Supporting information for

Cu(I)-Catalyzed Dearomatizing Cascade of Thiazoles using Two Molecules of an α-Aryl-α-Diazoester: A Novel Approach for the Synthesis of Densely Substituted 4-Thiazolines

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General Information:

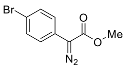
All chemicals were purchased from commercial sources and used without purification unless otherwise noted. Transition metal catalysts were purchased from commercial suppliers and stored at room temperature in a glove box filled with nitrogen gas, maintaining an oxygen and water level of less than 100 ppm for stability. Toluene was distilled under a nitrogen atmosphere using sodium metal as a desiccant to ensure purity during the process. All reactions were conducted in a nitrogen gas environment using standard Schlenk techniques for optimal conditions. The Schlenk tube, equipped with a PTFE-coated magnetic stirring bar, was washed with aqua regia before being thoroughly rinsed with deionized water and then dried in an oven at 130 degrees Celsius to ensure cleanliness and dryness. Prior to use, the Schlenk tube, equipped with a magnetic stirring bar, was transferred to a glove box for further handling. Analytical Thin Layer Chromatography (TLC) was performed on 0.25 mm precoated silica gel 60F254 plates, which were used for visualization under UV light at either 254 or 365 nm wavelengths. Alternatively, TLC plates could be stained with anisaldehyde, cerium ammonium molybdate or potassium permanganate and then heated for better visualization of the separated components. Unless otherwise specified, column chromatography was performed on silica gel (500-800 mesh) as the stationary phase and elution was performed with a mixture of hexanes/ethyl acetate (EtOAc).

Nuclear magnetic resonance (NMR) spectra were acquired using a high-resolution 400 MHz spectrometer with deuterated solvent as the medium. The resulting ^{1}H NMR spectra are presented in the following format: chemical shifts (δ ppm), multiplicities, coupling constants (Hz), and integrals. To ensure accurate referencing, the ^{1}H chemical shifts have been referenced to the residual solvent signal (δ H 7.26 for $CDCl_3$). The multiplicities are indicated as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), brs (broad singlet), and so on, depending on the number of peaks observed. For ^{13}C NMR spectra, data were collected at 100 MHz resolution. The resulting ^{13}C NMR spectra are reported in terms of chemical shifts with respect to the solvent signal (δ C 77.0 for $CDCl_3$).

Nuclear magnetic resonance (NMR) spectra were obtained in collaboration with the Analytical Center of Wuhan Textile University, which provided the necessary equipment and expertise for data collection. High-resolution mass spectrometry was performed using a conventional instrument equipped with a time-of-flight (TOF) analyzer. The service for this test was outsourced to ShanGuan Technology Services (Guangzhou) Co, which provided the necessary resources and expertise for data acquisition. For single crystal X-ray analysis, high-quality crystals were grown by slowly evaporating a solution containing **3b** in ethyl acetate at room temperature. The single crystal samples were then sent to ShanGuan Technology Services (Guangzhou) Co. for data collection and interpretation.

List of organic compounds used and prepared as starting materials:

Aryl diazoacetates (**1a**-**1r**) were synthesized in accordance with a well-established procedure.[1] Thiazole **2a** were prepared by modifying the reaction solvent from diethyl ether to tetrahydrofuran (THF) under otherwise identical conditions, as reported in the literature. The thiazoles (**2b**-**2j**) employed in this study were sourced from commercial suppliers to guarantee their availability and quality. Prior to utilization in the experimental procedures, both sets of compounds underwent high-performance liquid chromatography (HPLC) analysis to verify their purity levels. The results confirmed a minimum purity of 95% or higher for the aryl diazoacetates (**1a**-**1r**) and thiazoles (**2a**-**2k**).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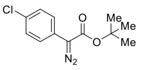
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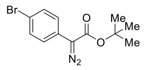
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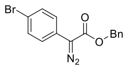
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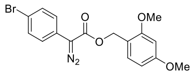
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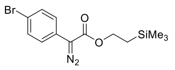
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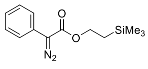
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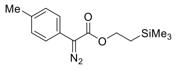
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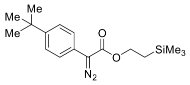
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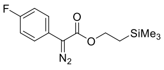
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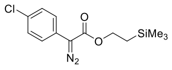
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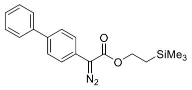
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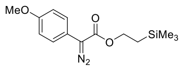
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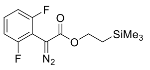
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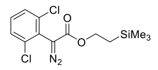
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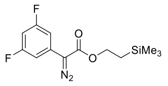
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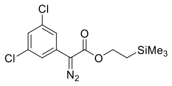
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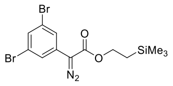
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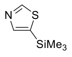
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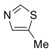
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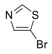
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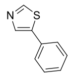
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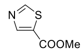
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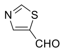
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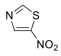
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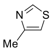
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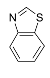
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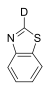
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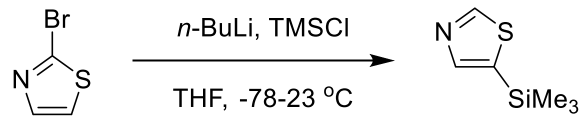
Reference:

1. (a) D. Maiti, R. Das, S. Sen, *J. Org. Chem.* **2021**, *86*, 2522-2533; (b) J. Zhu, R. Li, Y. Su, P. Gu, *J. Org. Chem.* **2019**, *84*, 5813-5820.

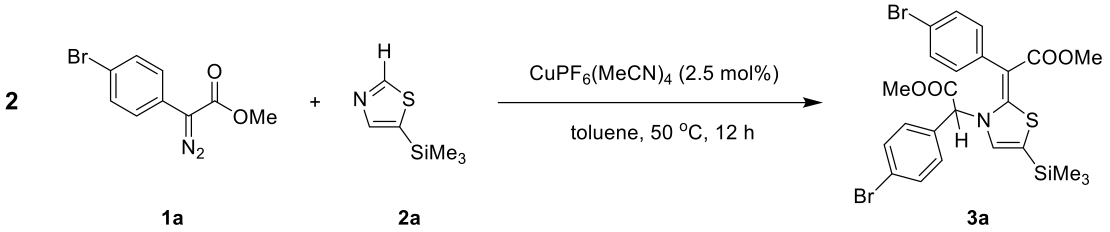
The preparation of 5-trimethylsilylthiazole 2a:



2a

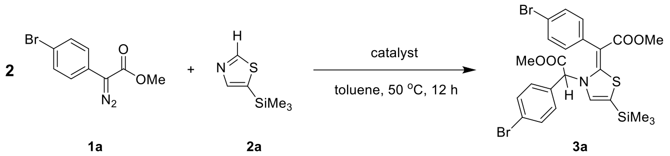
A dry, clean 250 mL Schlenk tube equipped with a stir bar was placed in a low-temperature bath precooled to -78 °C. The Schlenk line was purged with nitrogen gas three times via standard vacuum/pressure cycling techniques. The tube was then sealed with a rubber stopper under an inert nitrogen atmosphere. Under continued nitrogen protection, anhydrous tetrahydrofuran (THF) solution (50 mL) and *n*-butyl lithium (*n*-BuLi) solution (17 mL, 33.6 mmol) were added to the Schlenk tube via syringe. The reaction mixture was stirred for 15 minutes at -78 °C. Subsequently, 2-bromothiazole (5.000 g, 30.5 mmol) was introduced into the reaction mixture dropwise via a syringe pump over 30 minutes. Trimethylchlorosilane (3.310 g, 30.5 mmol) was added using a syringe in one portion. Stirring continued for an additional 2 hours at -78 °C. The Schlenk tube was sealed and allowed to slowly warm to room temperature over several hours while stirring. The reaction mixture was stirred overnight at room temperature. The reaction was quenched by carefully adding a saturated sodium bicarbonate solution (30 mL). The resulting mixture was extracted with dichloromethane (DCM, 20 mL × 3). The combined organic layers were dried over anhydrous sodium sulfate and filtered. The solvent was removed under reduced pressure using a rotary evaporator. The crude product was purified by distillation to yield 5-(trimethylsilyl)thiazole 2a (2.543 g, 53% yield).

Representative procedure for the preparation of 4-thiazoline 3a (the same procedure has been applied for the synthesis of 3a-3f, 4a-4i, 5a-5l):



A 25 mL Schlenk tube, equipped with a magnetic stirring bar, was transferred to a glove box maintained at a controlled atmosphere filled with nitrogen and the water and oxygen levels were preserved below 100 ppm. $CuPF_6(MeCN)_4$ (1.864 mg, 5.000 μmol) was weighed within the glove box and added to the Schlenk tube. Using a microliter syringe, 5-(trimethylsilyl)thiazole **2a** (31.0 mg, 0.200 mmol) was subsequently added to the Schlenk tube. The Schlenk tube was then added a solution of methyl 2-(4-bromophenyl)-2-diazoacetate 1a (107 mg, 0.420 mmol) dissolved in toluene (1.50 mL) in one portion. The Schlenk tube was sealed and then removed from the glove box and heated in an oil bath at 50 °C with stirring for 12 hours. After cooling to room temperature, the reaction mixture was then transferred to a glass vial and concentrated under reduced pressure, resulting in the formation of a residue. The crude product was subsequently purified using a silica gel column, eluting with a mixture of hexanes and EtOAc. Collected fractions yielded methyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-methoxy-2-oxoethyl)-5-(trimethylsilyl)thiazol-2(3*H*)-ylidene)acetate **3a** (101 mg, 0.166 mmol, 83% yield), which appeared as a yellow solid.

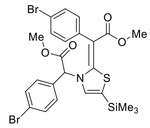
Optimizing of the reaction conditions:



Entry[a]	Catalyst	Catalyst loading	Solvent	concentration（mol/L）	Temperature	Molar ratio of **1a**:**2a**	Yield of **3a**[b]
1	$CuPF_6(MeCN)_4$	5 mol%	1.0 mL	0.20	50 °C	1.10:1.00	33%
2	$CuPF_6(MeCN)_4$	5 mol%	1.0 mL	0.20	50 °C	2.10:1.00	63%
3	$CuPF_6(MeCN)_4$	1.0 mol%	1.0 mL	0.20	50 °C	2.10:1.00	57%
4	$CuPF_6(MeCN)_4$	2.5 mol%	1.0 mL	0.20	50 °C	2.10:1.00	76%
5	$CuPF_6(MeCN)_4$	5 mol%	1.0 mL	0.20	50 °C	2.10:1.00	50%
6	$CuPF_6(MeCN)_4$	10 mol%	1.0 mL	0.20	50 °C	2.10:1.00	27%
7	none	N.A.	1.0 mL	0.20	50 °C	2.10:1.00	No reaction
8	$Cu(OTf)_2$	2.5 mol%	1.0 mL	0.20	50 °C	2.10:1.00	No reaction
9	$Rh_2(OAc)_4$	2.5 mol%	1.0 mL	0.20	50 °C	2.10:1.00	Complex mixture
10	$Rh_2(esp)_2$	2.5 mol%	1.0 mL	0.20	50 °C	2.10:1.00	Complex mixture
11	$CuPF_6(MeCN)_4$	2.5 mol%	1.0 mL	0.20	23 °C	2.10:1.00	13%
12	$CuPF_6(MeCN)_4$	2.5 mol%	1.0 mL	0.20	60 °C	2.10:1.00	82%
13	$CuPF_6(MeCN)_4$	2.5 mol%	0.5 mL	0.40	50 °C	2.10:1.00	74%
14	$CuPF_6(MeCN)_4$	2.5 mol%	1.0 mL	0.20	50 °C	2.10:1.00	76%
15	$CuPF_6(MeCN)_4$	2.5 mol%	1.5 mL	0.13	50 °C	2.10:1.00	83%
16	$CuPF_6(MeCN)_4$	2.5 mol%	2.0 mL	0.10	50 °C	2.10:1.00	76%
17	$CuPF_6(MeCN)_4$	2.5 mol%	2.5 mL	0.08	50 °C	2.10:1.00	79%

[a] The reaction was performed on a scale of 0.20 mmol, with **2a** serving as the limiting reagent, under a nitrogen atmosphere. [b] isolated yield.

List of organic compounds prepared as products: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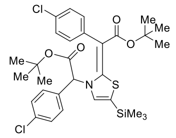
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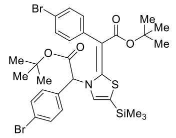
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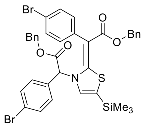
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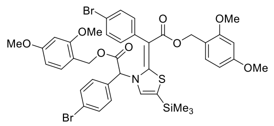
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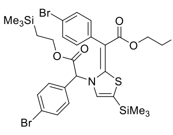
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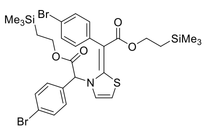
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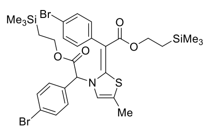
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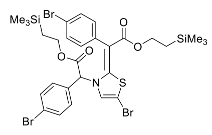
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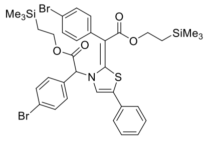
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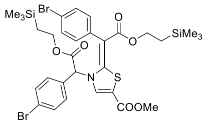
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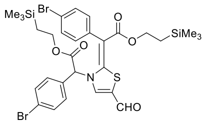
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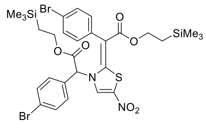
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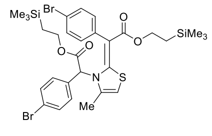
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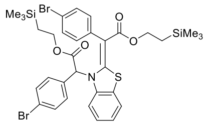
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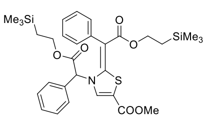
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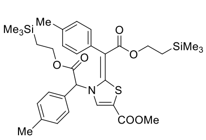
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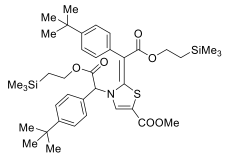
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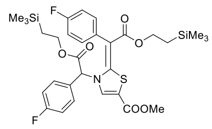
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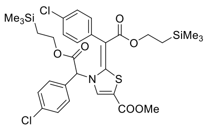
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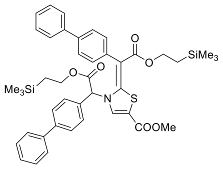
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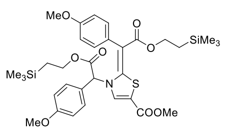
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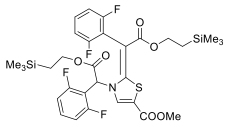
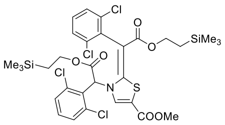
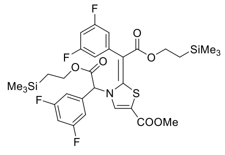
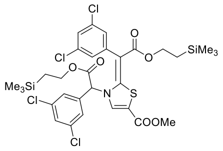
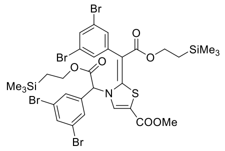

5h

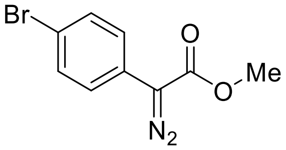

5i


5j

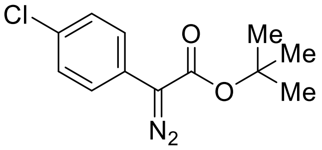

5k


5l

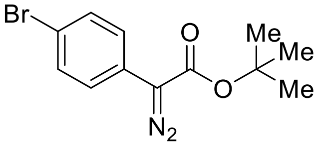
Characterization data of 1a-1r:



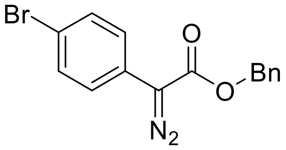
methyl 2-(4-bromophenyl)-2-diazoacetate (**1a**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H).



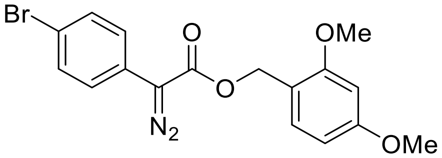
***tert*-butyl 2-(4-chlorophenyl)-2-diazoacetate** (**1b**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 1.54 (s, 9H).



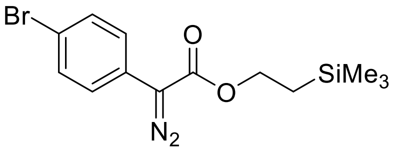
***tert*-butyl 2-(4-bromophenyl)-2-diazoacetate** (**1c**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 1.54 (s, 9H).



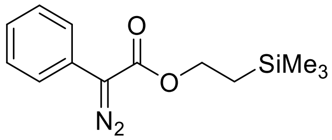
benzyl 2-(4-bromophenyl)-2-diazoacetate (**1d**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, *J* = 8.7 Hz, 2H), 7.41 – 7.37 (m, 5H), 7.37 – 7.33 (m, 2H), 5.31 (s, 2H).



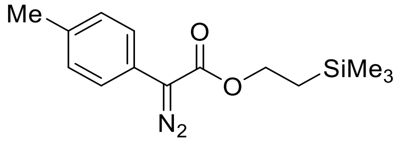
2,4-dimethoxybenzyl 2-(4-bromophenyl)-2-diazoacetate (**1e**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.28 – 7.26 (m, 1H), 6.49 – 6.47 (m, 1H), 6.47 – 6.45 (m, 1H), 5.28 (s, 2H), 3.83 (s, 3H), 3.82 (s, 3H).



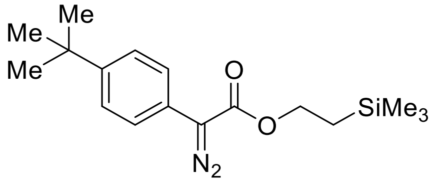
2-(trimethylsilyl)ethyl 2-(4-bromophenyl)-2-diazoacetate (**1f**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 4.37 (t, *J* = 8.4 Hz, 2H), 1.07 (t, *J* = 8.4 Hz, 2H), 0.06 (s, 9H).



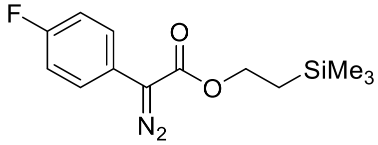
2-(trimethylsilyl)ethyl 2-diazo-2-phenylacetate (1g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 4.38 (t, *J* = 8.5 Hz, 2H), 1.08 (t, *J* = 8.5 Hz, 2H), 0.06 (s, 9H).



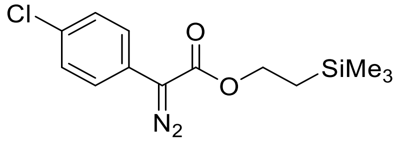
2-(trimethylsilyl)ethyl 2-diazo-2-(*p*-tolyl)acetate (**1h**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 4.36 (t, *J* = 8.5 Hz, 2H), 2.34 (s, 3H), 1.07 (t, *J* = 8.5 Hz, 2H), 0.06 (s, 9H).



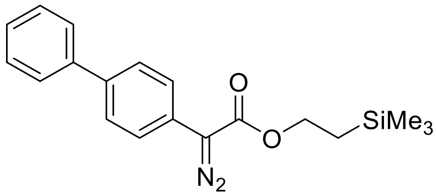
2-(trimethylsilyl)ethyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate (**1i**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 4H), 4.37 (t, *J* = 8.5 Hz, 2H), 1.32 (s, 9H), 1.08 (t, *J* = 8.5 Hz, 2H), 0.06 (s, 9H).



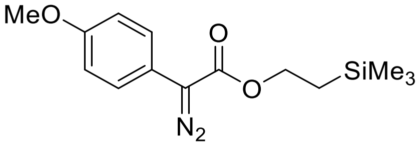
2-(trimethylsilyl)ethyl 2-diazo-2-(4-fluorophenyl)acetate (**1j**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.08 (t, *J* = 8.8 Hz, 2H), 4.37 (t, *J* = 8.5 Hz, 2H), 1.07 (t, *J* = 8.5 Hz, 2H), 0.06 (s, 9H).



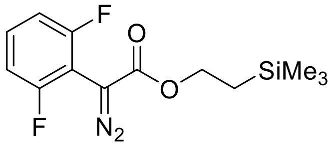
2-(trimethylsilyl)ethyl 2-(4-chlorophenyl)-2-diazoacetate (**1k**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 4.36 (t, *J* = 8.4 Hz, 2H), 1.07 (t, *J* = 8.4 Hz, 2H), 0.06 (s, 9H).



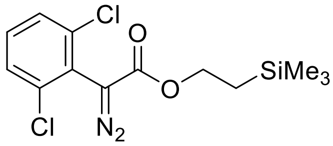
2-(trimethylsilyl)ethyl 2-([1,1'-biphenyl]-4-yl)-2-diazoacetate (**1l**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (tt, *J* = 7.6, 1.4 Hz, 1H), 4.40 (t, *J* = 8.5 Hz, 2H), 1.10 (t, *J* = 8.5 Hz, 2H), 0.08 (s, 9H).



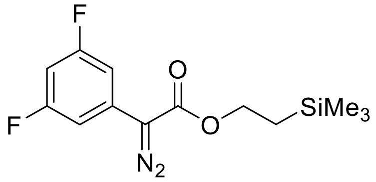
2-(trimethylsilyl)ethyl 2-diazo-2-(4-methoxyphenyl)acetate (**1m**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.36 (t, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 1.07 (t, *J* = 8.4 Hz, 2H), 0.06 (s, 9H).



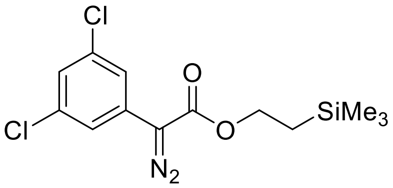
2-(trimethylsilyl)ethyl 2-diazo-2-(2,6-difluorophenyl)acetate (**1n**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 (tt, *J* = 8.4, 6.3 Hz, 1H), 6.97 (t, *J* = 8.4 Hz, 2H), 4.34 (t, *J* = 8.5 Hz, 2H), 1.04 (t, *J* = 8.5 Hz, 2H), 0.03 (s, 9H).



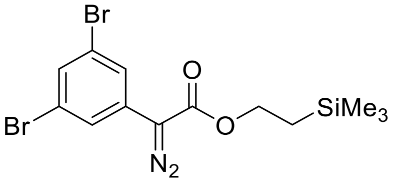
2-(trimethylsilyl)ethyl 2-diazo-2-(2,6-dichlorophenyl)acetate (**1o**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 4.34 (s, 2H), 1.04 (s, 2H), 0.09 – -0.06 (m, 9H).



2-(trimethylsilyl)ethyl 2-diazo-2-(3,5-difluorophenyl)acetate (**1p**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.11 – 7.02 (m, 2H), 6.60 (tt, *J* = 8.8, 2.2 Hz, 1H), 4.38 (t, *J* = 8.5 Hz, 2H), 1.08 (t, *J* = 8.5 Hz, 2H), 0.07 (s, 9H).

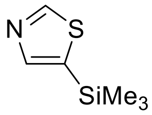


2-(trimethylsilyl)ethyl 2-diazo-2-(3,5-dichlorophenyl)acetate (**1q**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 1.8 Hz, 2H), 7.14 (t, *J* = 1.8 Hz, 1H), 4.38 (t, *J* = 8.5 Hz, 2H), 1.08 (t, *J* = 8.5 Hz, 2H), 0.07 (s, 9H).

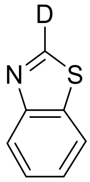


2-(trimethylsilyl)ethyl 2-diazo-2-(3,5-dibromophenyl)acetate (**1r**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.7 Hz, 2H), 7.44 (t, *J* = 1.7 Hz, 1H), 4.38 (t, *J* = 8.4 Hz, 2H), 1.08 (t, *J* = 8.4 Hz, 2H), 0.07 (s, 9H).

Characterization data of 2a and 2k:

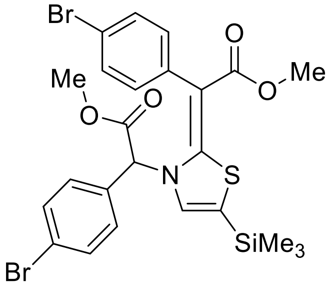


5-(trimethylsilyl)thiazole (**2a**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.00 (s, 1H), 7.94 (s, 1H), 0.34 (s, 9H).

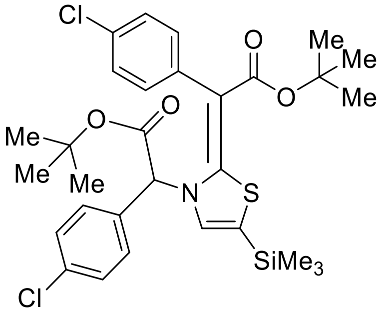


benzo[*d*]thiazole-2-*d* (**2k**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 (ddd, *J* = 8.3, 1.2, 0.5 Hz, 1H), 7.97 (ddd, *J* = 8.3, 1.2, 0.5 Hz, 1H), 7.53 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.45 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H).

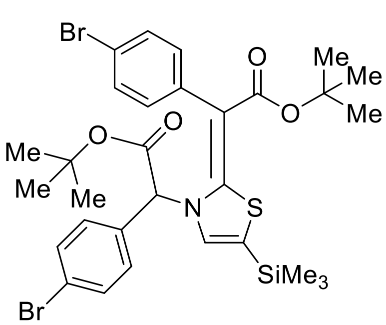
Characterization data of 3a-3f, 4a-4i, 5a-5l:



methyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-methoxy-2-oxoethyl)-5-(trimethylsilyl)thiazol-2(3*H*)-ylidene)acetate (**3a**), 101 mg (Yellow solid, 83% yield); TLC R$_f$= 0.38 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.41 (m, 4H), 7.11 (s, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.35 (s, 1H), 5.58 (s, 1H), 3.66 (s, 6H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.8, 168.5, 165.3, 136.4, 133.9, 133.5, 133.3, 132.3, 132.0, 129.1, 123.4, 121.0, 119.1, 92.0, 64.1, 52.9, 51.5, -0.9; HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{24}H_{26}Br_2NO_4SSi^+$, 611.9693; found, 611.9699.

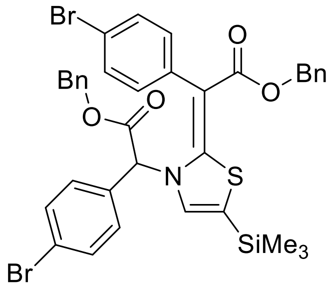


***tert*-butyl (*Z*)-2-(3-(2-(*tert*-butoxy)-1-(4-chlorophenyl)-2-oxoethyl)-5-(trimethylsilyl)thiazol-2(3*H*)-ylidene)-2-(4-chlorophenyl)acetate** (**3b**), 85 mg (Yellow liquid, 70% yield); TLC R$_f$= 0.45 (Hexanes/EtOAc = 20:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.10 (m, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.51 (s, 1H), 5.35 (s, 1H), 1.34 (s, 9H), 1.30 (s, 9H), 0.15 (s, 9H); (This compound decomposes in CDCl$_3$ and the ^{13}C NMR spectra could not be collected successfully.); HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{30}H_{38}Cl_2NO_4SSi^+$, 606.1663; found, 606.1672.

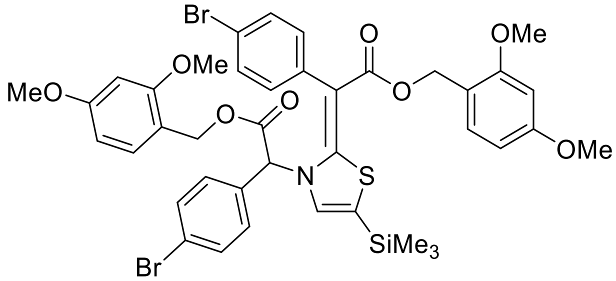


***tert*-butyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-(*tert*-butoxy)-2-oxoethyl)-5-(trimethylsilyl)thiazol-2(3*H*)-ylidene)acetate** (**3c**), 115 mg (Yellow solid, 83% yield); TLC R$_f$= 0.38 (Hexanes/EtOAc = 20:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ

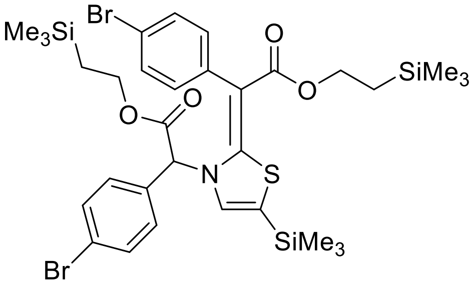
7.42 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.41 (s, 1H), 5.44 (s, 1H), 1.41 (s, 9H), 1.39 (s, 9H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 167.4, 163.7, 137.3, 134.8, 133.2, 132.7, 132.1, 131.8, 129.1, 122.9, 120.3, 117.9, 93.9, 83.6, 79.2, 63.9, 28.7, 27.9, -0.8; HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{30}H_{38}Br_2NO_4SSi^+$, 696.0632; found, 696.0643.



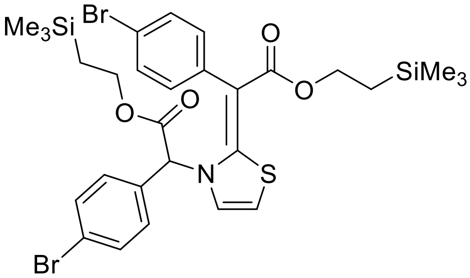
benzyl (*Z*)-2-(3-(2-(benzyloxy)-1-(4-bromophenyl)-2-oxoethyl)-5-(trimethylsilyl)thiazol-2(3*H*)-ylidene)-2-(4-bromophenyl)acetate (**3d**), 122 mg (Yellow liquid, 80% yield); TLC R$_f$ = 0.46 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 6H), 7.30 – 7.23 (m, 6H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.08 (s, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.32 (s, 1H), 5.64 (s, 1H), 5.22 (d, *J* = 13.0 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 5.10 (d, *J* = 13.0 Hz, 1H), 5.03 (d, *J* = 12.0 Hz, 1H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 167.6, 165.0, 137.6, 136.1, 134.5, 133.8, 133.5, 132.4, 132.2, 132.0, 129.2, 129.0, 128.9, 128.8, 128.4, 127.5, 127.3, 123.3, 121.0, 118.9, 91.9, 68.0, 65.3, 63.8, -0.9; HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{36}H_{34}Br_2NO_4SSi^+$, 764.0319; found, 764.0341.



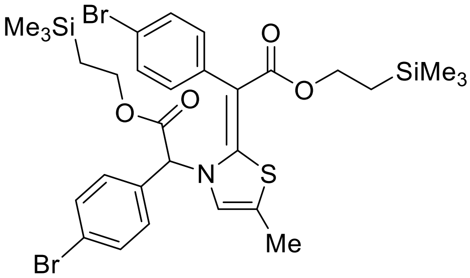
2,4-dimethoxybenzyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-((2, 4-dimethoxybenzyl)oxy)-2-oxoethyl)-5-(trimethylsilyl)thiazol-2(3*H*)-ylidene)acetate (**3e**), 122 mg (Yellow liquid, 69% yield); TLC R$_f$ = 0.31 (Hexanes/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.08 (s, 2H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 2H), 6.46 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.43 (d, *J* = 2.3 Hz, 1H), 6.40 – 6.36 (m, 2H), 6.31 (s, 1H), 5.58 (s, 1H), 5.30 (d, *J* = 11.6 Hz, 1H), 5.18 (d, *J* = 13.0 Hz, 1H), 5.06 (d, *J* = 13.0 Hz, 1H), 4.89 (d, *J* = 11.6 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.73 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 167.9, 164.9, 161.9, 160.5, 159.1, 158.4, 136.3, 134.3, 133.6, 132.7, 132.4, 132.0, 131.7, 129.5, 129.3, 123.0, 120.7, 118.6, 118.5, 115.3, 104.2, 103.8, 98.6, 98.4, 92.2, 64.0, 63.5, 61.1, 55.5, 55.5, 55.5, 55.4, -0.9; HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{40}H_{42}Br_2NO_8SSi^+$, 884.0742; found, 884.0765.



2-(trimethylsilyl)ethyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-5-(trimethylsilyl)thiazol-2(3*H*)-ylidene)acetate (**3f**), 146 mg (Yellow solid, 93% yield); TLC R*f* = 0.50 (Hexanes/EtOAc = 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.11 (s, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.38 (s, 1H), 5.54 (s, 1H), 4.26 – 4.07 (m, 4H), 0.96 – 0.89 (m, 4H), 0.17 (s, 9H), 0.02 (s, 9H), -0.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 168.3, 164.9, 136.6, 134.3, 133.3, 132.5, 132.2, 131.9, 129.1, 123.1, 120.7, 118.8, 92.4, 64.8, 64.1, 62.1, 17.7, 17.3, -0.9, -1.4, -1.5; HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{32}H_{46}Br_2NO_4SSi_3^+$, 784.0797; found, 784.0815.

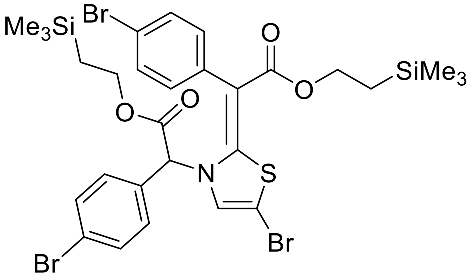


2-(trimethylsilyl)ethyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)thiazol-2(3*H*)-ylidene)acetate (**4a**), 114 mg (Yellow liquid, 80% yield); TLC R*f* = 0.31 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 4H), 7.13 (s, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 4.7 Hz, 1H), 6.28 (d, *J* = 4.7 Hz, 1H), 5.55 (s, 1H), 4.27 – 4.07 (m, 4H), 0.95 – 0.88 (m, 4H), 0.02 (s, 9H), -0.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.3, 162.5, 136.4, 134.3, 133.7, 132.4, 132.0, 129.3, 127.8, 123.3, 120.8, 107.4, 92.6, 64.9, 64.3, 62.1, 17.6, 17.3, -1.4, -1.5; HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{29}H_{38}Br_2NO_4SSi_2^+$, 712.0401; found, 712.0417.

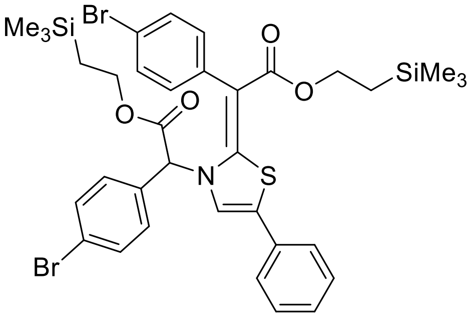


2-(trimethylsilyl)ethyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-5-methylthiazol-2(3*H*)-ylidene)acetate (**4b**), 109 mg (Yellow liquid, 75% yield); TLC R*f* = 0.42 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400

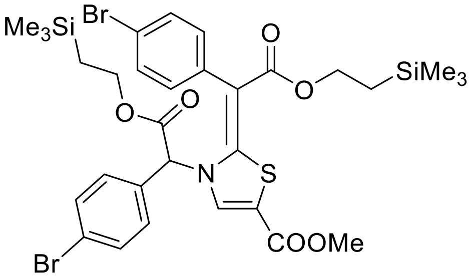
MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 4H), 7.13 (s, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.12 (s, 1H), 5.49 (s, 1H), 4.25 – 4.06 (m, 4H), 2.06 (s, 3H), 0.95 – 0.88 (m, 4H), 0.02 (s, 9H), -0.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 168.2, 163.1, 136.7, 134.4, 133.4, 132.3, 131.9, 129.3, 123.1, 123.1, 120.6, 119.3, 92.0, 64.7, 64.2, 62.0, 17.7, 17.3, 12.2, -1.4, -1.5; HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{30}H_{40}Br_2NO_4SSi_2^+$, 726.0558; found, 726.0602.



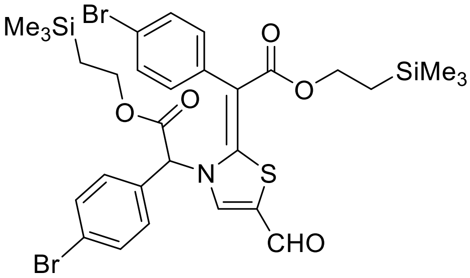
2-(trimethylsilyl)ethyl (*Z*)-2-(5-bromo-2-(1-(4-bromophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)thiazol-3(2*H*)-yl)-2-(4-bromophenyl)acetate (**4c**), 136 mg (Yellow solid, 86% yield); TLC R$_f$= 0.46 (Hexanes/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 3H), 7.42 (d, *J* = 6.8 Hz, 1H), 7.22 (d, *J* = 6.8 Hz, 1H), 7.03 (d, *J* = 6.8 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.40 (s, 1H), 5.47 (s, 1H), 4.23 – 4.08 (m, 4H), 0.94 – 0.88 (m, 4H), 0.02 (s, 9H), -0.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 168.1, 162.4, 135.6, 133.9, 133.7, 132.5, 132.1, 129.3, 127.4, 123.6, 121.3, 97.0, 94.2, 65.0, 64.3, 62.6, 17.6, 17.3, -1.5, -1.5; HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{29}H_{36}Br_3NNaO_4SSi_2^+$, 811.9326; found, 811.9321.



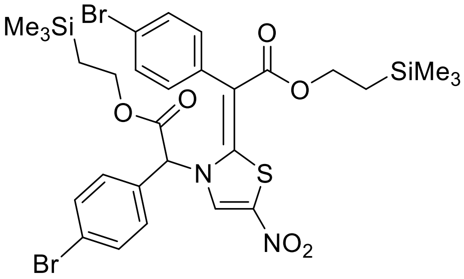
2-(trimethylsilyl)ethyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-5-phenylthiazol-2(3*H*)-ylidene)acetate (**4d**), 120 mg (Yellow solid, 76% yield); TLC R$_f$= 0.42 (Hexanes/EtOAc = 20:1); ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 7.1 Hz, 2H), 7.48 – 7.31 (m, 5H), 7.28 (t, *J* = 7.1 Hz, 1H), 7.20 (s, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.03 (s, 1H), 5.48 (s, 1H), 4.17 – 4.07 (m, 4H), 0.89 – 0.82 (m, 4H), -0.05 (s, 9H), -0.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.3, 161.8, 136.2, 134.2, 132.7, 132.5, 132.0, 131.1, 129.2, 128.9, 127.8, 125.3, 123.7, 123.4, 122.7, 121.0, 93.1, 65.0, 64.5, 62.3, 17.7, 17.3, -1.4, -1.5; HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{35}H_{42}Br_2NO_4SSi_2^+$, 788.0714; found, 788.0720.



methyl (*Z*)-3-(1-(4-bromophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(1-(4-bromophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**4e**), 146 mg (Yellow solid, 95% yield); TLC R_f= 0.29 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.41 (m, 4H), 7.23 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.21 (s, 1H), 7.01 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 2H), 5.51 (s, 1H), 4.24 – 4.08 (m, 4H), 3.77 (s, 3H), 0.94 – 0.88 (m, 4H), 0.02 (s, 9H), -0.06 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.1, 167.8, 161.7, 161.0, 136.2, 135.2, 133.9, 133.5, 132.7, 132.2, 132.1, 129.3, 123.8, 121.6, 113.9, 95.6, 65.2, 64.3, 62.7, 52.2, 17.6, 17.3, -1.5, -1.5; HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{31}H_{39}Br_2NNaO_6SSi_2^+$, 792.0276; found, 792.0287.

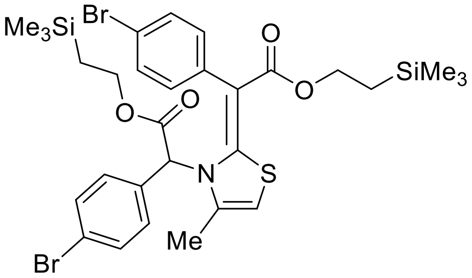


2-(trimethylsilyl)ethyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-5-formylthiazol-2(3*H*)-ylidene)acetate (**4f**), 38 mg (Yellow solid, 26% yield); TLC R_f= 0.54 (Hexanes/EtOAc = 5:1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.61 (s, 1H), 7.82 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.58 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.55 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.48 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.03 (dd, *J* = 8.2, 1.8 Hz, 1H), 5.49 (s, 1H), 4.18 – 4.07 (m, 4H), 0.88 – 0.78 (m, 4H), -0.06 (s, 9H), -0.10 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 180.7, 167.9, 167.9, 159.6, 141.5, 134.9, 133.8, 133.4, 132.9, 132.6, 132.3, 132.3, 129.3, 124.8, 124.1, 122.0, 97.5, 65.5, 64.5, 63.1, 17.6, 17.3, -1.5, -1.5; HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{30}H_{37}Br_2NNaO_5SSi_2^+$, 762.0170; found, 762.0185.

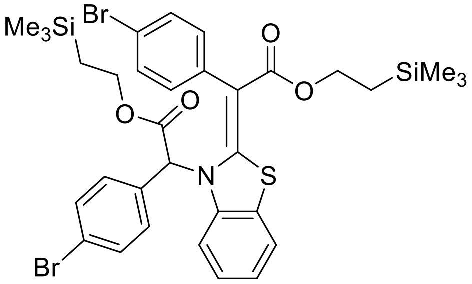


2-(trimethylsilyl)ethyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-oxo-2-

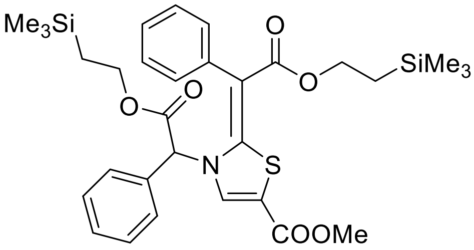
(2-(trimethylsilyl)ethoxy)ethyl)-5-nitrothiazol-2(3*H*)-ylidene)acetate (**4g**), 104 mg (Orange solid, 69% yield); TLC R_f= 0.54 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.54 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.47 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.23 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.01 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 5.50 (s, 1H), 4.25 – 4.07 (m, 4H), 0.95 – 0.86 (m, 4H), 0.02 (s, 9H), -0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 167.4, 157.6, 134.7, 134.4, 133.8, 133.4, 133.1, 132.6, 132.6, 132.5, 132.5, 129.5, 124.6, 122.5, 99.0, 65.7, 64.8, 63.6, 17.6, 17.4, -1.5, -1.5; HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{29}H_{36}Br_2N_2NaO_6SSi_2^+$, 779.0072; found, 779.0086.



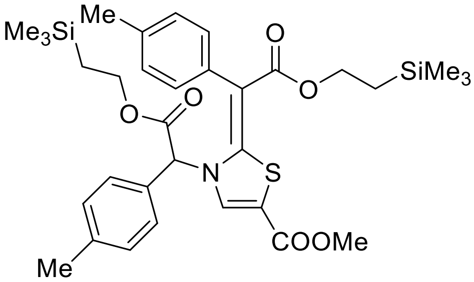
2-(trimethylsilyl)ethyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-4-methylthiazol-2(3*H*)-ylidene)acetate (**4h**), 74 mg (Yellow liquid, 51% yield); TLC R_f= 0.54 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.06 (d, *J* = 1.9 Hz, 1H), 6.11 (s, 1H), 4.45 – 4.40 (m, 2H), 4.33 – 4.28 (m, 2H), 1.65 (s, 3H), 1.22 – 1.16 (m, 2H), 0.98 – 0.88 (m, 2H), 0.07 (s, 9H), -0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 167.3, 161.2, 141.5, 138.4, 132.0, 131.6, 130.0, 129.5, 129.2, 127.8, 125.1, 122.8, 116.3, 106.5, 89.0, 72.7, 66.0, 62.5, 18.1, 17.2, 16.6, -1.3, -1.5; HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{30}H_{40}Br_2NO_4SSi_2^+$, 726.0558; found, 726.0626.



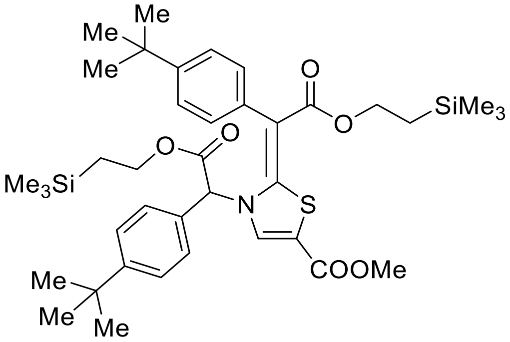
2-(trimethylsilyl)ethyl (*Z*)-2-(4-bromophenyl)-2-(3-(1-(4-bromophenyl)-2-oxo-2-(2-trimethylsilyl)ethoxy)ethyl)benzo[*d*]thiazol-2(3*H*)-ylidene)acetate (**4i**), 128 mg (Yellow solid, 84% yield); TLC R_f= 0.44 (Hexanes/EtOAc = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.07 – 6.97 (m, 3H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.83 (s, 1H), 4.23 (t, *J* = 8.6 Hz, 2H), 4.09 (td, *J* = 11.2, 6.4 Hz, 1H), 3.96 (td, *J* = 11.2, 6.4 Hz, 1H), 0.92 (t, *J* = 8.6 Hz, 2H), 0.75 – 0.63 (m, 2H), -0.02 (s, 9H), -0.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 167.8, 162.0, 140.2, 135.0, 133.6, 133.2, 132.0, 131.3, 129.2, 127.9, 125.4, 123.1, 122.3, 121.3, 121.2, 113.5, 97.0, 66.5, 64.9, 62.7, 17.6, 17.2, -1.5, -1.5; HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{33}H_{39}Br_2NNaO_4SSi_2^+$, 784.0377; found, 784.0322.



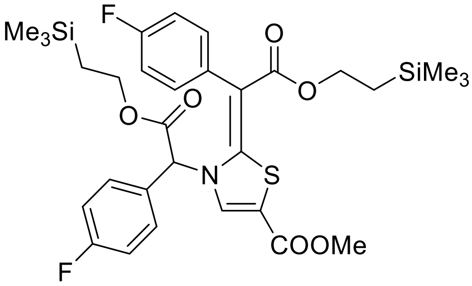
methyl (*Z*)-3-(2-oxo-1-phenyl-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(2-oxo-1-phenyl-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5a**), 109 mg (Yellow solid, 89% yield); TLC R*f* = 0.22 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.27 (m, 5H), 7.21 (s, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.99 – 6.95 (m, 2H), 5.54 (s, 1H), 4.23 – 4.07 (m, 4H), 3.75 (s, 3H), 0.94 – 0.84 (m, 4H), -0.01 (s, 9H), -0.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 168.4, 162.1, 160.5, 136.8, 136.2, 134.6, 132.2, 131.4, 129.4, 129.4, 129.1, 129.0, 128.1, 127.6, 112.9, 97.1, 64.8, 64.7, 62.5, 52.1, 17.6, 17.3, -1.4, -1.5; HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{31}H_{41}NNaO_6SSi_2^+$, 634.2086; found, 634.2092.



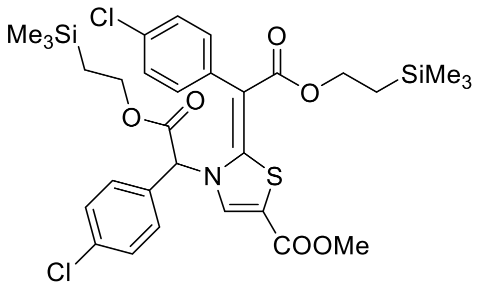
methyl (*Z*)-3-(2-oxo-1-(*p*-tolyl)-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(2-oxo-1-(*p*-tolyl)-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5b**), 99 mg (Yellow solid, 77% yield); TLC R*f* = 0.22 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.30 – 7.26 (m, 2H), 7.19 – 7.15 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.63 (s, 1H), 4.29 – 4.12 (m, 4H), 3.80 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H), 1.00 – 0.89 (m, 4H), 0.05 (s, 9H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 168.6, 162.1, 160.3, 139.4, 137.1, 137.0, 133.0, 131.9, 131.7, 131.1, 130.1, 129.8, 129.7, 128.0, 112.6, 96.8, 64.5, 64.3, 62.4, 52.0, 21.4, 21.2, 17.6, 17.3, -1.5, -1.6; HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{33}H_{46}NO_6SSi_2^+$, 640.2579; found, 640.2582.



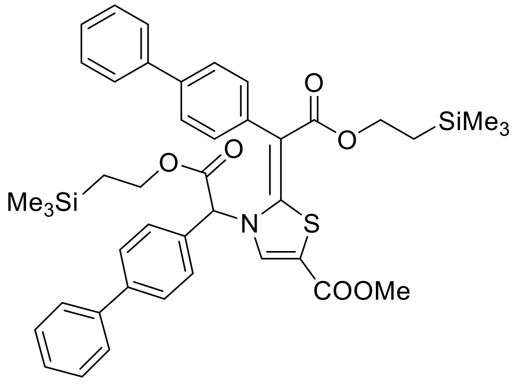
methyl (*Z*)-3-(1-(4-(*tert*-butyl)phenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(1-(4-(*tert*-butyl)phenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5c**), 90 mg (Yellow solid, 62% yield); TLC R$_f$= 0.26 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.28 (m, 4H), 7.26 – 7.23 (m, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 2H), 5.55 (s, 1H), 4.27 – 4.19 (m, 3H), 4.09 – 4.01 (m, 1H), 3.76 (s, 3H), 1.31 (s, 9H), 1.28 (s, 9H), 0.97 – 0.86 (m, 4H), -0.02 (s, 9H), -0.10 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.9, 168.7, 162.2, 160.3, 152.3, 150.3, 137.2, 132.9, 131.7, 130.7, 127.8, 126.3, 125.9, 112.5, 96.8, 64.6, 64.1, 62.4, 52.0, 34.7, 34.6, 31.4, 31.3, 17.5, 17.4, -1.4, -1.5; HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{39}H_{57}NNaO_6SSi_2^+$, 746.3338; found, 746.3345.



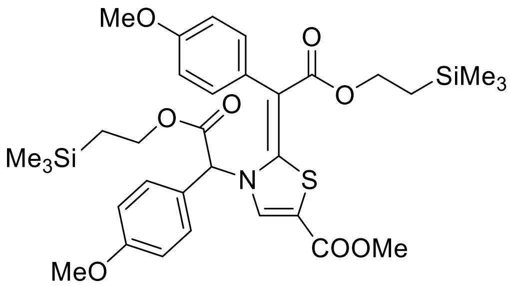
methyl (*Z*)-3-(1-(4-fluorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(1-(4-fluorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5d**), 106 mg (Yellow solid, 82% yield); TLC R$_f$= 0.22 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 (td, *J* = 8.0, 5.5, 2.2 Hz, 1H), 7.32 (s, 1H), 7.18 (td, *J* = 8.0, 5.5, 2.2 Hz, 1H), 7.13 (td, *J* = 8.5, 2.6 Hz, 1H), 7.11 – 7.08 (m, 1H), 7.08 – 7.04 (m, 2H), 7.03 – 6.99 (m, 2H), 5.59 (s, 1H), 4.28 – 4.14 (m, 4H), 3.82 (s, 3H), 0.98 – 0.90 (m, 4H), 0.05 (s, 9H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.5, 168.2, 164.3, 163.4, 161.9, 161.8, 161.0, 160.8, 136.3, 133.8, 133.7, 133.0, 132.9, 132.1, 132.1, 130.3, 130.3, 129.9, 129.8, 116.7, 116.5, 116.1, 116.1, 115.9, 115.9, 113.5, 95.9, 65.1, 64.1, 62.7, 52.2, 17.6, 17.2, -1.5, -1.6 (there are more signals than the number of carbons in the molecular formula due to the coupling of F atoms); HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{31}H_{40}F_2NO_6SSi_2^+$, 648.2078; found, 648.1988.



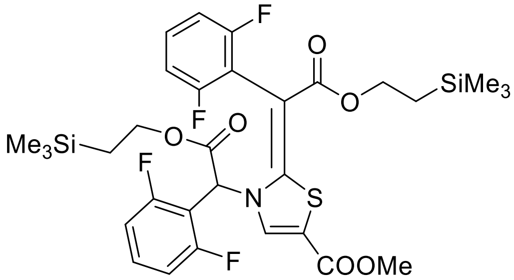
methyl (*Z*)-3-(1-(4-chlorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(1-(4-chlorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5e**), 124 mg (Yellow solid, 91% yield); TLC R_f= 0.33 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.27 (m, 5H), 7.21 (s, 1H), 7.08 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 2H), 5.53 (s, 1H), 4.24 – 4.09 (m, 4H), 3.77 (s, 3H), 0.93 – 0.88 (m, 4H), 0.01 (s, 9H), -0.06 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.3, 167.9, 161.8, 161.0, 136.3, 135.7, 134.8, 133.6, 133.5, 133.0, 132.4, 129.8, 129.3, 129.2, 129.2, 113.9, 95.7, 65.2, 64.3, 62.7, 52.2, 17.6, 17.3, -1.4, -1.5; HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{31}H_{40}Cl_2NO_6SSi_2^+$, 680.1487; found, 680.1495.



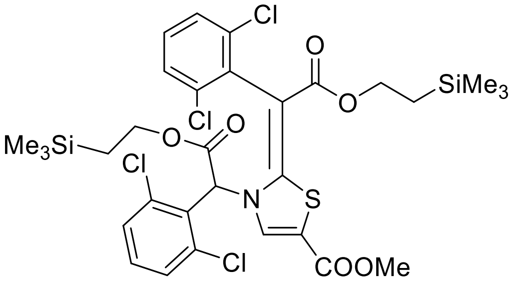
methyl (*Z*)-3-(1-([1,1'-biphenyl]-4-yl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(1-([1,1'-biphenyl]-4-yl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5f**), 110 mg (Yellow solid, 72% yield); TLC R_f= 0.56 (Hexanes/EtOAc = 5:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 4H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.41 (m, 4H), 7.39 – 7.32 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 5.74 (s, 1H), 4.32 – 4.21 (m, 2H), 4.19 – 4.11 (m, 1H), 4.07 – 3.98 (m, 1H), 3.77 (s, 3H), 0.94 (t, *J* = 8.4 Hz, 2H), 0.82 – 0.66 (m, 2H), -0.07 (s, 9H), -0.12 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.7, 168.5, 162.0, 160.8, 142.3, 140.5, 140.1, 139.9, 136.9, 135.3, 133.6, 132.7, 131.5, 129.0, 128.9, 128.3, 128.1, 128.0, 127.6, 127.2, 127.0, 113.3, 96.5, 64.9, 64.6, 62.6, 52.1, 17.6, 17.1, -1.4, -1.7; HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{43}H_{49}NNaO_6SSi_2^+$, 786.2712; found, 786.2718.



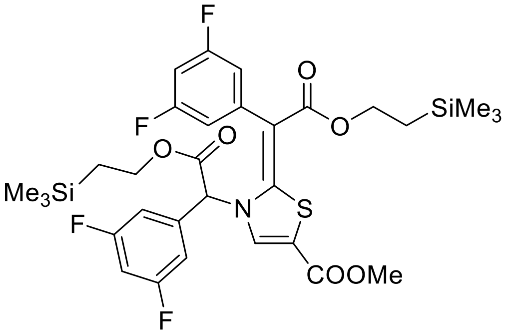
methyl (*Z*)-3-(1-(4-methoxyphenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(1-(4-methoxyphenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5g**), 74 mg (Yellow solid, 55% yield); TLC R_f= 0.56 (Hexanes/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.31 – 7.29 (m, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 7.00 – 6.95 (m, 3H), 6.92 – 6.89 (m, 1H), 6.88 (d, *J* = 8.1 Hz, 2H), 5.66 (s, 1H), 4.28 – 4.10 (m, 4H), 3.85 (s, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 0.99 – 0.89 (m, 4H), 0.04 (s, 9H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 168.7, 162.2, 160.3, 160.2, 158.9, 136.9, 133.1, 132.4, 129.5, 128.1, 126.5, 114.7, 114.7, 114.0, 112.5, 96.5, 64.6, 64.1, 62.4, 55.4, 55.2, 52.0, 17.6, 17.2, -1.4, -1.5; HRMS (ESI$^+$) m/z: $[M + Na]^+$ calcd for $C_{33}H_{45}NaO_8SSi_2^+$, 694.2297; found, 694.2309.



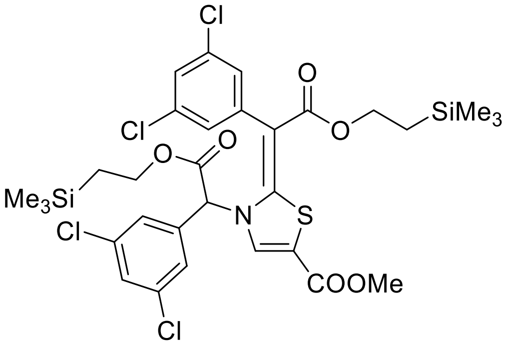
methyl (*Z*)-3-(1-(2,6-difluorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(1-(2,6-difluorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5h**), 119 mg (Yellow liquid, 87% yield); TLC R_f= 0.63 (Hexanes/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 1H), 7.33 – 7.27 (m, 1H), 7.22 (s, 1H), 7.00 – 6.90 (m, 3H), 6.87 (t, *J* = 8.0 Hz, 1H), 5.85 (s, 1H), 4.24 – 4.13 (m, 4H), 3.78 (s, 3H), 0.94 – 0.84 (m, 4H), -0.02 (s, 9H), -0.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 166.7, 163.5, 163.5, 162.2, 162.2, 162.0, 162.0, 161.8, 161.6, 161.1, 161.0, 159.8, 159.7, 159.5, 159.4, 135.3, 132.6, 132.5, 132.4, 130.3, 130.2, 130.1, 114.2, 112.8, 112.6, 112.5, 112.5, 112.4, 112.3, 112.3, 111.9, 111.8, 111.6, 111.6, 111.5, 111.4, 111.3, 82.6, 65.5, 62.7, 54.3, 52.2, 17.4, 17.0, -1.5, -1.6 (there are more signals than the number of carbons in the molecular formula due to the coupling of F atoms); HRMS (ESI$^+$) m/z: $[M + Na]^+$ calcd for $C_{31}H_{37}F_4NNaO_6SSi_2^+$, 706.1709 ; found, 706.1709.



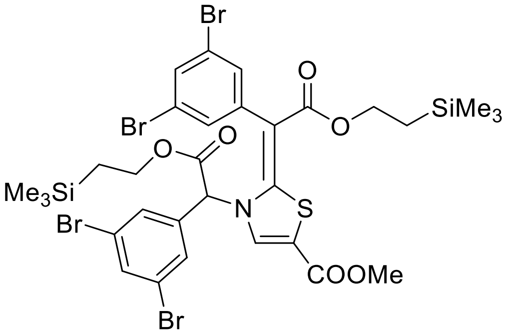
methyl (*Z*)-3-(1-(2,6-dichlorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(1-(2,6-dichlorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5i**), 114 mg (Yellow solid, 76% yield); TLC R$_f$= 0.56 (Hexanes/EtOAc = 5:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.31 (m, 4H), 7.28 (s, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 5.77 (s, 1H), 4.22 – 4.17 (m, 2H), 4.11 – 4.02 (m, 2H), 3.78 (s, 3H), 0.91 – 0.82 (m, 4H), -0.04 (s, 9H), -0.07 – -0.09 (m, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.3, 166.2, 163.8, 161.9, 139.9, 139.4, 136.9, 135.4, 133.6, 131.4, 130.5, 129.9, 129.6, 128.2, 128.2, 114.3, 93.5, 65.4, 63.1, 62.7, 52.2, 17.5, 16.7, -1.5, -1.5; HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{31}H_{37}Cl_4NNaO_6SSi_2^+$, 772.0497; found, 772.0517.



methyl (*Z*)-3-(1-(3,5-difluorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(1-(3,5-difluorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5j**), 85 mg (Yellow solid, 62% yield); TLC R$_f$= 0.42 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.23 (s, 1H), 6.85 – 6.78 (m, 2H), 6.73 (tt, *J* = 8.9, 2.0 Hz, 2H), 6.52 (d, *J* = 5.6 Hz, 2H), 5.43 (s, 1H), 4.27 – 4.18 (m, 4H), 3.78 (s, 3H), 0.96 – 0.89 (m, 4H), 0.02 (s, 9H), -0.06 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.6, 167.2, 164.7, 164.6, 162.2, 162.1, 161.6, 161.3, 139.5, 139.4, 139.3, 137.7, 137.6, 137.5, 135.8, 115.2, 114.9, 114.6, 114.2, 113.9, 111.1, 111.0, 110.9, 110.8, 105.7, 105.4, 105.2, 103.6, 103.3, 103.1, 94.8, 65.9, 64.0, 63.0, 52.4, 17.6, 17.3, -1.5, -1.5 (there are more signals than the number of carbons in the molecular formula due to the coupling of F atoms); HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{31}H_{37}F_4NNaO_6SSi_2^+$, 706.1709; found, 706.1718.

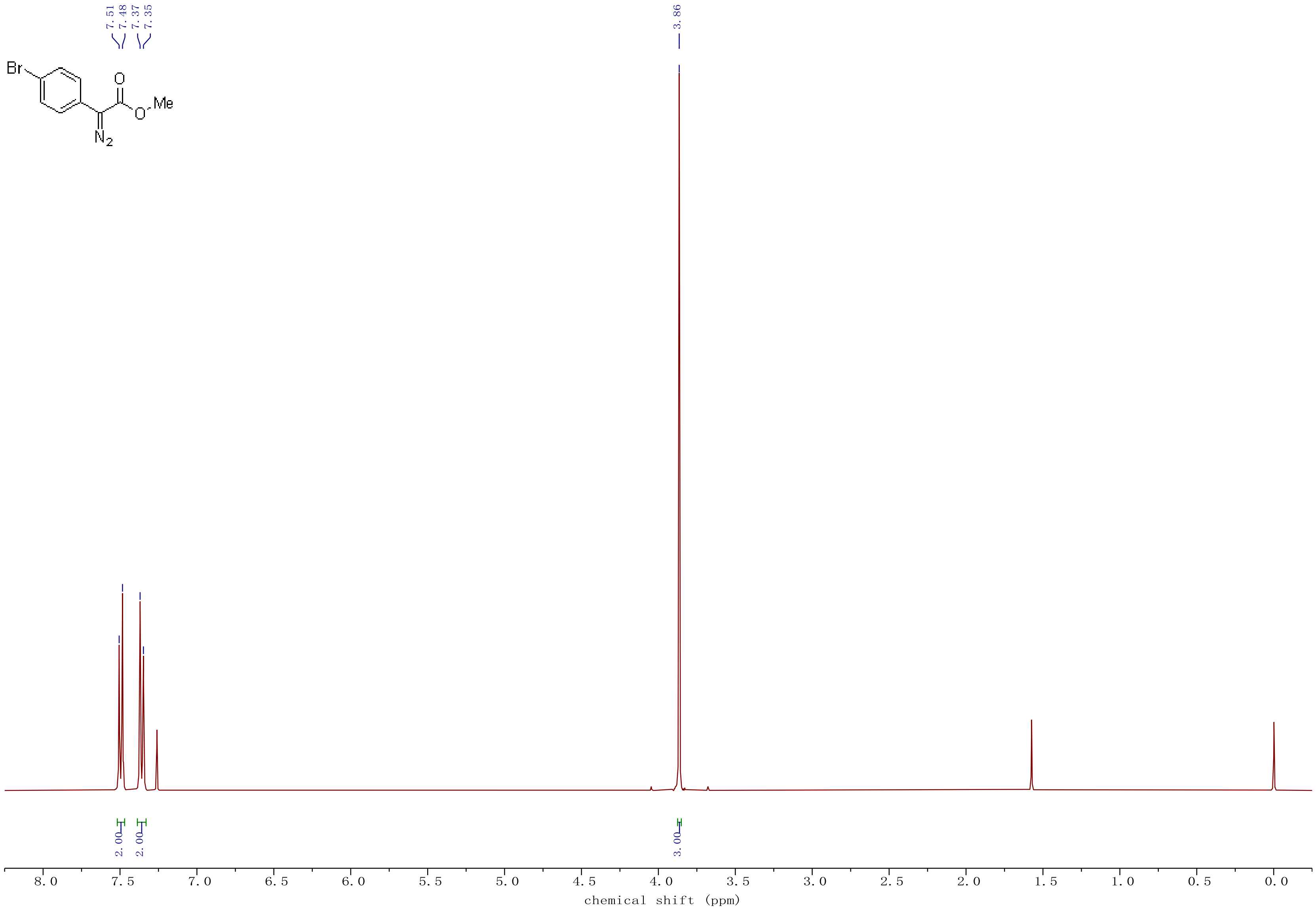


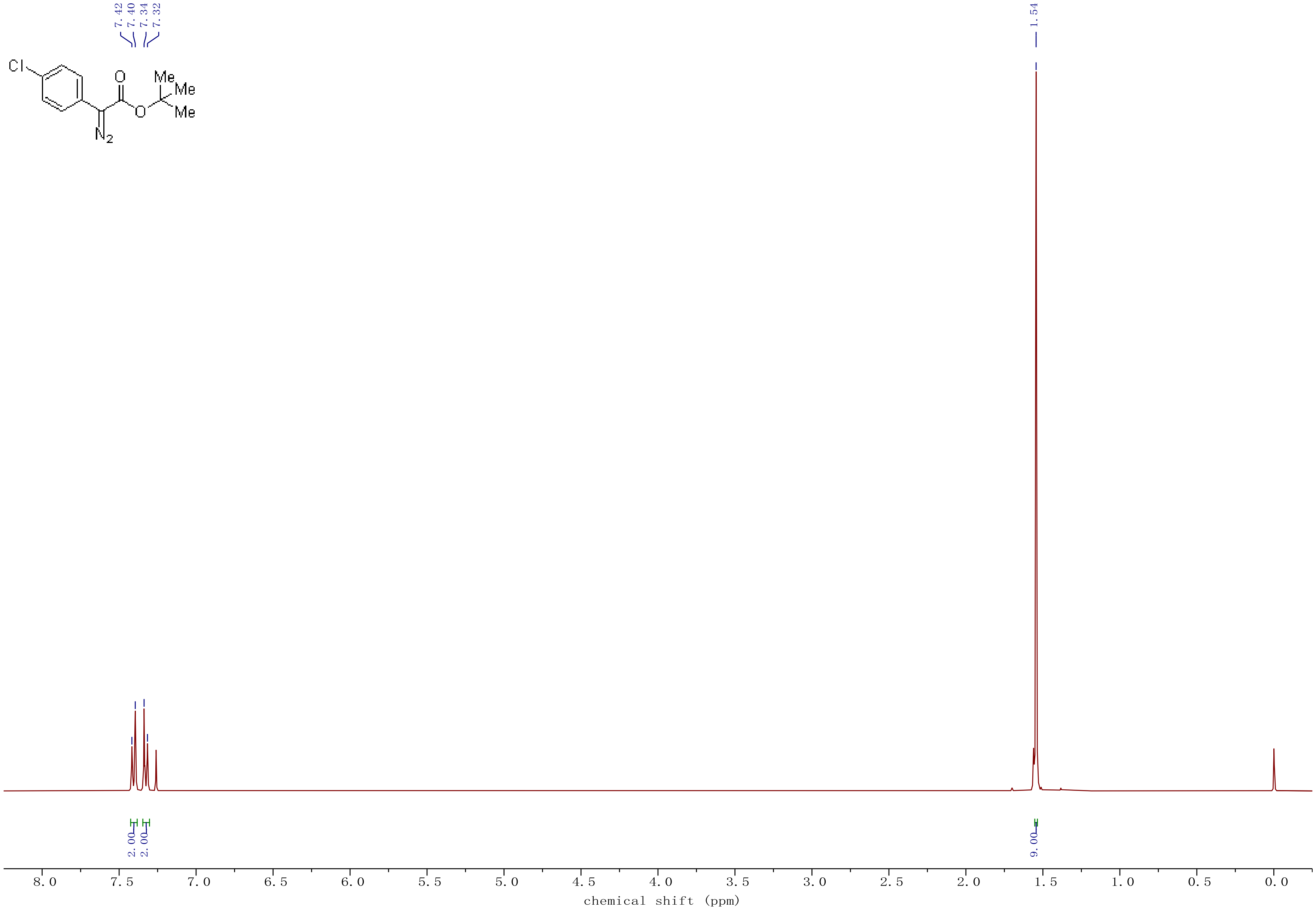
methyl (*Z*)-3-(1-(3,5-dichlorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(1-(3,5-dichlorophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5k**), 42 mg (Yellow solid, 28% yield); TLC R*f*= 0.45 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 1.9 Hz, 1H), 7.29 (t, *J* = 1.9 Hz, 1H), 7.24 (s, 1H), 7.14 (s, 2H), 6.85 (d, *J* = 1.9 Hz, 2H), 5.41 (s, 1H), 4.29 – 4.19 (m, 4H), 3.81 (s, 3H), 0.99 – 0.90 (m, 4H), 0.02 (s, 9H), -0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.0, 161.6, 139.1, 137.0, 136.3, 135.6, 135.5, 130.3, 130.0, 129.6, 127.8, 126.2, 114.8, 94.7, 66.1, 64.0, 63.1, 52.4, 17.5, 17.4, -1.4, -1.5; HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{31}H_{37}Cl_4NNaO_6SSi_2^+$, 772.0497; found, 772.0516.



methyl (*Z*)-3-(1-(3,5-dibromophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethyl)-2-(1-(3,5-dibromophenyl)-2-oxo-2-(2-(trimethylsilyl)ethoxy)ethylidene)-2,3-dihydrothiazole-5-carboxylate (**5l**), 108 mg (Yellow liquid, 58% yield); TLC R*f*= 0.42 (Hexanes/EtOAc = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, *J* = 1.7 Hz, 1H), 7.59 (t, *J* = 1.7 Hz, 1H), 7.38 (s, 1H), 7.30 (s, 1H), 7.23 (s, 1H), 7.04 (s, 2H), 5.39 (s, 1H), 4.32 – 4.18 (m, 4H), 3.81 (s, 3H), 1.02 – 0.89 (m, 4H), 0.02 (s, 9H), -0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.0, 161.6, 139.7, 137.3, 135.6, 135.6, 133.5, 133.3, 133.1, 129.5, 124.1, 123.5, 114.7, 94.6, 66.2, 63.8, 63.1, 52.4, 17.5, -1.4, -1.5 (one carbon signal is missing due to ovelapping); HRMS (ESI$^+$) m/z: [M + Na]$^+$ calcd for $C_{31}H_{37}Br_4NNaO_6SSi_2^+$, 949.8465; found, 949.8471.

Copies of ^{1}H NMR spectra of 1a-1r, 2a and 2k, 3a-3f, 4a-4i, 5a-5l:

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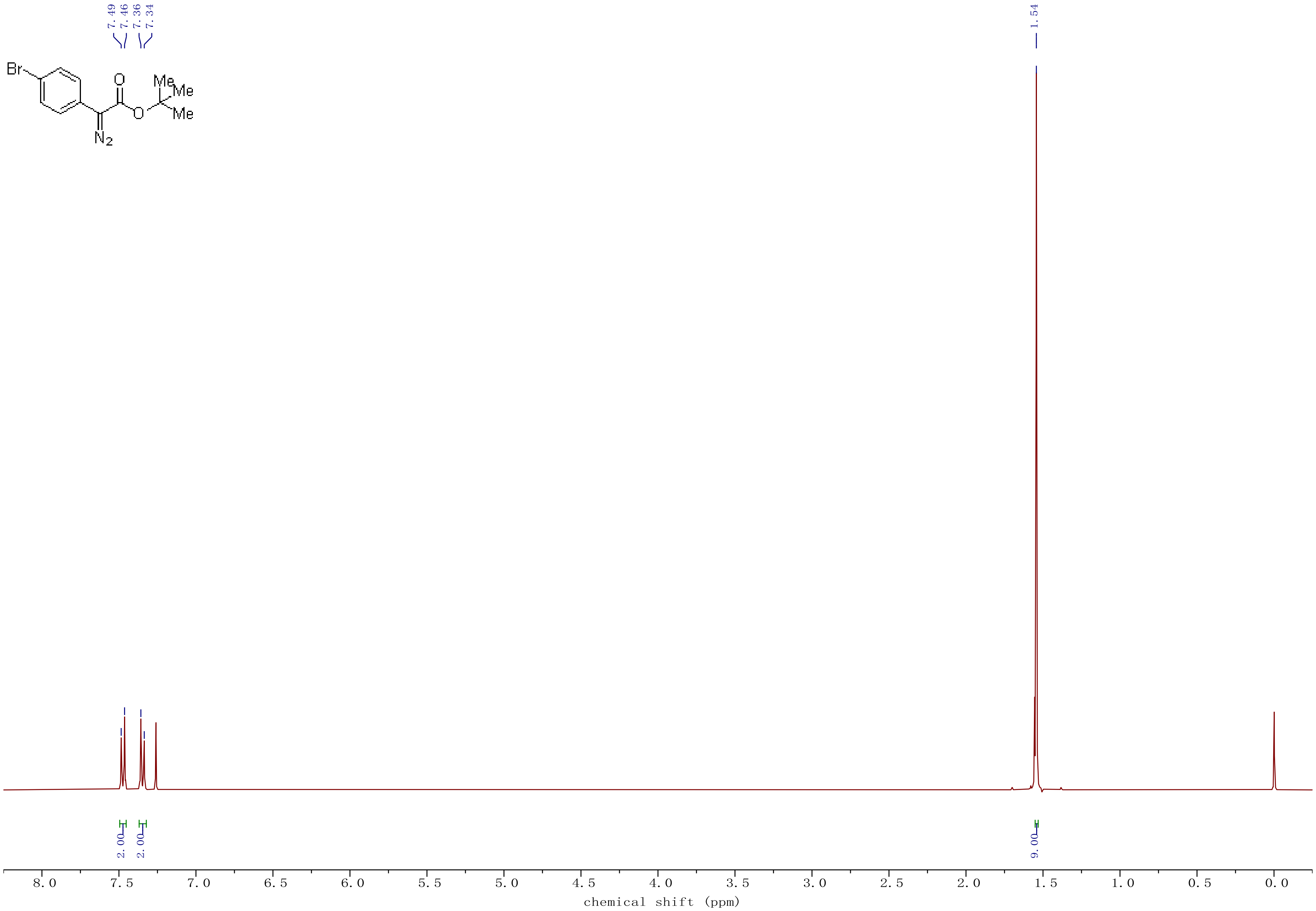
chemical shift (ppm)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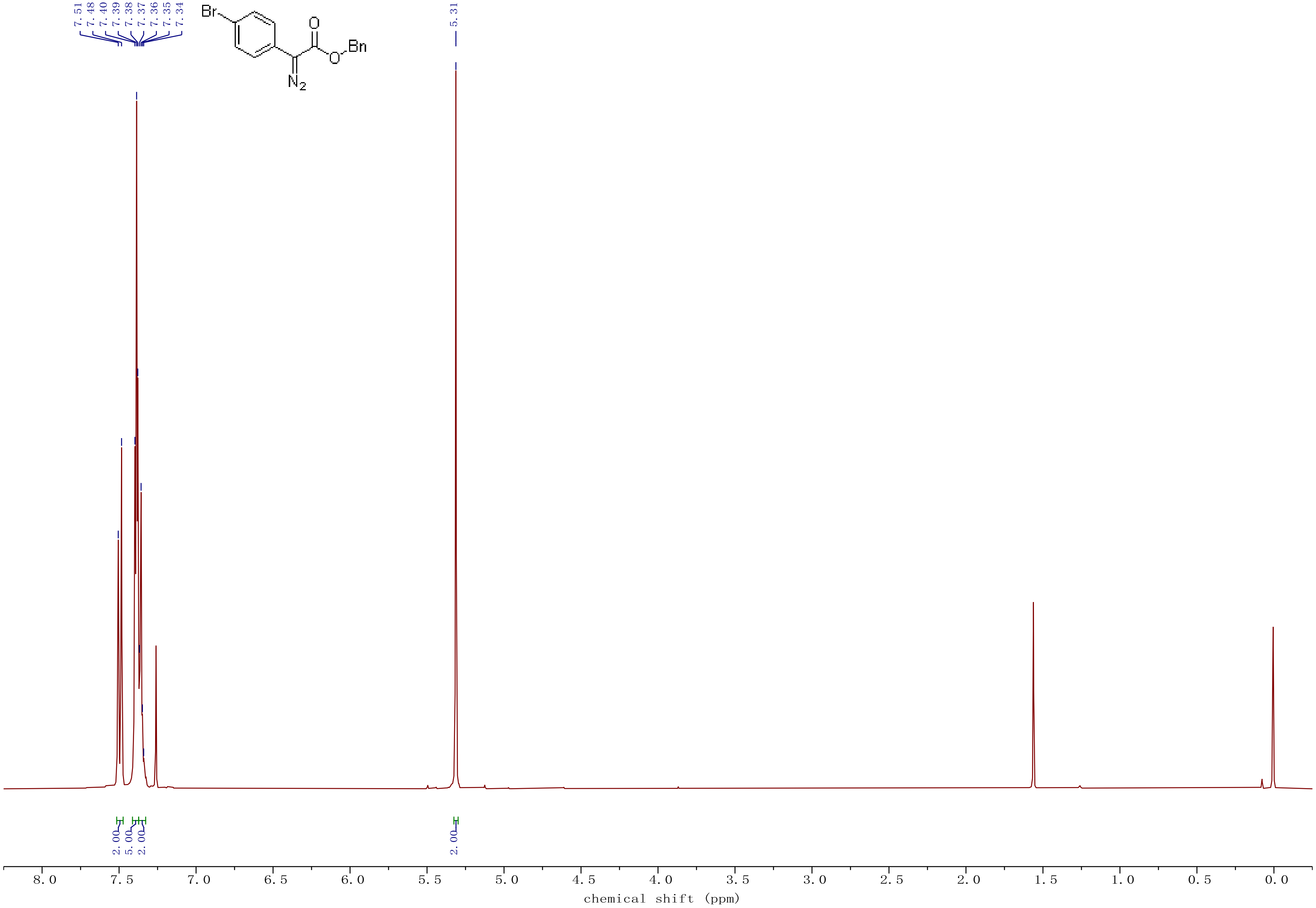
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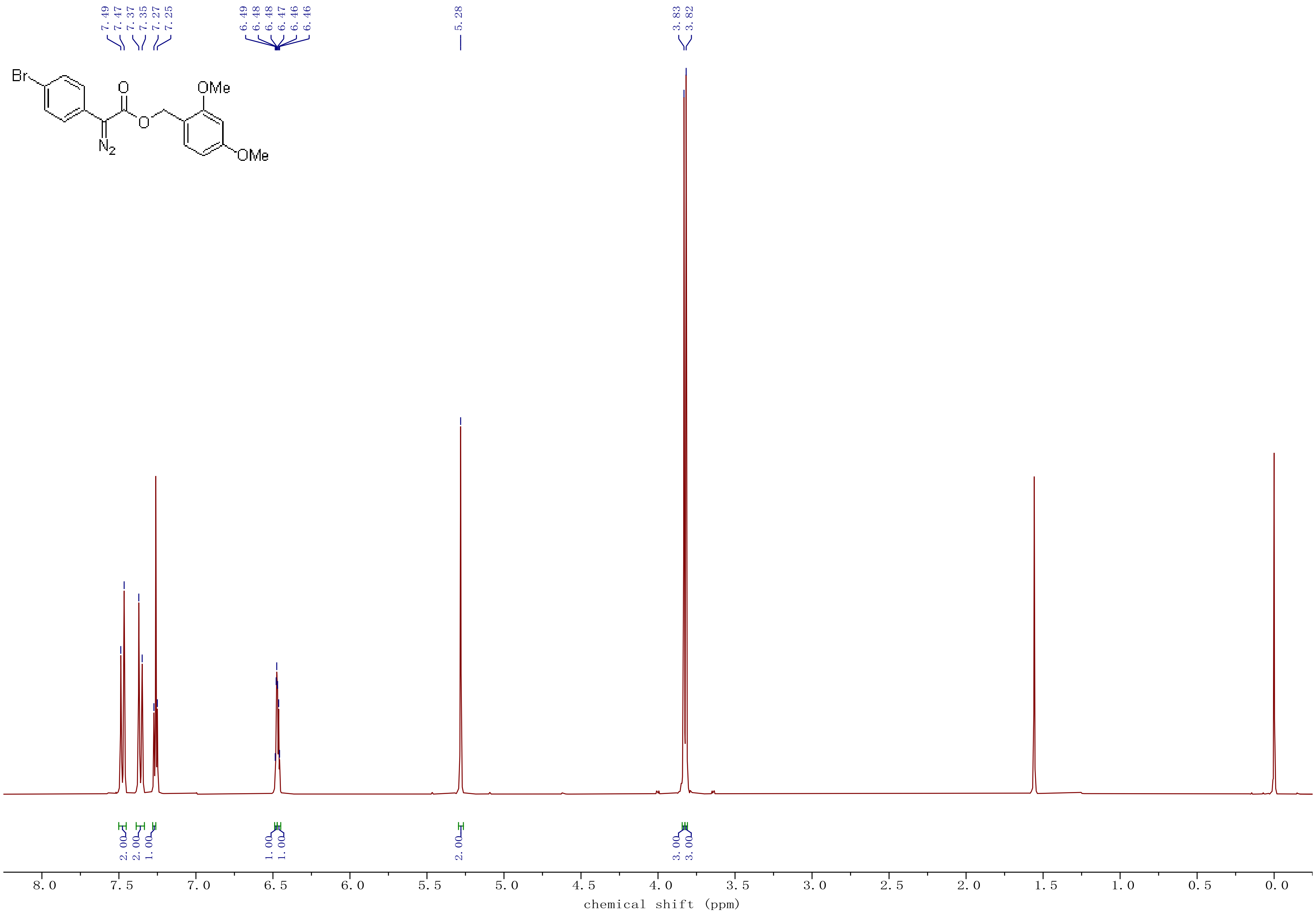
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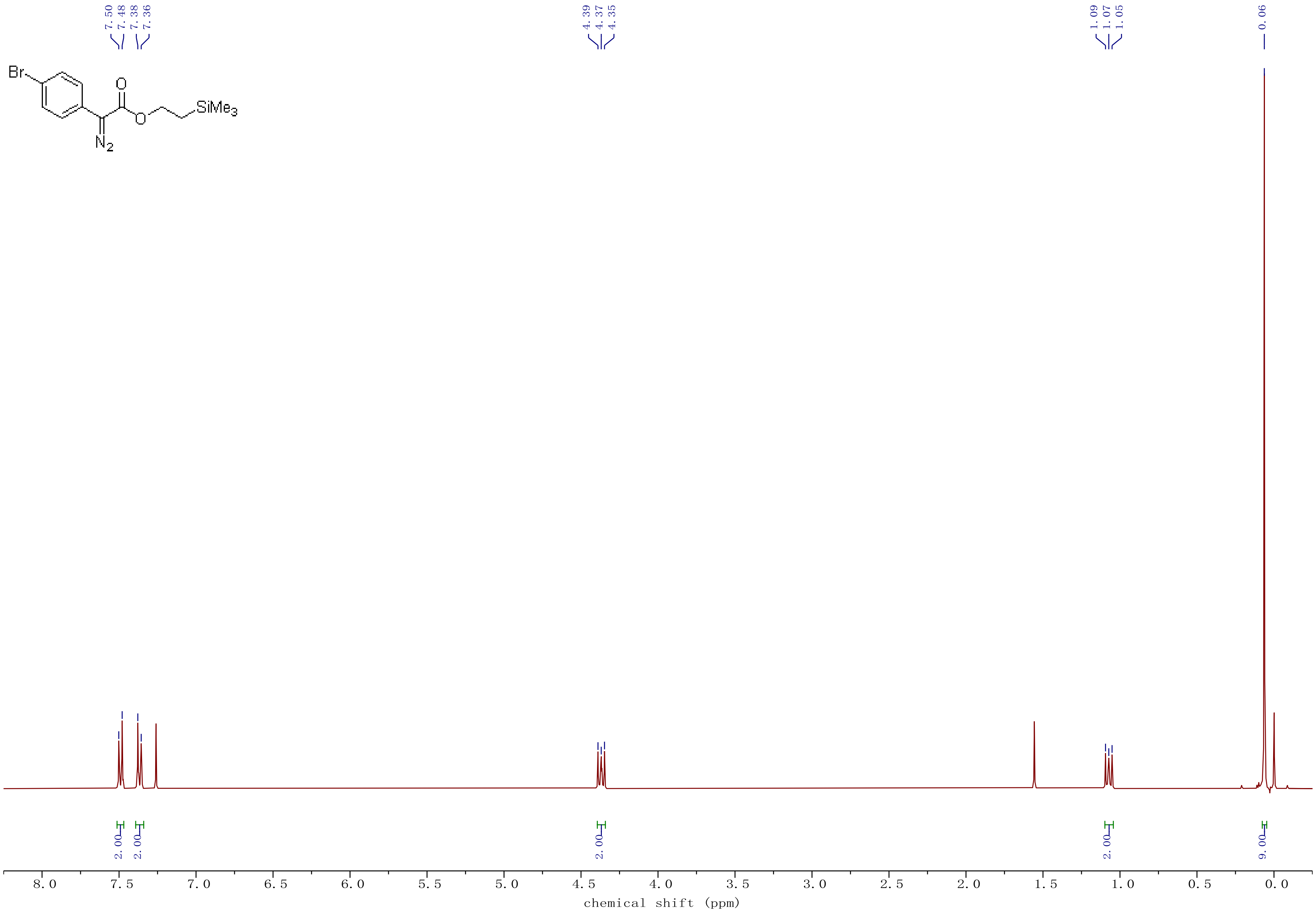

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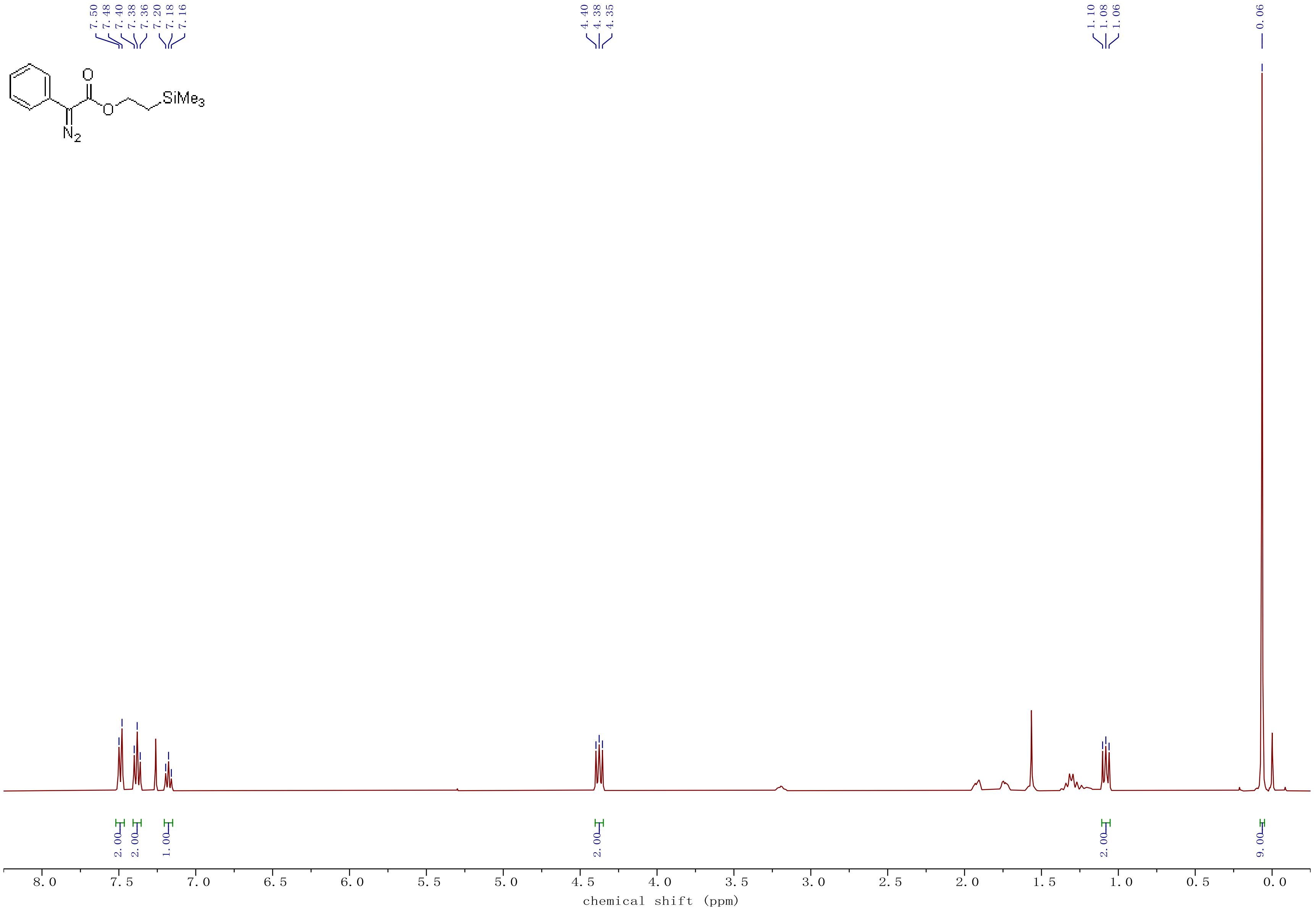
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4.40
4.38
4.35
1.10
1.08
1.06
0.06
O
O
SiMe3
N2
2.00
2.00
1.00
2.00
2.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
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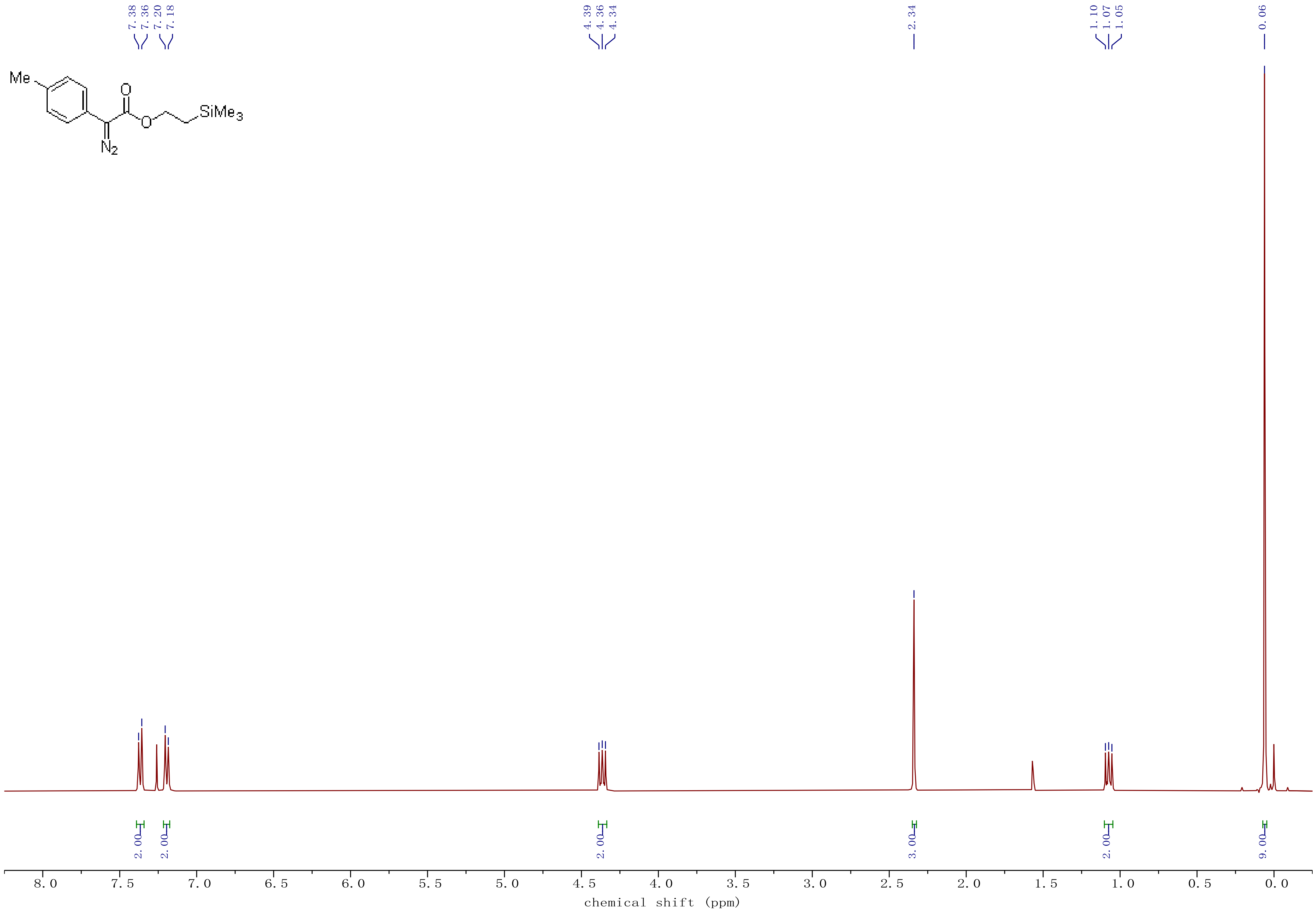
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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4.36
4.34
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1.07
1.05
0.06
Me
O
O
SiMe3
N2
2.00
2.00
2.00
3.00
2.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
1.0
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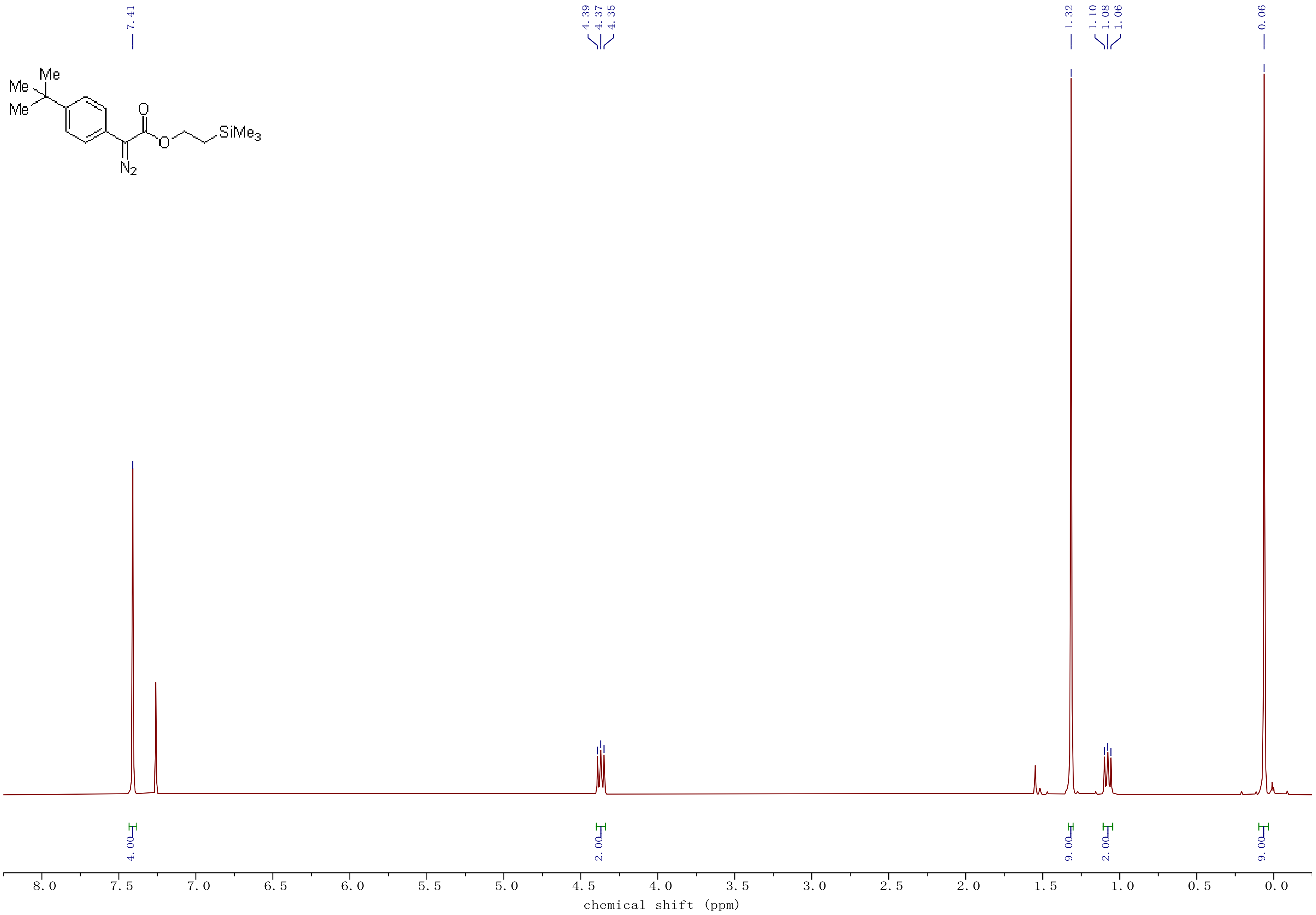
0.0
chemical shift (ppm)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1.10
1.08
1.06
0.06
Me
Me
Me
O
O
SiMe3
N2
4.00
2.00
9.00
2.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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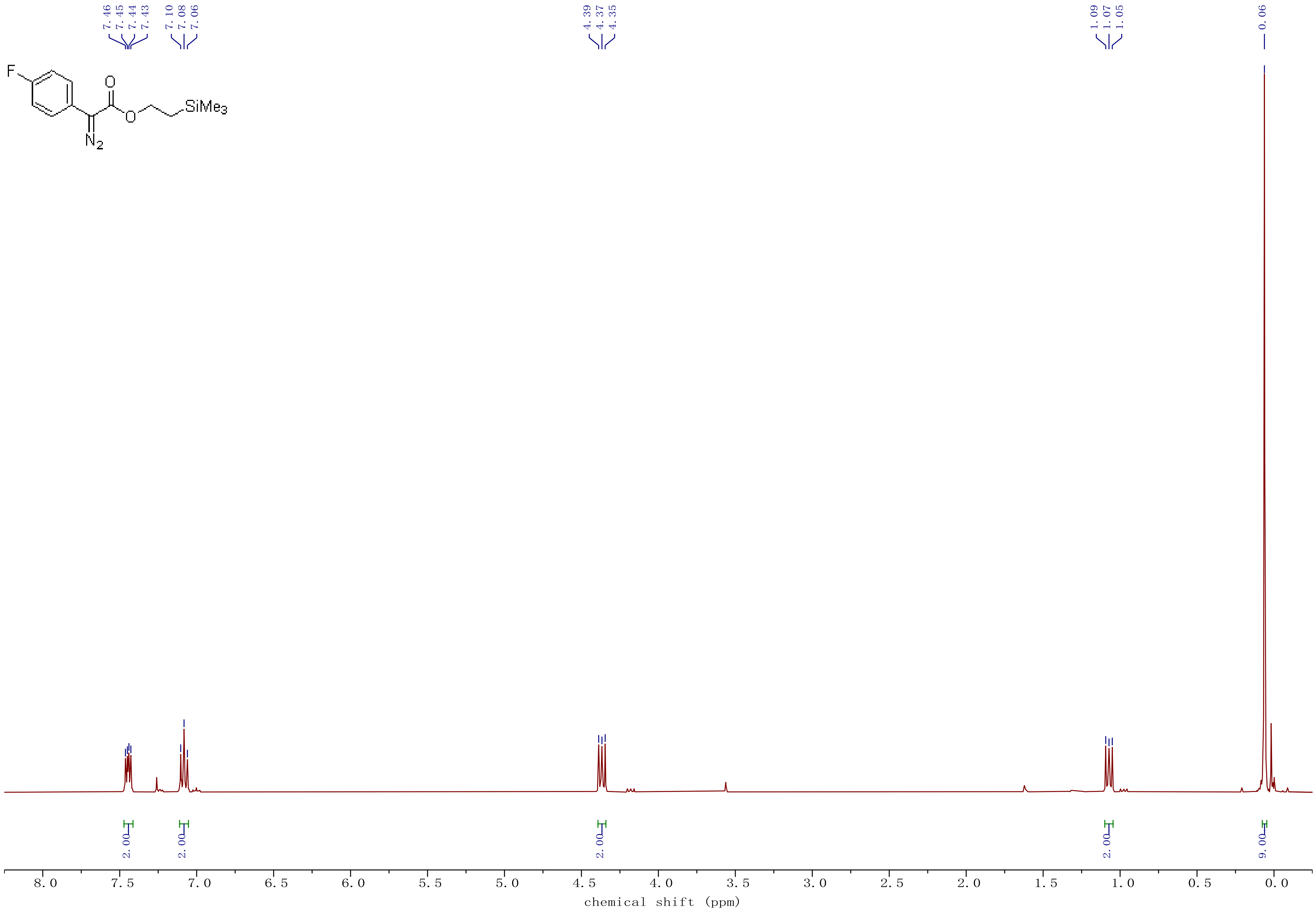
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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7.08
7.06
4.39
4.37
4.35
1.09
1.07
1.05
0.06
F
O
O
SiMe3
N2
2.00
2.00
2.00
2.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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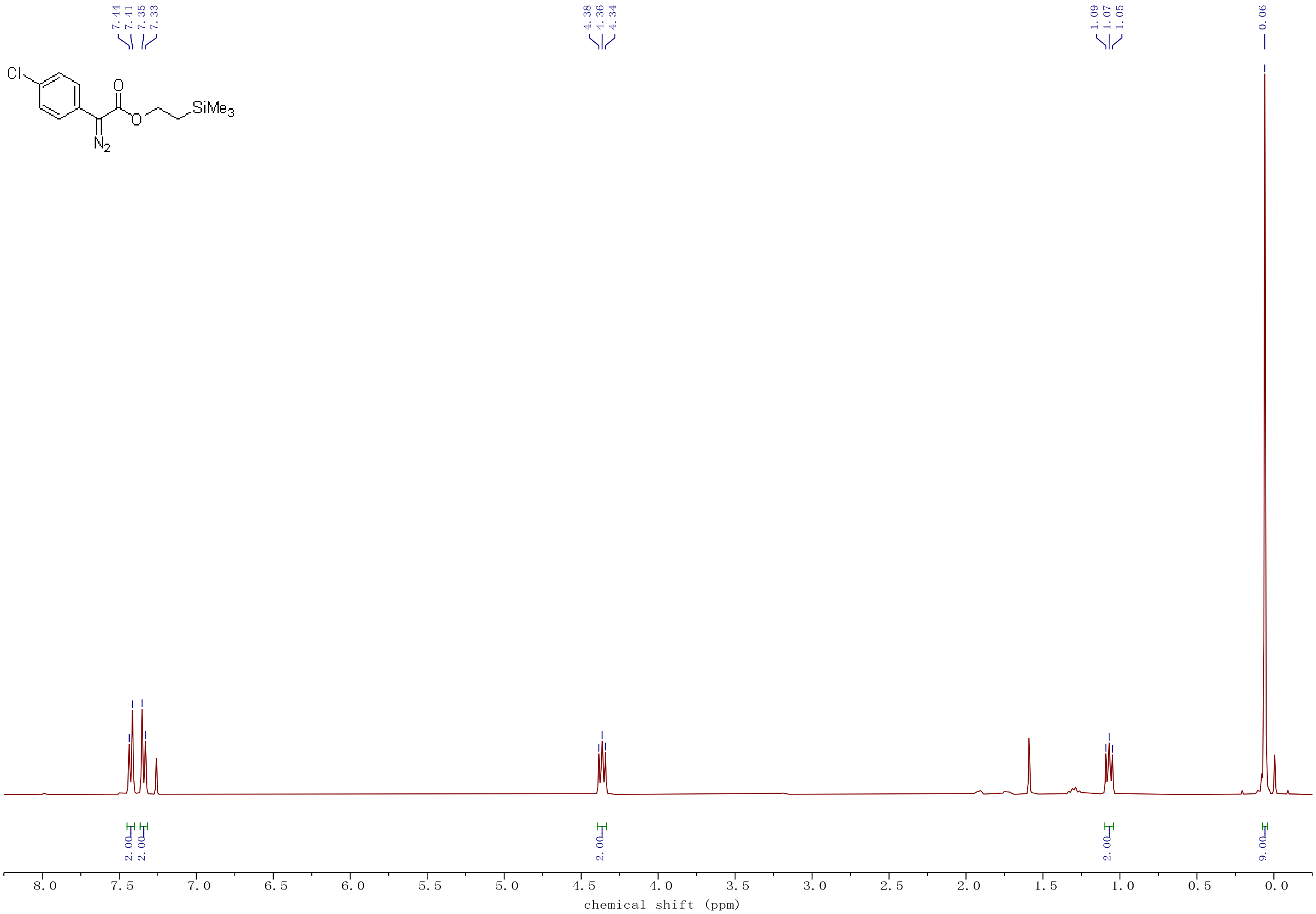
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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O
SiMe3
N2
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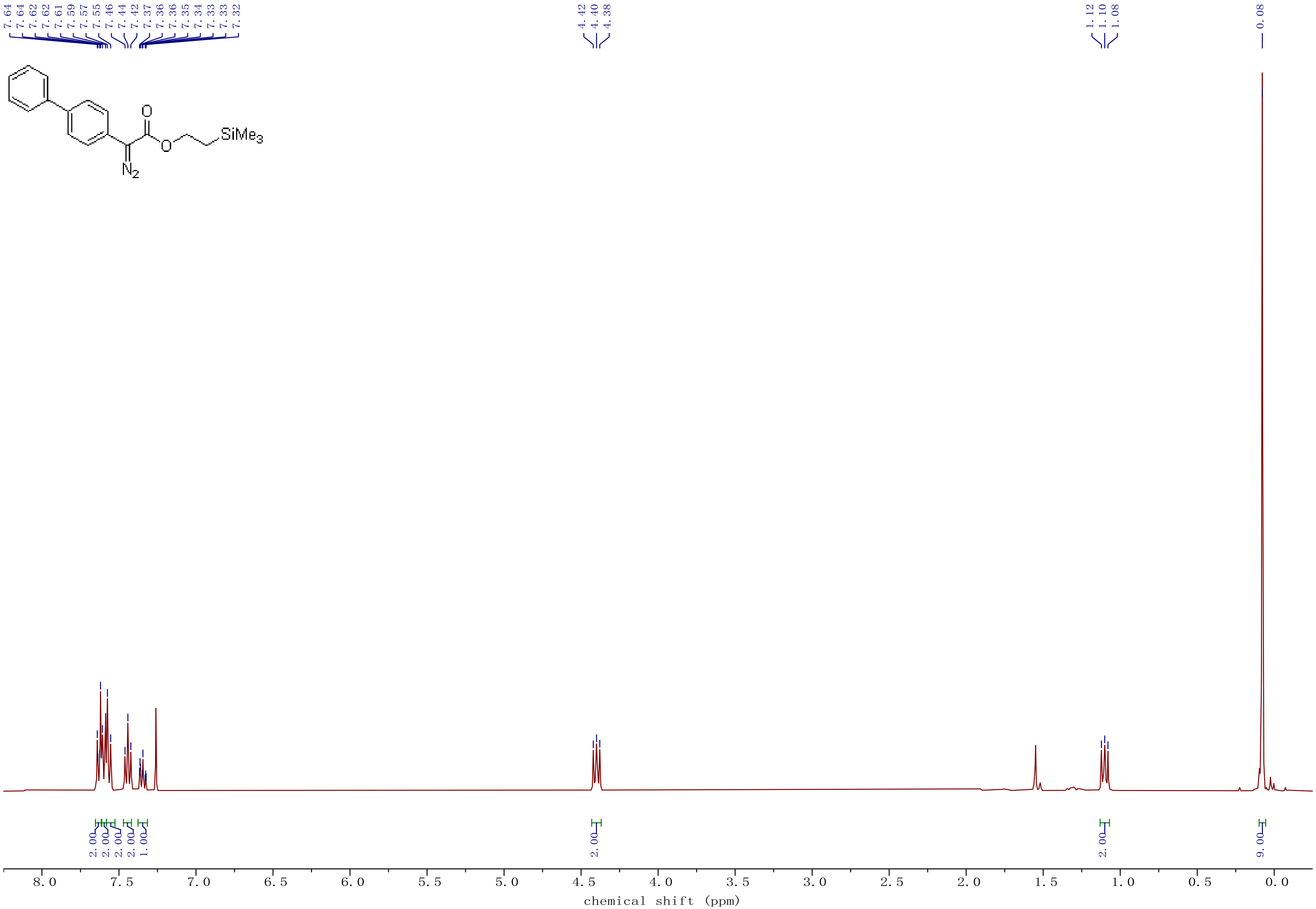
7.41
7.35
7.33
4.38
4.36
4.34
1.09
1.07
1.05
0.06
2.00
2.00
2.00
2.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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7.57
7.55
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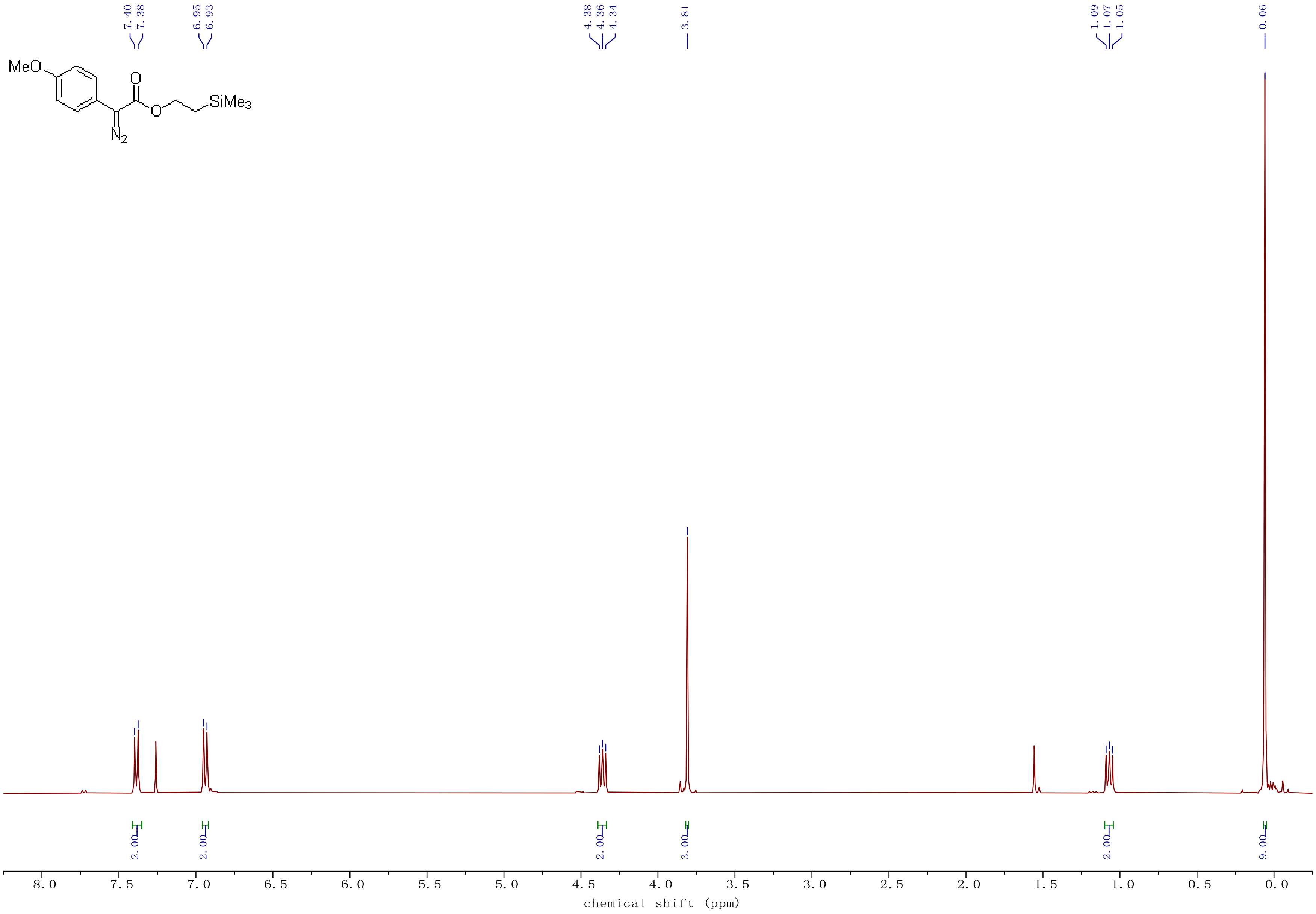
7.42
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.32
4.42
4.40
4.38
1.12
1.10
1.08
0.08
O
O
SiMe3
N2
2.00
2.00
2.00
2.00
1.00
2.00
2.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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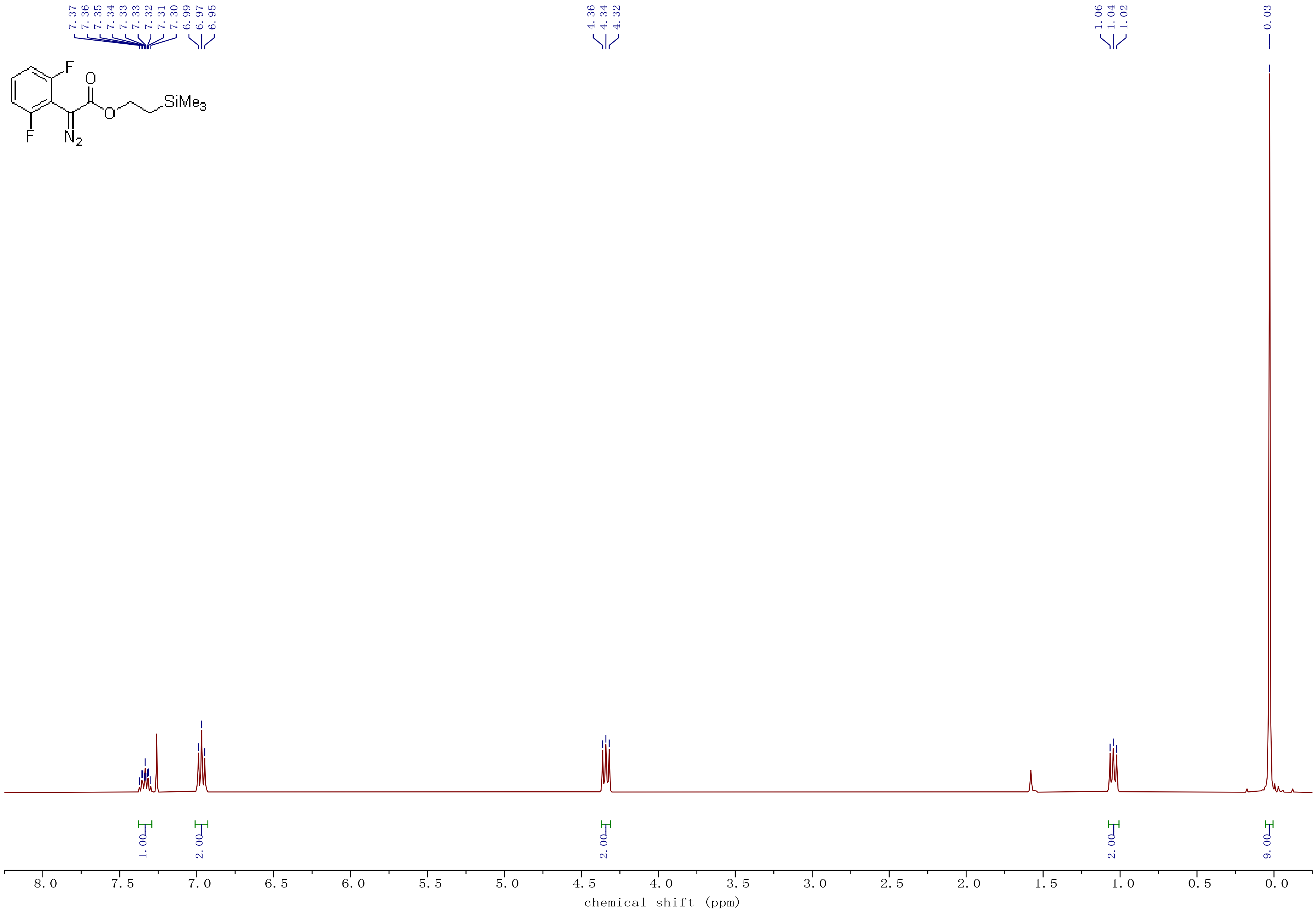
6.95
6.93
4.38
4.36
4.34
3.81
1.09
1.07
1.05
0.06
MeO
O
O
SiMe3
N2
2.00
2.00
2.00
3.00
2.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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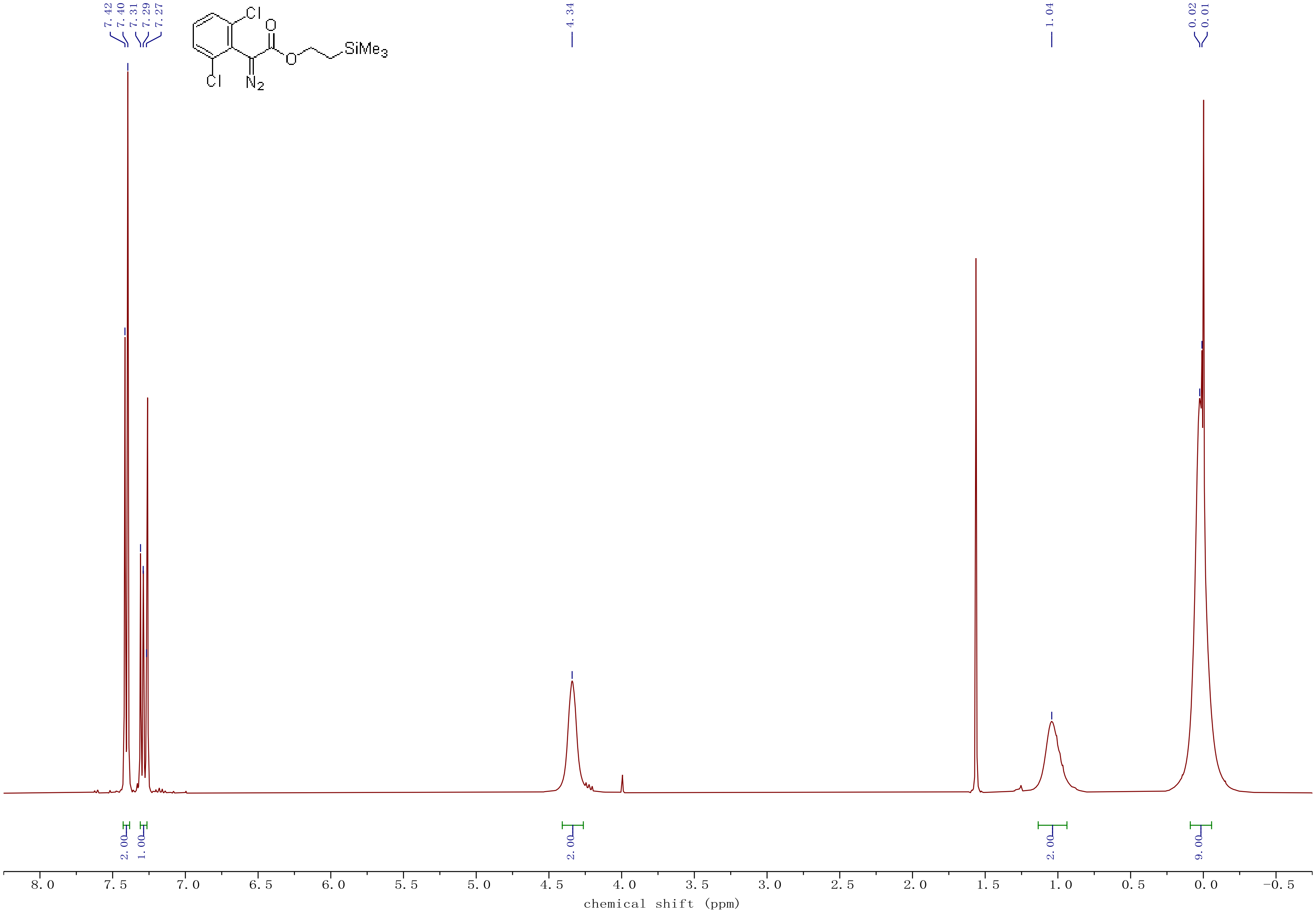
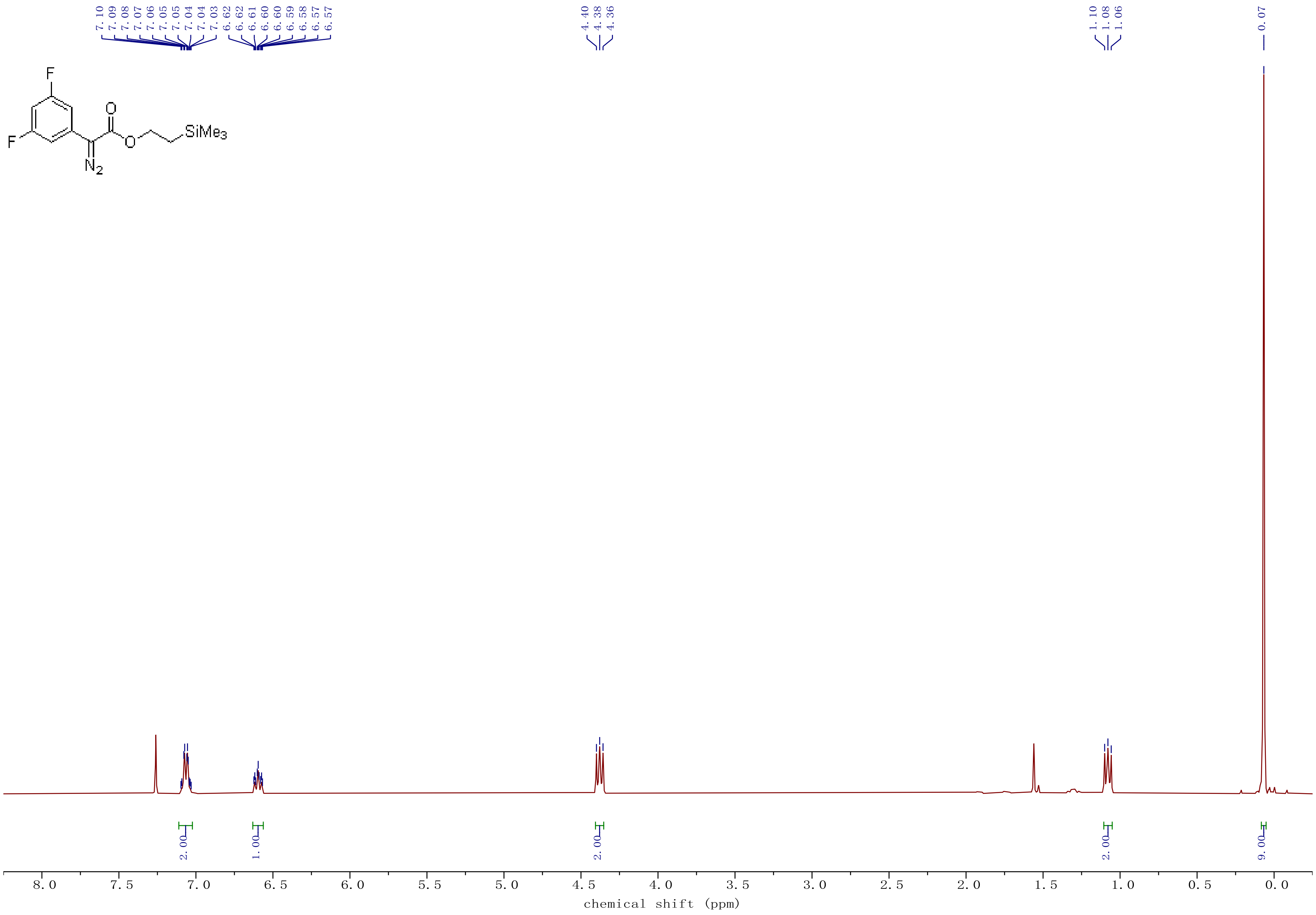
7.33
7.32
7.31
7.30
6.99
6.97
6.95
4.36
4.34
4.32
1.06
1.04
1.02
0.03
F
O
O
SiMe3
F
N2
1.00
2.00
2.00
2.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)



7.42
7.40
7.31
7.29
7.27
4.34
1.04
0.02
0.01
Cl
O
O
SiMe3
Cl
N2
2.00
1.00
2.00
2.00
9.00
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
chemical shift (ppm)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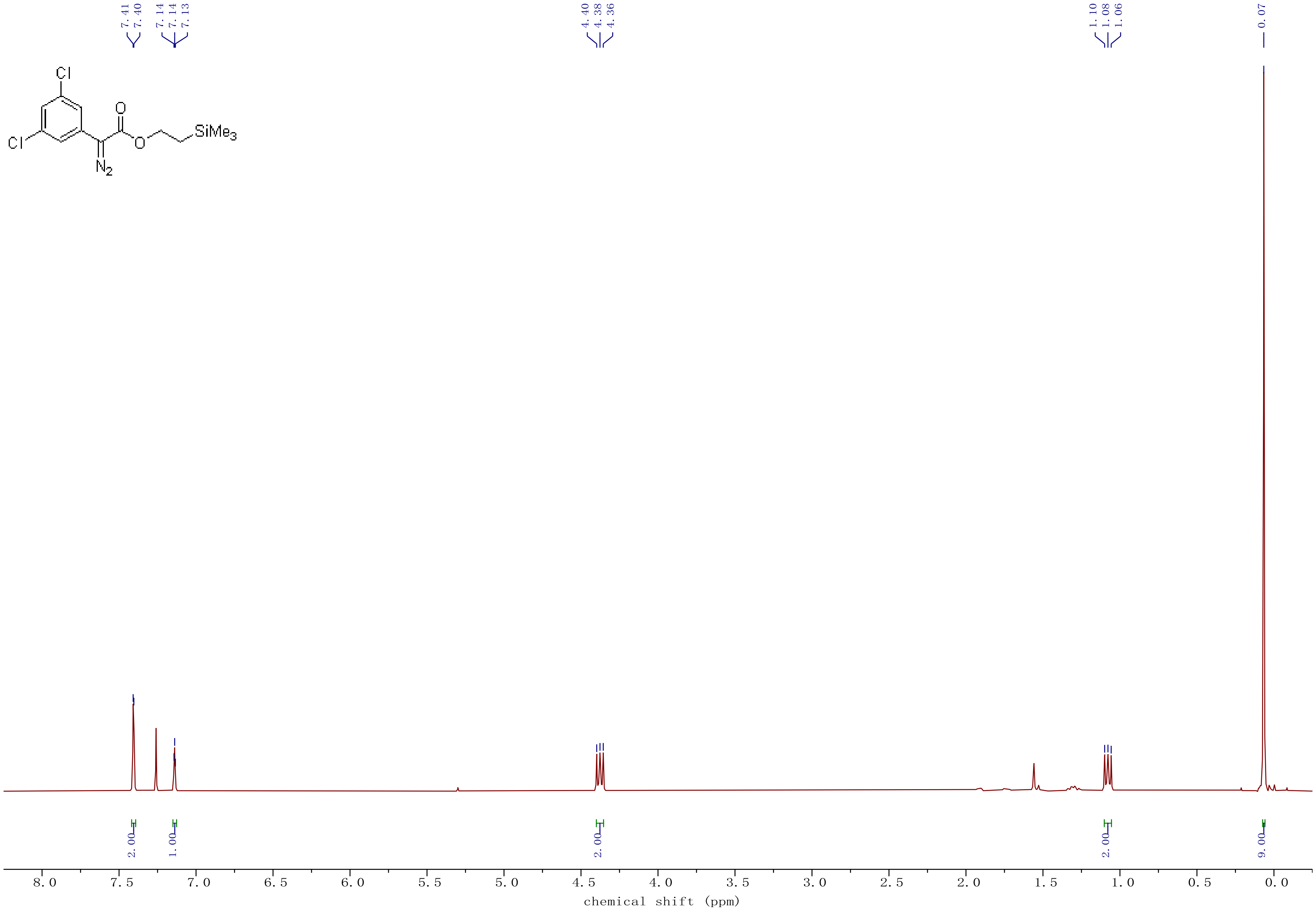
7.09
7.08
7.07
7.06
7.05
7.04
7.04
7.03
6.62
6.61
6.60
6.60
6.59
6.58
6.57
6.57
4.40
4.38
4.36
1.10
1.08
1.06
0.07
F
F
O
O
SiMe3
N2
2.00
1.00
2.00
2.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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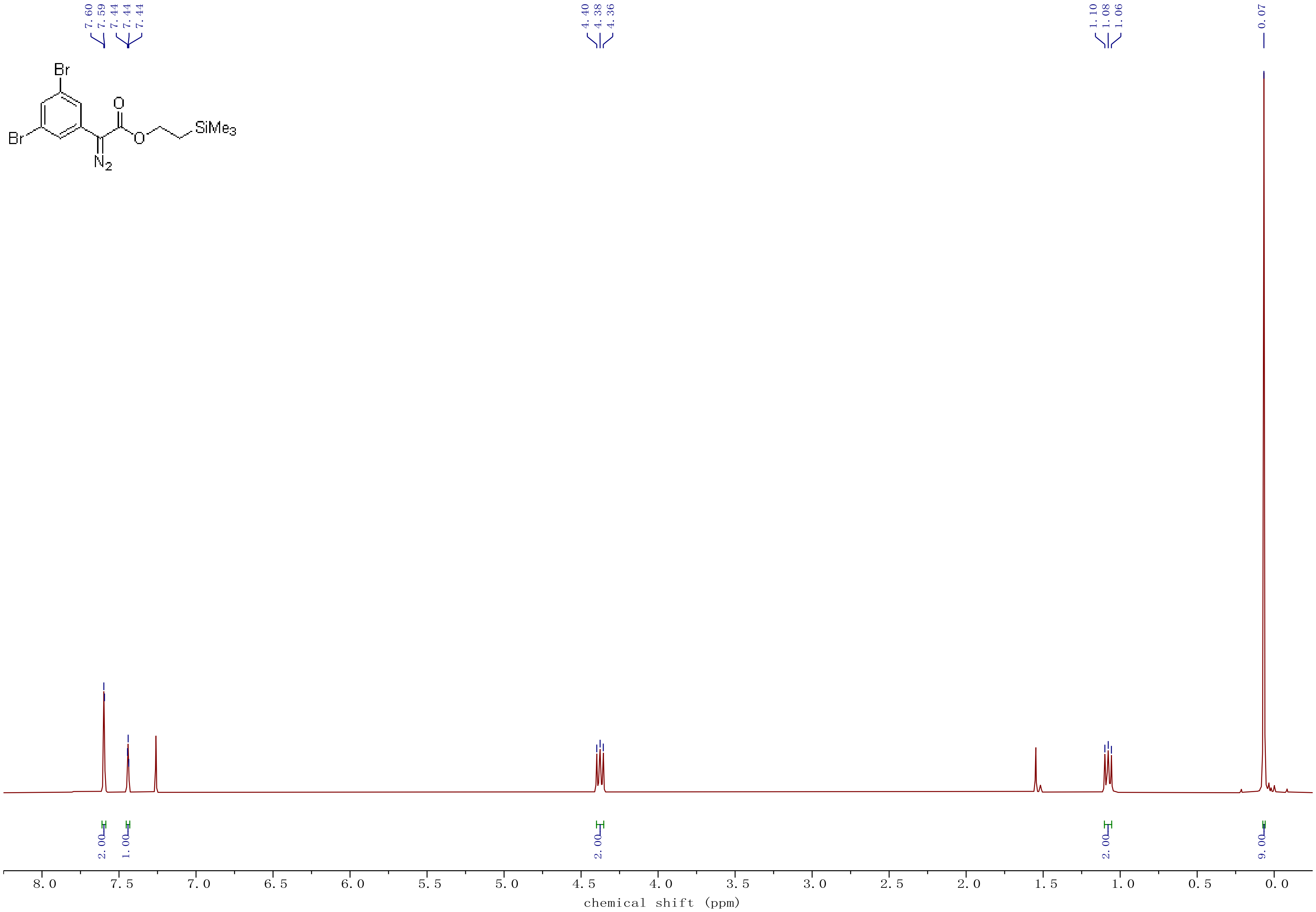
7.14
7.14
7.13
4.40
4.38
4.36
1.10
1.08
1.06
0.07
Cl
Cl
O
O
SiMe3
N2
2.00
1.00
2.00
2.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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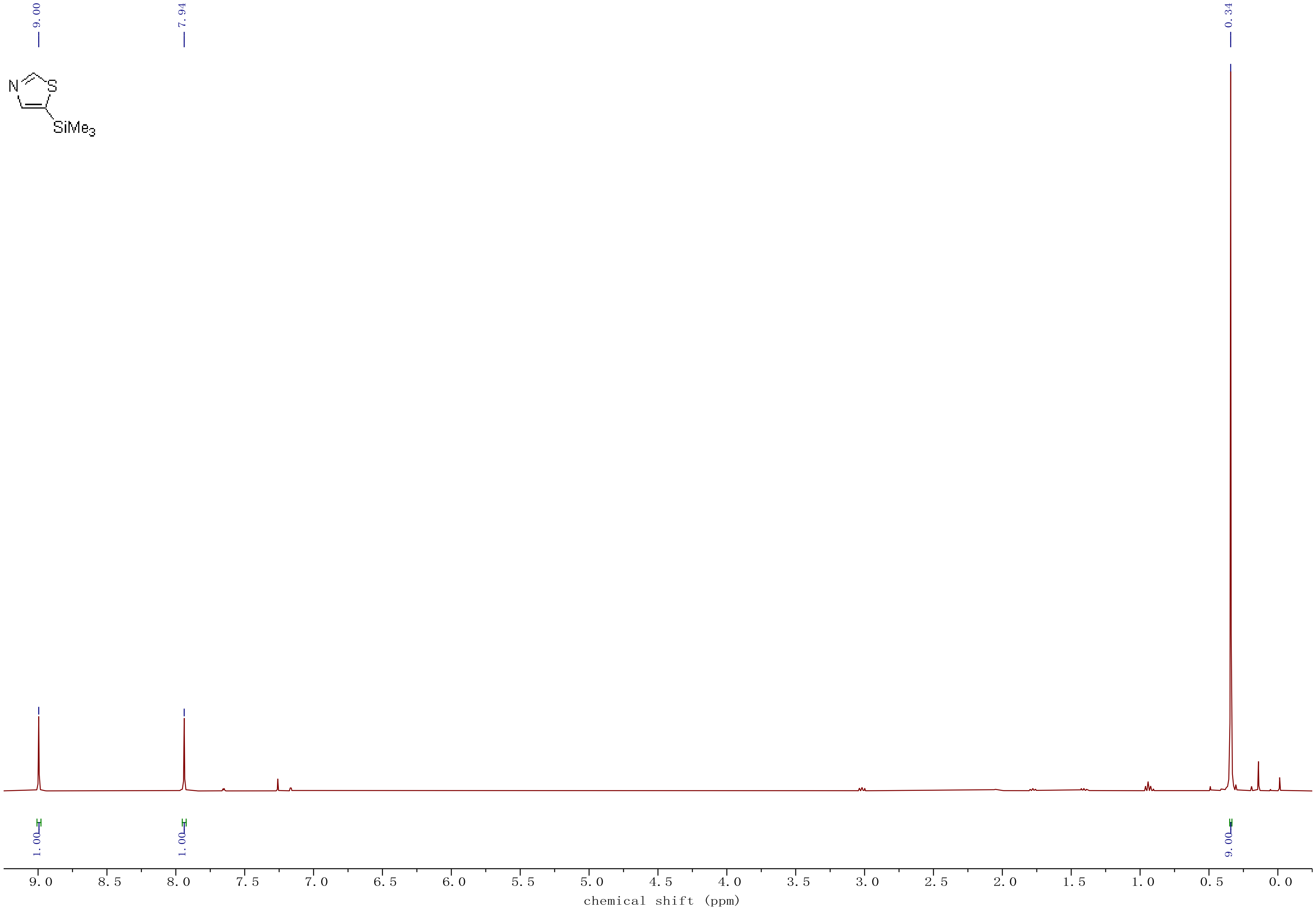
7.59
7.44
7.44
7.44
4.40
4.38
4.36
1.10
1.08
1.06
0.07
Br
Br
O
O
SiMe3
N2
2.00
1.00
2.00
2.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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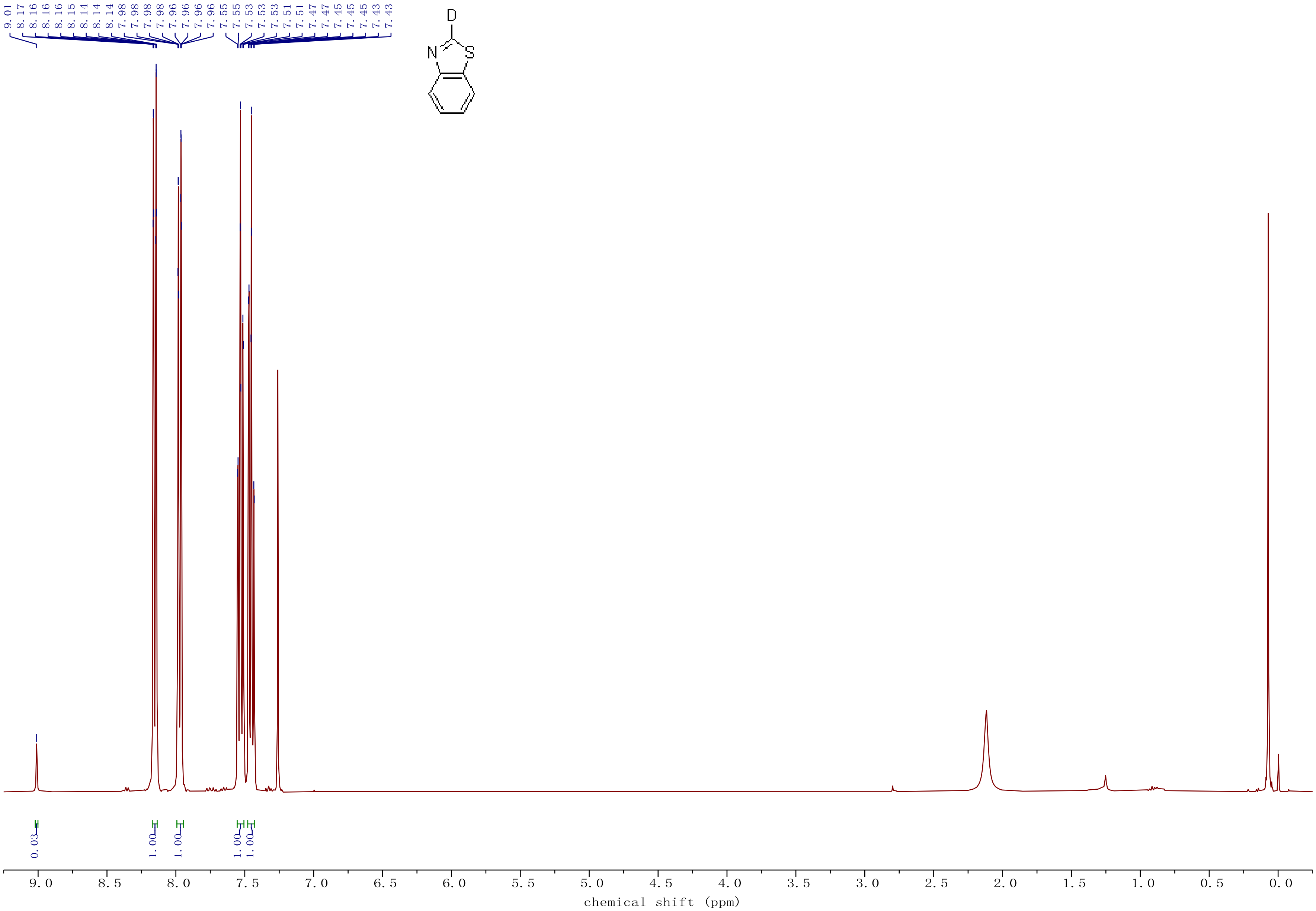
N
S
SiMe3
1.00
1.00
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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8.14
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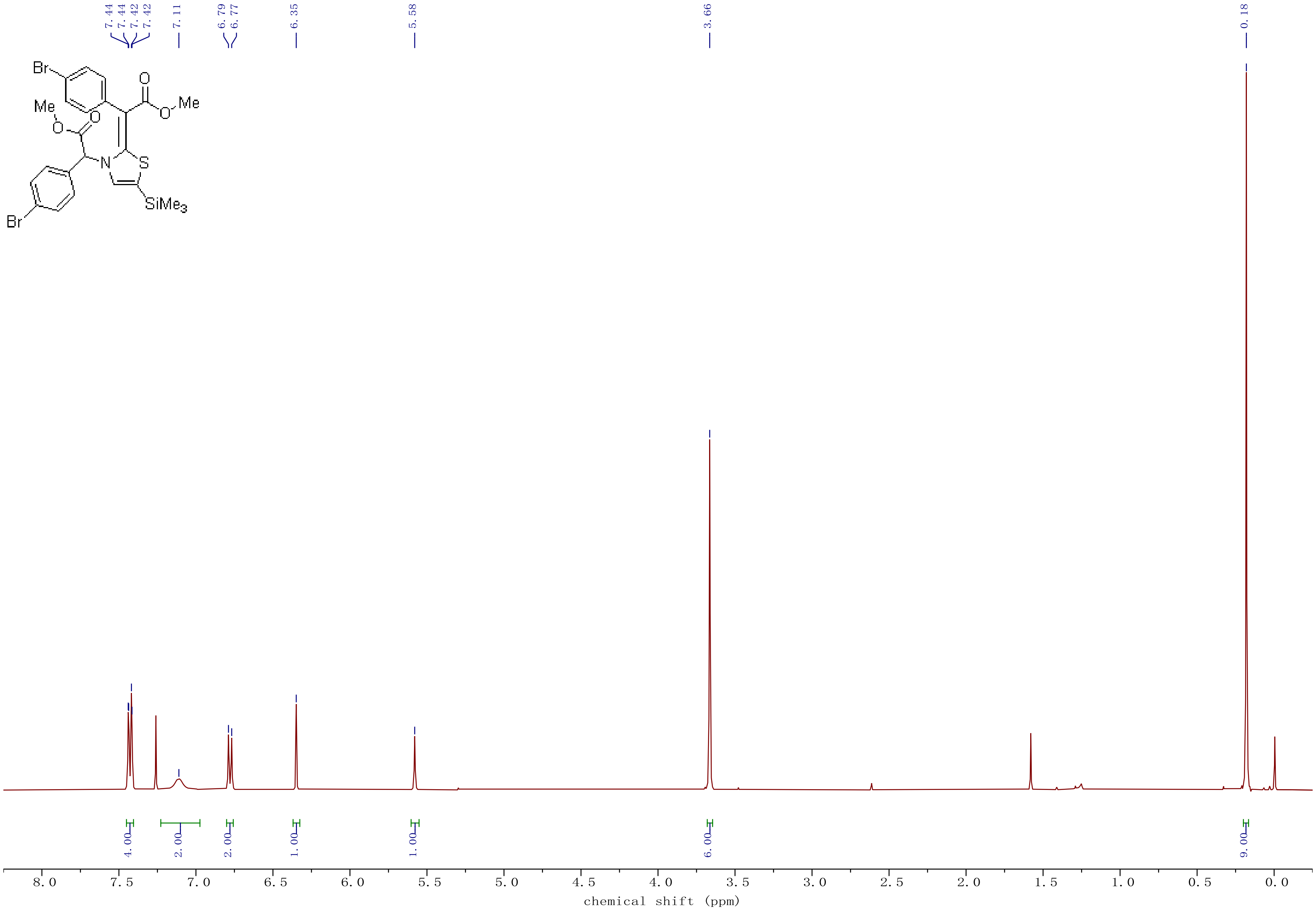
7.98
7.96
7.96
7.96
7.55
7.55
7.53
7.53
7.53
7.51
7.51
7.47
7.45
7.45
7.45
7.43
7.43
D
N
S
0.03
1.00
1.00
1.00
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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6.79
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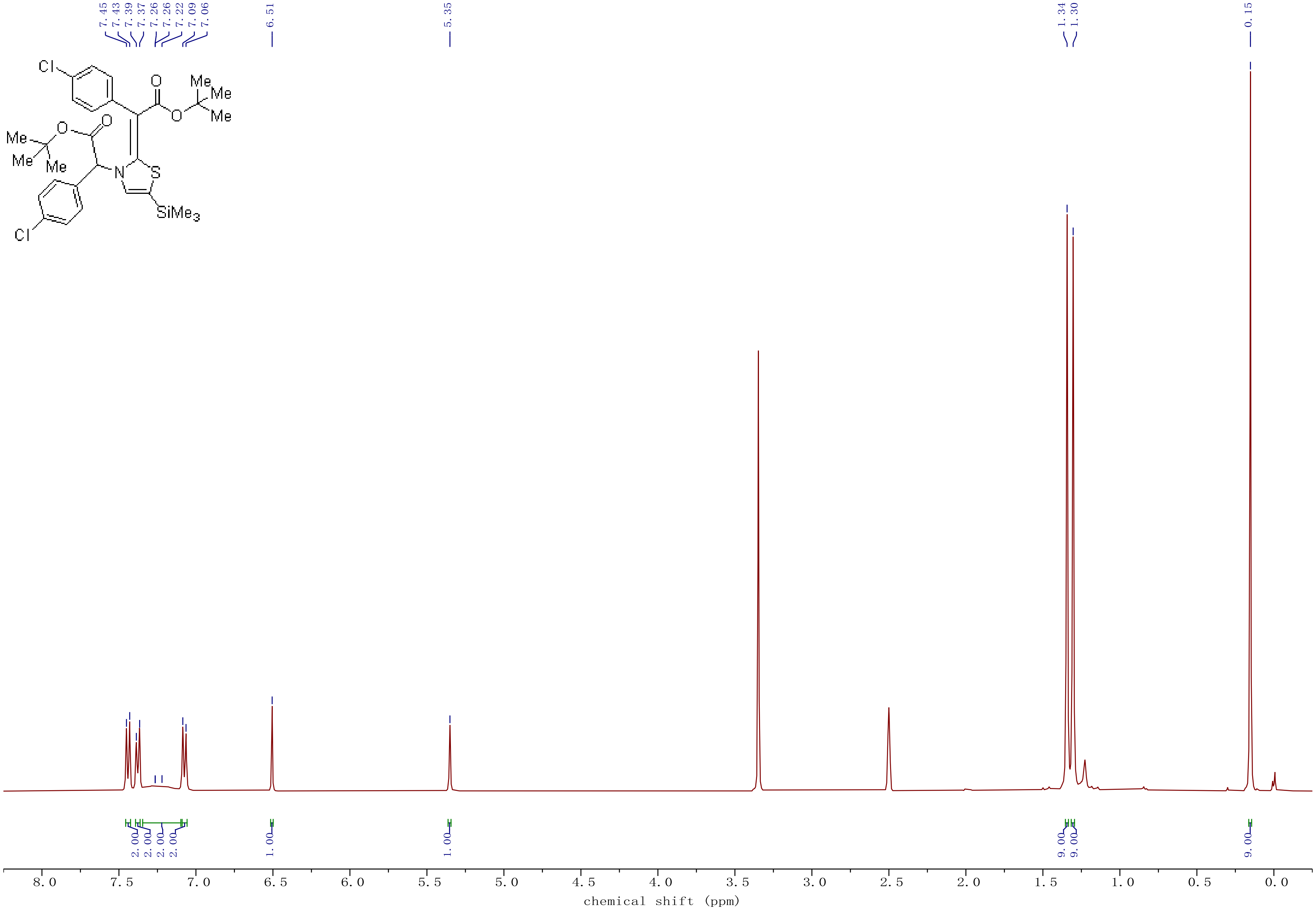
3.66
0.18
Br
O
Me
O
Me
O
O
N
S
SiMe3
Br
4.00
2.00
2.00
1.00
1.00
6.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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5.35
1.34
1.30
0.15
Cl
O
Me
Me
Me
O
O
Me
Me
Me
O
N
S
SiMe3
Cl
2.00
2.00
2.00
2.00
1.00
1.00
9.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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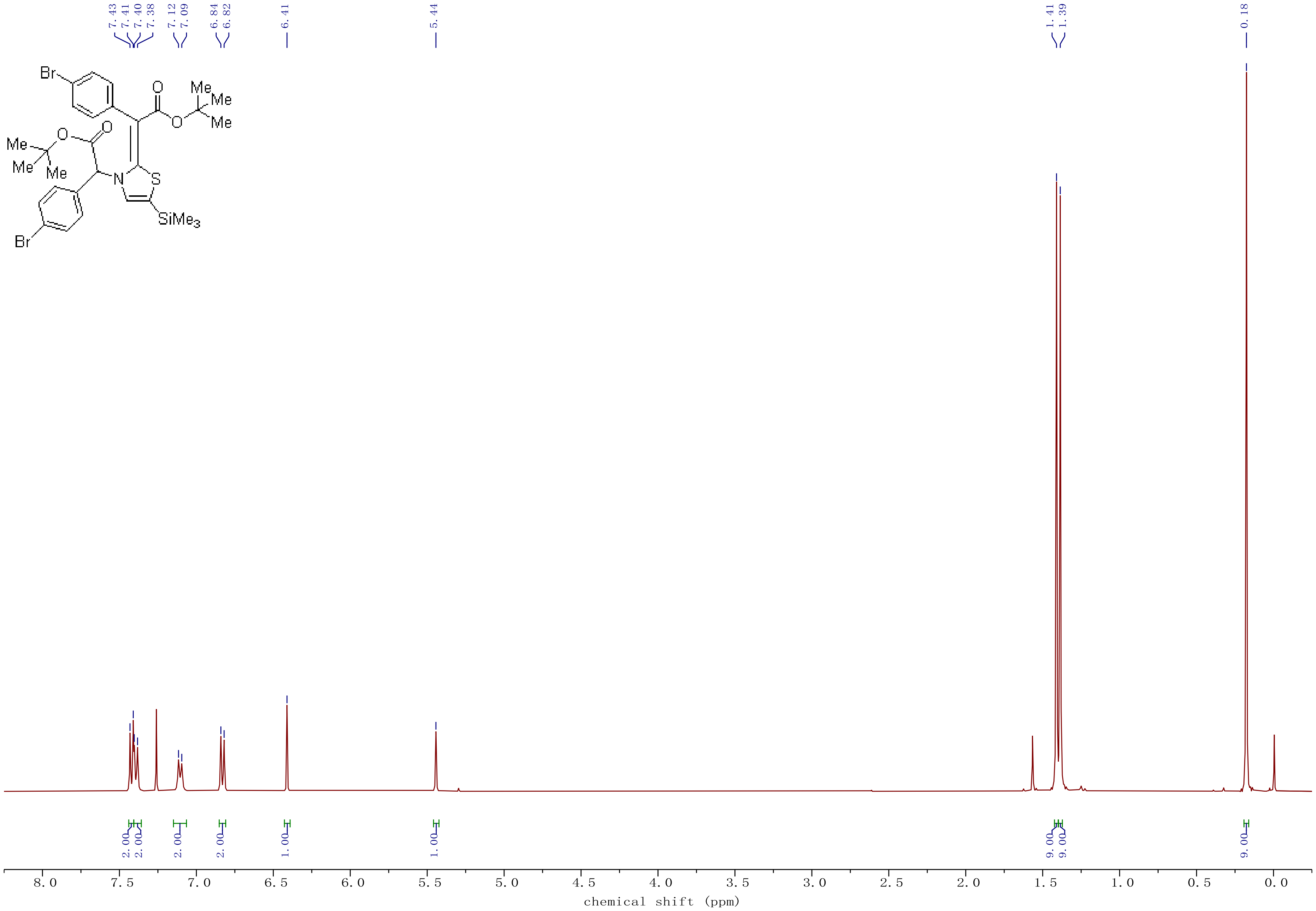
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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7.09
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6.82
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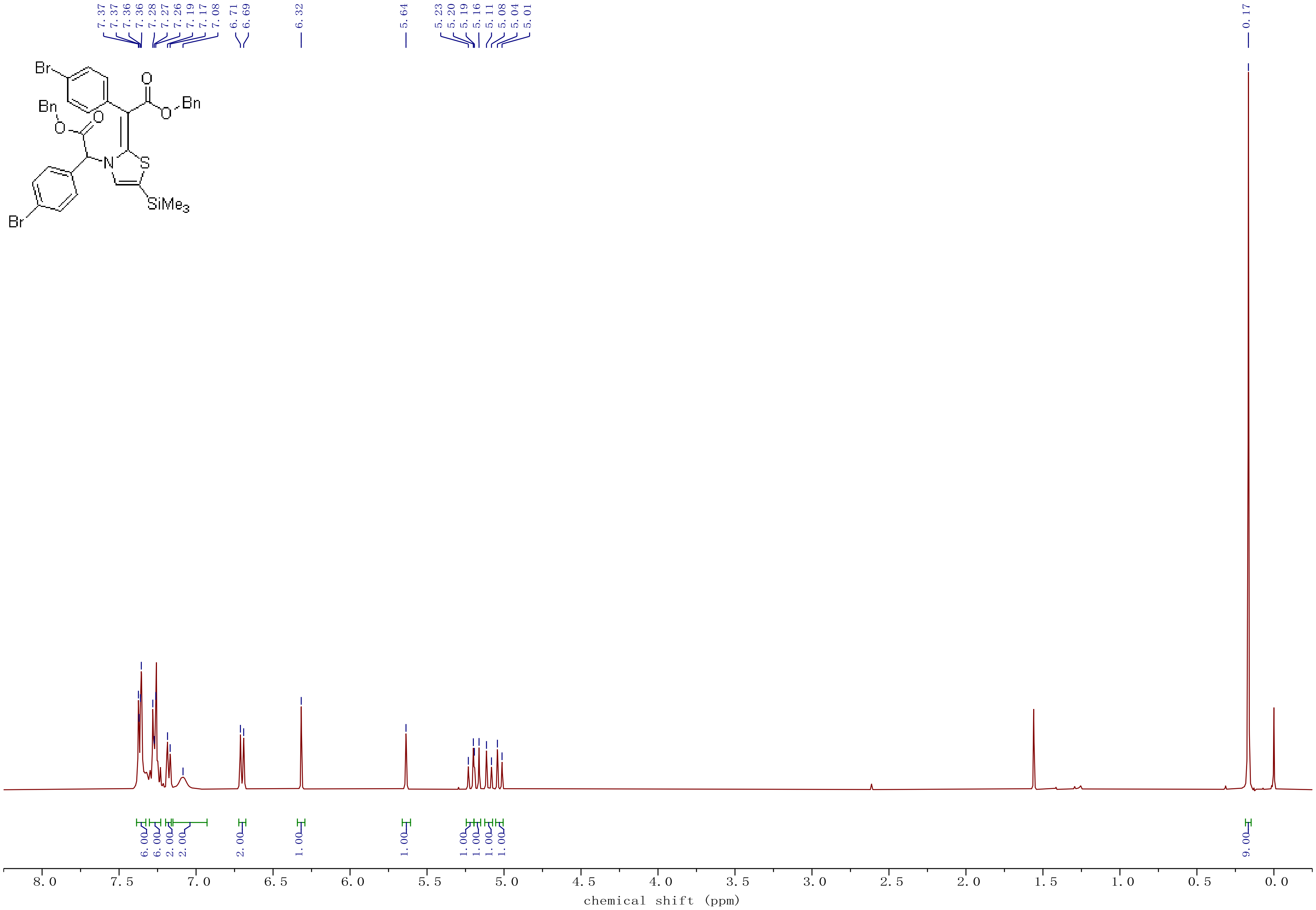
5.44
1.41
1.39
0.18
Br
O
Me
Me
Me
O
Me
O
O
Me
Me
Me
N
S
SiMe3
Br
2.00
2.00
2.00
2.00
1.00
1.00
9.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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5.23
5.20
5.19
5.16
5.11
5.08
5.04
5.01
0.17
Br
Bn
O
O
Bn
O
O
N
S
SiMe3
Br
6.00
6.00
2.00
2.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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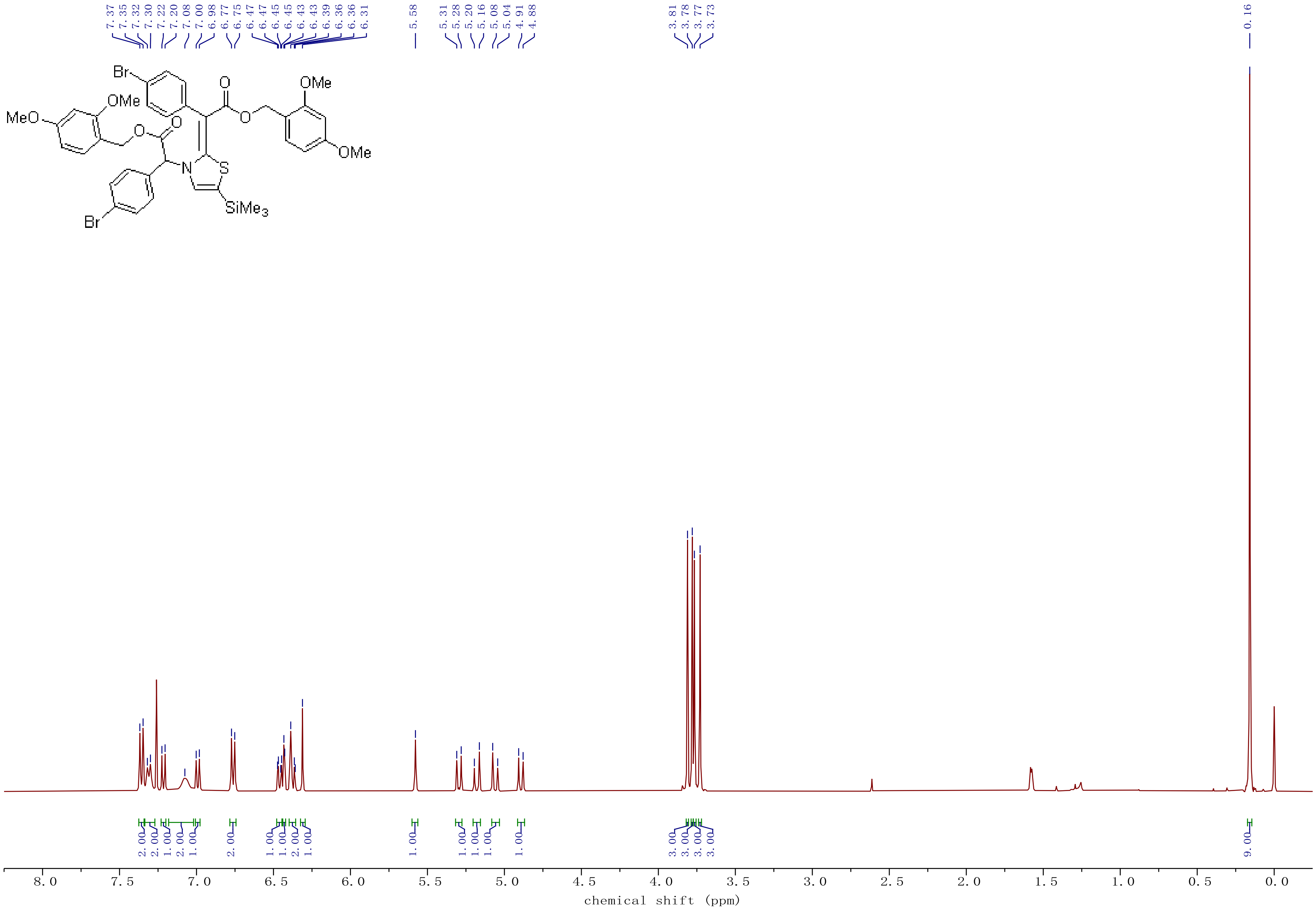
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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6.45
6.45
6.43
6.43
6.39
6.36
6.36
6.31
5.58
5.31
5.28
5.20
5.16
5.08
5.04
4.91
4.88
3.81
3.78
3.77
3.73
0.16
Br
OMe
MeO
O
O
N
S
SiMe3
Br
O
O
OMe
OMe
Br
2.00
2.00
1.00
2.00
1.00
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1.00
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2.00
1.00
1.00
1.00
1.00
1.00
1.00
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3.00
3.00
3.00
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6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
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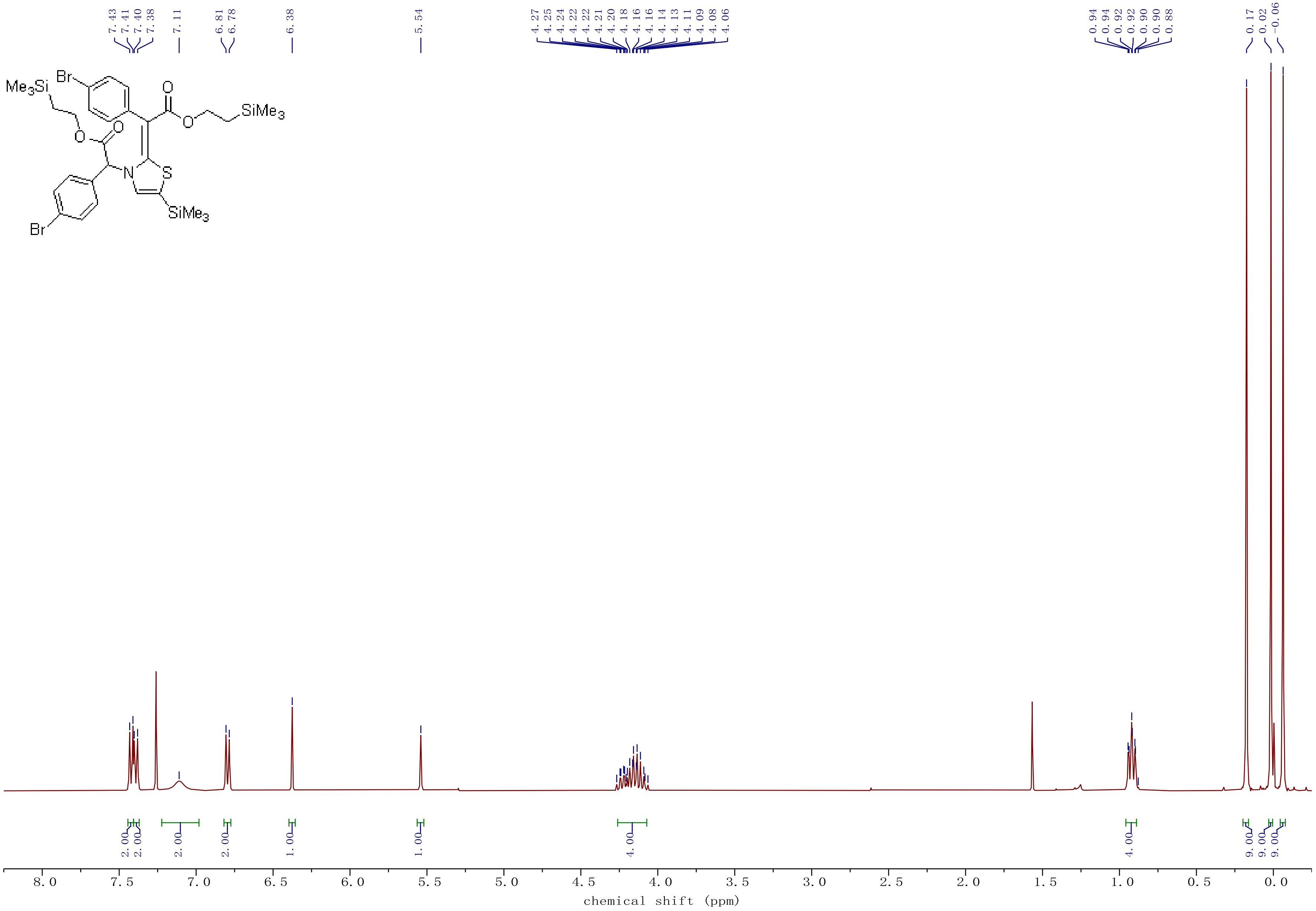
1.0
0.5
0.0
chemical shift (ppm)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7.38
7.11
6.81
6.78
6.38
5.54
4.27
4.25
4.24
4.22
4.22
4.21
4.20
4.18
4.16
4.16
4.14
4.13
4.11
4.09
4.08
4.06
0.94
0.94
0.92
0.92
0.90
0.90
0.88
0.17
0.02
-0.06
Me3Si
Br
O
O
SiMe3
O
O
N
S
SiMe3
Br
2.00
2.00
2.00
2.00
1.00
1.00
4.00
4.00
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9.00
9.00
8.0
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6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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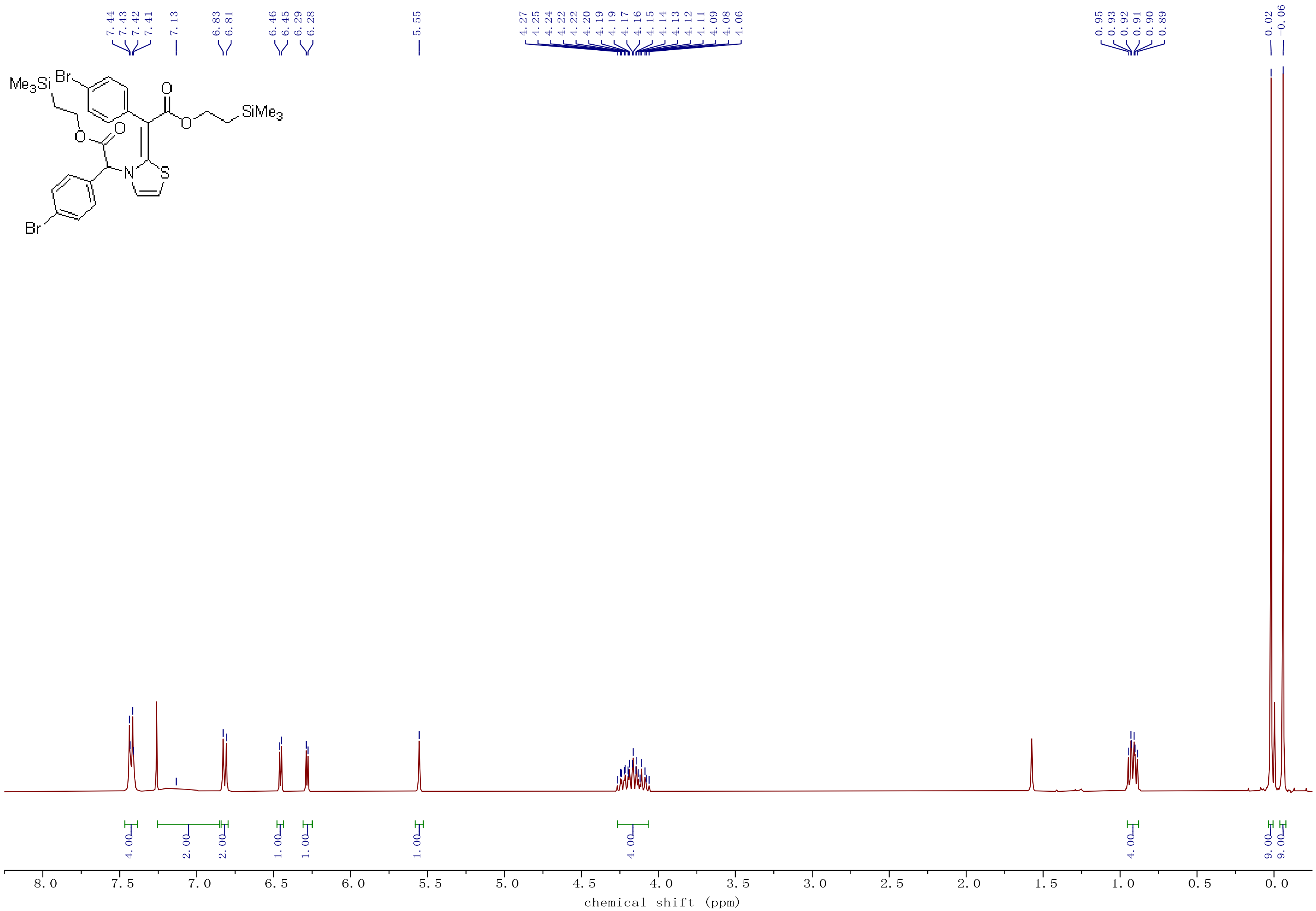
0.0
chemical shift (ppm)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4.27
4.25
4.24
4.22
4.22
4.20
4.19
4.19
4.17
4.16
4.15
4.14
4.13
4.12
4.11
4.09
4.08
4.06
0.95
0.93
0.92
0.91
0.90
0.89
0.02
-0.06
Me3Si
Br
O
O
SiMe3
O
O
N
S
Br
4.00
2.00
2.00
1.00
1.00
1.00
4.00
4.00
9.00
9.00
8.0
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7.0
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6.0
5.5
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2.0
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1.0
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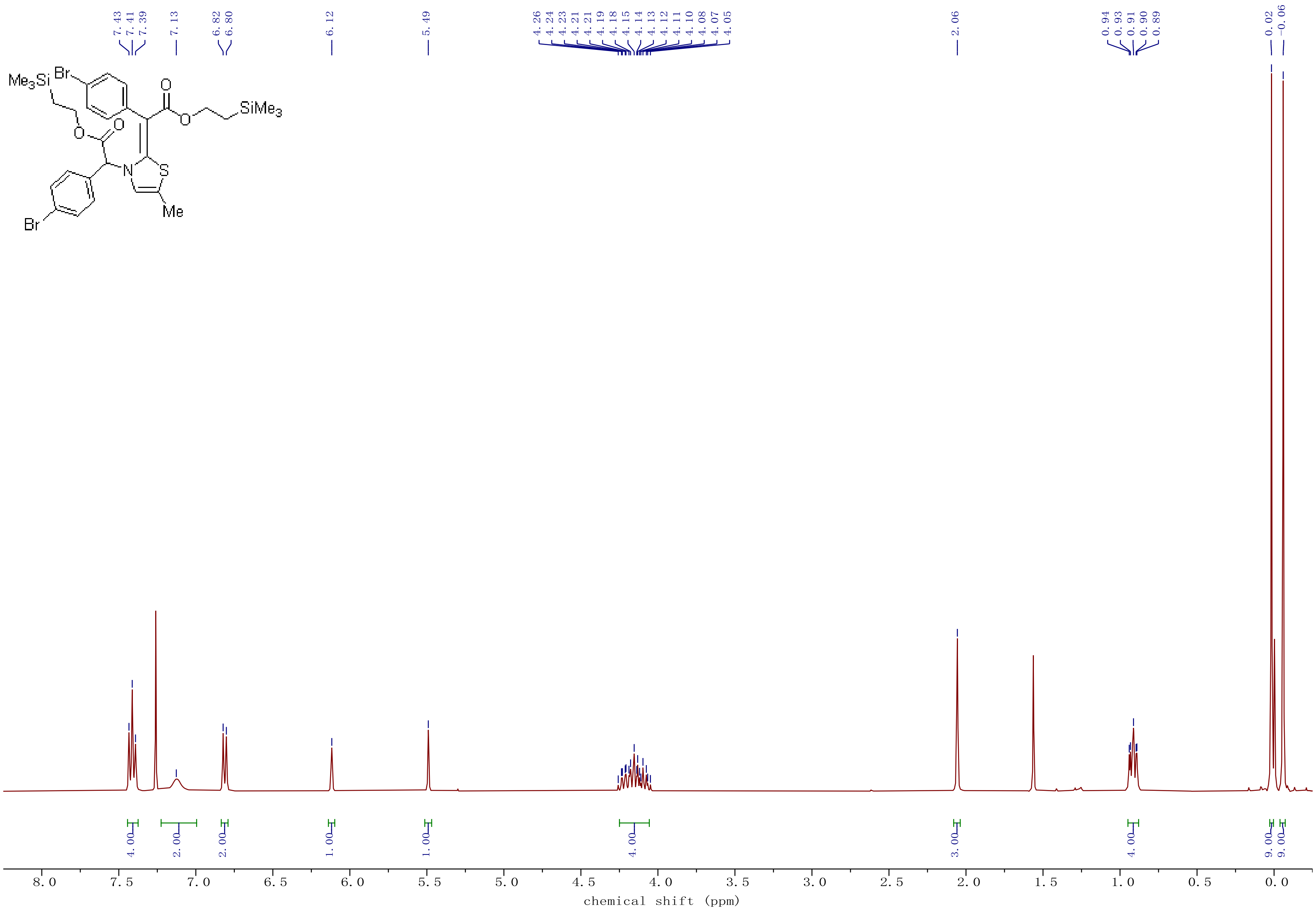
0.0
chemical shift (ppm)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4.21
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4.19
4.18
4.15
4.14
4.13
4.12
4.11
4.10
4.08
4.07
4.05
2.06
0.94
0.93
0.91
0.90
0.89
0.02
-0.06
Me3Si
Br
O
O
SiMe3
O
O
N
S
Me
Br
4.00
2.00
2.00
1.00
1.00
4.00
3.00
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8.0
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6.0
5.5
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3.5
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2.5
2.0
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1.0
0.5
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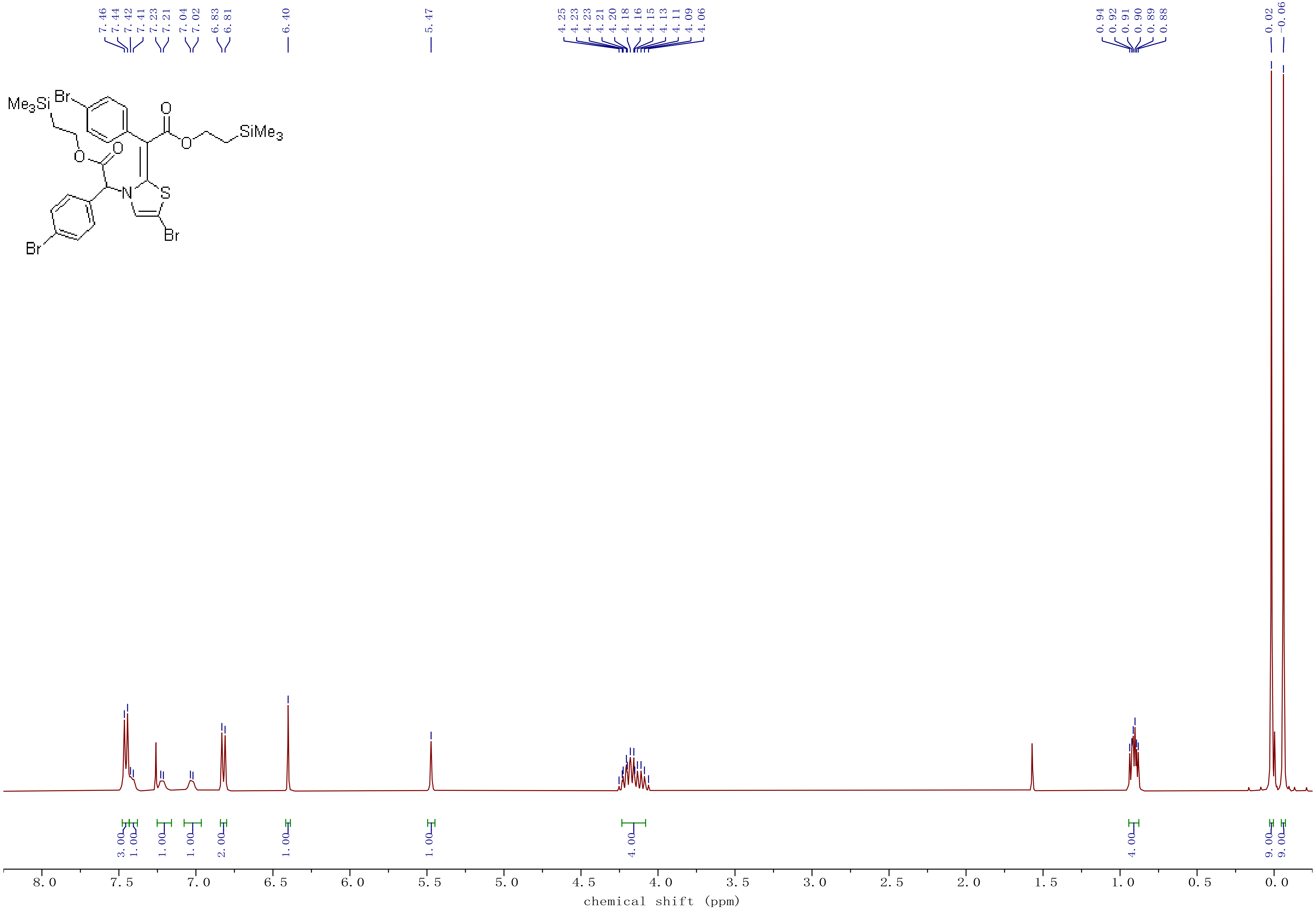
chemical shift (ppm)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7.04
7.02
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6.81
6.40
5.47
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4.23
4.23
4.21
4.20
4.18
4.16
4.15
4.13
4.11
4.09
4.06
0.94
0.92
0.91
0.90
0.89
0.88
0.02
-0.06
Me3Si
Br
O
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SiMe3
O
O
N
S
Br
Br
3.00
1.00
1.00
1.00
2.00
1.00
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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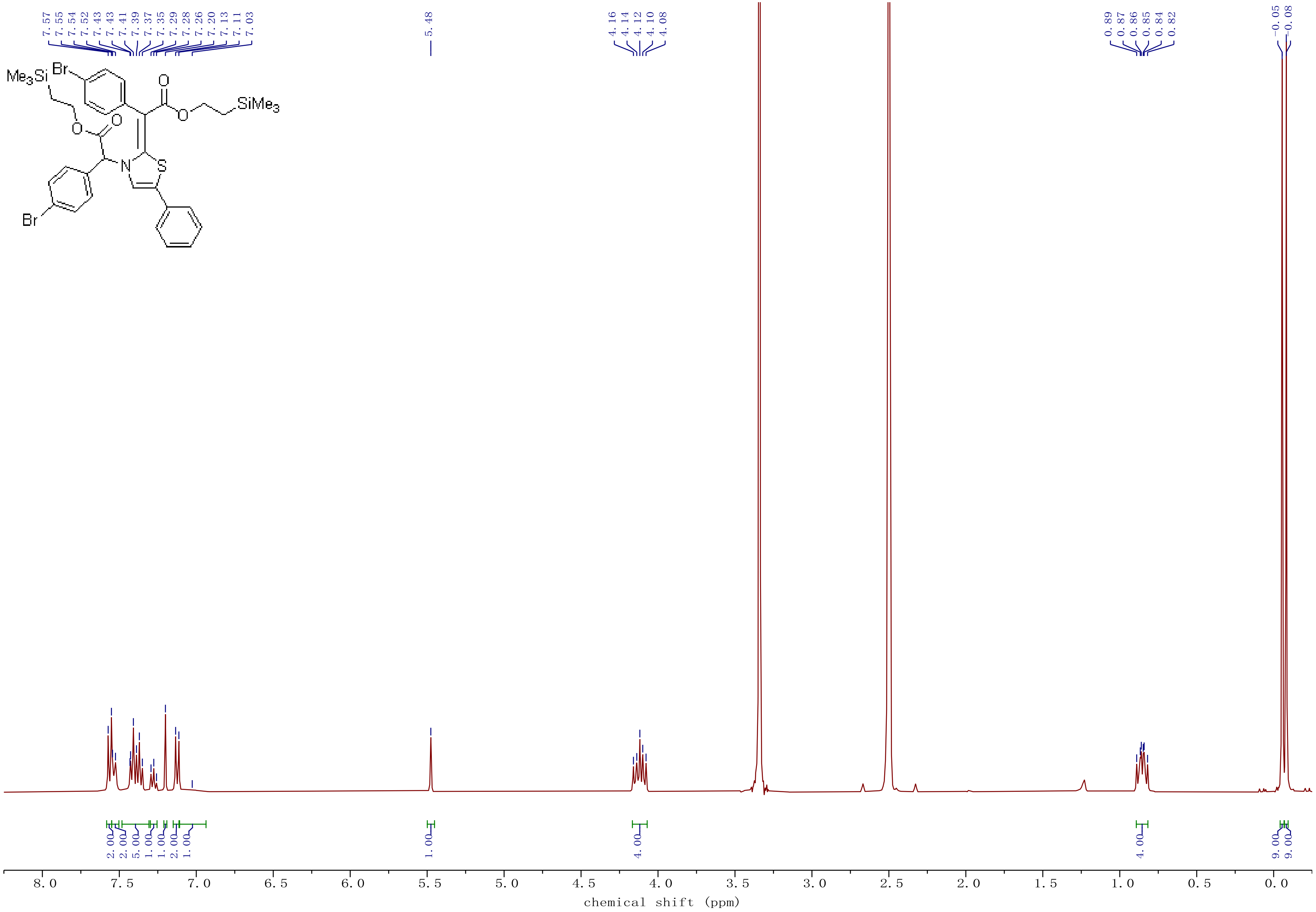
chemical shift (ppm)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7.13
7.11
7.03
5.48
4.16
4.14
4.12
4.10
4.08
0.89
0.87
0.86
0.85
0.84
0.82
-0.05
-0.08
Br
Me3Si
O
O
O
O
SiMe3
N
S
Br
2.00
2.00
5.00
1.00
1.00
2.00
1.00
1.00
4.00
4.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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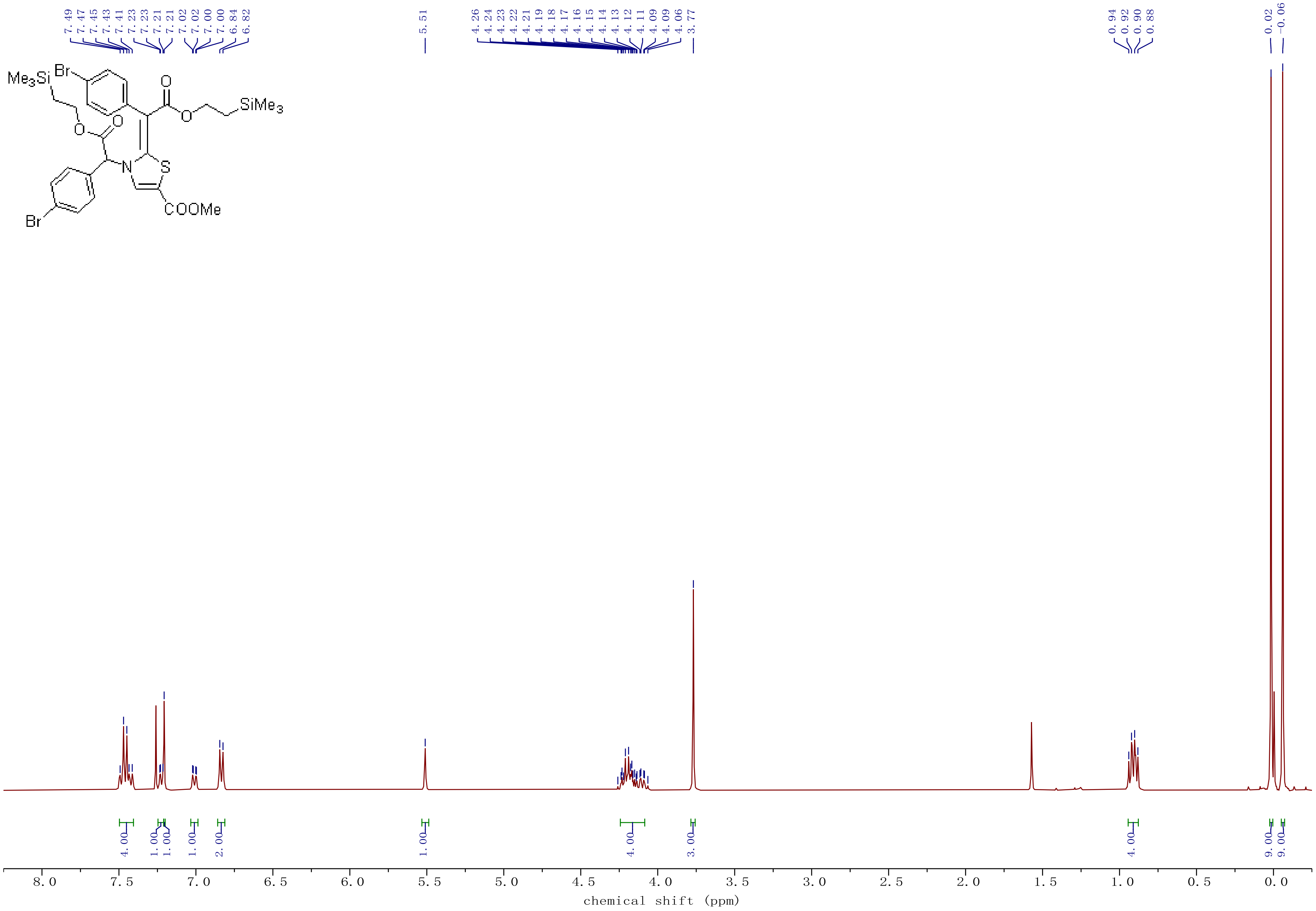
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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7.02
7.00
7.00
6.84
6.82
5.51
4.26
4.24
4.23
4.22
4.21
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.12
4.11
4.09
4.06
3.77
0.94
0.92
0.90
0.88
0.02
-0.06
Me3Si
Br
O
O
SiMe3
O
O
N
S
Br
COOMe
4.00
1.00
1.00
1.00
2.00
1.00
4.00
3.00
4.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
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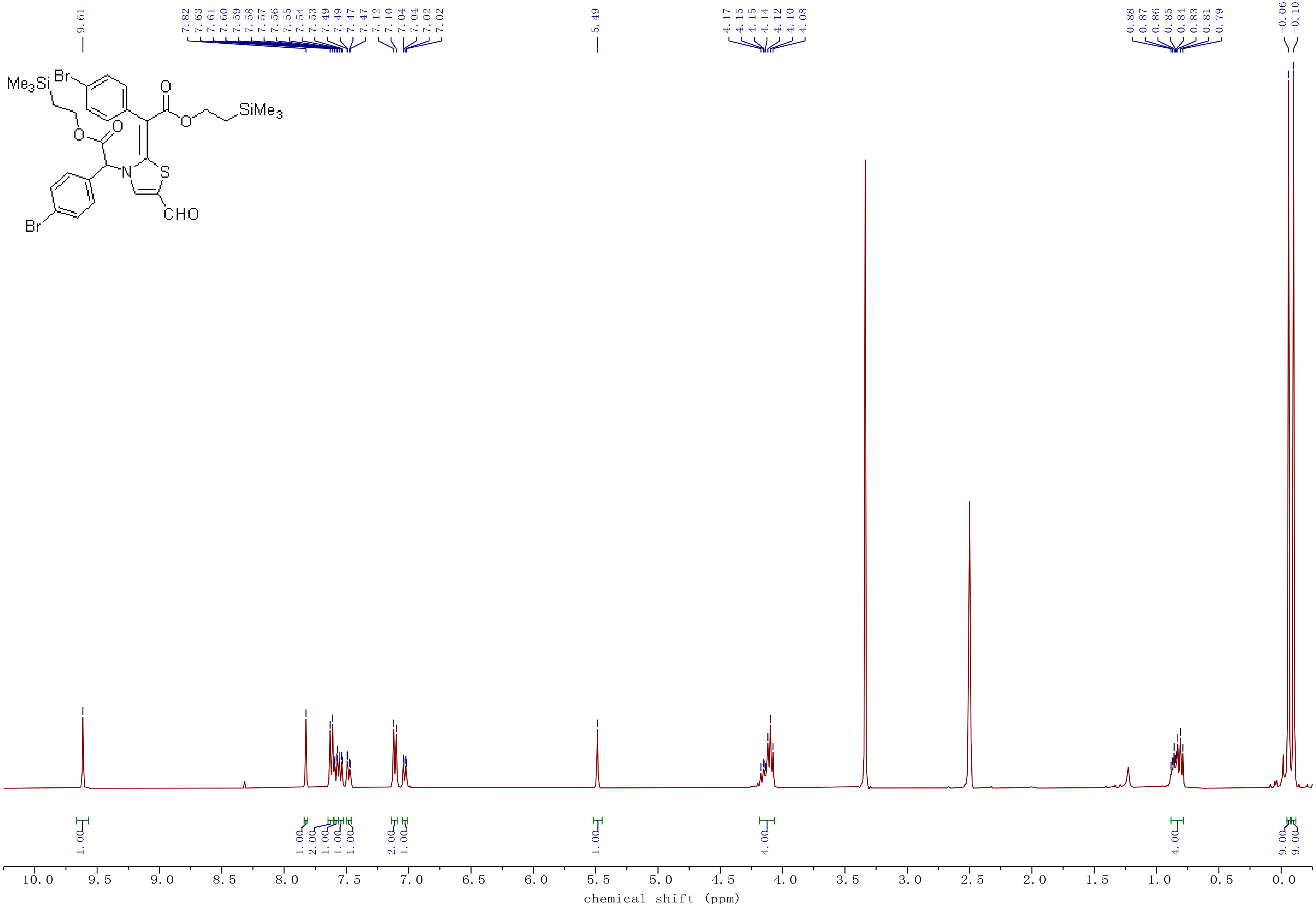
1.0
0.5
0.0
chemical shift (ppm)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7.49
7.47
7.47
7.12
7.10
7.04
7.04
7.02
7.02
5.49
4.17
4.15
4.15
4.14
4.12
4.10
4.08
0.88
0.87
0.86
0.85
0.84
0.83
0.81
0.79
-0.06
-0.10
Me3Si
Br
O
O
SiMe3
O
O
N
S
CHO
Br
1.00
1.00
2.00
1.00
1.00
1.00
2.00
1.00
1.00
4.00
4.00
9.00
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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1.0
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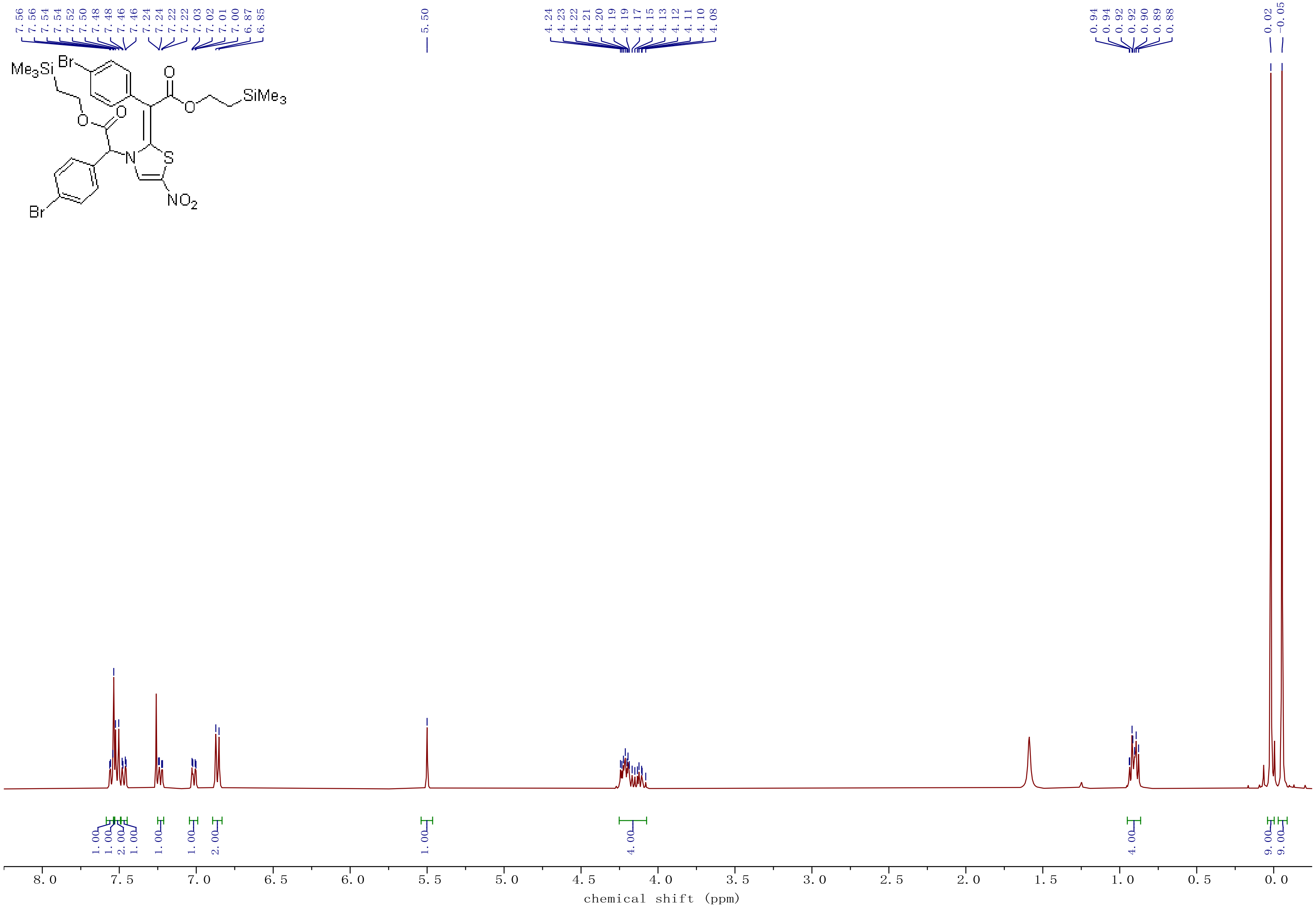
0.0
chemical shift (ppm)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7.22
7.03
7.02
7.01
7.00
6.87
6.85
5.50
4.24
4.23
4.22
4.21
4.20
4.19
4.19
4.17
4.15
4.13
4.12
4.11
4.10
4.08
0.94
0.94
0.92
0.92
0.90
0.89
0.88
0.02
-0.05
Me3Si
Br
O
SiMe3
O
O
O
N
S
NO2
Br
1.00
1.00
2.00
1.00
1.00
1.00
2.00
1.00
4.00
4.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
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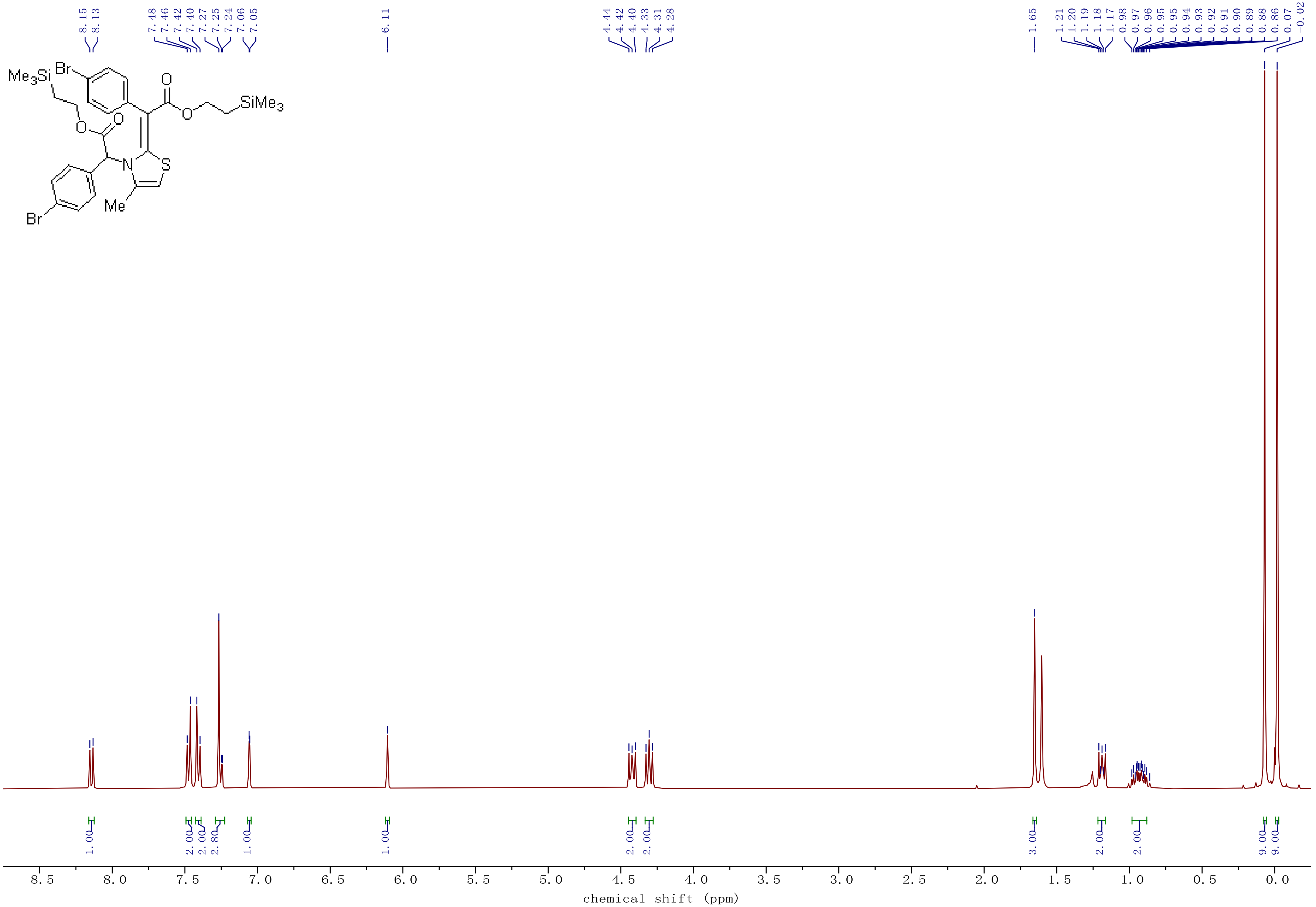
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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7.06
7.05
6.11
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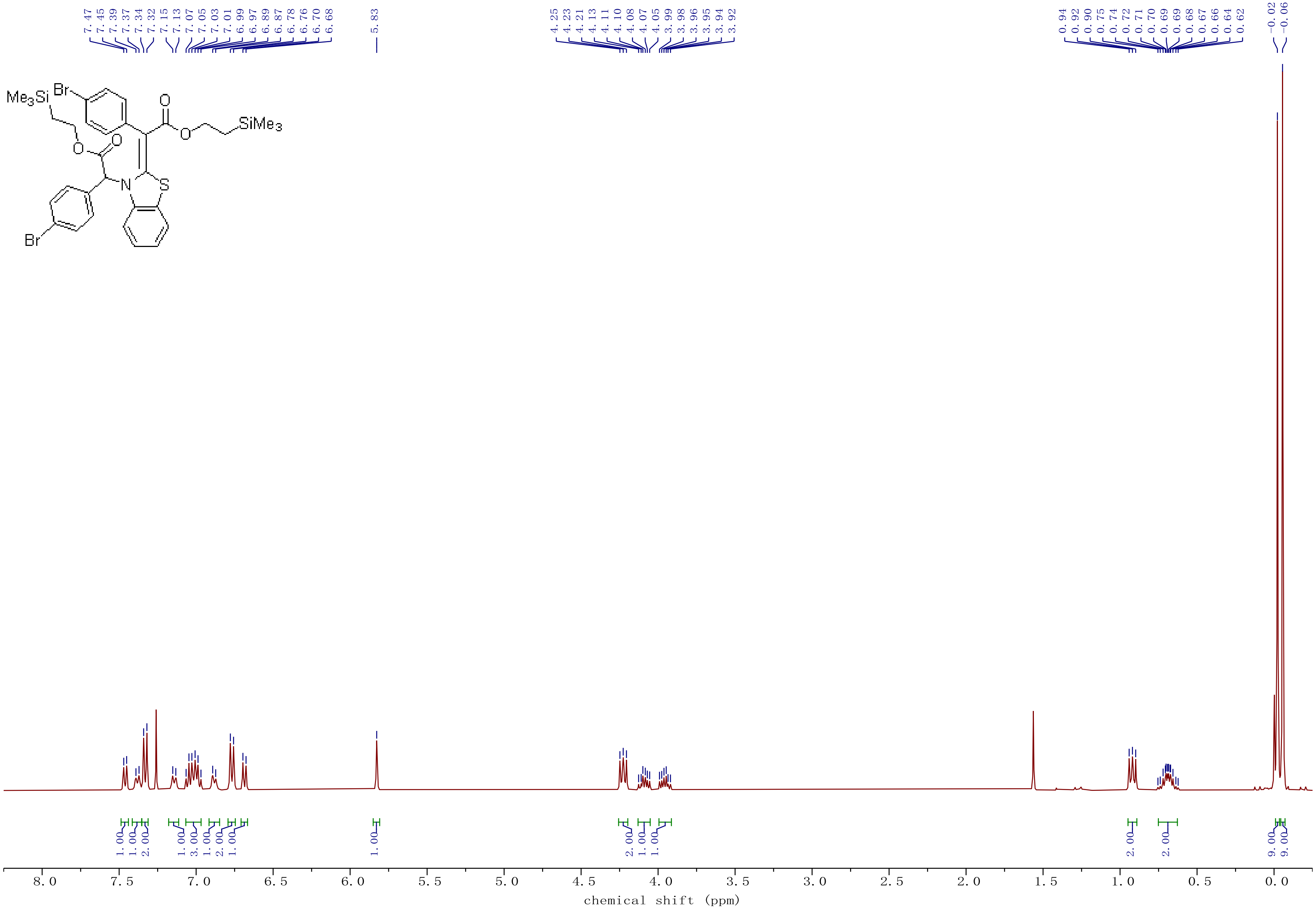
4.42
4.40
4.33
4.31
4.28
1.65
1.21
1.20
1.19
1.18
1.17
0.98
0.97
0.96
0.95
0.95
0.94
0.93
0.92
0.91
0.90
0.89
0.88
0.86
0.07
-0.02
Me3Si
Br
O
O
SiMe3
O
O
N
S
Me
Br
1.00
2.00
2.00
2.80
1.00
1.00
2.00
2.00
3.00
2.00
2.00
9.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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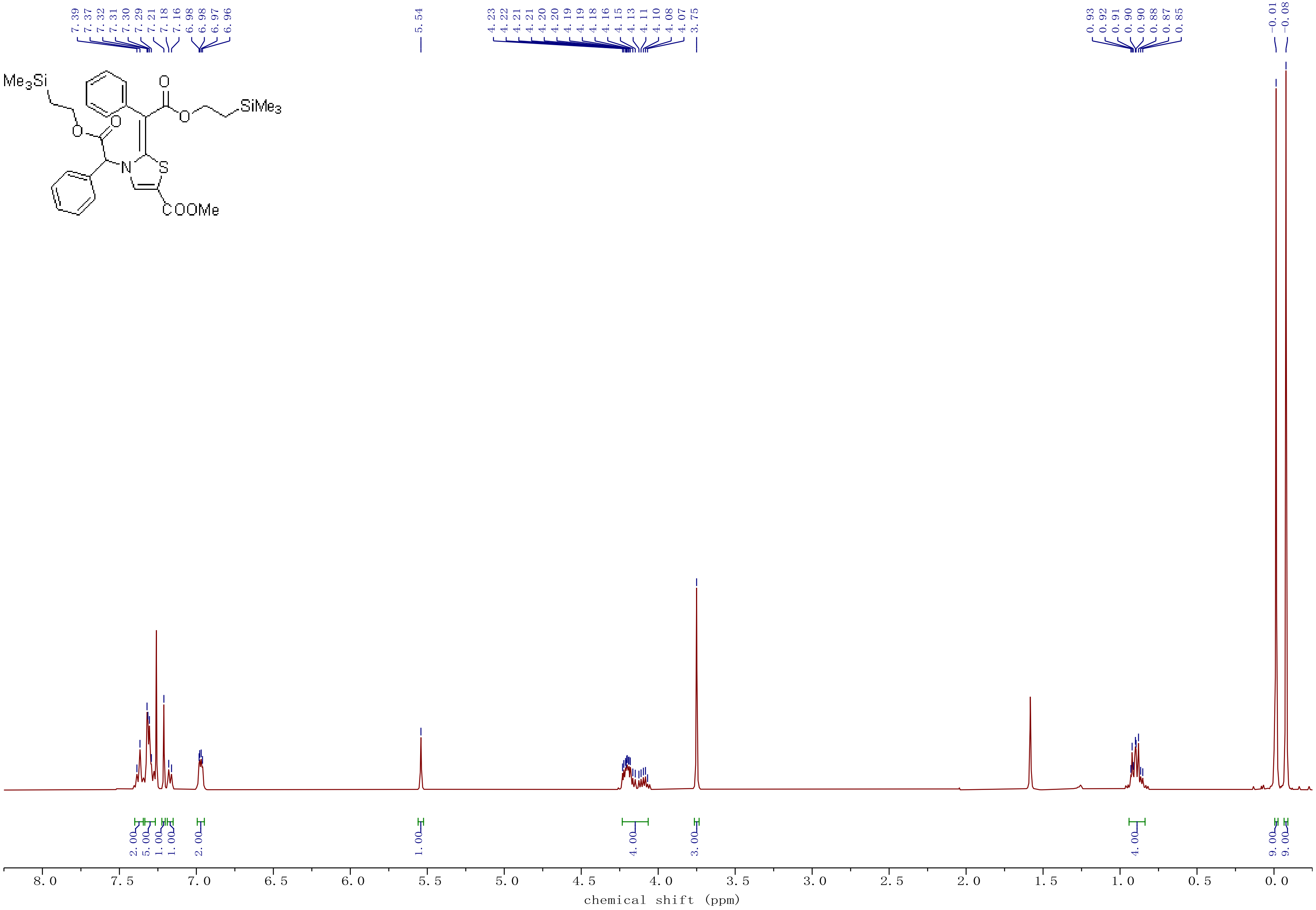
7.32
7.15
7.13
7.07
7.05
7.03
7.01
6.99
6.97
6.89
6.87
6.78
6.76
6.70
6.68
5.83
4.25
4.23
4.21
4.13
4.11
4.10
4.08
4.07
4.05
3.99
3.98
3.96
3.95
3.94
3.92
0.94
0.92
0.90
0.75
0.74
0.72
0.71
0.70
0.69
0.68
0.67
0.66
0.64
0.62
-0.02
-0.06
Me$_3$Si
Br
O
O
SiMe$_3$
O
O
N
S
Br
1.00
1.00
2.00
1.00
3.00
1.00
2.00
1.00
1.00
2.00
1.00
1.00
2.00
2.00
9.00
9.00
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
chemical shift (ppm)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7.18
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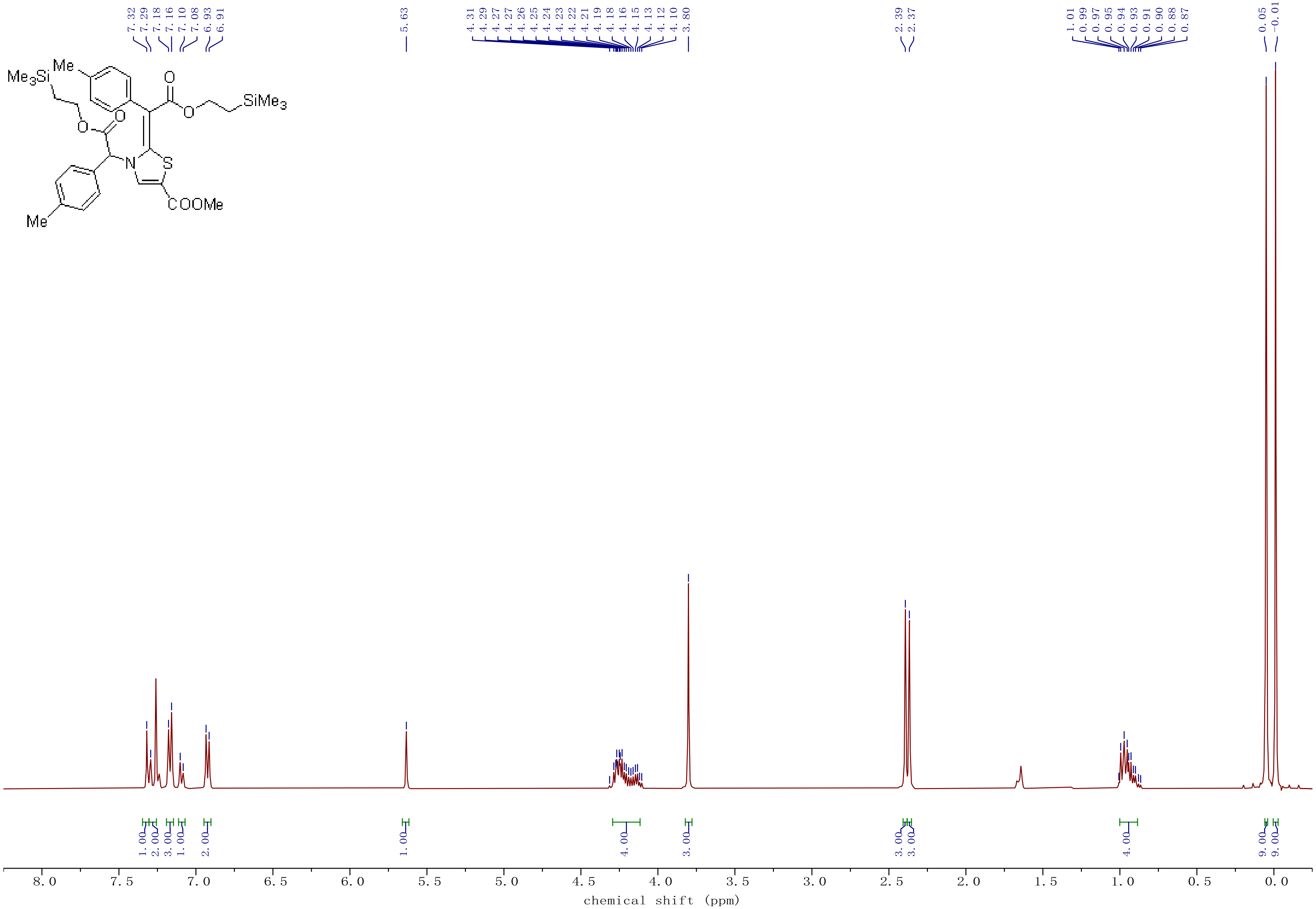
6.98
6.98
6.97
6.96
5.54
4.23
4.22
4.21
4.21
4.20
4.20
4.19
4.19
4.18
4.16
4.15
4.13
4.11
4.10
4.08
4.07
3.75
0.93
0.92
0.91
0.90
0.90
0.88
0.87
0.85
-0.01
-0.08
Me3Si
O
O
SiMe3
O
O
N
S
COOMe
2.00
5.00
1.00
1.00
2.00
1.00
4.00
3.00
4.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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7.10
7.08
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6.91
5.63
4.31
4.29
4.27
4.27
4.26
4.25
4.24
4.23
4.22
4.21
4.19
4.18
4.16
4.15
4.13
4.12
4.10
3.80
2.39
2.37
1.01
0.99
0.97
0.95
0.94
0.93
0.91
0.90
0.88
0.87
0.05
-0.01
Me
Me3Si
O
O
O
SiMe3
O
N
S
COOMe
Me
1.00
2.00
3.00
1.00
2.00
1.00
4.00
3.00
3.00
3.00
4.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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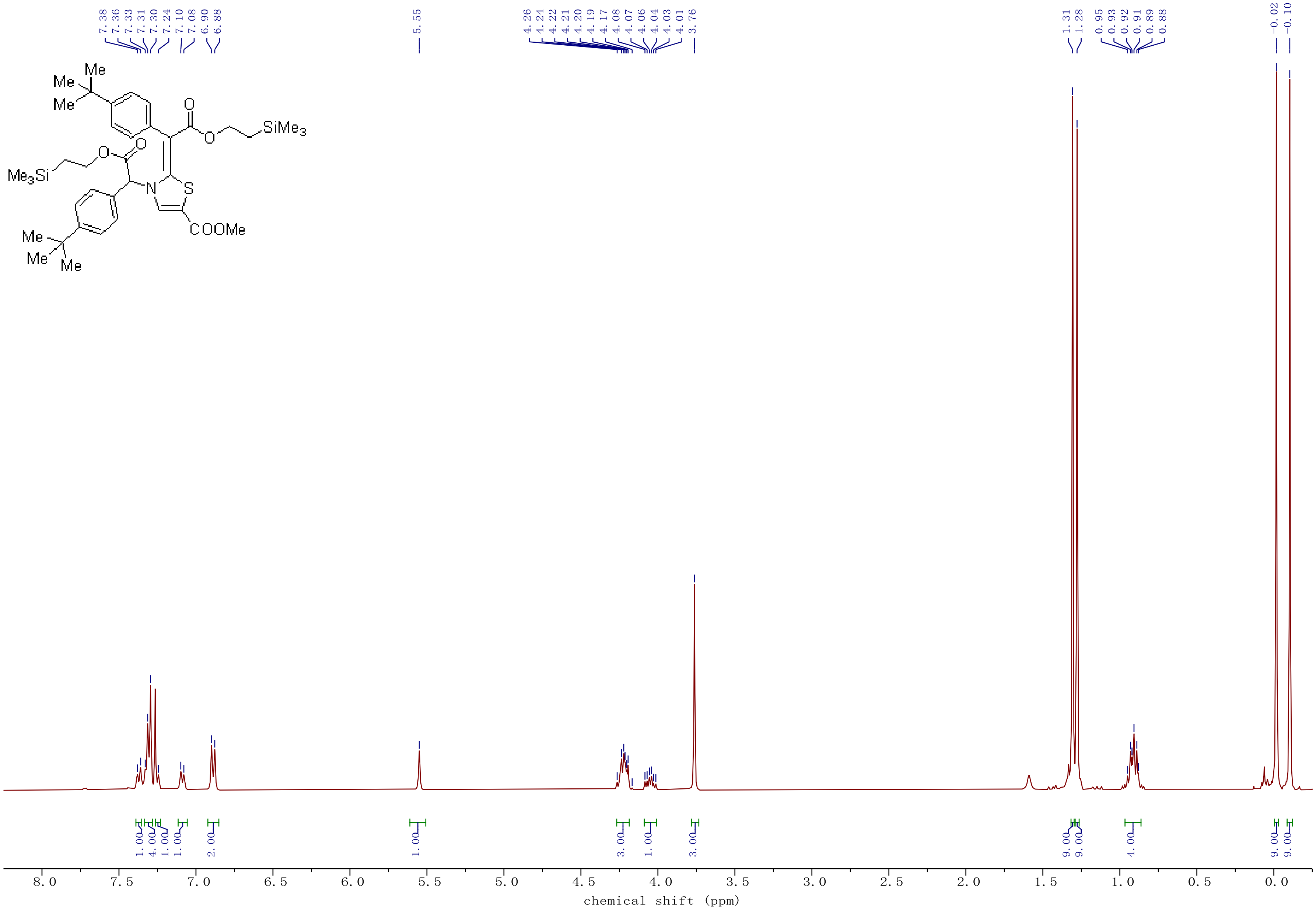
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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6.88
5.55
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4.24
4.22
4.21
4.20
4.19
4.17
4.08
4.07
4.06
4.04
4.03
4.01
3.76
1.31
1.28
0.95
0.93
0.92
0.91
0.89
0.88
-0.02
-0.10
Me
Me
Me
O
O
SiMe3
O
O
Me3Si
N
S
COOMe
Me
Me
Me
1.00
4.00
1.00
1.00
2.00
1.00
3.00
1.00
3.00
9.00
9.00
4.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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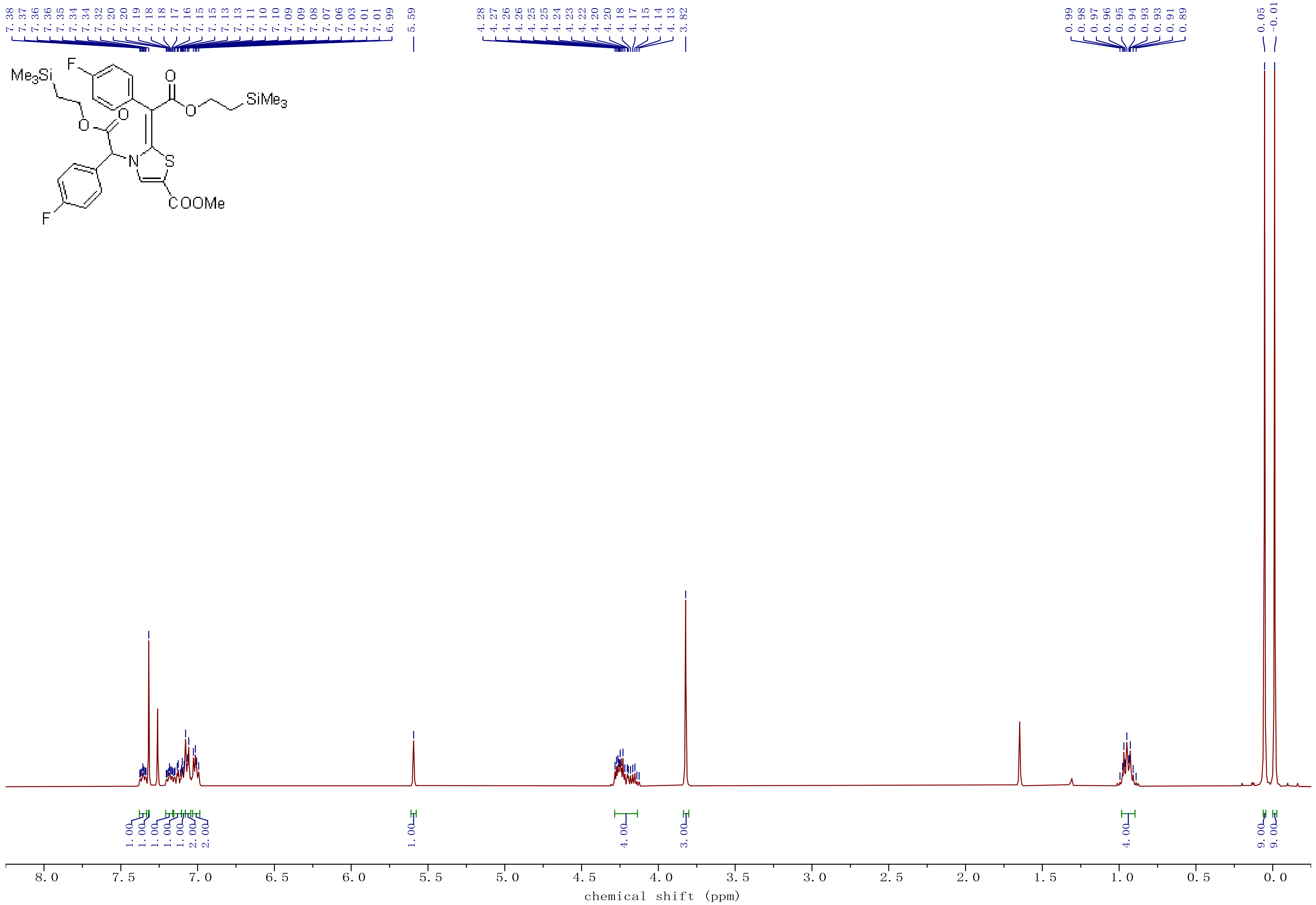
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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7.19
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7.18
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7.15
7.13
7.13
7.11
7.10
7.10
7.09
7.09
7.08
7.07
7.06
7.03
7.01
7.01
6.99
5.59
4.28
4.27
4.26
4.26
4.25
4.25
4.24
4.23
4.22
4.20
4.20
4.18
4.17
4.15
4.14
4.13
3.82
0.99
0.98
0.97
0.96
0.95
0.94
0.93
0.93
0.91
0.89
0.05
-0.01
Me$_3$Si
F
O
O
O
O
SiMe$_3$
N
S
COOMe
F
1.00
1.00
1.00
1.00
1.00
2.00
2.00
1.00
4.00
3.00
4.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
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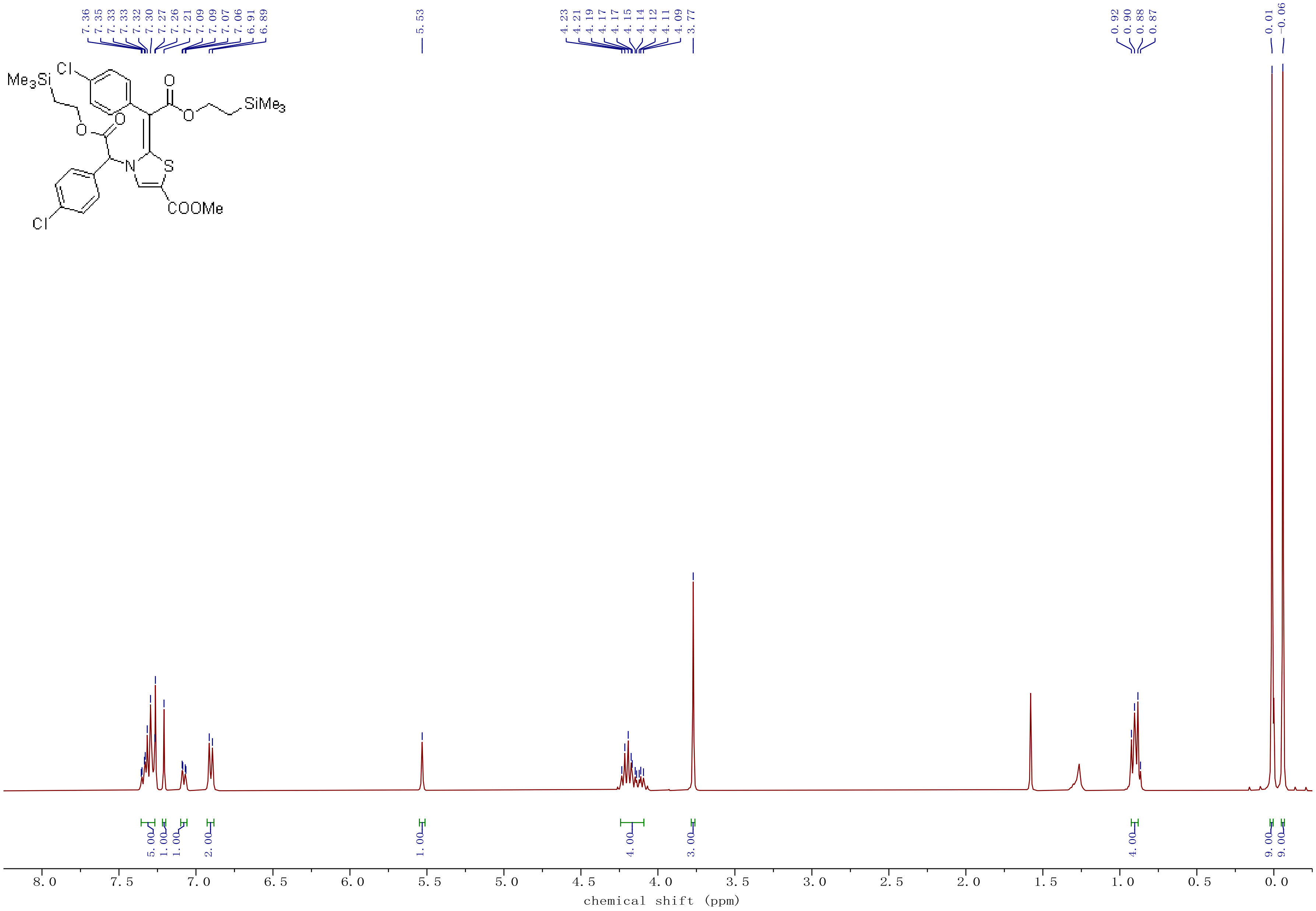
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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7.09
7.09
7.07
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6.89
5.53
4.23
4.21
4.19
4.17
4.17
4.15
4.14
4.12
4.11
4.09
3.77
0.92
0.90
0.88
0.87
0.01
-0.06
Me3Si
Cl
O
O
SiMe3
O
O
N
S
COOMe
Cl
5.00
1.00
1.00
2.00
1.00
4.00
3.00
4.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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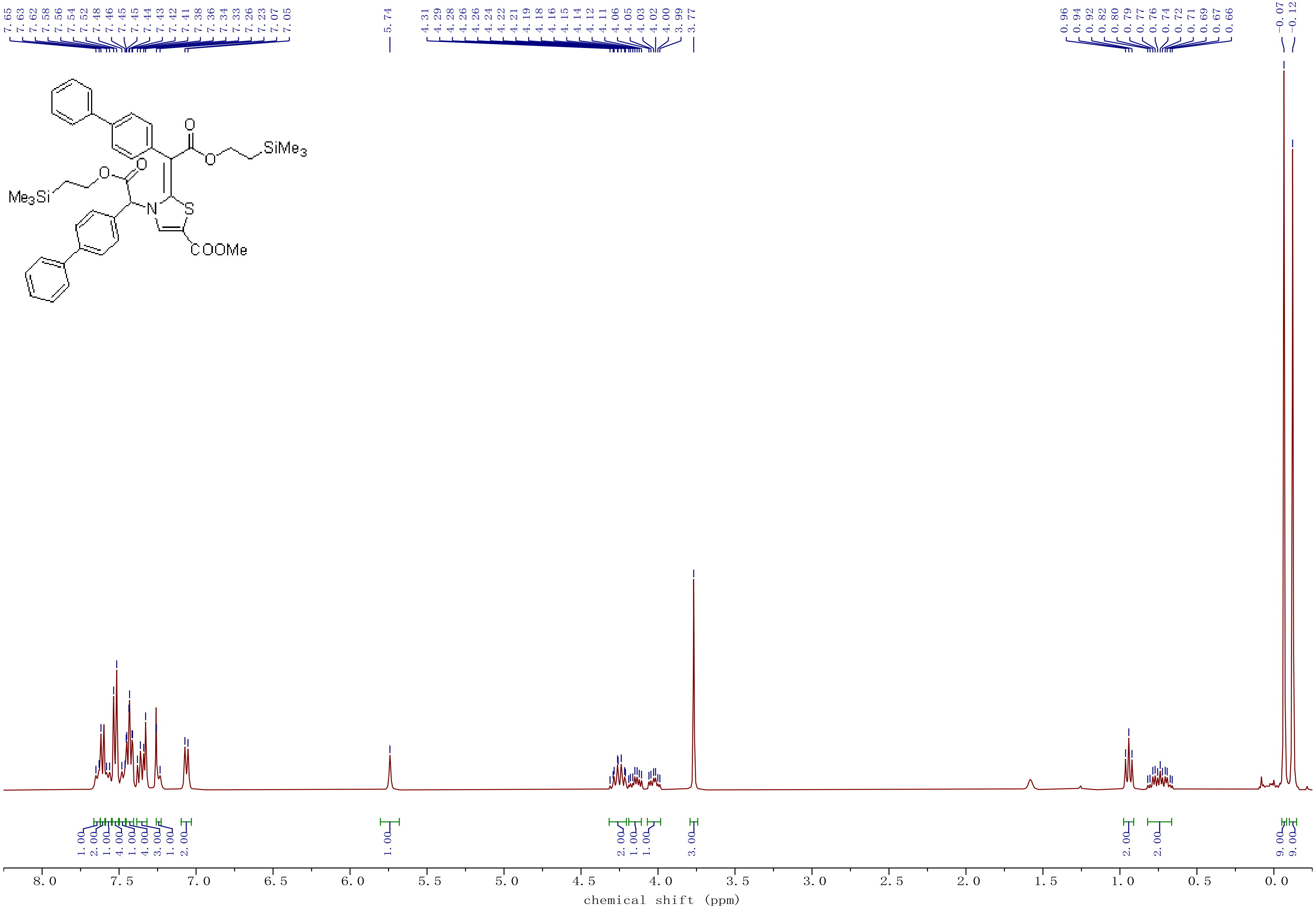
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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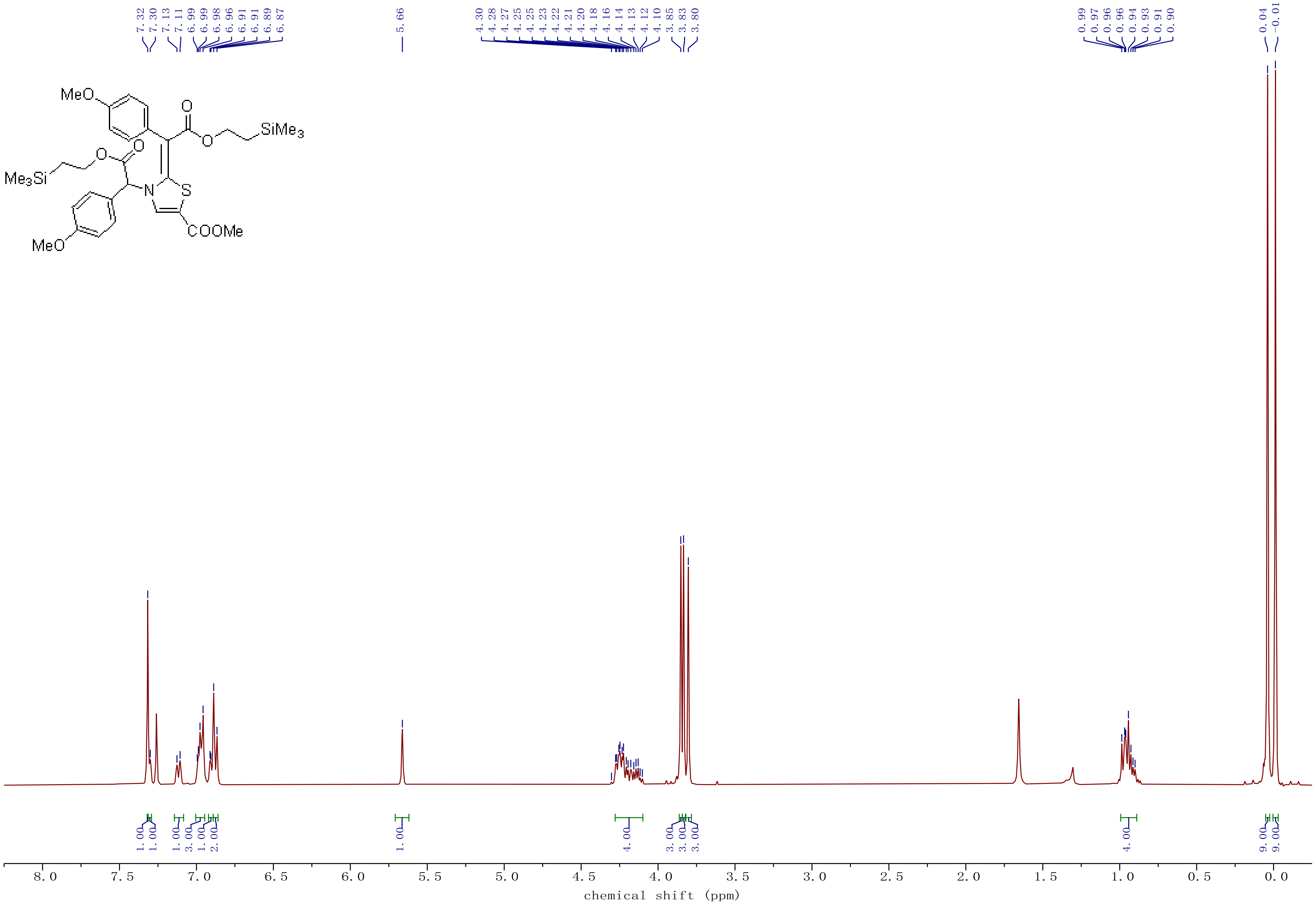
5.74
4.31 4.29 4.28 4.26 4.26 4.24 4.22 4.21 4.19 4.18 4.16 4.15 4.14 4.12 4.11 4.06 4.05 4.03 4.02 4.00 3.99 3.77
0.96 0.94 0.92 0.82 0.80 0.79 0.77 0.76 0.74 0.72 0.71 0.69 0.67 0.66
-0.07 -0.12
O
SiMe3
Me3Si
O
O
O
N
S
COOMe
1.00 2.00 1.00 4.00 1.00 4.00 3.00 1.00 2.00
1.00
2.00 1.00 1.00
3.00
2.00 2.00
9.00 9.00
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
chemical shift (ppm)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7.13
7.11
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6.99
6.98
6.96
6.91
6.91
6.89
6.87
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4.30
4.28
4.27
4.25
4.25
4.23
4.22
4.21
4.20
4.18
4.16
4.14
4.13
4.12
4.10
3.85
3.83
3.80
0.99
0.97
0.96
0.96
0.94
0.93
0.91
0.90
0.04
-0.01
MeO
O
SiMe3
O
O
O
Me3Si
N
S
MeO
COOMe
1.00
1.00
1.00
3.00
1.00
2.00
1.00
4.00
3.00
3.00
3.00
4.00
9.00
9.00
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6.5
6.0
5.5
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1.0
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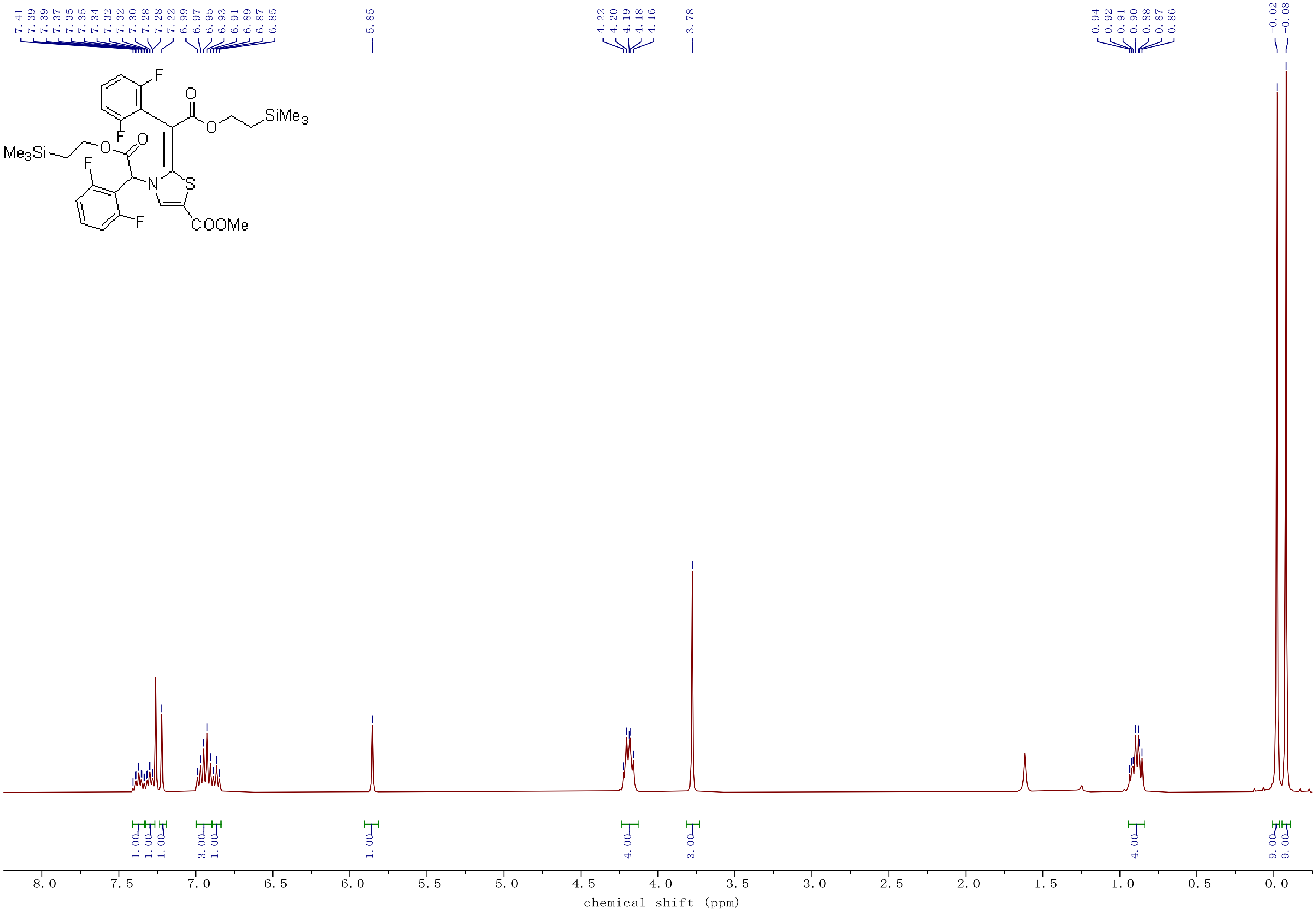
0.0
chemical shift (ppm)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7.30
7.28
7.28
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6.99
6.97
6.95
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6.91
6.89
6.87
6.85
5.85
4.22
4.20
4.19
4.18
4.16
3.78
0.94
0.92
0.91
0.90
0.88
0.87
0.86
-0.02
-0.08
F
O
SiMe3
O
F
Me3Si
O
O
F
N
S
F
COOMe
1.00
1.00
1.00
3.00
1.00
1.00
4.00
3.00
4.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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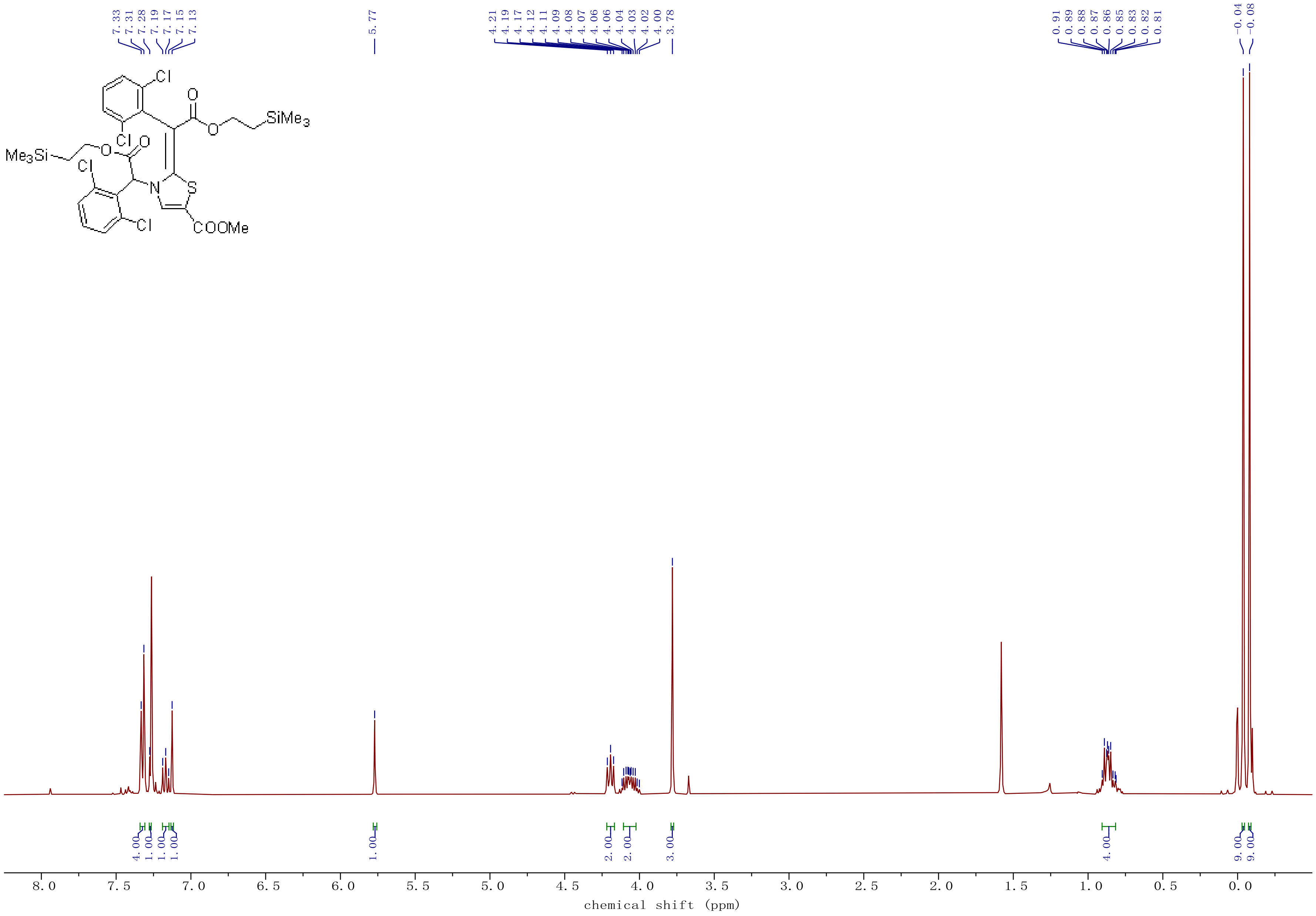
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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7.15
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5.77
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4.19
4.17
4.12
4.11
4.09
4.08
4.07
4.06
4.04
4.03
4.02
4.00
3.78
0.91
0.89
0.88
0.87
0.86
0.85
0.83
0.82
0.81
-0.04
-0.08
Cl
O
SiMe3
O
Cl
O
Me3Si
O
Cl
N
S
Cl
COOMe
4.00
1.00
1.00
1.00
1.00
2.00
2.00
3.00
4.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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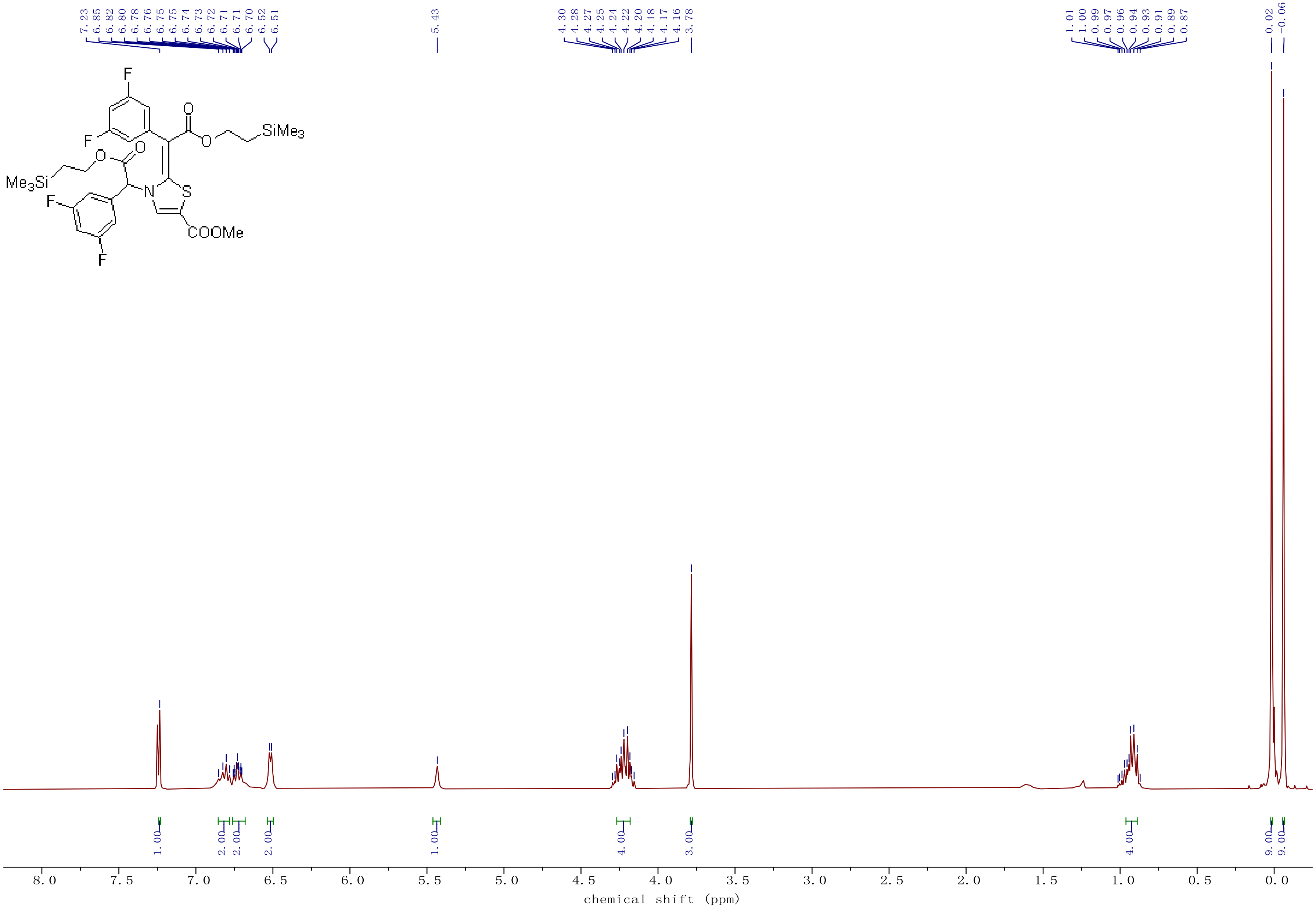
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)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6.76
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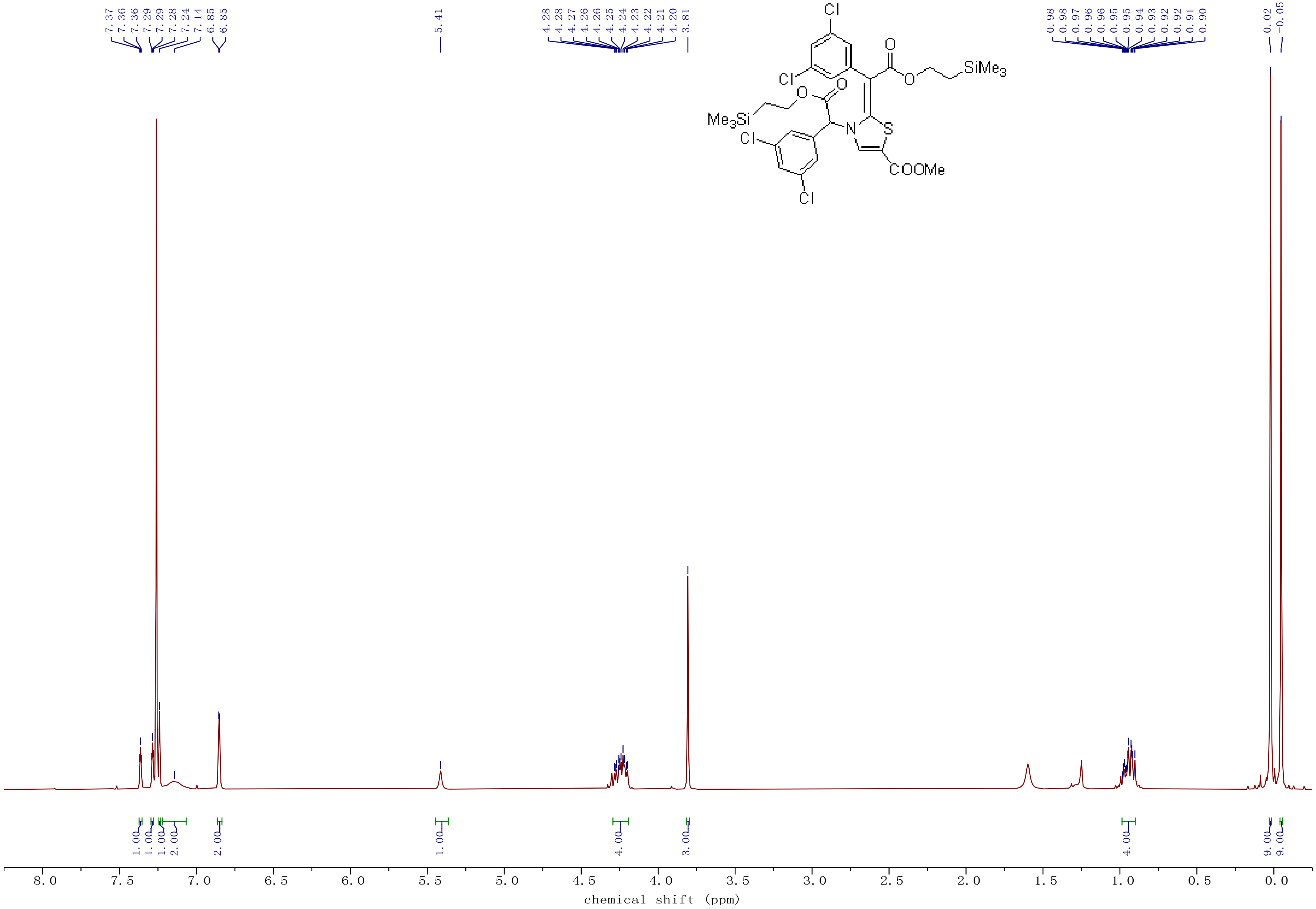
6.75
6.74
6.73
6.72
6.71
6.71
6.70
6.52
6.51
5.43
4.30
4.28
4.27
4.25
4.24
4.22
4.20
4.18
4.17
4.16
3.78
1.01
1.00
0.99
0.97
0.96
0.94
0.93
0.91
0.89
0.87
0.02
-0.06
1.00
2.00
2.00
2.00
1.00
4.00
3.00
4.00
9.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
chemical shift (ppm)
F
F
O
O
SiMe3
O
O
Me3Si
F
N
S
F
COOMe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7.24
7.14
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4.26
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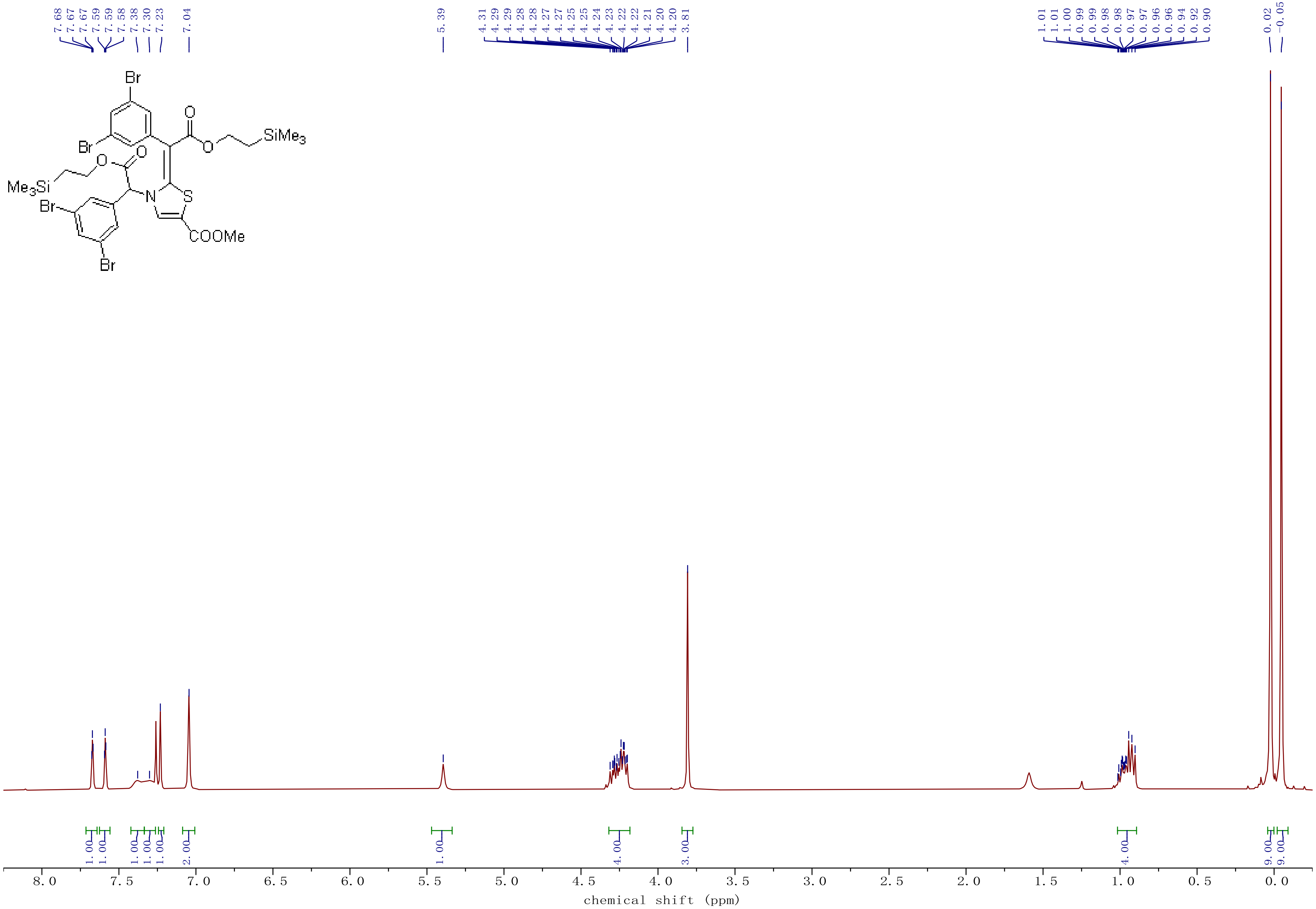
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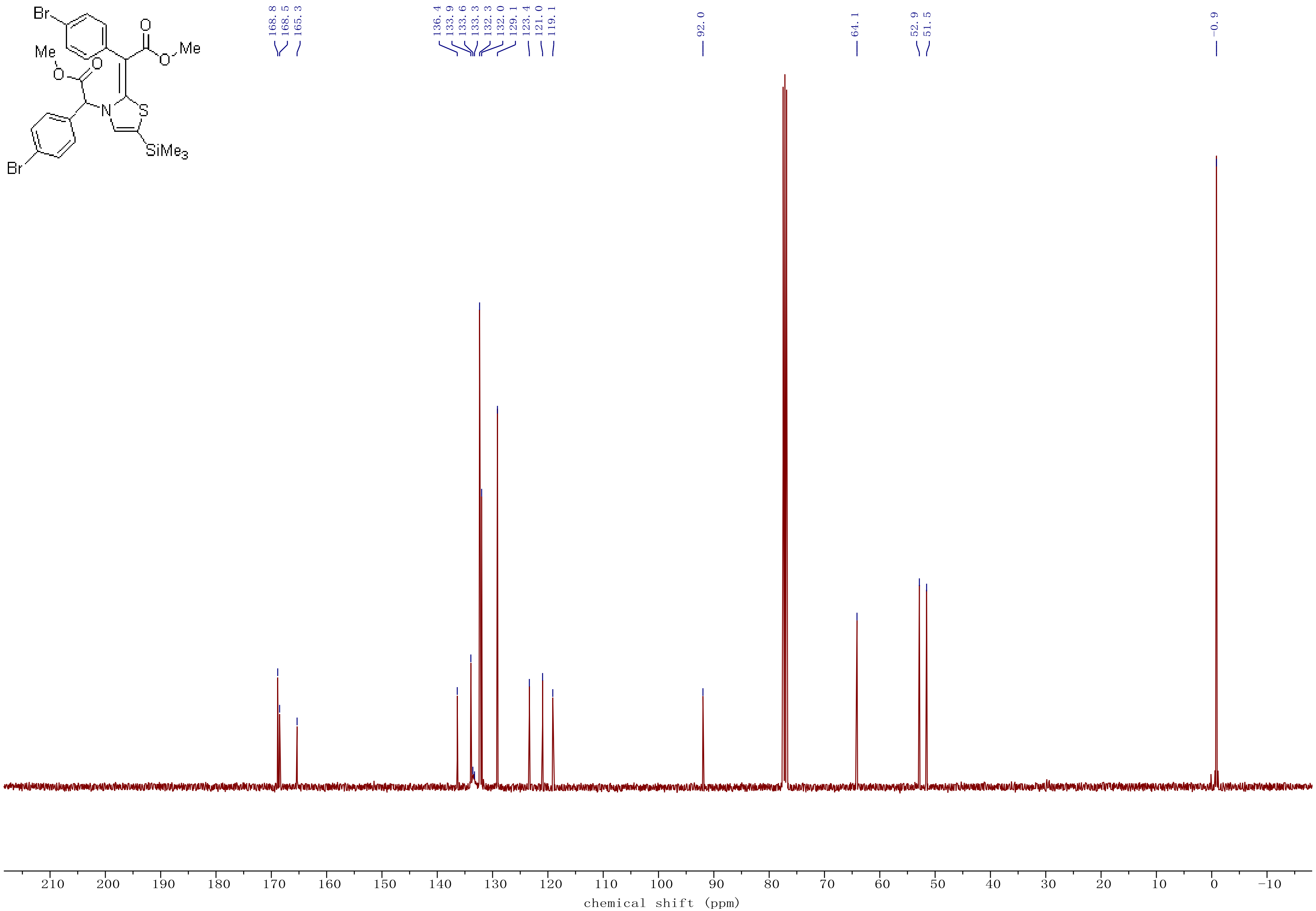
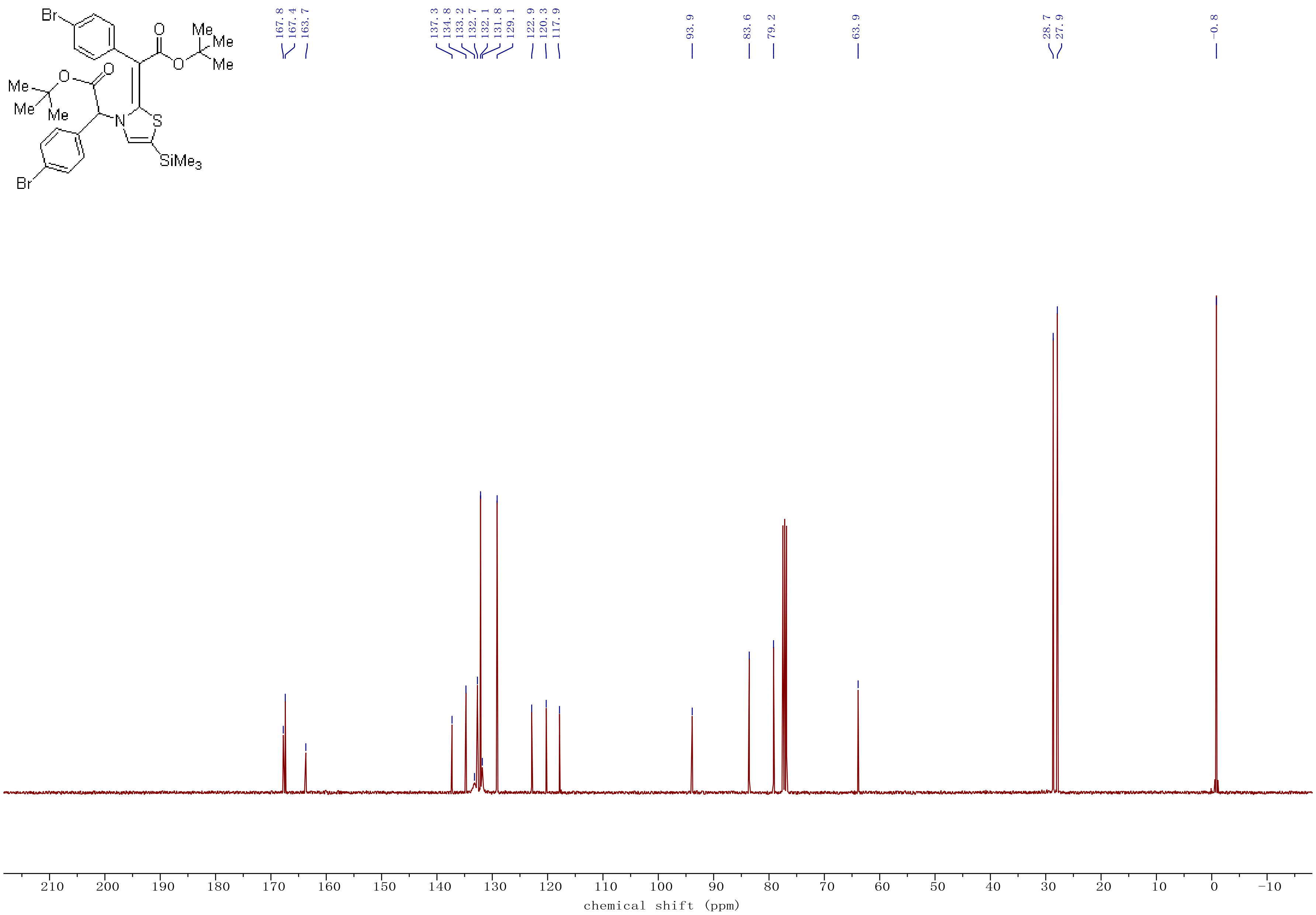
chemical shift (ppm)

Copies of ^{13}C NMR spectra of 3a, 3c-3f, 4a-4i, 5a-5l:

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137.3
134.8
133.2
132.7
132.1
131.8
129.1
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120.3
117.9
93.9
83.6
79.2
63.9
28.7
27.9
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180
170
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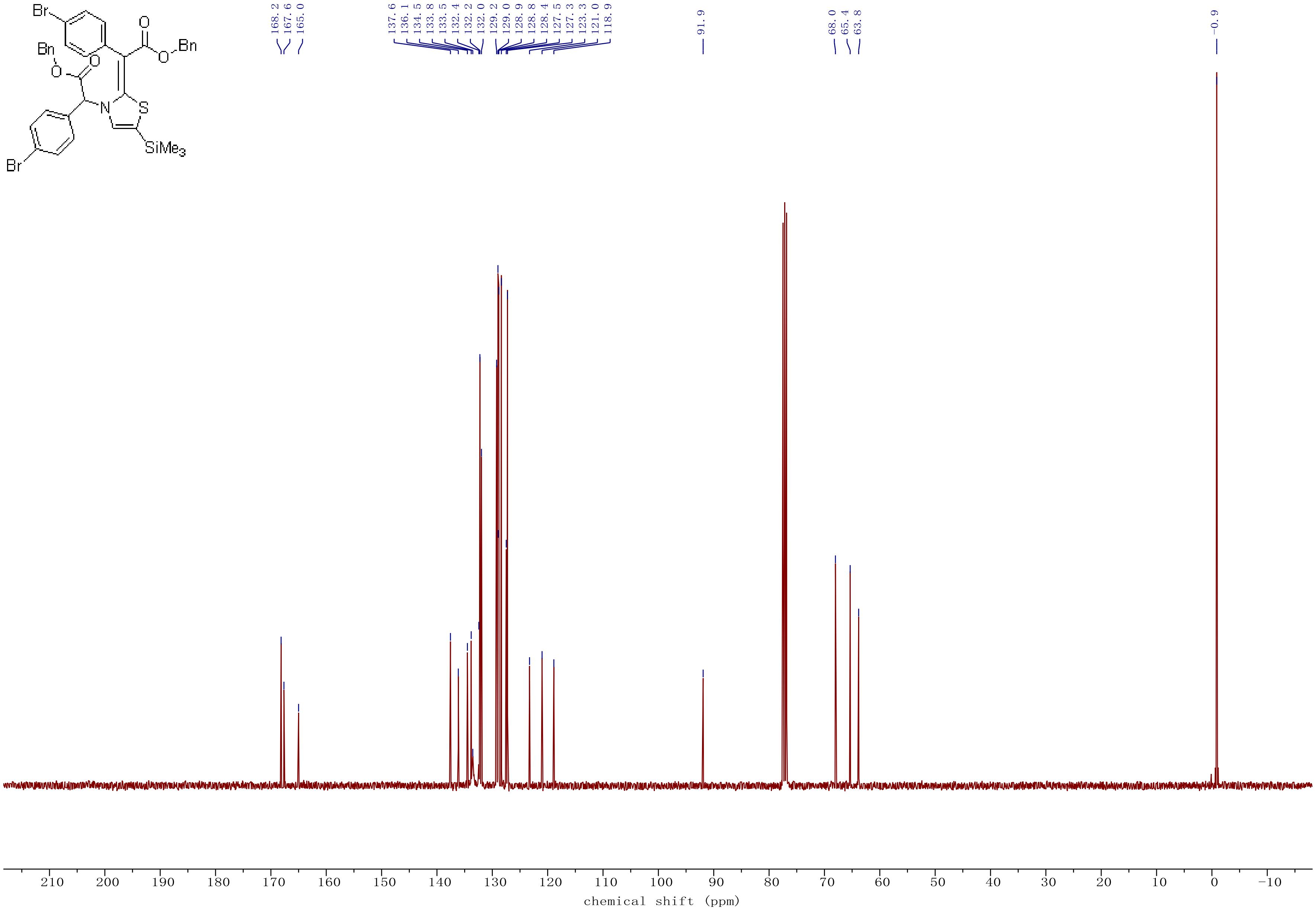
−10
chemical shift (ppm)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132.4
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129.0
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128.8
128.4
127.5
127.3
123.3
121.0
118.9
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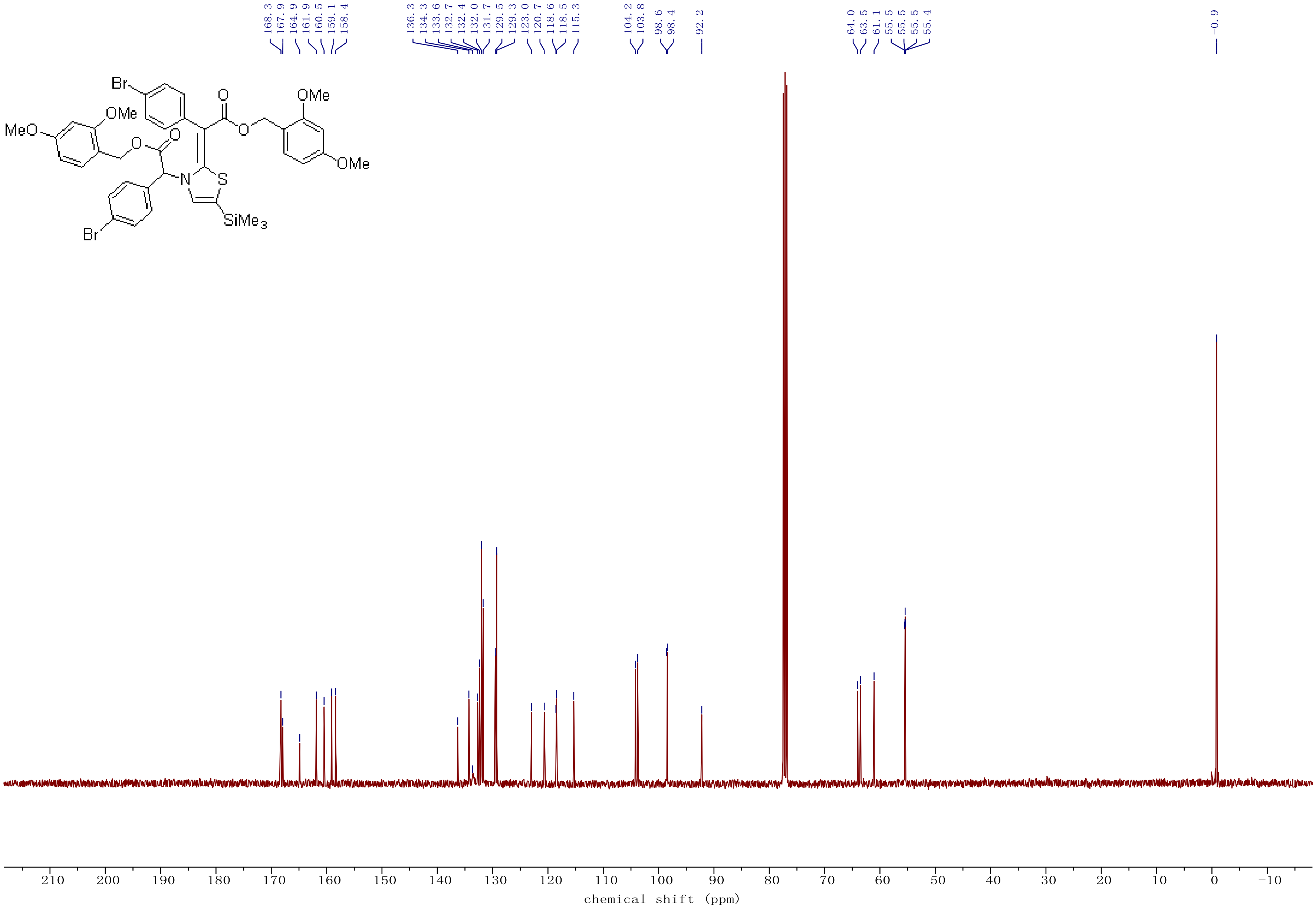
chemical shift (ppm)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55.4
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O
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S
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Br
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170
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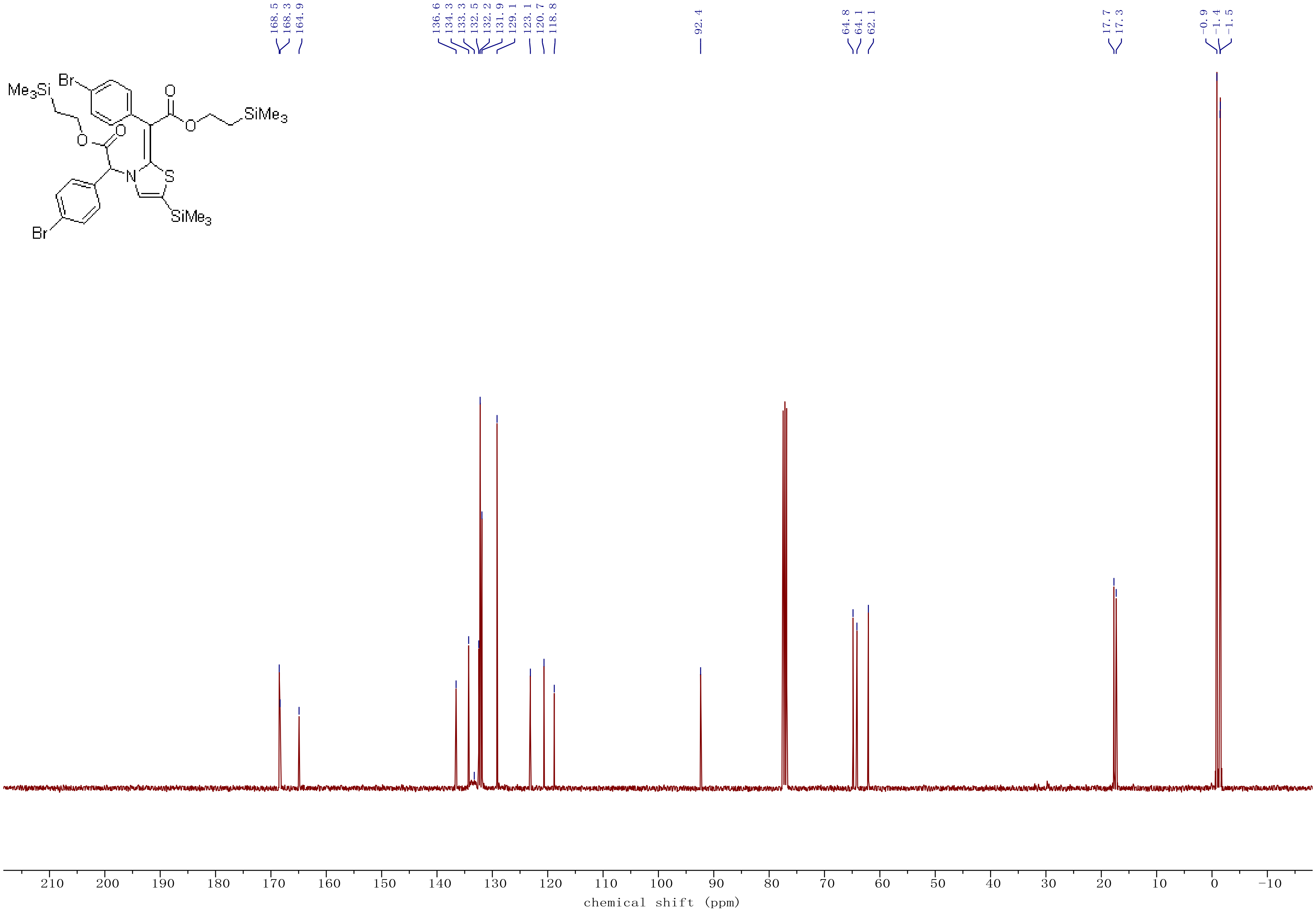
chemical shift (ppm)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64.1
62.1
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N
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80
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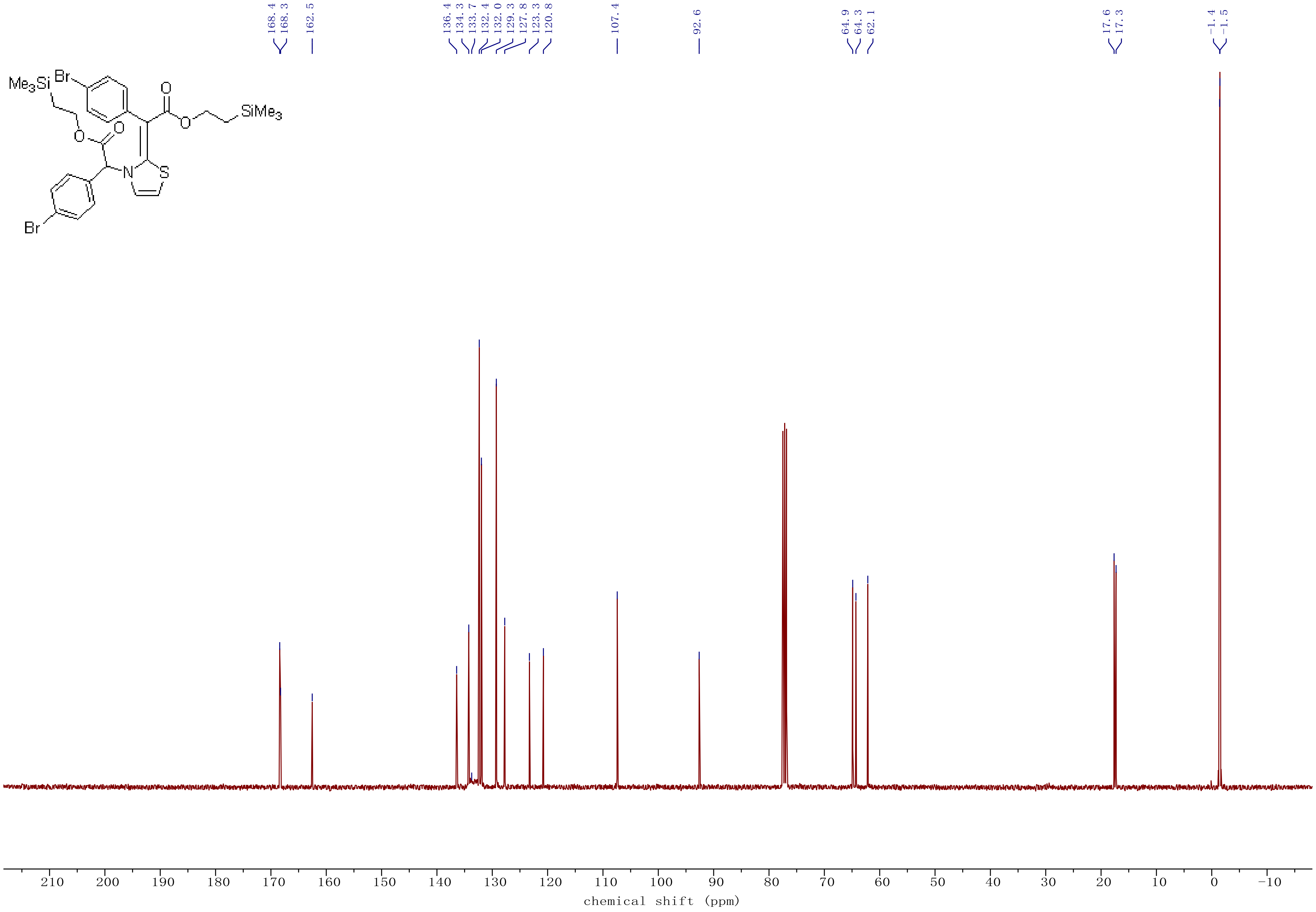
chemical shift (ppm)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64.3
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17.6
17.3
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-1.5
Me3Si
Br
O
SiMe3
O
O
N
S
Br
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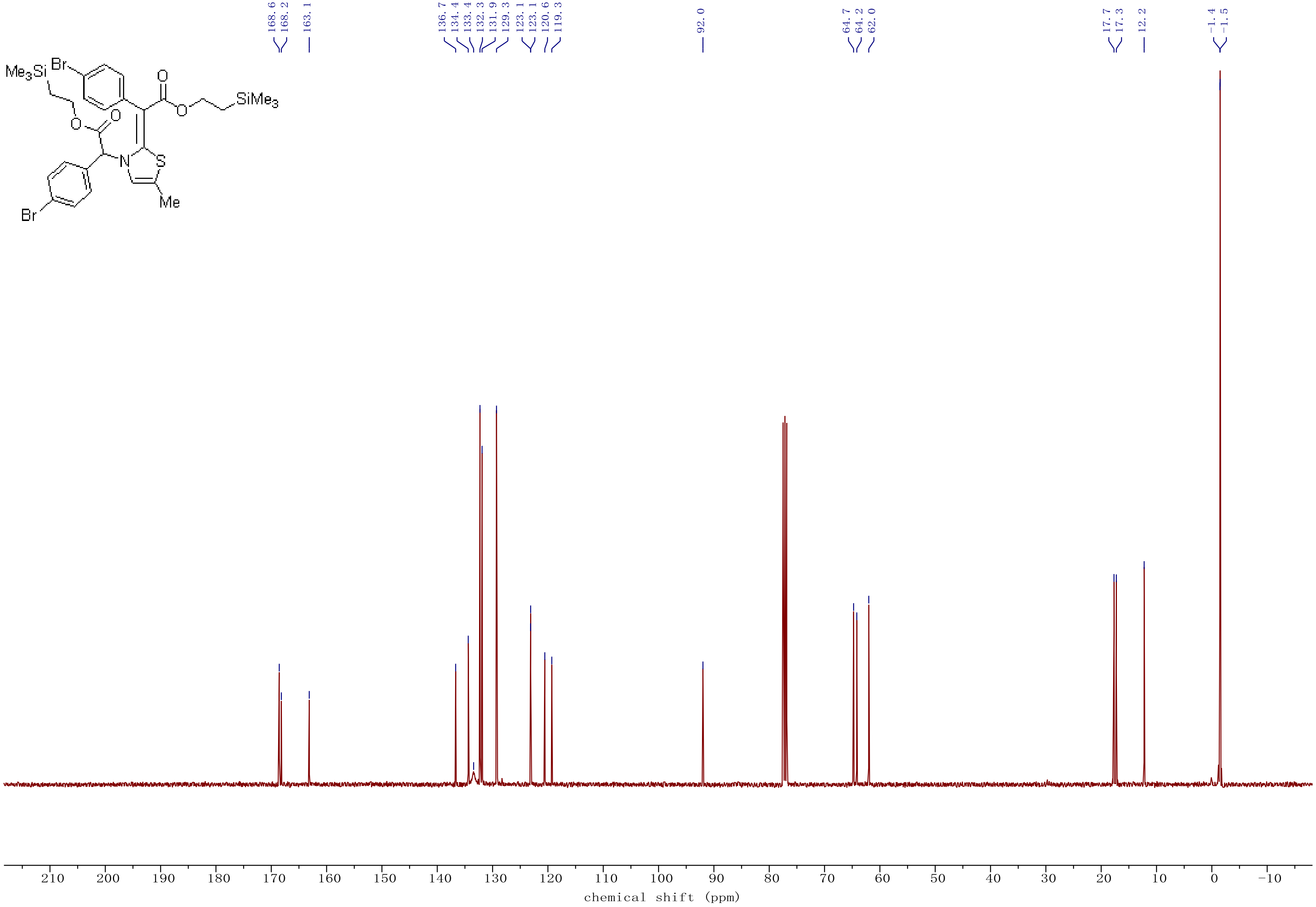
chemical shift (ppm)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64.2
62.0
17.7
17.3
12.2
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-1.5
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Me3Si
O
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O
SiMe3
O
N
S
Me
Br
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180
170
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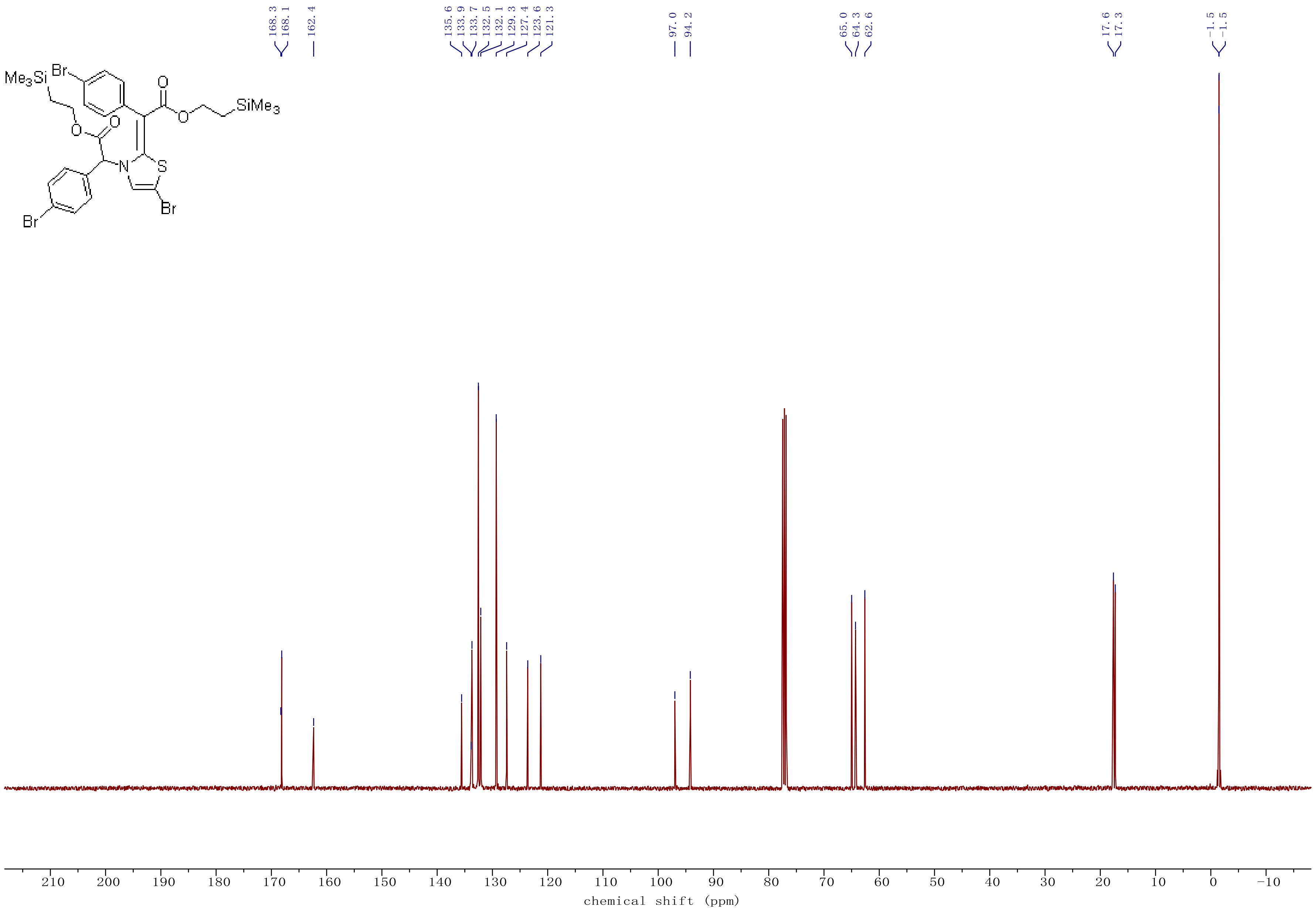
chemical shift (ppm)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94.2
65.0
64.3
62.6
17.6
17.3
-1.5
-1.5
Me3Si
Br
O
O
SiMe3
O
O
N
S
Br
Br
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200
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180
170
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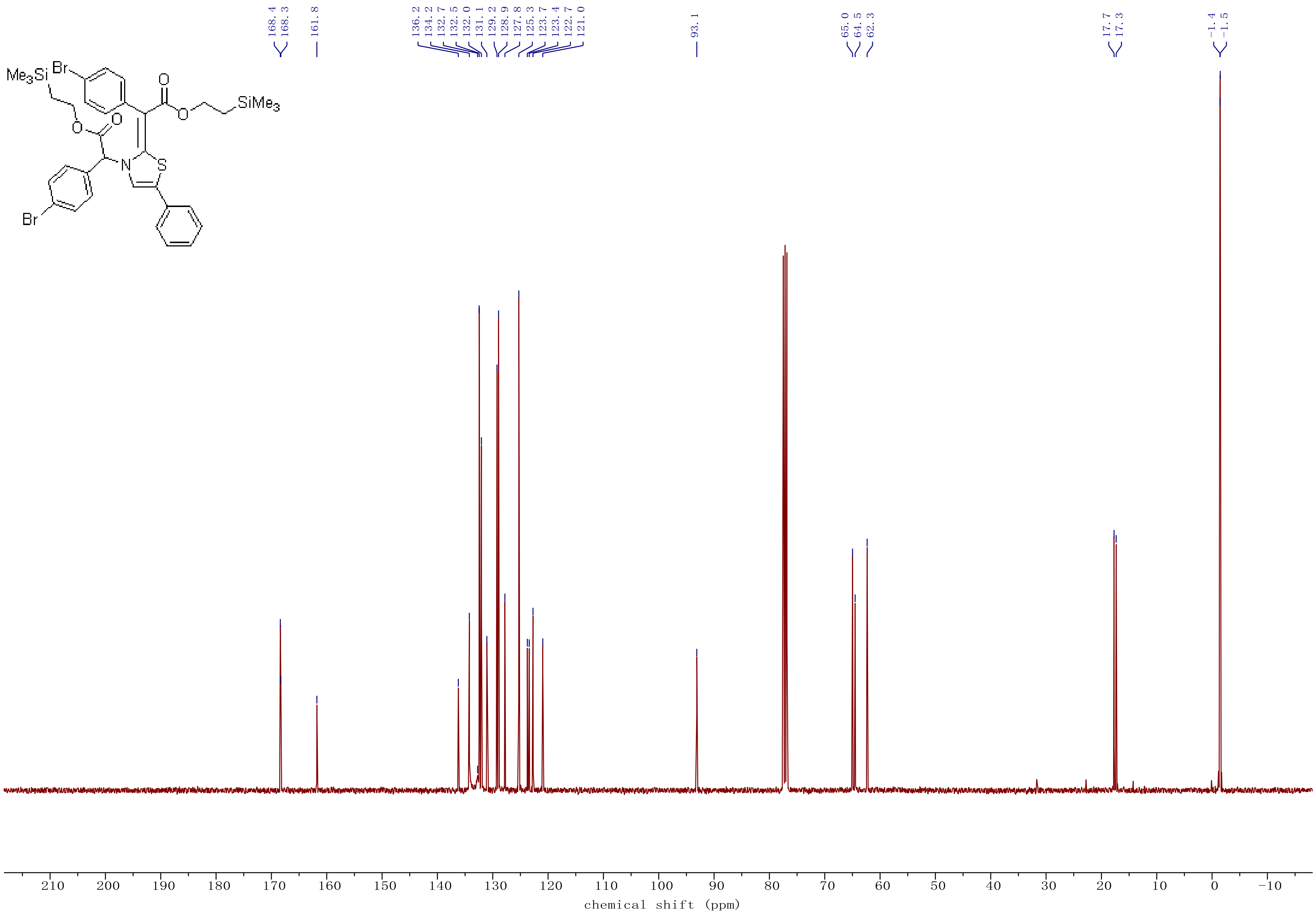
chemical shift (ppm)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SiMe3
O
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N
S
Br
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132.7
132.5
132.0
131.1
129.2
128.9
127.8
125.3
123.7
123.4
122.7
121.0
93.1
65.0
64.5
62.3
17.7
17.3
-1.4
-1.5
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200
190
180
170
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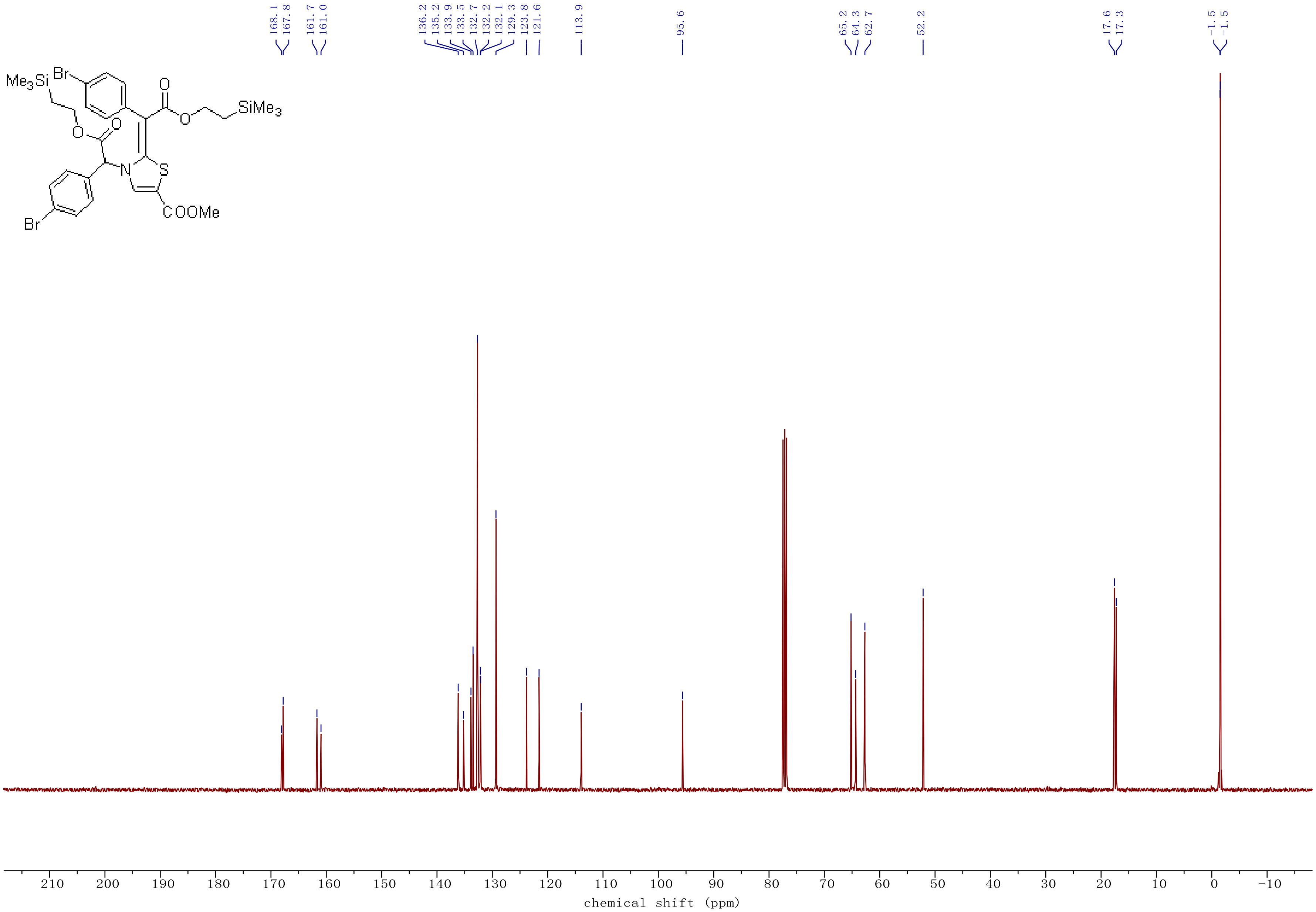
chemical shift (ppm)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121.6
113.9
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64.3
62.7
52.2
17.6
17.3
-1.5
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Br
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SiMe3
O
O
N
S
COOMe
Br
210
200
190
180
170
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140
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120
110
100
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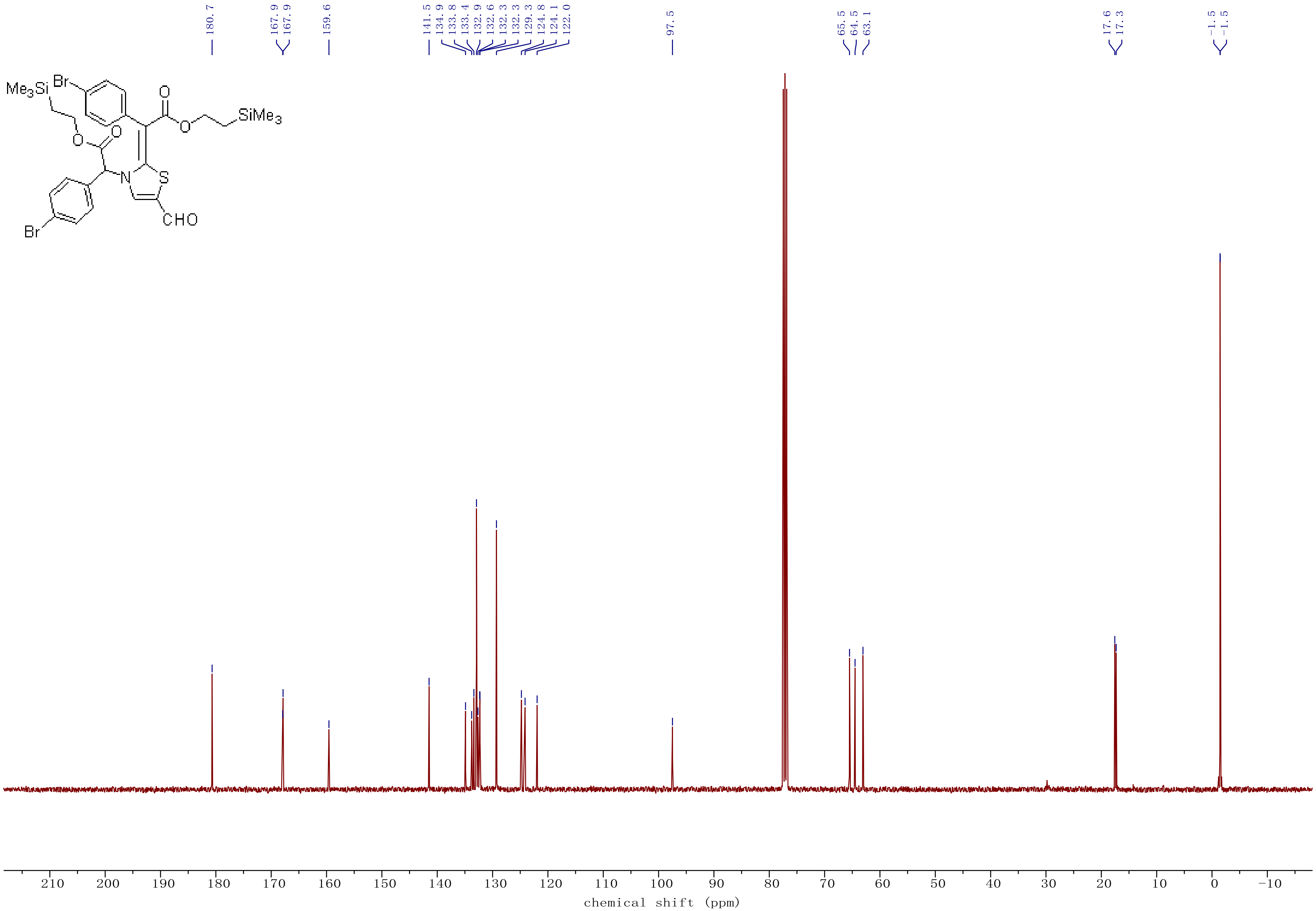
chemical shift (ppm)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124.8
124.1
122.0
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65.5
64.5
63.1
17.6
17.3
-1.5
-1.5
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Br
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N
S
Br
CHO
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180
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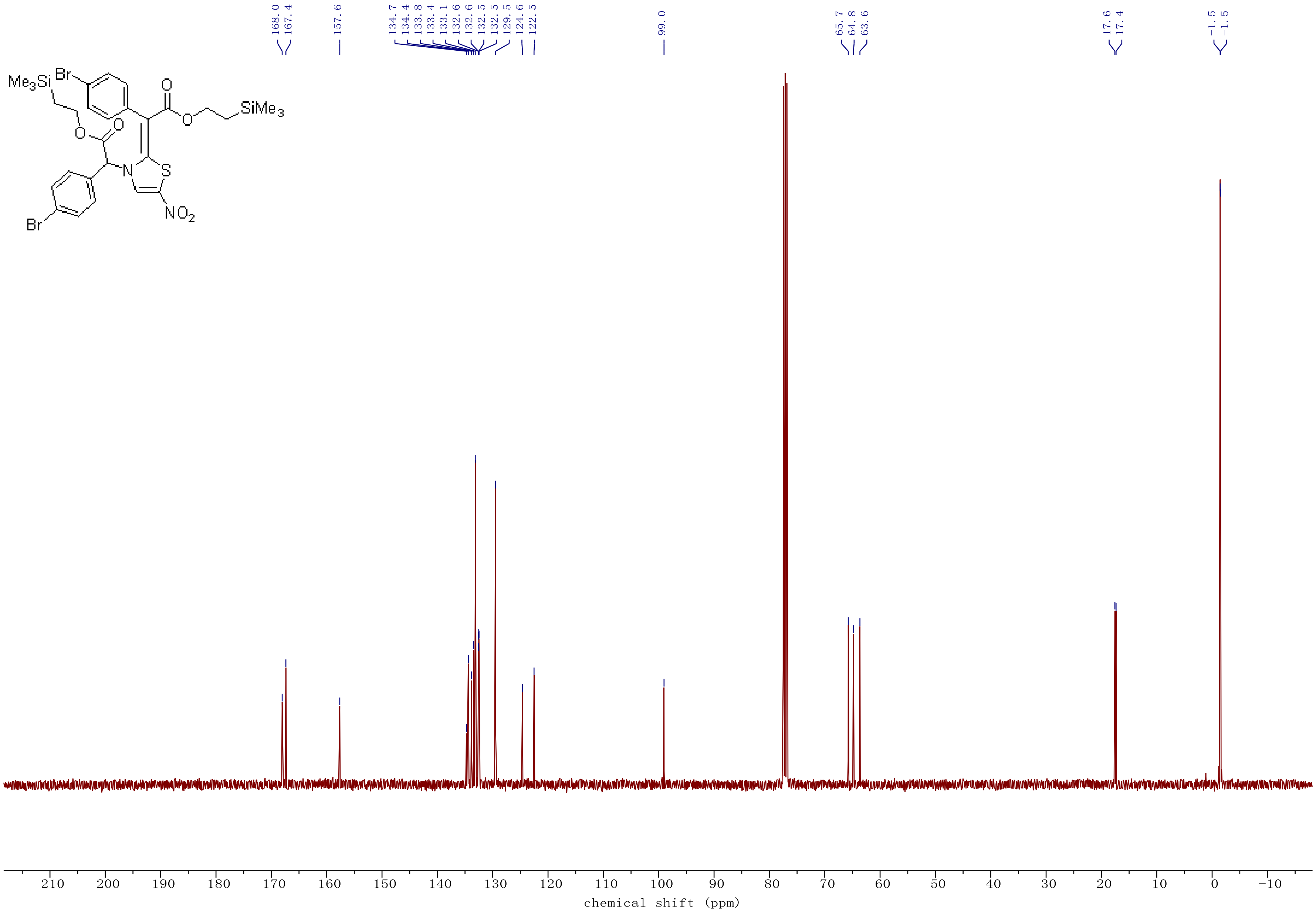
chemical shift (ppm)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63.6
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17.4
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-1.5
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Br
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N
S
NO2
Br
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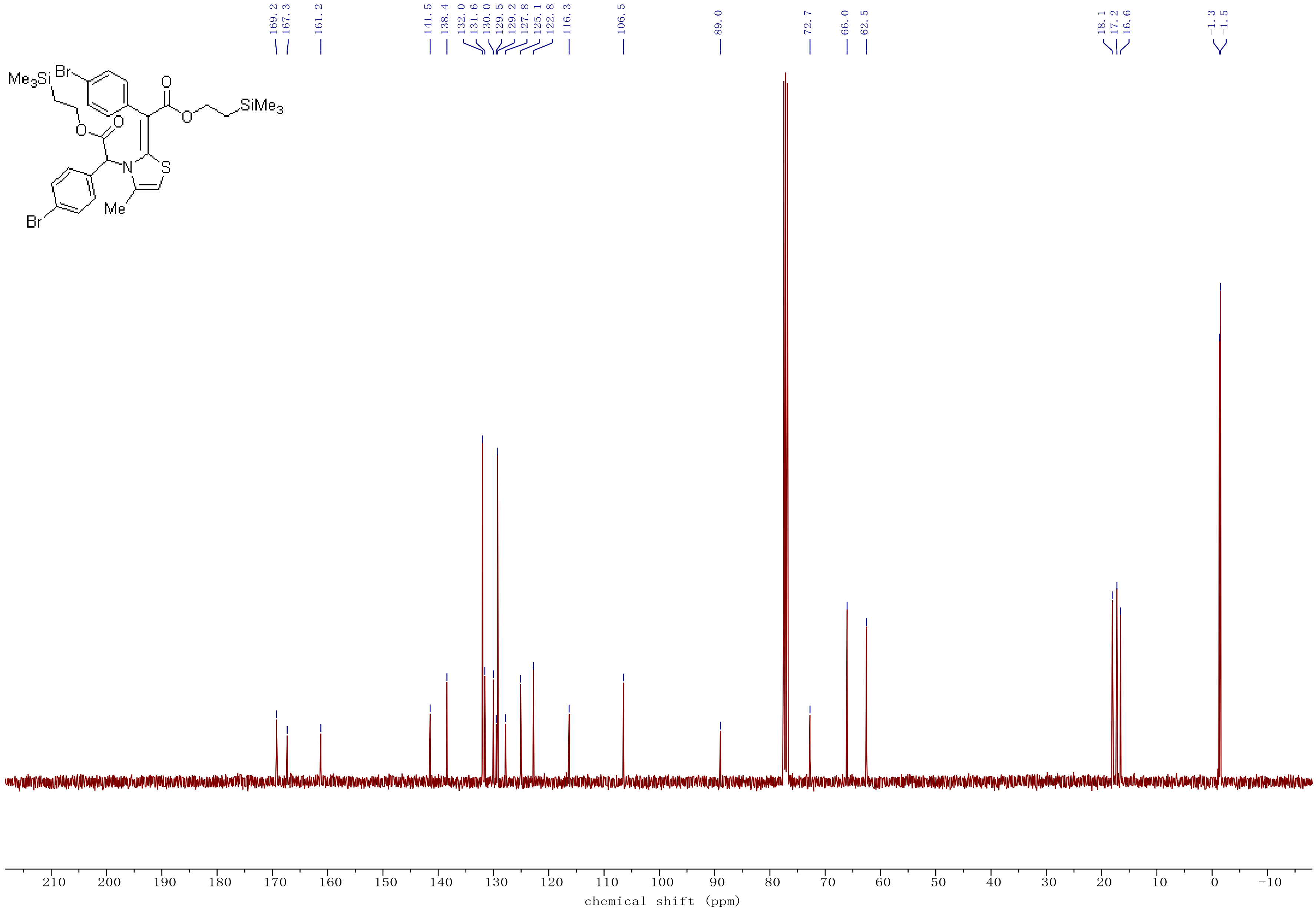
chemical shift (ppm)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66.0
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17.2
16.6
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-1.5
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Br
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O
SiMe3
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O
N
S
Me
Br
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200
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180
170
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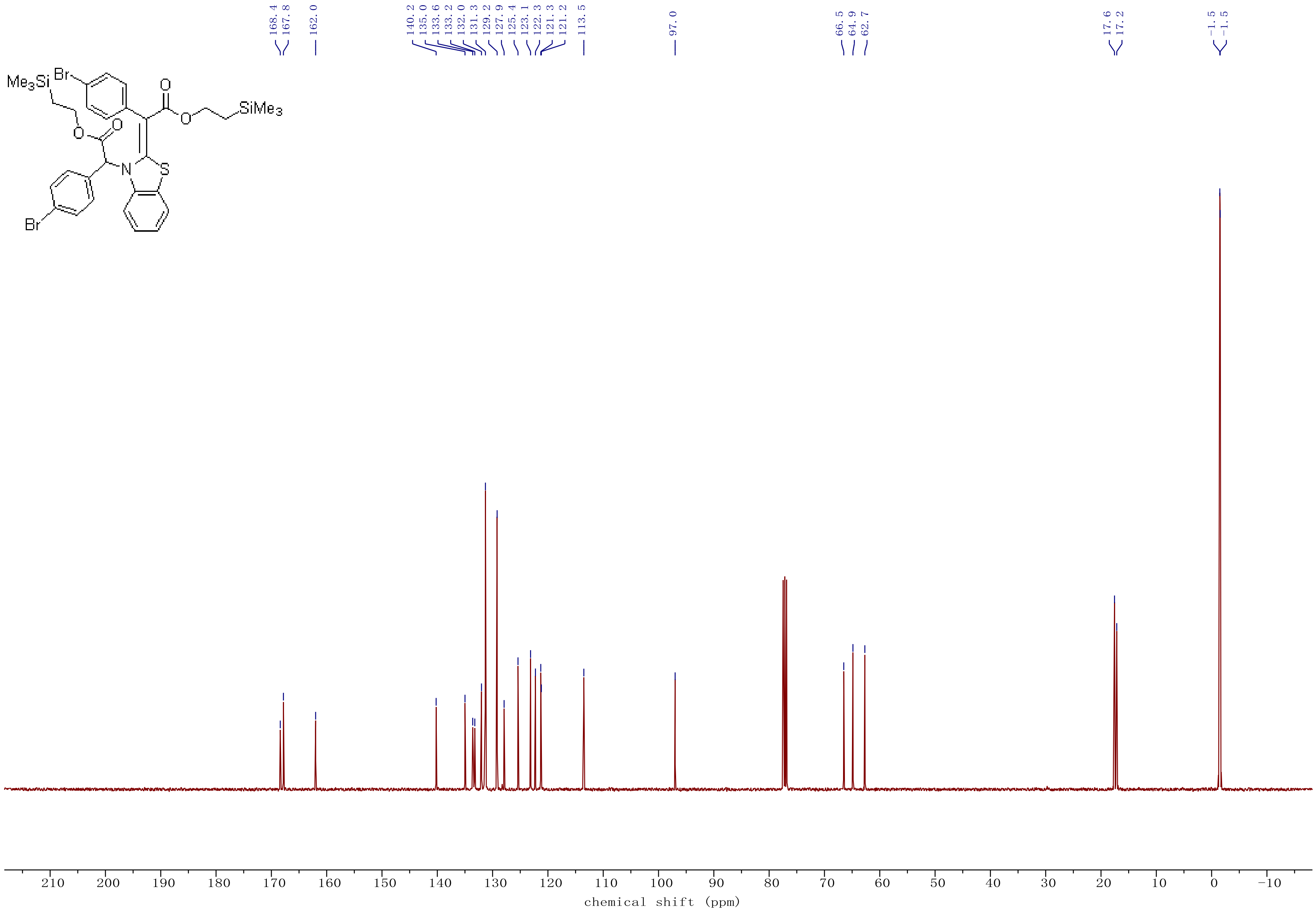
chemical shift (ppm)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121.3
121.2
113.5
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66.5
64.9
62.7
17.6
17.2
-1.5
-1.5
Me3Si
Br
O
O
SiMe3
O
O
N
S
Br
210
200
190
180
170
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100
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80
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60
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30
20
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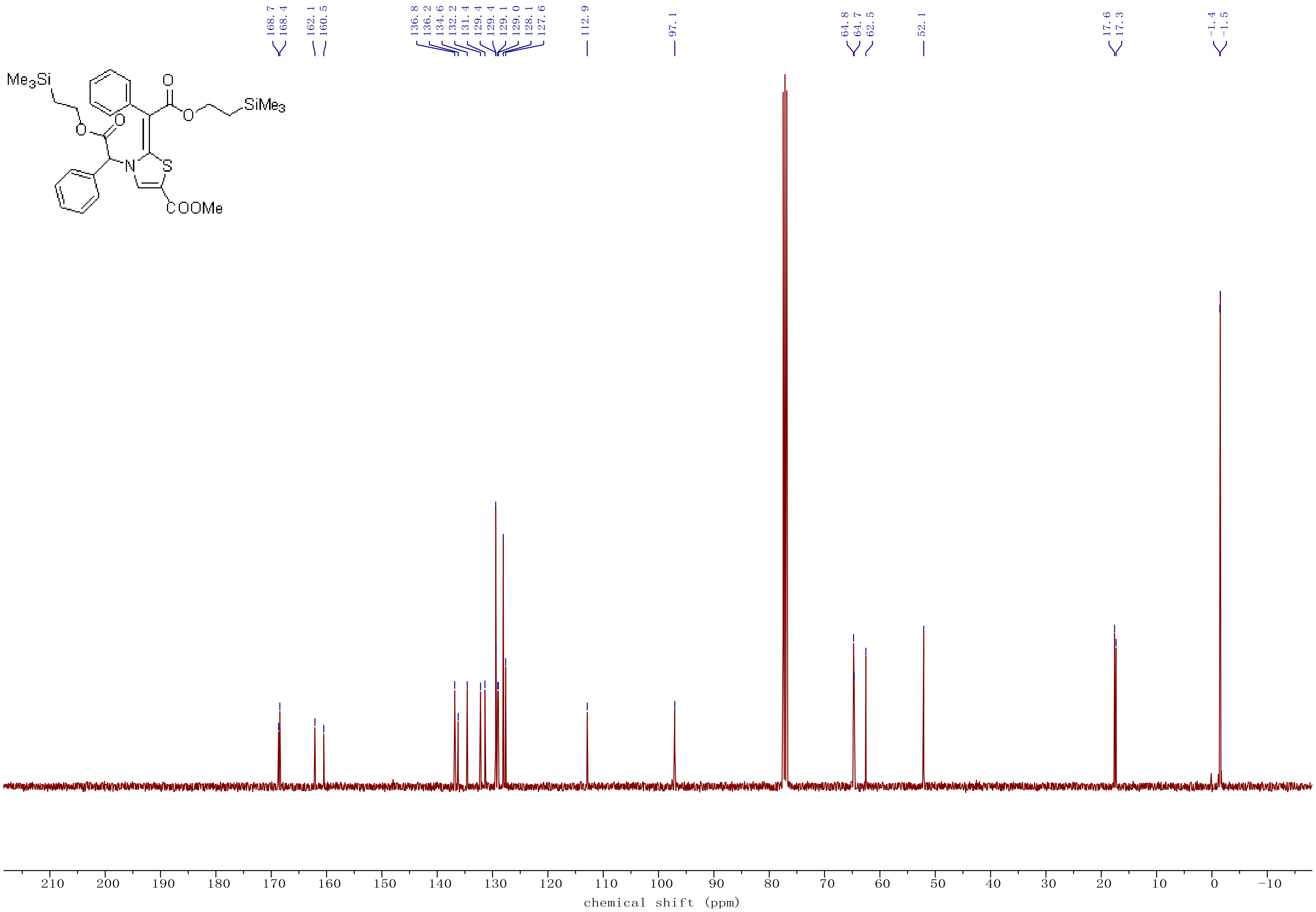
chemical shift (ppm)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17.6
17.3
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−1.5
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O
O
O
SiMe3
O
O
N
S
COOMe
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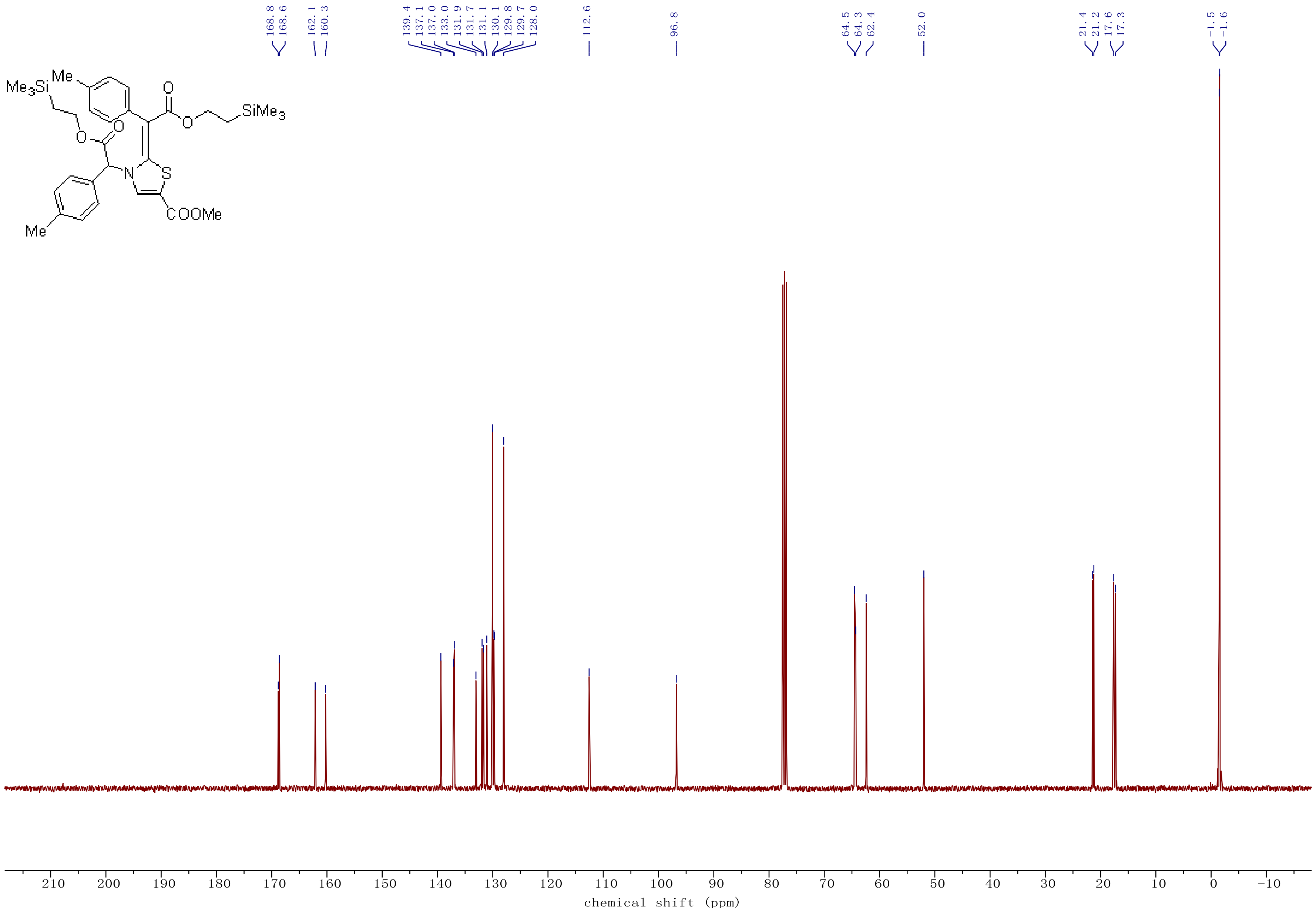
chemical shift (ppm)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64.5
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62.4
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21.2
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N
S
COOMe
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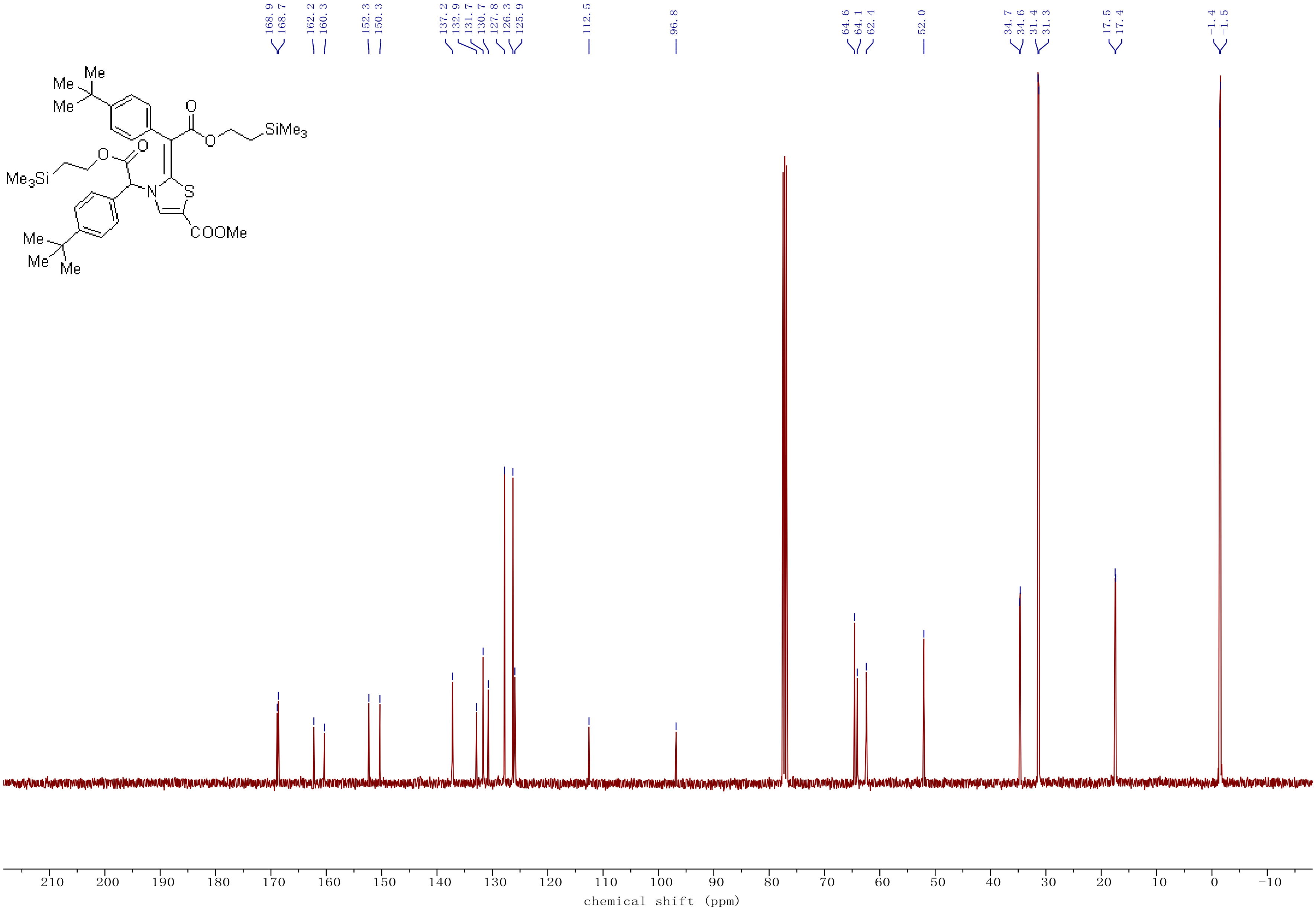
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Me
O
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COOMe
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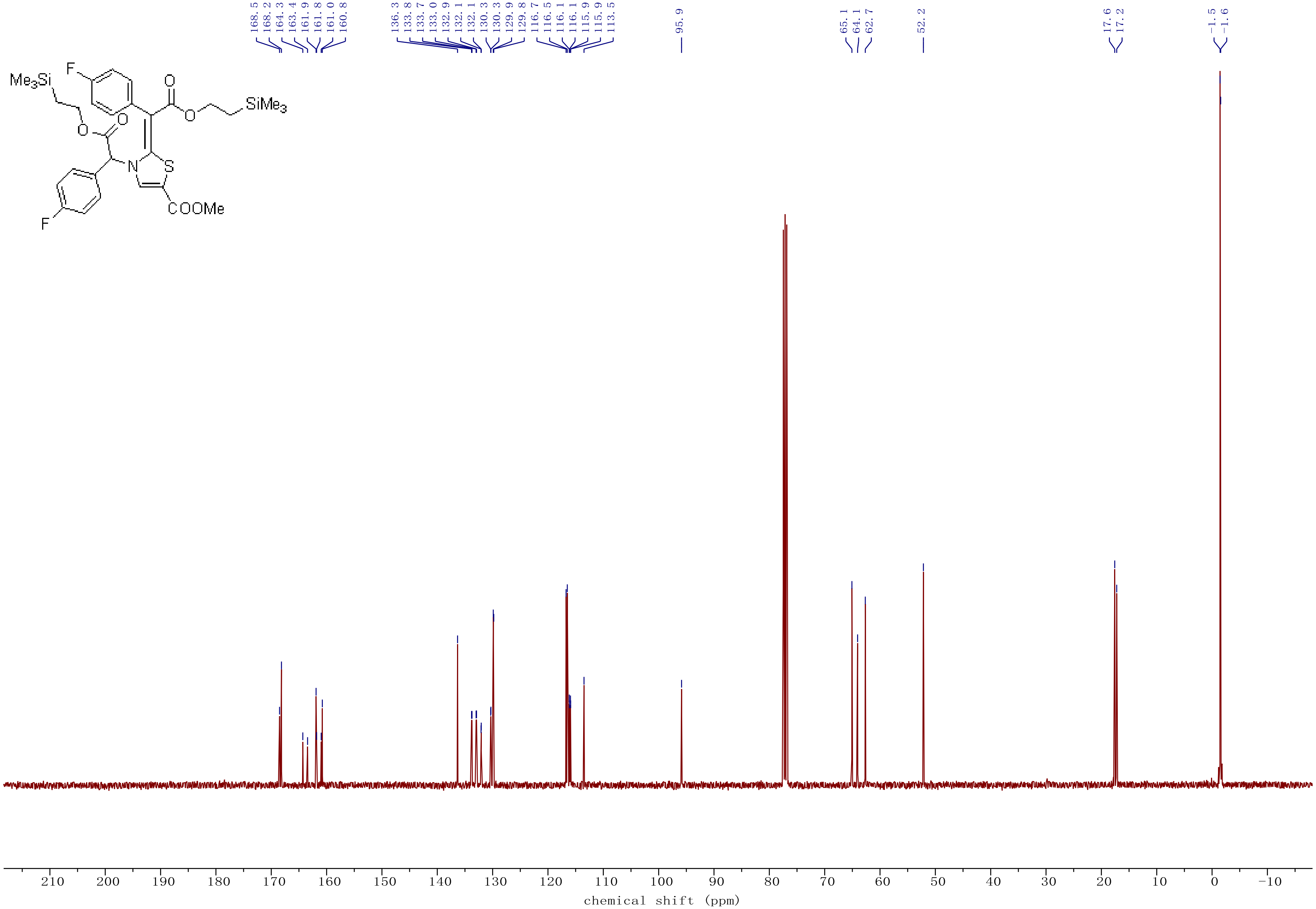
chemical shift (ppm)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Me$_3$Si
O
O
O
O
SiMe$_3$
N
S
F
COOMe
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80
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30
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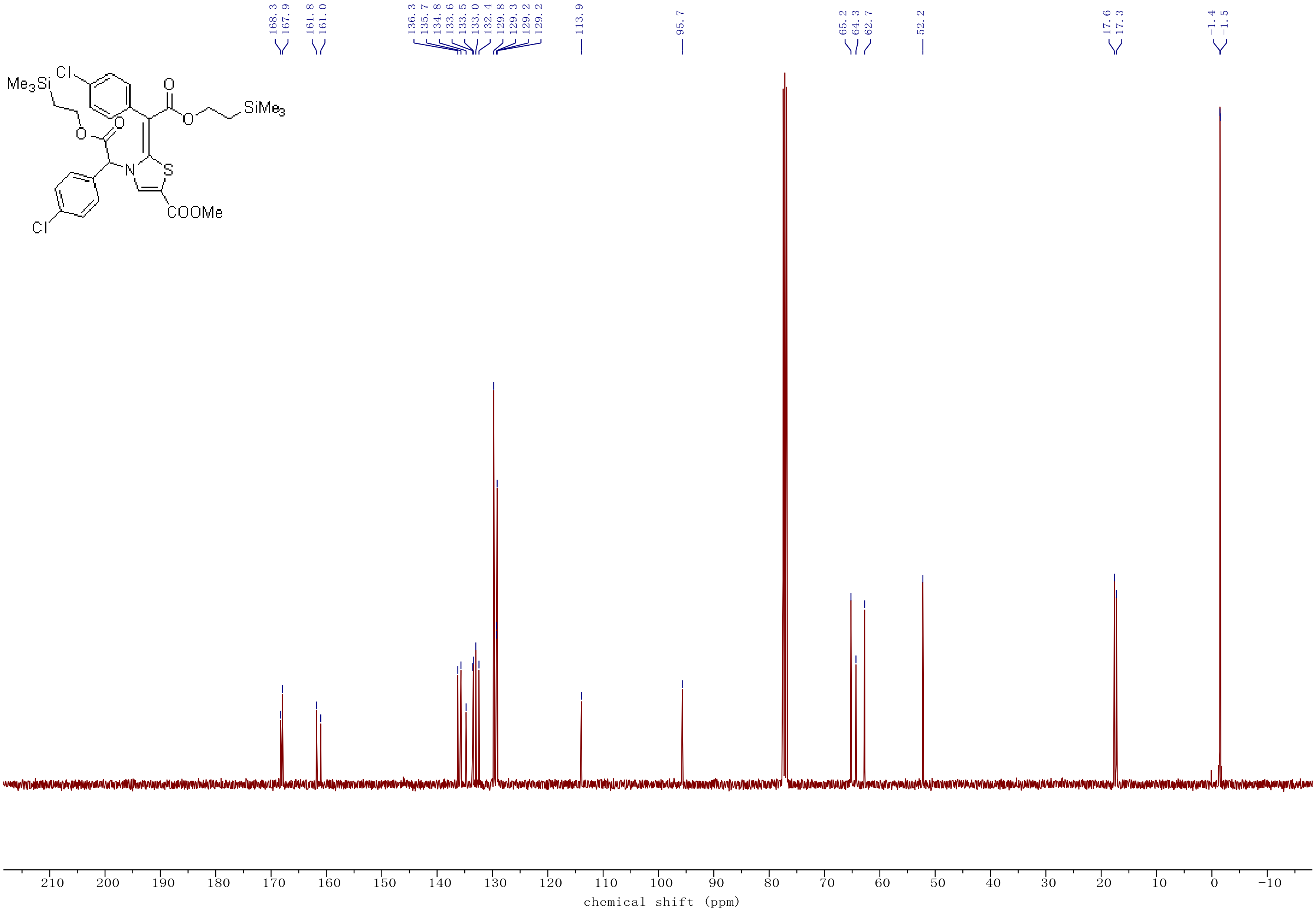
chemical shift (ppm)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17.3
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180
170
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150
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120
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100
90
80
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60
50
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S
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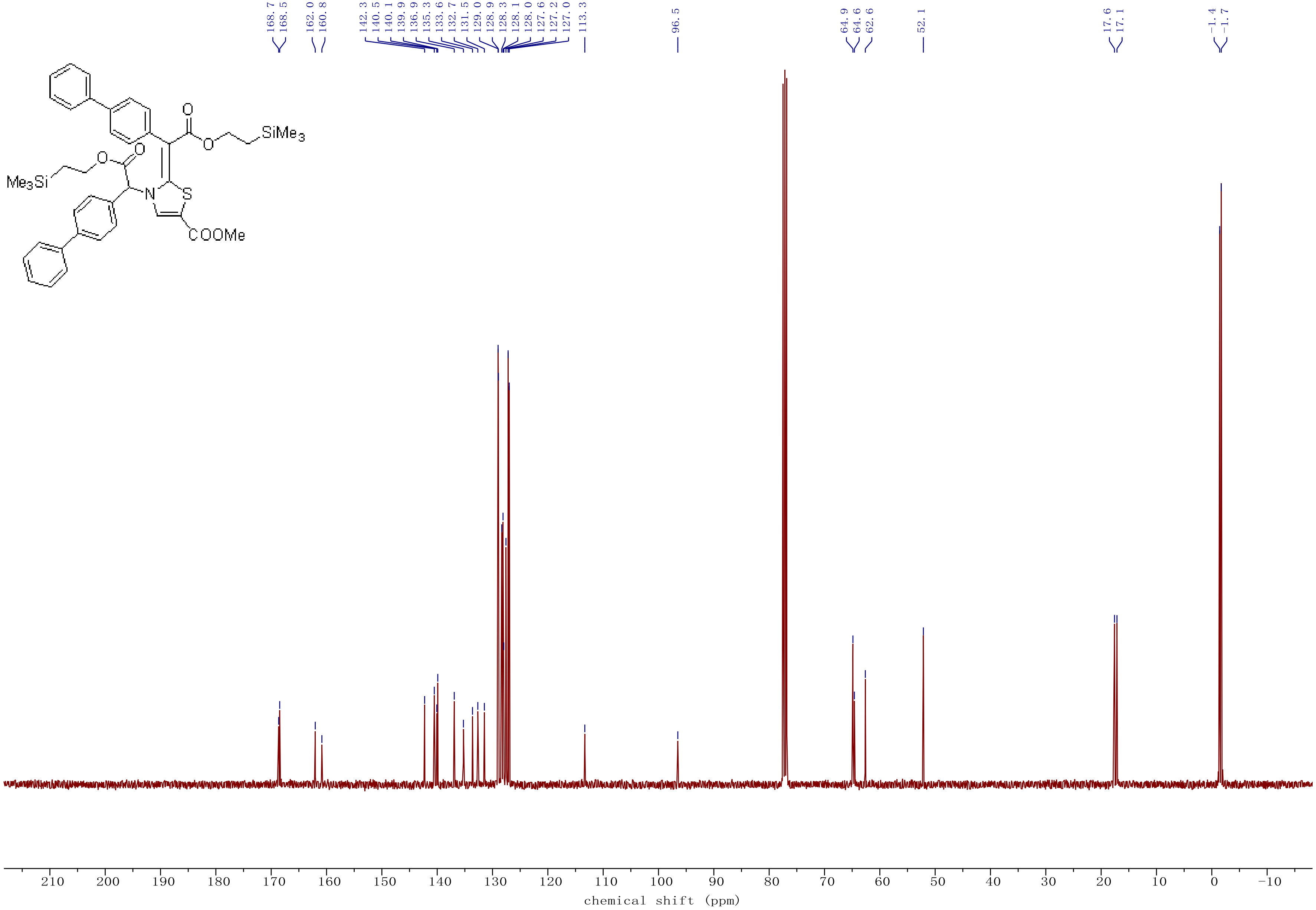
COOMe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N
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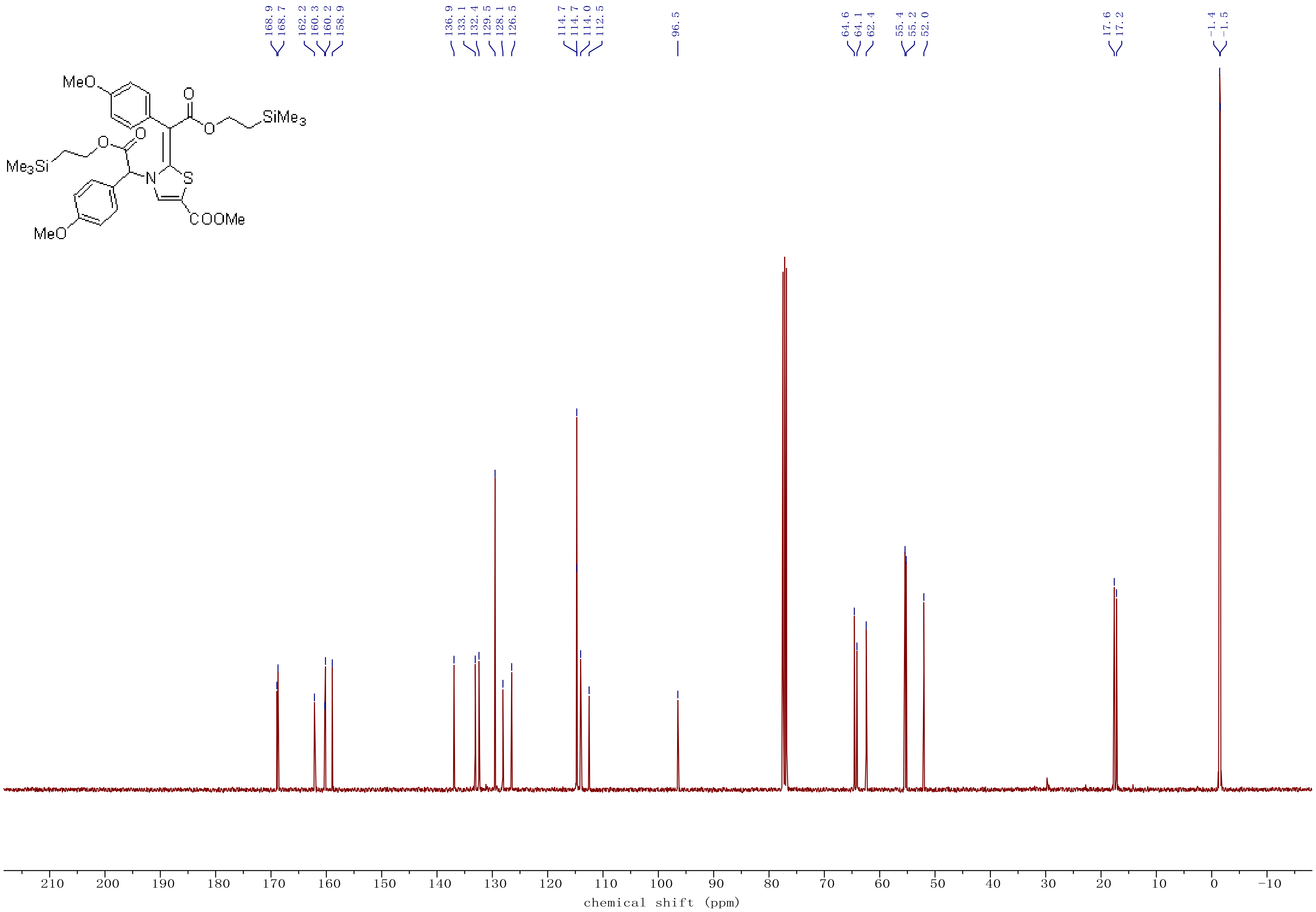
chemical shift (ppm)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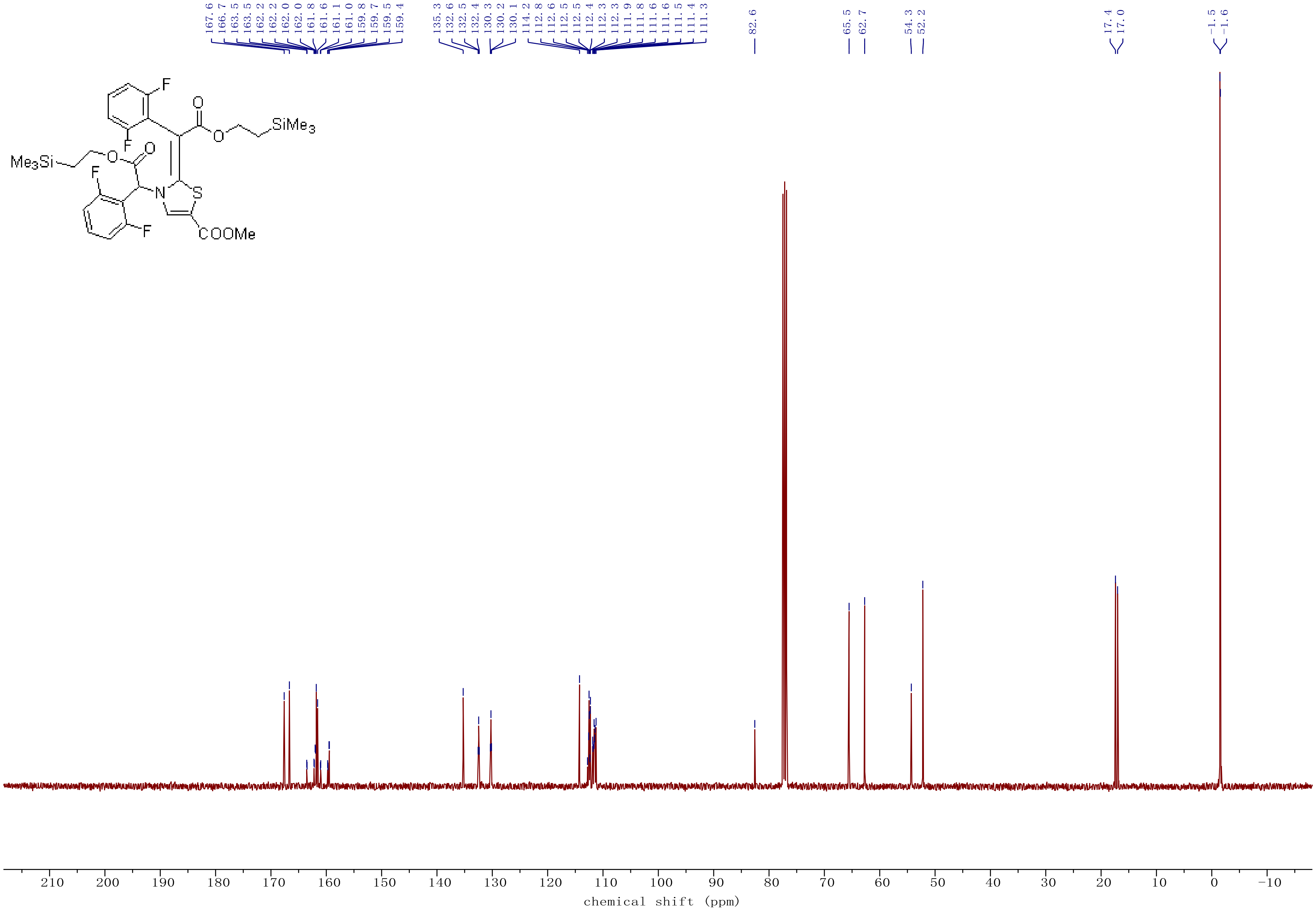
chemical shift (ppm)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O
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O
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N
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COOMe
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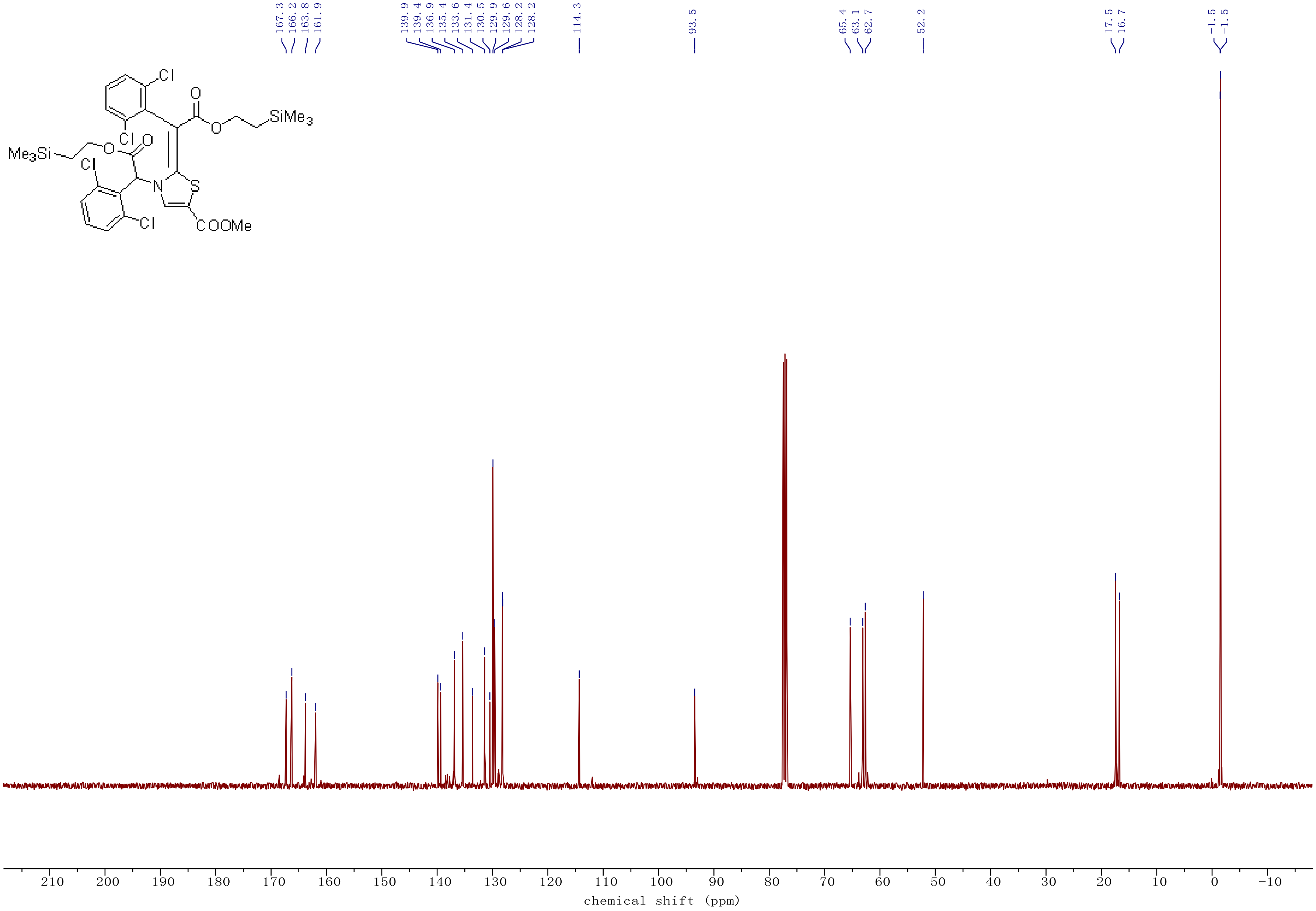
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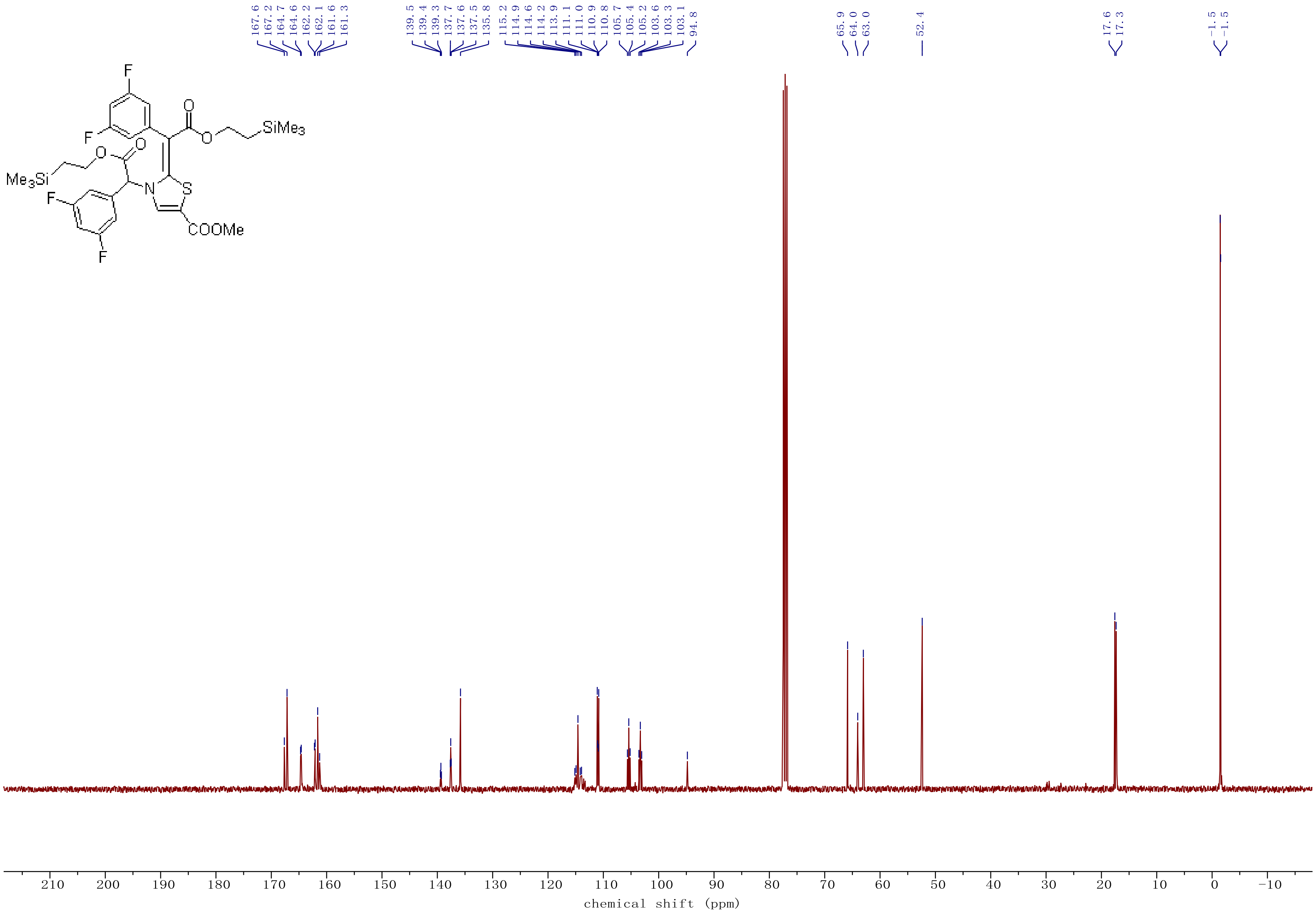
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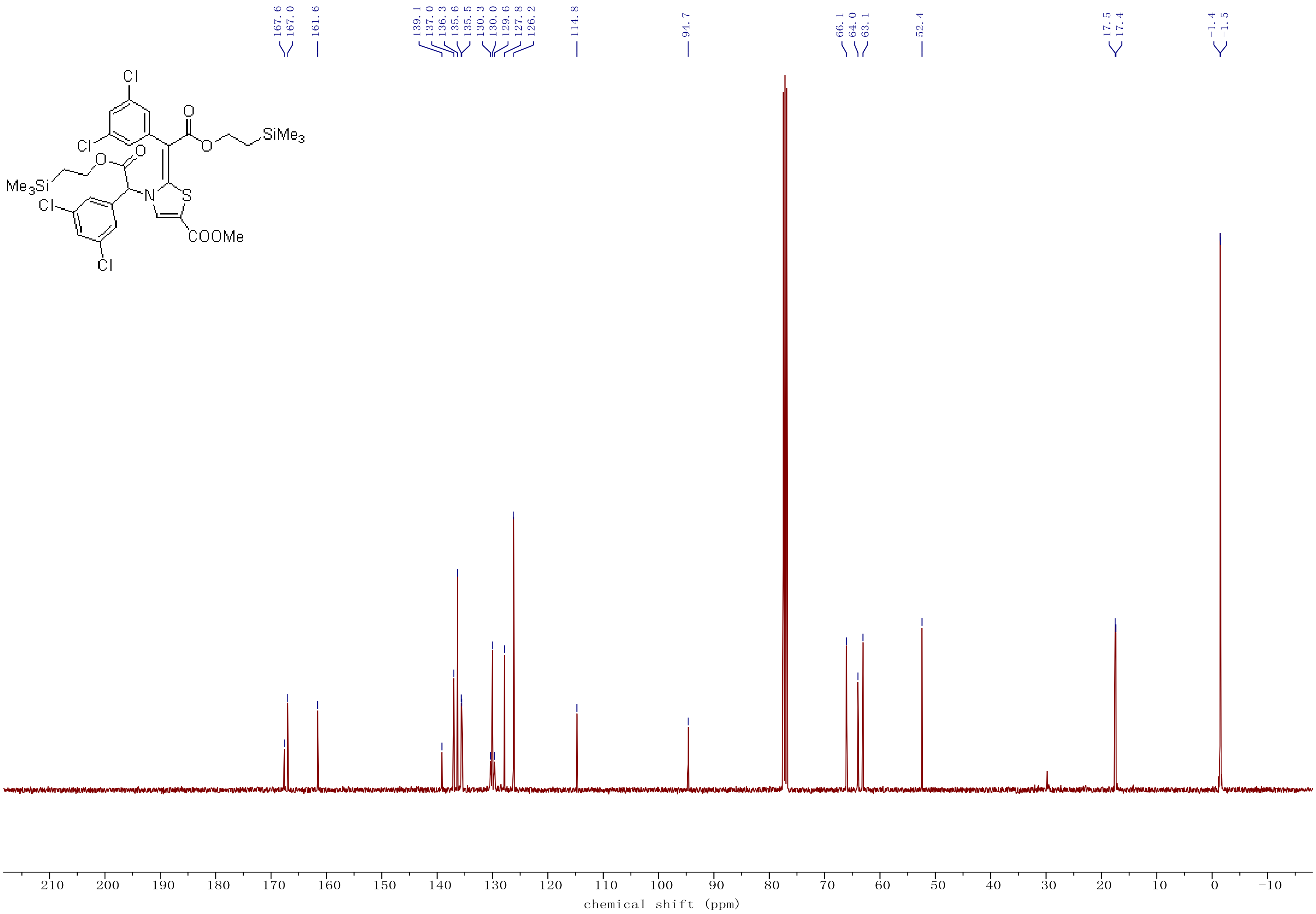
chemical shift (ppm)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94.7
66.1
64.0
63.1
52.4
17.5
17.4
−1.4
−1.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
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N
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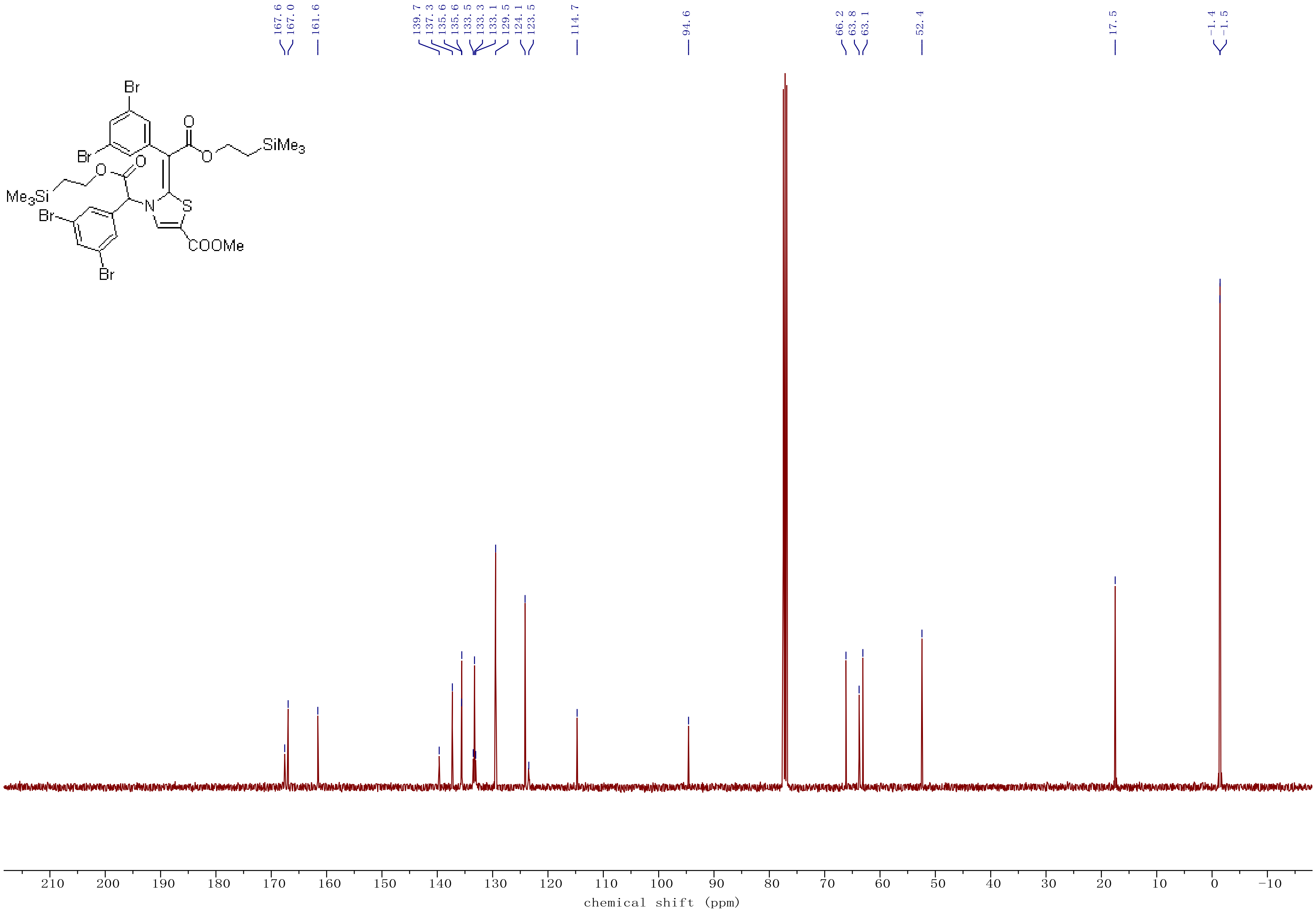
COOMe
Cl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66.2
63.8
63.1
52.4
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-1.5
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Br
O
O
SiMe3
Br
O
O
Me3Si
N
S
Br
COOMe
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
chemical shift (ppm)

X-Ray crystallographic data of 3b:

Experimental

Crystallization of $C_{30}H_{37}C_{l2}NO_4SSi$ (**3b**) was successfully carried out using a solution containing ethyl acetate as the solvent, leading to the formation of crystals that were then carefully selected for analysis on an XtaLAB AFC12 (RINC): Kappa single diffractometer. The crystal was kept at 120.0(2) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Number of restraints - 0, number of constraints - unknown.

Details:
1. Fixed Uiso
At 1.2 times of:
All C(H) groups
At 1.5 times of:
All C(H, H, H) groups
2.a Ternary CH refined with riding coordinates:
C19(H19)
2.b Aromatic/amide H refined with riding coordinates:
C2(H2), C6(H6), C7(H7), C9(H9), C10(H10), C21(H21), C22(H22), C24(H24), C25(H25)
2.c Idealised Me refined as rotating group:
C12(H12A, H12B, H12C), C14(H14A, H14B, H14C), C15(H15A, H15B, H15C), C16(H16A, H16B,
H16C), C17(H17A, H17B, H17C), C18(H18A, H18B, H18C), C27(H27A, H27B, H27C), C29(H29A,
H29B, H29C), C30(H30A, H30B, H30C)

This report has been created with Olex2, compiled on 2022.04.07 svn.rca3783a0 for OlexSys.

Table 1 Crystal data and structure refinement for 3b.

Identification code	3b
Empirical formula	$C_{30}H_{37}Cl_2NO_4SSi$
Formula weight	606.65
Temperature/K	120.0(2)

Crystal system	triclinic
Space group	P-1
a/Å	11.6650(6)
b/Å	11.8161(8)
c/Å	14.0653(9)
α/°	70.874(6)
β/°	66.157(6)
γ/°	67.903(6)
Volume/Å^3	1607.3(2)
Z	2
ρ_{calc}g/cm^3	1.253
μ/mm^{-1}	3.052
F(000)	640.0
Crystal size/mm^3	0.14 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.024 to 133.2
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 12$, $-16 \leq l \leq 16$
Reflections collected	13065
Independent reflections	5521 [R_{int} = 0.0398, R_{sigma} = 0.0420]
Data/restraints/parameters	5521/0/361
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0529, wR_2 = 0.1524
Final R indexes [all data]	R_1 = 0.0580, wR_2 = 0.1573
Largest diff. peak/hole / e Å^{-3}	0.68/-0.44

Crystal structure determination of 3b

Crystal Data for $C_{30}H_{37}Cl_2NO_4SSi$ (*M* =606.65 g/mol): triclinic, space group P-1 (no. 2), *a* = 11.6650(6) Å, *b* = 11.8161(8) Å, *c* = 14.0653(9) Å, *α* = 70.874(6)°, *β* = 66.157(6)°, *γ* = 67.903(6)°, *V* = 1607.3(2) Å^3, *Z* = 2, *T* = 120.0(2) K, μ(Cu Kα) = 3.052 mm^{-1}, *Dcalc* = 1.253 g/cm^3, 13065 reflections measured (7.024° ≤ 2Θ ≤ 133.2°), 5521 unique (R_{int} = 0.0398, R_{sigma} = 0.0420) which were used in all calculations. The final R_1 was 0.0529 (I > 2σ(I)) and wR_2 was 0.1573 (all data).

Refinement model description

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3b. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Cl1	8440.1(6)	5147.5(6)	11094.6(5)	46.91(19)
Cl2	9217.5(8)	4786.5(7)	3250.6(6)	62.9(2)
S1	5097.5(5)	10179.2(5)	7216.4(4)	35.63(18)
Si1	2694.2(6)	10021.6(6)	9359.0(5)	36.51(19)
O1	6883.7(16)	10999.2(15)	5525.4(13)	42.6(4)
O2	8234.3(14)	10021.1(14)	4161.0(11)	34.5(4)
O3	4702.2(14)	5907.9(15)	7553.8(14)	41.5(4)
O4	6750.7(14)	4627.3(14)	7054.5(12)	34.2(4)
N1	5677.3(16)	7835.5(17)	7315.0(14)	31.1(4)
C1	4150(2)	9304(2)	8302.0(18)	36.0(5)
C2	4602(2)	8115(2)	8216.4(17)	33.7(5)
C3	6060.6(19)	8870(2)	6637.0(16)	30.1(4)
C4	7006(2)	8910(2)	5651.6(16)	30.9(5)
C5	7558(2)	7888(2)	5057.5(15)	29.6(4)
C6	8886(2)	7294(2)	4737.8(17)	33.5(5)
C7	9406(2)	6350(2)	4171.0(18)	37.7(5)
C8	8567(2)	6000(2)	3933.3(17)	39.1(5)
C9	7243(2)	6577(2)	4224.3(18)	40.2(5)
C10	6738(2)	7526(2)	4785.9(17)	34.8(5)
C11	7345(2)	10080(2)	5133.4(17)	32.4(5)
C12	9544(3)	10635(3)	2444(2)	51.3(7)
C13	8674(2)	11115(2)	3461.0(17)	34.9(5)
C14	7533(3)	12206(3)	3271(2)	54.8(7)
C15	9481(3)	11414(3)	3910(2)	49.0(6)
C16	1746(2)	11511(2)	8699(2)	49.6(6)
C17	3225(2)	10344(3)	10307(2)	48.8(6)
C18	1741(2)	8859(2)	10075.3(19)	43.5(6)
C19	6547(2)	6539(2)	7346.2(16)	30.3(4)
C20	7025.5(19)	6127(2)	8301.4(16)	30.4(4)
C21	6773(2)	5130(2)	9121.1(18)	41.5(5)
C22	7222(3)	4805(3)	9984.2(19)	45.5(6)
C23	7918(2)	5503(2)	10006.8(17)	36.3(5)
C24	8178(2)	6504(2)	9200(2)	41.7(5)
C25	7733(2)	6807(2)	8350.3(19)	39.7(5)
C26	5863(2)	5669(2)	7329.7(16)	31.9(5)
C27	7626(2)	2590(3)	6752(3)	57.9(8)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3b. U$_{eq}$ is defined as 1/3 of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	*x*	*y*	*z*	**U(eq)**
C28	6349(2)	3583(2)	7009.7(18)	35.7(5)
C29	5736(3)	4018(3)	6139(2)	54.0(7)
C30	5435(3)	3136(3)	8083(2)	51.8(6)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 3b. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	**U$_{11}$**	**U$_{22}$**	**U$_{33}$**	**U$_{23}$**	**U$_{13}$**	**U$_{12}$**
Cl1	50.7(4)	57.1(4)	41.1(3)	-12.7(3)	-16.9(2)	-19.4(3)
Cl2	89.3(5)	48.8(4)	64.0(4)	-35.4(3)	-34.9(4)	-2.1(4)
S1	36.7(3)	29.0(3)	36.1(3)	-13.7(2)	0.3(2)	-10.8(2)
Si1	30.9(3)	35.0(4)	39.9(3)	-16.1(3)	-0.8(2)	-9.6(3)
O1	50.0(9)	31.9(9)	40.9(8)	-15.8(7)	1.6(7)	-17.0(7)
O2	39.7(8)	30.7(8)	31.5(7)	-10.9(6)	-1.6(6)	-15.1(7)
O3	31.3(8)	35.0(9)	60.3(10)	-16.0(8)	-12.5(7)	-8.9(7)
O4	32.4(8)	33.4(9)	43.3(8)	-19.4(7)	-8.7(6)	-10.2(6)
N1	29.3(9)	28.9(10)	33.4(9)	-12.1(7)	-3.1(7)	-9.3(7)
C1	31.0(10)	35.9(13)	37.5(11)	-12.0(9)	-3.0(9)	-10.5(9)
C2	29.5(10)	34.0(12)	35.7(11)	-14.0(9)	-0.9(8)	-11.4(9)
C3	29.9(10)	31.0(11)	31.8(10)	-11.7(8)	-7.0(8)	-9.9(9)
C4	30.7(10)	29.2(11)	32.3(10)	-10.6(9)	-5.9(8)	-8.8(9)
C5	35.6(11)	28.5(11)	26.9(9)	-8.1(8)	-6.1(8)	-13.7(9)
C6	33.8(11)	33.4(12)	36.5(11)	-13.8(9)	-7.6(9)	-11.4(9)
C7	38.9(12)	33.3(12)	38.3(11)	-15.3(10)	-6.9(9)	-6.8(10)
C8	55.7(14)	30.5(12)	33.0(11)	-12.7(9)	-14.3(10)	-8.9(10)
C9	53.0(14)	40.2(13)	40.1(12)	-9.7(10)	-20.5(10)	-19.2(11)
C10	35.6(11)	36.8(12)	35.6(11)	-9.7(9)	-10.8(9)	-12.7(9)
C11	33.2(10)	31.1(12)	31.8(10)	-11.1(9)	-5.5(8)	-9.4(9)
C12	64.9(16)	48.6(16)	34.2(12)	-11.8(11)	3.0(11)	-27.2(13)
C13	39.0(11)	30.2(12)	33.0(10)	-7.1(9)	-4.7(9)	-14.1(9)
C14	48.9(15)	45.3(15)	52.8(15)	3.5(12)	-12.2(12)	-11.0(12)
C15	53.3(15)	53.0(16)	48.5(13)	-11.8(12)	-8.9(11)	-30.1(13)
C16	40.2(13)	40.0(14)	59.5(15)	-14.2(12)	-9.5(11)	-5.3(11)
C17	41.7(13)	52.4(16)	54.0(14)	-27.6(12)	-3.7(11)	-13.7(12)
C18	38.3(12)	47.5(15)	41.3(12)	-14.6(11)	-1.9(10)	-15.9(11)
C19	28.5(10)	28.0(11)	32.6(10)	-11.5(8)	-3.5(8)	-8.5(8)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 3b. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
C20	27.2(10)	31.1(11)	33.0(10)	-15.9(9)	-2.5(8)	-8.0(8)
C21	50.9(13)	45.9(14)	37.2(11)	-7.4(10)	-11.6(10)	-27.6(11)
C22	57.1(15)	50.0(15)	35.5(12)	-4.0(11)	-10.7(10)	-30.5(12)
C23	35.5(11)	40.8(13)	35.9(11)	-16.7(9)	-7.9(9)	-10.7(10)
C24	44.1(12)	39.1(13)	52.0(13)	-10.4(11)	-18.6(11)	-18.1(11)
C25	40.4(12)	35.2(12)	46.0(12)	-5.9(10)	-14.2(10)	-15.3(10)
C26	35.2(11)	27.9(11)	32.2(10)	-9.5(8)	-8.1(8)	-8.9(9)
C27	41.9(14)	49.0(16)	97(2)	-46.8(16)	-19.5(14)	-4.5(12)
C28	37.2(11)	33.3(12)	44.8(12)	-17.3(10)	-11.8(9)	-12.3(9)
C29	73.8(18)	48.4(16)	61.0(16)	-12.6(13)	-33.7(14)	-25.7(14)
C30	62.6(16)	39.2(14)	52.8(15)	-11.2(12)	-8.5(13)	-22.9(13)

Table 4 Bond Lengths for 3b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C23	1.740(2)	C5	C6	1.386(3)
Cl2	C8	1.746(2)	C5	C10	1.398(3)
S1	C1	1.756(2)	C6	C7	1.390(3)
S1	C3	1.760(2)	C7	C8	1.379(3)
Si1	C1	1.874(2)	C8	C9	1.377(4)
Si1	C16	1.864(3)	C9	C10	1.391(3)
Si1	C17	1.867(3)	C12	C13	1.524(3)
Si1	C18	1.864(2)	C13	C14	1.509(3)
O1	C11	1.219(3)	C13	C15	1.512(3)
O2	C11	1.346(3)	C19	C20	1.525(3)
O2	C13	1.470(2)	C19	C26	1.530(3)
O3	C26	1.199(3)	C20	C21	1.378(3)
O4	C26	1.329(3)	C20	C25	1.383(3)
O4	C28	1.502(3)	C21	C22	1.397(3)
N1	C2	1.402(3)	C22	C23	1.372(3)
N1	C3	1.381(3)	C23	C24	1.375(3)
N1	C19	1.483(3)	C24	C25	1.381(3)
C1	C2	1.331(3)	C27	C28	1.502(3)
C3	C4	1.378(3)	C28	C29	1.514(3)
C4	C5	1.488(3)	C28	C30	1.515(3)
C4	C11	1.455(3)			

Table 5 Bond Angles for 3b.

Atom	Atom	Atom	Angle/˚
C1	S1	C3	92.25(10)
C16	Si1	C1	108.08(11)
C16	Si1	C17	109.74(13)
C17	Si1	C1	110.42(11)
C18	Si1	C1	106.54(11)
C18	Si1	C16	112.37(12)
C18	Si1	C17	109.64(12)
C11	O2	C13	121.23(17)
C26	O4	C28	120.83(16)
C2	N1	C19	118.97(17)
C3	N1	C2	113.46(18)
C3	N1	C19	123.77(16)
S1	C1	Si1	122.89(13)
C2	C1	S1	109.56(16)
C2	C1	Si1	127.50(17)
C1	C2	N1	115.88(19)
N1	C3	S1	108.68(14)
C4	C3	S1	124.39(17)
C4	C3	N1	126.9(2)
C3	C4	C5	123.22(18)
C3	C4	C11	116.88(19)
C11	C4	C5	119.47(18)
C6	C5	C4	121.47(18)
C6	C5	C10	118.4(2)
C10	C5	C4	120.1(2)
C5	C6	C7	121.6(2)
C8	C7	C6	118.5(2)
C7	C8	Cl2	118.42(19)
C9	C8	Cl2	119.86(18)
C9	C8	C7	121.7(2)
C8	C9	C10	119.1(2)
C9	C10	C5	120.7(2)
O1	C11	O2	124.15(19)
O1	C11	C4	124.54(19)
O2	C11	C4	111.31(18)
O2	C13	C12	101.77(18)
O2	C13	C14	110.97(18)
O2	C13	C15	109.83(19)
C14	C13	C12	110.8(2)
C14	C13	C15	113.0(2)
C15	C13	C12	109.9(2)
N1	C19	C20	109.19(17)
N1	C19	C26	110.74(17)
C20	C19	C26	113.55(17)
C21	C20	C19	123.60(19)
C21	C20	C25	118.6(2)
C25	C20	C19	117.83(19)
C20	C21	C22	121.1(2)
C23	C22	C21	118.7(2)
C22	C23	Cl1	119.52(19)
C22	C23	C24	121.2(2)
C24	C23	Cl1	119.23(17)
C23	C24	C25	119.3(2)
C24	C25	C20	121.1(2)
O3	C26	O4	126.7(2)
O3	C26	C19	124.0(2)
O4	C26	C19	109.30(17)
O4	C28	C27	102.51(17)
O4	C28	C29	109.37(19)
O4	C28	C30	110.20(19)
C27	C28	C29	111.8(2)
C27	C28	C30	110.4(2)
C29	C28	C30	112.2(2)

Table 6 Torsion Angles for 3b.

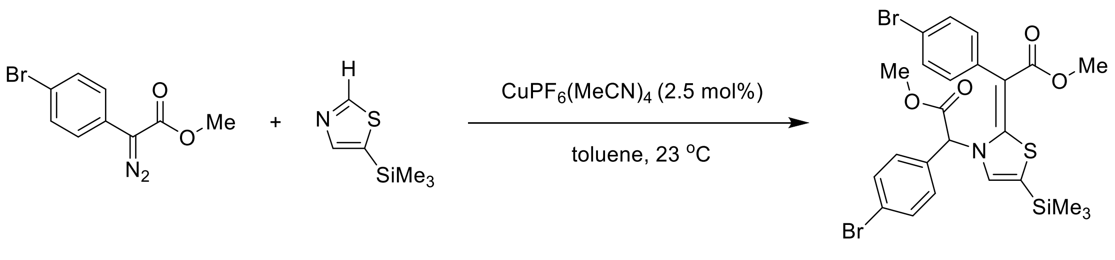
A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C23	C24	C25	-178.24(19)	C8	C9	C10	C5	-0.3(3)
Cl2	C8	C9	C10	178.74(16)	C10	C5	C6	C7	-0.7(3)
S1	C1	C2	N1	-0.6(3)	C11	O2	C13	C12	-174.6(2)
S1	C3	C4	C5	-163.38(16)	C11	O2	C13	C14	-56.6(3)
S1	C3	C4	C11	9.0(3)	C11	O2	C13	C15	69.0(3)
Si1	C1	C2	N1	177.03(16)	C11	C4	C5	C6	65.3(3)
N1	C3	C4	C5	14.4(3)	C11	C4	C5	C10	-113.1(2)
N1	C3	C4	C11	-173.2(2)	C13	O2	C11	O1	-3.3(3)
N1	C19	C20	C21	118.8(2)	C13	O2	C11	C4	176.59(18)
N1	C19	C20	C25	-60.1(2)	C16	Si1	C1	S1	42.07(18)
N1	C19	C26	O3	-18.9(3)	C16	Si1	C1	C2	-135.3(2)
N1	C19	C26	O4	162.34(16)	C17	Si1	C1	S1	-77.97(18)
C1	S1	C3	N1	-3.66(16)	C17	Si1	C1	C2	104.7(2)
C1	S1	C3	C4	174.48(19)	C18	Si1	C1	S1	163.04(14)
C2	N1	C3	S1	4.0(2)	C18	Si1	C1	C2	-14.3(3)
C2	N1	C3	C4	-174.1(2)	C19	N1	C2	C1	156.6(2)
C2	N1	C19	C20	-54.4(2)	C19	N1	C3	S1	-153.72(16)
C2	N1	C19	C26	71.4(2)	C19	N1	C3	C4	28.2(3)
C3	S1	C1	Si1	-175.30(15)	C19	C20	C21	C22	-179.1(2)
C3	S1	C1	C2	2.45(18)	C19	C20	C25	C24	178.8(2)
C3	N1	C2	C1	-2.3(3)	C20	C19	C26	O3	104.3(2)
C3	N1	C19	C20	102.2(2)	C20	C19	C26	O4	-74.4(2)
C3	N1	C19	C26	-132.0(2)	C20	C21	C22	C23	0.3(4)
C3	C4	C5	C6	-122.5(2)	C21	C20	C25	C24	-0.1(4)
C3	C4	C5	C10	59.1(3)	C21	C22	C23	Cl1	177.9(2)
C3	C4	C11	O1	2.5(3)	C21	C22	C23	C24	-0.2(4)
C3	C4	C11	O2	-177.34(18)	C22	C23	C24	C25	-0.2(4)
C4	C5	C6	C7	-179.16(19)	C23	C24	C25	C20	0.3(4)
C4	C5	C10	C9	179.54(19)	C25	C20	C21	C22	-0.2(4)
C5	C4	C11	O1	175.2(2)	C26	O4	C28	C27	-176.0(2)
C5	C4	C11	O2	-4.6(3)	C26	O4	C28	C29	65.3(3)
C5	C6	C7	C8	-0.4(3)	C26	O4	C28	C30	-58.4(3)
C6	C5	C10	C9	1.1(3)	C26	C19	C20	C21	-5.3(3)
C6	C7	C8	Cl2	-178.39(17)	C26	C19	C20	C25	175.80(19)
C6	C7	C8	C9	1.3(3)	C28	O4	C26	O3	-0.8(3)
C7	C8	C9	C10	-1.0(4)	C28	O4	C26	C19	177.92(17)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3b.

Atom	*x*	*y*	*z*	U(eq)
H2	4219.73	7492.47	8733.99	40
H6	9455.2	7538.58	4910.23	40
H7	10319.22	5954.58	3952.13	45
H9	6682.55	6331.1	4043.72	48
H10	5826.66	7931.4	4987.13	42
H12A	10273.22	9923.49	2586.6	77
H12B	9884.99	11302.34	1899.17	77
H12C	9032.9	10371.71	2192.31	77
H14A	6979.01	11929.92	3075.87	82
H14B	7857.03	12860.4	2692.89	82
H14C	7022.48	12537.39	3919.77	82
H15A	8925.22	11681.16	4582.83	74
H15B	9848.39	12086.63	3404.47	74
H15C	10191.6	10669.07	4034.68	74
H16A	2283.02	12092.66	8337.34	74
H16B	954.66	11880.2	9234.74	74
H16C	1503.53	11342.39	8179.33	74
H17A	3821.12	9580.17	10578.8	73
H17B	2458.91	10624.2	10900.21	73
H17C	3674.74	10996.41	9939.64	73
H18A	1499.23	8661.52	9569.65	65
H18B	948.77	9207.8	10620.85	65
H18C	2274.68	8096.06	10411.92	65
H19	7326.88	6545.05	6690.58	36
H21	6285.87	4656.68	9098.92	50
H22	7047.96	4114.45	10544.62	55
H24	8659.05	6980.73	9226.19	50
H25	7915.65	7495.33	7789.78	48
H27A	8217.19	2902.59	6067.61	87
H27B	7474.97	1847.9	6711.29	87
H27C	8020.22	2370.88	7308.86	87
H29A	4894.35	4645.35	6344.16	81
H29B	5600.31	3304.79	6032.57	81
H29C	6317.38	4385.14	5477.82	81
H30A	5824.9	2961.35	8634.75	78
H30B	5290.57	2373.31	8078.13	78
H30C	4598.33	3784.35	8232.05	78

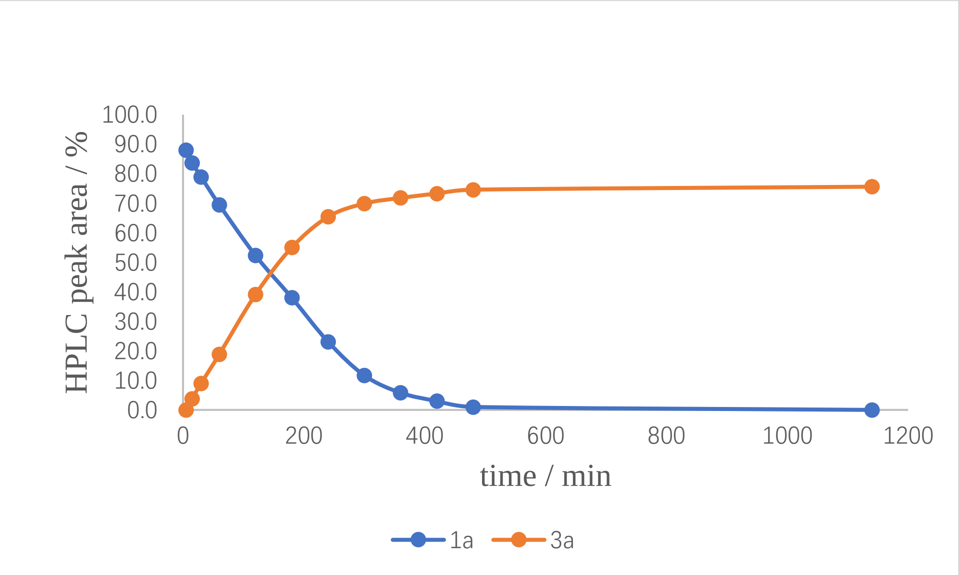
Representative procedure for monitoring of the reaction progress by HPLC analysis:

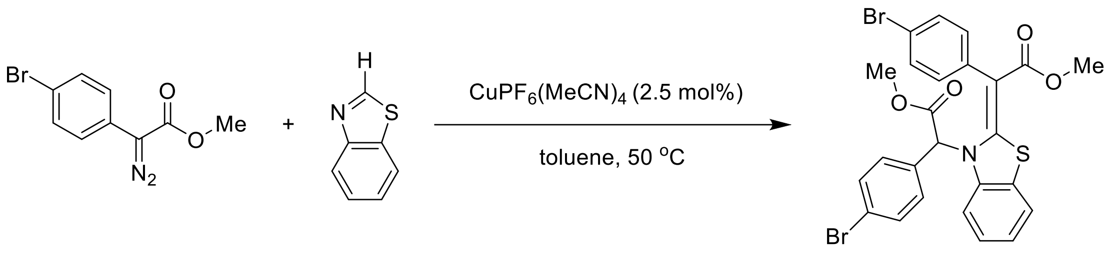
A Schlenk tube with a magnetic stirring bar was transferred to a glove box with a controlled atmosphere. The glove box maintained a nitrogen environment with water and oxygen levels below 100 ppm. $CuPF_6(MeCN)_4$ (1.864 mg, 5.000 umol) was weighed within the glove box and added to the Schlenk tube. Using a microliter syringe, 5-(trimethylsilyl)thiazole **2a** (31.0 mg, 0.200 mmol) was subsequently added to the Schlenk tube. The Schlenk tube was then added a solution of methyl 2-(4-bromophenyl)-2-diazoacetate **1a** (107 mg, 0.420 mmol) dissolved in toluene (1.50 mL) in one portion. The Schlenk tube was sealed and then stirred inside the glove box at room temperature. At different reaction time intervals denoted, the screwable cap of the Schlenk tube was opened, and a small amount of sample was acquired using a glass pipette. The glass pipette was removed from the glove box, and the sample was diluted with HPLC-grade acetonitrile (1.0 mL). The diluted sample was analyzed by HPLC analysis using a Supersil ODS2 3μm column and an eluent comprising a mixture of acetonitrile and water (80:20) at a flow rate of 1.67 mL/min with a detection wavelength of 220 nm. The same operation was repeated for the reaction time intervals denoted in the table below. The resulting data constitute the peak area percentages under HPLC analysis, excluding toluene peaks.



1a **2a** **3a**

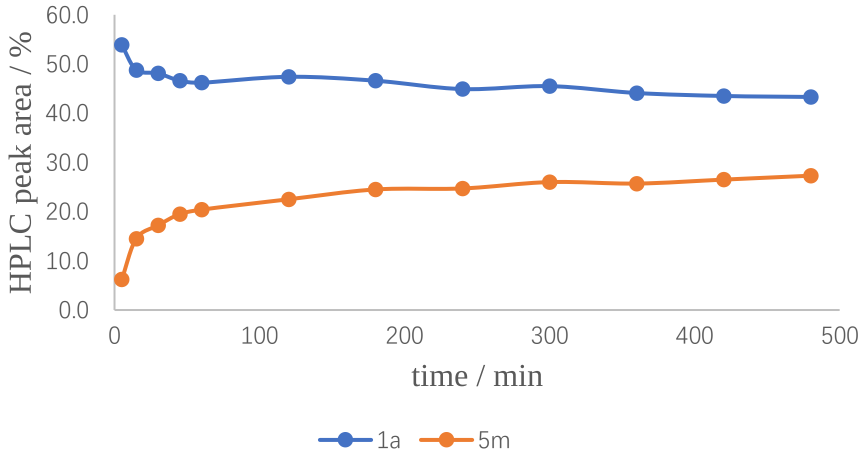
Time/min	HPLC peak area of **1a**	HPLC peak area of **3a**
5	88.0	0
15	83.7	3.8
30	78.9	9.0
60	69.5	18.8
120	52.3	39.1
180	38.0	55.0
240	23.1	65.4
300	11.7	69.9
360	5.8	71.8
420	3.0	73.3
480	1.0	74.6
1140	0	75.6

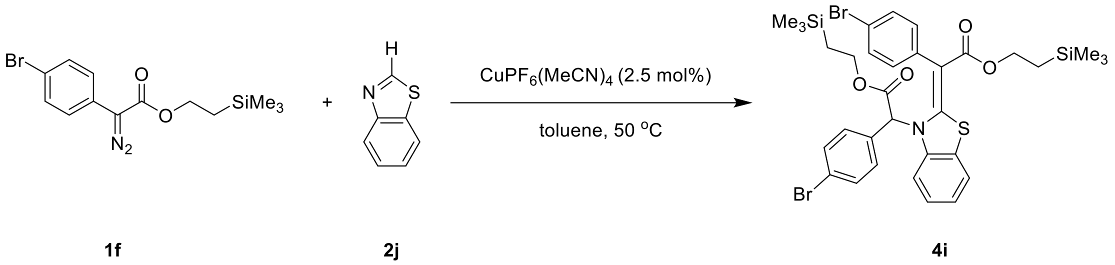




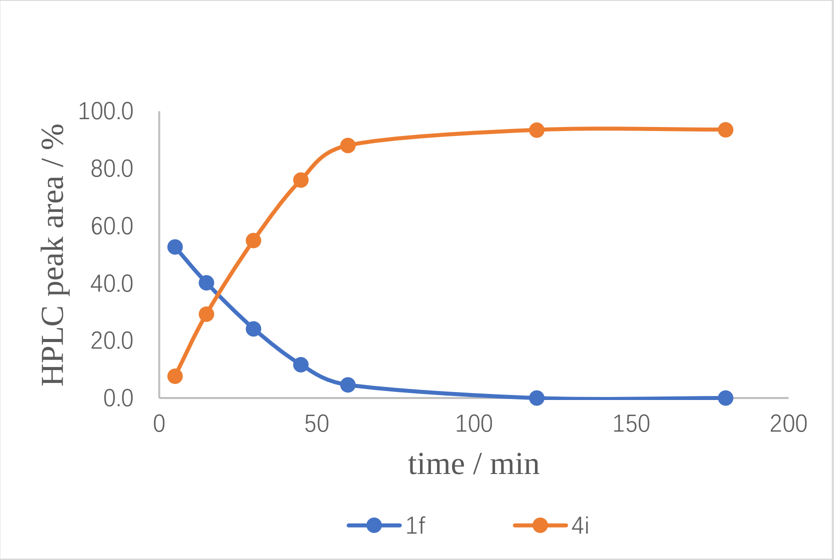
1a **2j** **5m**

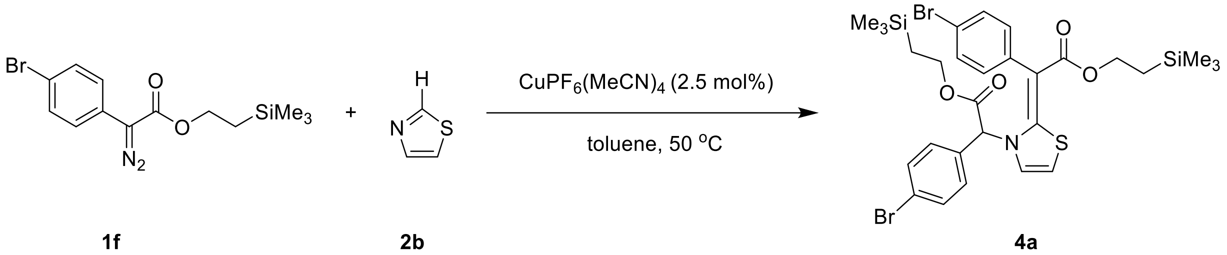
Time/min	HPLC peak area of **1a**	HPLC peak area of **5m**
5	53.9	6.2
15	48.8	14.5
30	48.1	17.2
45	46.6	19.5
60	46.2	20.4
120	47.4	22.5
180	46.6	24.5
240	44.9	24.7
300	45.5	26.0
360	44.1	25.7
420	43.5	26.5
480	43.3	27.3



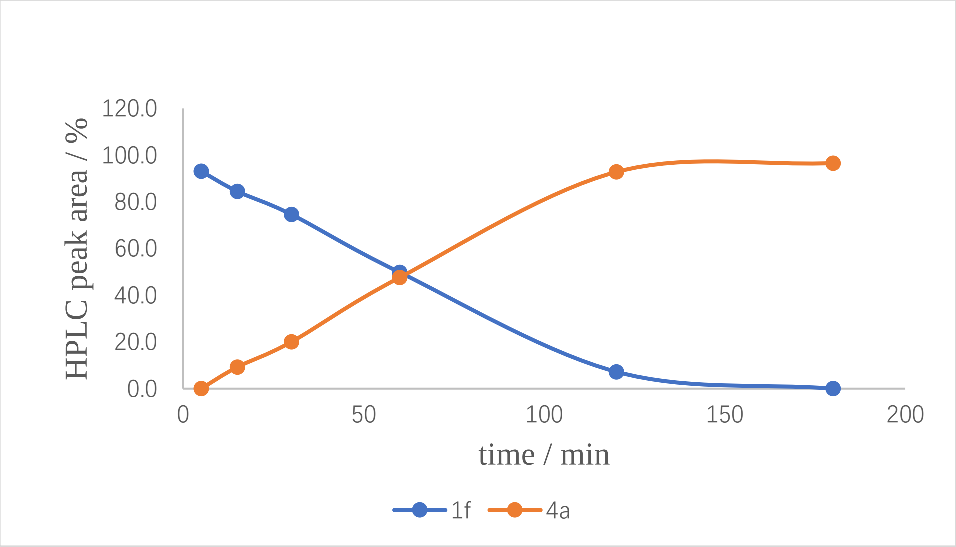


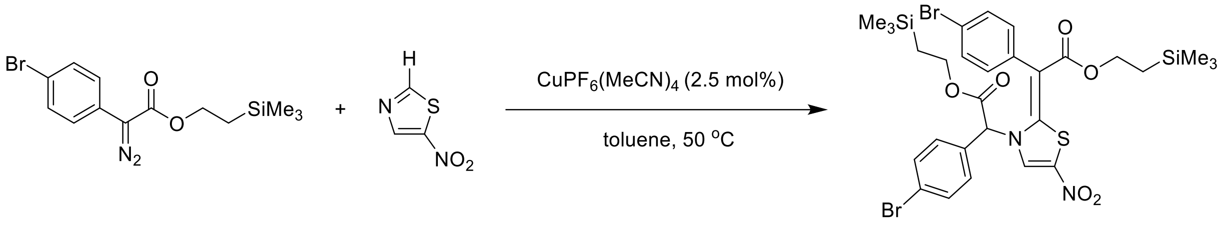
Time/min	HPLC peak area of **1f**	HPLC peak area of **4i**
5	52.7	7.6
15	40.2	29.3
30	24.2	55.0
45	11.7	76.0
60	4.6	88.1
120	0	93.5
180	0	93.6





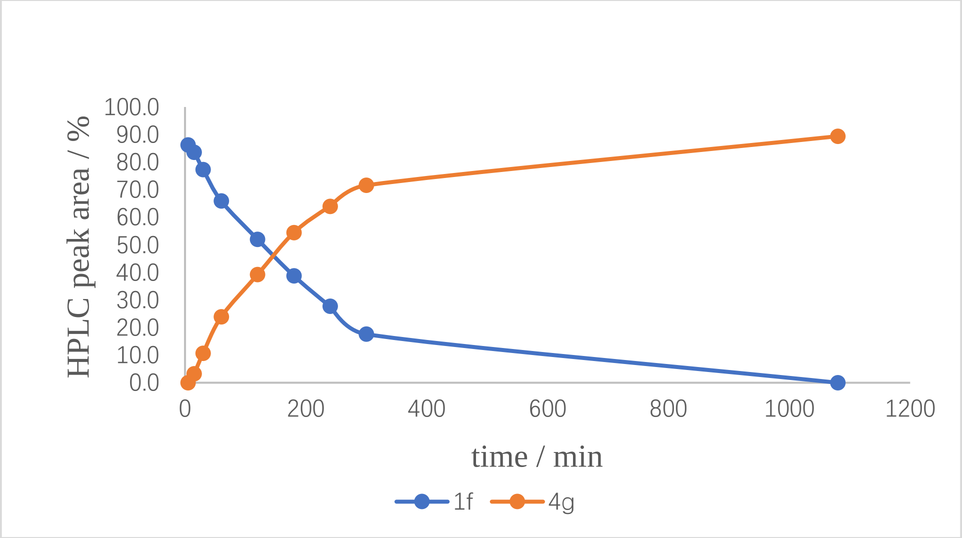
Time/min	HPLC peak area of **1f**	HPLC peak area of **4a**
5	93.1	0
15	84.5	9.2
30	74.6	20.0
60	49.8	47.6
120	7.2	92.8
180	0	96.6





1f **2h** **4g**

Time/min	HPLC peak area of **1f**	HPLC peak area of **4g**
5	86.3	0
15	83.6	3.3
30	77.3	10.7
60	65.9	23.9
120	52.0	39.2
180	38.8	54.4
240	27.7	64.0
300	17.6	71.6
1080	0	89.4



The study of the kinetic isotope effect: