1p 0.5 mmol

2p 83%

Following **Typical Procedure VI**, the reaction of **1p** (172.9 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), Cu(CH_3CN)$_4$$PF_6$ (3.7 mg, 0.01 mmol), and **L1** (7.1 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2p** (147.0 mg, 83%) as an oil [eluent: petroleum ether/ethyl acetate = 5/2 (490 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2 H, ArH), 7.40-7.20 (m, 7 H, ArH), 5.54 (t, *J* = 3.2 Hz, 1 H, =CH), 5.15-5.00 (m, 1 H, NH), 3.02 (q, *J* = 6.6 Hz, 2 H, NCH_2), 2.54 (td, J_1 = 7.5 Hz, J_2 = 3.2 Hz, 2 H, CH_2), 2.40 (s, 3 H, CH_3), 1.82-1.64 (m, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.2, 143.5, 136.7, 131.9, 129.8, 128.9, 128.8, 127.0, 126.6, 113.1, 111.6, 70.6, 42.4, 27.3, 26.6, 21.4; IR (neat) *v* (cm^{-1}) 3281, 2224, 1945, 1598, 1495, 1450, 1326; MS (EI): *m/z* (%) 352 (M$^+$, 14.91), 131 (100); HRMS (ESI) Calcd for $C_{20}H_{21}N_2O_2S$ [(M + H)$^+$]: 353.1318; Found: 353.1318.

3.17. Synthesis of *N*-(6-cyano-4-hexylhepta-4,5-allenyl)-4-methylbenzenesulfonamide **2q**. (zdj-4-187, zdj-4-035)



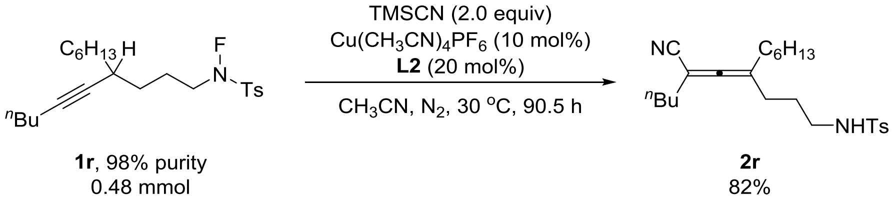
1q 0.5 mmol

2q 66%

Following **Typical Procedure VI**, the reaction of **1q** (183.5 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), Cu(CH_3CN)$_4$$PF_6$ (18.8 mg, 0.05 mmol), and **L2** (18.0 mg, 0.1 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2q** (122.8

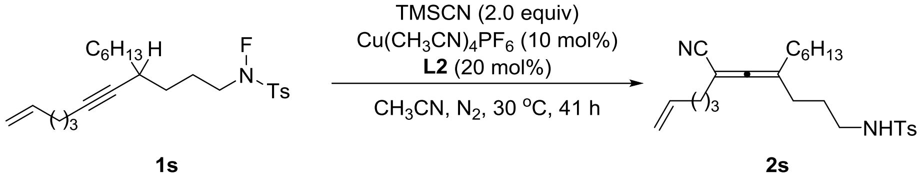
mg, 66%) as an oil [eluent: petroleum ether/ethyl acetate = 5/1 (480 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 2 H, ArH), 7.32 (d, *J* = 8.0 Hz, 2 H, ArH), 5.16 (t, *J* = 6.0 Hz, 1 H, NH), 2.94 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.02 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.96 (t, *J* = 7.0 Hz, 2 H, CH_2), 1.83 (s, 3 H, CH_3), 1.65-1.53 (m, 2 H, CH_2), 1.44-1.17 (m, 8 H, CH_2 × 4), 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.0, 143.3, 136.8, 129.6, 126.9, 116.8, 109.9, 77.8, 42.4, 32.1, 31.4, 28.9, 28.6, 27.1, 26.9, 22.4, 21.4, 17.6, 13.9; IR (neat) *ν* (cm^{-1}) 3281, 2216, 1954, 1599, 1495, 1439, 1328; MS (EI): *m/z* (%) 374 (M^+, 1.76), 219 (100); HRMS (ESI) Calcd for $C_{21}H_{30}N_2NaO_2S$ [$(M + Na)^+$]: 397.1920; Found: 397.1922.

3.18. Synthesis of *N*-(6-cyano-4-hexyldeca-4,5-allenyl)-4-methylbenzenesulfonamide **2r**. (zdj-4-183)



Following **Typical Procedure VI**, the reaction of **1r** (208.7 mg, 98% purity, 0.48 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (18.6 mg, 0.05 mmol), and **L2** (18.1 mg, 0.1 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2r** (170.6 mg, 82%) as an oil [eluent: petroleum ether/ethyl acetate = 11/2 (390 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2 H, ArH), 7.32 (d, *J* = 8.0 Hz, 2 H, ArH), 5.25-5.04 (m, 1 H, NH), 2.94 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.17-1.87 (m, 6 H, CH_2 × 3), 1.66-1.52 (m, 2 H, CH_2), 1.51-1.16 (m, 12 H, CH_2 × 6), 0.99-0.80 (m, 6 H, CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.2, 143.3, 136.8, 129.6, 126.9, 116.4, 110.3, 83.1, 42.4, 32.2, 31.4, 31.2, 29.8, 29.0, 28.7, 27.2, 27.0, 22.4, 21.7, 21.4, 13.9, 13.6; IR (neat) *v* (cm^{-1}) 3281, 2215, 1952, 1599, 1495, 1456; MS (EI): *m/z* (%) 416 (M$^+$, 1.21), 261 (100); HRMS (ESI) Calcd for $C_{24}H_{36}N_2NaO_2S$ [(M + Na)$^+$]: 439.2390; Found: 439.2392.

3.19. Synthesis of *N*-(6-cyano-4-hexylundeca-4,5,10-trienyl)-4-methylbenzenesulfonamide **2s**. (zdj-4-199)

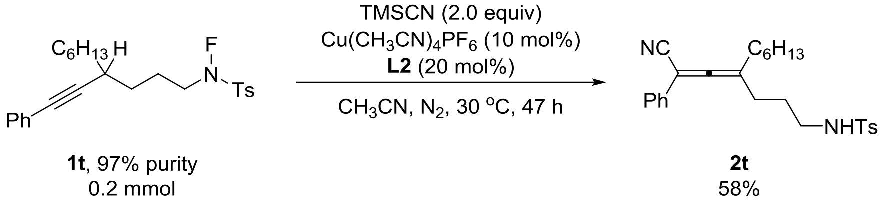


1s
0.2 mmol

2s
79%

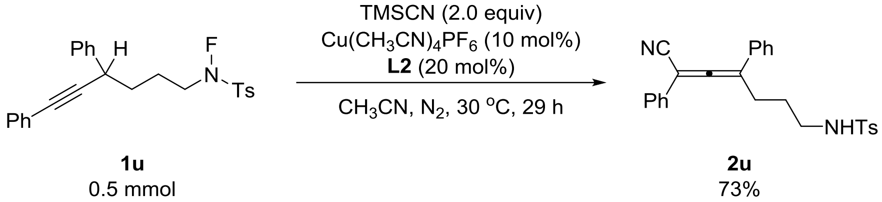
Following **Typical Procedure VI**, the reaction of **1s** (85.3 mg, 0.2 mmol), TMSCN (50 μL, d = 0.793 g/mL, 39.7 mg, 0.4 mmol), $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol), and **L2** (7.2 mg, 0.04 mmol) in CH_3CN (1 + 1 mL) afforded **2s** (68.6 mg, 79%) as an oil [eluent: petroleum ether/ethyl acetate = 6/1 (420 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2 H, ArH), 7.32 (d, *J* = 8.0 Hz, 2 H, ArH), 5.84-5.69 (m, 1 H, =CH), 5.10-4.93 (m, 2 H, =CH_2), 4.88-4.75 (m, 1 H, NH), 2.95 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.21-1.93 (m, 8 H, CH_2 × 4), 1.65-1.51 (m, 4 H, CH_2 × 2), 1.44-1.19 (m, 8 H, CH_2 × 4), 0.89 (t, *J* = 7.0 Hz, 3 H, CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 143.4, 137.5, 136.8, 129.7, 127.0, 116.3, 115.3, 110.6, 82.9, 42.5, 32.6, 32.2, 31.5, 30.9, 29.0, 28.7, 27.3, 27.04, 26.95, 22.5, 21.4, 13.9; IR (neat) *v* (cm^{-1}) 3282, 2214, 1951, 1641, 1599, 1495; MS (EI): *m/z* (%) 428 (M$^+$, 15.55), 133 (100); HRMS (ESI) Calcd for $C_{25}H_{36}N_2NaO_2S$ [(M + Na)$^+$]: 451.2390; Found: 451.2392.

3.20. Synthesis of *N*-(6-cyano-4-hexyl-6-phenylhexa-4,5-allenyl)-4-methylbenzenesulfonamide **2t**. (zdj-6-175)



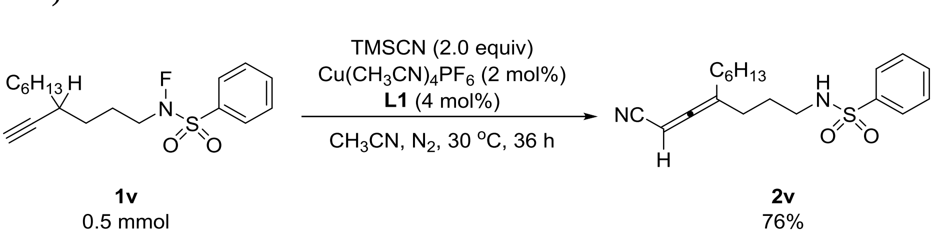
Following **Typical Procedure VI**, the reaction of **1t** (85.8 mg, 97% purity, 0.2 mmol), TMSCN (50 μL, d = 0.793 g/mL, 39.7 mg, 0.4 mmol), $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol), and **L2** (7.1 mg, 0.04 mmol) in CH_3CN (1 + 1 mL) afforded **2t** (49.2 mg, 58%) as an oil [eluent: petroleum ether/ethyl acetate = 4/1 (400 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2 H, ArH), 7.46-7.20 (m, 7 H, ArH), 4.84 (t, *J* = 6.3 Hz, 1 H, NH), 2.96 (q, *J* = 6.6 Hz, 2 H, NCH_2), 2.40 (s, 3 H, CH_3), 2.32-2.10 (m, 4 H, CH_2 × 2), 1.72-1.59 (m, 2 H, CH_2), 1.53-1.38 (m, 2 H, CH_2), 1.38-1.16 (m, 6 H, CH_2 × 3), 0.85 (t, *J* = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.4, 143.4, 136.7, 130.2, 129.7, 128.9, 128.4, 126.9, 125.3, 114.9, 114.6, 87.4, 42.5, 32.6, 31.4, 29.3, 28.8, 27.3, 27.1, 22.5, 21.4, 13.9; IR (neat) *v* (cm^{-1}) 3282, 2219, 1937, 1598, 1495, 1453, 1328; MS (EI): *m/z* (%) 436 (M$^+$, 14.16), 281 (100); HRMS (ESI) Calcd for $C_{26}H_{32}N_2NaO_2S$ [(M + Na)$^+$]: 459.2077; Found: 459.2077.

3.21. Synthesis of *N*-(6-cyano-4,6-diphenylhexa-4,5-allenyl)-4-methylbenzenesulfonamide **2u**. (zdj-7-026)



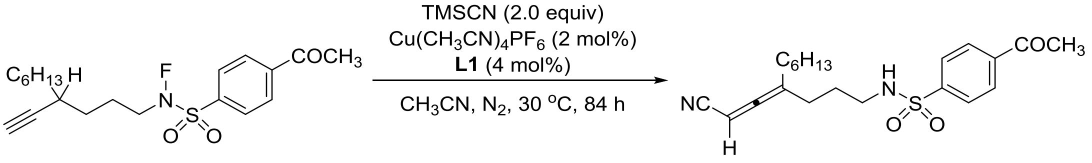
Following **Typical Procedure VI**, the reaction of **1u** (212.0 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (18.5 mg, 0.05 mmol), and **L2** (18.1 mg, 0.1 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2u** (156.7 mg, 73%) as an oil [eluent: petroleum ether/ethyl acetate = 5/2 (420 mL)]: ^1H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2 H, ArH), 7.51-7.43 (m, 2 H, ArH), 7.43-7.28 (m, 8 H, ArH), 7.24 (d, *J* = 7.8 Hz, 2 H, ArH), 4.97-4.80 (m, 1 H, NH), 3.04 (q, *J* = 6.6 Hz, 2 H, NCH_2), 2.80-2.61 (m, 2 H, CH_2), 2.38 (s, 3 H, CH_3), 1.88-1.63 (m, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.8, 143.4, 136.6, 132.1, 129.6, 129.3, 129.1, 128.91, 128.88, 126.9, 126.6, 125.5, 115.4, 113.7, 89.5, 42.5, 27.3, 27.2, 21.4; IR (neat) *v* (cm^{-1}) 3281, 2220, 1924, 1598, 1494, 1447, 1327; MS (ESI): 451 [$(M + Na)^+$], 446 [$(M + NH_4)^+$], 429 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{26}H_{24}N_2NaO_2S$ [$(M + Na)^+$]: 451.1451; Found: 451.1449.

3.22. Synthesis of *N*-(6-cyano-4-hexylhexa-4,5-allenyl)benzenesulfonamide **2v**. (zdj-4-019)



Following **Typical Procedure VI**, the reaction of **1v** (169.9 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.6 mg, 0.01 mmol), and **L1** (7.2 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2v** (132.5 mg, 76%) as an oil [eluent: petroleum ether/ethyl acetate = 9/2 (440 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93-7.83 (m, 2 H, ArH), 7.64-7.57 (m, 1 H, ArH), 7.57-7.48 (m, 2 H, ArH), 5.20-5.10 (m, 1 H, =CH), 5.00 (t, *J* = 6.3 Hz, 1 H, NH), 2.98 (q, *J* = 6.5 Hz, 2 H, NCH_2), 2.13-1.91 (m, 4 H, $CH_2 \times 2$), 1.67-1.55 (m, 2 H, CH_2), 1.46-1.34 (m, 2 H, CH_2), 1.34-1.18 (m, 6 H, $CH_2 \times 3$), 0.89 (t, *J* = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.7, 139.7, 132.7, 129.2, 126.9, 114.2, 110.7, 68.2, 42.4, 31.7, 31.4, 28.7, 28.4, 27.1, 26.8, 22.5, 14.0; IR (neat) *v* (cm^{-1}) 3283, 2223, 1957, 1447, 1328; MS (EI): *m/z* (%) 346 (M$^+$, 39.17), 205 (100); HRMS (ESI) Calcd for $C_{19}H_{26}N_2NaO_2S$ [(M + Na)$^+$]: 369.1607; Found: 369.1610.

3.23. Synthesis of *N*-(6-cyano-4-hexylhexa-4,5-allenyl)-4-acetylbenzenesulfonamide **2w**. (fjj-6-108)



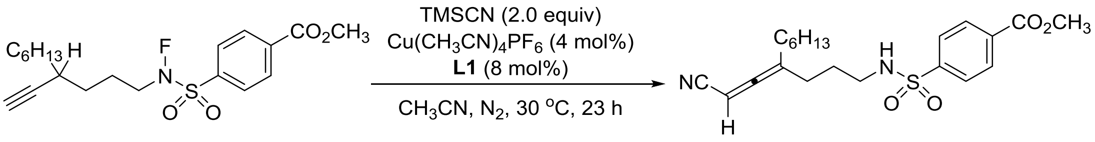
1w
0.51 mmol

2w
68%

Following **Typical Procedure VI**, the reaction of **1w** (194.8 mg, 0.51 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.8 mg, 0.01 mmol), and **L1** (7.2 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2w** (135.3 mg, 68%) as an oil [eluent: petroleum ether/ethyl acetate = 5/1 (500 mL) to 3/1 (500 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2 H, ArH), 7.97 (d, *J* = 8.5 Hz, 2 H, ArH), 5.45 (t, *J* = 6.3 Hz, 1 H, NH), 5.23-5.15 (m, 1 H, =CH), 3.00 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.67 (s, 3 H, CH_3), 2.13-2.04 (m, 2 H, CH_2), 2.04-1.97 (m, 2 H, CH_2), 1.69-

1.58 (m, 2 H, CH_2), 1.44-1.34 (m, 2 H, CH_2), 1.33-1.19 (m, 6 H, CH_2 × 3), 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 197.0, 143.7, 139.8, 128.9, 127.2, 114.1, 110.6, 68.2, 42.4, 31.6, 31.3, 28.6, 28.3, 27.0, 26.8, 22.4, 13.9; IR (neat) *v* (cm^{-1}) 3281, 2223, 1957, 1694, 1597, 1572, 1427, 1398; MS (EI): *m/z* (%) 388 (M^+, 46.6), 205 (100); HRMS (ESI) Calcd for $C_{21}H_{28}N_2NaO_3S$ [$(M + Na)^+$]: 411.1713; Found: 411.1715.

3.24. Synthesis of *N*-(6-cyano-4-hexylhexa-4,5-allenyl)-4-methoxycarbonyl-benzenesulfonamide **2x**. (syq-4-072)



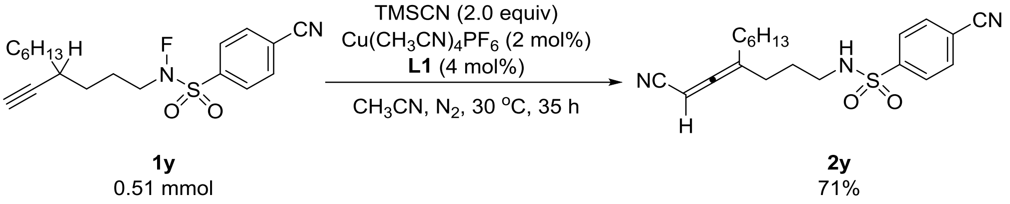
1x
0.5 mmol

2x
72%, 98% purity

Following **Typical Procedure VI**, the reaction of **1x** (199.4 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (7.7 mg, 0.02 mmol), and **L1** (14.3 mg, 0.04 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2x** (149.4 mg, 72%, 98% purity) as an oil [eluent: petroleum ether/ethyl acetate = 5/1 (300 mL) to 4/1 (300 mL) to 3/1 (400 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 2 H, ArH), 7.95 (d, *J* = 8.5 Hz, 2 H, ArH), 5.40-5.23 (m, 1 H, NH), 5.23-5.14 (m, 1 H, =CH), 3.97 (s, 3 H, CH_3), 3.00 (q, *J* = 6.5 Hz, 2 H, NCH_2), 2.20-1.88 (m, 4 H, CH_2 × 2), 1.73-1.57 (m, 2 H, CH_2), 1.47-1.17 (m, 8 H, CH_2 × 4), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.7, 165.5, 143.8, 133.7, 130.3, 126.9, 114.1, 110.6, 68.2, 52.6, 42.4, 31.6, 31.3, 28.6, 28.3, 27.0, 26.8, 22.4, 13.9; IR (neat) *v* (cm^{-1}) 3285, 2224, 1955, 1731, 1436, 1336; MS (EI): *m/z* (%) 404 (M^+, 37.78), 205

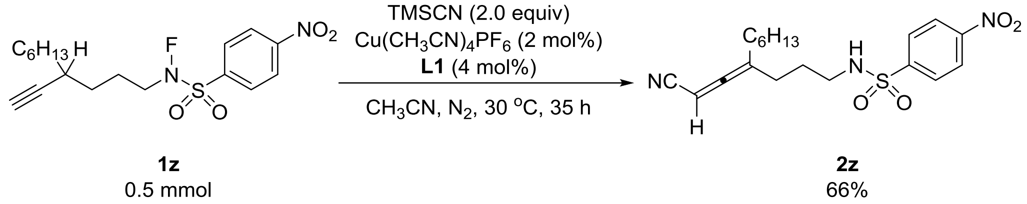
(100); HRMS (ESI) Calcd for $C_{21}H_{28}N_2NaO_4S$ [(M + Na)$^+$]: 427.1662; Found: 427.1664.

3.25. Synthesis of *N*-(6-cyano-4-hexylhexa-4,5-allenyl)-4-cyanobenzenesulfonamide **2y**. (syq-4-056)



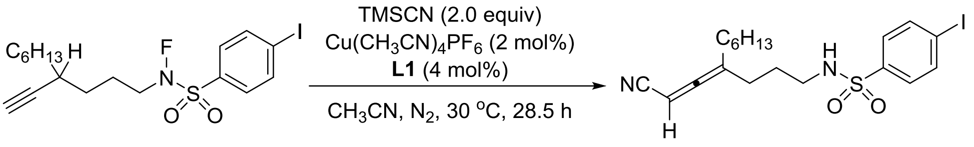
Following **Typical Procedure VI**, the reaction of **1y** (185.5 mg, 0.51 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.9 mg, 0.01 mmol), and **L1** (7.3 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) to afforded **2y** (134.2 mg, 71%) as a solid (m.p. 81.6-84.1 °C, diethyl ether/hexane) [eluent: petroleum ether/ethyl acetate = 5/1 (600 mL) to 4/1 (600 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2 H, ArH), 7.84 (d, *J* = 8.5 Hz, 2 H, ArH), 5.24-5.16 (m, 2 H, =CH and NH), 3.07-2.95 (m, 2 H, CH_2), 2.15-1.98 (m, 4 H, CH_2 × 2), 1.72-1.61 (m, 2 H, CH_2), 1.47-1.36 (m, 2 H, CH_2), 1.36-1.20 (m, 6 H, CH_2 × 3), 0.89 (t, *J* = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.7, 144.1, 133.0, 127.6, 117.2, 116.3, 114.2, 110.6, 68.4, 42.4, 31.7, 31.4, 28.6, 28.3, 27.1, 26.8, 22.4, 13.9; IR (neat) *v* (cm^{-1}) 3285, 2237, 2223, 1953, 1397, 1337; MS (EI): *m/z* (%) 371 (M$^+$, 34.30), 205 (100); Anal. Calcd. for $C_{20}H_{25}N_3O_2S$ (%): C, 64.66; H, 6.78; N, 11.31; Found: C, 64.64; H, 6.83; N, 11.35.

3.26. Synthesis of *N*-(6-cyano-4-hexylhexa-4,5-allenyl)-4-nitrobenzenesulfonamide **2z**. (zdj-4-033)



Following **Typical Procedure VI**, the reaction of **1z** (192.0 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), Cu(CH_3CN)$_4$$PF_6$ (3.6 mg, 0.01 mmol), and **L1** (7.3 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2z** (128.1 mg, 66%) as an oil [eluent: petroleum ether/ethyl acetate = 7/2 (450 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.5 Hz, 2 H, ArH), 8.07 (d, *J* = 9.0 Hz, 2 H, ArH), 5.25-5.19 (m, 1 H, =CH), 5.13 (t, *J* = 6.3 Hz, 1 H, NH), 3.12-2.95 (m, 2 H, NCH_2), 2.20-1.95 (m, 4 H, CH_2 × 2), 1.75-1.61 (m, 2 H, CH_2), 1.47-1.36 (m, 2 H, CH_2), 1.35-1.20 (m, 6 H, CH_2 × 3), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.8, 150.1, 145.7, 128.3, 124.4, 114.2, 110.6, 68.4, 42.5, 31.7, 31.4, 28.7, 28.4, 27.2, 26.9, 22.5, 14.0; IR (neat) *v* (cm^{-1}) 3288, 2223, 1957, 1607, 1531, 1433, 1401, 1349; MS (EI): *m/z* (%) 391 (M$^+$, 23.79), 205 (100); HRMS (ESI) Calcd for $C_{19}H_{26}N_3O_4S$ [(M + H)$^+$]: 392.1639; Found: 392.1638.

3.27. Synthesis of *N*-(6-cyano-4-hexylhexa-4,5-allenyl)-4-iodobenzenesulfonamide **2aa**. (zdj-4-127)

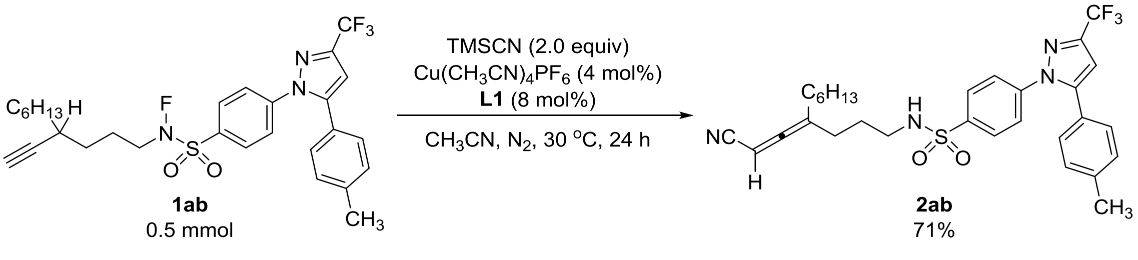


1aa, 98% purity
0.49 mmol

2aa
73%

Following **Typical Procedure VI**, the reaction of **1aa** (233.1 mg, 98% purity, 0.49 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.8 mg, 0.01 mmol), and **L1** (7.3 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2aa** (169.6 mg, 73%) as an oil [eluent: petroleum ether/ethyl acetate = 9/2 (440 mL)]: ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2 H, ArH), 7.59 (d, J = 8.5 Hz, 2 H, ArH), 5.26 (t, J = 6.3 Hz, 1 H, NH), 5.22-5.13 (m, 1 H, =CH), 2.95 (q, J = 6.7 Hz, 2 H, NCH_2), 2.16-1.84 (m, 4 H, $CH_2 \times 2$), 1.68-1.56 (m, 2 H, CH_2), 1.46-1.18 (m, 8 H, $CH_2 \times 4$), 0.89 (t, J = 7.0 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.7, 139.4, 138.3, 128.3, 114.2, 110.6, 99.9, 68.2, 42.3, 31.6, 31.3, 28.6, 28.3, 26.9, 26.8, 22.4, 13.9; IR (neat) v (cm^{-1}) 3281, 2223, 1957, 1570, 1470, 1384, 1331; MS (EI): m/z (%) 472 (M^+, 51.78), 205 (100); HRMS (ESI) Calcd for $C_{19}H_{25}IN_2NaO_2S$ [$(M + Na)^+$]: 495.0574; Found: 495.0576.

3.28. Synthesis of *N*-(6-cyano-4-hexylhexa-4,5-allenyl)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-*1H*-pyrazol-1-yl)benzenesulfonamide **2ab**. (fjj-6-123)

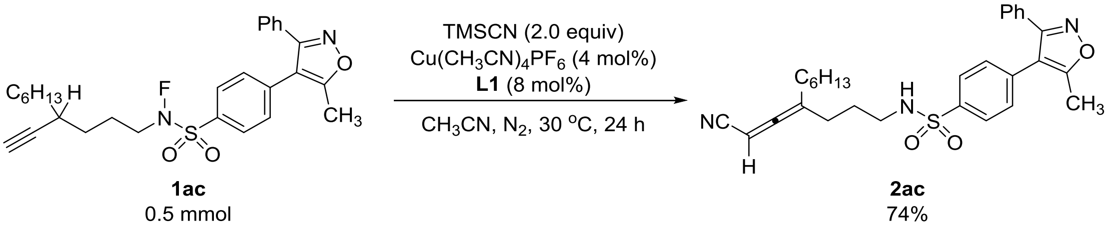


1ab
0.5 mmol

2ab
71%

Following **Typical Procedure VI**, the reaction of **1ab** (282.2 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol), and **L1** (14.4 mg, 0.04 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2ab** (202.3 mg, 71%) as an oil [eluent: petroleum ether/ethyl acetate = 4/1 (500 mL)]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 2 H, ArH), 7.48 (d, *J* = 8.5 Hz, 2 H, ArH), 7.17 (d, *J* = 8.5 Hz, 2 H, ArH), 7.11 (d, *J* = 8.5 Hz, 2 H, ArH), 6.75 (s, 1 H, ArH), 5.25-5.16 (m, 1 H, NH), 5.12 (t, *J* = 6.3 Hz, 1 H, =CH), 2.96 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.37 (s, 3 H, CH_3), 2.13-1.95 (m, 4 H, CH_2 × 2), 1.69-1.57 (m, 2 H, CH_2), 1.47-1.36 (m, 2 H, CH_2), 1.34-1.20 (m, 6 H, CH_2 × 3), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.7, 145.2, 143.9 (q, *J* = 38.3 Hz), 142.4, 139.7, 139.3, 129.6, 128.6, 128.0, 125.5, 121.0 (q, *J* = 267.4 Hz), 114.1, 110.6, 106.2, 68.3, 42.4, 31.6, 31.4, 28.6, 28.4, 27.1, 26.8, 22.4, 21.2, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.9; IR (neat) *ν* (cm^{-1}) 3281, 2223, 1955, 1598, 1499, 1472, 1450, 1374; MS (ESI): *m/z* 571 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{30}H_{33}F_3N_4NaO_2S$ [$(M + Na)^+$]: 593.2169; Found: 593.2169.

3.29. Synthesis of *N*-(6-cyano-4-hexylhexa-4,5-allenyl)-4-(5-methyl-3-phenylisoxazol-4-yl)benzenesulfonamide **2ac**. (hyk-2-021)

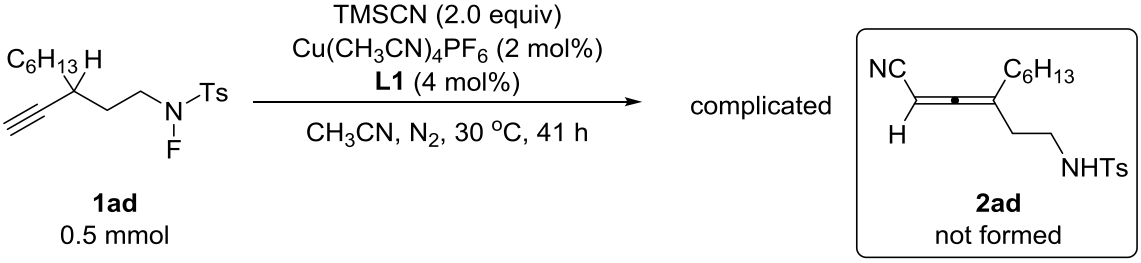


Following **Typical Procedure VI**, the reaction of **1ac** (247.6 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (7.6 mg, 0.02 mmol), and **L1** (14.5 mg, 0.04 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **2ac** (185.0

mg, 74%) as an oil [eluent: petroleum ether/ethyl acetate = 5/2 (700 mL)]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2 H, ArH), 7.39-7.10 (m, 7 H, ArH), 5.16-5.03 (m, 1 H, =CH), 4.87 (t, *J* = 6.3 Hz, 1 H, NH), 2.95 (q, *J* = 6.6 Hz, 2 H, NCH_2), 2.42 (s, 3 H, CH_3), 2.12-1.88 (m, 4 H, CH_2 × 2), 1.69-1.51 (m, 2 H, CH_2), 1.41-1.07 (m, 8 H, CH_2 × 4), 0.81 (t, *J* = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.7, 167.2, 161.0, 138.9, 135.0, 130.2, 129.6, 128.6, 128.4, 128.3, 127.3, 114.4, 114.1, 110.7, 68.3, 42.4, 31.6, 31.4, 28.6, 28.4, 27.2, 26.8, 22.4, 13.9, 11.7; IR (neat) *ν* (cm^{-1}) 3280, 2222, 1955, 1620, 1465, 1444, 1421, 1395, 1332; MS (ESI): *m/z* 526 [(M + Na)$^+$], 504 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{29}H_{33}N_3NaO_3S$ [(M + Na)$^+$]: 526.2135; Found: 526.2138.

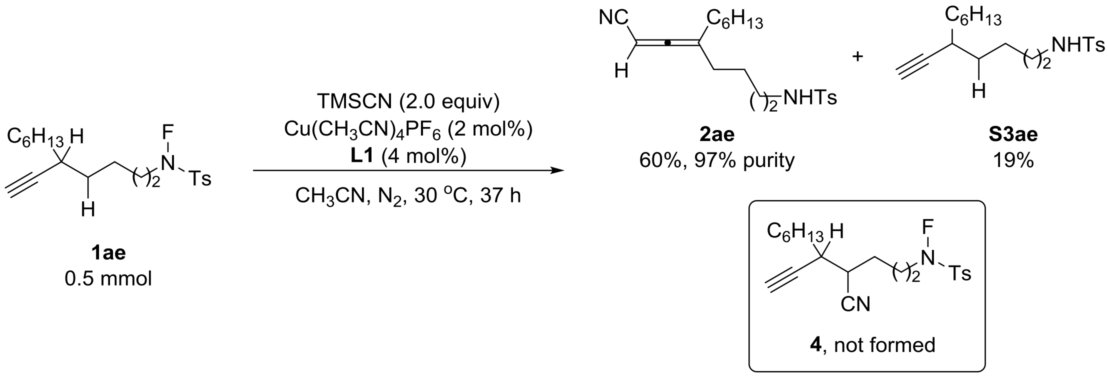
4. The Reaction for 1, n-HAT (n ≠ 5)

4.1. The reaction of **1ad** for 1,4-HAT. (zdj-7-006)



Following **Typical Procedure VI**, the reaction of **1ad** (169.9 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.9 mg, 0.01 mmol), and **L1** (7.2 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) was complicated.

4.2. The reaction of **1ae** for 1,6-HAT. (zdj-6-184)



1ae
0.5 mmol

2ae
60%, 97% purity

S3ae
19%

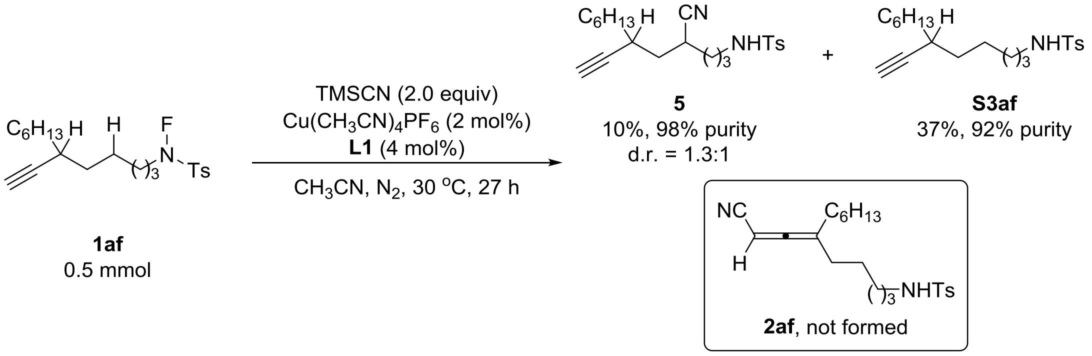
4, not formed

Following **Typical Procedure VI**, the reaction of **1ae** (184.2 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol), and **L1** (7.1 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **S3ae** (33.2 mg, 19%) and **2ae** (115.7 mg, 60%, 97% purity) [eluent: petroleum ether/ethyl acetate = 4/1 (450 mL)].

S3ae: oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2 H, ArH), 7.31 (d, *J* = 8.1 Hz, 2 H, ArH), 4.71 (t, *J* = 6.2 Hz, 1 H, NH), 2.94 (q, *J* = 6.5 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.31-2.15 (m, 1 H, CH), 2.02 (d, *J* = 2.4 Hz, 1 H, ≡CH), 1.57-1.18 (m, 16 H, $CH_2 \times 8$), 0.88 (t, *J* = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 137.0, 129.7, 127.1, 87.7, 69.3, 43.0, 34.9, 34.2, 31.7, 31.3, 29.3, 29.1, 27.1, 24.2, 22.6, 21.5, 14.0; IR (neat) *v* (cm^{-1}) 3289, 2110, 1599, 1459, 1326; MS (EI): *m/z* 388 [$(M + K)^+$], 372 [$(M + Na)^+$], 350 [$(M + H)^+$]; HRMS (ESI) Calcd for $C_{20}H_{31}NNaO_2S$ [$(M + Na)^+$]: 372.1968; Found: 372.1968.

2ae: oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2 H, ArH), 7.31 (d, *J* = 8.1 Hz, 2 H, ArH), 5.22-5.04 (m, 2 H, =CH and NH), 2.91 (q, *J* = 6.5 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.05-1.92 (m, 4 H, $CH_2 \times 2$), 1.58-1.18 (m, 12 H, $CH_2 \times 6$), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.9, 143.3, 136.8, 129.6, 127.0, 114.3, 110.9, 67.7, 42.6, 31.5, 31.4, 30.9, 28.8, 28.6, 26.8, 23.8, 22.4, 21.4, 13.9; IR (neat) *v* (cm^{-1}) 3282, 2222, 1957, 1599, 1456, 1327; MS (EI): *m/z* (%) 374 (M$^+$, 16.68), 219 (100); HRMS (ESI) Calcd for $C_{21}H_{30}N_2NaO_2S$ [(M + Na)$^+$]: 397.1920; Found: 397.1920.

4.3. The reaction of **1n** for 1,7-HAT. (zdj-7-034)



Following **Typical Procedure VI**, the reaction of **1af** (191.2 mg, 0.5 mmol), TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol), $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol), and **L1** (7.4 mg, 0.02 mmol) in CH_3CN (2.5 + 2.5 mL) afforded **S3af** (72.9 mg, 37%, 92% purity) and **5** (19.2 mg, 10%, 98% purity, dr = 1.3:1 was determined by quantitative ^{13}C NMR analysis) [eluent: petroleum ether/ethyl acetate = 9/2 (440 mL) to 3/1 (400 mL)].

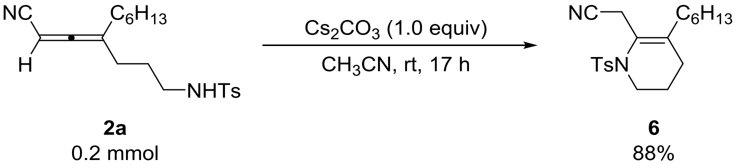
S3af: oil, ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2 H, ArH), 7.31 (d, *J* = 8.1 Hz, 2 H, ArH), 5.05 (t, *J* = 6.2 Hz, 1 H, NH), 2.91 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.31-2.17 (m, 1 H, CH), 2.02 (d, *J* = 2.4 Hz, 1 H, ≡CH), 1.56-1.16 (m, 18 H, $CH_2 \times 9$), 0.88 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 136.9, 129.6, 127.0, 87.9, 69.1, 43.0, 34.8, 34.6, 31.7, 31.3, 29.3, 29.0, 27.1, 26.6, 26.2, 22.5, 21.4, 14.0; IR (neat) *v* (cm^{-1}) 3289, 2110, 1599, 1457, 1327; MS (EI): *m/z* 386

[(M + Na)$^+$], 364 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{21}H_{33}NNaO_2S$ [(M + Na)$^+$]: 386.2124; Found: 386.2123.

5: oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2 H, ArH), 7.32 (d, *J* = 8.1 Hz, 2 H, ArH), 4.82 (t, *J* = 6.2 Hz, 1 H, NH), 3.06-2.73 (m, 3 H, NCH_2 and CH), 2.66-2.37 (m, 4 H, CH_3 and CH], 2.12 (dd, J_1 = 2.4 Hz, J_2 = 0.9 Hz, 1 H, ≡CH), 1.90-1.16 (m, 16 H, $CH_2 \times 8$), 0.89 (t, *J* = 6.6 Hz, 3 H, CH_3); IR (neat) *v* (cm^{-1}) 3287, 2239, 2112, 1598, 1456, 1328; MS (ESI): 411 [(M + Na)$^+$], 389 [(M + H)$^+$]; HRMS (ESI) Calcd for $C_{22}H_{32}N_2NaO_2S$ [(M + Na)$^+$]: 411.2077; Found: 411.2076.

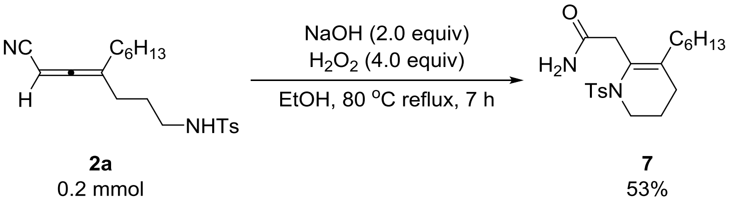
5. Transformations of Products

5.1. Synthesis of 6-cyanomethyl-5-hexyl-1-tosyl-1,2,3,4-tetrahydropyridine **6**. (zdj-4-111)



To a 25 mL Schlenk tube were added Cs_2CO_3 (65.8 mg, 0.20 mmol) and a solution of **2a** (71.9 mg, 0.2 mmol) in CH_3CN (2 mL). The resulting mixture was stirred at room temperature for 17 hours as monitored by TLC, filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3), concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 7/1 (320 mL)] to afford **6** (63.2 mg, 88%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2 H, ArH), 7.31 (d, *J* = 8.0 Hz, 2 H, ArH), 3.71 (s, 2 H, CH_2), 3.44 (t, *J* = 5.8 Hz, 2 H, CH_2), 2.44 (s, 3 H, CH_3), 2.09 (t, *J* = 8.0 Hz, 2 H, CH_2), 1.82 (t, *J* = 6.8 Hz, 2 H, CH_2), 1.49-1.12 (m, 10 H, $CH_2 \times 5$), 0.90 (t, *J* = 6.8 Hz, 3 H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 136.0, 134.8, 129.7, 127.5, 122.4, 117.9, 46.3, 33.4, 31.5, 29.1, 27.9, 26.4, 22.5, 21.5, 21.4, 20.4, 13.9; IR (neat) *v* (cm^{-1}) 2251, 1598, 1494, 1457, 1414, 1341, 1306; MS (EI): *m/z* (%) 360 (M^+, 43.21), 205 (100); HRMS (ESI) Calcd for $C_{20}H_{28}N_2NaO_2S$ [$(M + Na)^+$]: 383.1764; Found: 383.1765.

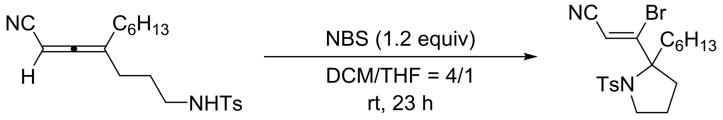
5.2. Synthesis of 6-(2-amino-2-oxoethyl)-5-hexyl-1-tosyl-1,2,3,4-tetrahydropyridine **7**.[9] (zdj-4-099)



To a 25 mL Schlenk tube were added NaOH (17.0 mg, 0.43 mmol), a solution of **2a** (72.5 mg, 0.2 mmol) in EtOH (2 mL), and H_2O_2 (30% wt, 91.9 mg, 0.81 mmol) sequentially. The Schlenk tube was then equipped with a condenser. The resulting mixture was stirred at 80 °C for 7 hours as monitored by TLC, filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3), concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 1/1 (400 mL)] to afford **7** (40.1 mg, 53%) as an oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2 H, ArH), 7.28 (d, *J* = 8.0 Hz, 2 H, ArH), 6.20 (s, 1 H, one proton of $CONH_2$), 5.78 (s, 1 H, one proton of $CONH_2$), 3.59 (s, 2 H, CH_2), 3.55-3.45 (m, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.08 (t, *J* = 7.5 Hz, 2 H, CH_2), 1.78 (t, *J* = 7.0 Hz, 2 H, CH_2), 1.46-1.18 (m, 10 H, $CH_2 \times 5$), 0.89 (t, *J* = 7.0 Hz, 3 H, CH_2); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 172.8, 143.6, 136.5, 133.7, 129.5, 127.3, 126.7, 46.8, 39.0, 33.5, 31.6, 29.1, 28.4, 26.5, 22.5, 21.5, 20.7, 14.0; IR (neat) *v* (cm^{-1}) 3463, 3365, 3193, 3064, 1679, 1598, 1495, 1456, 1381, 1337; MS (EI): *m/z* (%) 223 [(M – Ts)$^+$, 100]; HRMS (ESI) Calcd for $C_{20}H_{30}N_2NaO_3S$ [(M + Na)$^+$]: 401.1869; Found: 401.1870.

5.3. Synthesis of (*Z*)-2-(1-bromo-2-cyanovinyl)-2-hexyl-*N*-tosylpyrrolidin (*Z*)-**8**.[10] (zdj-4-094)

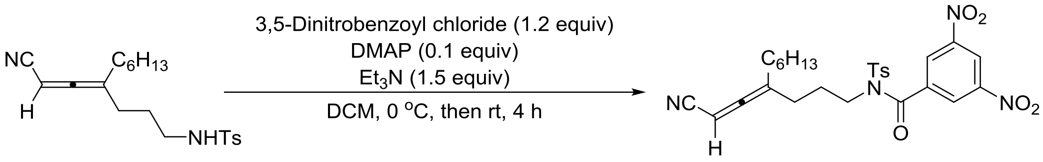


2a
0.2 mmol

(*Z*)-**8**
70%

To a 25 mL Schlenk tube were added NBS (42.7 mg, 0.24 mmol), THF (0.4 mL), and a solution of **2a** (71.9 mg, 0.2 mmol) in DCM (1.6 mL). The resulting mixture was stirred at room temperature for 23 hours as monitored by TLC, transferred to a round-bottomed flask, concentrated in vacuo, and purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 9/1 (450 mL)] to afford (*Z*)-**8** (61.6 mg, 70%) as a soild (m.p.106.3-106.6 °C, dichloromethane/hexane): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 2 H, ArH), 7.31 (d, *J* = 8.5 Hz, 2 H, ArH), 6.29 (s, 1 H, =CH), 3.64-3.48 (m, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.37-2.19 (m, 2 H, CH_2), 2.09-1.81 (m, 4 H, $CH_2 \times 2$), 1.34-1.04 (m, 8 H, $CH_2 \times 4$), 0.88 (t, *J* = 7.3 Hz, 3 H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.3, 143.5, 137.1, 129.4, 127.0, 116.0, 103.2, 74.5, 50.2, 38.6, 36.8, 31.6, 29.4, 24.6, 22.9, 22.5, 21.4, 14.0; IR (neat) *v* (cm^{-1}) 3063, 2225, 1599, 1495, 1460, 1342; MS (EI): *m/z* (%) 359 [(M – Br)$^+$, 23.51], 155 (100); Anal. Calcd. for $C_{20}H_{27}BrN_2O_2S$ (%): C, 54.67; H, 6.19; N, 6.38; Found: C, 54.59; H, 6.19; N, 6.21.

5.4. Synthesis of *N*-(6-cyano-4-hexylhexa-4,5-allenyl)-*N*-tosyl-3,5-dinitrobenzamide **9**. (zdj-4-164)



2a
0.2 mmol

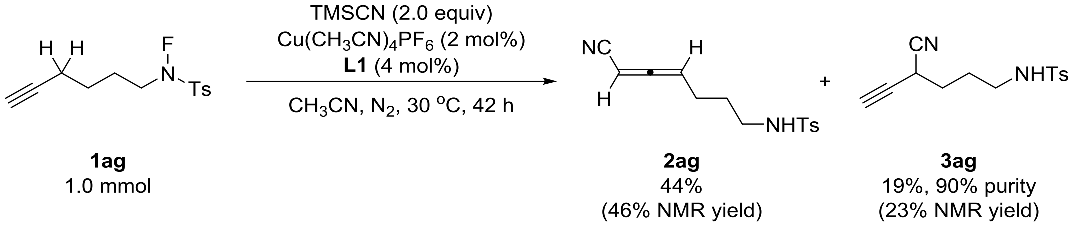
9
91%

To a 25 mL Schlenk tube were added a solution of **2a** (72.2 mg, 0.2 mmol) in DCM (0.5 mL). The resulting mixture was cooled down to 0 °C with an ice-water bath followed by the sequential addition of DMAP (2.4 mg, 0.02 mmol), Et_3N (41.8 μL, d = 0.728 g/mL, 30.4 mg, 0.3 mmol), and a solution of 3,5-dinitrobenzoyl chloride (57.1 mg, 0.25 mmol) in DCM (1.5 mL). The resulting mixture was stirred at room temperature for 4 hours as monitored by TLC, transferred to a round-bottomed flask, concentrated in vacuo, purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 5/1 (300 mL)] to afford **9** (101.0 mg, 91%) as a solid (m.p. 84.5-85.9 °C, diethyl ether/hexane): ^1H NMR (500 MHz, $CDCl_3$) δ 9.11 (s, 1 H, ArH), 8.50 (d, *J* = 2.0 Hz, 2 H, ArH), 7.50 (d, *J* = 8.0 Hz, 2 H, ArH), 7.35 (d, *J* = 8.0 Hz, 2 H, ArH), 5.35-5.17 (m, 1 H, =CH), 3.93-3.74 (m, 2 H, NCH_2), 2.46 (s, 3 H, CH_3), 2.27-2.08 (m, 4 H, $CH_2 \times 2$), 2.01-1.86 (m, 2 H, CH_2), 1.54-1.40 (m, 2 H, CH_2), 1.39-1.19 (m, 6 H, $CH_2 \times 3$), 0.90 (t, *J* = 6.8 Hz, 3 H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 166.8, 147.8, 146.4, 138.9, 134.9, 130.3, 127.8, 127.4, 120.5, 114.1, 110.3, 68.6, 46.6, 31.6, 31.4, 28.9, 28.7, 26.9, 26.1, 22.5, 21.6, 14.0; IR (neat) *v* (cm^{-1}) 3100, 2223, 1958, 1683, 1627, 1595, 1548, 1494, 1457, 1344; MS (EI): *m/z* (%) 360 [(M – $C_7H_3N_2O_5$ + H)$^+$, 45.06], 205 (100); Anal. Calcd. for $C_{27}H_{30}N_4O_7S$ (%): C, 58.47; H, 5.45; N, 10.10; Found: C, 58.50; H, 5.47; N, 10.09.

6. Regioselectivity and Mechanistic Studies

6.1. Regioselectivity

6.1.1 Cyanation of secondary propargylic C-H bond in **1ag**. (zdj-5-149, zdj-4-115)

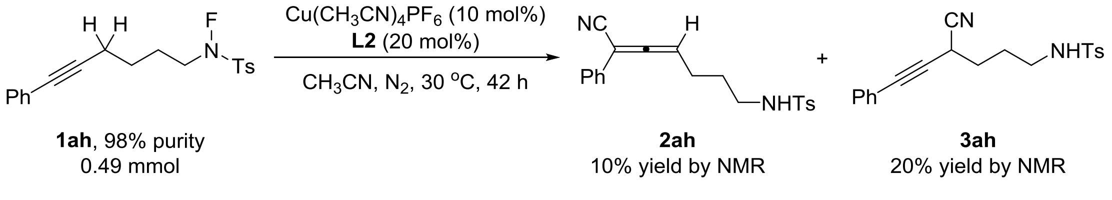


To a 25 mL flame-dried Schlenk tube with a polytetrafluoroethylene plug was added **L1** (14.5 mg, 0.04 mmol). Then the Schlenk tube was taken into a glove box, $Cu(CH_3CN)_4PF_6$ (7.5 mg, 0.02 mmol) and CH_3CN (5 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **1ag** (269.1 mg, 1.0 mmol), CH_3CN (5 mL), and TMSCN (250 μL, d = 0.793 g/mL, 198.3 mg, 2.0 mmol). The Schlenk tube was taken out from the glove box. The resulting mixture was stirred at 30 °C for 42 hours as monitored by TLC and filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3). After evaporation, 19.0 μL of CH_3NO_2 was added as the internal standard: 23% NMR yield of **3ag** and 46% NMR yield of **2ag** were determined by ^{1}H NMR analysis of the crude product. The crude product was then purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 3/1 (600 mL)] to afford afforded **3ag** (58.3 mg, 19%, 90% purity) and **2ag** (121.7 mg, 44%).

3ag: oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2 H, ArH), 7.32 (d, *J* = 8.0 Hz, 2 H, ArH), 5.15-5.06 (m, 1 H, NH), 3.55 (td, J_1 = 6.8 Hz, J_2 = 2.4 Hz, 1 H, CH), 2.99 (q, *J* = 6.5 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.32 (d, *J* = 2.8 Hz, 1 H, ≡CH), 1.95-1.86 (m, 2 H, CH_2), 1.79-1.66 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 136.5, 129.8, 127.0, 116.8, 75.4, 73.0, 41.9, 29.8, 26.3, 22.4, 21.4; IR (neat) *v* (cm^{-1}) 3282, 2249, 2129, 1598, 1495, 1426, 1326; MS (EI): *m/z* (%) 276 (M^+, 42.81), 155 (100); HRMS (ESI) Calcd for $C_{14}H_{16}N_2NaO_2S$ [$(M + Na)^+$]: 299.0825; Found: 299.0827.

2ag: oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2 H, ArH), 7.33 (d, *J* = 8.0 Hz, 2 H, ArH), 5.68 (q, *J* = 6.8 Hz, 1 H, =CH), 5.25-5.18 (m, 1 H, =CH), 5.18-5.07 (m, 1 H, NH), 2.96 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.44 (s, 3 H, CH_3), 2.16 (qd, J_1 = 7.2 Hz, J_2 = 3.1 Hz, 2 H, CH_2), 1.69-1.59 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.0, 143.5, 136.6, 129.7, 126.9, 113.4, 95.8, 67.9, 42.1, 28.2, 24.0, 21.4; IR (neat) *v* (cm^{-1}) 3282, 2225, 1960, 1598, 1426, 1326; MS (EI): *m/z* (%) 276 (M^+, 74.30), 99 (100); HRMS (ESI) Calcd for $C_{14}H_{16}N_2NaO_2S$ [$(M + Na)^+$]: 299.0825; Found: 299.0827.

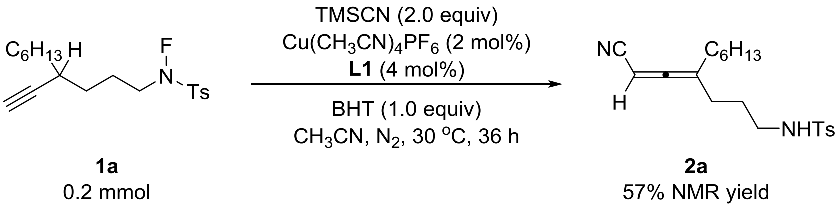
6.1.2. Cyanation of secondary propargylic C-H bond in **1ah**. (zdj-7-055)



To a 25 mL flame-dried Schlenk tube with a polytetrafluoroethylene plug was added **L2** (18.2 mg, 0.10 mmol). Then the Schlenk tube was taken into a glove box, $Cu(CH_3CN)_4PF_6$ (18.2 mg, 0.05 mmol) and CH_3CN (2.5 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **1ah** (173.1 mg, 98% purity, 0.49 mmol), CH_3CN (2.5 mL), and TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol). The Schlenk tube was taken out from the glove box. The resulting mixture was stirred at 30 °C for 42 hours as monitored by TLC and filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3). After evaporation, 9.0 μL of CH_3NO_2 was added as the internal standard: 20% yield of **3ah** and 10% yield of **2ah** were determined by ^{1}H NMR analysis of the crude product.

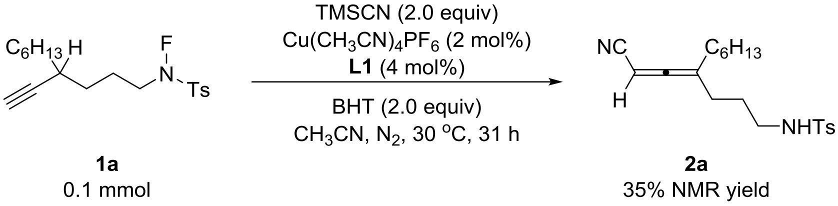
6.2. Radical trapping experiments with BHT.

6.2.1. The reaction of **1a** under the standard conditions with 1.0 equiv BHT. (zdj-5-143)



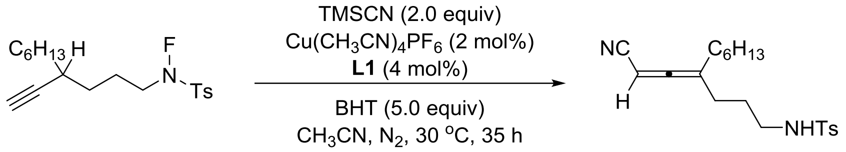
To a 25 mL flame-dried Schlenk tube with a polytetrafluoroethylene plug was added **L1** (3.0 mg, 0.008 mmol). Then the Schlenk tube was taken to a glove box, $Cu(CH_3CN)_4PF_6$ (1.5 mg, 0.004 mmol) and CH_3CN (1 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **1a** (71.0 mg, 0.2 mmol), BHT (44.3 mg, 0.2 mmol), CH_3CN (1 mL), and TMSCN (50 μL, d = 0.793 g/mL, 39.7 mg, 0.4 mmol). The Schlenk tube was taken out from the glove box. The resulting mixture was stirred at 30 °C for 36 hours as monitored by TLC and filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3). After evaporation, 3.6 μL of CH_3NO_2 was added as the internal standard: 57% NMR yield of **2a** as determined by ^1H NMR analysis of the crude product.

6.2.2. The reaction of **1a** under standard conditions with 2.0 equiv BHT. (zdj-5-153)



To a 25 mL flame-dried Schlenk tube with a polytetrafluoroethylene plug was added **L1** (1.5 mg, 0.004 mmol). Then the Schlenk tube was taken to the glove box, $Cu(CH_3CN)_4PF_6$ (0.8 mg, 0.002 mmol) and CH_3CN (0.5 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **1a** (35.2 mg, 0.2 mmol), BHT (43.7 mg, 0.2 mmol), CH_3CN (0.5 mL), and TMSCN (25 μL, d = 0.793 g/mL, 19.8 mg, 0.2 mmol). The tube was taken out from the glove box. The resulting mixture was stirred at 30 °C for 31 hours as monitored by TLC and filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3). After evaporation, 1.8 μL of CH_3NO_2 was added as the internal standard: 35% NMR yield of **2a** as determined by ^1H NMR analysis of the crude product.

6.2.3. The reaction of **1a** under standard conditions with 5.0 equiv BHT. (zdj-5-156)



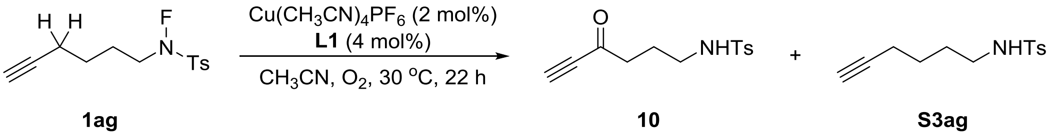
1a 0.1 mmol

2a not formed

To a 25 mL flame-dried Schlenk tube with a polytetrafluoroethylene plug was added **L1** (1.4 mg, 0.004 mmol). Then the Schlenk tube was taken into a glove box, $Cu(CH_3CN)_4PF_6$ (0.7 mg, 0.002 mmol) and CH_3CN (0.5 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **1a** (35.4 mg, 0.2 mmol), BHT (110.2 mg, 1.0 mmol), CH_3CN (0.5 mL), and TMSCN (25 μL, d = 0.793 g/mL, 19.8 mg, 0.2 mmol). The tube was taken out from the glove box. The resulting mixture was stirred at 30 °C for 35 hours as monitored by TLC and filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3). After evaporation, 1.8 μL of CH_3NO_2 was added as the internal standard: no signal of **2a** was determined by ^{1}H NMR analysis of the crude product.

6.3. Radical trapping experiments with O_2.

6.3.1. The reaction of **1ag** under the standard conditions using O_2 instead of N_2. (zdj-5-151, zdj-4-194)



1ag 0.4 mmol 9% recovery

10 27%, 94% purity (33% NMR yield)

S3ag 38% (42% NMR yield)

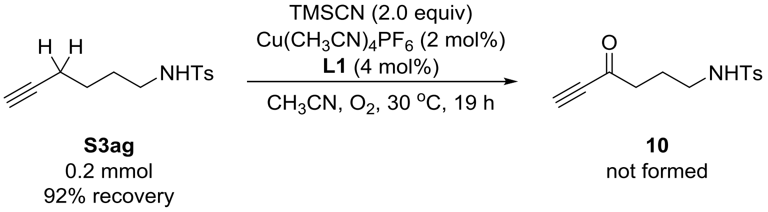
To a 25 mL flame-dried Schlenk tube was added **L1** (5.9 mg, 0.016 mmol). Then the Schlenk tube was taken to the glove box, $Cu(CH_3CN)_4PF_6$ (3.0 mg, 0.008 mmol), and CH_3CN (2 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **1ag** (107.5 mg, 0.4 mmol) and CH_3CN (2 mL). The tube was taken out from the glove box. The resulting mixture was frozen with a liquid nitrogen bath and the tube's nitrogen inside was completely replaced with a O_2 balloon for three times. The Schlenk tube was then allowed to stand until the mixture was warmed up to room temperature followed by the addition of TMSCN (100 μL, d = 0.793 g/mL, 79.3 mg, 0.8 mmol). The resulting mixture was stirred at 30 °C for 22 hours as monitored by TLC and filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3). After evaporation, 7.2 μL of CH_3NO_2 was added as the internal standard: 33% NMR yield of **10**, 42% NMR yield of **S3ag** and 9% recovery of **1ag** as determined by ^1H NMR analysis of the crude product. The crude product was then purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 5/1 (300 mL) to 3/1 (400 mL)] to afford **S3ag** (38.2 mg, 38%) and **10** (30.7 mg, 27%, 94% purity).

S3ag:[11] solid (m.p. 56.9-59.6 °C, dichloromethane/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2 H, ArH), 7.31 (d, J = 8.4 Hz, 2 H, ArH), 4.97-4.86 (m, 1 H, NH), 2.95 (q, J = 6.7 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.14 (td, J_1 = 6.7 Hz, J_2 = 2.5 Hz, 2 H, CH_2), 1.92 (t, J = 2.6 Hz, 1 H, ≡CH), 1.64-1.45 (m, 4 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 136.8, 129.7, 127.0, 83.7, 68.7, 42.6, 28.4, 25.2, 21.4, 17.8; IR (neat) ν (cm^{-1}) 3289, 2116, 1598, 1429; MS (EI): m/z (%) 250 $[(M-H)^+$, 0.48], 155 (100).

10: oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2 H, ArH), 7.31 (d, J =

8.0 Hz, 2 H, ArH), 5.02-4.85 (m, 1 H, NH), 3.25 (s, 1 H, ≡CH), 2.96 (q, *J* = 6.5 Hz, 2 H, NCH_2), 2.67 (t, *J* = 7.0 Hz, 2 H, CH_2), 2.43 (s, 3 H, CH_3), 1.87-1.78 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.2, 143.5, 136.7, 129.7, 127.0, 81.1, 79.1, 42.11, 42.09, 23.3, 21.5; IR (neat) *v* (cm^{-1}) 3269, 1682, 1598, 1425, 1376, 1359, 1325, 1306; MS (EI): *m/z* (%) 265 (M^+, 100); HRMS (ESI) Calcd for $C_{13}H_{15}NNaO_3S$ [$(M + Na)^+$]: 288.0665; Found: 288.0667.

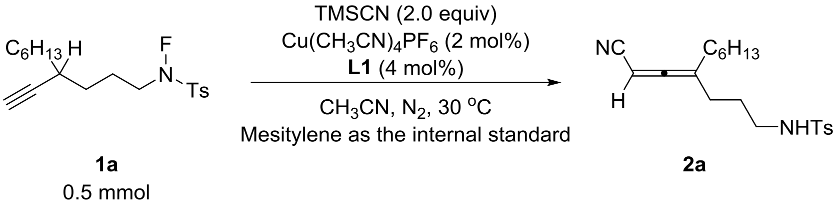
6.3.2. The reaction of **S3ag** under the standard conditions using O_2 instead of N_2. (zdj-5-154)



To a 25 mL flame-dried Schlenk tube was added **L1** (2.9 mg, 0.008 mmol). Then the Schlenk tube was taken to the glove box, $Cu(CH_3CN)_4PF_6$ (1.4 mg, 0.004 mmol), and CH_3CN (1 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **S3ag** (50.1 mg, 0.4 mmol) and CH_3CN (1 mL). The tube was taken out from the glove box. The resulting mixture was frozen with a liquid nitrogen bath and the nitrogen inside the tube was completely replaced with O_2 using a oxygen balloon for three times. The Schlenk tube was then allowed to stand until the mixture was warmed up to room temperature followed by the addition of TMSCN (50 μL, d = 0.793 g/mL, 39.7 mg, 0.4 mmol). The resulting mixture was stirred at 30 °C for 19 hours as monitored by TLC and filtrated through a short column of silica gel eluted with ethyl acetate (10 mL × 3). After evaporation, 3.6 μL of CH_3NO_2 was added as the internal standard: no signal of **10** and 92% recovery of **S3ag** were determined by ^1H NMR analysis of the crude product.

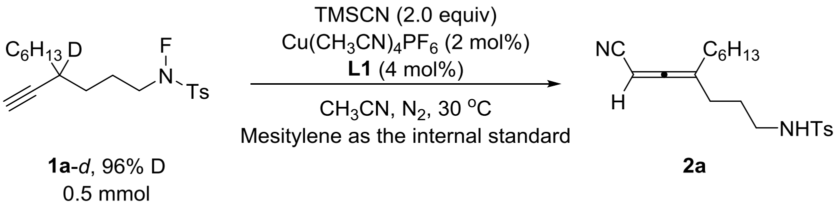
6.4. The Kinetic Isotopic Effect Experiments

6.4.1. Monitoring the Reaction of **1a** afforded **2a**.



To a 25 mL flame-dried Schlenk tube with a polytetrafluoroethylene plug was added **L1** (7.2 mg, 0.02 mmol). Then the Schlenk tube was taken into a glove box, $Cu(CH_3CN)_4PF_6$ (3.7 mg, 0.01 mmol) and CH_3CN (2.5 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **1a** (176.7 mg, 0.5 mmol), CH_3CN (2.5 mL), and TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol). Next, mesitylene (23 μL) was added as the internal standard. The tube was taken out from the glove box, the resulting mixture was stirred at 30 °C. Analiquot of the resulting mixture was taken at each indicated time shown in **Table S5**.

6.4.2. Monitoring the Reaction of **1a-*d*** afforded **2a**.



To a 25 mL flame-dried Schlenk tube with a polytetrafluoroethylene plug were added **L1** (7.1 mg, 0.02 mmol). Then the Schlenk tube was taken into a glove box, $Cu(CH_3CN)_4PF_6$ (3.8 mg, 0.01 mmol) and CH_3CN (2.5 mL) were added. The resulting mixture was stirred for 30 minutes followed by the sequential addition of **1a**-*d* (96% D, 177.2 mg, 0.5 mmol), CH_3CN (2.5 mL), and TMSCN (125 μL, d = 0.793 g/mL, 99.1 mg, 1.0 mmol). Next, mesitylene (23 μL) was added as the internal standard. The tube was taken out from the glove box, the resulting mixture was stirred at 30 °C. Analiquot of the resulting mixture was taken at each indicated time shown in **Table S5**.

Table S5. Monitoring the copper-catalyzed propargylic C-H cyanation of **1a** and **1a**-*d* under the standard conditions.

Entry	Reaction time (h)	NMR Yield of **2a** (%)	NMR Yield of **2a**-*d* (%)
1	0.5	5	3
2	1	10	7
3	1.5	14	10
4	2	20	13
5	2.5	24	16

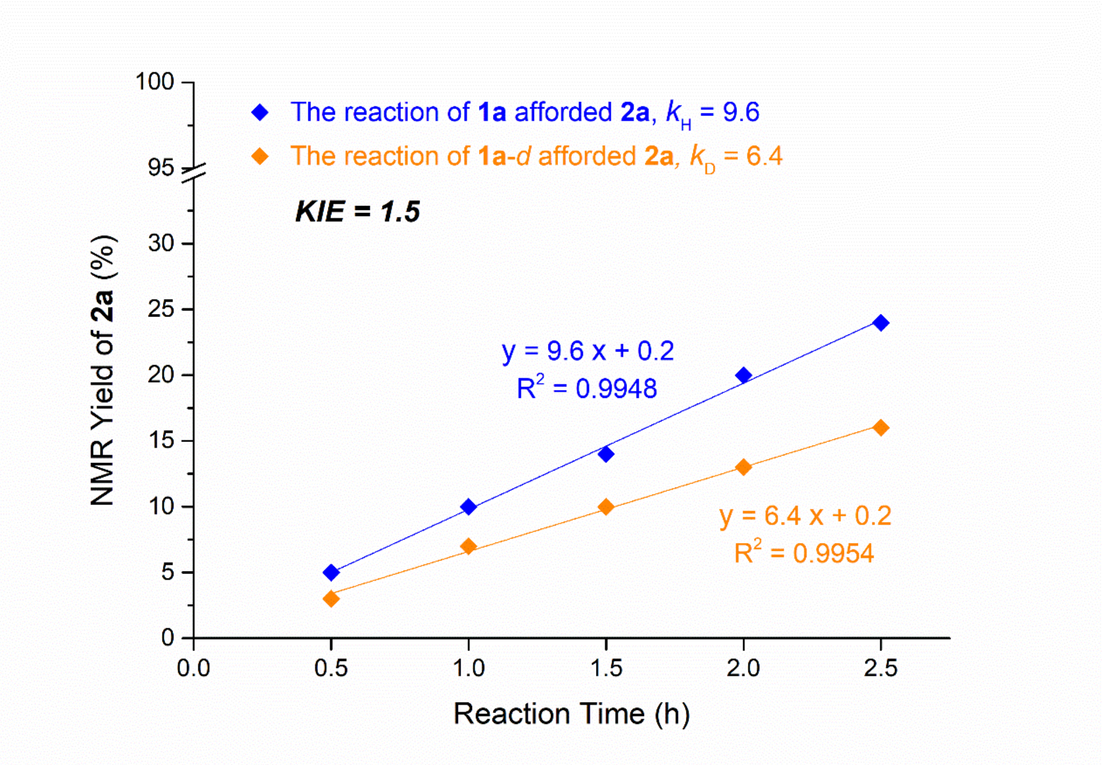
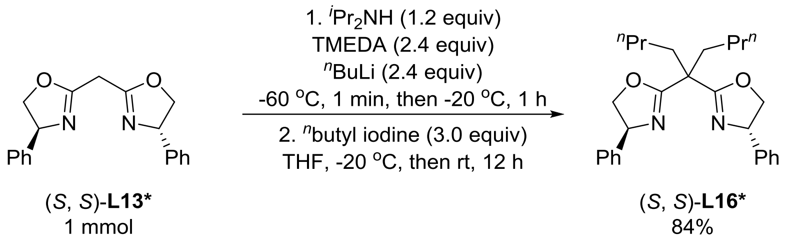


Figure S1. The Kinetic Isotope Effect Experiments

7. Preliminary Result on the Asymmetric Version

7.1. Synthesis of Chiral Ligands

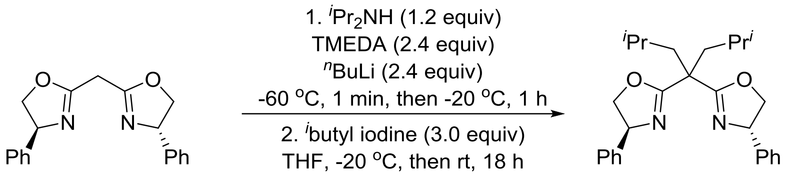
7.1.1. Synthesis of (4*S*,4'*S*)-2,2'-(nonane-5,5-diyl)bis(4-phenyl-4,5-dihydrooxazole) (*S*,*S*)-**L16*** (zdj-6-011)



Typical Procedure VII: To a 100 mL flame-dried Schlenk flask were added a solution of (*S*,*S*)-**L13*** (307.8 mg, 1 mmol) in THF (18 mL), TMEDA (279.4 mg, 2.4 mmol), and $^{i}Pr_2NH$ (122.0 mg, 1.2 mmol) under a N_2 atmosphere. The resulting solution was cooled down to -60 °C and ^{n}BuLi (2.4 M in hexane, 1.0 mL, 2.4 mmol) was added dropwise at -60 °C within 1 minute. The resulting mixture was transfer to a -20 °C cooling bath and stirred at that temperature for 1 hour followed by the addition of ^{n}butyl iodine (555.0 mg, 3 mmol). The cooling bath was removed, the resulting mixture was stirred at room temperature for 12 hours as monitored by TLC, quenched with H_2O (20 mL) slowly, and extracted with ethyl acetate (20 mL × 3). The combined organic layer was washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtrated, and concentrated in vacuo. The crude residual was purified by chromatography on silica gel [eluent: petroleum ether/ethyl acetate = 3/1 (320 mL)] to afford (*S*, *S*)-**L16*** (351.6 mg, 84%) as an oil: $[\alpha]_D^{19.9}$= -147.5 (*c* = 0.975, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.30 (m, ArH, 4 H), 7.30-7.23 (m, ArH, 6 H), 5.24 (dd, J_1 = 10.3 Hz, J_2 = 8.3 Hz, 2 H, one proton OCH_2 × 2), 4.66 (dd, J_1 = 10.0 Hz, J_2 = 8.5 Hz, 2 H, one proton OCH_2 × 2), 4.12 (t, *J* = 8.3 Hz, 2 H, NCH × 2), 2.19-2.03 (m, 4 H, CH_2 × 2), 1.44-1.23 (m, 8 H, CH_2 × 4), 0.93 (t, *J* = 7.3 Hz, 6 H, CH_3 × 2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 142.4, 128.6, 127.5, 126.7, 75.0, 69.6, 46.1, 32.3, 26.2, 22.9, 14.0; IR (neat) *ν* (cm^{-1}) 1653, 1494, 1455; MS (EI): *m/z* (%) 375 [$(M - C_2H_5)^+$, 10.77], 319 (100); Anal. Calcd.

for $C_{27}H_{34}N_2O_2$ (%): C, 77.48; H, 8.19, N, 6.69; Found: C, 77.21; H, 8.06, N, 6.52.

7.1.2. Synthesis of (4*S*,4'*S*)-2,2'-(2,6-dimethylheptane-4,4-diyl)bis(4-phenyl-4,5-dihydrooxazole) (*S*,*S*)-**L17***. (zdj-6-027)

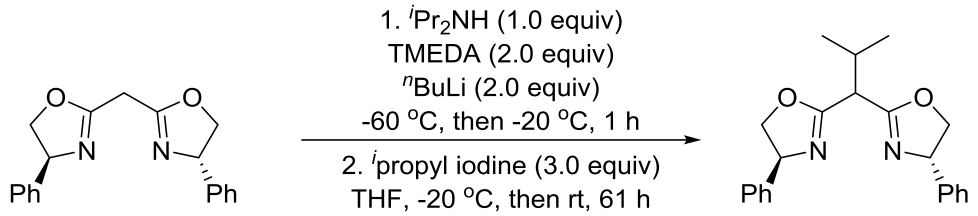


(*S*, *S*)-**L13***
1 mmol

(*S*, *S*)-**L17***
53%

Following Typical Procedure VII: The reaction of (*S*, *S*)-**L13*** (308.0 mg, 1 mmol), TMEDA (278.0 mg, 2.4 mmol), ^{i}Pr$_2$NH (121.9 mg, 1.2 mmol), ^{n}BuLi (2.4 M in hexane, 1.0 mL, 2.4 mmol), and ^{i}butyl iodine (553.4 mg, 3 mmol) in THF (18 mL) afforded (*S*,*S*)-**L17*** (221.4 mg, 53%). [eluent: petroleum ether/ethyl acetate = 5/2 (350 mL)]: $[\alpha]_D^{20}$= -203.1 (c = 0.905, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.18 (m, ArH, 10 H), 5.20 (dd, J_1 = 10.2 Hz, J_2 = 8.4 Hz, 2 H, one proton OCH_2 × 2), 4.64 (dd, J_1 = 10.2 Hz, J_2 = 8.4 Hz, 2 H, one proton OCH_2 × 2), 4.08 (t, J = 8.4 Hz, 2 H, NCH × 2), 2.25-2.09 (m, 4 H, CH_2 × 2), 1.87-1.72 (m, 2 H, CH × 2), 0.97 (t, J = 6.8 Hz, 12 H, CH_3 × 4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 142.3, 128.6, 127.5, 126.7, 74.8, 69.7, 45.2, 40.9, 24.8, 24.1, 23.0; IR (neat) v (cm^{-1}) 1651, 1494, 1470, 1454; MS (EI): *m/z* (%) 375 [(M – ^{i}Pr)$^+$, 20.18], 319 (100); HRMS (ESI) Calcd for $C_{27}H_{35}N_2O_2$ (%): [(M + H)$^+$]: 419.2693; Found: 419.2694.

7.1.3. Synthesis of (4*S*,4'*S*)-2,2'-(2-methylpropane-1,1-diyl)bis(4-phenyl-4,5-dihydrooxazole) (*S*, *S*)-**L20***. (zdj-5-157)



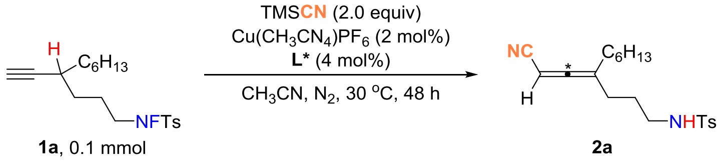
(*S*, *S*)-**L13***
1 mmol

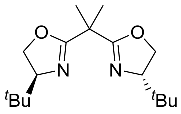
(*S*, *S*)-**L20***
59%

Following Typical Procedure VII, the reaction of (*S*, *S*)-**L13*** (304.9 mg, 1 mmol), TMEDA (0.3 mL, d = 0.775 g/mL, 232.5 mg, 2 mmol), $^{i}Pr_2NH$ (0.14 mL, d = 0.718 g/mL, 100.5 mg, 1 mmol), $^{n}BuLi$ (2.4 M in hexane, 0.84 mL, 2 mmol), and ^{i}propyl iodine (0.3 mL, d = 1.703 g/mL, 510.9 mg, 3 mmol) afforded (*S*, *S*)-**L20*** (203.0 mg, 59%) as an oil [eluent: petroleum ether/ethyl acetate = 3/2 (400 mL)]. (This reaction was quenched with a saturated aqueous solution of NH_4Cl): $[\alpha]_D^{20}$= -96.7 (*c* = 0.91, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.22 (m, ArH, 10 H), 5.34-5.18 (m, 2 H, one proton $OCH_2 \times 2$), 4.75-4.63 (m, 2 H, one proton $OCH_2 \times 2$), 4.16 (dt, J_1 = 12.9 Hz, J_2 = 8.3 Hz, 2 H, NCH × 2), 3.47 (d, *J* = 9.2 Hz, 1 H, CH), 2.61-2.44 (m, 1 H, CH), 1.14 (d, *J* = 6.8 Hz, 6 H, $CH_3 \times 2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 142.2, 142.1, 128.6, 127.5, 126.6, 74.94, 74.90, 69.6, 69.4, 46.8, 29.3, 20.8, 20.7; IR (neat) *v* (cm^{-1}) 1660, 1494, 1471, 1455; MS (EI): *m/z* (%) 348 (M^+, 7.30), 306 (100); HRMS (ESI) Calcd for $C_{22}H_{25}N_2O_2$ [$(M + H)^+$]: 349.1911; Found: 349.1913.

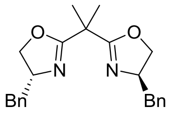
7.2. Optimization of Reaction Conditions with Chiral Ligands

Table S6. Optimization of Chiral Ligands [a, b, c]

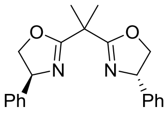




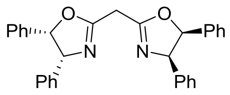
L1*
2a: 25% (8% ee)
recovery of **1a**: 67%



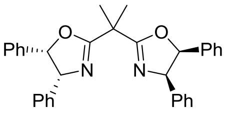
L2*
2a: 72% (-4% ee)
recovery of **1a**: 0%



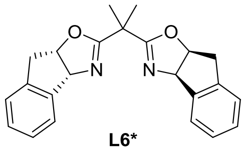
L3*
2a: 65% (-29% ee)
recovery of **1a**: 9%



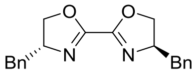
L4*
2a: 35% (16% ee)
recovery of **1a**: 55%



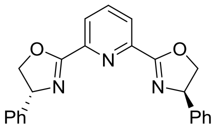
L5*
2a: 27% (22% ee)
recovery of **1a**: 56%



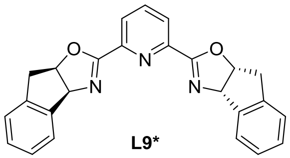
L6*
2a: 82% (18% ee)
recovery of **1a**: 0%



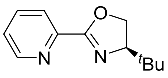
L7*
2a: 3% (n.d.)
recovery of **1a**: 88%



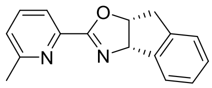
L8*
2a: 12% (9% ee)
recovery of **1a**: 81%



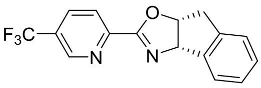
L9*
2a: 17% (-8% ee)
recovery of **1a**: 67%



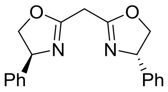
L10*
2a: 59% (0% ee)
recovery of **1a**: 0%



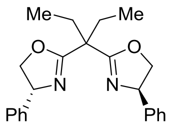
L11*
2a: 84% (-3% ee)
recovery of **1a**: 11%



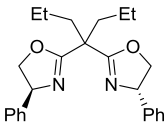
L12*
2a: 26% (-2% ee)
recovery of **1a**: 50%



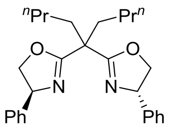
L13*
2a: 49% (-16% ee)
recovery of **1a**: 29%



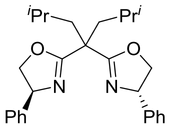
L14*
2a: 71% (34% ee)
recovery of **1a**: 0%



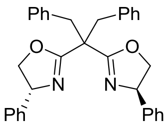
L15*[d]
2a: 83% (-36% ee)
recovery of **1a**: 0%



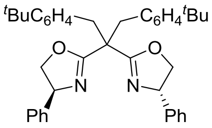
L16*
2a: 79% (-36% ee)
recovery of **1a**: 7%



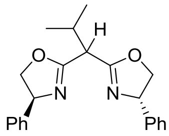
L17*
2a: 39% (-34% ee)
recovery of **1a**: 33%



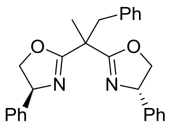
L18*
2a: 67% (11% ee)
recovery of **1a**: 7%



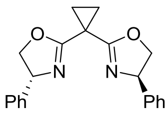
L19*
2a: 50% (-9% ee)
recovery of **1a**: 43%



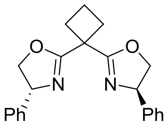
L20*
2a: 76% (-21% ee)
recovery of **1a**: 0%



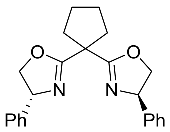
L21*
2a: 64% (-26% ee)
recovery of **1a**: 9%



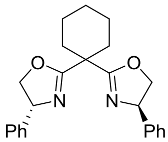
L22*
2a: 76% (21% ee)
recovery of **1a**: 0%



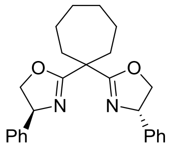
L23*
2a: 42% (24% ee)
recovery of **1a**: 37%



L24*
2a: 69% (29% ee)
recovery of **1a**: 22%



L25*
2a: 3% (n.d.)
recovery of **1a**: 94%

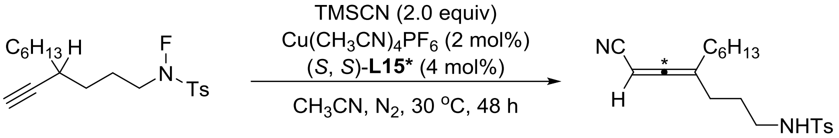


L26*
2a: 10% (-23% ee)
recovery of **1a**: 86%

[a] All reactions were run on 0.1 mmol scale in CH_3CN (1 mL) at 30 °C for 48 hours under a nitrogen atmosphere. [b] Yield and recovery were determined via crude ^1H NMR analysis with CH_3NO_2 as internal standard. [c] ee values of isolated **2a** was determined by chiral HPLC. [d] 0.2 mmol scale and mesitylene was used as internal standard.

7.3. Catalytic Propargylic C-H Cyanation with Chiral Ligands.

7.3.1. Asymmetric Synthesis of (-)-**2a**. (zdj-7-011)

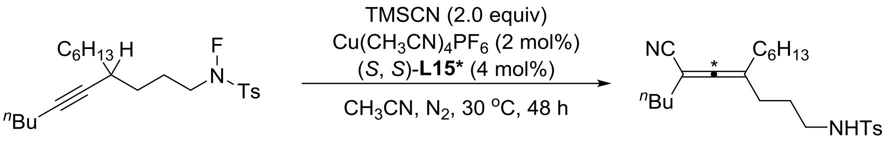


1a
0.2 mmol

(-)-**2a**
79%, -36% ee

Following **Typical Procedure VI**, the reaction of **1a** (70.9 mg, 0.2 mmol), TMSCN (50 μL, d = 0.793 g/mL, 39.7 mg, 0.4 mmol), Cu(CH$_3$CN)$_4$PF$_6$ (1.5 mg, 0.004 mmol), and (*S*,*S*)-**L15*** (3.1 mg, 0.008 mmol) in CH$_3$CN (1 + 1 mL) afforded (-)-**2a** (57.0 mg, 79%) as an oil [eluent: petroleum ether/ethyl acetate = 4/1 (400 mL)]: -36% ee (HPLC conditions: Chiralcel IC column, *n*-Hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 214 nm, t_R(major) = 16.2 min, t_R(minor) = 14.6 min); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.4 Hz, 2 H, ArH), 7.33 (d, *J* = 8.1 Hz, 2 H, ArH), 5.20-5.11 (m, 1 H, =CH), 4.72 (t, *J* = 6.0 Hz, 1 H, NH), 2.96 (q, *J* = 6.6 Hz, 2 H, NCH$_2$), 2.44 (s, 3 H, CH$_3$), 2.12-1.95 (m, 4 H, CH$_2$ × 2), 1.70-1.55 (m, 2 H, CH$_2$), 1.46-1.19 (m, 8 H, CH$_2$ × 4), 0.89 (t, *J* = 6.8 Hz, 3 H, CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 212.7, 143.6, 136.8, 129.8, 127.0, 114.2, 110.7, 68.3, 42.4, 31.7, 31.5, 28.7, 28.5, 27.1, 26.9, 22.5, 21.5, 14.0; IR (neat) *v* (cm^{-1}) 3282, 2223, 1957, 1598, 1455, 1328; MS (EI): *m/z* (%) 360 (M$^+$, 29.9), 205 (100); HRMS (ESI) Calcd for C$_{20}$H$_{28}$N$_2$NaO$_2$S [(M + Na)$^+$]: 383.1764; Found: 383.1764.

7.3.2. Asymmetric Synthesis of (+)-**2r**. (zdj-7-015)



1r
0.2 mmol

(+)-**2r**
33%, 23% ee

Following **Typical Procedure VI**, the reaction of **1r** (84.1 mg, 98% purity, 0.2 mmol), TMSCN (50 μL, d = 0.793 g/mL, 39.7 mg, 0.4 mmol), $Cu(CH_3CN)_4PF_6$ (1.5 mg, 0.004 mmol), and (*S*,*S*)-**L15*** (3.2 mg, 0.008 mmol) in CH_3CN (1 + 1 mL) afforded (+)-**2a** (27.3 mg, 79%) as an oil [eluent: petroleum ether/ethyl acetate = 11/2 (390 mL) to 5/1 (60 mL)]: -23% ee (HPLC conditions: Chiralcel IC column, *n*-Hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 214 nm, t_R(major) = 9.8 min, t_R(minor) = 9.0 min); $[\alpha]_D^{20}$= + 5.0 (*c* = 1.365, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2 H, ArH), 7.32 (d, *J* = 8.1 Hz, 2 H, ArH), 4.97-4.80 (m, 1 H, NH), 2.95 (q, *J* = 6.7 Hz, 2 H, NCH_2), 2.43 (s, 3 H, CH_3), 2.17-1.91 (m, 6 H, CH_2 × 3), 1.65-1.53 (m, 2 H, CH_2), 1.51-1.18 (m, 12 H, CH_2 × 6), 0.96-0.82 (m, 6 H, CH_3 × 2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.3, 143.4, 136.8, 129.7, 127.0, 116.4, 110.4, 83.2, 42.5, 32.2, 31.5, 31.3, 29.8, 29.0, 28.7, 27.3, 27.1, 22.5, 21.8, 21.4, 14.0, 13.6; IR (neat) *ν* (cm^{-1}) 3282, 2928, 2858, 2215, 1952, 1599, 1456, 1328; MS (EI): *m/z* (%) 416 (M^+, 2.38), 261 (100); HRMS (ESI) Calcd for $C_{24}H_{36}N_2NaO_2S$ [$(M + Na)^+$]: 439.2390; Found: 439.2389.

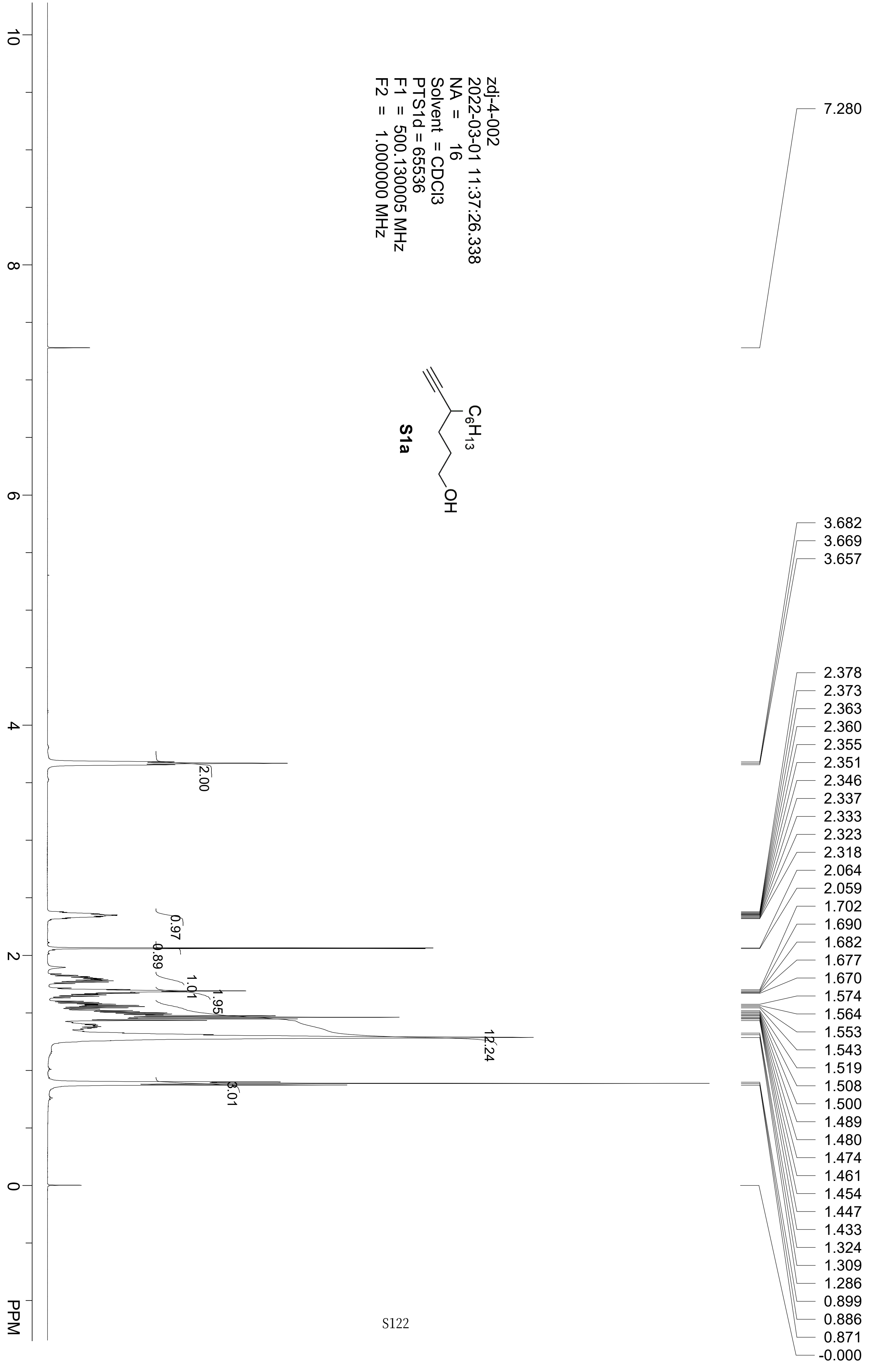
8. References

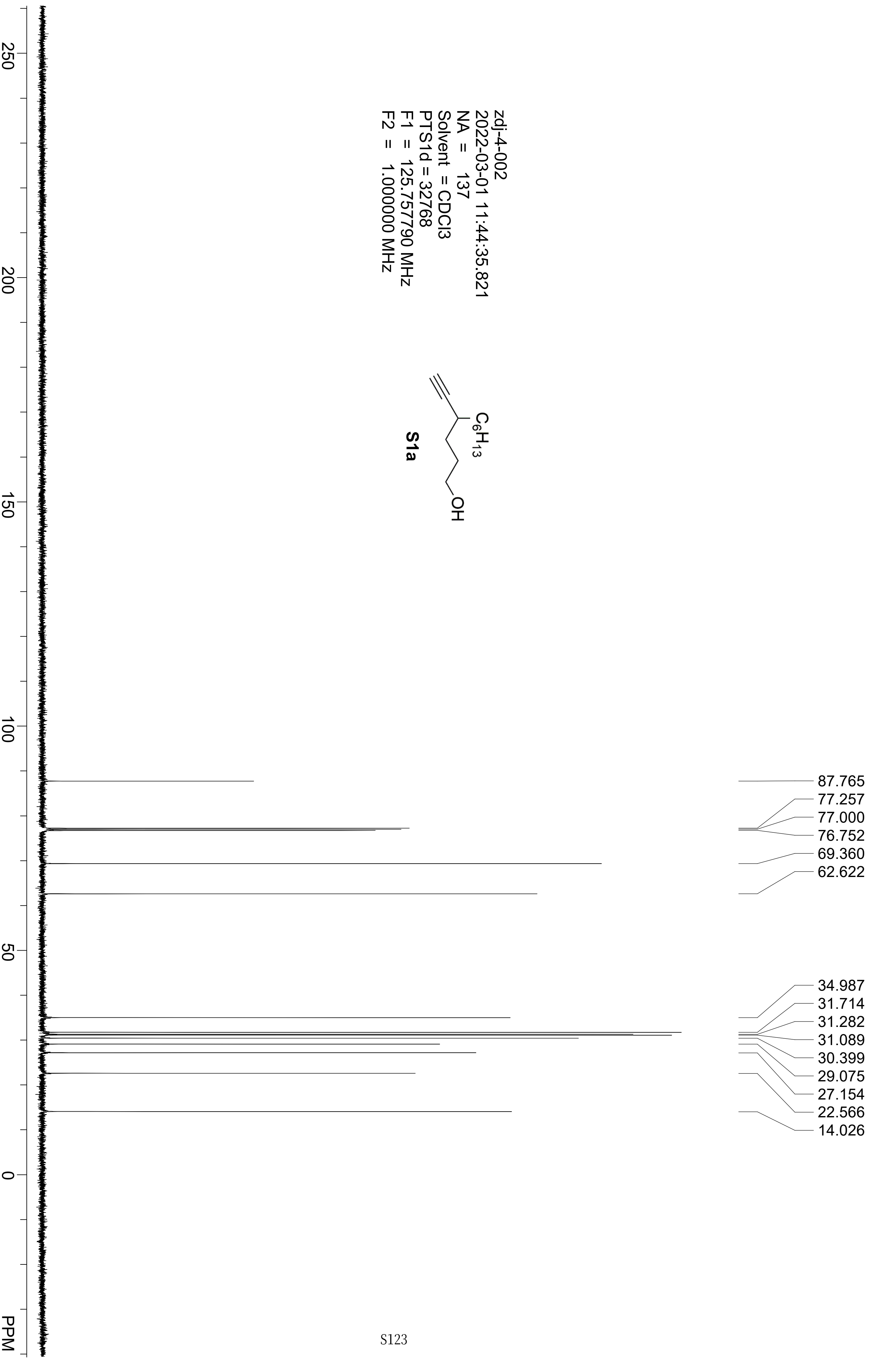
1. Li, S.; Wang, Y.; Wu, Z.; Shi, W.; Lei, Y.; Davies, P. W.; Shu, W. *Org. Lett.* **2021**, *23*, 7209.
2. Feldman, K. S.; Bruendl, M. M.; Schildknegt, K.; Bohnstedt, A. C. *J. Org.*

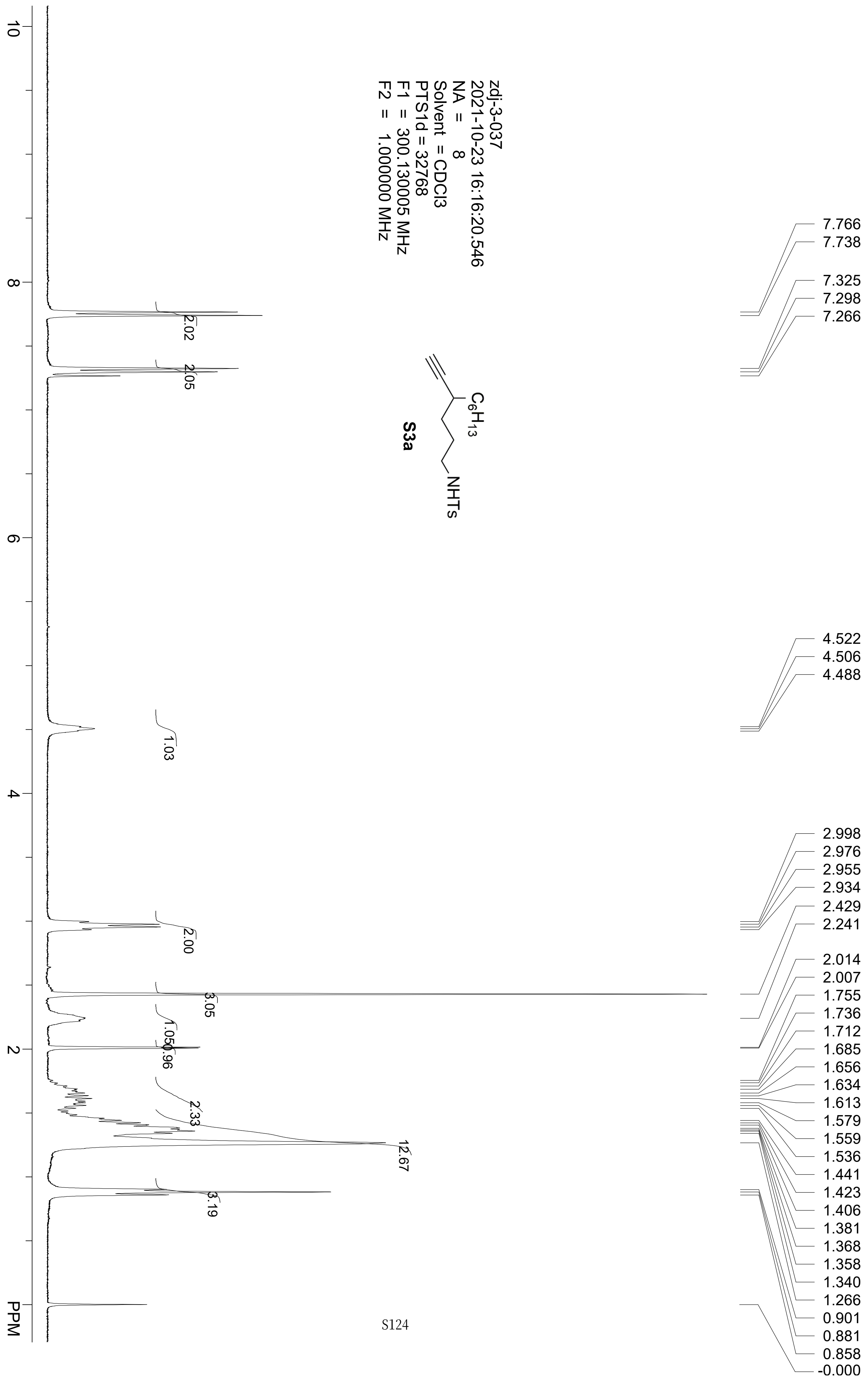
Chem. **1996**, *61*, 5440.

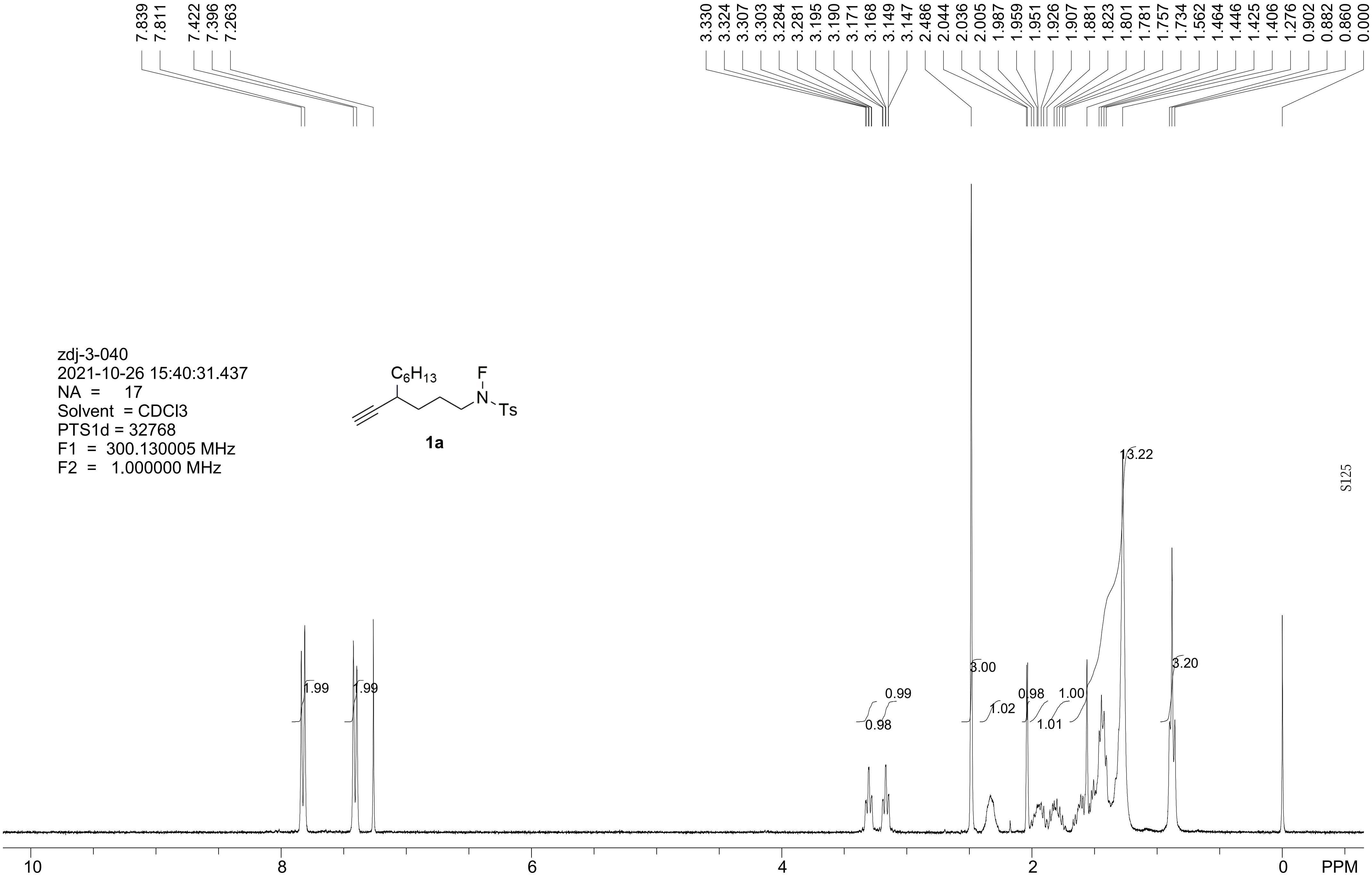
3. Grell, Y.; Demirel, N.; Harms, K.; Meggers, E. *Organometallics* **2019**, *38*, 3852.
4. Joo, J. M.; Yuan, Y.; Lee, C. *J. Am. Chem. Soc.* **2006***, 128,* 14818.
5. Yang, C.-H.; Han, M.; Li, W.; Zhu, N.; Sun, Z.; Wang, J.; Yang, Z.; Li, Y.-M. *Org. Lett.* **2020**, *22*, 5090.
6. Zhang, Z.; Zhang, X.; Nagib, D. A. *Chem* **2019**, *5*, 3127.
7. Kiyotsuka, Y.; Kobayashi, Y. *J. Org. Chem.* **2009**, *74*, 7489.
8. Xu, W.; Wang, G.; Xie, X.; Liu, Y. *Org. Lett.* **2018**, *20*, 3273.
9. Chen, Y.; Wang, J.; Lu, Y. *Chem. Sci.* **2021**, *12*, 11316.
10. Jonasson, C.; Horváth, A.; Bäckvall, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 9600.
11. Nilsson, B. L., Overman, L. E., Read de Alaniz, J., and Rohde, J. M. *J. Am. Chem. Soc*. **2008**, *130*, 11297.

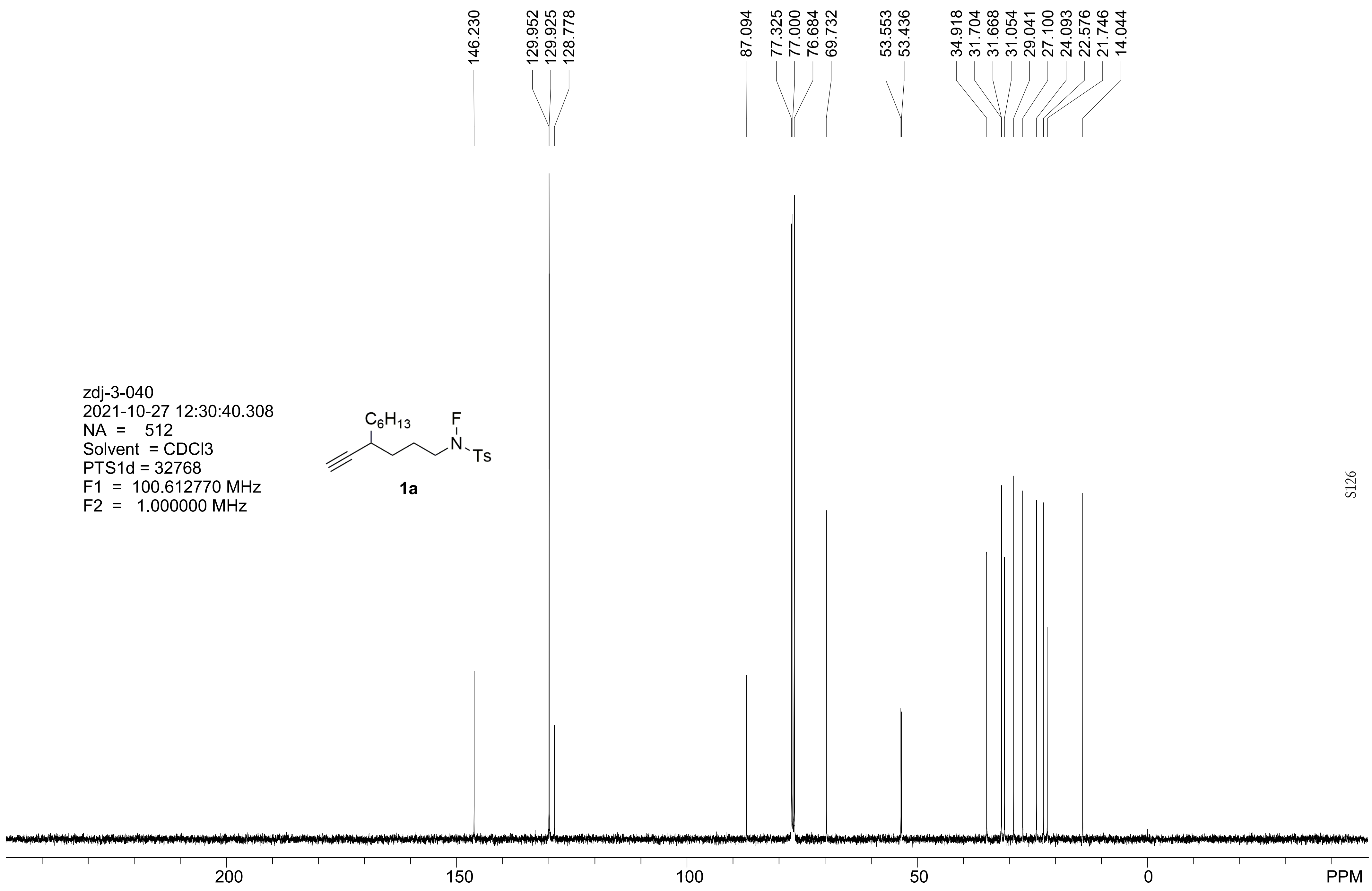
9. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra of the Compounds Prepared

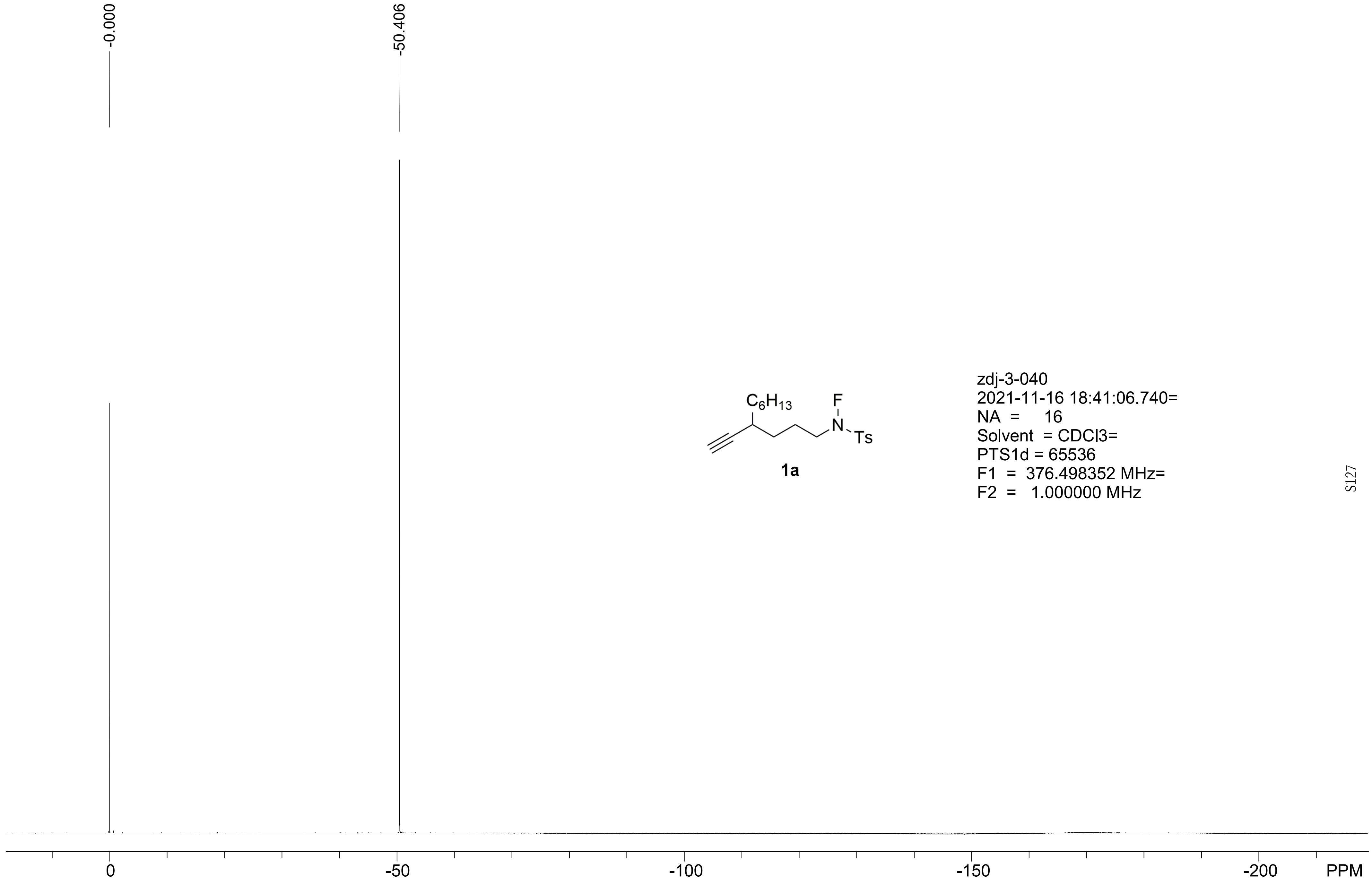



zdj-4-002
2022-03-01 11:44:35.821
NA = 137
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
C6H13
OH
S1a
87.765
77.257
77.000
76.752
69.360
62.622
34.987
31.714
31.282
31.089
30.399
29.075
27.154
22.566
14.026
250
200
150
100
50
0
PPM


zdj-3-037
2021-10-23 16:16:20.546
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C$_6$H$_{13}$
NHTs
S3a
10
8
6
4
2
PPM
2.02
2.05
1.03
2.00
3.05
1.05
0.96
2.33
12.67
3.19
7.766
7.738
7.325
7.298
7.266
4.522
4.506
4.488
2.998
2.976
2.955
2.934
2.429
2.241
2.014
2.007
1.755
1.736
1.712
1.685
1.656
1.634
1.613
1.579
1.559
1.536
1.441
1.423
1.406
1.381
1.368
1.358
1.340
1.266
0.901
0.881
0.858
-0.000

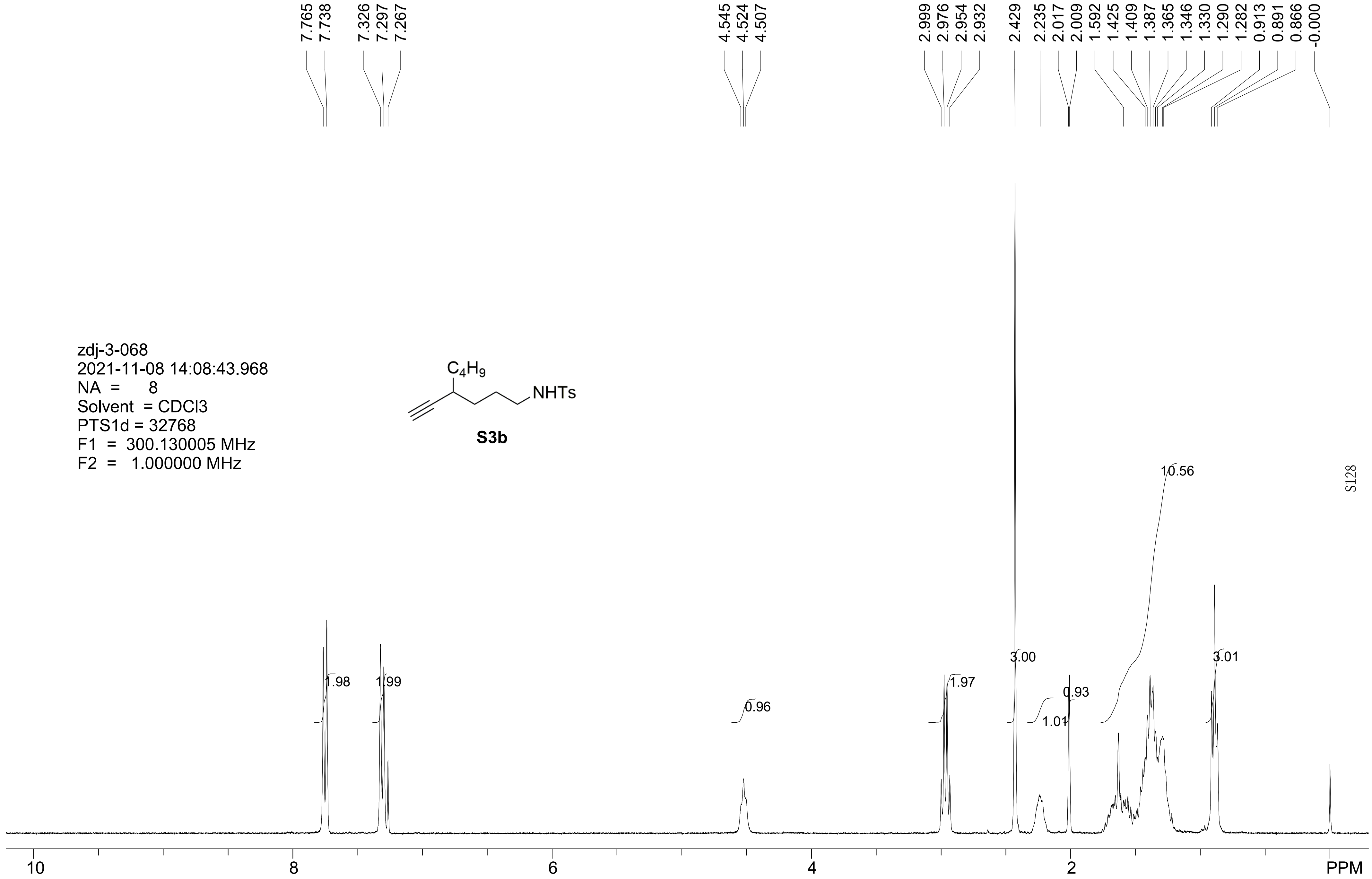
zdj-3-040
2021-10-26 15:40:31.437
NA = 17
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C6H13
F
N
Ts
1a
7.839
7.811
7.422
7.396
7.263
3.330
3.324
3.307
3.303
3.284
3.281
3.195
3.190
3.171
3.168
3.149
3.147
2.486
2.044
2.036
2.005
1.987
1.959
1.951
1.926
1.907
1.881
1.823
1.801
1.781
1.757
1.734
1.562
1.464
1.446
1.425
1.406
1.276
0.902
0.882
0.860
0.000
1.99
1.99
0.99
0.98
3.00
1.02
0.98
1.00
1.01
13.22
3.20
10
8
6
4
2
0
PPM

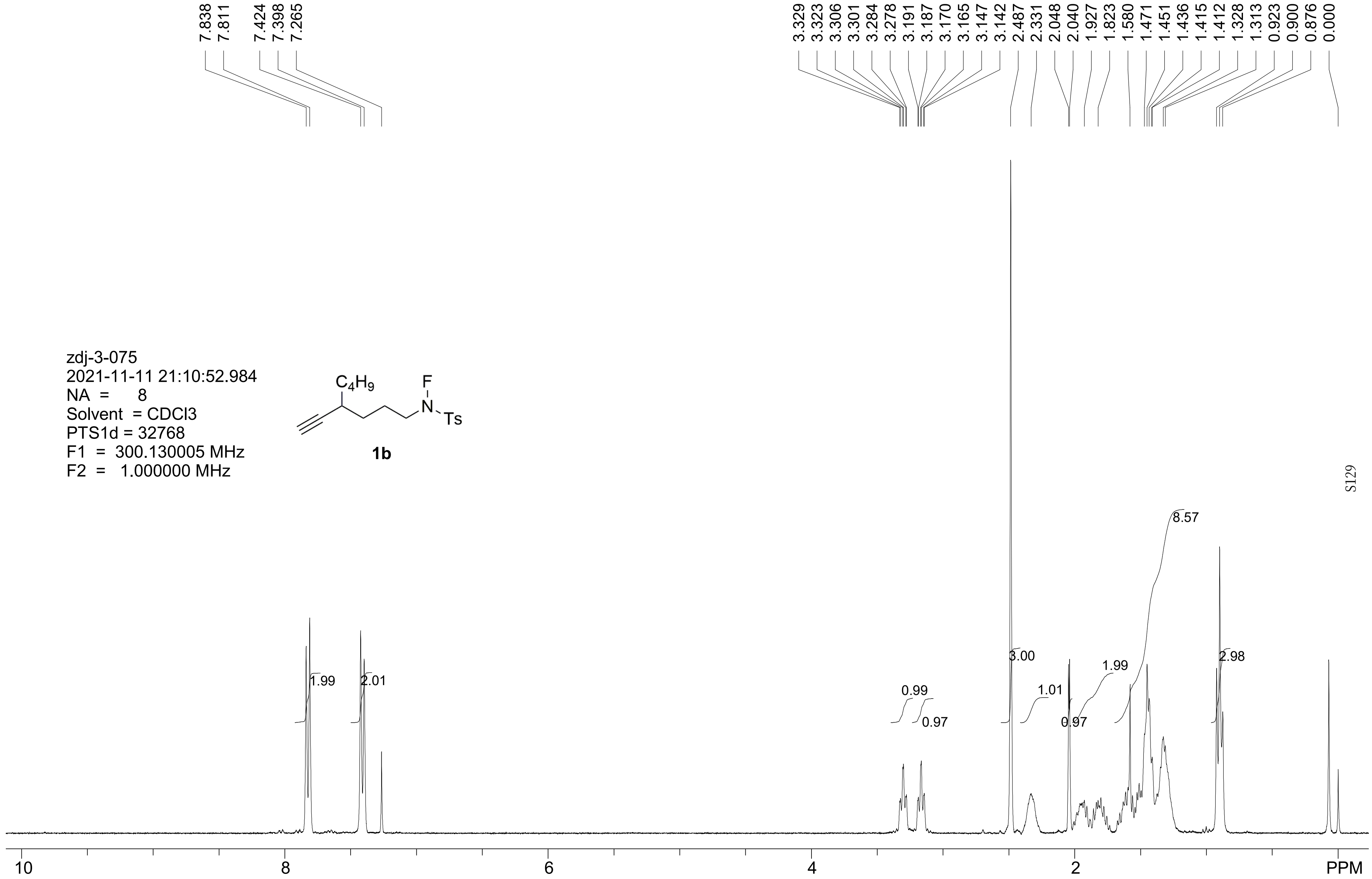

146.230
129.952
129.925
128.778
87.094
77.325
77.000
76.684
69.732
53.553
53.436
34.918
31.704
31.668
31.054
29.041
27.100
24.093
22.576
21.746
14.044
zdj-3-040
2021-10-27 12:30:40.308
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
C6H13
F
N
Ts
1a
200
150
100
50
0
PPM



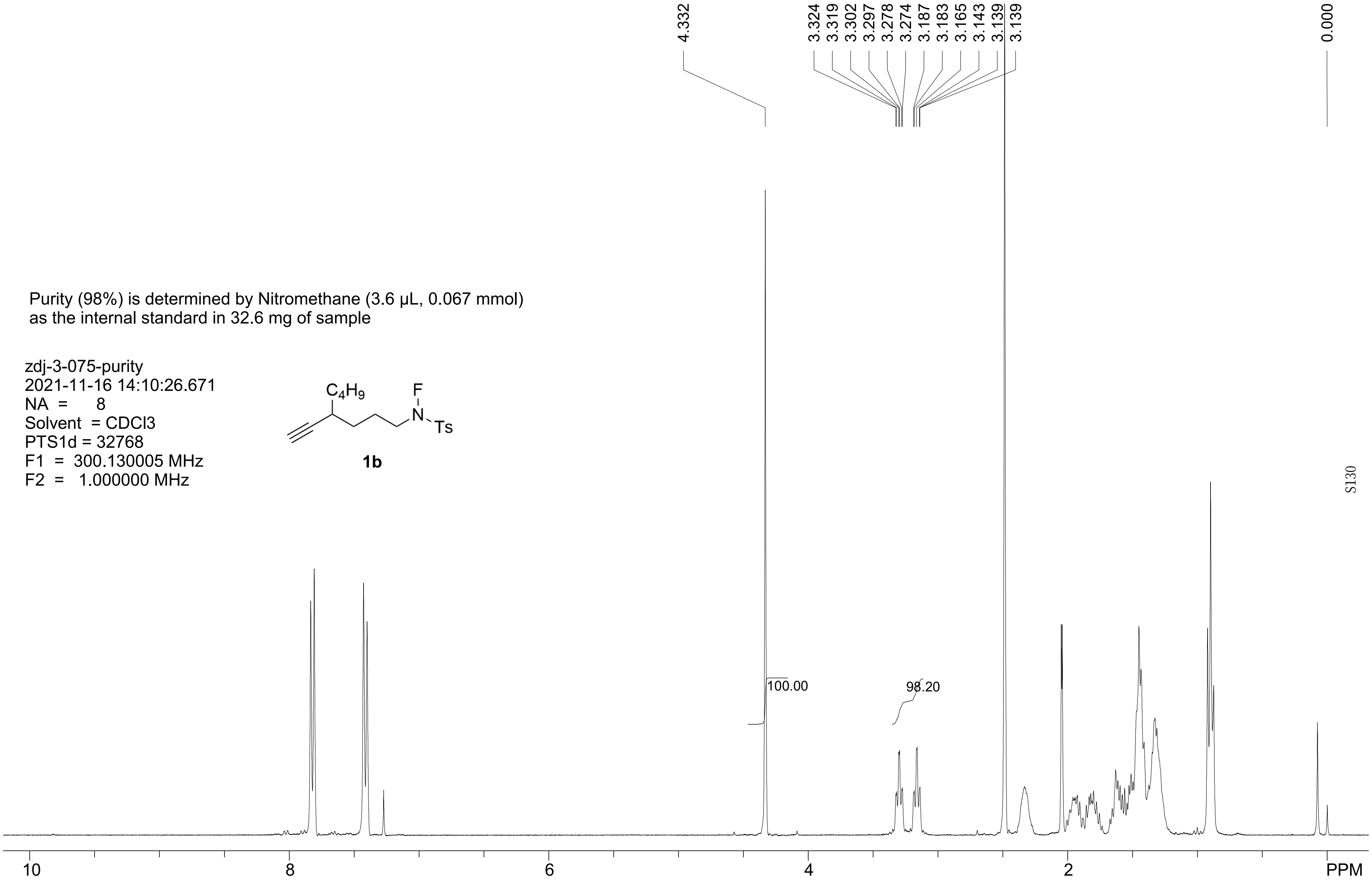
1a

zdj-3-040
2021-11-16 18:41:06.740=
NA = 16
Solvent = CDCl3=
PTS1d = 65536
F1 = 376.498352 MHz=
F2 = 1.000000 MHz


7.765
7.738
7.326
7.297
7.267
4.545
4.524
4.507
2.999
2.976
2.954
2.932
2.429
2.235
2.017
2.009
1.592
1.425
1.409
1.387
1.365
1.346
1.330
1.290
1.282
0.913
0.891
0.866
-0.000
zdj-3-068
2021-11-08 14:08:43.968
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C4H9
NHTs
S3b
1.98
1.99
0.96
1.97
3.00
1.01
0.93
10.56
3.01
10
8
6
4
2
PPM


zdj-3-075
2021-11-11 21:10:52.984
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

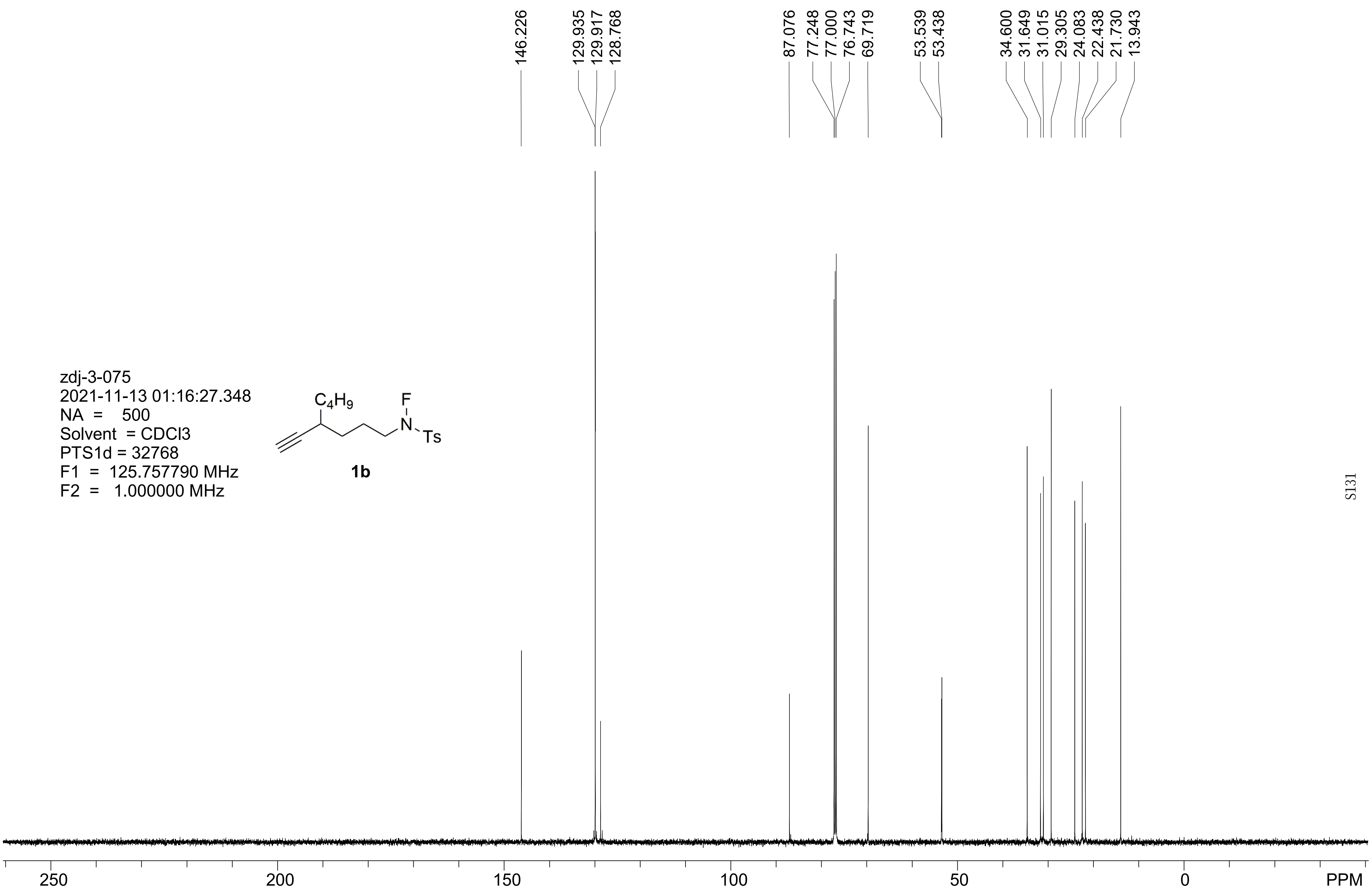
1b

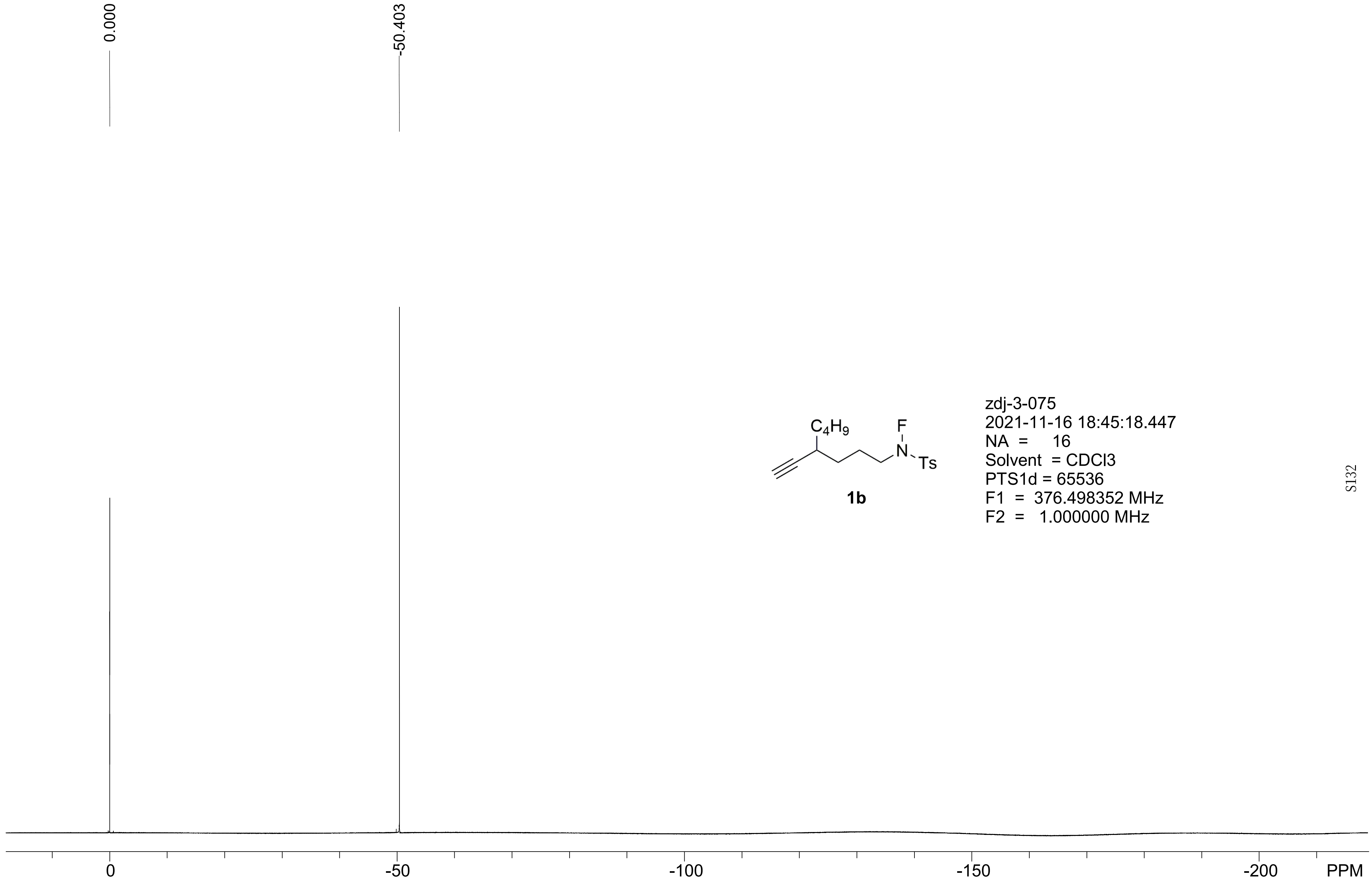


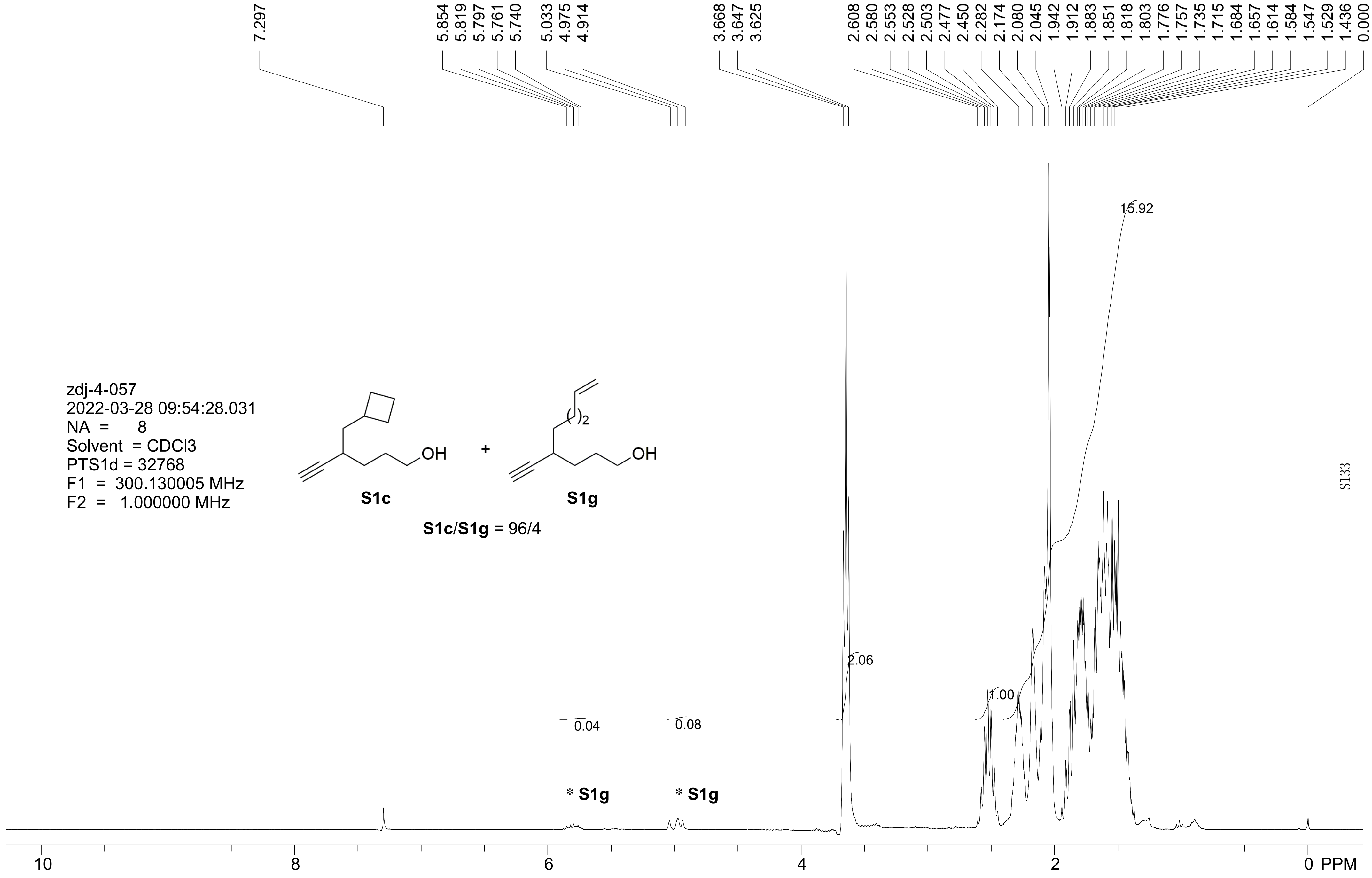
1b

Purity (98%) is determined by Nitromethane (3.6 μL, 0.067 mmol)
as the internal standard in 32.6 mg of sample

zdj-3-075-purity
2021-11-16 14:10:26.671
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz


zdj-3-075
2021-11-13 01:16:27.348
NA = 500
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
C4H9
F
N
Ts
1b
146.226
129.935
129.917
128.768
87.076
77.248
77.000
76.743
69.719
53.539
53.438
34.600
31.649
31.015
29.305
24.083
22.438
21.730
13.943
250
200
150
100
50
0
PPM

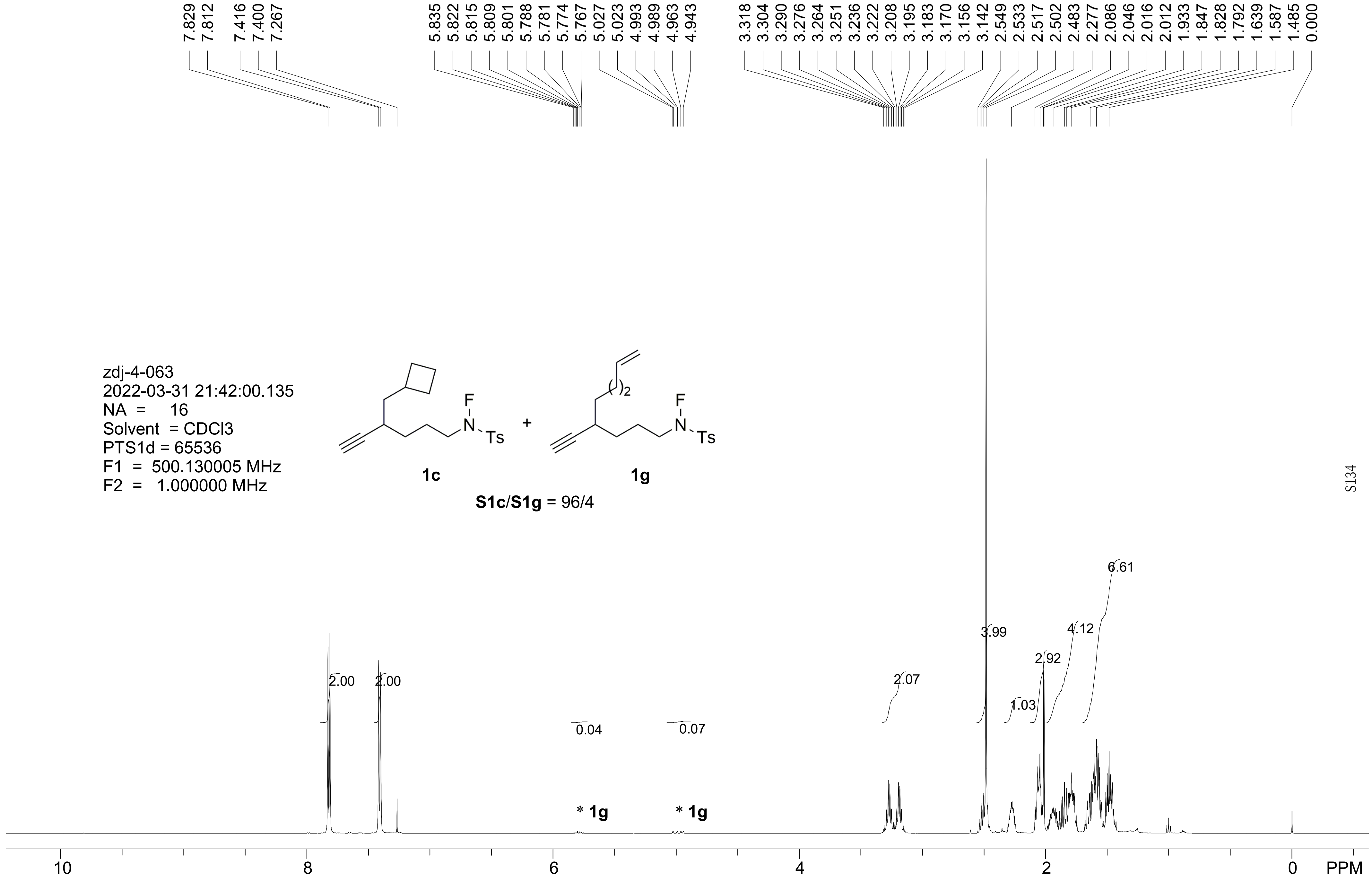

0.000
-50.403
C_4H_9
F
N
Ts
1b
zdj-3-075
2021-11-16 18:45:18.447
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz
0
-50
-100
-150
-200
PPM

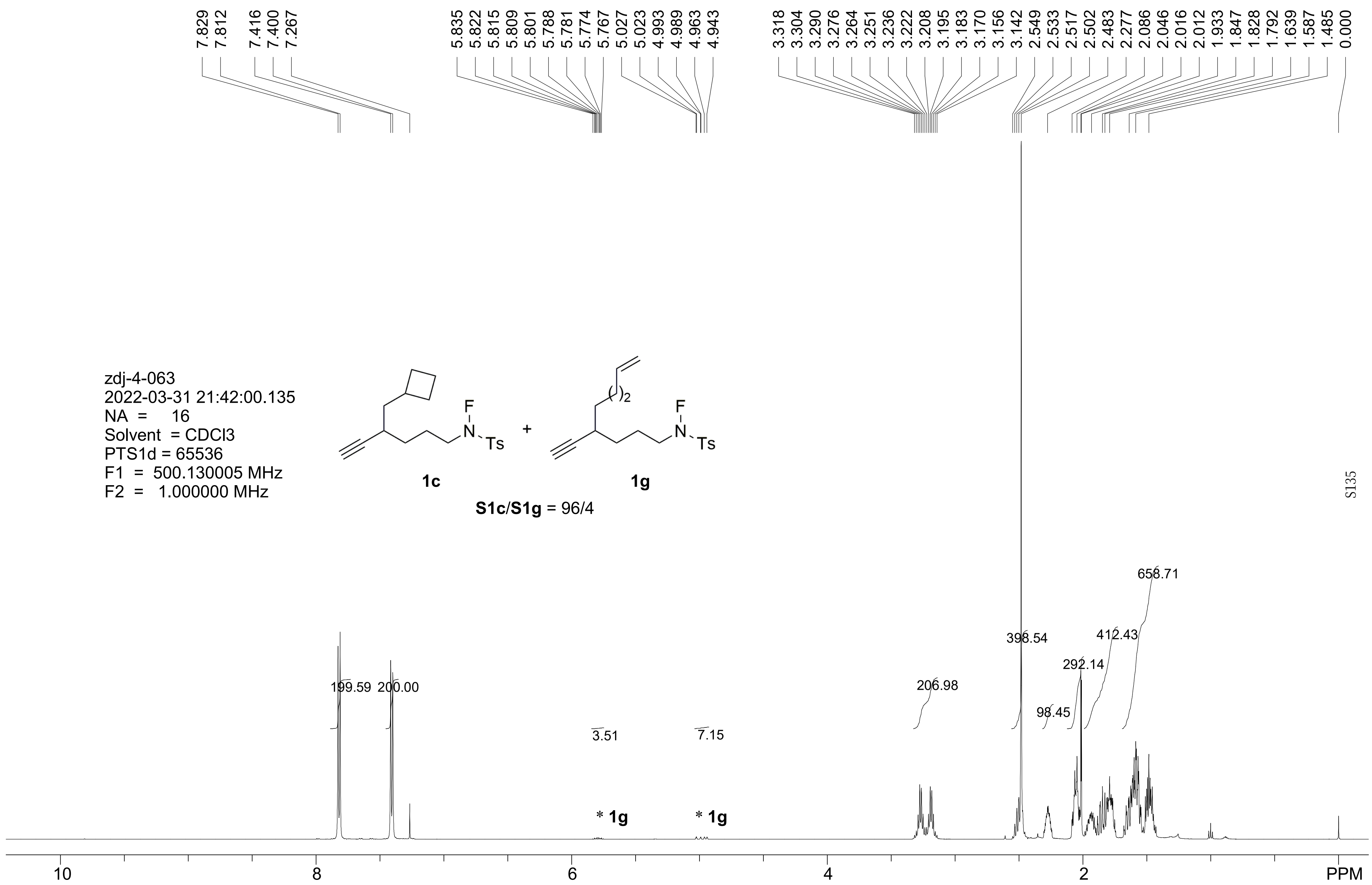


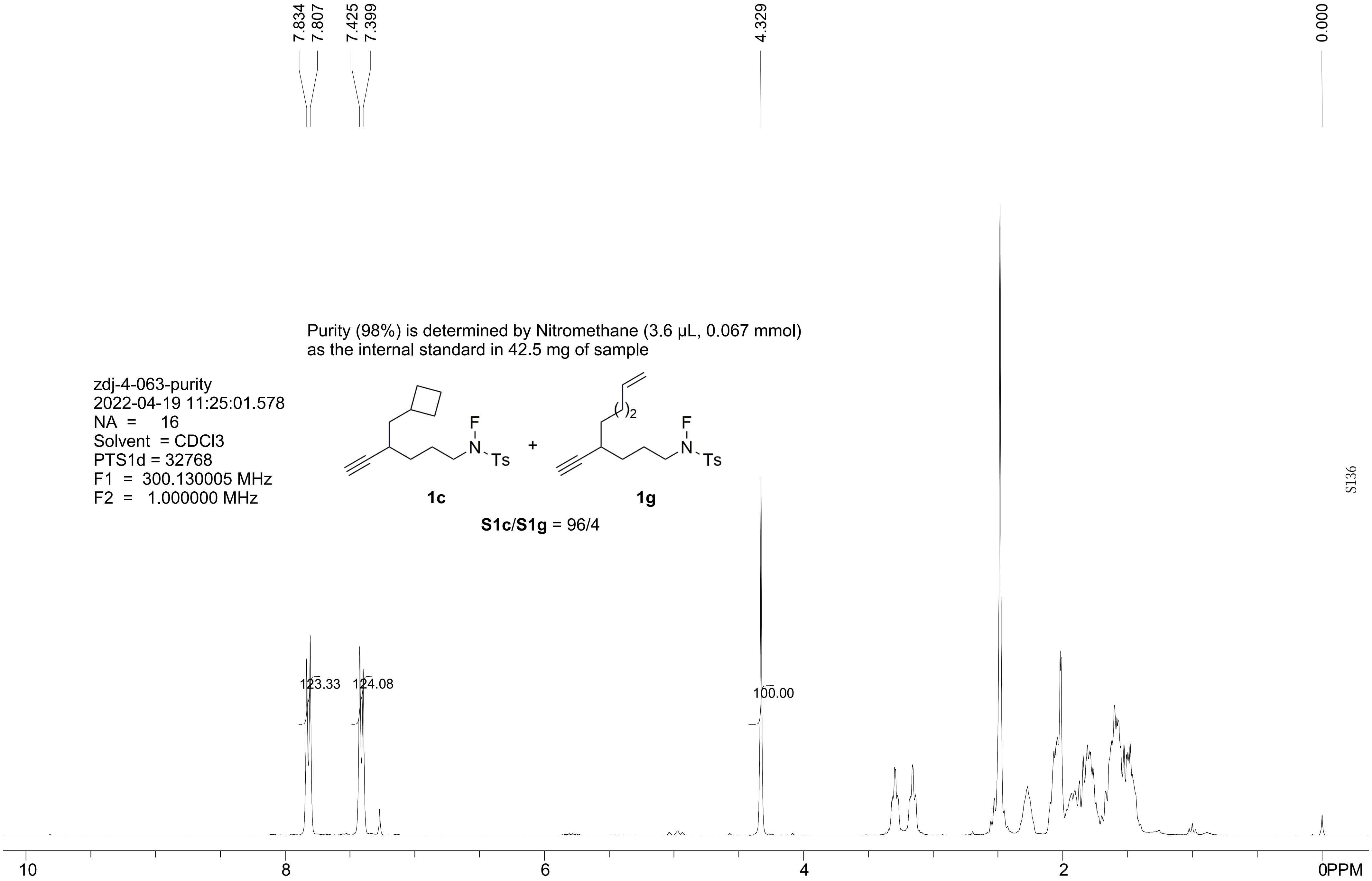
zdj-4-057
2022-03-28 09:54:28.031
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

S1c + **S1g**

S1c/S1g = 96/4


zdj-4-063
2022-03-31 21:42:00.135
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
F
N
Ts
+
F
N
Ts
( )2
1c
1g
S1c/S1g = 96/4
7.829
7.812
7.416
7.400
7.267
5.835
5.822
5.815
5.809
5.801
5.788
5.781
5.774
5.767
5.027
5.023
4.993
4.989
4.963
4.943
3.318
3.304
3.290
3.276
3.264
3.251
3.236
3.222
3.208
3.195
3.183
3.170
3.156
3.142
2.549
2.533
2.517
2.502
2.483
2.277
2.086
2.046
2.016
2.012
1.933
1.847
1.828
1.792
1.639
1.587
1.485
0.000
2.00
2.00
0.04
0.07
2.07
3.99
1.03
2.92
4.12
6.61
* 1g
* 1g
10
8
6
4
2
0
PPM


7.829
7.812
7.416
7.400
7.267
5.835
5.822
5.815
5.809
5.801
5.788
5.781
5.774
5.767
5.027
5.023
4.993
4.989
4.963
4.943
3.318
3.304
3.290
3.276
3.264
3.251
3.236
3.222
3.208
3.195
3.183
3.170
3.156
3.142
2.549
2.533
2.517
2.502
2.483
2.277
2.086
2.046
2.016
2.012
1.933
1.847
1.828
1.792
1.639
1.587
1.485
0.000
zdj-4-063
2022-03-31 21:42:00.135
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
F
N
Ts
+
( )2
F
N
Ts
1c
1g
S1c/S1g = 96/4
199.59
200.00
3.51
7.15
* 1g
* 1g
206.98
398.54
98.45
292.14
412.43
658.71
10
8
6
4
2
PPM



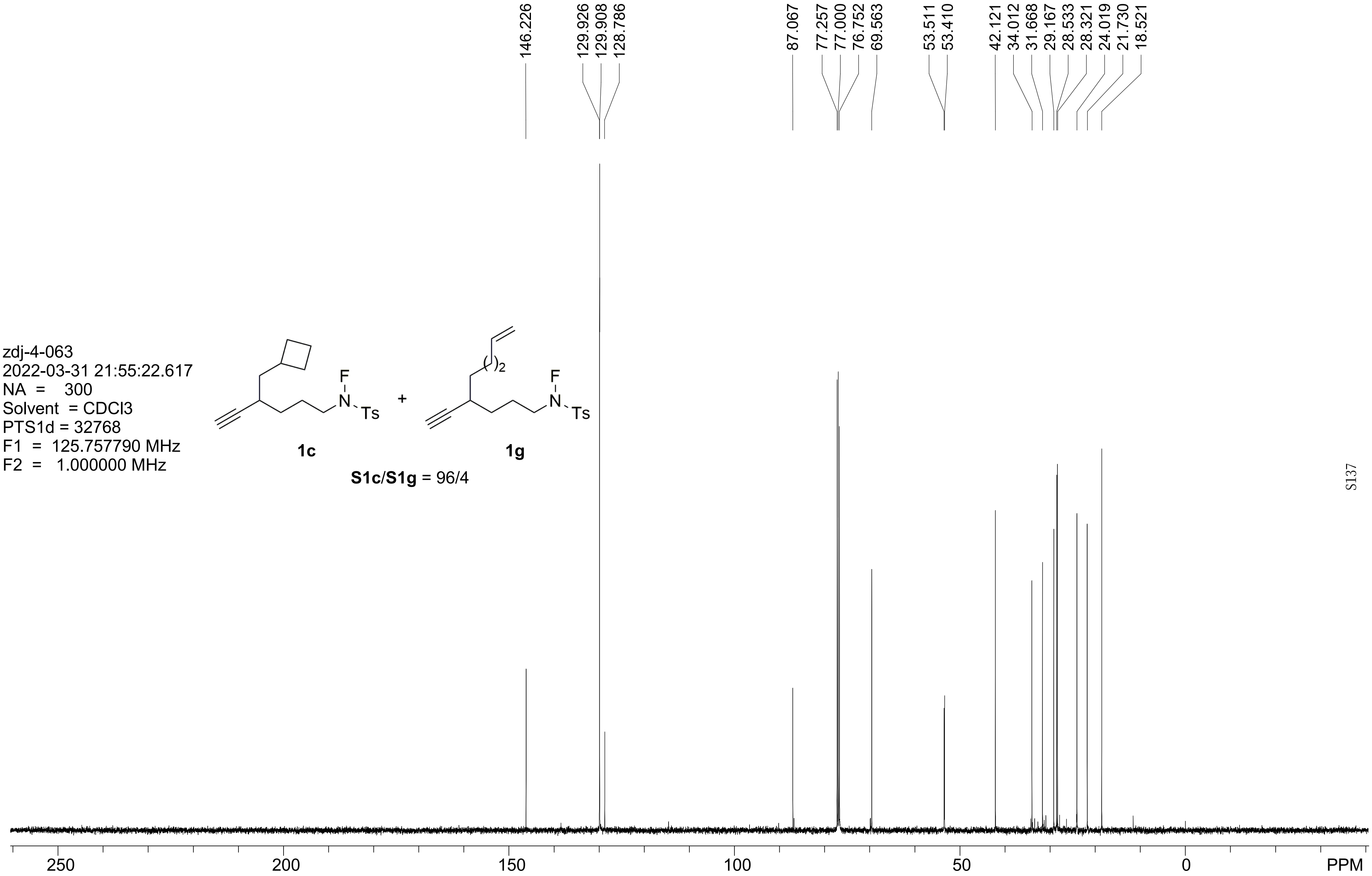
zdj-4-063-purity
2022-04-19 11:25:01.578
NA = 16
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

Purity (98%) is determined by Nitromethane (3.6 μL, 0.067 mmol) as the internal standard in 42.5 mg of sample

1c

1g

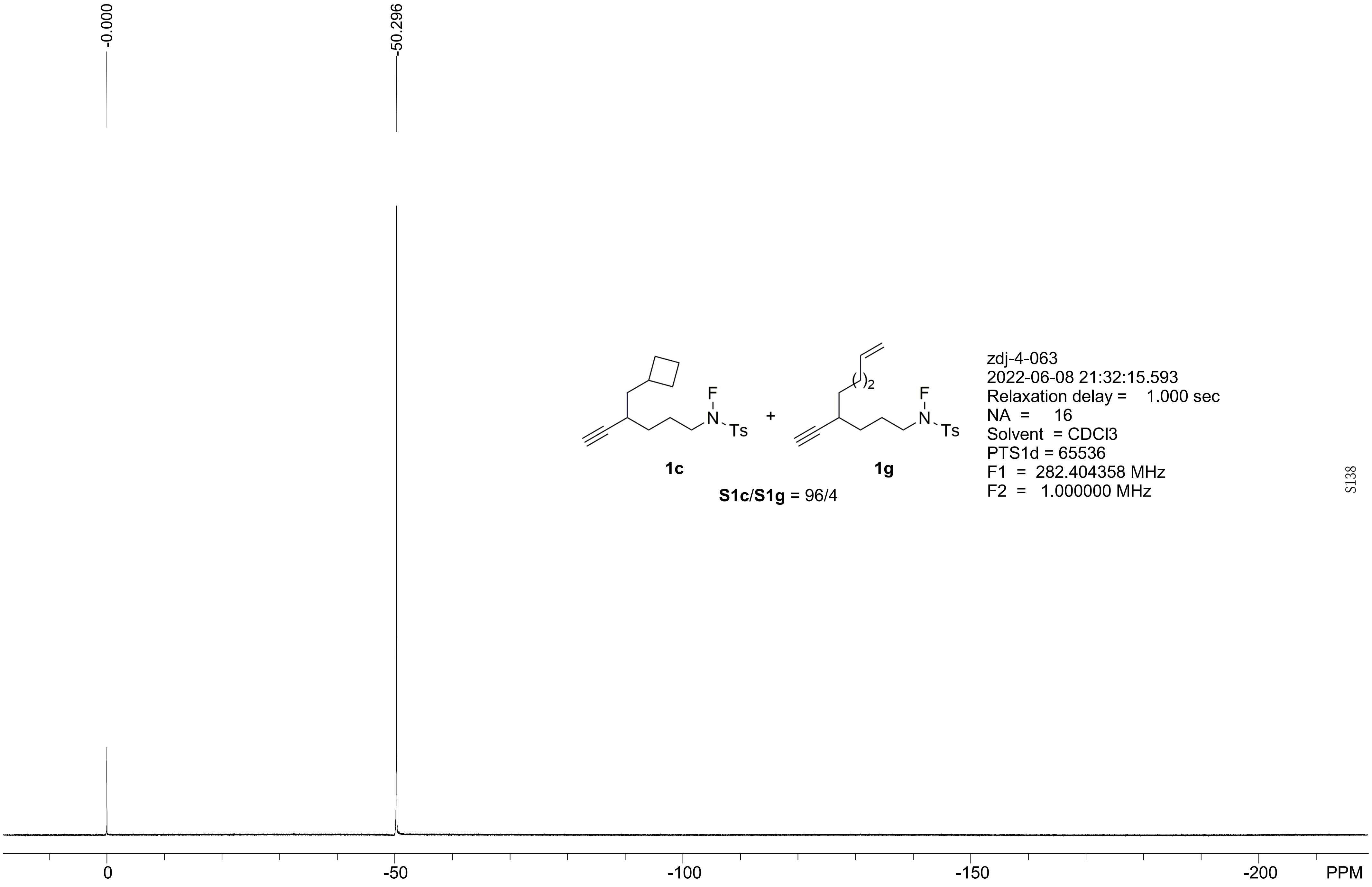
S1c/**S1g** = 96/4



zdj-4-063
2022-03-31 21:55:22.617
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz

1c + **1g**

S1c/**S1g** = 96/4

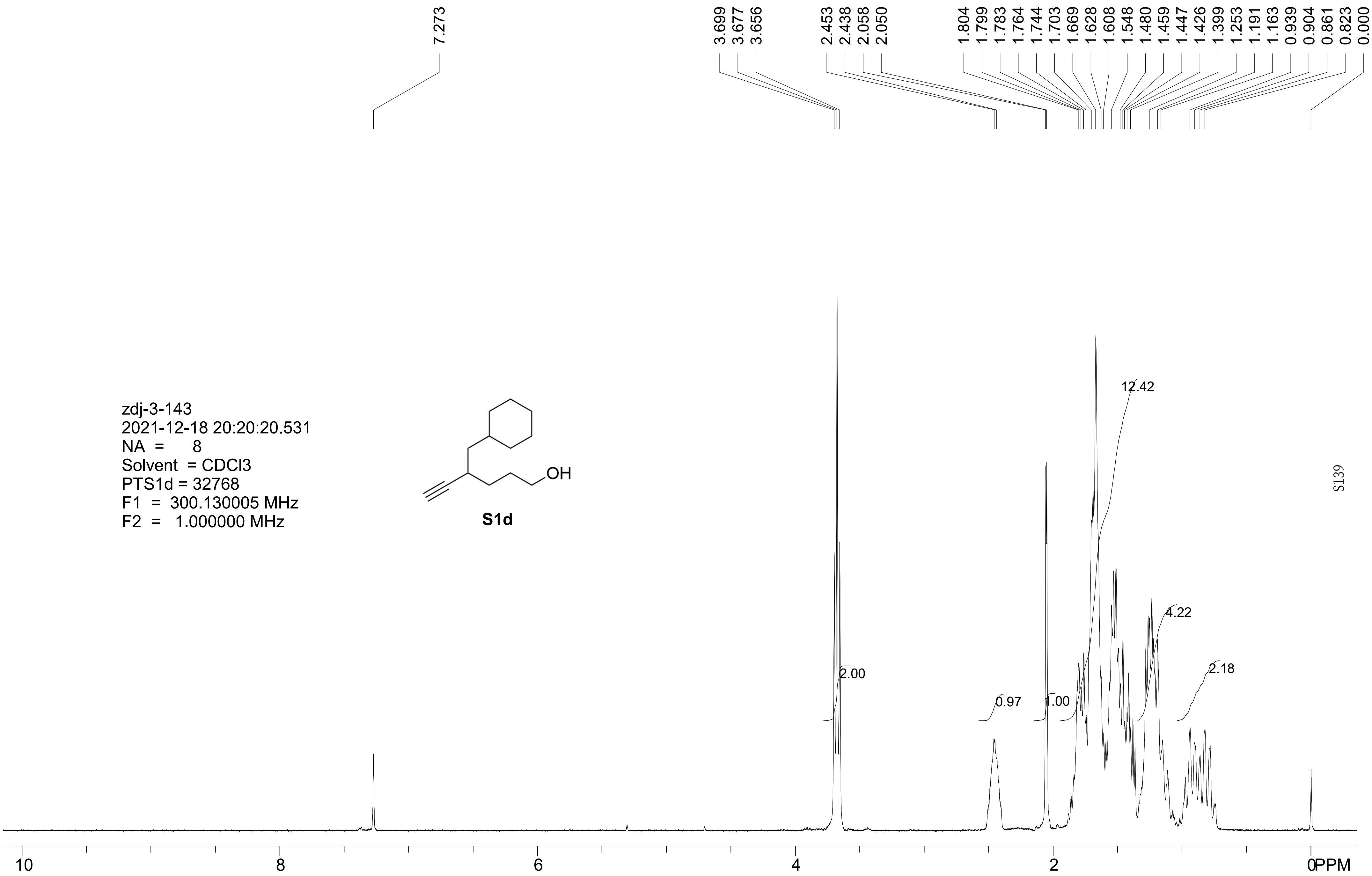


1c

1g

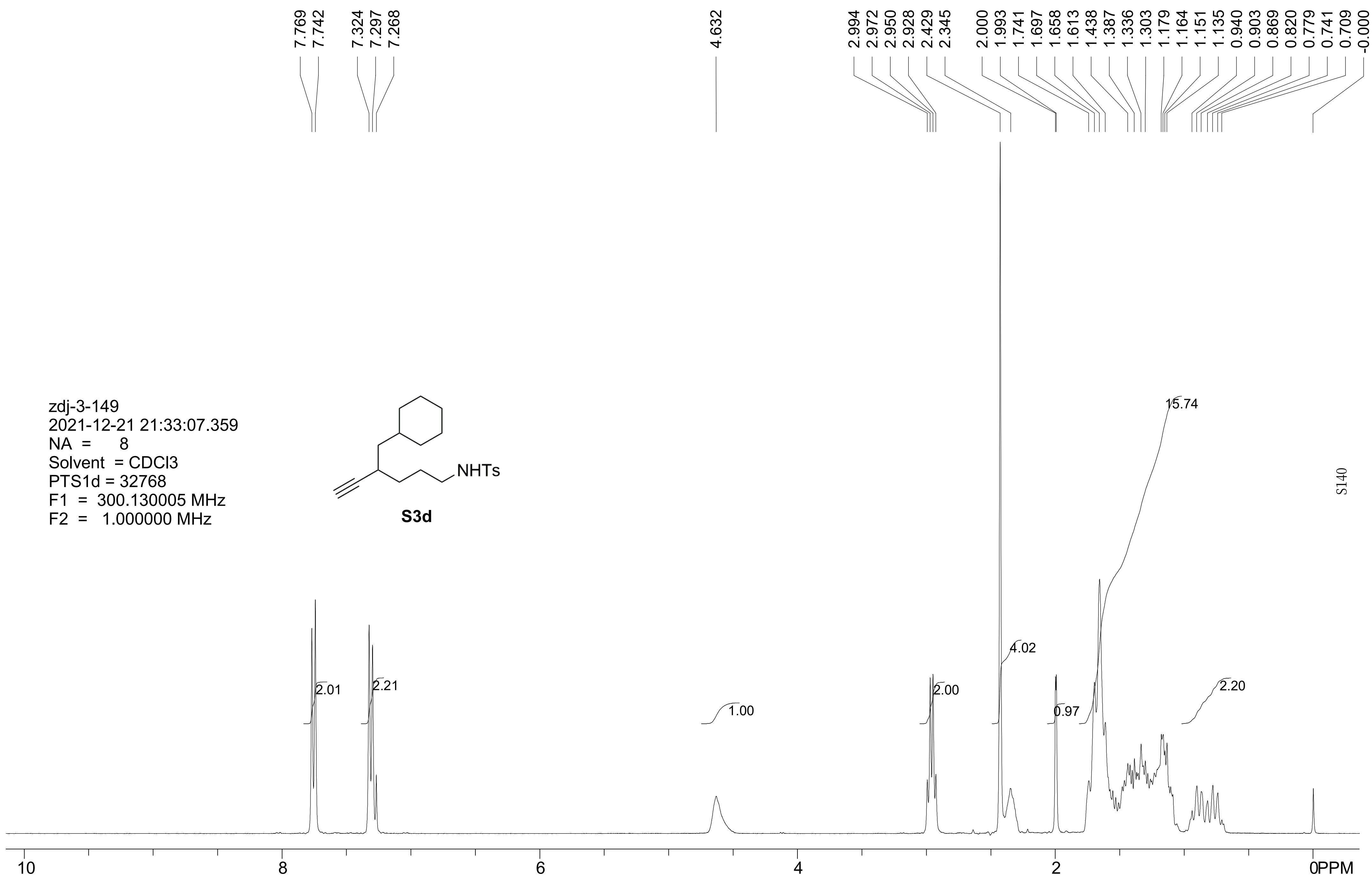
S1c/**S1g** = 96/4

zdj-4-063
2022-06-08 21:32:15.593
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz

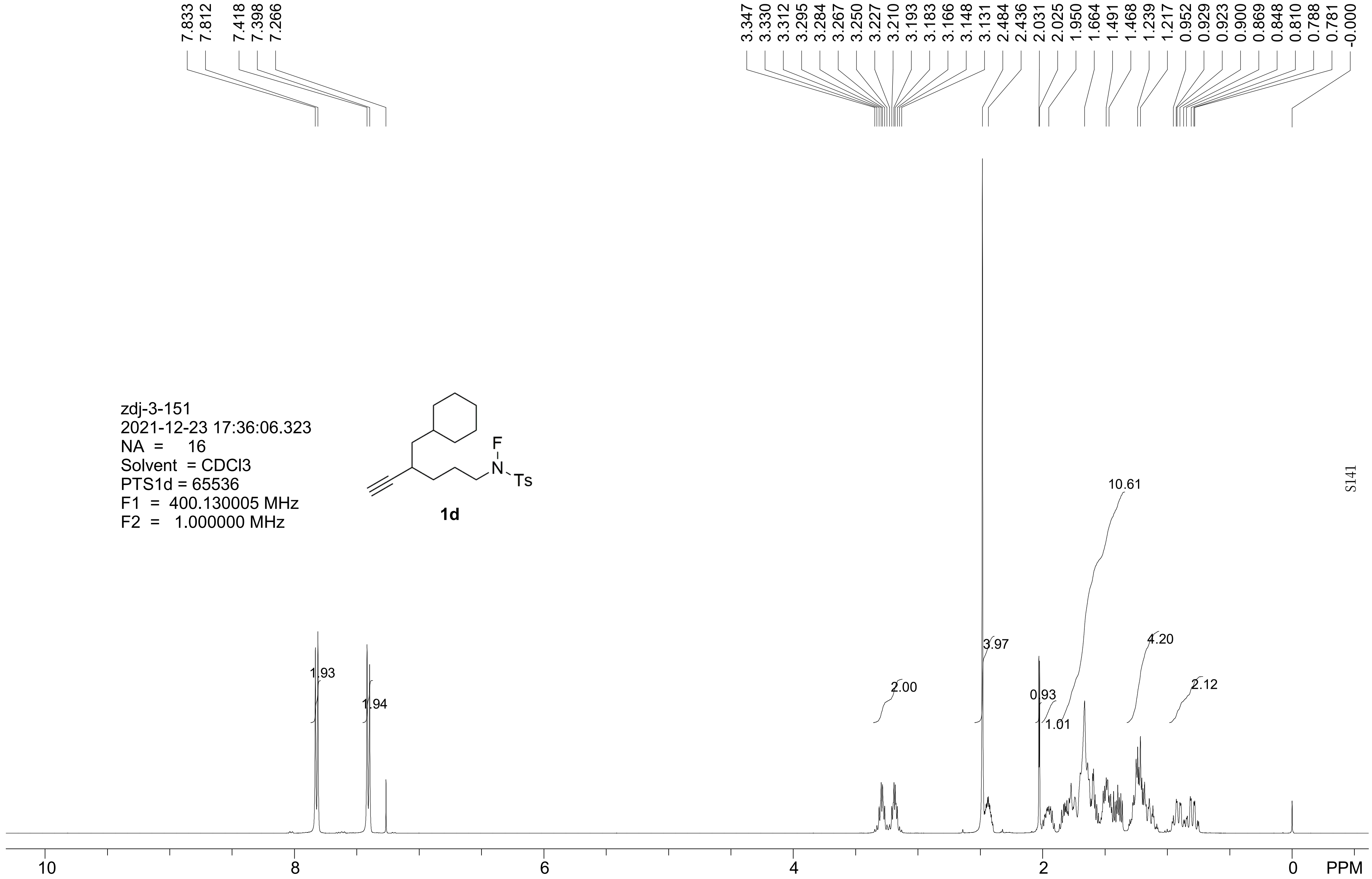


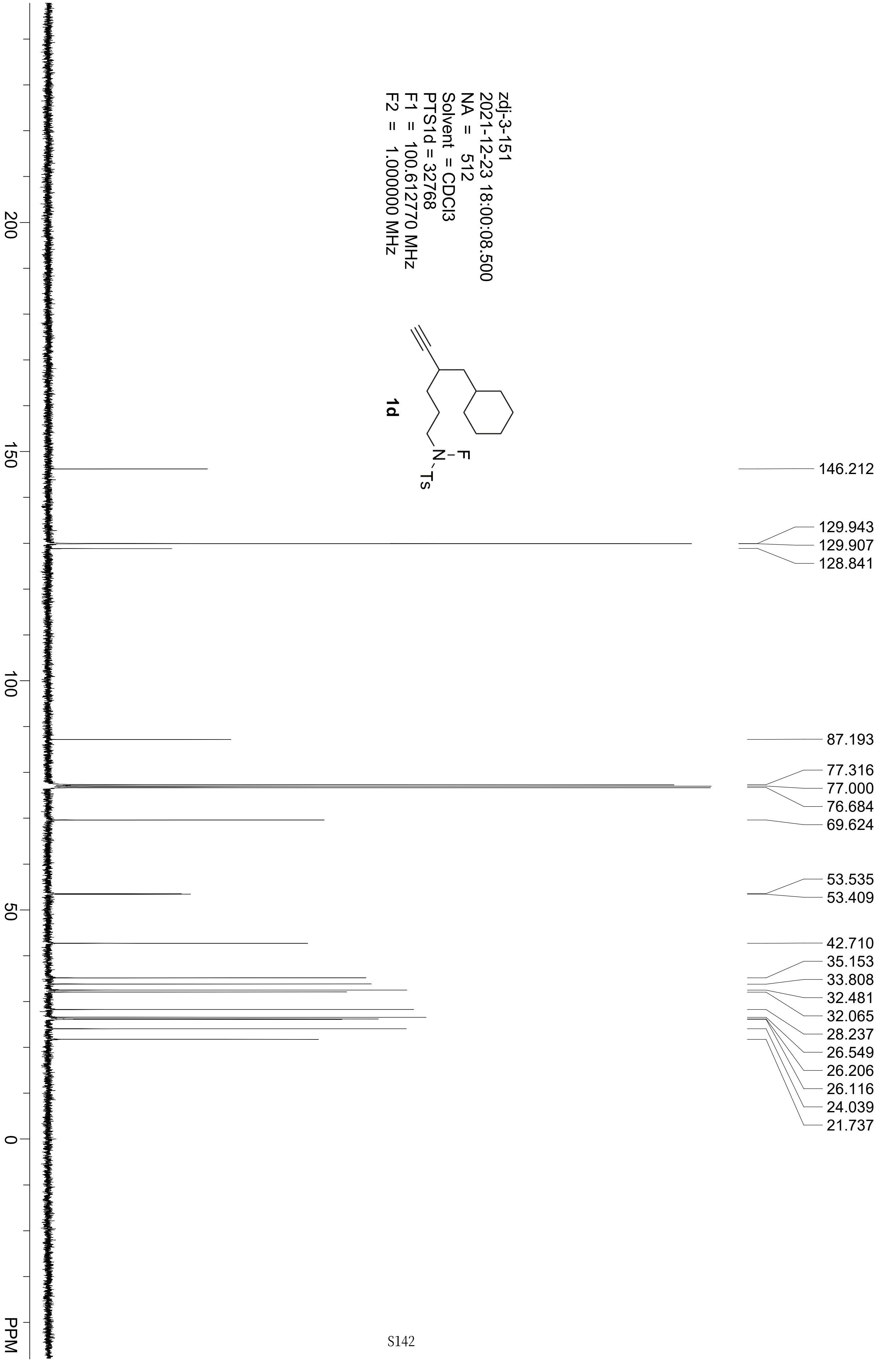
zdj-3-143
2021-12-18 20:20:20.531
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

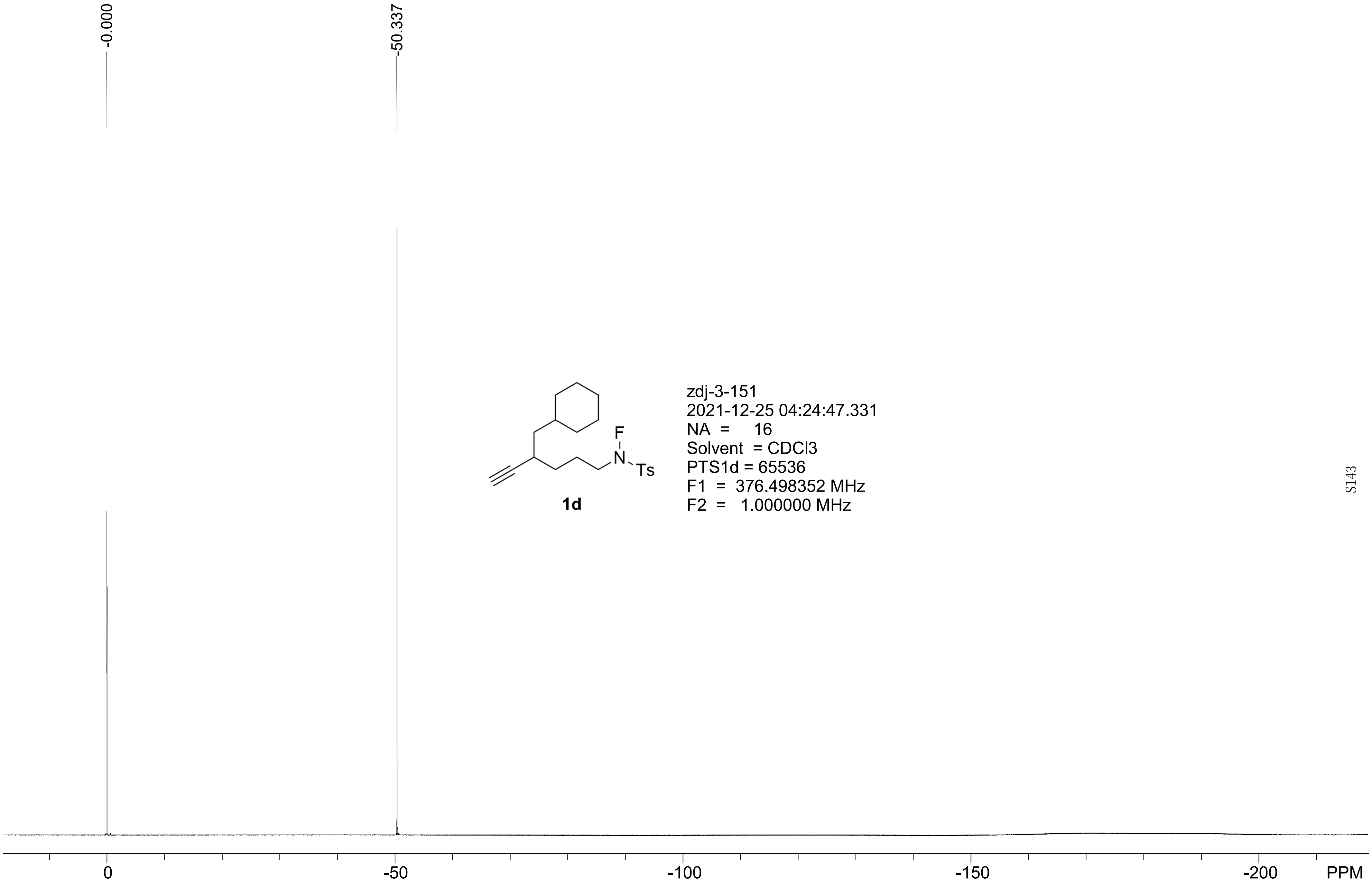
S1d


zdj-3-149
2021-12-21 21:33:07.359
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NHTs
7.769
7.742
7.324
7.297
7.268
4.632
2.994
2.972
2.950
2.928
2.429
2.345
2.000
1.993
1.741
1.697
1.658
1.613
1.438
1.387
1.336
1.303
1.179
1.164
1.151
1.135
0.940
0.903
0.869
0.820
0.779
0.741
0.709
-0.000
2.01
2.21
1.00
2.00
4.02
0.97
15.74
2.20
10
8
6
4
2
0PPM

S3d

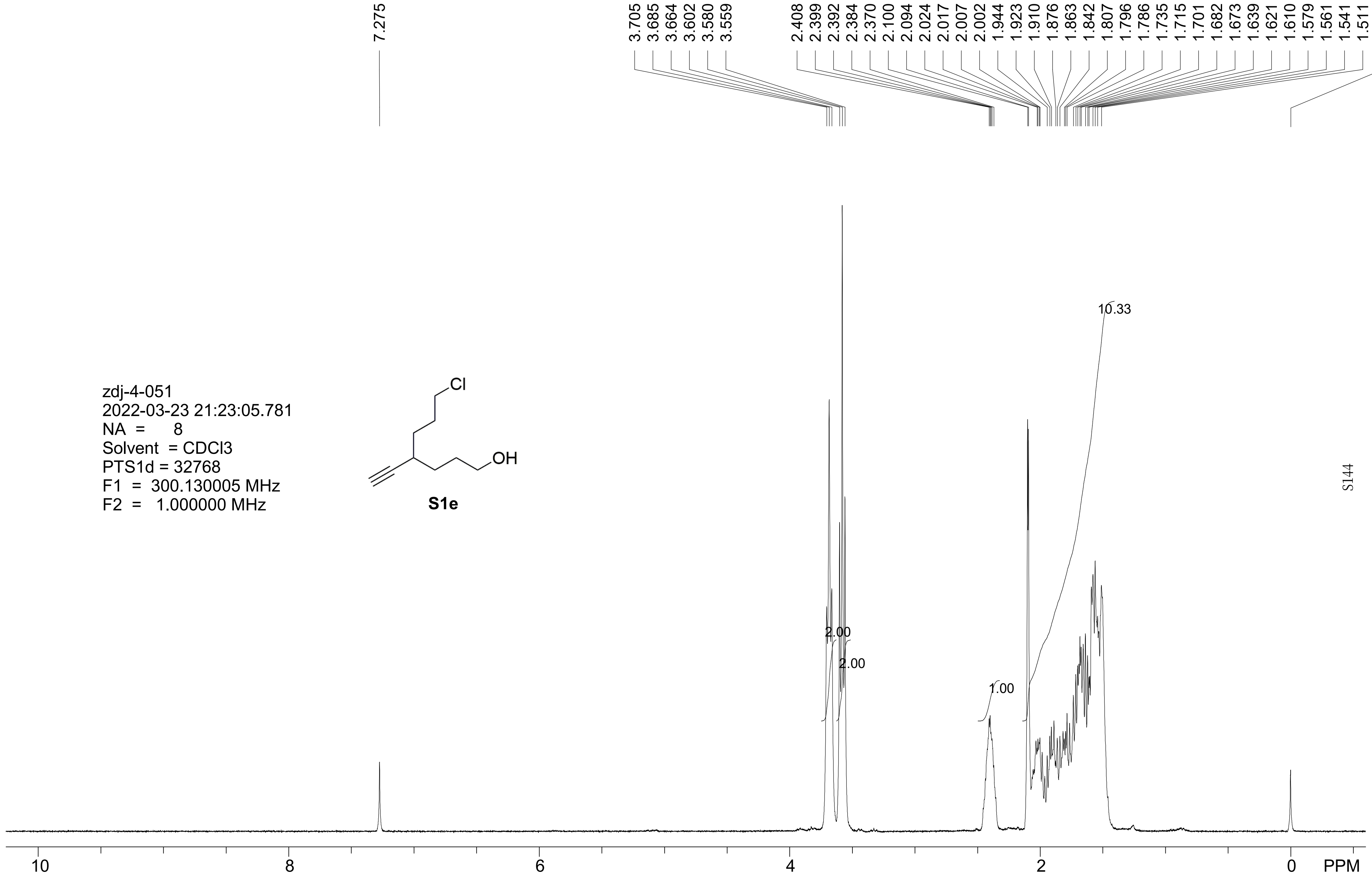

zdj-3-151
2021-12-23 17:36:06.323
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
F
N
Ts
1d
7.833
7.812
7.418
7.398
7.266
3.347
3.330
3.312
3.295
3.284
3.267
3.250
3.227
3.210
3.193
3.183
3.166
3.148
3.131
2.484
2.436
2.031
2.025
1.950
1.664
1.491
1.468
1.239
1.217
0.952
0.929
0.923
0.900
0.869
0.848
0.810
0.788
0.781
-0.000
1.93
1.94
2.00
3.97
0.93
1.01
10.61
4.20
2.12
10
8
6
4
2
0
PPM


zdj-3-151
2021-12-23 18:00:08.500
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
F
N
Ts
1d
146.212
129.943
129.907
128.841
87.193
77.316
77.000
76.684
69.624
53.535
53.409
42.710
35.153
33.808
32.481
32.065
28.237
26.549
26.206
26.116
24.039
21.737
200
150
100
50
0
PPM



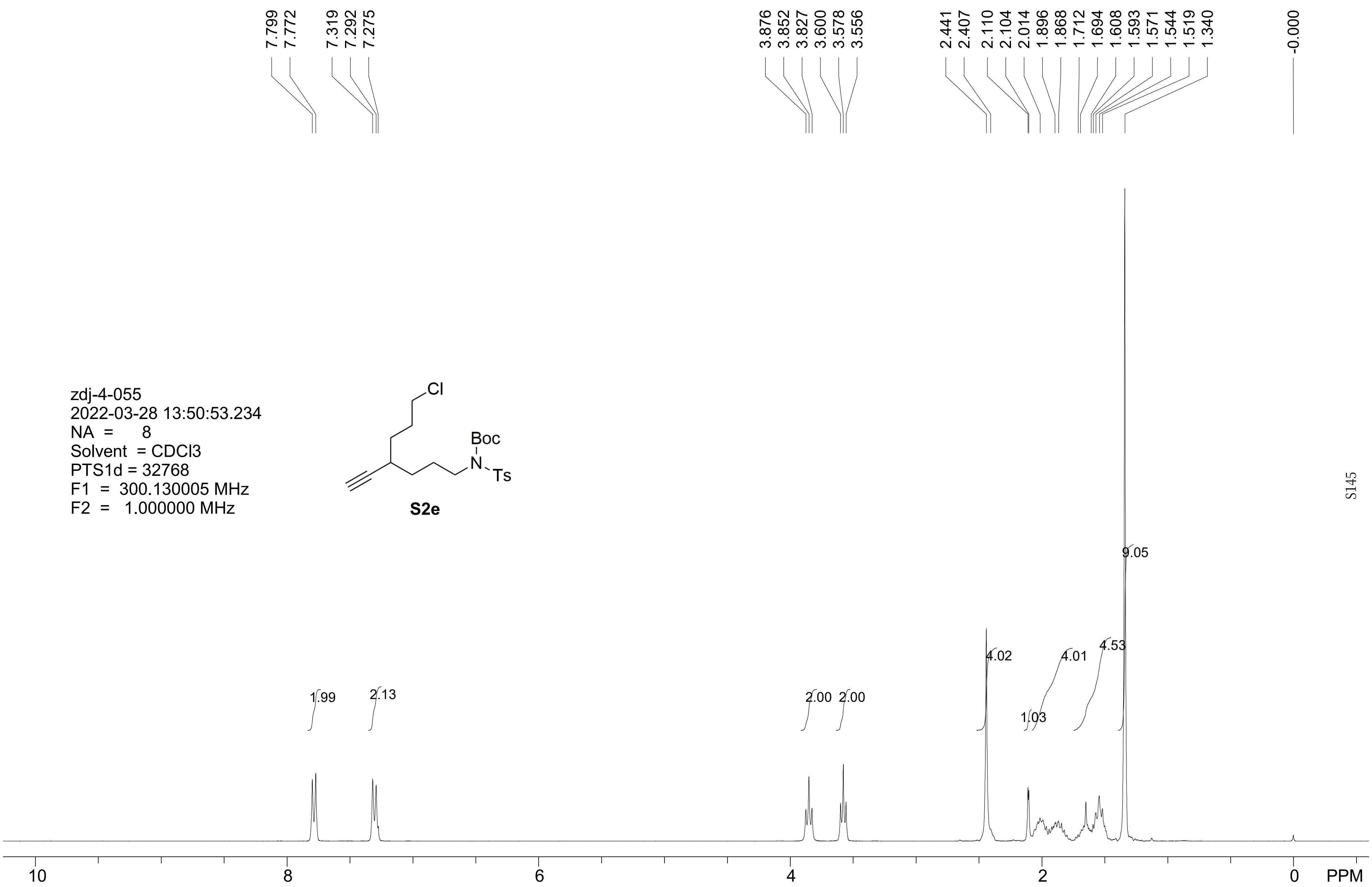
1d

zdj-3-151
2021-12-25 04:24:47.331
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz



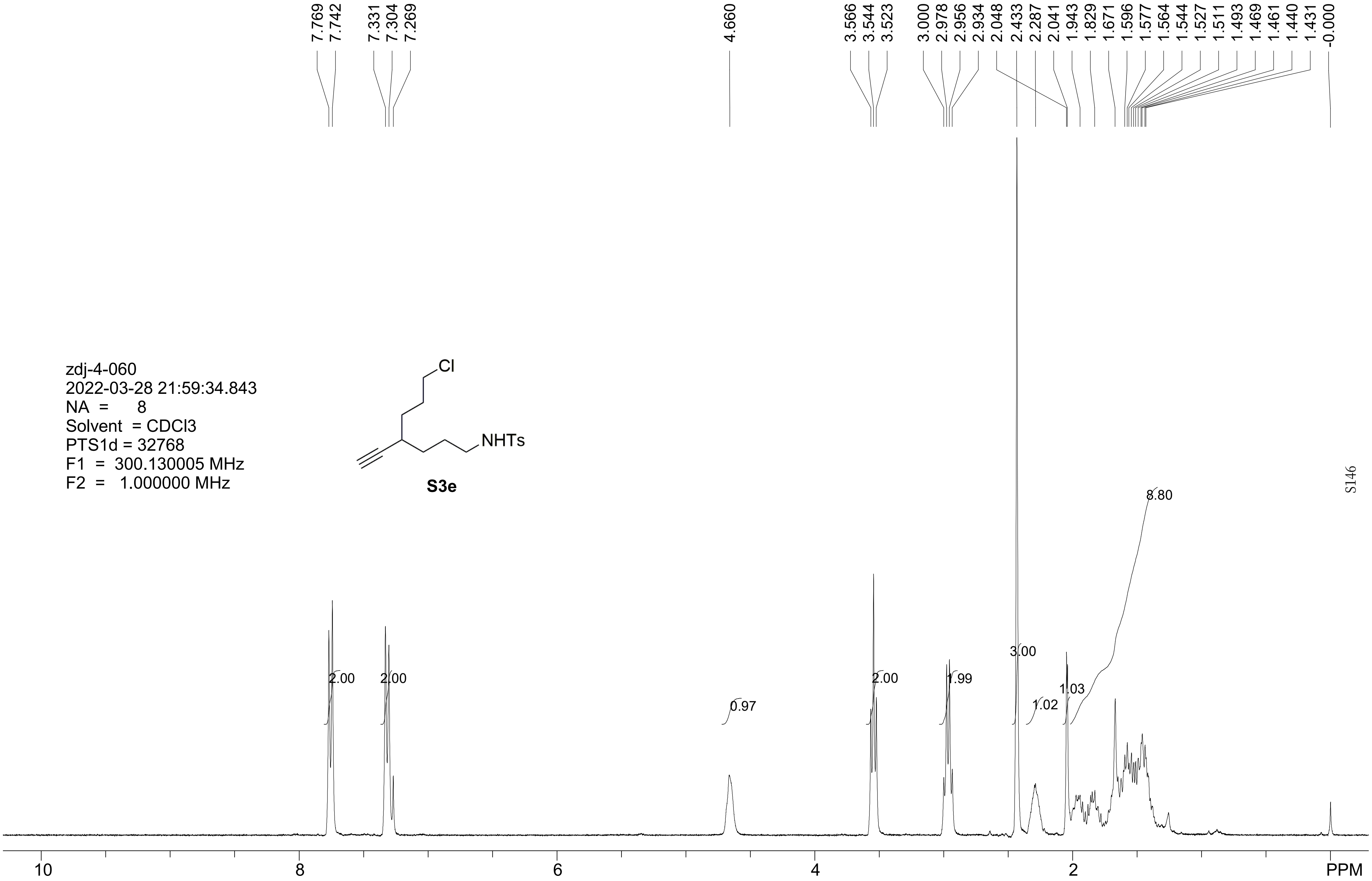
zdj-4-051
2022-03-23 21:23:05.781
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

S1e

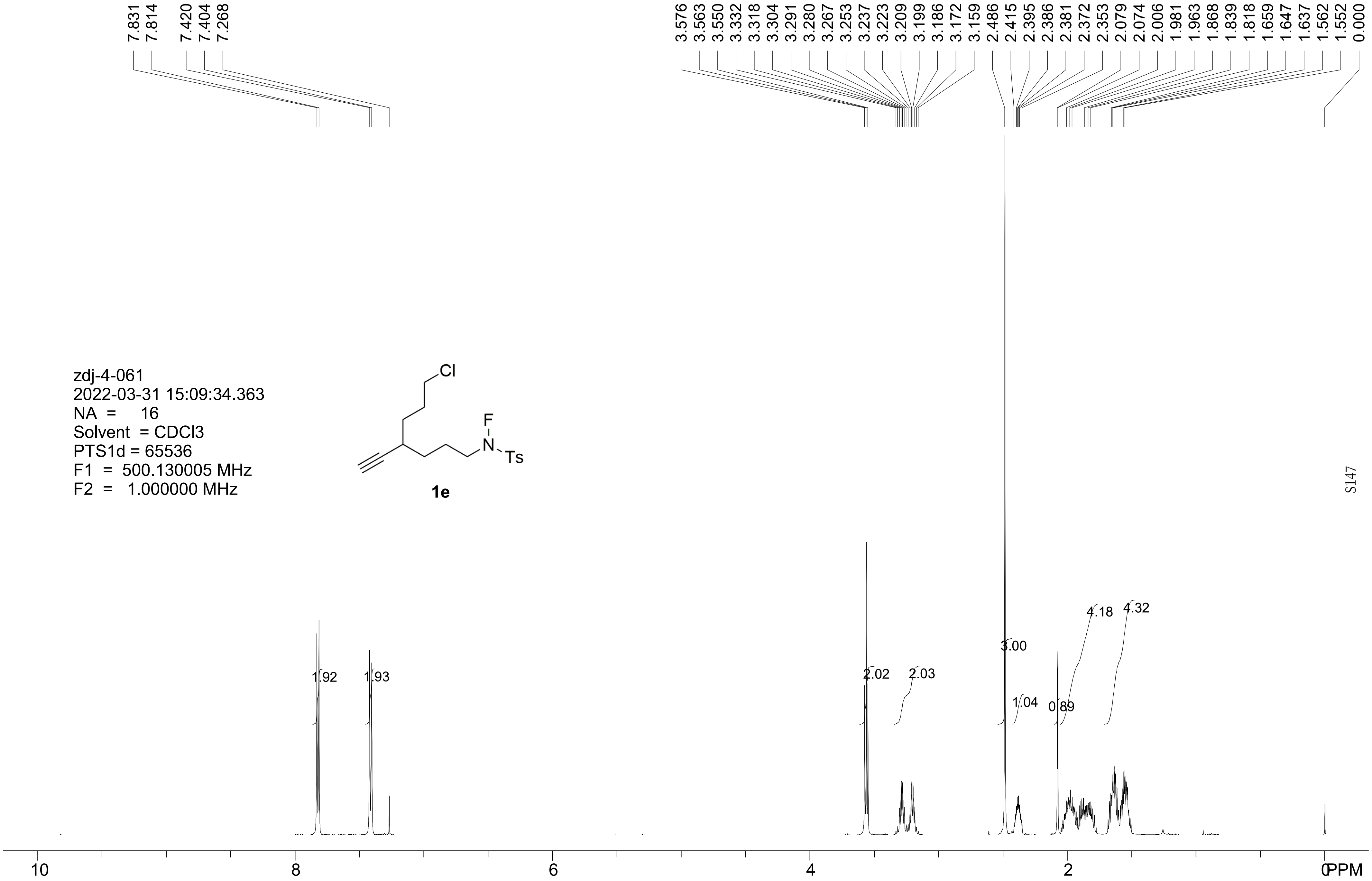


7.799
7.772
7.319
7.292
7.275
3.876
3.852
3.827
3.600
3.578
3.556
2.441
2.407
2.110
2.104
2.014
1.896
1.868
1.712
1.694
1.608
1.593
1.571
1.544
1.519
1.340
-0.000
zdj-4-055
2022-03-28 13:50:53.234
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Cl
Boc
N
Ts
1.99
2.13
2.00
2.00
4.02
1.03
4.01
4.53
9.05
10
8
6
4
2
0
PPM

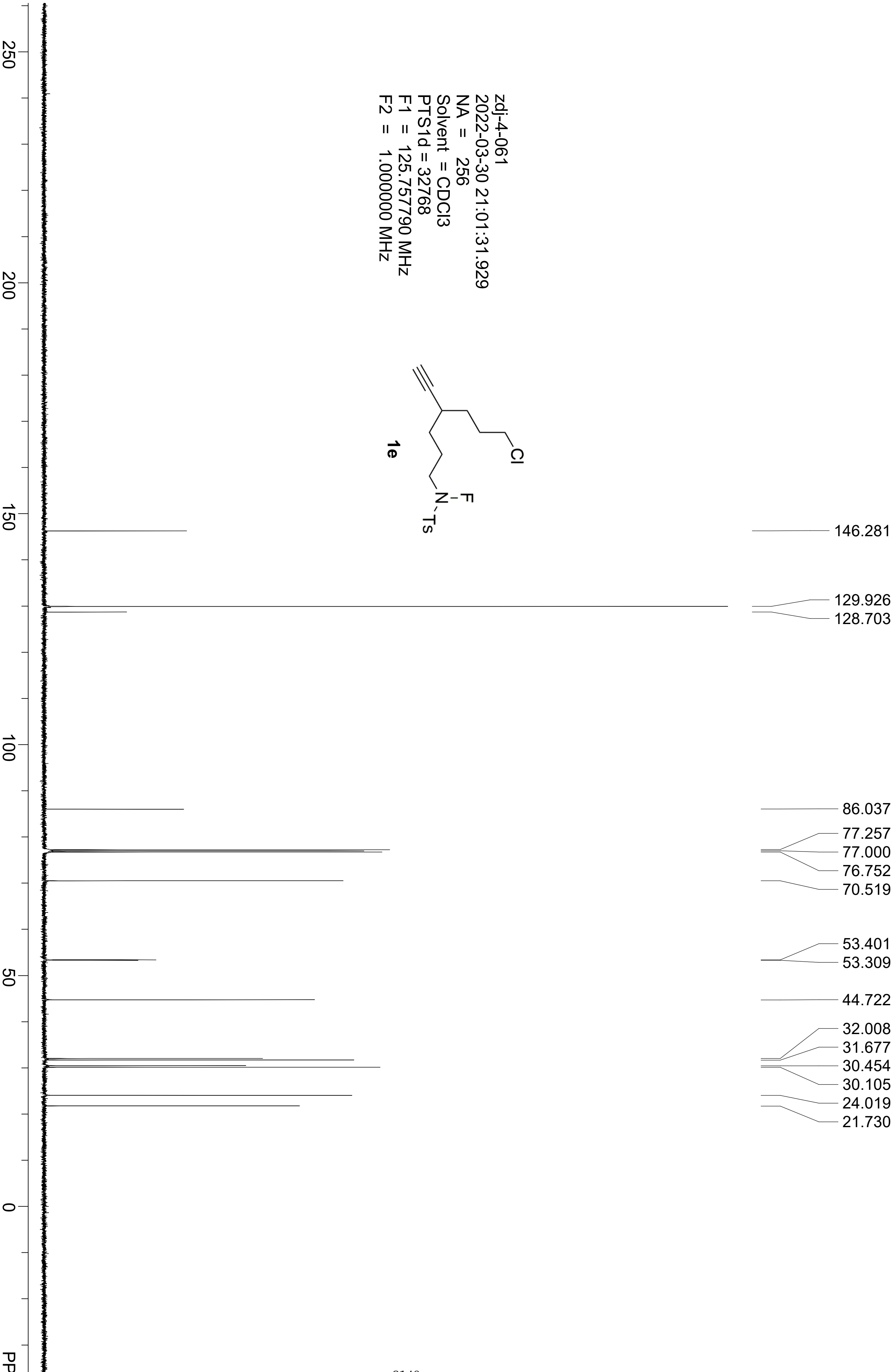
S2e

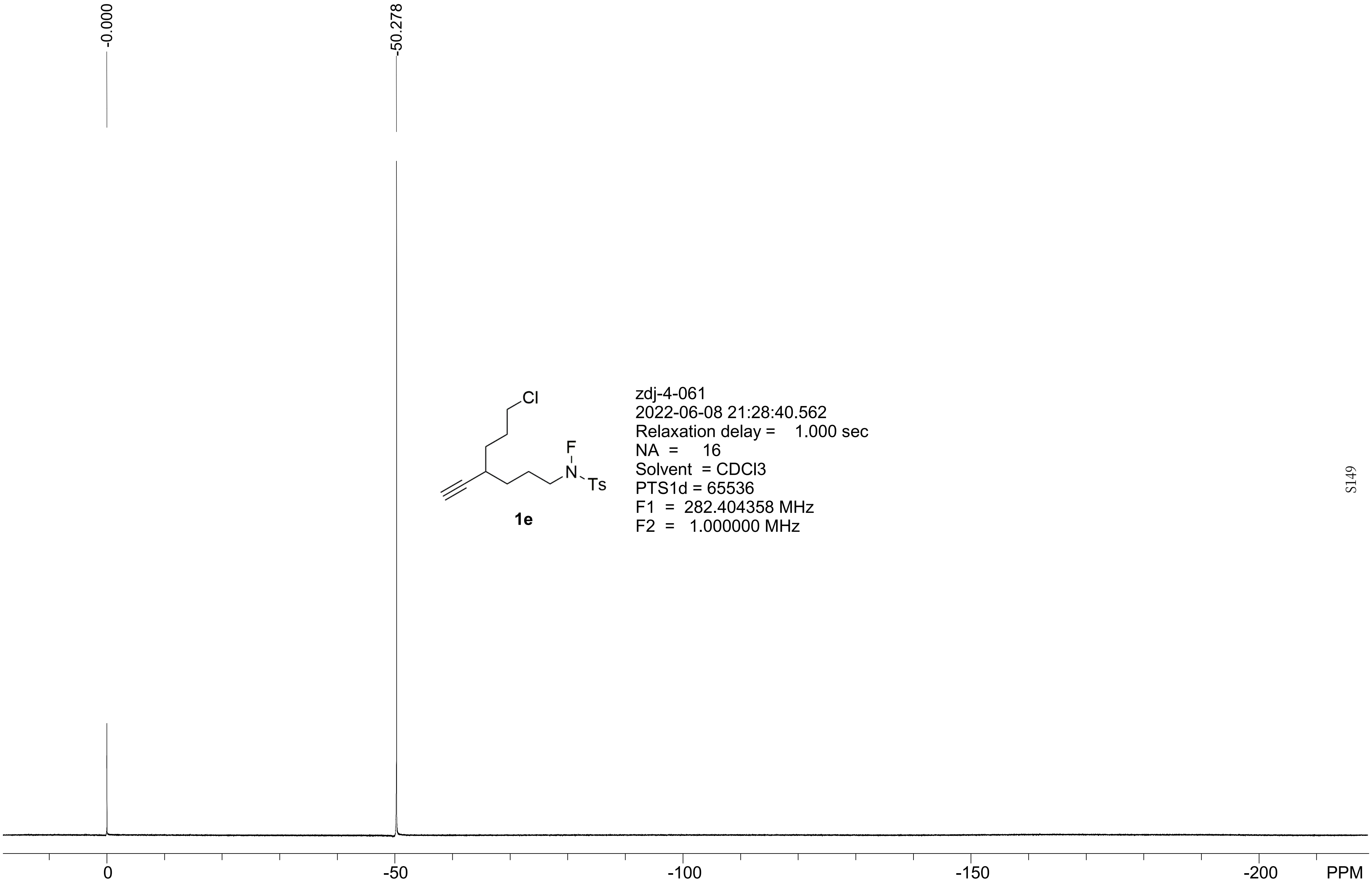

zdj-4-060
2022-03-28 21:59:34.843
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Cl
NHTs
7.769
7.742
7.331
7.304
7.269
4.660
3.566
3.544
3.523
3.000
2.978
2.956
2.934
2.048
2.433
2.287
2.041
1.943
1.829
1.671
1.596
1.577
1.564
1.544
1.527
1.511
1.493
1.469
1.461
1.440
1.431
-0.000
2.00
2.00
0.97
2.00
1.99
3.00
1.02
1.03
8.80
10
8
6
4
2
PPM

S3e


zdj-4-061
2022-03-31 15:09:34.363
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz

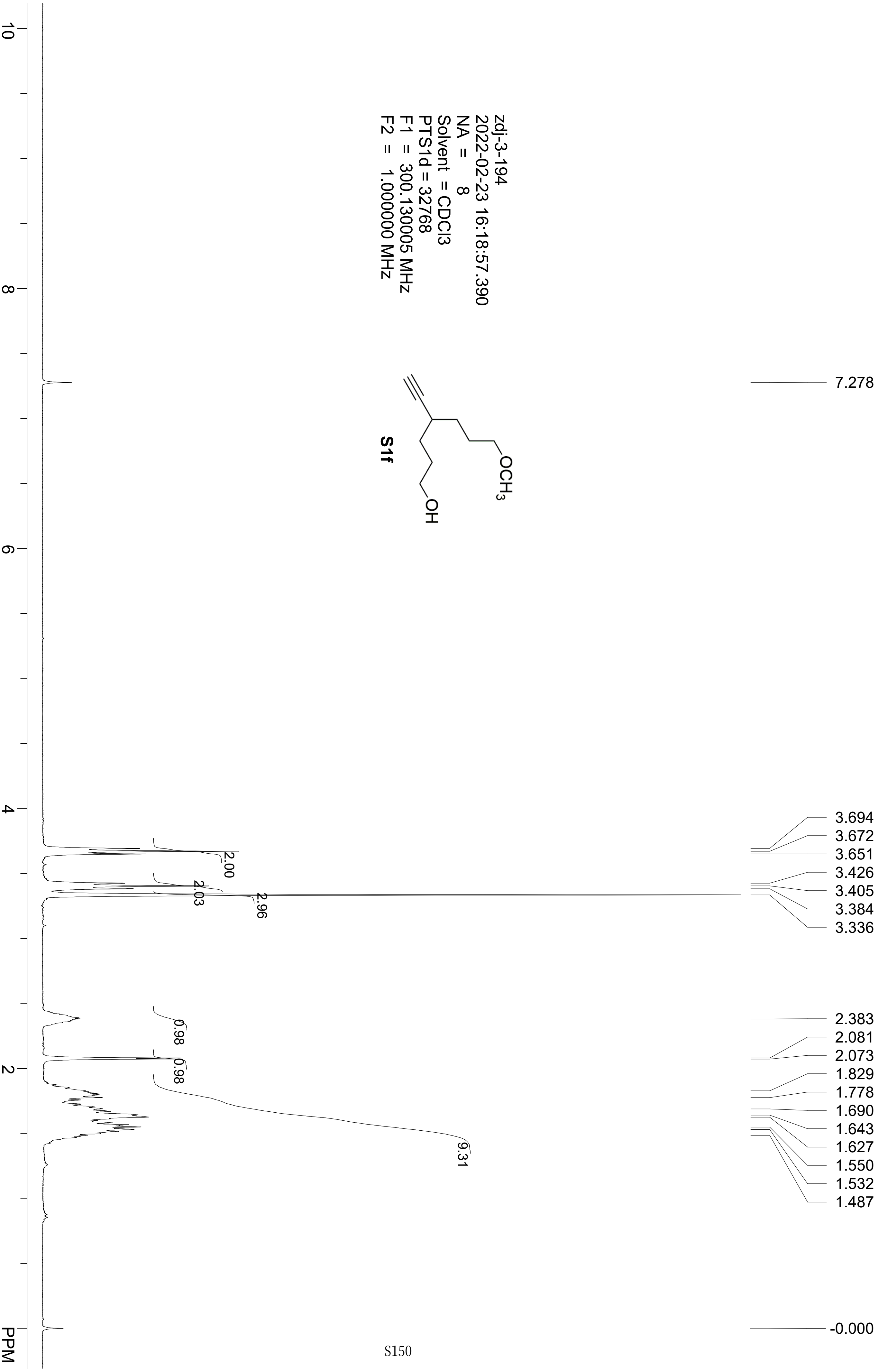
1e


zdj-4-061
2022-03-30 21:01:31.929
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
Cl
F
N
Ts
1e
146.281
129.926
128.703
86.037
77.257
77.000
76.752
70.519
53.401
53.309
44.722
32.008
31.677
30.454
30.105
24.019
21.730
250
200
150
100
50
0
PPM

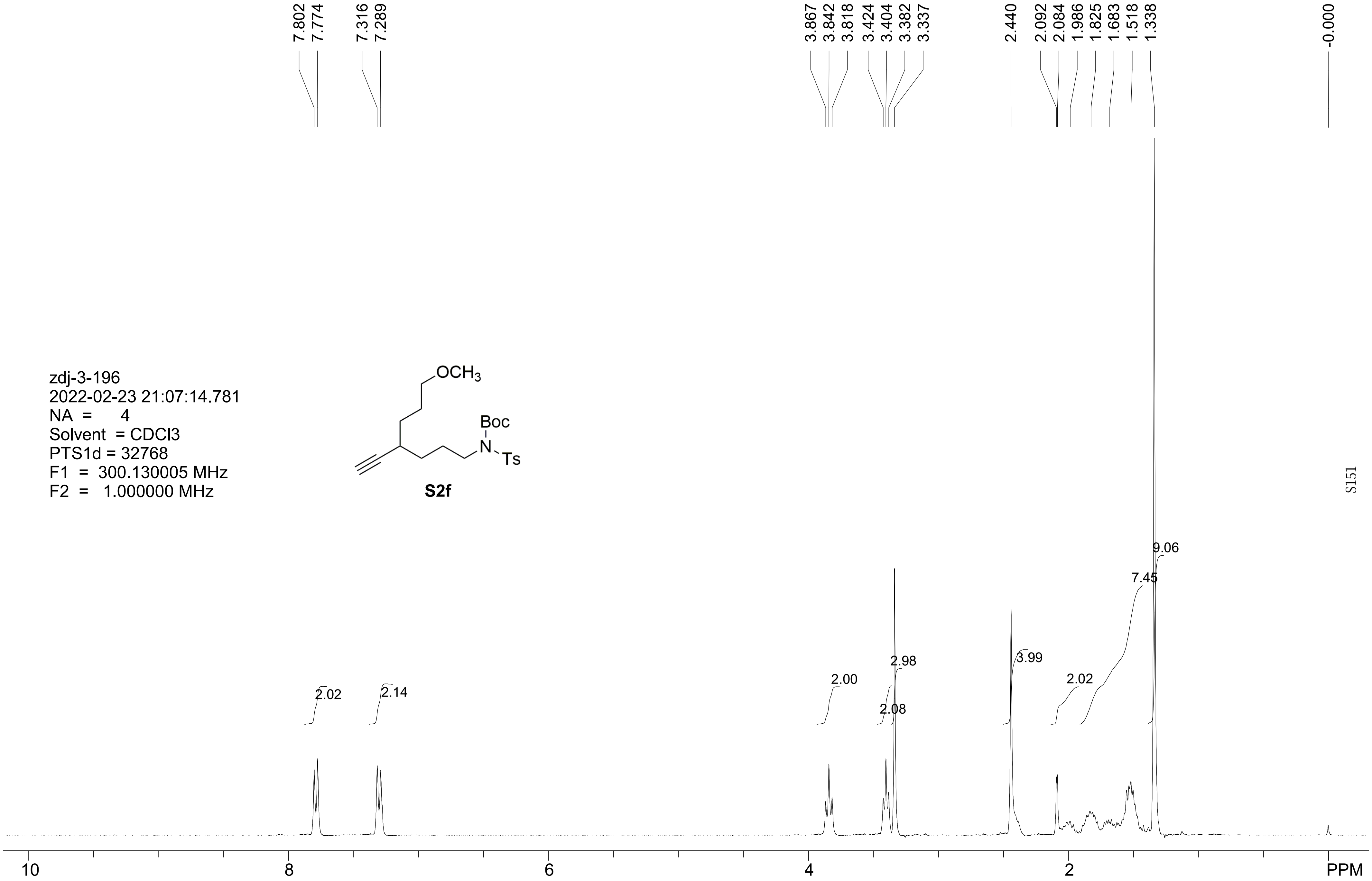


1e

zdj-4-061
2022-06-08 21:28:40.562
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz

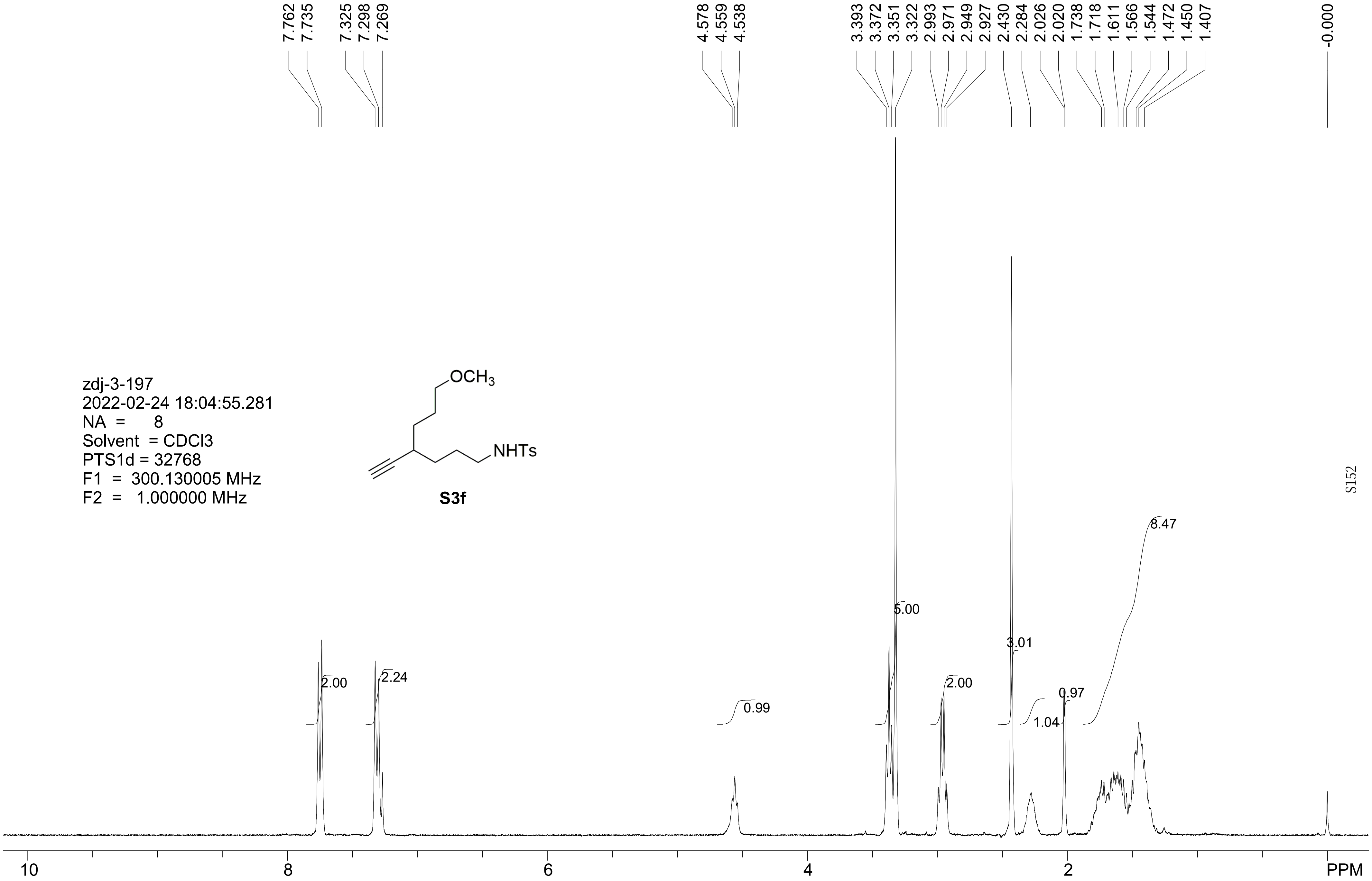

zdj-3-194
2022-02-23 16:18:57.390
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
OCH3
OH
7.278
3.694
3.672
3.651
3.426
3.405
3.384
3.336
2.383
2.081
2.073
1.829
1.778
1.690
1.643
1.627
1.550
1.532
1.487
-0.000
2.00
2.03
2.96
0.98
0.98
9.31
10
8
6
4
2
PPM

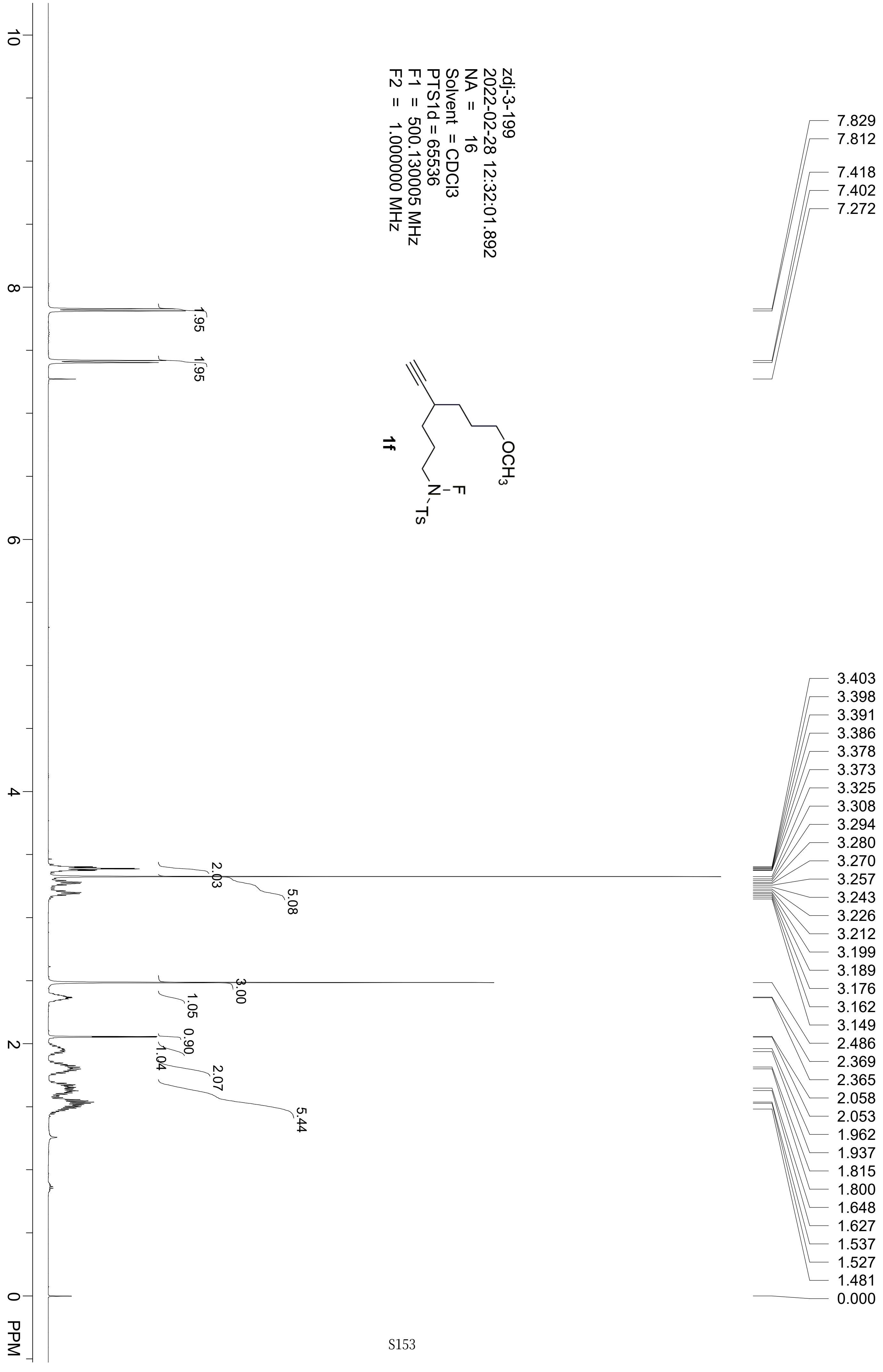
S1f

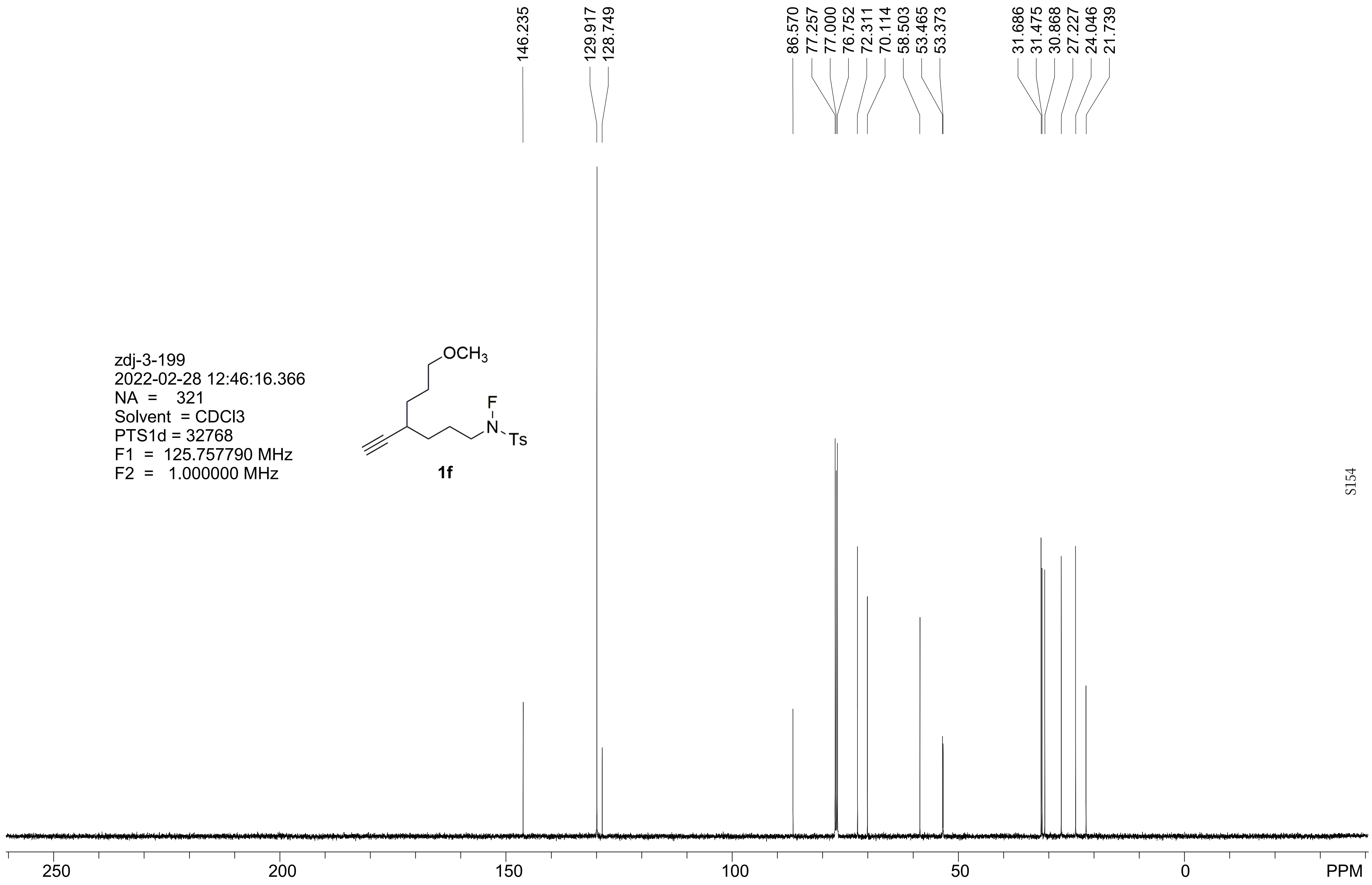


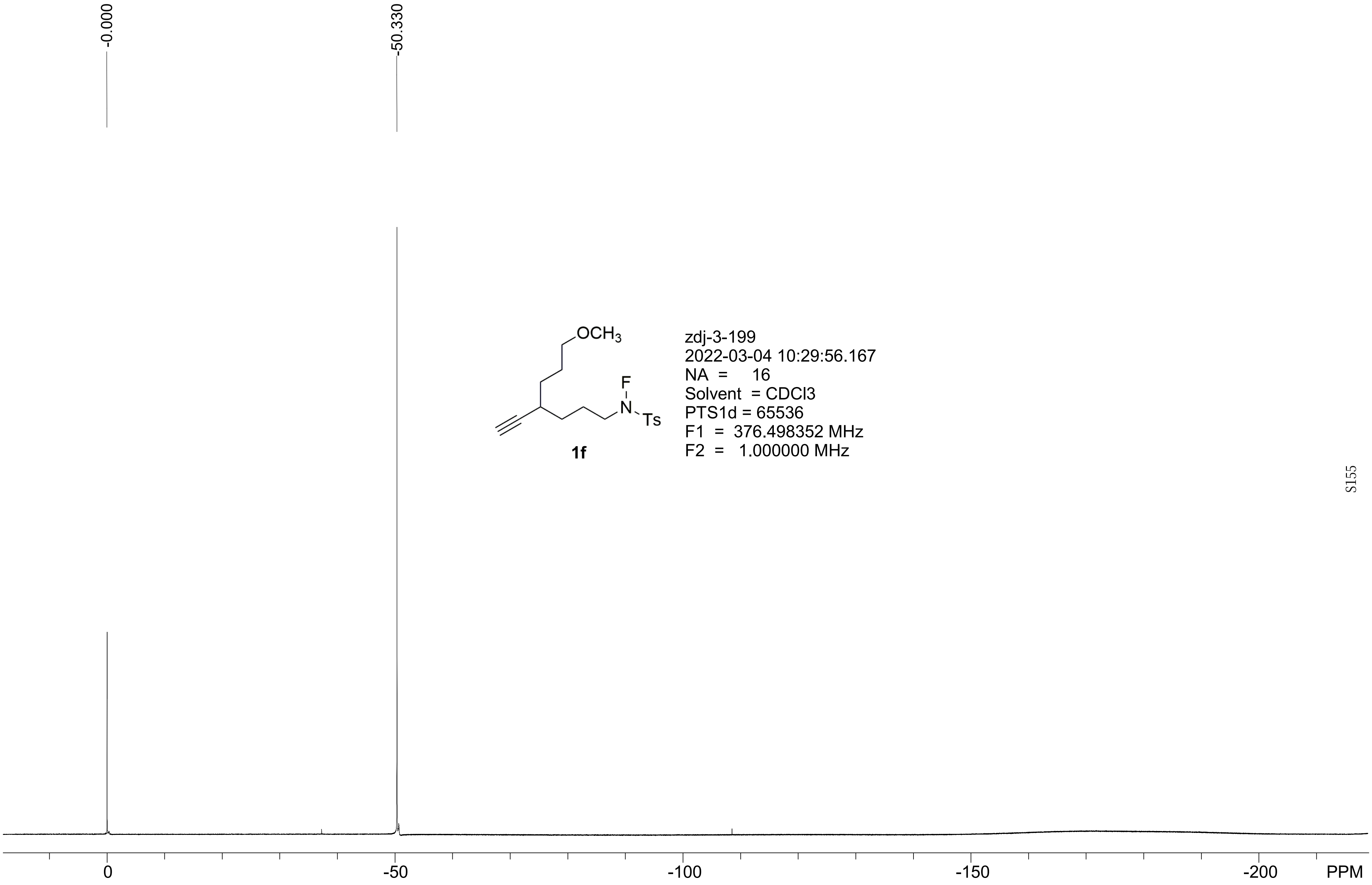
zdj-3-196
2022-02-23 21:07:14.781
NA = 4
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

S2f


7.762
7.735
7.325
7.298
7.269
4.578
4.559
4.538
3.393
3.372
3.351
3.322
2.993
2.971
2.949
2.927
2.430
2.284
2.026
2.020
1.738
1.718
1.611
1.566
1.544
1.472
1.450
1.407
-0.000
zdj-3-197
2022-02-24 18:04:55.281
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
OCH3
NHTs
S3f
2.00
2.24
0.99
5.00
2.00
3.01
1.04
0.97
8.47
10
8
6
4
2
PPM

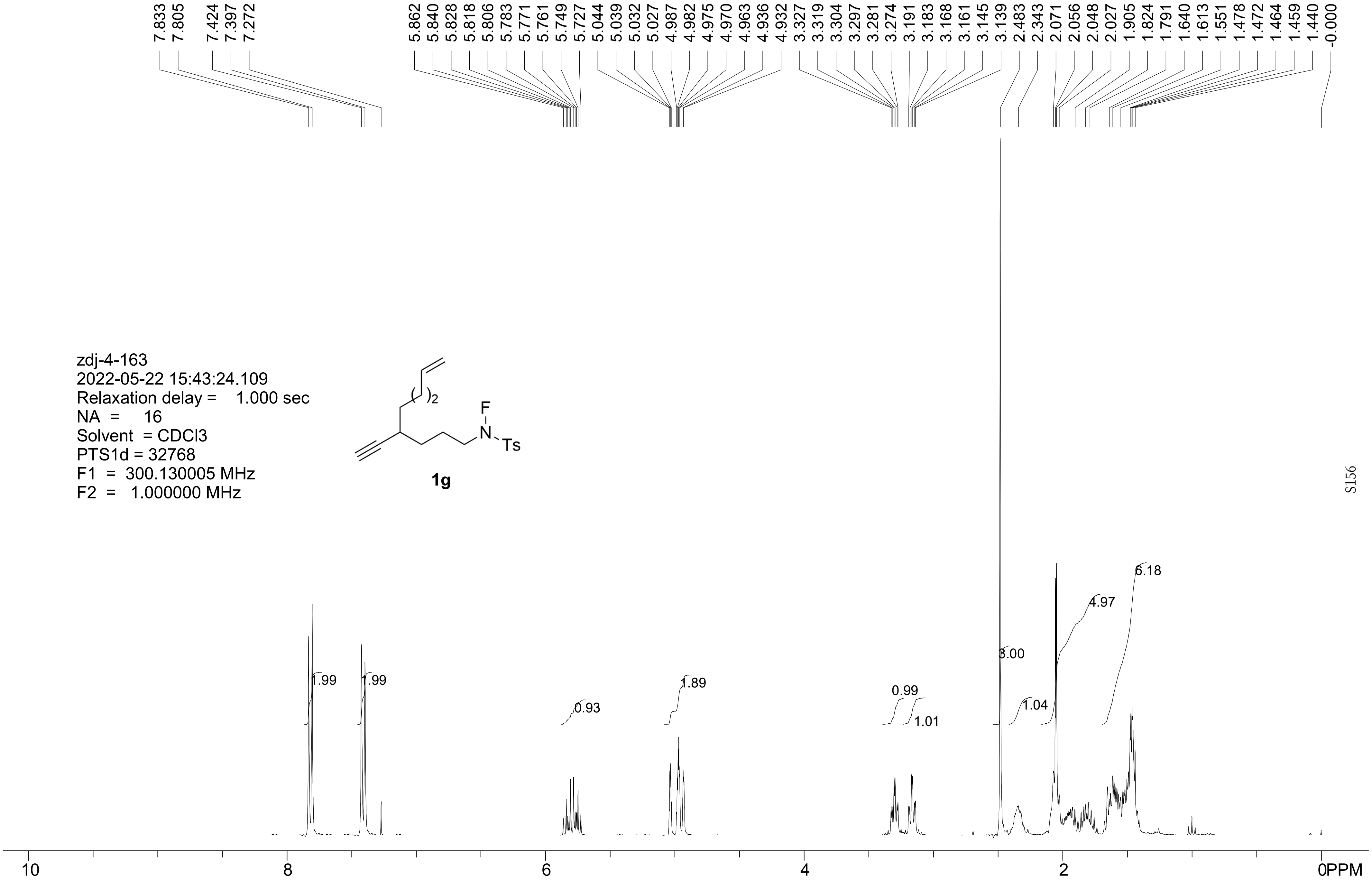

zdj-3-199
2022-02-28 12:32:01.892
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
OCH3
F
N
Ts
1f
7.829
7.812
7.418
7.402
7.272
3.403
3.398
3.391
3.386
3.378
3.373
3.325
3.308
3.294
3.280
3.270
3.257
3.243
3.226
3.212
3.199
3.189
3.176
3.162
3.149
2.486
2.369
2.365
2.058
2.053
1.962
1.937
1.815
1.800
1.648
1.627
1.537
1.527
1.481
0.000
1.95
1.95
2.03
5.08
3.00
1.05
0.90
1.04
2.07
5.44
10
8
6
4
2
0
PPM

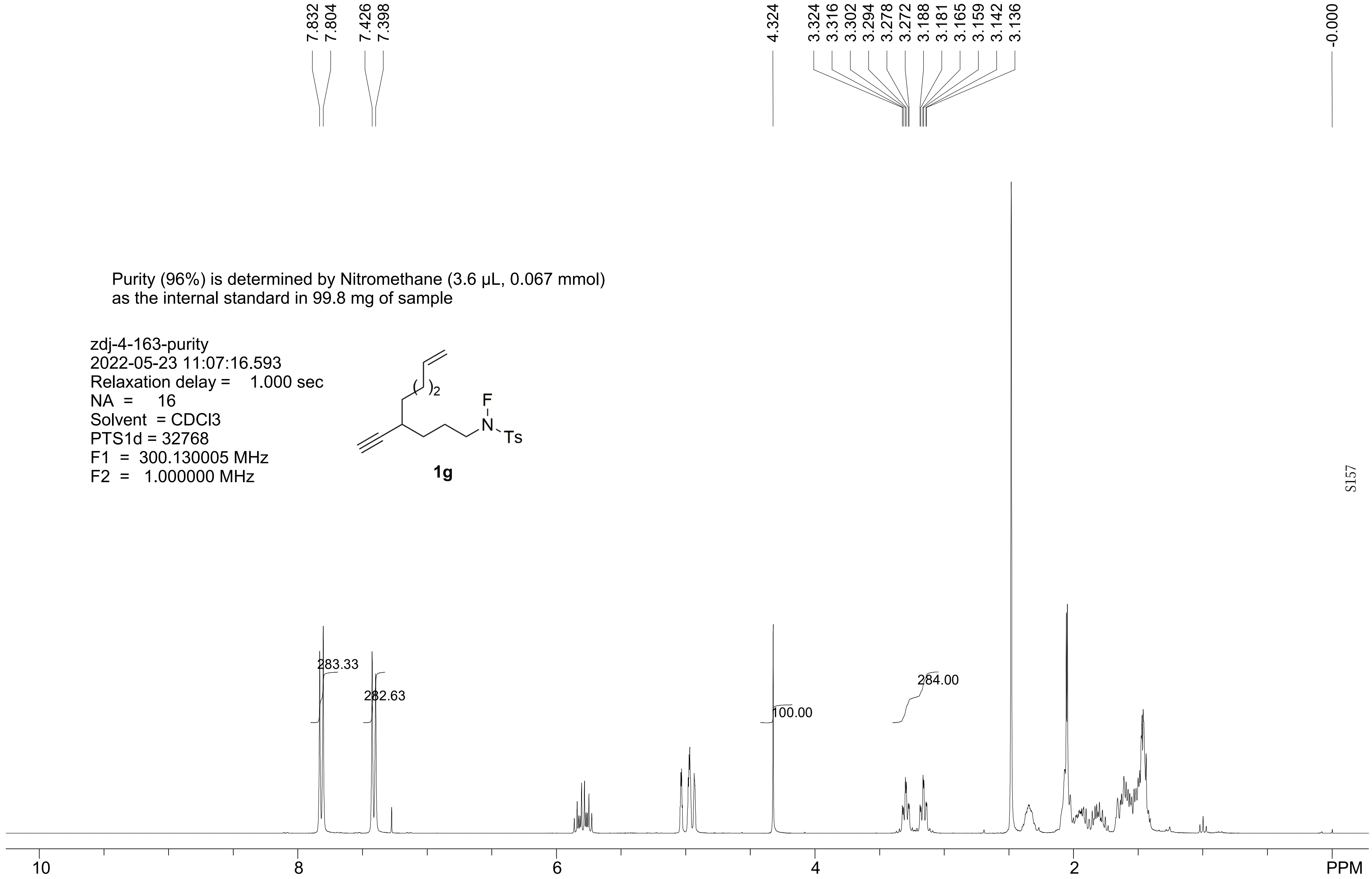

146.235
129.917
128.749
86.570
77.257
77.000
76.752
72.311
70.114
58.503
53.465
53.373
31.686
31.475
30.868
27.227
24.046
21.739
zdj-3-199
2022-02-28 12:46:16.366
NA = 321
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
OCH3
F
N
Ts
1f
250
200
150
100
50
0
PPM



1f

zdj-3-199
2022-03-04 10:29:56.167
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz

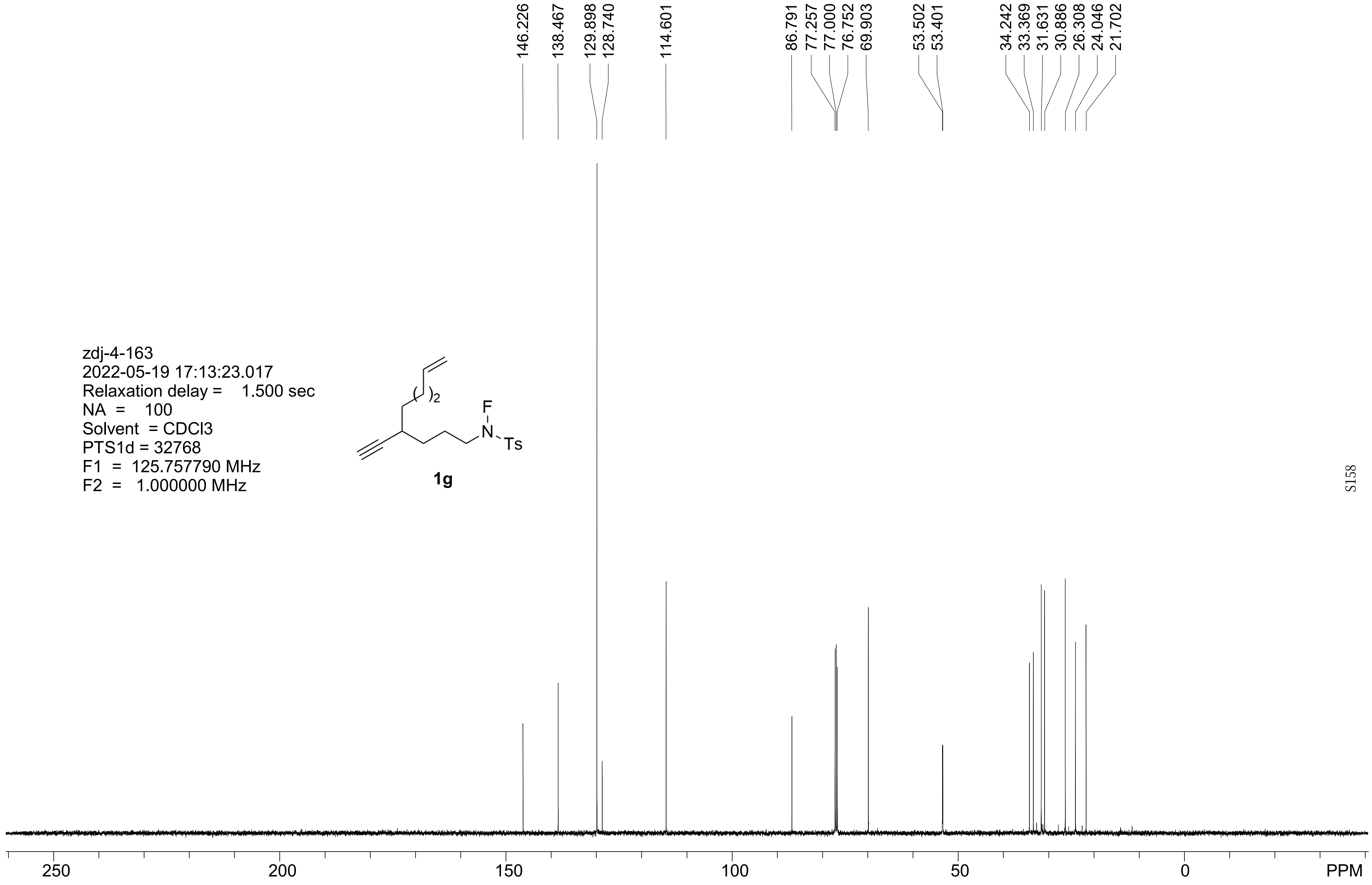

zdj-4-163
2022-05-22 15:43:24.109
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
F
N
Ts
2
1g
7.833
7.805
7.424
7.397
7.272
5.862
5.840
5.828
5.818
5.806
5.783
5.771
5.761
5.749
5.727
5.044
5.039
5.032
5.027
4.987
4.982
4.975
4.970
4.963
4.936
4.932
3.327
3.319
3.304
3.297
3.281
3.274
3.191
3.183
3.168
3.161
3.145
3.139
2.483
2.343
2.071
2.056
2.048
2.027
1.905
1.824
1.791
1.640
1.613
1.551
1.478
1.472
1.464
1.459
1.440
-0.000
1.99
1.99
0.93
1.89
0.99
1.01
3.00
1.04
4.97
6.18
10
8
6
4
2
0PPM

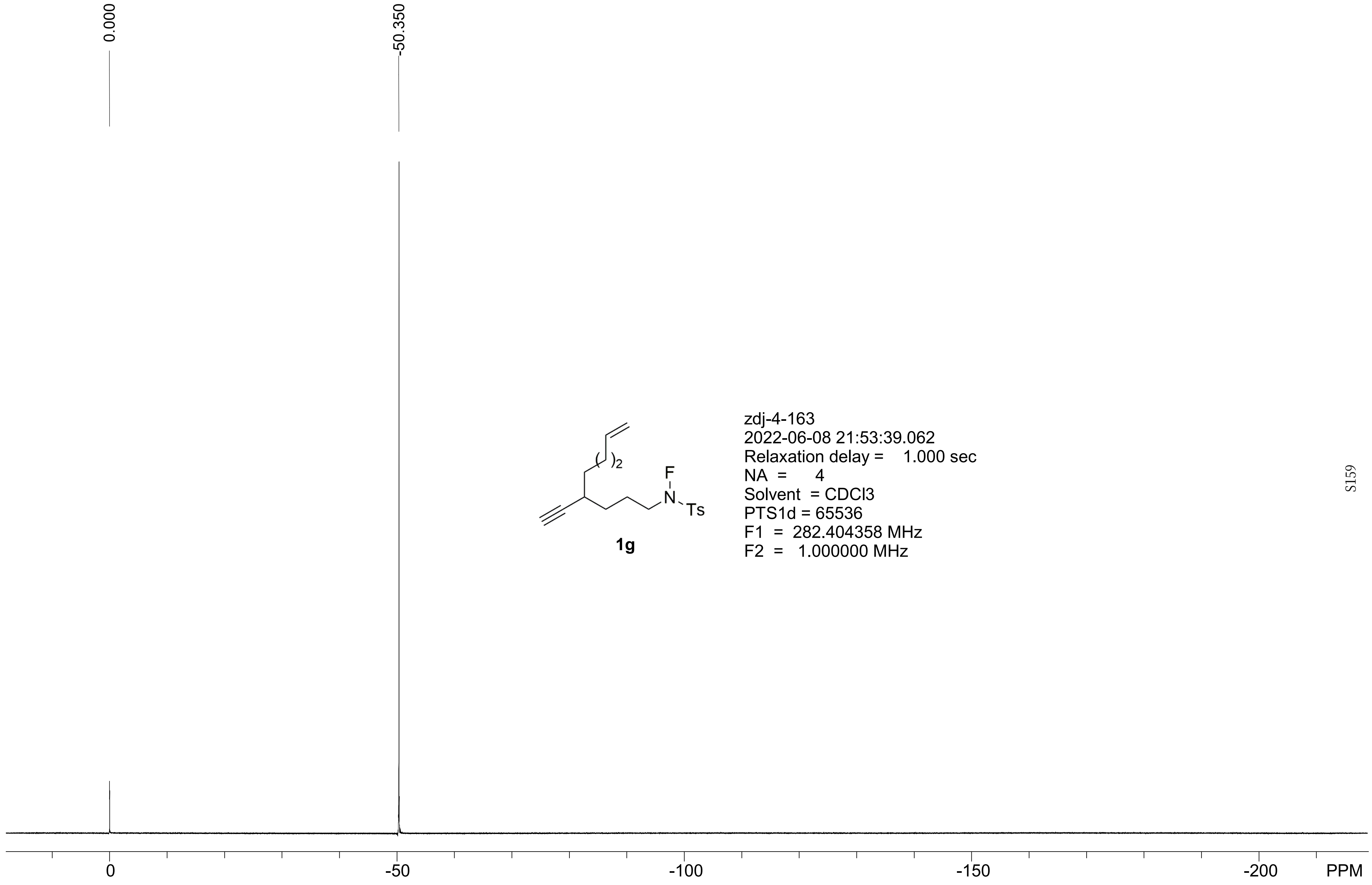


Purity (96%) is determined by Nitromethane (3.6 μL, 0.067 mmol)
as the internal standard in 99.8 mg of sample

zdj-4-163-purity
2022-05-23 11:07:16.593
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

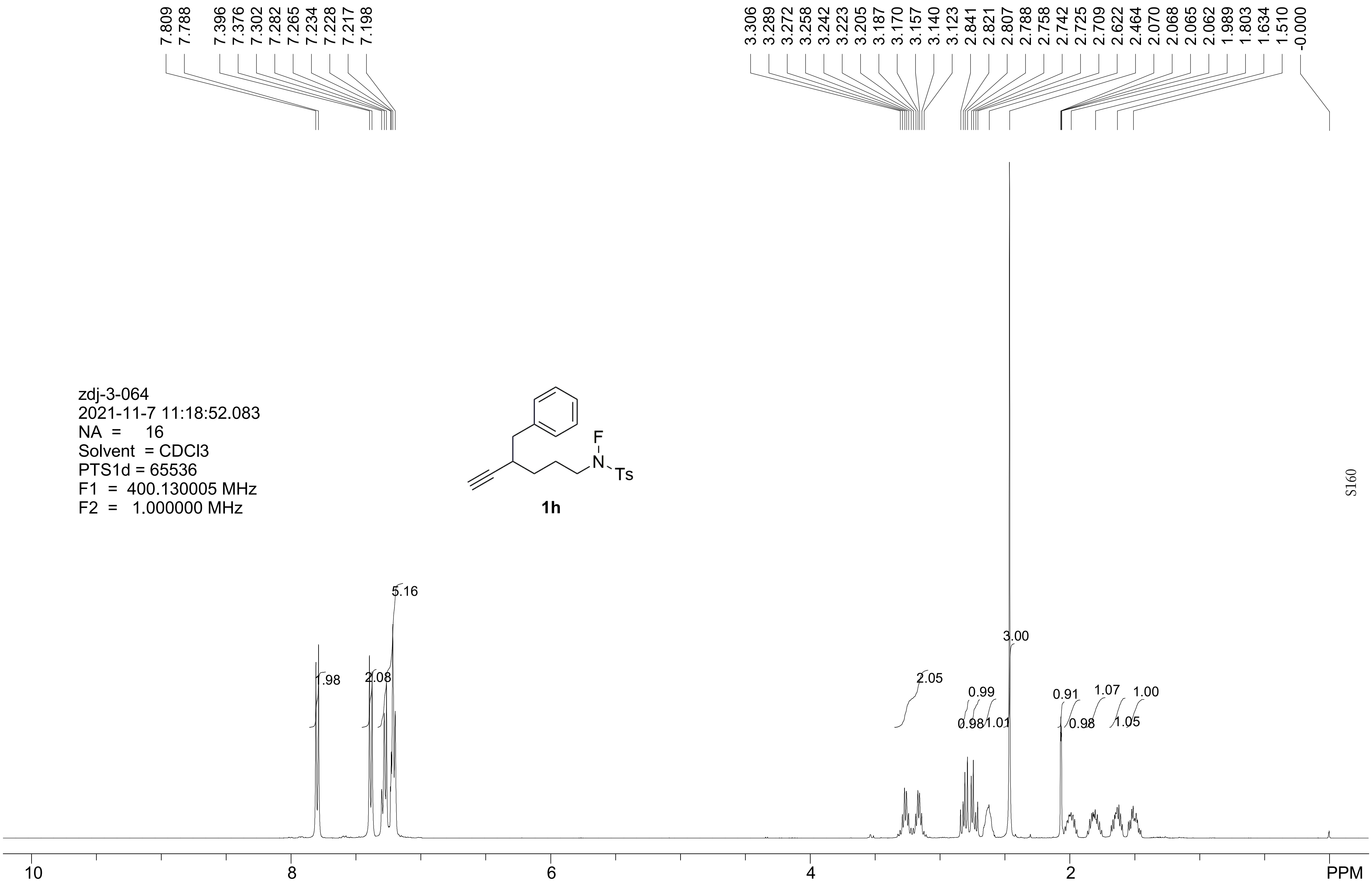
1g

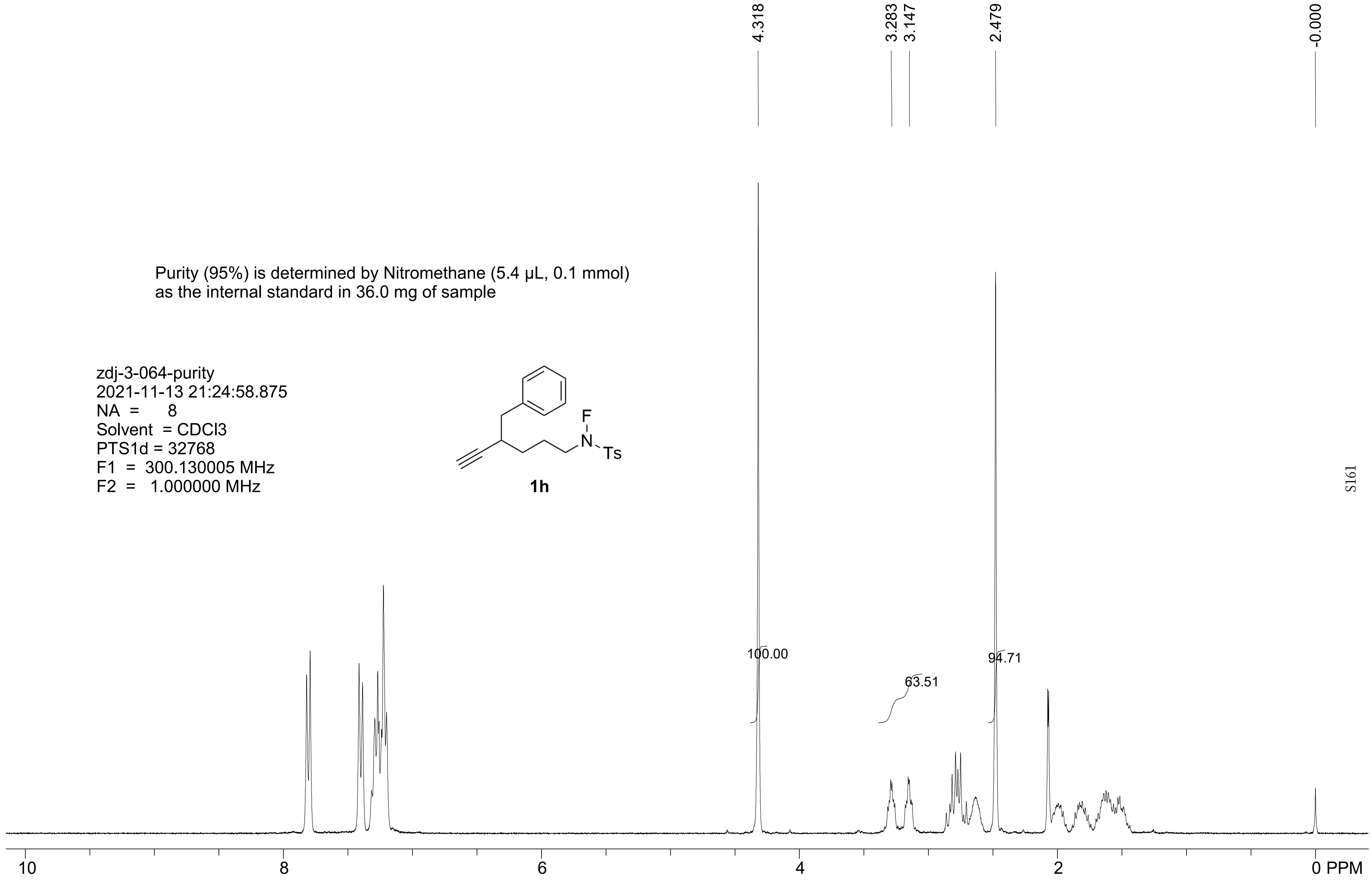

146.226
138.467
129.898
128.740
114.601
86.791
77.257
77.000
76.752
69.903
53.502
53.401
34.242
33.369
31.631
30.886
26.308
24.046
21.702
zdj-4-163
2022-05-19 17:13:23.017
Relaxation delay = 1.500 sec
NA = 100
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
F
N
Ts
2
1g
250
200
150
100
50
0
PPM



1g

zdj-4-163
2022-06-08 21:53:39.062
Relaxation delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz

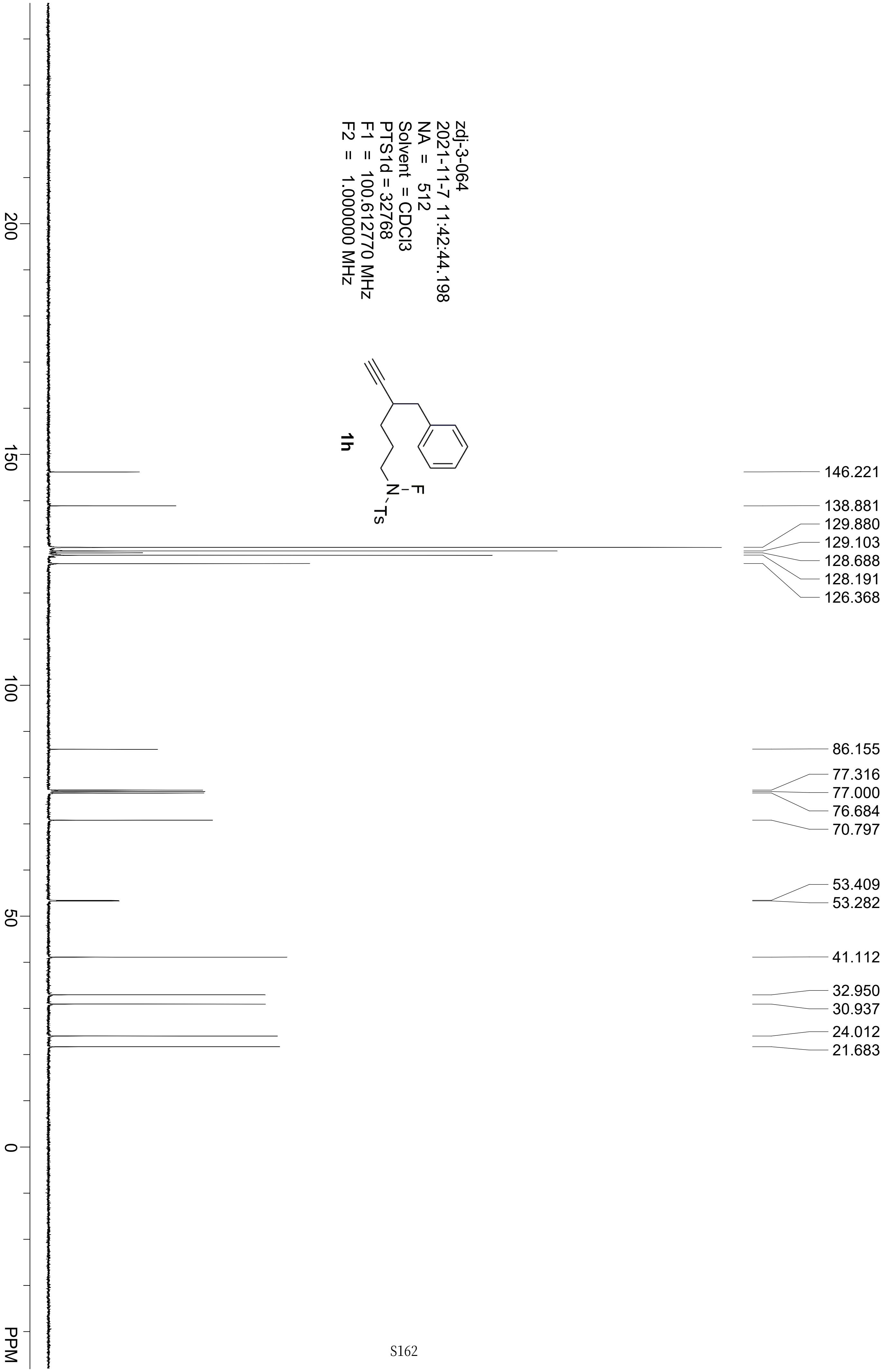

7.809
7.788
7.396
7.376
7.302
7.282
7.265
7.234
7.228
7.217
7.198
3.306
3.289
3.272
3.258
3.242
3.223
3.205
3.187
3.170
3.157
3.140
3.123
2.841
2.821
2.807
2.788
2.758
2.742
2.725
2.709
2.622
2.464
2.070
2.068
2.065
2.062
1.989
1.803
1.634
1.510
-0.000
zdj-3-064
2021-11-7 11:18:52.083
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
F
N
Ts
1h
1.98
2.08
5.16
2.05
0.99
0.98
1.01
3.00
0.91
0.98
1.07
1.05
1.00
10
8
6
4
2
PPM

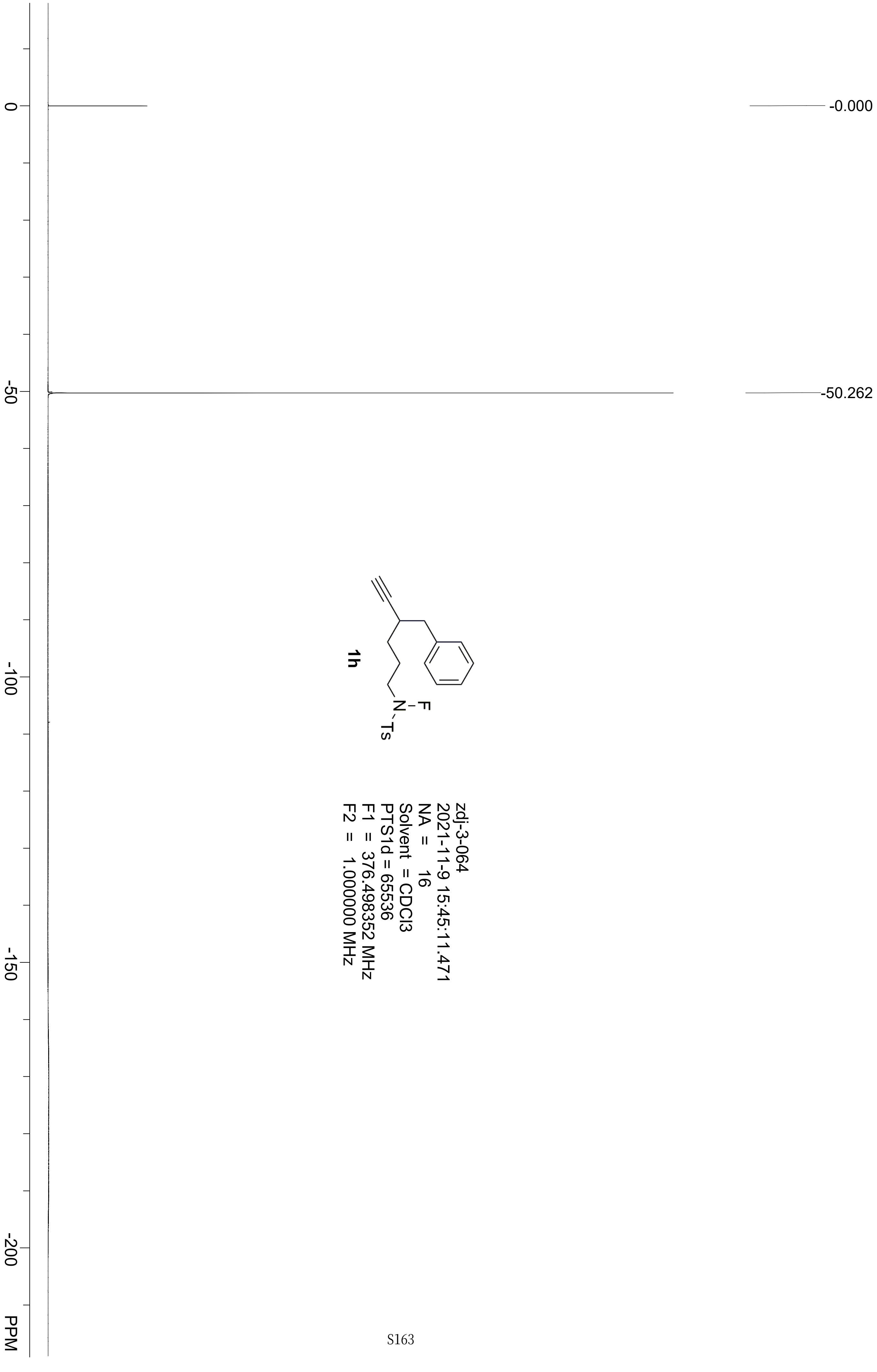


Purity (95%) is determined by Nitromethane (5.4 μL, 0.1 mmol) as the internal standard in 36.0 mg of sample

zdj-3-064-purity
2021-11-13 21:24:58.875
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

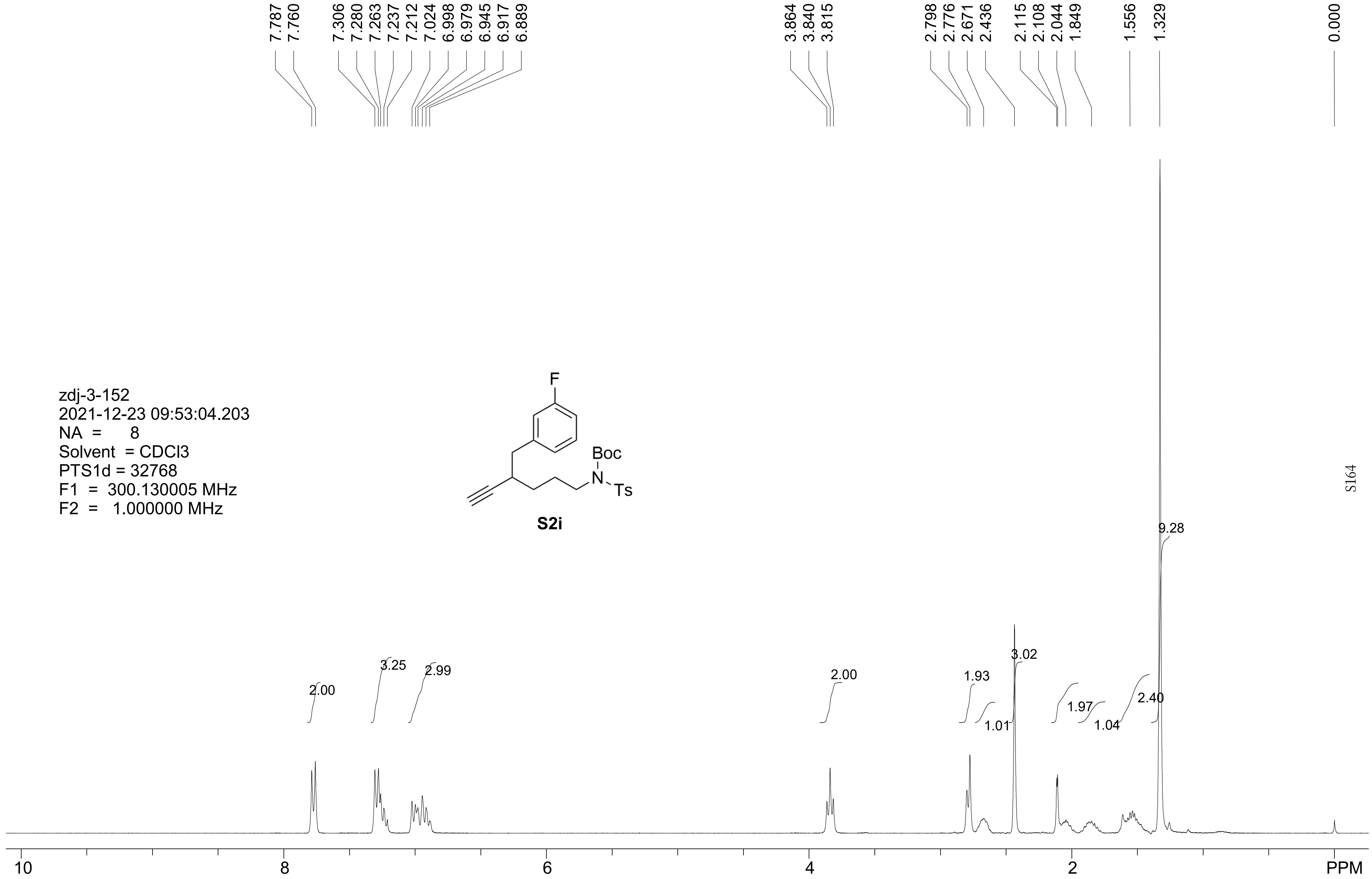
1h


zdj-3-064
2021-11-7 11:42:44.198
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
1h
F
N
Ts
146.221
138.881
129.880
129.103
128.688
128.191
126.368
86.155
77.316
77.000
76.684
70.797
53.409
53.282
41.112
32.950
30.937
24.012
21.683
200
150
100
50
0
PPM

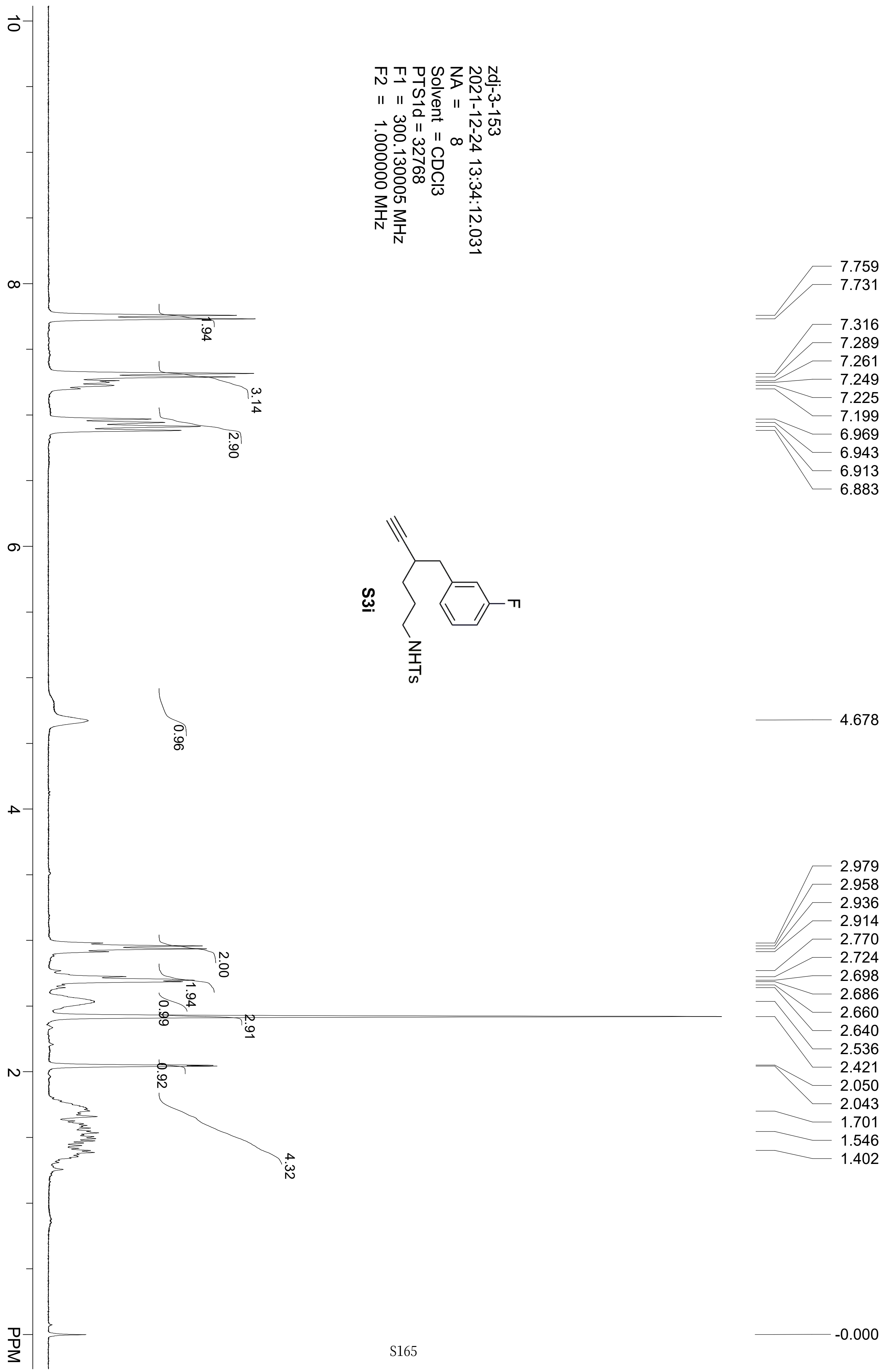


-0.000
-50.262
0
-50
-100
-150
-200
PPM
F
N
Ts
zdj-3-064
2021-11-9 15:45:11.471
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz

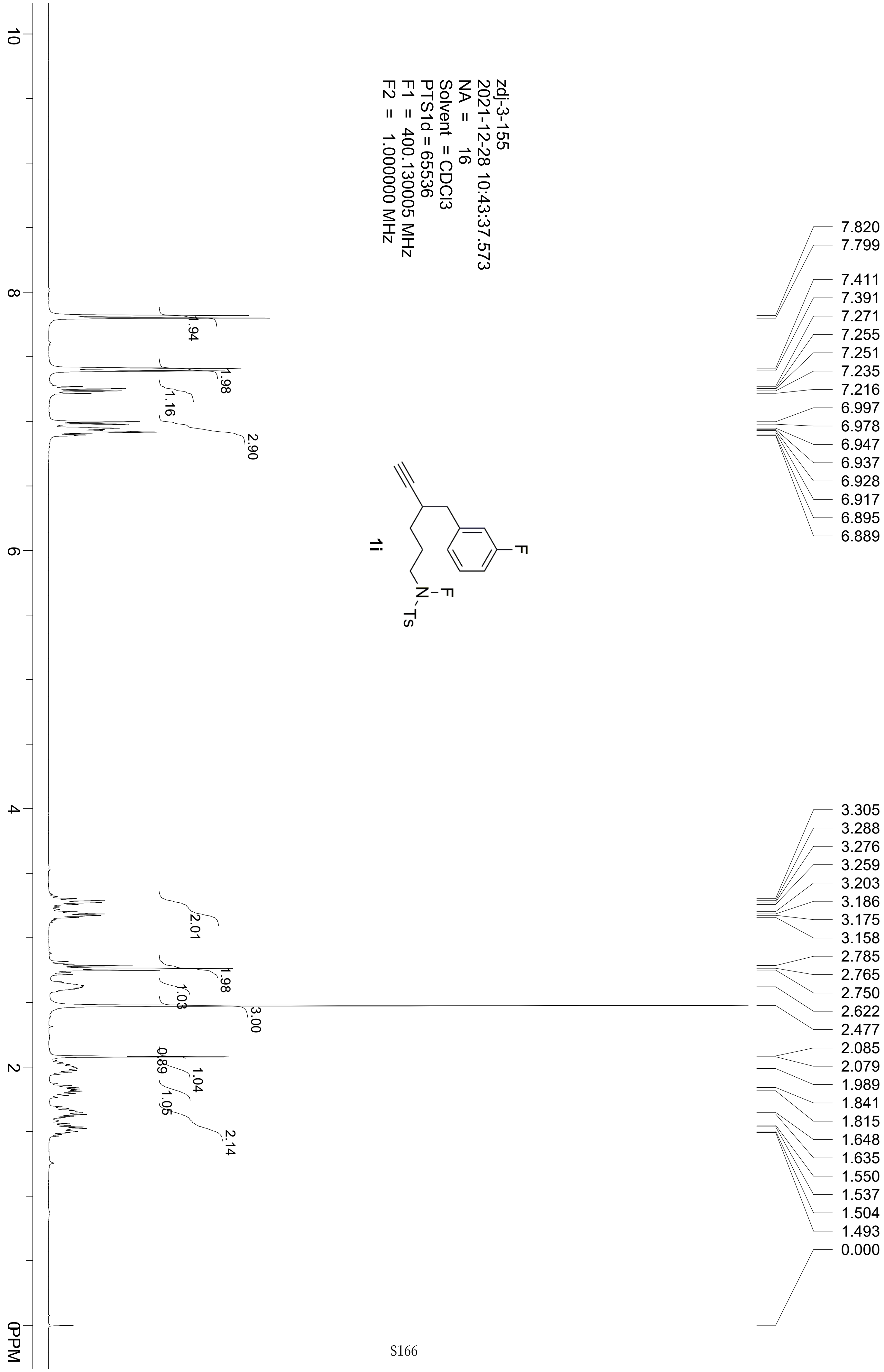
1h

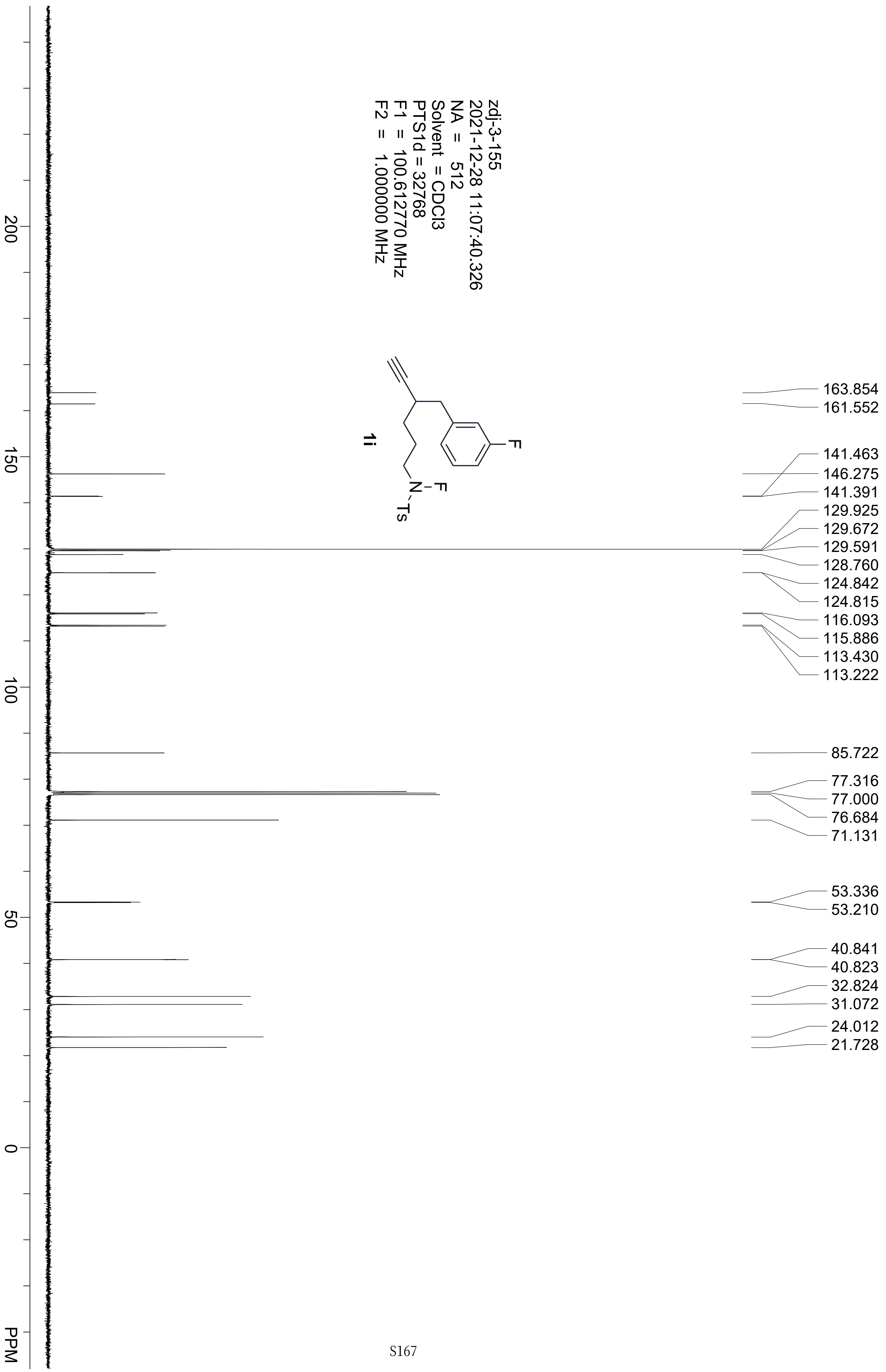

zdj-3-152
2021-12-23 09:53:04.203
NA =   8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

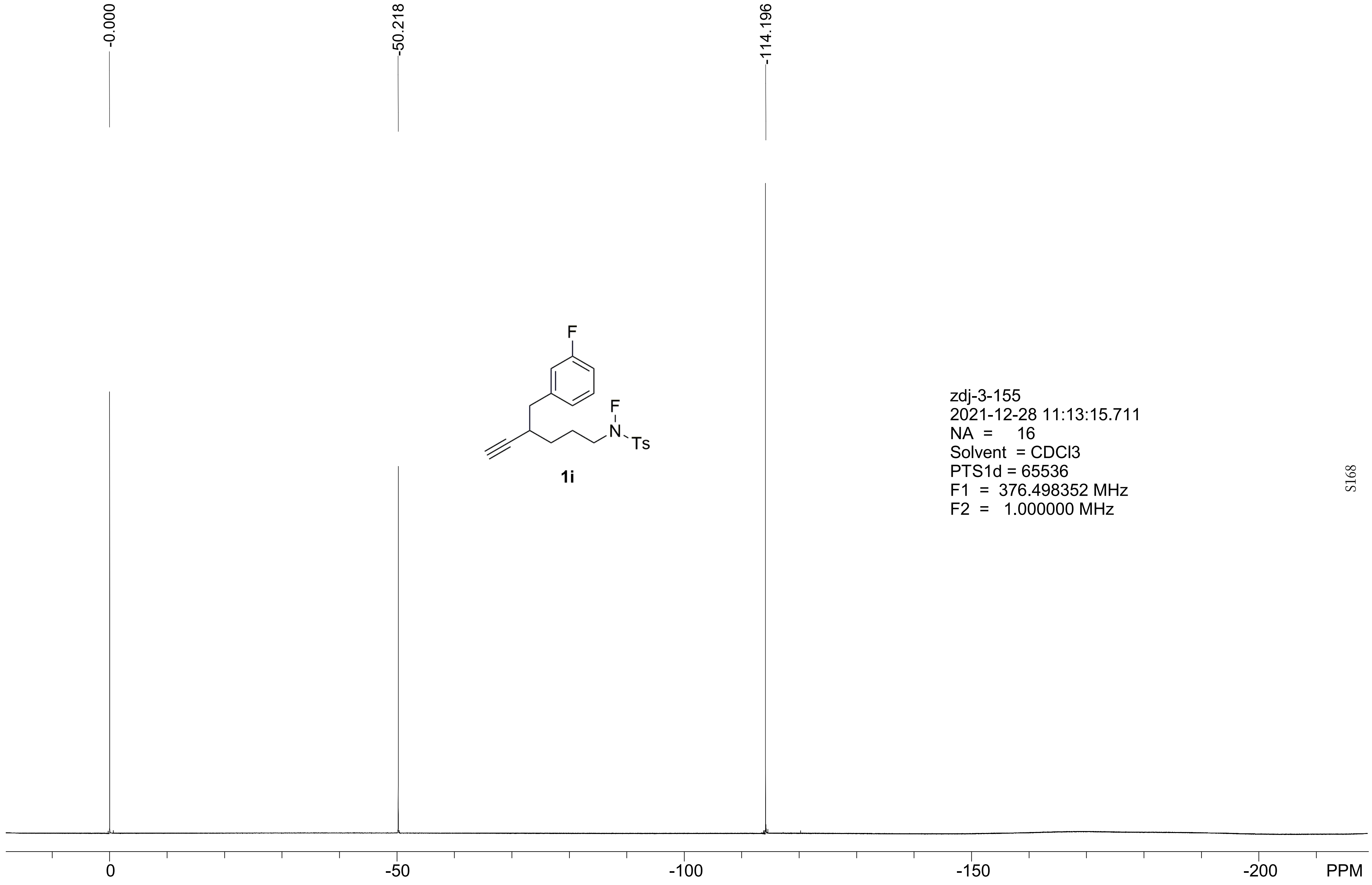
S2i


zdj-3-153
2021-12-24 13:34:12.031
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
F
NHTs
10
8
6
4
2
PPM
1.94
3.14
2.90
0.96
2.00
1.94
0.99
2.91
0.92
4.32
7.759
7.731
7.316
7.289
7.261
7.249
7.225
7.199
6.969
6.943
6.913
6.883
4.678
2.979
2.958
2.936
2.914
2.770
2.724
2.698
2.686
2.660
2.640
2.536
2.421
2.050
2.043
1.701
1.546
1.402
-0.000

S3i

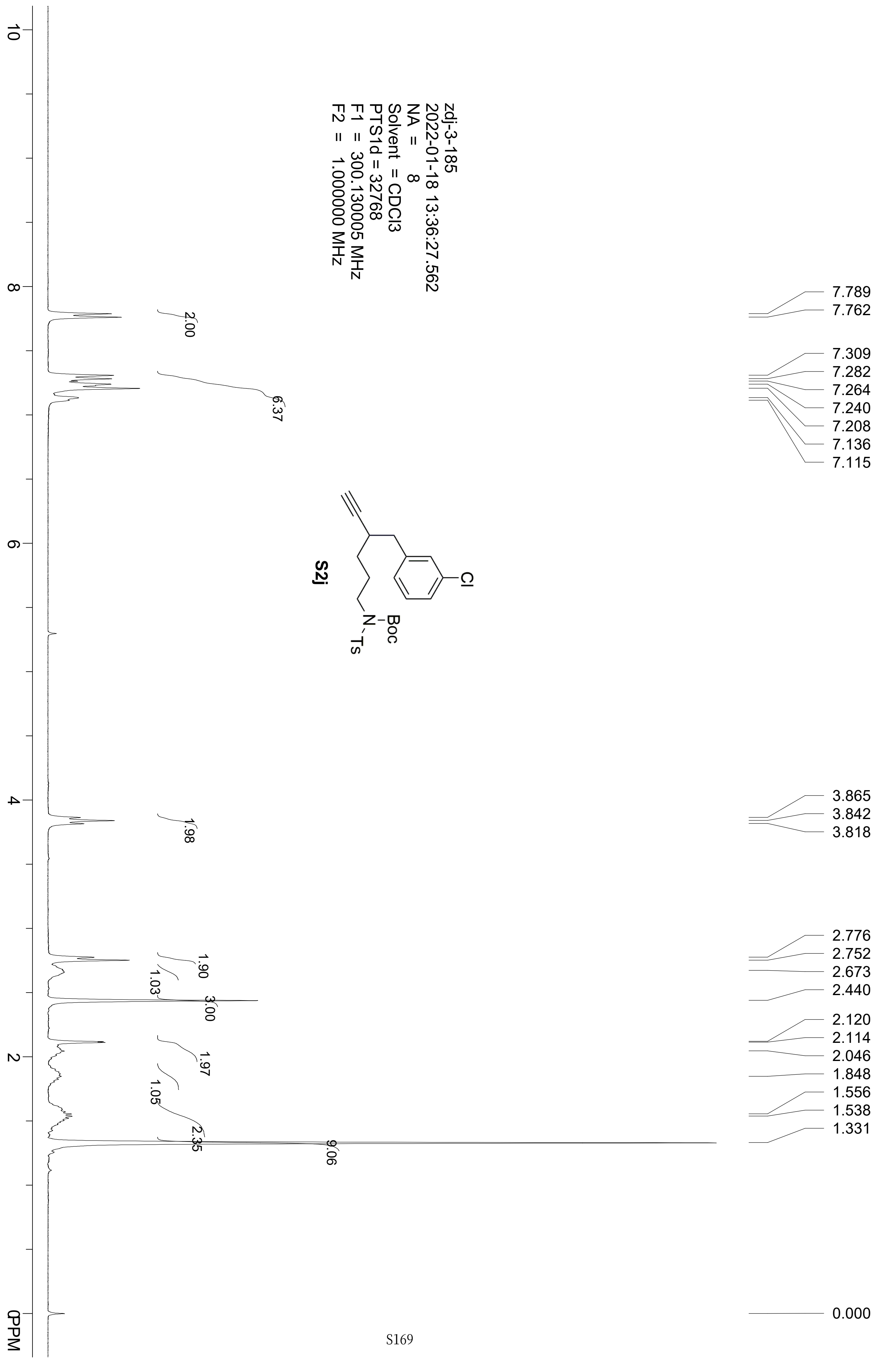

zdj-3-155
2021-12-28 10:43:37.573
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
1i
F
F
N
Ts
7.820
7.799
7.411
7.391
7.271
7.255
7.251
7.235
7.216
6.997
6.978
6.947
6.937
6.928
6.917
6.895
6.889
3.305
3.288
3.276
3.259
3.203
3.186
3.175
3.158
2.785
2.765
2.750
2.622
2.477
2.085
2.079
1.989
1.841
1.815
1.648
1.635
1.550
1.537
1.504
1.493
0.000
1.94
1.98
1.16
2.90
2.01
1.98
1.03
3.00
0.89
1.04
1.05
2.14
10
8
6
4
2
0
PPM

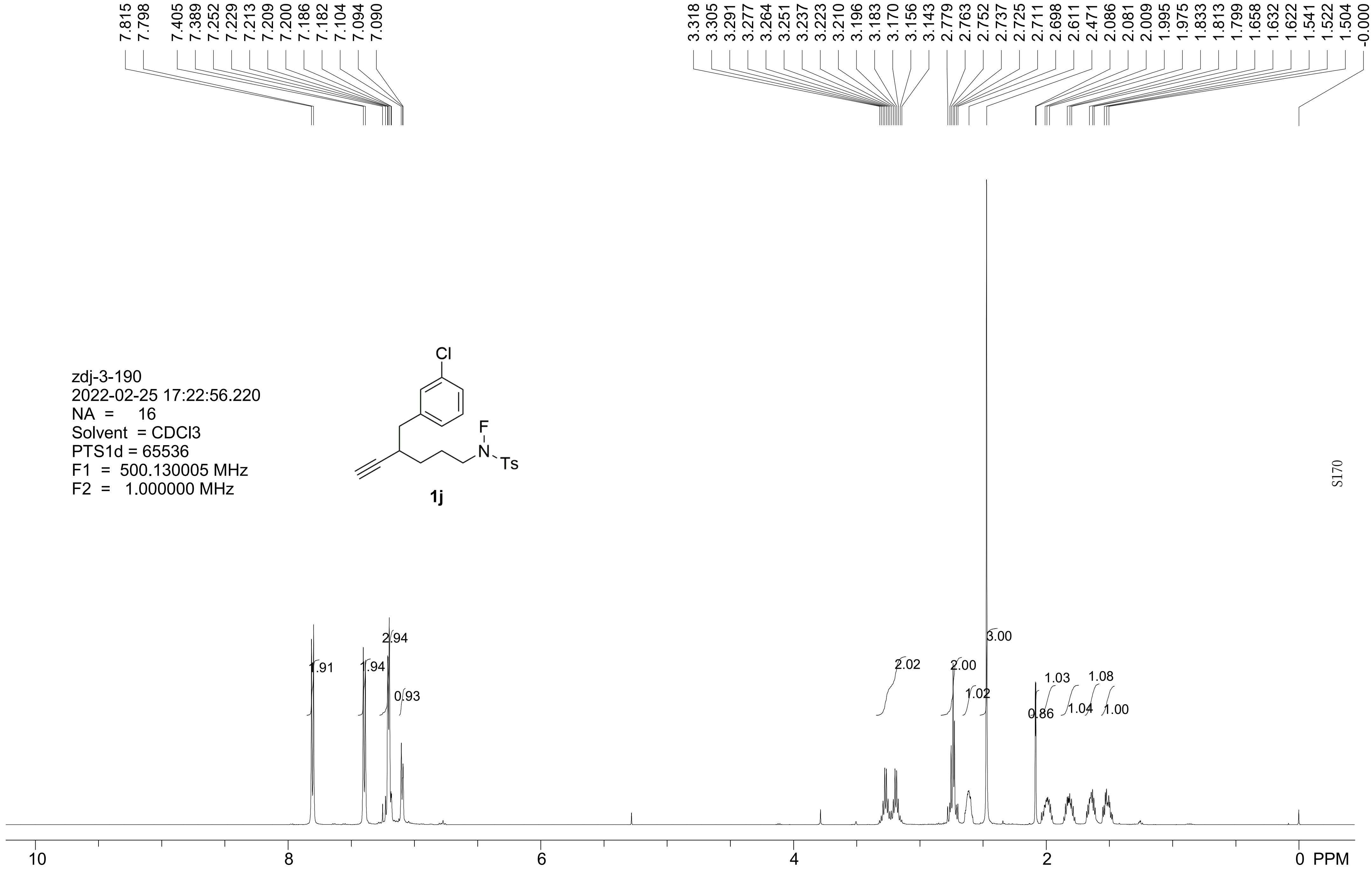

zdj-3-155
2021-12-28 11:07:40.326
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
F
F
N
Ts
1i
163.854
161.552
141.463
146.275
141.391
129.925
129.672
129.591
128.760
124.842
124.815
116.093
115.886
113.430
113.222
85.722
77.316
77.000
76.684
71.131
53.336
53.210
40.841
40.823
32.824
31.072
24.012
21.728
200
150
100
50
0
PPM

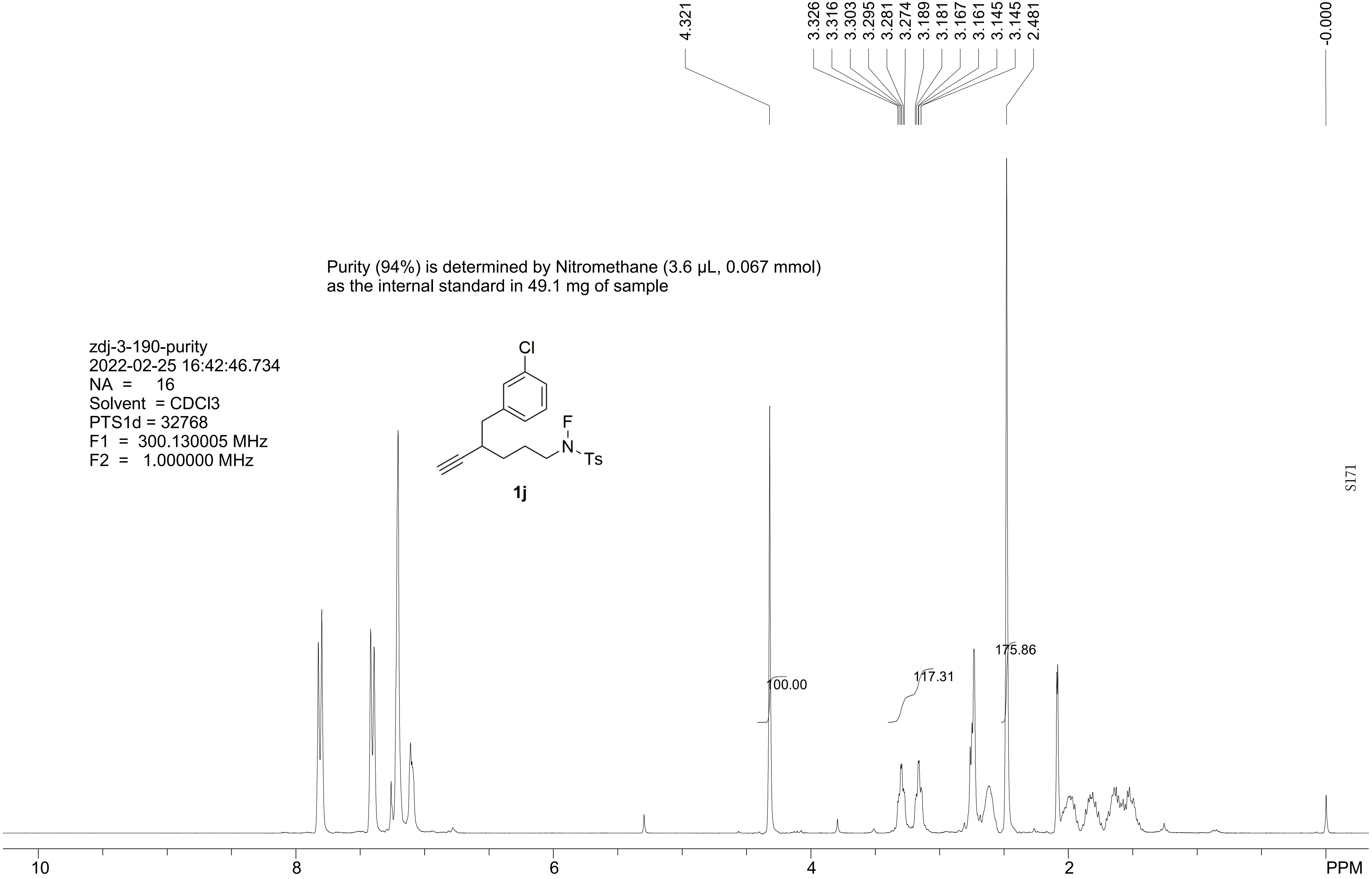


1i

zdj-3-155
2021-12-28 11:13:15.711
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz


zdj-3-185
2022-01-18 13:36:27.562
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
S2j
Cl
Boc
N
Ts
7.789
7.762
7.309
7.282
7.264
7.240
7.208
7.136
7.115
3.865
3.842
3.818
2.776
2.752
2.673
2.440
2.120
2.114
2.046
1.848
1.556
1.538
1.331
0.000
2.00
6.37
1.98
1.90
1.03
3.00
1.97
1.05
2.35
9.06
10
8
6
4
2
0
PPM

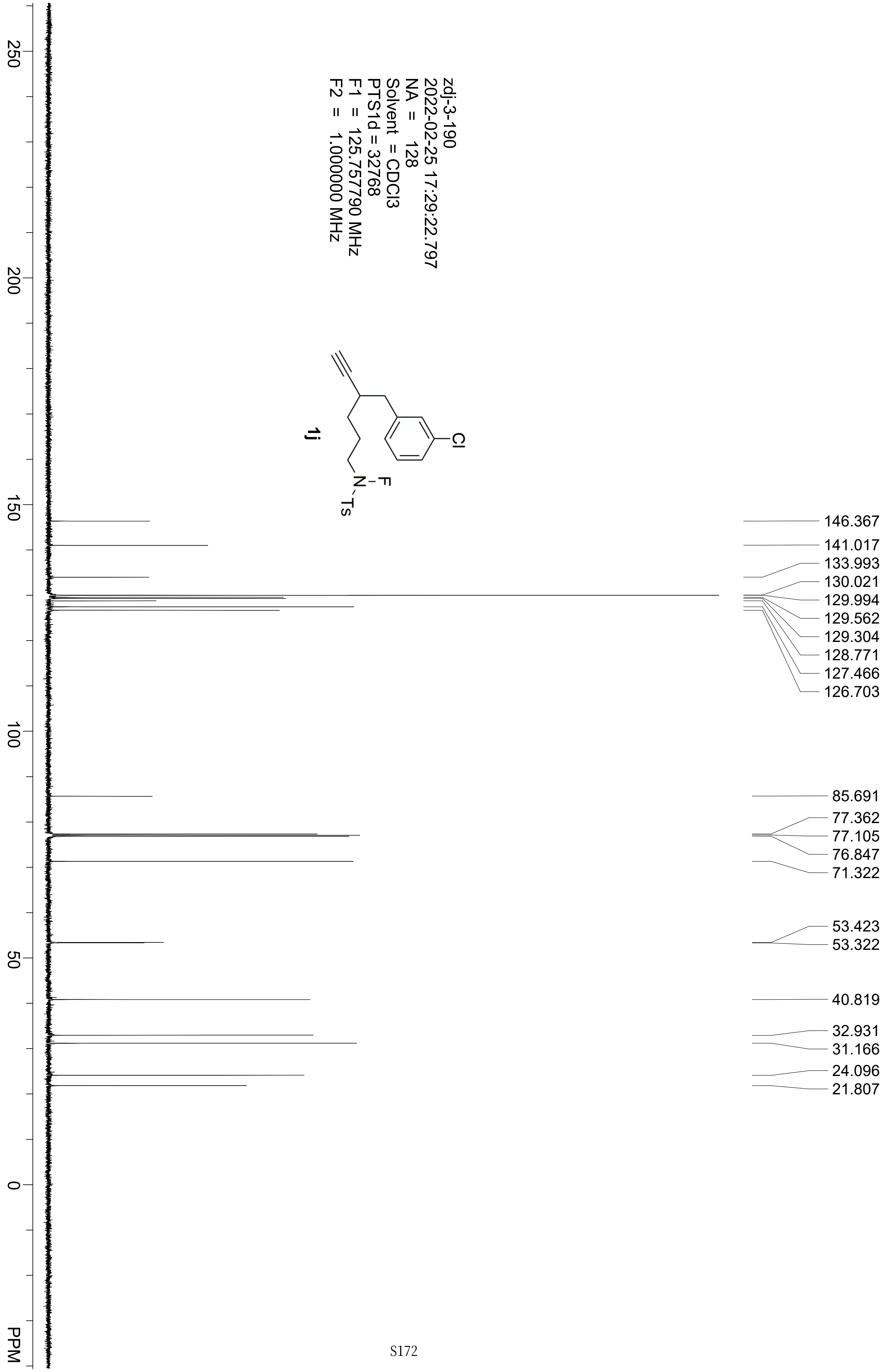

zdj-3-190
2022-02-25 17:22:56.220
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
Cl
F
N
Ts
1j
7.815
7.798
7.405
7.389
7.252
7.229
7.213
7.209
7.200
7.186
7.182
7.104
7.094
7.090
3.318
3.305
3.291
3.277
3.264
3.251
3.237
3.223
3.210
3.196
3.183
3.170
3.156
3.143
2.779
2.763
2.752
2.737
2.725
2.711
2.698
2.611
2.471
2.086
2.081
2.009
1.995
1.975
1.833
1.813
1.799
1.658
1.632
1.622
1.541
1.522
1.504
-0.000
1.91
1.94
2.94
0.93
2.02
2.00
1.02
3.00
0.86
1.03
1.04
1.08
1.00
10
8
6
4
2
0 PPM



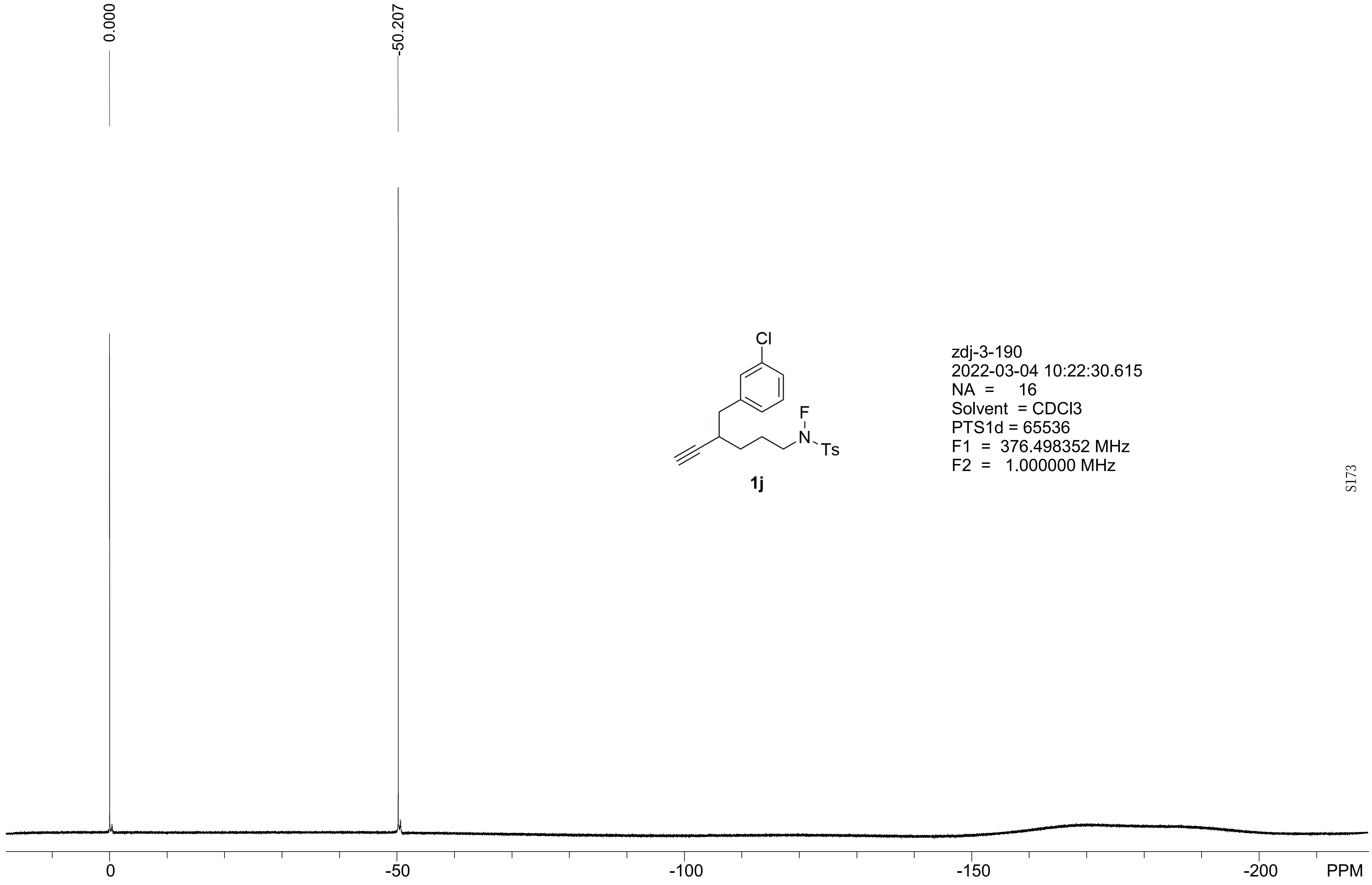
1j

Purity (94%) is determined by Nitromethane (3.6 μL, 0.067 mmol)
as the internal standard in 49.1 mg of sample

zdj-3-190-purity
2022-02-25 16:42:46.734
NA = 16
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

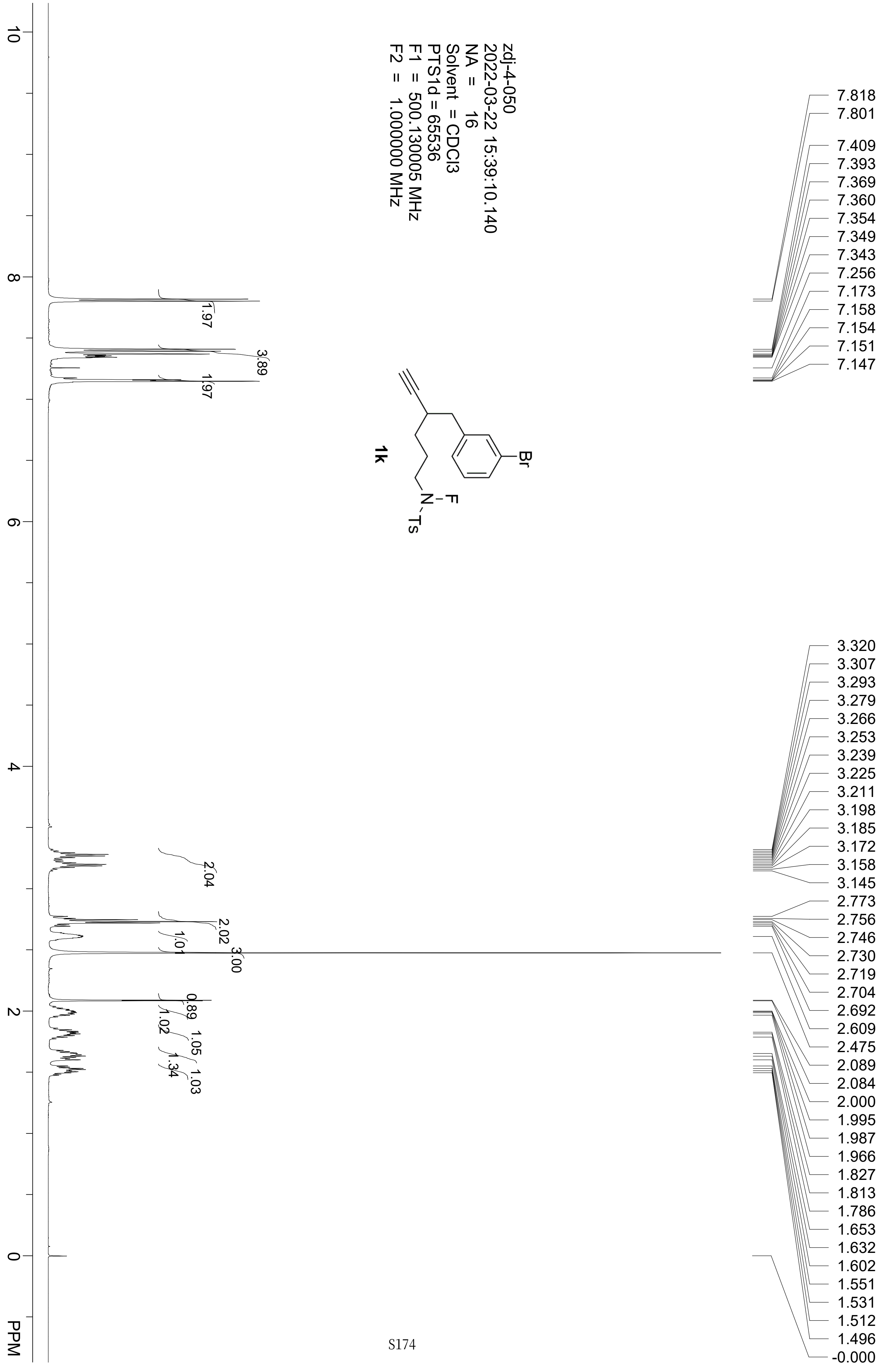

zdj-3-190
2022-02-25 17:29:22.797
NA = 128
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
Cl
F
N
Ts
146.367
141.017
133.993
130.021
129.994
129.562
129.304
128.771
127.466
126.703
85.691
77.362
77.105
76.847
71.322
53.423
53.322
40.819
32.931
31.166
24.096
21.807
250
200
150
100
50
0
PPM

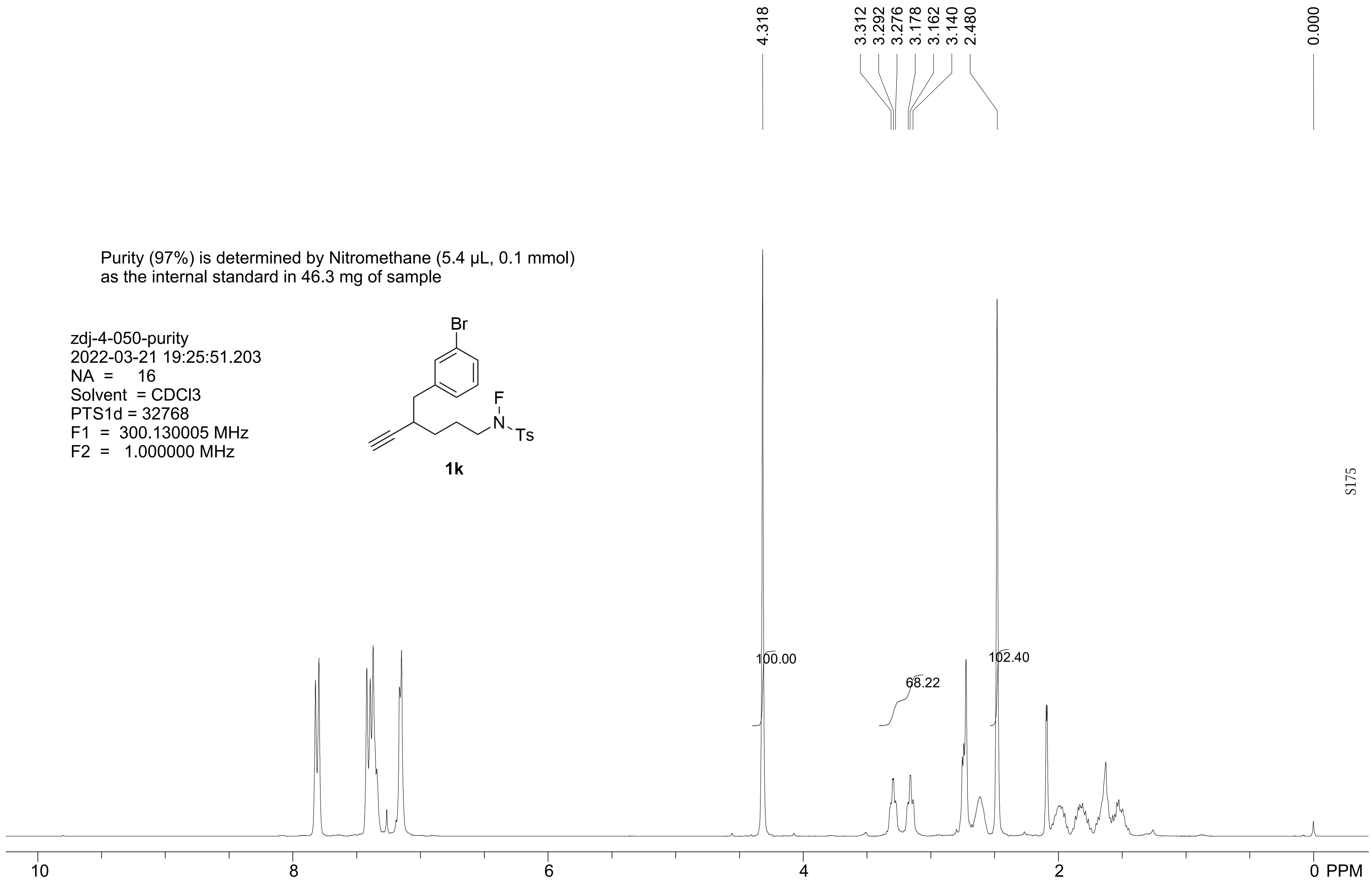
1j



1j

zdj-3-190
2022-03-04 10:22:30.615
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz

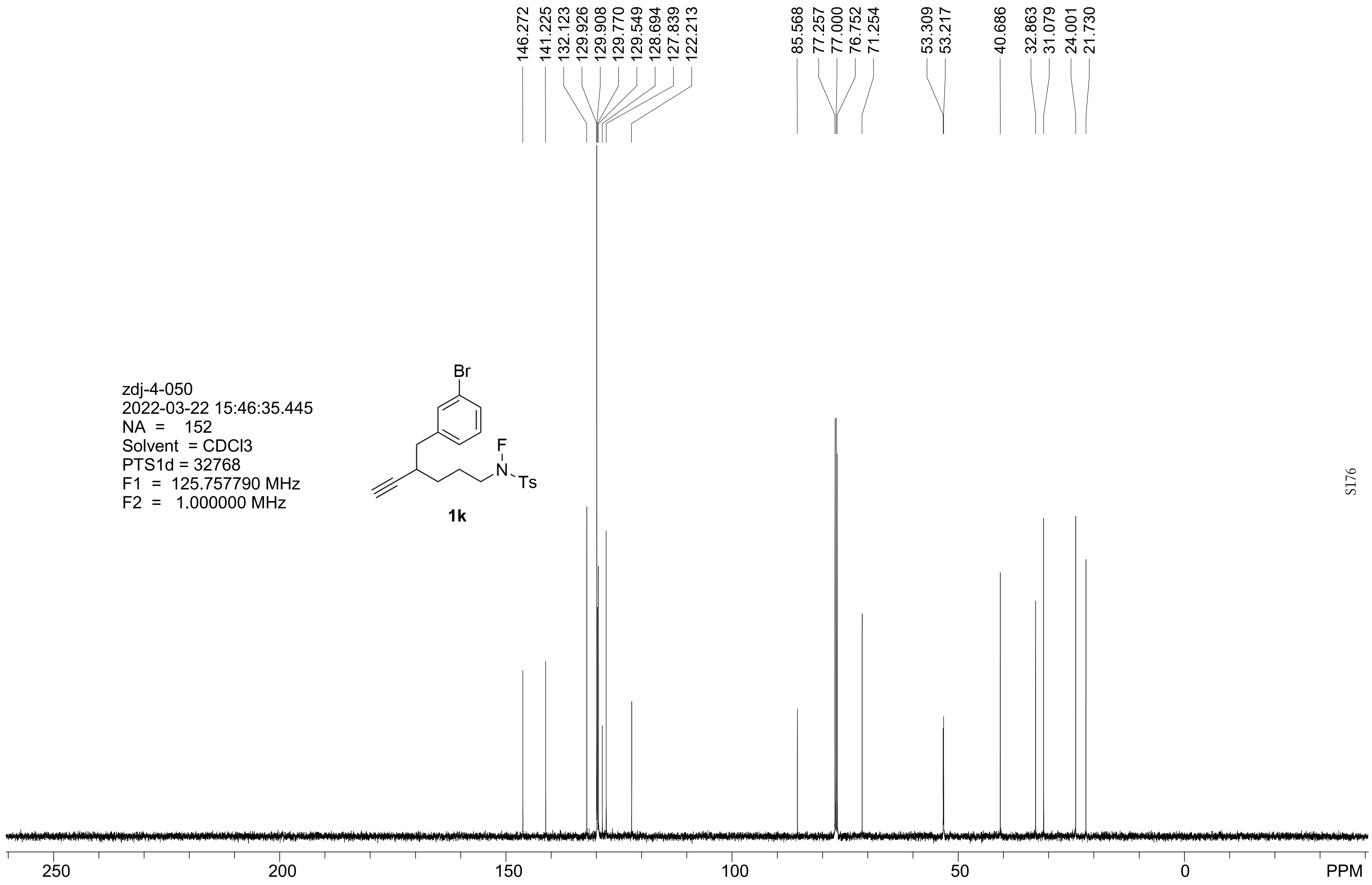

zdj-4-050
2022-03-22 15:39:10.140
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
Br
F
N
Ts
1k
7.818
7.801
7.409
7.393
7.369
7.360
7.354
7.349
7.343
7.256
7.173
7.158
7.154
7.151
7.147
3.320
3.307
3.293
3.279
3.266
3.253
3.239
3.225
3.211
3.198
3.185
3.172
3.158
3.145
2.773
2.756
2.746
2.730
2.719
2.704
2.692
2.609
2.475
2.089
2.084
2.000
1.995
1.987
1.966
1.827
1.813
1.786
1.653
1.632
1.602
1.551
1.531
1.512
1.496
-0.000
1.97
3.89
1.97
2.04
2.02
1.01
3.00
0.89
1.02
1.05
1.34
1.03
10
8
6
4
2
0
PPM

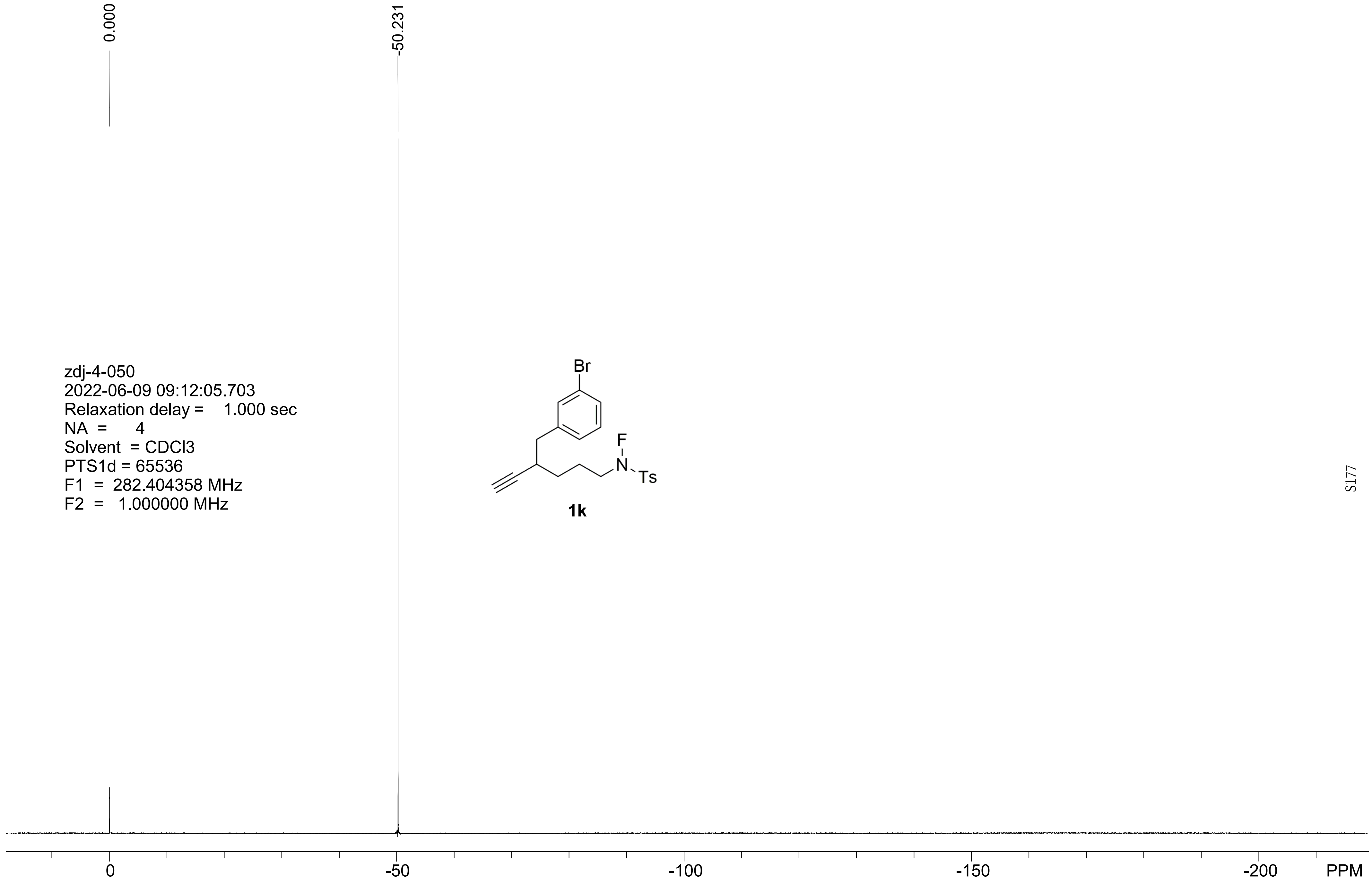


Purity (97%) is determined by Nitromethane (5.4 µL, 0.1 mmol)
as the internal standard in 46.3 mg of sample

zdj-4-050-purity
2022-03-21 19:25:51.203
NA = 16
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

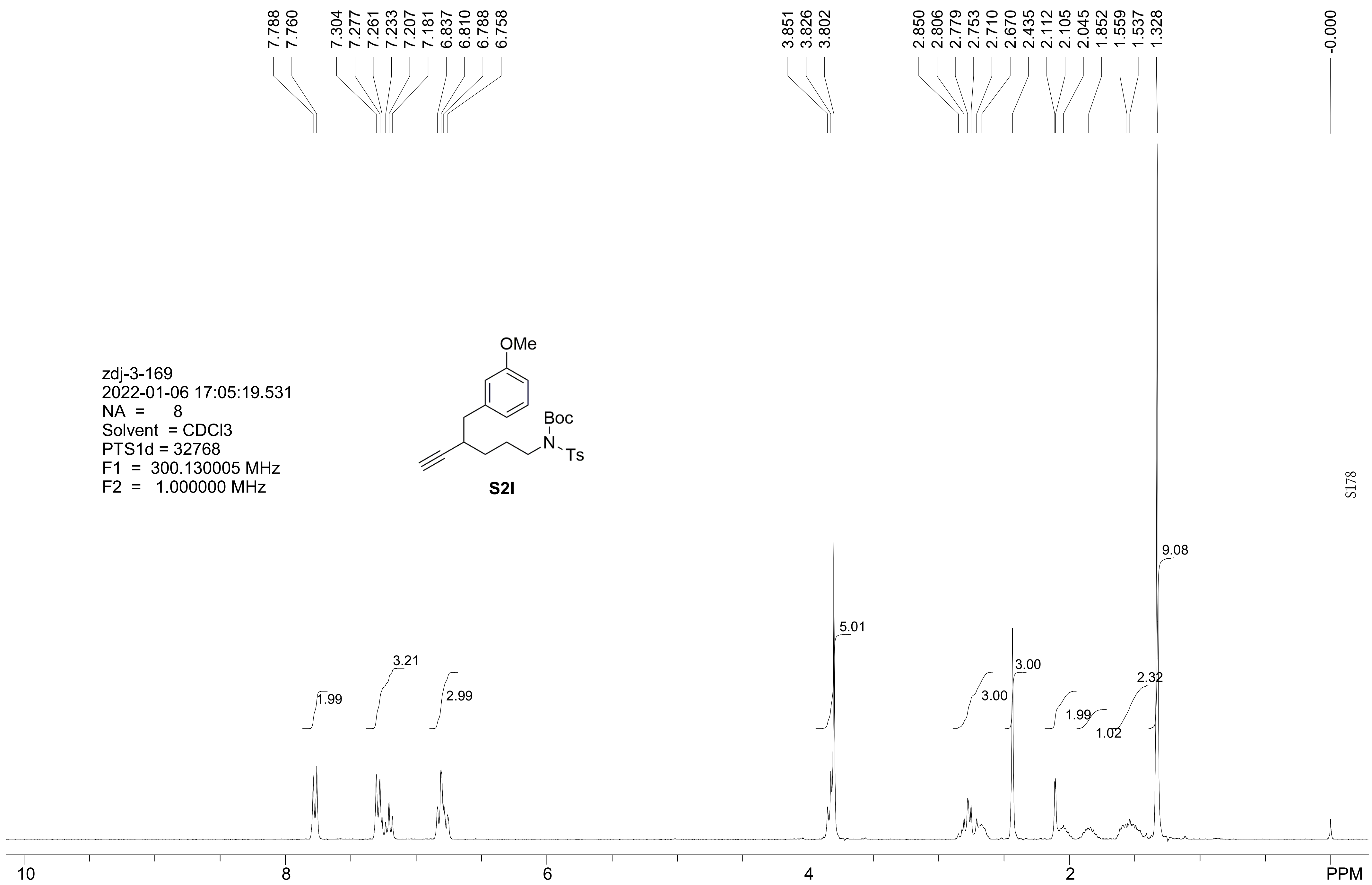
1k


zdj-4-050
2022-03-22 15:46:35.445
NA = 152
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
Br
F
N
Ts
1k
146.272
141.225
132.123
129.926
129.908
129.770
129.549
128.694
127.839
122.213
85.568
77.257
77.000
76.752
71.254
53.309
53.217
40.686
32.863
31.079
24.001
21.730
250
200
150
100
50
0
PPM



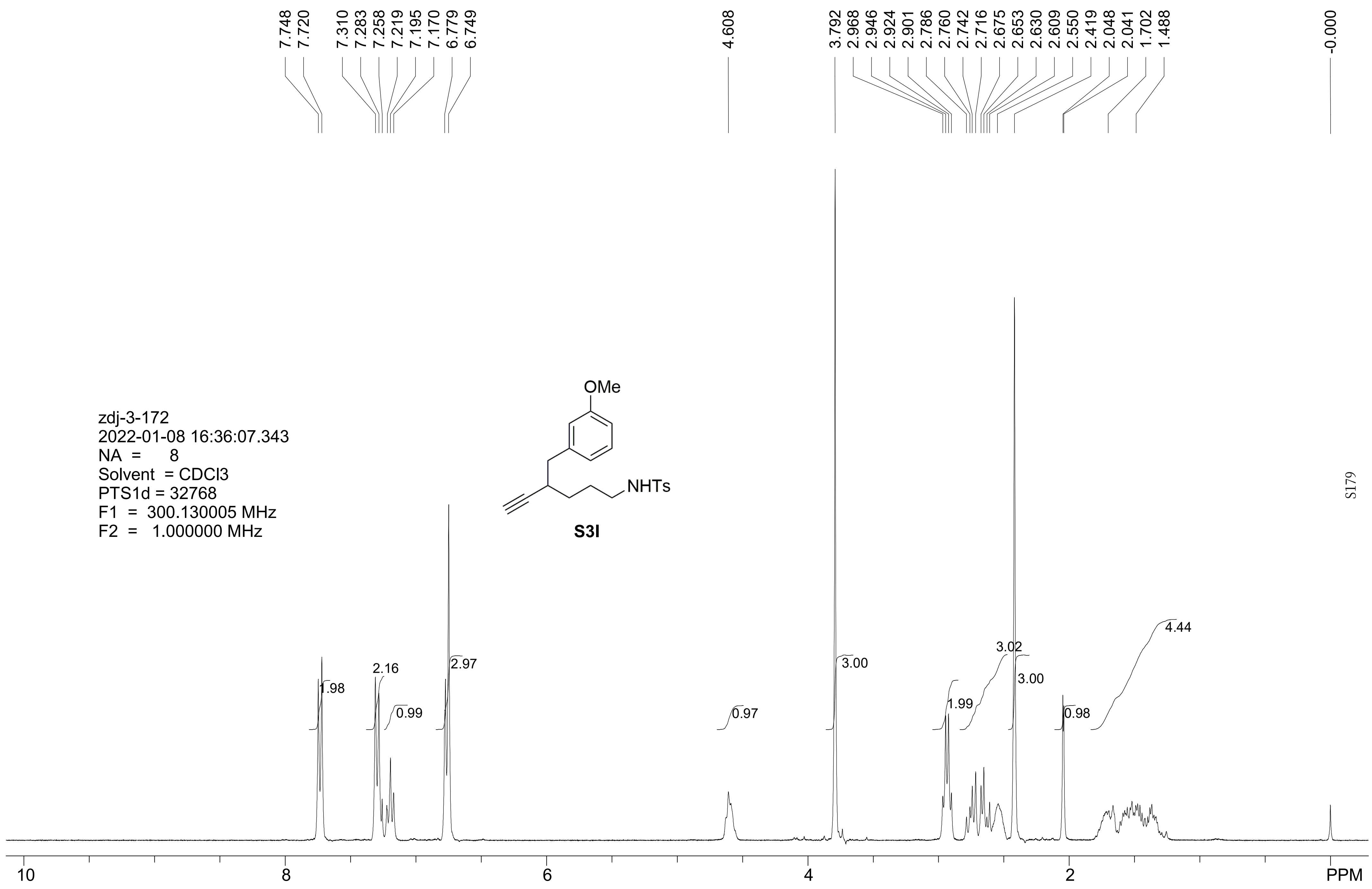
zdj-4-050
2022-06-09 09:12:05.703
Relaxation delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz

1k



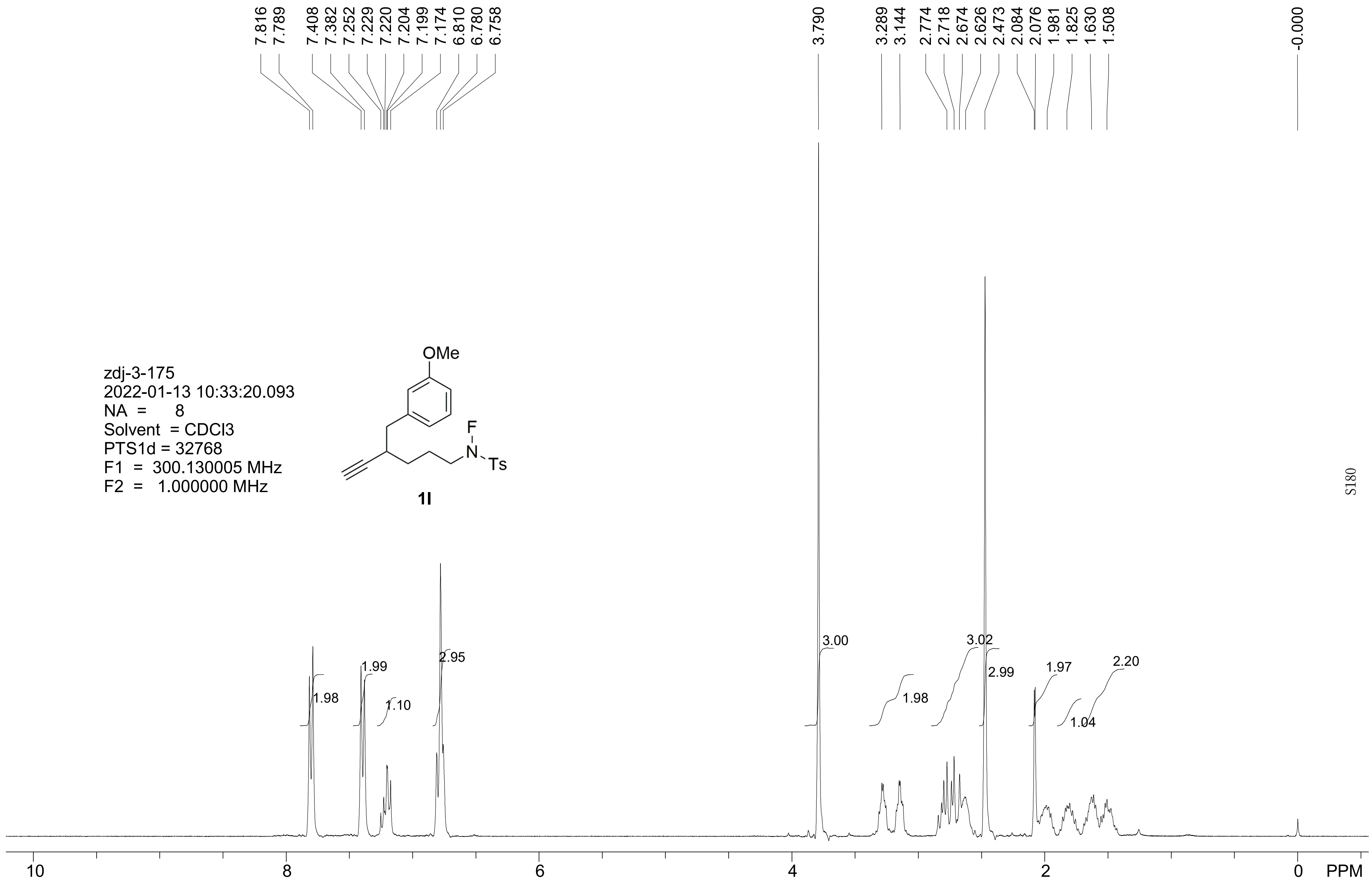
zdj-3-169
2022-01-06 17:05:19.531
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

S2l

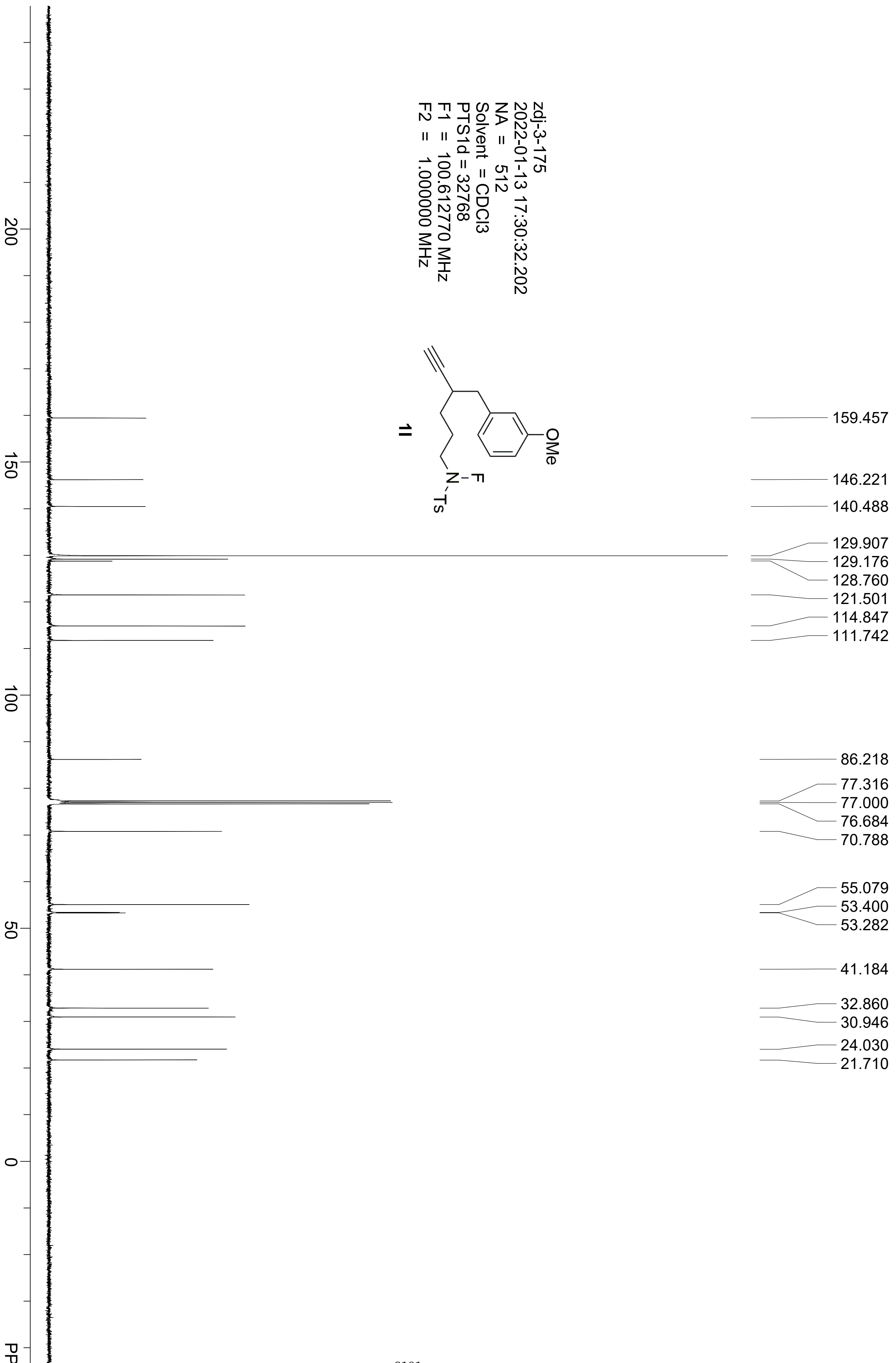


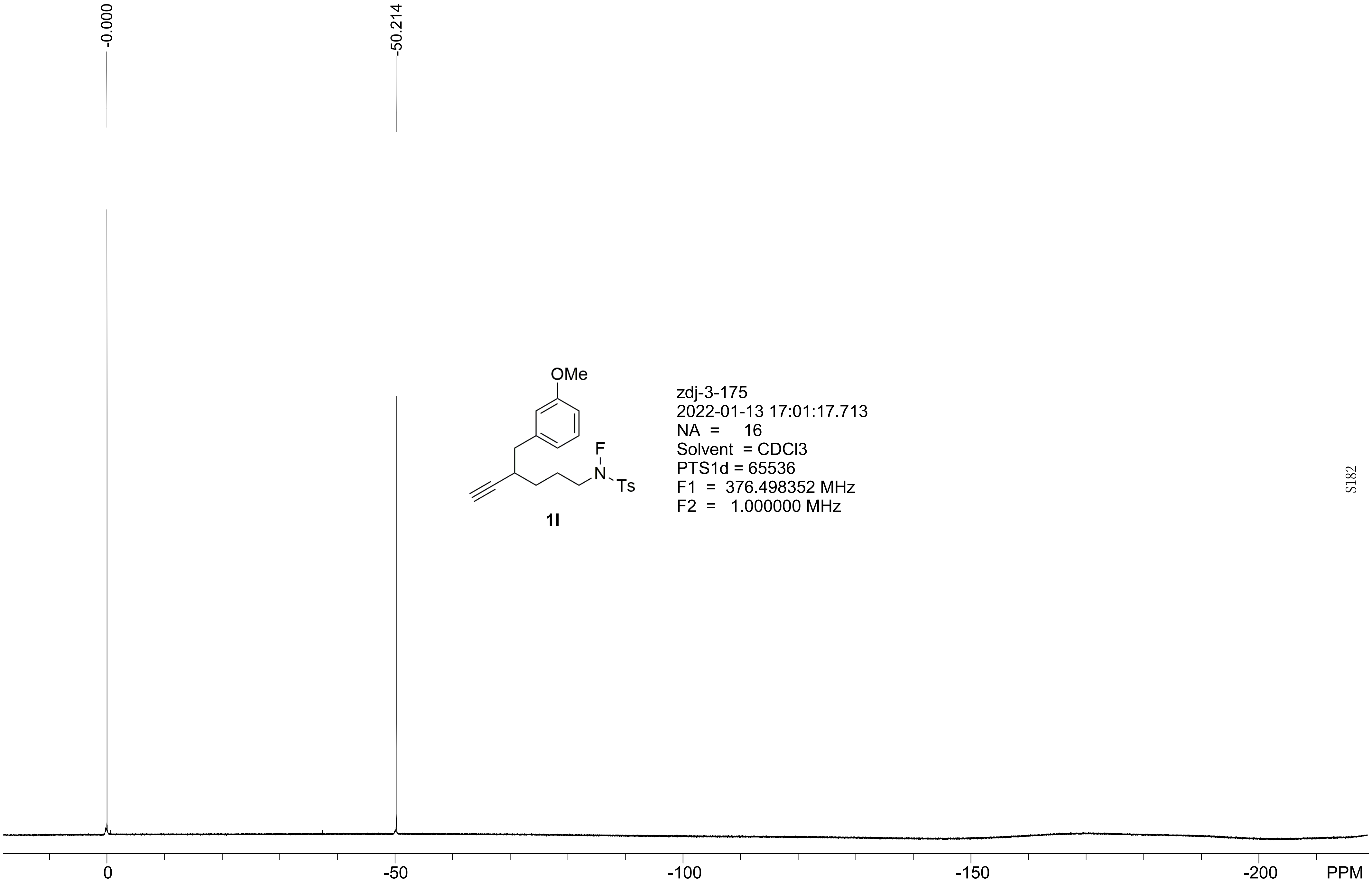
zdj-3-172
2022-01-08 16:36:07.343
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

S3l



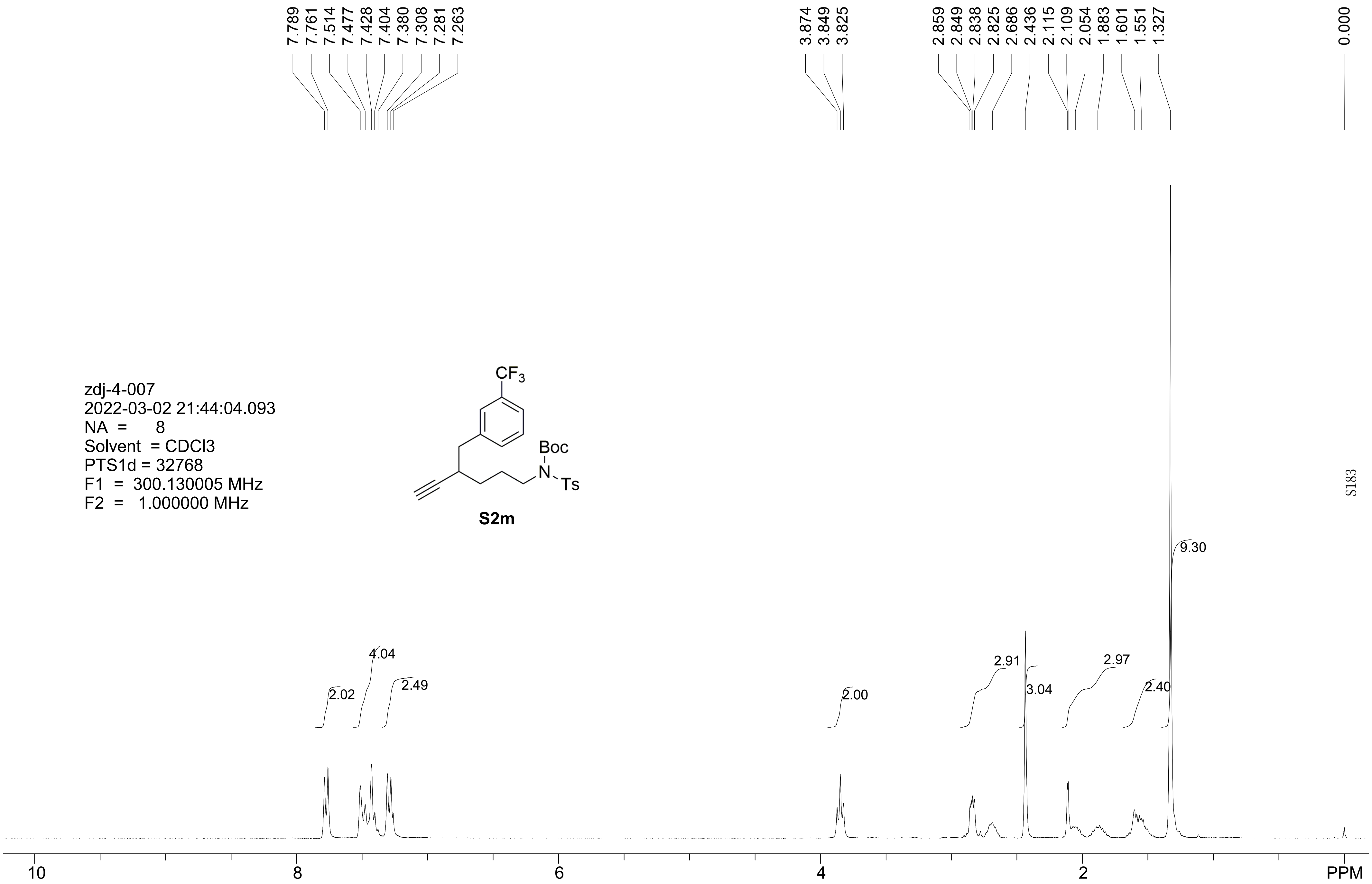
7.816
7.789
7.408
7.382
7.252
7.229
7.220
7.204
7.199
7.174
6.810
6.780
6.758
3.790
3.289
3.144
2.774
2.718
2.674
2.626
2.473
2.084
2.076
1.981
1.825
1.630
1.508
-0.000
zdj-3-175
2022-01-13 10:33:20.093
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
OMe
F
N
Ts
1l
1.98
1.99
1.10
2.95
3.00
1.98
3.02
2.99
1.97
1.04
2.20
10
8
6
4
2
0
PPM


zdj-3-175
2022-01-13 17:30:32.202
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
OMe
F
N
Ts
1l
159.457
146.221
140.488
129.907
129.176
128.760
121.501
114.847
111.742
86.218
77.316
77.000
76.684
70.788
55.079
53.400
53.282
41.184
32.860
30.946
24.030
21.710
200
150
100
50
0
PPM

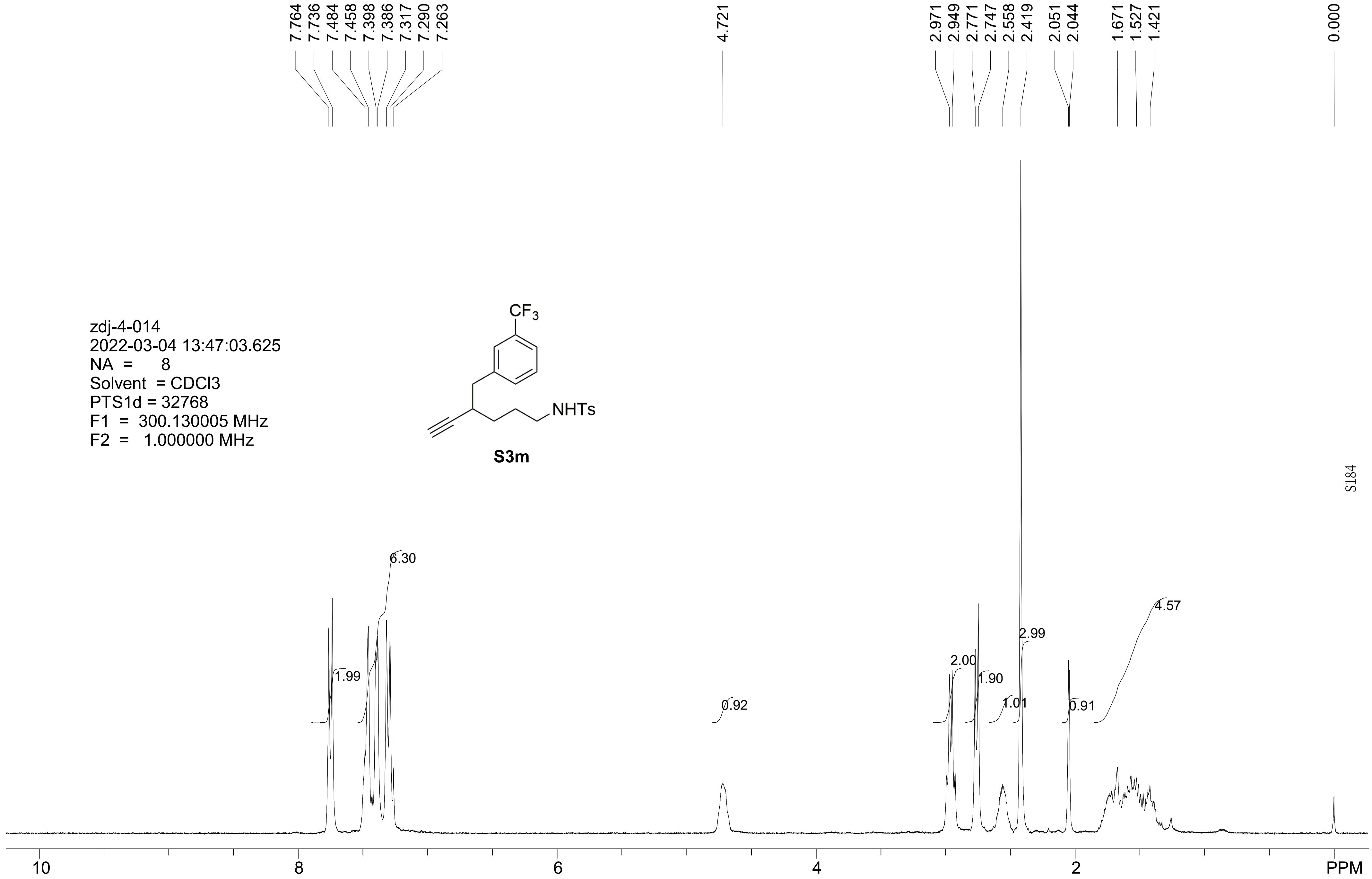


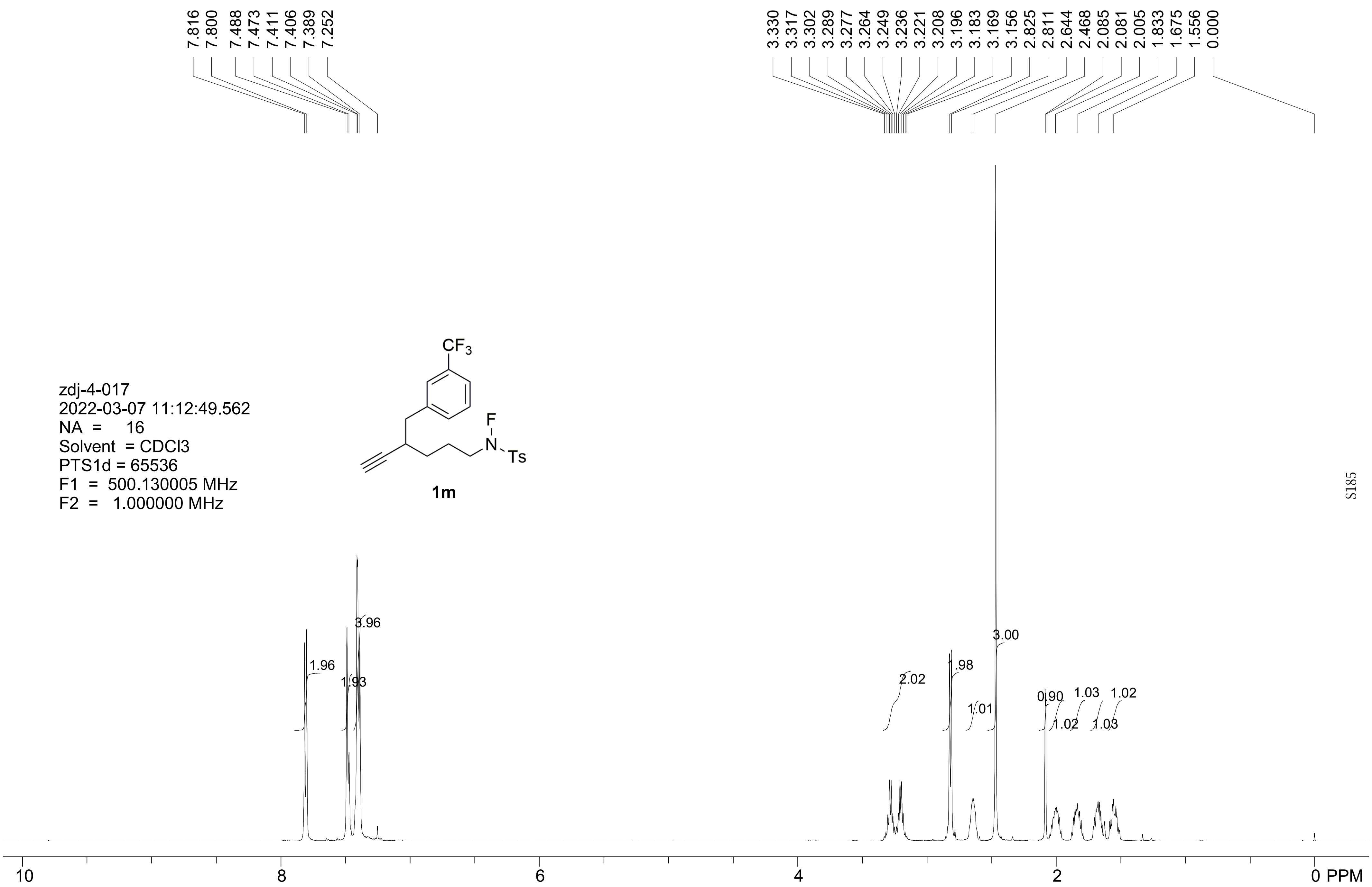
1l

zdj-3-175
2022-01-13 17:01:17.713
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz


zdj-4-007
2022-03-02 21:44:04.093
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
CF3
Boc
N
Ts
7.789
7.761
7.514
7.477
7.428
7.404
7.380
7.308
7.281
7.263
3.874
3.849
3.825
2.859
2.849
2.838
2.825
2.686
2.436
2.115
2.109
2.054
1.883
1.601
1.551
1.327
0.000
2.02
4.04
2.49
2.00
2.91
3.04
2.97
2.40
9.30
10
8
6
4
2
PPM

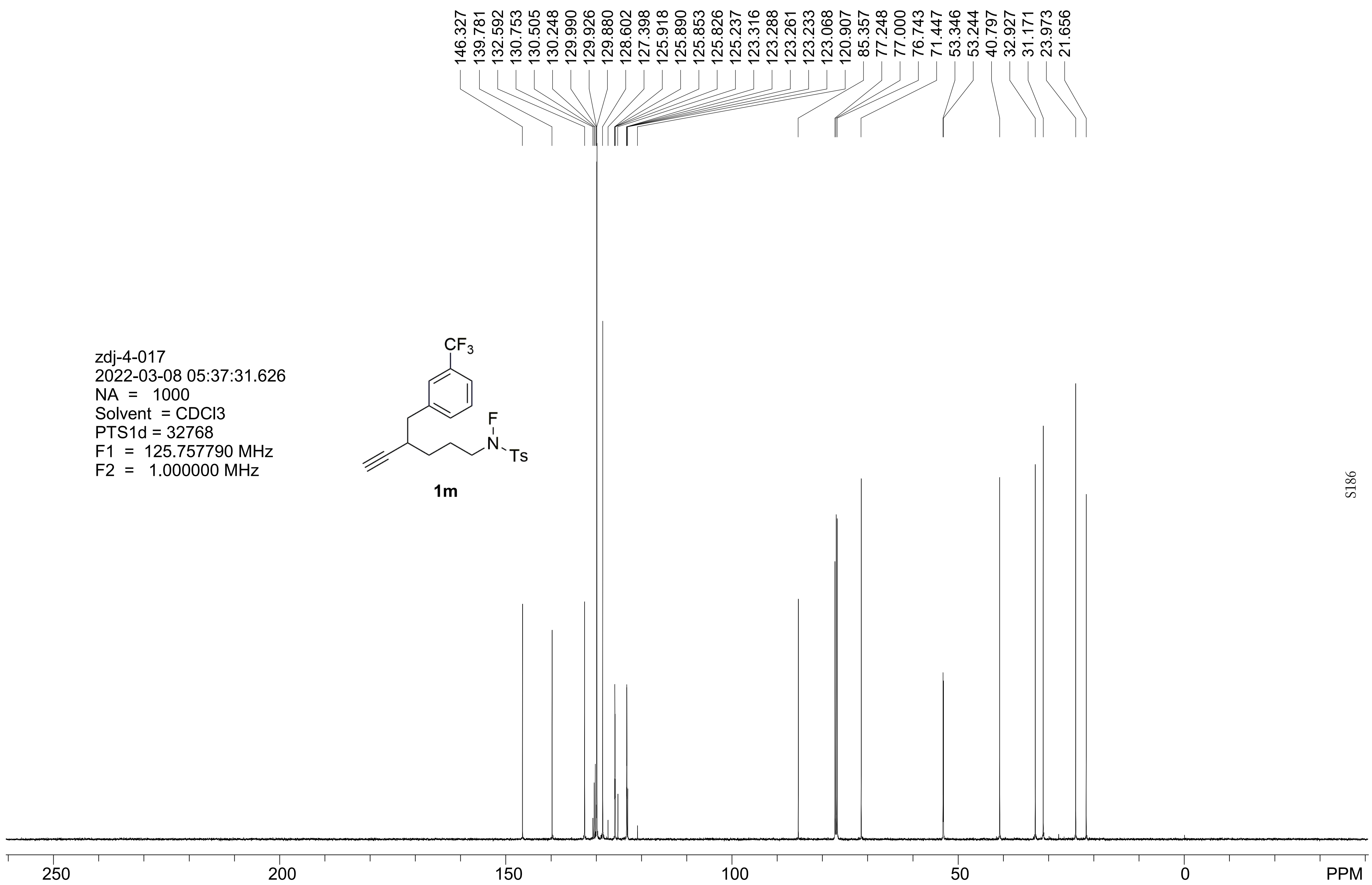
S2m

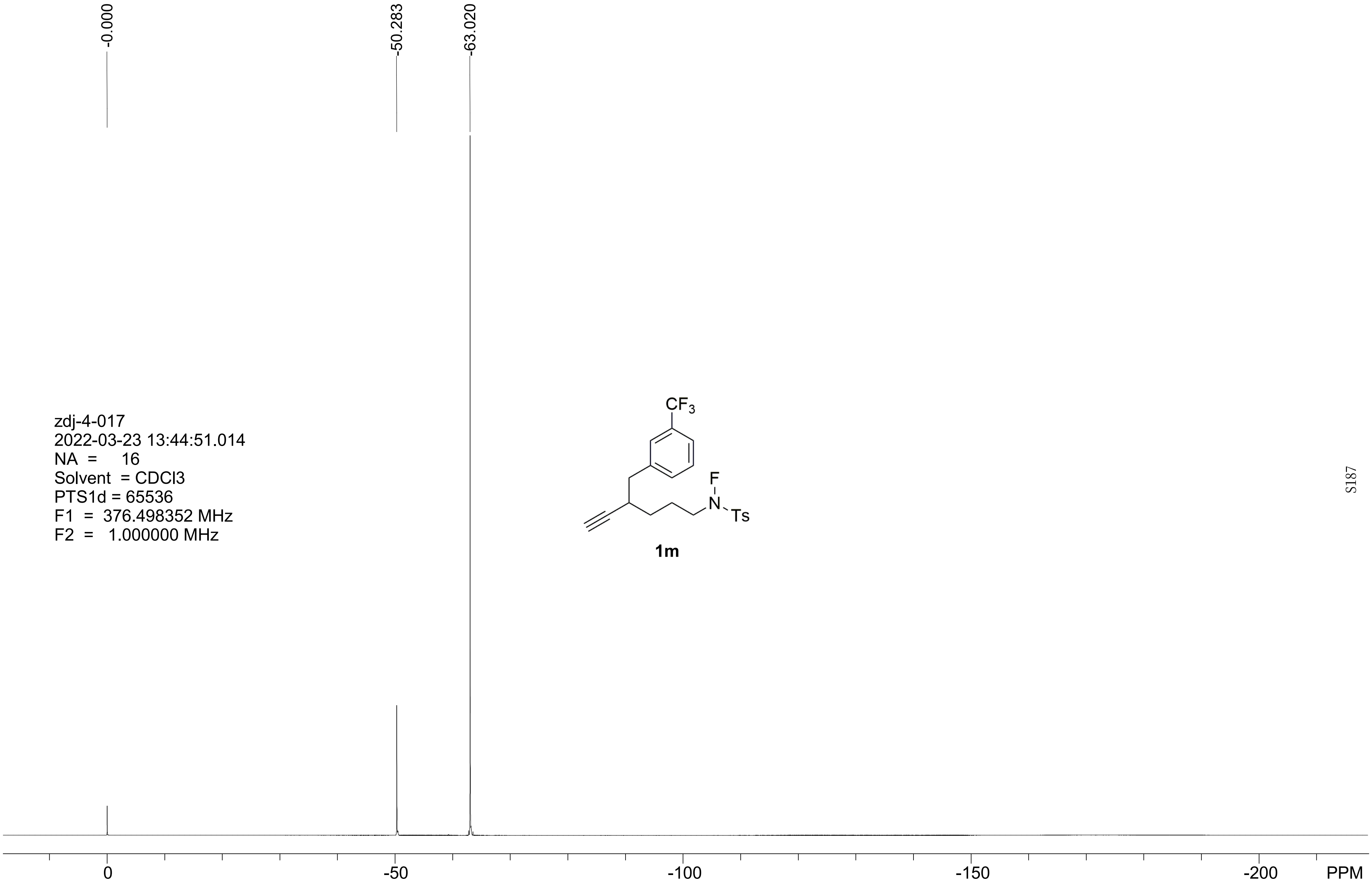

7.764
7.736
7.484
7.458
7.398
7.386
7.317
7.290
7.263
4.721
2.971
2.949
2.771
2.747
2.558
2.419
2.051
2.044
1.671
1.527
1.421
0.000
zdj-4-014
2022-03-04 13:47:03.625
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
CF3
NHTs
S3m
6.30
1.99
0.92
2.00
1.90
1.01
2.99
0.91
4.57
10
8
6
4
2
PPM



zdj-4-017
2022-03-07 11:12:49.562
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz

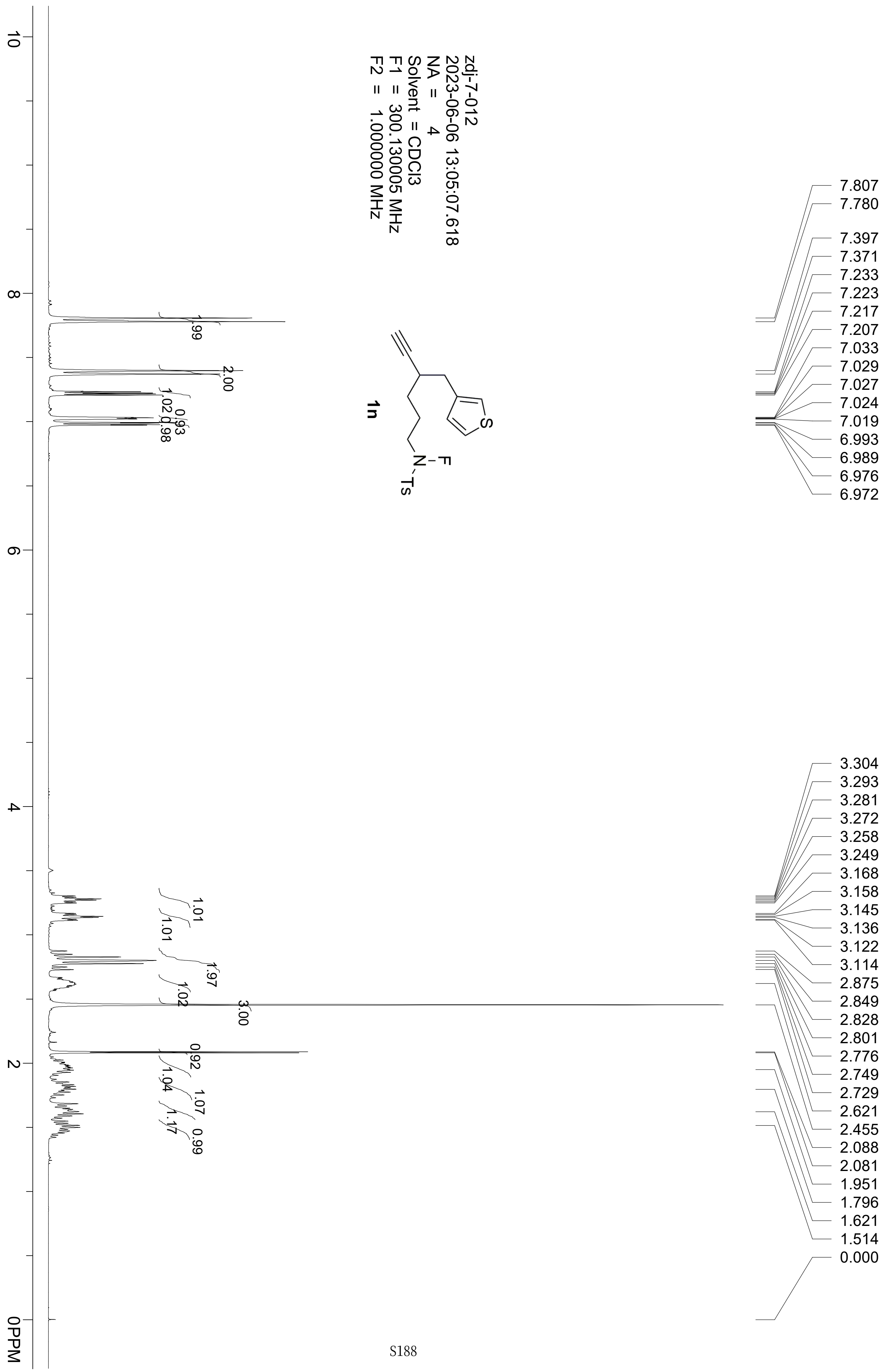
1m

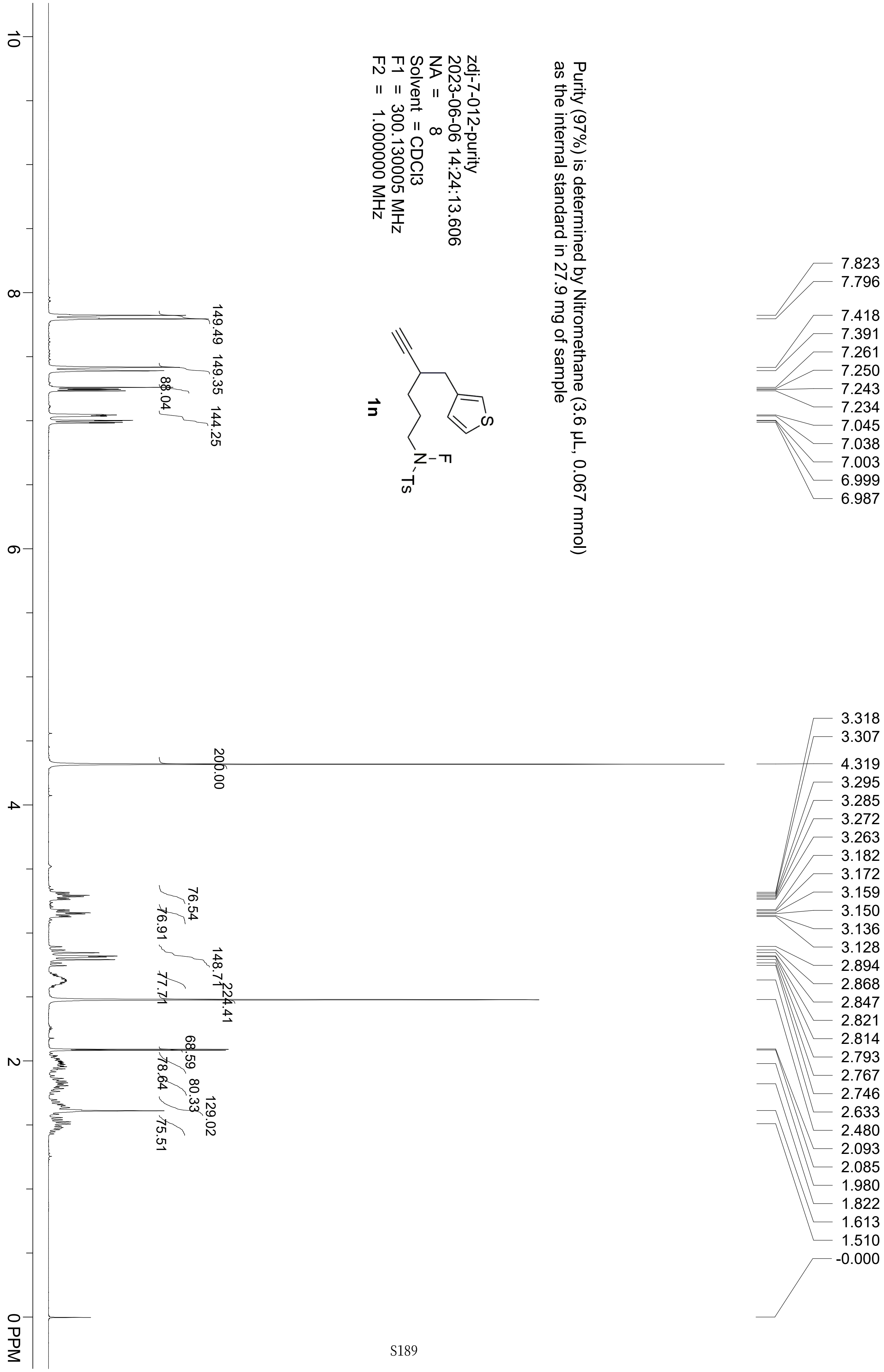

146.327
139.781
132.592
130.753
130.505
130.248
129.990
129.926
129.880
128.602
127.398
125.918
125.890
125.853
125.826
125.237
123.316
123.288
123.261
123.233
123.068
120.907
85.357
77.248
77.000
76.743
71.447
53.346
53.244
40.797
32.927
31.171
23.973
21.656
zdj-4-017
2022-03-08 05:37:31.626
NA = 1000
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
CF3
F
N
Ts
1m
250
200
150
100
50
0
PPM



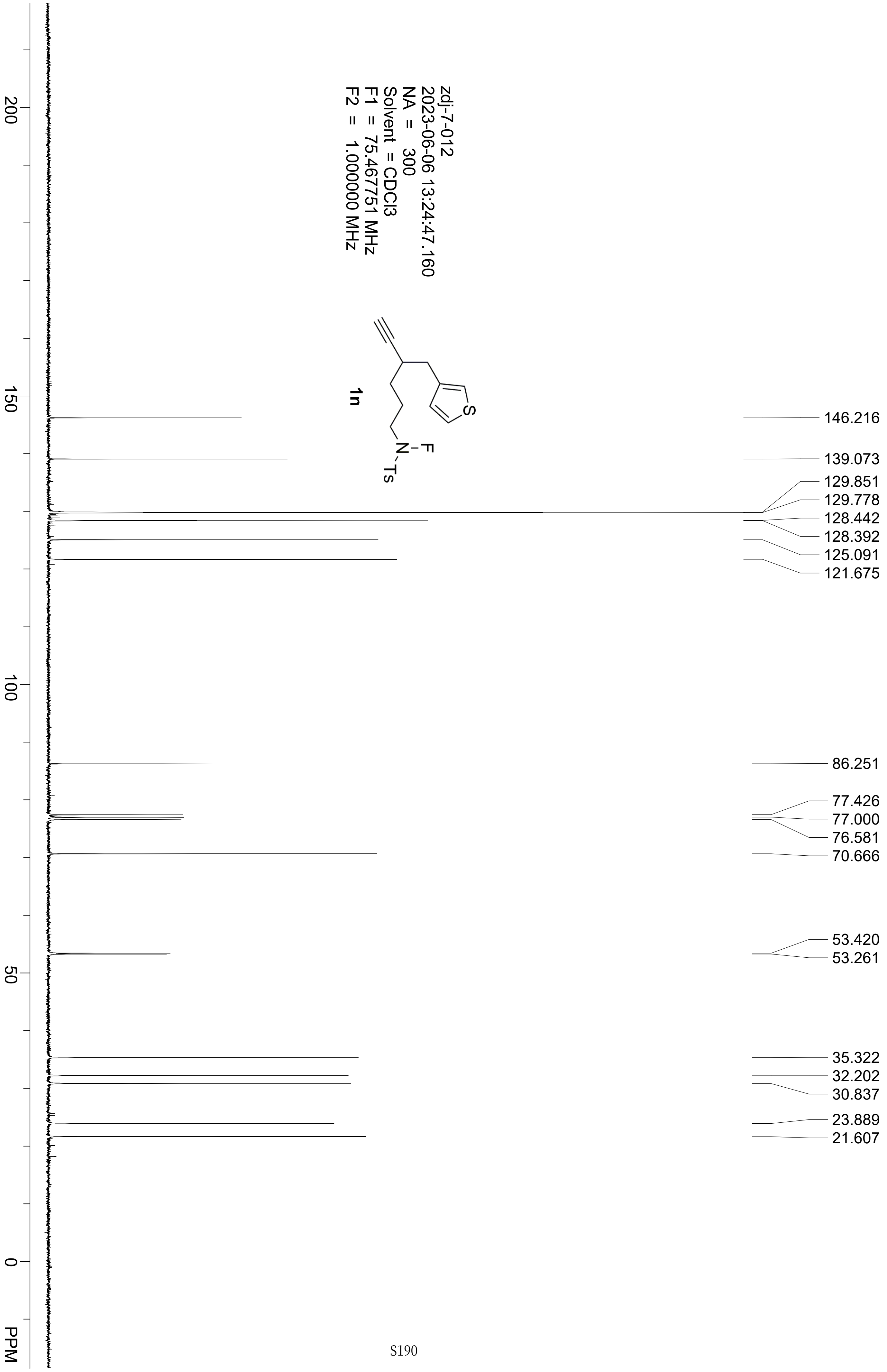
zdj-4-017
2022-03-23 13:44:51.014
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz

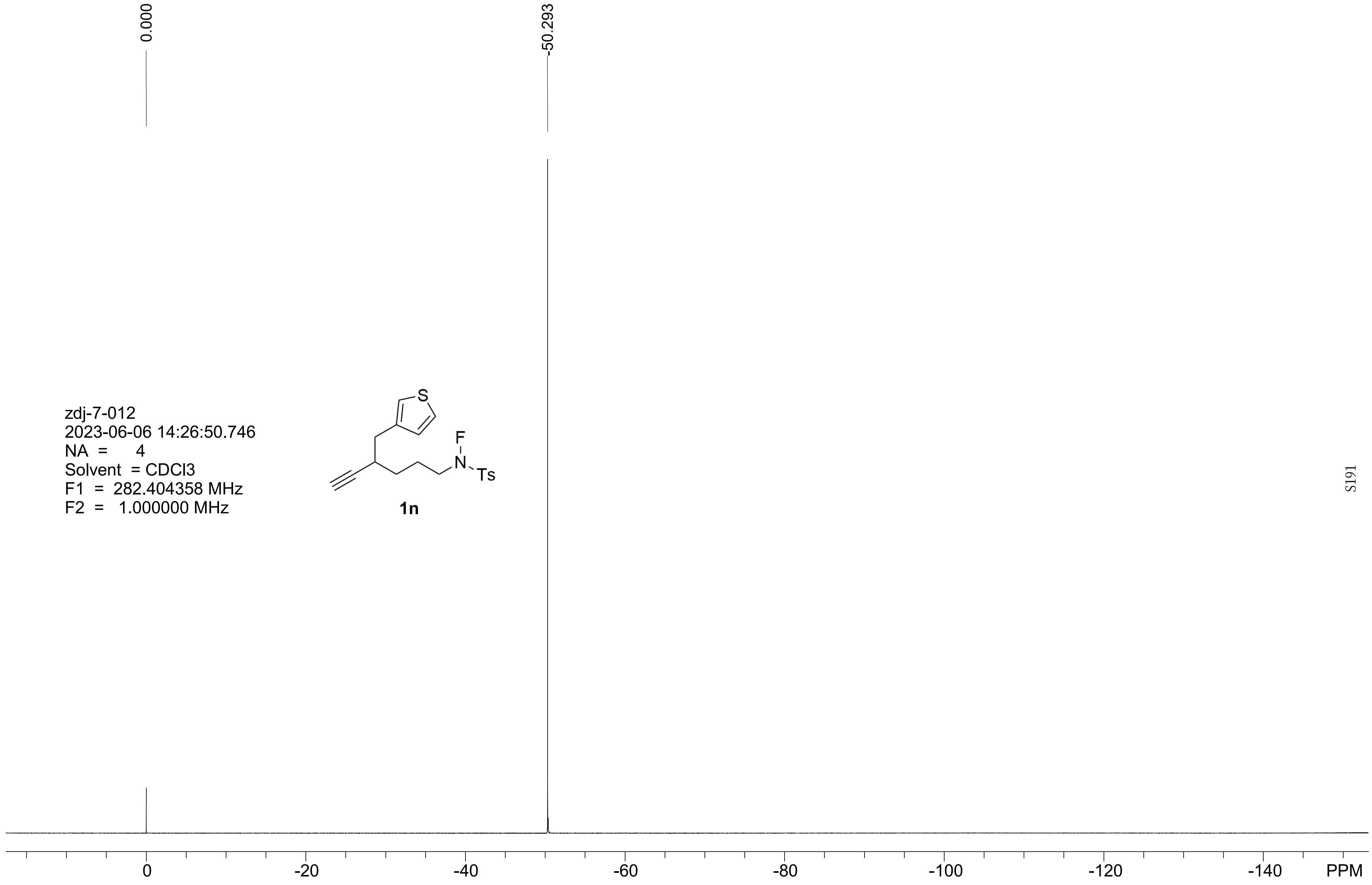
1m

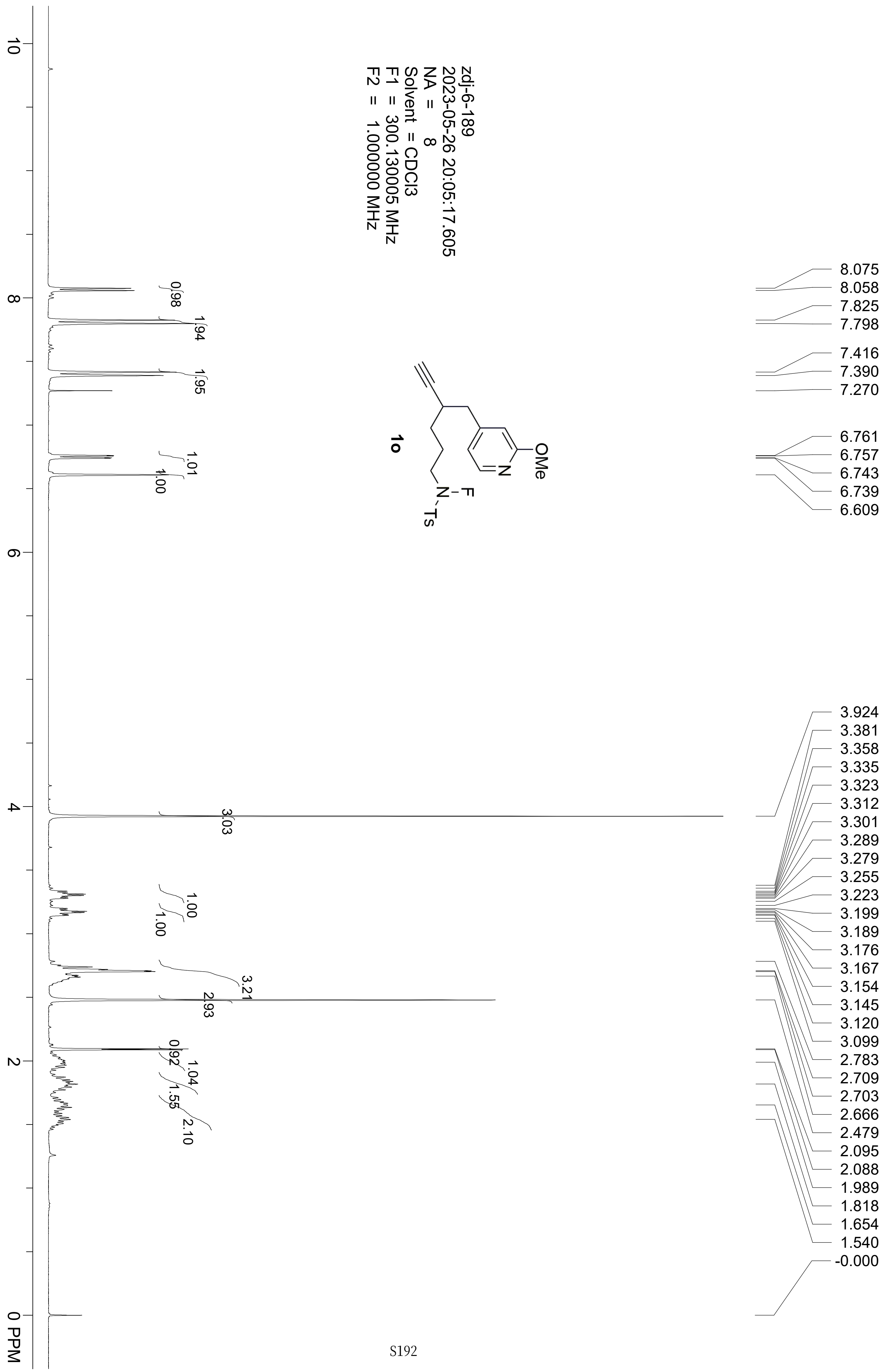

zdj-7-012
2023-06-06 13:05:07.618
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
1n
F
N
Ts
S
7.807
7.780
7.397
7.371
7.233
7.223
7.217
7.207
7.033
7.029
7.027
7.024
7.019
6.993
6.989
6.976
6.972
3.304
3.293
3.281
3.272
3.258
3.249
3.168
3.158
3.145
3.136
3.122
3.114
2.875
2.849
2.828
2.801
2.776
2.749
2.729
2.621
2.455
2.088
2.081
1.951
1.796
1.621
1.514
0.000
1.99
2.00
1.02
0.93
0.98
1.01
1.01
1.97
1.02
3.00
0.92
1.04
1.07
1.17
0.99
10
8
6
4
2
0PPM

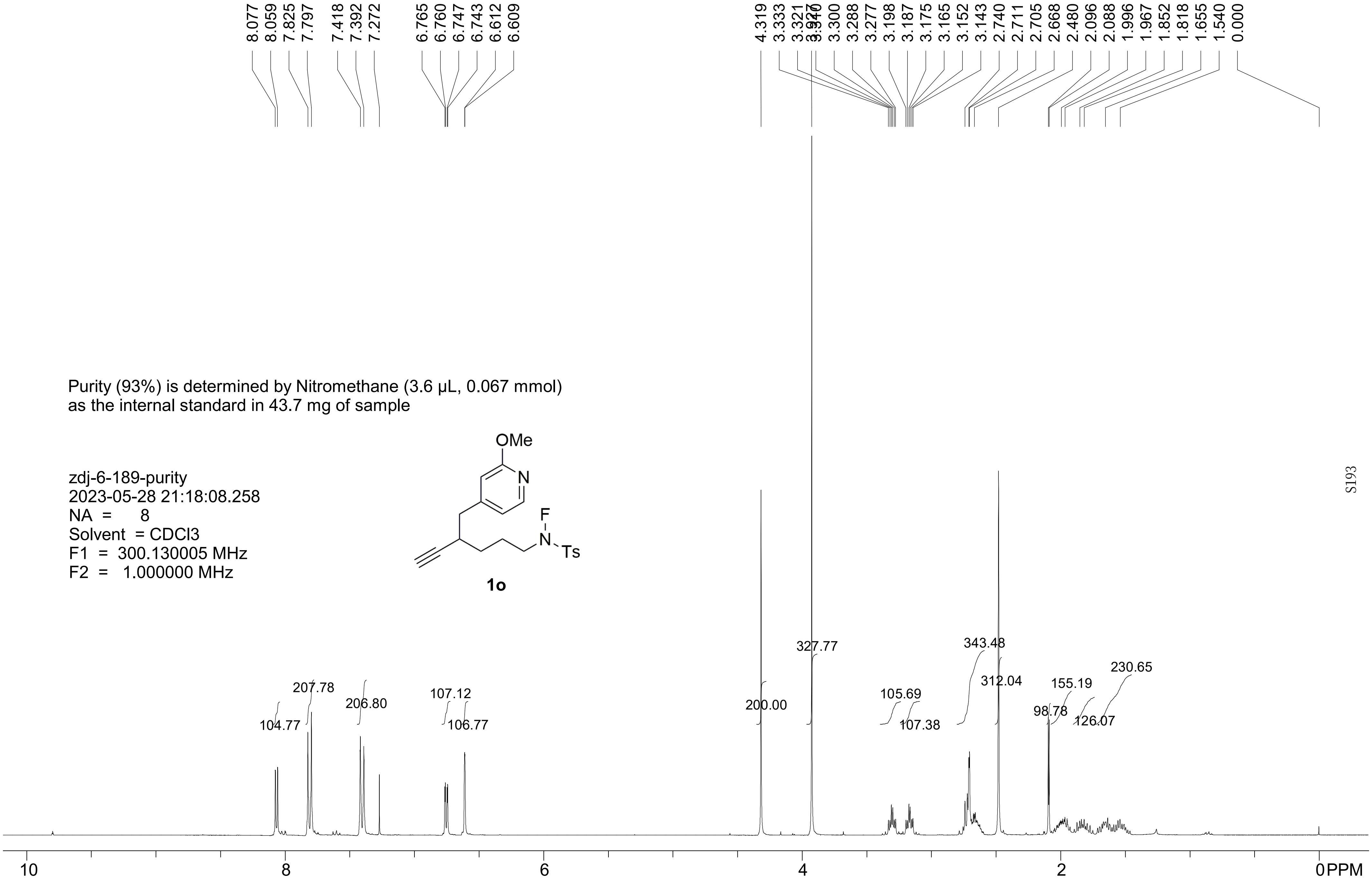

Purity (97%) is determined by Nitromethane (3.6 μL, 0.067 mmol) as the internal standard in 27.9 mg of sample

1n


zdj-7-012
2023-06-06 13:24:47.160
NA = 300
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
S
F
N
Ts
1n
146.216
139.073
129.851
129.778
128.442
128.392
125.091
121.675
86.251
77.426
77.000
76.581
70.666
53.420
53.261
35.322
32.202
30.837
23.889
21.607
200
150
100
50
0
PPM


0.000
-50.293
zdj-7-012
2023-06-06 14:26:50.746
NA = 4
Solvent = CDCl3
F1 = 282.404358 MHz
F2 = 1.000000 MHz
S
F
N
Ts
1n
0
-20
-40
-60
-80
-100
-120
-140
PPM

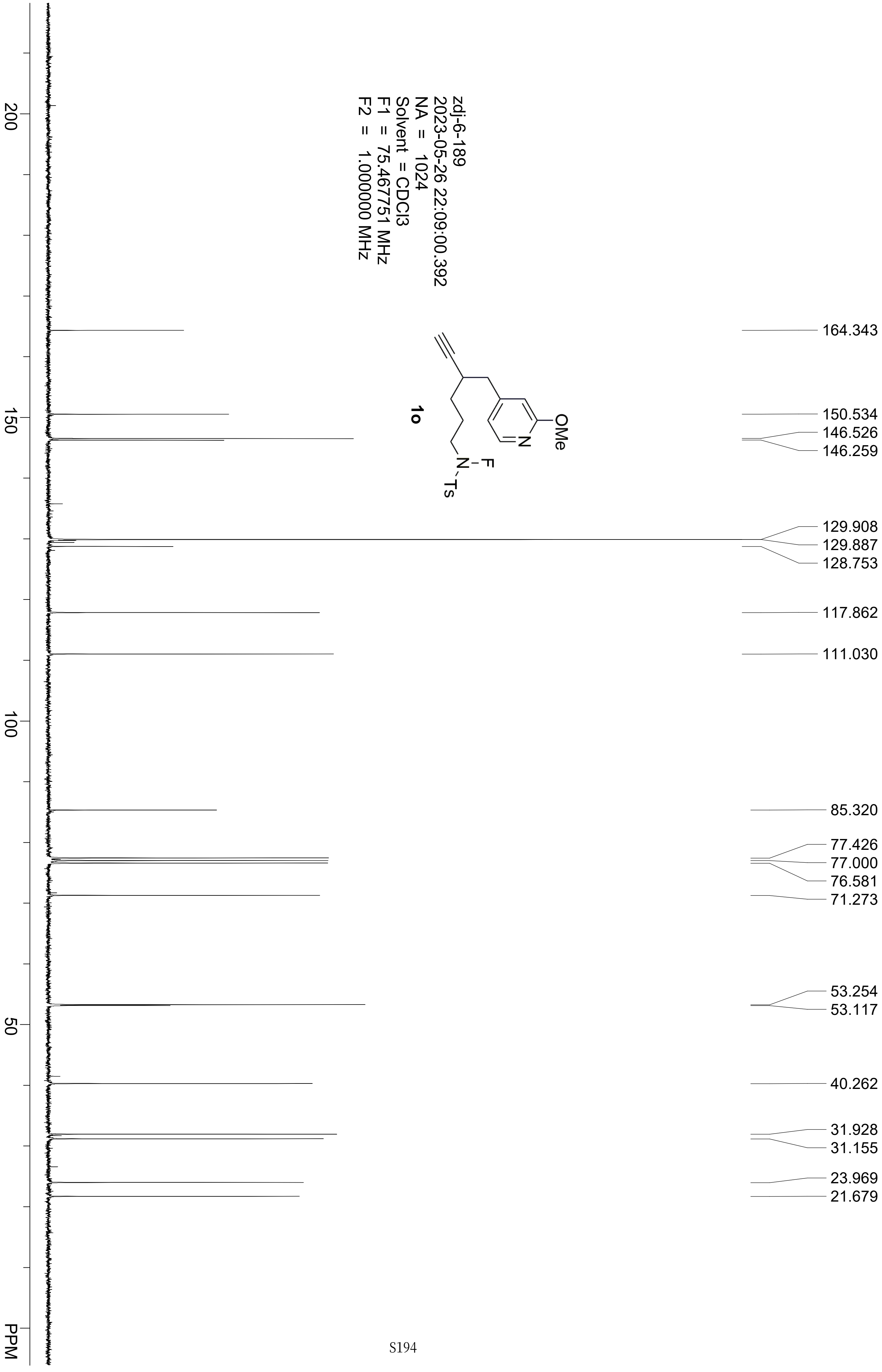

zdj-6-189
2023-05-26 20:05:17.605
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
OMe
N
F
N
Ts
1o
10
8
6
4
2
0 PPM
0.98
1.94
1.95
1.01
1.00
3.03
1.00
1.00
3.21
2.93
0.92
1.04
1.55
2.10
8.075
8.058
7.825
7.798
7.416
7.390
7.270
6.761
6.757
6.743
6.739
6.609
3.924
3.381
3.358
3.335
3.323
3.312
3.301
3.289
3.279
3.255
3.223
3.199
3.189
3.176
3.167
3.154
3.145
3.120
3.099
2.783
2.709
2.703
2.666
2.479
2.095
2.088
1.989
1.818
1.654
1.540
-0.000



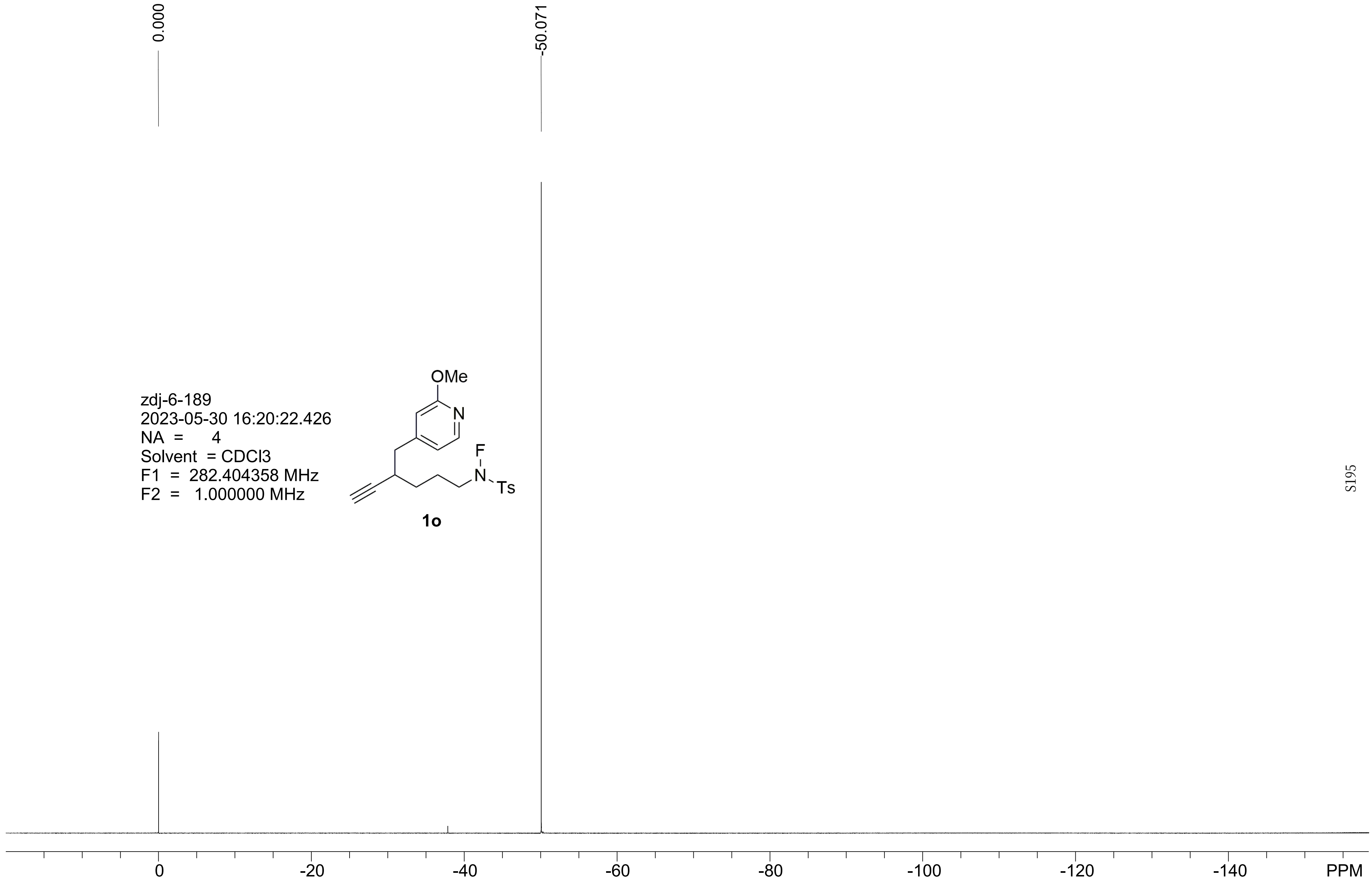
Purity (93%) is determined by Nitromethane (3.6 μL, 0.067 mmol)
as the internal standard in 43.7 mg of sample

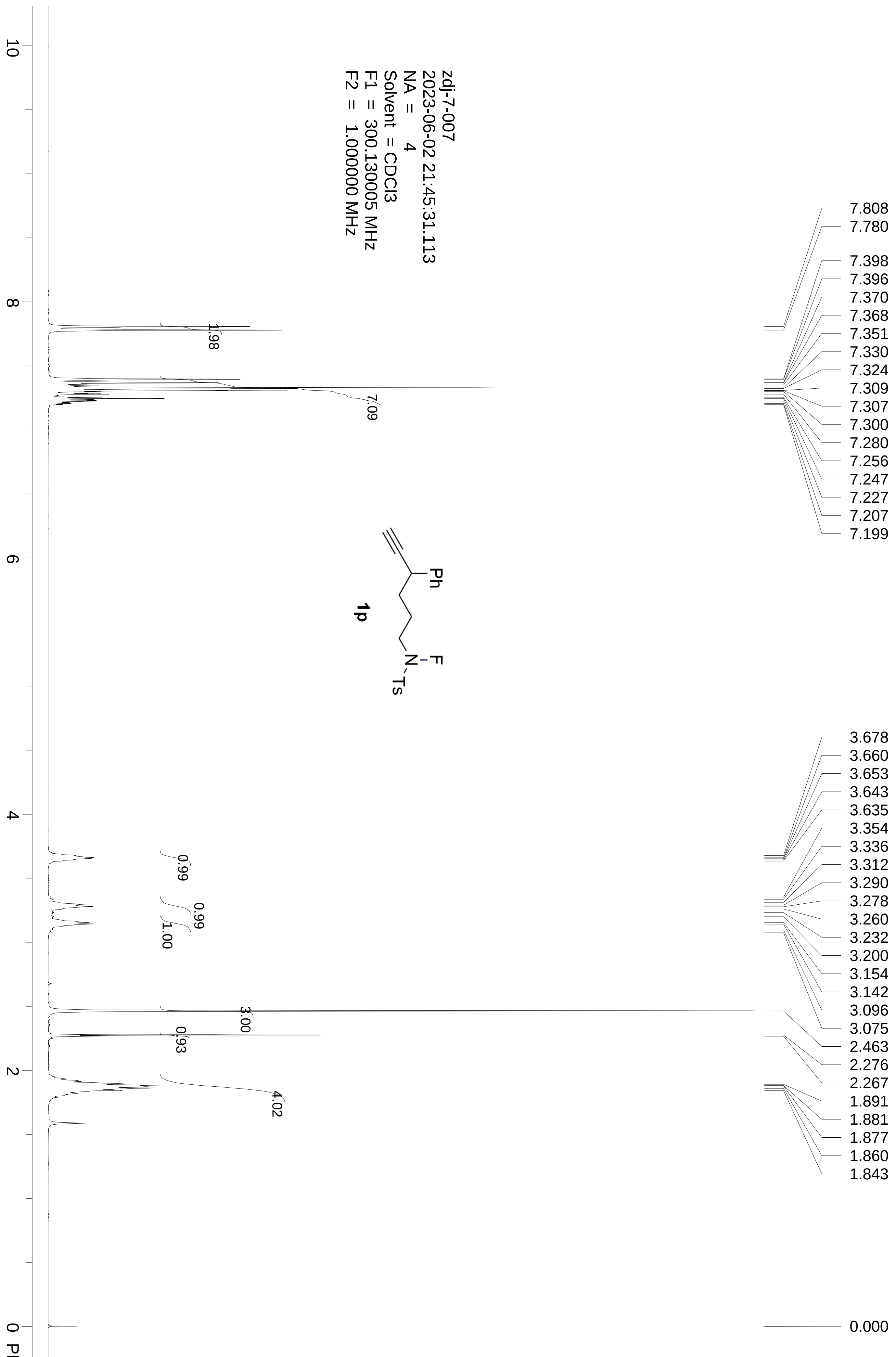
zdj-6-189-purity
2023-05-28 21:18:08.258
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz

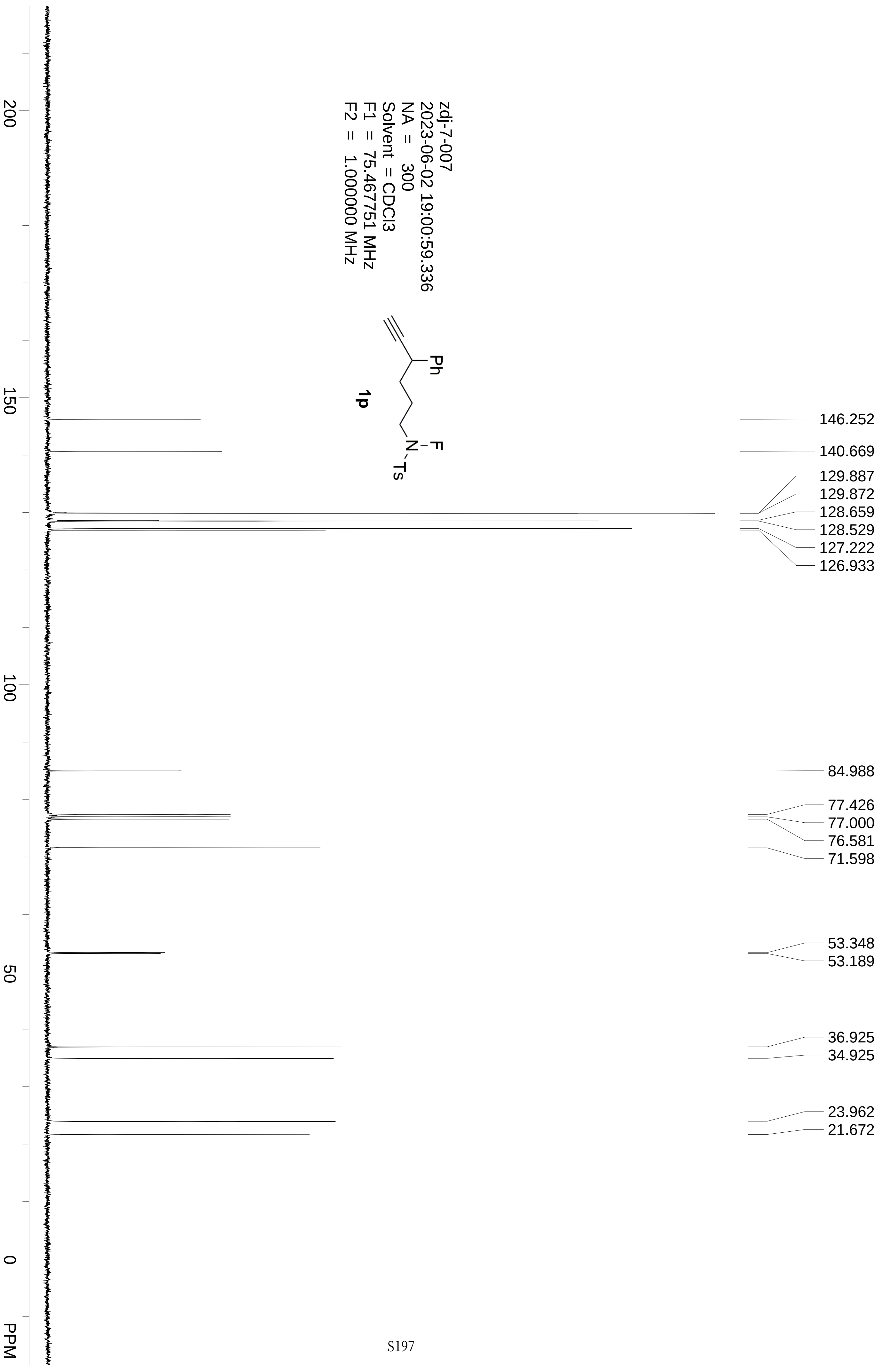
1o

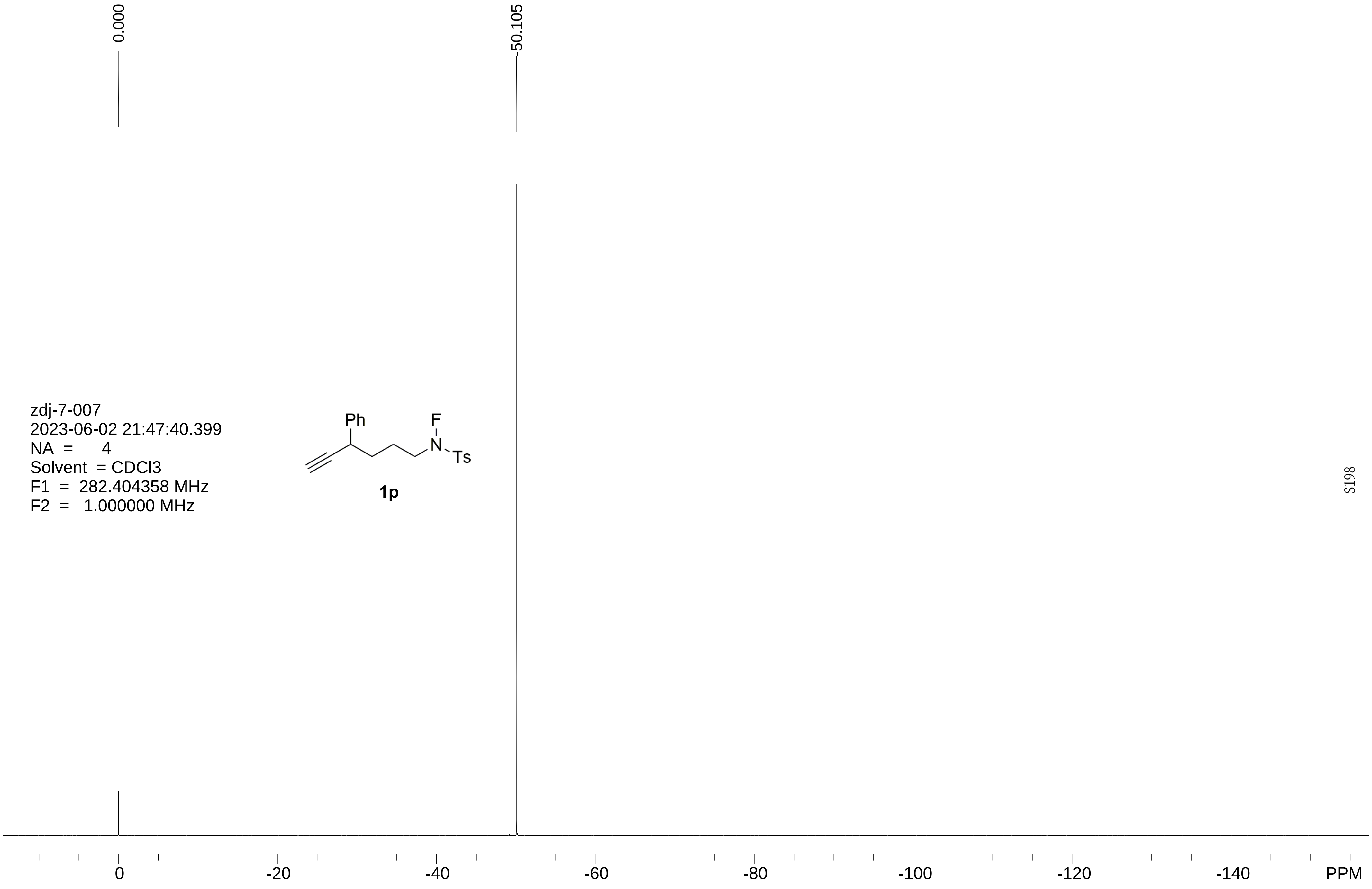

zdj-6-189
2023-05-26 22:09:00.392
NA = 1024
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
OMe
N
F
N
Ts
164.343
150.534
146.526
146.259
129.908
129.887
128.753
117.862
111.030
85.320
77.426
77.000
76.581
71.273
53.254
53.117
40.262
31.928
31.155
23.969
21.679
200
150
100
50
PPM

1o

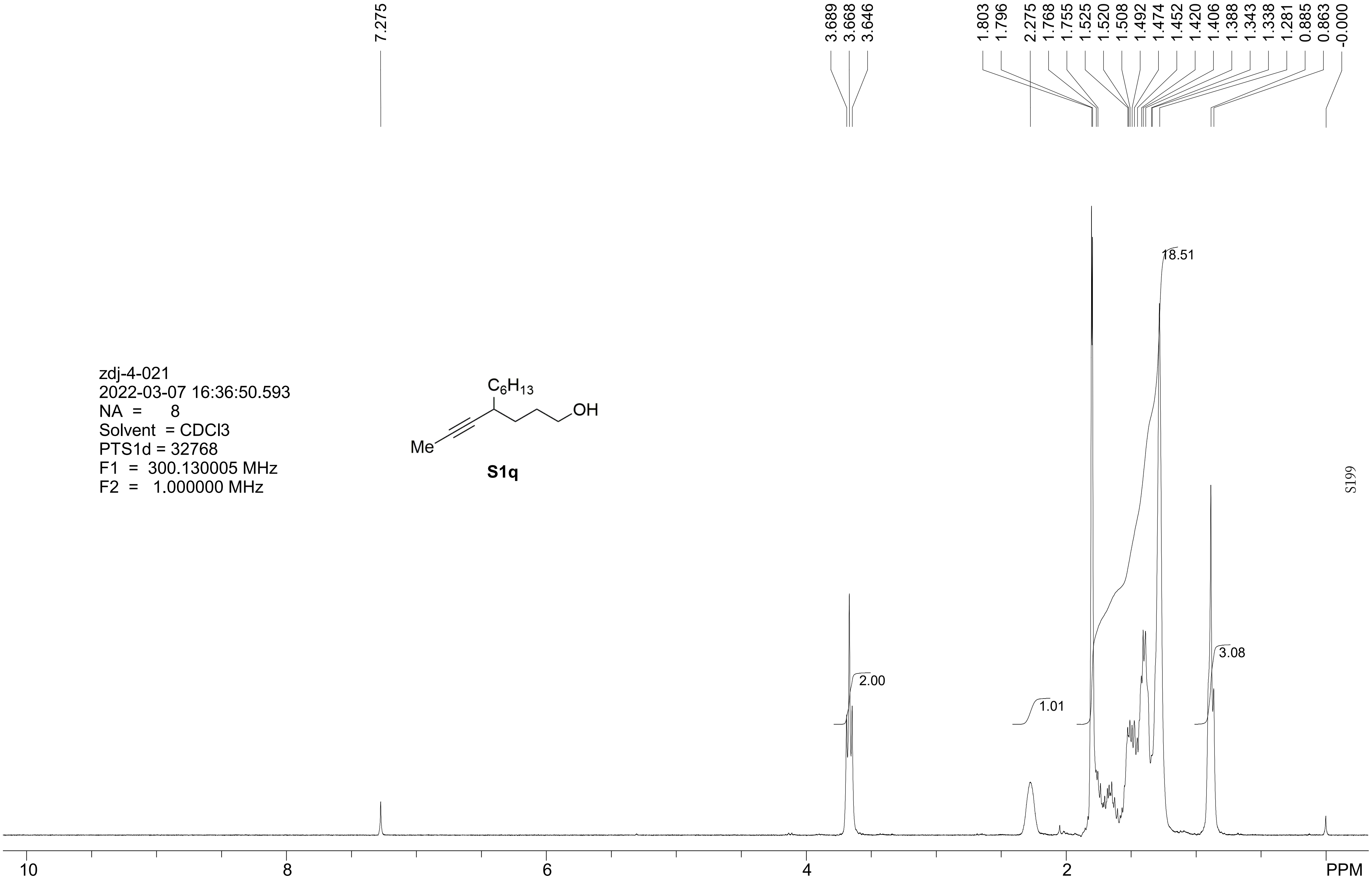

0.000
-50.071
zdj-6-189
2023-05-30 16:20:22.426
NA = 4
Solvent = CDCl3
F1 = 282.404358 MHz
F2 = 1.000000 MHz
OMe
N
F
N
Ts
1o
0
-20
-40
-60
-80
-100
-120
-140
PPM


zdj-7-007
2023-06-02 21:45:31.113
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Ph
1p
N
F
Ts
10
8
6
4
2
0 PPM
1.98
7.09
0.99
0.99
1.00
3.00
0.93
4.02
7.808
7.780
7.398
7.396
7.370
7.368
7.351
7.330
7.324
7.309
7.307
7.300
7.280
7.256
7.247
7.227
7.207
7.199
3.678
3.660
3.653
3.643
3.635
3.354
3.336
3.312
3.290
3.278
3.260
3.232
3.200
3.154
3.142
3.096
3.075
2.463
2.276
2.267
1.891
1.881
1.877
1.860
1.843
0.000

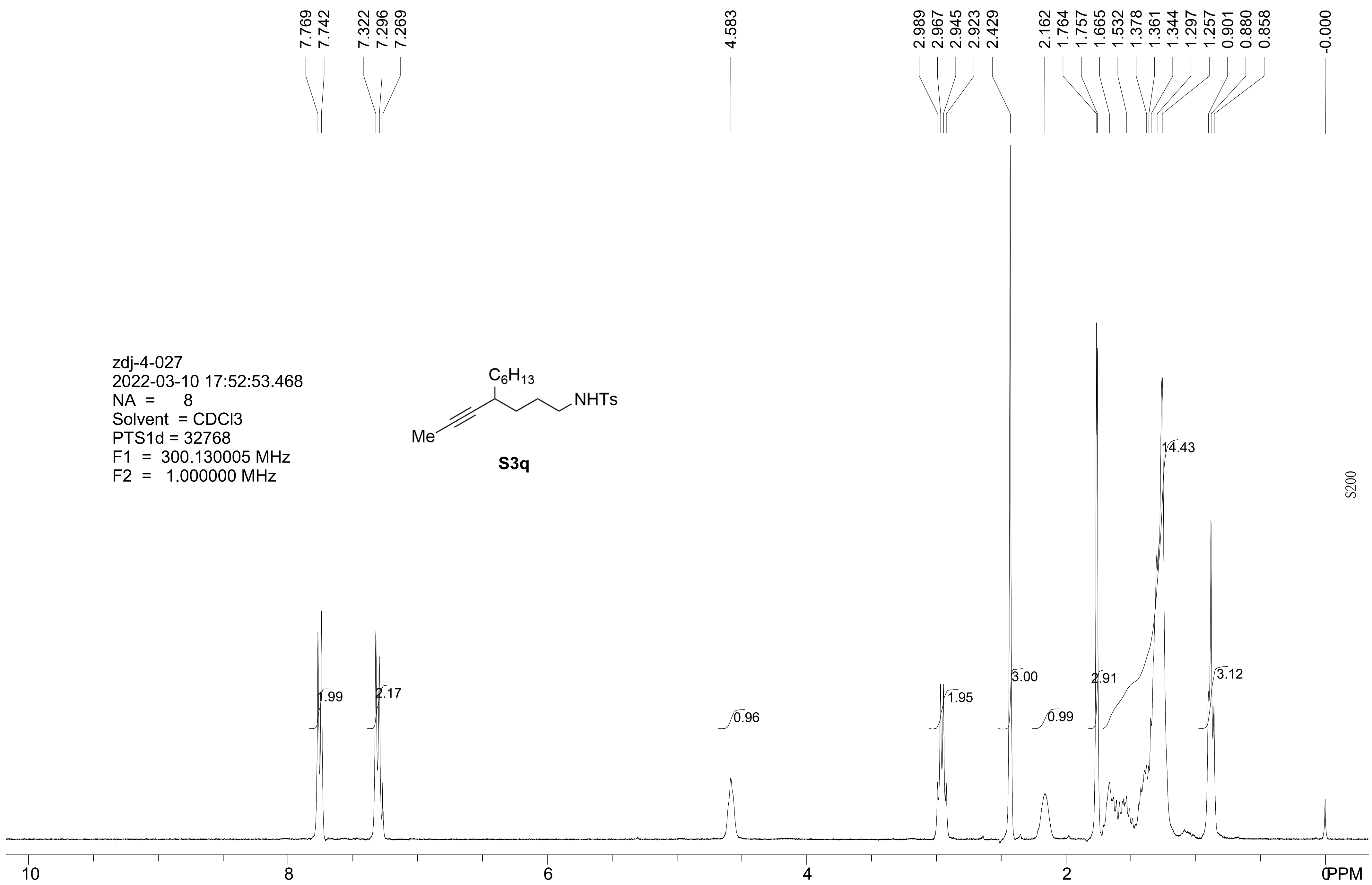

zdj-7-007
2023-06-02 19:00:59.336
NA = 300
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Ph
N
F
Ts
1p
146.252
140.669
129.887
129.872
128.659
128.529
127.222
126.933
84.988
77.426
77.000
76.581
71.598
53.348
53.189
36.925
34.925
23.962
21.672
200
150
100
50
0
PPM


0.000
-50.105
zdj-7-007
2023-06-02 21:47:40.399
NA = 4
Solvent = CDCl3
F1 = 282.404358 MHz
F2 = 1.000000 MHz
Ph
F
N
Ts
0
-20
-40
-60
-80
-100
-120
-140
PPM

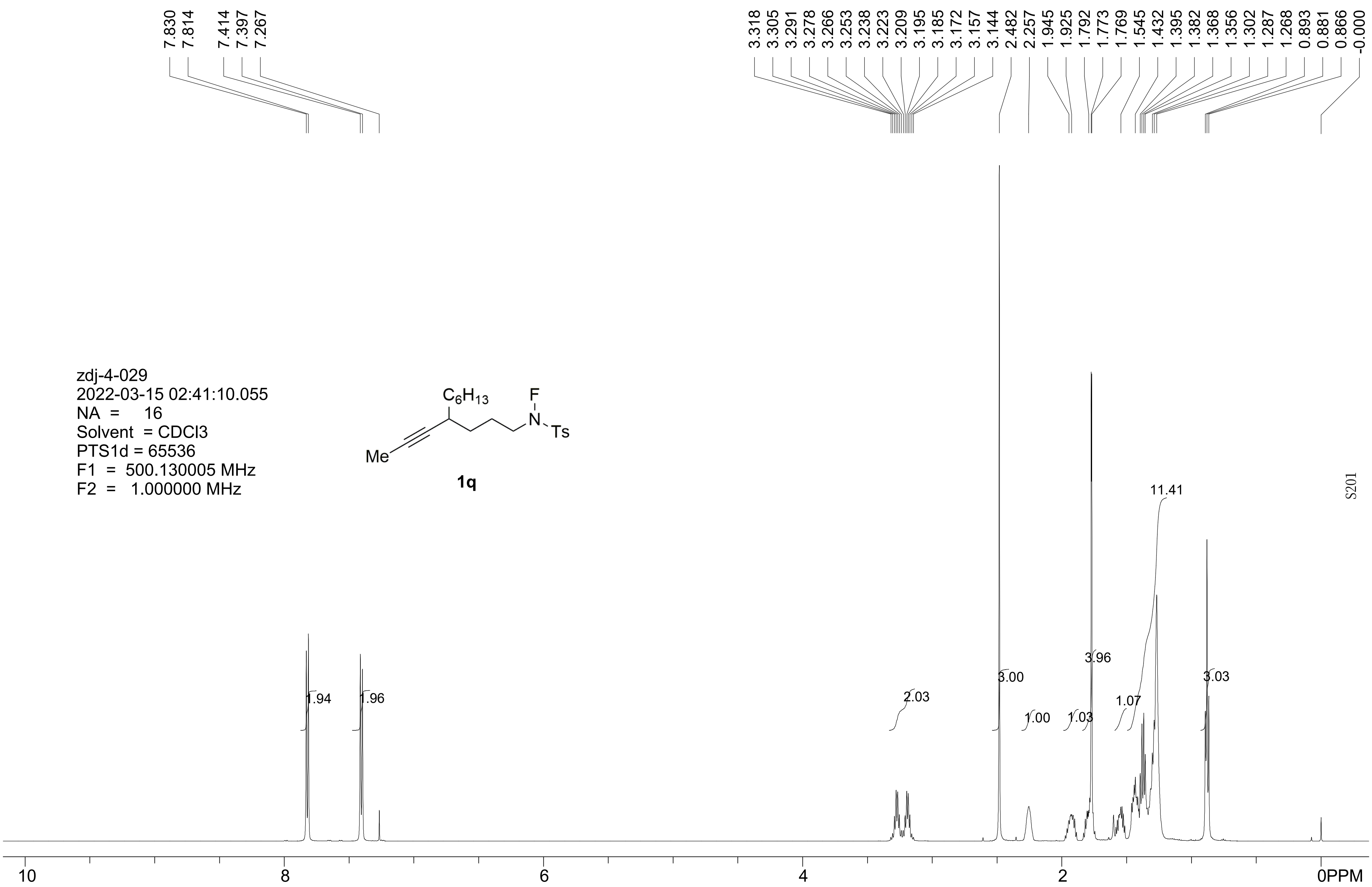
1p


zdj-4-021
2022-03-07 16:36:50.593
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C6H13
OH
Me
7.275
3.689
3.668
3.646
1.803
1.796
2.275
1.768
1.755
1.525
1.520
1.508
1.492
1.474
1.452
1.420
1.406
1.388
1.343
1.338
1.281
0.885
0.863
-0.000
2.00
1.01
18.51
3.08
10
8
6
4
2
PPM

S1q

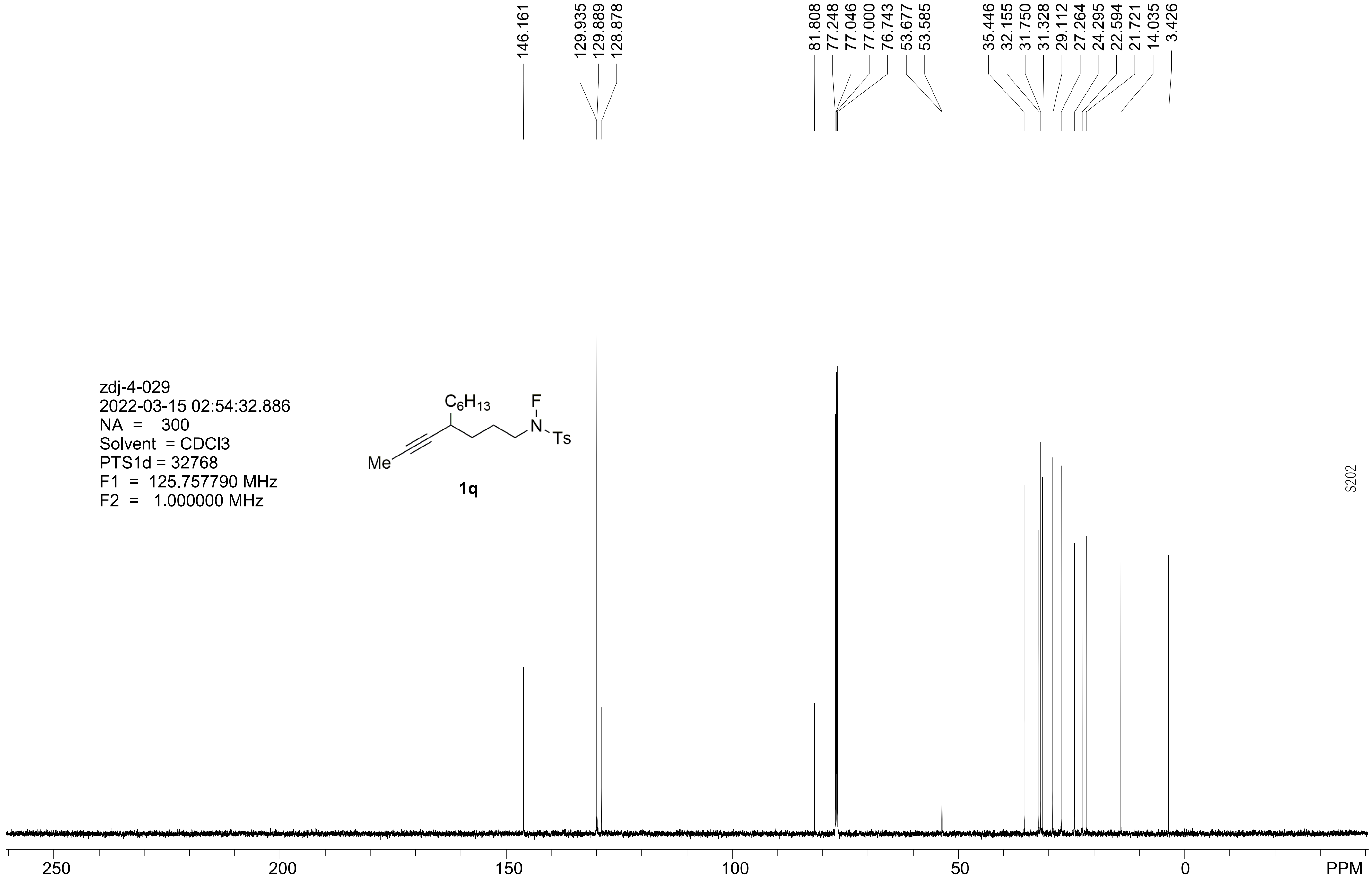

zdj-4-027
2022-03-10 17:52:53.468
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

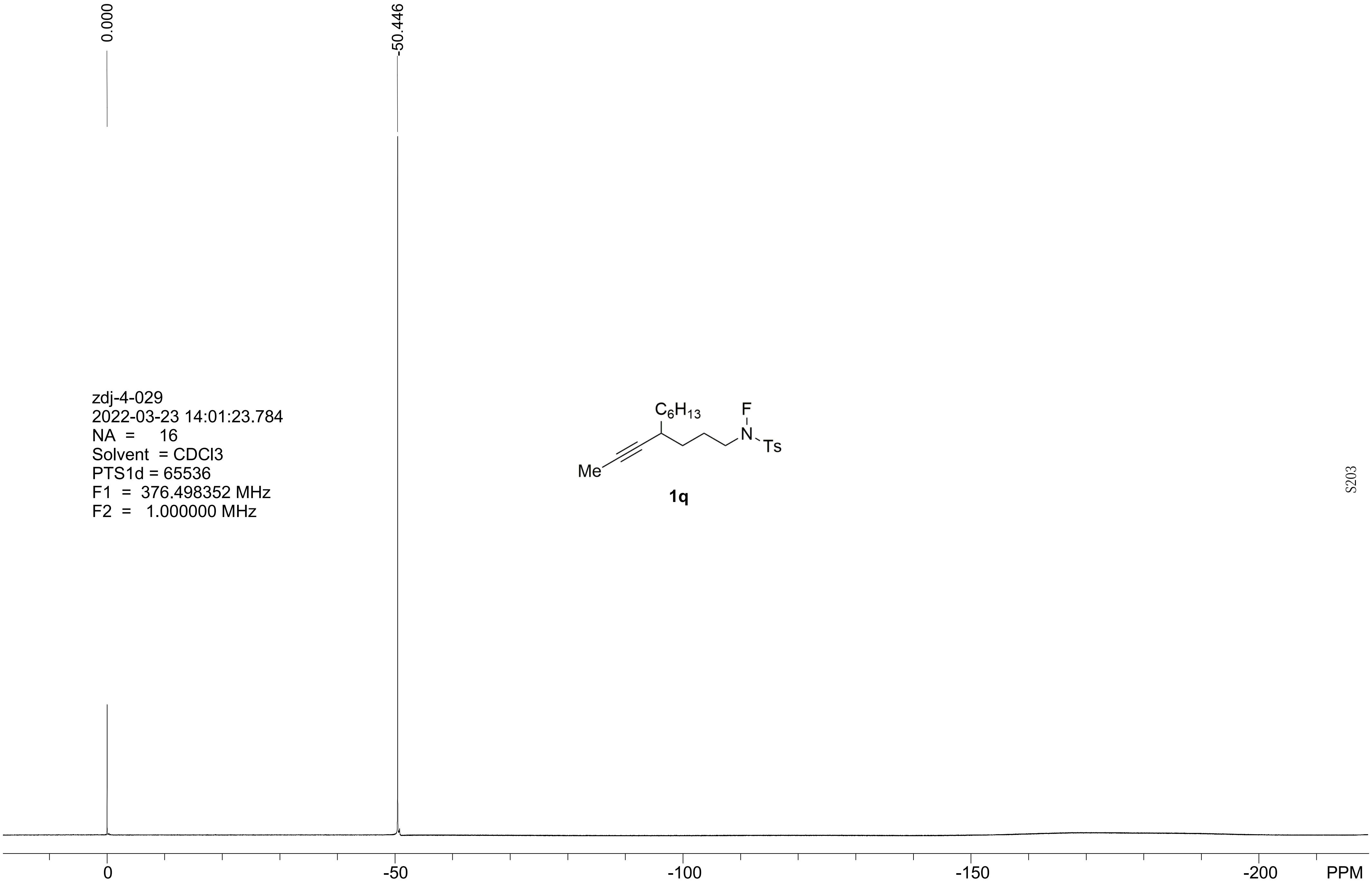
S3q



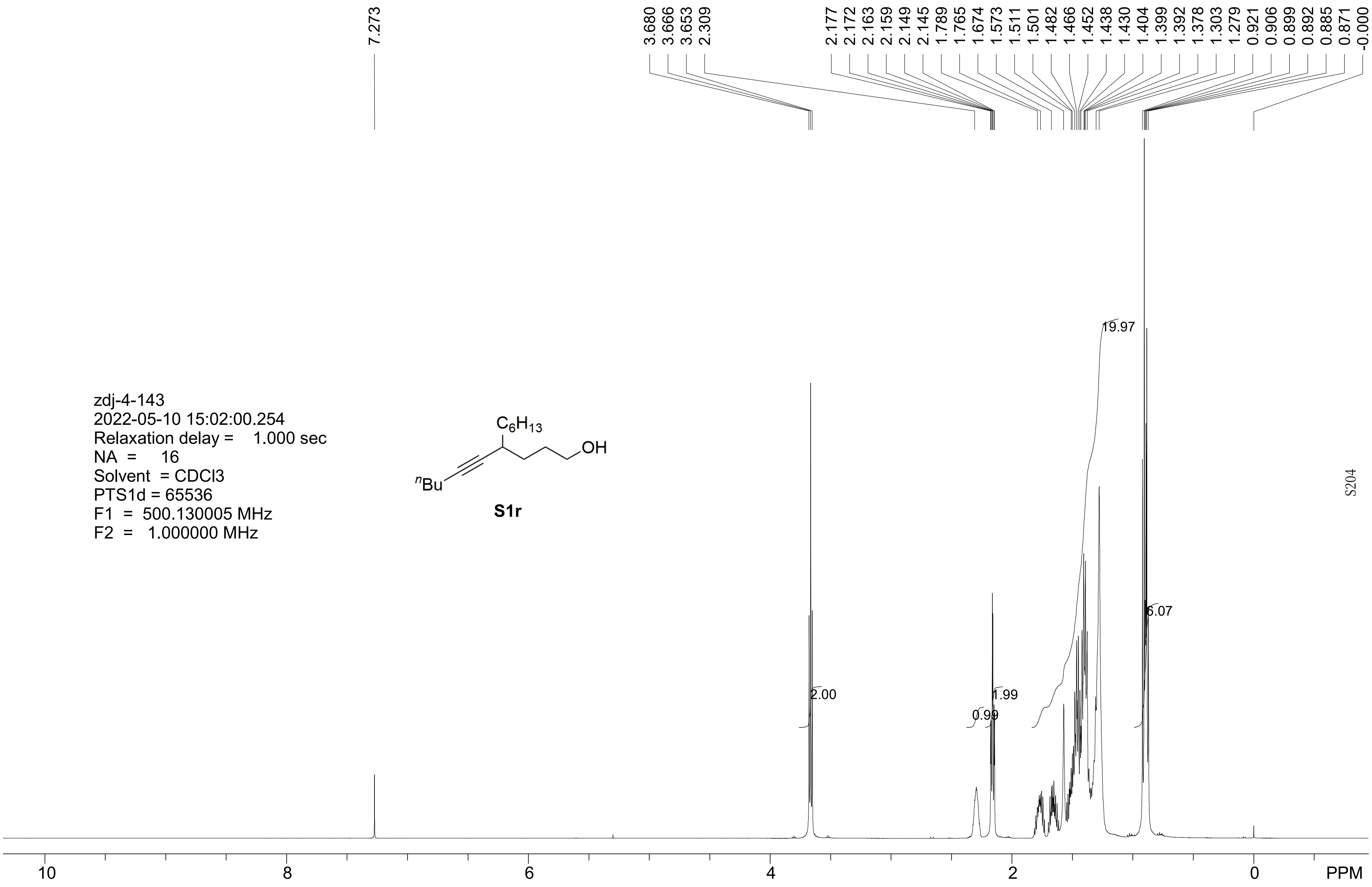
zdj-4-029
2022-03-15 02:41:10.055
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz

1q

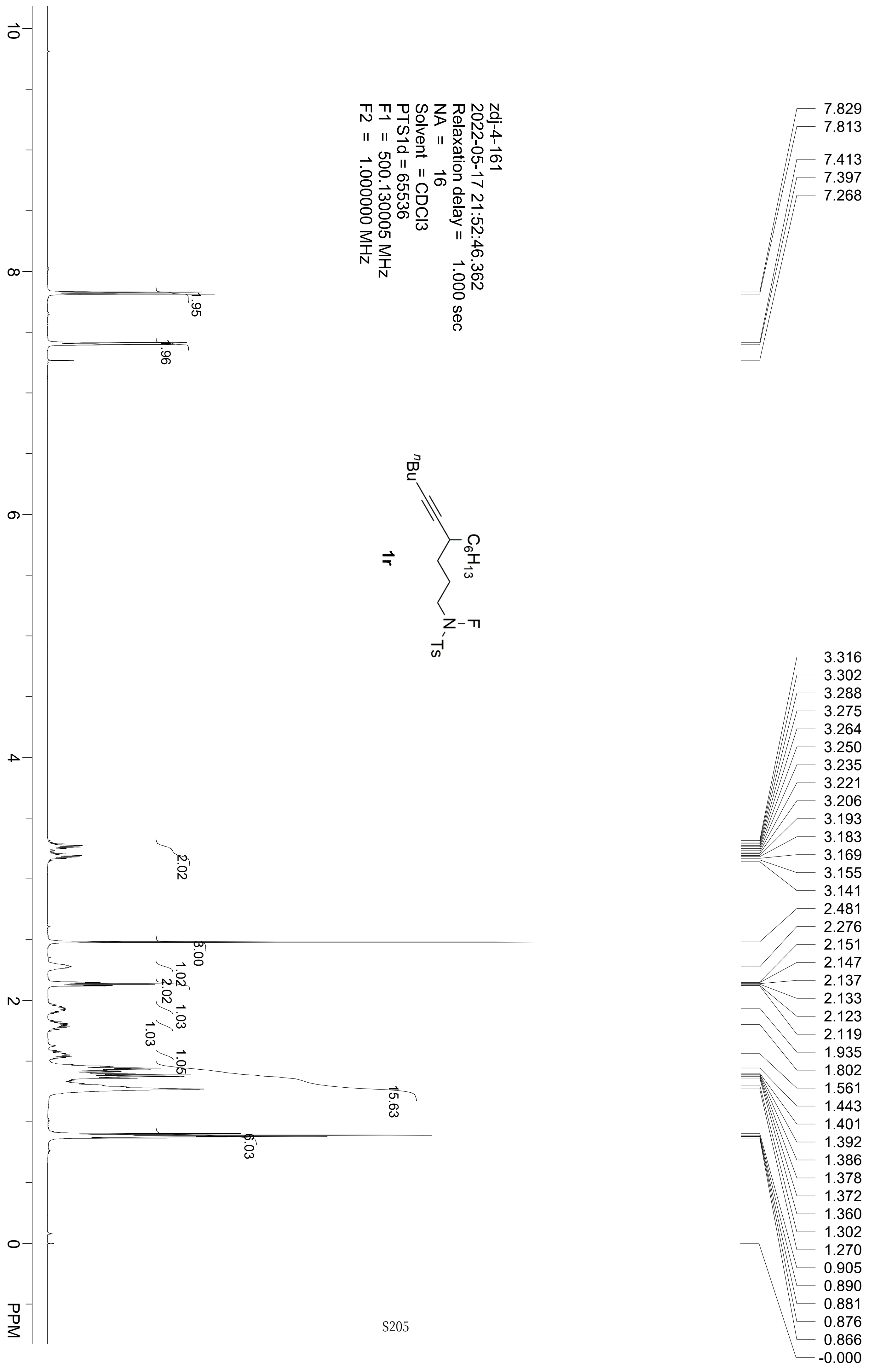

146.161
129.935
129.889
128.878
81.808
77.248
77.046
77.000
76.743
53.677
53.585
35.446
32.155
31.750
31.328
29.112
27.264
24.295
22.594
21.721
14.035
3.426
zdj-4-029
2022-03-15 02:54:32.886
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
C_6H_{13}
F
N
Ts
Me
1q
250
200
150
100
50
0
PPM

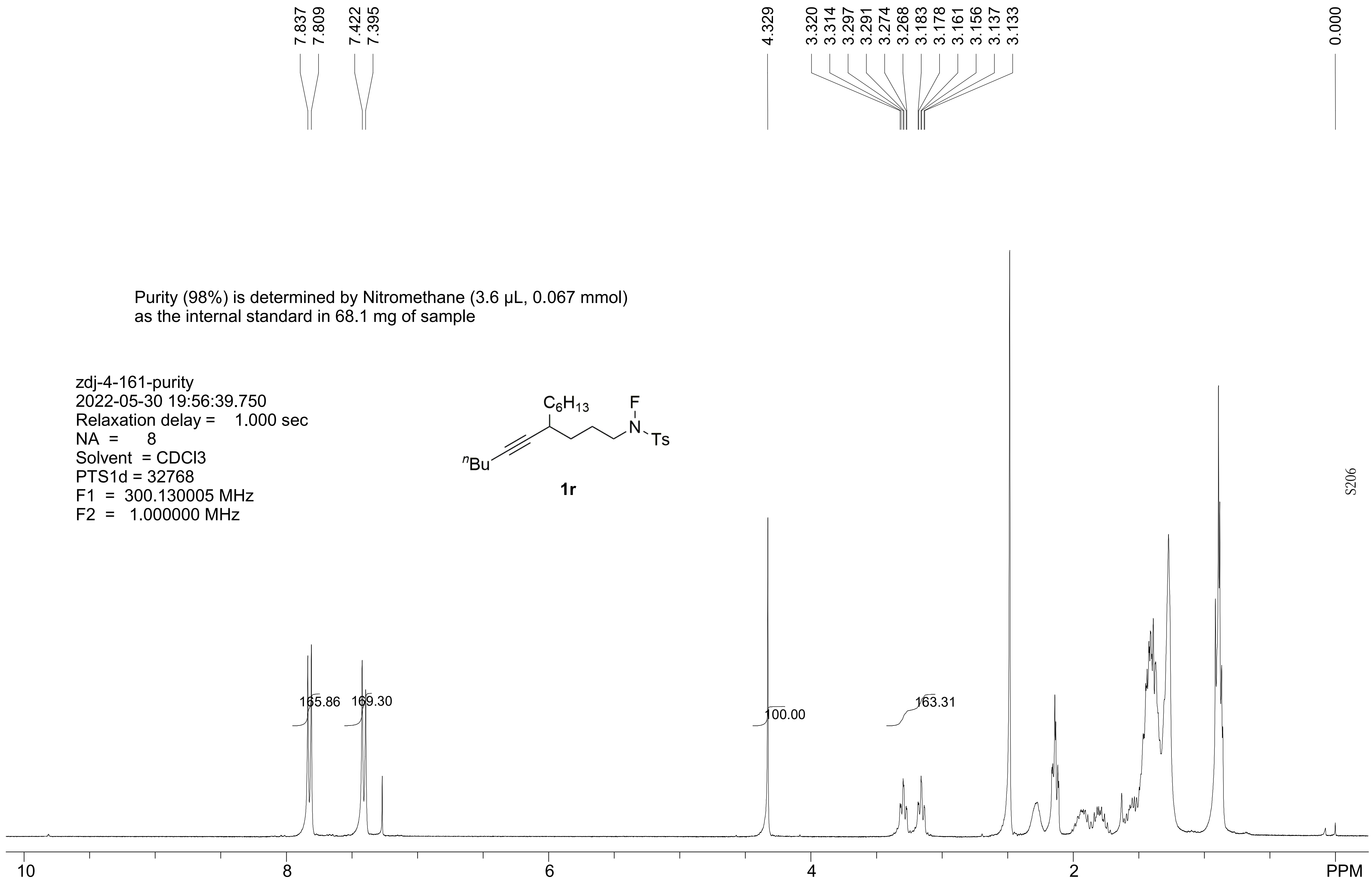

0.000
-50.446
zdj-4-029
2022-03-23 14:01:23.784
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz
Me
C6H13
F
N
Ts
0
-50
-100
-150
-200
PPM

1q


7.273
3.680
3.666
3.653
2.309
2.177
2.172
2.163
2.159
2.149
2.145
1.789
1.765
1.674
1.573
1.511
1.501
1.482
1.466
1.452
1.438
1.430
1.404
1.399
1.392
1.378
1.303
1.279
0.921
0.906
0.899
0.892
0.885
0.871
-0.000
zdj-4-143
2022-05-10 15:02:00.254
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
C6H13
OH
nBu
19.97
6.07
2.00
1.99
0.99
10
8
6
4
2
0
PPM

S1r

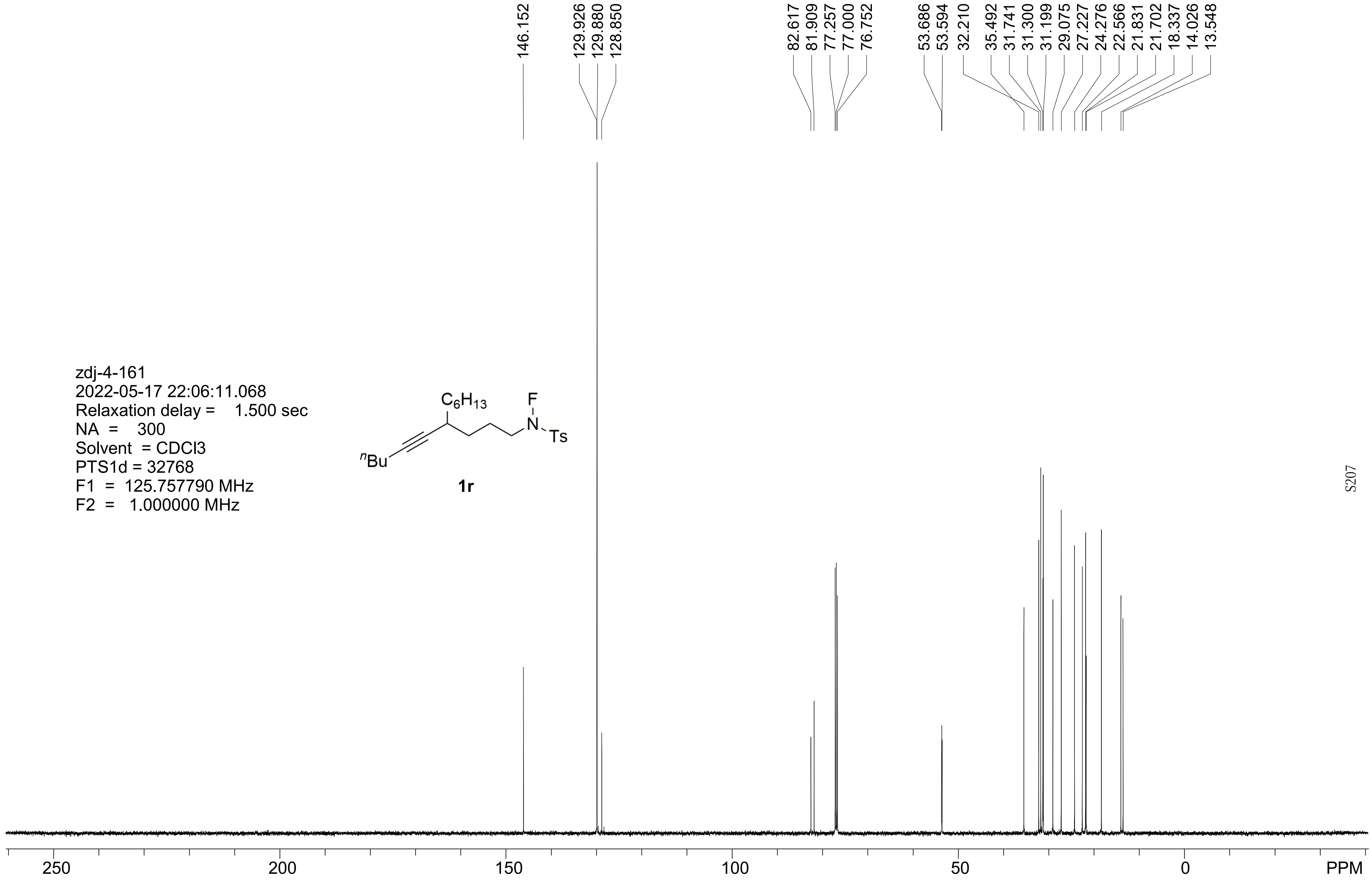

zdj-4-161
2022-05-17 21:52:46.362
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
nBu
C6H13
N
F
Ts
1r
7.829
7.813
7.413
7.397
7.268
3.316
3.302
3.288
3.275
3.264
3.250
3.235
3.221
3.206
3.193
3.183
3.169
3.155
3.141
2.481
2.276
2.151
2.147
2.137
2.133
2.123
2.119
1.935
1.802
1.561
1.443
1.401
1.392
1.386
1.378
1.372
1.360
1.302
1.270
0.905
0.890
0.881
0.876
0.866
-0.000
1.95
1.96
2.02
3.00
1.02
2.02
1.03
1.03
1.05
15.63
6.03
10
8
6
4
2
0
PPM



1r

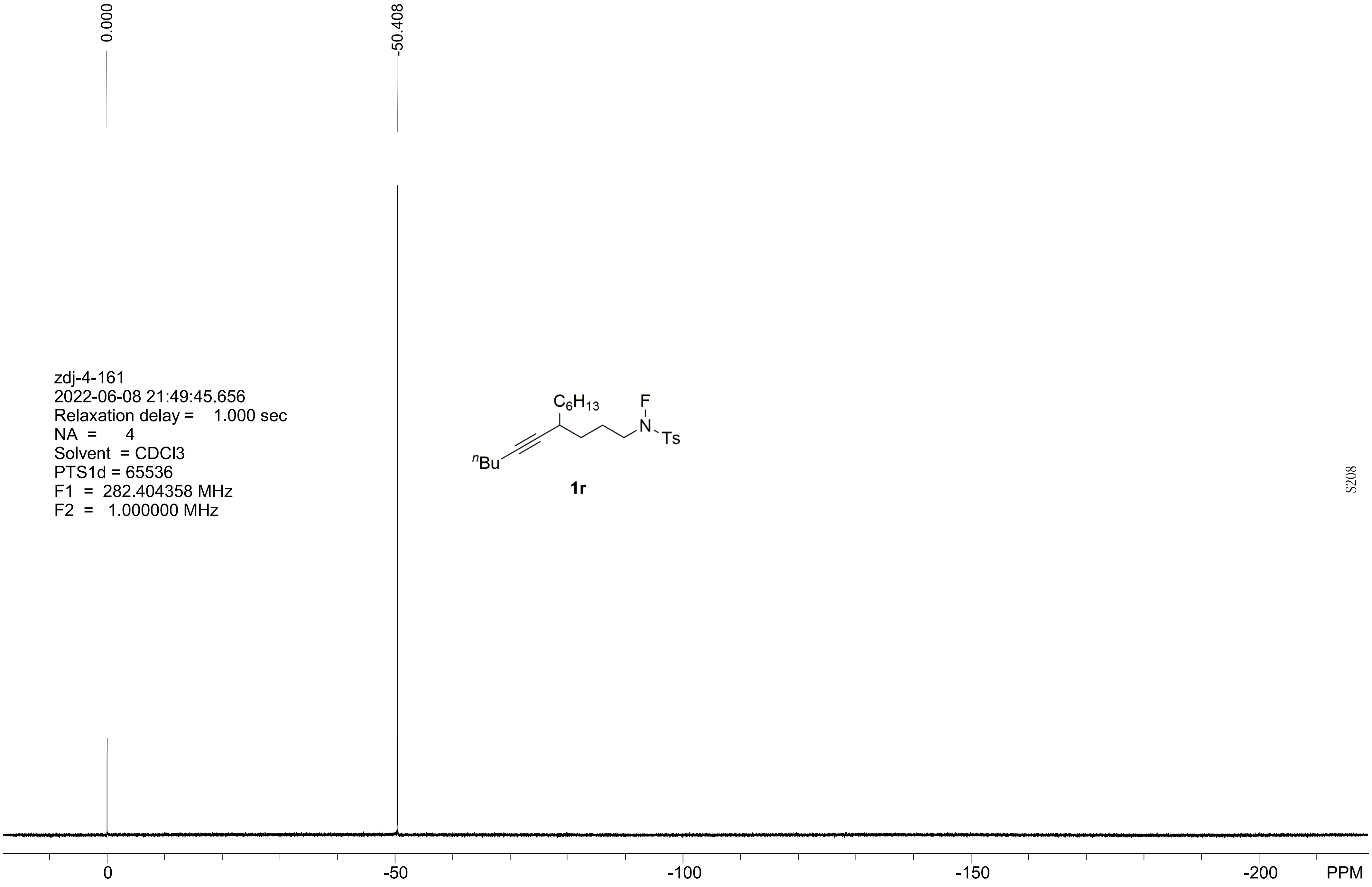
Purity (98%) is determined by Nitromethane (3.6 μL, 0.067 mmol)
as the internal standard in 68.1 mg of sample

zdj-4-161-purity
2022-05-30 19:56:39.750
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

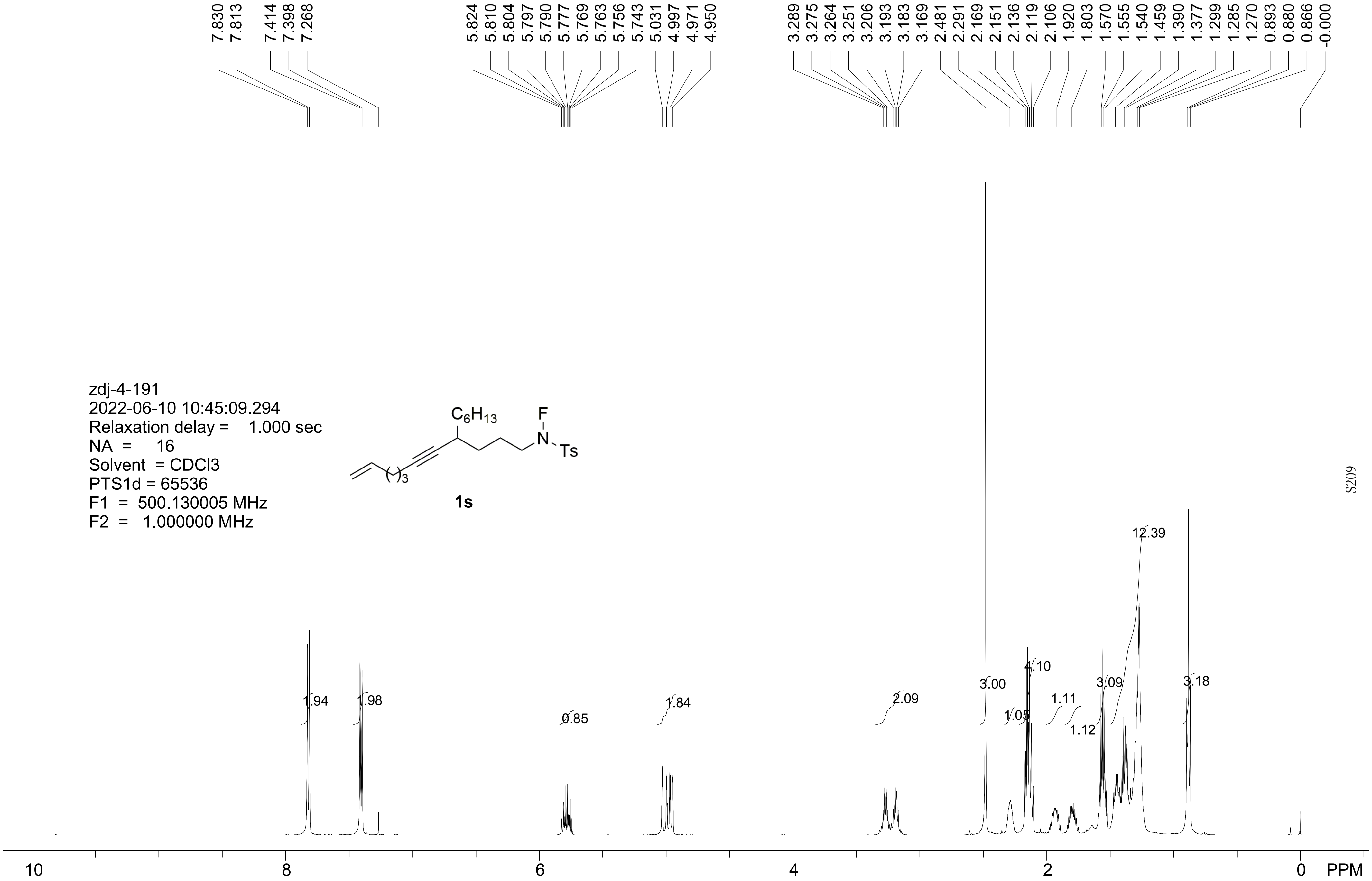


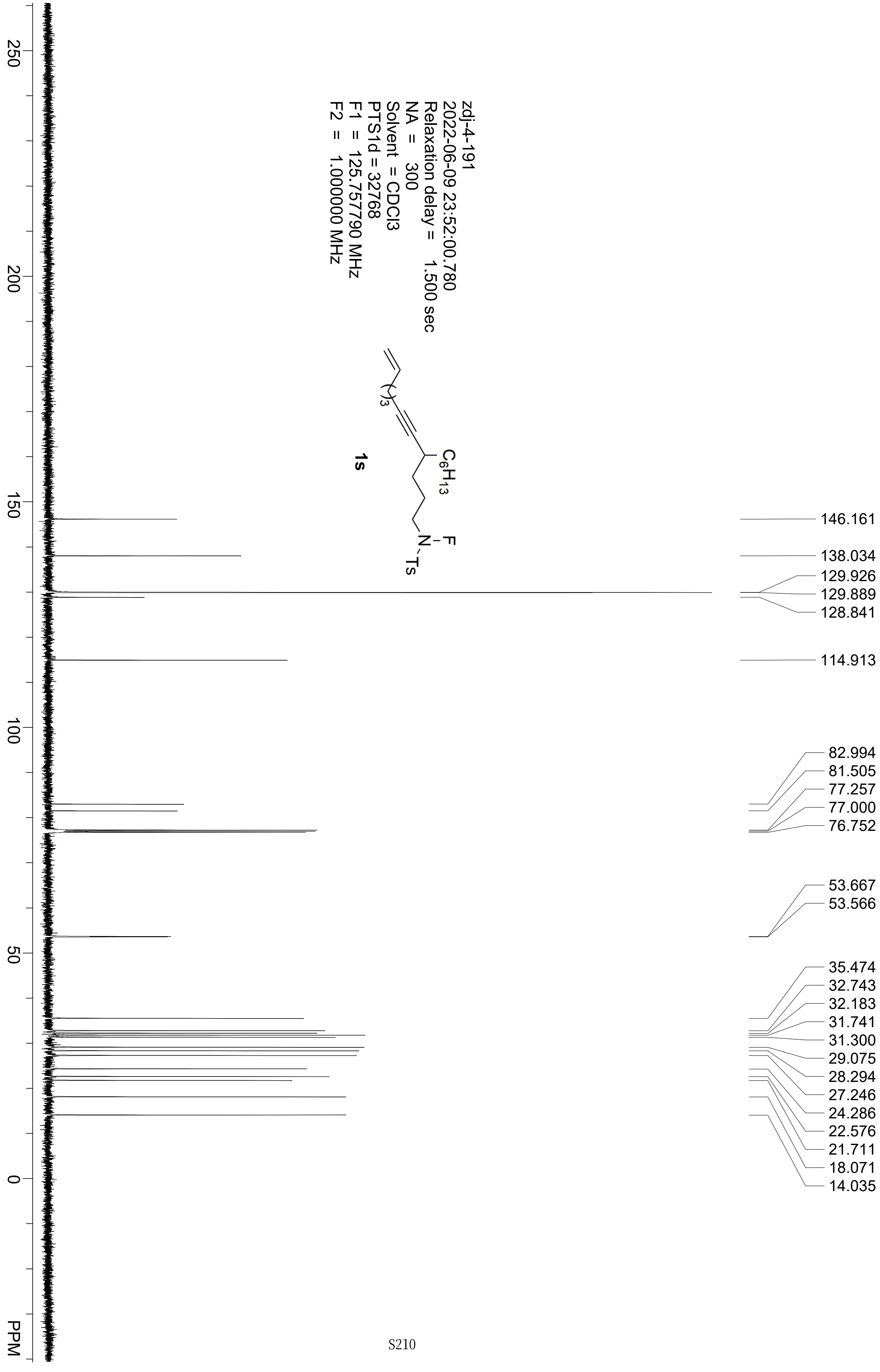
zdj-4-161
2022-05-17 22:06:11.068
Relaxation delay = 1.500 sec
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz

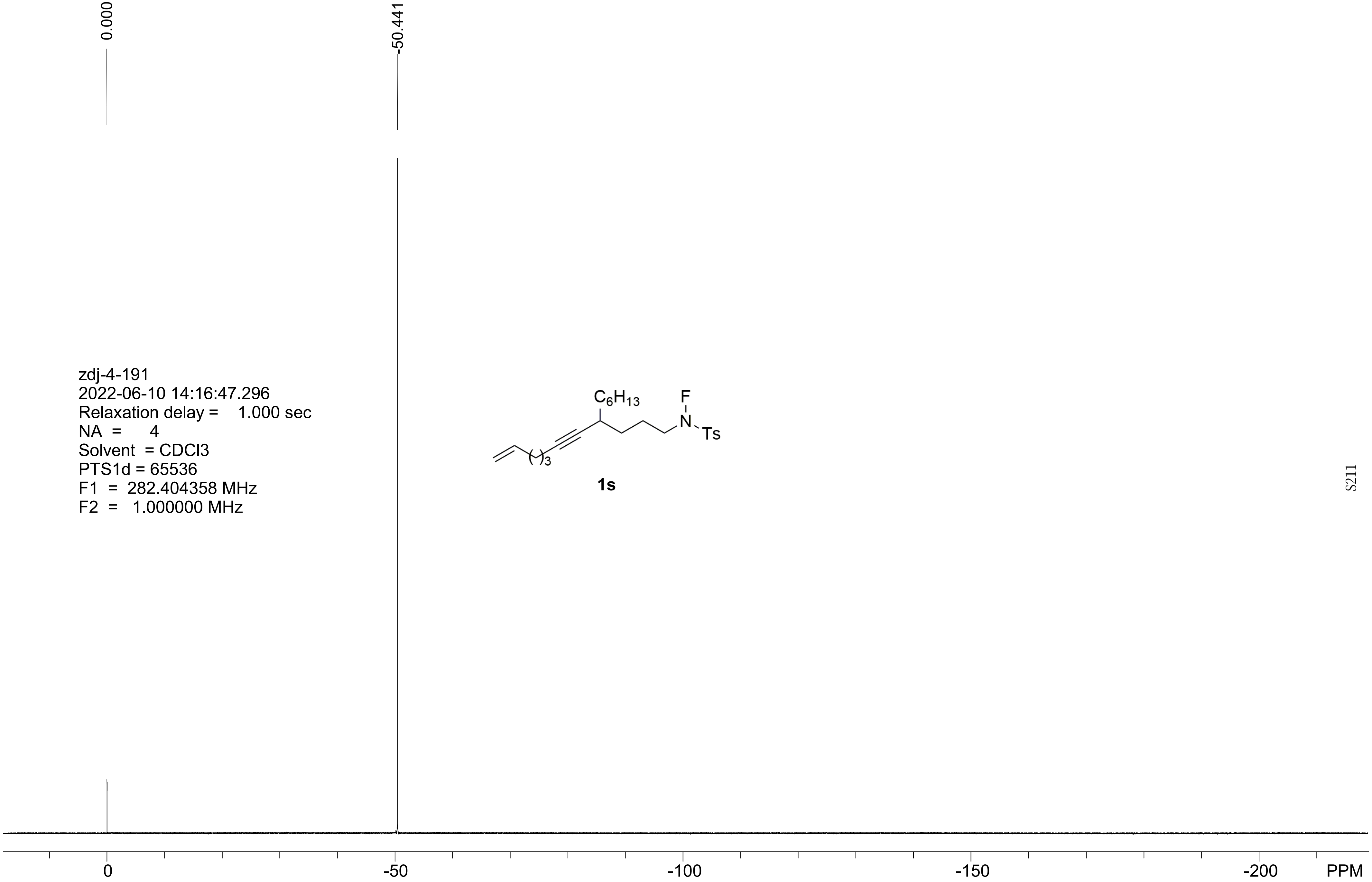
1r


0.000
-50.408
zdj-4-161
2022-06-08 21:49:45.656
Relaxation delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz
C6H13
F
N
Ts
nBu
0
-50
-100
-150
-200
PPM

1r

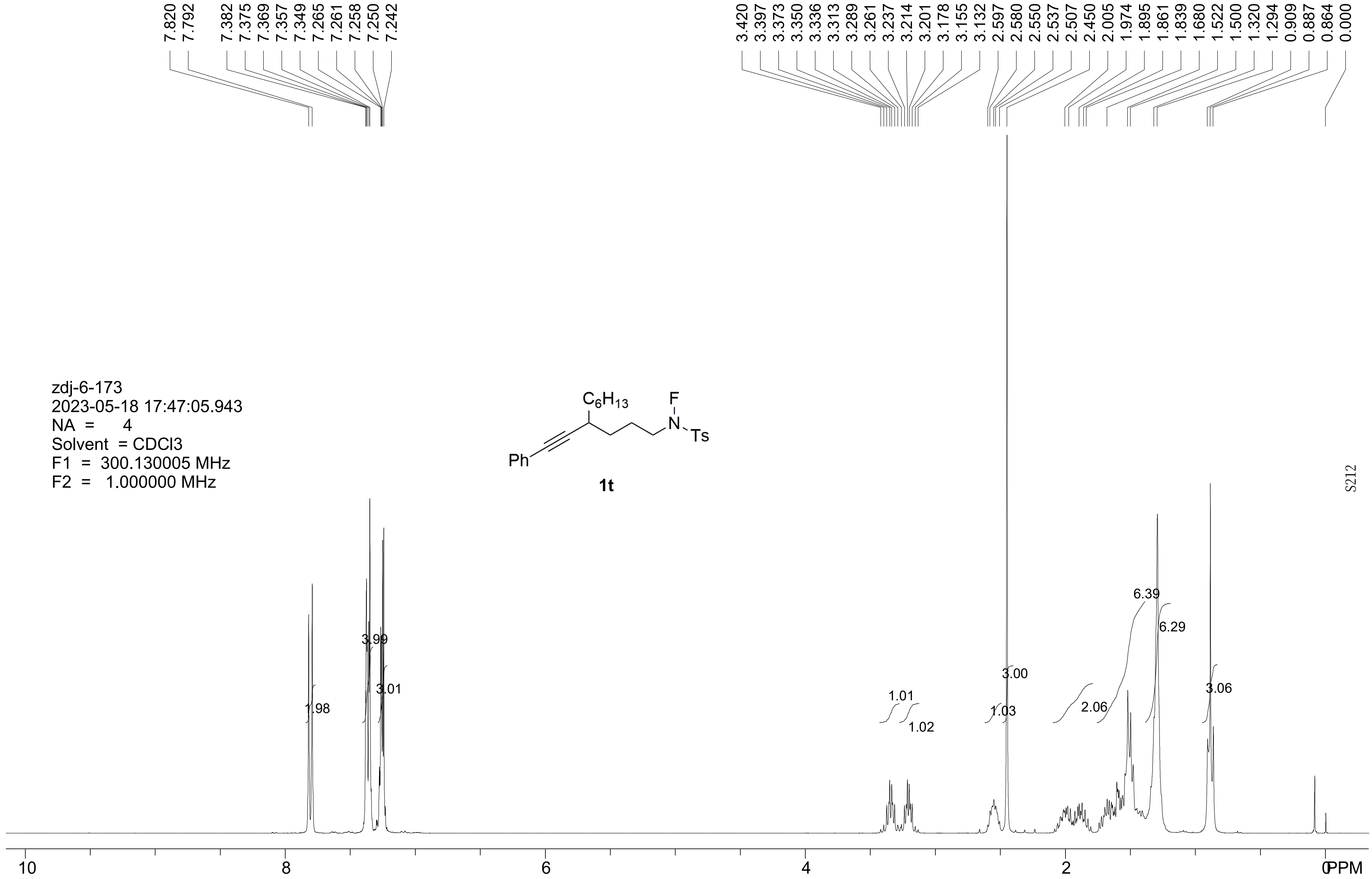

7.830
7.813
7.414
7.398
7.268
5.824
5.810
5.804
5.797
5.790
5.777
5.769
5.763
5.756
5.743
5.031
4.997
4.971
4.950
3.289
3.275
3.264
3.251
3.206
3.193
3.183
3.169
2.481
2.291
2.169
2.151
2.136
2.119
2.106
1.920
1.803
1.570
1.555
1.540
1.459
1.390
1.377
1.299
1.285
1.270
0.893
0.880
0.866
-0.000
zdj-4-191
2022-06-10 10:45:09.294
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
C6H13
F
N
Ts
3
1s
1.94
1.98
0.85
1.84
2.09
3.00
1.05
4.10
1.11
1.12
3.09
12.39
3.18
10
8
6
4
2
0
PPM


zdj-4-191
2022-06-09 23:52:00.780
Relaxation delay = 1.500 sec
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
C6H13
F
N
Ts
3
1s
146.161
138.034
129.926
129.889
128.841
114.913
82.994
81.505
77.257
77.000
76.752
53.667
53.566
35.474
32.743
32.183
31.741
31.300
29.075
28.294
27.246
24.286
22.576
21.711
18.071
14.035
250
200
150
100
50
0
PPM

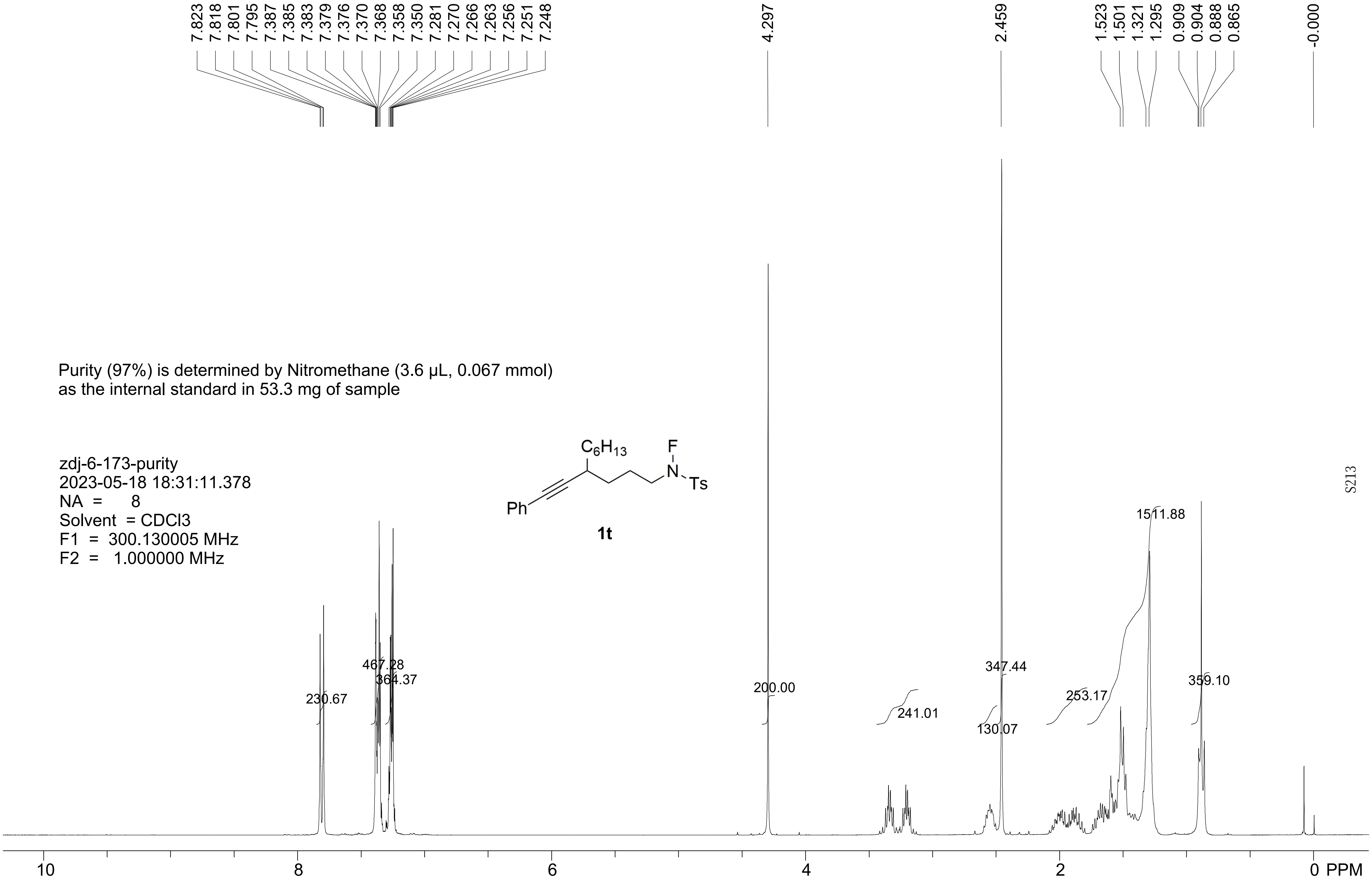


zdj-4-191
2022-06-10 14:16:47.296
Relaxation delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz

1s


zdj-6-173
2023-05-18 17:47:05.943
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz

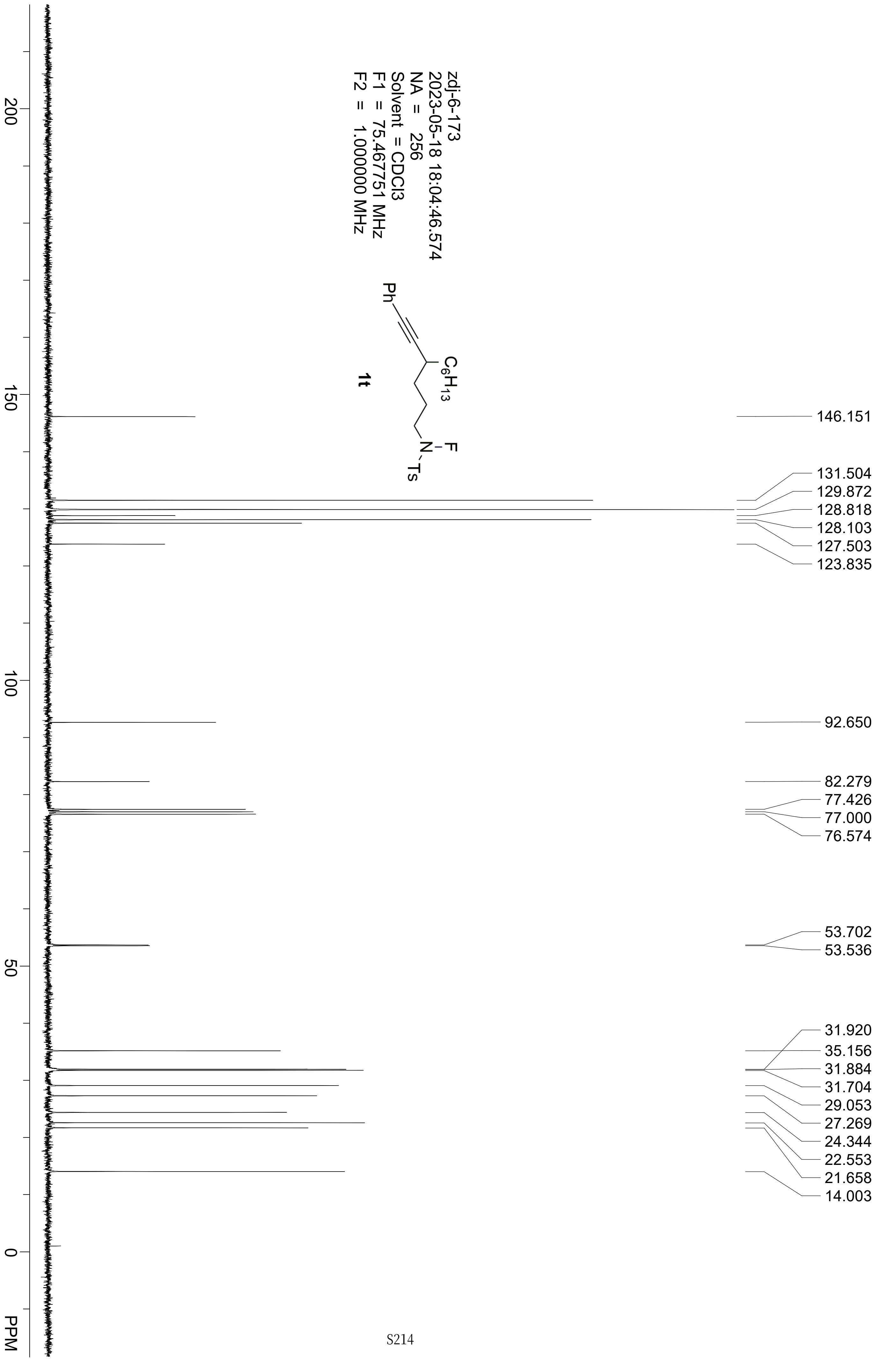
1t

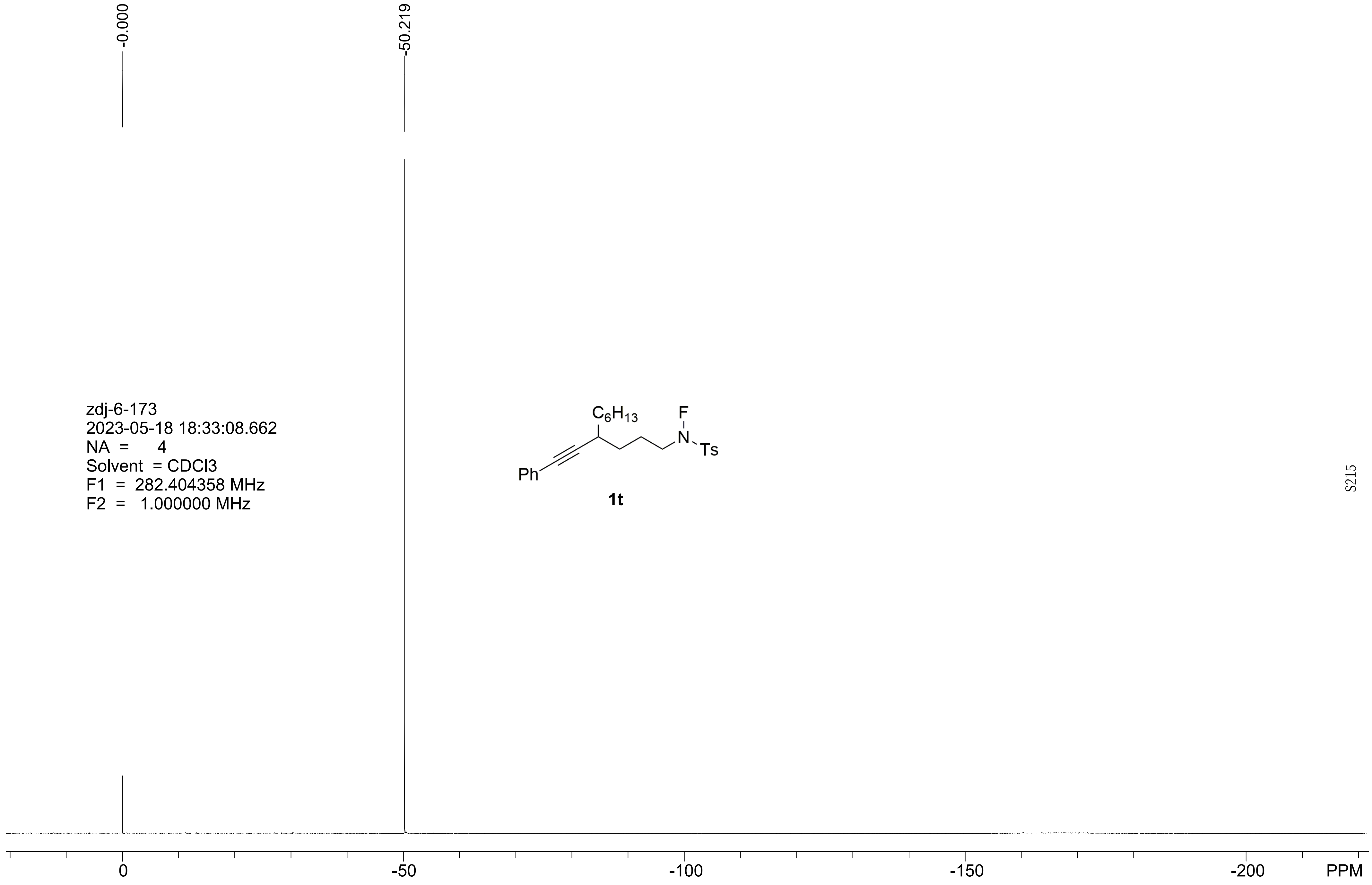


Purity (97%) is determined by Nitromethane (3.6 μL, 0.067 mmol)
as the internal standard in 53.3 mg of sample

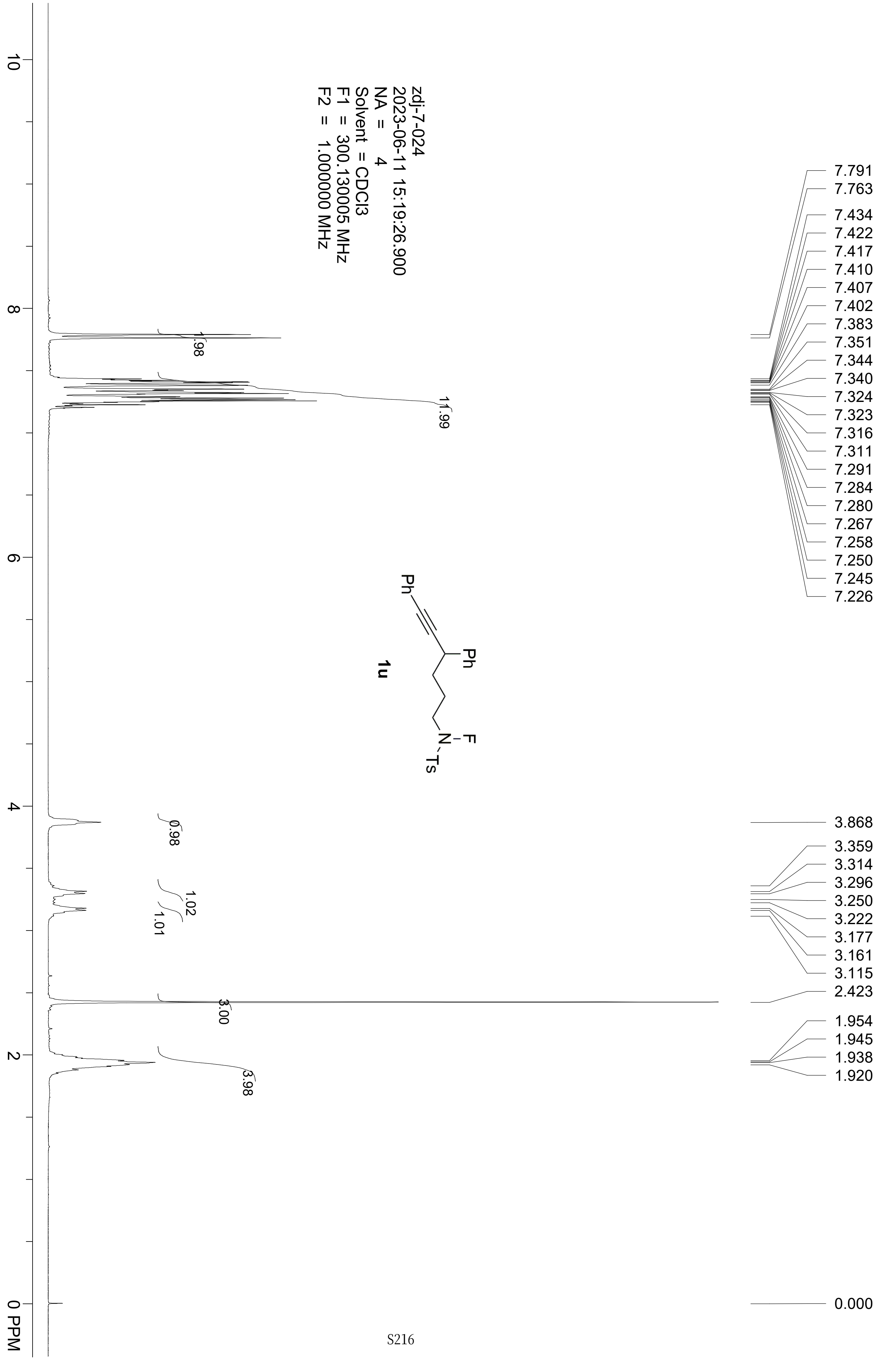
zdj-6-173-purity
2023-05-18 18:31:11.378
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz

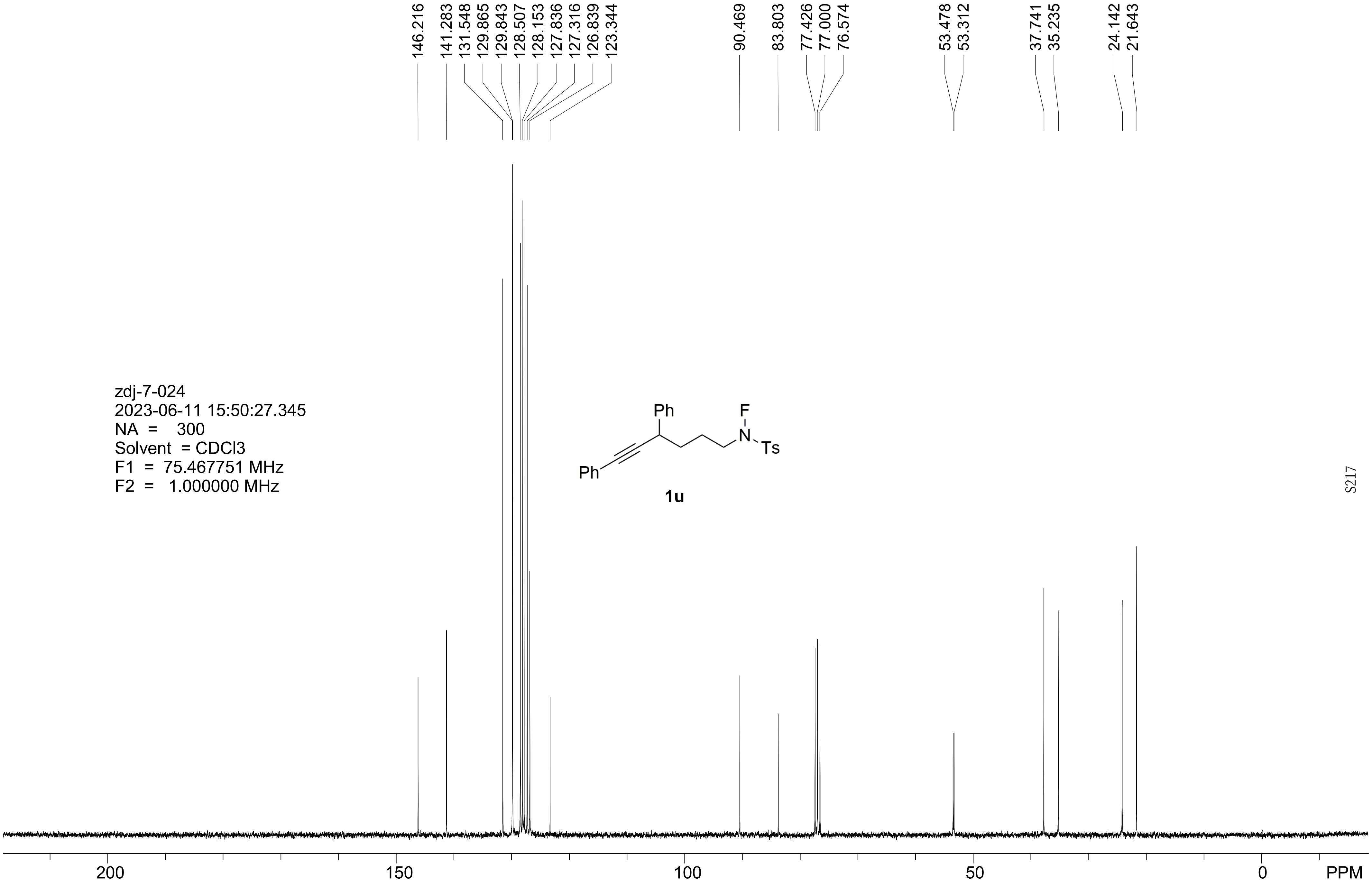
1t


zdj-6-173
2023-05-18 18:04:46.574
NA = 256
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Ph
C6H13
N
F
Ts
1t
200
150
100
50
0
PPM
146.151
131.504
129.872
128.818
128.103
127.503
123.835
92.650
82.279
77.426
77.000
76.574
53.702
53.536
31.920
35.156
31.884
31.704
29.053
27.269
24.344
22.553
21.658
14.003

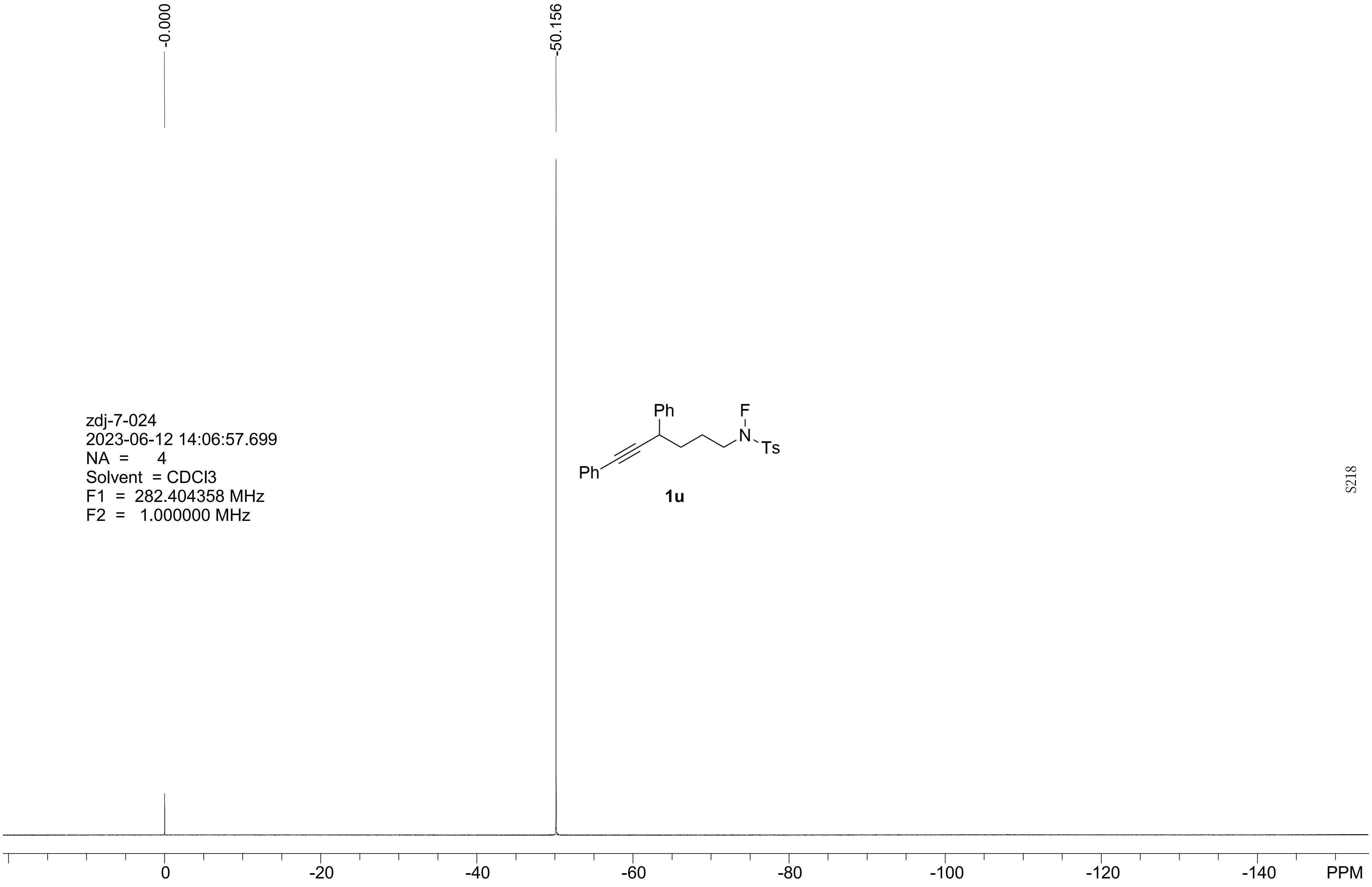

-0.000
-50.219
zdj-6-173
2023-05-18 18:33:08.662
NA = 4
Solvent = CDCl3
F1 = 282.404358 MHz
F2 = 1.000000 MHz
C_6H_{13}
F
N
Ts
Ph
0
-50
-100
-150
-200
PPM

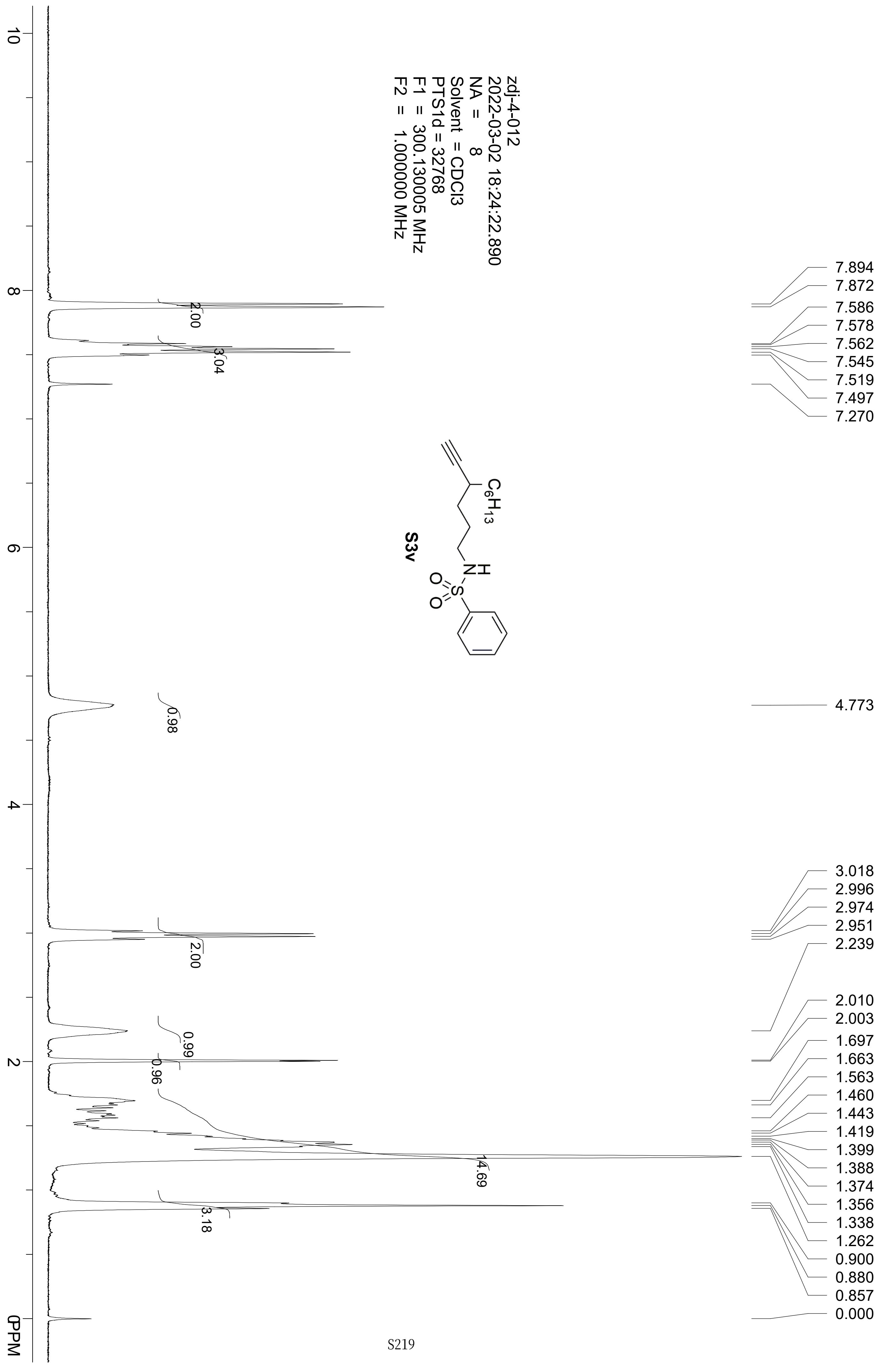
1t

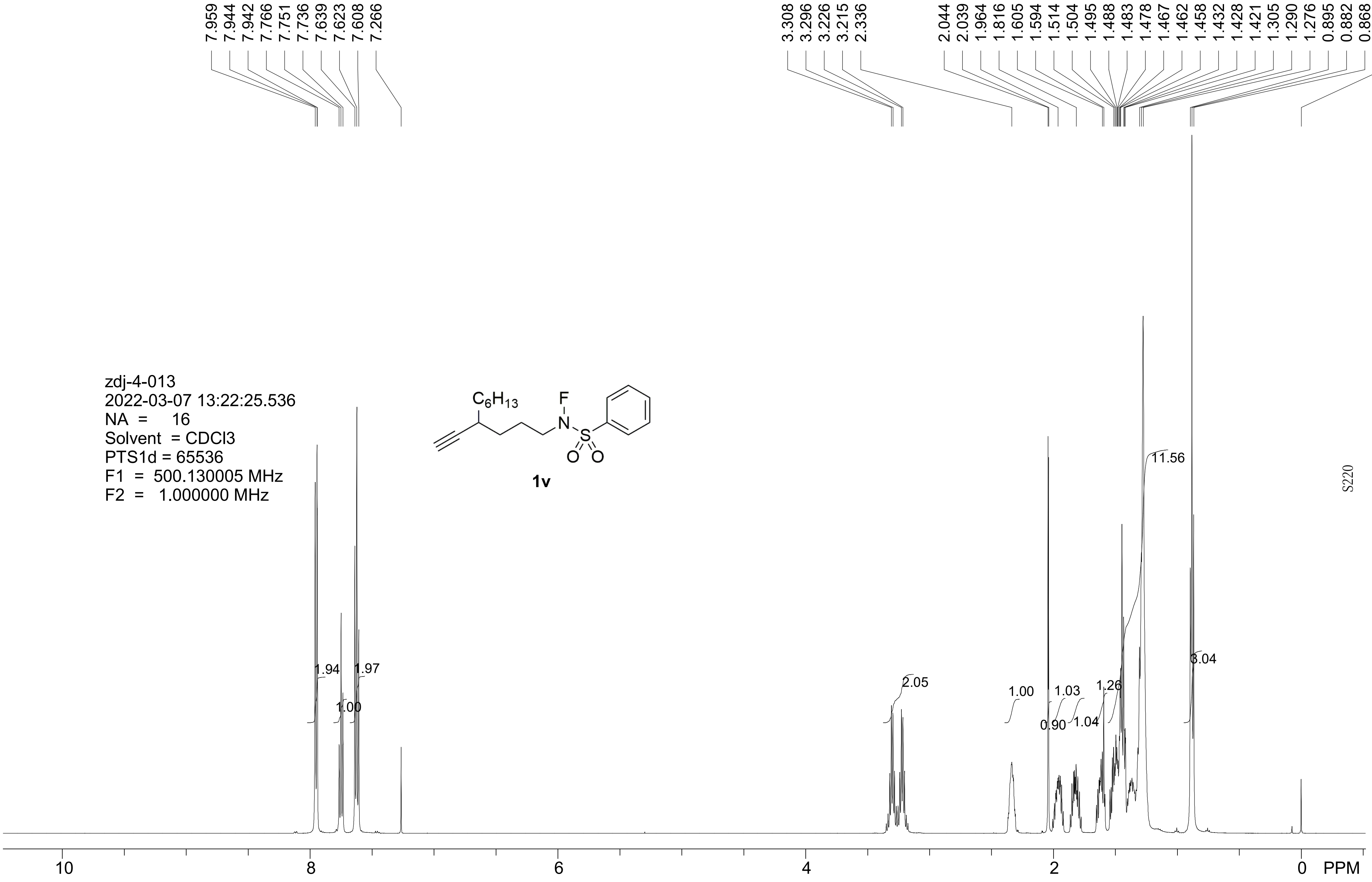

zdj-7-024
2023-06-11 15:19:26.900
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Ph
Ph
N
F
Ts
1u
10
8
6
4
2
0 PPM
1.98
11.99
0.98
1.02
1.01
3.00
3.98
7.791
7.763
7.434
7.422
7.417
7.410
7.407
7.402
7.383
7.351
7.344
7.340
7.324
7.323
7.316
7.311
7.291
7.284
7.280
7.267
7.258
7.250
7.245
7.226
3.868
3.359
3.314
3.296
3.250
3.222
3.177
3.161
3.115
2.423
1.954
1.945
1.938
1.920
0.000

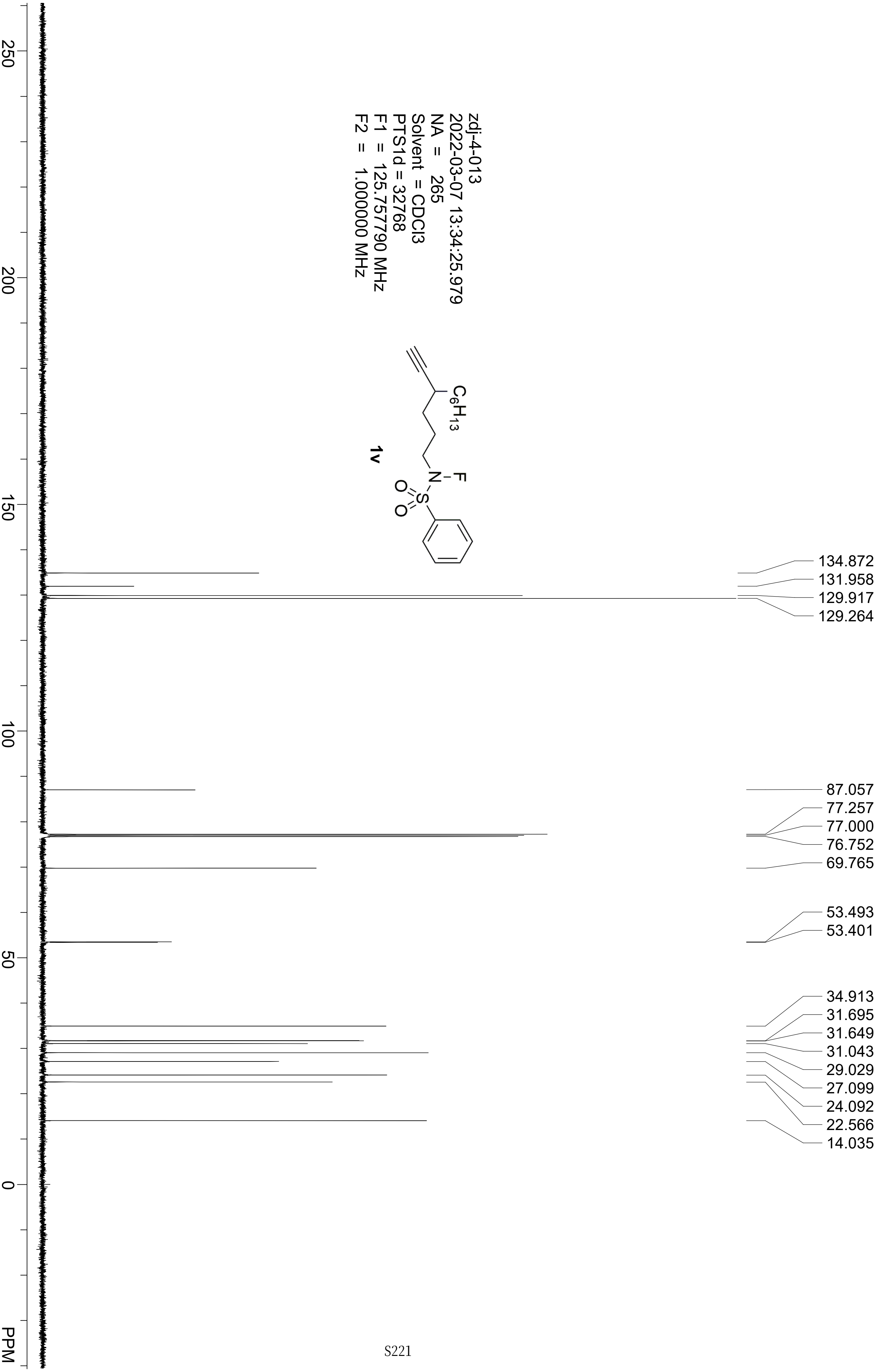

146.216
141.283
131.548
129.865
129.843
128.507
128.153
127.836
127.316
126.839
123.344
90.469
83.803
77.426
77.000
76.574
53.478
53.312
37.741
35.235
24.142
21.643
zdj-7-024
2023-06-11 15:50:27.345
NA = 300
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Ph
Ph
F
N
Ts
200
150
100
50
0
PPM

1u

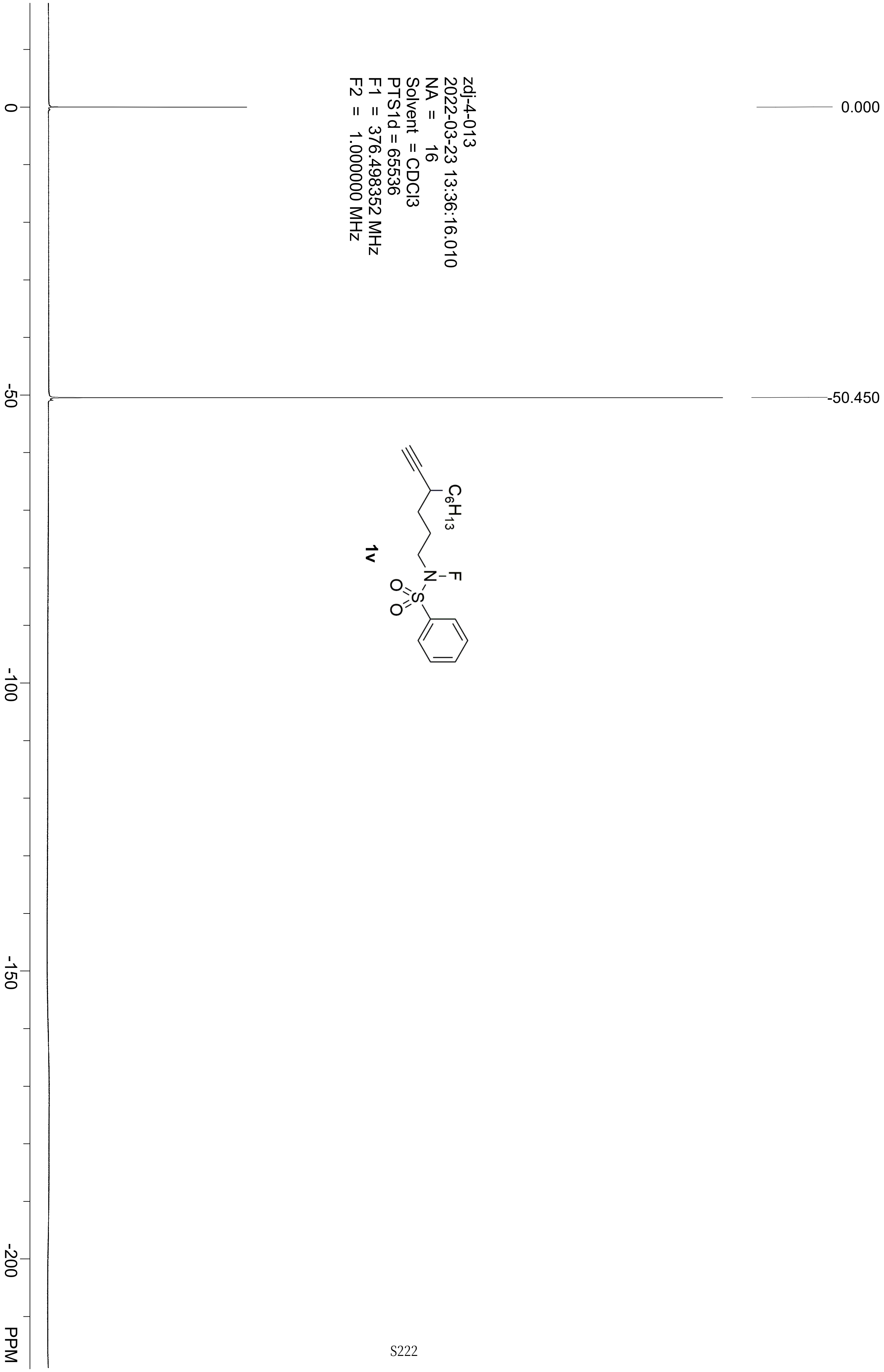

-0.000
-50.156
zdj-7-024
2023-06-12 14:06:57.699
NA = 4
Solvent = CDCl3
F1 = 282.404358 MHz
F2 = 1.000000 MHz
Ph
Ph
F
N
Ts
1u
0
-20
-40
-60
-80
-100
-120
-140
PPM

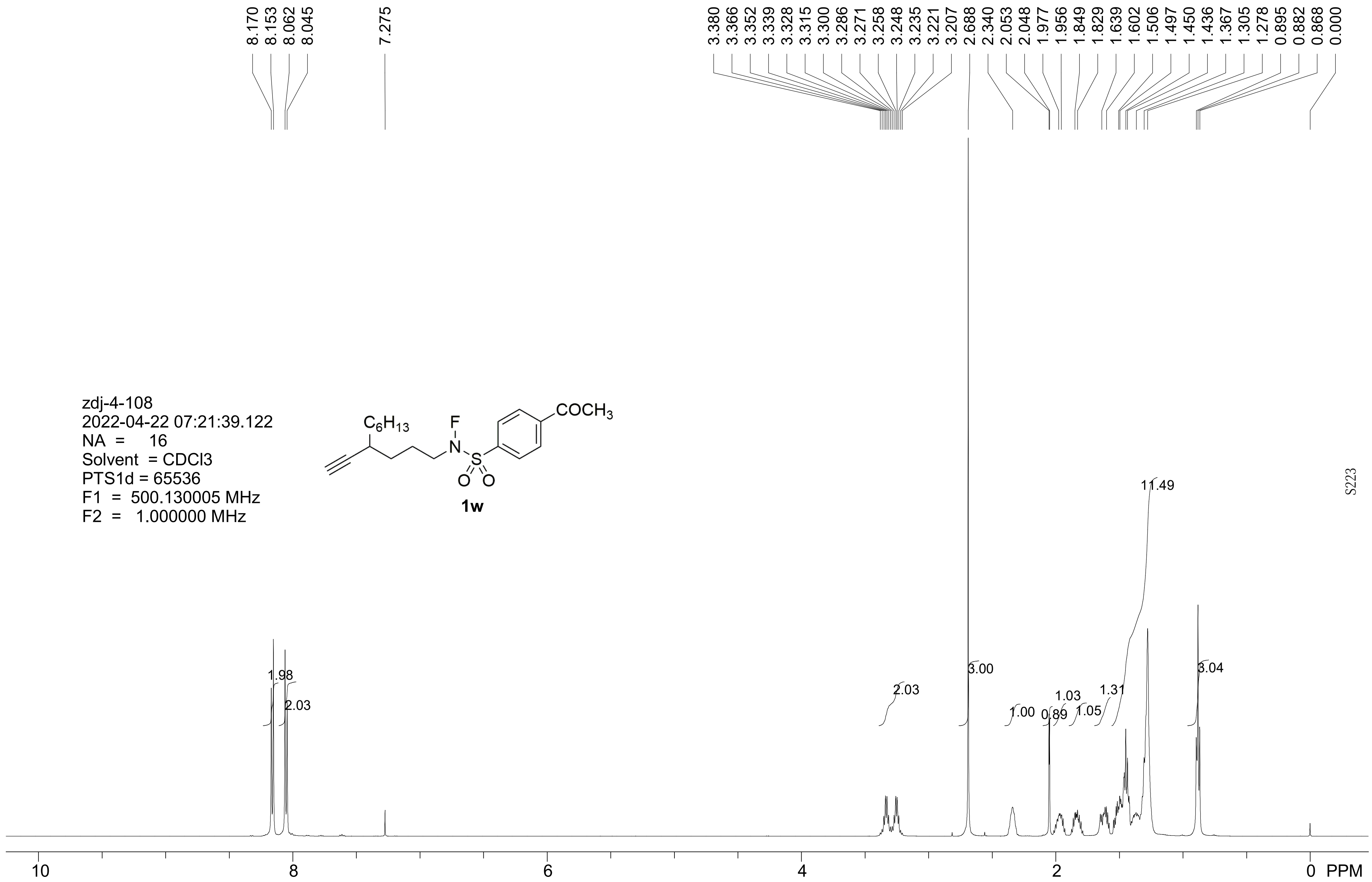

zdj-4-012
2022-03-02 18:24:22.890
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C6H13
H
N
S
O
O
S3v
7.894
7.872
7.586
7.578
7.562
7.545
7.519
7.497
7.270
4.773
3.018
2.996
2.974
2.951
2.239
2.010
2.003
1.697
1.663
1.563
1.460
1.443
1.419
1.399
1.388
1.374
1.356
1.338
1.262
0.900
0.880
0.857
0.000
2.00
3.04
0.98
2.00
0.99
0.96
14.69
3.18
10
8
6
4
2
0
PPM

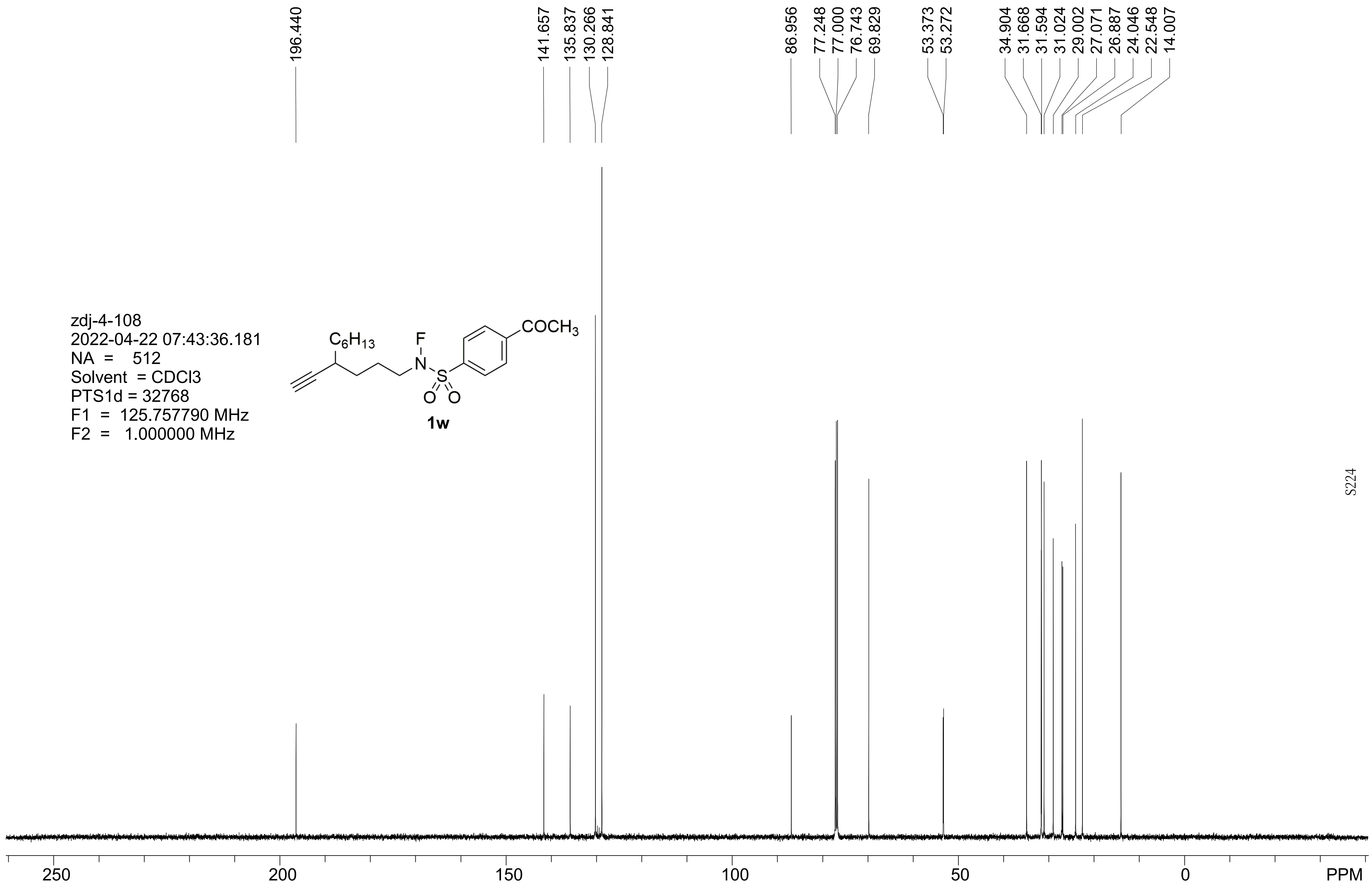

7.959
7.944
7.942
7.766
7.751
7.736
7.639
7.623
7.608
7.266
3.308
3.296
3.226
3.215
2.336
2.044
2.039
1.964
1.816
1.605
1.594
1.514
1.504
1.495
1.488
1.483
1.478
1.467
1.462
1.458
1.432
1.428
1.421
1.305
1.290
1.276
0.895
0.882
0.868
0.000
zdj-4-013
2022-03-07 13:22:25.536
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
C6H13
F
N
S
O
O
1v
1.94
1.00
1.97
2.05
1.00
0.90
1.03
1.04
1.26
11.56
3.04
10
8
6
4
2
0
PPM

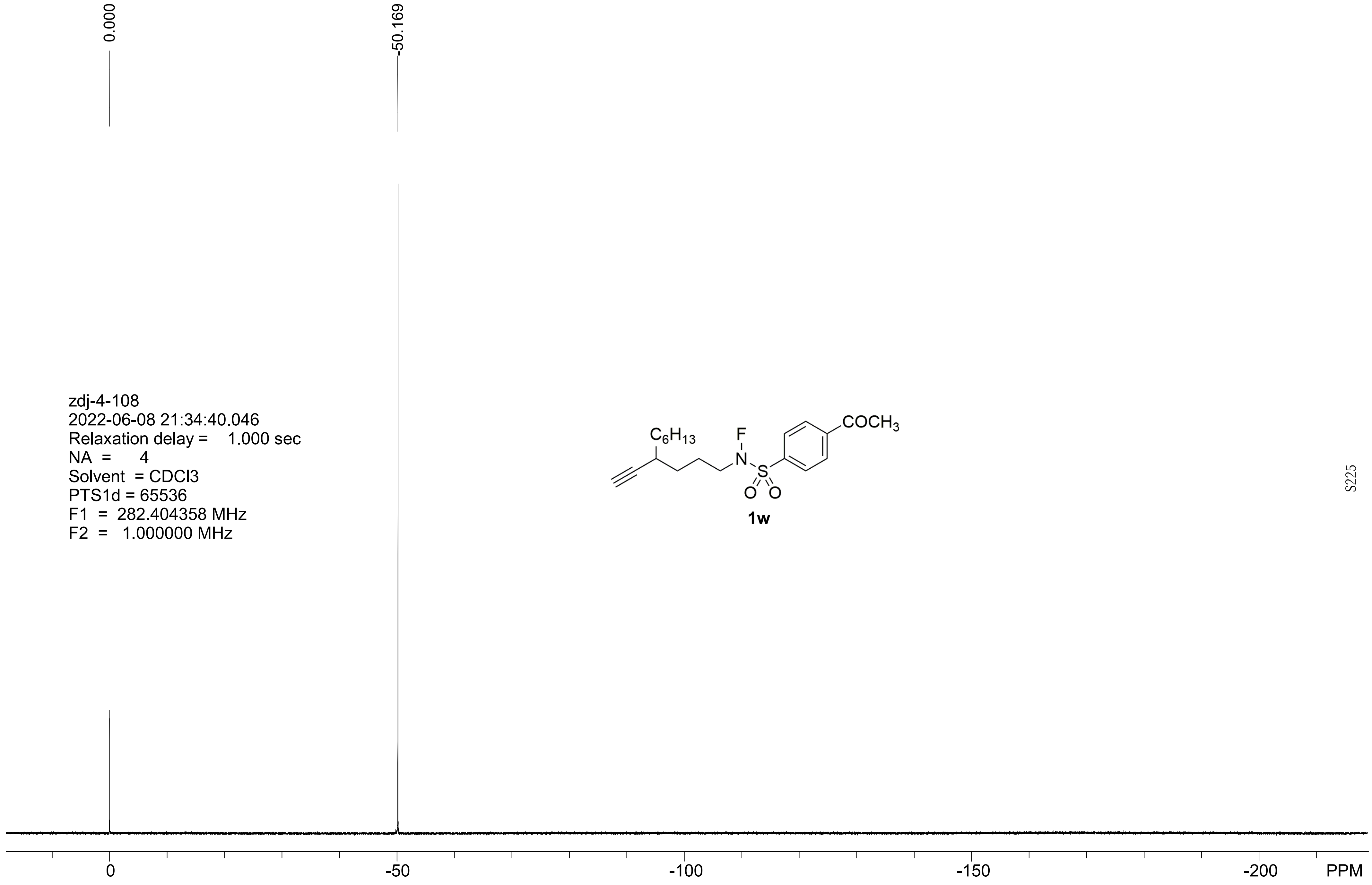

zdj-4-013
2022-03-07 13:34:25.979
NA = 265
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
C6H13
N
F
S
O
O
134.872
131.958
129.917
129.264
87.057
77.257
77.000
76.752
69.765
53.493
53.401
34.913
31.695
31.649
31.043
29.029
27.099
24.092
22.566
14.035
250
200
150
100
50
0
PPM

1v

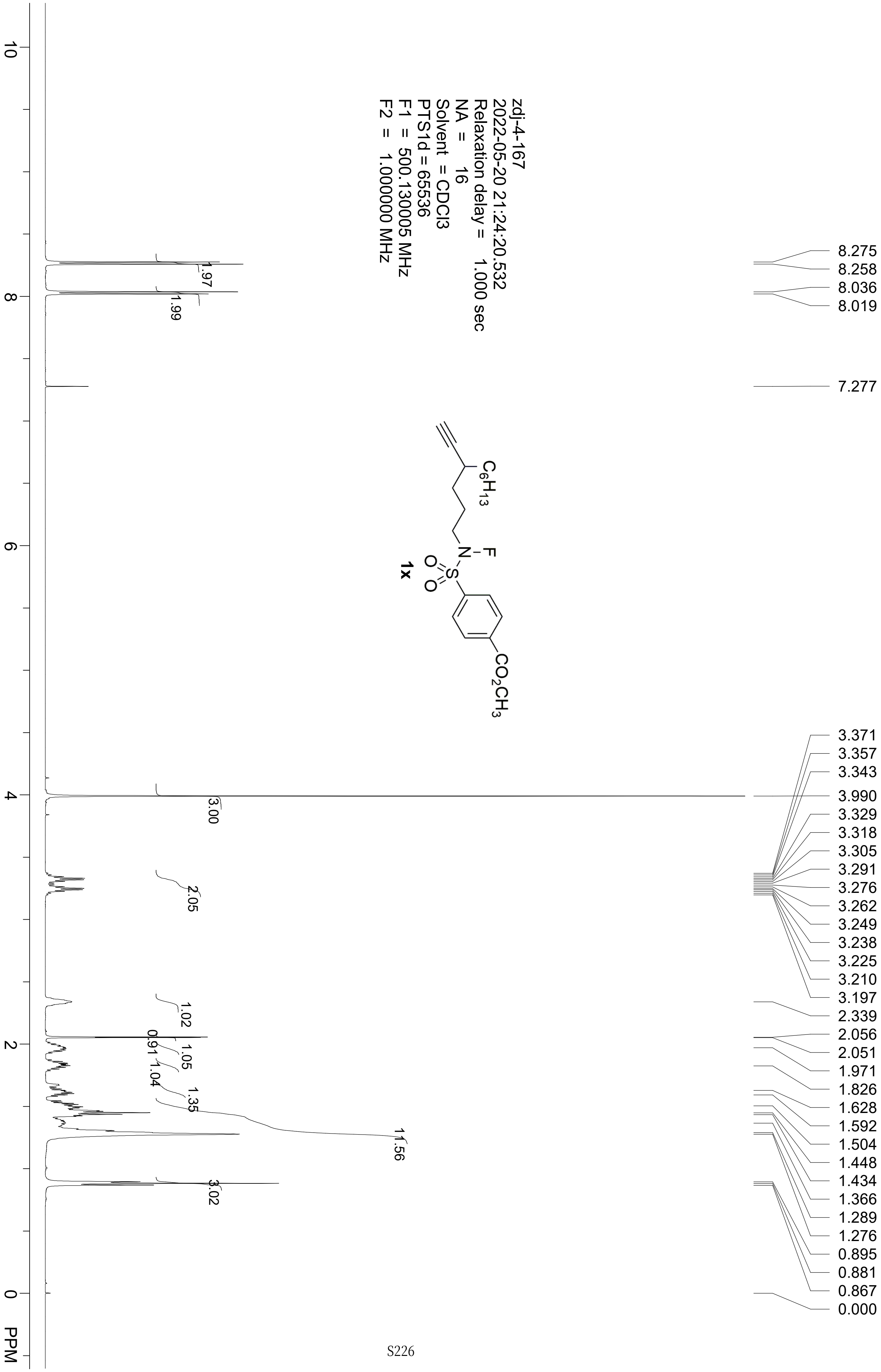

zdj-4-013
2022-03-23 13:36:16.010
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz
0.000
-50.450
C6H13
N
F
S
O
O
1v
0
-50
-100
-150
-200
PPM

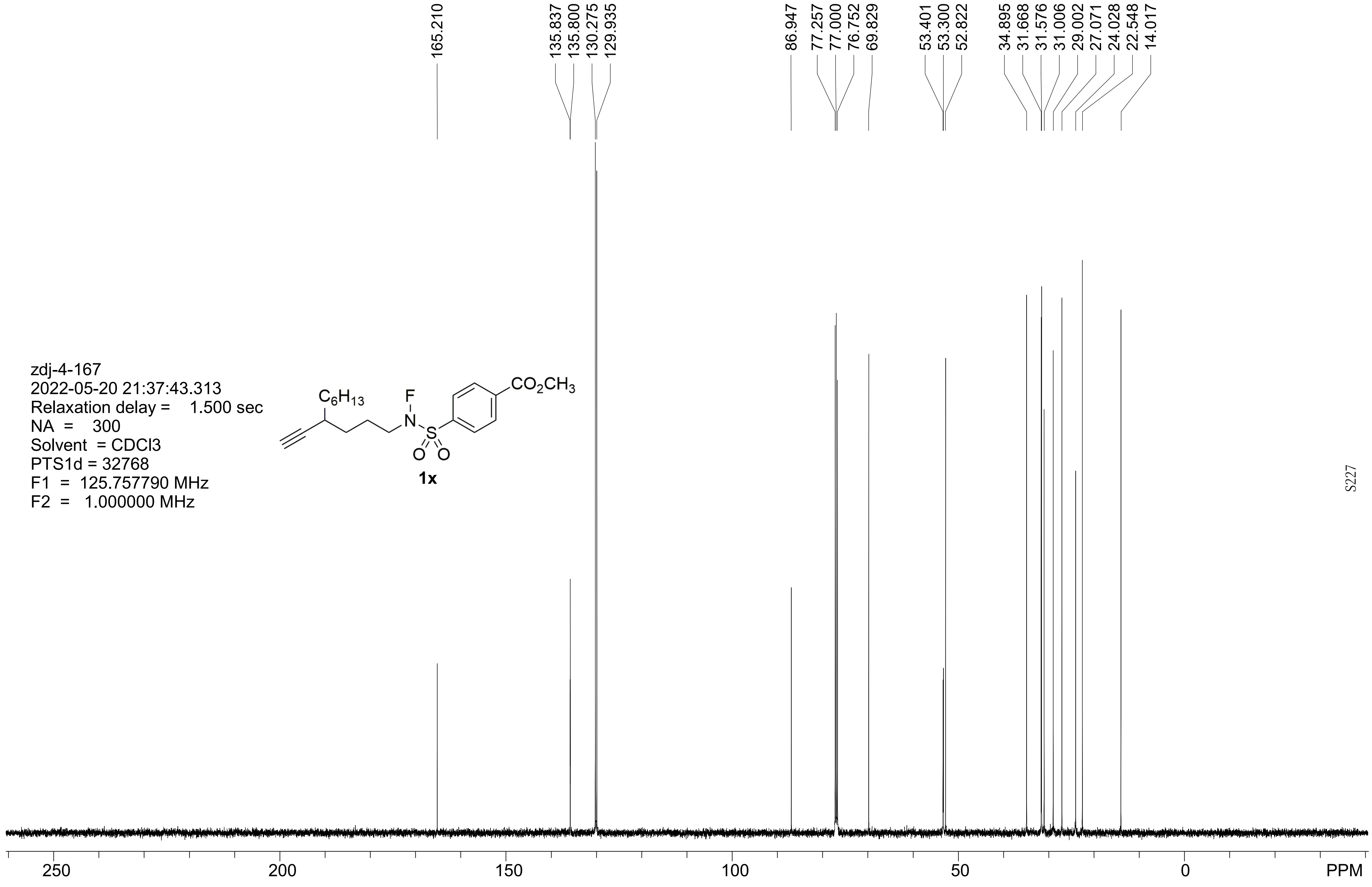

8.170
8.153
8.062
8.045
7.275
3.380
3.366
3.352
3.339
3.328
3.315
3.300
3.286
3.271
3.258
3.248
3.235
3.221
3.207
2.688
2.340
2.053
2.048
1.977
1.956
1.849
1.829
1.639
1.602
1.506
1.497
1.450
1.436
1.367
1.305
1.278
0.895
0.882
0.868
0.000
zdj-4-108
2022-04-22 07:21:39.122
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
C6H13
F
N
S
O
O
COCH3
1w
1.98
2.03
2.03
3.00
1.00
0.89
1.03
1.05
1.31
11.49
3.04
10
8
6
4
2
0 PPM


zdj-4-108
2022-04-22 07:43:36.181
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
C_6H_{13}
F
N
S
O
O
$COCH_3$
1w
196.440
141.657
135.837
130.266
128.841
86.956
77.248
77.000
76.743
69.829
53.373
53.272
34.904
31.668
31.594
31.024
29.002
27.071
26.887
24.046
22.548
14.007
250
200
150
100
50
0
PPM


0.000
-50.169
zdj-4-108
2022-06-08 21:34:40.046
Relaxation delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz
C6H13
F
N
S
O
O
COCH3
0
-50
-100
-150
-200
PPM

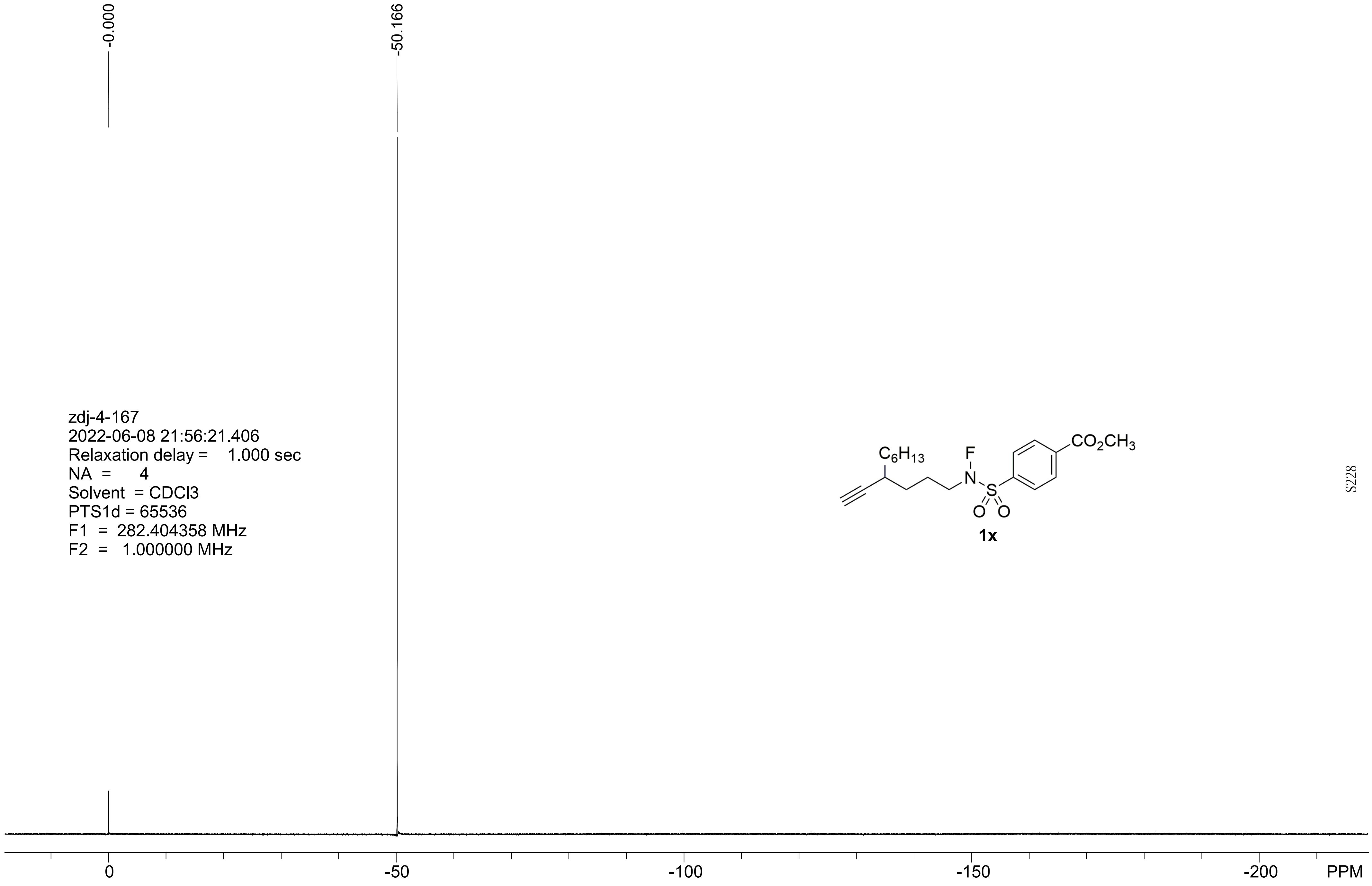
1w

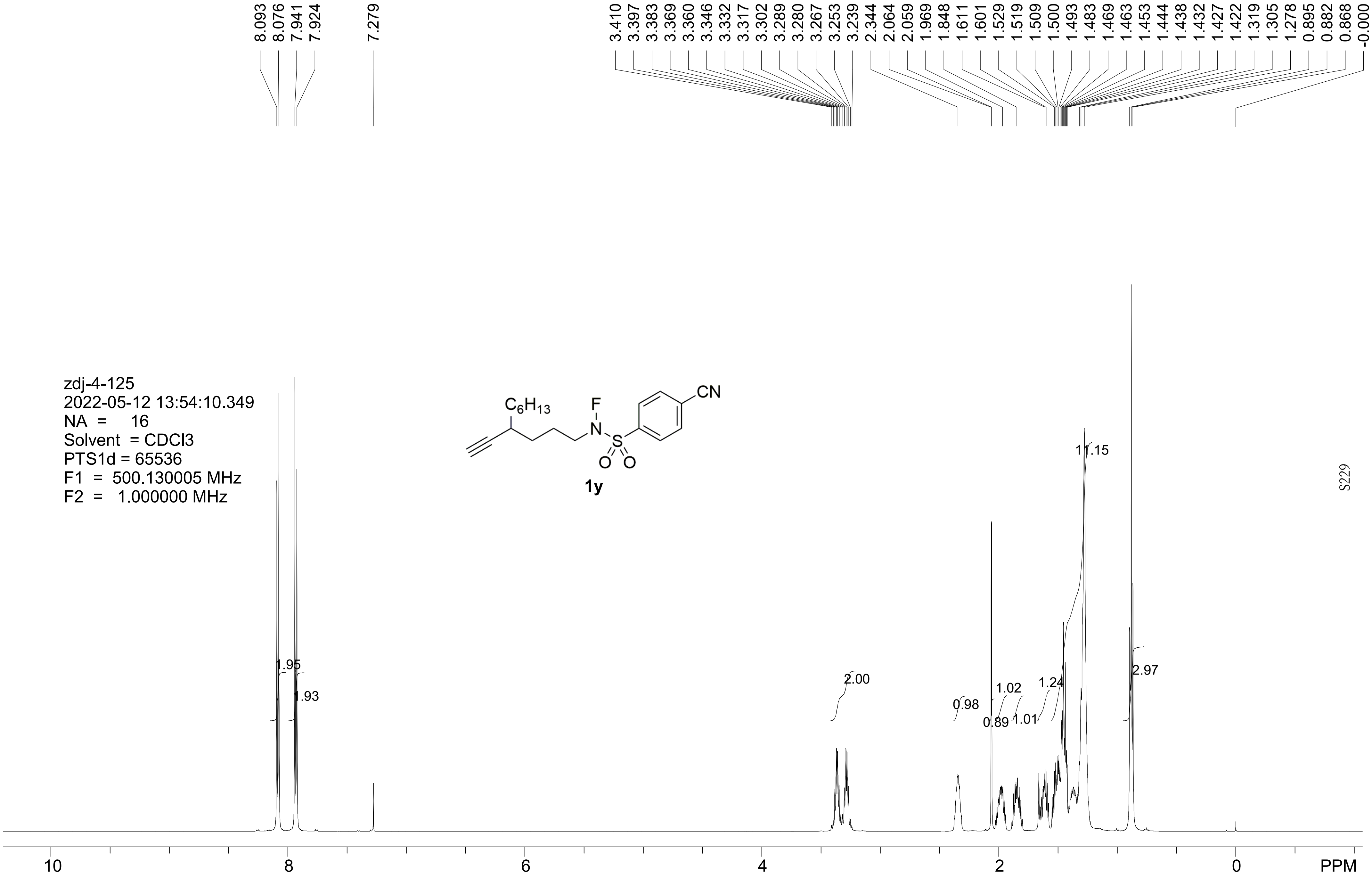

zdj-4-167
2022-05-20 21:24:20.532
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
C6H13
F
N
S
O
O
CO2CH3
1x
10
8
6
4
2
0
PPM
1.97
1.99
3.00
2.05
1.02
0.91
1.05
1.04
1.35
11.56
3.02
8.275
8.258
8.036
8.019
7.277
3.371
3.357
3.343
3.990
3.329
3.318
3.305
3.291
3.276
3.262
3.249
3.238
3.225
3.210
3.197
2.339
2.056
2.051
1.971
1.826
1.628
1.592
1.504
1.448
1.434
1.366
1.289
1.276
0.895
0.881
0.867
0.000



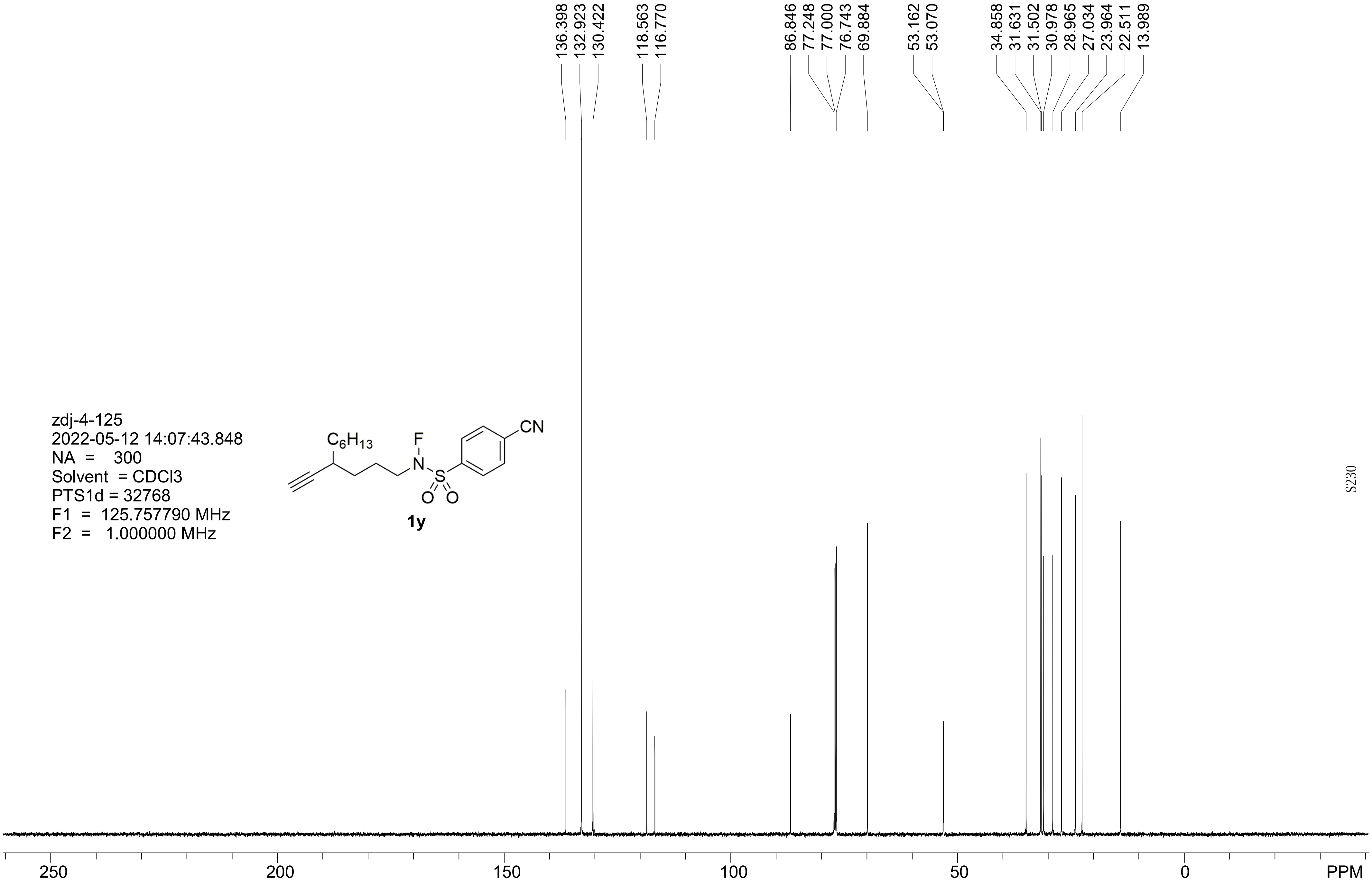
zdj-4-167
2022-05-20 21:37:43.313
Relaxation delay = 1.500 sec
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz

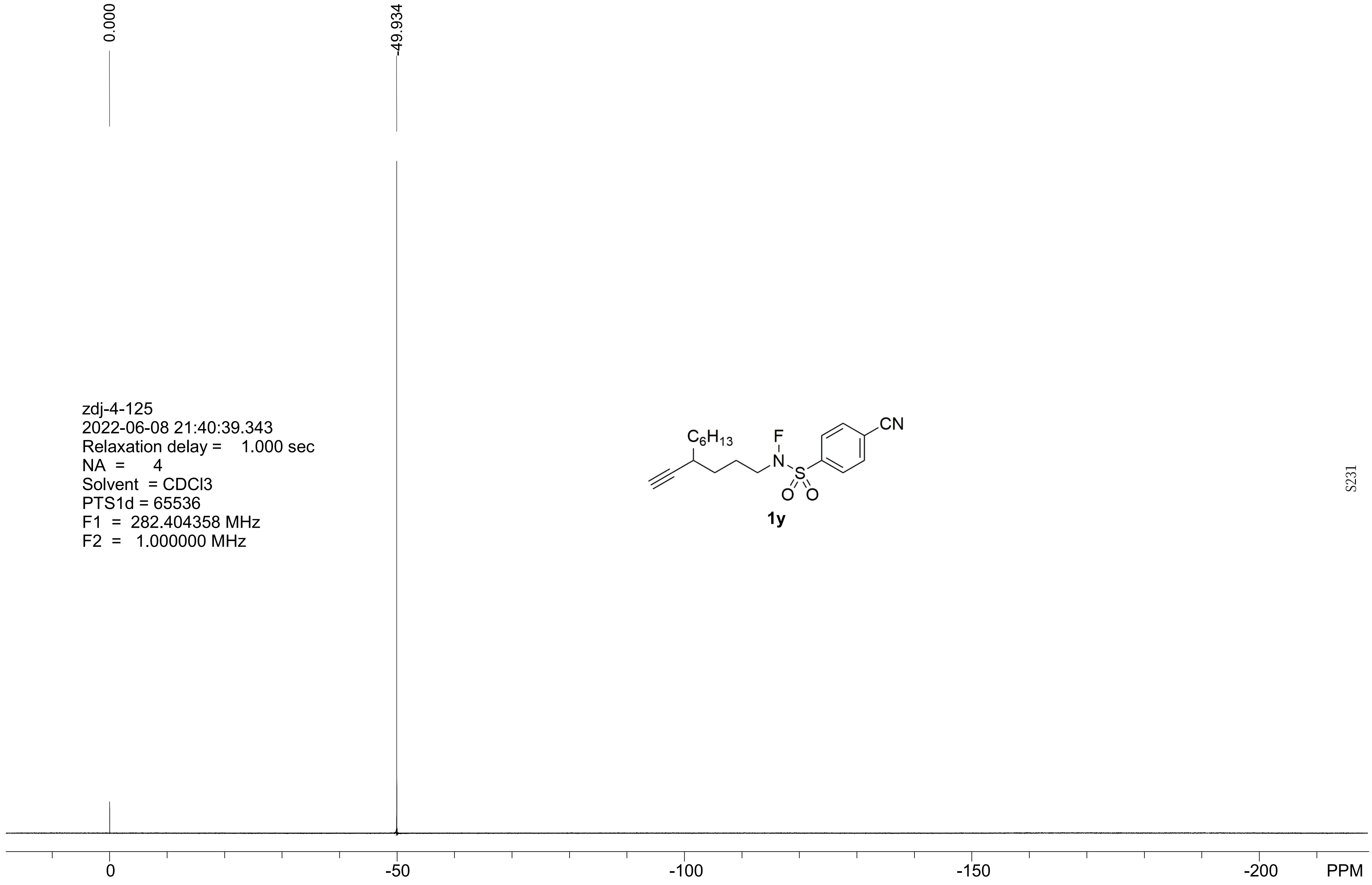
1x


-0.000
-50.166
zdj-4-167
2022-06-08 21:56:21.406
Relaxation delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz
C6H13
F
N
S
O
O
CO2CH3
1x
0
-50
-100
-150
-200
PPM


8.093
8.076
7.941
7.924
7.279
3.410
3.397
3.383
3.369
3.360
3.346
3.332
3.317
3.302
3.289
3.280
3.267
3.253
3.239
2.344
2.064
2.059
1.969
1.848
1.611
1.601
1.529
1.519
1.509
1.500
1.493
1.483
1.469
1.463
1.453
1.444
1.438
1.432
1.427
1.422
1.319
1.305
1.278
0.895
0.882
0.868
-0.000
zdj-4-125
2022-05-12 13:54:10.349
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
C6H13
F
N
S
O
O
CN
1.95
1.93
2.00
0.98
1.02
0.89
1.01
1.24
11.15
2.97
10
8
6
4
2
0
PPM

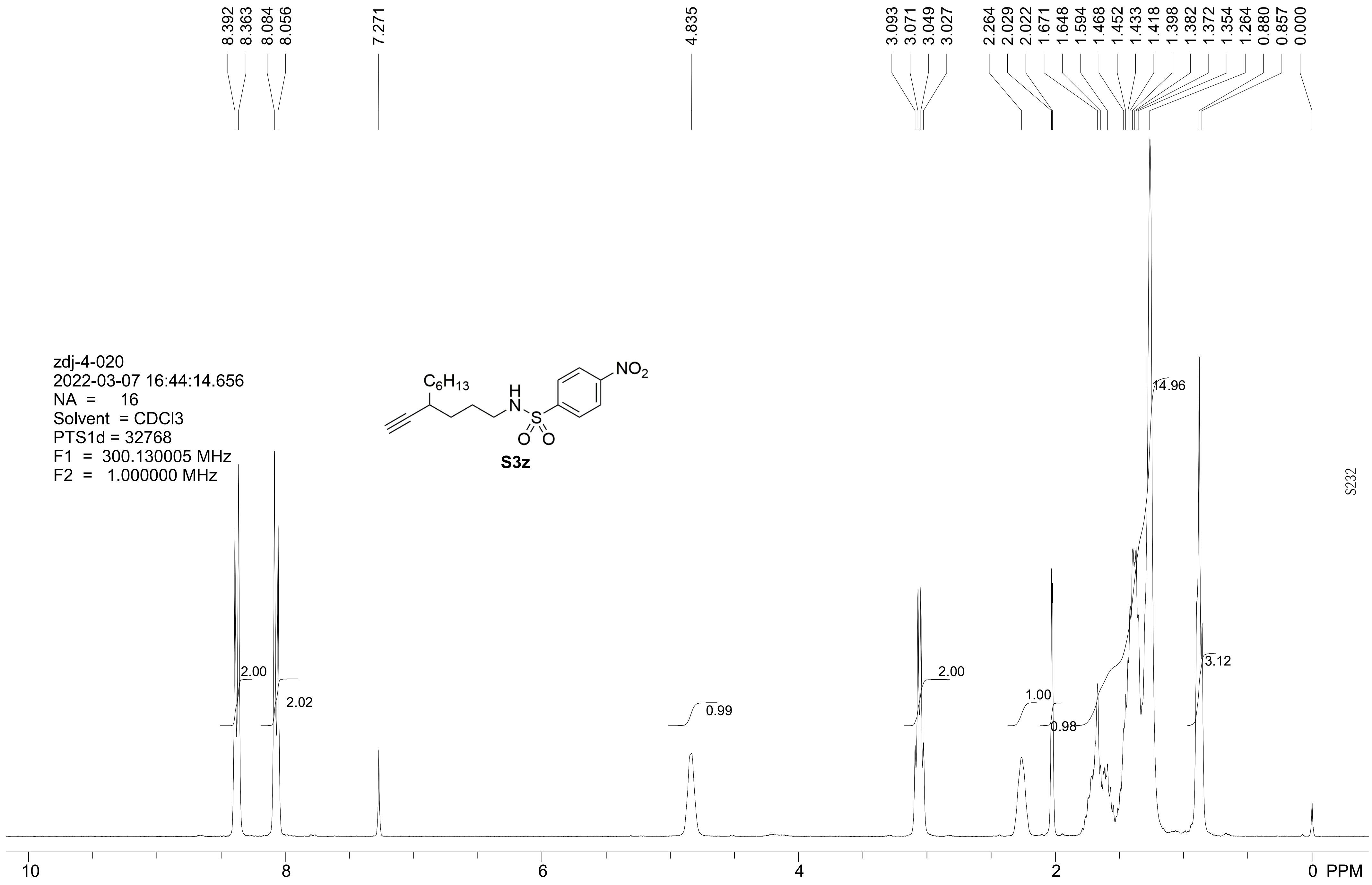
1y

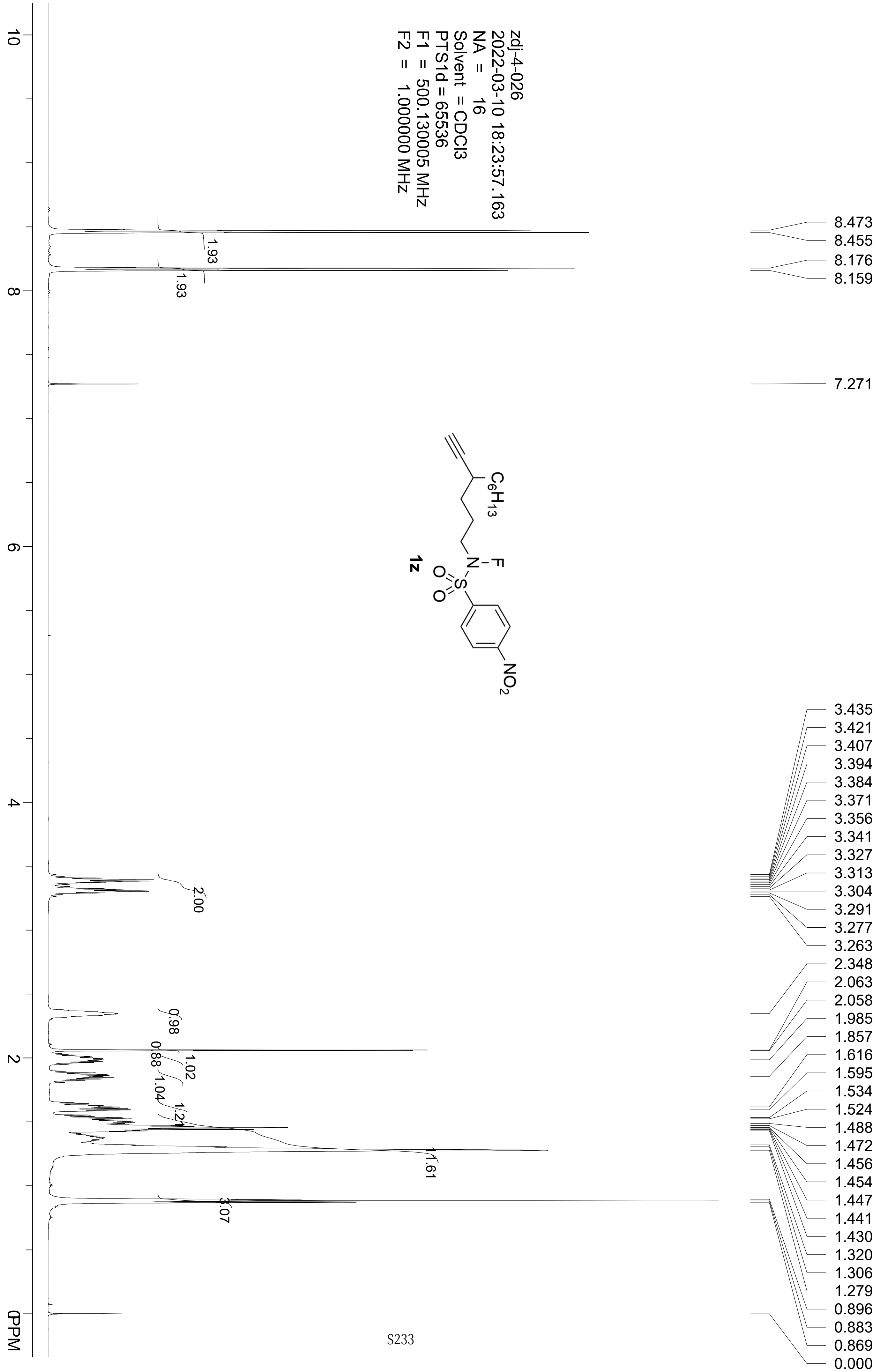

136.398
132.923
130.422
118.563
116.770
86.846
77.248
77.000
76.743
69.884
53.162
53.070
34.858
31.631
31.502
30.978
28.965
27.034
23.964
22.511
13.989
zdj-4-125
2022-05-12 14:07:43.848
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
C6H13
F
N
S
O
O
CN
1y
250
200
150
100
50
0
PPM

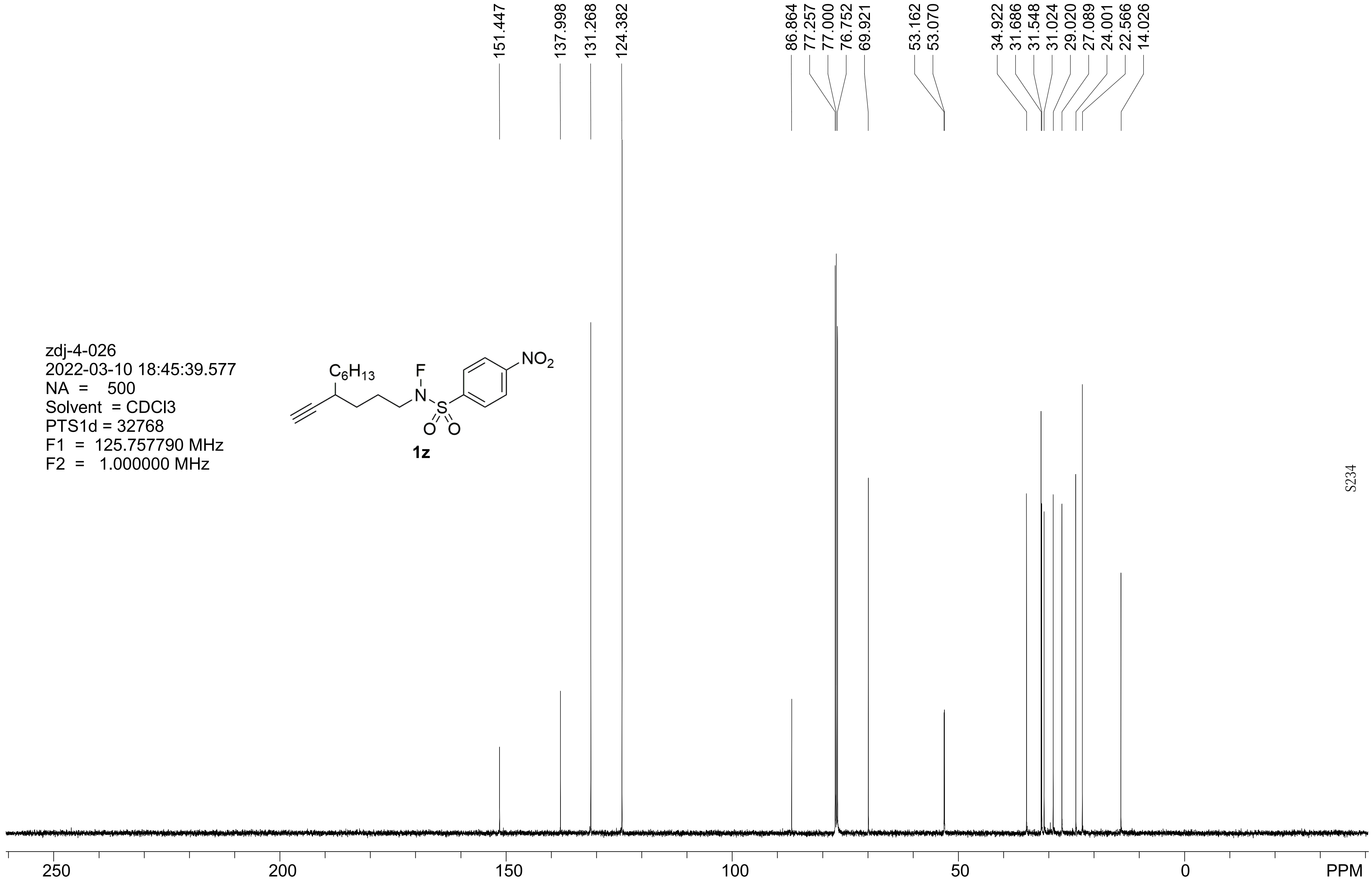


zdj-4-125
2022-06-08 21:40:39.343
Relaxation delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz

1y

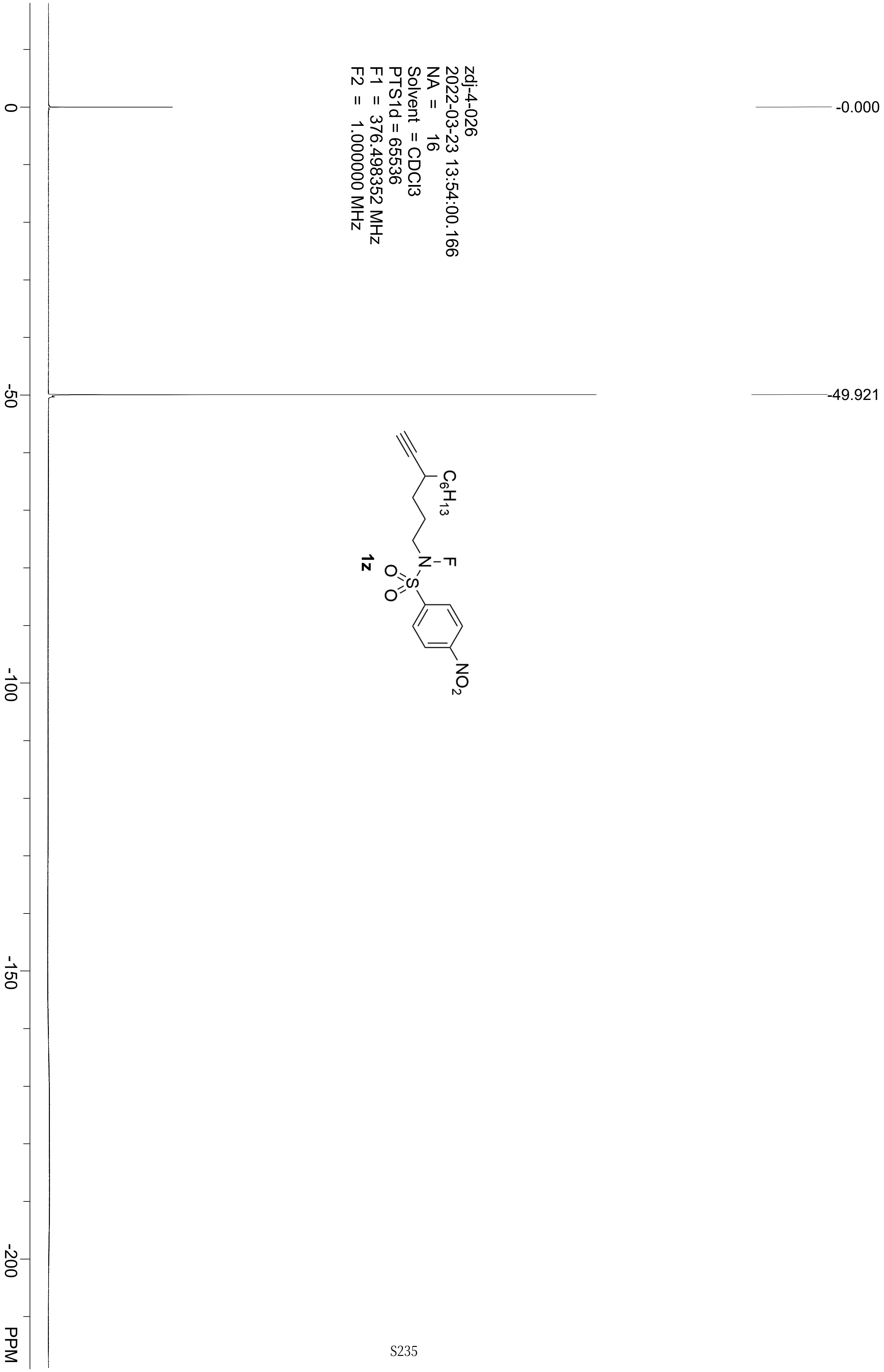

S3z
zdj-4-020
2022-03-07 16:44:14.656
NA = 16
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C6H13
H
N
S
O
O
NO2
8.392
8.363
8.084
8.056
7.271
4.835
3.093
3.071
3.049
3.027
2.264
2.029
2.022
1.671
1.648
1.594
1.468
1.452
1.433
1.418
1.398
1.382
1.372
1.354
1.264
0.880
0.857
0.000
2.00
2.02
0.99
2.00
1.00
0.98
14.96
3.12
10
8
6
4
2
0 PPM

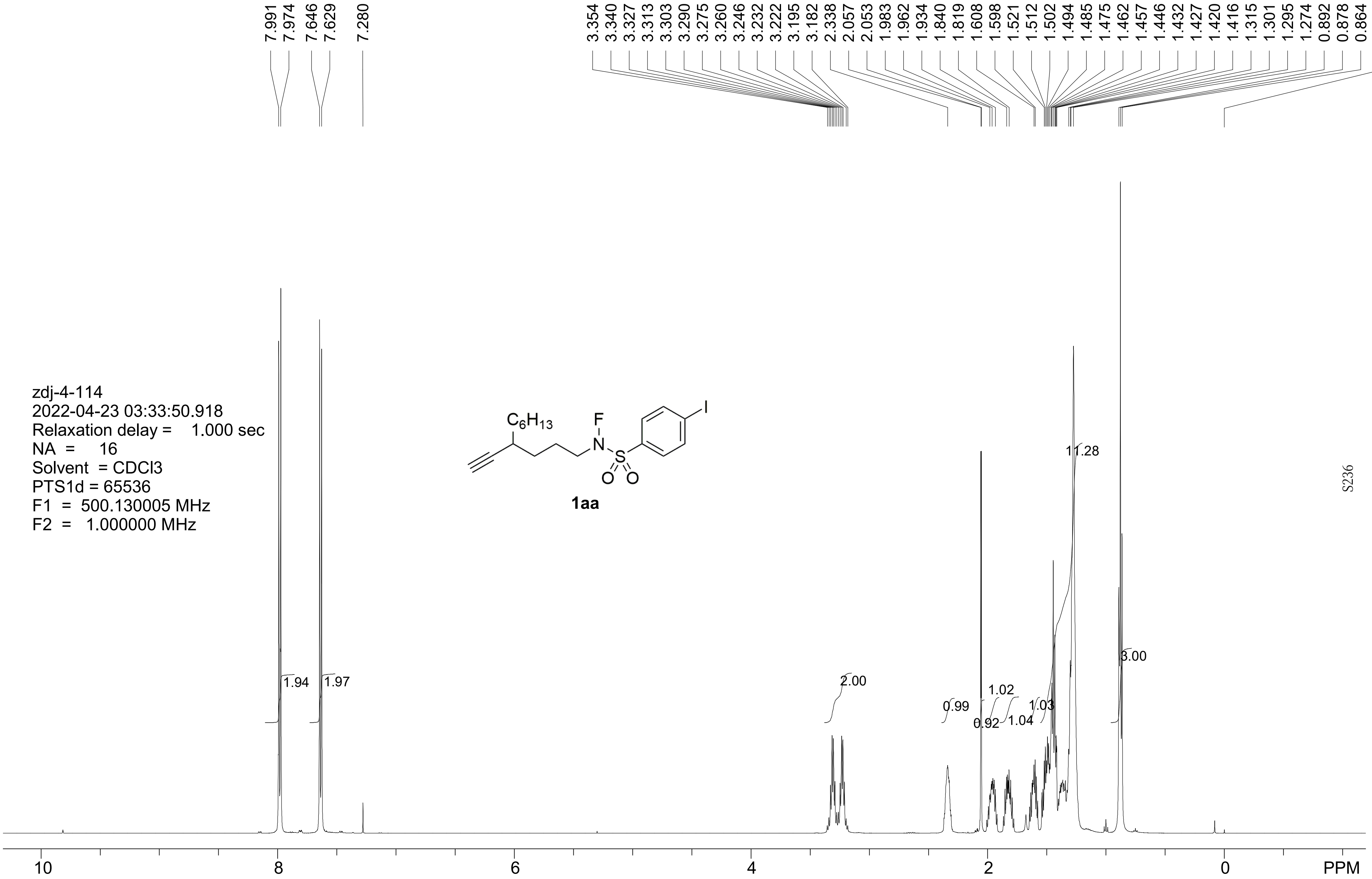

zdj-4-026
2022-03-10 18:23:57.163
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
C6H13
F
N
S
O
O
NO2
1z
10
8
6
4
2
0
PPM
1.93
1.93
2.00
0.98
0.88
1.02
1.04
1.21
1.61
3.07
8.473
8.455
8.176
8.159
7.271
3.435
3.421
3.407
3.394
3.384
3.371
3.356
3.341
3.327
3.313
3.304
3.291
3.277
3.263
2.348
2.063
2.058
1.985
1.857
1.616
1.595
1.534
1.524
1.488
1.472
1.456
1.454
1.447
1.441
1.430
1.320
1.306
1.279
0.896
0.883
0.869
0.000



zdj-4-026
2022-03-10 18:45:39.577
NA =   500
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 =   1.000000 MHz

1z

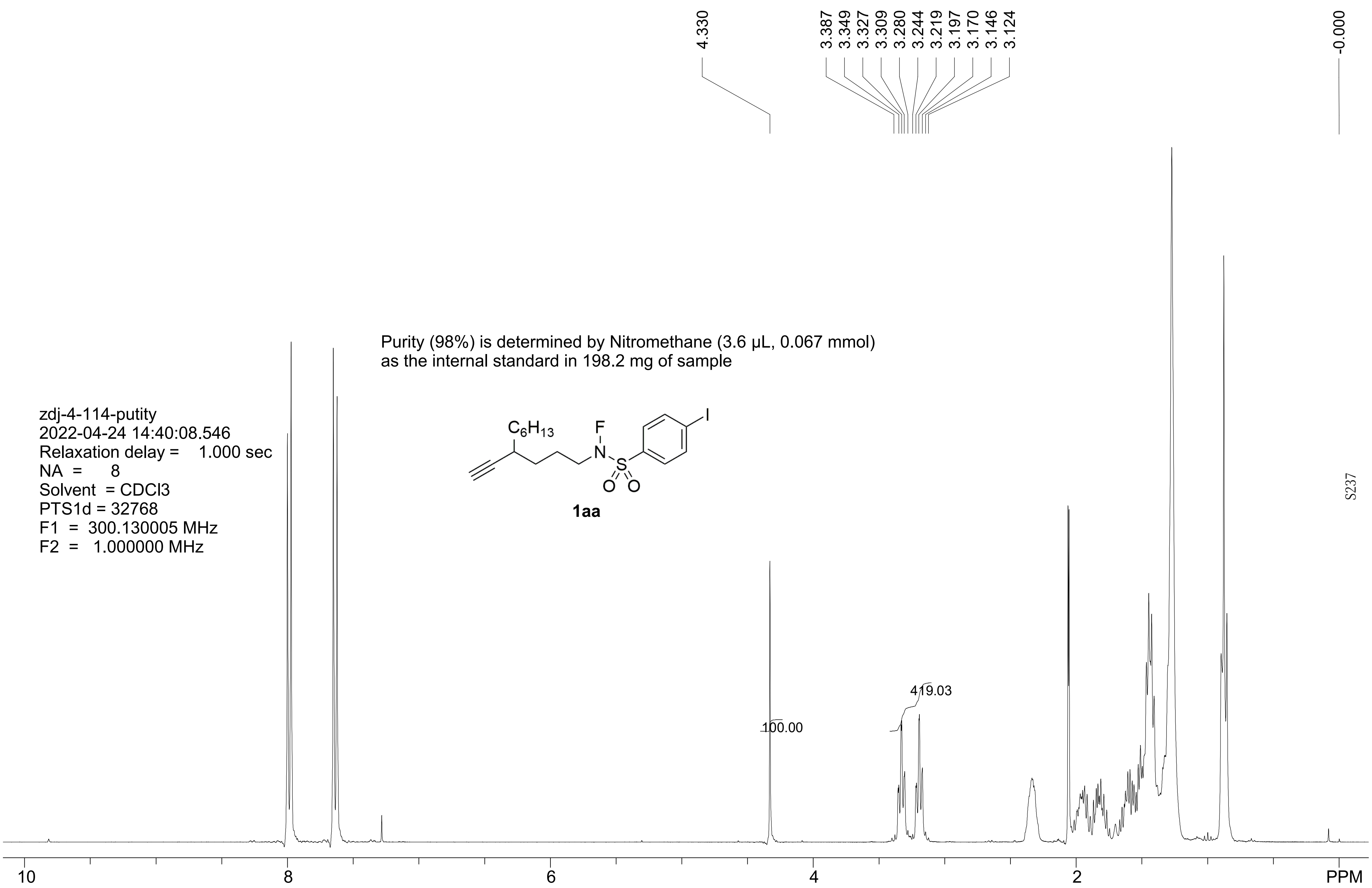

zdj-4-026
2022-03-23 13:54:00.166
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz
-0.000
-49.921
0
-50
-100
-150
-200
PPM
C6H13
F
N
S
O
O
NO2
1z


zdj-4-114
2022-04-23 03:33:50.918
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
7.991
7.974
7.646
7.629
7.280
3.354
3.340
3.327
3.313
3.303
3.290
3.275
3.260
3.246
3.232
3.222
3.195
3.182
2.338
2.057
2.053
1.983
1.962
1.934
1.840
1.819
1.608
1.598
1.521
1.512
1.502
1.494
1.485
1.475
1.462
1.457
1.446
1.432
1.427
1.420
1.416
1.315
1.301
1.295
1.274
0.892
0.878
0.864
-0.000
1.94
1.97
2.00
0.99
0.92
1.02
1.04
1.03
11.28
3.00
C_6H_{13}
F
N
S
O
O
I
10
8
6
4
2
0
PPM

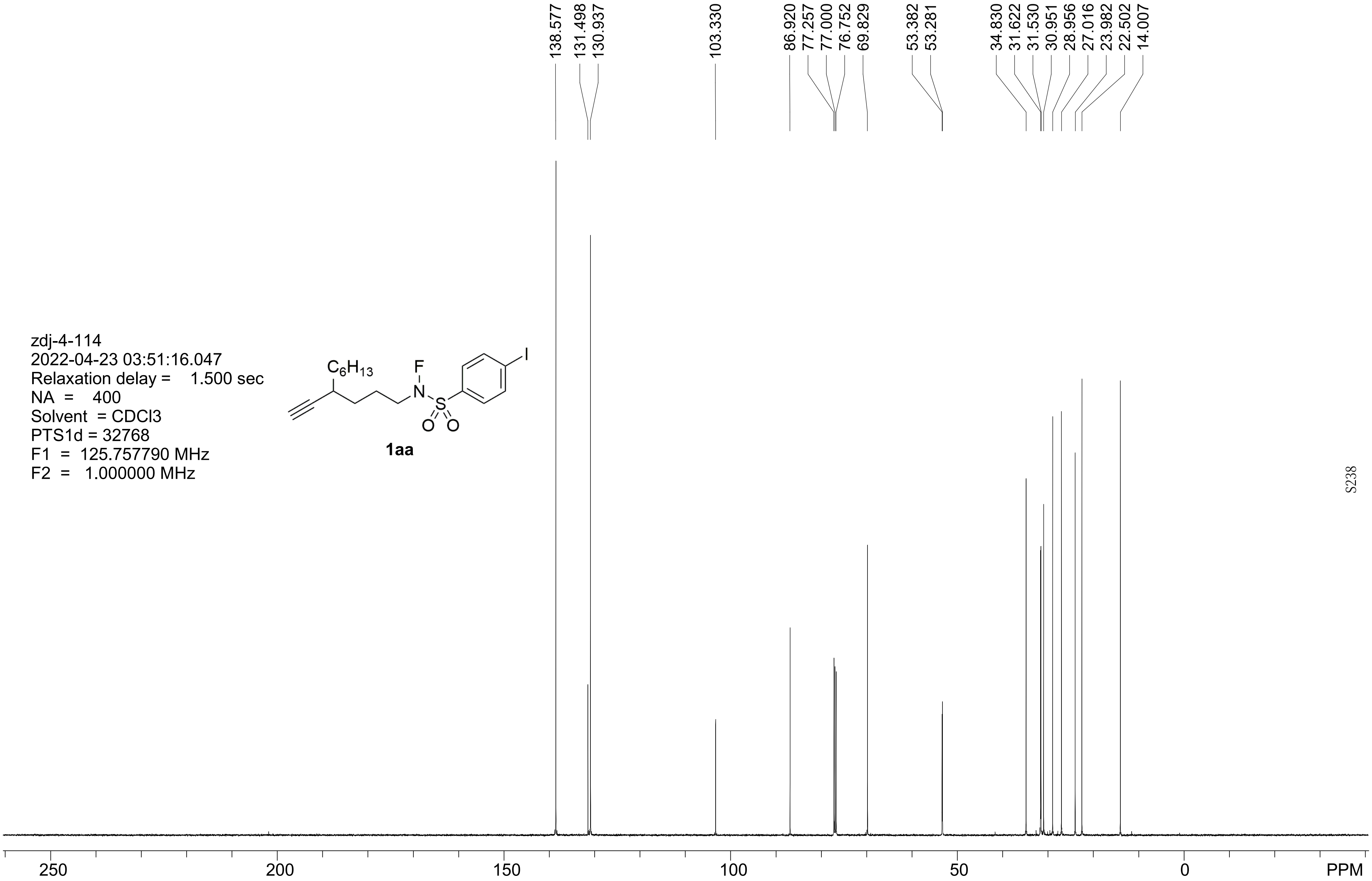
1aa

zdj-4-114-putity
2022-04-24 14:40:08.546
Relaxation delay = 1.000 sec
NA = 8
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

Purity (98%) is determined by Nitromethane (3.6 μL, 0.067 mmol) as the internal standard in 198.2 mg of sample

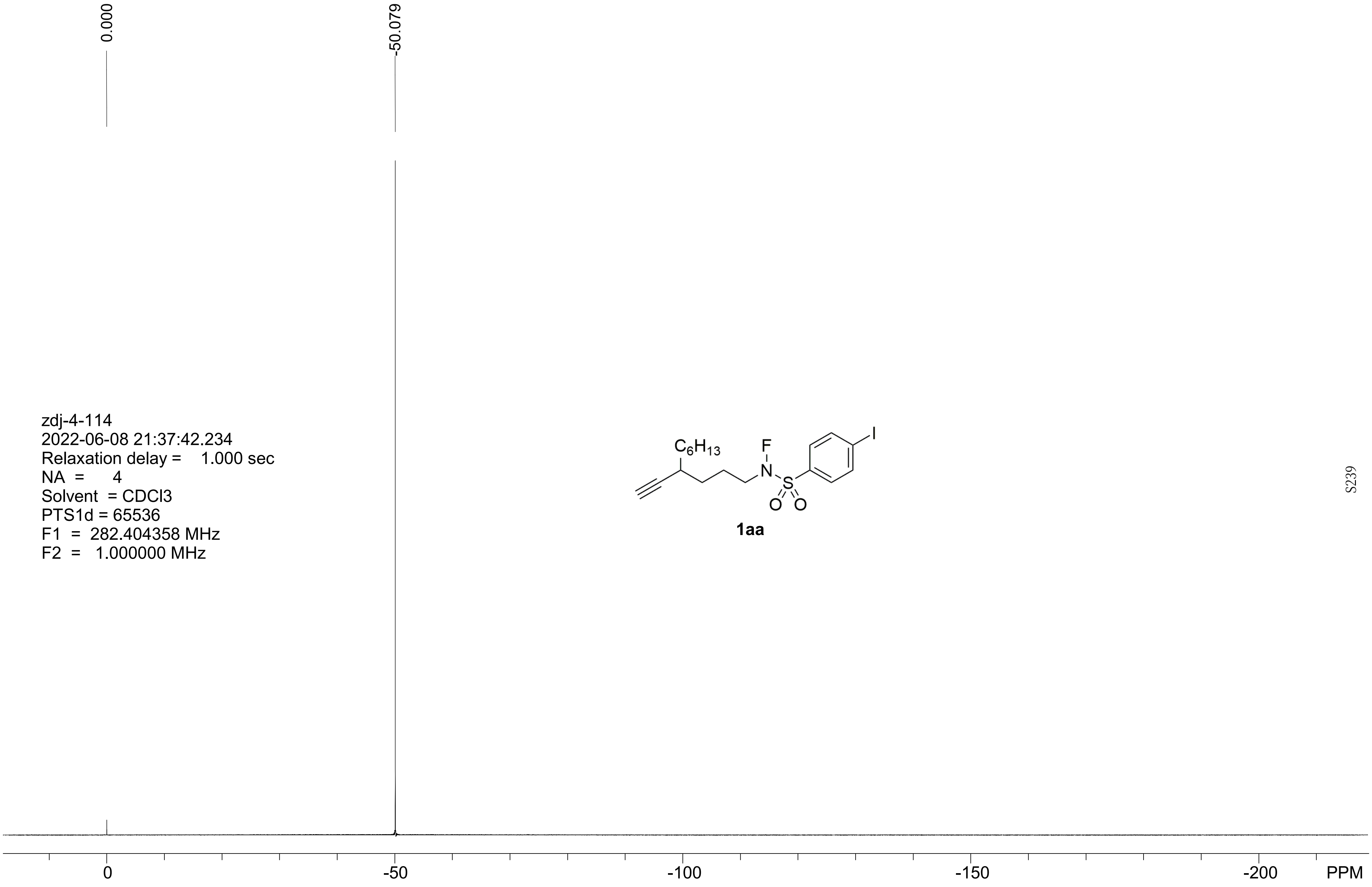


1aa



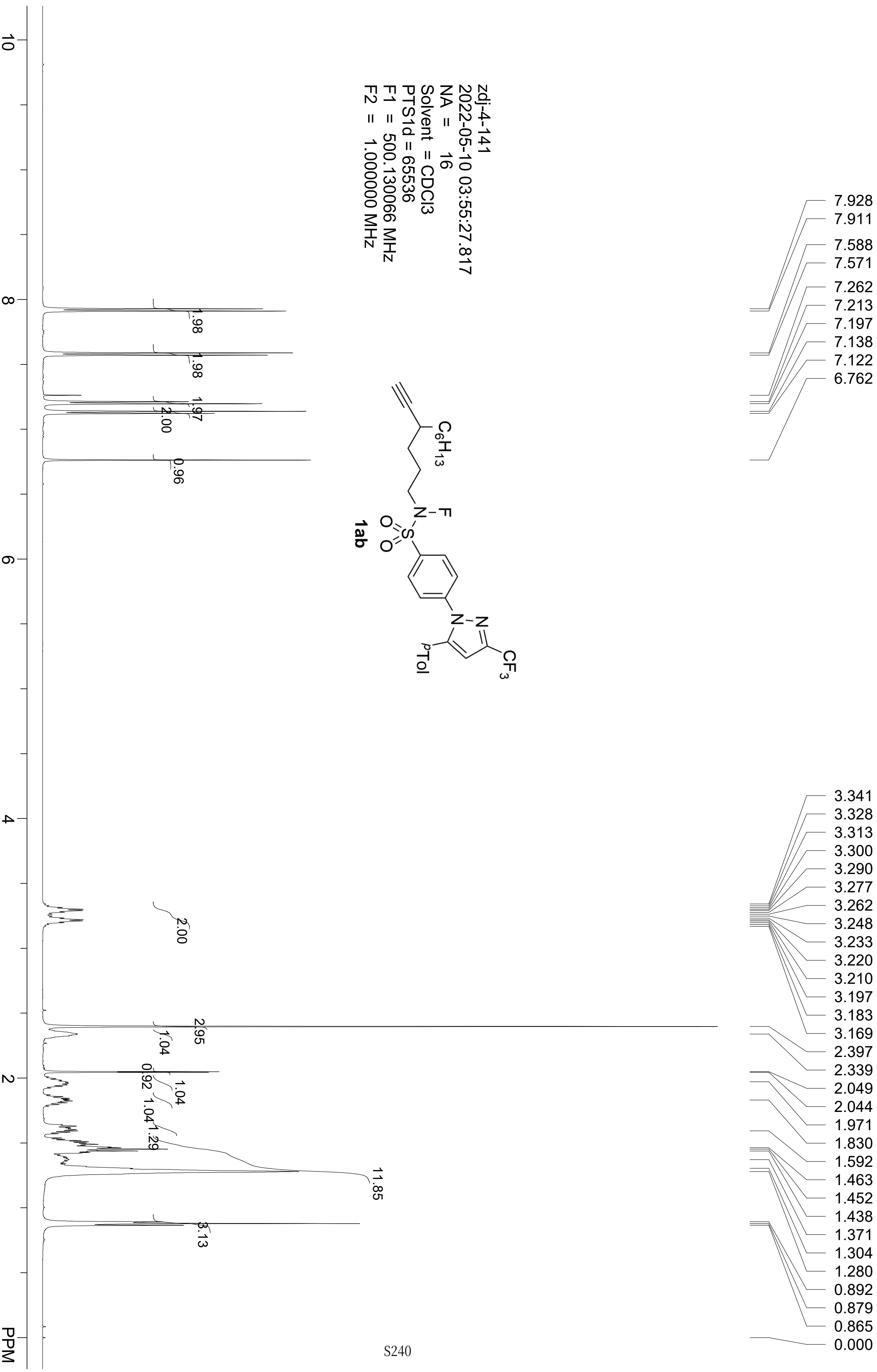
zdj-4-114
2022-04-23 03:51:16.047
Relaxation delay = 1.500 sec
NA = 400
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz

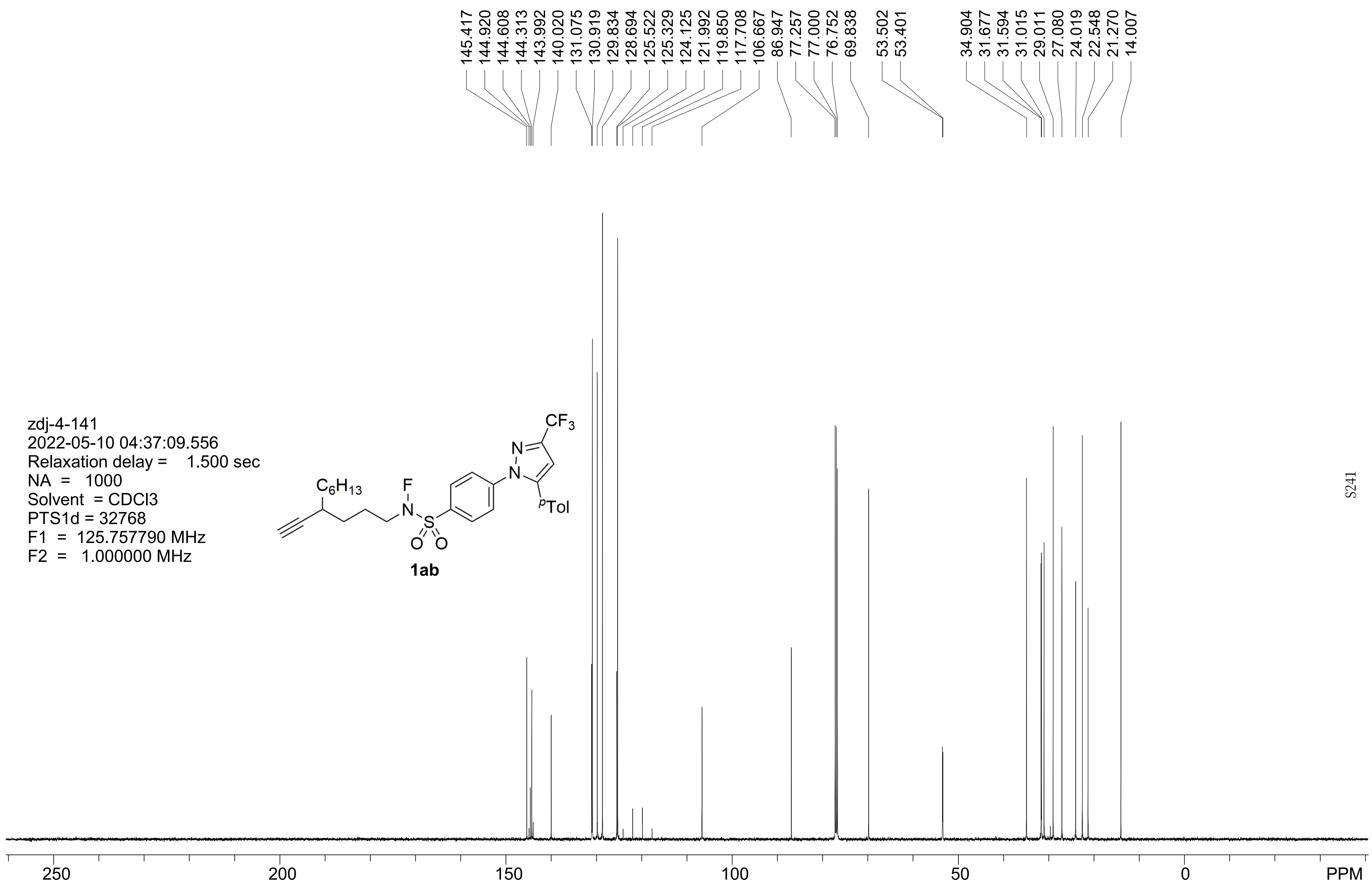
1aa

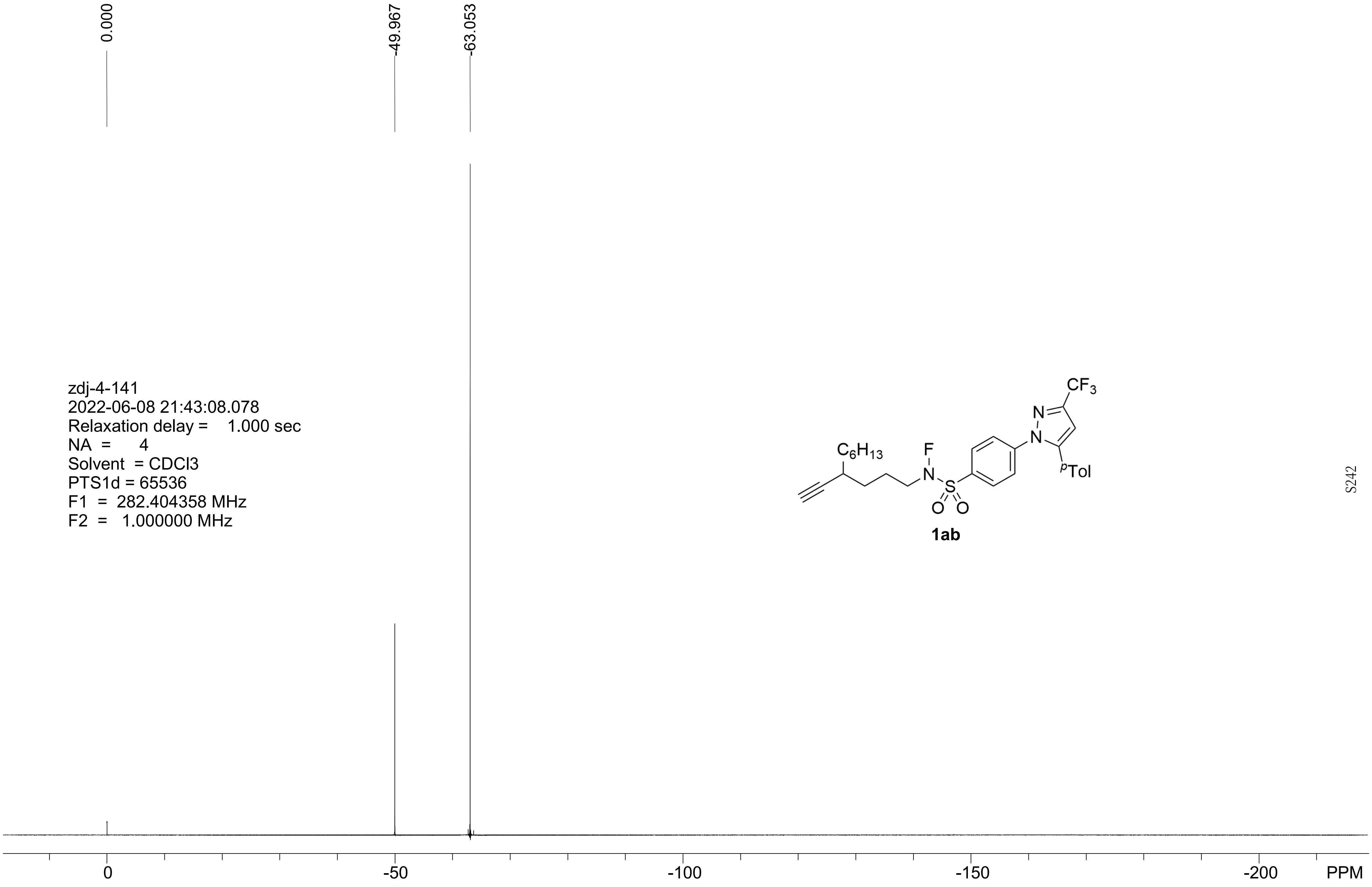


zdj-4-114
2022-06-08 21:37:42.234
Relaxation delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz

1aa

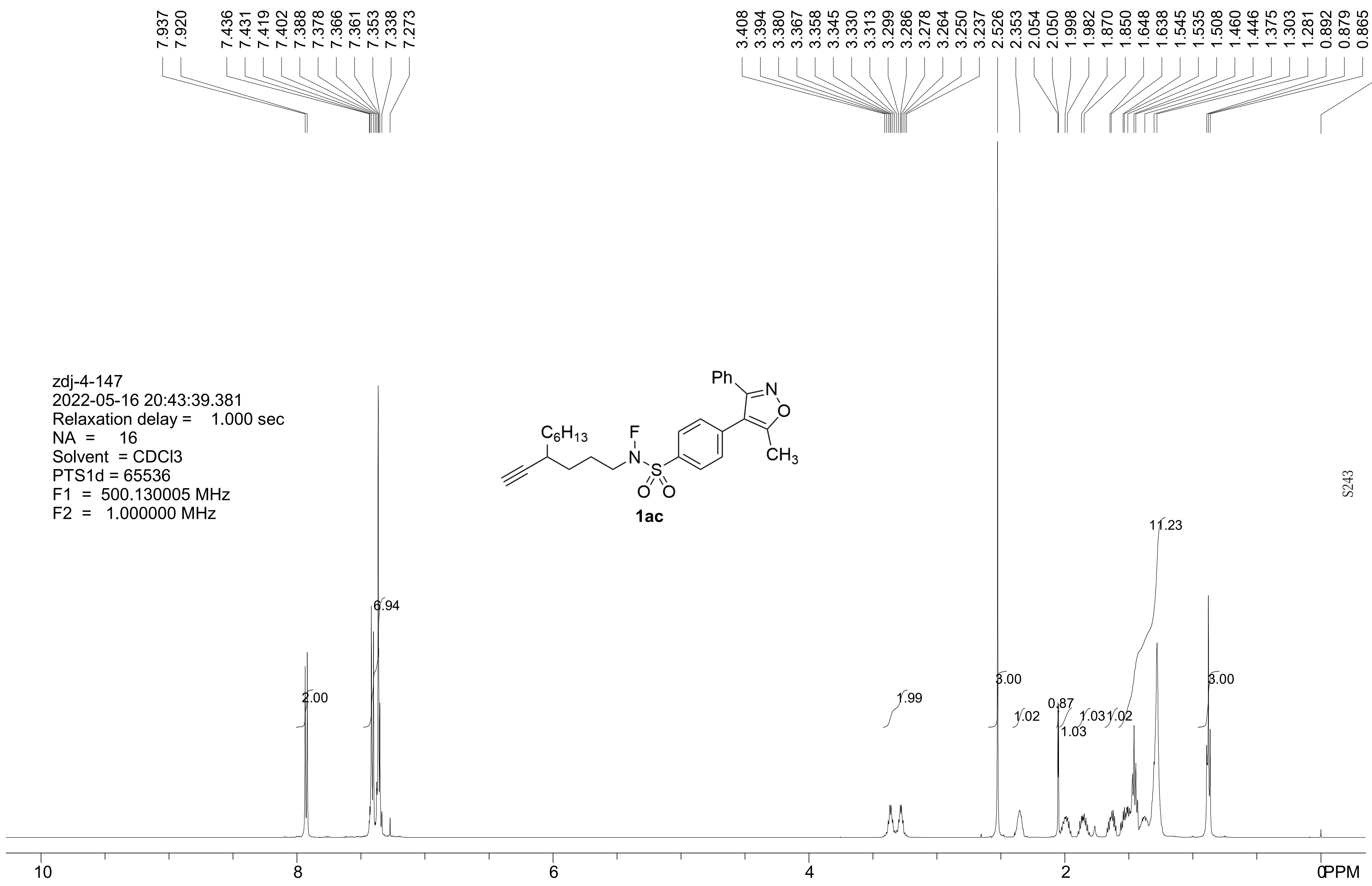

zdj-4-141
2022-05-10 03:55:27.817
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130066 MHz
F2 = 1.000000 MHz
1ab
N
F
S
O
O
N
N
CF3
pTol
C6H13
7.928
7.911
7.588
7.571
7.262
7.213
7.197
7.138
7.122
6.762
3.341
3.328
3.313
3.300
3.290
3.277
3.262
3.248
3.233
3.220
3.210
3.197
3.183
3.169
2.397
2.339
2.049
2.044
1.971
1.830
1.592
1.463
1.452
1.438
1.371
1.304
1.280
0.892
0.879
0.865
0.000
1.98
1.98
1.97
2.00
0.96
2.00
2.95
1.04
0.92
1.04
1.04
1.29
11.85
3.13
10
8
6
4
2
PPM

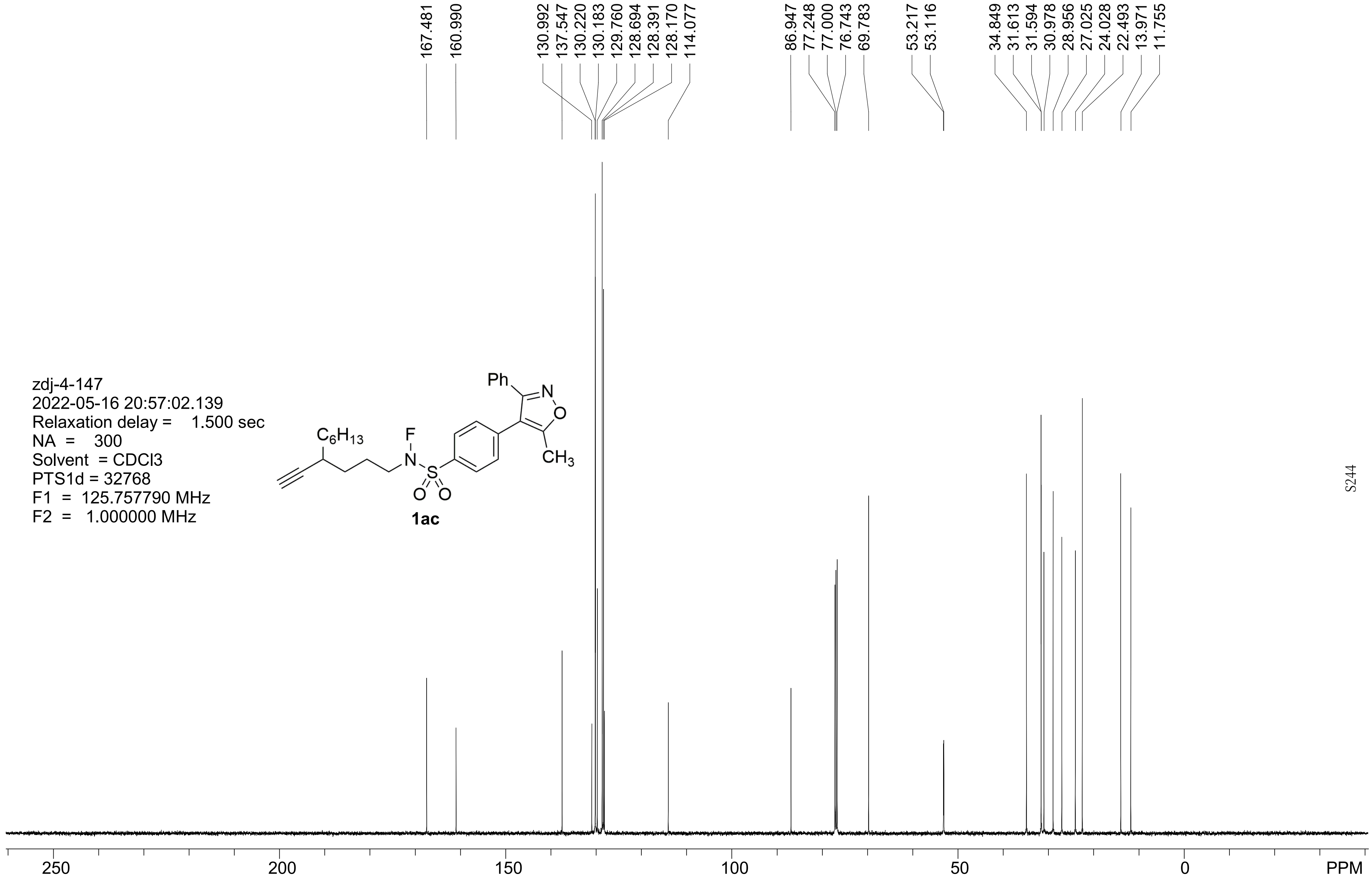

145.417
144.920
144.608
144.313
143.992
140.020
131.075
130.919
129.834
128.694
125.522
125.329
124.125
121.992
119.850
117.708
106.667
86.947
77.257
77.000
76.752
69.838
53.502
53.401
34.904
31.677
31.594
31.015
29.011
27.080
24.019
22.548
21.270
14.007
zdj-4-141
2022-05-10 04:37:09.556
Relaxation delay =   1.500 sec
NA =   1000
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 =   1.000000 MHz
C6H13
F
N
S
O
O
N
N
CF3
pTol
1ab
250
200
150
100
50
0
PPM

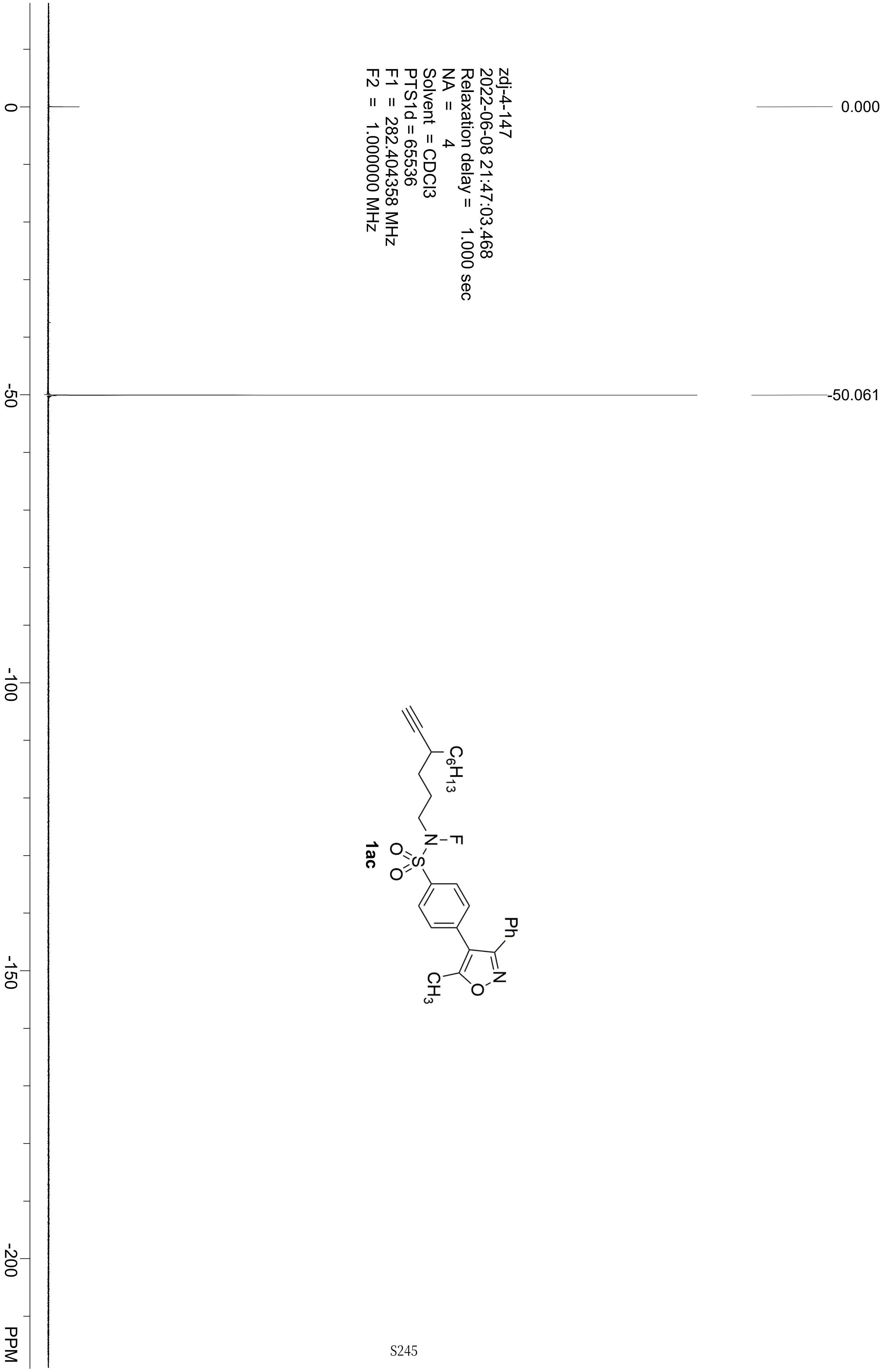


1ab

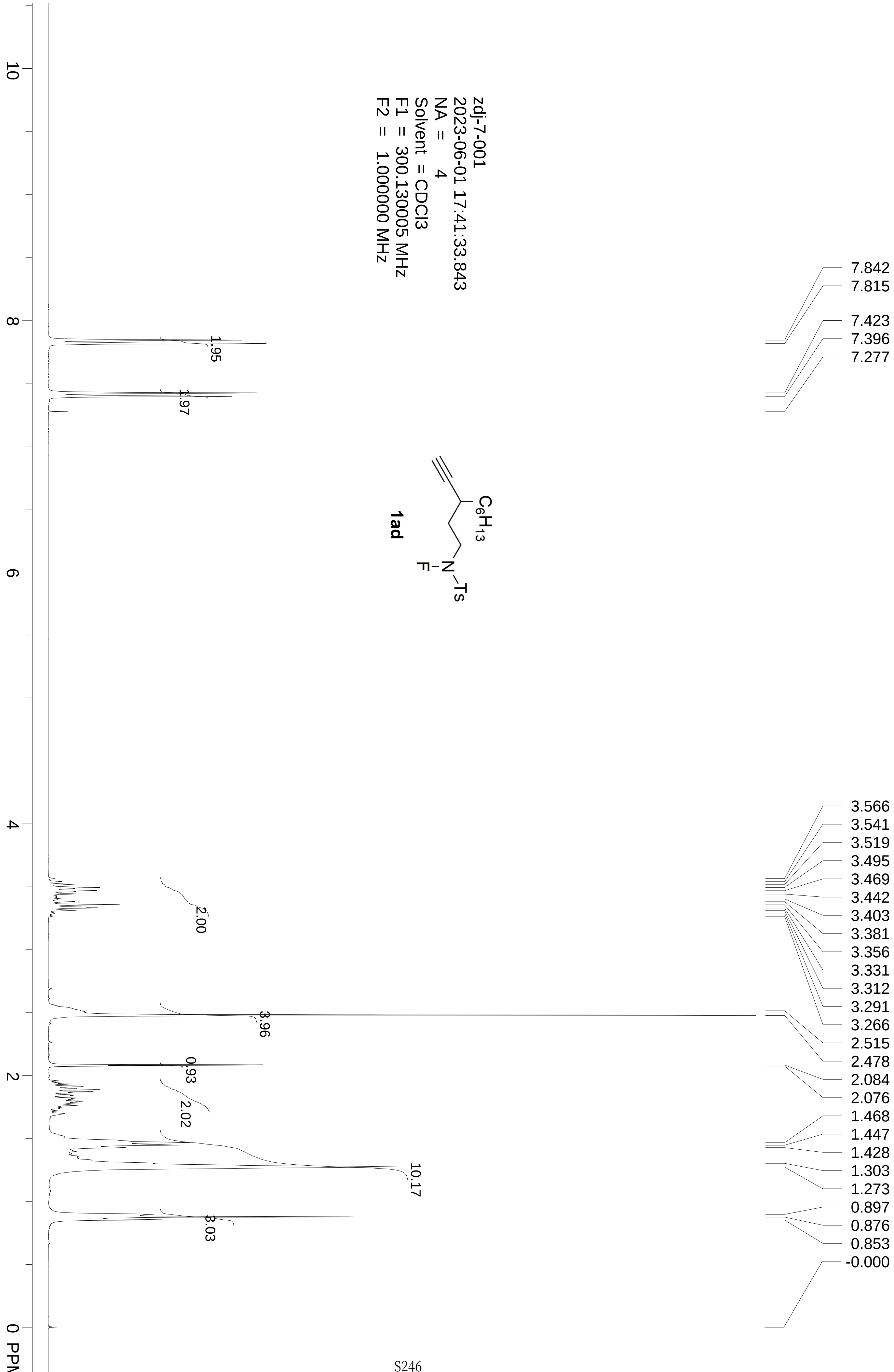
zdj-4-141
2022-06-08 21:43:08.078
Relaxation delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz

7.937
7.920
7.436
7.431
7.419
7.402
7.388
7.378
7.366
7.361
7.353
7.338
7.273
3.408
3.394
3.380
3.367
3.358
3.345
3.330
3.313
3.299
3.286
3.278
3.264
3.250
3.237
2.526
2.353
2.054
2.050
1.998
1.982
1.870
1.850
1.648
1.638
1.545
1.535
1.508
1.460
1.446
1.375
1.303
1.281
0.892
0.879
0.865
-0.000
zdj-4-147
2022-05-16 20:43:39.381
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
Ph
N
O
C6H13
F
N
S
O
O
CH3
1ac
2.00
6.94
1.99
3.00
1.02
0.87
1.03
1.03
1.02
11.23
3.00
10
8
6
4
2
0
PPM

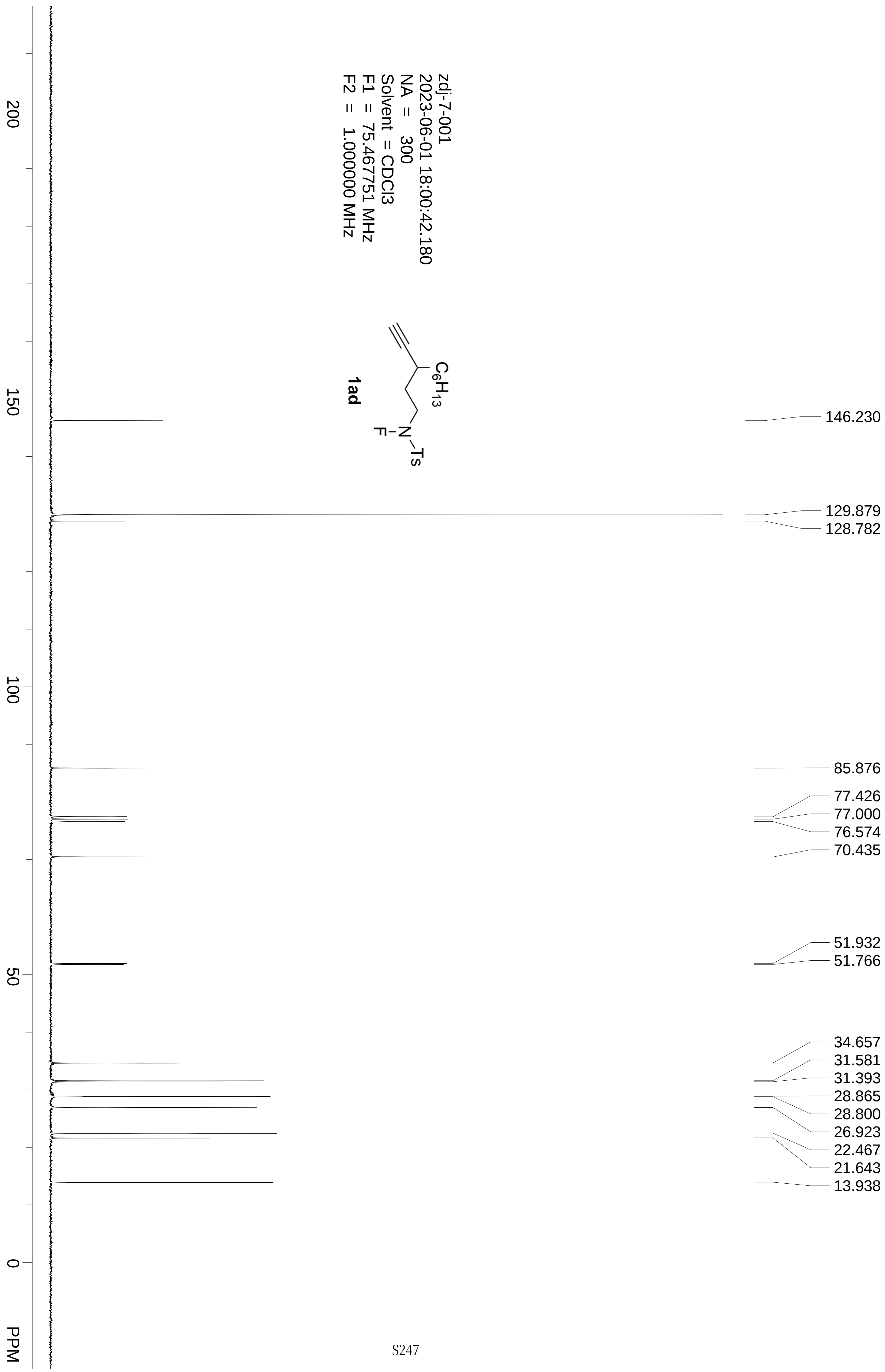

zdj-4-147
2022-05-16 20:57:02.139
Relaxation delay = 1.500 sec
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
1ac
Ph
N
O
CH3
C6H13
F
N
S
O
O
167.481
160.990
130.992
137.547
130.220
130.183
129.760
128.694
128.391
128.170
114.077
86.947
77.248
77.000
76.743
69.783
53.217
53.116
34.849
31.613
31.594
30.978
28.956
27.025
24.028
22.493
13.971
11.755
250
200
150
100
50
0
PPM

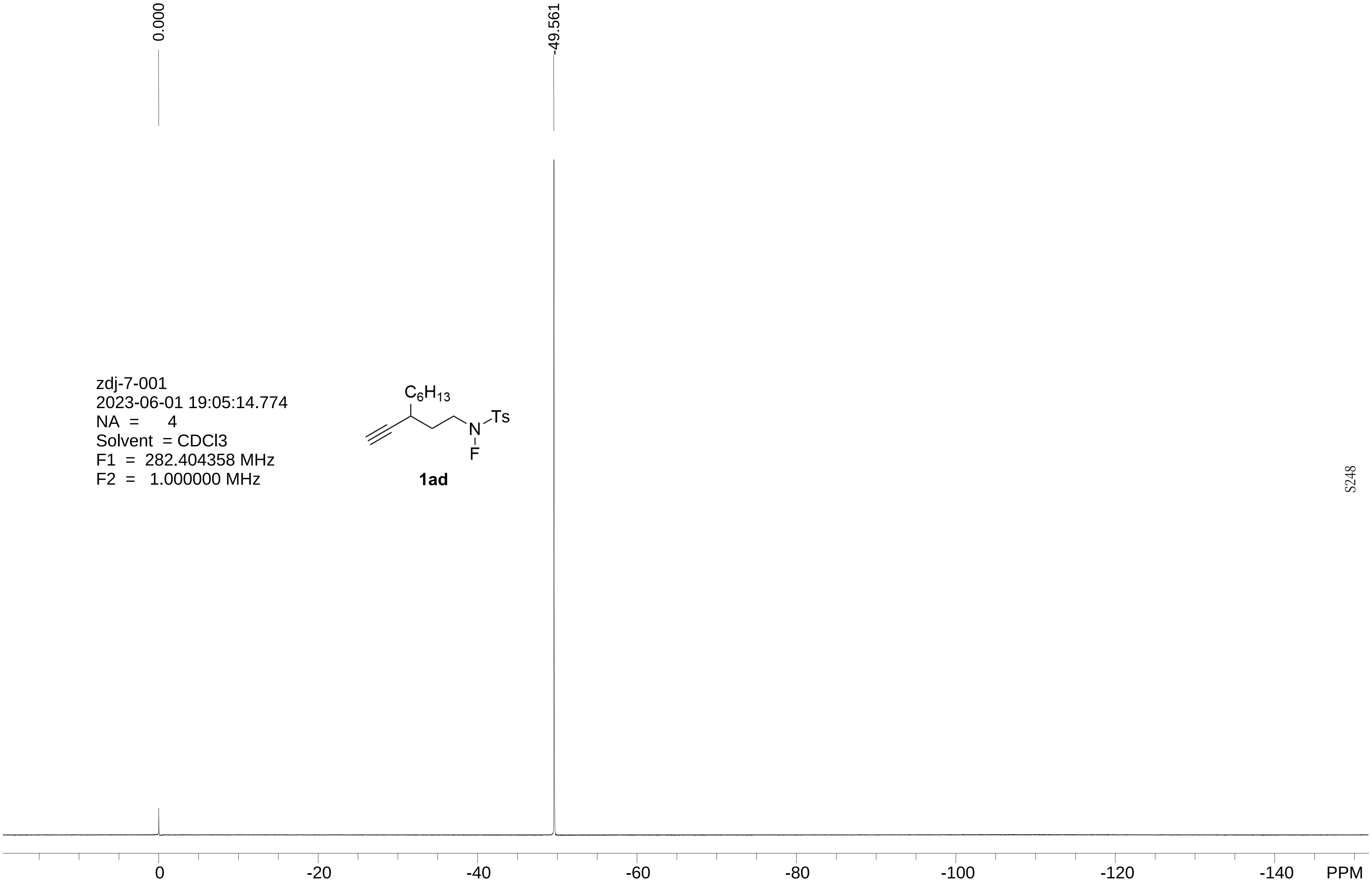

zdj-4-147
2022-06-08 21:47:03.468
Relaxation delay = 1.000 sec
NA = 4
Solvent = CDCl3
PTS1d = 65536
F1 = 282.404358 MHz
F2 = 1.000000 MHz
0.000
-50.061
0
-50
-100
-150
-200
PPM
C6H13
F
N
S
O
O
Ph
N
O
CH3

1ac

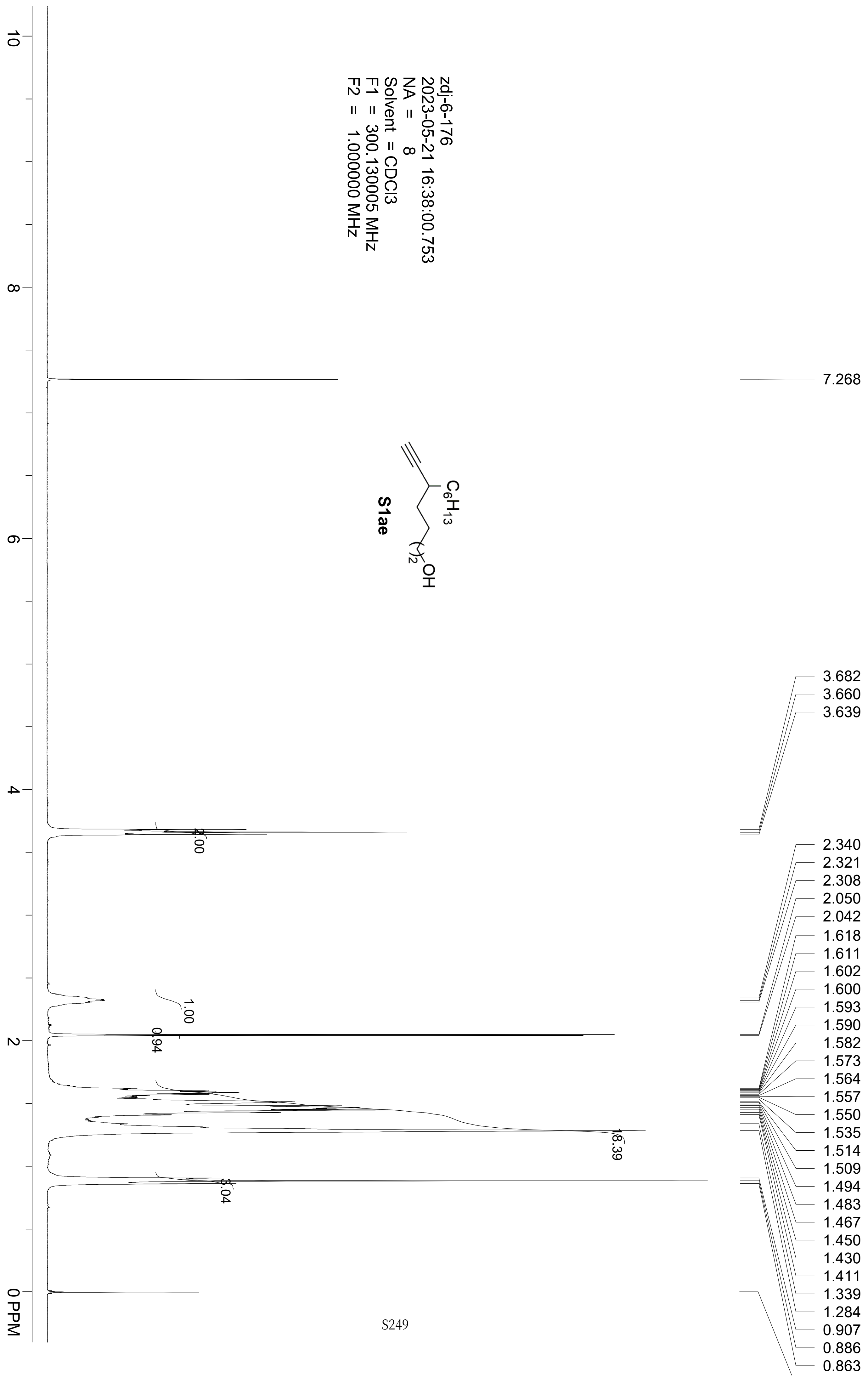

zdj-7-001
2023-06-01 17:41:33.843
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C_6H_{13}
N
Ts
F
7.842
7.815
7.423
7.396
7.277
3.566
3.541
3.519
3.495
3.469
3.442
3.403
3.381
3.356
3.331
3.312
3.291
3.266
2.515
2.478
2.084
2.076
1.468
1.447
1.428
1.303
1.273
0.897
0.876
0.853
-0.000
1.95
1.97
2.00
3.96
0.93
2.02
10.17
3.03
10
8
6
4
2
0 PPM

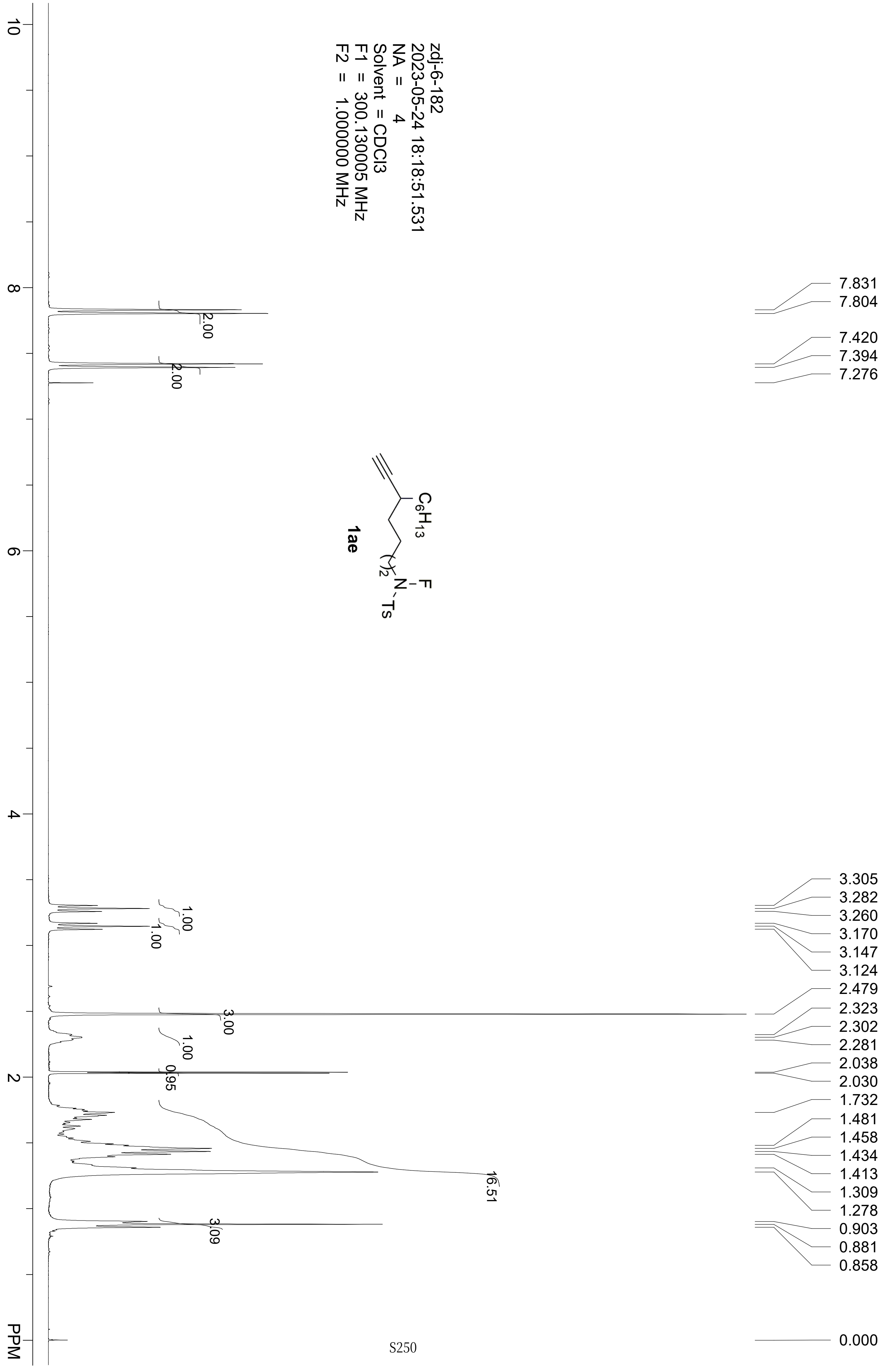
1ad

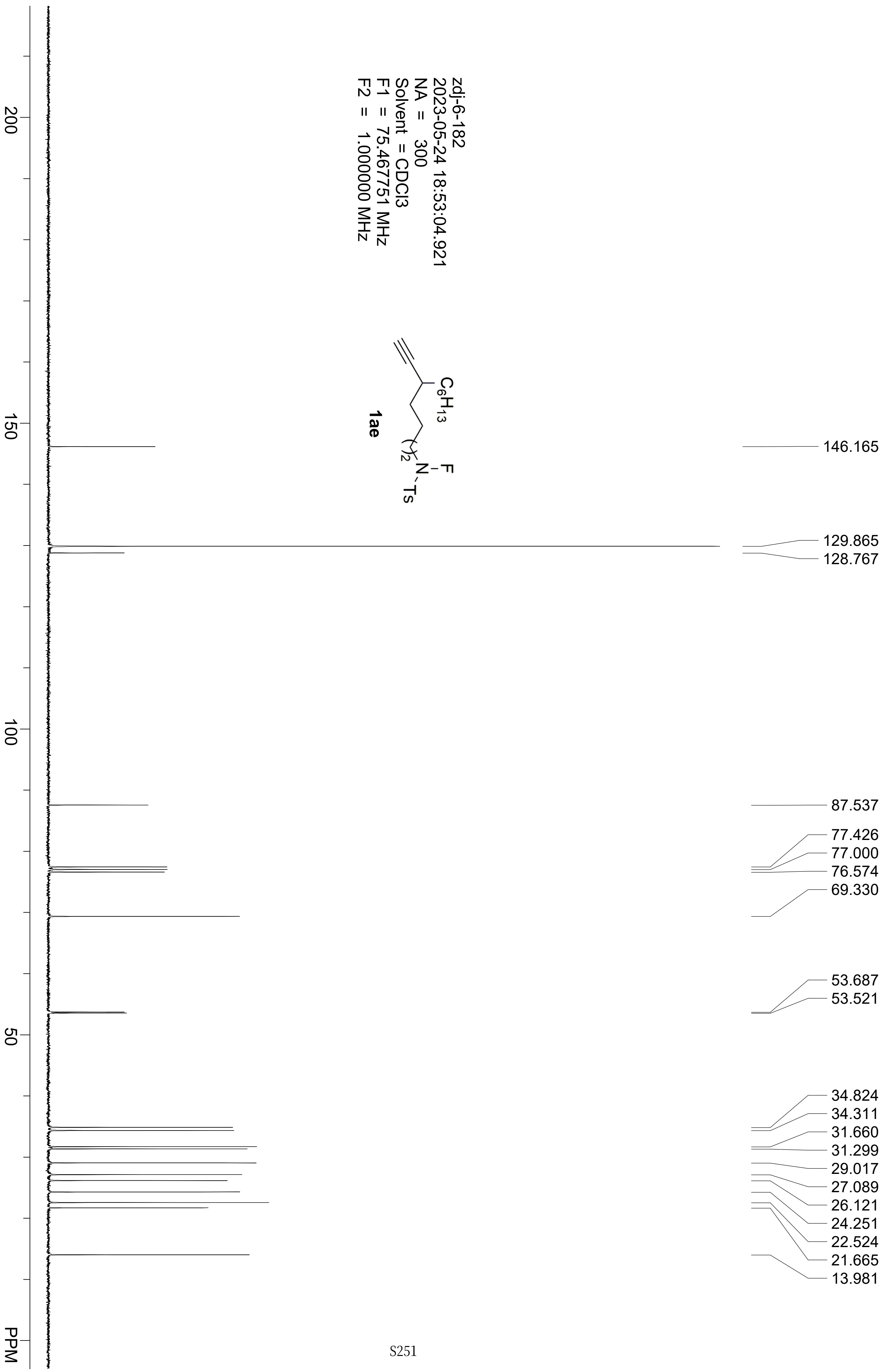

zdj-7-001
2023-06-01 18:00:42.180
NA = 300
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
C6H13
N
Ts
F
1ad
146.230
129.879
128.782
85.876
77.426
77.000
76.574
70.435
51.932
51.766
34.657
31.581
31.393
28.865
28.800
26.923
22.467
21.643
13.938
200
150
100
50
0
PPM

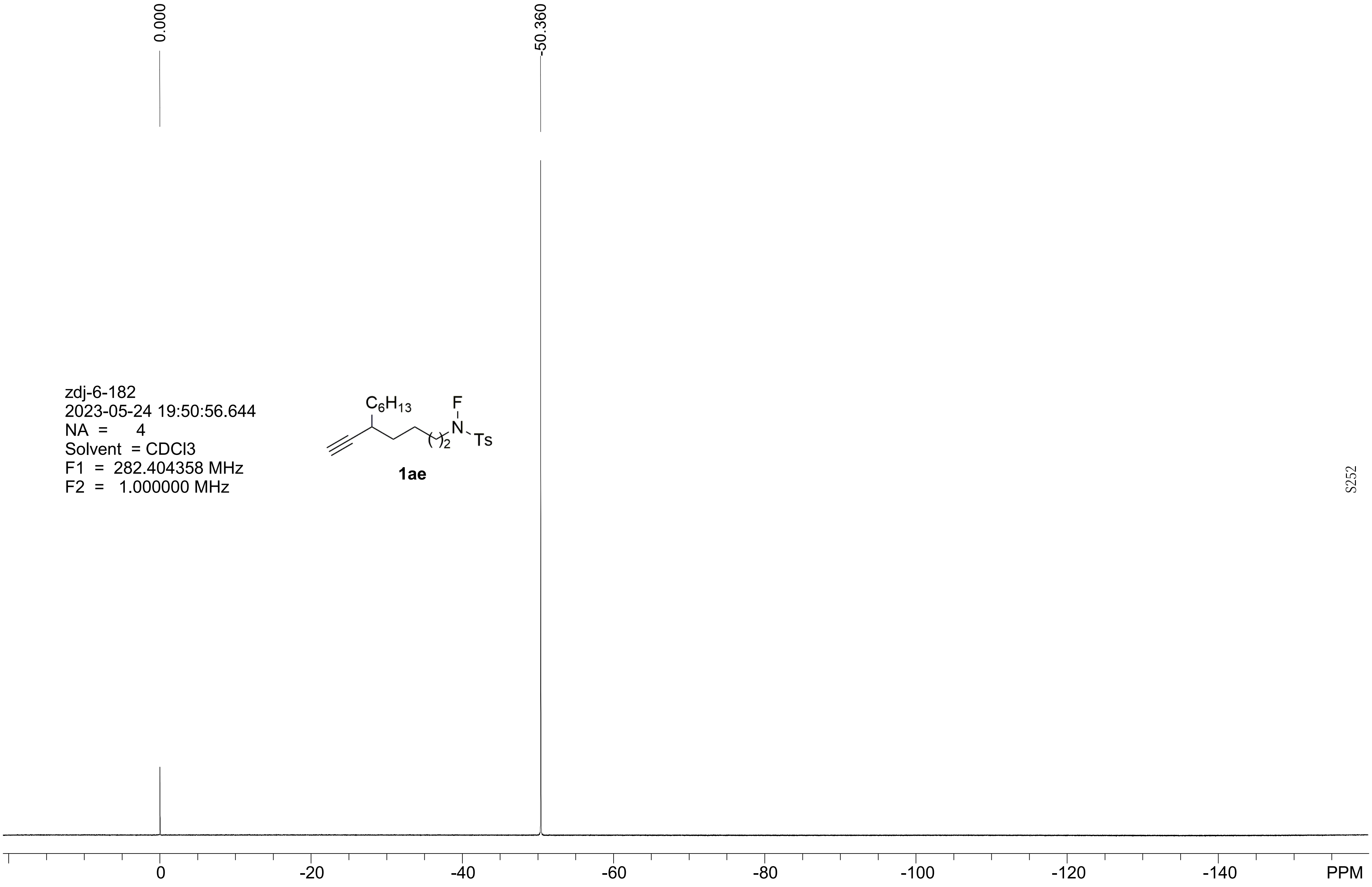

0.000
-49.561
zdj-7-001
2023-06-01 19:05:14.774
NA = 4
Solvent = CDCl3
F1 = 282.404358 MHz
F2 = 1.000000 MHz
C6H13
N
Ts
F
0
-20
-40
-60
-80
-100
-120
-140
PPM

1ad

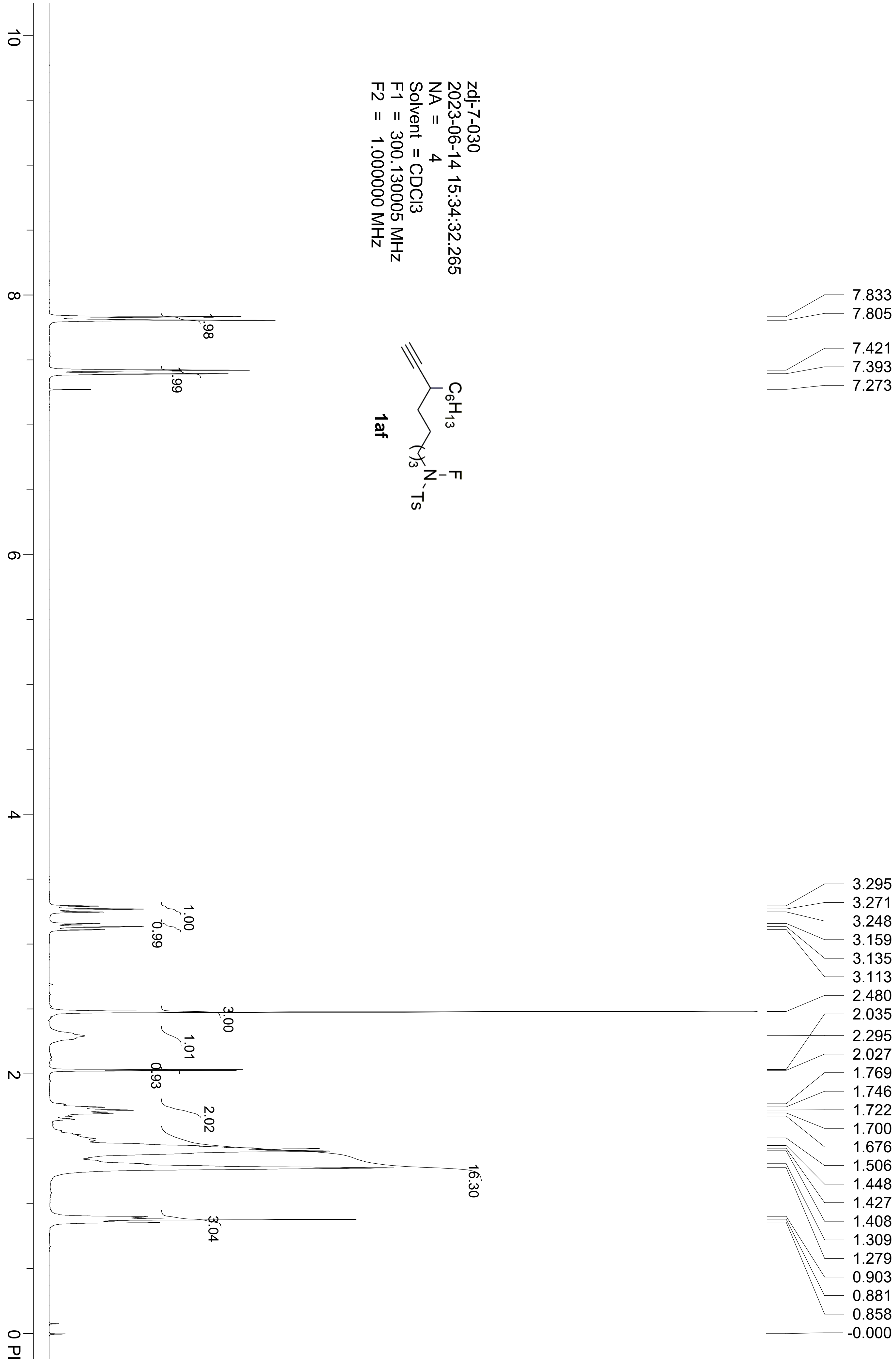

zdj-6-176
2023-05-21 16:38:00.753
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C6H13
OH
2
S1ae
7.268
3.682
3.660
3.639
2.340
2.321
2.308
2.050
2.042
1.618
1.611
1.602
1.600
1.593
1.590
1.582
1.573
1.564
1.557
1.550
1.535
1.514
1.509
1.494
1.483
1.467
1.450
1.430
1.411
1.339
1.284
0.907
0.886
0.863
2.00
1.00
0.94
18.39
3.04
10
8
6
4
2
0 PPM

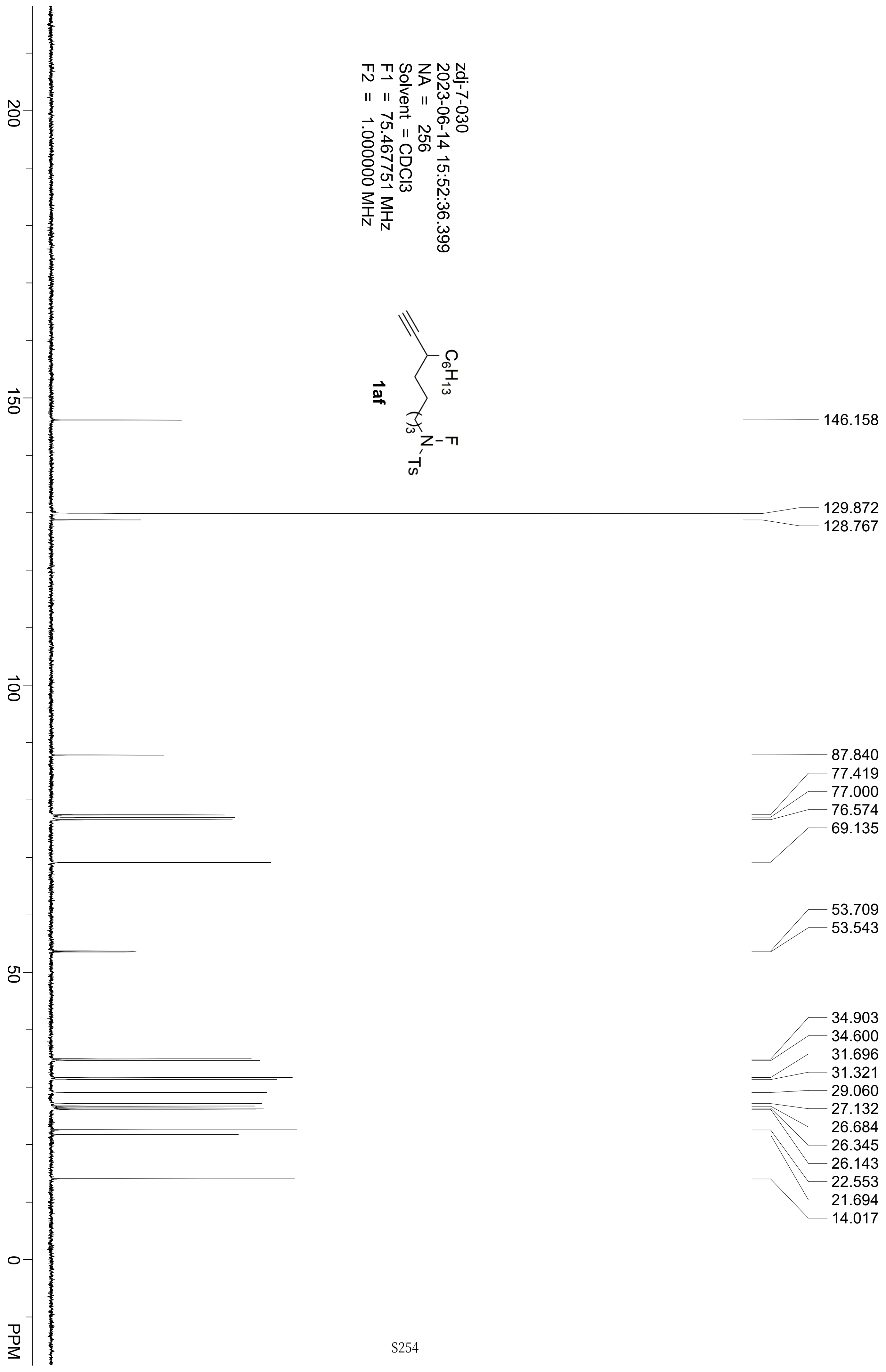

zdj-6-182
2023-05-24 18:18:51.531
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C6H13
F
N
Ts
( )2
1ae
10
8
6
4
2
PPM
2.00
2.00
1.00
1.00
3.00
1.00
0.95
16.51
3.09
7.831
7.804
7.420
7.394
7.276
3.305
3.282
3.260
3.170
3.147
3.124
2.479
2.323
2.302
2.281
2.038
2.030
1.732
1.481
1.458
1.434
1.413
1.309
1.278
0.903
0.881
0.858
0.000

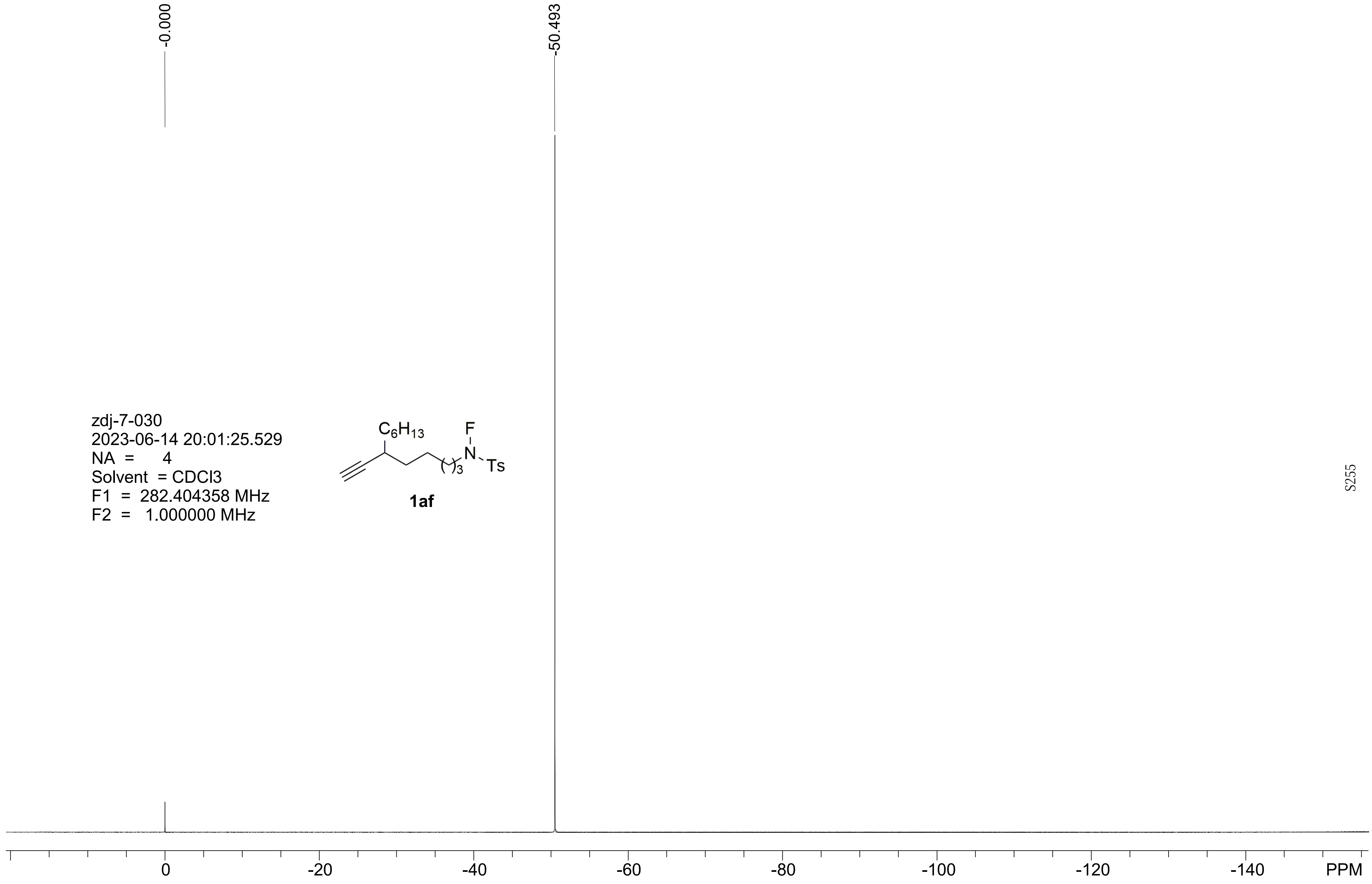

zdj-6-182
2023-05-24 18:53:04.921
NA = 300
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
C_6H_{13}
$(\ )_2$
N
F
Ts
1ae
146.165
129.865
128.767
87.537
77.426
77.000
76.574
69.330
53.687
53.521
34.824
34.311
31.660
31.299
29.017
27.089
26.121
24.251
22.524
21.665
13.981
200
150
100
50
PPM

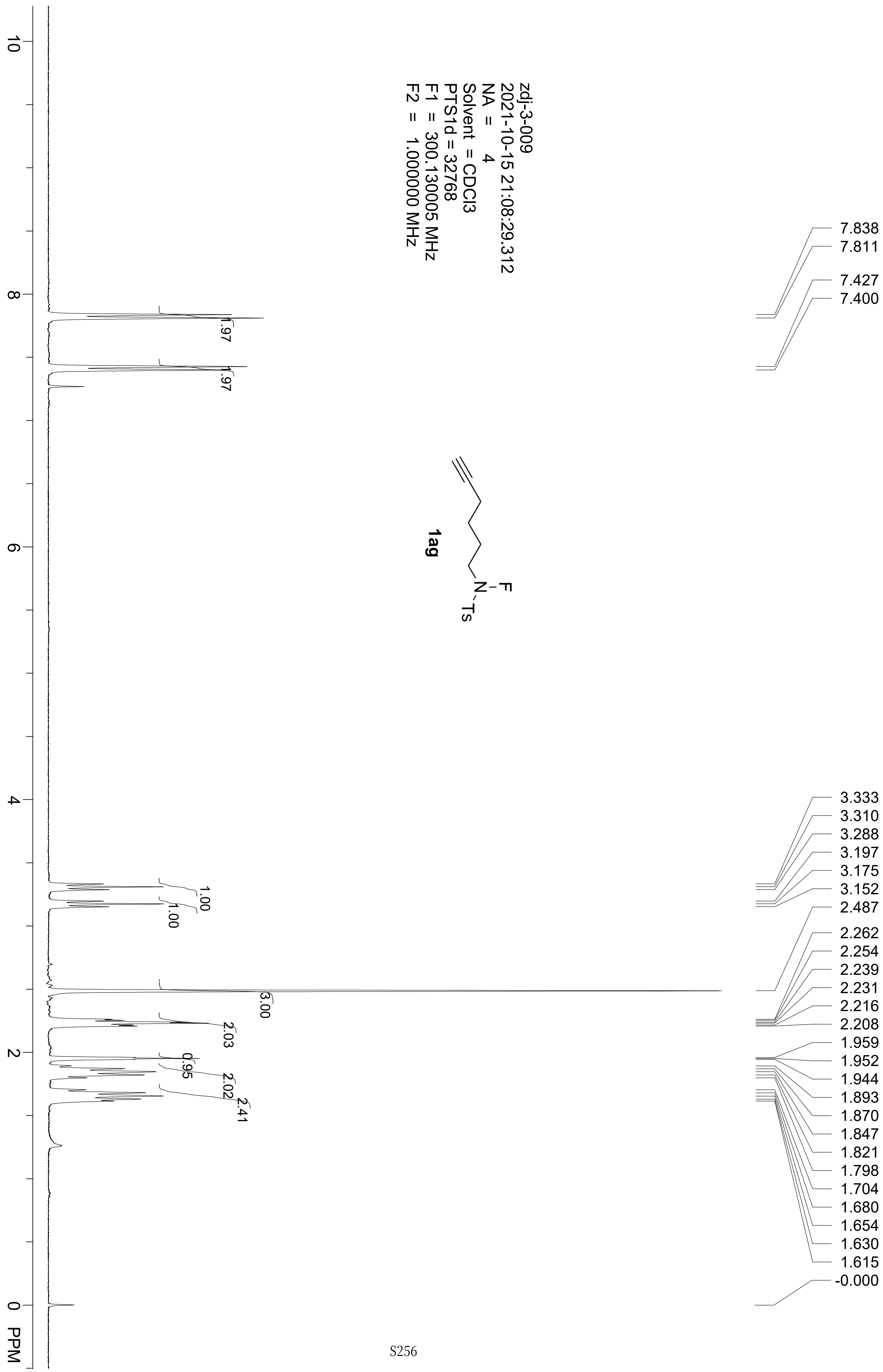

0.000
-50.360
zdj-6-182
2023-05-24 19:50:56.644
NA = 4
Solvent = CDCl3
F1 = 282.404358 MHz
F2 = 1.000000 MHz
C6H13
F
N
Ts
2
0
-20
-40
-60
-80
-100
-120
-140
PPM

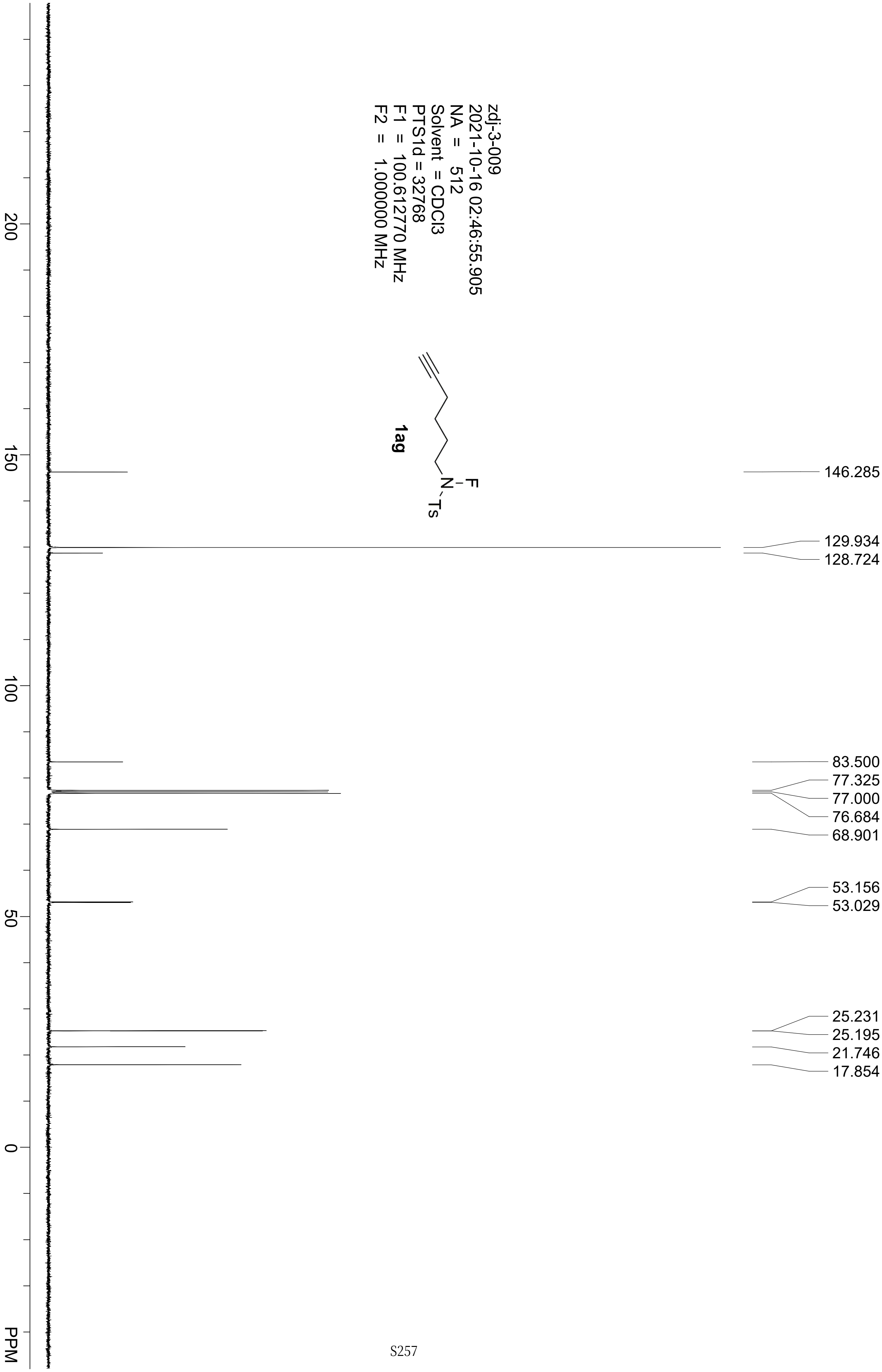
1ae

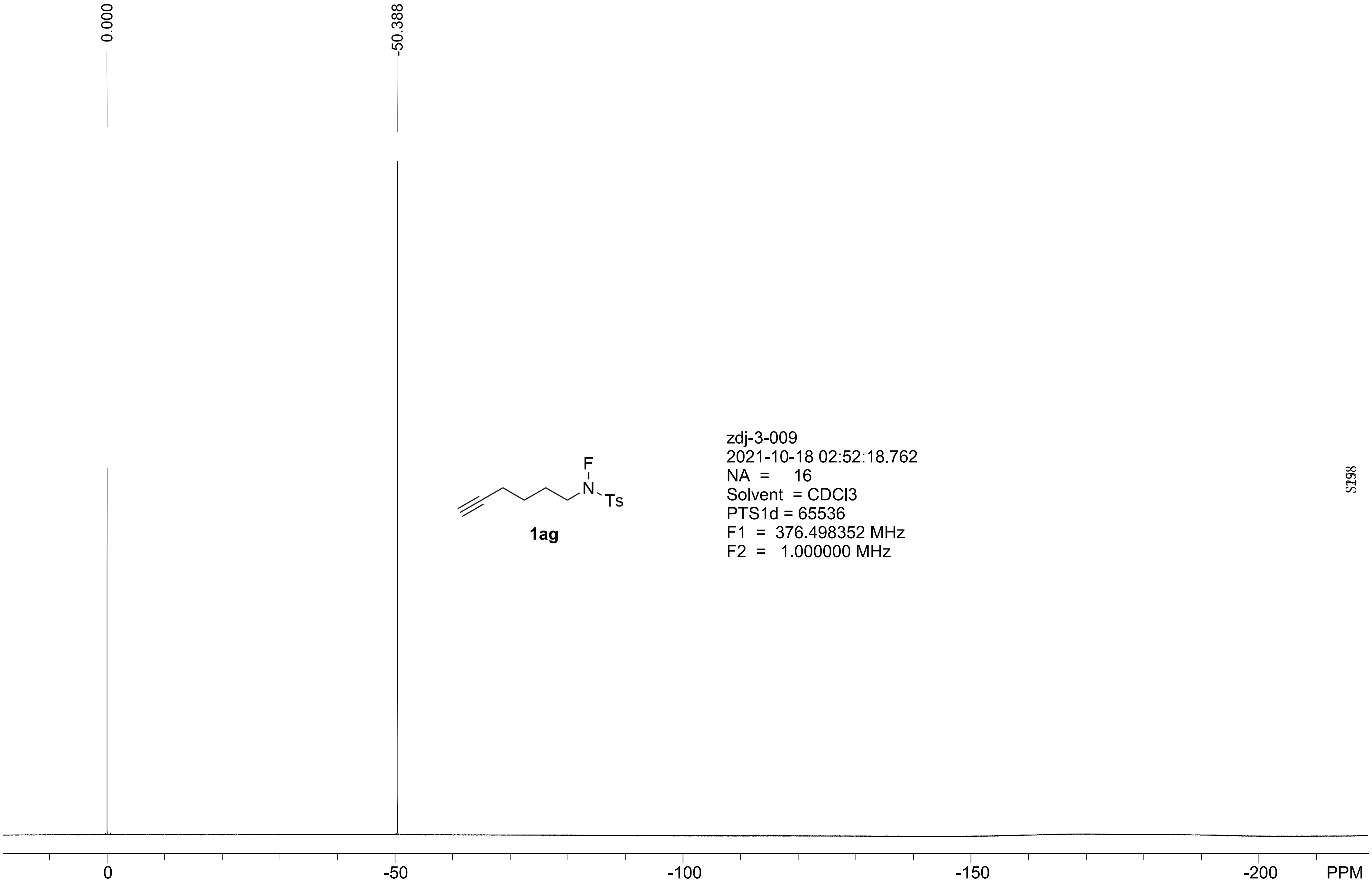

zdj-7-030
2023-06-14 15:34:32.265
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C6H13
F
N
Ts
3
1af
10
8
6
4
2
0 PPM
1.98
1.99
1.00
0.99
3.00
1.01
0.93
2.02
16.30
3.04
7.833
7.805
7.421
7.393
7.273
3.295
3.271
3.248
3.159
3.135
3.113
2.480
2.035
2.295
2.027
1.769
1.746
1.722
1.700
1.676
1.506
1.448
1.427
1.408
1.309
1.279
0.903
0.881
0.858
-0.000

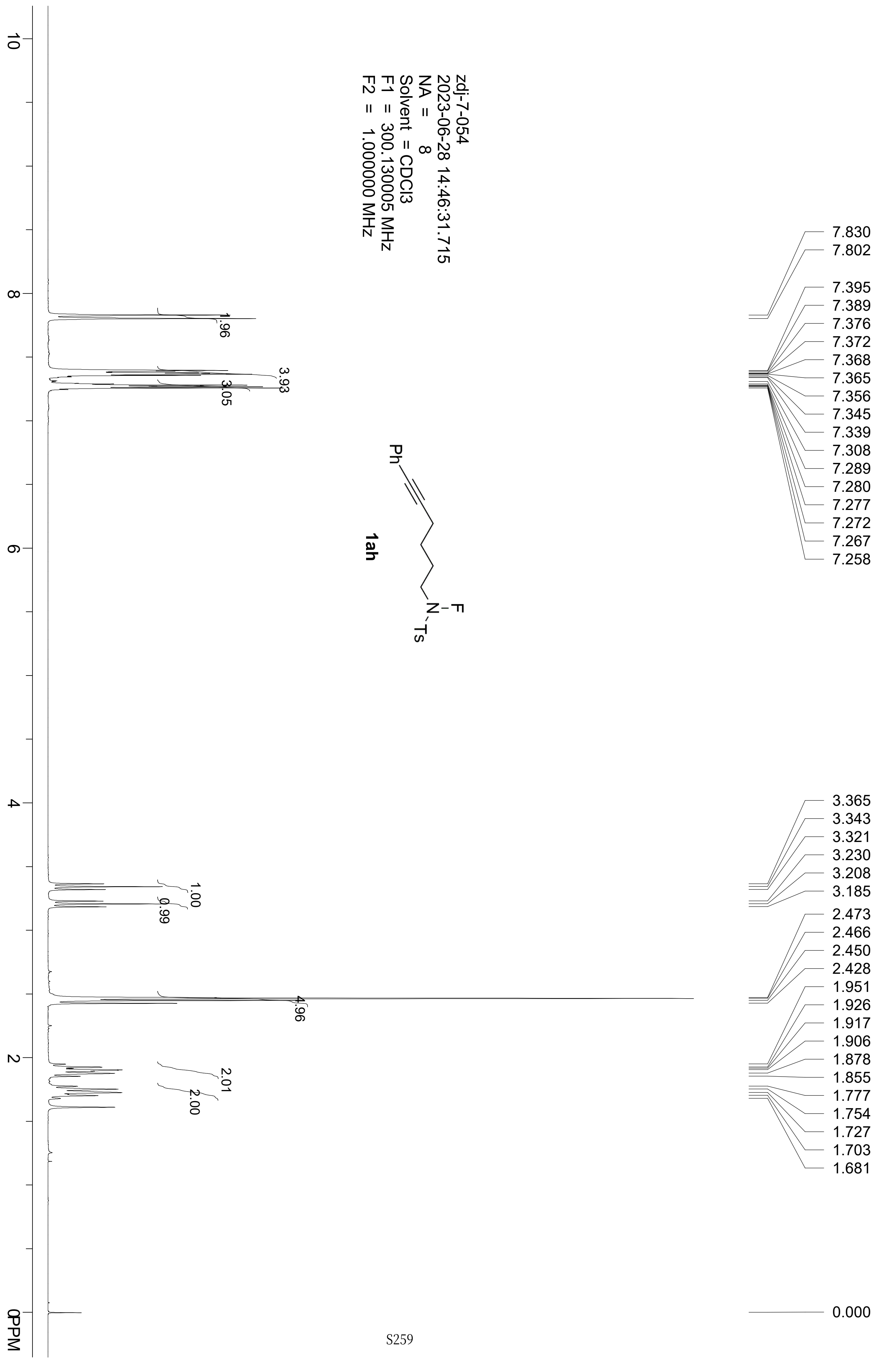

zdj-7-030
2023-06-14 15:52:36.399
NA = 256
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
C6H13
F
N
Ts
3
1af
146.158
129.872
128.767
87.840
77.419
77.000
76.574
69.135
53.709
53.543
34.903
34.600
31.696
31.321
29.060
27.132
26.684
26.345
26.143
22.553
21.694
14.017
200
150
100
50
0
PPM

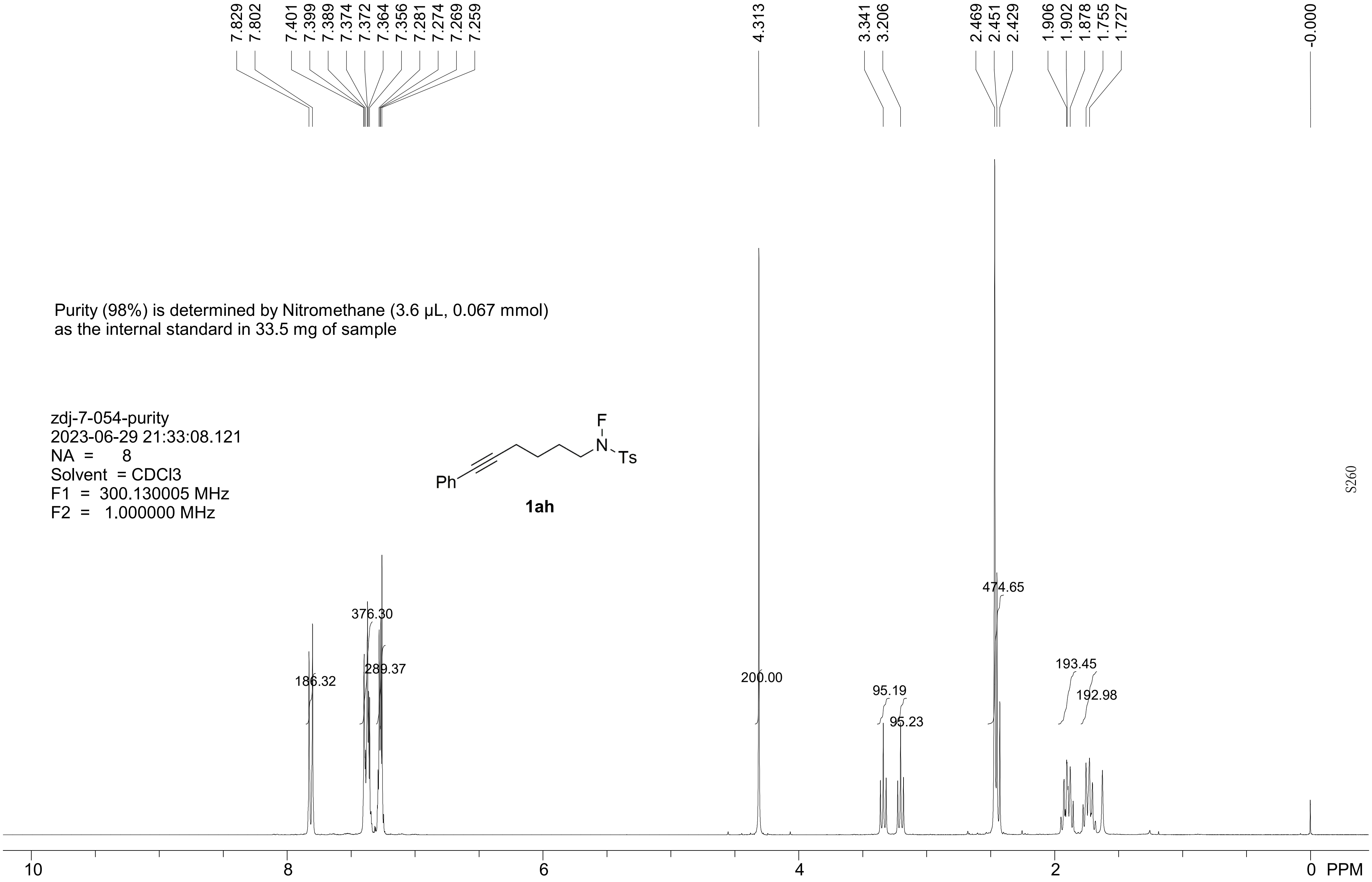

-0.000
-50.493
zdj-7-030
2023-06-14 20:01:25.529
NA = 4
Solvent = CDCl3
F1 = 282.404358 MHz
F2 = 1.000000 MHz
C6H13
F
N
Ts
3
1af
0
-20
-40
-60
-80
-100
-120
-140
PPM


zdj-3-009
2021-10-15 21:08:29.312
NA = 4
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
F
N
Ts
1ag
7.838
7.811
7.427
7.400
3.333
3.310
3.288
3.197
3.175
3.152
2.487
2.262
2.254
2.239
2.231
2.216
2.208
1.959
1.952
1.944
1.893
1.870
1.847
1.821
1.798
1.704
1.680
1.654
1.630
1.615
-0.000
1.97
1.97
1.00
1.00
3.00
2.03
0.95
2.02
2.41
10
8
6
4
2
0
PPM


zdj-3-009
2021-10-16 02:46:55.905
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
1ag
F
N
Ts
146.285
129.934
128.724
83.500
77.325
77.000
76.684
68.901
53.156
53.029
25.231
25.195
21.746
17.854
200
150
100
50
0
PPM


0.000
-50.388
F
N
Ts
1ag
zdj-3-009
2021-10-18 02:52:18.762
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz
0
-50
-100
-150
-200
PPM

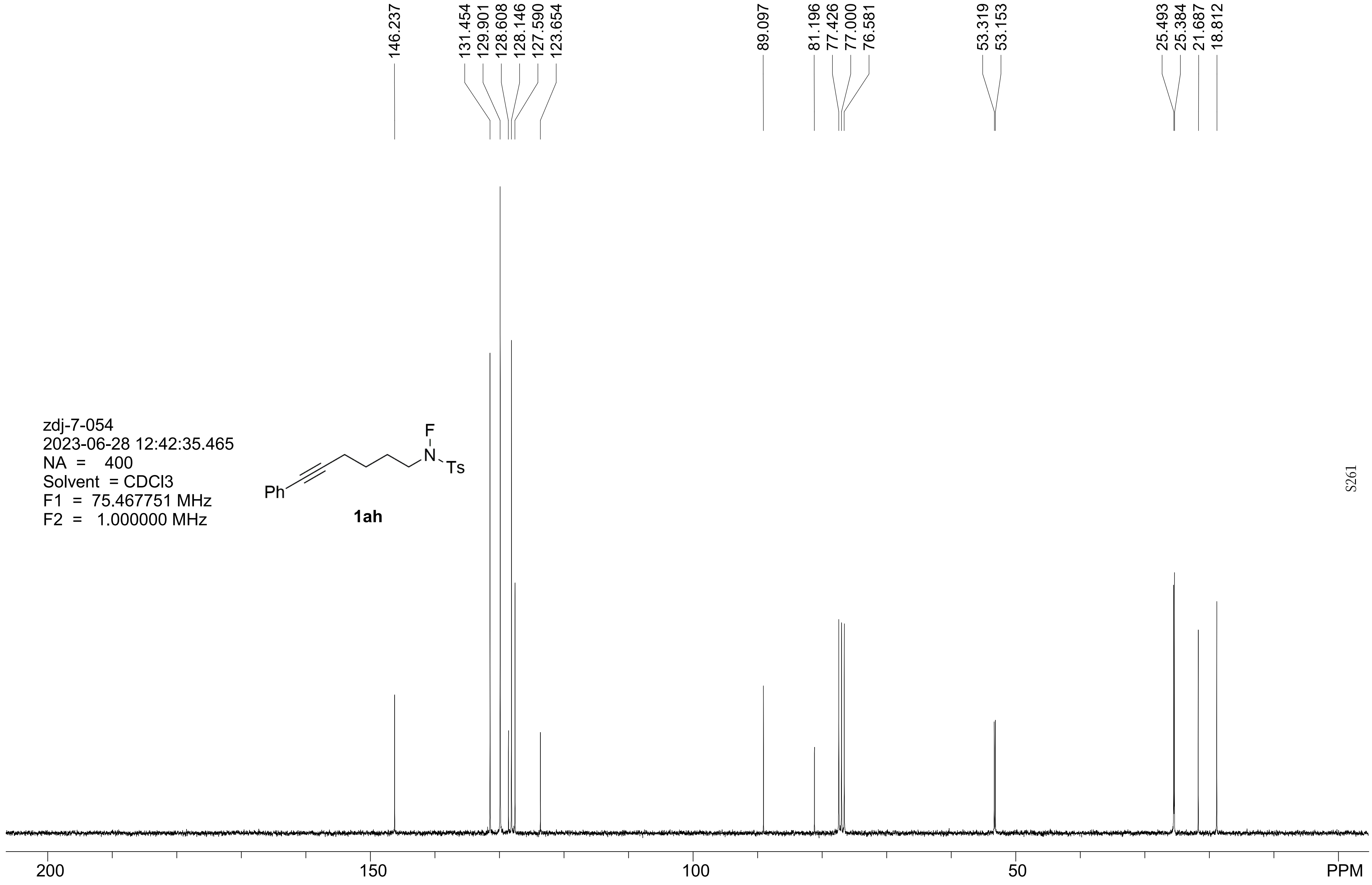

zdj-7-054
2023-06-28 14:46:31.715
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
Ph
F
N
Ts
1ah
7.830
7.802
7.395
7.389
7.376
7.372
7.368
7.365
7.356
7.345
7.339
7.308
7.289
7.280
7.277
7.272
7.267
7.258
3.365
3.343
3.321
3.230
3.208
3.185
2.473
2.466
2.450
2.428
1.951
1.926
1.917
1.906
1.878
1.855
1.777
1.754
1.727
1.703
1.681
0.000
1.96
3.93
3.05
1.00
0.99
4.96
2.01
2.00
10
8
6
4
2
0PPM



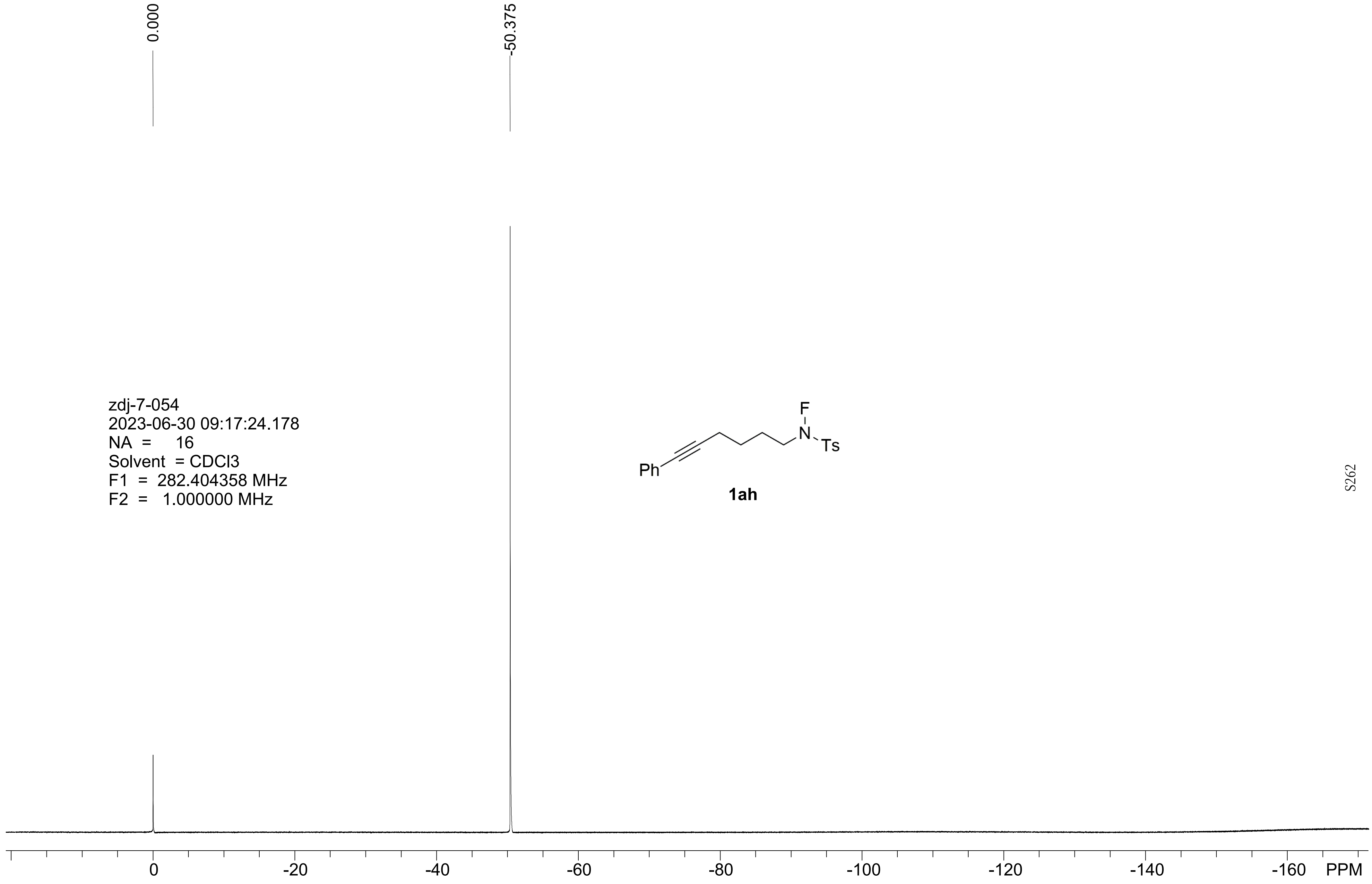
Purity (98%) is determined by Nitromethane (3.6 μL, 0.067 mmol)
as the internal standard in 33.5 mg of sample

zdj-7-054-purity
2023-06-29 21:33:08.121
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz

1ah

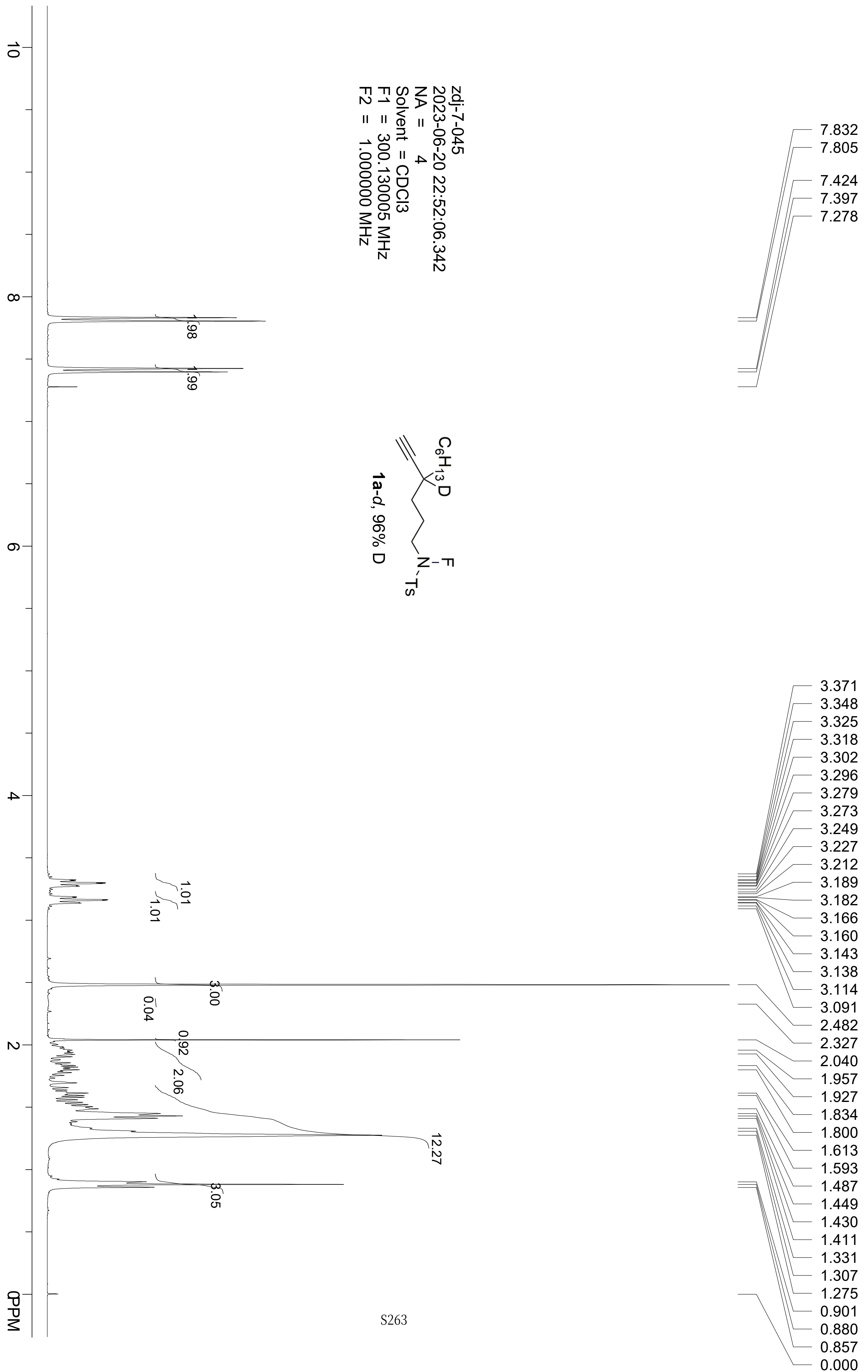

zdj-7-054
2023-06-28 12:42:35.465
NA = 400
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
Ph
F
N
Ts
146.237
131.454
129.901
128.608
128.146
127.590
123.654
89.097
81.196
77.426
77.000
76.581
53.319
53.153
25.493
25.384
21.687
18.812
200
150
100
50
PPM

1ah

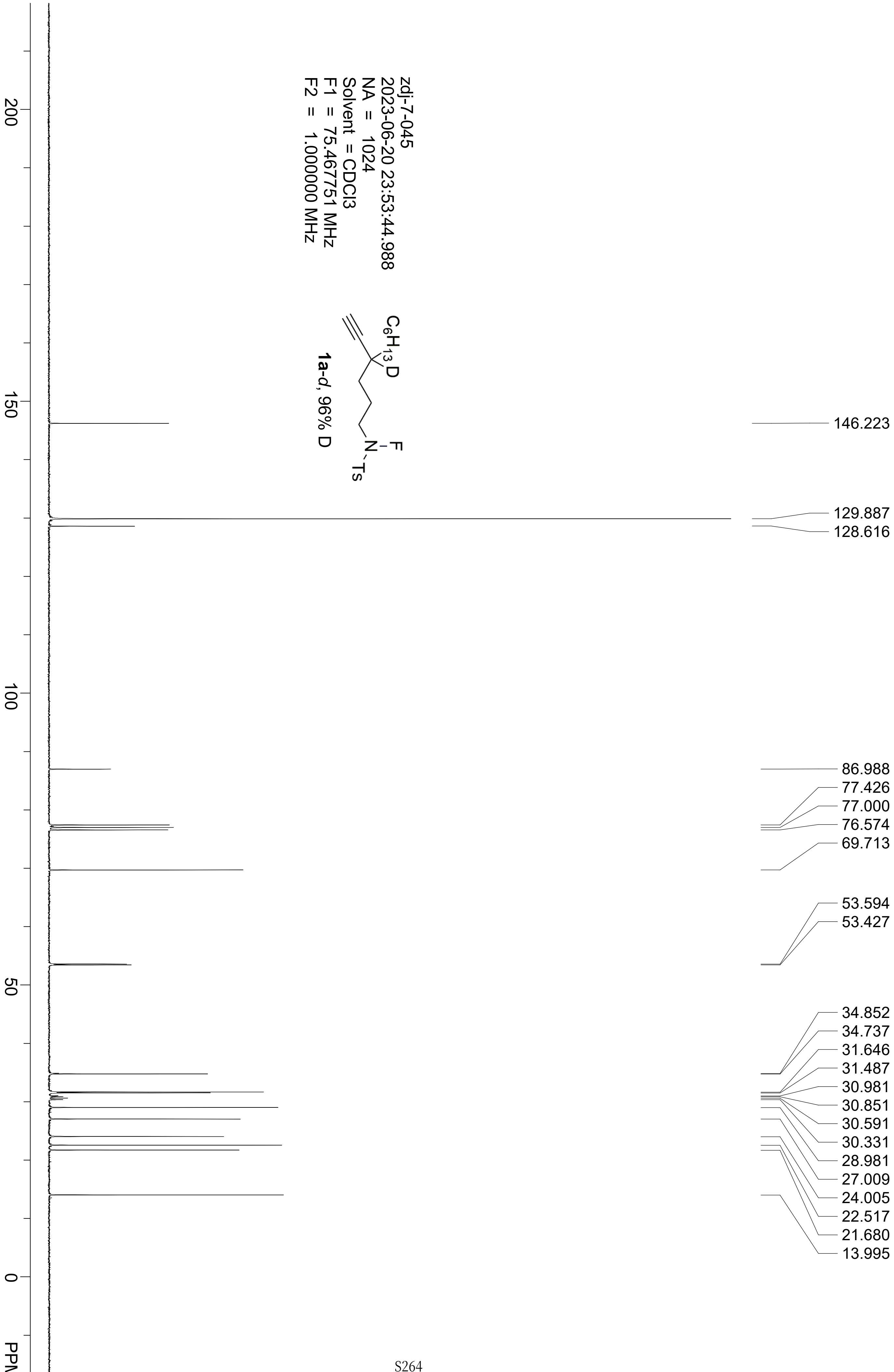


zdj-7-054
2023-06-30 09:17:24.178
NA = 16
Solvent = CDCl3
F1 = 282.404358 MHz
F2 = 1.000000 MHz

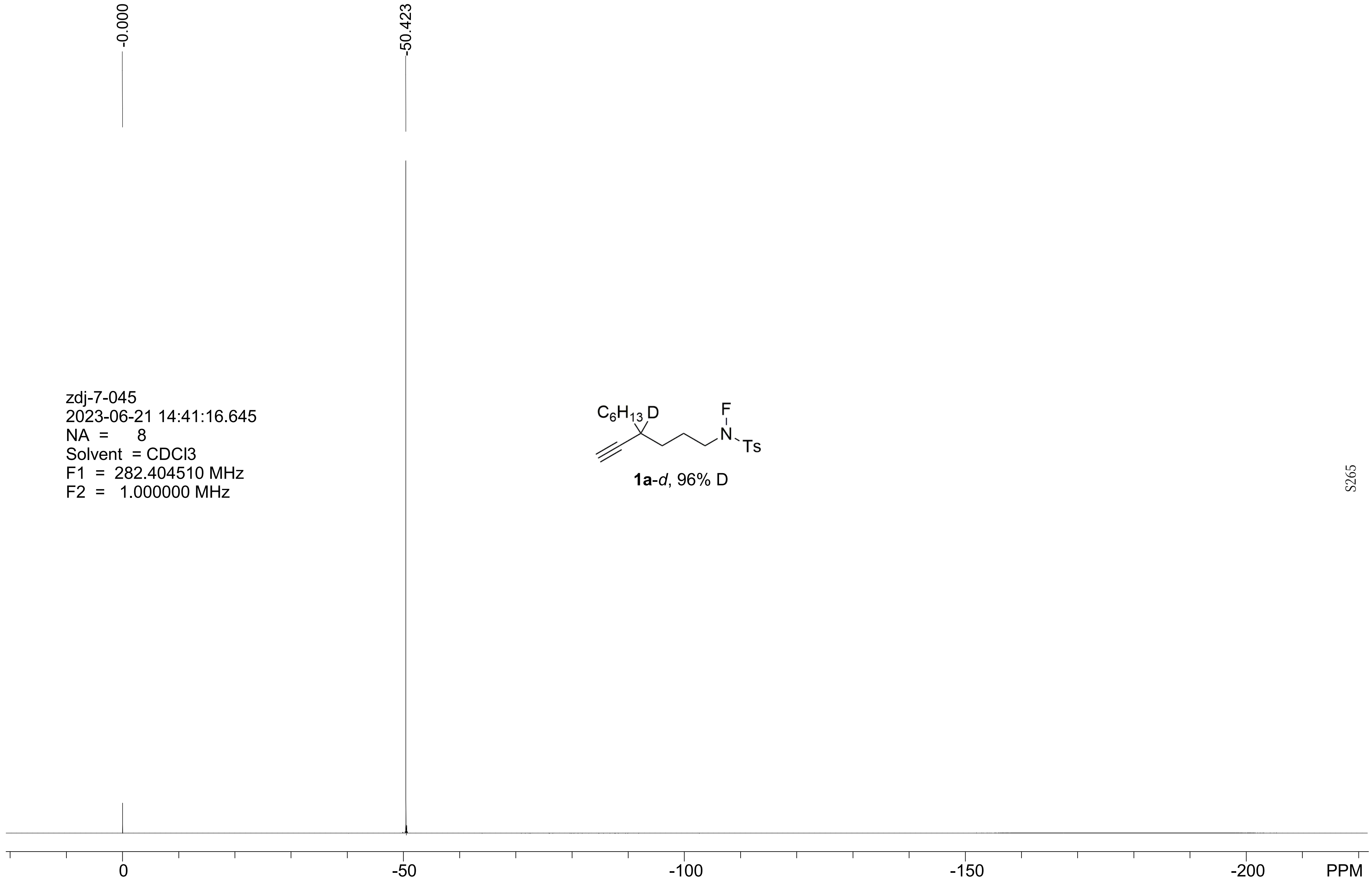
1ah


zdj-7-045
2023-06-20 22:52:06.342
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C_6H_{13}
D
F
N
Ts
7.832
7.805
7.424
7.397
7.278
3.371
3.348
3.325
3.318
3.302
3.296
3.279
3.273
3.249
3.227
3.212
3.189
3.182
3.166
3.160
3.143
3.138
3.114
3.091
2.482
2.327
2.040
1.957
1.927
1.834
1.800
1.613
1.593
1.487
1.449
1.430
1.411
1.331
1.307
1.275
0.901
0.880
0.857
0.000
1.98
1.99
1.01
1.01
3.00
0.04
0.92
2.06
12.27
3.05
10
8
6
4
2
0PPM

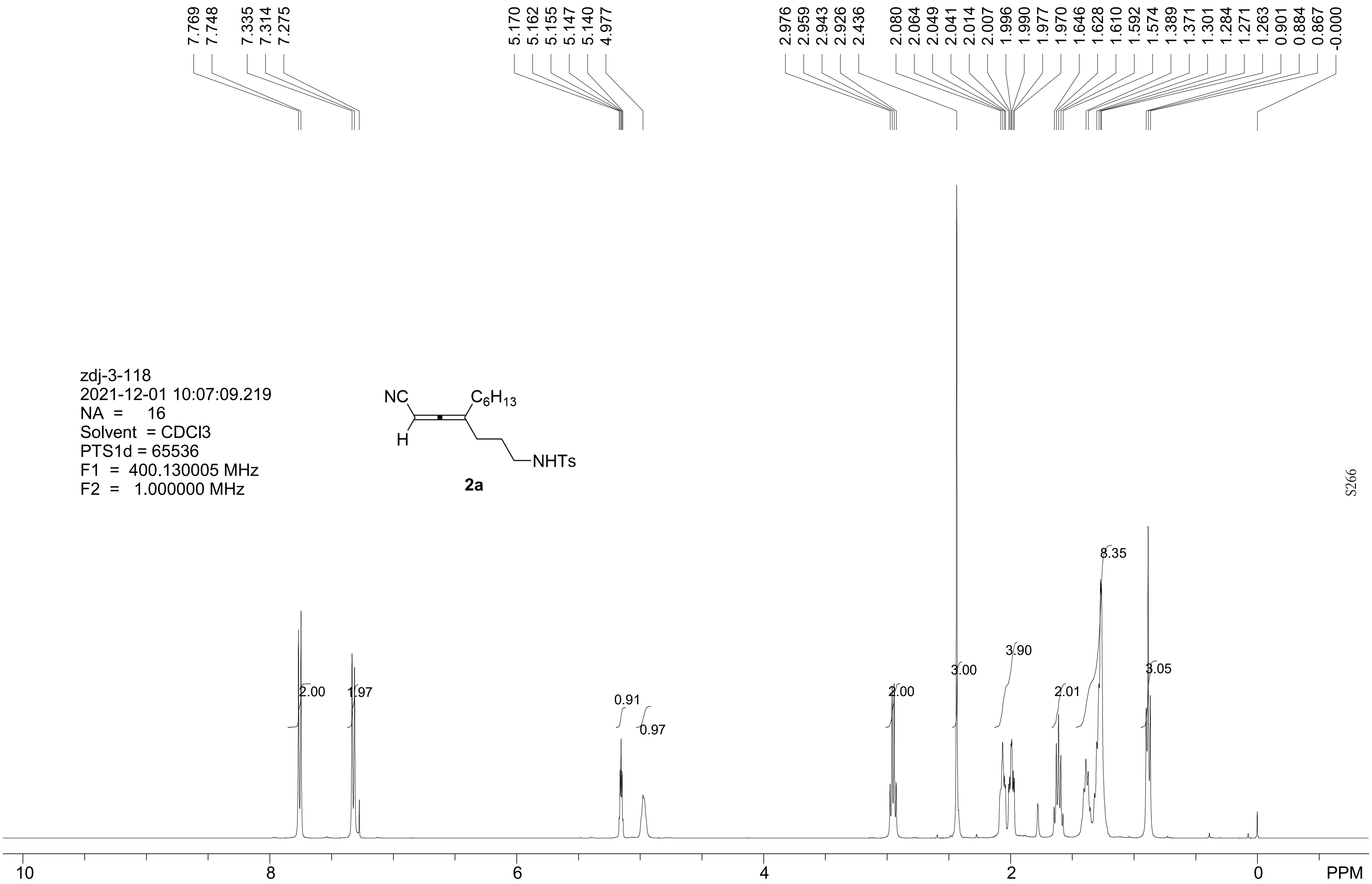
1a-*d*, 96% D

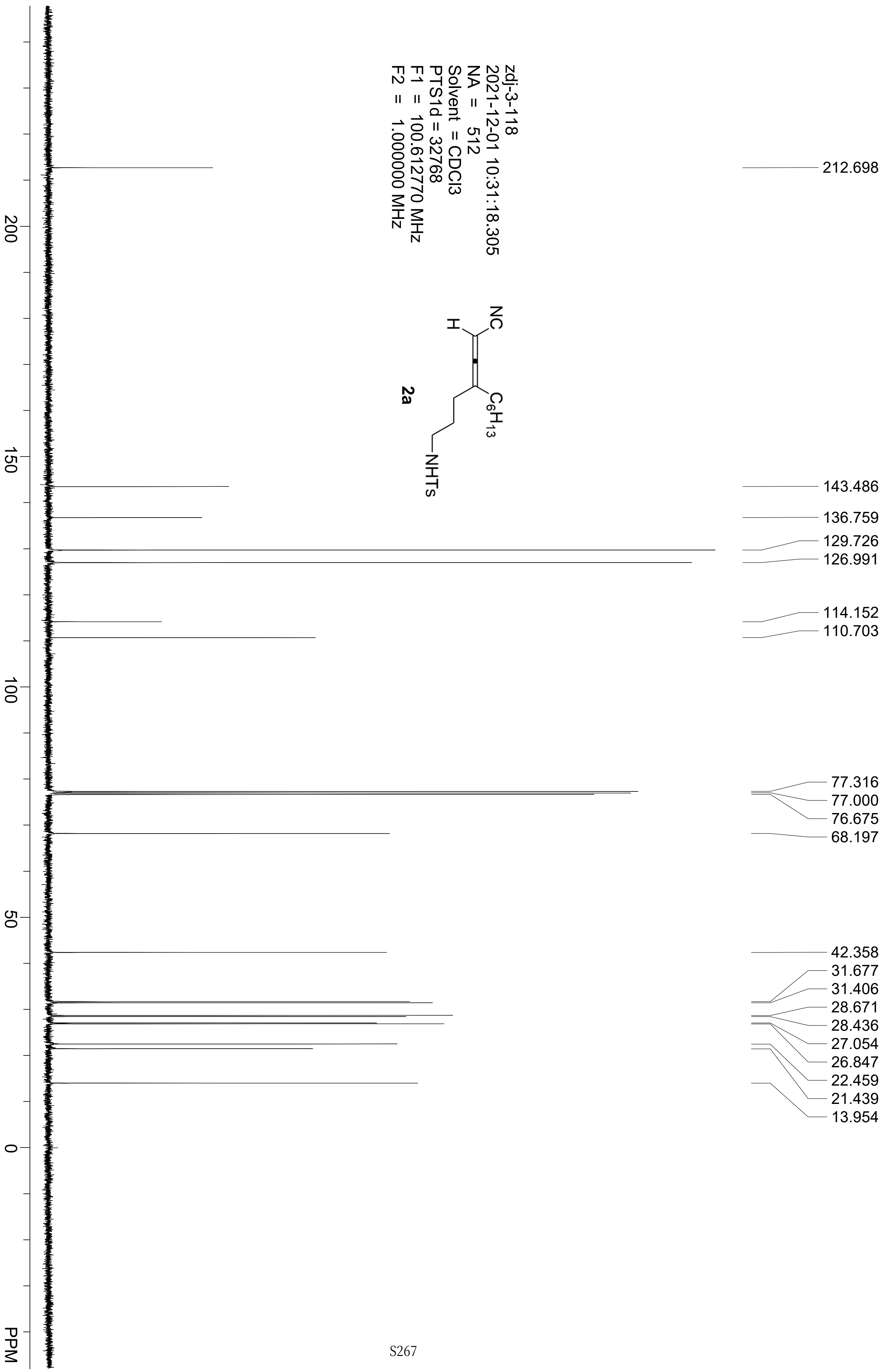

zdj-7-045
2023-06-20 23:53:44.988
NA = 1024
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
C_6H_{13}
D
F
N
Ts
200
150
100
50
0
PPM
146.223
129.887
128.616
86.988
77.426
77.000
76.574
69.713
53.594
53.427
34.852
34.737
31.646
31.487
30.981
30.851
30.591
30.331
28.981
27.009
24.005
22.517
21.680
13.995

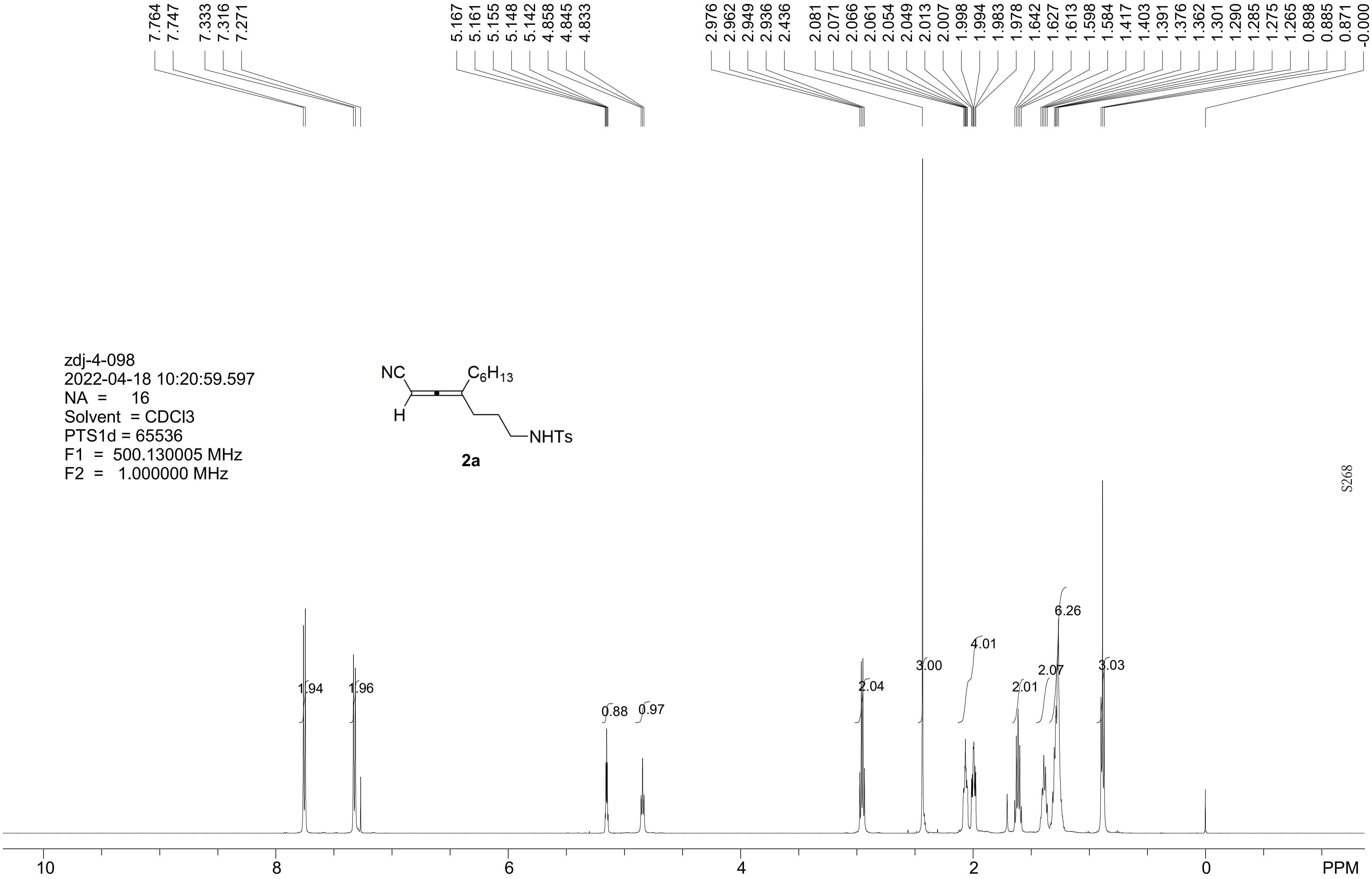
1a-*d*, 96% D

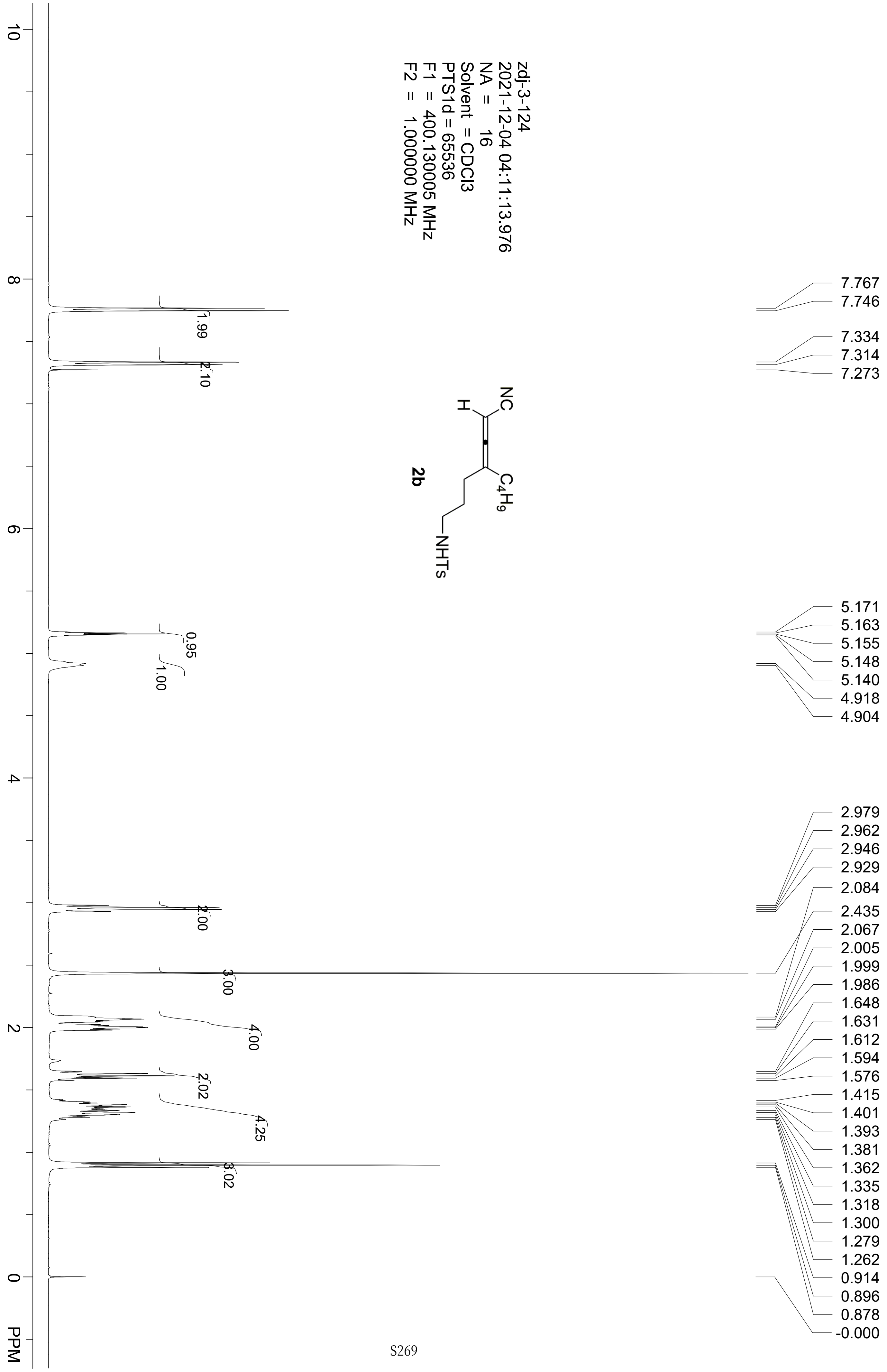

-0.000
-50.423
zdj-7-045
2023-06-21 14:41:16.645
NA = 8
Solvent = CDCl3
F1 = 282.404510 MHz
F2 = 1.000000 MHz
C6H13 D
F
N
Ts
0
-50
-100
-150
-200
PPM

1a-*d*, 96% D

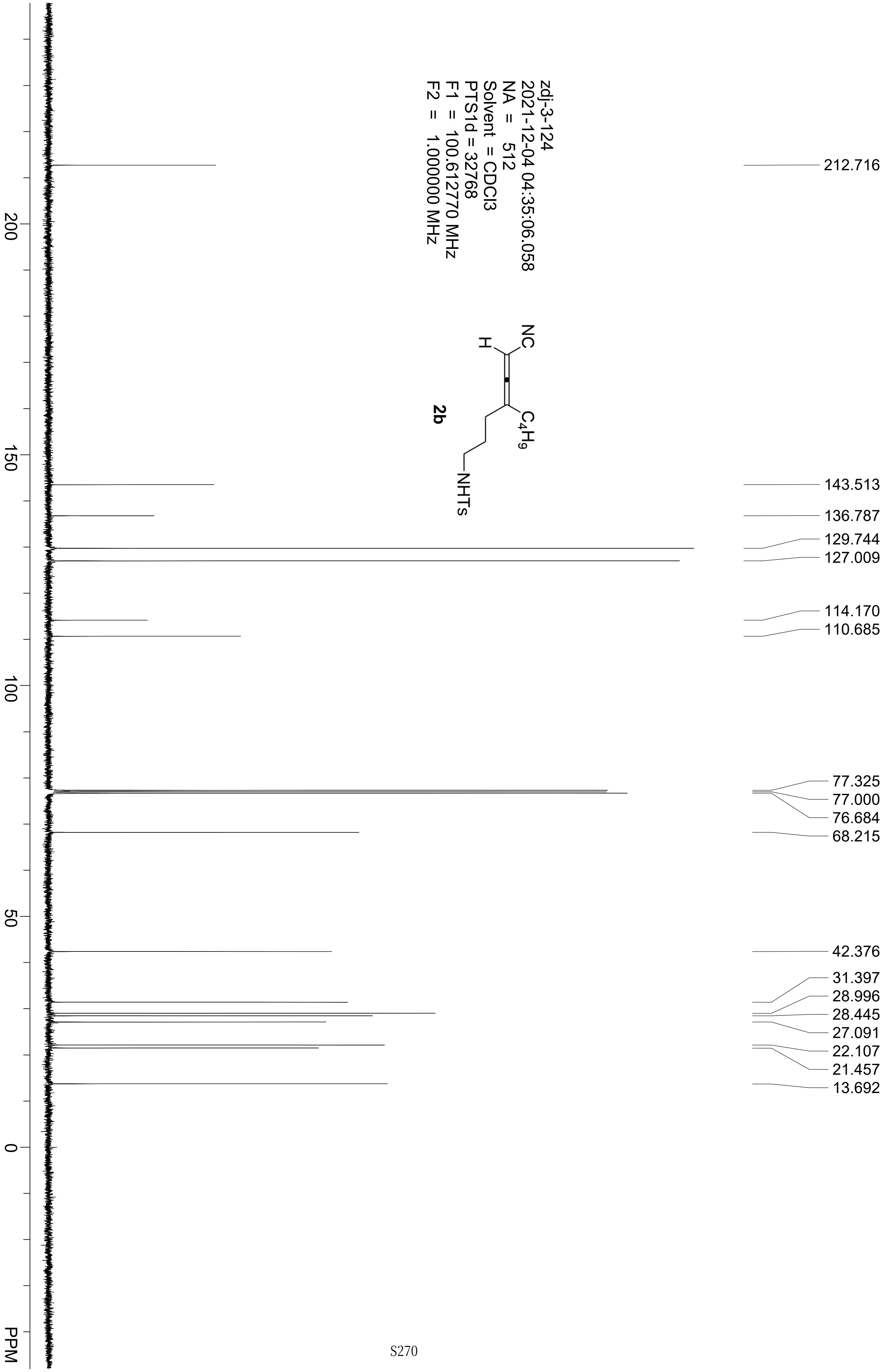

7.769
7.748
7.335
7.314
7.275
5.170
5.162
5.155
5.147
5.140
4.977
2.976
2.959
2.943
2.926
2.436
2.080
2.064
2.049
2.041
2.014
2.007
1.996
1.990
1.977
1.970
1.646
1.628
1.610
1.592
1.574
1.389
1.371
1.301
1.284
1.271
1.263
0.901
0.884
0.867
-0.000
zdj-3-118
2021-12-01 10:07:09.219
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
NC
C_6H_{13}
H
NHTs
2a
2.00
1.97
0.91
0.97
2.00
3.00
3.90
2.01
8.35
3.05
10
8
6
4
2
0
PPM

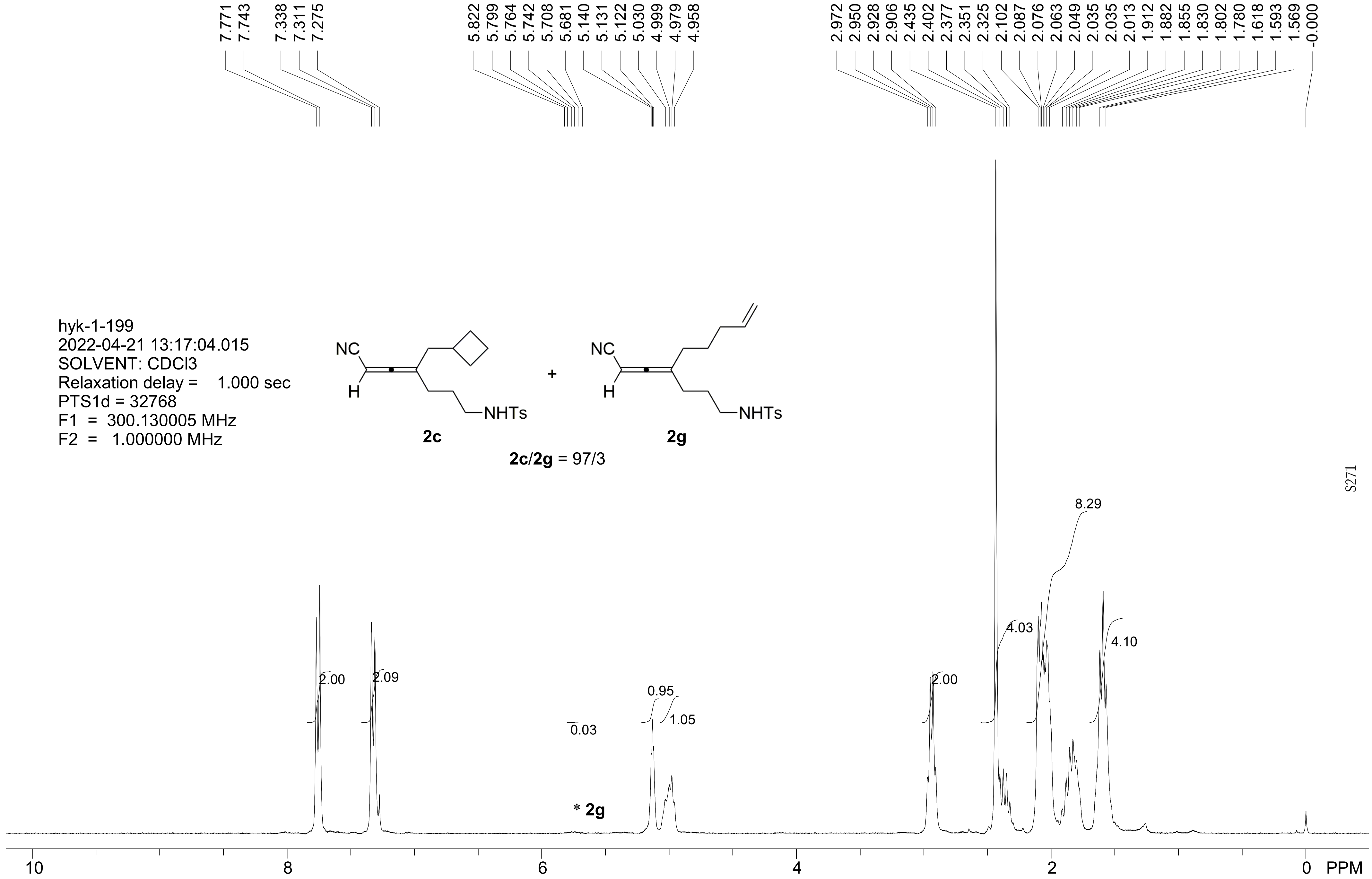

zdj-3-118
2021-12-01 10:31:18.305
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
NC
H
C6H13
NHTs
2a
212.698
143.486
136.759
129.726
126.991
114.152
110.703
77.316
77.000
76.675
68.197
42.358
31.677
31.406
28.671
28.436
27.054
26.847
22.459
21.439
13.954
200
150
100
50
0
PPM

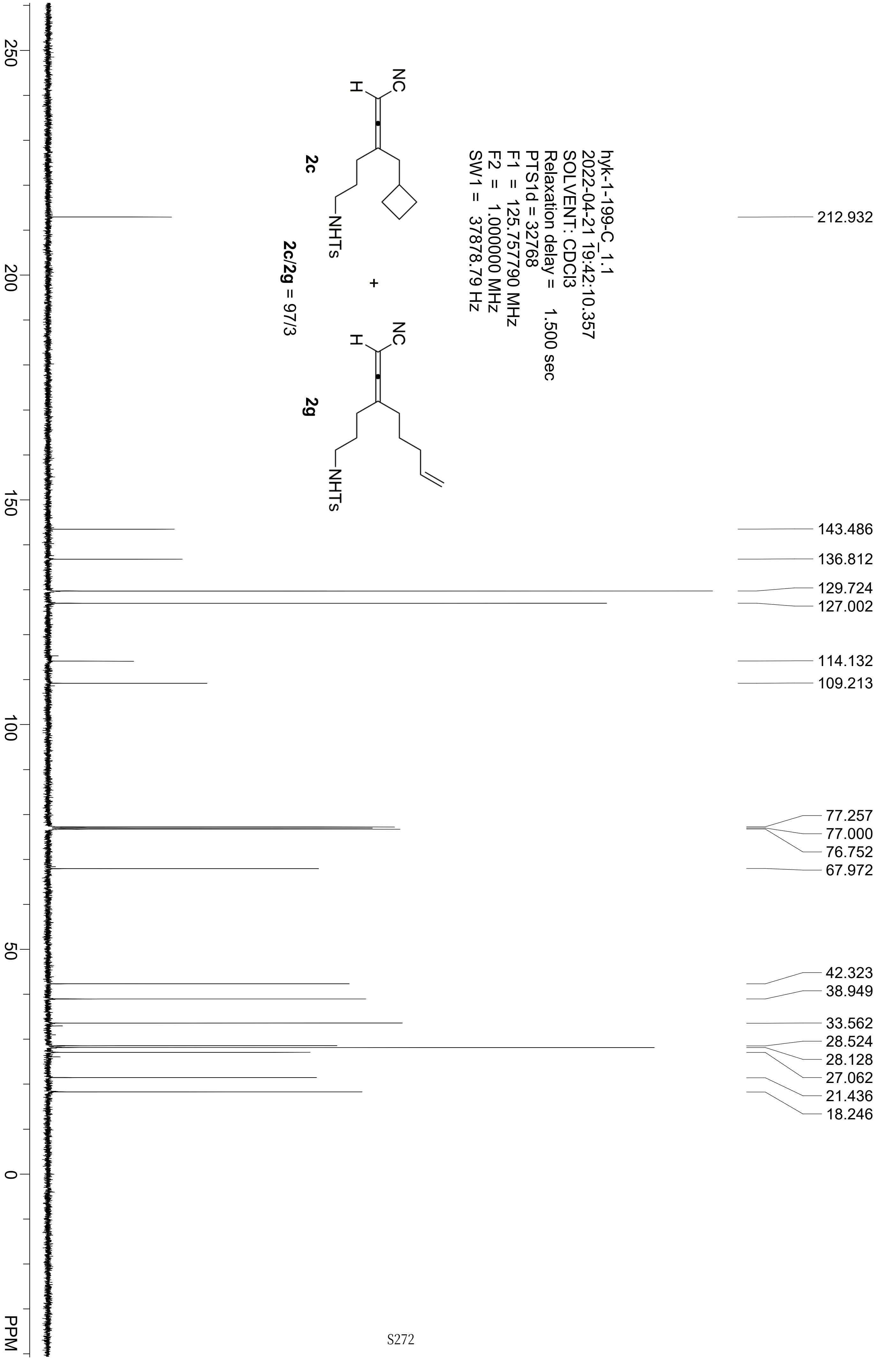

zdj-4-098
2022-04-18 10:20:59.597
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
NC
H
C_6H_{13}
NHTs
2a
7.764
7.747
7.333
7.316
7.271
5.167
5.161
5.155
5.148
5.142
4.858
4.845
4.833
2.976
2.962
2.949
2.936
2.436
2.081
2.071
2.066
2.061
2.054
2.049
2.013
2.007
1.998
1.994
1.983
1.978
1.642
1.627
1.613
1.598
1.584
1.417
1.403
1.391
1.376
1.362
1.301
1.290
1.285
1.275
1.265
0.898
0.885
0.871
-0.000
1.94
1.96
0.88
0.97
2.04
3.00
4.01
2.01
2.07
6.26
3.03
10
8
6
4
2
0
PPM

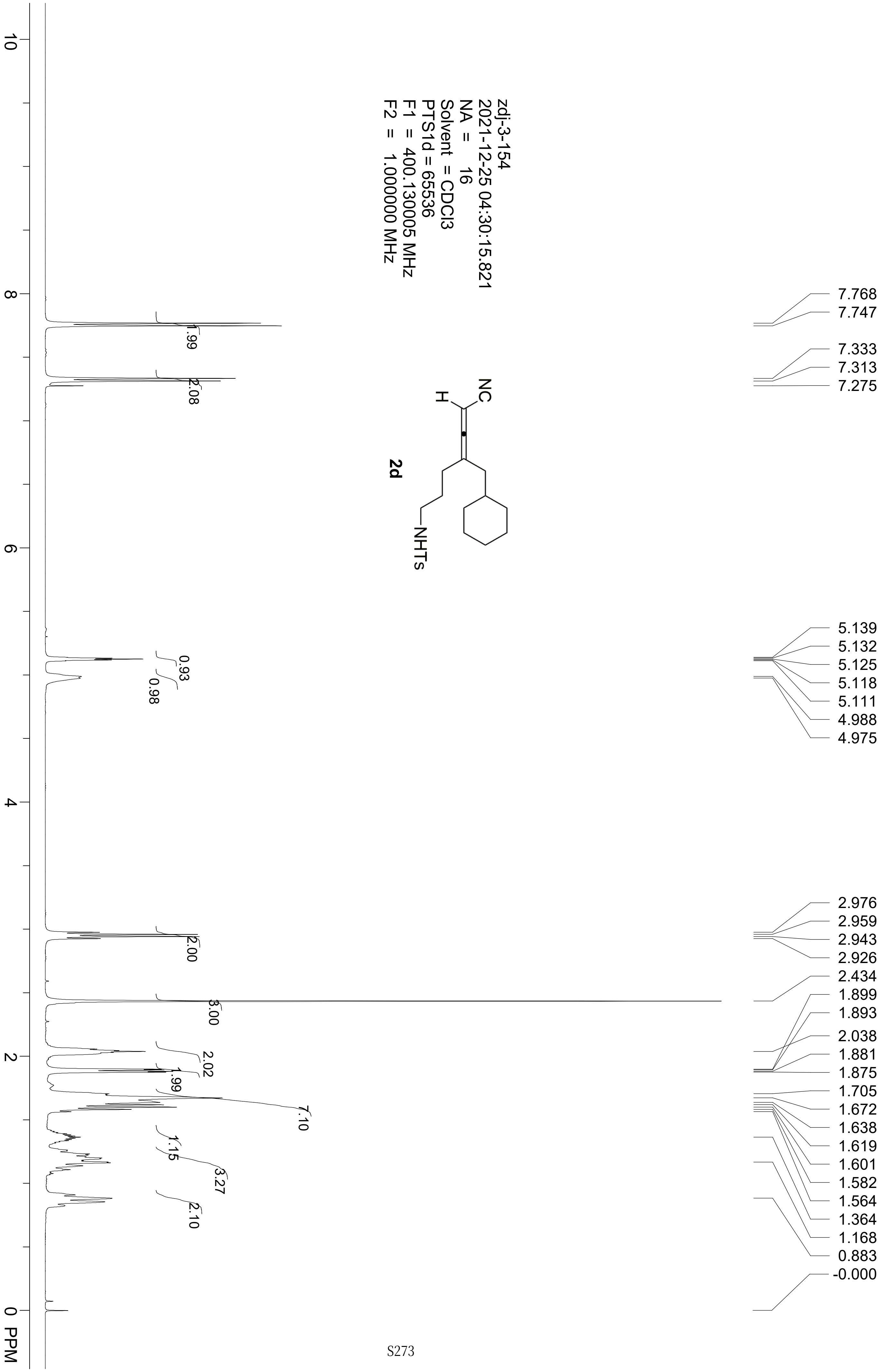

zdj-3-124
2021-12-04 04:11:13.976
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
NC
H
C4H9
NHTs
7.767
7.746
7.334
7.314
7.273
5.171
5.163
5.155
5.148
5.140
4.918
4.904
2.979
2.962
2.946
2.929
2.084
2.435
2.067
2.005
1.999
1.986
1.648
1.631
1.612
1.594
1.576
1.415
1.401
1.393
1.381
1.362
1.335
1.318
1.300
1.279
1.262
0.914
0.896
0.878
-0.000
1.99
2.10
0.95
1.00
2.00
3.00
4.00
2.02
4.25
3.02
10
8
6
4
2
0
PPM

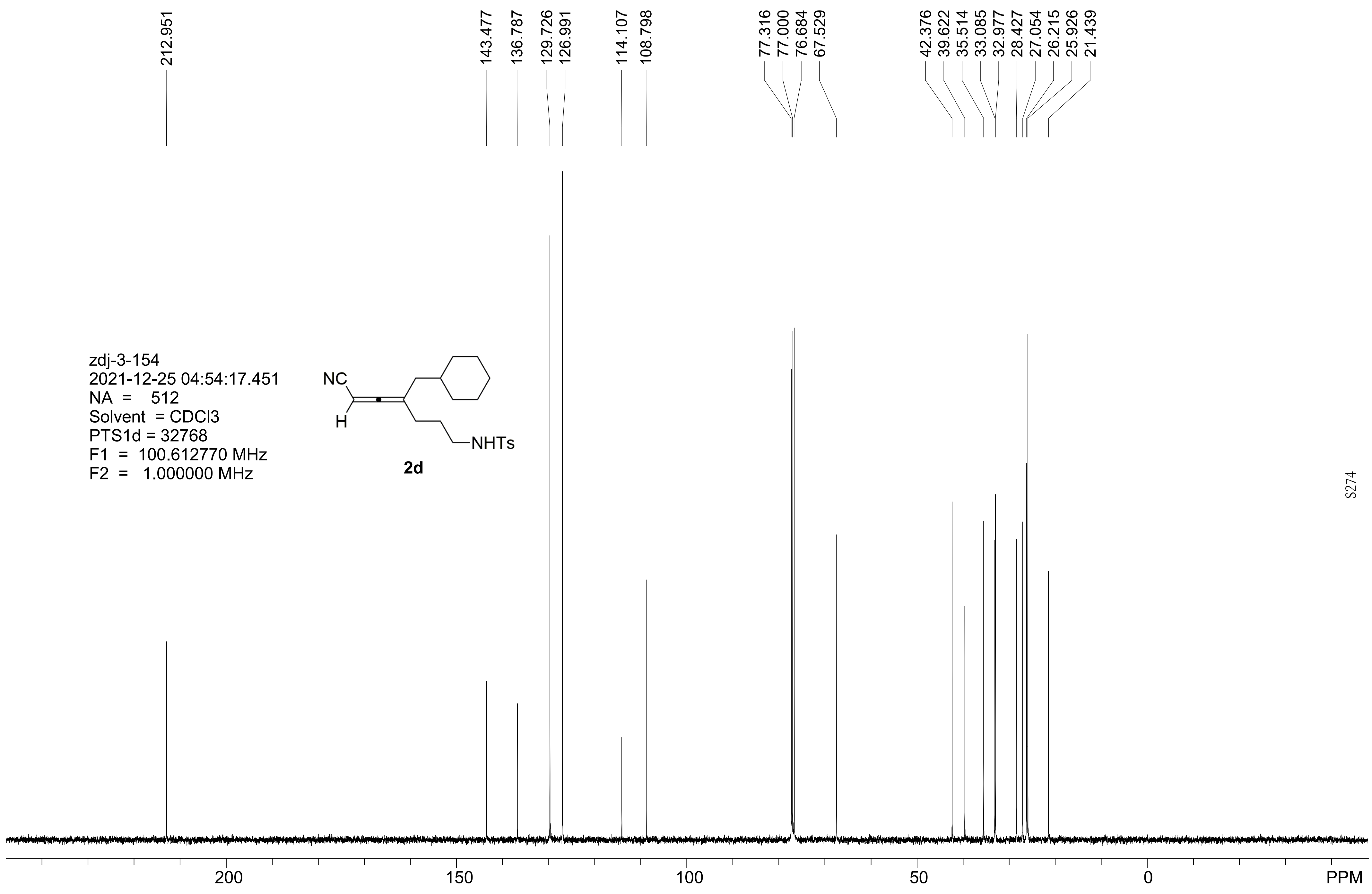
2b

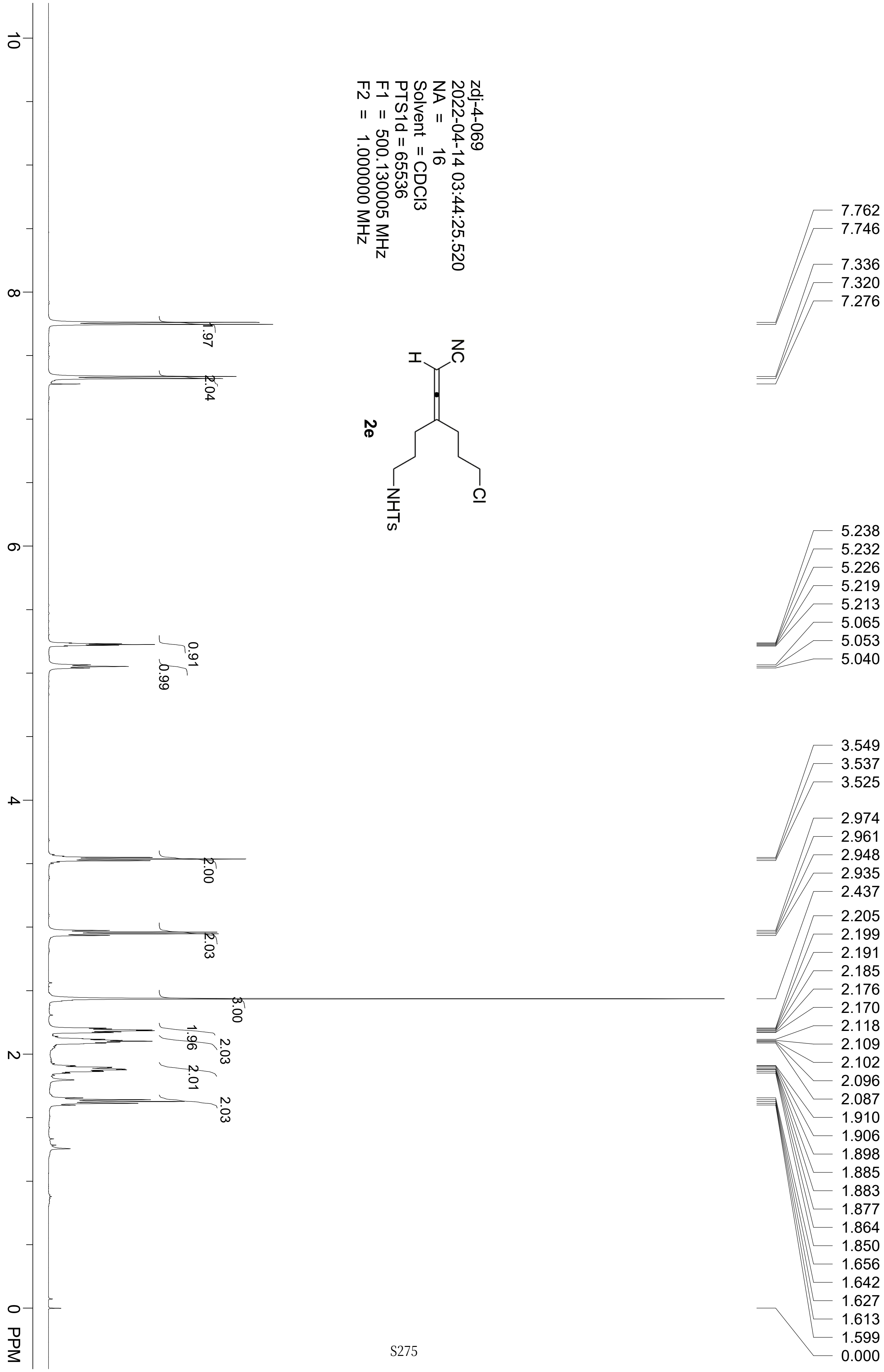

zdj-3-124
2021-12-04 04:35:06.058
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
NC
H
C4H9
NHTs
2b
212.716
143.513
136.787
129.744
127.009
114.170
110.685
77.325
77.000
76.684
68.215
42.376
31.397
28.996
28.445
27.091
22.107
21.457
13.692
200
150
100
50
0
PPM

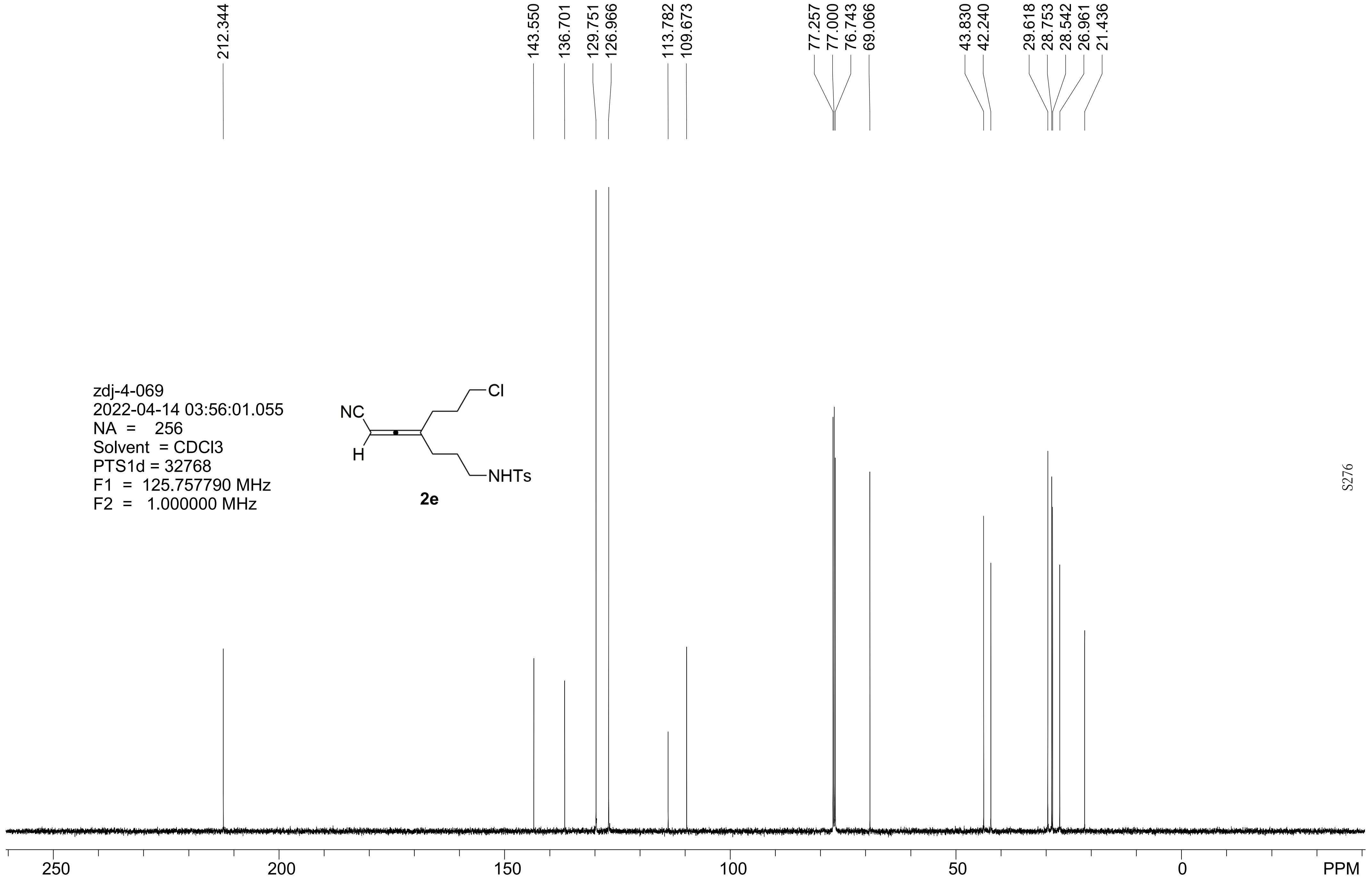

7.771
7.743
7.338
7.311
7.275
5.822
5.799
5.764
5.742
5.708
5.681
5.140
5.131
5.122
5.030
4.999
4.979
4.958
2.972
2.950
2.928
2.906
2.435
2.402
2.377
2.351
2.325
2.102
2.087
2.076
2.063
2.049
2.035
2.035
2.013
1.912
1.882
1.855
1.830
1.802
1.780
1.618
1.593
1.569
-0.000
hyk-1-199
2022-04-21 13:17:04.015
SOLVENT: CDCl3
Relaxation delay = 1.000 sec
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
H
NHTs
2c
+
NC
H
NHTs
2g
2c/2g = 97/3
8.29
4.03
4.10
2.00
2.09
2.00
0.95
1.05
0.03
* 2g
10
8
6
4
2
0 PPM

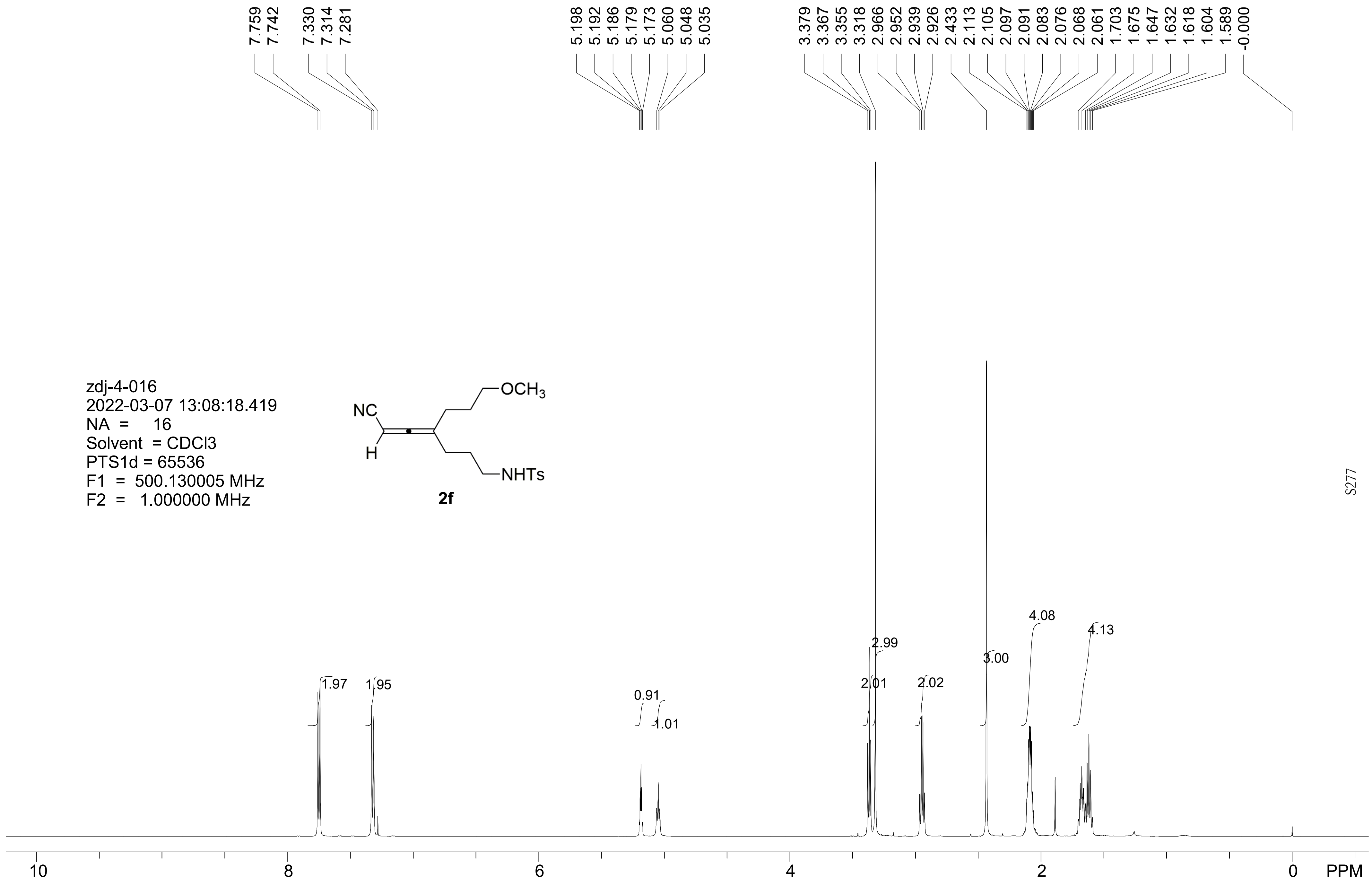

hyk-1-199-C_1.1
2022-04-21 19:42:10.357
SOLVENT: CDCl3
Relaxation delay = 1.500 sec
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
SW1 = 37878.79 Hz
NC
H
NHTs
2c
+
NC
H
NHTs
2g
2c/2g = 97/3
212.932
143.486
136.812
129.724
127.002
114.132
109.213
77.257
77.000
76.752
67.972
42.323
38.949
33.562
28.524
28.128
27.062
21.436
18.246
250
200
150
100
50
0
PPM

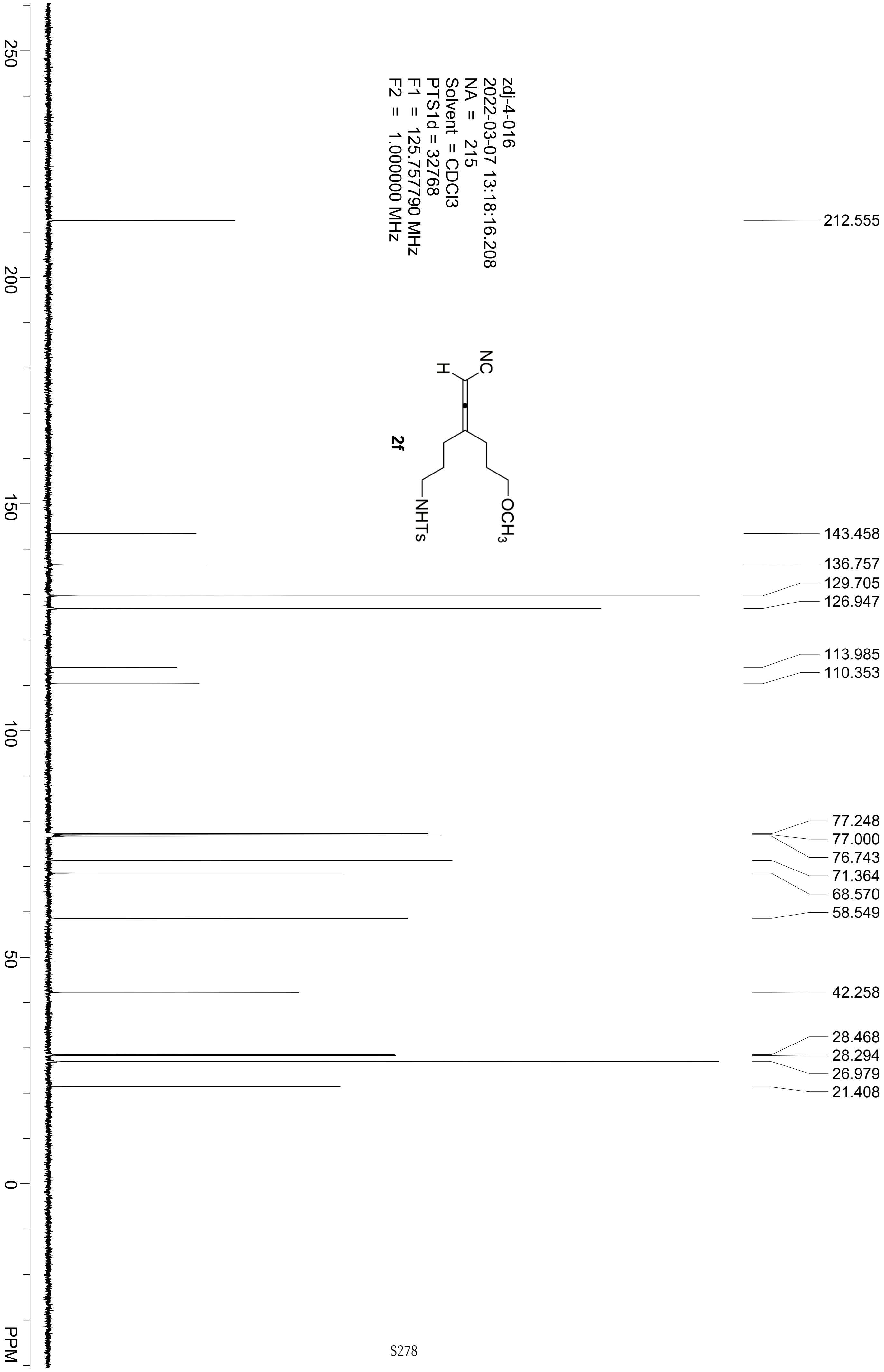

zdj-3-154
2021-12-25 04:30:15.821
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
NC
H
NHTs
2d
10
8
6
4
2
0 PPM
1.99
2.08
0.93
0.98
2.00
3.00
2.02
1.99
7.10
1.15
3.27
2.10
7.768
7.747
7.333
7.313
7.275
5.139
5.132
5.125
5.118
5.111
4.988
4.975
2.976
2.959
2.943
2.926
2.434
1.899
1.893
2.038
1.881
1.875
1.705
1.672
1.638
1.619
1.601
1.582
1.564
1.364
1.168
0.883
-0.000

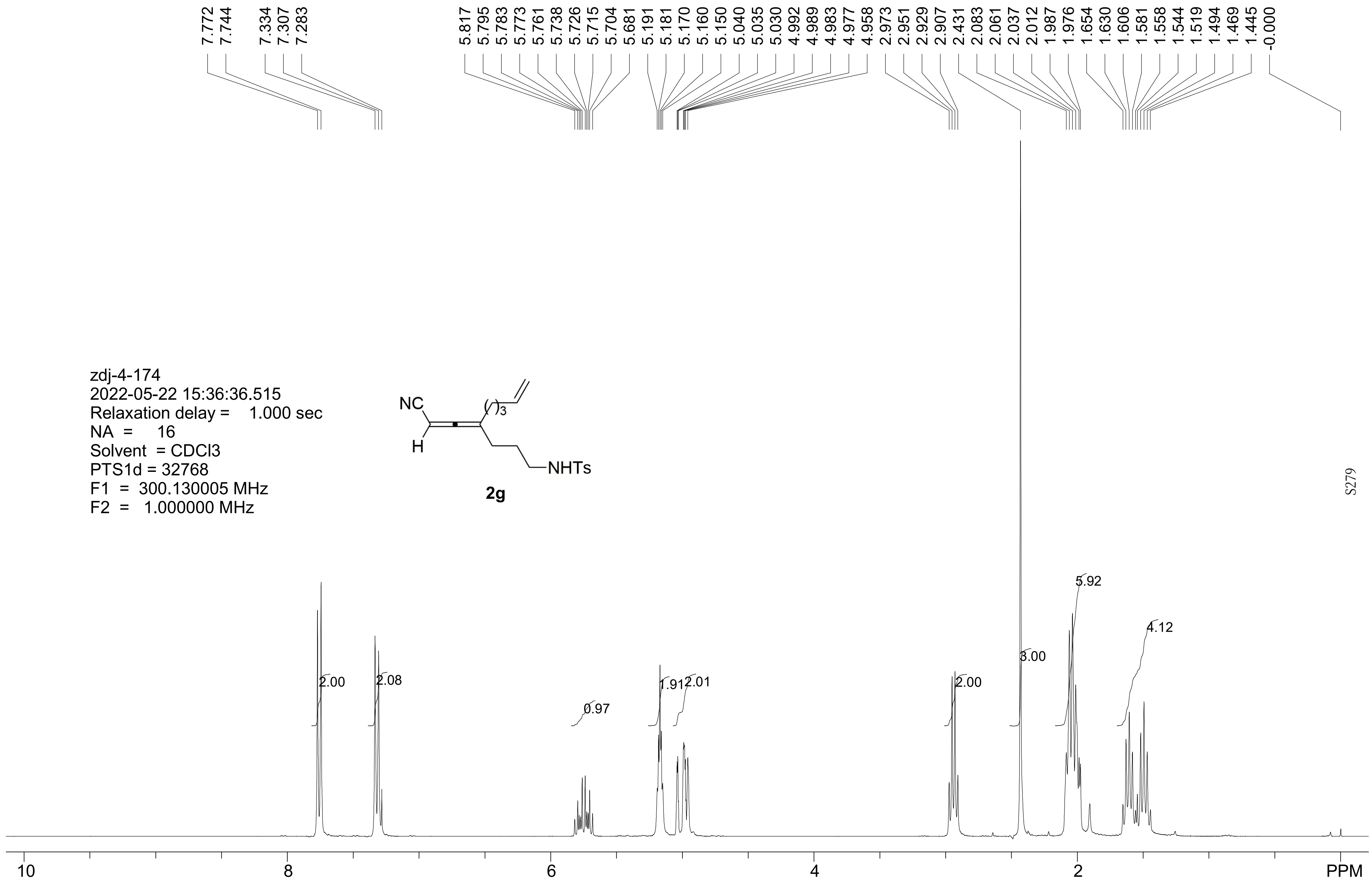

212.951
143.477
136.787
129.726
126.991
114.107
108.798
77.316
77.000
76.684
67.529
42.376
39.622
35.514
33.085
32.977
28.427
27.054
26.215
25.926
21.439
zdj-3-154
2021-12-25 04:54:17.451
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
NC
H
NHTs
2d
200
150
100
50
0
PPM


zdj-4-069
2022-04-14 03:44:25.520
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
NC
H
Cl
NHTs
2e
7.762
7.746
7.336
7.320
7.276
5.238
5.232
5.226
5.219
5.213
5.065
5.053
5.040
3.549
3.537
3.525
2.974
2.961
2.948
2.935
2.437
2.205
2.199
2.191
2.185
2.176
2.170
2.118
2.109
2.102
2.096
2.087
1.910
1.906
1.898
1.885
1.883
1.877
1.864
1.850
1.656
1.642
1.627
1.613
1.599
0.000
1.97
2.04
0.91
0.99
2.00
2.03
3.00
1.96
2.03
2.01
2.03
10
8
6
4
2
0 PPM

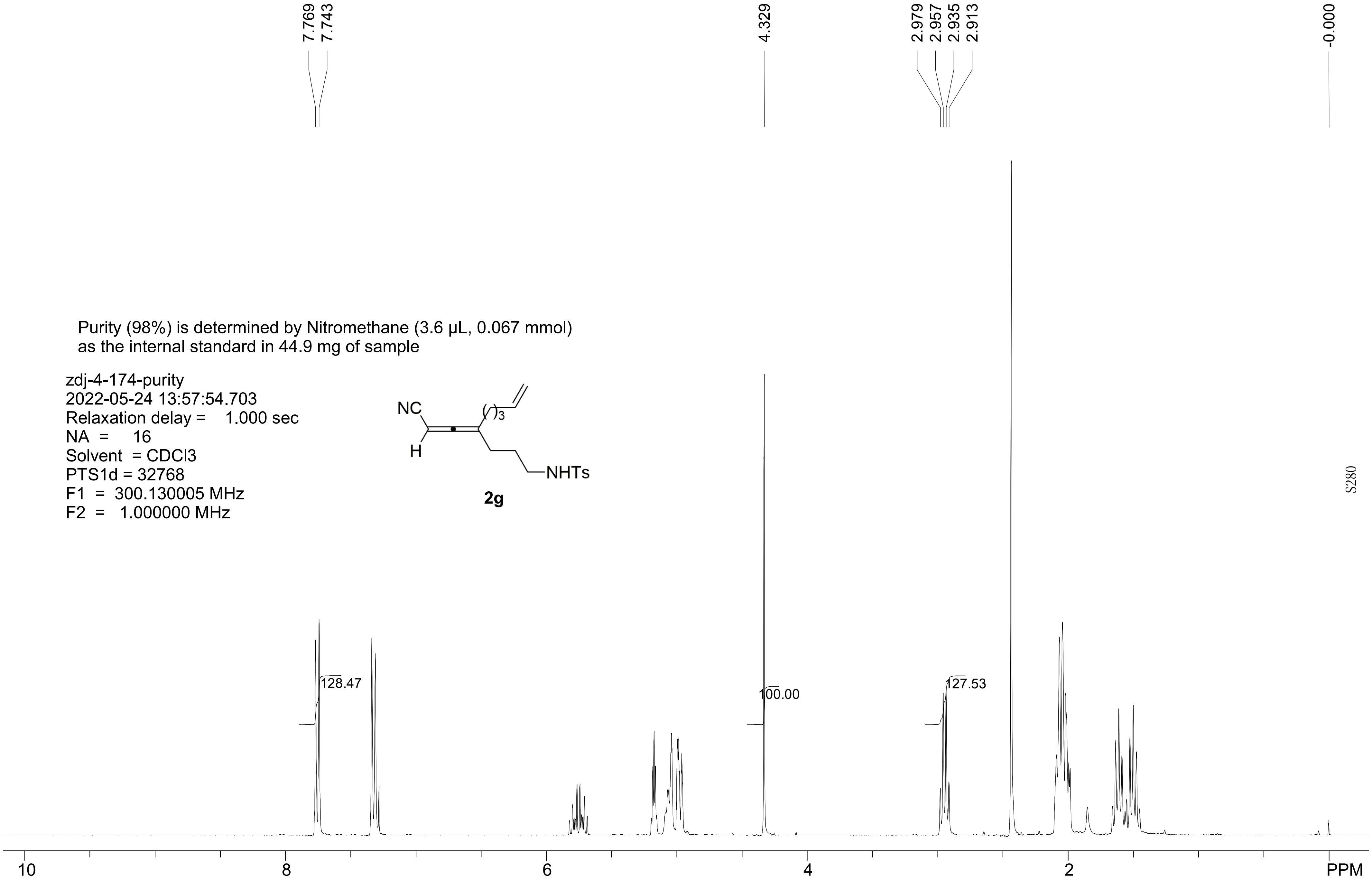

212.344
143.550
136.701
129.751
126.966
113.782
109.673
77.257
77.000
76.743
69.066
43.830
42.240
29.618
28.753
28.542
26.961
21.436
zdj-4-069
2022-04-14 03:56:01.055
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
Cl
NHTs
2e
250
200
150
100
50
0
PPM


zdj-4-016
2022-03-07 13:08:18.419
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
NC
H
OCH$_3$
NHTs
2f
7.759
7.742
7.330
7.314
7.281
5.198
5.192
5.186
5.179
5.173
5.060
5.048
5.035
3.379
3.367
3.355
3.318
2.966
2.952
2.939
2.926
2.433
2.113
2.105
2.097
2.091
2.083
2.076
2.068
2.061
1.703
1.675
1.647
1.632
1.618
1.604
1.589
-0.000
1.97
1.95
0.91
1.01
2.01
2.99
2.02
3.00
4.08
4.13
10
8
6
4
2
0
PPM


zdj-4-016
2022-03-07 13:18:16.208
NA = 215
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
OCH3
NHTs
2f
212.555
143.458
136.757
129.705
126.947
113.985
110.353
77.248
77.000
76.743
71.364
68.570
58.549
42.258
28.468
28.294
26.979
21.408
250
200
150
100
50
0
PPM


zdj-4-174
2022-05-22 15:36:36.515
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
H
3
NHTs
7.772
7.744
7.334
7.307
7.283
5.817
5.795
5.783
5.773
5.761
5.738
5.726
5.715
5.704
5.681
5.191
5.181
5.170
5.160
5.150
5.040
5.035
5.030
4.992
4.989
4.983
4.977
4.958
2.973
2.951
2.929
2.907
2.431
2.083
2.061
2.037
2.012
1.987
1.976
1.654
1.630
1.606
1.581
1.558
1.544
1.519
1.494
1.469
1.445
-0.000
2.00
2.08
0.97
1.91
2.01
2.00
3.00
5.92
4.12
10
8
6
4
2
PPM

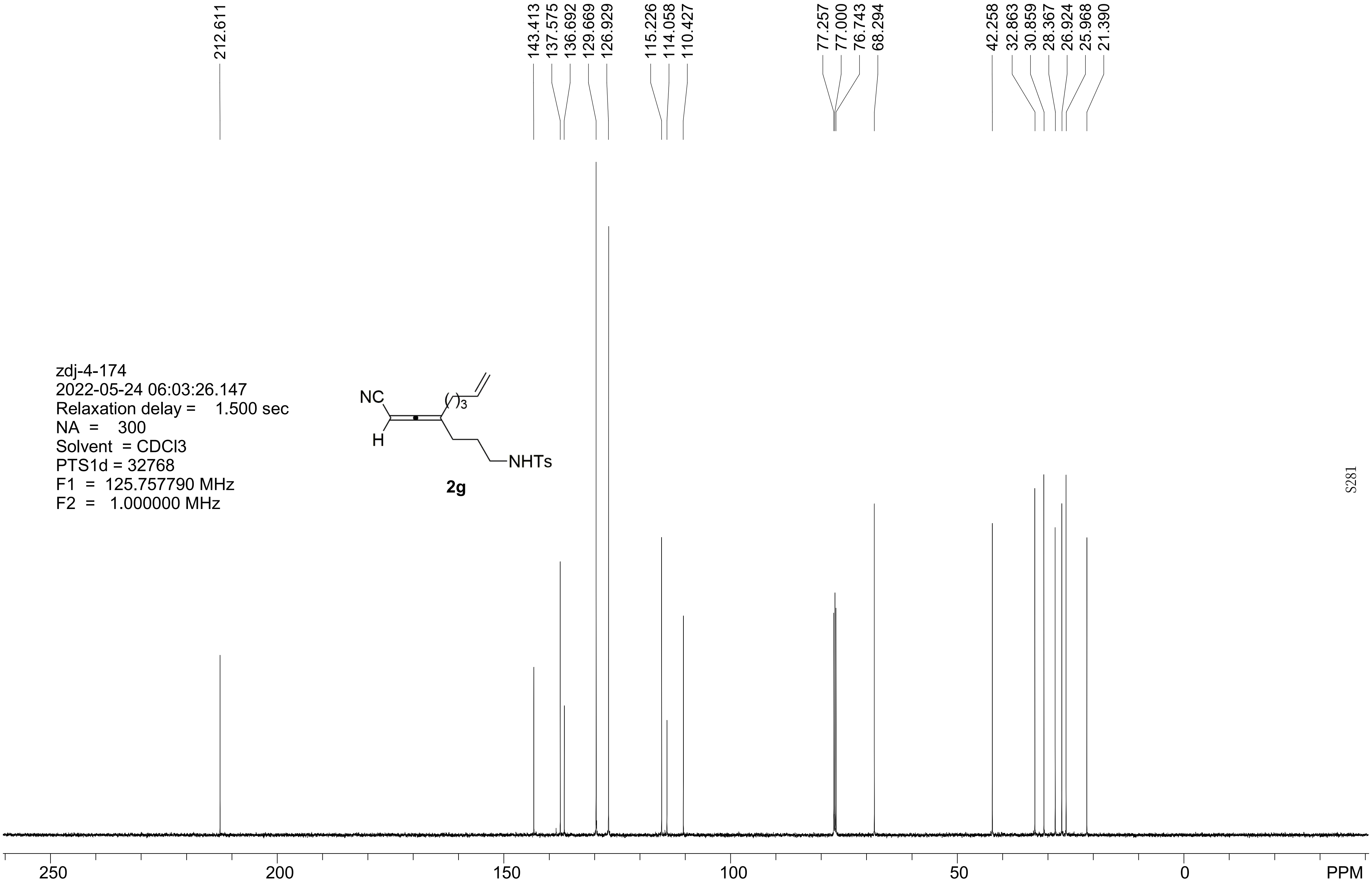
2g



Purity (98%) is determined by Nitromethane (3.6 μL, 0.067 mmol)
as the internal standard in 44.9 mg of sample

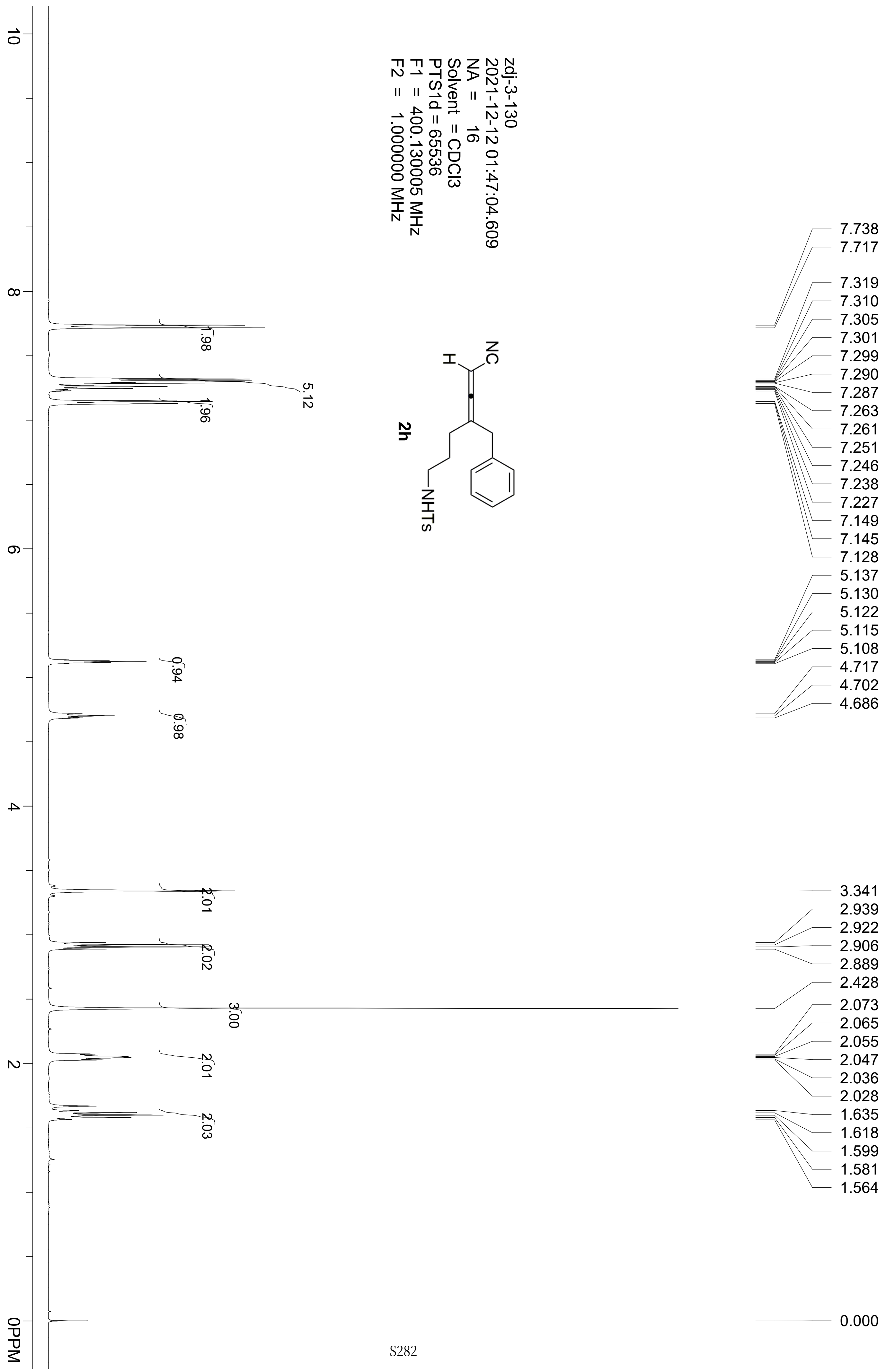
zdj-4-174-purity
2022-05-24 13:57:54.703
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

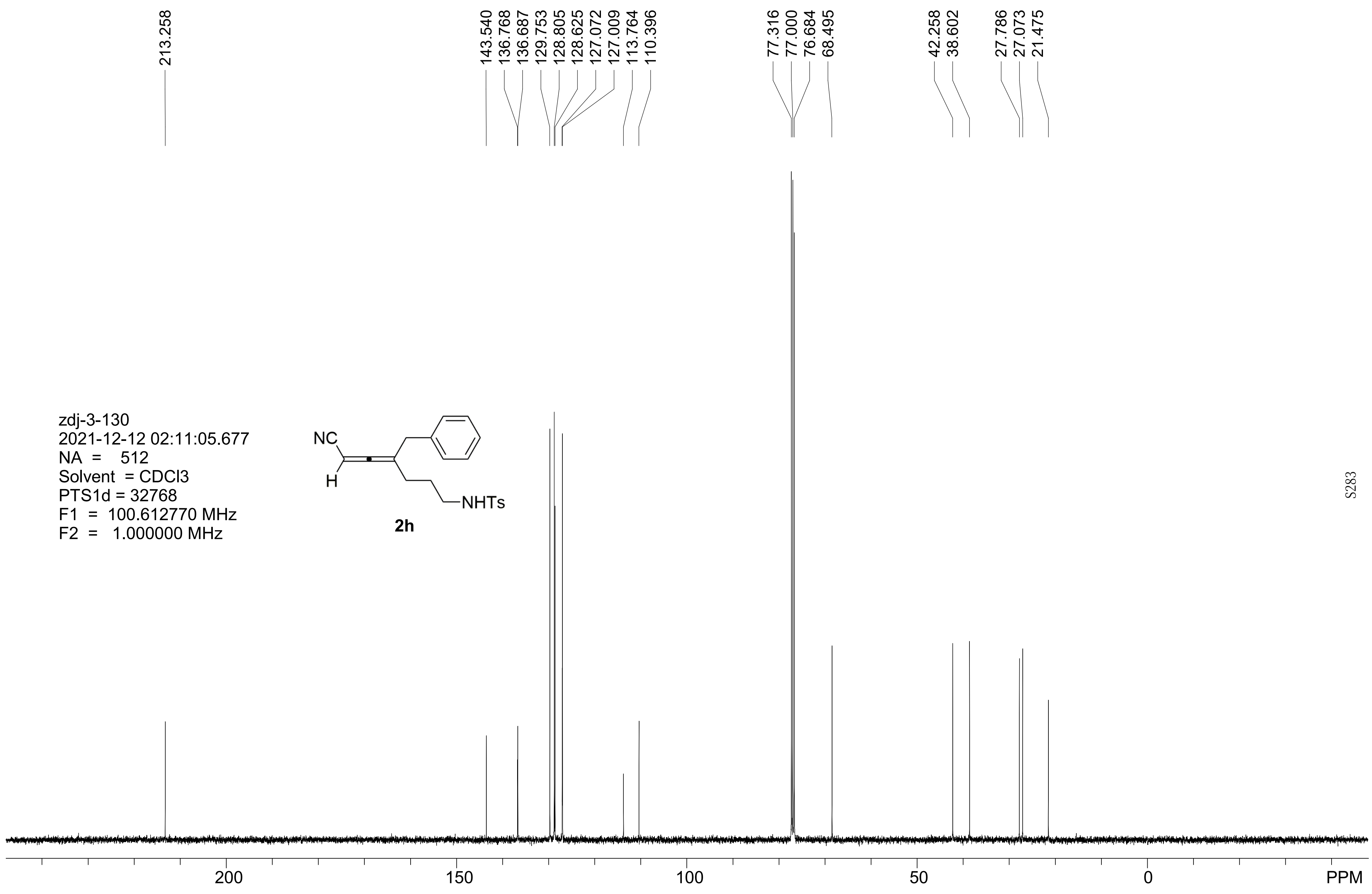
2g

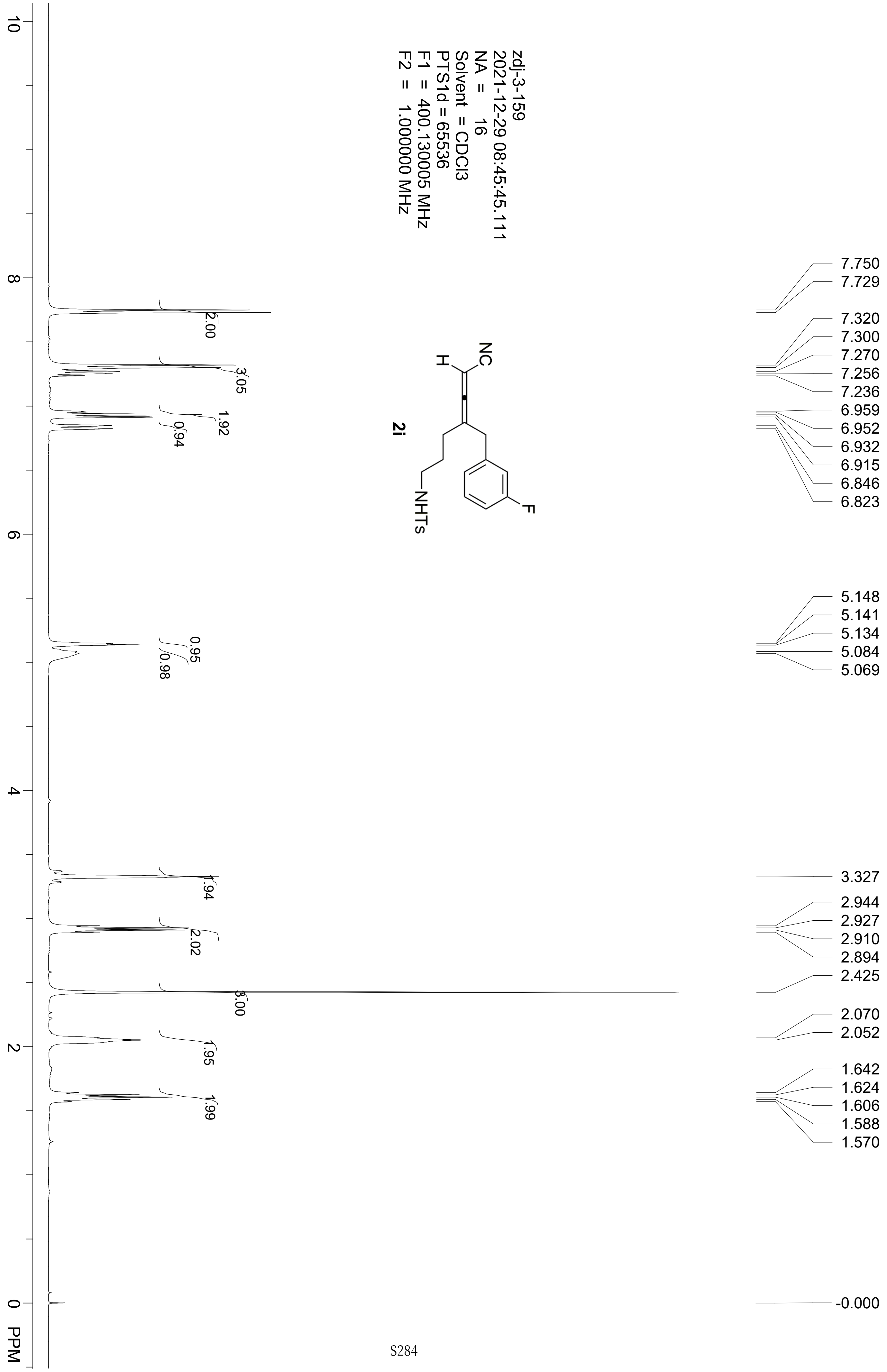


zdj-4-174
2022-05-24 06:03:26.147
Relaxation delay = 1.500 sec
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz

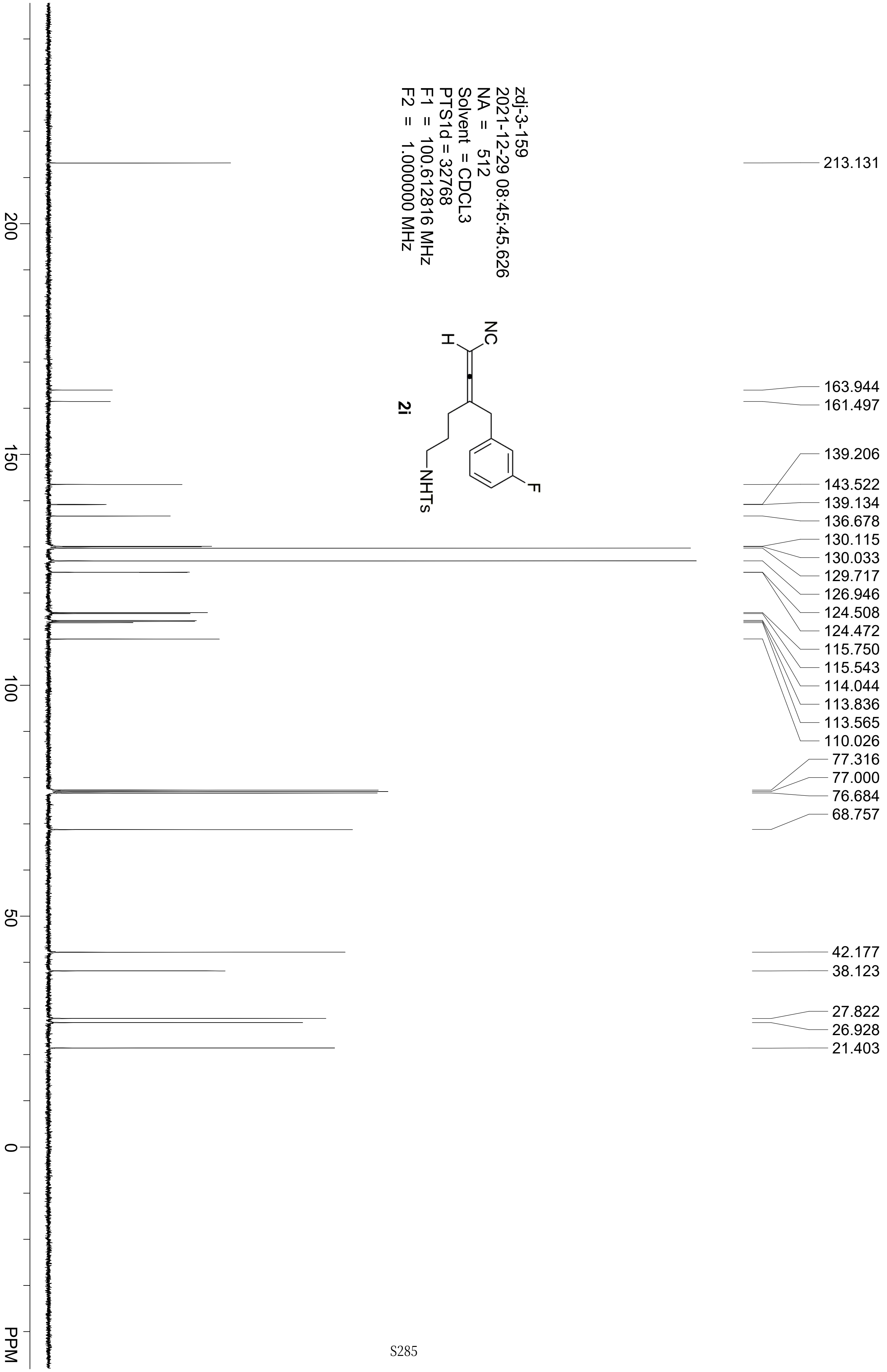
2g

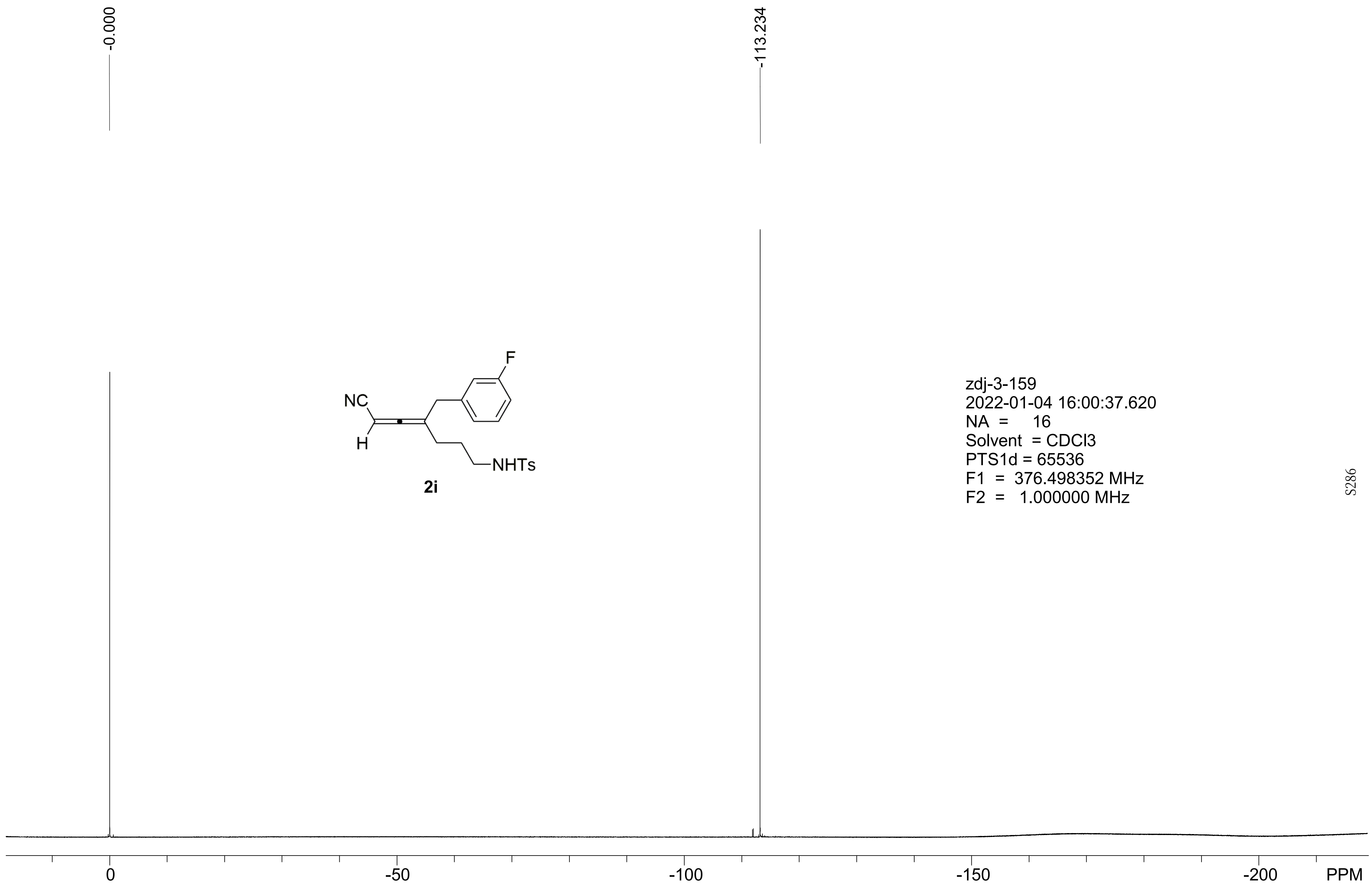

zdj-3-130
2021-12-12 01:47:04.609
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
NC
H
NHTs
2h
10
8
6
4
2
0PPM
1.98
5.12
1.96
0.94
0.98
2.01
2.02
3.00
2.01
2.03
7.738
7.717
7.319
7.310
7.305
7.301
7.299
7.290
7.287
7.263
7.261
7.251
7.246
7.238
7.227
7.149
7.145
7.128
5.137
5.130
5.122
5.115
5.108
4.717
4.702
4.686
3.341
2.939
2.922
2.906
2.889
2.428
2.073
2.065
2.055
2.047
2.036
2.028
1.635
1.618
1.599
1.581
1.564
0.000

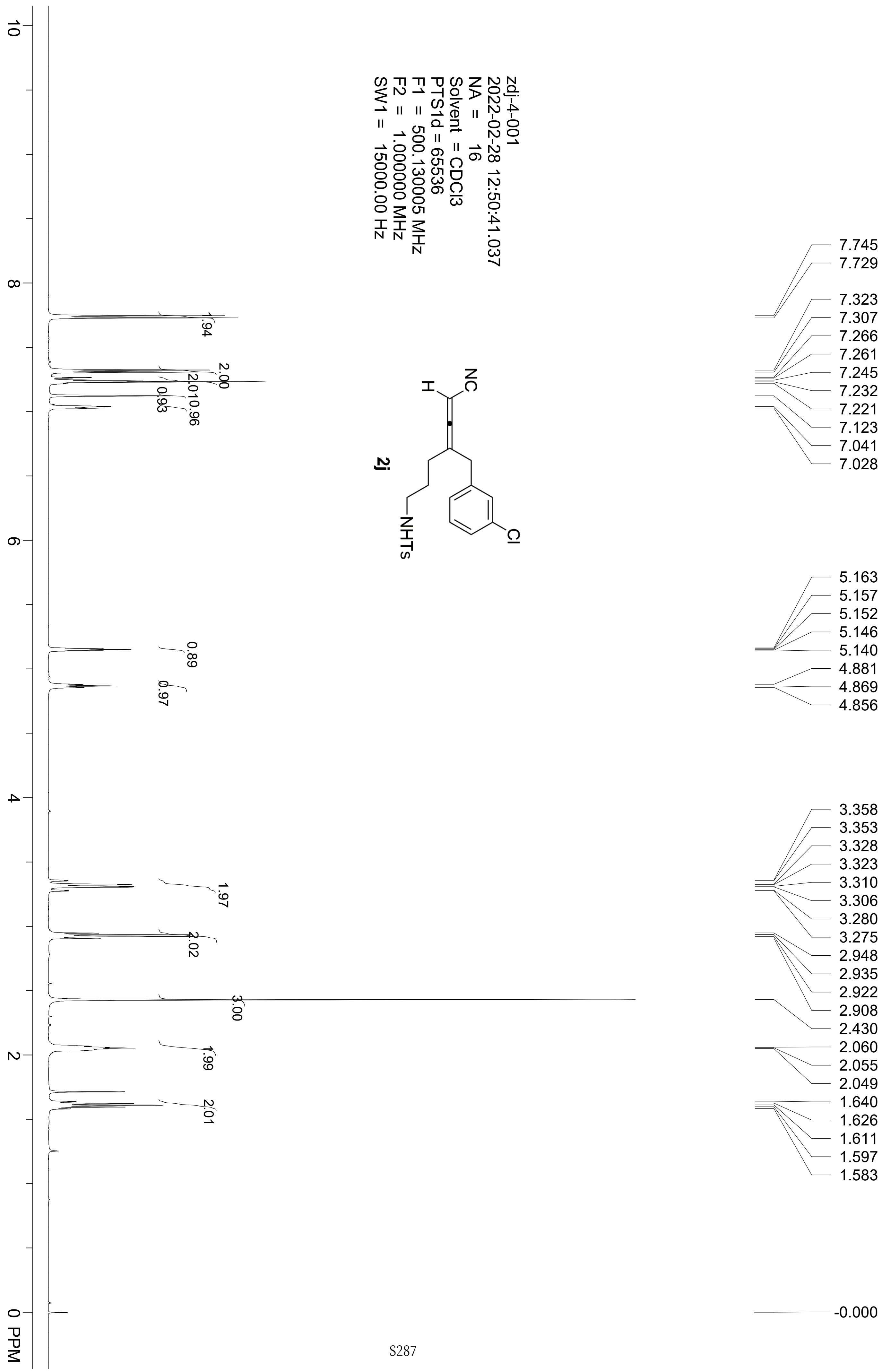

213.258
143.540
136.768
136.687
129.753
128.805
128.625
127.072
127.009
113.764
110.396
77.316
77.000
76.684
68.495
42.258
38.602
27.786
27.073
21.475
zdj-3-130
2021-12-12 02:11:05.677
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz
NC
H
NHTs
2h
200
150
100
50
0
PPM

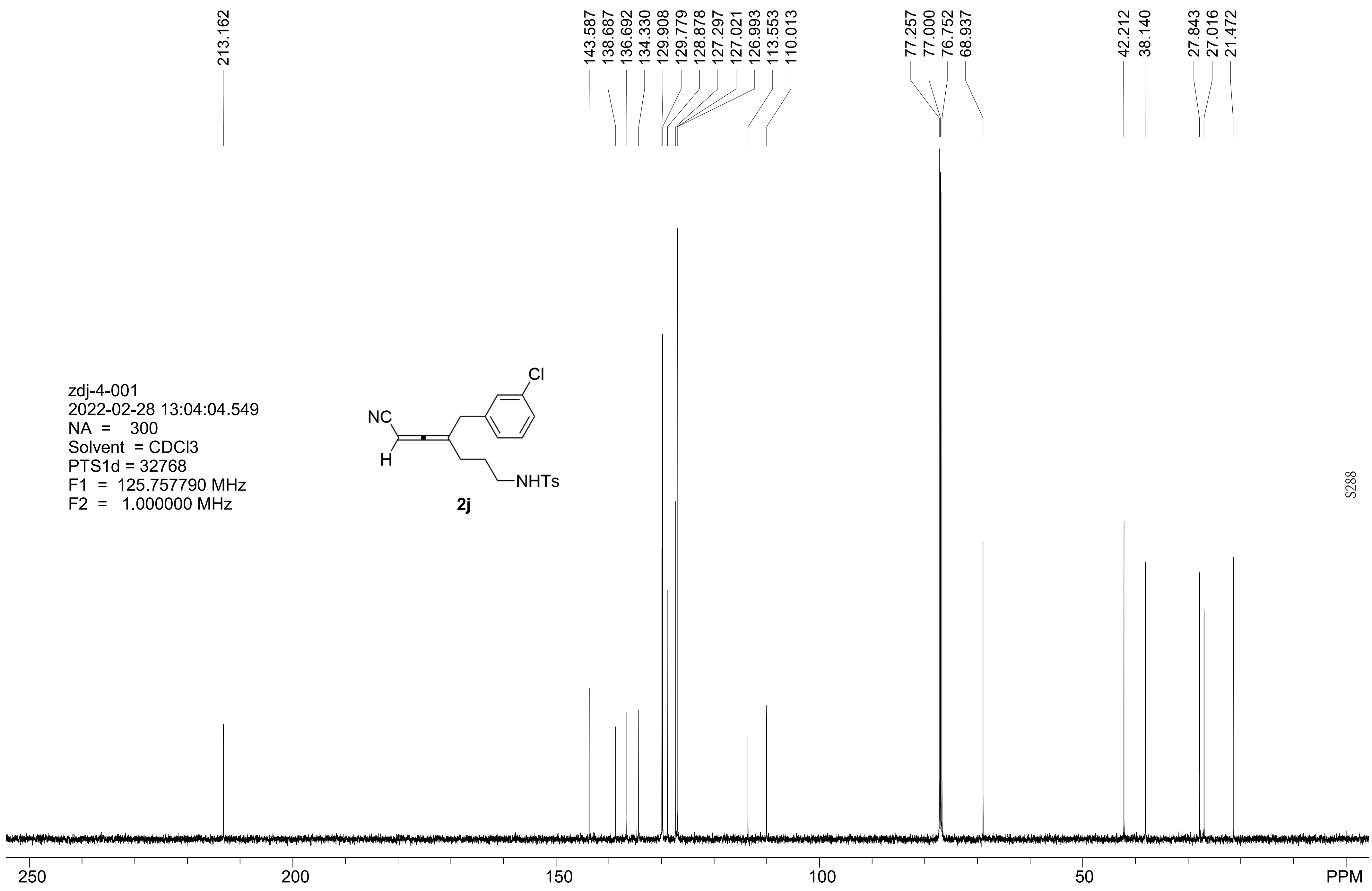

zdj-3-159
2021-12-29 08:45:45.111
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
NC
H
F
NHTs
10
8
6
4
2
0
PPM
2.00
3.05
1.92
0.94
0.95
0.98
1.94
2.02
3.00
1.95
1.99
7.750
7.729
7.320
7.300
7.270
7.256
7.236
6.959
6.952
6.932
6.915
6.846
6.823
5.148
5.141
5.134
5.084
5.069
3.327
2.944
2.927
2.910
2.894
2.425
2.070
2.052
1.642
1.624
1.606
1.588
1.570
-0.000

2i

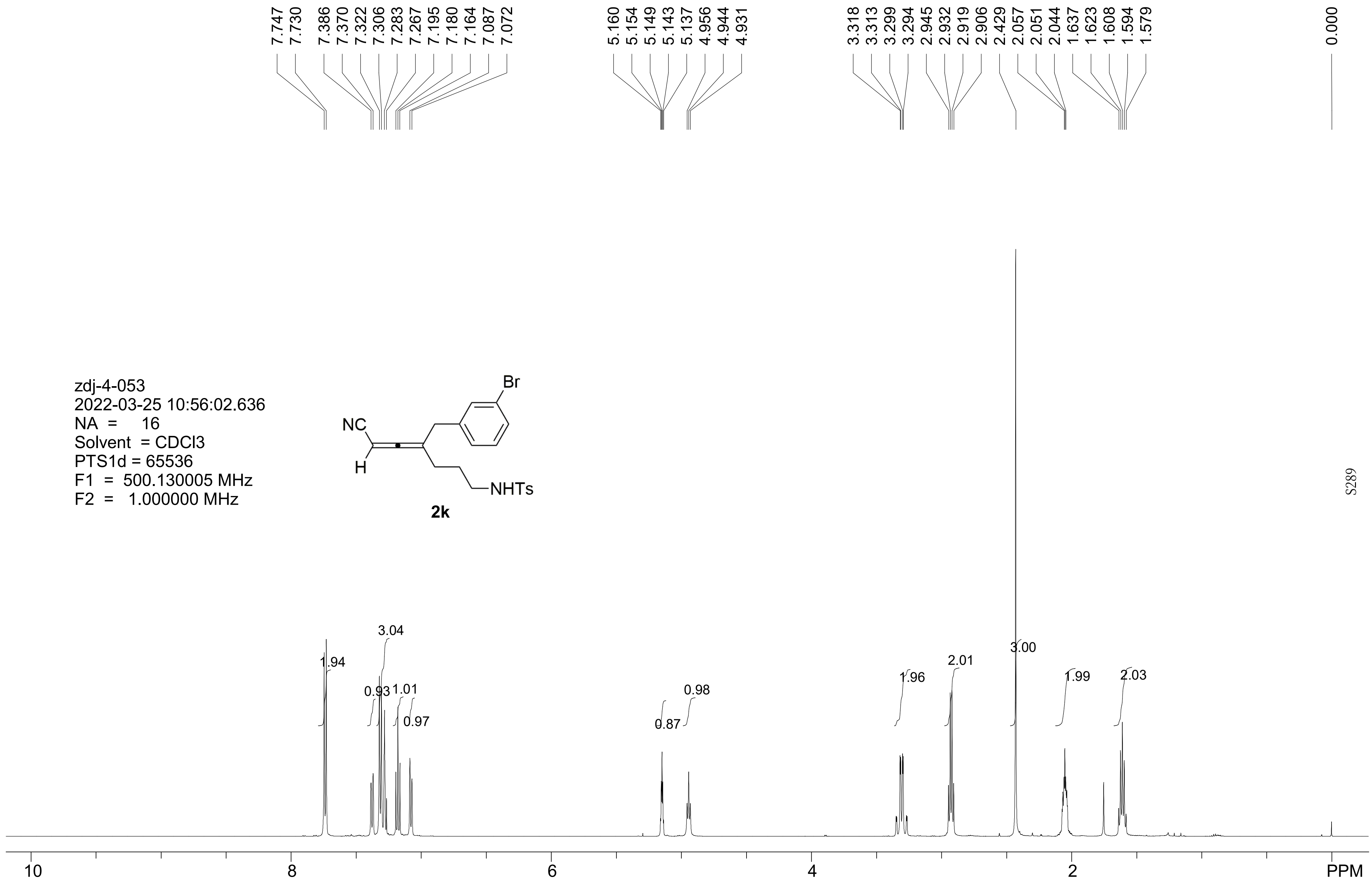

zdj-3-159
2021-12-29 08:45:45.626
NA = 512
Solvent = CDCL3
PTS1d = 32768
F1 = 100.612816 MHz
F2 = 1.000000 MHz
NC
H
F
NHTs
2i
213.131
163.944
161.497
139.206
143.522
139.134
136.678
130.115
130.033
129.717
126.946
124.508
124.472
115.750
115.543
114.044
113.836
113.565
110.026
77.316
77.000
76.684
68.757
42.177
38.123
27.822
26.928
21.403
200
150
100
50
0
PPM


2i
-0.000
-113.234
NC
H
F
NHTs
zdj-3-159
2022-01-04 16:00:37.620
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 376.498352 MHz
F2 = 1.000000 MHz
0
-50
-100
-150
-200
PPM


zdj-4-001
2022-02-28 12:50:41.037
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
SW1 = 15000.00 Hz
NC
H
Cl
NHTs
2j
7.745
7.729
7.323
7.307
7.266
7.261
7.245
7.232
7.221
7.123
7.041
7.028
5.163
5.157
5.152
5.146
5.140
4.881
4.869
4.856
3.358
3.353
3.328
3.323
3.310
3.306
3.280
3.275
2.948
2.935
2.922
2.908
2.430
2.060
2.055
2.049
1.640
1.626
1.611
1.597
1.583
-0.000
1.94
2.00
2.01
0.96
0.93
0.89
0.97
1.97
2.02
3.00
1.99
2.01
10
8
6
4
2
0 PPM

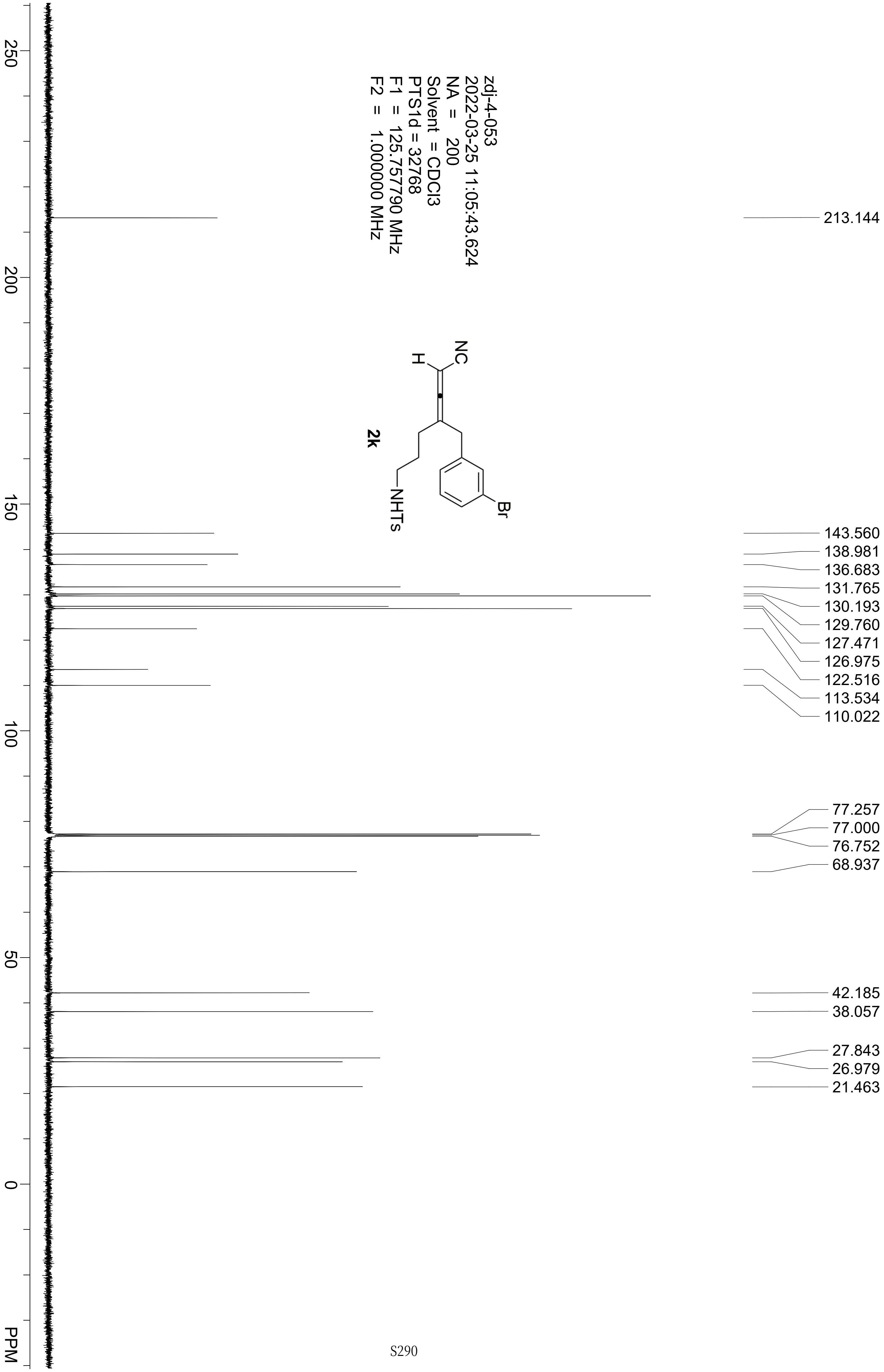

213.162
143.587
138.687
136.692
134.330
129.908
129.779
128.878
127.297
127.021
126.993
113.553
110.013
77.257
77.000
76.752
68.937
42.212
38.140
27.843
27.016
21.472
zdj-4-001
2022-02-28 13:04:04.549
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
Cl
NHTs
250
200
150
100
50
PPM

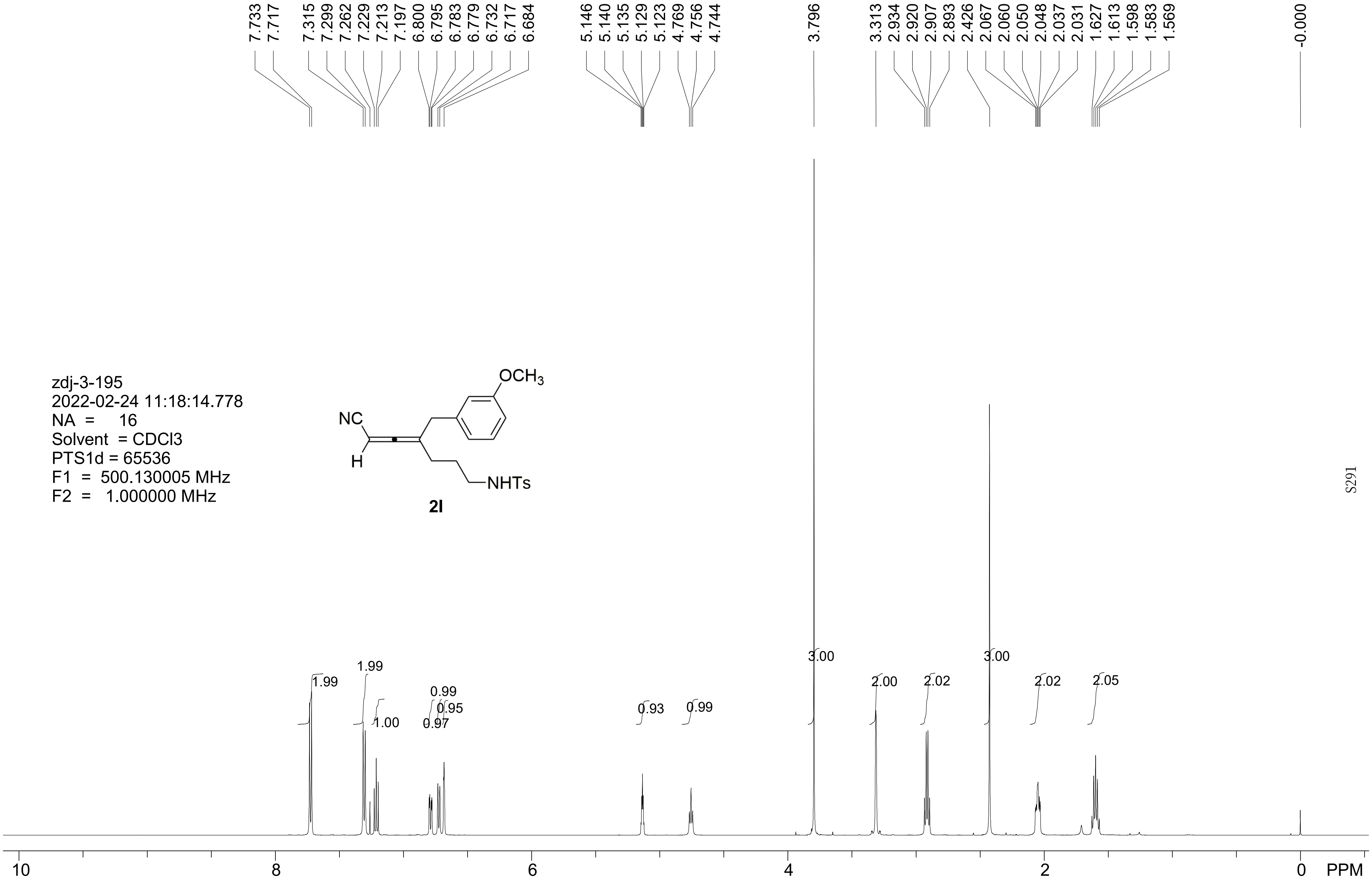
2j



zdj-4-053
2022-03-25 10:56:02.636
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz

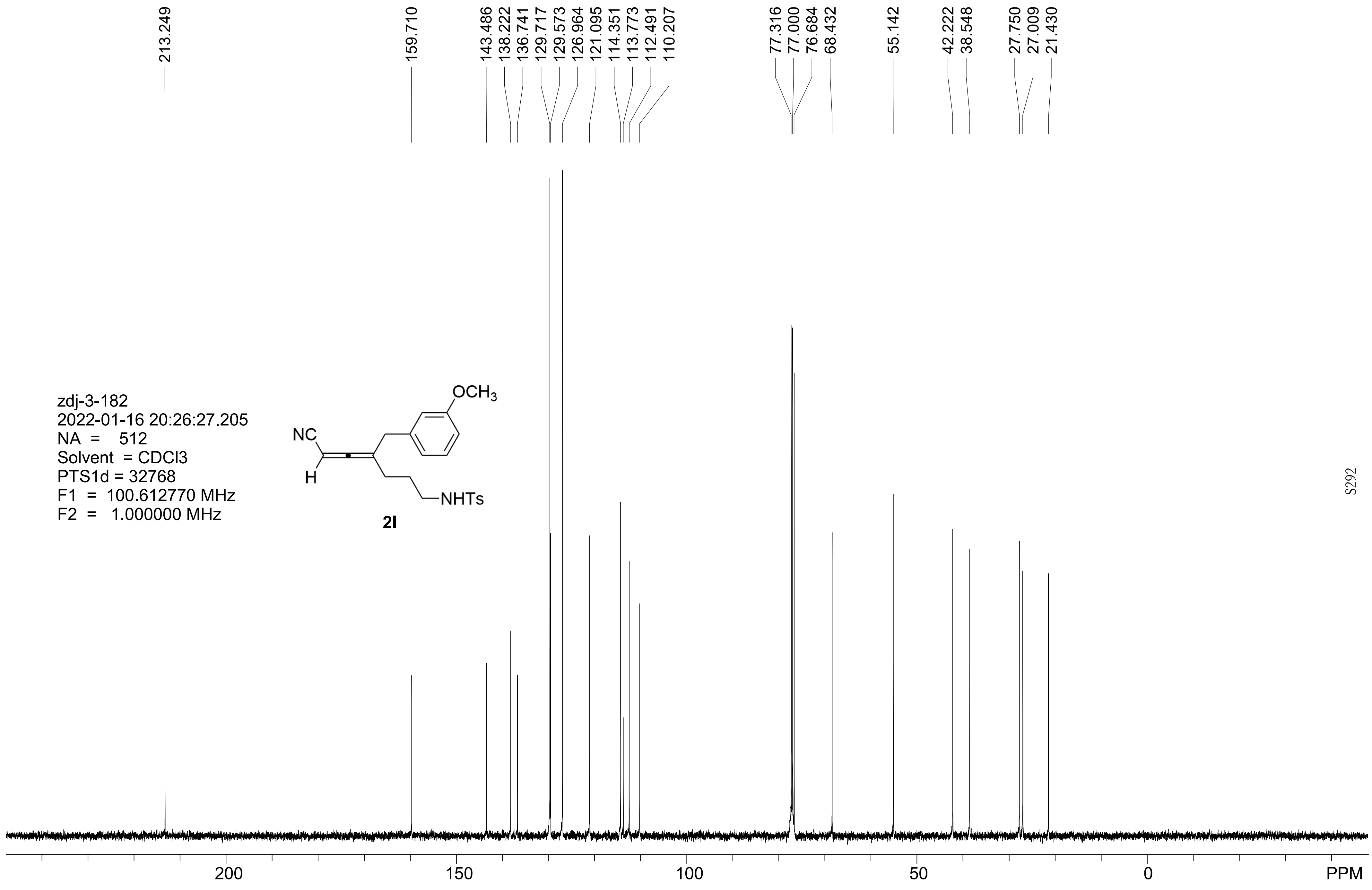
2k


zdj-4-053
2022-03-25 11:05:43.624
NA = 200
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
Br
NHTs
2k
213.144
143.560
138.981
136.683
131.765
130.193
129.760
127.471
126.975
122.516
113.534
110.022
77.257
77.000
76.752
68.937
42.185
38.057
27.843
26.979
21.463
250
200
150
100
50
0
PPM



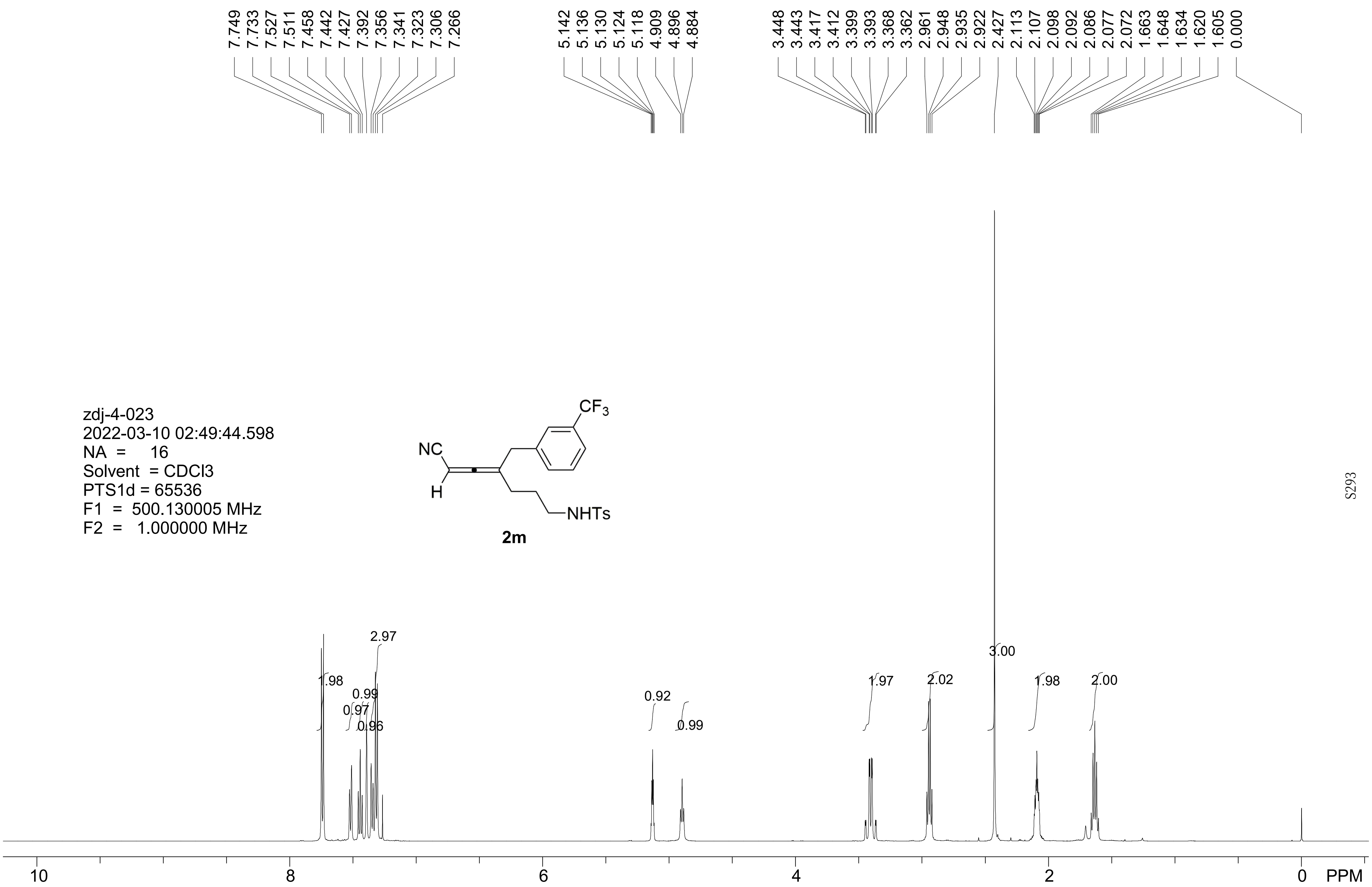
2l

zdj-3-195
2022-02-24 11:18:14.778
NA =   16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 =   1.000000 MHz
NC
H
OCH$_3$
NHTs
7.733
7.717
7.315
7.299
7.262
7.229
7.213
7.197
6.800
6.795
6.783
6.779
6.732
6.717
6.684
5.146
5.140
5.135
5.129
5.123
4.769
4.756
4.744
3.796
3.313
2.934
2.920
2.907
2.893
2.426
2.067
2.060
2.050
2.048
2.037
2.031
1.627
1.613
1.598
1.583
1.569
-0.000
1.99
1.99
1.00
0.99
0.95
0.97
0.93
0.99
3.00
2.00
2.02
3.00
2.02
2.05
10
8
6
4
2
0
PPM

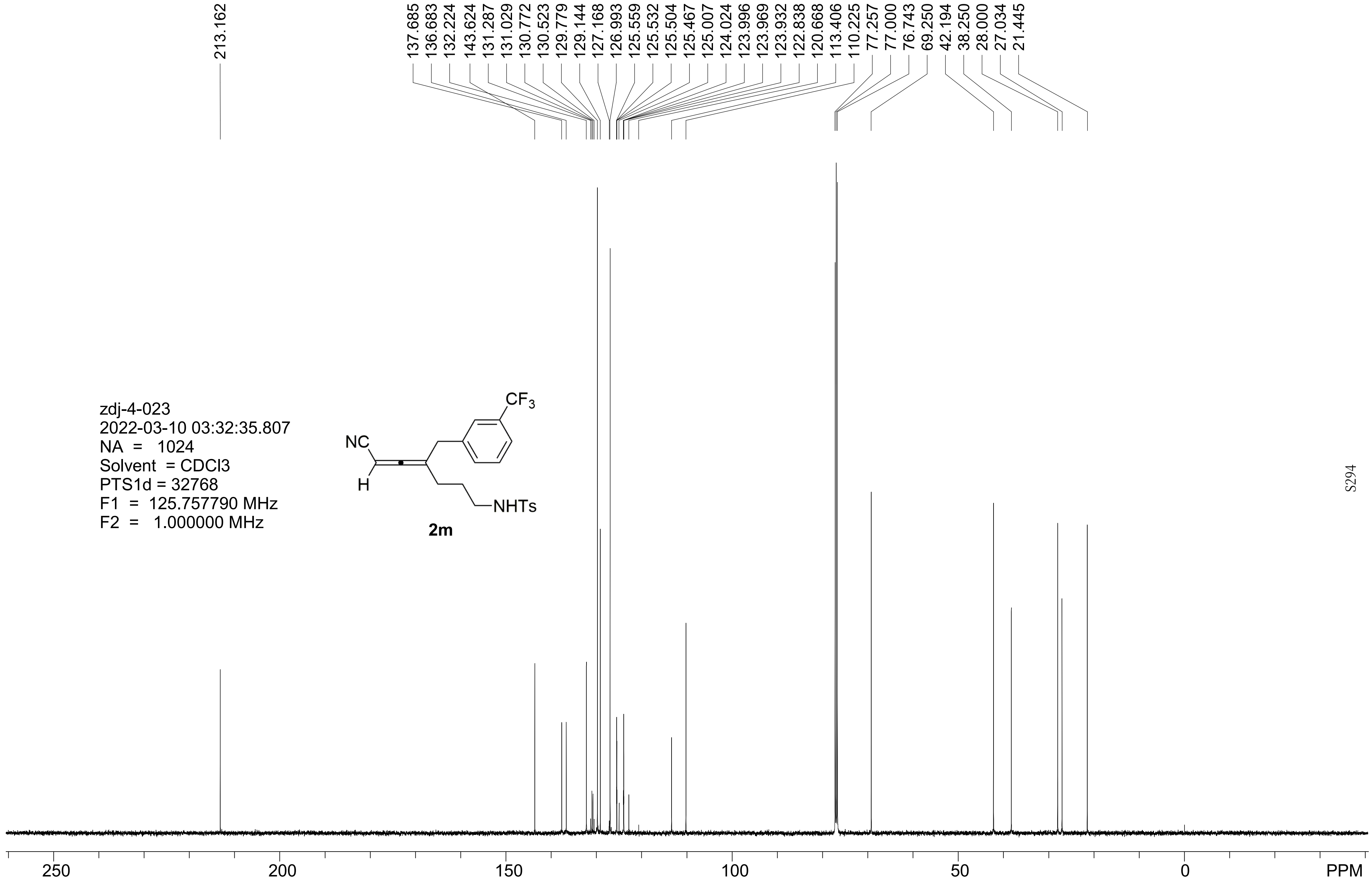


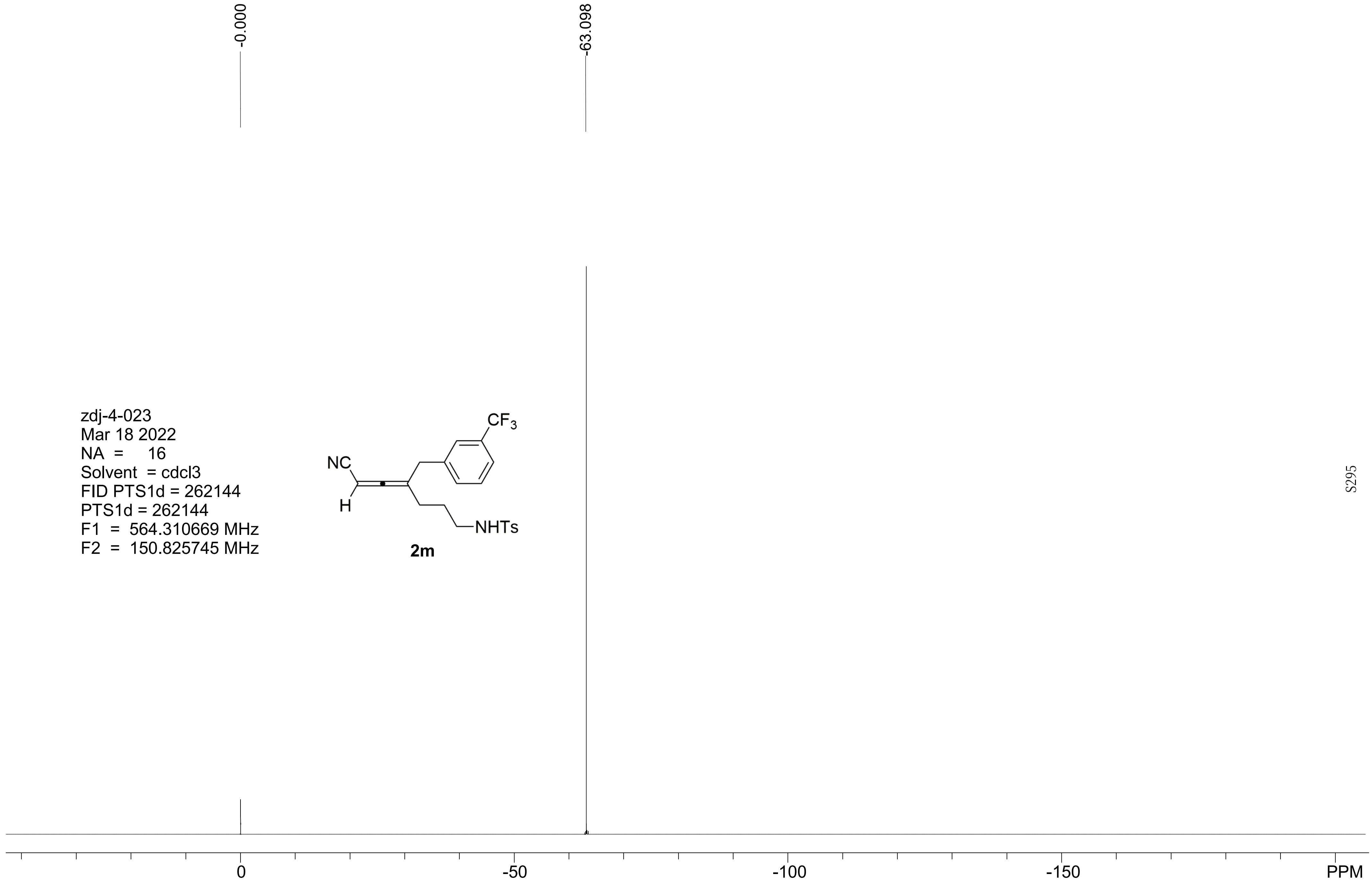
zdj-3-182
2022-01-16 20:26:27.205
NA = 512
Solvent = CDCl3
PTS1d = 32768
F1 = 100.612770 MHz
F2 = 1.000000 MHz

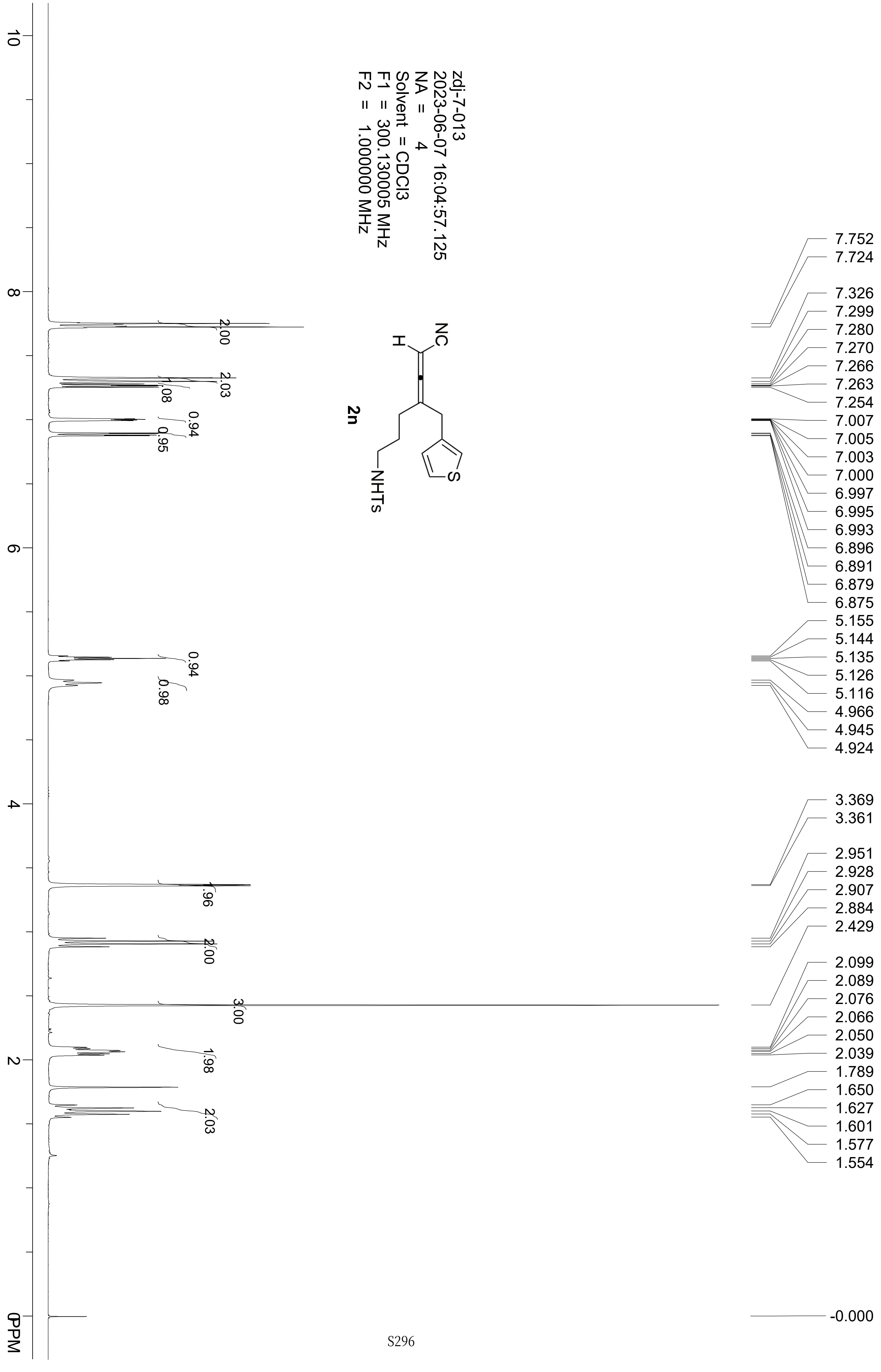
2l

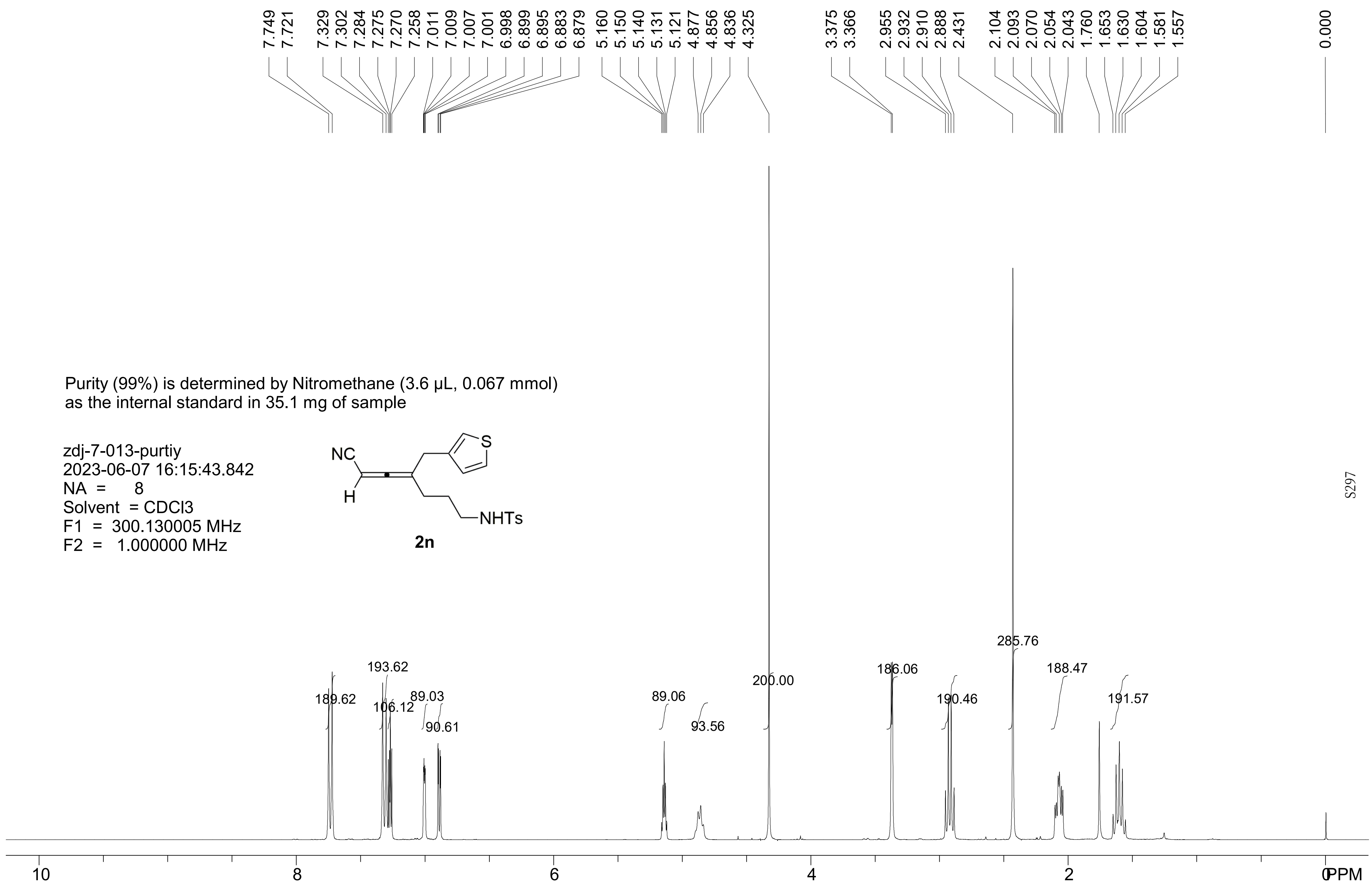

zdj-4-023
2022-03-10 02:49:44.598
NA =   16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz

2m


213.162
137.685
136.683
132.224
143.624
131.287
131.029
130.772
130.523
129.779
129.144
127.168
126.993
125.559
125.532
125.504
125.467
125.007
124.024
123.996
123.969
123.932
122.838
120.668
113.406
110.225
77.257
77.000
76.743
69.250
42.194
38.250
28.000
27.034
21.445
zdj-4-023
2022-03-10 03:32:35.807
NA = 1024
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
CF3
NHTs
2m
250
200
150
100
50
0
PPM


-0.000
-63.098
zdj-4-023
Mar 18 2022
NA =   16
Solvent = cdcl3
FID PTS1d = 262144
PTS1d = 262144
F1 = 564.310669 MHz
F2 = 150.825745 MHz
NC
H
CF$_3$
NHTs
2m
0
-50
-100
-150
PPM

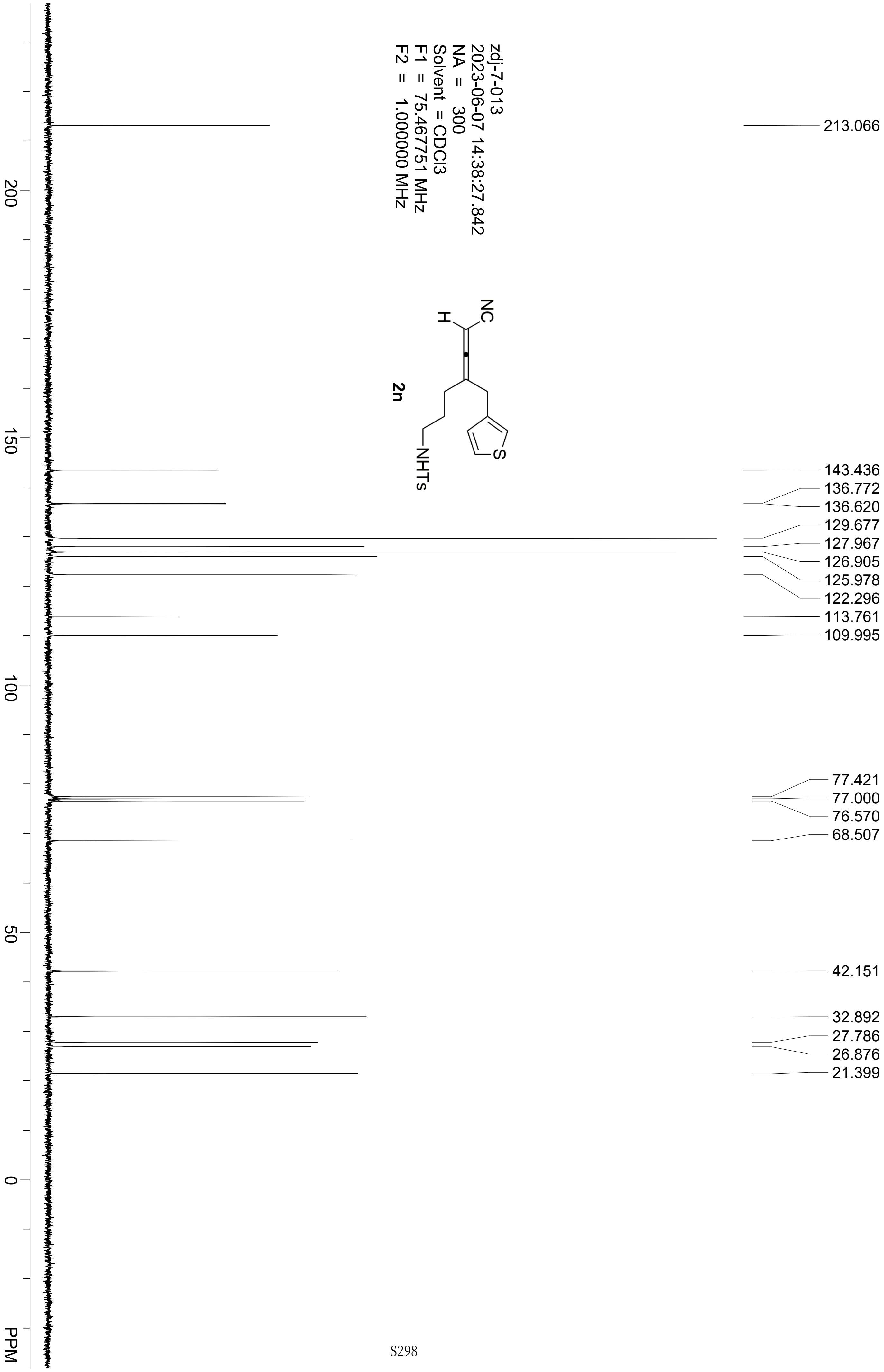

zdj-7-013
2023-06-07 16:04:57.125
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
H
S
NHTs
2n
10
8
6
4
2
0
PPM
2.00
2.03
1.08
0.94
0.95
0.94
0.98
1.96
2.00
3.00
1.98
2.03
7.752
7.724
7.326
7.299
7.280
7.270
7.266
7.263
7.254
7.007
7.005
7.003
7.000
6.997
6.995
6.993
6.896
6.891
6.879
6.875
5.155
5.144
5.135
5.126
5.116
4.966
4.945
4.924
3.369
3.361
2.951
2.928
2.907
2.884
2.429
2.099
2.089
2.076
2.066
2.050
2.039
1.789
1.650
1.627
1.601
1.577
1.554
-0.000

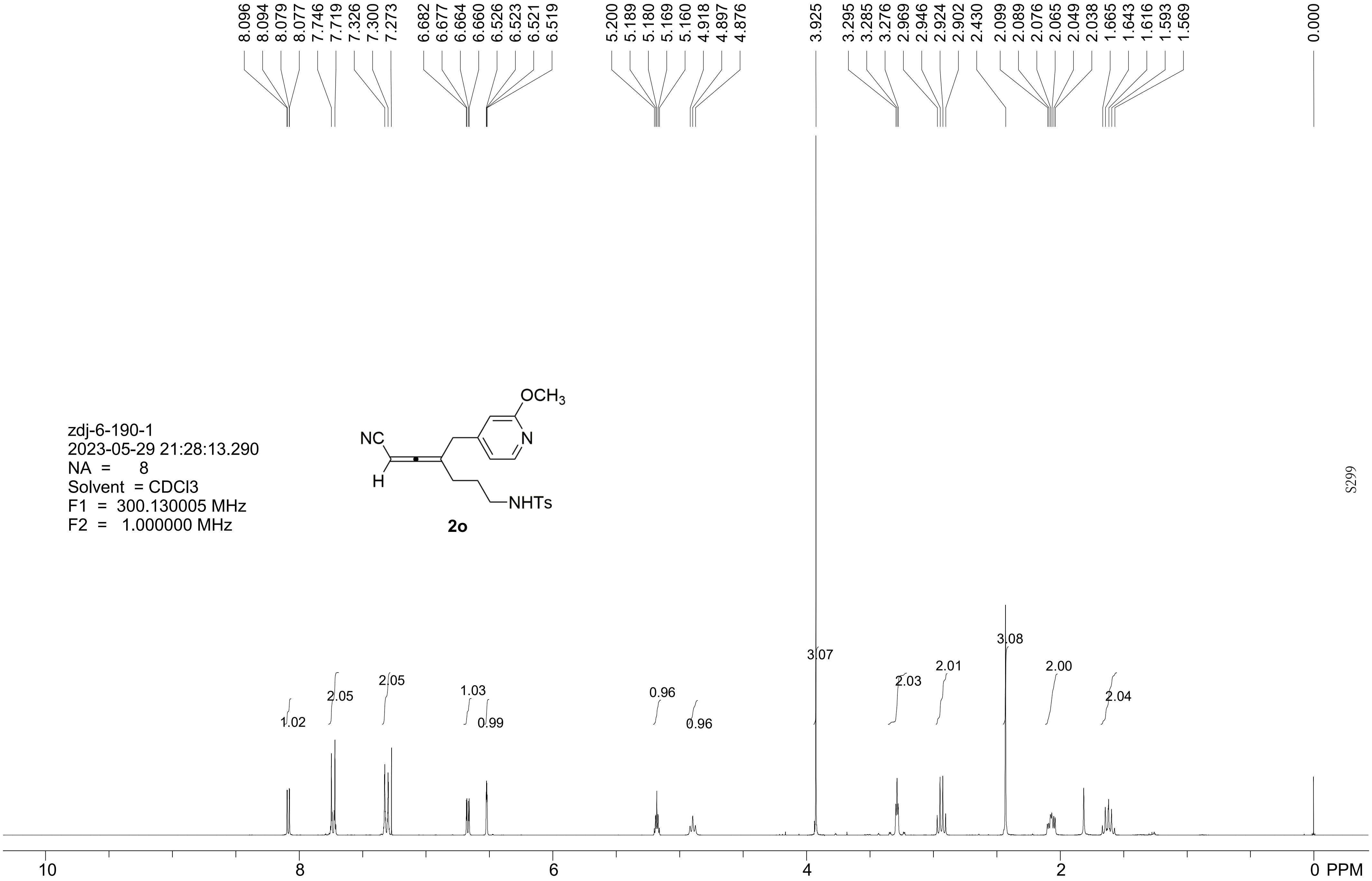


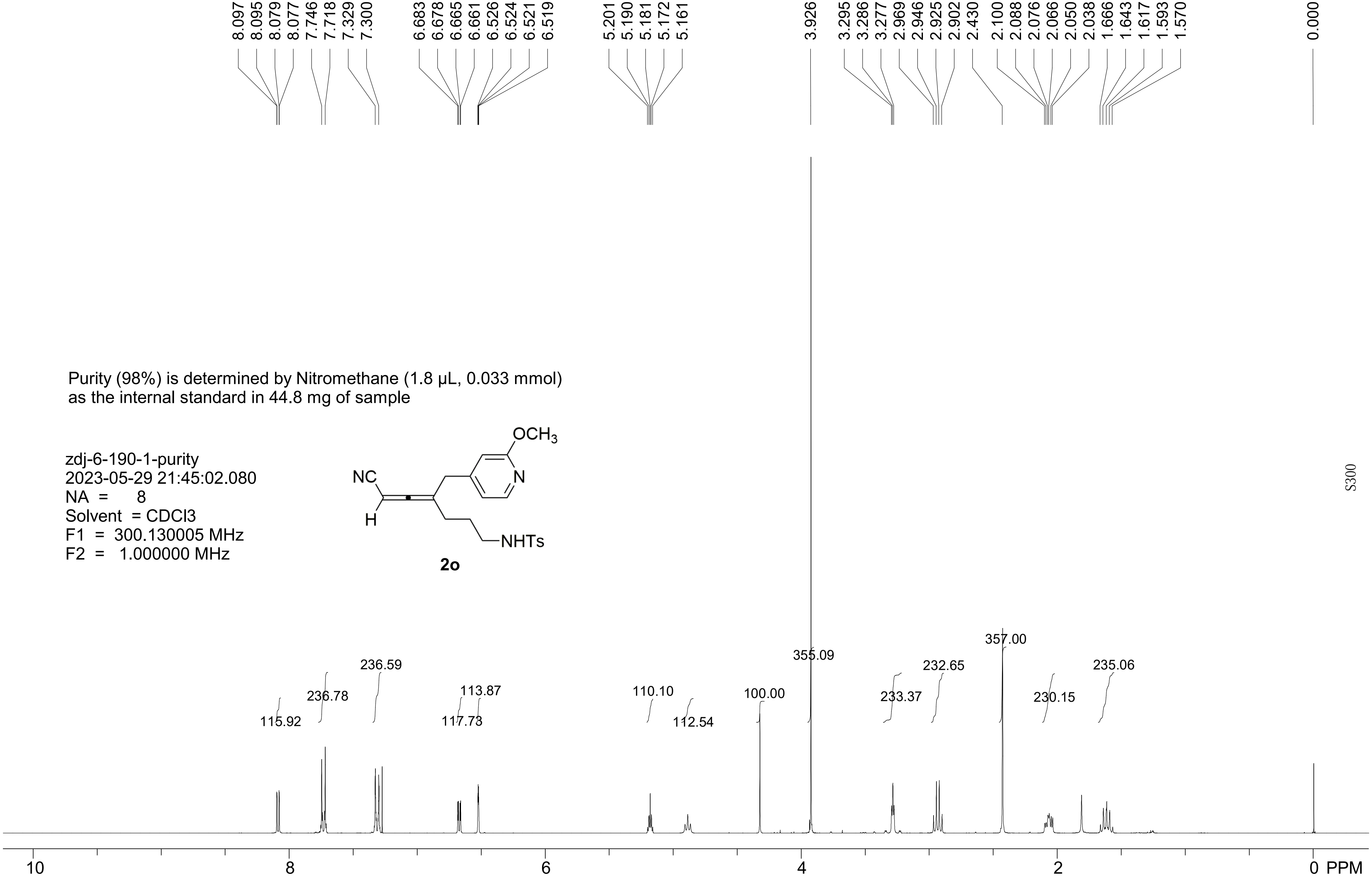
Purity (99%) is determined by Nitromethane (3.6 μL, 0.067 mmol)
as the internal standard in 35.1 mg of sample

zdj-7-013-purtiy
2023-06-07 16:15:43.842
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz

2n


zdj-7-013
2023-06-07 14:38:27.842
NA = 300
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
NC
H
S
NHTs
2n
213.066
143.436
136.772
136.620
129.677
127.967
126.905
125.978
122.296
113.761
109.995
77.421
77.000
76.570
68.507
42.151
32.892
27.786
26.876
21.399
200
150
100
50
0
PPM

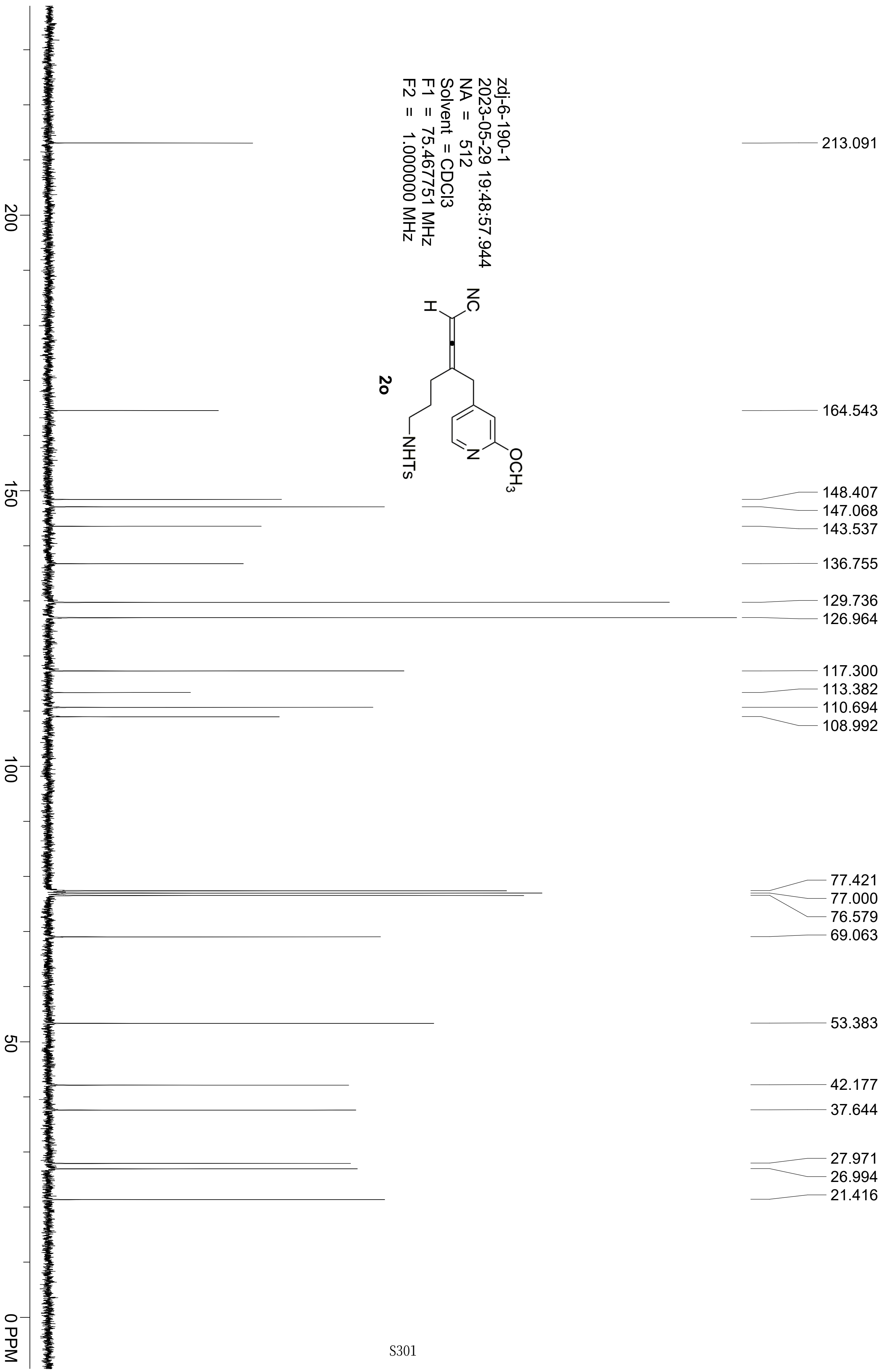

zdj-6-190-1
2023-05-29 21:28:13.290
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
H
OCH3
N
NHTs
2o
8.096
8.094
8.079
8.077
7.746
7.719
7.326
7.300
7.273
6.682
6.677
6.664
6.660
6.526
6.523
6.521
6.519
5.200
5.189
5.180
5.169
5.160
4.918
4.897
4.876
3.925
3.295
3.285
3.276
2.969
2.946
2.924
2.902
2.430
2.099
2.089
2.076
2.065
2.049
2.038
1.665
1.643
1.616
1.593
1.569
0.000
1.02
2.05
2.05
1.03
0.99
0.96
0.96
3.07
2.03
2.01
3.08
2.00
2.04
10
8
6
4
2
0 PPM



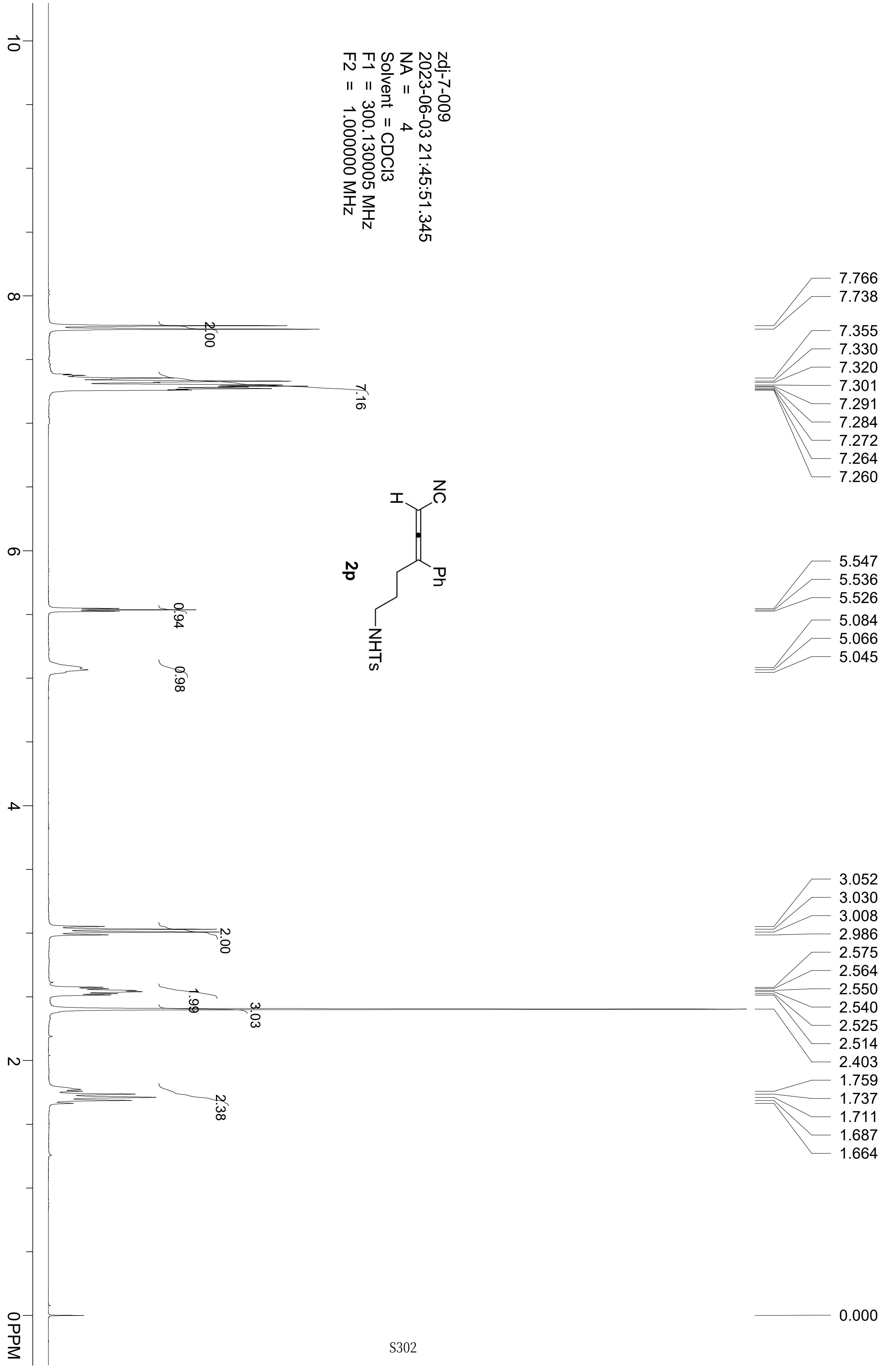
2o

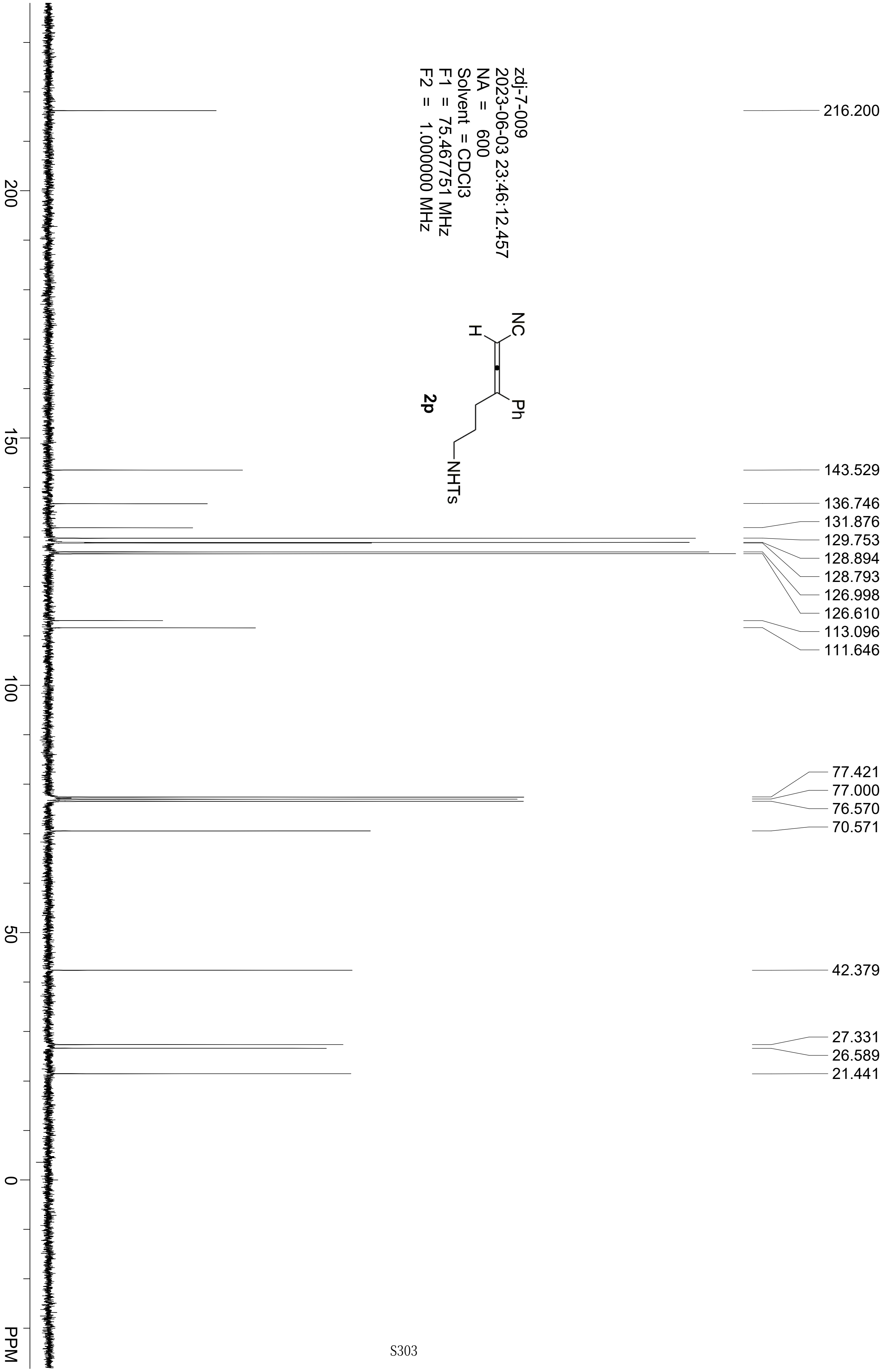
Purity (98%) is determined by Nitromethane (1.8 μL, 0.033 mmol)
as the internal standard in 44.8 mg of sample

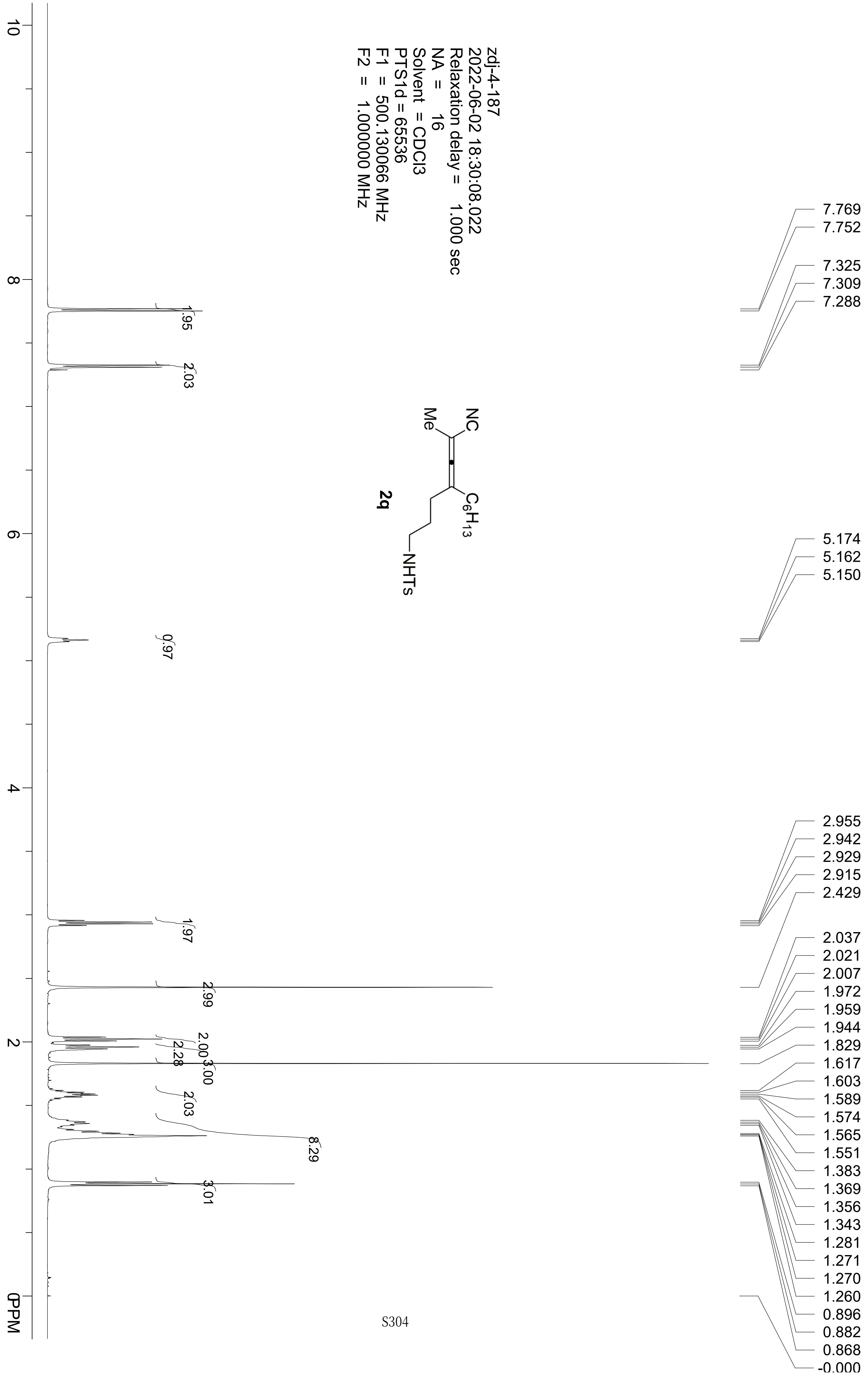
zdj-6-190-1-purity
2023-05-29 21:45:02.080
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz

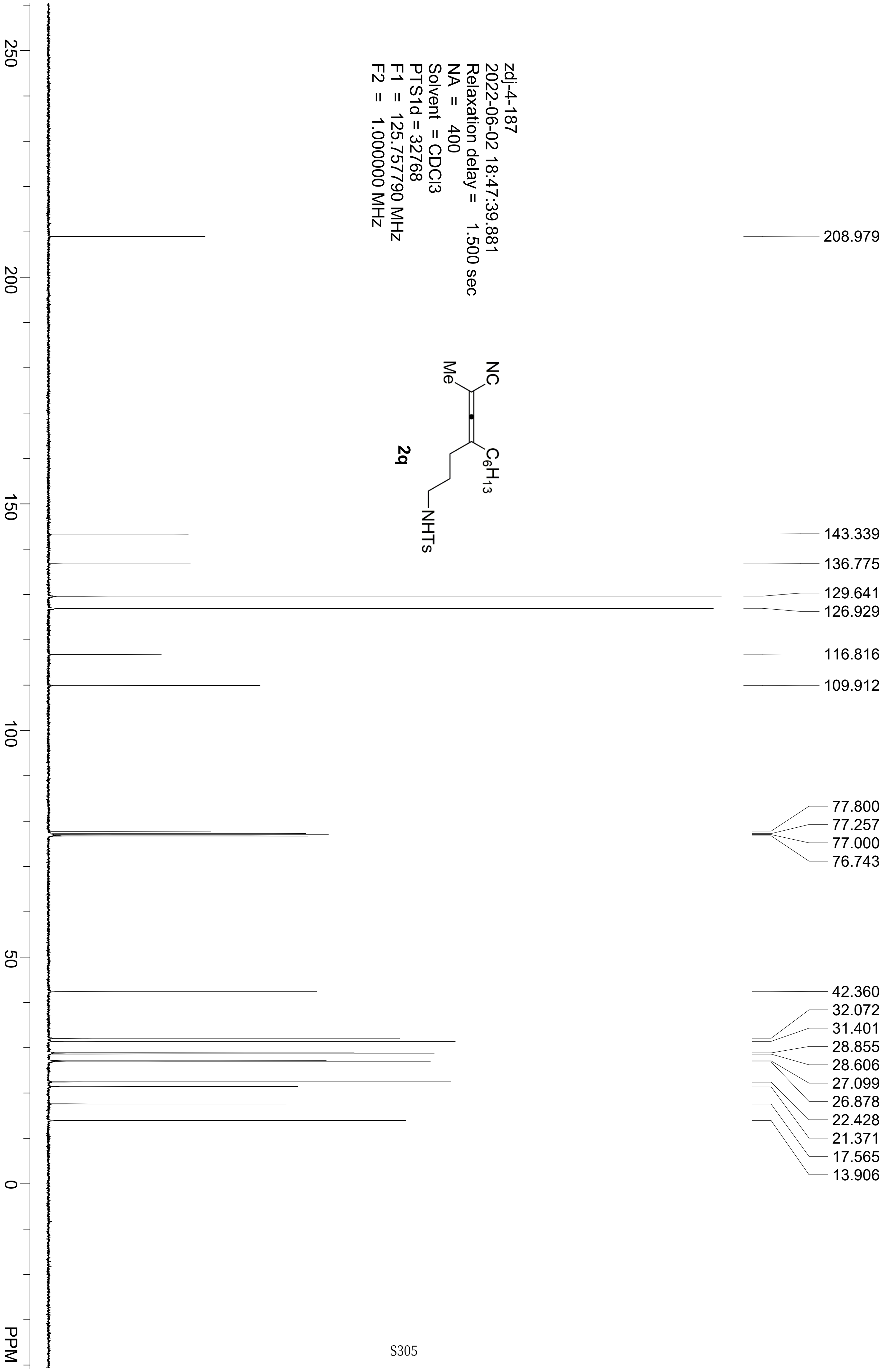

zdj-6-190-1
2023-05-29 19:48:57.944
NA = 512
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
NC
H
OCH$_3$
N
NHTs
213.091
164.543
148.407
147.068
143.537
136.755
129.736
126.964
117.300
113.382
110.694
108.992
77.421
77.000
76.579
69.063
53.383
42.177
37.644
27.971
26.994
21.416
200
150
100
50
0 PPM

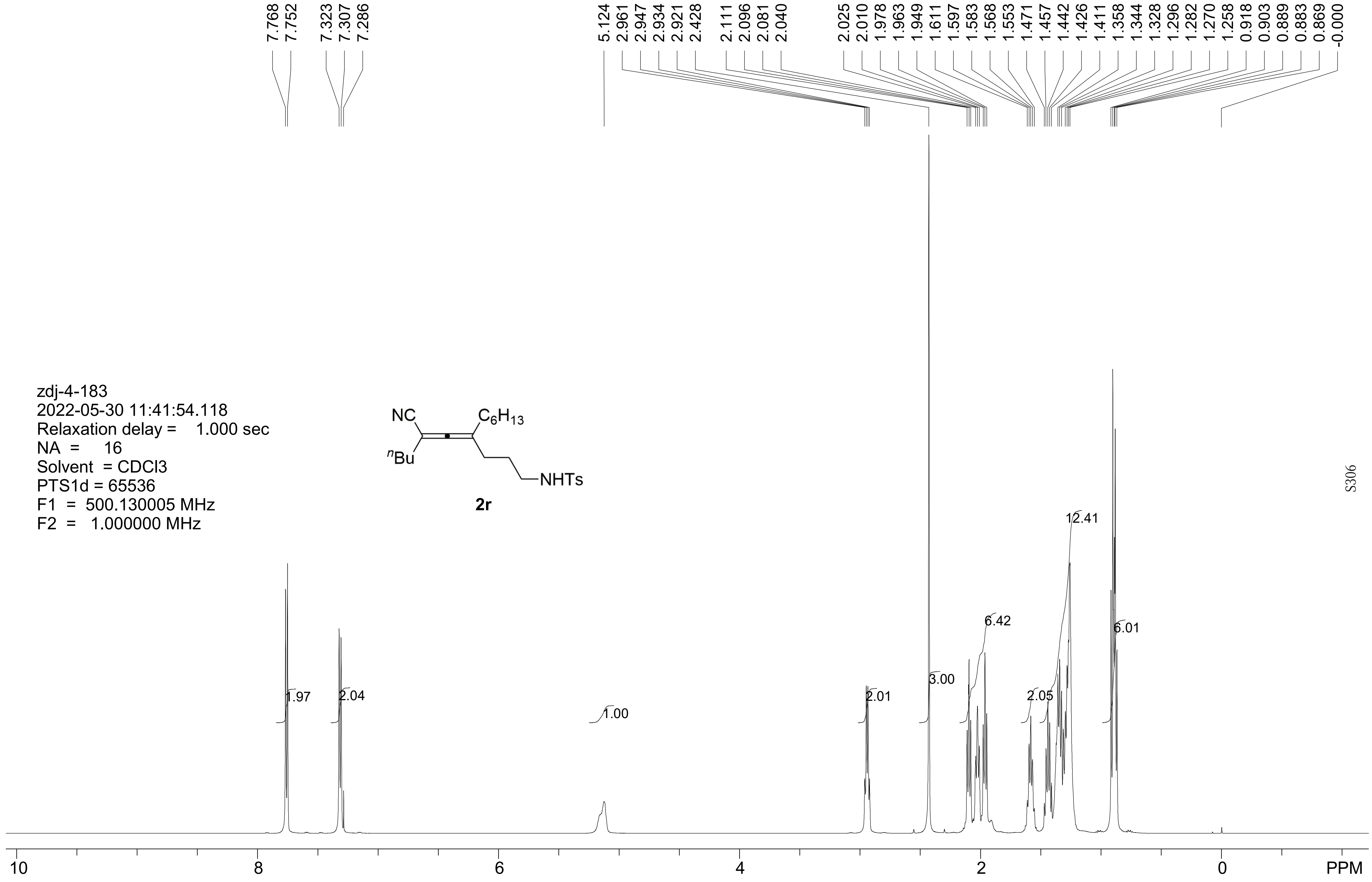
2o


zdj-7-009
2023-06-03 21:45:51.345
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
H
Ph
NHTs
2p
10
8
6
4
2
0PPM
2.00
7.16
0.94
0.98
2.00
1.99
3.03
2.38
7.766
7.738
7.355
7.330
7.320
7.301
7.291
7.284
7.272
7.264
7.260
5.547
5.536
5.526
5.084
5.066
5.045
3.052
3.030
3.008
2.986
2.575
2.564
2.550
2.540
2.525
2.514
2.403
1.759
1.737
1.711
1.687
1.664
0.000

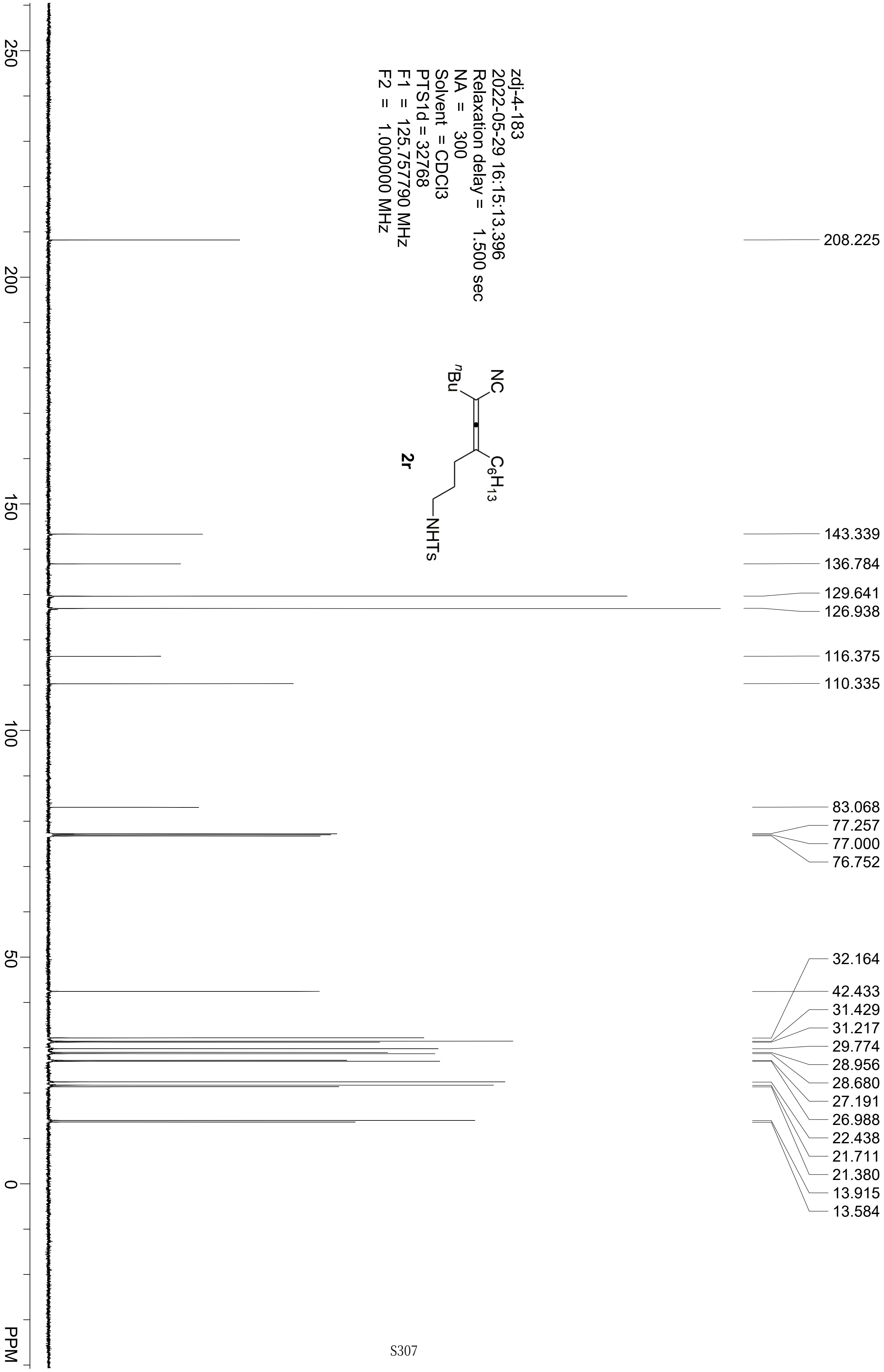

zdj-7-009
2023-06-03 23:46:12.457
NA = 600
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
NC
H
Ph
NHTs
2p
216.200
143.529
136.746
131.876
129.753
128.894
128.793
126.998
126.610
113.096
111.646
77.421
77.000
76.570
70.571
42.379
27.331
26.589
21.441
200
150
100
50
0
PPM

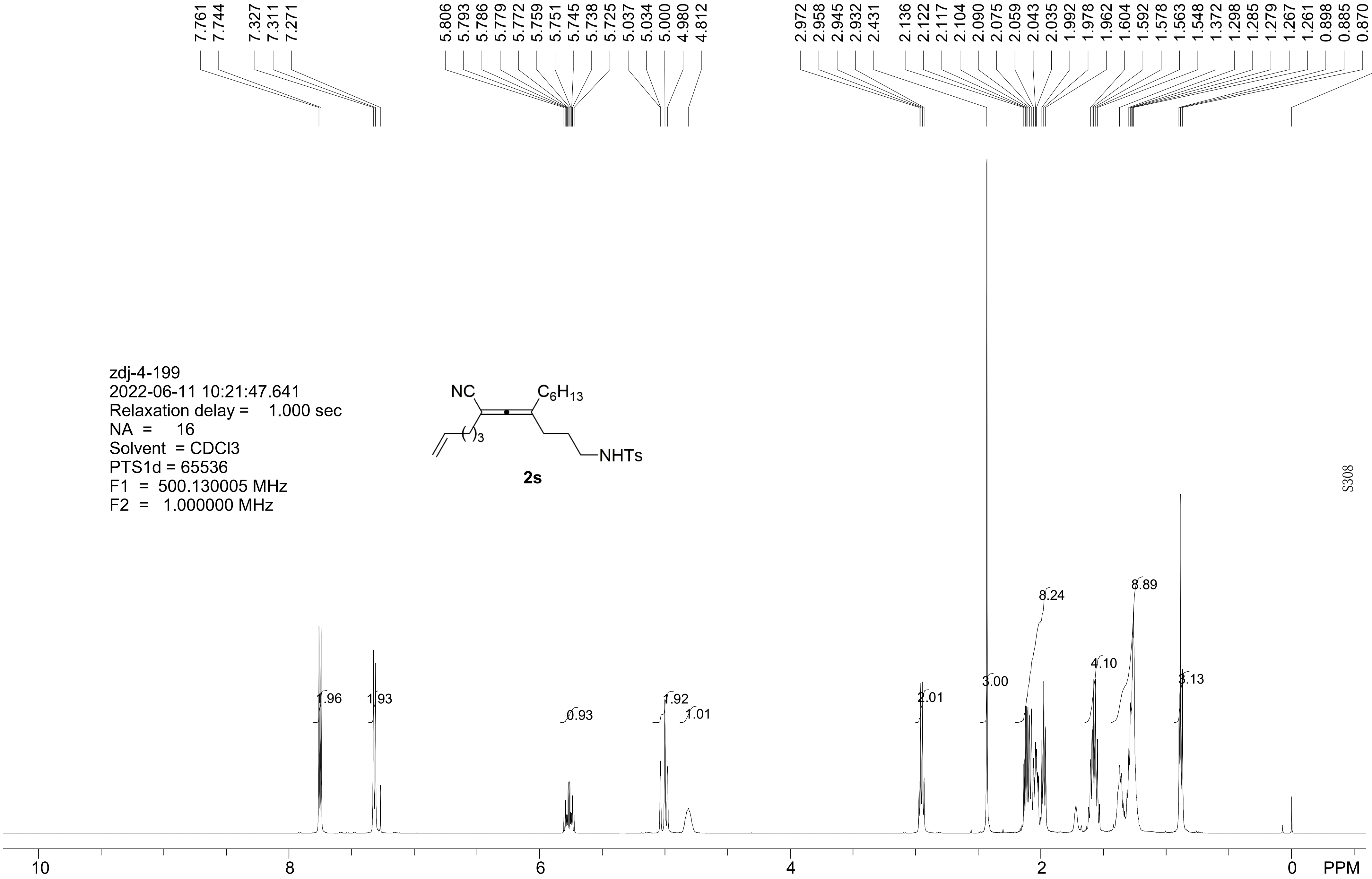

zdj-4-187
2022-06-02 18:30:08.022
Relaxation delay = 1.000 sec
NA = 16
PTS1d = 65536
Solvent = CDCl3
F1 = 500.130066 MHz
F2 = 1.000000 MHz
NC
Me
C_6H_{13}
NHTs
2q
10
8
6
4
2
0
PPM
1.95
2.03
0.97
1.97
2.99
2.00
2.28
3.00
2.03
8.29
3.01
7.769
7.752
7.325
7.309
7.288
5.174
5.162
5.150
2.955
2.942
2.929
2.915
2.429
2.037
2.021
2.007
1.972
1.959
1.944
1.829
1.617
1.603
1.589
1.574
1.565
1.551
1.383
1.369
1.356
1.343
1.281
1.271
1.270
1.260
0.896
0.882
0.868
-0.000


zdj-4-187
2022-06-02 18:47:39.881
Relaxation delay = 1.500 sec
NA = 400
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
Me
C6H13
NHTs
2q
208.979
143.339
136.775
129.641
126.929
116.816
109.912
77.800
77.257
77.000
76.743
42.360
32.072
31.401
28.855
28.606
27.099
26.878
22.428
21.371
17.565
13.906
250
200
150
100
50
0
PPM


zdj-4-183
2022-05-30 11:41:54.118
Relaxation delay =   1.000 sec
NA =   16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 =   1.000000 MHz

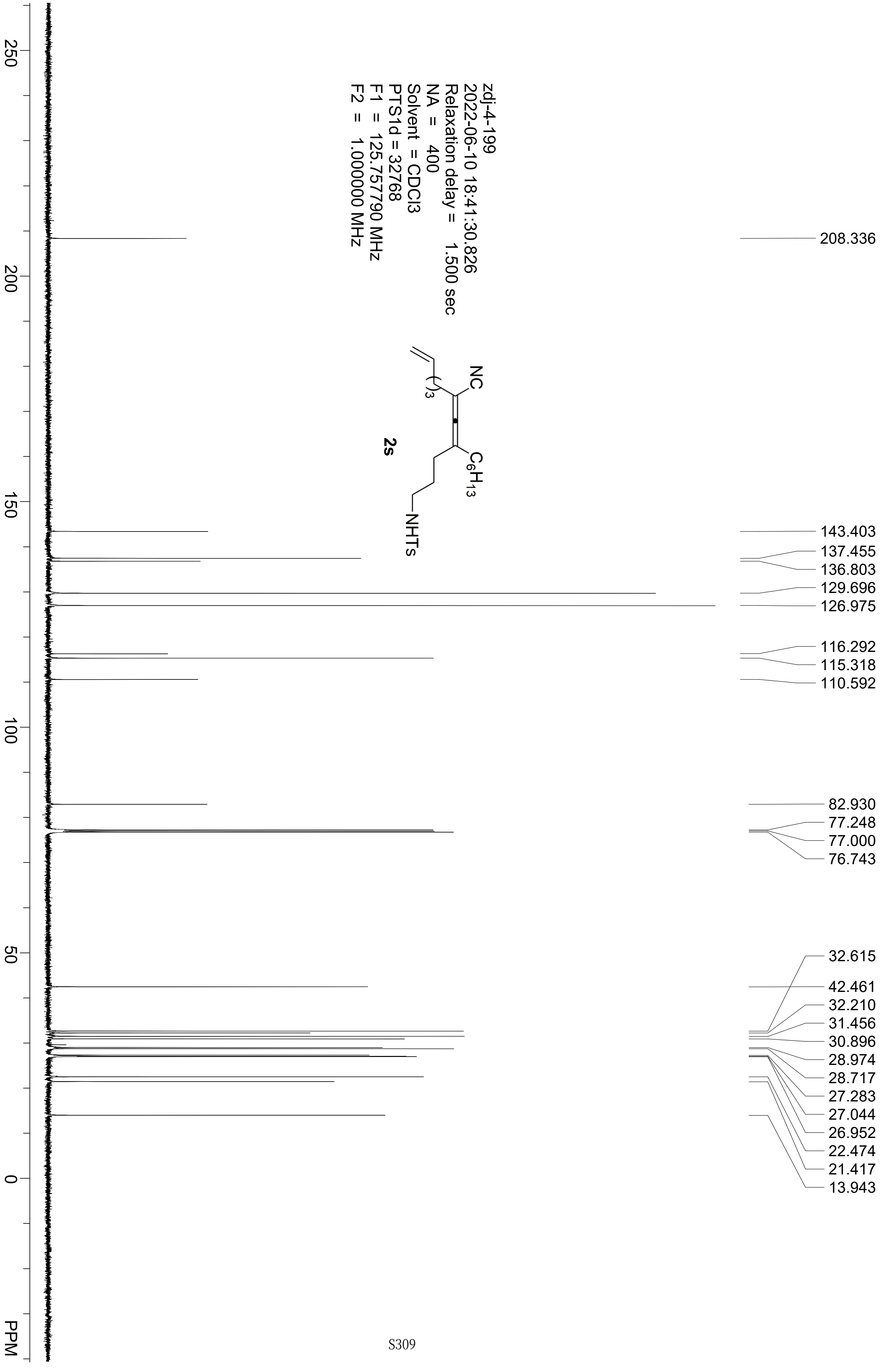
2r


zdj-4-183
2022-05-29 16:15:13.396
Relaxation delay = 1.500 sec
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
^{n}Bu
C_6H_{13}
NHTs
2r
250
200
150
100
50
0
PPM
208.225
143.339
136.784
129.641
126.938
116.375
110.335
83.068
77.257
77.000
76.752
32.164
42.433
31.429
31.217
29.774
28.956
28.680
27.191
26.988
22.438
21.711
21.380
13.915
13.584

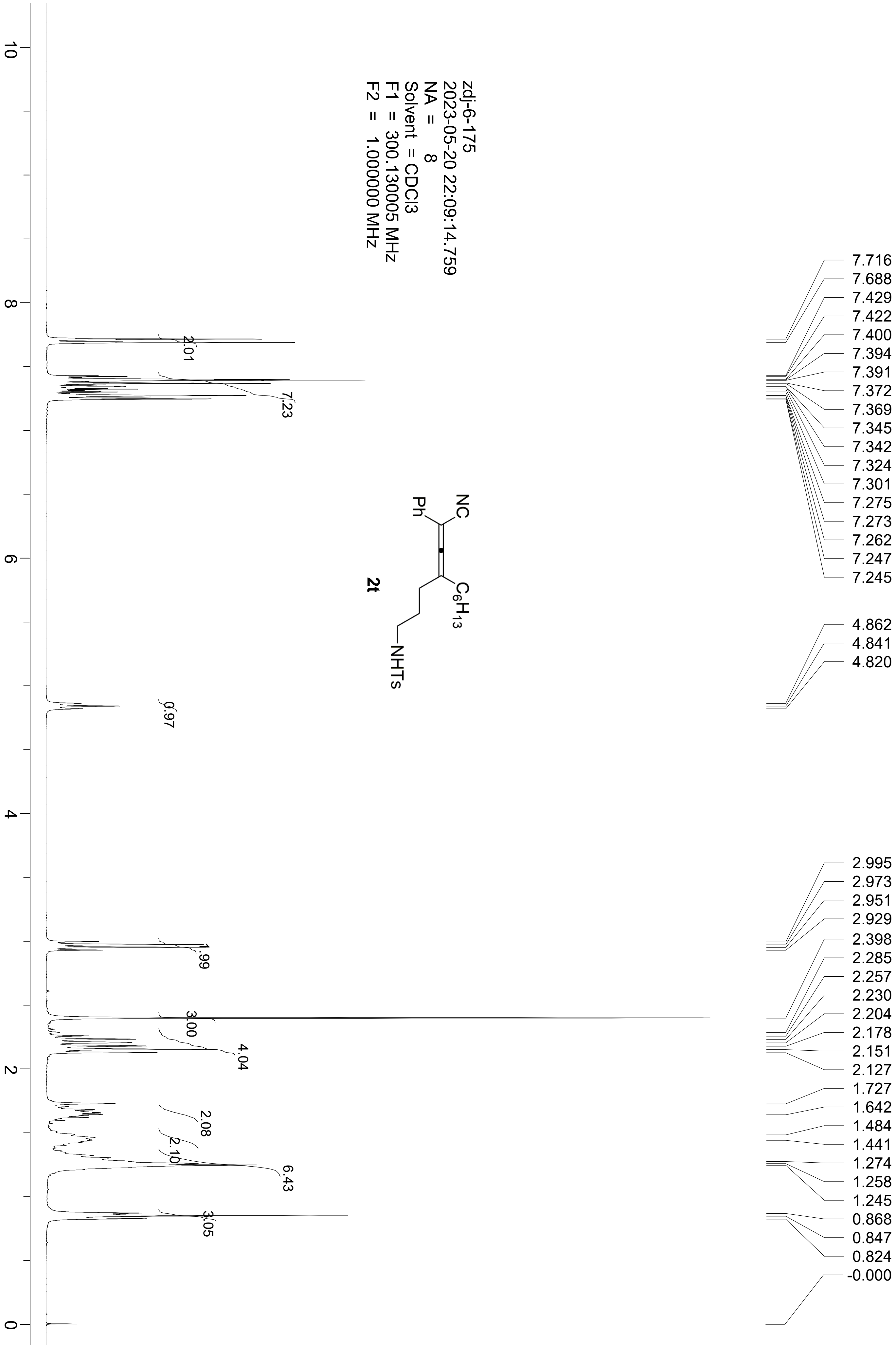


zdj-4-199
2022-06-11 10:21:47.641
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz

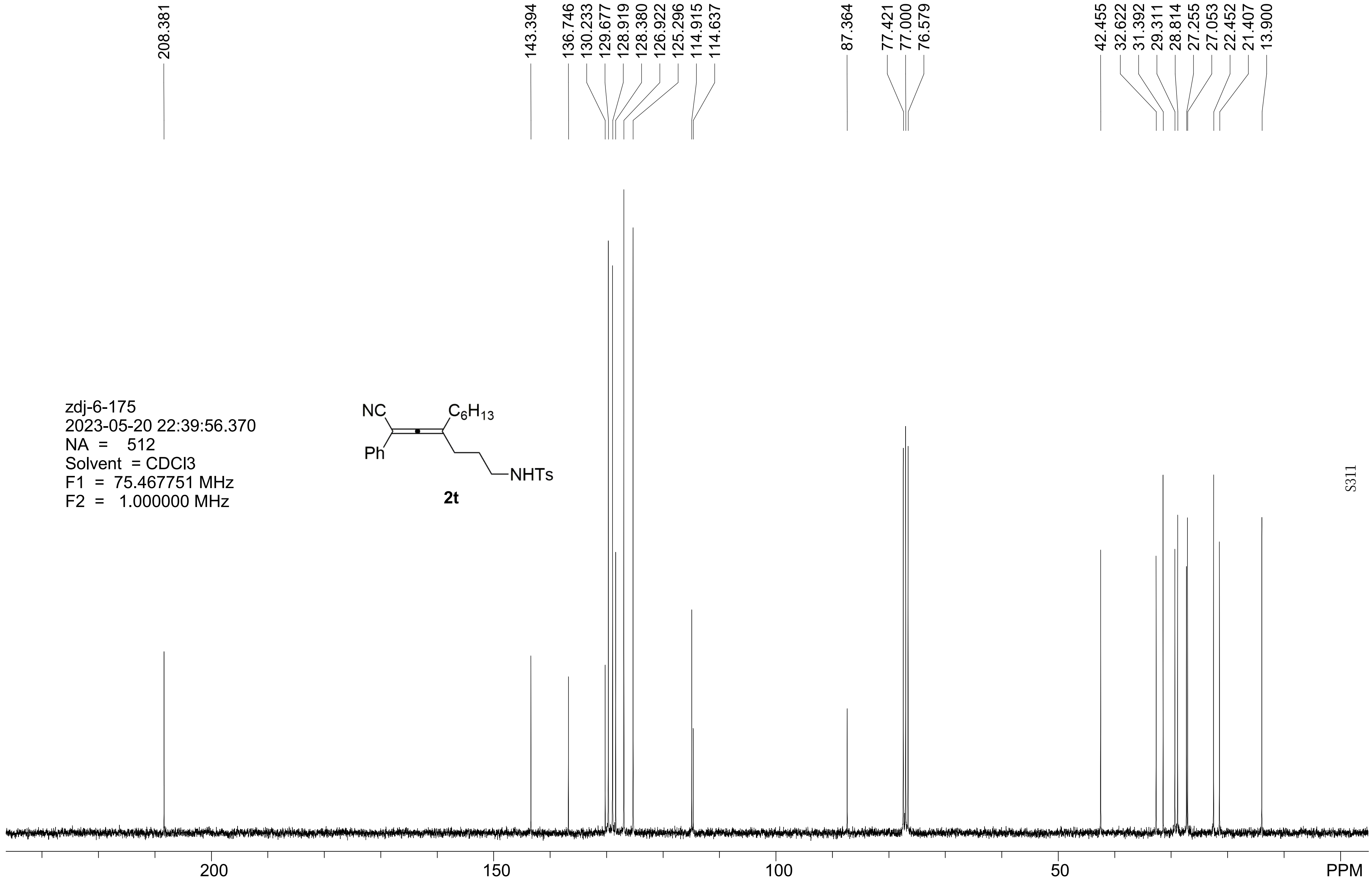
2s

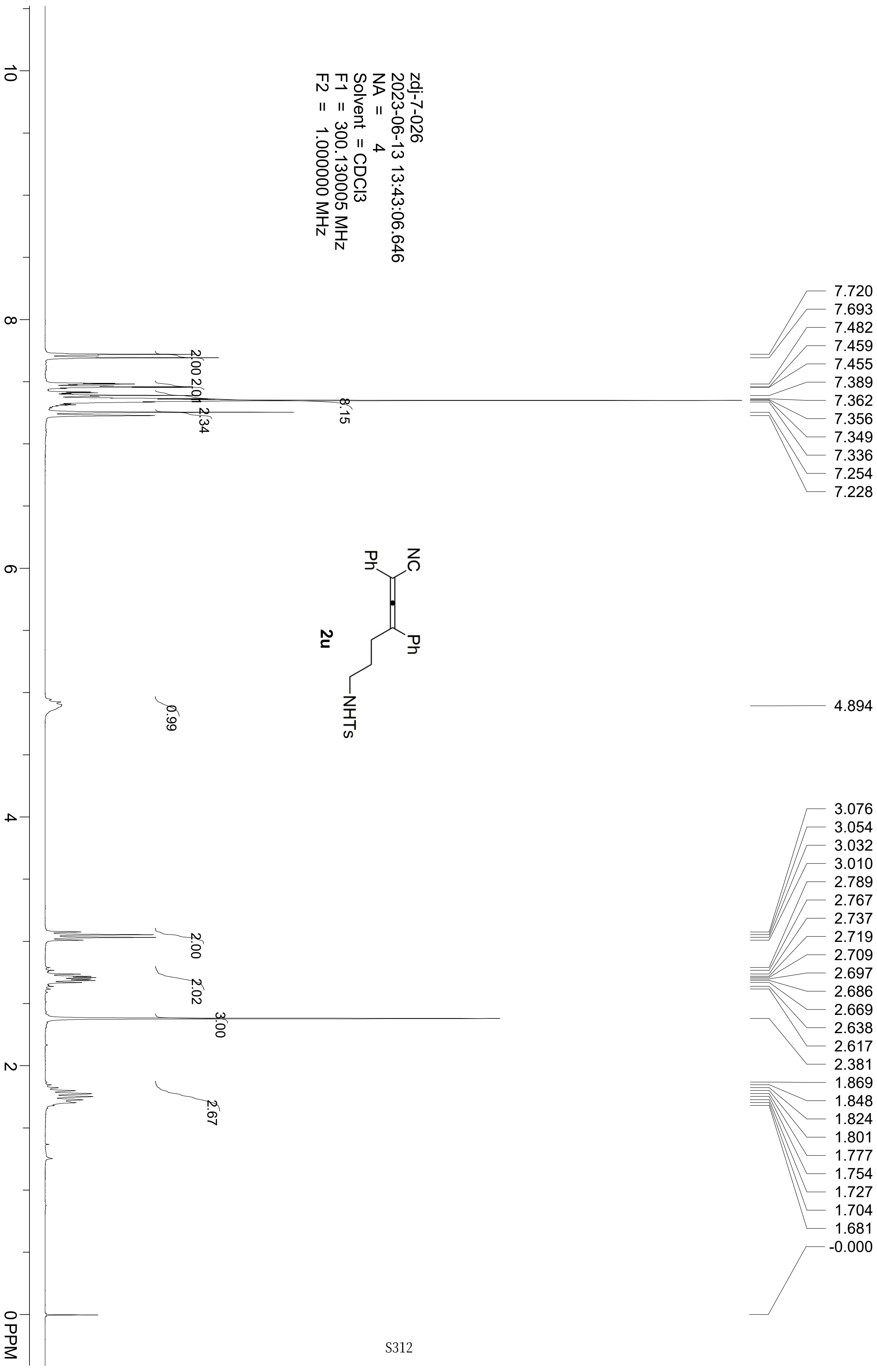

zdj-4-199
2022-06-10 18:41:30.826
Relaxation delay = 1.500 sec
NA = 400
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
C6H13
NHTs
3
250
200
150
100
50
0
PPM
208.336
143.403
137.455
136.803
129.696
126.975
116.292
115.318
110.592
82.930
77.248
77.000
76.743
32.615
42.461
32.210
31.456
30.896
28.974
28.717
27.283
27.044
26.952
22.474
21.417
13.943

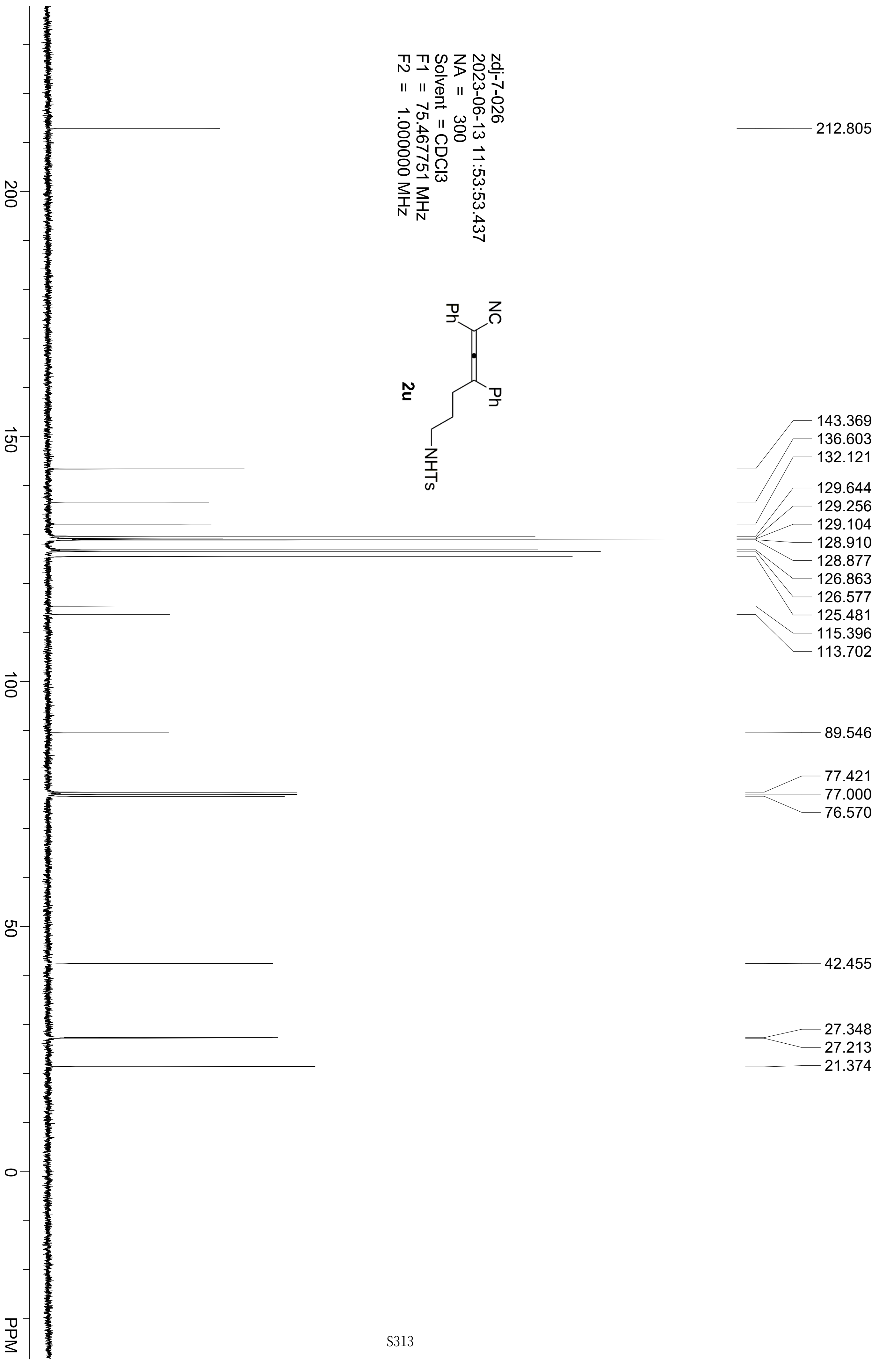
2s


zdj-6-175
2023-05-20 22:09:14.759
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
Ph
C6H13
NHTs
10
8
6
4
2
0
PPM
2.01
7.23
0.97
1.99
3.00
4.04
2.08
2.10
6.43
3.05
7.716
7.688
7.429
7.422
7.400
7.394
7.391
7.372
7.369
7.345
7.342
7.324
7.301
7.275
7.273
7.262
7.247
7.245
4.862
4.841
4.820
2.995
2.973
2.951
2.929
2.398
2.285
2.257
2.230
2.204
2.178
2.151
2.127
1.727
1.642
1.484
1.441
1.274
1.258
1.245
0.868
0.847
0.824
-0.000

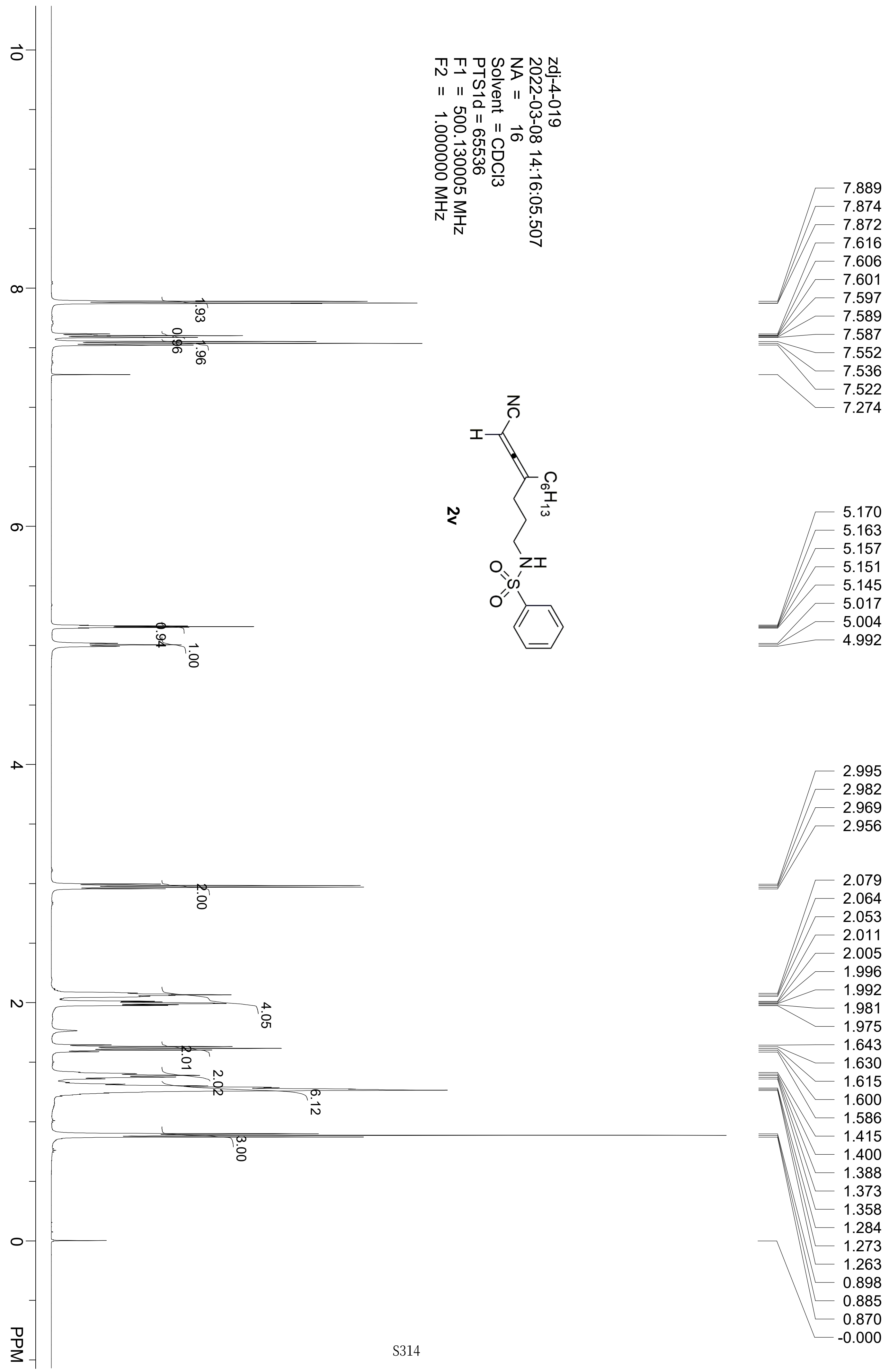
2t


208.381
143.394
136.746
130.233
129.677
128.919
128.380
126.922
125.296
114.915
114.637
87.364
77.421
77.000
76.579
42.455
32.622
31.392
29.311
28.814
27.255
27.053
22.452
21.407
13.900
zdj-6-175
2023-05-20 22:39:56.370
NA = 512
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
NC
Ph
C_6H_{13}
NHTs
2t
200
150
100
50
PPM

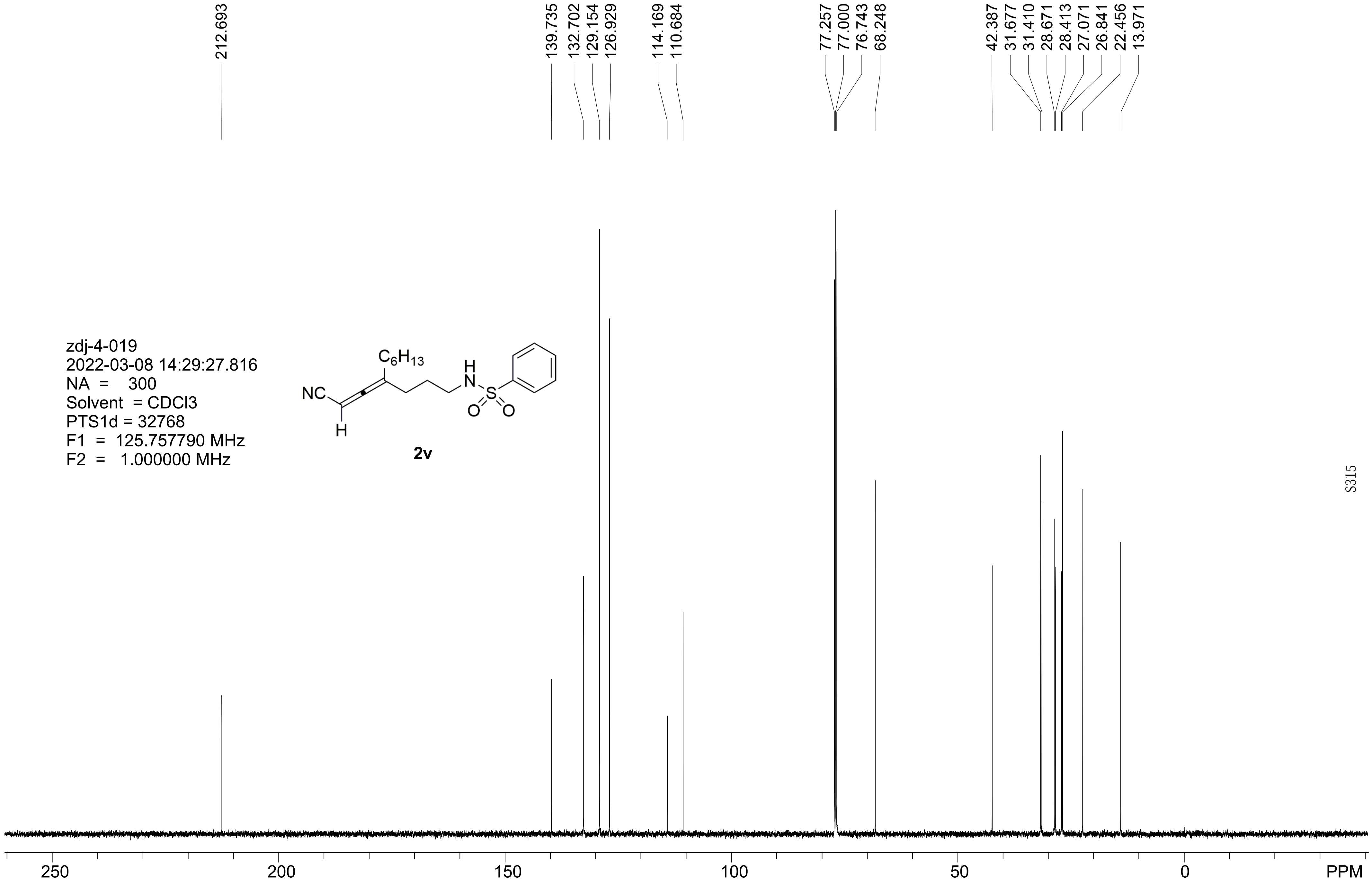

zdj-7-026
2023-06-13 13:43:06.646
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
Ph
Ph
NHTs
2u
10
8
6
4
2
0 PPM
2.00
2.01
2.34
8.15
0.99
2.00
2.02
3.00
2.67
7.720
7.693
7.482
7.459
7.455
7.389
7.362
7.356
7.349
7.336
7.254
7.228
4.894
3.076
3.054
3.032
3.010
2.789
2.767
2.737
2.719
2.709
2.697
2.686
2.669
2.638
2.617
2.381
1.869
1.848
1.824
1.801
1.777
1.754
1.727
1.704
1.681
-0.000

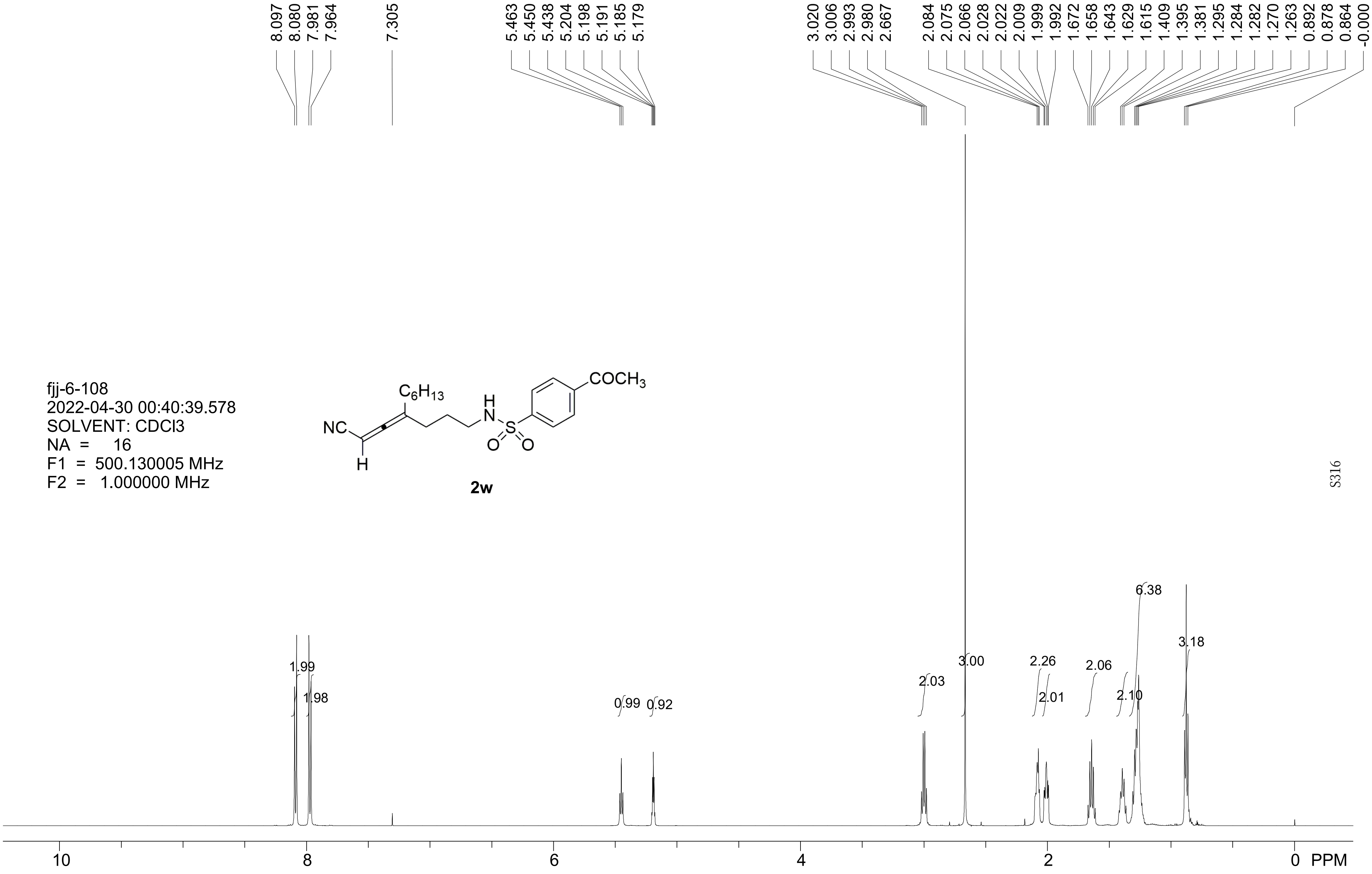

zdj-7-026
2023-06-13 11:53:53.437
NA = 300
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
NC
Ph
Ph
NHTs
212.805
143.369
136.603
132.121
129.644
129.256
129.104
128.910
128.877
126.863
126.577
125.481
115.396
113.702
89.546
77.421
77.000
76.570
42.455
27.348
27.213
21.374
200
150
100
50
0
PPM

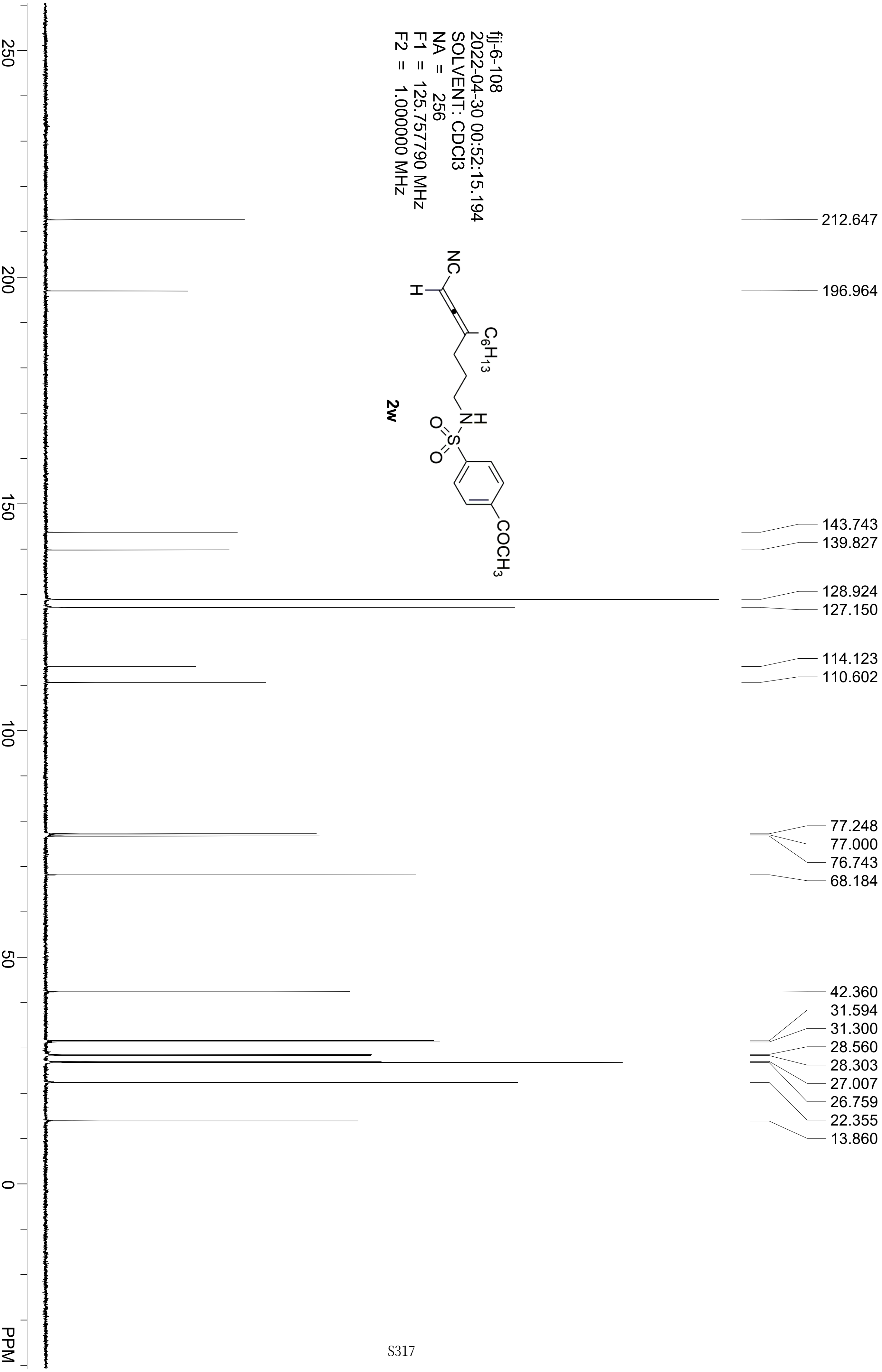
2u

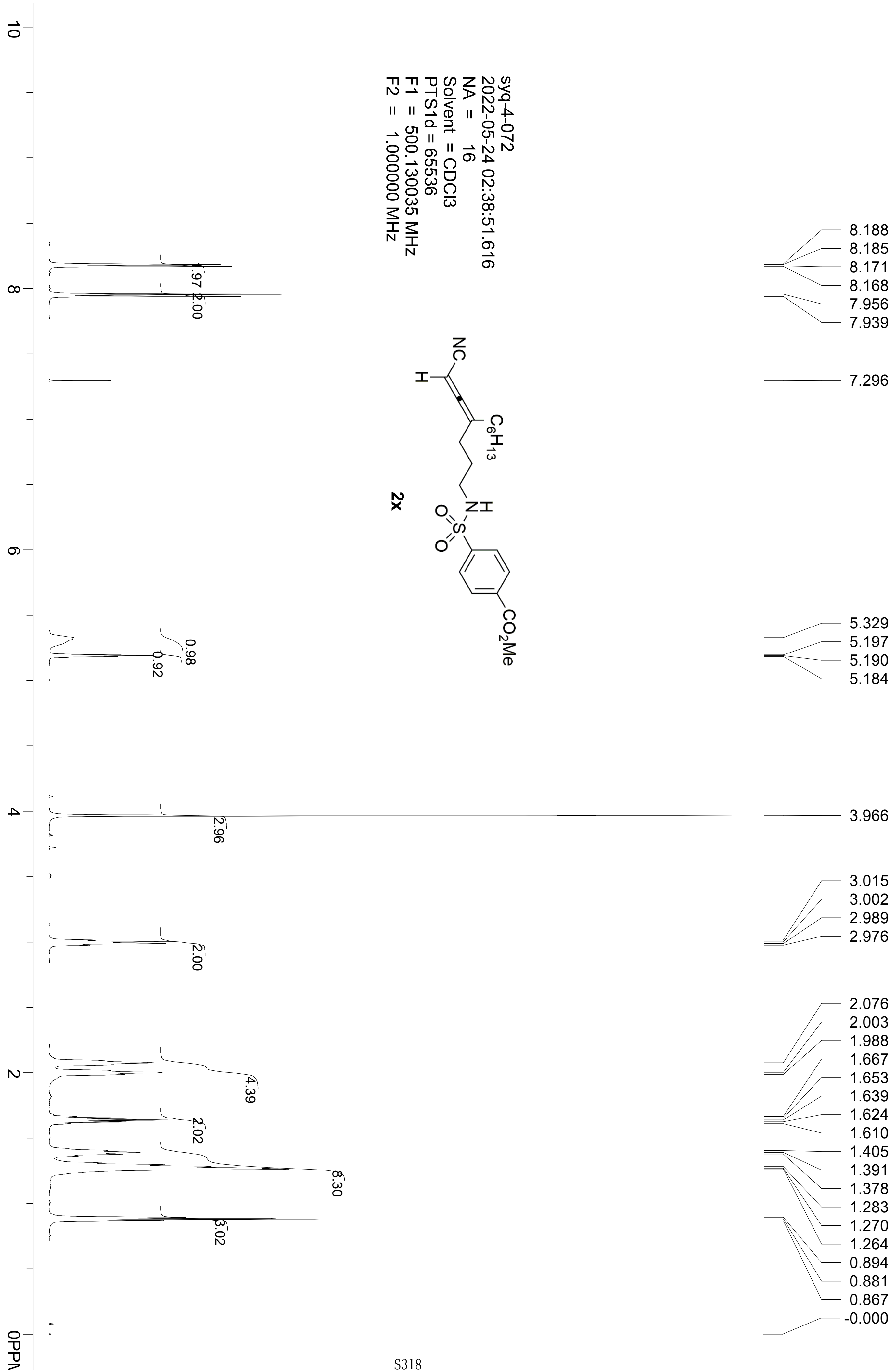

zdj-4-019
2022-03-08 14:16:05.507
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
NC
H
C_6H_{13}
H
N
S
O
O
7.889
7.874
7.872
7.616
7.606
7.601
7.597
7.589
7.587
7.552
7.536
7.522
7.274
5.170
5.163
5.157
5.151
5.145
5.017
5.004
4.992
2.995
2.982
2.969
2.956
2.079
2.064
2.053
2.011
2.005
1.996
1.992
1.981
1.975
1.643
1.630
1.615
1.600
1.586
1.415
1.400
1.388
1.373
1.358
1.284
1.273
1.263
0.898
0.885
0.870
-0.000
1.93
0.96
1.96
0.94
1.00
2.00
4.05
2.01
2.02
6.12
3.00
10
8
6
4
2
0
PPM

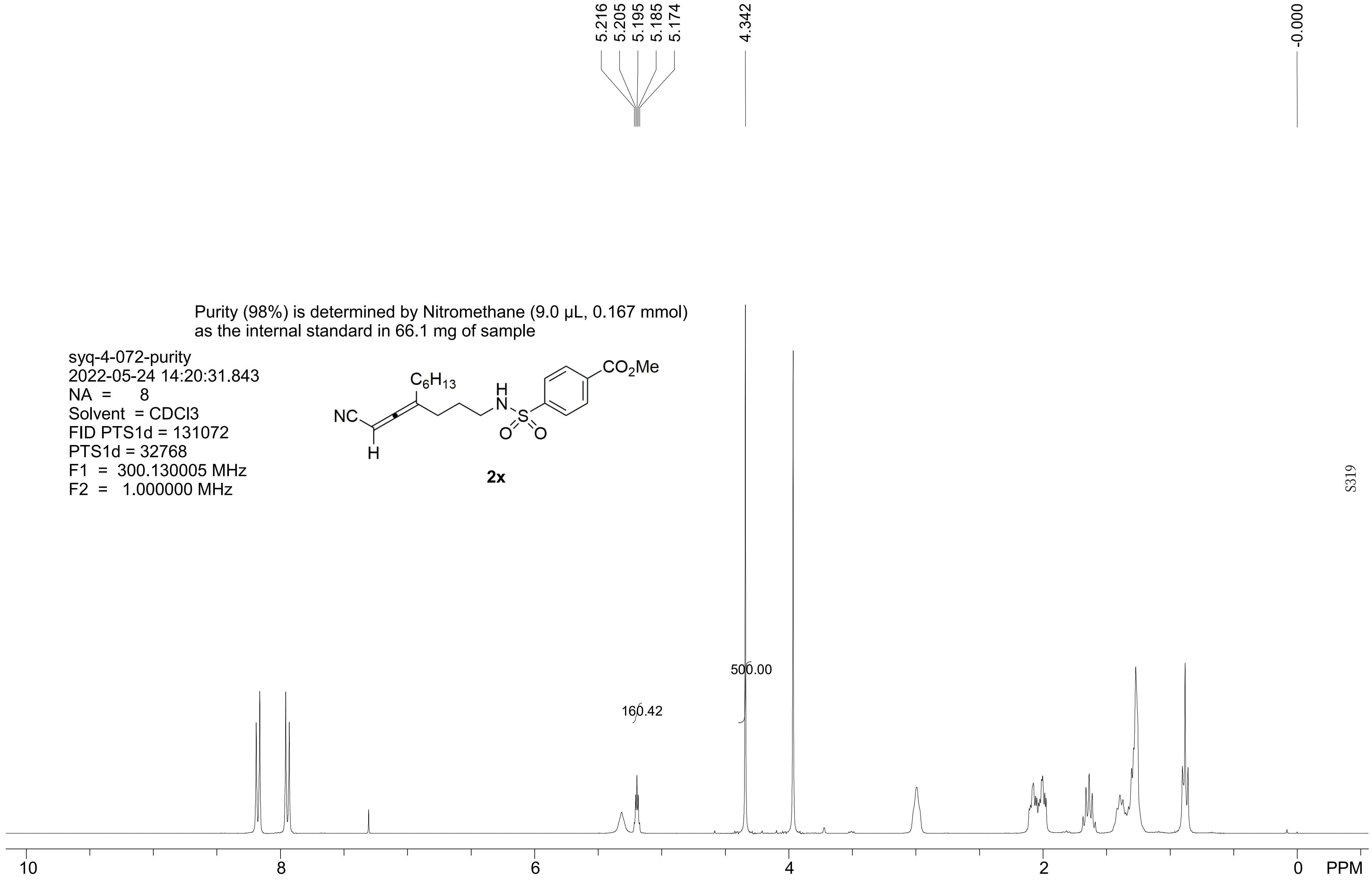
2v


212.693
139.735
132.702
129.154
126.929
114.169
110.684
77.257
77.000
76.743
68.248
42.387
31.677
31.410
28.671
28.413
27.071
26.841
22.456
13.971
zdj-4-019
2022-03-08 14:29:27.816
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
C6H13
H
N
S
O
O
2v
250
200
150
100
50
0
PPM


fjj-6-108
2022-04-30 00:40:39.578
SOLVENT: CDCl3
NA = 16
F1 = 500.130005 MHz
F2 = 1.000000 MHz
NC
H
C_6H_{13}
H
N
S
O
O
$COCH_3$
2w
8.097
8.080
7.981
7.964
7.305
5.463
5.450
5.438
5.204
5.198
5.191
5.185
5.179
3.020
3.006
2.993
2.980
2.667
2.084
2.075
2.066
2.028
2.022
2.009
1.999
1.992
1.672
1.658
1.643
1.629
1.615
1.409
1.395
1.381
1.295
1.284
1.282
1.270
1.263
0.892
0.878
0.864
-0.000
1.99
1.98
0.99
0.92
2.03
3.00
2.26
2.01
2.06
2.10
6.38
3.18
10
8
6
4
2
0 PPM


fjj-6-108
2022-04-30 00:52:15.194
SOLVENT: CDCl3
NA = 256
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
C6H13
H
N
S
O
O
COCH3
2w
250
200
150
100
50
0
PPM
212.647
196.964
143.743
139.827
128.924
127.150
114.123
110.602
77.248
77.000
76.743
68.184
42.360
31.594
31.300
28.560
28.303
27.007
26.759
22.355
13.860

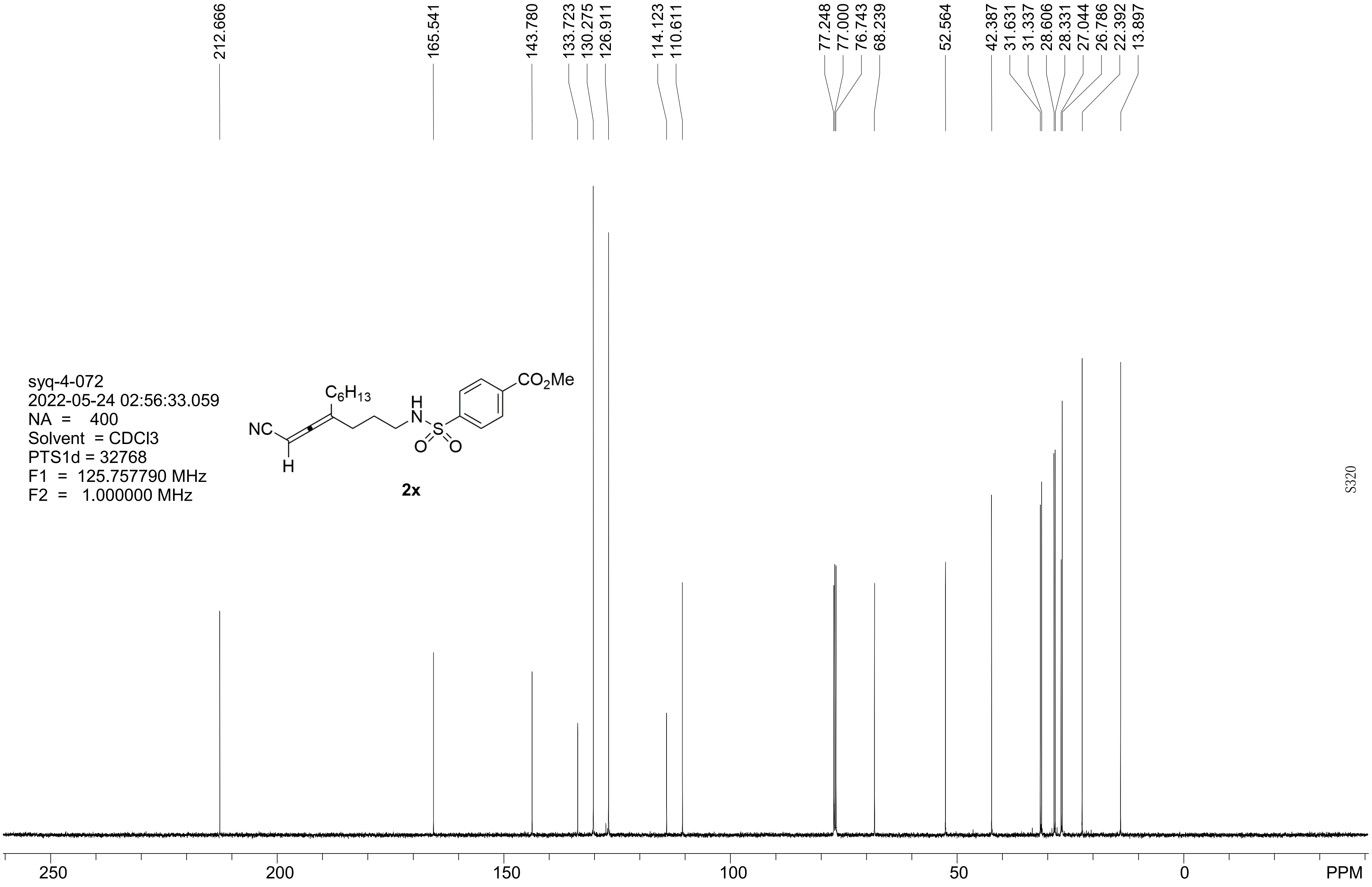

syq-4-072
2022-05-24 02:38:51.616
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130035 MHz
F2 = 1.000000 MHz
NC
H
C6H13
H
N
S
O
O
CO2Me
2x
8.188
8.185
8.171
8.168
7.956
7.939
7.296
5.329
5.197
5.190
5.184
3.966
3.015
3.002
2.989
2.976
2.076
2.003
1.988
1.667
1.653
1.639
1.624
1.610
1.405
1.391
1.378
1.283
1.270
1.264
0.894
0.881
0.867
-0.000
1.97
2.00
0.98
0.92
2.96
2.00
4.39
2.02
8.30
3.02
10
8
6
4
2
0PPM

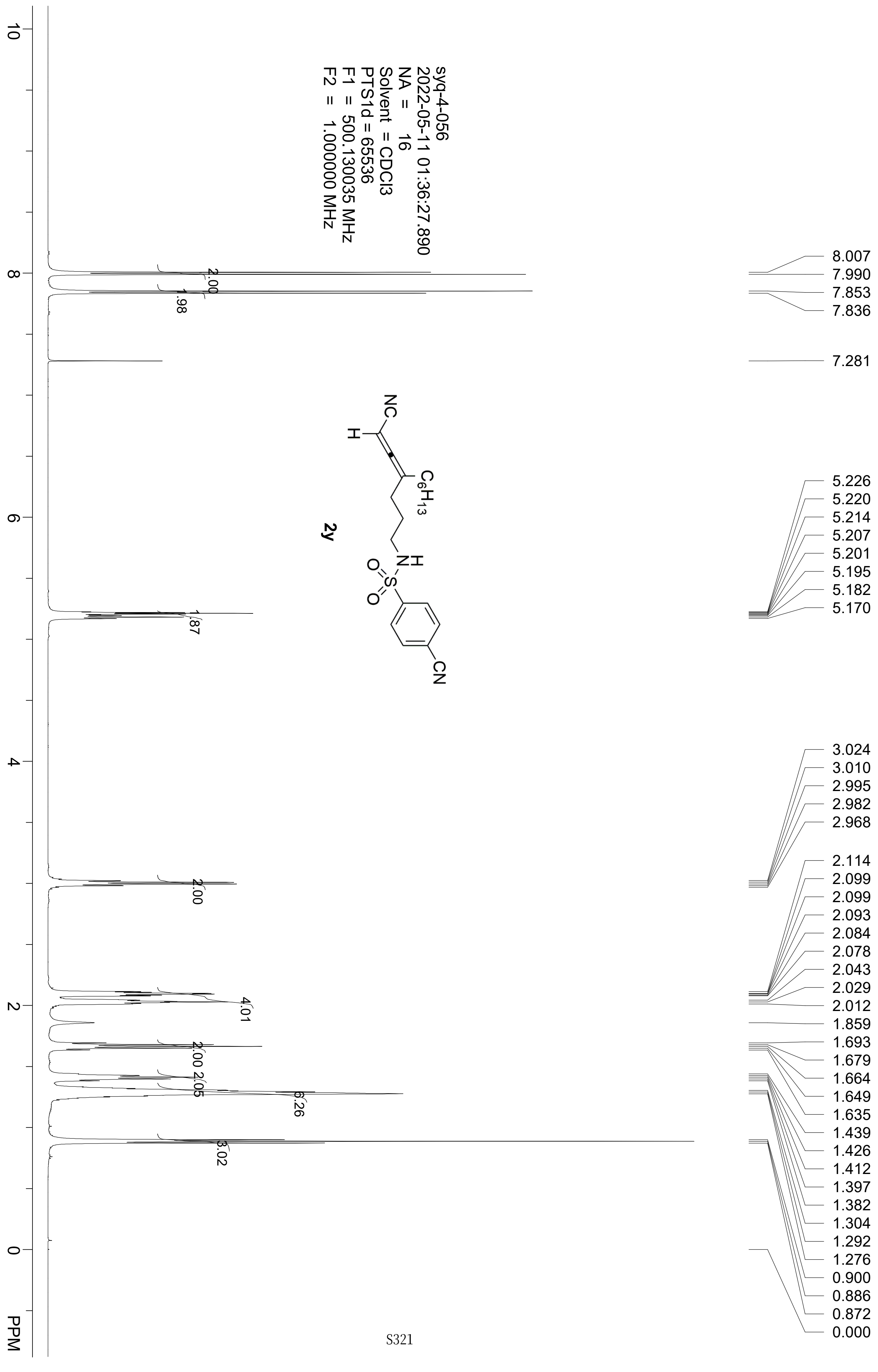


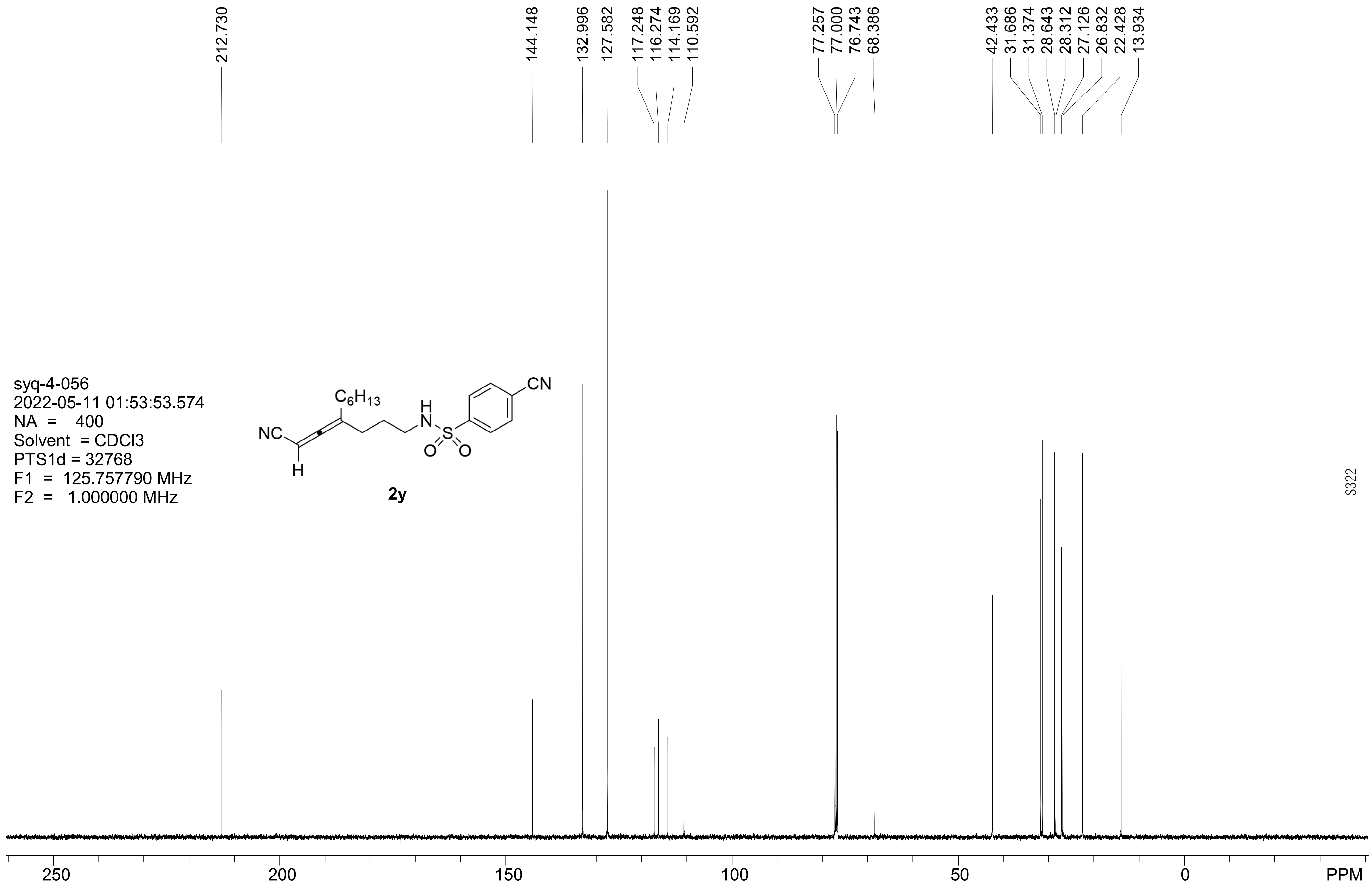
Purity (98%) is determined by Nitromethane (9.0 μL, 0.167 mmol)
as the internal standard in 66.1 mg of sample

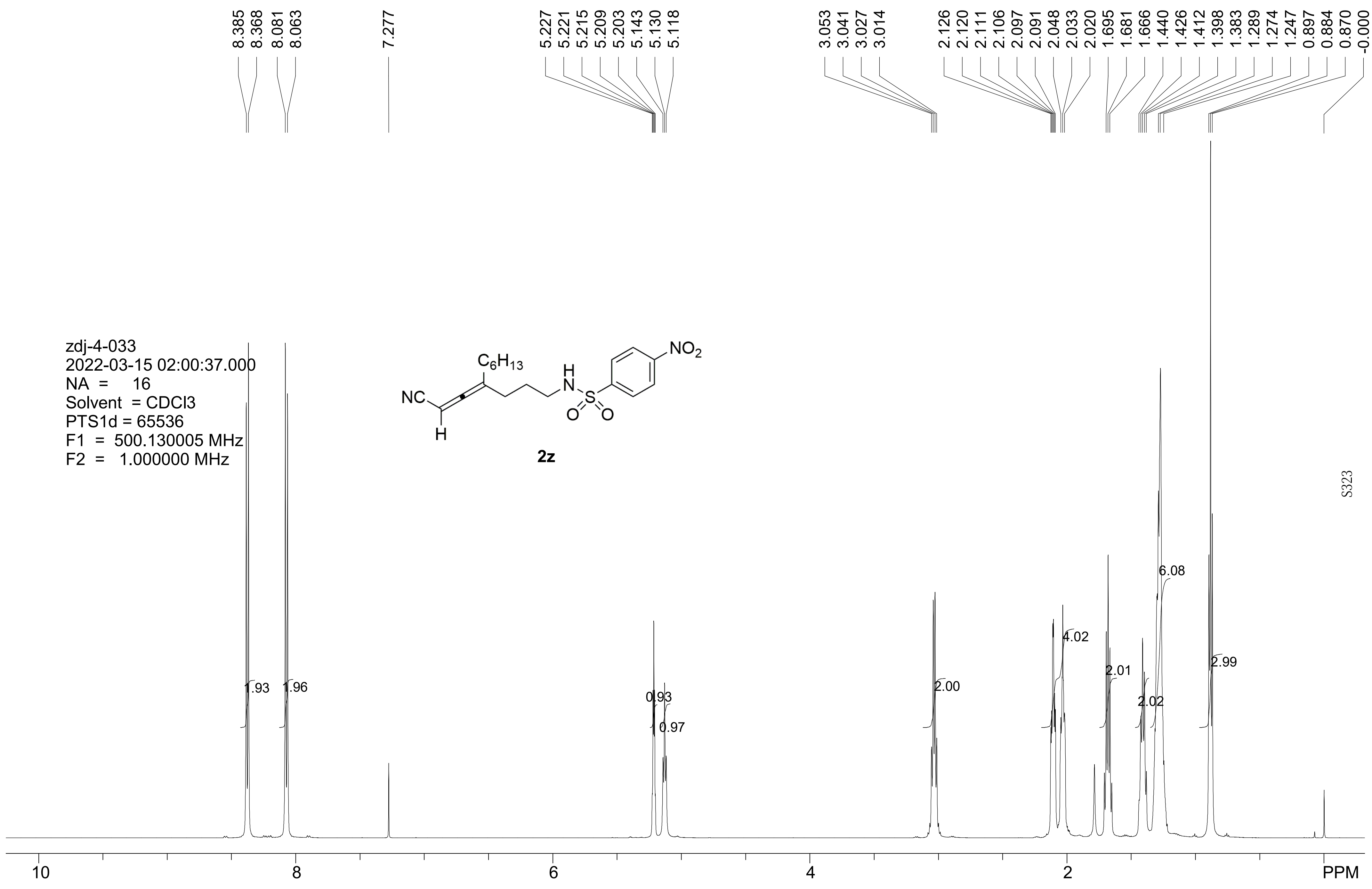
syq-4-072-purity
2022-05-24 14:20:31.843
NA = 8
Solvent = CDCl3
FID PTS1d = 131072
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz

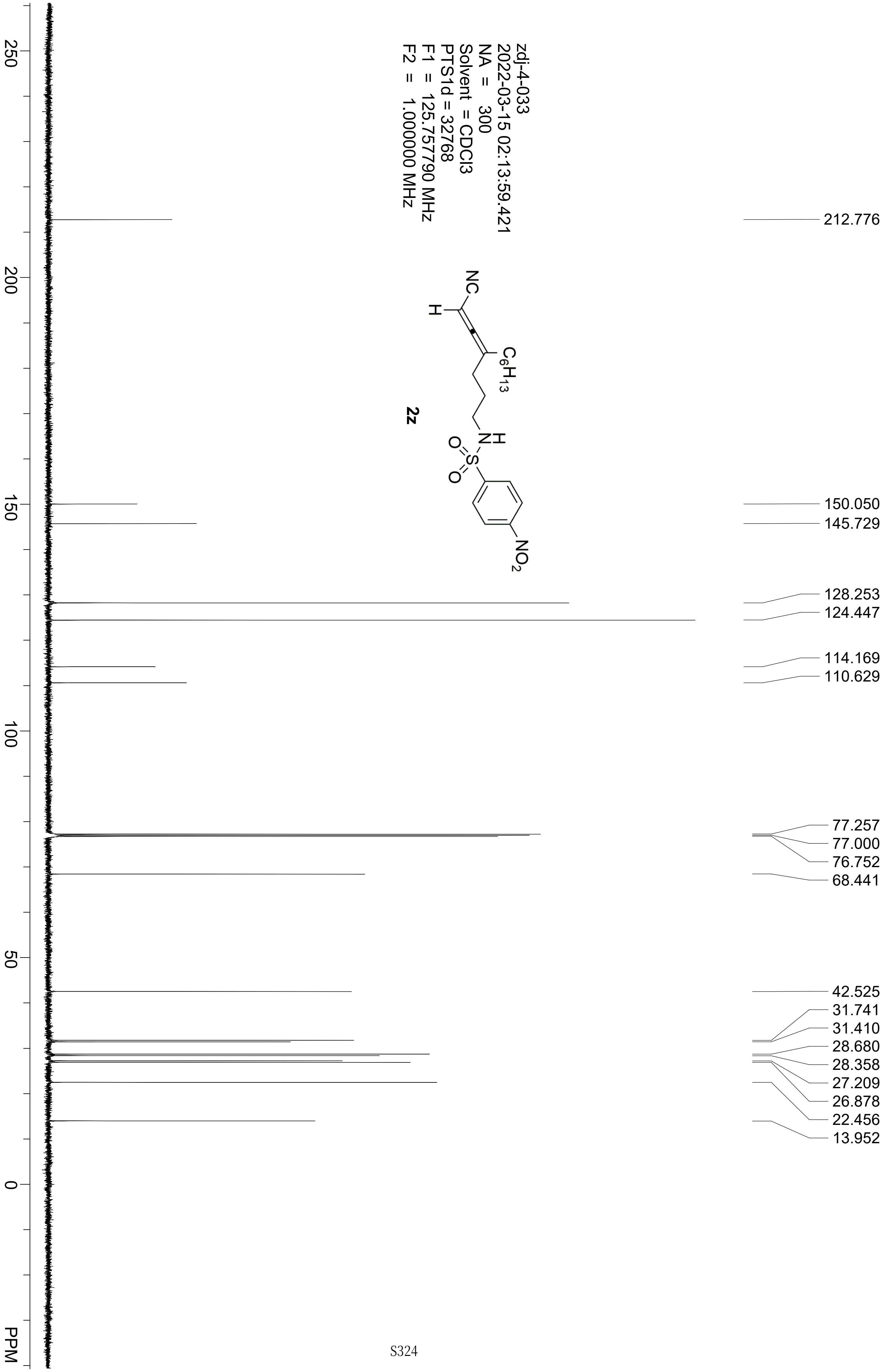
2x

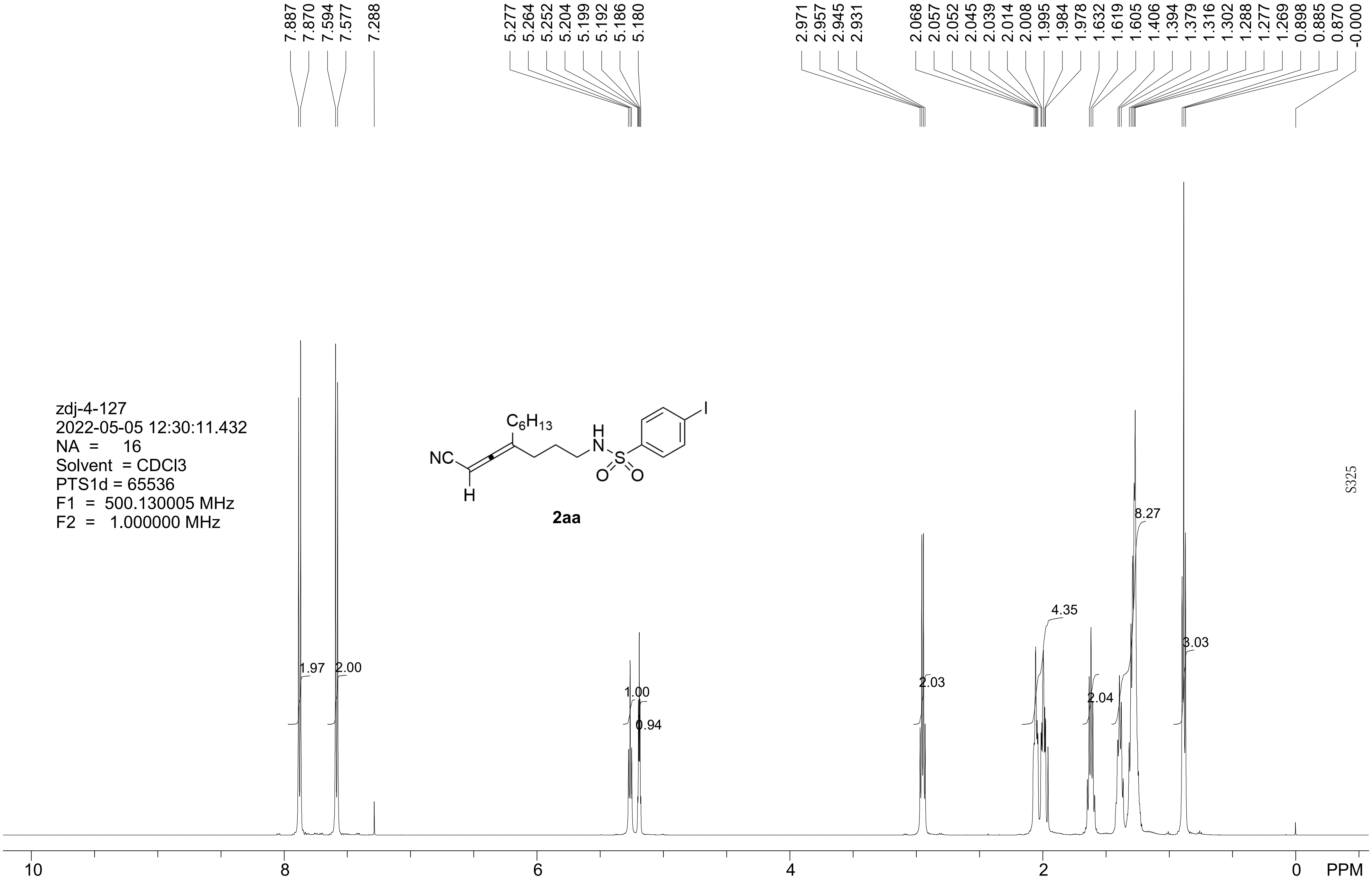

212.666
165.541
143.780
133.723
130.275
126.911
114.123
110.611
77.248
77.000
76.743
68.239
52.564
42.387
31.631
31.337
28.606
28.331
27.044
26.786
22.392
13.897
syq-4-072
2022-05-24 02:56:33.059
NA = 400
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
C_6H_{13}
H
N
S
O
O
CO_2Me
2x
250
200
150
100
50
0
PPM

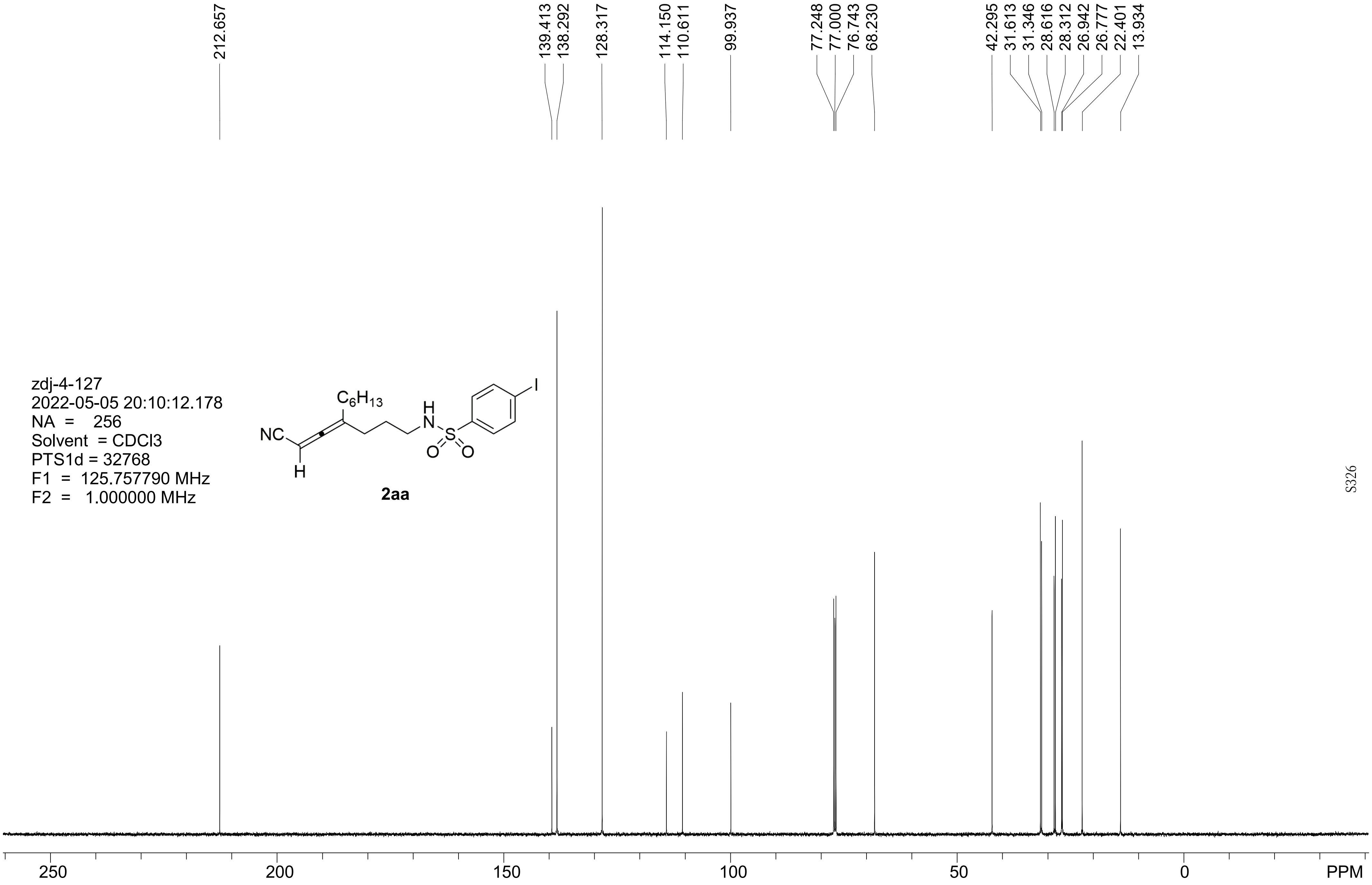

syq-4-056
2022-05-11 01:36:27.890
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130035 MHz
F2 = 1.000000 MHz
NC
H
C6H13
H
N
S
O
O
CN
2y
10
8
6
4
2
0
PPM
2.00
1.98
1.87
2.00
4.01
2.00
2.05
6.26
3.02
8.007
7.990
7.853
7.836
7.281
5.226
5.220
5.214
5.207
5.201
5.195
5.182
5.170
3.024
3.010
2.995
2.982
2.968
2.114
2.099
2.099
2.093
2.084
2.078
2.043
2.029
2.012
1.859
1.693
1.679
1.664
1.649
1.635
1.439
1.426
1.412
1.397
1.382
1.304
1.292
1.276
0.900
0.886
0.872
0.000

212.730
144.148
132.996
127.582
117.248
116.274
114.169
110.592
77.257
77.000
76.743
68.386
42.433
31.686
31.374
28.643
28.312
27.126
26.832
22.428
13.934
syq-4-056
2022-05-11 01:53:53.574
NA = 400
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
C6H13
H
N
S
O
O
CN
2y
250
200
150
100
50
0
PPM

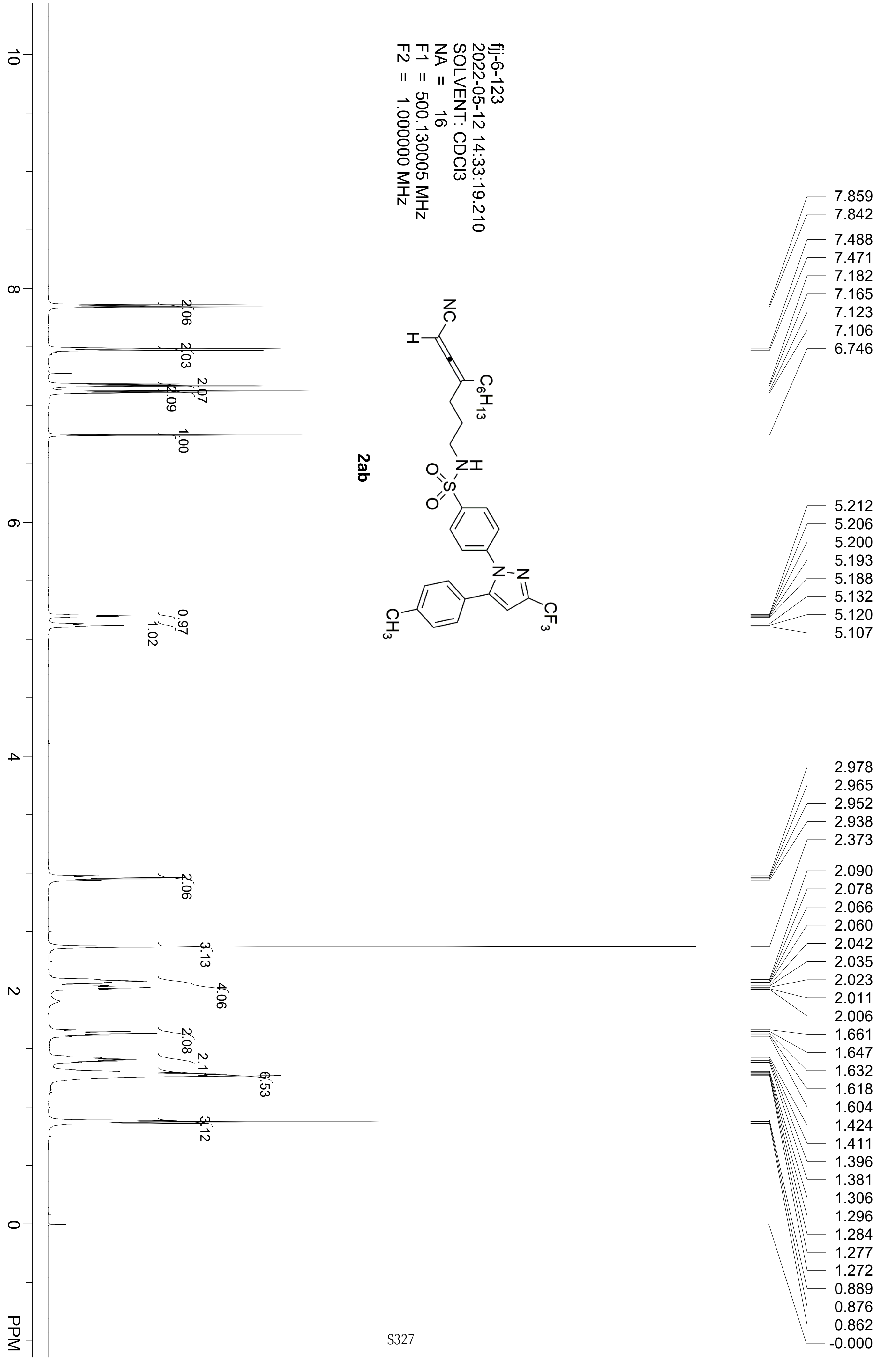

8.385
8.368
8.081
8.063
7.277
5.227
5.221
5.215
5.209
5.203
5.143
5.130
5.118
3.053
3.041
3.027
3.014
2.126
2.120
2.111
2.106
2.097
2.091
2.048
2.033
2.020
1.695
1.681
1.666
1.440
1.426
1.412
1.398
1.383
1.289
1.274
1.247
0.897
0.884
0.870
-0.000
zdj-4-033
2022-03-15 02:00:37.000
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
C6H13
NC
H
H
N
S
O
O
NO2
2z
1.93
1.96
0.93
0.97
2.00
4.02
2.01
2.02
6.08
2.99
10
8
6
4
2
PPM


zdj-4-033
2022-03-15 02:13:59.421
NA = 300
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
C6H13
H
N
S
O
O
NO2
2z
212.776
150.050
145.729
128.253
124.447
114.169
110.629
77.257
77.000
76.752
68.441
42.525
31.741
31.410
28.680
28.358
27.209
26.878
22.456
13.952
250
200
150
100
50
0
PPM

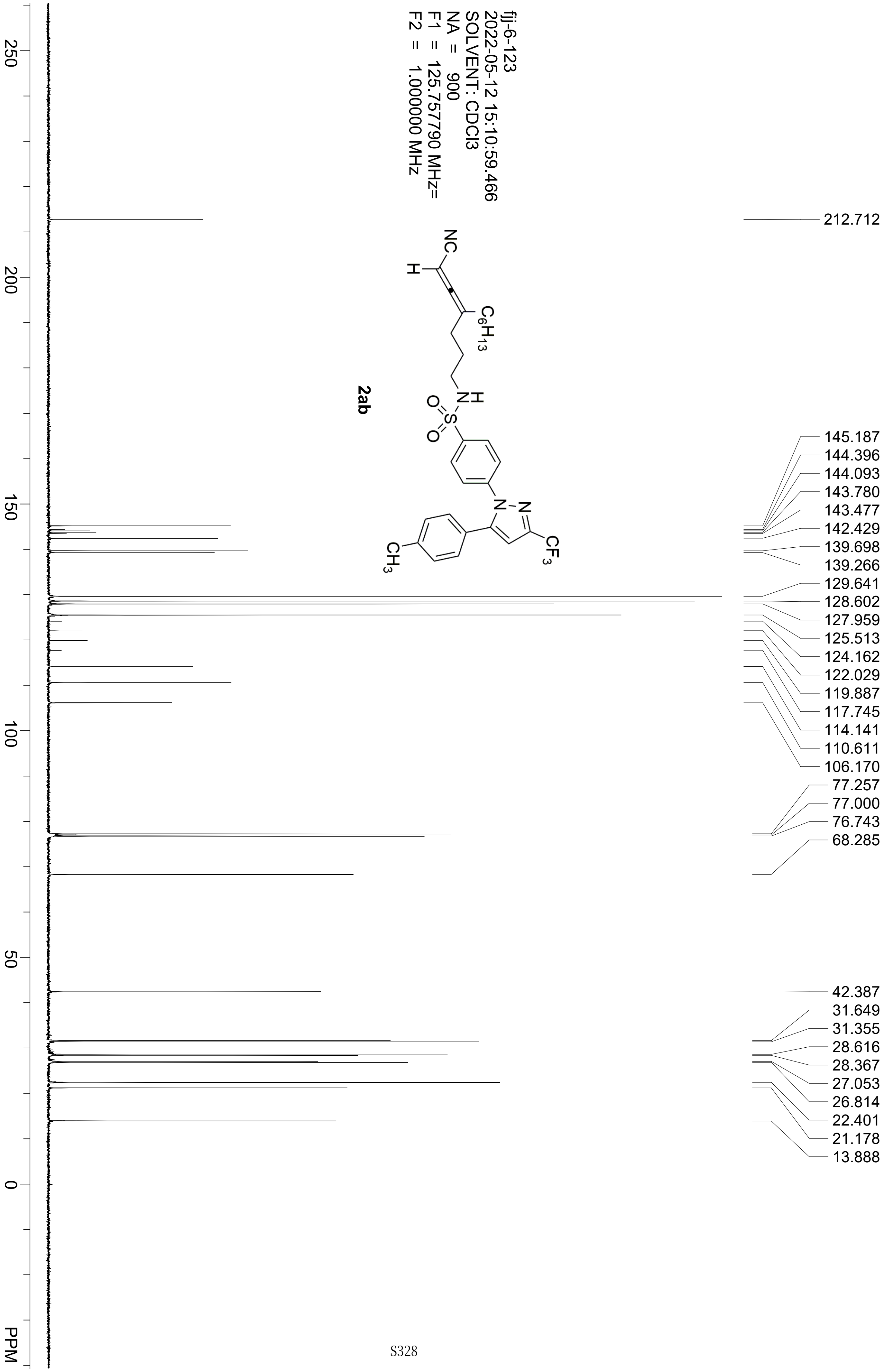

zdj-4-127
2022-05-05 12:30:11.432
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
NC
H
C6H13
H
N
S
O
O
I
2aa
7.887
7.870
7.594
7.577
7.288
5.277
5.264
5.252
5.204
5.199
5.192
5.186
5.180
2.971
2.957
2.945
2.931
2.068
2.057
2.052
2.045
2.039
2.014
2.008
1.995
1.984
1.978
1.632
1.619
1.605
1.406
1.394
1.379
1.316
1.302
1.288
1.277
1.269
0.898
0.885
0.870
-0.000
1.97
2.00
1.00
0.94
2.03
4.35
2.04
8.27
3.03
10
8
6
4
2
0
PPM


212.657
139.413
138.292
128.317
114.150
110.611
99.937
77.248
77.000
76.743
68.230
42.295
31.613
31.346
28.616
28.312
26.942
26.777
22.401
13.934
zdj-4-127
2022-05-05 20:10:12.178
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
C6H13
H
N
S
O
O
I
250
200
150
100
50
0
PPM

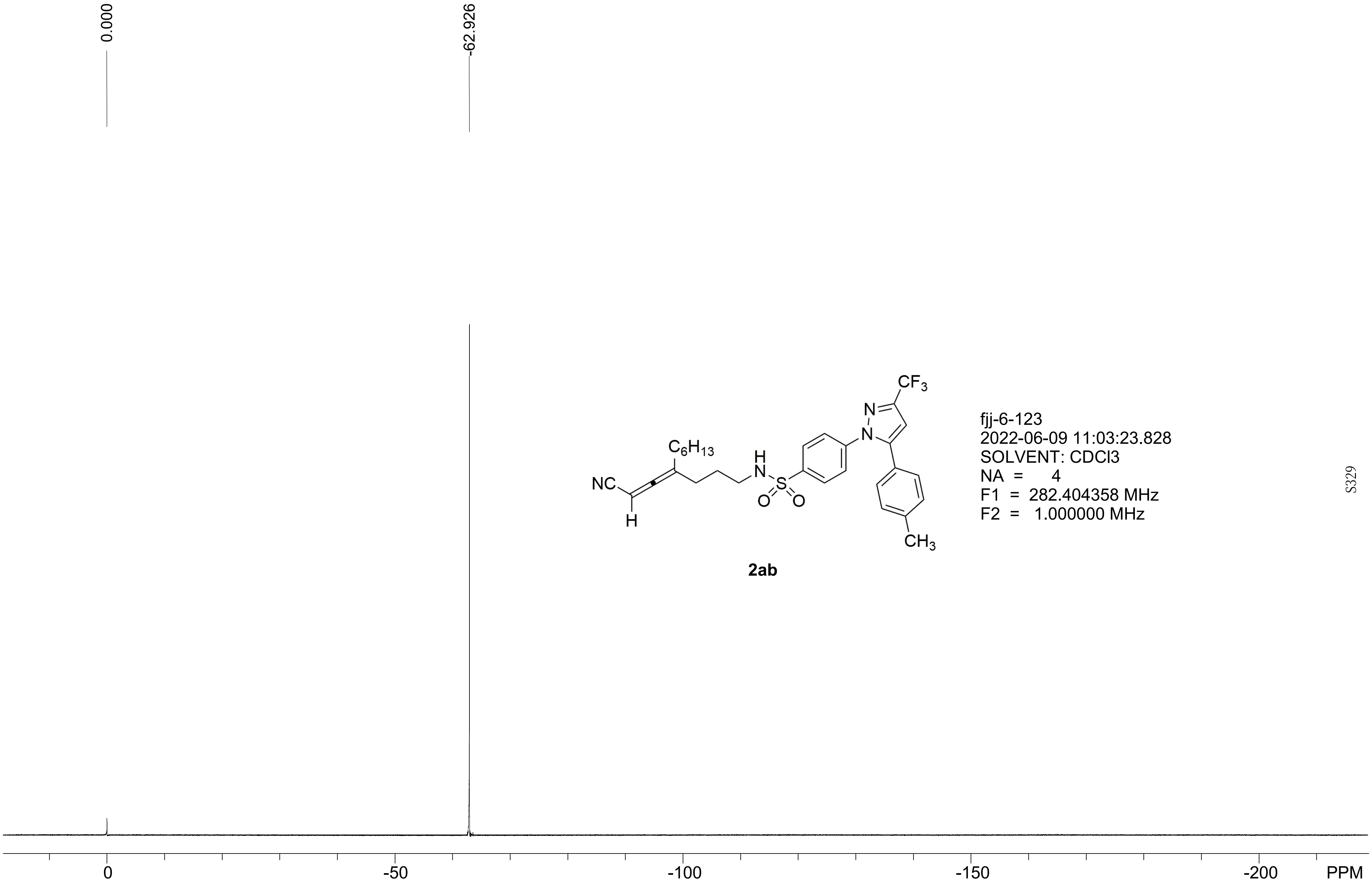
2aa


fjj-6-123
2022-05-12 14:33:19.210
SOLVENT: CDCl3
NA = 16
F1 = 500.130005 MHz
F2 = 1.000000 MHz
NC
H
C6H13
H
N
O
S
O
N
N
CF3
CH3
10
8
6
4
2
0
PPM
2.06
2.03
2.07
2.09
1.00
0.97
1.02
2.06
3.13
4.06
2.08
2.11
6.53
3.12
7.859
7.842
7.488
7.471
7.182
7.165
7.123
7.106
6.746
5.212
5.206
5.200
5.193
5.188
5.132
5.120
5.107
2.978
2.965
2.952
2.938
2.373
2.090
2.078
2.066
2.060
2.042
2.035
2.023
2.011
2.006
1.661
1.647
1.632
1.618
1.604
1.424
1.411
1.396
1.381
1.306
1.296
1.284
1.277
1.272
0.889
0.876
0.862
-0.000

2ab

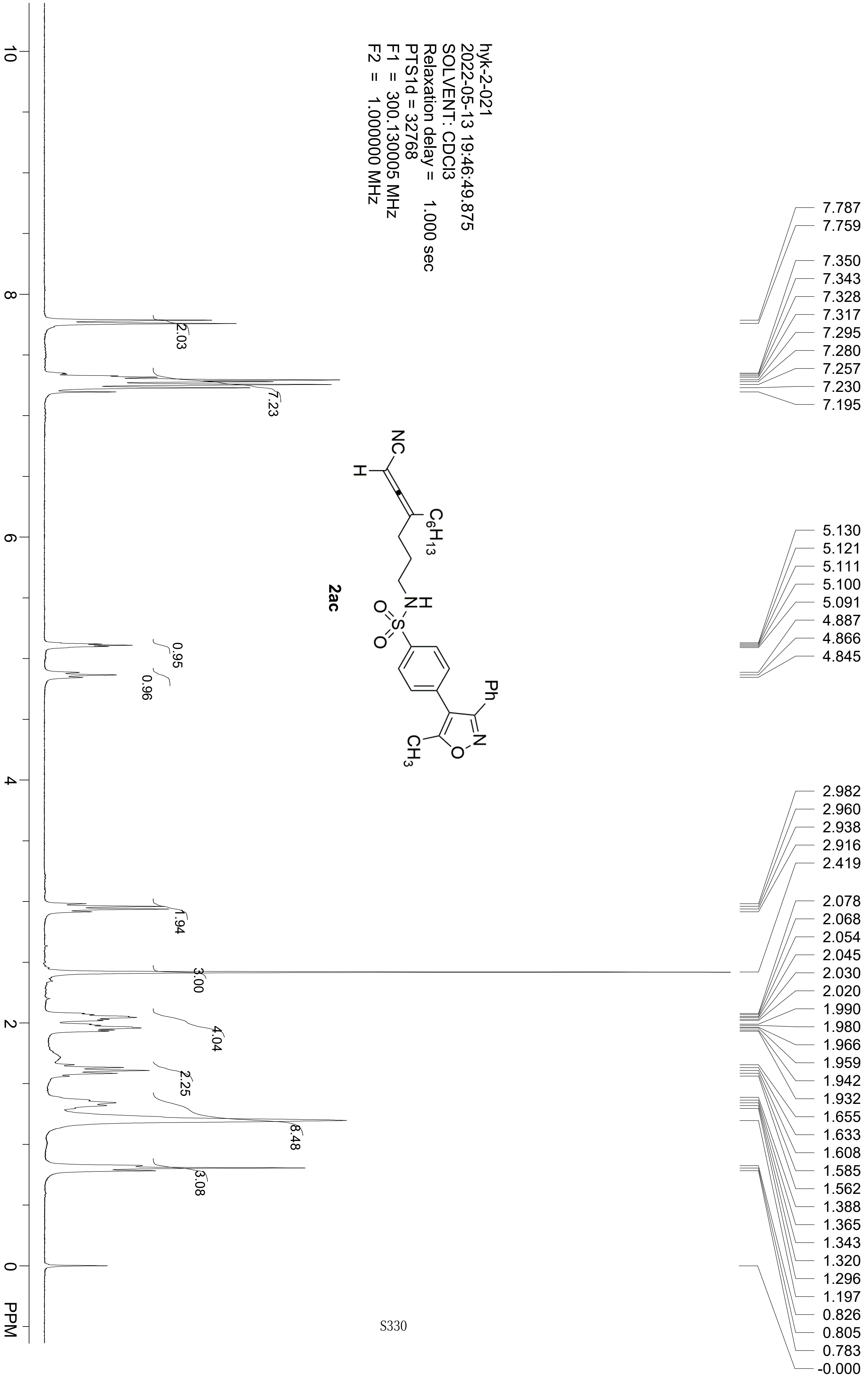

fjj-6-123
2022-05-12 15:10:59.466
SOLVENT: CDCl3
NA = 900
F1 = 125.757790 MHz=
F2 = 1.000000 MHz
NC
H
C6H13
H
N
O
S
O
N
N
CF3
CH3
250
200
150
100
50
0
PPM
212.712
145.187
144.396
144.093
143.780
143.477
142.429
139.698
139.266
129.641
128.602
127.959
125.513
124.162
122.029
119.887
117.745
114.141
110.611
106.170
77.257
77.000
76.743
68.285
42.387
31.649
31.355
28.616
28.367
27.053
26.814
22.401
21.178
13.888

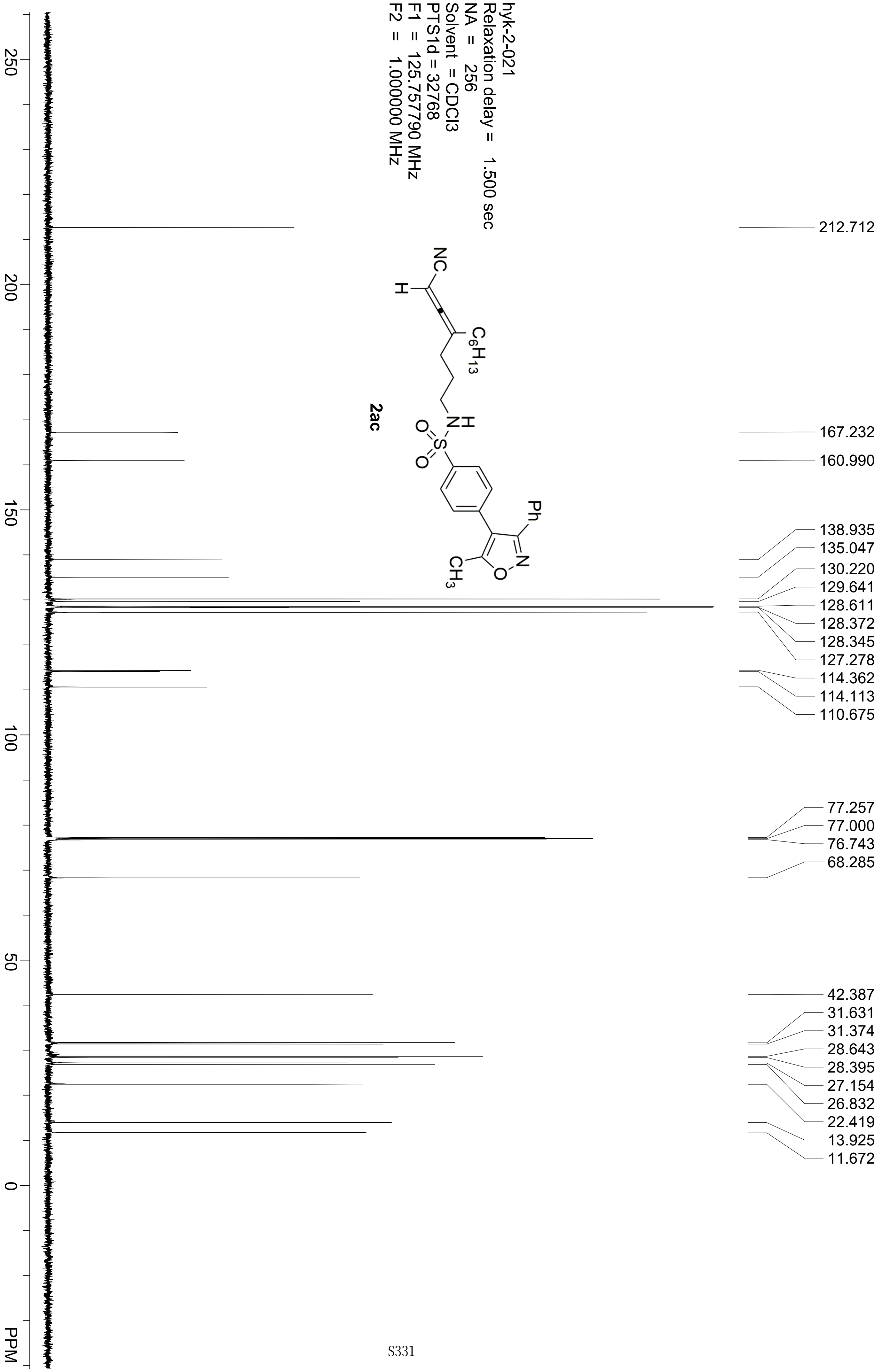
2ab

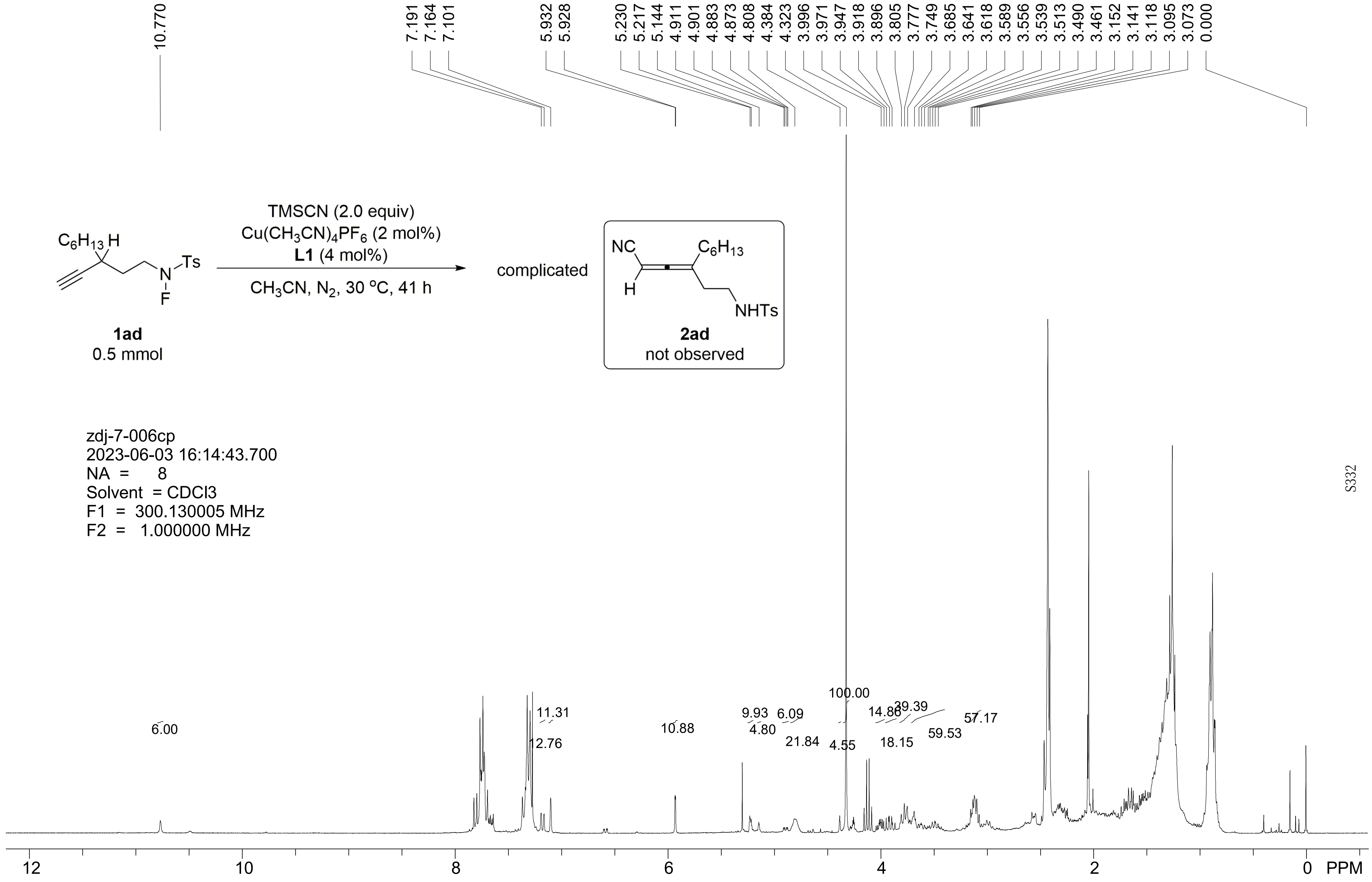


2ab

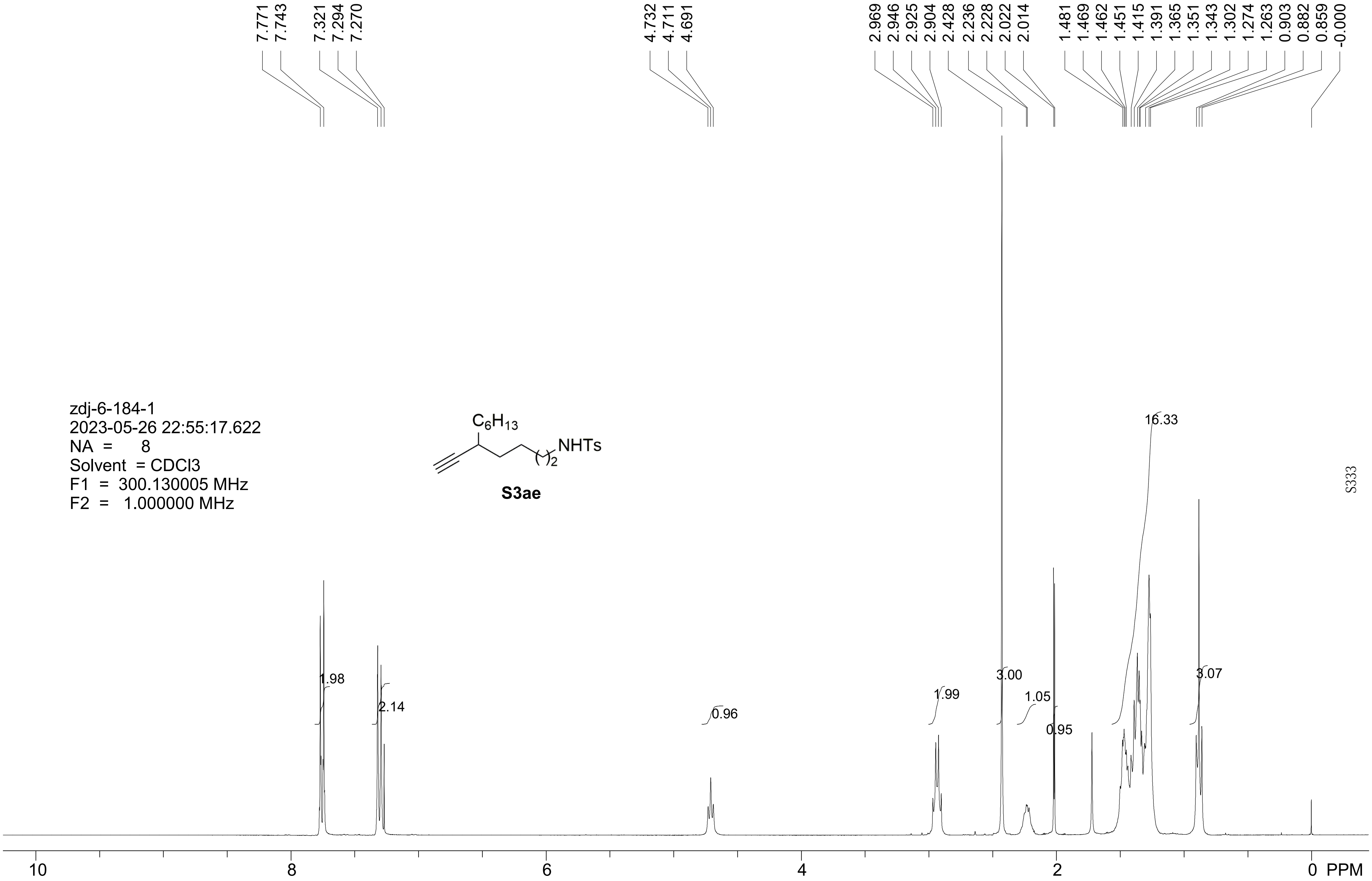
fjj-6-123
2022-06-09 11:03:23.828
SOLVENT: CDCl3
NA = 4
F1 = 282.404358 MHz
F2 = 1.000000 MHz

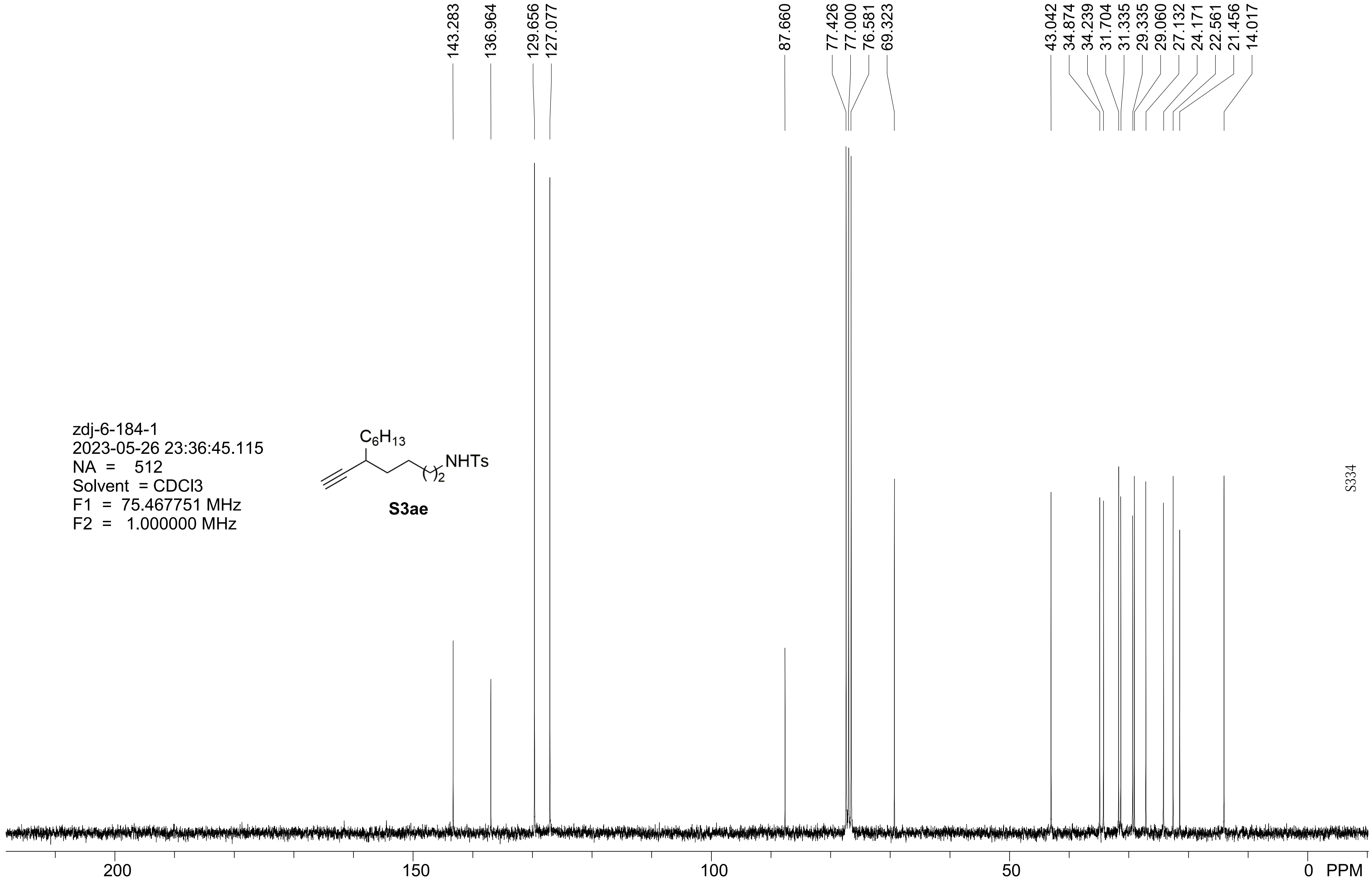

hyk-2-021
2022-05-13 19:46:49.875
SOLVENT: CDCl3
Relaxation delay = 1.000 sec
PTS1d = 32768
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
H
C6H13
H
N
S
O
O
Ph
N
O
CH3
2ac
10
8
6
4
2
0
PPM
2.03
7.23
0.95
0.96
1.94
3.00
4.04
2.25
8.48
3.08
7.787
7.759
7.350
7.343
7.328
7.317
7.295
7.280
7.257
7.230
7.195
5.130
5.121
5.111
5.100
5.091
4.887
4.866
4.845
2.982
2.960
2.938
2.916
2.419
2.078
2.068
2.054
2.045
2.030
2.020
1.990
1.980
1.966
1.959
1.942
1.932
1.655
1.633
1.608
1.585
1.562
1.388
1.365
1.343
1.320
1.296
1.197
0.826
0.805
0.783
-0.000


hyk-2-021
Relaxation delay = 1.500 sec
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
2ac
NC
H
C6H13
H
N
S
O
O
Ph
N
O
CH3
212.712
167.232
160.990
138.935
135.047
130.220
129.641
128.611
128.372
128.345
127.278
114.362
114.113
110.675
77.257
77.000
76.743
68.285
42.387
31.631
31.374
28.643
28.395
27.154
26.832
22.419
13.925
11.672
250
200
150
100
50
0
PPM



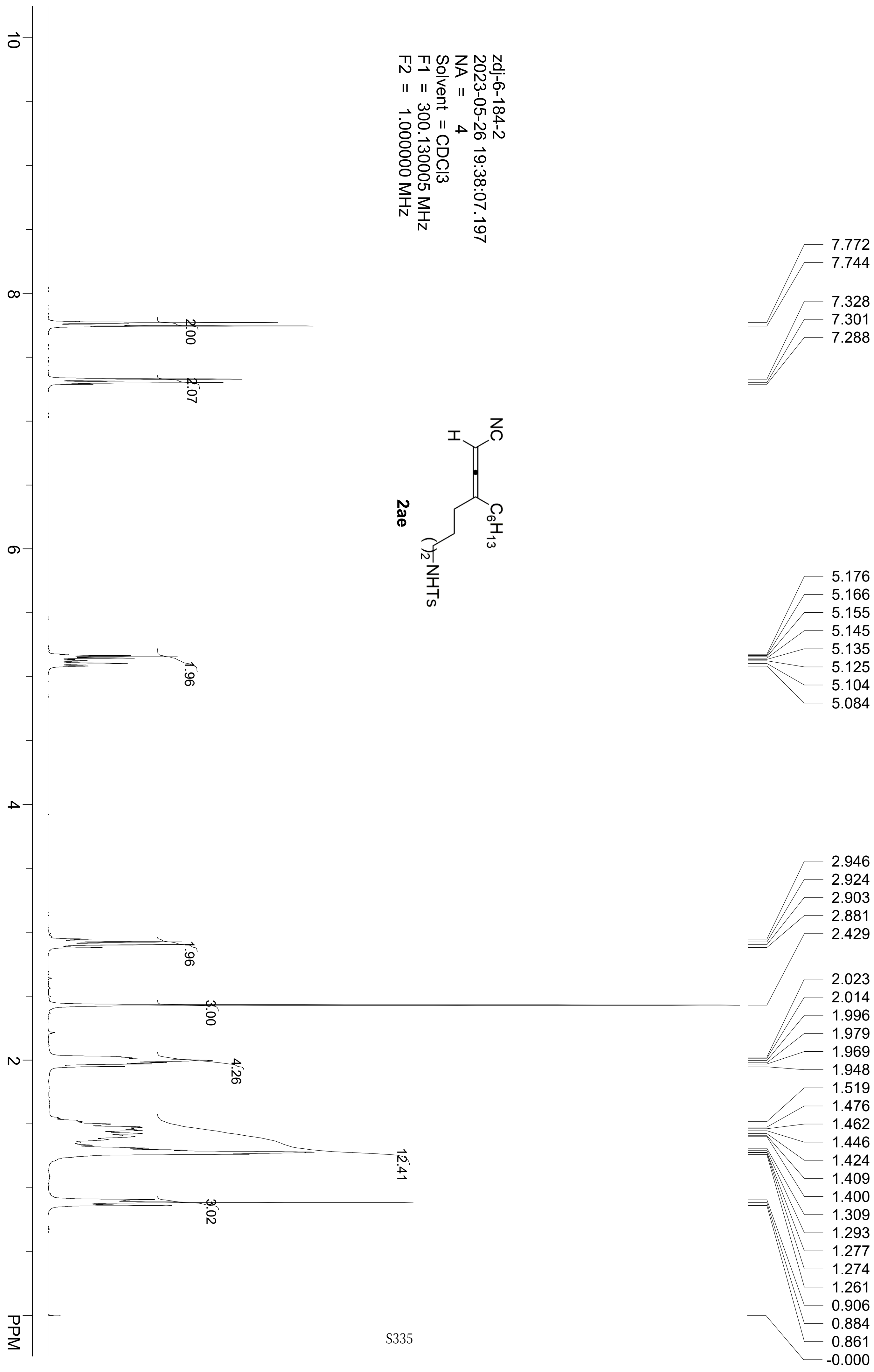
zdj-7-006cp
2023-06-03 16:14:43.700
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz

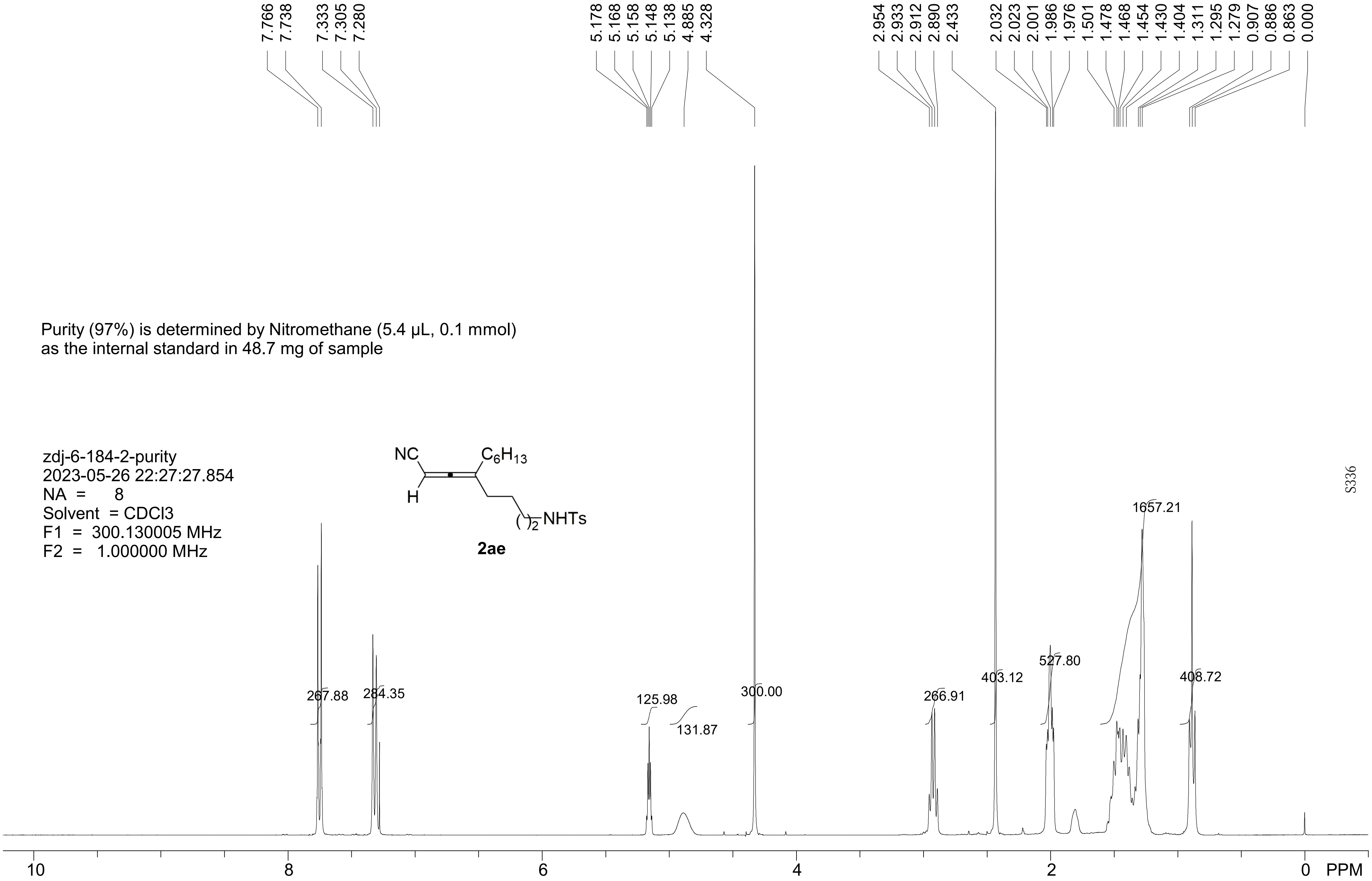

zdj-6-184-1
2023-05-26 22:55:17.622
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C6H13
NHTs
2
S3ae
7.771
7.743
7.321
7.294
7.270
4.732
4.711
4.691
2.969
2.946
2.925
2.904
2.428
2.236
2.228
2.022
2.014
1.481
1.469
1.462
1.451
1.415
1.391
1.365
1.351
1.343
1.302
1.274
1.263
0.903
0.882
0.859
-0.000
1.98
2.14
0.96
1.99
3.00
1.05
0.95
16.33
3.07
10
8
6
4
2
0 PPM



zdj-6-184-1
2023-05-26 23:36:45.115
NA = 512
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz

S3ae

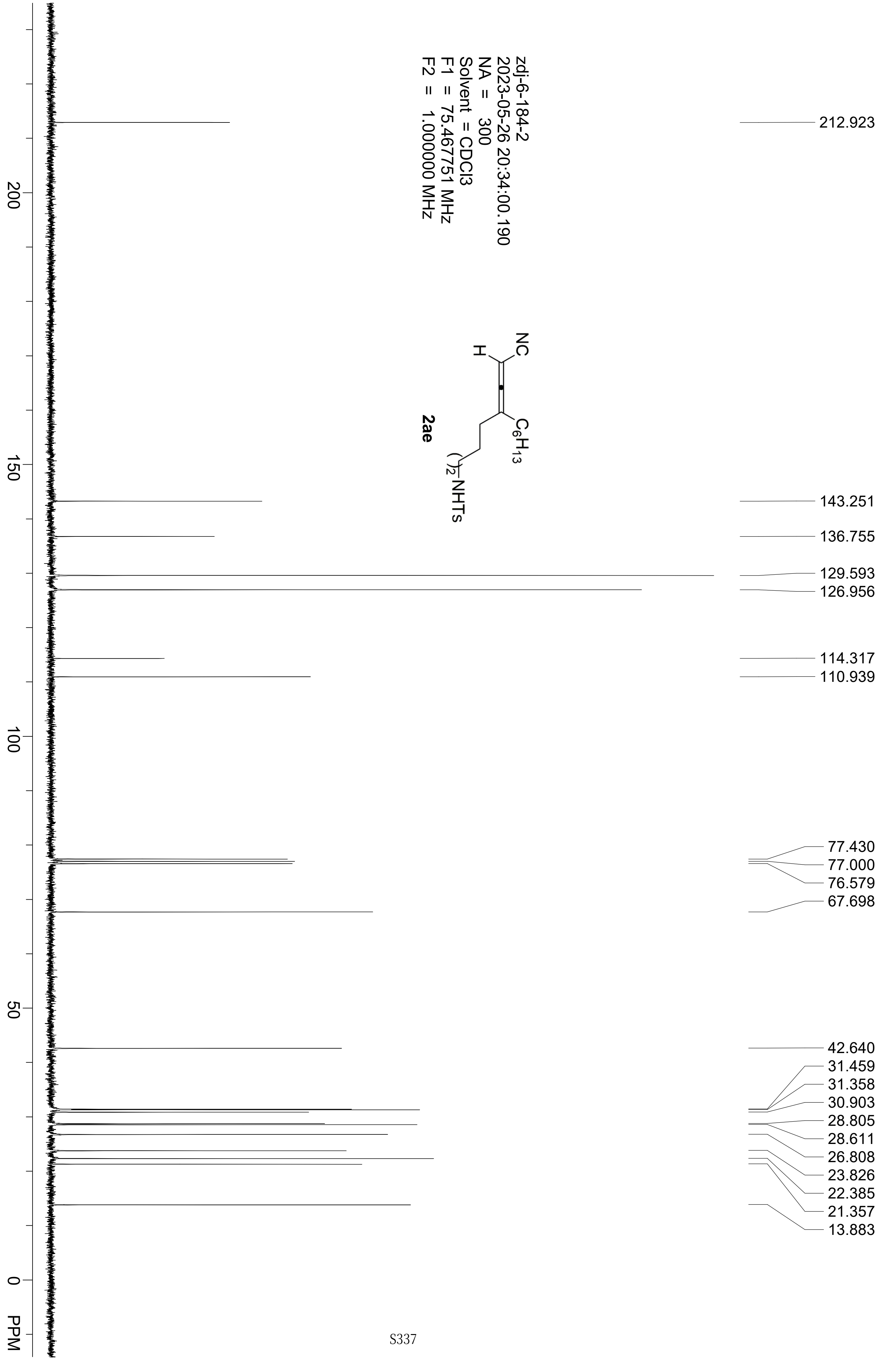

zdj-6-184-2
2023-05-26 19:38:07.197
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
H
C6H13
( )2 NHTs
2ae
7.772
7.744
7.328
7.301
7.288
5.176
5.166
5.155
5.145
5.135
5.125
5.104
5.084
2.946
2.924
2.903
2.881
2.429
2.023
2.014
1.996
1.979
1.969
1.948
1.519
1.476
1.462
1.446
1.424
1.409
1.400
1.309
1.293
1.277
1.274
1.261
0.906
0.884
0.861
-0.000
2.00
2.07
1.96
1.96
3.00
4.26
12.41
3.02
10
8
6
4
2
PPM

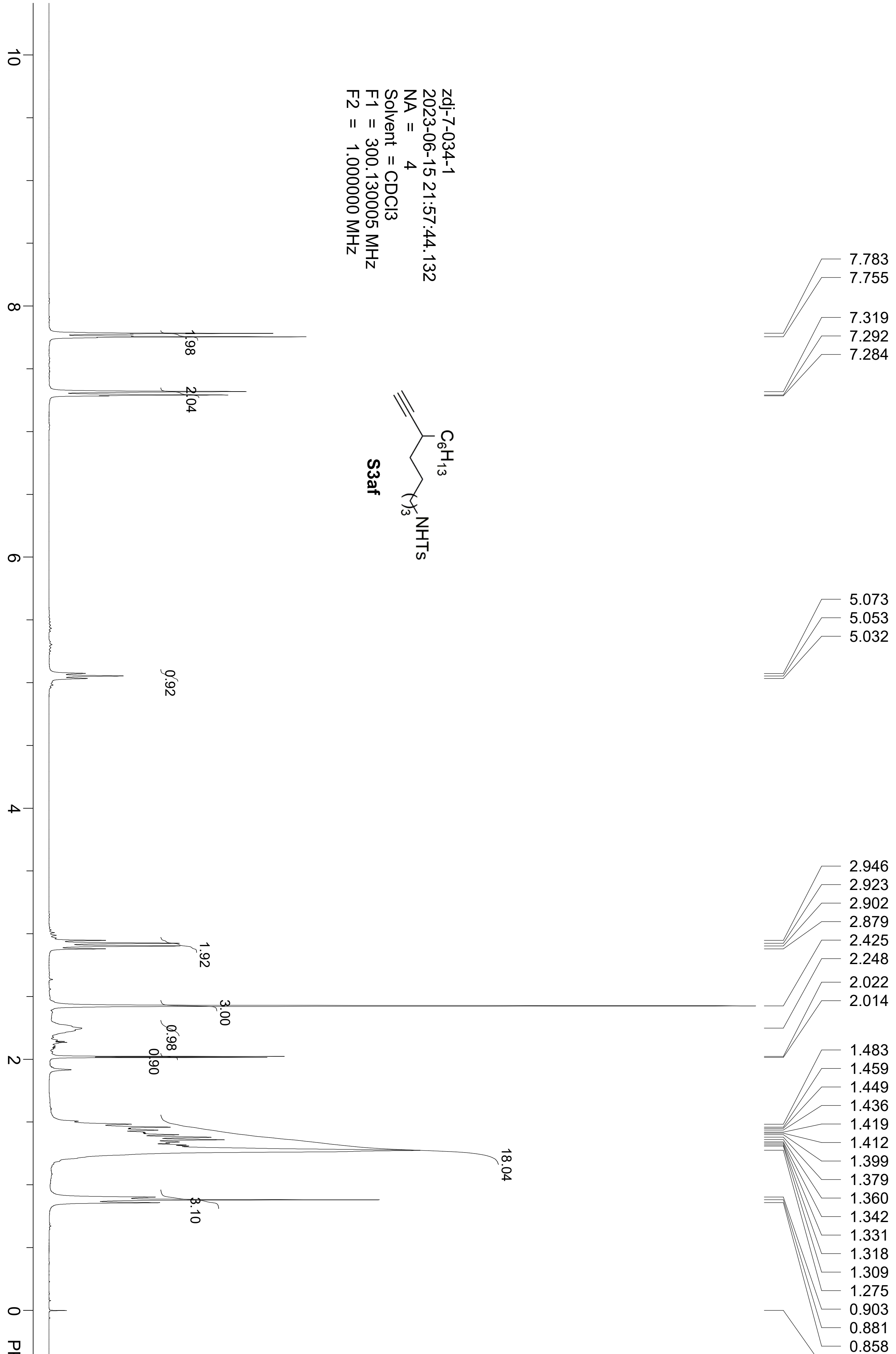


Purity (97%) is determined by Nitromethane (5.4 µL, 0.1 mmol)
as the internal standard in 48.7 mg of sample

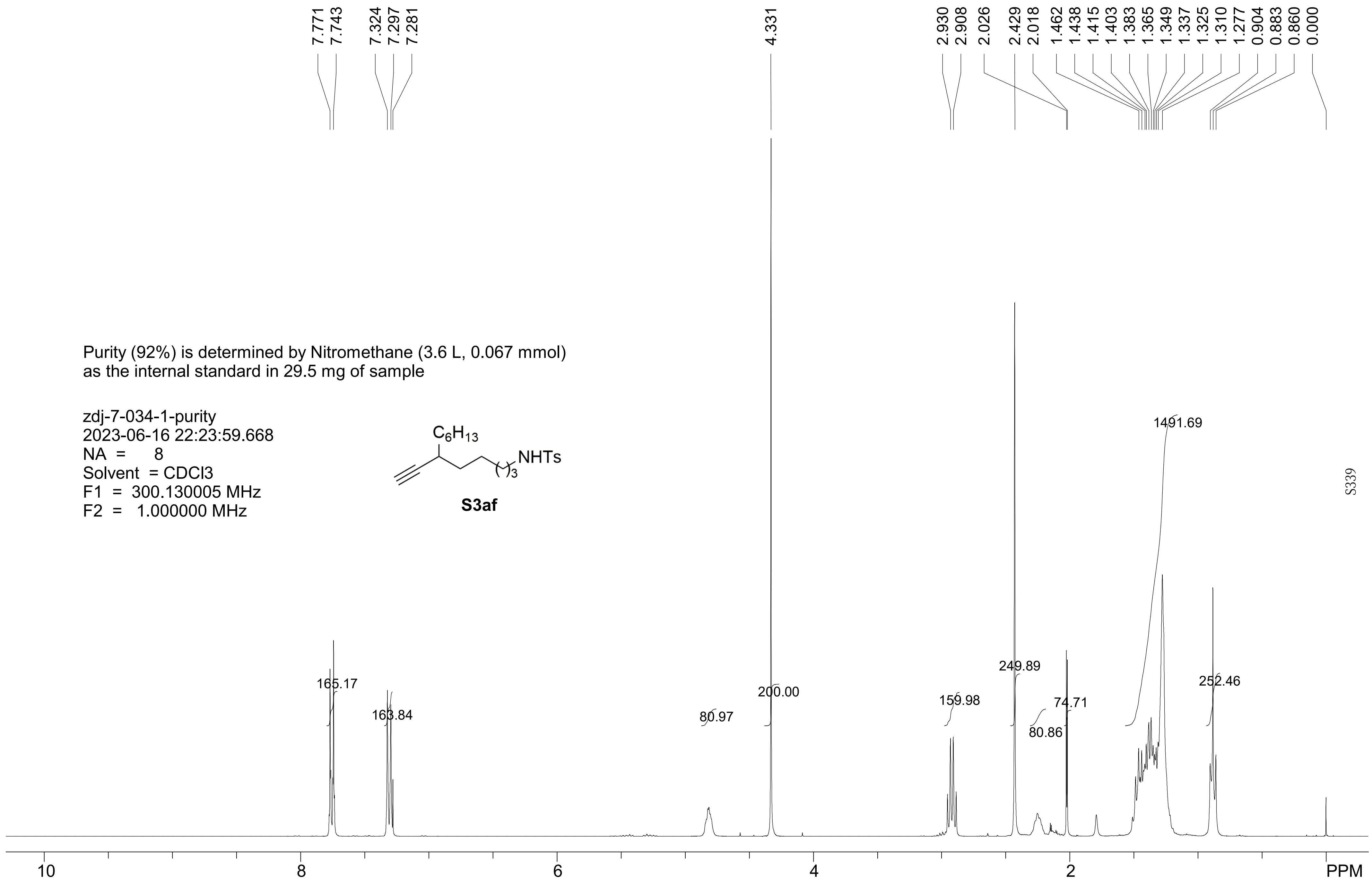
zdj-6-184-2-purity
2023-05-26 22:27:27.854
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz

2ae


zdj-6-184-2
2023-05-26 20:34:00.190
NA = 300
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
NC
H
C6H13
NHTs
2
2ae
212.923
143.251
136.755
129.593
126.956
114.317
110.939
77.430
77.000
76.579
67.698
42.640
31.459
31.358
30.903
28.805
28.611
26.808
23.826
22.385
21.357
13.883
200
150
100
50
0
PPM


zdj-7-034-1
2023-06-15 21:57:44.132
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C6H13
NHTs
3
7.783
7.755
7.319
7.292
7.284
5.073
5.053
5.032
2.946
2.923
2.902
2.879
2.425
2.248
2.022
2.014
1.483
1.459
1.449
1.436
1.419
1.412
1.399
1.379
1.360
1.342
1.331
1.318
1.309
1.275
0.903
0.881
0.858
0.000
1.98
2.04
0.92
1.92
3.00
0.98
0.90
18.04
3.10
10
8
6
4
2
0
PPM

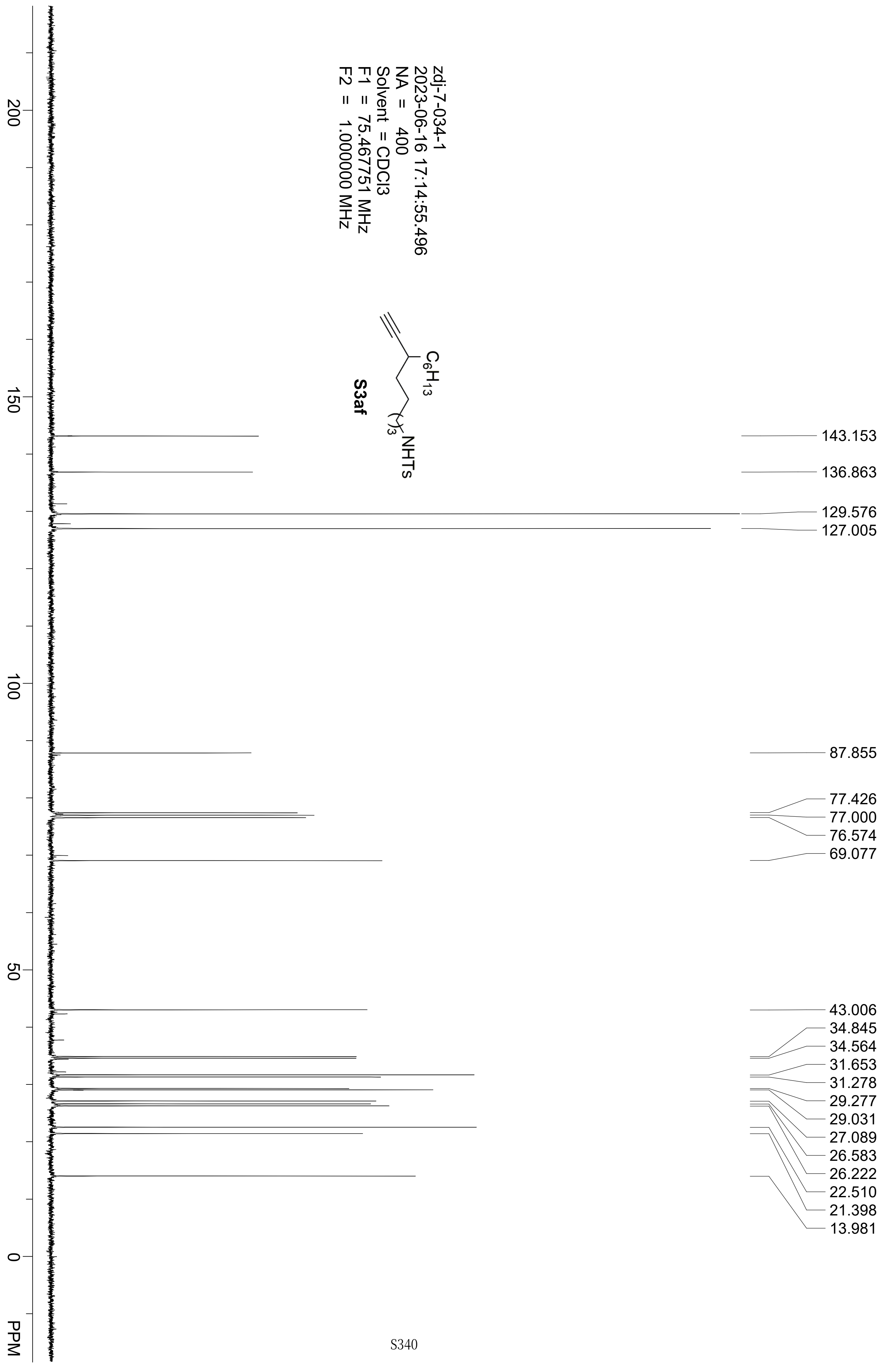
S3af

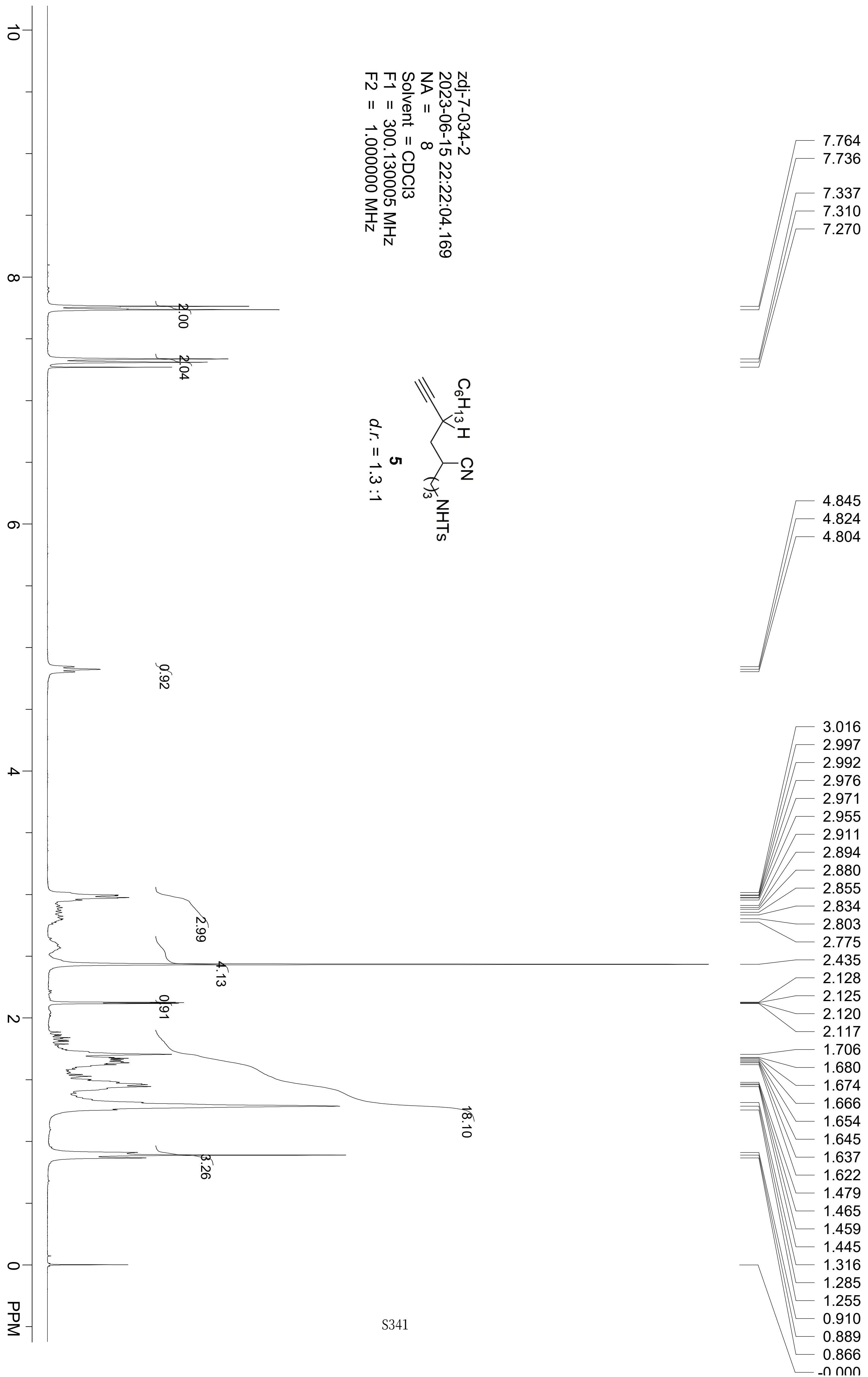


Purity (92%) is determined by Nitromethane (3.6 L, 0.067 mmol)
as the internal standard in 29.5 mg of sample

zdj-7-034-1-purity
2023-06-16 22:23:59.668
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz

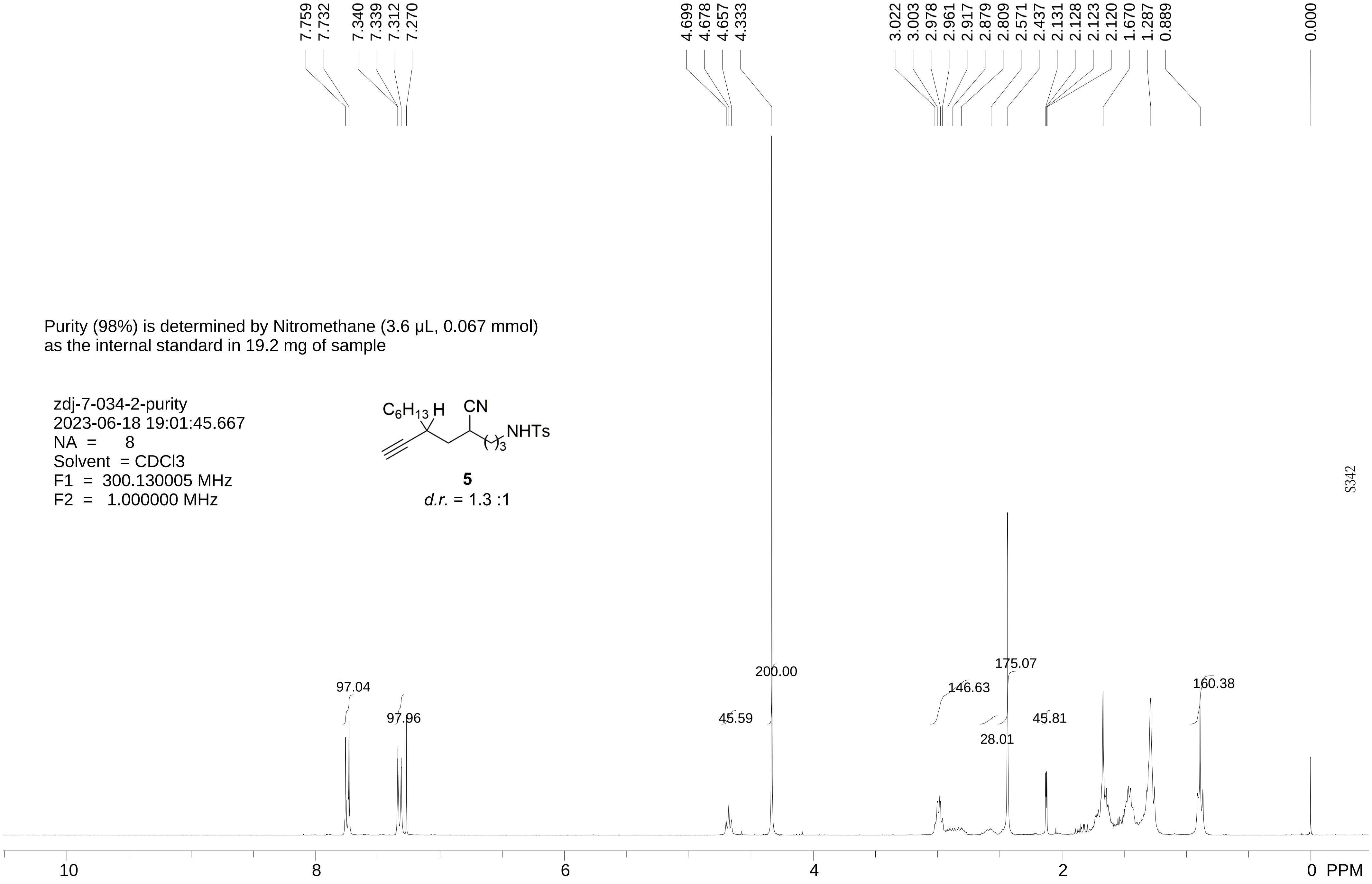
S3af


zdj-7-034-1
2023-06-16 17:14:55.496
NA = 400
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
C_6H_{13}
$()_3$
NHTs
S3af
143.153
136.863
129.576
127.005
87.855
77.426
77.000
76.574
69.077
43.006
34.845
34.564
31.653
31.278
29.277
29.031
27.089
26.583
26.222
22.510
21.398
13.981
200
150
100
50
0
PPM


zdj-7-034-2
2023-06-15 22:22:04.169
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
C6H13 H CN
NHTs
3
10
8
6
4
2
0
PPM
2.00
2.04
0.92
2.99
4.13
0.91
18.10
3.26
7.764
7.736
7.337
7.310
7.270
4.845
4.824
4.804
3.016
2.997
2.992
2.976
2.971
2.955
2.911
2.894
2.880
2.855
2.834
2.803
2.775
2.435
2.128
2.125
2.120
2.117
1.706
1.680
1.674
1.666
1.654
1.645
1.637
1.622
1.479
1.465
1.459
1.445
1.316
1.285
1.255
0.910
0.889
0.866
-0.000

5

d.r. = 1.3 :1

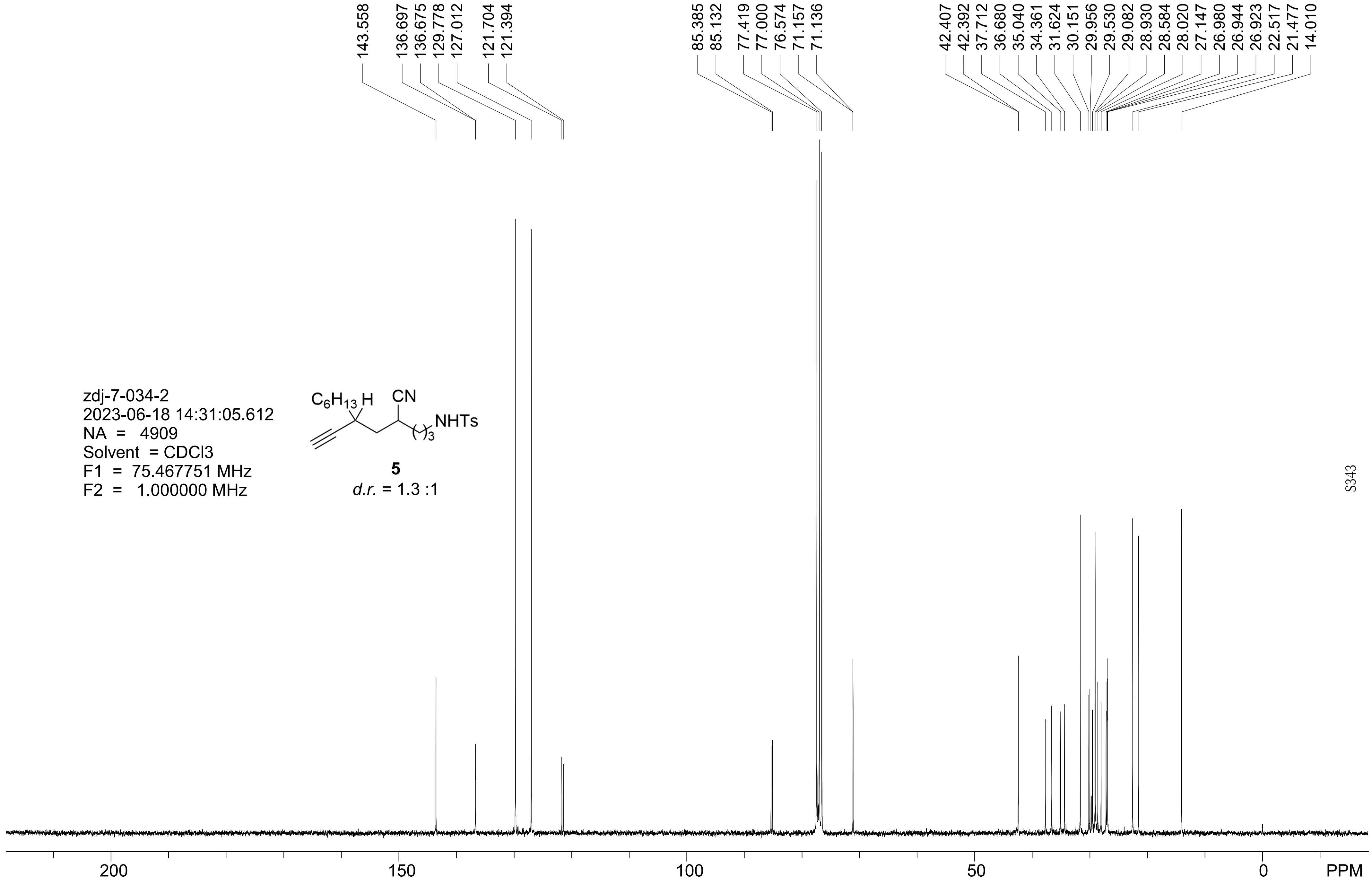


Purity (98%) is determined by Nitromethane (3.6 μL, 0.067 mmol)
as the internal standard in 19.2 mg of sample

zdj-7-034-2-purity
2023-06-18 19:01:45.667
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz

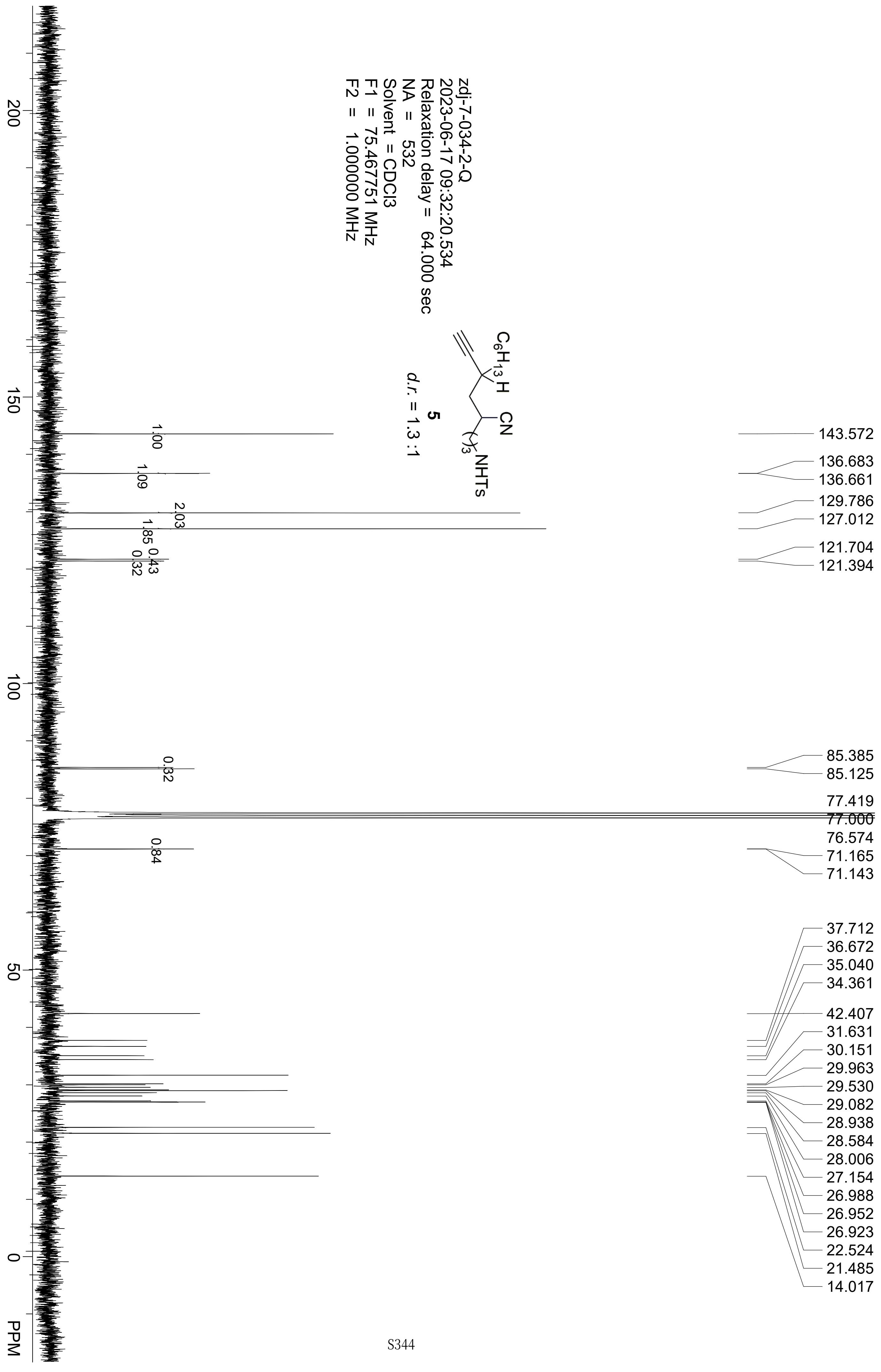
5

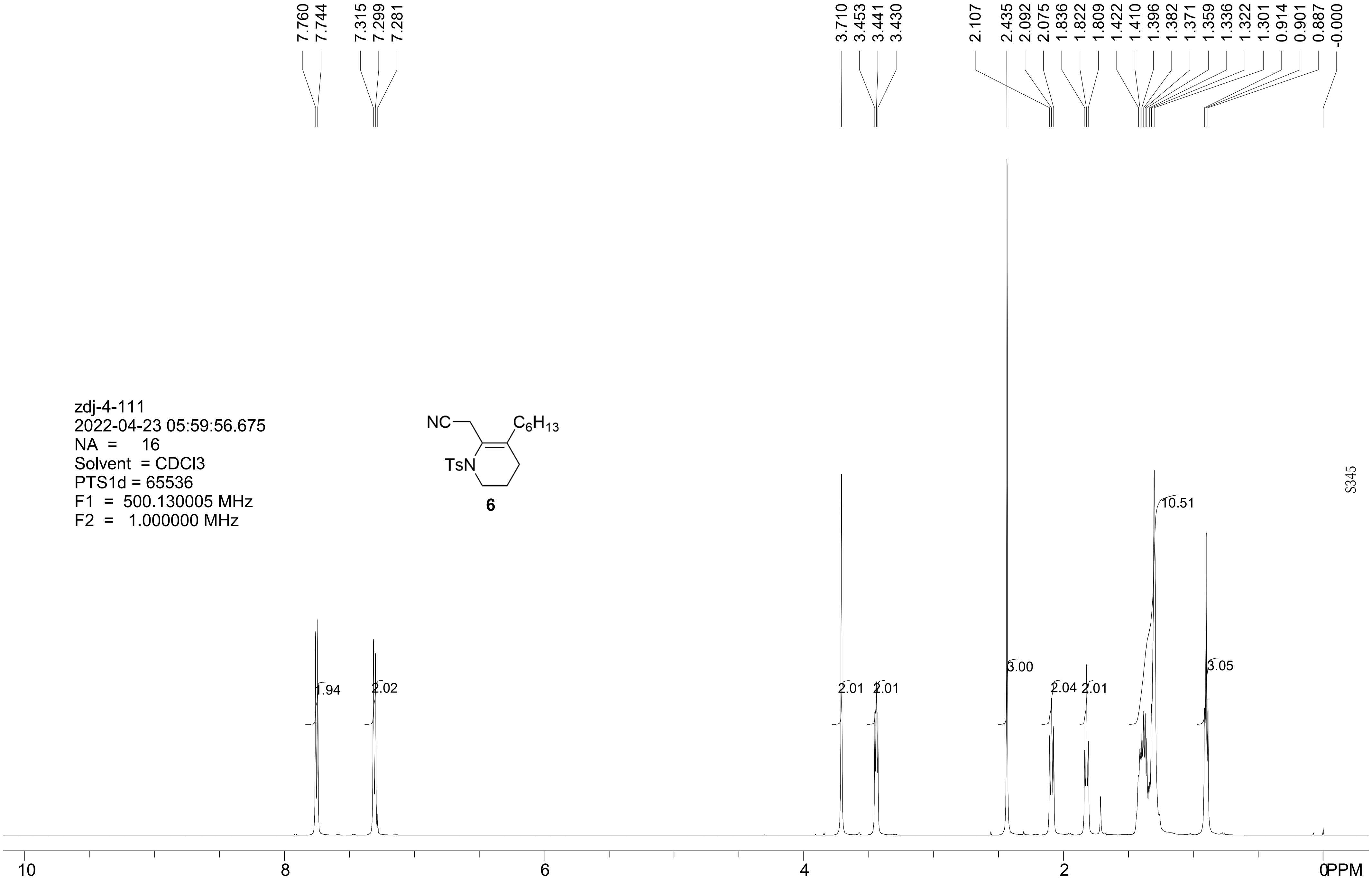
d.r. = 1.3 :1


zdj-7-034-2
2023-06-18 14:31:05.612
NA = 4909
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
C6H13 H
CN
NHTs
3
143.558
136.697
136.675
129.778
127.012
121.704
121.394
85.385
85.132
77.419
77.000
76.574
71.157
71.136
42.407
42.392
37.712
36.680
35.040
34.361
31.624
30.151
29.956
29.530
29.082
28.930
28.584
28.020
27.147
26.980
26.944
26.923
22.517
21.477
14.010
200
150
100
50
0
PPM

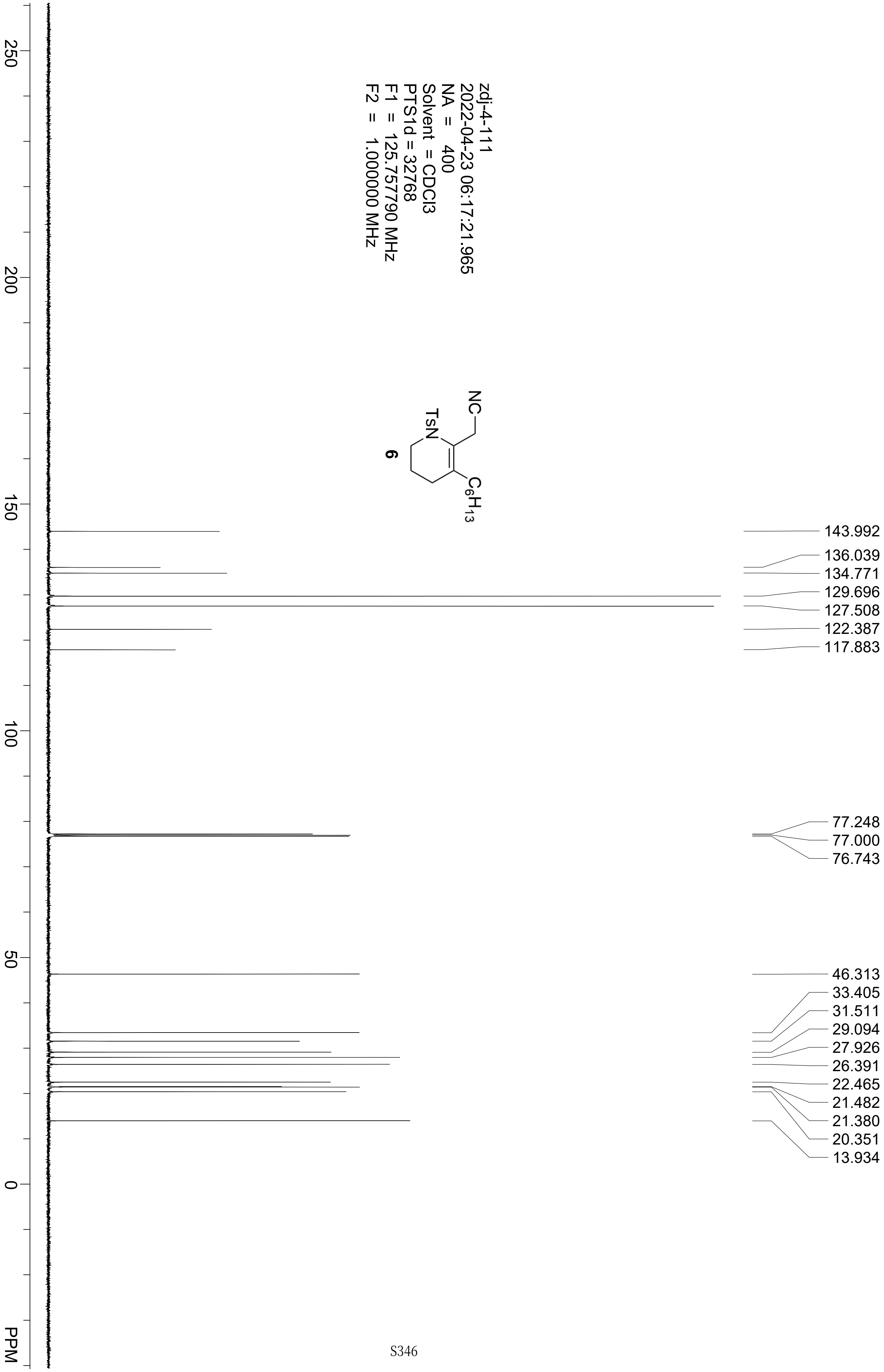
5

d.r. = 1.3 :1

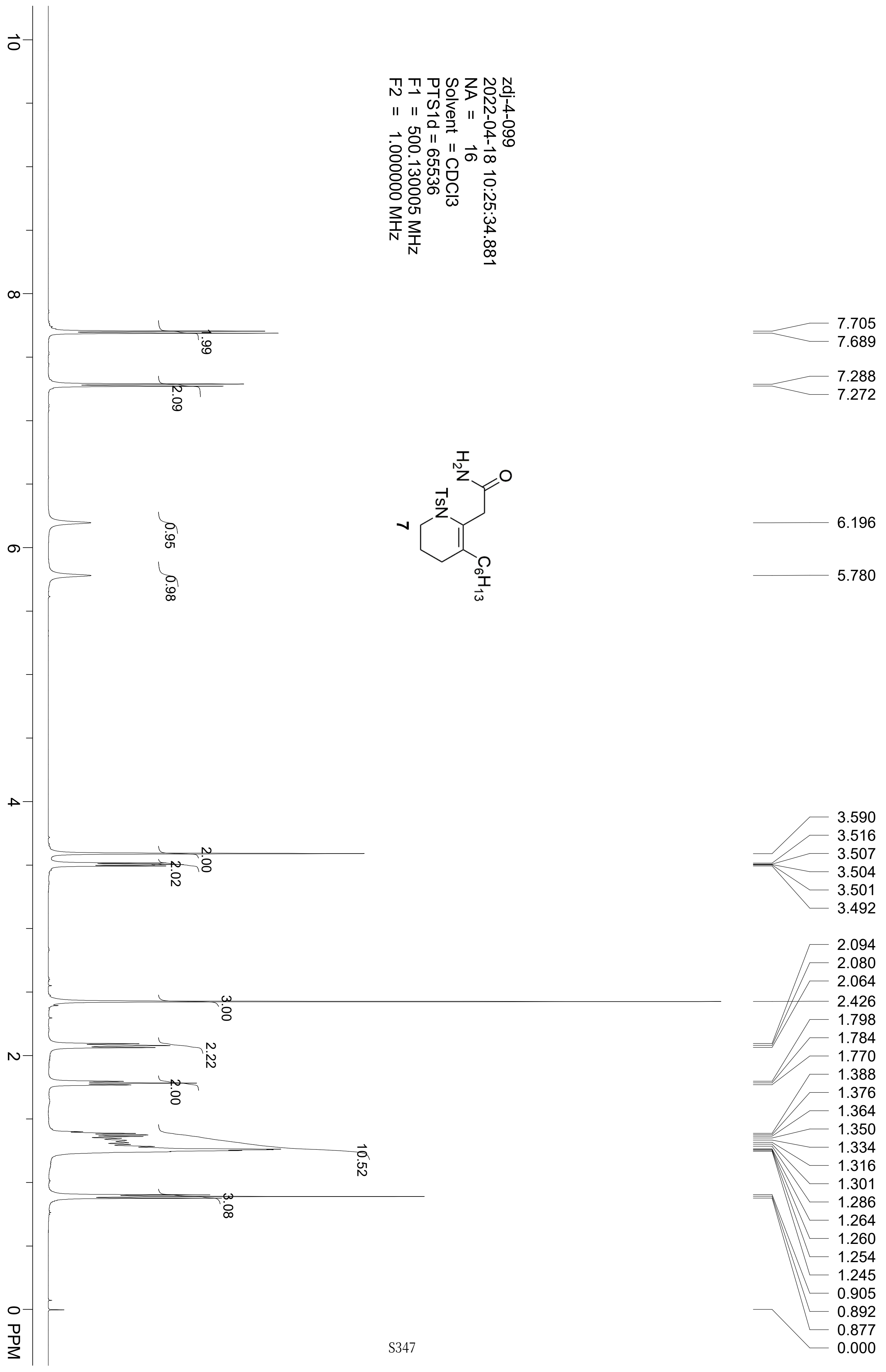

zdj-7-034-2-Q
2023-06-17 09:32:20.534
Relaxation delay = 64.000 sec
NA = 532
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
C6H13 H
CN
NHTs
3
5
d.r. = 1.3 :1
1.00
1.09
2.03
1.85
0.43
0.32
0.32
0.84
143.572
136.683
136.661
129.786
127.012
121.704
121.394
85.385
85.125
77.419
77.000
76.574
71.165
71.143
37.712
36.672
35.040
34.361
42.407
31.631
30.151
29.963
29.530
29.082
28.938
28.584
28.006
27.154
26.988
26.952
26.923
22.524
21.485
14.017
200
150
100
50
0
PPM

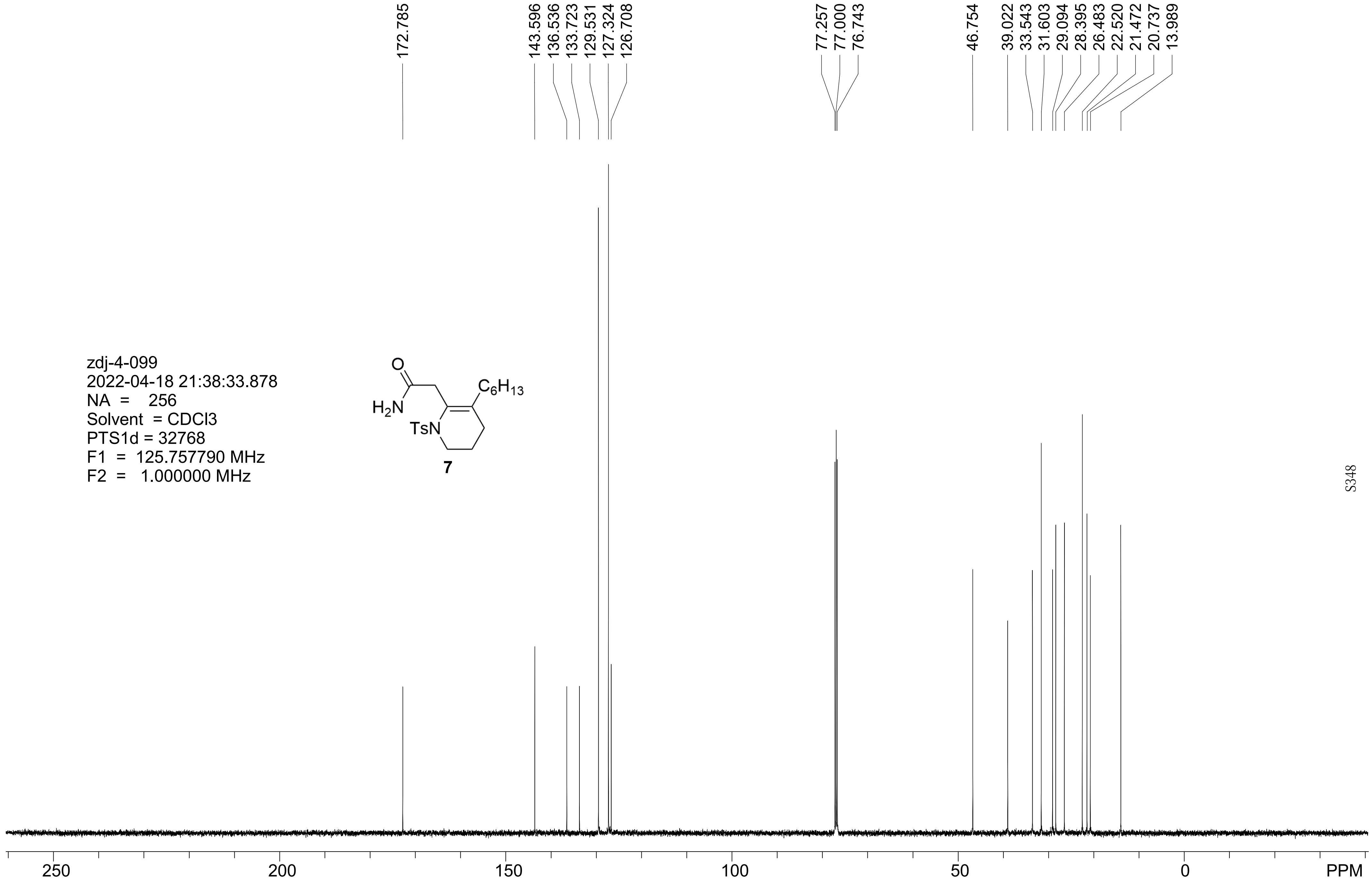

zdj-4-111
2022-04-23 05:59:56.675
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
NC
TsN
C_6H_{13}
7.760
7.744
7.315
7.299
7.281
3.710
3.453
3.441
3.430
2.107
2.435
2.092
2.075
1.836
1.822
1.809
1.422
1.410
1.396
1.382
1.371
1.359
1.336
1.322
1.301
0.914
0.901
0.887
-0.000
1.94
2.02
2.01
2.01
3.00
2.04
2.01
10.51
3.05
10
8
6
4
2
0PPM

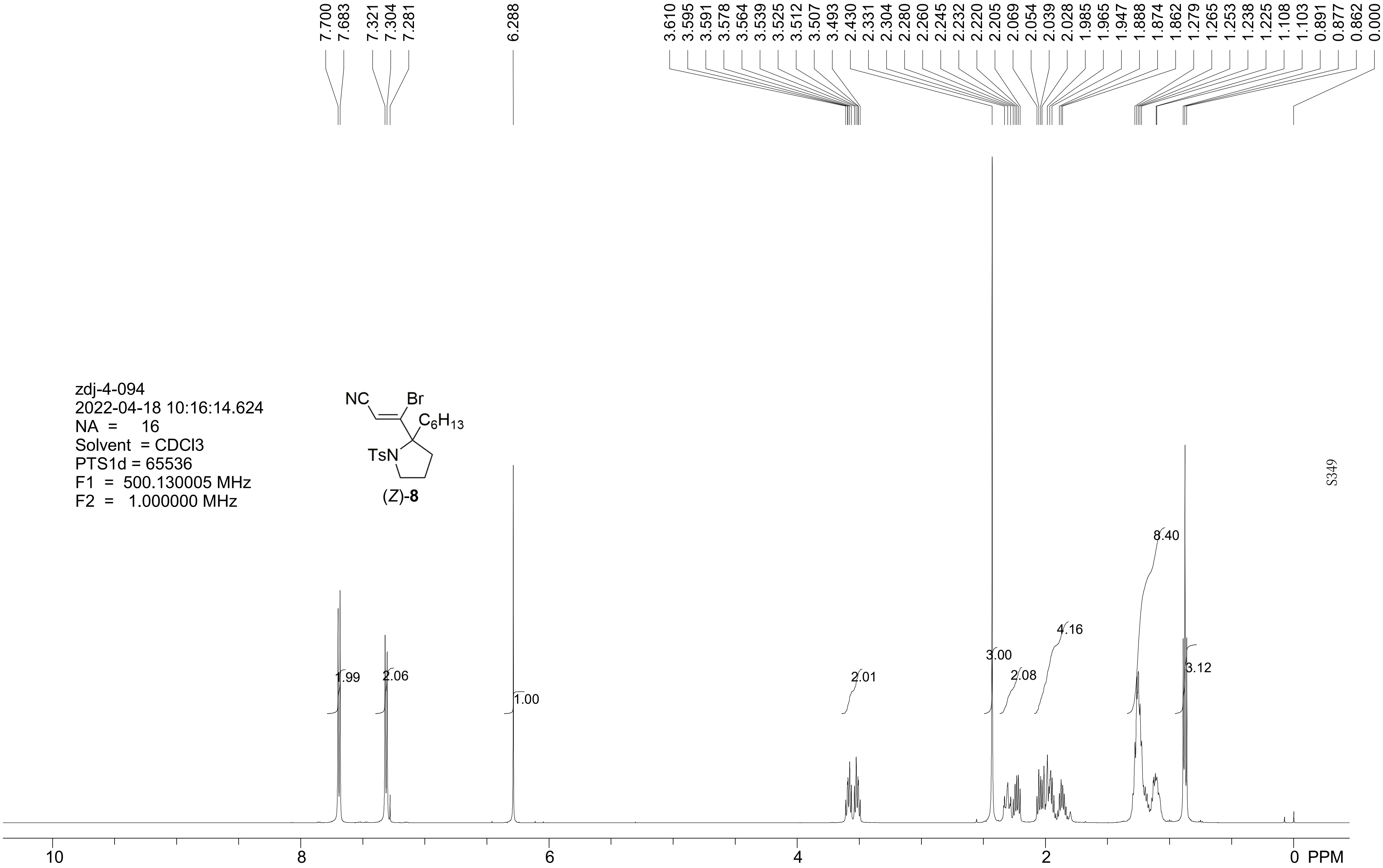
6


zdj-4-111
2022-04-23 06:17:21.965
NA = 400
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
TsN
C6H13
250
200
150
100
50
0
PPM
143.992
136.039
134.771
129.696
127.508
122.387
117.883
77.248
77.000
76.743
46.313
33.405
31.511
29.094
27.926
26.391
22.465
21.482
21.380
20.351
13.934

6

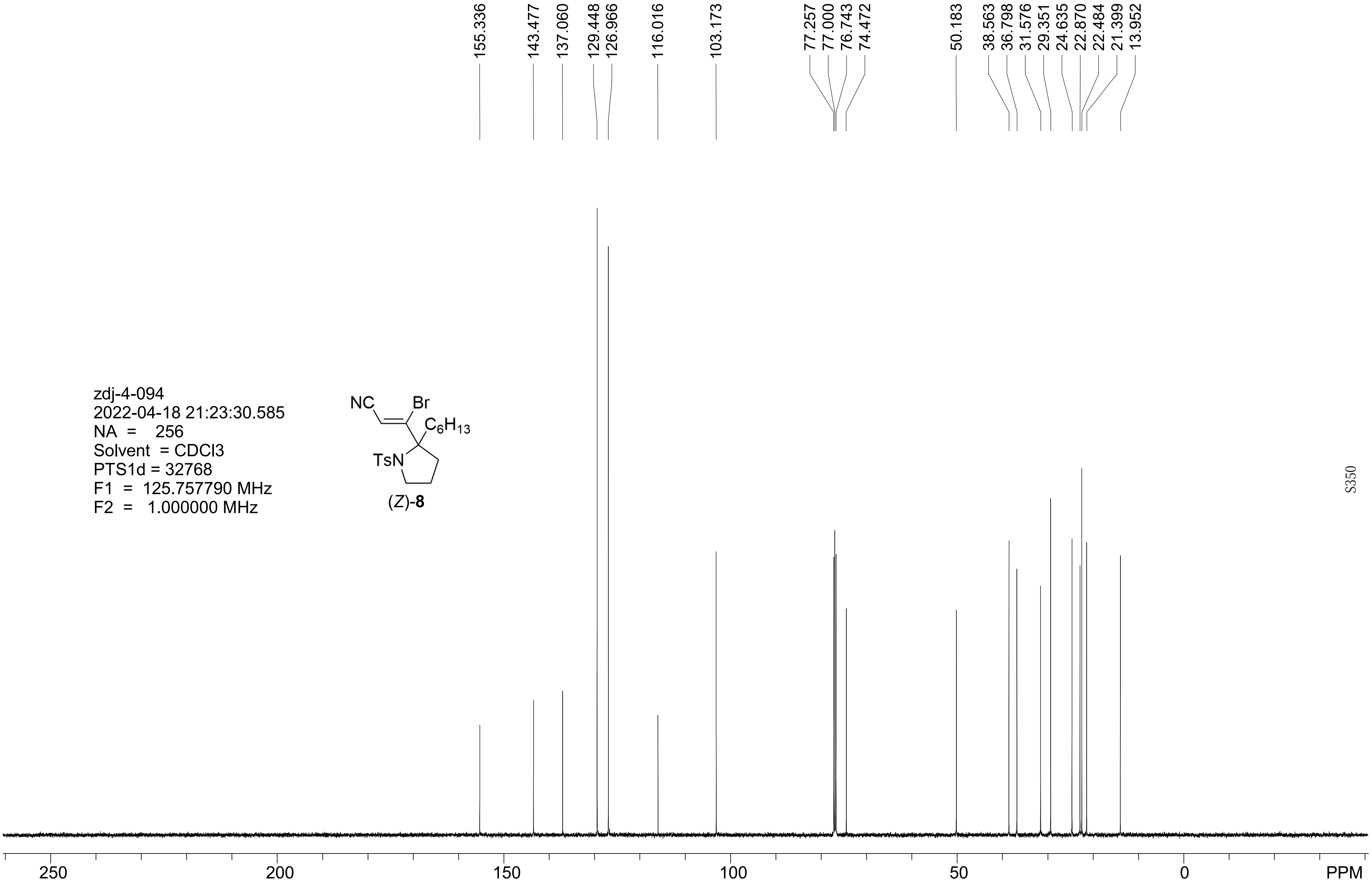

7
zdj-4-099
2022-04-18 10:25:34.881
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
H2N
O
TsN
C6H13
10
8
6
4
2
0 PPM
1.99
2.09
0.95
0.98
2.00
2.02
3.00
2.22
2.00
10.52
3.08
7.705
7.689
7.288
7.272
6.196
5.780
3.590
3.516
3.507
3.504
3.501
3.492
2.094
2.080
2.064
2.426
1.798
1.784
1.770
1.388
1.376
1.364
1.350
1.334
1.316
1.301
1.286
1.264
1.260
1.254
1.245
0.905
0.892
0.877
0.000


zdj-4-099
2022-04-18 21:38:33.878
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
O
H2N
TsN
C6H13
7
172.785
143.596
136.536
133.723
129.531
127.324
126.708
77.257
77.000
76.743
46.754
39.022
33.543
31.603
29.094
28.395
26.483
22.520
21.472
20.737
13.989
250
200
150
100
50
0
PPM



zdj-4-094
2022-04-18 10:16:14.624
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz

(*Z*)-**8**


155.336
143.477
137.060
129.448
126.966
116.016
103.173
77.257
77.000
76.743
74.472
50.183
38.563
36.798
31.576
29.351
24.635
22.870
22.484
21.399
13.952
zdj-4-094
2022-04-18 21:23:30.585
NA = 256
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
Br
C6H13
TsN
(Z)-8
250
200
150
100
50
0
PPM

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 220506_zdj_4_094

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: 220506_zdj_4_094

```
Bond precision:   C-C = 0.0099 A          Wavelength=0.71073

Cell:             a=8.3288(2)     b=22.8188(8)        c=10.9506(3)
                  alpha=90        beta=90.530(2)      gamma=90
Temperature:      293 K

                 Calculated                        Reported
Volume           2081.11(11)                       2081.11(11)
Space group      P 21                              P 1 21 1
Hall group       P 2yb                             P 2yb
Moiety formula   C20 H27 Br N2 O2 S                C20 H27 Br N2 O2 S
Sum formula      C20 H27 Br N2 O2 S                C20 H27 Br N2 O2 S
Mr               439.40                            439.40
Dx,g cm-3        1.402                             1.402
Z                4                                 4
Mu (mm-1)        2.092                             2.092
F000             912.0                             912.0
F000'            911.65
h,k,lmax         11,31,15                          11,30,15
Nref             11515[ 5894]                      9055
Tmin,Tmax        0.500,0.580                       0.811,1.000
Tmin'            0.386

Correction method= # Reported T Limits: Tmin=0.811 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.54/0.79       Theta(max)= 29.426

                                                    wR2(reflections)=
R(reflections)= 0.0488( 5914)                       0.1120( 9055)

S = 1.011                    Npar= 473
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

● Alert level A

```
EXPT005_ALERT_1_A  _exptl_crystal_description is missing
            Crystal habit description.
            The following tests will not be performed.
            CRYSR_01
PLAT699_ALERT_1_A Missing _exptl_crystal_description Value .......     Please Do !
```

● Alert level C

```
PLAT220_ALERT_2_C NonSolvent   Resd 2  C   Ueq(max)/Ueq(min) Range        3.1 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C30      --C31      .       0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C39      --C40      .       0.18 Ang.
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of       C30 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C29 Check
PLAT341_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00992 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.361 Check
PLAT915_ALERT_3_C No Flack x Check Done: Low Friedel Pair Coverage         68 %
```

● Alert level G

```
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
PLAT791_ALERT_4_G Model has Chirality at C8           (Sohnke SpGr)         R Verify
PLAT791_ALERT_4_G Model has Chirality at C28          (Sohnke SpGr)         S Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        661 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          1 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          1 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.0 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          0 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by          2 Check
```

```
   2 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   8 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  11 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   5 ALERT type 2 Indicator that the structure model may be wrong or deficient
   6 ALERT type 3 Indicator that the structure quality may be low
   5 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

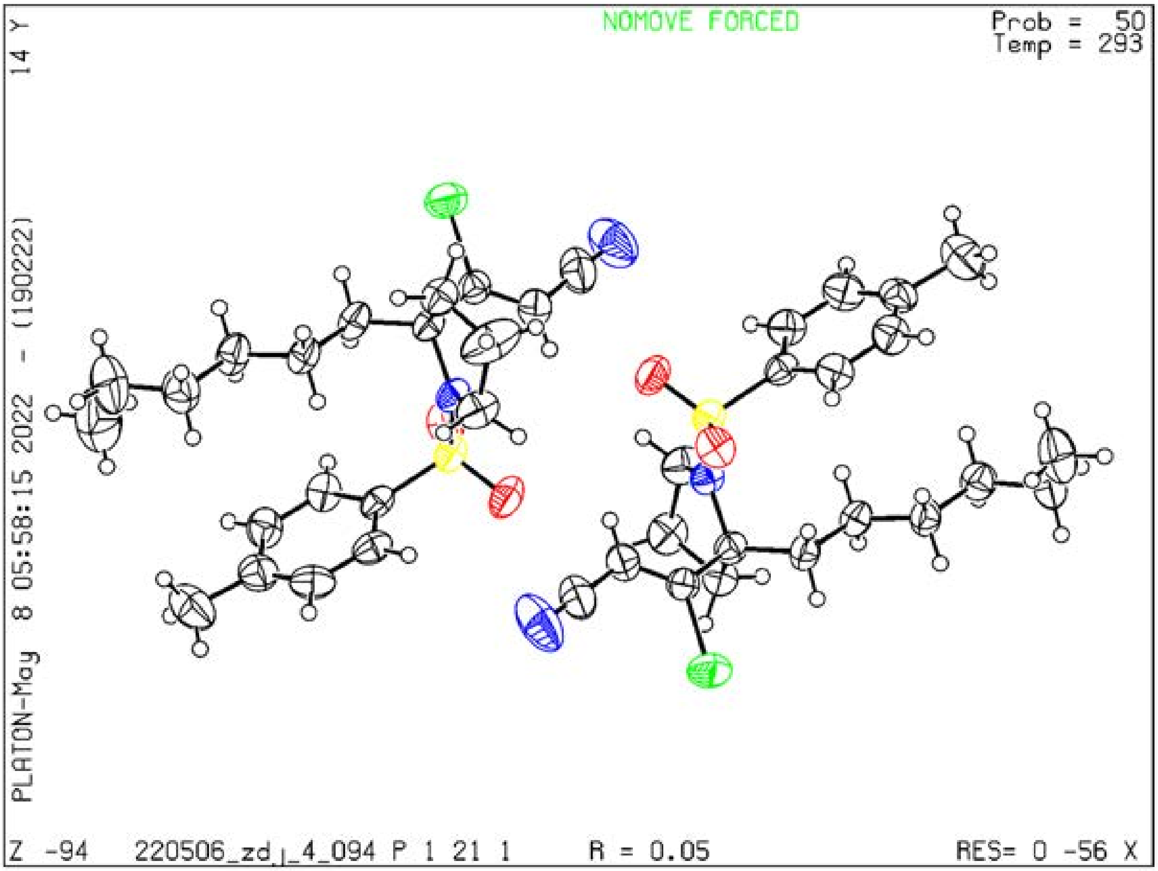
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

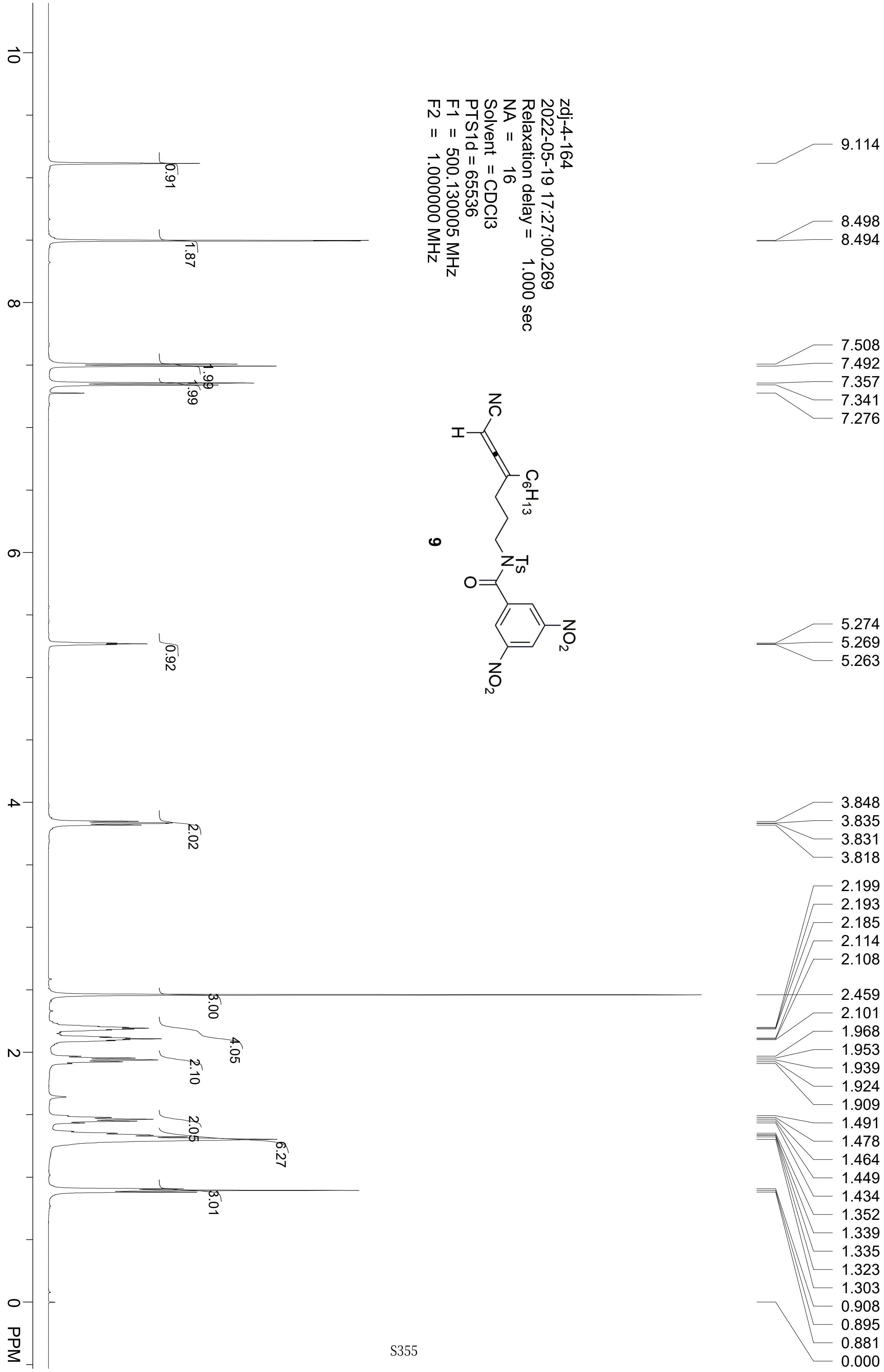
Publication of your CIF in other journals

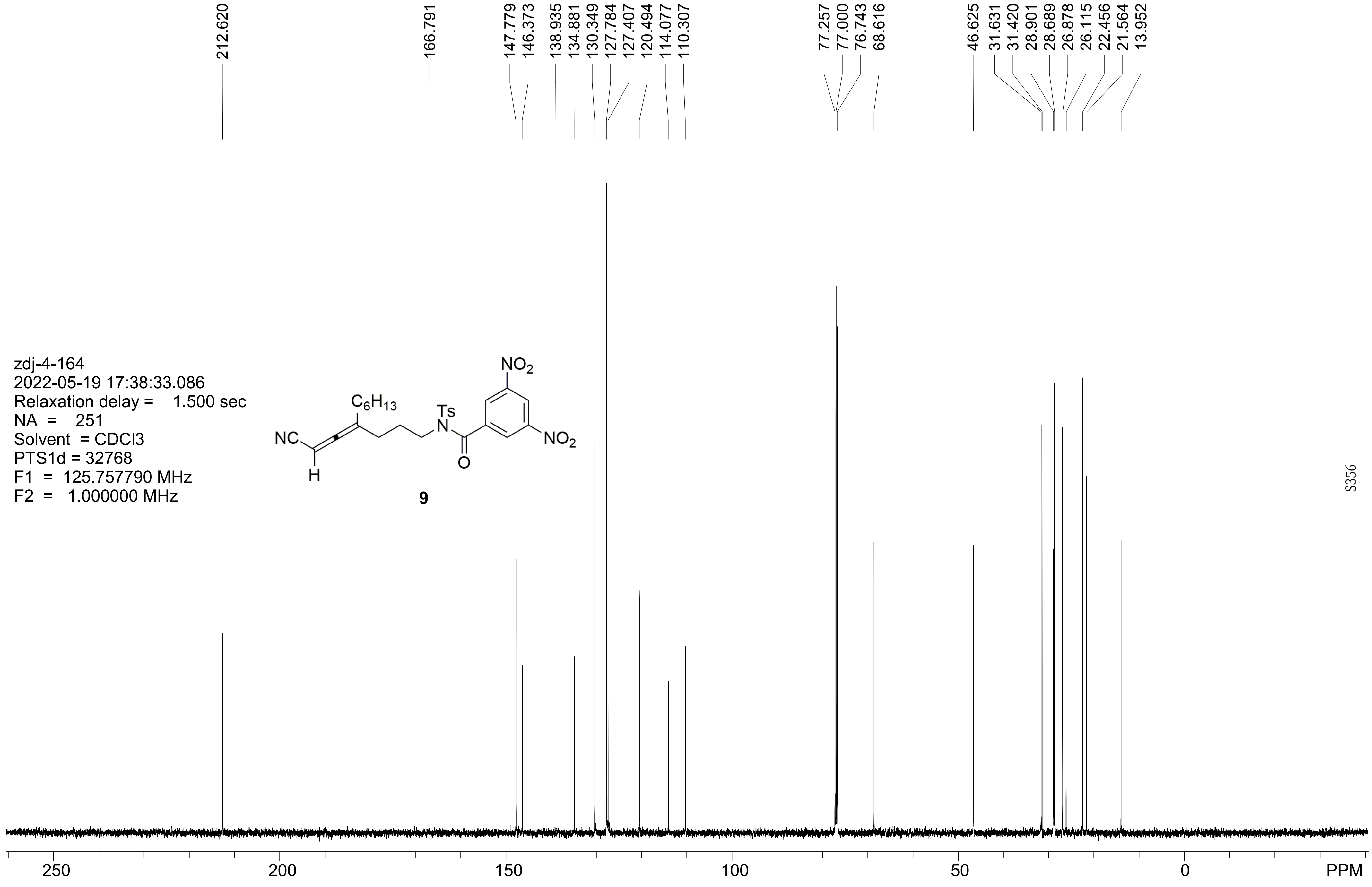
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/02/2022; check.def file version of 19/02/2022

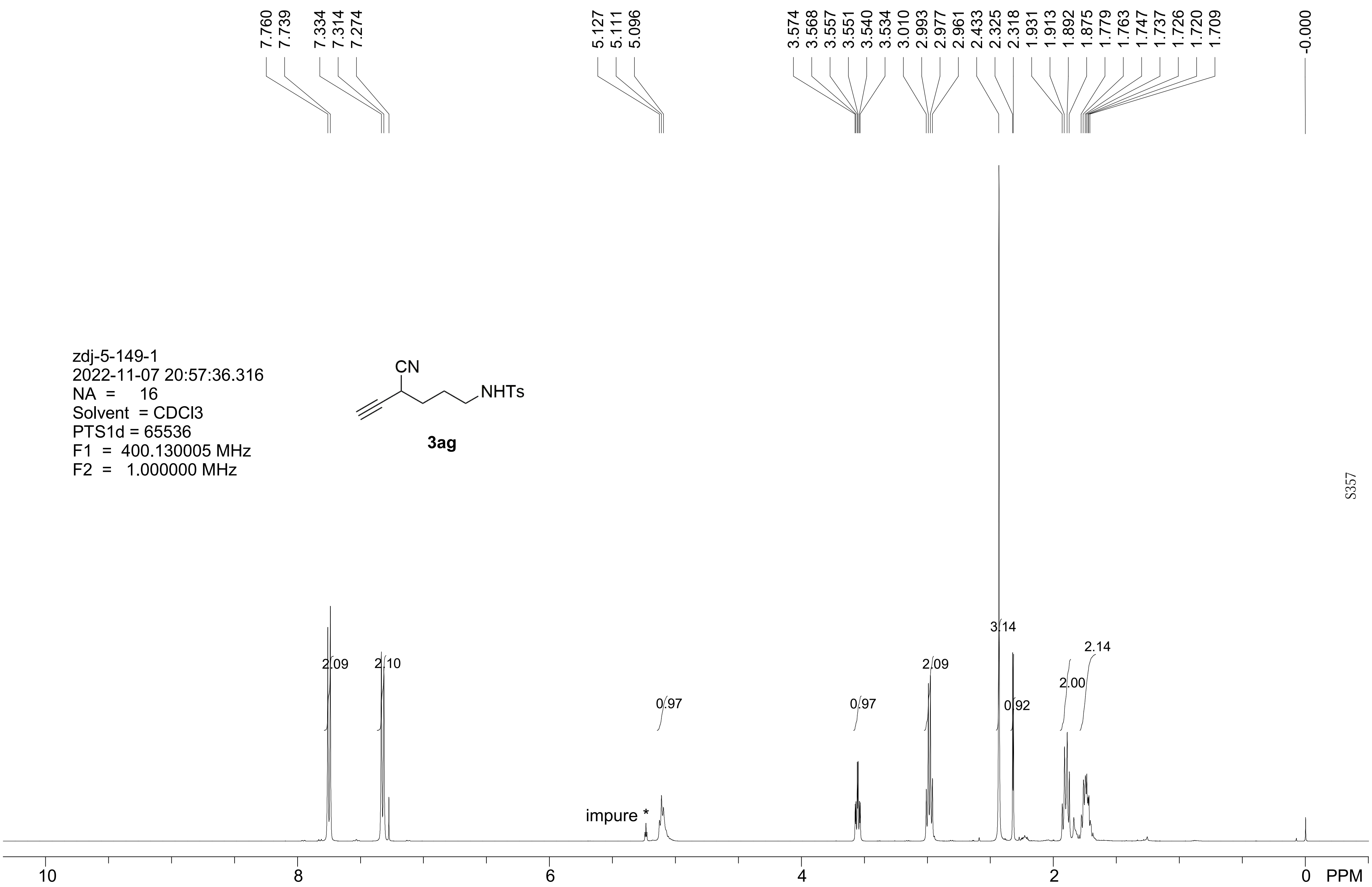
Datablock 220506_zdj_4_094 - ellipsoid plot

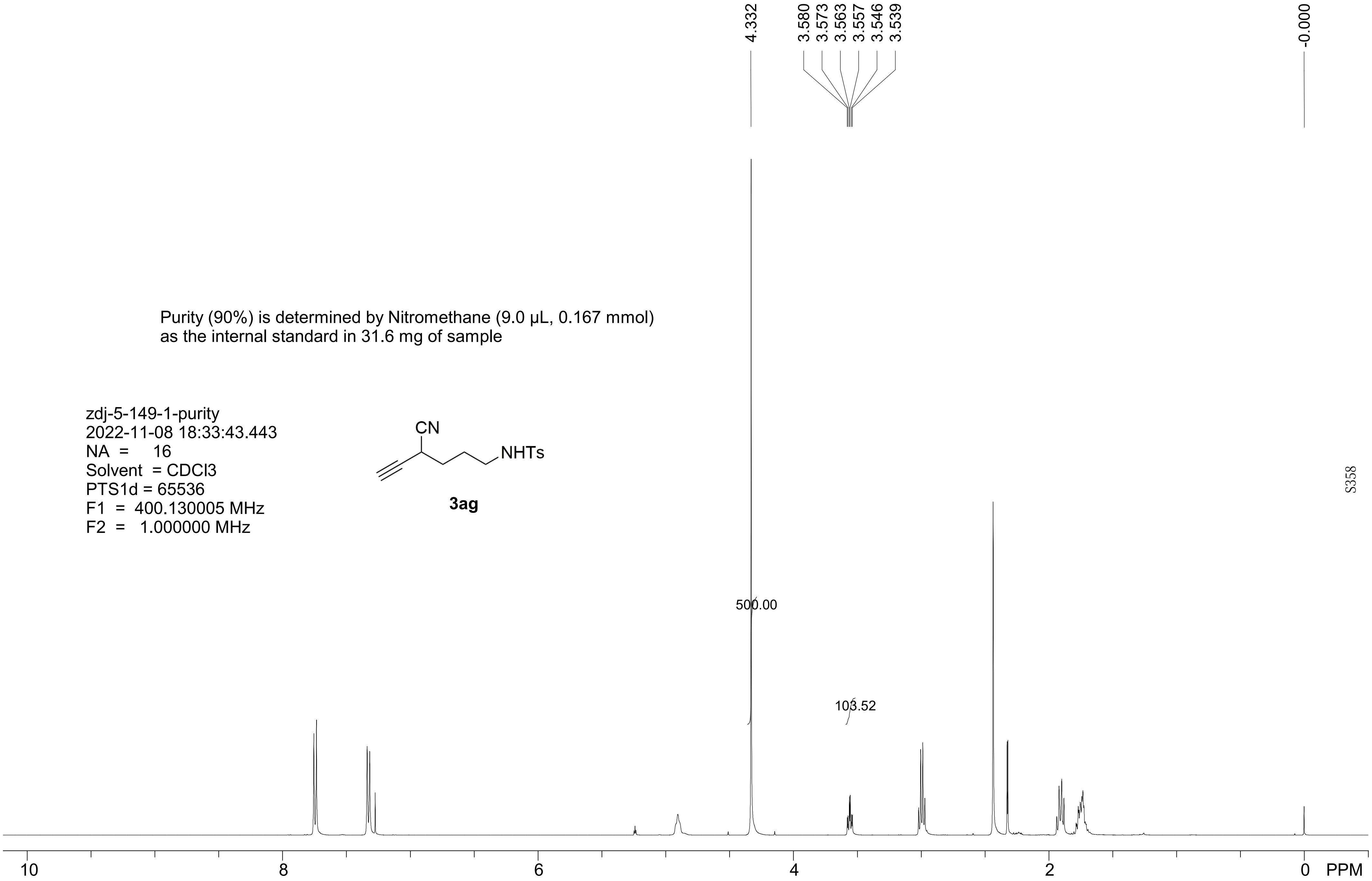



zdj-4-164
2022-05-19 17:27:00.269
Relaxation delay = 1.000 sec
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 500.130005 MHz
F2 = 1.000000 MHz
NC
H
C6H13
N
Ts
O
NO2
NO2
9
9.114
8.498
8.494
7.508
7.492
7.357
7.341
7.276
5.274
5.269
5.263
3.848
3.835
3.831
3.818
2.199
2.193
2.185
2.114
2.108
2.459
2.101
1.968
1.953
1.939
1.924
1.909
1.491
1.478
1.464
1.449
1.434
1.352
1.339
1.335
1.323
1.303
0.908
0.895
0.881
0.000
0.91
1.87
1.99
1.99
0.92
2.02
3.00
4.05
2.10
2.05
6.27
3.01
10
8
6
4
2
0
PPM


212.620
166.791
147.779
146.373
138.935
134.881
130.349
127.784
127.407
120.494
114.077
110.307
77.257
77.000
76.743
68.616
46.625
31.631
31.420
28.901
28.689
26.878
26.115
22.456
21.564
13.952
zdj-4-164
2022-05-19 17:38:33.086
Relaxation delay = 1.500 sec
NA = 251
Solvent = CDCl3
PTS1d = 32768
F1 = 125.757790 MHz
F2 = 1.000000 MHz
NC
H
C6H13
Ts
N
O
NO2
NO2
250
200
150
100
50
0
PPM

9

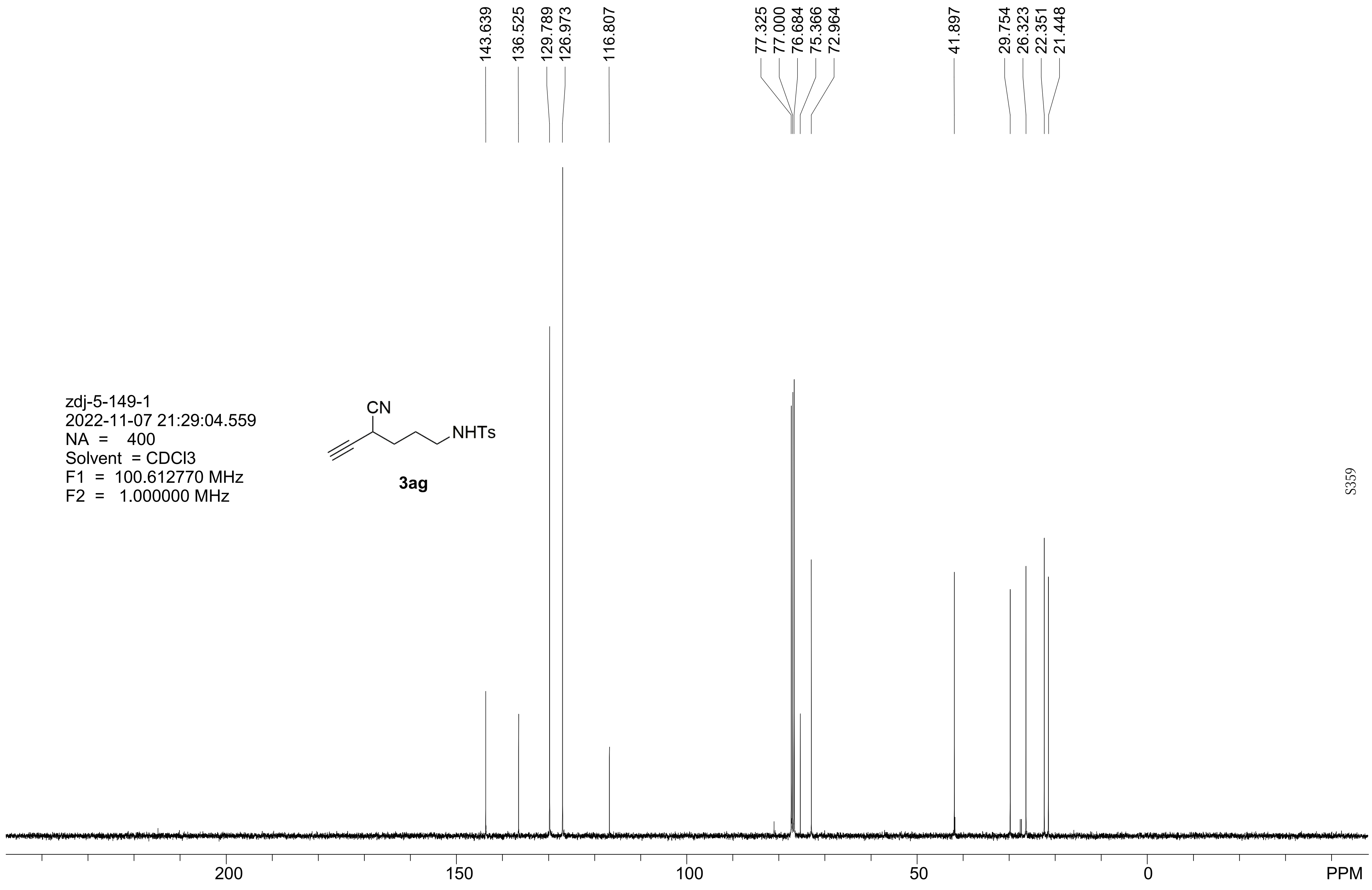

7.760
7.739
7.334
7.314
7.274
5.127
5.111
5.096
3.574
3.568
3.557
3.551
3.540
3.534
3.010
2.993
2.977
2.961
2.433
2.325
2.318
1.931
1.913
1.892
1.875
1.779
1.763
1.747
1.737
1.726
1.720
1.709
-0.000
zdj-5-149-1
2022-11-07 20:57:36.316
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
CN
NHTs
3ag
2.09
2.10
impure *
0.97
0.97
2.09
3.14
0.92
2.00
2.14
10
8
6
4
2
0
PPM

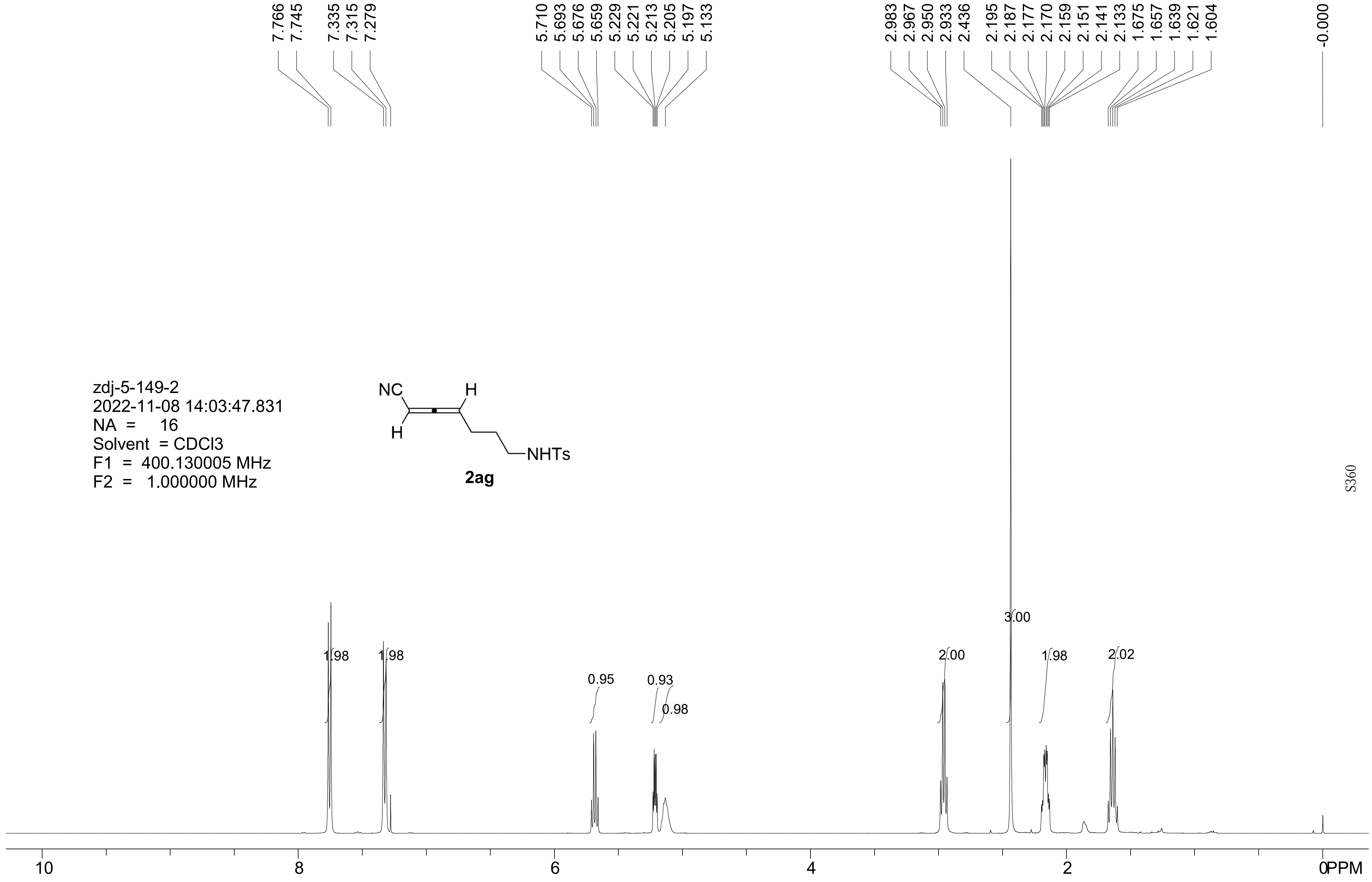


Purity (90%) is determined by Nitromethane (9.0 µL, 0.167 mmol)
as the internal standard in 31.6 mg of sample

zdj-5-149-1-purity
2022-11-08 18:33:43.443
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz

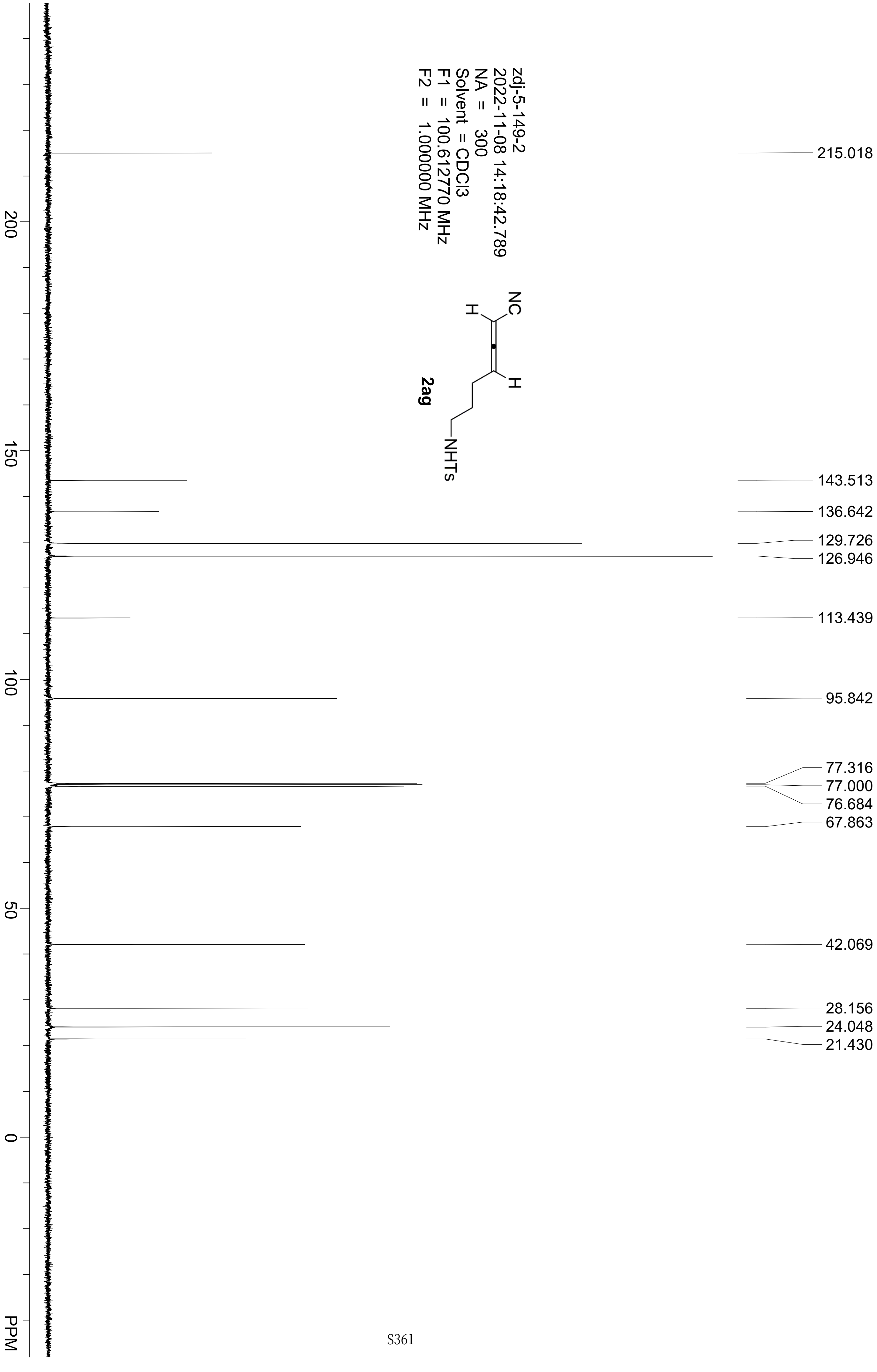
3ag

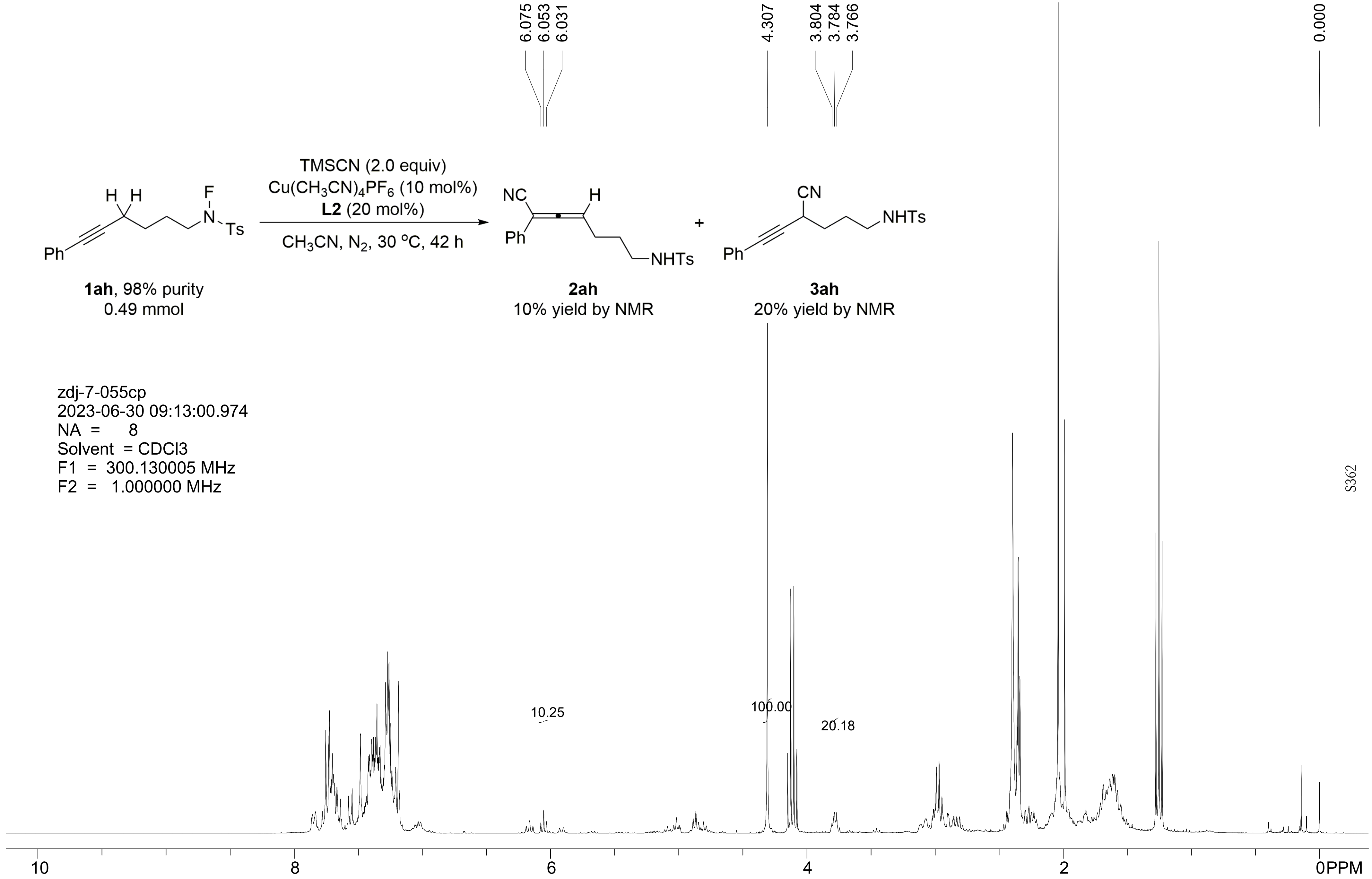

143.639
136.525
129.789
126.973
116.807
77.325
77.000
76.684
75.366
72.964
41.897
29.754
26.323
22.351
21.448
zdj-5-149-1
2022-11-07 21:29:04.559
NA = 400
Solvent = CDCl3
F1 = 100.612770 MHz
F2 = 1.000000 MHz
CN
NHTs
3ag
200
150
100
50
0
PPM

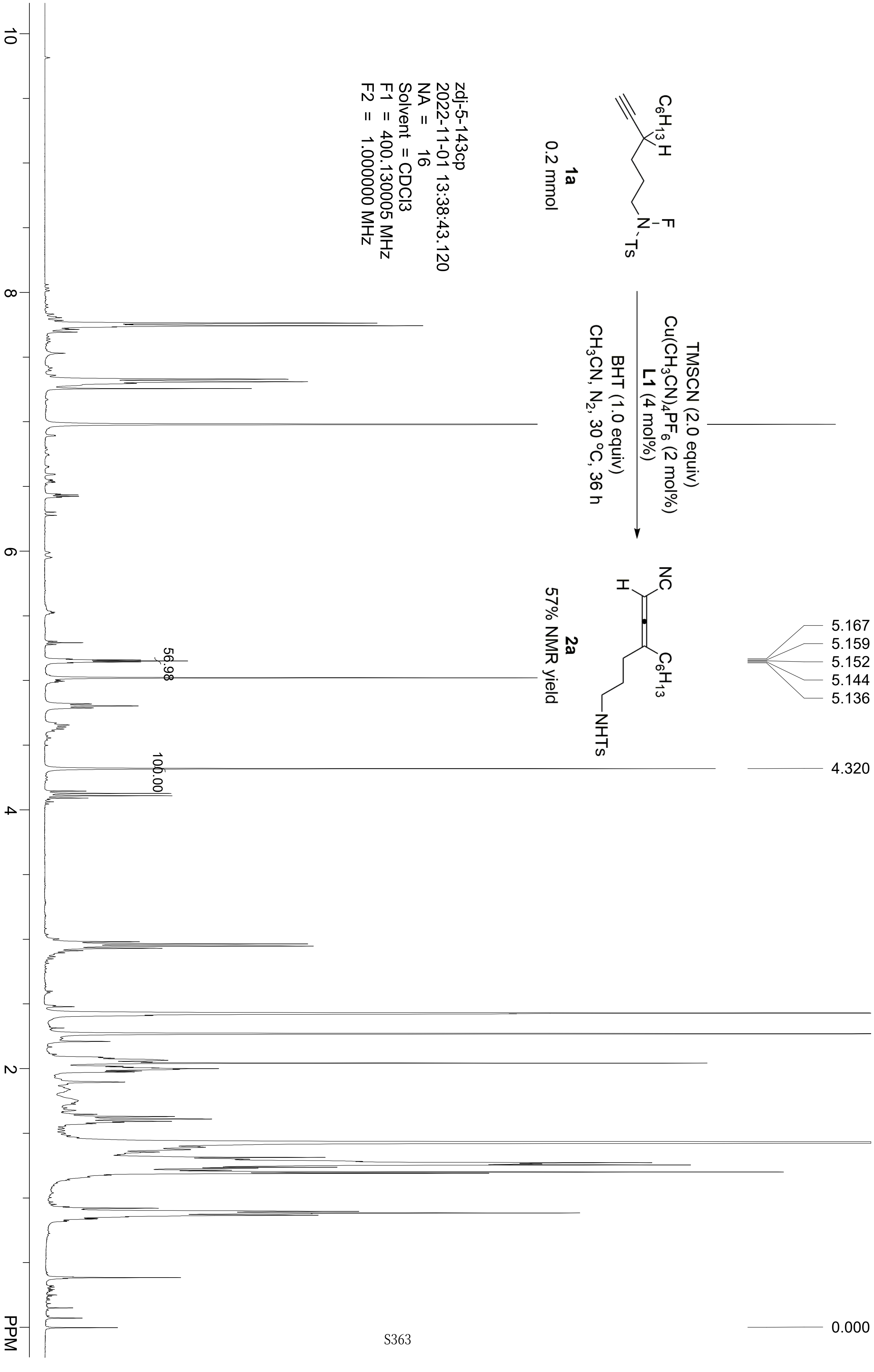


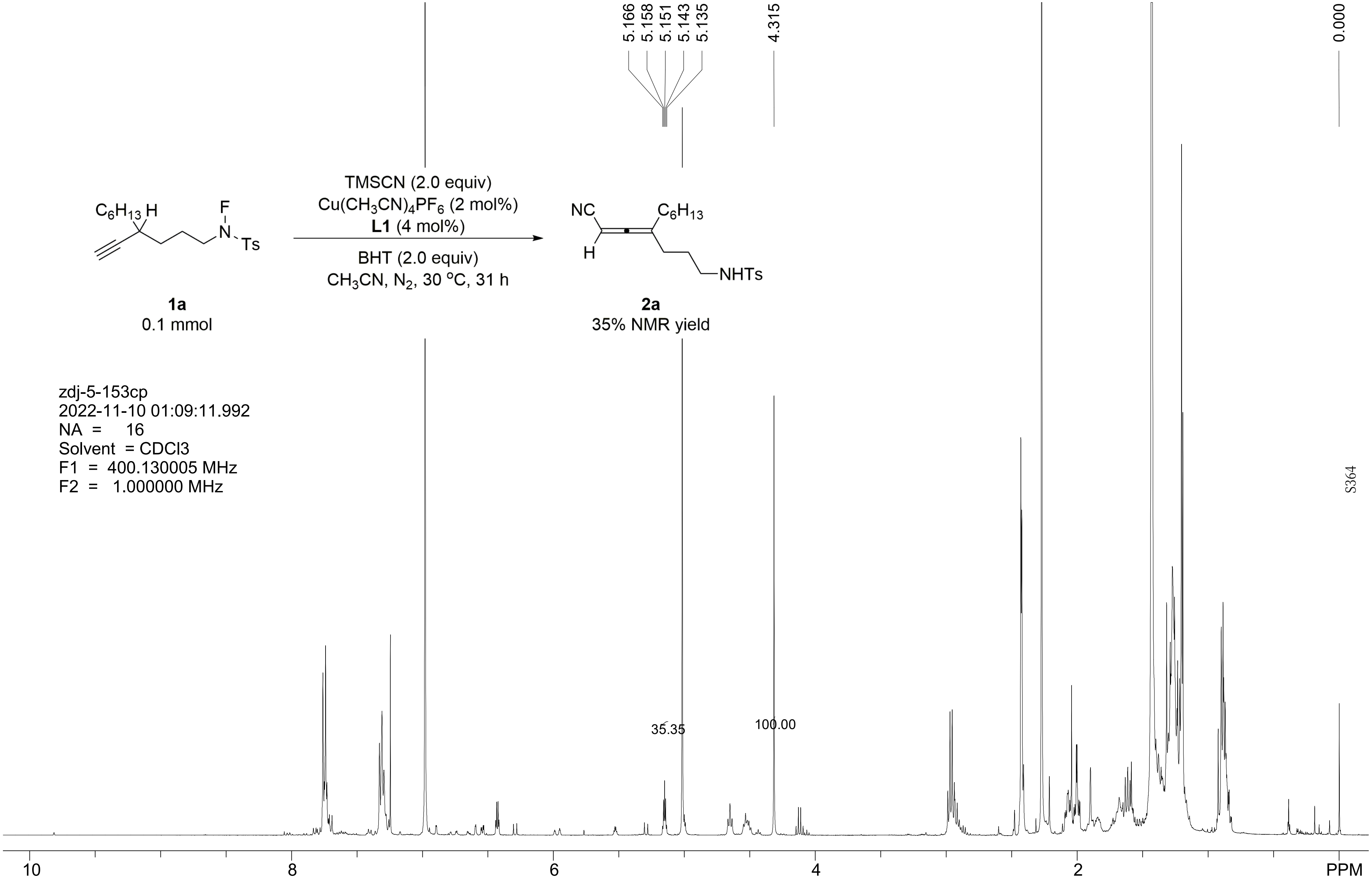
zdj-5-149-2
2022-11-08 14:03:47.831
NA = 16
Solvent = CDCl3
F1 = 400.130005 MHz
F2 = 1.000000 MHz

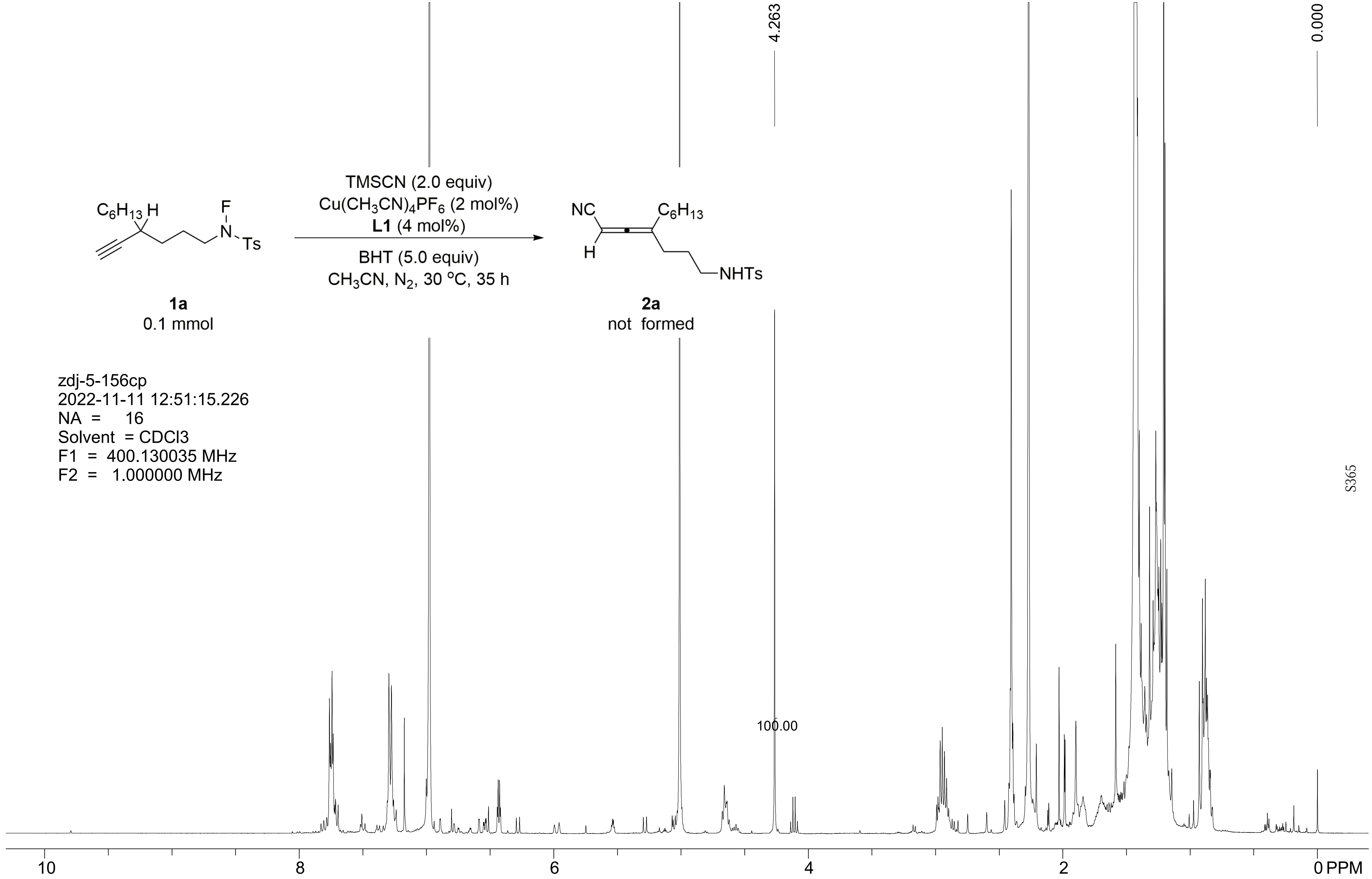
2ag


zdj-5-149-2
2022-11-08 14:18:42.789
NA = 300
Solvent = CDCl3
F1 = 100.612770 MHz
F2 = 1.000000 MHz
NC
H
H
NHTs
2ag
215.018
143.513
136.642
129.726
126.946
113.439
95.842
77.316
77.000
76.684
67.863
42.069
28.156
24.048
21.430
200
150
100
50
0
PPM

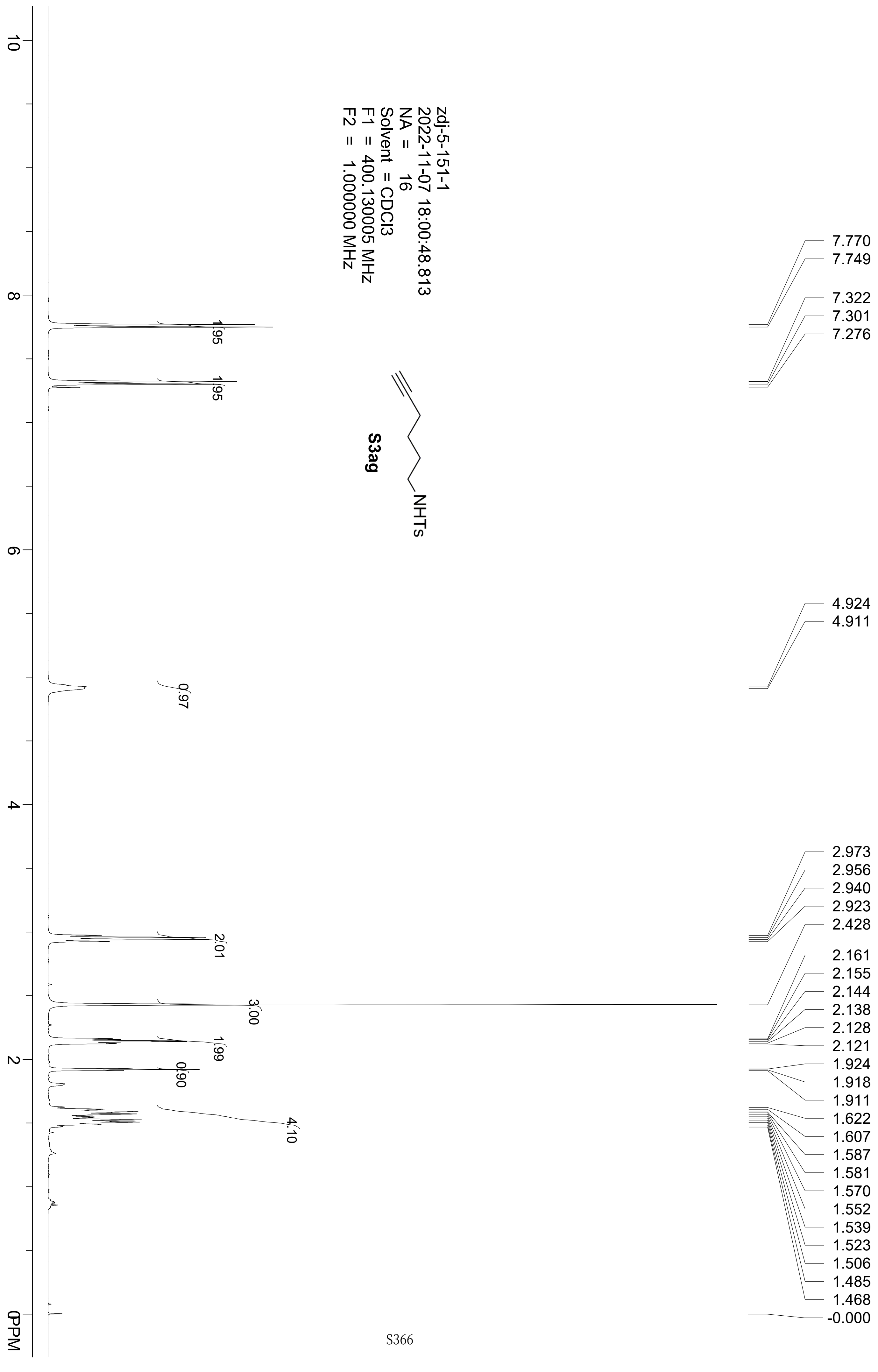

6.075
6.053
6.031
4.307
3.804
3.784
3.766
0.000
TMSCN (2.0 equiv)
Cu(CH3CN)4PF6 (10 mol%)
L2 (20 mol%)
CH3CN, N2, 30 °C, 42 h
H H
F
N
Ts
Ph
NC
H
Ph
NHTs
+
CN
NHTs
Ph
1ah, 98% purity
0.49 mmol
2ah
10% yield by NMR
3ah
20% yield by NMR
zdj-7-055cp
2023-06-30 09:13:00.974
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
10.25
100.00
20.18
10
8
6
4
2
0PPM

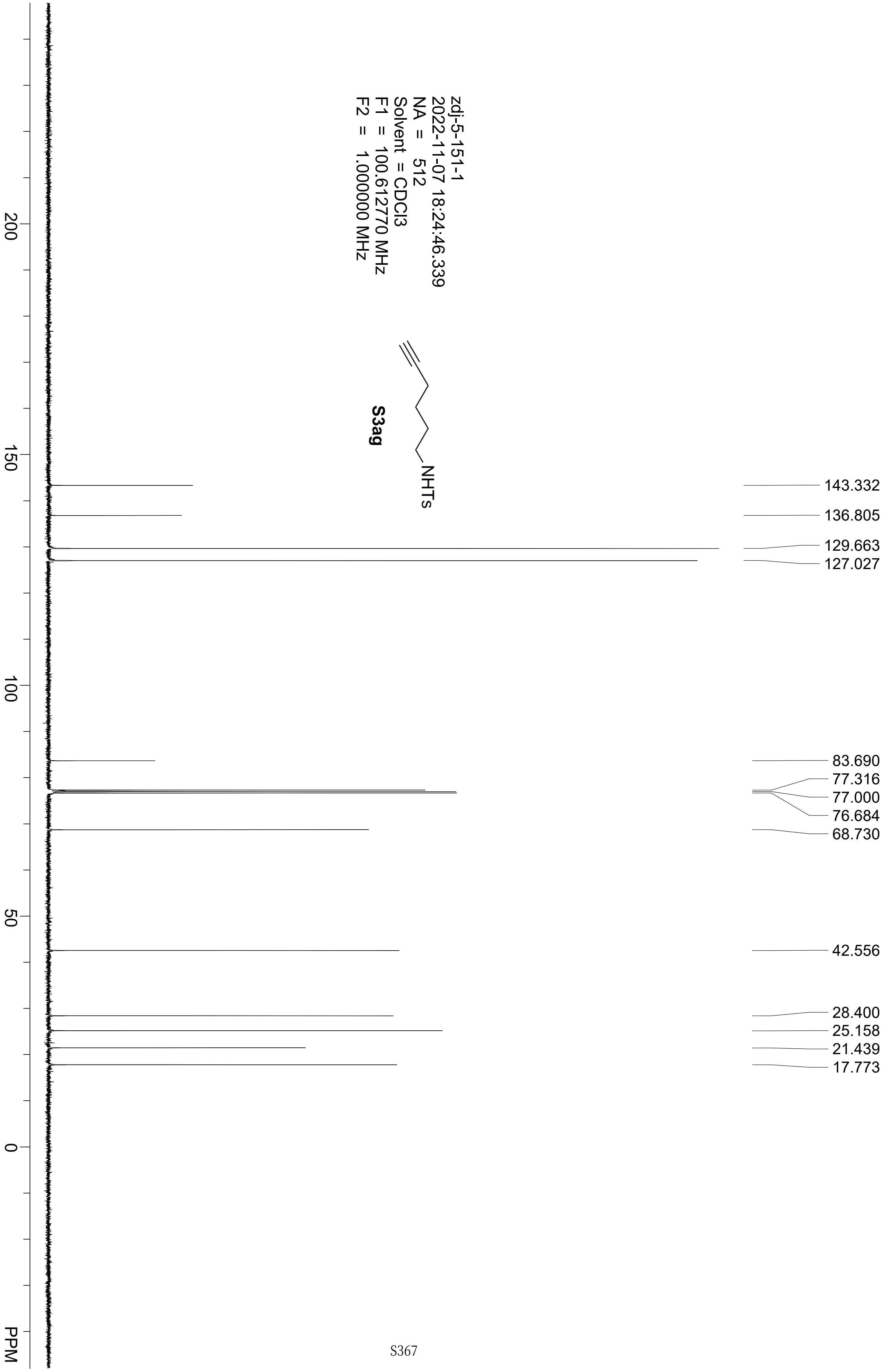

C6H13 H
N
F
Ts
1a
0.2 mmol
TMSCN (2.0 equiv)
Cu(CH3CN)4PF6 (2 mol%)
L1 (4 mol%)
BHT (1.0 equiv)
CH3CN, N2, 30 °C, 36 h
NC
H
C6H13
NHTs
2a
57% NMR yield
zdj-5-143cp
2022-11-01 13:38:43.120
NA = 16
Solvent = CDCl3
F1 = 400.130005 MHz
F2 = 1.000000 MHz
5.167
5.159
5.152
5.144
5.136
4.320
0.000
56.98
100.00
10
8
6
4
2
PPM


5.166
5.158
5.151
5.143
5.135
4.315
0.000
C_6H_{13} H
F
N
Ts
1a
0.1 mmol
TMSCN (2.0 equiv)
$Cu(CH_3CN)_4PF_6$ (2 mol%)
L1 (4 mol%)
BHT (2.0 equiv)
CH_3CN, N_2, 30 °C, 31 h
NC
H
C_6H_{13}
NHTs
2a
35% NMR yield
zdj-5-153cp
2022-11-10 01:09:11.992
NA = 16
Solvent = CDCl3
F1 = 400.130005 MHz
F2 = 1.000000 MHz
35.35
100.00
10
8
6
4
2
PPM

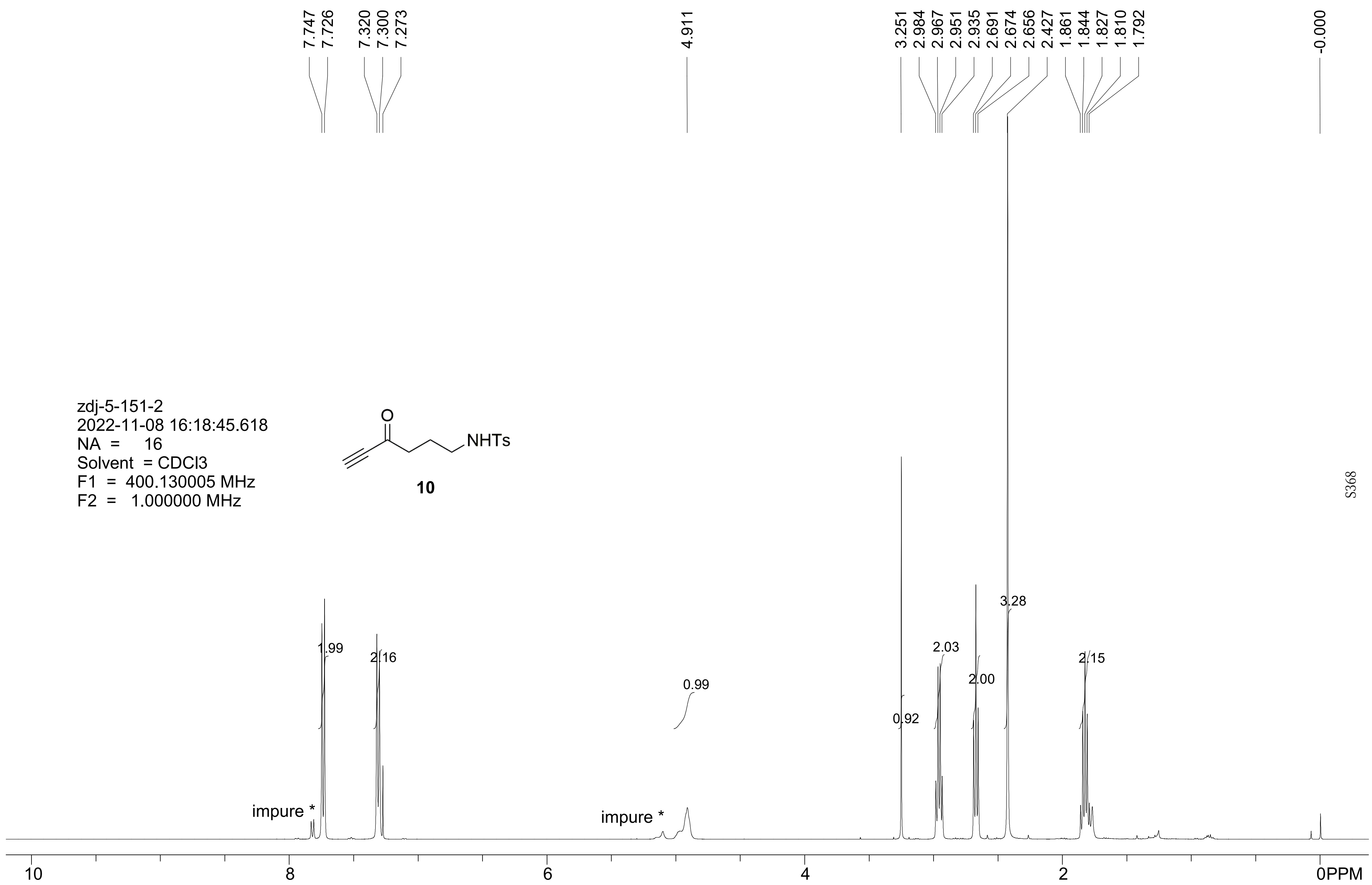


1a
0.1 mmol
TMSCN (2.0 equiv)
$Cu(CH_3CN)_4PF_6$ (2 mol%)
L1 (4 mol%)
BHT (5.0 equiv)
CH_3CN, N_2, 30 °C, 35 h
2a
not formed
zdj-5-156cp
2022-11-11 12:51:15.226
NA = 16
Solvent = CDCl3
F1 = 400.130035 MHz
F2 = 1.000000 MHz
4.263
0.000
100.00
10
8
6
4
2
0 PPM


zdj-5-151-1
2022-11-07 18:00:48.813
NA = 16
Solvent = CDCl3
F1 = 400.130005 MHz
F2 = 1.000000 MHz
NHTs
S3ag
7.770
7.749
7.322
7.301
7.276
4.924
4.911
2.973
2.956
2.940
2.923
2.428
2.161
2.155
2.144
2.138
2.128
2.121
1.924
1.918
1.911
1.622
1.607
1.587
1.581
1.570
1.552
1.539
1.523
1.506
1.485
1.468
-0.000
1.95
1.95
0.97
2.01
3.00
1.99
0.90
4.10
10
8
6
4
2
0
PPM

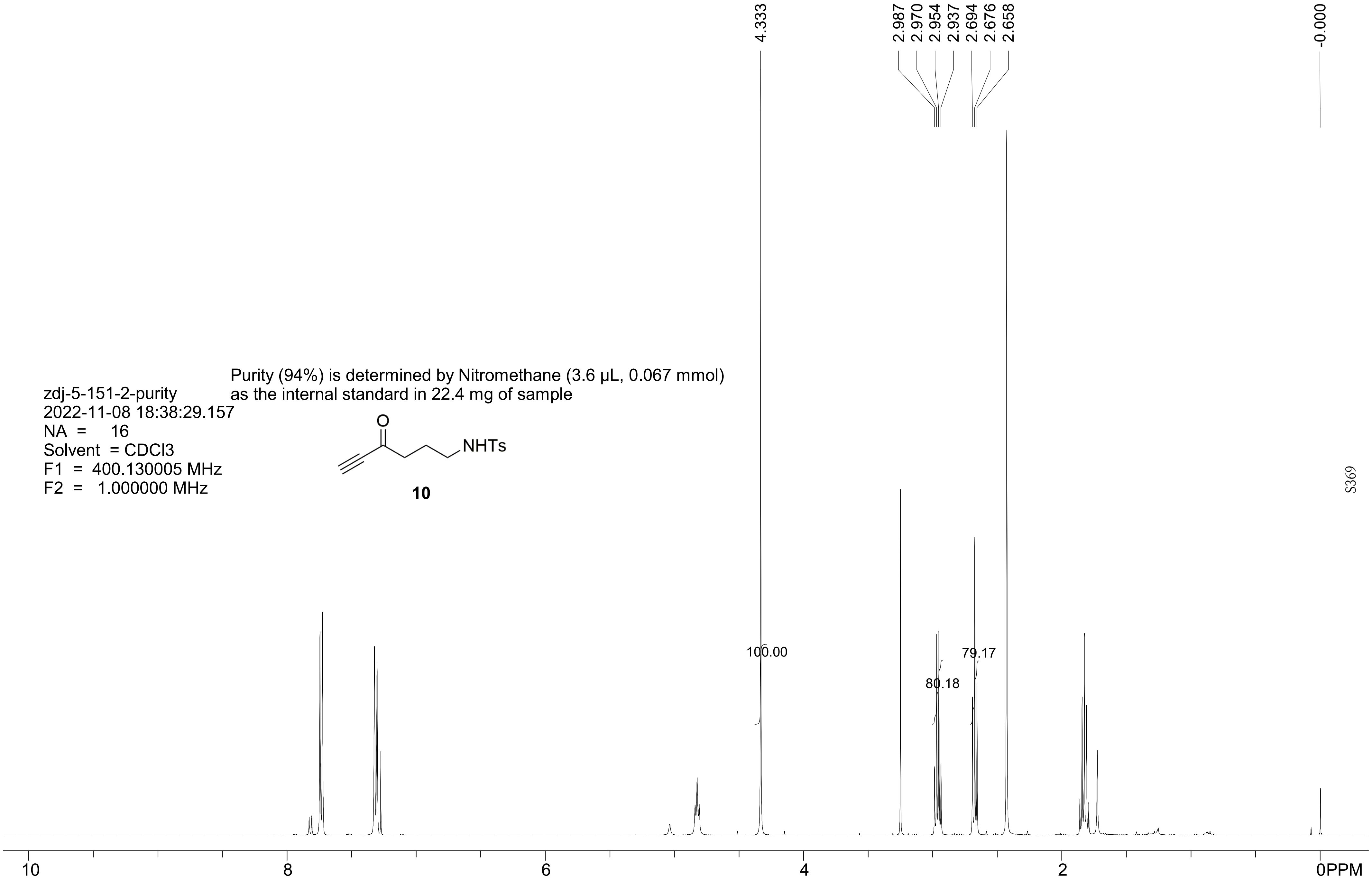

zdj-5-151-1
2022-11-07 18:24:46.339
NA = 512
Solvent = CDCl3
F1 = 100.612770 MHz
F2 = 1.000000 MHz
NHTs
143.332
136.805
129.663
127.027
83.690
77.316
77.000
76.684
68.730
42.556
28.400
25.158
21.439
17.773
200
150
100
50
0
PPM

S3ag



10

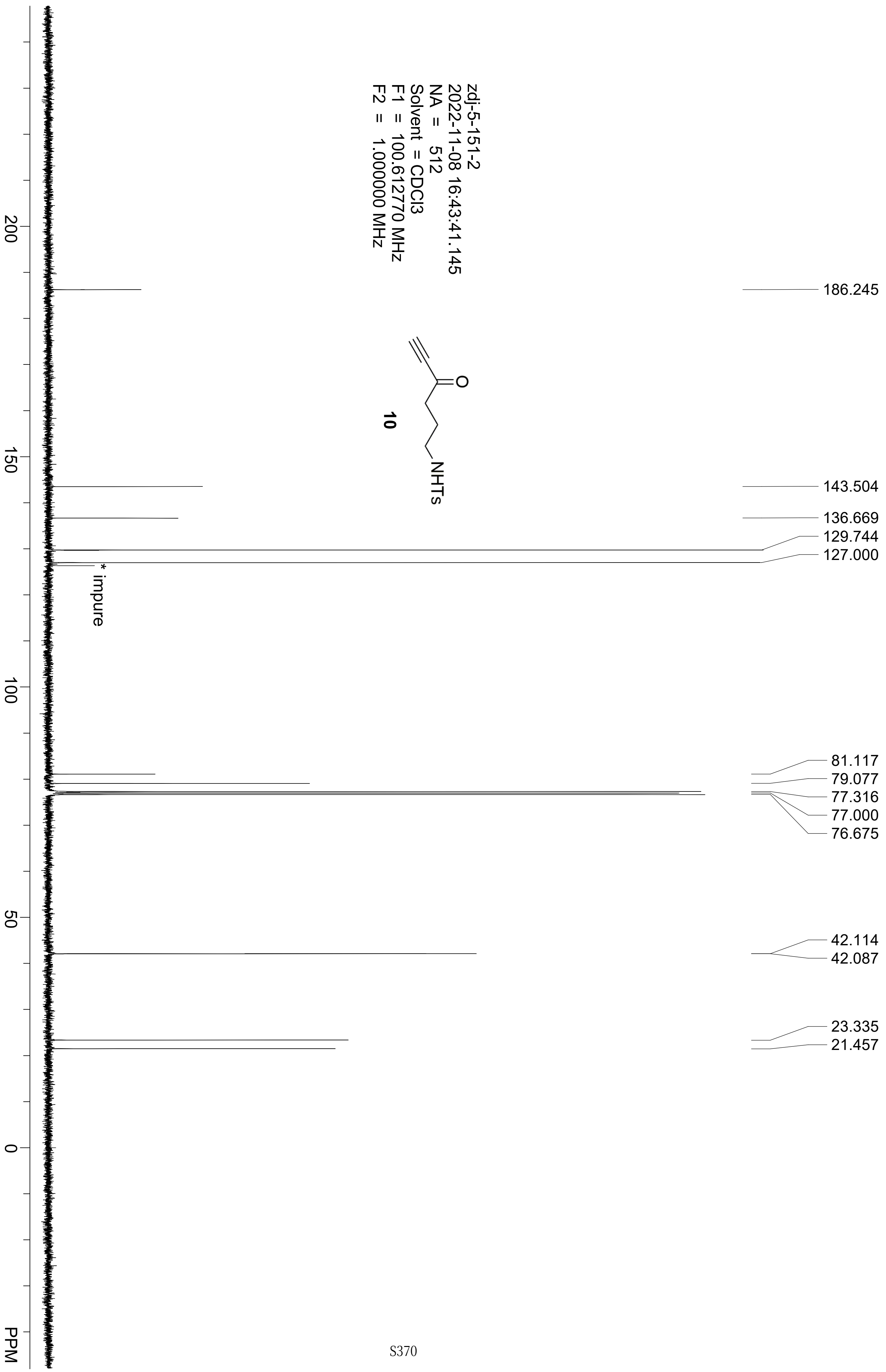
zdj-5-151-2
2022-11-08 16:18:45.618
NA = 16
Solvent = CDCl3
F1 = 400.130005 MHz
F2 = 1.000000 MHz
O
NHTs
7.747
7.726
7.320
7.300
7.273
4.911
3.251
2.984
2.967
2.951
2.935
2.691
2.674
2.656
2.427
1.861
1.844
1.827
1.810
1.792
-0.000
impure *
1.99
2.16
impure *
0.99
0.92
2.03
2.00
3.28
2.15
10
8
6
4
2
0PPM

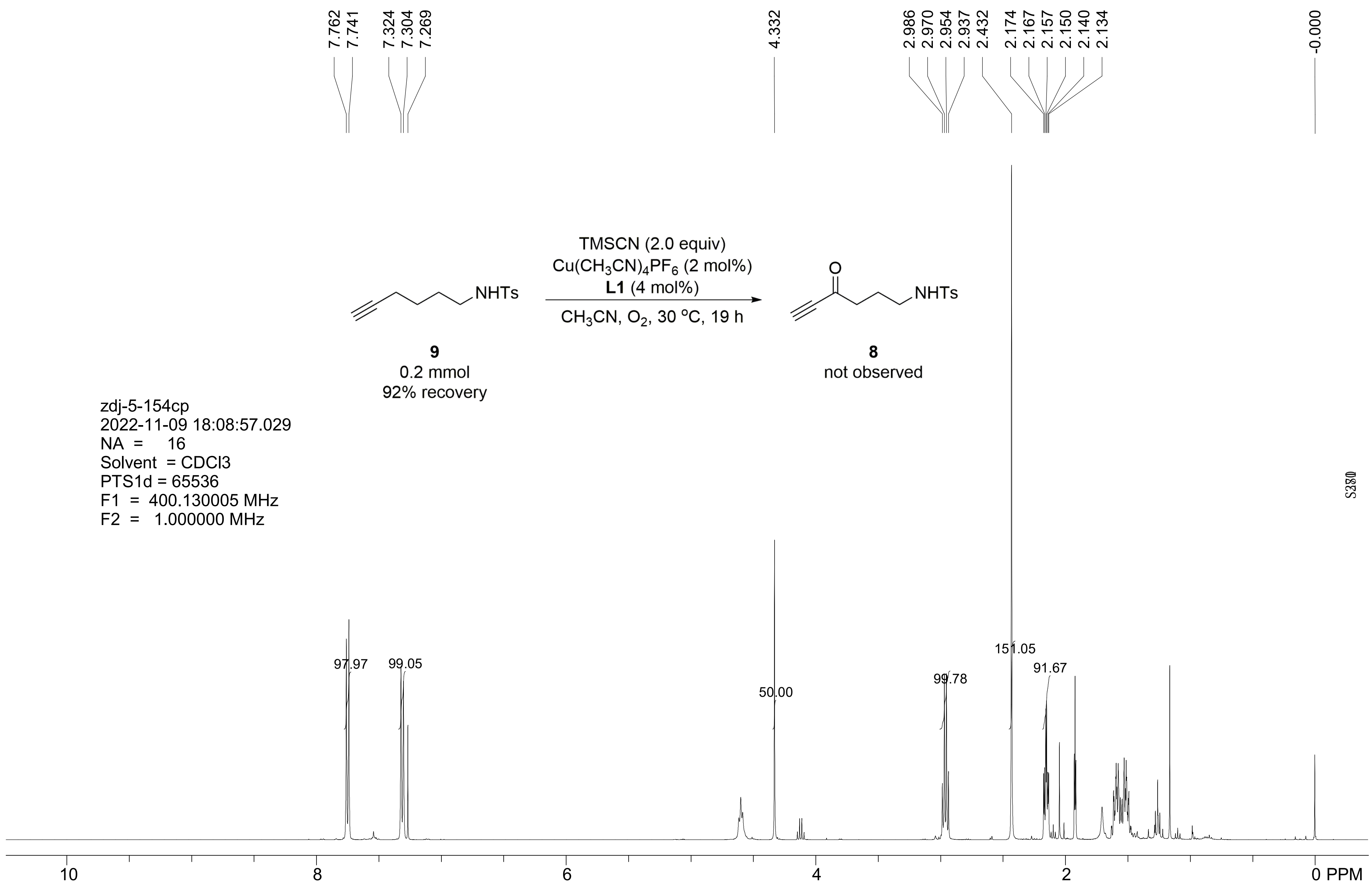


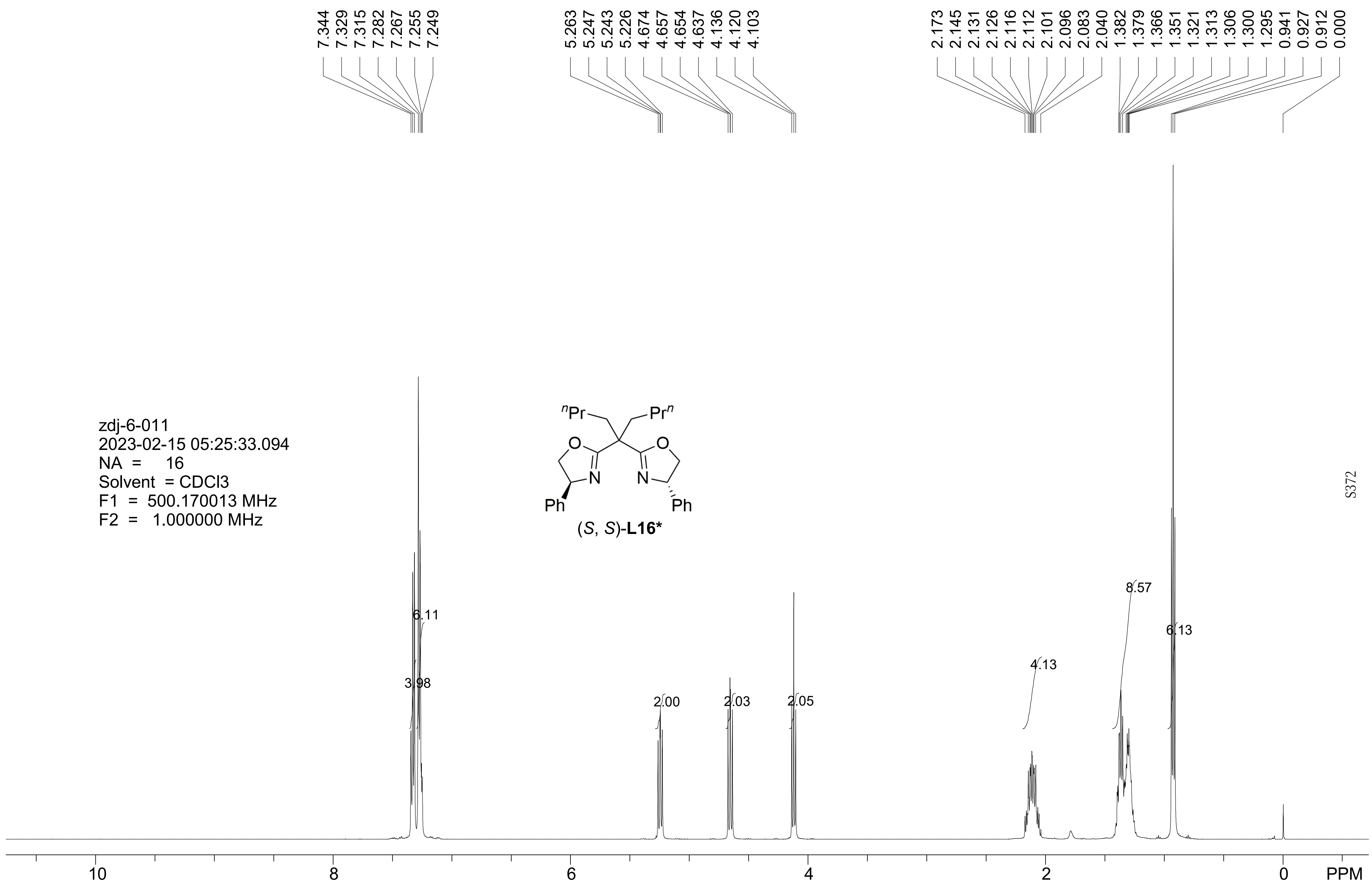
10

Purity (94%) is determined by Nitromethane (3.6 μL, 0.067 mmol) as the internal standard in 22.4 mg of sample

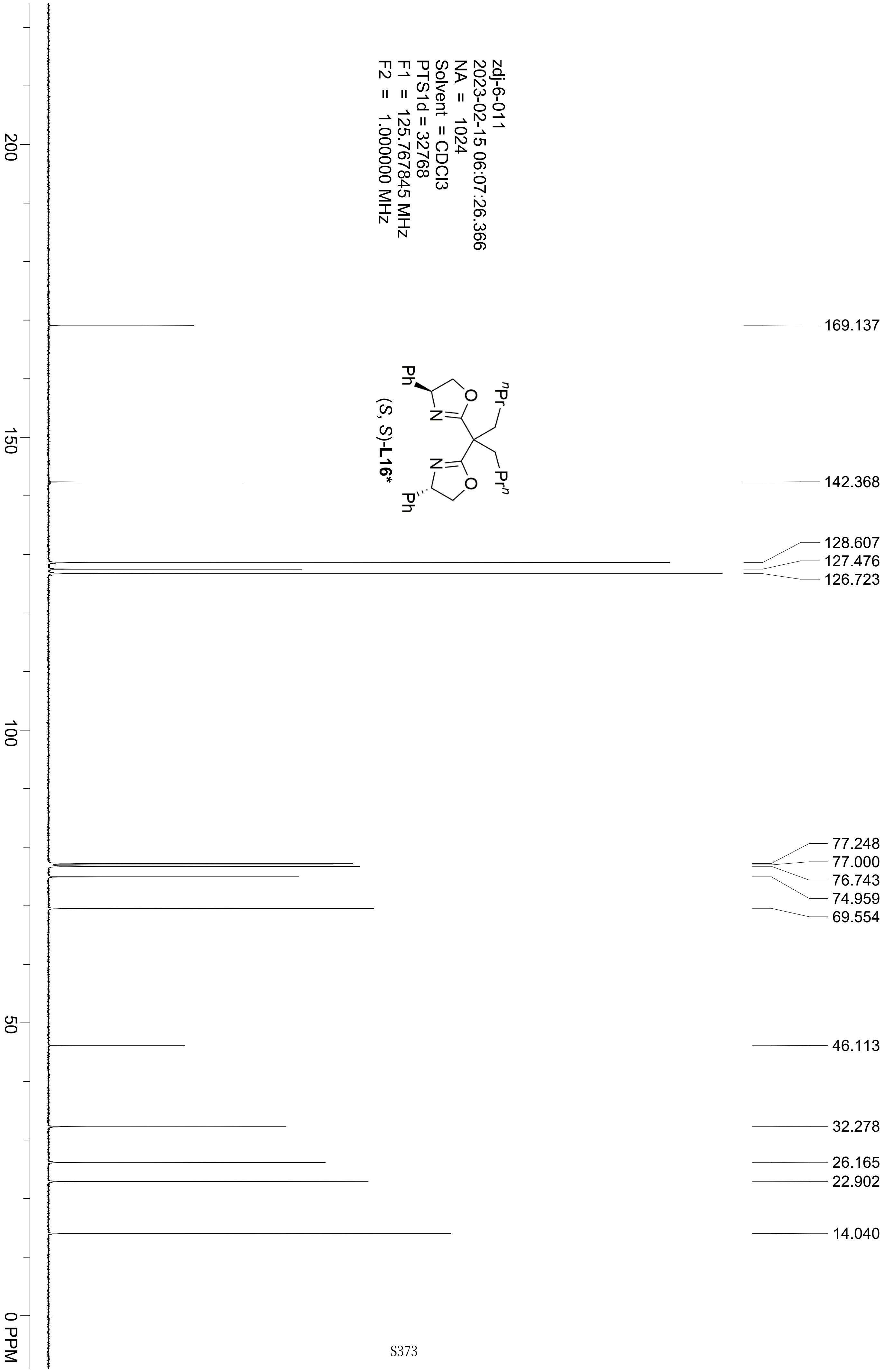
zdj-5-151-2-purity
2022-11-08 18:38:29.157
NA = 16
Solvent = CDCl3
F1 = 400.130005 MHz
F2 = 1.000000 MHz


zdj-5-151-2
2022-11-08 16:43:41.145
NA = 512
Solvent = CDCl3
F1 = 100.612770 MHz
F2 = 1.000000 MHz
O
NHTs
10
* impure
186.245
143.504
136.669
129.744
127.000
81.117
79.077
77.316
77.000
76.675
42.114
42.087
23.335
21.457
200
150
100
50
0
PPM

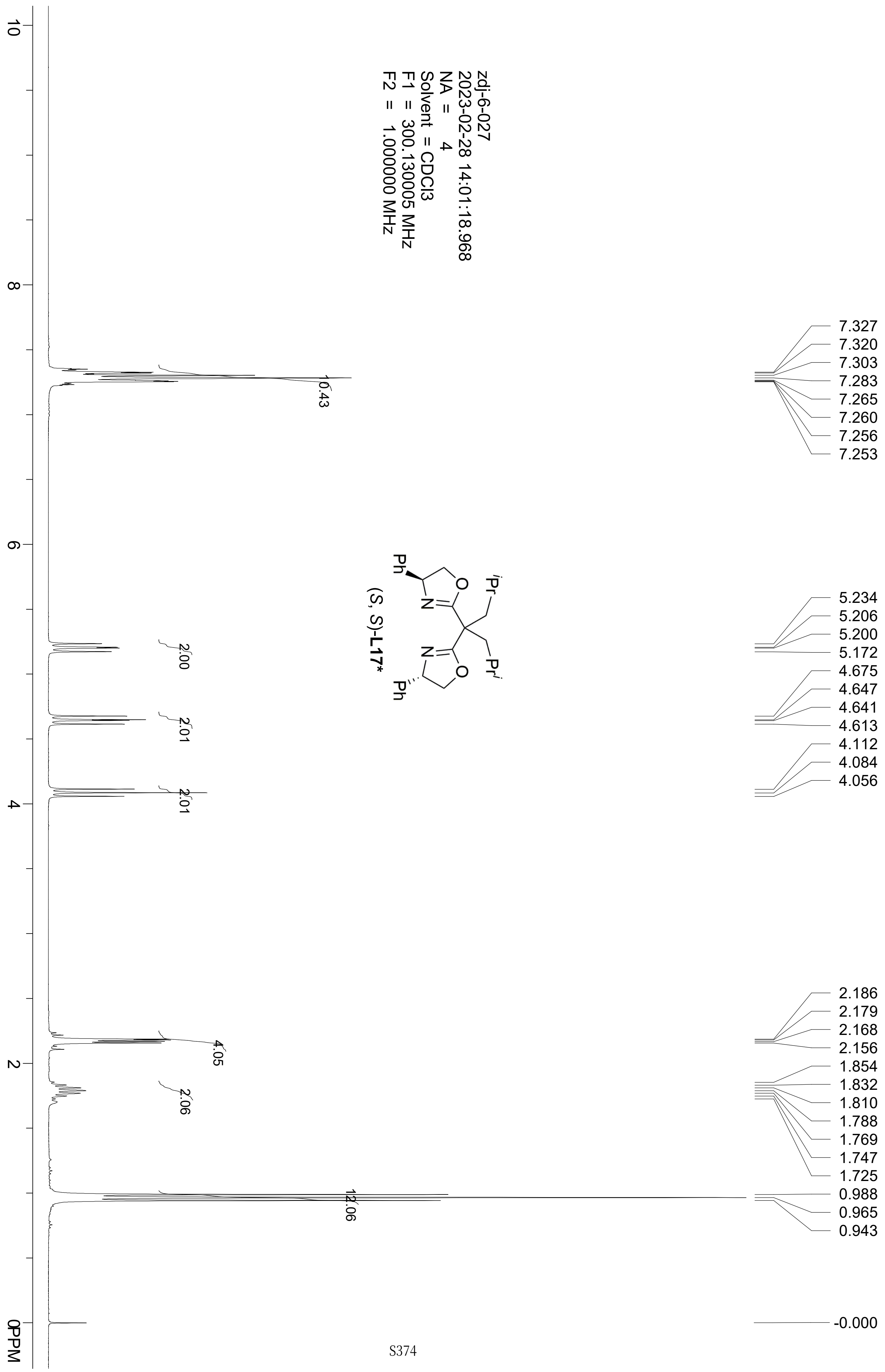

7.762
7.741
7.324
7.304
7.269
4.332
2.986
2.970
2.954
2.937
2.432
2.174
2.167
2.157
2.150
2.140
2.134
-0.000
TMSCN (2.0 equiv)
Cu(CH3CN)4PF6 (2 mol%)
L1 (4 mol%)
CH3CN, O2, 30 °C, 19 h
NHTs
O
NHTs
9
0.2 mmol
92% recovery
8
not observed
zdj-5-154cp
2022-11-09 18:08:57.029
NA = 16
Solvent = CDCl3
PTS1d = 65536
F1 = 400.130005 MHz
F2 = 1.000000 MHz
97.97
99.05
50.00
99.78
151.05
91.67
10
8
6
4
2
0 PPM

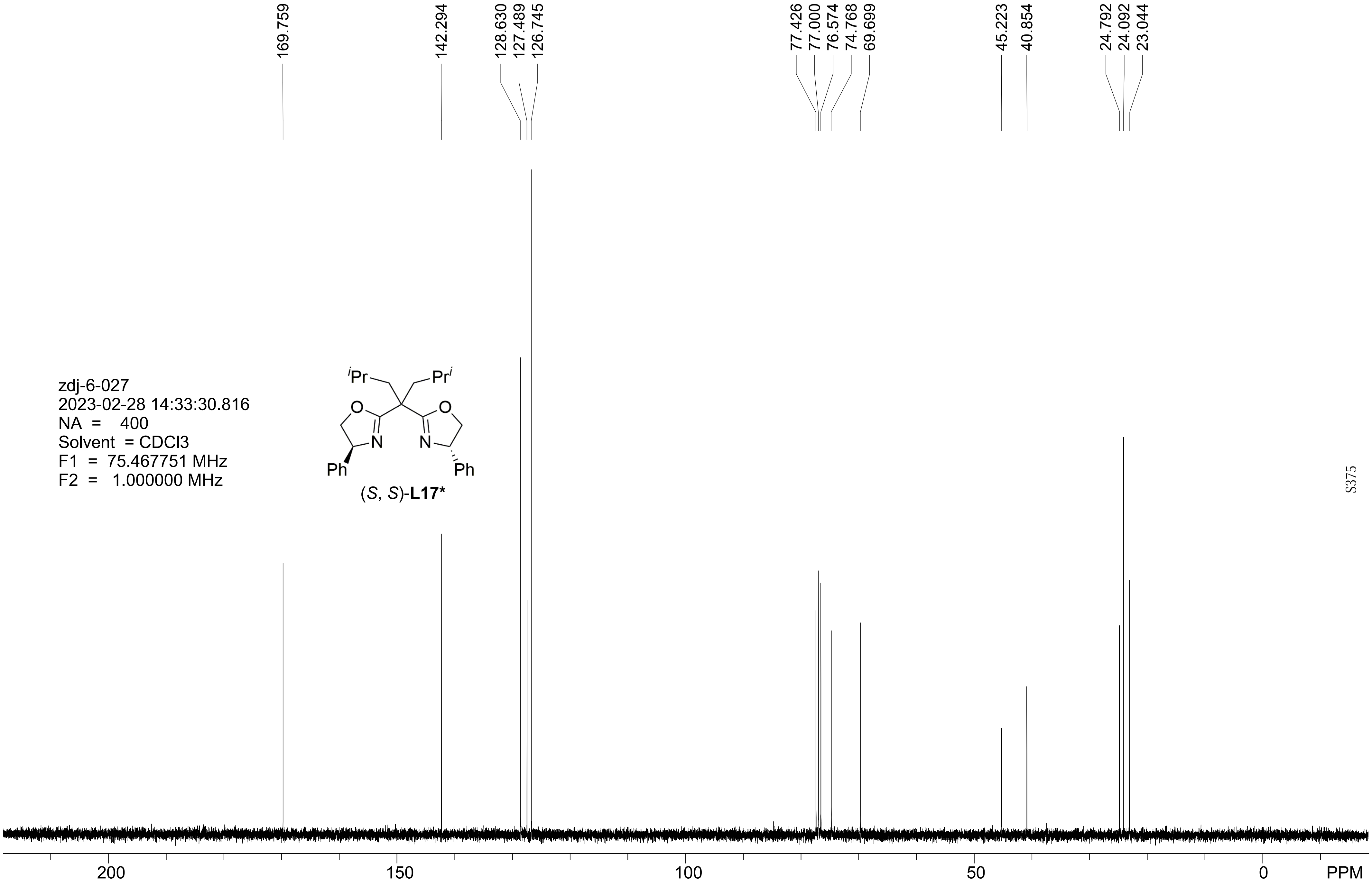

(*S*, *S*)-**L16***

zdj-6-011
2023-02-15 05:25:33.094
NA = 16
Solvent = CDCl3
F1 = 500.170013 MHz
F2 = 1.000000 MHz
ⁿPr
Prⁿ
O
N
Ph
7.344
7.329
7.315
7.282
7.267
7.255
7.249
5.263
5.247
5.243
5.226
4.674
4.657
4.654
4.637
4.136
4.120
4.103
2.173
2.145
2.131
2.126
2.116
2.112
2.101
2.096
2.083
2.040
1.382
1.379
1.366
1.351
1.321
1.313
1.306
1.300
1.295
0.941
0.927
0.912
0.000
3.98
6.11
2.00
2.03
2.05
4.13
8.57
6.13
10
8
6
4
2
0
PPM

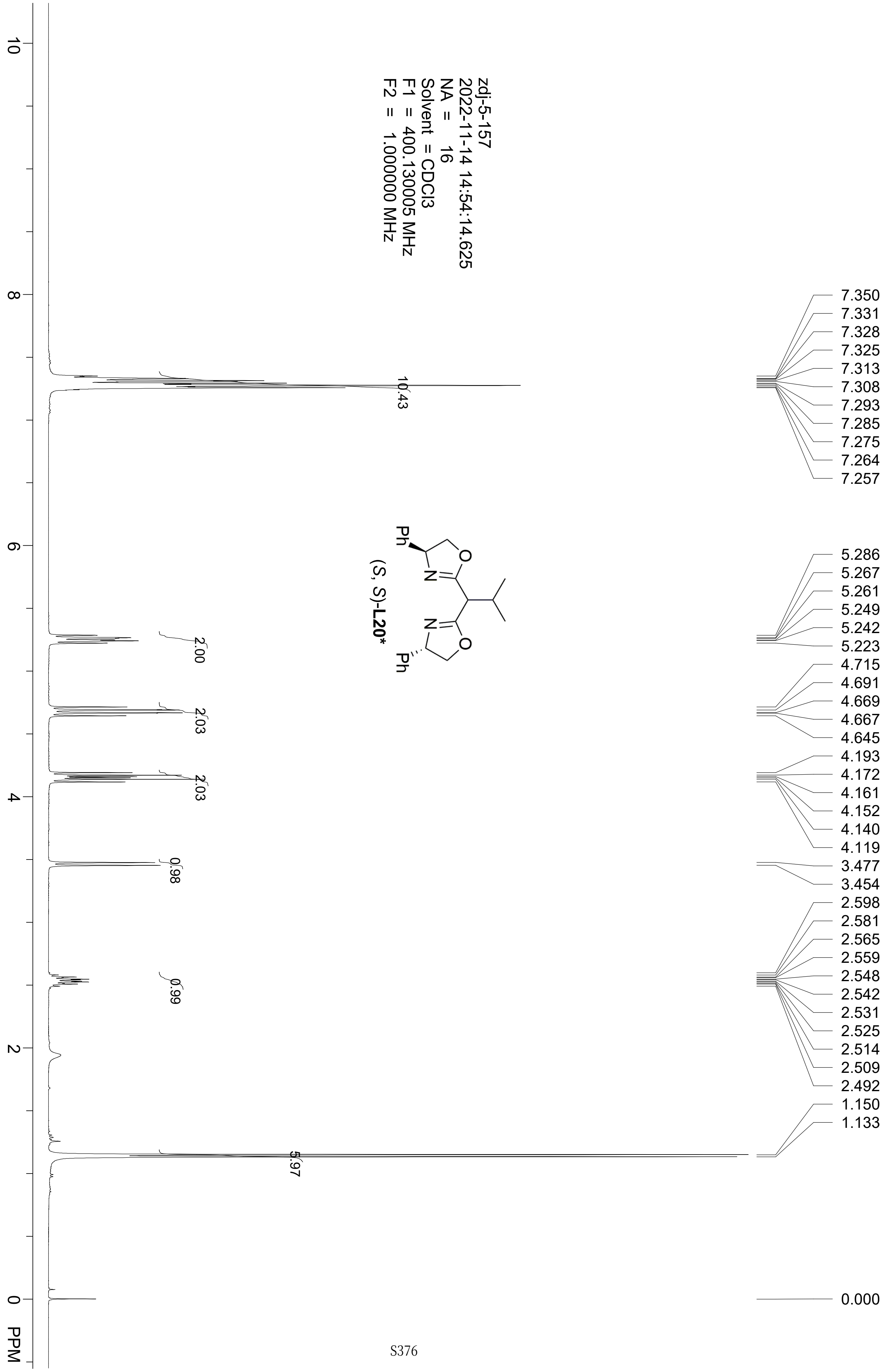

(S, S)-**L16***

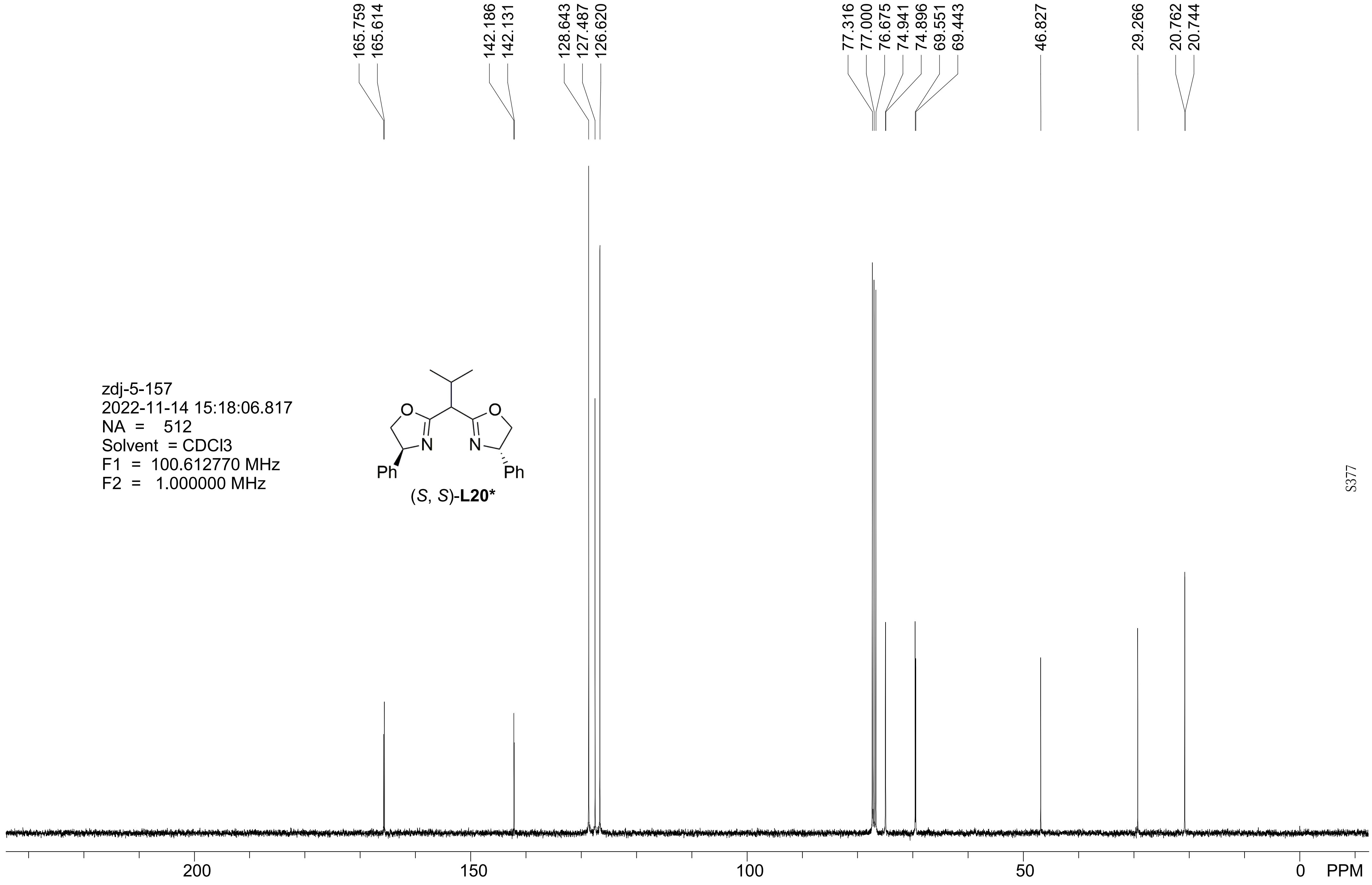
zdj-6-011
2023-02-15 06:07:26.366
NA = 1024
Solvent = CDCl3
PTS1d = 32768
F1 = 125.767845 MHz
F2 = 1.000000 MHz
ⁿPr
Prⁿ
O
N
Ph
169.137
142.368
128.607
127.476
126.723
77.248
77.000
76.743
74.959
69.554
46.113
32.278
26.165
22.902
14.040
200
150
100
50
0 PPM


zdj-6-027
2023-02-28 14:01:18.968
NA = 4
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
(S, S)-**L17***
^{i}Pr
^{i}Pr
O
N
O
N
Ph
Ph
7.327
7.320
7.303
7.283
7.265
7.260
7.256
7.253
5.234
5.206
5.200
5.172
4.675
4.647
4.641
4.613
4.112
4.084
4.056
2.186
2.179
2.168
2.156
1.854
1.832
1.810
1.788
1.769
1.747
1.725
0.988
0.965
0.943
-0.000
10.43
2.00
2.01
2.01
4.05
2.06
12.06
10
8
6
4
2
0PPM


169.759
142.294
128.630
127.489
126.745
77.426
77.000
76.574
74.768
69.699
45.223
40.854
24.792
24.092
23.044
zdj-6-027
2023-02-28 14:33:30.816
NA = 400
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
^{i}Pr
Pr^i
O
N
Ph
200
150
100
50
0
PPM

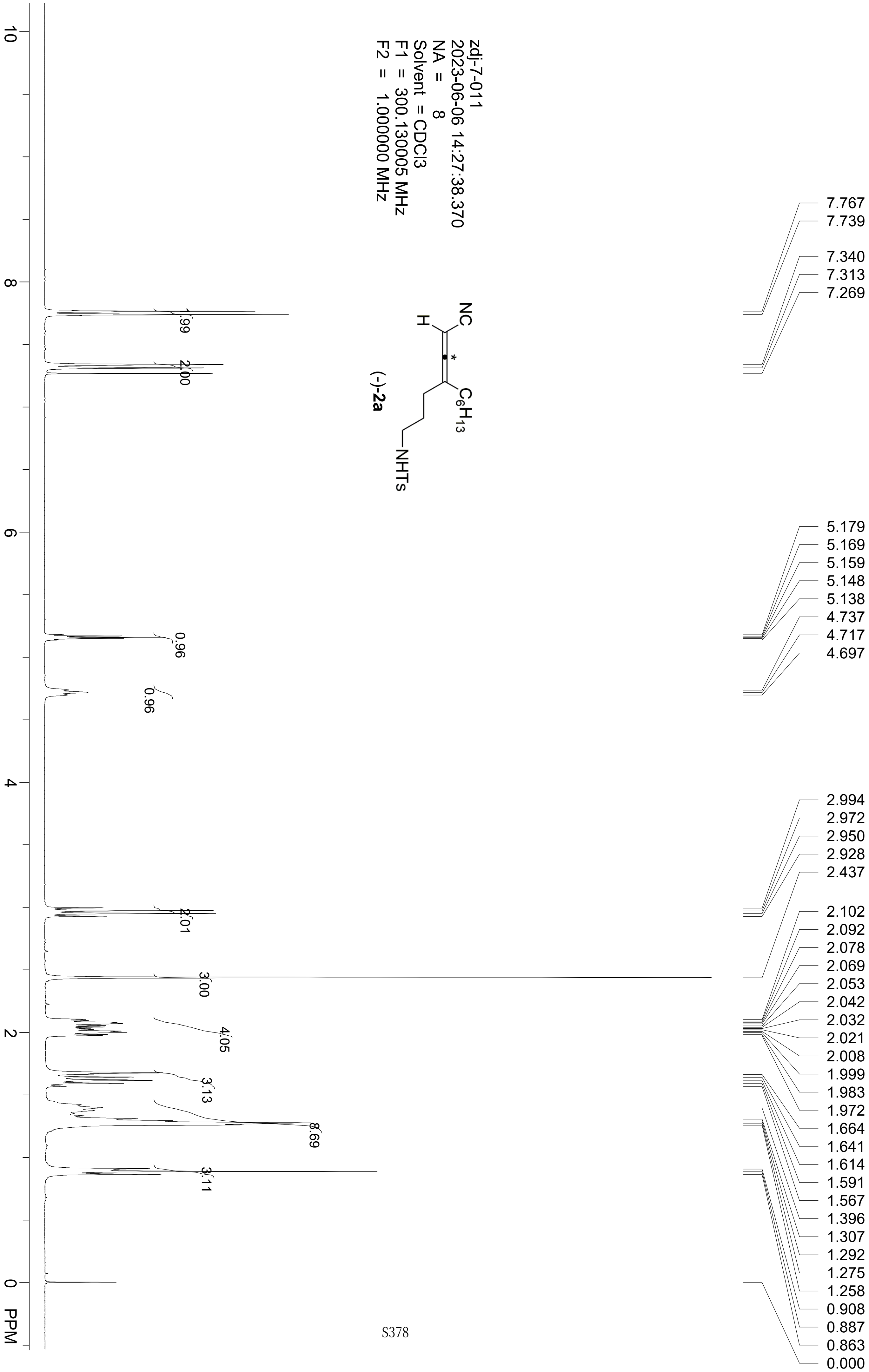
(*S*, *S*)-**L17***

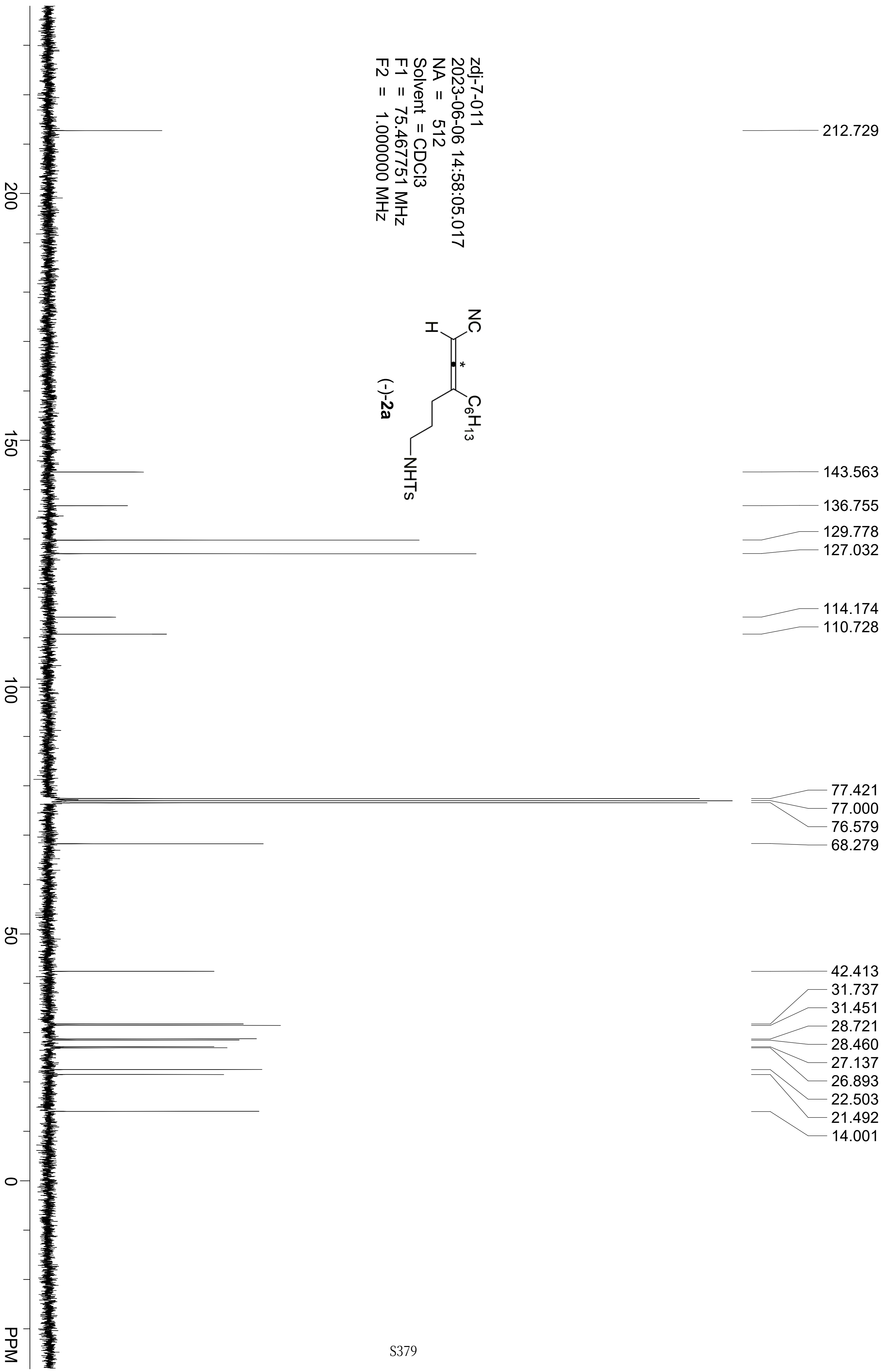

zdj-5-157
2022-11-14 14:54:14.625
NA = 16
Solvent = CDCl3
F1 = 400.130005 MHz
F2 = 1.000000 MHz
Ph
O
N
N
O
Ph
(S, S)-**L20***
10
8
6
4
2
0
PPM
10.43
2.00
2.03
2.03
0.98
0.99
5.97
7.350
7.331
7.328
7.325
7.313
7.308
7.293
7.285
7.275
7.264
7.257
5.286
5.267
5.261
5.249
5.242
5.223
4.715
4.691
4.669
4.667
4.645
4.193
4.172
4.161
4.152
4.140
4.119
3.477
3.454
2.598
2.581
2.565
2.559
2.548
2.542
2.531
2.525
2.514
2.509
2.492
1.150
1.133
0.000



zdj-5-157
2022-11-14 15:18:06.817
NA = 512
Solvent = CDCl3
F1 = 100.612770 MHz
F2 = 1.000000 MHz

(*S*, *S*)-**L20***


zdj-7-011
2023-06-06 14:27:38.370
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
H
*
C6H13
NHTs
(-)-2a
10
8
6
4
2
0
PPM
1.99
2.00
0.96
0.96
2.01
3.00
4.05
3.13
8.69
3.11
7.767
7.739
7.340
7.313
7.269
5.179
5.169
5.159
5.148
5.138
4.737
4.717
4.697
2.994
2.972
2.950
2.928
2.437
2.102
2.092
2.078
2.069
2.053
2.042
2.032
2.021
2.008
1.999
1.983
1.972
1.664
1.641
1.614
1.591
1.567
1.396
1.307
1.292
1.275
1.258
0.908
0.887
0.863
0.000

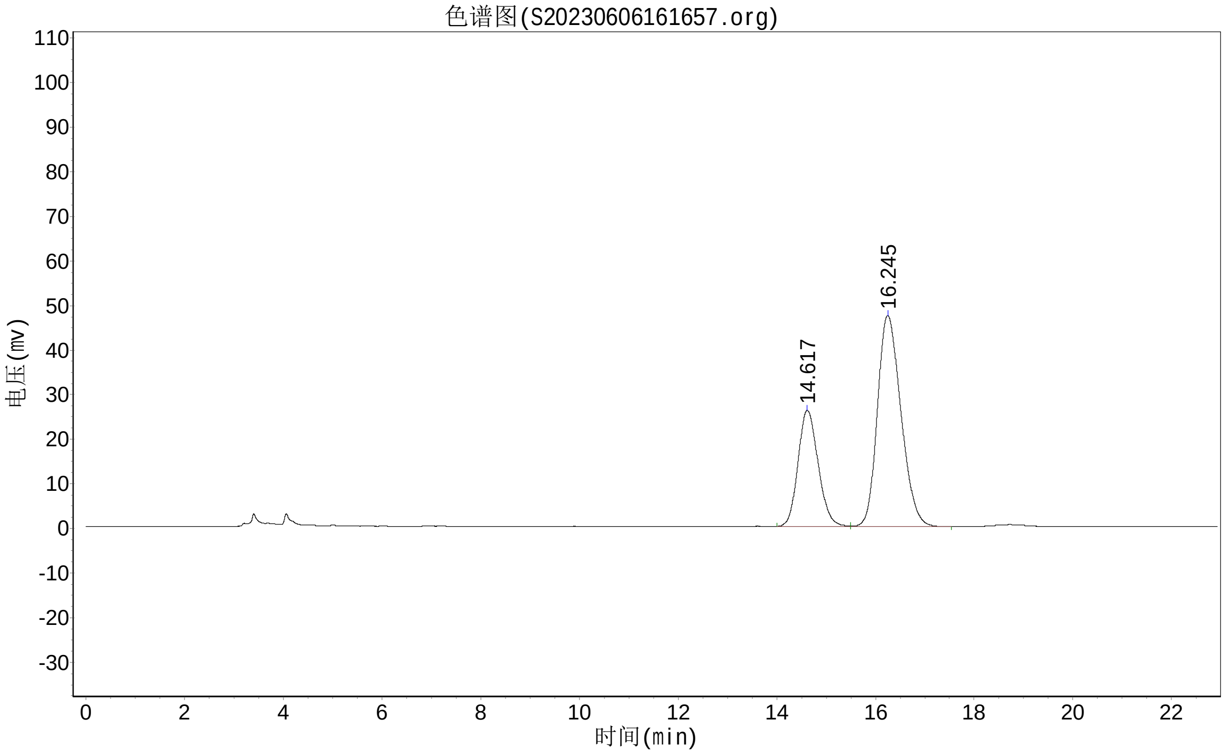

zdj-7-011
2023-06-06 14:58:05.017
NA = 512
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
NC
H
*
C_6H_{13}
NHTs
(-)-2a
212.729
143.563
136.755
129.778
127.032
114.174
110.728
77.421
77.000
76.579
68.279
42.413
31.737
31.451
28.721
28.460
27.137
26.893
22.503
21.492
14.001
200
150
100
50
0
PPM

zdj-7-011

实验时间：2023-06-06,16:16:57
谱图文件:D:\浙大智达\N2000\样品\S20230606161657.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者：zdj
报告时间：2023-06-06,16:43:10
积分方法:面积归一法

实验内容简介：
IC,n-hexane/i-PrOH = 60/40,1.0,214



分析结果表

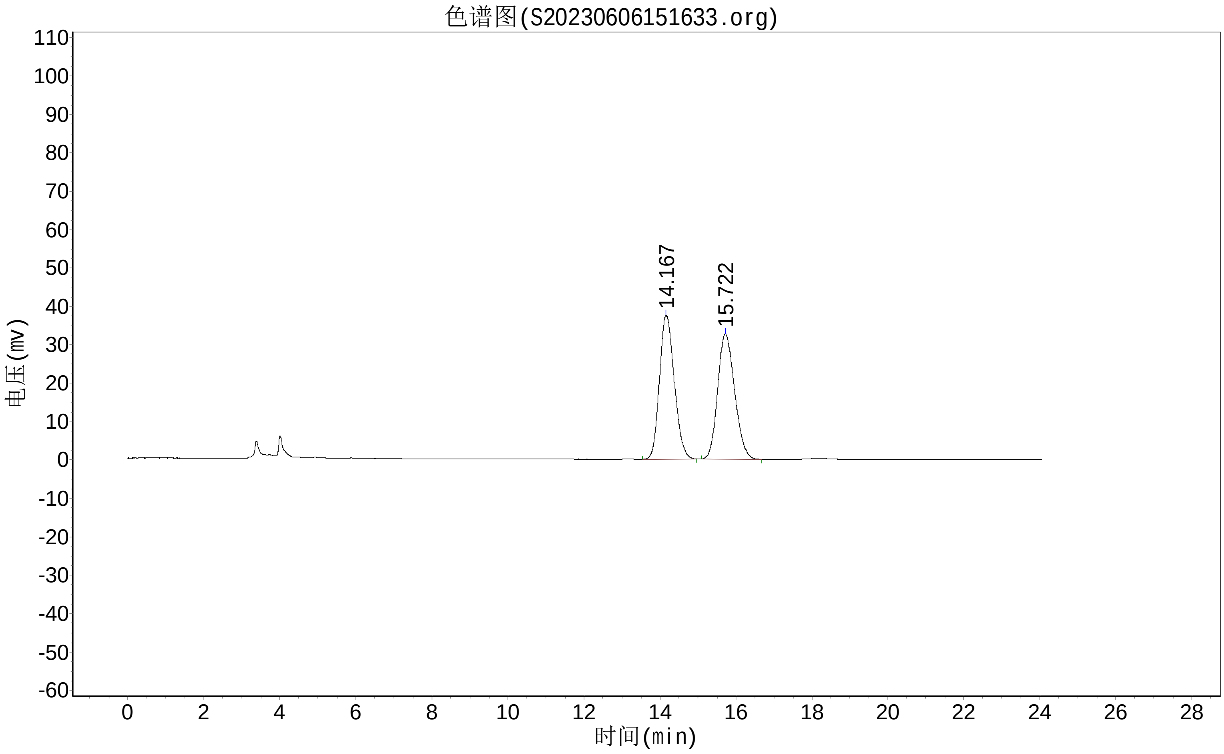
峰号	峰名	保留时间	峰高	峰面积	含量
1		14.617	25968.787	735344.750	31.9764
2		16.245	47246.141	1564304.125	68.0236
总计			73214.928	2299648.875	100.0000

zdj-4-098

实验时间：2023-06-06,15:16:33
谱图文件:D:\浙大智达\N2000\样品\S20230606151633.org
方法文件:D:\浙大智达\N2000\djx.mtd

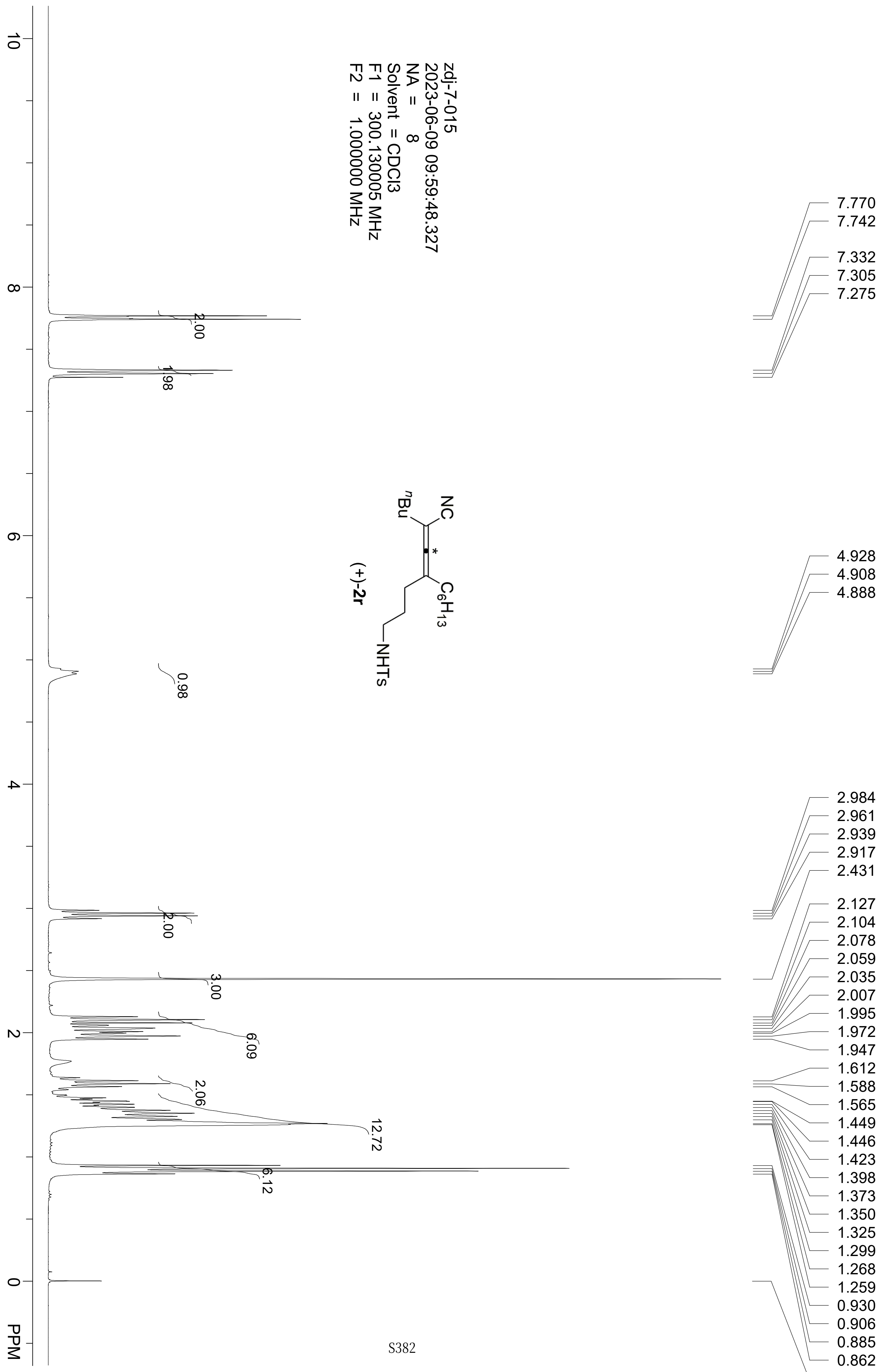
实验者：zdj
报告时间：2023-06-06,15:42:48
积分方法:面积归一法

实验内容简介：
IC,n-hexane/i-PrOH = 60/40,1.0,214

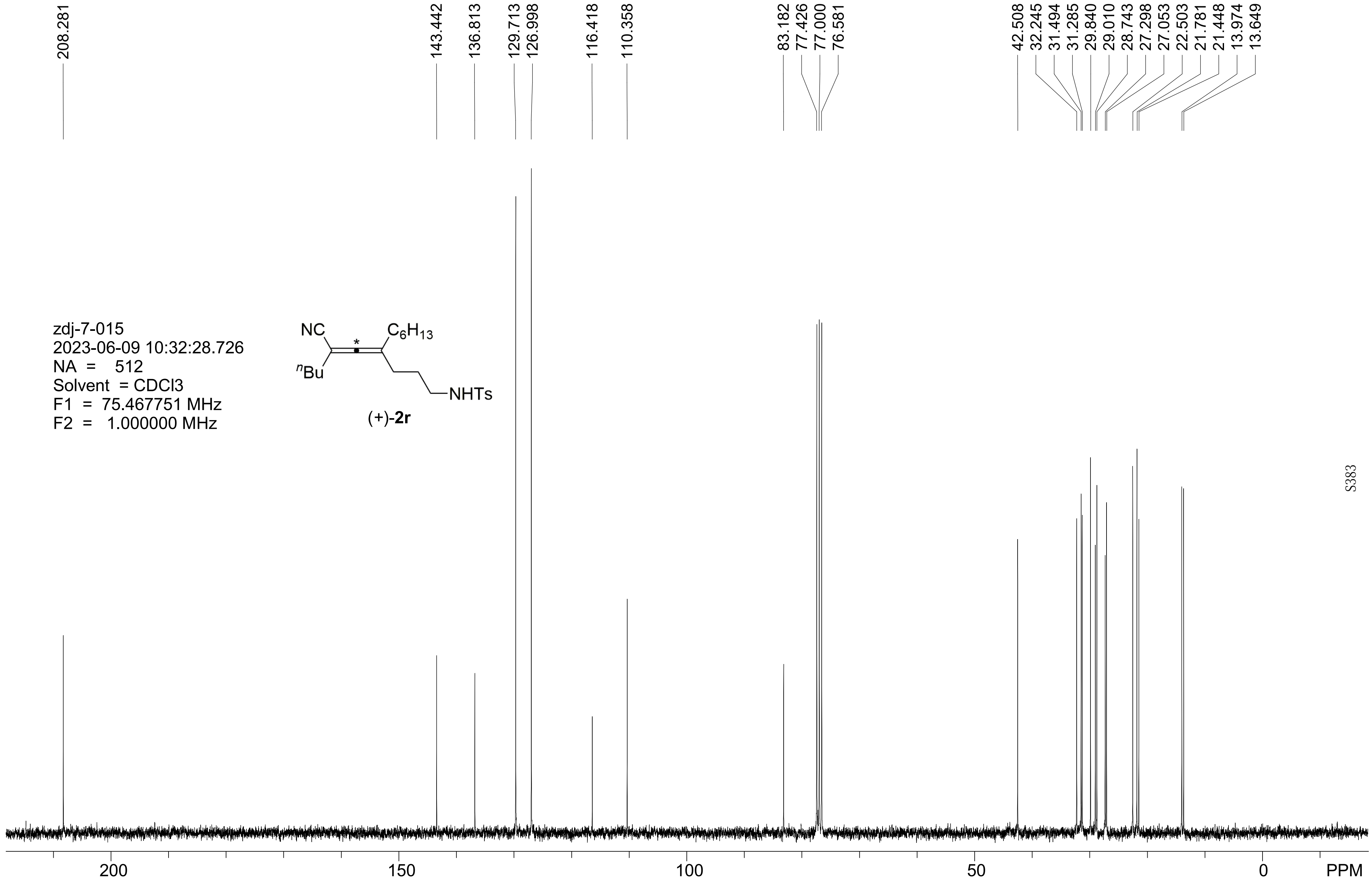


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		14.167	37506.824	1018020.500	50.0757
2		15.722	32686.047	1014941.375	49.9243
总计			70192.871	2032961.875	100.0000


zdj-7-015
2023-06-09 09:59:48.327
NA = 8
Solvent = CDCl3
F1 = 300.130005 MHz
F2 = 1.000000 MHz
NC
*
C6H13
nBu
NHTs
7.770
7.742
7.332
7.305
7.275
4.928
4.908
4.888
2.984
2.961
2.939
2.917
2.431
2.127
2.104
2.078
2.059
2.035
2.007
1.995
1.972
1.947
1.612
1.588
1.565
1.449
1.446
1.423
1.398
1.373
1.350
1.325
1.299
1.268
1.259
0.930
0.906
0.885
0.862
-0.000
2.00
1.98
0.98
2.00
3.00
6.09
2.06
12.72
6.12
10
8
6
4
2
0
PPM

(+)-**2r**


208.281
143.442
136.813
129.713
126.998
116.418
110.358
83.182
77.426
77.000
76.581
42.508
32.245
31.494
31.285
29.840
29.010
28.743
27.298
27.053
22.503
21.781
21.448
13.974
13.649
zdj-7-015
2023-06-09 10:32:28.726
NA = 512
Solvent = CDCl3
F1 = 75.467751 MHz
F2 = 1.000000 MHz
NC
C_6H_{13}
*
^{n}Bu
NHTs
(+)-**2r**
200
150
100
50
0
PPM

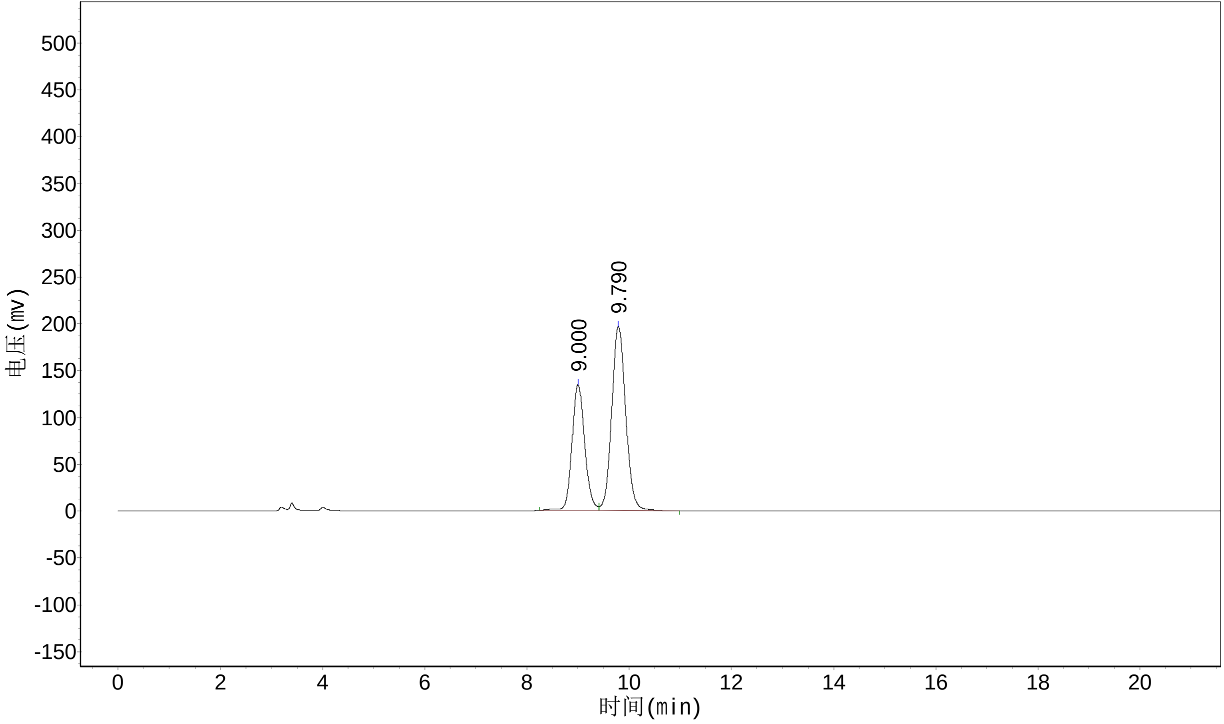
zdj-7-015

实验时间：2023-06-09,10:50:24
谱图文件:D:\浙大智达\N2000\样品\S20230609105025.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者：zdj
报告时间：2023-06-09,11:15:27
积分方法:面积归一法

实验内容简介：
IC,n-hexane/i-PrOH = 60/40,1.0,214

色谱图(S20230609105025.org)



分析结果表

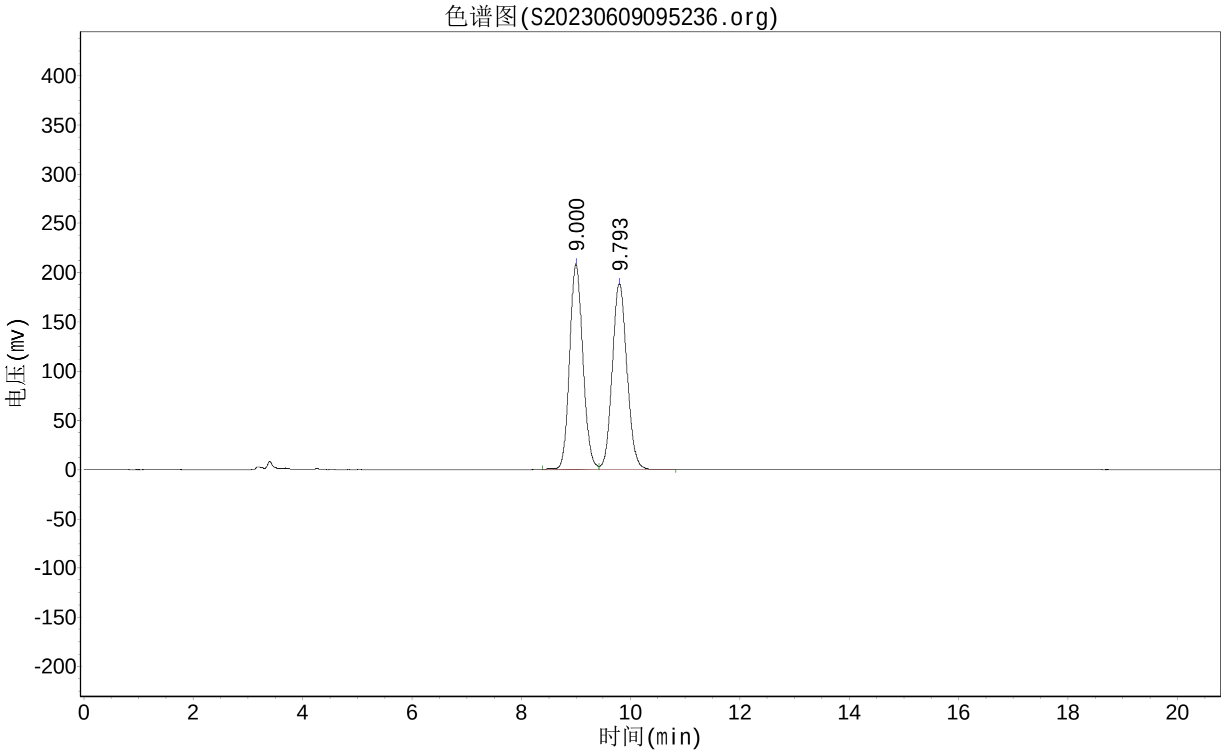
峰号	峰名	保留时间	峰高	峰面积	含量
1		9.000	134847.094	2346348.500	38.3995
2		9.790	197042.313	3764011.500	61.6005
总计			331889.406	6110360.000	100.0000

zdj-4-183

实验时间：2023-06-09,9:52:36
谱图文件:D:\浙大智达\N2000\样品\S20230609095236.org
方法文件:D:\浙大智达\N2000\djx.mtd

实验者：zdj
报告时间：2023-06-09,10:16:50
积分方法:面积归一法

实验内容简介：
IC,n-hexane/i-PrOH = 60/40,1.0,214



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.000	208616.344	3539921.750	50.1111
2		9.793	188456.625	3524224.250	49.8889
总计			397072.969	7064146.000	100.0000