Enantioselective Synthesis of 1,2-Benzothiazine 1-Imines via Ru^{II}/Chiral Carboxylic Acid-Catalyzed C–H Alkylation/Cyclization

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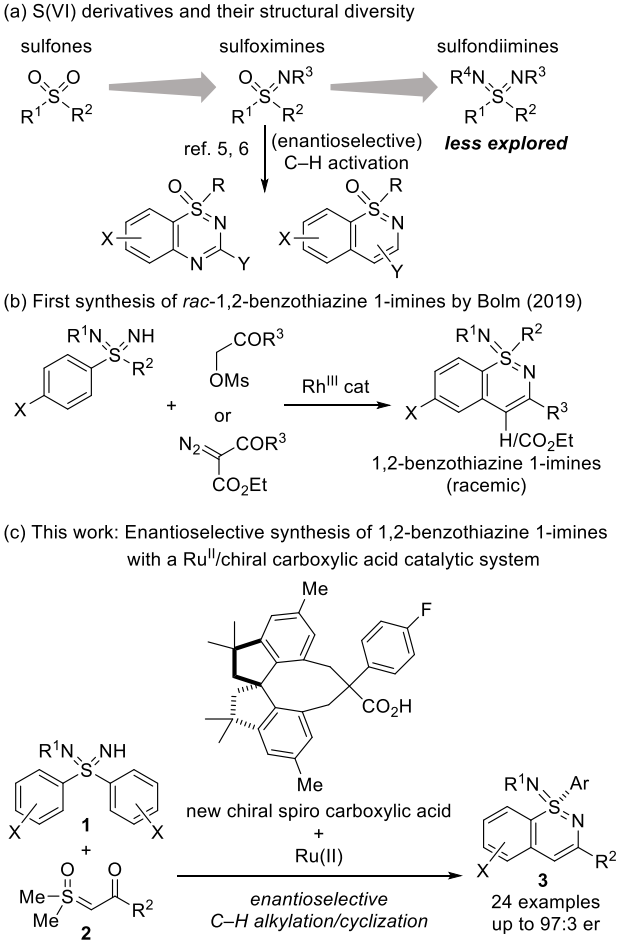
Abstract: Sulfondiimines are diaza-analogues of sulfones with a chiral sulfur center. Compared to sulfones and sulfoximines, their synthesis and transformations have so far been studied to a lesser extent. Here, we report the enantioselective synthesis of 1,2-benzothiazine 1-imines, i.e., cyclic sulfondiimine derivatives from sulfondiimines and sulfoxonium ylides via C–H alkylation/cyclization reactions. The combination of $[Ru(p\text{-cymene})Cl_2]_2$ and a newly developed chiral spiro carboxylic acid is key to achieving high enantioselectivity.

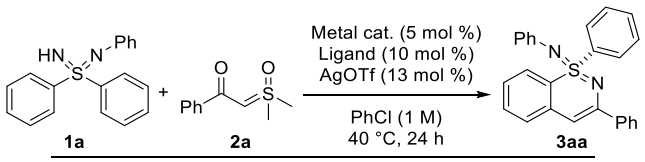
Hexavalent sulfur centers with two S=O bonds, such as sulfones and sulfonamides, are fundamental functional groups in organic chemistry that are widely found in drugs and other biologically active molecules.[1] Replacement of one or two of the oxygen atoms of sulfones with nitrogen substituents results in sulfoximines[2] and sulfondiimines, respectively (Scheme 1a).[3] These aza-analogues of sulfones adopt a tetrahedral chiral sulfur center and provide the opportunity to deploy different substructures in a three-dimensional manner, which significantly increases their structural diversity and complexity. In this context, sulfoximines have attracted great attention, and various synthetic and transformation methods have been developed.[2] Most recently, transition-metal-catalyzed directed C–H functionalizations[4] of sulfoximines have been exploited for the synthesis of cyclic and acyclic derivatives.[5,6] Moreover, enantioselective variants have been developed using chiral metal catalysts or chiral carboxylic acid co-catalysts.[6] Compared to the notable advances in the synthetic chemistry of sulfoximines, the synthesis and transformations of sulfondiimines are much less developed, thus providing an unexplored promising chemical space in which to seek biologically relevant molecules.[3] In 2019, Bolm and co-workers reported Rh^{III}-catalyzed C–H alkylation/cyclization reactions of sulfondiimines for the synthesis of 1,2-benzothiazine 1-imines as unprecedented cyclic organosulfur compounds (Scheme 1b).[7] While 1,2-benzothiazine 1-imines possess *S*-chirality and their stereochemistry can influence their biological properties, enantioselective synthesis of 1,2-benzothiazine 1-imines has not yet been reported.[8]



Scheme 1. Various hexavalent organosulfur compounds and synthesis of 1,2-benzothiazine 1-imines.

Here, we report the enantioselective synthesis of 1,2-benzothiazine 1-imines **3** from diaryl sulfondiimines **1** and sulfoxonium ylides **2** via Ru^{II}-catalyzed C–H functionalization reactions (Scheme 1c).[9,10] Even though the desymmetrization-

Table 1. Effects of chiral carboxylic acid ligands and metal catalysts.[a]



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

Entry	Metal cat.	Ligand	% Yield[b]	Er[c]
1	[Ru(*p*-cymene)Cl_2]$_2$	**L1**	<5	–
2	[Ru(*p*-cymene)Cl_2]$_2$	**L2**	63	55:45
3	[Ru(*p*-cymene)Cl_2]$_2$	**L3**	66	60:40
4	[Ru(*p*-cymene)Cl_2]$_2$	**L4**	70	77:23
5	[Ru(*p*-cymene)Cl_2]$_2$	**L5**	64	73:27
6	[Ru(*p*-cymene)Cl_2]$_2$	**L6**	44	80:20
7	[Ru(*p*-cymene)Cl_2]$_2$	**L7**	67	95:5
8	[Ru(*p*-cymene)Cl_2]$_2$	**L8**	84	97:3
9	[Ru(*p*-cymene)Cl_2]$_2$	**L9**	68	96:4
10	Ru(*p*-cymene)Cl_2]$_2$	**L10**	36	94:6
11	Ru(*p*-cymene)Cl_2]$_2$	**L11**	88	91:9
12	[Ru(benzene)Cl_2]$_2$	**L8**	20	92:8
13	[Cp*$RhCl_2$]$_2$	**L8**	<5	–
14	[Cp*$IrCl_2$]$_2$	**L8**	<5	–
15	Cp*Co(CO)I_2[d]	**L8**	<5	–

[a] Reaction conditions: **1a** (0.05 mmol), **2a** (0.055 mmol), metal catalyst (0.0025 mmol), ligand (0.005 mmol), and AgOTf (0.0065 mmol) in PhCl (0.05 mL) at 40 °C for 24 h unless otherwise noted. [b] Determined by ^{1}H NMR analysis of the crude mixture using 1,1,2,2-tetrabromoethane as the internal standard. [c] Determined by chiral HPLC analysis. [d] 10 mol %.

type enantioselective C–H functionalization of diaryl sulfoximines is well established,[6] the straightforward expansion to diaryl sulfondiimines **1** is not trivial because two sterically different nitrogen atoms of **1** can work competitively as the directing group, which can potentially lead to low enantioselectivity. We found that the combination of [Ru(*p*-cymene)Cl_2]$_2$ and a newly developed chiral spiro carboxylic acid is of crucial importance to achieve reasonable yield and high enantioselectivity.

With previous reports on enantioselective C–H alkylation/cyclization reactions of sulfoximines with sulfoxonium ylides by Shi[6d] and our group[6f] in mind, we investigated the reaction of sulfondiimine **1a** and sulfoxonium ylide **2a** using the combination of a metal catalyst and chiral carboxylic acid, which enables carboxylate-assisted enantioselective C–H activation (Table 1).[11-13] After intensive screening of the reaction conditions, we found that the desired product (**3aa**) was obtained in the presence of [Ru(*p*-cymene)Cl_2]$_2$, AgOTf, and a chiral carboxylic acid ligand. Among the chiral acids **L1**–**L6** (Figure 1), which have been developed in our group,[6g,14] the pseudo-C_2-symmetric acids (**L4**–**L6**)[6g,14d] exhibited moderate enantioselectivity (entries 4–6). Despite these promising results, further improvement by minor tuning was not feasible, which prompted us to develop new chiral spiro carboxylic acids **L7**–**L10**. These acids were successfully synthesized from known compound **4**[15] via double enolate alkylation and subsequent demethylation (Scheme 2). To our delight, **L7**–**L10** significantly improved the enantioselectivity (Table 1, entries 7–10), and we selected **L8** as the best ligand (entry 8, 84% yield, 97:3 er). Although rationalization of the improvement requires further

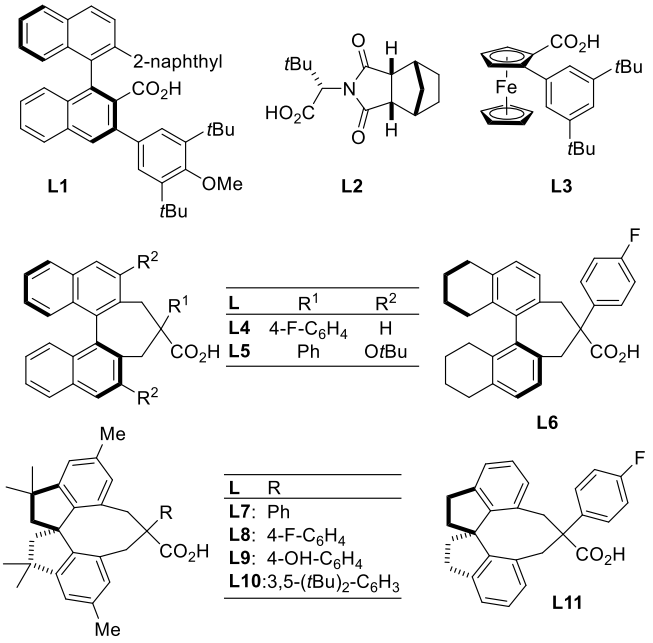
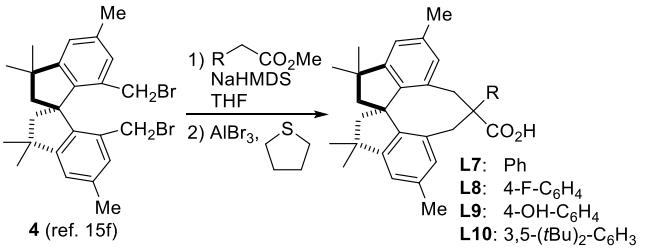


Figure 1. Structures of the chiral carboxylic acids used in this work.

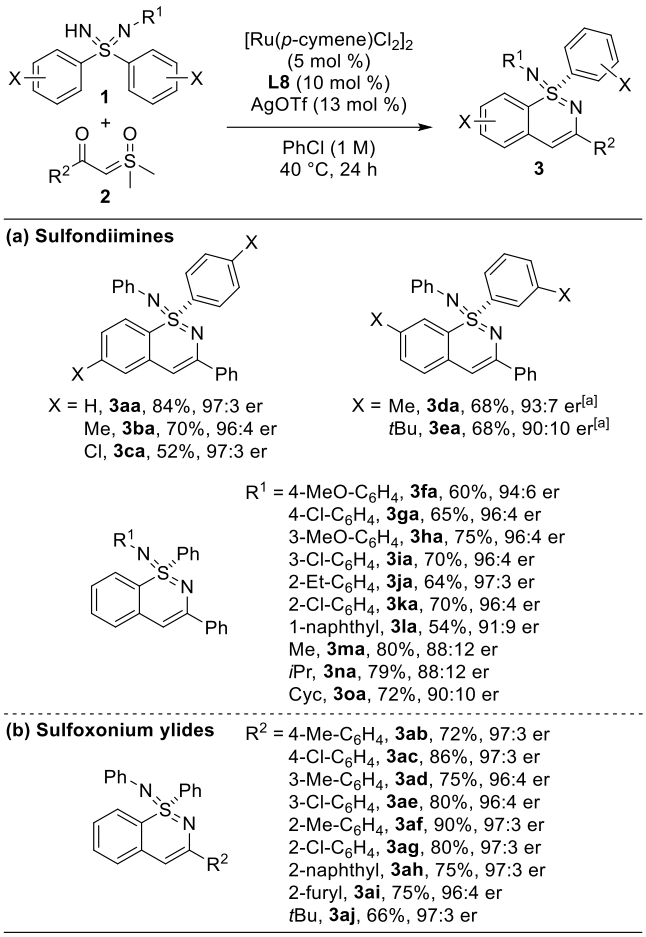


Scheme 2. Synthesis of new chiral spiro carboxylic acids **L7**–**L10**; for details, see the Supporting Information.

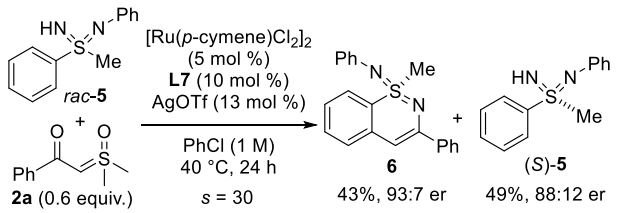
intensive computational studies, we speculate that the conformational rigidity of **L7**–**L10** might be important for high enantioselectivity as the structure of **L4** and **L8** are very similar.[16] A chiral spiro carboxylic acid derived from a simple commercially available SPINOL (**L11**) exhibited enantioselectivity lower than **L8** but much higher than **L6**, which implies that the methyl substituents of **L7** would have a moderate influence on the selectivity (entry 11). When the metal catalyst was changed to [Ru(benzene)Cl_2]$_2$, both reactivity and enantioselectivity dropped (entry 12), indicating that the arene ligand did not dissociate during the catalytic process. As control experiments, Cp*M^{III} catalysts (M = Rh, Ir, Co) were evaluated, albeit that the desired reaction scarcely proceeded (entries 13–15).

We then examined the scope of sulfondiimines (**1**) under the optimized conditions (Table 1, entry 8), and the results are shown in Scheme 3a.[17] In some cases, the use of **L7** afforded slightly improved results. Substituents at the para and meta positions of the *S*-aryl groups were well tolerated to afford the product in 90:10–97:3 er (**3ba**–**3ea**). In the presence of *meta*-substituents, the less hindered position was selectively alkylated. As the *N*-substituent, both aryl (**3fa**–**3la**) and alkyl groups (**3ma**–**3oa**) were acceptable, although the enantioselectivity was slightly diminished for the alkyl substituent. The scope of

sulfoxonium ylides (**2**) was also investigated (Scheme 3b). Various substituted phenyl groups, as well as 2-naphthyl and 2-furyl groups, were successfully introduced at the 3-position of the product (**3ab**–**3ah**, 96:4–97:3 er) by employing the corresponding sulfoxonium ylide (**2**). Furthermore, *t*Bu-substituted sulfoxonium ylide also provided the product in high enantioselectivity (**3aj**, 97:3 er). We also examined the kinetic resolution of a racemic alkyl-aryl sulfondiimine (Scheme 4; *rac*-**5**), and a reasonably good selectivity factor (*s* = 30) was observed.[18,19]

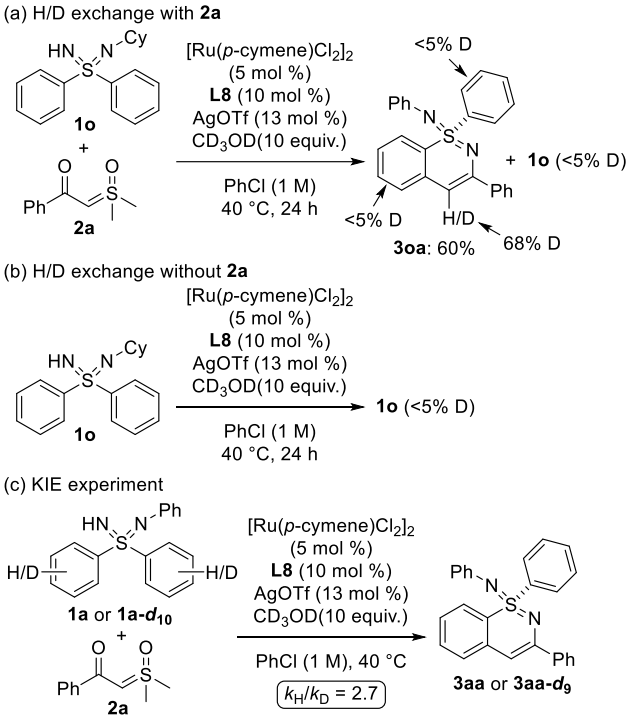


Scheme 3. Substrate scope of the enantioselective C–H alkylation/cyclization of diaryl sulfondiimines. Reaction conditions: **1** (0.05 mmol), **2** (0.055 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (0.0025 mmol), **L8** (0.005 mmol), and AgOTf (0.0065 mmol) in PhCl (0.05 mL) at 40 °C for 24 h unless otherwise noted. [a] **L7** was used instead of **L8**.



Scheme 4. Kinetic resolution of alkyl-aryl sulfondiimine **5**. The selectivity factor (*s*) was calculated as $s = \ln[(1 - c)(1 - ee_5)] / \ln[(1 - c)(1 + ee_5)]$, where the conversion *c* was calculated as $c = ee_5 / (ee_5 + ee_6)$.[20]

Finally, we performed several experiments to gain insight into the nature of the key enantio-determining C–H activation step. When the reaction using **1o** was performed under the optimized conditions, except for the addition of CD_3OD, deuterium incorporation was observed at the 4-position of product **3oa**, but not at the other positions of **3oa** or recovered **1o** (Scheme 5a). The same experiment without reactant **2a** did not afford deuterium-incorporated **1o** (Scheme 5b). These results indicate that the C–H bond cleavage of **1o** by the Ru^{II}/carboxylic acid catalyst system is irreversible. This irreversibility may explain the independence of the enantioselectivity from the structure of reactant **2** (Scheme 3b)**.** The deuterium incorporation at the 4-position of **3oa** could be feasibly interpreted by the H/D exchange from **2a** or the intermediate of the C–H alkylation before cyclization. We also checked the kinetic isotope effect, and a k_H/k_D value of 2.7 was observed from parallel experiments (Scheme 5c), suggesting that the C–H activation step would be involved in the rate-determining step. This is in line with our experimental observation that the reactivity depends on the structure of the chiral carboxylic acid (Table 1).



Scheme 5. Experimental mechanistic studies.

In summary, we have demonstrated that the combination of [Ru(*p*-cymene)Cl_2]$_2$ and a newly developed chiral spiro carboxylic acid (**L7** or **L8**) enables the enantioselective synthesis of 1,2-benzothiazine 1-imines from sulfondiimines via C–H alkylation/cyclization with a sulfoxonium ylide as the reactant, thus expanding the accessible chemical space with respect to compounds with a chiral S(VI) center. Moreover, the newly developed chiral carboxylic acids will hopefully expand the applicability of the metal/chiral carboxylic acid system for enantioselective C–H functionalization reactions.

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Keywords: asymmetric catalysis • 1,2-benzothiazine 1-imine • C–H activation • ruthenium • sulfondiimine

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[14] a) S. Fukagawa, Y. Kato, R. Tanaka, M. Kojima, T. Yoshino, S. Matsunaga, *Angew. Chem. Int. Ed.* **2019**, *58*, 1153; *Angew. Chem.* **2019**, *131*, 1165; b) D. Sekine, K. Ikeda, S. Fukagawa, M. Kojima, T. Yoshino, S. Matsunaga, *Organometallics* **2019**, *38*, 3921; c) S. Fukagawa, M. Kojima, T. Yoshino, S. Matsunaga, *Angew. Chem. Int. Ed.* **2019**, *58*, 18154; *Angew. Chem.* **2019**, *131*, 18322; d) Y. Kato, L. Lin, M. Kojima, T. Yoshino, S. Matsunaga, *ACS Catal.* **2021**, *11*, 4271.

[15] a) S. Chang, L. Wang, X. Lin, *Org. Biomol. Chem.* **2018**, *16*, 2239; b) H. Gu, Z. Han, H. Xie, X. Lin, *Org. Lett.* **2018**, *20*, 6544; c) H. Shan, Q. Zhou, J. Yu, S. Zhang, X. Hong, X. Lin, *J. Org. Chem.* **2018**, *83*, 11873;

d) W. Sun, H. Gu, X. Lin, *J. Org. Chem.* **2018**, *83*, 4034; e) L. Wang, J. Zhong, X. Lin, *Angew. Chem. Int. Ed.* **2019**, *58*, 15824; *Angew. Chem.* **2019**, *131*, 15971; f) Z. Han, X. Lin, *Synthesis* **2020**, *52*, 1131; g) Z. Han, J. Jin, A. G. Woldegiorgis, X. Lin, *RSC Adv.* **2022**, *12*, 27012; h) L. Yao, A. G. Woldegiorgis, X. Lin, *Tetrahedron Lett.* **2022**, *109*, 154157.

[16] For the calculated structures of **L4** and **L8**, see the Supporting Information.

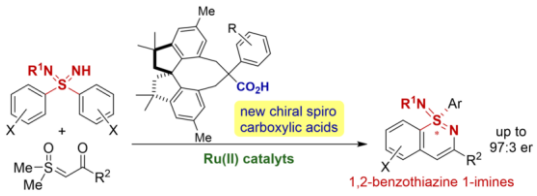
[17] The absolute configuration of **3ka** was determined via single-crystal X-ray diffraction analysis. Deposition number 2257084 (for **3ka**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

[18] The absolute configuration of the major isomer of the recovered sulfondiimine (**5**) was determined by the comparison of its retention time in chiral HPLC analysis and specific rotation with those were previously reported: S. Dong, M. Frings, H. Cheng, J. Wen, D. Zhang, G. Raabe, C. Bolm, *J. Am. Chem. Soc.* **2016**, *138*, 2166 and ref. 3c. See the Supporting Information for details.

[19] For preliminary results of a parallel kinetic resolution of an unsymmetrically substituted diaryl sulfondiimine, see the Supporting Information.

[20] C. S. Chen, Y. Fujimoto, G. Girdaukas, C. J. Sih, *J. Am. Chem. Soc.* **1982**, *104*, 7294.

Entry for the Table of Contents



Enantioselective C–H alkylation/cyclization of sulfondiimines with sulfoxonium ylides using a Ru^{II} catalyst and a newly developed chiral spiro carboxylic acid enables the synthesis of 1,2-benzothiazine 1-imines, thus expanding the accessible chemical space of chiral hexavalent organosulfur scaffolds relevant to biologically active compounds.

Institute and/or researcher Twitter usernames: @MatsunagaGroup

Supporting Information

Enantioselective Synthesis of 1,2-Benzothiazine 1-Imines via Ru^{II}/Chiral Carboxylic Acid-Catalyzed C–H Alkylation/Cyclization.

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Table of Contents

1. General S2

2. Experimental procedures S3

2.1. Preparation of L7-L10 ..... S3

2.2. Preparation of L11 ..... S8

2.3. Preparation of sulfondiimines S9

2.4. Ru(II)-catalyzed enantioselective C–H alkylation/cyclization S16

2.5. Kinetic resolution of racemic sulfondiimine S49

2.6. Parallel kinetic resolution of sulfondiimine S52

2.7. H/D exchange experiments S54

2.8. Kinetic isotopic effect S57

2.9. Determination of the absolute configuration S58

3. DFT calculation of the structures of chiral carboxylic acids S60

4. Reference S62

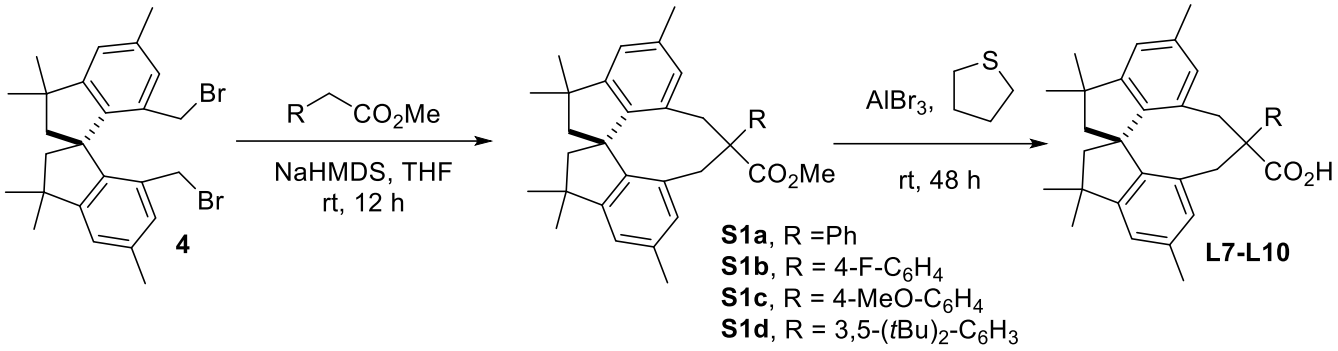
5. NMR spectra S63

1. General

Reactions were carried out under argon atmosphere unless otherwise noted. Enantioselectivities were determined by high performance liquid chromatography (HPLC) using 4.6 nm × 25 cm Daicel Chiralpak columns. NMR spectra were recorded on JEOL JNM-ECS400 spectrometers operating at 391.78 MHz for ^{1}H NMR, 98.52 MHz for ^{13}C NMR and 368.59 Hz for ^{19}F NMR, JOEL JNM-ECX400 spectrometers operating at 395.88 MHz for ^{1}H NMR, 99.55 MHz for ^{13}C NMR and 372.48 MHz for ^{19}F NMR, JOEL JNM-ECZ400 spectrometers operating at 399.78 MHz for ^{1}H NMR, 100.53 MHz for ^{13}C NMR and 368.61 MHz for ^{19}F NMR, JNM-ECZ500 spectrometers operating at 500.16 MHz for ^{1}H NMR and 125.77 MHz for ^{13}C NMR. NMR chemical shifts are given in ppm relative to $SiMe_4$, with the solvent resonance used as an internal reference: $CHCl_3$ (7.26 ppm for ^{1}H NMR), $CDCl_3$ (77.16 ppm for ^{13}C NMR), hexafluorobenzene (161.64 ppm for ^{19}F NMR in $CDCl_3$). ESI mass spectra were measured on Thermo Scientific Exactive spectrometer. Optical rotations were measured on a JASCO P-1010 polarimeter. Column chromatography was performed with silica gel Kanto Silica gel 60 N (40-50 mesh) or Yamazen YFLC AI-580 using Universal Column SiOH. Dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), diethyl ether (Et_2O), and toluene were purified by Glass Contour solvent purification system before use. 1,2-Dichloroethane (DCE), ethanol, Dimethylformamide (DMF), chloroform and acetonitrile (CH_3CN) were purchased from Kanto Chemicals (dehydrated grade) and used as received. Chlorobenzene and methanol were purchased from Aldrich (dehydrated grade) and used as received. **1a**,[S1] **2a**-**2j**[S2] were prepared according to the literatures. All other reagents were commercially available and used as received unless otherwise noted.

2. Experimental procedures

2.1. Preparation of L7-L10



General Procedure A for S1a–S1d

To a solution of compound **4** (100 mg, 1.0 equiv.) in THF (4 mL) was added NaHMDS (1 M in THF, 0.31 mL, 1.5 equiv.) dropwise at –78 ºC, and then corresponding methyl-α-arylacetate (1.1 equiv.) in THF (2 mL) was added at –78 ºC. The reaction mixture was stirred for 1 h at –78 ºC and then stirred for 1 h at 0 ºC. The reaction mixture was cooled to –78 ºC again and stirred for 30 min. To the reaction mixture was added NaHMDS (1 M in THF, 0.31 mL, 1.5 equiv.) dropwise at –78 ºC and then stirred for 12 h at room temperature. The rection was quenched by adding water at 0 °C, and extracted with AcOEt three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by silica gel column chromatography (hexane/AcOEt) to give **S1a–S1d.**

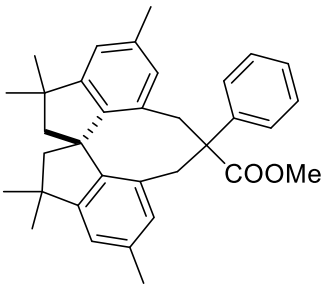
General Procedure B for L7-L10

To a solution of compound **S1a–S1d** (1.0 equiv.) in tetrahydrothiophene (2 mL) was added $AlBr_3$ (4.0 equiv.) and the reaction mixture was stirred for 48 h at room temperature. The rection was quenched by adding water at 0 °C, and extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by silica gel column chromatography (hexane/AcOEt) to give **L7-L10**.

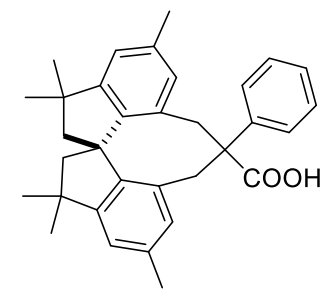
Methyl

2,4,4,7,7,9-hexamethyl-12-phenyl-4,5,6,7,12,13-hexahydro-11H-cycloocta[1,2,3-cd:1,8,7-c'd']diindene-12-car

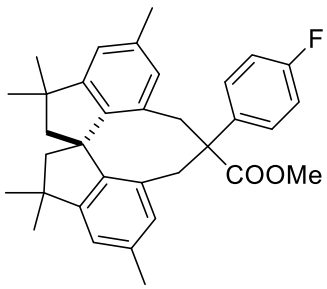
boxylate (S1a): Prepared according to **GP-A** using compound **4** (0.21 mmol, 100 mg, 1.0 equiv.), methyl-α-phenylacetate (0.23 mmol, 35 mg, 1.1 equiv.), NaHMDS (1 M in THF, 0.31 mmol, 0.31 mL, 1.5 equiv. x 2). **S1a** was isolated as a colorless solid (70 mg, 70%). **IR** (KBr) 2959, 2949, 2916, 2857, 1731, 1446, 1220, 1174, 1048, 860, 696 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.21-7.19 (m, 3H), 6.87 (s, 1H), 6.81-6.77 (m, 2H), 6.74 (s, 1H), 6.64 (s, 1H), 5.48 (s, 1H), 3.63 (s, 3H), 3.28 (d, *J* = 13.3 Hz, 1H), 3.21 (d, *J* = 12.6 Hz, 1H), 2.97 (d, *J* = 12.5 Hz, 1H), 2.63 (d, *J* = 13.3 Hz, 1H), 2.40 (d, *J* = 12.7 Hz, 1H), 2.37 (d, *J* = 12.7 Hz, 1H), 2.31 (s, 3H), 2.00 (d, *J* = 8.9 Hz, 1H), 1.97 (d, *J* = 8.9 Hz, 1H), 1.92 (s, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.29 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 175.3, 151.6, 151.0, 145.7, 145.3, 141.8, 136.8, 135.6, 132.2, 131.2, 130.5, 128.7, 127.8, 126.8, 126.6, 122.2, 121.4, 58.2, 57.2, 57.0, 56.7, 51.6, 42.0, 41.9, 38.9, 34.2, 32.4, 32.3, 30.4, 30.3, 21.3, 20.9. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{34}H_{38}O_2Na^+$: 501.2764; Found 501.2757. **$[\alpha]_D^{24.1}$** = –54.2 (*c* = 0.50, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 10:1).



2,4,4,7,7,9-hexamethyl-12-phenyl-4,5,6,7,12,13-hexahydro-11H-cycloocta[1,2,3-cd:1,8,7-c'd']diindene-12-car boxylic acid (L7): Prepared according to **GP-B** using compound **S1a** (0.15 mmol, 70 mg, 1.0 equiv.) in tetrahydrothiophene (2 mL), $AlBr_3$ (0.60 mmol, 140 mg, 4.0 equiv.). **L7** was isolated as a colorless solid (70 mg, >99%). **IR** (KBr) 2956, 2919, 2860, 1737, 1698, 1448, 1278, 860, 696 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.25-7.19 (m, 3H), 6.92-8.85 (m, 3H), 6.82 (s, 1H), 6.74 (s, 1H), 5.51 (s, 1H), 3.29-3.18 (m, 2H), 3.01 (d, *J* = 12.6 Hz, 1H), 2.66 (d, *J* = 13.3 Hz, 1H), 2.41 (d, *J* = 12.5 Hz, 1H), 2.38 (d, *J* = 12.5 Hz, 1H), 2.24 (s, 3H), 2.00 (s, 1H), 1.97 (s, 1H), 1.92 (s, 3H), 1.50 (s, 3H), 1.46 (s, 3H), 1.28 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 181.26, 151.5, 151.1, 145.6, 145.3, 141.3, 137.1, 135.6, 131.8, 131.0, 130.5, 129.2, 127.9, 127.0, 126.7, 122.3, 121.5, 58.2, 57.1, 57.0, 56.8, 42.0, 41.9, 38.2, 34.1, 32.5, 32.3, 30.4, 30.3, 21.3, 20.8. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{36}O_2Na^+$: 487.2608; Found 487.2603. **$[\alpha]_D^{23.2}$** = –45.5 (*c* = 0.50, $CHCl_3$). **Rf** 0.34 (hexane/AcOEt = 2:1).

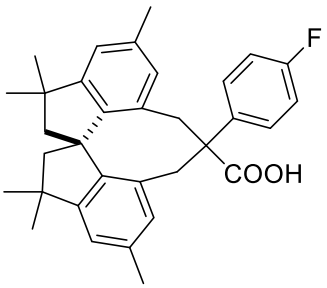


Methyl 12-(4-fluorophenyl)-2,4,4,7,7,9-hexamethyl-4,5,6,7,12,13-hexahydro -11H-cycloocta[1,2,3-cd:1,8,7-c'd']diindene-12-carboxylate (S1b): Prepared according to **GP-A** using compound **4** (0.21 mmol, 100 mg, 1.0 equiv.),

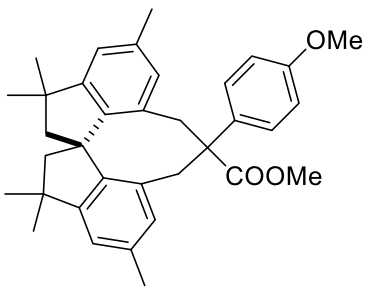


methyl-α-(4-fluorophenyl)acetate (0.23 mmol, 39 mg, 1.1 equiv.), NaHMDS (1 M in THF, 0.31 mmol, 0.31 mL, 1.5 equiv. x 2). **S1b** was isolated as a colorless solid (70 mg, 67%). **IR** (KBr) 2960, 2931, 2859, 1731, 1509, 1458, 1235, 1175, 1051, 858, 835, 818, 720 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.94-6.87 (m, 3H), 6.77-6.73 (m, 3H), 6.63 (s, 1H), 5.52 (s, 1H), 3.63 (s, 3H), 3.27 (d, *J* = 13.4 Hz, 1H), 3.16 (d, *J* = 12.5 Hz, 1H), 2.95 (d, *J* = 12.6, 1H), 2.59 (d, *J* = 13.4 Hz, 1H), 2.42-2.35 (m, 2H), 2.01-1.95 (m, 5H), 1.49 (s, 3H), 1.46 (s, 3H), 1.28 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 175.2, 161.2 (d, *J* = 254.1 Hz), 151.7, 151.2, 145.6, 145.3, 137.7 (d, *J* = 2.9 Hz), 136.9, 135.7, 131.9, 131.0, 130.4, 128.6, 128.3 (d, *J* = 7.6 Hz), 122.3, 121.5, 114.6 (d, *J* = 21.0 Hz), 58.2, 57.1, 56.7, 56.5, 51.7, 42.0, 41.9, 38.9, 34.5, 32.4, 32.3, 30.4, 30.3, 21.3, 20.9. **^{19}F NMR** (370 MHz, $CDCl_3$) δ: –116.1. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{34}H_{37}O_2FNa^+$: 519.2670; Found 519.2665. **$[\alpha]_D^{23.6}$** = –36.7 (*c* = 0.50, $CHCl_3$). **Rf** 0.65 (hexane/AcOEt = 10:1).

12-(4-fluorophenyl)-2,4,4,7,7,9-hexamethyl-4,5,6,7,12,13-hexahydro-11H-cycloocta[1,2,3-cd:1,8,7-c'd']diindene-12-carboxylic acid (L8): Prepared according to **GP-B** using compound **S1b** (0.20 mmol, 100 mg, 1.0 equiv.) in tetrahydrothiophene (2 mL), $AlBr_3$ (0.80 mmol, 213 mg, 4.0 equiv.). **L8** was isolated as a colorless solid (80 mg, 83%). **IR** (KBr) 2955, 2918, 2864, 1708, 1509, 1459, 1235, 1168, 860, 830, 732 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.96-6.90 (m, 3H), 6.88-6.82 (m, 2H), 6.80 (s, 1H), 6.75 (s, 1H), 5.55 (s, 1H), 3.26 (d, *J* = 13.3 Hz, 1H), 3.19 (d, *J* = 12.6 Hz, 1H), 2.98 (d, *J* = 12.6, 1H), 2.62 (d, *J* = 13.3 Hz, 1H), 2.43-2.36 (m, 2H), 2.24 (s, 3H), 1.99-1.95 (m, 5H), 1.50 (s, 3H), 1.47 (s, 3H), 1.28 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.2, 161.7 (d, *J* = 246.6 Hz), 151.6, 151.2, 145.5, 145.3, 137.1 (d, *J* = 2.9 Hz) (one peak is overlap), 135.7, 131.5, 130.7, 130.4, 129.1, 128.4 (d, *J* = 8.7 Hz), 122.4, 121.6, 114.7 (d, *J* = 22.2 Hz), 58.2, 57.0, 56.8, 56.4, 42.0, 41.9, 38.3, 34.4, 32.5, 32.3, 30.4, 30.3, 21.3, 20.9. **^{19}F NMR** (370MHz, $CDCl_3$) δ: –115.1. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{35}O_2FNa^+$: 505.2513; Found 505.2511. **$[\alpha]_D^{23.4}$** = –49.1 (*c* = 0.50, $CHCl_3$). **Rf** 0.35 (hexane/AcOEt = 2:1).

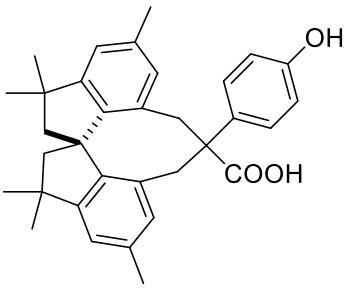


Methyl-12-(4-methoxyphenyl)-2,4,4,7,7,9-hexamethyl-4,5,6,7,12,13-hexahydro-11H-cycloocta[1,2,3-cd:1,8,7-c'd']diindene-12-carboxylate (S1c): Prepared according to **GP-A** using compound **4** (0.21 mmol, 100 mg, 1.0 equiv.), methyl-α-(4-methoxphenyl)acetate (0.23 mmol, 41 mg, 1.1 equiv.), NaHMDS (1

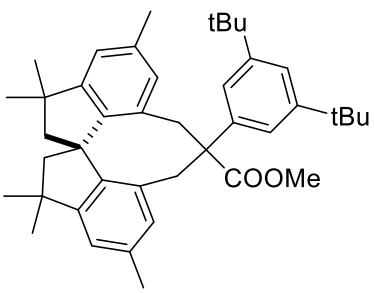


M in THF, 0.31 mmol, 0.31 mL, 1.5 equiv. x 2). **S1c** was isolated as a colorless solid (50 mg, 47%). **IR** (KBr) 2952, 2921, 2860, 1732, 1512, 1464, 1250, 1186, 1038, 860, 827 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.86 (s, 1H), 6.76-6.68 (m, 5H), 6.63 (s, 1H), 5.55 (s, 1H), 3.78 (s, 3H), 3.63 (s, 3H), 3.25 (d, *J* = 13.3 Hz, 1H), 3.15 (d, *J* = 12.6 Hz, 1H), 2.94 (d, *J* = 12.5 Hz, 1H), 2.59 (d, *J* = 13.3, 1H), 2.42-2.35 (m, 2H), 2.31 (s, 3H), 2.01-1.94 (m, 5H), 1.49 (s, 3H), 1.46 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 175.5, 158.3, 151.6, 151.0, 145.7, 145.3, 136.8, 135.5, 133.9, 132.3, 131.4, 130.7, 128.7, 127.7, 122.1, 121.3, 113.2, 58.2, 57.2, 56.7, 56.4, 55.3, 51.6, 42.0, 41.9, 38.8, 34.4, 32.4, 32.3, 30.4, 30.3, 21.3, 20.9. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{35}H_{40}O_3Na^+$: 531.2870; Found 531.2868. **$[\alpha]_D^{23.4}$** = –78.9 (*c* = 0.50, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 10:1).

2,4,4,7,7,9-hexamethyl-12-phenyl-4,5,6,7,12,13-hexahydro-11H-cycloocta[1,2,3-cd:1,8,7-c'd']diindene-12-carboxylic acid (L9): Prepared according to **GP-B** using compound **S1c** (0.089 mmol, 45 mg, 1.0 equiv.) in tetrahydrothiophene (2 mL), $AlBr_3$ (0.354 mmol, 94 mg, 4.0 equiv.). **L9** was isolated as a cololress solid (43 mg, >99%). **IR** (KBr) 3400, 2956, 2919, 2861, 1701, 1514, 1449, 1262, 1180, 859, 827 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 6.89 (s, 1H), 6.81 (s, 1H), 6.77-6.74 (m, 3H), 6.69-6.66 (m, 2H), 5.60 (s, 1H), 3.23 (d, *J* = 13.3 Hz, 1H), 3.15 (d, *J* = 12.6 Hz, 1H), 2.97 (d, *J* = 12.6 Hz, 1H), 2.62 (d, *J* = 13.3, 1H), 2.42-2.35 (m, 2H), 2.23 (s, 3H), 2.00-1.95 (m, 5H), 1.50 (s, 3H), 1.46 (s, 3H), 1.27 (s, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 181.1, 154.4, 151.5, 151.1, 145.6, 145.2, 137.1, 135.6, 133.5, 131.8, 131.1, 130.6, 129.1, 128.0, 122.3, 121.5, 114.7, 58.2, 57.1, 56.7, 56.2, 42.0, 41.9, 38.1, 34.3, 32.5, 32.3, 30.4, 30.3, 21.3, 21.0. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{36}O_3Na^+$: 503.2557; Found 531.2554. **$[\alpha]_D^{24.3}$** = –78.7 (*c* = 0.50, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 2:1).

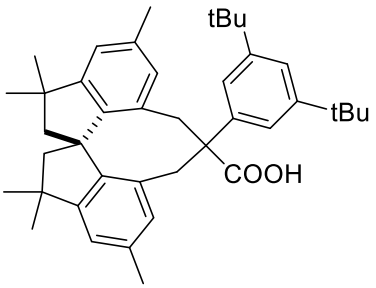


Methyl-12-(3,5-di-tert-butylphenyl)-2,4,4,7,7,9-hexamethyl-4,5,6,7,12,13-hexahydro-11H-cycloocta[1,2,3-cd:1,8,7-c'd']diindene-12-carboxylate (S1d): Prepared according to **GP-A** using compound **4** (0.21 mmol, 100 mg, 1.0 equiv.), methyl-α-(3,5-di-tert-butylphenyl)acetate (0.23 mmol, 60 mg, 1.1 equiv.), NaHMDS (1 M in THF, 0.31 mmol, 0.31 mL, 1.5 equiv. x 2). **S1d** was isolated as a colorless solid (50 mg, 47%). **IR** (KBr) 2960, 2947, 2918, 2859, 1731, 1596, 1449, 1360, 1172, 1051 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.24 (s, 1H), 6.87 (s, 1H), 6.68 (s, 1H), 6.66 (s, 1H), 6.63 (s, 2H), 5.43 (s, 1H), 3.65 (s, 3H), 3.32 (d, *J* = 12.6 Hz, 1H), 3.21 (d, *J* = 13.3 Hz, 1H), 3.00 (d, *J* = 12.5,

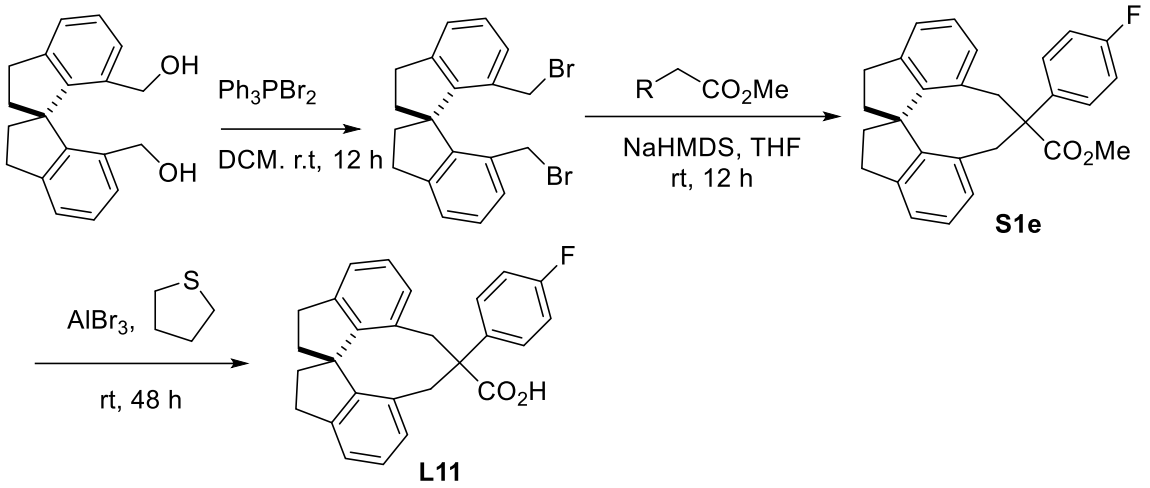


1H), 2.62 (d, *J* = 13.3 Hz, 1H), 2.42-2.35 (m, 2H), 2.32 (s, 3H), 2.02 (d, *J* = 12.5 Hz, 1H), 1.94 (d, *J* = 12.8 Hz, 1H), 1.88 (s, 3H), 1.48-1.47 (m, 6H), 1.26 (s, 6H), 1.23 (s, 18H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 175.5, 151.6, 150.8, 149.9, 145.6, 145.3, 140.5, 136.9, 135.4, 132.6, 131.2, 130.5, 128.5, 122.1, 121.2, 120.7, 120.5, 58.3, 57.1, 57.0, 56.8, 51.6, 42.0, 41.8, 39.2, 34.8, 34.1, 32.8, 32.1, 31.4, 30.4, 30.2, 21.4, 21.1. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{42}H_{54}O_2Na^+$: 613.4016; Found 613.4010. **$[\alpha]_D^{23.1}$** = –31.4 (*c* = 0.50, $CHCl_3$). **Rf** 0.6 (hexane/AcOEt = 10:1).

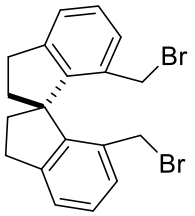
12-(3,5-di-tert-butylphenyl)-2,4,4,7,7,9-hexamethyl-4,5,6,7,12,13-hexahydro-11H-cycloocta[1,2,3-cd:1,8,7-c'd']diindene-12-carboxylic acid (L10): Prepared according to **GP-B** using compound **S1d** (0.19 mmol, 110 mg, 1.0 equiv.) in tetrahydrothiophene (2 mL), $AlBr_3$ (0.8 mmol, 213 mg, 4.0 equiv.). **L10** was isolated as a colorless solid (70 mg, 64%). **IR** (KBr) 2960, 2955, 2920, 2863, 1700, 1598, 1465, 1448, 1361, 1248, 860, 712 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.25 (s, 1H), 6.88 (s, 1H), 6.86 (s, 1H), 6.75 (s, 2H), 6.66 (s, 1H), 5.45 (s, 1H), 3.33 (d, *J* = 12.6 Hz, 1H), 3.20 (d, *J* = 13.1 Hz, 1H), 3.07 (d, *J* = 12.6, 1H), 2.68 (d, *J* = 13.1 Hz, 1H), 2.40 (d, *J* = 12.8 Hz, 1H), 2.34 (d, *J* = 12.8 Hz, 1H), 2.17 (s, 3H), 2.02 (d, *J* = 12.7 Hz, 1H), 1.93 (d, *J* = 12.8 Hz, 1H), 1.85 (s, 3H), 1.49 (s, 3H), 1.47 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H), 1.22 (s, 18H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 179.8, 151.5, 150.8, 150.1, 145.4, 145.2, 139.7, 137.2, 135.4, 132.2, 130.9, 130.5, 129.0, 122.2, 121.2, 120.8, 120.6, 58.2, 57.2, 56.7, 56.6, 42.0, 41.8, 38.7, 34.8, 33.8, 32.8, 32.2, 31.4, 30.4, 30.2, 21.3, 20.9. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{52}O_2Na^+$: 599.3860; Found 599.3854. **$[\alpha]_D^{23.7}$** = –27.4 (*c* = 0.50, $CHCl_3$). **Rf** 0.2 (hexane/AcOEt = 6:1).



2.2. Preparation of L11

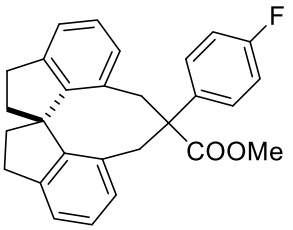


(*R*)-7,7'-bis(bromomethyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]:



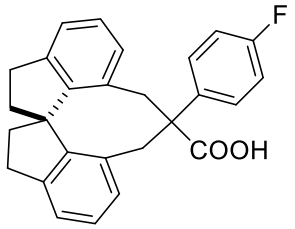
To a solution of (*R*)-(2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)dimethanol (0.36 mmol, 100 mg, 1.0 equiv.)[S3] in DCM (5 mL) was added Ph_3PBr_2 (1.8 mmol, 760 mg, 5.0 equiv.) in several portions at room temperature. The reaction mixture was stirred for 12 h at room temperature. The rection was quenched by adding water at 0 °C, and extracted with DCM three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was purified by silica gel column chromatography (hexane/AcOEt) to give (*R*)-7,7'-bis(bromomethyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] as a colorless solid (135 mg, 93%). **IR** (KBr) 2957, 2947, 2843, 1448, 1434, 1215, 1203, 785, 752 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.28-7.21 (m, 6H), 4.13 (d, *J* = 10.4 Hz, 2H), 4.05 (d, *J* = 10.4 Hz, 2H), 3.07-3.02 (m, 4H), 2.41-2.29 (m, 4H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 147.0, 144.1, 133.8, 130.6, 128.2, 125.2, 61.6, 38.2, 30.7, 30.3. **HRMS** (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{18}Br_2^+$: 403.9775; Found 403.9751. **$[\alpha]_D^{22.0}$** = +280.9 (*c* = 0.25, $CHCl_3$). **Rf** 0.7 (hexane/AcOEt = 10:1).

methyl 12-(4-fluorophenyl)-4,5,6,7,12,13-hexahydro-11H-cycloocta[1,2,3-cd:1,8,7-c'd']diindene-12-carboxylate (S1e): Prepared according to **GP-A** using compound (*R*)-7,7'-bis(bromomethyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] (0.1 mmol, 40 mg, 1.0 equiv.), methyl-α-(4-fluorophenyl)acetate (0.11 mmol, 18 mg, 1.1 equiv.), NaHMDS (1 M in THF, 0.15 mmol, 0.15 mL, 1.5 equiv. x 2). **S1e** was isolated as a colorless solid (20 mg, 50%). **IR** (KBr) 2936, 1721, 1509, 1455, 1276, 1243, 1228, 1176, 841 cm^{-1}. **^{1}H NMR**

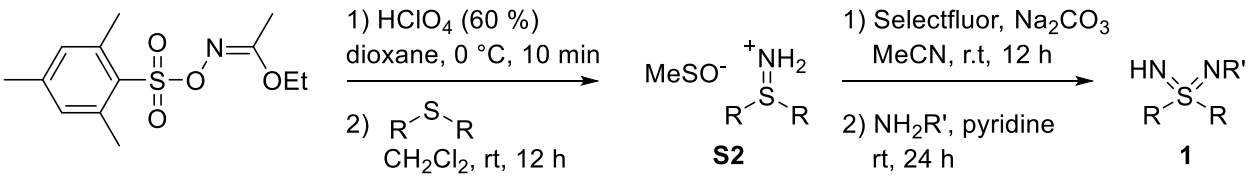


($CDCl_3$, 400 MHz) δ 7.15 (d, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.93-6.91 (m, 4H), 6.83 (d, *J* = 7.2 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 5.80 (d, *J* = 7.6 Hz, 1H), 3.65 (s, 3H), 3.42 (d, *J* = 13.5 Hz, 1H), 3.31 (d, *J* = 12.6 Hz, 1H), 3.10-2.98 (m, 3H), 2.86-2.74 (m, 3H), 2.30-2.21 (m, 2H), 2.00-1.88 (m, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 175.1, 161.7 (d, *J* = 246.6 Hz), 149.0, 148.8, 143.2, 142.6, 137.5 (d, *J* = 2.9 Hz), 132.2, 131.5, 129.1, 128.3 (d, *J* = 8.7 Hz), 127.7, 127.1, 125.9, 123.9, 123.1, 114.9 (d, *J* = 21.2 Hz), 61.2, 55.9, 51.9, 38.5, 38.0, 34.5, 30.4, 30.4. (one aliphatic signal was missing probably due to overlap) **^{19}F NMR** (370MHz, $CDCl_3$) δ: –114.9. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{25}FO_2Na^+$: 435.1731; Found 435.1718. **$[\alpha]_D^{22.1}$** = –60.7 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 10:1).

12-(4-fluorophenyl)-4,5,6,7,12,13-hexahydro-11H-cycloocta[1,2,3-cd:1,8,7-c'd']diindene-12-carboxylic acid (L11): Prepared according to **GP-B** using compound **S1e** (0.05 mmol, 20 mg, 1.0 equiv.) in tetrahydrothiophene (2 mL), $AlBr_3$ (0.2 mmol, 54 mg, 4.0 equiv.). **L10** was isolated as a colorless solid (10 mg, 50%). **IR** (KBr) 3068, 2942, 1705, 1510, 1456, 1085, 1240, 719 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.23-7.20 (m, 1H), 7.14-7.10 (m, 1H), 7.03-6.94 (m, 6H), 6.74-6.69 (m, 1H), 5.82 (d, *J* = 7.4 Hz, 1H), 3.40 (d, *J* = 13.4 Hz, 1H), 3.32 (d, *J* = 12.6 Hz, 1H), 3.14-2.99 (m, 3H), 2.90-2.74 (m, 3H), 2.31-2.22 (m, 2H), 2.00-1.89 (m, 2H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 180.1, 161.8 (d, J = 246.6 Hz), 149.1, 148.8, 143.3, 142.7, 136.8 (d, J = 2.9 Hz), 131.9, 131.3, 129.1, 128.4 (d, J = 7.7 Hz), 128.1, 127.2, 126.0, 123.9, 123.2, 115.0 (d, J = 21.2 Hz), 61.2, 55.7, 38.4, 38.1, 37.9, 34.3, 30.5, 30.4. **^{19}F NMR** (370MHz, $CDCl_3$) δ: –114.5. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{23}FO_2Na^+$: 421.1574; Found 421.1559. **$[\alpha]_D^{22.2}$** = –82.4 (*c* = 0.25, $CHCl_3$). **Rf** 0.4 (hexane/AcOEt = 2:1).



2.3. Preparation of sulfondiimines

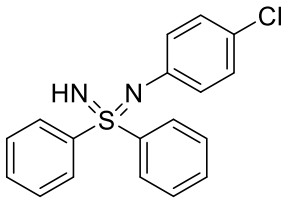


General Procedure C for 1a-1o[S1]

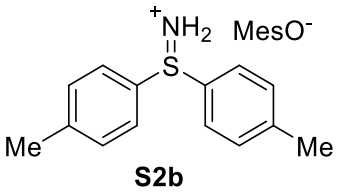
To ethyl o-(mesitylenesulfonyl)acetohydroxamate (1.0 g, 3.51 mmol, 1 equiv.) in 1,4-dioxane (4 mL) was added 60% perchloric acid (2.5 mL) dropwise at 0 °C. After additional vigorous stirring for 10 min at 0 °C, cold water was added and the product was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried

over Na_2SO_4, filtered, and evaporated under vacuum to approximately 1 mL. This mixture was slowly added to a solution of the corresponding sulfide (3.51 mmol, 1 equiv.) in CH_2Cl_2 (4 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h. Half of the CH_2Cl_2 was evaporated and diethyl ether (20 mL) was added. The product crystallized upon storage at –30 °C overnight and was collected by filtration and dried in high vacuum to give the corresponding sulfiliminium salt **S2**.

To a solution of the obtained sulfiliminium salt **S2** (1.0 equiv.) and Na_2CO_3 (5.0 equiv.) in MeCN (8 mL) was added Selectfluor® (1.0 equiv.) at 0 °C and the mixture was stirred for 12 h at room temperature. The mixture was quenched by water and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated under vacuum. To the residue was added to a solution of $R'NH_2$ (3.0 equiv.) and pyridine (1.2 equiv.) and the mixture was stirred for 24 h at room temperature. The residue was purified by silica gel column chromatography (hexane/AcOEt) and evaporated under vacuum. The residual solid was washed by hexane and filtered to give the desired sulfondiimine **1**. When necessary, **1** was further purified by GPC.

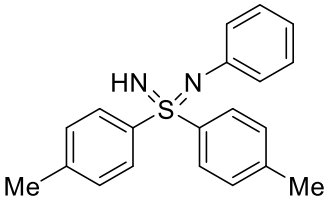


Bis(4-methylphenyl)sulfiliminium mesitylenesulfonate (S2b): Prepared according to **GP-C** using bis(4-methylphenyl) sulfide (3.51 mmol, 750 mg, 1.0 equiv.), **S2b** was isolated as a colorless solid (1.2 g, 79%). **IR** (KBr) 3180, 3046, 2983, 2934, 1593, 1453, 1403, 1215, 1080, 1015, 809, 678 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.62-7.59 (m, 4H), 7.23-7.20 (m, 4H), 6.76 (s, 2H), 2.50 (s, 6H), 2.34 (s, 6H), 2.23 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 144.2, 138.8, 137.4, 130.9, 130.7, 129.8, 128.4, 22.8, 21.5, 20.8; one aromatic signal was missing probably due to overlap. **HRMS** (ESI) m/z: $[M\text{-}MesO^-]^+$ Calcd for $C_{14}H_{16}NS^+$: 230.0998; Found 230.0994.



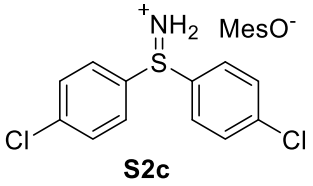
S2b

N-phenyl-1,1-di-p-tolyl-λ^6-sulfondiimine (1b): Prepared according to **GP-C** using compound **S2b** (2.7 mmol, 1.2 g, 1.0 equiv.), Na_2CO_3 (13.5 mmol, 1.4 g, 5.0 equiv.), Selectfluor® (2.7 mmol, 990 mg, 1.0 equiv.), aniline (8.1 mmol, 0.8 mL, 3.0 equiv.), pyridine (3.24 mmol, 0.28 mL, 1.2 equiv.). **1b** was isolated as a colorless solid (0.2 g, 23%). **IR** (KBr) 3180, 3057, 1595, 1485, 1283, 1254, 1086, 1074, 1044, 954, 946, 765, 759, 749 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.04 (d, J = 8.3 Hz, 4H), 7.24 (d, J = 8.5 Hz, 4H), 7.17-7.10 (m, 4H), 6.86-6.81 (m, 1H), 2.35 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 146.0, 142.6, 140.3, 129.8, 128.8, 127.9, 123.3, 120.6, 21.4. **HRMS**



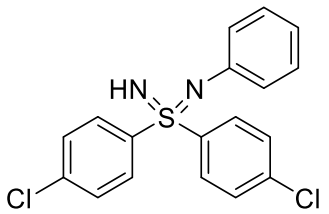
(ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}N_2S^+$: 321.1420; Found 321.1415. **Rf** 0.4 (hexane/AcOEt = 3:1).

Bis(4-chlorophenyl)sulfiliminium mesitylenesulfonate (S2c): Prepared according to **GP-C** using bis(4-chlorophenyl) sulfide (3.51 mmol, 900 mg, 1.0 equiv.), **S2c** was isolated as a colorless solid (1.2 g, 72%). **IR** (KBr) 3152, 3079, 2971, 2937, 1603, 1569, 1478, 1398, 1224, 1172, 1085, 1015, 818, 680 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.83 (brs, 2H), 7.72 (d, *J* = 8.6 Hz, 4H), 7.37 (d, *J* = 8.6 Hz, 4H), 6.80 (s, 2H), 2.51 (s, 6H), 2.25 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 140.3, 139.5, 138.7, 137.0, 131.2, 130.8, 130.7, 129.9, 22.9, 20.8. **HRMS** (ESI) m/z: $[M\text{-}MesO^-]^+$ Calcd for $C_{12}H_{10}NSCl_2^+$: 269.9906; Found 269.9901.

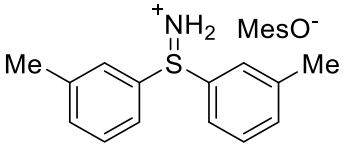


S2c

1,1-bis(4-chlorophenyl)-N-phenyl-λ^6-sulfondiimine (1c): Prepared according to **GP-C** using compound **S2c** (2.12 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (10.6 mmol, 1.12 g, 5.0 equiv.), Selectfluor® (2.12 mmol, 750 mg, 1.0 equiv.), aniline (6.36 mmol, 0.6 mL, 3.0 equiv.), pyridine (2.54 mmol, 0.22 mL, 1.2 equiv.). **1c** was isolated as a colorless solid (0.42 g, 42%). **IR** (KBr) 3150, 1591, 1573, 1483, 1471, 1391, 1283, 1255, 1083, 948, 755, 749 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.10 (dd, *J* = 8.8, 2.0 Hz, 4H), 7.43 (dd, *J* = 8.8, 2.0 Hz, 4H), 7.17-7.10 (m, 4H), 6.90-6.87 (m, 1H), 2.26 (brs, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 145.0, 141.4, 138.9, 129.5, 129.5, 129.0, 123.3, 121.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}N_2SCl_2^+$: 361.0328; Found 361.0321. **Rf** 0.6 (hexane/AcOEt = 3:1).

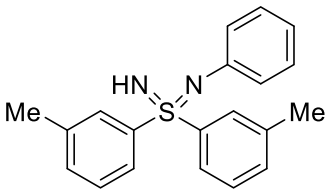


Bis(3-methylphenyl)sulfiliminium mesitylenesulfonate (S2d): Prepared according to **GP-C** using bis(3-methylphenyl) sulfide (3.5 mmol, 750 mg, 1.0 equiv.), **S2d** was isolated as a colorless solid (1.1 g, 72%). **IR** (KBr) 3174, 3041, 2968, 2959, 1598, 1477, 1451, 1225, 1186, 1083, 1013, 850, 781, 669 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.60 (s, 2H), 7.53-7.50 (m, 2H), 7.34-7.30 (m, 4H), 6.75 (s, 2H), 2.52 (s, 6H), 2.32 (s, 6H), 2.21 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 140.9, 139.3, 138.5, 137.2, 134.0, 132.9, 130.6, 130.0, 128.5, 125.4, 22.9, 21.3, 20.8. **HRMS** (ESI) m/z: $[M\text{-}MesO^-]^+$ Calcd for $C_{14}H_{16}NS^+$: 230.0998; Found 230.0993.

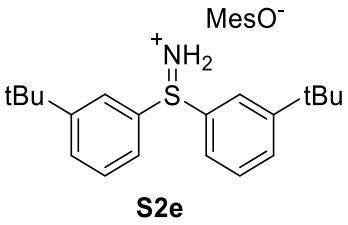


S2d

N-phenyl-1,1-di-m-tolyl-λ^6-sulfondiimine (1d): Prepared according to **GP-C** using compound **S2d** (2.3 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (11.6 mmol, 1.4 g, 5.0 equiv.), Selectfluor® (2.3 mmol, 820 mg, 1.0 equiv.), aniline (6.9 mmol, 0.8 mL, 3.0 equiv.), pyridine (8.3 mmol, 0.4 mL, 1.2 equiv.). **1d** was isolated as a colorless solid (0.25 g, 34%). **IR** (KBr) 3243, 3062, 1593, 1486, 1293, 1262, 1088, 933, 795, 749, 684 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.00 (s, 2H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.15-7.13 (m, 4H), 6.87-6.83 (m, 1H), 2.39 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 143.0, 139.3, 132.8, 128.9, 128.8, 128.2, 125.1, 123.4, 120.7, 21.5; one aromatic signal was missing probably due to overlap. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_2SNa^+$: 343.1239; Found 343.1237. **Rf** 0.4 (hexane/AcOEt = 3:1).

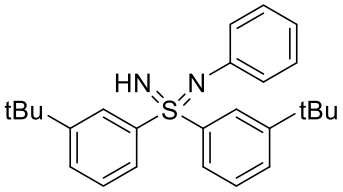


Bis(3-tert-butylphenyl)sulfiliminium mesitylenesulfonate (S2e): Prepared according to **GP-C** using bis(2-methylphenyl) sulfide (1.0 mmol, 310 mg, 1.0 equiv.), **S2e** was isolated as a color solid (0.6 g, >99%). **IR** (KBr) 3206, 3190, 3174, 3142, 3070, 3050, 2957, 2877, 1593, 1481, 1365, 1183, 1082, 1008, 717 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.68-7.62 (m, 4H), 7.59-7.54 (m, 4H), 7.43-7.37 (m, 2H), 6.75 (s, 2H), 2.54 (s, 6H), 2.22(s, 3H), 1.26 (s, 18H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 153.5, 139.9, 138.0, 137.0, 133.0, 130.4, 130.1, 130.1, 125.6, 125.3, 35.1, 30.9, 22.9, 20.7. **HRMS** (ESI) m/z: $[M\text{-}MesO^-]^+$ Calcd for $C_{20}H_{28}NS^+$: 314.1937; Found 314.1930.

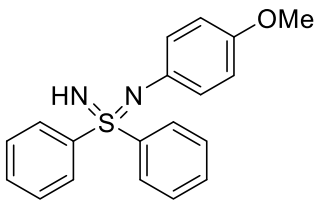


S2e

1,1-bis(3-(tert-butyl)phenyl)-N-phenyl-λ^6-sulfondiimine (1e): Prepared according to **GP-C** using compound **S2e** (1.0 mmol, 514 mg, 1.0 equiv.), Na_2CO_3 (5 mmol, 550 mg, 5.0 equiv.), Selectfluor® (1 mmol, 354 mg, 1.0 equiv.), aniline (3.0 mmol, 0.3 mL, 3.0 equiv.), pyridine (1.2 mmol, 0.1 mL, 1.2 equiv.). **1e** was isolated as a brown solid (0.12 g, 30%). **IR** (KBr) 3214, 2954, 2864, 1593, 1479, 1291, 1255, 1089, 957, 754 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.22 (t, *J* = 1.8 Hz, 2H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.50-7.47 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.19-7.11 (m, 4H), 6.86-6.82 (m, 1H), 2.21 (brs, 1H), 1.30 (s, 18H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.4, 146.0, 142.9, 128.9, 128.8, 128.7, 125.1, 124.8, 123.5, 120.7, 35.0, 31.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{33}N_2S^+$: 405.2359; Found 405.2353. **Rf** 0.7 (hexane/AcOEt = 3:1).

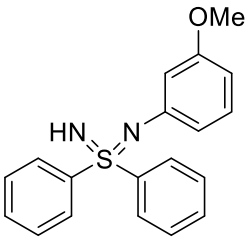


N-**(4-methoxyphenyl)-1,1-diphenyl-λ⁶-sulfondiimine (1f)**: Prepared according to **GP-C** using diphenylsulfiliminium mesitylenesulfonate (2.49 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (12.47 mmol, 1.3 g, 5.0 equiv.), Selectfluor® (2.49 mmol, 881 mg, 1.0 equiv.), 4-methoxyaniline (7.47 mmol, 919 mg, 3.0 equiv.), pyridine (2.97 mmol, 0.24 mL, 1.2 equiv.). **1f** was isolated by GPC as a brown solid (0.27 g, 37%). **IR** (KBr) 3281, 1500, 1444, 1272, 1229, 1084, 1038, 958, 835, 721, 687 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.20-8.15 (m, 4H), 7.47-7.44 (m, 6H), 7.08 (d, *J* = 9.1 Hz, 2H), 6.71 (d, *J* = 8.6, 1H), 3.71 (s, 3H), 2.17 (brs, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 154.2, 143.1, 138.6, 131.9, 129.1, 128.1, 124.3, 114.2, 55.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2SO^+$: 323.1213; Found 323.1210. **Rf** 0.5 (hexane/AcOEt = 2:1).



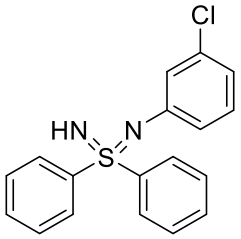
N-(4-chlorophenyl)-1,1-diphenyl-λ⁶-sulfondiimine (1g): Prepared according to **GP-C** using diphenylsulfiliminium mesitylenesulfonate (2.49 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (12.47 mmol, 1.3 g, 5.0 equiv.), Selectfluor® (2.49 mmol, 881 mg, 1.0 equiv.), 4-chloroaniline (7.47 mmol, 949 mg, 3.0 equiv.), pyridine (2.97 mmol, 0.24 mL, 1.2 equi.v). **1g** was isolated by GPC as a brown solid (0.18 g, 22%). **IR** (KBr) 1482, 1444, 1278, 1244, 1081, 1038, 950, 828, 718, 685 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.16 (d, *J* = 8.2 Hz, 4H), 7.52-7.43 (m, 6H), 7.11-7.05 (m, 4H), 2.21 (brs, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 144.5, 142.6, 132.2, 129.2, 128.8, 128.0, 125.8, 124.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}N_2SCl^+$: 327.0717; Found 327.0714. **Rf** 0.5 (hexane/AcOEt = 3:1).

N-(3-methoxyphenyl)-1,1-diphenyl-λ⁶-sulfondiimine (1h): Prepared according to **GP-C** using diphenylsulfiliminium mesitylenesulfonate (2.49 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (12.47 mmol, 1.3 g, 5.0 equiv.), Selectfluor® (2.49 mmol, 881 mg, 1.0 equiv.), 3-methoxyaniline (7.47 mmol, 0.80 mL, 3.0 equiv.), pyridine (2.97 mmol, 0.24 mL, 1.2 equiv.). **1h** was isolated as a brown solid (0.27 g, 37%). **IR** (KBr)3178, 1579, 1490, 1444, 1289, 1208, 1151, 1081, 1037, 979, 884, 772, 725, 691 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.19-8.17 (m, 4H), 7.48-7.42 (m, 6H), 7.03-7.01 (m, 1H), 6.78 -6.74 (m, 2H), 6.44-6.42 (m, 1H), 3.70 (s, 3H), 2.24 (brs, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 160.1, 147.0, 143.0, 132.0, 129.3, 129.1, 128.0, 115.6, 109.0, 106.8, 55.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2SO^+$: 323.1213; Found 323.1208. **Rf** 0.5 (hexane/AcOEt = 2:1).

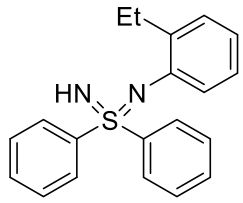


N-**(3-chlorophenyl)-1,1-diphenyl-λ⁶-sulfondiimine (1i)**: Prepared according to **GP-C** uisng

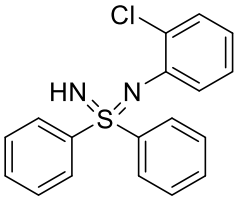
diphenylsulfiliminium mesitylenesulfonate (2.49 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (12.47 mmol, 1.3 g, 5.0 equiv.), Selectfluor® (2.49 mmol, 881 mg, 1.0 equiv.), 3-chloroaniline (7.47 mmol, 0.72 mL, 3.0 equiv.), pyridine (2.97 mmol, 0.24 mL, 1.2 equiv.). **1i** was isolated as a brown solid (0.37 g, 50%). **IR** (KBr) 3170, 1588, 1553, 1472, 1442, 1313, 1257, 1094, 1043, 971, 786, 716, 684 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.17 (dd, *J* = 7.5, 1.6 Hz, 4H), 7.52-7.44 (m, 6H), 7.19 (s, 1H), 7.06-6.99 (m, 2H), 6.84-6.78 (m, 1H), 2.24 (brs, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 147.3, 142.6, 134.2, 132.2, 129.6, 129.2, 127.9, 123.4, 121.1, 120.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}N_2SCl^+$: 327.0717; Found 327.0713. **Rf** 0.5 (hexane/AcOEt = 2:1).



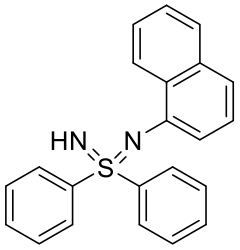
N-(2-ethylphenyl)-1,1-diphenyl-λ^6-sulfondiimine (1j): Prepared according to **GP-C** using diphenylsulfiliminium mesitylenesulfonate (2.49 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (12.47 mmol, 1.3 g, 5.0 equiv.), Selectfluor® (2.49 mmol, 881 mg, 1.0 equiv.), 2-ethylaniline (7.47 mmol, 0.87 mL, 3.0 equiv.), pyridine (2.97 mmol, 0.24 mL, 1.2 equiv.). **1j** was isolated as a colorless solid (0.27 g, 37%). **IR** (KBr) 3273, 3246, 2964, 1592, 1481, 1445, 1302, 1282, 1252, 1119, 1078, 1056, 955, 757, 686 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.19-8.16 (m, 4H), 7.49-7.43 (m, 6H), 7.19-7.13 (m, 2H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.81 (t, *J* = 7.3 Hz, 1H), 2.94 (q, *J* = 7.1 Hz, 2H), 2.22 (brs, 1H), 1.40-1.33 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 143.6, 143.4, 138.5, 131.9, 129.1, 128.6, 127.9, 126.0, 120.7, 120.6, 25.5, 14.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}N_2S^+$: 321.1420; Found 321.1418. **Rf** 0.6 (hexane/AcOEt = 2:1).



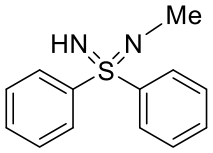
N-(2-chlorophenyl)-1,1-diphenyl-λ^6-sulfondiimine (1k): Prepared according to **GP-C** using diphenylsulfiliminium mesitylenesulfonate (2.49 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (12.47 mmol, 1.3 g, 5.0 equiv.), Selectfluor® (2.49 mmol, 881 mg, 1.0 equiv.), 2-chloroaniline (7.47 mmol, 0.72 mL, 3.0 equiv.), pyridine (2.97 mmol, 0.24 mL, 1.2 equiv.). **1k** was isolated as a colorless solid (0.15 g, 20%). **IR** (KBr) 3201, 1584, 1471, 1437, 1309, 1287, 1249, 1079, 1061, 1032, 958, 751, 717, 678, 620 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.26-8.21 (m, 4H), 7.49 - 7.43 (m, 6H), 7.38-7.29 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.76 (t, *J* = 7.7, 1H), 2.37 (brs, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 142.8, 142.7, 132.2, 129.8, 129.2, 128.2, 126.9, 122.5, 121.4; one aromatic signal was missing probably due to overlap. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}N_2SCl^+$: 327.0717; Found 327.0715. **Rf** 0.5 (hexane/AcOEt = 2:1).



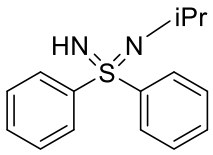
N-(naphthalen-1-yl)-1,1-diphenyl-λ^6-sulfondiimine (1l): Prepared according to **GP-C** using diphenylsulfiliminium mesitylenesulfonate (2.49 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (12.47 mmol, 1.3 g, 5.0 equiv.), Selectfluor® (2.49 mmol, 881 mg, 1.0 equiv.), naphthalen-1-amine (7.47 mmol, 973 mg, 3.0 equiv.), pyridine (2.97 mmol, 0.24 mL, 1.2 equiv.). **1l** was isolated as a colorless solid (0.13 g, 18%). **IR** (KBr) 3198, 1568, 1396, 1270, 1240, 1186, 1113, 1078, 937, 769, 727 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.77 (d, *J* = 8.2 Hz, 1H), 8.29-8.24 (m, 4H), 7.77 (d *J* = 8.2 Hz, 1H), 7.54-7.44 (m, 8H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 2.35 (brs, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 143.1, 142.0, 134.7, 132.1, 130.9, 129.2, 128.0, 127.8, 126.0, 125.7, 124.7, 124.0, 120.3, 115.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}N_2S^+$: 343.1263; Found 343.1259. **Rf** 0.4 (hexane/AcOEt = 2:1).



N-methyl-1,1-diphenyl-λ^6-sulfondiimine (1m): Prepared according to **GP-C** using diphenylsulfiliminium mesitylenesulfonate (2.49 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (12.47 mmol, 1.3 g, 5.0 equiv.), Selectfluor® (2.49 mmol, 881 mg, 1.0 equiv.), methanamine (7.47 mmol, 33 wt% in EtOH 1.0 mL, 3.0 equiv.), pyridine (2.97 mmol, 0.24 mL, 1.2 equiv.). **1m** was isolated as a colorless solid (0.1 g, 19%). **IR** (KBr) 3152, 2909, 2852, 2786, 1444, 1181, 1089, 1091, 995, 837, 757, 716, 688 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.10-8.04 (m, 4H), 7.52-7.39 (m, 6H), 2.80 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 142.4, 131.7 129.0, 127.9, 29.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}N_2S^+$: 231.0950; Found 231.0947. **Rf** 0.2 (hexane/AcOEt = 2:1).

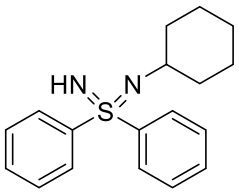


N-isopropyl-1,1-diphenyl-λ^6-sulfondiimine (1n): Prepared according to **GP-C** using diphenylsulfiliminium mesitylenesulfonate (2.49 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (12.47 mmol, 1.3 g, 5.0 equiv.), Selectfluor® (2.49 mmol, 881 mg, 1.0 equiv.), propan-2-amine (7.47 mmol, 0.6 mL, 3.0 equiv.), pyridine (2.97 mmol, 0.24 mL, 1.2 equiv.). **1n** was isolated as a colorless solid (50 mg, 9%). **IR** (KBr) 3202, 2969, 2924, 2858, 1442, 1177, 1142, 1069, 982, 758, 709, 689 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.13-8.08 (m, 4H), 7.49-7.39 (m, 6H), 3.52-3.45 (m, 1H), 1.87 (brs, 1H), 1.25-1.19 (m, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 143.7, 131.5, 128.8, 128.0, 45.2, 27.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2S^+$: 259.1263; Found 259.1261. **Rf** 0.3 (hexane/AcOEt = 2:1).

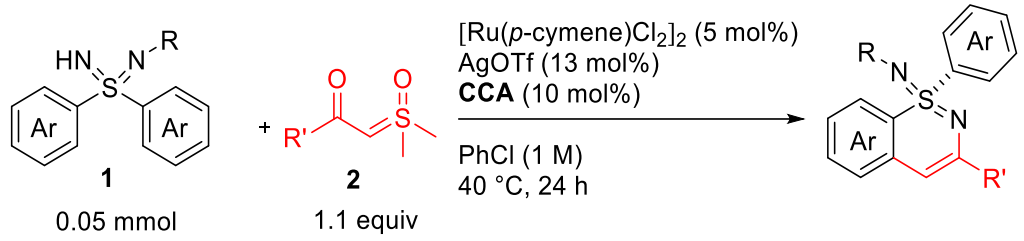


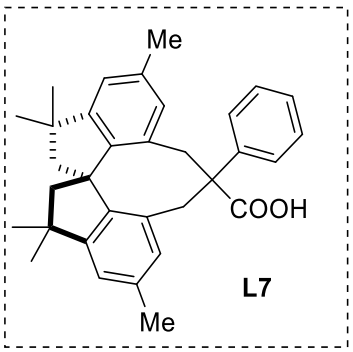
N-cyclohexyl-1,1-diphenyl-λ^6-sulfondiimine (1o): Prepared according to **GP-C** using diphenylsulfiliminium

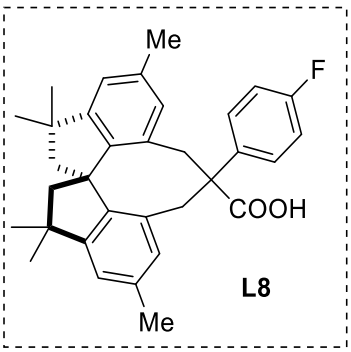
mesitylenesulfonate (2.49 mmol, 1.0 g, 1.0 equiv.), Na_2CO_3 (12.47 mmol, 1.3 g, 5.0 equiv.), Selectfluor® (2.49 mmol, 881 mg, 1.0 equiv.), cyclohexanamine (7.47 mmol, 0.8 mL, 3.0 equiv.), pyridine (2.97 mmol, 0.24 mL, 1.2 equiv.). **1o** was isolated as a colorless solid (0.18 g, 26%). **IR** (KBr) 3302, 3062, 2913, 2850, 1473, 1445, 1167, 1087, 1082, 962, 696, 679 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.12-8.07 (m, 4H), 7.46-7.39 (m, 6H), 3.17-3.09 (m, 1H), 1.89-1.82 (m, 2H), 1.75-1.67 (m, 3H), 1.57-1.39 (m, 3H), 1.29-1.13 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 144.2, 131.2, 128.8, 128.0, 52.8, 37.4, 25.8, 25.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}N_2S^+$: 299.1576; Found 299.1574. **Rf** 0.5 (hexane/AcOEt = 2:1).



2.4. Ru(II)-catalyzed enantioselective C–H alkylation/cyclization



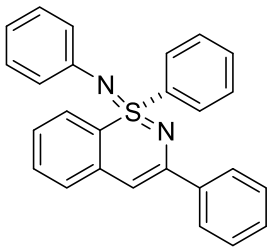




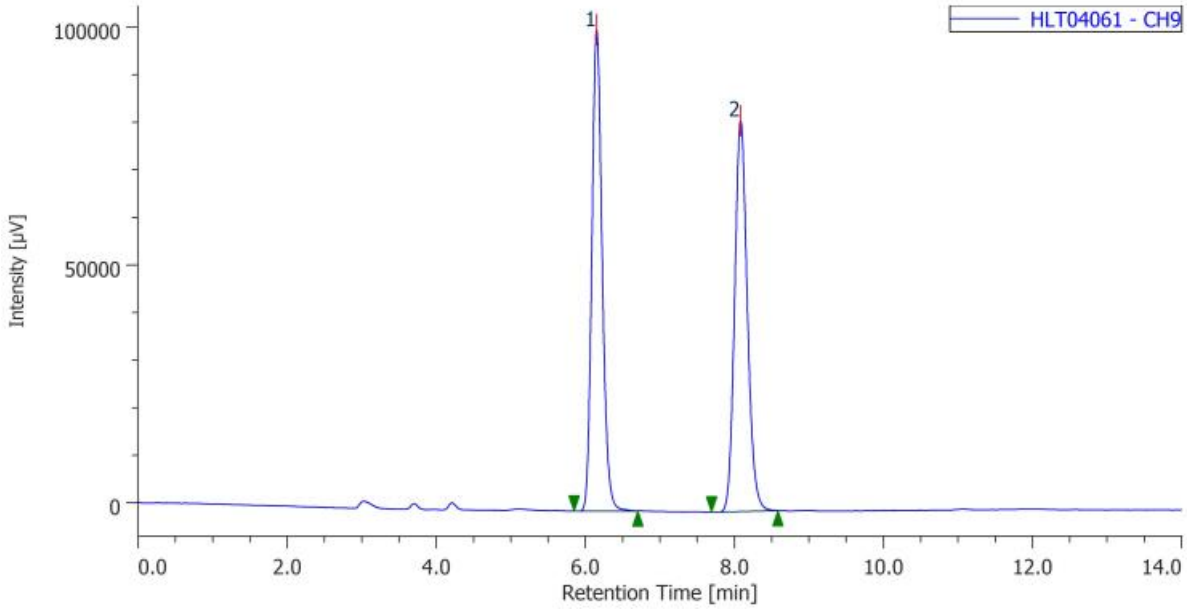
General Procedure D: Ru(II)-catalyzed enantioselective C–H alkylation/cyclization

In an argon-filled glovebox, a screw-capped test tube was charged with chiral carboxylic acid **CCA** (0.005 mmol, 10 mol%), [Ru(*p*-cymene)Cl_2]$_2$ (1.6 mg, 0.0025 mmol, 5 mol%), AgOTf (1.6 mg, 0.0065 mmol, 13 mol%), sulfondiimine **1** (0.05 mmol, 1.0 equiv.), and sulfoxonium ylide **2** (0.055 mmol, 1.1 equiv.). After the addition of chlorobenzene (0.05 mL), the test tube was capped and brought out of the glovebox. The reaction mixture was stirred at 40 °C for 24 h. The resulting mixture was directly purified by silica gel column chromatography (hexane/AcOEt) to afford **3**.

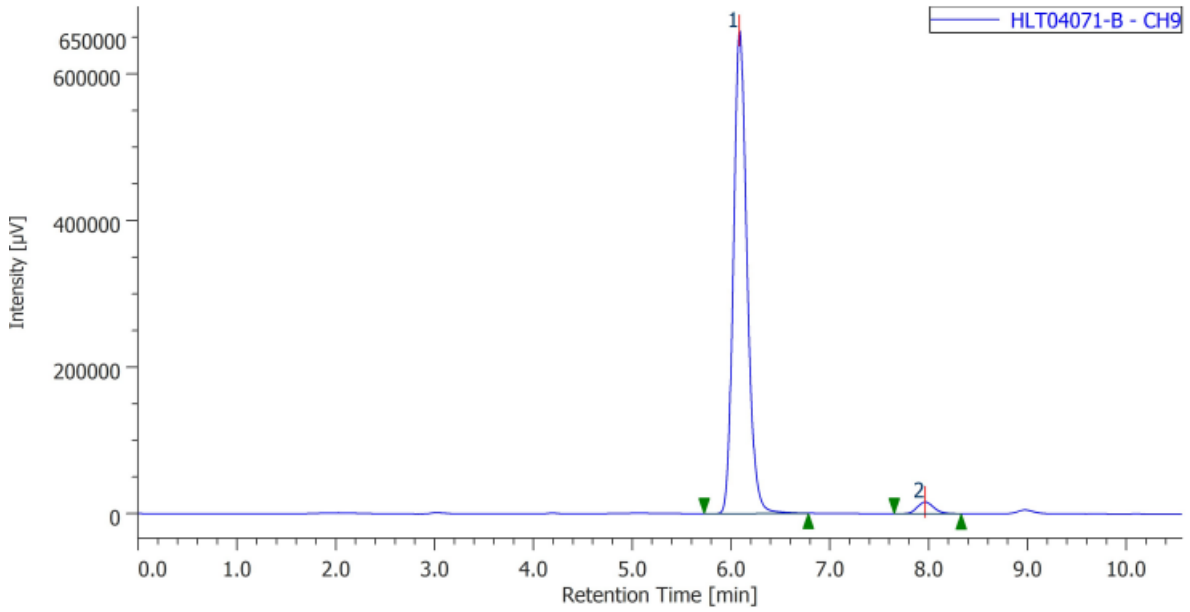
(*S*)-N,1,3-triphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3aa): Prepared according to **GP-D** using compound **1a** (0.05 mmol, 14.6 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3aa**



was isolated as a yellow solid (16.5 mg, 84%). **IR** (KBr) 3055, 2957, 2923, 1585, 1530, 1483, 1472, 1445, 1362, 1283, 1256, 1117, 1040, 752, 691 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.21 (m, 2H), 8.02-7.98 (m, 2H), 7.58-7.53 (m, 3H), 7.46-7.34 (m, 5H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.15-7.09 (m, 1H), 7.09-7.04 (m, 2H), 6.87 - 6.80 (m, 3H), 6.63 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 149.2, 144.6, 143.0, 139.7, 139.1, 132.5, 132.1, 128.9, 128.8, 128.7, 128.5, 128.3, 126.5, 126.4, 126.3, 125.9, 123.5, 121.5, 116.3, 96.4. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 6.09 min (major) and 7.97 min (minor). **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{20}N_2SNa^+$: 415.1239; Found 415.1235. **$[\alpha]_D^{22.1}$** = +142.1 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 2:1).

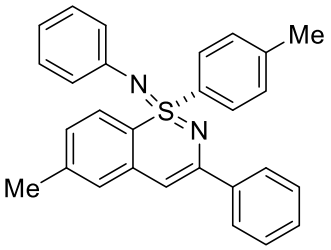


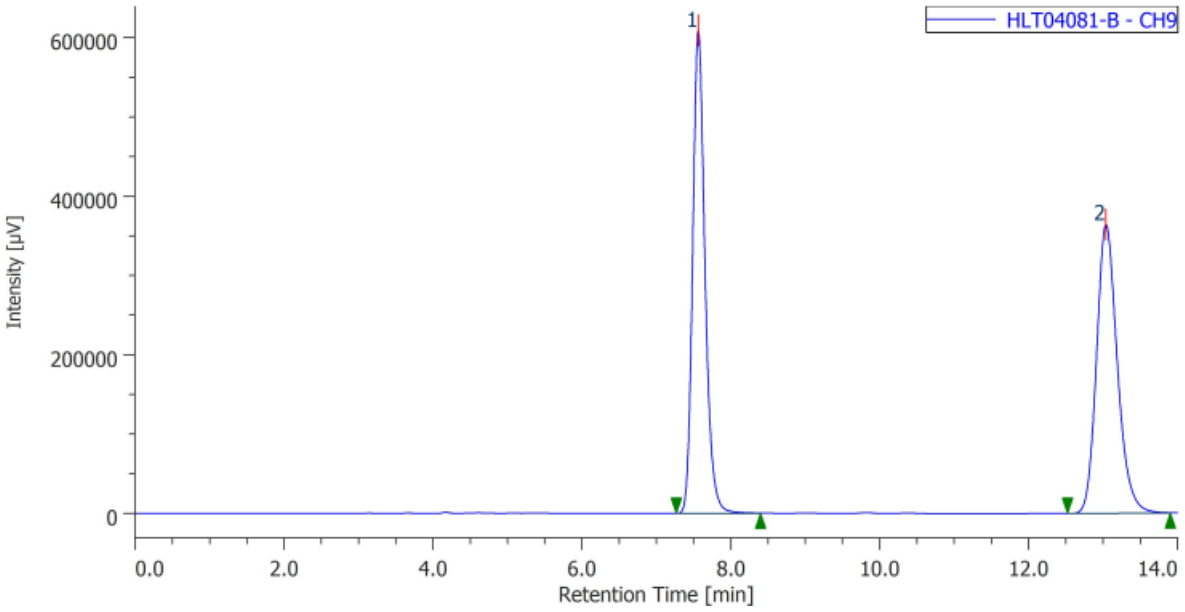
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.150	50.045
2	Unknown	9	8.080	49.955



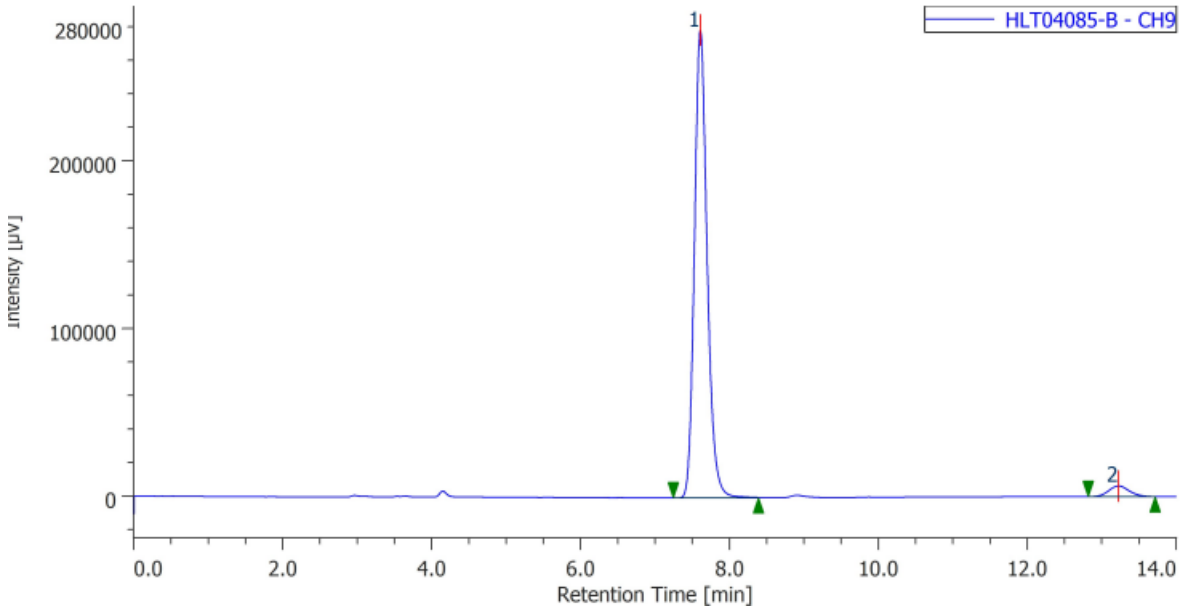
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.083	97.113
2	Unknown	9	7.963	2.887

(*S*)-6-methyl-N,3-diphenyl-1-(p-tolyl)-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ba): Prepared according to **GP-D** using compound **1b** (0.05 mmol, 16.0 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ba** was isolated as a yellow solid (14.7 mg, 70%). **IR** (KBr) 3051, 2954, 2915, 1591, 1534, 1485, 1468, 1352, 1282, 1259, 1115, 1088, 1013, 754, 695 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.99 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.42-7.30 (m, 6H), 7.08-7.03 (m, 3H), 6.94-6.90 (m, 1H), 6.85-6.79 (m, 3H), 6.56 (s, 1H), 2.41 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 149.2, 144.9, 143.3, 142.6, 140.5, 139.8, 139.3, 129.5, 128.8, 128.6, 128.5, 128.3, 127.8, 126.5, 126.1, 125.8, 123.4, 121.3, 113.9, 96.2, 21.6, 21.4. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 7.61 min (major) and 13.22 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{25}N_2S^+$: 421.1733; Found 421.1726. **$[\alpha]_D^{19.1}$** = +218.1 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).

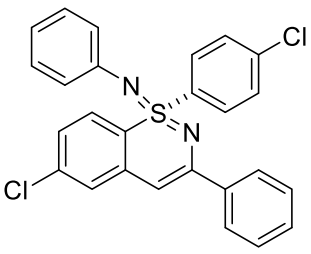




#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	7.560	49.766
2	Unknown	9	13.033	50.234

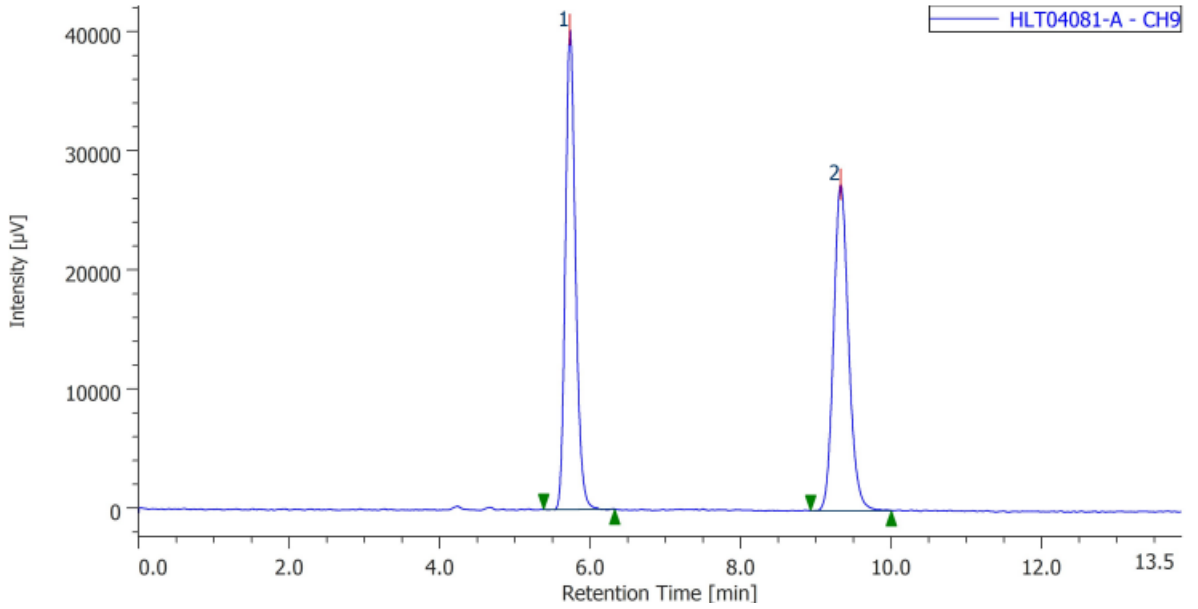


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	7.607	96.438
2	Unknown	9	13.223	3.562

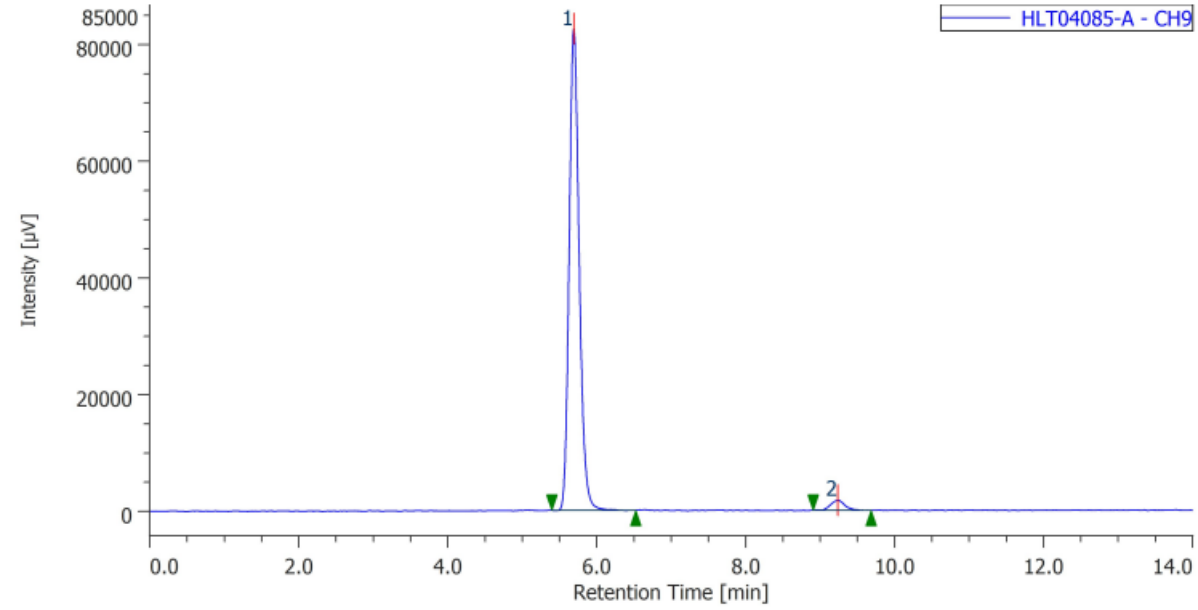


(*S*)-6-chloro-1-(4-chlorophenyl)-N,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ca): Prepared according to **GP-D** using compound **1c** (0.05 mmol, 18.0 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ca** was isolated as a yellow solid (12.0 mg, 52%). **IR** (KBr) 1567, 1484, 1390, 1257, 1083, 821, 757, 694, 669 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.10-8.07 (m, 2H),

7.98-7.95 (m, 2H), 7.54-7.51 (m, 2H), 7.45-7.36 (m, 3H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 2.3 Hz, 1H), 7.10-7.05 (m, 3H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.81 (dd, *J* = 8.4, 1.1 Hz, 2H), 6.56 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 150.6, 143.8, 141.3, 141.2, 139.6, 138.6, 138.5, 129.9, 129.3, 129.2, 129.0, 128.5, 127.4, 126.7, 126.6, 125.6, 123.4, 122.1, 114.0, 95.7. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 350 nm): t_R = 5.69 min (major) and 9.23 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{19}N_2SCl_2^+$: 461.0641; Found 461.0631. **$[\alpha]_D^{23.3}$** = +88.7 (*c* = 0.25, $CHCl_3$). **Rf** 0.8 (hexane/AcOEt = 3:1).

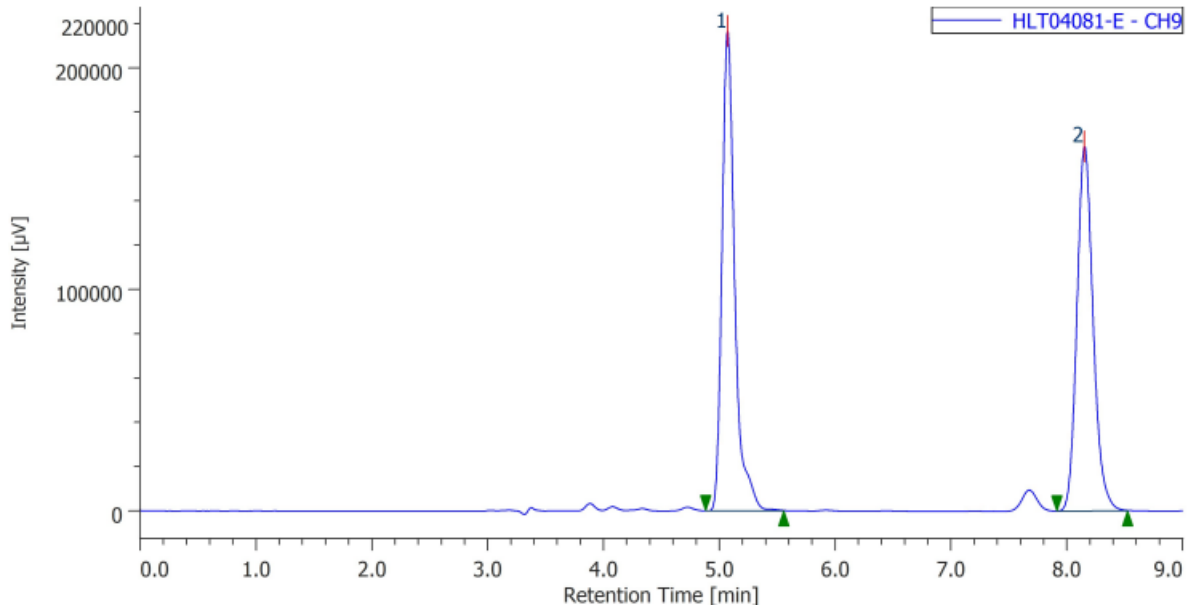


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.730	49.815
2	Unknown	9	9.327	50.185

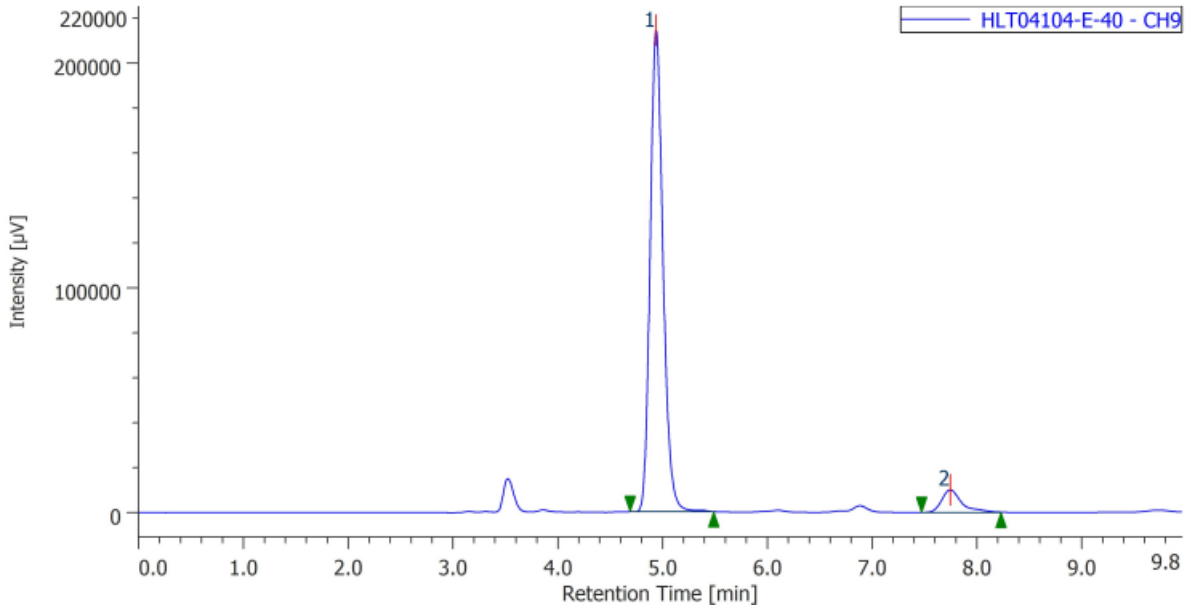


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.690	96.985
2	Unknown	9	9.233	3.015

(*S*)-7-methyl-N,3-diphenyl-1-(m-tolyl)-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3da): Prepared according to **GP-D** using compound **1d** (0.05 mmol, 16.0 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L7** (0.005 mmol, 2.4 mg, 10 mol%). **3da** was isolated as a yellow solid (14.3 mg, 68%). **IR** (KBr) 3051, 3023, 2947, 1588, 1483, 1358, 1285, 1255, 1114, 1037, 758, 685 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.99-7.96 (m, 4H), 7.45-7.32 (m, 6H), 7.22-7.19 (m, 2H), 7.06 (t, *J* = 7.9 Hz, 2H), 6.83-6.80 (m, 3H), 6.61 (s, 1H), 2.43 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 148.2, 144.8, 143.0, 139.3, 139.1, 137.3, 136.5, 133.7, 133.3, 128.8, 128.7, 128.4, 128.3, 126.4, 126.3, 125.9, 125.2, 123.3, 121.3, 116.2, 96.2, 21.5, 21.3; one aromatic signal was missing probably due to overlap. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 2/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 4.94 min (major) and 7.74 min (minor). **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{24}N_2SNa^+$: 443.1352; Found 443.1548. **$[\alpha]_D^{20.8}$** = +107.8 (*c* = 0.25, $CHCl_3$). **Rf** 0.6 (hexane/AcOEt = 3:1).

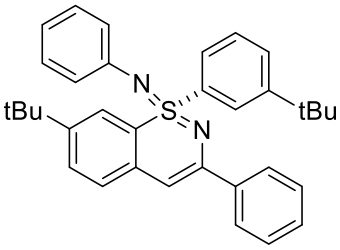


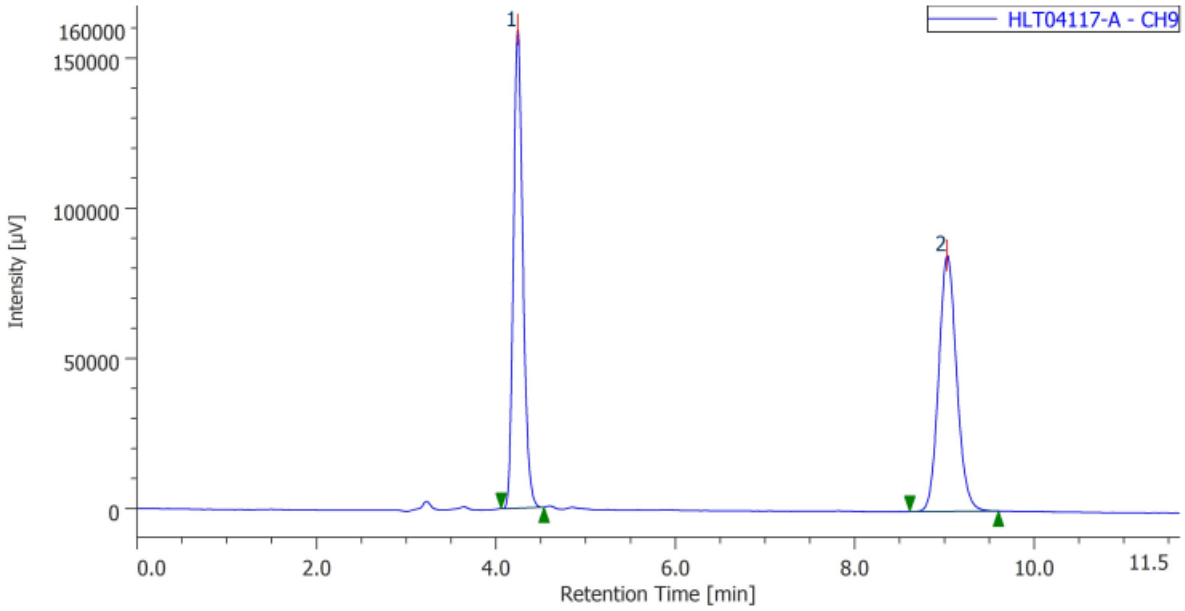
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.070	50.891
2	Unknown	9	8.150	49.109



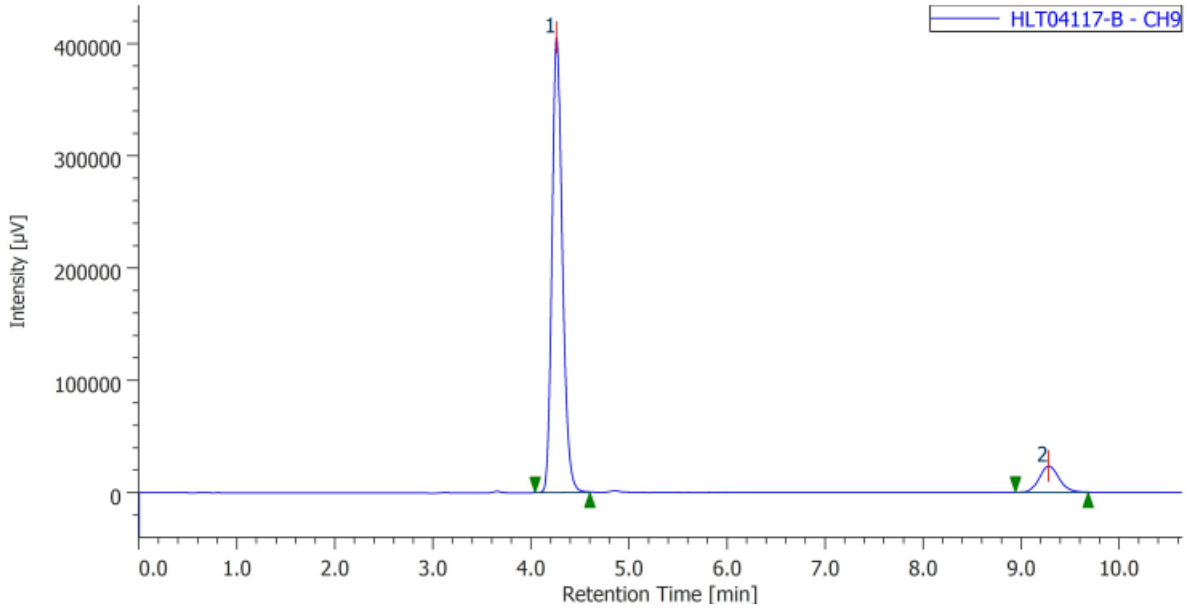
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	4.937	93.235
2	Unknown	9	7.743	6.765

(*S*)-7-(tert-butyl)-1-(3-(tert-butyl)phenyl)-N,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ea): Prepared according to **GP-D** using compound **1e** (0.05 mmol, 16.0 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L7** (0.005 mmol, 2.4 mg, 10 mol%). **3ea** was isolated as a yellow oil (17.2 mg, 68%). **IR** (neat) 2962, 2934, 2927, 1592, 1486, 1360, 1290, 1256, 1127 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.25 (s, 1H), 8.01 (d, *J* = 6.8 Hz, 2H), 7.86-7.83 (m, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.48-7.34 (m, 6H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.08-7.03 (m, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.57 (s, 1H), 1.33 (s, 9H), 1.19 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.2, 149.6, 148.3, 145.1, 142.4, 139.4, 137.2, 130.0, 129.4, 128.8, 128.7, 128.4, 128.3, 126.4, 126.2, 125.8, 124.8, 124.0, 121.6, 121.5, 116.0, 96.4, 35.1, 34.7, 31.2, 30.9. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 4.24 min (major) and 9.28 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{37}N_2S^+$: 505.2672; Found 505.2666. **$[\alpha]_D^{23.4}$** = +157.0 (*c* = 0.25, $CHCl_3$). **Rf** 0.8 (hexane/AcOEt = 3:1).



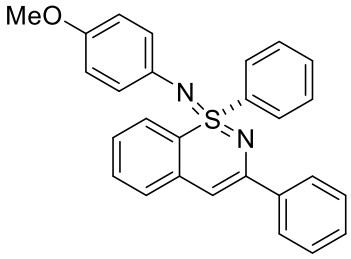


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	4.240	49.669
2	Unknown	9	9.027	50.331

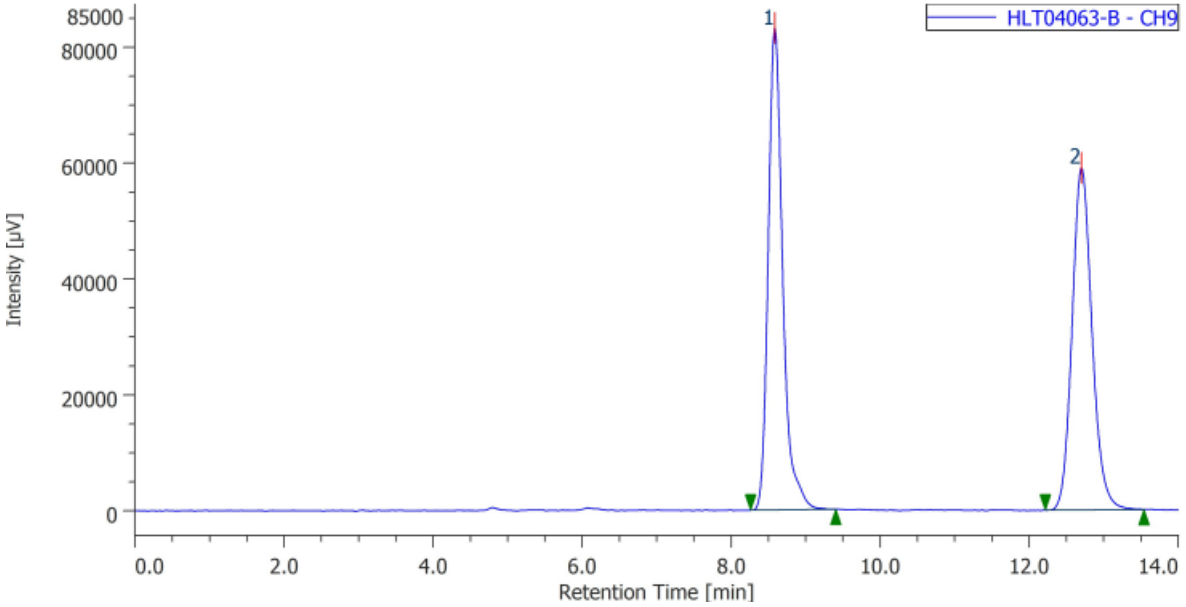


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	4.260	90.104
2	Unknown	9	9.280	9.896

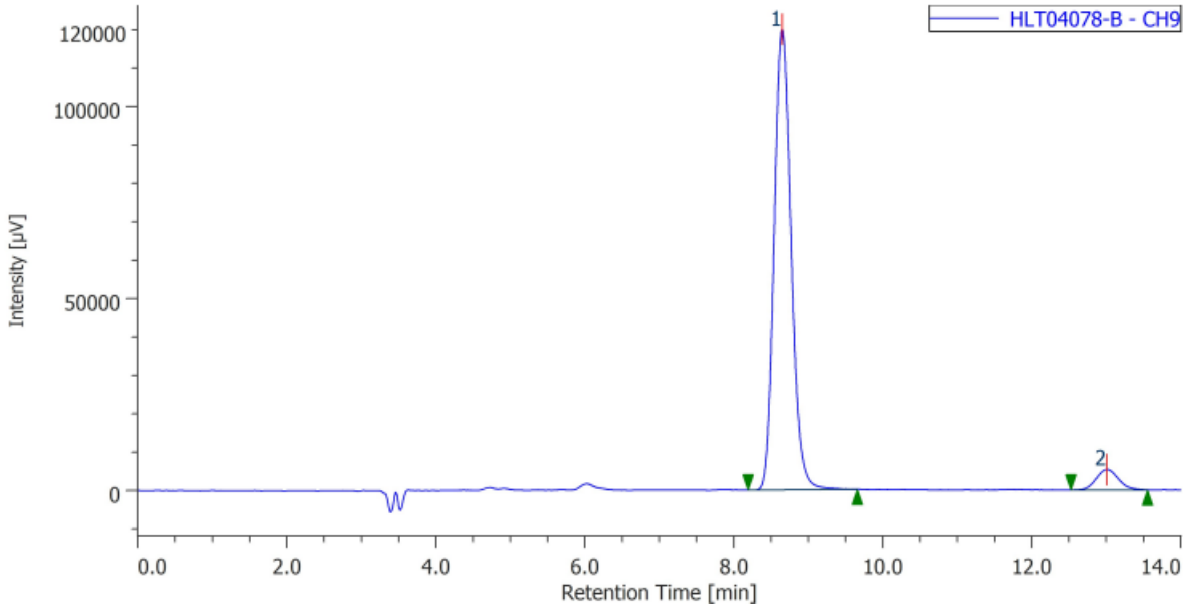
(*S*)-N-(4-methoxyphenyl)-1,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3fa): Prepared according to **GP-D** using compound **1f** (0.05 mmol, 16.1 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3fa** was isolated as a yellow solid (12.7 mg, 60%). **IR** (KBr) 2957, 2925, 2851, 1665, 1572, 1501, 1470, 1445, 1363, 1260, 1236, 1101, 1030, 801, 684 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ



8.18-8.15 (m, 2H), 8.00 (d, J = 8.1 Hz, 2H), 7.55-7.53 (m, 3H), 7.45-7.34 (m, 5H), 7.28 (d, J = 8.1 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 6.79 (d, J = 7.2 Hz, 2H), 6.61 (d, J = 7.2 Hz, 2H), 6.58 (s, 1H), 3.65 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 154.8, 149.2, 142.9, 139.8, 139.2, 137.5, 132.4, 132.1, 128.9, 128.7, 128.6, 128.3, 126.5, 126.4, 126.2, 126.0, 124.5, 116.4, 114.2, 96.3, 55.3. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 350 nm): t_R = 8.65 min (major) and 13.00 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{23}N_2SO^+$: 423.1526; Found 423.1519. **$[\alpha]_D^{20.1}$** = +28.3 (c = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).

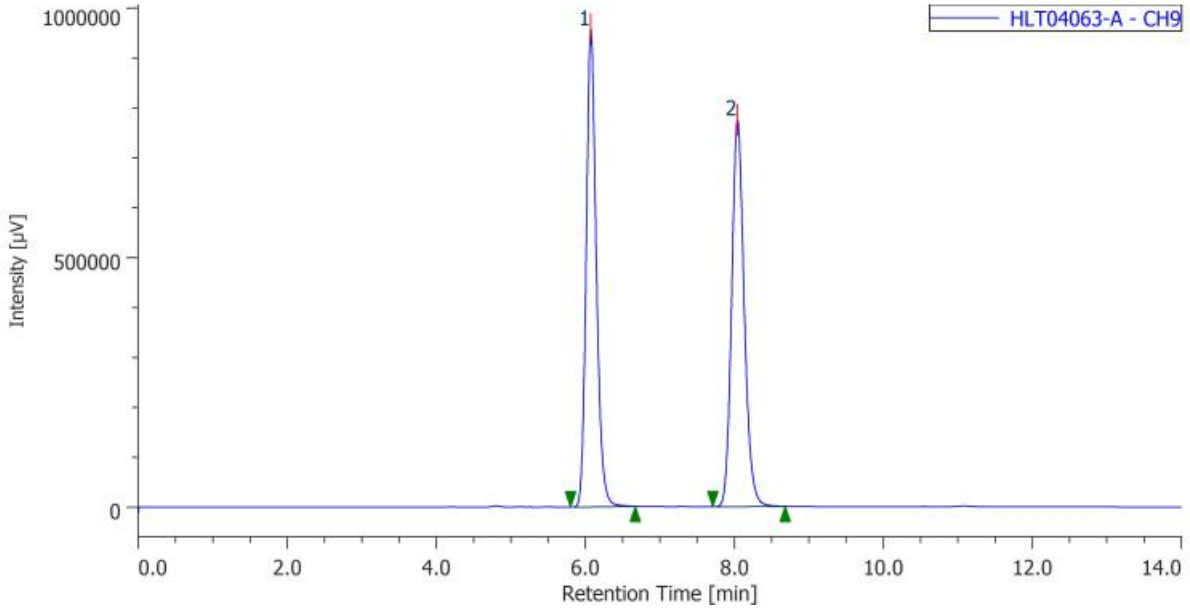


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	8.583	50.634
2	Unknown	9	12.697	49.366

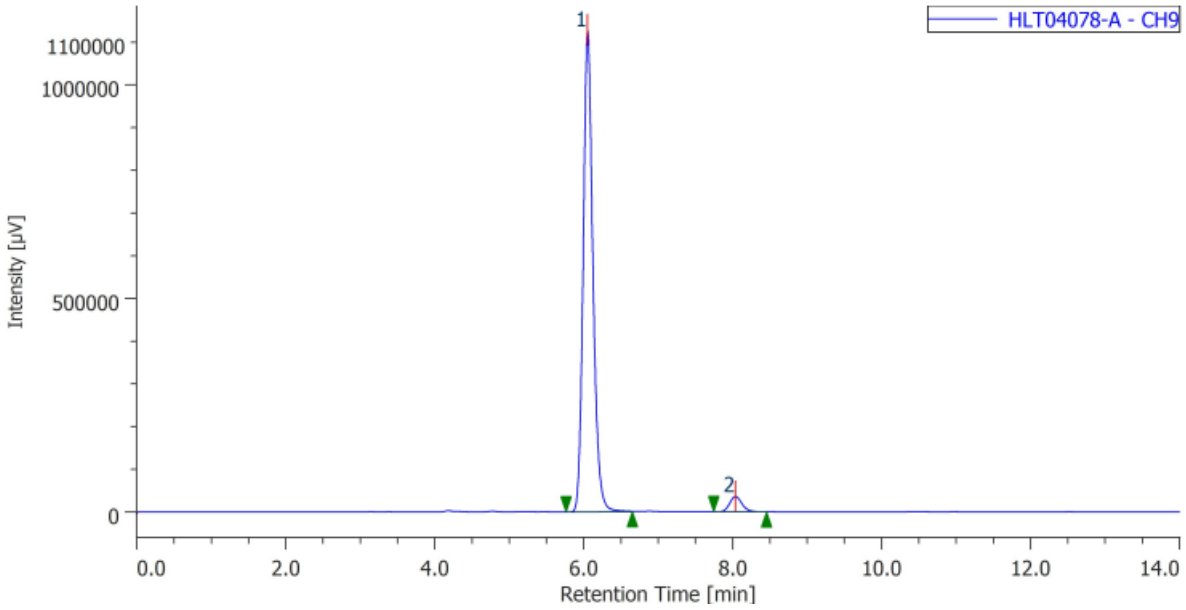


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	8.647	94.479
2	Unknown	9	13.003	5.521

(*S*)-N-(4-chlorophenyl)-1,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ga): Prepared according to **GP-D** using compound **1g** (0.05 mmol, 16.3 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ga** was isolated as a yellow solid (13.8 mg, 65%). **IR** (KBr) 1584, 1530, 1484, 1446, 1362, 1277, 1250, 1116, 1085, 824, 755 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.17-8.15 (m, 2H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.58-7.56 (m, 3H), 7.44-7.36 (m, 5H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.64 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 149.0, 147.6, 143.4, 142.7, 139.7, 138.9, 132.7, 132.3, 129.0, 128.8, 128.6, 128.4, 126.8, 126.5, 126.5, 125.8, 124.6, 115.8, 96.5; one aromatic signal was missing probably due to overlap. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 6.05 min (major) and 8.03 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{20}N_2SCl^+$: 427.1030; Found 427.1028. **$[\alpha]_D^{21.5}$** = +155.6 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).

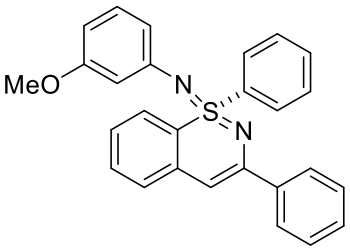


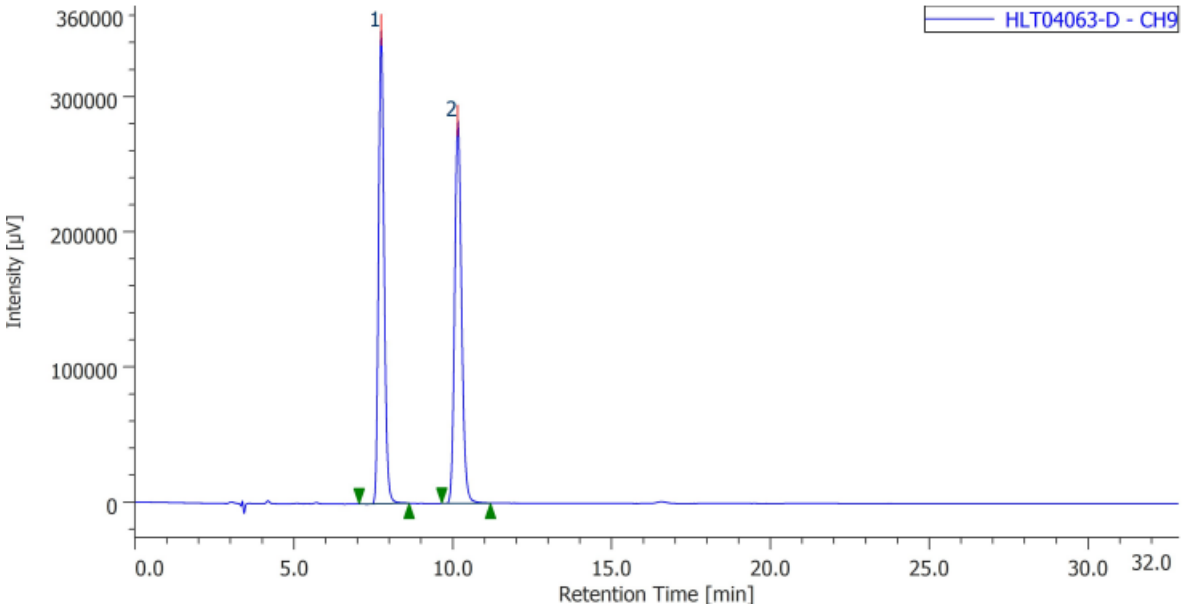
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.070	49.736
2	Unknown	9	8.040	50.264



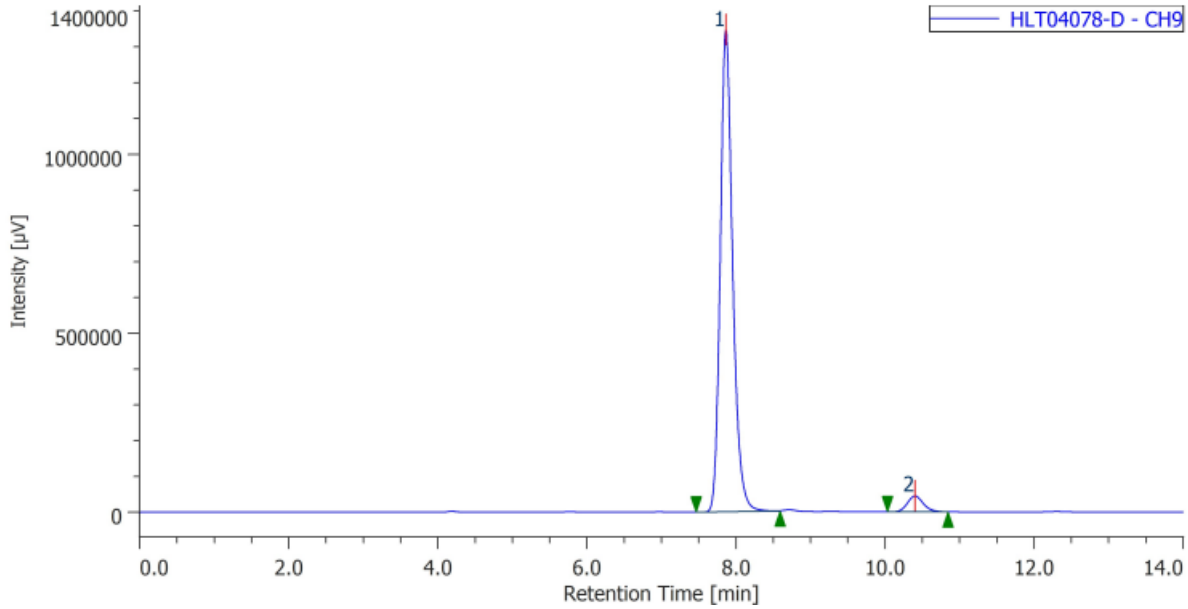
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.050	96.060
2	Unknown	9	8.033	3.940

(*S*)-N-(3-methoxyphenyl)-1,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ha): Prepared according to **GP-D** using compound **1h** (0.05 mmol, 16.1 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ha** was isolated as a yellow solid (15.8 mg, 75%). **IR** (KBr) 3056, 2928, 1585, 1530, 1471, 1445, 1362, 1282, 1209, 1162, 1116, 1085, 758, 720 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.20-8.18 (m, 2H), 8.01-7.98 (m, 2H), 7.58-7.54 (m, 3H), 7.44-7.33 (m, 5H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.14-7.10 (m, 1H), 6.97-6.93 (m, 1H), 6.64 (s, 1H), 6.46-6.39 (m, 3H), 3.58 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 160.0, 149.1, 145.9, 142.8, 139.7, 139.1, 132.6, 132.2, 129.4, 128.9, 128.7, 128.7, 128.3, 126.5, 126.4, 126.4, 125.9, 116.3, 115.9, 108.3, 108.3, 96.4, 54.9. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 7.86 min (major) and 10.40 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{23}N_2SO^+$: 423.1526; Found 423.1520. **$[\alpha]_D^{22.3}$** = +145.3 (*c* = 0.25, $CHCl_3$). **Rf** 0.6 (hexane/AcOEt = 3:1).



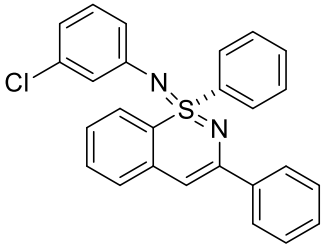


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	7.743	49.888
2	Unknown	9	10.157	50.112

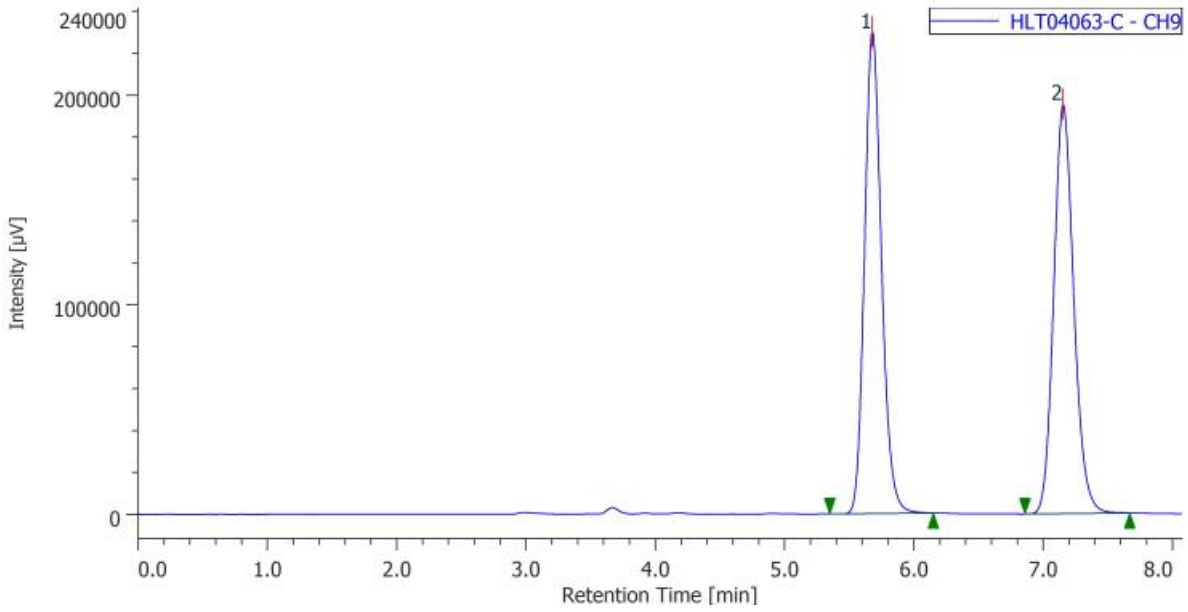


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	7.860	95.843
2	Unknown	9	10.397	4.157

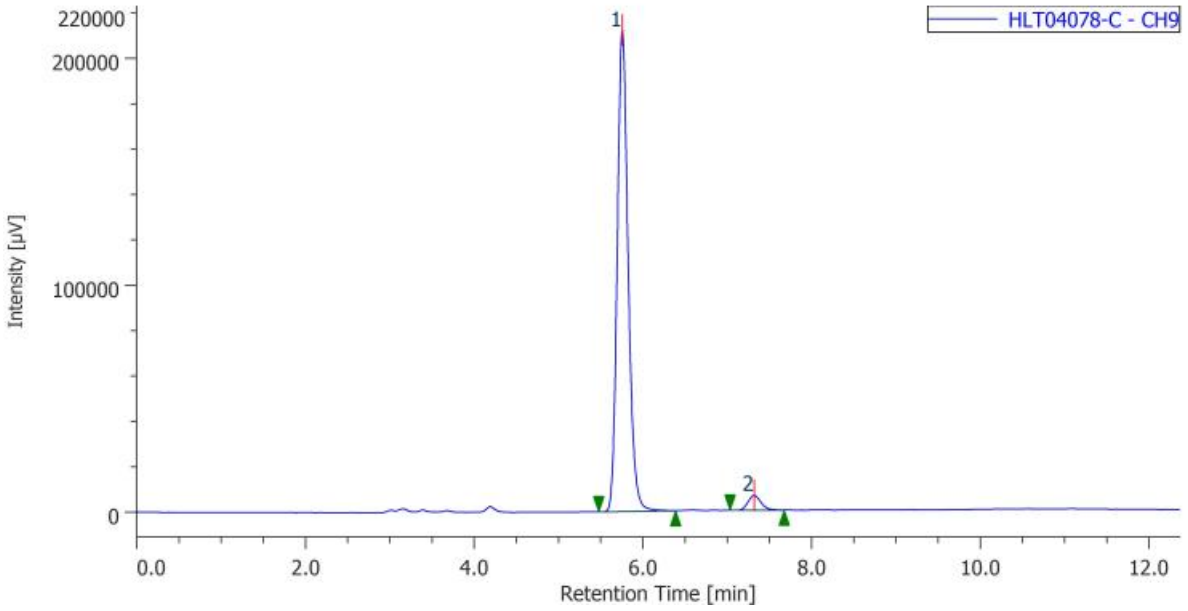
(*S*)-N-(3-chlorophenyl)-1,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ia): Prepared according to **GP-D** using compound **1i** (0.05 mmol, 16.3 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ia** was isolated as a yellow solid (14.9 mg, 70%). **IR** (KBr) 1584, 1530, 1469, 1445, 1263, 1238, 1115, 1022, 936, 757, 684 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.18-8.14 (m, 2H), 7.99 (d, *J* = 8.2 Hz, 2H),



7.58-7.54 (m, 3H), 7.44-7.36 (m, 5H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.96-6.91 (m, 2H), 6.81-6.77 (m, 1H), 6.67 (s, 1H), 6.64-6.60 (m, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 149.1, 146.1, 142.6, 139.7, 138.9, 134.2, 132.7, 132.4, 129.6, 129.0, 128.8, 128.6, 128.4, 126.6, 126.5, 125.8, 125.3, 124.0, 121.5, 121.0, 115.8, 96.6. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 350 nm): t_R = 5.75 min (major) and 7.32 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{20}N_2SCl^+$: 427.1030; Found 427.1027. **$[\alpha]_D^{22.3}$** = +118.1 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).

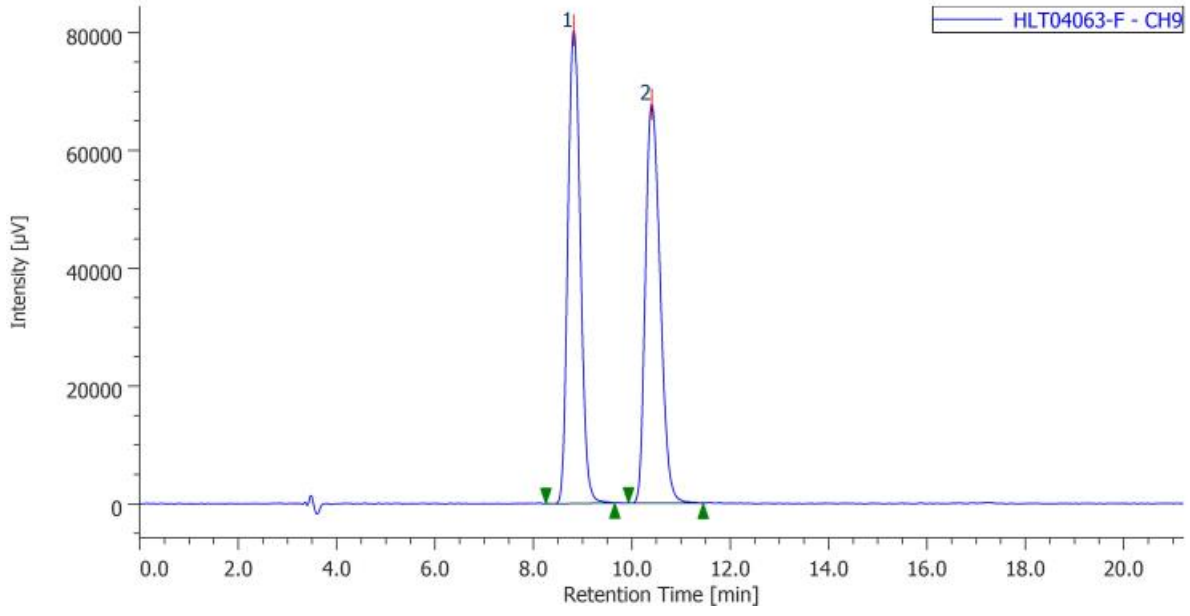


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.677	50.030
2	Unknown	9	7.150	49.970

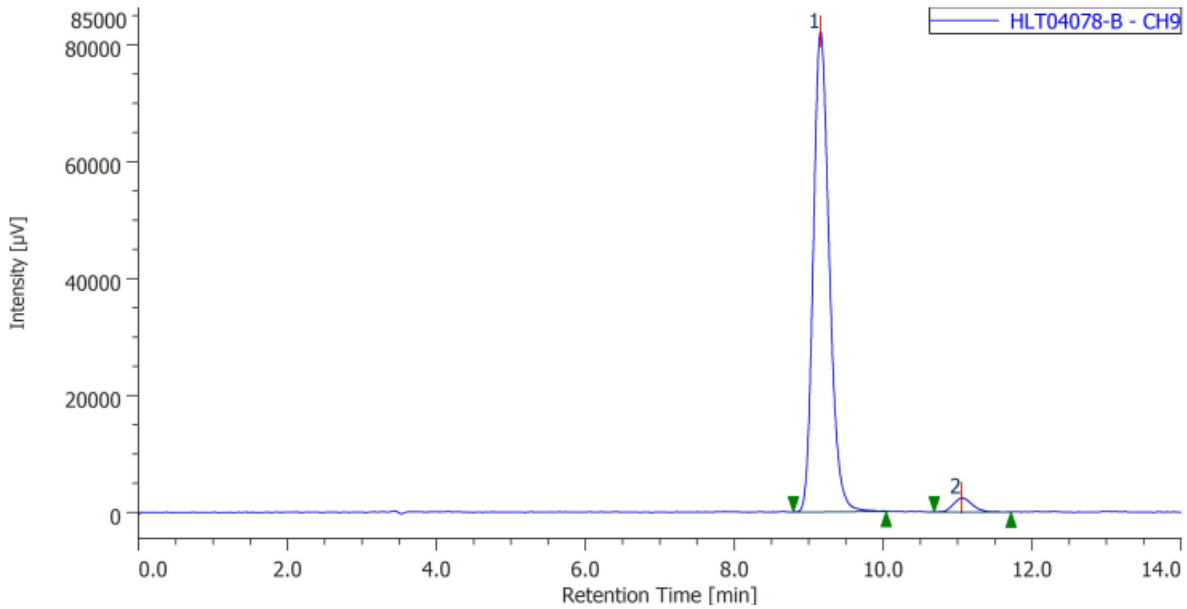


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.753	96.409
2	Unknown	9	7.317	3.591

(*S*)-N-(2-ethylphenyl)-1,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ja): Prepared according to **GP-D** using compound **1j** (0.05 mmol, 16.0 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ja** was isolated as a yellow amorphous (13.4 mg, 65%). **IR** (neat) 3059, 2959, 2925, 1583, 1530, 1472, 1446, 1363, 1281, 1257, 1126, 767, 753, 685 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.20-8.18 (m, 2H), 7.99 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.58-7.54 (m, 3H), 7.42-7.29 (m, 6H), 7.12-7.04 (m, 2H), 6.80-6.74 (m, 2H), 6.66 (s, 1H), 6,36-6.34 (m, 1H), 2.98-2.87 (m, 2H), 1.33 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 149.3, 144.0, 142.3, 140.0, 139.2, 138.9, 132.4, 132.1, 128.9, 128.7, 128.6, 128.3, 126.5, 126.3, 126.1, 125.8, 121.5, 120.6, 116.6, 96.3, 25.5, 14.5; two aromatic signals were missing probably due to overlap. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 350 nm): t_R = 9.16 min (major) and 11.05 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{25}N_2S^+$: 421.1733; Found 421.1727. **$[\alpha]_D^{18.7}$** = +70.5 (*c* = 0.25, $CHCl_3$). **Rf** 0.7 (hexane/AcOEt = 3:1).

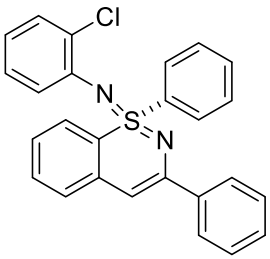


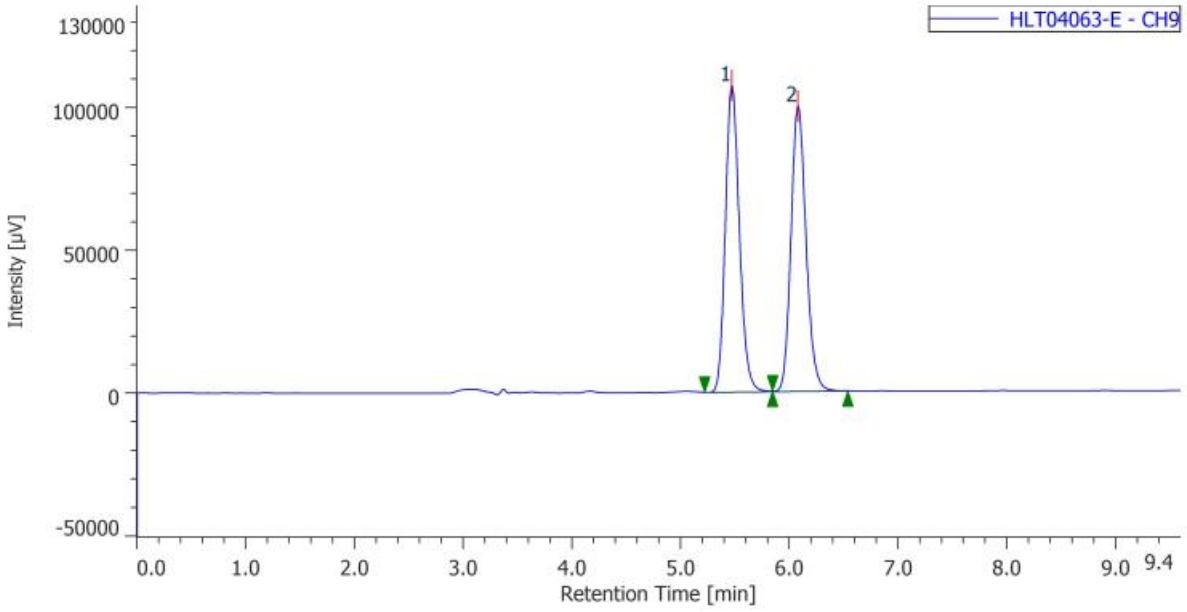
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	8.817	50.050
2	Unknown	9	10.400	49.950



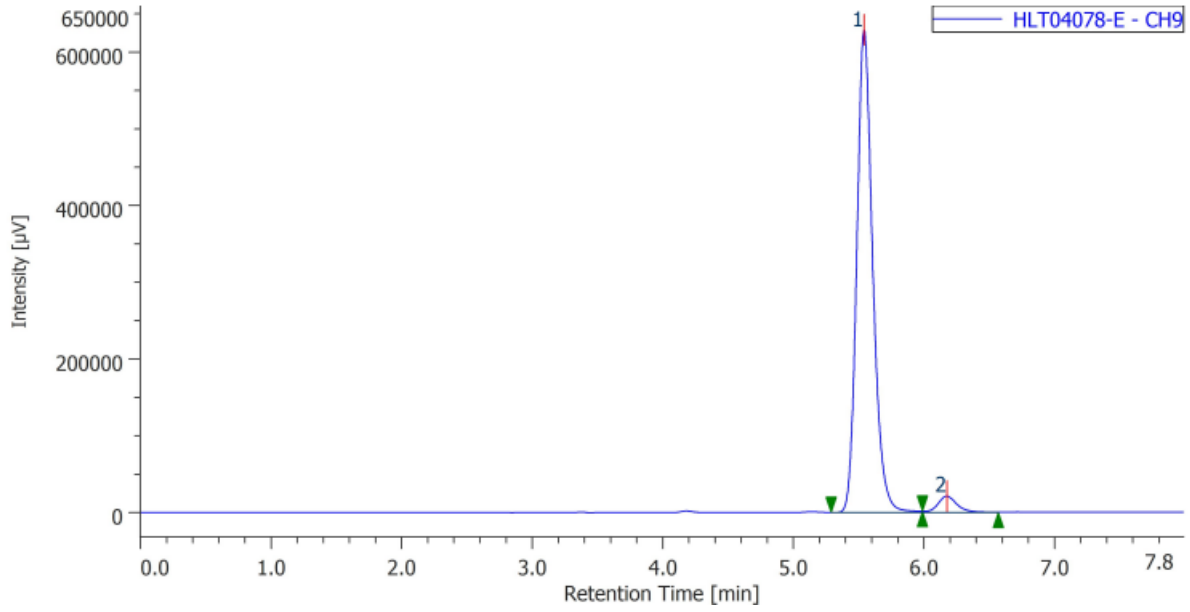
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	9.157	96.618
2	Unknown	9	11.050	3.382

(*S*)-N-(2-chlorophenyl)-1,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ka): Prepared according to **GP-D** using compound **1k** (0.05 mmol, 16.3 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ka** was isolated as a yellow solid (14.9 mg, 70%). **IR** (KBr) 1583, 1530, 1471, 1362, 1308, 1280, 1249, 1116, 1019, 751, 720, 679 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.31-8.29 (m, 2H), 8.04-8.02 (m, 2H), 7.58-7.56 (m, 3H), 7.47-7.33 (m, 5H), 7.30-7.27 (m, 2H), 7.13-7.09 (m, 1H), 6.82 (td, *J* = 7.7, 1.8 Hz, 1H), 6.74 (td, *J* = 7.6, 1.7 Hz, 1H), 6.67 (s, 1H), 6.57 (dd, *J* = 7.9, 1.6 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 148.7, 143.3, 141.8, 139.9, 138.9, 132.7, 132.4, 129.8, 129.7 129.0, 128.9, 128.8, 128.4, 127.0, 126.6, 126.5, 126.4, 126.0. 122.4, 122.3, 115.8, 96.4. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 5.54 min (major) and 6.17 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{20}N_2SCl^+$: 427.1030; Found 427.1025. **$[\alpha]_D^{22.6}$** = +69.6 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).



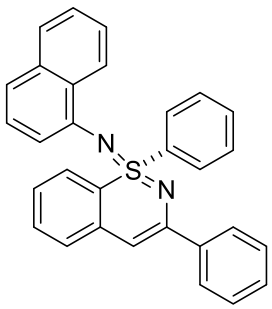


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.470	49.960
2	Unknown	9	6.077	50.040



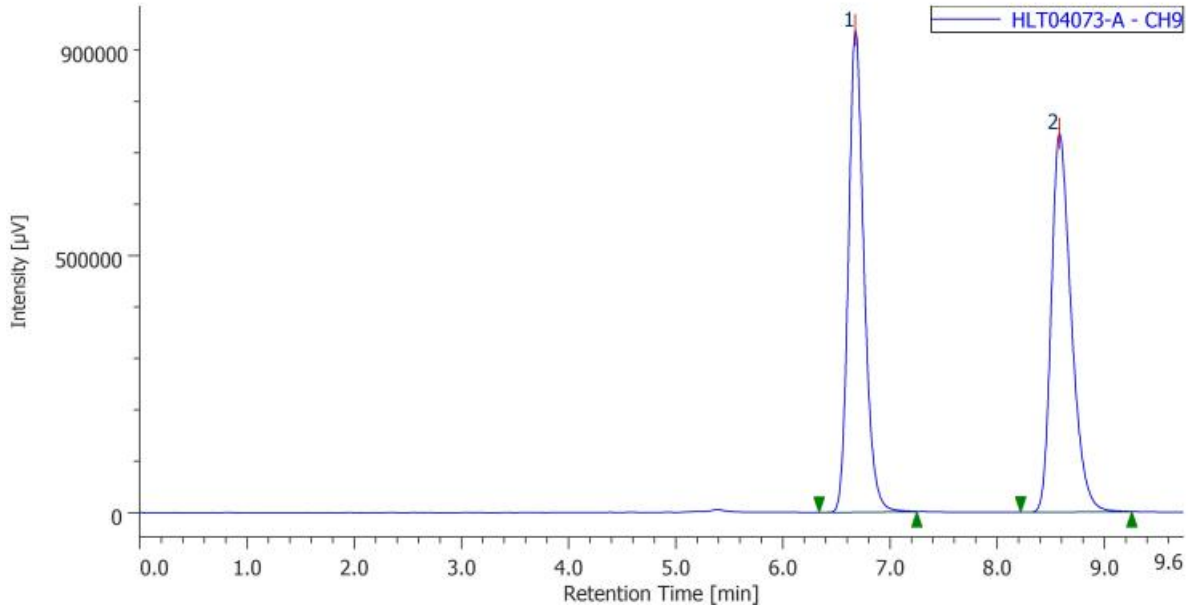
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.540	96.181
2	Unknown	9	6.173	3.819

(*S*)-N-(naphthalen-1-yl)-1,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3la):

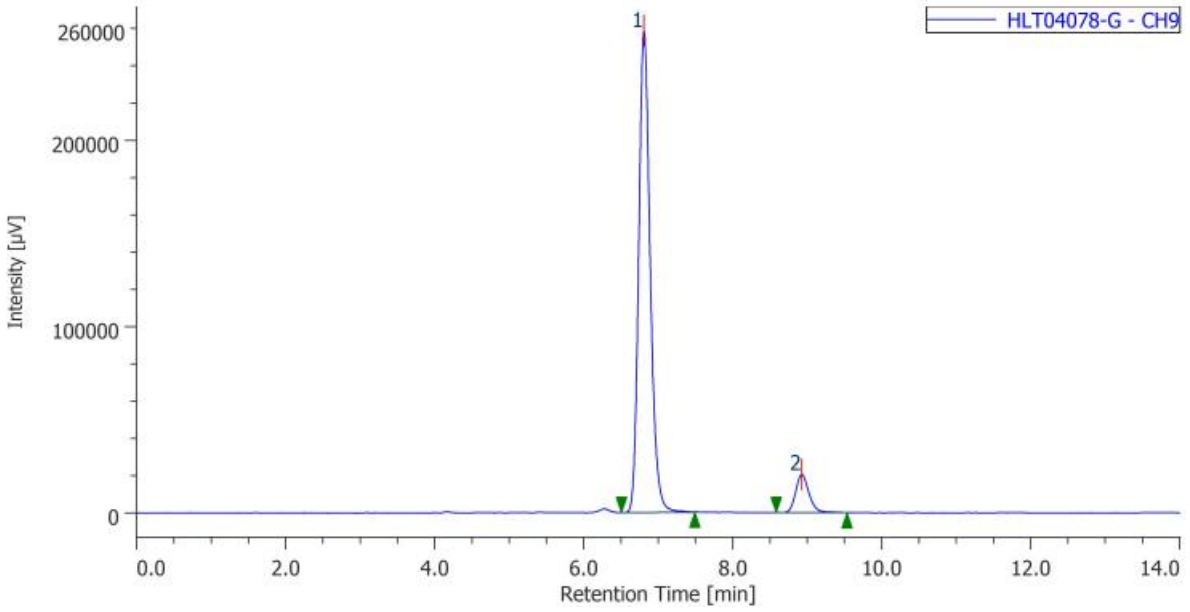


Prepared according to **GP-D** using compound **1l** (0.05 mmol, 17.1 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3la** was isolated as a yellow solid (11.9 mg, 54%). **IR** (KBr) 1570, 1530, 1470, 1394, 1362, 1278, 1112, 794, 750, 684 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.72 (d, *J* = 7.7 Hz, 1H), 8.33-8.29

(m, 2H), 8.04-8.00 (m, 2H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.63-7.60 (m, 3H), 7.54-7.49 (m, 1H), 7.48-7.30 (m, 8H), 7.05 (t, *J* = 7.9 Hz, 2H), 6.70 (s, 1H), 6.49 (d, *J* = 6.3 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 149.3, 143.6, 141.1, 140.1, 139.1, 134.6, 132.6, 132.3, 130.9, 129.0, 128.7, 128.6, 128.4, 127.7, 126.5, 126.5, 126.3, 126.0, 125.8, 125.8, 124.8, 124.3, 121.3, 115.9, 115.6, 96.5. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 320 nm): t_R = 6.80 min (major) and 8.92 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{23}N_2S^+$: 443.1576; Found 443.1571. **$[\alpha]_D^{19.9}$** = +9.3 (*c* = 0.25, $CHCl_3$). **Rf** 0.6 (hexane/AcOEt = 3:1).

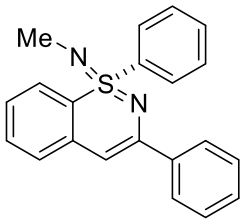


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.673	49.737
2	Unknown	9	8.577	50.263

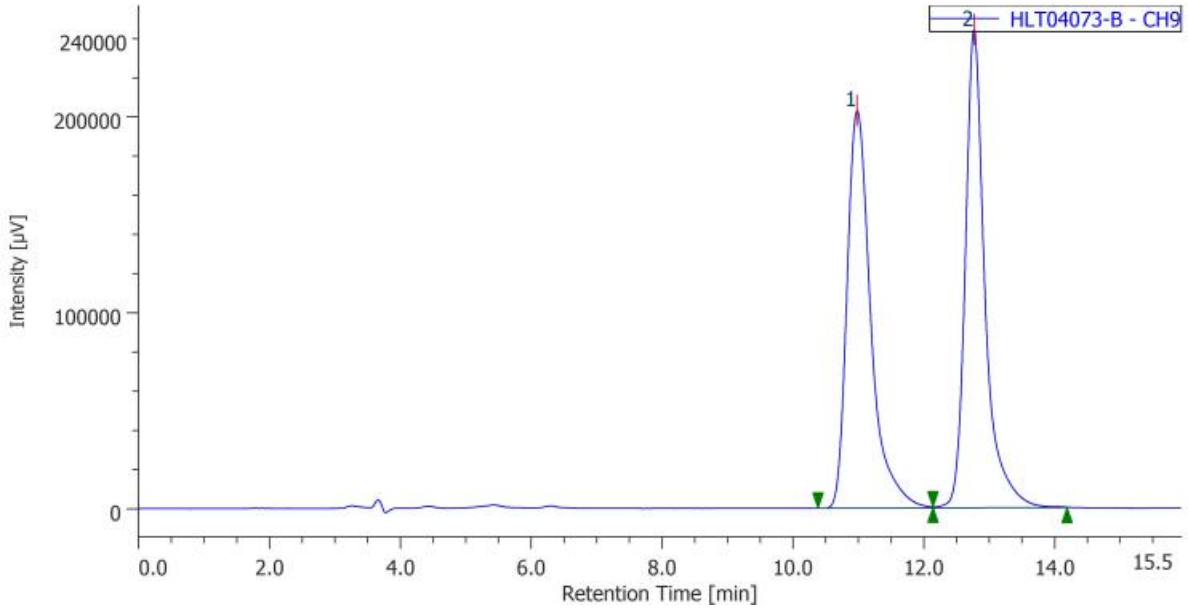


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.803	91.461
2	Unknown	9	8.923	8.539

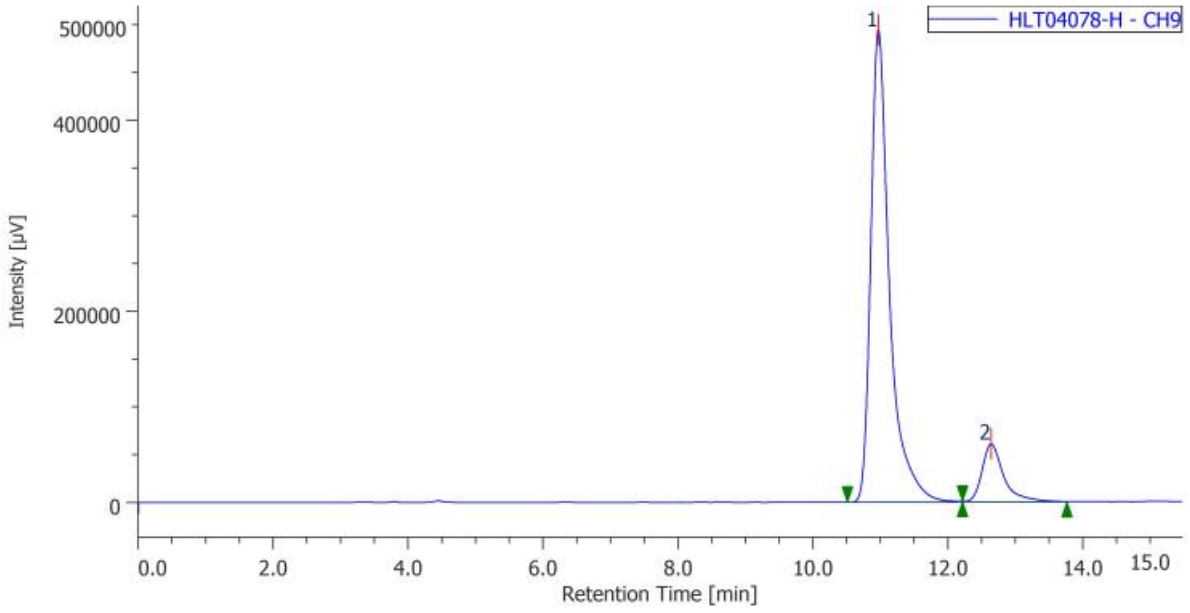
(*S*)-N-methyl-1,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ma): Prepared according to **GP-D** using compound **1m** (0.05 mmol, 11.5 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ma** was isolated as a yellow solid (13.2 mg, 80%).



IR (KBr) 3056, 2861, 1582, 1528, 1471, 1445, 1361, 1199, 1102, 947, 766 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.04-7.95 (m, 4H), 7.52-7.36 (m, 8H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.52 (s, 1H), 2.75 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 150.2, 142.5, 140.0, 139.4, 132.3, 132.0, 128.8, 128.6, 128.3, 127.8, 126.5, 126.3, 126.0, 125.8, 115.3, 96.1, 29.6. **HPLC** (chiral column: DAICEL CHIRALPAK IA; solvent: hexane/2-propanol = 19/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 11.00 min (major) and 12.64 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}N_2S^+$: 331.1263; Found 331.1257. **$[\alpha]_D^{19.8}$** = –130.0 (*c* = 0.25, $CHCl_3$). **Rf** 0.2 (hexane/AcOEt = 3:1).

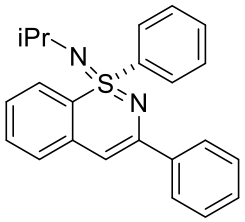


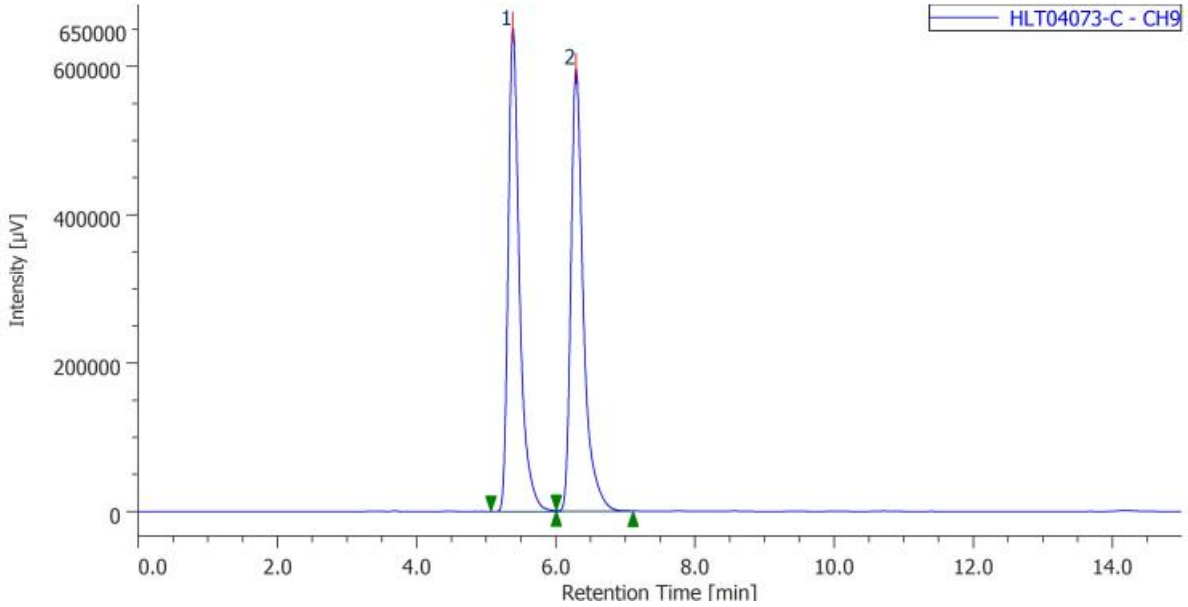
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	10.977	50.072
2	Unknown	9	12.763	49.928



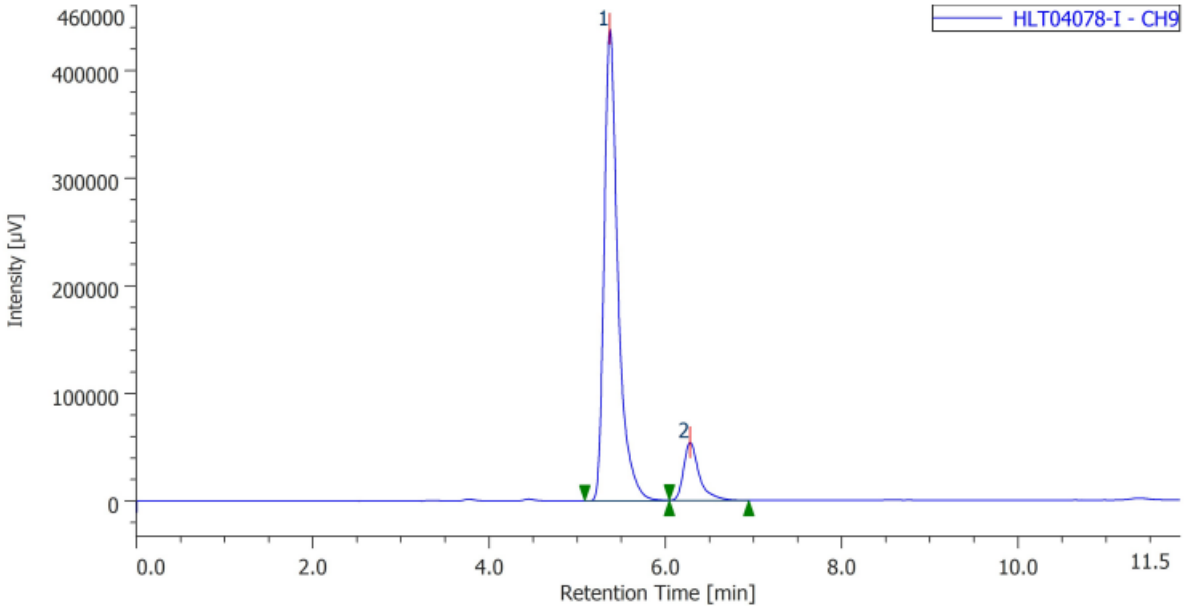
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	10.967	87.592
2	Unknown	9	12.637	12.408

(*S*)-N-isopropyl-1,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3na): Prepared according to **GP-D** using compound **1n** (0.05 mmol, 12.9 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3na** was isolated as a yellow solid (14.4 mg, 79%). **IR** (KBr) 3061, 2965, 2922, 2857, 1571, 1530, 1473, 1445, 1366, 1287, 1181, 1116, 940, 821, 756, 682 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.08-8.00 (m, 4H), 7.51-7.46 (m, 3H), 7.44-7.33 (m, 5H), 7.32-7.29 (m, 1H), 7.19-7.14 (m, 1H), 6.52 (s, 1H), 3.30-3.24 (m, 1H), 1.18 (d, *J* = 6.3 Hz, 3H), 1.09 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 149.6, 142.6, 139.7, 139.6, 132.1, 131.6, 128.7, 128.5, 128.4, 128.3, 126.5, 126.1, 125.9, 125.7, 117.3, 95.6, 46.0, 26.4, 26.1. **HPLC** (chiral column: DAICEL CHIRALPAK IA; solvent: hexane/2-propanol = 19/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 5.37 min (major) and 6.28 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{23}N_2S^+$: 359.1576; Found 359.1572. **$[\alpha]_D^{23.1}$** = +227.1 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).



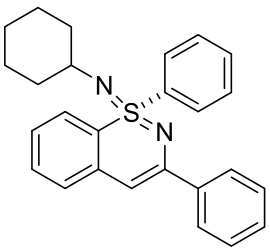


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.380	49.871
2	Unknown	9	6.290	50.129

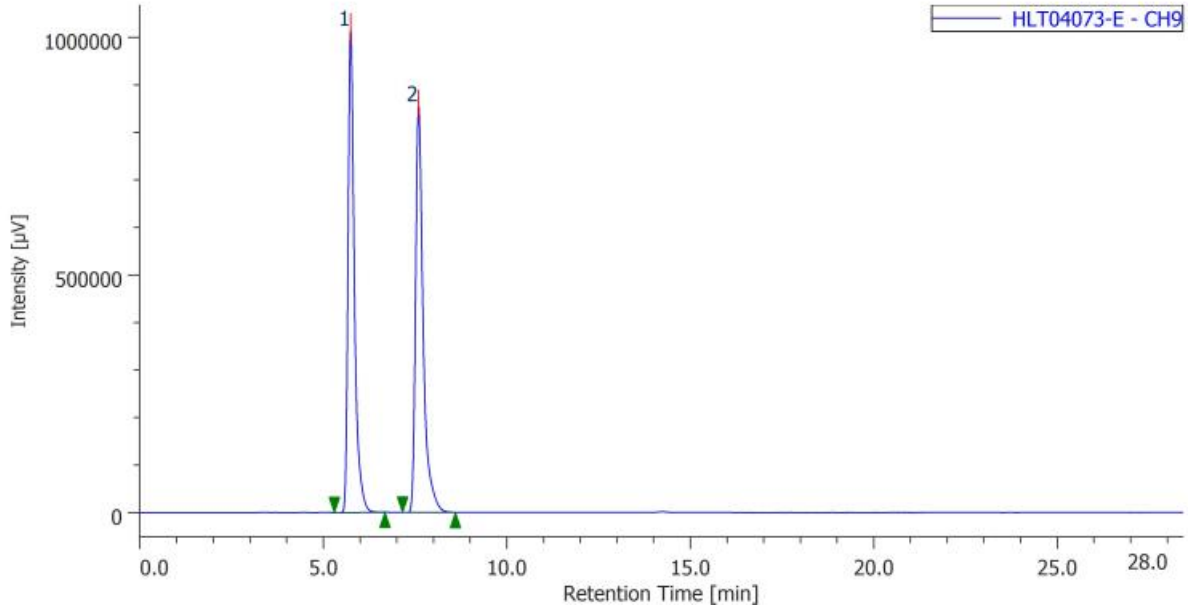


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.367	87.803
2	Unknown	9	6.277	12.197

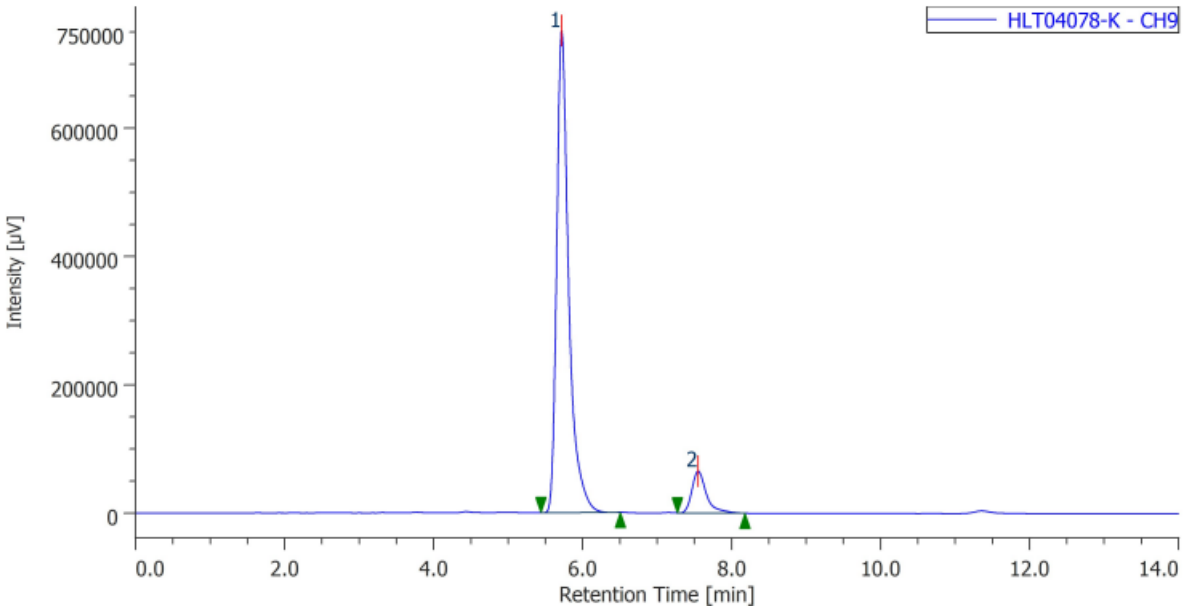
(*S*)-N-cyclohexyl-1,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3oa): Prepared according to **GP-D** using compound **1o** (0.05 mmol, 14.9 mg, 1.0 equiv.), **2a** (0.055 mmol, 10.8 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3oa** was isolated as a yellow solid (14.3 mg, 72%). **IR** (KBr) 3059, 2926, 2850, 1571, 1527, 1472, 1444, 1366,



1181, 1106, 945, 765, 720 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.05-7.98 (m, 4H), 7.49-7.45 (m, 3H), 7.44-7.33 (m, 5H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.51 (s, 1H), 2.99-2.90 (m, 1H), 1.86-1.79 (m, 1H), 1.70-1.58 (m, 3H), 1.52-1.34 (m, 3H), 1.19-1.05 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 149.6, 143.0, 139.8, 139.5, 132.0, 131.6, 128.7, 128.4, 128.3, 128.2, 126.5, 126.1, 126.0, 125.6, 117.7, 95.6, 53.4, 36.7, 36.2, 25.8, 25.3, 25.2. **HPLC** (chiral column: DAICEL CHIRALPAK IA; solvent: hexane/2-propanol = 19/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 5.72 min (major) and 7.55 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{27}N_2S^+$: 399.1889; Found 399.1886. **$[\alpha]_D^{23.6}$** = +195.2 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).

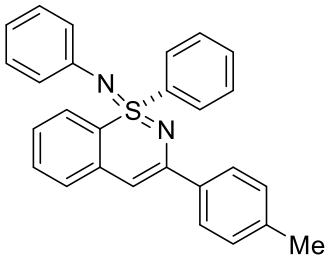


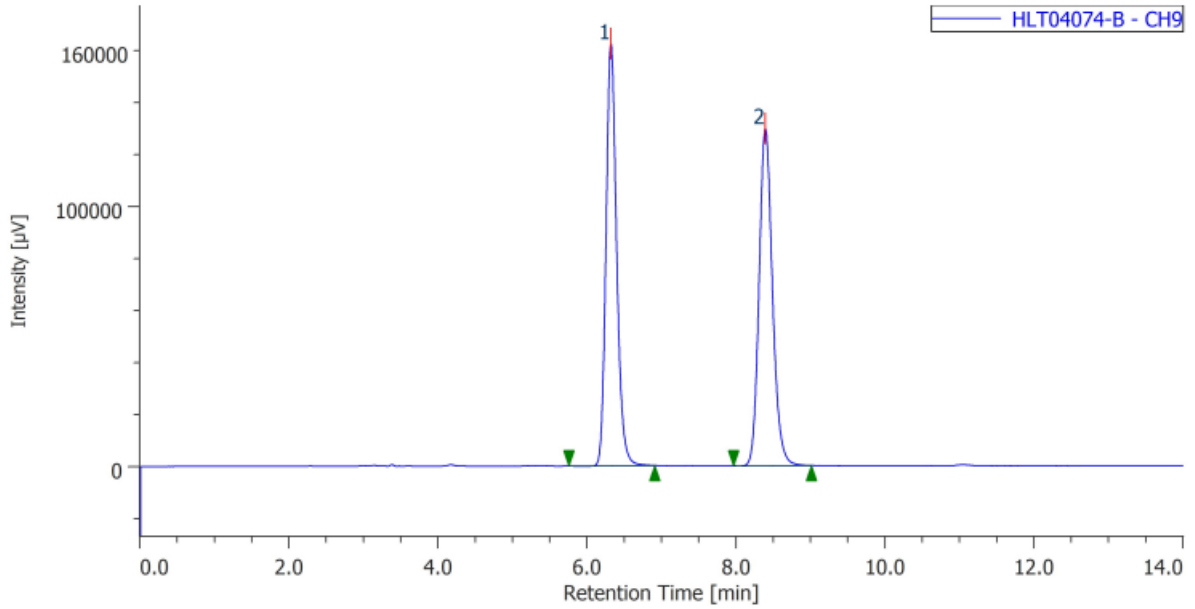
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.740	49.730
2	Unknown	9	7.593	50.270



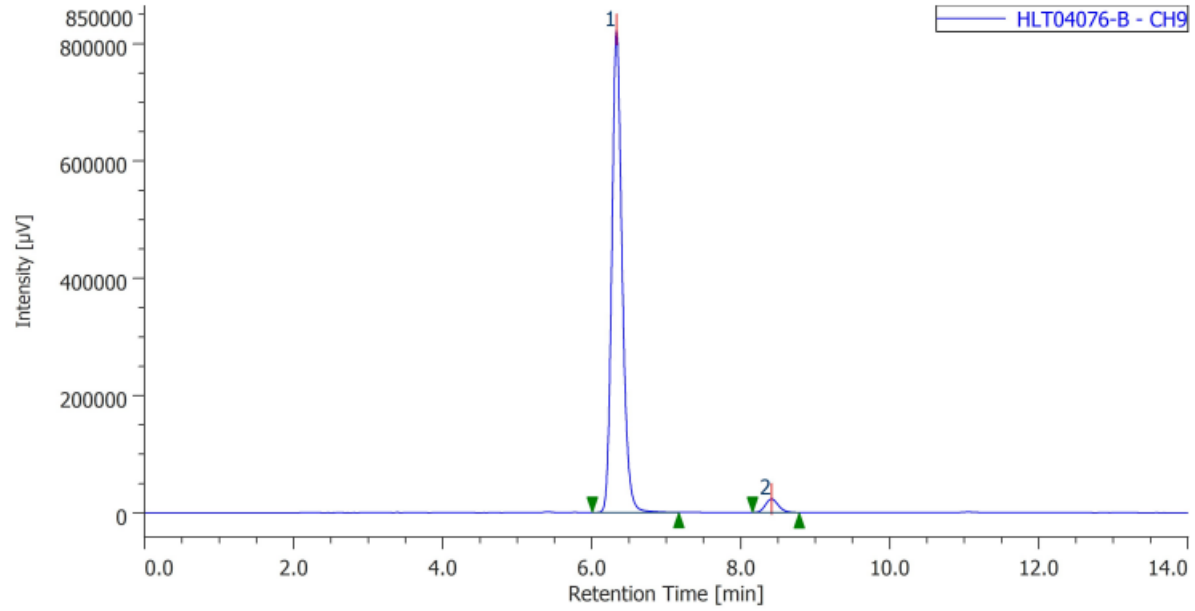
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.717	90.486
2	Unknown	9	7.547	9.514

(*S*)-N,1-diphenyl-3-(p-tolyl)-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ab): Prepared according to **GP-D** using compound **1a** (0.05 mmol, 14.6 mg, 1.0 equiv.), **2b** (0.055 mmol, 11.6 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ab** was isolated as a yellow solid (14.6 mg, 72%). **IR** (KBr) 3056, 1579, 1506, 1471, 1283, 1256, 1116, 1086, 749, 682, 607 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.19-8.16 (m, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.56-7.53 (m, 3H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.35 (td, *J* = 7.6, 1.1 Hz, 1H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.12-7.03 (m, 3H), 6.86-6.80 (m, 3H), 6.60 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 149.2, 144.7, 143.1, 139.9, 138.8, 136.3, 132.5, 132.1, 129.1, 128.9, 128.8, 128.5, 126.4, 126.3, 126.1, 125.9, 123.5, 121.5, 116.1, 95.8, 21.3. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 6.33 min (major) and 8.41 min (minor). **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{22}N_2SNa^+$: 429.1396; Found 429.1394. **$[\alpha]_D^{22.6}$** = +150.2 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).



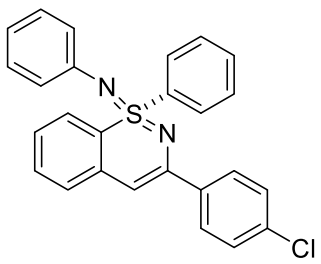


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.320	49.816
2	Unknown	9	8.390	50.184

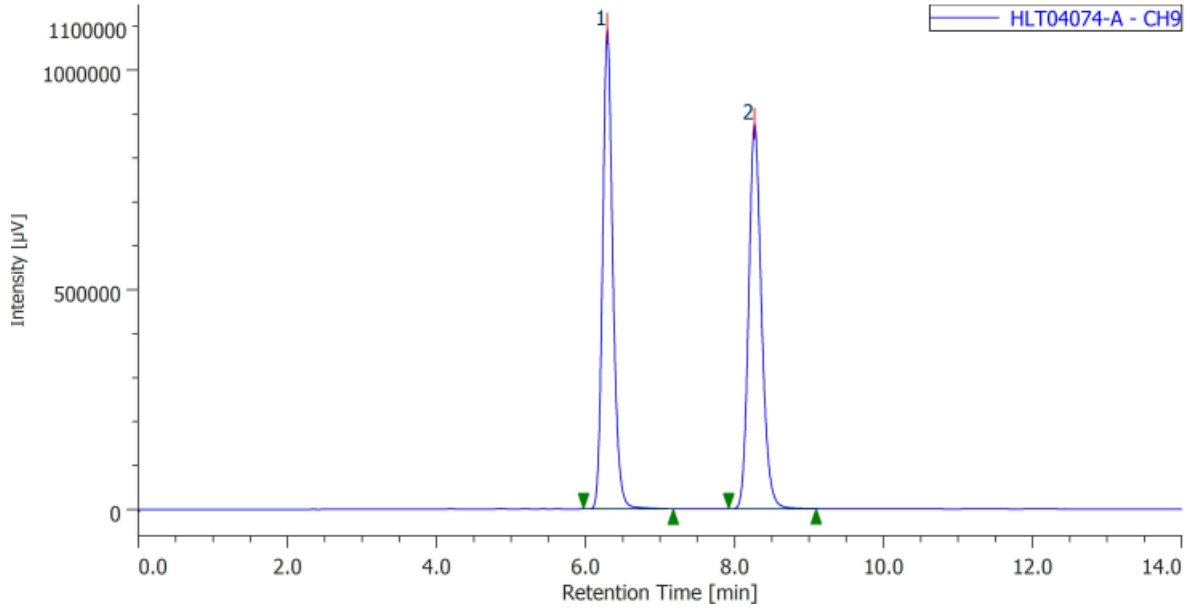


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.330	96.543
2	Unknown	9	8.410	3.457

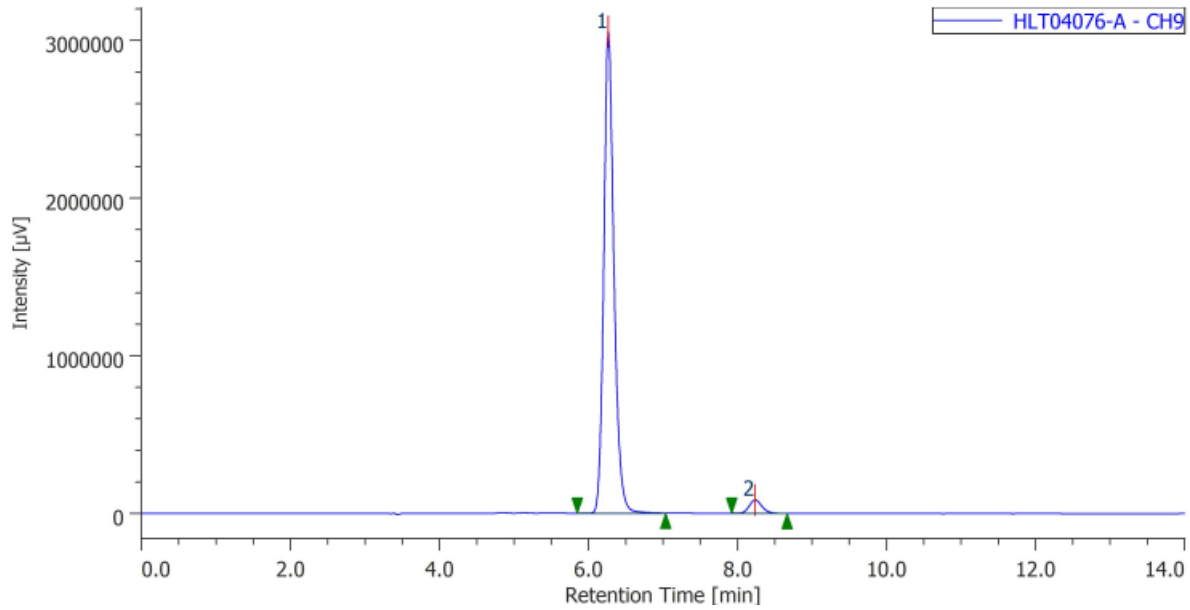
(*S*)-3-(4-chlorophenyl)-N,1-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ac): Prepared according to **GP-D** using compound **1a** (0.05 mmol, 14.6 mg, 1.0 equiv.), **2c** (0.055 mmol, 12.7 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ac** was isolated as a yellow solid (18.3 mg, 86%). **IR** (KBr) 1579, 1531, 1471, 1402, 1283, 1256, 1115, 1086, 756 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.18-8.15 (m, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.58-7.55 (m, 3H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.40-7.36 (m, 3H), 7.29 (d, *J* = 8.2 Hz,



1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.85-6.80 (m, 3H), 6.60 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 147.9, 144.4, 142.8, 139.5, 137.6, 134.6, 132.6, 132.2, 129.0, 128.9, 128.6, 128.5, 127.8, 126.6, 126.4, 125.9, 123.5, 121.7, 116.5, 96.4. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 6.26 min (major) and 8.23 min (minor). **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{19}N_2SClNa^+$: 449.0850; Found 449.0845. **$[\alpha]_D^{22.9}$** = +127.5 (*c* = 0.25, $CHCl_3$). **Rf** 0.6 (hexane/AcOEt = 3:1).

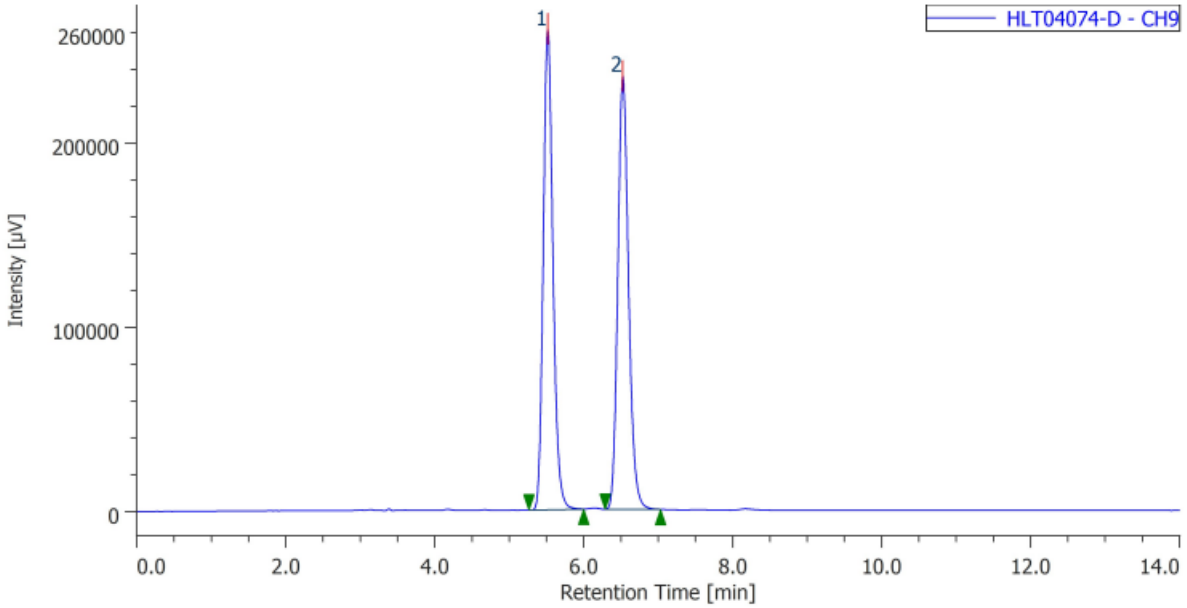


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.290	49.711
2	Unknown	9	8.267	50.289

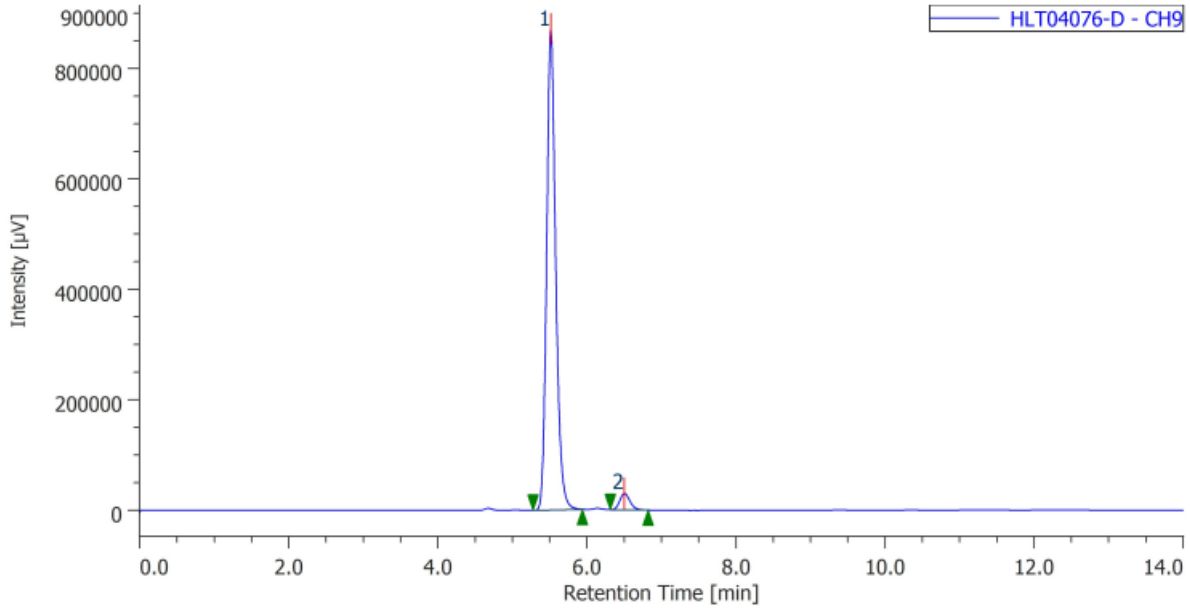


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.263	96.546
2	Unknown	9	8.233	3.454

(*S*)-N,1-diphenyl-3-(m-tolyl)-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ad): Prepared according to **GP-D** using compound **1a** (0.05 mmol, 14.6 mg, 1.0 equiv.), **2d** (0.055 mmol, 11.6 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ad** was isolated as a yellow solid (15.2 mg, 75%). **IR** (KBr) 1590, 1573, 1529, 1471, 1286, 1257, 1116, 1086, 754 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.19-8.17 (m, 2H), 7.83-7.78 (m, 2H), 7.56-7.55 (m, 3H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.38-7.28 (m, 3H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.12-7.04 (m, 3H), 6.85-6.83 (m, 3H), 6.62 (s, 1H), 2.40 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 149.4, 144.6, 143.1, 139.1, 138.0, 132.5, 132.1, 129.5, 128.9, 128.8, 128.8, 128.7, 128.2, 127.2, 126.4, 126.3, 125.9, 123.6, 123.4, 121.5, 116.2, 96.3, 21.5. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 5.51 min (major) and 6.50 min (minor). **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{22}N_2SNa^+$: 429.1396; Found 429.1390. **$[\alpha]_D^{20.0}$** = +231.0 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).

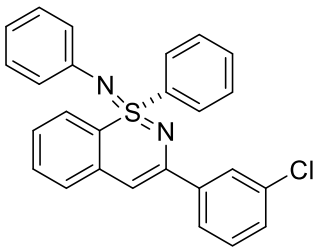


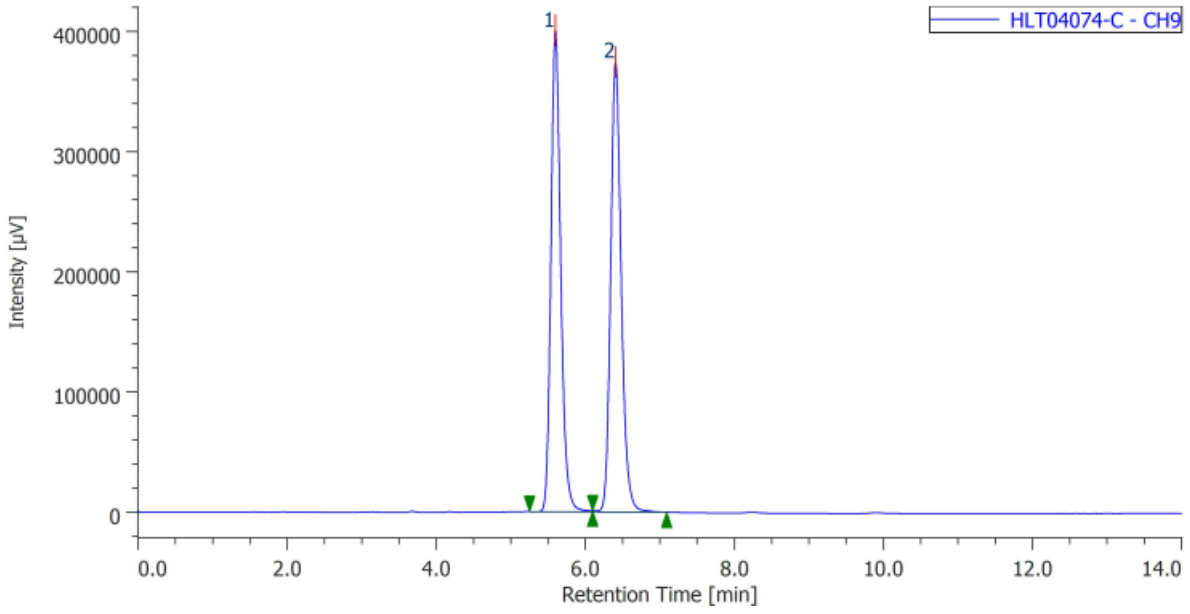
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.513	49.980
2	Unknown	9	6.520	50.020



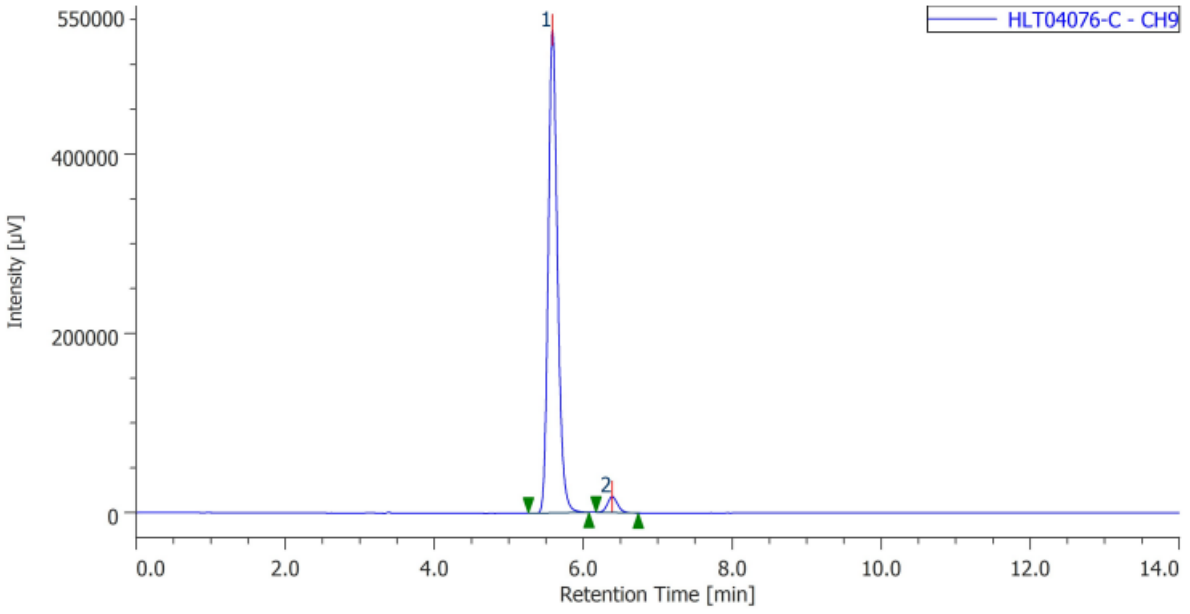
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.513	96.246
2	Unknown	9	6.500	3.754

(*S*)-3-(3-chlorophenyl)-N,1-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ae): Prepared according to **GP-D** using compound **1a** (0.05 mmol, 14.6 mg, 1.0 equiv.), **2e** (0.055 mmol, 12.7 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ae** was isolated as a yellow solid (16.9 mg, 80%). **IR** (KBr) 1591, 1472, 1261, 1116, 1085, 948, 748 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.19-8.16 (m, 2H), 7.99 (s, 1H), 7.88-7.86 (m, 1H), 7.59-7.57 (m, 3H), 7.45-7.37 (m, 2H), 7.34-7.30 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.0 Hz, 2H), 6.86-6.81 (m, 3H), 6.62 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 147.6, 144.4, 142.7, 141.0, 139.4, 134.4, 132.7, 132.3, 129.5, 129.0, 128.9, 128.6, 126.8, 126.6, 126.5, 125.9, 124.6, 123.4, 121.7, 116.6, 96.9; one aromatic signal was missing probably due to overlap. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 5.58 min (major) and 6.39 min (minor). **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{19}N_2SClNa^+$: 449.0850; Found 449.0847. **$[\alpha]_D^{20.7}$** = +132.8 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).

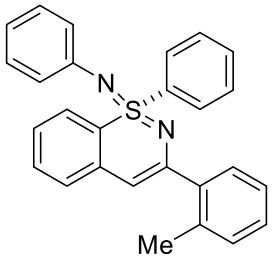




#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.597	49.623
2	Unknown	9	6.403	50.377

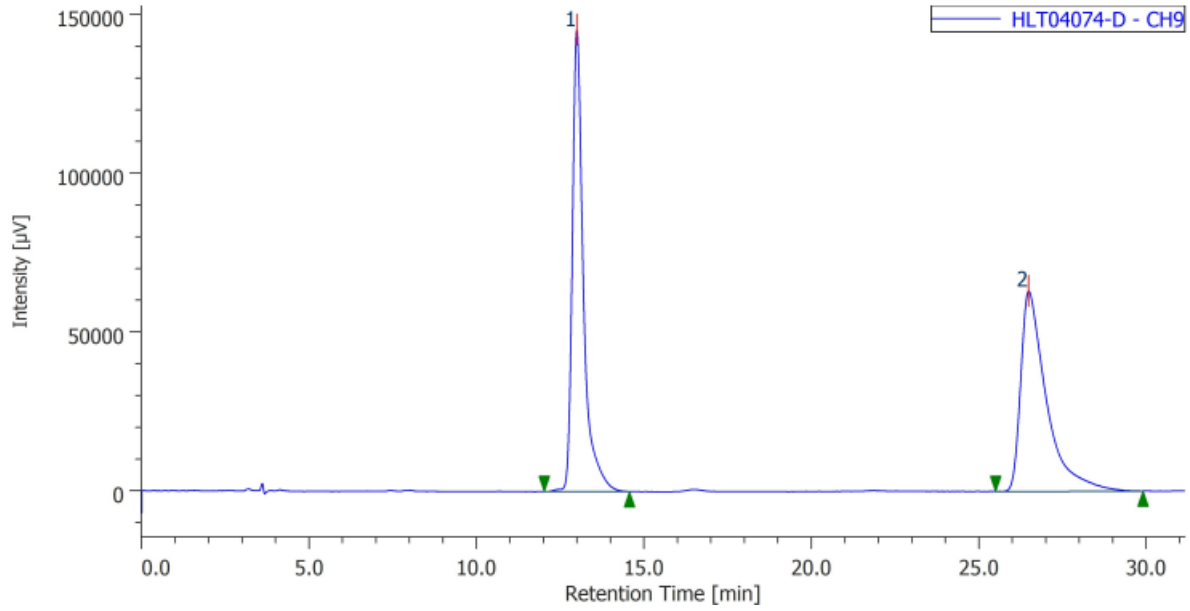


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.583	96.474
2	Unknown	9	6.387	3.526

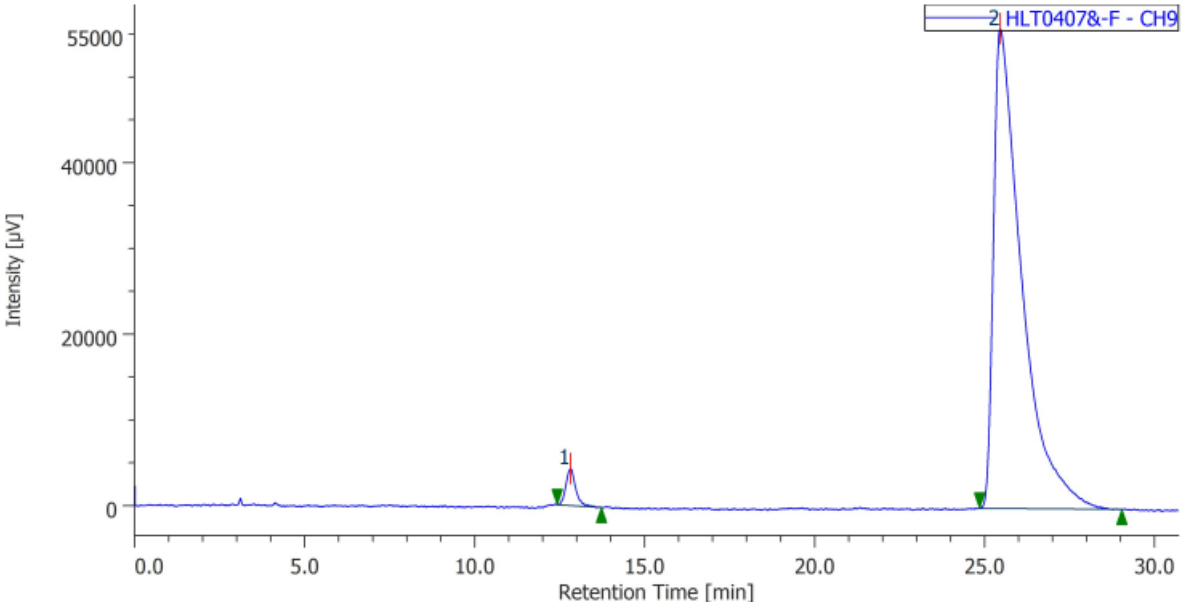


(*S*)-N,1-diphenyl-3-(o-tolyl)-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3af): Prepared according to **GP-D** using compound **1a** (0.05 mmol, 14.6 mg, 1.0 equiv.), **2f** (0.055 mmol, 11.6 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3af** was isolated as a yellow solid (18.3 mg, 90%). **IR** (KBr) 1577, 1528, 1469, 1358, 1255, 1116, 1086, 758, 720 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.21-8.19 (m, 2H), 7.57-7.56 (m, 3H), 7.49-7.47 (m, 1H), 7.42-7.37 (m, 2H), 7.26-7.19 (m, 4H), 7.15-7.09 (m, 3H), 6.88-6.83 (m, 3H), 6.19 (s, 1H), 2.42

(s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.2, 144.4, 142.8, 140.6, 139.6, 136.0, 132.5, 132.2, 130.7, 129.0, 128.9, 128.8, 128.7, 128.0, 126.4, 126.0, 125.9, 125.6, 123.5, 121.5, 115.4, 99.6, 20.5. **HPLC** (chiral column: DAICEL CHIRALPAK IA; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 300 nm): t_R = 12.82 min (minor) and 25.45 min (major). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{23}N_2S^+$: 407.1577; Found 407.1571. **$[\alpha]_D^{18.9}$** = +125.3 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).

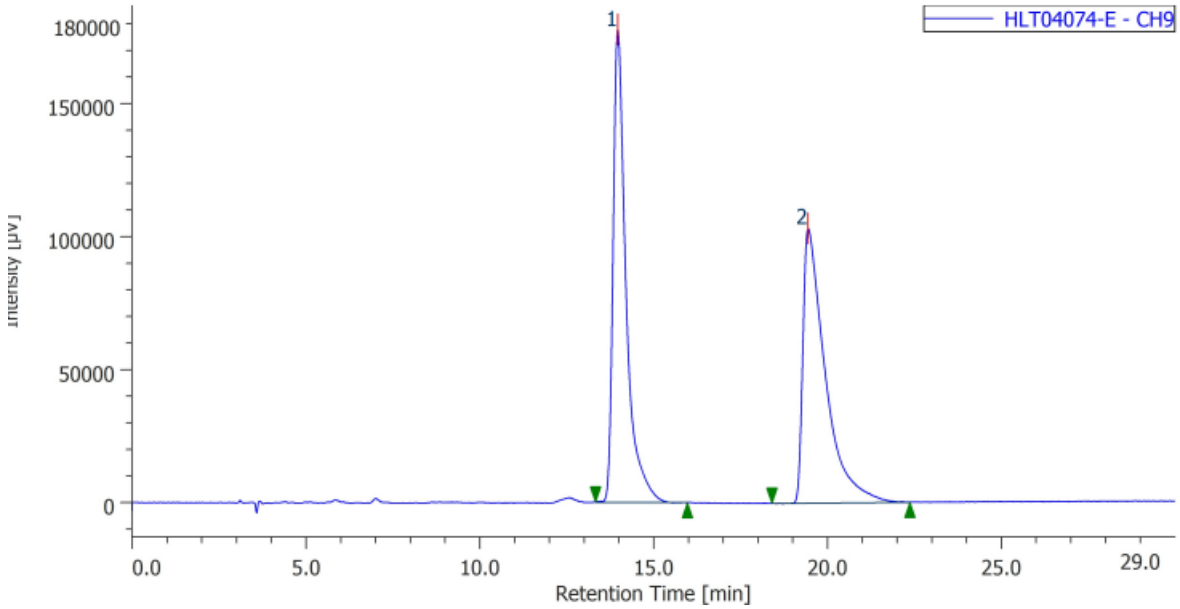


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	12.993	50.069
2	Unknown	9	26.480	49.931

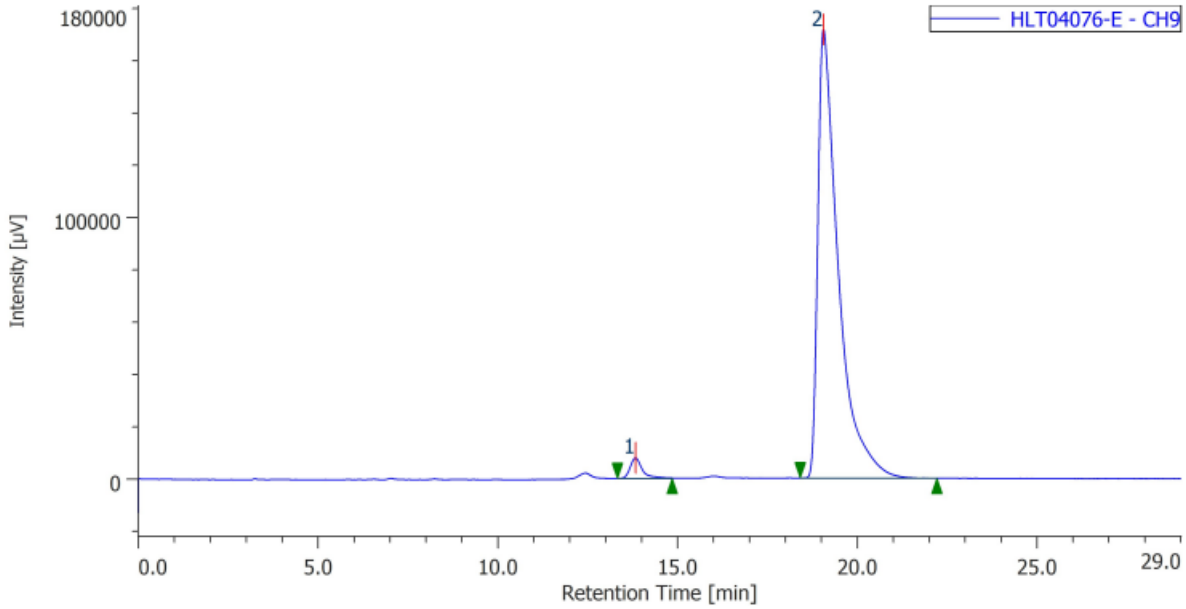


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	12.820	2.567
2	Unknown	9	25.453	97.433

(*S*)-3-(2-chlorophenyl)-N,1-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ag): Prepared according to **GP-D** using compound **1a** (0.05 mmol, 14.6 mg, 1.0 equiv.), **2g** (0.055 mmol, 12.7 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ag** was isolated as a yellow solid (16.9 mg, 80%). **IR** (KBr) 1579, 1482, 1469, 1359, 1287, 1261, 1115, 1078, 751 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.26-8.24 (m, 2H), 7.60-7.57 (m, 4H), 7.44-7.42 (m, 2H), 7.41-7.37 (m, 1H), 7.29-7.24 (m, 3H), 7.18-7.14 (m, 1H), 7.13-7.10 (m, 2H), 6.89-6.86 (m, 3H), 6.37-6.36 (m, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 148.6, 144.3, 142.8, 139.5, 139.1, 132.6, 132.2, 132.2, 130.9, 130.1, 129.1, 128.9, 128.8, 126.8, 126.7, 126.2, 126.0, 123.6, 121.7, 116.0, 100.8; one aromatic signal was missing probably due to overlap. **HPLC** (chiral column: DAICEL CHIRALPAK IA; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 13.82 min (minor) and 19.05 min (major). **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{19}N_2SClNa^+$: 449.0850; Found 449.0845. **$[\alpha]_D^{19.8}$** = +208.9 (*c* = 0.25, $CHCl_3$). **Rf** 0.6 (hexane/AcOEt = 3:1).

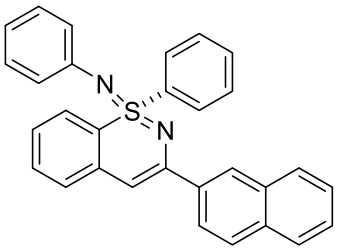


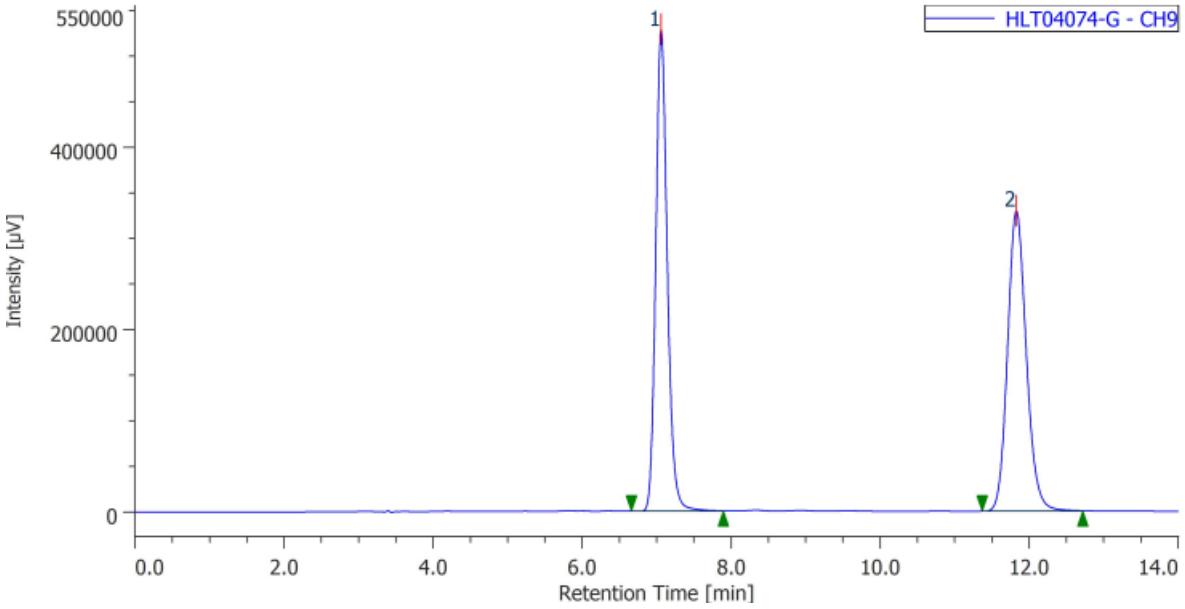
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	13.963	49.903
2	Unknown	9	19.437	50.097



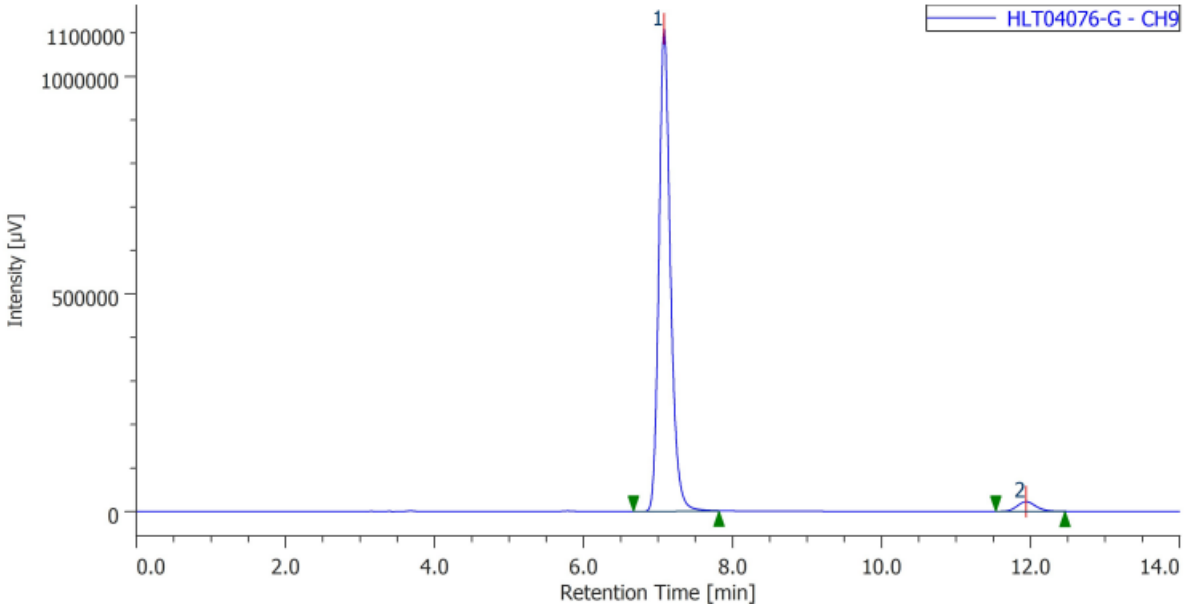
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	13.823	2.627
2	Unknown	9	19.053	97.373

(*S*)-3-(naphthalen-2-yl)-N,1-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ah): Prepared according to **GP-D** using compound **1a** (0.05 mmol, 14.6 mg, 1.0 equiv.), **2h** (0.055 mmol, 13.6 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ah** was isolated as a yellow solid (16.1 mg, 75%). **IR** (KBr) 3854, 3751, 3649, 3055, 1576, 1527, 1472, 1374, 1259, 1114, 755 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.56 (s, 1H), 8.24-8.21 (m, 2H), 8.08 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.92-7.83 (m, 3H), 7.59-7.56 (m, 3H), 7.49-7.45 (m, 3H), 7.42-7.37 (m, 1H), 7.36-7.33 (m, 1H), 7.16-7.12 (m, 1H), 7.09-7.03 (m, 2H), 6.90 - 6.87 (m, 2H), 6.90-6.81 (m, 1H), 6.79 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 148.9, 144.6, 143.0, 139.8, 136.3, 133.6, 133.4, 132.6, 132.2, 129.0, 128.9, 128.8, 128.6, 127.8, 127.5, 126.5, 126.4, 126.3, 126.2, 126.1, 126.0, 124.0, 123.5, 121.6, 116.5, 96.9. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 7.08 min (major) and 11.94 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{23}N_2S^+$: 443.1577; Found 443.1573. **$[\alpha]_D^{20.5}$** = +69.5 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).



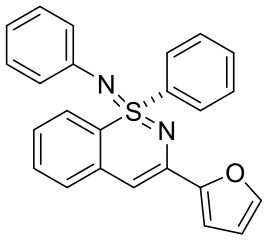


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	7.057	49.773
2	Unknown	9	11.823	50.227

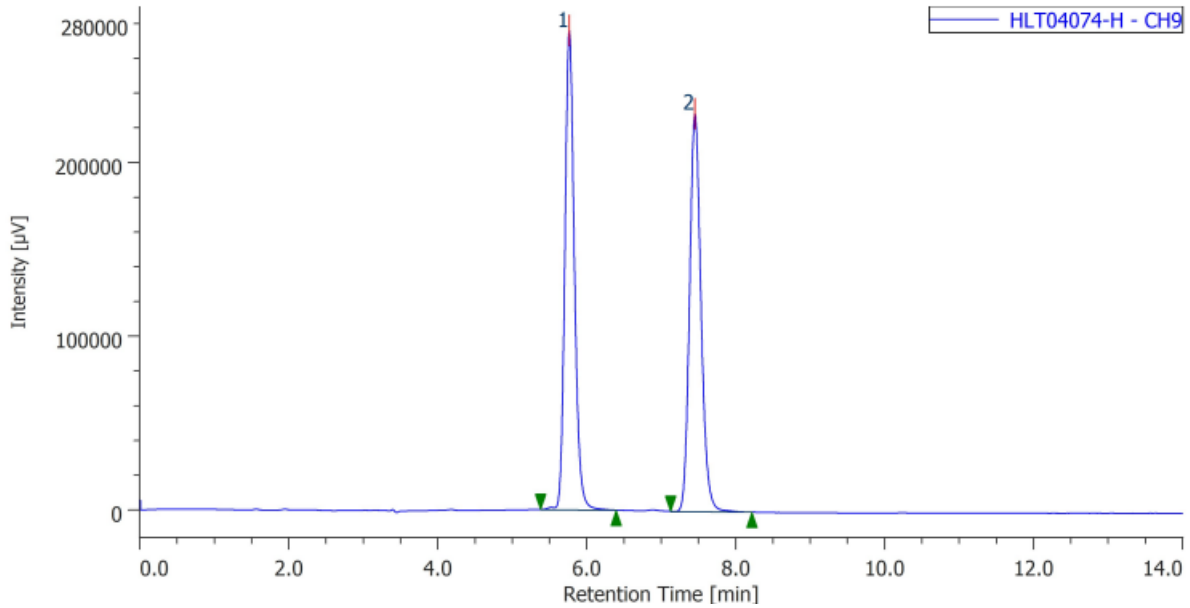


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	7.080	96.785
2	Unknown	9	11.937	3.215

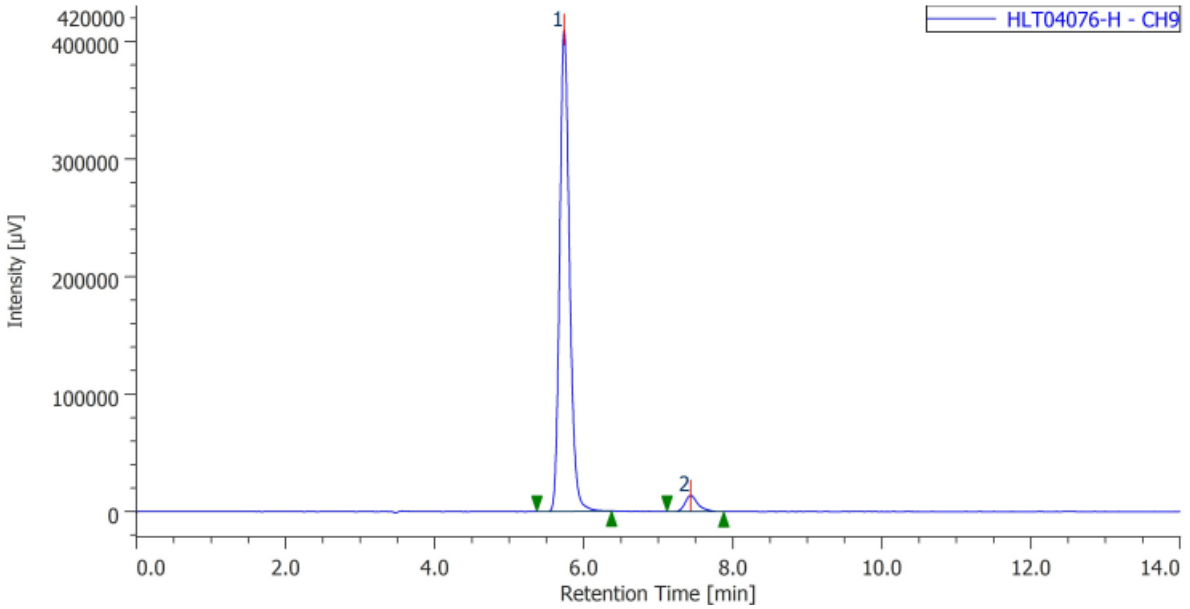
(*S*)-3-(furan-2-yl)-N,1-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3ai): Prepared according to **GP-D** using compound **1a** (0.05 mmol, 14.6 mg, 1.0 equiv.), **2i** (0.055 mmol, 10.2 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3ai** was isolated as a yellow solid (14.3 mg, 75%). **IR** (KBr) 1586, 1526, 1483, 1468, 1310, 1292, 1261, 1216, 1119, 1086, 795, 752, 737 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.18-8.15 (m, 2H), 7.57-7.54 (m, 3H), 7.49 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.36-7.33 (m, 1H), 7.27 (d, *J* = 6.9 Hz, 1H),



7.11-7.06 (m, 3H), 6.90 (dd, *J* = 3.3, 0.9 Hz, 1H), 6.88-6.82 (m, 3H), 6.63 (s, 1H), 6.48 (dd, *J* = 3.3, 1.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.5, 144.5, 143.0, 142.9, 140.7, 139.6, 132.6, 132.2, 128.9, 128.9, 128.5, 126.4, 126.2, 126.0, 123.6, 121.6, 117.0, 111.9, 109.2, 94.6. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 300 nm): t_R = 5.73 min (major) and 7.43 min (minor). **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{18}N_2SONa^+$: 405.1032; Found 405.1028. **$[\alpha]_D^{19.5}$** = +103.2 (*c* = 0.25, $CHCl_3$). **Rf** 0.5 (hexane/AcOEt = 3:1).

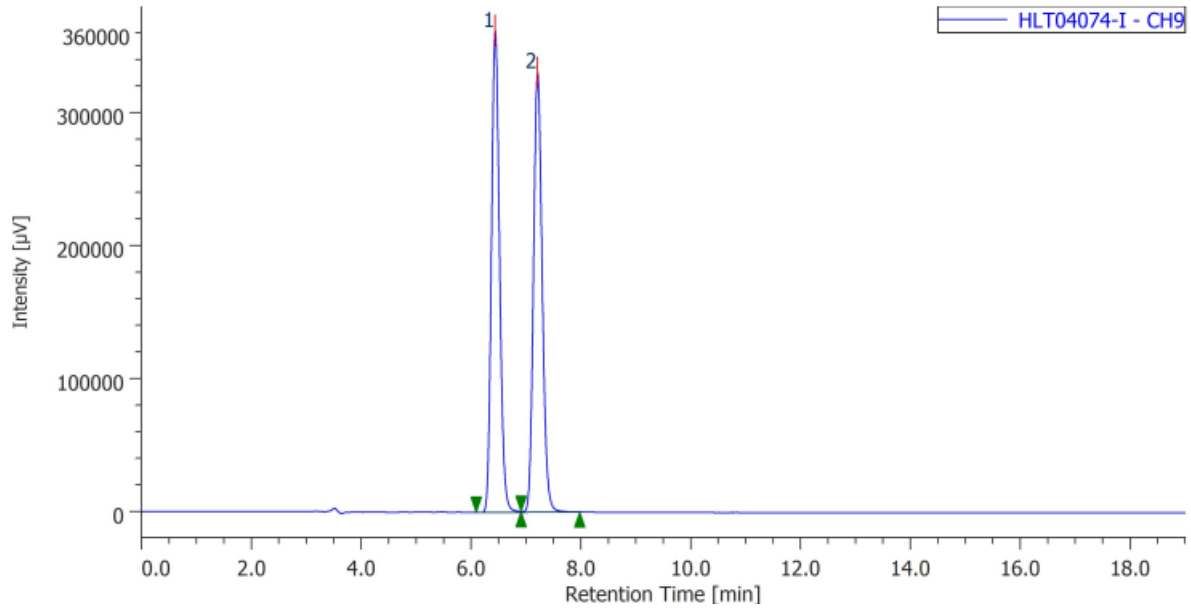


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.763	50.008
2	Unknown	9	7.450	49.992

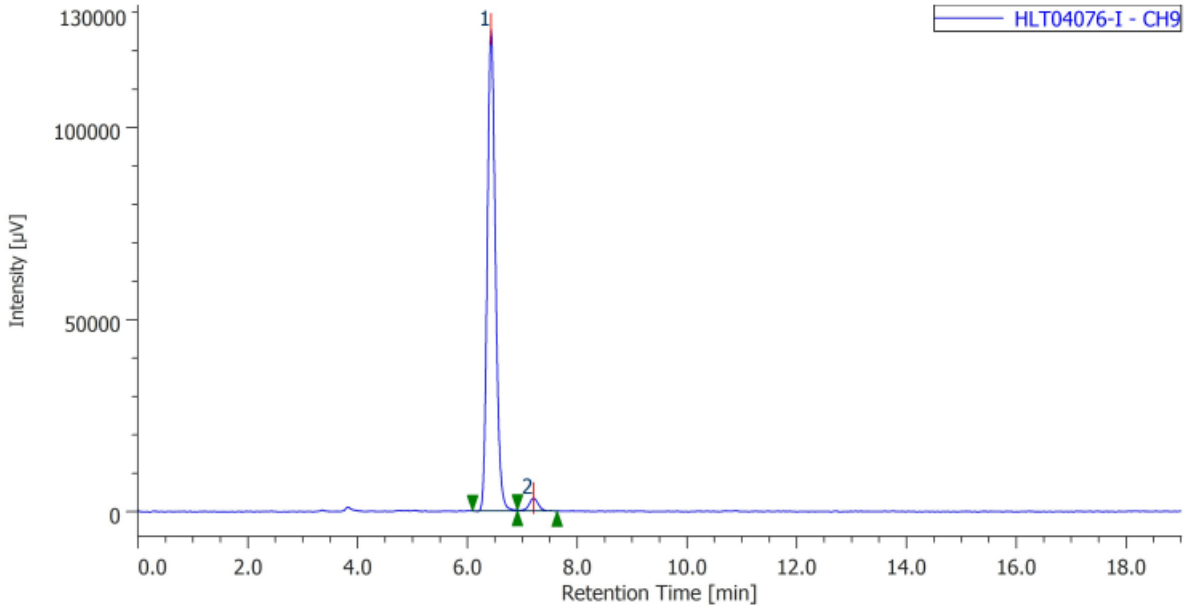


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	5.733	95.837
2	Unknown	9	7.433	4.163

(*S*)-3-(tert-butyl)-N,1-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (3aj): Prepared according to **GP-D** using compound **1a** (0.05 mmol, 14.6 mg, 1.0 equiv.), **2j** (0.055 mmol, 9.7 mg, 1.1 equiv.), **L8** (0.005 mmol, 2.4 mg, 10 mol%). **3aj** was isolated as a yellow oil (12.3 mg, 66%). **IR** (neat) 2960, 2924, 1577, 1532, 1486, 1472, 1350, 1283, 1257, 1148, 1087, 748, 719 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.13 - 8.11 (m, 2H), 7.56 - 7.54 (m, 3H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.31 - 7.28 (m, 1H), 7.18-7.16 (m, 1H), 7.09 - 7.04 (m, 3H), 6.85-6.81 (m, 1H), 6.79 - 6.76 (m, 2H), 6.03-6.03 (m, 1H), 1.33 (s, 9H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 162.0, 144.9, 143.6, 139.9, 132.3, 131.9, 128.8, 128.6, 128.4, 126.1, 125.8, 125.8, 123.5, 121.3, 115.1, 93.0, 38.1, 29.1. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 97/3; flow rate: 1.0 mL/min; detection: at 300 nm): t_R = 6.43 min (major) and 7.21 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}N_2S^+$: 373.1733; Found 373.1730. **$[\alpha]_D^{21.0}$** = +185.4 (*c* = 0.25, $CHCl_3$). **Rf** 0.7 (hexane/AcOEt = 3:1).

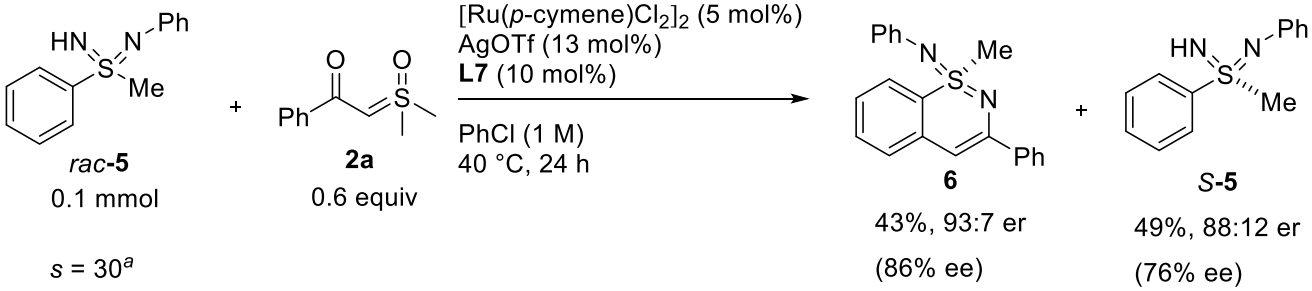


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.437	50.516
2	Unknown	9	7.207	49.484



#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.427	97.050
2	Unknown	9	7.207	2.950

2.5. Kinetic resolution of racemic sulfondiimine



rac-**5**
0.1 mmol

2a
0.6 equiv

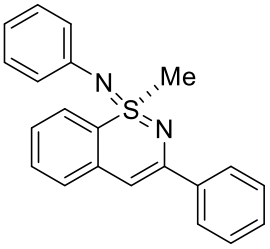
6
43%, 93:7 er
(86% ee)

S-**5**
49%, 88:12 er
(76% ee)

$s = 30^a$

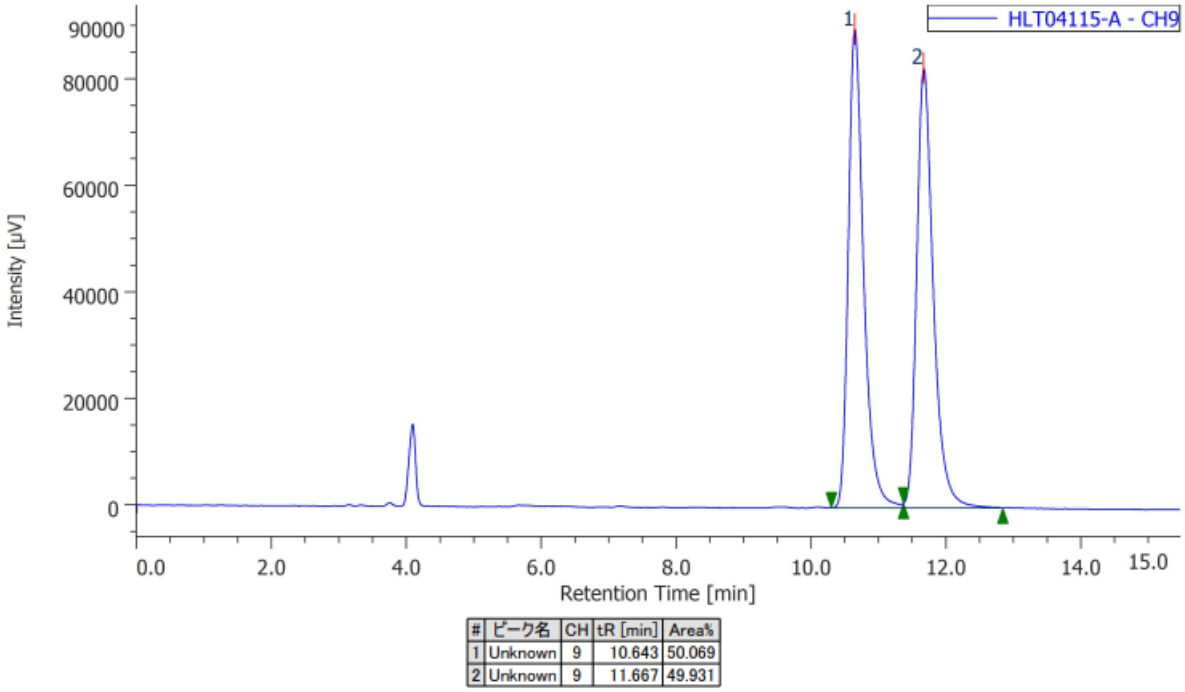
a) Selectivity factor is given: $S = \ln[(1 - C)(1 - ee_5)]/\ln[(1 - C)(1 + ee_5)]$, $C = ee_5/(ee_5 + ee_6)$

In an argon-filled glovebox, a screw-capped test tube was charged with chiral carboxylic acid **L7** (4.8 mg, 0.01 mmol, 10 mol%), [Ru(*p*-cymene)Cl_2]$_2$ (3.2 mg, 0.005 mmol, 5 mol%), AgOTf (3.2 mg, 0.013 mmol, 13 mol%), sulfondiimine *rac*-**5** (23.0 mg, 0.1 mmol, 1.0 equiv.), and sulfoxonium ylide **2a** (11.8 mg, 0.06 mmol, 0.6 equiv.). After the addition of chlorobenzene (0.1 mL), the test tube was capped and brought out of the glovebox. The reaction mixture was stirred at 40 °C for 24 h. The resulting mixture was directly purified by silica gel column chromatography (hexane/AcOEt) to afford **6** and *S*-**5**.

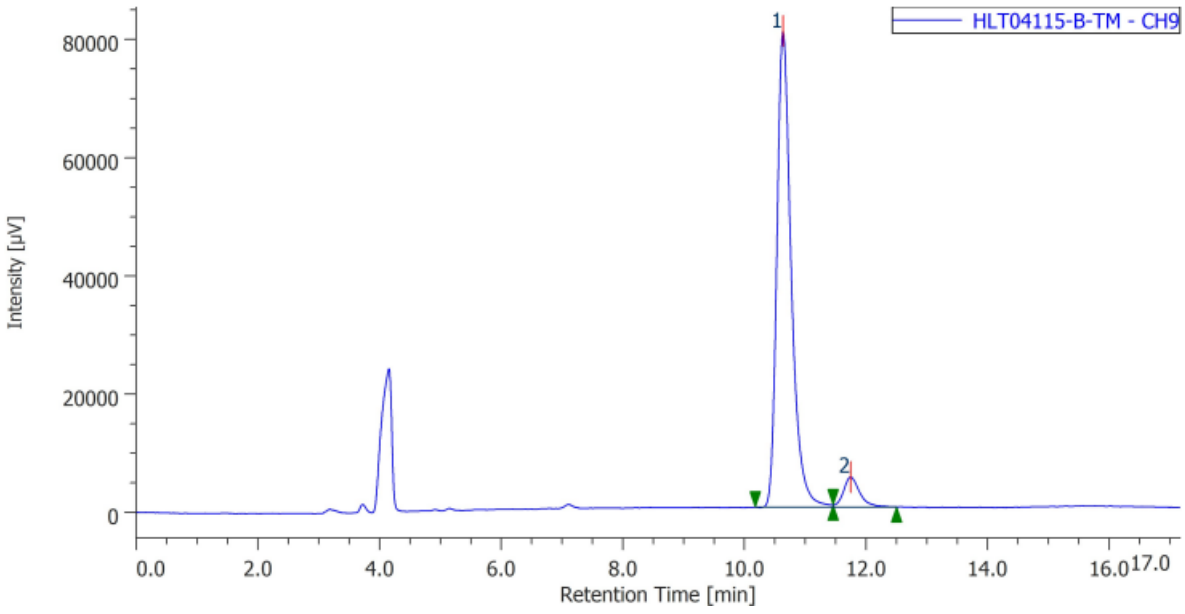


(*S*)-1-methyl-N,3-diphenyl-1λ^6-benzo[*e*][1,2]thiazin-1-imine (6): **6** was isolated as a yellow oil (14.2 mg, 43%). **IR** (KBr) 1571, 1530, 1472, 1364, 1284, 1256, 1117, 1041, 758, 694 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.93-7.90 (m, 2H), 7.74 (d, *J* = 8.2 Hz,

1H), 7.47-7.33 (m, 4H), 7.29-7.25 (m, 2H), 7.04-7.00 (m, 2H), 6.81 (t, *J* = 7.5 Hz, 1H), 6.74-6.71 (m, 2H), 6.48 (s, 1H), 3.66 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 149.2, 144.9, 140.0, 138.9, 132.8, 128.8, 128.8, 128.3, 126.5, 126.4, 126.4, 124.8, 123.0, 121.6, 114.8, 96.5, 50.1. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 19/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 10.62 min (major) and 11.72 min (minor). **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{18}N_2SNa^+$: 353.1083; Found 353.1075. **$[\alpha]_D^{24.7}$** = –8.5 (*c* = 0.25, $CHCl_3$). **Rf** 0.8 (hexane/AcOEt = 3:1).

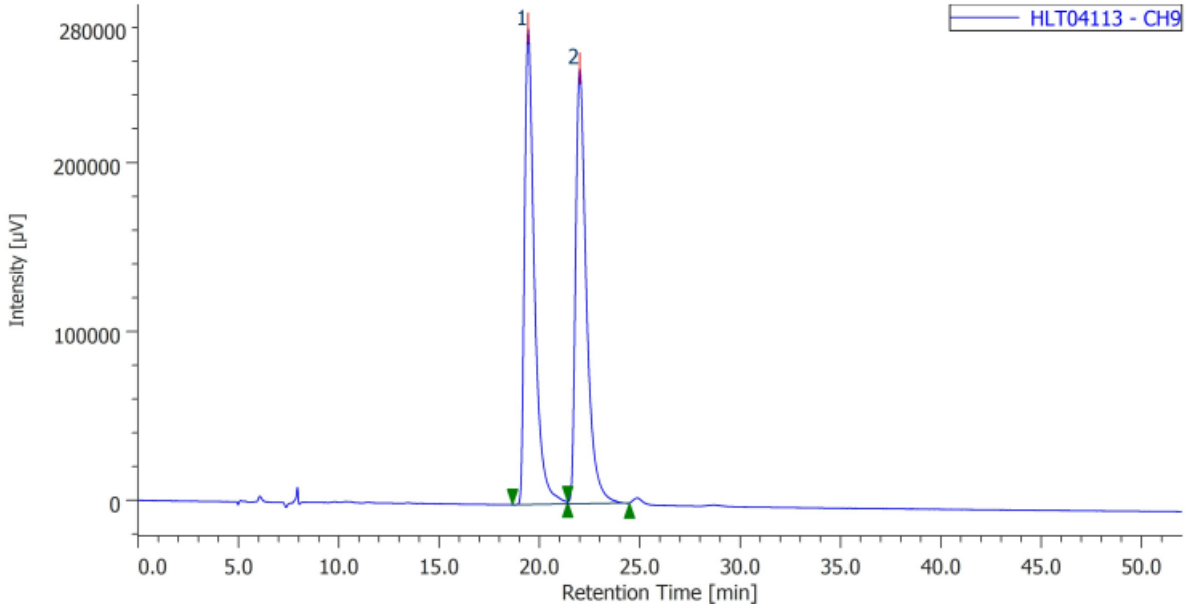


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	10.643	50.069
2	Unknown	9	11.667	49.931

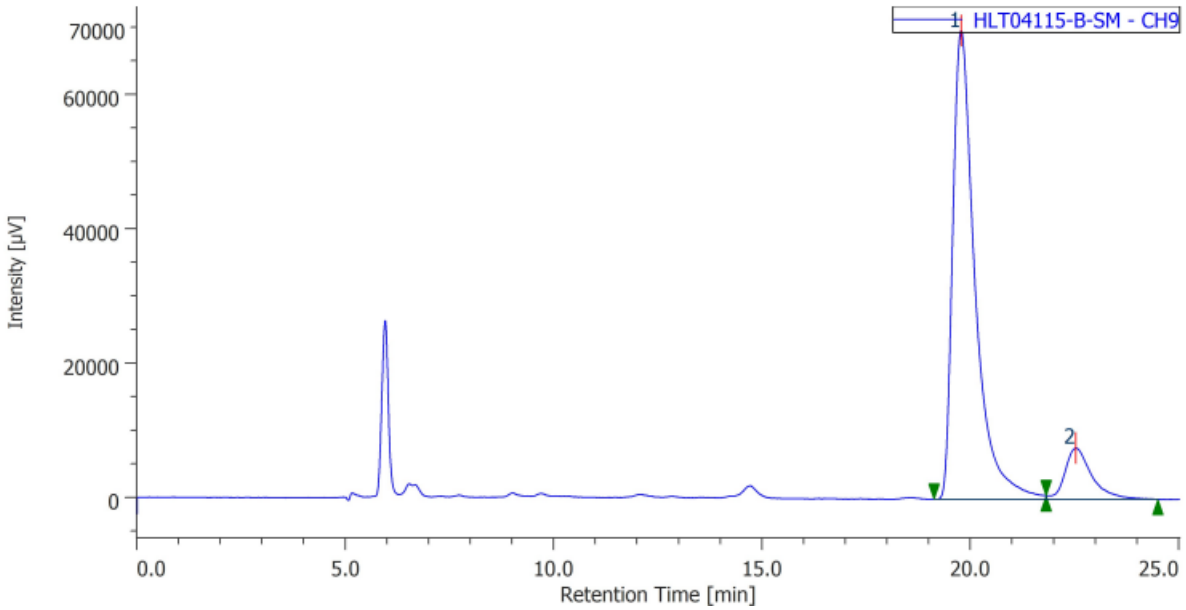


#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	10.630	93.325
2	Unknown	9	11.743	6.675

(*S*)-1-methyl-N,1-diphenyl-λ^6-sulfanediimine (5): **5** was isolated as a pale brown solid (11.3 mg, 49%). **IR** (KBr) 3120, 3106, 1595, 1485, 1284, 1256, 1088, 1060, 963, 768, 756, 735 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.19 (d, *J* = 8.2 Hz, 2H), 7.63-7.55 (m, 3H), 7.17 (t, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 3.27 (s, 3H), 2.17 (brs, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 145.9, 142.0, 132.7, 129.4, 129.0, 127.8, 123.1, 121.0, 48.3. **HPLC** (chiral column: DAICEL CHIRALPAK IA; solvent: hexane/2-propanol = 9/1; flow rate: 0.6 mL/min; detection: at 254 nm): t_R = 19.77 min (major) and 22.53 min (minor). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}N_2S^+$: 231.0951; Found 231.0947. **$[\alpha]_D^{23.0}$** = –41.0 (*c* = 0.25, $CHCl_3$). **Rf** 0.8 (hexane/AcOEt = 3:1).



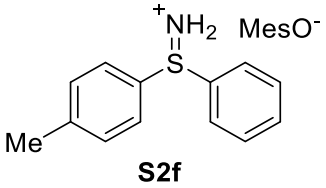
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	19.433	50.163
2	Unknown	9	22.000	49.837



#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	19.773	88.451
2	Unknown	9	22.527	11.549

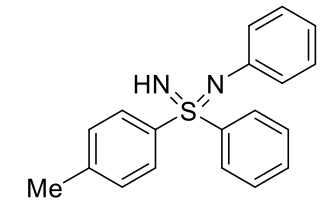
2.6. Parallel kinetic resolution of sulfondiimine

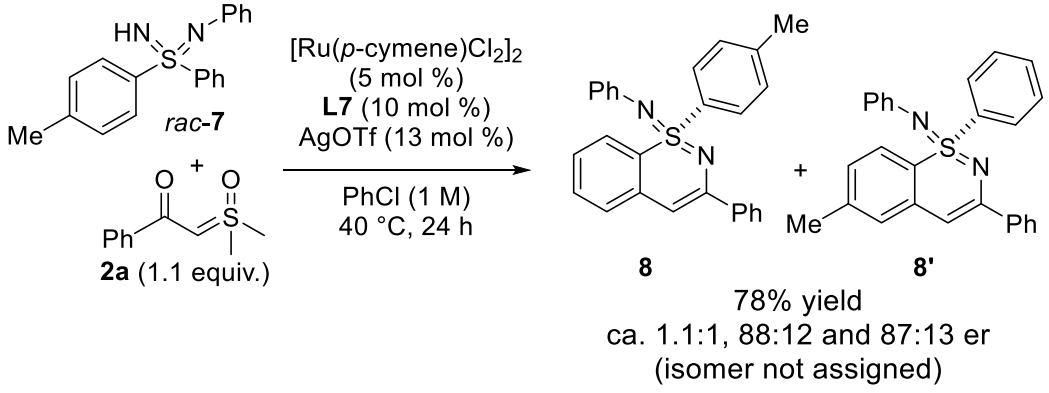
(4-tolyl-phenyl)sulfiliminium mesitylenesulfonate (S2f): Prepared according to **GP-C** using (4-tolylphenyl) sulfide (3.5 mmol, 750 mg, 1.0 equiv.), **S2f** was isolated as a colorless solid (1.3 g, 72%). **IR** (KBr) 3042, 1603, 1445, 1218, 1189, 1176, 1085, 676 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.58-7.46 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.76 (s, 2H), 2.53 (s, 6H), 2.34 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 144.2, 138.3, 137.1, 133.4, 132.8, 130.9, 130.5, 130.1, 130.0, 129.9, 128.6, 128.2, 67.0, 22.9, 21.5, 20.7. **HRMS** (ESI) m/z: $[M\text{-}MesO^-]^+$ Calcd for $C_{13}H_{14}NS^+$: 216.0842; Found 216.0838.



S2f

N,1-diphenyl-1-(p-tolyl)-λ^6-sulfondiimine (*rac*-7): Prepared according to **GP-C** using compound **S2f** (3.2 mmol, 1.3 g, 1.0 equiv.), Na_2CO_3 (16 mmol, 1.68 g, 5.0 equiv.), Selectfluor® (3.2 mmol, 1.13 g, 1.0 equiv.), aniline (9.6 mmol, 0.9 mL, 3.0 equiv.), pyridine (3.84 mmol, 0.3 mL, 1.2 equiv.). *rac*-**7** was isolated as a colorless solid (0.27 g, 27%). **IR** (KBr) 3191, 3152, 3058, 1594, 1482, 1443, 1282, 1257, 1176, 1085, 1039, 949, 750 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.20-8.17 (m, 2H), 8.06 (d, *J* = 7.9 Hz, 2H), 7.47-7.45 (m, 3H), 7.26-7.24 (m, 2H), 7.17-7.11 (m, 4H), 6.87-6.83 (m, 1H), 2.36 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 145.7, 143.4, 142.8, 139.8, 131.9, 129.8, 129.1, 128.8, 128.1, 127.9, 123.4, 120.7, 21.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_2S^+$: 307.1264; Found 307.1257. **Rf** 0.4 (hexane/AcOEt = 3:1).

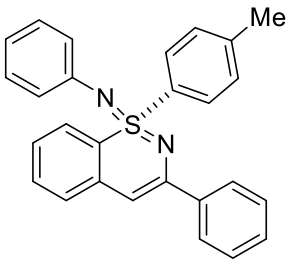


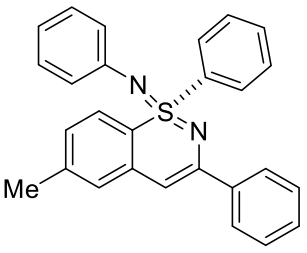


In an argon-filled glovebox, a screw-capped test tube was charged with chiral carboxylic acid **L7** (4.8 mg, 0.01

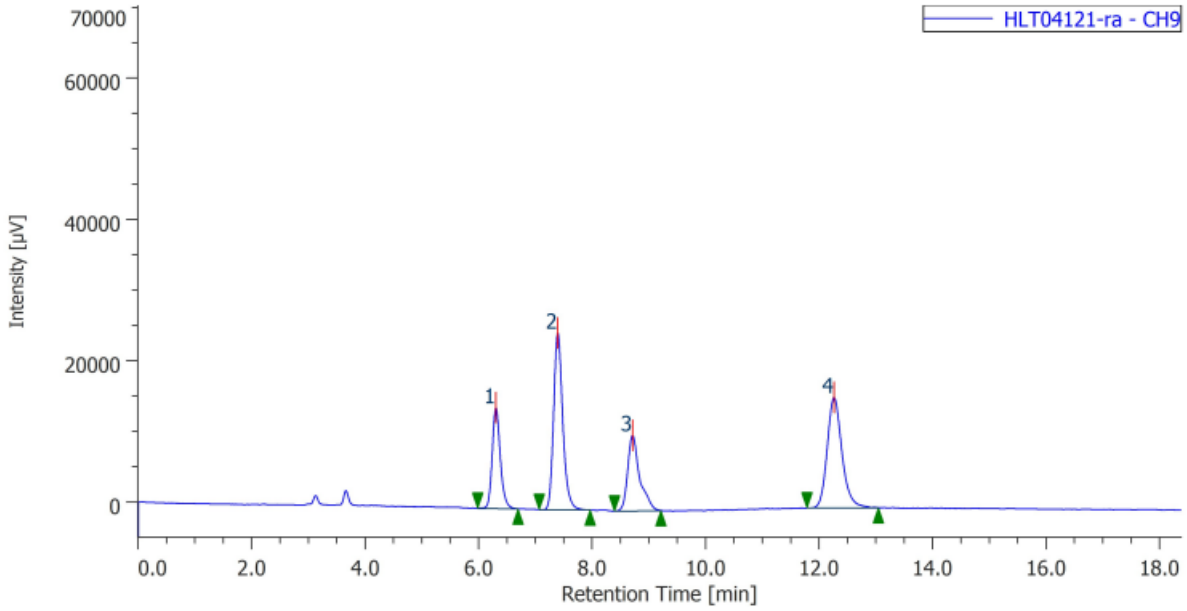
mmol, 10 mol%), [Ru(*p*-cymene)Cl_2]$_2$ (3.2 mg, 0.005 mmol, 5 mol%), AgOTf (3.2 mg, 0.013 mmol, 13 mol%), sulfondiimine *rac*-**7** (30.6 mg, 0.1 mmol, 1.0 equiv.), and sulfoxonium ylide **2a** (11.8 mg, 0.06 mmol, 0.6 equiv.). After the addition of chlorobenzene (0.1 mL), the test tube was capped and brought out of the glovebox. The reaction mixture was stirred at 40 °C for 24 h. The resulting mixture was directly purified by silica gel column chromatography (hexane/AcOEt) to afford an inseparable mixture of **8** and **8'** as a yellow solid (15.8 mg, 78%, ca. 1.1:1 ratio). Due to the structural similarity and inseparable nature, the ^{1}H and ^{13}C NMR signals could not be assigned and the structure of the isomers were not assigned.

(S)-N,3-diphenyl-1-(p-tolyl)-1λ^6-benzo[e][1,2]thiazin-1-imine and **(S)-6-methyl-N,1,3-triphenyl-1λ^6-benzo[e][1,2]thiazin-1-imine (8** and **8'**, not assigned**)**:

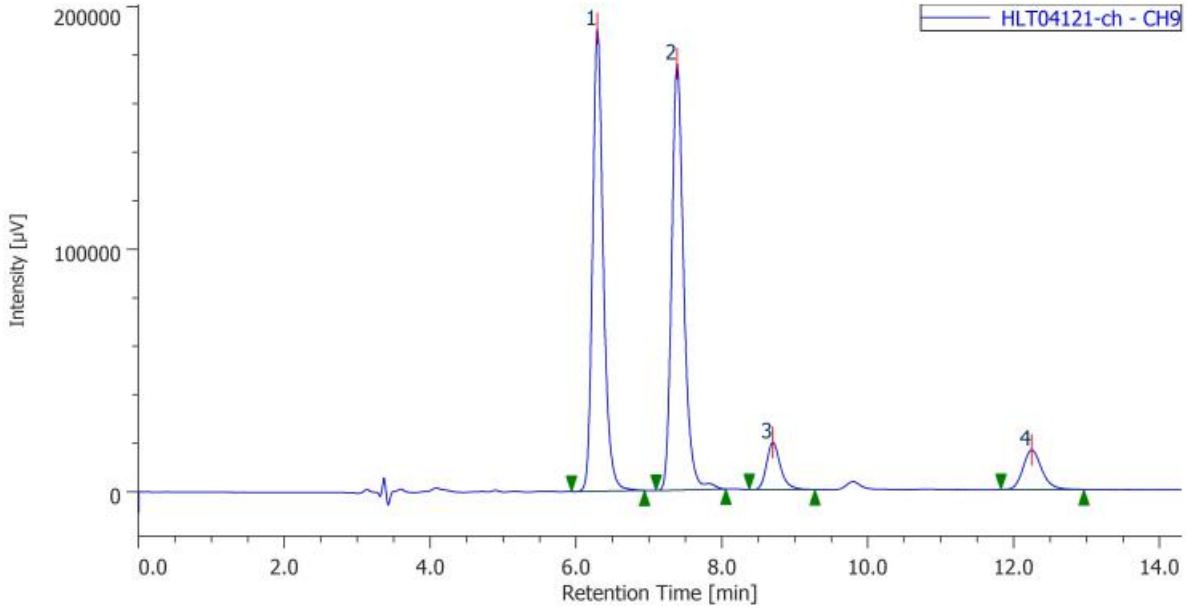




IR (KBr) 1585, 1531, 1486, 1471, 1445, 1282, 1256, 1114, 1088, 754 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.17-8.14 (m, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 8.01-7.89 (m, 4H), 7.54-7.52 (m, 3H), 7.43-7.33 (m, 11H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.13-7.03 (m, 6H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.87-6.79 (m, 6H), 6.62 (s, 1H), 6.57 (s, 1H), 2.42 (s, 3H), 2.31 (3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 149.3, 149.2, 144.8, 144.7, 143.5, 143.4, 142.8, 140.0, 139.6, 139.3, 132.3, 132.0, 129.6, 128.9, 128.8, 128.8, 128.7, 128.6, 128.4, 128.3, 127.9, 126.5, 126.5, 126.3, 126.2, 126.2, 125.9, 125.8, 123.5, 123.5, 121.4, 121.4, 116.6, 113.7, 96.3, 96.3, 21.6, 21.5. (four aromatic signals were missing probably due to overlap) **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 4/1; flow rate: 1.0 mL/min; detection: at 250 nm): t_R = 6.29 min (major), 7.38 (major), 8.70 (minor), 12.24 (minor). **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{22}N_2SNa^+$: 429.1396; Found 429.1389. **$[\alpha]_D^{22.0}$** = +87.7 (*c* = 0.25, $CHCl_3$). **Rf** 0.7 (hexane/AcOEt = 2:1).



#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.300	16.486
2	Unknown	9	7.393	32.569
3	Unknown	9	8.710	18.216
4	Unknown	9	12.260	32.729

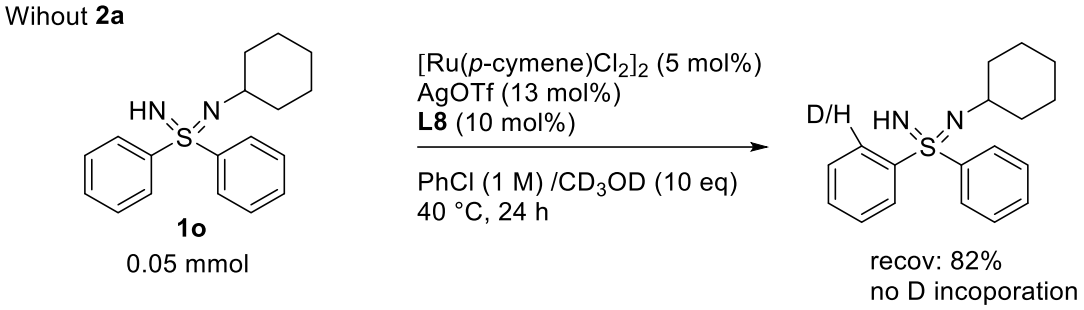


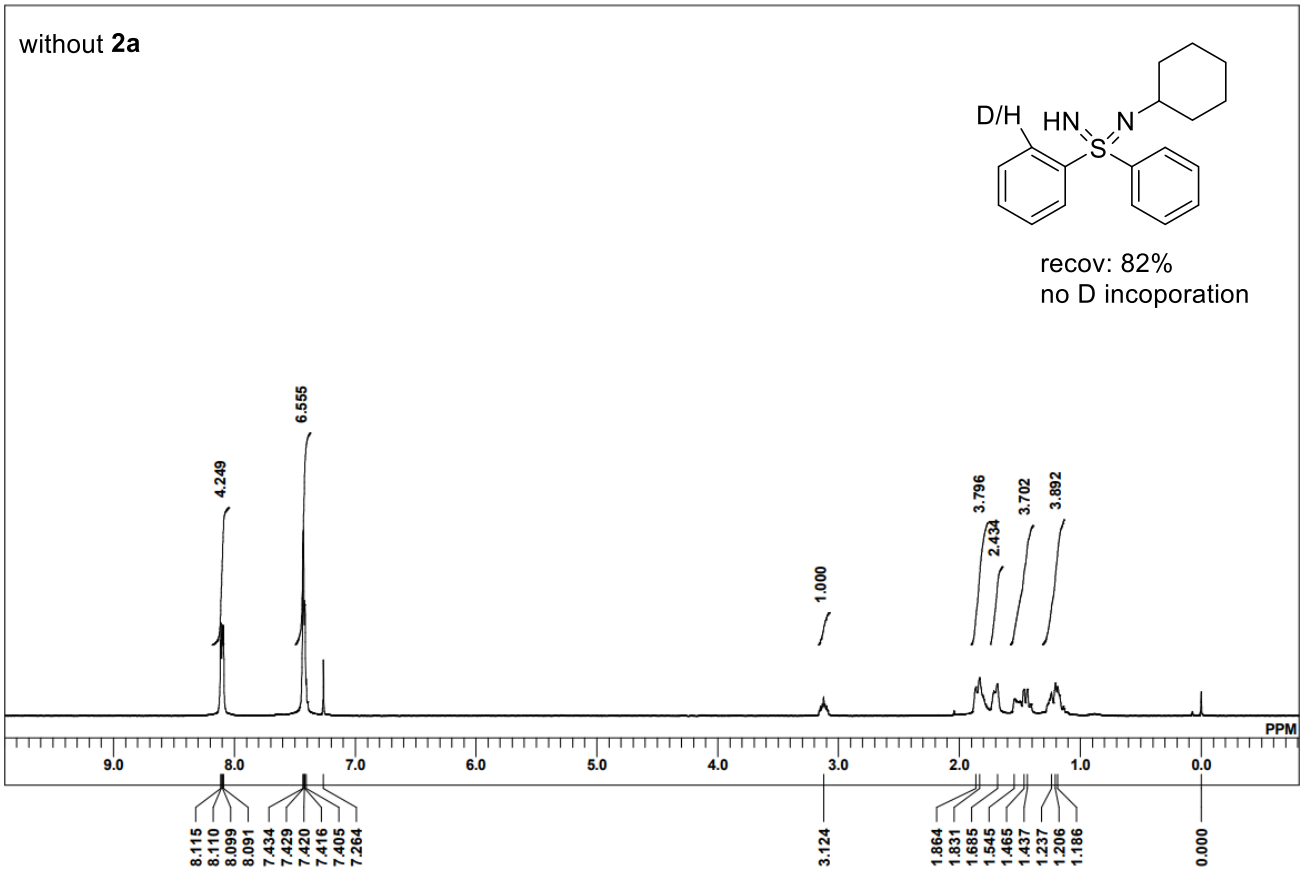
#	ピーク名	CH	tR [min]	Area%
1	Unknown	9	6.290	43.132
2	Unknown	9	7.383	44.637
3	Unknown	9	8.697	5.759
4	Unknown	9	12.243	6.473

2.7. H/D exchange experiments

Without 2a: To a screw-cap vial were added **L8** (2.4 mg, 0.005 mmol, 10 mol%) and CD_3OD (ca. 0.2 mL), and the

mixture was stirred for 30 min at room temperature. The mixture was concentrated in vacuo and moved into an argon-filled glovebox. The vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (1.6 mg, 0.0025 mmol, 5 mol%), AgOTf (1.6 mg, 0.0065 mmol, 13 mol%) and sulfondiimine **1o** (14.9 mg, 0.05 mmol, 1.0 equiv.). After the addition of chlorobenzene (0.5 mL) and CD_3OD (10.0 equiv.), the test tube was capped and brought out of the glovebox. The reaction mixture was stirred at 40 °C for 24 h. The resulting mixture was directly purified by silica gel column chromatography (hexane/AcOEt) to afford **1o** (12.2 mg, 82%). The ^{1}H NMR analysis of the recovered **1o** indicated no H/D exchange.

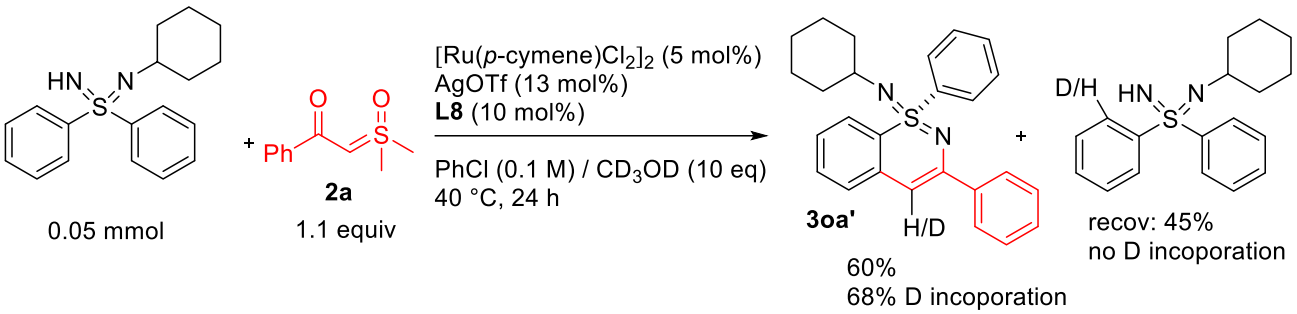


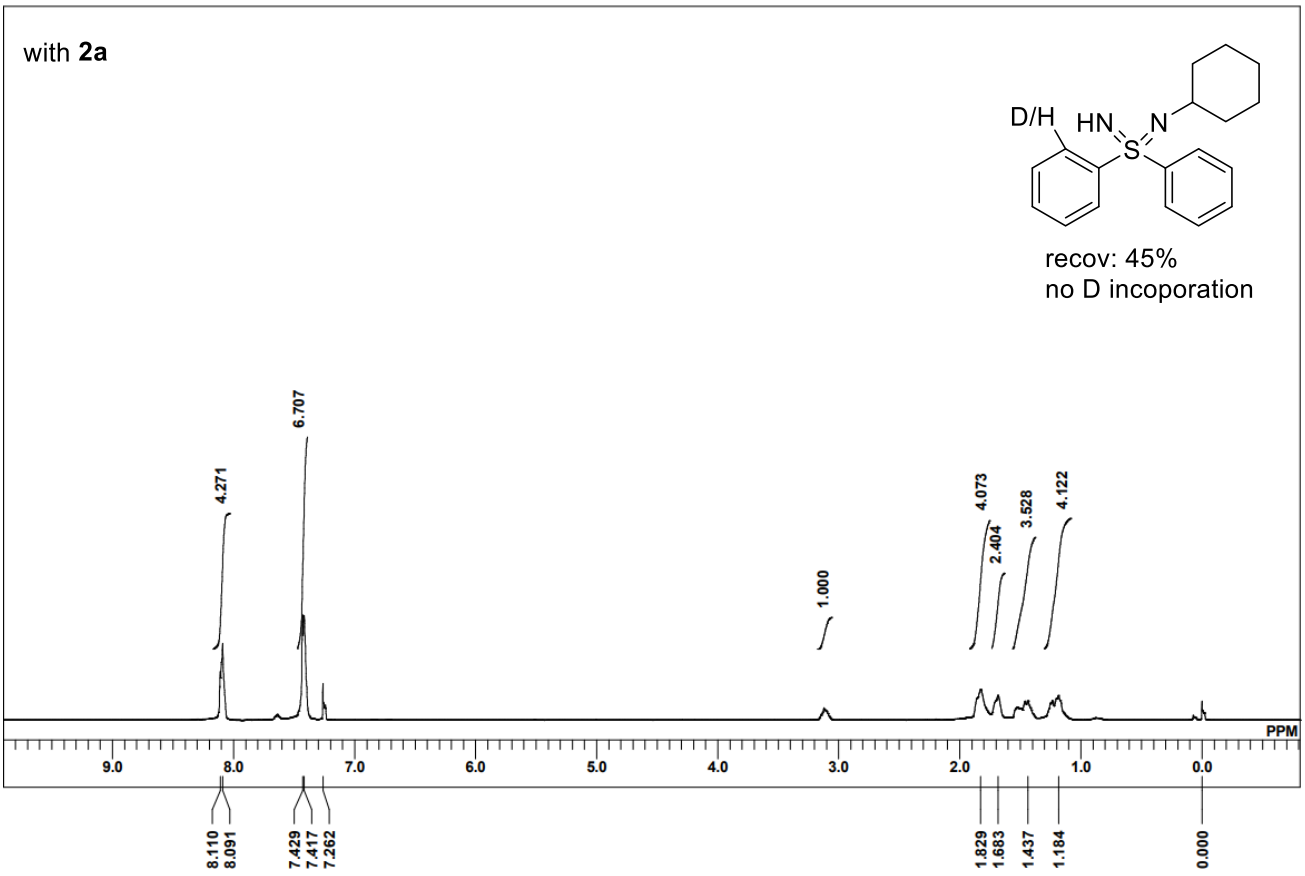


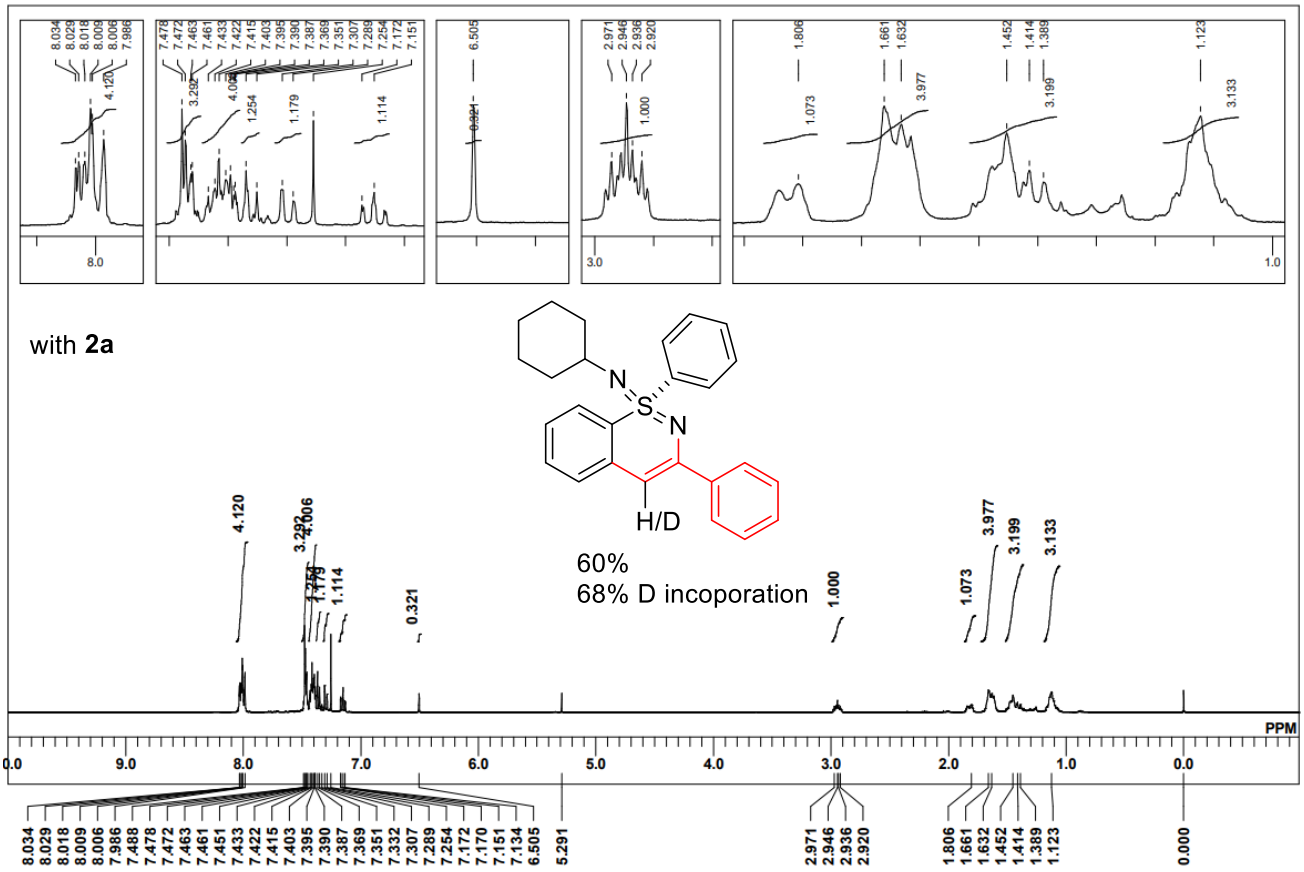
With 2a: To a screw-cap vial were added **L8** (2.4 mg, 0.005 mmol, 10 mol%) and CD_3OD (ca. 0.2 mL), and the mixture was stirred for 30 min at room temperature. The mixture was concentrated in vacuo and moved into an

argon-filled glovebox. The vial was charged with [Ru(*p*-cymene)Cl_2]$_2$ (1.6 mg, 0.0025 mmol, 5 mol%), AgOTf (1.6 mg, 0.0065 mmol, 13 mol %), sulfondiimine **1o** (14.9 mg, 0.05 mmol, 1.0 equiv.), and sulfoxonium ylide **2a** (10.8 mg, 0.055 mmol, 1.1 equiv.). After the addition of chlorobenzene (0.5 mL) and CD_3OD (10.0 equiv.), the test tube was capped and brought out of the glovebox. The reaction mixture was stirred at 40 °C for 24 h. The resulting mixture was directly purified by silica gel column chromatography (hexane/AcOEt) to afford **3oa'** (12.0 mg, 60%) and **1o** (6.7 mg, 45%, with a small amount of some impurity). The ^{1}H NMR analysis of the recovered **1o** indicated no H/D exchange.

With **2a**

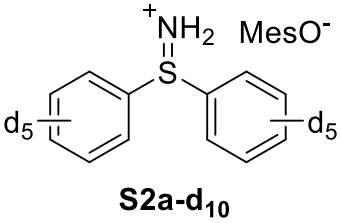






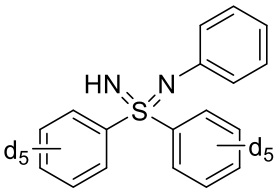
2.8. Kinetic isotopic effect

Bis(phenyl-d_5)sulfiliminium mesitylenesulfonate (S2a-d_{10}) : Prepared according to **GP-C** using bis(phenyl-d_5) sulfide (3.51 mmol, 690 mg, 1.0 equiv.), **S2a-d_{10}** was isolated as a colorless solid (1.4 g, 96%). **IR** (KBr) 2989, 1603, 1455, 1320, 1223, 1084, 1077, 1020, 682, 665 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.62 (brs, 2H), 7.77 (s, 2H), 2.52 (s, 6H), 2.22 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 139.6, 138.4, 137.1, 132.9, 132.5 (t, J = 23.5 Hz), 130.6, 129.7 (t, J = 25.4 Hz), 128.0 (t, J = 25.8 Hz), 22.9, 20.7. **HRMS** (ESI) m/z: $[M\text{-}MesO^-]^+$ Calcd for $C_{12}H_2D_{10}NS^+$: 212.1313; Found 212.1309.

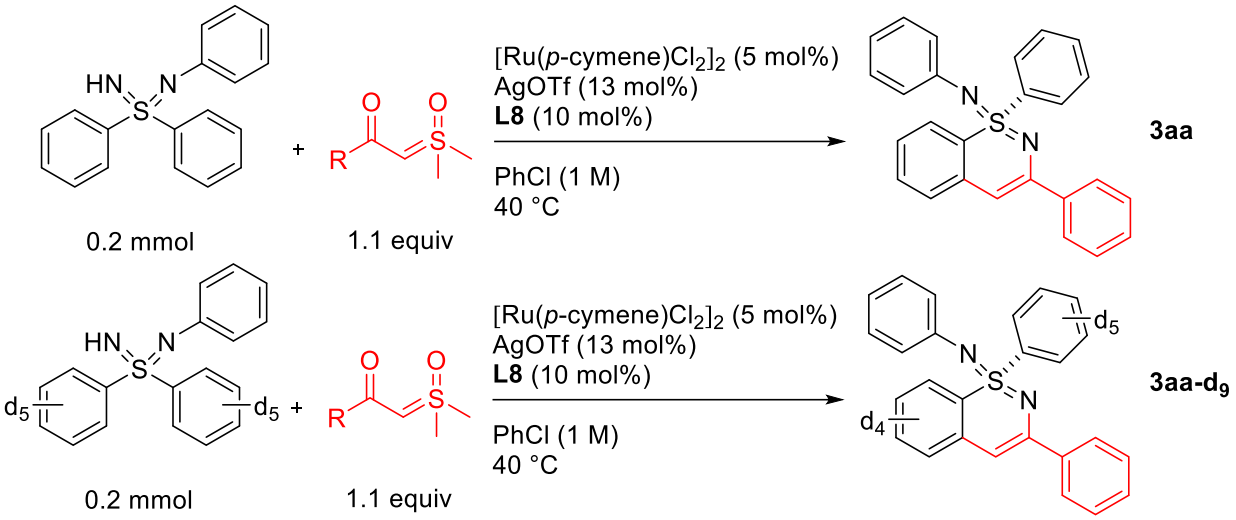


S2a-d_{10}

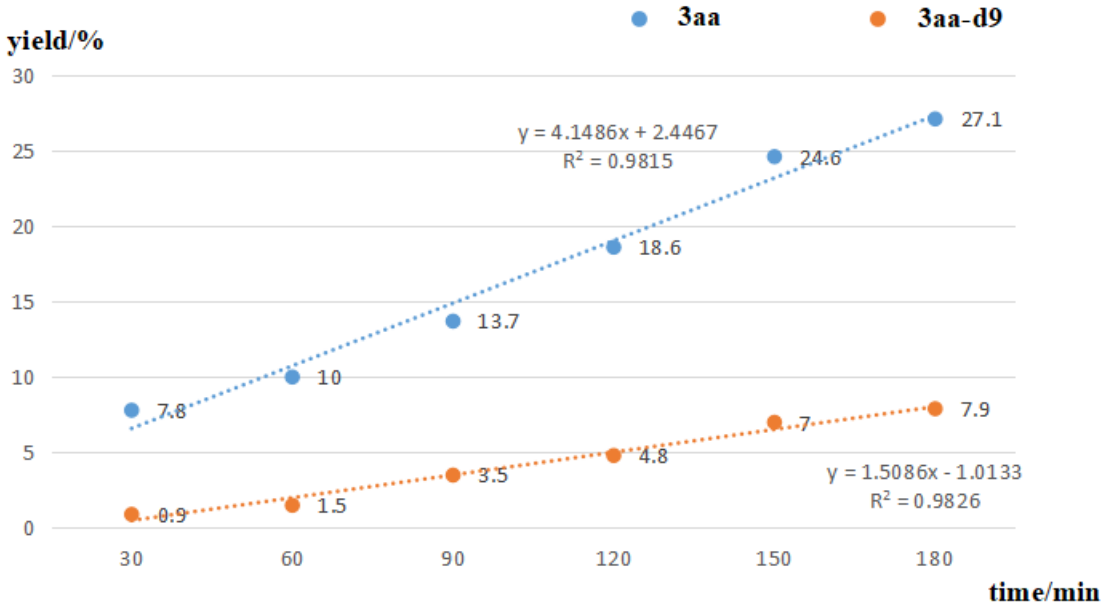
N-Phenyl-S,S-di(phenyl-d_5) sulfondiimine (1a-d_{10}) : Prepared according to **GP-C** using compound **S2a-d_{10}** (3.2 mmol, 1.3 g, 1.0 equiv.), Na_2CO_3 (16.0 mmol, 1.7 g, 5.0 equiv.), Selectfluor (3.2 mmol, 1.14 g, 1.0 equiv.), aniline (9.6 mmol, 0.90 mL, 3.0 equiv.), pyridine (3.81 mmol, 0.33 mL, 1.2 equiv.). **1a-d_{10}** was isolated as a brown solid (0.30 g, 31%). **IR** (KBr) 3169, 1597, 1485, 1294, 1263, 1056, 964, 817, 750, 692 cm^{-1}. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.18-7.11 (m, 4H), 6.85 (t, J = 6.3 Hz, 1H), 2.22 (brs, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ



145.7, 142.9, 131.5 (t, J = 23.5 Hz), 128.8, 128.6 (t, J = 24.0 Hz), 127.6 (t, J = 25.4 Hz), 123.3, 120.8. **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_6D_{10}N_2SNa^+$: 325.1554; Found 325.1549. **Rf** 0.3 (hexane/AcOEt = 3:1).



In an argon-filled glovebox, a screw-capped test tube was charged with chiral carboxylic acid **L8** (9.6 mg, 0.02 mmol, 10 mol%), [Ru(*p*-cymene)Cl_2]$_2$ (6.4 mg, 0.01 mmol, 5 mol%), AgOTf (6.4 mg, 0.026 mmol, 13 mol%), sulfondiimine **1** (0.2 mmol, 1.0 equiv.), and sulfoxonium ylides **2a** (0.22 mmol, 43.2 mg, 1.1 equiv.). After the addition of chlorobenzene (0.2 mL), the test tube was stirred at 40 °C in the glovebox. An aliquot of the mixture (25 μL) was taken by syringe at each reaction time (30, 60, 90, 120, 180 min) and filtrated through Celite using ethyl acetate. The yield was calculated by ^{1}H NMR analysis using $CHBr_2CHBr_2$ as the internal standard.



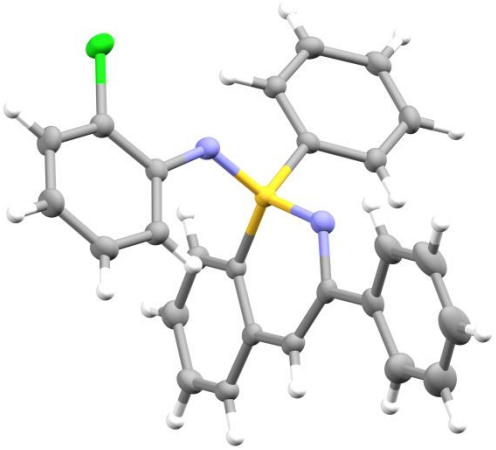
2.9. Determination of the absolute configuration

A single crystal of **3ka** suitable for X-ray crystallography was grown by slow vapor diffusion of pentane to asolution of **3ka** in ethyl acetate. Single crystal X-ray diffraction analysis was performed on a Rigaku R-AXIS RAPID/S equipped with an imaging plate area detector, a graphite-monochromated Cu-Kα radiation source (λ = 1.5418 Å) and a low temperature system using cold nitrogen stream (133 K). The detailed data were available in a crystallographic information file (CIF) deposited in CCDC (@@@@@).

Table 1. Crystal data and structure refinement for **3ka**.

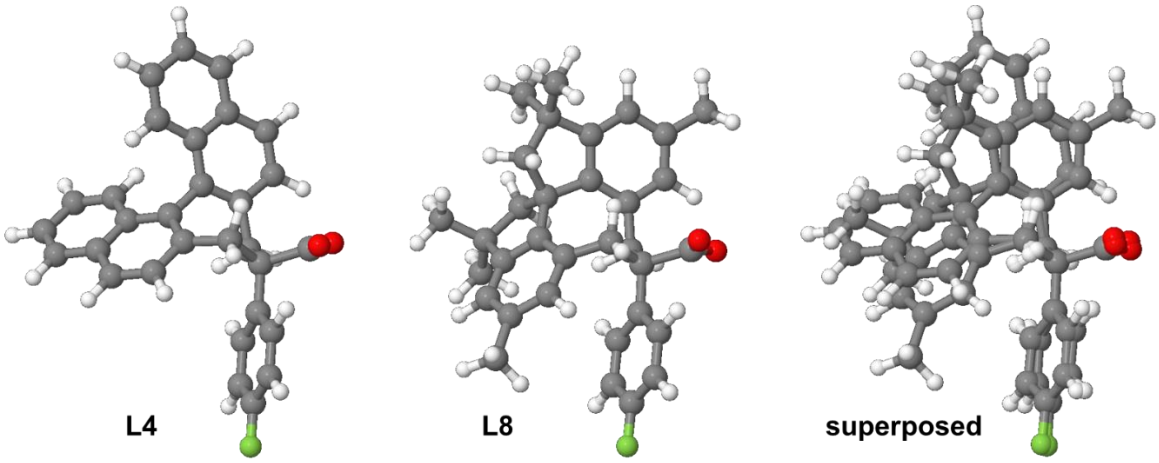
Identification code	**3ka**	
Empirical formula	C26 H19 Cl N2 S	
Formula weight	426.94	
Temperature	133(2) K	
Wavelength	1.54187 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.5685(2) Å	a= 90Å
	b = 13.1219(2) Å	b= 90Å
	c = 16.8024(3) Å	g = 90Å
Volume	2109.66(7) $Å^3$	
Z	4	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	2.637 mm^{-1}	
F(000)	888	
Crystal size	0.428 x 0.348 x 0.295 mm^3	
Theta range for data collection	4.275 to 68.224°	
Index ranges	-11<=h<=11, -15<=k<=15, -20<=l<=20	
Reflections collected	24033	
Independent reflections	3844 [R(int) = 0.0396]	
Completeness to theta = 67.687°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7999	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3844 / 0 / 272	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0248, wR2 = 0.0656	
R indices (all data)	R1 = 0.0250, wR2 = 0.0658	
Absolute structure parameter	0.053(3)	
Extinction coefficient	0.0025(3)	

Largest diff. peak and hole 0.206 and -0.205 e.Å^{-3}



3. DFT calculation of the structures of chiral carboxylic acids

The structures of **L4** and **L8** as their carboxylate anion forms were optimized with ωB97X-D functional[S4] and def2-SVP basis set[S5] using Gaussian 16 Rev. C.01 program.[S6] The structures and superposed structures with their carbonyl carbon atom, α-carbon atom, and adjacent carbon atom of the α-aryl moiety are shown below.



Cartesian coordinates of **L4** and **L8**:

L4: charge=-1, multiplicity=1

C	0.95186900	0.77246700	0.27268200
C	-0.20282500	0.66294000	1.04086200
C	1.44509000	2.06530600	-0.10009800
C	-0.81761800	-0.68661500	1.29720800
C	-0.84671700	1.83975200	1.50357200
C	1.58255200	-0.49015600	-0.21847900
C	2.54883400	2.23916500	-0.98533000
C	0.79263300	3.23445100	0.39351100
C	-1.53748000	-1.24431100	0.03306600
H	-1.52740700	-0.64302700	2.13132400
H	-0.04365900	-1.40747800	1.59455400
C	-0.35852700	3.08653000	1.21030100
H	-1.75659000	1.73119000	2.09918500
C	0.78730800	-1.37227000	-0.93790100
C	2.92694600	-0.85210300	0.12471000
C	3.00007500	3.49084200	-1.32574900
H	3.03384300	1.35468300	-1.40074900

C	1.29095200	4.51686500	0.03192100
C	-0.65323300	-1.02867700	-1.20991700
C	-2.90503400	-0.58147700	-0.11289700
H	-0.86410800	3.98252400	1.58059100
C	1.31364600	-2.62197700	-1.35637500
C	3.75763100	-0.04330000	0.95287600
C	3.45497500	-2.09035900	-0.34826300
C	2.37223900	4.64785900	-0.80343400
H	3.84634800	3.59454600	-2.00914000
H	0.78503500	5.40240400	0.42691100
H	-1.05440800	-1.66834200	-2.00557700
H	-0.68954600	0.02205100	-1.53624800
C	-3.27539700	0.22294000	-1.19631200
C	-3.86408300	-0.78192600	0.89800800
C	2.61483000	-2.96001500	-1.09384000
H	0.62993500	-3.31615300	-1.84835900
C	5.04530200	-0.41599700	1.25448400
H	3.35476200	0.88597600	1.35823100
C	4.79460700	-2.44321700	-0.02700700
H	2.74154900	5.63938200	-1.07663500
C	-4.53381300	0.82717400	-1.26856300
H	-2.57956700	0.39420500	-2.01759100
C	-5.11948600	-0.18734700	0.84392000
H	-3.60317800	-1.46494300	1.71070100
H	3.01358700	-3.92329300	-1.42358100
C	5.57850400	-1.62625100	0.74993000
H	5.65897200	0.22297000	1.89420900
H	5.18665600	-3.39200600	-0.40409100
C	-5.43849500	0.62009500	-0.24180400
H	-4.81372600	1.45627500	-2.11579700
H	-5.86104900	-0.35221500	1.62830500
H	6.60468100	-1.91359200	0.99213600
F	-6.65009500	1.20314200	-0.29831800
C	-1.77655600	-2.82112300	0.25452000
O	-2.09120600	-3.13372100	1.41530400
O	-1.63175000	-3.52990800	-0.75369800

L8: charge=-1, multiplicity=1

C	1.68899348	0.73073959	-0.08386583
C	2.77326311	0.77986409	1.02981243
C	2.03588596	1.63337742	-1.29995400
C	3.79585163	-0.34950243	0.74672078
H	3.25111923	1.76596635	1.12064919
H	2.27417330	0.57498859	1.99022123
C	0.39341329	1.38255151	0.38798556
C	1.72831673	-0.75068399	-0.44264362
C	1.43664322	3.03866892	-1.03270811
H	3.11416953	1.67267895	-1.50957454
H	1.55272704	1.19963360	-2.18998669
C	4.27892384	-0.98072291	2.05851388
C	5.01829054	0.13216750	-0.05135691
C	2.94672340	-1.31630378	-0.06281646
C	-0.65283770	0.83710729	1.14921446
C	0.32885483	2.70838438	-0.04464919
C	0.73965325	-1.54263916	-1.04457616
C	0.87011363	3.63831704	-2.32631781
C	2.45458106	4.02284874	-0.43476277
H	4.99942287	-1.79327465	1.87236833
H	4.77900594	-0.22755793	2.69034646
H	3.43425074	-1.40162881	2.62434257
H	5.69254907	-0.71274693	-0.26458236
H	5.58726670	0.88724816	0.51651579
H	4.73098201	0.57199953	-1.01604564
C	3.24554934	-2.64283626	-0.36167062
C	-0.84277541	-0.64769623	1.30365775
C	-1.66508573	1.70944250	1.56442769
C	-0.70381999	3.55099754	0.36081171
C	-0.66606912	-1.03439527	-1.23404558
C	1.05154412	-2.87665189	-1.32326048
H	0.42825737	4.63226090	-2.15033743
H	1.66567428	3.75317191	-3.08136349
H	0.08667450	2.98996425	-2.74729761
H	1.97227002	4.98962996	-0.21845342
H	3.28377184	4.20593044	-1.13818397
H	2.87989608	3.65058083	0.50698947
C	2.29790214	-3.43424019	-1.01528781
H	4.20325866	-3.07736176	-0.05643149
C	-1.52900787	-1.24264621	0.03312822
H	-1.47969962	-0.88885309	2.16306418
H	0.10577989	-1.17474948	1.47231154
C	-1.70673970	3.05903506	1.19859726
H	-2.49494824	1.29532928	2.14481080
H	-0.74681809	4.58622232	0.00679264
H	-1.16443165	-1.58802099	-2.04033086
H	-0.62257547	0.02937338	-1.51129389
H	0.25038680	-3.50603122	-1.71873990
C	2.56906969	-4.88210614	-1.33641933
C	-2.90613123	-0.59078471	-0.11157848

C	-2.86911576	3.91756695	1.62762147	H	-2.45240460	0.70616877	-1.78253433
H	3.52784504	-5.21919479	-0.91455024	C	-5.15410376	-0.29626575	0.79919349
H	2.60226167	-5.04883027	-2.42543196	H	-3.70005176	-1.72239433	1.52846519
H	1.77064139	-5.52488974	-0.93519974	C	-5.39858123	0.69686006	-0.14151576
C	-3.20228665	0.40044763	-1.05288793	H	-4.65800107	1.83017903	-1.80660787
C	-3.91665883	-0.93165620	0.80465240	H	-5.93457081	-0.56455181	1.51417985
H	-3.80489950	3.55618094	1.17099049	F	-6.58924445	1.32509845	-0.14611849
H	-3.00849757	3.88789441	2.71965782	C	-1.78393091	-2.81348007	0.25313925
H	-2.72971778	4.96764569	1.33068278	O	-1.92178860	-3.16492517	1.43762334
C	-4.43896797	1.04954603	-1.07542944	O	-1.86429499	-3.48477419	-0.78908759

4. Reference

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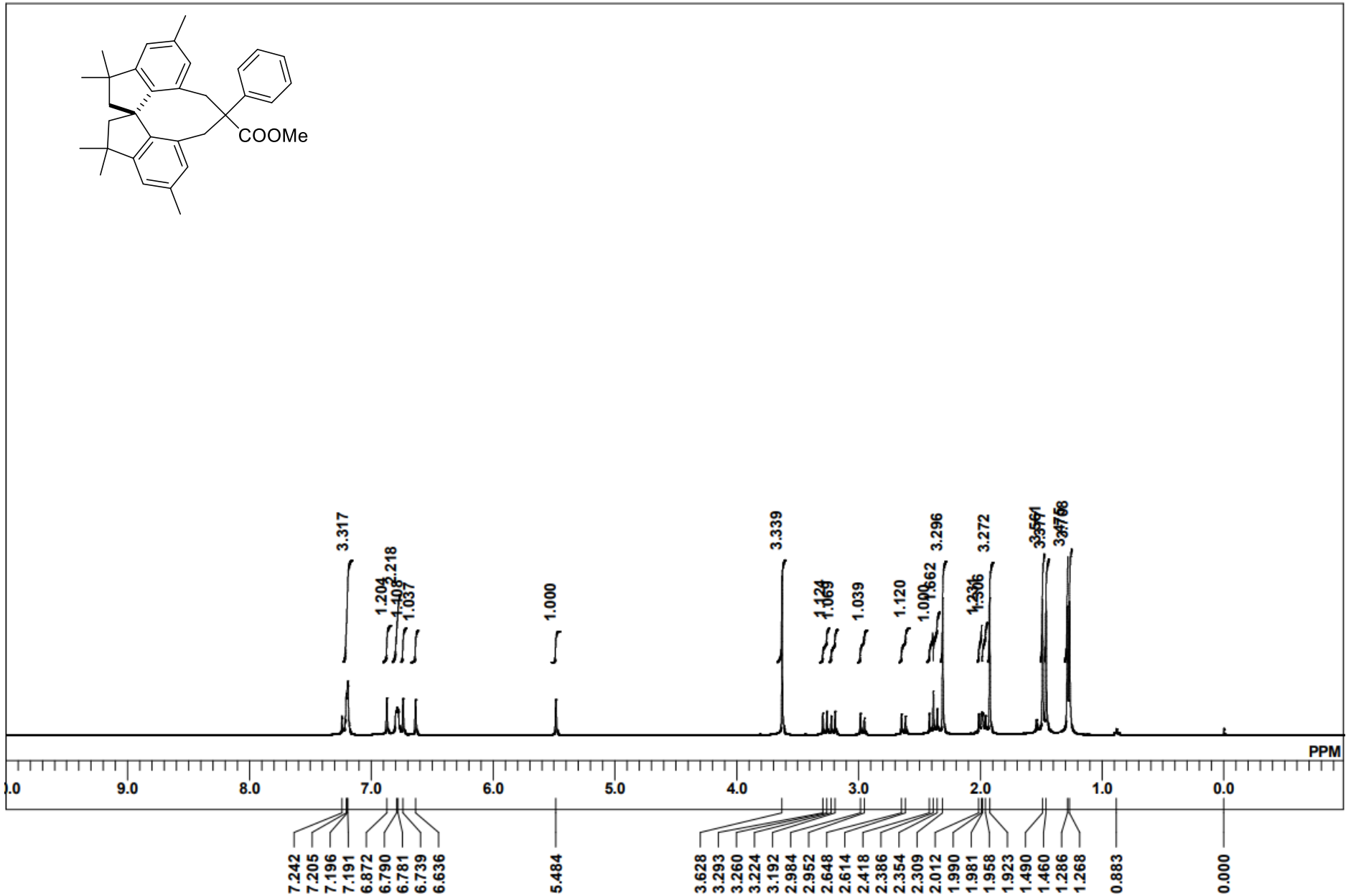
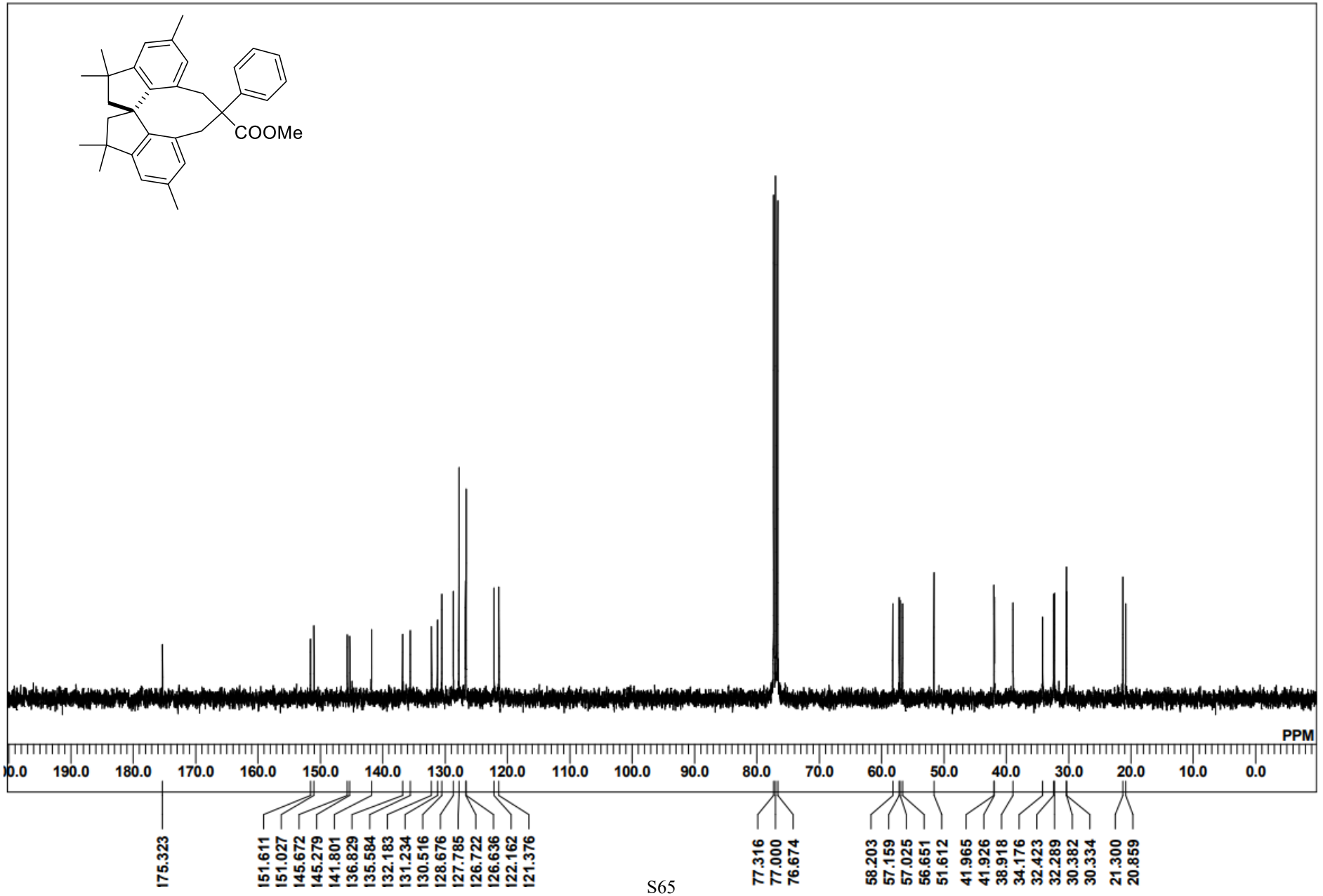
5. NMR spectra

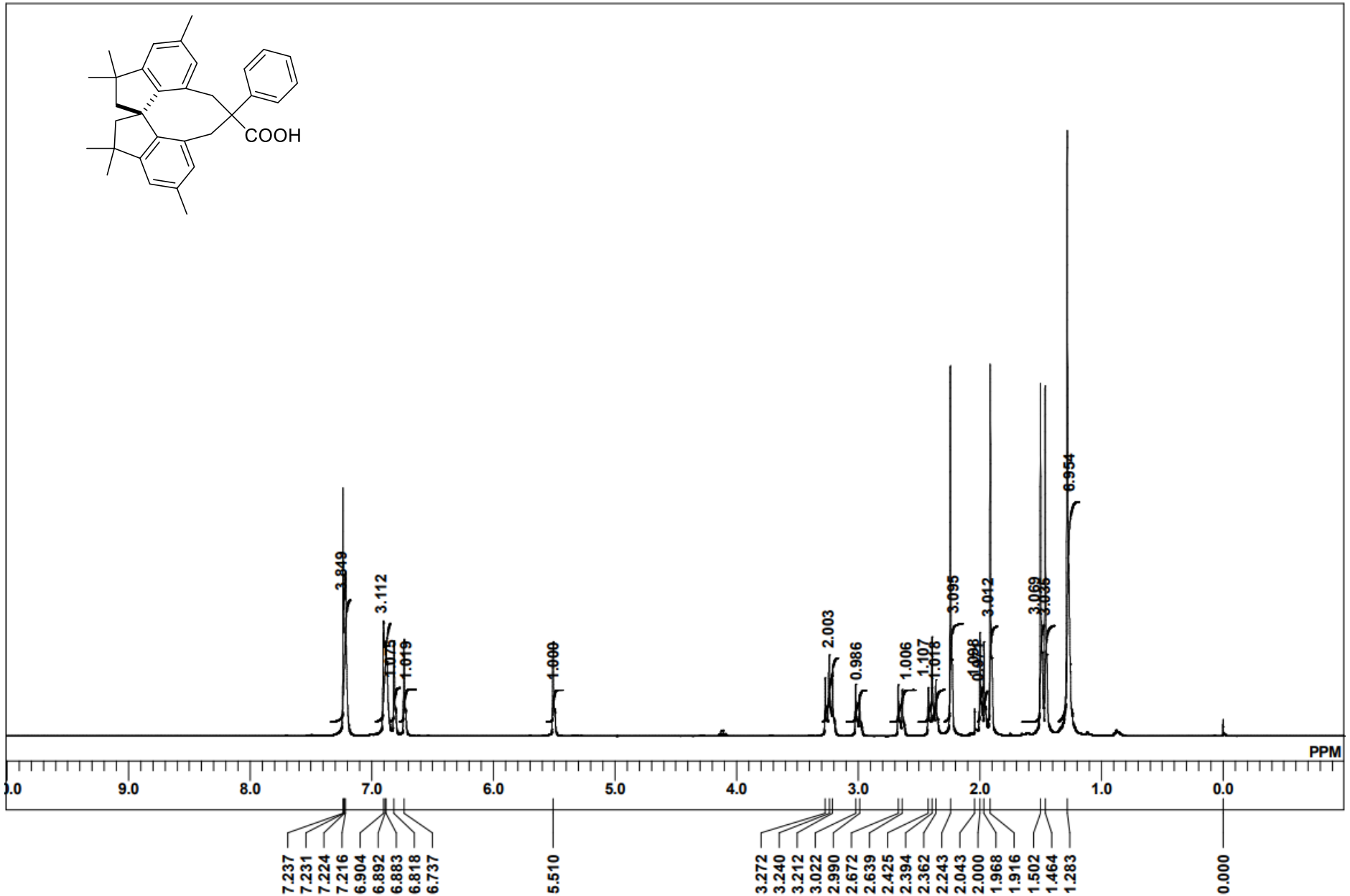
^{1}H NMR spectrum of **S1a**



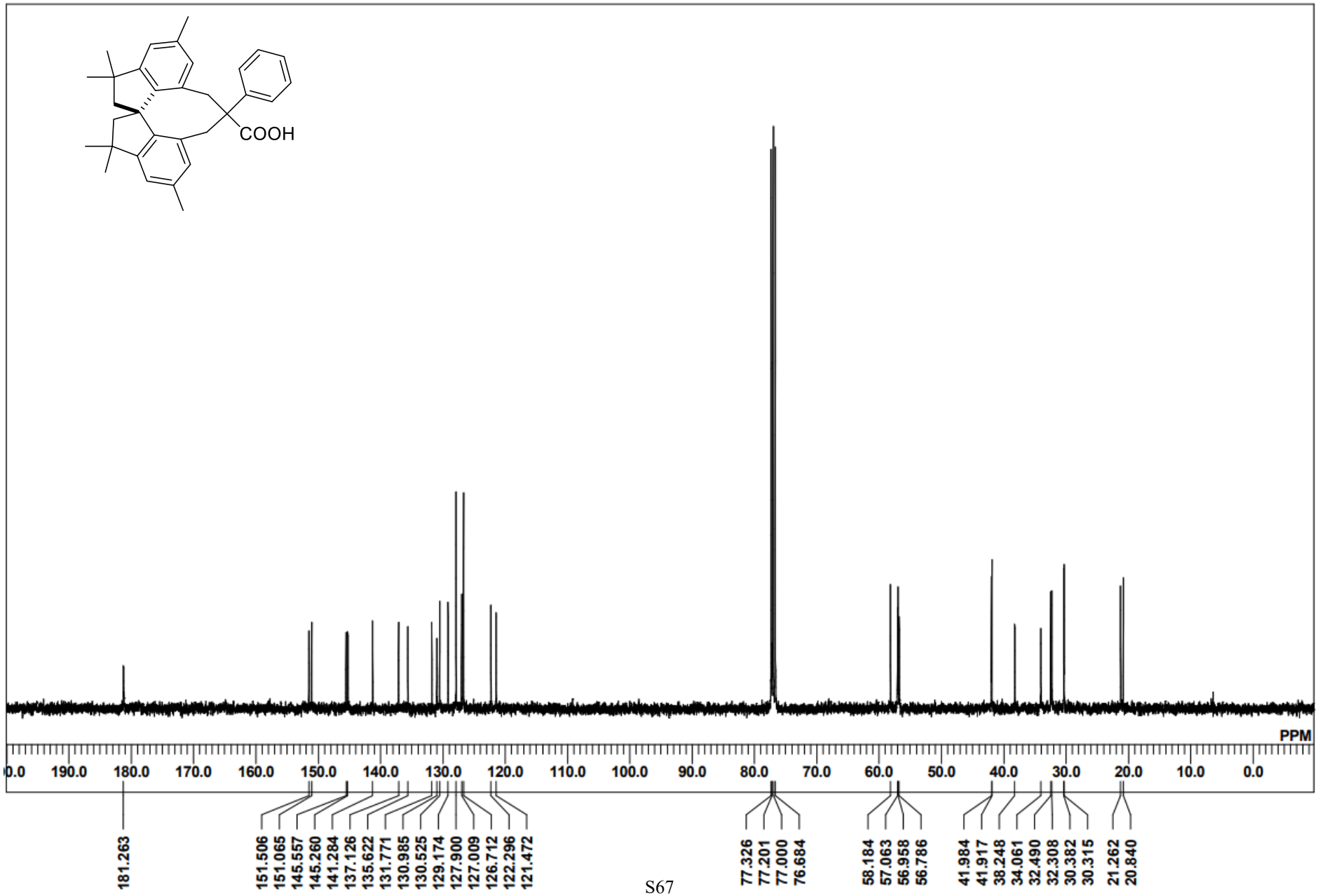
^{13}C NMR spectrum of **S1a**



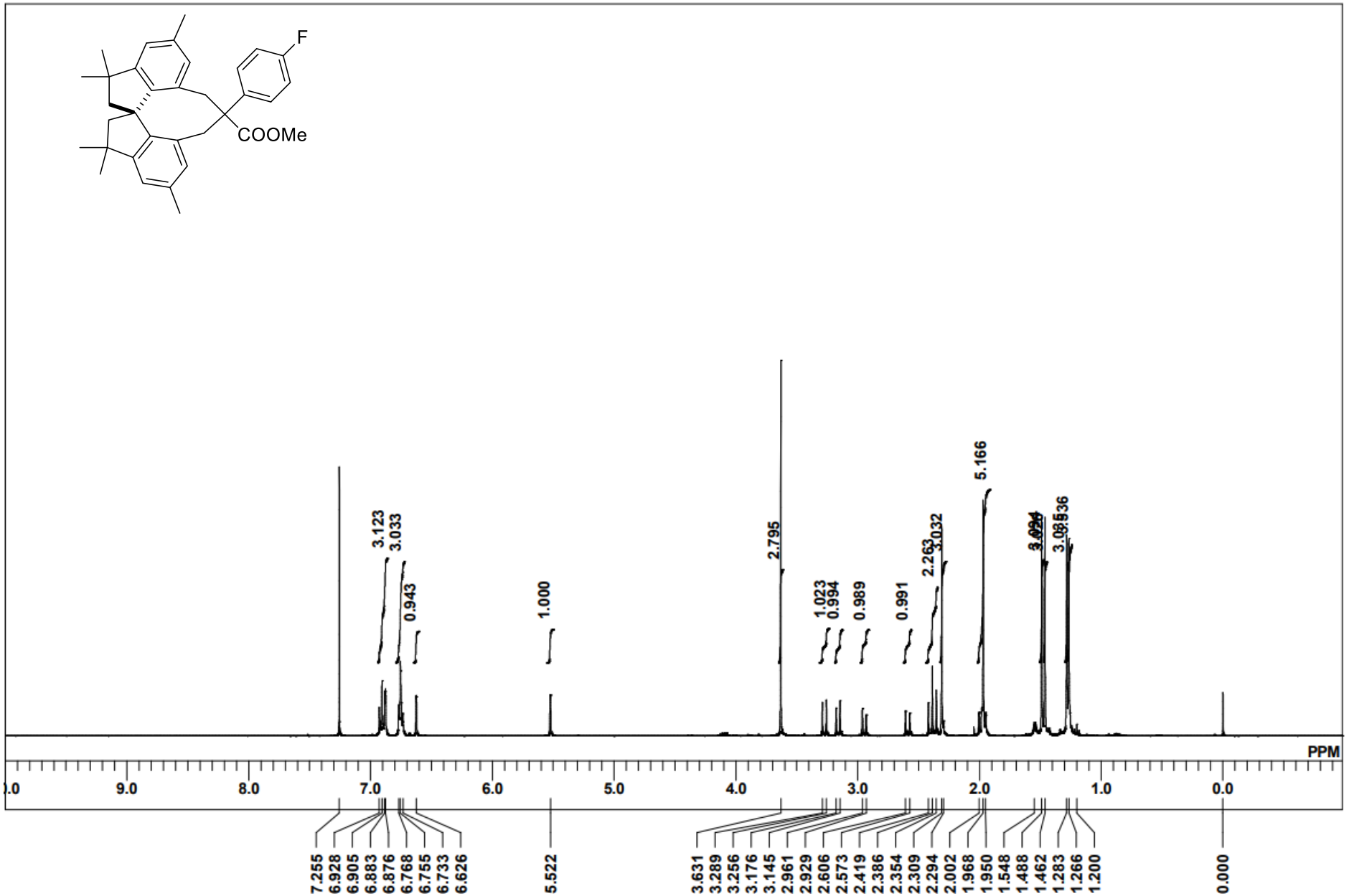
^{1}H NMR spectrum of **L7**



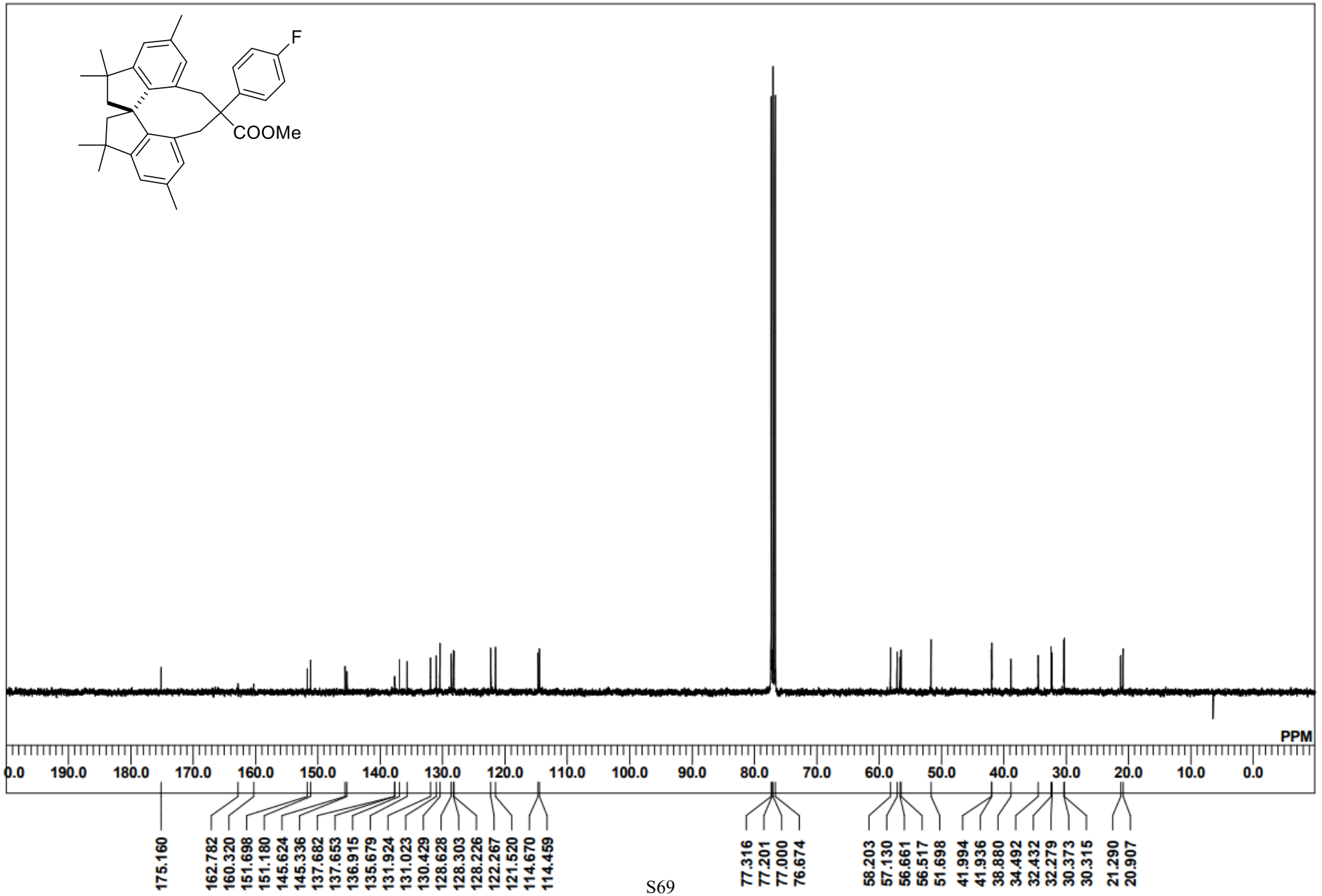
^{13}C NMR spectrum of **L7**



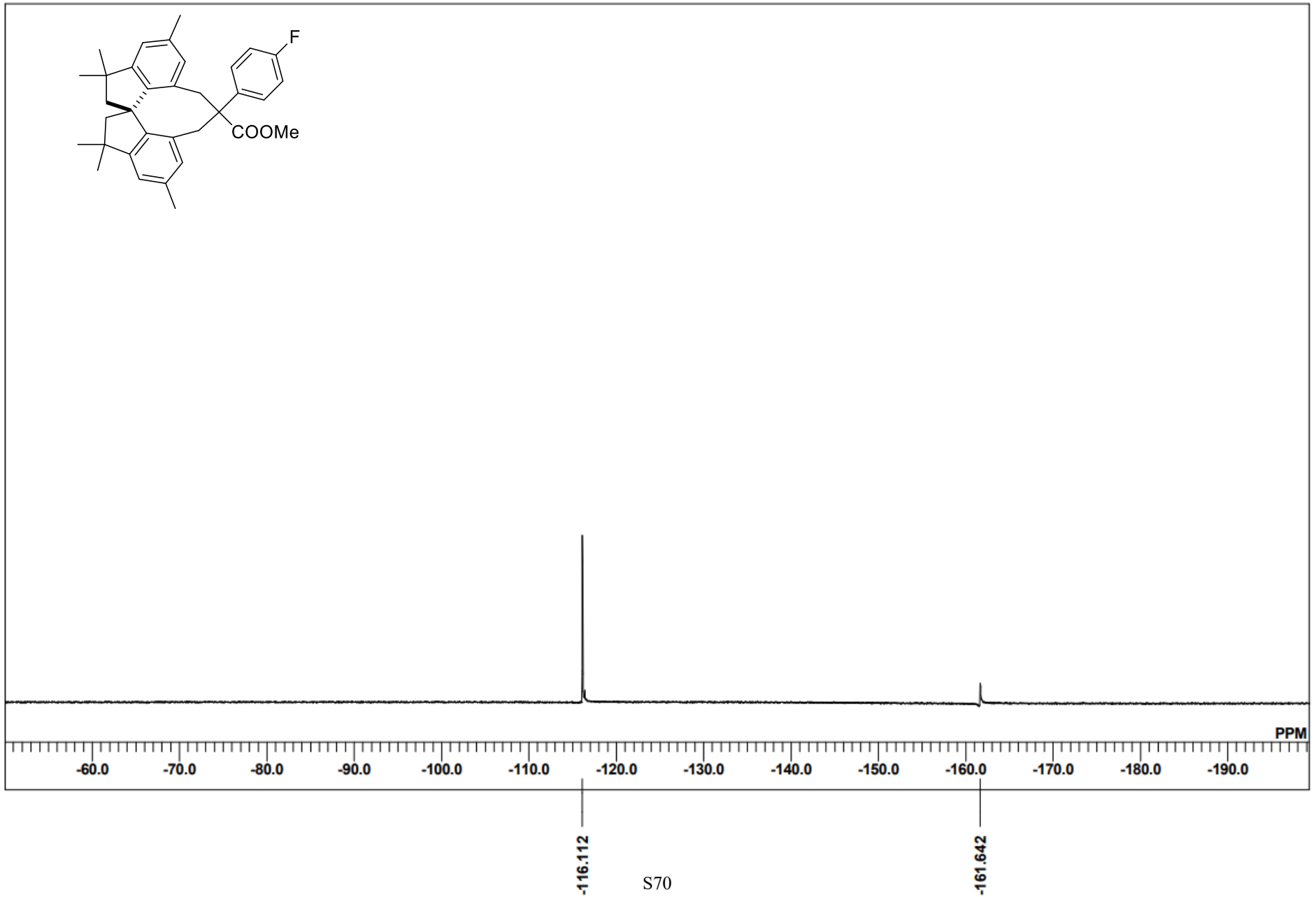
^{1}H NMR spectrum of **S1b**



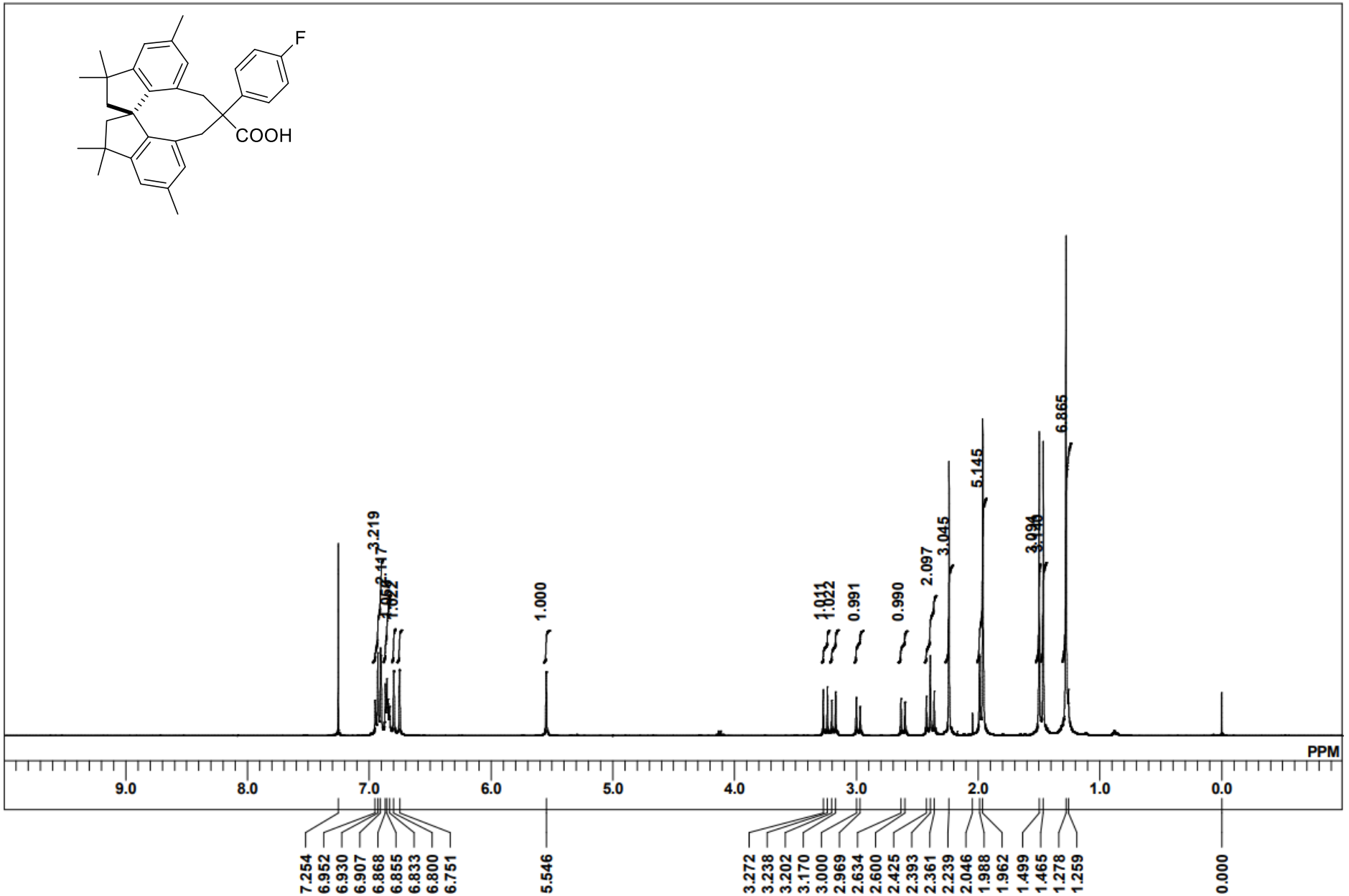
^{13}C NMR spectrum of **S1b**



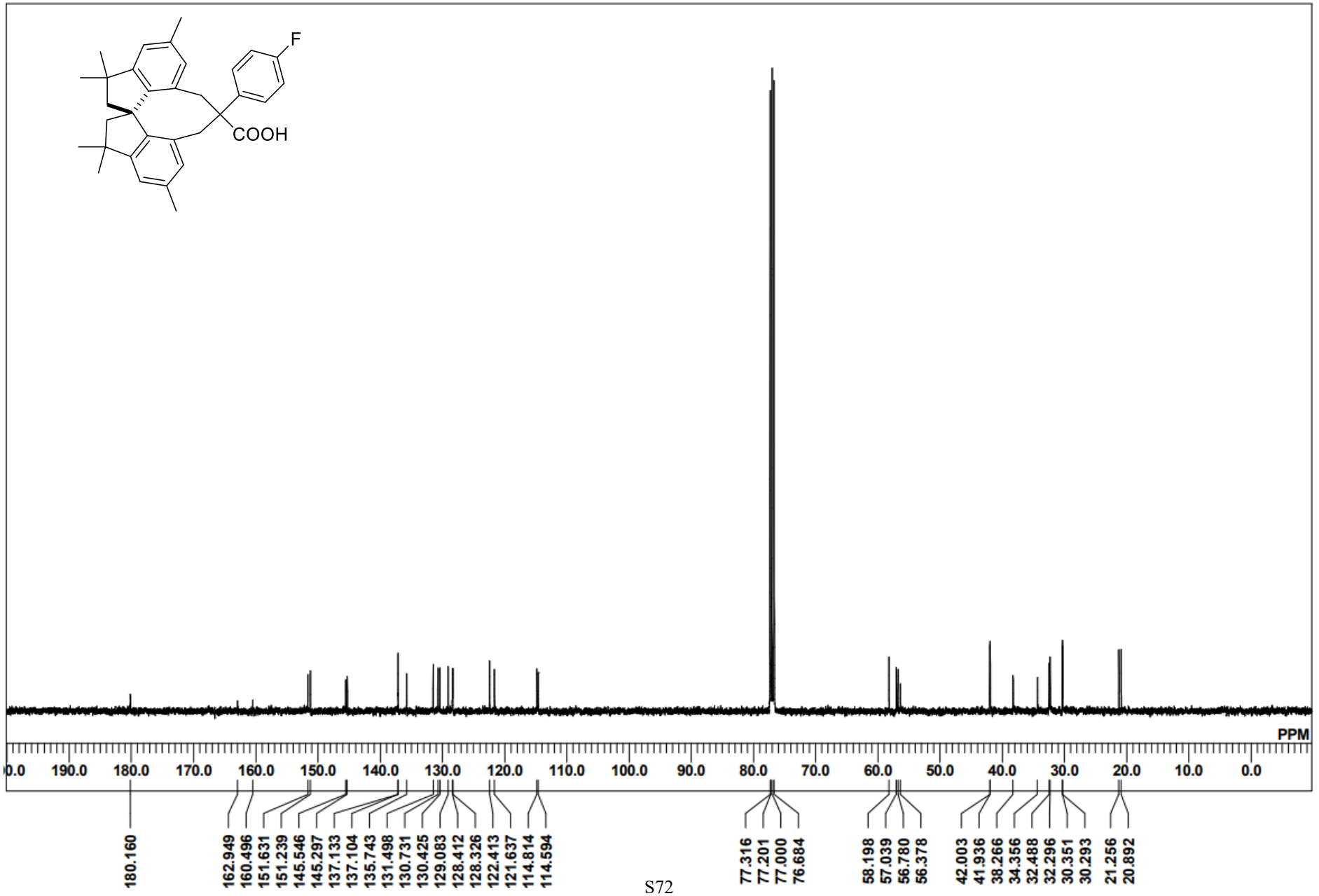
^{19}F NMR spectrum of **S1b**



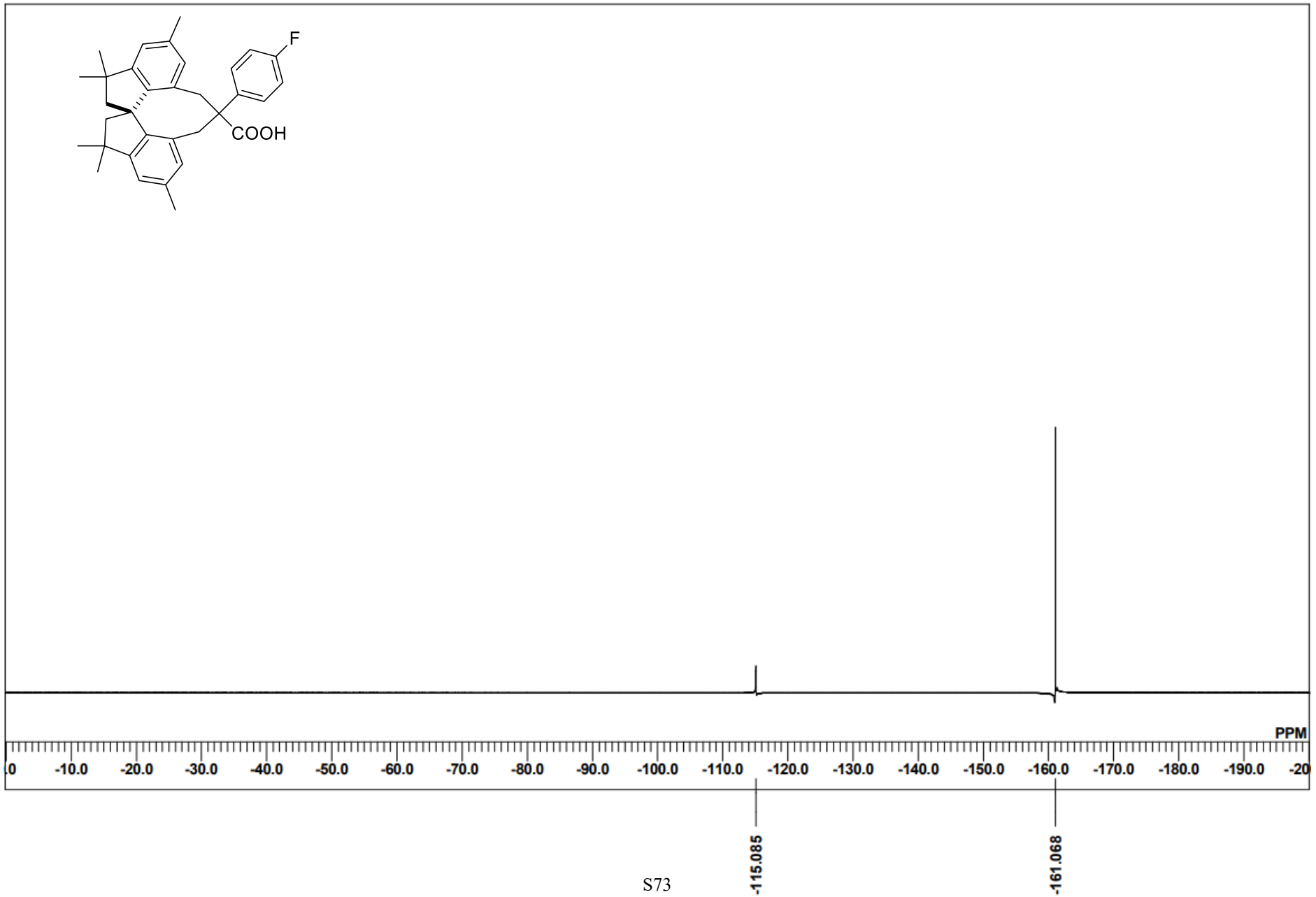
^{1}H NMR spectrum of **L8**



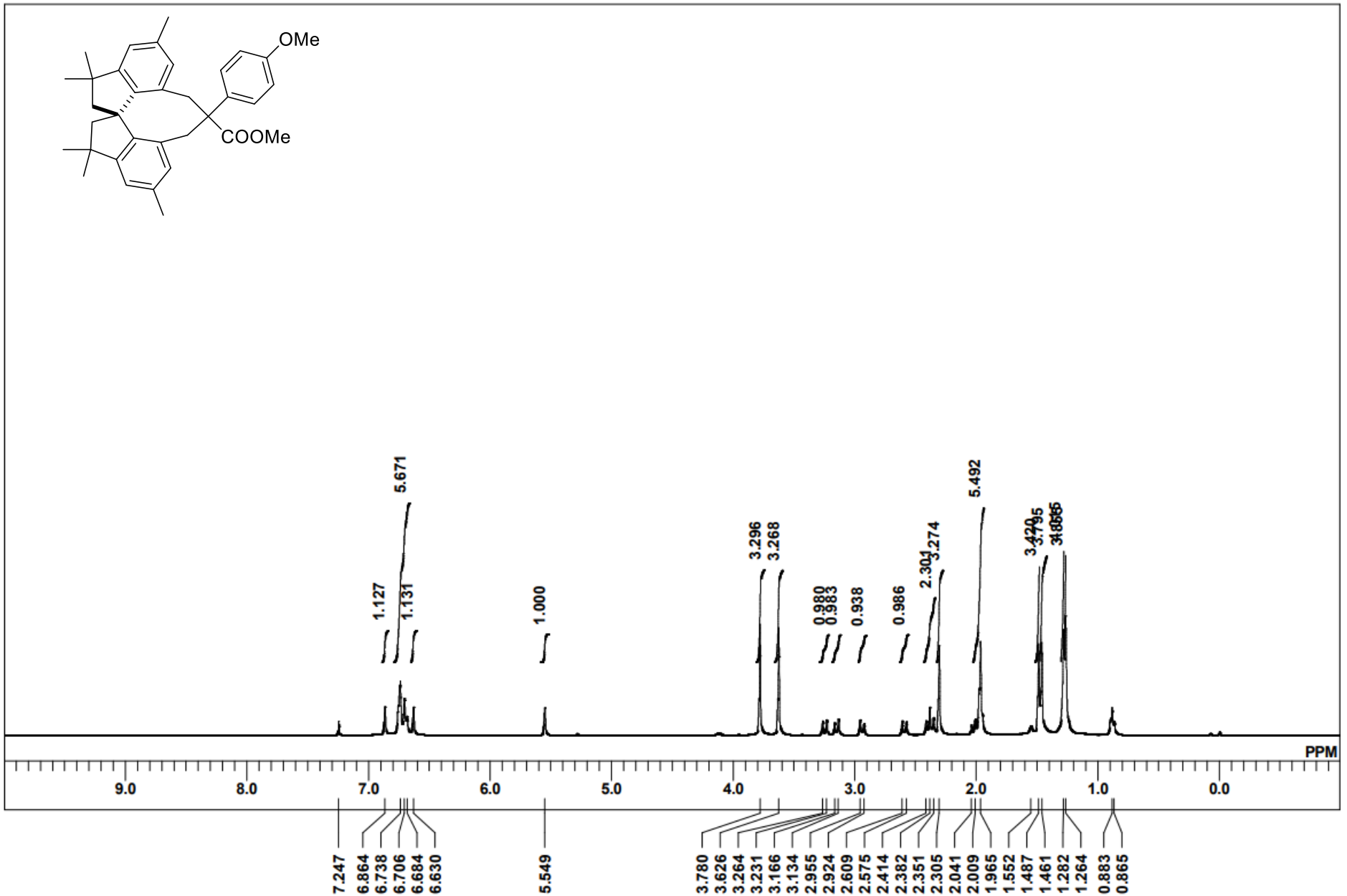
^{13}C NMR spectrum of **L8**



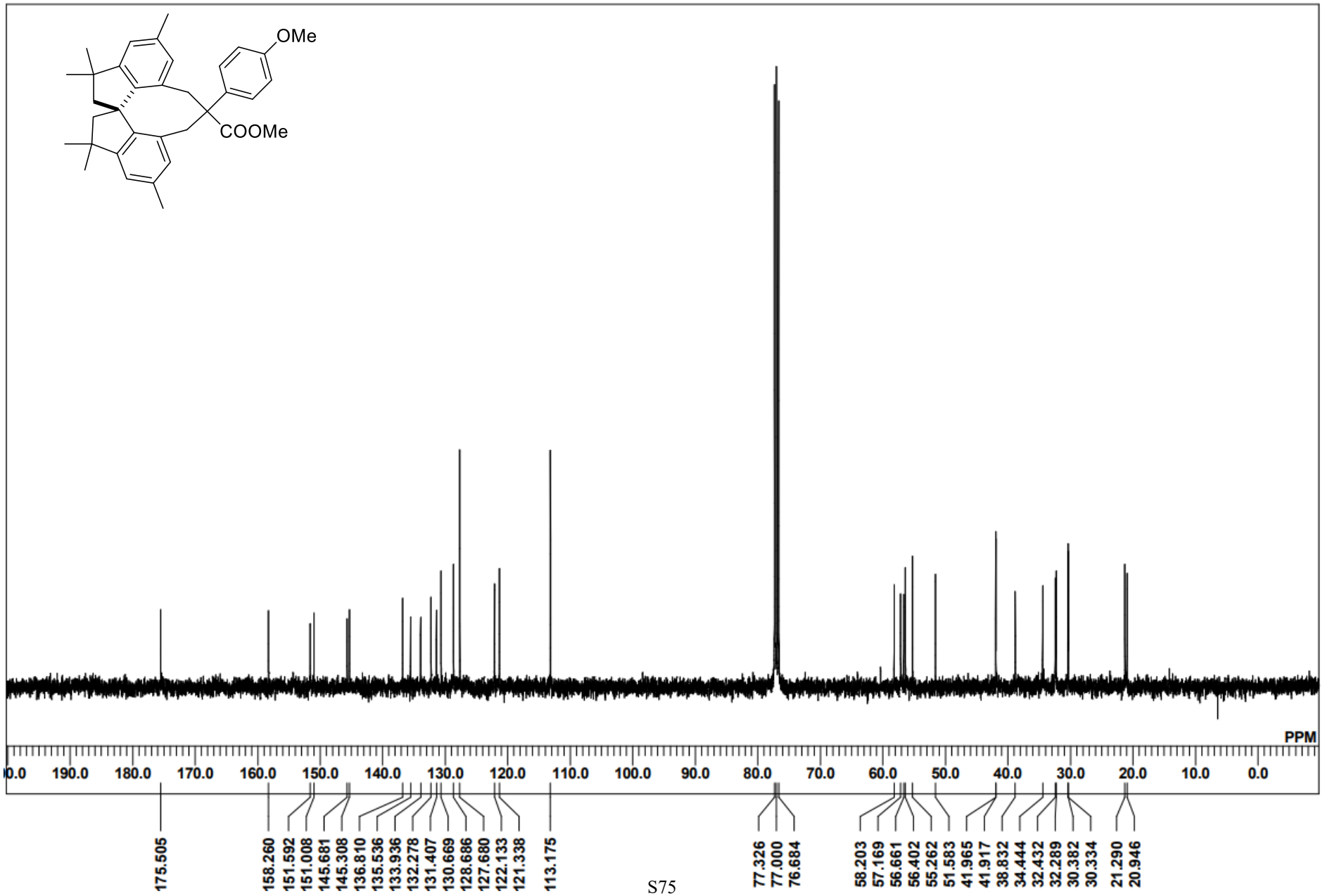
^{19}F NMR spectrum of **L8**



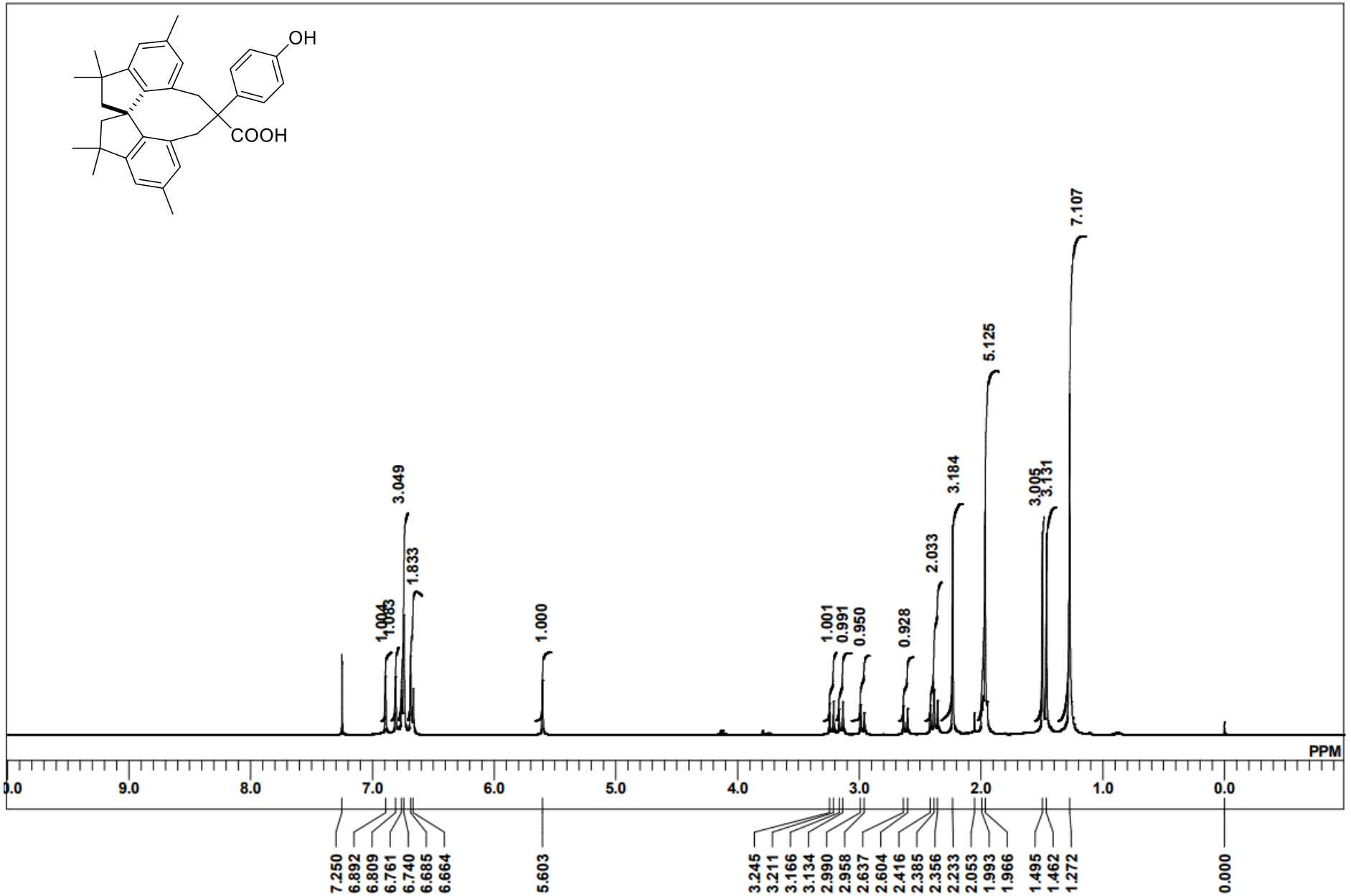
^{1}H NMR spectrum of **S1c**



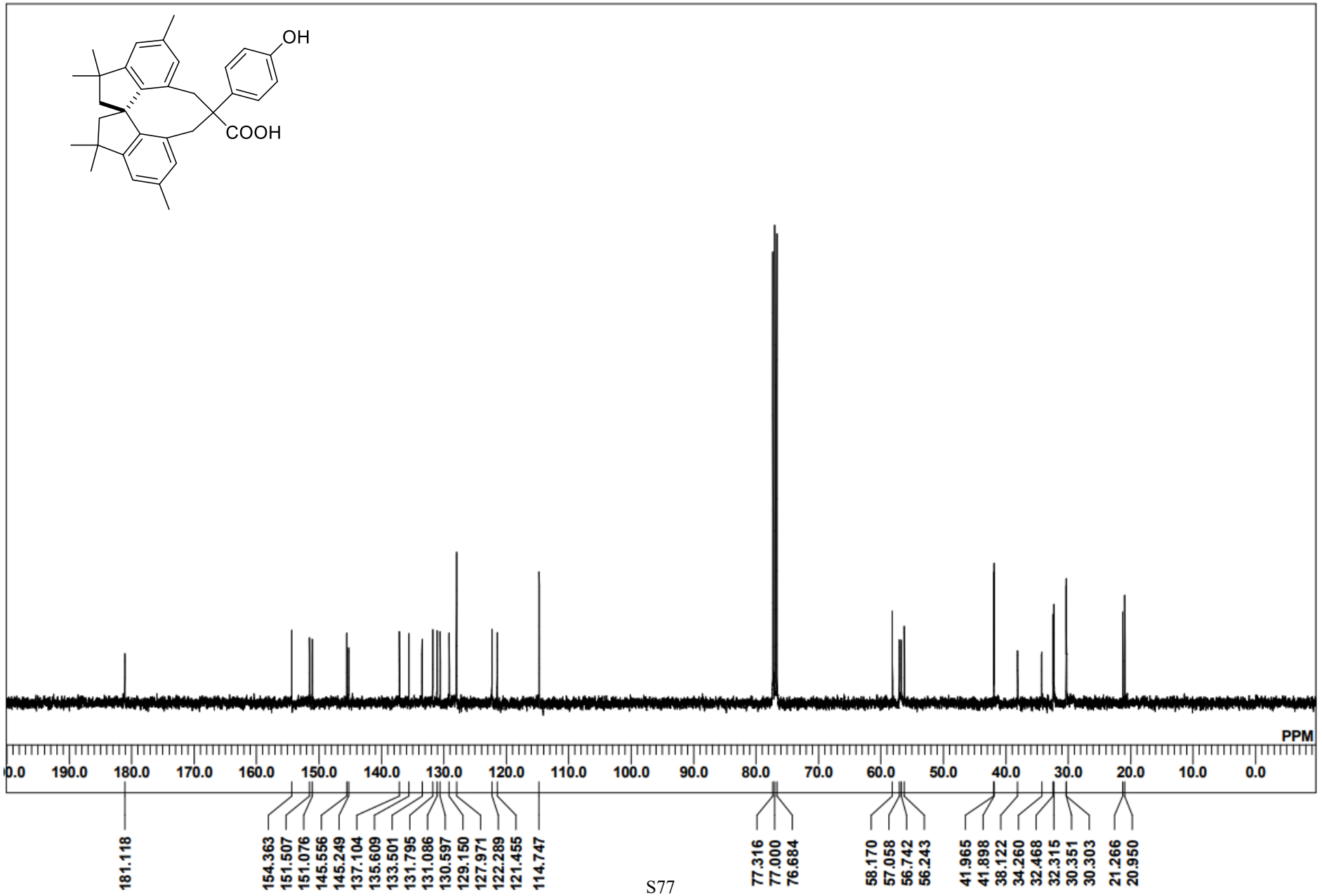
^{13}C NMR spectrum of **S1c**



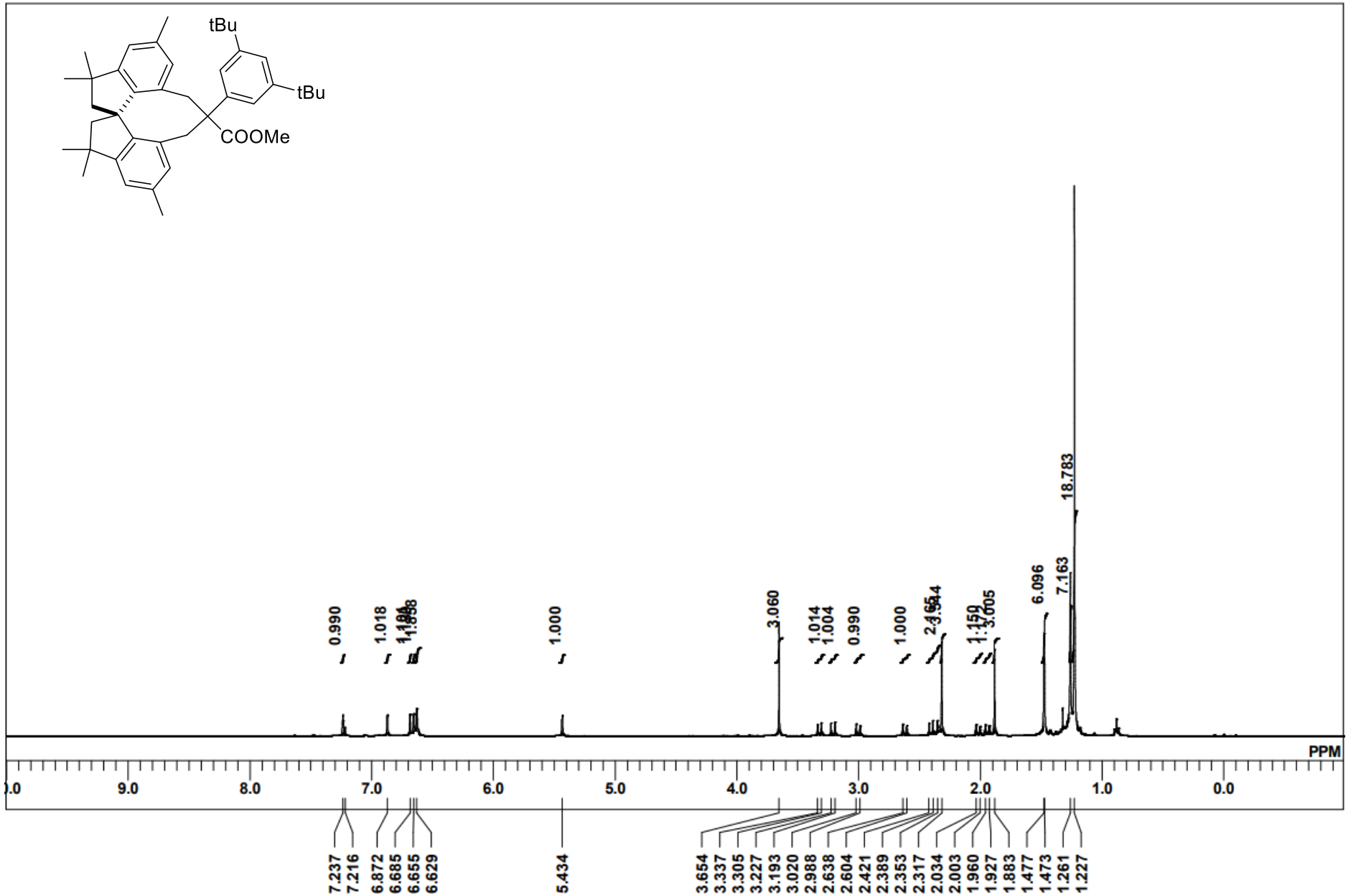
^{1}H NMR spectrum of **L9**



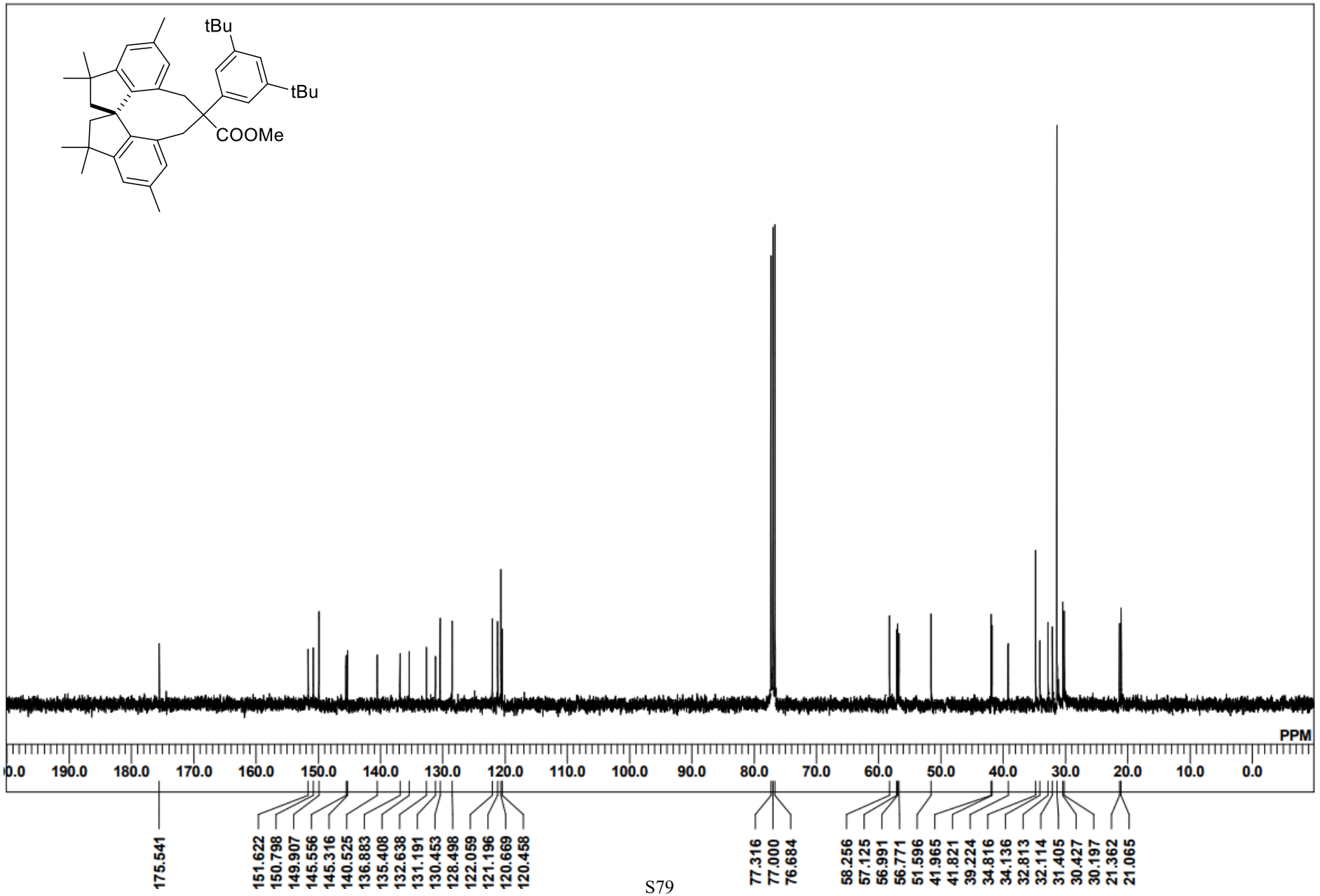
^{13}C NMR spectrum of **L9**



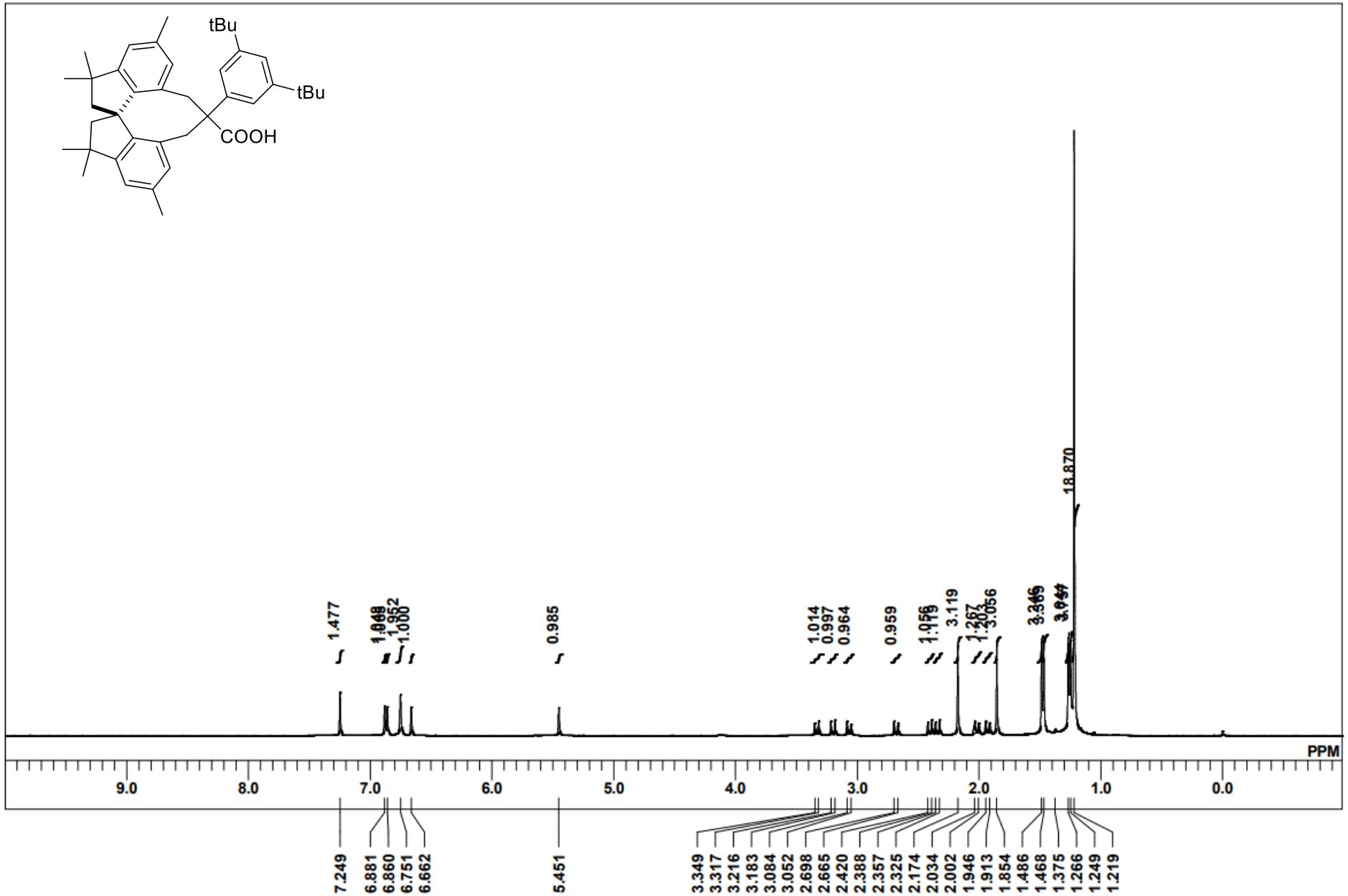
^{1}H NMR spectrum of **S1d**



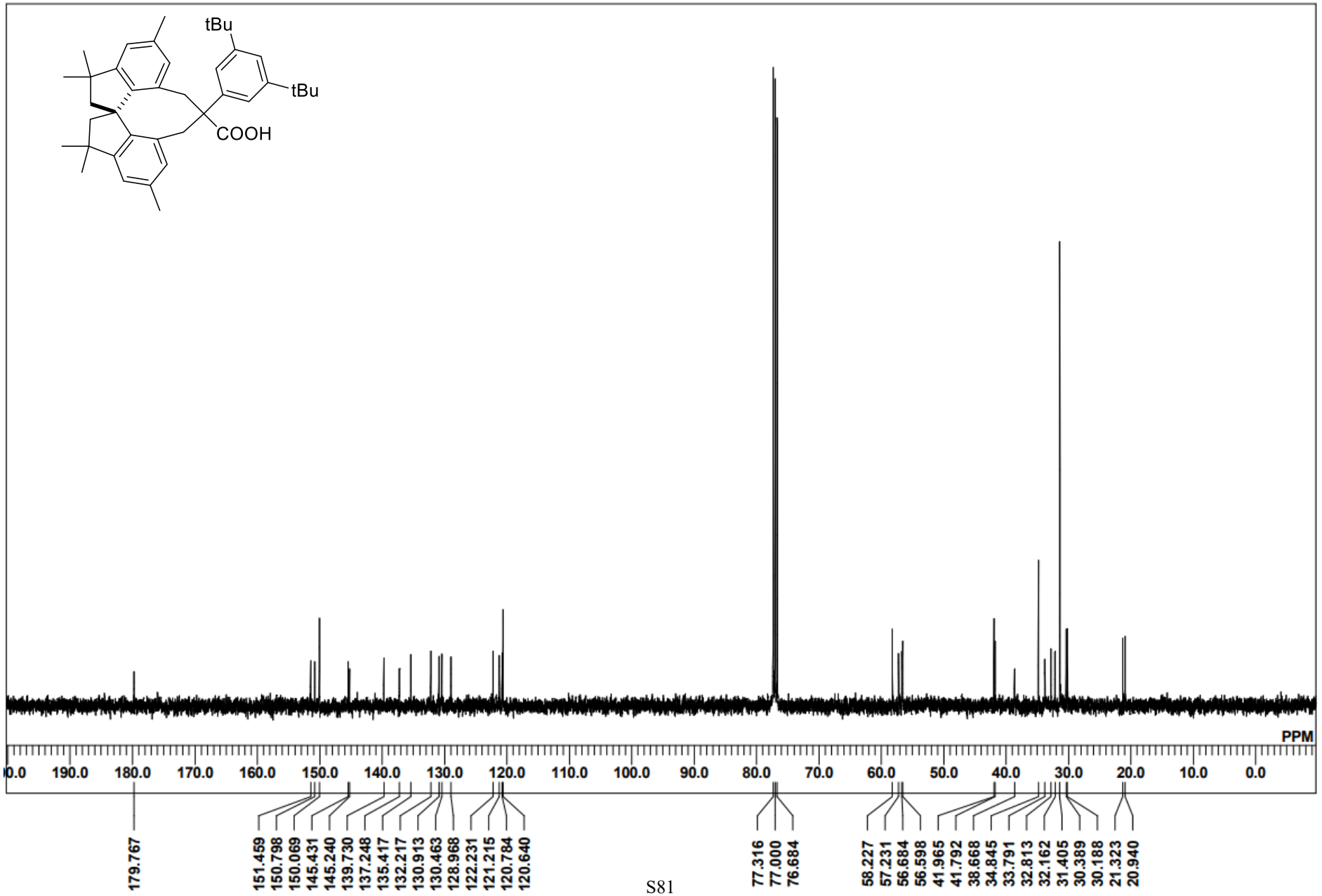
^{13}C NMR spectrum of **S1d**



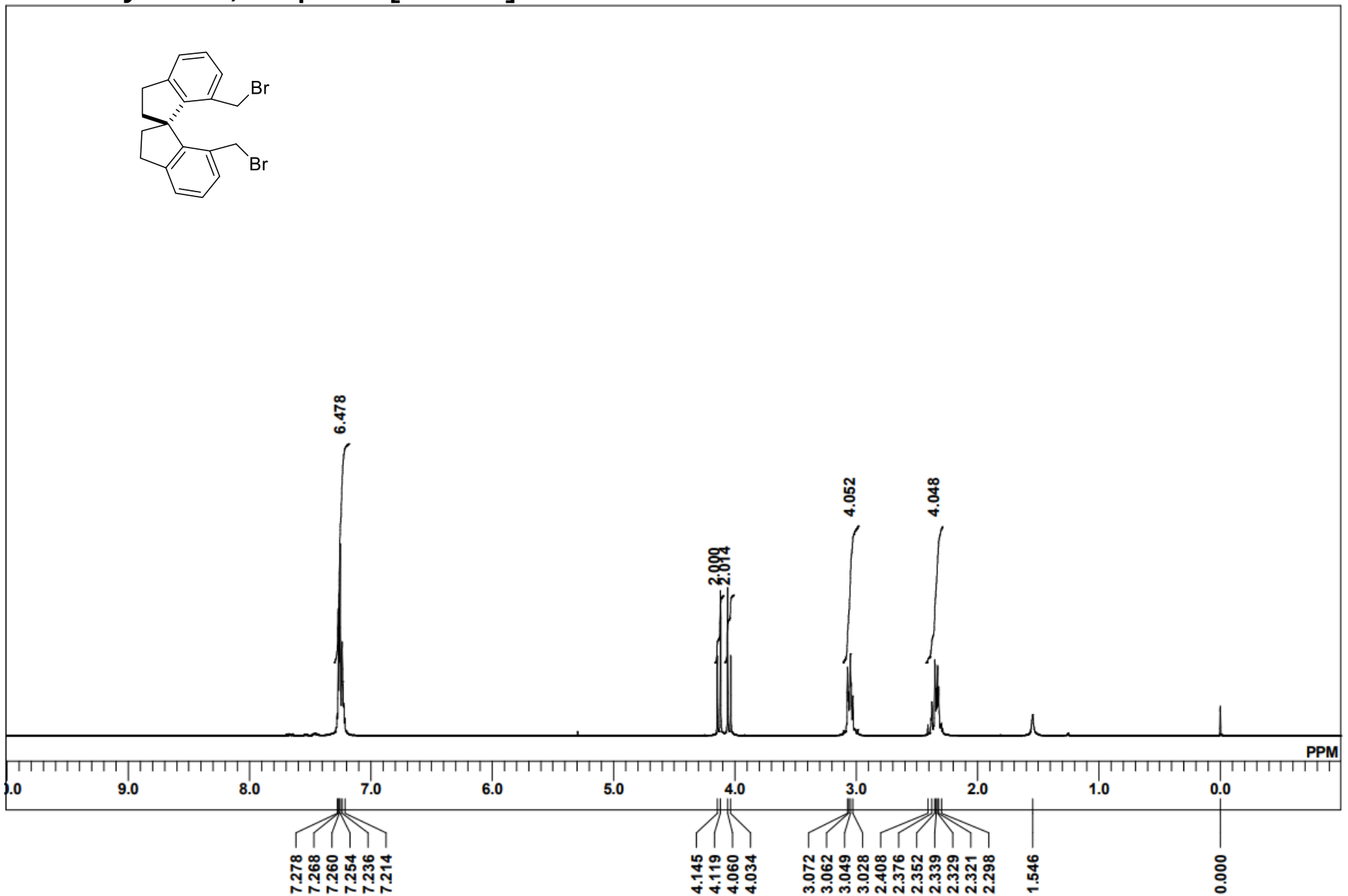
^{1}H NMR spectrum of **L10**



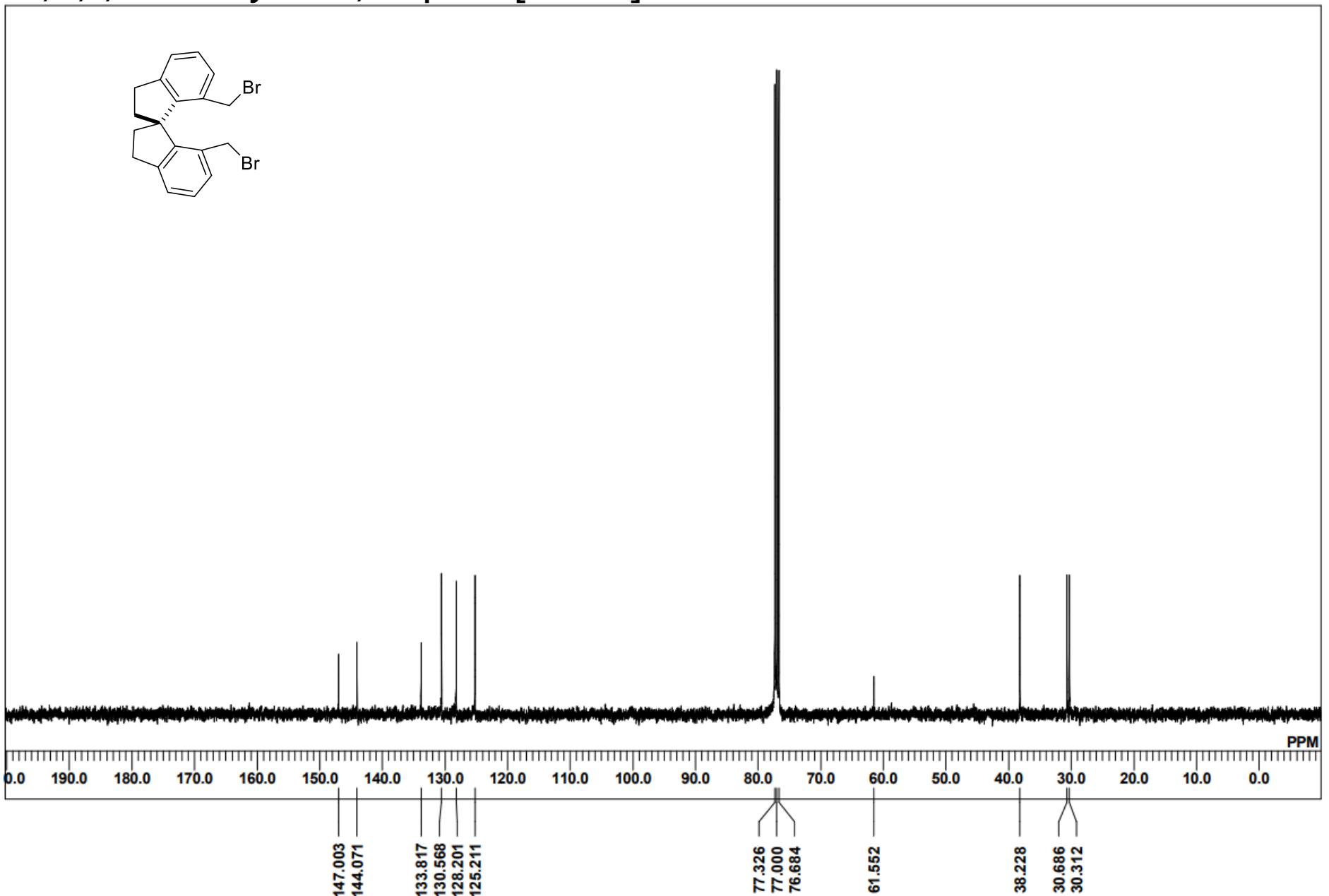
^{13}C NMR spectrum of **L10**



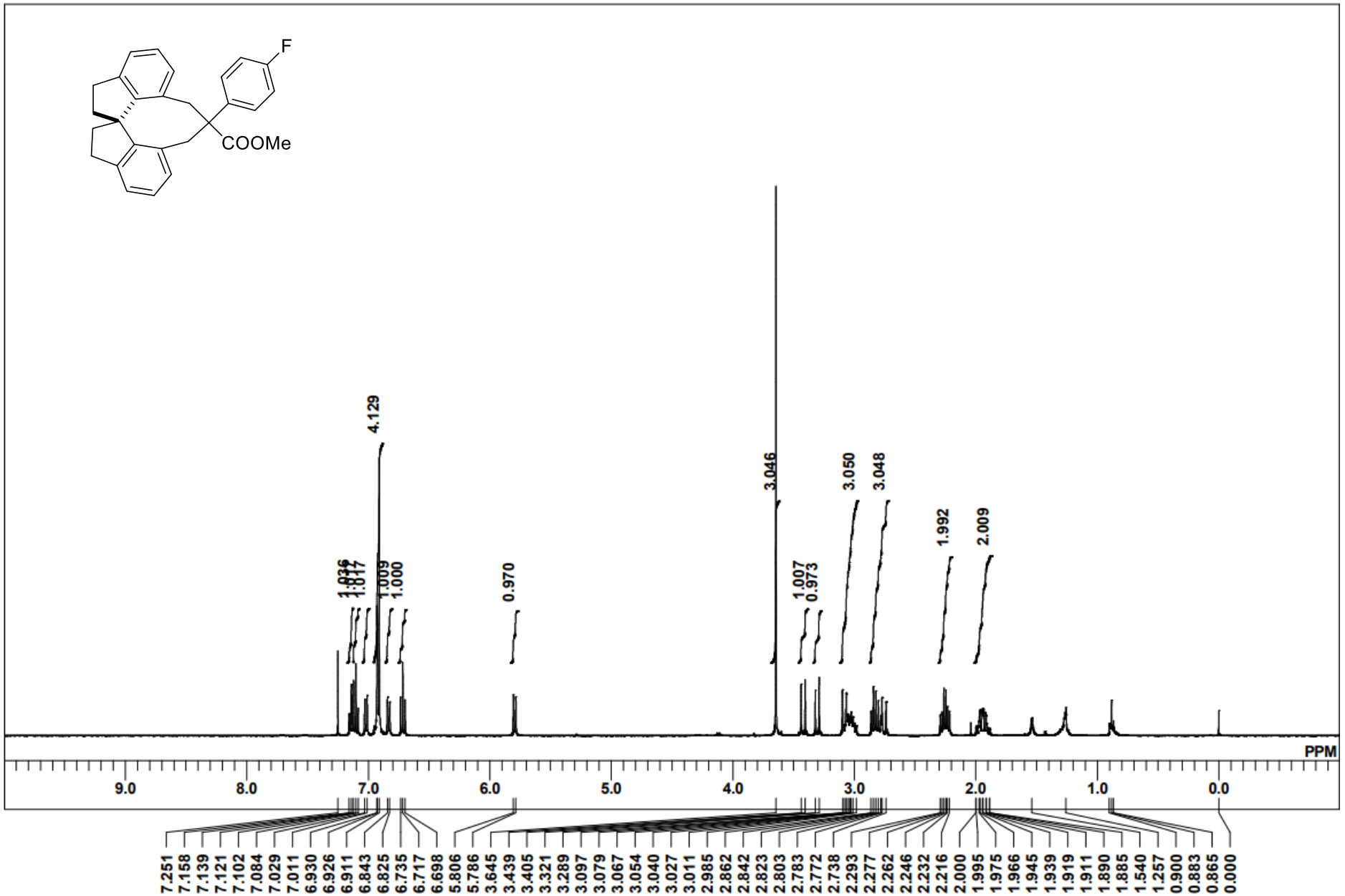
^{1}H NMR spectrum of **(R)-7,7'-bis(bromomethyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]**



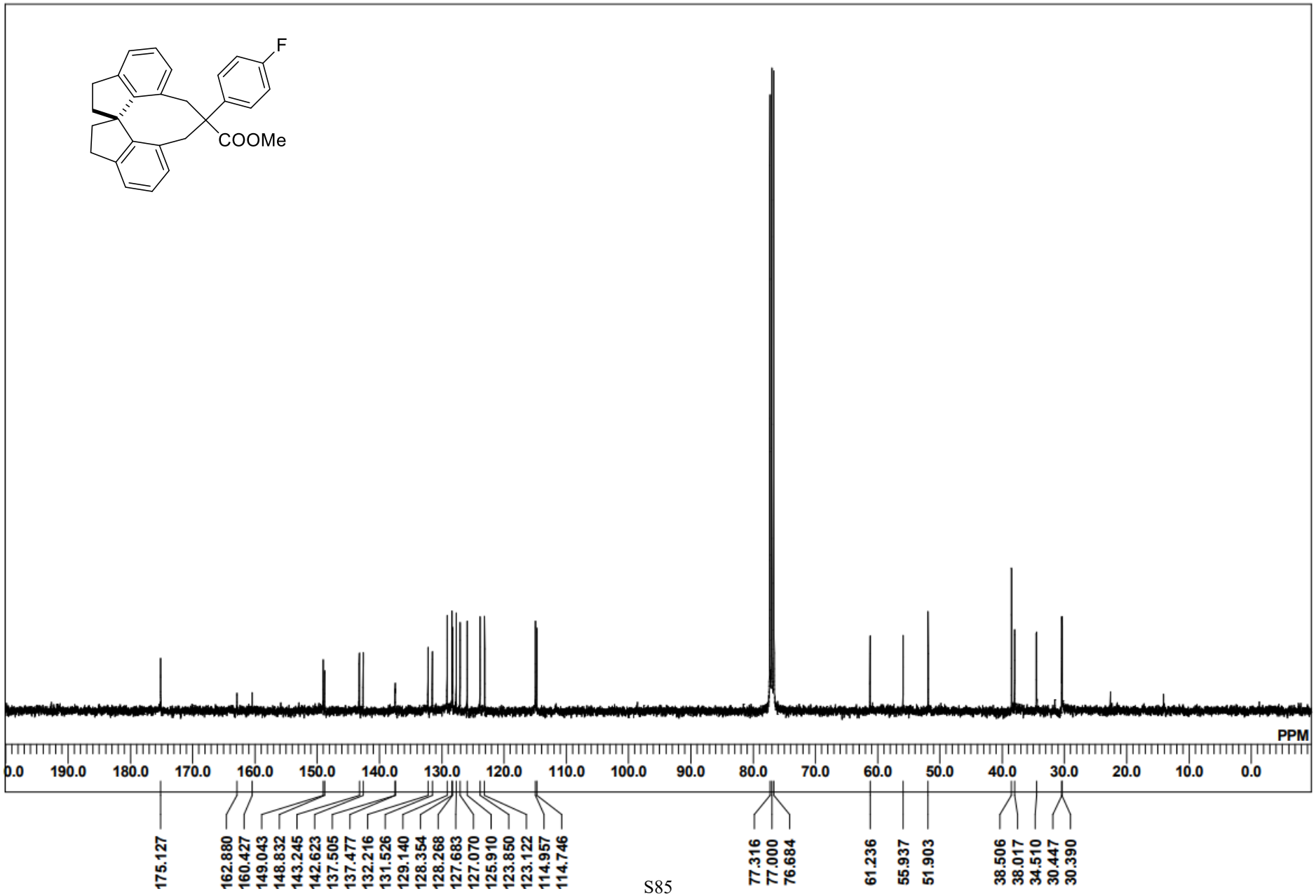
^{13}C NMR spectrum of **(R)-7,7'-bis(bromomethyl)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]**



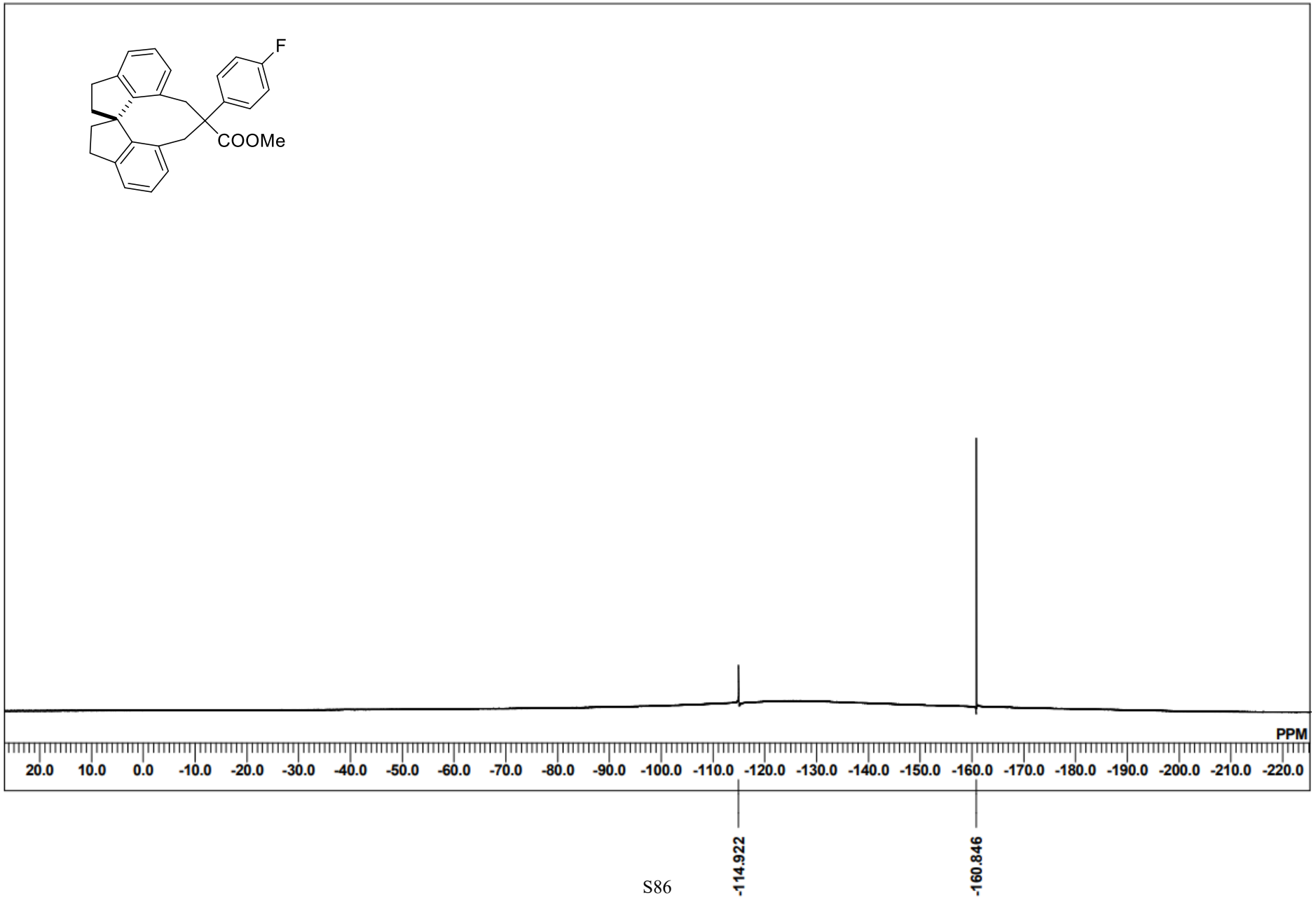
^{1}H NMR spectrum of **S1e**



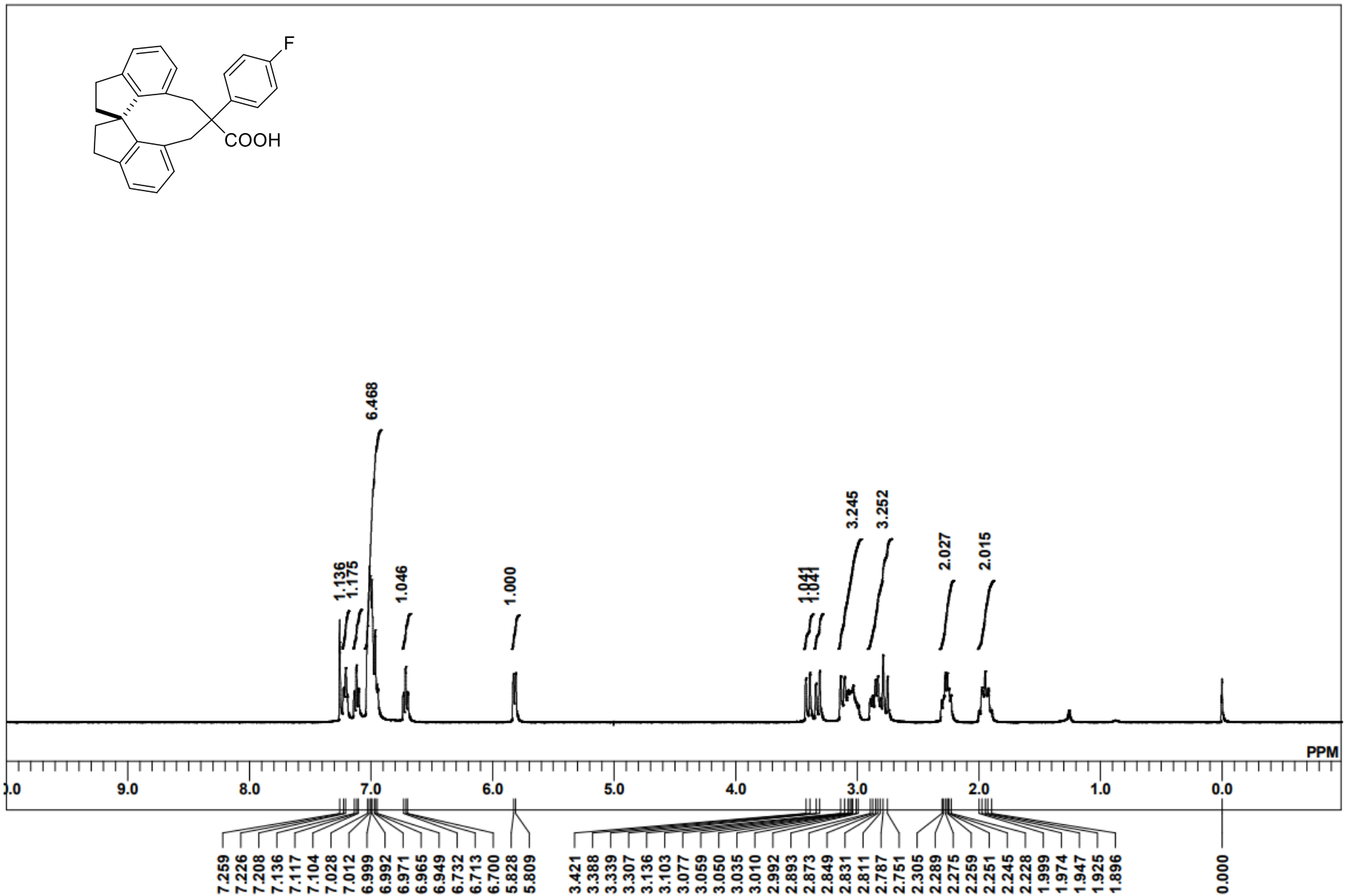
^{13}C NMR spectrum of **S1e**



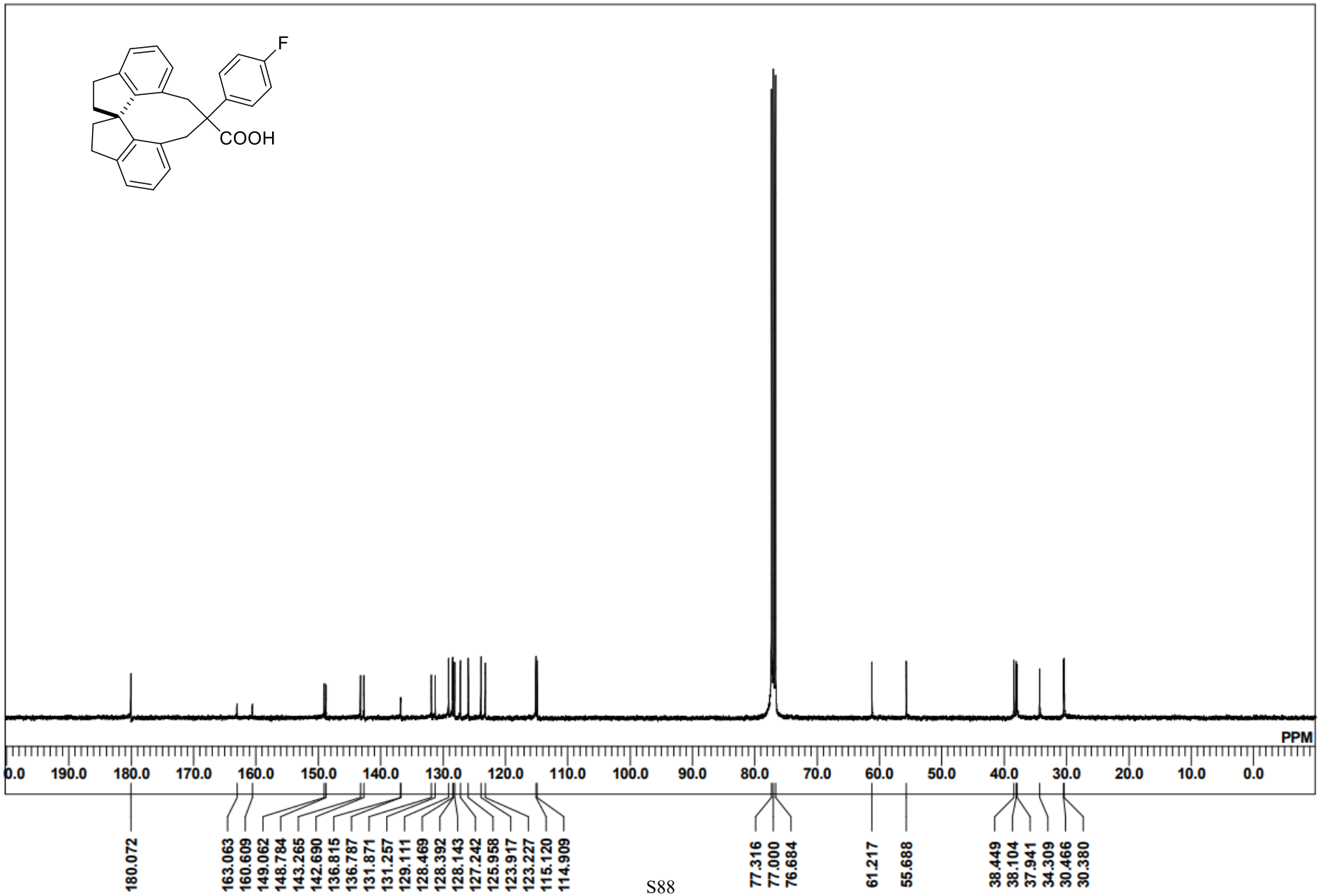
^{19}F NMR spectrum of **S1e**



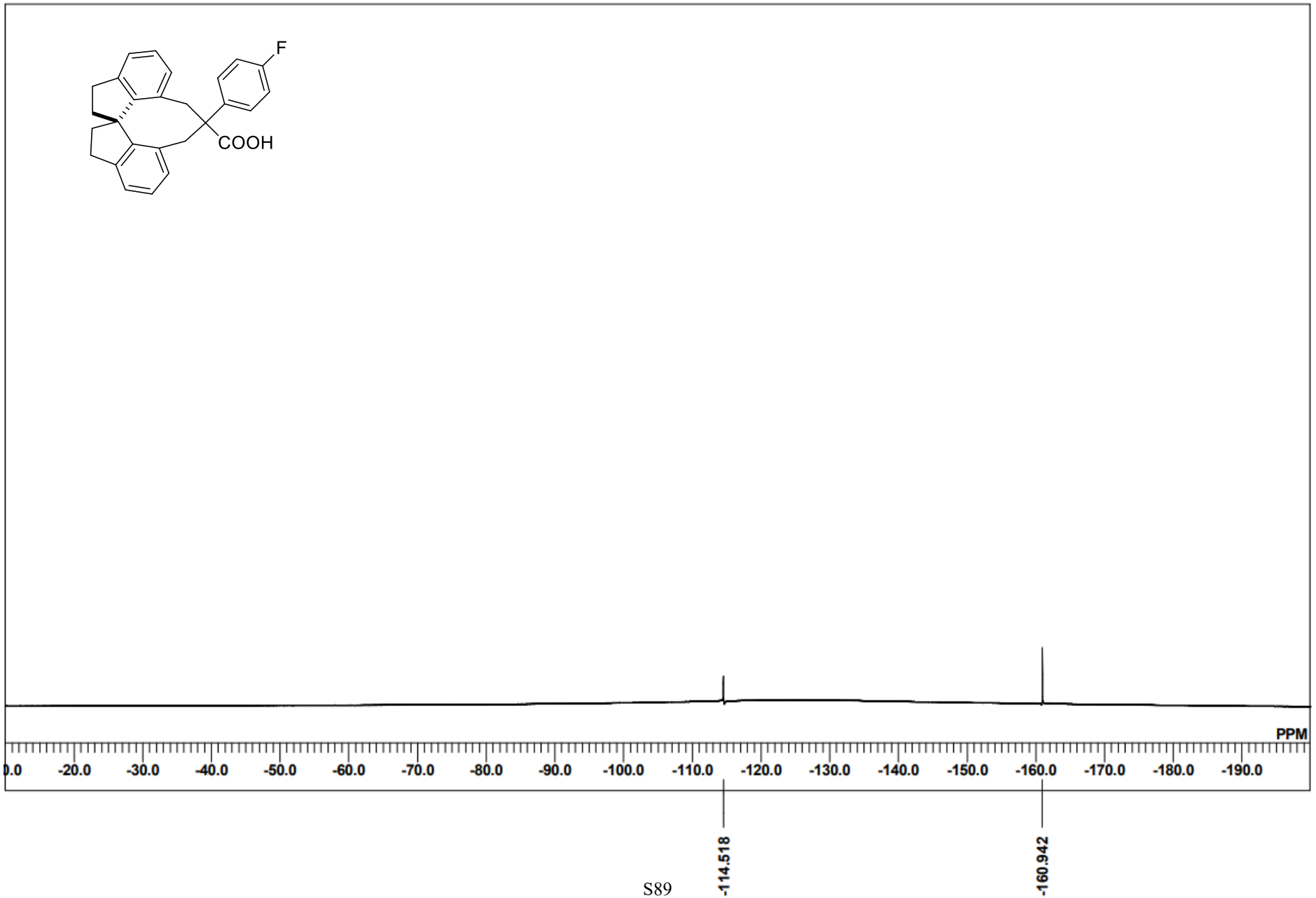
^{1}H NMR spectrum of **L11**



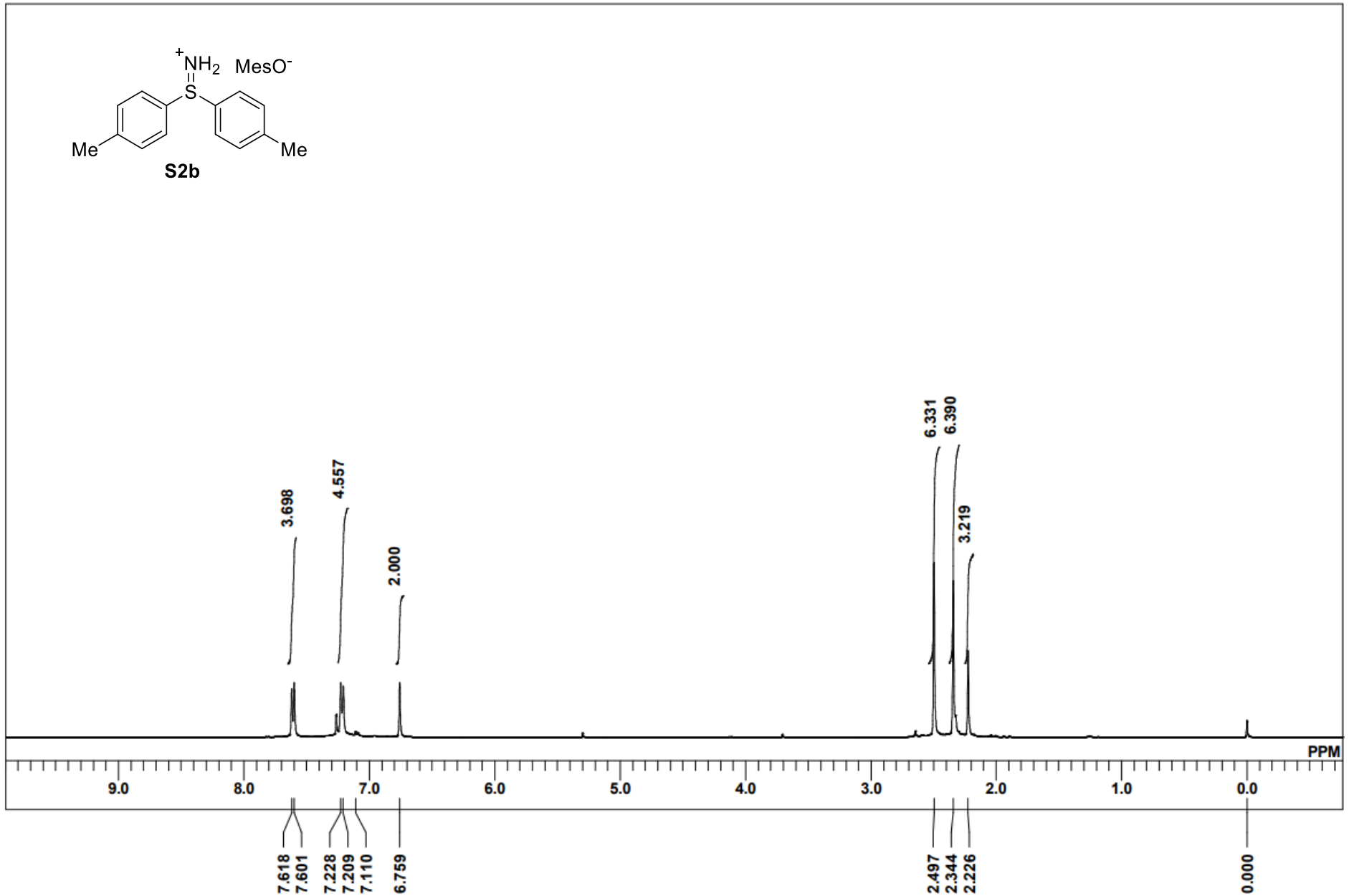
^{13}C NMR spectrum of **L11**



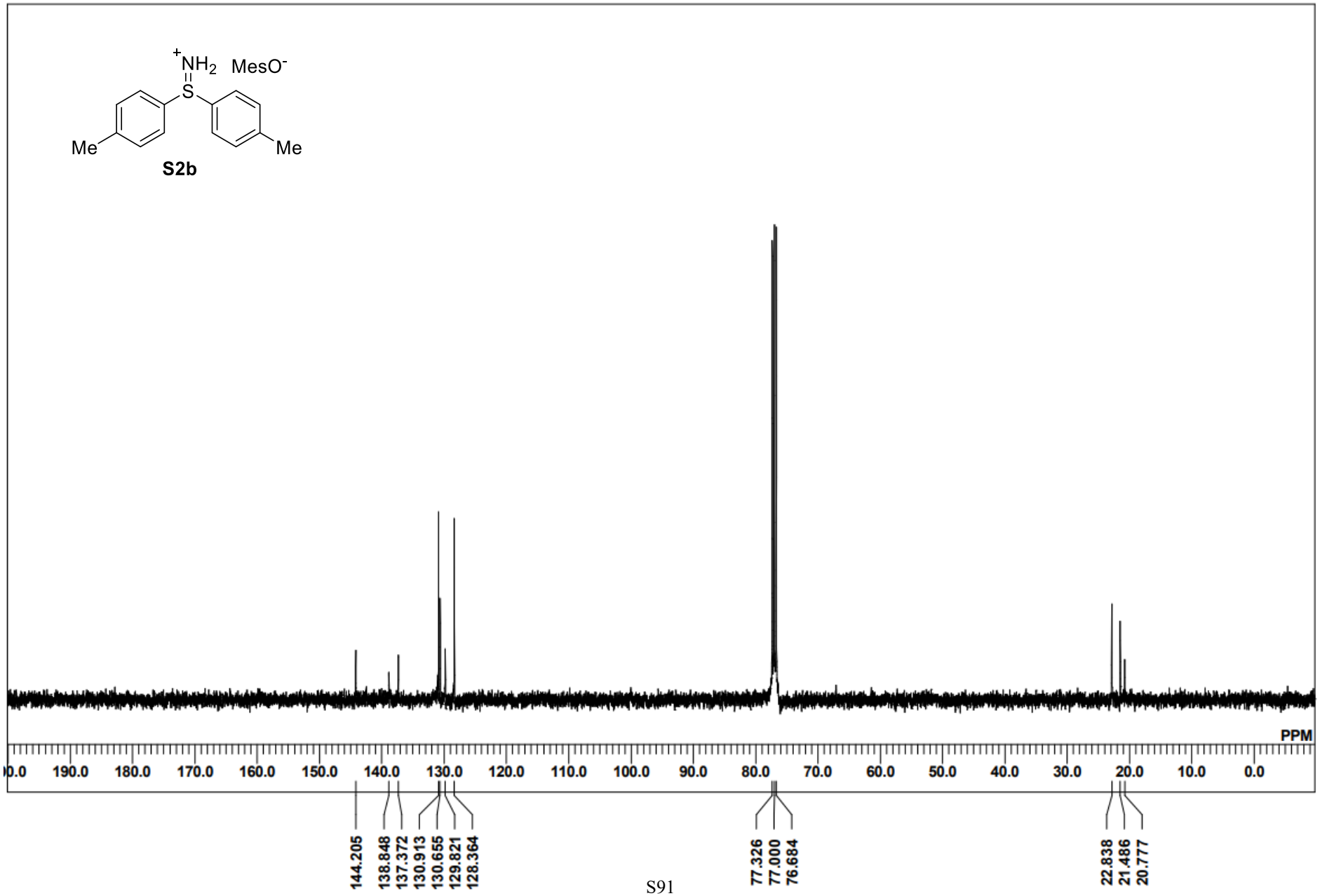
^{19}F NMR spectrum of **L11**



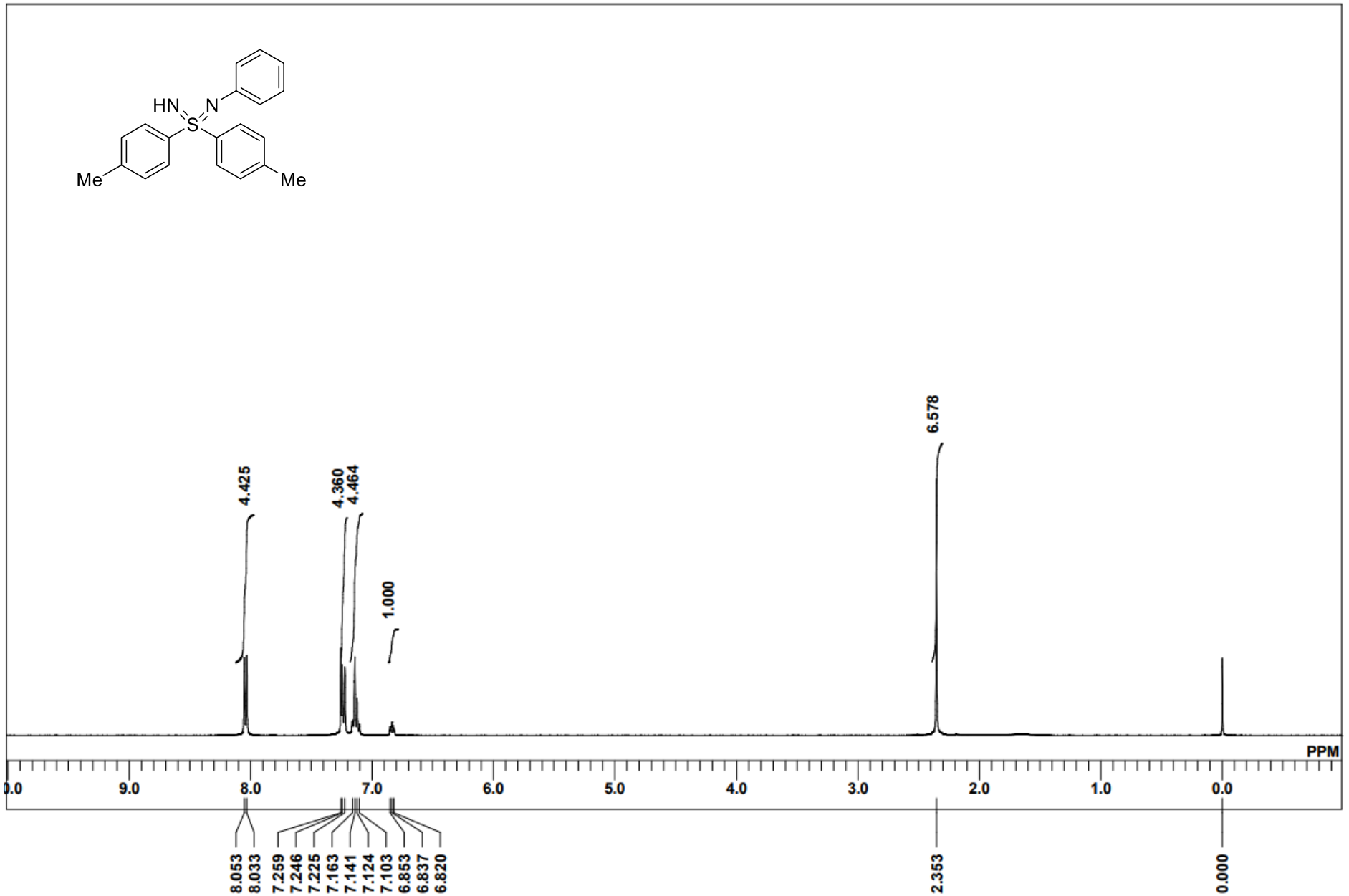
^{1}H NMR spectrum of **S2b**



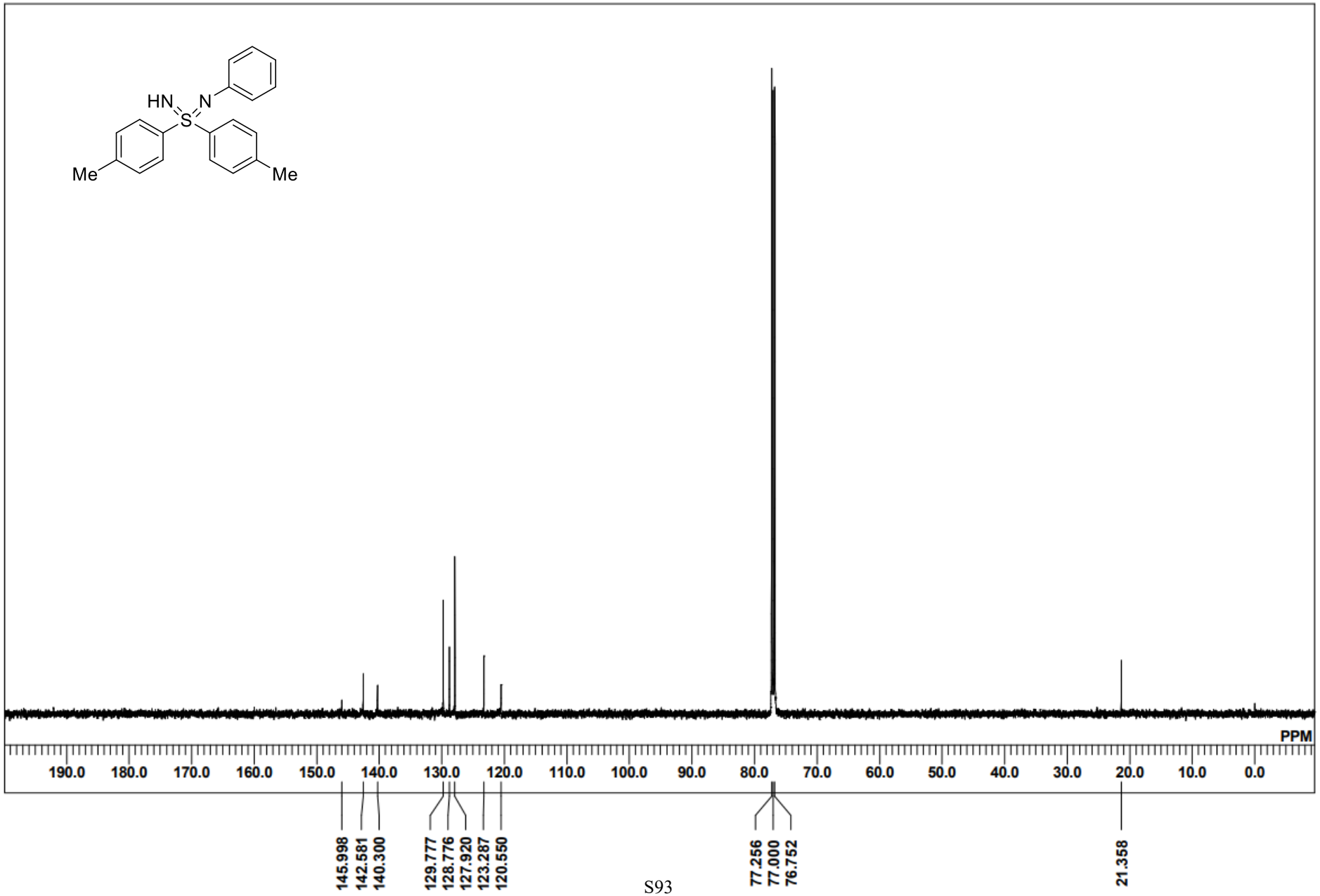
^{13}C NMR spectrum of **S2b**



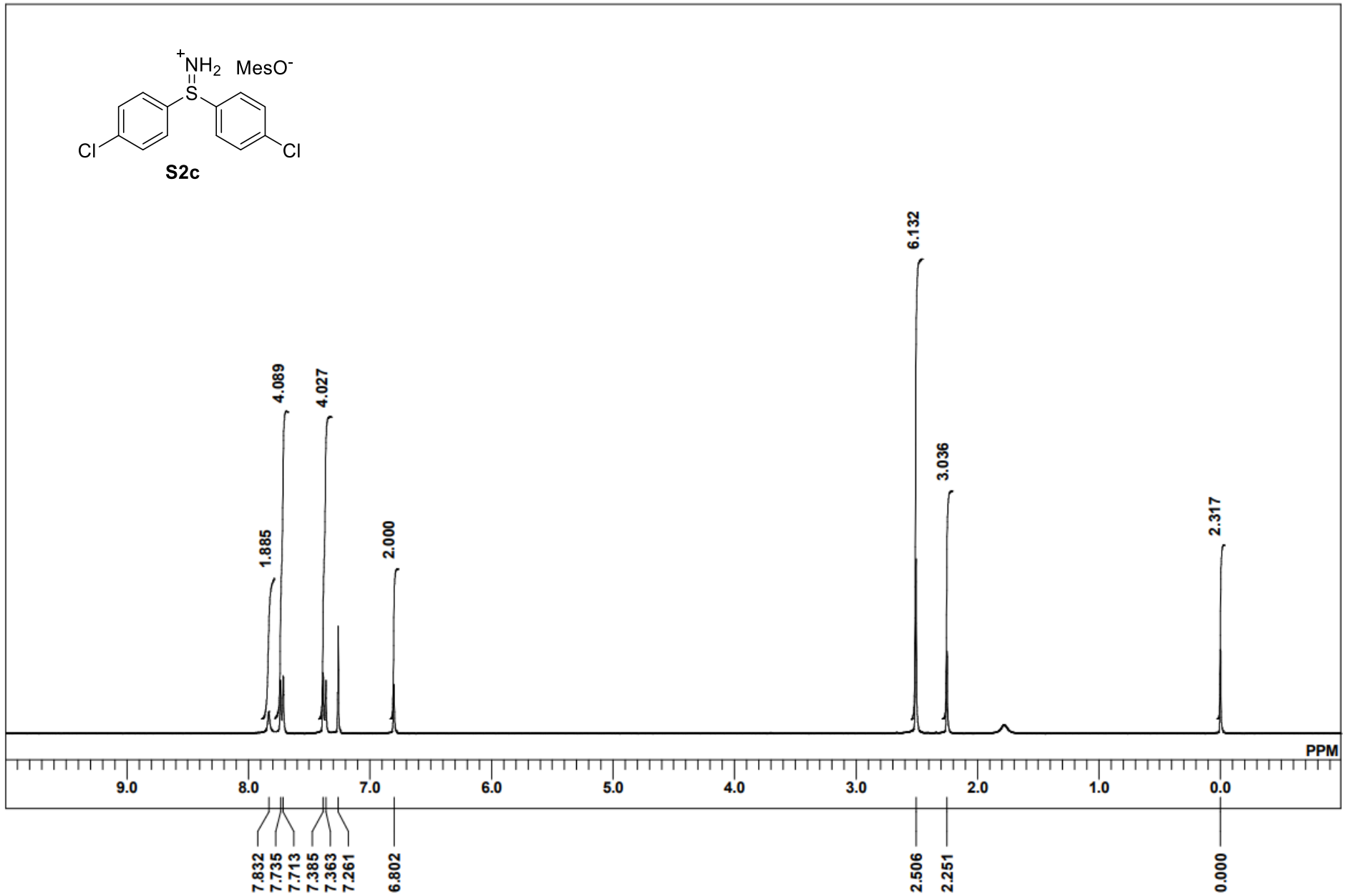
^{1}H NMR spectrum of **1b**



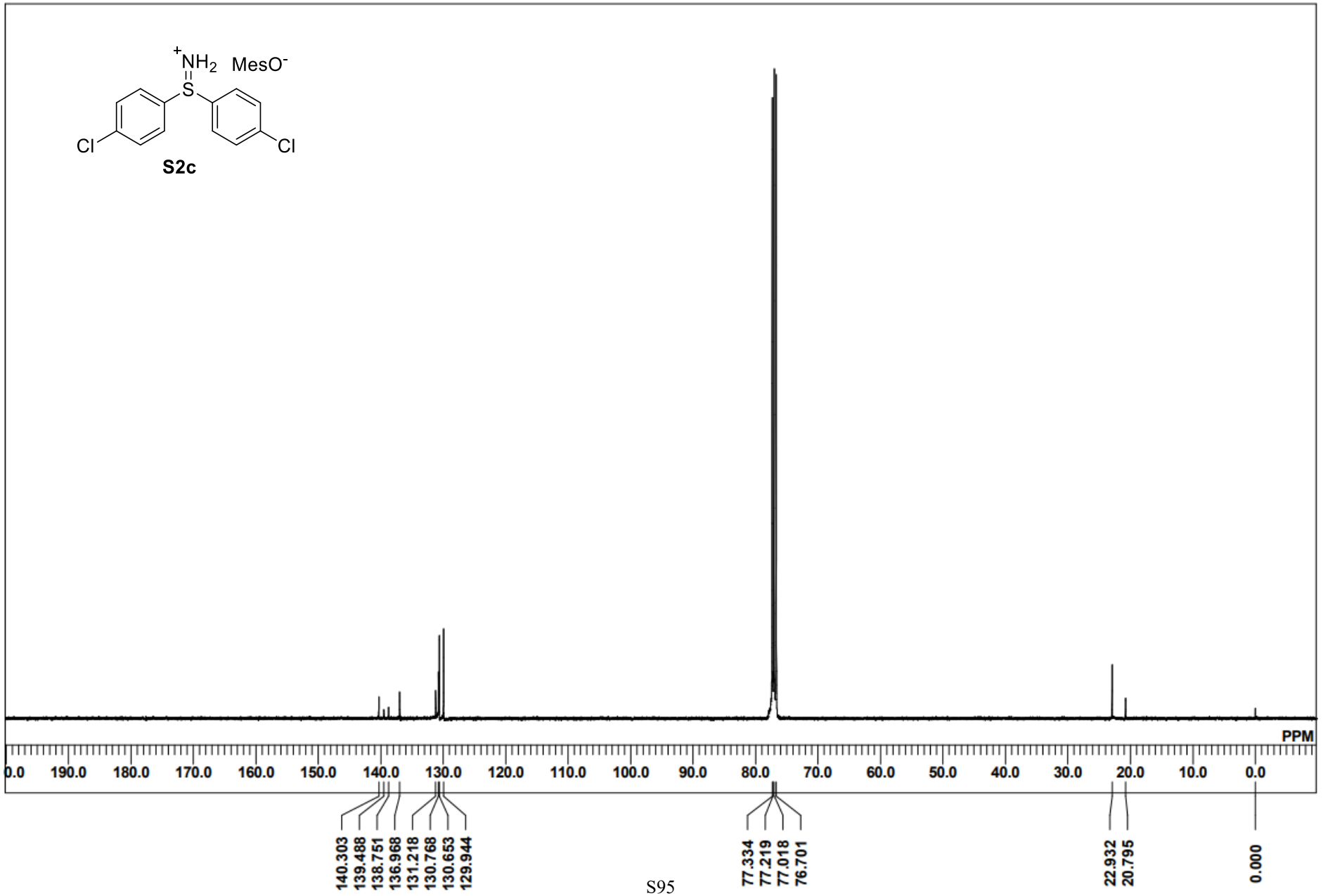
^{13}C NMR spectrum of **1b**



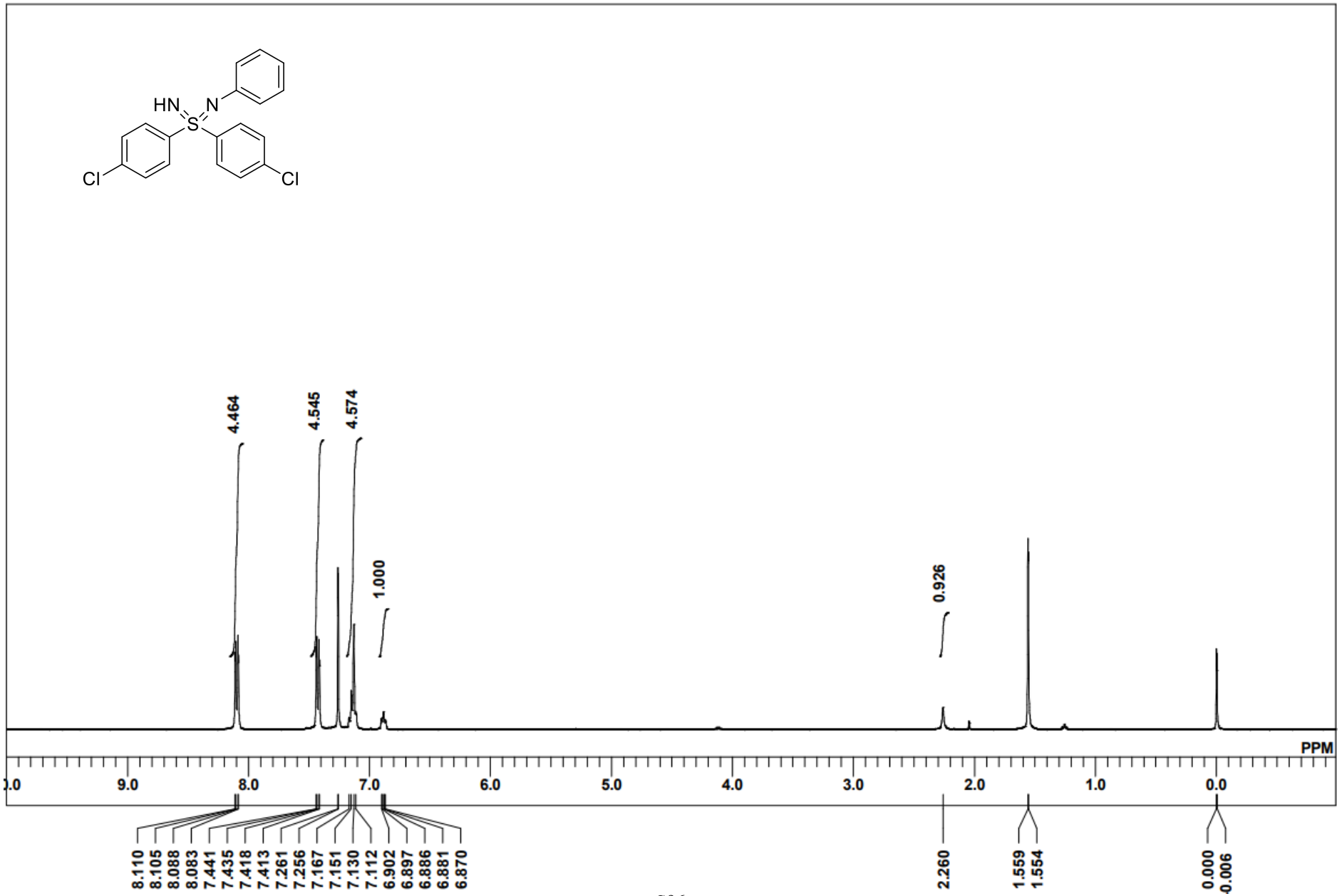
^{1}H NMR spectrum of **S2c**



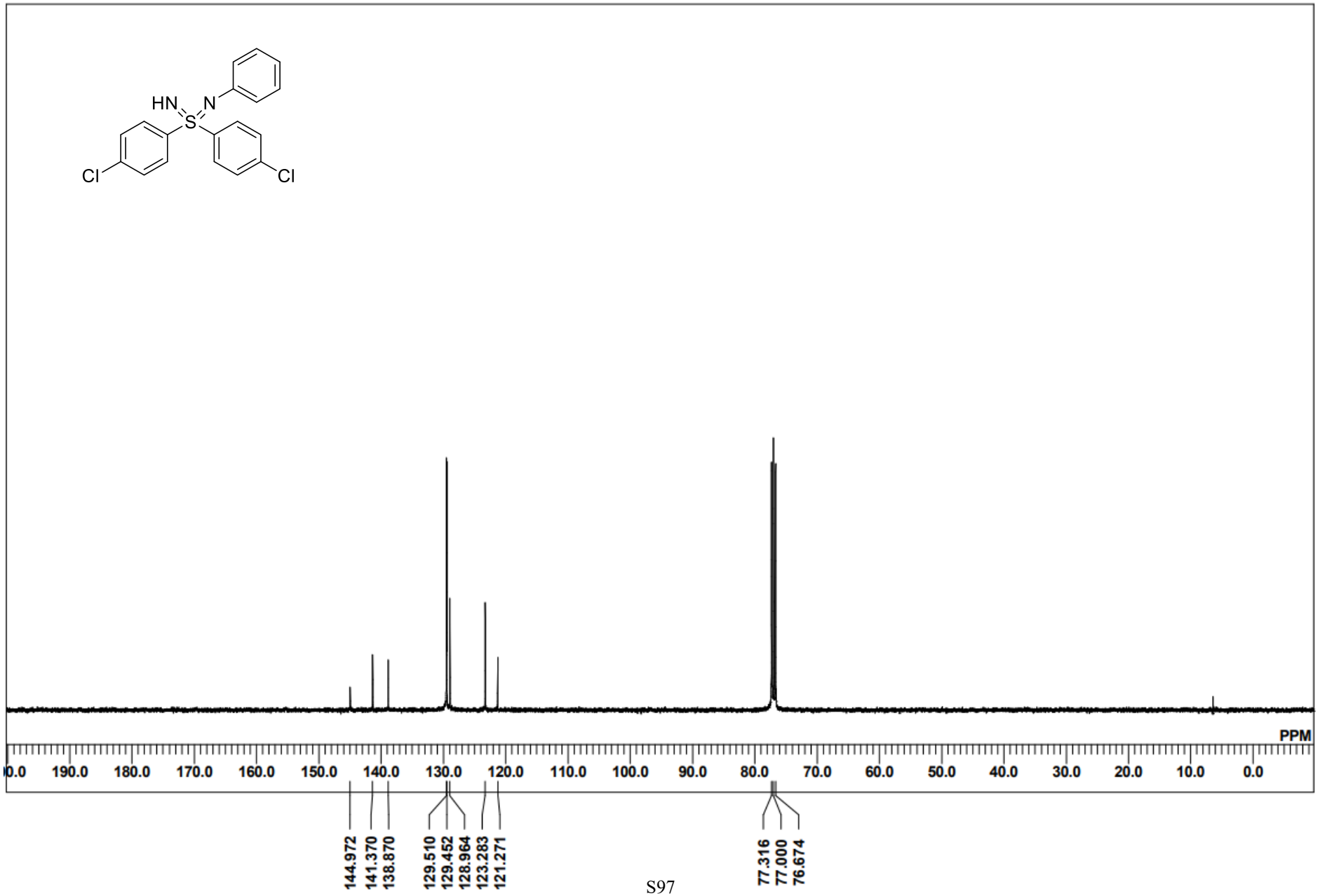
^{13}C NMR spectrum of **S2c**



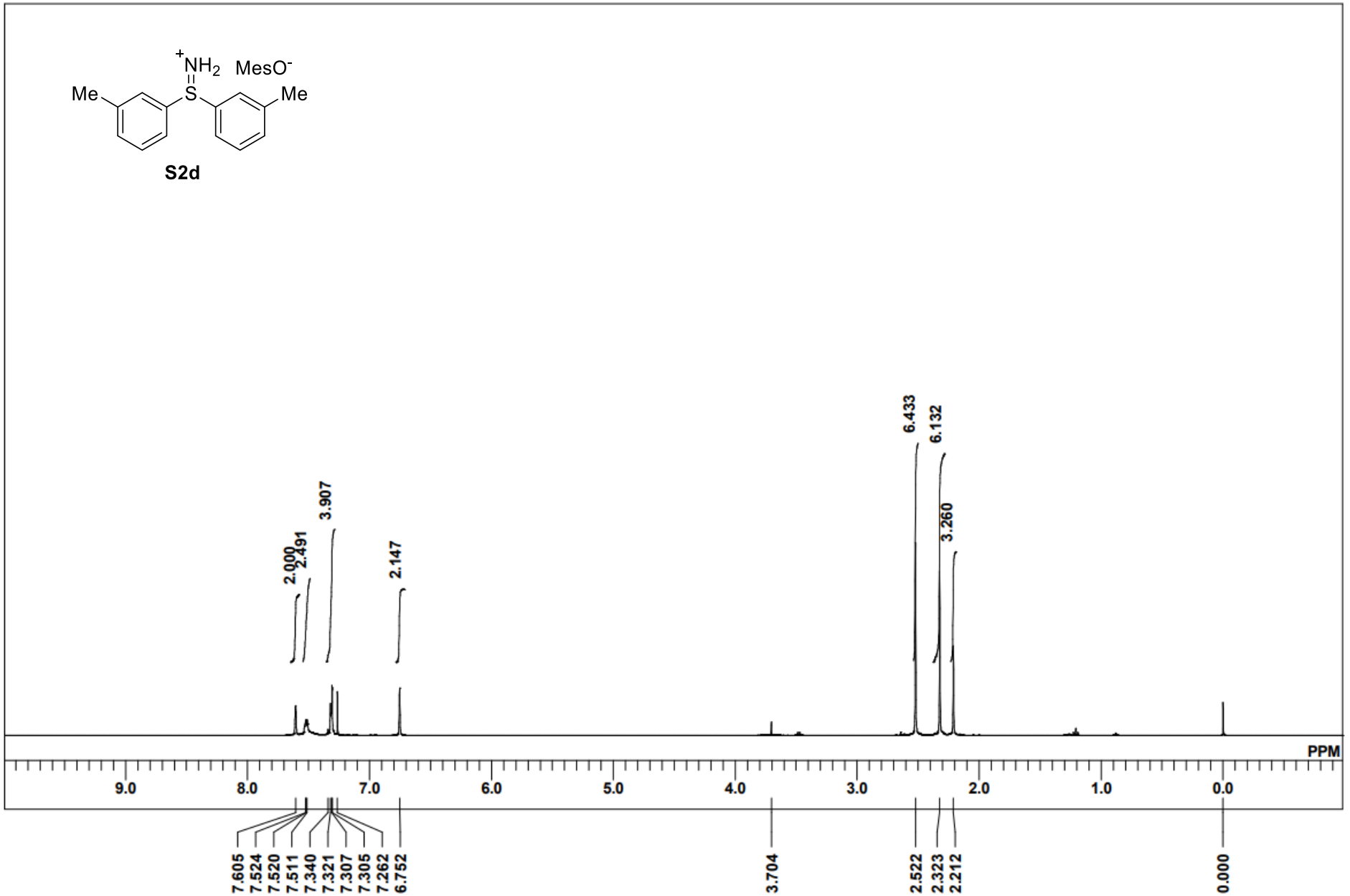
^{1}H NMR spectrum of **1c**



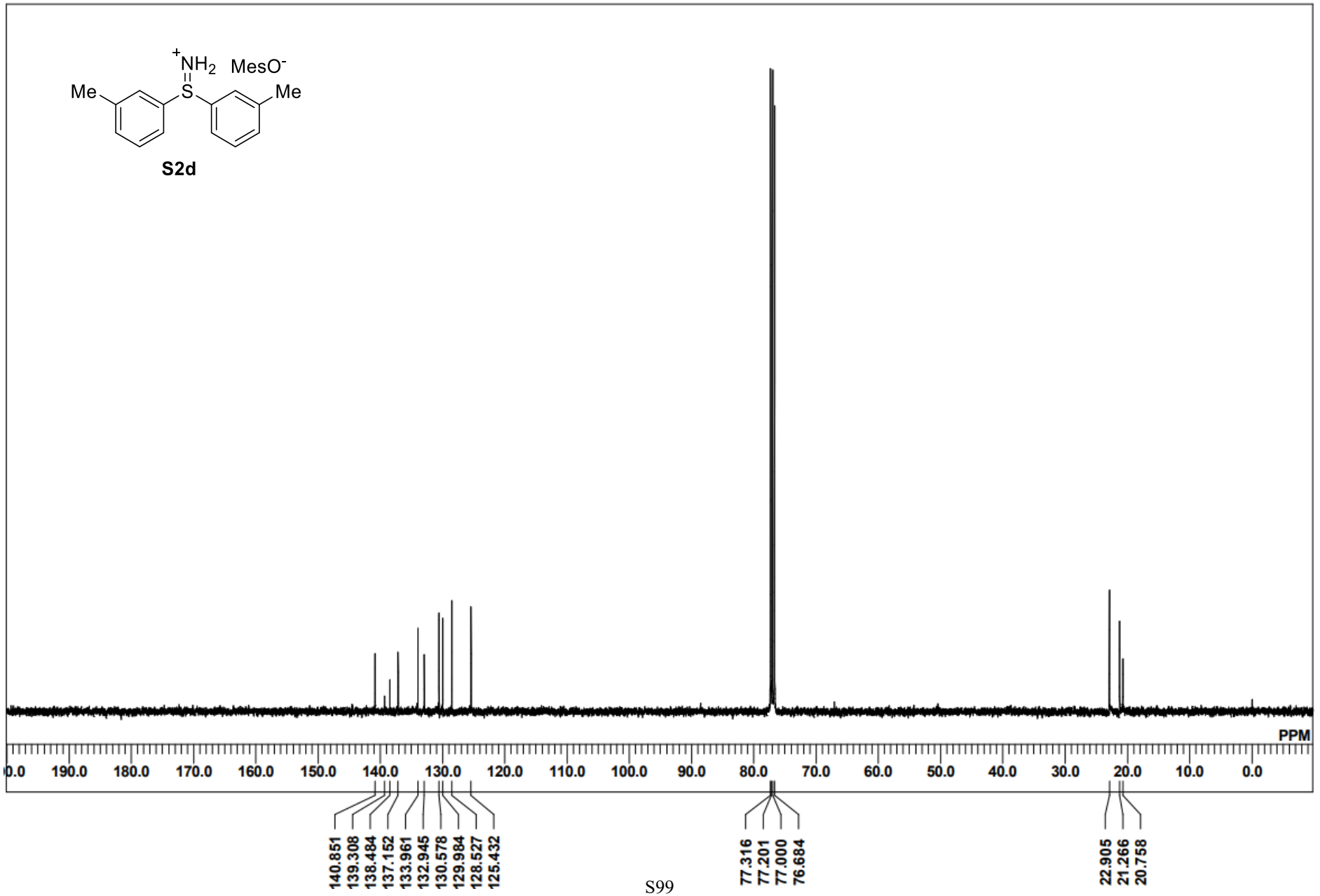
^{13}H NMR spectrum of **1c**



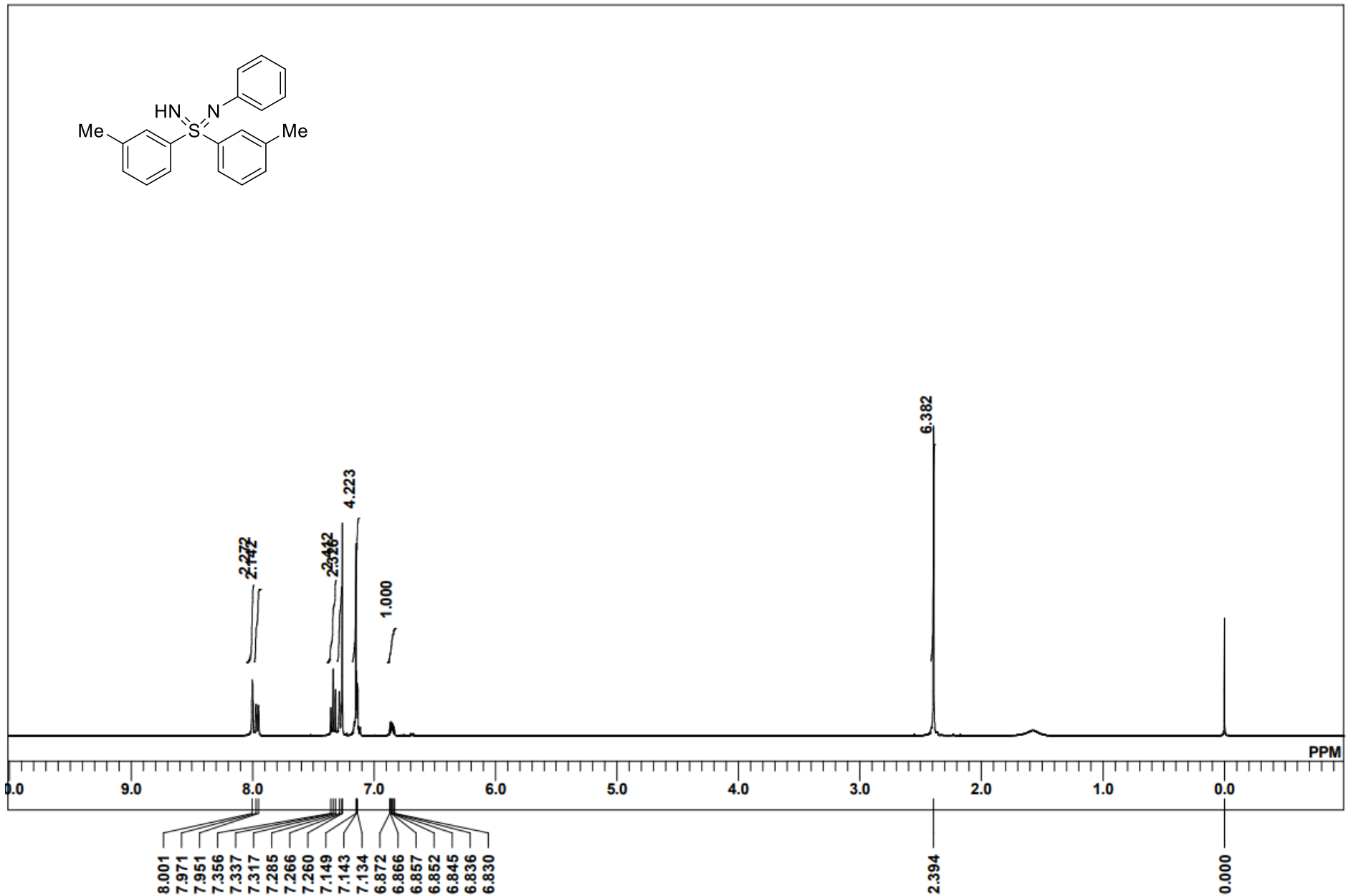
^{1}H NMR spectrum of **S2d**



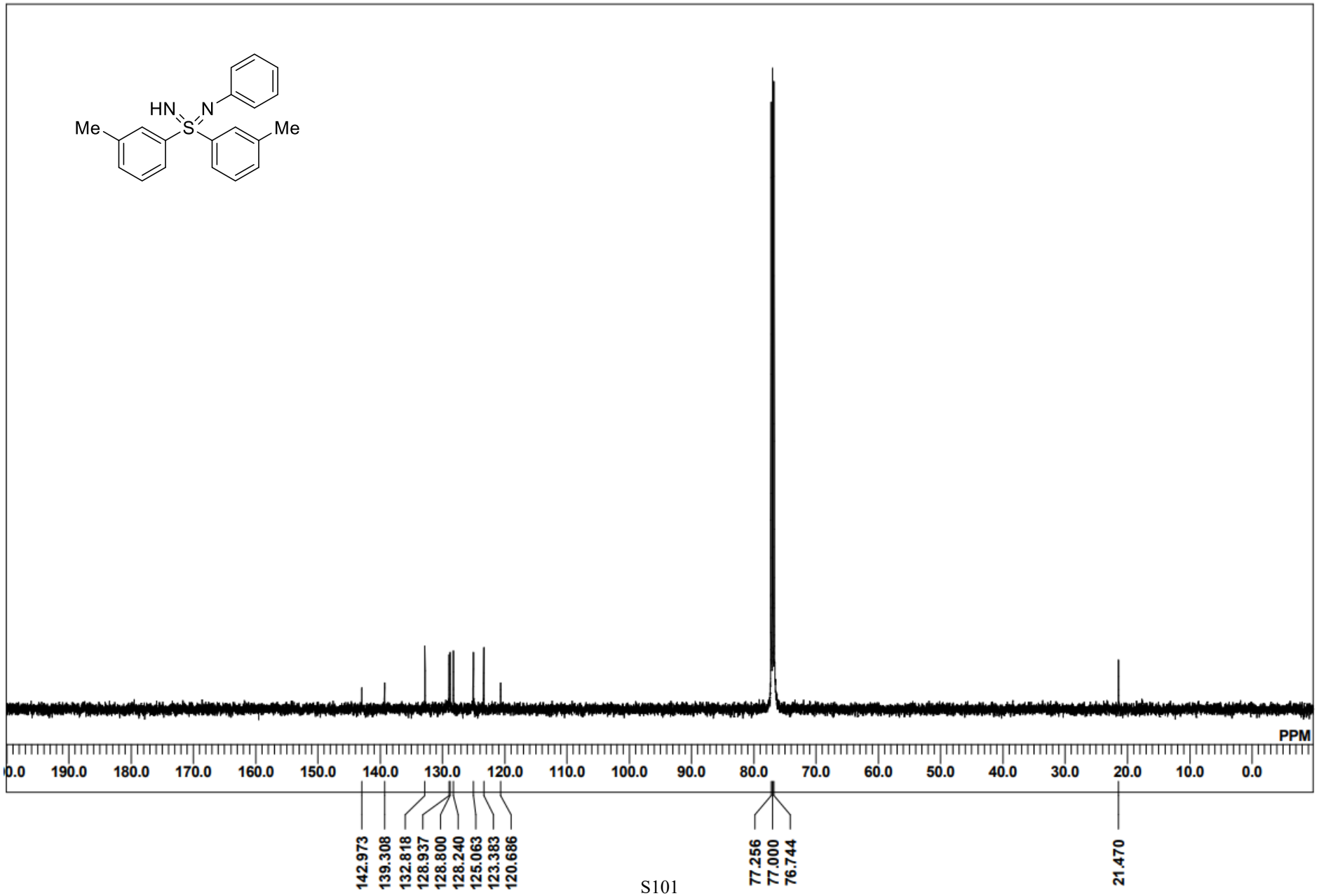
^{13}C NMR spectrum of **S2d**



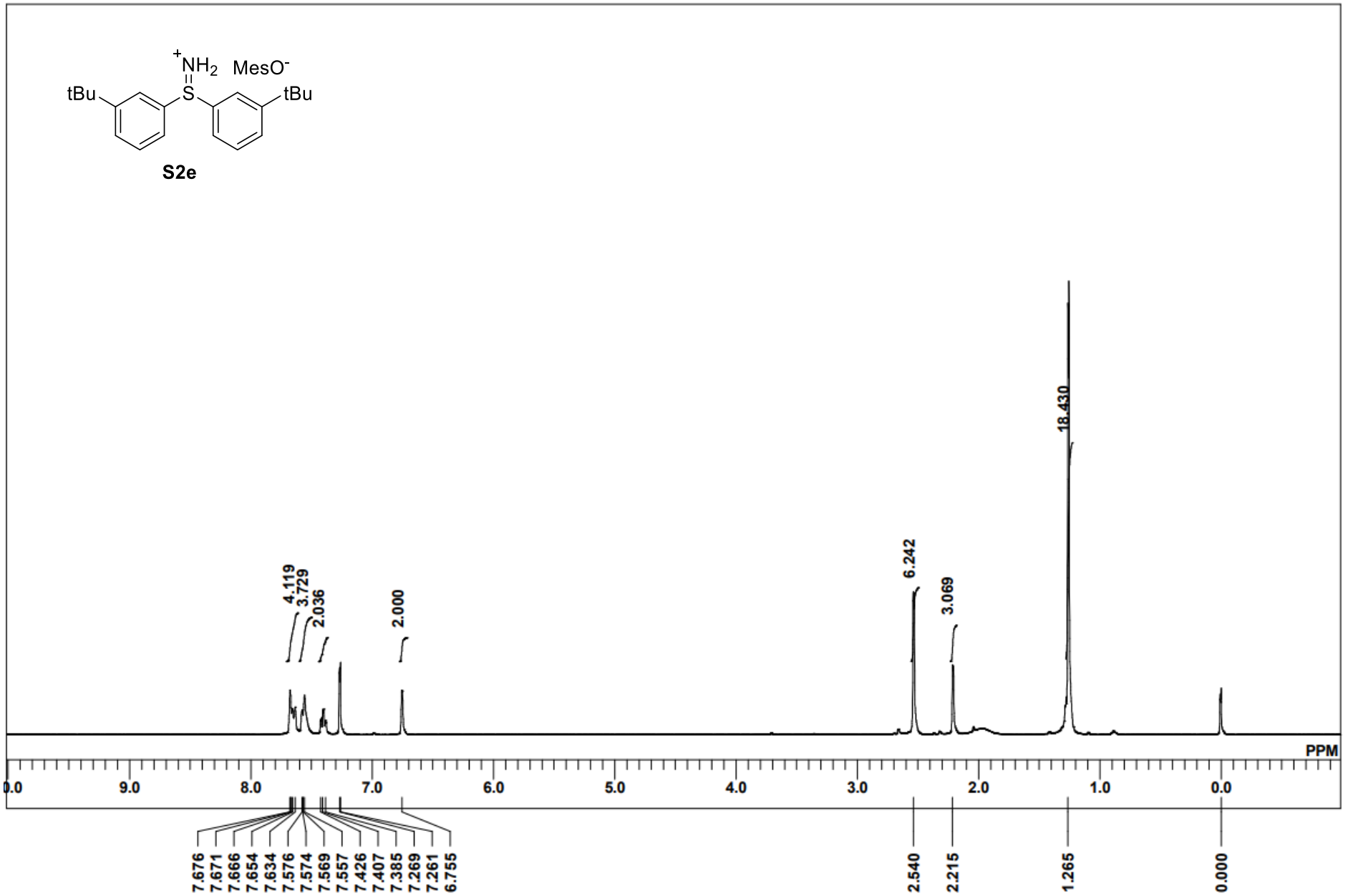
^{1}H NMR spectrum of **1d**



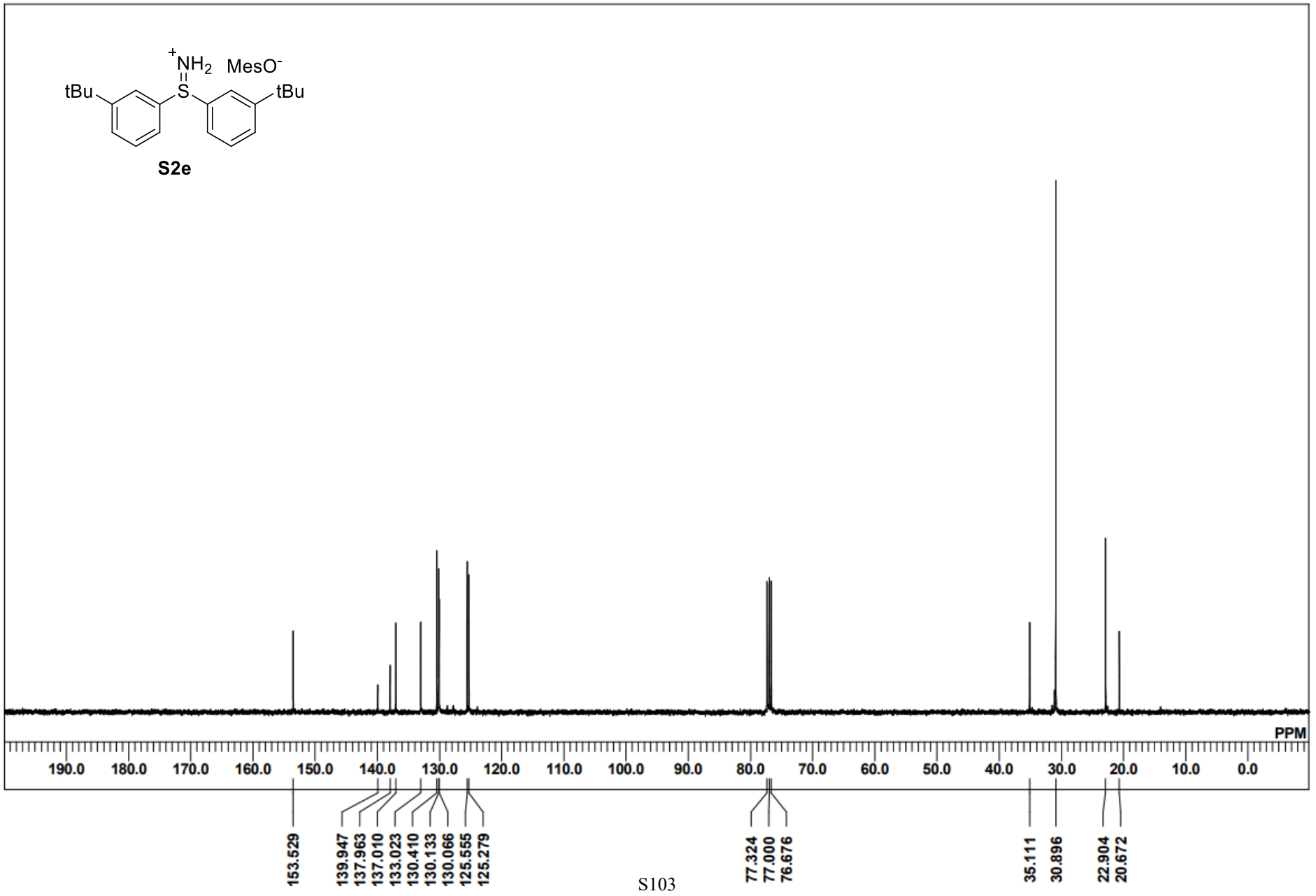
^{13}C NMR spectrum of **1d**



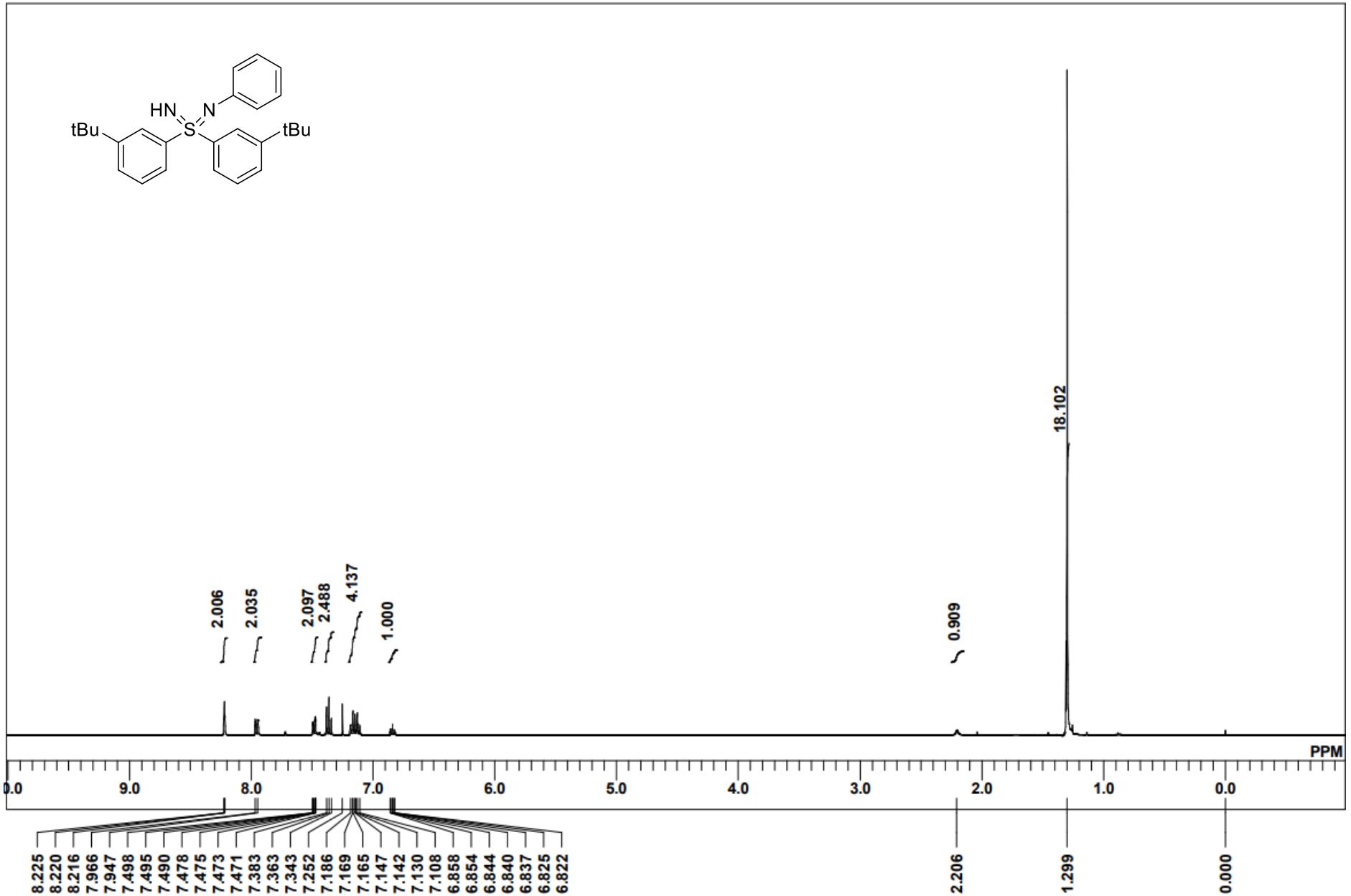
^{1}H NMR spectrum of **S2e**



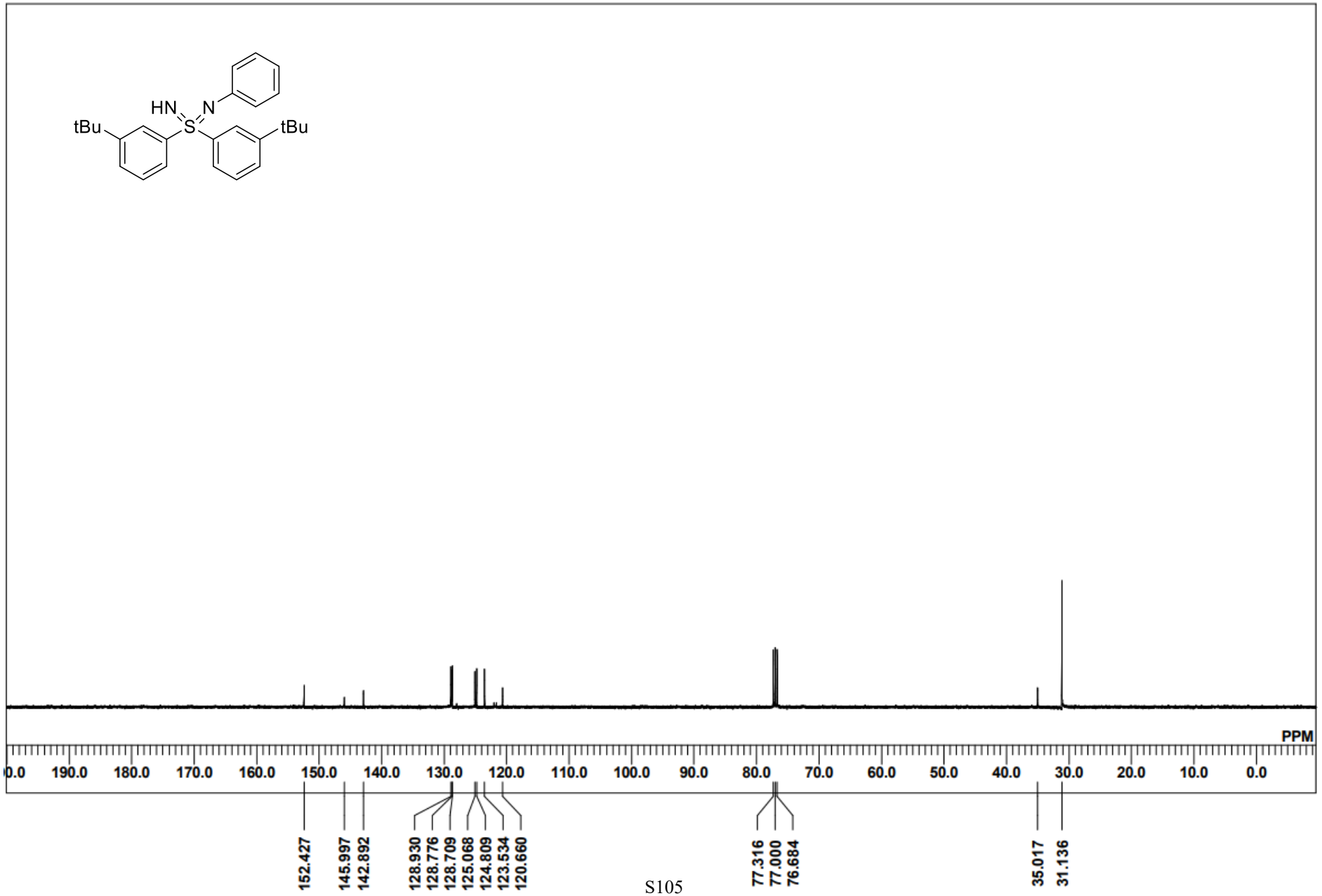
^{13}C NMR spectrum of **S2e**



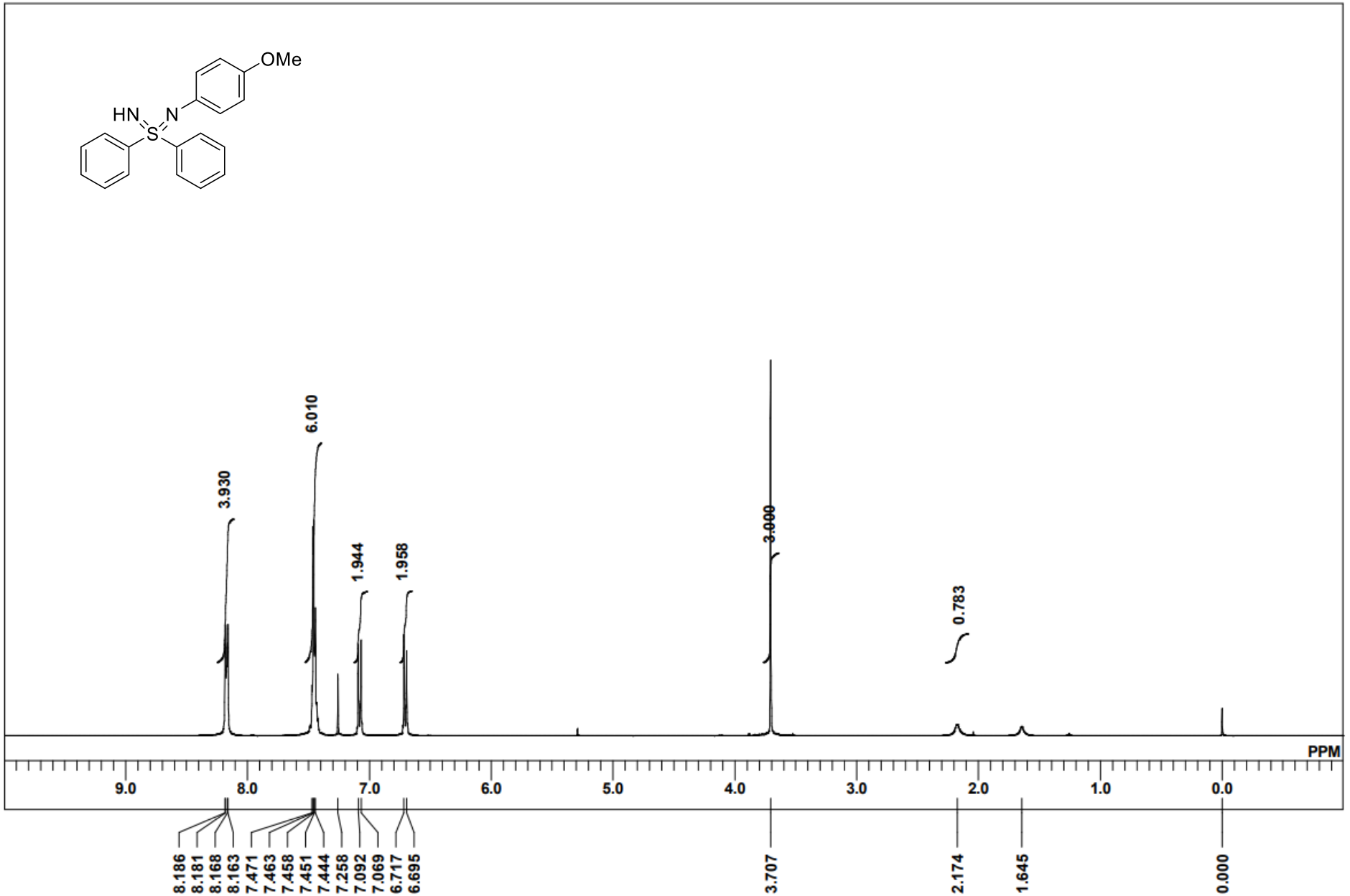
^{1}H NMR spectrum of **1e**



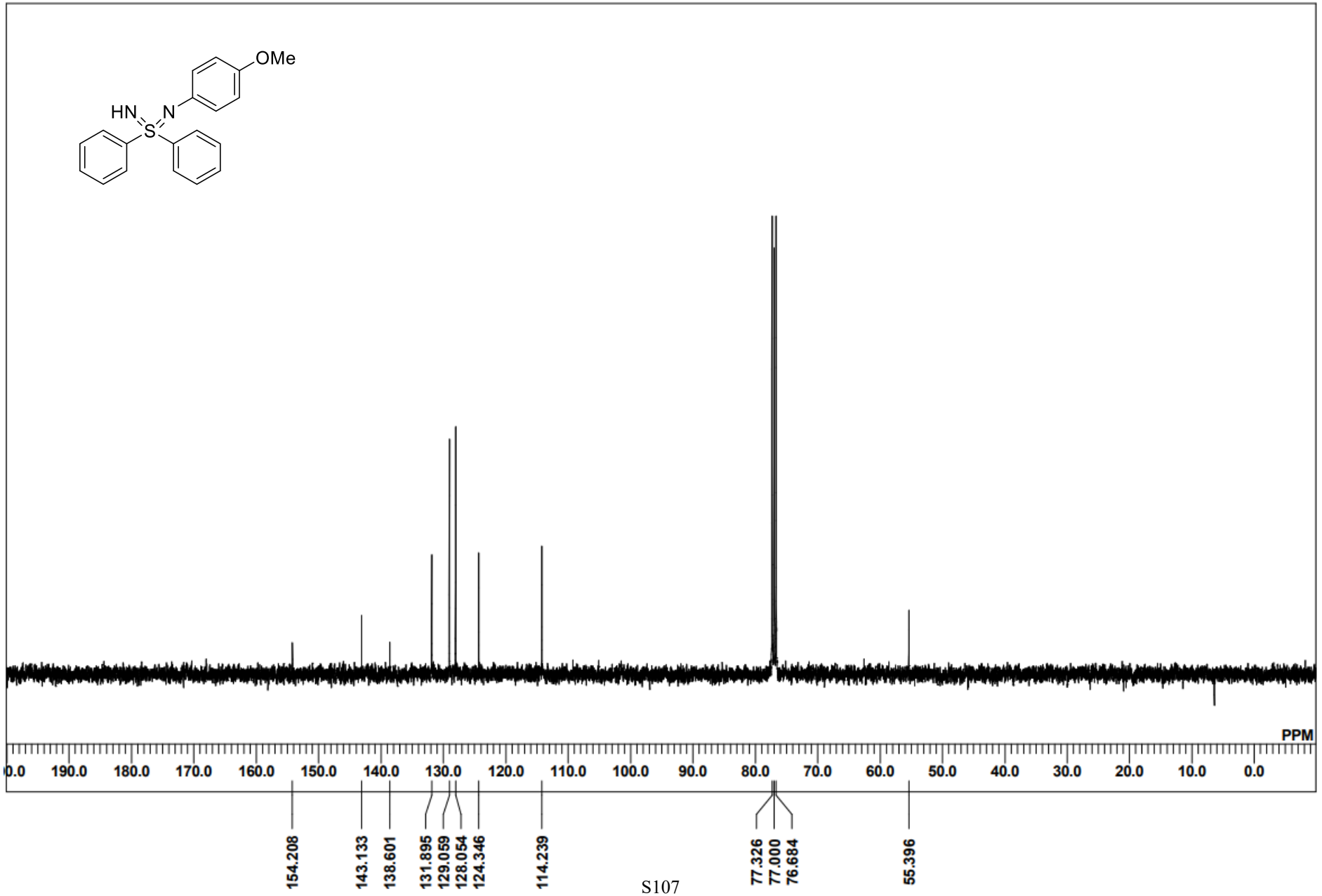
^{13}C NMR spectrum of **1e**



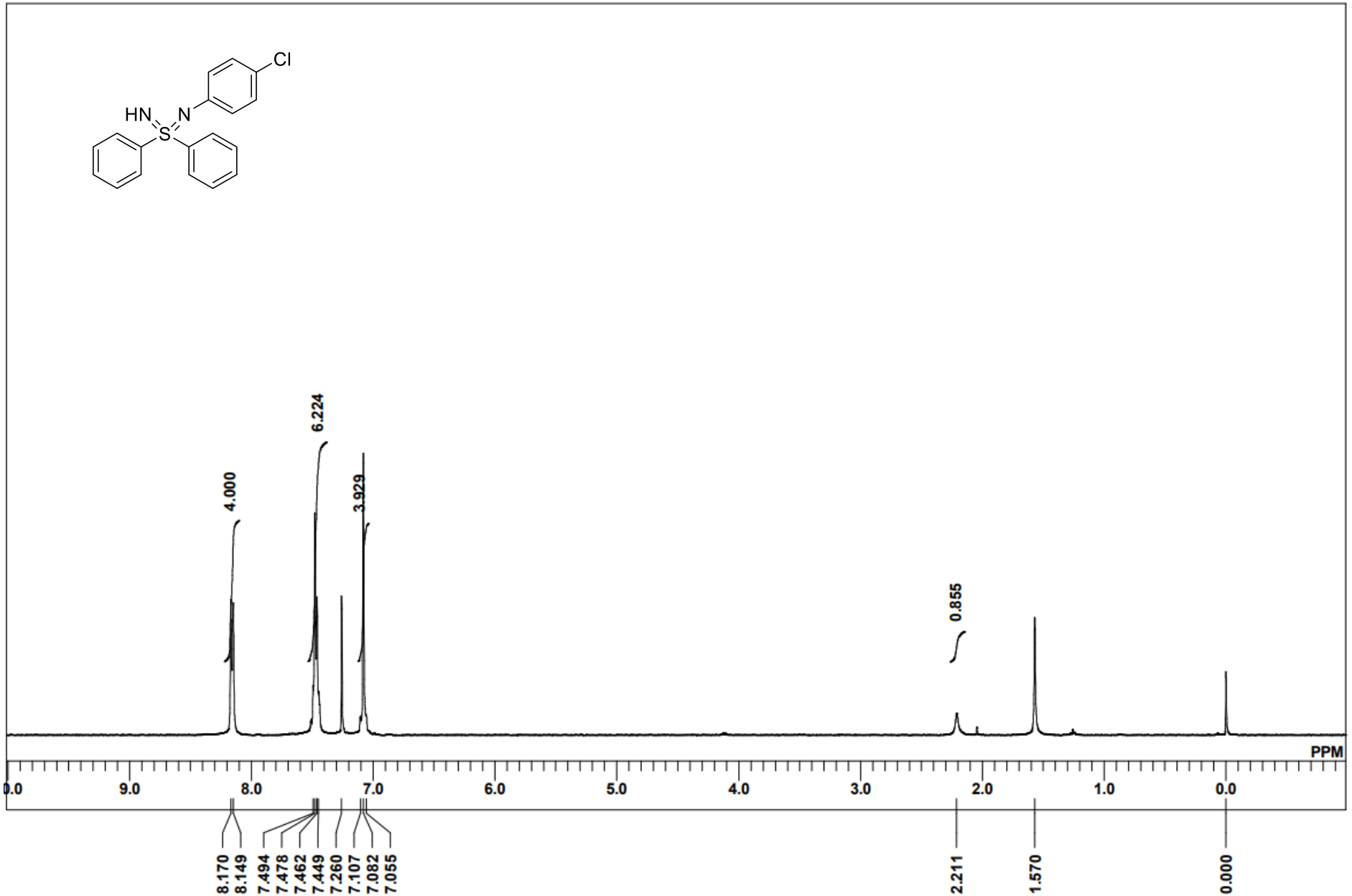
^{1}H NMR spectrum of **1f**



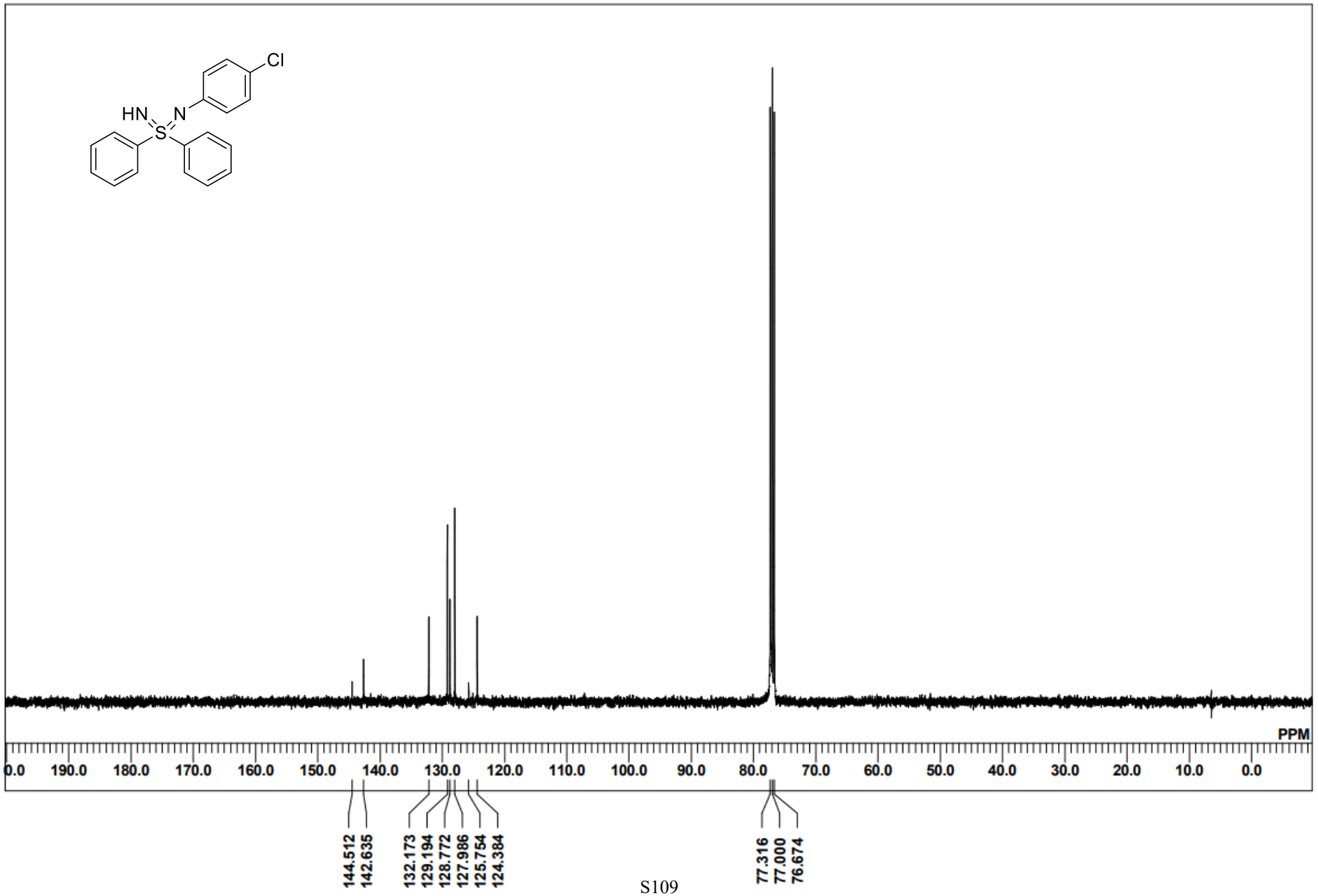
^{13}C NMR spectrum of **1f**



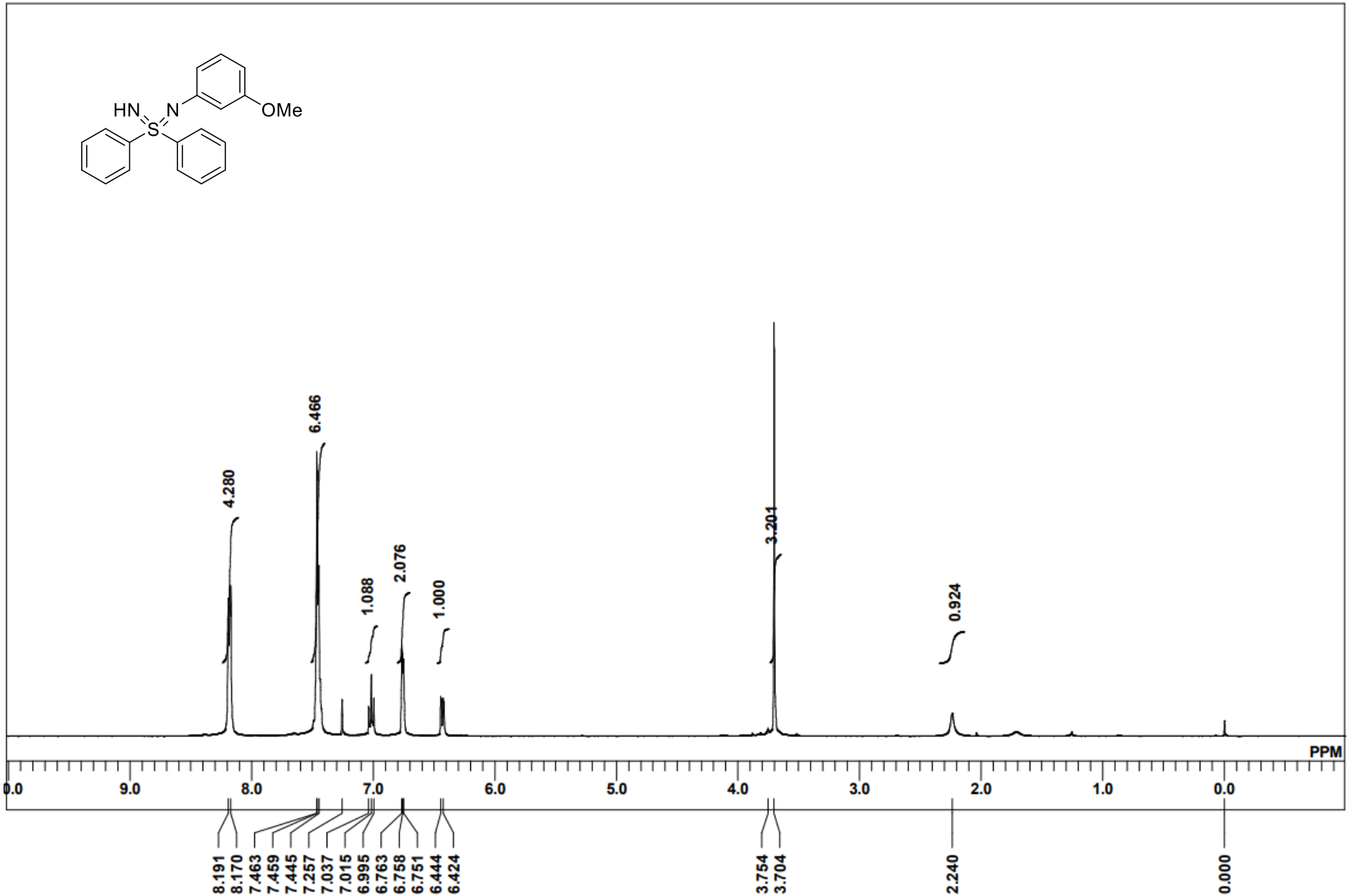
^{1}H NMR spectrum of **1g**



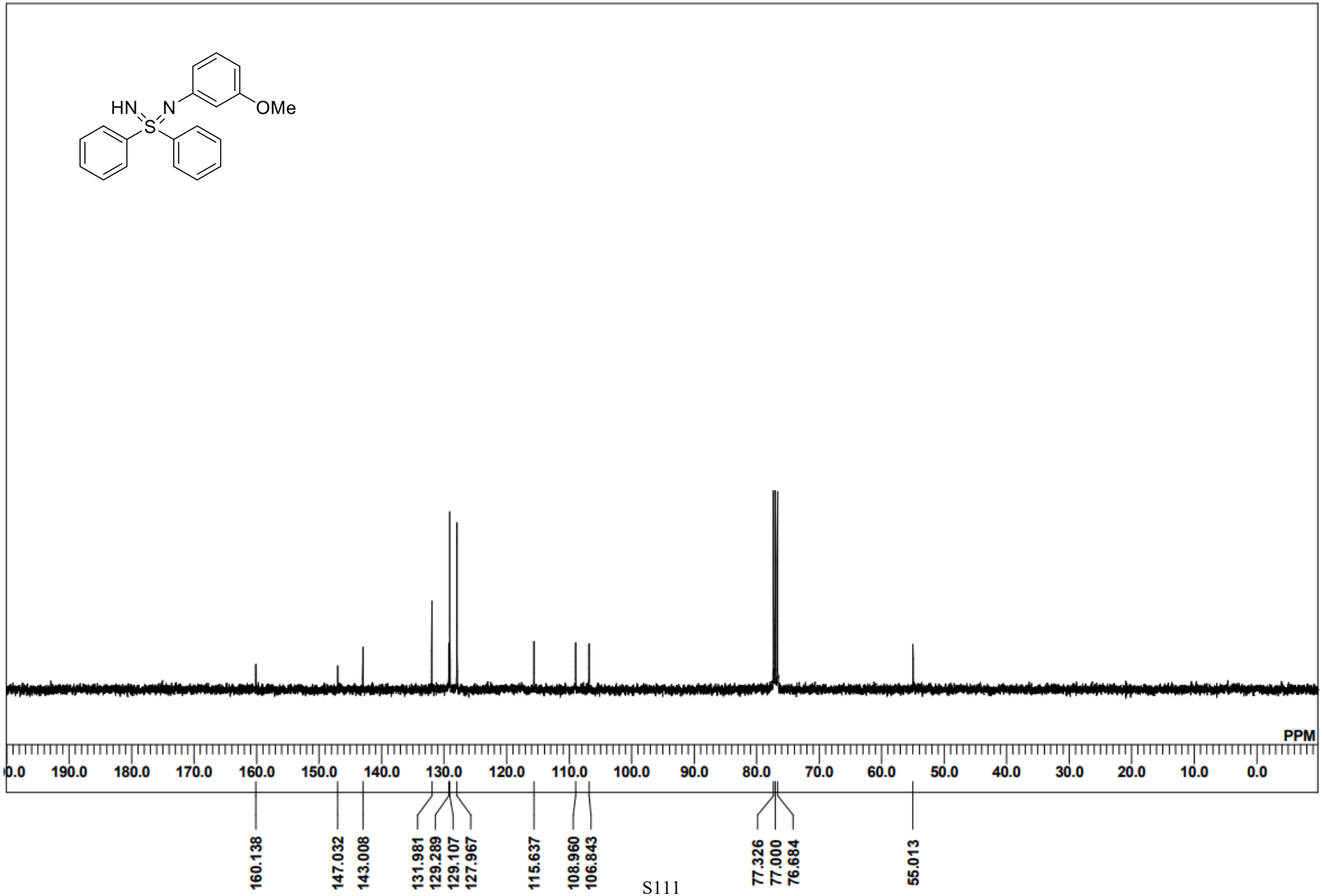
^{13}C NMR spectrum of **1g**



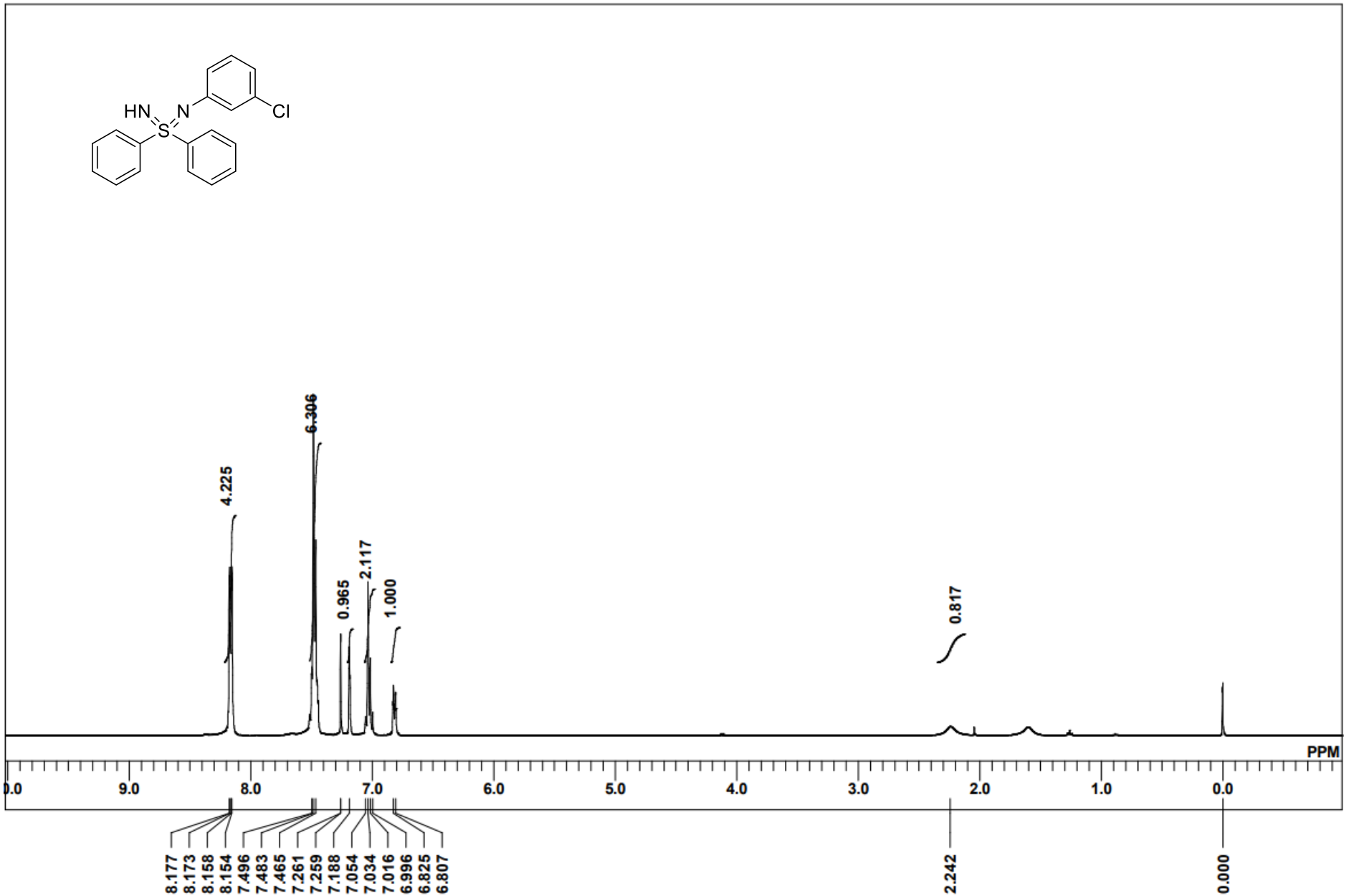
^{1}H NMR spectrum of **1h**



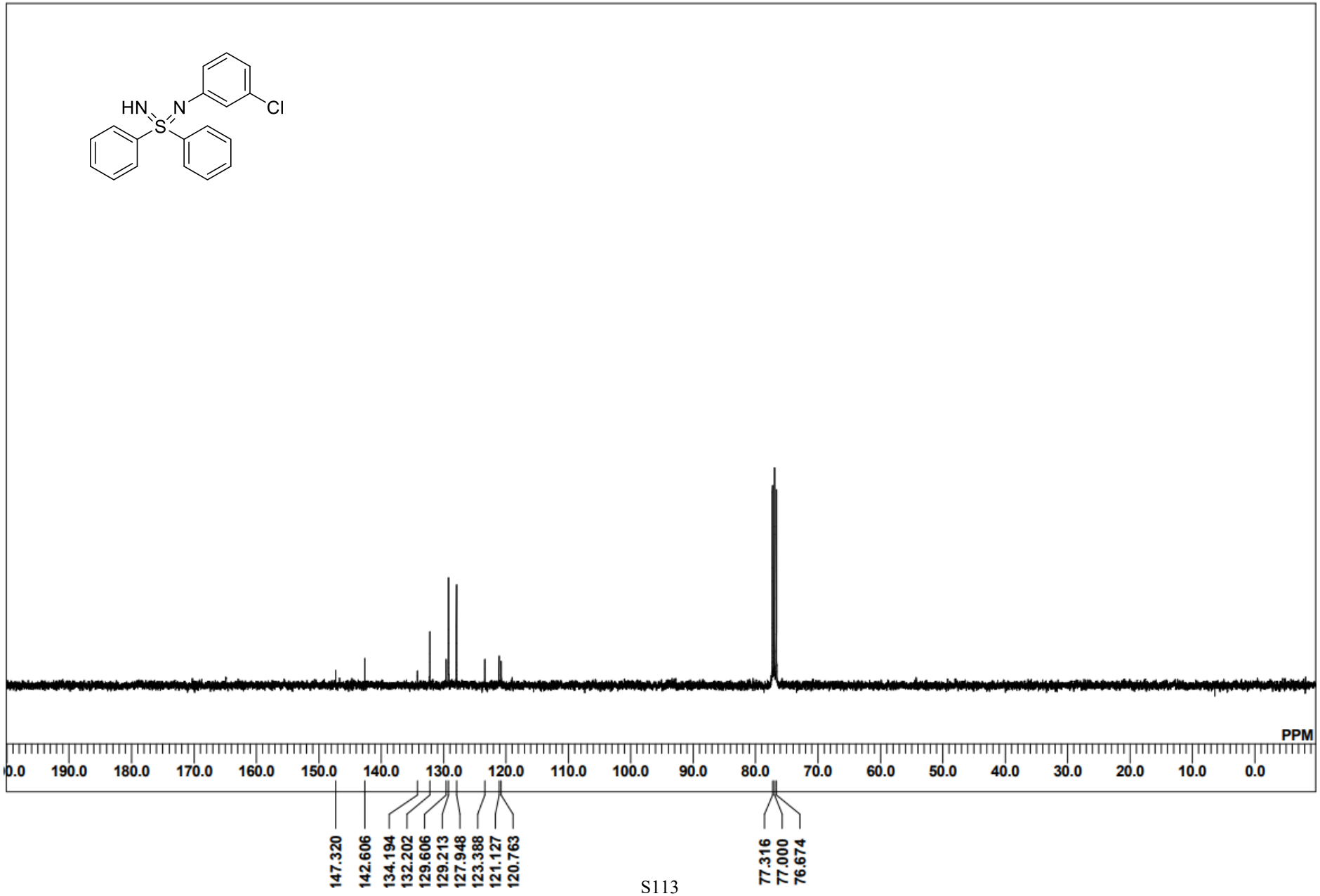
^{13}C NMR spectrum of **1h**



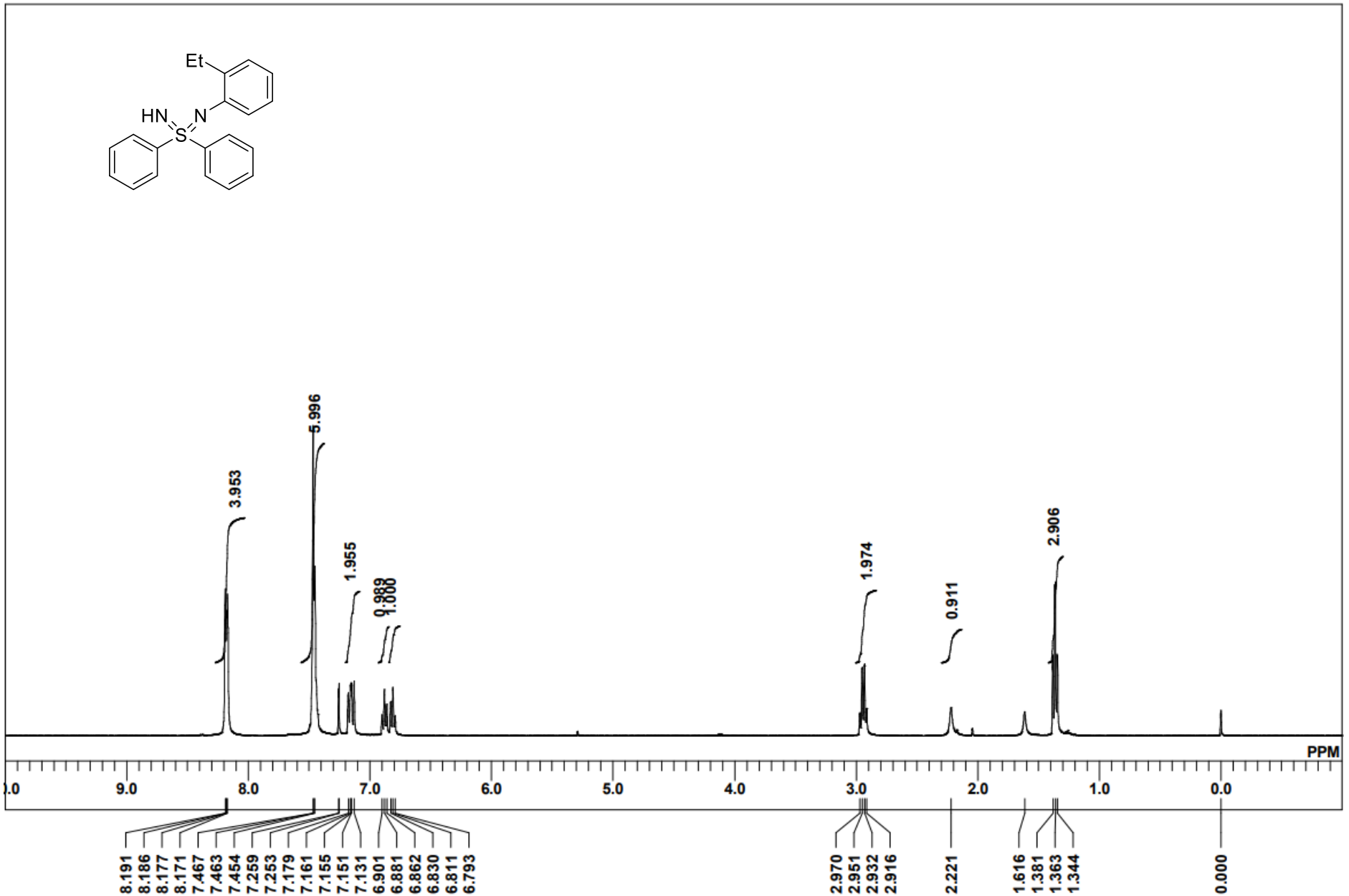
^{1}H NMR spectrum of **1i**



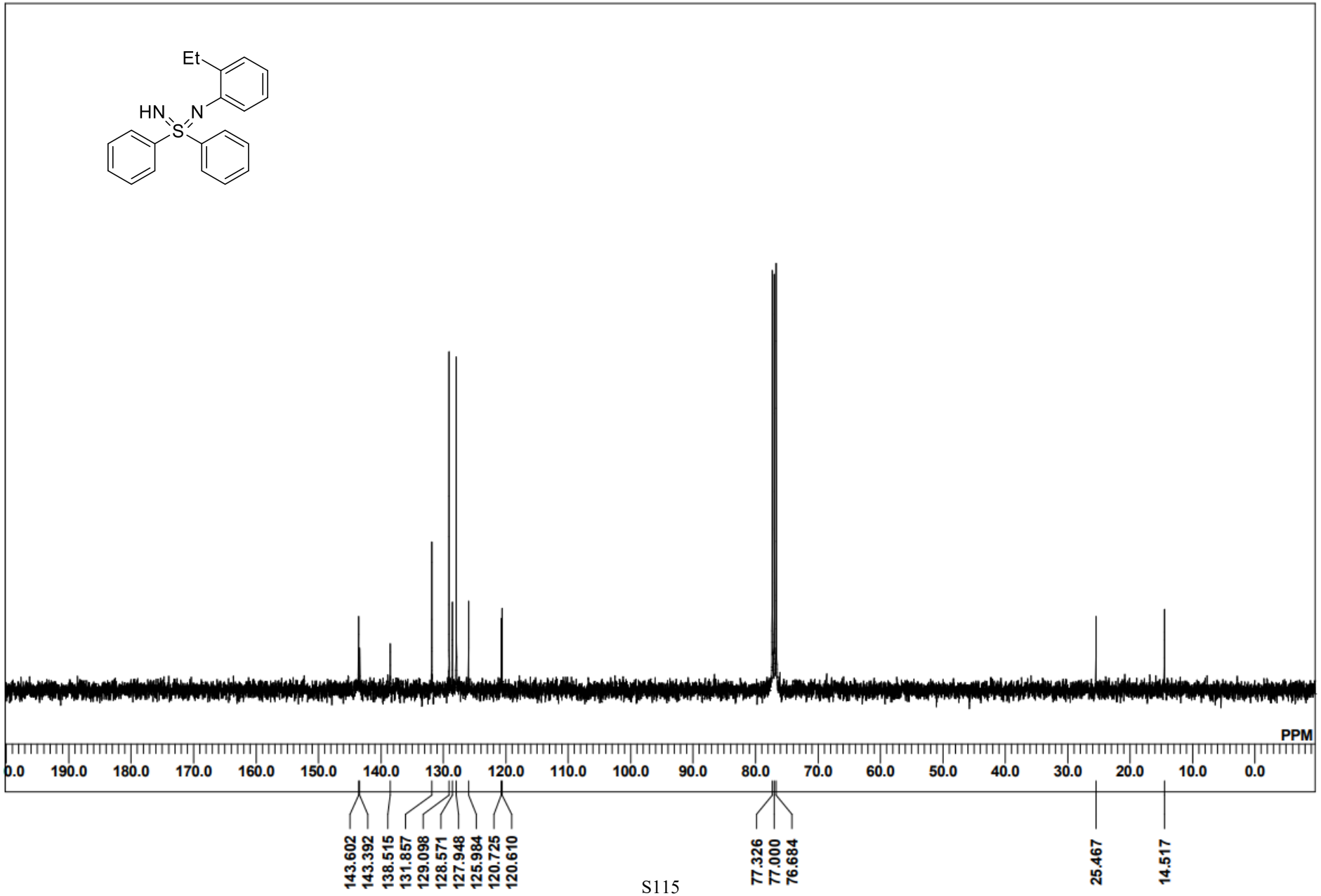
^{13}C NMR spectrum of **1i**



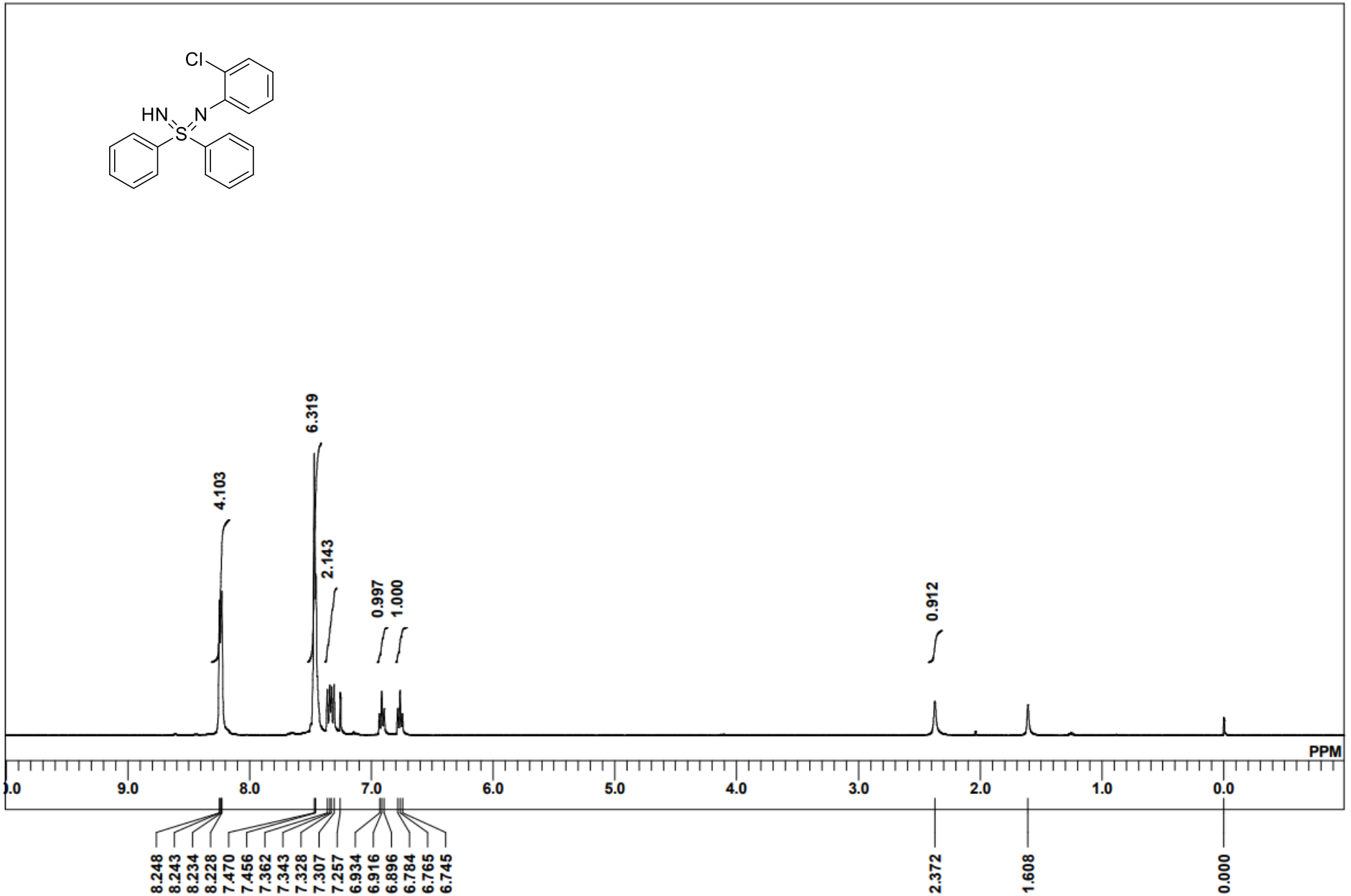
^{1}H NMR spectrum of **1i**



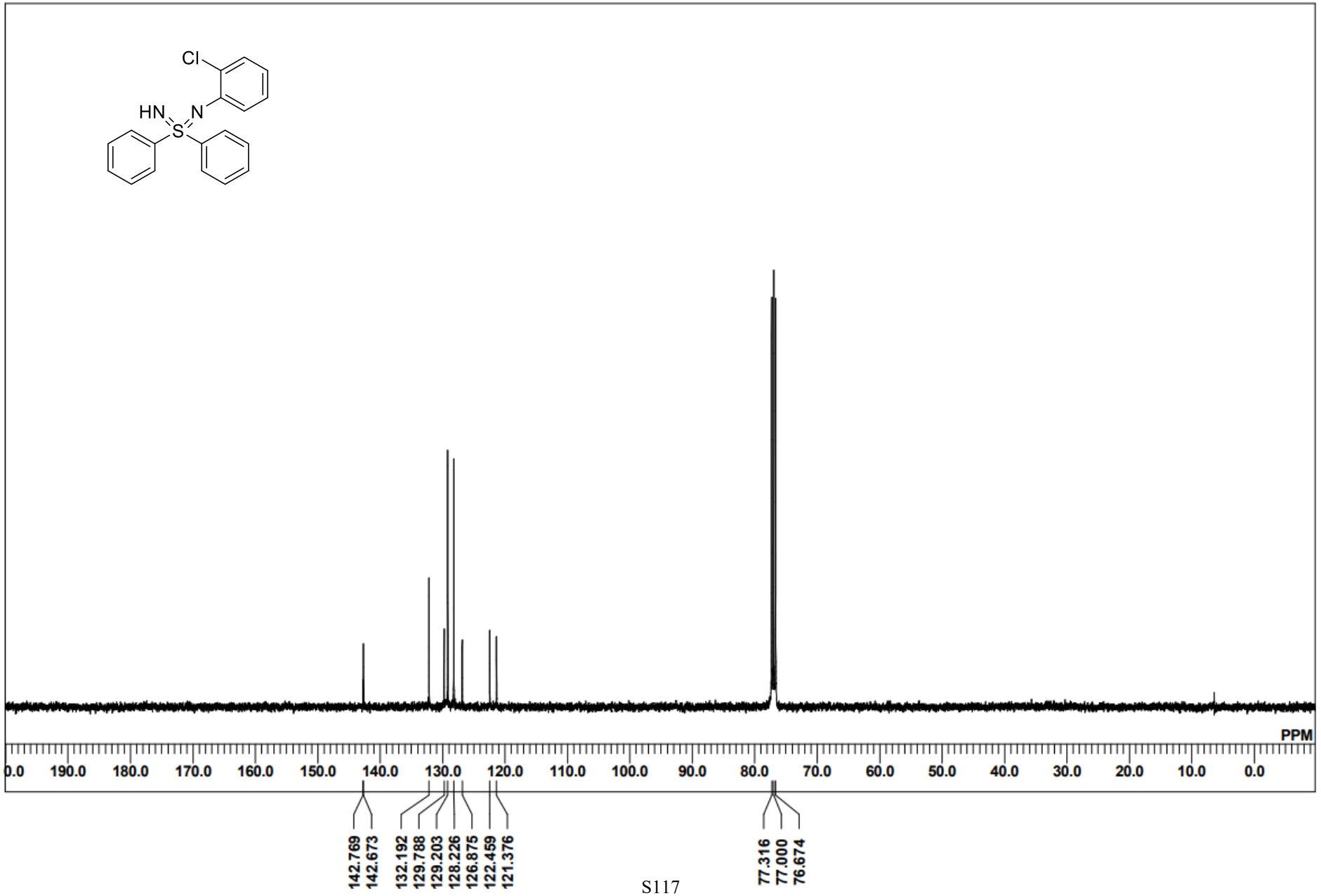
^{13}C NMR spectrum of **1i**



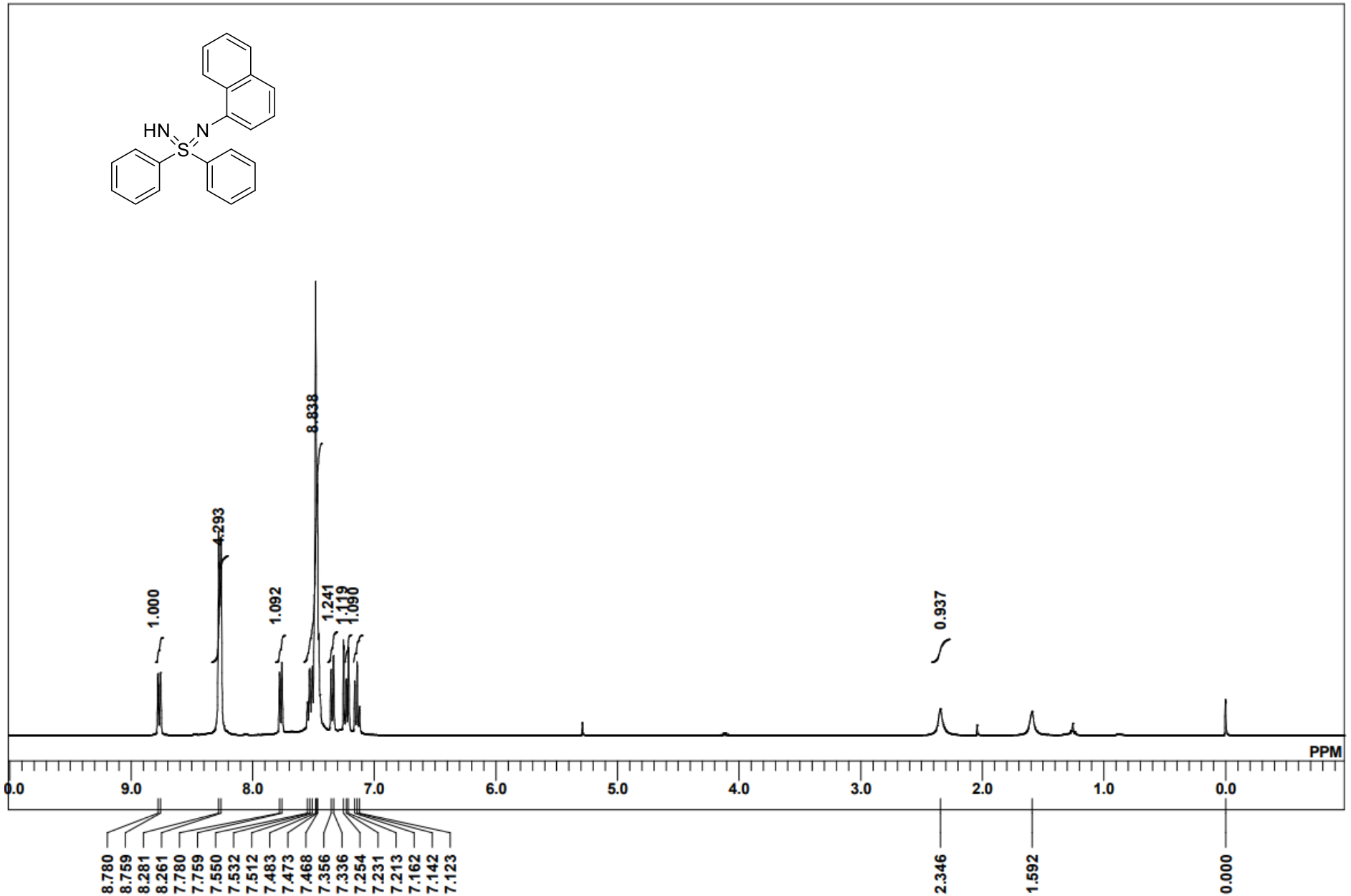
^{1}H NMR spectrum of **1k**



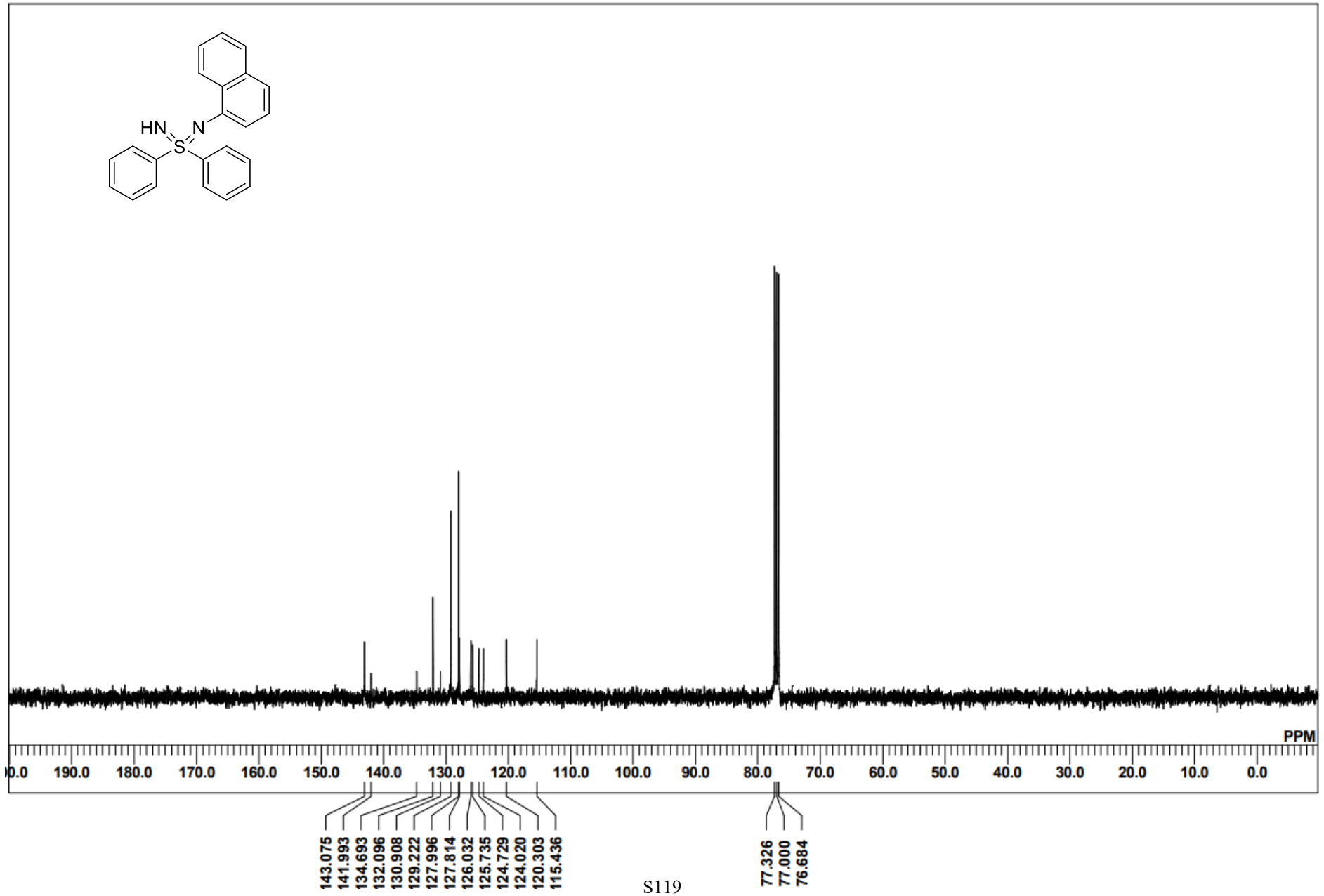
^{13}C NMR spectrum of **1k**



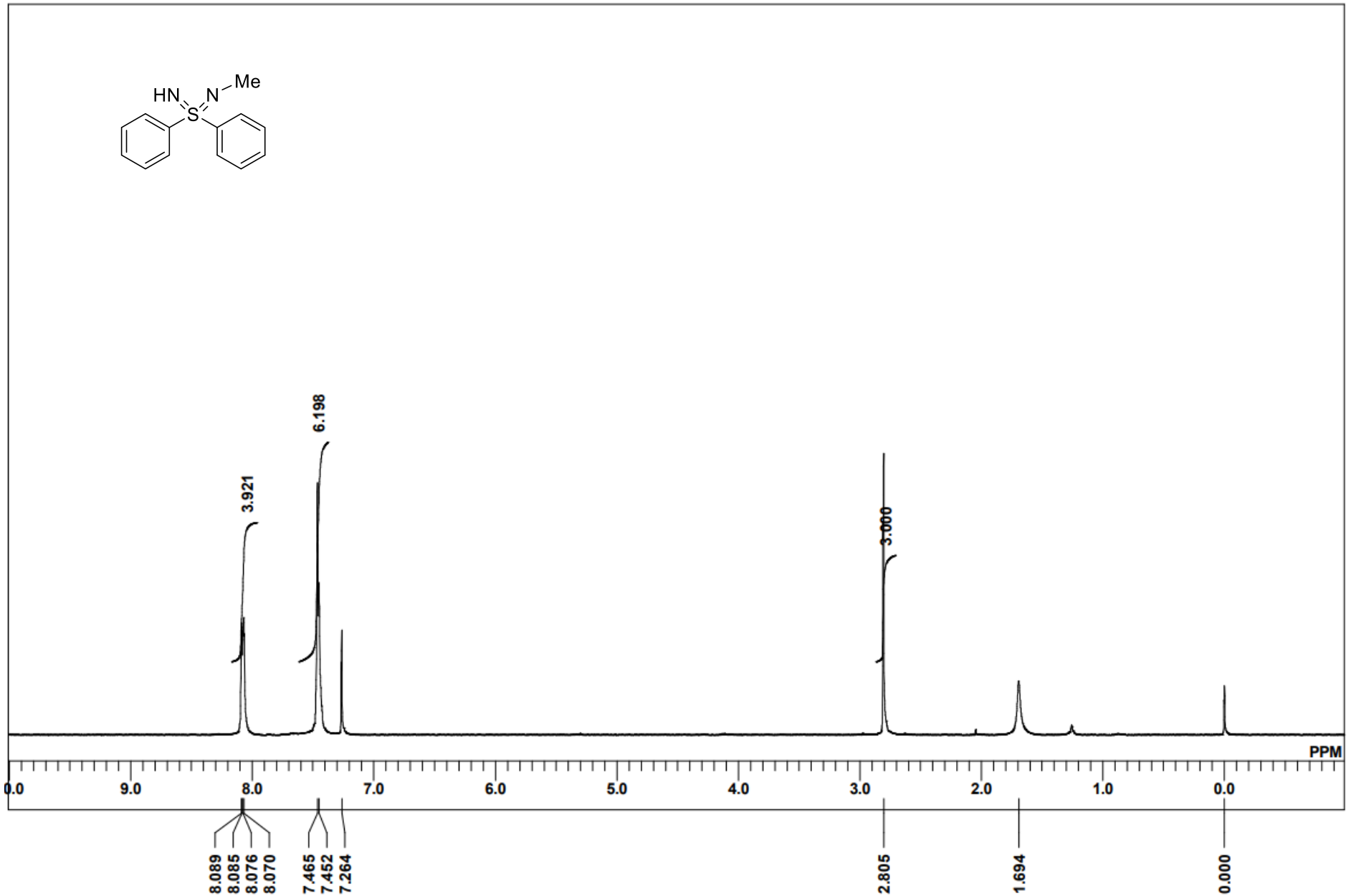
^{1}H NMR spectrum of **1l**



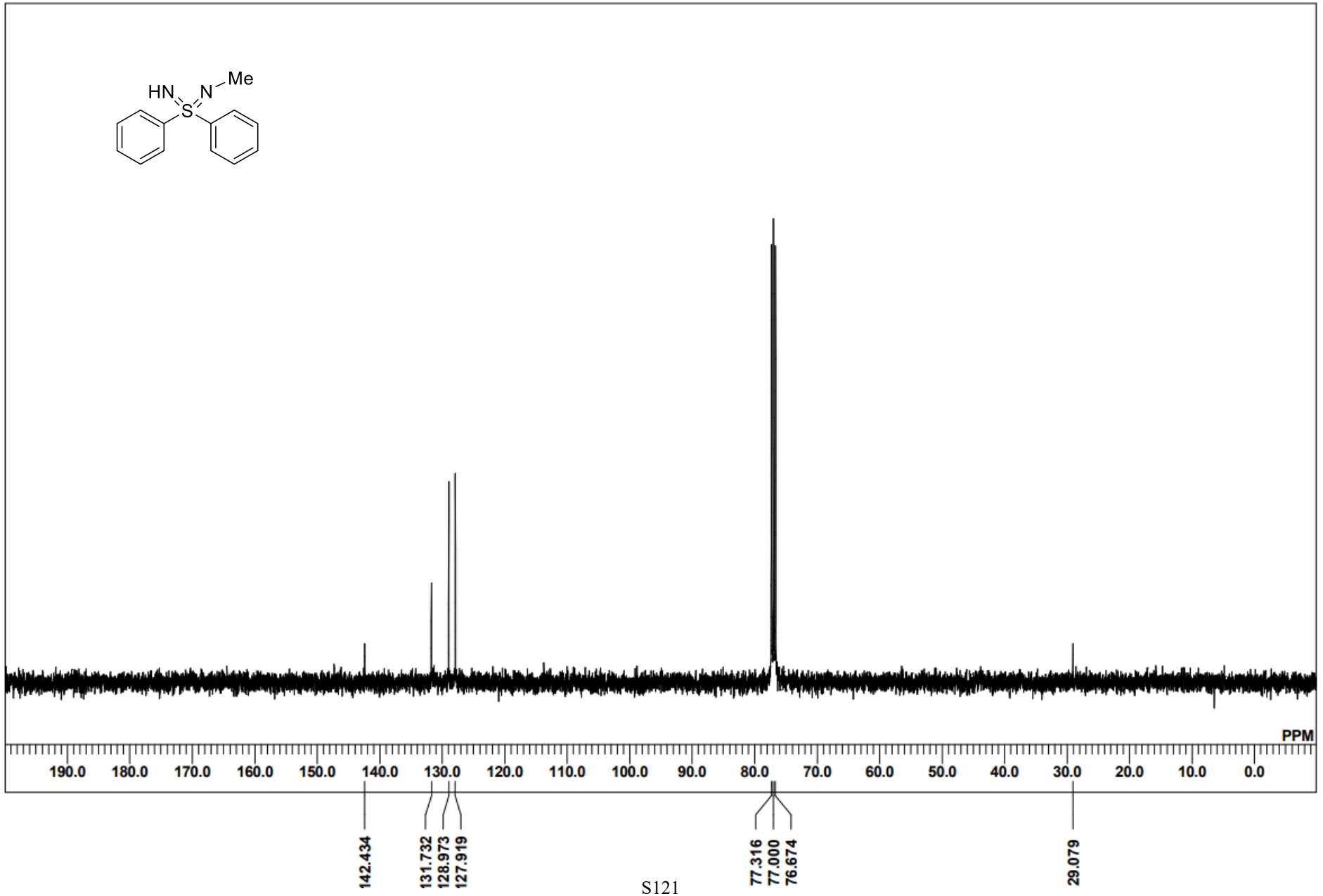
^{13}C NMR spectrum of **1l**



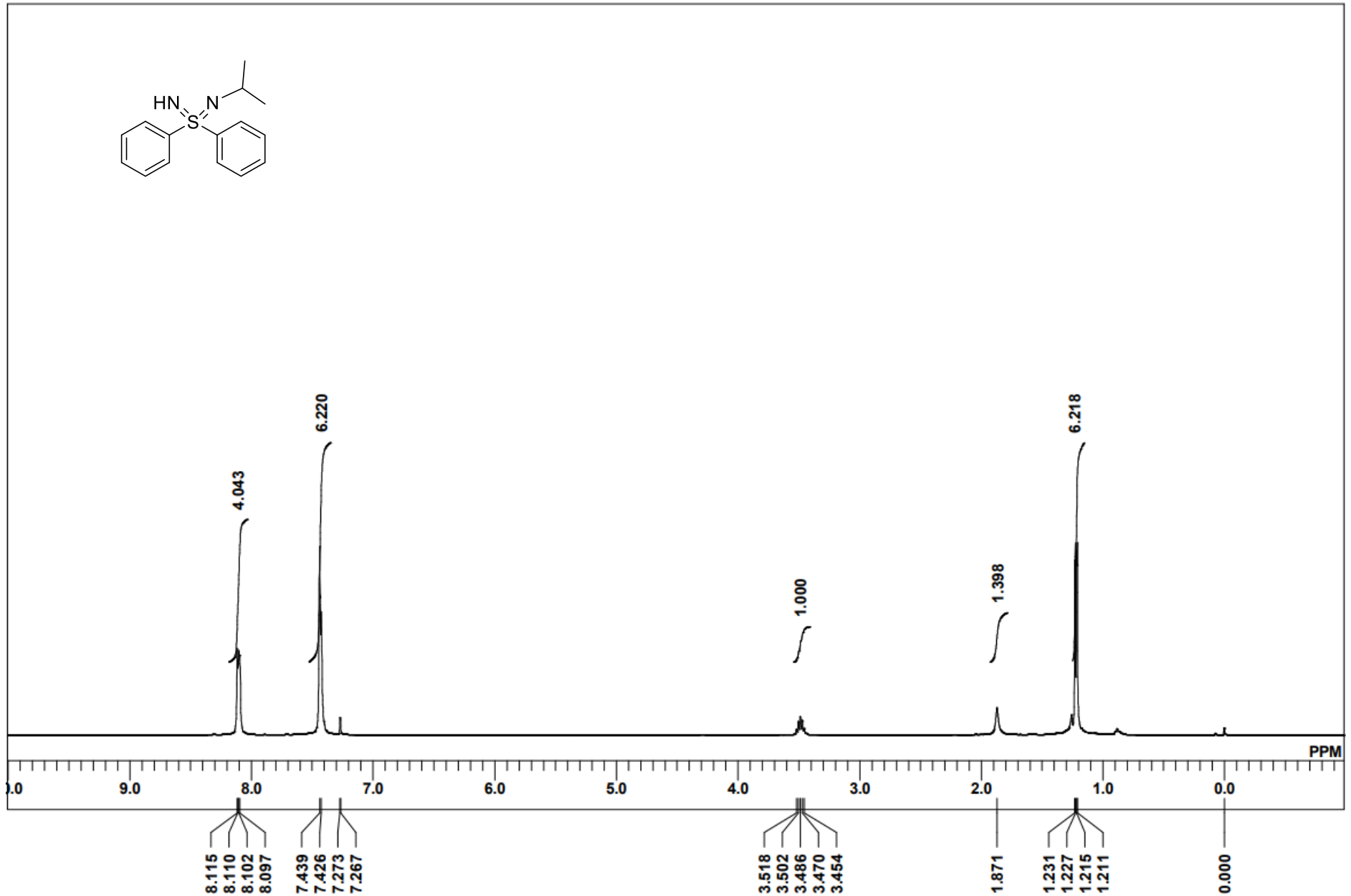
^{1}H NMR spectrum of **1m**



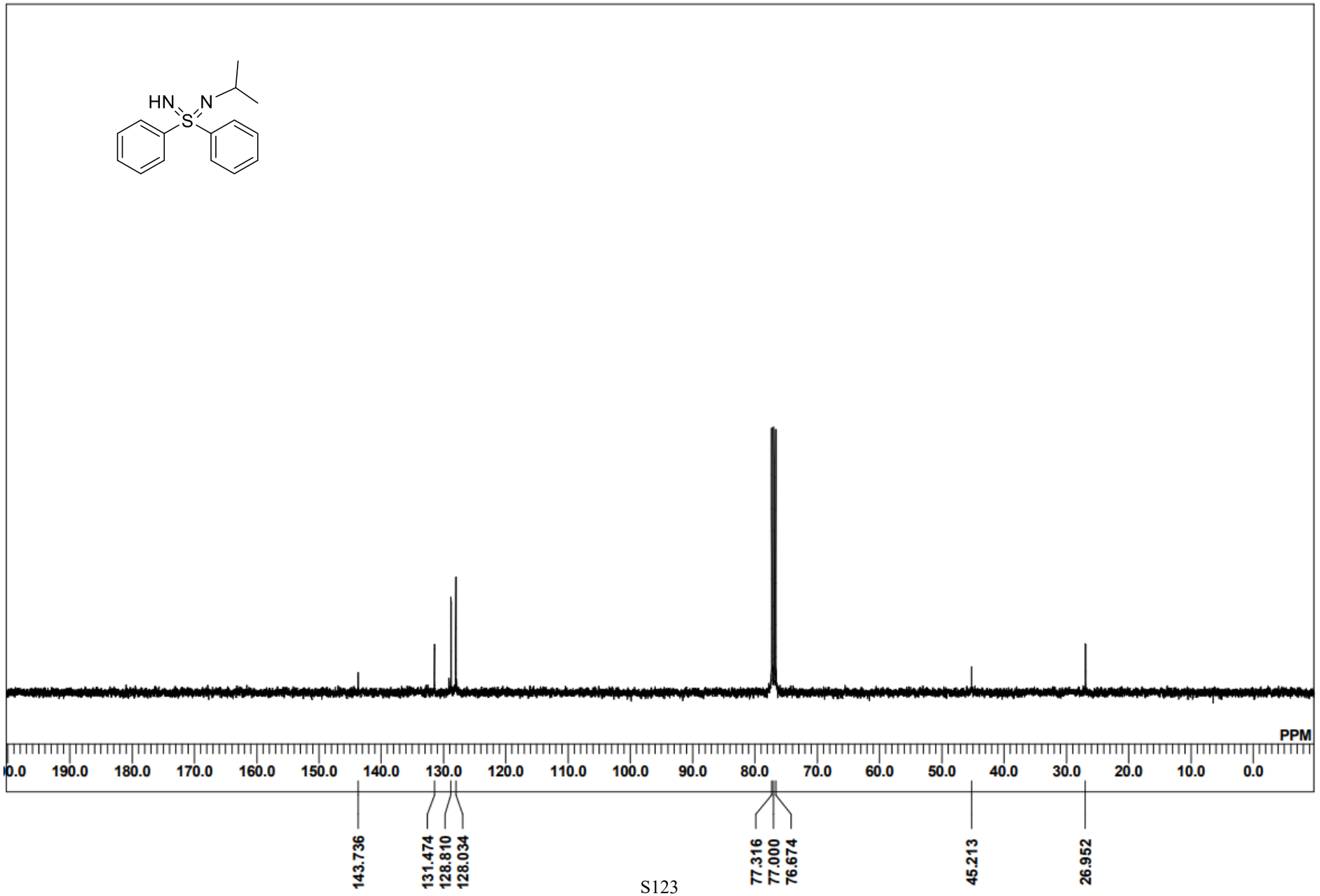
^{13}C NMR spectrum of **1m**



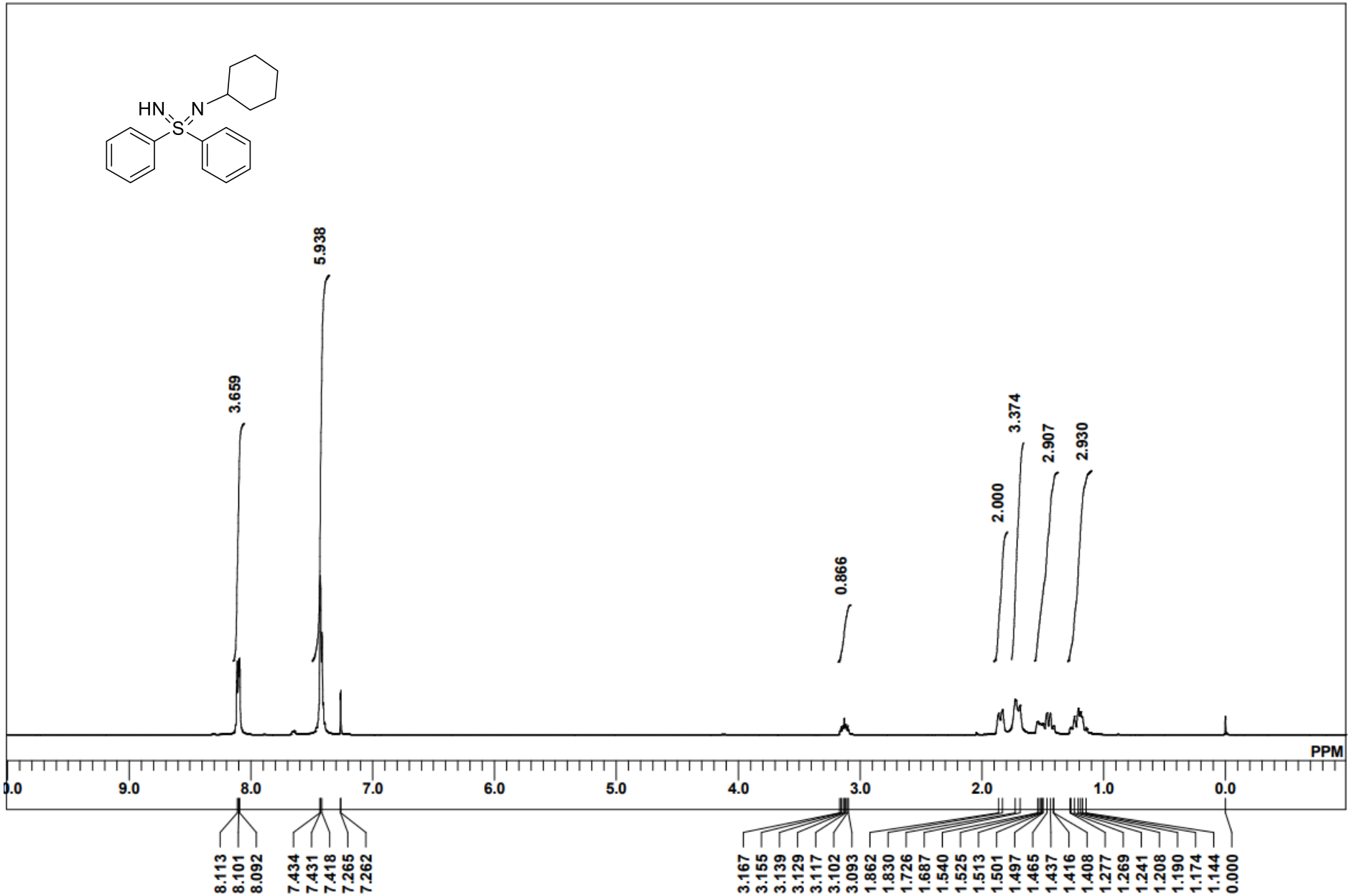
^{1}H NMR spectrum of **1n**



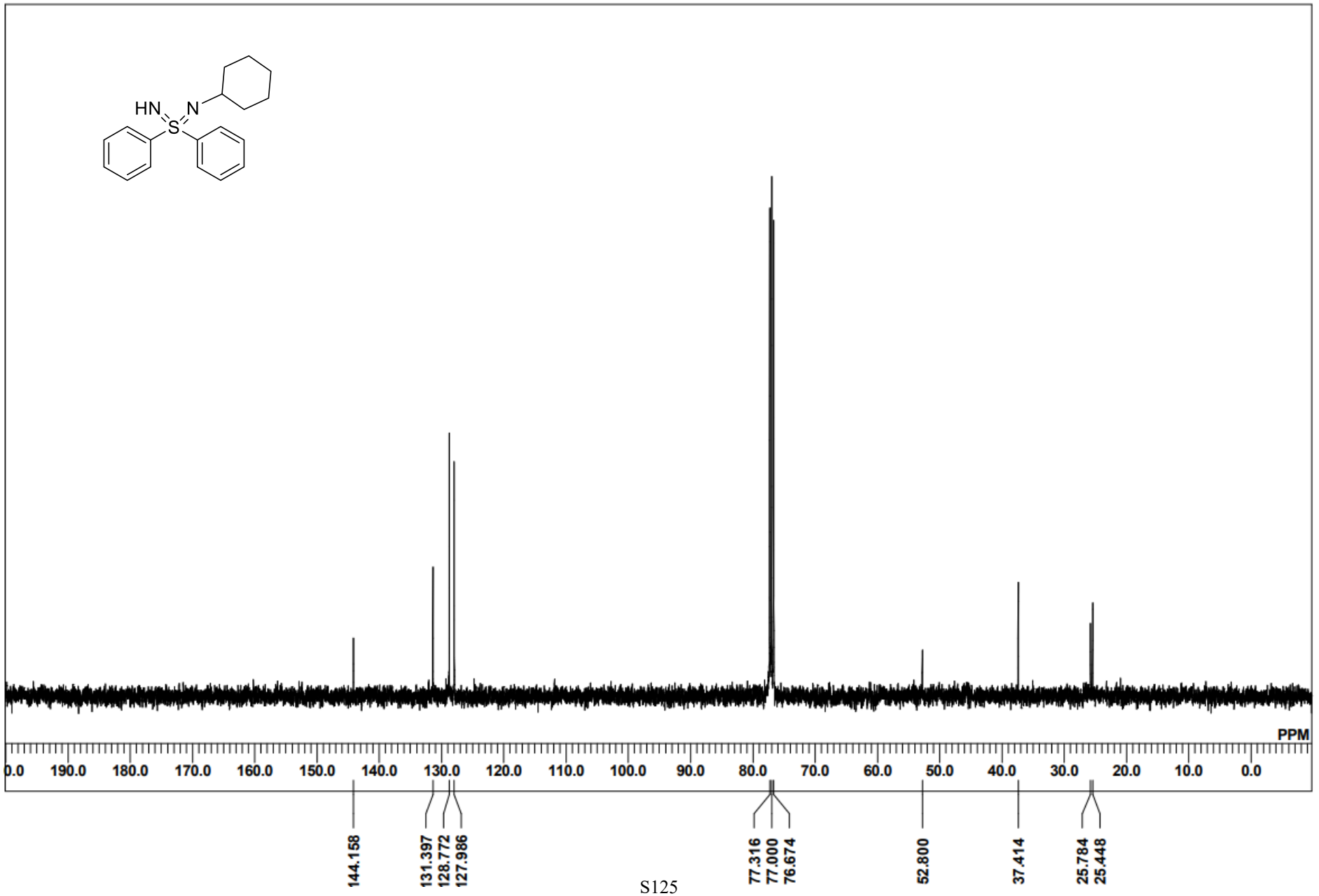
^{13}C NMR spectrum of **1n**



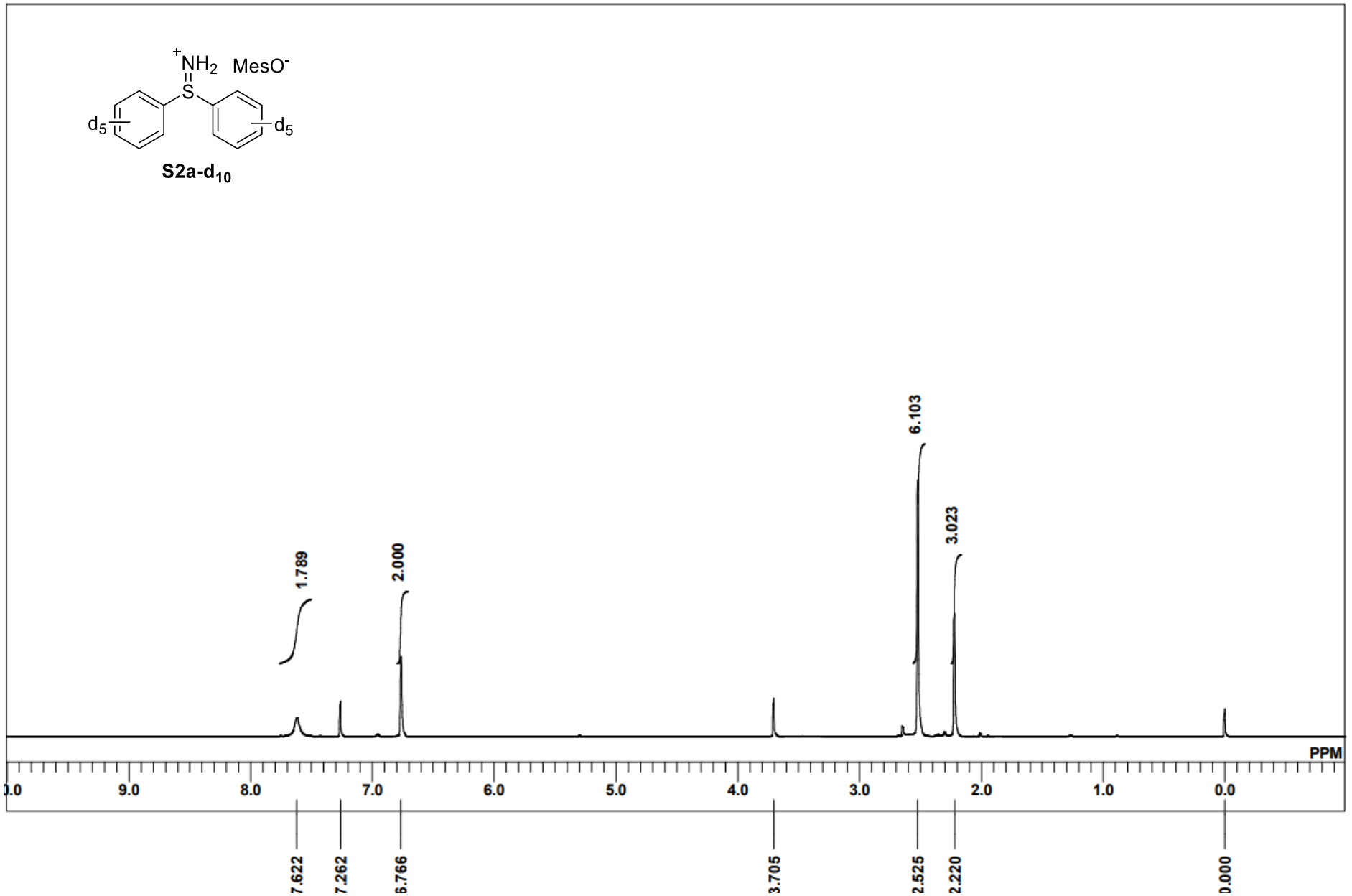
^{1}H NMR spectrum of **1o**



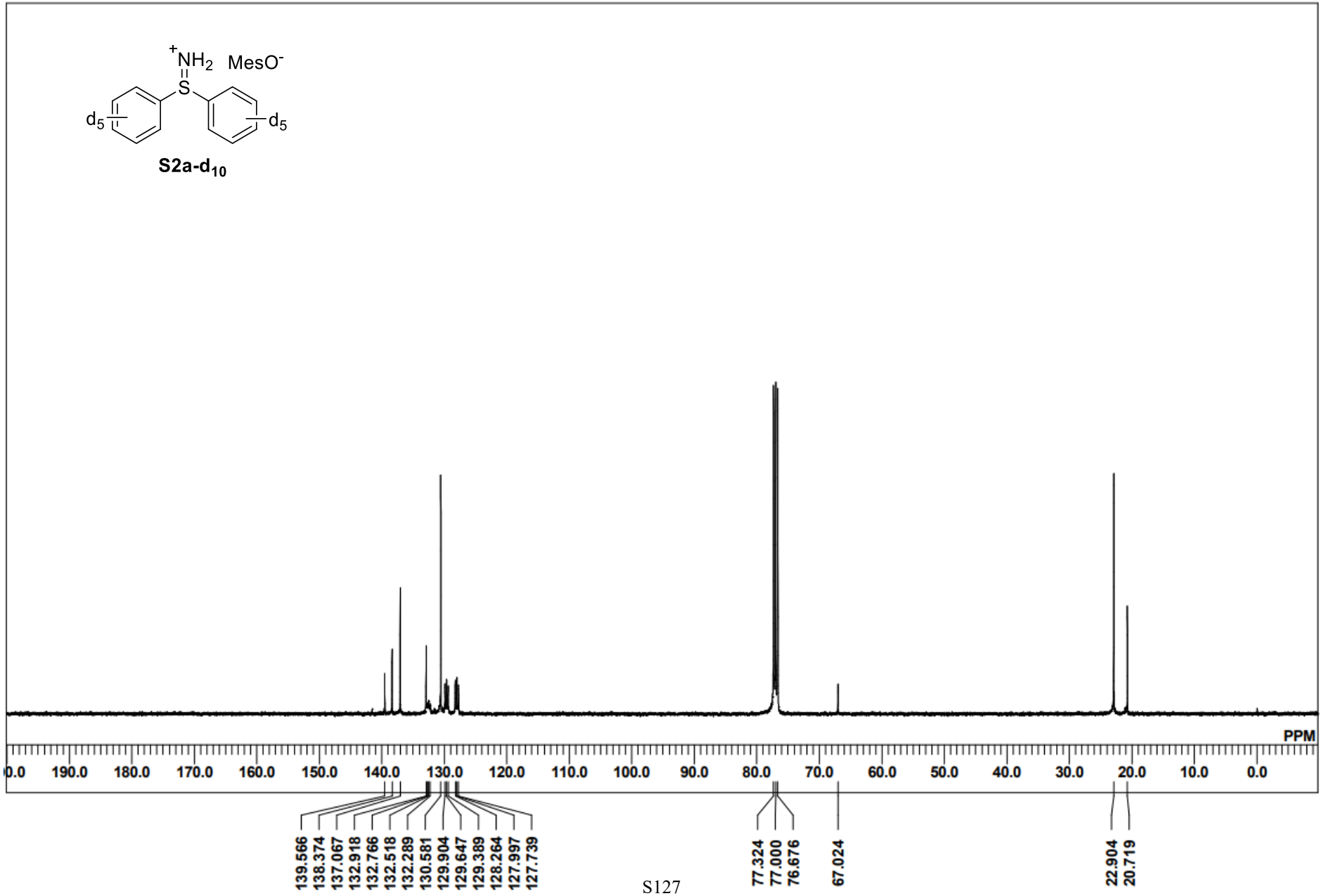
^{13}C NMR spectrum of **1o**



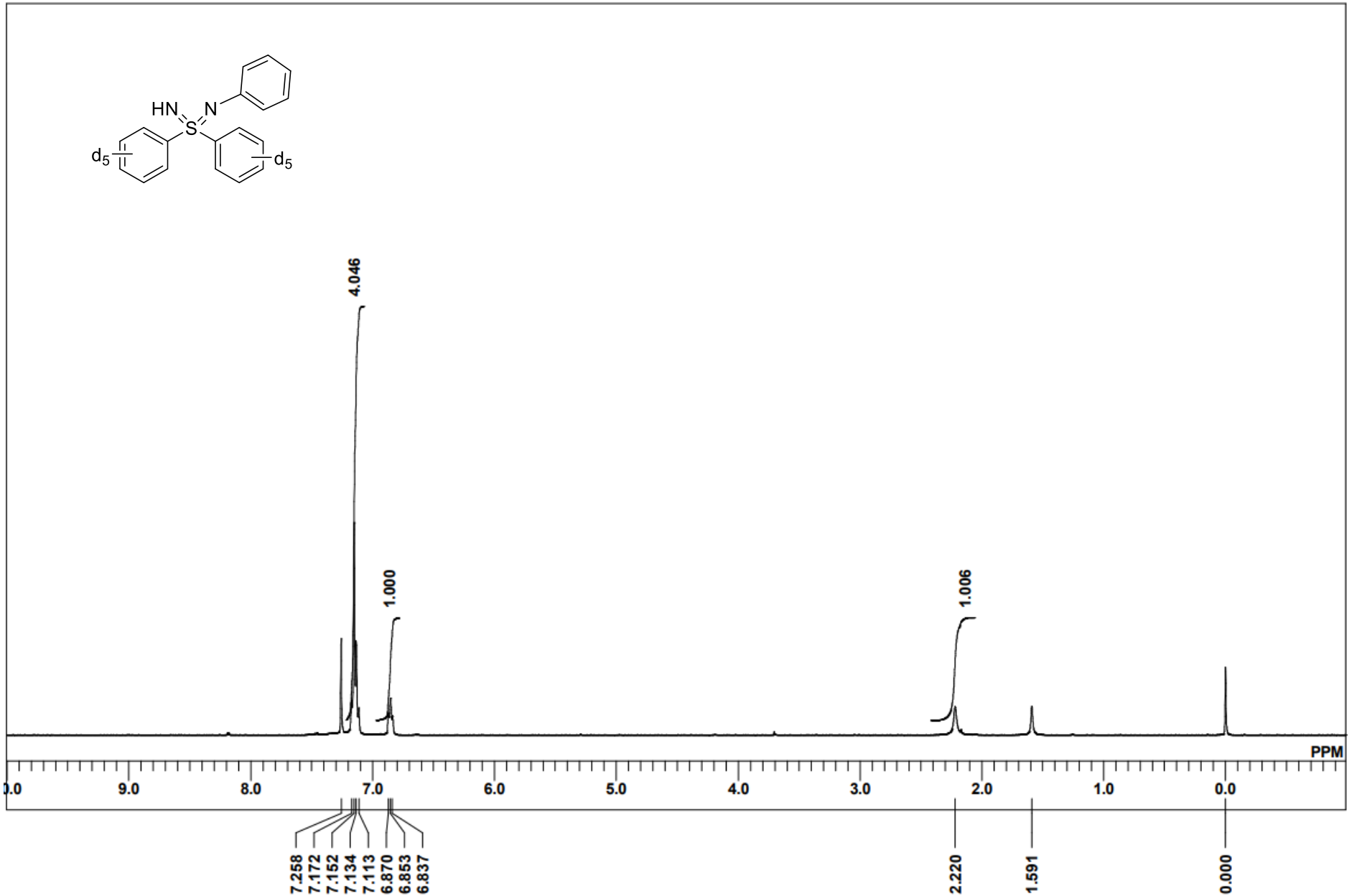
^{1}H NMR spectrum of **S2a-**d10 (contain the peak of dioxane: 3.7 ppm)



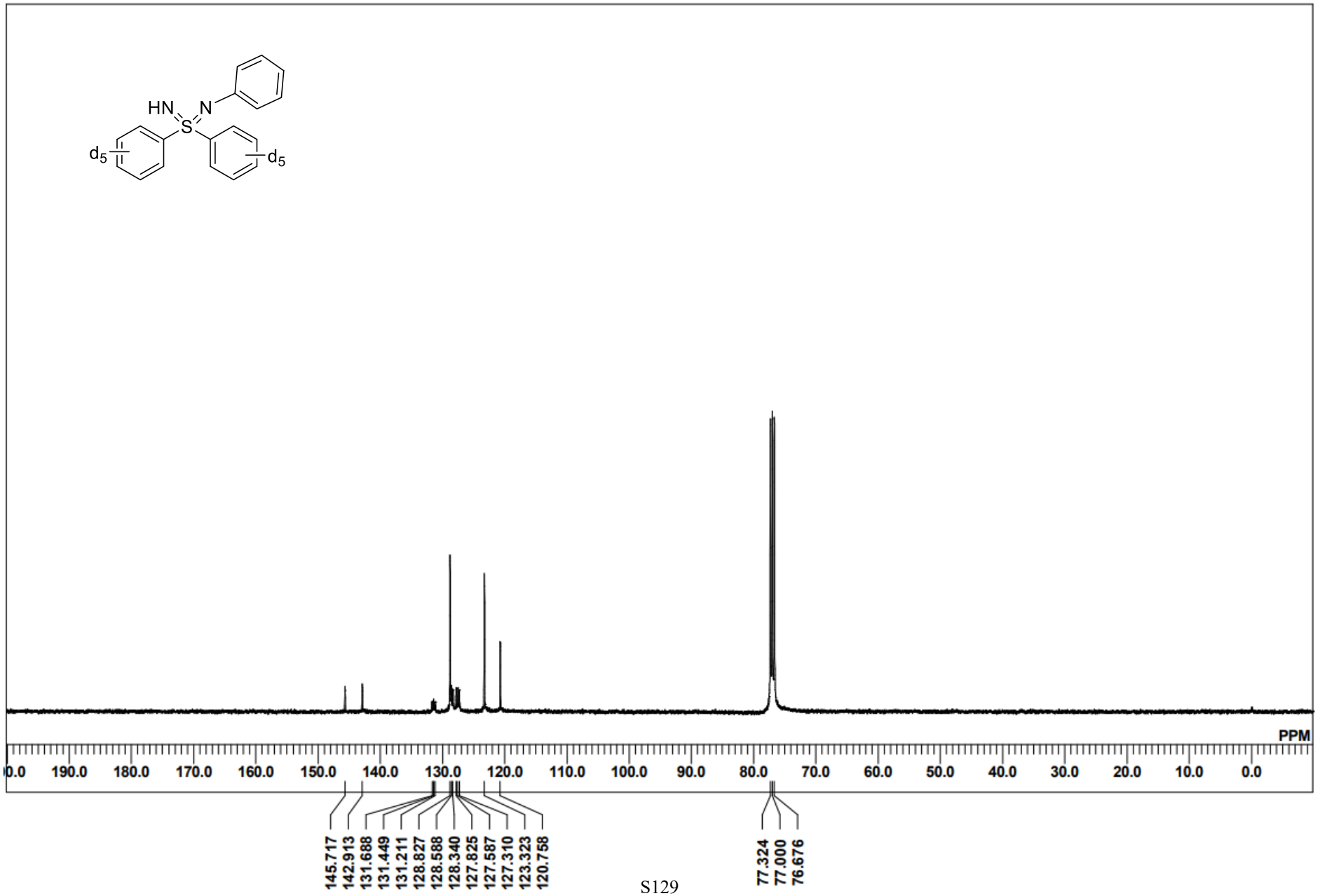
^{13}C NMR spectrum of **S2a-**d10 (contain the peak of dioxane: 67 ppm)



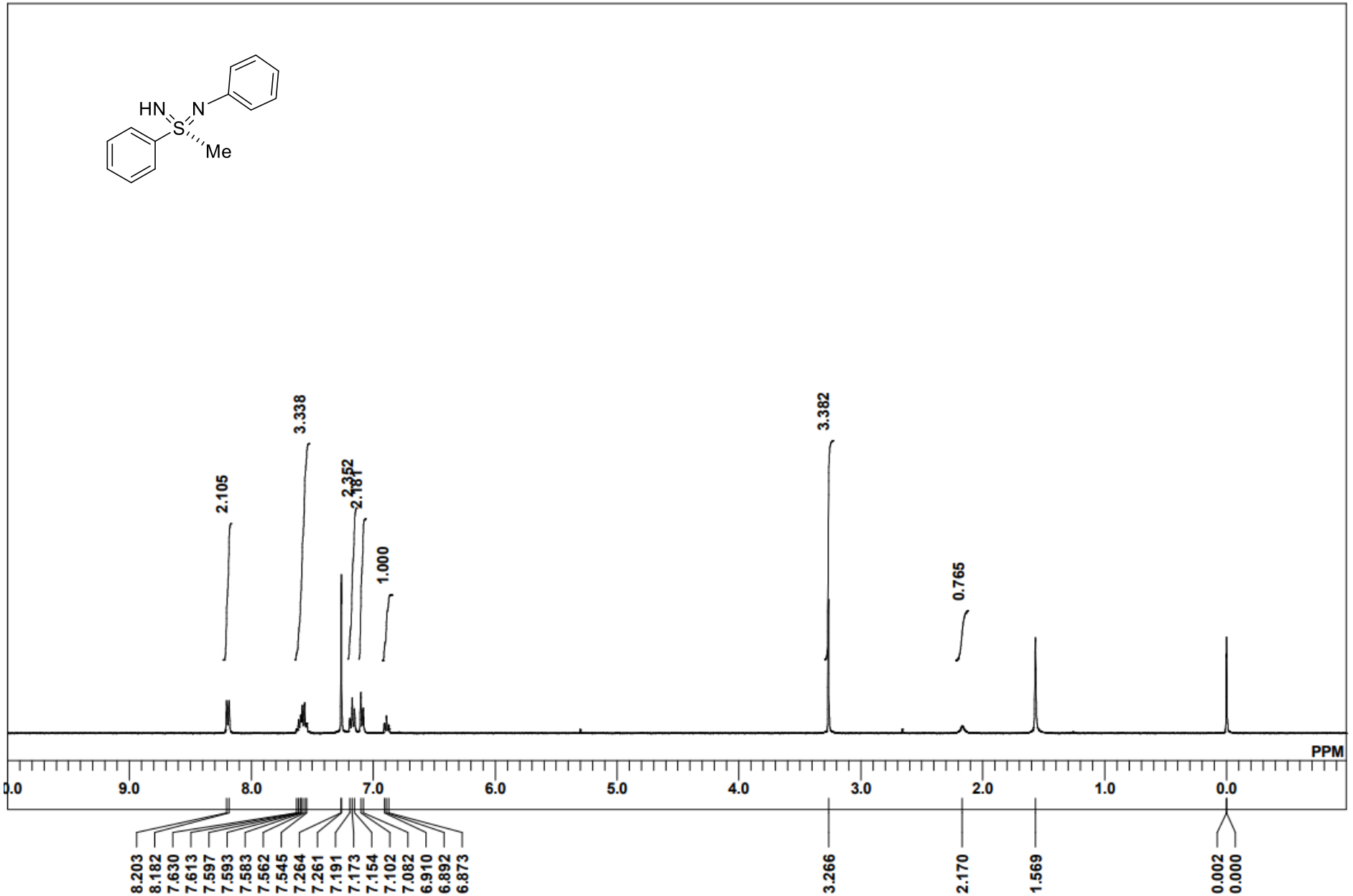
^{1}H NMR spectrum of **1a-d10**



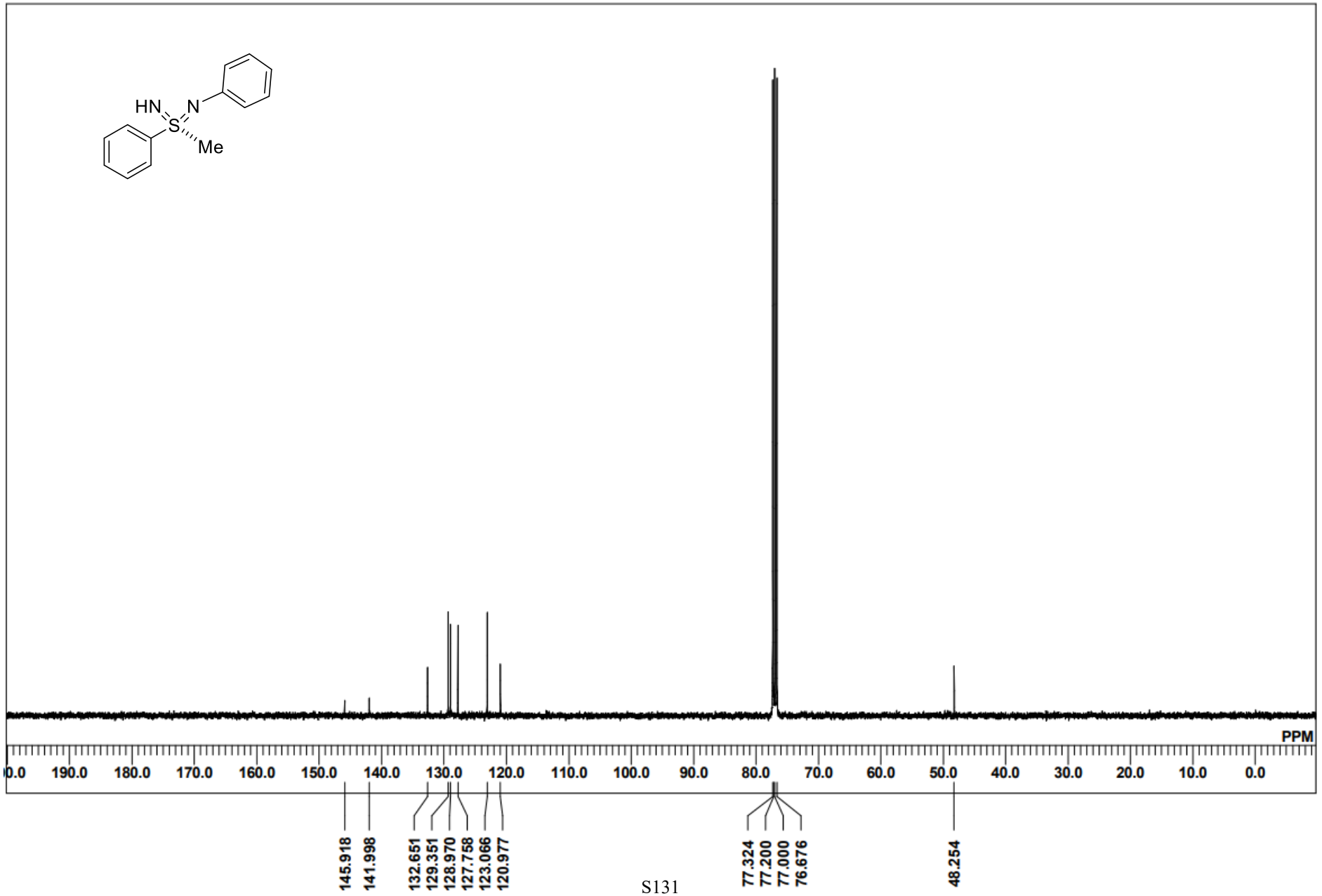
^{13}C NMR spectrum of **1a-d10**



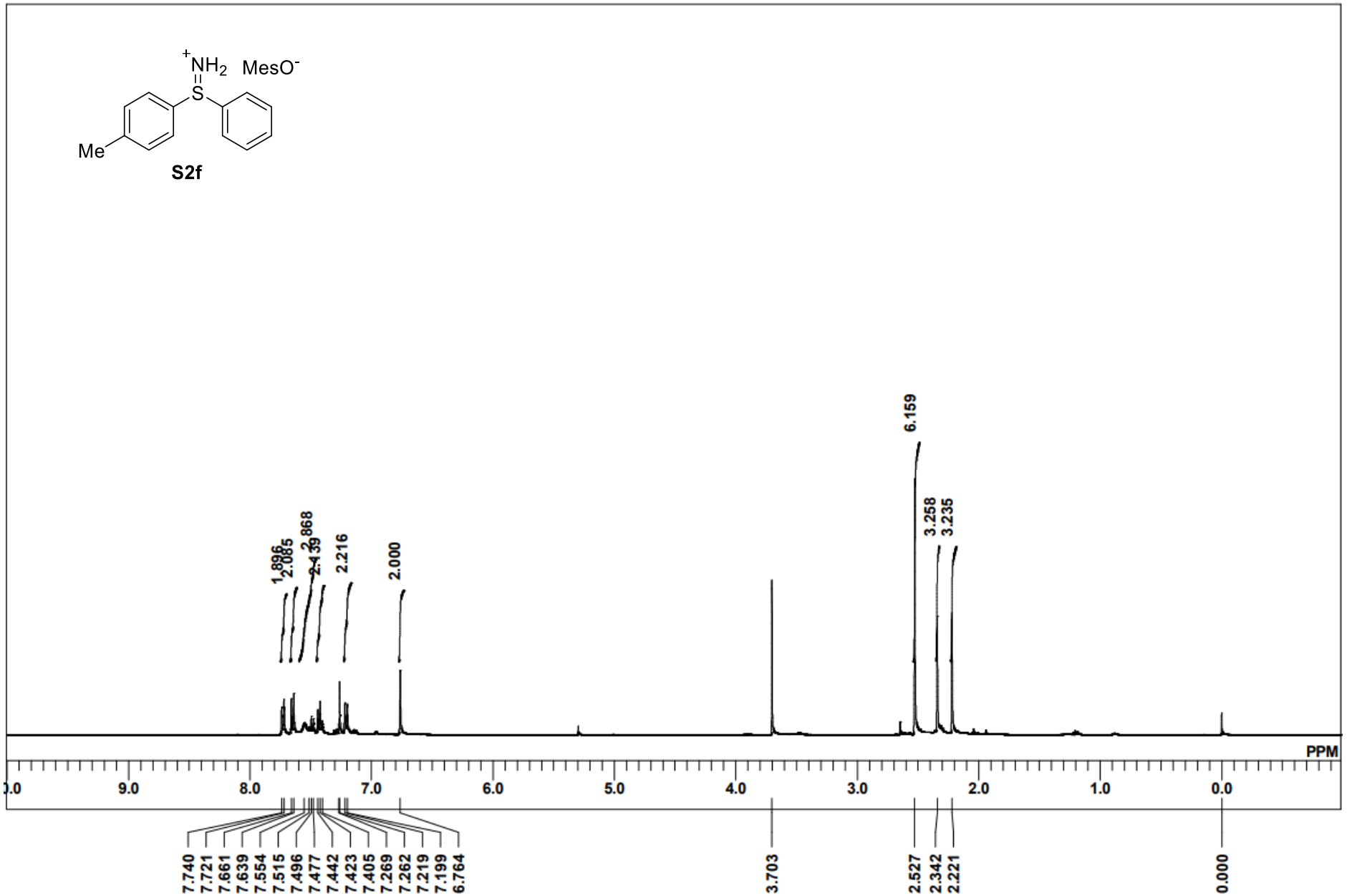
^{1}H NMR spectrum of **5**



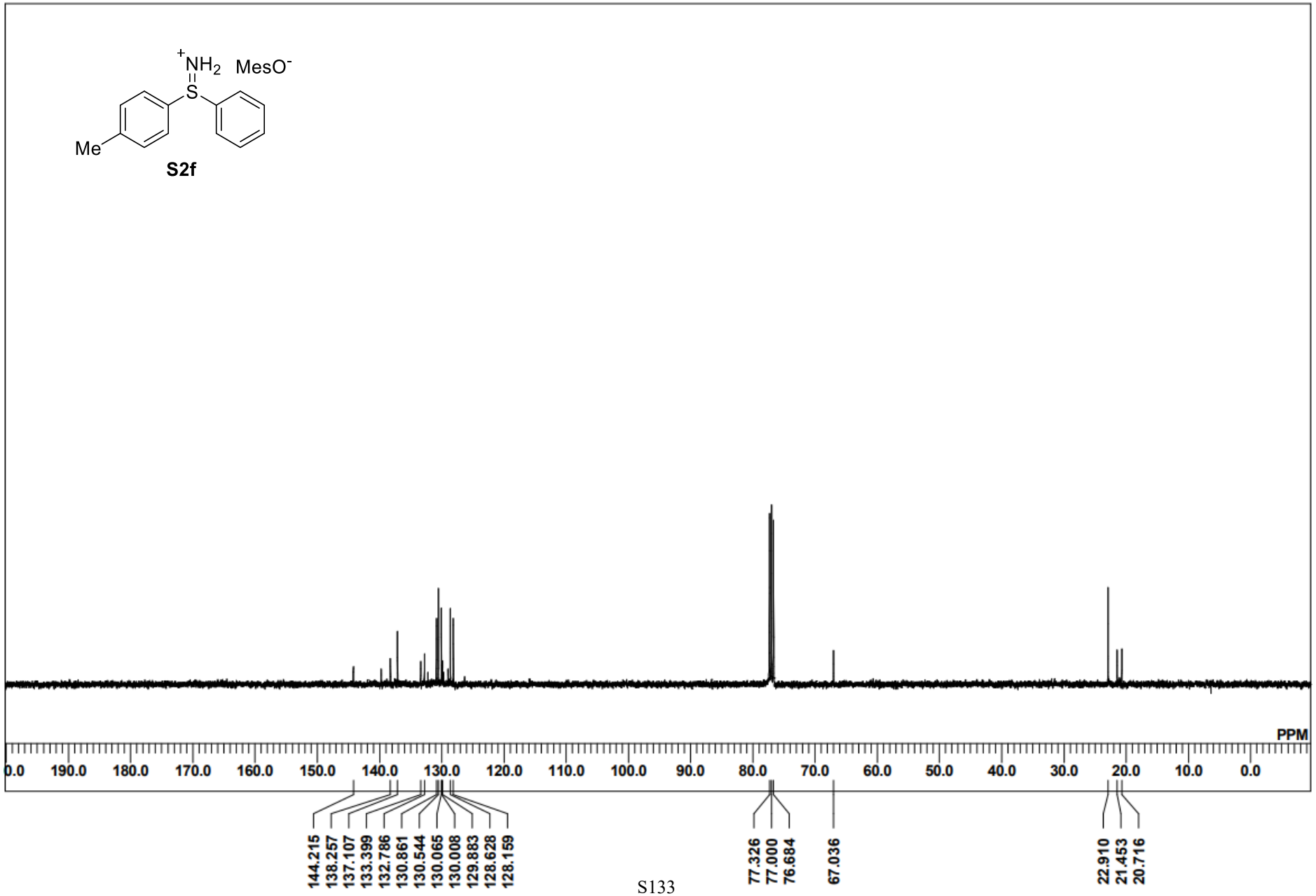
^{13}C NMR spectrum of **5**



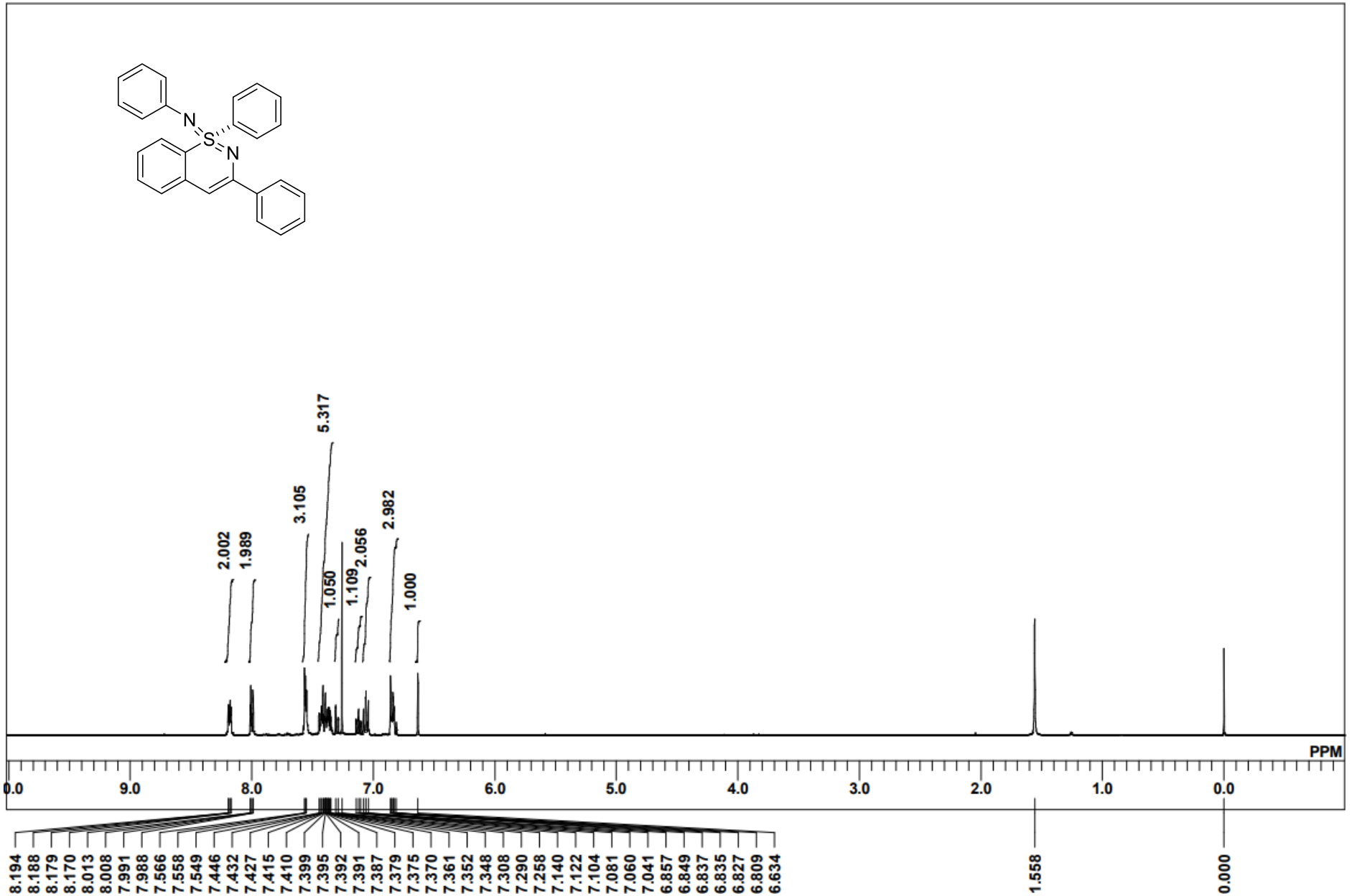
^{1}H NMR spectrum of **S2f** (contain the peak of dioxane: 3.7 ppm)



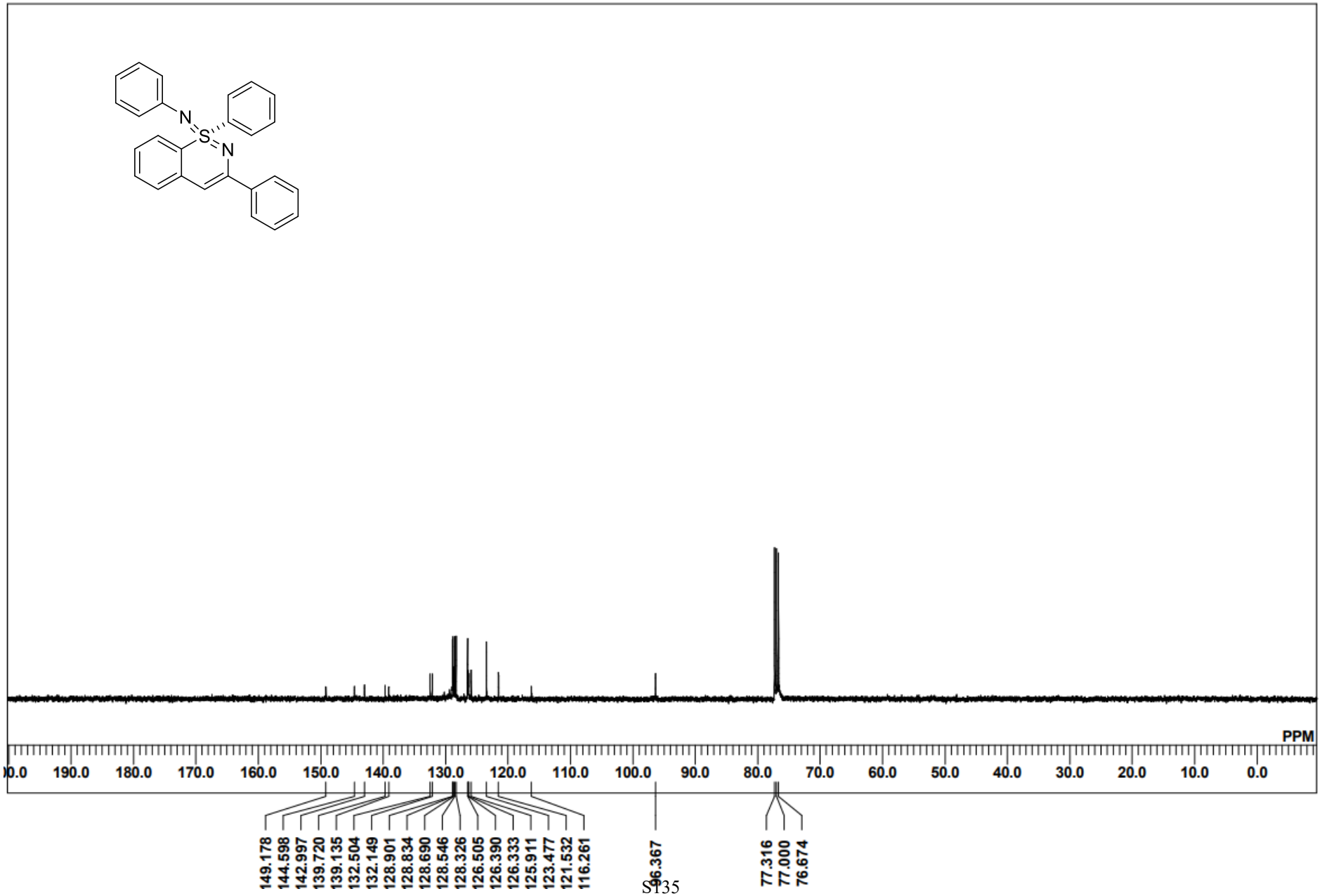
^{13}C NMR spectrum of **S2f** (contain the peak of dioxane: 67 ppm)



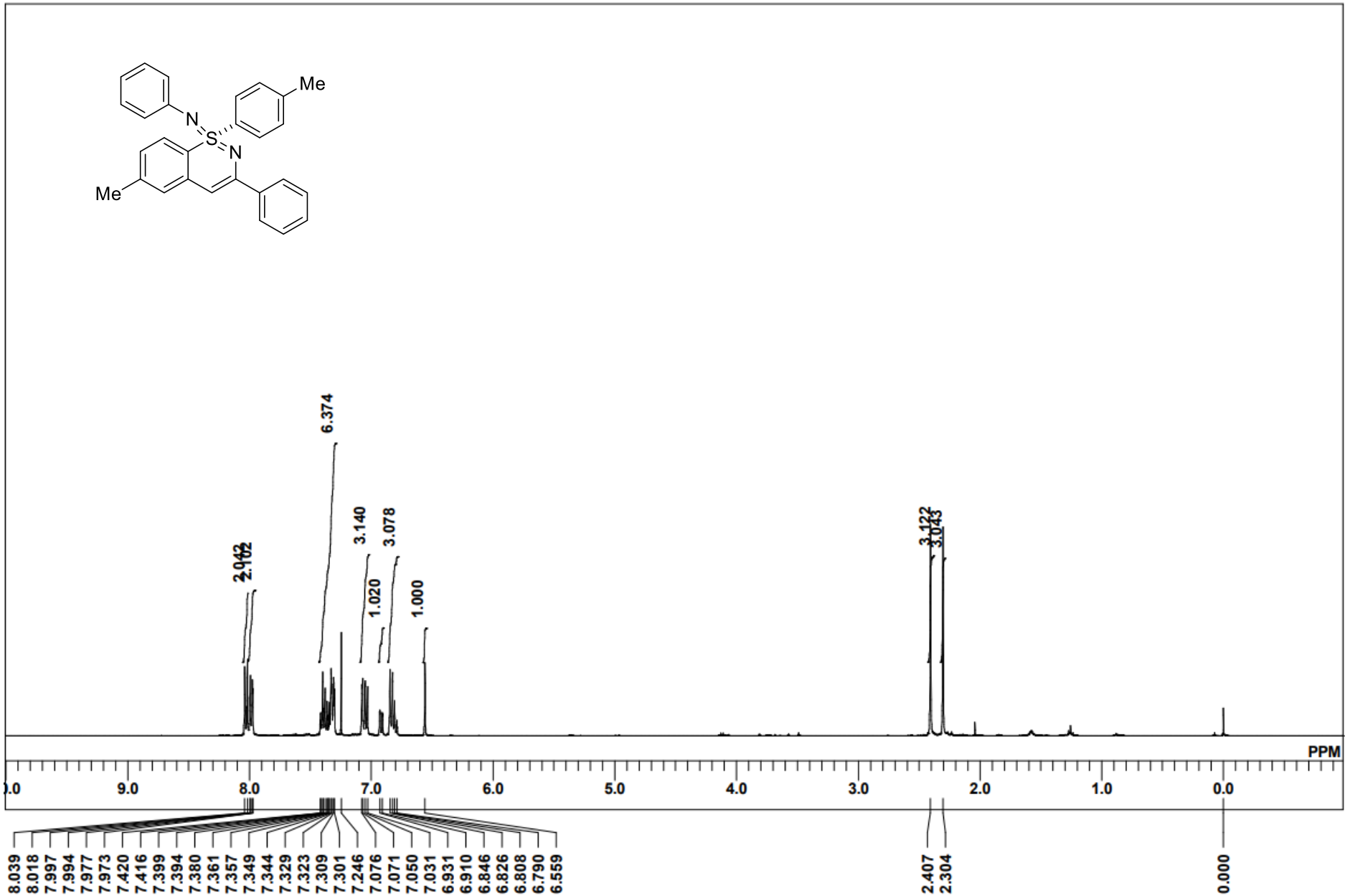
^{1}H NMR spectrum of **3aa**



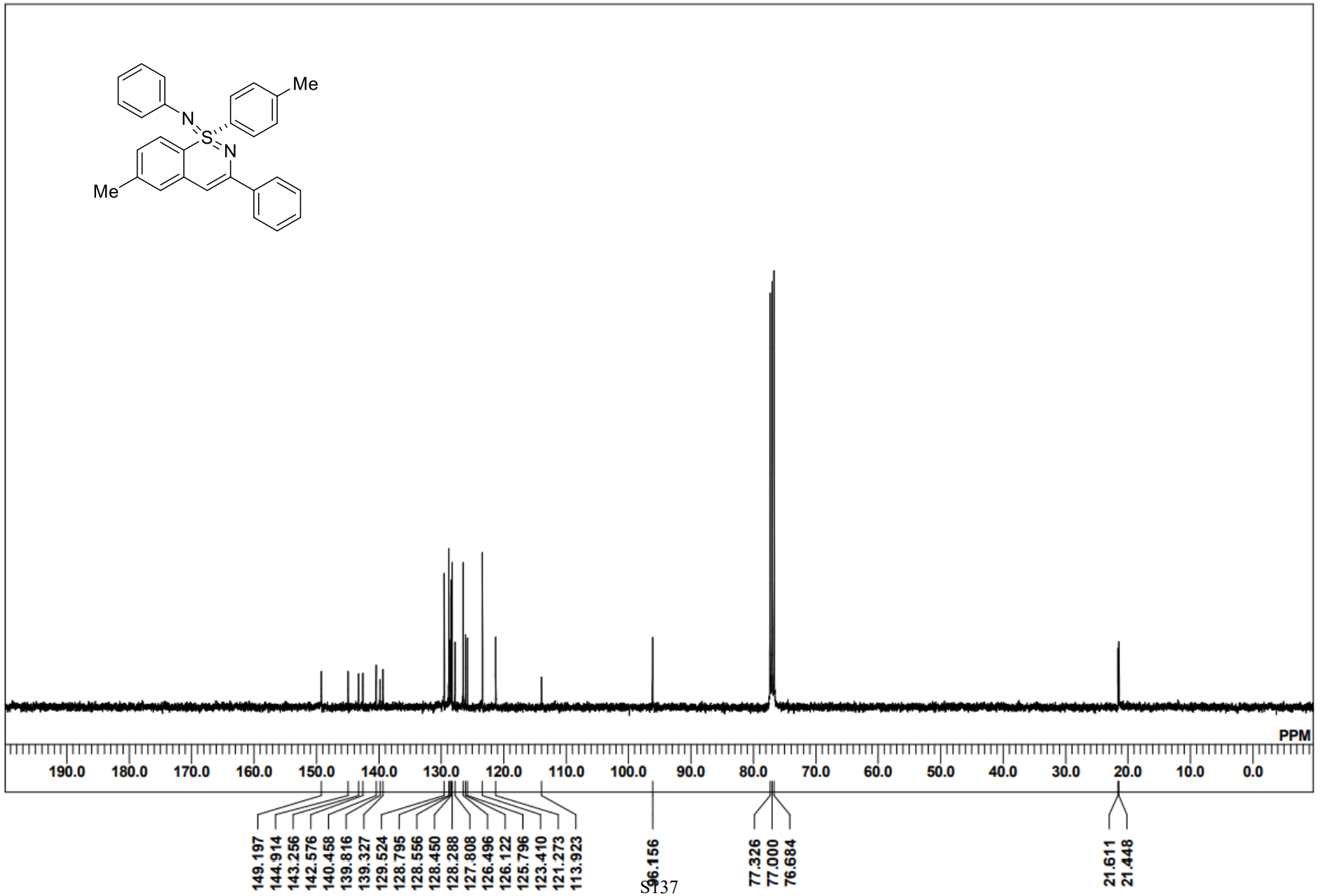
^{13}C NMR spectrum of **3aa**



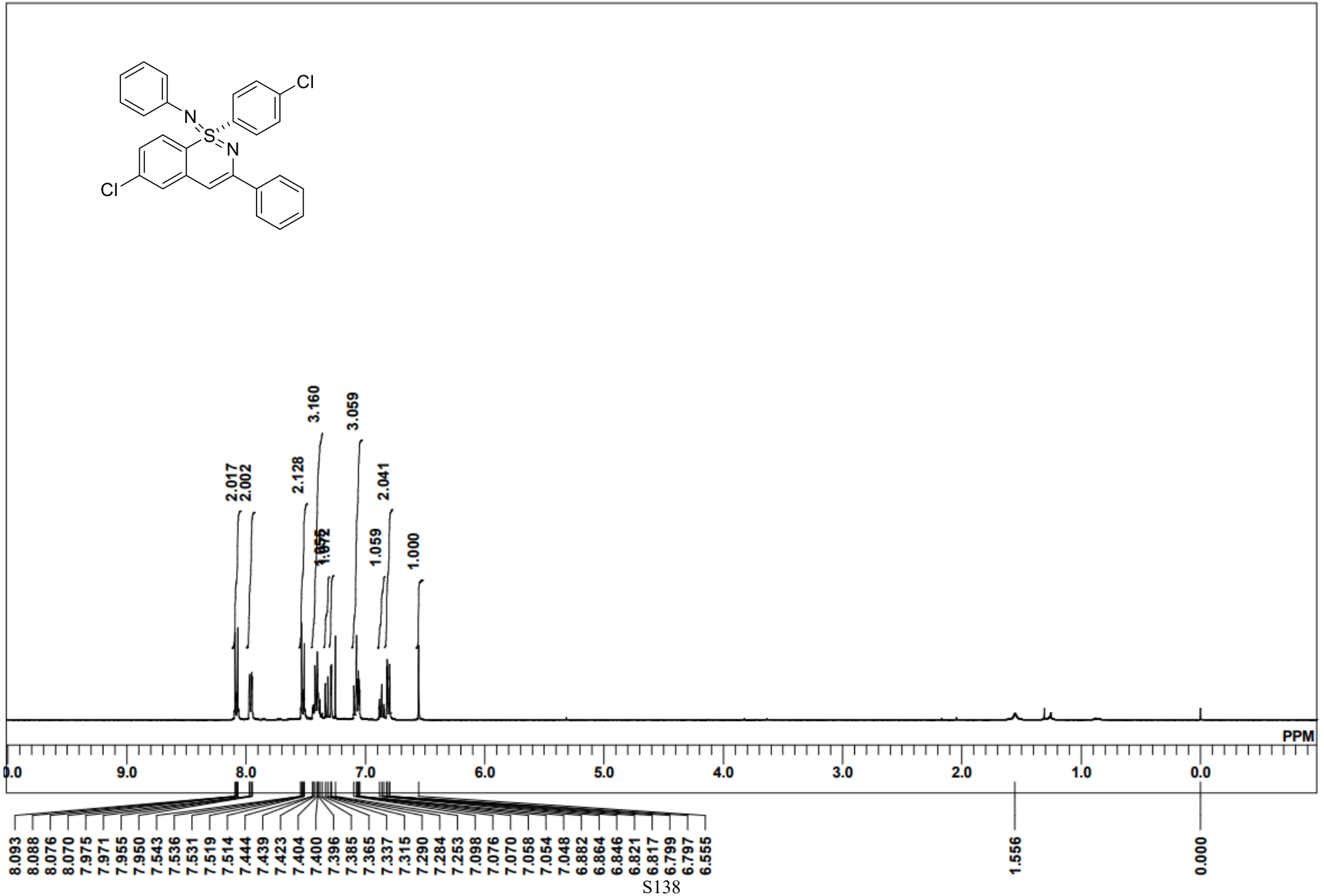
^{1}H NMR spectrum of **3ba**



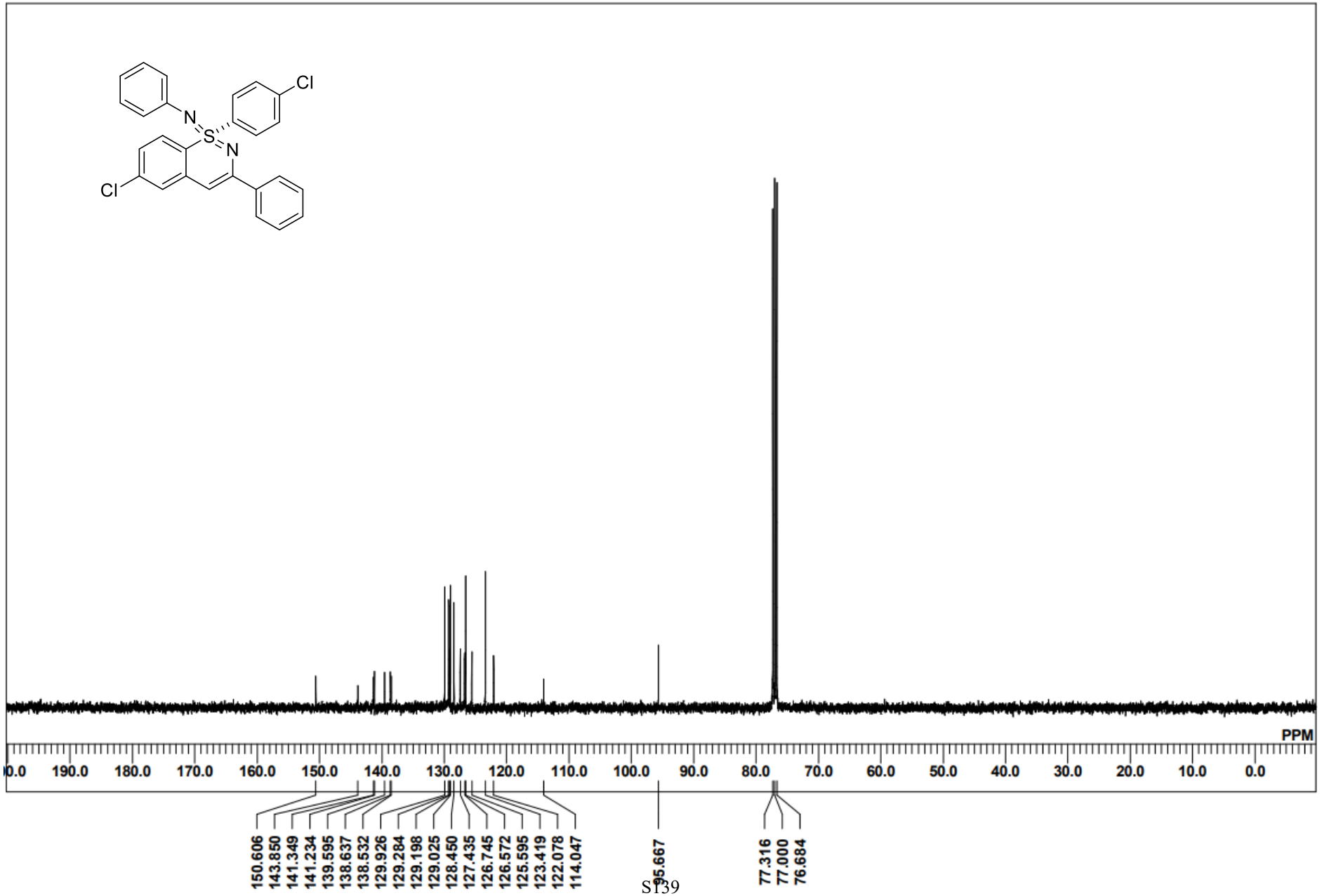
^{13}C NMR spectrum of **3ba**



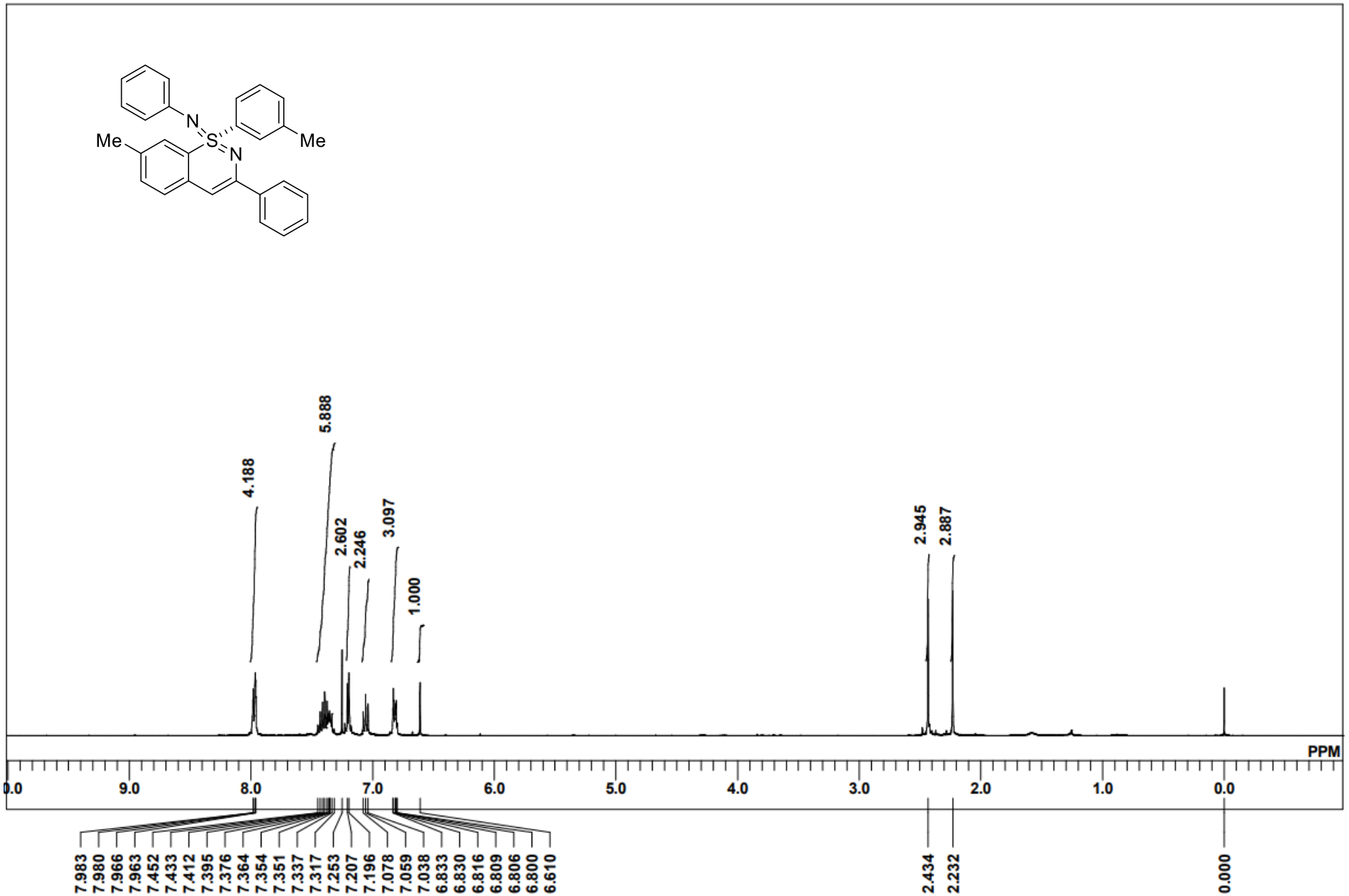
^{1}H NMR spectrum of **3ca**



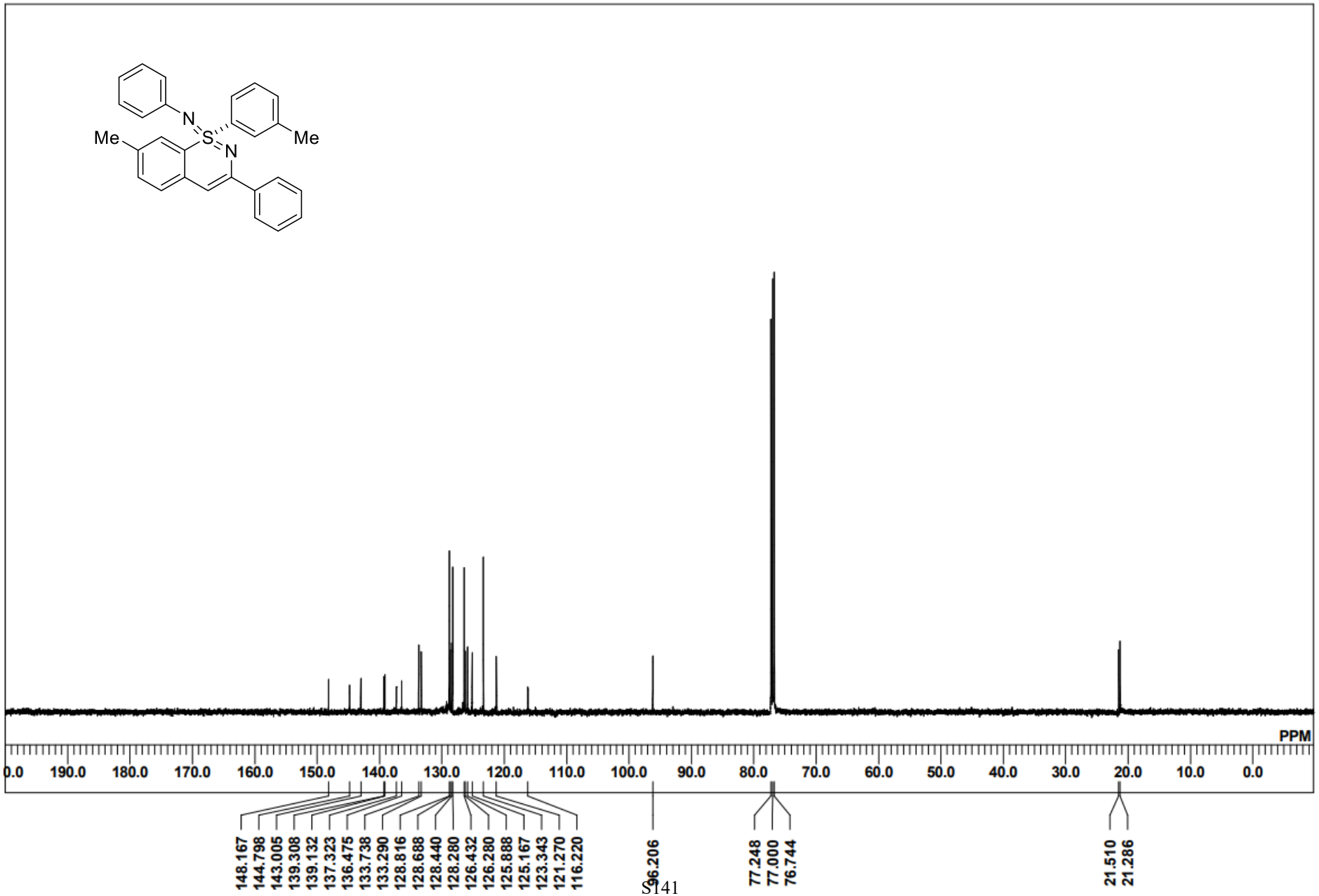
^{13}C NMR spectrum of **3ca**



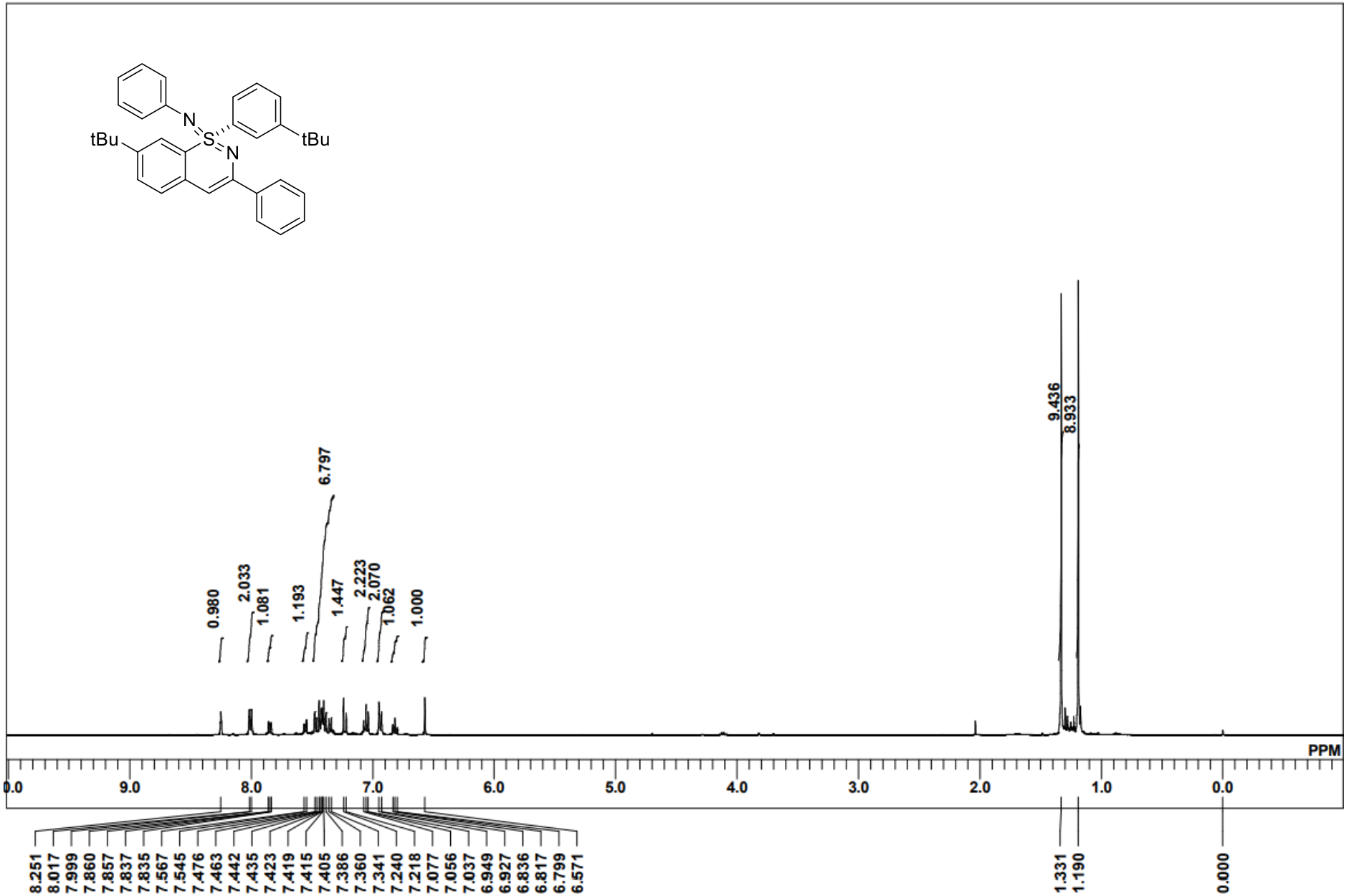
^{1}H NMR spectrum of **3da**



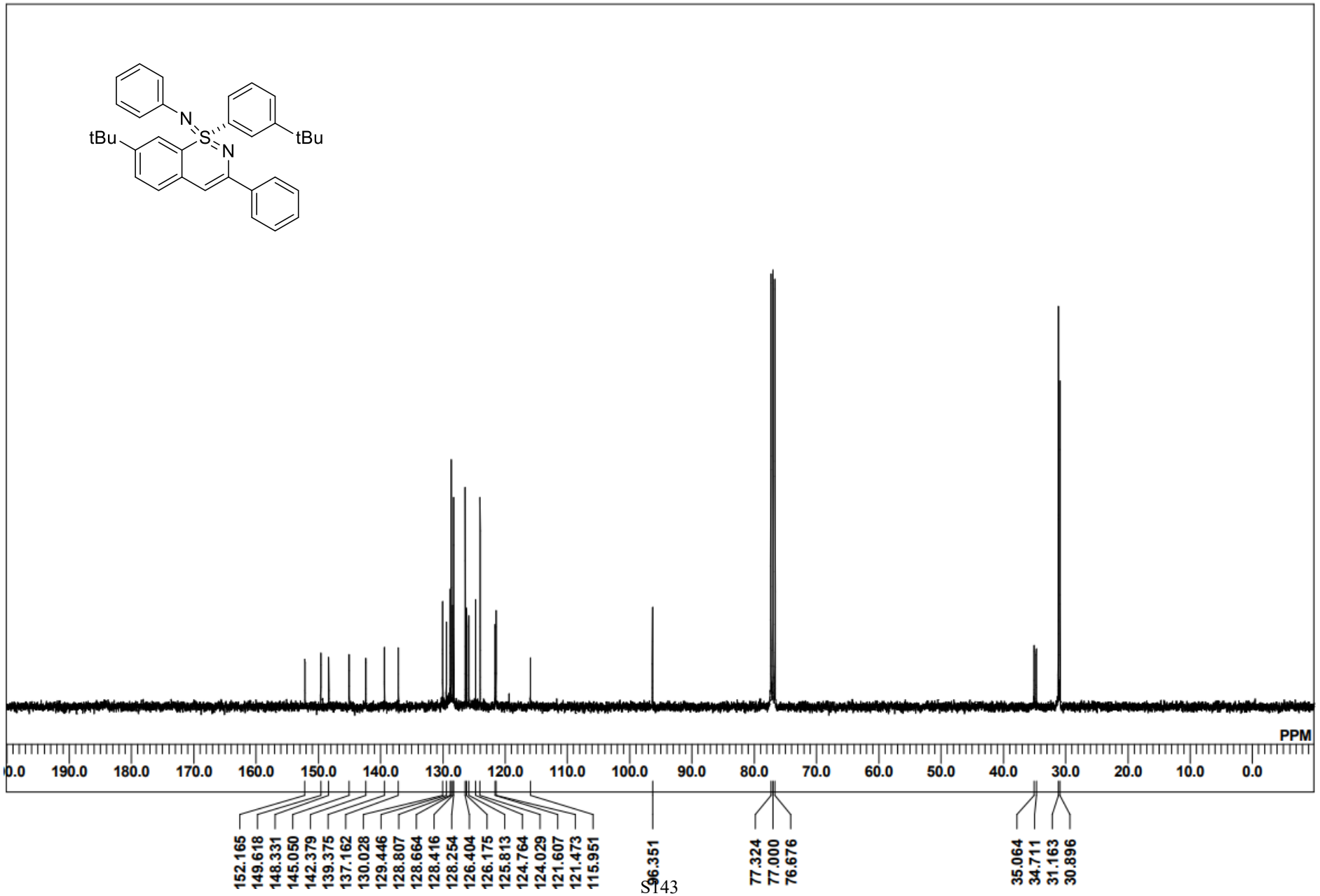
^{13}C NMR spectrum of **3da**



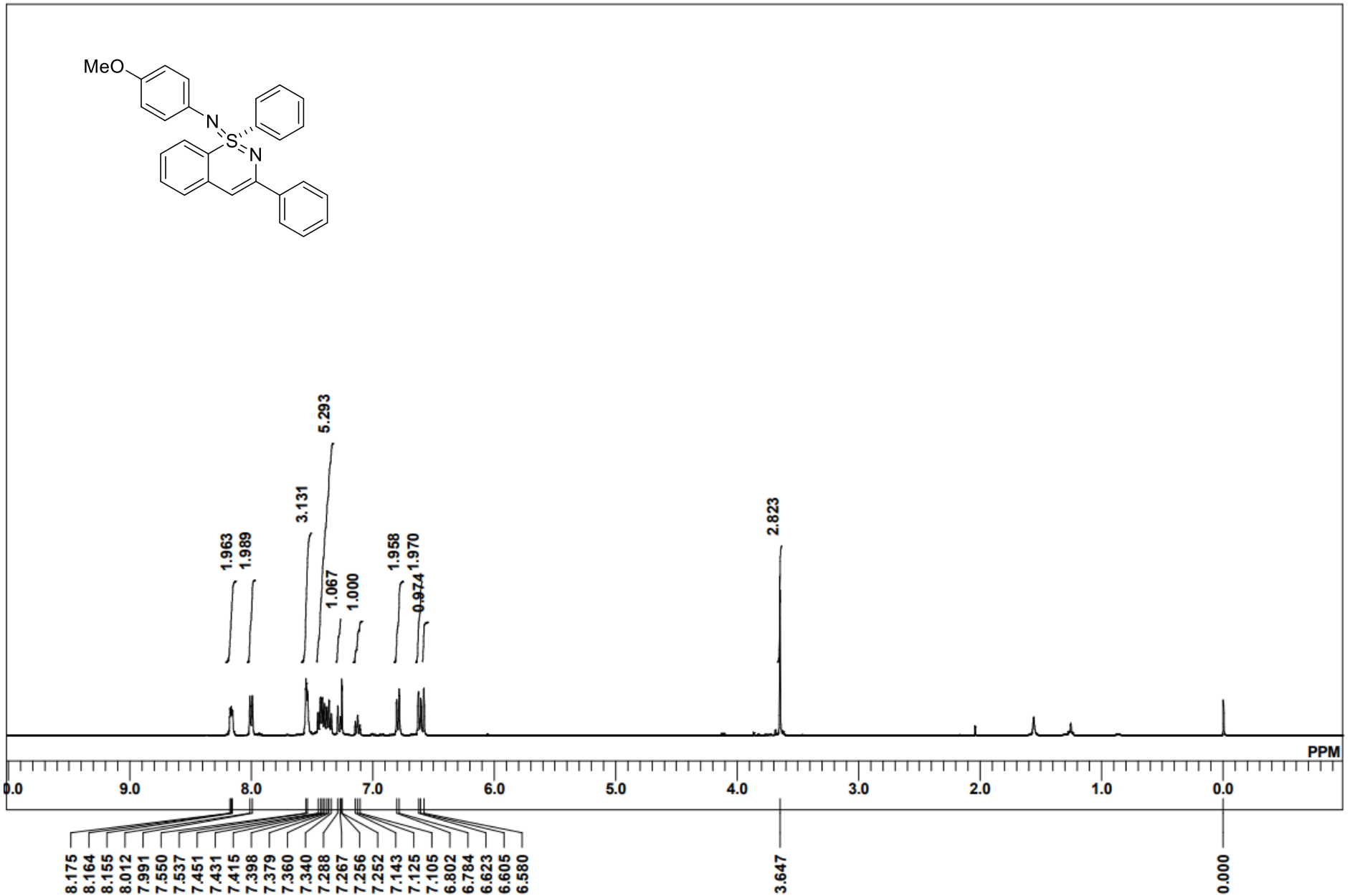
^{1}H NMR spectrum of **3ea**



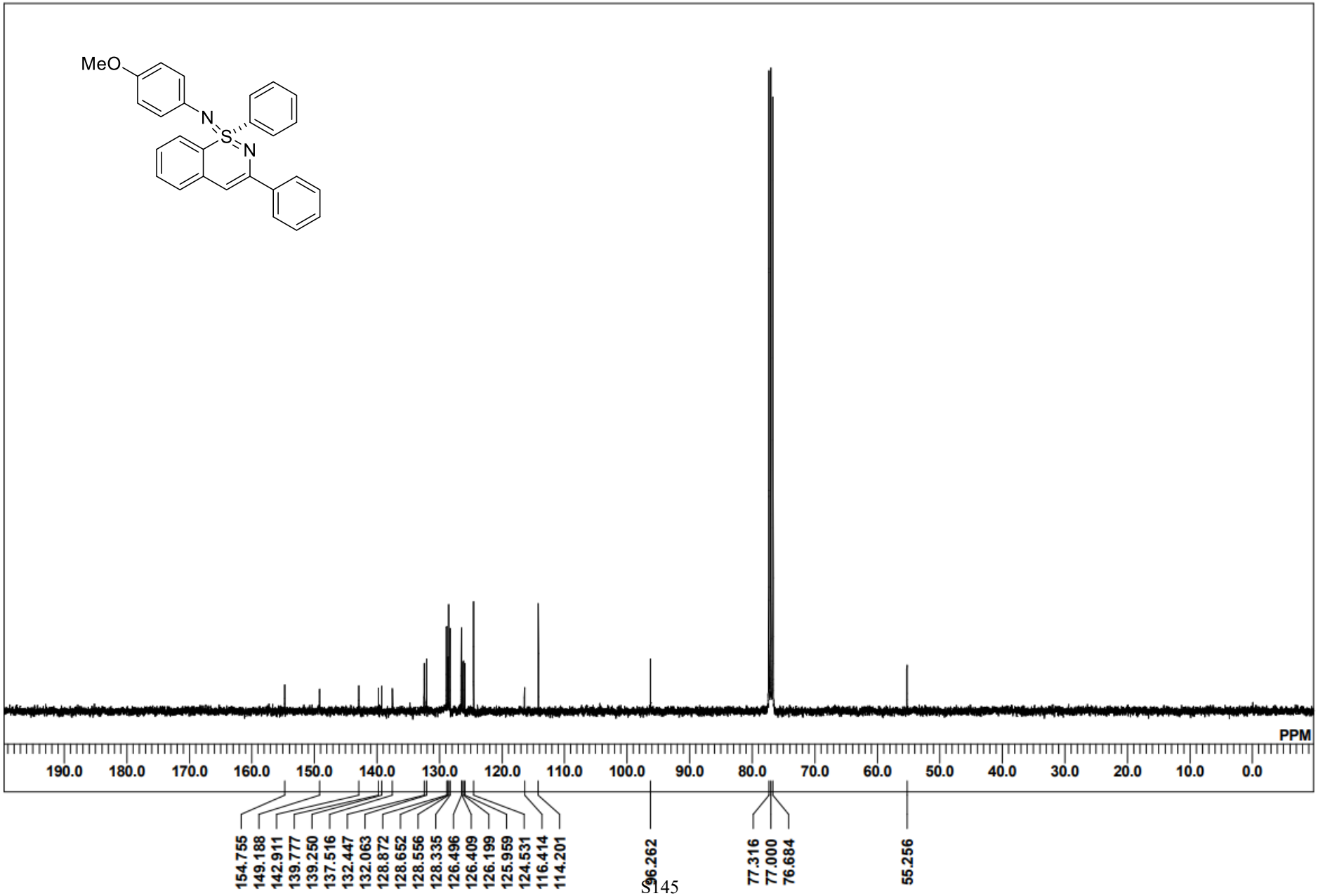
^{13}C NMR spectrum of **3ea**



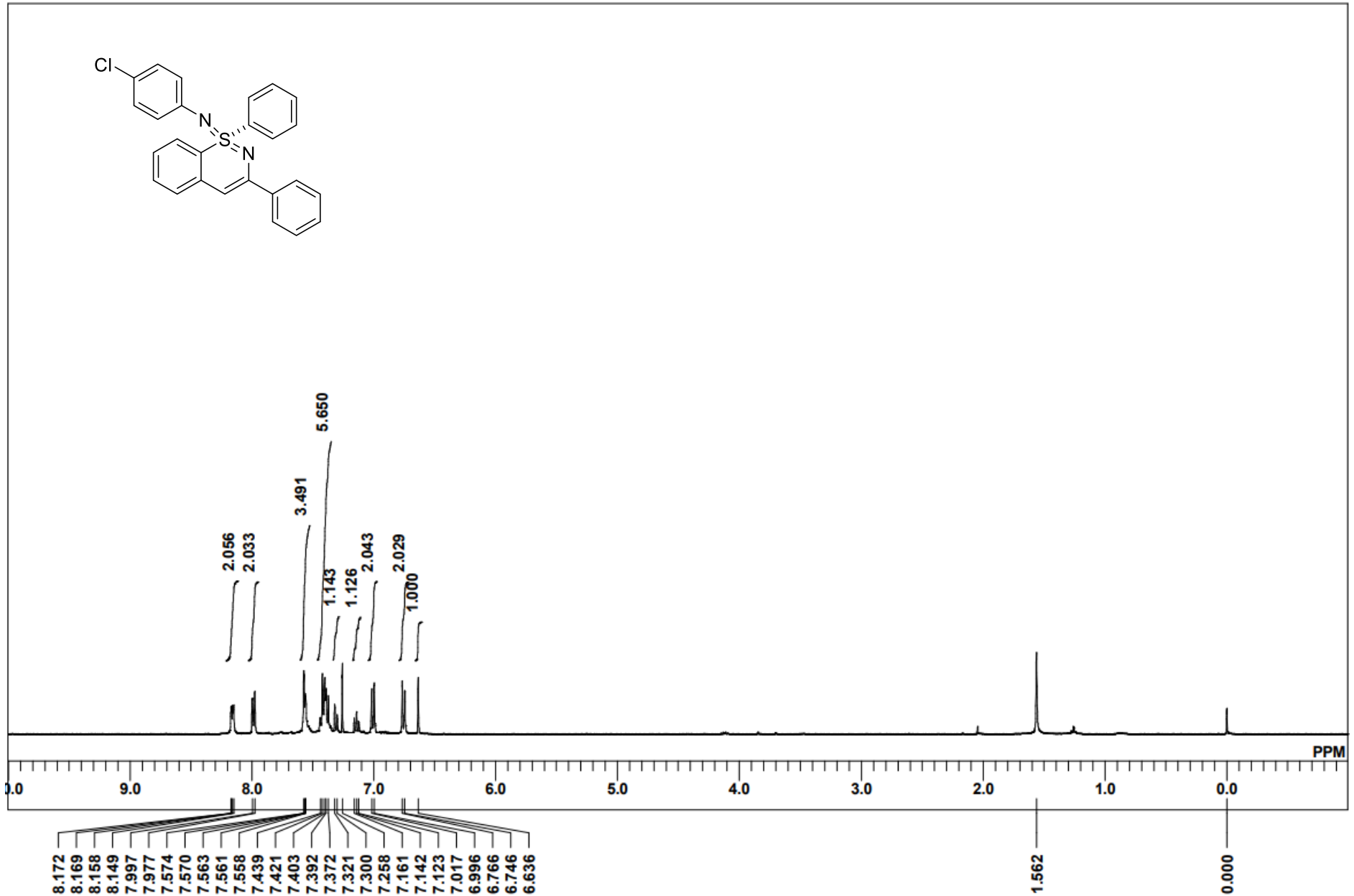
^{1}H NMR spectrum of **3fa**



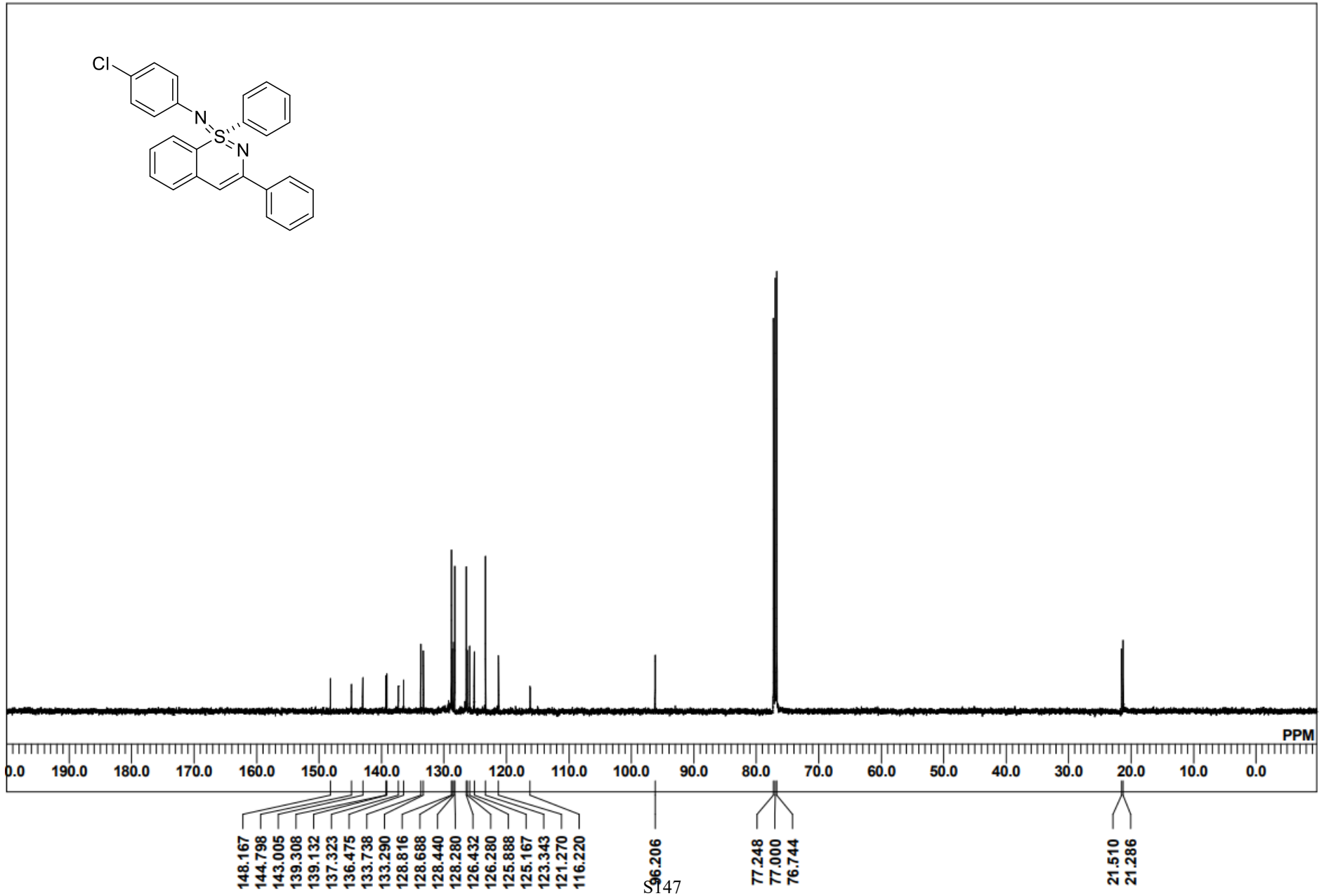
^{13}C NMR spectrum of **3fa**



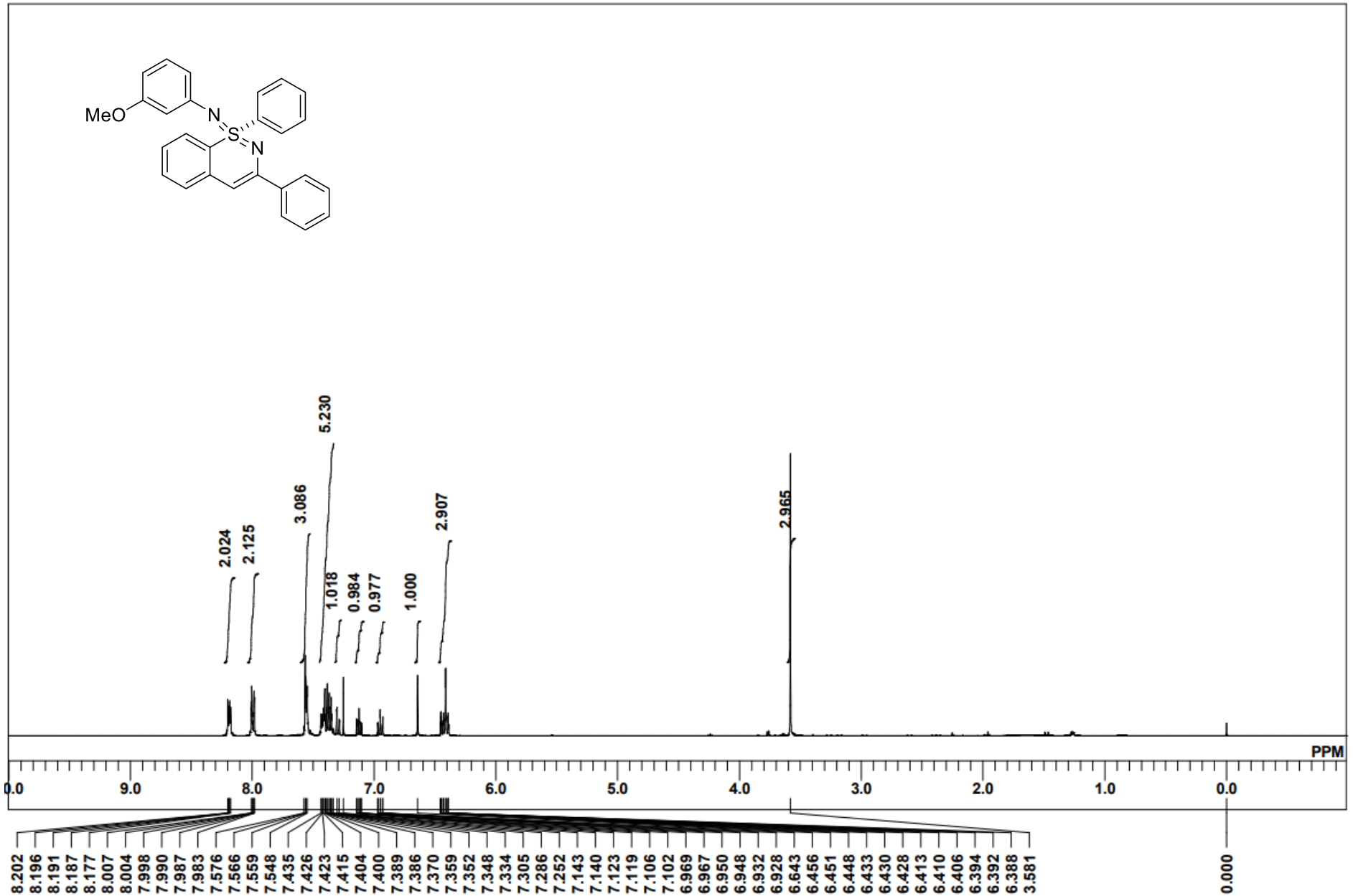
^{1}H NMR spectrum of **3ga**



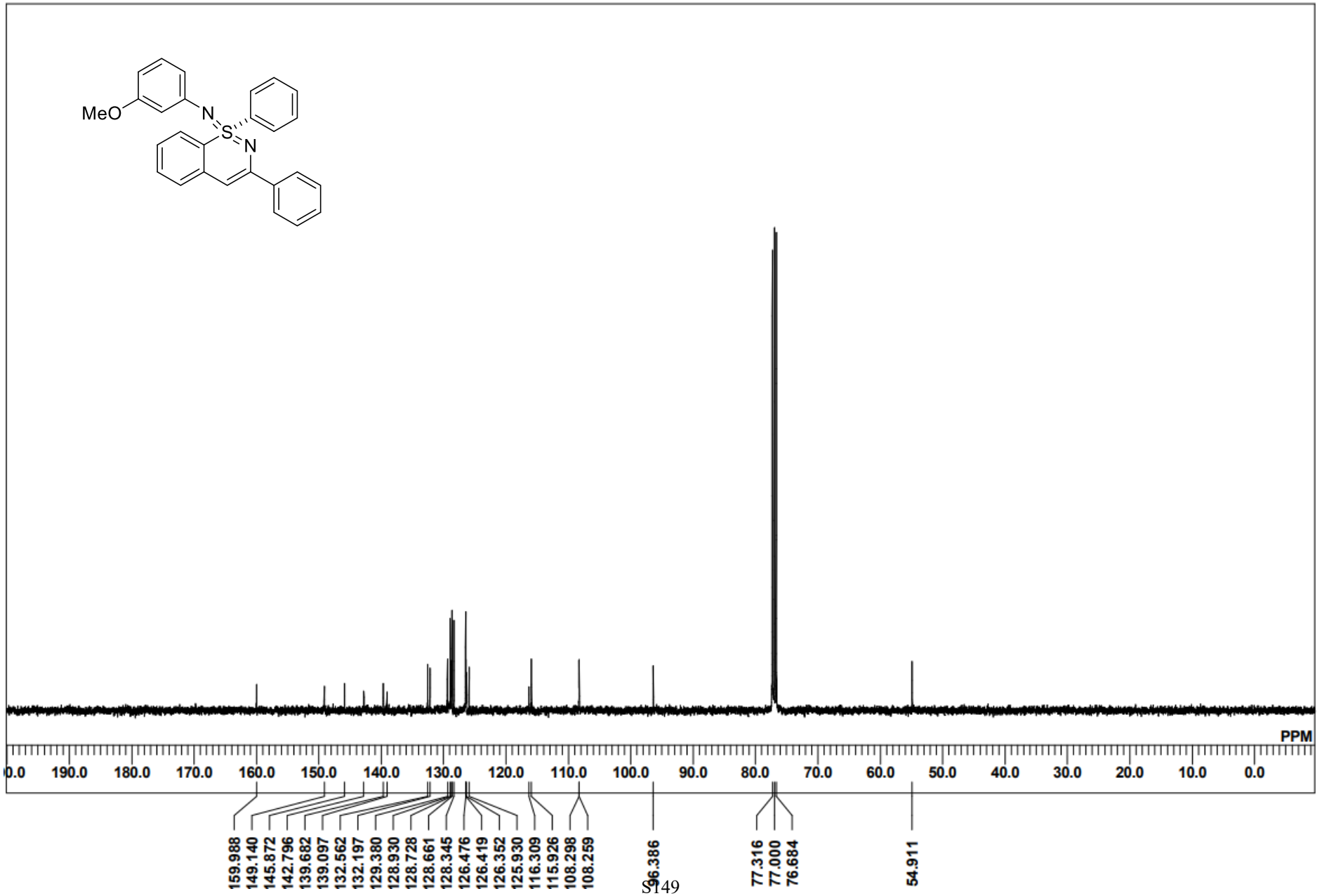
^{13}C NMR spectrum of **3ga**



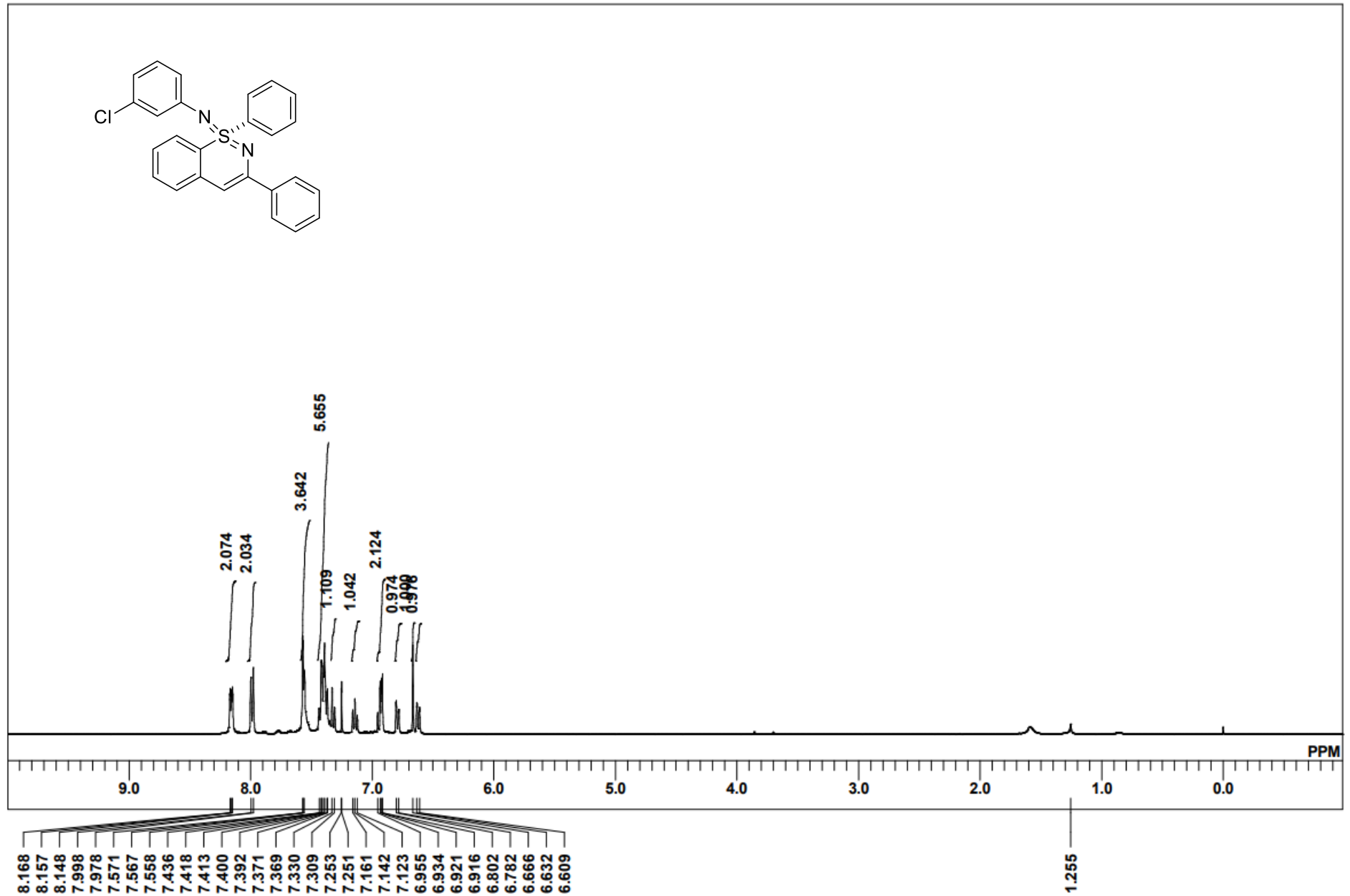
^{1}H NMR spectrum of **3ha**



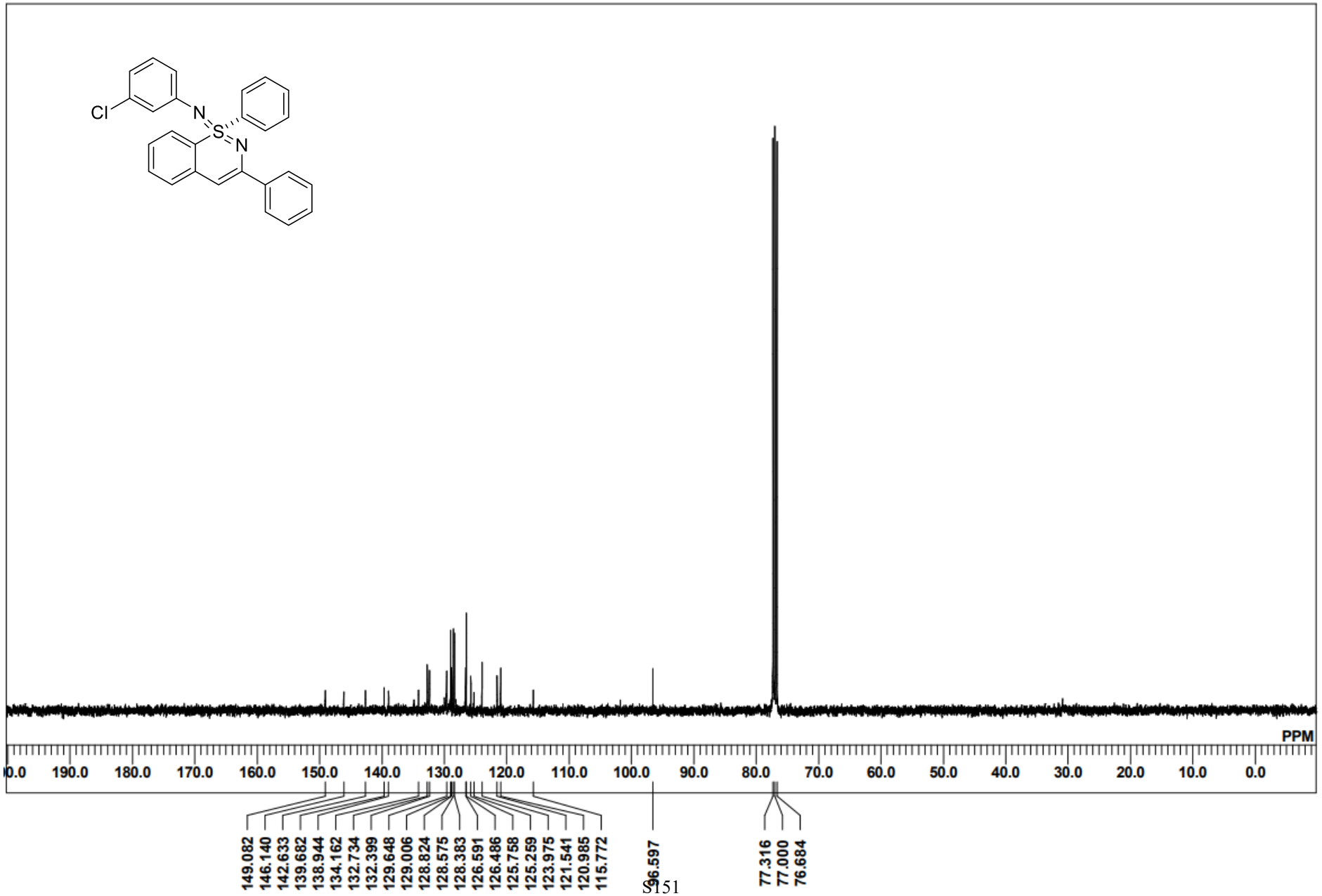
^{13}C NMR spectrum of **3ha**



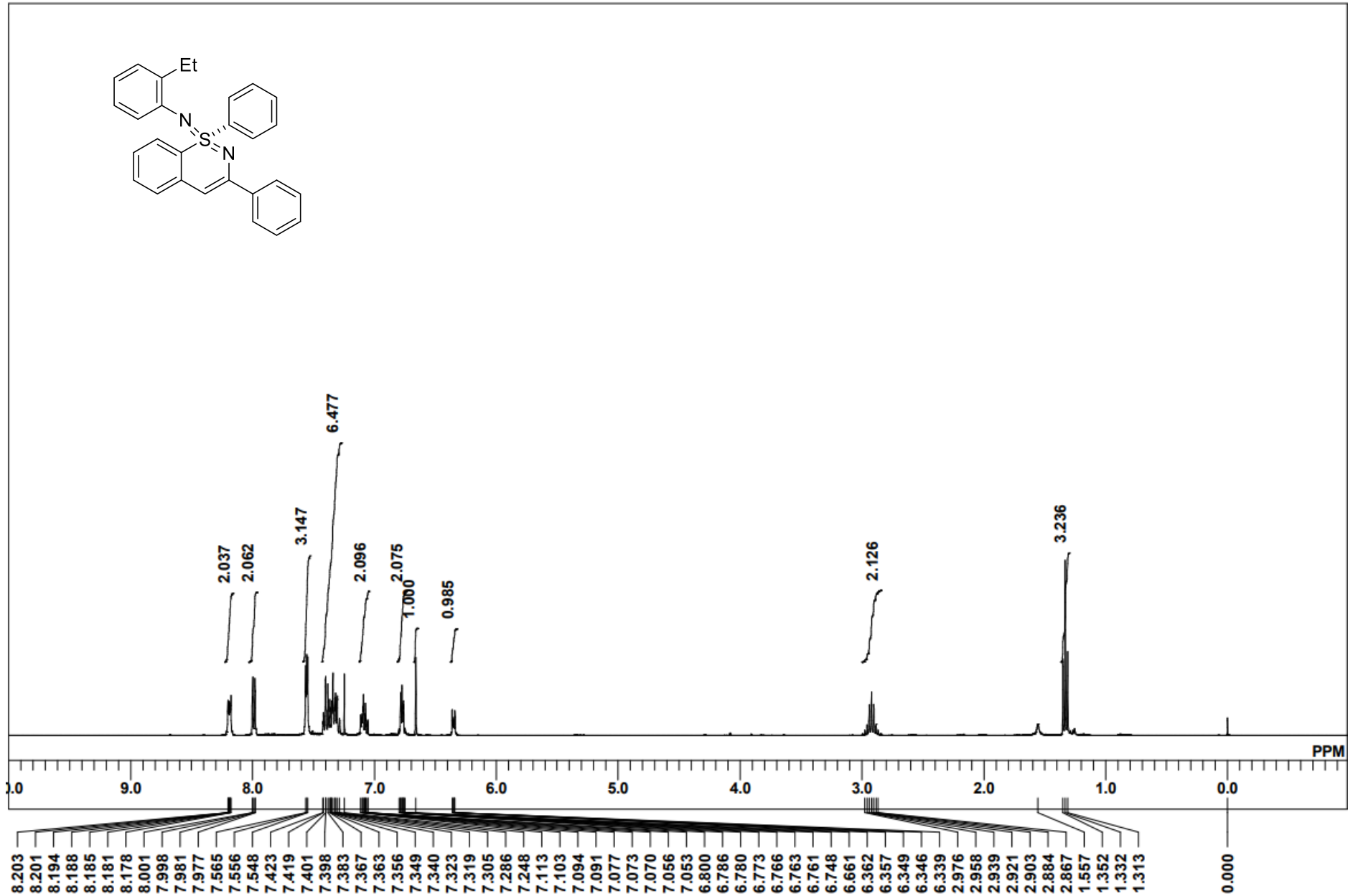
^{1}H NMR spectrum of **3ia**



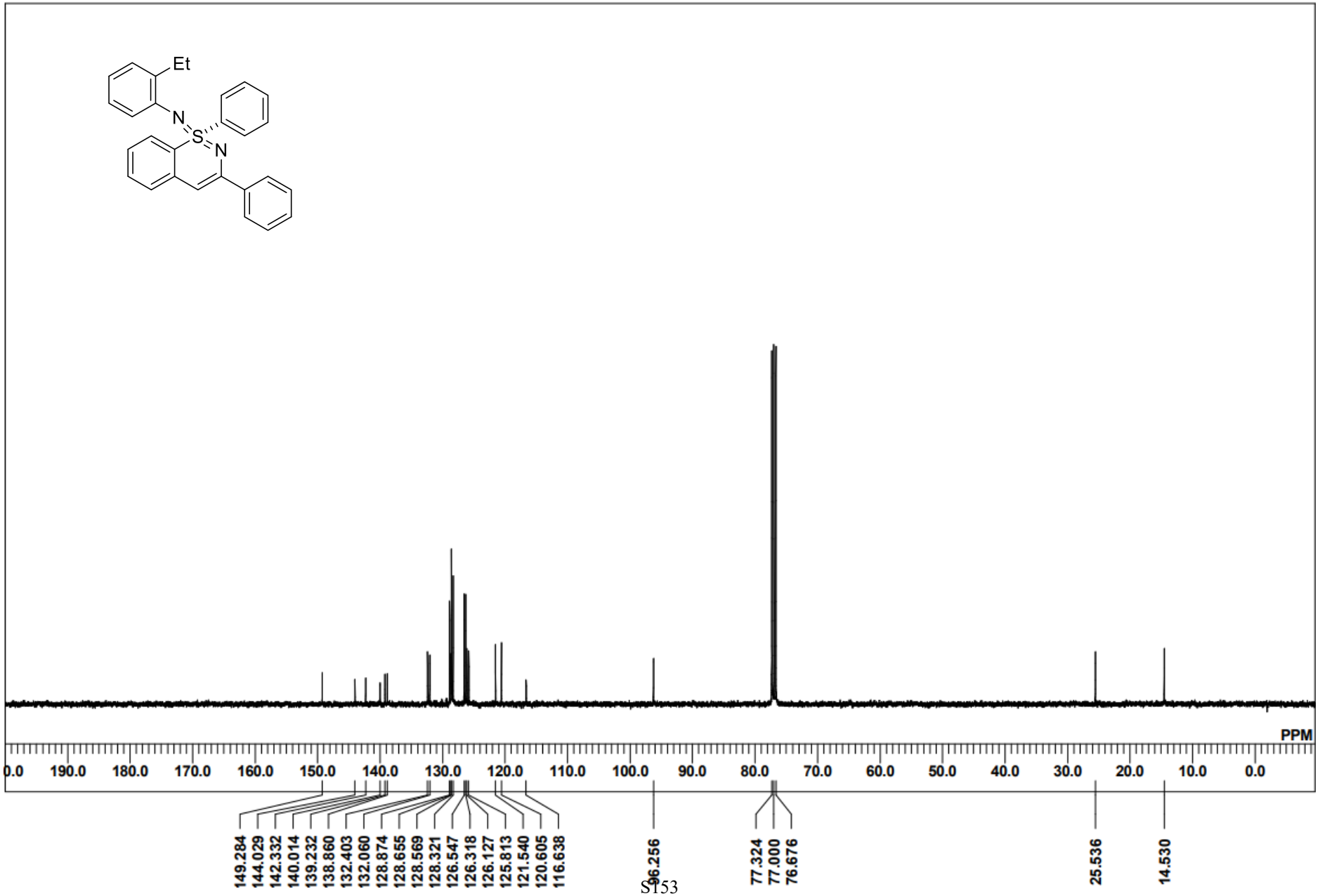
^{13}C NMR spectrum of **3ia**



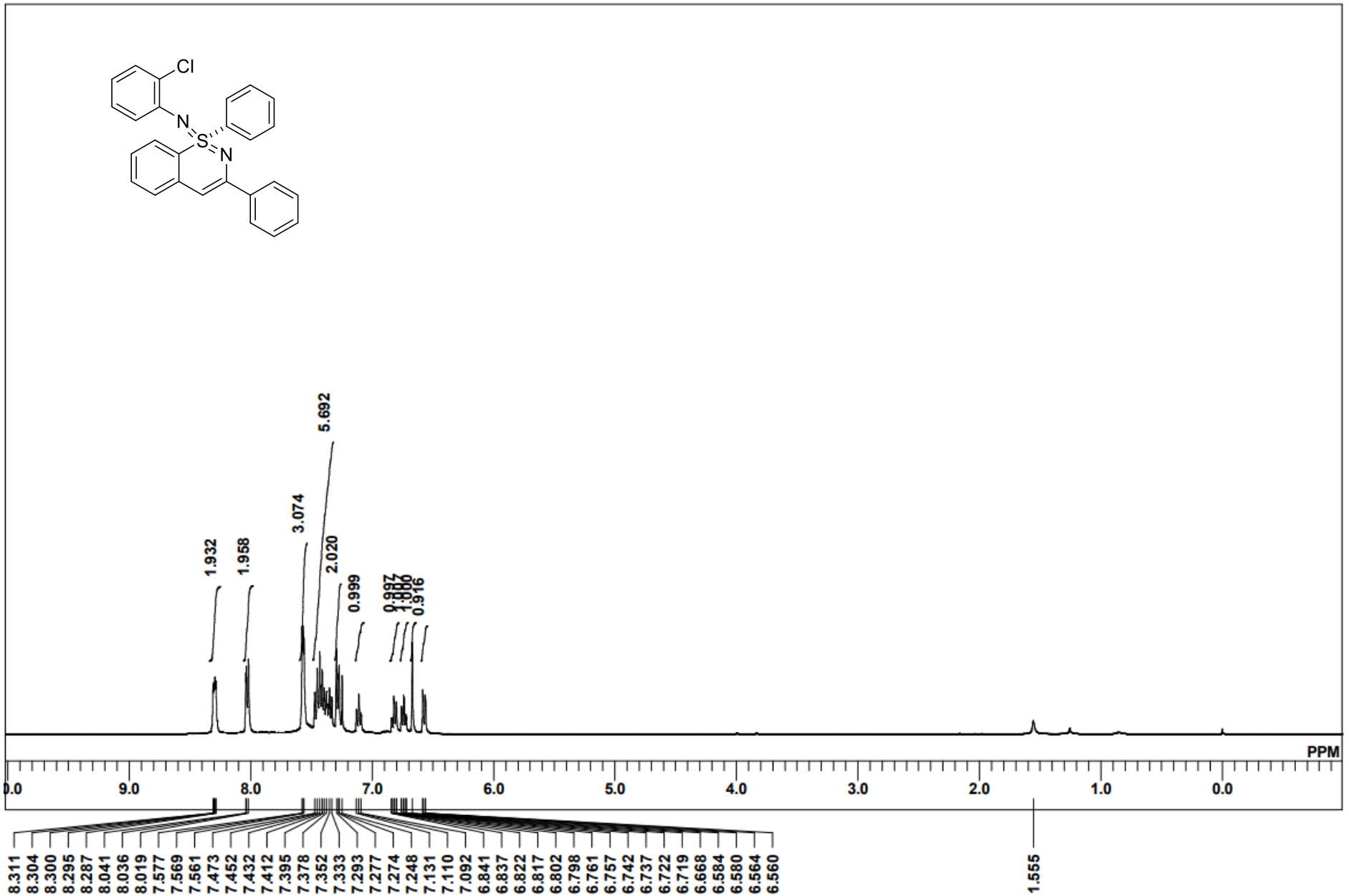
^{1}H NMR spectrum of **3ja**



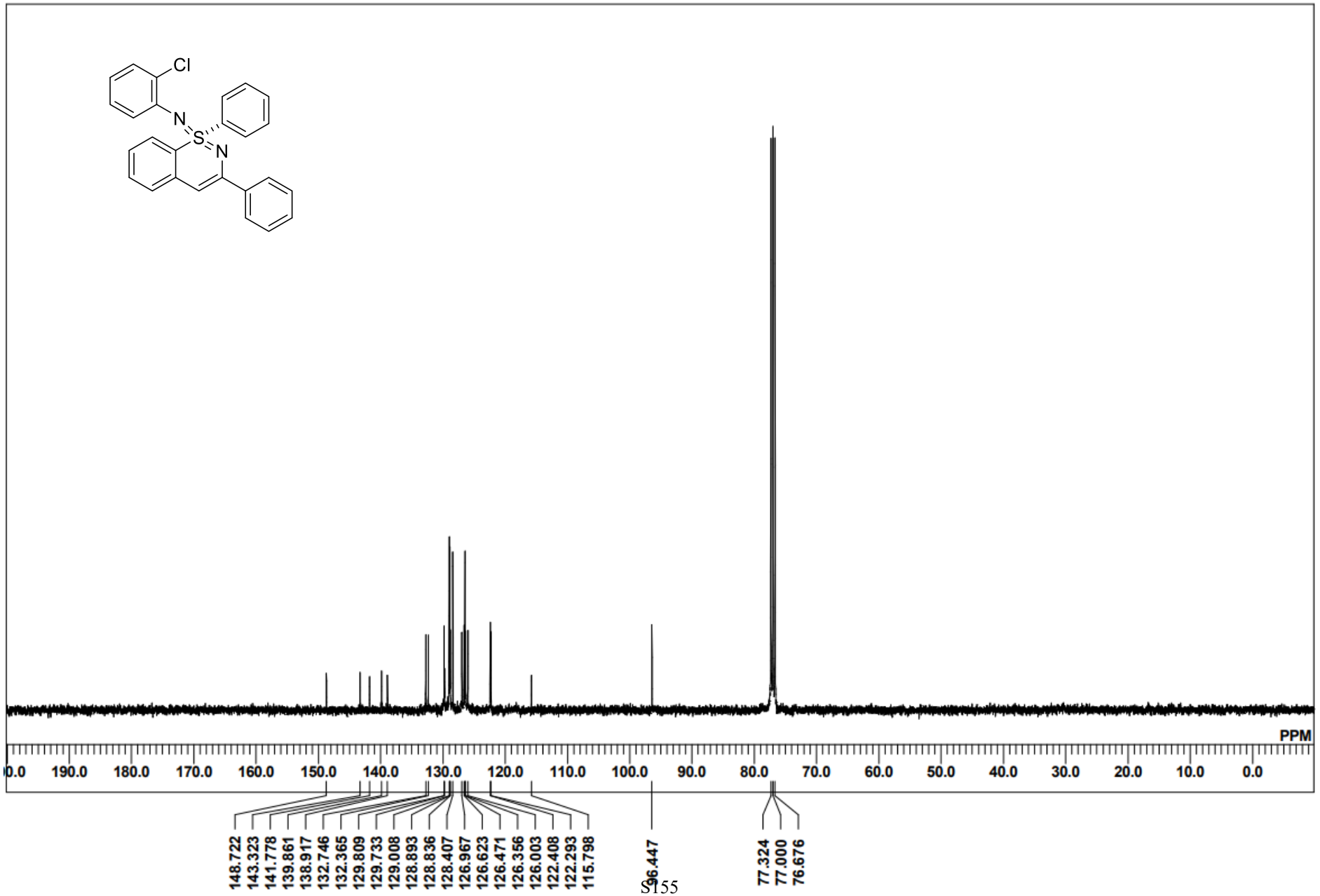
^{13}C NMR spectrum of **3ja**



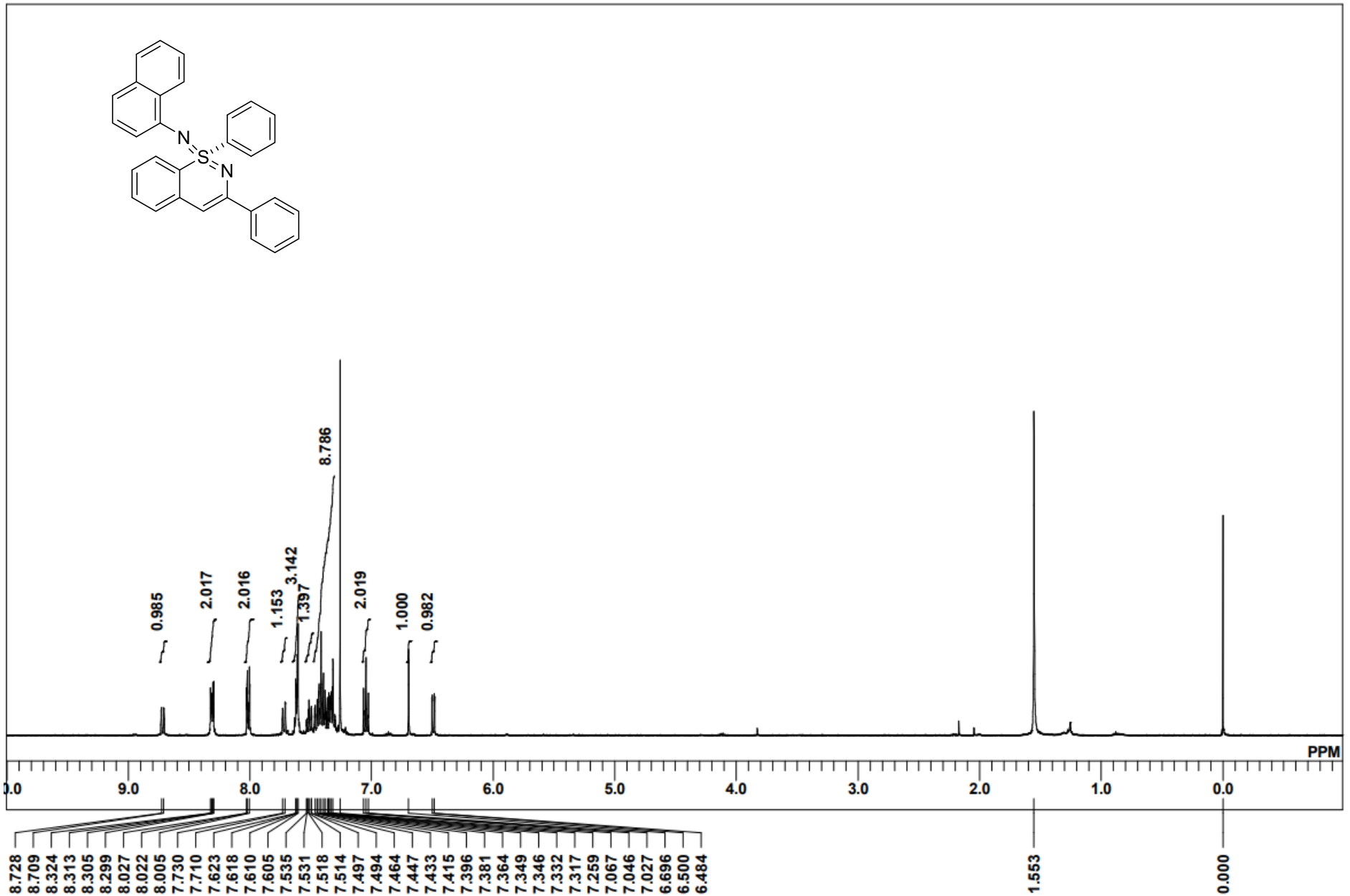
^{1}H NMR spectrum of **3ka**



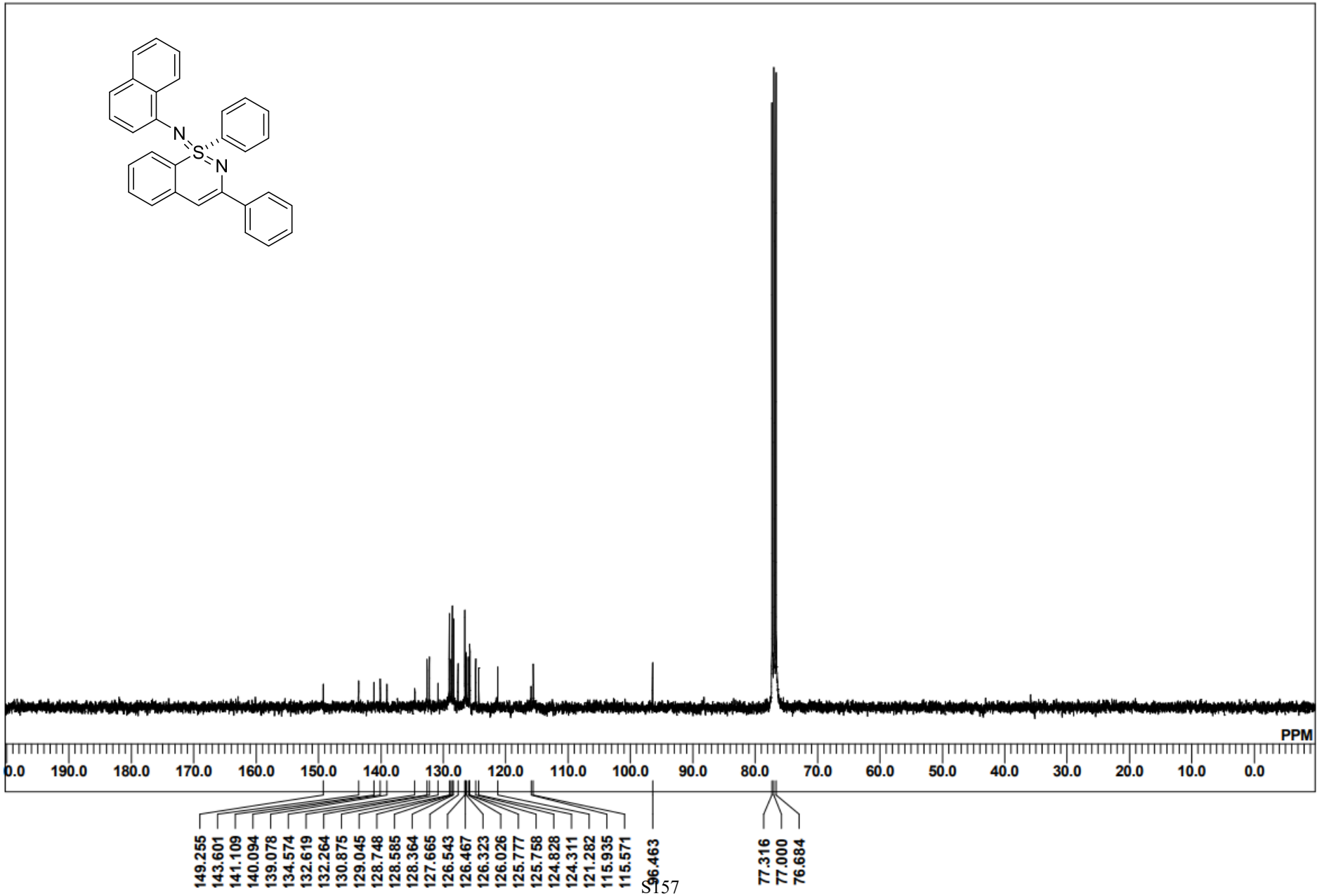
^{13}C NMR spectrum of **3ka**



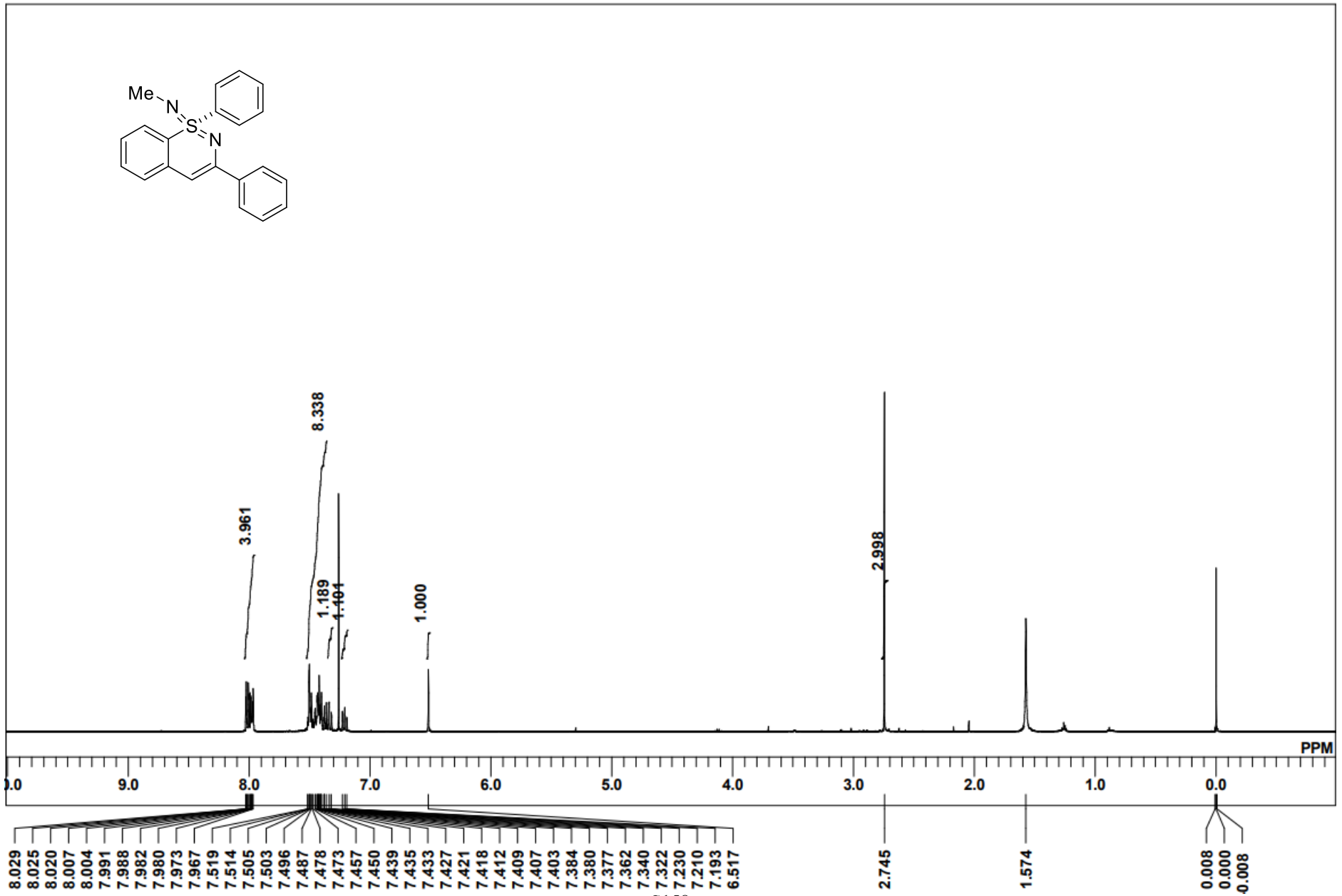
^{1}H NMR spectrum of **3la**



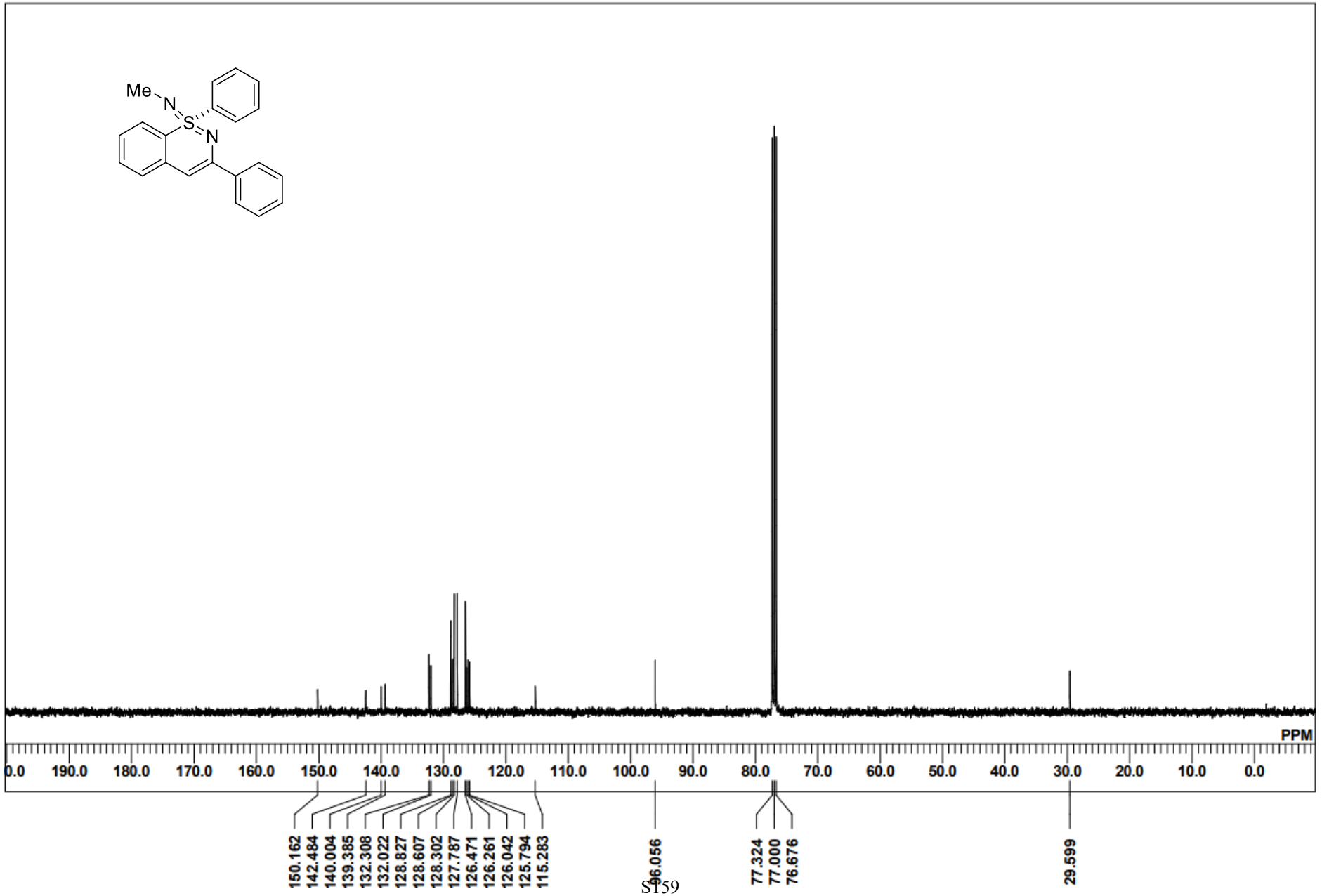
^{13}C NMR spectrum of **3la**



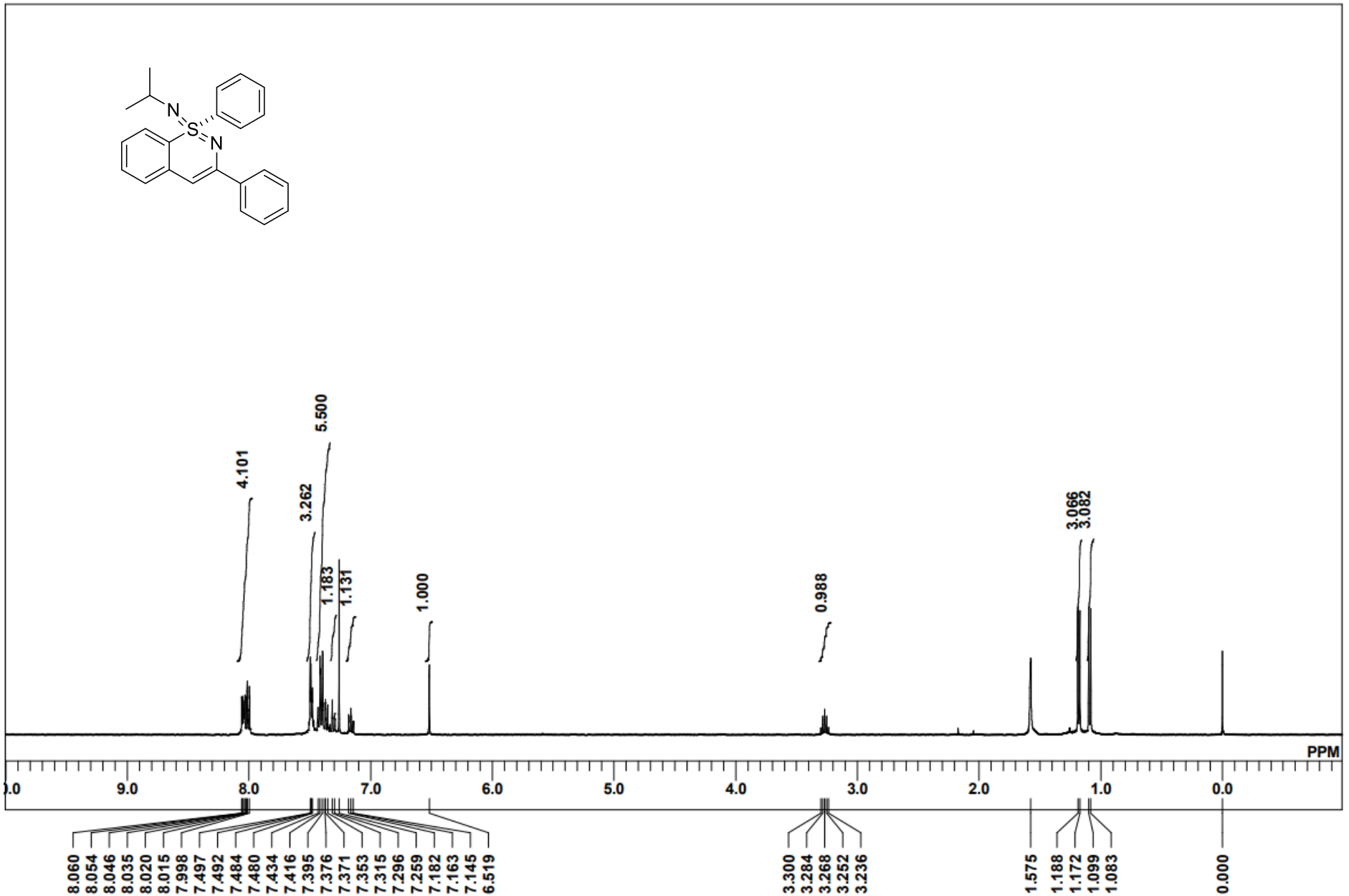
^{1}H NMR spectrum of **3ma**



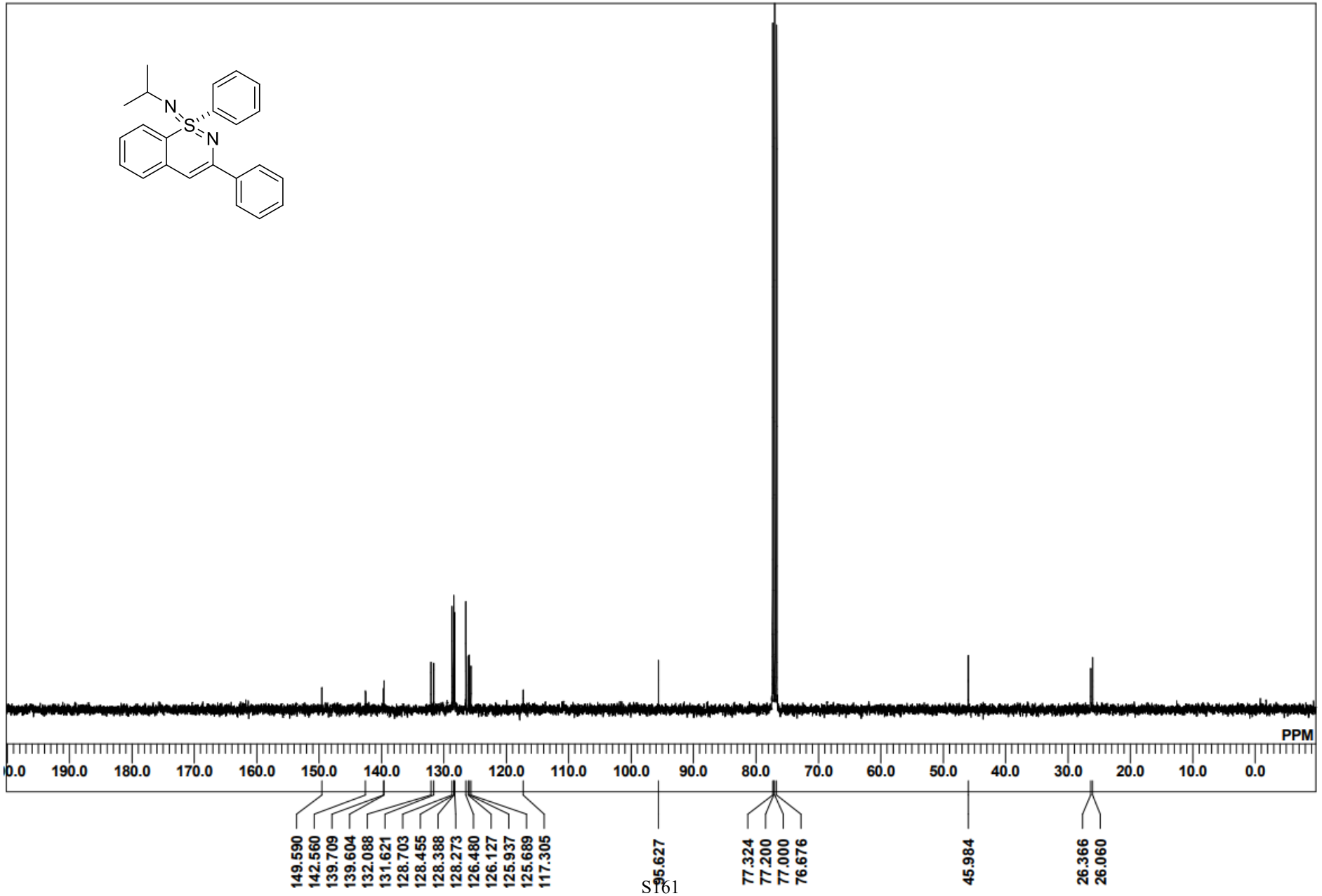
^{13}C NMR spectrum of **3ma**



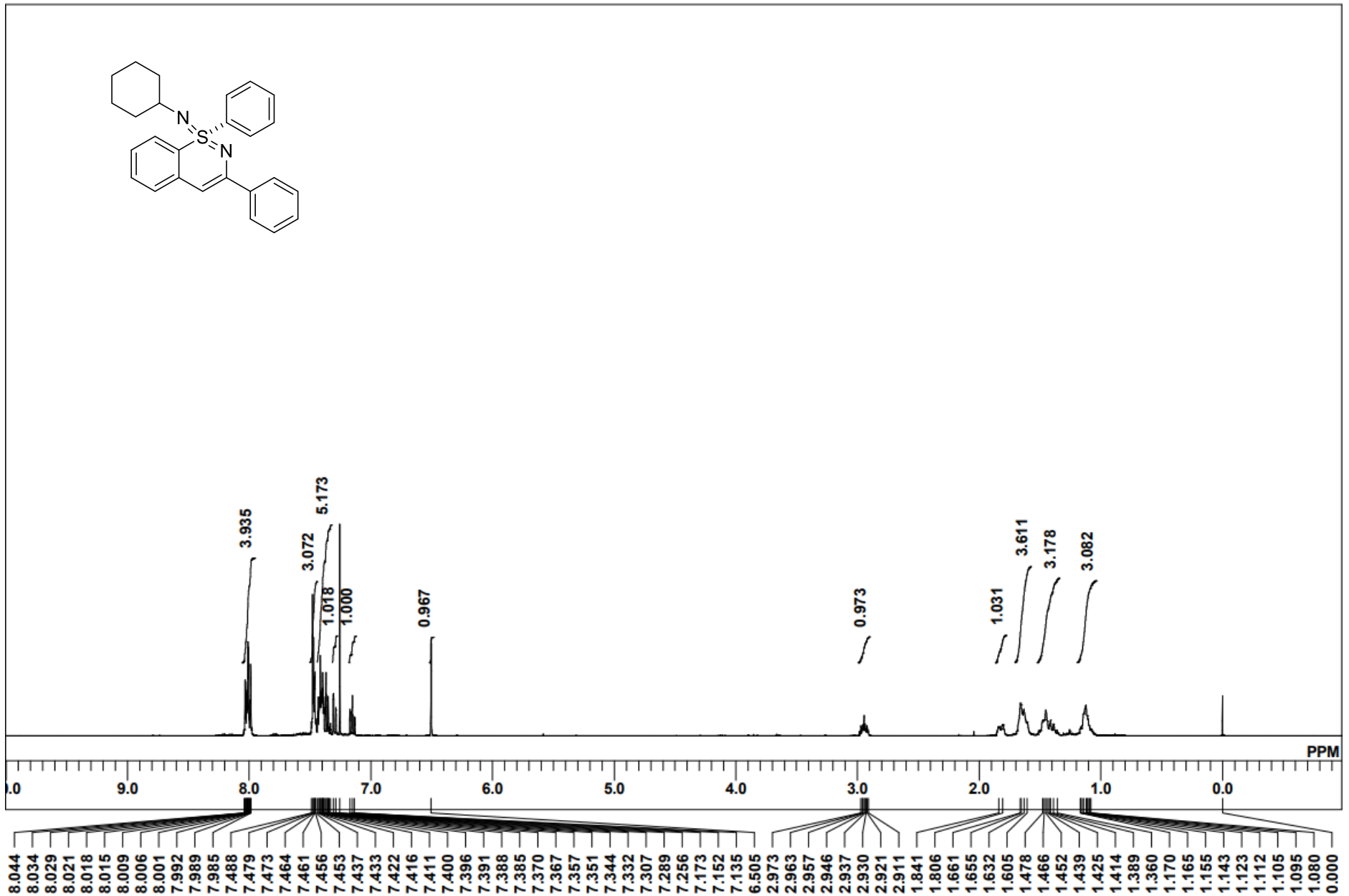
^{1}H NMR spectrum of **3na**



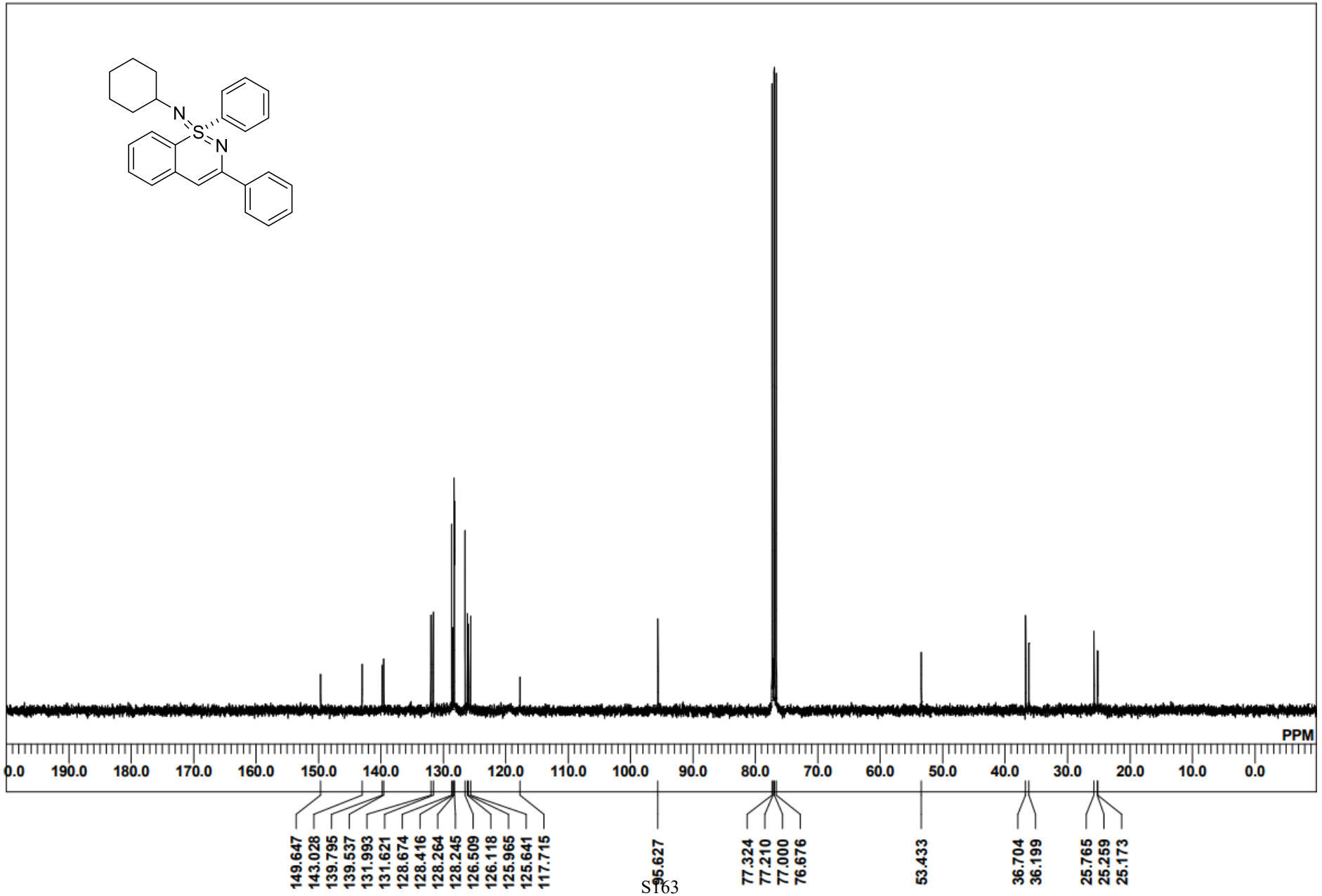
^{13}C NMR spectrum of **3na**



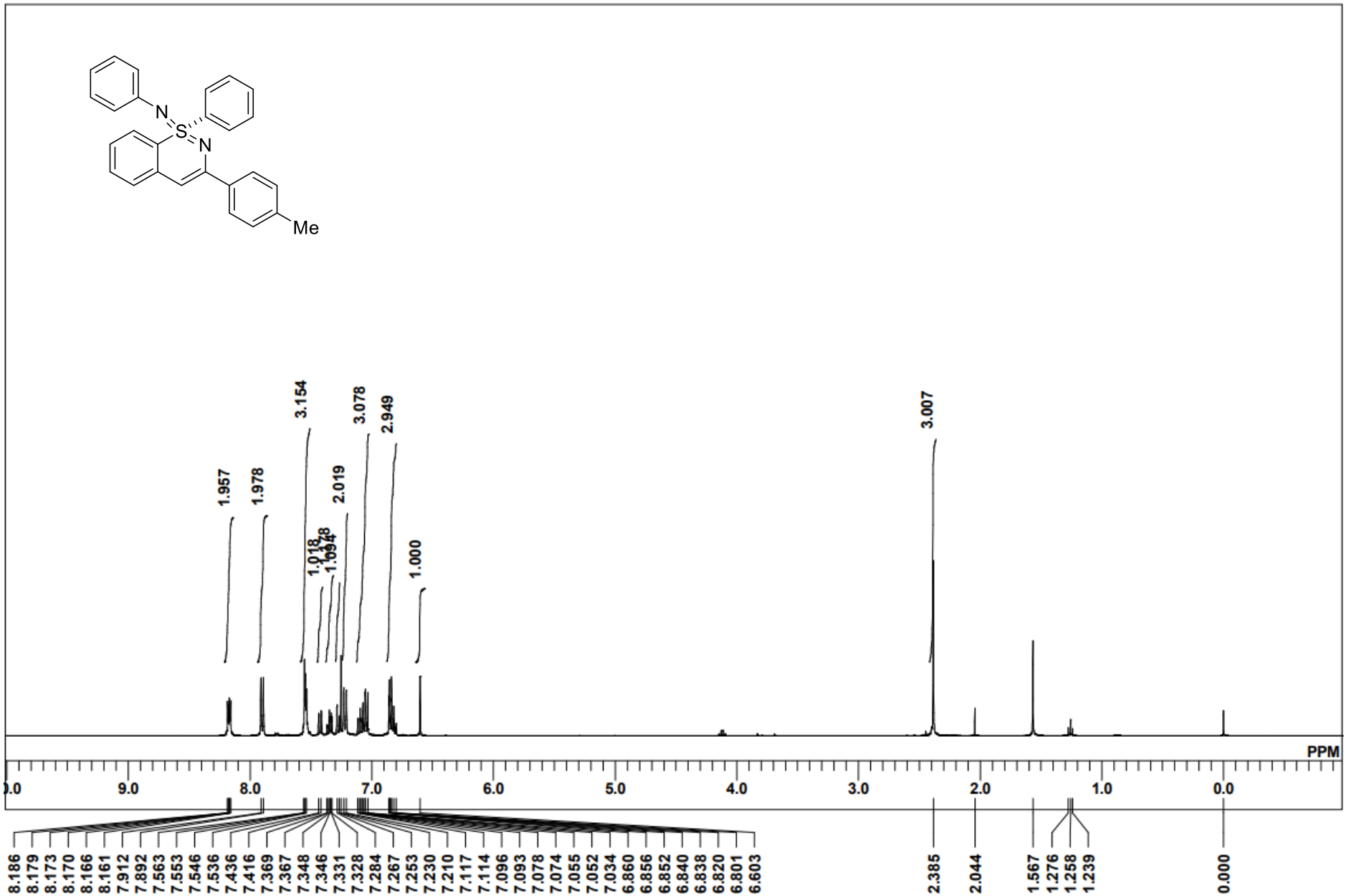
^{1}H NMR spectrum of **3oa**



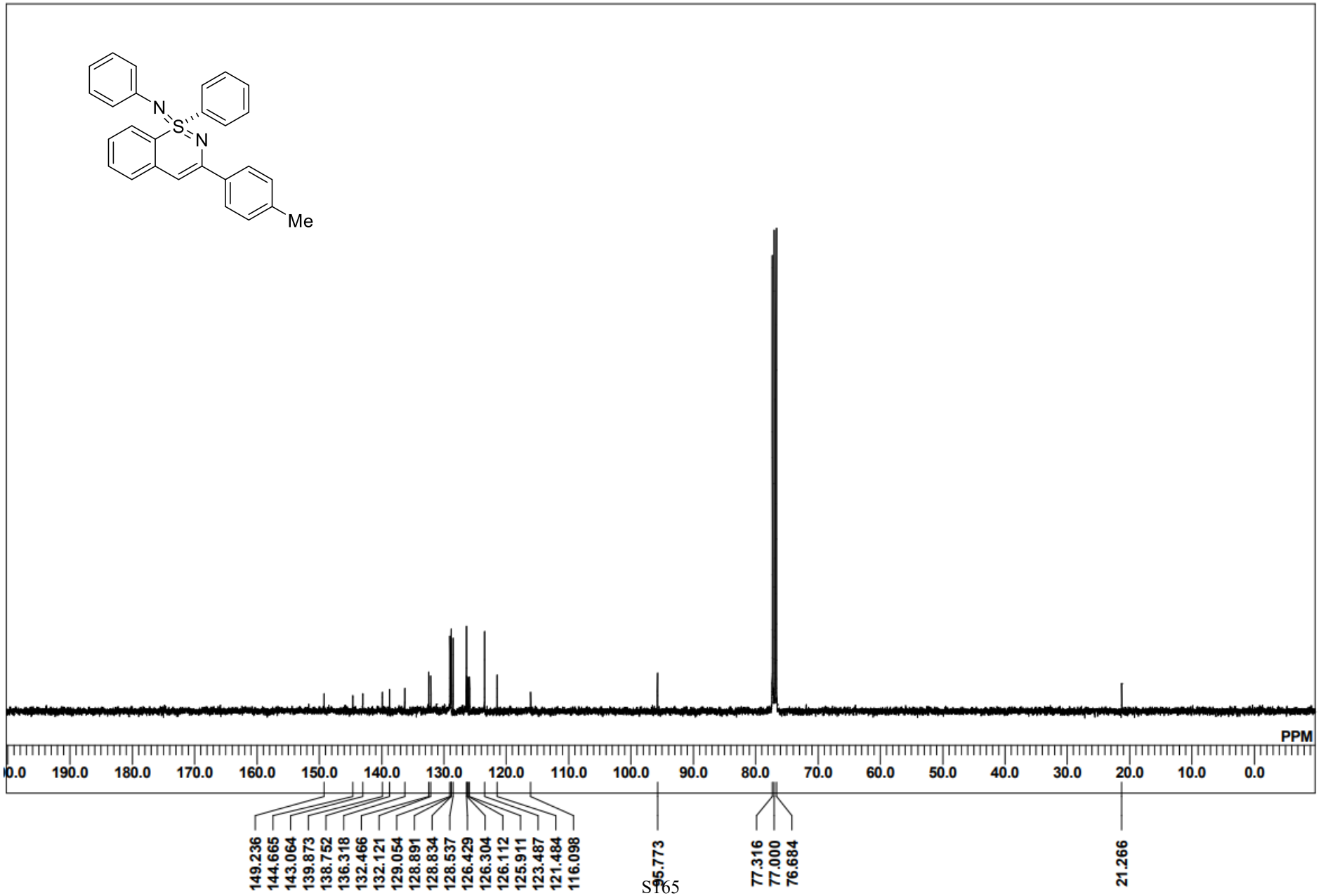
^{13}C NMR spectrum of **3oa**



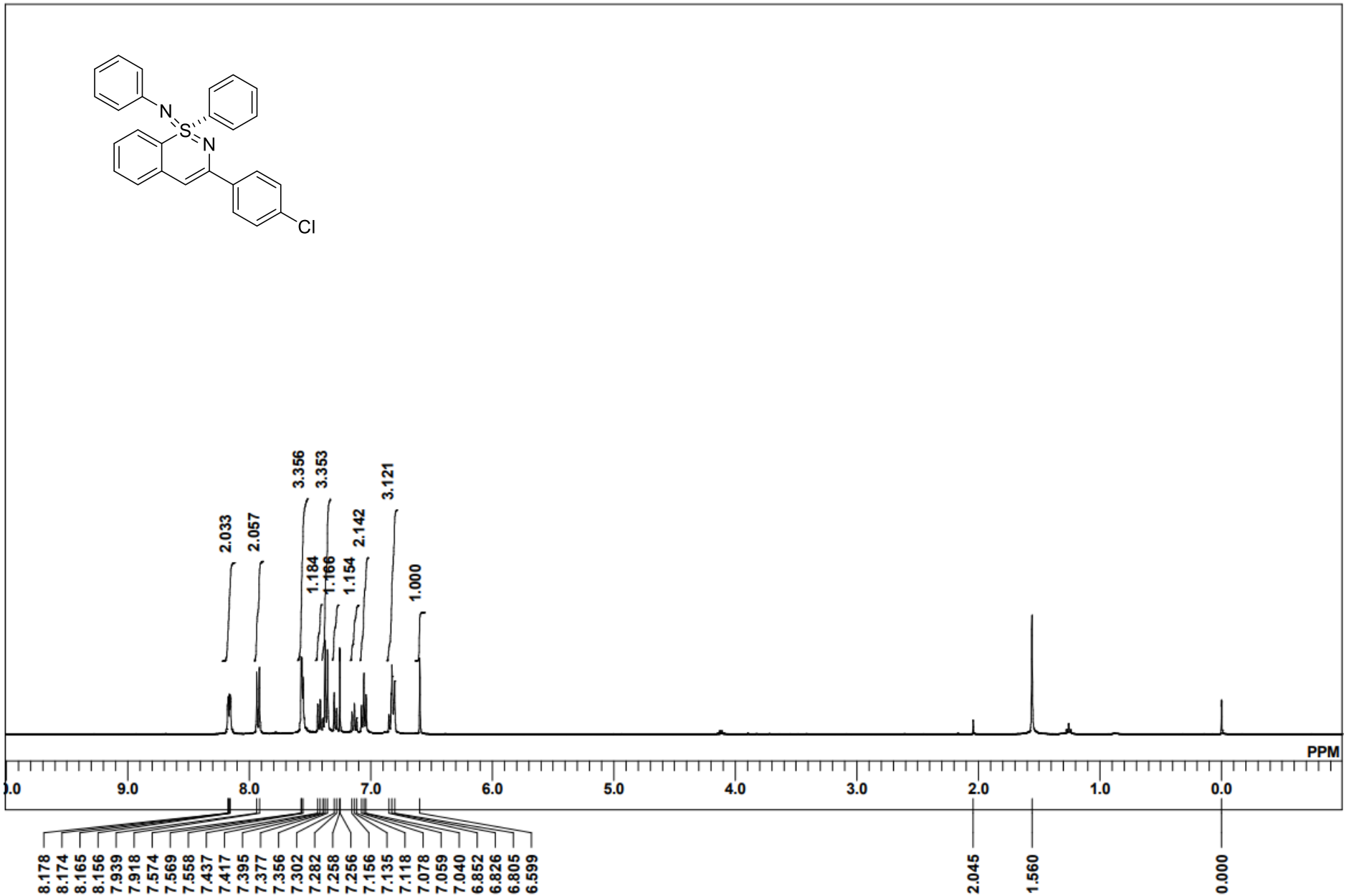
^{1}H NMR spectrum of **3ab**



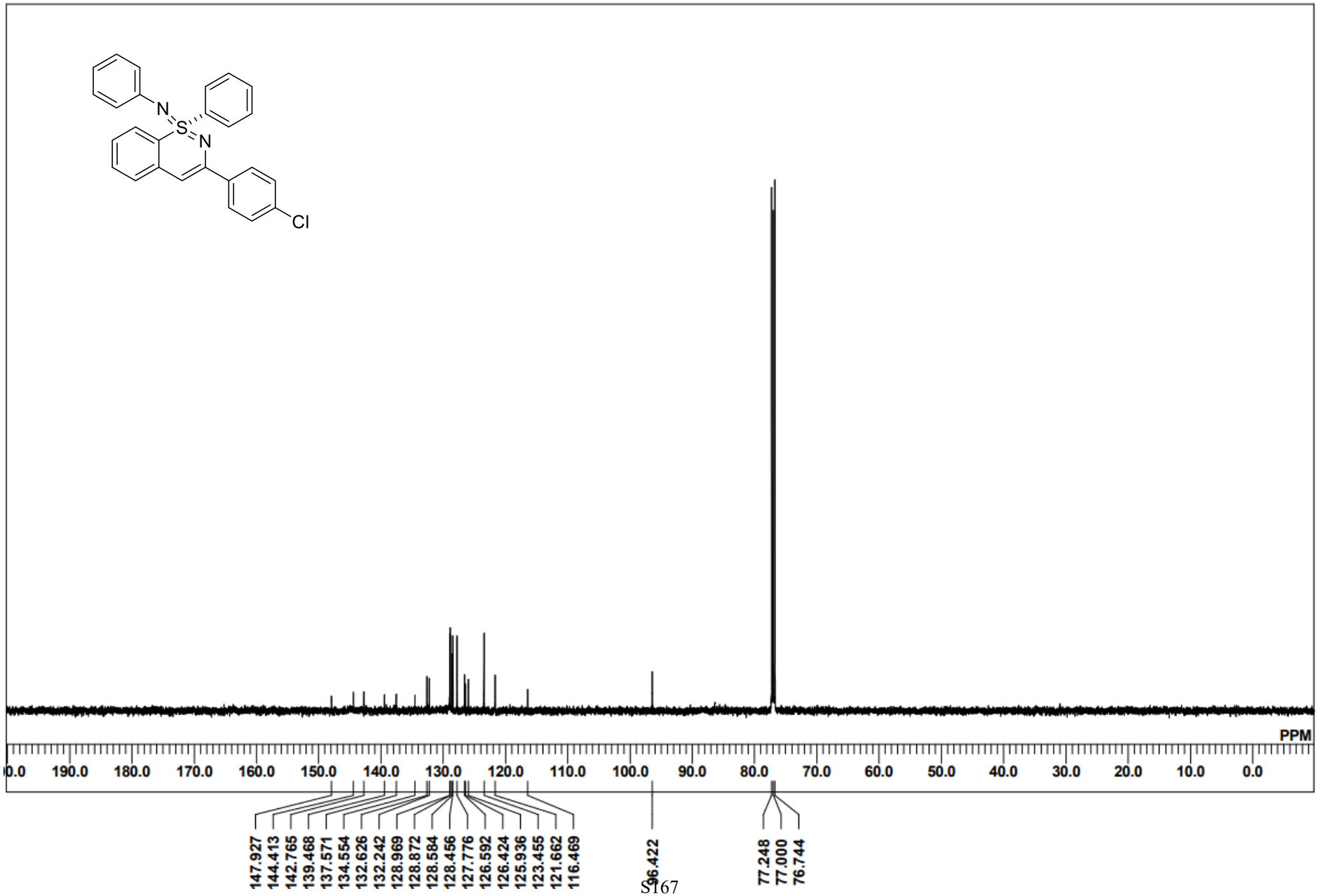
^{13}C NMR spectrum of **3ab**



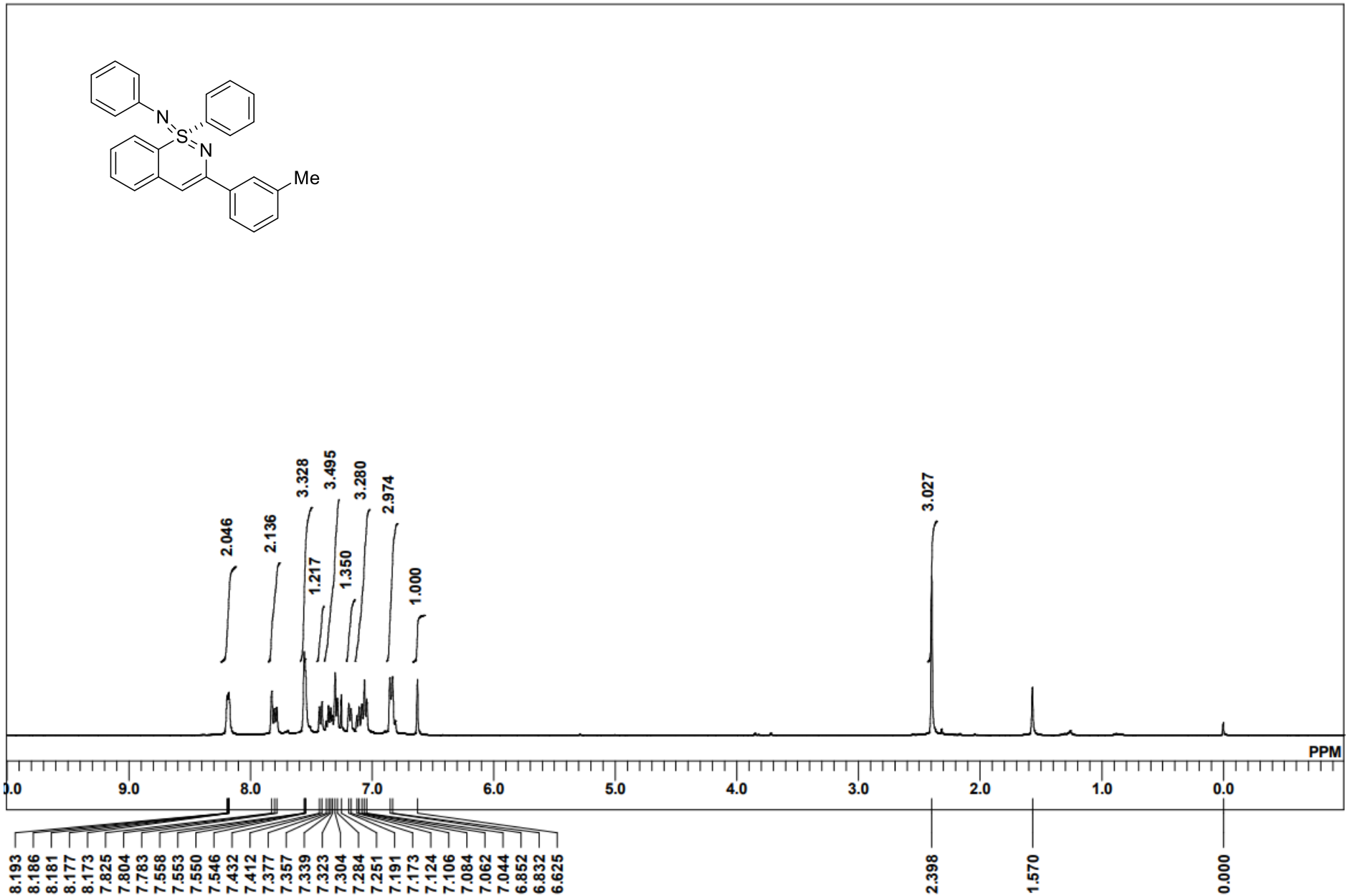
^{1}H NMR spectrum of **3ac**



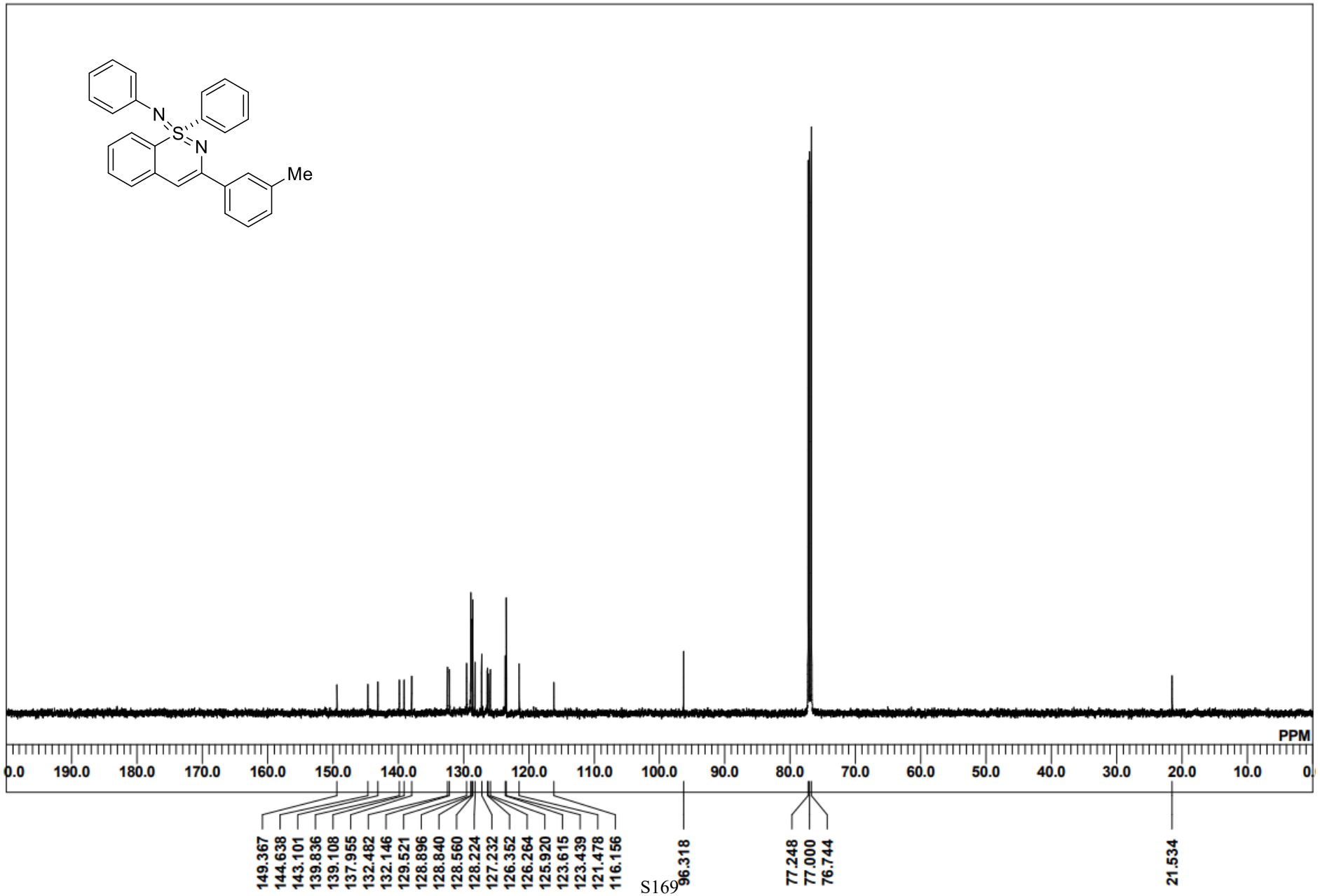
^{13}C NMR spectrum of **3ac**



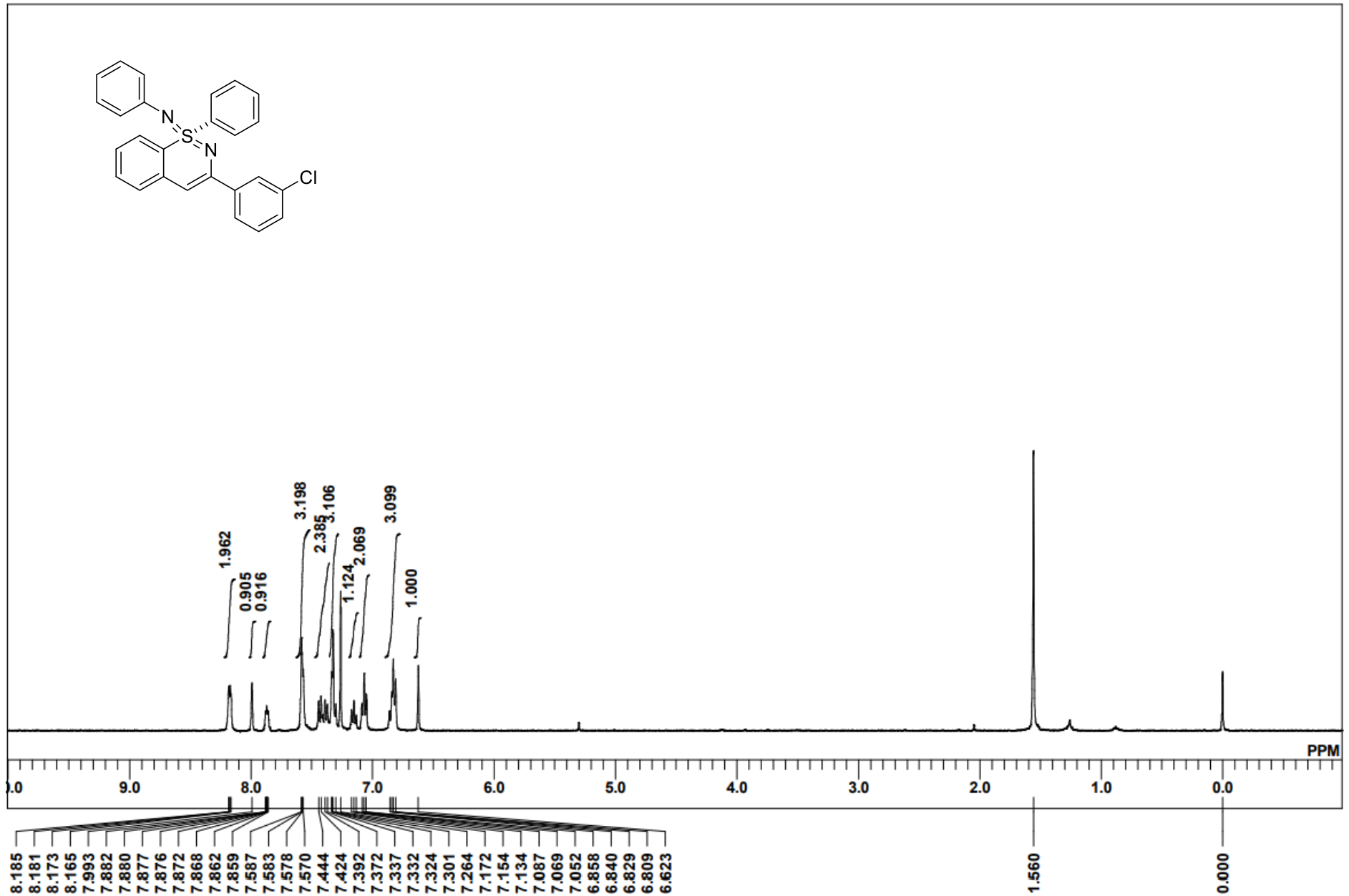
^{1}H NMR spectrum of **3ad**



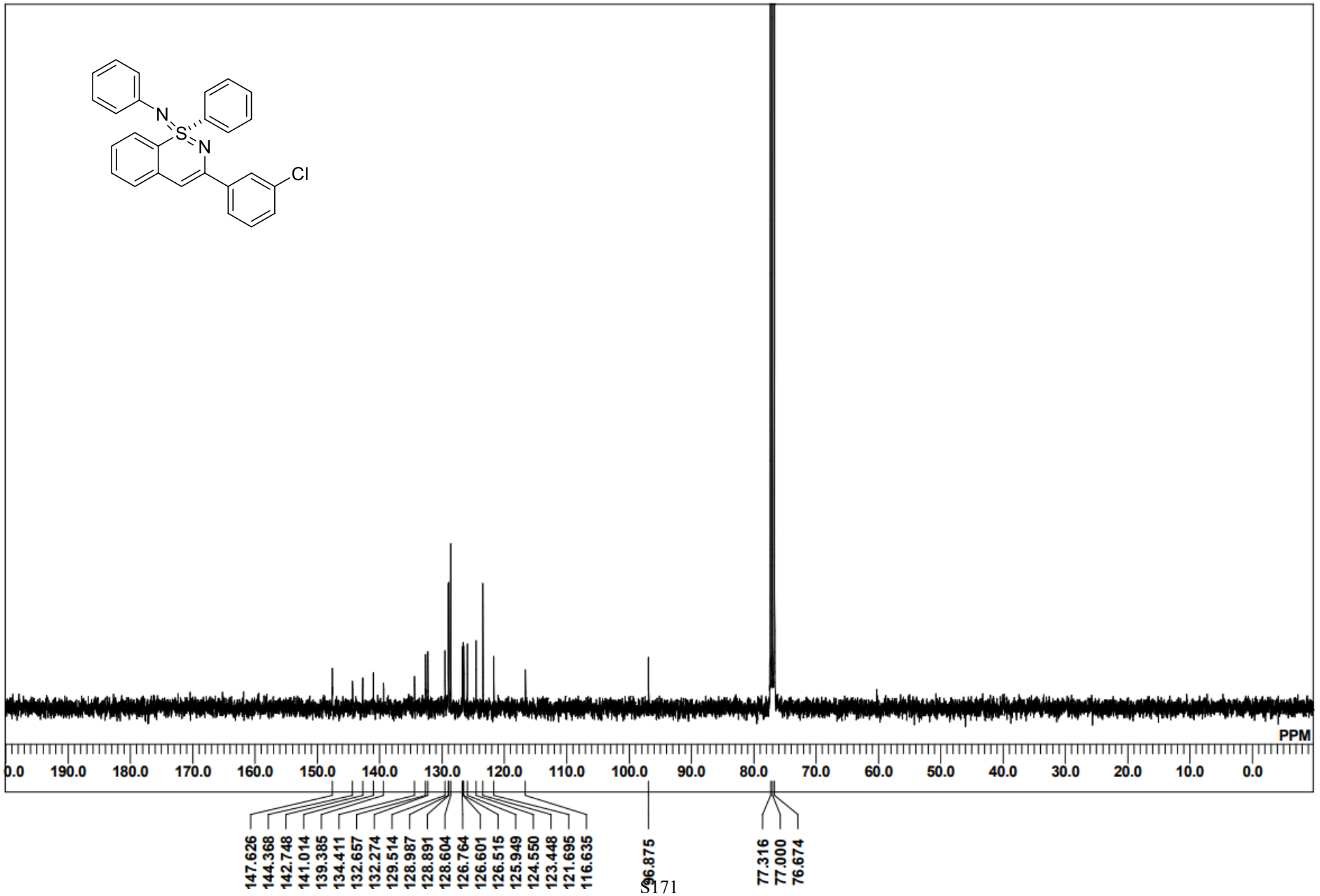
^{13}C NMR spectrum of **3ad**



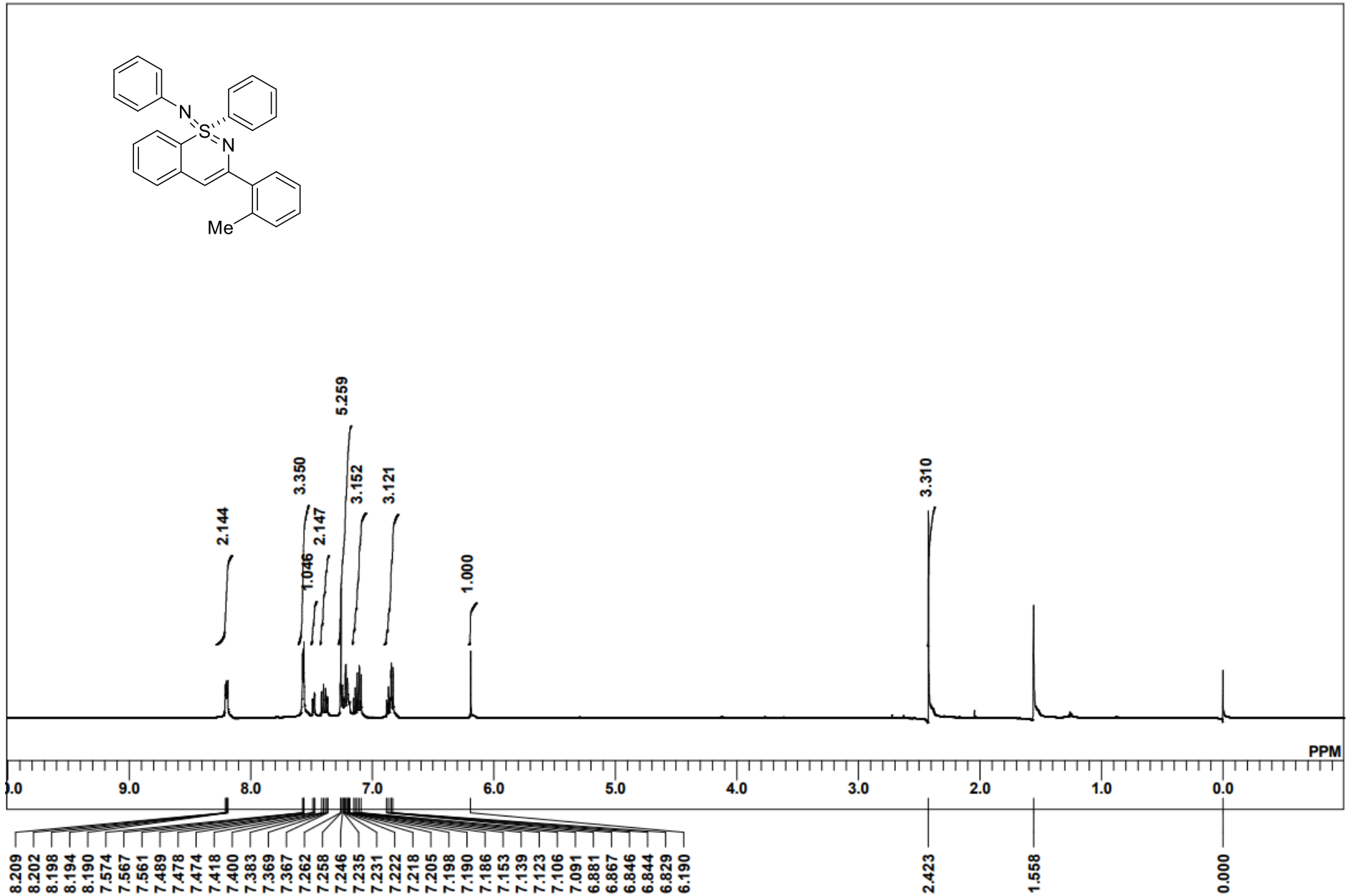
^{1}H NMR spectrum of **3ae**



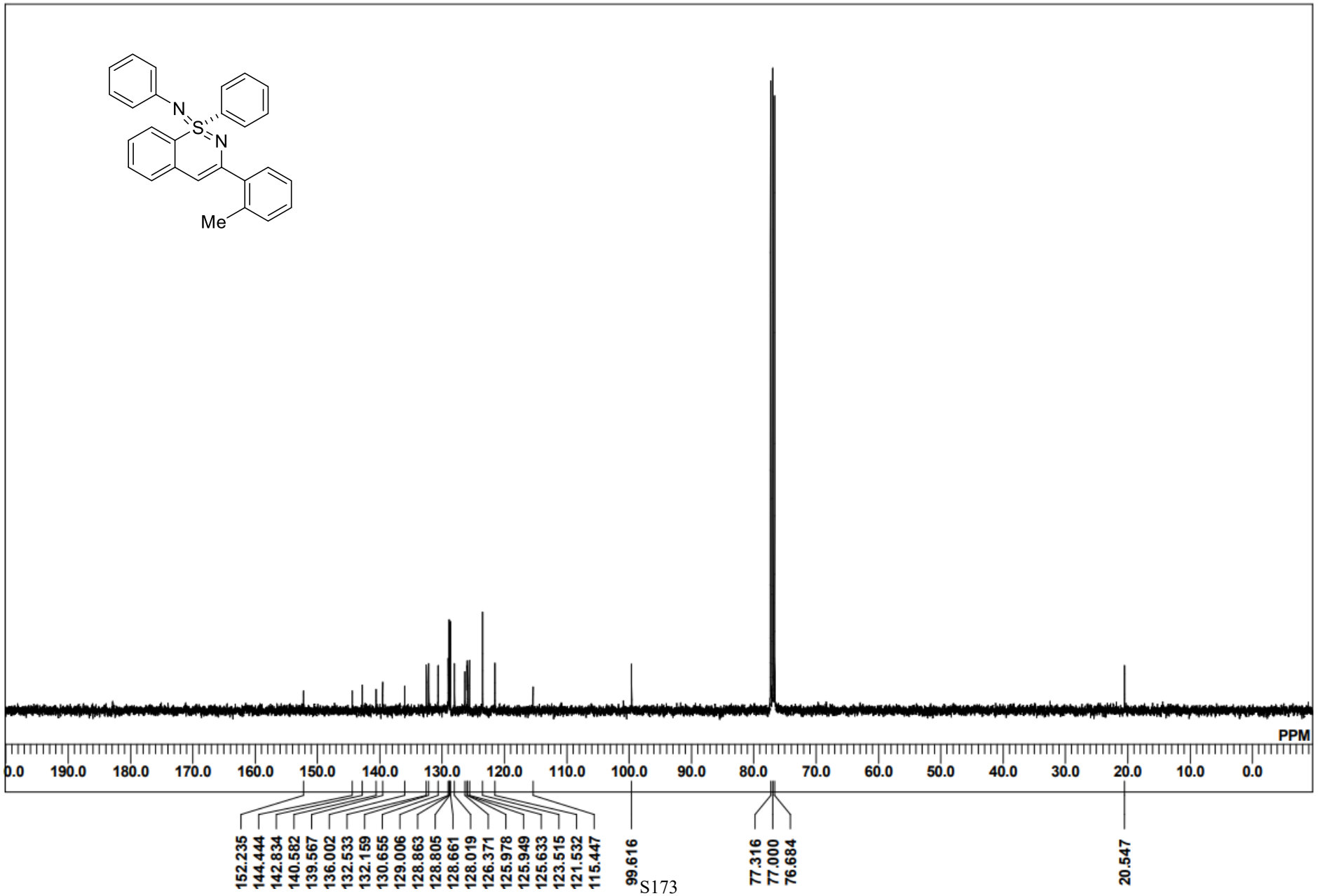
^{13}C NMR spectrum of **3ae**



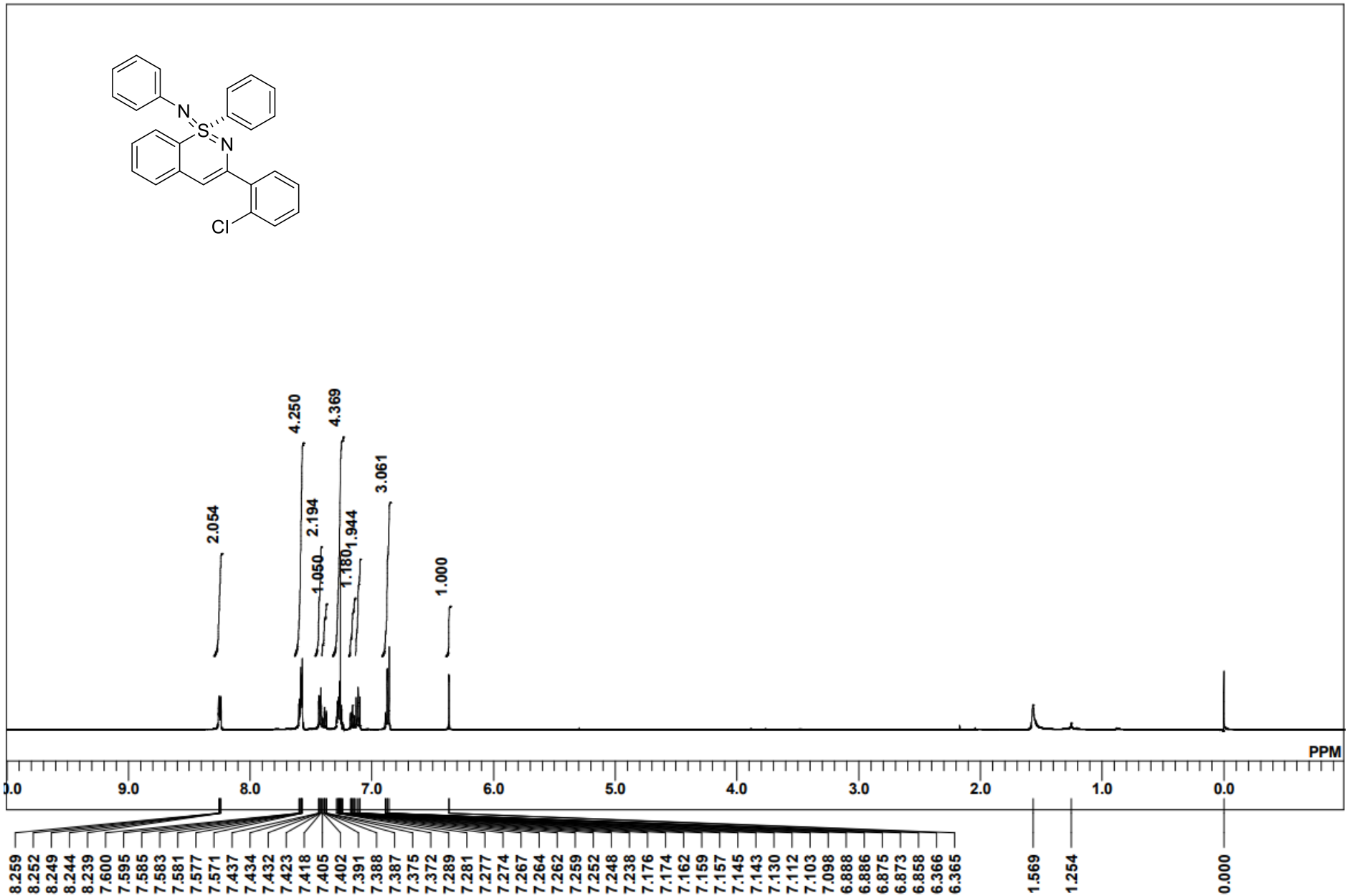
^{1}H NMR spectrum of **3af**



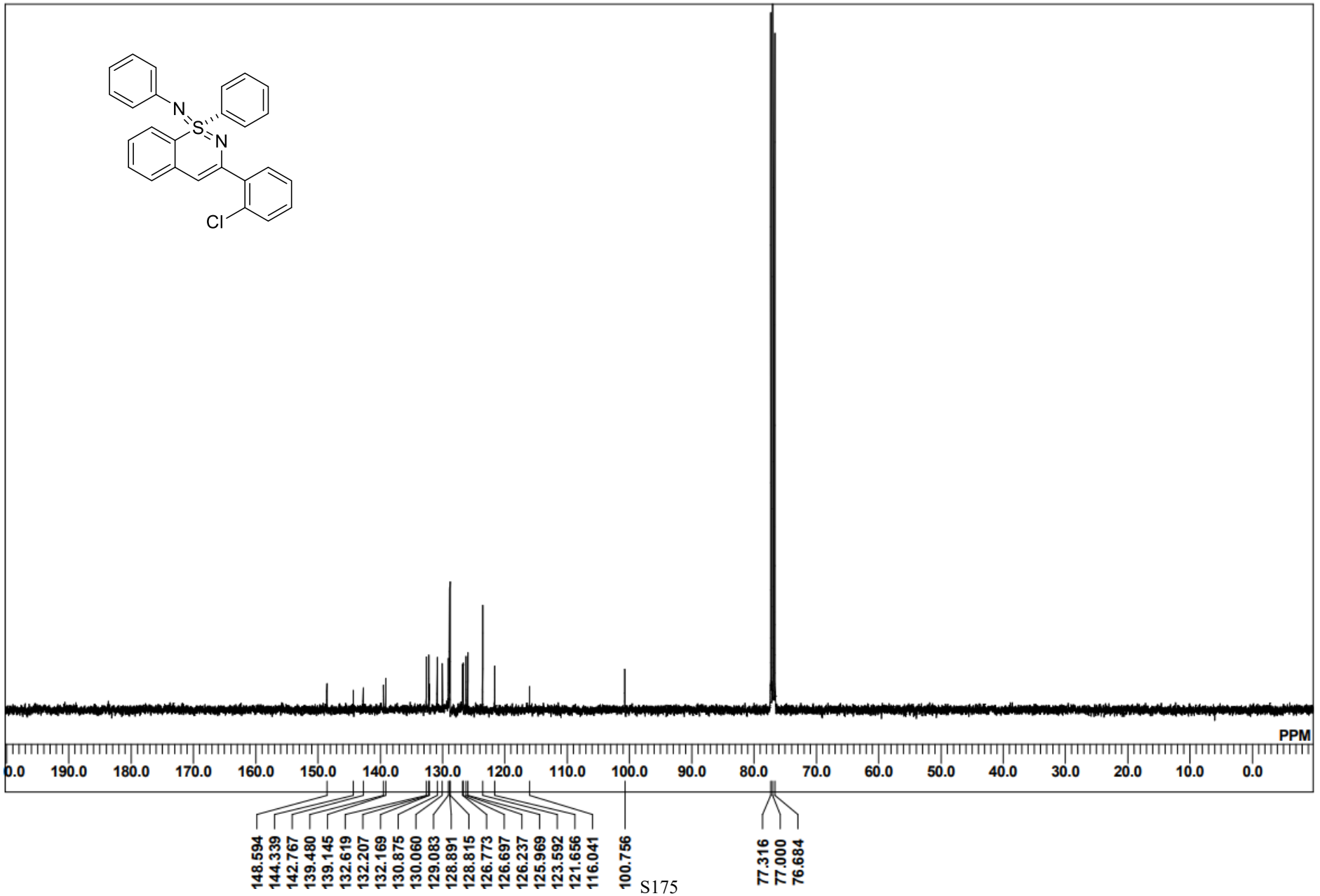
^{13}C NMR spectrum of **3af**



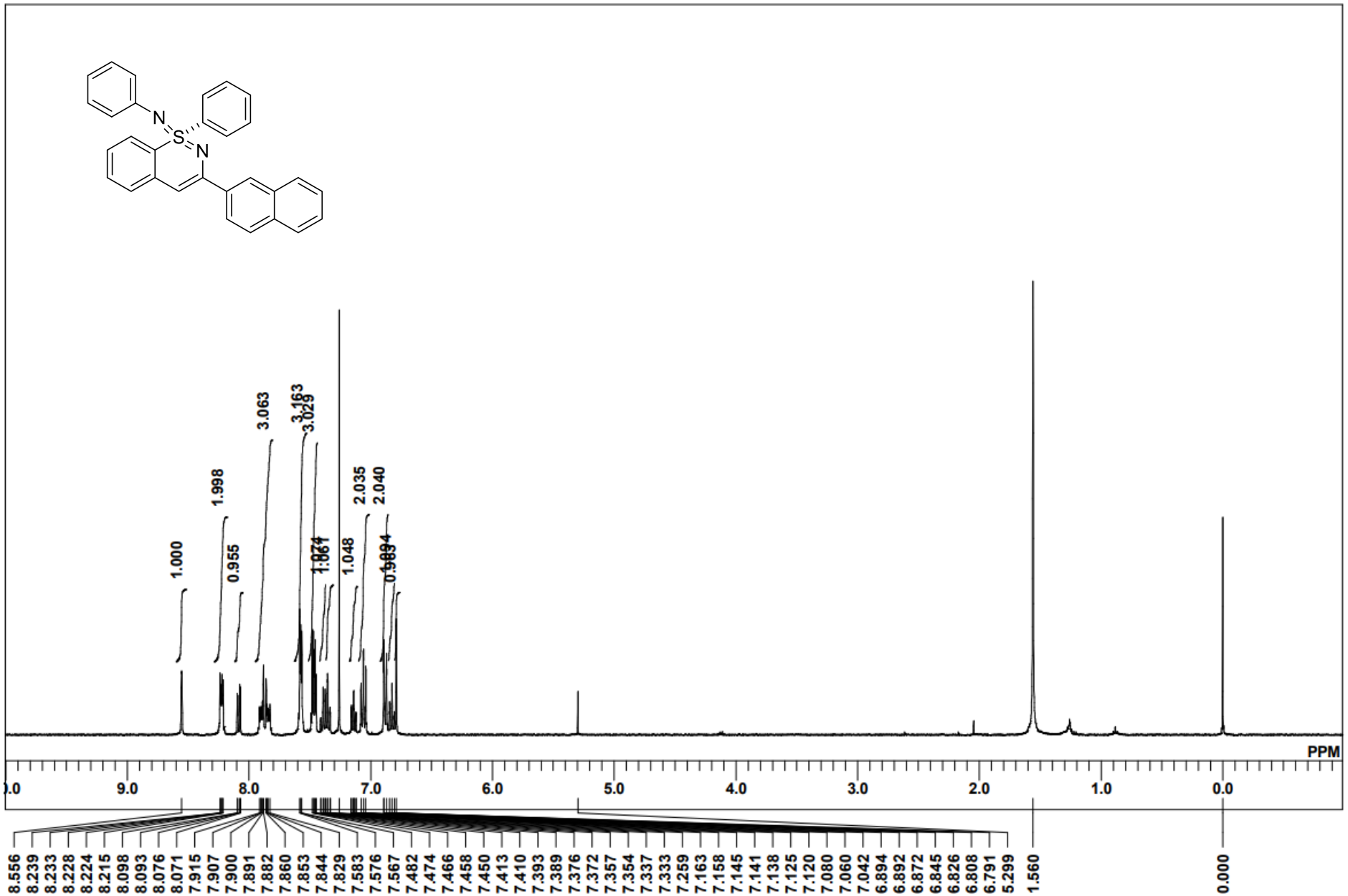
^{1}H NMR spectrum of **3ag**



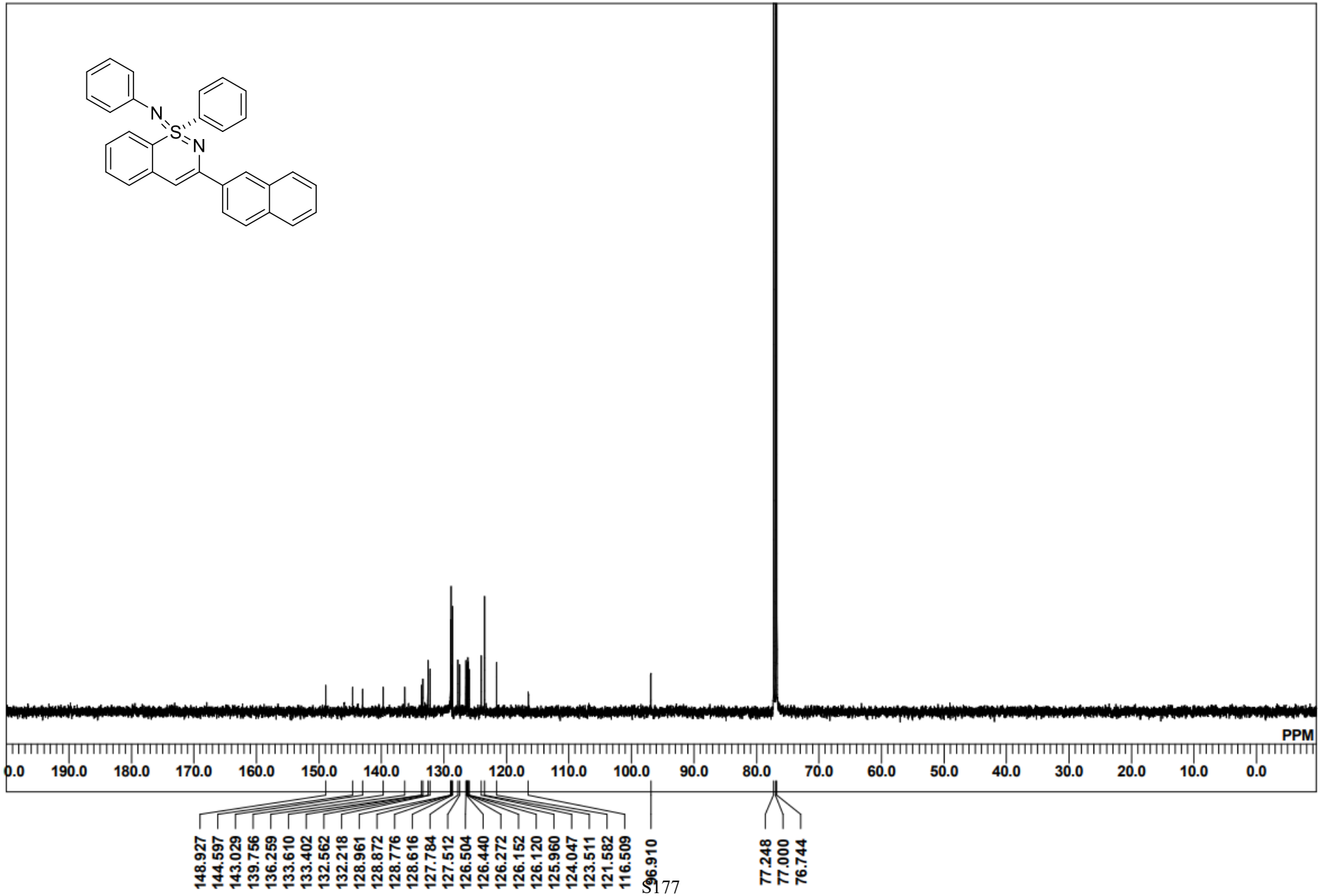
^{13}C NMR spectrum of **3ag**



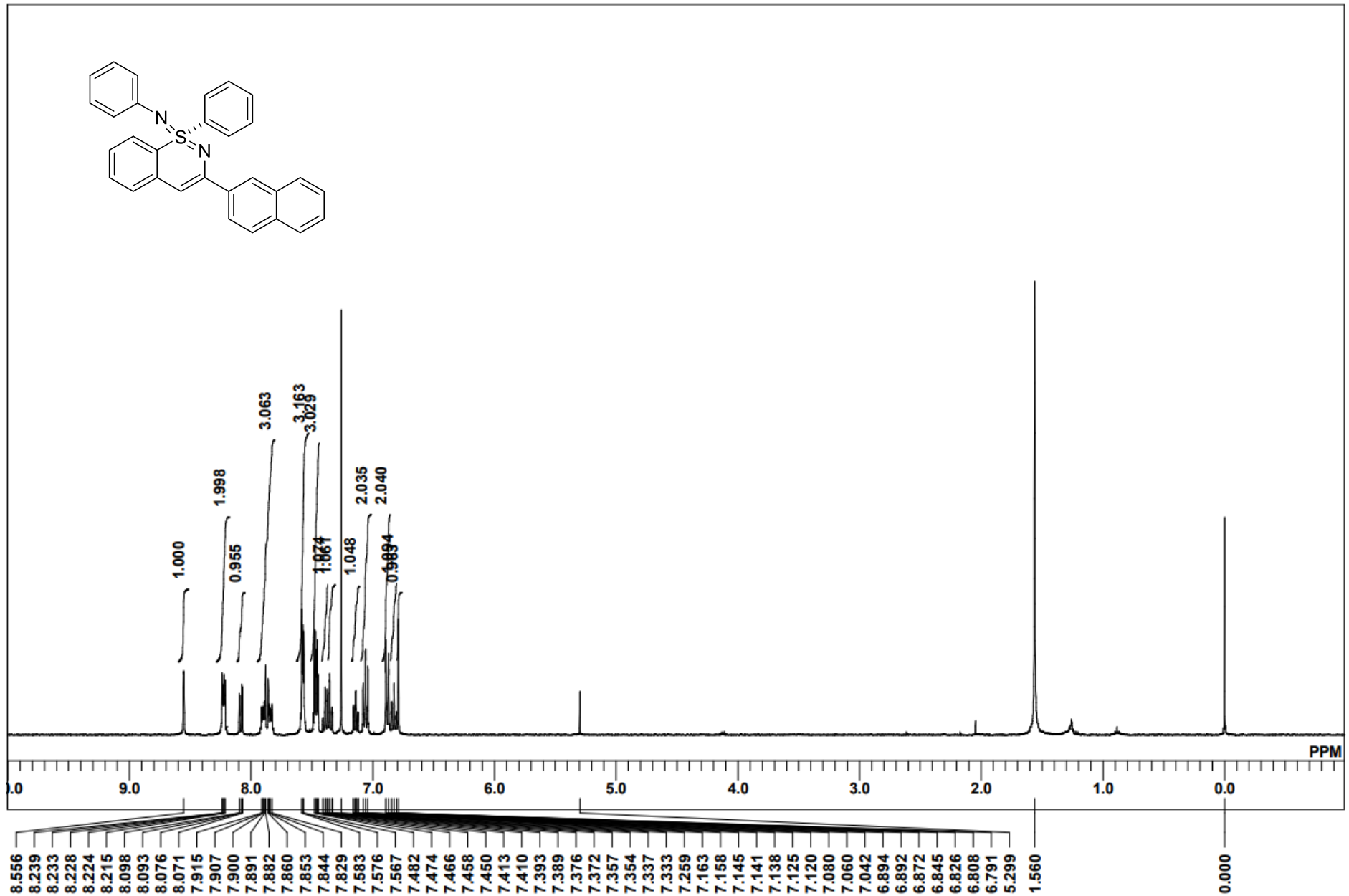
^{1}H NMR spectrum of **3ah**



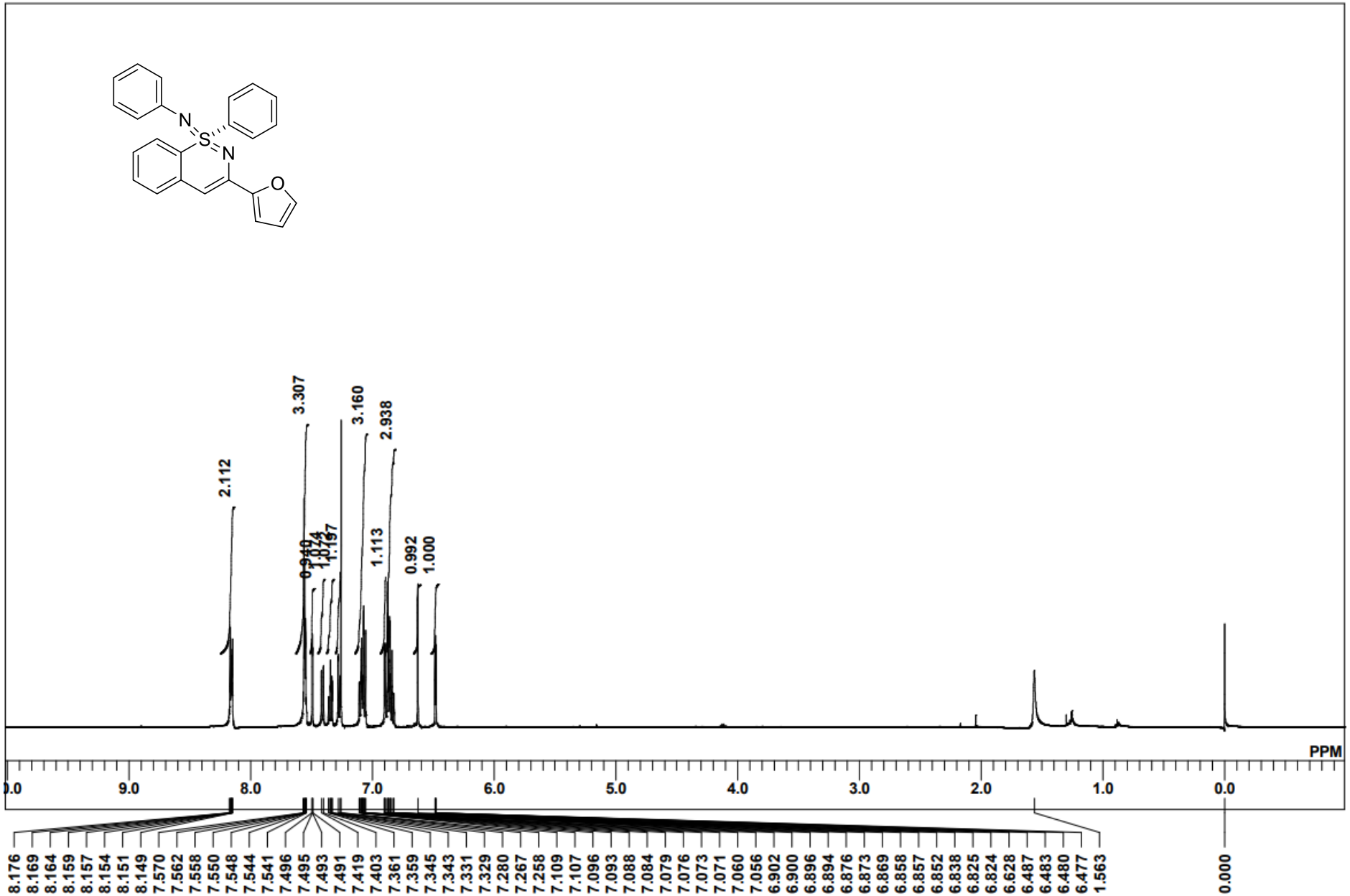
^{13}C NMR spectrum of **3ah**



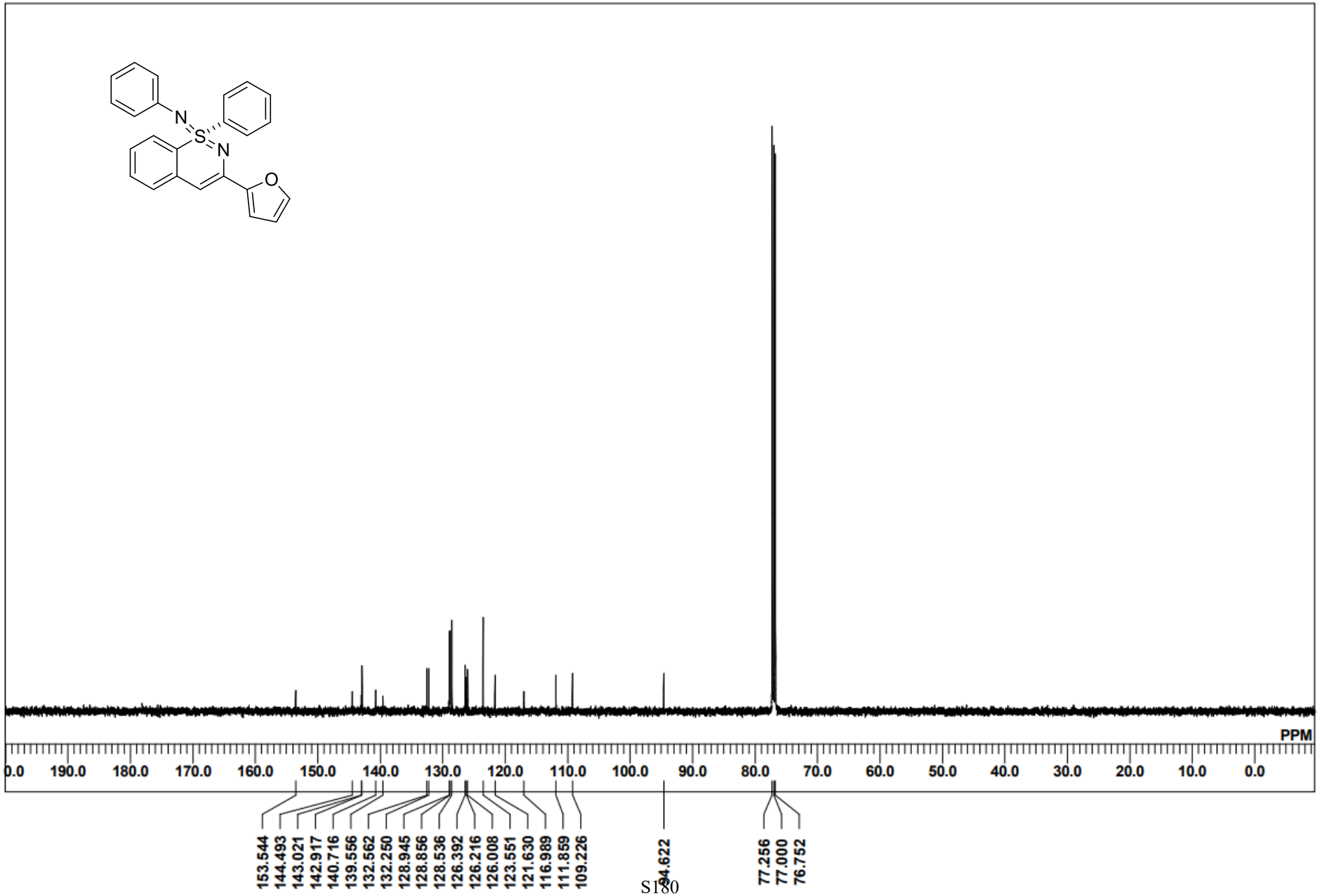
^{1}H NMR spectrum of **3ah**



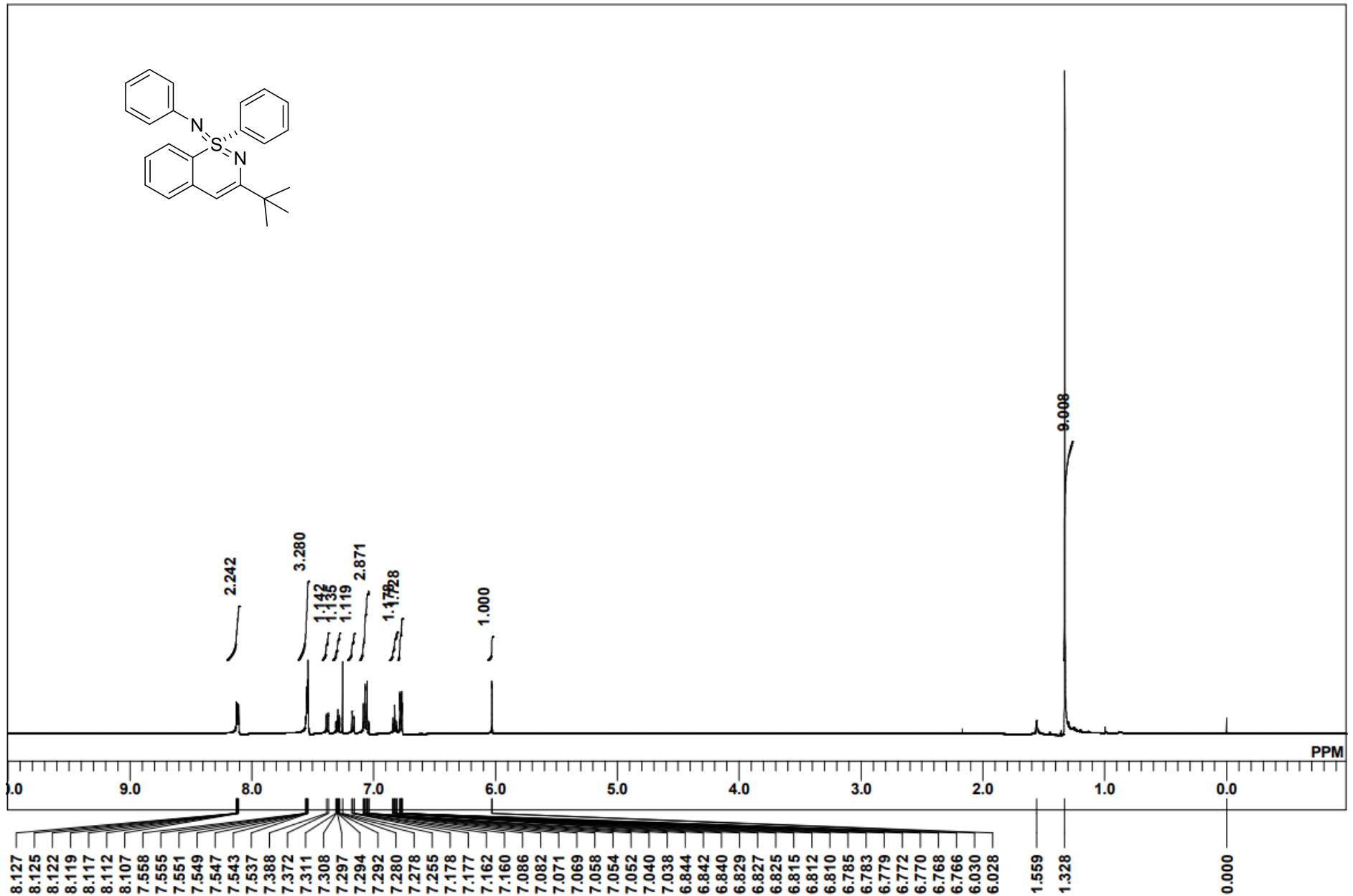
^{1}H NMR spectrum of **3ai**



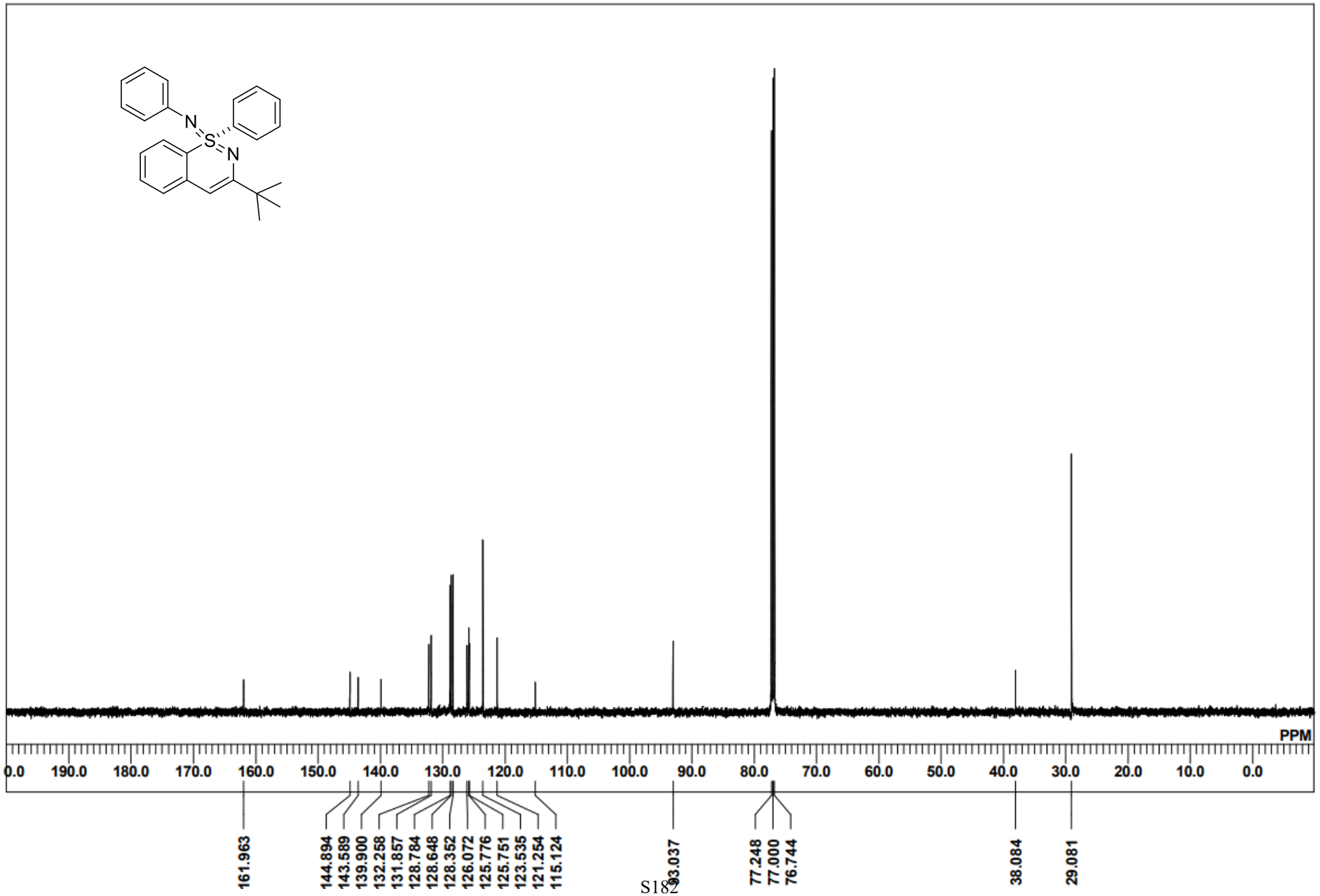
^{13}C NMR spectrum of **3ai**



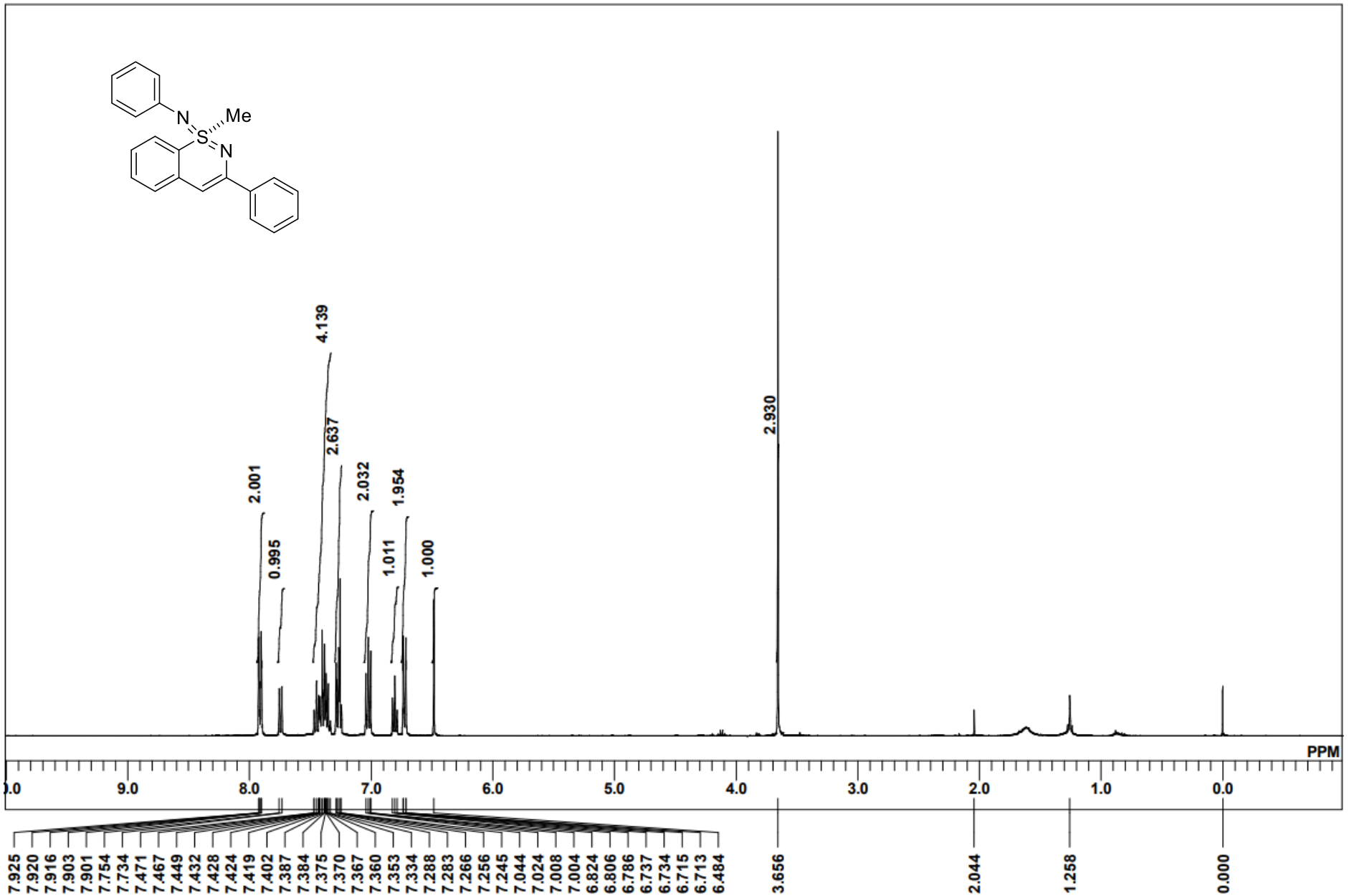
^{1}H NMR spectrum of **3aj**



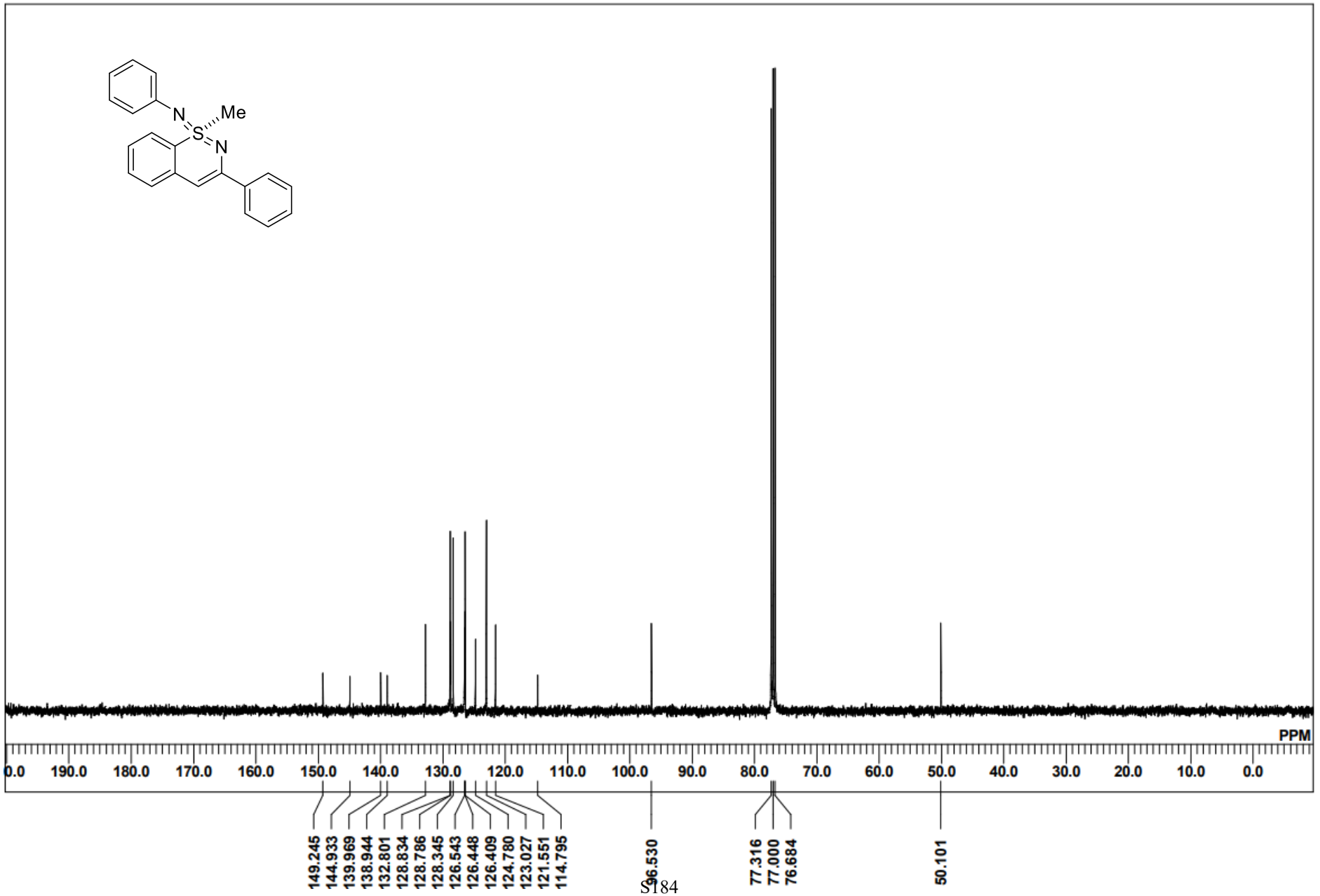
^{13}C NMR spectrum of **3aj**



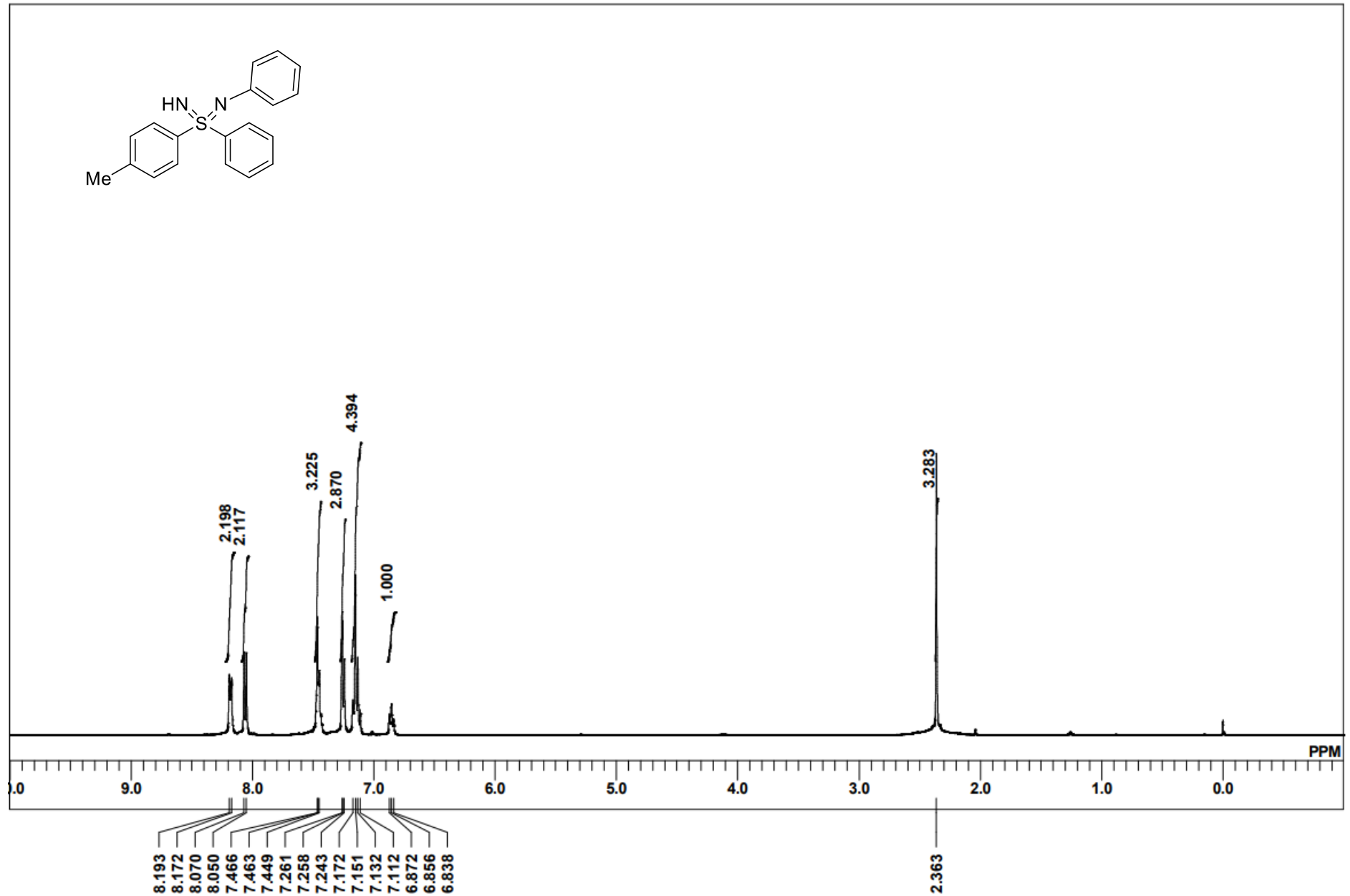
^{1}H NMR spectrum of **6**



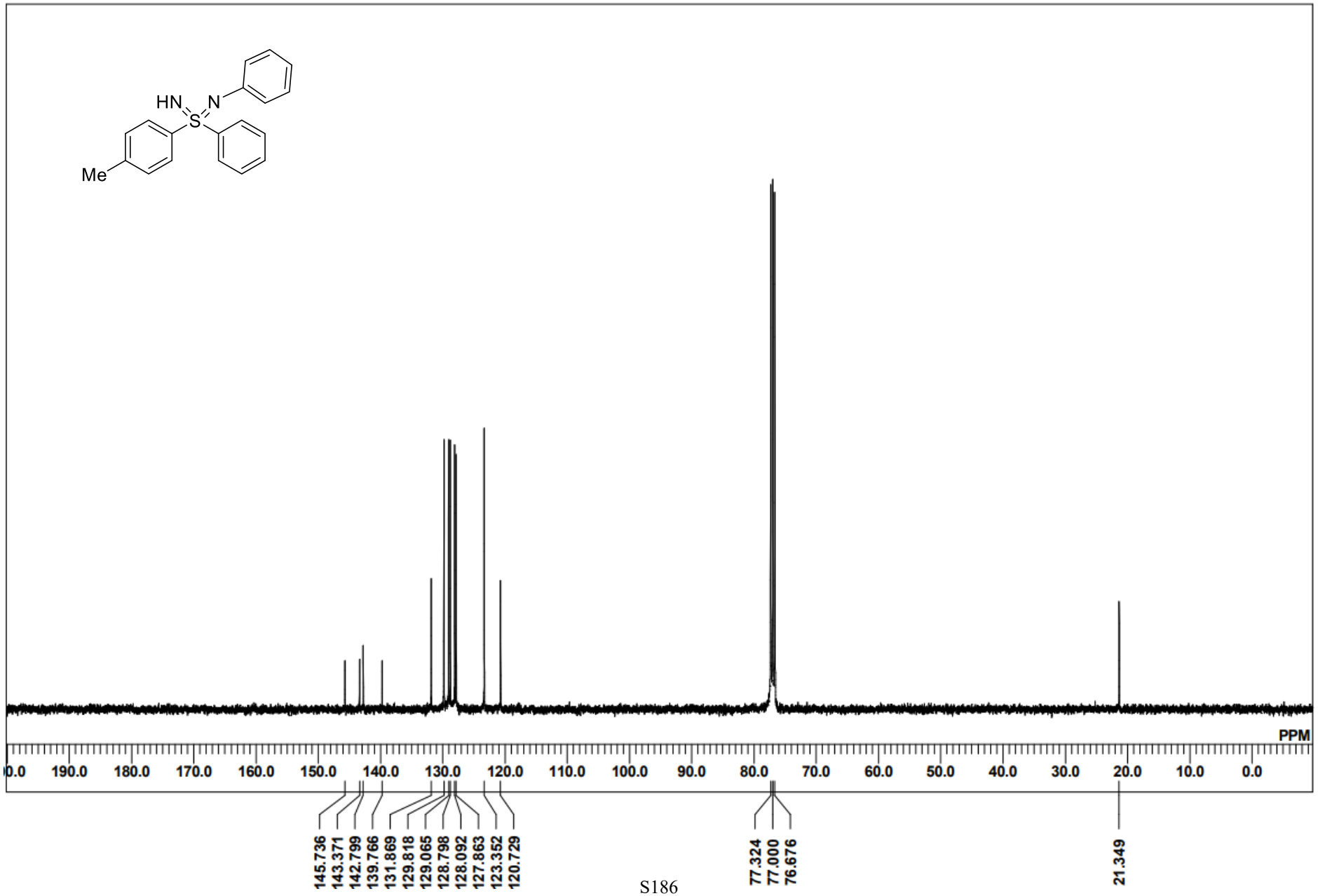
^{13}C NMR spectrum of **6**



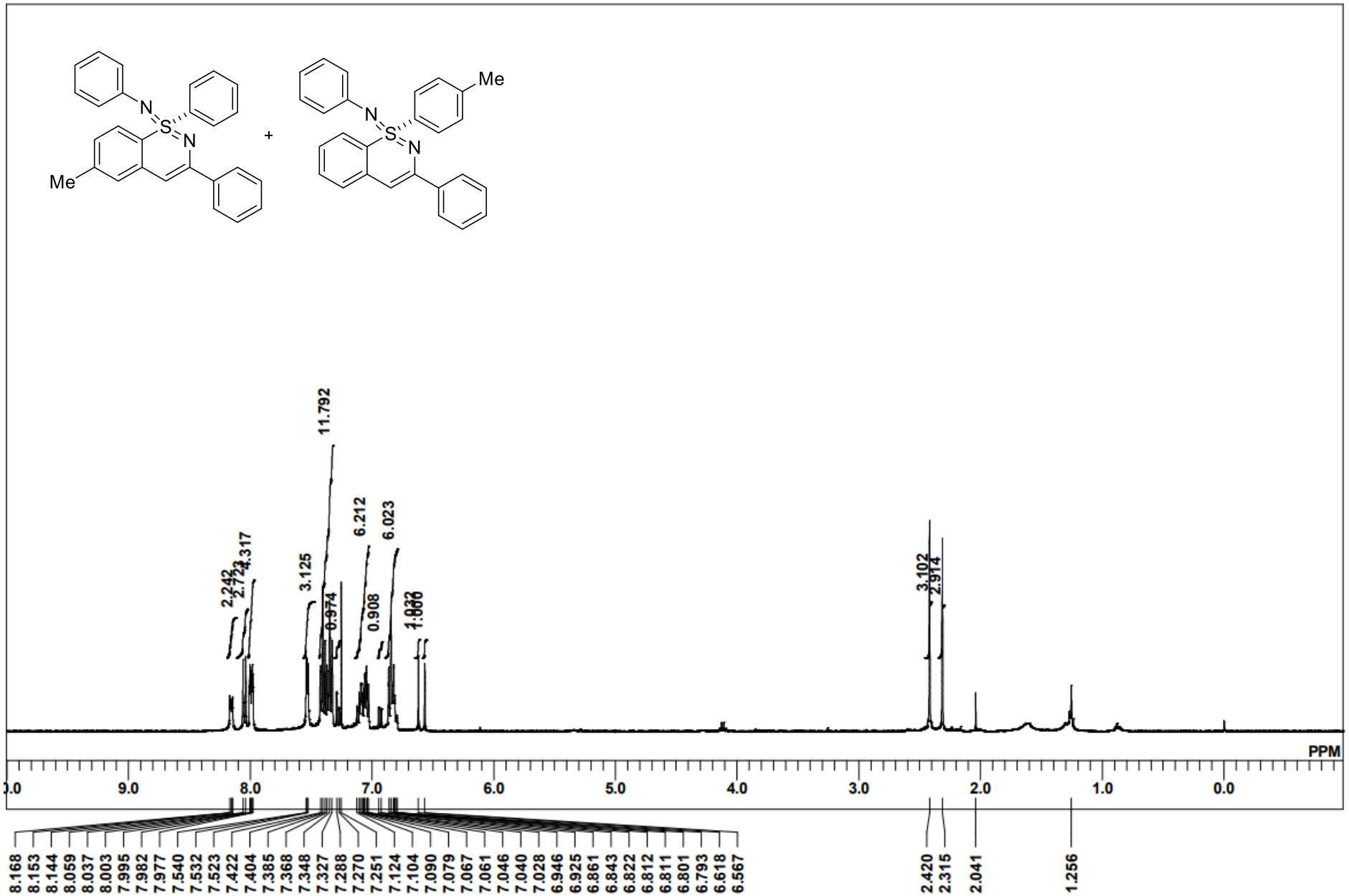
^{1}H NMR spectrum of **rac-7**



^{13}C NMR spectrum of **rac-7**



^{1}H NMR spectrum of **8**



^{13}C NMR spectrum of **8**