Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of Silafluorenes and Silaindenes via Silyl Radicals from Arylhydrosilanes: Intramolecular Cyclization and Intermolecular Annulation with Alkynes

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1. General considerations

General. Unless otherwise noted, all reactions were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Preparative thin-layer chromatography (PTLC) was performed on pre-coated, glass-backed GF254 silica gel plates. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with PTLC or standard silica gel chromatography. Column chromatography was performed on silica gel (200–300 mesh) using standard methods.

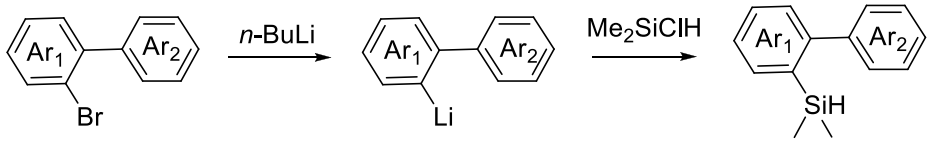
Structural analysis. NMR spectra were measured on a Bruker Avance-400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents ($CDCl_{3,}$) and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to corresponding solvent resonance. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (ν max) are reported in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were acquired with an EI source. Single crystal X-ray diffraction analysis of **5c** was carried out by Mr. Yousong Ding on a Bruker apex duo equipment at Center for Applied Chemistry Research, Frontier Institute of Science and Technology, Xi'an Jiaotong University.

Materials. Commercial reagents were purchased from J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, Strem Chemicals, TCI and used as received unless otherwise stated. Hexane, THF, Et_2O, benzene were purified by distillation over sodium and stored under N_2.

2. Intramolecular homolytic aromatic silylation of biphenylhydrosilanes

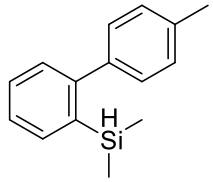
2.1 Preparation of starting materials

A. General procedure A for synthesis of biphenylhydrosilanes:



n-BuLi (1.5 mL, 3.75 mmol, 1.5 eq.) was added dropwise to a solution of 2-bromo-1,1'-biphenyl (582.8 mg, 2.5 mmol, 1.0 eq.) in THF (10 mL) at -78 ℃ under an atmosphere of N_2. After stirring for 15 min, dimethylchlorosilane (354.8 mg, 3.75 mmol, 1.5 eq.) was added dropwise at -78 ℃ to the mixture, then the mixture was warmed to 25 ℃ slowly. After 24 h, a saturated solution of NH_4Cl in H_2O was added and the mixture was extracted using EA (ethyl acetate). The organic layer was dried over MgSO4, filtered, and concentrated under reduced pressure. The product was isolated by column chromatography on silica gel (PE, petroleum ether) to give 2-(dimethylsilyl)biphenyl.[1]

(1b) dimethyl(4'-methyl-[1,1'-biphenyl]-2-yl)silane



Chemical Formula: $C_{15}H_{18}Si$
Exact Mass: 226.1178
Molecular Weight: 226.3940

The general procedure A was followed using 2-bromo-4'-methyl-1,1'-biphenyl (617.9 mg, 2.5 mmol, 1.0 eq.) as starting material, **1b** was obtained as a colorless liquid.

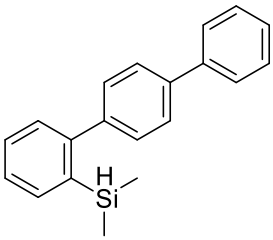
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.2 Hz, 1H), 7.41 (td, *J* = 7.4, 1.2 Hz, 1H), 7.34 (td, *J* = 7.2, 1.2 Hz, 1H), 7.29-7.19 (m, 5H), 4.48 (m, 1H), 2.41 (s, 3H), 0.07 (dd, *J* = 4.0, 1.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 149.5, 141.0, 136.9, 136.2, 135.2, 129.5, 129.2, 128.7, 126.4, 21.4, -2.8.

HRMS (EI^+): Calculated for $C_{15}H_{18}Si$ (M^+): 226.1178, Found: 226.1174.

IR (cm^{-1}): 3050, 2956, 2117, 1464, 1249, 1124, 881, 835, 762, 731, 708 .

(1g) [1,1':4',1''-terphenyl]-2-yldimethylsilane



Chemical Formula: $C_{20}H_{20}Si$
Exact Mass: 288.1334
Molecular Weight: 288.4650

The general procedure A was followed using 2-bromo-1,1':4',1"-terphenyl (773.0 mg, 2.5 mmol, 1.0 eq.) as starting material, **1g** was obtained as a white solid.

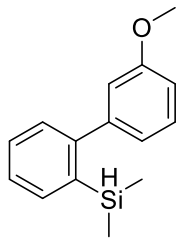
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.66 (t, *J* = 8.0 Hz, 5H), 7.49-7.43 (m, 5H), 7.39-7.34 (m, 3H), 4.39 (d, *J* = 3.6 Hz, 1H), 0.11 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 149.0, 142.9, 140.9, 140.1, 136.2, 135.3, 129.8, 129.4, 129.3, 128.9, 127.5, 127.2, 126.7, 126.6, -2.8.

HRMS (EI^+): Calculated for $C_{20}H_{20}Si$ (M^+): 288.1334, Found: 288.1339.

IR (cm^{-1}): 3026, 2955, 2096, 1465, 1426, 1249, 1123, 891, 756, 697.

(1i) (3'-methoxy-[1,1'-biphenyl]-2-yl)dimethylsilane



Chemical Formula: $C_{15}H_{18}OSi$
Exact Mass: 242.1127
Molecular Weight: 242.3930

The general procedure A was followed using 2-bromo-3'-methoxy-1,1'-biphenyl (657.8 mg, 2.5 mmol, 1.0 eq.) as starting material, **1j** was obtained as a colorless liquid.

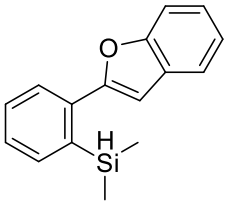
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.62 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.42 (td, *J* = 7.6, 1.6 Hz, 1H), 7.35 (td, *J* = 7.6, 1.6 Hz, 1H), 7.32-7.28 (m, 2H), 6.94-6.90 (m, 3H), 4.36 (m, 1H), 3.83 (s, 3H), 0.09 (d, *J* = 3.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 159.30, 149.3, 145.3, 136.1, 135.3, 129.2, 129.1, 126.6, 121.9, 114.8, 113.1, 55.4, -2.8.

HRMS (EI^+): Calculated for $C_{15}H_{18}OSi$ (M^+): 242.1127, Found: 242.1121.

IR (cm^{-1}): 3052, 3000, 2955, 2902, 2833, 2116, 1583, 1463, 1247, 1216, 1209, 877, 836, 761, 730, 701 .

(1k) 2-(benzofuran-2-yl)phenyl)dimethylsilane



Chemical Formula: $C_{16}H_{16}OSi$
Exact Mass: 252.0970
Molecular Weight: 252.3880

The general procedure A was followed using 2-(2-bromophenyl)benzofuran (682.8 mg, 2.5 mmol, 1.0 eq.) as starting material, **1k** was obtained as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.74 (dd, *J* = 7.6, 6.4 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.32-7.24 (m, 2H), 6.94 (s, 1H), 4.56 (m, 1H), 0.34 (dd, *J* = 3.6, 2.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 154.6, 136.6, 136.3, 136.2, 129.5, 129.2, 128.0, 127.8, 124.2, 123.1, 121.1, 111.1, 103.2, -2.6.

HRMS (EI^+): Calculated for $C_{16}H_{16}OSi$ (M^+): 252.0970, Found: 252.0967.

IR (cm^{-1}): 3053, 2954, 2923, 2111, 1445, 1247, 898, 877, 764, 747, 724.

2.2. Synthesis of silafluorenes

A. Optimization of reaction parameters

Table S1. Optimization of radical initiator[a]

Entry	Radical initiator	Yield (%)[b]
1	di-*tert*-butyl peroxide	79
2	benzoyl peroxide	19
3	azodiisobutyronitrile	trace
4	*tert*-butyl hydroperoxide [c]	n.r.

[a]Reaction conditions: biphenyl-2-yldimethylsilane (0.1 mmol), radical initiator (0.3 mmol), benzene (0.5 ml) under 130 °C and N_2 atomosphere for 24 h. [b]Yields based on ^{1}H NMR analysis of the crude products with 1,3,5-trimethoxybenzene added as an internal standard. [c]70% solvent in H_2O.

Table S2. Optimization of additive[a]

Entry	Additive	Yield (%)[b]
1	K_2CO_3(3.0 eq)	75
2	^{t}BuLi(3.0 eq)	64
3	K_3PO_4(3.0 eq)	60
4	$CsCO_3$(3.0 eq)	43

5	LiOMe(3.0 eq)	68
6	^{t}BuOK(3.0 eq)	n.r.
7	LiOAc(3.0 eq)	67
8	PhCOONa(3.0 eq)	65
9	Na_2CO_3(3.0 eq)	67
10	KOAc(3.0 eq)	72
11	$KHCO_3$(3.0 eq)	72
12	Na_3PO_4(3.0 eq)	72
13	K_2CO_3(3.0 eq), Phenanthroline(20 mol%)	23
14	K_2CO_3(3.0 eq), TMEDA(20 mol%)	8
15	K_2CO_3(3.0 eq), DMEDA(20 mol%)	10

[a]Reaction conditions: biphenyl-2-yldimethylsilane (0.1 mmol), DTBP (0.3 mmol), additive, benzene (0.5 ml) under 130 ^{o}C and N_2 atomosphere for 24 h. [b]Yields based on ^{1}H NMR analysis of the crude products with 1,3,5-trimethoxybenzene added as an internal standard.

Table S3. Optimization of solvent[a]

Entry	Solvent	Yield (%)[b]
1	acetonitrile	47
2	benzene	66[c]
3	toluene	39
4	dioxane	57
5	1,2-dichloroethane	36
6	water	7
7	trifluorotoluene	84 (77)[d]
8	chlorobenzene	78
9	1,2-dichlorobenzene	63
10	*tert*-butylbenzene	65
11	tetrachloromethane	trace
12	1,1,2,2-tetrachloroethane	trace

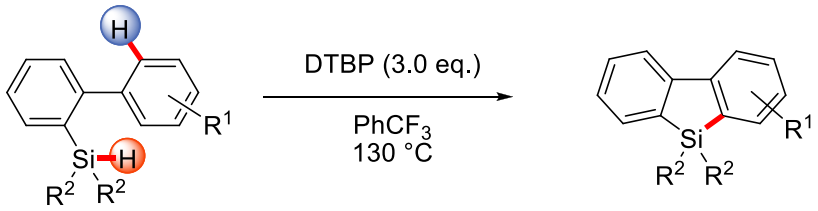
[a]Reaction conditions: biphenyl-2-yldimethylsilane (0.1 mmol), DTBP (0.3 mmol), solvent (0.5 ml) under 130 ^{o}C and N_2 atomosphere for 24 h. [b]Yields based on ^{1}H NMR analysis of the crude products with 1,3,5-trimethoxybenzene added as an internal standard. [c]The reaction was performed under air. [d]Isolated yield shown in parenthesis.

Table S4. Optimization of other reaction parameters [a]

Entry	Radical initiator	Temperature (^{o}C)	Time (h)	Yield (%)[b]
1	DTBP(2.0 eq)	130	24	61
2	DTBP(4.0 eq)	130	24	72
3	DTBP(3.0 eq)	130	20	80
4	DTBP(3.0 eq)	130	36	81
5	DTBP(3.0 eq)	130	48	72
6	DTBP(3.0 eq)	120	24	73
7	DTBP(3.0 eq)	140	24	75
8	DTBP(3.0 eq)	150	24	75

[a]Reaction conditions: biphenyl-2-yldimethylsilane (0.1 mmol), DTBP, trifluorotoluene (0.5 ml) under certain temperature and N_2 atomosphere for a certain period of time. [b]Yields based on ^{1}H NMR analysis of the crude products with 1,3,5-trimethoxybenzene added as an internal standard.

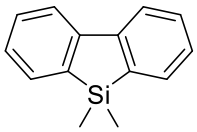
B. General procedure B for synthesis of silafluorenes:



In a dried Schlenk flask (25 mL in volume) equipped with a stirring bar were placed with biphenylhydrosilanes (0.25 mmol, 1.0 eq, if solid). After evacuation and refill with dry nitrogen for three times, DTBP (137.8 uL, 0.75 mmol, 3.0 eq.) and $PhCF_3$ (1.0 mL) were added with syringes under a stream of nitrogen. The resulting mixture was allowed to stir at 130 ℃ for 36 h. After cooling to room temperature, the reaction mixture was concentrated and then purified by column chromatography on silica gel or PTLC (PE as the eluting solvent) to give the target products.

C. Spectra data of silafluorenes:

(2a) 5,5-dimethyl-5*H*-dibenzo[*b*,*d*]silole,[1] CAS: 13688-68-1



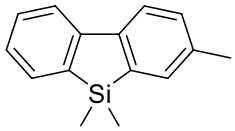
Chemical Formula: $C_{14}H_{14}Si$
Exact Mass: 210.0865
Molecular Weight: 210.3510

The general procedure B was followed using biphenyl-2-yldimethylsilane **1a** (53.1 mg, 0.25 mmol, 1.0 eq.) as starting material. **2a** was obtained as yellow oil (40.6 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.43 (s, 6H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm -3.1, 121.0, 127.5, 130.3, 132.9, 139.1, 147.9..

(2b) 3,5,5-trimethyl-5*H*-dibenzo[*b*,*d*]silole



Chemical Formula: $C_{15}H_{16}Si$
Exact Mass: 224.1021
Molecular Weight: 224.3780

The general procedure B was followed using dimethyl(4'-methylbiphenyl-2-yl)silane **1b** (56.6 mg, 0.25 mmol, 1.0 eq.) as starting material. **2b** was obtained as yellow oil (37.1 mg, 66%).

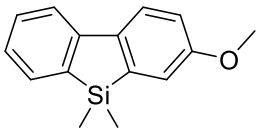
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.41 (s, 6H), 2.38 (s, 3H), 7.24 (t, *J* = 5.6 Hz, 2H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.44 (s, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm -3.1, 21.5, 120.7, 120.8, 127.1, 130.3, 131.1, 132.8, 133.6, 137.1, 138.8, 139.1, 145.3, 148.0.

HRMS (EI^+): Calculated for $C_{15}H_{16}Si$ (M^+): 224.1021, Found: 224.1022.

IR (cm^{-1}): 2919, 1619, 1275, 1259, 1062, 764, 750, 672.

(2c) 3-methoxy-5,5-dimethyl-5*H*-dibenzo[*b*,*d*]silole,[1] CAS: 1252259-64-5



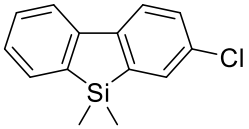
Chemical Formula: $C_{15}H_{16}OSi$
Exact Mass: 240.0970
Molecular Weight: 240.3770

The general procedure B was followed using (4'-methoxybiphenyl-2-yl)dimethylsilane **1c** (60.6 mg, 0.25 mmol, 1.0 eq.) as starting material. **2c** was obtained as yellow oil (40.7 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.43 (s, 6H), 3.87 (s, 3H), 6.97 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 6.8 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm -3.1, 55.5, 115.7, 118.0, 120.3, 122.1, 126.5, 130.4, 132.8, 138.3, 140.8, 141.1, 147.9, 159.4.

(2d) 3-chloro-5,5-dimethyl-5*H*-dibenzo[*b,d*]silole,[1] CAS: 1252259-63-4



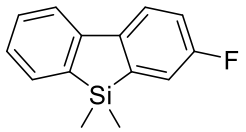
Chemical Formula: $C_{14}H_{13}ClSi$
Exact Mass: 244.0475
Molecular Weight: 244.7930

The general procedure B was followed using (4'-chlorobiphenyl-2-yl)dimethylsilane **1d** (74.0 mg, 0.3 mmol, 1.0 eq.) as starting material. **2d** was obtained as yellow solid (58.0 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.43 (s, 6H), 7.29 (t, *J* = 7.2Hz, 1H), 7.38 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.62 (d, *J* = 6.8 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm -3.2, 121.0, 122.2, 127.7, 130.3, 130.5, 132.7, 133.0, 133.6, 138.7, 141.6, 146.2, 146.9.

(2e) 3-fluoro-5,5-dimethyl-5*H*-dibenzo[*b,d*]silole,[1] CAS: 1252259-62-3



Chemical Formula: $C_{14}H_{13}FSi$
Exact Mass: 228.0771
Molecular Weight: 228.3414

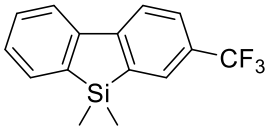
The general procedure B was followed using (4'-fluorobiphenyl-2-yl)dimethylsilane **1e** (69.0 mg, 0.3 mmol, 1.0 eq.) as starting material. **2e** was obtained as yellow oil (46.6 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.42 (s, 6H), 7.08 (td, *J* = 8.8, 2.8 Hz, 1H), 7.23-7.29 (m, 2H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.61 (d, *J* = 6.8 Hz, 1H), 7.73-7.77 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm -3.2, 117.1 (d, *J* = 23 Hz), 119.1 (d, *J* = 20 Hz), 120.7, 122.4 (d, *J* = 7 Hz), 127.2, 130.5, 133.0, 138.6, 142.0 (d, *J* = 5 Hz), 143.8 (d, *J* = 3 Hz), 147.1, 162.8 (d, *J* = 247 Hz).

^{19}F NMR (377 MHz, CDCl3): δ ppm -115.81.

(2f) 5,5-dimethyl-3-(trifluoromethyl)-5*H*-dibenzo[*b,d*]silole,[1] CAS: 1252259-61-2



Chemical Formula: $C_{15}H_{13}F_3Si$
Exact Mass: 278.0739
Molecular Weight: 278.3492

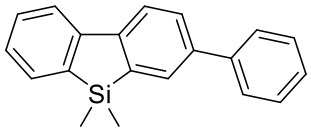
The general procedure B was followed using dimethyl(4'-(trifluoromethyl)biphenyl-2-yl)silane **1f** (70.1 mg, 0.25 mmol, 1.0 eq.) as starting material. **2f** was obtained as white solid (56.7 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.46 (s, 6H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.86-7.91 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm -3.3, 120.9, 121.7, 124.8 (q, *J* = 271 Hz), 127.4 (q, *J* = 4 Hz), 128.5, 129.2 (q, *J* = 32 Hz), 129.5 (q, *J* = 4 Hz), 130.6, 133.1, 139.6, 140.0, 146.5, 151.3.

^{19}F NMR (377 MHz, CDCl3): δ ppm -62.20.

(2g) 5,5-dimethyl-3-phenyl-5*H*-dibenzo[*b,d*]silole



Chemical Formula: $C_{20}H_{18}Si$
Exact Mass: 286.1178
Molecular Weight: 286.4490

The general procedure B was followed using [1,1':4',1"-terphenyl]-2-yldimethylsilane **1g** (72.1 mg, 0.25 mmol, 1.0 eq.) as starting material. **2g** was obtained as yellow solid (53 mg, 74%).

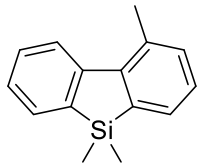
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.52 (s, 6H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.48-7.53 (m, 3H). 7.71 (d, *J* = 7.6 Hz, 4H), 7.89-7.94 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm -3.1, 121.1, 121.3, 127.2, 127.3, 127.5, 128.9, 129.3, 130.4, 131.6, 132.9, 139.2, 139.8, 140.3, 141.4, 147.1, 147.6.

HRMS (EI^+): Calculated for $C_{20}H_{18}Si$ (M^+): 286.1178, Found: 286.1181.

IR (cm^{-1}): 3045, 2957, 1594, 1464, 1433, 1388, 1246, 1130, 1064, 841, 779, 754, 692.

(2h) 1,5,5-trimethyl-5*H*-dibenzo[*b,d*]silole[1], CAS: 252259-84-9



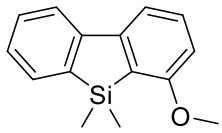
Chemical Formula: $C_{15}H_{16}Si$
Exact Mass: 224.1021
Molecular Weight: 224.3780

The general procedure B was followed using dimethyl(2'-methylbiphenyl-2-yl)silane **1h** (56.6 mg, 0.25 mmol, 1.0 eq.) as starting material. **2h** was obtained as yellow oil (35.7 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.41 (s, 6H), 2.77 (s, 3H), 7.19-7.25 (m, 2H). 7.29 (t, *J* = 6.8 Hz, 1H), 7.45 (td, *J* = 7.6, 1.6 Hz, 1H), 7.51 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.68 (dd, *J* = 6.8, 0.4 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm -3.1, 24.4, 125.8, 126.6, 127.0, 130.1, 130.5, 132.9, 134.4, 134.5, 140.5, 140.7, 146.2, 149.8.

(2i) 4-methoxy-5,5-dimethyl-5*H*-dibenzo[*b,d*]silole



Chemical Formula: $C_{15}H_{16}OSi$
Exact Mass: 240.0970
Molecular Weight: 240.3770

The general procedure B was followed using (3'-methoxybiphenyl-2-yl)dimethylsilane **1i** (60.6 mg, 0.25 mmol, 1.0 eq.) as starting material. **2i** was obtained as yellow oil (48 mg, 67%).

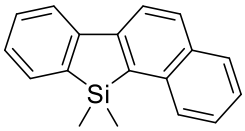
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.44 (s, 6H), 3.85 (s, 3H), 6.75 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.38-7.45 (m, 3H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm -3.6, 55.5, 109.1, 114.1, 121.3, 125.7, 127.6, 130.0, 132.5, 132.7, 140.0, 147.7, 149.7, 164.2.

HRMS (EI^+): Calculated for $C_{15}H_{16}OSi$ (M^+): 240.0970, Found: 240.0972.

IR (cm^{-1}): 3058, 2955, 1591, 1568, 1558, 1472, 1430, 1243, 1107, 842, 799, 782, 756, 724.

(2j) 11,11-dimethyl-11*H*-benzo[*b*]naphtho[2,1-*d*]silole



Chemical Formula: $C_{18}H_{16}Si$
Exact Mass: 260.1021
Molecular Weight: 260.4110

The general procedure B was followed using dimethyl(2-(naphthalen-2-yl)phenyl)silane **1j** (65.6 mg, 0.25 mmol, 1.0 eq.) as starting material. **2j** was obtained as yellow oil (33.6 mg, 52%).

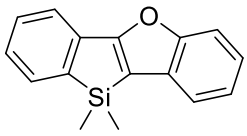
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.62 (s, 6H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.46-7.55 (m, 3H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.88-8.02 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ -2.5, 120.1, 121.4, 125.8, 127.0, 127.7, 128.8, 129.3, 130.6, 131.3, 133.0, 133.4, 137.1, 137.4, 139.5, 147.1, 148.4.

HRMS (EI^+): Calculated for $C_{18}H_{16}Si$ (M^+): 260.1021, Found: 260.1024.

IR (cm^{-1}): 3045, 2956, 2918, 2850, 1585, 1455, 1247, 1147, 1128, 993, 843, 824, 776, 760, 744, 716, 686.

(2k) 10,10-dimethyl-10*H*-benzo[4,5]silolo[3,2-*b*]benzofuran



Chemical Formula: $C_{16}H_{14}OSi$
Exact Mass: 250.0814
Molecular Weight: 250.3720

The general procedure B was followed using 2-(benzofuran-2-yl)phenyl)dimethylsilane **1k** (63.1 mg, 0.25 mmol, 1.0 eq.) as starting material. **2k** was obtained as yellow oil (36.3 mg, 58%).

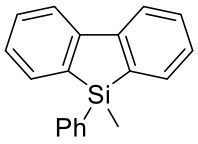
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.50 (s, 6H), 7.31-7.23 (m, 3H), 7.42 (td, *J* = 7.6, 1.1 Hz, 1H), 7.59-7.53 (m, 3H), 7.65 (d, *J* = 7.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) -3.4, 111.8, 113.3, 119.5, 122.0, 123.4, 123.9, 127.8, 130.0, 130.9, 132.7, 139.0, 142.3, 158.6, 169.5.

HRMS (EI^+): Calculated for $C_{16}H_{14}OSi$ (M^+): 250.0814, Found: 250.0818.

IR (cm^{-1}): 2955, 2922, 2849, 1733, 1455, 1257, 1123, 841, 814, 784, 746.

(2l) 5-methyl-5-phenyl-5*H*-dibenzo[*b*,*d*]silole[1], CAS: 87522-65-4



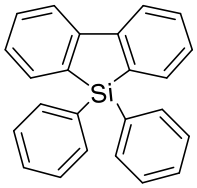
Chemical Formula: $C_{19}H_{16}Si$
Exact Mass: 272.1021
Molecular Weight: 272.4220

The general procedure B was followed using 2-(benzofuran-2-yl)phenyl)dimethylsilane **1l** (68.6 mg, 0.25 mmol, 1.0 eq.) as starting material. **2k** was obtained as yellow oil (33.4 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.73 (s, 3H), 7.22-7.34 (m, 5H), 7.44 (td, *J* = 7.6, 0.8 Hz, 2H), 7.57-7.53 (m, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) -4.9, 121.1, 127.7, 128.2, 130.0, 130.6, 133.5, 134.6, 134.8, 137.5, 148.5.

(2m) 5,5-diphenyl-5*H*-dibenzo[*b*,*d*]silole[2], CAS: 5550-08-3



Chemical Formula: $C_{24}H_{18}Si$
Exact Mass: 334.1178
Molecular Weight: 334.4930

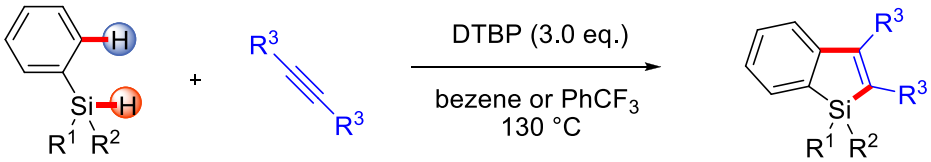
The general procedure B was followed using [1,1'-biphenyl]-2-yldiphenylsilane **1m** (101.0 mg, 0.3 mmol, 1.0 eq.) as starting material. **2m** was obtained as yellow solid (66.8 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.30-7.42 (m, 8H), 7.48 (td, *J* = 7.6, 1.2 Hz, 2H), 7.65 (dd, *J* = 8.0, 1.6 Hz, 4H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 121.3, 127.9, 128.3, 130.2, 130.9, 132.8, 134.1, 135.7, 136.0, 148.9.

3. Intermolecular silyl radical cascades with alkynes

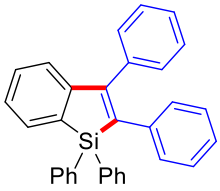
A. General procedure C for synthesis of silafluorenes:



In a dried Schlenk flask (25 mL in volume) equipped with a stirring bar were placed with alkynes (0.30 mmol, 1.5 eq, if solid) and arylhydrosilanes (0.20 mmol, 1.0 eq, if solid). After evacuation and refill with dry N_2 for three times, alkynes (0.30 mmol, 1.5 eq, if liquid) and arylhydrosilanes (0.20 mmol, 1.0 eq, if liquid), DTBP (110.8 uL, 0.60 mmol, 3.0 eq.) and $PhCF_3$ or bezene (0.8 mL) were added with syringes under a stream of N_2. The resulting mixture was allowed to stir at 130 ℃ for 24 h. After cooling to room temperature, the reaction mixture was concentrated and then purified by column chromatography on silica gel or PTLC (hexane as the eluting solvent) to give the target products.

B. Spectra data of silaindenes:

(5a) 1,1,2,3-tetraphenyl-1*H*-benzo[*b*]silole



Chemical Formula: $C_{32}H_{24}Si$
Exact Mass: 436.1647
Molecular Weight: 436.6290

The general procedure C was followed using triphenylsilane (52.1 mg, 0.20 mmol, 1.0 eq.) and 1,2-diphenylethyne (53.4 mg, 0.30 mmol, 1.5 eq.) as starting material, $PhCF_3$ as solvent. **5a** was obtained as a white-yellow solid (58.5 mg, 67%).

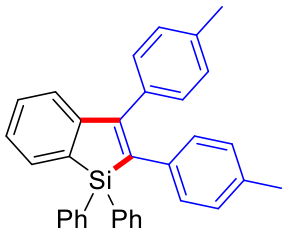
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.92-6.94 (m, 2H), 7.00-7.06 (m, 3H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.16-7.36 (m, 12H), 7.43 (t, *J* = 7.6, 2H), 7.63 (d, *J* = 7.2 Hz, 3H), 7.71 (d, *J* = 6.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 124.6, 126.0, 127.4, 127.4, 128.0, 128.3, 128.6, 129.3, 129.9, 130.3, 130.4, 132.5, 133.1, 135.7, 135.9, 138.1, 139.8, 140.1, 151.7, 155.8.

HRMS (EI$^+$): Calculated for $C_{32}H_{24}Si$ (M^+): 436.1647, Found: 436.1650.

IR (cm^{-1}): 3050, 2923, 1584, 1483, 1439, 1428, 1111, 762, 739, 695, 669.

(5b) 1,1-diphenyl-2,3-di-p-tolyl-1*H*-benzo[*b*]silole



Chemical Formula: $C_{34}H_{28}Si$
Exact Mass: 464.1960
Molecular Weight: 464.6830

The general procedure C was followed using triphenylsilane (52.1 mg, 0.20 mmol, 1.0 eq.) and 1,2-di-p-tolylethyne (61.9 mg, 0.30 mmol, 1.5 eq.) as starting material, PhH as solvent. **5b** was obtained as white solid (65.7 mg, 71%).

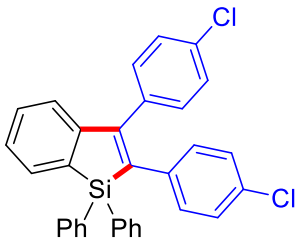
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.20 (s, 3H), 2.38 (s, 3H), 6.75-6.92 (m, 4H), 7.10-7.19 (m, 5H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.28-7.43 (m, 8H), 7.63 (dd, *J* = 6.8, 1.2 Hz, 3H), 7.68 (d, *J* = 6.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 21.2, 21.5, 124.5, 127.1, 128.3, 128.8, .129.3, 129.4, 129.7, 130.2, 130.3, 132.8, 133.0, 135.3, 135.5, 135.7, 135.9, 136.8, 136.9, 139.4, 152.1, 155.4.

HRMS (EI$^+$): Calculated for $C_{34}H_{28}Si$ (M^+): 464.1960, Found: 464.1965.

IR (cm^{-1}): 3062, 2920, 1583, 1511, 1428, 1111, 837, 818, 773, 739, 726, 697.

(5c) 2,3-bis(4-chlorophenyl)-1,1-diphenyl-1*H*-benzo[*b*]silole



Chemical Formula: $C_{32}H_{22}Cl_2Si$
Exact Mass: 504.0868
Molecular Weight: 505.5130

The general procedure C was followed using triphenylsilane (52.1 mg, 0.20 mmol, 1.0 eq.) and 1,2-bis(4-chlorophenyl)ethyne (74.1 mg, 0.30 mmol, 1.5 eq.) as starting material, $PhCF_3$ as solvent. **5c** was obtained as white solid (71.4 mg, 71%).

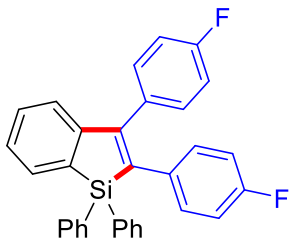
^{1}H NMR (100 MHz, $CDCl_3$): δ ppm 6.83-6.85 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.35-7.40 (m, 7H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.61 (dd, *J* = 8.0, 1.2 Hz, 4H), 7.74 (d, *J* = 6.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 124.5, 127.7, 128.4, 128.4, 129.0, 130.4, 130.5, 130.6, 131.2, 131.8, 131.9, 133.4, 133.5, 135.4, 135.8, 136.0, 138.1, 139.8, 150.9, 155.0.

HRMS (EI$^+$): Calculated for $C_{32}H_{22}Cl_2Si$ (M^+): 504.0868, Found: 504.0864.

IR (cm^{-1}): 3066, 2924, 1588, 1559, 1467, 1112, 773, 746, 695.

(5d) 2,3-bis(4-fluorophenyl)-1,1-diphenyl-1*H*-benzo[*b*]silole



Chemical Formula: $C_{32}H_{22}F_2Si$
Exact Mass: 472.1459
Molecular Weight: 472.6098

The general procedure C was followed using triphenylsilane (52.1 mg, 0.20 mmol, 1.0 eq.) and 1,2-bis(4-fluorophenyl)ethyne (64.3 mg, 0.30 mmol, 1.5 eq.) as starting material, PhH as solvent. **5d** was obtained as white-yellow solid (76.4 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.75 (t, *J* = 8.4 Hz, 2H), 6.84-6.88 (m, 2H), 7.07 (t, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.21 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.34-7.38 (m, 5H), 7.43-7.49 (m, 2H), 7.60 (d, *J* = 6.8 Hz, 4H), 7.72 (d, *J* = 6.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 115.2 (d, *J* = 21 Hz), 115.7 (d, *J* = 21 Hz), 124.4, 127.6, 128.4, 130.5, 130.5, 130.7 (d, *J* = 8 Hz), 131.6 (d, *J* = 8 Hz), 132.1, 133.3, 133.6 (d, *J* = 4 Hz), 135.4, 135.7 (d, *J* = 4 Hz), 135.8, 139.7, 151.3, 154.8, 161.3 (d, *J* = 245

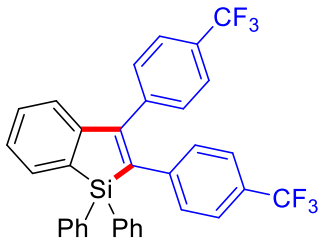
Hz), 162.2 (d, J = 245 Hz).

^{19}F NMR (377 MHz, CDCl3): δ ppm -116.19, -114.34.

HRMS (EI$^+$): Calculated for $C_{32}H_{22}F_2Si$ (M^+): 472.1459, Found: 472.1461.

IR (cm^{-1}): 3049, 2927, 1601, 1507, 1496, 1223, 1112, 835, 818, 741, 729.

(5e) 1,1-diphenyl-2,3-bis(4-(trifluoromethyl)phenyl)-1*H*-benzo[*b*]silole



Chemical Formula: $C_{34}H_{22}F_6S$
Exact Mass: 572.1395
Molecular Weight: 572.6254

The general procedure C was followed using triphenylsilane (52.1 mg, 0.20 mmol, 1.0 eq.) and 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (94.3 mg, 0.30 mmol, 1.5 eq.) as starting material, $PhCF_3$ as solvent. **5e** was obtained as a colorless liquid (71.0 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.98 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.2 Hz, 1H), 7.16-7.23 (m, 1H), 7.30-7.48 (m, 12H), 7.60-7.65 (m, 5H), 7.77 (dd, J = 6.4, 1.2 Hz, 1H).

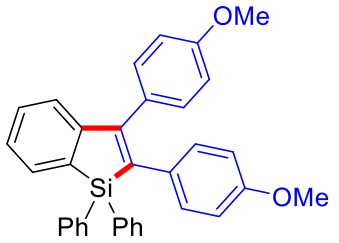
^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 124.6, 125.1 (q, J = 3 Hz), 125.6 (q, J = 3 Hz), 126.8 (q, J = 271 Hz), 126.9 (q, J = 271 Hz), 127.8, 128.0, 128.4, 128.7 (q, J = 28 Hz), 129.0, 130.0, 130.6, 130.6, 131.3, 133.4, 135.3, 135.7, 136.2, 140.4, 141.2, 143.2, 150.4, 155.5.

^{19}F NMR (377 MHz, CDCl3): δ ppm -62.48, -62.45.

HRMS (EI$^+$): Calculated for $C_{34}H_{22}F_6Si$ (M^+): 572.1395, Found: 572.1398.

IR (cm^{-1}): 3052, 1614, 1429, 1320, 1164, 1106, 852, 742, 709, 696.

(5f) 2,3-bis(4-methoxyphenyl)-1,1-diphenyl-1*H*-benzo[*b*]silole



Chemical Formula: $C_{34}H_{28}O_2Si$
Exact Mass: 496.1859
Molecular Weight: 496.6810

The general procedure C was followed using triphenylsilane (52.1 mg, 0.20 mmol, 1.0 eq.) and 1,2-bis(4-methoxyphenyl)ethyne (71.5 mg, 0.30 mmol, 1.5 eq.) as starting material, PhH as solvent. **5f** was obtained as white solid (55.6 mg, 56%).

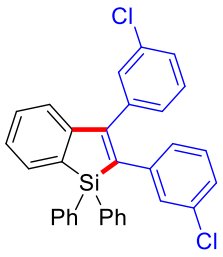
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 3.69 (s, 3H), 3.84 (s, 3H), 6.58 (d, J = 8.8 Hz, 2H), 6.90 (t, J = 8.8 Hz, 4H), 7.13 (d, J = 7.6 Hz, 1H), 7.17-7.23 (m, 3H), 7.29-7.36 (m, 5H), 7.42 (t, J = 7.2 Hz, 2H), 7.63 (d, J = 7.2 Hz, 4H), 7.67 (d, J = 6.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 55.2, 55.4, 113.5, 114.2, 124.3, 127.0, 128.3, 130.2, 130.3, 130.6, 130.7, 131.1, 132.3, 132.8, 133.0, 135.6, 135.9, 138.9, 152.2, 154.2, 157.8, 158.9.

HRMS (EI$^+$): Calculated for $C_{34}H_{28}O_2Si$ (M^+): 496.1859, Found: 496.1864.

IR (cm^{-1}): 3011, 2957, 1606, 1497, 1244, 1116, 1100, 833, 746, 725, 698.

(5g) 2,3-bis(3-chlorophenyl)-1,1-diphenyl-1*H*-benzo[*b*]silole



Chemical Formula: $C_{32}H_{22}Cl_2Si$
Exact Mass: 504.0868
Molecular Weight: 505.5130

The general procedure C was followed using triphenylsilane (52.1 mg, 0.20 mmol, 1.0 eq.) and 1,2-bis(3-chlorophenyl)ethyne (74.1 mg, 0.30 mmol, 1.5 eq.) as starting material, PhH as solvent. **5g** was obtained as white solid (67.7 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.78 (d, J = 7.2 Hz, 1H), 6.86 (s, 1H), 6.95-7.02 (m, 2H), 7.09-7.12 (m, 2H), 7.25 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 6.8 Hz, 3H), 7.36 (t, J = 7.6 Hz, 5H), 7.45 (t, J = 7.2 Hz, 2H), 7.60 (d, J = 6.8 Hz, 4H), 7.72 (d, J = 6.8 Hz, 1H).

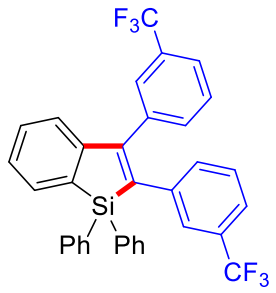
^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 124.7, 126.4, 127.3, 127.9, 128.1, 128.5, 128.9, 129.4, 129.6, 130.0, 130.6, 130.6, 131.6, 133.4, 133.9, 134.6, 135.4, 135.8,

136.3, 139.4, 140.0, 141.4, 150.7, 155.2.

HRMS (EI$^+$): Calculated for $C_{32}H_{22}Cl_2Si$ (M^+): 504.0868, Found: 504.0874.

IR (cm^{-1}): 3067, 2922, 2851, 1468, 1112, 1100, 780, 738, 725, 696.

(5h) 1,1-diphenyl-2,3-bis(3-(trifluoromethyl)phenyl)-1*H*-benzo[*b*]silole



Chemical Formula: $C_{34}H_{22}F_6Si$
Exact Mass: 572.1395
Molecular Weight: 572.6254

The general procedure C was followed using triphenylsilane (52.1 mg, 0.20 mmol, 1.0 eq.) and 1,2-bis(3-(trifluoromethyl)phenyl)ethyne (94.3 mg, 0.30 mmol, 1.5 eq.) as starting material, PhH as solvent. **5h** was obtained as white solid (97.3 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.04-7.22 (m, 4H), 7.23-7.41 (m, 8H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 6.4 Hz, 2H), 7.60 (t, *J* = 8.2 Hz, 5H), 7.76 (d, *J* = 6.8 Hz, 1H).

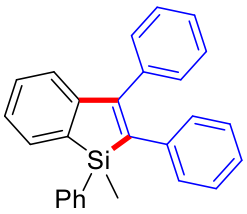
^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 122.9 (q, *J* = 4 Hz), 124.6, 124.6 (q, *J* = 4 Hz), 125.8 (q, *J* = 4 Hz), 126.6 (q, *J* = 4 Hz), 126.7 (q, *J* = 272 Hz), 126.8 (q, *J* = 272 Hz), 127.9, 128.1, 128.6, 128.7, 129.3, 129.7, 130.3 (q, *J* = 32 Hz), 130.7, 130.8, 131.4, 132.2, 133.1, 133.6, 135.3, 135.8, 136.2, 138.2, 140.2, 140.6, 150.5, 155.5.

^{19}F NMR (377 MHz, CDCl3): δ ppm -62.78, -63.15.

HRMS (EI$^+$): Calculated for $C_{34}H_{22}F_6Si$ (M^+): 572.1395, Found: 572.1399.

IR (cm^{-1}): 3048, 2997, 2954, 1497, 1177, 1110, 833, 737, 699.

(5i) 1-methyl-1,2,3-triphenyl-1*H*-benzo[*b*]silole,[3] CAS: 1309154-21-9



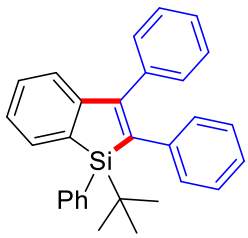
Chemical Formula: $C_{27}H_{22}$
Exact Mass: 374.1491

The general procedure C was followed using methyldiphenylsilane (39.7 mg, 0.20 mmol, 1.0 eq.) and 1,2-diphenylethyne (53.5 mg, 0.30 mmol, 1.5 eq.) as starting material, PhH as solvent. **5i** was obtained as white solid (44.9 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.76 (s, 3H), 6.91 (d, *J* = 6.8 Hz, 2H), 6.97-7.00 (m, 3H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.21-7.30 (m, 10H), 7.58 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm -5.6, 124.3, 125.9, 127.1, 127.3, 128.0, 128.3, 128.6, 129.0, 129.8, 130.0, 130.2, 132.4, 134.3, 134.7, 136.9, 138.2, 139.7, 141.5, 151.5, 154.7.

(5j) 1-(*tert*-butyl)-1,2,3-triphenyl-1*H*-benzo[*b*]silole



Chemical Formula: $C_{30}H_{28}Si$
Exact Mass: 416.1960
Molecular Weight: 416.6390

The general procedure C was followed using *tert*-butyldiphenylsilane (48.1 mg, 0.20 mmol, 1.0 eq.) and 1,2-diphenylethyne (53.5 mg, 0.30 mmol, 1.5 eq.) as starting material, PhH as solvent. **5j** was obtained as white solid (18.3 mg, 22%).

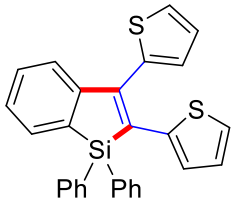
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 1.07 (s, 9H), 6.93-6.95 (m, 2H), 6.99-7.10 (m, 4H), 6.21-7.41 (m, 10H), 7.73 (td, *J* = 6.4, 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 18.8, 27.3, 124.5, 125.6, 126.9, 127.1, 127.9, 128.1, 129.1, 129.8, 129.9, 130.0, 132.8, 133.3, 135.7, 135.9, 138.0, 141.2, 141.4, 151.7, 155.9.

HRMS (EI$^+$): Calculated for $C_{30}H_{28}Si$ (M^+): 416.1960, Found: 416.1964.

IR (cm^{-1}): 3066, 2925, 2855, 1598, 1437, 1109, 820, 741, 698, 679.

(5k) 1,1-diphenyl-2,3-di(thiophen-2-yl)-1*H*-benzo[*b*]silole



Chemical Formula: $C_{28}H_{20}S_2Si$
Exact Mass: 448.0776
Molecular Weight: 448.6730

The general procedure C was followed using triphenylsilane (52.1 mg, 0.20 mmol, 1.0 eq.) and 1,2-di(thiophen-2-yl)ethyne (57.1 mg, 0.30 mmol, 1.5 eq.) as starting material. **5k** was obtained as yellow solid (14.4 mg, 16%).

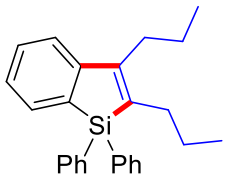
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 6.80 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.98 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.05-7.07 (m, 2H), 7.12 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.21-7.26 (m, 2H), 7.31-7.47 (m, 7H), 7.59 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.64 (d, *J* = 6.8 Hz, 1H), 7.72 (dd, *J* = 8.0, 1.6 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 124.3, 126.3, 127.4, 127.5, 127.6, 128.2, 128.4, 128.5, 129.9, 130.5, 130.8, 131.9, 132.7, 134.2, 136.1, 136.6, 137.7, 142.1, 145.0, 152.3.

HRMS (EI$^+$): Calculated for $C_{28}H_{20}S_2Si$ (M^+): 448.0776, Found: 448.0774.

IR (cm^{-1}): 3066, 2920, 2850, 1583, 1427, 1262, 1109, 848, 820, 773, 733, 694.

(5l) 1,1-diphenyl-2,3-dipropyl-1*H*-benzo[*b*]silole



Chemical Formula: $C_{26}H_{28}Si$
Exact Mass: 368.1960
Molecular Weight: 368.5950

The general procedure C was followed using triphenylsilane (52.1 mg, 0.20 mmol, 1.0 eq.) and oct-4-yne (33.1 mg, 0.30 mmol, 1.5 eq.) as starting material. **5l** was obtained as white solid (22.9 mg, 31%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.79 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H), 1.34 (qt, *J* = 8.0 Hz, 2H), 1.62 (qt, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 8.0 Hz, 2H), 2.63 (t, *J* = 8.0 Hz, 2H), 7.15-7.19 (m, 1H), 7.33-7.43 (m, 8H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.2 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 13.6, 13.7, 21.3, 23.0, 28.5, 31.6, 120.6, 125.3, 127.1, 128.9, 129.2, 131.8, 132.4, 134.7, 135.0, 138.4, 150.4, 153.6.

HRMS (EI$^+$): Calculated for $C_{26}H_{28}Si$ (M^+): 368.1960, Found: 368.1956.

(1) T. Ureshino, T. Yoshida, Y. Kuninobu and K. Takai, *J. Am. Chem. Soc.*, 2010, **132**, 14324.

(2) Y. Yabusaki, N. Ohshima, H. Kondo, T. Kusamoto, Y. Yamanoi and H. Nishihara, *Chem.—Eur. J.*, 2010, **16**, 5581.

(3) M. Onoe, K. Baba, Y. Kim, Y. Kita, M. Tobisu and N. Chatani, *J. Am. Chem. Soc.*, 2012, **134**, 19477.

4. X-ray diffraction data of 5c. (CCDC 1037609)

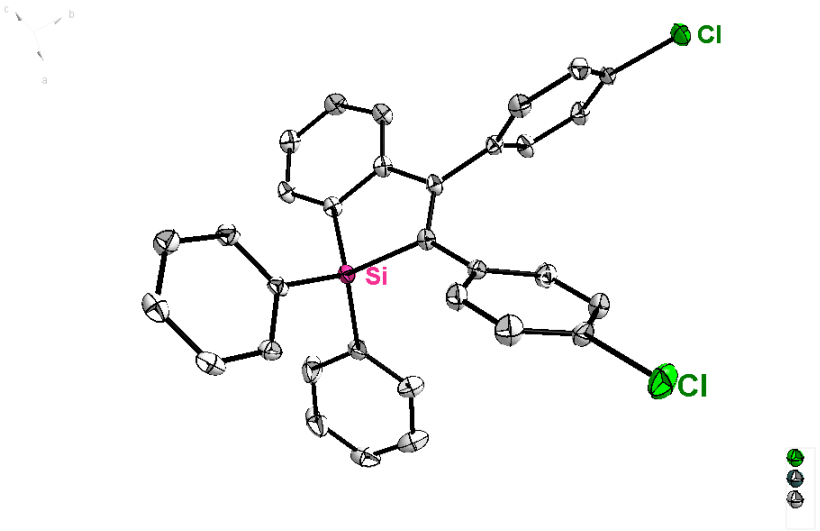


Table S5. Crystal data and structure refinement for **5c**.

Identification code	2
Empirical formula	C_{32} H_{22} Cl_2 Si
Formula weight	505.49
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.9590(11) Å alpha = 90 deg.
	b = 24.396(3) Å beta = 108.6020(10) deg.
	c = 11.0384(12) Å gamma = 90 deg.
Volume	2541.8(5) Å^3
Z, Calculated density	4, 1.321 Mg/m^3
Absorption coefficient	0.322 mm^-1
F(000)	1048
Crystal size	? x ? x ? mm
Theta range for data collection	1.67 to 27.64 deg.
Limiting indices	-12<=h<=12, -31<=k<=31, -14<=l<=14
Reflections collected / unique	41982 / 5888 [R(int) = 0.0356]
Completeness to theta = 27.64	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5888 / 0 / 316
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.0883
R indices (all data)	R1 = 0.0494, wR2 = 0.0941
Largest diff. peak and hole	0.409 and -0.334 e.A^-3

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	3857(1)	4568(1)	1183(1)	26(1)
Cl(2)	11981(1)	3363(1)	3459(1)	36(1)
Si(1)	6652(1)	1237(1)	2765(1)	16(1)
C(1)	4271(2)	3882(1)	1579(2)	19(1)
C(2)	5083(2)	3742(1)	2810(2)	22(1)
C(3)	5438(2)	3193(1)	3082(2)	21(1)
C(4)	4990(2)	2793(1)	2141(2)	18(1)
C(5)	4160(2)	2948(1)	914(2)	22(1)
C(6)	3797(2)	3493(1)	625(2)	23(1)
C(7)	5392(2)	2205(1)	2393(1)	18(1)
C(8)	4255(2)	1797(1)	2328(1)	18(1)
C(9)	2850(2)	1934(1)	2179(2)	21(1)
C(10)	1881(2)	1521(1)	2156(2)	25(1)
C(11)	2299(2)	978(1)	2294(2)	24(1)
C(12)	3707(2)	837(1)	2468(2)	21(1)
C(13)	4701(2)	1244(1)	2484(1)	17(1)
C(14)	7671(2)	925(1)	4336(1)	17(1)
C(15)	7030(2)	821(1)	5271(2)	21(1)
C(16)	7778(2)	589(1)	6439(2)	25(1)
C(17)	9205(2)	465(1)	6713(2)	25(1)
C(18)	9874(2)	567(1)	5806(2)	24(1)
C(19)	9114(2)	789(1)	4628(2)	21(1)
C(20)	7240(2)	897(1)	1499(2)	21(1)
C(21)	8064(2)	1160(1)	860(2)	25(1)
C(22)	8588(2)	875(1)	8(2)	32(1)
C(23)	8276(2)	326(1)	-224(2)	33(1)
C(24)	7440(3)	59(1)	373(2)	41(1)
C(25)	6925(3)	341(1)	1226(2)	37(1)
C(26)	6727(2)	2005(1)	2669(1)	17(1)
C(27)	8008(2)	2343(1)	2817(2)	17(1)
C(28)	8064(2)	2761(1)	1962(2)	22(1)
C(29)	9283(2)	3073(1)	2154(2)	23(1)
C(30)	10454(2)	2971(1)	3209(2)	23(1)
C(31)	10440(2)	2558(1)	4064(2)	27(1)
C(32)	9223(2)	2246(1)	3855(2)	23(1)

Table S7. Bond lengths [Å] and angles [deg] for b.

Cl(1)-C(1)	1.7446(16)
Cl(2)-C(30)	1.7435(16)
Si(1)-C(13)	1.8671(16)
Si(1)-C(14)	1.8692(16)
Si(1)-C(20)	1.8721(16)
Si(1)-C(26)	1.8799(16)
C(1)-C(2)	1.385(2)
C(1)-C(6)	1.385(2)
C(2)-C(3)	1.393(2)
C(3)-C(4)	1.391(2)
C(4)-C(5)	1.396(2)
C(4)-C(7)	1.491(2)
C(5)-C(6)	1.387(2)
C(7)-C(26)	1.357(2)
C(7)-C(8)	1.492(2)
C(8)-C(9)	1.397(2)
C(8)-C(13)	1.414(2)
C(9)-C(10)	1.389(2)
C(10)-C(11)	1.383(2)
C(11)-C(12)	1.397(2)
C(12)-C(13)	1.397(2)
C(14)-C(15)	1.399(2)
C(14)-C(19)	1.408(2)
C(15)-C(16)	1.387(2)
C(16)-C(17)	1.389(2)
C(17)-C(18)	1.389(2)
C(18)-C(19)	1.390(2)
C(20)-C(21)	1.397(2)
C(20)-C(25)	1.402(2)
C(21)-C(22)	1.398(2)
C(22)-C(23)	1.380(3)
C(23)-C(24)	1.379(3)
C(24)-C(25)	1.390(3)
C(26)-C(27)	1.484(2)
C(27)-C(32)	1.396(2)
C(27)-C(28)	1.401(2)
C(28)-C(29)	1.391(2)
C(29)-C(30)	1.382(2)
C(30)-C(31)	1.384(2)
C(31)-C(32)	1.387(2)
C(13)-Si(1)-C(14)	112.70(7)
C(13)-Si(1)-C(20)	115.91(7)
C(14)-Si(1)-C(20)	107.82(7)

C(13)-Si(1)-C(26)	92.26(7)
C(14)-Si(1)-C(26)	115.97(7)
C(20)-Si(1)-C(26)	111.84(7)
C(2)-C(1)-C(6)	121.77(15)
C(2)-C(1)-Cl(1)	120.09(13)
C(6)-C(1)-Cl(1)	118.12(13)
C(1)-C(2)-C(3)	118.60(15)
C(4)-C(3)-C(2)	120.99(15)
C(3)-C(4)-C(5)	118.91(15)
C(3)-C(4)-C(7)	122.18(14)
C(5)-C(4)-C(7)	118.89(14)
C(6)-C(5)-C(4)	120.91(15)
C(1)-C(6)-C(5)	118.80(15)
C(26)-C(7)-C(4)	125.01(14)
C(26)-C(7)-C(8)	116.42(14)
C(4)-C(7)-C(8)	118.57(13)
C(9)-C(8)-C(13)	120.46(14)
C(9)-C(8)-C(7)	124.23(14)
C(13)-C(8)-C(7)	115.26(13)
C(10)-C(9)-C(8)	119.54(15)
C(11)-C(10)-C(9)	120.65(15)
C(10)-C(11)-C(12)	120.25(15)
C(11)-C(12)-C(13)	120.29(15)
C(12)-C(13)-C(8)	118.78(14)
C(12)-C(13)-Si(1)	133.74(12)
C(8)-C(13)-Si(1)	107.39(11)
C(15)-C(14)-C(19)	117.43(14)
C(15)-C(14)-Si(1)	121.21(12)
C(19)-C(14)-Si(1)	121.36(12)
C(16)-C(15)-C(14)	121.57(15)
C(15)-C(16)-C(17)	120.00(16)
C(16)-C(17)-C(18)	119.81(16)
C(17)-C(18)-C(19)	120.00(15)
C(18)-C(19)-C(14)	121.17(15)
C(21)-C(20)-C(25)	117.57(16)
C(21)-C(20)-Si(1)	123.17(13)
C(25)-C(20)-Si(1)	119.13(13)
C(20)-C(21)-C(22)	121.06(17)
C(23)-C(22)-C(21)	119.88(18)
C(24)-C(23)-C(22)	120.24(17)
C(23)-C(24)-C(25)	119.90(19)
C(24)-C(25)-C(20)	121.31(19)
C(7)-C(26)-C(27)	124.78(14)
C(7)-C(26)-Si(1)	108.53(11)
C(27)-C(26)-Si(1)	126.65(11)
C(32)-C(27)-C(28)	117.75(14)

C(32)-C(27)-C(26)	119.01(14)
C(28)-C(27)-C(26)	123.24(14)
C(29)-C(28)-C(27)	121.08(15)
C(30)-C(29)-C(28)	119.36(15)
C(29)-C(30)-C(31)	121.10(15)
C(29)-C(30)-Cl(2)	119.57(13)
C(31)-C(30)-Cl(2)	119.33(13)
C(30)-C(31)-C(32)	118.97(15)
C(31)-C(32)-C(27)	121.72(15)

Symmetry transformations used to generate equivalent atoms:

Table S8. Anisotropic displacement parameters ($Å^2$ x 10^3) for b. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$

	U11	U22	U33	U23	U13	U12
Cl(1)	26(1)	14(1)	42(1)	4(1)	15(1)	3(1)
Cl(2)	22(1)	32(1)	52(1)	3(1)	12(1)	-11(1)
Si(1)	17(1)	14(1)	18(1)	0(1)	6(1)	0(1)
C(1)	17(1)	12(1)	33(1)	3(1)	12(1)	2(1)
C(2)	20(1)	19(1)	28(1)	-5(1)	9(1)	-3(1)
C(3)	18(1)	21(1)	22(1)	1(1)	4(1)	-1(1)
C(4)	13(1)	15(1)	25(1)	1(1)	6(1)	-2(1)
C(5)	20(1)	19(1)	23(1)	-1(1)	2(1)	-2(1)
C(6)	21(1)	19(1)	25(1)	4(1)	4(1)	0(1)
C(7)	18(1)	16(1)	18(1)	0(1)	4(1)	-1(1)
C(8)	18(1)	17(1)	17(1)	-1(1)	3(1)	-2(1)
C(9)	18(1)	19(1)	23(1)	-1(1)	2(1)	0(1)
C(10)	16(1)	28(1)	28(1)	-1(1)	3(1)	-2(1)
C(11)	21(1)	22(1)	28(1)	-3(1)	5(1)	-8(1)
C(12)	23(1)	15(1)	24(1)	-2(1)	5(1)	-3(1)
C(13)	18(1)	17(1)	17(1)	-1(1)	3(1)	-1(1)
C(14)	18(1)	11(1)	20(1)	-2(1)	6(1)	0(1)
C(15)	18(1)	21(1)	23(1)	0(1)	7(1)	0(1)
C(16)	25(1)	30(1)	22(1)	3(1)	8(1)	-1(1)
C(17)	27(1)	21(1)	23(1)	3(1)	3(1)	4(1)
C(18)	20(1)	19(1)	31(1)	-2(1)	6(1)	6(1)
C(19)	22(1)	19(1)	25(1)	-2(1)	12(1)	3(1)
C(20)	24(1)	22(1)	17(1)	1(1)	6(1)	5(1)
C(21)	19(1)	33(1)	22(1)	-5(1)	5(1)	-3(1)
C(22)	21(1)	54(1)	23(1)	-7(1)	9(1)	-3(1)
C(23)	35(1)	44(1)	18(1)	-3(1)	7(1)	17(1)
C(24)	75(2)	23(1)	28(1)	0(1)	22(1)	12(1)
C(25)	68(1)	22(1)	32(1)	0(1)	30(1)	0(1)

C(26)	18(1)	15(1)	18(1)	1(1)	5(1)	-1(1)
C(27)	17(1)	15(1)	21(1)	-1(1)	8(1)	1(1)
C(28)	21(1)	22(1)	24(1)	4(1)	6(1)	-1(1)
C(29)	26(1)	19(1)	28(1)	3(1)	13(1)	-3(1)
C(30)	17(1)	21(1)	32(1)	-3(1)	11(1)	-5(1)
C(31)	18(1)	28(1)	30(1)	4(1)	1(1)	-3(1)
C(32)	21(1)	21(1)	25(1)	7(1)	5(1)	-1(1)

Table S9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for b.

	x	y	z	U(eq)
H(2)	5391	4013	3456	26
H(3)	5995	3090	3922	25
H(5)	3840	2677	267	26
H(6)	3233	3597	-213	27
H(9)	2559	2307	2095	25
H(10)	922	1613	2043	30
H(11)	1625	699	2271	29
H(12)	3990	464	2575	26
H(15)	6060	911	5102	25
H(16)	7314	515	7051	31
H(17)	9723	312	7517	30
H(18)	10851	484	5992	29
H(19)	9575	850	4008	25
H(21)	8271	1539	1006	30
H(22)	9157	1058	-410	39
H(23)	8639	131	-797	39
H(24)	7216	-318	202	49
H(25)	6349	154	1632	45
H(28)	7257	2831	1240	27
H(29)	9311	3354	1566	28
H(31)	11251	2490	4784	33
H(32)	9216	1958	4432	27

5. Optical Property Characterization

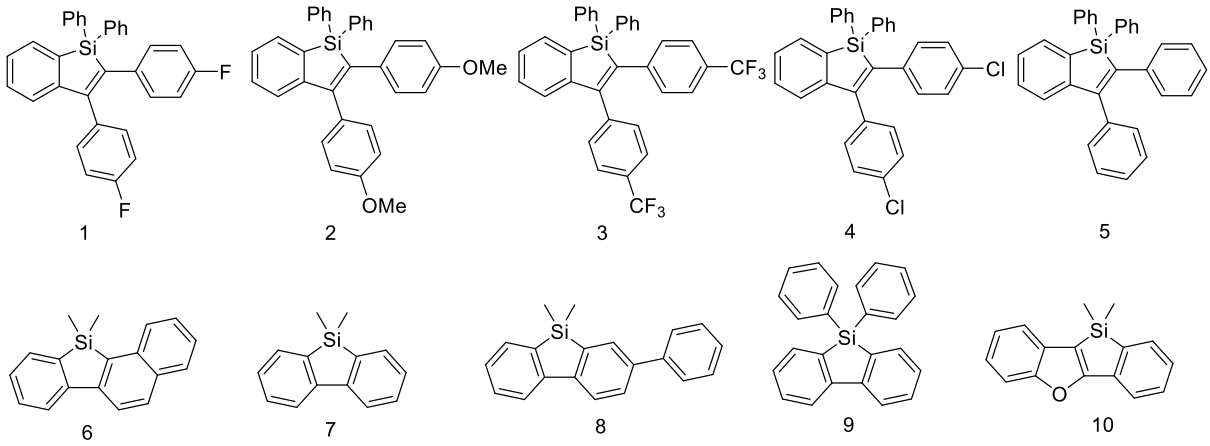


Figure 1. UV absorption of compounds 1-5 in CH_2Cl_2.

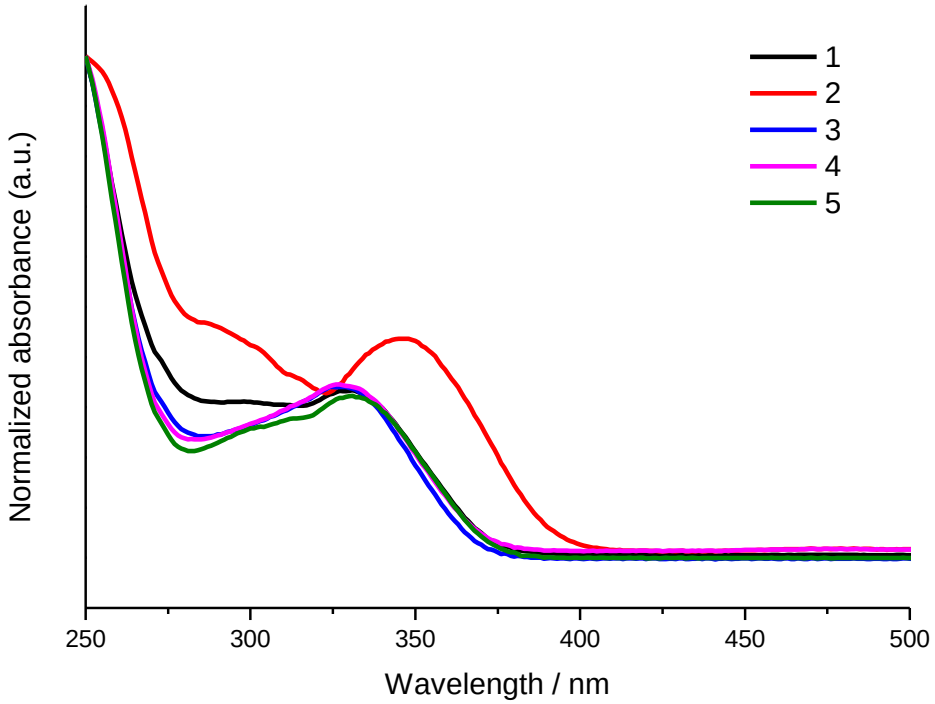


Figure 2. UV absorption of compounds 6-10 in CH_2Cl_2.

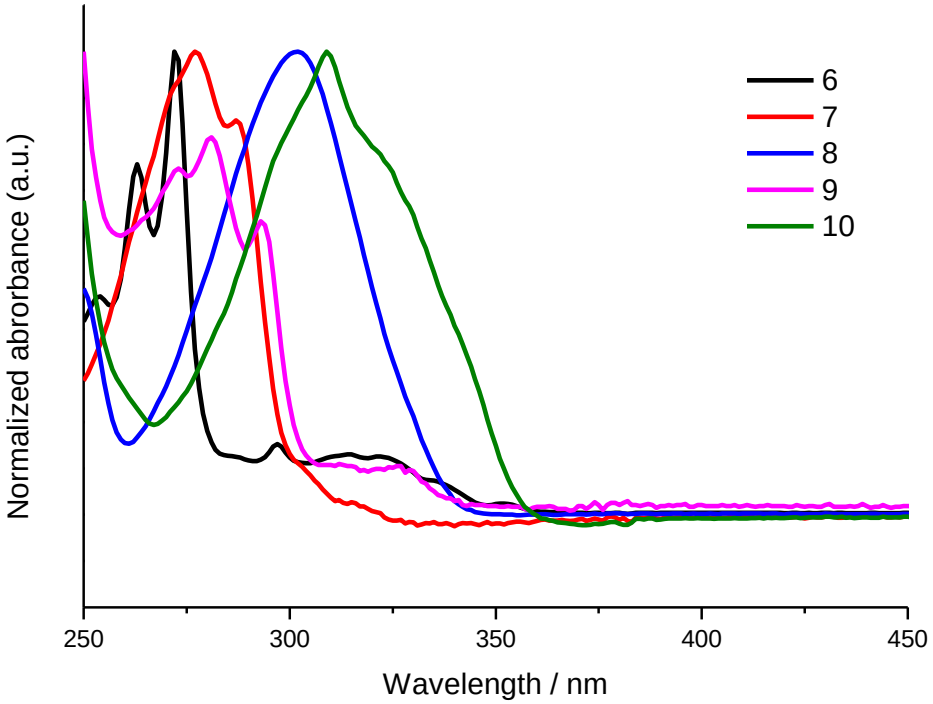


Figure 3. Fluorescence emission of compounds 1-5 in CH_2Cl_2 with excitation wavelength 250 nm.

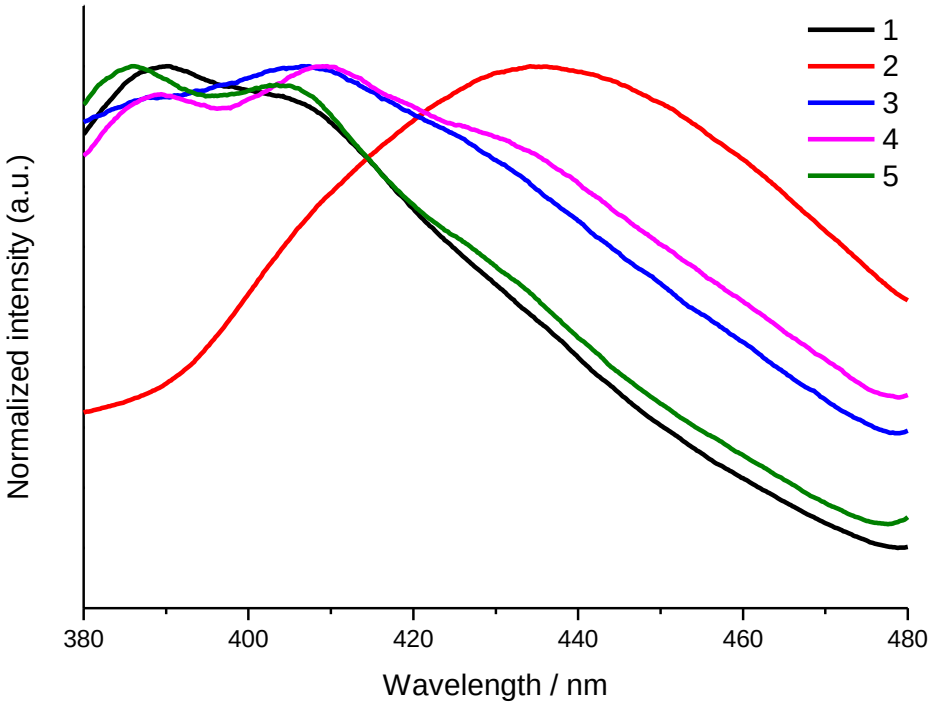


Figure 4. Fluorescence emission of compounds 6-10 in CH_2Cl_2 with excitation wavelength 250 nm.

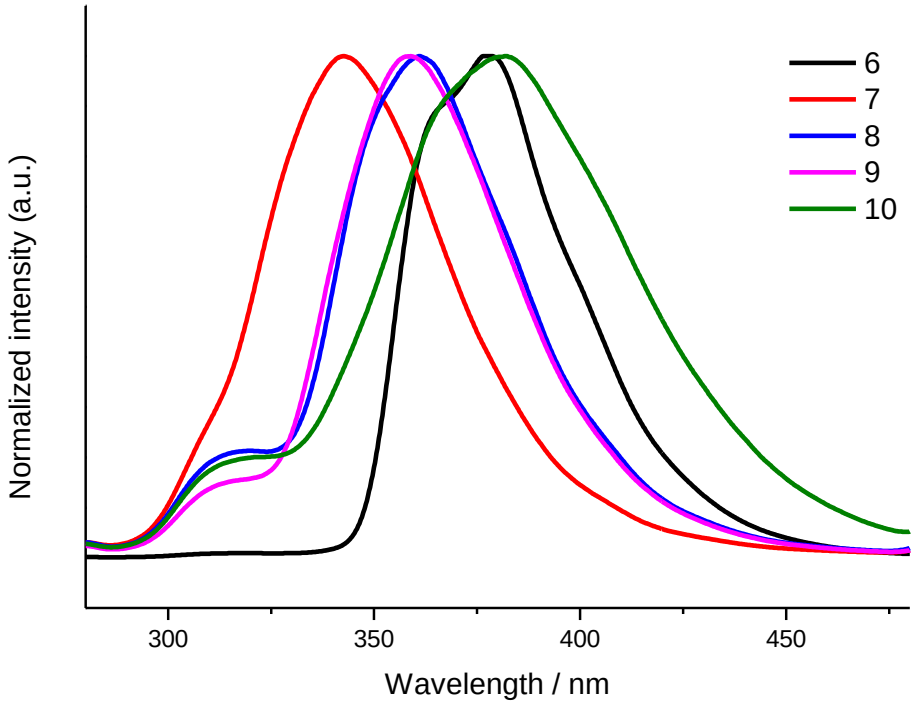


Figure 5. Fluorescence emission of compounds 1-5 in CH_2Cl_2 with excitation wavelength 320 nm.

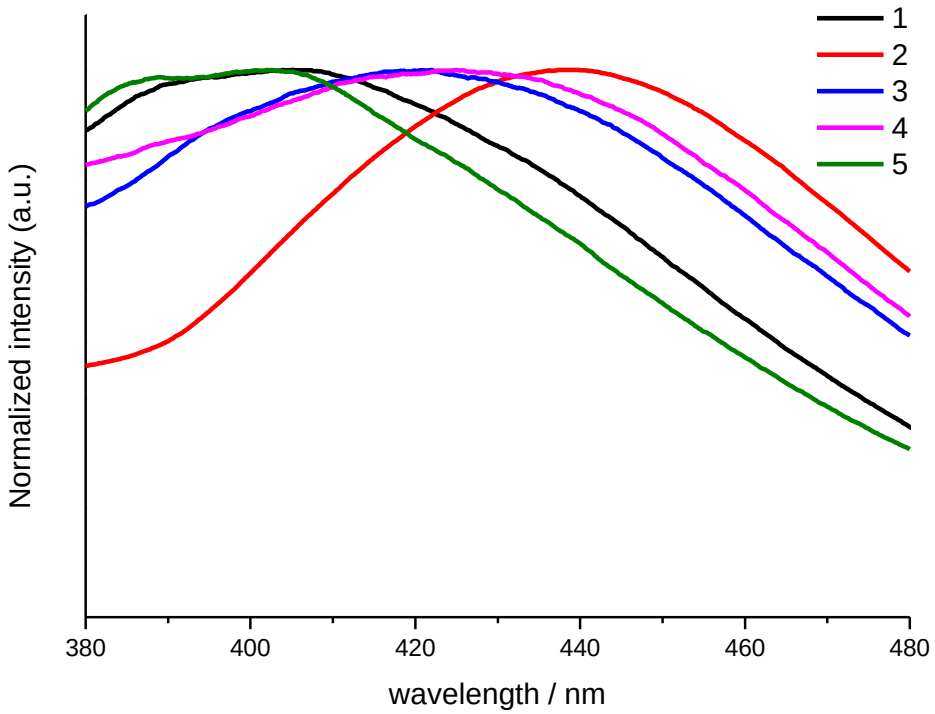
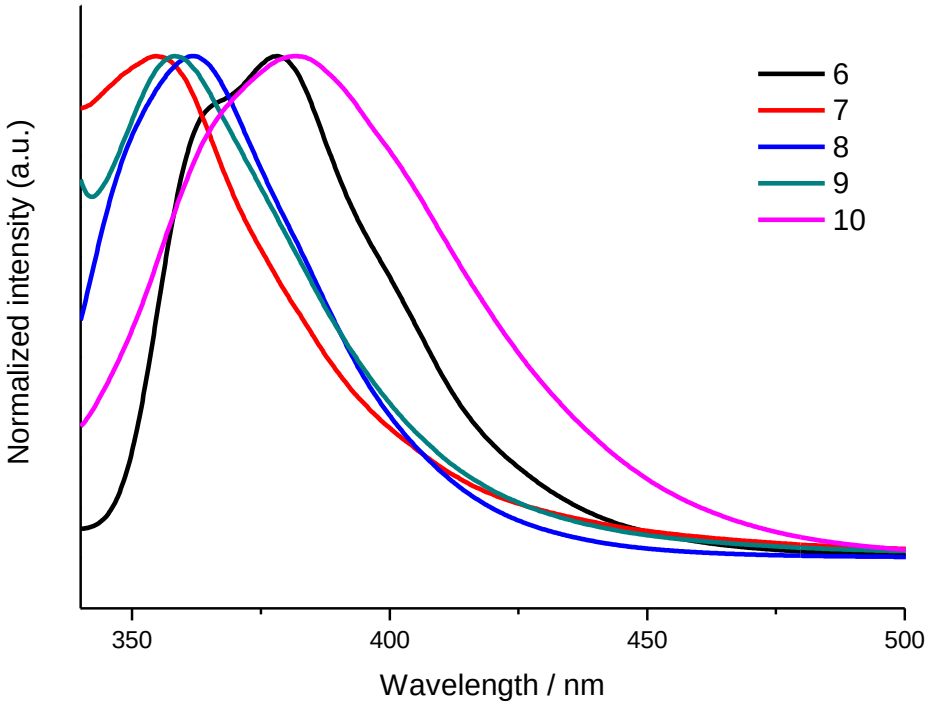
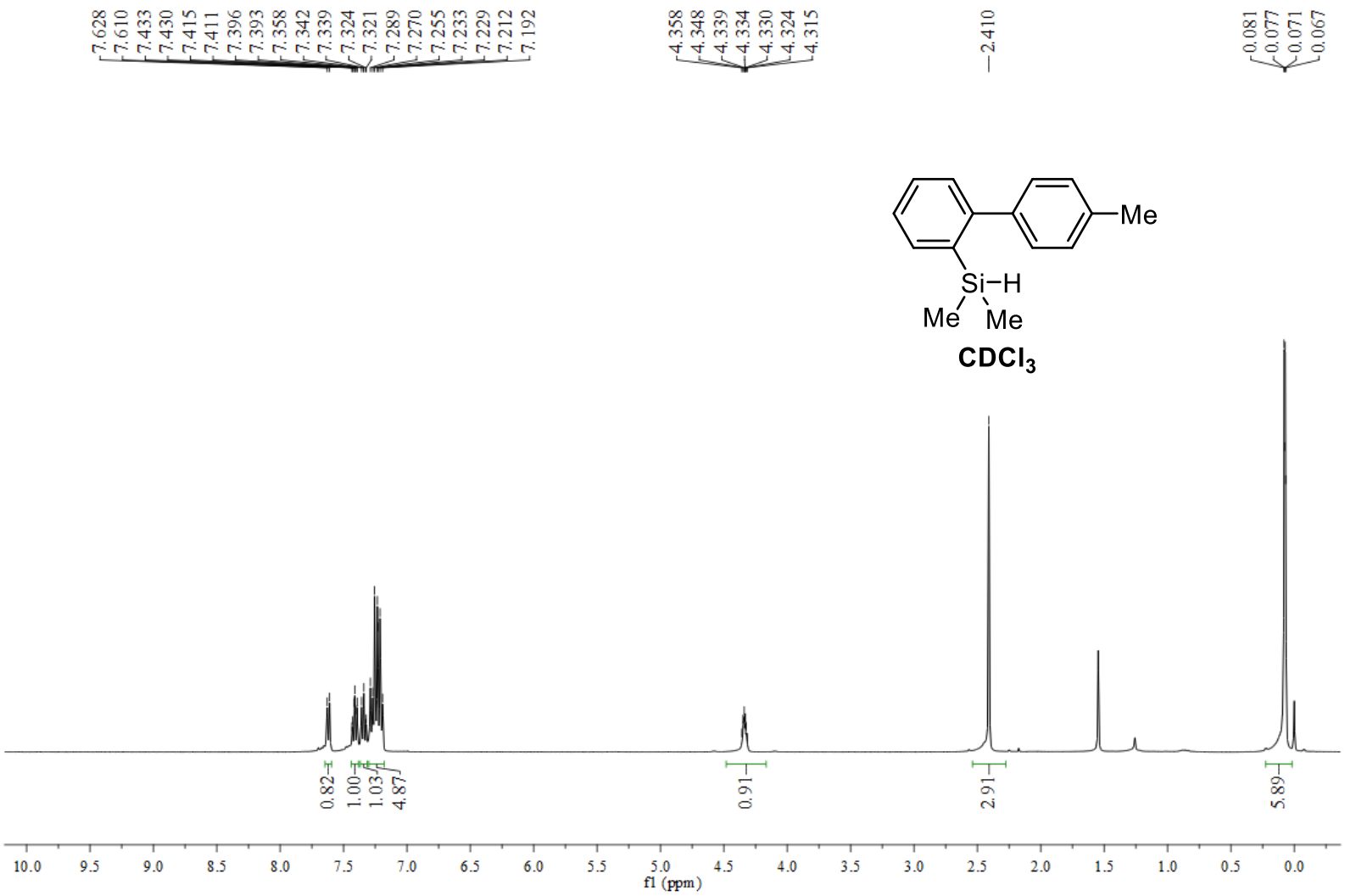
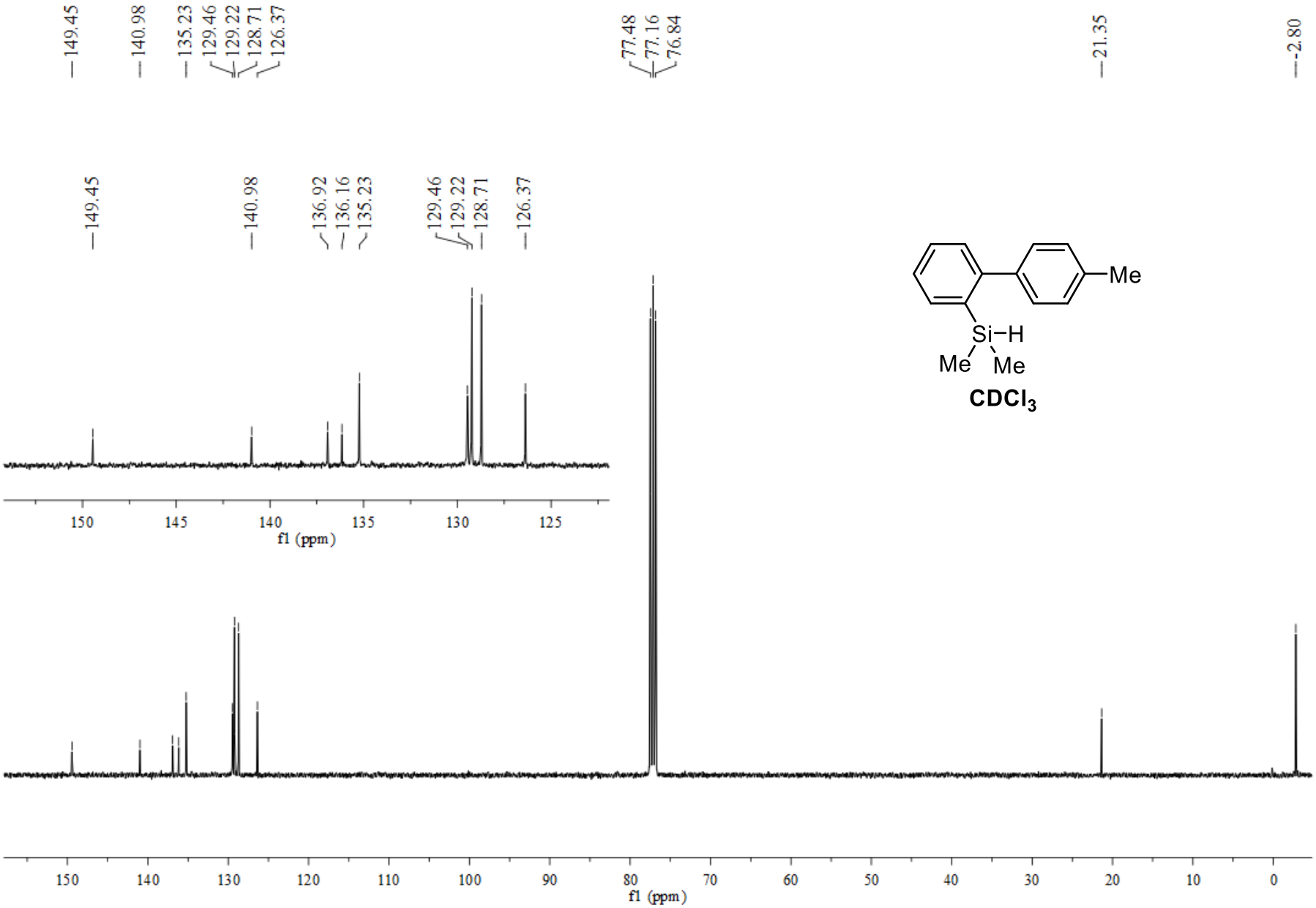


Figure 6. Fluorescence emission of compounds 6-10 in CH_2Cl_2 with excitation wavelength 320 nm.



6. Copy of NMR spectra

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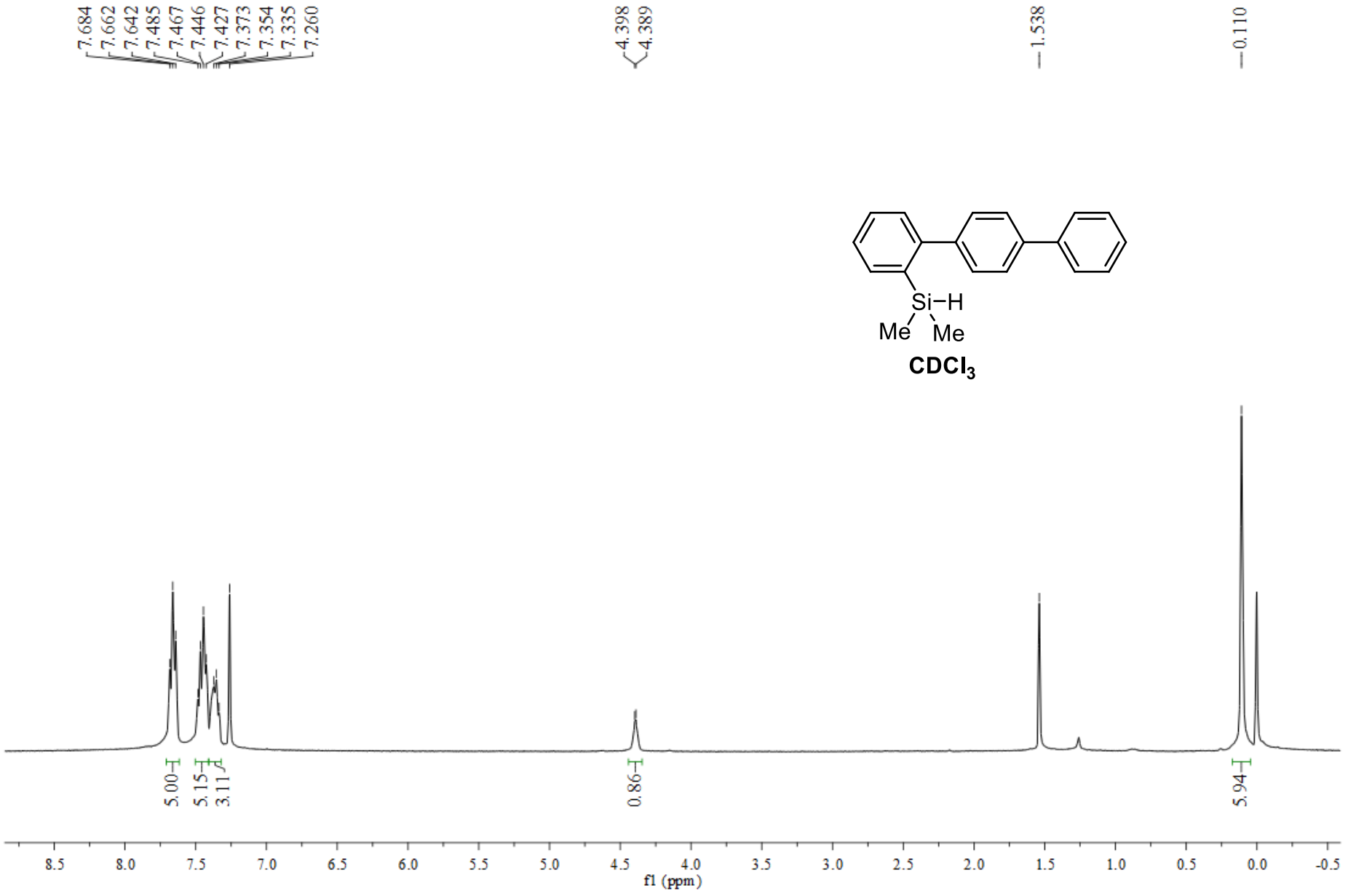
135.23
129.46
129.22
128.71
126.37
77.48
77.16
76.84
21.35
-2.80
Me
Si–H
Me
Me
CDCl3
f1 (ppm)
f1 (ppm)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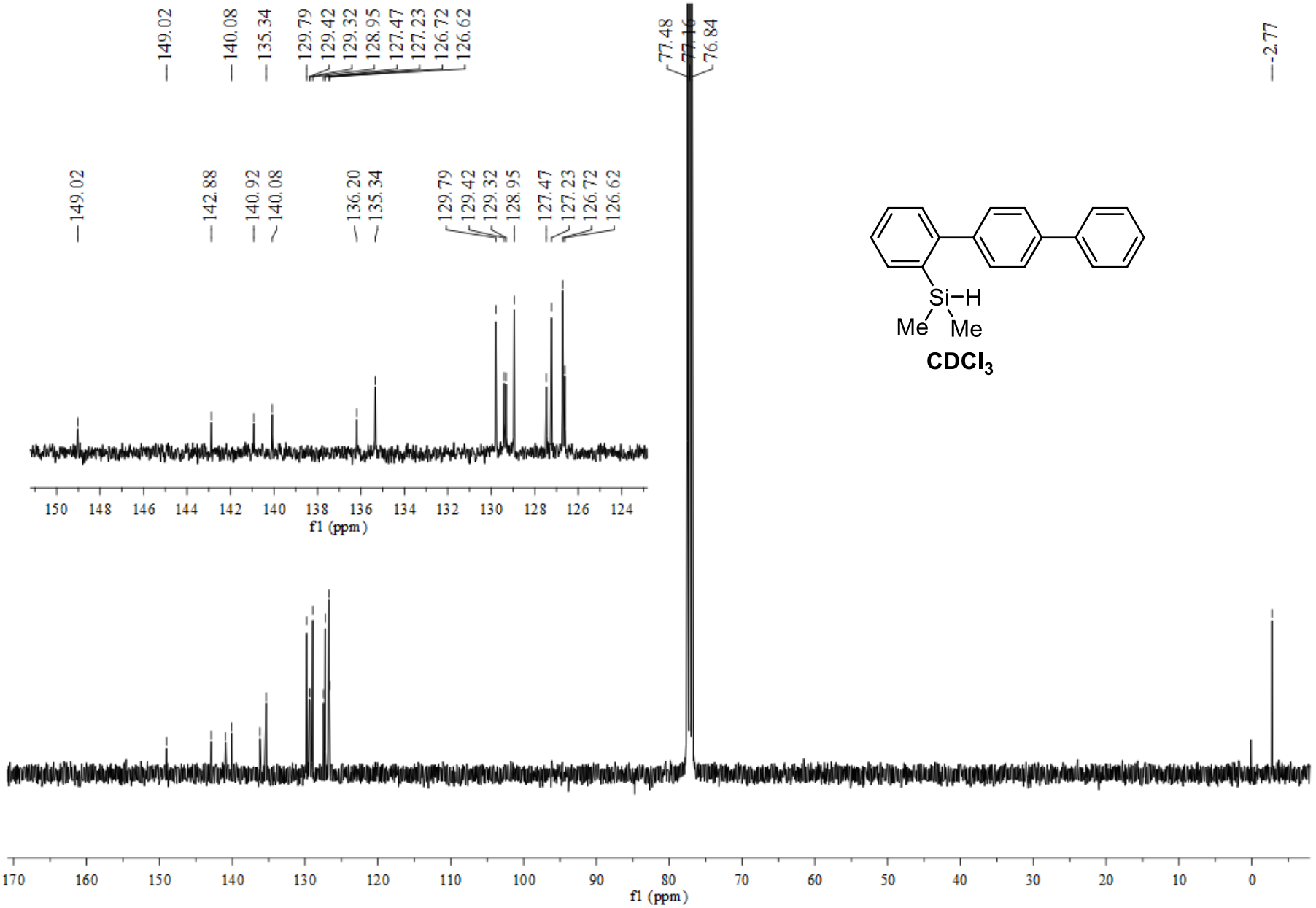
7.662
7.642
7.485
7.467
7.446
7.427
7.373
7.354
7.335
7.260
4.398
4.389
1.538
0.110
Si–H
Me
Me
CDCl3
5.00
5.15
3.11
0.86
5.94
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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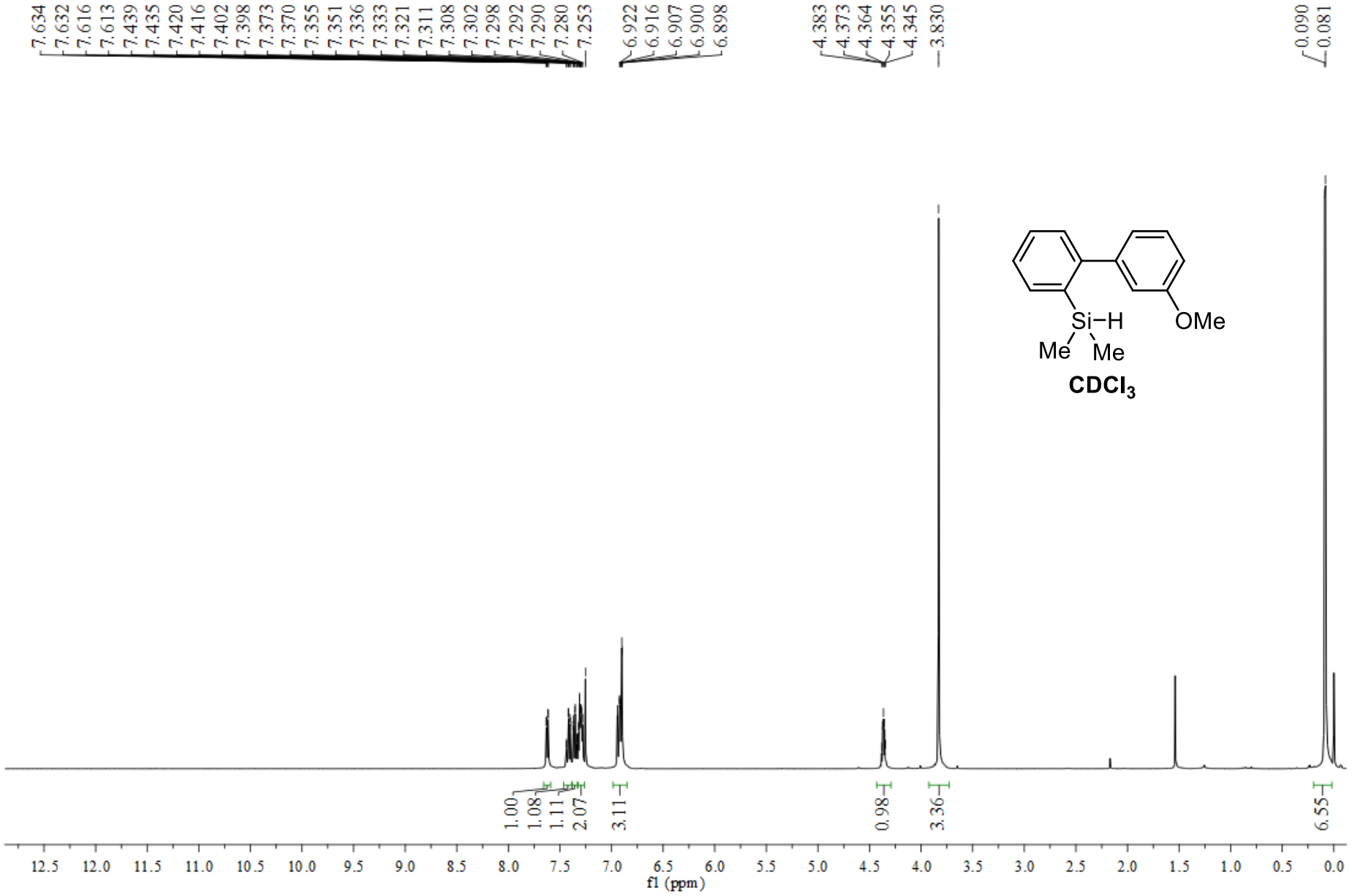
140.08
135.34
129.79
129.42
129.32
128.95
127.47
127.23
126.72
126.62
77.48
76.84
-2.77
149.02
142.88
140.92
140.08
136.20
135.34
129.79
129.42
129.32
128.95
127.47
127.23
126.72
126.62
150 148 146 144 142 140 138 136 134 132 130 128 126 124
f1 (ppm)
Si–H
Me
Me
CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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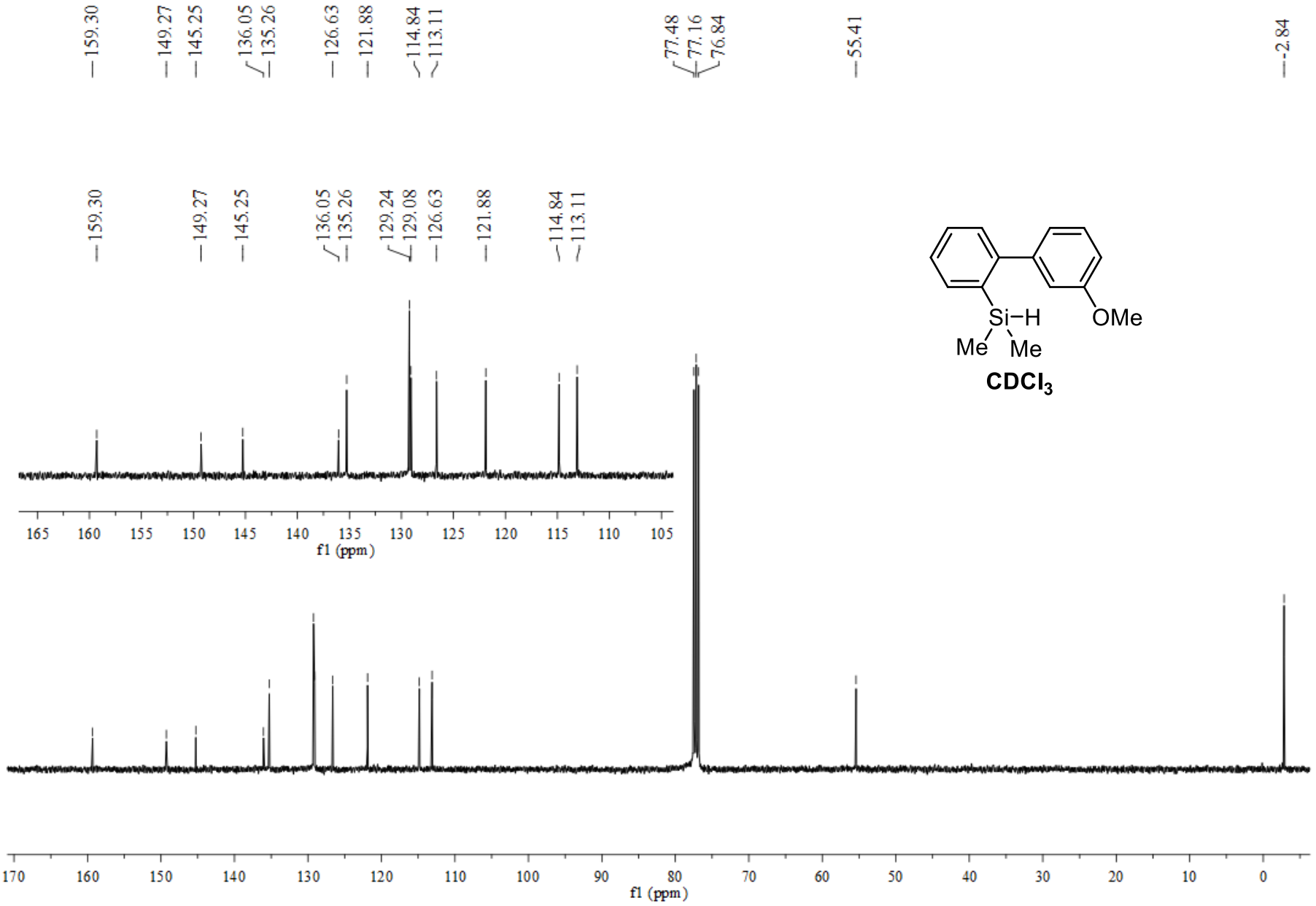
7.616
7.613
7.439
7.435
7.420
7.416
7.402
7.398
7.373
7.370
7.355
7.351
7.336
7.333
7.321
7.311
7.308
7.302
7.298
7.292
7.290
7.280
7.253
6.922
6.916
6.907
6.900
6.898
4.383
4.373
4.364
4.355
4.345
3.830
0.090
0.081
Si–H
Me
Me
OMe
CDCl3
1.00
1.08
1.11
2.07
3.11
0.98
3.36
6.55
f1 (ppm)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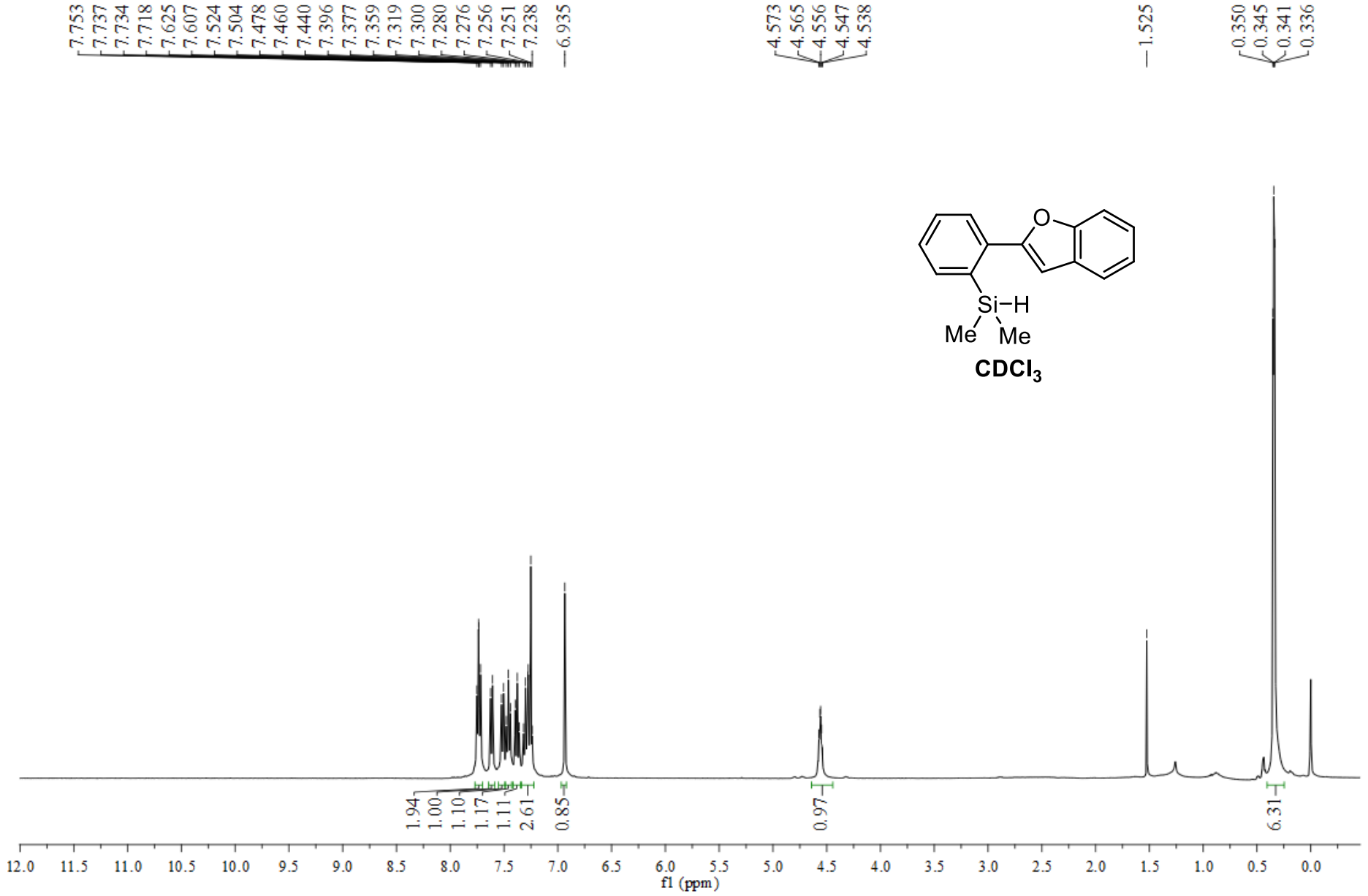
145.25
136.05
135.26
126.63
121.88
114.84
113.11
77.48
77.16
76.84
55.41
2.84
159.30
149.27
145.25
136.05
135.26
129.24
129.08
126.63
121.88
114.84
113.11
Si–H
OMe
Me
Me
CDCl3
165 160 155 150 145 140 135 130 125 120 115 110 105
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.625
7.607
7.524
7.504
7.478
7.460
7.440
7.396
7.377
7.359
7.319
7.300
7.280
7.276
7.256
7.251
7.238
6.935
4.573
4.565
4.556
4.547
4.538
1.525
0.350
0.345
0.341
0.336
O
Si–H
Me
Me
CDCl3
1.94
1.00
1.10
1.17
1.11
2.61
0.85
0.97
6.31
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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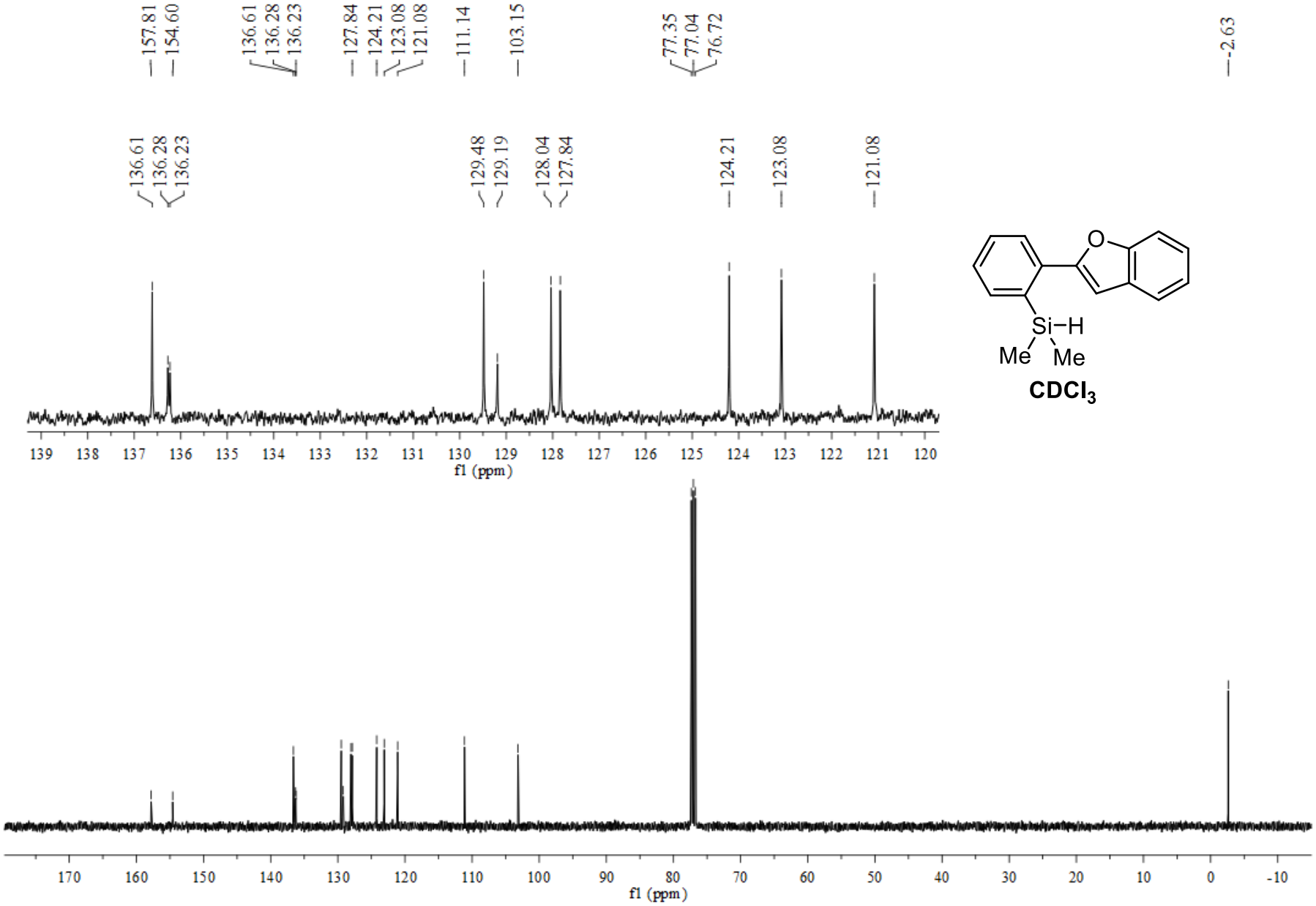
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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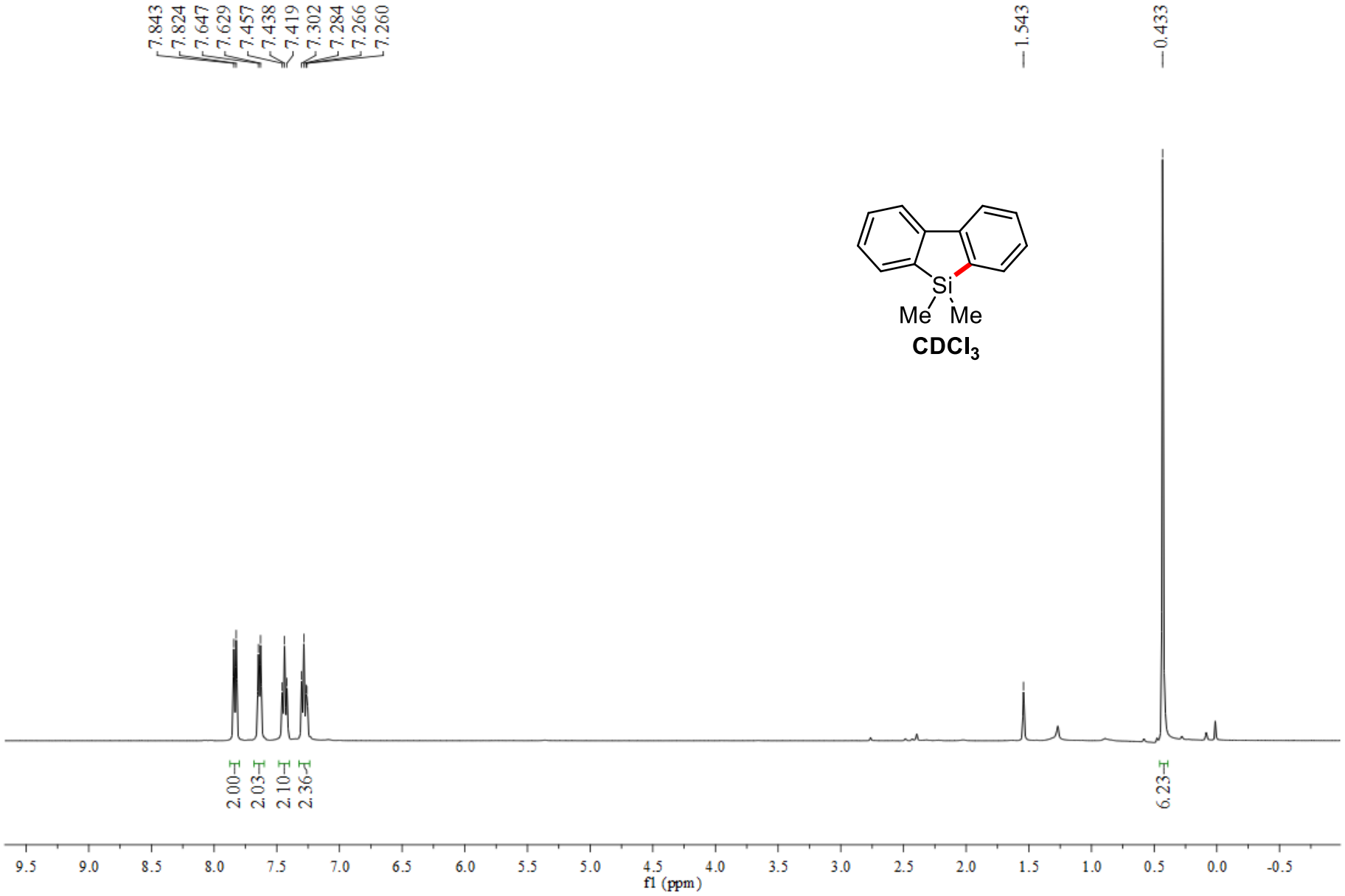
154.60
136.61
136.28
136.23
127.84
124.21
123.08
121.08
111.14
103.15
77.35
77.04
76.72
-2.63
129.48
129.19
128.04
127.84
124.21
123.08
121.08
O
Si–H
Me
Me
CDCl3
f1 (ppm)
f1 (ppm)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7.629
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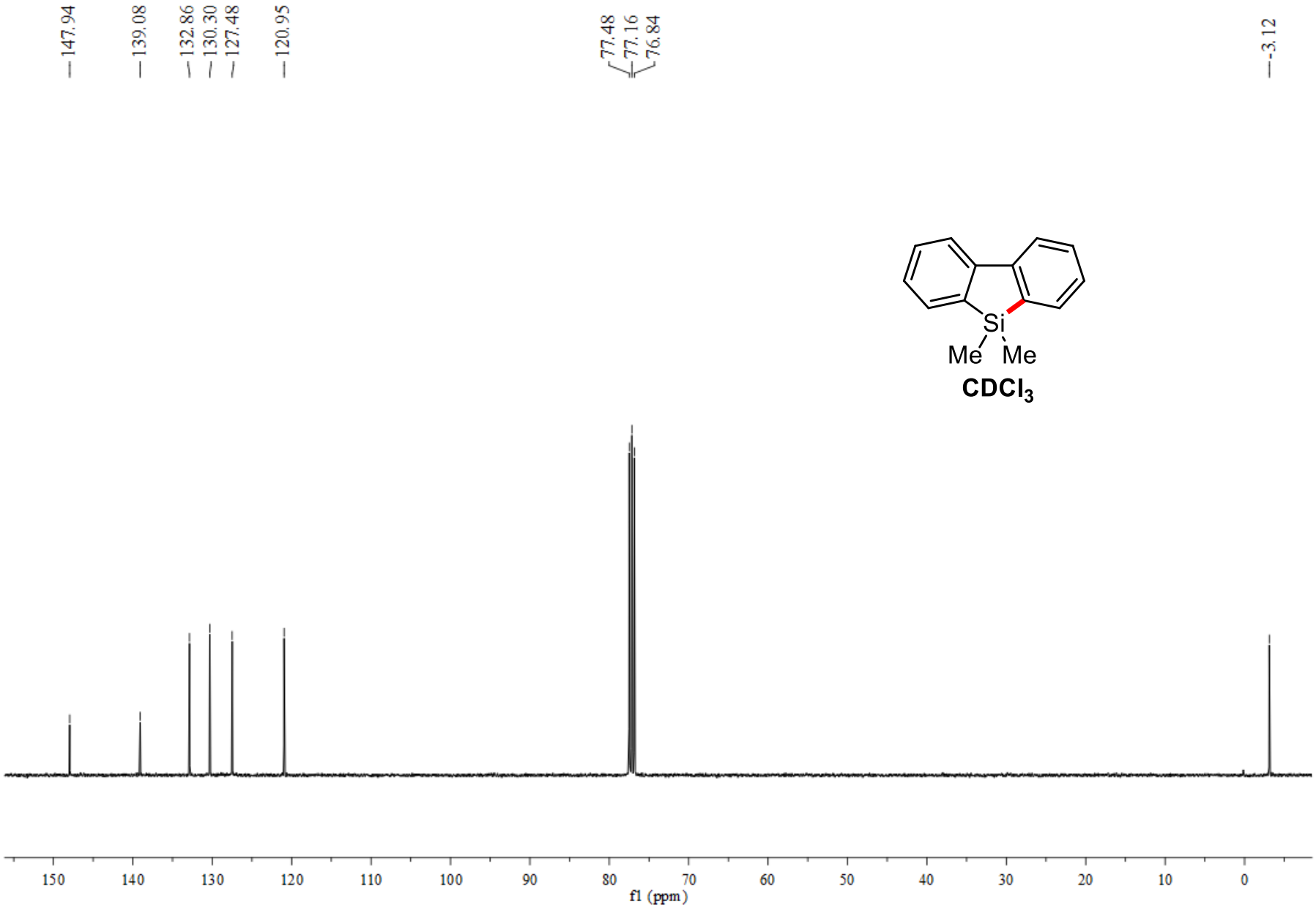
7.438
7.419
7.302
7.284
7.266
7.260
1.543
0.433
Si
Me
Me
CDCl3
2.00
2.03
2.10
2.36
6.23
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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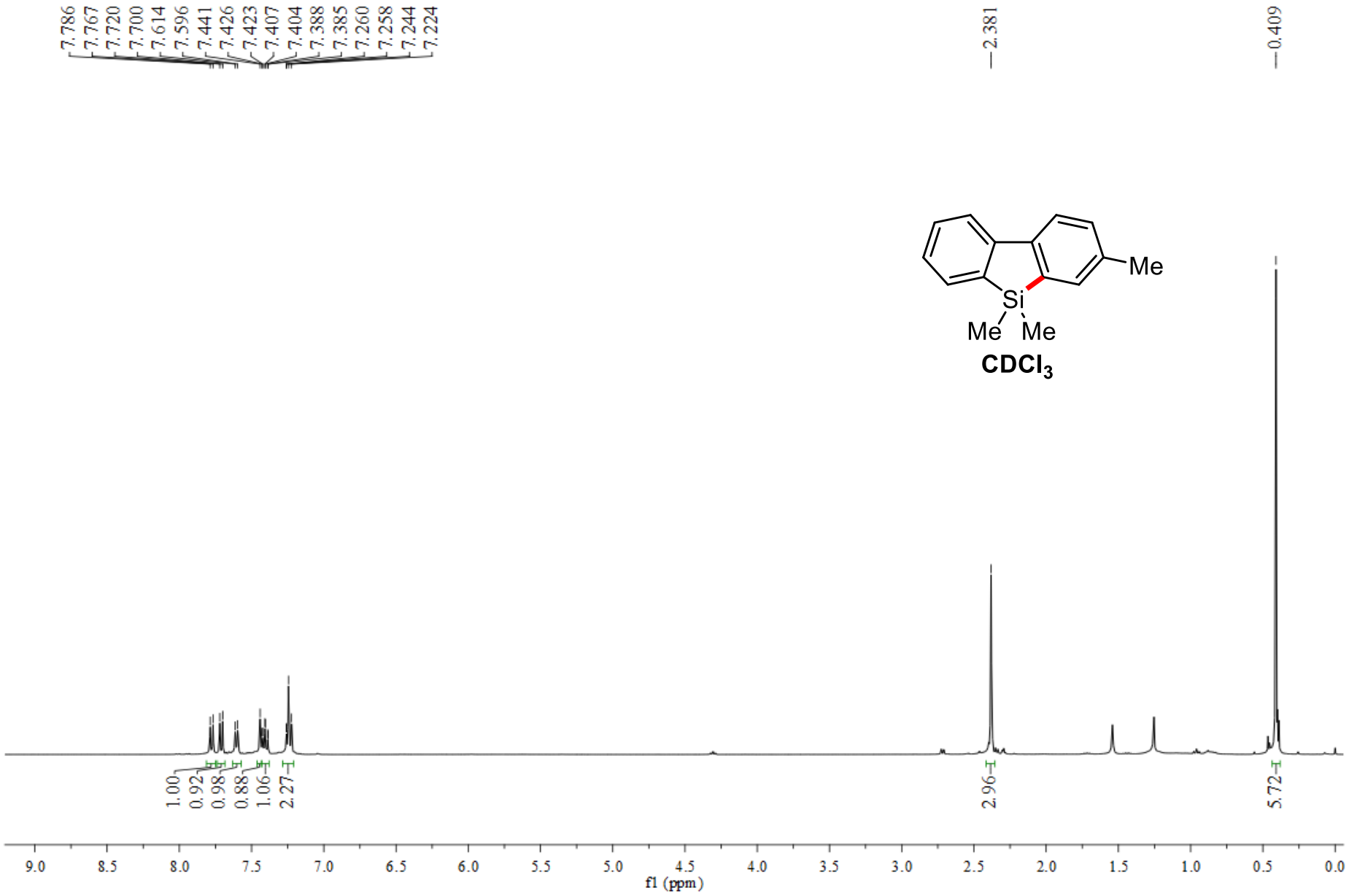
139.08
132.86
130.30
127.48
120.95
77.48
77.16
76.84
-3.12
Si
Me
Me
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.404
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7.385
7.260
7.258
7.244
7.224
2.381
0.409
Me
Si
Me
Me
CDCl3
1.00
0.92
0.98
0.88
1.06
2.27
2.96
5.72
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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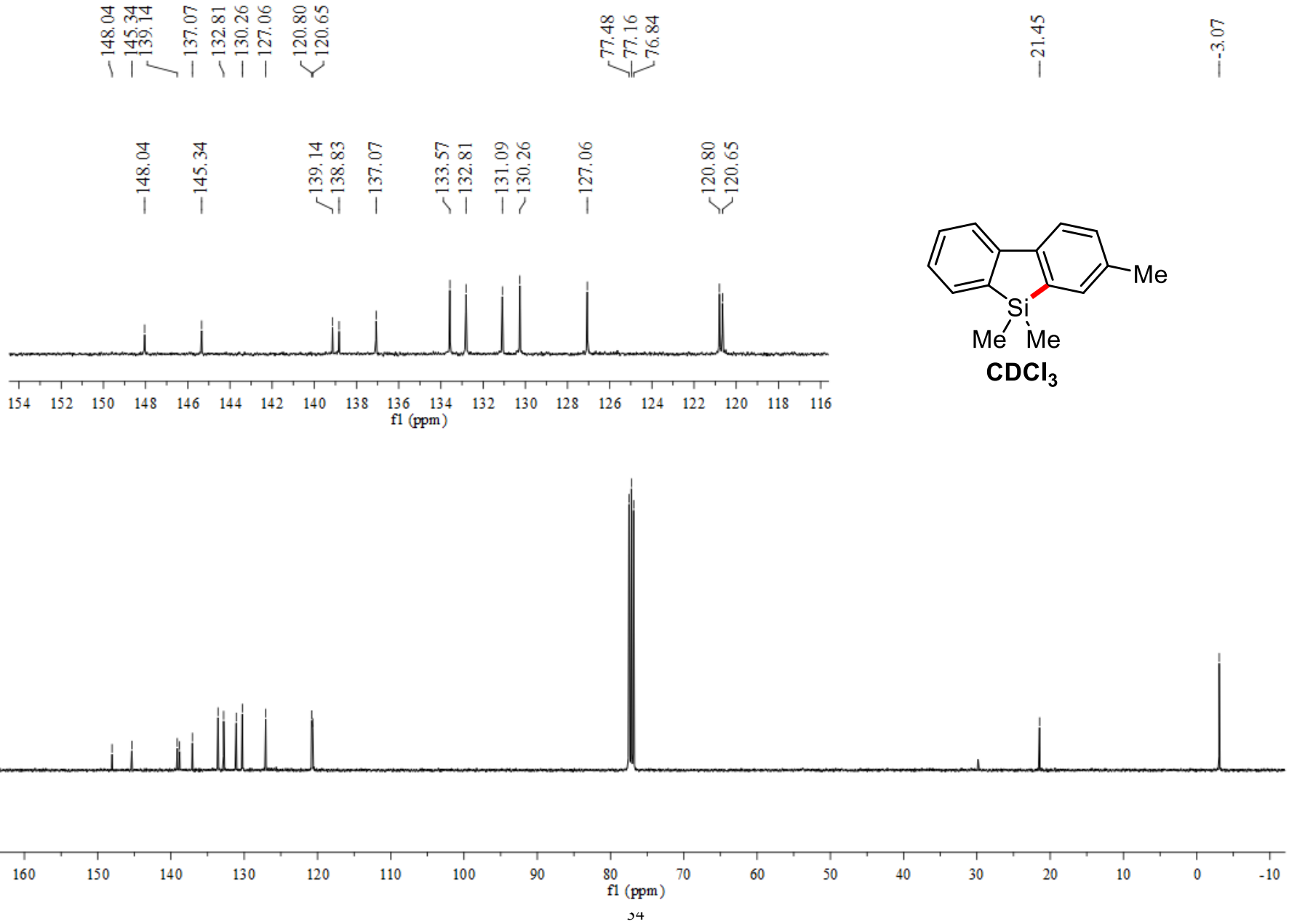
1.5
1.0
0.5
0.0
f1 (ppm)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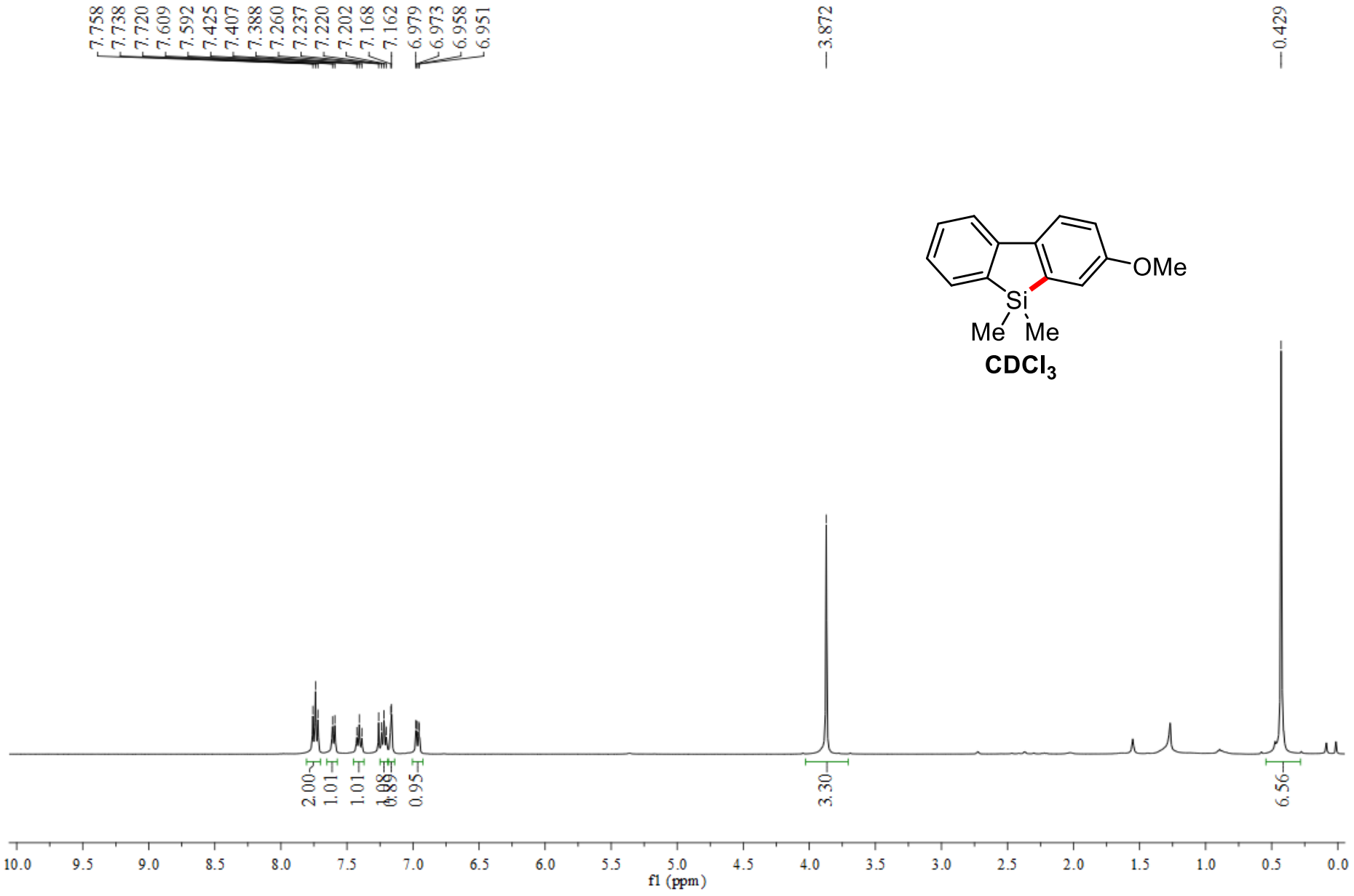
137.07
132.81
130.26
127.06
120.80
120.65
77.48
77.16
76.84
21.45
-3.07
148.04
145.34
139.14
138.83
137.07
133.57
132.81
131.09
130.26
127.06
120.80
120.65
Me
Si
Me
Me
CDCl3
f1 (ppm)
f1 (ppm)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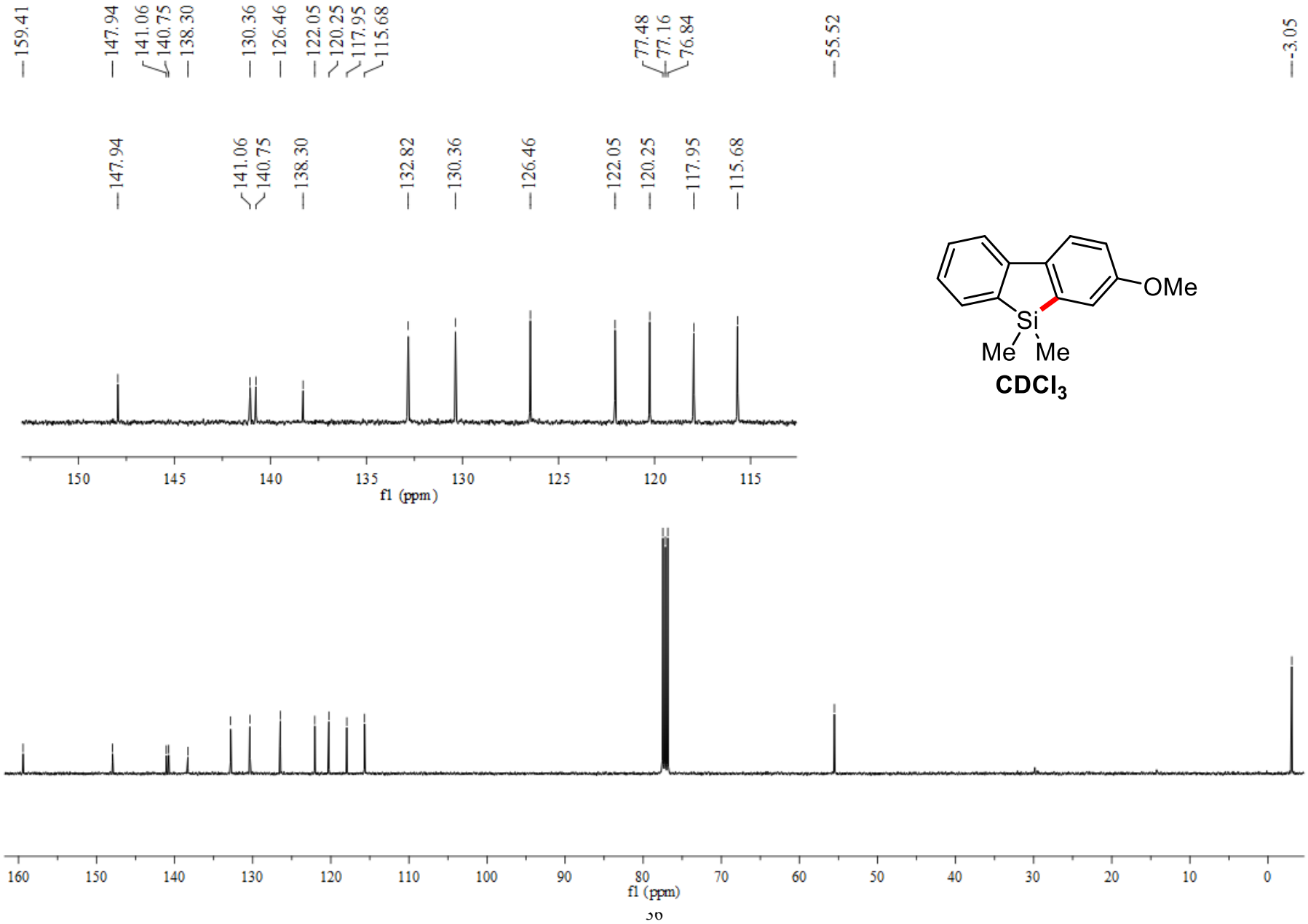
7.592
7.425
7.407
7.388
7.260
7.237
7.220
7.202
7.168
7.162
6.979
6.973
6.958
6.951
3.872
0.429
OMe
Si
Me
Me
CDCl3
2.00
1.01
1.01
1.08
0.95
3.30
6.56
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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141.06
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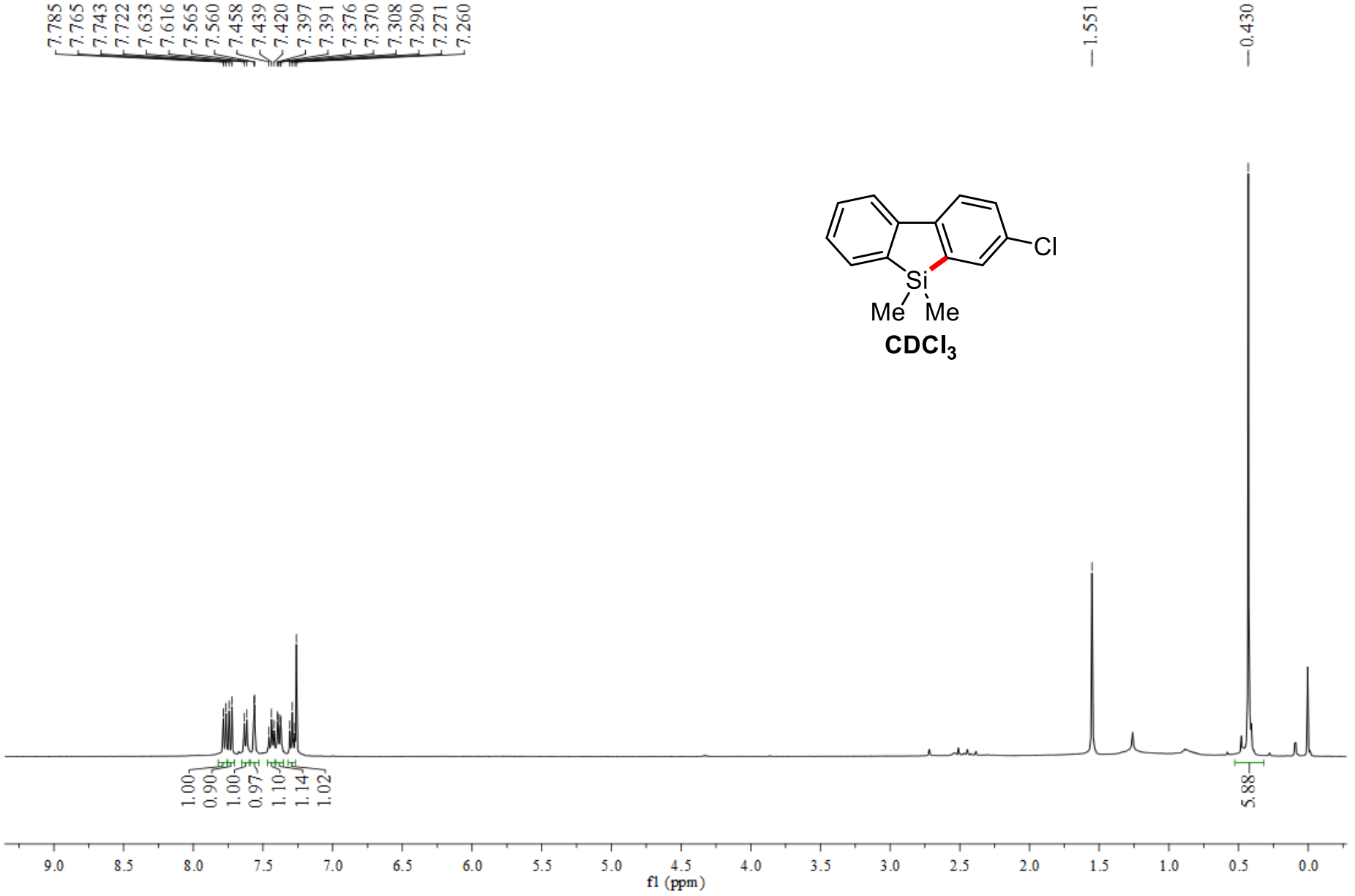
138.30
130.36
126.46
122.05
120.25
117.95
115.68
77.48
77.16
76.84
55.52
-3.05
147.94
141.06
140.75
138.30
132.82
130.36
126.46
122.05
120.25
117.95
115.68
OMe
Si
Me
Me
CDCl3
150
145
140
135
130
125
120
115
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.560
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7.439
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7.391
7.376
7.370
7.308
7.290
7.271
7.260
1.551
0.430
Cl
Si
Me
Me
CDCl3
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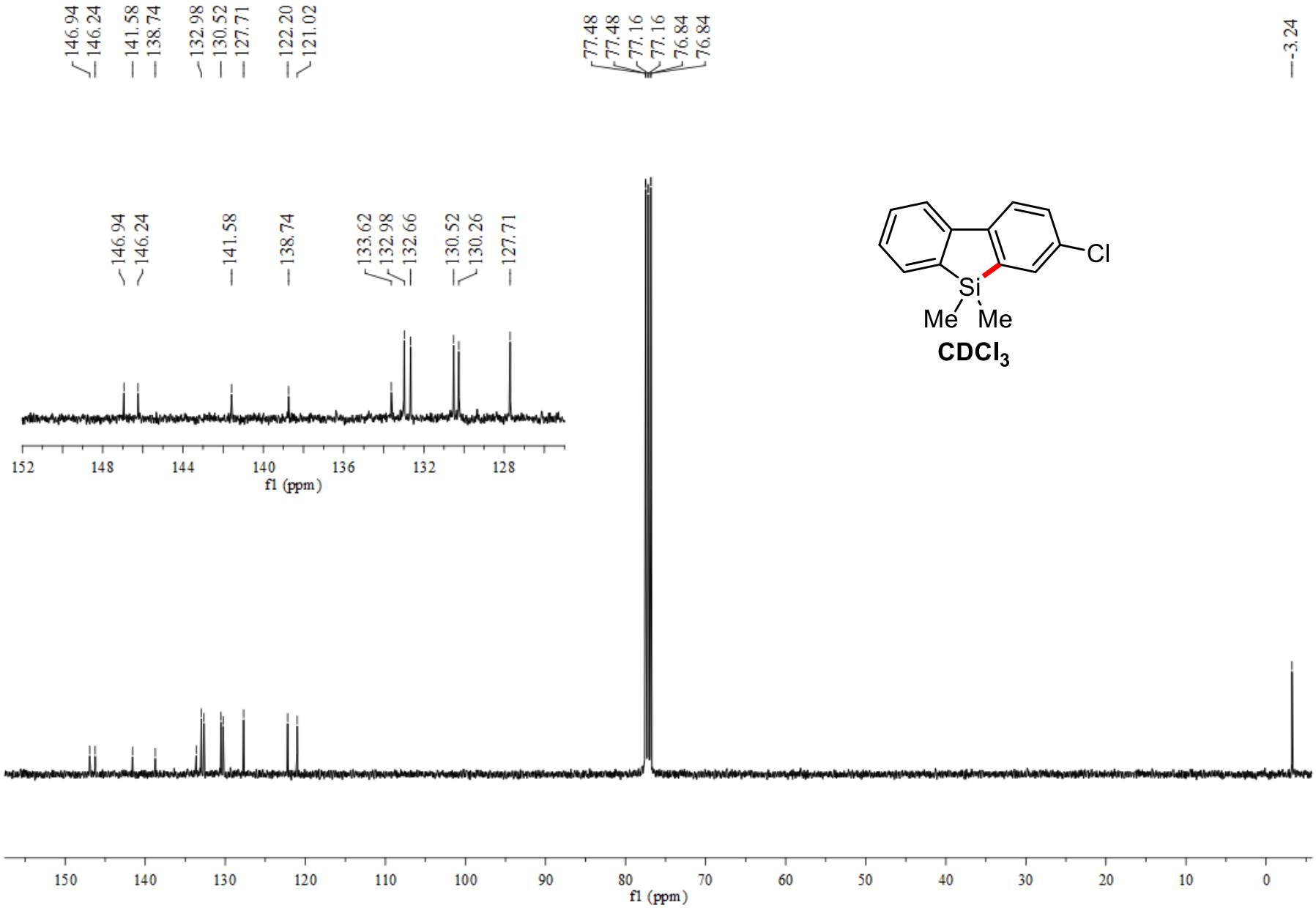
0.90
1.00
0.97
1.10
1.14
1.02
5.88
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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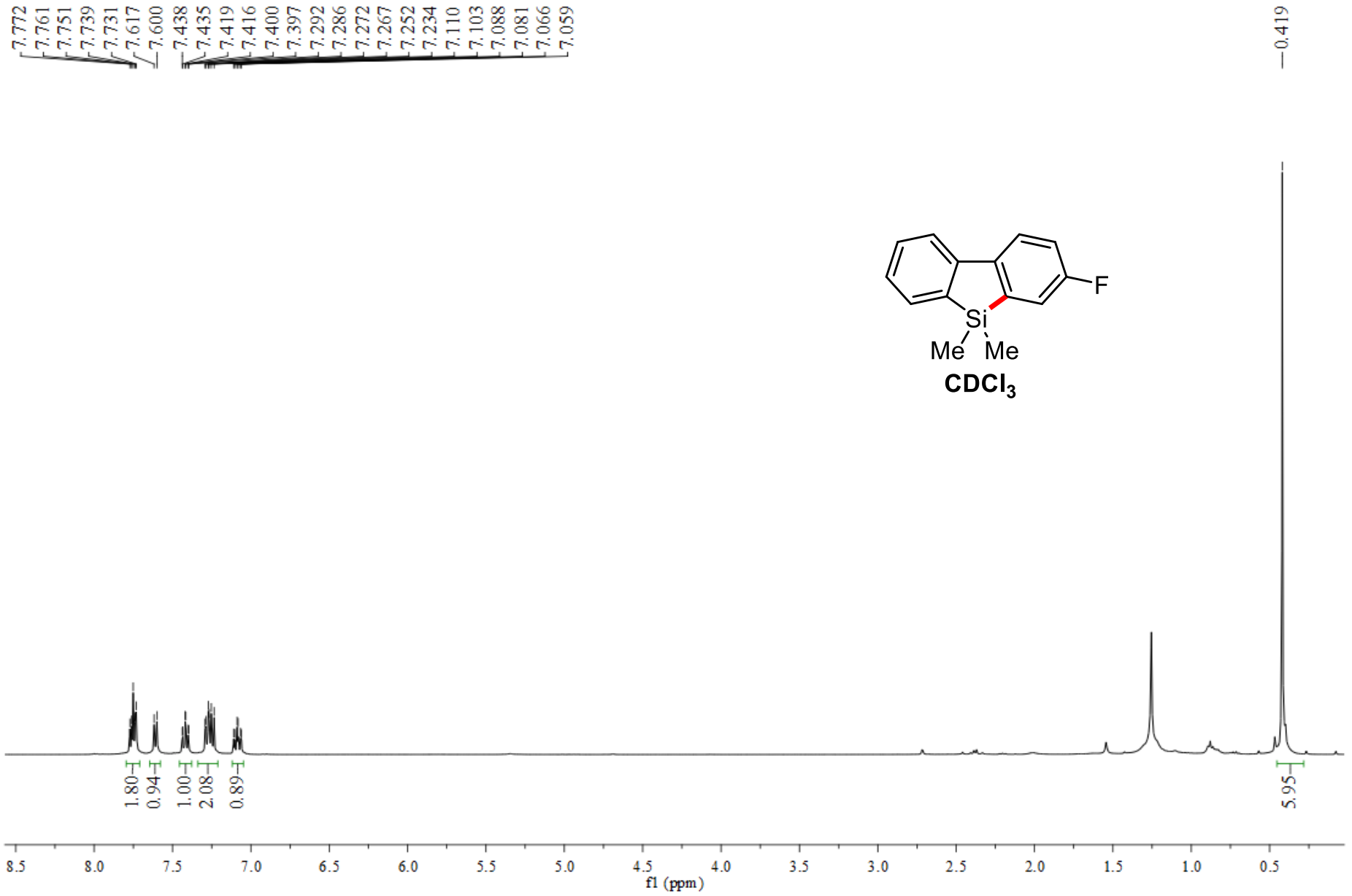
76.84
76.84
-3.24
146.94
146.24
141.58
138.74
133.62
132.98
132.66
130.52
130.26
127.71
152
148
144
140
136
132
128
f1 (ppm)
Cl
Si
Me
Me
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.419
7.416
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7.397
7.292
7.286
7.272
7.267
7.252
7.234
7.110
7.103
7.088
7.081
7.066
7.059
0.419
F
Si
Me
Me
CDCl3
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0.94
1.00
2.08
0.89
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
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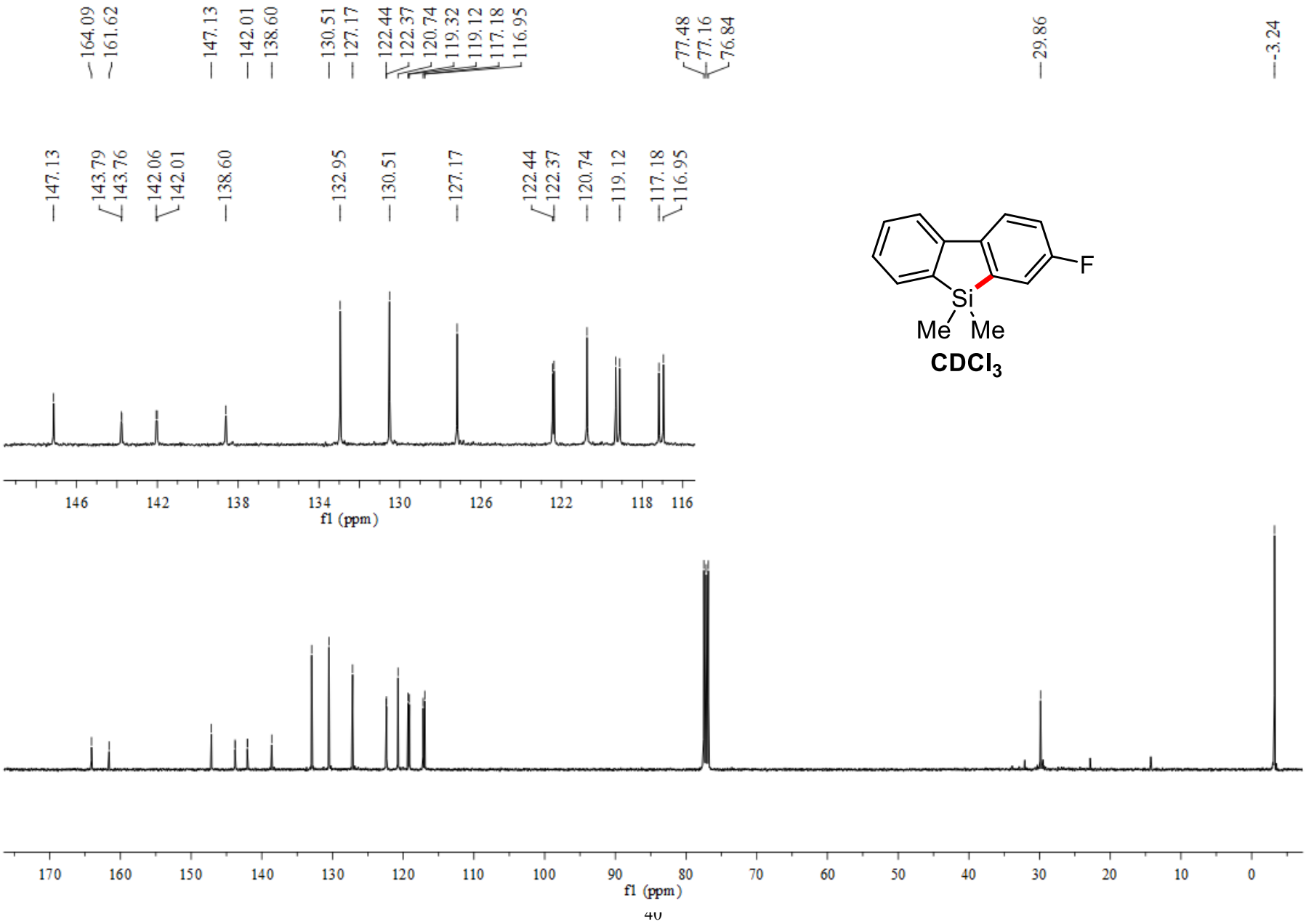
1.5
1.0
0.5
f1 (ppm)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161.62
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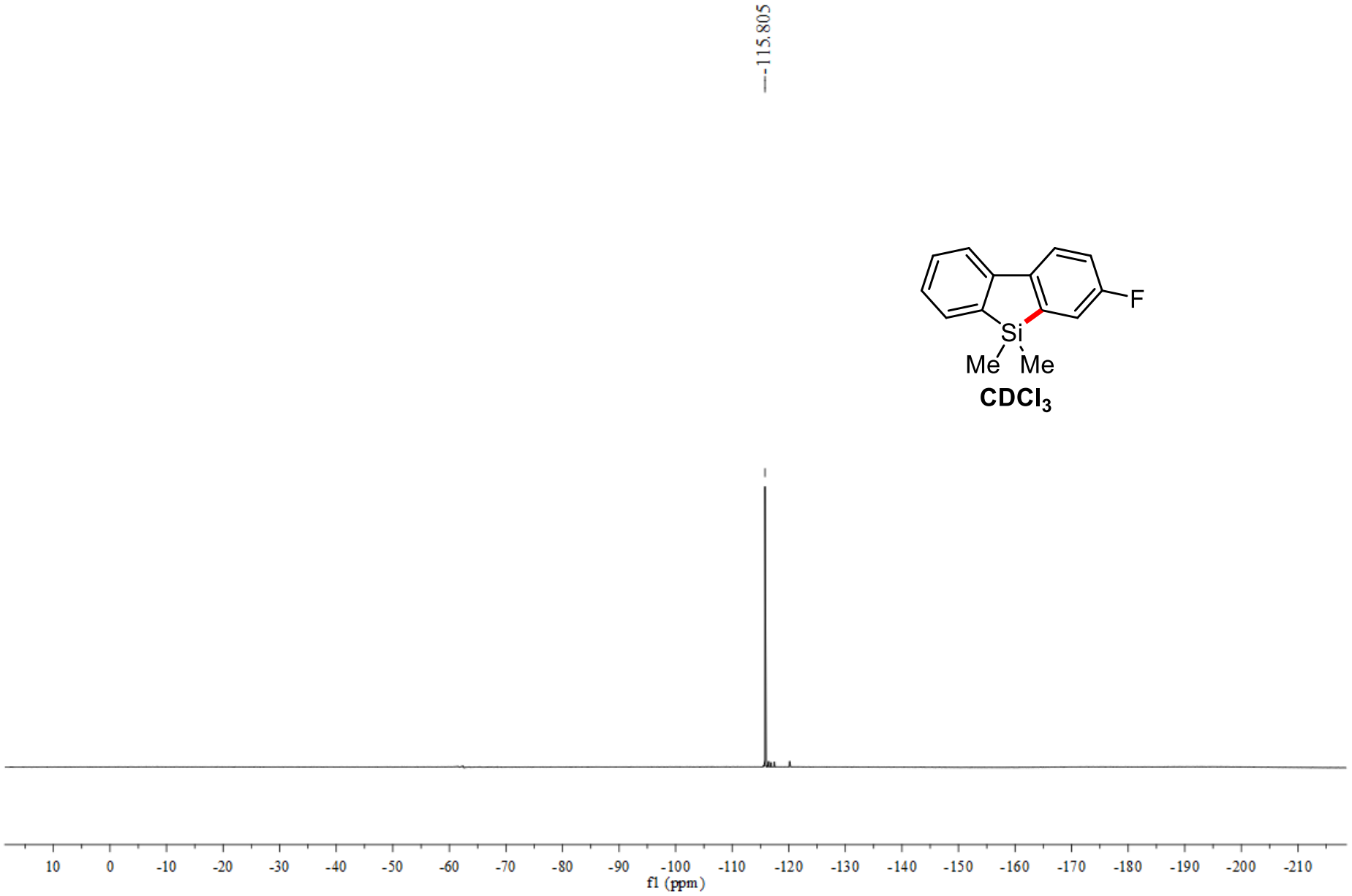
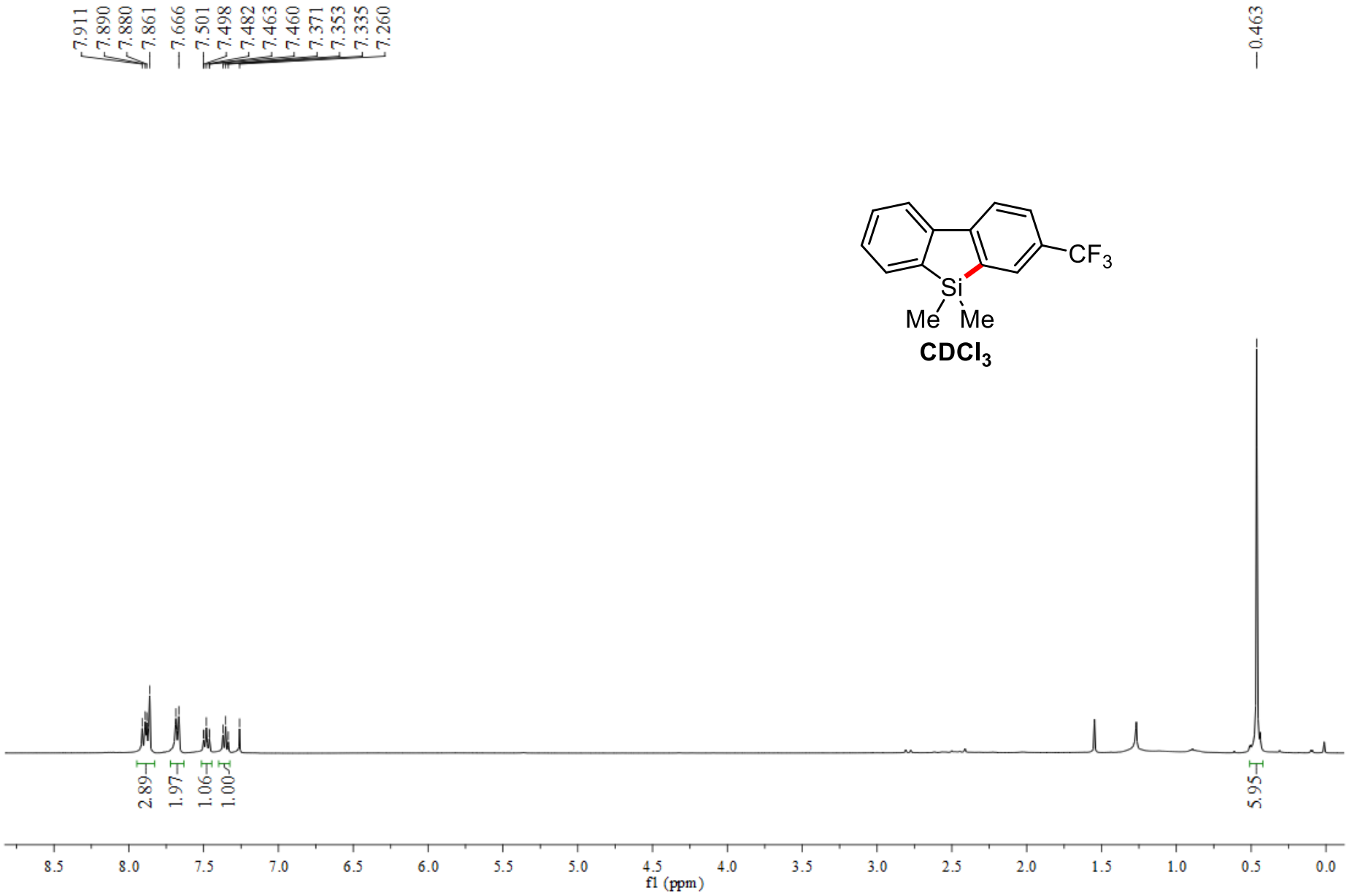
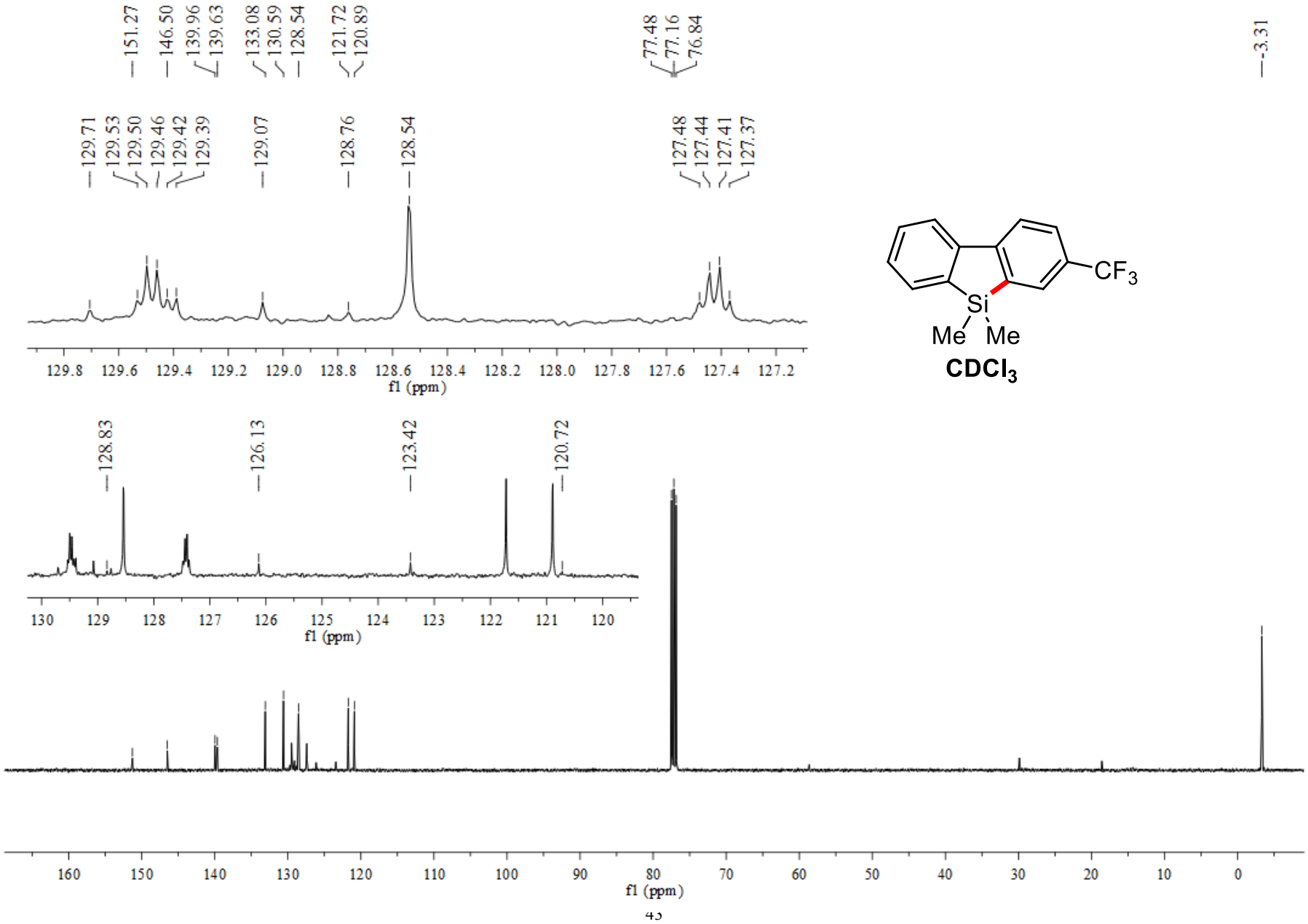
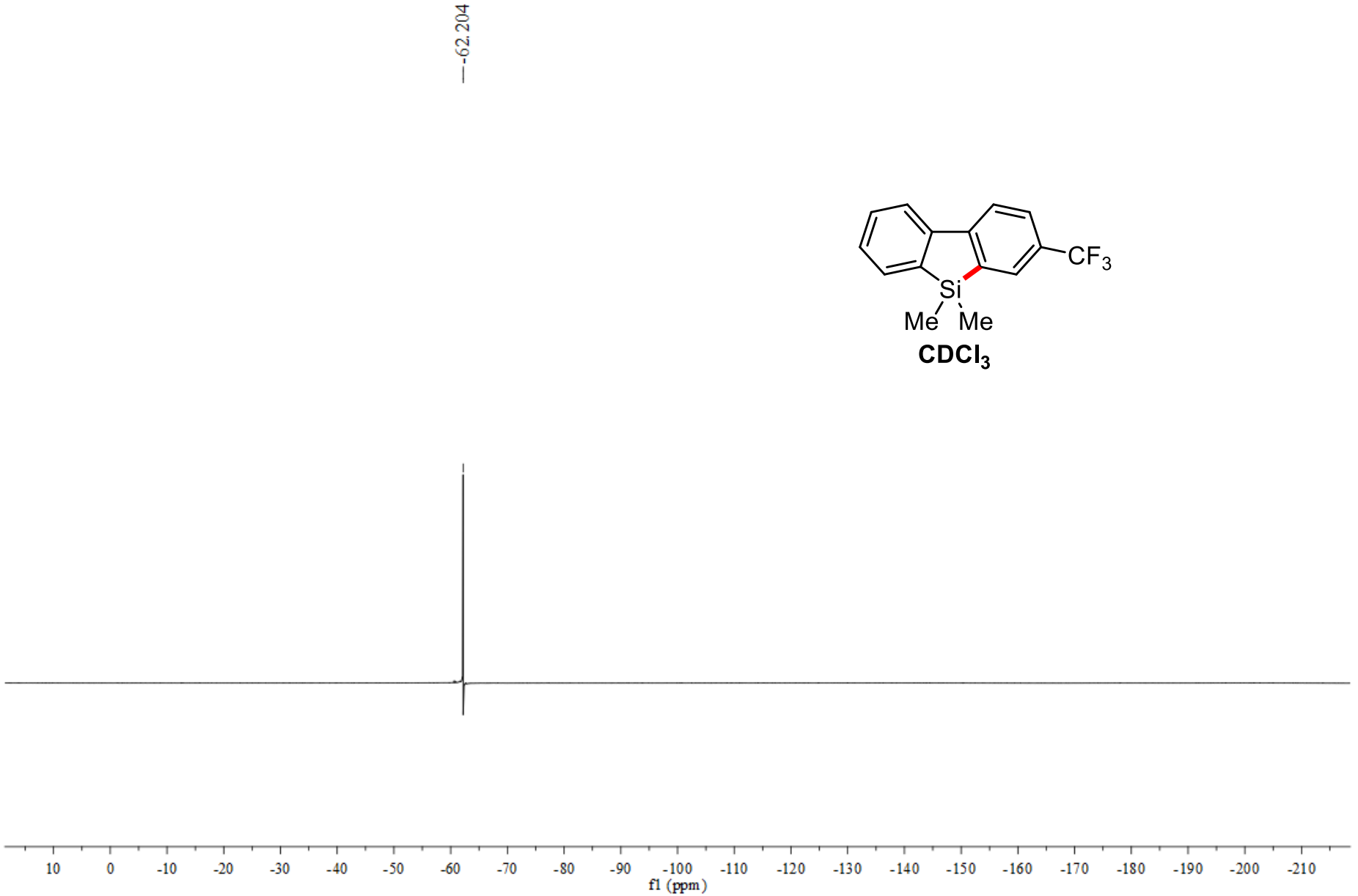
142.01
138.60
130.51
127.17
122.44
122.37
120.74
119.32
119.12
117.18
116.95
77.48
77.16
76.84
29.86
-3.24
147.13
143.79
143.76
142.06
142.01
138.60
132.95
130.51
127.17
122.44
122.37
120.74
119.12
117.18
116.95
F
Si
Me
Me
CDCl3
f1 (ppm)
f1 (ppm)


-115.805
F
Si
Me
Me
CDCl3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.911
7.890
7.880
7.861
7.666
7.501
7.498
7.482
7.463
7.460
7.371
7.353
7.335
7.260
0.463
CF3
Si
Me
Me
CDCl3
2.89
1.97
1.06
1.00
5.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


151.27
146.50
139.96
139.63
133.08
130.59
128.54
121.72
120.89
77.48
77.16
76.84
-3.31
129.71
129.53
129.50
129.46
129.42
129.39
129.07
128.76
128.54
127.48
127.44
127.41
127.37
129.8 129.6 129.4 129.2 129.0 128.8 128.6 128.4 128.2 128.0 127.8 127.6 127.4 127.2
f1 (ppm)
128.83
126.13
123.42
120.72
130 129 128 127 126 125 124 123 122 121 120
f1 (ppm)
CF3
Si
Me Me
CDCl3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.204
CF3
Si
Me
Me
CDCl3
10
0
-10
-20
-30
-40
-50
-60
-70
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-110
-120
-130
-140
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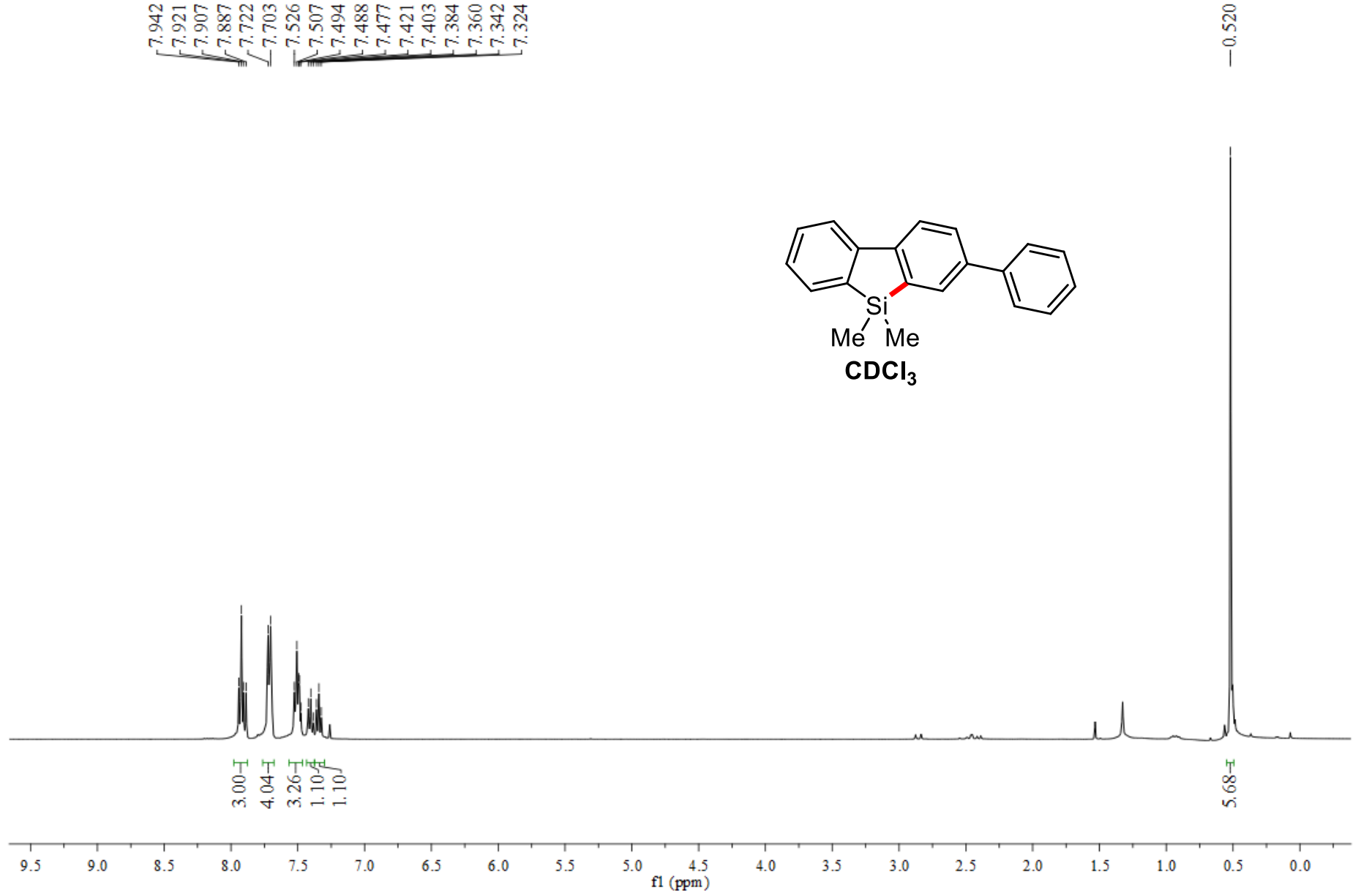
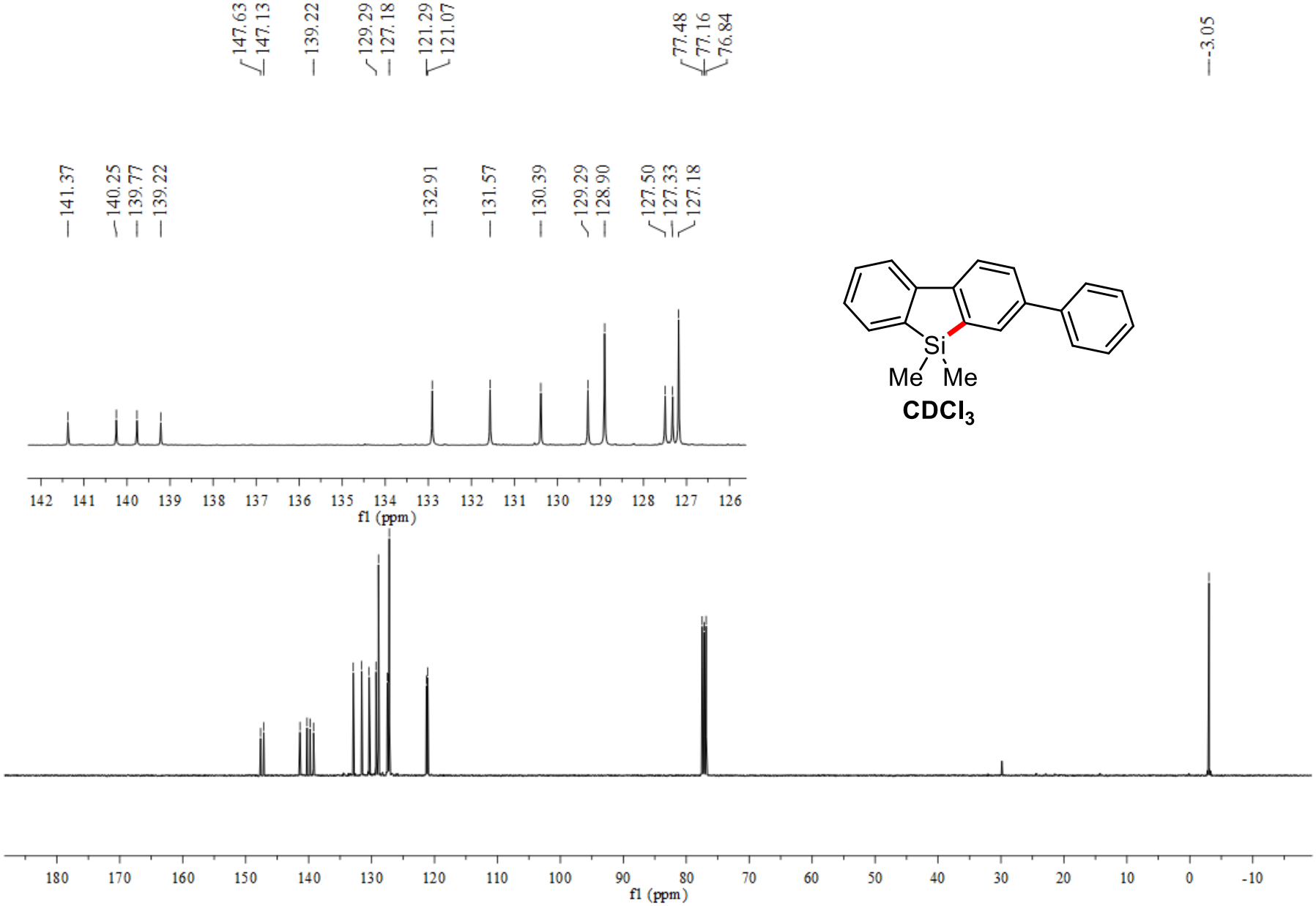
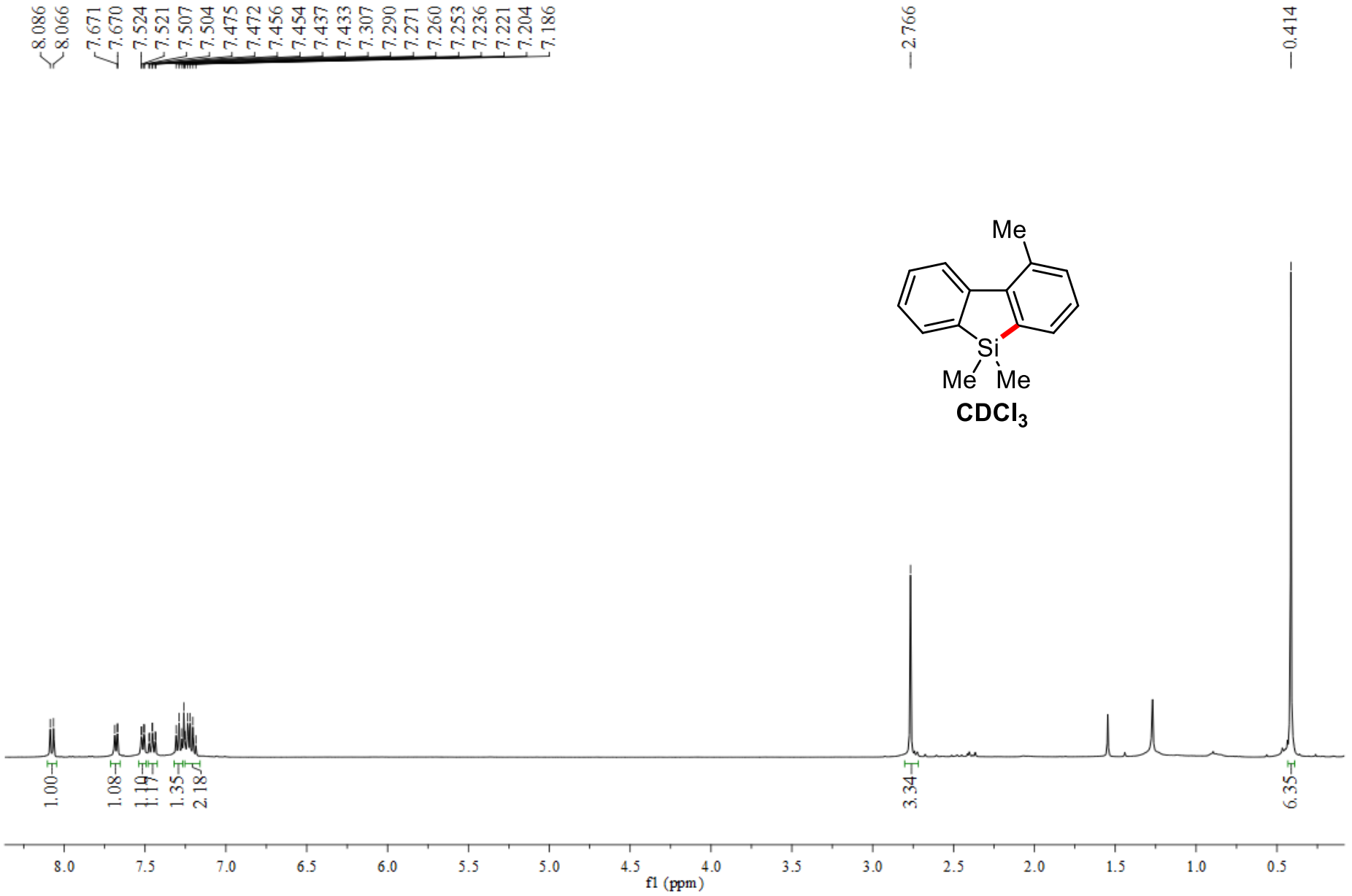
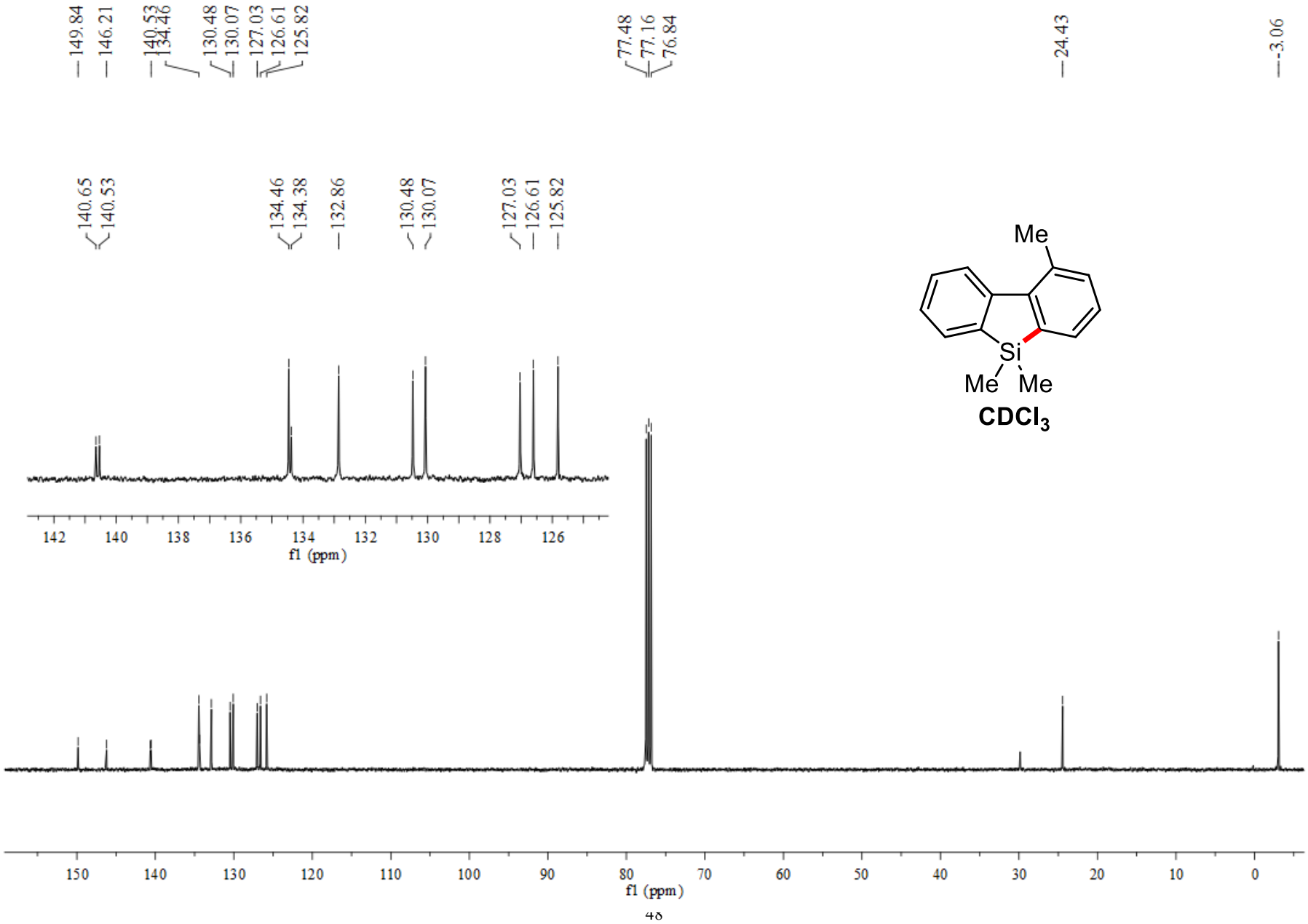
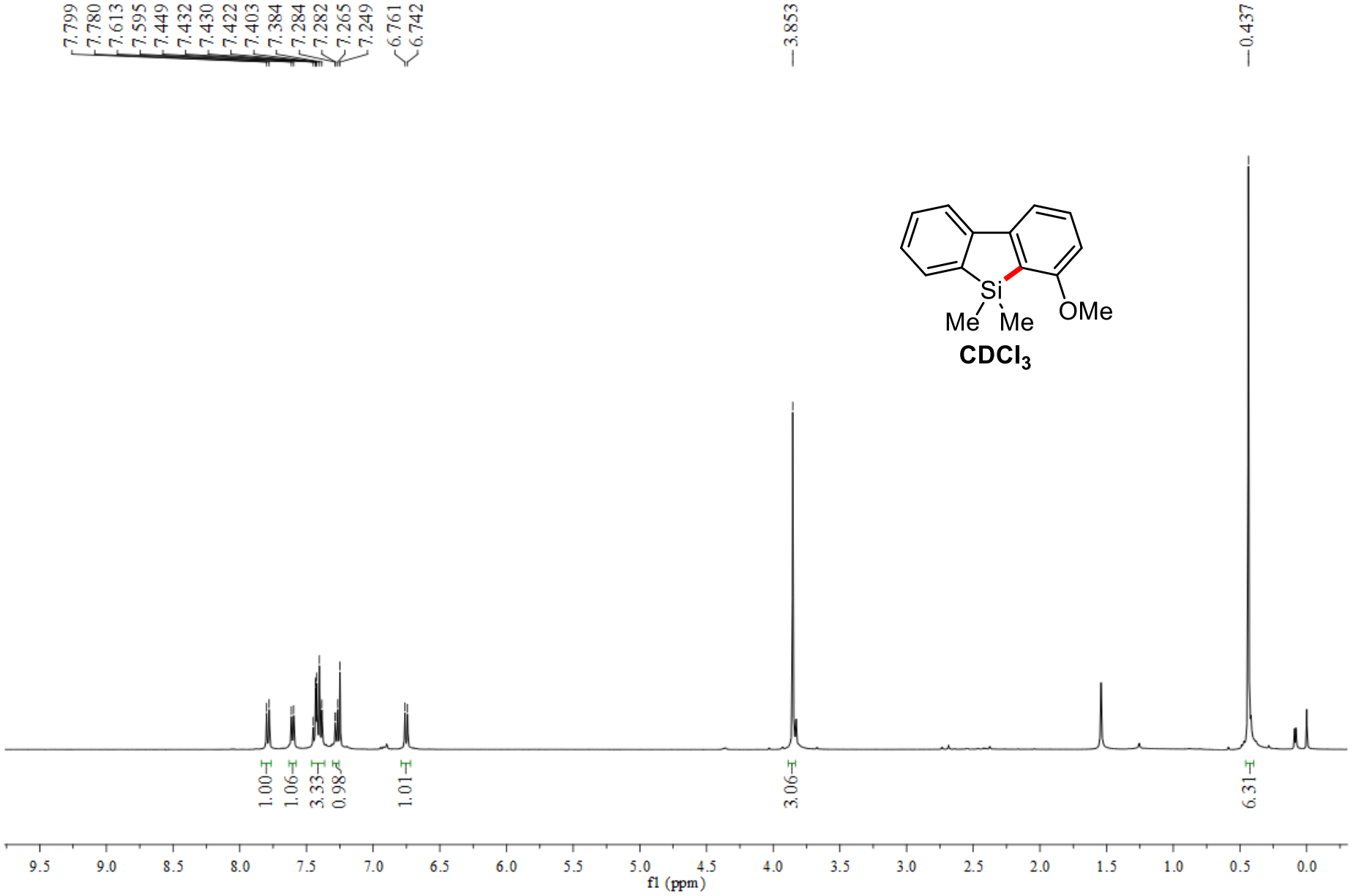
-160
-170
-180
-190
-200
-210
f1 (ppm)

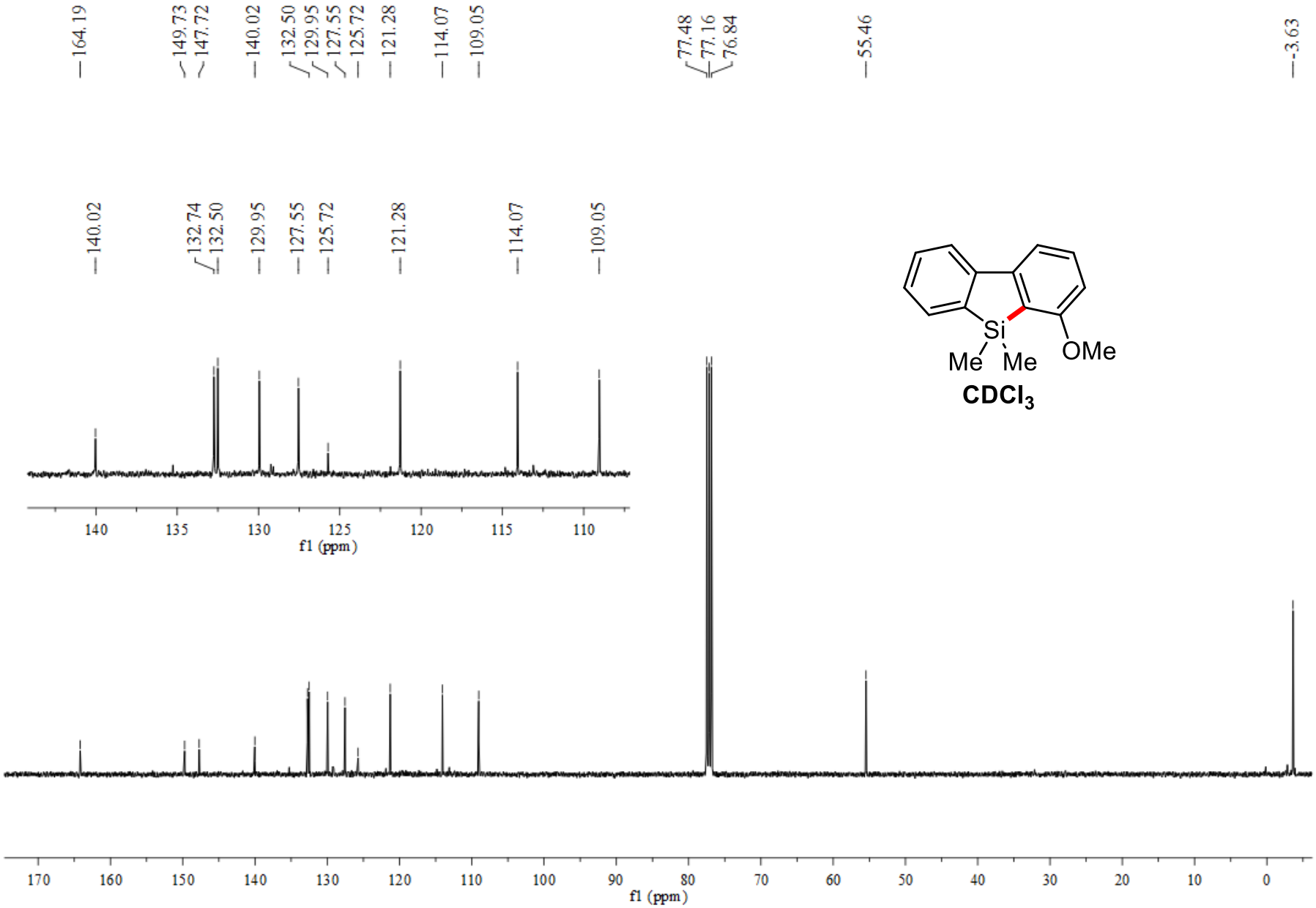

7.942
7.921
7.907
7.887
7.722
7.703
7.526
7.507
7.494
7.488
7.477
7.421
7.403
7.384
7.360
7.342
7.324
0.520
Si
Me
Me
CDCl3
3.00
4.04
3.26
1.10
1.10
5.68
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

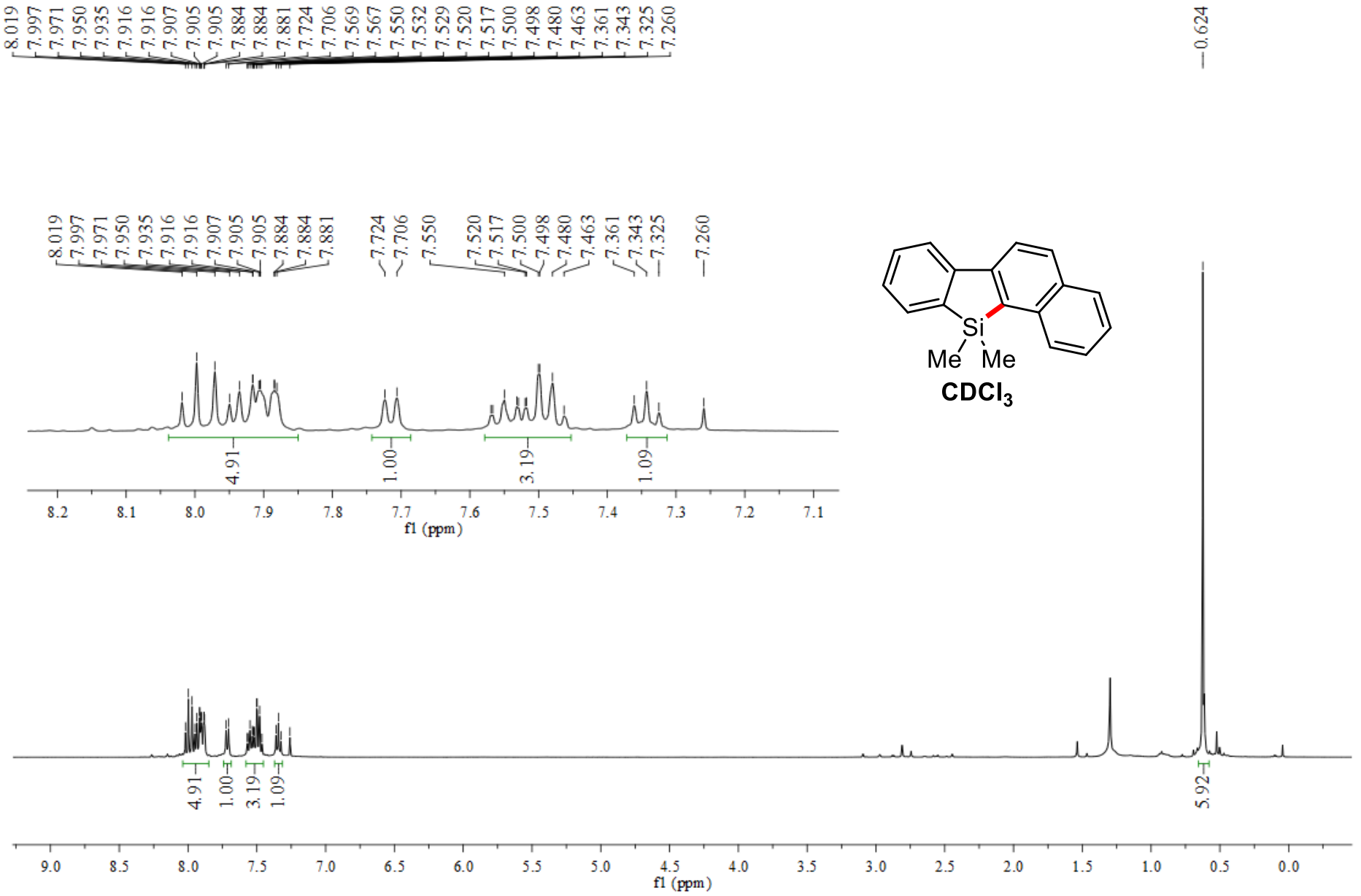

147.63
147.13
139.22
129.29
127.18
121.29
121.07
77.48
77.16
76.84
-3.05
141.37
140.25
139.77
139.22
132.91
131.57
130.39
129.29
128.90
127.50
127.33
127.18
142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126
f1 (ppm)
Si
Me
Me
CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

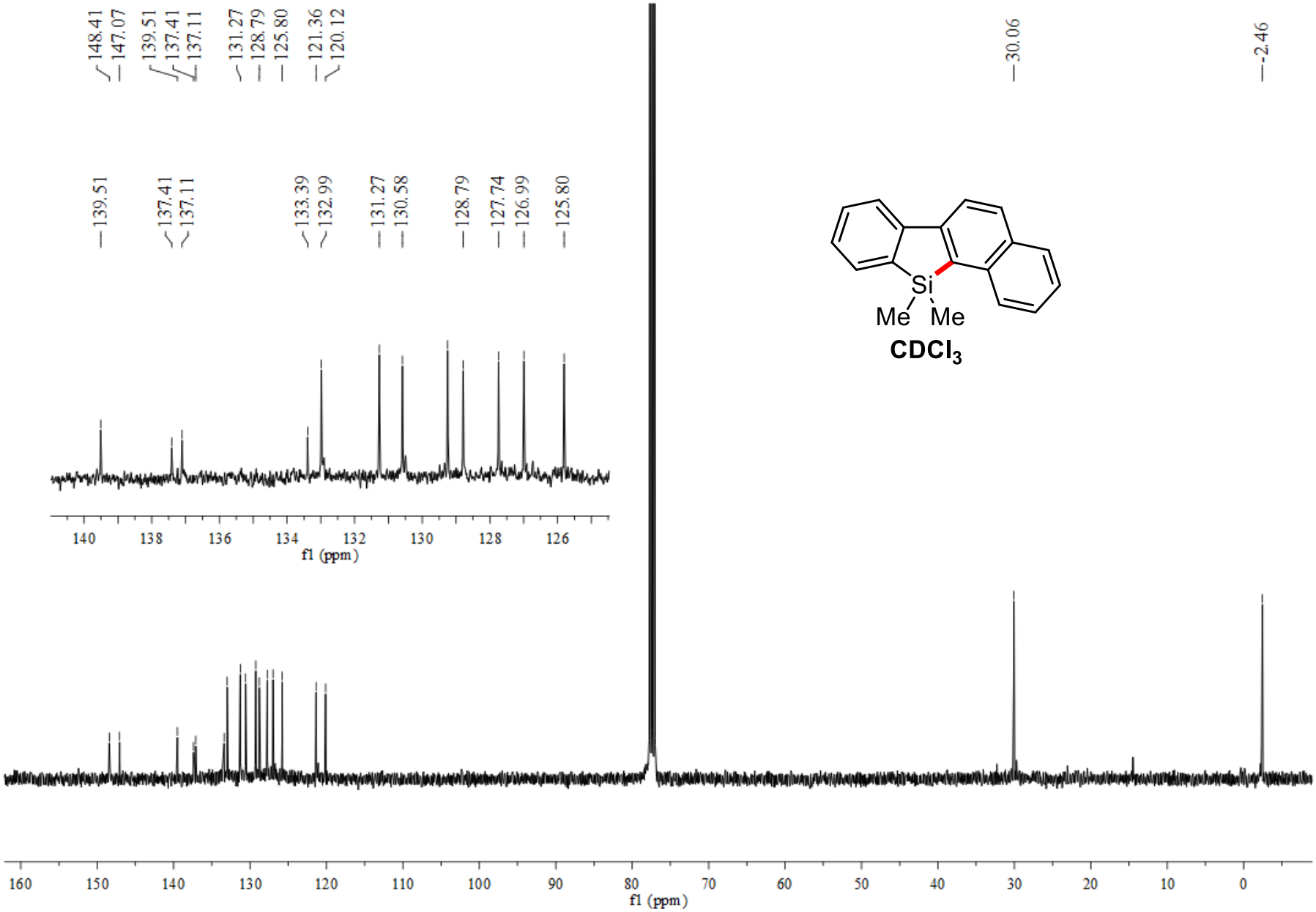

8.086
8.066
7.671
7.670
7.524
7.521
7.507
7.504
7.475
7.472
7.456
7.454
7.437
7.433
7.307
7.290
7.271
7.260
7.253
7.236
7.221
7.204
7.186
2.766
0.414
Me
Si
Me
Me
CDCl3
1.00
1.08
1.19
1.35
2.18
3.34
6.35
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

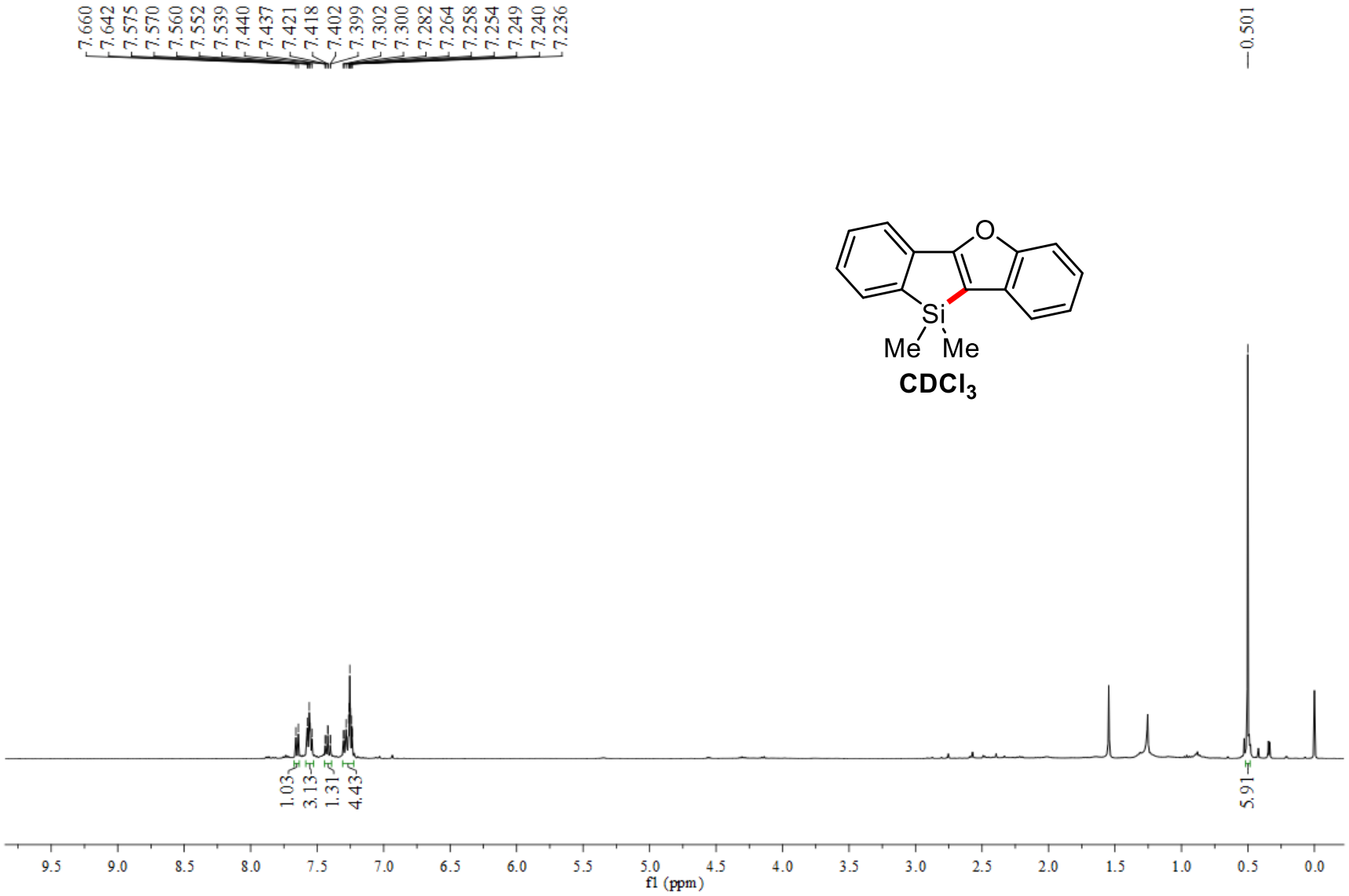

149.84
146.21
140.53
134.46
130.48
130.07
127.03
126.61
125.82
77.48
77.16
76.84
24.43
-3.06
140.65
140.53
134.46
134.38
132.86
130.48
130.07
127.03
126.61
125.82
Me
Si
Me
Me
CDCl3
142
140
138
136
134
132
130
128
126
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

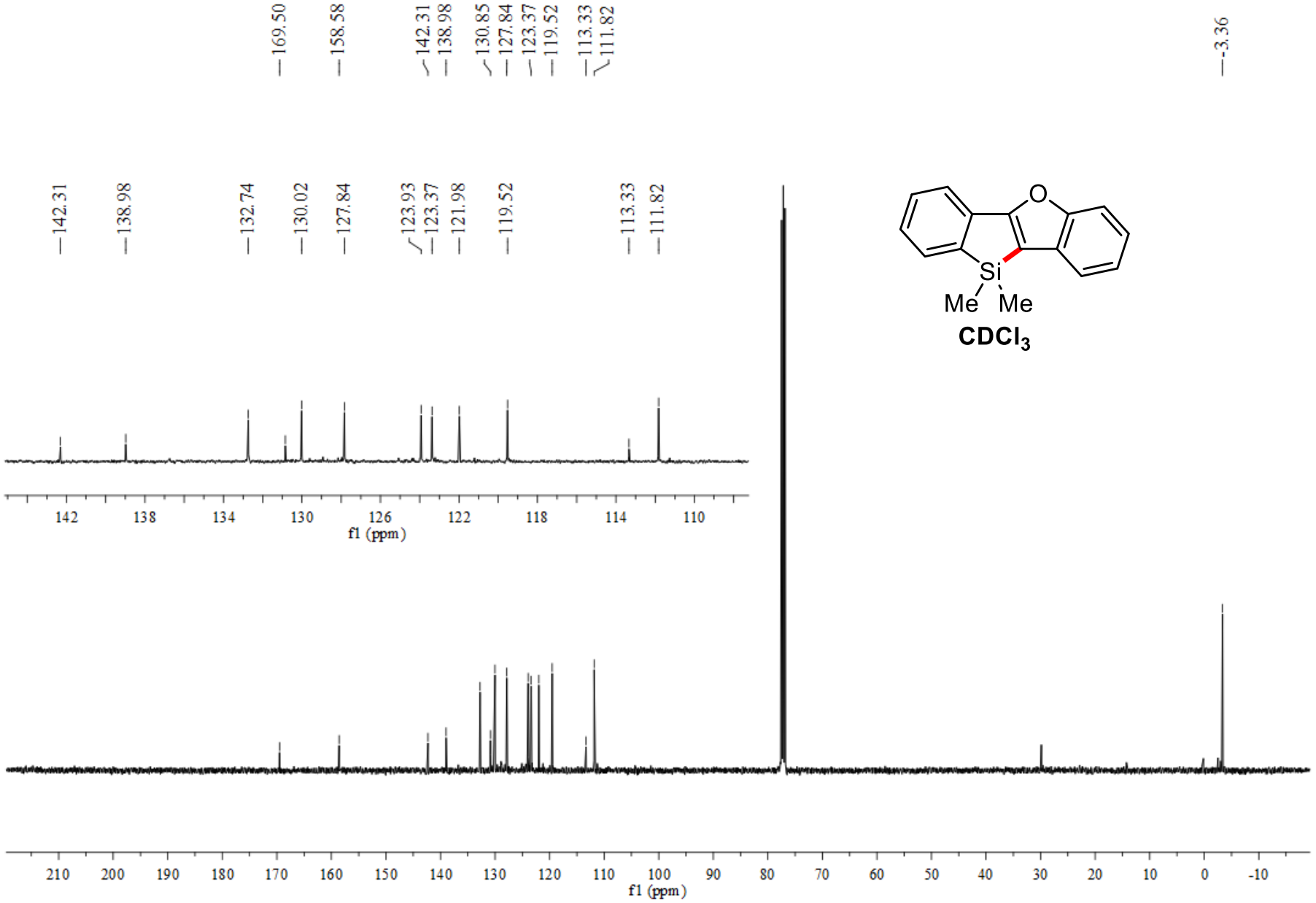

7.799
7.780
7.613
7.595
7.449
7.432
7.430
7.422
7.403
7.384
7.284
7.282
7.265
7.249
6.761
6.742
3.853
0.437
Si
Me
Me
OMe
CDCl3
1.00
1.06
3.33
0.98
1.01
3.06
6.31
f1 (ppm)

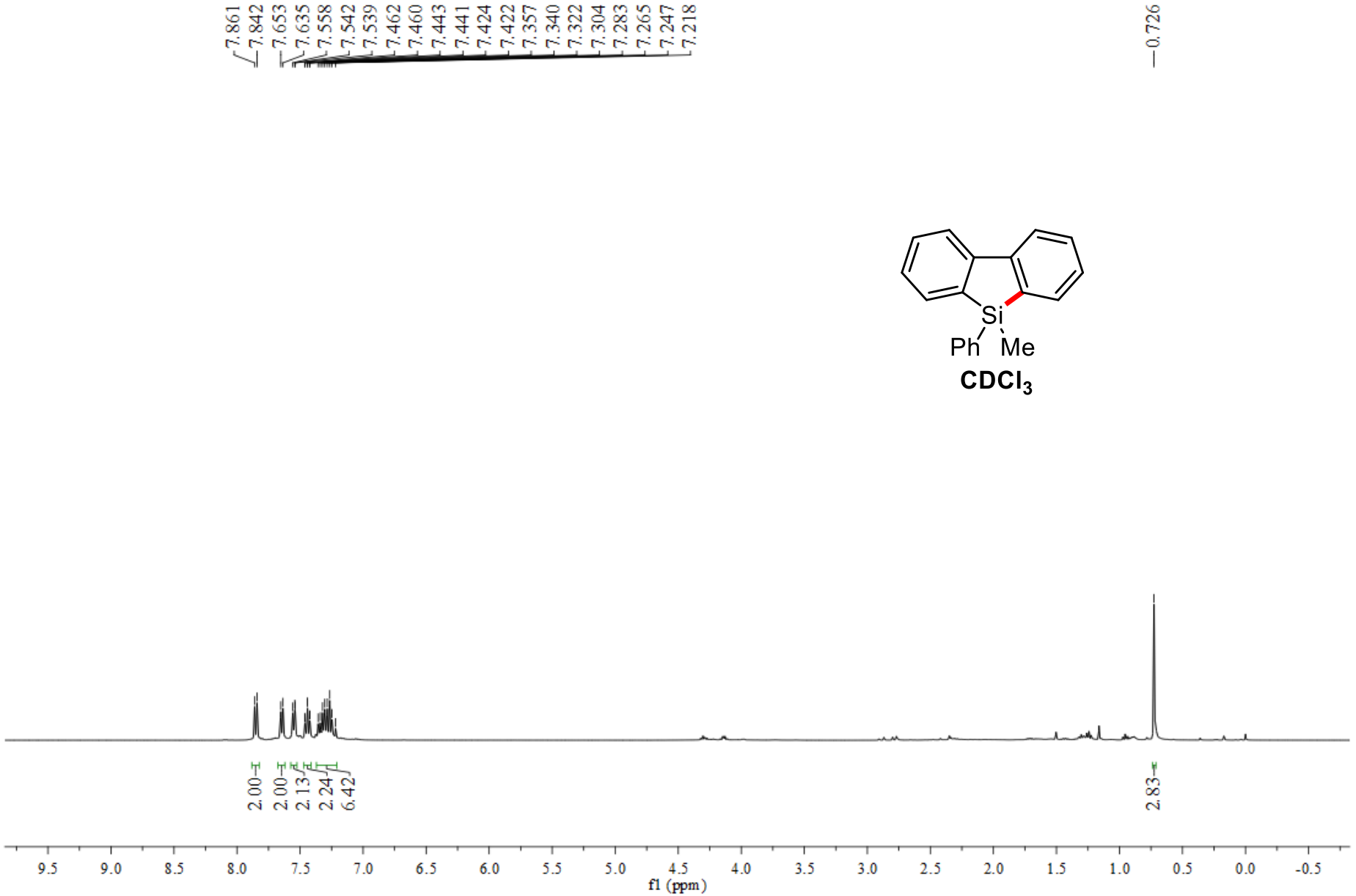

164.19
149.73
147.72
140.02
132.50
129.95
127.55
125.72
121.28
114.07
109.05
77.48
77.16
76.84
55.46
-3.63
140.02
132.74
132.50
129.95
127.55
125.72
121.28
114.07
109.05
Si
Me
Me
OMe
CDCl3
140
135
130
125
120
115
110
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.019
7.997
7.971
7.950
7.935
7.916
7.916
7.907
7.905
7.905
7.884
7.884
7.881
7.724
7.706
7.569
7.567
7.550
7.532
7.529
7.520
7.517
7.500
7.498
7.480
7.463
7.361
7.343
7.325
7.260
0.624
Si
Me
Me
CDCl3
4.91
1.00
3.19
1.09
5.92
f1 (ppm)


148.41
147.07
139.51
137.41
137.11
131.27
128.79
125.80
121.36
120.12
30.06
2.46
139.51
137.41
137.11
133.39
132.99
131.27
130.58
128.79
127.74
126.99
125.80
Si
Me
Me
CDCl3
f1 (ppm)
f1 (ppm)


7.660
7.642
7.575
7.570
7.560
7.552
7.539
7.440
7.437
7.421
7.418
7.402
7.399
7.302
7.300
7.282
7.264
7.258
7.254
7.249
7.240
7.236
0.501
O
Si
Me
Me
CDCl3
1.03
3.13
1.31
4.43
5.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


169.50
158.58
142.31
138.98
130.85
127.84
123.37
119.52
113.33
111.82
-3.36
142.31
138.98
132.74
130.02
127.84
123.93
123.37
121.98
119.52
113.33
111.82
O
Si
Me
Me
CDCl3
142
138
134
130
126
122
118
114
110
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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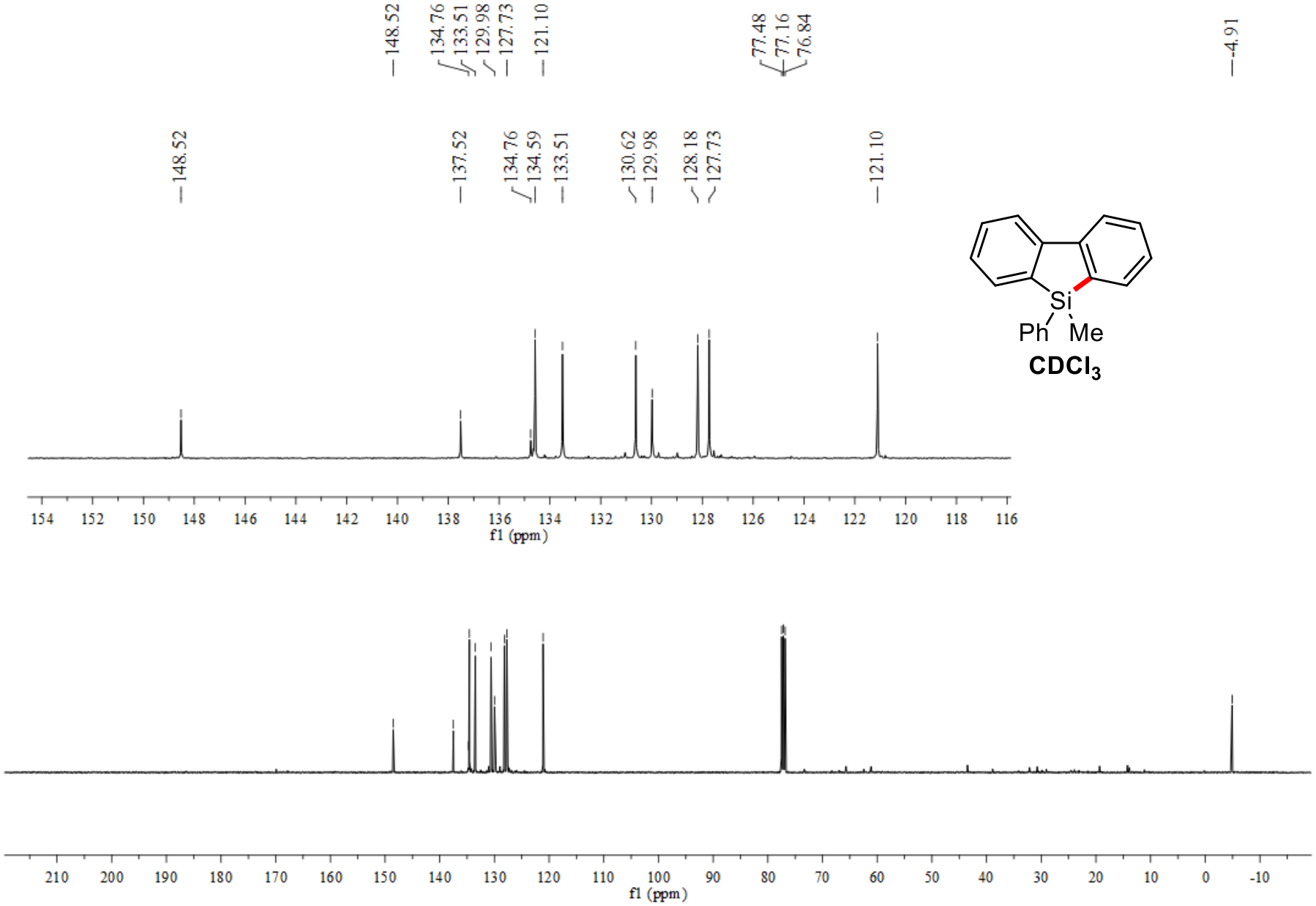
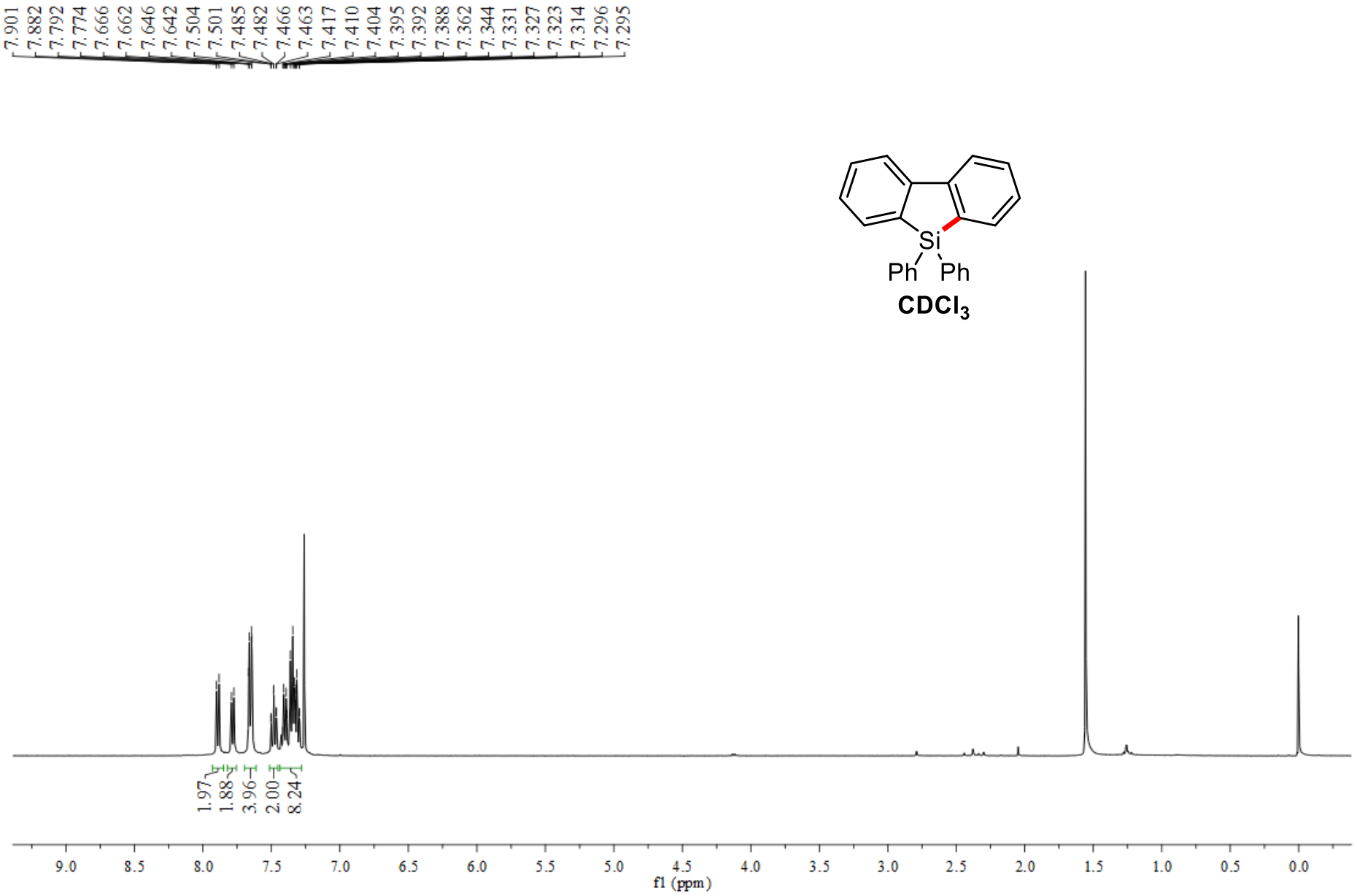
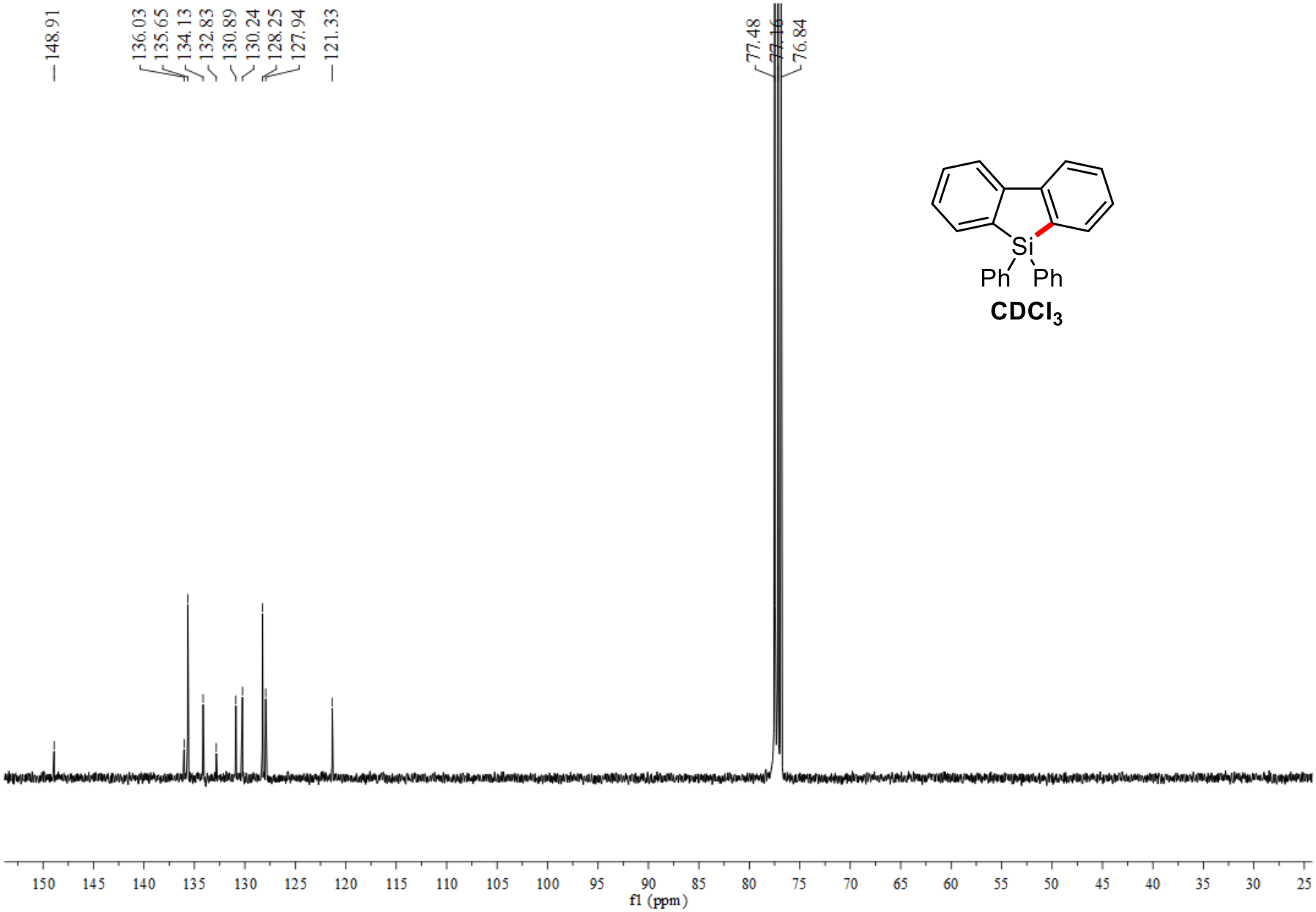
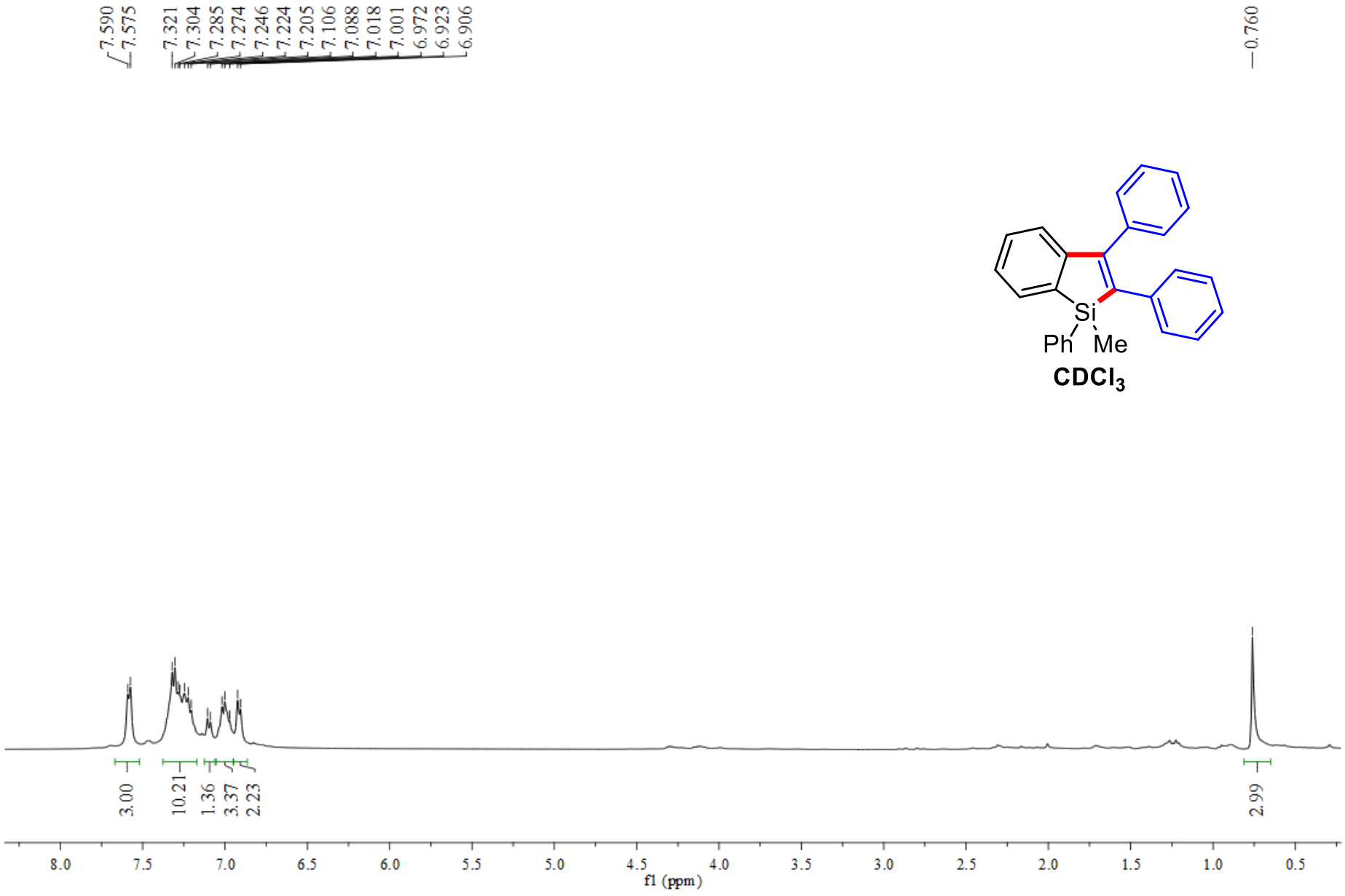
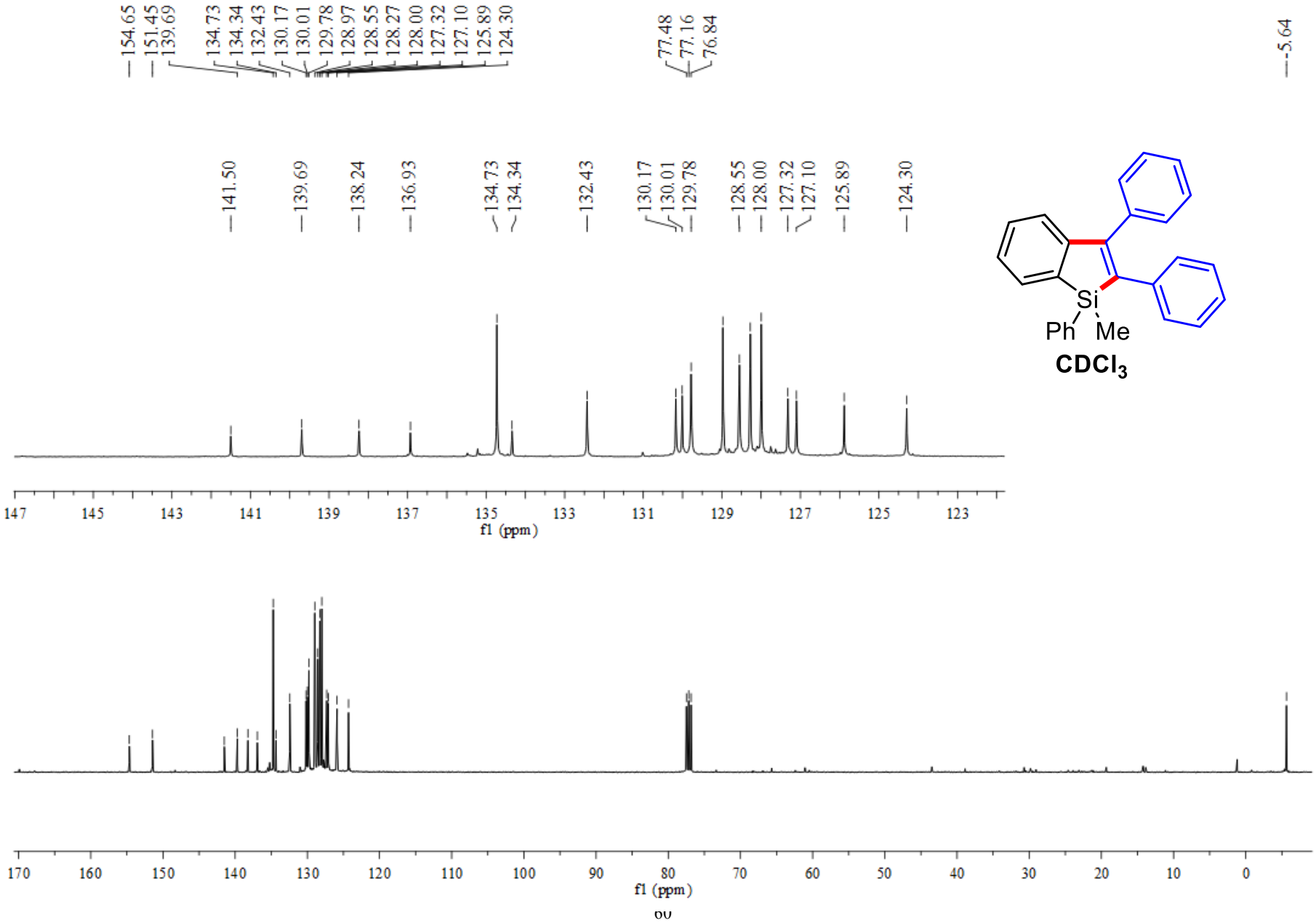
7.653
7.635
7.558
7.542
7.539
7.462
7.460
7.443
7.441
7.424
7.422
7.357
7.340
7.322
7.304
7.283
7.265
7.247
7.218
0.726
Si
Ph
Me
CDCl3
2.00
2.00
2.13
2.24
6.42
2.83
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


148.52
134.76
133.51
129.98
127.73
121.10
77.48
77.16
76.84
-4.91
148.52
137.52
134.76
134.59
133.51
130.62
129.98
128.18
127.73
121.10
Si
Ph
Me
CDCl3
f1 (ppm)
f1 (ppm)


7.901
7.882
7.792
7.774
7.666
7.662
7.646
7.642
7.504
7.501
7.485
7.482
7.466
7.463
7.417
7.410
7.404
7.395
7.392
7.388
7.362
7.344
7.331
7.327
7.323
7.314
7.296
7.295
Si
Ph
Ph
CDCl3
1.97
1.88
3.96
2.00
8.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


148.91
136.03
135.65
134.13
132.83
130.89
130.24
128.25
127.94
121.33
77.48
77.16
76.84
Si
Ph
Ph
CDCl3
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)


7.590
7.575
7.321
7.304
7.285
7.274
7.246
7.224
7.205
7.106
7.088
7.018
7.001
6.972
6.923
6.906
0.760
Si
Ph
Me
CDCl3
3.00
10.21
1.36
3.37
2.23
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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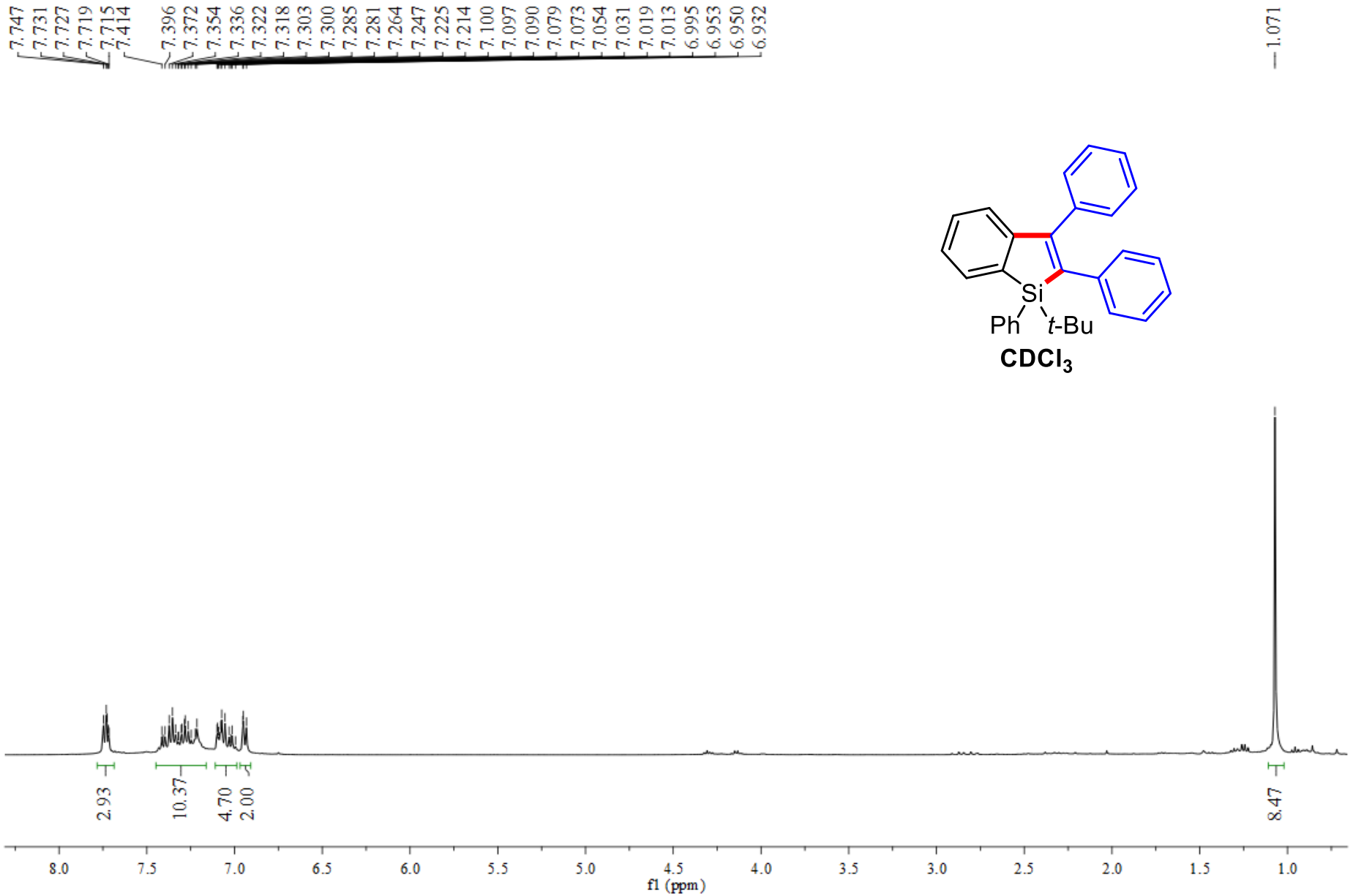
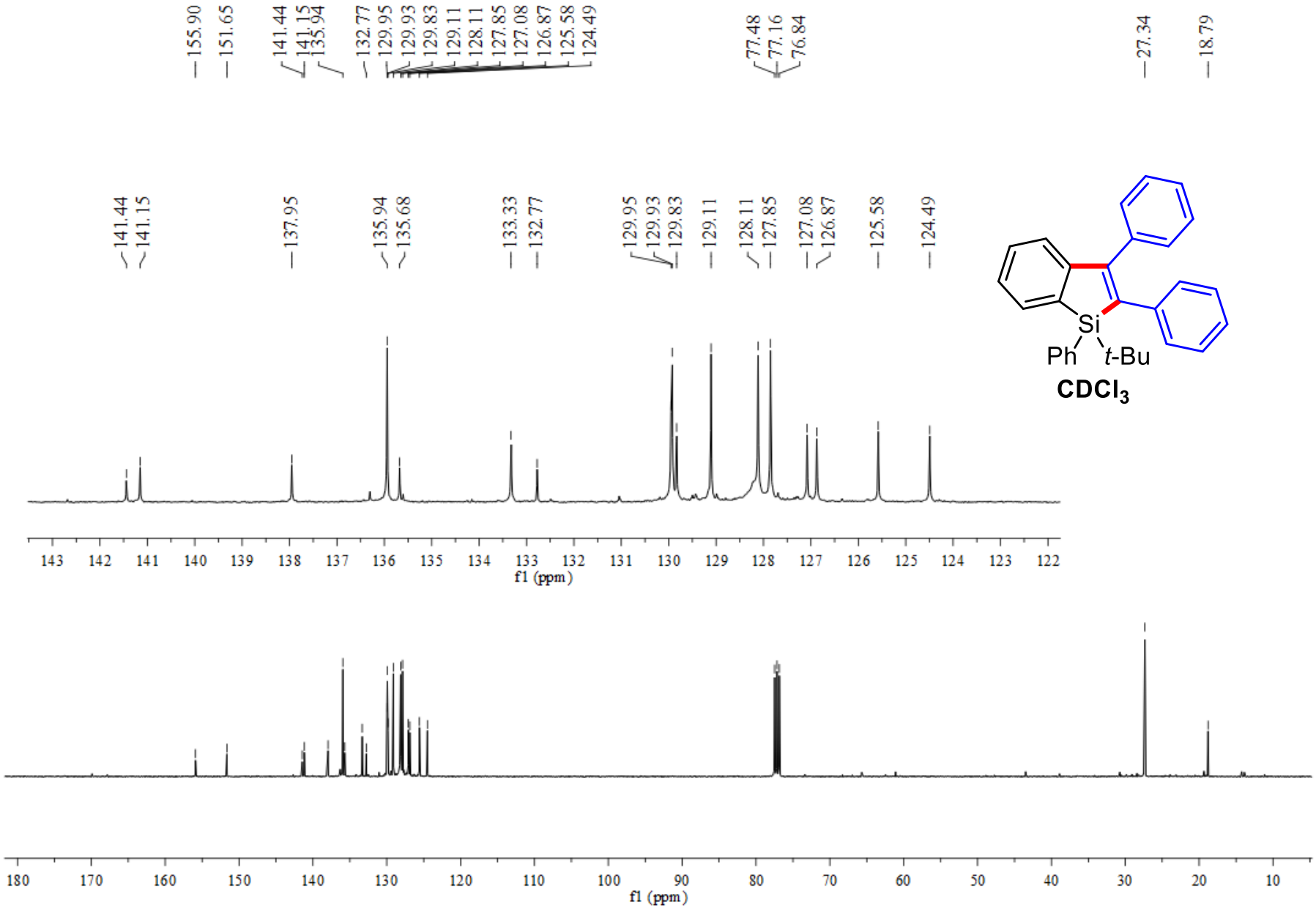
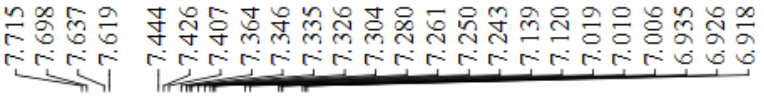
134.73
134.34
132.43
130.17
130.01
129.78
128.97
128.55
128.27
128.00
127.32
127.10
125.89
124.30
77.48
77.16
76.84
-5.64
141.50
139.69
138.24
136.93
134.73
134.34
132.43
130.17
130.01
129.78
128.55
128.00
127.32
127.10
125.89
124.30
Si
Ph
Me
CDCl3
147
145
143
141
139
137
135
133
131
129
127
125
123
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.747
7.731
7.727
7.719
7.715
7.414
7.396
7.372
7.354
7.336
7.322
7.318
7.303
7.300
7.285
7.281
7.264
7.247
7.225
7.214
7.100
7.097
7.090
7.079
7.073
7.054
7.031
7.019
7.013
6.995
6.953
6.950
6.932
1.071
Si
Ph
t-Bu
CDCl3
2.93
10.37
4.70
2.00
8.47
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


155.90
151.65
141.44
141.15
135.94
132.77
129.95
129.93
129.83
129.11
128.11
127.85
127.08
126.87
125.58
124.49
77.48
77.16
76.84
27.34
18.79
141.44
141.15
137.95
135.94
135.68
133.33
132.77
129.95
129.93
129.83
129.11
128.11
127.85
127.08
126.87
125.58
124.49
Si
Ph
t-Bu
CDCl3
143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.715
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7.619
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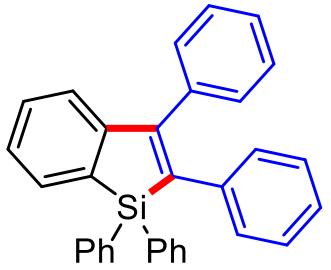
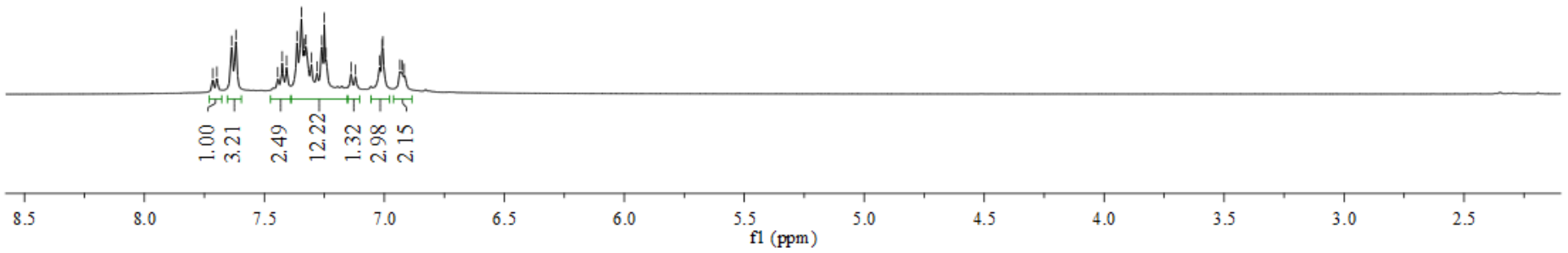
7.426
7.407
7.364
7.346
7.335
7.326
7.304
7.280
7.261
7.250
7.243
7.139
7.120
7.019
7.010
7.006
6.935
6.926
6.918


Si
Ph
Ph

$CDCl_3$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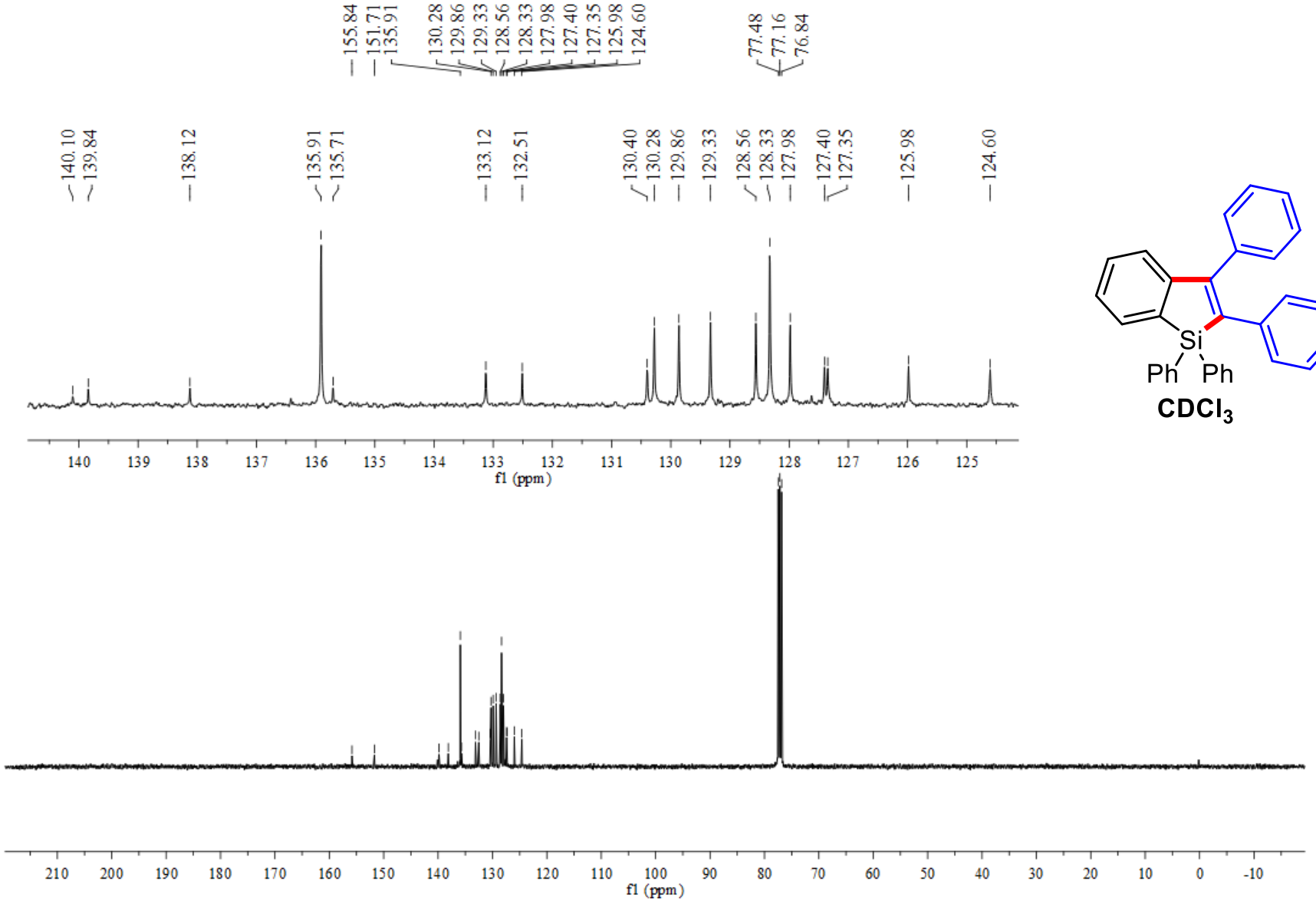
3.21
2.49
12.22
1.32
2.98
2.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)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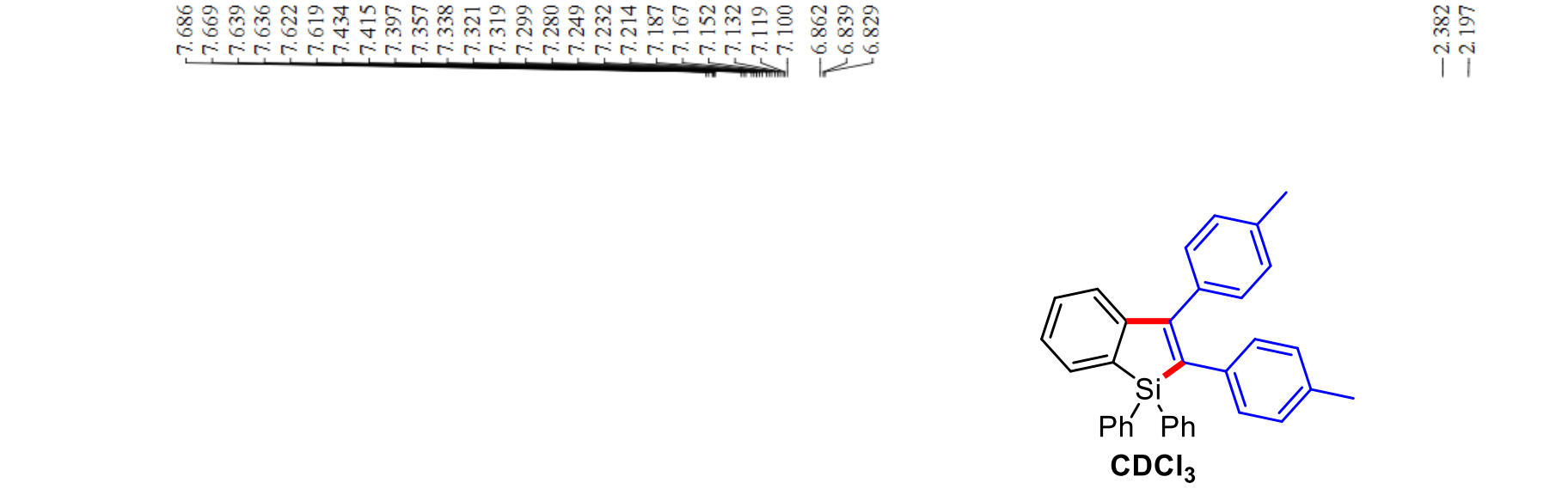
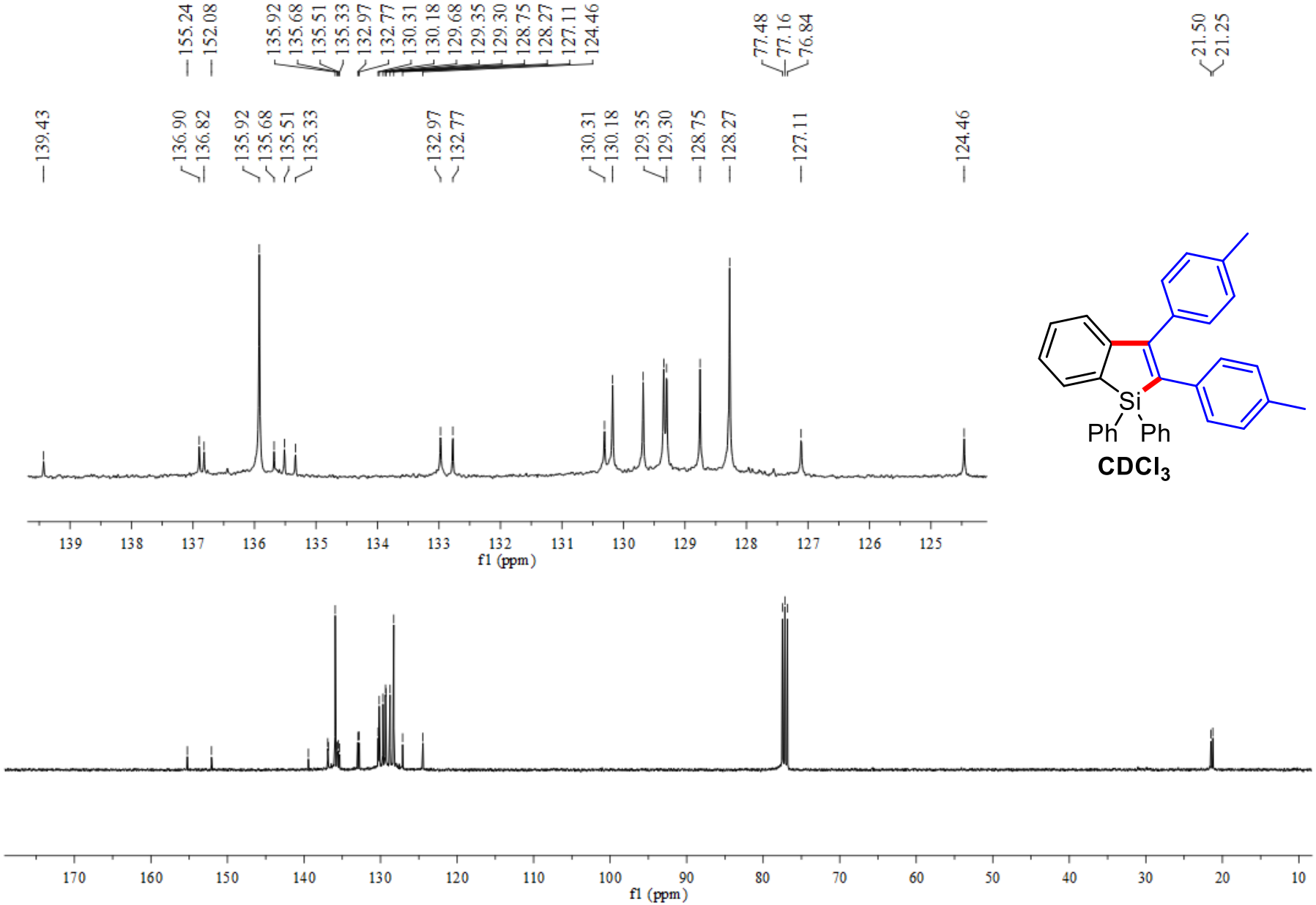
151.71
135.91
130.28
129.86
129.33
128.56
128.33
127.98
127.40
127.35
125.98
124.60
77.48
77.16
76.84
140.10
139.84
138.12
135.91
135.71
133.12
132.51
130.40
130.28
129.86
129.33
128.56
128.33
127.98
127.40
127.35
125.98
124.60
f1 (ppm)
f1 (ppm)
Si
Ph
Ph
CDCl3


7.686
7.669
7.639
7.636
7.622
7.619
7.434
7.415
7.397
7.357
7.338
7.321
7.319
7.299
7.280
7.249
7.232
7.214
7.187
7.167
7.152
7.132
7.119
7.100
6.862
6.839
6.829
2.382
2.197
Si
Ph
Ph
CDCl3
1.06
3.26
8.28
0.94
5.05
4.00
2.88
2.92
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)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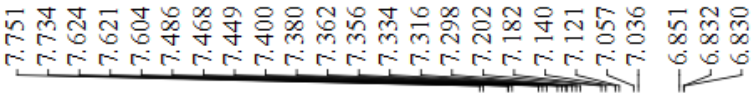
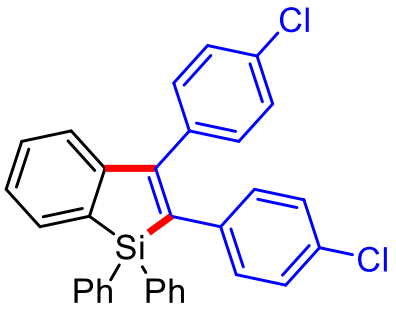
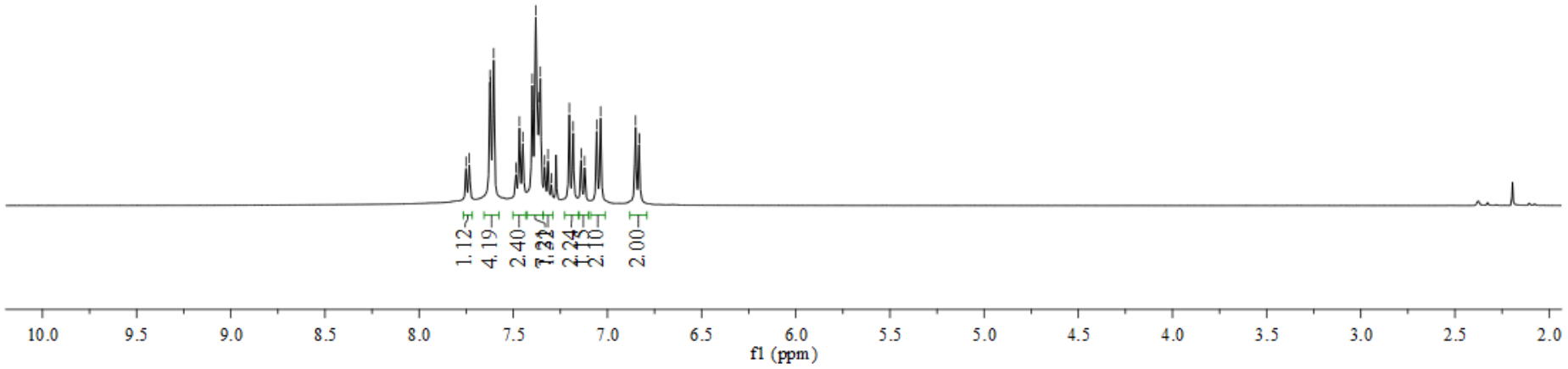
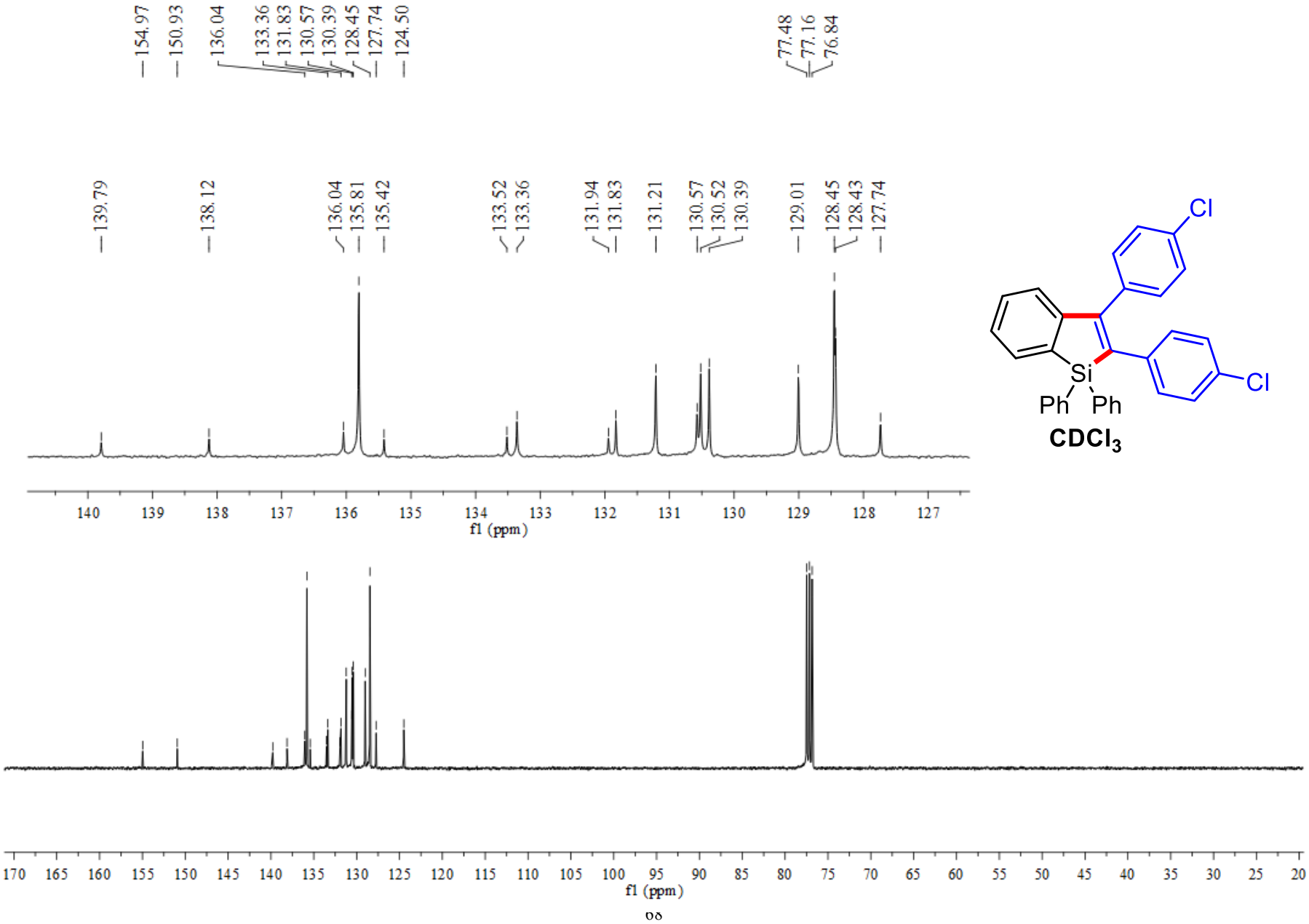
152.08
135.92
135.68
135.51
135.33
132.97
132.77
130.31
130.18
129.68
129.35
129.30
128.75
128.27
127.11
124.46
77.48
77.16
76.84
21.50
21.25
139.43
136.90
136.82
135.92
135.68
135.51
135.33
132.97
132.77
130.31
130.18
129.35
129.30
128.75
128.27
127.11
124.46
f1 (ppm)
Si
Ph
Ph
CDCl3

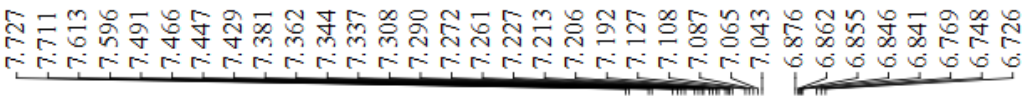

7.751
7.734
7.624
7.621
7.604
7.486
7.468
7.449
7.400
7.380
7.362
7.356
7.334
7.316
7.298
7.202
7.182
7.140
7.121
7.057
7.036
6.851
6.832
6.830

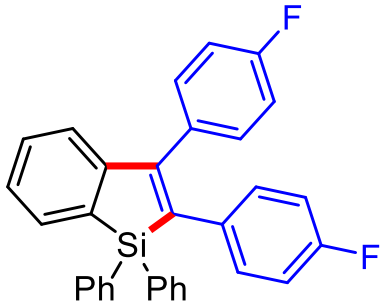

Cl
Si
Ph
Ph
Cl

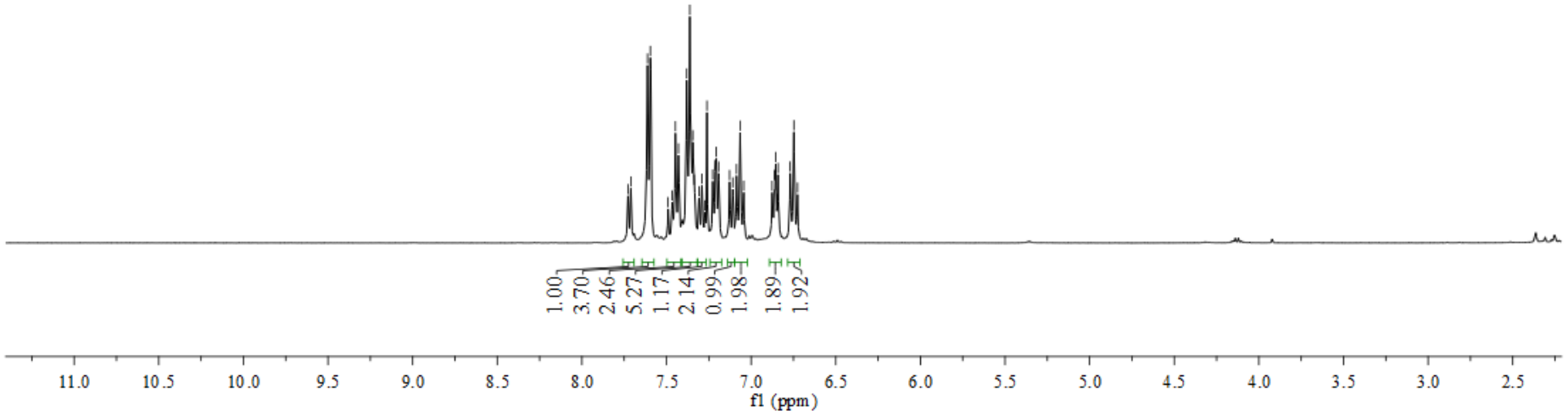
$CDCl_3$


1.12
4.19
2.40
2.24
2.10
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


154.97
150.93
136.04
133.36
131.83
130.57
130.39
128.45
127.74
124.50
77.48
77.16
76.84
139.79
138.12
136.04
135.81
135.42
133.52
133.36
131.94
131.83
131.21
130.57
130.52
130.39
129.01
128.45
128.43
127.74
f1 (ppm)
Cl
Si
Ph
Ph
Cl
CDCl3
f1 (ppm)


7.727
7.711
7.613
7.596
7.491
7.466
7.447
7.429
7.381
7.362
7.344
7.337
7.308
7.290
7.272
7.261
7.227
7.213
7.206
7.192
7.127
7.108
7.087
7.065
7.043
6.876
6.862
6.855
6.846
6.841
6.769
6.748
6.726


F
Si
Ph
Ph
F
CDCl3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3.70
2.46
5.27
1.17
2.14
0.99
1.98
1.89
1.92
11.0
10.5
10.0
9.5
9.0
8.5
8.0
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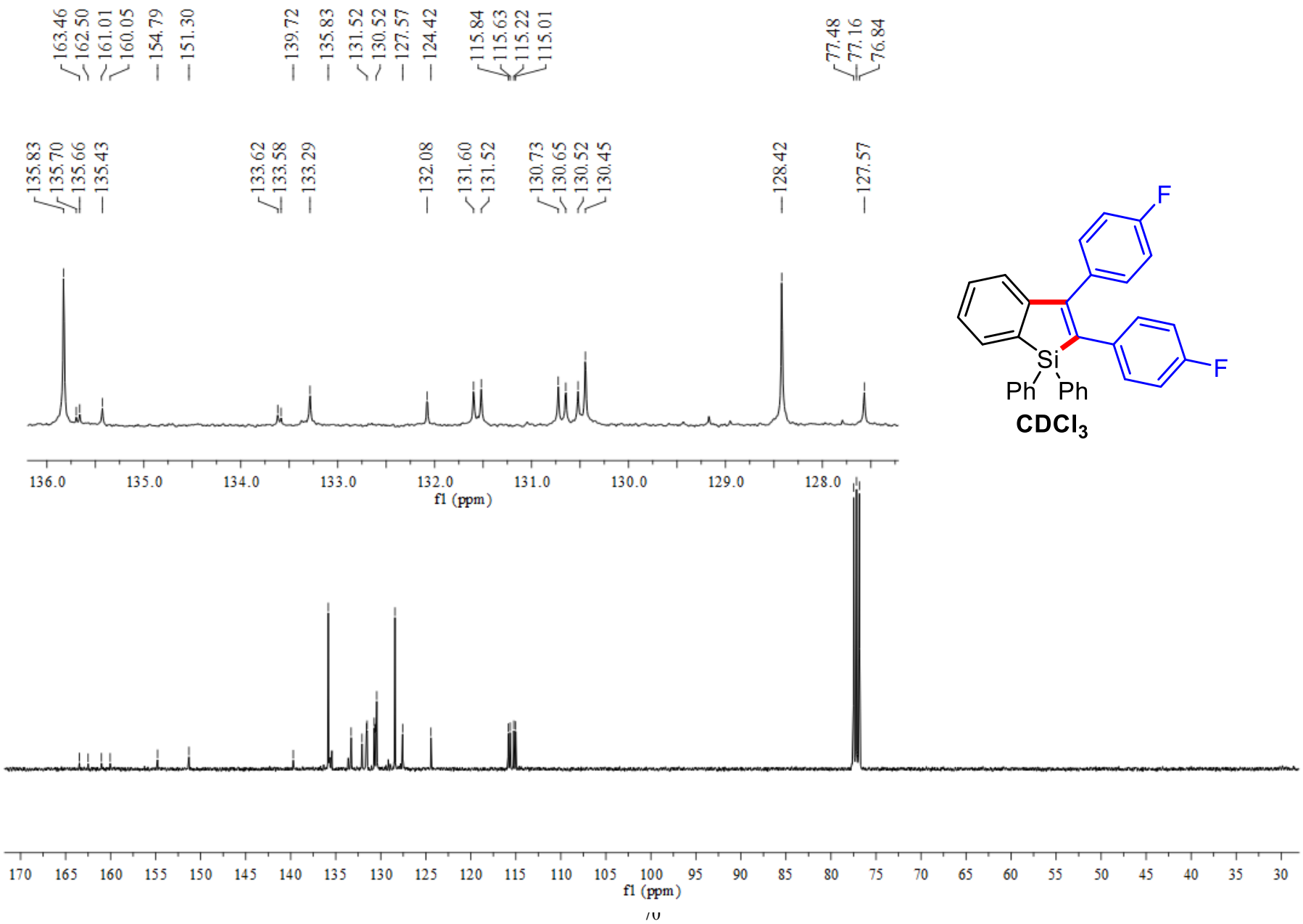
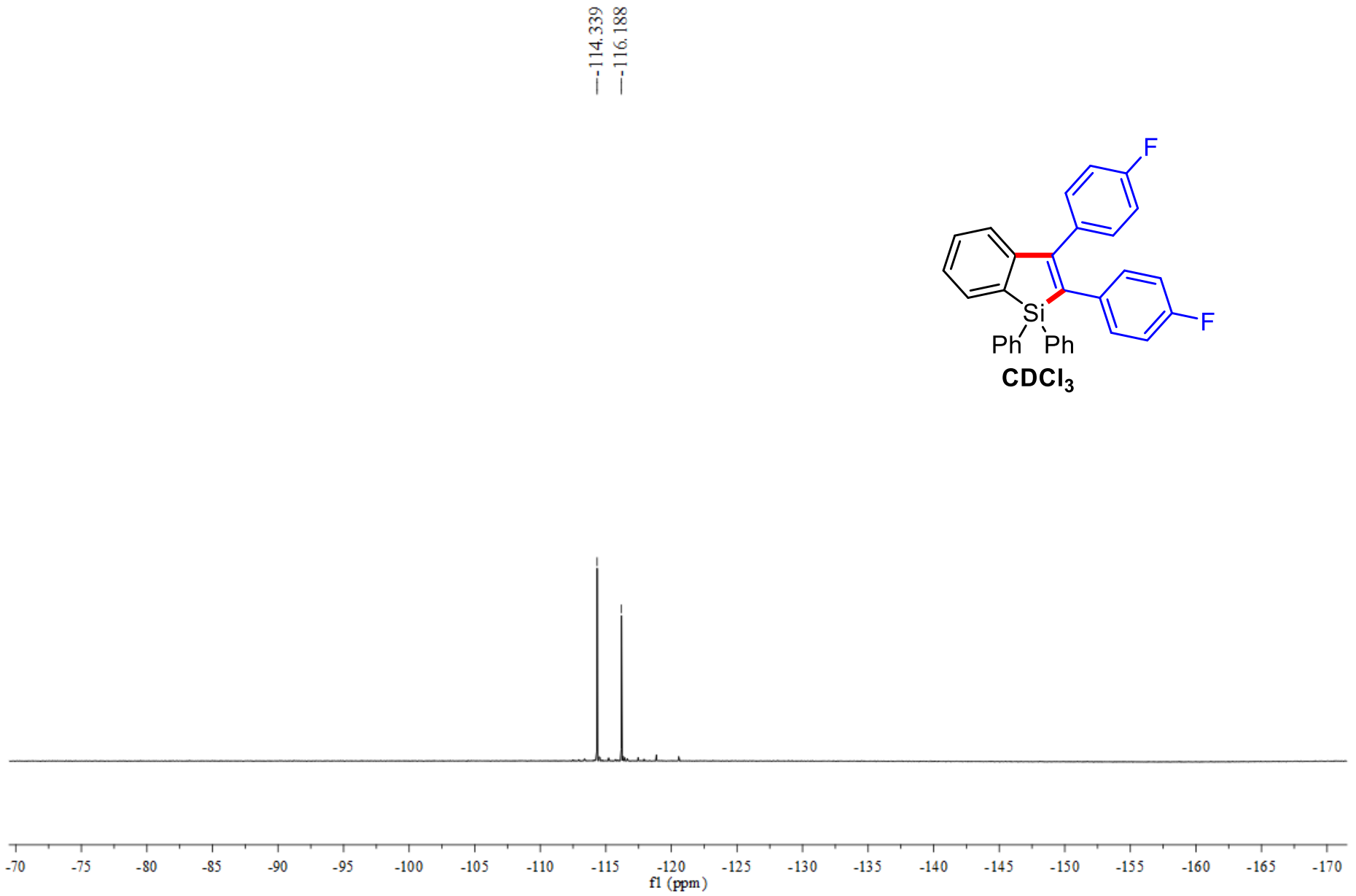
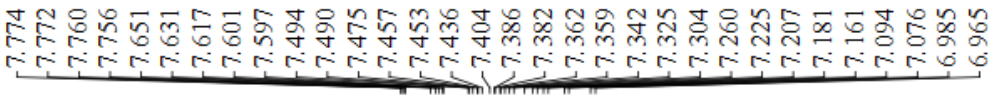
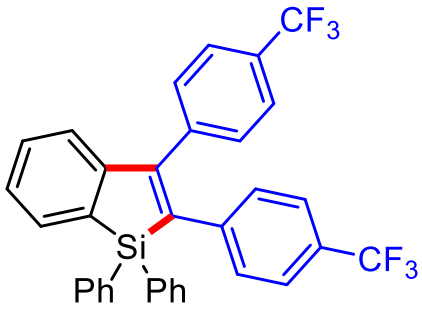
4.0
3.5
3.0
2.5
f1 (ppm)

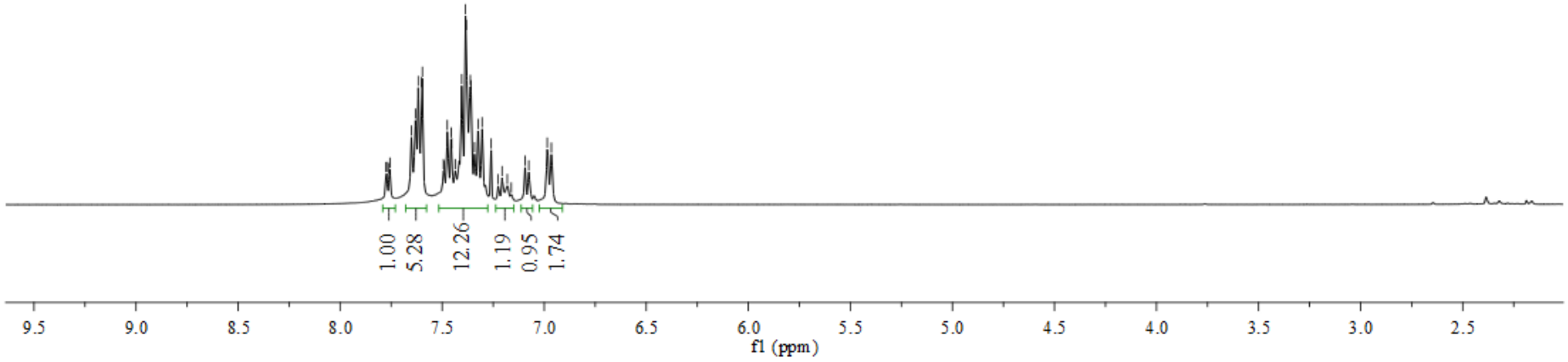

163.46
162.50
161.01
160.05
154.79
151.30
139.72
135.83
131.52
130.52
127.57
124.42
115.84
115.63
115.22
115.01
77.48
77.16
76.84
135.83
135.70
135.66
135.43
133.62
133.58
133.29
132.08
131.60
131.52
130.73
130.65
130.52
130.45
128.42
127.57
F
F
Si
Ph
Ph
CDCl3
136.0
135.0
134.0
133.0
132.0
131.0
130.0
129.0
128.0
f1 (ppm)
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)

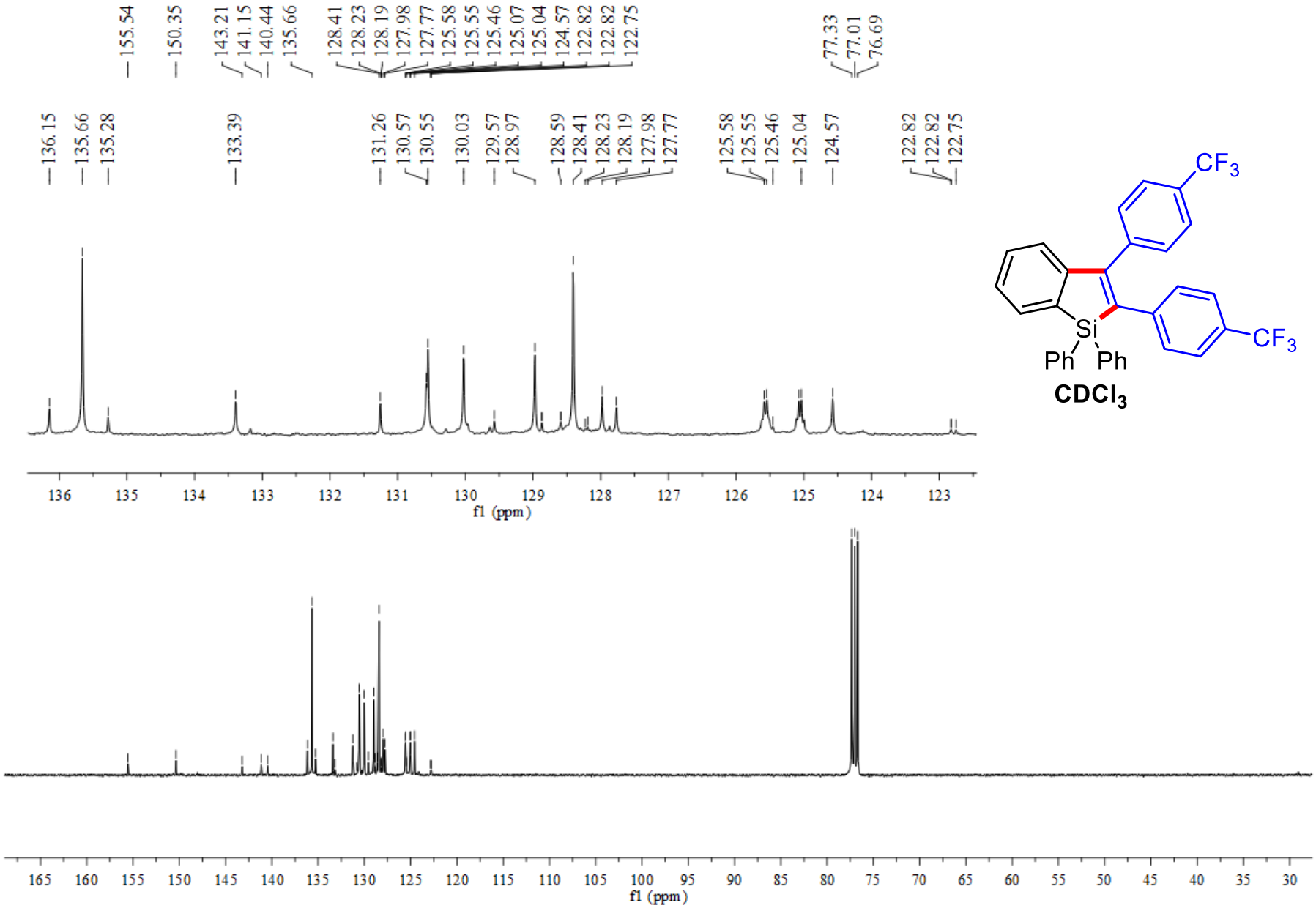

-114.339
-116.188
F
F
Si
Ph
Ph
CDCl3
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
f1 (ppm)

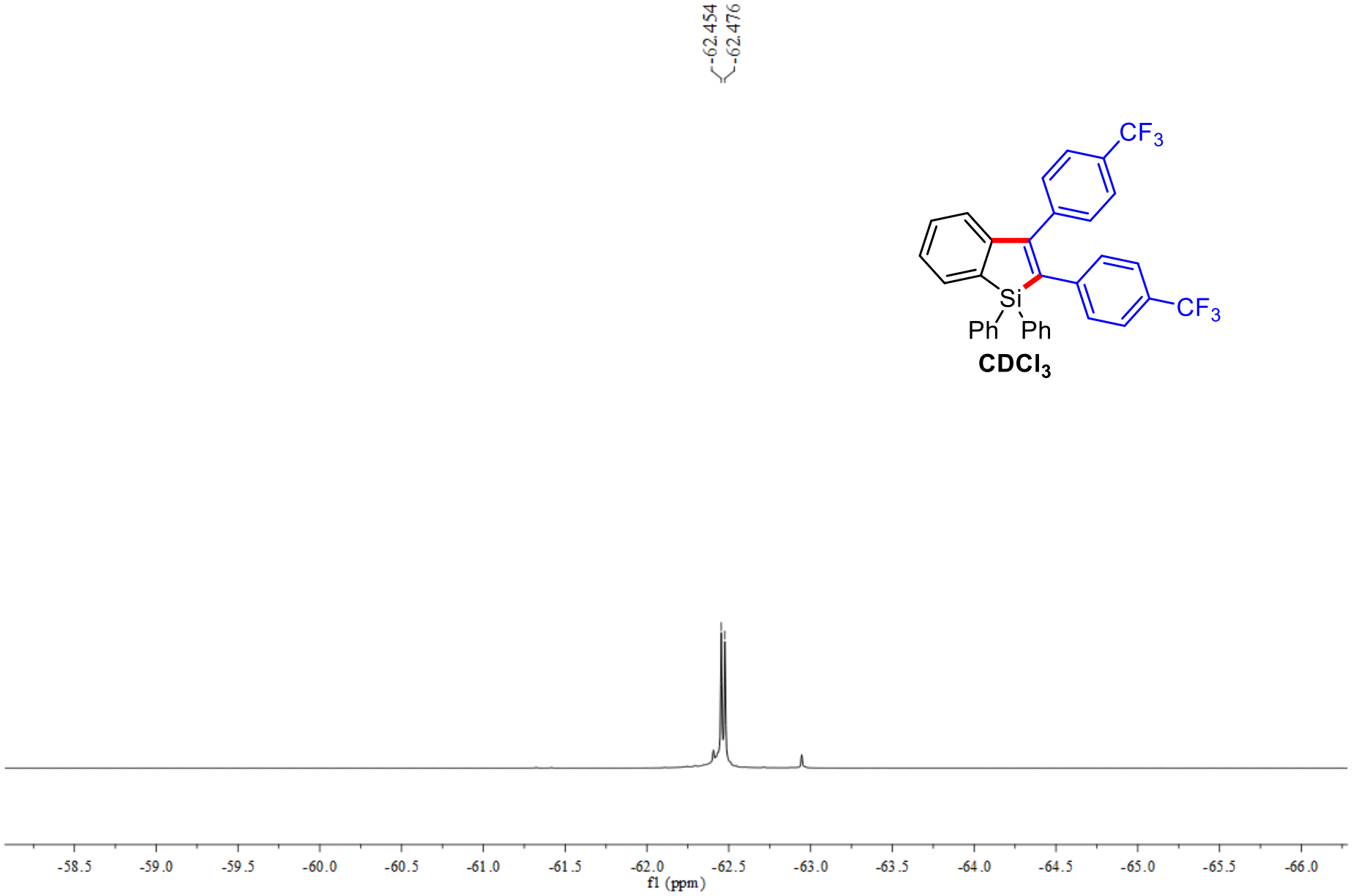

7.774
7.772
7.760
7.756
7.651
7.631
7.617
7.601
7.597
7.494
7.490
7.475
7.457
7.453
7.436
7.404
7.386
7.382
7.362
7.359
7.342
7.325
7.304
7.260
7.225
7.207
7.181
7.161
7.094
7.076
6.985
6.965

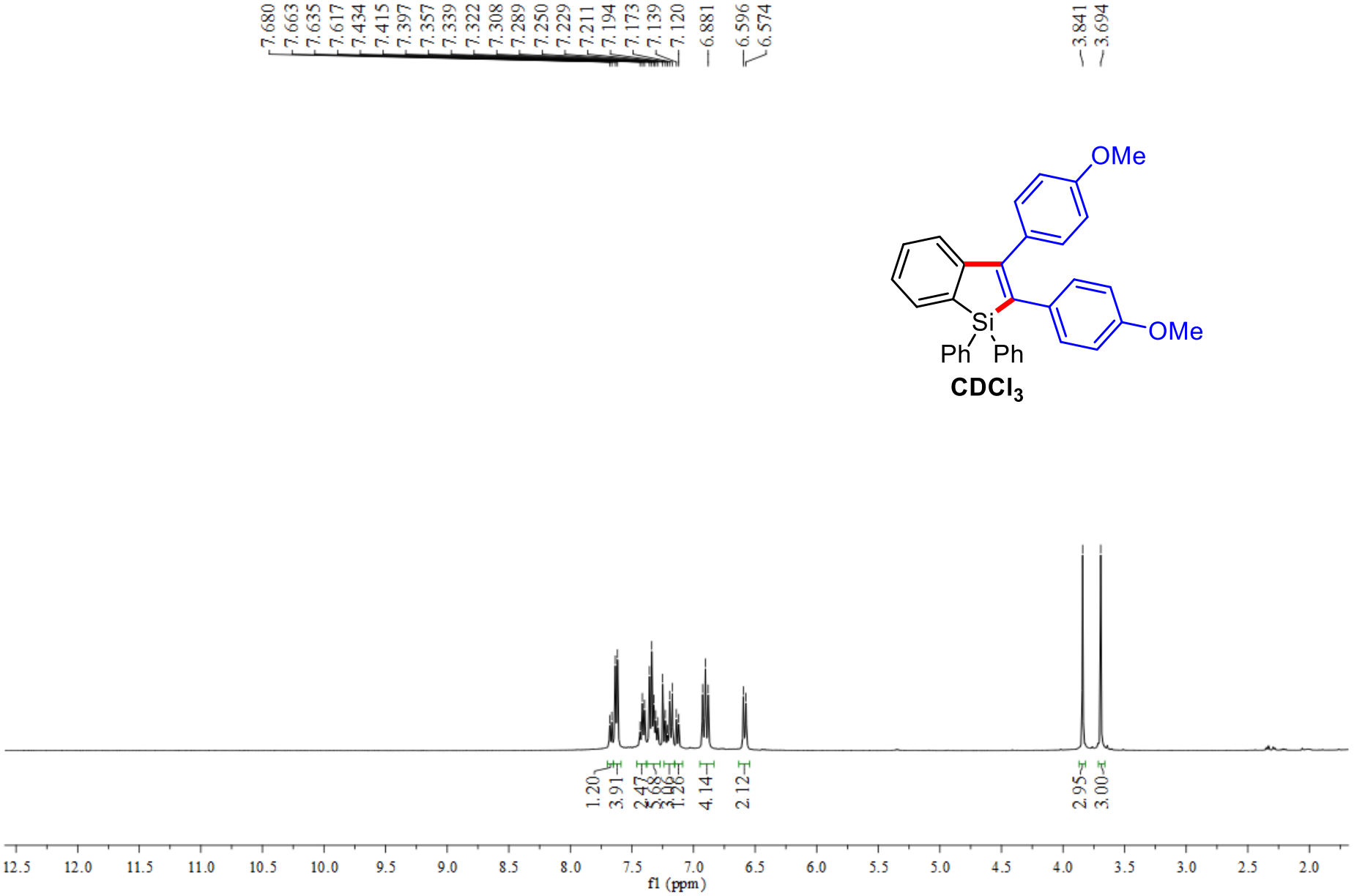

CF3
Si
Ph
Ph
CF3

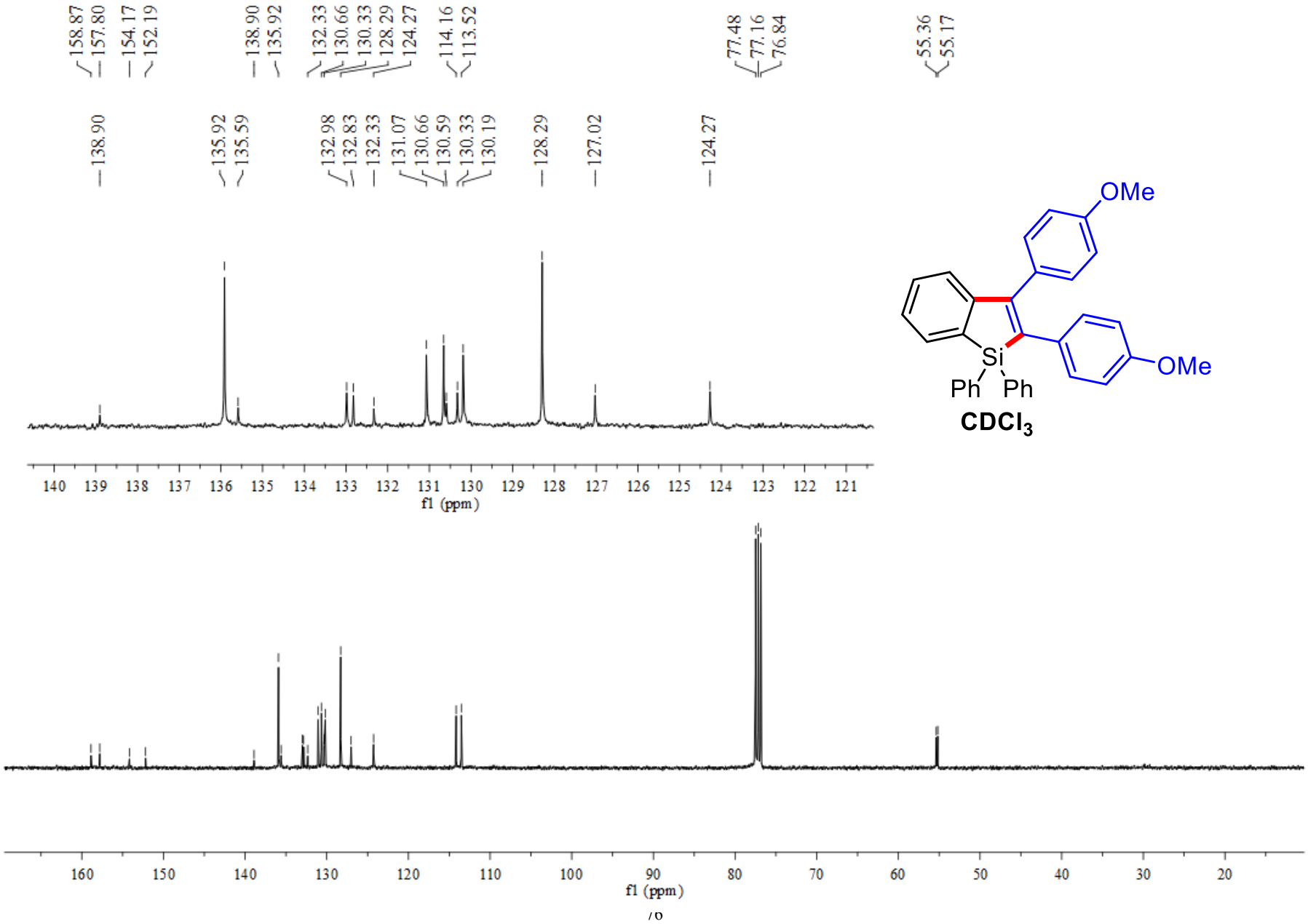
$CDCl_3$

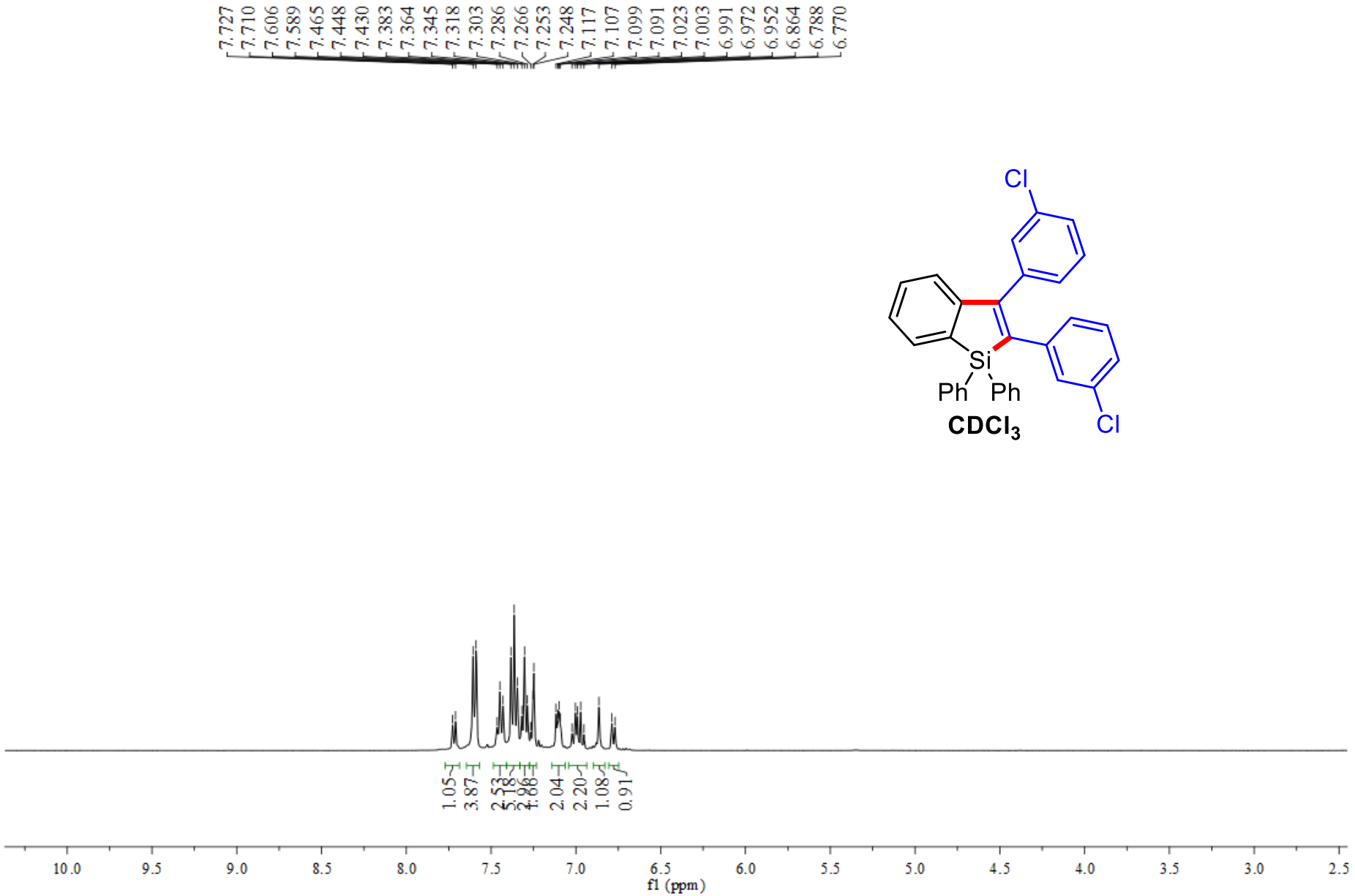

1.00
5.28
12.26
1.19
0.95
1.74
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)


155.54
150.35
143.21
141.15
140.44
135.66
128.41
128.23
128.19
127.98
127.77
125.58
125.55
125.46
125.07
125.04
124.57
122.82
122.82
122.75
77.33
77.01
76.69
136.15
135.66
135.28
133.39
131.26
130.57
130.55
130.03
129.57
128.97
128.59
128.41
128.23
128.19
127.98
127.77
125.58
125.55
125.46
125.04
124.57
122.82
122.82
122.75
136
135
134
133
132
131
130
129
128
127
126
125
124
123
f1 (ppm)
CF3
CF3
Si
Ph
Ph
CDCl3
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)

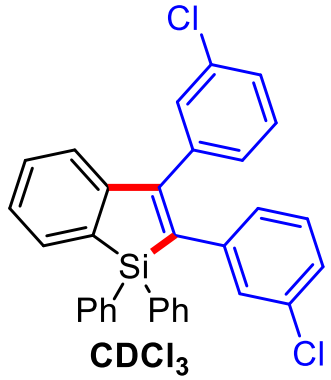

-62.454
-62.476
CF3
CF3
Si
Ph
Ph
CDCl3
-58.5
-59.0
-59.5
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
f1 (ppm)


7.680
7.663
7.635
7.617
7.434
7.415
7.397
7.357
7.339
7.322
7.308
7.289
7.250
7.229
7.211
7.194
7.173
7.139
7.120
6.881
6.596
6.574
3.841
3.694
OMe
OMe
Si
Ph
Ph
CDCl3
1.20
3.91
2.47
2.68
3.46
1.28
4.14
2.12
2.95
3.00
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

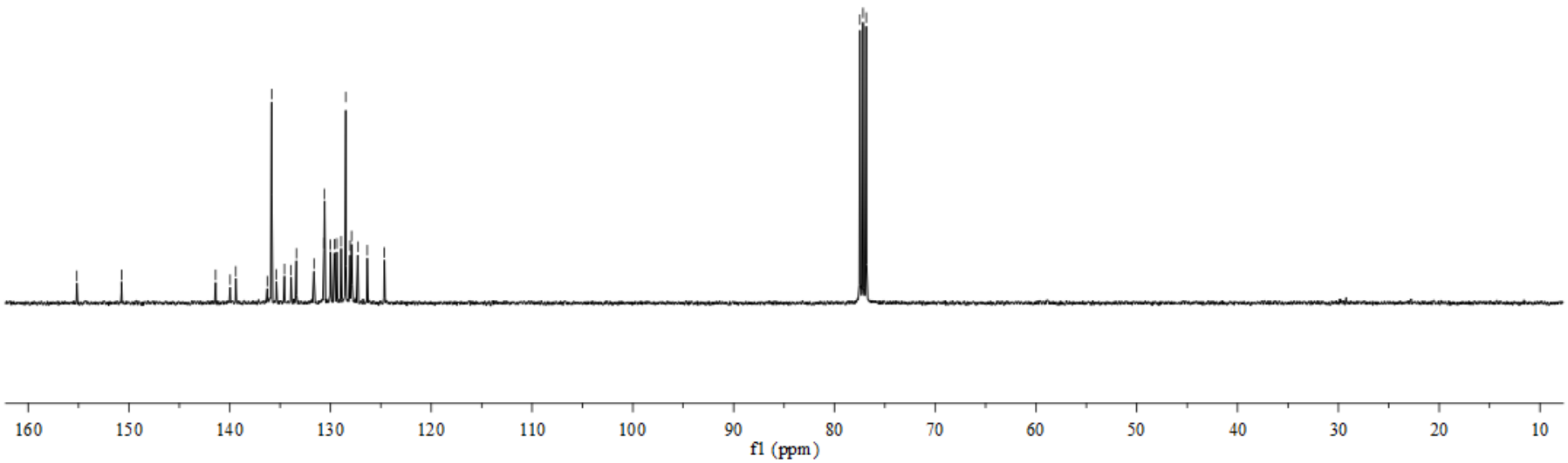

158.87
157.80
154.17
152.19
138.90
135.92
132.33
130.66
130.33
128.29
124.27
114.16
113.52
77.48
77.16
76.84
55.36
55.17
138.90
135.92
135.59
132.98
132.83
132.33
131.07
130.66
130.59
130.33
130.19
128.29
127.02
124.27
OMe
OMe
Si
Ph
Ph
CDCl3
f1 (ppm)
f1 (ppm)

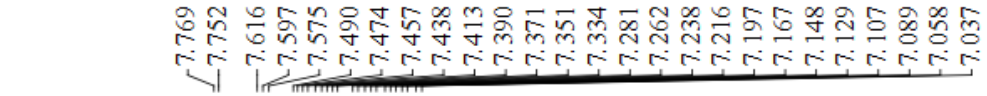

7.727
7.710
7.606
7.589
7.465
7.448
7.430
7.383
7.364
7.345
7.318
7.303
7.286
7.266
7.253
7.248
7.117
7.107
7.099
7.091
7.023
7.003
6.991
6.972
6.952
6.864
6.788
6.770
Cl
Si
Ph
Ph
Cl
CDCl3
1.05
3.87
2.53
5.18
4.86
2.04
2.20
1.08
0.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

155.17
150.72
141.40
139.96
139.39
135.83
130.64
130.59
130.01
129.61
129.37
128.94
128.48
128.06
127.91
127.30
126.35
124.66
77.48
77.16
76.84



$CDCl_3$

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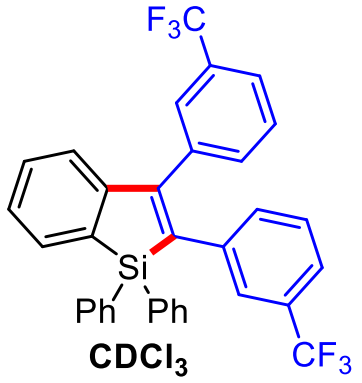
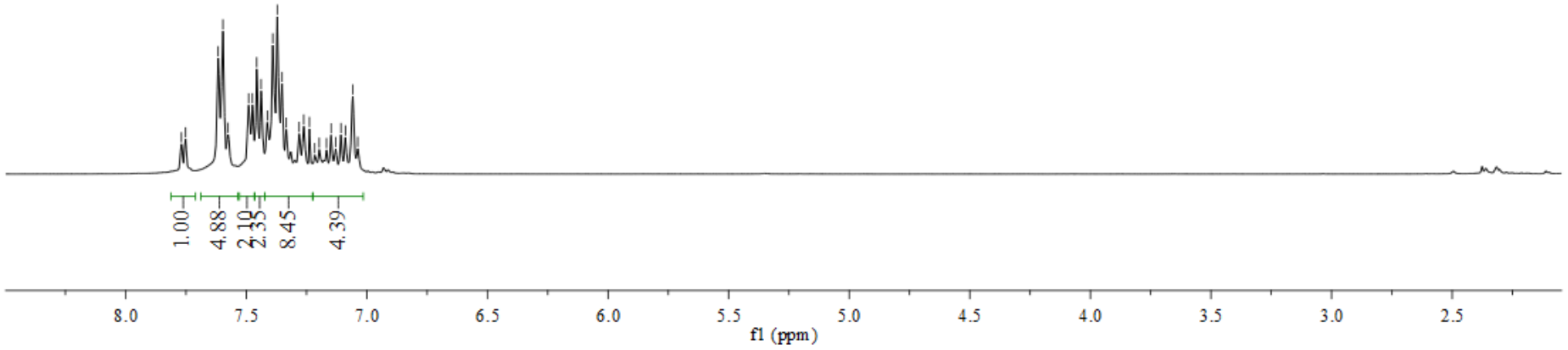
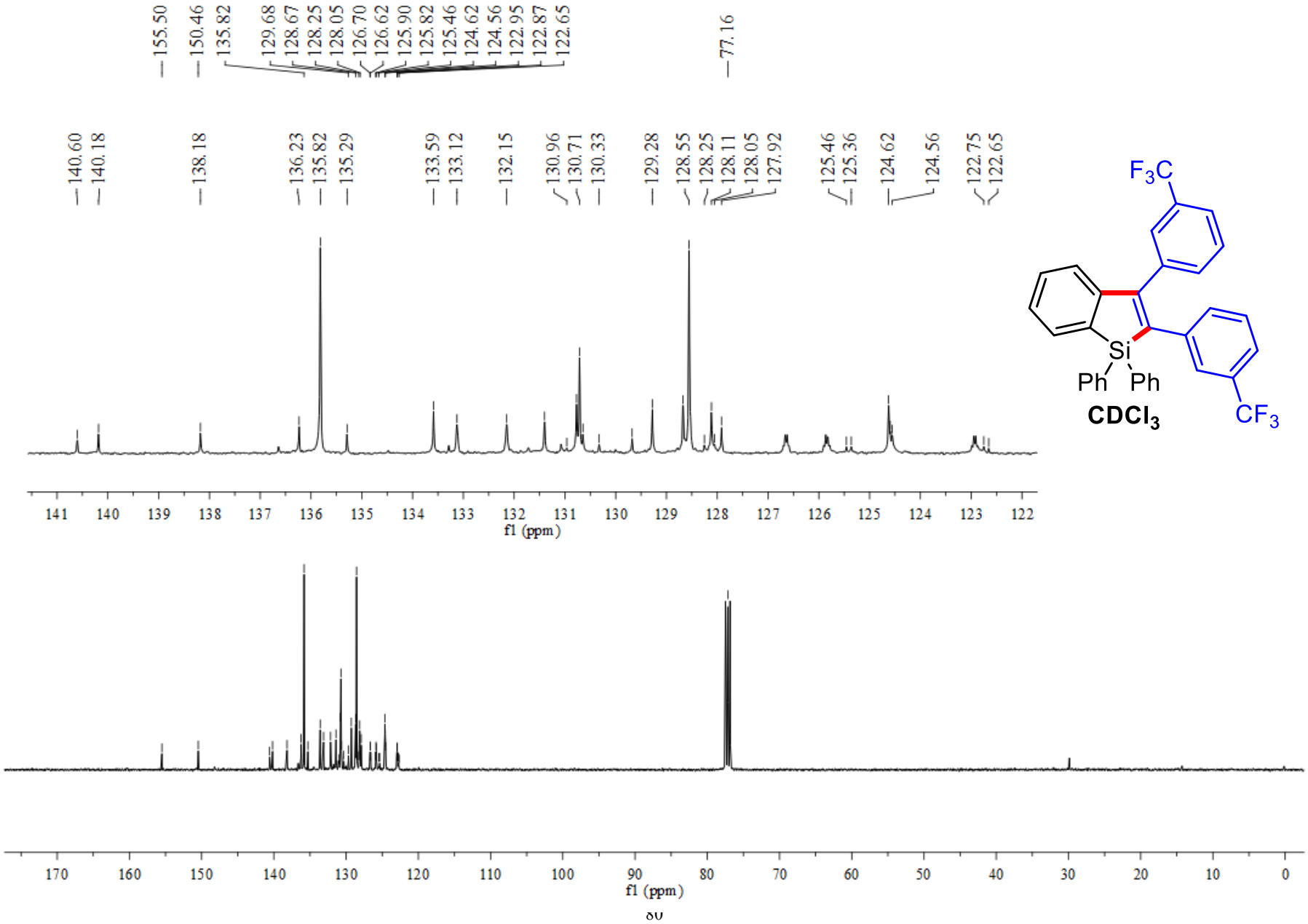
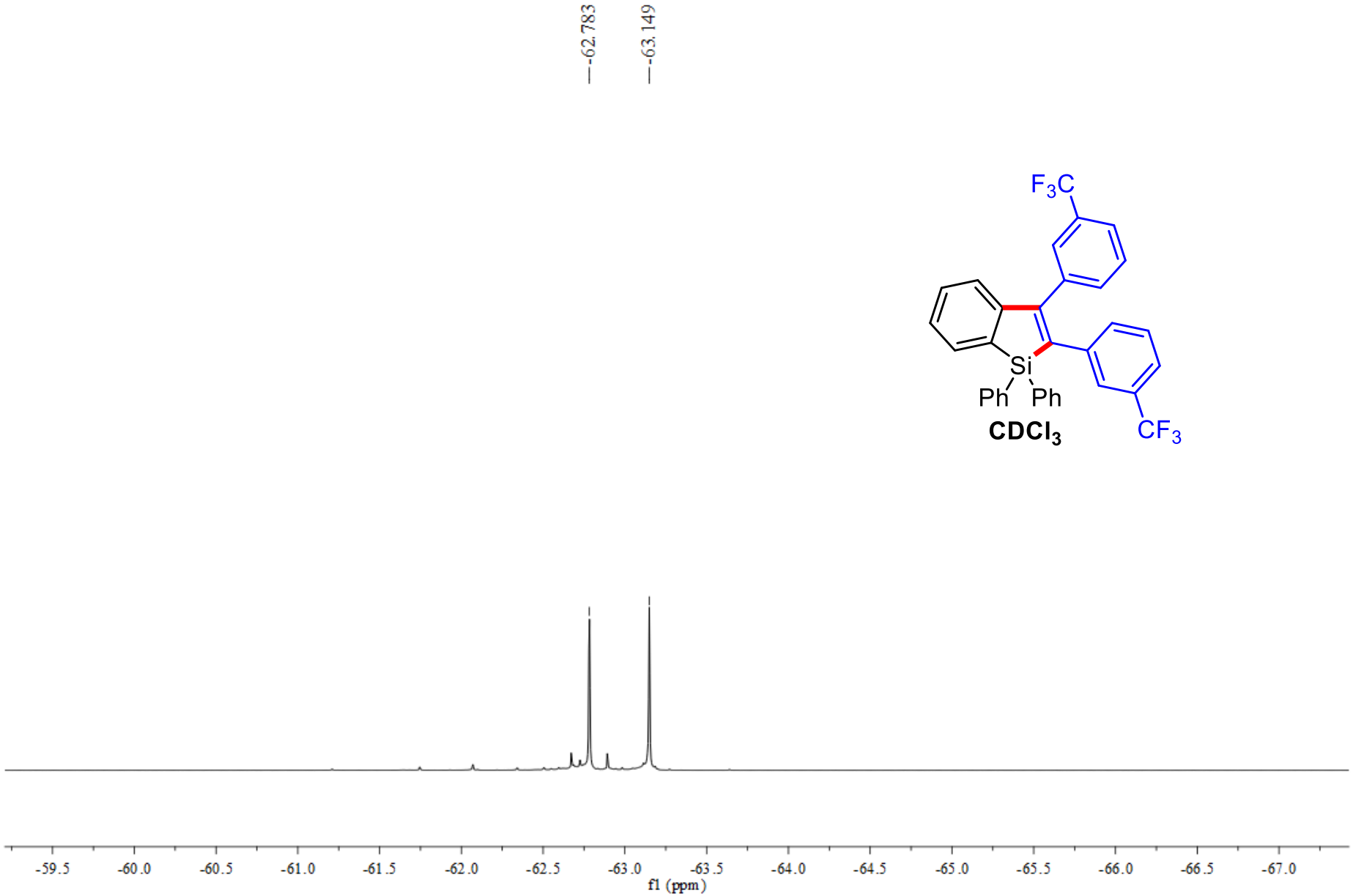
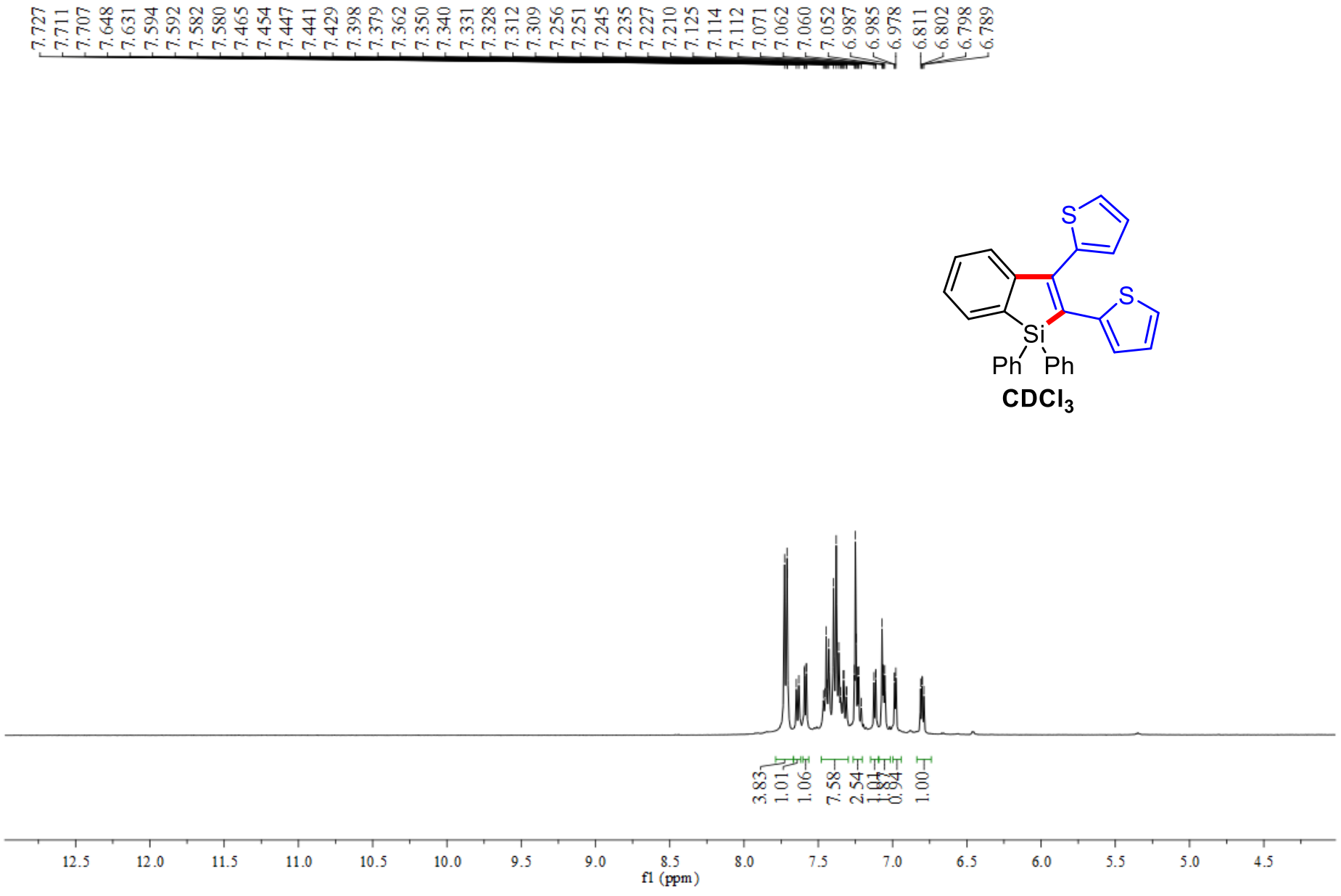
7.752
7.616
7.597
7.575
7.490
7.474
7.457
7.438
7.413
7.390
7.371
7.351
7.334
7.281
7.262
7.238
7.216
7.197
7.167
7.148
7.129
7.107
7.089
7.058
7.037


F3C
Si
Ph
Ph
CF3
CDCl3


1.00
4.88
2.10
2.35
8.45
4.39
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)


155.50
150.46
135.82
129.68
128.67
128.25
128.05
126.70
126.62
125.90
125.82
125.46
124.62
124.56
122.95
122.87
122.65
77.16
140.60
140.18
138.18
136.23
135.82
135.29
133.59
133.12
132.15
130.96
130.71
130.33
129.28
128.55
128.25
128.11
128.05
127.92
125.46
125.36
124.62
124.56
122.75
122.65
141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
F3C
Si
Ph
Ph
CF3
CDCl3


-62.783
-63.149
F3C
Si
Ph
Ph
CF3
CDCl3
-59.5
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
-67.0
f1 (ppm)


7.727
7.711
7.707
7.648
7.631
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7.582
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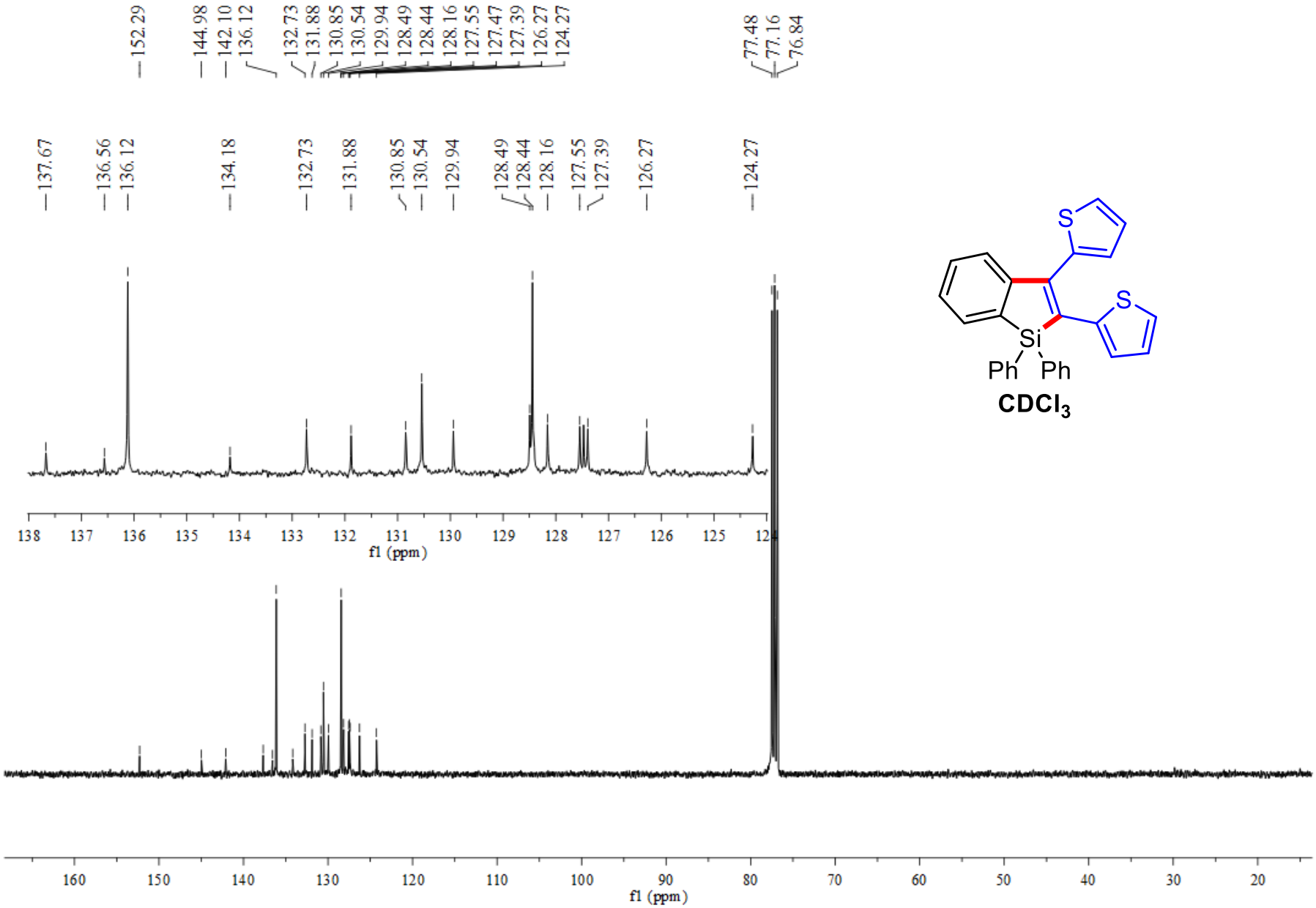
7.447
7.441
7.429
7.398
7.379
7.362
7.350
7.340
7.331
7.328
7.312
7.309
7.256
7.251
7.245
7.235
7.227
7.210
7.125
7.114
7.112
7.071
7.062
7.060
7.052
6.987
6.985
6.978
6.811
6.802
6.798
6.789
S
S
Si
Ph
Ph
CDCl3
3.83
1.01
1.06
7.58
2.54
1.04
1.87
0.94
1.00
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f1 (ppm)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142.10
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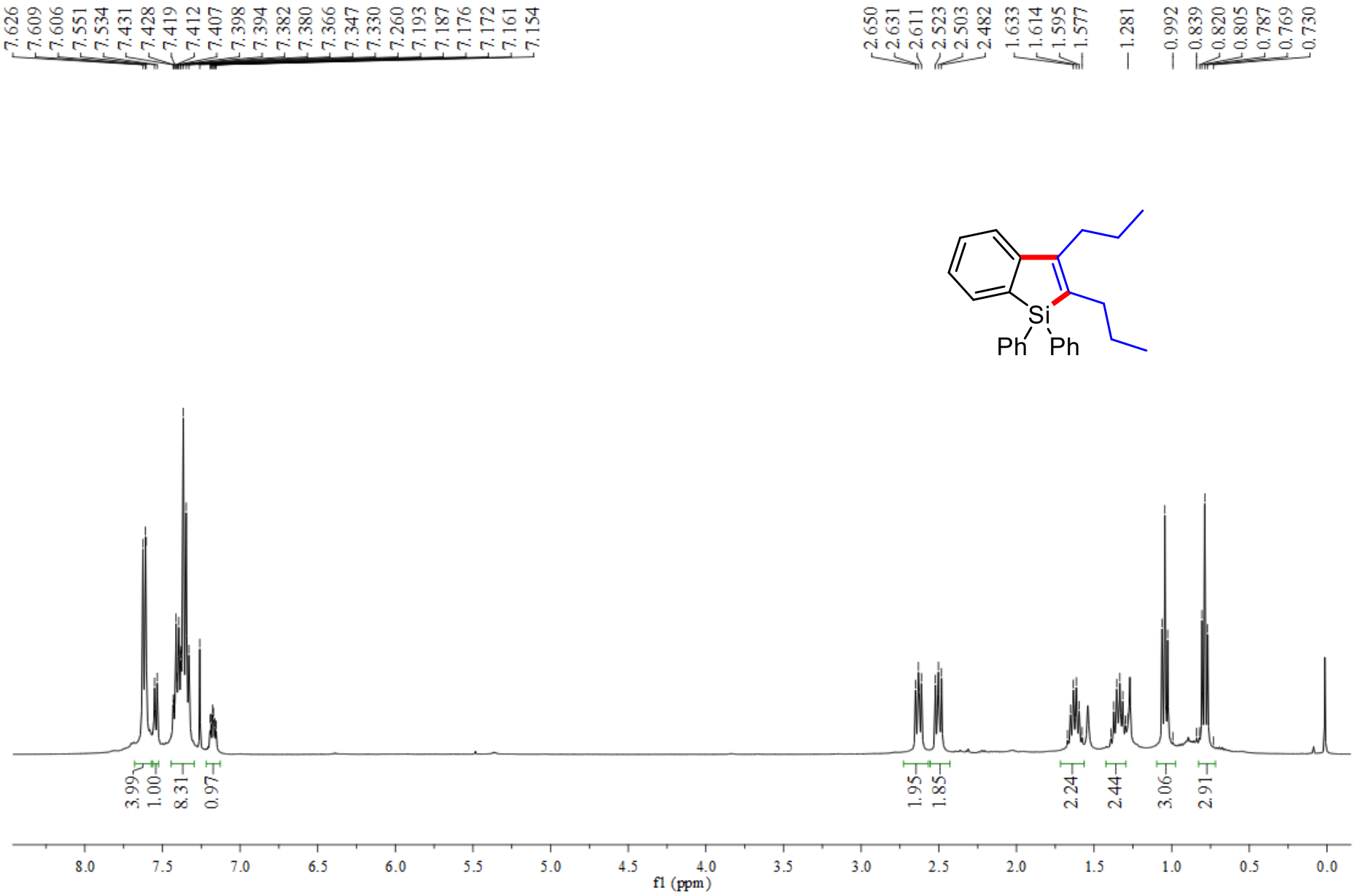
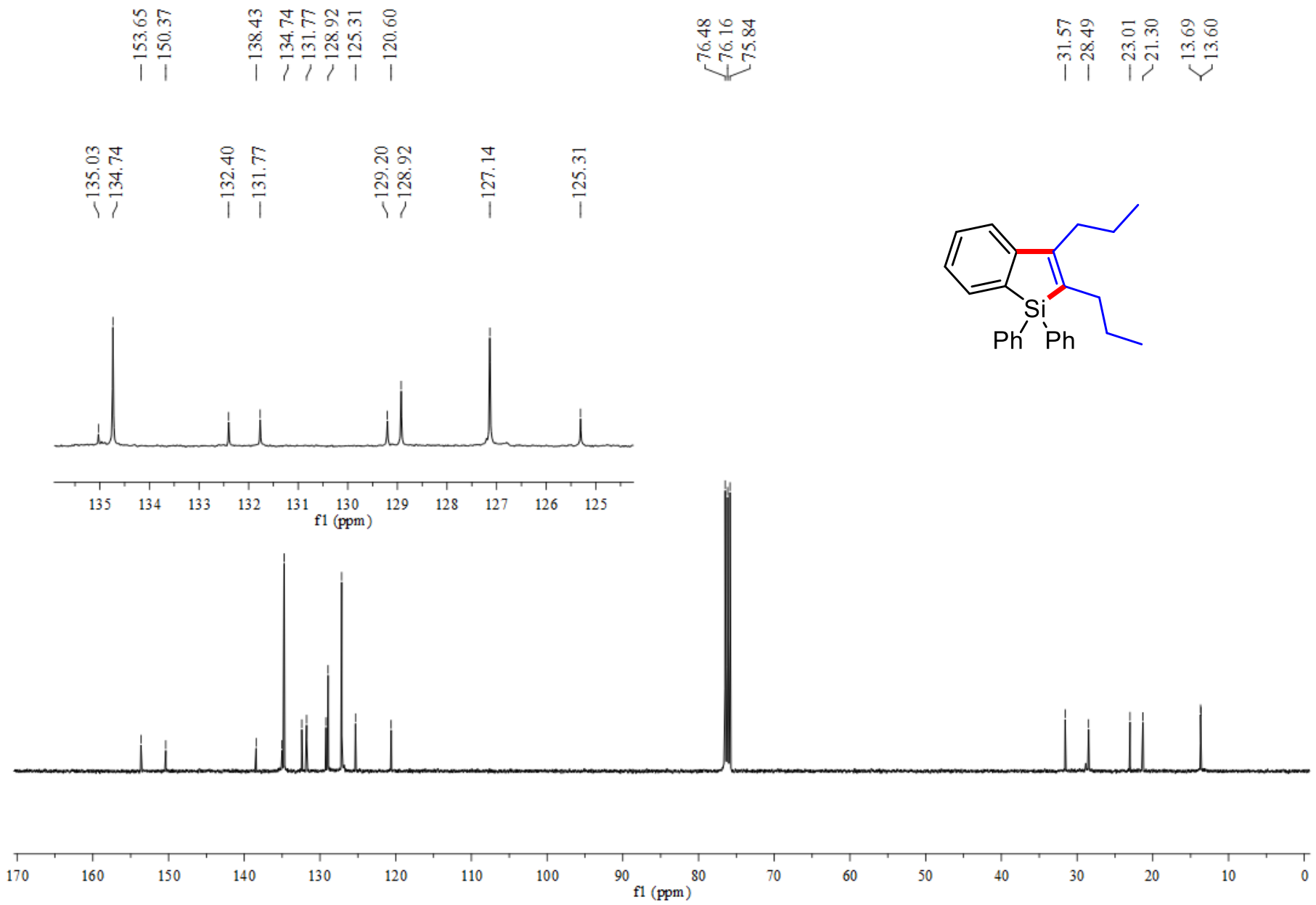
132.73
131.88
130.85
130.54
129.94
128.49
128.44
128.16
127.55
127.47
127.39
126.27
124.27
77.48
77.16
76.84
137.67
136.56
136.12
134.18
132.73
131.88
130.85
130.54
129.94
128.49
128.44
128.16
127.55
127.39
126.27
124.27
S
S
Si
Ph
Ph
CDCl3
f1 (ppm)
f1 (ppm)


7.626
7.609
7.606
7.551
7.534
7.431
7.428
7.419
7.412
7.407
7.398
7.394
7.382
7.380
7.366
7.347
7.330
7.260
7.193
7.187
7.176
7.172
7.161
7.154
2.650
2.631
2.611
2.523
2.503
2.482
1.633
1.614
1.595
1.577
1.281
0.992
0.839
0.820
0.805
0.787
0.769
0.730
Si
Ph
Ph
3.99
1.00
8.31
0.97
1.95
1.85
2.24
2.44
3.06
2.91
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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138.43
134.74
131.77
128.92
125.31
120.60
76.48
76.16
75.84
31.57
28.49
23.01
21.30
13.69
13.60
135.03
134.74
132.40
131.77
129.20
128.92
127.14
125.31
Si
Ph
Ph
f1 (ppm)
f1 (ppm)