Supporting Information

Synthesis of Cyclic Silyl Enol Ethers from *α*-Aryl-*α*-Diazoketones: New Building Blocks for Preparation of Indanones and *α*,*β*-Unsaturated Ketones

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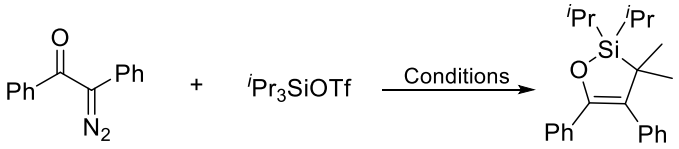
Table of Contents

1 General information

Unless otherwise noted, all reactions were carried out in oven-dried 25-mL Schlenk tubes under a nitrogen atmosphere. Solvents were purified by standard techniques without special instructions. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 spectrometer (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR), a Varian DLG400 spectrometer (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR), a Bruker Avance III-500 spectrometer (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR), and a Bruker Avance NEO 600 NMR Spectrometer (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR); All chemical shifts were reported in ppm (δ) relative to the internal standard TMS (0 ppm). The coupling constants *J* are given in Hz. The peak patterns are indicated below: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a NEXUS EURO (Thermo Nicolet) FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on either an LTQ Orbitrap XL (Thermo Scientific) mass spectrometer or a G6224A (Agilent Technologies) mass spectrometer. TLC was carried out on SiO_2 (silica gel 60 F254, Bide Pharmatech Ltd.), and the spots were located with UV light. Column chromatography was carried out on silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., LTD.) or basic aluminium oxide (200–300 mesh, Sinopharm Group Co. LTD). Melting points were determined using a micro-melting point apparatus and were uncorrected. Unless otherwise noted, starting materials are commercially available.

2 Optimization of reaction conditions

Table S1 Screening of reaction condition of diazoketones with silyl triflates



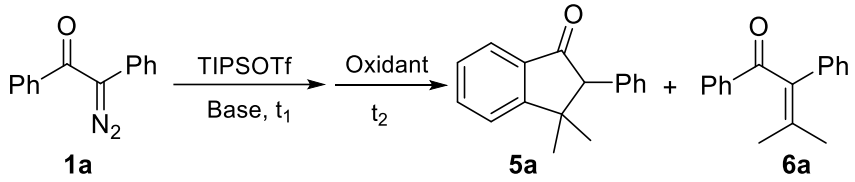
1a **2a**

Entry	Solvent	Base	Yield (%)[a,b]
1	CH_2Cl_2	None	20
2	CH_2Cl_2	$^{i}Pr_2NEt$	83
3	CH_2Cl_2	2,6-dimethylpyridine	91
4	CH_2Cl_2	2,6-DTBPy	95
5	DCE	2,6-DTBPy	89
6	Chlorobenzene	2,6-DTBPy	91
7	CH_3CN	2,6-DTBPy	78
8	Toluene	2,6-DTBPy	NR[c]
9	THF	2,6-DTBPy	NR[c]
10	DMF	2,6-DTBPy	NR[c]

[a]Reaction conditions: **1a** (0.2 mmol), $^{i}Pr_3SiOTf$ (0.22 mmol), and base (0.3 mmol) in solvent (2.0 mL) at 20 °C under N_2 for 30 min. [b]Isolated yield. [c]No reaction; starting material **1a** was recovered.

2-Diazo-1,2-diphenylethan-1-one (**1a**) and triisopropylsilyl triflate ($^{i}Pr_3SiOTf$) were selected as model substrates to optimize the reaction conditions for exploring the proposed C(sp^3)–H insertion reaction (Table S1). The reaction parameters, including solvent and base, were then screened. The desired product **2a** was obtained in only 20% yield when **1a** was reacted with $^{i}Pr_3SiOTf$ in CH_2Cl_2 at 20 °C under a nitrogen atmosphere for 30 min (Table S1, entry 1). The low yield was attributed to the generation of triflic acid, which led to the decomposition of **1a**. Various Lewis bases were then evaluated to enhance the yield (entries 2–4). Among the tested bases, using 2,6-di-*tert*-butylpyridine (2,6-DTBPy) led to excellent yield of **2a** (entry 4). Subsequently, the solvents were screened using 2,6-DTBPy as the base, revealing that CH_2Cl_2 was the optimal solvent for the current reaction (entries 4–10). Therefore, the reactions of *α*-aryl-*α*-diazoketone (0.2 mmol) with silyl triflate (1.1 equiv.) were performed in the presence of 2,6-DTBPy (1.5 equiv.) as the base in CH_2Cl_2 (3.0 mL) solvent at 20 °C under a nitrogen atmosphere for 30 min.

Table S1 Screening of reaction conditions of one-pot synthesis of multi-substituted indanones



1a **5a** **6a**

Entry	Base	Oxidant	Yield/**5a** (%)[a,b]	Yield/**6a** (%)[a,b]
1	2,6-DTBPy	$FeCl_3$	ND[c]	ND[c]
2	$^{i}Pr_2NEt$	$FeCl_3$	ND[c]	ND[c]
3	2,6-dimethylpyridine	$FeCl_3$	ND[c]	ND[c]
4	2-fluoropyridine	$FeCl_3$	ND[c]	ND[c]
5	2,4-difluoropyridine	$FeCl_3$	ND[c]	ND[c]
6	4-cyanopyridine	$FeCl_3$	ND[c]	21
7	pyrazine	$FeCl_3$	65	ND[c]
8	pyrimidine	$FeCl_3$	66	ND[c]
9	pyridazine	$FeCl_3$	76	ND[c]
10	1,2,3-triazine	$FeCl_3$	<10	<10
11	pyridazine	$CuCl_2$	ND[c]	<10
12	pyridazine	*m*-CPBA	ND[c]	<10
13	pyridazine	$K_2S_2O_8$	ND[c]	<10
14[d]	pyridazine	$PhI(OAc)_2$	ND[c]	43
15[d]	pyridazine	DMP	ND[c]	35
16	pyridazine	$FeCl_3·6H_2O$	ND[c]	63

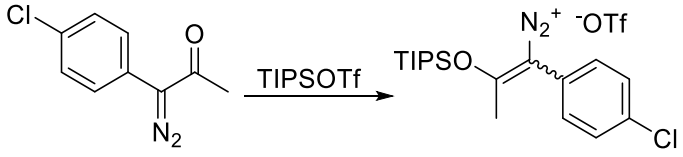
[a] Reaction conditions: **1a** (0.2 mmol), $^{i}Pr_3SiOTf$ (0.22 mmol), base (0.22 mmol), oxidant (0.4 mmol), CH_2Cl_2 (3.0 mL), 20 ºC, N_2, t_1 = 2 h, t_2 = 12 h. [b]Isolated yield. [c]Not detected; starting material **1a** disappeared. [d]The reaction temperature was 40 ºC. *m*-CPBA = *meta*-chloroperoxybenzoic acid, DMP = Dess-Martin periodinane.

Considering the limited reports on the synthetic applications of cyclic silyl enol ethers, we explored their potential applications in organic synthesis. It was found that

these compounds can be transformed into indanones and *α,β*-unsaturated ketones using specific oxidants, respectively. The conditions of one-pot two-step reactions were explored (Table S2). Upon conducting the reaction of **1a** with $^{i}Pr_3SiOTf$ in the presence of 2,6-DTBPy under a nitrogen atmosphere for 2 hours, $FeCl_3$ was added to the resulting mixture and stirred for an additional 12 h (Table S2, entry 1). However, no indanone **5a** and *α,β*-unsaturated ketone **6a** formation was observed. This outcome may be attributed to the strong coordination between 2,6-DTBPy and $FeCl_3$. Other bases were then evaluated, and the results are summarized in Table S2. It was found that $^{i}Pr_2NEt$ and pyridine derivatives were unsuitable as they resulted in messy mixtures (entries 2–5). To our delight, *α,β*-unsaturated ketone **6a** was obtained as a sole product in 21% yield when utilizing 4-cyanopyridine as the base (entry 6). However, only the indanone **5a** was obtained with yields of 65%, 66%, and 76%, respectively, when electron-deficient heterocycles such as pyrazine, pyrimidine, and pyridazine were used as the base, (entries 7–9). It should be noted that the more electron-deficient trisubstituted triazine was not suitable for the current reaction (entry 10). Furthermore, various oxidants, including $CuCl_2$, peroxides and hypervalent iodines were evaluated (entries 11–15). Nevertheless, these oxidants demonstrated lower efficiency compared to $FeCl_3$. Therefore, the optimal reaction conditions for obtaining indanones are as below: 2-diazo-1,2-diarylketone (0.2 mmol), $^{i}Pr_3SiOTf$ (1.1 equiv.), pyridazine (1.1 equiv.) in CH_2Cl_2 (3.0 mL) under N_2 at 20 °C for 2 h (first step), followed by treating with $FeCl_3$ (2.0 equiv.) under N_2 at 20 °C for 12 h (second step).

Additionally, *α,β*-unsaturated ketone **6a** was obtained as a sole product in 63% yield when $FeCl_3·6H_2O$ was used instead of $FeCl_3$ (Table S2, entry 16). Thus, the optimal reaction conditions for obtaining *α,β*-unsaturated ketones are as below: *α*-aryl-*α*-diazoketone (0.2 mmol), $^{i}Pr_3SiOTf$ (1.1 equiv.), pyridazine (1.1 equiv.) in CH_2Cl_2 (3.0 mL) under N_2 at 20 °C for 2 h (first step), followed by treating with $FeCl_3·6H_2O$ (2.0 equiv.) under N_2 at 20 °C for 12 h (second step).

3 In-situ NMR analysis of the vinyldiazonium salt derived from 1v



1v *Vinyldiazonium salt **I***

The procedure for the preparation of vinyldiazonium salt was shown below: in a glovebox, a J-Young NMR tube was charged with **1v** (19 mg, 0.1 mmol) and CD_2Cl_2 (0.6 mL), followed by shaking until complete dissolution. The NMR tube was transferred to liquid nitrogen until the solution solidified into a solid state. After $^{i}Pr_3SiOTf$ (0.1 mmol, 31 mg) was added carefully, the NMR tube was sealed and removed from the glovebox while maintaining liquid nitrogen temperature. Subsequently, it was placed in an ethanol low-temperature bath (-80 °C) and shaken until complete dissolution of $^{i}Pr_3SiOTf$. After standing for 3 h in the low-temperature

bath, the NMR tube was rapidly removed and placed into liquid nitrogen. Ethanol adhered on the surface of the NMR tube was wiped off. The tube was inserted quickly into an NMR spectrometer at -70 °C for analysis. The peaks of ^{1}H and ^{13}C NMR spectra were assigned according to the literature.[1]

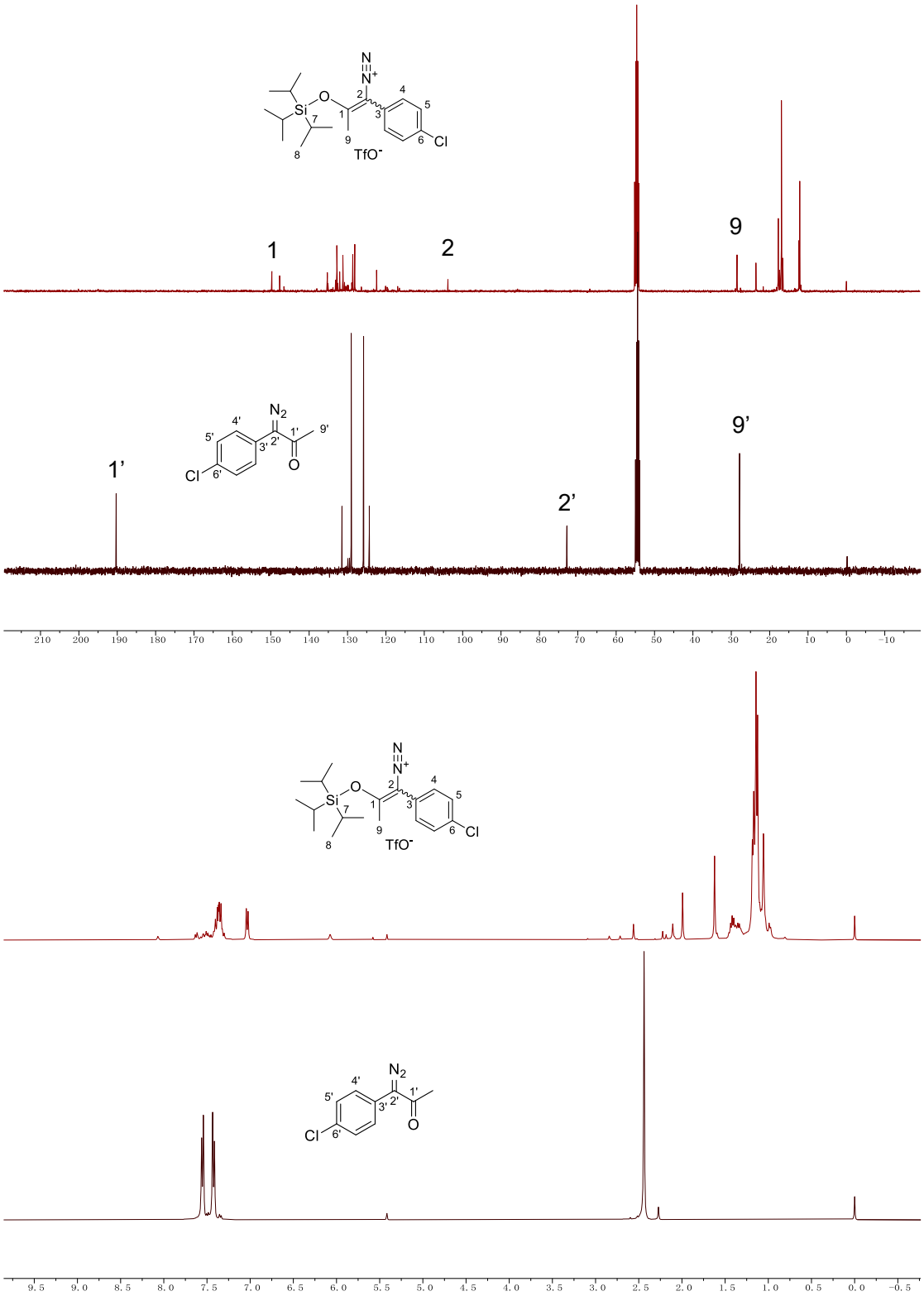
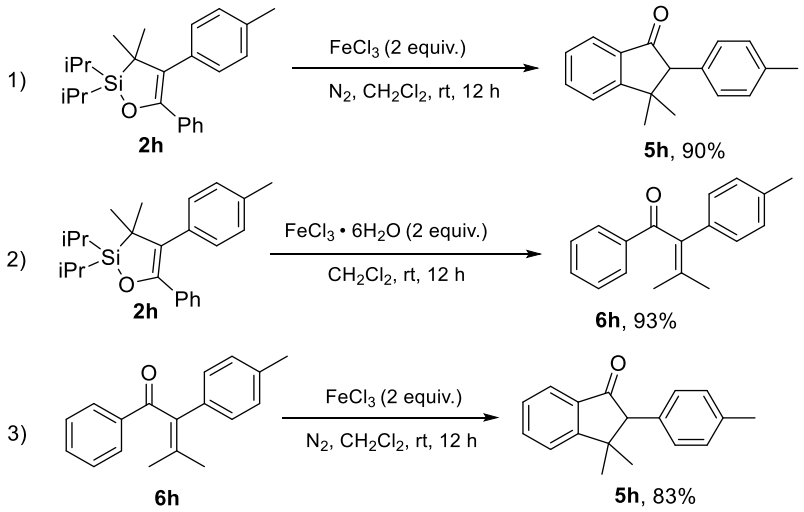


Figure S1 ^{1}H and ^{13}C NMR spectra of compound **1v** and diazonium salt **I**

4 Details of control experiments and GC–MS analysis results

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **2h** (73 mg, 0.2 mmol), CH_2Cl_2 (3.0 mL), and $FeCl_3$ (65 mg, 0.4 mmol) under a nitrogen atmosphere. The mixture was stirred at room temperature for 12 h. Upon completion of the reaction as monitored by TLC, the mixture was quenched with water and extracted with ethyl acetate (3 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified via silica gel column chromatography (eluent: hexane/ethyl acetate = 20:1) to afford indanone **5h** (45 mg, 90%; eq. 1). The *α,β*-unsaturated ketone **6h** (47 mg, 93%; eq. 2) was obtained when $FeCl_3·6H_2O$ was used instead of anhydrous $FeCl_3$. Furthermore, it was found that the *α,β*-unsaturated ketone **6h** can be transformed to indanone **5h** (42 mg, 83%; eq. 3) in the presence of anhydrous $FeCl_3$.



Scheme S1 Control experiments of the formation of indanone **5h**

These results revealed that *α,β*-unsaturated ketone **6h** is an intermediate in the transformation of **2h** to indanone **5h**. The reaction mixture (Scheme S1, eq. 1) was subjected to GC–MS analysis after filtration through a microporous membrane. The results are presented in the figure S2. The indanone **5h** and *α,β*-unsaturated ketone **6h** were simultaneously detected, further indicating that *α,β*-unsaturated ketone **6h** is an intermediate in the transformation of **2h** to indanone **5h**. The trimer and tetramer of diisopropylsiloxane were generated via the hydrolysis of $^{i}Pr_2SiCl_2$.

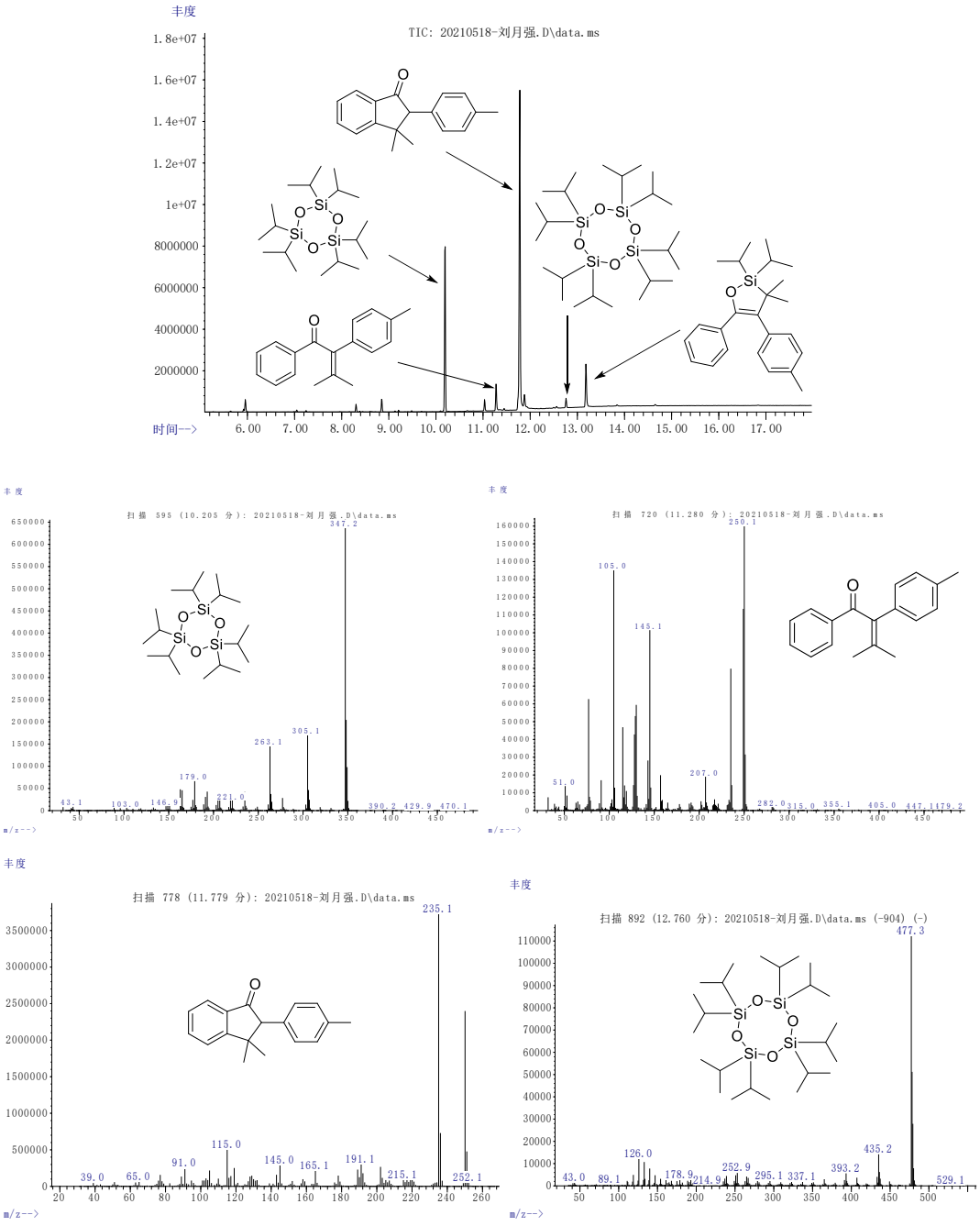


Figure S2 Gas chromatogram and MS spectra

5 Computational details

5.1 Computational method

DFT calculations were carried out to study the vinyl cation intermediate II using the Gaussian 16 software package[2]. The geometry optimizations were performed using m06-2x functional with 6-311G (d, p) basis set. The vibrational frequencies were computed using the same level of theory as employed for the geometry optimizations to confirm the status of the optimized stationary point as an energy minimum.

Additionally, natural bond orbital analysis was performed to confirm the electronic structure and bonding characteristics of the vinyl cation intermediate II.

5.2 Results of geometry optimization and natural bond orbital analysis

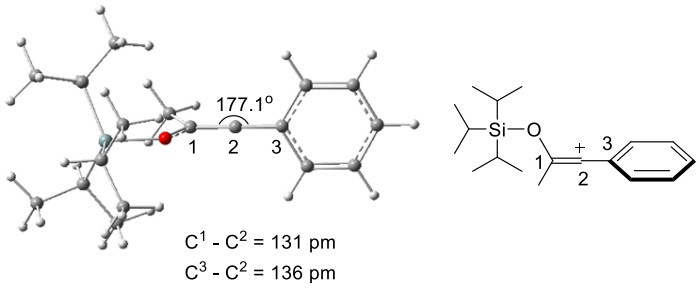
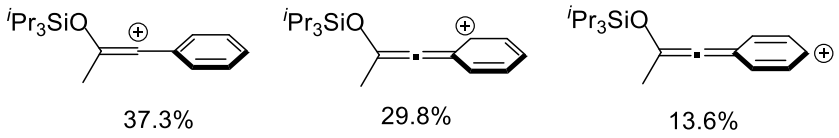


Figure S3 Structure and partial bond lengths as well as the angle of intermediate II

Figure S4 Main resonance structures of intermediate II



37.3% 29.8% 13.6%

Table S3 Results of bond order analysis of intermediate II

	C^1–C^2 bond	C^2–C^3 bond
Fuzzy-atom bond order	1.69	1.47
Wiberg bond order	1.74	1.45
Mayer bond order	1.66	1.37

The optimized structure of intermediate II in Figure S3 shows the C^1–C^2 bond length is measured to be 131 pm, slightly shorter than the C^2–C^3 bond length by 5 pm. The C^1–C^2–C^3 bond angle is nearly linear, measuring at 177.1°. These findings suggest that the C^2 atom exhibits sp hybridization with a vinyl cation character. This finding is substantiated by the main resonance structure analysis presented in Figure S4, where the predominant characteristics of intermediate II observed is a vinyl cation (37.3%) rather than the other two types of conjugated diene (29.8% and 13.6%). Additionally, fuzzy-atom bond orders, Wiberg bond order, and Mayer bond order analysis (Table S3) consistently indicate that the bond orders for the C^1–C^2 bonds are larger compared to those involving the C^2–C^3 bond, providing additional evidence for the vinyl cation character of intermediate II.

5.3 Cartesian coordinates for the optimized structure of intermediate II

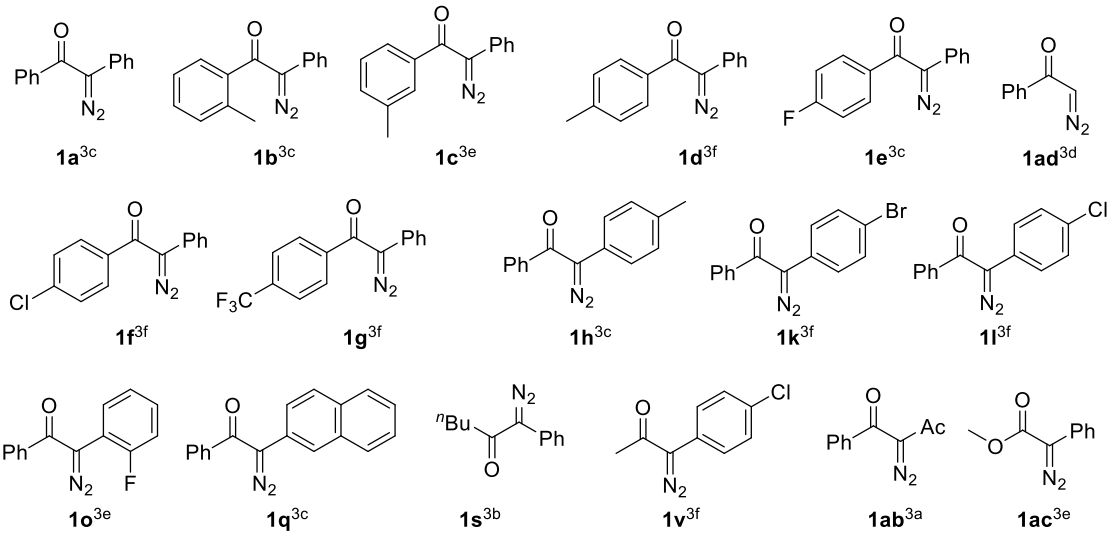
C	3.33298	-0.00322	-0.14938
C	4.03411	-1.23911	0.01261
C	5.37581	-1.22707	0.31098
C	6.03588	0.00093	0.45227
C	5.37432	1.22690	0.30077

C	4.03260	1.23482	0.00226
H	3.48534	-2.16597	-0.10181
H	5.92178	-2.15259	0.43790
H	7.09450	0.00256	0.68812
H	5.91915	2.15411	0.42000
H	3.48270	2.16002	-0.11988
C	2.00064	-0.00515	-0.42662
C	0.72896	-0.00827	-0.75827
C	0.42726	-0.01517	-2.23962
H	-0.15720	0.87373	-2.48566
H	-0.15195	-0.90946	-2.47826
H	1.33801	-0.01489	-2.83820
O	-0.22438	-0.00588	0.14901
Si	-1.96274	0.00126	-0.00715
C	-2.44471	-1.56122	-0.95129
C	-2.48483	0.00538	1.79231
C	-2.43221	1.56682	-0.95288
C	-3.90304	-1.94734	-0.64167
H	-4.19672	-2.81966	-1.23077
H	-4.60625	-1.14477	-0.87461
H	-4.02909	-2.20641	0.41282
C	-1.99272	1.26326	2.52636
H	-2.26086	1.20867	3.58450
H	-2.43263	2.17783	2.12528
H	-0.90427	1.35297	2.46560
C	-1.48466	2.75373	-0.71418
H	-1.77815	3.60130	-1.33908
H	-0.44079	2.52059	-0.94315
H	-1.51793	3.08731	0.32468
C	-2.01132	-1.25877	2.52772
H	-2.27678	-1.19814	3.58622
H	-0.92452	-1.36592	2.46539
H	-2.46644	-2.16688	2.12896
H	-2.39555	1.30769	-2.01930
C	-3.88394	1.97114	-0.63542
H	-4.17150	2.84396	-1.22678
H	-3.99981	2.23664	0.41861
H	-4.59794	1.17564	-0.85956
H	-2.39858	-1.30506	-2.01805
C	-1.51265	-2.7586	-0.70414
H	-1.55864	-3.09136	0.33447
H	-0.46427	-2.53729	-0.92402

H	-1.81038	-3.60309	-1.33121
H	-3.58276	0.01353	1.79472

6 Preparation of diazoketones and silyl triflates

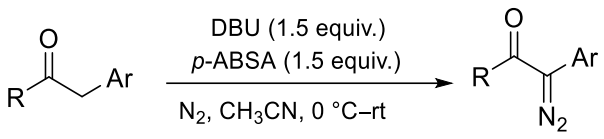
6.1 Preparation of known diazoketones according to literature procedures



Scheme S2 Details of known diazoketones

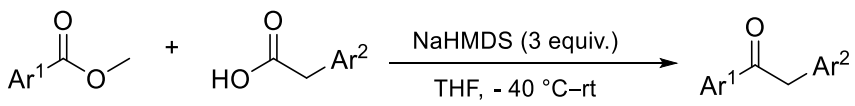
Most of the diazoketones were prepared according to known procedures reported in literatures.[3] The details are shown in Scheme S.

6.2 General procedure for preparation of unknown diazoketones



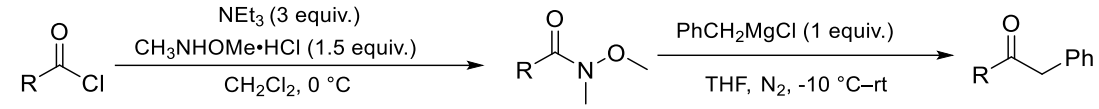
In a glove box, an oven-dried 50 mL flask equipped with a Teflon-coated magnetic stir bar was charged with 2-arylethanone (2.0 mmol), 4-acetamidobenzenesulfonyl azide (*p*-ABSA, 0.72 g, 3.0 mmol), and acetonitrile (10.0 mL). Then, the flask was sealed with a rubber septum. The flask was taken out of the glove box and cooled to 0 °C with an ice bath. Subsequently, DBU (0.46 g, 3.0 mmol in 3 mL acetonitrile) was added dropwise, and the mixture was slowly warmed to room temperature overnight. The solvent was removed under reduced pressure, maintaining the temperature below 30 °C. The resulting residue was purified by column chromatography (eluent: hexane/CH_2Cl_2 = 1:1) on basic aluminium oxide to afford the corresponding diazoketone.

6.3 General procedure for preparation of 1,2-diarylethan-1-ones



A Schlenk tube (100 mL) equipped with a magnetic stir bar was charged with methyl arylcarboxylate (5.0 mmol), arylacetic acid (5.0 mmol), and dry THF (20 mL) under a nitrogen atmosphere. After the mixture was cooled to -40 °C, NaHMDS (2.5 M in THF, 6 mL) was added dropwise, and the temperature was slowly warmed to room temperature over 10 h. The mixture was quenched with saturated aqueous NH_4Cl solution, and the residue was extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over a short silica gel pad and concentrated under reduced pressure. The resulting residue was purified via silica gel column chromatography (eluent: hexane/ethyl acetate = 20:1) to obtain the corresponding 1,2-diarylethan-1-one.

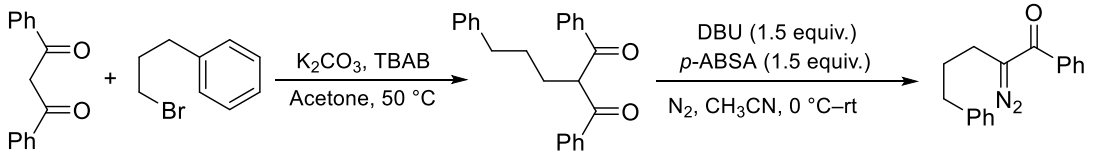
6.4 General procedure for preparation of 1-aryl-1-alkyl-2-ones



An oven-dried 100 mL flask equipped with a magnetic stir bar was charged successively with *N*,*O*-dimethylhydroxylamine hydrochloride (1.46 g, 15 mmol), aliphatic acyl chloride (10 mmol), and CH_2Cl_2 (50 mL). After the resulting mixture was cooled to 0 °C with an ice bath, Et_3N (4.2 mL, 30 mmol) was added slowly. The mixture was gradually warmed to room temperature for 12 h, and then the mixture was quenched with water and extracted with ethyl acetate (40 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The Weinreb amide was used in the next step without further purification.

In the next step, a Schlenk tube (100 mL) equipped with a magnetic stir bar was charged with Weinreb amide prepared in the first step and THF (20.0 mL) under a nitrogen atmosphere. After the mixture was cooled to -10 °C, $PhCH_2MgCl$ (5.5 mL, 2 M, 11 mmol) was added dropwise. The resulting mixture was then warmed to room temperature over 3 h. The reaction progress was monitored by TLC. After completion of the reaction, the resulting solution was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with brine (30 mL × 3), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified via silica gel column chromatography (eluent: hexane/ethyl acetate = 20:1) to obtain the corresponding ketone.

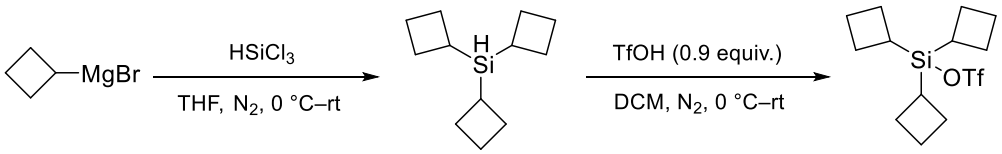
6.5 Procedure for preparation of diazoketone 1rr



An oven-dried 100 mL flask equipped with a magnetic stir bar was charged successively with 1,3-diphenylpropane-1,3-dione (4.5 g, 20.0 mmol), K_2CO_3 (2.76 g,

20.0 mmol), tetrabutylammonium bromide (TBAB, 160 mg, 0.5 mmol), (3-bromopropyl)benzene (2.0 g, 10.0 mmol), and acetone (40 mL). The mixture was then stirred at 50 °C for 12 h. The reaction progress was monitored by TLC. After reaction finished, water (50 mL) was added to the mixture and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: hexane/ethyl acetate = 20:1) to obtain the desired product 1,3-diphenyl-2-(3-phenylpropyl)propane-1,3-dione. The corresponding diazoketone (2-diazo-1,5-diphenylpentan-1-one, **1rr**) was obtained by following the procedure for the preparation of diazoketones.

6.6 Representative procedure for preparation of silyl triflates

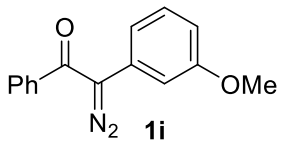


Tricyclobutylsilane was synthesized by a modified procedure.[4] An oven-dried 100 mL Schlenk tube was charged with cyclobutylmagnesium bromide (2.0 M in THF, 16 mL, 32 mmol) under a nitrogen atmosphere and cooled with an ice bath. $HSiCl_3$ (1.0 mL, 10 mmol) was added dropwise at 0 °C, and the resulting mixture was warmed to room temperature overnight. The mixture was quenched with water and extracted with pentane (20 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via silica gel column chromatography (eluent: pentane) to afford tricyclobutylsilane (1.20 g, 62%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 1H), 2.19–2.03 (m, 9H), 2.06–1.91 (m, 12H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 25.0, 23.8, 18.4; IR (neat): ν_{max} 2927, 2860, 2085, 1628, 1441, 1239, 1052, 906, 790, 758 cm^{-1}; MS (EI-TOF) *m/z*: 57.1, 83.0, 97.0, 111.0, 139.1, 194.1.

Tricyclobutylsilyl triflate was generated in situ by a modified procedure.[5] An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with tricyclobutylsilane (194 mg, 1 mmol) and CH_2Cl_2 (5.0 mL) under nitrogen atmosphere and cooled in an ice bath. Triflic acid (80 μL, 0.9 mmol) was added dropwise by a microsyringe, and the mixture was slowly warmed up to room temperature overnight. The solution was used directly in the next step without further purification. Tricyclopentylsilane,[6] tricyclohexylsilane,[7] and 1-(*tert*-butyl)silinane[8] were synthesized according to reported procedures, and the corresponding silyl triflates were synthesized in situ by the same procedure for the synthesis of tricyclobutylsilyl triflate.

6.7 Characterization data of diazoketones and silanes

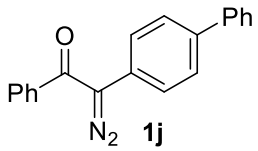
2-diazo-2-(3-methoxyphenyl)-1-phenylethan-1-one (1i)



1i

262 mg, 52% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.56 (m, 2H), 7.55–7.46 (m, 1H), 7.47–7.37 (m, 2H), 7.30 (dd, J = 8.0, 8.0 Hz, 1H), 7.12 (dd, J = 2.2, 2.2 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 6.80 (ddd, J = 8.4, 2.6, 0.9 Hz, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 188.4, 160.1, 138.0, 131.7, 130.0, 128.6, 127.7, 127.5, 118.0, 112.8, 111.6, 73.2, 55.3; IR (KBr): ν_{max} 3060, 2851, 2075, 1626, 1486, 1343, 1262, 1227, 1037, 775, 698, 682 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na - N_2)^+$ $C_{15}H_{12}O_2Na^+$ 247.0735, found 247.0729.

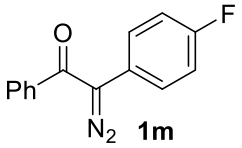
2-([1,1'-biphenyl]-4-yl)-2-diazo-1-phenylethan-1-one (1j)[9]



1j

465 mg, 78% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.57 (m, 6H), 7.58–7.48 (m, 3H), 7.49–7.39 (m, 4H), 7.36 (dd, J = 7.4, 7.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 188.4, 140.2, 139.8, 138.0, 131.8, 128.9, 128.6, 127.8, 127.7, 127.6, 127.0, 126.3, 124.9, 73.0.

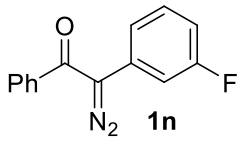
2-diazo-2-(4-fluorophenyl)-1-phenylethan-1-one (1m)[10]



1m

360 mg, 75% yield; Orange solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, J = 7.2 Hz, 2H), 7.51 (dd, J = 7.4, 7.4 Hz, 1H), 7.47 (dd, J = 8.7, 5.1 Hz, 2H), 7.43 (dd, J = 7.6, 7.6 Hz, 2H), 7.12 (dd, J = 8.6, 8.6 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 188.3, 161.7 (d, J = 247.5 Hz), 137.7, 131.8, 128.6, 128.0 (d, J = 7.8 Hz), 127.7, 121.9, 116.2 (d, J = 22.6 Hz), 72.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.30.

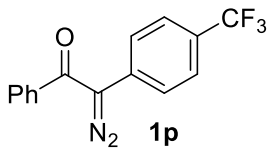
2-diazo-2-(3-fluorophenyl)-1-phenylethan-1-one (1n)



1n

303 mg, 63% yield; Orange solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.0 Hz, 2H), 7.50–7.40 (m, 1H), 7.44–7.32 (m, 3H), 7.33–7.20 (m, 1H), 7.17–7.06 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 188.0, 159.0 (d, J = 248.3 Hz), 137.3, 131.8, 131.2 (d, J = 2.1 Hz), 129.9 (d, J = 8.3 Hz), 128.5, 127.8, 124.7 (d, J = 3.6 Hz), 116.1 (d, J = 21.3 Hz), 114.6 (d, J = 13.1 Hz), 68.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.44; IR (KBr): ν_{max} 3062, 2087, 1626, 1493, 1448, 1340, 1281, 1249, 911, 866, 756, 698, 641 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H + CH_3CN - N_2)^+$ $C_{16}H_{13}FNO^+$ 254.0976, found 254.0978.

2-diazo-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-one (1p)

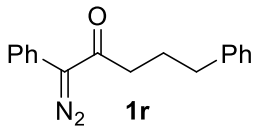


1p

441 mg, 76% yield; Orange solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64–7.78 (m, 6H), 7.54–7.58 (m, 1H), 7.45–7.50 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 188.0, 137.6, 132.1, 130.5, 128.8, 128.6 (q, J = 32.7 Hz), 127.6, 125.9 (q, J = 3.8 Hz), 125.3, 124.0 (q, J = 271.5 Hz), 72.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.54; IR (KBr): ν_{max}

2921, 2088, 1728, 1602, 1446, 1337, 1240, 1116, 841, 702, 477 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H + CH_3CN - N_2)^+$ $C_{17}H_{13}F_3NO^+$ 304.0944, found 304.0941.

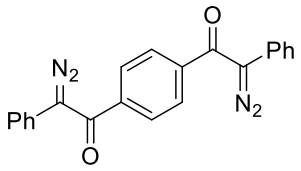
1-diazo-1,5-diphenylpentan-2-one (1r)



1r

428 mg, 81% yield; Orange oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 7.9 Hz, 2H), 7.38 (dd, J = 7.8, 7.8 Hz, 2H), 7.28 (dd, J = 7.5, 7.5 Hz, 2H), 7.23 (dd, J = 7.5, 7.5 Hz, 1H), 7.22–7.14 (m, 3H), 2.68 (t, J = 7.6 Hz, 2H), 2.58 (t, J = 7.4 Hz, 2H), 2.01–2.06 (m, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 192.6, 141.4, 129.1, 128.51, 128.47, 127.0, 126.1, 126.0, 125.6, 77.3, 77.1, 76.9, 72.2, 38.2, 35.1, 26.1; IR (neat): ν_{max} 2933, 2070, 1715, 1648, 1496, 1453, 1372, 1221, 1115, 1029, 910, 753, 699 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na - N_2)^+$ $C_{17}H_{16}ONa^+$ 259.1099, found 259.1093.

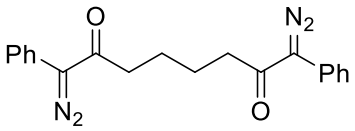
1,1'-(1,4-phenylene)bis(2-diazo-2-phenylethan-1-one) (1t)



1t

293 mg, 40% yield; Orange solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 4H), 7.46–7.35 (m, 8H), 7.32–7.25 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 187.3, 140.5, 129.2, 128.0, 127.4, 126.4, 125.7, 73.7; IR (KBr): ν_{max} 2921, 2087, 1613, 1495, 1353, 1236, 1184, 869, 812, 748, 687, 494 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na - N_2)^+$ $C_{22}H_{14}N_2O_2Na^+$ 361.0947, found 361.0950.

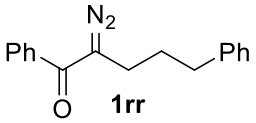
1,8-bis(diazo)-1,8-diphenyloctane-2,7-dione (1u)



1u

312 mg, 45% yield; Orange solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 6.9 Hz, 4H), 7.44–7.33 (m, 4H), 7.31–7.20 (m, 2H), 2.69–2.55 (m, 4H), 1.86–1.69 (m, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 192.4, 129.1, 127.1, 126.0, 125.5, 72.2, 38.7, 24.0; IR (KBr): ν_{max} 2067, 2066, 1650, 1486, 1368, 1315, 1247, 1180, 1102, 886, 743, 694, 661 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na - 2\ N_2)^+$ $C_{20}H_{18}O_2Na^+$ 313.1204, found 313.1203.

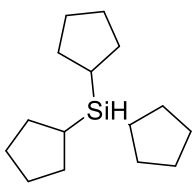
2-diazo-1,5-diphenylpentan-1-one (1rr)



1rr

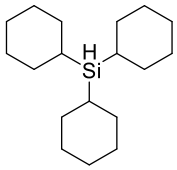
53 mg, 10% yield; Orange oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.5 Hz, 2H), 7.50–7.42 (m, 1H), 7.39 (dd, J = 7.5, 7.5 Hz, 2H), 7.28 (dd, J = 7.5, 7.5 Hz, 2H), 7.19 (d, J = 7.1 Hz, 3H), 2.72 (t, J = 7.7 Hz, 2H), 2.55 (t, J = 7.6 Hz, 2H), 1.95–1.87 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 189.6, 141.3, 137.8, 131.4, 128.6, 128.5, 128.4, 127.2, 126.1, 67.0, 35.1, 28.8, 23.4; IR (neat): ν_{max} 3019, 2921, 2843, 2067, 1621, 1499, 1433, 1331, 1078, 902, 780, 743, 698 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{16}N_2ONa^+$ 287.1155, found 287.1157.

Tricyclopentylsilane[6]



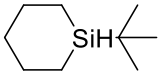
Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 3.56 (q, J = 2.9 Hz, 1H), 1.93–1.72 (m, 6H), 1.70–1.53 (m, 6H), 1.56–1.41 (m, 6H), 1.44–1.30 (m, 6H), 1.09–0.94 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 29.8, 26.9, 22.5.

Tricyclohexylsilane[7]



Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (q, J = 2.3 Hz, 1H), 1.70–1.72 (s, 16H), 1.16–1.31 (m, 14H), 0.94–0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 29.5, 28.3, 27.0, 22.1.

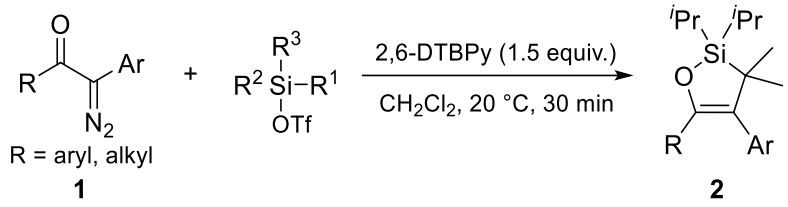
1-(tert-butyl)silinane[8]



Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.47 (tt, J = 6.7, 1.7 Hz, 1H), 1.97–1.81 (m, 2H), 1.65–1.51 (m, 1H), 1.47–1.30 (m, 2H), 1.14–0.99 (m, 1H), 0.85 (s, 9H), 0.81–0.71 (m, 2H), 0.56–0.35 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 30.0, 27.3, 25.3, 16.0, 8.2.

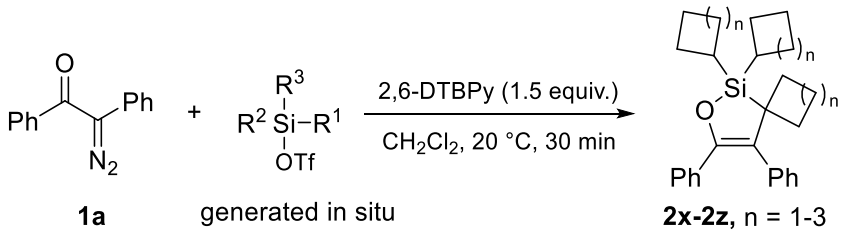
7 The reaction of diazoketones with silyl triflates

7.1 General procedure for obtaining products 2a–2w and 3



An oven-dried Schlenk tube equipped with a magnetic stir bar was charged successively with 2,6-DTBPy (0.3 mmol, 58 mg), silyl triflate (0.22 mmol), and CH_2Cl_2 (3.0 mL) under nitrogen atmosphere. After the resulting mixture was stirred for 1 min, α-aryl-α-diazoketone (0.2 mmol) was added, and the mixture was stirred at 20 °C for 30 min. Then, the mixture was quenched with triethylamine (0.5 mL), and the solvent was removed under reduced pressure. The resulting residue was purified via silica gel column chromatography (eluent: hexane/ethyl acetate = 100:1) to afford the corresponding cyclic silyl enol ether. Notably, compounds **1ab**, **1ac**, **1ad**, and **1rr** are unsuitable for the current reaction.

7.2 General procedure for obtaining products 2x–2z, 2y' and 4

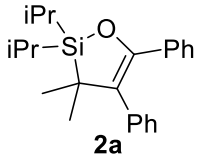


A Schlenk tube equipped with the solution of silyl triflate in CH_2Cl_2 (5.0 mL) generated in situ was charged with DTBPy (1 mmol, 191 mg) under a nitrogen atmosphere. After the resulting mixture was stirred for 1 min, **1a** (0.5 mmol, 111 mg) was added, and the resulting mixture was stirred at 20 °C for 30 minutes. Then, the mixture was quenched with triethylamine (0.5 mL), and the solvent was removed under

reduced pressure. The resulting residue was purified via silica gel column chromatography (eluent: hexane/ethyl acetate = 100:1) to afford the corresponding cyclic silyl enol ether. It is worth noting that compound **4** was also obtained by this procedure.

7.3 Characterization data of the cyclic silyl enol ethers and byproducts

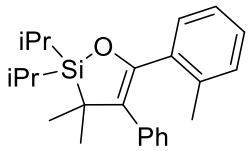
2,2-diisopropyl-3,3-dimethyl-4,5-diphenyl-2,3-dihydro-1,2-oxasilole (2a)



2a

67 mg, 95% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.10 (m, 5H), 7.05–6.94 (m, 5H), 1.43–1.27 (m, 2H), 1.25–1.09 (m, 12H), 1.10 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.9, 136.8, 135.0, 130.9, 128.2, 127.9, 127.5, 127.2, 126.5, 125.7, 30.2, 23.6, 17.8, 12.3; IR (neat): ν_{max} 3054, 2943, 2866, 1613, 1463, 1314, 1228, 1065, 882, 848, 811, 713, 694 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{23}H_{31}OSi^+$ 351.2139, found 351.2140.

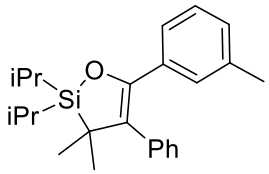
2,2-diisopropyl-3,3-dimethyl-4-phenyl-5-(o-tolyl)-2,3-dihydro-1,2-oxasilole (2b)



2b

67 mg, 92% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17–7.05 (m, 3H), 7.08–6.98 (m, 3H), 7.00–6.87 (m, 3H), 2.27 (s, 3H), 1.51–1.37 (m, 2H), 1.30–1.20 (m, 18H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 151.3, 136.6, 135.9, 135.4, 130.9, 130.2, 129.8, 127.7, 127.4, 126.5, 126.0, 125.0, 29.6, 24.1, 19.9, 17.9, 17.7, 12.3; IR (neat): ν_{max} 3054, 2945, 2866, 1721, 1601, 1460, 1310, 1261, 1080, 966, 880, 816, 726, 699 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{24}H_{33}OSi^+$ 365.2301, found 365.2307.

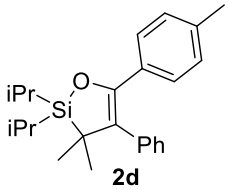
2,2-diisopropyl-3,3-dimethyl-4-phenyl-5-(m-tolyl)-2,3-dihydro-1,2-oxasilole (2c)



2c

69 mg, 94% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.26 (m, 3H), 7.18–7.07 (m, 3H), 7.04–6.90 (m, 3H), 2.20 (s, 3H), 1.47 (dt, J = 7.4 Hz, 2H), 1.33–1.23 (m, 12H), 1.21 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.0, 136.9, 134.9, 130.9, 128.5, 128.1, 128.0, 127.3, 126.4, 125.6, 125.1, 30.2, 23.6, 21.5, 17.83, 17.79, 12.3; IR (neat): ν_{max} 3437, 2943, 2866, 1726, 1602, 1461, 1384, 1186, 881, 838, 769, 737, 701 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{24}H_{33}OSi^+$ 365.2301, found 365.2302.

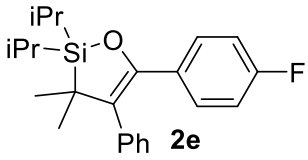
2,2-diisopropyl-3,3-dimethyl-4-phenyl-5-(p-tolyl)-2,3-dihydro-1,2-oxasilole (2d)



2d

69 mg, 94% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.22 (m, 3H), 7.12 (d, J = 8.2 Hz, 2H), 7.11–7.03 (m, 2H), 6.90 (d, J = 8.0 Hz, 2H), 2.22 (s, 3H), 1.50–1.35 (m, 2H), 1.25 (d, J = 7.4 Hz, 6H), 1.22 (d, J = 7.5 Hz, 6H), 1.16 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.9, 137.0, 136.9, 132.2, 130.9, 128.20, 128.17, 127.8, 126.4, 124.9, 30.2, 23.6, 21.2, 17.8, 17.8, 12.2; IR (neat): ν_{max} 3027, 2943, 2866, 1609, 1503, 1463, 1319, 1180, 1082, 968, 882, 853, 826, 604 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{24}H_{33}OSi^+$ 365.2301, found 365.2309.

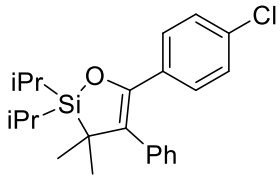
5-(4-fluorophenyl)-2,2-diisopropyl-3,3-dimethyl-4-phenyl-2,3-dihydro-1,2-oxasilole (2e)



2e

68 mg, 92% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.24 (m, 3H), 7.26–7.15 (m, 2H), 7.06 (d, J = 6.9 Hz, 2H), 6.76 (dd, J = 8.7, 8.7 Hz, 2H), 1.47–1.38 (m, 2H), 1.25 (d, J = 7.4 Hz, 6H), 1.22 (d, J = 7.5 Hz, 6H), 1.16 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.8 (d, J = 247.0 Hz), 148.0, 136.6, 131.1 (d, J = 3.4 Hz), 130.9, 129.6 (d, J = 7.9 Hz), 128.3, 126.7, 125.4, 114.4 (d, J = 21.4 Hz), 30.2, 23.6, 17.8, 12.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.48; IR (neat): ν_{max} 2944, 2866, 1604, 1507, 1463, 1310, 1230, 1081, 882, 855, 783, 710, 682, 598 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for (M + H)$^{+}$ $C_{23}H_{30}FOSi^{+}$ 369.2050, found 369.2056.

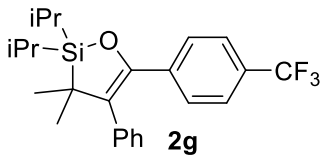
5-(4-chlorophenyl)-2,2-diisopropyl-3,3-dimethyl-4-phenyl-2,3-dihydro-1,2-oxasilole (2f)



2f

72 mg, 93% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 3H), 7.15 (d, J = 8.0 Hz, 2H), 7.11–6.97 (m, 4H), 1.47–1.38 (m, 2H), 1.30–1.19 (m, 12H), 1.16 (s, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.9, 136.4, 133.5, 132.8, 130.7, 129.1, 128.4, 127.6, 126.8, 126.4, 30.3, 23.5, 17.8, 12.2; IR (neat): ν_{max} 2944, 2866, 1609, 1485, 1463, 1224, 1092, 962, 881, 851, 831, 806, 762, 717, 699, 492 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for (M + H)$^{+}$ $C_{23}H_{30}O^{35}ClSi^{+}$ 385.1749, found 385.1759.

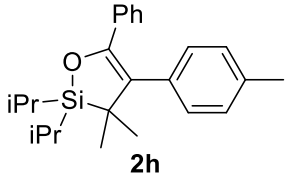
2,2-diisopropyl-3,3-dimethyl-4-phenyl-5-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1,2-oxasilole (2g)



2g

75 mg, 90% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.25 (m, 7H), 7.07 (d, J = 7.0 Hz, 2H), 1.51–1.36 (m, 2H), 1.25 (d, J = 7.6 Hz, 6H), 1.23 (d, J = 7.4 Hz, 6H), 1.18 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.6, 138.4, 136.1, 130.7, 128.8 (q, J = 32.3 Hz), 128.5, 128.1, 127.9, 127.0, 124.4 (q, J = 4.0 Hz), 124.2 (q, J = 271.4 Hz),30.5, 23.4, 17.73, 17.71, 12.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.57; IR (neat): ν_{max} 2945, 2867, 1616, 1463, 1325, 1165, 1125, 1015, 964, 882, 855, 815, 766, 712, 683 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for (M + H)$^{+}$ $C_{24}H_{30}F_3OSi^{+}$ 419.2013, found 419.2017.

2,2-diisopropyl-3,3-dimethyl-5-phenyl-4-(p-tolyl)-2,3-dihydro-1,2-oxasilole (2h)

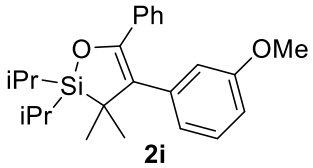


2h

69 mg, 95% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 2H), 7.23–7.06 (m, 5H), 7.00 (d, J = 7.4 Hz, 2H), 2.39 (s, 3H), 1.54–1.39 (m, 2H), 1.30 (d, J = 7.5 Hz, 6H), 1.27 (d, J = 7.5 Hz, 6H), 1.20 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.7, 136.0, 135.2, 133.6, 130.7, 129.0, 127.9, 127.4, 127.1, 125.7, 30.2, 23.6, 21.3, 17.8, 12.3; IR (neat): ν_{max} 2943, 2866, 1598, 1463,

1314, 1224, 1186, 1065, 967, 882, 817, 767, 692 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{24}H_{33}OSi^+$ 365.2301, found 365.2309.

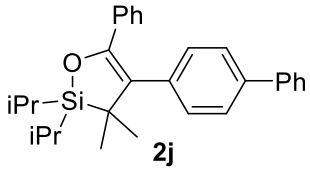
2,2-diisopropyl-4-(3-methoxyphenyl)-3,3-dimethyl-5-phenyl-2,3-dihydro-1,2-oxasilole (2i)



2i

72 mg, 95% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 2H), 7.23–7.16 (m, 1H), 7.14–7.04 (m, 3H), 6.80 (ddd, J = 8.3, 2.7, 1.0 Hz, 1H), 6.67 (d, J = 7.5 Hz, 1H), 6.64 (d, J = 2.6 Hz, 1H), 3.75 (s, 3H), 1.48–1.36 (m, 2H), 1.25 (d, J = 7.5 Hz, 6H), 1.22 (d, J = 7.5 Hz, 6H), 1.18 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 148.9, 138.3, 135.0, 129.1, 127.9, 127.5, 127.3, 125.5, 123.5, 116.6, 111.8, 55.2, 30.3, 23.6, 17.82, 17.81, 12.3; IR (neat): ν_{max} 3055, 2944, 2866, 1604, 1575, 1463, 1251, 1065, 983, 882, 847, 812 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{24}H_{33}O_2Si^+$ 381.2244, found 381.2254.

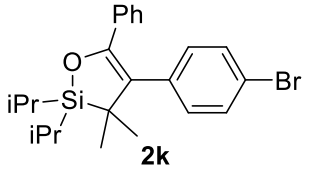
4-([1,1'-biphenyl]-4-yl)-2,2-diisopropyl-3,3-dimethyl-5-phenyl-2,3-dihydro-1,2-oxasilole (2j)



2j

80 mg, 94% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.2 Hz, 2H), 7.47 (d, J = 7.8 Hz, 2H), 7.35 (dd, J = 7.5, 7.5 Hz, 2H), 7.28–7.18 (m, 3H), 7.07 (d, J = 7.8 Hz, 2H), 7.04–6.97 (m, 3H), 1.41–1.31 (m, 2H), 1.19 (d, J = 7.5 Hz, 6H), 1.16 (d, J = 7.5 Hz, 6H), 1.13 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.1, 140.9, 139.0, 136.0, 135.0, 131.3, 128.8, 128.0, 127.5, 127.3, 127.2, 126.9, 126.8, 125.3, 30.3, 23.7, 17.8, 12.3; IR (neat): ν_{max} 2943, 2866, 1687, 1594, 1491, 1463, 1314, 1228, 1087, 1066, 962, 882, 830, 804, 765, 694 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{29}H_{35}OSi^+$ 427.2452, found 427.2458.

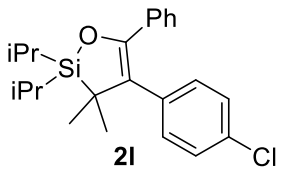
4-(4-bromophenyl)-2,2-diisopropyl-3,3-dimethyl-5-phenyl-2,3-dihydro-1,2-oxasilole (2k)



2k

82 mg, 96% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.4 Hz, 2H), 7.19–7.12 (m, 2H), 7.08–6.95 (m, 3H), 6.86 (d, J = 8.4 Hz, 2H), 1.41–1.27 (m, 2H), 1.16 (d, J = 7.3 Hz, 6H), 1.14 (d, J = 7.6 Hz, 6H), 1.07 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.6, 135.9, 134.7, 132.6, 131.4, 128.0, 127.6, 127.5, 124.4, 120.7, 30.1, 23.6, 17.80, 17.78, 12.2; IR (neat): ν_{max} 2943, 2866, 1597, 1568, 1462, 1384, 1143, 1121, 1087, 1067, 966, 881, 819, 767 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{23}H_{30}O^{79}BrSi^+$ 429.1244, found 429.1248.

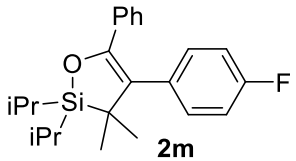
4-(4-chlorophenyl)-2,2-diisopropyl-3,3-dimethyl-5-phenyl-2,3-dihydro-1,2-oxasilole (2l)



2l

72 mg, 93% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.0 Hz, 2H), 7.29–7.22 (m, 2H), 7.19–7.10 (m, 3H), 7.03 (d, J = 8.4 Hz, 2H), 1.54–1.38 (m, 2H), 1.27 (d, J = 7.6 Hz, 6H), 1.25 (d, J = 7.3 Hz, 6H), 1.18 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.5, 135.4, 134.7, 132.5, 132.2, 128.5, 128.0, 127.6, 127.5, 124.4, 30.1, 23.6, 17.8, 17.7, 12.2; IR (neat): ν_{max} 2943, 2866, 1631, 1590, 1464, 1317, 1224, 1089, 882, 821, 767, 739, 697, 589, 482 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{23}H_{30}O^{35}ClSi^+$ 385.1749, found 385.1758.

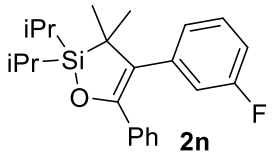
4-(4-fluorophenyl)-2,2-diisopropyl-3,3-dimethyl-5-phenyl-2,3-dihydro-1,2-oxasilole (2m)



2m

70 mg, 95% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.20 (m, 2H), 7.16–7.07 (m, 3H), 7.07–6.92 (m, 4H), 1.49–1.38 (m, 2H), 1.25 (d, J = 7.4 Hz, 6H), 1.22 (d, J = 7.5 Hz, 6H), 1.15 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.9 (d, J = 244.9 Hz), 149.4, 134.9, 132.6 (d, J = 3.6 Hz), 132.4 (d, J = 7.9 Hz), 127.9, 127.5, 127.4, 124.6, 115.2 (d, J = 21.0 Hz), 30.1, 23.6, 17.78, 17.76, 12.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.45; IR (neat): ν_{max} 3054, 2944, 2866, 1597, 1505, 1317, 1226, 1087, 1066, 968, 828, 768, 692, 602 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{23}H_{30}FOSi^+$ 369.2050, found 369.2051.

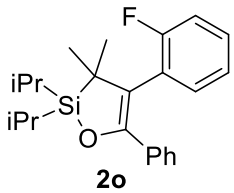
4-(3-fluorophenyl)-2,2-diisopropyl-3,3-dimethyl-5-phenyl-2,3-dihydro-1,2-oxasilole (2n)



2n

69 mg, 94% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.17 (m, 3H), 7.13–7.09 (m, 3H), 7.01–6.90 (m, 1H), 6.90–6.76 (m, 2H), 1.47–1.40 (m, 2H), 1.25 (d, J = 7.4 Hz, 6H), 1.22 (d, J = 7.5 Hz, 6H), 1.18 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.7 (d, J = 245.8 Hz), 149.6, 139.3 (d, J = 7.6 Hz), 134.7, 129.5 (d, J = 8.6 Hz), 127.9, 127.6, 127.5, 126.8 (d, J = 2.8 Hz), 124.5, 117.6 (d, J = 20.3 Hz), 113.4 (d, J = 20.8 Hz), 30.2, 23.6, 17.8, 17.7, 12.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.72; IR (neat): ν_{max} 3070, 2945, 2867, 1594, 1463, 1444, 1314, 1261, 1206, 1066, 966, 881, 842, 811, 757, 693, 691 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{23}H_{30}FOSi^+$ 369.2050, found 369.2055.

4-(2-fluorophenyl)-2,2-diisopropyl-3,3-dimethyl-5-phenyl-2,3-dihydro-1,2-oxasilole (2o)

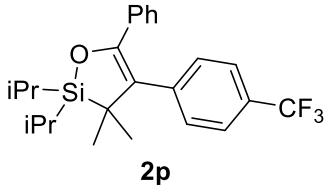


2o

67 mg, 91% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.14 (m, 3H), 7.07–6.88 (m, 6H), 1.45–1.30 (m, 2H), 1.23–1.02 (m, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.1 (d, J = 241.9 Hz), 150.4, 135.0, 133.4 (d, J = 3.5 Hz), 128.7 (d, J = 7.9 Hz), 127.6, 127.5, 127.3, 124.0 (d, J = 17.8 Hz), 123.7 (d, J = 3.7 Hz), 118.9, 115.6 (d, J = 23.3 Hz), 30.7, 24.1, 22.6, 17.7, 12.2; ^{19}F NMR (376 MHz,

$CDCl_3$) δ -113.61; IR (neat): ν_{max} 3062, 2945, 2867, 1616, 1579, 1463, 1421, 1244, 1209, 1142, 1067, 1003, 934, 855, 811, 767, 713, 693, 604 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{23}H_{30}FOSi^+$ 369.2050, found 369.2057.

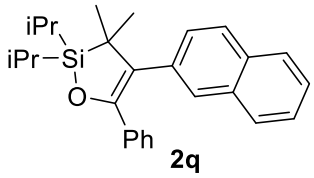
2,2-diisopropyl-3,3-dimethyl-5-phenyl-4-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1,2-oxasilole (2p)



2p

43 mg, 51% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.9 Hz, 2H), 7.27–7.14 (m, 4H), 7.14–7.10 (m, 3H), 1.48–1.39 (m, 2H), 1.26 (d, J = 7.2 Hz, 6H), 1.23 (d, J = 7.6 Hz, 6H), 1.18 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 150.1, 141.2, 134.6, 131.2, 129.6 (d, J = 34.7 Hz), 128.5, 128.1, 127.6, 125.1 (q, J = 3.7 Hz), 124.4 (q, J = 273.4 Hz), 124.3, 30.3, 23.7, 17.7, 12.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.30; IR (neat): ν_{max} 2946, 2868, 1616, 1463, 1325, 1165, 1126, 1067, 969, 830, 694, 611 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{24}H_{30}F_3OSi^+$ 419.2013, found 419.2020.

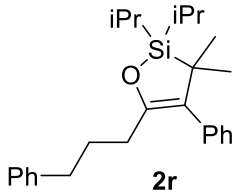
2,2-diisopropyl-3,3-dimethyl-4-(naphthalen-2-yl)-5-phenyl-2,3-dihydro-1,2-oxasilole (2q)



2q

75 mg, 93% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02–7.87 (m, 1H), 7.87–7.79 (m, 2H), 7.66 (s, 1H), 7.58–7.46 (m, 2H), 7.41–7.31 (m, 2H), 7.31–7.25 (m, 1H), 7.22–6.98 (m, 3H), 1.51–1.42 (m, 2H), 1.36 (d, J = 7.5 Hz, 6H), 1.33 (d, J = 7.5 Hz, 6H), 1.29 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.3, 135.0, 134.6, 133.6, 132.3, 129.8, 129.1, 128.01, 127.98, 127.7, 127.6, 127.3, 125.8, 125.5, 30.6, 23.7, 17.9, 12.3; IR (neat): ν_{max} 3047, 2944, 2865, 1598, 1463, 1184, 1065, 928, 882, 848, 818, 766, 746, 693, 649, 477 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{27}H_{33}OSi^+$ 401.2295, found 401.2304.

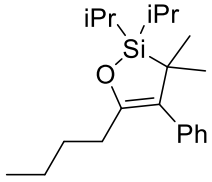
2,2-diisopropyl-3,3-dimethyl-4-phenyl-5-(3-phenylpropyl)-2,3-dihydro-1,2-oxasilole (2r)



2r

69 mg, 88% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.18 (m, 5H), 7.13 (dd, J = 7.2, 7.2 Hz, 1H), 7.09 (d, J = 7.6 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 2.56–2.41 (m, 2H), 1.99 (t, J = 7.3 Hz, 2H), 1.91–1.71 (m, 2H), 1.43–1.28 (m, 1H), 1.21 (d, J = 7.8 Hz, 6H), 1.19 (d, J = 7.2 Hz, 6H), 1.09 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.4, 142.7, 136.4, 131.2, 128.4, 128.2, 127.7, 126.2, 125.6, 123.7, 35.6, 30.0, 29.2, 29.0, 23.9, 17.9, 17.8, 12.2; IR (neat): ν_{max} 3023, 2943, 2865, 1642, 1460, 1217, 1139, 949, 882, 761, 699, 486 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{26}H_{37}OSi^+$ 393.2608, found 393.2614.

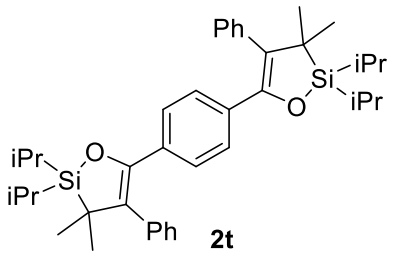
5-butyl-2,2-diisopropyl-3,3-dimethyl-4-phenyl-2,3-dihydro-1,2-oxasilole (2s)



2s

45 mg, 68% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.28–7.19 (m, 1H), 7.09–6.97 (m, 2H), 1.90 (t, J = 7.6 Hz, 2H), 1.55–1.27 (m, 6H), 1.20 (d, J = 7.6 Hz, 6H), 1.18 (d, J = 7.6 Hz, 6H), 1.08 (s, 6H), 0.79 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.9, 136.6, 131.2, 127.6, 126.1, 123.2, 29.9, 29.5, 29.0, 23.9, 22.3, 17.8, 17.7, 14.0, 12.2; IR (neat): ν_{max} 2954, 2867, 1643, 1464, 1365, 1262, 1187, 881, 826, 802, 737, 701 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{21}H_{35}OSi^+$ 331.2452, found 331.2460.

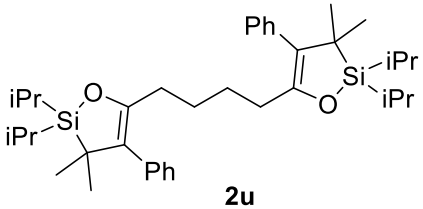
1,4-bis(2,2-diisopropyl-3,3-dimethyl-4-phenyl-2,3-dihydro-1,2-oxasilol-5-yl)benzene (2t)



2t

91 mg, 73% yield; White solid, Mp 190.7–191.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.20 (m, 6H), 7.01 (d, J = 7.0 Hz, 4H), 6.97 (s, 4H), 1.32–1.41 (m, 4H), 1.20 (d, J = 8.4 Hz, 12H), 1.18 (d, J = 8.4 Hz, 12H), 1.11 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.7, 136.8, 133.7, 130.8, 128.2, 127.0, 126.4, 125.8, 30.2, 23.5, 17.78, 17.76, 12.2; IR (KBr): ν_{max} 2942, 2867, 1613, 1456, 1220, 1142, 1085, 964, 917, 880, 838, 795, 758, 589 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{40}H_{54}O_2Si_2Na^+$ 645.3555, found 645.3550.

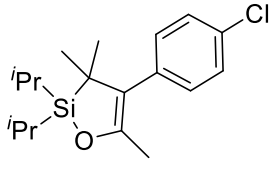
1,4-bis(2,2-diisopropyl-3,3-dimethyl-4-phenyl-2,3-dihydro-1,2-oxasilol-5-yl)butane (2u)



2u

77 mg, 64% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.17 (m, 6H), 7.09–6.90 (m, 4H), 1.90–1.74 (m, 4H), 1.42–1.27 (m, 8H), 1.18 (d, J = 4.9 Hz, 12H), 1.16 (d, J = 4.9 Hz, 12H), 1.06 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.8, 136.5, 131.2, 127.5, 126.1, 123.2, 30.1, 28.9, 26.9, 23.9, 17.8, 17.7, 12.1; IR (neat): ν_{max} 2944, 2866, 1643, 1460, 1224, 1126, 1071, 1014, 950, 882, 810, 761, 710, 700, 681 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{38}H_{58}O_2Si_2Na^+$ 625.3868, found 625.3866.

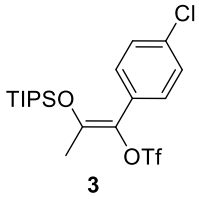
4-(4-chlorophenyl)-2,2-diisopropyl-3,3,5-trimethyl-2,3-dihydro-1,2-oxasilole (2v)



2v

36 mg, 55% yield; Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, J = 8.3 Hz, 2H), 6.89 (d, J = 8.3 Hz, 2H), 1.55 (s, 3H), 1.33–1.21 (m, 2H), 1.11 (d, J = 7.5 Hz, 6H), 1.09 (d, J = 7.5 Hz, 6H), 0.99 (s, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 149.9, 135.2, 132.3, 127.9, 122.3, 28.8, 23.8, 17.7, 17.6, 16.3, 12.1; IR (neat): ν_{max} 2944, 2866, 1649, 1464, 1377, 1220, 1140, 948, 881, 800, 685 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{18}H_{28}O^{35}ClSi^+$ 323.1592, found 323.1595.

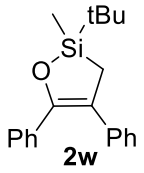
(E)-1-(4-chlorophenyl)-2-((triisopropylsilyl)oxy)prop-1-en-1-yl trifluoromethanesulfonate (3)



3

26 mg, 27% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 1H), 2.17 (s, 3H), 1.12–0.90 (m, 21H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.2, 134.0, 133.7, 130.5, 129.5, 128.2, 118.2 (q, J = 320.3 Hz), 18.7, 17.7, 13.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ -74.18; IR (neat): ν_{max} 2949, 2870, 1666, 1417, 1383, 1314, 1298, 1141, 1093, 1028, 1015, 883, 854, 748, 662 cm^{-1}; HRMS (EI-TOF) *m/z* calculated for $(M)^+$ $C_{19}H_{28}{}^{35}ClF_3O_4SSi^+$ 472.1113, found 472.1112.

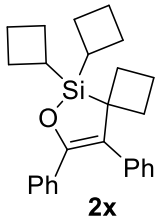
2-(tert-butyl)-2-methyl-4,5-diphenyl-2,3-dihydro-1,2-oxasilole (2w)



2w

36 mg, 58% yield; Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66–7.42 (m, 10H), 1.32 (s, 9H), 0.31 (s, 5H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 146.5, 134.8, 133.9, 132.0, 129.7, 129.6, 129.2, 128.6, 128.15, 128.13, 25.7, 18.3, 1.0, -4.0; IR (neat): ν_{max} 3060, 2920, 2859, 1654, 1470, 1419, 1266, 1206, 1142, 988, 910, 834, 784, 696, 592, 514 cm^{-1}; HRMS (APCI-TOF) *m/z* calculated for $(M + H)^+$ $C_{20}H_{25}OSi^+$ 309.1669, found 309.1675.

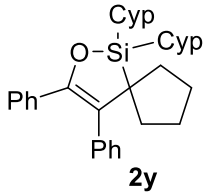
5,5-dicyclobutyl-7,8-diphenyl-6-oxa-5-silaspiro[3.4]oct-7-ene (2x)



2x

166 mg, 86% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.25 (m, 5H), 7.18–6.94 (m, 5H), 2.49–2.04 (m, 14H), 2.04–1.82 (m, 4H), 1.69–1.41 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 150.1, 137.7, 135.1, 131.3, 128.3, 127.9, 127.5, 127.2, 126.5, 123.2, 37.5, 28.1, 24.0, 23.8, 23.7, 20.2, 19.8; IR (neat): ν_{max} 3022, 2965, 2860, 1608, 1494, 1443, 1320, 1182, 1132, 1059, 906, 799, 693, 561 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{26}H_{30}OSiNa^+$ 409.1958, found 409.1960.

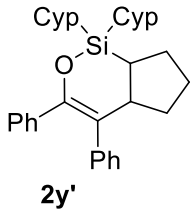
1,1-dicyclopentyl-3,4-diphenyl-2-oxa-1-silaspiro[4.4]non-3-ene (2y)



2y

114 mg, 53% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.15 (m, 5H), 7.14–7.00 (m, 5H), 2.09–1.81 (m, 6H), 1.80–1.60 (m, 8H), 1.62–1.40 (m, 12H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.9, 137.7, 135.2, 131.4, 128.2, 127.8, 127.4, 127.0, 126.5, 123.5, 42.5, 32.9, 28.3, 28.2, 27.1, 26.9, 25.5, 23.8; IR (neat): ν_{max} 2949, 2864, 1609, 1495, 1444, 1320, 1225, 1115, 1012, 898, 816, 767, 726, 694, 547 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{29}H_{37}OSi^+$ 429.2608, found 429.2612.

1,1-dicyclopentyl-3,4-diphenyl-1,4a,5,6,7,7a-hexahydrocyclopenta[c][1,2]oxasiline (2y')

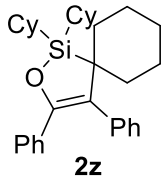


2y'

47 mg, 22% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.06 (m, 5H), 7.03 (d, J = 6.2 Hz, 5H), 3.15–3.21 (m, 1H), 2.05–1.75 (m, 7H), 1.76–1.37 (m, 16H), 1.32–1.15 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.8, 143.3, 139.2, 130.0, 129.2, 127.9, 127.1, 126.6, 125.6, 120.1, 46.6, 34.4, 28.02, 27.96, 27.9, 27.8, 27.03, 26.99, 26.8, 25.9, 24.8, 24.2, 22.9; IR (neat): ν_{max} 2920, 2848, 1601, 1237, 1139,

1066, 1008, 963, 910, 829, 747, 695, 514 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{29}H_{37}OSi^+$ 429.2608, found 429.2613.

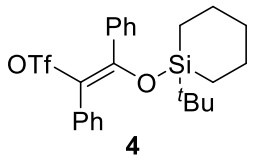
1,1-dicyclohexyl-3,4-diphenyl-2-oxa-1-silaspiro[4.5]dec-3-ene (2z)



2z

146 mg, 62% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 3H), 7.19 (dd, J = 6.8, 3.1 Hz, 2H), 7.11–7.04 (m, 5H), 2.13–1.88 (m, 6H), 1.87–1.67 (m, 10H), 1.61–1.41 (m, 4H), 1.33–1.23 (m, 12H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.6, 137.7, 135.1, 131.3, 128.1, 127.8, 127.4, 127.1, 126.5, 125.6, 41.4, 32.2, 28.4, 28.1, 27.9, 27.0, 26.3, 25.7; IR (neat): ν_{max} 2920, 2847, 1600, 1493, 1444, 1235, 1138, 1018, 975, 914, 829, 750, 695, 520 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{32}H_{43}OSi^+$ 471.3078, found 471.3070.

(E)-2-((1-(tert-butyl)silinan-1-yl)oxy)-1,2-diphenylvinyl trifluoromethanesulfonate (4)

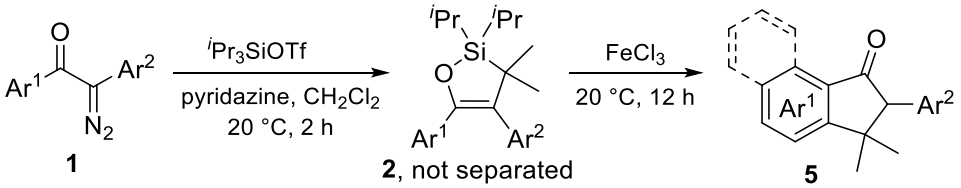


4

177 mg, 71% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63–6.55 (m, 10H), 1.81–1.62 (m, 2H), 1.61–1.39 (m, 3H), 1.23–1.07 (m, 1H), 1.00 (s, 9H), 0.74–0.34 (m, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.8, 134.7, 133.8, 132.1, 129.6, 129.2, 128.6, 128.2, 128.0, 29.4, 26.4, 24.2, 18.3, 10.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.12; IR (neat): ν_{max} 2921, 2857, 1643, 1413, 1263, 1215, 1199, 1141, 944, 793, 696, 522 cm^{-1}; HRMS (EI-TOF) *m/z* calculated for $(M)^+$ $C_{24}H_{29}F_3O_4SSi^+$ 498.1502, found 498.1510.

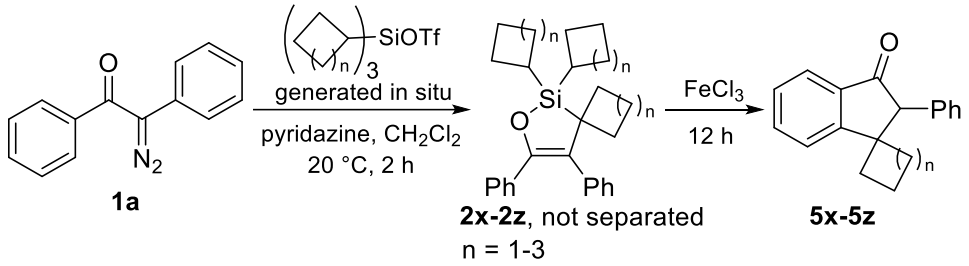
8 One-pot synthesis of multi-substituted indanones

8.1 General procedure for obtaining indanones 5a, 5b, 5d–5f, 5h–5o, and 5n



An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with pyridazine (18 mg, 0.22 mmol), CH_2Cl_2 (3.0 mL), and $^iPr_3SiOTf$ (0.22 mmol, 68 mg) under a nitrogen atmosphere. After the resulting mixture was stirred for 1 min, α-aryl-α-diazoketone (0.2 mmol) was added, and the resulting mixture was stirred at 20 °C for 2 h. Then, anhydrous $FeCl_3$ (65 mg, 0.4 mmol) was added, and the mixture was stirred under a nitrogen atmosphere for an additional 12 h. Upon completion of the reaction, as monitored by TLC, the mixture was quenched with water and extracted with ethyl acetate (3 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via silica gel column chromatography (eluent: hexane/ethyl acetate = 20:1) to afford the corresponding indanone.

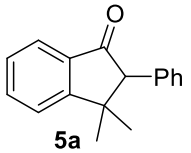
8.2 General procedure for obtaining indanones 5x–5z



A Schlenk tube equipped with the solution of silyl triflate in CH_2Cl_2 (5.0 mL) generated in situ was charged with pyridazine (50 mg, 0.6 mmol) under a nitrogen atmosphere. After the resulting mixture was stirred for 1 min, **1a** (0.5 mmol, 111 mg) was added, and the resulting mixture was stirred at 20 °C for 2 h. Then, anhydrous $FeCl_3$ (163 mg, 1.0 mmol) was added, and the mixture was stirred under a nitrogen atmosphere for an additional 12 h. Upon completion of the reaction as monitored by TLC, the mixture was quenched with water and extracted with ethyl acetate (3 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via silica gel column chromatography (eluent: hexane/ethyl acetate = 20:1) to afford the corresponding indanone.

8.3 Characterization data of the indanones

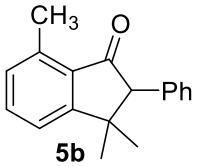
3,3-dimethyl-2-phenyl-2,3-dihydro-1H-inden-1-one (5a)



5a

36 mg, 76% yield; White solid, Mp 136.8–137.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.6 Hz, 1H), 7.75–7.62 (m, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.49–7.41 (m, 1H), 7.42–7.33 (m, 2H), 7.36–7.28 (m, 1H), 7.20–7.13 (m, 2H), 3.80 (s, 1H), 1.61 (s, 3H), 0.93 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.5, 162.3, 136.7, 135.2, 135.0, 130.1, 128.4, 127.6, 127.1, 123.9, 123.6, 67.0, 43.8, 28.6 28.5; IR (KBr): ν_{max} 2961, 2926, 1710, 1601, 1496, 1362, 1327, 1211, 886, 758, 705, 522 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{16}ONa^+$ 259.1093, found 259.1094.

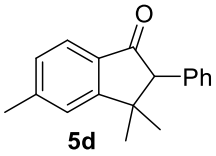
3,3,7-trimethyl-2-phenyl-2,3-dihydro-1H-inden-1-one (5b)



5b

39 mg, 77% yield; White solid, Mp 105.5–106.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 5.6, 5.6 Hz, 1H), 7.38–7.36 (m, 3H), 7.32 (d, J = 5.3 Hz, 1H), 7.23–7.09 (m, 3H), 3.77 (s, 1H), 2.72 (s, 3H), 1.58 (s, 3H), 0.93 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.1, 162.9, 138.9, 136.9, 134.3, 132.5, 130.2, 129.4, 128.3, 127.0, 120.9, 67.3, 43.1, 28.6, 28.5, 18.5; IR (KBr): ν_{max} 3023, 2962, 1705, 1590, 1478, 1318, 1210, 1034, 878, 800, 753, 704 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{18}H_{18}ONa^+$ 273.1250, found 273.1248.

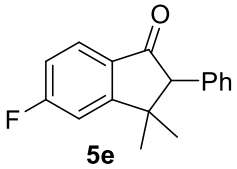
3,3,5-trimethyl-2-phenyl-2,3-dihydro-1H-inden-1-one (5d)



5d

37 mg, 73% yield; White solid, Mp 110.2–111.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.8 Hz, 1H), 7.39–7.29 (m, 3H), 7.29 (d, J = 7.1 Hz, 1H), 7.23 (d, J = 7.0 Hz, 1H), 7.12 (d, J = 6.8 Hz, 2H), 3.75 (s, 1H), 2.48 (s, 3H), 1.55 (s, 3H), 0.88 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.0, 162.8, 146.4, 137.0, 132.8, 130.1, 128.9, 128.3, 127.0, 124.0, 123.7, 67.1, 43.6, 28.7, 28.3, 22.3; IR (KBr): ν_{max} 2961, 2924, 1712, 1606, 1463, 1321, 1216, 1085, 1035, 826, 756, 710, 699, 617 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{18}H_{18}ONa^+$ 273.1250, found 273.1249.

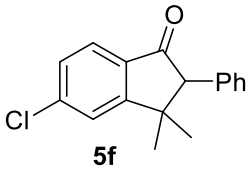
5-fluoro-3,3-dimethyl-2-phenyl-2,3-dihydro-1H-inden-1-one (5e)



5e

21 mg, 41% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, J = 8.4, 5.4 Hz, 1H), 7.42–7.35 (m, 2H), 7.35–7.29 (m, 1H), 7.20 (dd, J = 8.7, 2.3 Hz, 1H), 7.18–7.09 (m, 3H), 3.81 (s, 1H), 1.59 (s, 3H), 0.92 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.5, 167.6 (d, J = 256.4 Hz), 165.3 (d, J = 8.9 Hz), 136.4, 131.4 (d, J = 1.9 Hz), 130.1, 128.4, 127.3, 126.3 (d, J = 10.2 Hz), 115.9 (d, J = 23.7 Hz), 110.5 (d, J = 22.3 Hz), 67.1, 43.7 (d, J = 1.9 Hz), 28.5, 28.3; IR (neat): ν_{max} 2963, 2927, 1716, 1612, 1591, 1477, 1289, 1211, 1067, 867, 757, 711, 626, 532 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{15}FONa^+$ 277.0999, found 277.0991.

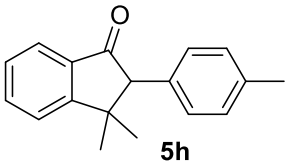
5-chloro-3,3-dimethyl-2-phenyl-2,3-dihydro-1H-inden-1-one (5f)



5f

24 mg, 45% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 6.1 Hz, 1H), 7.51 (d, J = 1.3 Hz, 1H), 7.40 (dd, J = 6.1, 1.3 Hz, 1H), 7.38–7.32 (m, 2H), 7.32–7.27 (m, 1H), 7.15–7.07 (m, 2H), 3.78 (s, 1H), 1.57 (s, 3H), 0.90 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.0, 163.7, 141.6, 136.2, 133.5, 130.1, 128.5, 128.4, 127.3, 125.1, 124.1, 67.0, 43.8, 28.4, 28.3; IR (neat): ν_{max} 2962, 2927, 1718, 1597, 1463, 1283, 1210, 1068, 861, 831, 755, 703 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{15}O^{35}ClNa^+$ 293.0704, found 293.0704.

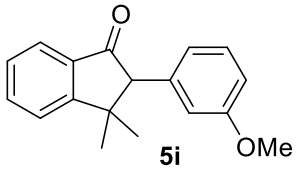
3,3-dimethyl-2-(p-tolyl)-2,3-dihydro-1H-inden-1-one (5h)



5h

38 mg, 75% yield; White solid, Mp 125.7–125.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.4 Hz, 1H), 7.65 (dd, J = 7.4, 7.4 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.41 (dd, J = 7.4, 7.4 Hz, 1H), 7.16 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 7.8 Hz, 2H), 3.73 (s, 1H), 2.34 (s, 3H), 1.56 (s, 3H), 0.90 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.7, 162.3, 136.7, 135.12, 135.06, 133.6, 130.0, 129.1, 127.6, 123.8, 123.6, 66.7, 43.7, 28.5, 21.1; IR (KBr): ν_{max} 2964, 2924, 1710, 1601, 1514, 1465, 1362, 1216, 1162, 1028, 848, 807, 769, 540 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{18}H_{18}ONa^+$ 273.1250, found 273.1248.

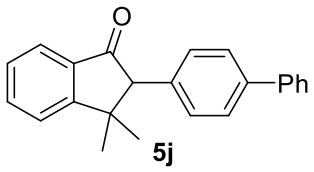
2-(3-methoxyphenyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (5i)



5i

39 mg, 74% yield; White solid, Mp 98.3–99.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.6 Hz, 1H), 7.76–7.58 (m, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.50–7.36 (m, 1H), 7.26 (dd, J = 7.9, 7.9 Hz, 1H), 6.84 (ddd, J = 8.3, 2.6, 1.0 Hz, 1H), 6.76–6.68 (m, 1H), 6.68 (dd, J = 2.1, 2.1 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 1H), 1.57 (s, 3H), 0.92 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.3, 162.3, 159.5, 138.2, 135.2, 135.0, 129.3, 127.6, 123.9, 123.7, 122.6, 116.1, 112.4, 66.9, 55.2, 43.8, 28.7, 28.3; IR (KBr): ν_{max} 3054, 2936, 1725, 1662, 1595, 1448, 1372, 1286, 1247, 1050, 783, 698, 566 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{18}H_{18}O_2Na^+$ 289.1199, found 289.1196.

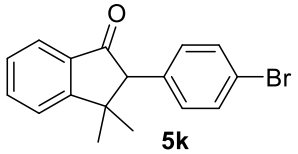
2-([1,1'-biphenyl]-4-yl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (5j)



5j

33 mg, 53% yield; White solid, Mp 139.7–141.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.6 Hz, 1H), 7.71 (td, J = 7.5, 1.3 Hz, 1H), 7.67–7.61 (m, 4H), 7.59 (d, J = 7.7 Hz, 1H), 7.53–7.42 (m, 3H), 7.38 (dd, J = 7.4, 7.4 Hz, 1H), 7.26 (d, J = 8.2 Hz, 2H), 3.86 (s, 1H), 1.65 (s, 3H), 1.00 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.4, 162.3, 140.9, 140.0, 135.8, 135.3, 135.0, 130.6, 128.8, 127.7, 127.3, 127.2, 127.1, 123.9, 123.7, 66.8, 43.9, 28.6, 28.5; IR (KBr): ν_{max} 3028, 2960, 1715, 1603, 1470, 1385, 1302, 1211, 1087, 1007, 851, 762, 698 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{23}H_{20}ONa^+$ 335.1406, found 335.1405.

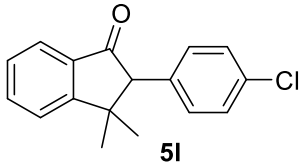
2-(4-bromophenyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (5k)



5k

43 mg, 68% yield; White solid, Mp 119.4–120.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.6 Hz, 1H), 7.73–7.62 (m, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.43 (dd, J = 7.4, 7.4 Hz, 1H), 7.02 (d, J = 8.3 Hz, 2H), 3.73 (s, 1H), 1.57 (s, 3H), 0.89 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.8, 162.0, 135.6, 135.4, 134.8, 131.8, 131.6, 127.8, 123.9, 123.6, 121.3, 66.4, 43.7, 28.5, 28.4; IR (KBr): ν_{max} 2962, 1707, 1601, 1488, 1469, 1456, 1324, 1211, 1010, 843, 801, 768 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{15}O^{79}BrNa^+$ 337.0198, found 337.0200.

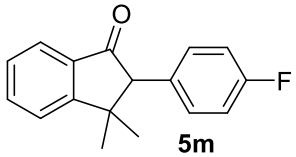
2-(4-chlorophenyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (5l)



5l

41 mg, 75% yield; White solid, Mp 122.8–123.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.7 Hz, 1H), 7.67 (dd, J = 7.5, 7.5 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.43 (dd, J = 7.4, 7.4 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.3 Hz, 2H), 3.75 (s, 1H), 1.57 (s, 3H), 0.89 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.8, 162.0, 135.3, 135.1, 134.8, 133.2, 131.4, 128.6, 127.8, 123.9, 123.6, 66.3, 43.8, 28.5, 28.4; IR (KBr): ν_{max} 2961, 2919, 1715, 1600, 1492, 1323, 1208, 1162, 1015, 885, 847, 806, 771, 707, 525 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{15}O^{35}ClNa^+$ 293.0704, found 293.0697.

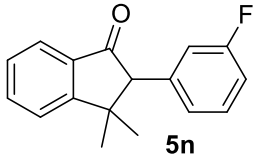
2-(4-fluorophenyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (5m)



5m

36 mg, 70% yield; White solid, Mp 125.3–126.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, J = 7.6 Hz, 1H), 7.73–7.63 (m, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.42 (dd, J = 7.4, 7.4 Hz, 1H), 7.18–7.07 (m, 2H), 7.04 (dd, J = 8.7, 8.7 Hz, 2H), 3.76 (s, 1H), 1.57 (s, 3H), 0.88 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 205.1, 162.1 (d, J = 245.9 Hz), 162.0, 135.3, 134.8, 132.3 (d, J = 3.3 Hz), 131.6 (d, J = 7.9 Hz), 127.7, 123.9, 123.6, 115.3 (d, J = 21.3 Hz), 66.2, 43.7, 28.5, 28.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -115.51; IR (KBr): ν_{max} 2966, 2927, 1716, 1602, 1509, 1466, 1363, 1301, 1225, 1162, 1011, 887, 821, 797, 772, 540 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{15}FONa^+$ 277.0999, found 277.1001.

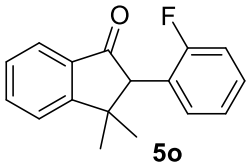
2-(3-fluorophenyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (5n)



5n

36 mg, 71% yield; White solid, Mp 108.2–109.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.7 Hz, 1H), 7.70 (dd, J = 7.5, 7.5 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.46 (dd, J = 7.5, 7.5 Hz, 1H), 7.39–7.29 (m, 1H), 7.08–6.98 (m, 1H), 6.95 (d, J = 7.7 Hz, 1H), 6.88 (d, J = 9.9 Hz, 1H), 3.79 (s, 1H), 1.61 (s, 3H), 0.94 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.6, 162.8 (d, J = 245.3 Hz), 162.0, 139.0 (d, J = 7.5 Hz), 135.4, 134.8, 129.8 (d, J = 8.3 Hz), 127.8, 125.9 (d, J = 2.8 Hz), 124.0, 123.6, 117.0 (d, J = 21.5 Hz), 114.1 (d, J = 21.0 Hz), 66.5 (d, J = 1.8 Hz), 43.8, 28.5, 28.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.13; IR (KBr): ν_{max} 2962, 2927, 1716, 1604, 1586, 1492, 1456, 1324, 1229, 1212, 1089, 758, 630 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{15}FONa^+$ 277.0999, found 277.0998.

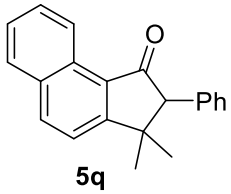
2-(2-fluorophenyl)-3,3-dimethyl-2,3-dihydro-1H-inden-1-one (5o)



5o

37 mg, 72% yield; White solid, Mp 89.7–90.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.7 Hz, 1H), 7.73–7.62 (m, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.48–7.39 (m, 1H), 7.35–7.22 (m, 1H), 7.17–7.04 (m, 3H), 4.02 (s, 1H), 1.60 (s, 3H), 0.98 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 204.6, 162.6, 161.6 (d, J = 245.4 Hz), 135.3, 134.7, 132.0, 129.0 (d, J = 8.3 Hz), 127.7, 124.3 (d, J = 15.4 Hz), 124.1 (d, J = 3.4 Hz), 123.9, 123.7, 115.6 (d, J = 22.6 Hz), 60.7, 43.8, 29.1, 27.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.40; IR (KBr): ν_{max} 2962, 2926, 1715, 1615, 1604, 1588, 1488, 1366, 1324, 1245, 1087, 944, 881, 795, 754, 700, 521 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{15}FONa^+$ 277.0999, found 277.0996.

3,3-dimethyl-2-phenyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (5q)

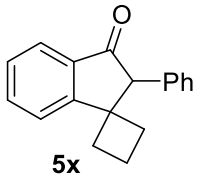


5q

32 mg, 55% yield; White solid, Mp 129.6–130.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.75–7.66 (m, 1H), 7.64–7.54 (m, 2H), 7.39–7.26 (m, 3H), 7.18 (d, J = 7.4 Hz, 2H), 3.90 (s, 1H), 1.63 (s, 3H), 0.97 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.9, 164.9, 137.3, 136.3, 132.7, 130.2, 129.3, 129.2, 128.8, 128.4, 128.1, 127.0, 126.7, 124.6, 120.9,

67.3, 43.4, 28.8, 27.9; IR (KBr): ν_{max} 3024, 2961, 1694, 1571, 1512, 1376, 1178, 1098, 884, 838, 767, 750, 700 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{21}H_{18}ONa^+$ 309.1250, found 309.1247.

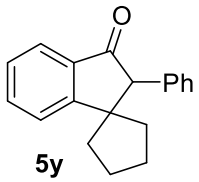
2'-phenylspiro[cyclobutane-1,1'-inden]-3'(2'H)-one (5x)



5x

52 mg, 42% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.7 Hz, 1H), 7.81–7.65 (m, 2H), 7.42 (dd, J = 7.4, 7.4 Hz, 1H), 7.37–7.23 (m, 3H), 7.03 (d, J = 7.7 Hz, 2H), 3.83 (s, 1H), 2.60–2.43 (m, 2H), 2.20–2.06 (m, 2H), 2.04–1.91 (m, 1H), 1.89–1.75 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 205.6, 161.8, 138.1, 135.7, 135.3, 129.4, 128.6, 127.7, 127.1, 123.8, 123.7, 66.5, 49.7, 36.3, 31.2, 16.4; IR (neat): ν_{max} 3064, 2930, 1712, 1603, 1495, 1463, 1325, 1284, 1157, 1013, 755, 700, 518 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{18}H_{16}ONa^+$ 271.1093, found 271.1095.

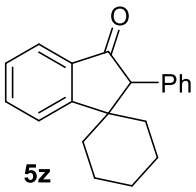
2'-phenylspiro[cyclopentane-1,1'-inden]-3'(2'H)-one (5y)



5y

66 mg, 50% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.6 Hz, 1H), 7.71–7.61 (m, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.47–7.36 (m, 1H), 7.34–7.22 (m, 3H), 7.04 (dd, J = 7.9, 1.7 Hz, 2H), 3.76 (s, 1H), 2.14–1.96 (m, 2H), 1.98–1.83 (m, 1H), 1.86–1.59 (m, 4H), 1.36–1.25 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 206.1, 162.3, 138.1, 135.9, 135.3, 129.8, 128.4, 127.5, 127.1, 124.0, 123.7, 66.5, 55.3, 43.4, 36.3, 25.3, 24.8; IR (neat): ν_{max} 2922, 1714, 1601, 1501, 1448, 1321, 1287, 1157, 1052, 760, 698 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{19}H_{18}ONa^+$ 285.1250, found 285.1247.

2'-phenylspiro[cyclohexane-1,1'-inden]-3'(2'H)-one (5z)

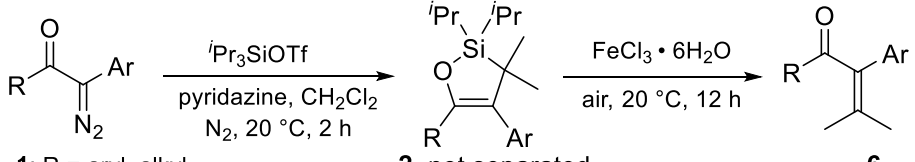


5z

64 mg, 46% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.6 Hz, 1H), 7.73–7.61 (m, 2H), 7.45 (dd, J = 7.3, 7.3 Hz, 1H), 7.27 (d, J = 7.1 Hz, 3H), 7.05 (d, J = 6.0 Hz, 2H), 3.83 (s, 1H), 1.83–1.56 (m, 8H), 1.42–1.29 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 206.5, 163.8, 138.2, 135.7, 135.0, 129.9, 128.3, 127.7, 127.0, 124.4, 124.2, 65.1, 47.4, 42.4, 32.2, 25.2, 24.1, 21.8; IR (neat): ν_{max} 2927, 2850, 1713, 1602, 1494, 1452, 1288, 1264, 1053, 910, 758, 703, 522 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{20}H_{20}ONa^+$ 299.1406, found 299.1401.

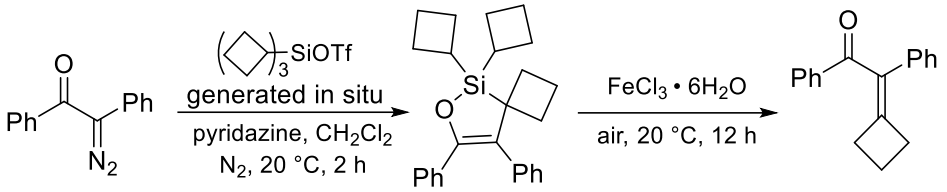
9 One-pot synthesis of multi-substituted *α,β*-unsaturated ketones

9.1 General procedure for synthesis of *α,β*-unsaturated ketones



1: R = aryl, alkyl **2**, not separated **6**

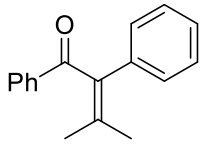
An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with pyridazine (18 mg, 0.22 mmol), CH_2Cl_2 (3 mL), $^iPr_3SiOTf$ (0.22 mmol, 68 mg) under a nitrogen atmosphere. After the resulting mixture was stirred for 1 min, *α*-aryl-*α*-diazoketone (0.2 mmol) was added, and the resulting mixture was stirred at 20 °C for 2 h. Then, $FeCl_3·6H_2O$ (108 mg, 0.4 mmol) was added, and the mixture was stirred under air for an additional 12 h. Upon completion of the reaction as monitored by TLC, the mixture was quenched with water and extracted with ethyl acetate (3 mL × 3). The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via silica gel column chromatography (eluent: hexane/ethyl acetate = 50:1) to afford the corresponding *α,β*-unsaturated ketone. It is worth noting that compound **6t** was obtained using bis-cyclic silyl enol ether **2t** as the starting material directly.



A Schlenk tube equipped with the solution of tricyclobutylsilyl triflate in CH_2Cl_2 (5.0 mL) generated in situ was charged with pyridazine (50 mg, 0.6 mmol) under a nitrogen atmosphere. After the resulting mixture was stirred for 1 min, **1a** (0.5 mmol, 111 mg) was added, and the resulting mixture was stirred at 20 °C for 2 h. Then, $FeCl_3·6H_2O$ (270 mg, 1.0 mmol) was added, and the mixture was stirred under a nitrogen atmosphere for an additional 12 h. Upon completion of the reaction as monitored by TLC, the mixture was quenched with water and extracted with ethyl acetate (3 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via silica gel column chromatography (eluent: hexane/ethyl acetate = 50:1) to afford compound **6x**.

9.2 Characterization data of the *α,β*-unsaturated carbon

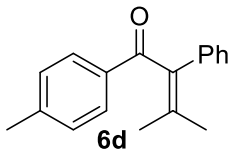
3-methyl-1,2-diphenylbut-2-en-1-one (6a)



6a

30 mg, 63% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.97 (d, *J* = 8.2 Hz, 2H), 7.54–7.45 (m, 1H), 7.41 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.35–7.25 (m, 4H), 7.25–7.14 (m, 1H), 1.88 (s, 3H), 1.78 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* 198.9, 137.1, 136.9, 136.7, 135.4, 133.1, 129.8, 129.3, 128.6, 128.4, 127.1, 22.6, 21.3; IR (neat): ν_{max} 3059, 2916, 1662, 1595, 1448, 1314, 1229, 1173, 1018, 853, 761, 700, 626, 503 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{16}ONa^+$ 259.1093, found 259.1094.

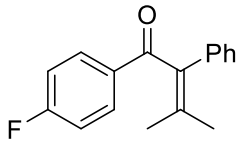
3-methyl-2-phenyl-1-(p-tolyl)but-2-en-1-one (6d)



6d

33mg, 66% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 6.1 Hz, 2H), 7.39–7.30 (m, 4H), 7.24 (d, J = 6.2 Hz, 3H), 2.40 (s, 4H), 1.90 (s, 4H), 1.80 (s, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.6, 144.0, 137.3, 136.9, 134.8, 134.5, 129.9, 129.3, 129.2, 128.3, 127.1, 22.5, 21.7, 21.3; IR (neat): ν_{max} 2917, 1732, 1661, 1604, 1442, 1270, 1175, 1016, 859, 786, 767, 701, 607, 507 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{18}H_{18}ONa^+$ 273.1250, found 273.1248.

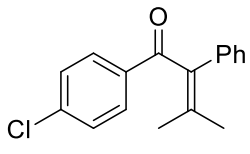
1-(4-fluorophenyl)-3-methyl-2-phenylbut-2-en-1-one (6e)



6e

40 mg, 79% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–7.86 (m, 2H), 7.38–7.25 (m, 4H), 7.26–7.18 (m, 1H), 7.14–7.00 (m, 2H), 1.88 (s, 3H), 1.78 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.3, 165.8 (d, J = 255.2 Hz), 137.0, 136.5, 135.7, 133.3, 132.4 (d, J = 9.5 Hz), 129.2, 128.4, 127.3, 115.8 (d, J = 22.0 Hz), 22.5, 21.3; IR (neat): ν_{max} 2917, 1663, 1595, 1503, 1295, 1231, 1151, 1020, 863, 844, 769, 702, 605, 512 cm^{-1}; ^{19}F NMR (377 MHz, $CDCl_3$) δ -105.07; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{15}FONa^+$ 277.0999, found 277.1001.

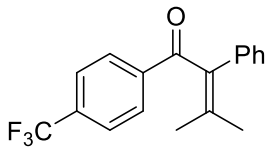
1-(4-chlorophenyl)-3-methyl-2-phenylbut-2-en-1-one (6f)



6f

45 mg, 83% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.34–7.26 (m, 4H), 7.25–7.18 (m, 1H), 1.88 (s, 3H), 1.78 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.5, 139.5, 136.9, 136.4, 136.2, 135.3, 131.1, 129.2, 129.0, 128.5, 127.3, 22.6, 21.4; IR (neat): ν_{max} 3055, 2914, 1666, 1586, 1570, 1442, 1226, 1169, 1084, 1012, 855, 836, 768, 627, 503 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{17}H_{16}{}^{35}ClO^+$ 271.0884, found 271.0885.

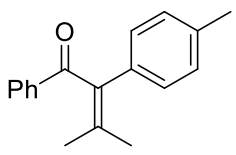
3-methyl-2-phenyl-1-(4-(trifluoromethyl)phenyl)but-2-en-1-one (6g)



6g

44 mg, 72% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–7.98 (m, 2H), 7.66 (d, J = 8.7 Hz, 2H), 7.38–7.19 (m, 5H), 1.91 (s, 3H), 1.81 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.5, 139.7, 137.3, 136.6, 136.3, 134.2 (q, J = 32.7 Hz), 129.9, 129.3, 128.5, 127.4, 125.7 (q, J = 3.8 Hz), 123.6 (q, J = 272.7 Hz), 22.6, 21.5; IR (neat): ν_{max} 3056, 2916, 1672, 1546, 1408, 1325, 1130, 1065, 1014, 859, 772, 700 cm^{-1}; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.12; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{18}H_{15}F_3ONa^+$ 327.0967, found 327.0971.

3-methyl-1-phenyl-2-(p-tolyl)but-2-en-1-one (6h)

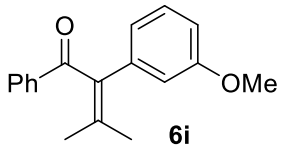


6h

34 mg, 67% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.92 (m, 2H), 7.53–7.44 (m, 1H), 7.45–7.35 (m, 2H), 7.19 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 2.29 (s, 3H), 1.88 (s, 3H), 1.77 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 199.1, 136.9, 136.8, 136.6, 135.0, 134.1, 133.0, 129.8, 129.11, 129.10, 128.6,

22.5, 21.3, 21.1; IR (neat): ν_{max} 2919, 1710, 1662, 1596, 1509, 1448, 1315, 1229, 1016, 857, 818, 702, 584, 508 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{18}H_{18}ONa^+$ 273.1250, found 273.1248.

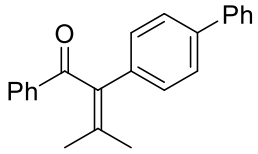
2-(3-methoxyphenyl)-3-methyl-1-phenylbut-2-en-1-one (6i)



6i

39 mg, 73% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 5.6 Hz, 2H), 7.53 (dd, J = 5.5, 5.5 Hz, 1H), 7.44 (dd, J = 5.7, 5.7 Hz, 2H), 7.31–7.20 (m, 1H), 6.92 (d, J = 5.7 Hz, 1H), 6.90–6.87 (m, 1H), 6.79 (dd, J = 6.2, 2.0 Hz, 1H), 3.79 (s, 3H), 1.92 (s, 3H), 1.80 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.8, 159.5, 138.4, 136.9, 136.6, 135.5, 133.1, 129.7, 129.3, 128.6, 121.8, 114.9, 112.7, 55.2, 22.5, 21.4; IR (neat): ν_{max} 3054, 2936, 1725, 1662, 1595, 1286, 1247, 1173, 1032, 925, 817, 783, 699, 641, 567 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{18}H_{18}O_2Na^+$ 289.1199, found 289.1201.

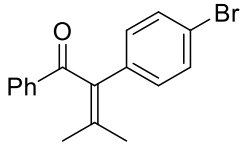
2-([1,1'-biphenyl]-4-yl)-3-methyl-1-phenylbut-2-en-1-one (6j)



6j

34 mg, 55% yield; White solid, Mp 101.5–102.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08–8.01 (m, 2H), 7.62–7.50 (m, 5H), 7.51–7.39 (m, 6H), 7.39–7.30 (m, 1H), 1.97 (s, 3H), 1.84 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.9, 140.6, 139.9, 137.0, 136.4, 136.1, 135.6, 133.2, 129.8, 129.6, 128.8, 128.7, 127.3, 127.1, 127.0, 22.6, 21.4; IR (KBr): ν_{max} 3058, 2914, 1662, 1578, 1448, 1315, 1230, 1015, 837, 790, 765, 734, 697 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{23}H_{20}ONa^+$ 335.1406, found 335.1408.

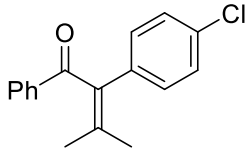
2-(4-bromophenyl)-3-methyl-1-phenylbut-2-en-1-one (6k)



6k

43 mg, 68% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03–7.85 (m, 2H), 7.56–7.49 (m, 1H), 7.47–7.32 (m, 4H), 7.18 (d, J = 8.4 Hz, 2H), 1.86 (s, 3H), 1.77 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.4, 136.7, 136.3, 136.1, 135.7, 133.3, 131.6, 130.9, 129.7, 128.7, 121.3, 22.6, 21.3; IR (neat): ν_{max} 2914, 1662, 1595, 1486, 1448, 1313, 1288, 1229, 1072, 1019, 859, 823, 788, 696, 517 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{17}H_{16}{}^{79}BrO^+$ 315.0379, found 315.0385.

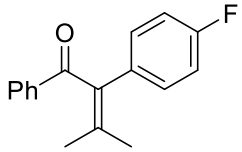
2-(4-chlorophenyl)-3-methyl-1-phenylbut-2-en-1-one (6l)



6l

40 mg, 74% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98–7.91 (m, 2H), 7.58–7.48 (m, 1H), 7.47–7.38 (m, 2H), 7.31–7.20 (m, 4H), 1.87 (s, 3H), 1.77 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.5, 136.8, 136.3, 135.6, 133.3, 133.1, 130.6, 129.7, 128.7, 128.6, 22.6, 21.3; IR (neat): ν_{max} 3059, 2927, 1763, 1667, 1586, 1399, 1271, 1170, 1092, 1013, 836, 701 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + H)^+$ $C_{17}H_{16}{}^{35}ClO^+$ 271.0884, found 271.0890.

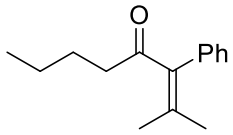
2-(4-fluorophenyl)-3-methyl-1-phenylbut-2-en-1-one (6m)



6m

28 mg, 56% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 5.3 Hz, 2H), 7.56–7.48 (m, 1H), 7.47–7.37 (m, 2H), 7.33–7.22 (m, 2H), 6.99 (dd, J = 6.6, 6.6 Hz, 2H), 1.86 (s, 3H), 1.77 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.8, 161.9 (d, J = 246.7 Hz), 136.8, 135.9, 135.6, 133.2, 133.1 (d, J = 3.5 Hz), 130.9 (d, J = 8.0 Hz), 129.7, 128.7, 115.3 (d, J = 21.4 Hz), 22.5, 21.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.93; IR (neat): ν_{max} 3055, 2916, 1662, 1596, 1505, 1448, 1314, 1226, 1157, 1020, 865, 834, 780, 701, 582, 520 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{17}H_{15}FONa^+$ 277.0999, found 277.0992.

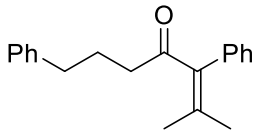
2-methyl-3-phenyloct-2-en-4-one (6r)



6r

32 mg, 75% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.33 (m, 2H), 7.32–7.27 (m, 1H), 7.22–7.09 (m, 2H), 2.25 (t, J = 5.5 Hz, 2H), 2.00 (s, 3H), 1.66 (s, 3H), 1.55–1.41 (m, 2H), 1.28–1.10 (m, 2H), 0.80 (t, J = 5.5 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.9, 140.9, 139.1, 138.5, 129.6, 128.5, 127.2, 77.2, 42.3, 26.1, 23.0, 22.3, 13.8; IR (neat): ν_{max} 3021, 2931, 1684, 1617, 1491, 1442, 1405, 1160, 1027, 883, 755, 702, 561 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{15}H_{20}ONa^+$ 239.1406, found 239.1411.

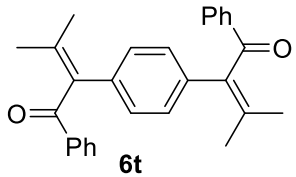
2-methyl-3,7-diphenylhept-2-en-4-one (6s)



6s

37 mg, 67% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, J = 8.1, 6.3 Hz, 2H), 7.32–7.26 (m, 1H), 7.26–7.18 (m, 2H), 7.18–7.10 (m, 3H), 7.06 (d, J = 7.5 Hz, 2H), 2.49 (dd, J = 8.7, 6.7 Hz, 2H), 2.28 (t, J = 7.2 Hz, 2H), 2.01 (s, 3H), 1.86–1.78 (m, 2H), 1.65 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 205.2, 141.9, 141.3, 139.0, 138.5, 129.6, 128.6, 128.4, 128.3, 127.2, 125.8, 41.9, 35.1, 25.7, 23.1, 22.3; IR (neat): ν_{max} 3060, 3025, 2931, 1682, 1604, 1493, 1442, 1370, 1177, 1071, 1027, 757, 701, 560, 493 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{20}H_{22}ONa^+$ 301.1563, found 301.1565.

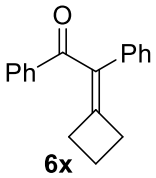
2,2'-(1,4-phenylene)bis(3-methyl-1-phenylbut-2-en-1-one) (6t)



6t

The title product was obtained using bis-cyclic silyl enol ether **2t** as starting material directly. 42 mg, 53% yield; White solid, Mp 190.2–191.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 4H), 7.31–7.24 (m, 8H), 7.24–7.16 (m, 2H), 1.87 (s, 6H), 1.76 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.1, 140.1, 136.7, 136.5, 129.8, 129.3, 128.51, 128.47, 127.3, 22.6, 21.5; IR (KBr): ν_{max} 1919, 1654, 1497, 1400, 1362, 1228, 1014, 863, 821, 775, 735, 621, 600 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{28}H_{26}O_2Na^+$ 417.1825, found 417.1817.

2-cyclobutylidene-1,2-diphenylethan-1-one (6x)



6x

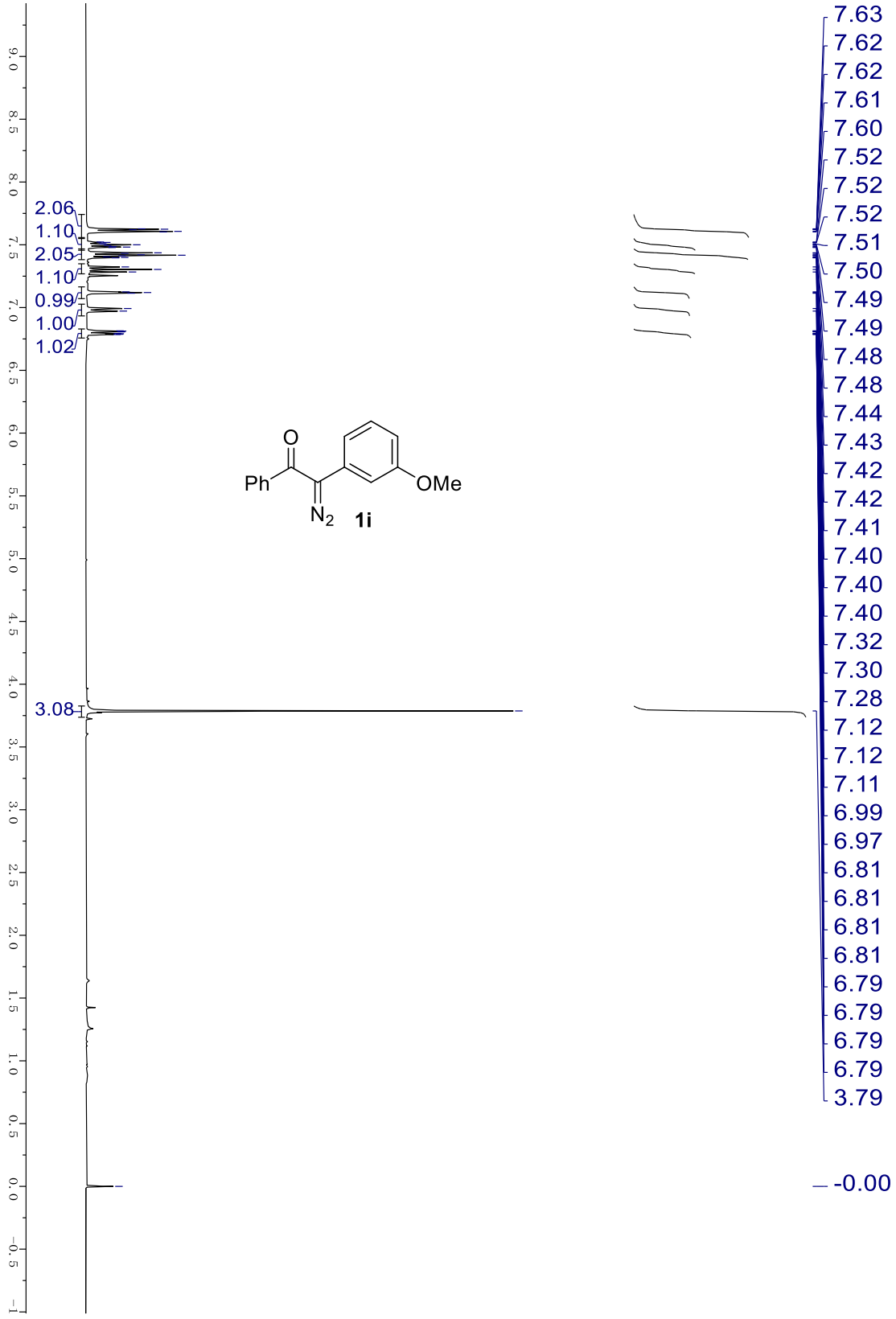
78 mg, 47% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.1 Hz, 2H), 7.54–7.47 (m, 1H), 7.41 (dd, J = 8.3, 6.9 Hz, 2H), 7.36–7.26 (m, 4H), 7.26–7.18 (m, 1H), 3.08 (t, J = 7.3 Hz, 2H), 2.79 (t, J = 7.2 Hz, 2H), 2.14–2.06 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.9, 151.2, 138.1, 136.5, 133.1, 132.6, 129.5, 128.42, 128.40, 127.8, 126.9, 32.9, 32.5, 17.6; IR (neat): ν_{max} 3080, 2955, 1665, 1596, 1495, 1446, 1317, 1239, 1174, 1074, 1023, 844, 762, 698, 625 cm^{-1}; HRMS (ESI-TOF) *m/z* calculated for $(M + Na)^+$ $C_{18}H_{16}ONa^+$ 271.1093, found 271.1096.

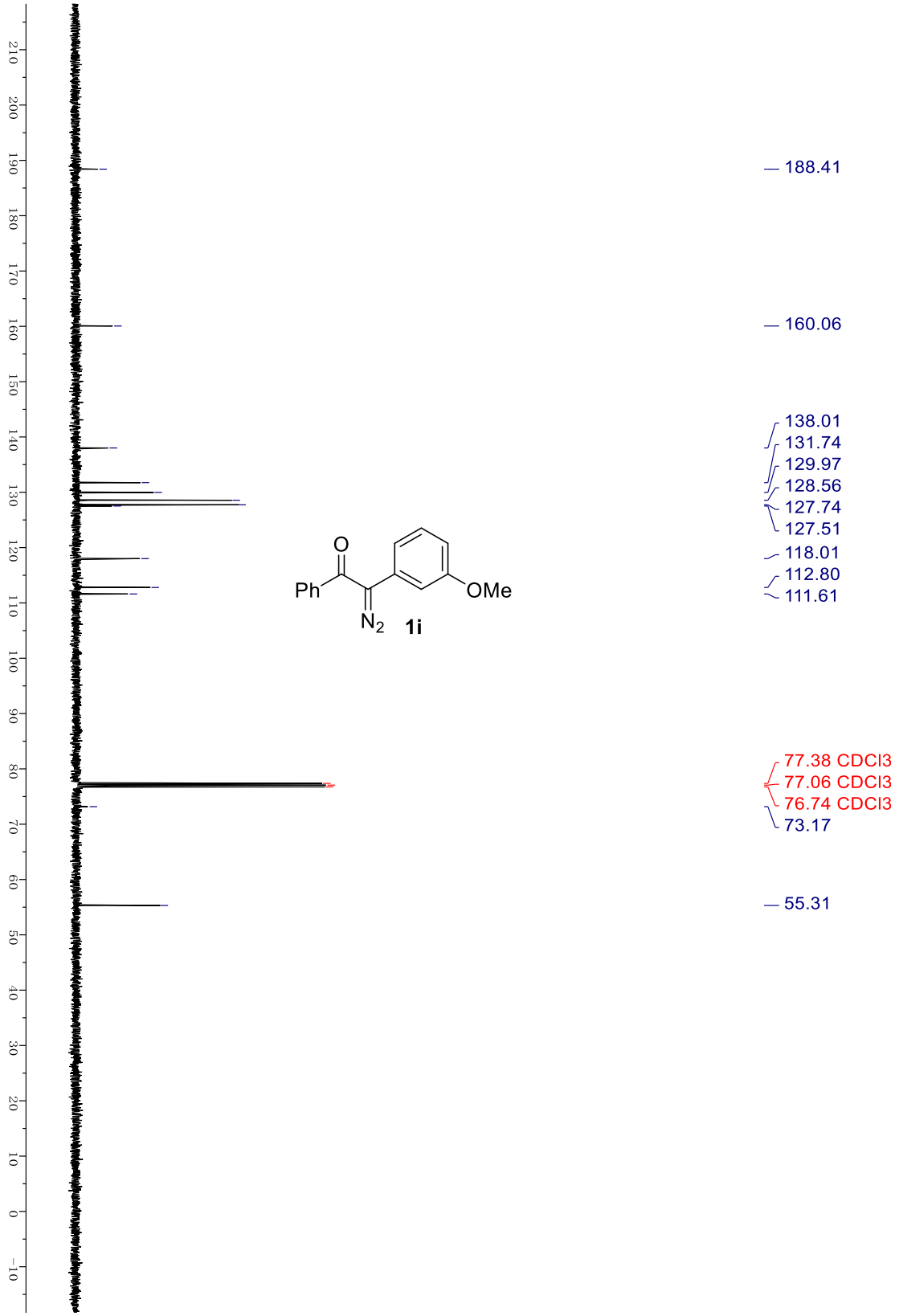
10 References

1. S. Darses, G. Michaud and J.-P. Genêt, *Eur. J. Org. Chem.*, **1999**, 1875.
2. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**
3. (a) H. Bel Abed, O. Mammoliti, O. Bande, G. Van Lommen and P. Herdewijn, *J. Org. Chem.*, **2013**, *78*, 7845. (b) B. Xu, S.-F. Zhu, X.-D. Zuo, Z.-C. Zhang and Q.-L. Zhou, **2014**, *53*, 3913. (c) D. Chen, X. Zhang, W.-Y. Qi, B. Xu and M.-H. Xu, *J. Am. Chem. Soc.*, **2015**, *137*, 5268. (d) J. Zhang, W. Chen, D. Huang, X. Zeng, X. Wang and Y. Hu, *J. Org. Chem.*, **2017**, *82*, 9171. (e) M. He, N. Chen, J. Wang and S. Peng, *Org. Lett.*, **2019**, *21*, 5167. (f) X.-S. Liu, M. Li, K. Dong, S. Peng and L. Liu, *Org. Lett.*, **2022**, *24*, 2175.
4. R. Shishido, M. Uesugi, R. Takahashi, T. Mita, T. Ishiyama, K. Kubota and H. Ito, *J. Am. Chem. Soc.*, **2020**, *142*, 14125.
5. M. Cianfanelli, G. Olivo, M. Milan, R. J. M. Klein Gebbink, X. Ribas, M. Bietti and M. Costas, *J. Am. Chem. Soc.*, **2020**, *142*, 1584.
6. M. P. Doyle and C. T. West, *J. Org. Chem.*, **1975**, *40*, 3821.
7. (a) W. H. Nebergall and O. H. Johnson, *J. Am. Chem. Soc.*, **1949**, *71*, 4022. (b) S. Masaoka, T. Banno and M. Ishikawa, *J. Organomet. Chem.*, **2006**, *691*, 174.
8. A. V. Belyakov, Y. Sigolaev, S. A. Shlykov, S. Ó. Wallevik, N. R. Jonsdottir, R. Bjornsson, S. Jonsdottir, Á. Kvaran, T. Kern, K. Hassler and I. Arnason, *Struct. Chem.*, **2015**, *26*, 445.
9. F. Ye, S. Qu, L. Zhou, C. Peng, C. Wang, J. Cheng, M. L. Hossain, Y. Liu, Y. Zhang, Z.-X. Wang and J. Wang, *J. Am. Chem. Soc.*, **2015**, *137*, 4435.
10. W. Jugelt and L. Berseck, *Tetrahedron*, **1970**, *26*, 5557.

11 Copies of NMR spectra

11.1 NMR spectra of diazoketones and silanes

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OMe
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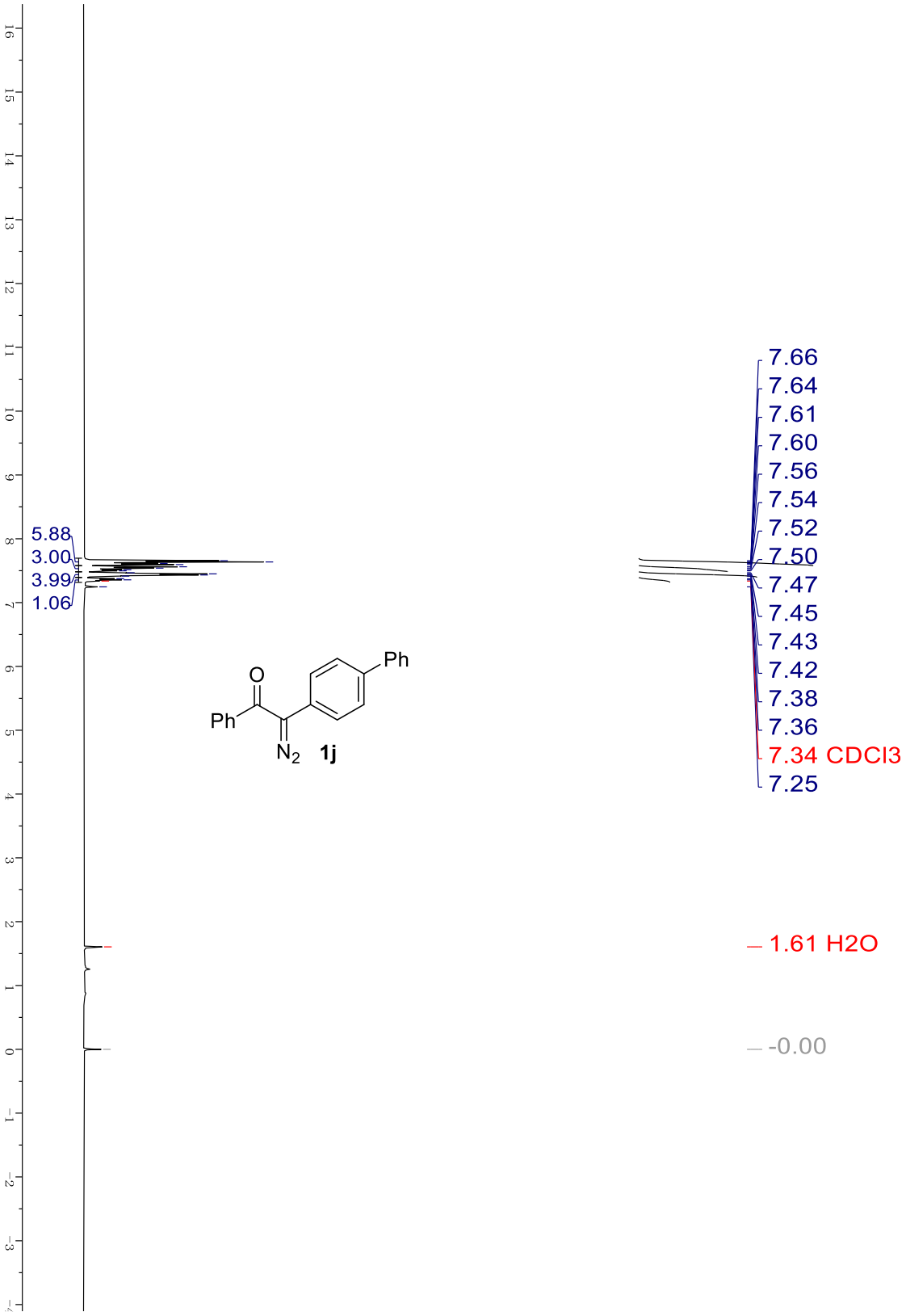
1i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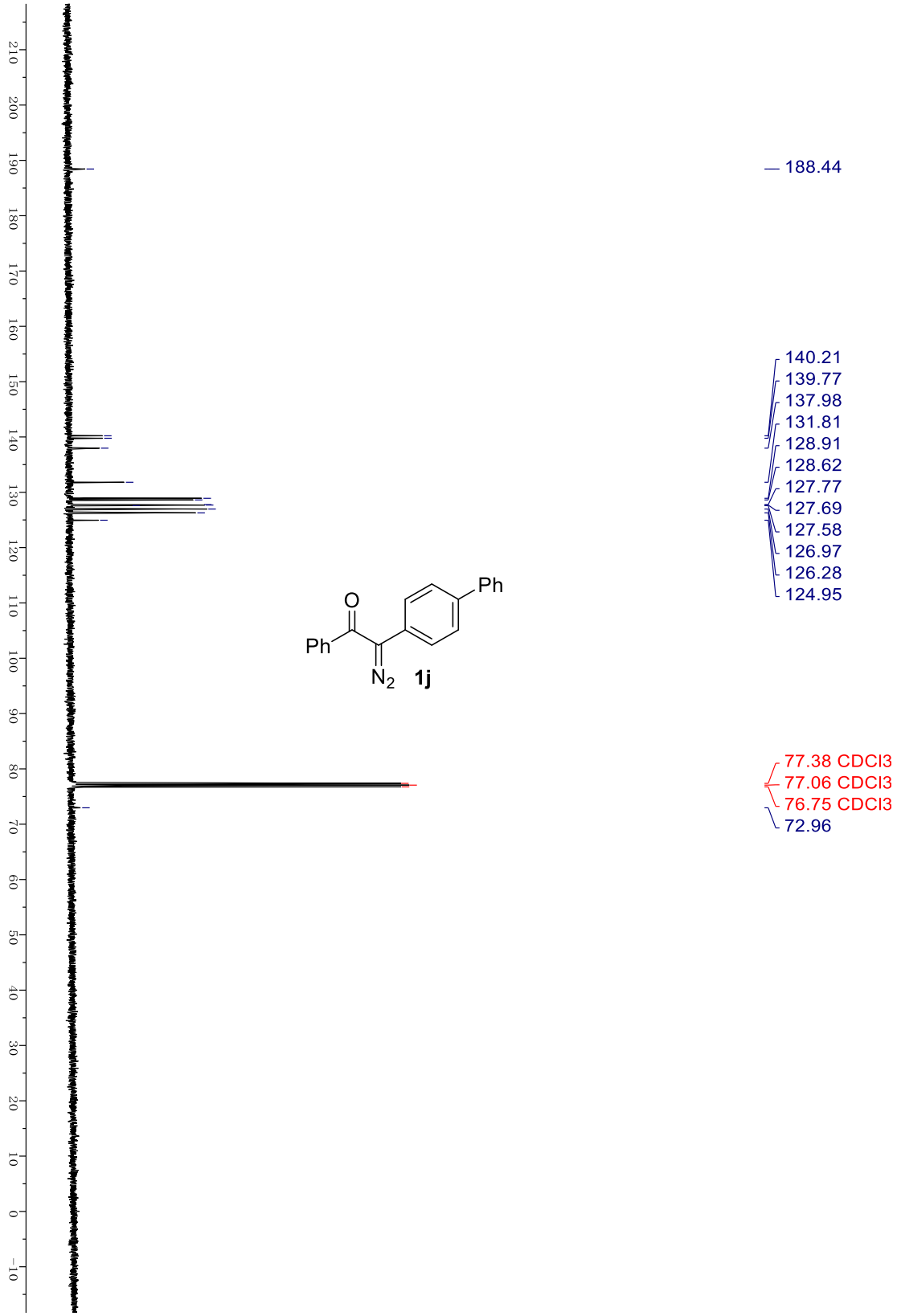
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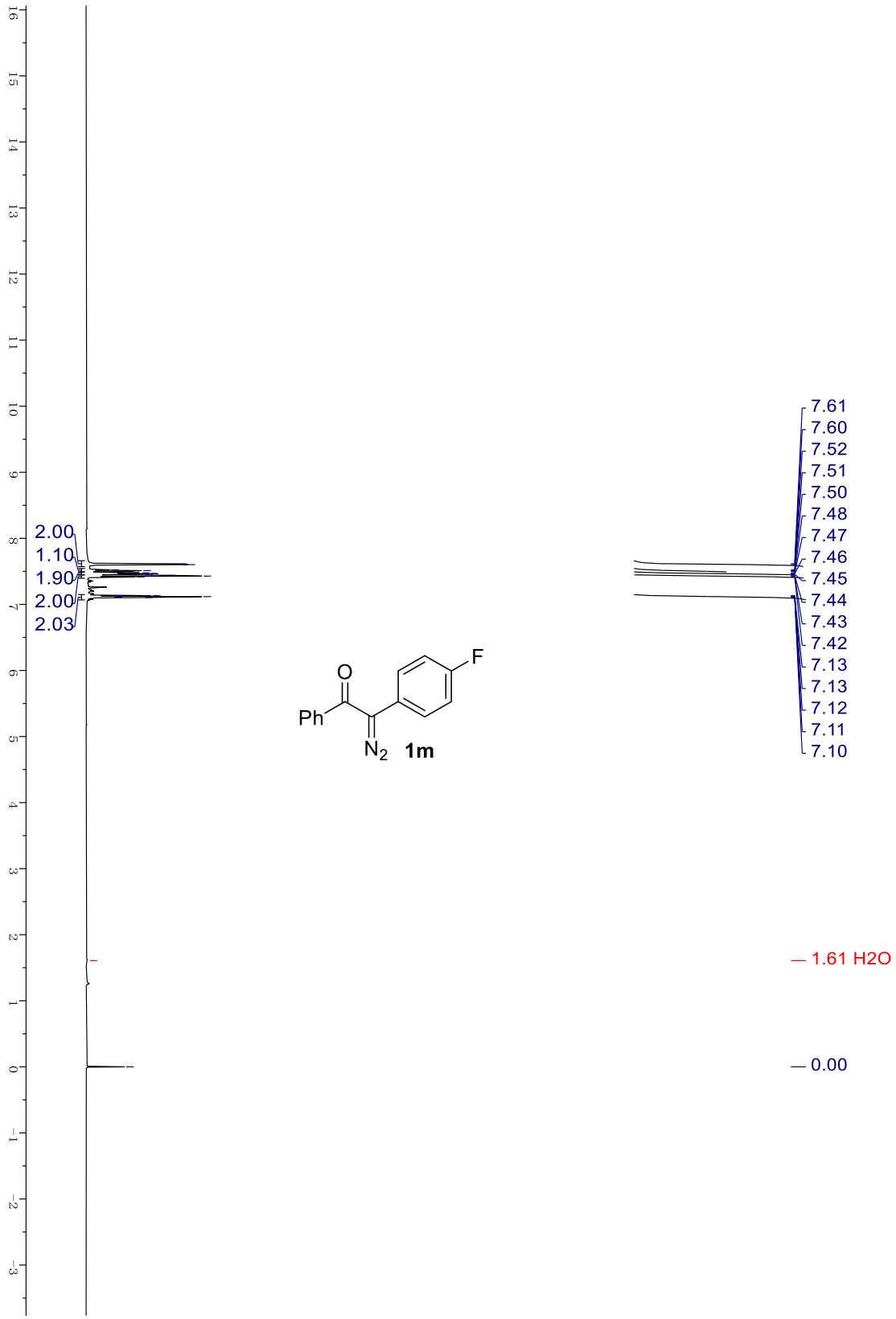
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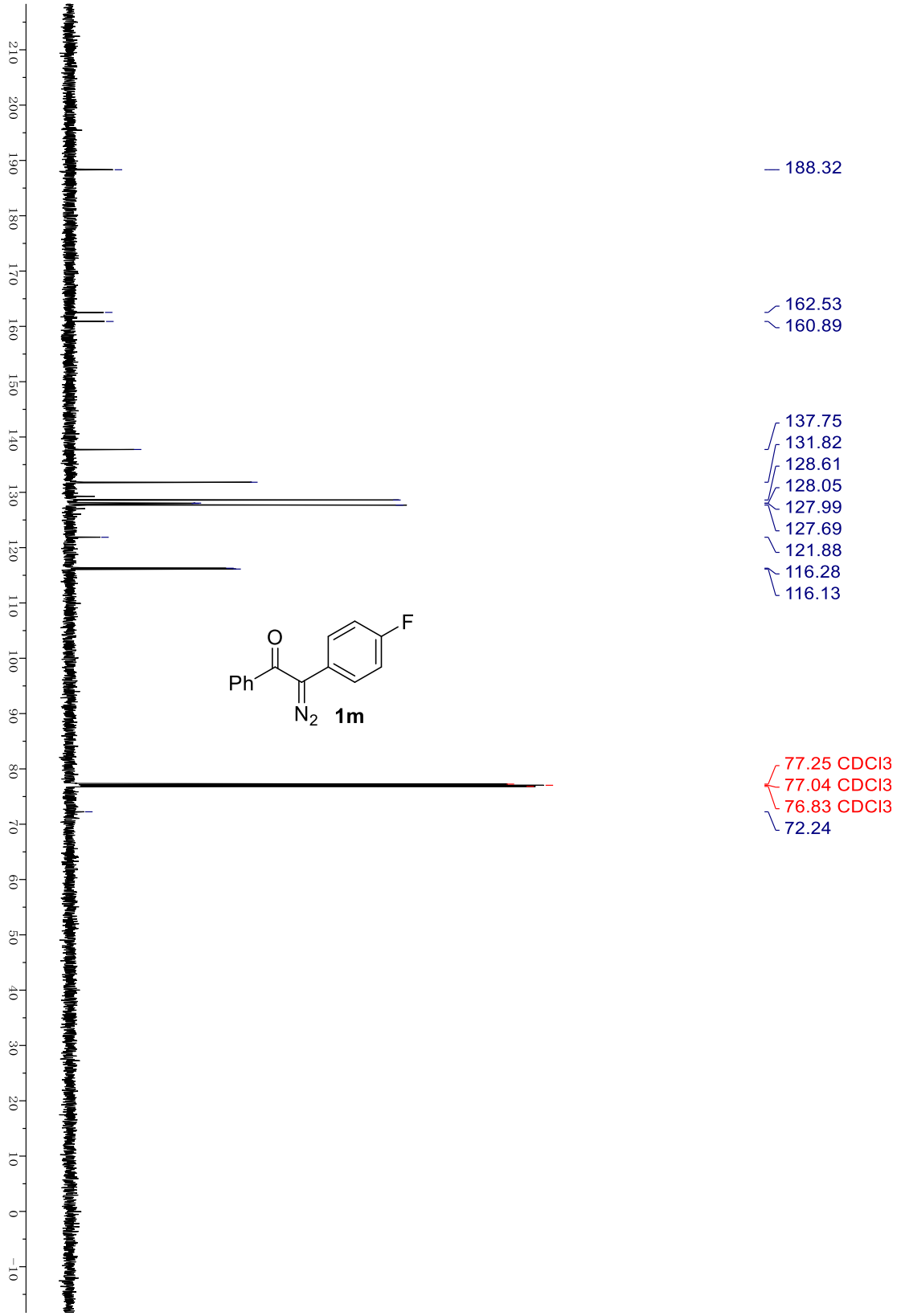
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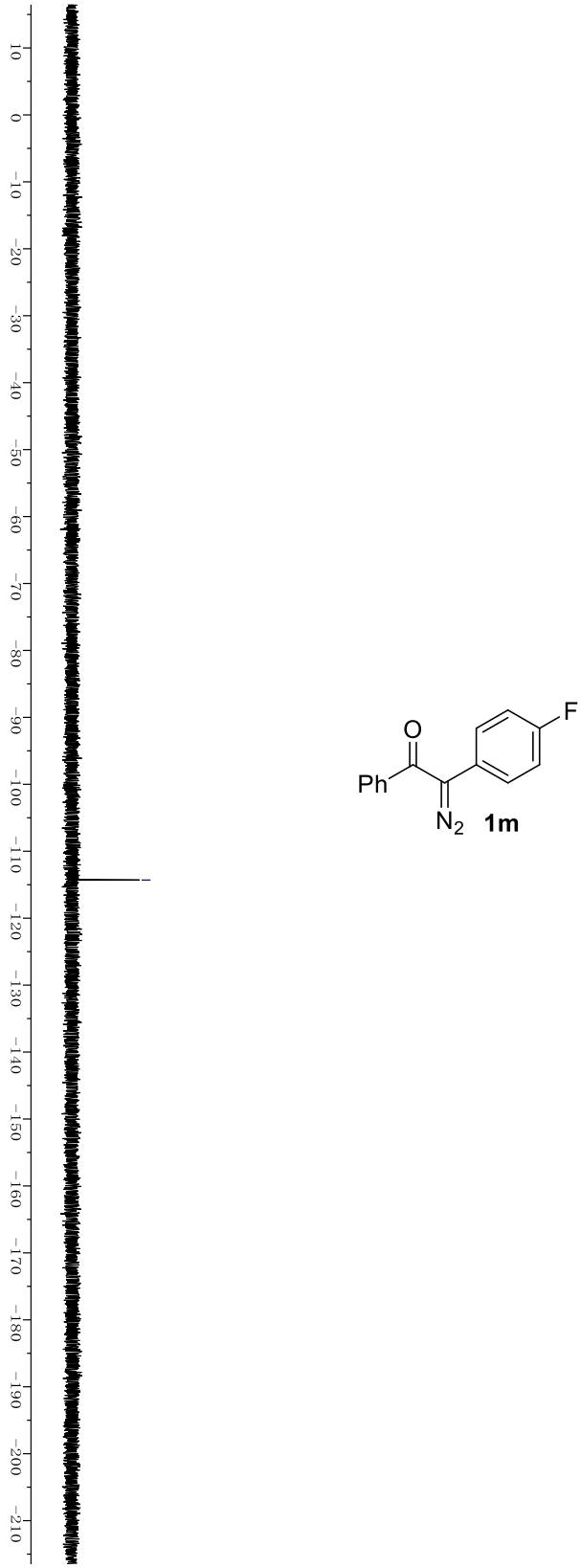
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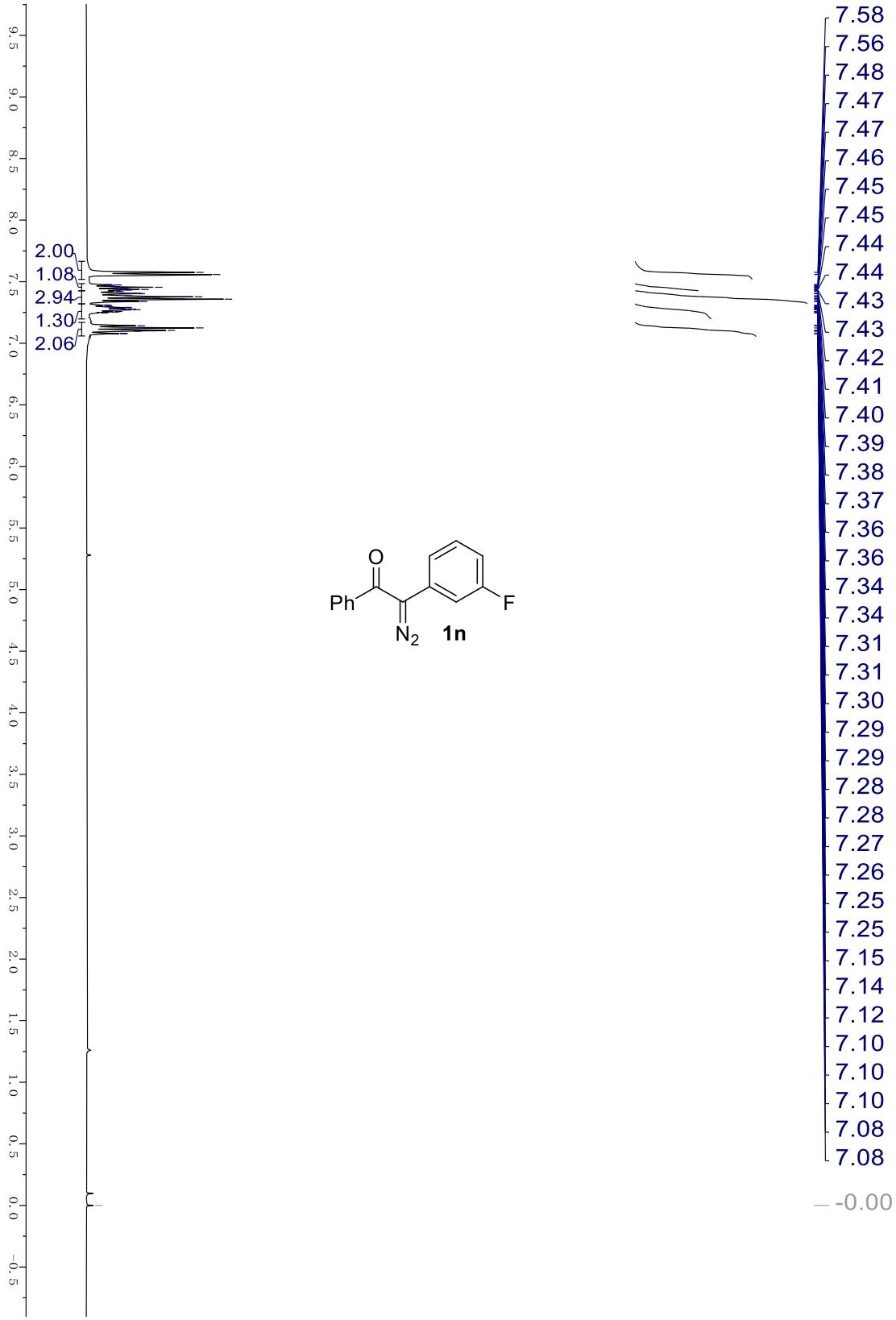
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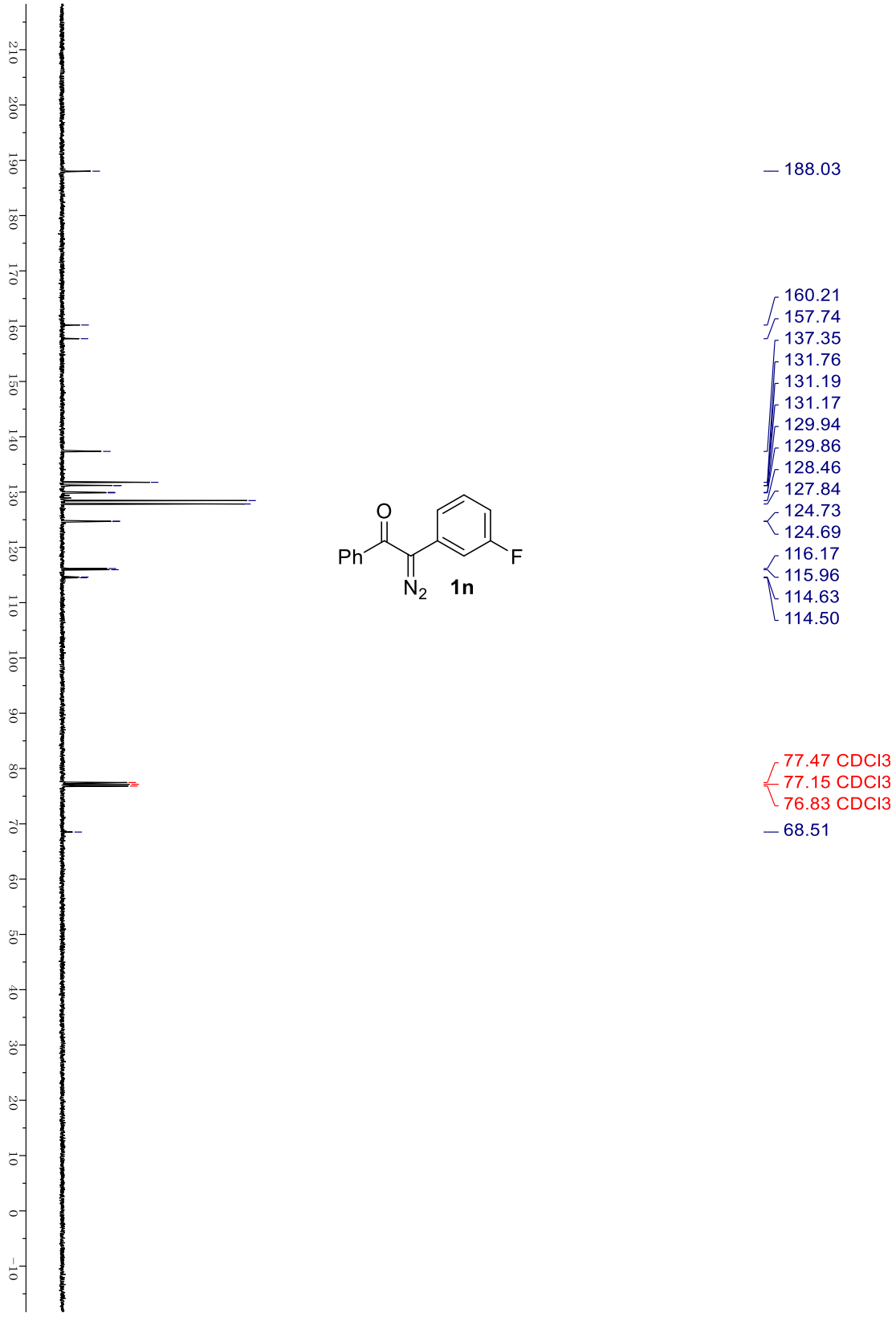
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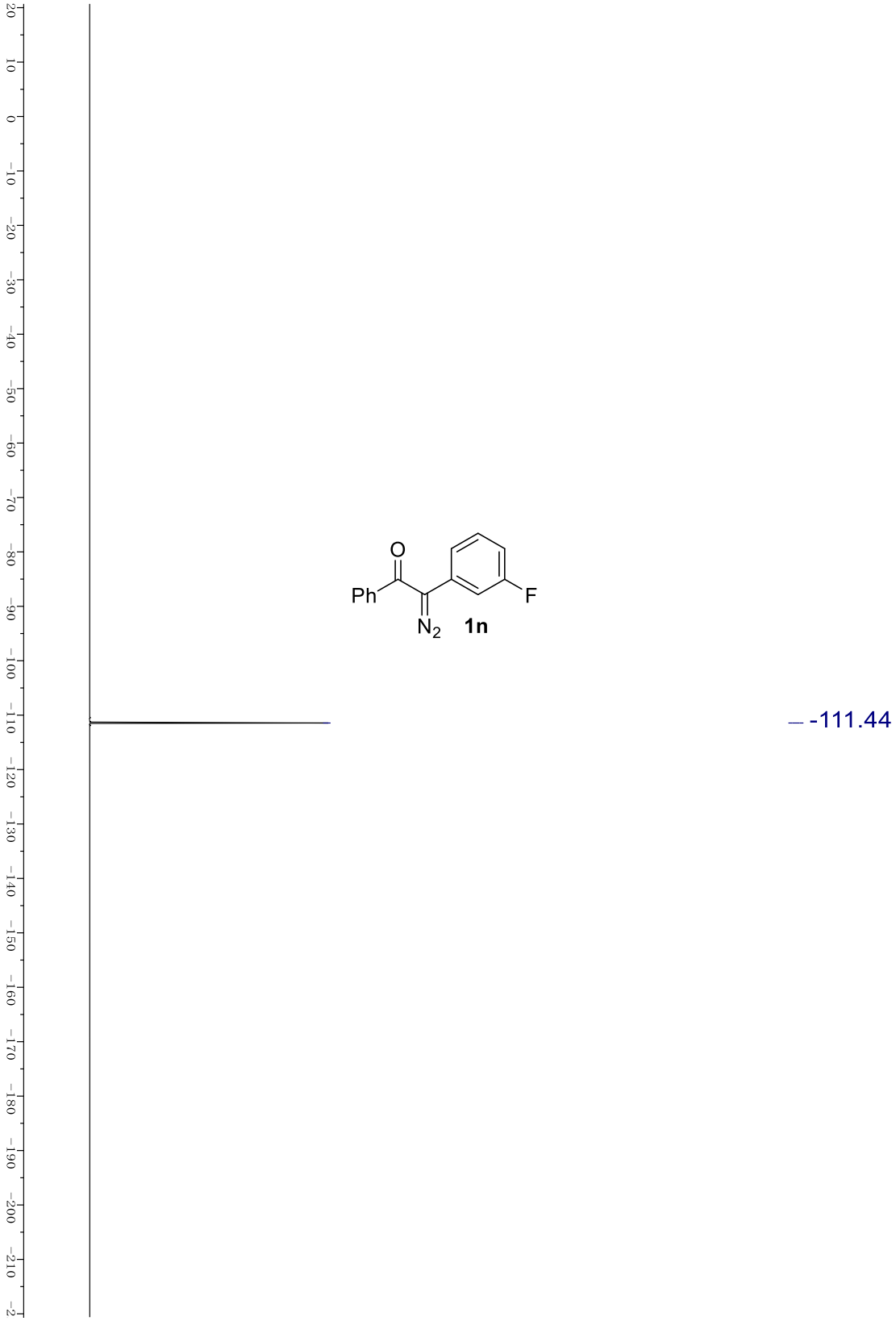
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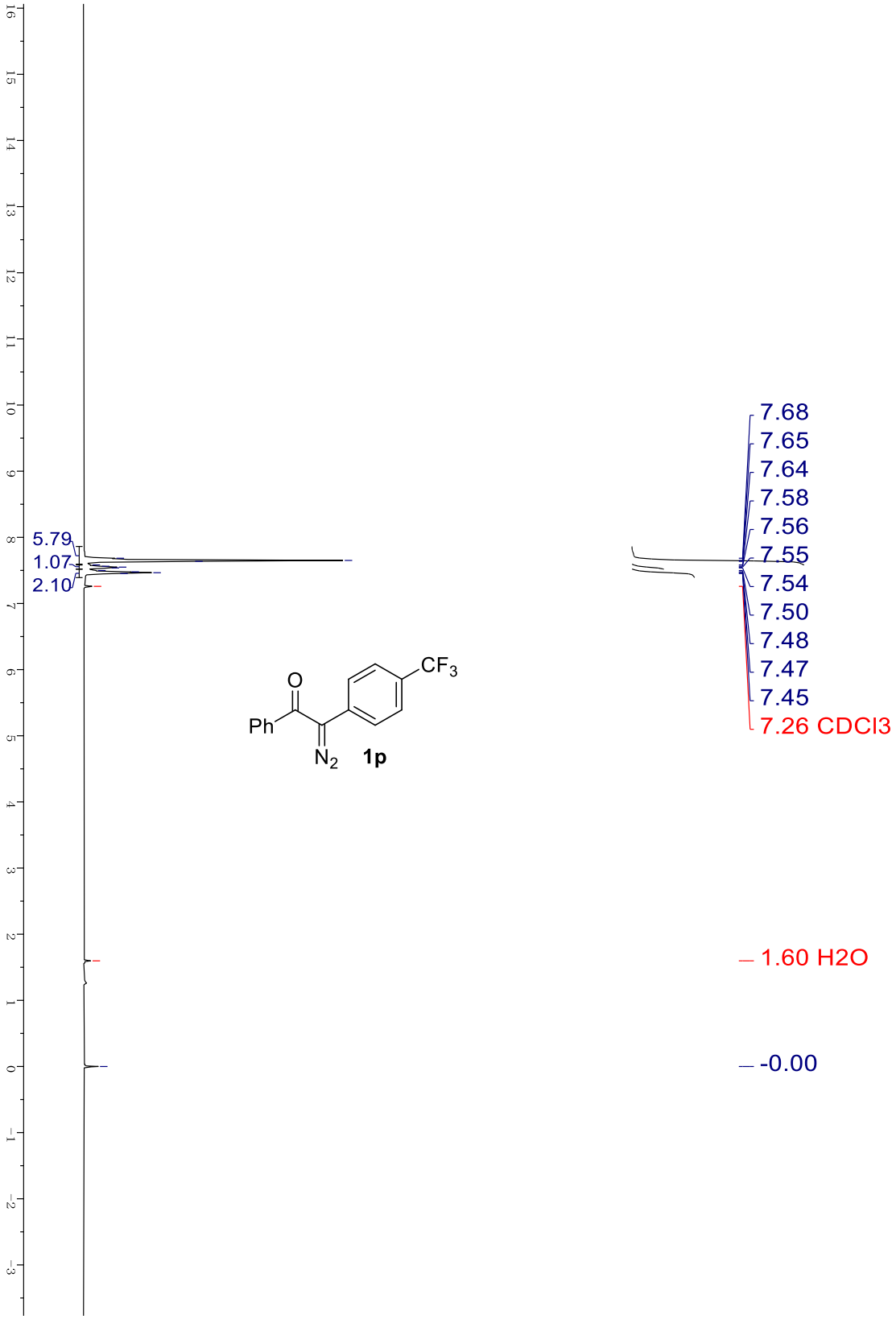
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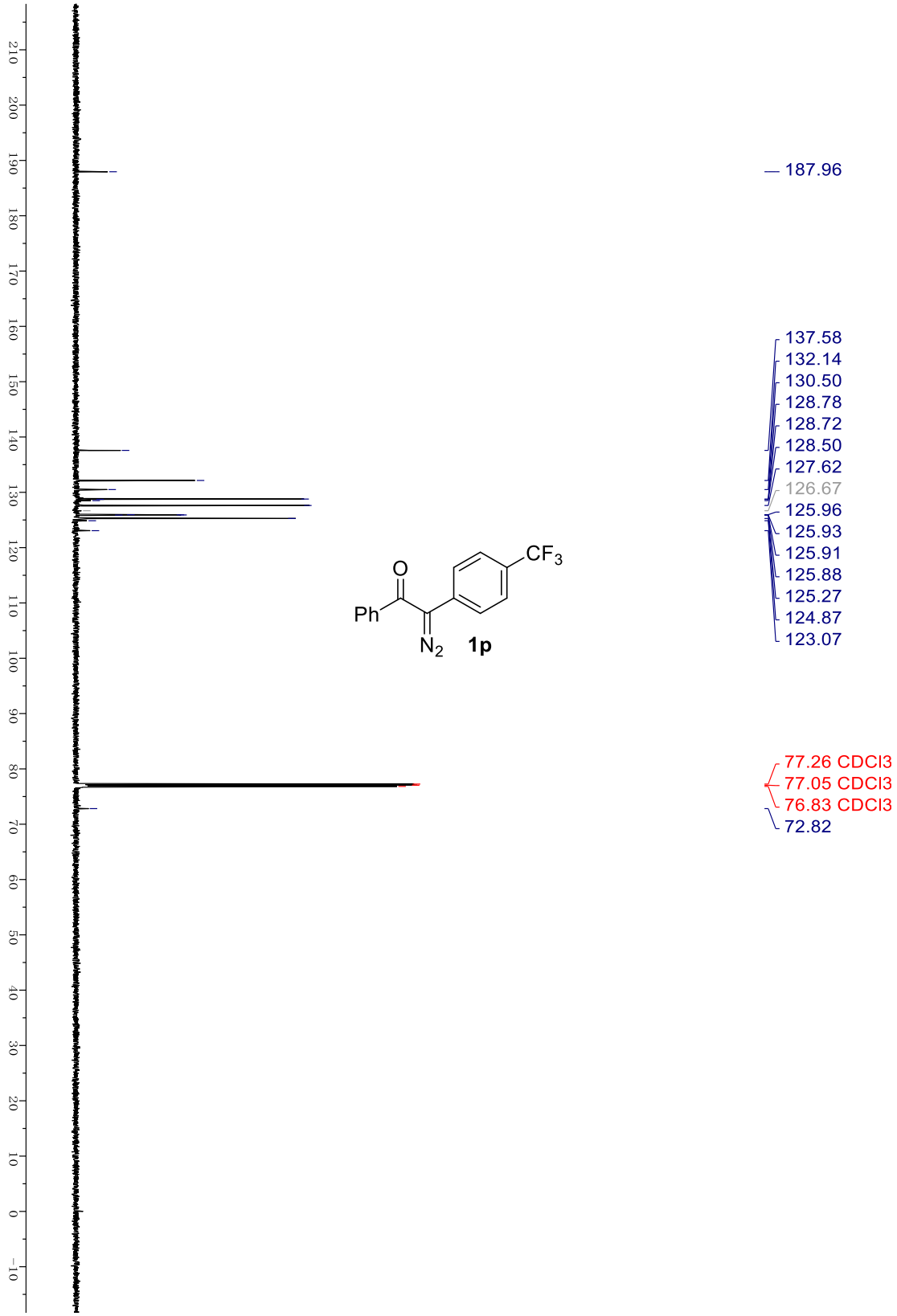
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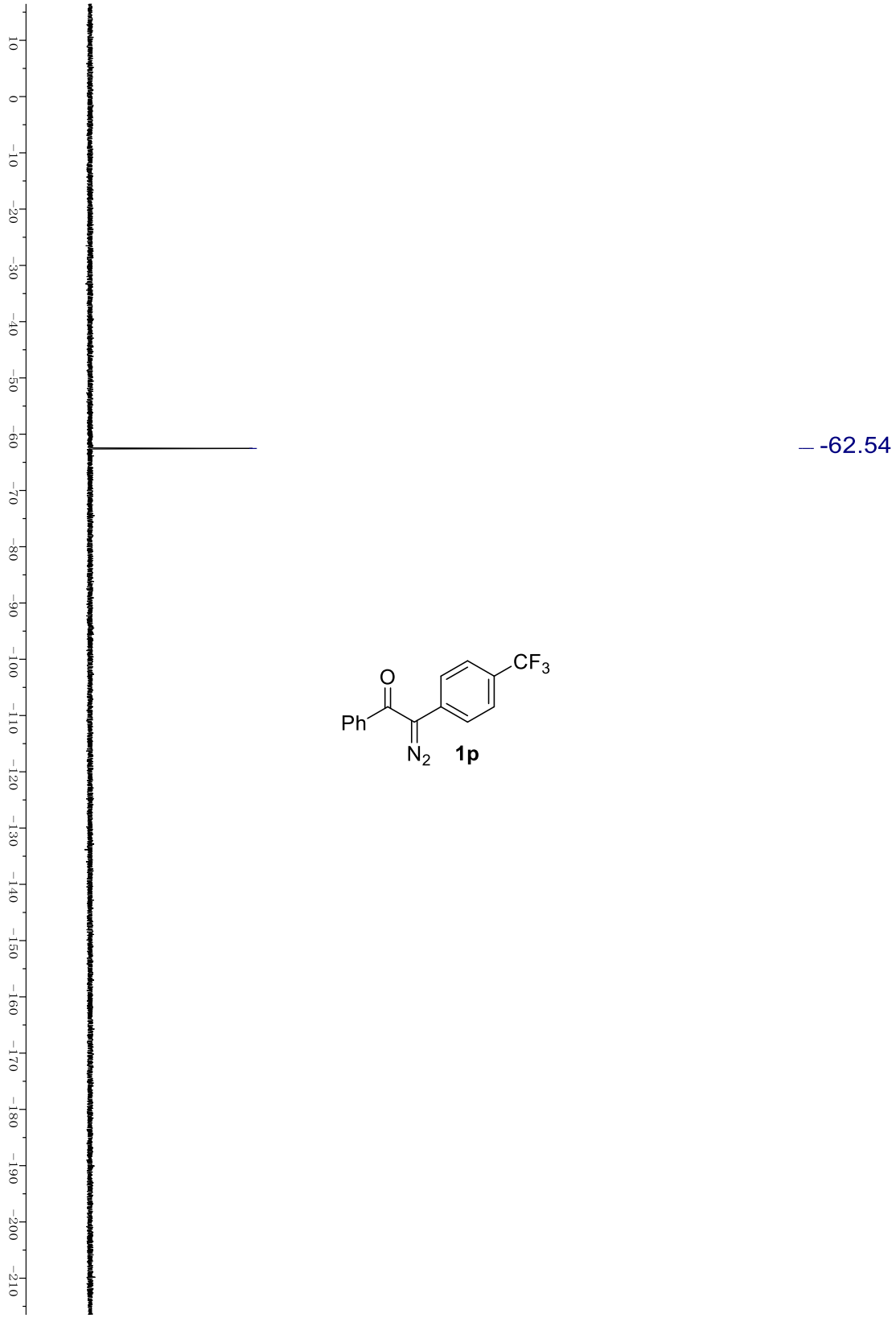
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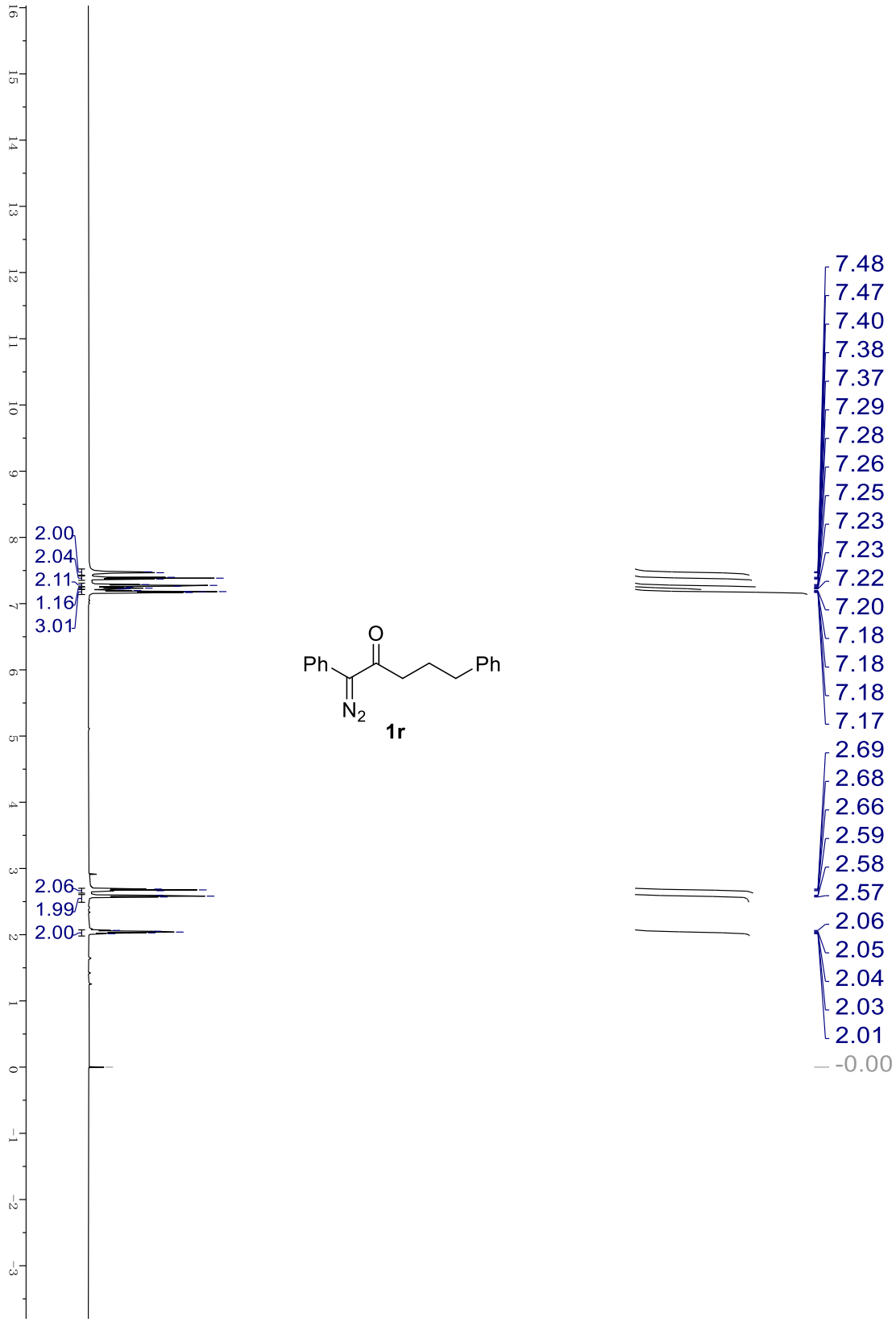
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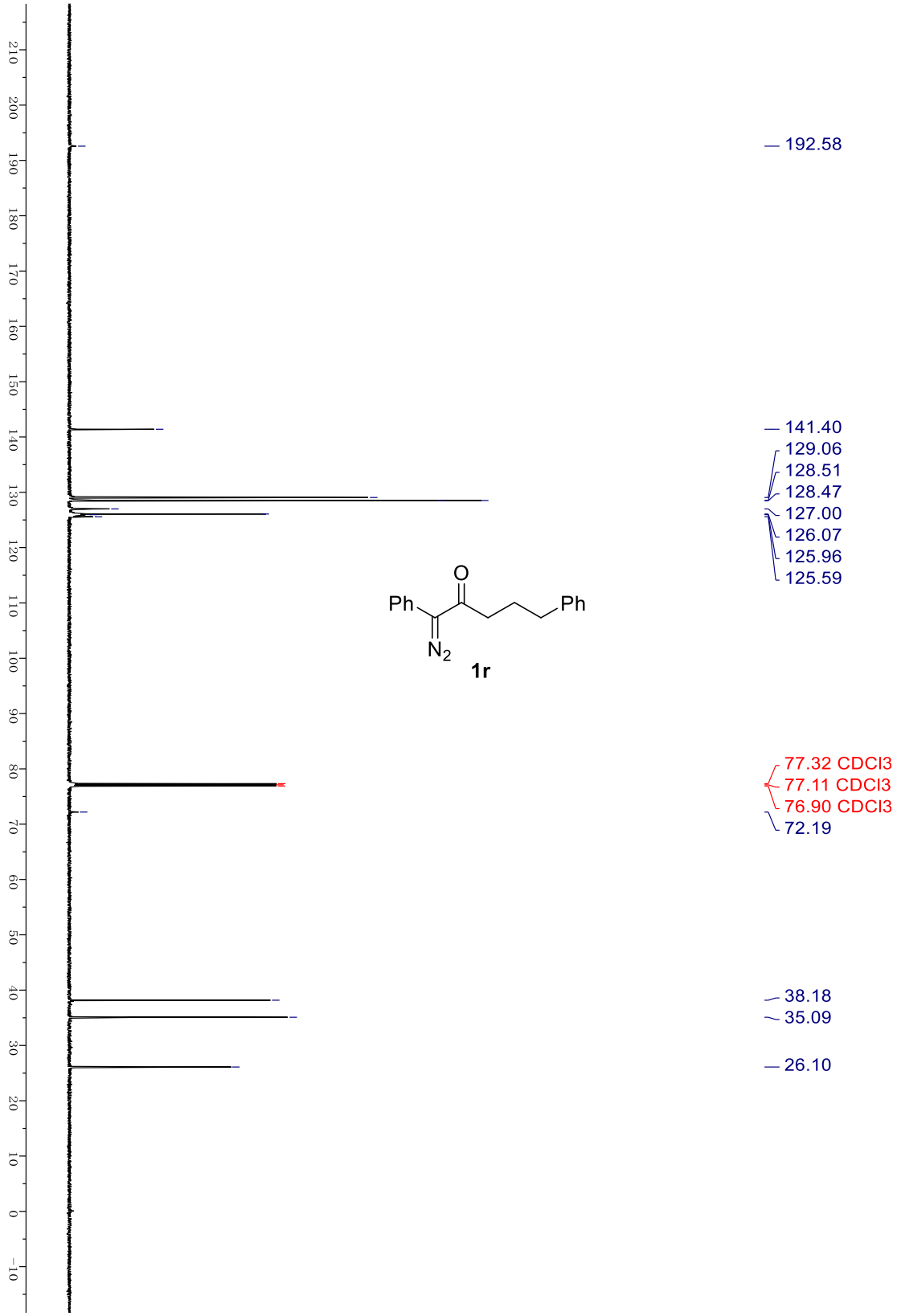
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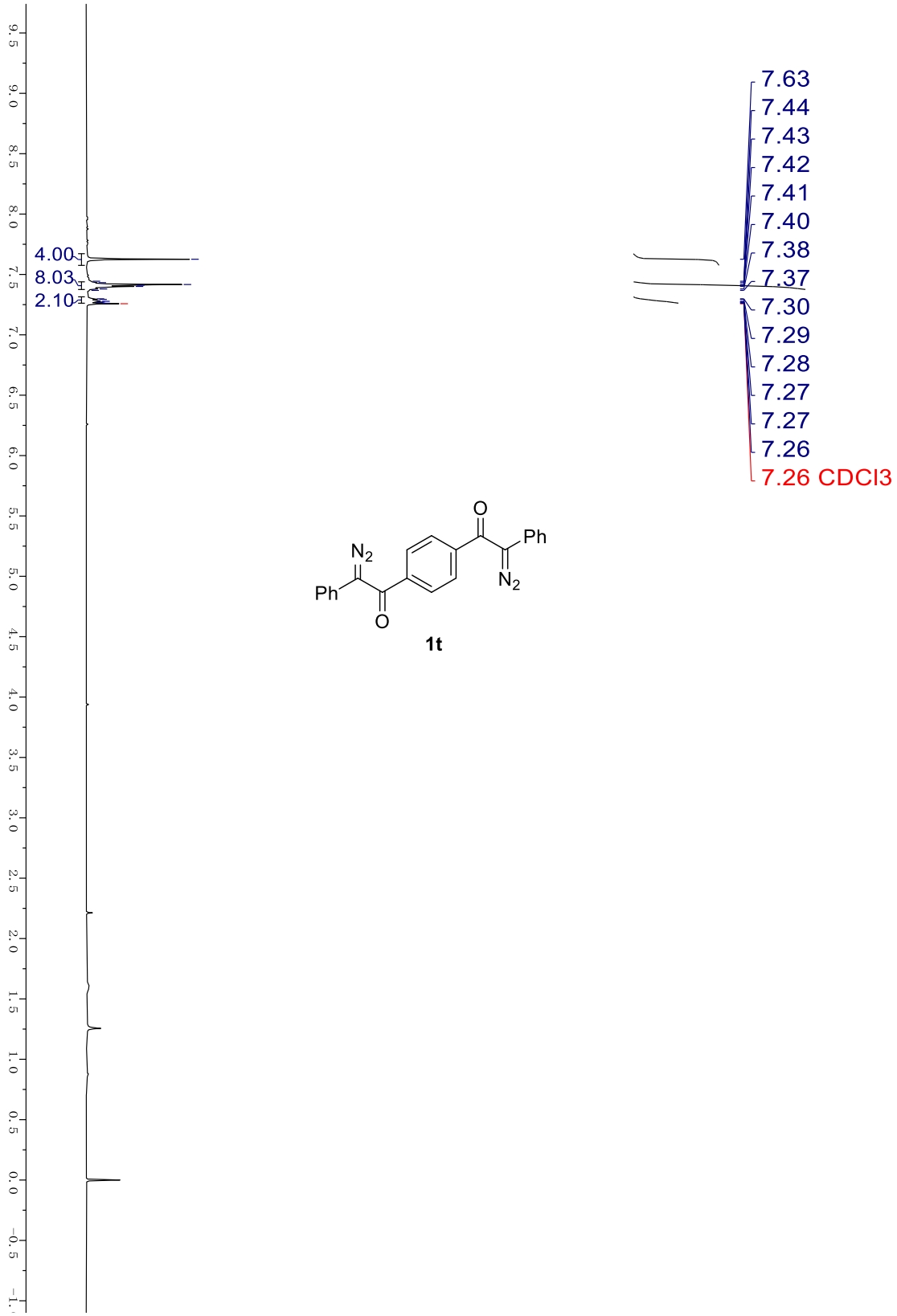
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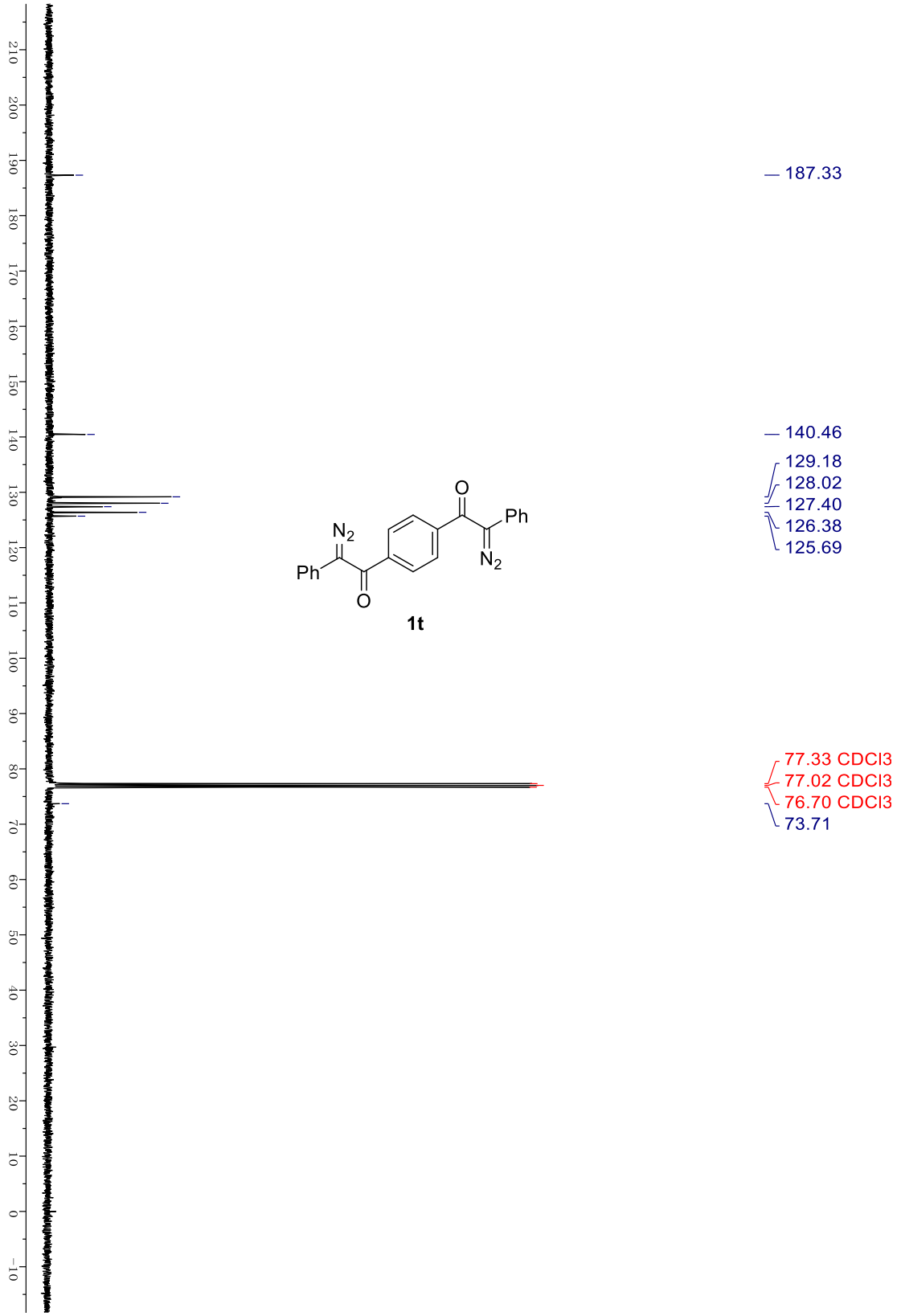
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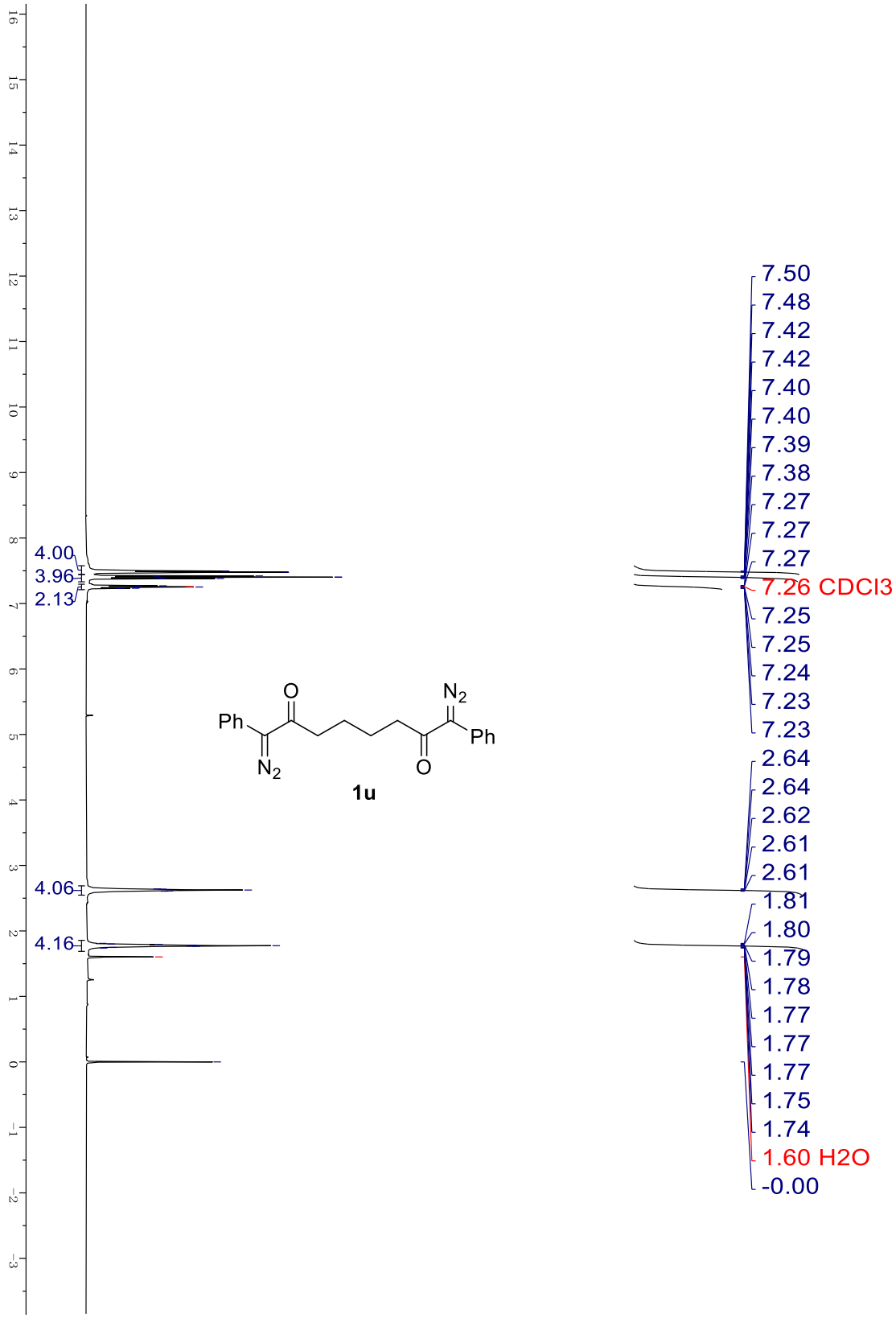
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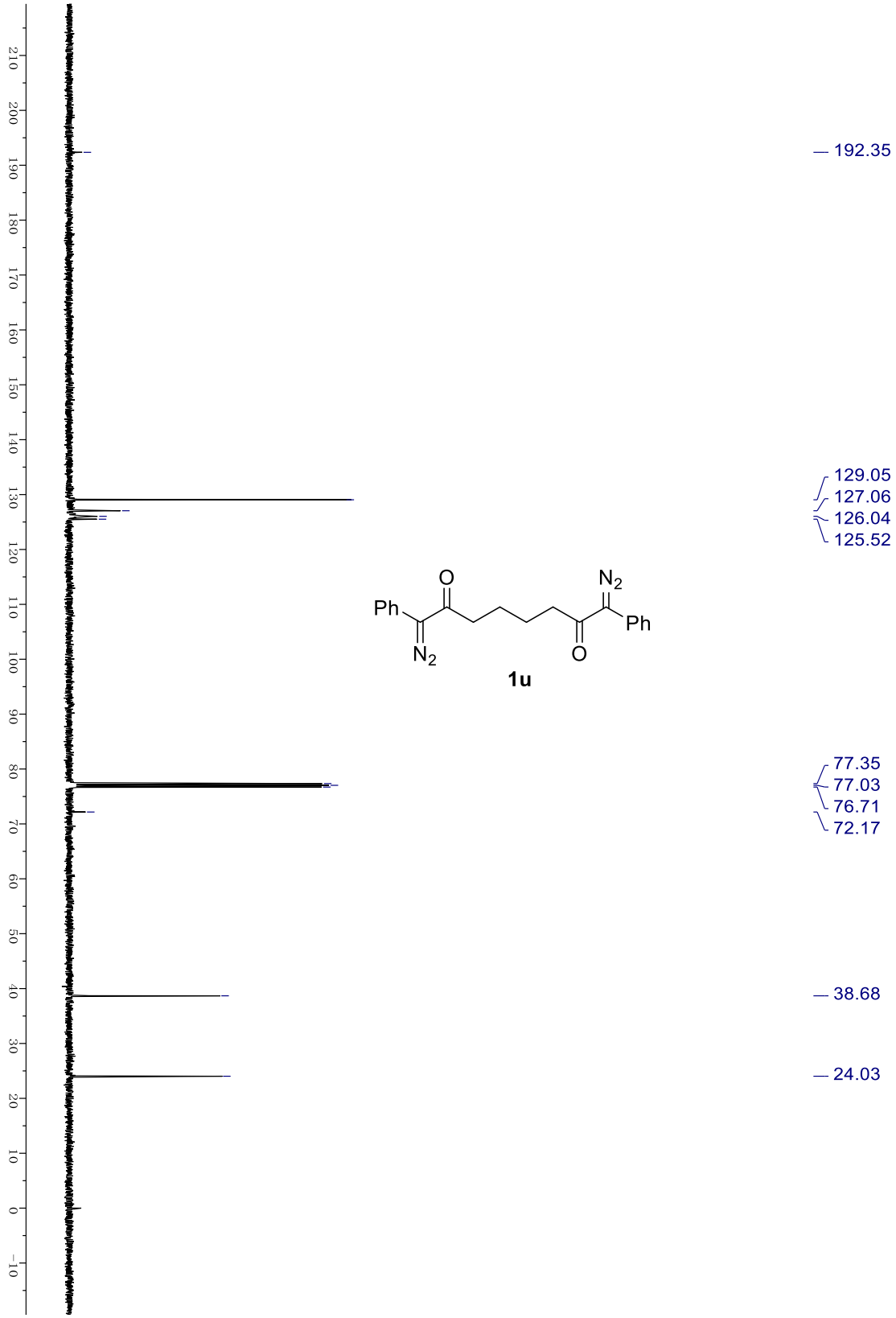
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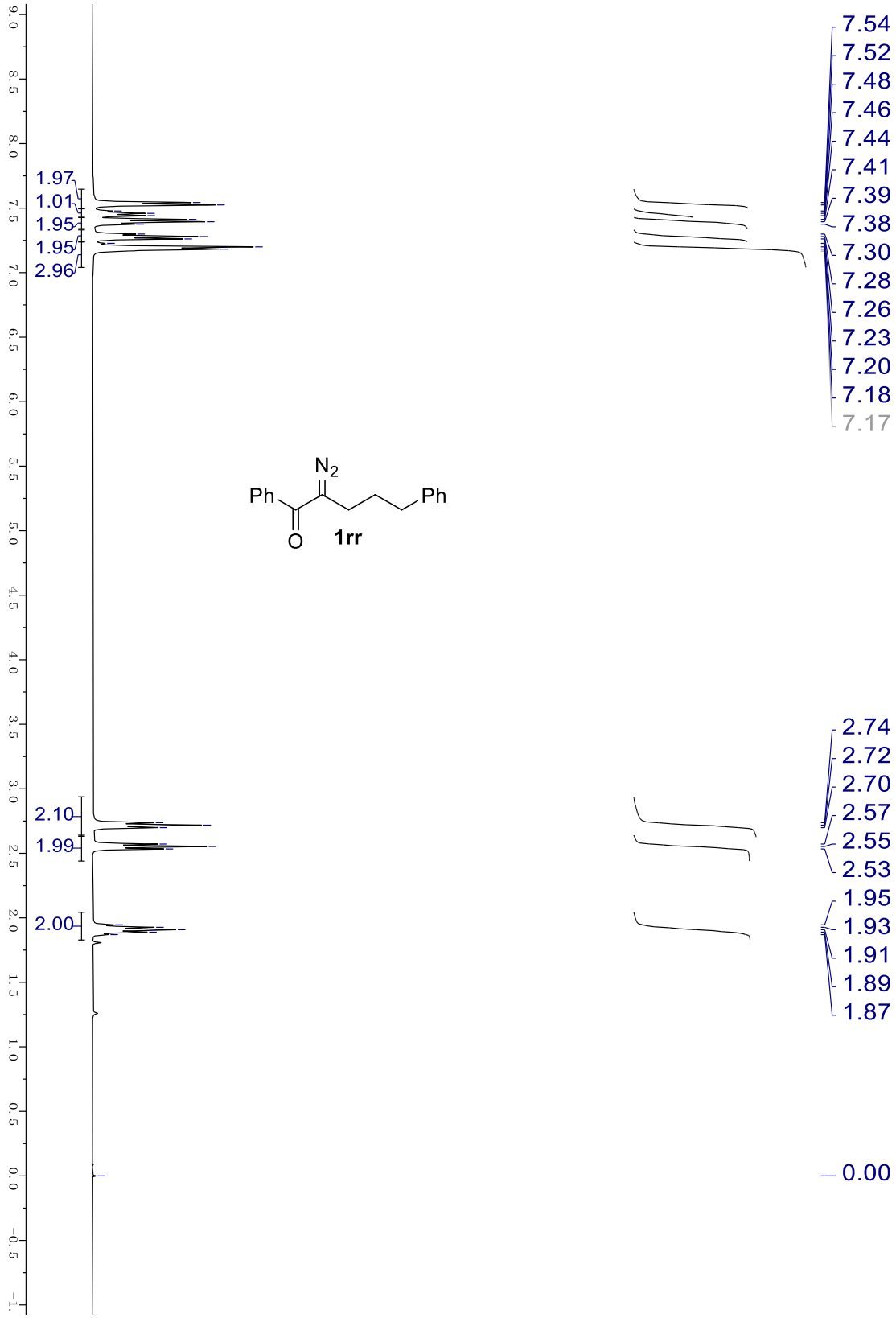
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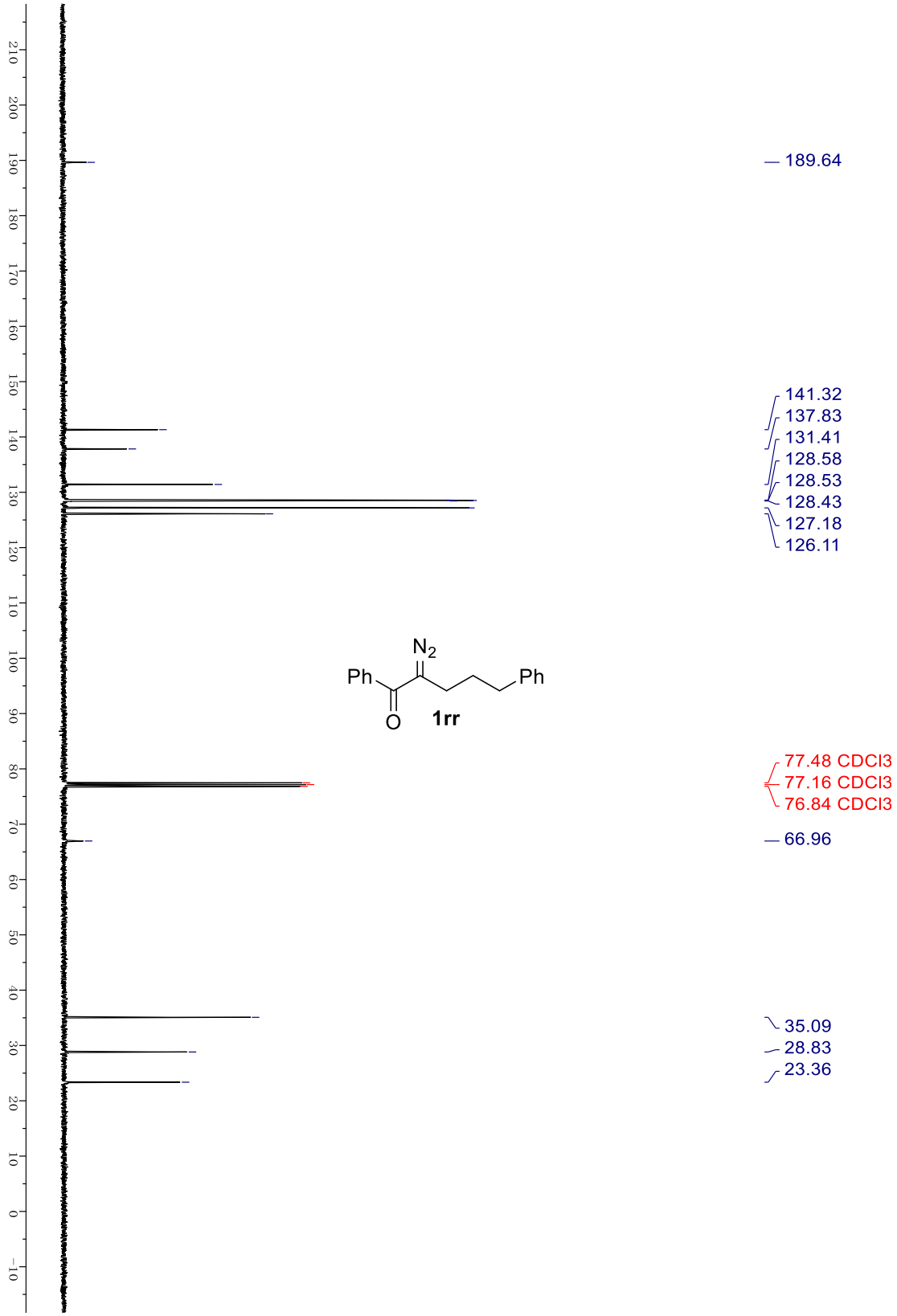
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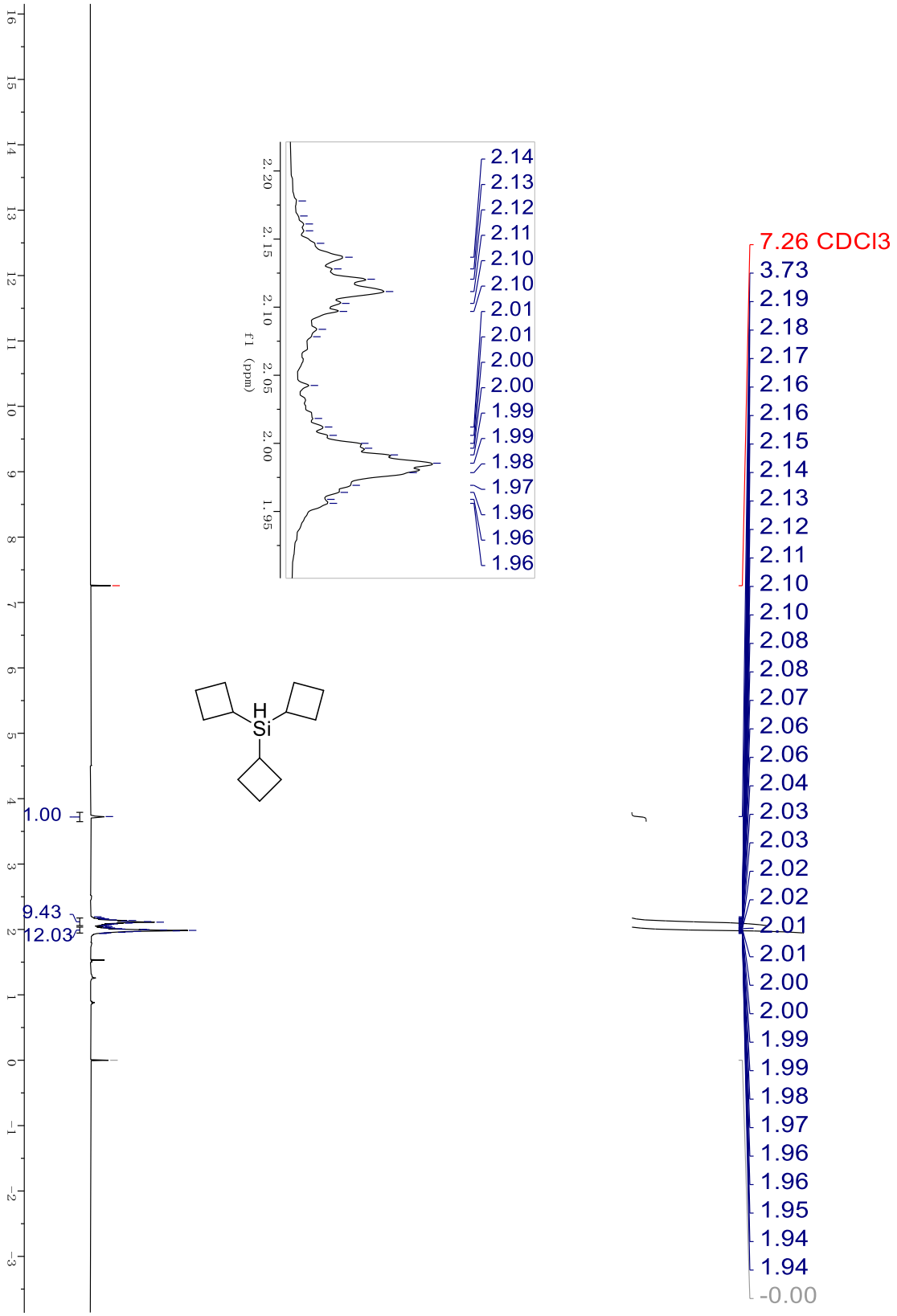
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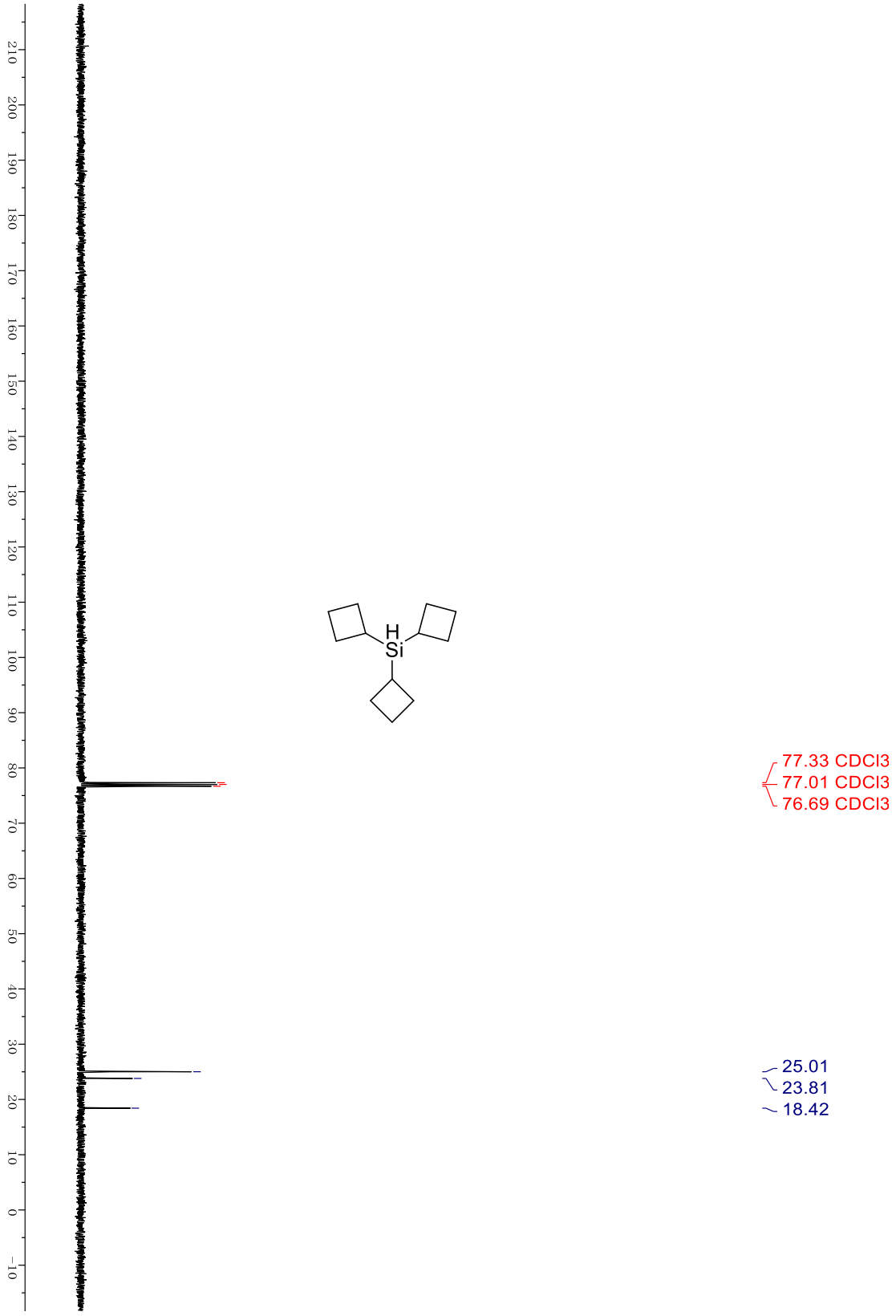
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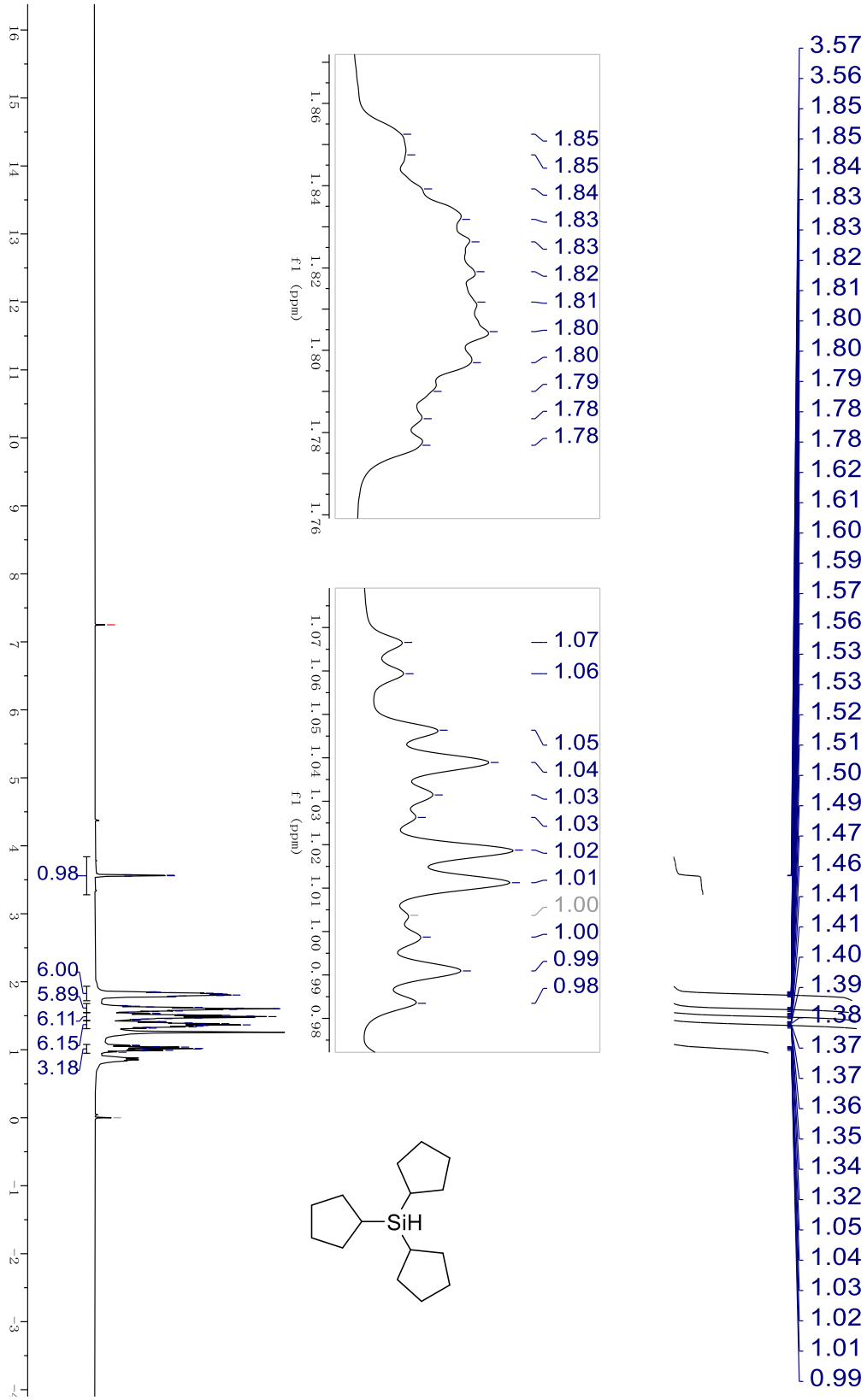
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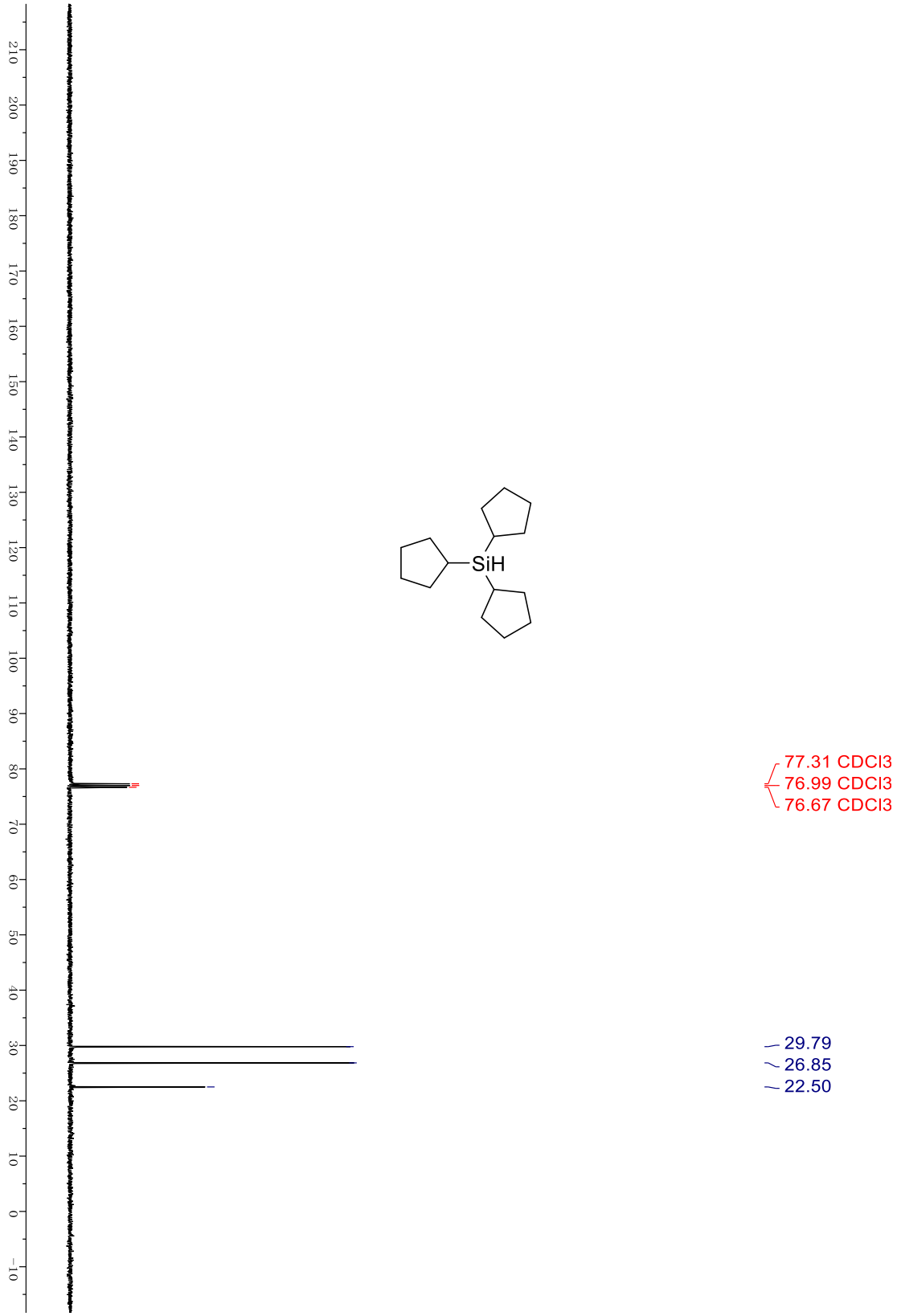
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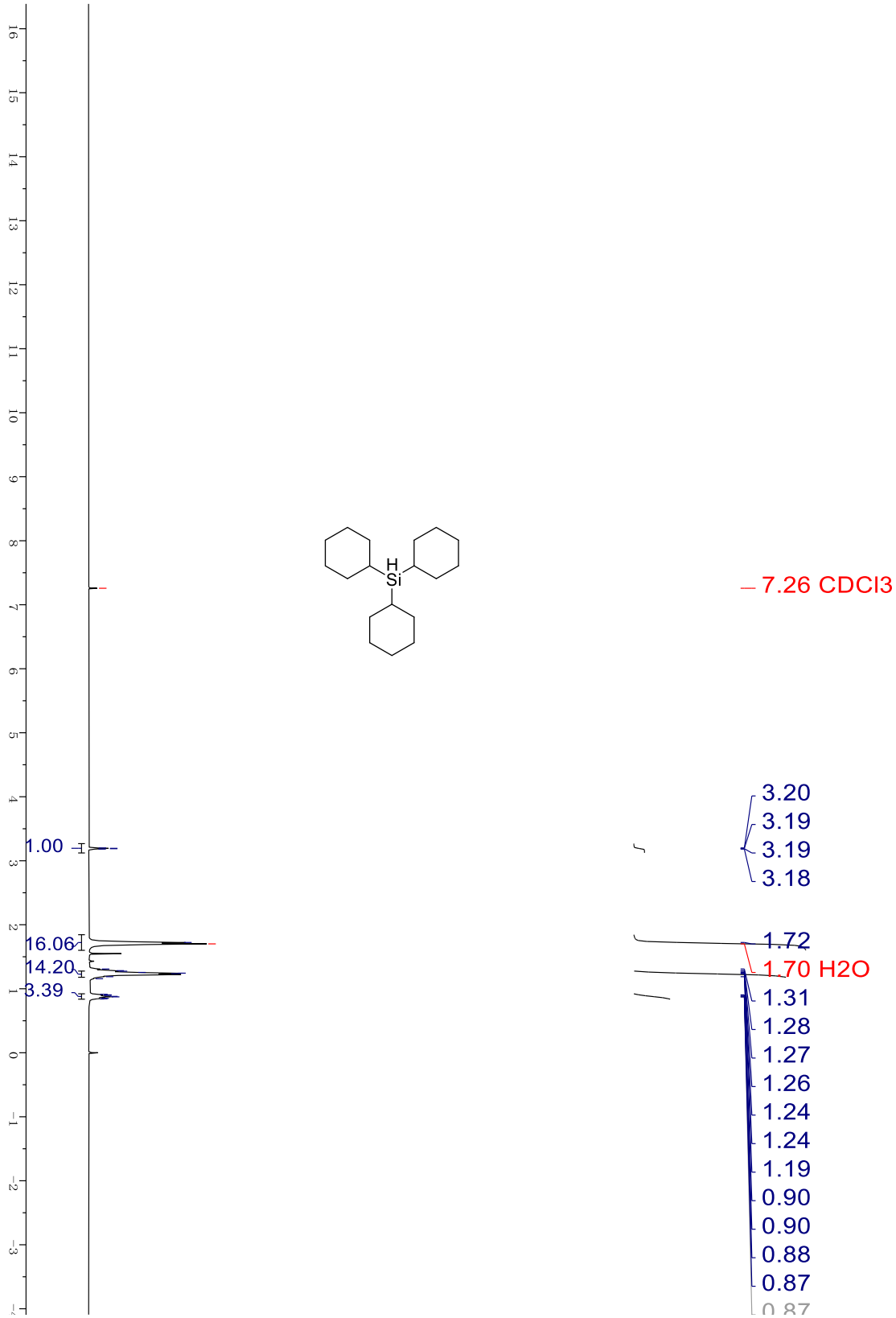
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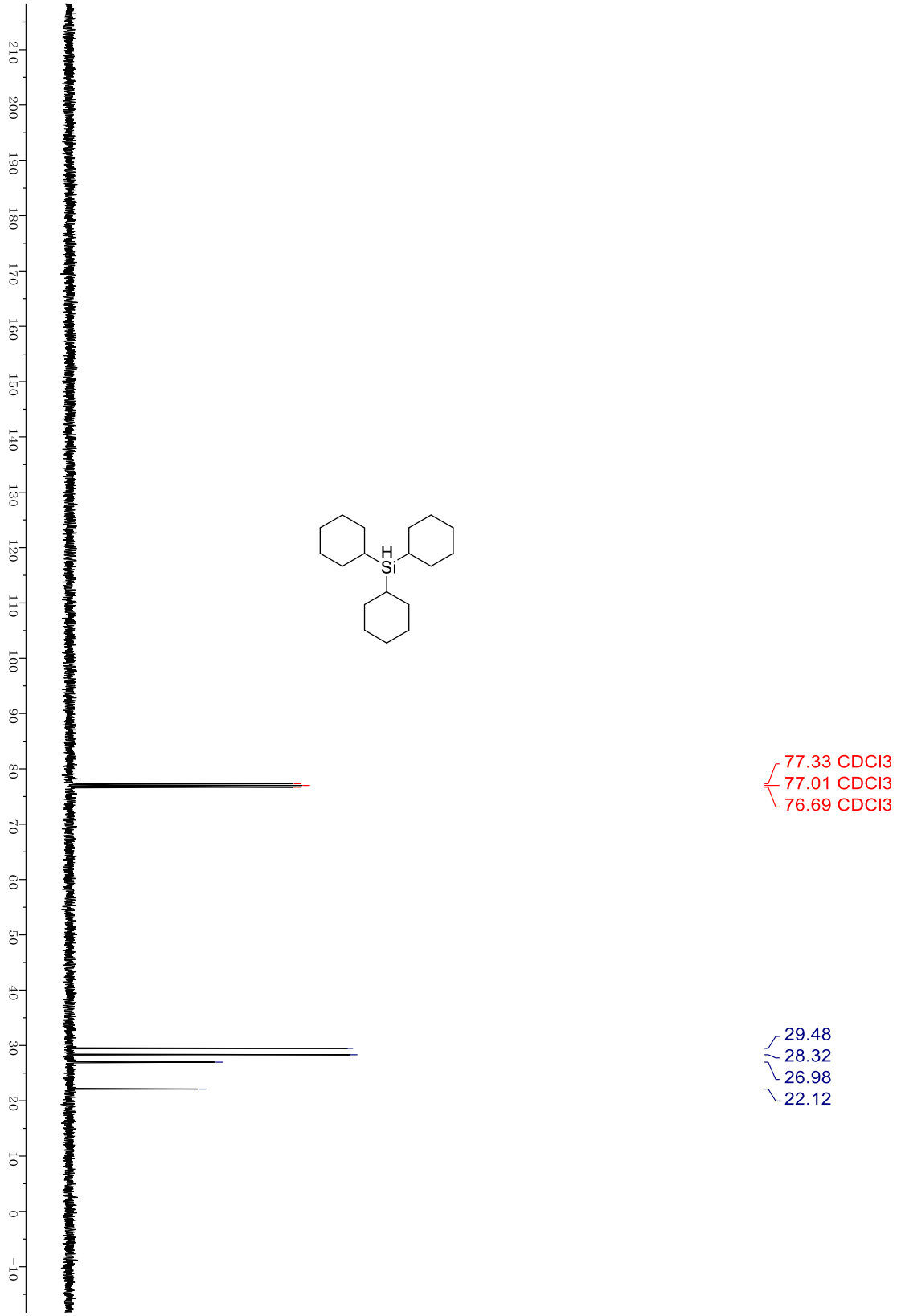
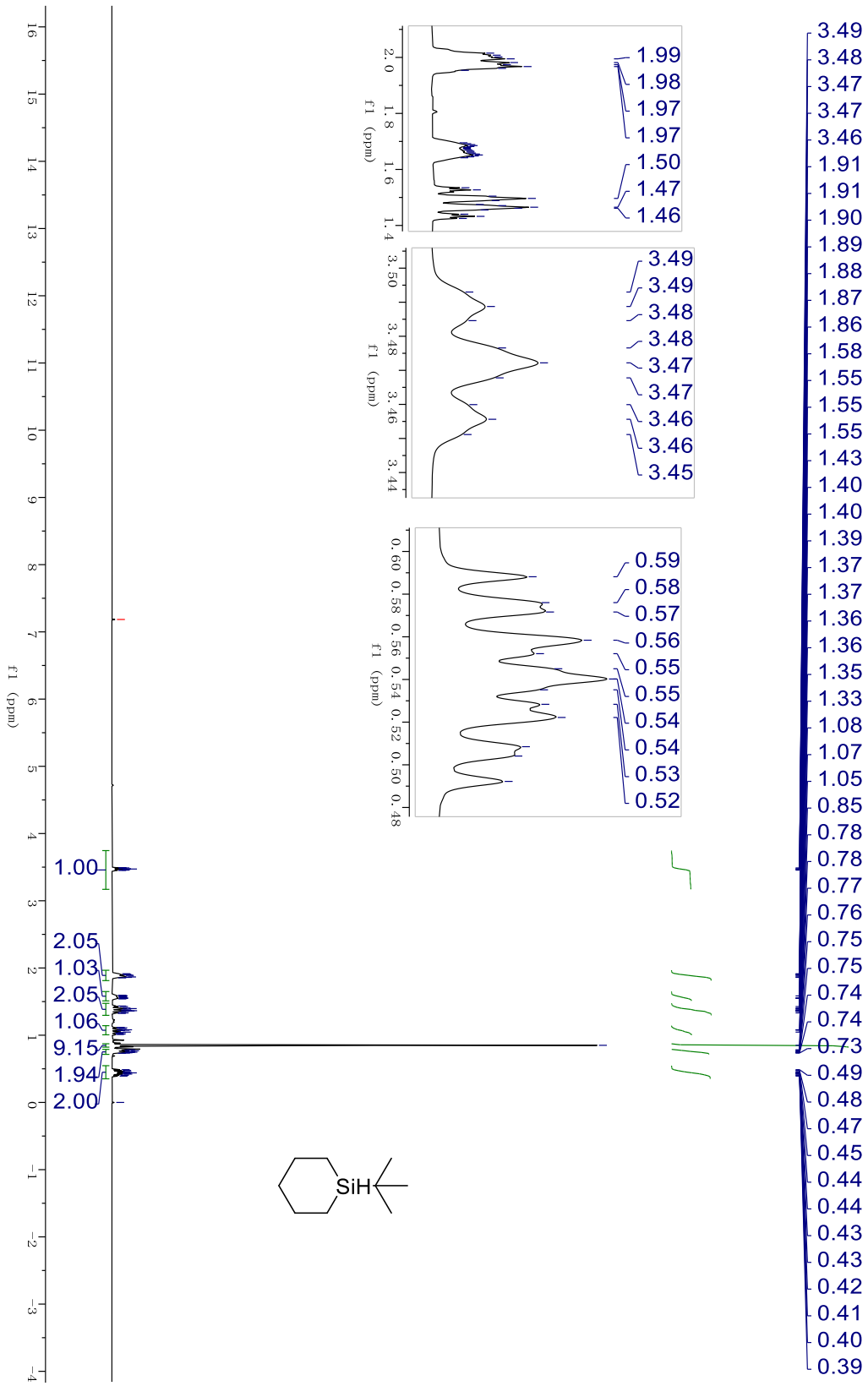
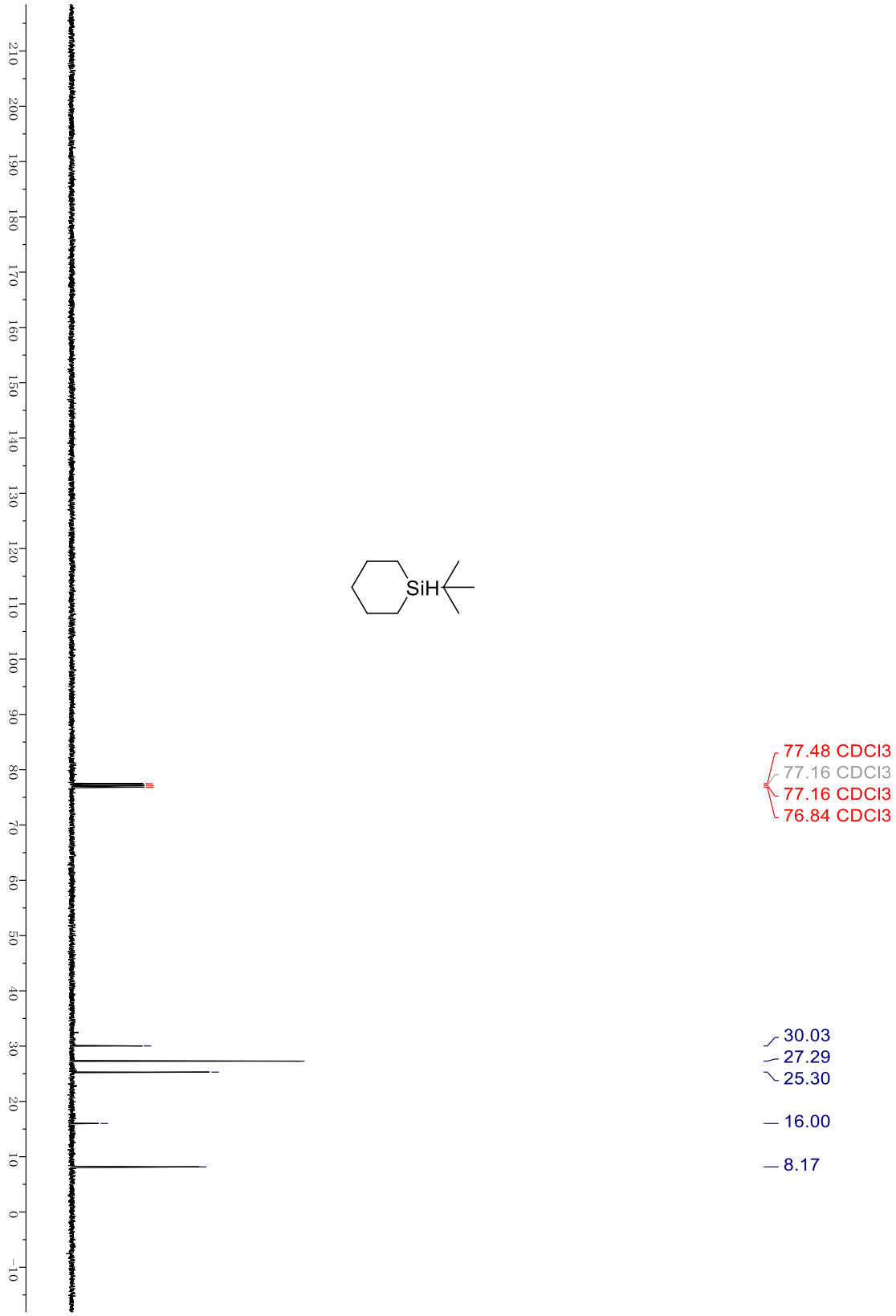
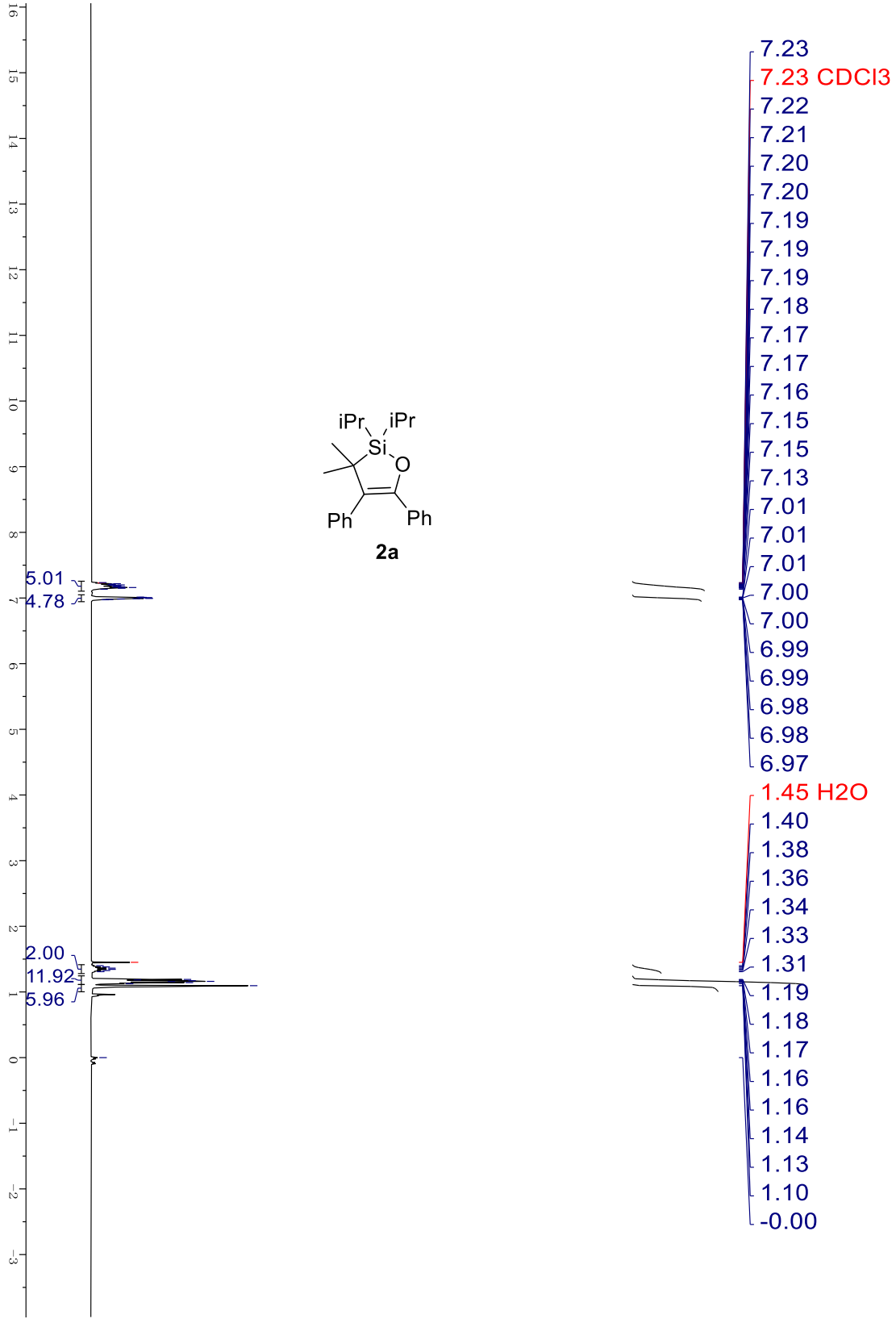
0.88
0.87

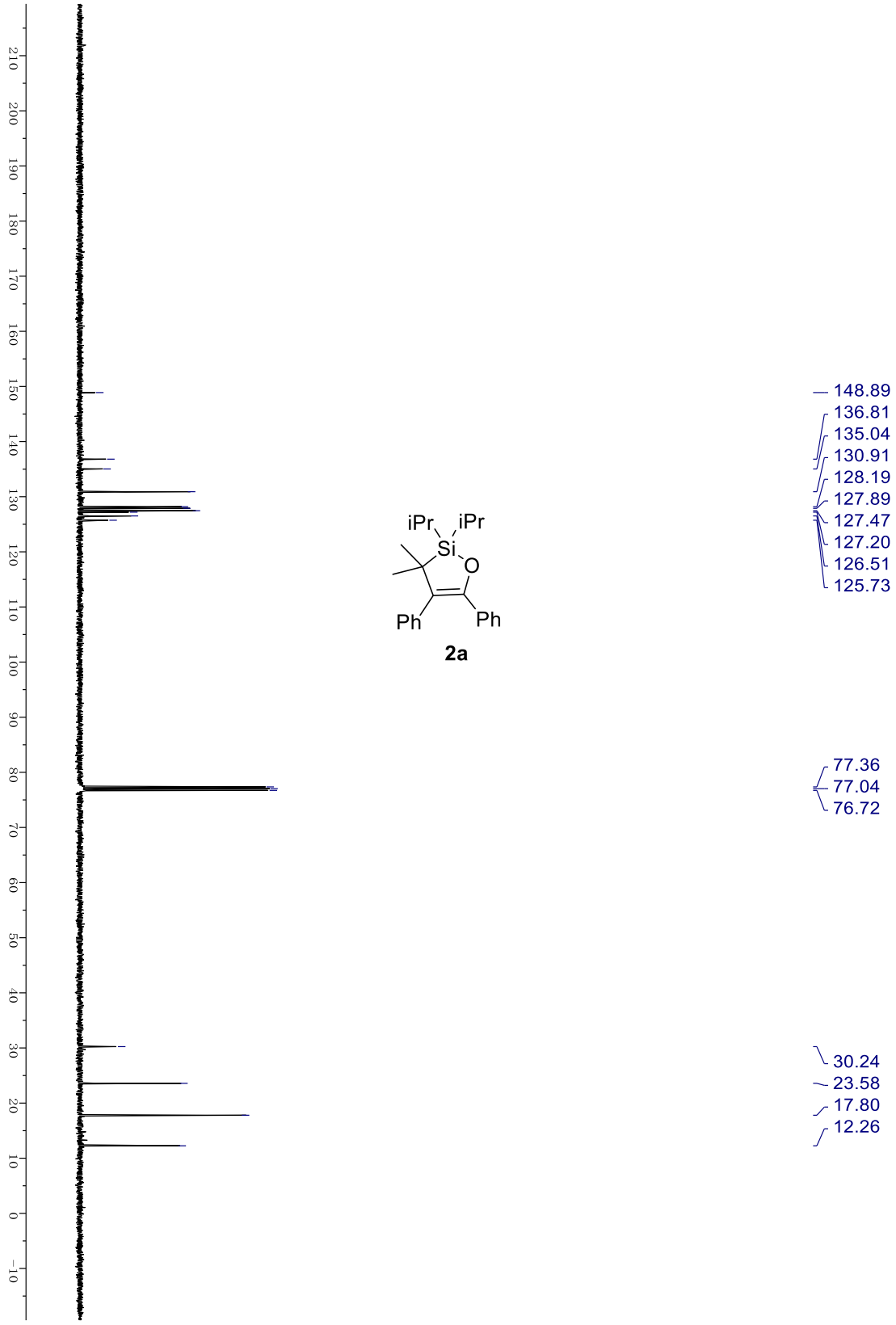

H
Si
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
29.48
28.32
26.98
22.12

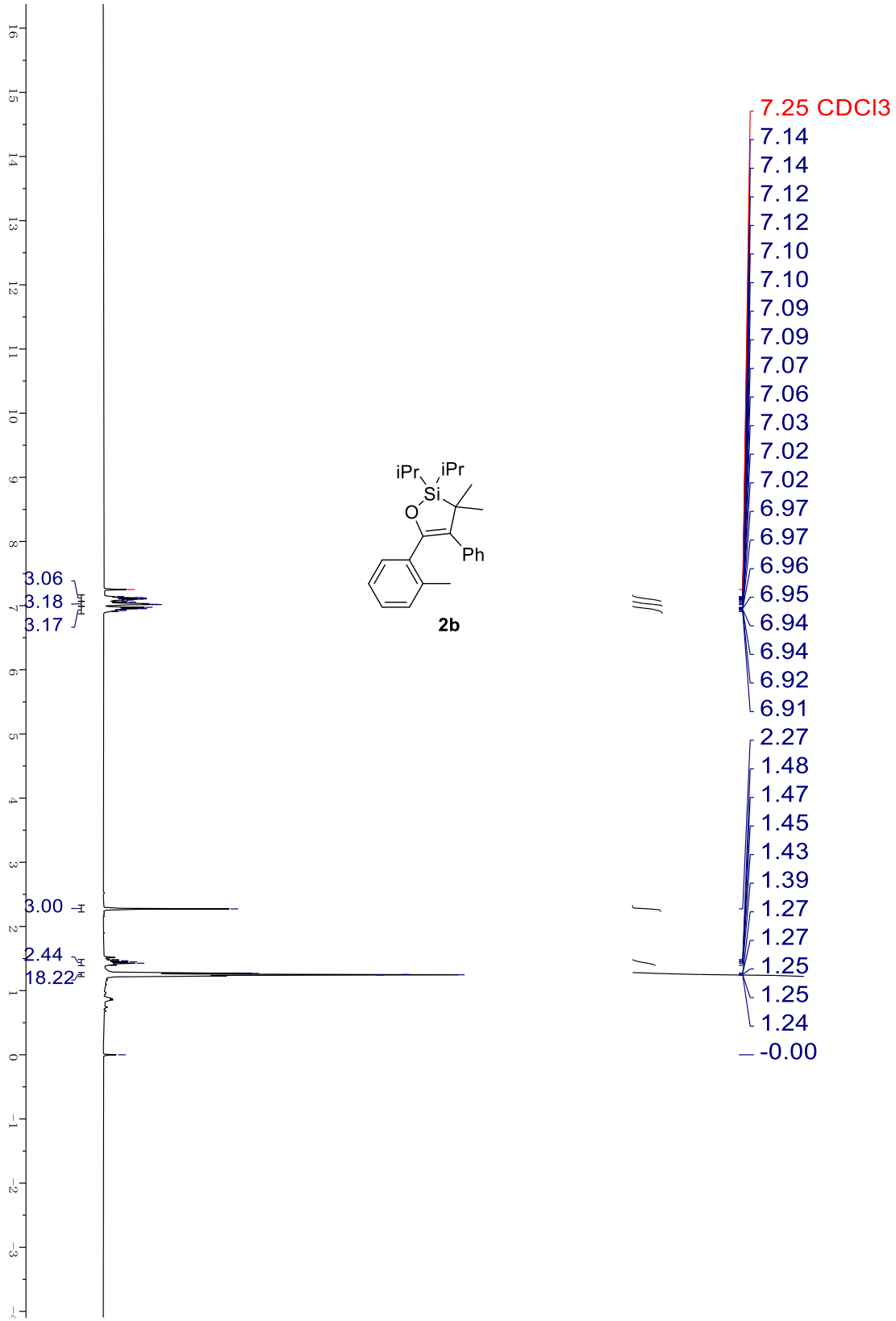

f1 (ppm)
1.00
2.05
1.03
2.05
1.06
9.15
1.94
2.00
SiH
1.99
1.98
1.97
1.97
1.50
1.47
1.46
3.49
3.49
3.48
3.48
3.47
3.47
3.46
3.46
3.45
0.59
0.58
0.57
0.56
0.55
0.55
0.54
0.54
0.53
0.52
3.49
3.48
3.47
3.47
3.46
1.91
1.91
1.90
1.89
1.88
1.87
1.86
1.58
1.55
1.55
1.55
1.43
1.40
1.40
1.39
1.37
1.37
1.36
1.36
1.35
1.33
1.08
1.07
1.05
0.85
0.78
0.78
0.77
0.76
0.75
0.75
0.74
0.74
0.73
0.49
0.48
0.47
0.45
0.44
0.44
0.43
0.43
0.42
0.41
0.40
0.39

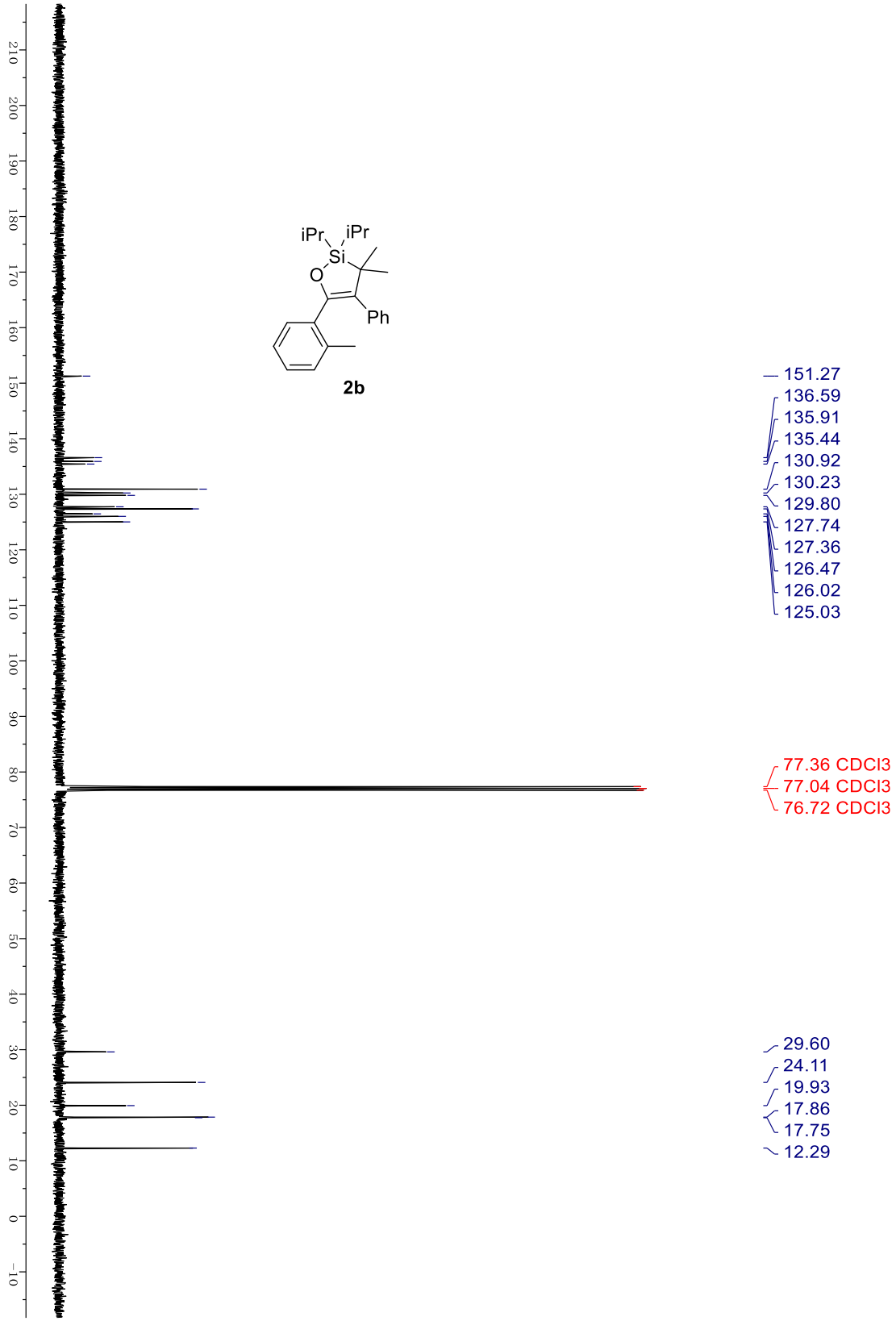

SiH
77.48 CDCl3
77.16 CDCl3
77.16 CDCl3
76.84 CDCl3
30.03
27.29
25.30
16.00
8.17

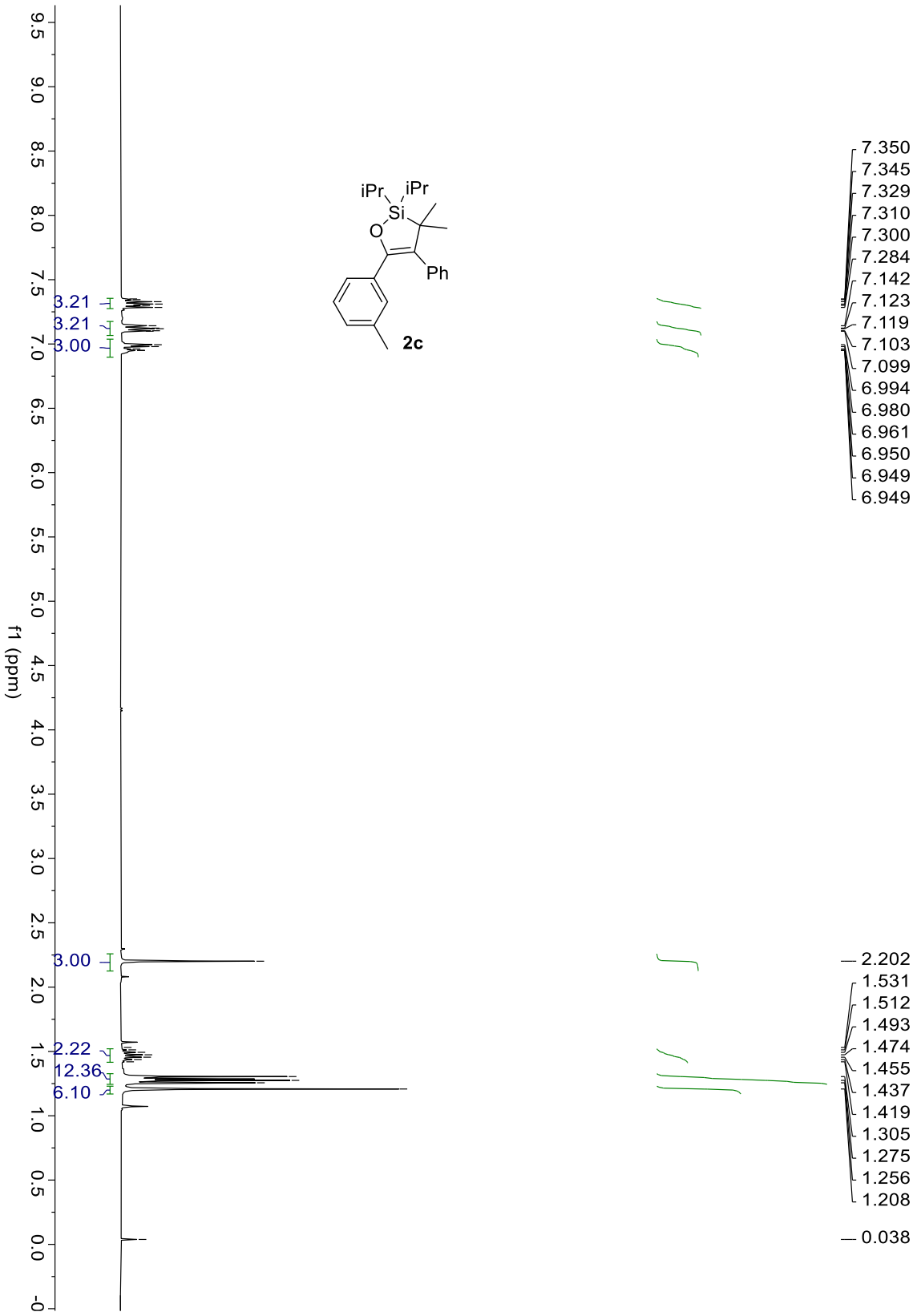
11.2 NMR spectra of cyclic silyl enol ethers and byproducts

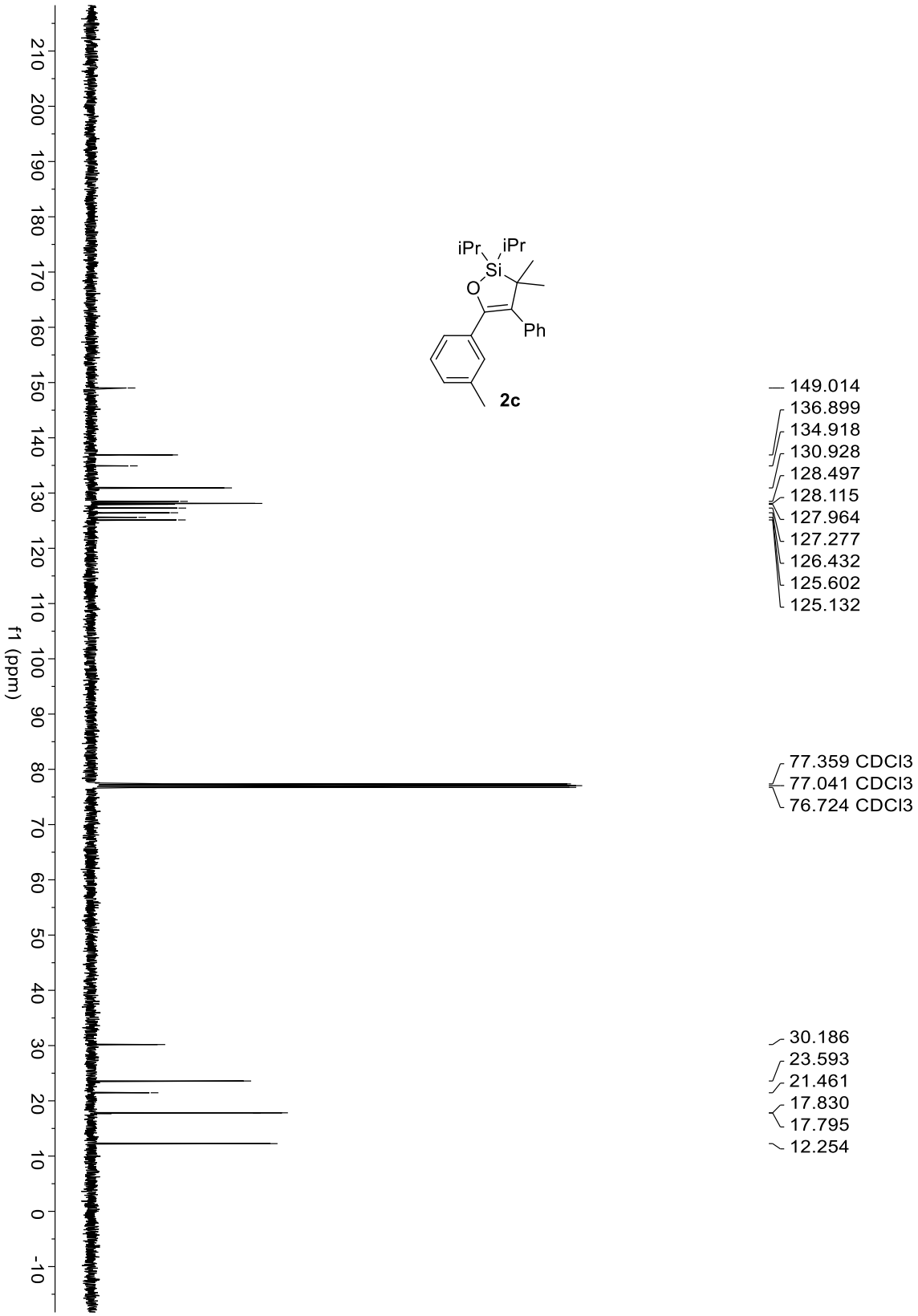


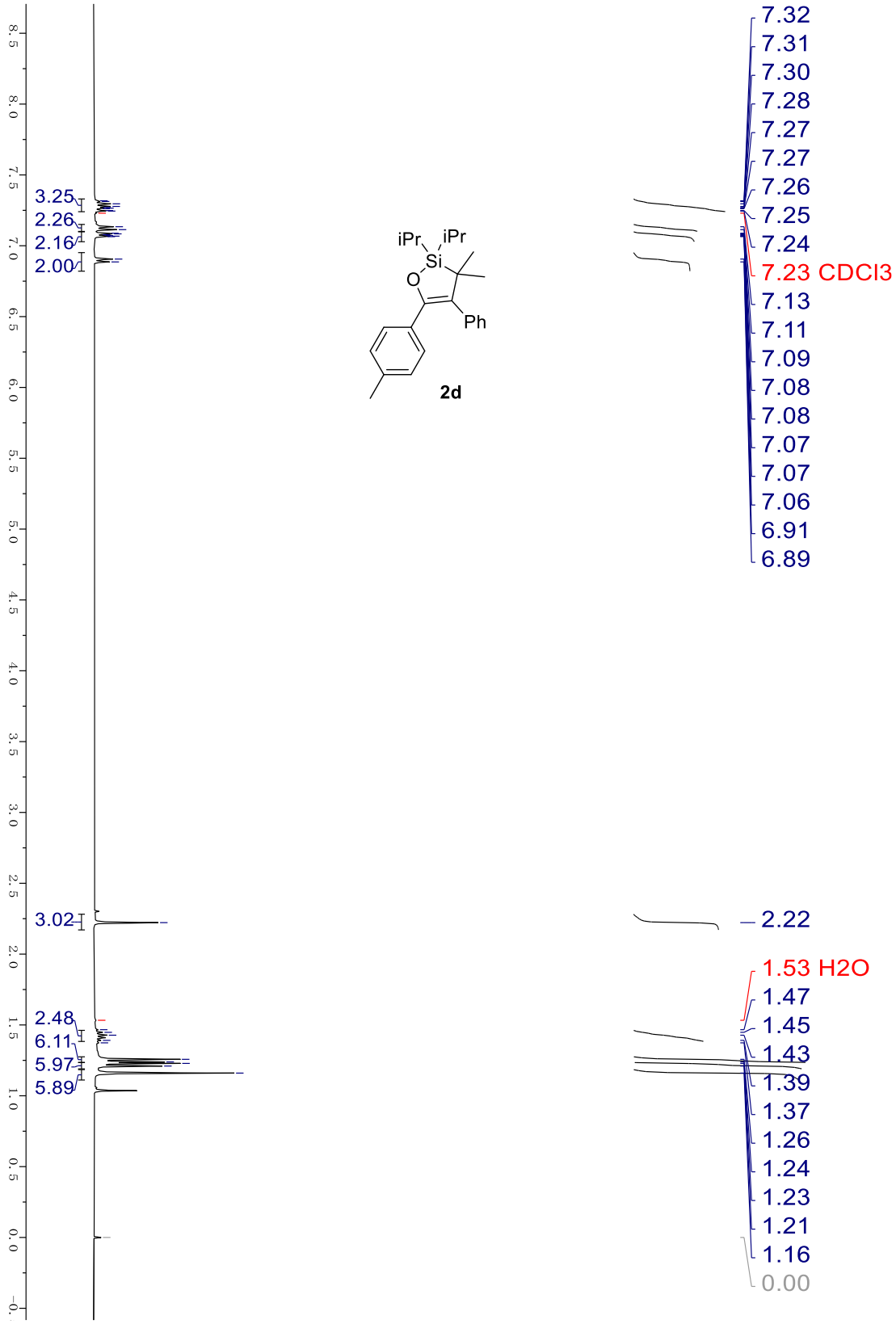

148.89
136.81
135.04
130.91
128.19
127.89
127.47
127.20
126.51
125.73
77.36
77.04
76.72
30.24
23.58
17.80
12.26
iPr
iPr
Si
O
Ph
Ph
2a

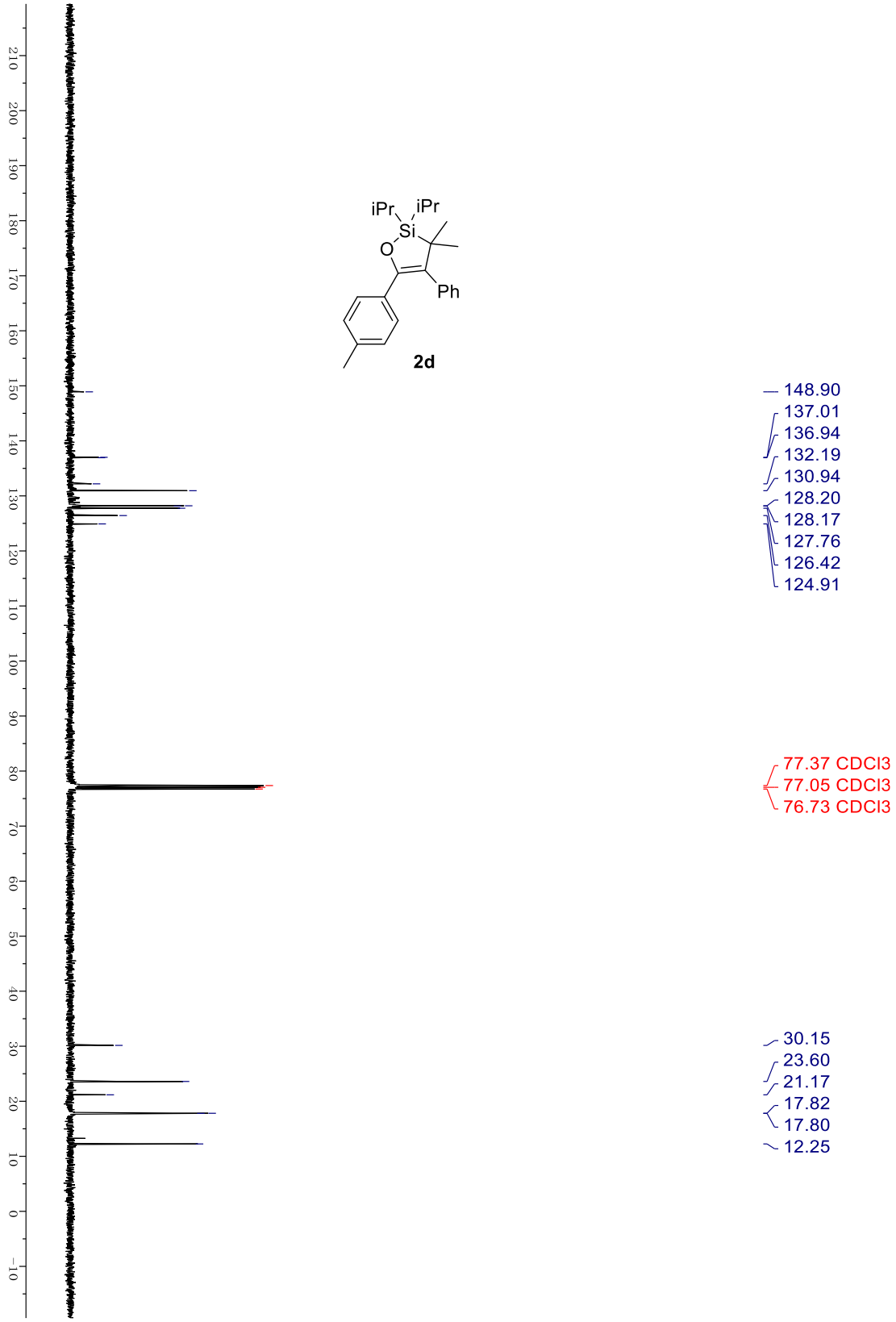

7.25 CDCl3
7.14
7.14
7.12
7.12
7.10
7.10
7.09
7.09
7.07
7.06
7.03
7.02
7.02
6.97
6.97
6.96
6.95
6.94
6.94
6.92
6.91
2.27
1.48
1.47
1.45
1.43
1.39
1.27
1.27
1.25
1.25
1.24
-0.00
3.06
3.18
3.17
3.00
2.44
18.22
iPr
iPr
Si
O
Ph
2b

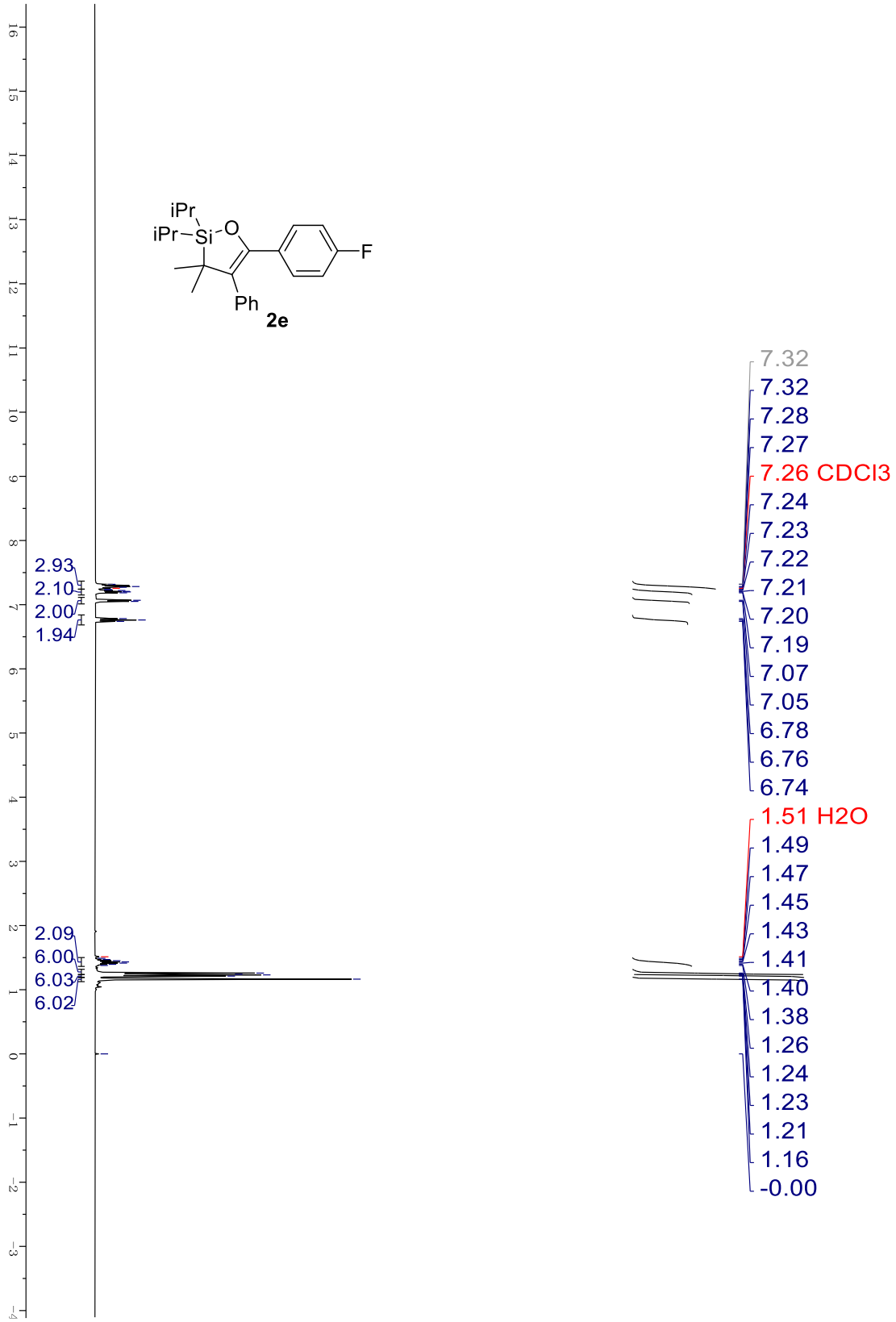

iPr
iPr
Si
O
Ph
2b
151.27
136.59
135.91
135.44
130.92
130.23
129.80
127.74
127.36
126.47
126.02
125.03
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
29.60
24.11
19.93
17.86
17.75
12.29

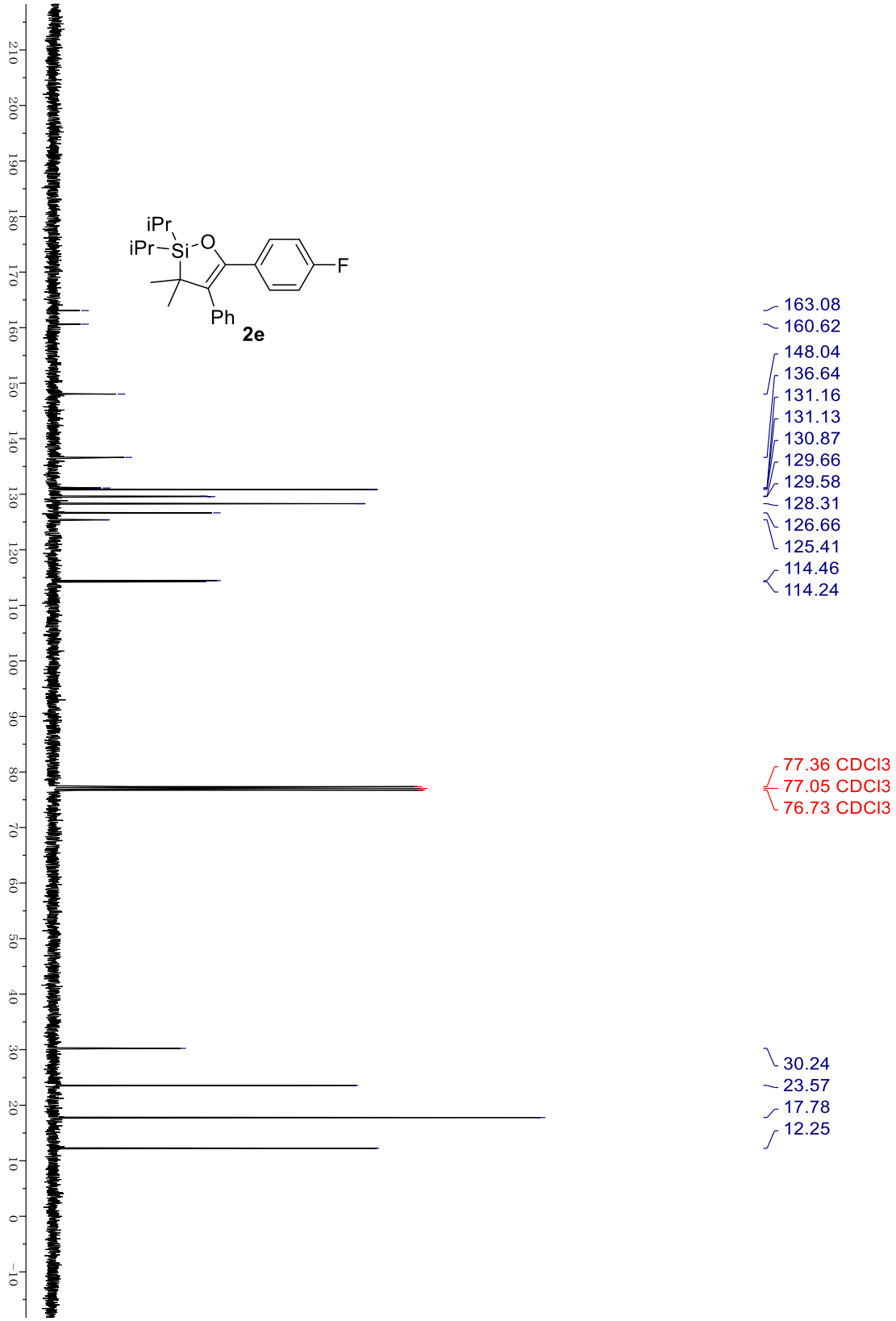

iPr
iPr
Si
O
Ph
2c
3.21
3.21
3.00
3.00
2.22
12.36
6.10
7.350
7.345
7.329
7.310
7.300
7.284
7.142
7.123
7.119
7.103
7.099
6.994
6.980
6.961
6.950
6.949
6.949
2.202
1.531
1.512
1.493
1.474
1.455
1.437
1.419
1.305
1.275
1.256
1.208
0.038
f1 (ppm)

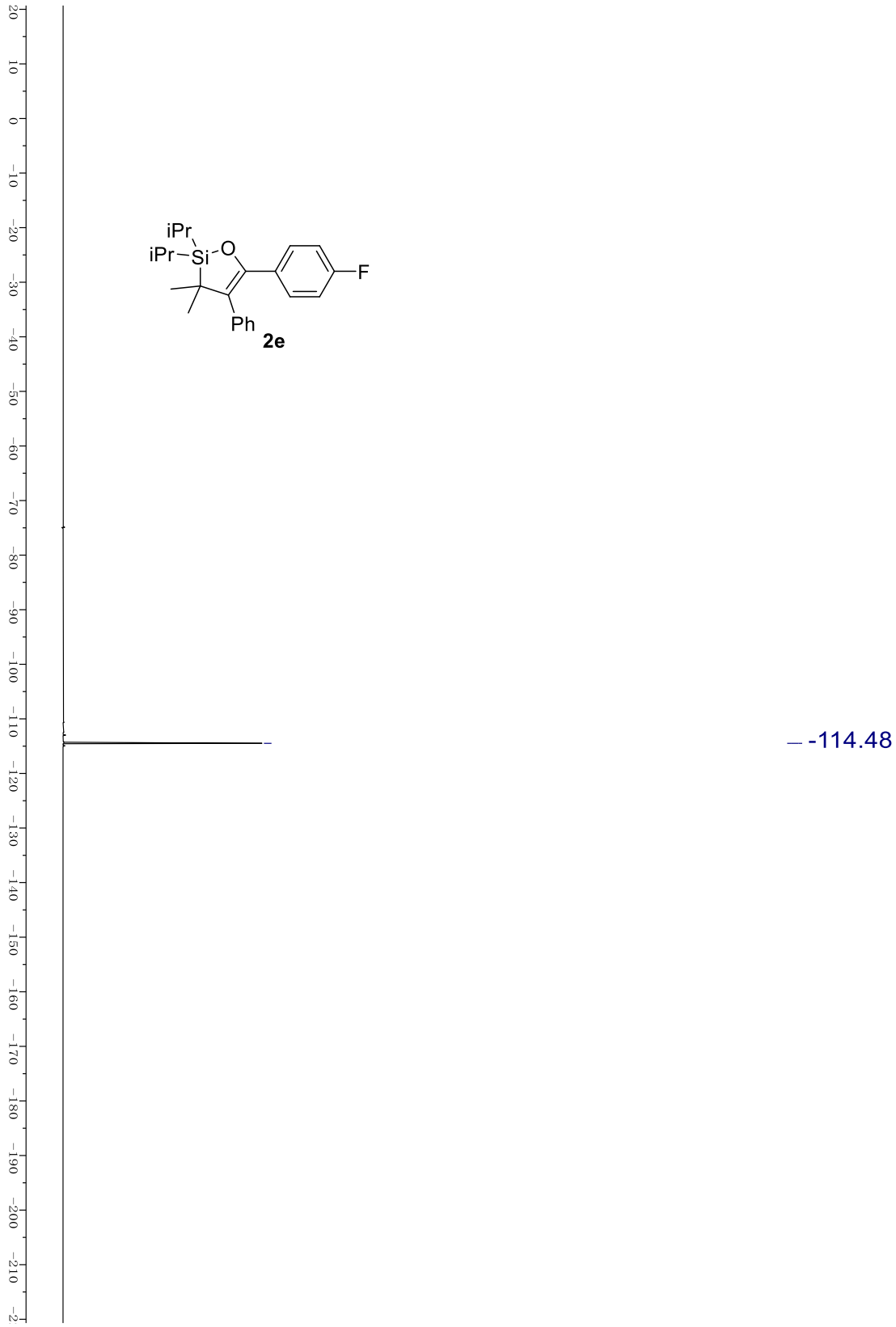

iPr
iPr
Si
O
Ph
2c
149.014
136.899
134.918
130.928
128.497
128.115
127.964
127.277
126.432
125.602
125.132
77.359 CDCl3
77.041 CDCl3
76.724 CDCl3
30.186
23.593
21.461
17.830
17.795
12.254
f1 (ppm)

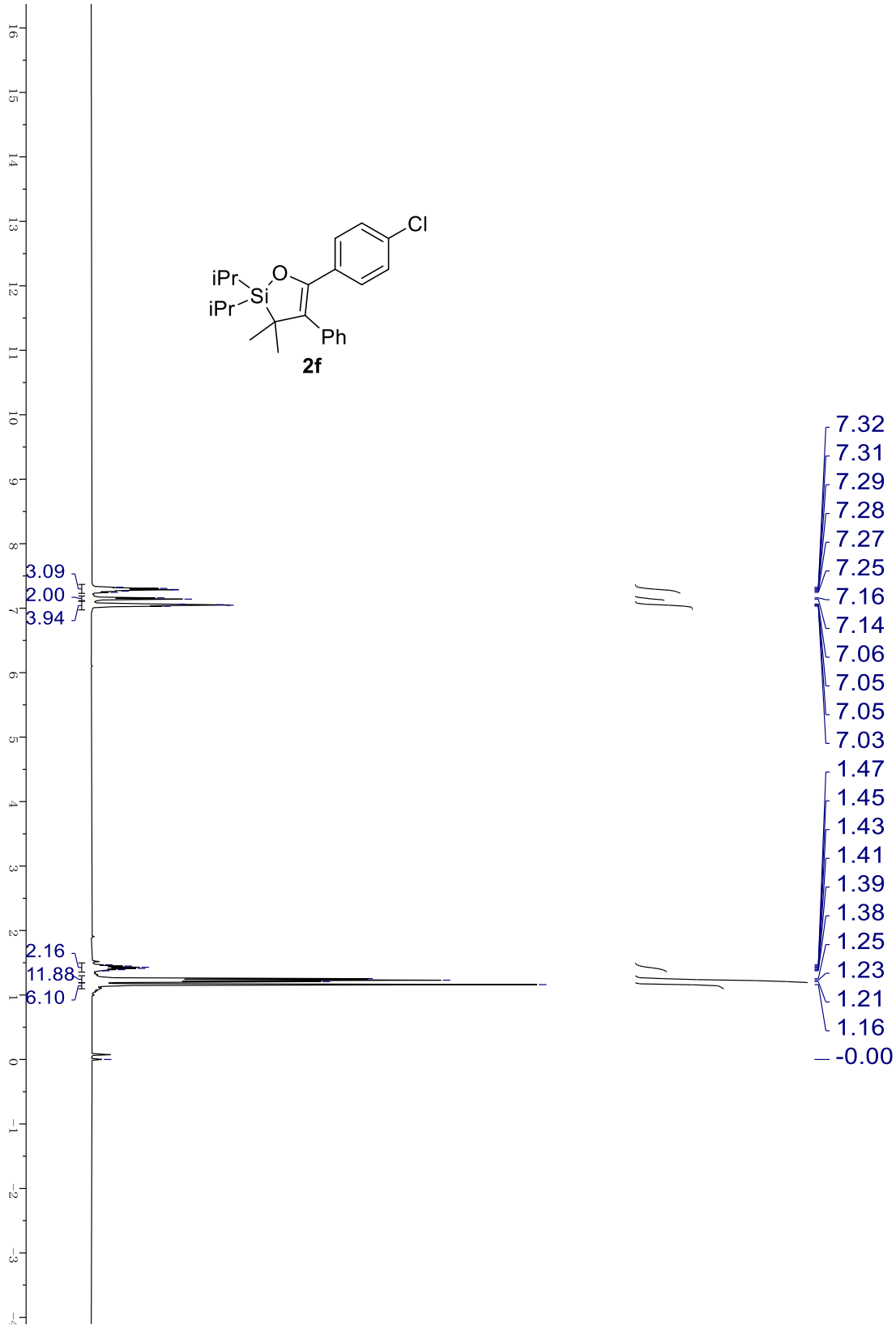

3.25
2.26
2.16
2.00
3.02
2.48
6.11
5.97
5.89
iPr
iPr
Si
O
Ph
2d
7.32
7.31
7.30
7.28
7.27
7.27
7.26
7.25
7.24
7.23 CDCl3
7.13
7.11
7.09
7.08
7.08
7.07
7.07
7.06
6.91
6.89
2.22
1.53 H2O
1.47
1.45
1.43
1.39
1.37
1.26
1.24
1.23
1.21
1.16
0.00

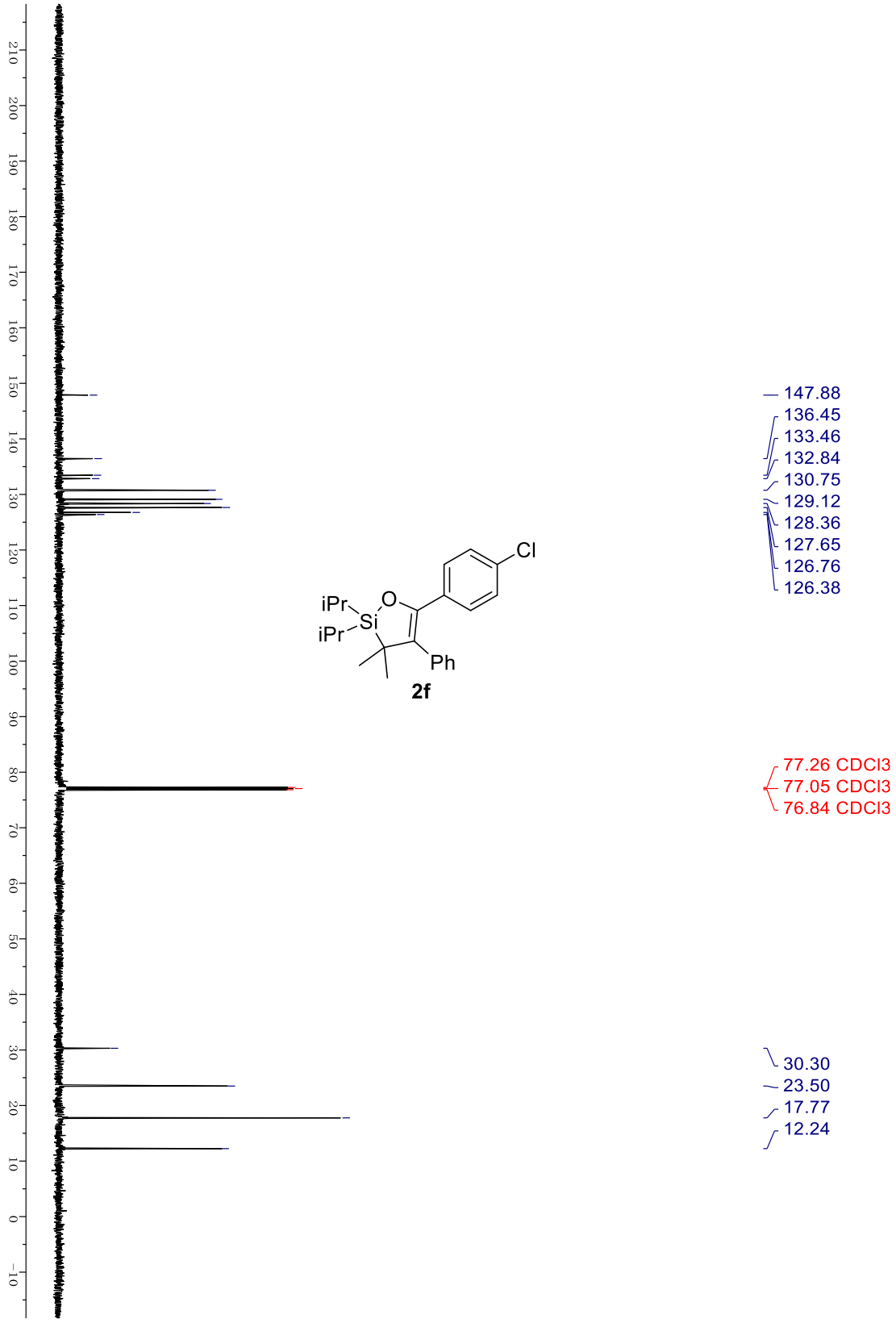

iPr
iPr
Si
O
Ph
2d
148.90
137.01
136.94
132.19
130.94
128.20
128.17
127.76
126.42
124.91
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
30.15
23.60
21.17
17.82
17.80
12.25

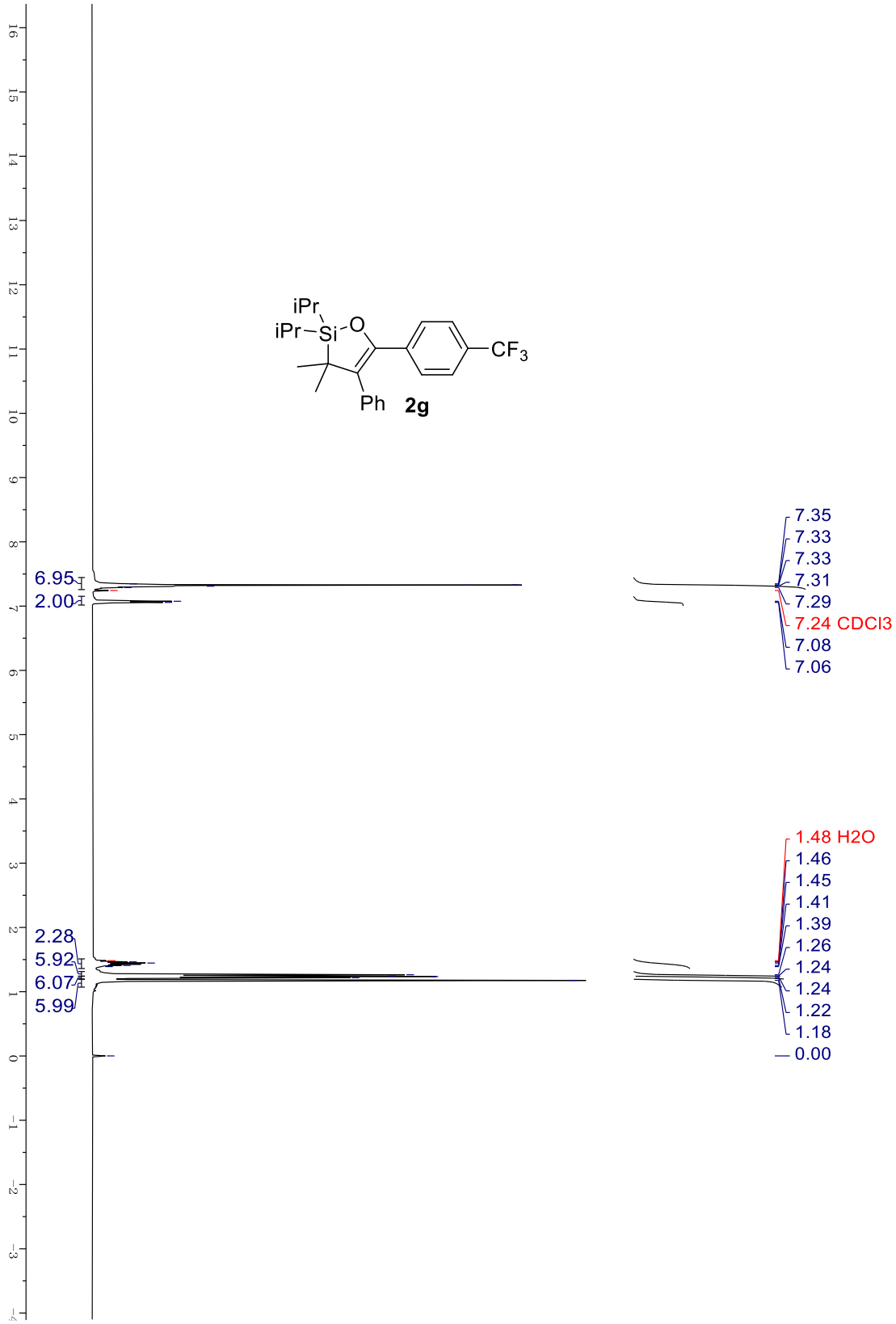

iPr
iPr
Si
O
F
Ph
2e
2.93
2.10
2.00
1.94
2.09
6.00
6.03
6.02
7.32
7.32
7.28
7.27
7.26 CDCl3
7.24
7.23
7.22
7.21
7.20
7.19
7.07
7.05
6.78
6.76
6.74
1.51 H2O
1.49
1.47
1.45
1.43
1.41
1.40
1.38
1.26
1.24
1.23
1.21
1.16
-0.00

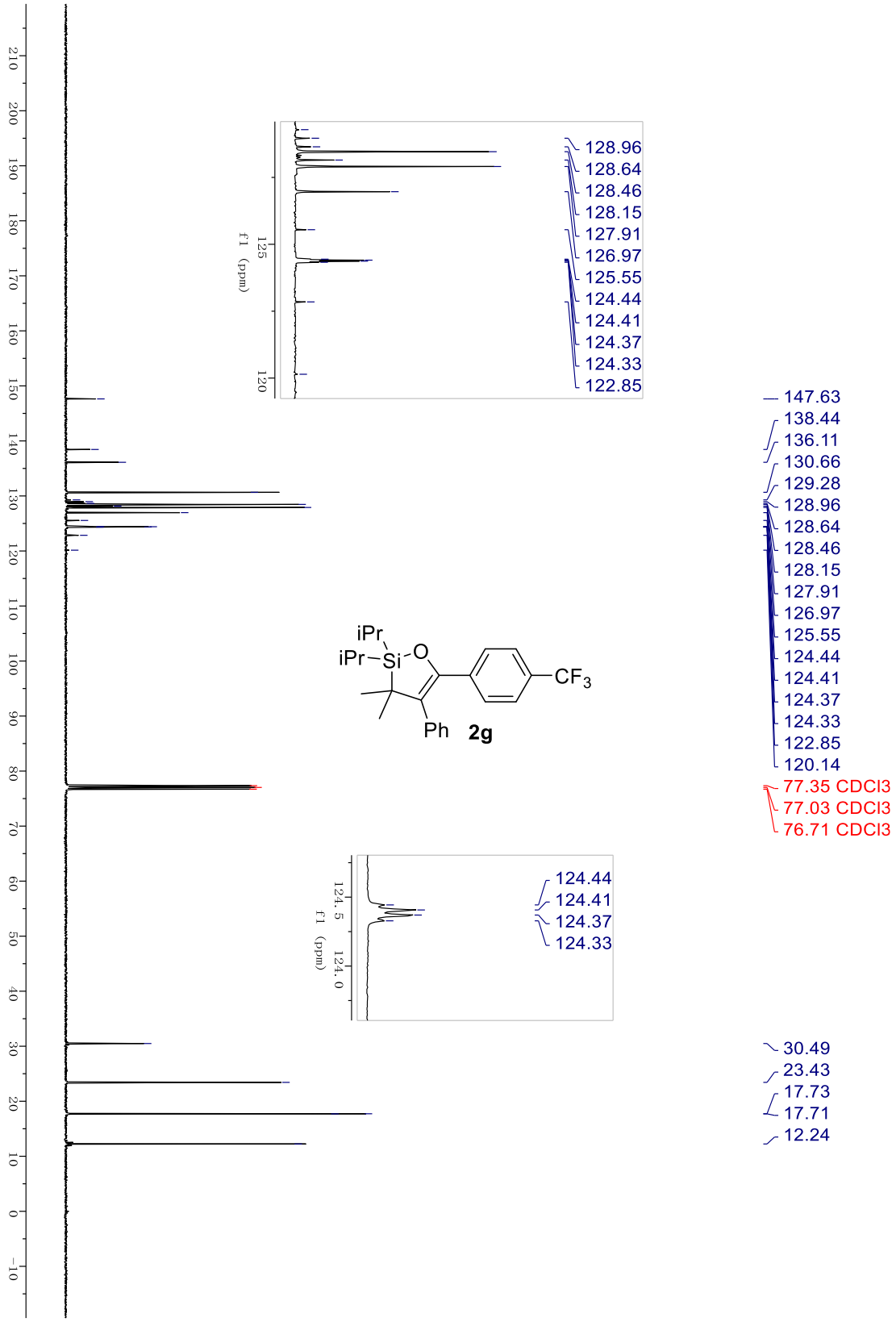

iPr
iPr
Si
O
F
Ph
2e
163.08
160.62
148.04
136.64
131.16
131.13
130.87
129.66
129.58
128.31
126.66
125.41
114.46
114.24
77.36 CDCl3
77.05 CDCl3
76.73 CDCl3
30.24
23.57
17.78
12.25

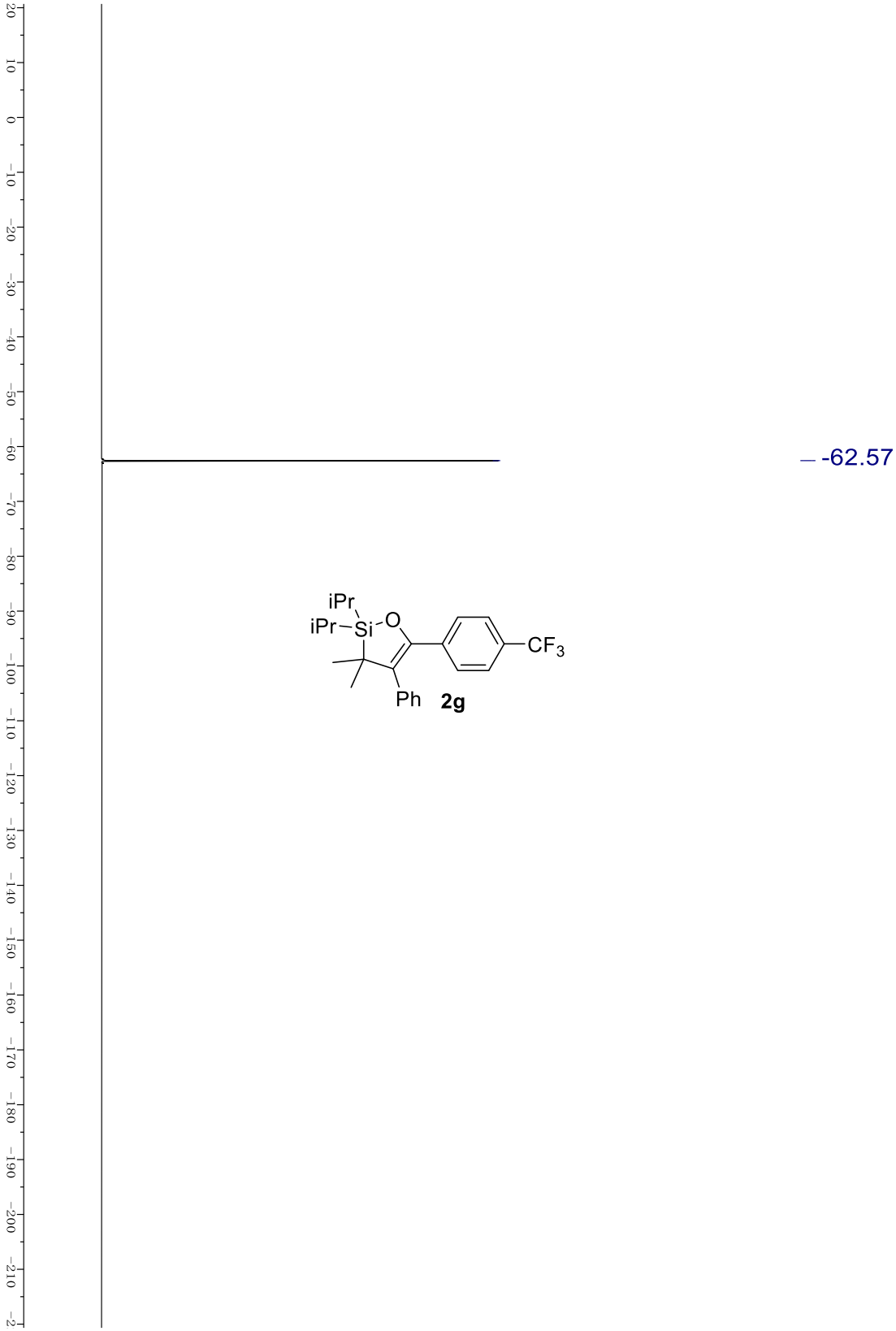

iPr
iPr
Si
O
F
Ph
2e
-114.48
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-2

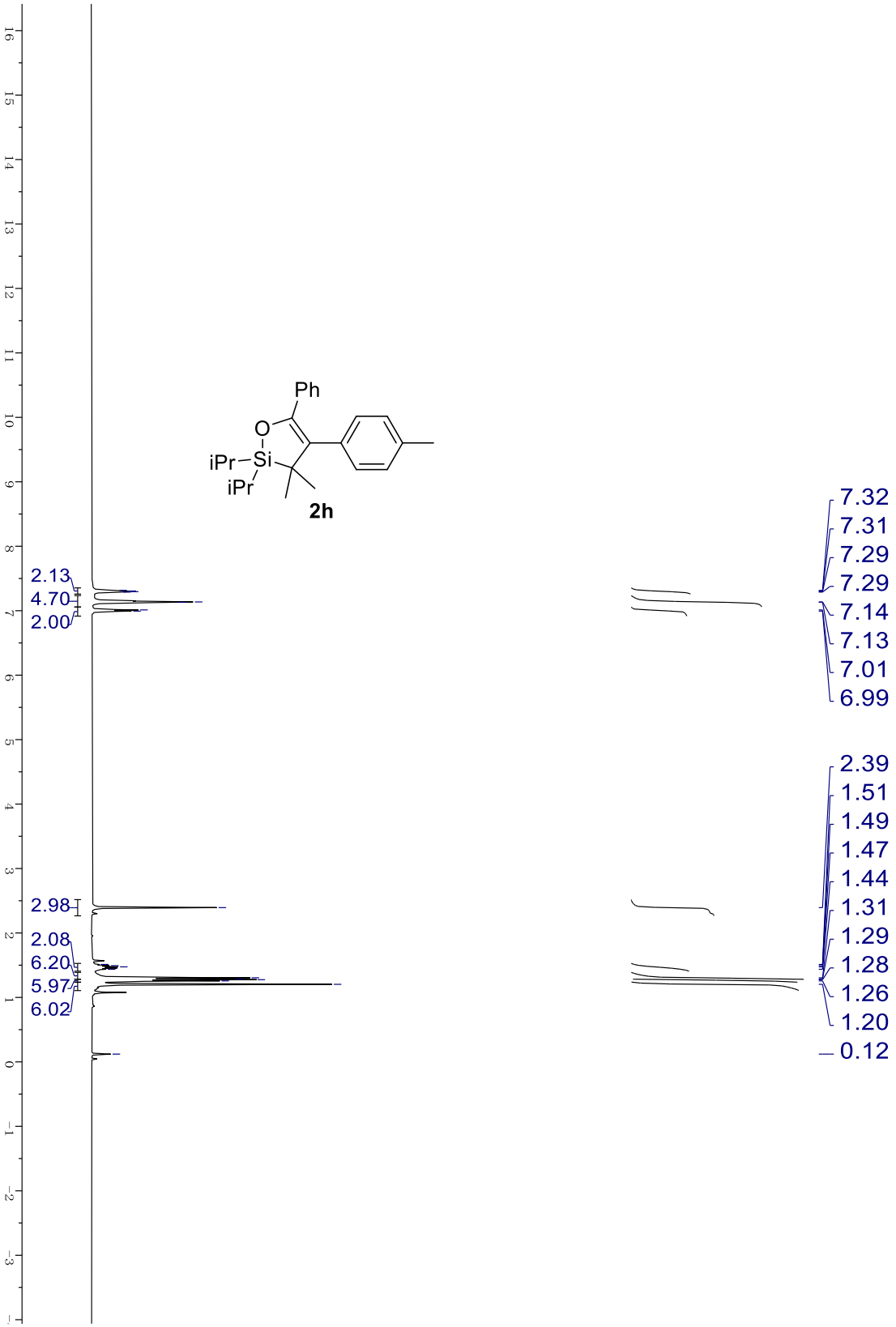

Cl
iPr
Si
O
iPr
Ph
2f
7.32
7.31
7.29
7.28
7.27
7.25
7.16
7.14
7.06
7.05
7.05
7.03
1.47
1.45
1.43
1.41
1.39
1.38
1.25
1.23
1.21
1.16
-0.00
3.09
2.00
3.94
2.16
11.88
6.10

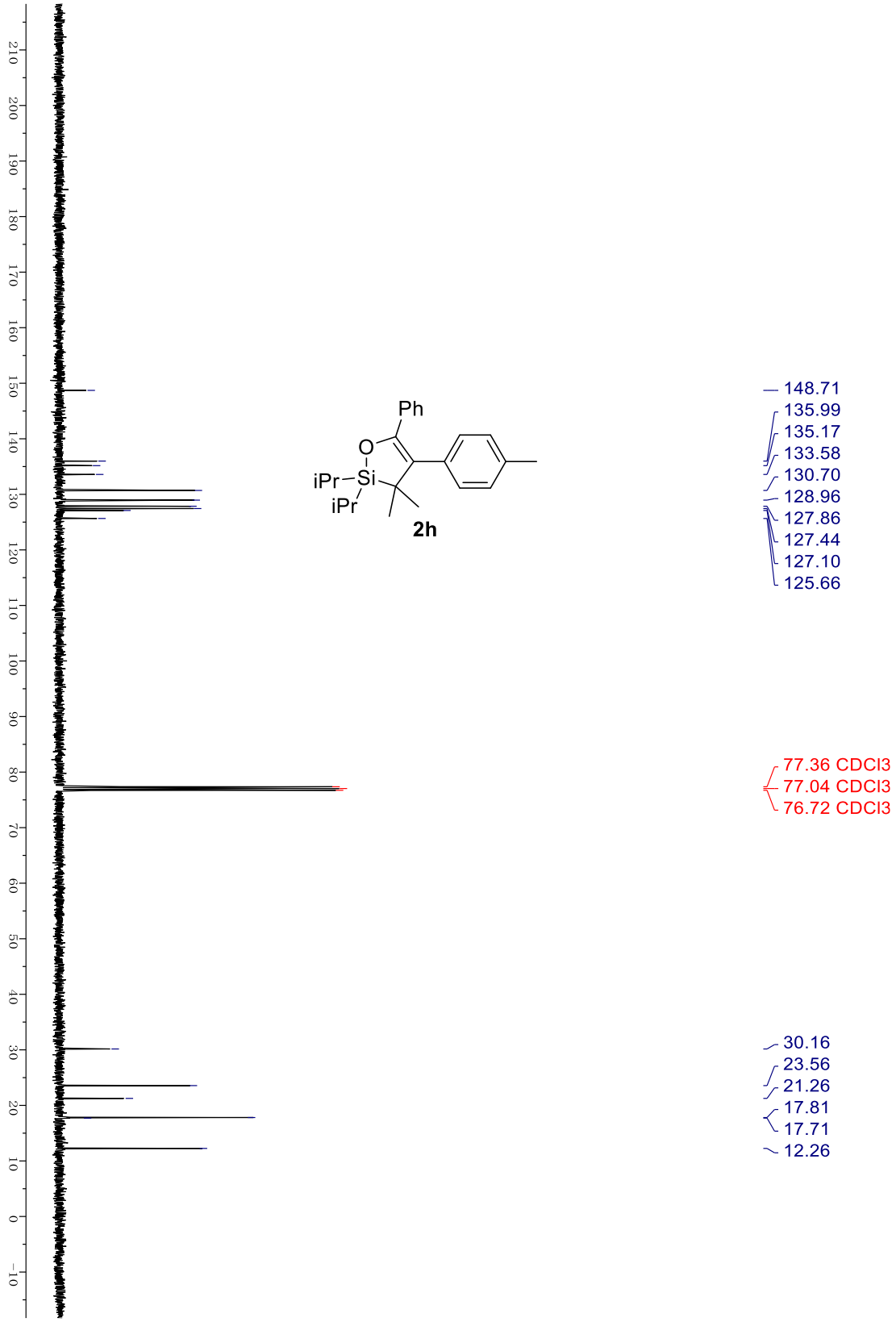

147.88
136.45
133.46
132.84
130.75
129.12
128.36
127.65
126.76
126.38
77.26 CDCl3
77.05 CDCl3
76.84 CDCl3
30.30
23.50
17.77
12.24
Cl
iPr
iPr
Si
O
Ph
2f

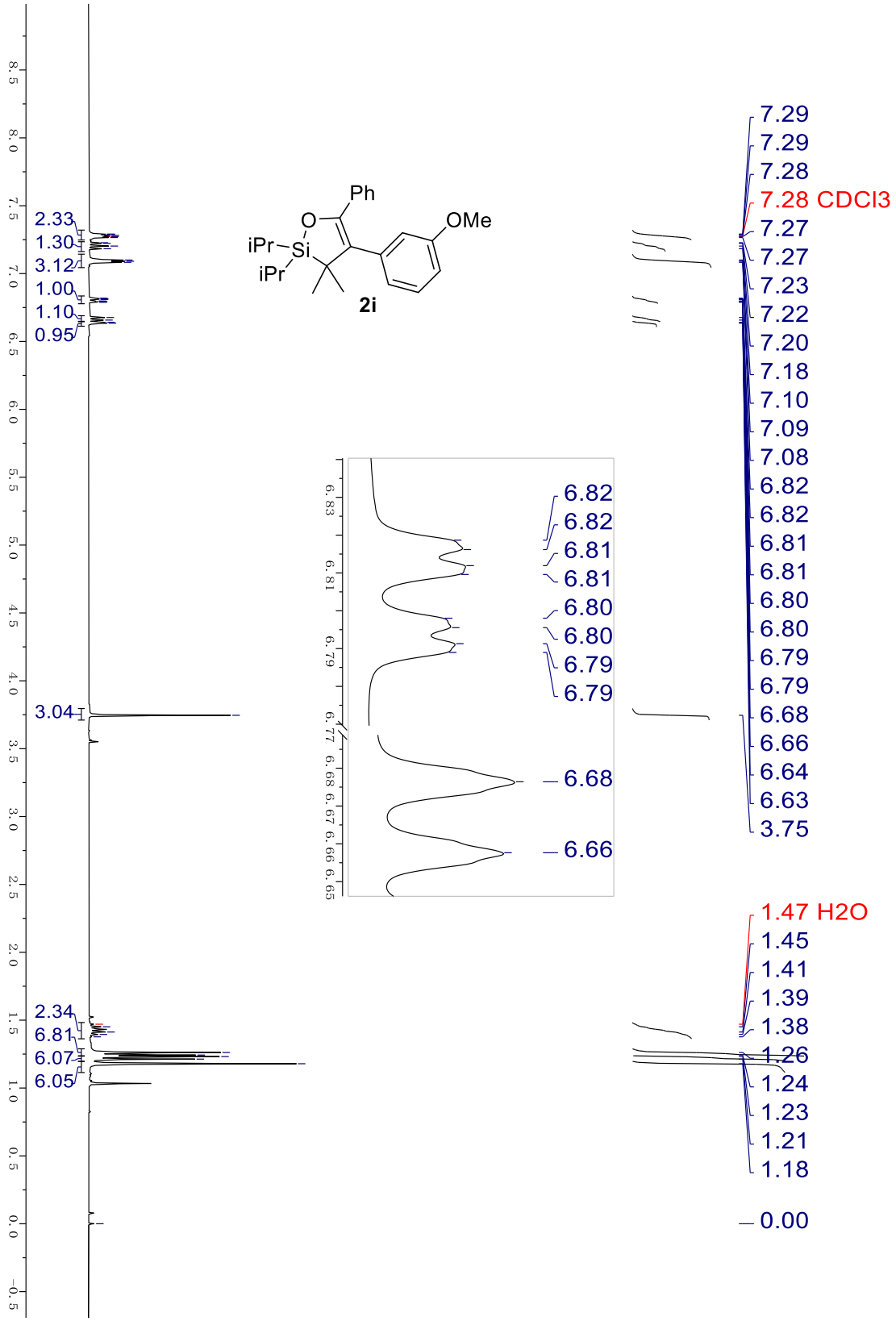

iPr
iPr
Si
O
CF3
Ph
2g
6.95
2.00
7.35
7.33
7.33
7.31
7.29
7.24 CDCl3
7.08
7.06
2.28
5.92
6.07
5.99
1.48 H2O
1.46
1.45
1.41
1.39
1.26
1.24
1.24
1.22
1.18
0.00

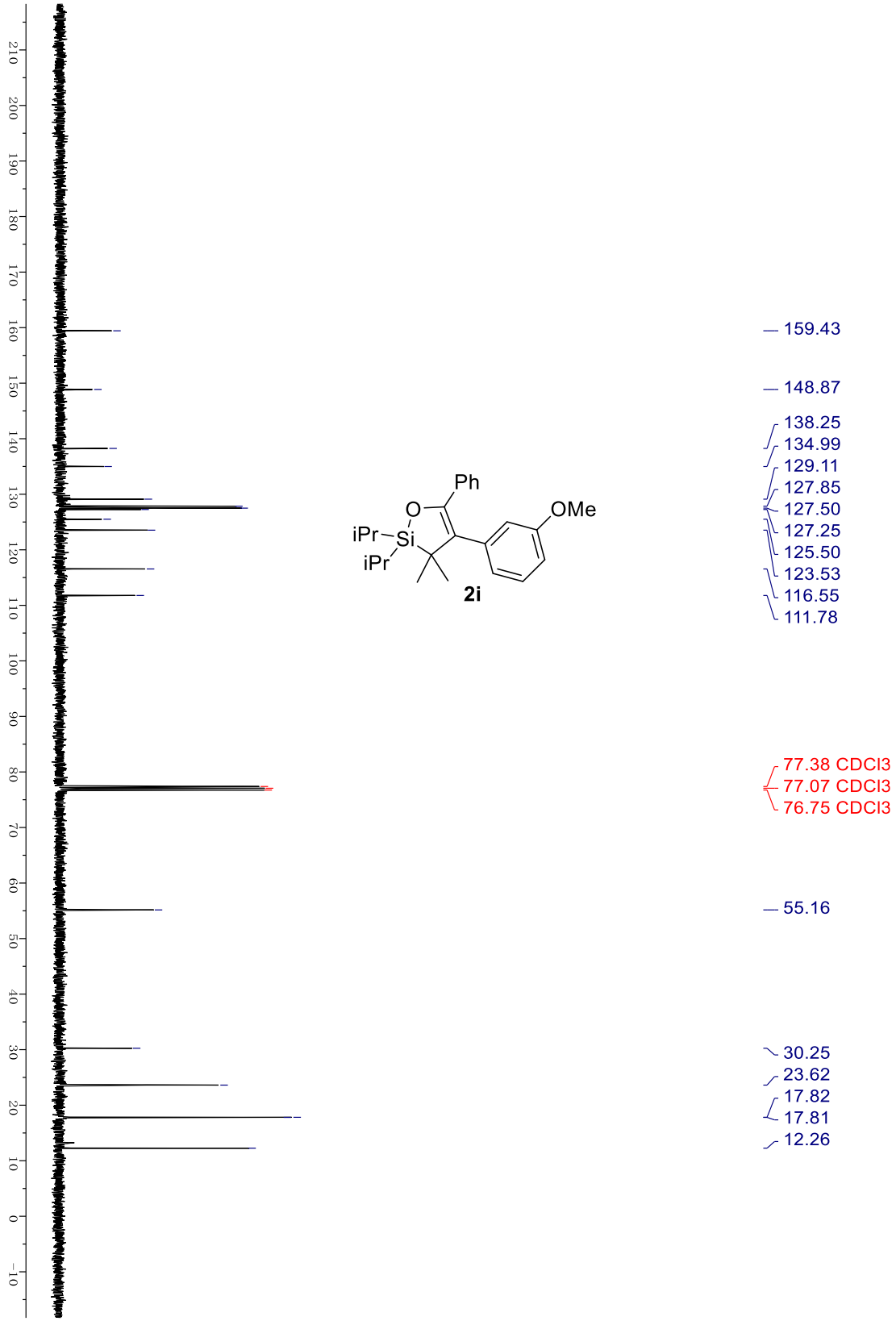

128.96
128.64
128.46
128.15
127.91
126.97
125.55
124.44
124.41
124.37
124.33
122.85
f1 (ppm)
125
120
147.63
138.44
136.11
130.66
129.28
128.96
128.64
128.46
128.15
127.91
126.97
125.55
124.44
124.41
124.37
124.33
122.85
120.14
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
iPr
iPr
Si
O
CF3
Ph
2g
124.44
124.41
124.37
124.33
f1 (ppm)
124.5
124.0
30.49
23.43
17.73
17.71
12.24

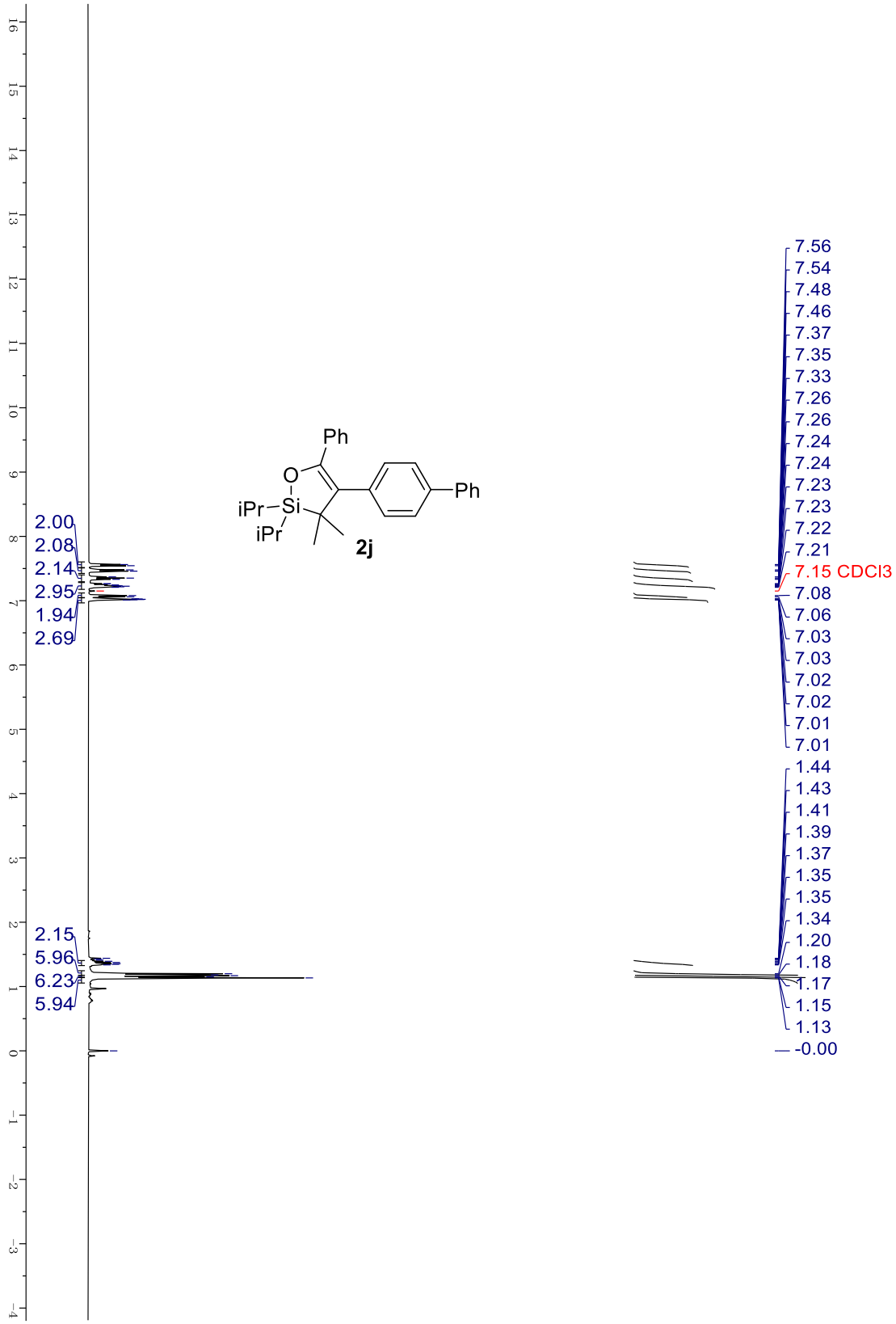

-62.57
iPr
iPr
Si
O
CF3
Ph
2g

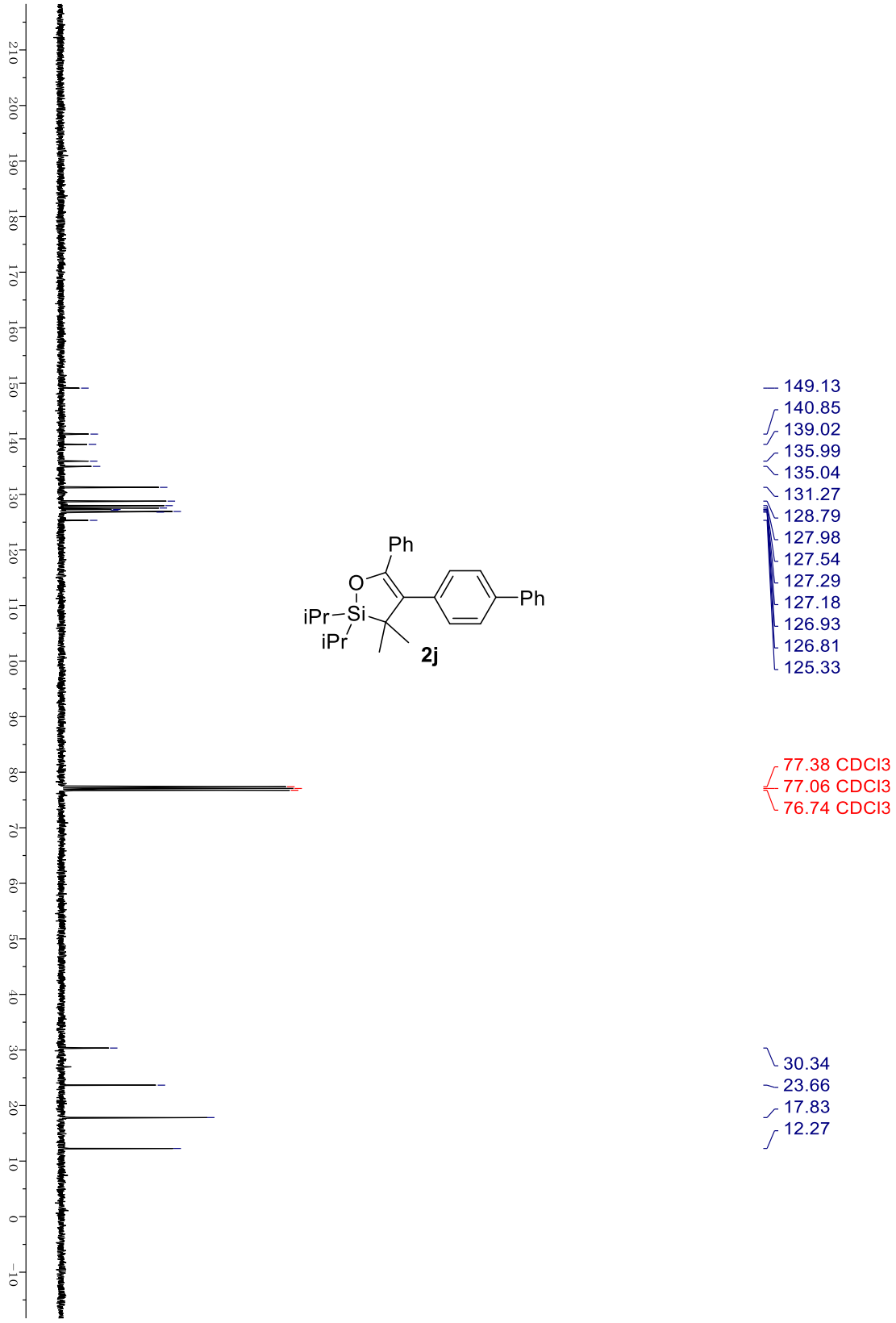

Ph
O
iPr
Si
iPr
2h
2.13
4.70
2.00
2.98
2.08
6.20
5.97
6.02
7.32
7.31
7.29
7.29
7.14
7.13
7.01
6.99
2.39
1.51
1.49
1.47
1.44
1.31
1.29
1.28
1.26
1.20
0.12

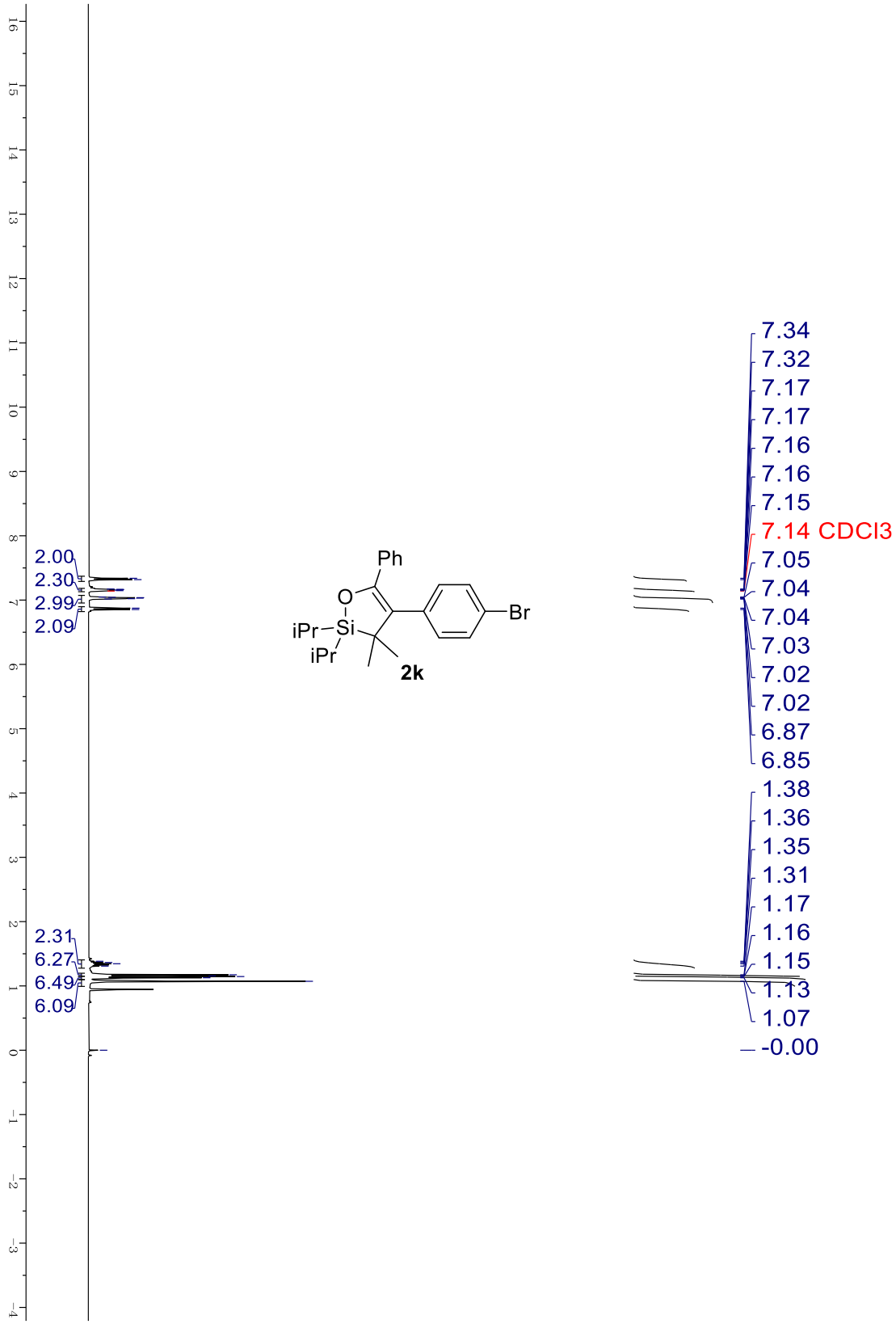

Ph
O
iPr
Si
iPr
2h
148.71
135.99
135.17
133.58
130.70
128.96
127.86
127.44
127.10
125.66
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
30.16
23.56
21.26
17.81
17.71
12.26

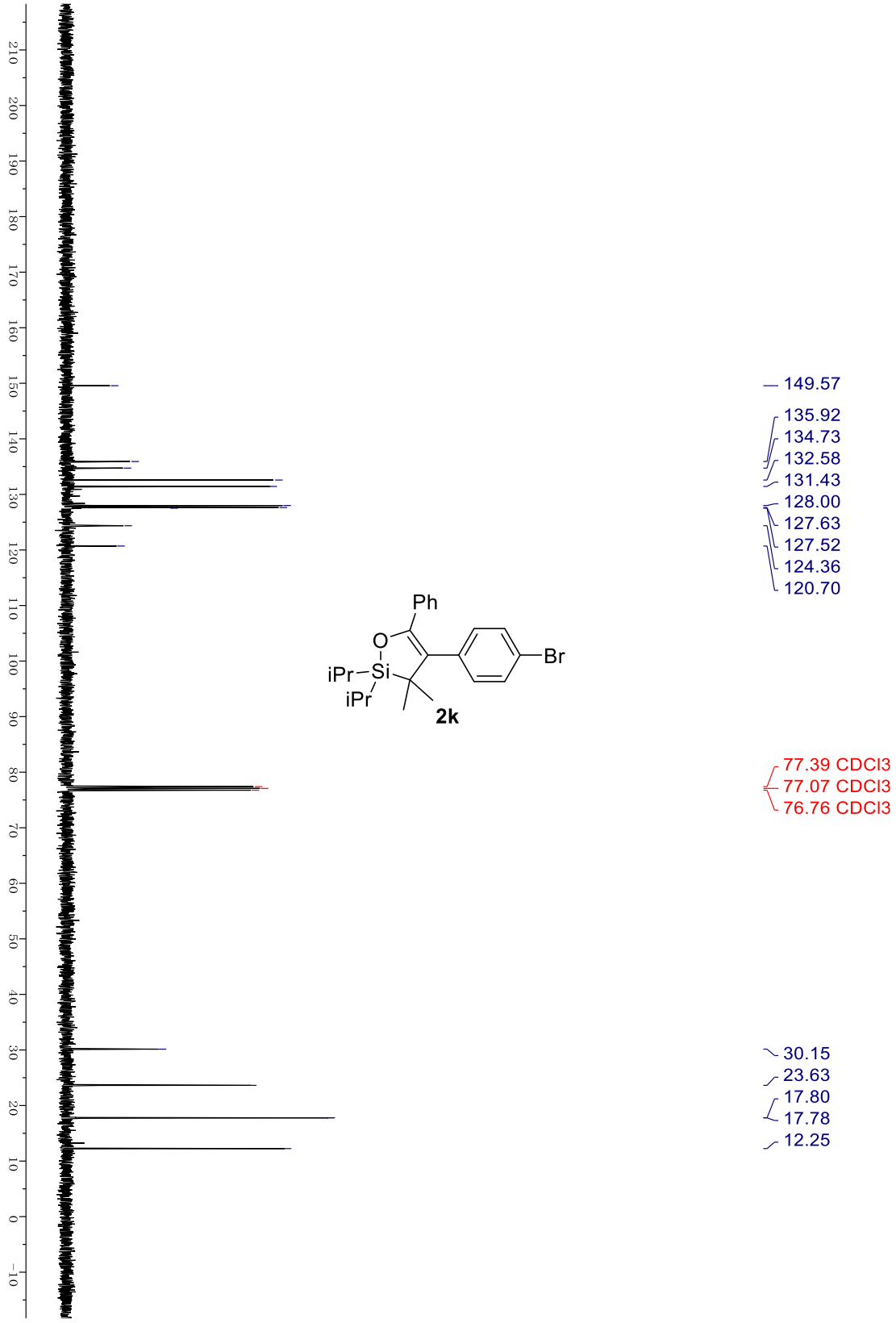

Ph
O
OMe
iPr
Si
iPr
2i
2.33
1.30
3.12
1.00
1.10
0.95
3.04
2.34
6.81
6.07
6.05
7.29
7.29
7.28
7.28 CDCl3
7.27
7.27
7.23
7.22
7.20
7.18
7.10
7.09
7.08
6.82
6.82
6.82
6.81
6.81
6.81
6.80
6.80
6.80
6.79
6.79
6.79
6.68
6.66
6.64
6.63
3.75
6.68
6.66
1.47 H2O
1.45
1.41
1.39
1.38
1.26
1.24
1.23
1.21
1.18
0.00

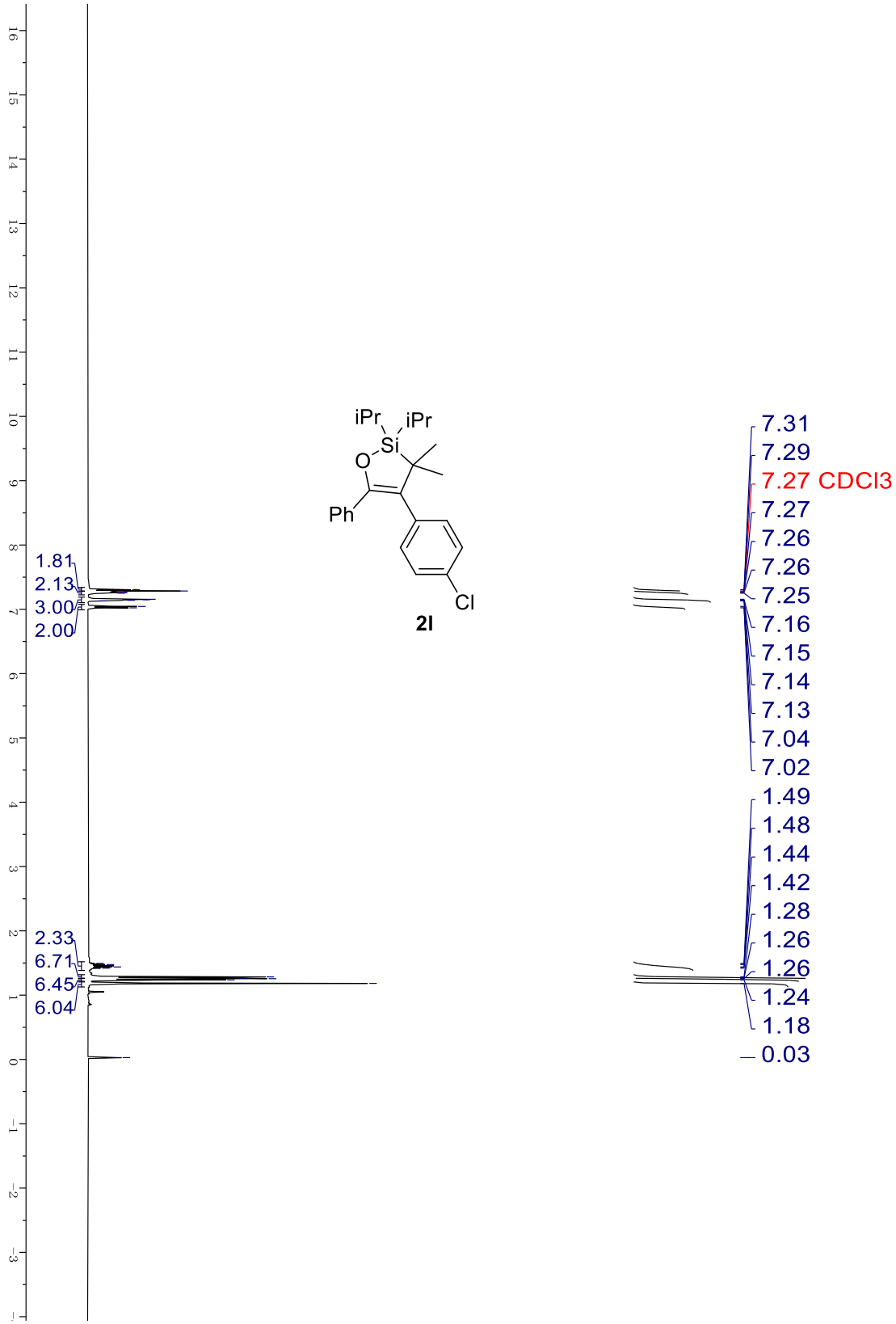

159.43
148.87
138.25
134.99
129.11
127.85
127.50
127.25
125.50
123.53
116.55
111.78
77.38 CDCl3
77.07 CDCl3
76.75 CDCl3
55.16
30.25
23.62
17.82
17.81
12.26
Ph
O
iPr
Si
iPr
OMe
2i


Ph
O
iPr
Si
iPr
Ph
2j
2.00
2.08
2.14
2.95
1.94
2.69
2.15
5.96
6.23
5.94
7.56
7.54
7.48
7.46
7.37
7.35
7.33
7.26
7.26
7.24
7.24
7.23
7.23
7.22
7.21
7.15 CDCl3
7.08
7.06
7.03
7.03
7.02
7.02
7.01
7.01
1.44
1.43
1.41
1.39
1.37
1.35
1.35
1.34
1.20
1.18
1.17
1.15
1.13
-0.00


149.13
140.85
139.02
135.99
135.04
131.27
128.79
127.98
127.54
127.29
127.18
126.93
126.81
125.33
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
30.34
23.66
17.83
12.27
Ph
O
iPr
Si
iPr
Ph
2j


2.00
2.30
2.99
2.09
2.31
6.27
6.49
6.09
Ph
O
iPr
Si
iPr
Br
2k
7.34
7.32
7.17
7.17
7.16
7.16
7.15
7.14 CDCl3
7.05
7.04
7.04
7.03
7.02
7.02
6.87
6.85
1.38
1.36
1.35
1.31
1.17
1.16
1.15
1.13
1.07
-0.00


149.57
135.92
134.73
132.58
131.43
128.00
127.63
127.52
124.36
120.70
77.39 CDCl3
77.07 CDCl3
76.76 CDCl3
30.15
23.63
17.80
17.78
12.25
Ph
O
iPr
Si
iPr
Br
2k


iPr
iPr
Si
O
Ph
Cl
2l
1.81
2.13
3.00
2.00
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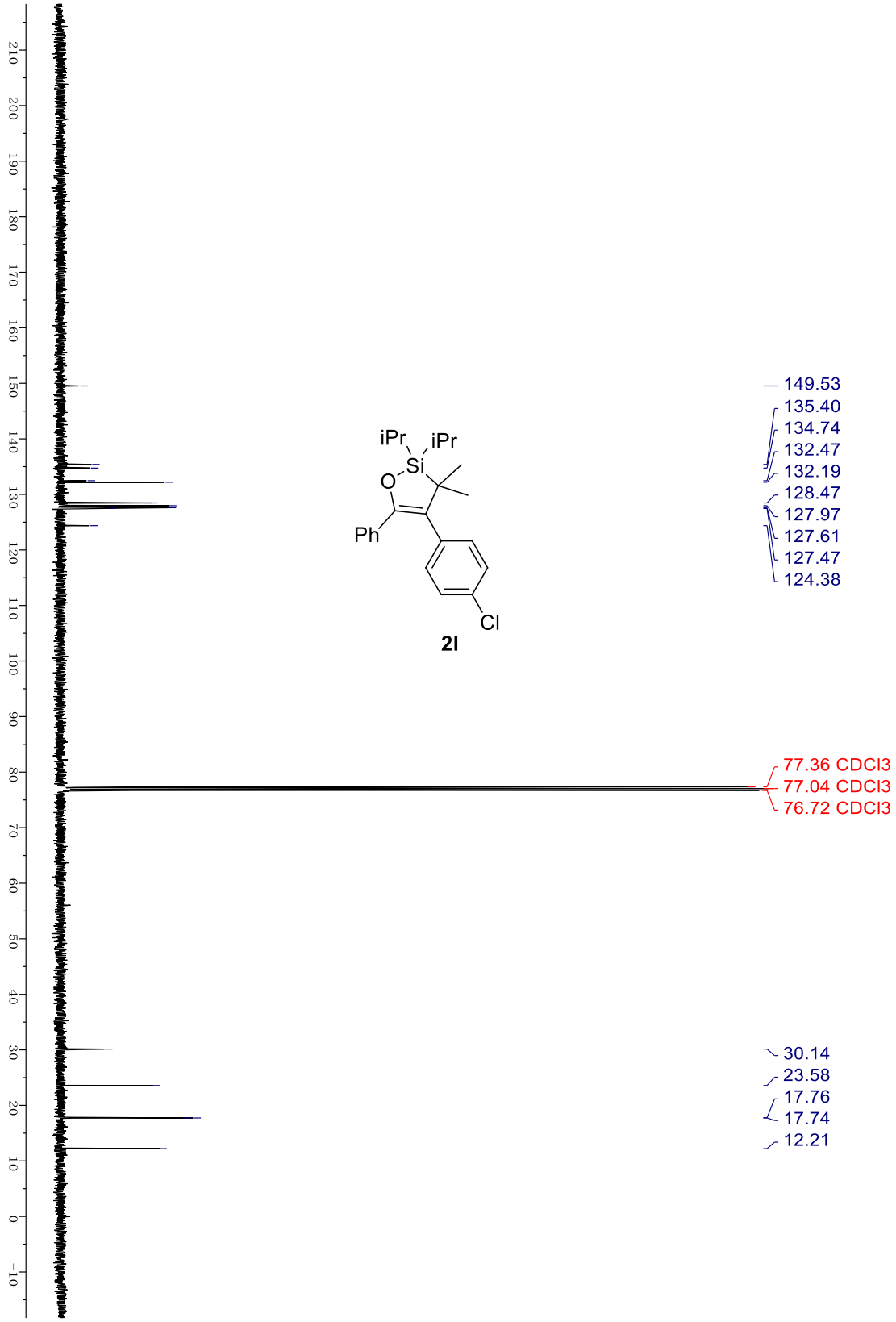
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Cl
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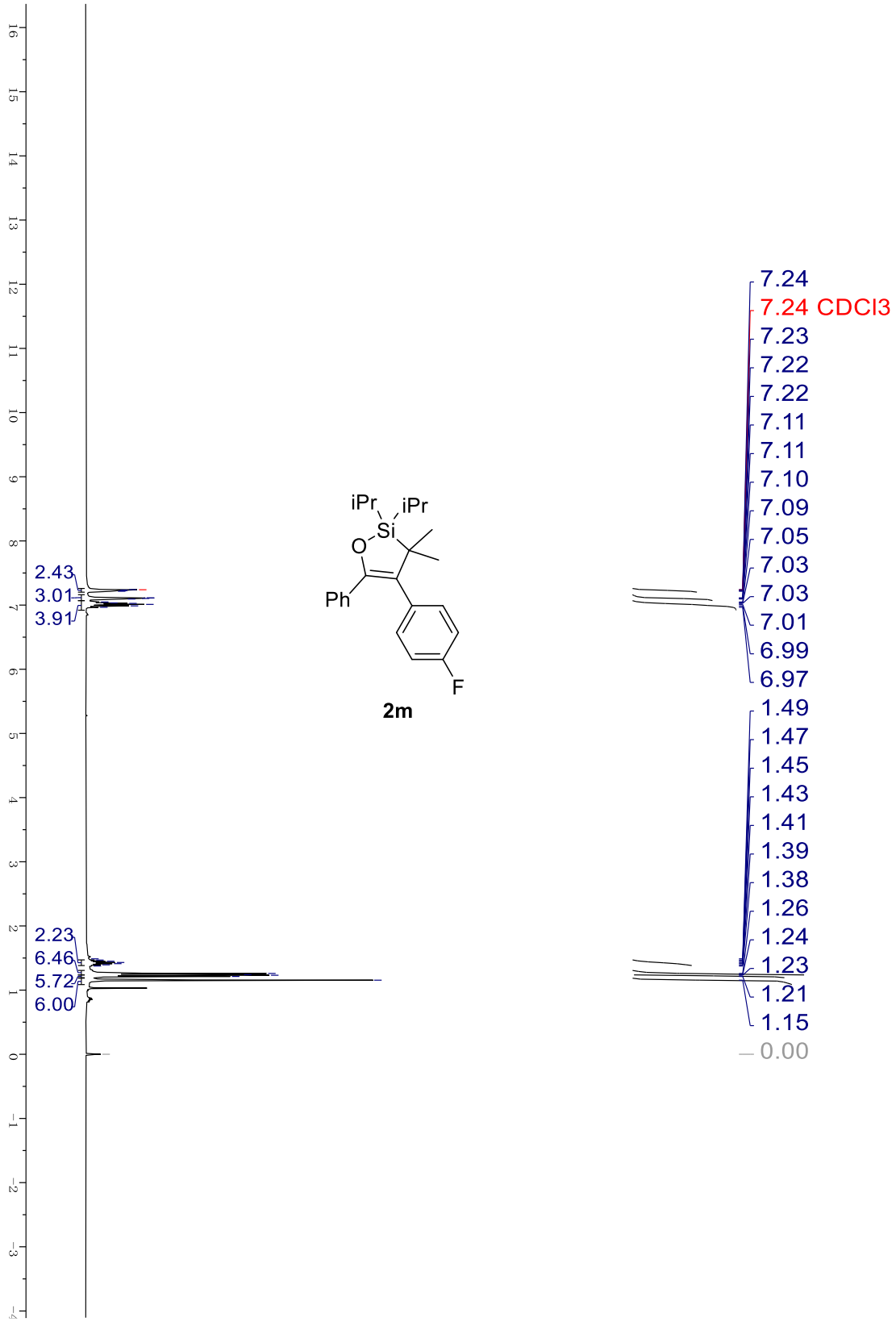
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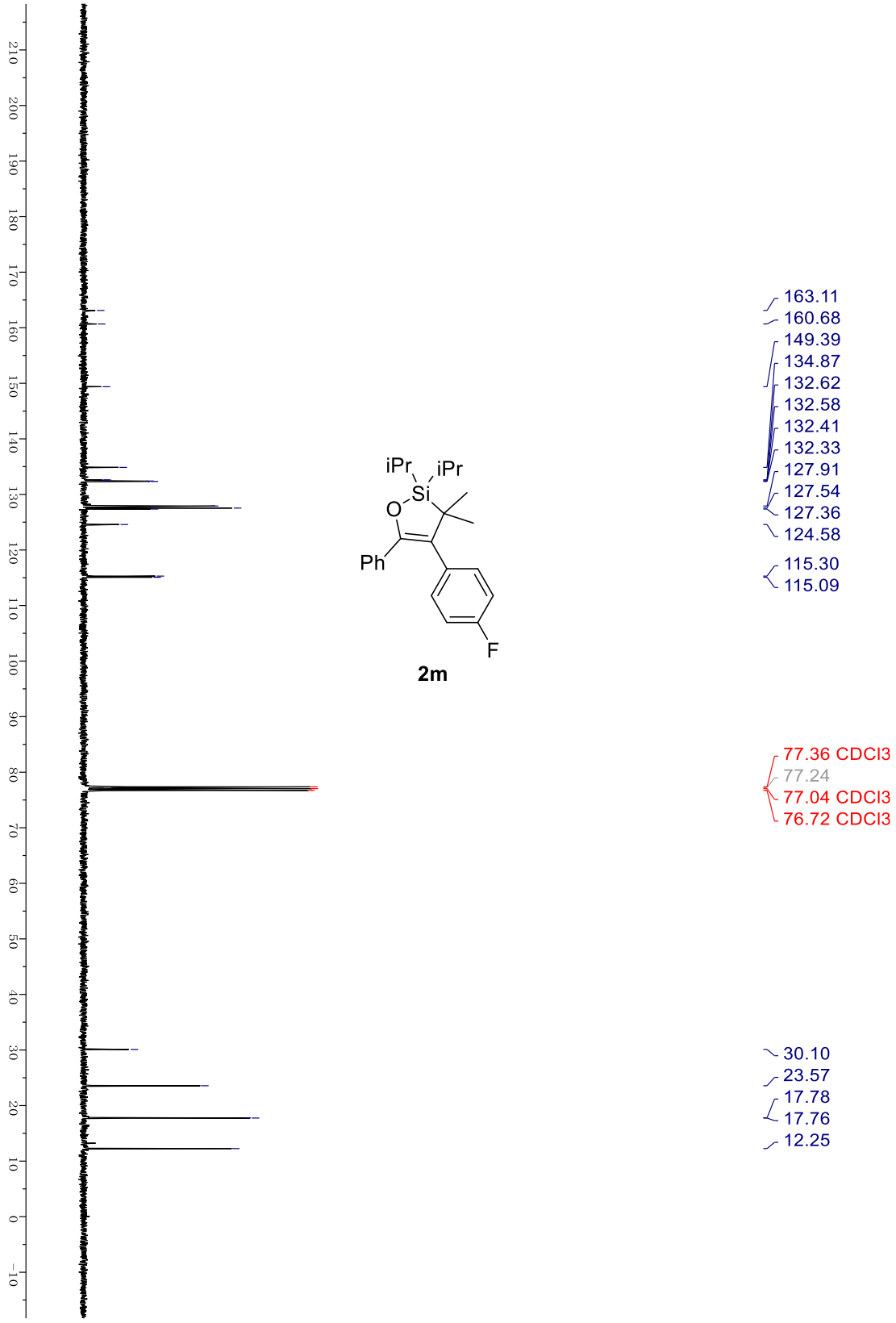
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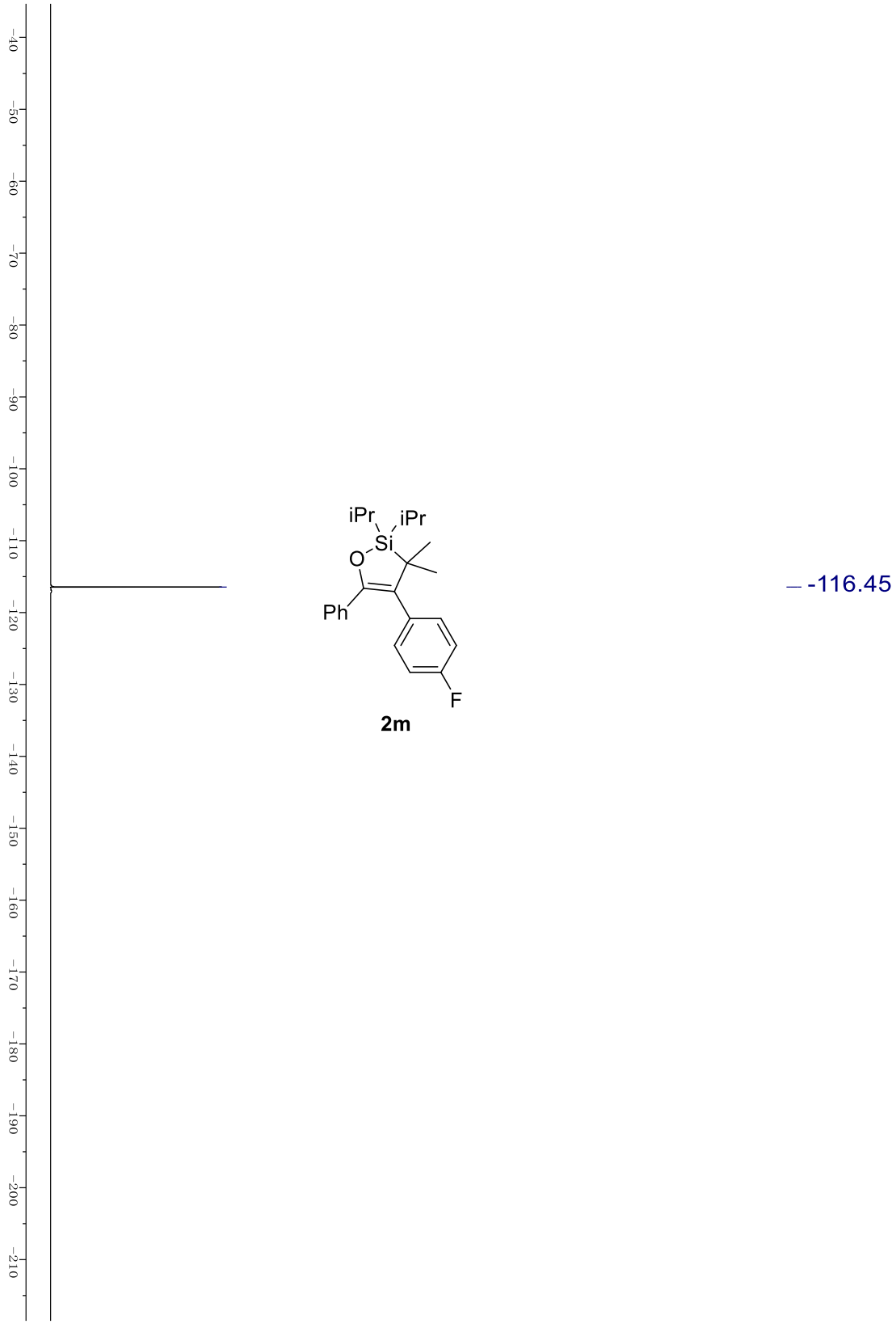
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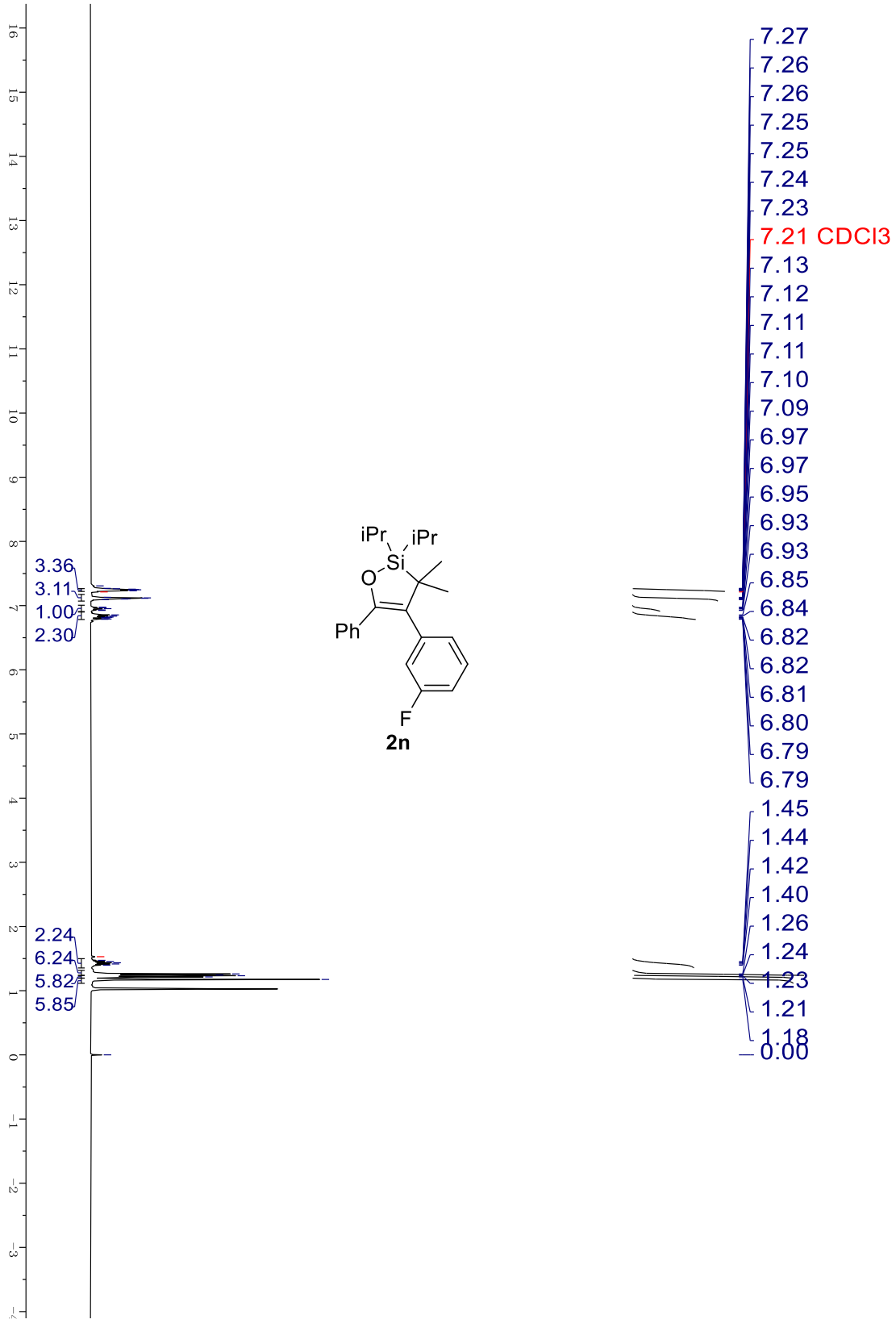
2m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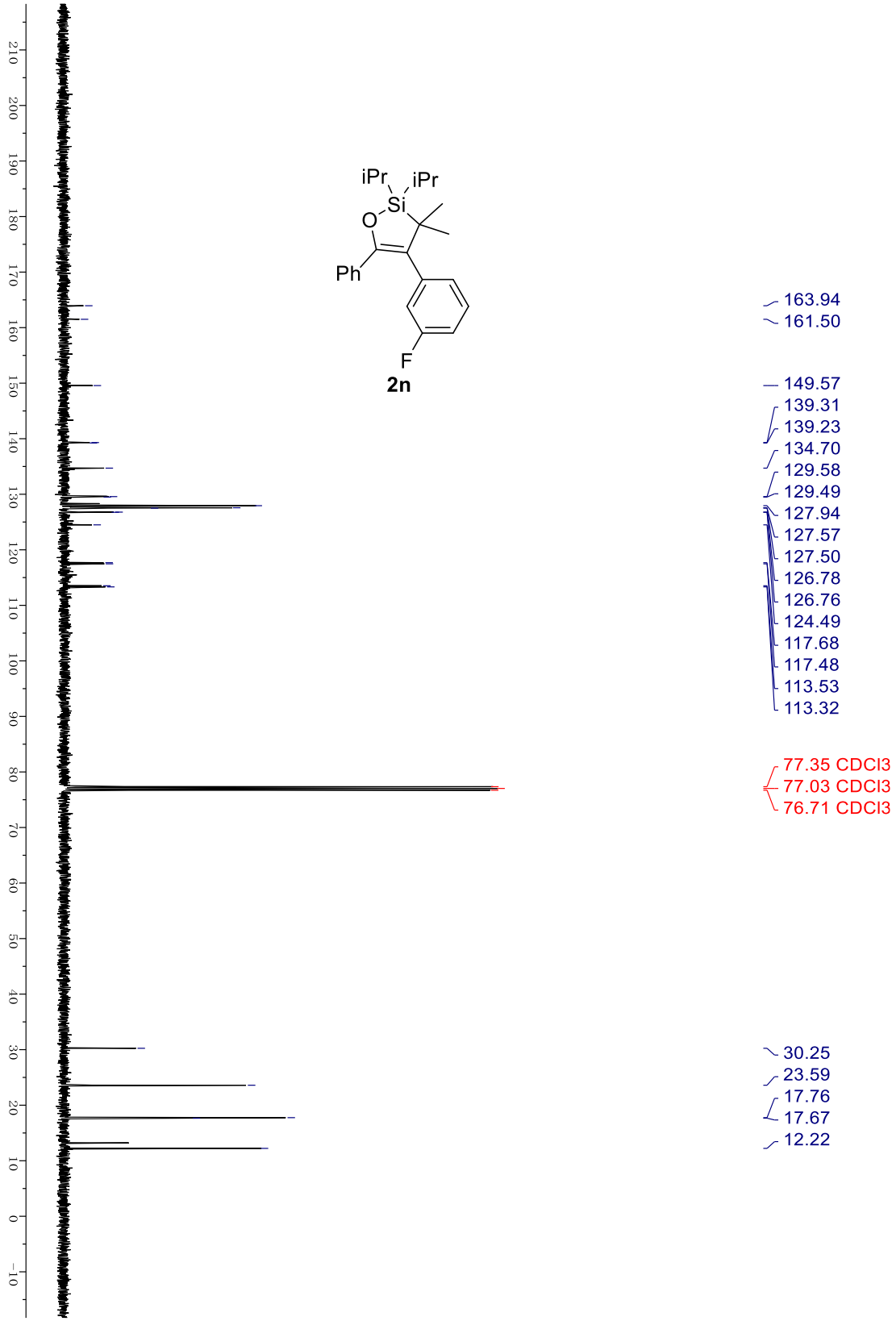
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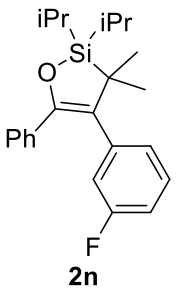
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2n

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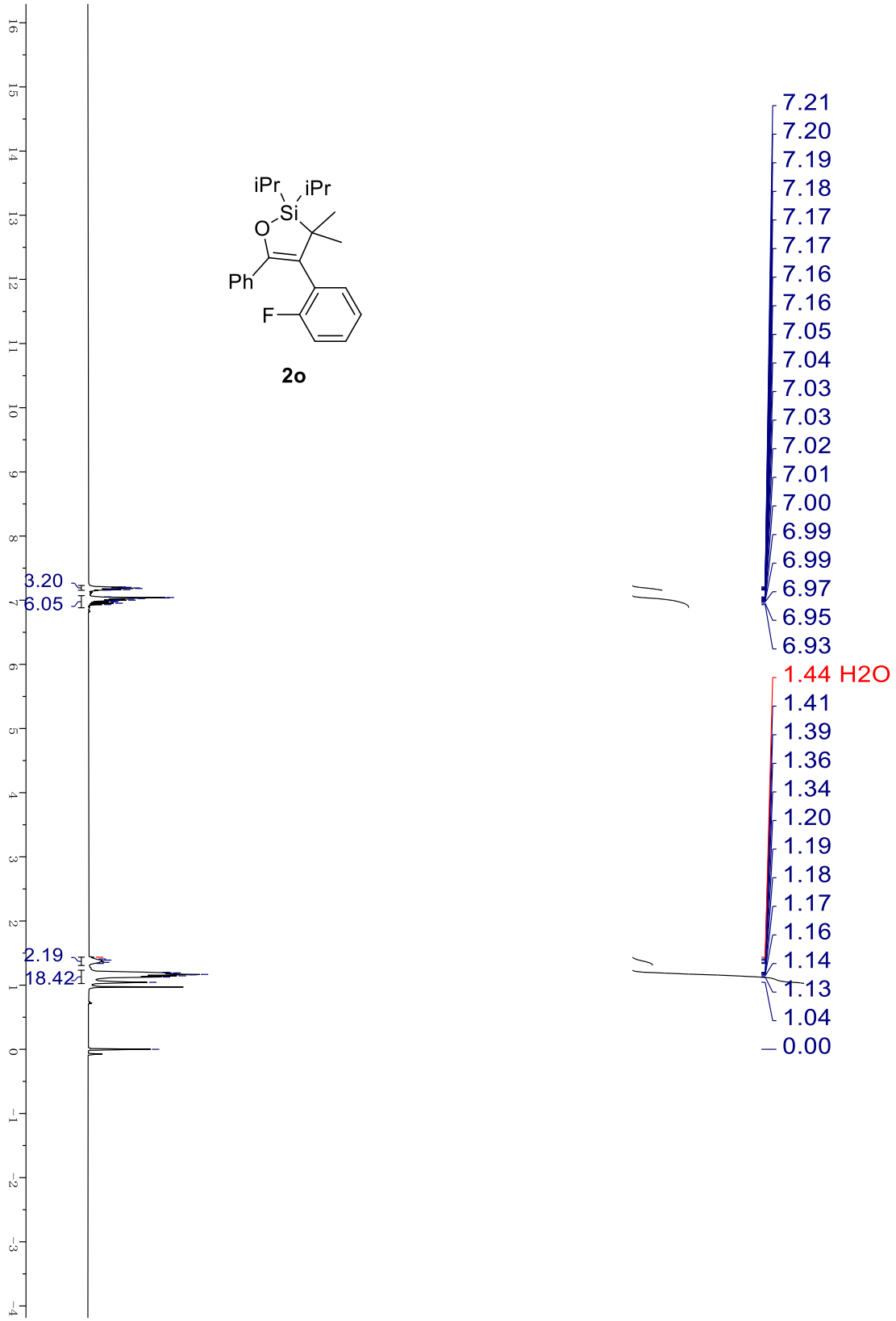
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7.18
7.17
7.17
7.16
7.16
7.05
7.04
7.03
7.03
7.02
7.01
7.00
6.99
6.99
6.97
6.95
6.93
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1.41
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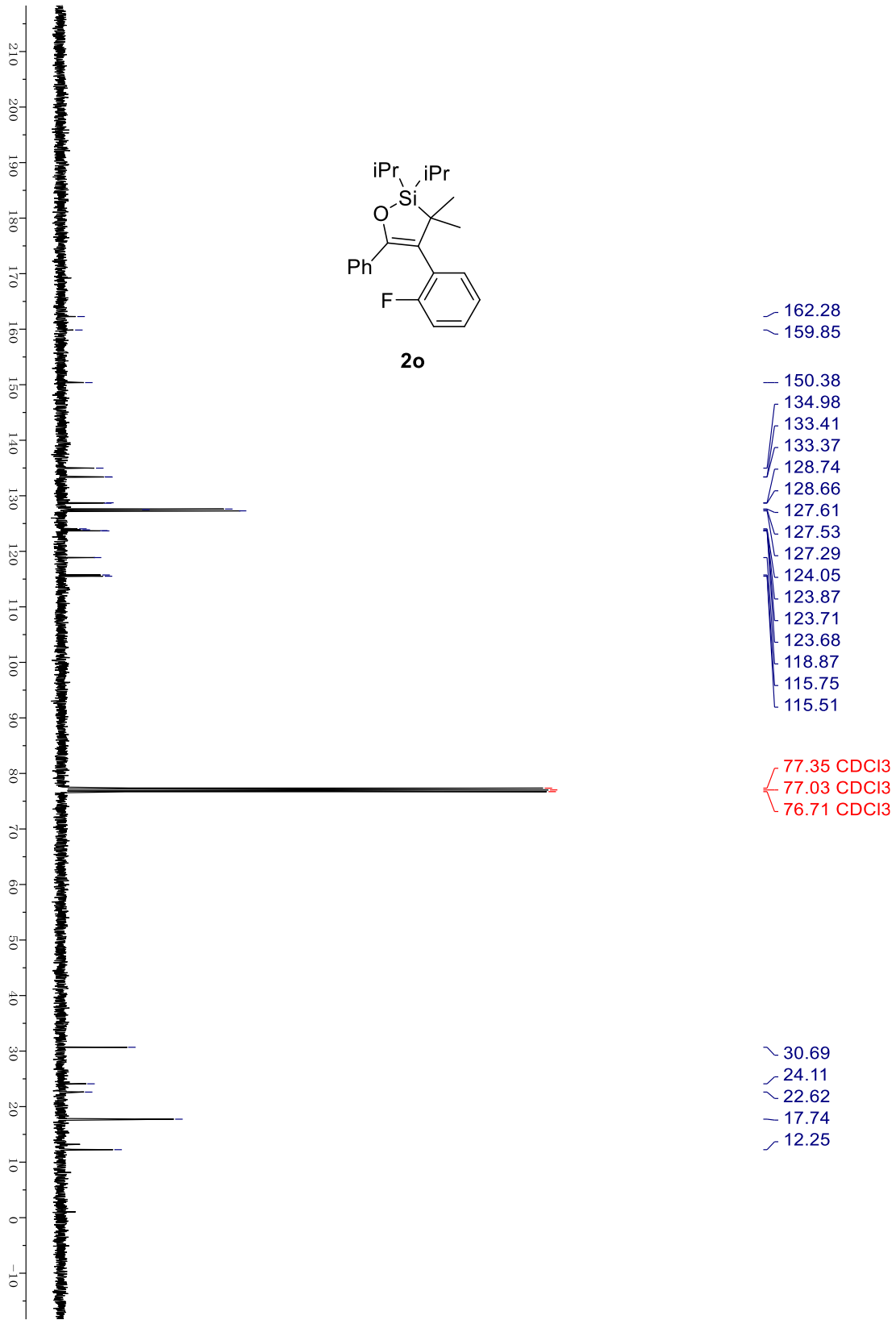
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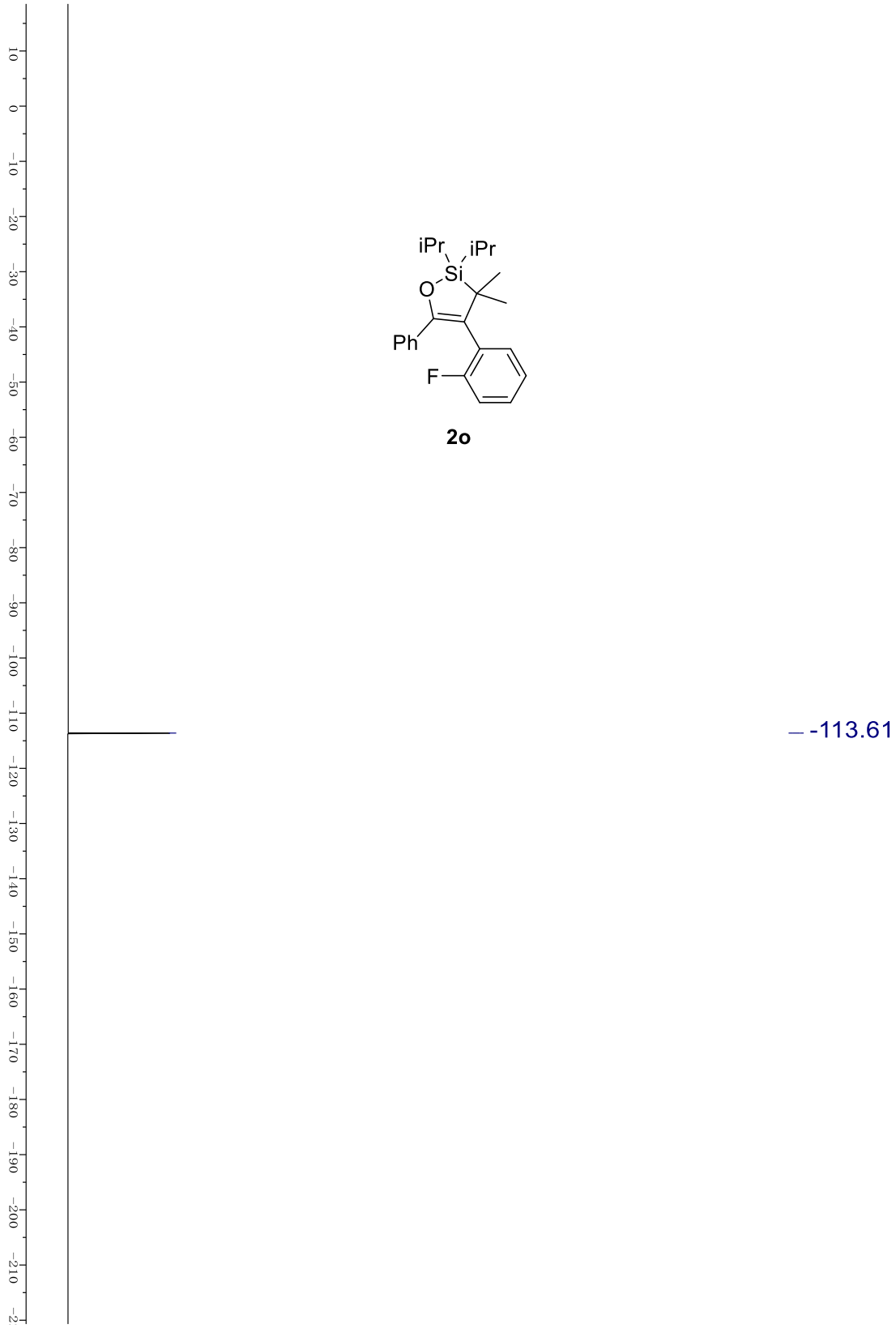
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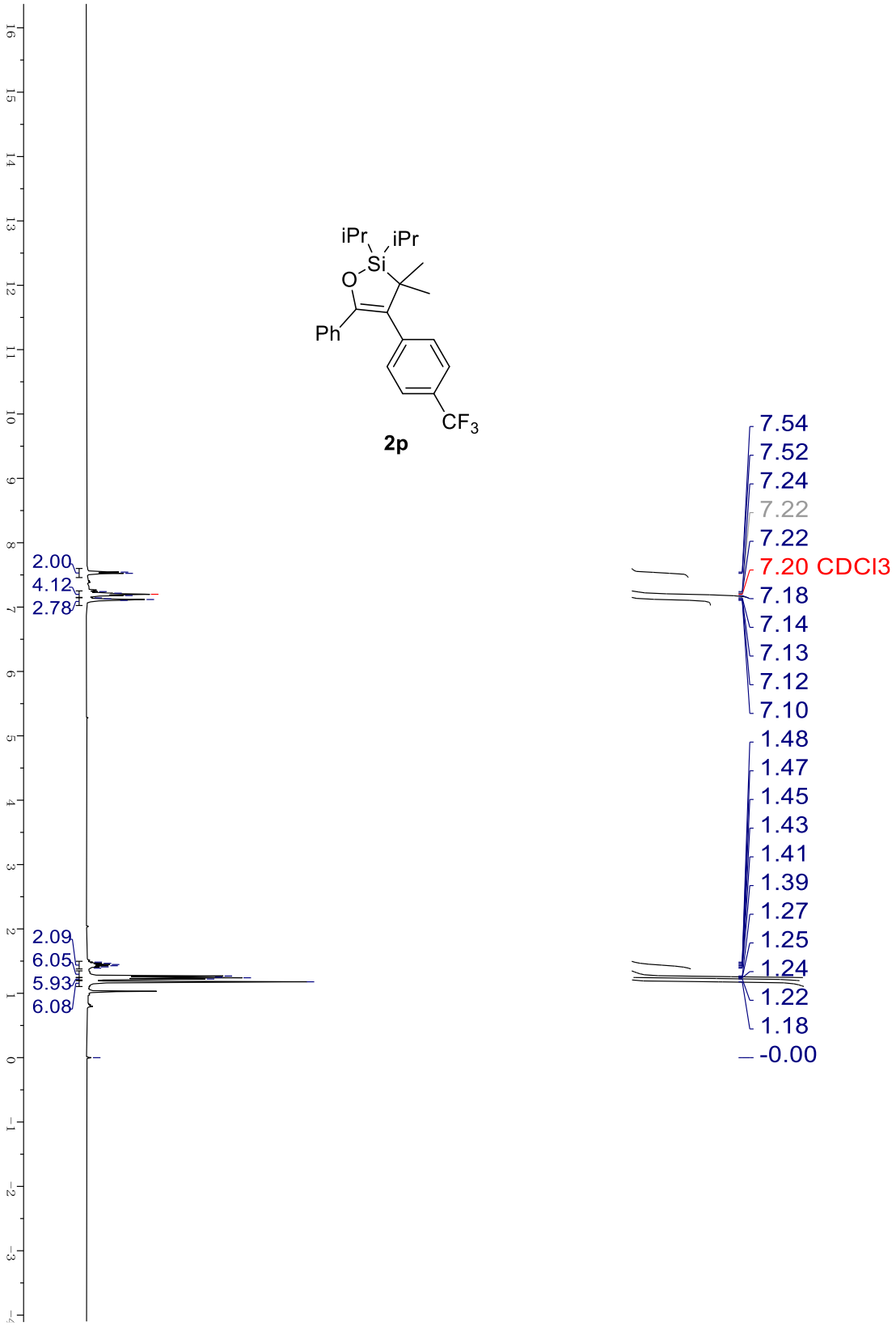
2o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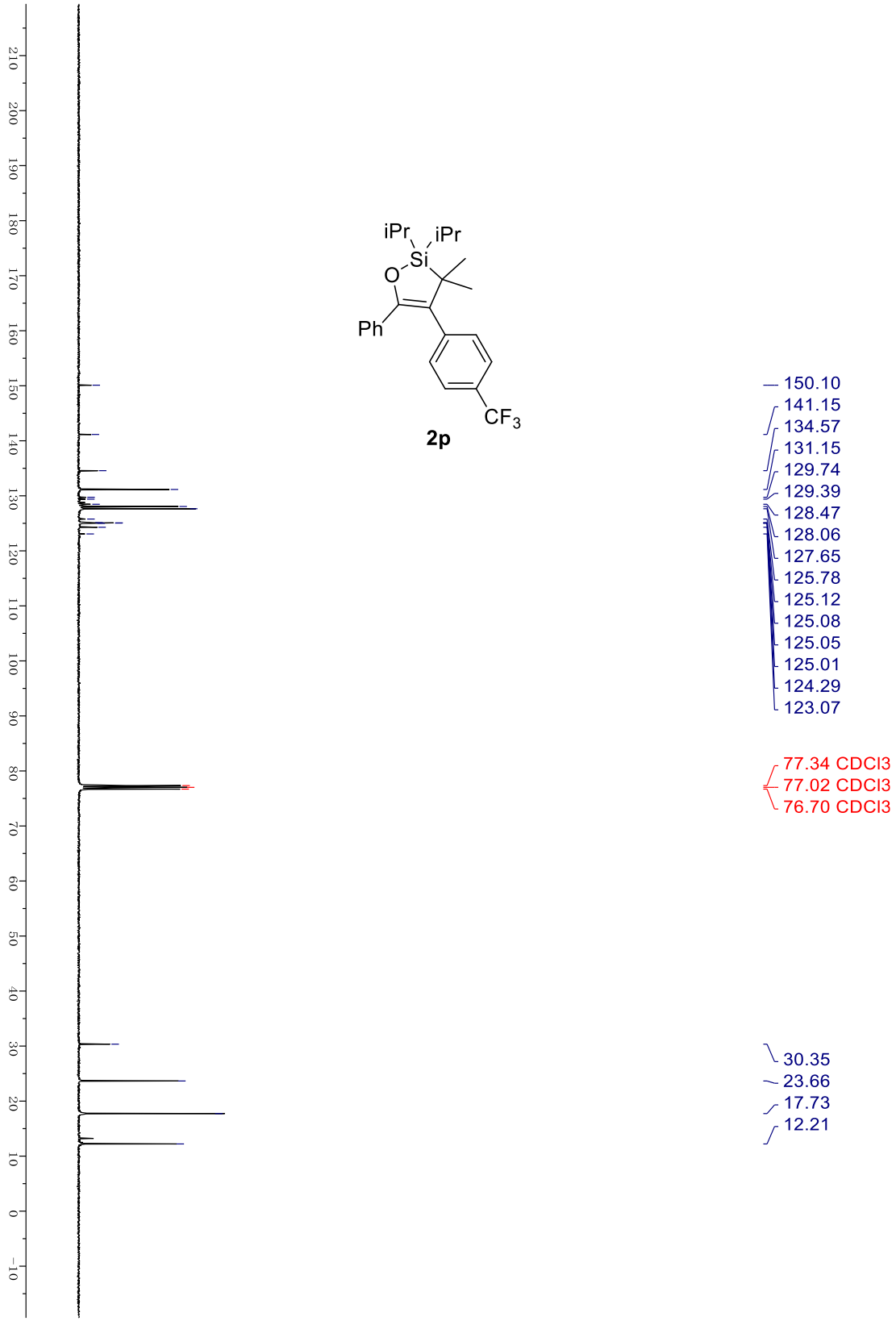
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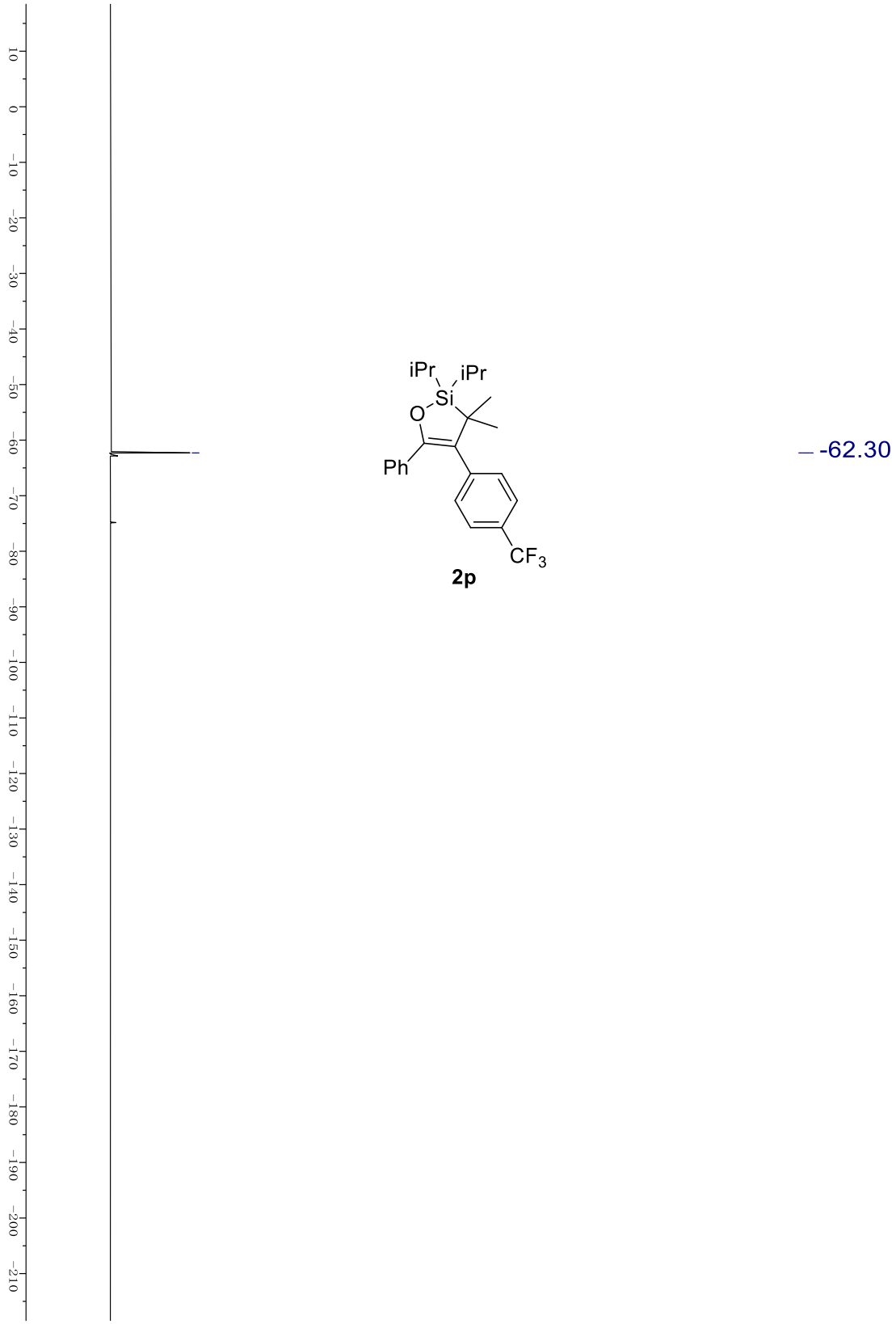
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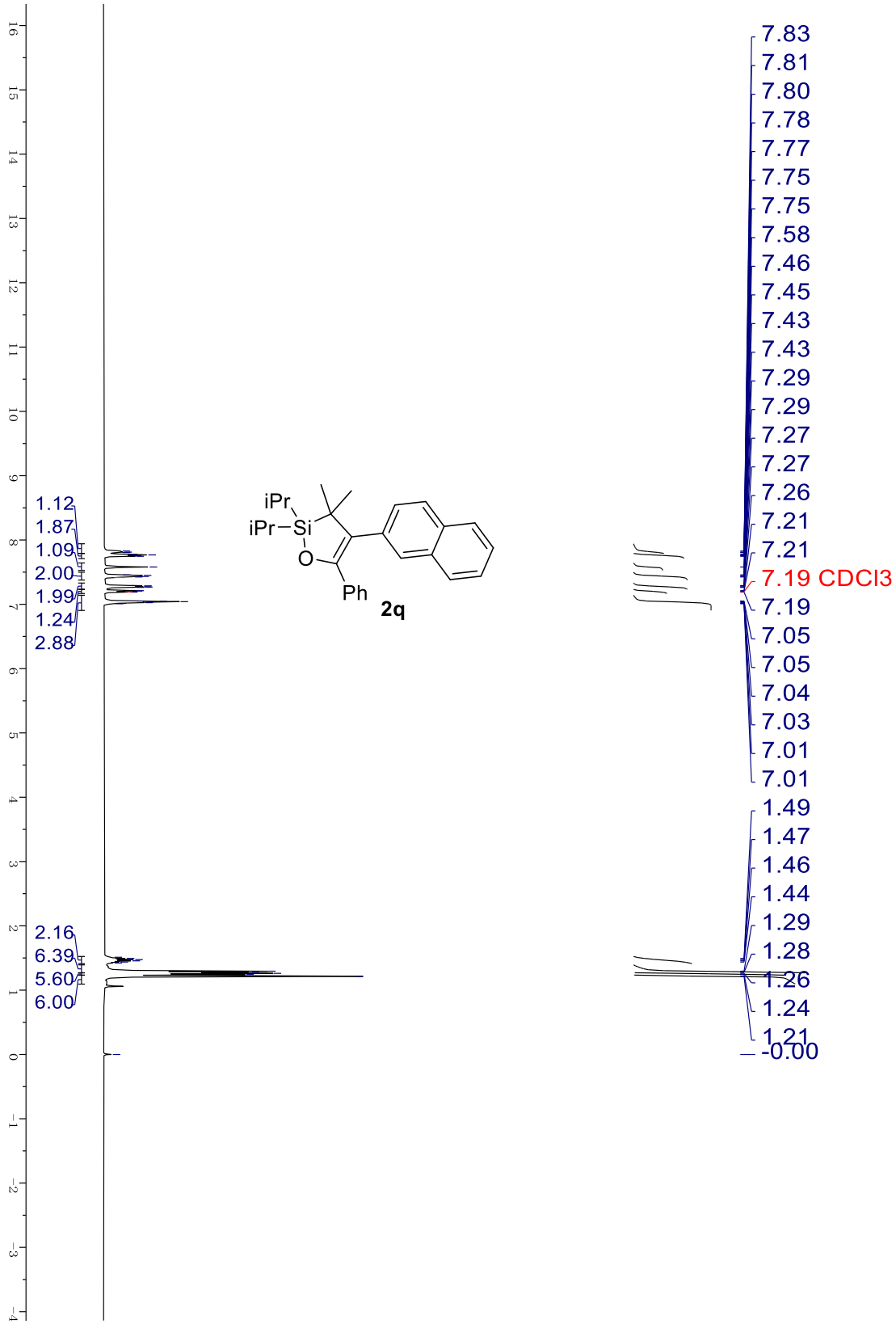
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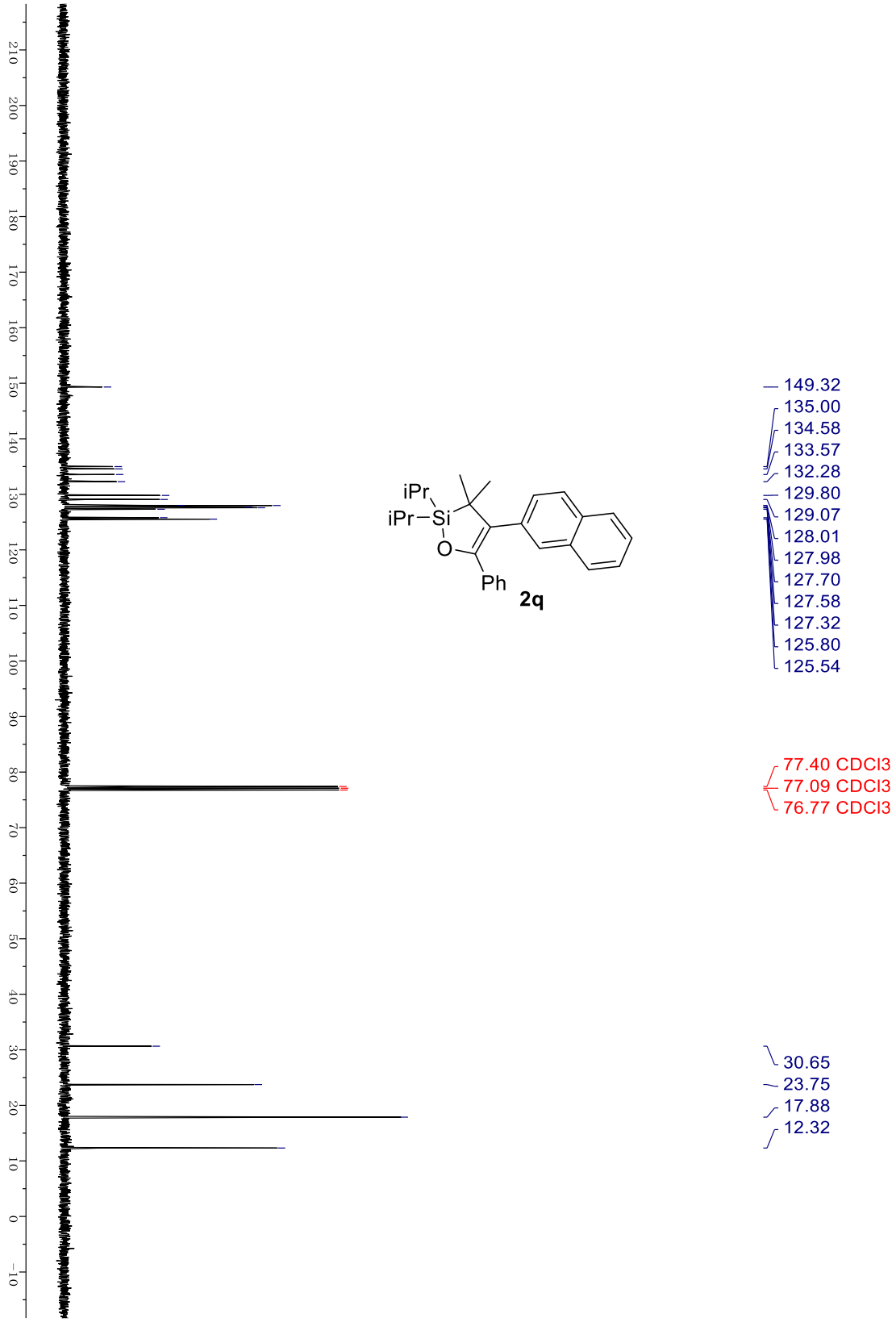
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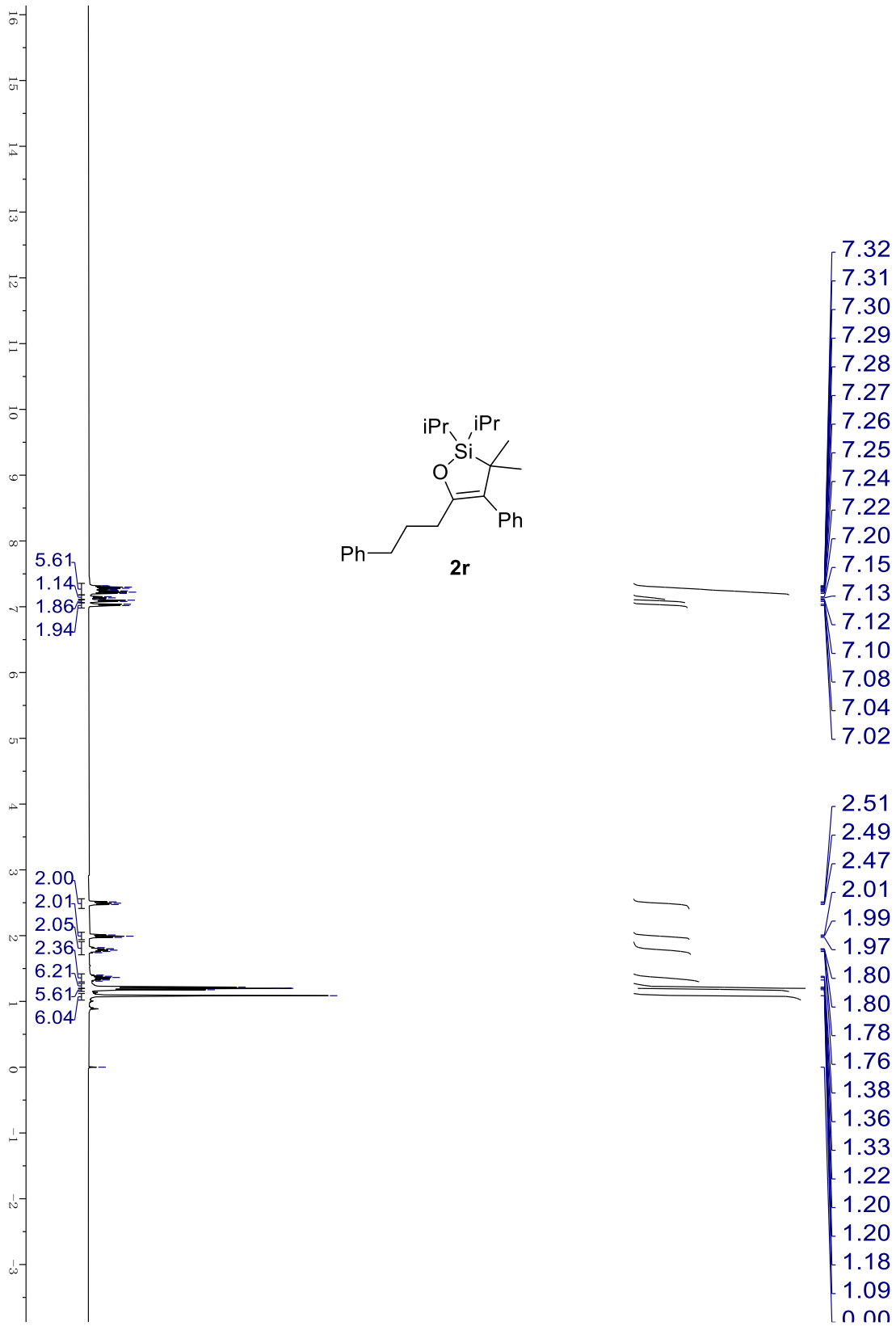
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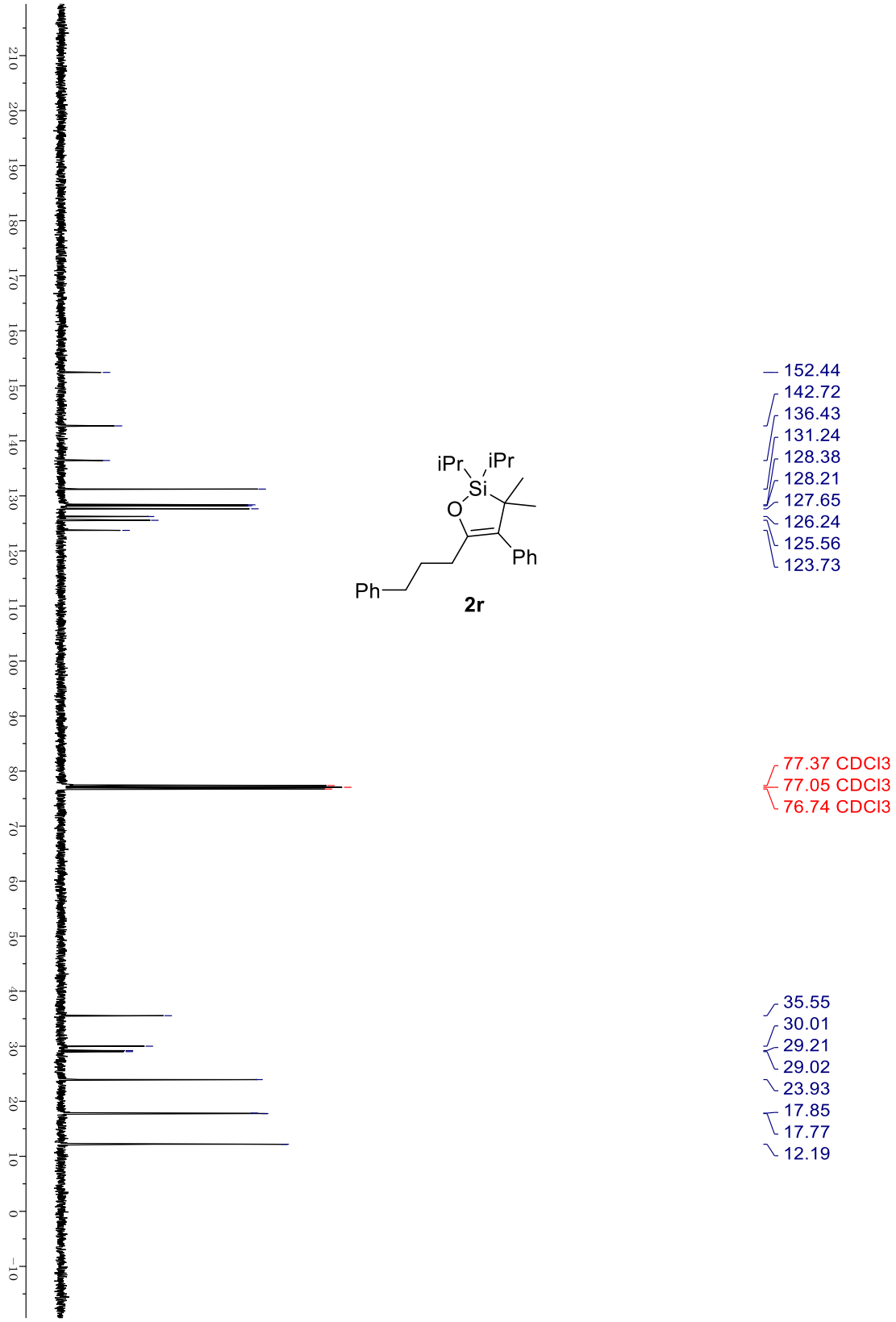
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Ph
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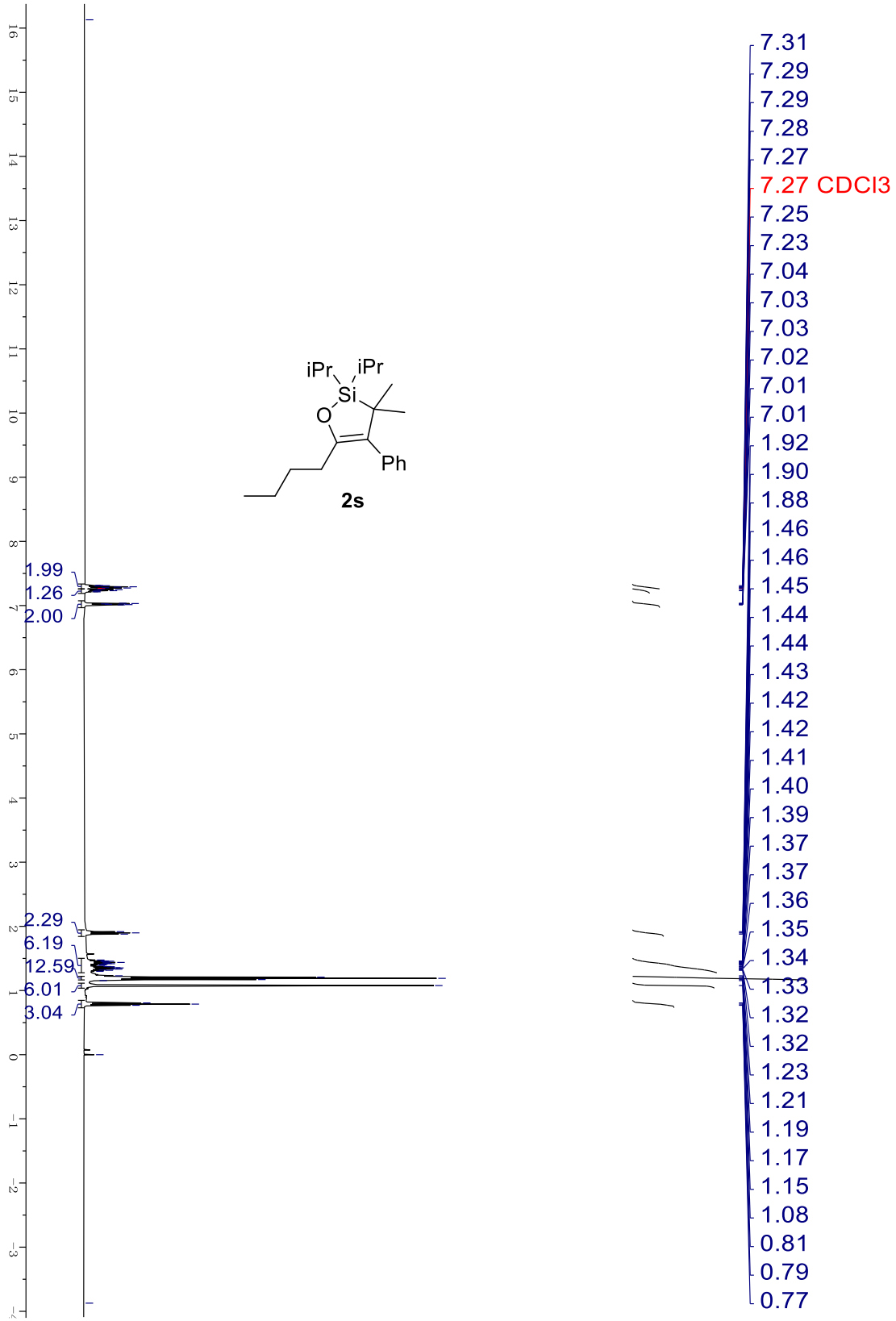
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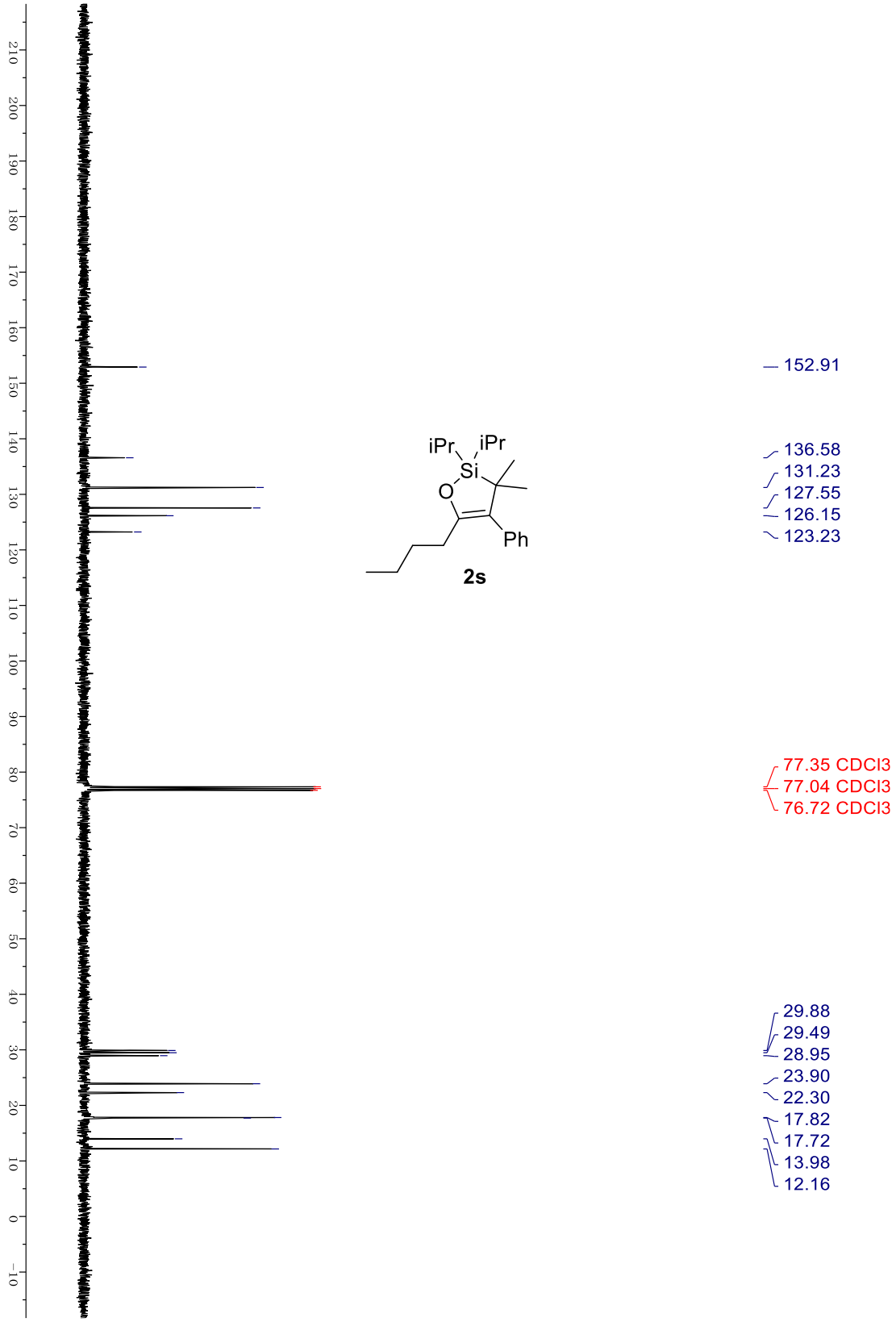
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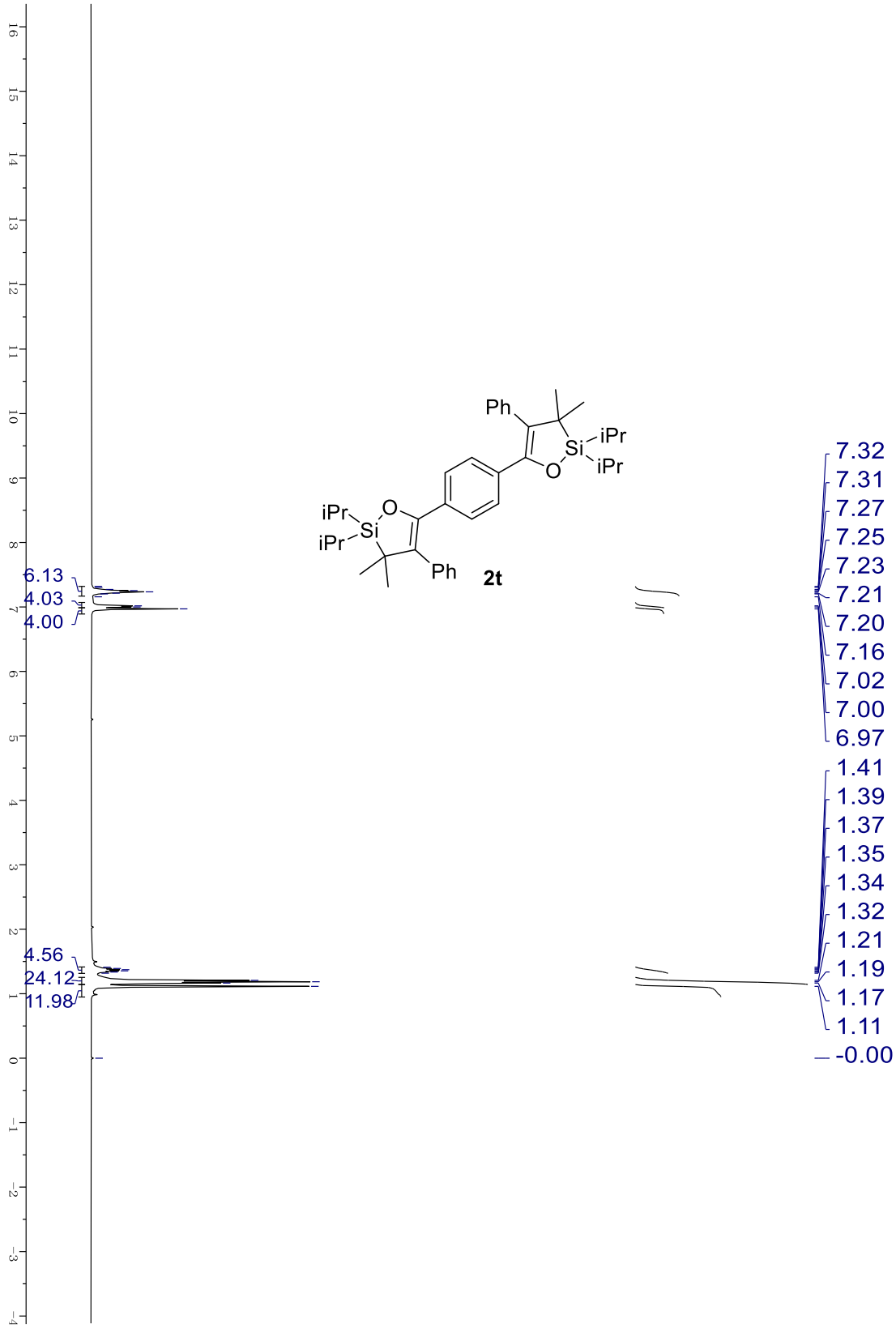
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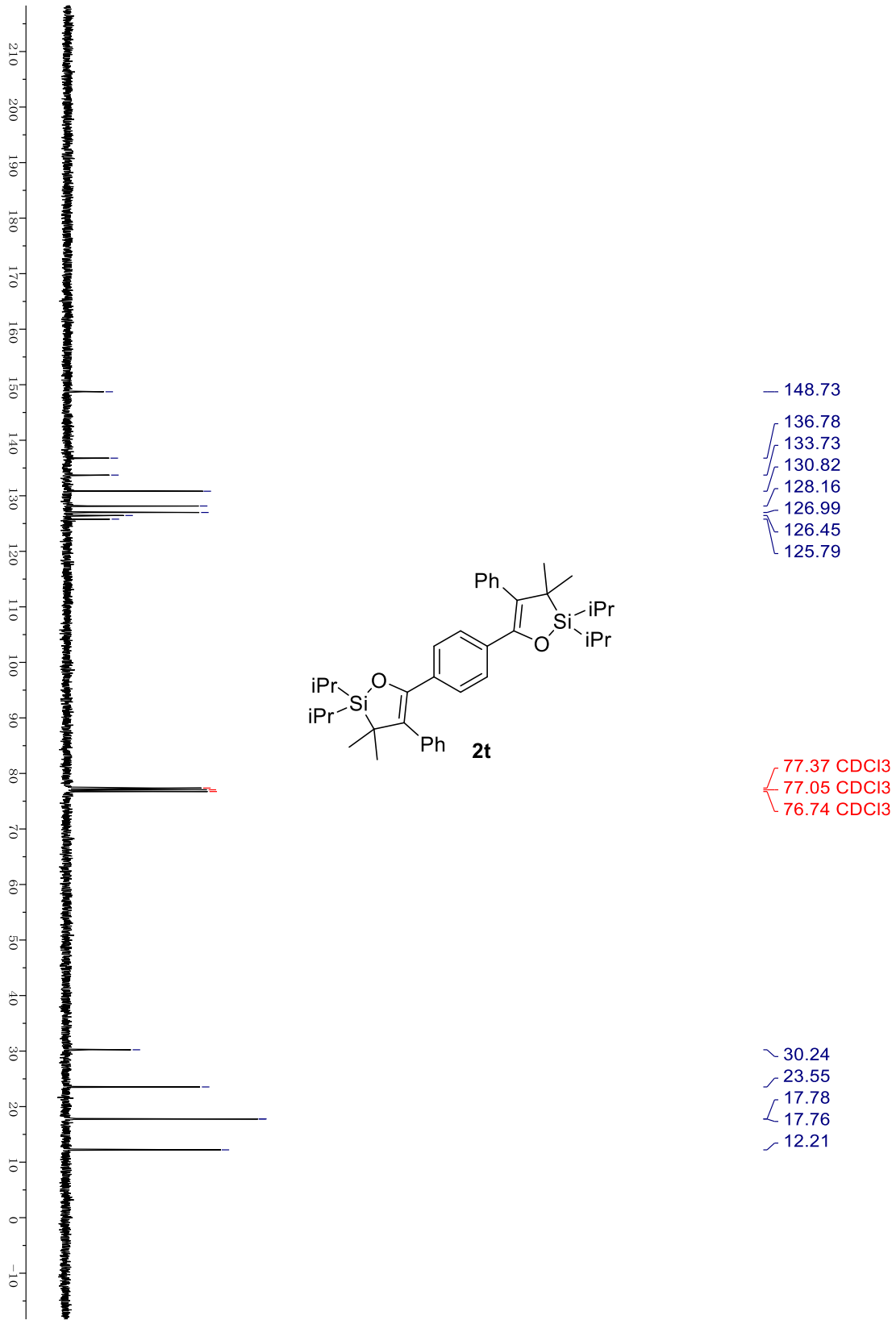
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O
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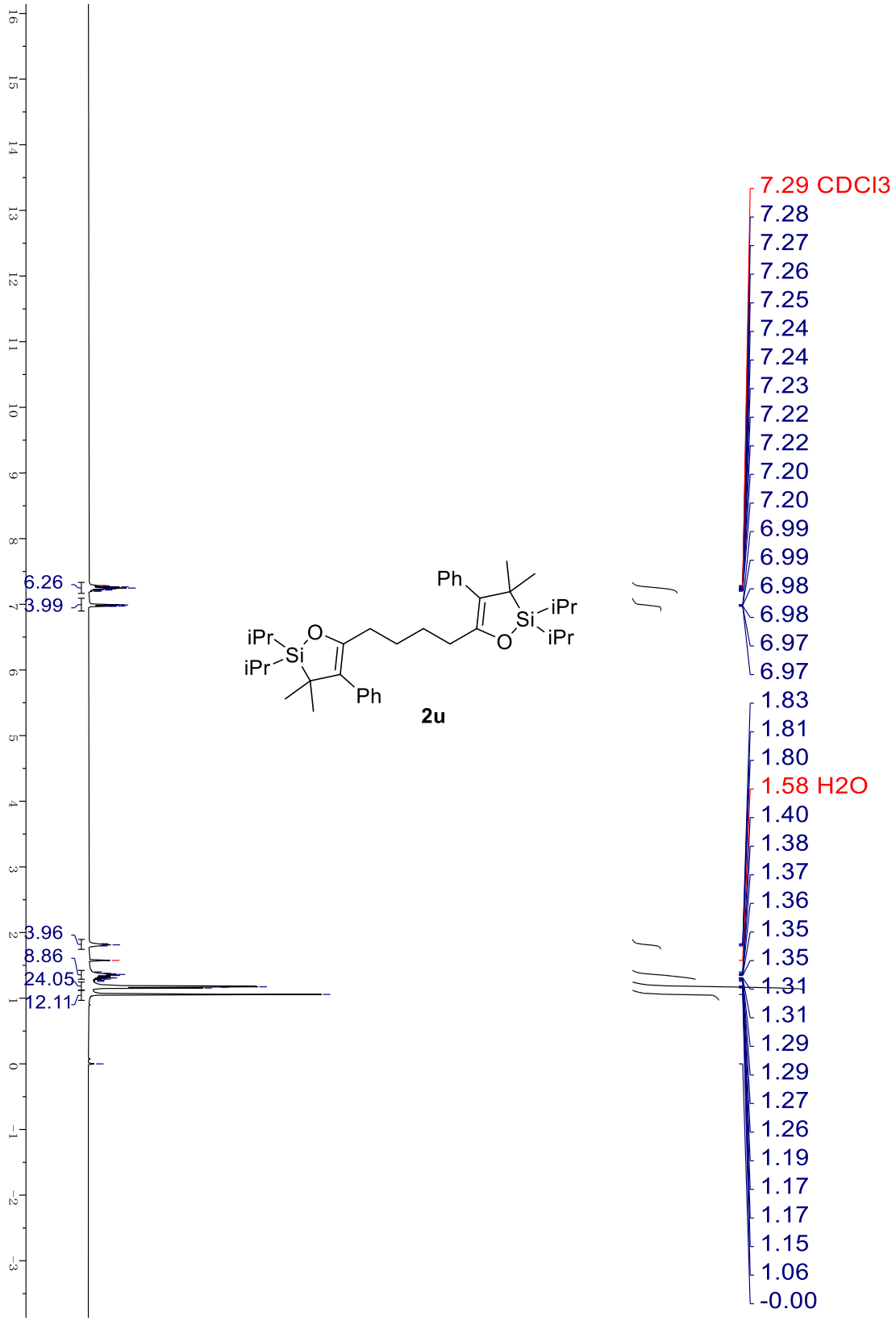
2t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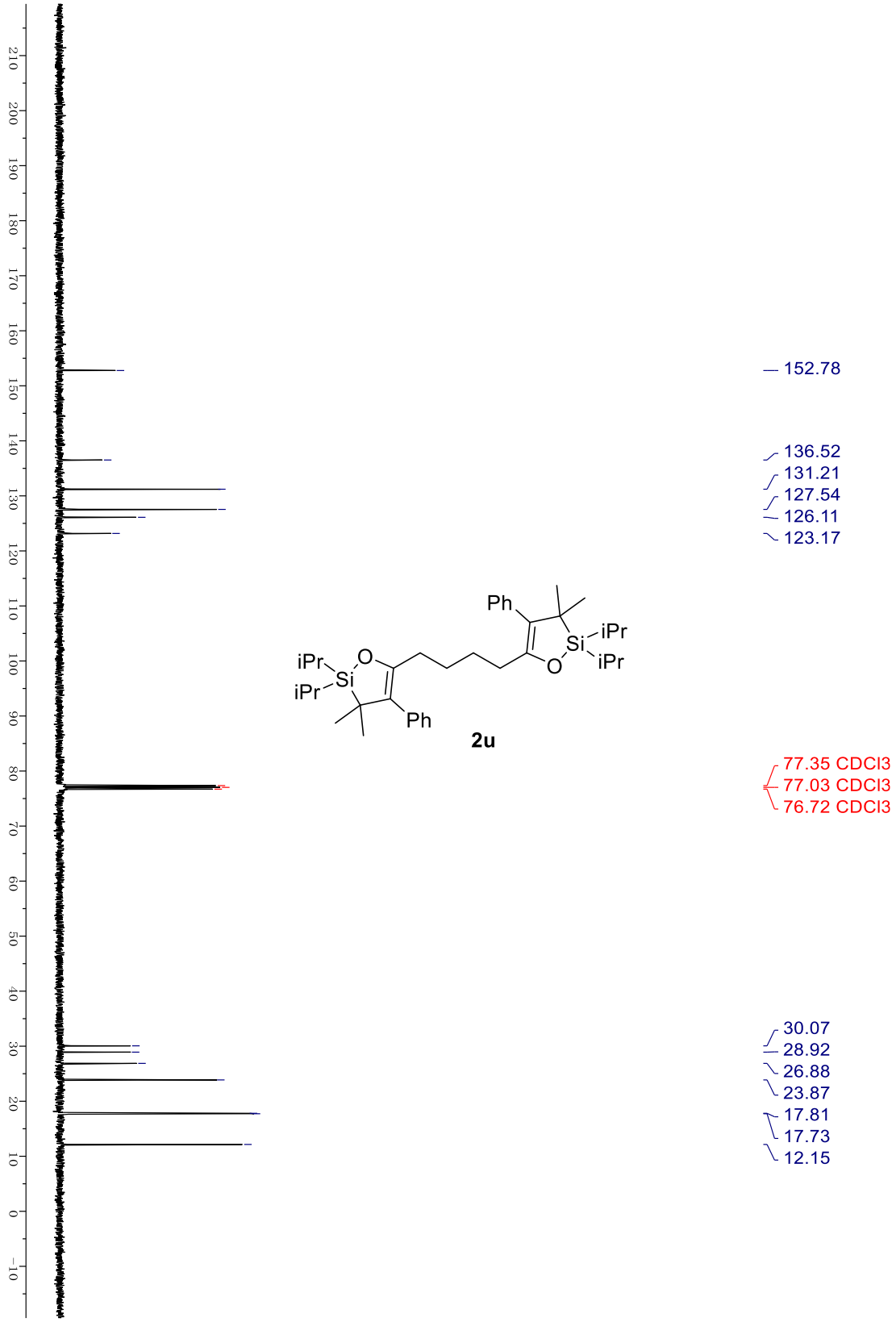
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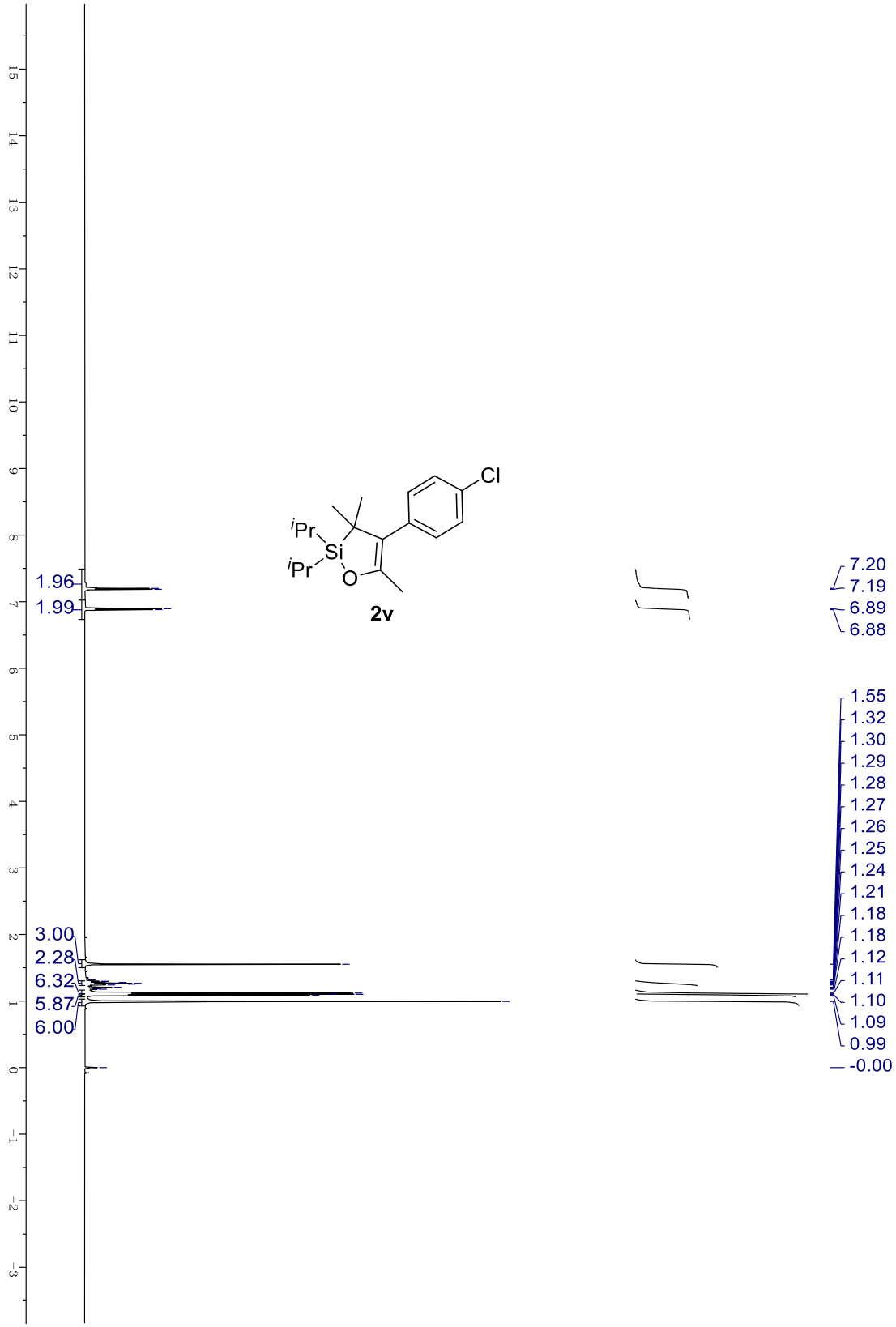
Ph

2u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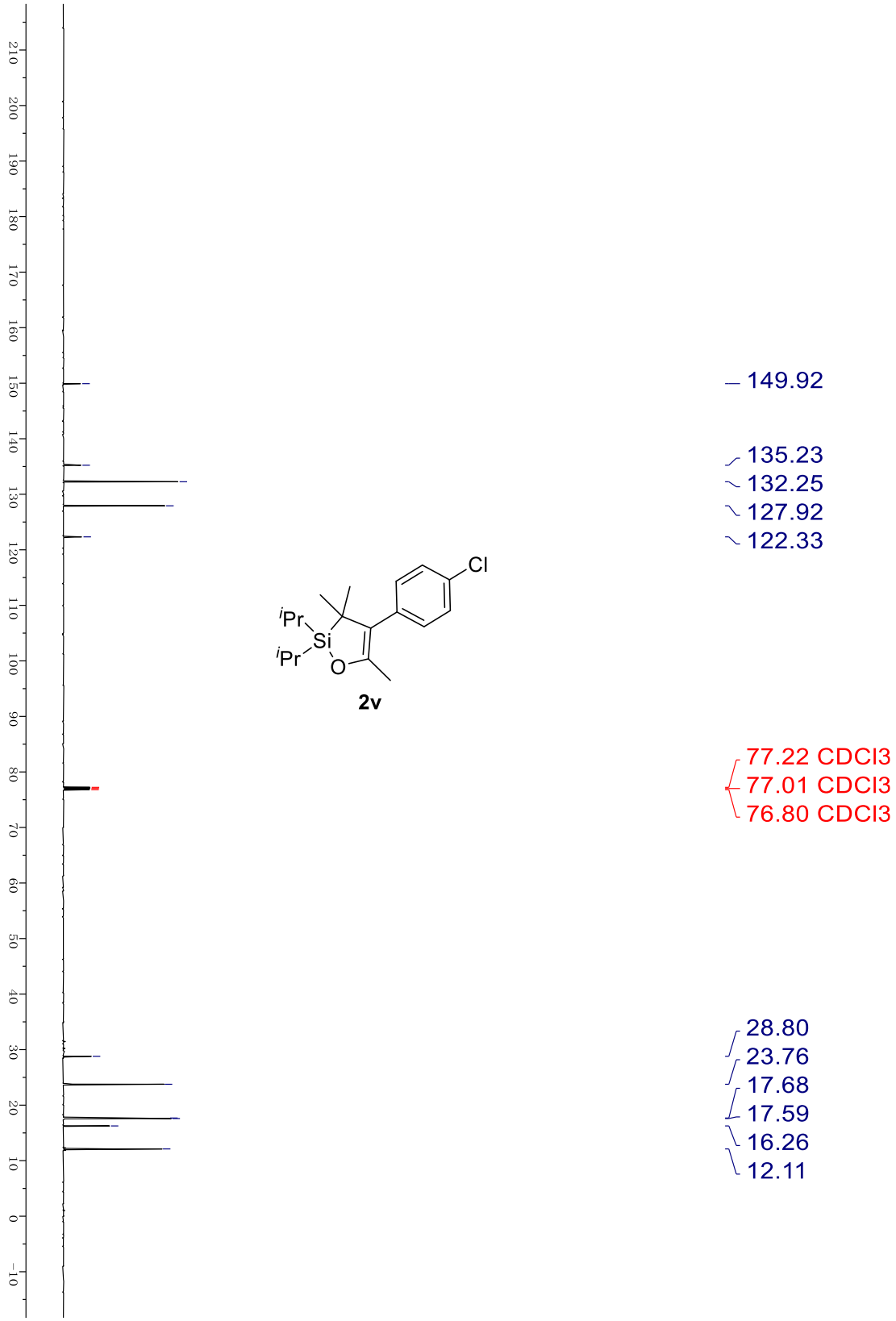
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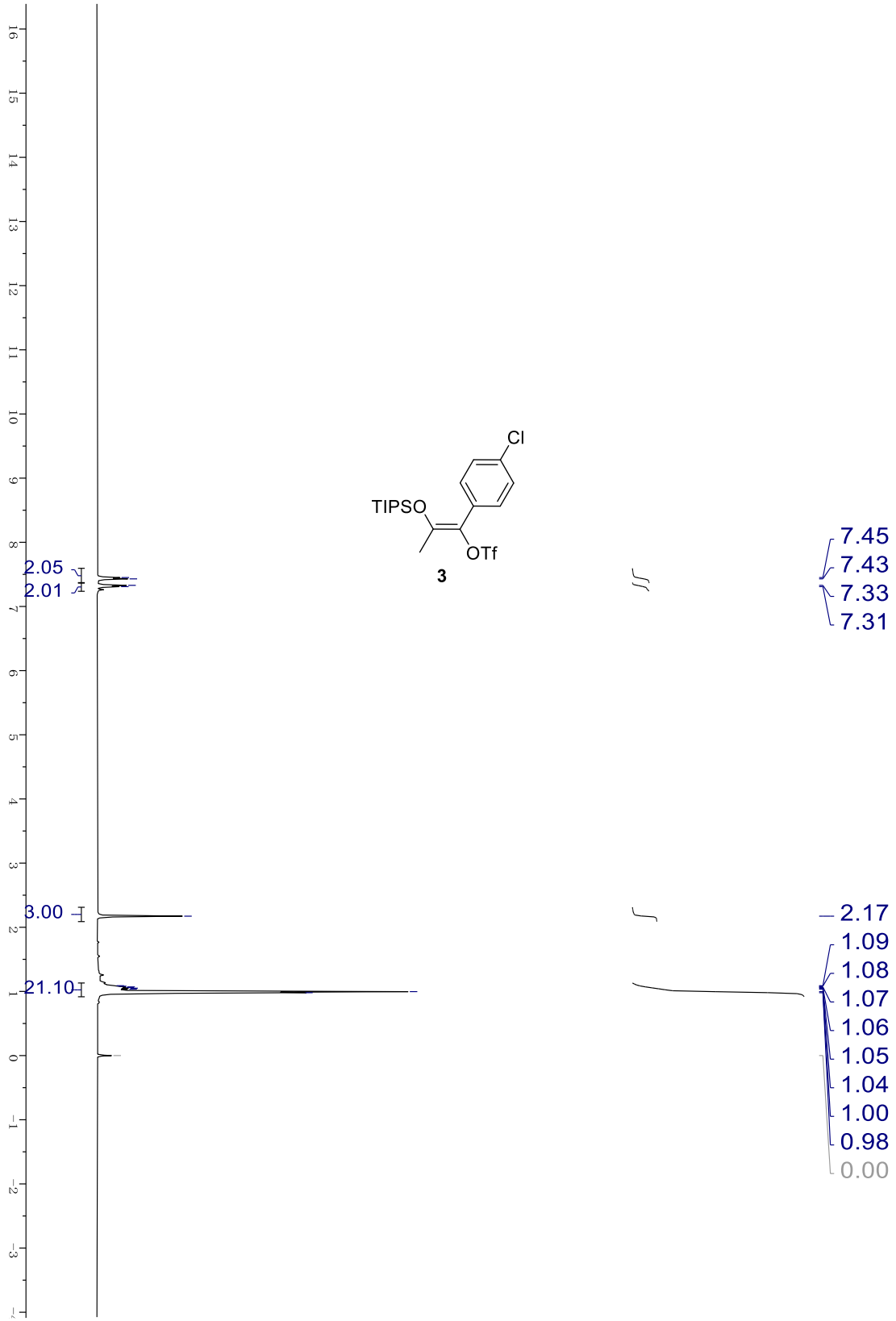
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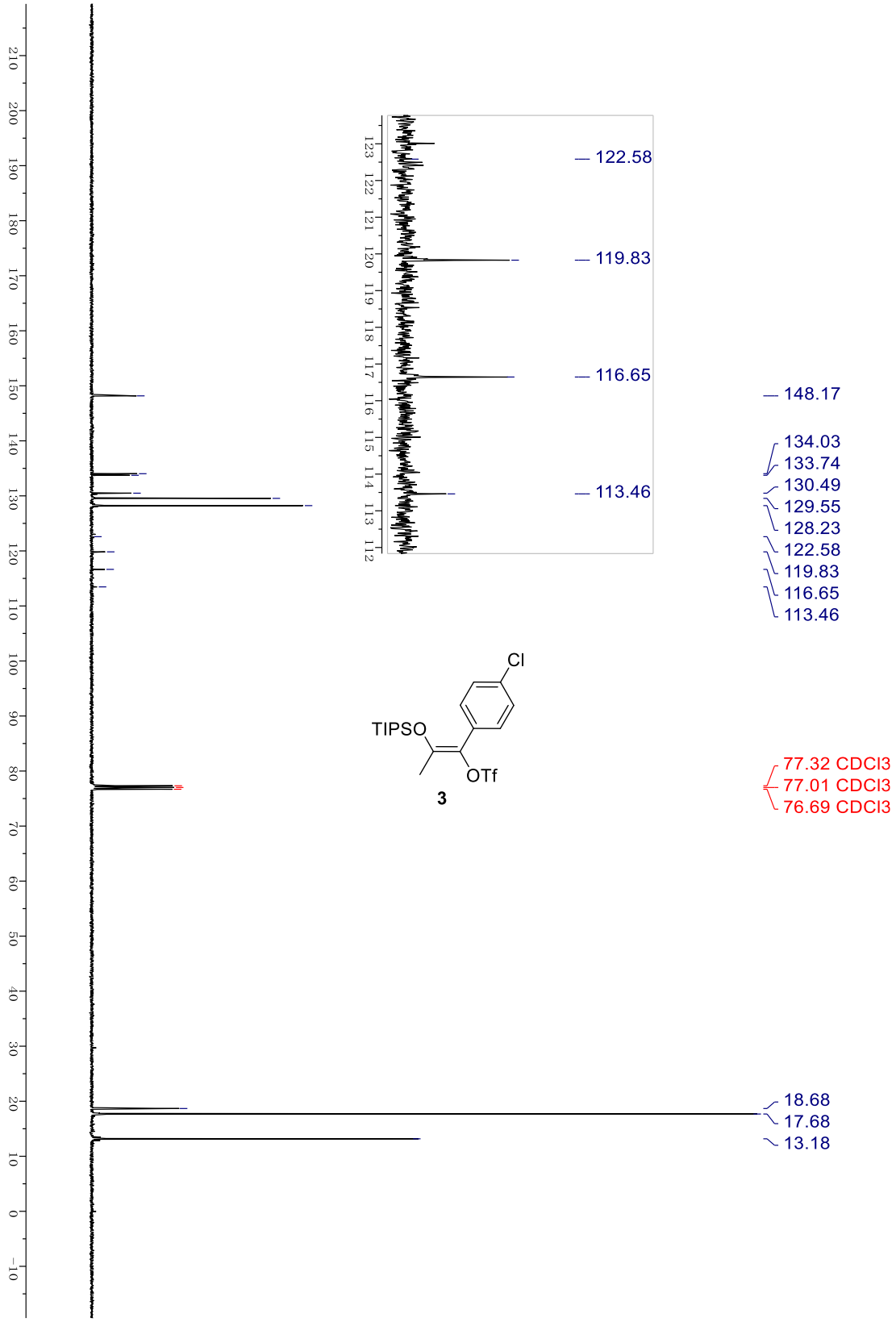
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113.46
Cl
TIPSO
OTf
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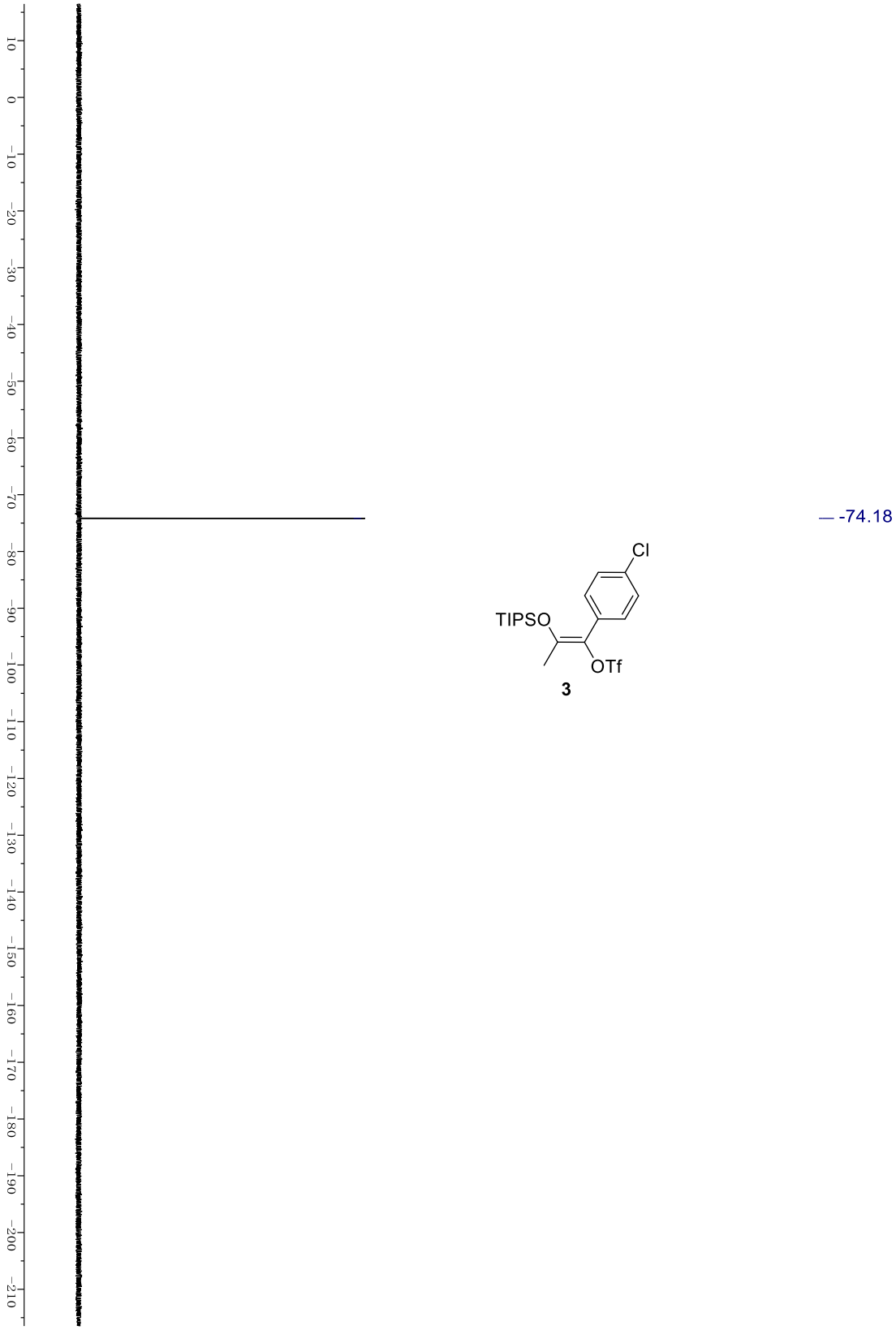
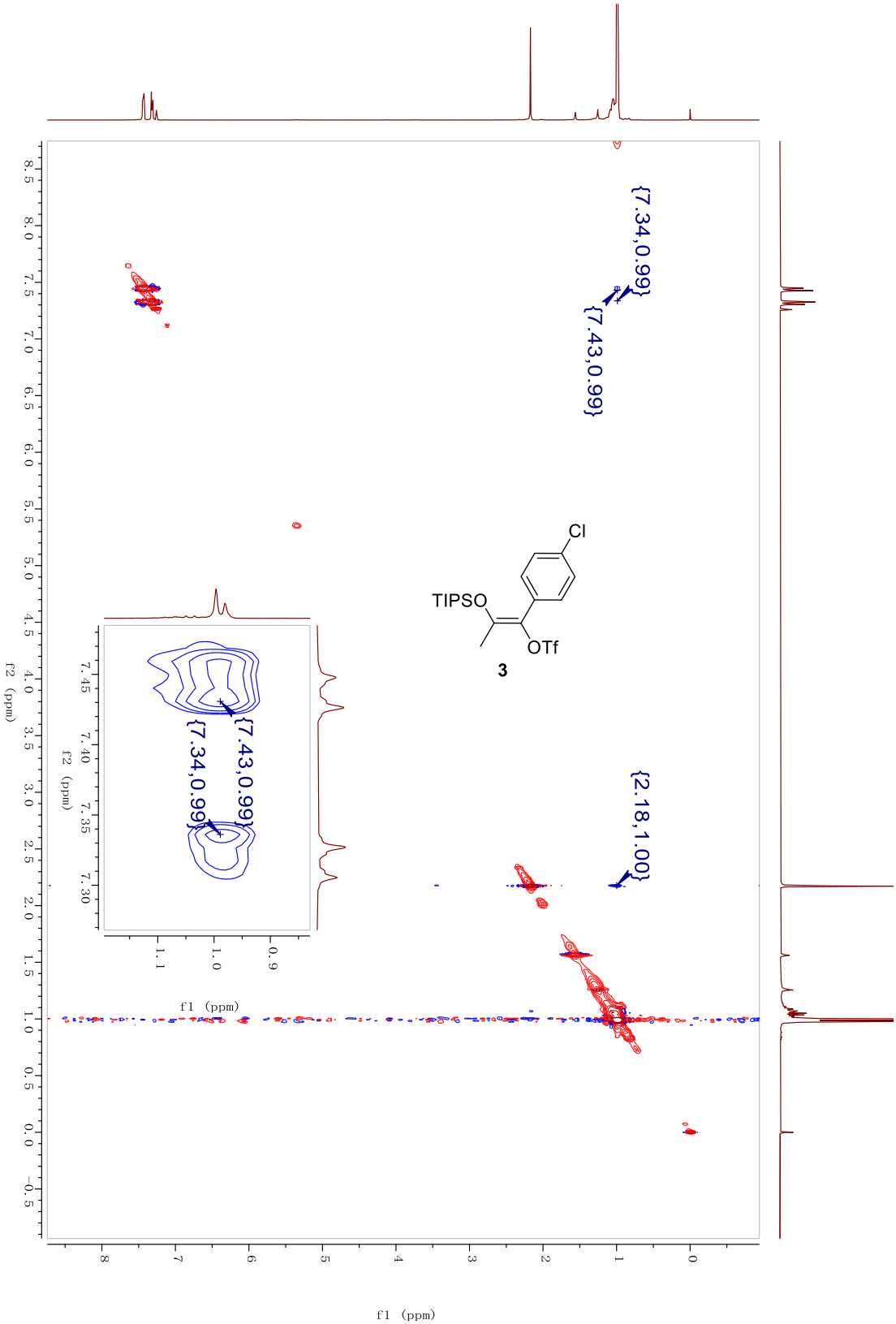
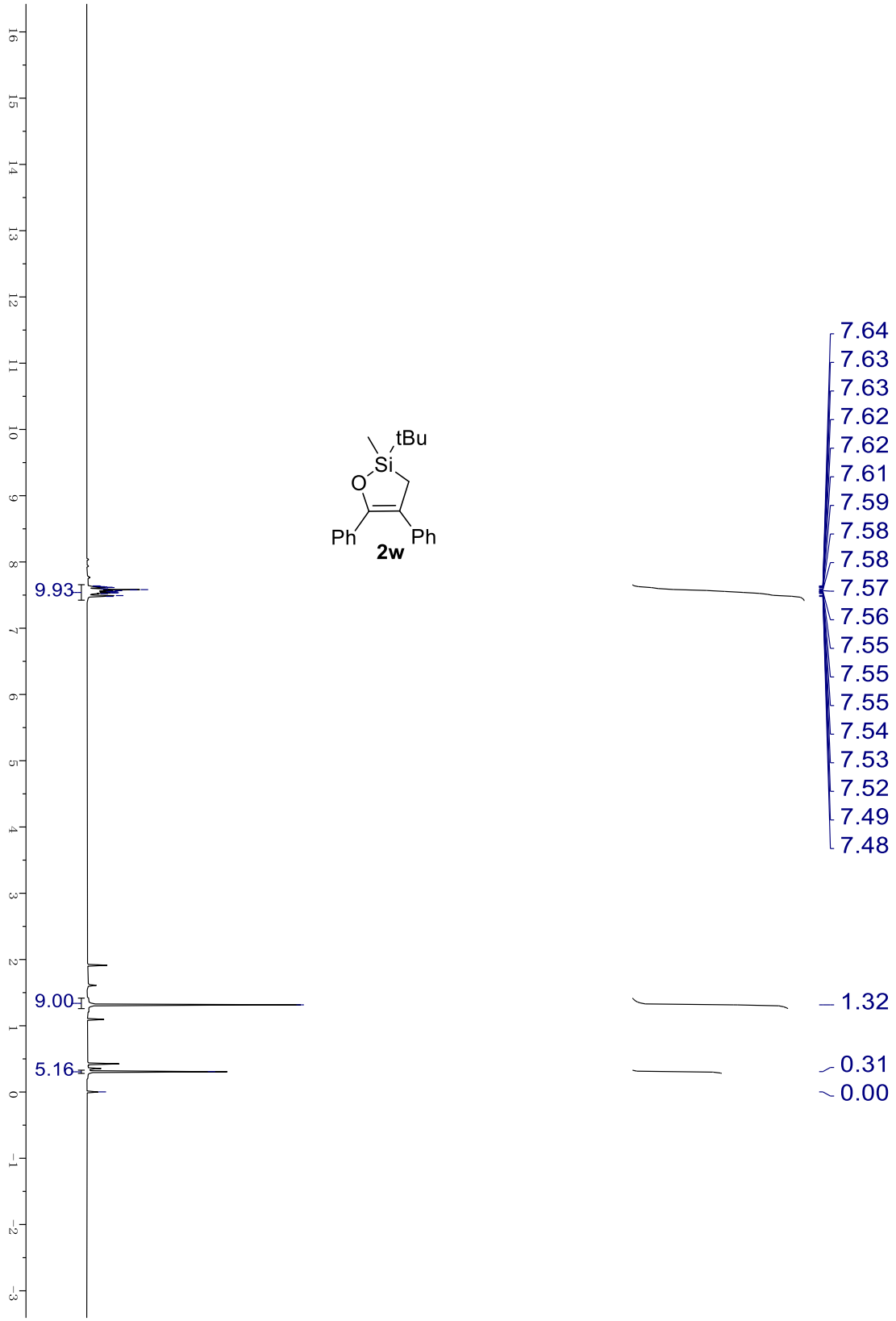
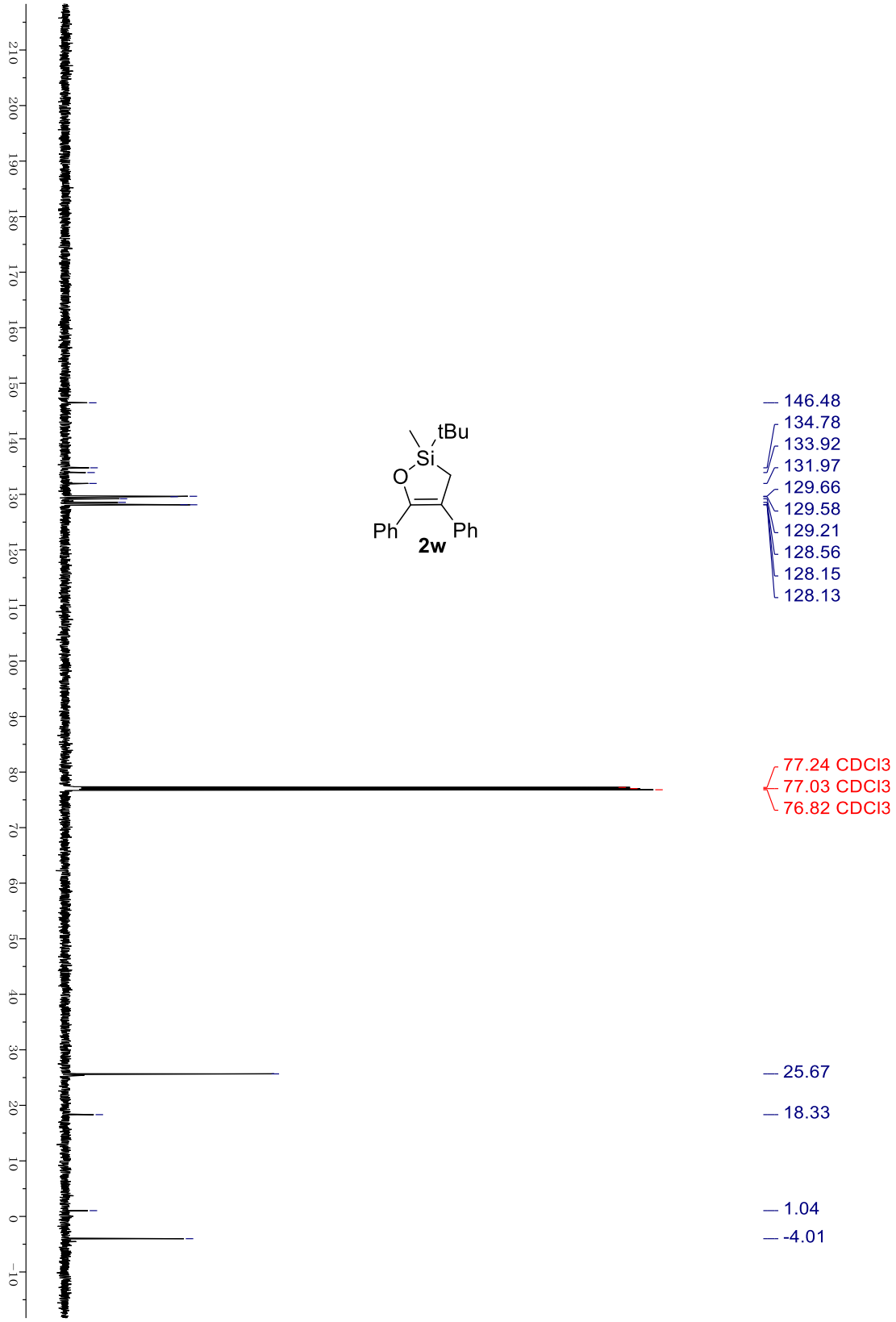
17.68
13.18

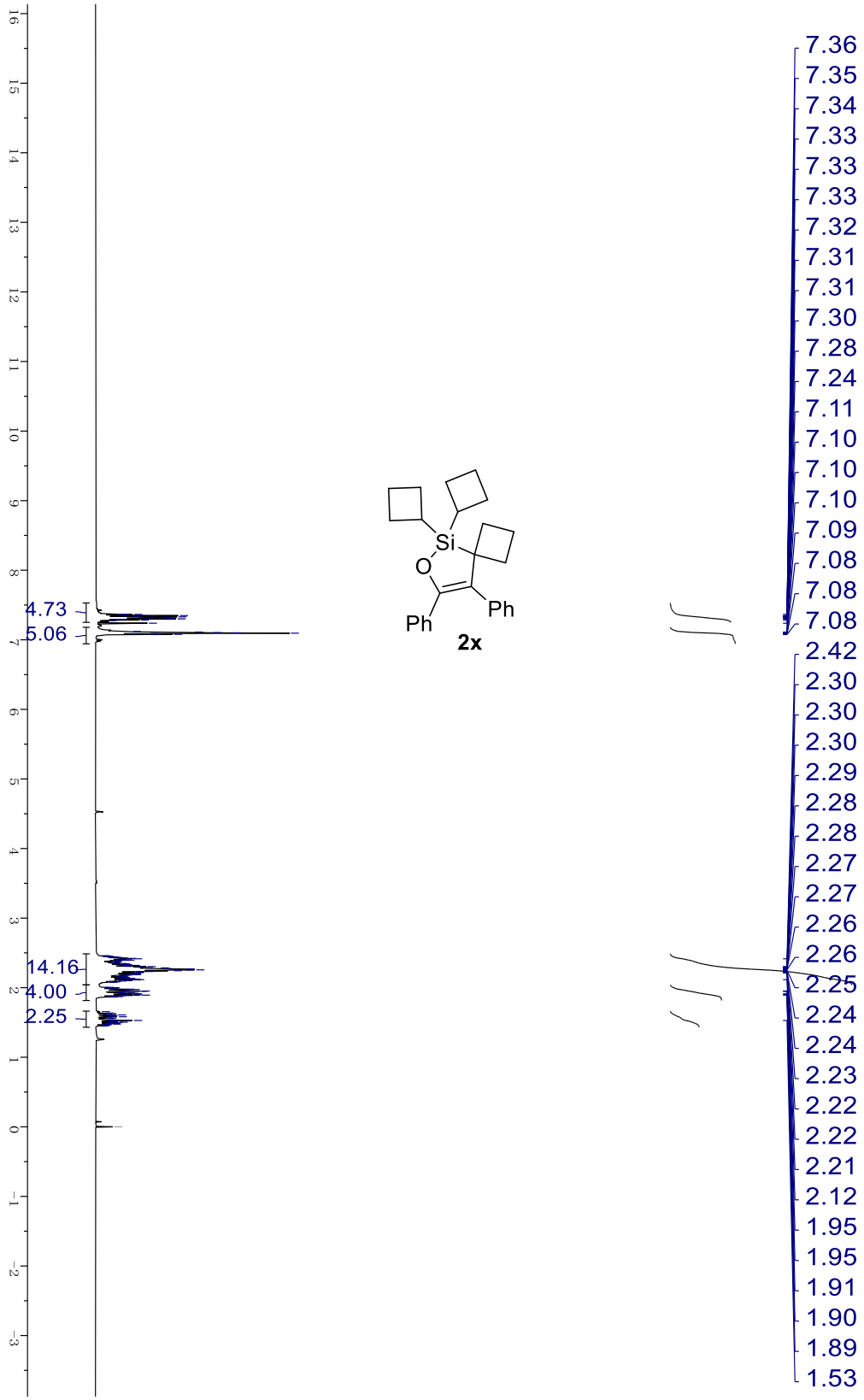

10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
-74.18
Cl
TIPSO
OTf
3

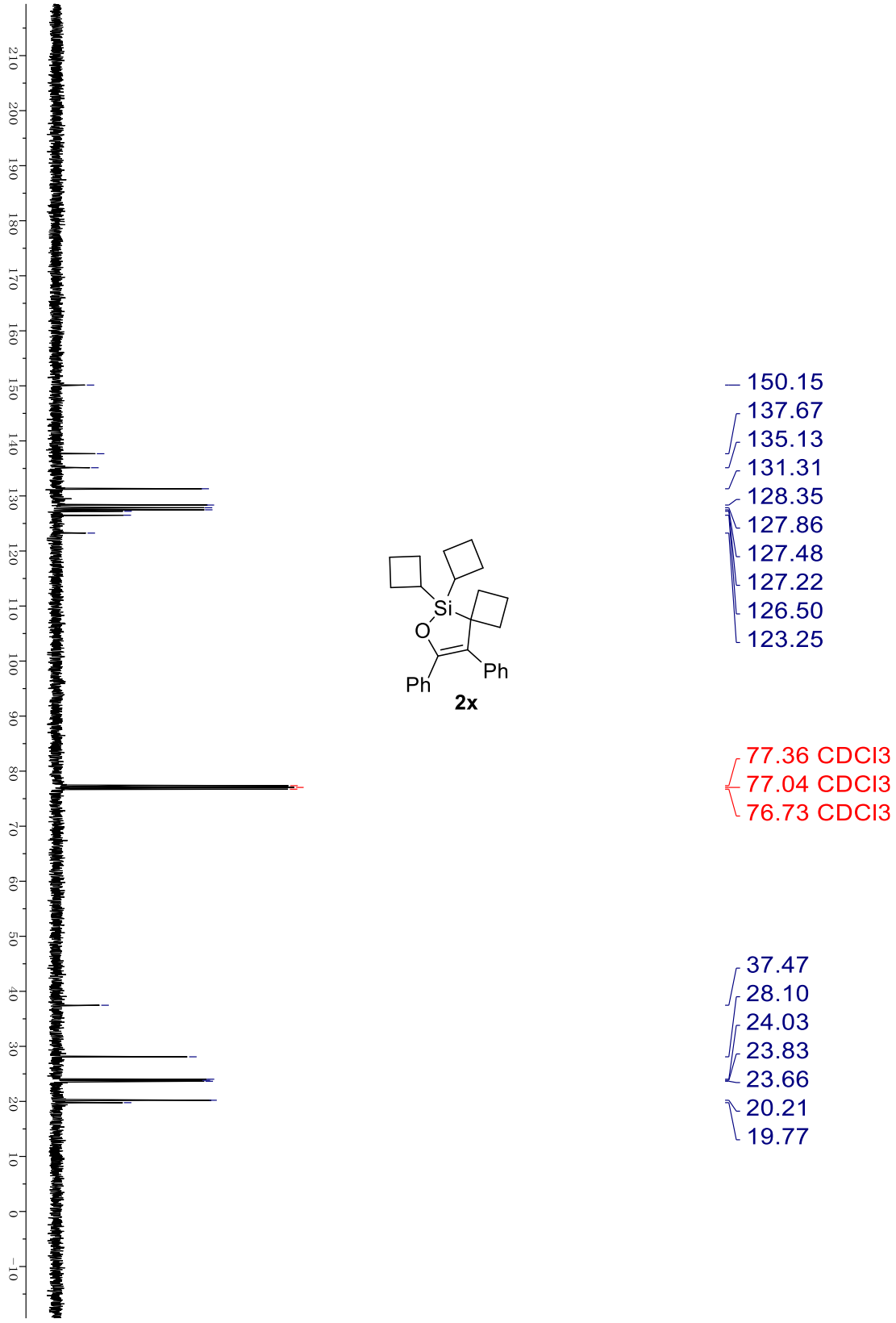


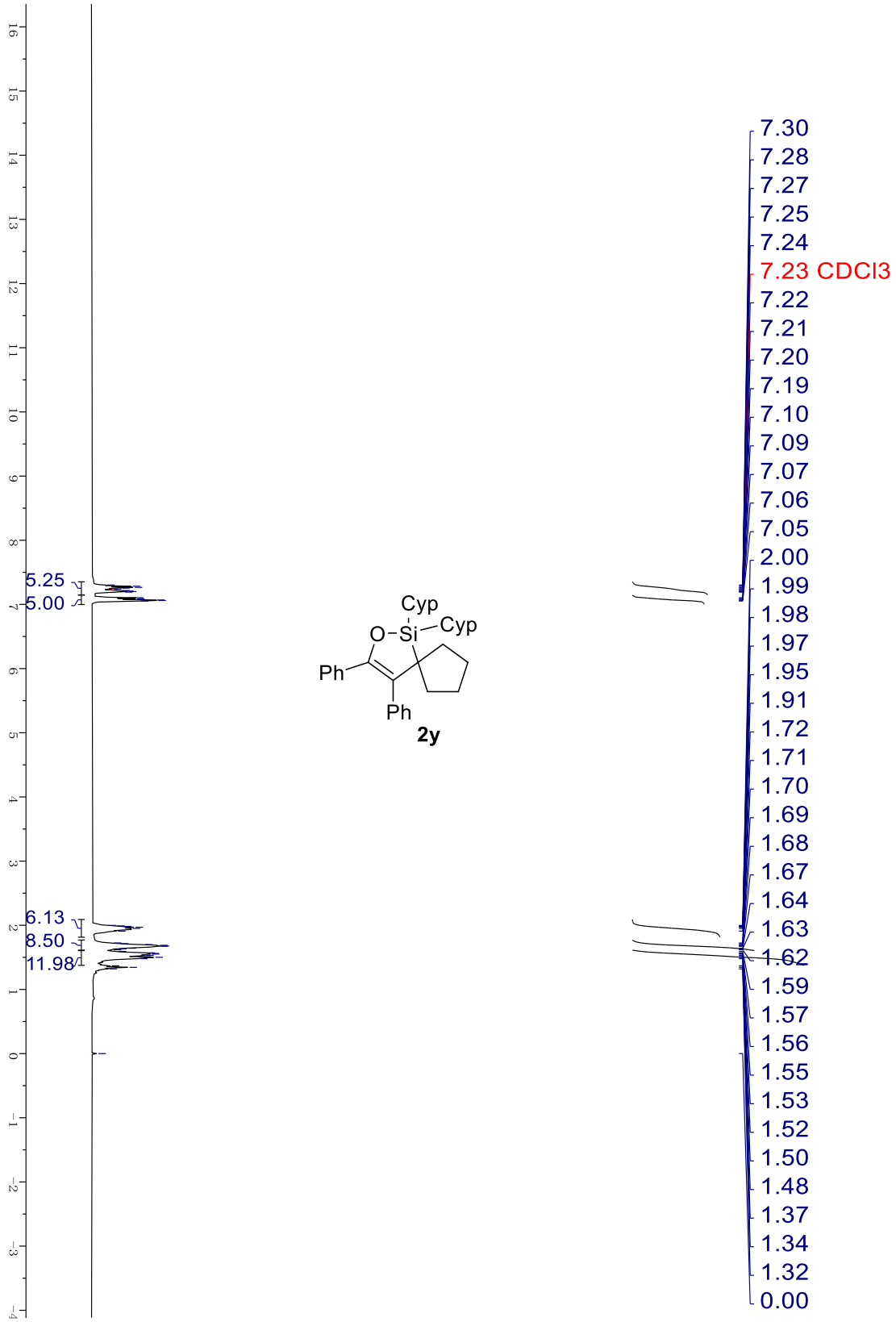
NOESY spectrum of product **3**

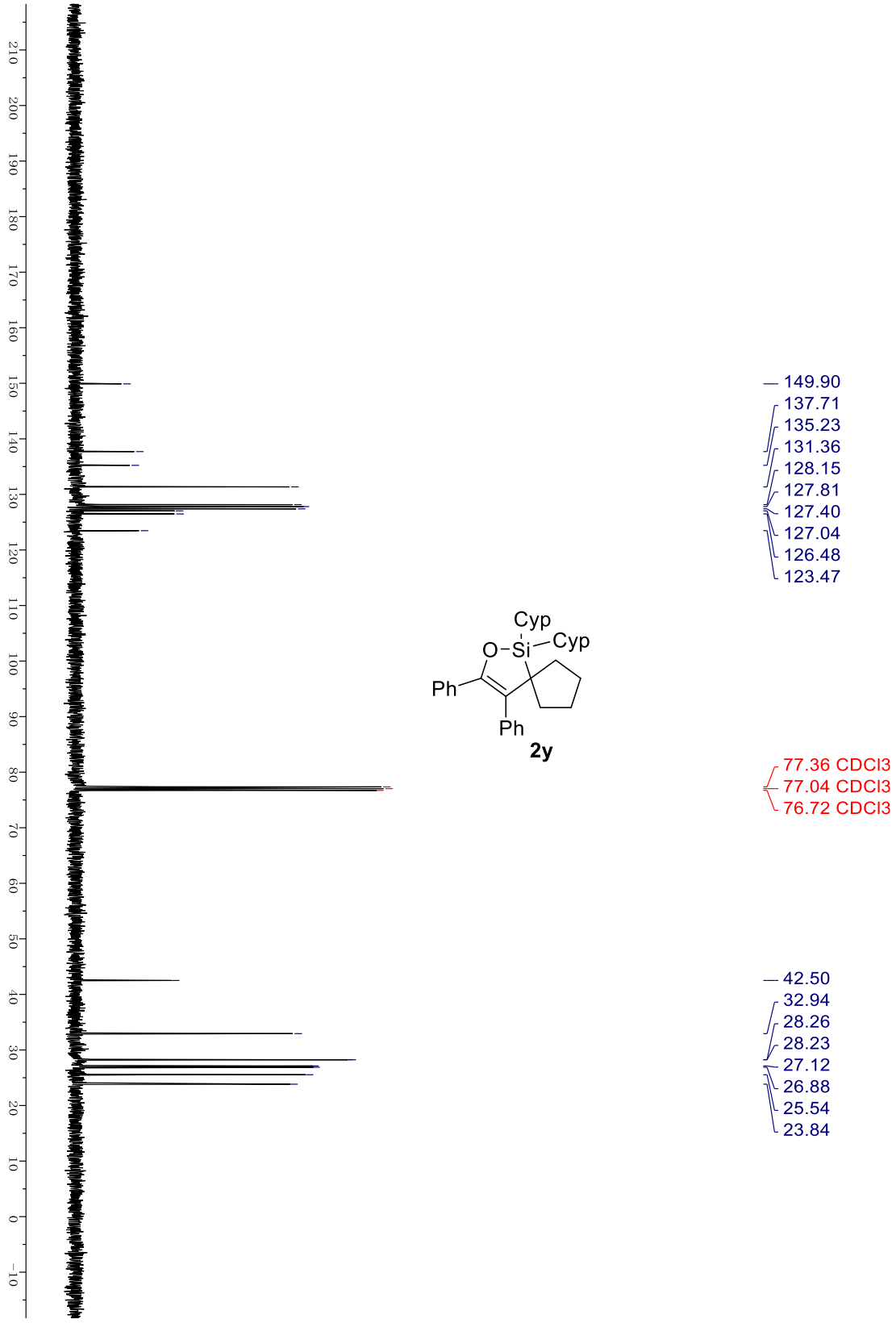

tBu
Si
O
Ph
Ph
2w
9.93
9.00
5.16
7.64
7.63
7.63
7.62
7.62
7.61
7.59
7.58
7.58
7.57
7.56
7.55
7.55
7.55
7.54
7.53
7.52
7.49
7.48
1.32
0.31
0.00

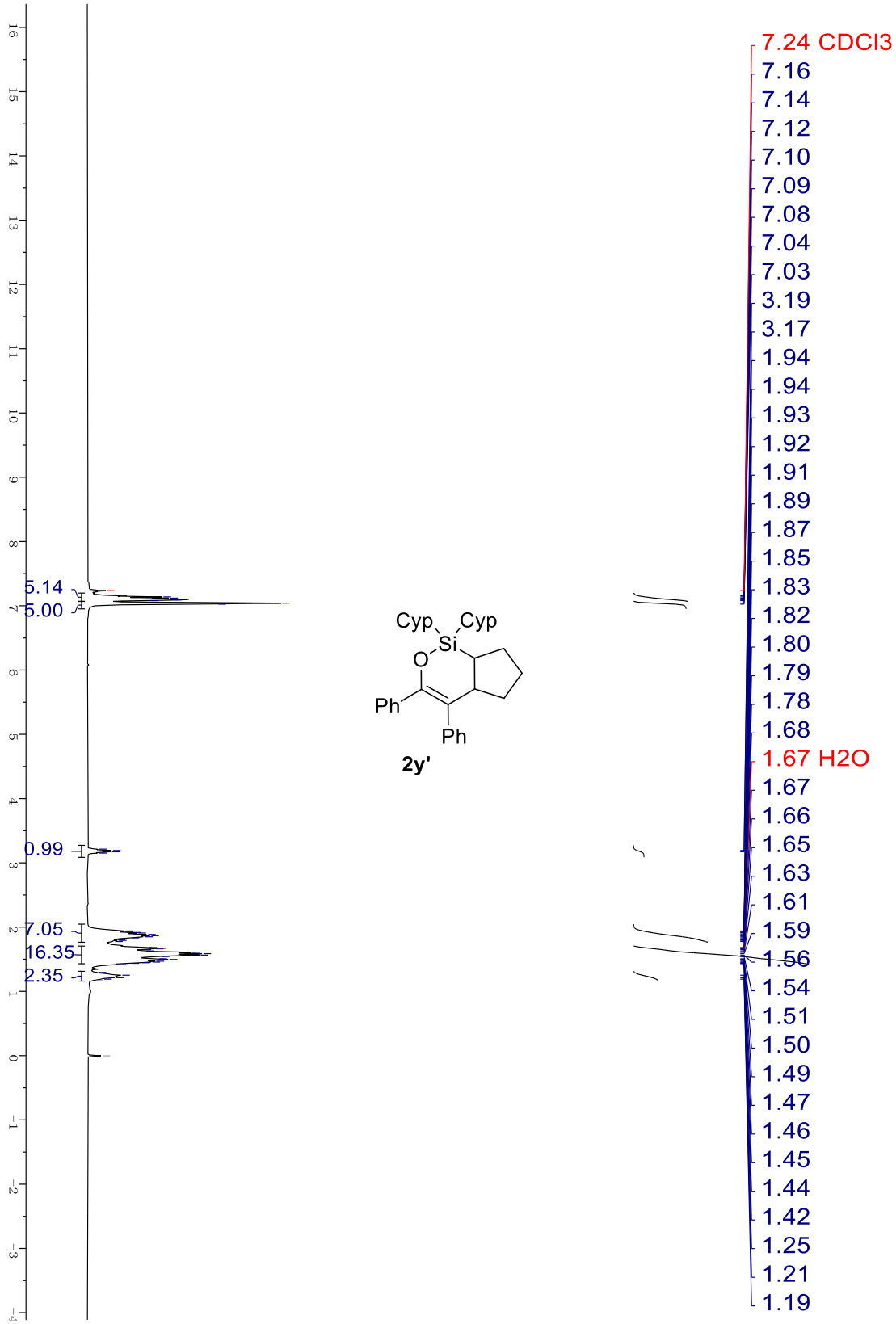

tBu
Si
O
Ph
Ph
2w
146.48
134.78
133.92
131.97
129.66
129.58
129.21
128.56
128.15
128.13
77.24 CDCl3
77.03 CDCl3
76.82 CDCl3
25.67
18.33
1.04
-4.01

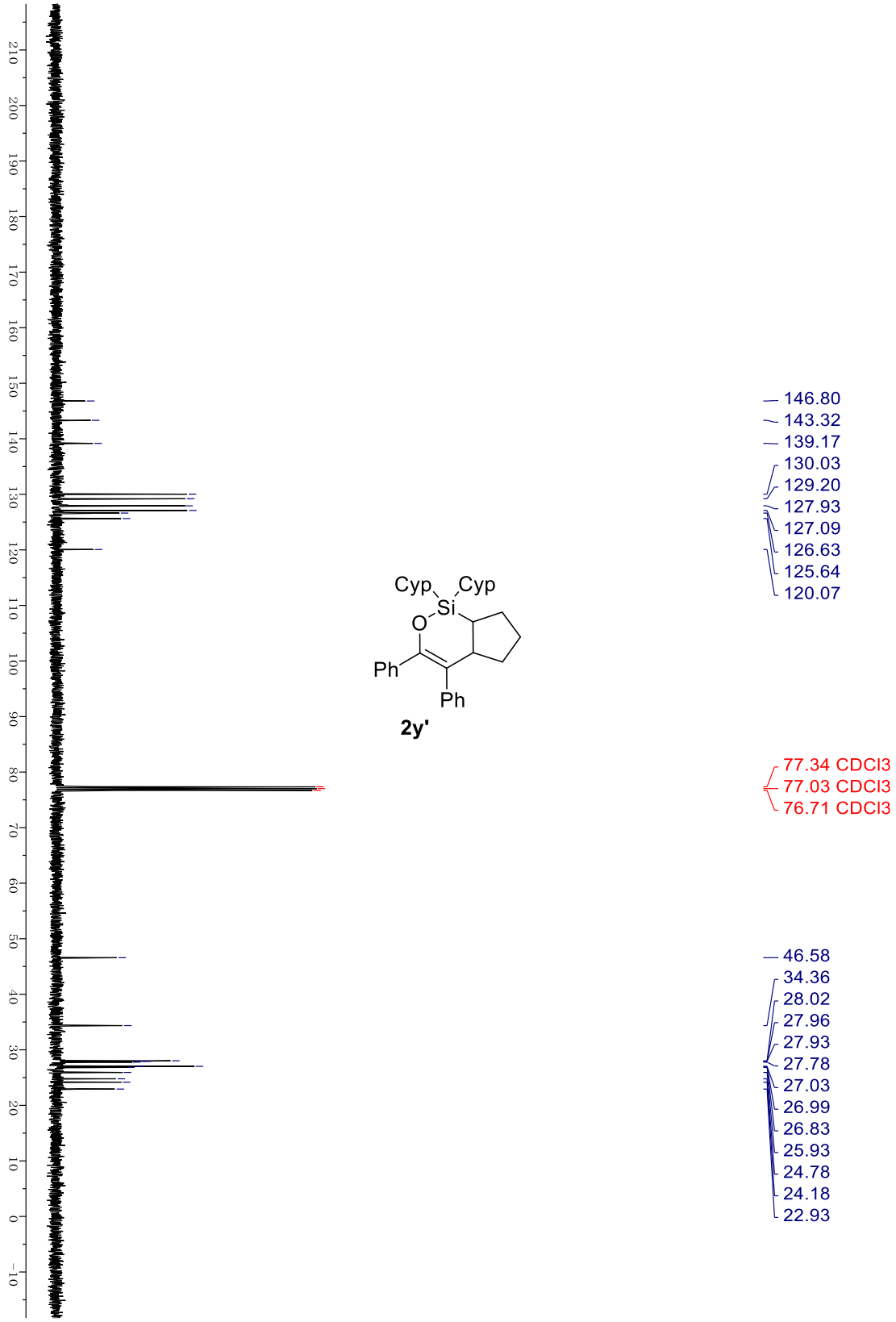

4.73
5.06
14.16
4.00
2.25
Si
O
Ph
Ph
2x
7.36
7.35
7.34
7.33
7.33
7.33
7.32
7.31
7.31
7.30
7.28
7.24
7.11
7.10
7.10
7.10
7.09
7.08
7.08
7.08
2.42
2.30
2.30
2.30
2.29
2.28
2.28
2.27
2.27
2.26
2.26
2.25
2.24
2.24
2.23
2.22
2.22
2.21
2.12
1.95
1.95
1.91
1.90
1.89
1.53

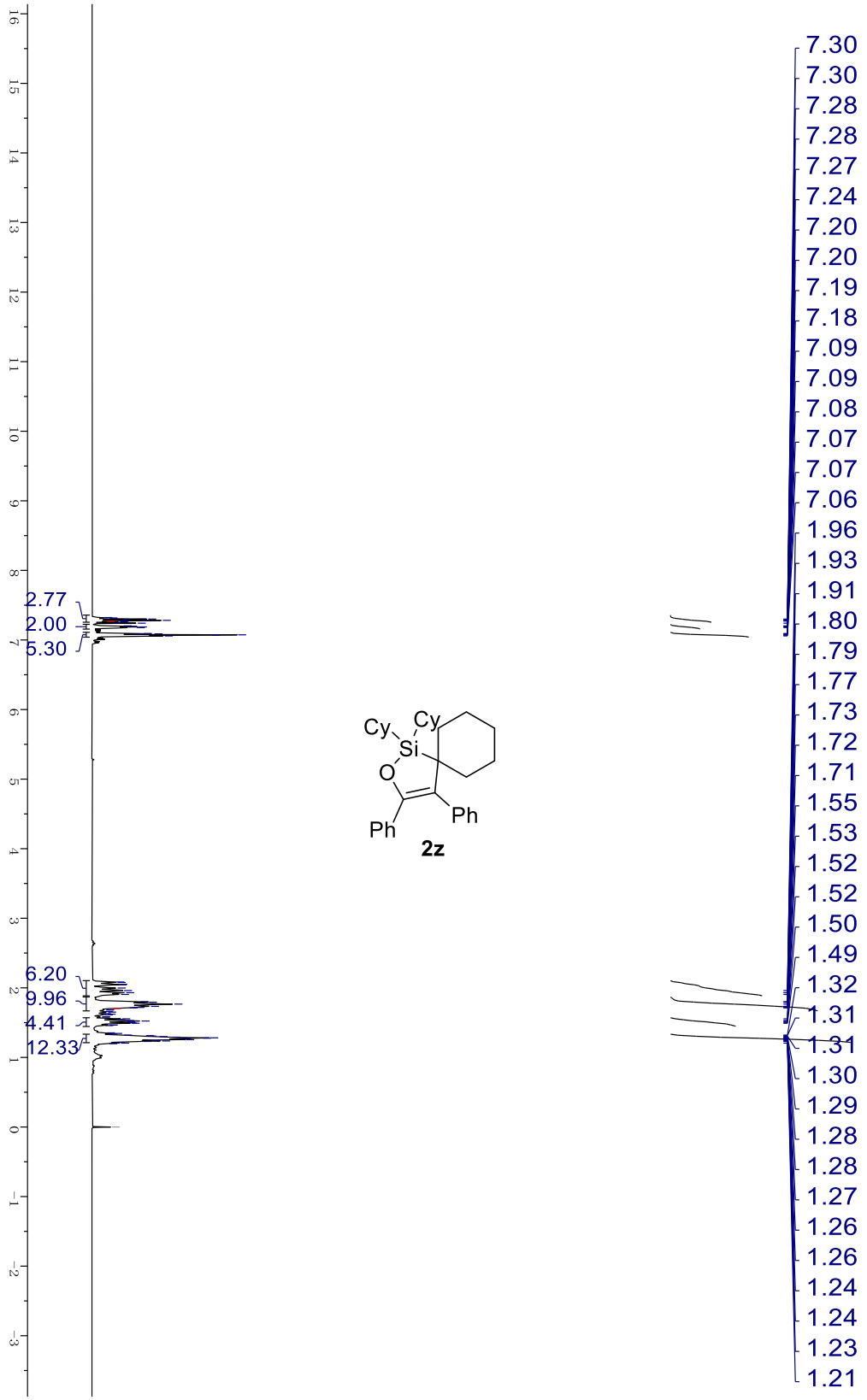

150.15
137.67
135.13
131.31
128.35
127.86
127.48
127.22
126.50
123.25
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
37.47
28.10
24.03
23.83
23.66
20.21
19.77
Si
O
Ph
Ph
2x

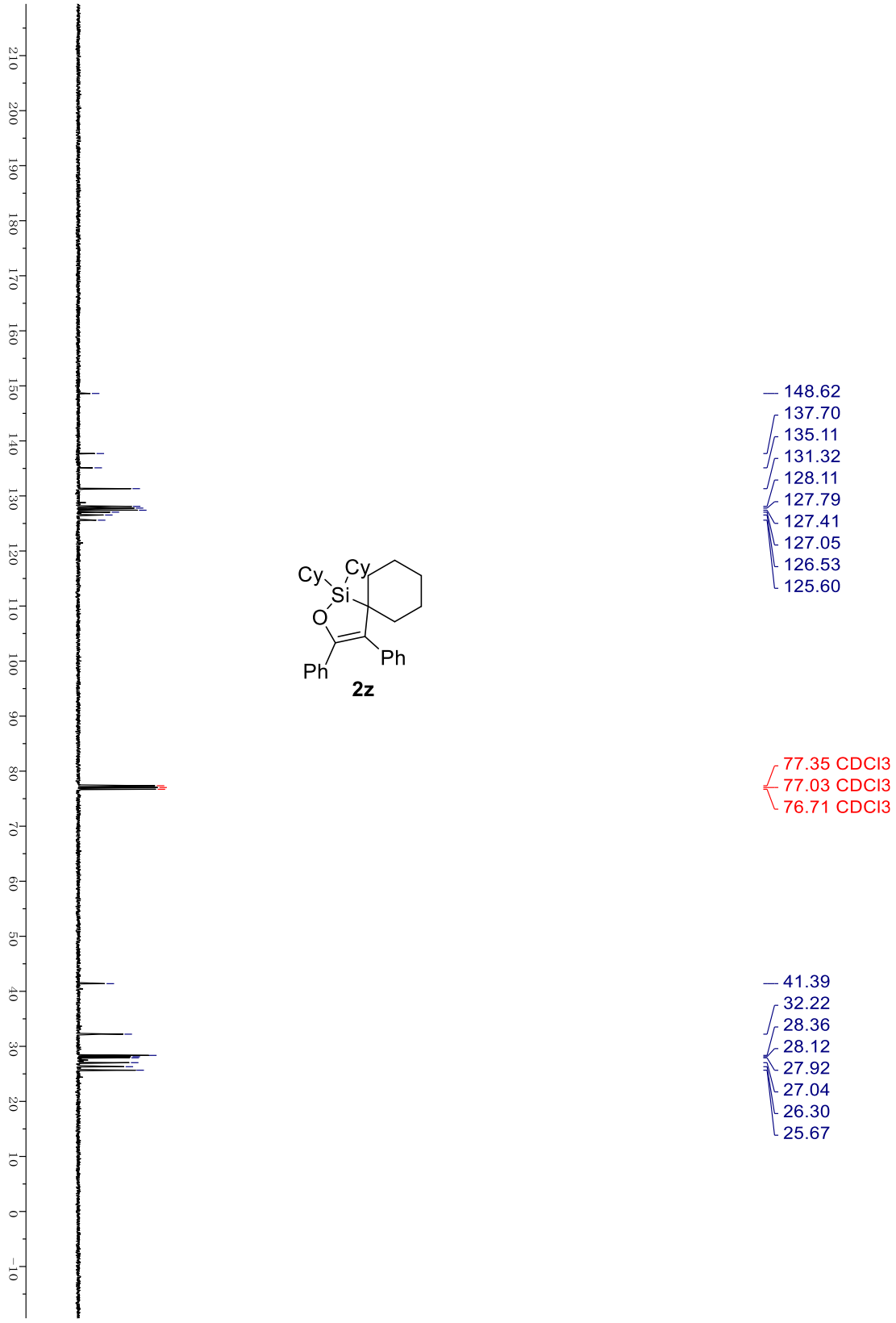

5.25
5.00
6.13
8.50
11.98
Cyp
O–Si
Cyp
Ph
Ph
2y
7.30
7.28
7.27
7.25
7.24
7.23 CDCl3
7.22
7.21
7.20
7.19
7.10
7.09
7.07
7.06
7.05
2.00
1.99
1.98
1.97
1.95
1.91
1.72
1.71
1.70
1.69
1.68
1.67
1.64
1.63
1.62
1.59
1.57
1.56
1.55
1.53
1.52
1.50
1.48
1.37
1.34
1.32
0.00

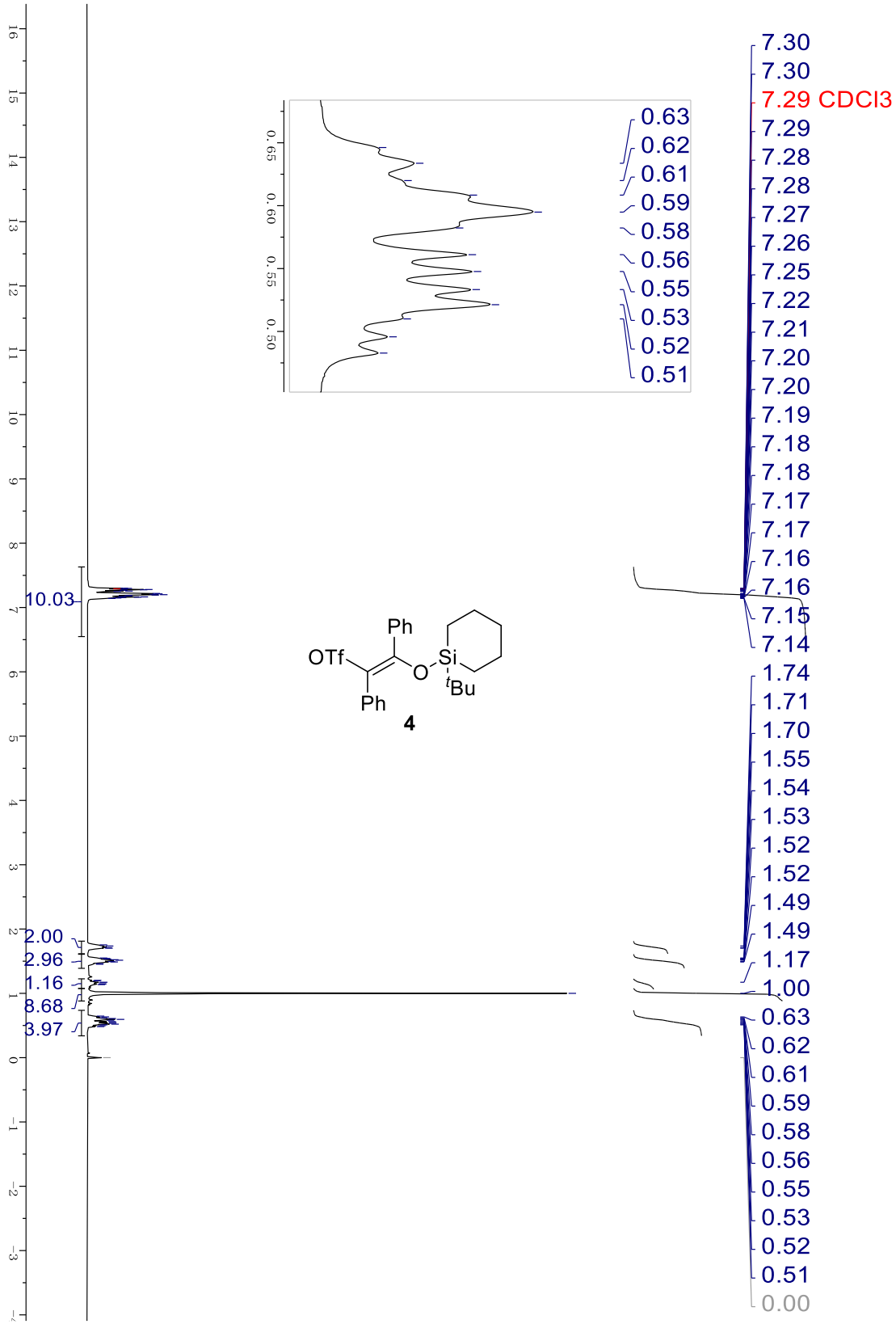

149.90
137.71
135.23
131.36
128.15
127.81
127.40
127.04
126.48
123.47
Cyp
O
Si
Cyp
Ph
Ph
2y
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
42.50
32.94
28.26
28.23
27.12
26.88
25.54
23.84

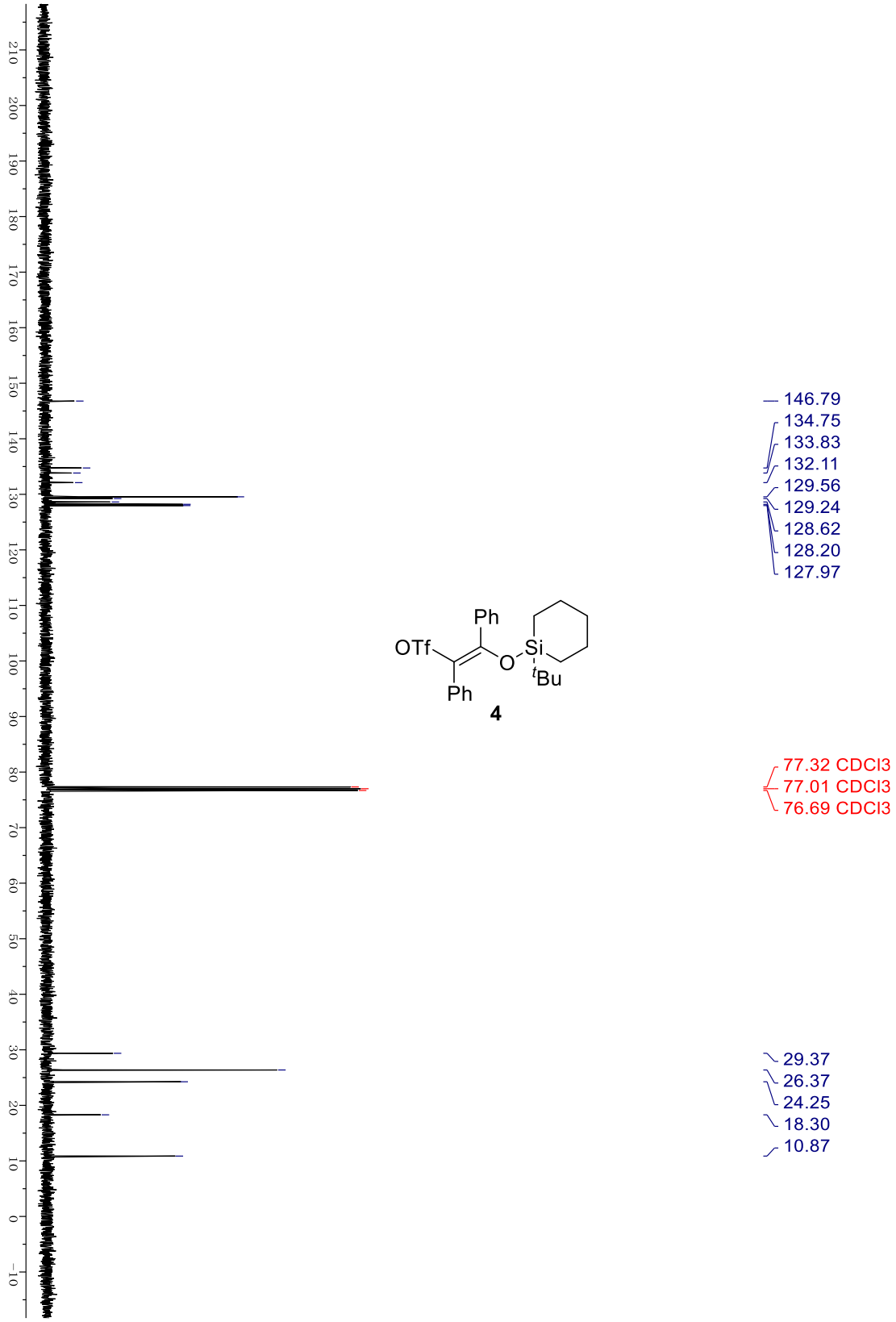

5.14
5.00
0.99
7.05
16.35
2.35
Cyp
Cyp
Si
O
Ph
Ph
2y'
7.24 CDCl3
7.16
7.14
7.12
7.10
7.09
7.08
7.04
7.03
3.19
3.17
1.94
1.94
1.93
1.92
1.91
1.89
1.87
1.85
1.83
1.82
1.80
1.79
1.78
1.68
1.67 H2O
1.67
1.66
1.65
1.63
1.61
1.59
1.56
1.54
1.51
1.50
1.49
1.47
1.46
1.45
1.44
1.42
1.25
1.21
1.19

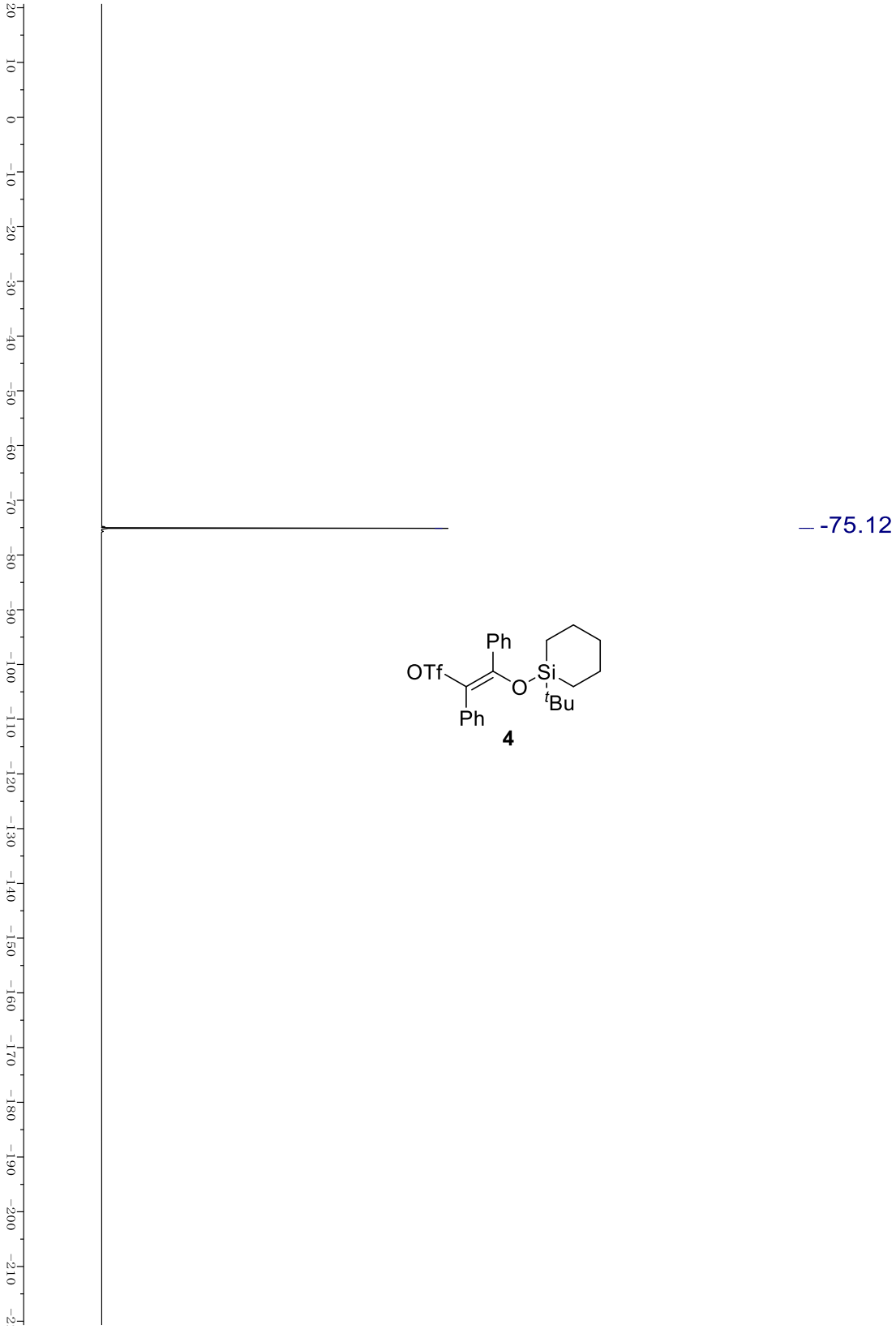

146.80
143.32
139.17
130.03
129.20
127.93
127.09
126.63
125.64
120.07
Cyp
Cyp
Si
O
Ph
Ph
2y'
77.34 CDCl3
77.03 CDCl3
76.71 CDCl3
46.58
34.36
28.02
27.96
27.93
27.78
27.03
26.99
26.83
25.93
24.78
24.18
22.93


2.77
2.00
5.30
6.20
9.96
4.41
12.33
Cy
Cy
Si
O
Ph
Ph
2z
7.30
7.30
7.28
7.28
7.27
7.24
7.20
7.20
7.19
7.18
7.09
7.09
7.08
7.07
7.07
7.06
1.96
1.93
1.91
1.80
1.79
1.77
1.73
1.72
1.71
1.55
1.53
1.52
1.52
1.50
1.49
1.32
1.31
1.31
1.30
1.29
1.28
1.28
1.27
1.26
1.26
1.24
1.24
1.23
1.21

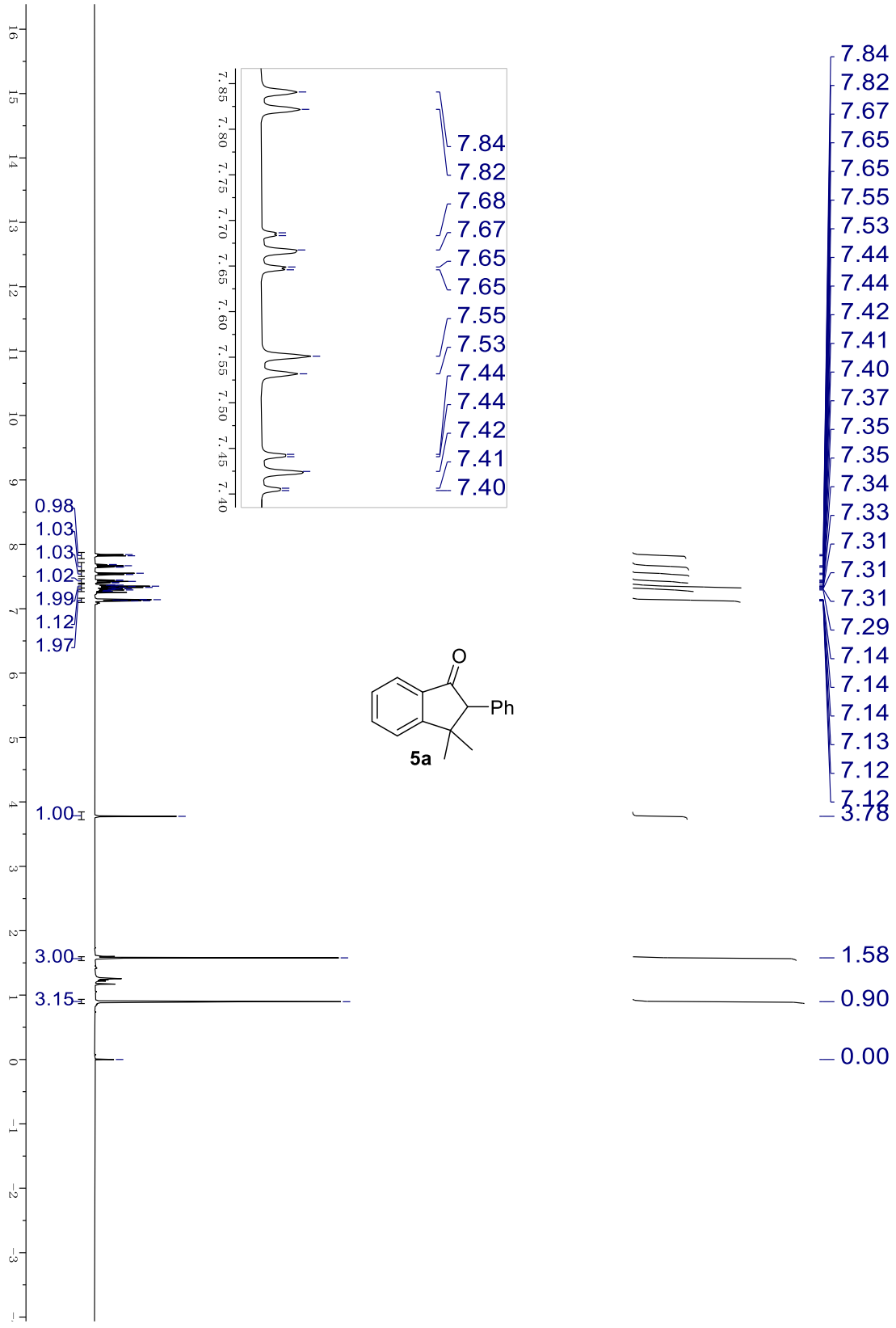

148.62
137.70
135.11
131.32
128.11
127.79
127.41
127.05
126.53
125.60
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
41.39
32.22
28.36
28.12
27.92
27.04
26.30
25.67
Cy
Cy
Si
O
Ph
Ph
2z

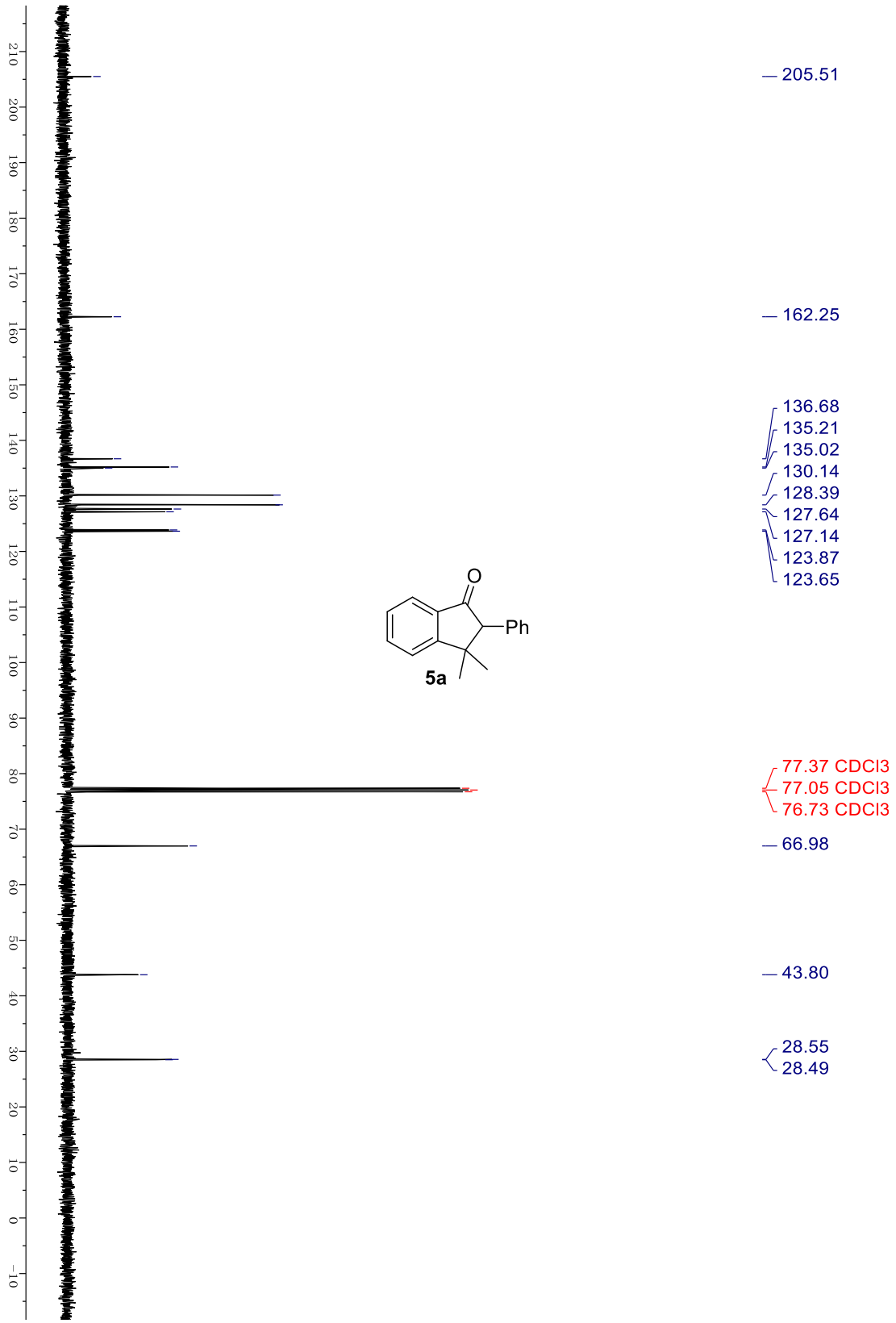

7.30
7.30
7.29 CDCl3
7.29
7.28
7.28
7.27
7.26
7.25
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.14
1.74
1.71
1.70
1.55
1.54
1.53
1.52
1.52
1.49
1.49
1.17
1.00
0.63
0.62
0.61
0.59
0.58
0.56
0.55
0.53
0.52
0.51
0.00
0.63
0.62
0.61
0.59
0.58
0.56
0.55
0.53
0.52
0.51
10.03
2.00
2.96
1.16
8.68
3.97
Ph
OTf
O
Si
tBu
Ph
4

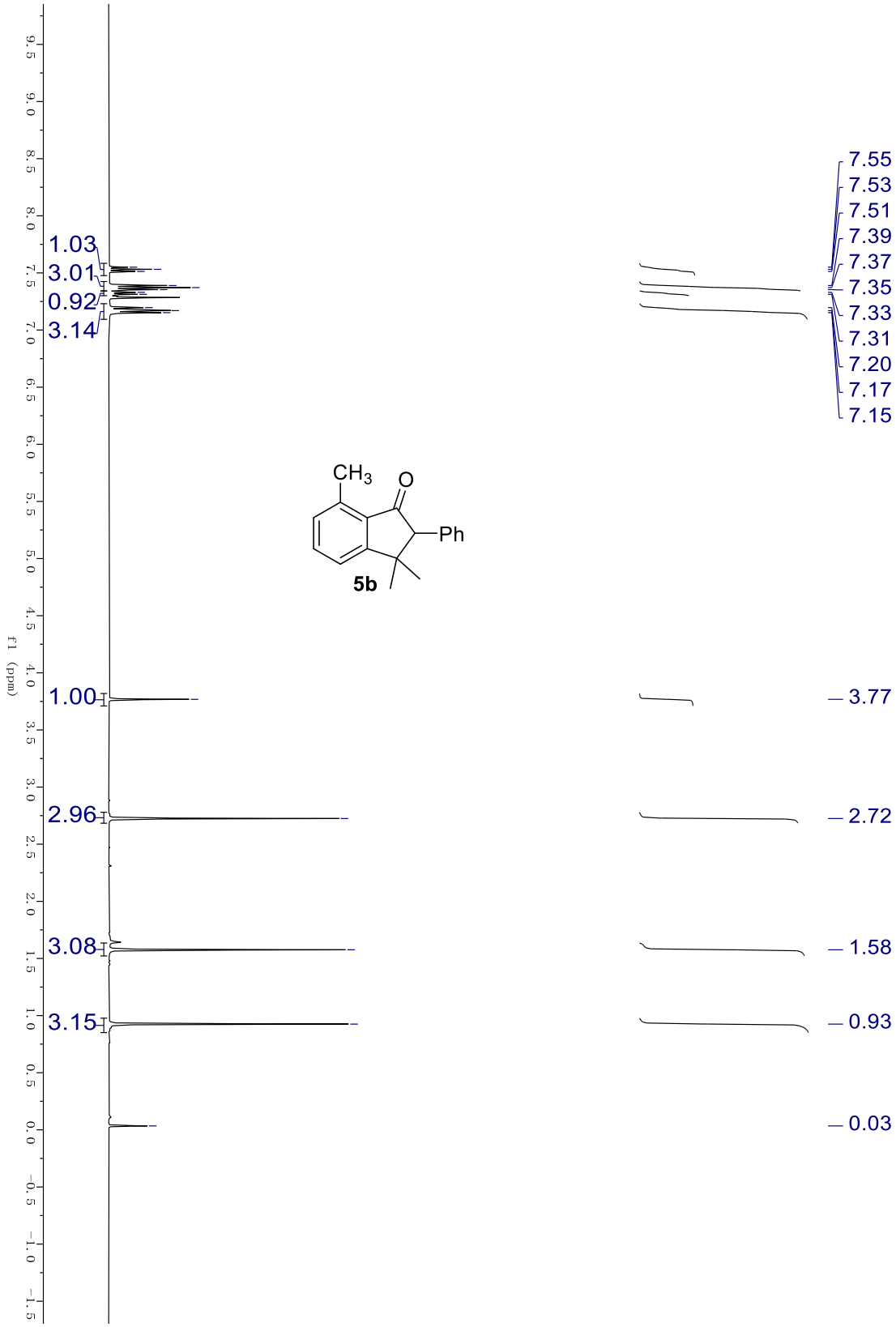

146.79
134.75
133.83
132.11
129.56
129.24
128.62
128.20
127.97
77.32 CDCl3
77.01 CDCl3
76.69 CDCl3
29.37
26.37
24.25
18.30
10.87
Ph
OTf
O
Si
tBu
Ph
4

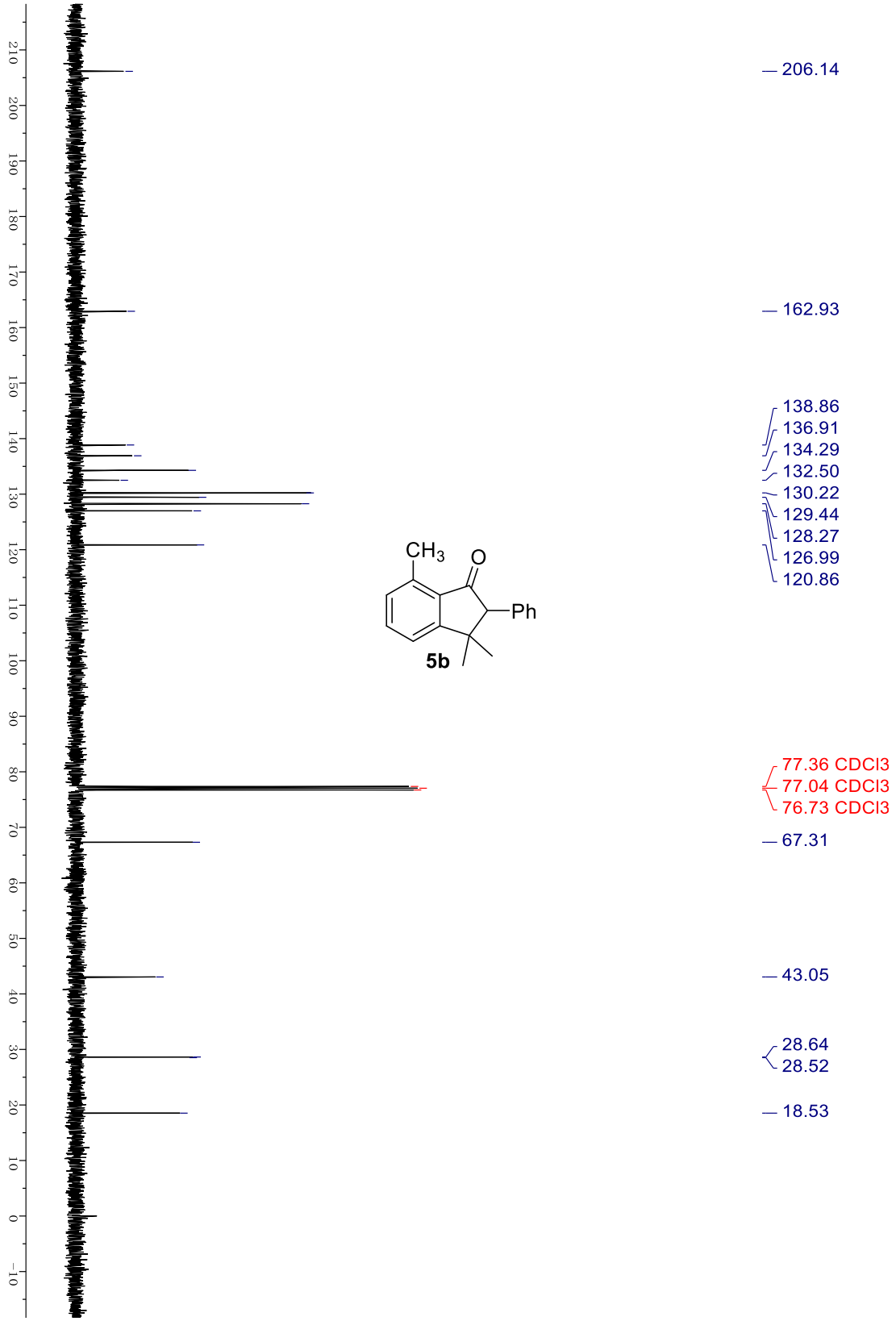

-75.12
Ph
OTf
Si
O
tBu
Ph
4

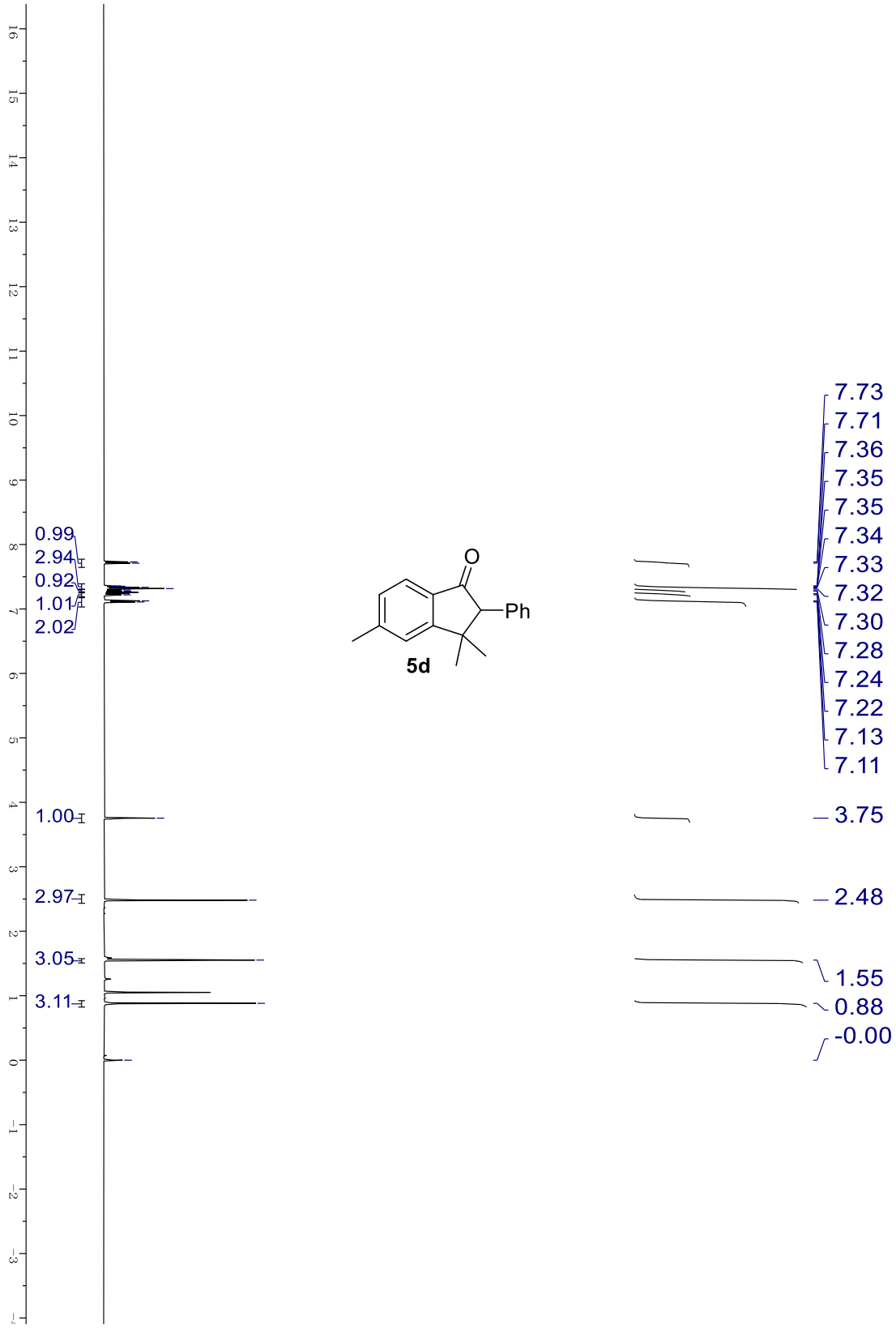
11.3 NMR spectra of indanones

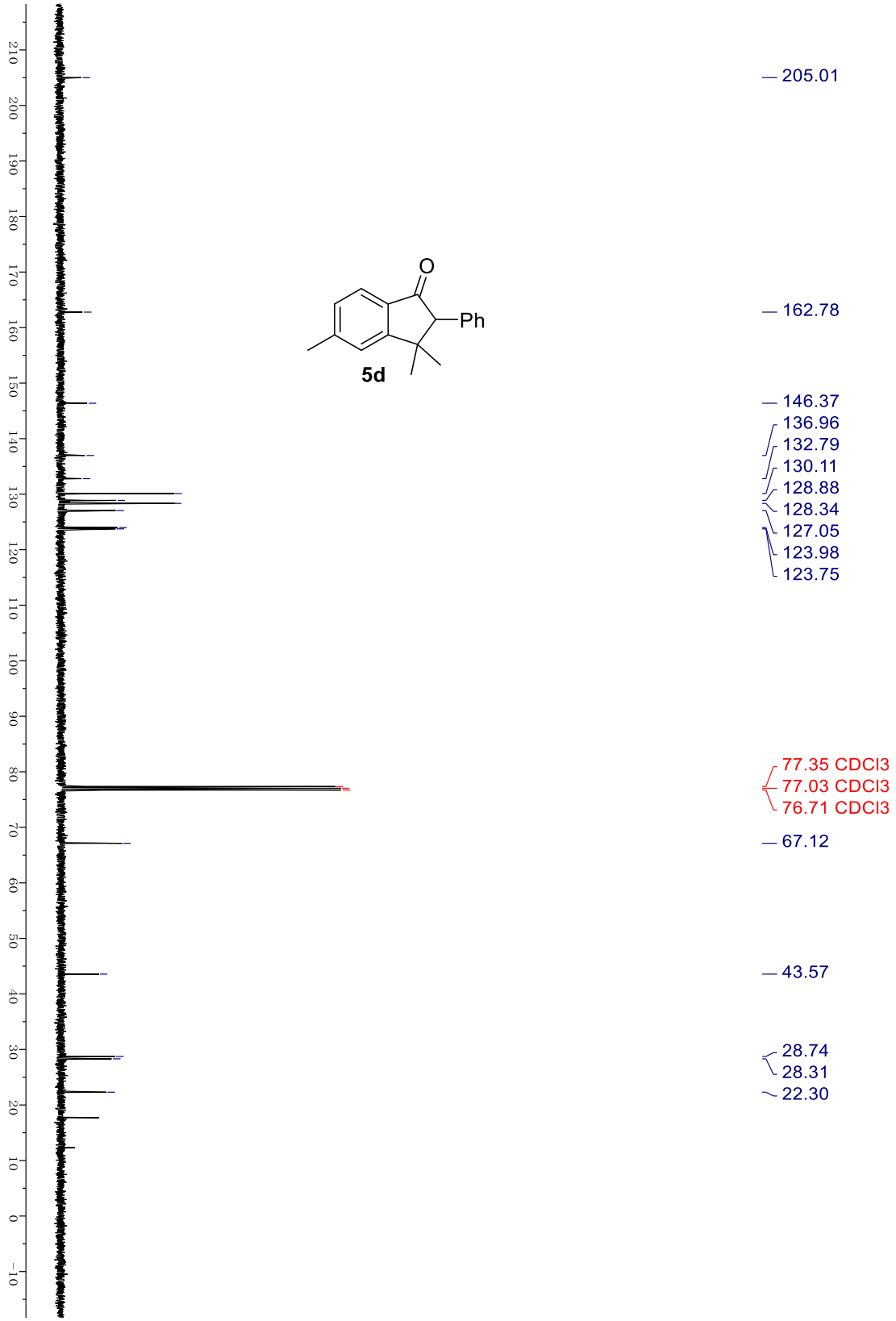


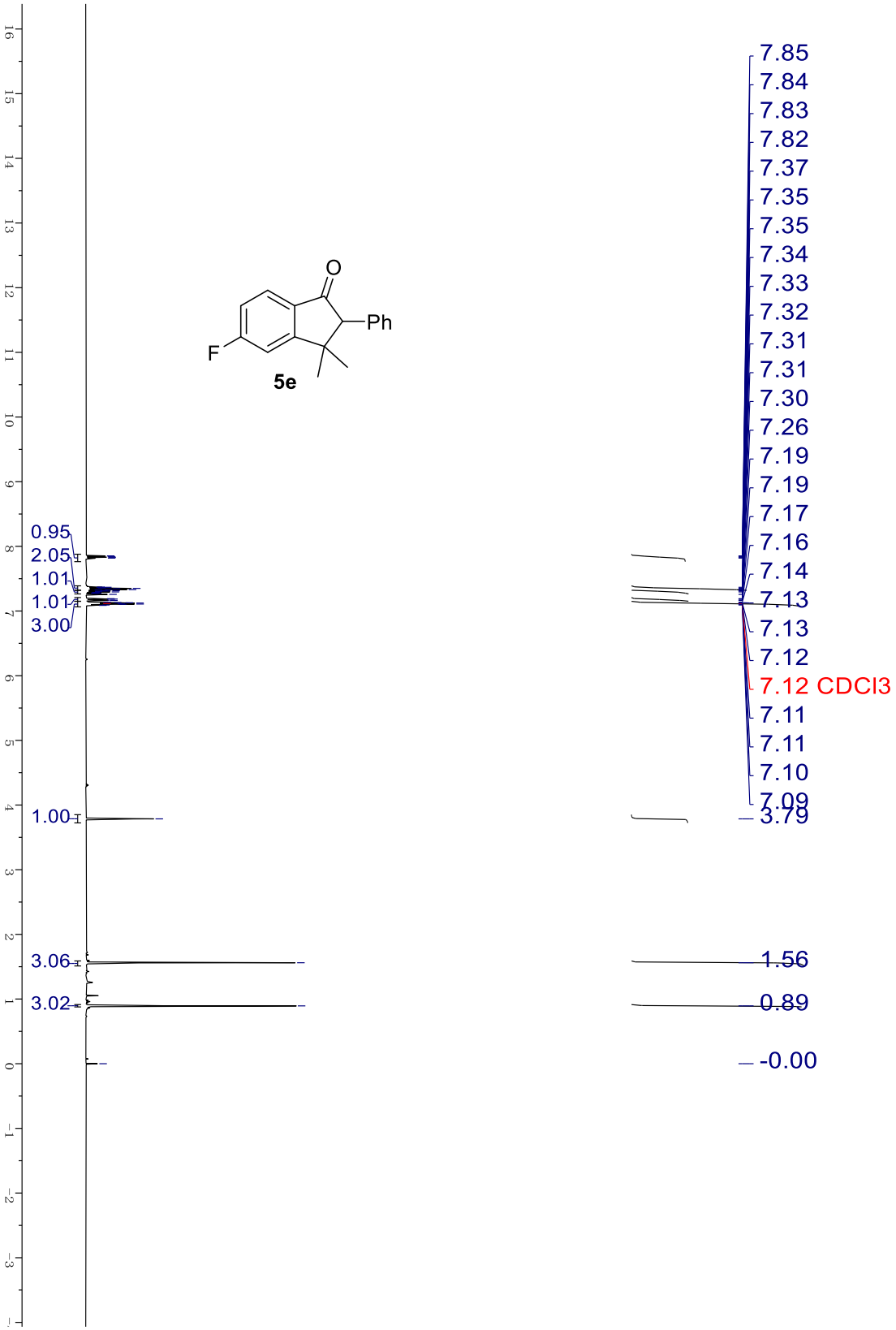

205.51
162.25
136.68
135.21
135.02
130.14
128.39
127.64
127.14
123.87
123.65
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
66.98
43.80
28.55
28.49
O
Ph
5a

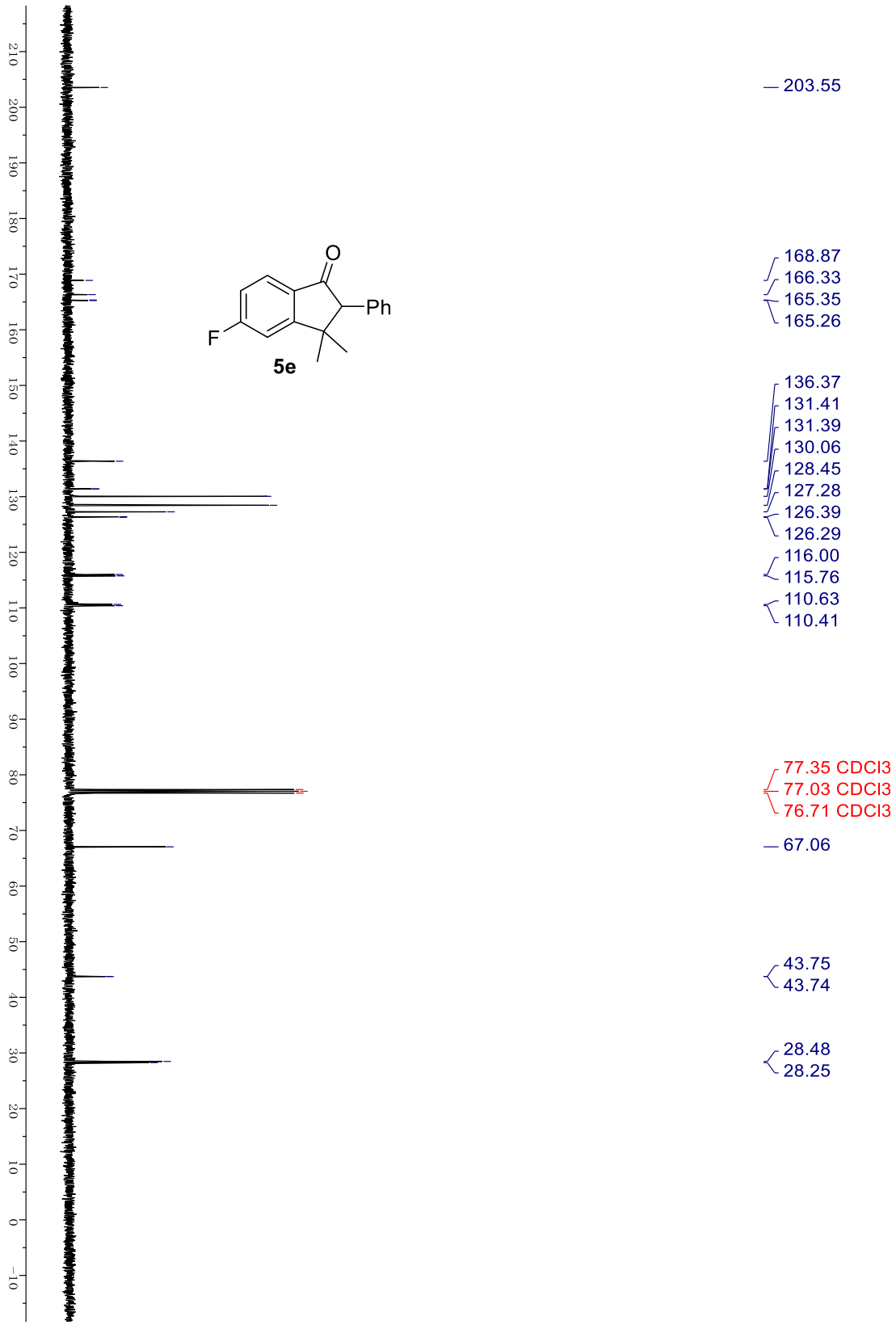

1.03
3.01
0.92
3.14
1.00
2.96
3.08
3.15
7.55
7.53
7.51
7.39
7.37
7.35
7.33
7.31
7.20
7.17
7.15
3.77
2.72
1.58
0.93
0.03
CH3
O
Ph
5b
f1 (ppm)

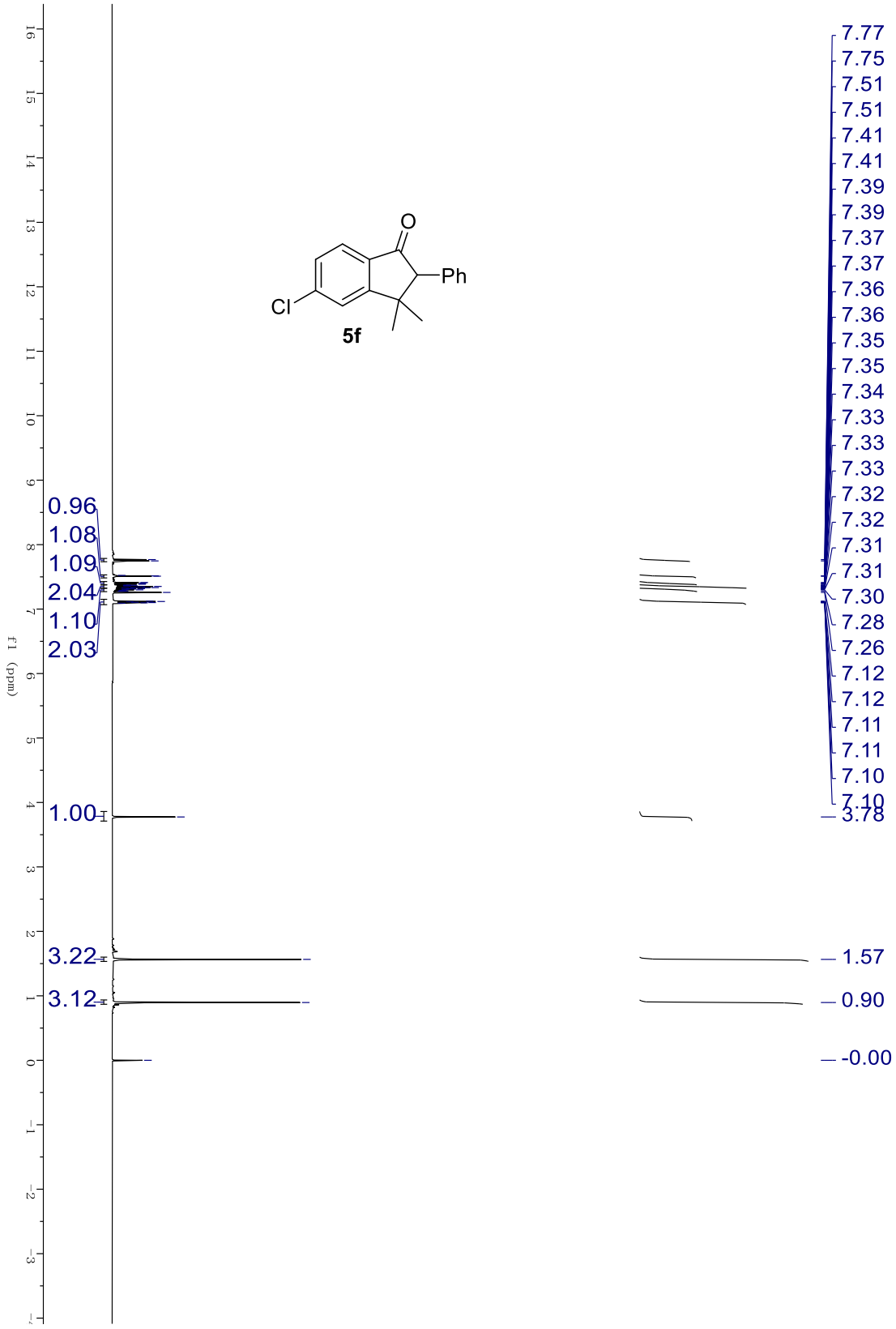

206.14
162.93
138.86
136.91
134.29
132.50
130.22
129.44
128.27
126.99
120.86
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
67.31
43.05
28.64
28.52
18.53
CH3
O
Ph
5b

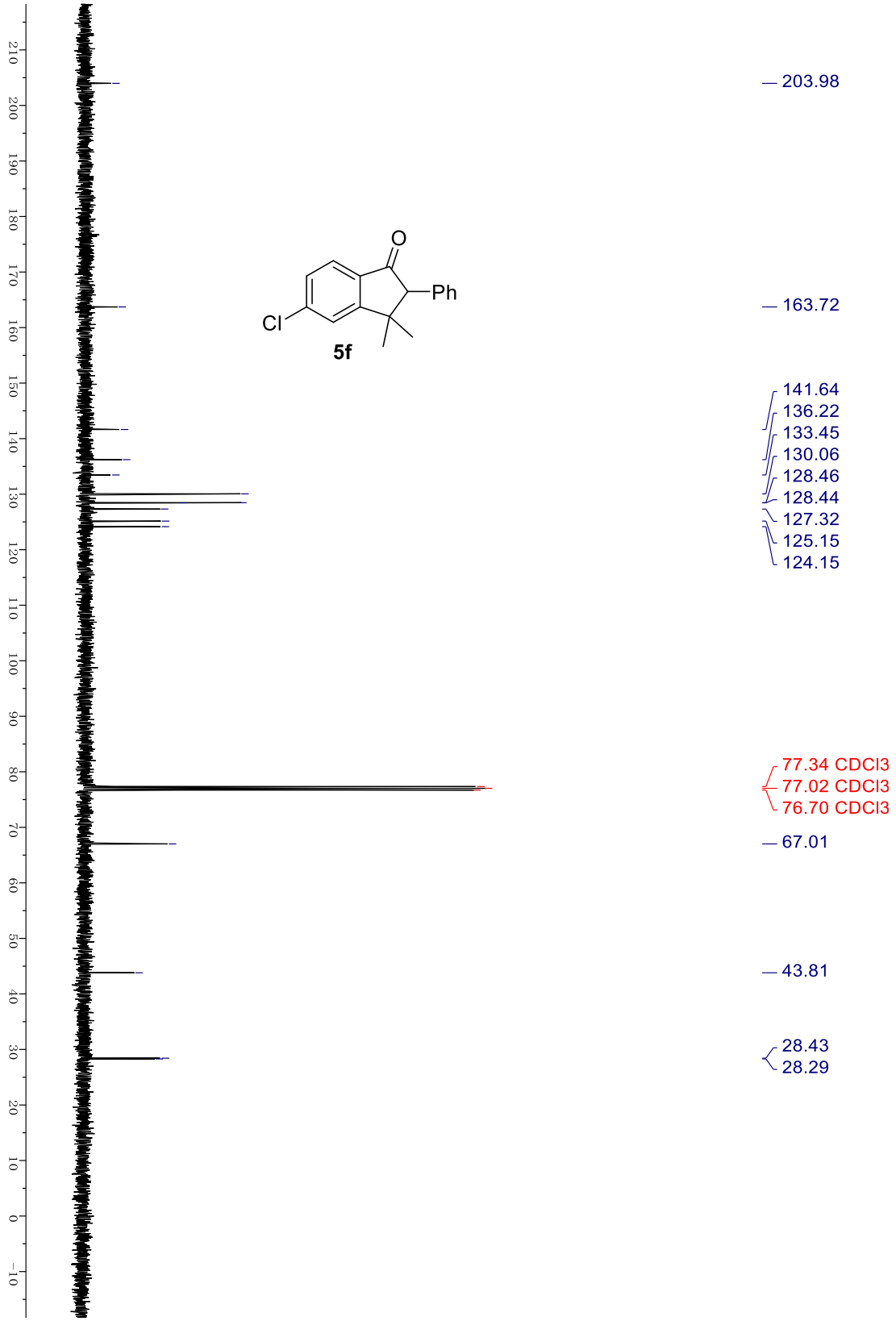

0.99
2.94
0.92
1.01
2.02
1.00
2.97
3.05
3.11
O
Ph
5d
7.73
7.71
7.36
7.35
7.35
7.34
7.33
7.32
7.30
7.28
7.24
7.22
7.13
7.11
3.75
2.48
1.55
0.88
-0.00

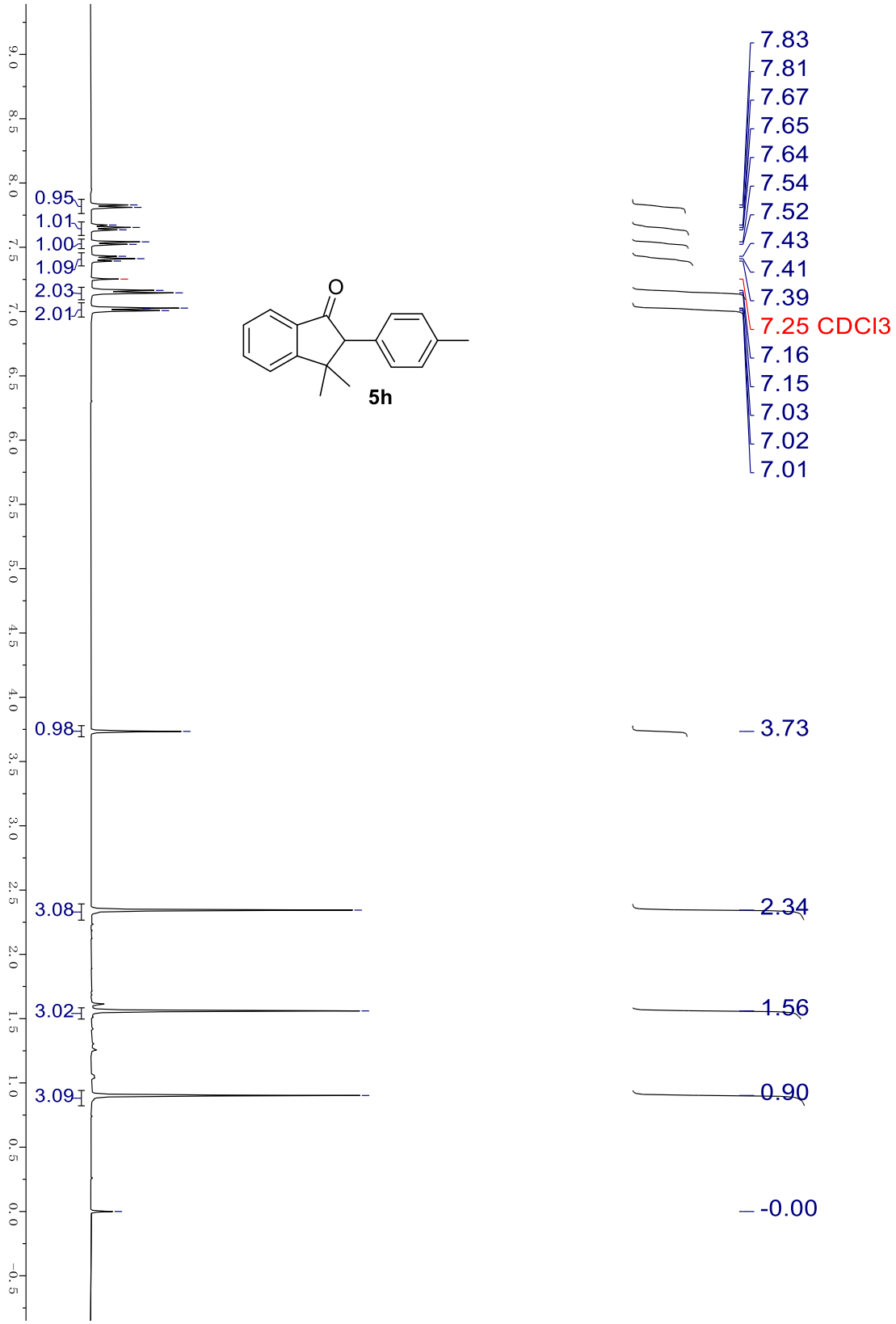

O
Ph
5d
205.01
162.78
146.37
136.96
132.79
130.11
128.88
128.34
127.05
123.98
123.75
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
67.12
43.57
28.74
28.31
22.30

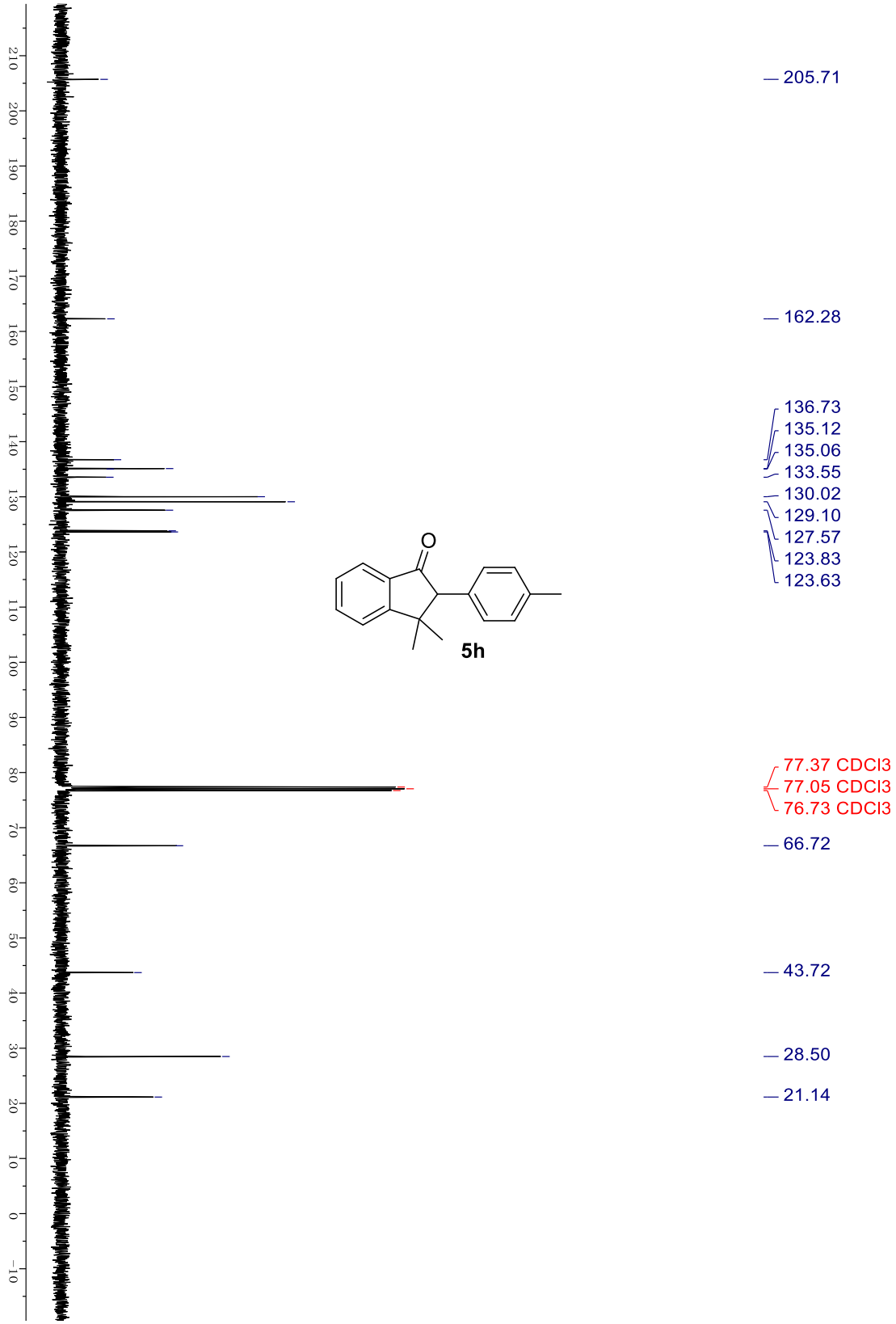

O
Ph
F
5e
0.95
2.05
1.01
1.01
3.00
1.00
3.06
3.02
7.85
7.84
7.83
7.82
7.37
7.35
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.26
7.19
7.19
7.17
7.16
7.14
7.13
7.13
7.12
7.12 CDCl3
7.11
7.11
7.10
7.09
3.79
1.56
0.89
-0.00

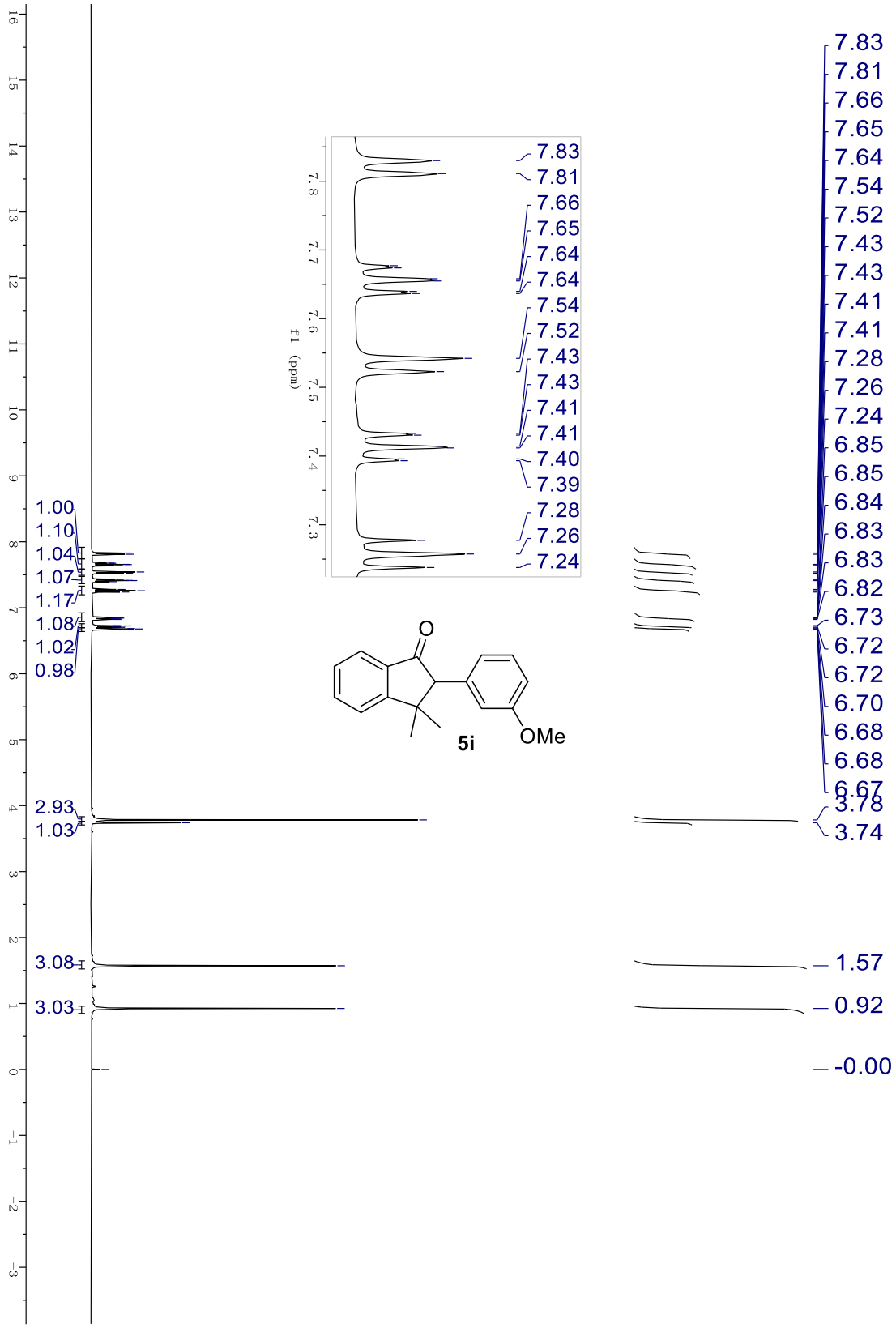

O
Ph
F
5e
203.55
168.87
166.33
165.35
165.26
136.37
131.41
131.39
130.06
128.45
127.28
126.39
126.29
116.00
115.76
110.63
110.41
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
67.06
43.75
43.74
28.48
28.25

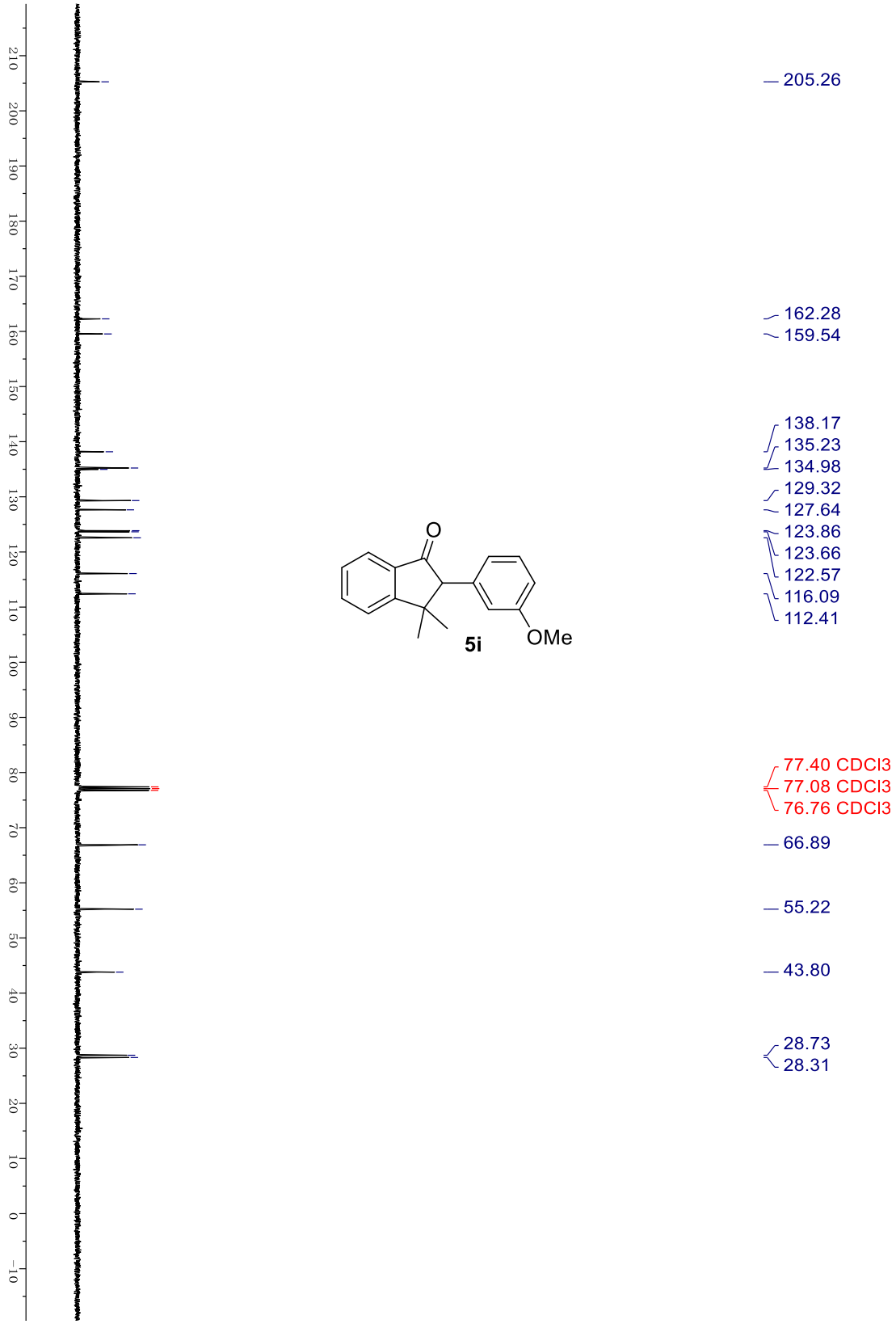

O
Ph
Cl
5f
f1 (ppm)
0.96
1.08
1.09
2.04
1.10
2.03
1.00
3.22
3.12
7.77
7.75
7.51
7.51
7.41
7.41
7.39
7.39
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.28
7.26
7.12
7.12
7.11
7.11
7.10
7.10
3.78
1.57
0.90
-0.00


O
Ph
Cl
5f
203.98
163.72
141.64
136.22
133.45
130.06
128.46
128.44
127.32
125.15
124.15
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
67.01
43.81
28.43
28.29


7.83
7.81
7.67
7.65
7.64
7.54
7.52
7.43
7.41
7.39
7.25 CDCl3
7.16
7.15
7.03
7.02
7.01
0.95
1.01
1.00
1.09
2.03
2.01
0.98
3.08
3.02
3.09
3.73
2.34
1.56
0.90
-0.00
O
5h


205.71
162.28
136.73
135.12
135.06
133.55
130.02
129.10
127.57
123.83
123.63
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
66.72
43.72
28.50
21.14
O
5h


7.83
7.81
7.66
7.65
7.64
7.54
7.52
7.43
7.43
7.41
7.41
7.28
7.26
7.24
6.85
6.85
6.84
6.83
6.83
6.82
6.73
6.72
6.72
6.70
6.68
6.68
6.67
3.78
3.74
1.57
0.92
-0.00
1.00
1.10
1.04
1.07
1.17
1.08
1.02
0.98
2.93
1.03
3.08
3.03
f1 (ppm)
O
OMe
5i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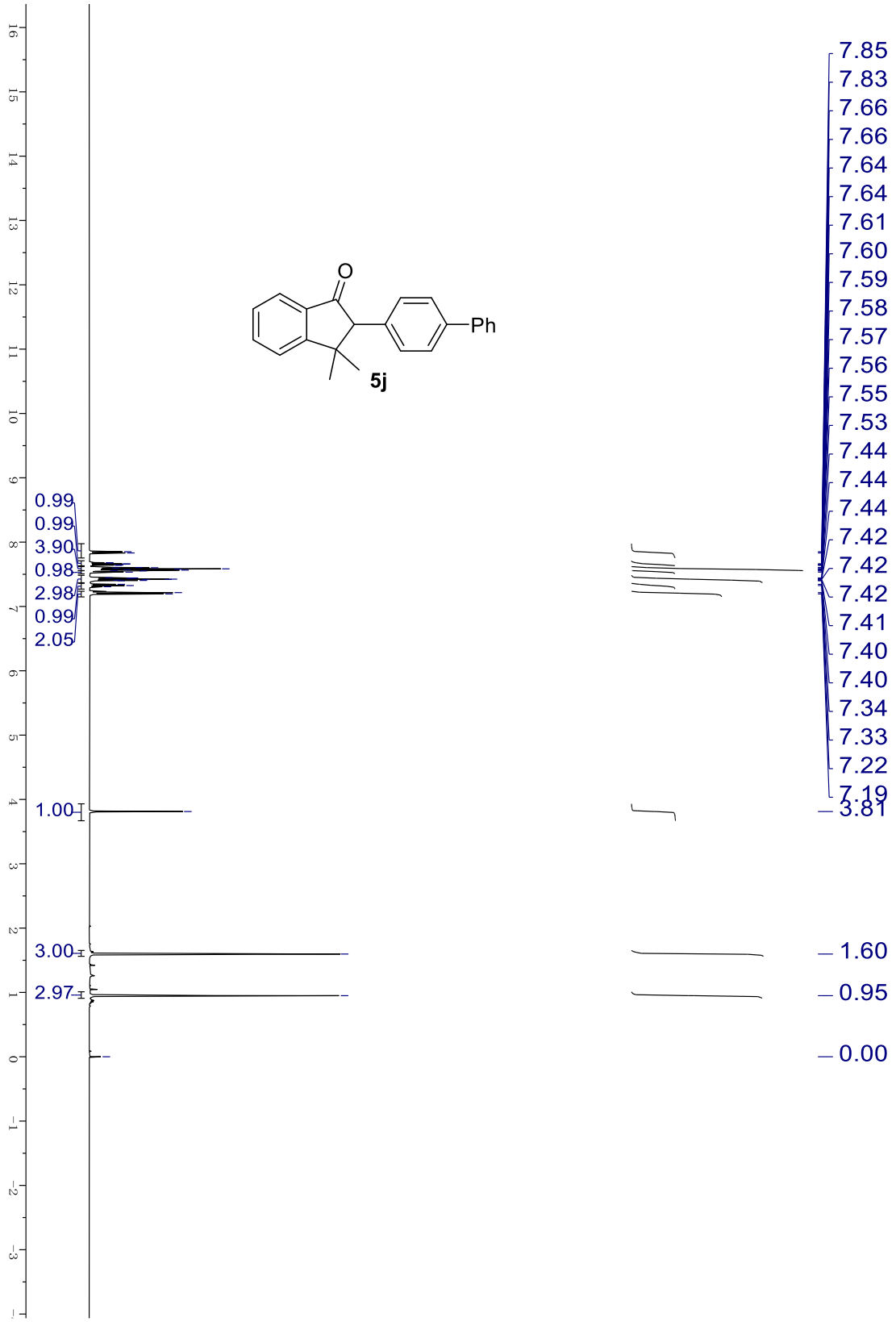
138.17
135.23
134.98
129.32
127.64
123.86
123.66
122.57
116.09
112.41
77.40 CDCl3
77.08 CDCl3
76.76 CDCl3
66.89
55.22
43.80
28.73
28.31
O
OMe
5i


O
Ph
5j
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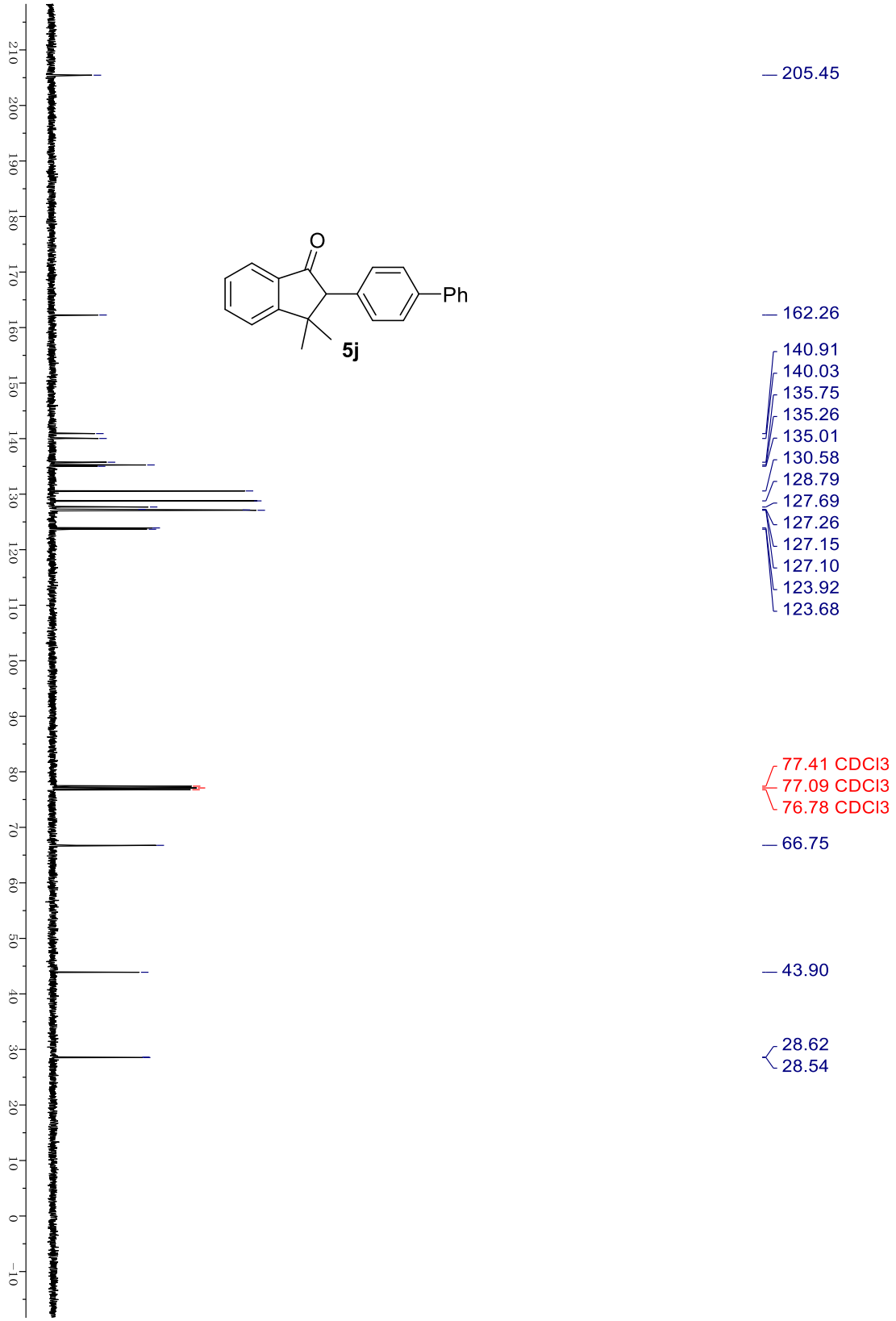
0.99
3.90
0.98
2.98
0.99
2.05
1.00
3.00
2.97
7.85
7.83
7.66
7.66
7.64
7.64
7.61
7.60
7.59
7.58
7.57
7.56
7.55
7.53
7.44
7.44
7.44
7.42
7.42
7.42
7.41
7.40
7.40
7.34
7.33
7.22
7.19
3.81
1.60
0.95
0.00


O
Ph
5j
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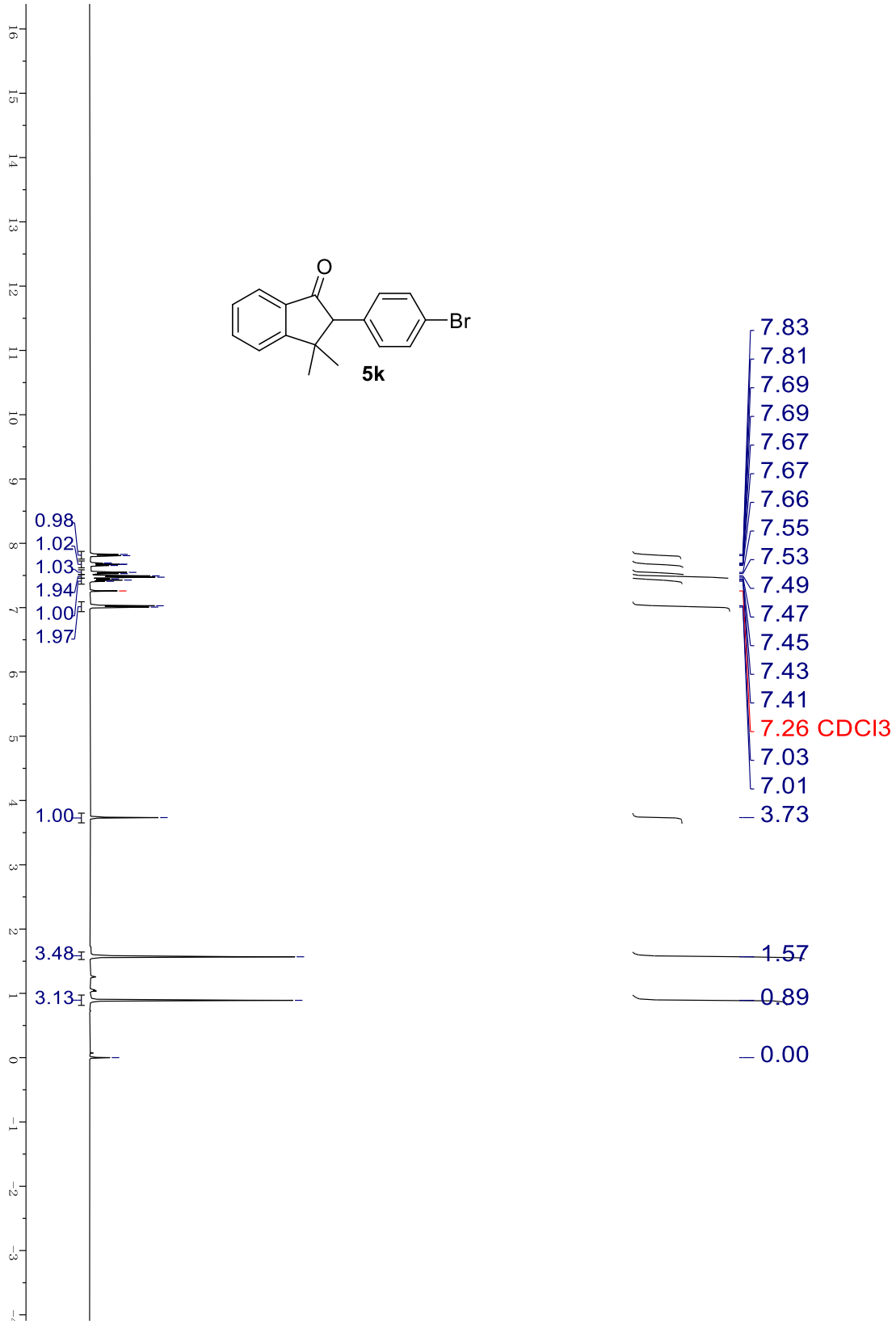
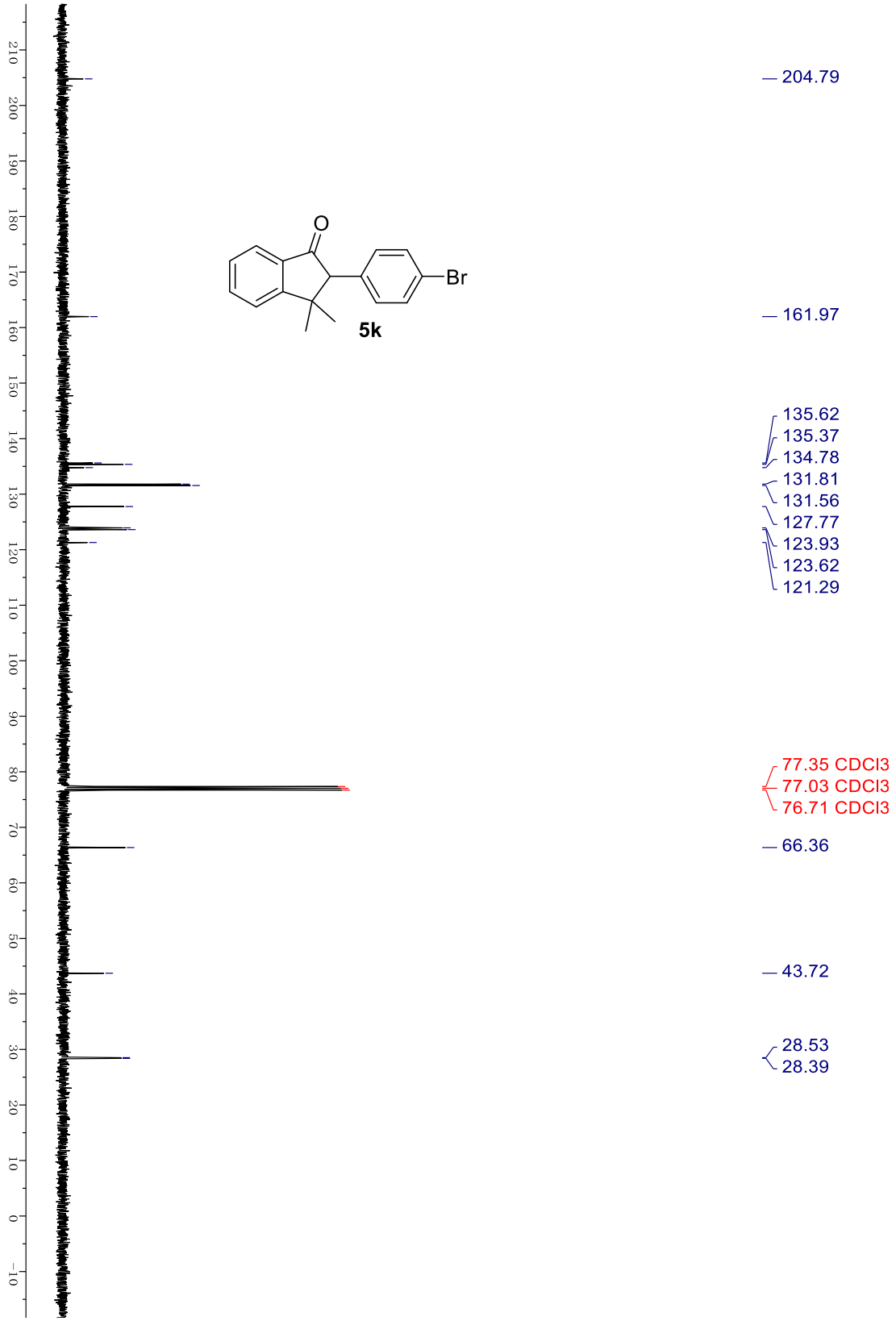
140.03
135.75
135.26
135.01
130.58
128.79
127.69
127.26
127.15
127.10
123.92
123.68
77.41 CDCl3
77.09 CDCl3
76.78 CDCl3
66.75
43.90
28.62
28.54


O
Br
5k
0.98
1.02
1.03
1.94
1.00
1.97
1.00
3.48
3.13
7.83
7.81
7.69
7.69
7.67
7.67
7.66
7.55
7.53
7.49
7.47
7.45
7.43
7.41
7.26 CDCl3
7.03
7.01
3.73
1.57
0.89
0.00


O
Br
5k
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135.62
135.37
134.78
131.81
131.56
127.77
123.93
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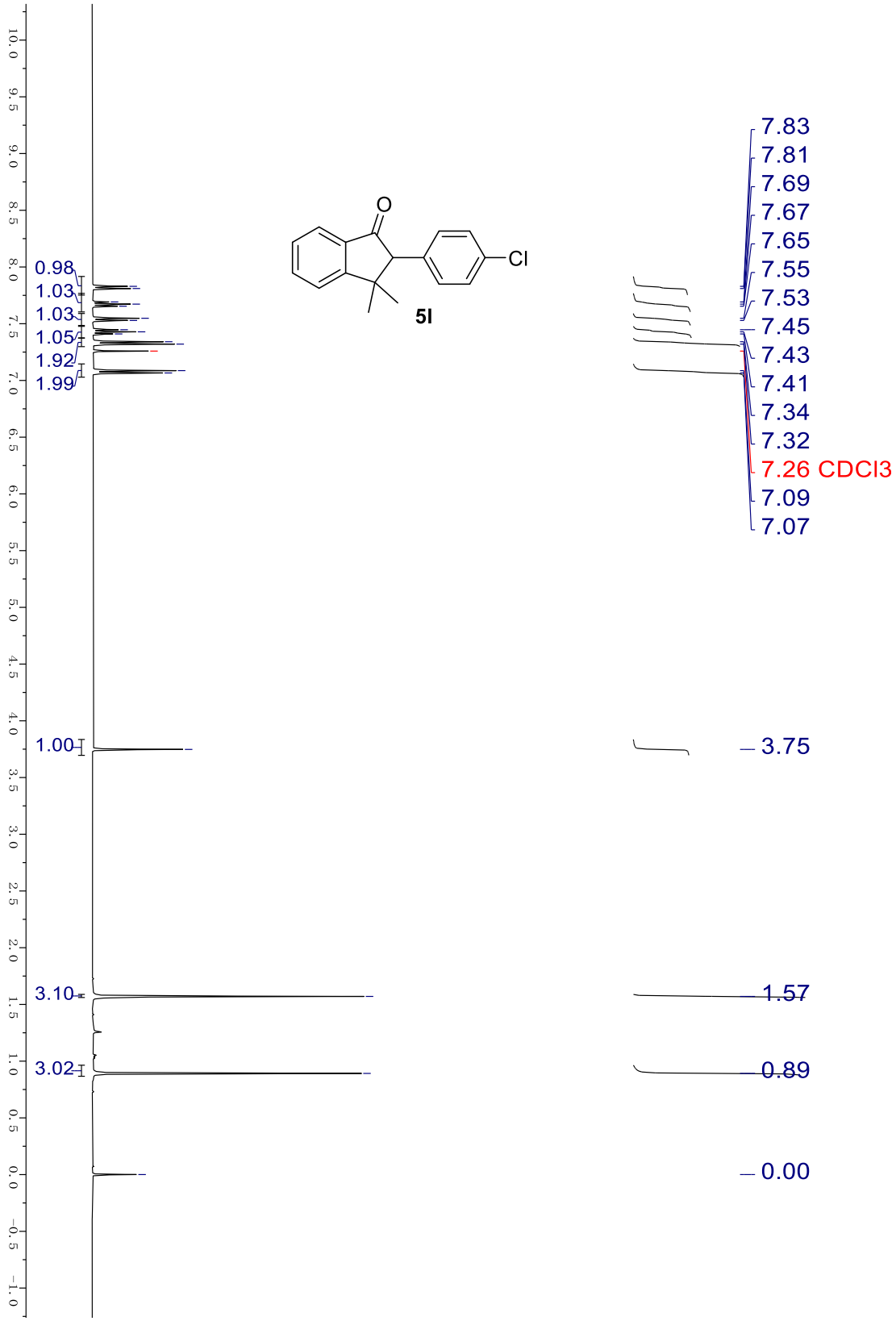
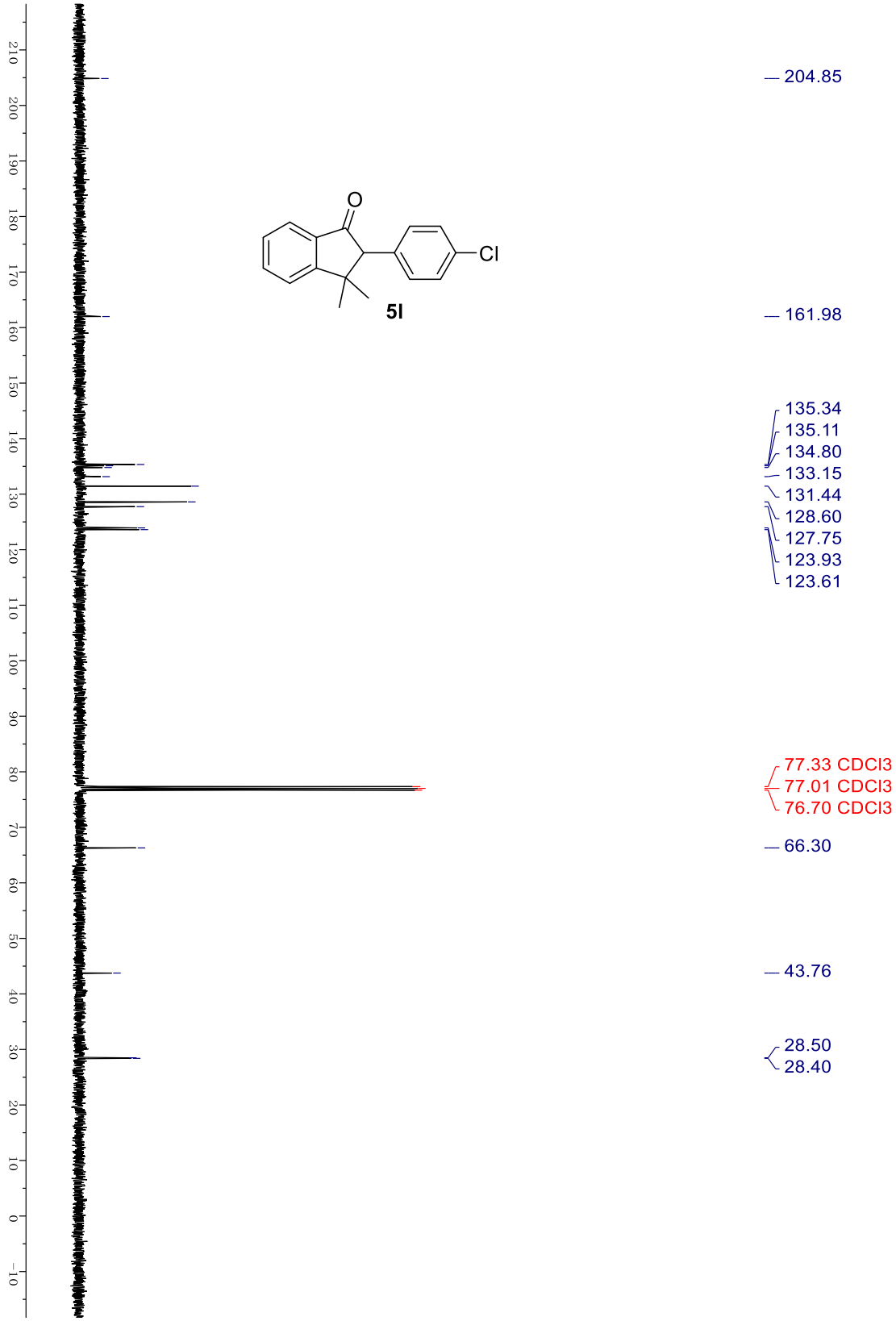
121.29
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
66.36
43.72
28.53
28.39


O
Cl
5l
7.83
7.81
7.69
7.67
7.65
7.55
7.53
7.45
7.43
7.41
7.34
7.32
7.26 CDCl3
7.09
7.07
3.75
1.57
0.89
0.00
0.98
1.03
1.03
1.05
1.92
1.99
1.00
3.10
3.02


O
Cl
5l
204.85
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135.34
135.11
134.80
133.15
131.44
128.60
127.75
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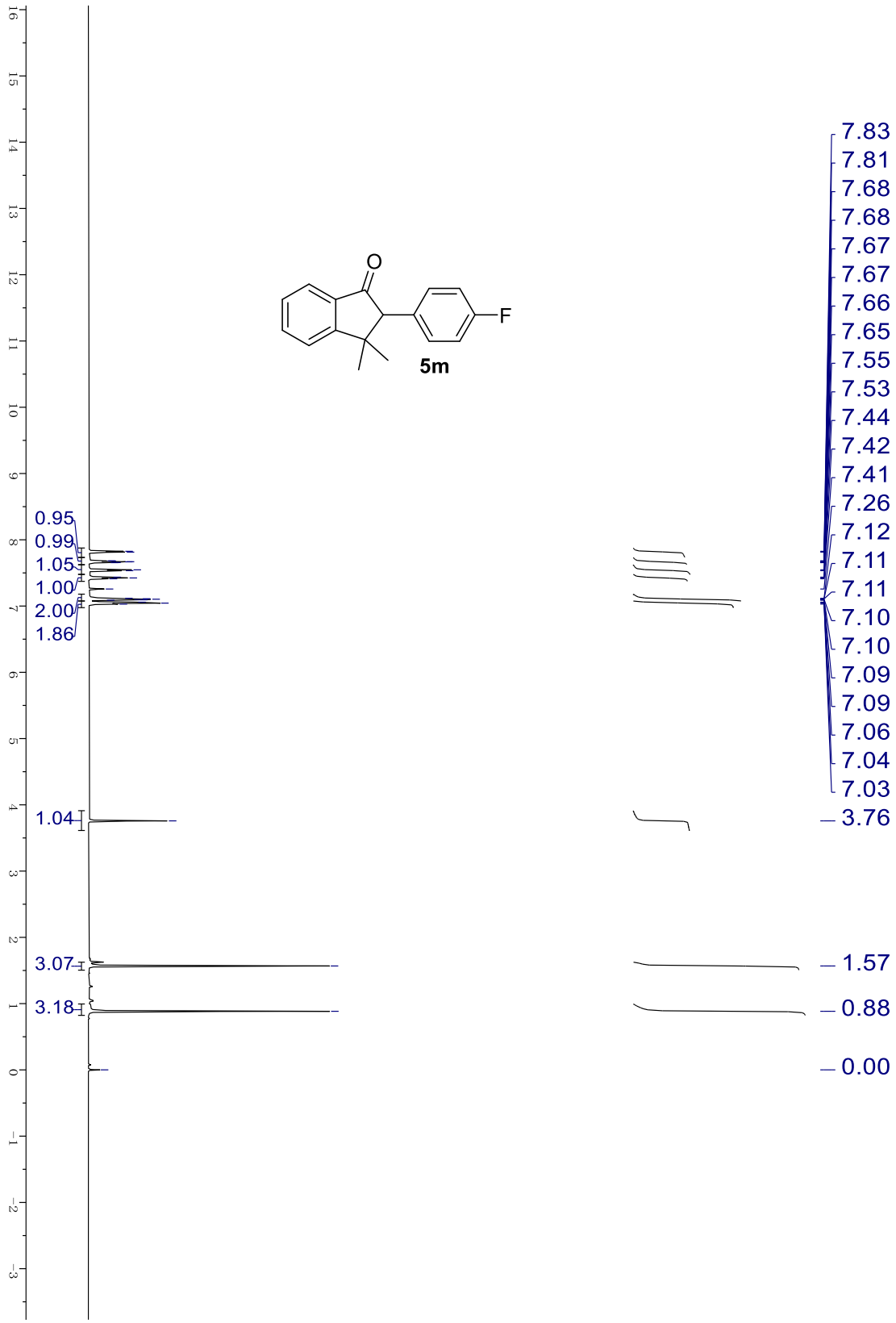
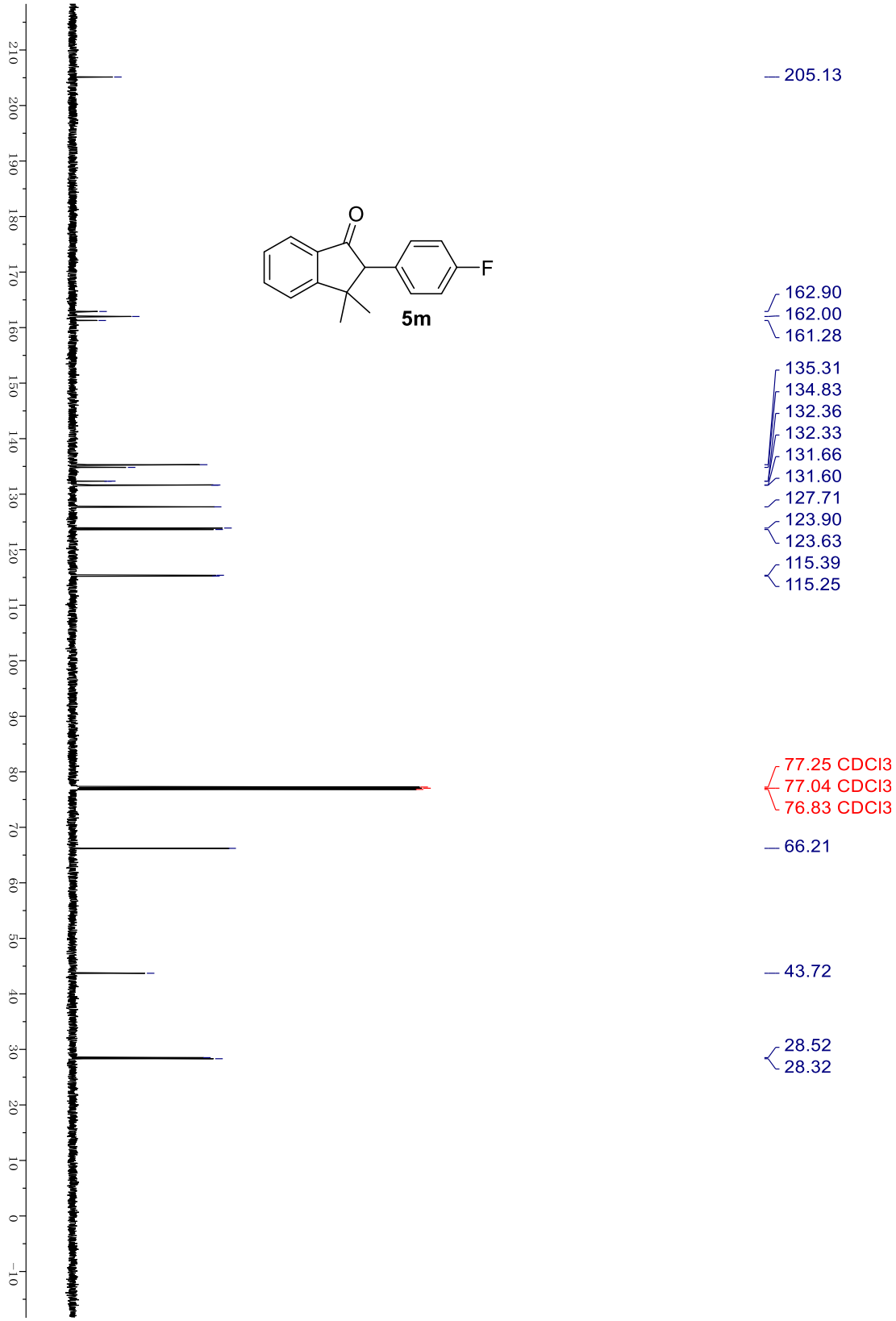
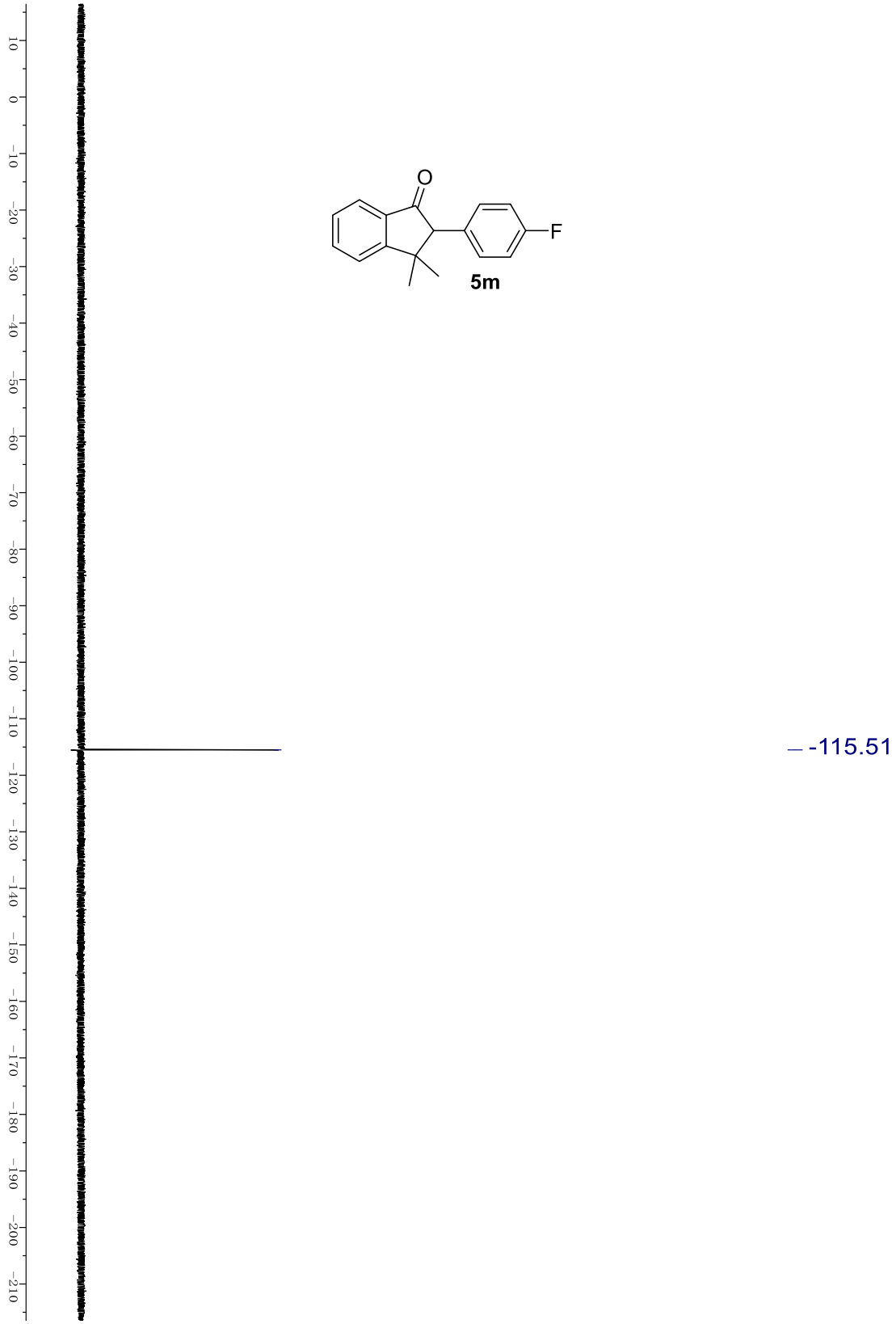
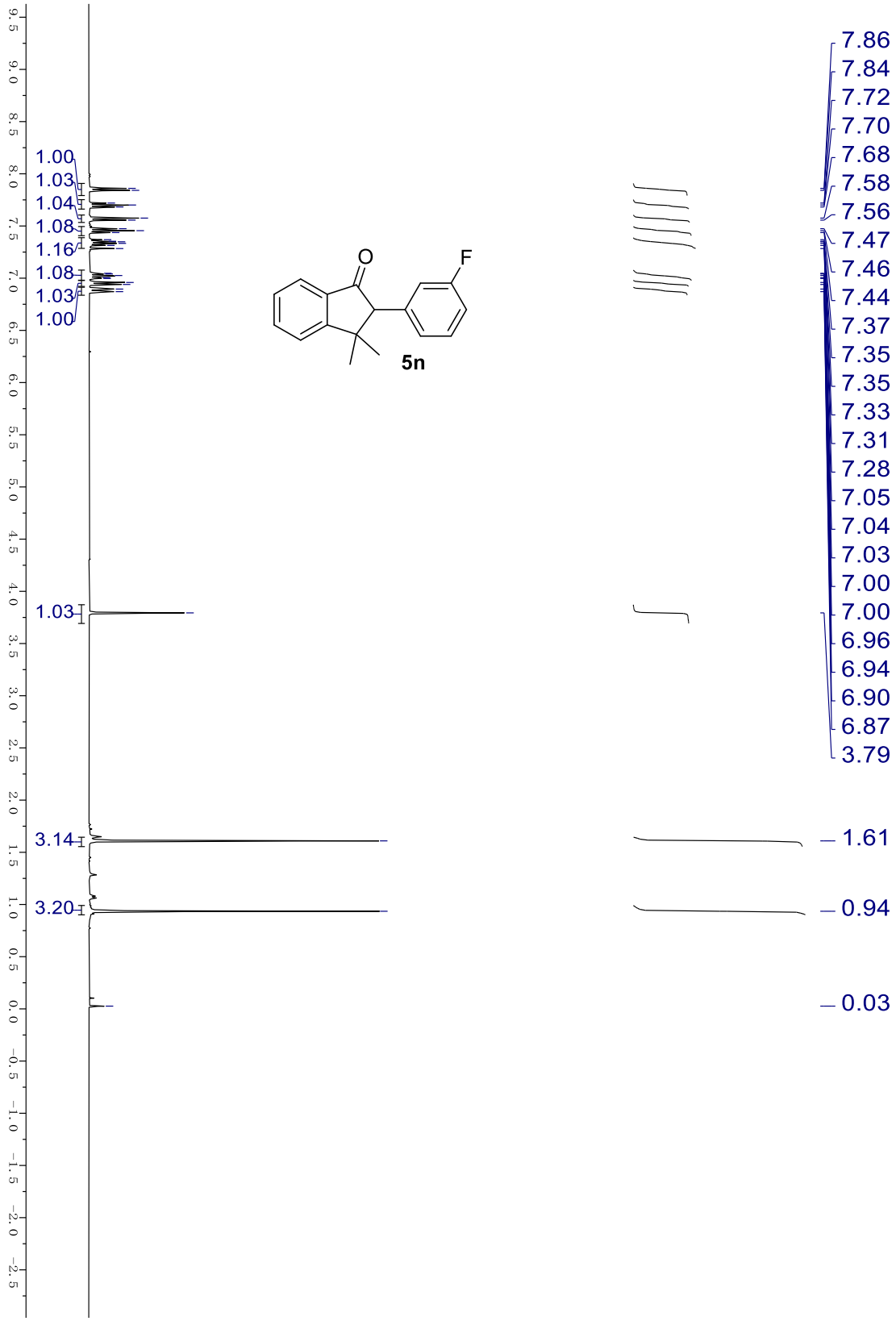
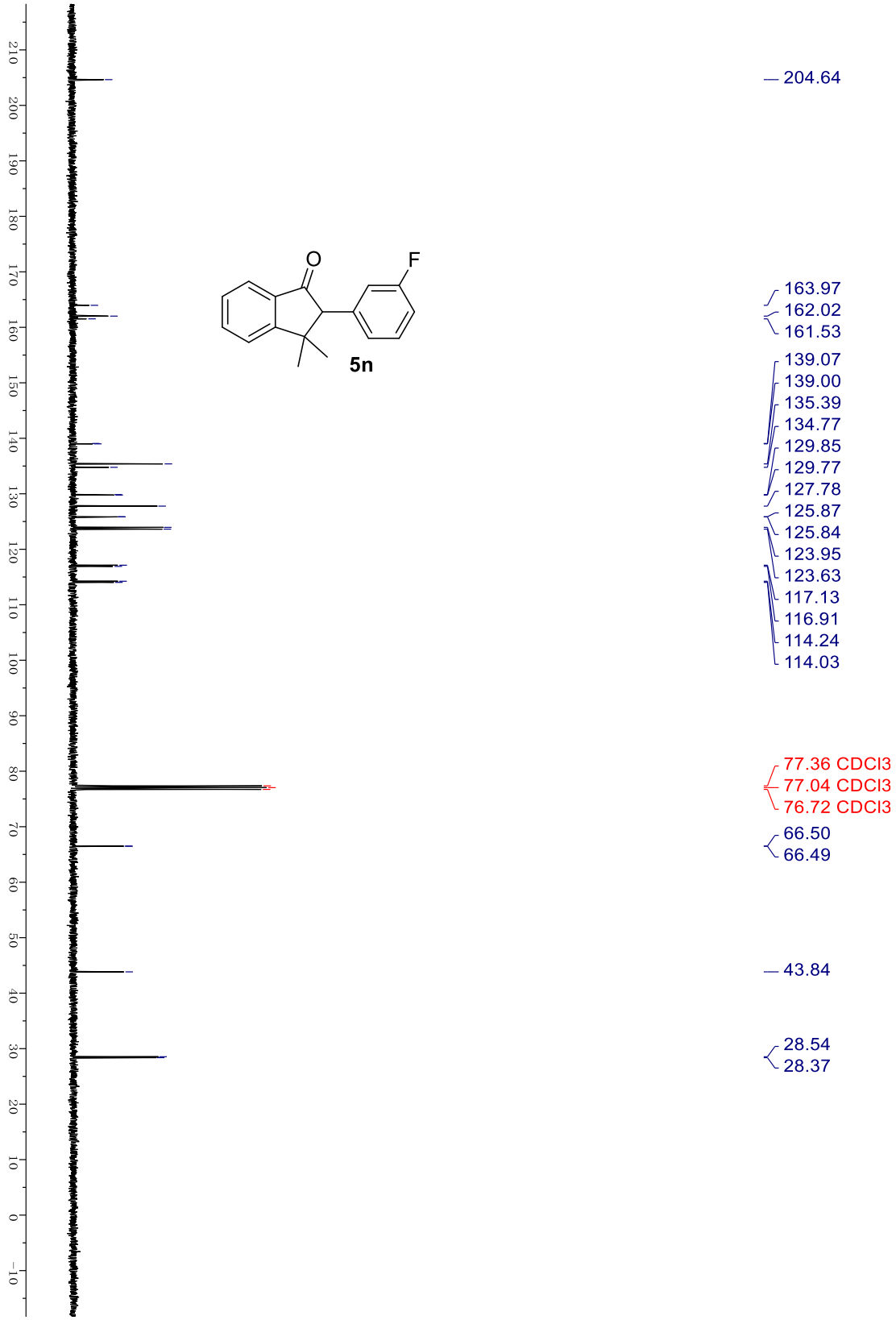
123.61
77.33 CDCl3
77.01 CDCl3
76.70 CDCl3
66.30
43.76
28.50
28.40

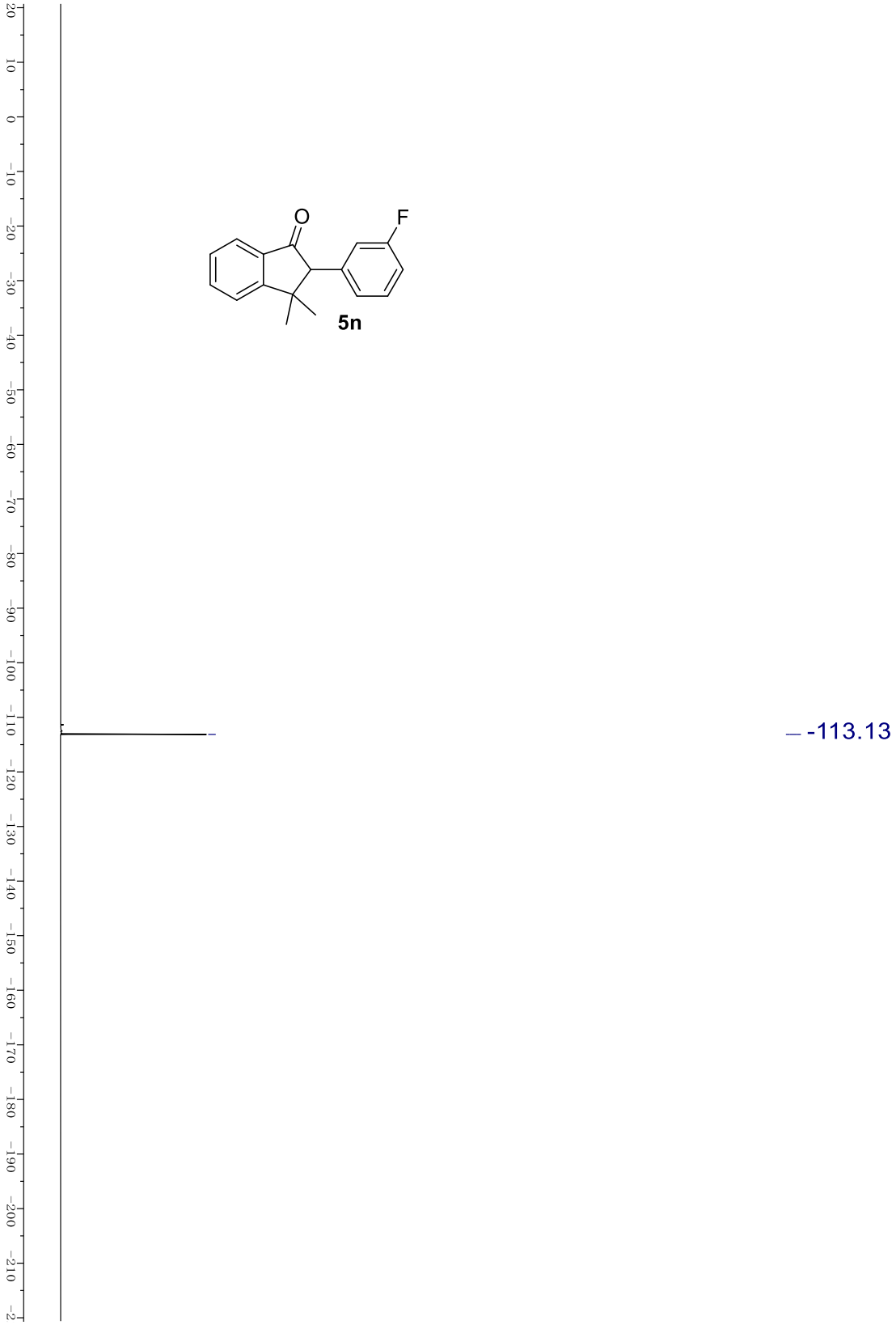

O
F
5m
0.95
0.99
1.05
1.00
2.00
1.86
1.04
3.07
3.18
7.83
7.81
7.68
7.68
7.67
7.67
7.66
7.65
7.55
7.53
7.44
7.42
7.41
7.26
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.06
7.04
7.03
3.76
1.57
0.88
0.00

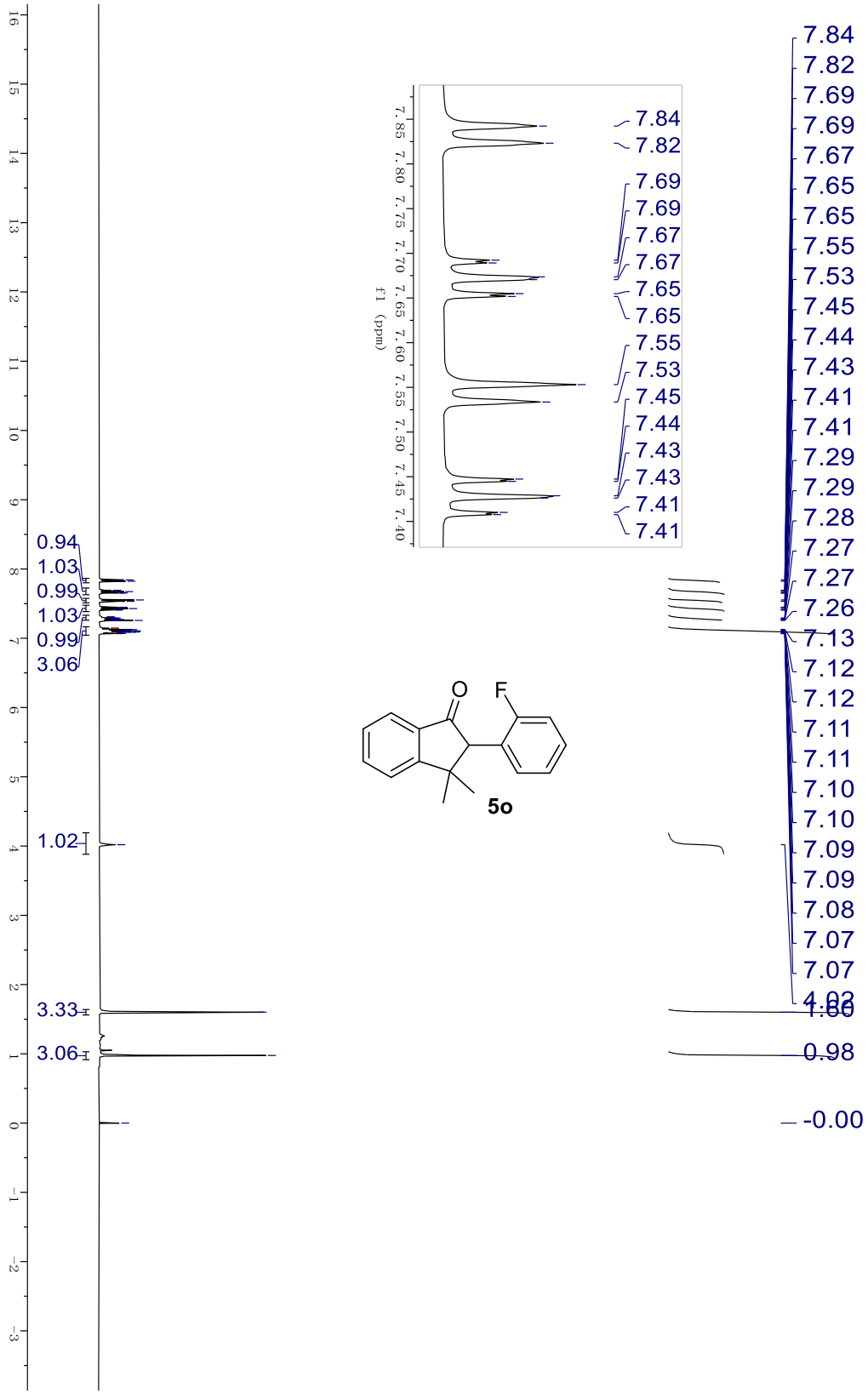

O
F
5m
205.13
162.90
162.00
161.28
135.31
134.83
132.36
132.33
131.66
131.60
127.71
123.90
123.63
115.39
115.25
77.25 CDCl3
77.04 CDCl3
76.83 CDCl3
66.21
43.72
28.52
28.32


O
F
5m
-115.51
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210


1.00
1.03
1.04
1.08
1.16
1.08
1.03
1.00
1.03
3.14
3.20
O
F
5n
7.86
7.84
7.72
7.70
7.68
7.58
7.56
7.47
7.46
7.44
7.37
7.35
7.35
7.33
7.31
7.28
7.05
7.04
7.03
7.00
7.00
6.96
6.94
6.90
6.87
3.79
1.61
0.94
0.03


O
F
5n
204.64
163.97
162.02
161.53
139.07
139.00
135.39
134.77
129.85
129.77
127.78
125.87
125.84
123.95
123.63
117.13
116.91
114.24
114.03
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
66.50
66.49
43.84
28.54
28.37


O
F
5n
-113.13
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-2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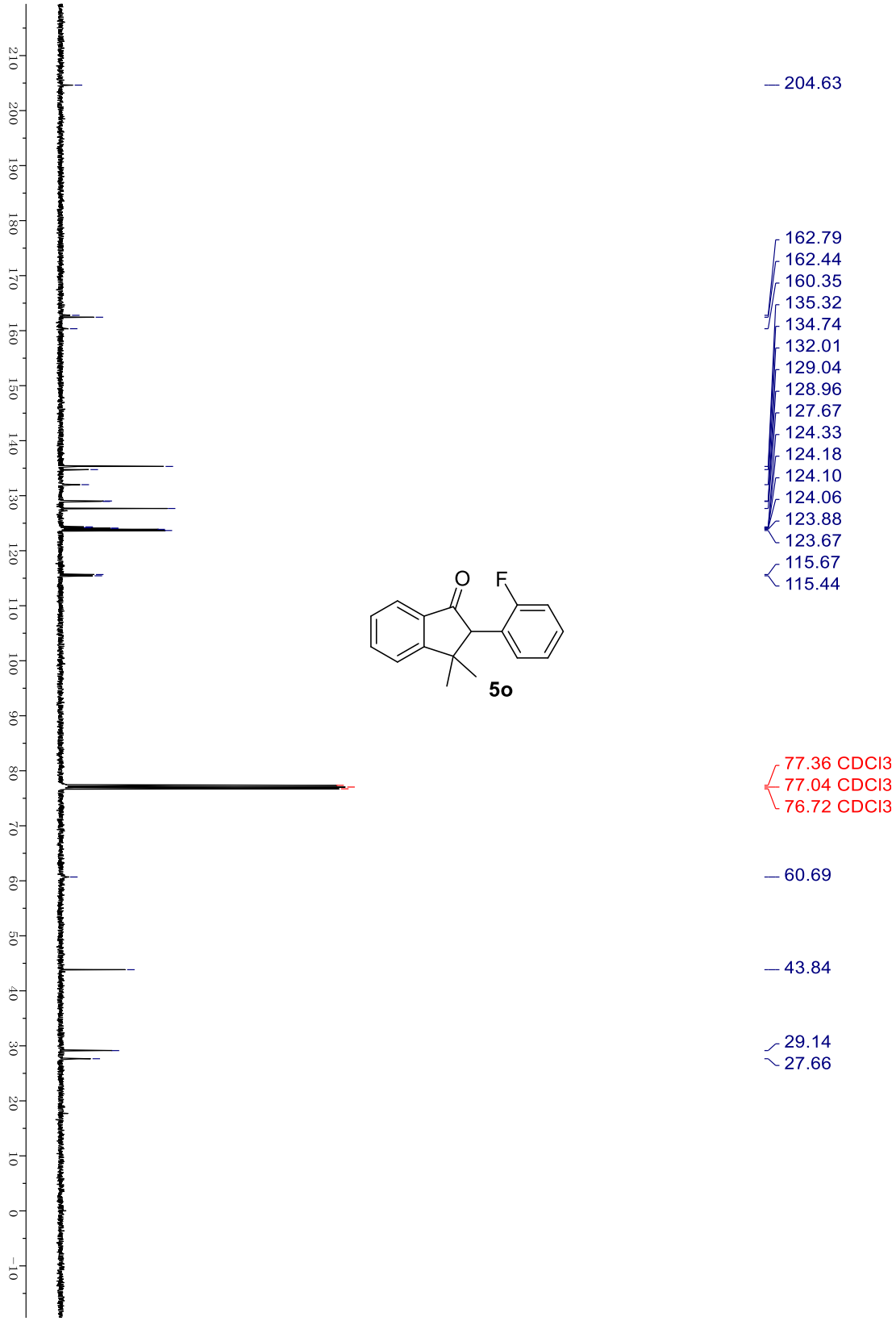
0.99
1.03
0.99
3.06
1.02
3.33
3.06
7.84
7.82
7.69
7.69
7.67
7.65
7.65
7.55
7.53
7.45
7.44
7.43
7.41
7.41
7.29
7.29
7.28
7.27
7.27
7.26
7.13
7.12
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.07
7.07
4.02
1.86
0.98
-0.00
O
F
5o
f1 (ppm)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160.35
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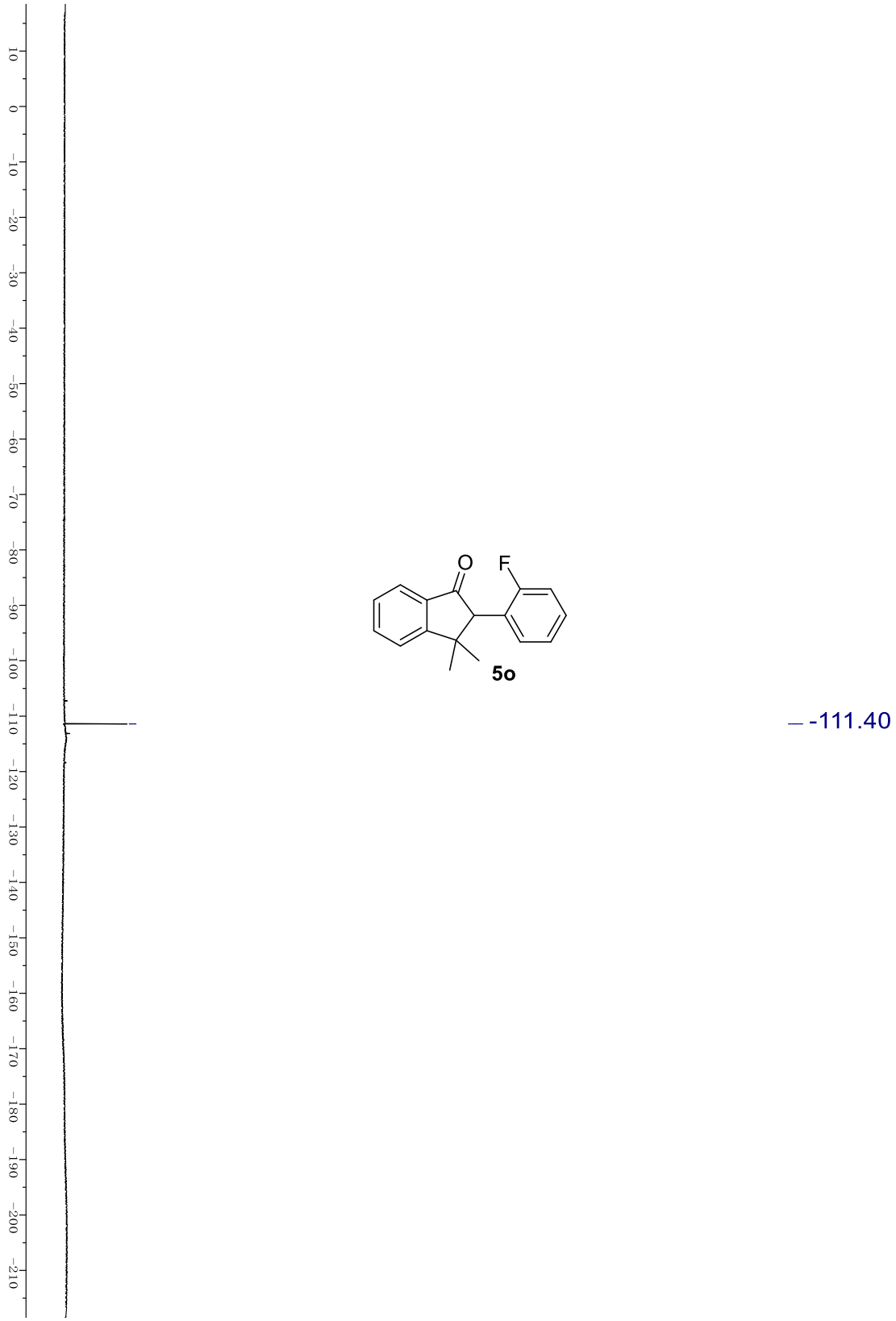
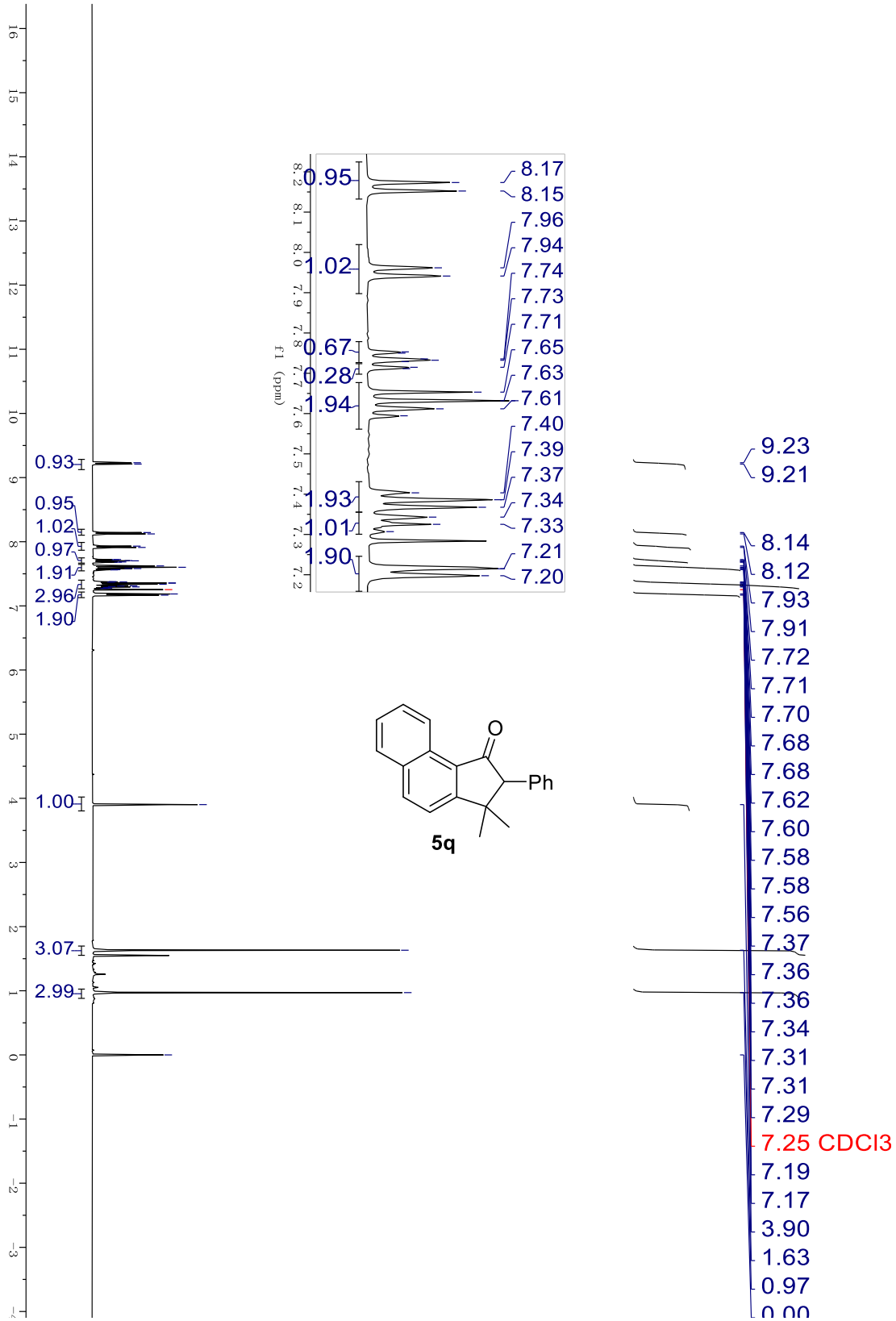
127.67
124.33
124.18
124.10
124.06
123.88
123.67
115.67
115.44
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
60.69
43.84
29.14
27.66
O
F
5o


10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
O
F
5o
-111.40


0.93
0.95
1.02
0.97
1.91
2.96
1.90
1.00
3.07
2.99
0.95
1.02
0.67
0.28
1.94
1.93
1.01
1.90
8.17
8.15
7.96
7.94
7.74
7.73
7.71
7.65
7.63
7.61
7.40
7.39
7.37
7.34
7.33
7.21
7.20
O
Ph
5q
9.23
9.21
8.14
8.12
7.93
7.91
7.72
7.71
7.70
7.68
7.68
7.62
7.60
7.58
7.58
7.56
7.37
7.36
7.36
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7.31
7.29
7.25 CDCl3
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7.17
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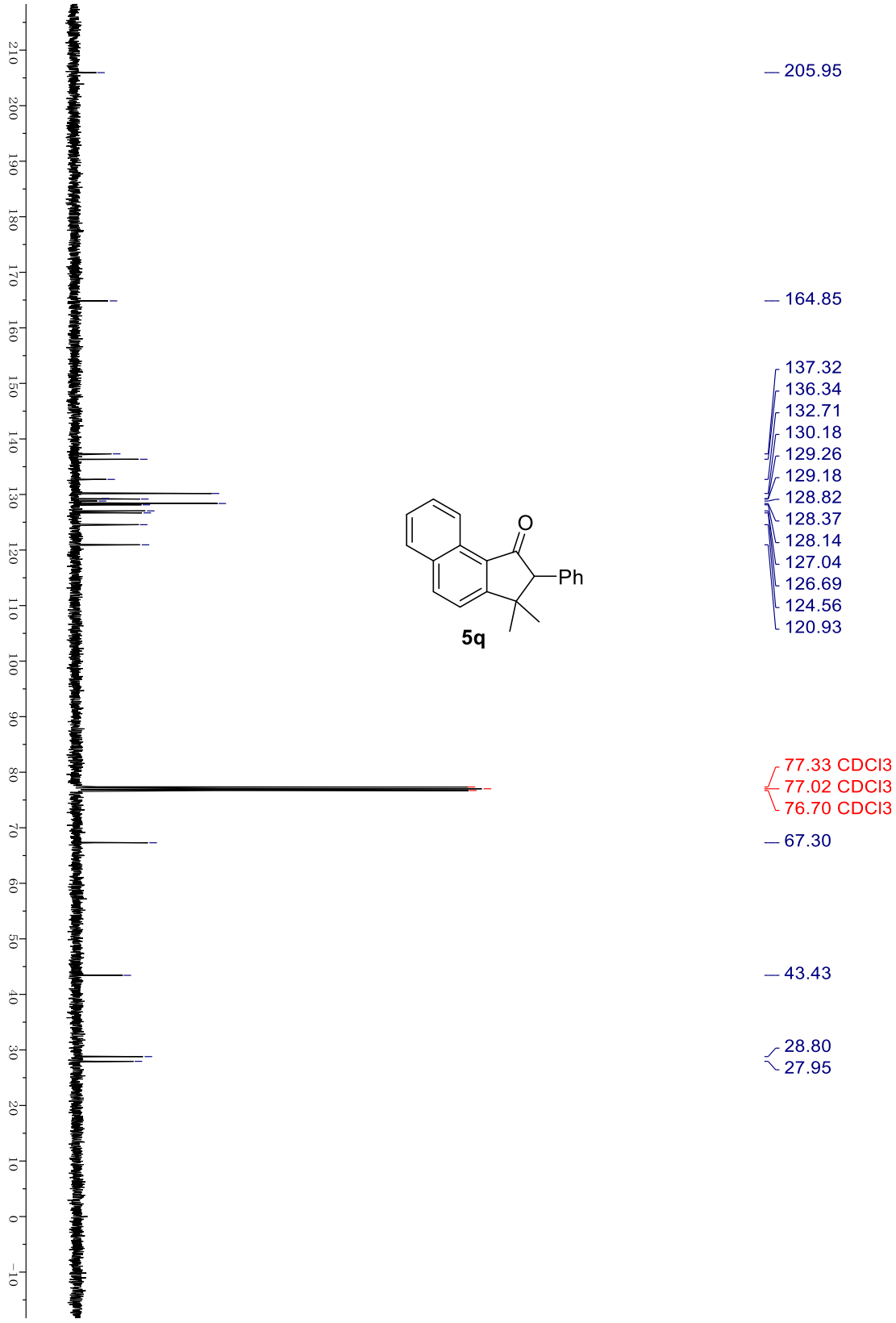
1.63
0.97
0.00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136.34
132.71
130.18
129.26
129.18
128.82
128.37
128.14
127.04
126.69
124.56
120.93
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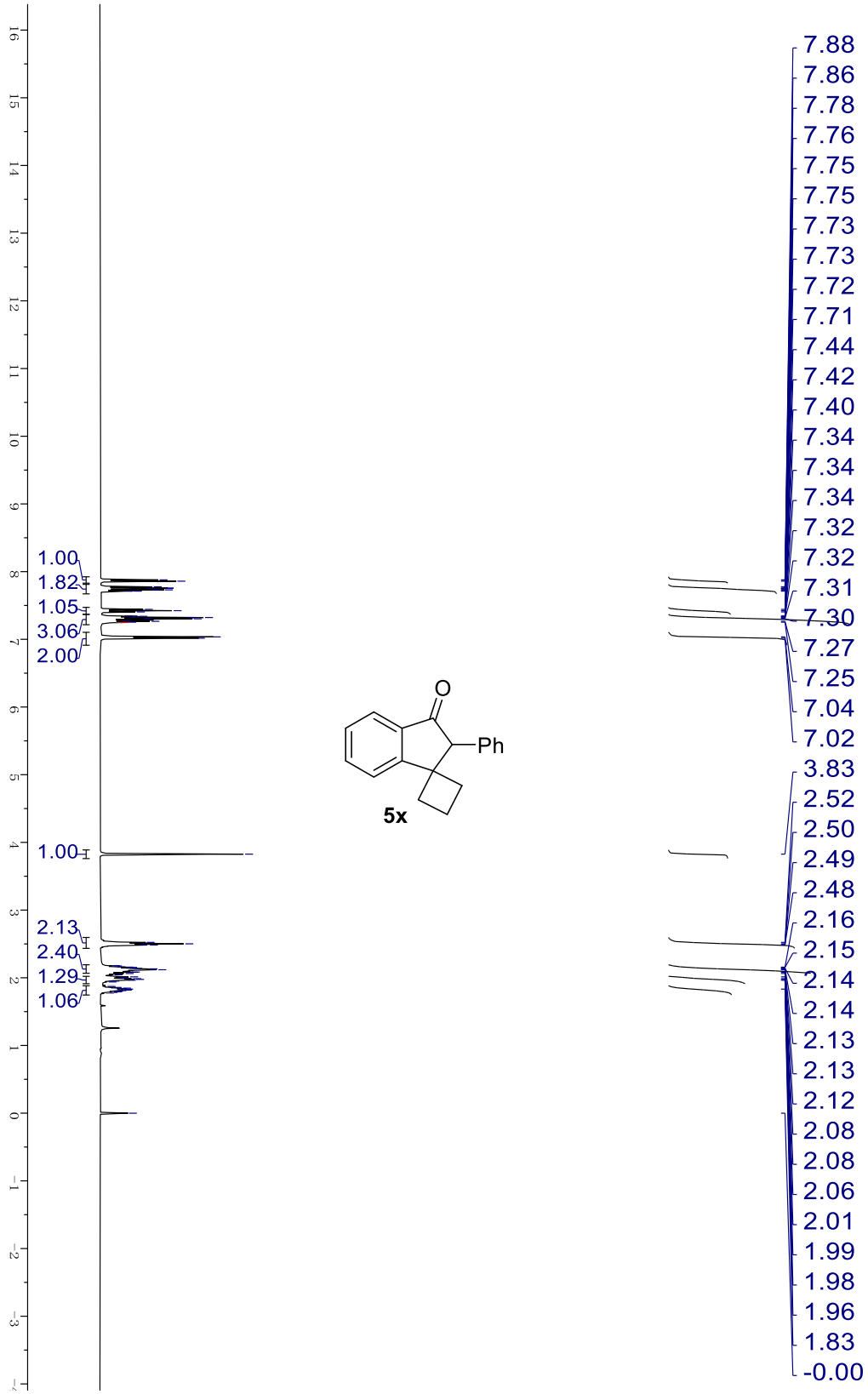
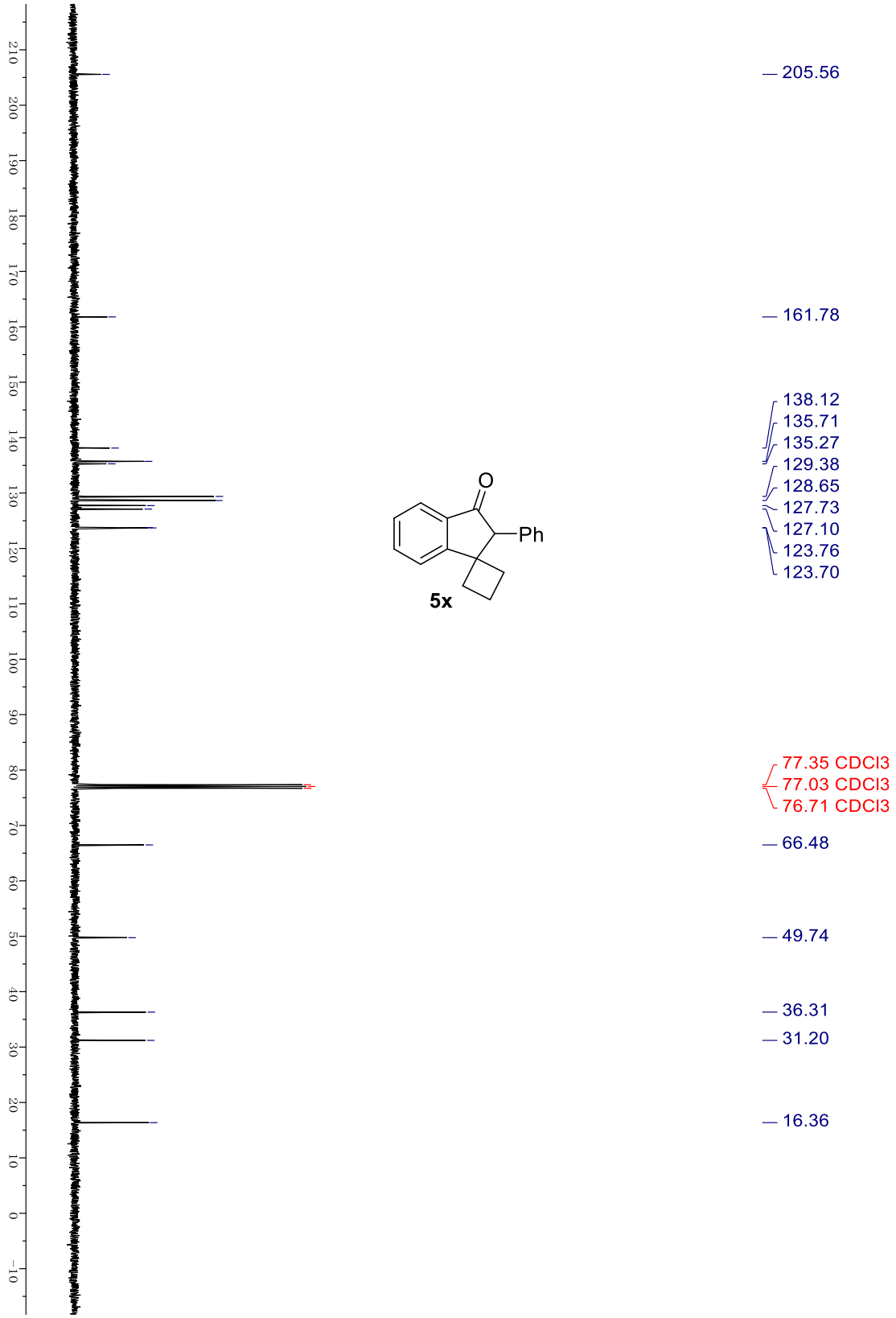
77.02 CDCl3
76.70 CDCl3
67.30
43.43
28.80
27.95
O
Ph
5q


1.00
1.82
1.05
3.06
2.00
1.00
2.13
2.40
1.29
1.06
O
Ph
5x
7.88
7.86
7.78
7.76
7.75
7.75
7.73
7.73
7.72
7.71
7.44
7.42
7.40
7.34
7.34
7.34
7.32
7.32
7.31
7.30
7.27
7.25
7.04
7.02
3.83
2.52
2.50
2.49
2.48
2.16
2.15
2.14
2.14
2.13
2.13
2.12
2.08
2.08
2.06
2.01
1.99
1.98
1.96
1.83
-0.00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129.38
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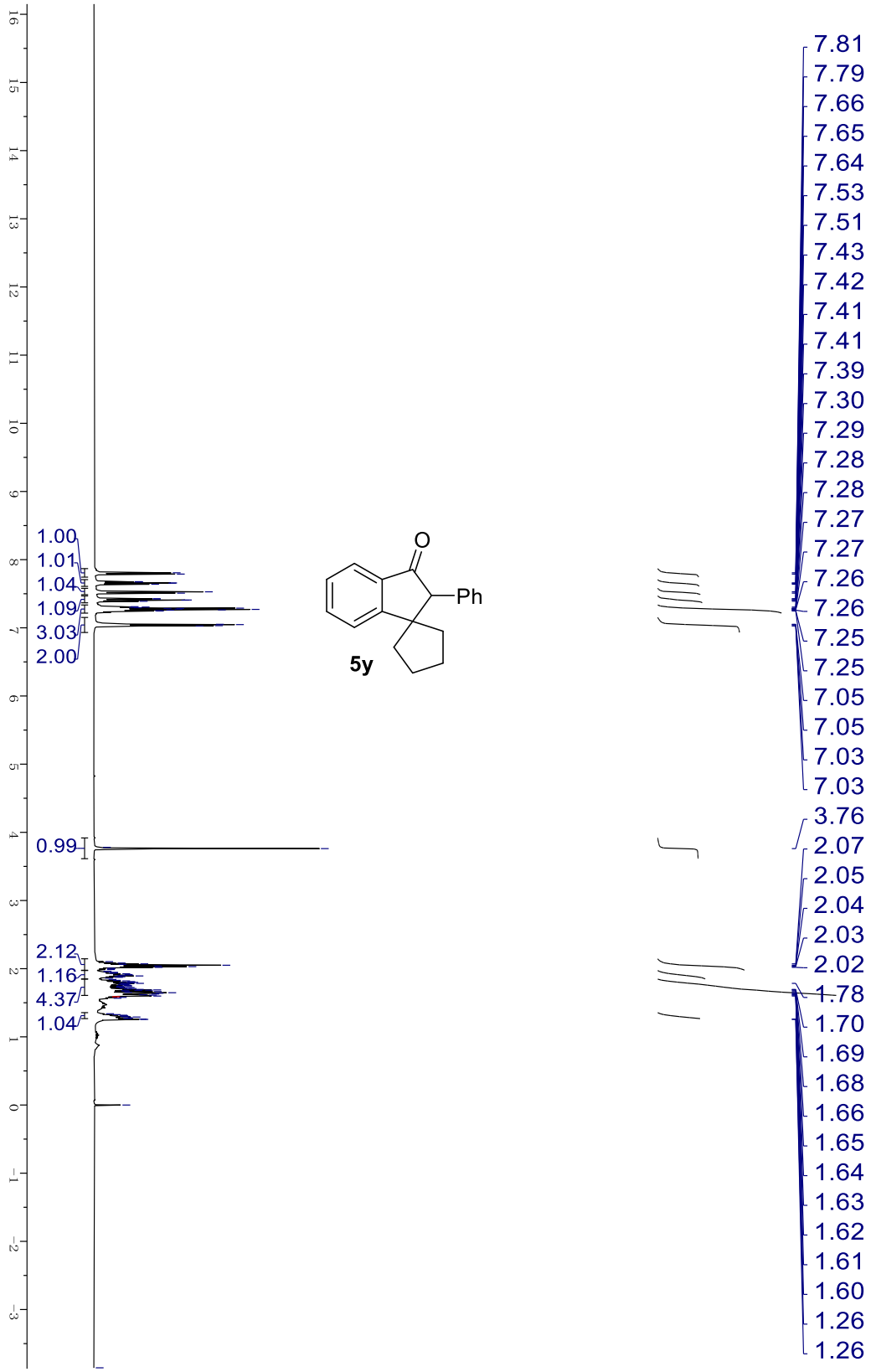
127.73
127.10
123.76
123.70
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
66.48
49.74
36.31
31.20
16.36
O
Ph
5x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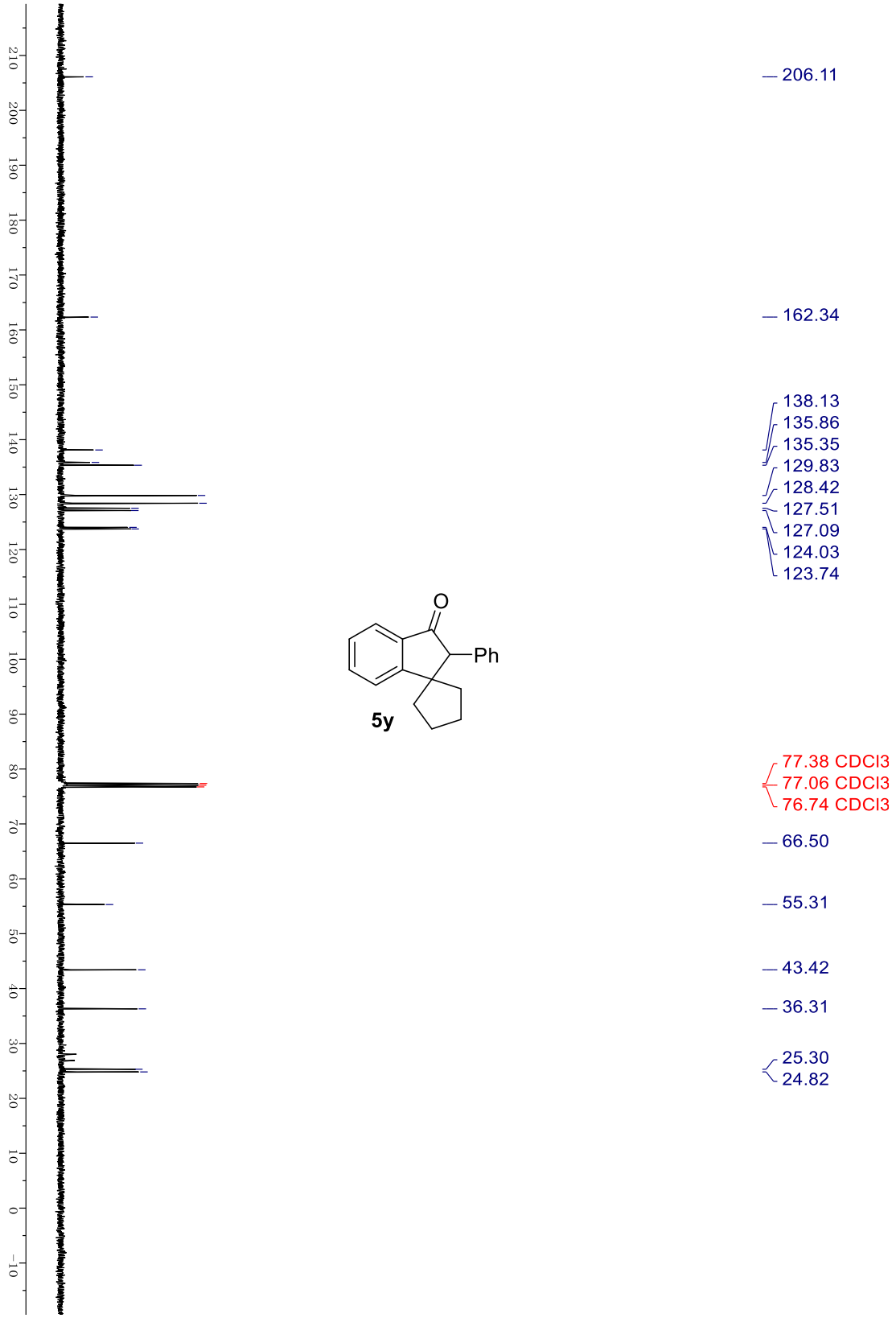
7.51
7.43
7.42
7.41
7.41
7.39
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.05
7.05
7.03
7.03
3.76
2.07
2.05
2.04
2.03
2.02
1.78
1.70
1.69
1.68
1.66
1.65
1.64
1.63
1.62
1.61
1.60
1.26
1.26
1.00
1.01
1.04
1.09
3.03
2.00
0.99
2.12
1.16
4.37
1.04
O
Ph
5y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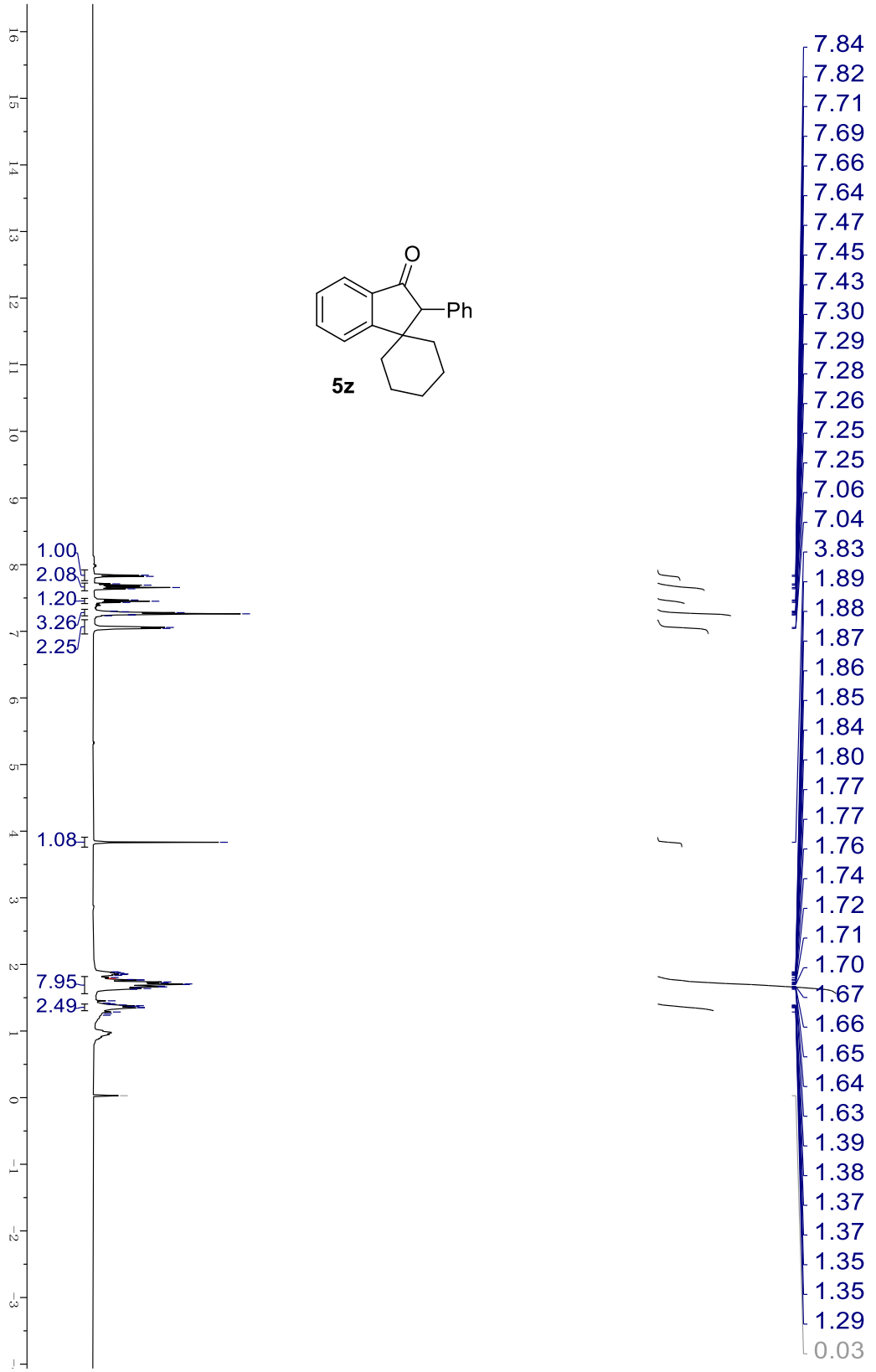
128.42
127.51
127.09
124.03
123.74
O
Ph
5y
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
66.50
55.31
43.42
36.31
25.30
24.82


O
Ph
5z
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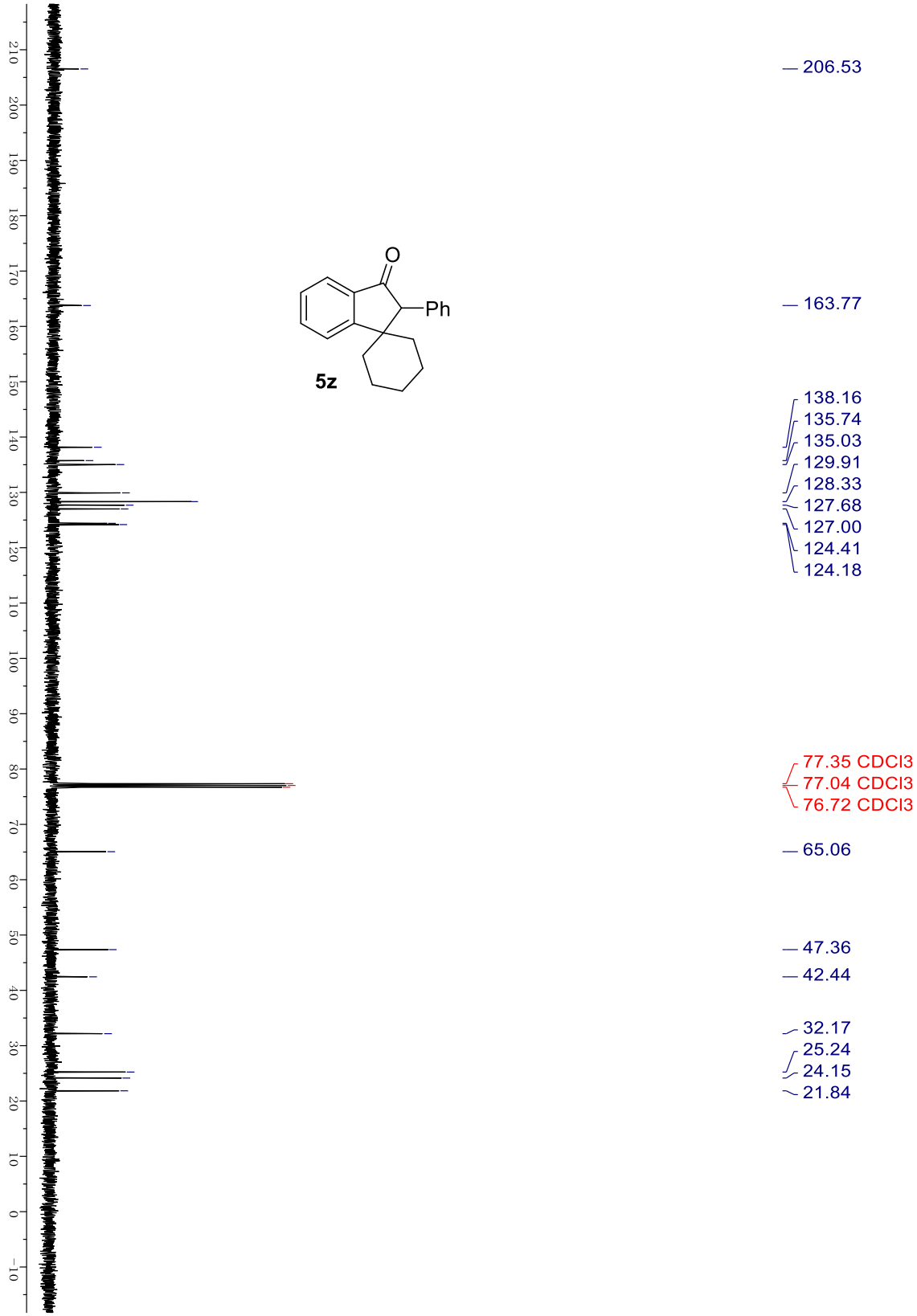
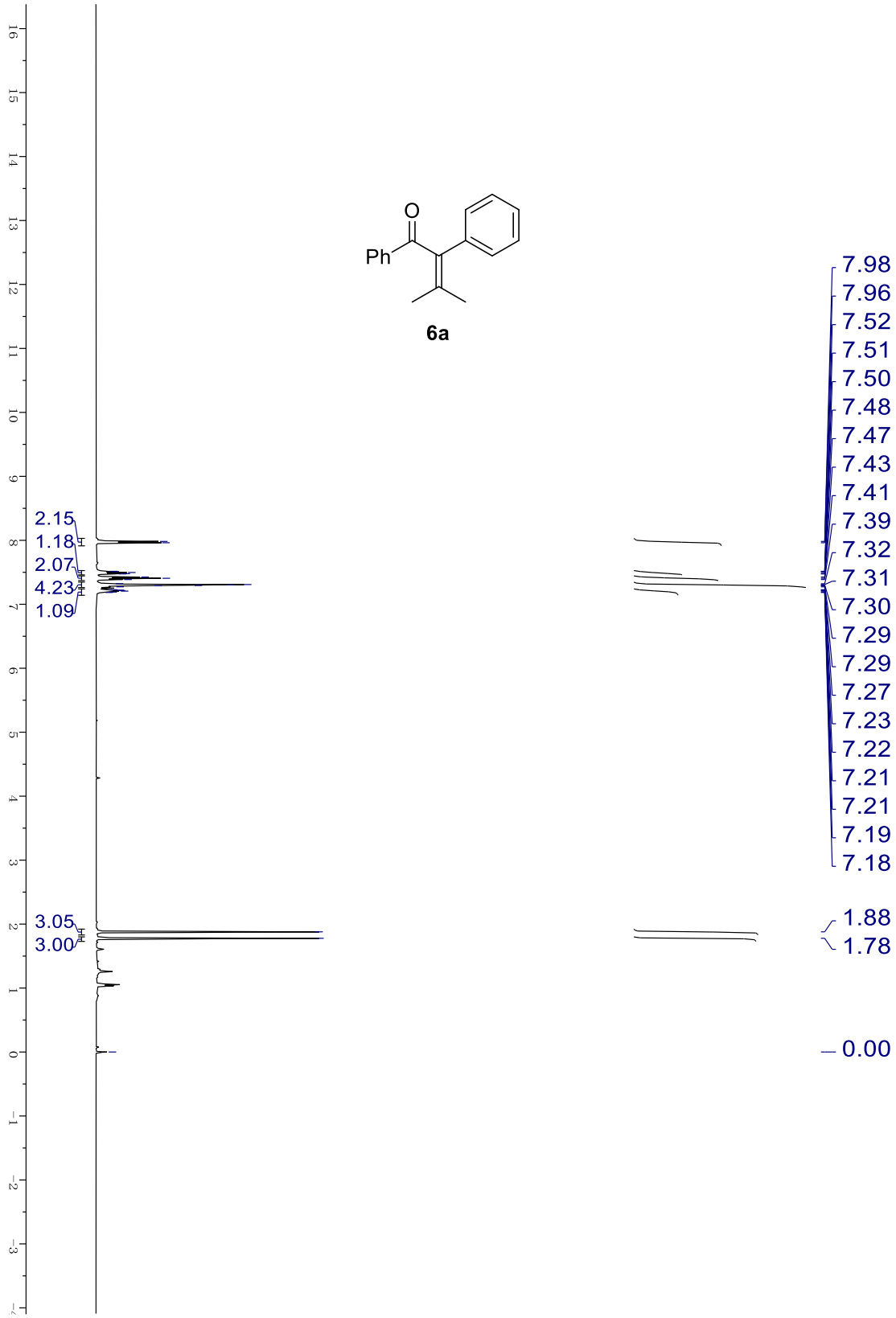
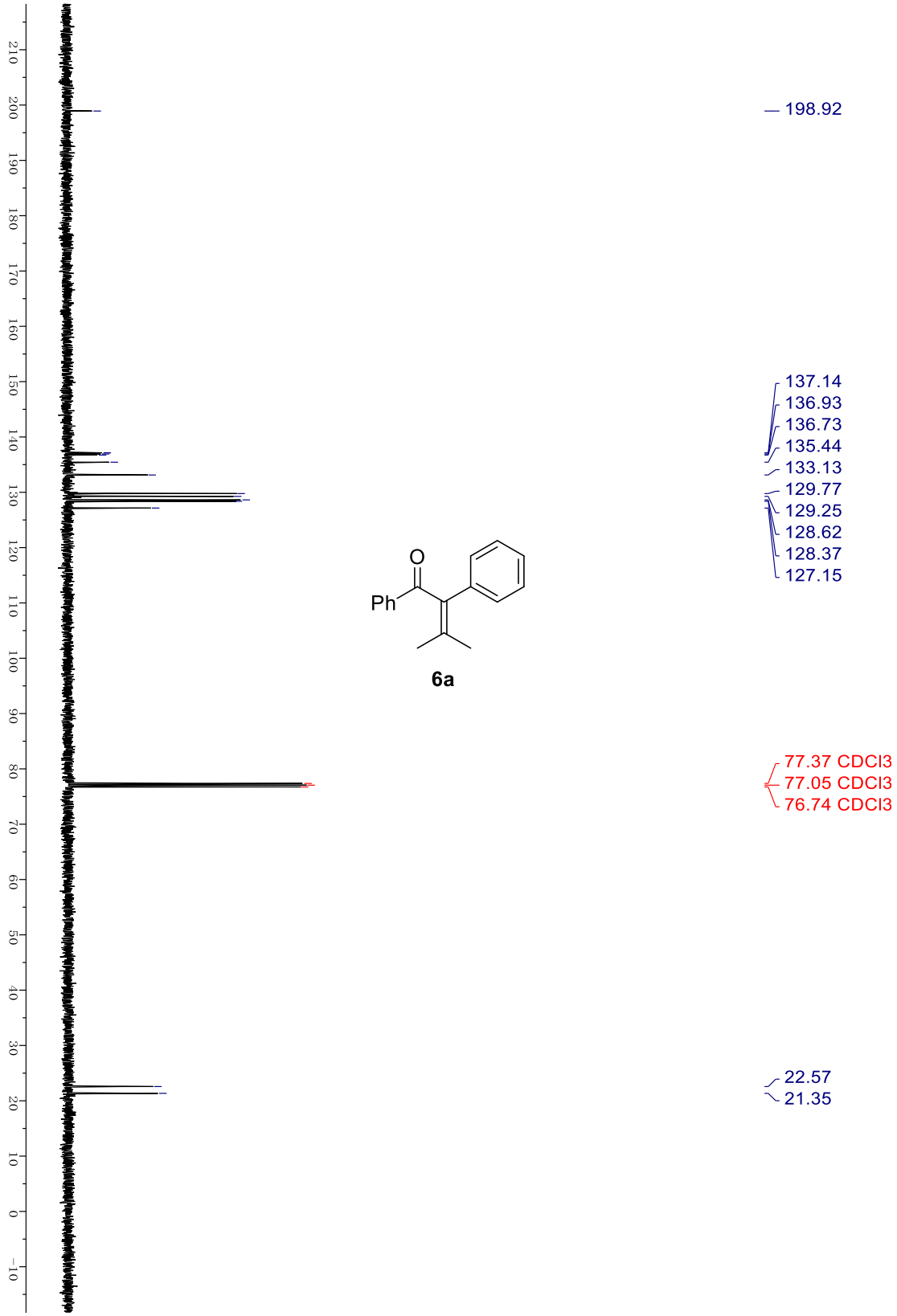
2.08
1.20
3.26
2.25
1.08
7.95
2.49
7.84
7.82
7.71
7.69
7.66
7.64
7.47
7.45
7.43
7.30
7.29
7.28
7.26
7.25
7.25
7.06
7.04
3.83
1.89
1.88
1.87
1.86
1.85
1.84
1.80
1.77
1.77
1.76
1.74
1.72
1.71
1.70
1.67
1.66
1.65
1.64
1.63
1.39
1.38
1.37
1.37
1.35
1.35
1.29
0.03


O
Ph
5z
206.53
163.77
138.16
135.74
135.03
129.91
128.33
127.68
127.00
124.41
124.18
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
65.06
47.36
42.44
32.17
25.24
24.15
21.84

11.4 NMR spectra of α,β-unsaturated carbonyls




198.92
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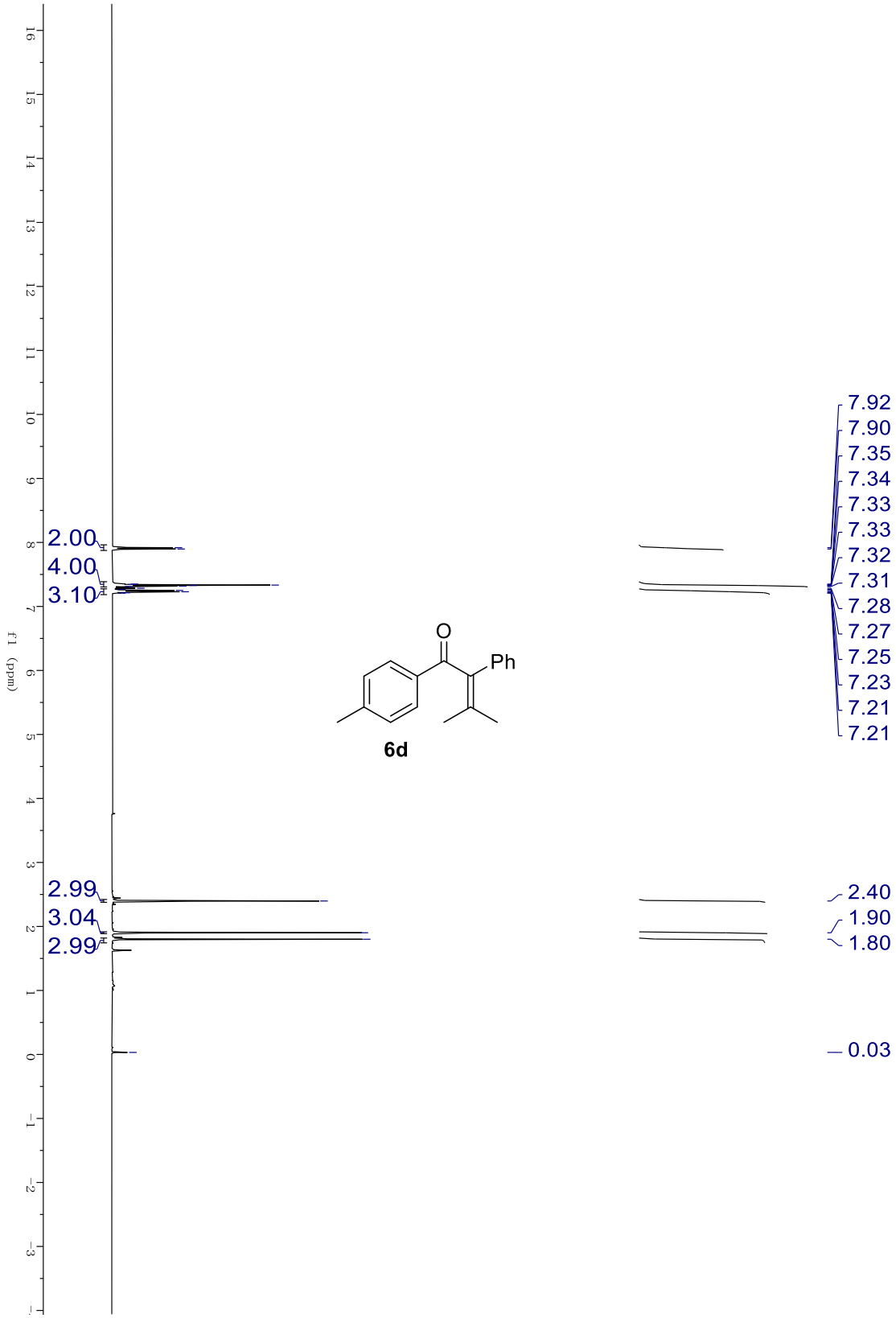
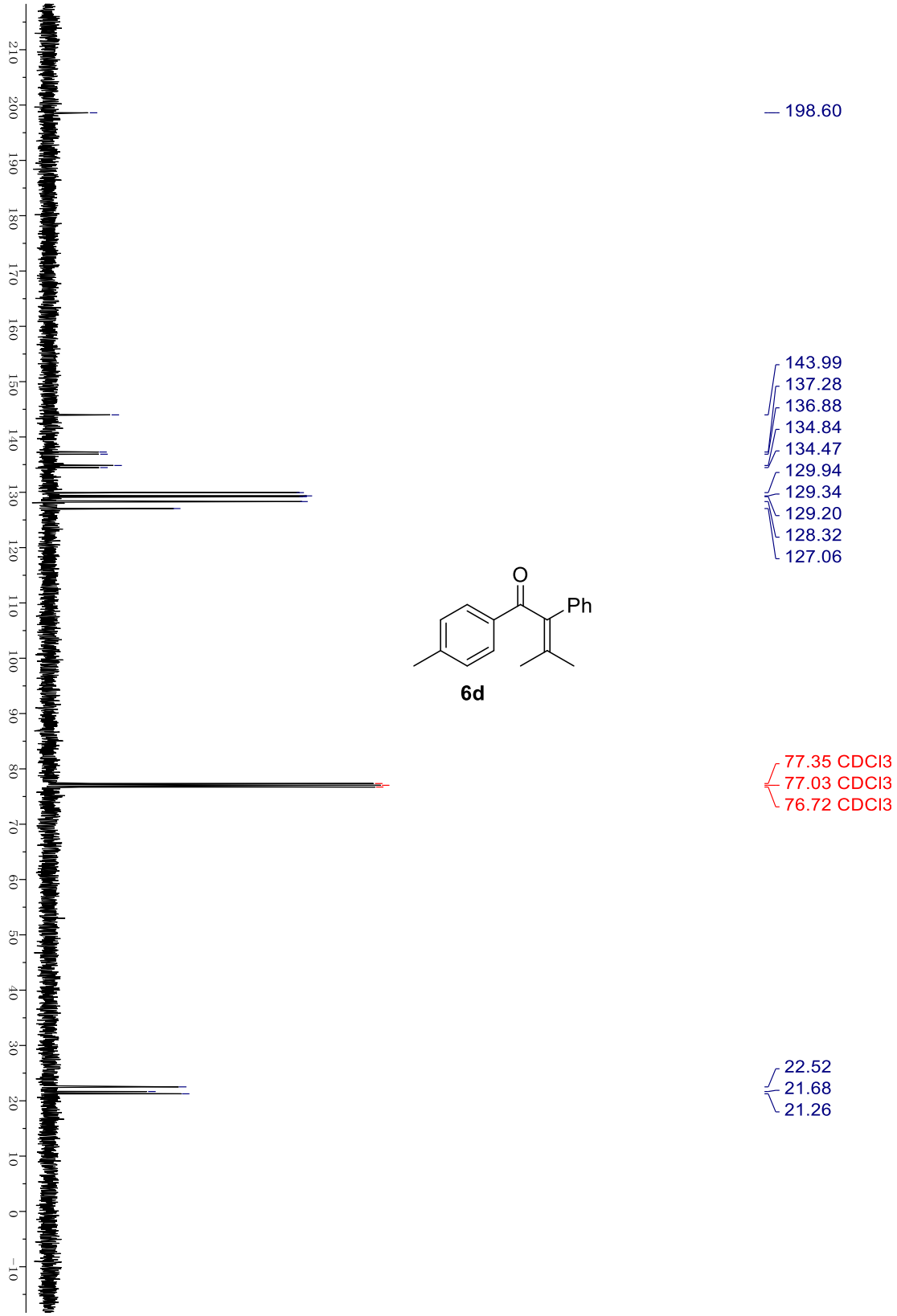
136.93
136.73
135.44
133.13
129.77
129.25
128.62
128.37
127.15
77.37 CDCl3
77.05 CDCl3
76.74 CDCl3
22.57
21.35
O
Ph

6a


f1 (ppm)
2.00
4.00
3.10
2.99
3.04
2.99
O
Ph
6d
7.92
7.90
7.35
7.34
7.33
7.33
7.32
7.31
7.28
7.27
7.25
7.23
7.21
7.21
2.40
1.90
1.80
0.03


198.60
143.99
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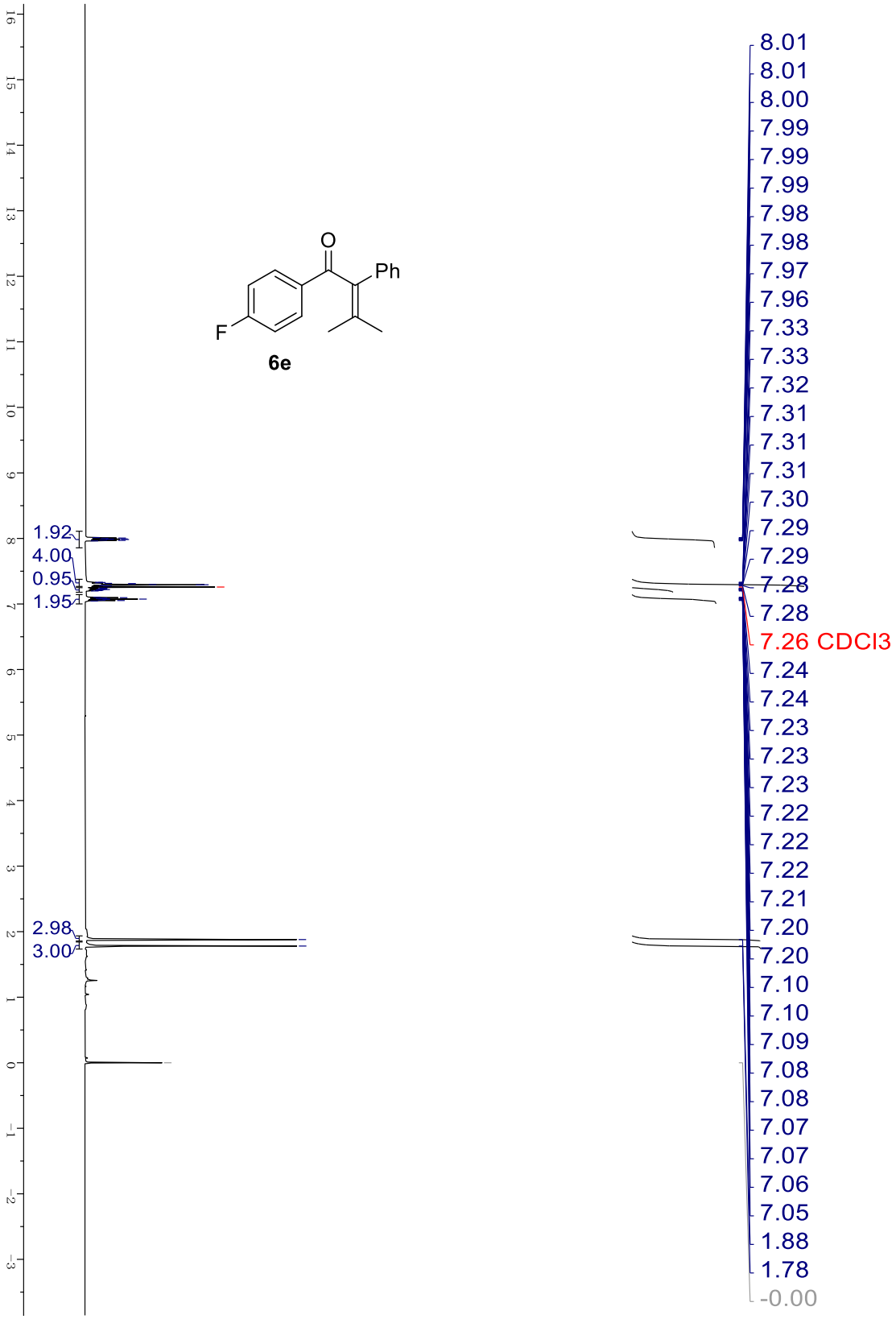
136.88
134.84
134.47
129.94
129.34
129.20
128.32
127.06
O
Ph
6d
77.35 CDCl3
77.03 CDCl3
76.72 CDCl3
22.52
21.68
21.26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Ph
F
6e
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0.95
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3.00
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8.01
8.00
7.99
7.99
7.99
7.98
7.98
7.97
7.96
7.33
7.33
7.32
7.31
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.26 CDCl3
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.22
7.21
7.20
7.20
7.10
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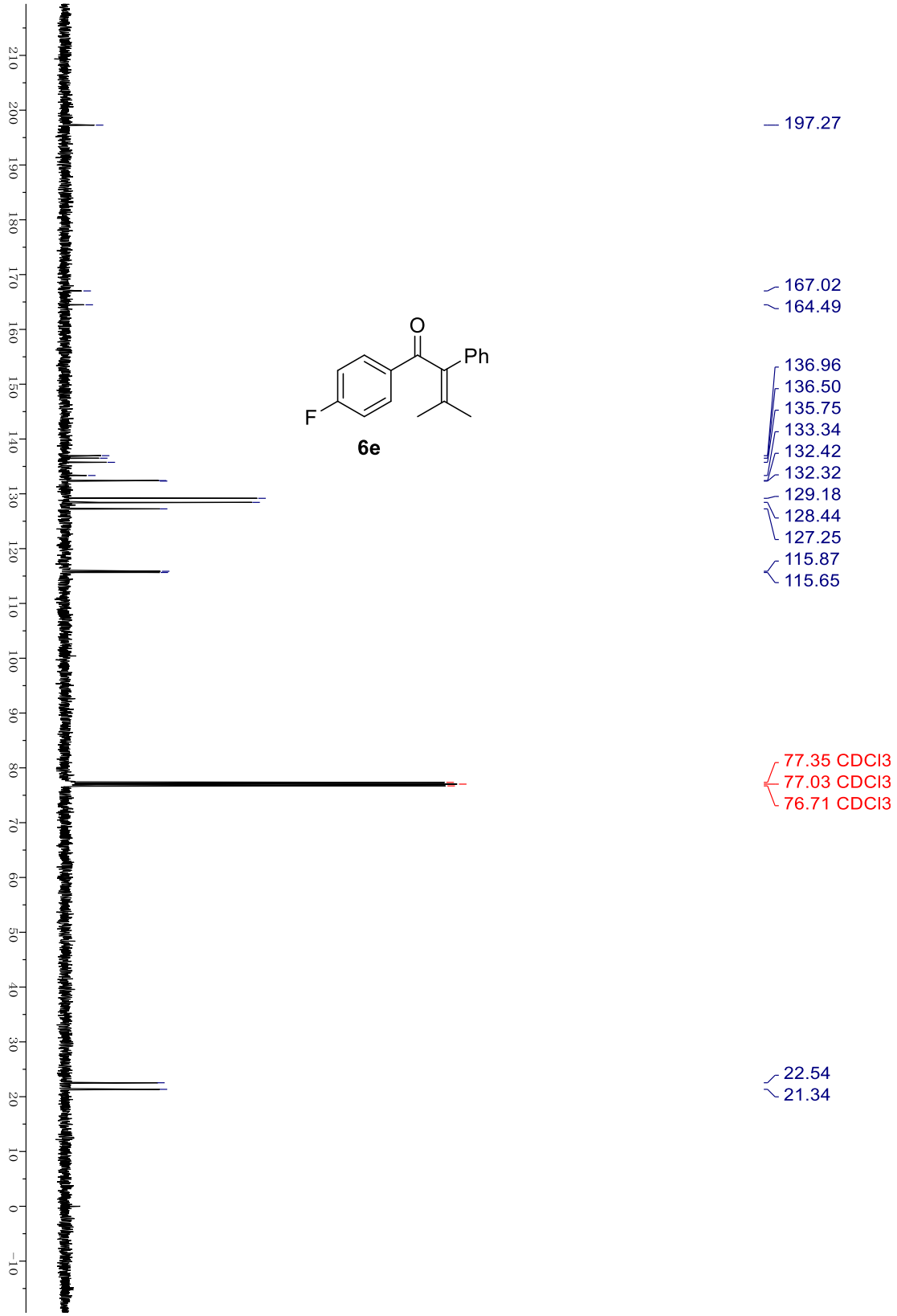
7.08
7.08
7.07
7.07
7.06
7.05
1.88
1.78
-0.00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Ph
F
6e
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164.49
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136.50
135.75
133.34
132.42
132.32
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127.25
115.87
115.65
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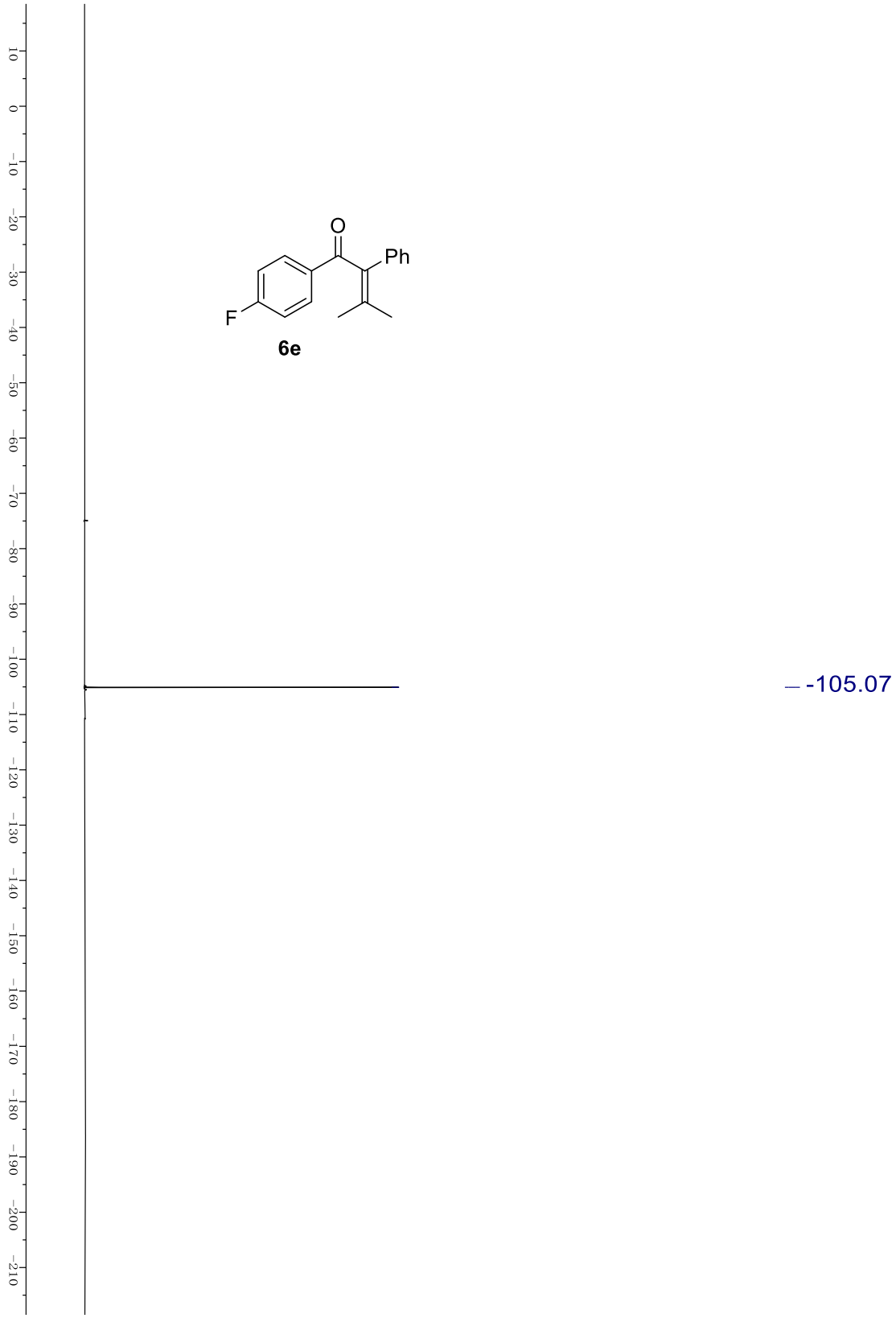
77.03 CDCl3
76.71 CDCl3
22.54
21.34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Ph
F
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-10
-20
-30
-40
-50
-60
-70
-80
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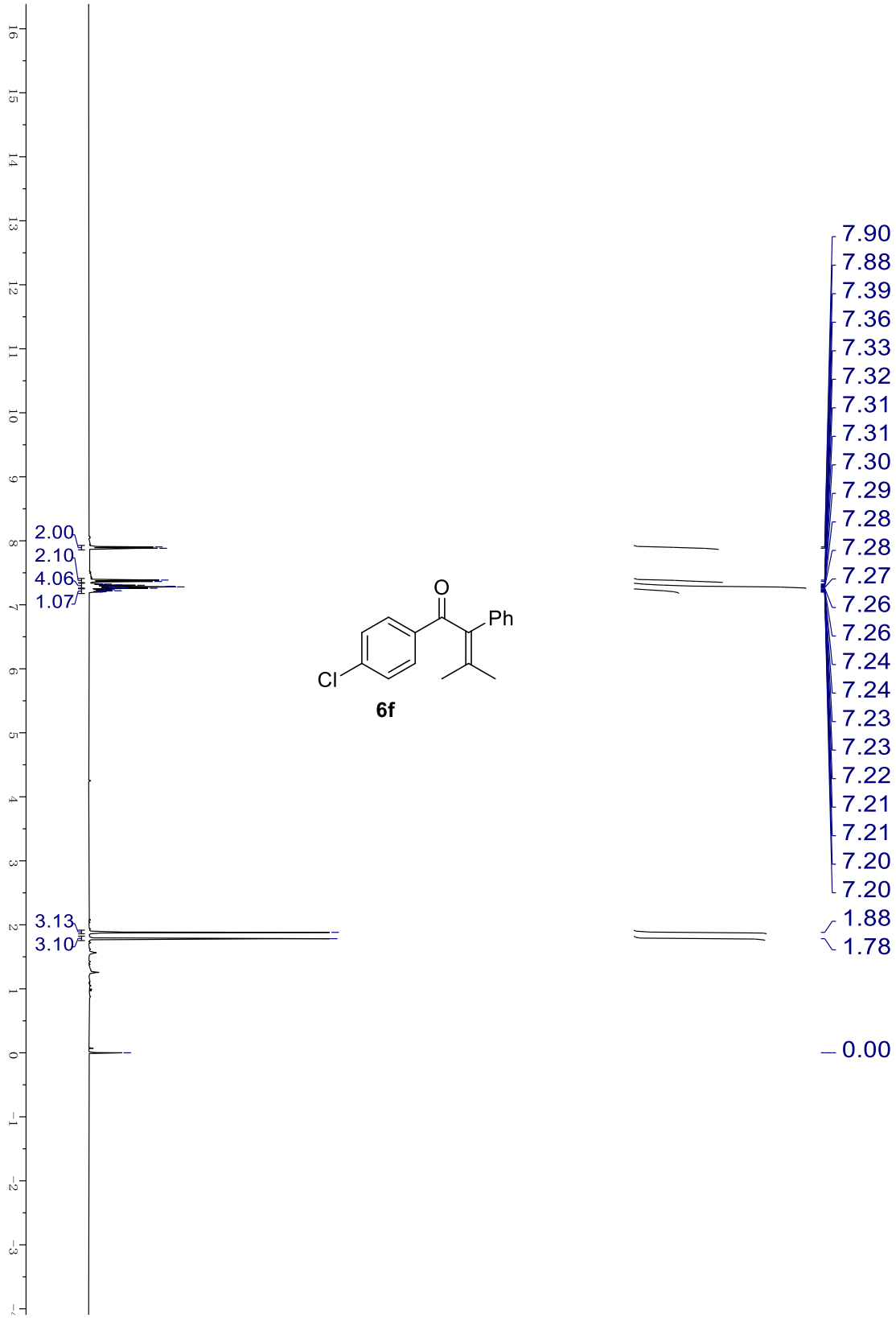
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

6e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7.31
7.31
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7.29
7.28
7.28
7.27
7.26
7.26
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.20
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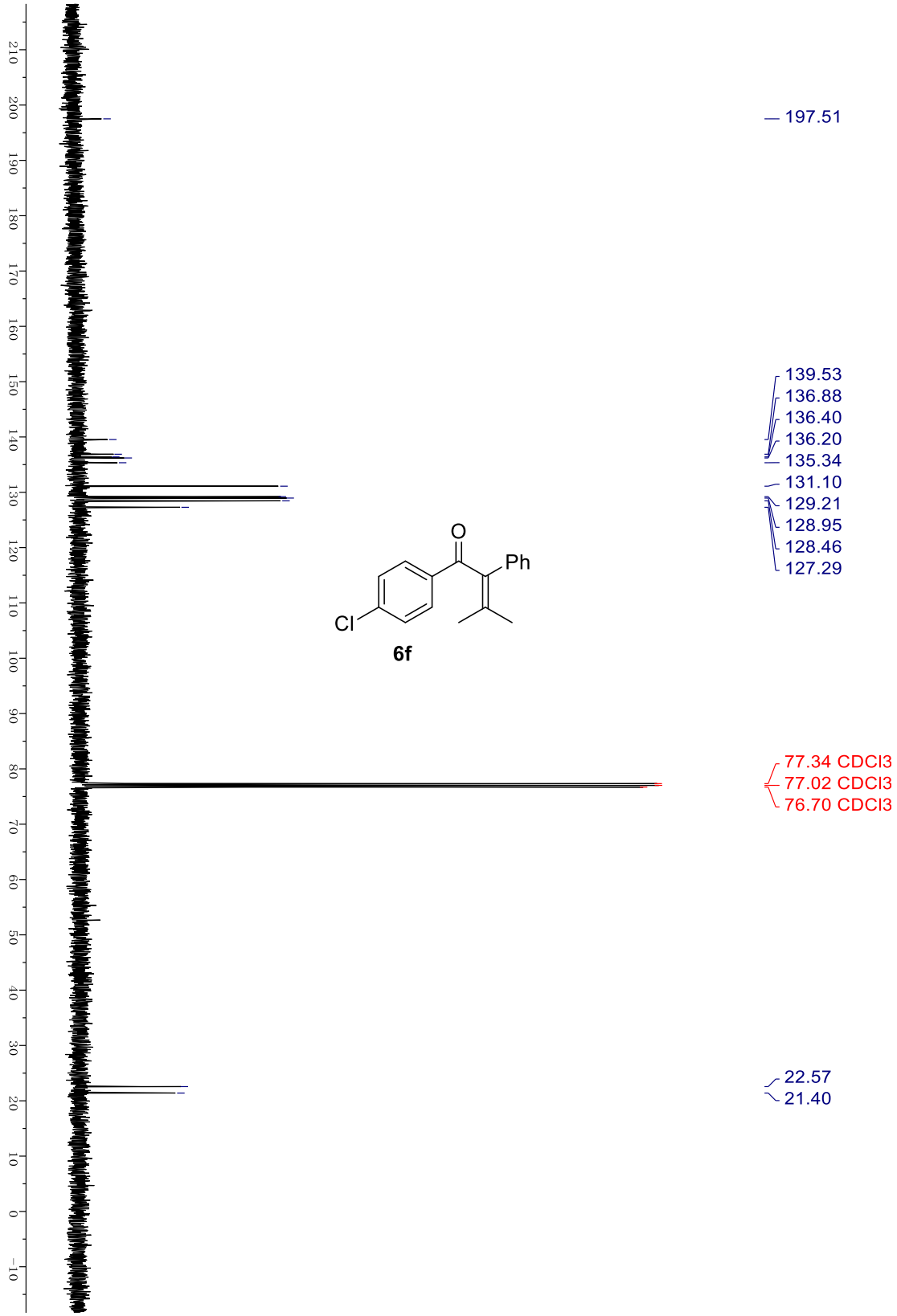
0.00
2.00
2.10
4.06
1.07
3.13
3.10
O
Ph
Cl
6f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129.21
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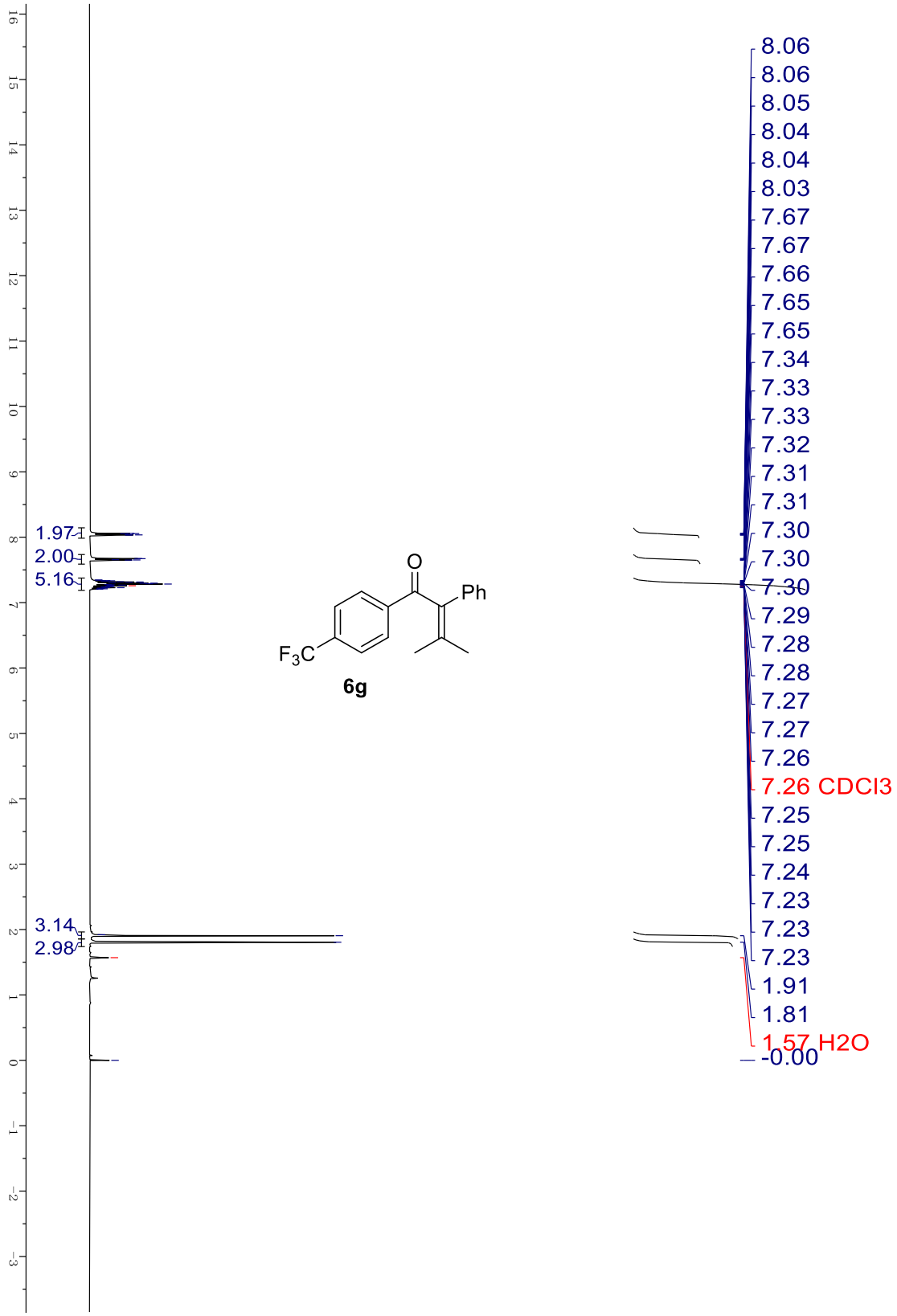
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
22.57
21.40
O
Ph
Cl
6f


1.97
2.00
5.16
3.14
2.98
O
Ph
F3C
6g
8.06
8.06
8.05
8.04
8.04
8.03
7.67
7.67
7.66
7.65
7.65
7.34
7.33
7.33
7.32
7.31
7.31
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7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26 CDCl3
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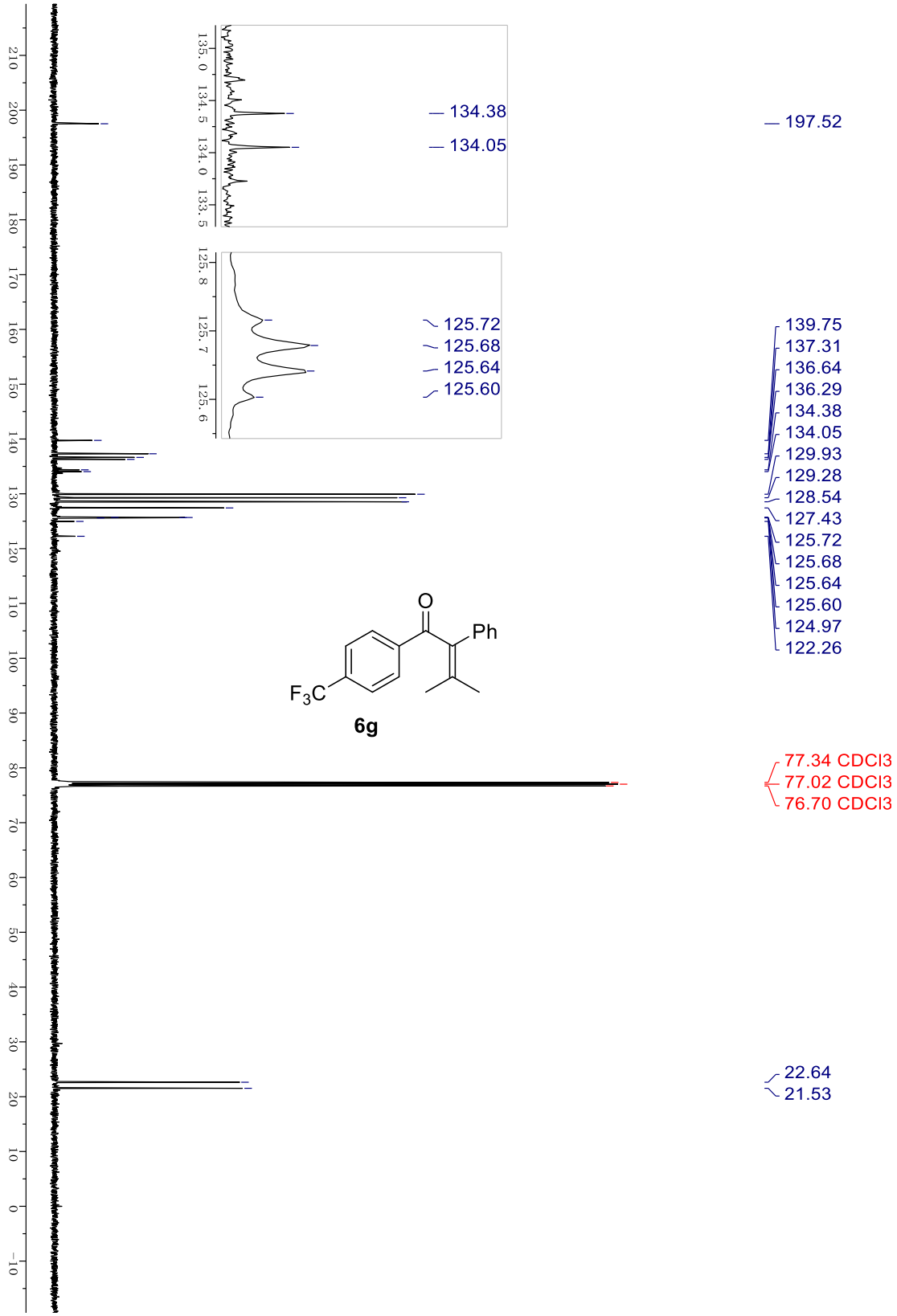
7.25
7.24
7.23
7.23
7.23
1.91
1.81
1.57 H2O
-0.00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136.64
136.29
134.38
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129.93
129.28
128.54
127.43
125.72
125.68
125.64
125.60
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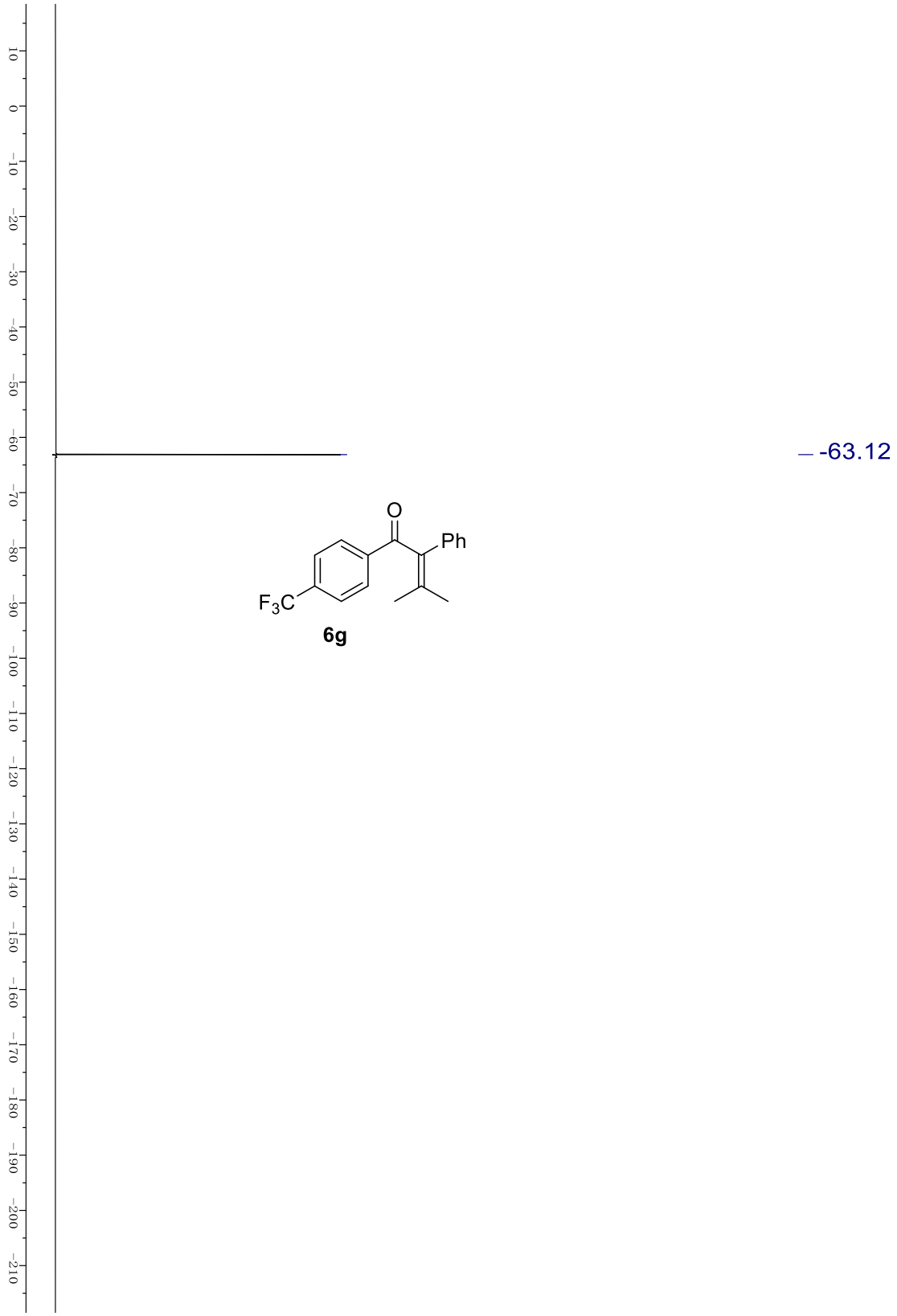
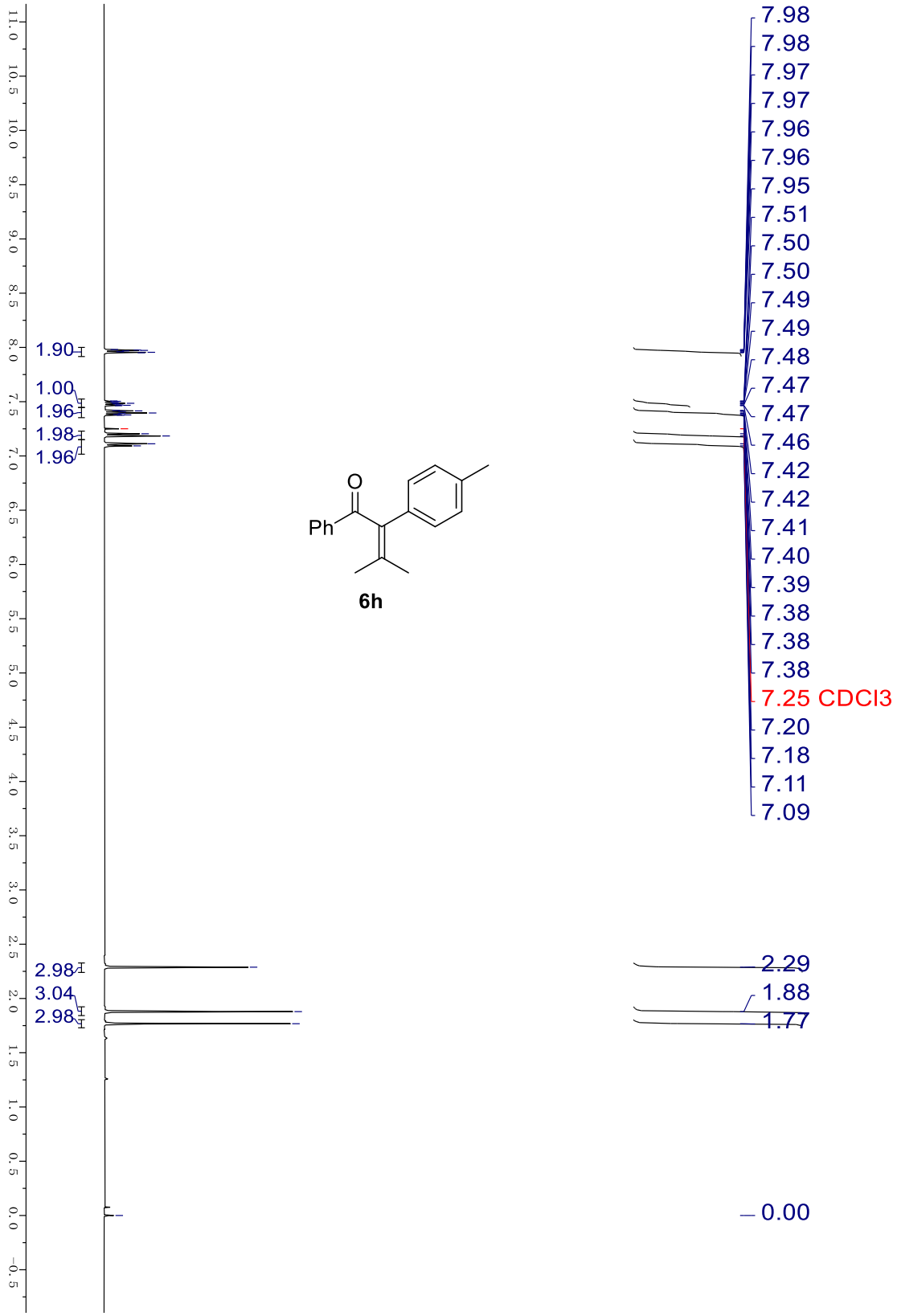
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
22.64
21.53
O
Ph
F3C
6g



6g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7.98
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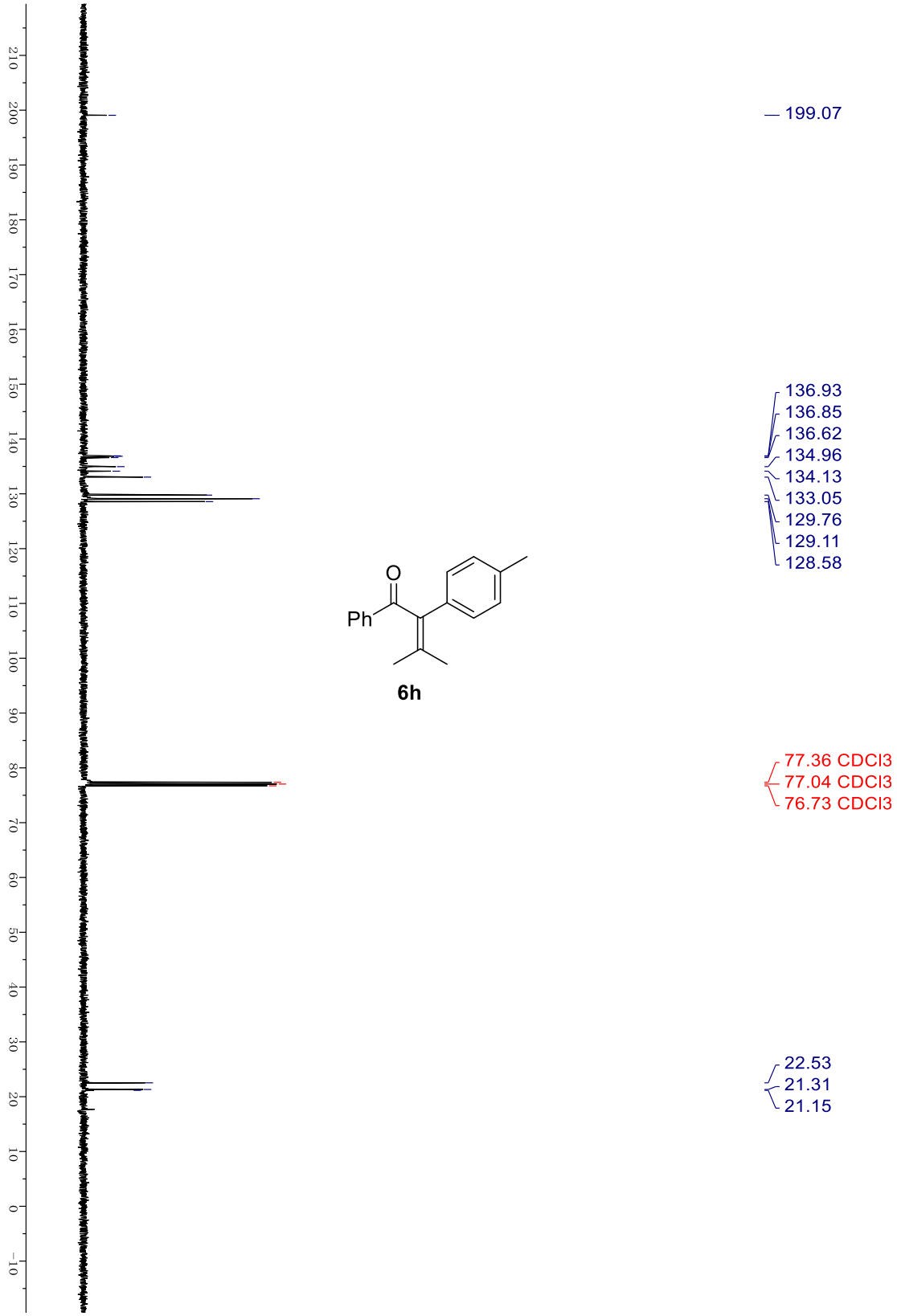
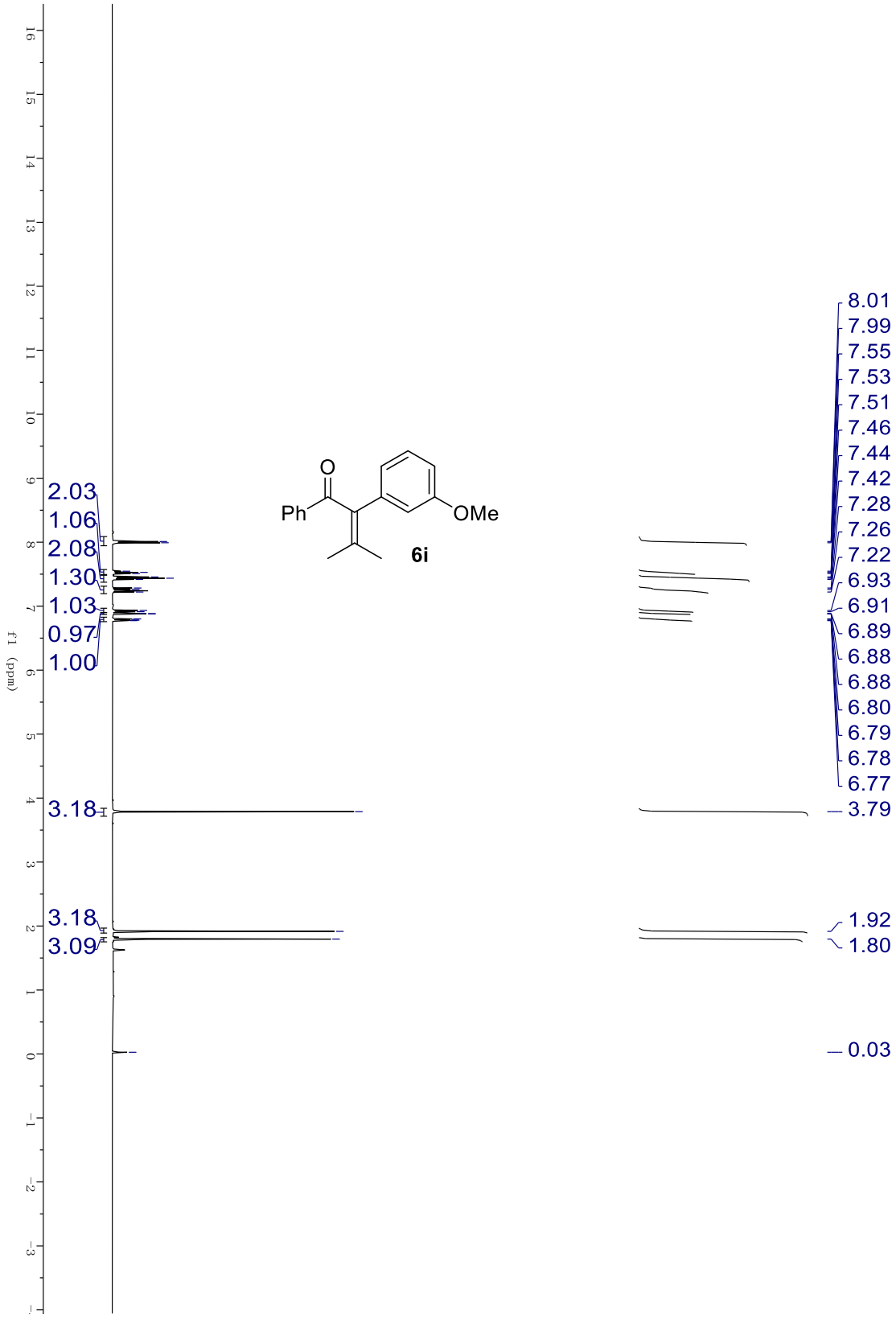
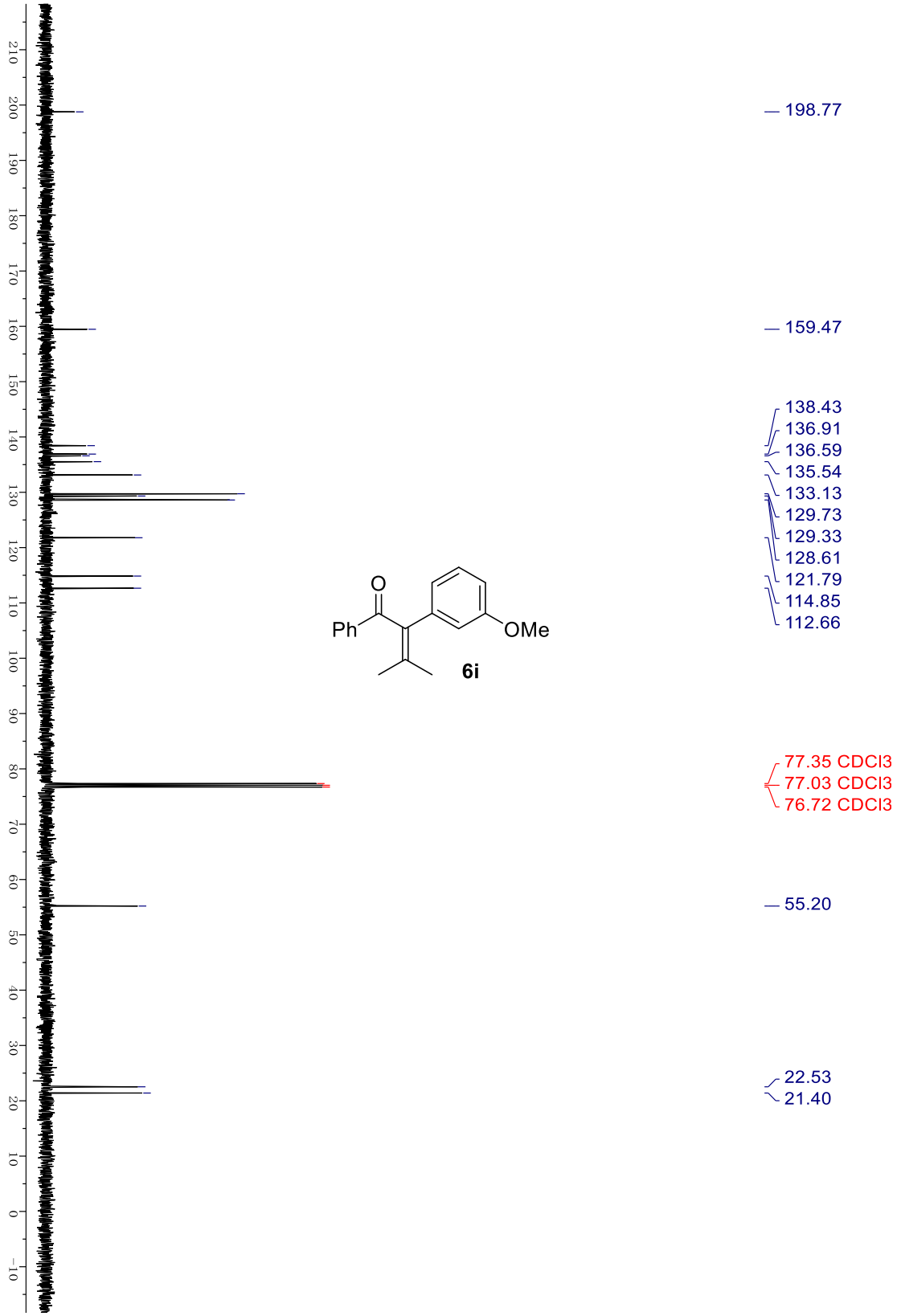
7.97
7.96
7.96
7.95
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.42
7.42
7.41
7.40
7.39
7.38
7.38
7.38
7.25 CDCl3
7.20
7.18
7.11
7.09
1.90
1.00
1.96
1.98
1.96
2.98
3.04
2.98
2.29
1.88
1.77
0.00
O
Ph

6h


199.07
136.93
136.85
136.62
134.96
134.13
133.05
129.76
129.11
128.58
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
22.53
21.31
21.15
O
Ph

6h


O
Ph
OMe
6i
2.03
1.06
2.08
1.30
1.03
0.97
1.00
3.18
3.18
3.09
8.01
7.99
7.55
7.53
7.51
7.46
7.44
7.42
7.28
7.26
7.22
6.93
6.91
6.89
6.88
6.88
6.80
6.79
6.78
6.77
3.79
1.92
1.80
0.03
f1 (ppm)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136.91
136.59
135.54
133.13
129.73
129.33
128.61
121.79
114.85
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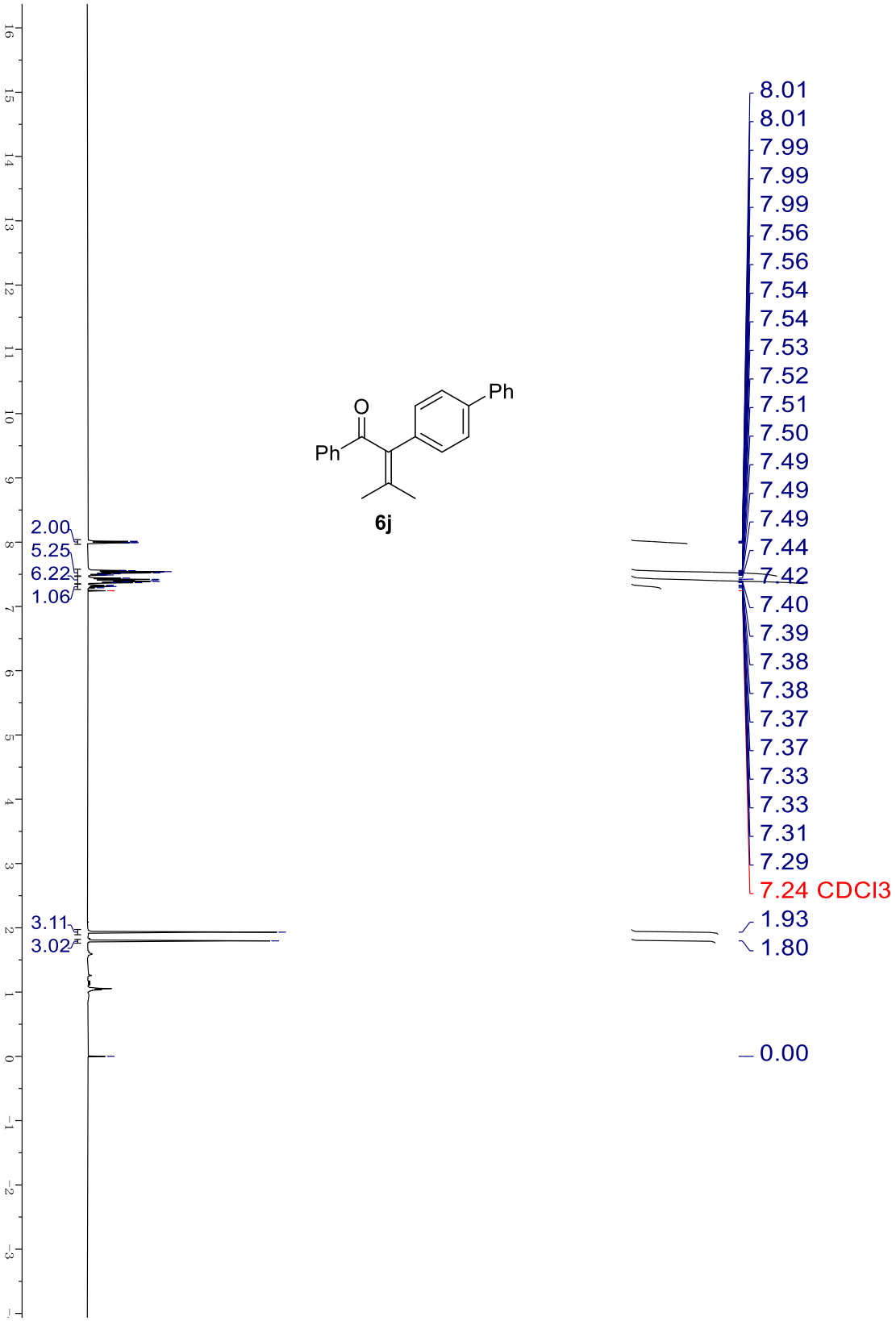
77.03 CDCl3
76.72 CDCl3
55.20
22.53
21.40
O
Ph
OMe
6i


8.01
8.01
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7.56
7.54
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7.52
7.51
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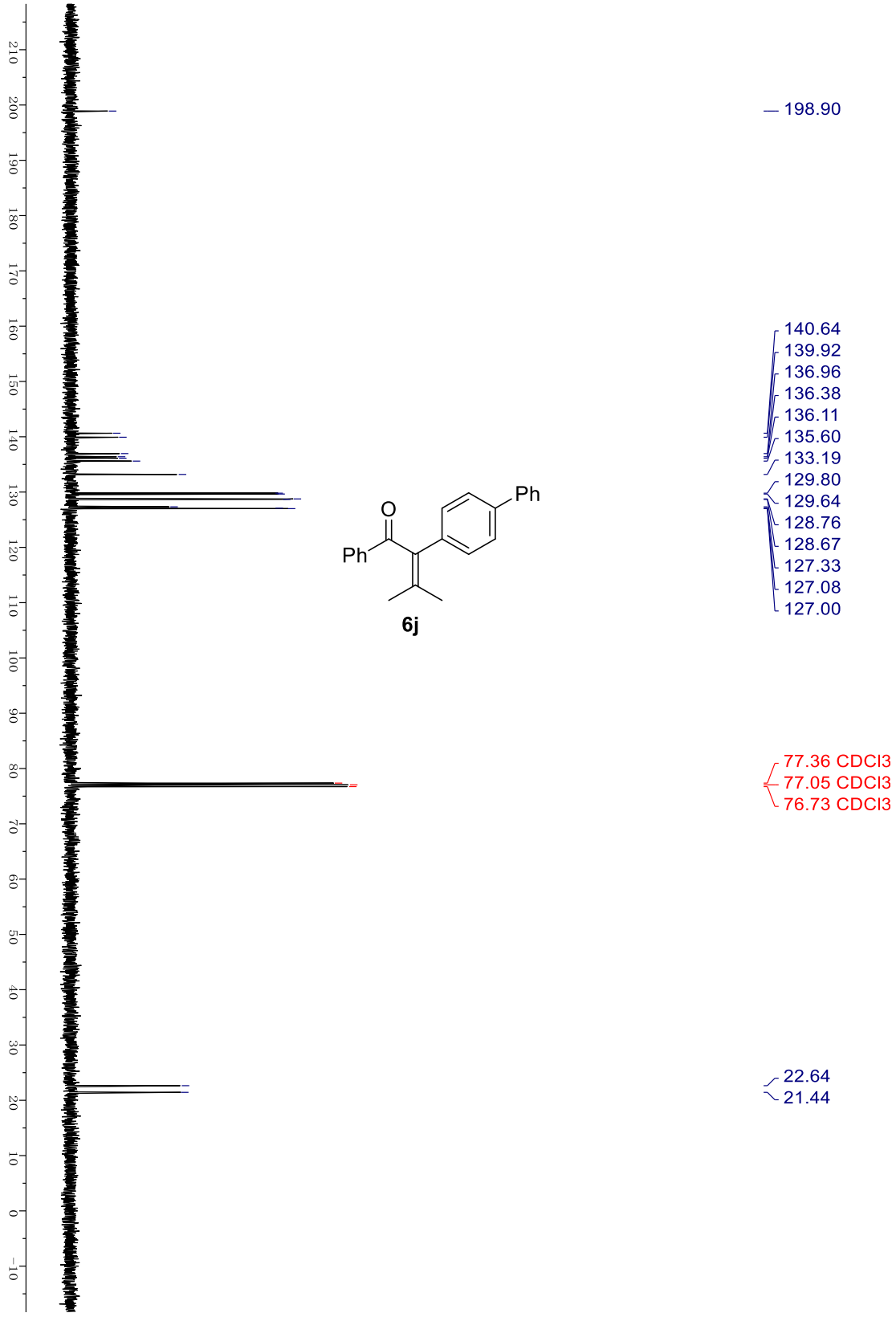
7.49
7.49
7.49
7.44
7.42
7.40
7.39
7.38
7.38
7.37
7.37
7.33
7.33
7.31
7.29
7.24 CDCl3
1.93
1.80
0.00
2.00
5.25
6.22
1.06
3.11
3.02
O
Ph
Ph
6j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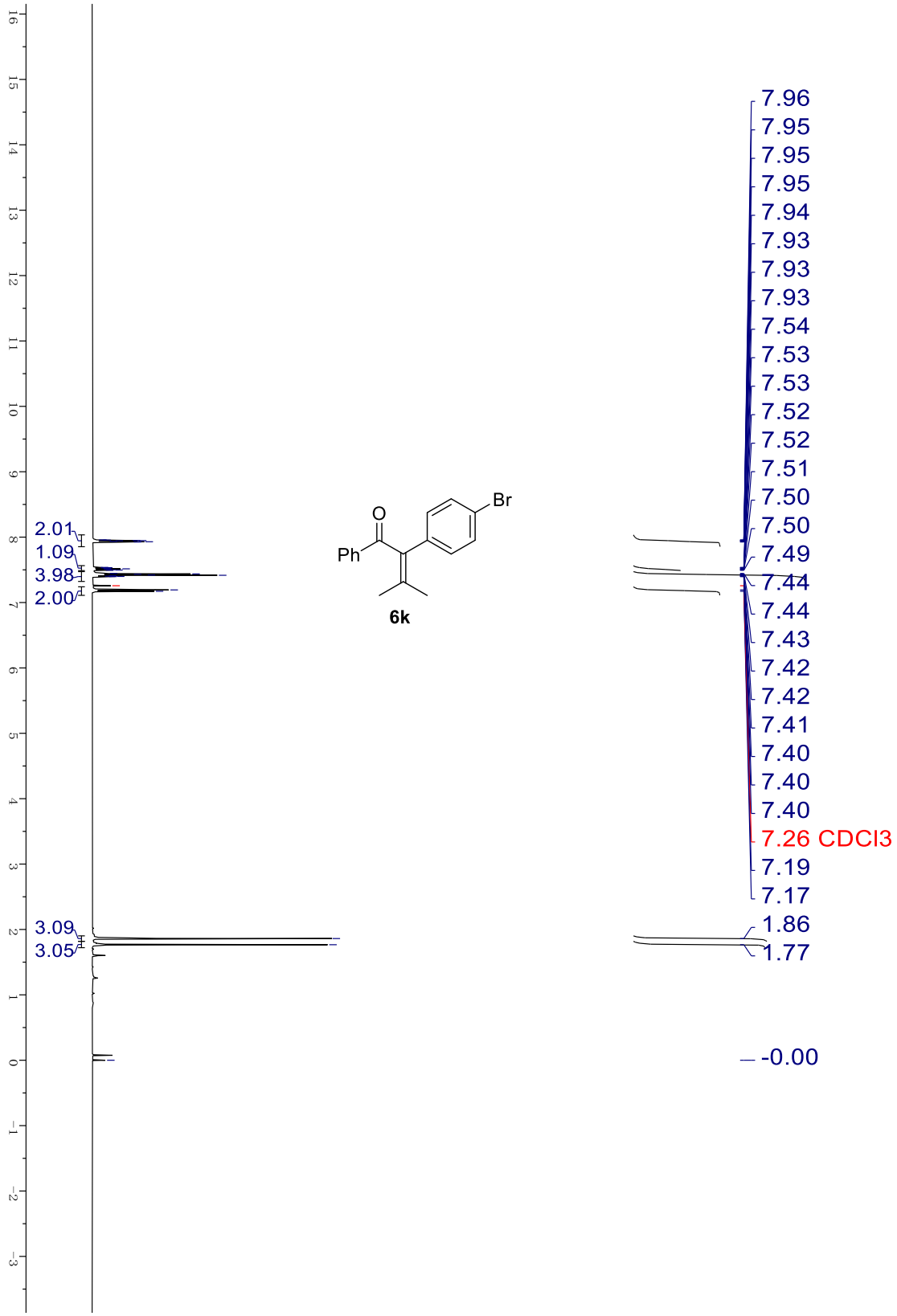
136.11
135.60
133.19
129.80
129.64
128.76
128.67
127.33
127.08
127.00
77.36 CDCl3
77.05 CDCl3
76.73 CDCl3
22.64
21.44
O
Ph
Ph
6j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1.09
3.98
2.00
3.09
3.05
O
Ph
Br
6k
7.96
7.95
7.95
7.95
7.94
7.93
7.93
7.93
7.54
7.53
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.44
7.44
7.43
7.42
7.42
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7.40
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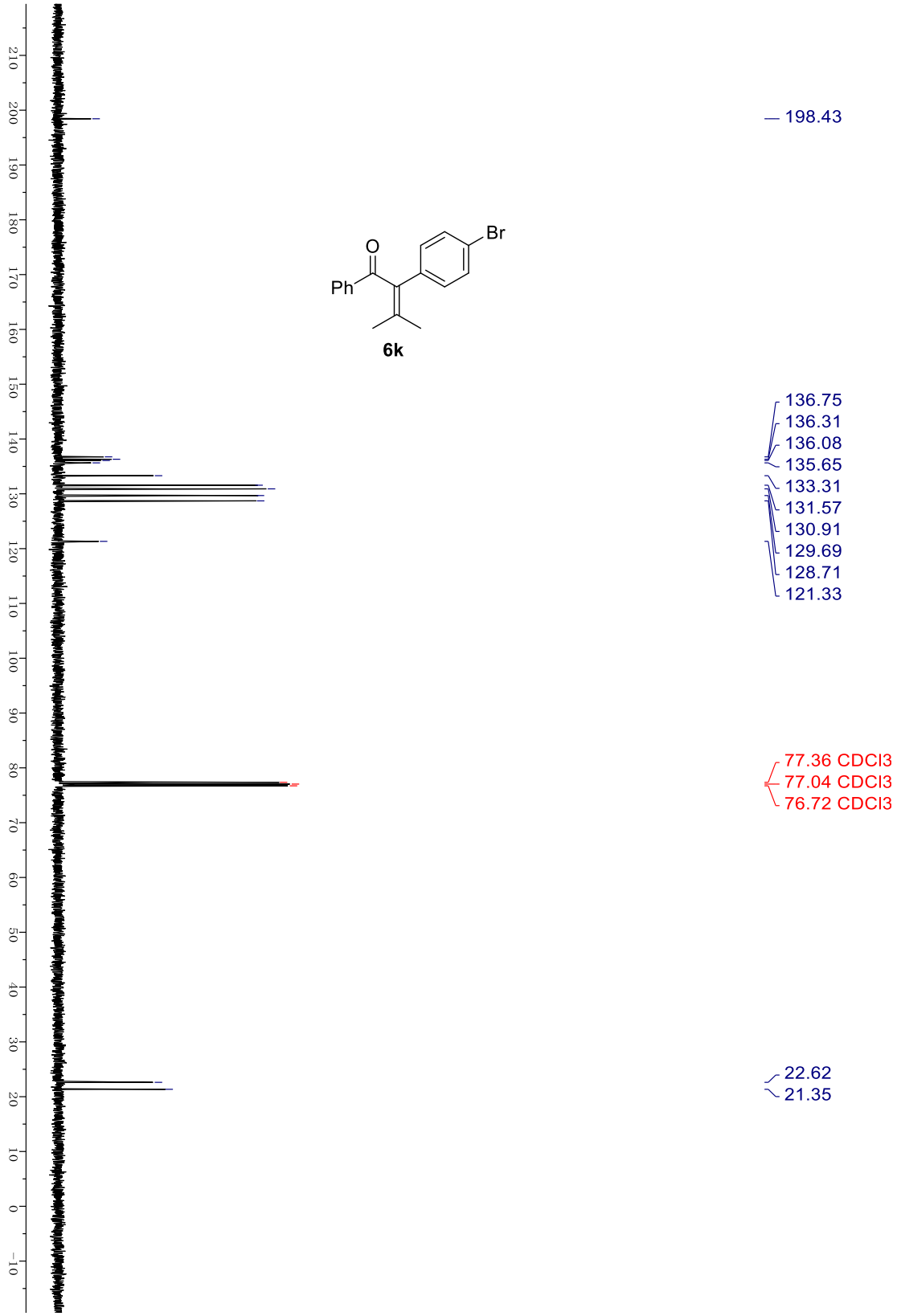
7.19
7.17
1.86
1.77
-0.00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131.57
130.91
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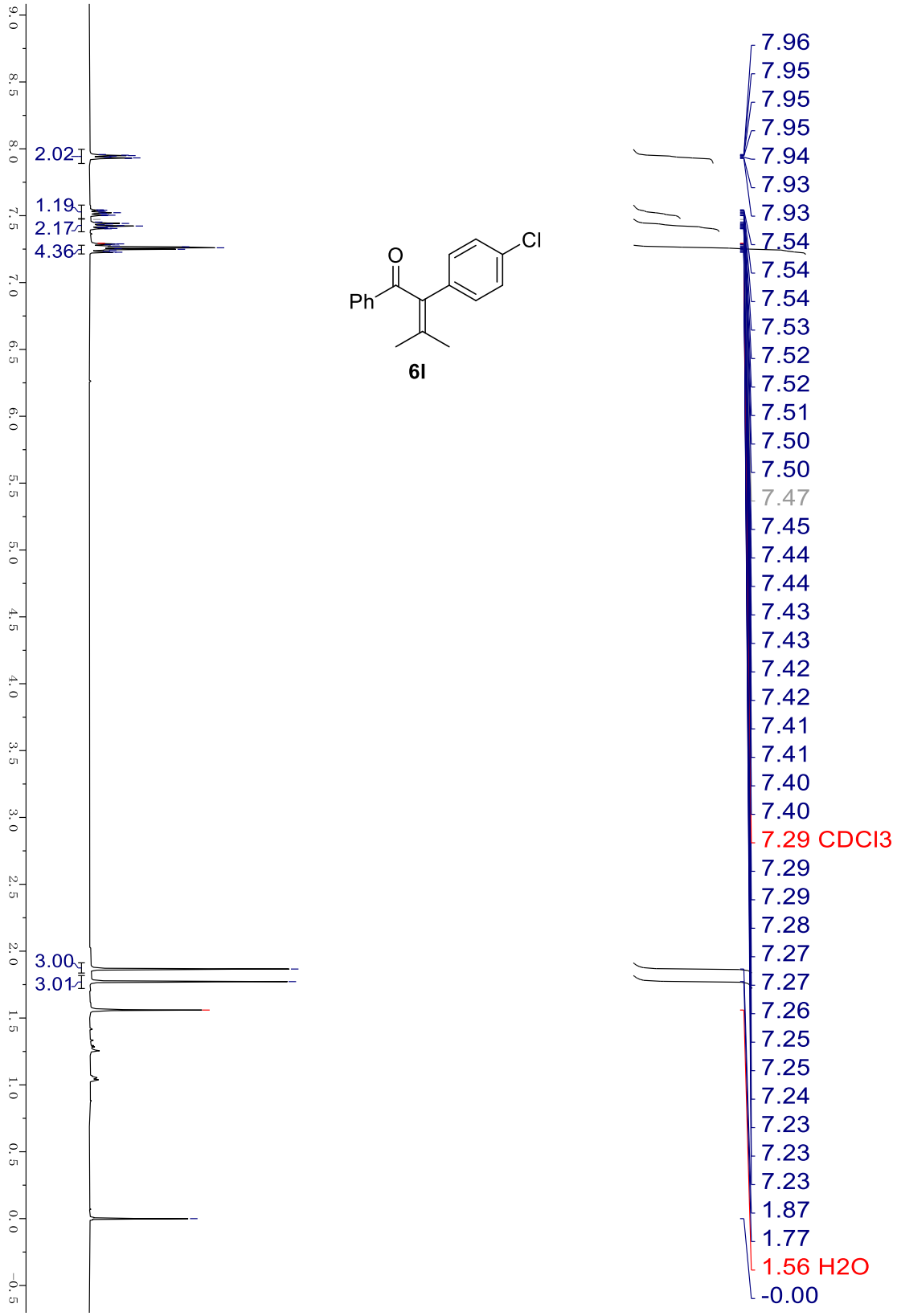
128.71
121.33
77.36 CDCl3
77.04 CDCl3
76.72 CDCl3
22.62
21.35
O
Ph
Br
6k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1.19
2.17
4.36
3.00
3.01
O
Cl
Ph
6l
7.96
7.95
7.95
7.95
7.94
7.93
7.93
7.54
7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.47
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
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7.40
7.29 CDCl3
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7.28
7.27
7.27
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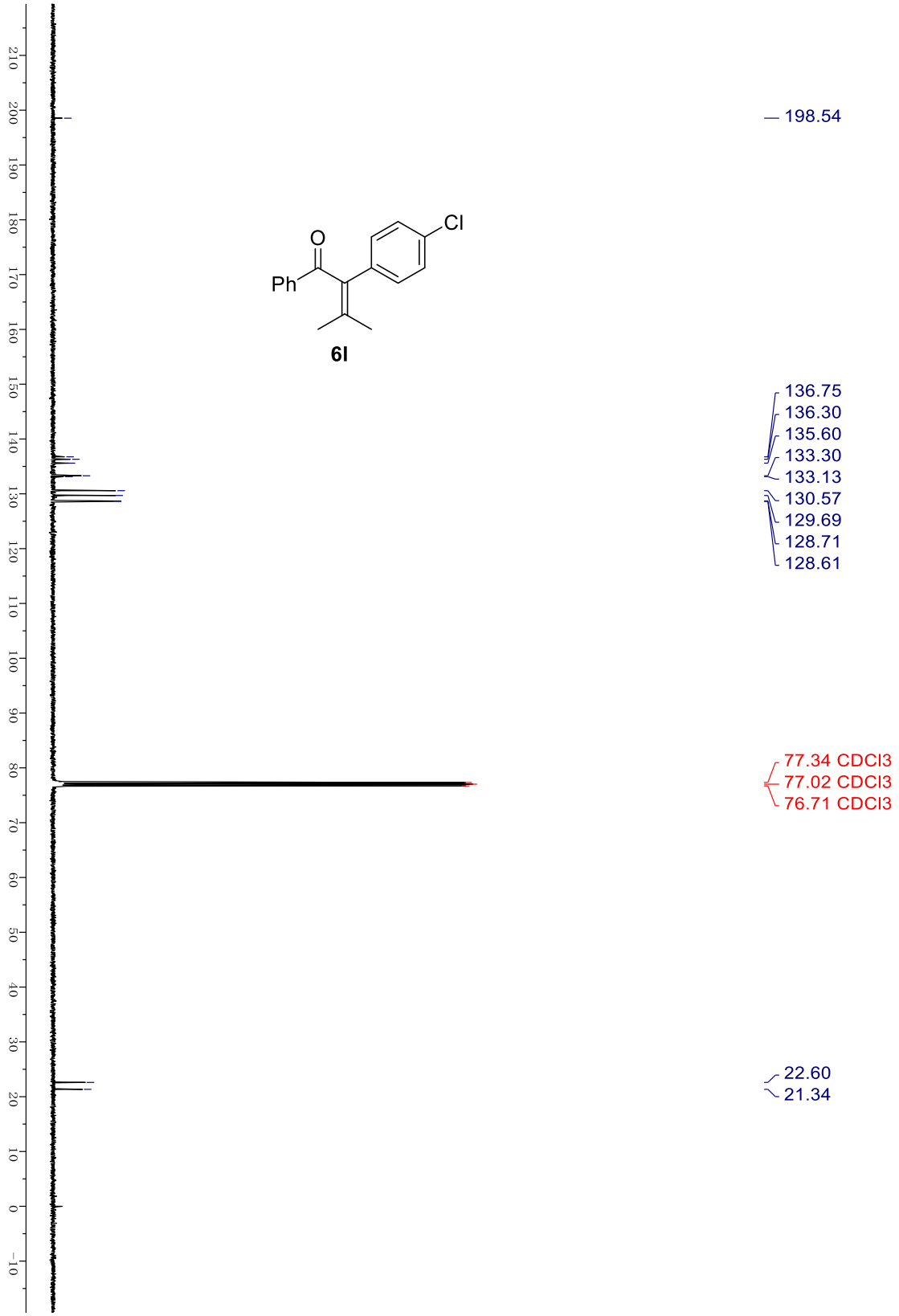
7.25
7.24
7.23
7.23
7.23
1.87
1.77
1.56 H2O
-0.00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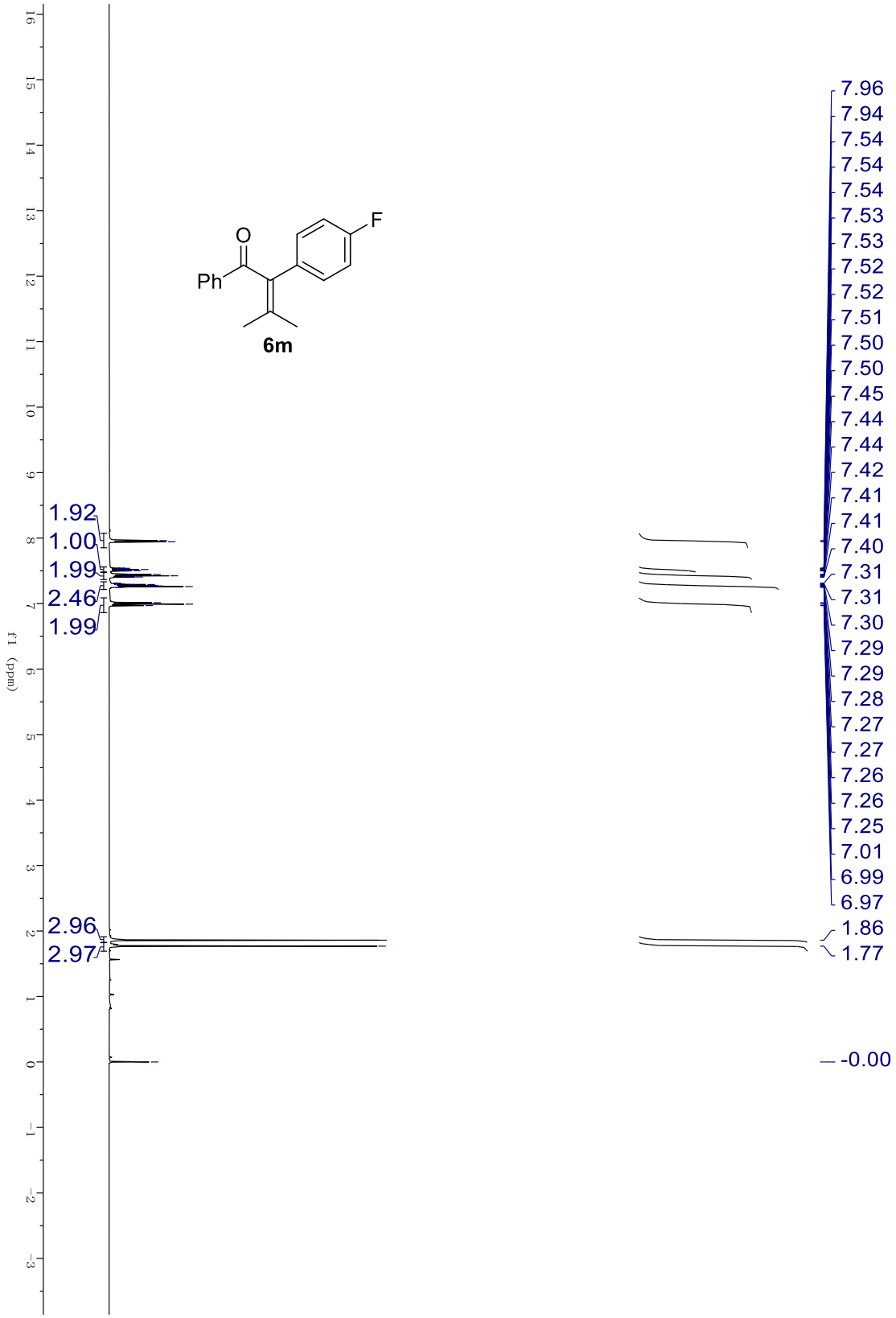
133.13
130.57
129.69
128.71
128.61
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
22.60
21.34
O
Cl
Ph
6l


O
Ph
F
6m
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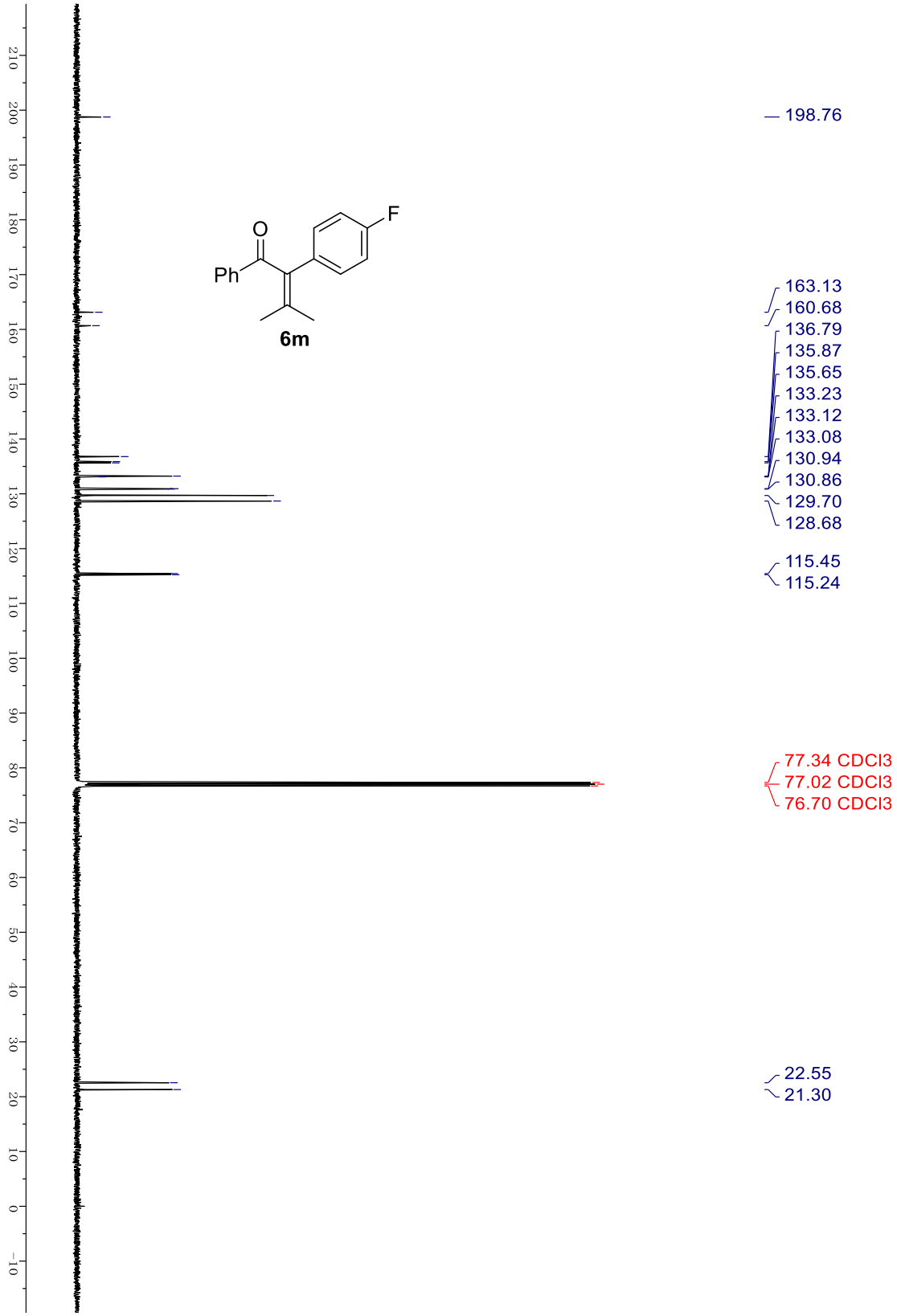
1.00
1.99
2.46
1.99
2.96
2.97
7.96
7.94
7.54
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.50
7.50
7.45
7.44
7.44
7.42
7.41
7.41
7.40
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.26
7.25
7.01
6.99
6.97
1.86
1.77
-0.00
f1 (ppm)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135.65
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133.12
133.08
130.94
130.86
129.70
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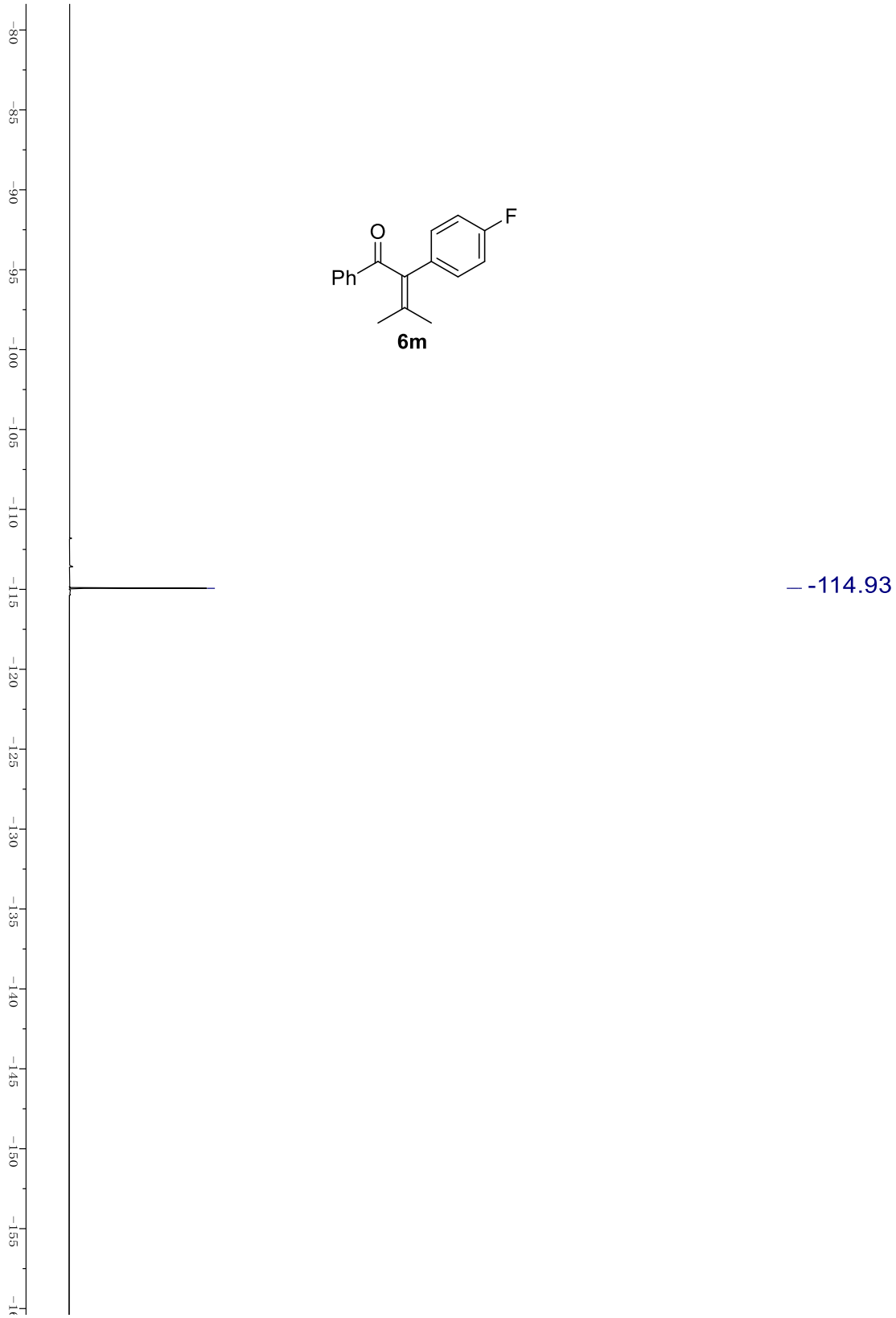
115.45
115.24
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
22.55
21.30
O
Ph
F
6m


O
Ph
F
6m
-114.93
-80
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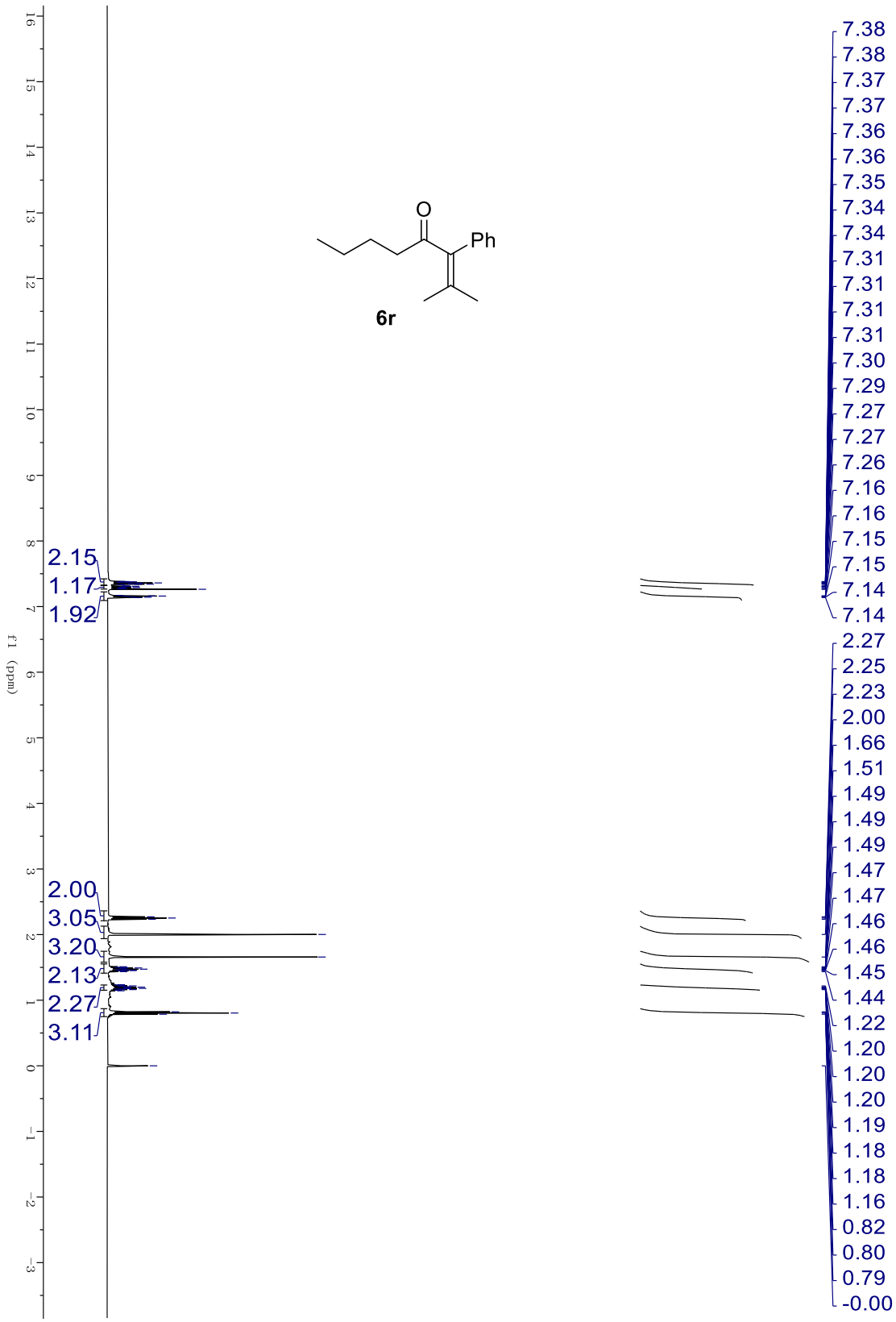
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155


O
Ph
6r
f1 (ppm)
2.15
1.17
1.92
2.00
3.05
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2.13
2.27
3.11
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.31
7.31
7.31
7.31
7.30
7.29
7.27
7.27
7.26
7.16
7.16
7.15
7.15
7.14
7.14
2.27
2.25
2.23
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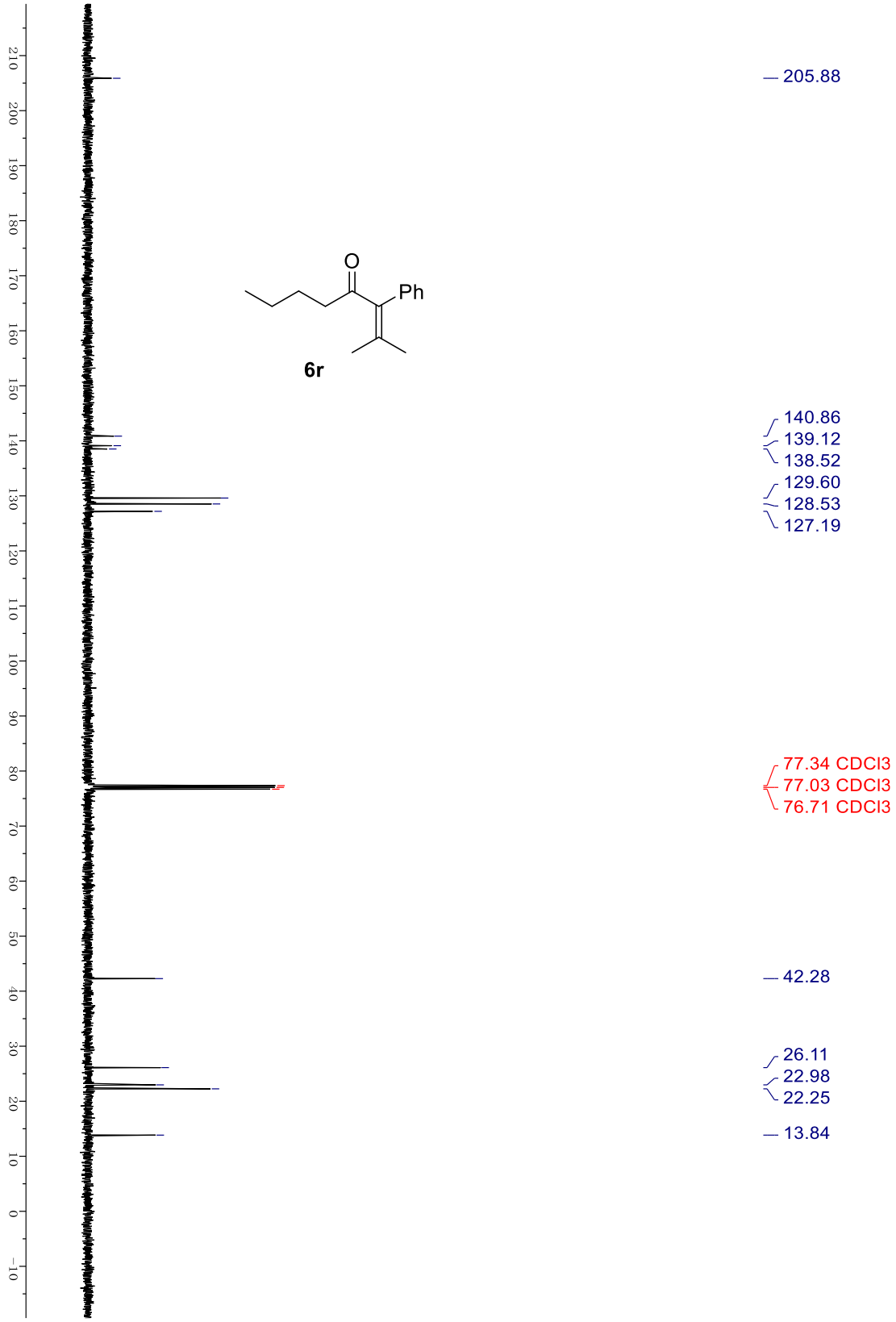
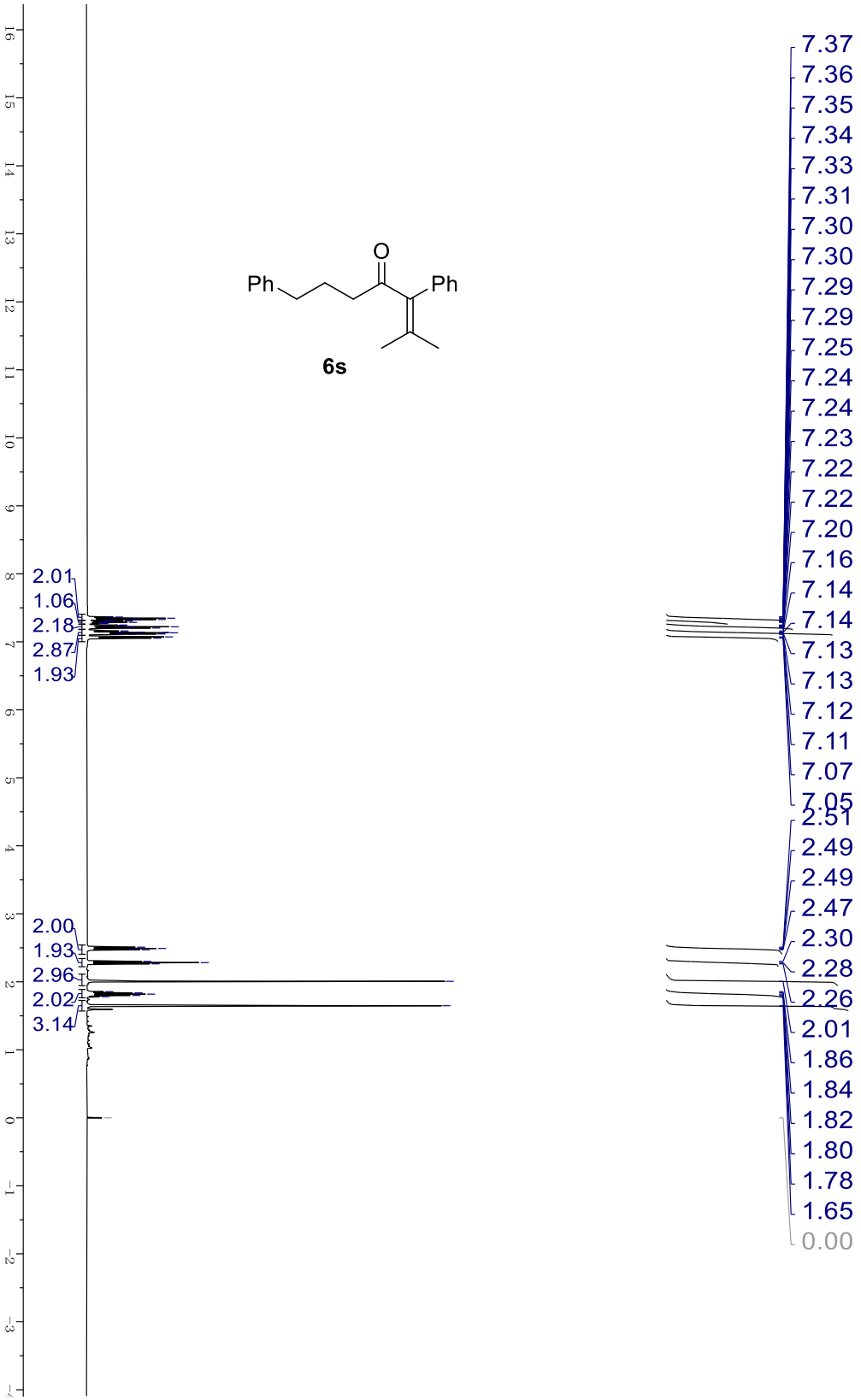
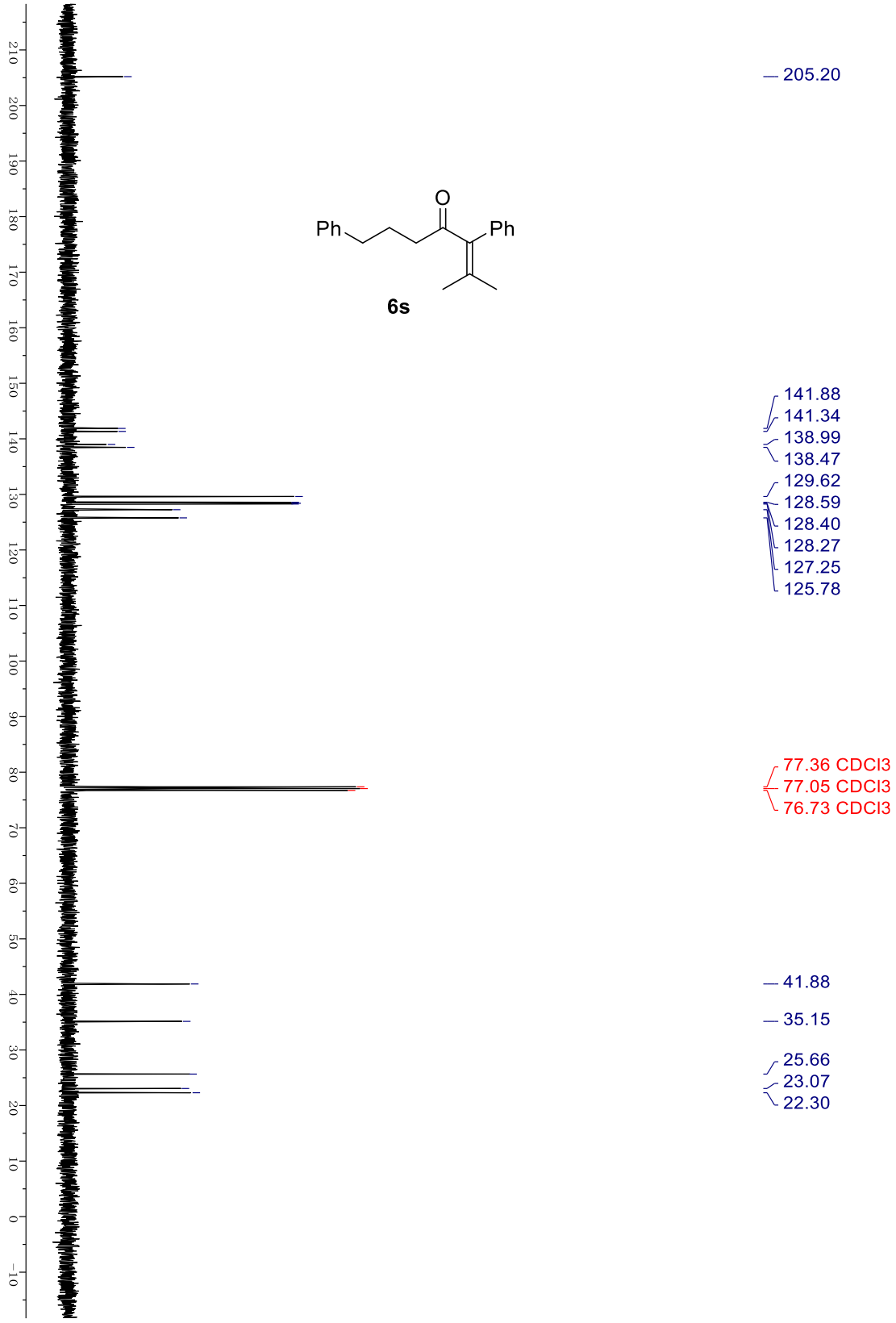
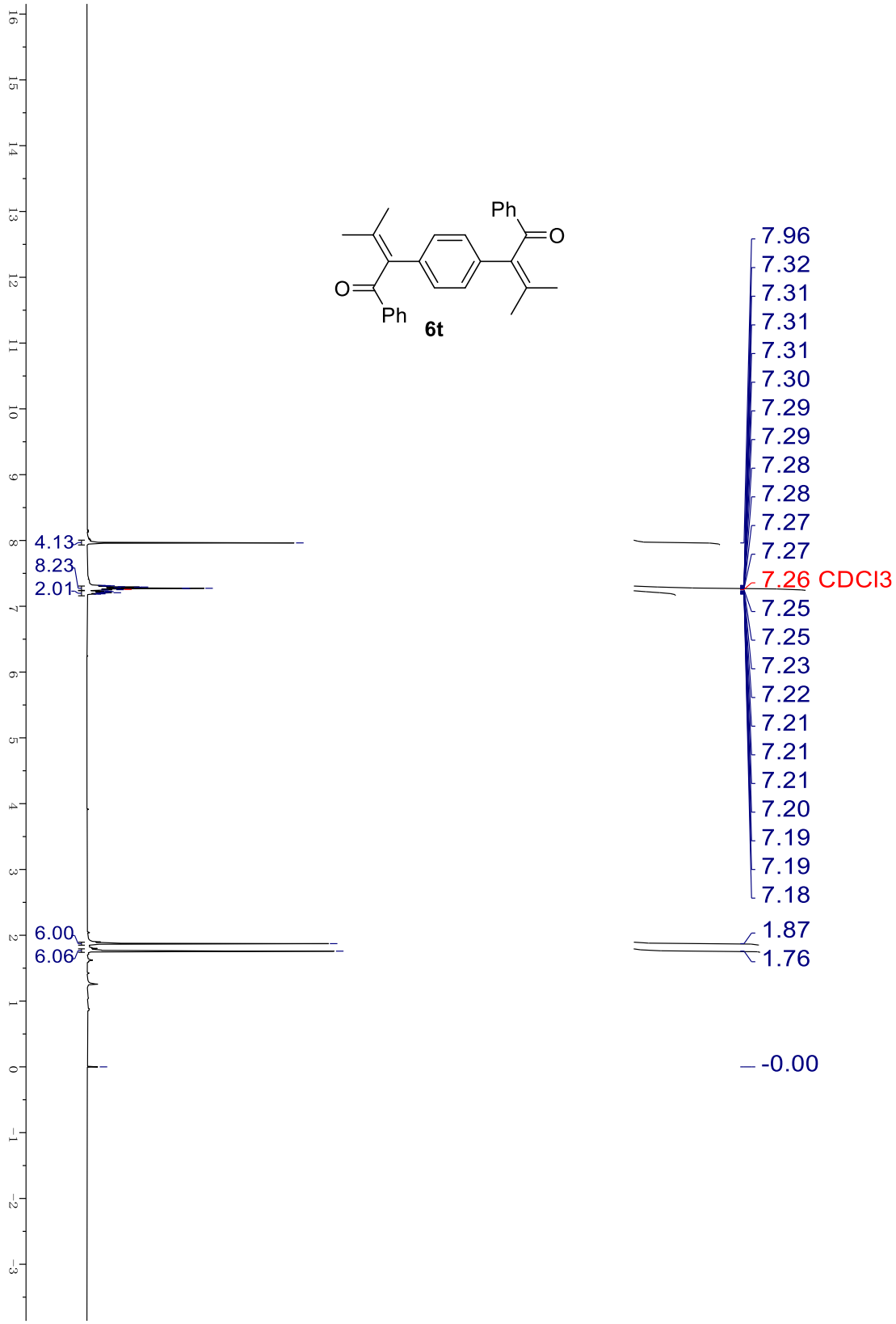
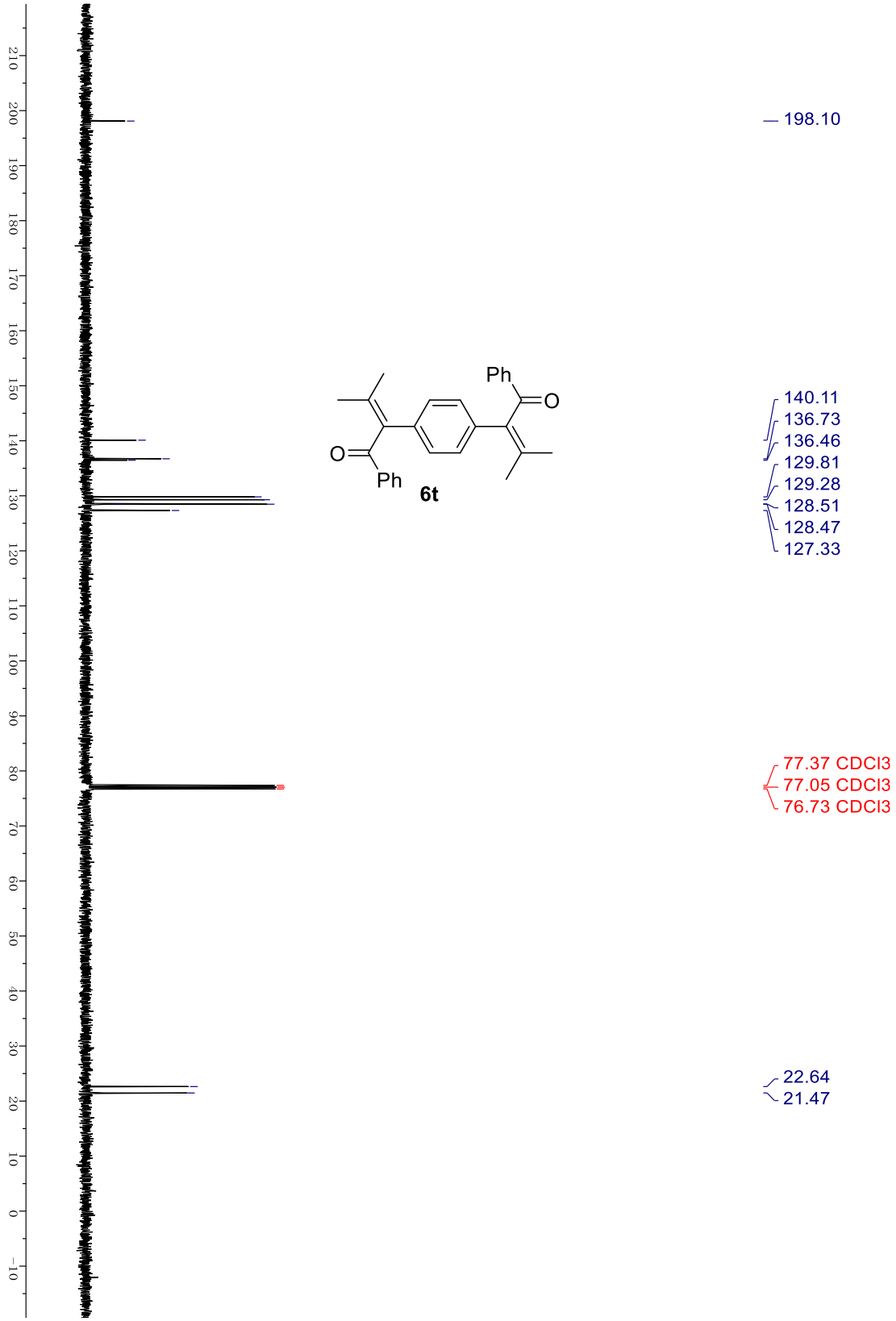
1.51
1.49
1.49
1.49
1.47
1.47
1.46
1.46
1.45
1.44
1.22
1.20
1.20
1.20
1.19
1.18
1.18
1.16
0.82
0.80
0.79
-0.00

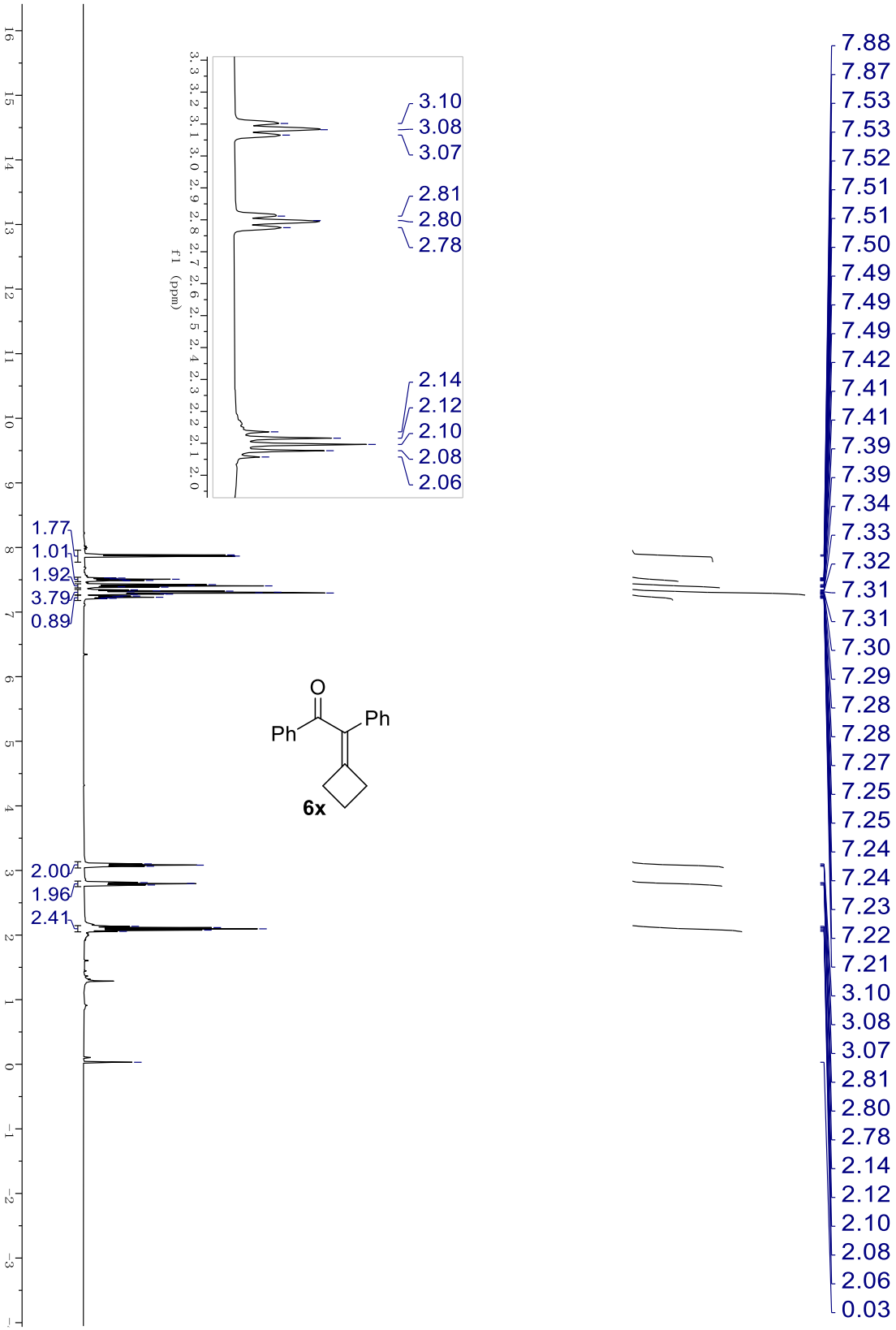

O
Ph
6r
205.88
140.86
139.12
138.52
129.60
128.53
127.19
77.34 CDCl3
77.03 CDCl3
76.71 CDCl3
42.28
26.11
22.98
22.25
13.84


O
Ph
Ph
6s
2.01
1.06
2.18
2.87
1.93
2.00
1.93
2.96
2.02
3.14
7.37
7.36
7.35
7.34
7.33
7.31
7.30
7.30
7.29
7.29
7.25
7.24
7.24
7.23
7.22
7.22
7.20
7.16
7.14
7.14
7.13
7.13
7.12
7.11
7.07
7.05
2.51
2.49
2.49
2.47
2.30
2.28
2.26
2.01
1.86
1.84
1.82
1.80
1.78
1.65
0.00


205.20
141.88
141.34
138.99
138.47
129.62
128.59
128.40
128.27
127.25
125.78
77.36 CDCl3
77.05 CDCl3
76.73 CDCl3
41.88
35.15
25.66
23.07
22.30
O
Ph
Ph
6s


Ph
O
O
Ph
6t
4.13
8.23
2.01
6.00
6.06
7.96
7.32
7.31
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26 CDCl3
7.25
7.25
7.23
7.22
7.21
7.21
7.21
7.20
7.19
7.19
7.18
1.87
1.76
-0.00


198.10
140.11
136.73
136.46
129.81
129.28
128.51
128.47
127.33
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
22.64
21.47
Ph
O
O
Ph
6t


3.10
3.08
3.07
2.81
2.80
2.78
2.14
2.12
2.10
2.08
2.06
f1 (ppm)
1.77
1.01
1.92
3.79
0.89
2.00
1.96
2.41
O
Ph
Ph
6x
7.88
7.87
7.53
7.53
7.52
7.51
7.51
7.50
7.49
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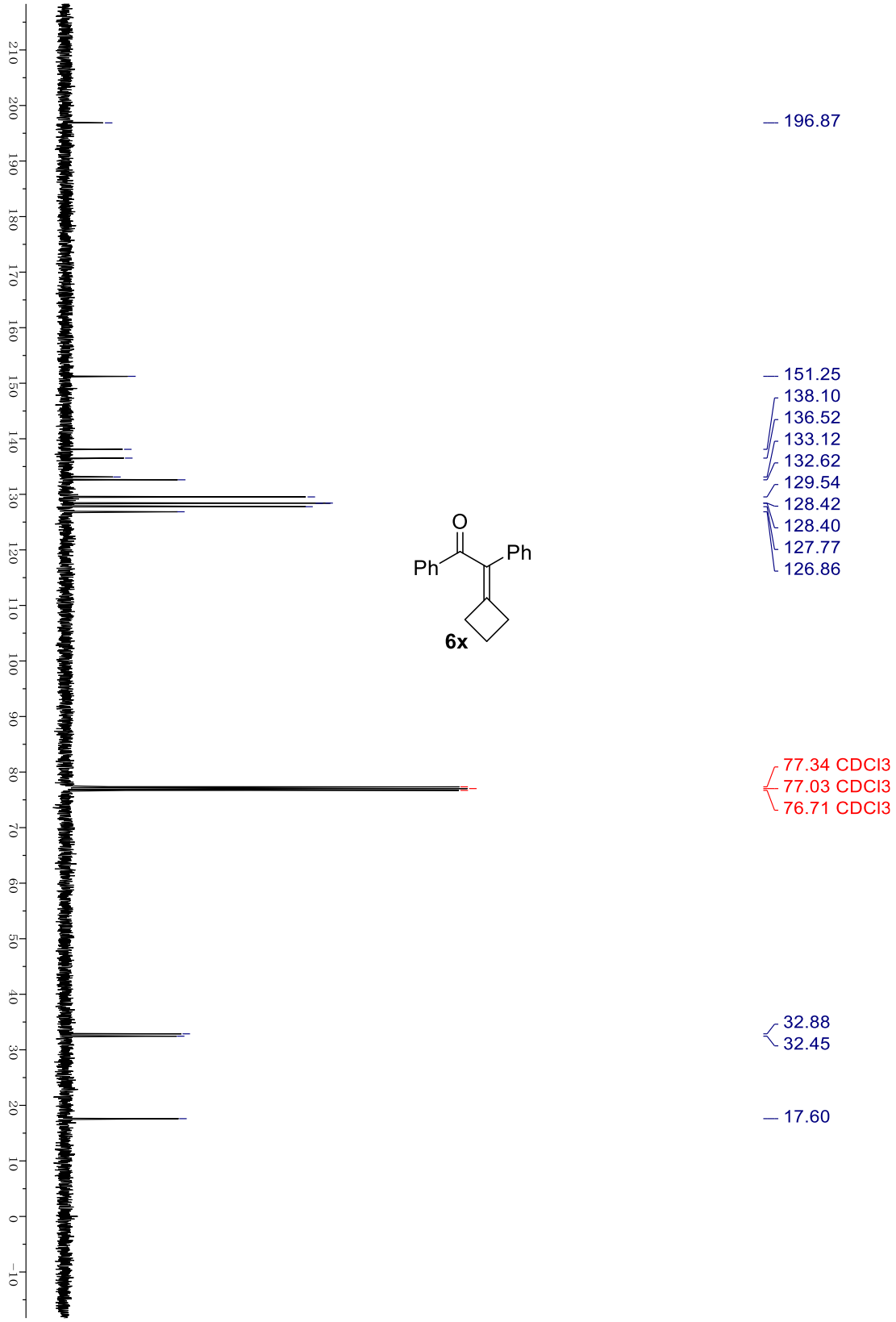
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