Supporting Information

Enantioselective C–H Amidation of Sulfondiimines for the Synthesis of 1,2,4-Benzothiadiazine-1-Imines under Cobalt Catalysis

Ayami Murata,[1] Tomonori Endo,[2] Yuki Hirata,[1] Kosuke Higashida,[2] Tatsuhiko Yoshino,[2]* Shigeki Matsunaga.[1,2]*

[1]Faculty of Pharmaceutical Sciences, Hokkaido University, Kita-ku, Sapporo, Japan.

[2]Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto, Japan.

Email: yoshino.tatsuhiko.5j@kyoto-u.ac.jp

matsunaga.shigeki.5x@kyoto-u.ac.jp

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1. General

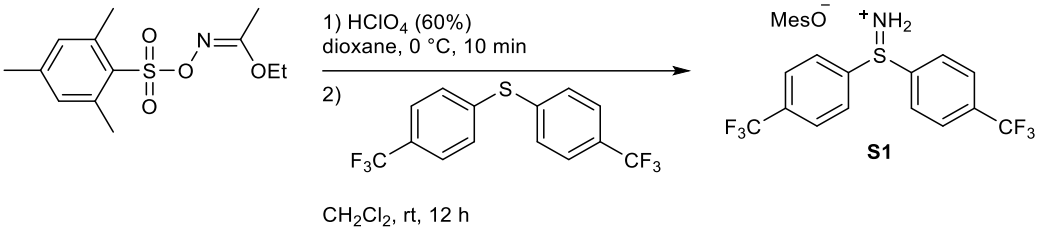
All non-aqueous reactions were carried out in a flame-dried glassware under argon atmosphere unless otherwise noted or in an argon-filled glovebox. NMR spectra were recorded on JEOL JNM-ECA600 spectrometers operating at 600.17 MHz for ^{1}H NMR, 150.92 MHz for ^{13}C NMR, and 564.69 Hz for ^{19}F NMR, JEOL JNM-ECA 600 spectrometers operating at 594.17 MHz for ^{1}H NMR, 149.41 MHz for ^{13}C NMR, JEOL JNM-ECZ 600 spectrometers operating at 599.67 MHz for ^{1}H NMR. Chemical shifts were reported in the scale relative to TMS (0.00 ppm for ^{1}H NMR in $CDCl_3$), $CHCl_3$ (7.26 ppm for ^{1}H NMR in $CDCl_3$), $CDCl_3$ (77.00 ppm for ^{13}C NMR in $CDCl_3$) and $PhCF_3$ (–63.72 ppm for ^{19}F NMR) as an internal reference, respectively. Column chromatography was performed with Kanto Silica gel 60 N (40-50 mesh) or Yamazen YFLC AI-580 using Universal Column SiOH. High resolution mass spectrometry (HRMS) was performed on a Bruker micrOTOF II-KR spectrometer in Atmospheric Pressure Chemical Ionization (APCI) method using "LC/MS tuning mix, for APCI, low concentration" as the internal standard. Optical rotations were measured on a JASCO P-1030 digital polarimeter at the sodium D line (589 nm). Analytical high performance liquid chromatography (HPLC) was performed on a JASCO PU-1580 intelligent HPLC pump with JASCO MD-4017 PDA detector using Daicel Chiralpak columns (0.46 cm × 25 cm). Retention times (tR) and peak ratios were determined with JASCO-ChromNAV analysis system.

Materials: Dichloromethane (DCM) and toluene were purified by Glass Contour solvent purification system before use. *t*AmOH was purchased from Aldrich (anhydrous grade) and used as received. Sulfondiimines **1**,[S1] dioxazolones **2**,[S2] chiral carboxylic acids (**A1**–**A5**),[S3] and Cp*Co(CO)I_2[S4] were synthesized according to the previously described methods. All other reagents were commercially available and used as received unless otherwise noted.

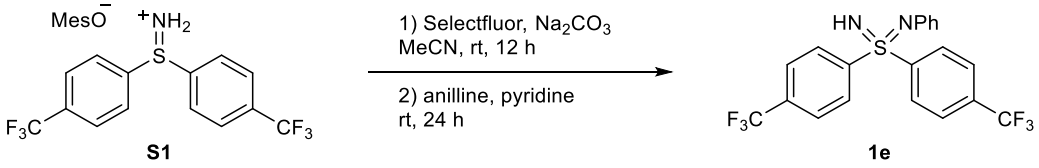
2. Experimental procedures

2-1. Preparation of substrates

Preparation of sulfondiimine 1d



To a solution of ethyl *O*-(mesitylenesulfonyl)acetohydroxamate (1.7 g, 6.0 mmol, 1 equiv.) in 1,4-dioxane (6 mL) was added 60% perchloric acid (3.9 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 bis(4-(trifluoromethyl)phenyl)sulfane (1.1 g, 6.0 mmol, 1 equiv.) in CH_2Cl_2 (6 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h. Approximately half of the CH_2Cl_2 was evaporated, and diethyl ether (12 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 **S1** (1.7 g, 3.6 mmol, 60%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.13 (s, 2H), 7.97 (d, *J* = 8.2 Hz, 4H), 7.62 (d, *J* = 8.2 Hz, 4H), 6.79 (s, 2H), 2.45 (s, 6H), 2.24 (s, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 139.3, 139.1, 136.9, 136.7, 135.2 (q, $^2J_{C\text{-}F}$ = 33.7 Hz), 130.8, 129.2, 127.4 (q, $^3J_{C\text{-}F}$ = 3.4 Hz), 122.7 (q, $^1J_{C\text{-}F}$ = 275.0 Hz), 22.8, 20.6. **^{19}F NMR** ($CDCl_3$, 564.67MHz) δ -63.6. **HRMS** (ESI) m/z: $[M\text{-}MesSO^-]^+$ Calcd for $C_{14}H_{10}F_6NS^+$: 388.0433; Found 388.0433.



To a solution of the obtained sulfiliminium salt **S1**(1.6 g, 3.0 mmol, 1.0 equiv.) and Na_2CO_3 (5.0 equiv.) in MeCN (12 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 $PhNH_2$ (0.81 mL, 9.0 mmol, 3.0 equiv.) and pyridine (0.29 mL, 3.6 mmol, 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 sulfondiimine **1e** (0.19 g, 0.44 mmol, 15%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.32 (d, *J* = 8.2 Hz, 4H), 7.74 (d, *J* = 8.2 Hz, 4H), 7.20-7.11 (m, 4H), 6.94-6.89 (m, 1H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 146.2, 144.5, 134.1 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 129.1, 128.7, 126.4 (q, $^3J_{C\text{-}F}$ = 3.4 Hz), 123.3, 123.2 (q, $^1J_{C\text{-}F}$ = 273.1 Hz), 121.7. **^{19}F NMR** ($CDCl_3$, 564.67MHz) δ -63.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}F_6N_2S^+$: 429.0855; Found 429.0857. **Rf** 0.1 (hexane/DCM = 1:3).

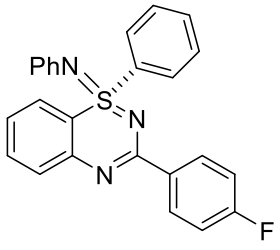
All other sulfondiimines were reported in our previous work.[S1]

2-2. Cobalt(III)/chiral carboxylic acid-catalyzed enantioselective C(sp^2)–H amidation of sulfondiimines

General Procedure

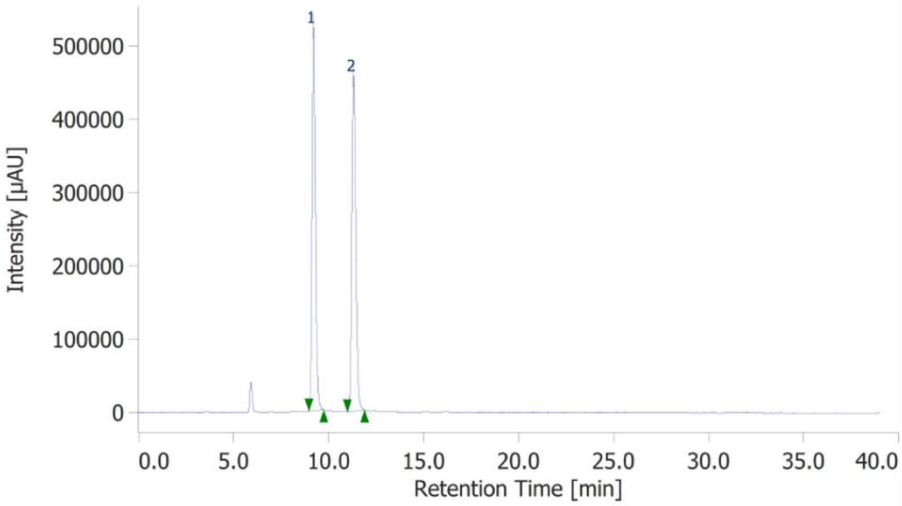
In an argon-filled glovebox, a screw-cap test tube was charged with Cp*Co(CO)I_2 (9.5 mg, 0.020 mmol, 10 mol %), AgOTf (10.3 mg, 0.040 mmol, 20 mol %), chiral acid **A5** (8.8 mg, 0.020 mmol, 10 mol %), sulfondiimine **1** (0.24 mmol, 1.2 equiv.), dioxazolone **2** (0.20 mmol, 1.0 equiv.), and *t*AmOH (400 μL). The test tube was capped, and then brought out of the glovebox. The reaction mixture was stirred for 24 h at 80 °C. The reaction mixture was filtered through a short pad of silica gel, eluted with AcOEt, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (DCM/hexane) to afford **3**.

(S)-3-(4-fluorophenyl)-N,1-diphenyl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3aa)

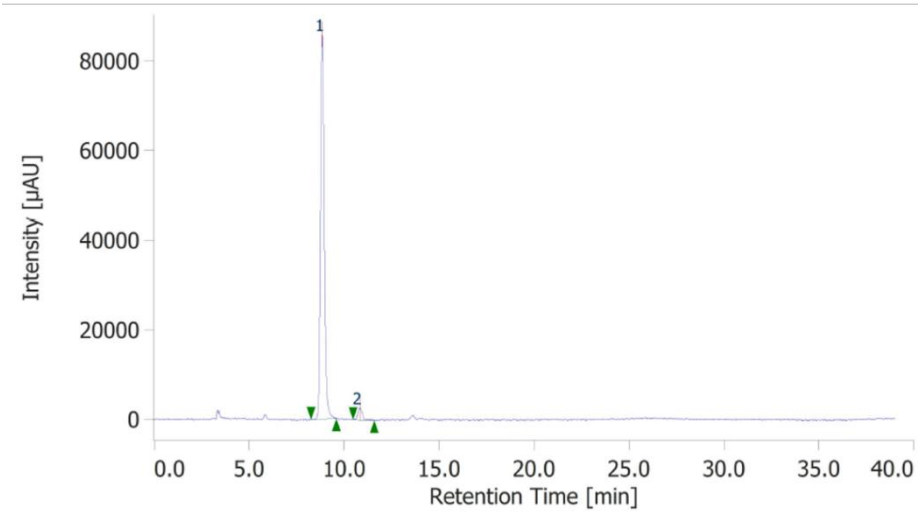


General Procedure 3aa using compound **1a** (70.2 mg, 0.24 mmol) and **2a** (36.2 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/hexane = 2/1) afforded **3aa** as a colorless solid (62.6 mg, 76%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.46-8.41 (m, 2H), 8.17-8.13 (m, 2H), 7.65-7.57 (m, 3H), 7.56-7.50 (m, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.19-7.15 (m, 1H), 7.15-7.10 (m, 2H), 7.09-7.05 (m, 2H), 6.90-6.83 (m, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 150.92 MHz) δ 164.8 (d, $^{1}J_{C\text{-}F}$ = 250.0 Hz), 159.0, 149.9, 143.2, 141.6, 134.2, 134.1 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 133.2, 130.6 (d, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 129.2, 129.1, 128.5, 128.2, 126.1, 125.3, 123.6, 122.6, 115.1 (d, $^{2}J_{C\text{-}F}$ = 21.7 Hz), 110.9. **^{19}F NMR** ($CDCl_3$, 564.67MHz) δ -111.1. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 8.9 (major) and 10.8 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}FN_3S^+$: 412.1278; Found 412.1284. **$[\alpha]_D^{23.7}$** = +138.9 (*c* = 0.50, $CHCl_3$). **Rf** 0.43 (hexane/DCM = 1/3).

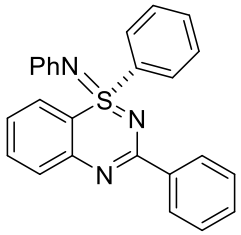


#	tR [min]	Area%
1	9.213	49.852
2	11.317	50.148

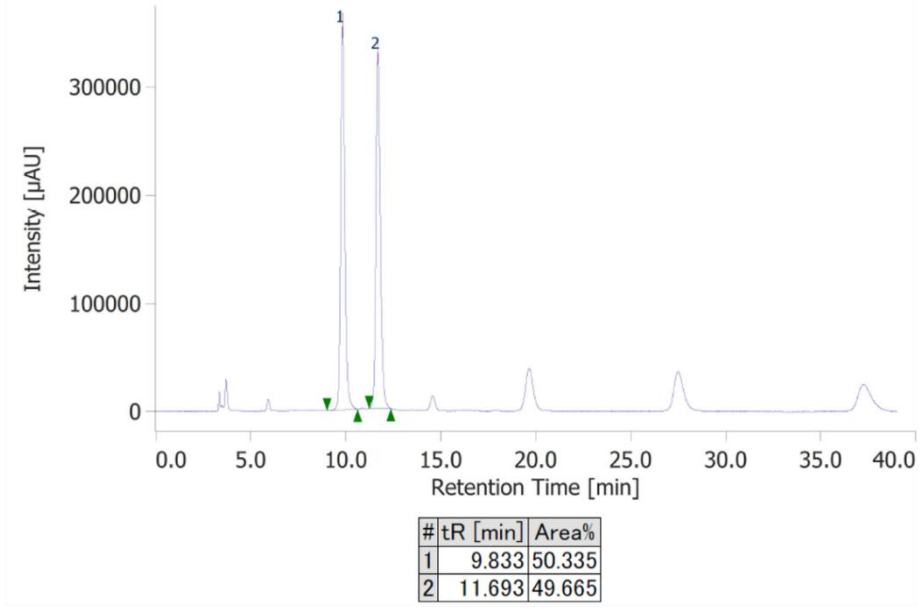


#	tR [min]	Area%
1	8.853	96.235
2	10.827	3.765

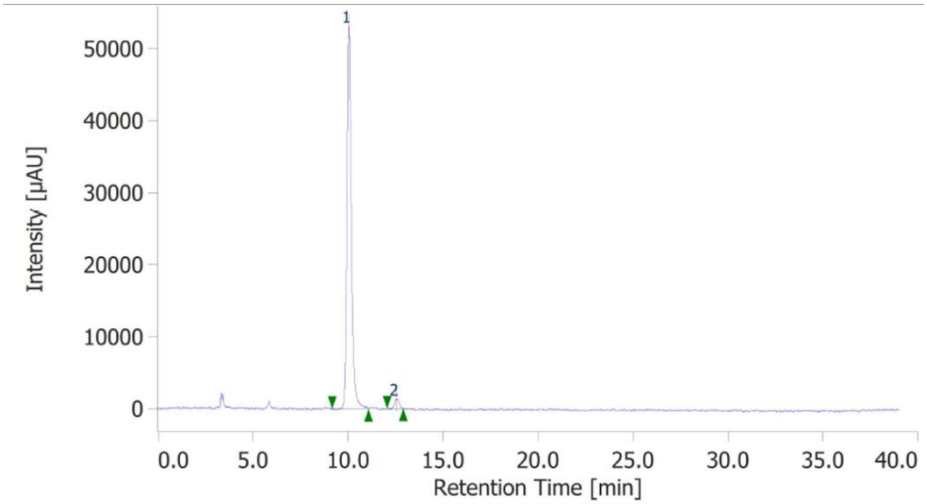
(S)-N,1,3-triphenyl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3ab)



General Procedure using compound **1a** (70.2 mg, 0.24 mmol) and **2b** (32.6 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/hexane = 2/1) afforded **3ab** as a colorless solid (55.6 mg, 71%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.46-8.41 (m, 2H), 8.19-8.14 (m, 2H), 7.66-7.51 (m, 5H), 7.51-7.42 (m, 4H), 7.21-7.14 (m, 1H), 7.11-7.03 (m, 2H), 6.91-6.84 (m, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 160.0, 150.0, 143.3, 141.7, 138.1, 134.2, 133.2, 130.8, 129.2, 129.1, 128.5, 128.3, 128.2, 128.2, 126.1, 125.3, 123.6, 122.6, 111.0. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 10.1 (major) and 12.6 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}N_3S^+$: 394.1372; Found 394.1373. **$[\alpha]_D^{23.3}$** = +130.1 (*c* = 0.50, $CHCl_3$). **Rf** 0.39 (hexane/AcOEt = 5/1).

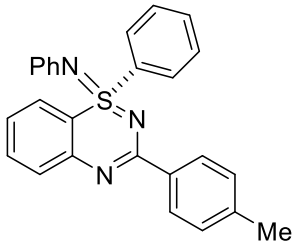


#	tR [min]	Area%
1	9.833	50.335
2	11.693	49.665

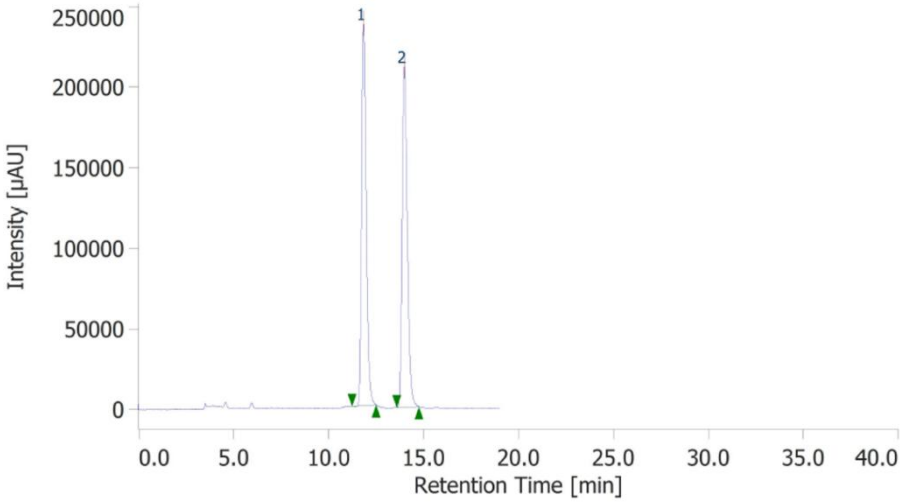


#	tR [min]	Area%
1	10.050	97.378
2	12.550	2.622

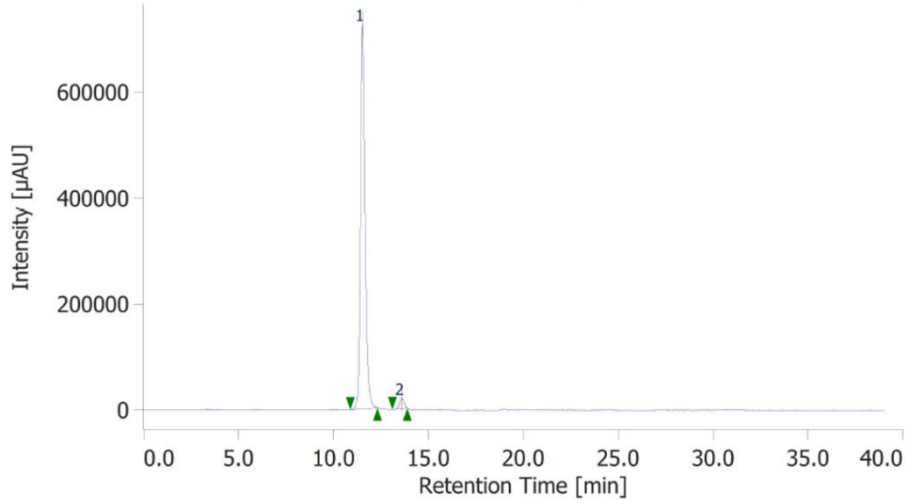
(S)-N,1-diphenyl-3-(p-tolyl)-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3ac)



General Procedure using compound **1a** (70.2 mg, 0.24 mmol) and **2c** (35.4 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/hexane = 3/2) afforded **3ac** as a colorless solid (54.9 mg, 67%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.33 (d, *J* = 8.1 Hz, 2H), 8.19-8.12 (m, 2H), 7.65-7.55 (m, 3H), 7.55-7.49 (m, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.29-7.25 (m, 2H), 7.17-7.12 (m, 1H), 7.10-7.03 (m, 3H), 6.90-6.83 (m, 3H), 2.42 (s, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 159.9, 150.1, 143.3, 141.7, 141.1, 135.2, 134.1, 133.1, 129.1, 129.0, 128.9, 128.4, 128.3, 128.1, 125.8, 125.2, 123.6, 122.4, 110.8, 21.5 **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 11.5 (major) and 13.6 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}N_3S^+$: 408.1529; Found 408.1525. **$[\alpha]_D^{23.6}$** = +112.0 (*c* = 0.50, $CHCl_3$). **Rf** 0.51 (DCM/hexane = 3/1).

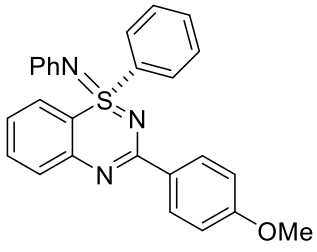


#	tR [min]	Area%
1	11.840	49.868
2	13.983	50.132

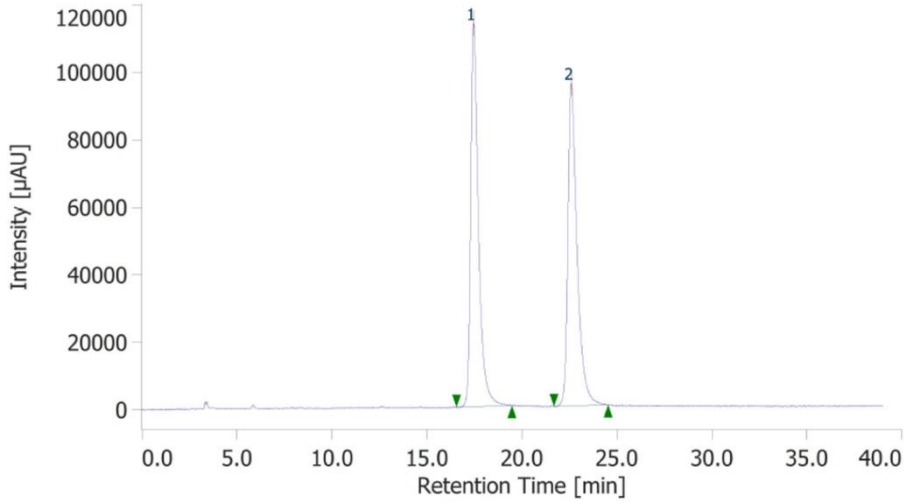


#	tR [min]	Area%
1	11.527	97.432
2	13.607	2.568

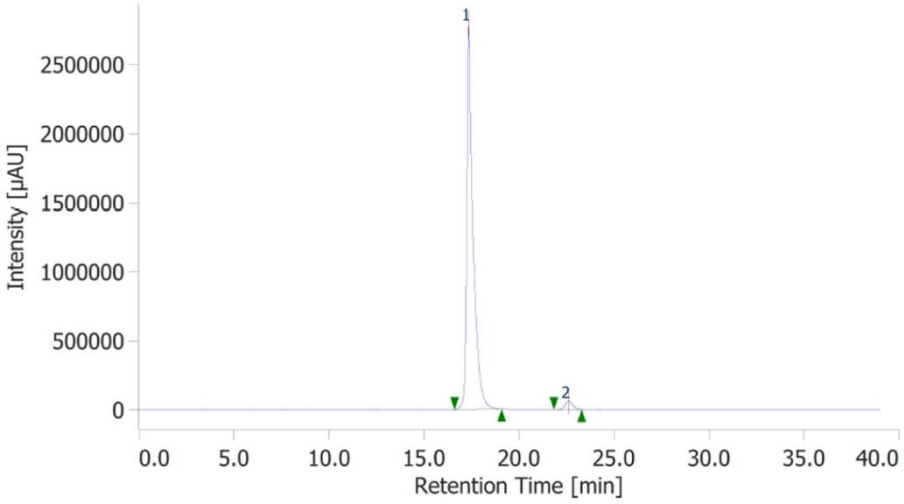
(S)-3-(4-methoxyphenyl)-N,1-diphenyl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3ad)



General Procedure using compound **1a** (70.2 mg, 0.24 mmol) and **2d** (38.6 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/hexane = 3/1) afforded **3ad** as a colorless solid (45.2 mg, 53%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.42-8.38 (m, 2H), 8.18-8.13 (m, 2H), 7.63-7.56 (m, 3H), 7.54-7.48 (m, 2H), 7.48-7.45 (m, 1H), 7.15-7.11 (m, 1H), 7.10-7.04 (m, 2H), 6.99-6.94 (m, 2H), 6.89-6.85 (m, 3H), 3.87 (s, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 161.9, 159.6, 150.2, 143.4, 141.7, 134.1, 133.0, 130.5, 130.2, 129.1, 129.0, 128.3, 128.0, 125.6, 125.2, 123.5, 122.4, 113.4, 110.7, 55.3 **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 17.4 (major) and 22.6 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}N_3OS^+$: 424.1478; Found 424.1486. **$[\alpha]_D^{23.4}$** = +73.0 (*c* = 0.50, $CHCl_3$). **Rf** 0.1 (hexane/DCM = 1/3).

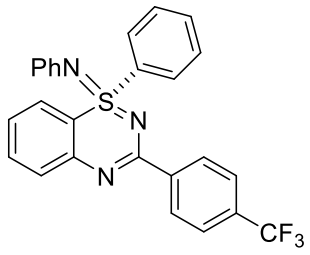


#	tR [min]	Area%
1	17.450	50.109
2	22.587	49.891

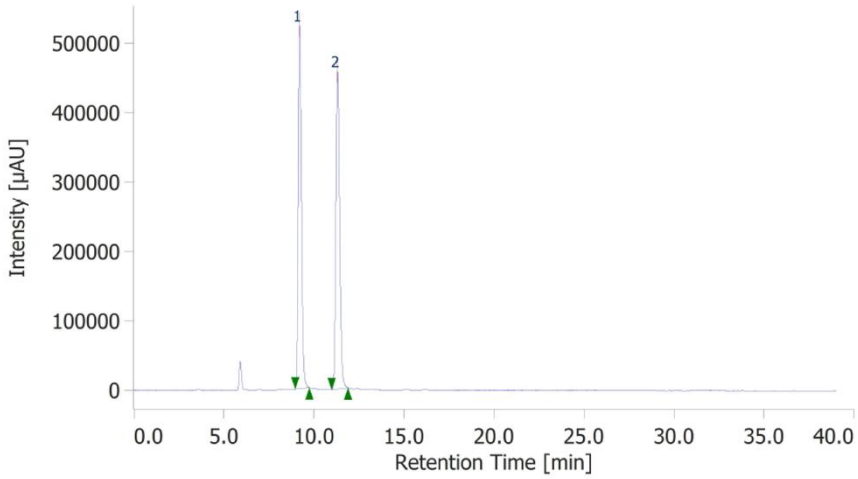


#	tR [min]	Area%
1	17.357	97.315
2	22.597	2.685

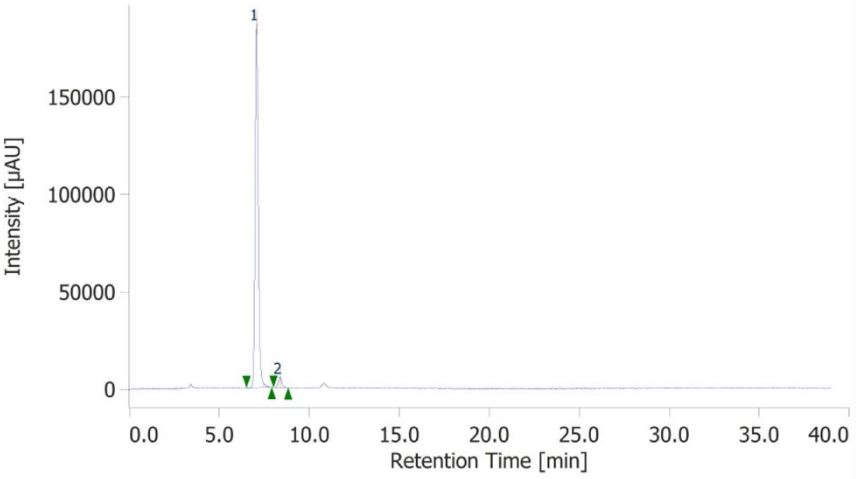
(S)-N,1-diphenyl-3-(4-(trifluoromethyl)phenyl)-1λ6-benzo[e][1,2,4]thiadiazin-1-imine (3ae)



General Procedure using compound **1a** (70.2 mg, 0.24 mmol) and **2e** (46.2 mg, 0.2 mmol) and purification by silica gel column chromatography (hexane/Et_2O = 2/1) afforded **3ae** as a colorless solid (90.1 mg, 97%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.54 (d, *J* = 8.2 Hz, 2H), 8.17-8.13 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.66-7.60 (m, 3H), 7.58-7.54 (m, 2H), 7.50 (d, *J* = 7.7 Hz 1H), 7.24-7.19 (m, 1H), 7.10-7.05 (m, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 2H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 158.4, 149.6, 143.0, 141.4, 141.3, 134.3, 133.3, 132.4 (q, $^2J_{C-F}$ = 32.8 Hz), 129.2, 129.1, 128.7, 128.4, 128.4, 126.8, 126.6, 125.2 (q, $^3J_{C-F}$ = 3.9 Hz), 124.3 (q, $^1J_{C-F}$ = 272.0 Hz), 123.6, 122.8, 111.3. **^{19}F NMR** ($CDCl_3$, 564.67MHz) δ -63.27. **HPLC** (chiral column: DAICEL CHIRALPAK IA; solvent: hexane/2-propanol = 95/5; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 7.1 (major) and 8.4 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{19}N_3SF_3^+$: 462.1246; Found 462.1246. **[α]$_D^{23.0}$** = +102.9 (*c* = 0.50, $CHCl_3$). **Rf** 0.45 (hexane/AcOEt = 5/1).

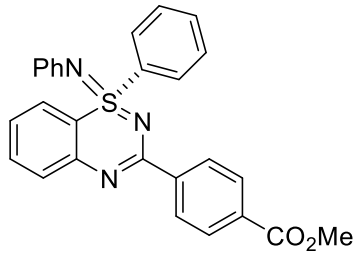


#	tR [min]	Area%
1	9.213	49.852
2	11.317	50.148

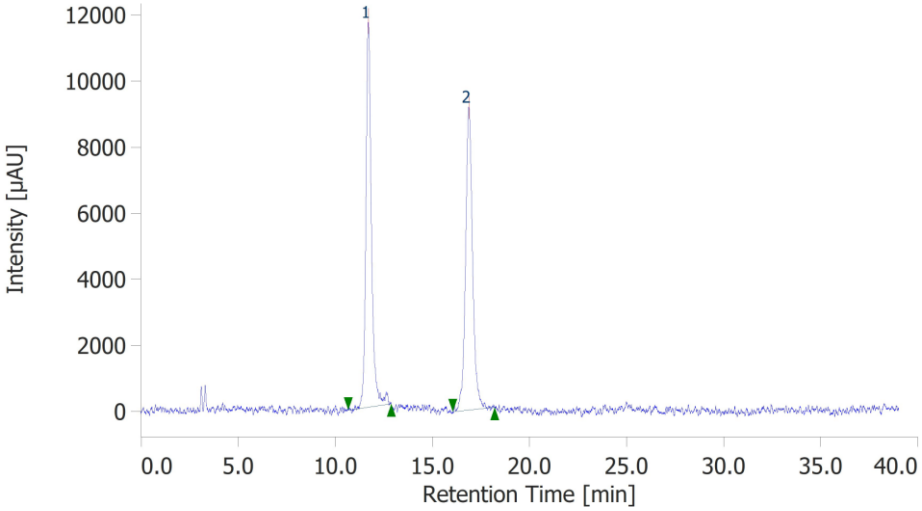


#	tR [min]	Area%
1	7.073	96.967
2	8.377	3.033

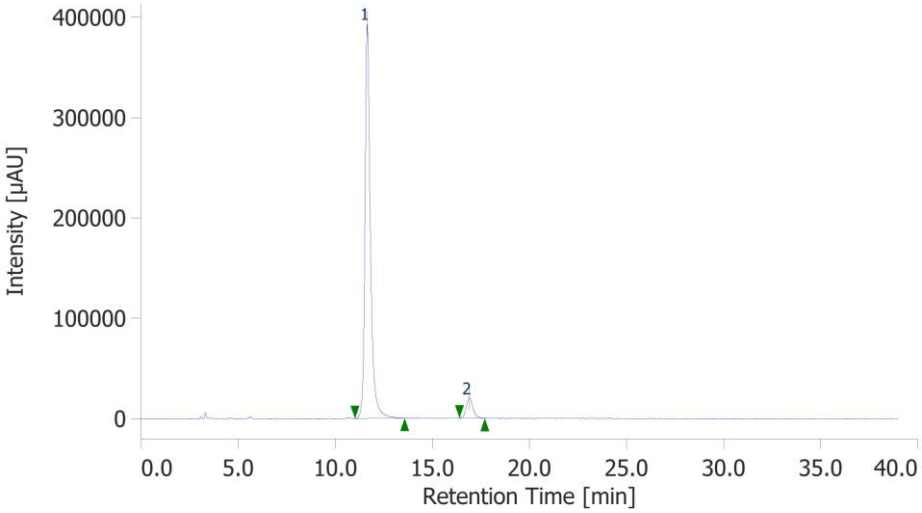
Methyl (*S*)-4-(1-phenyl-1-(phenylimino)-1l6-benzo[e][1,2,4]thiadiazin-3-yl)benzoate (3af)



General Procedure using compound **1a** (70.2 mg, 0.24 mmol) and **2f** (44.2 mg, 0.2 mmol) and purification by silica gel column chromatography (hexane/DCM/AcOEt = 8/1/1) afforded **3af** as a colorless solid (54.8 mg, 61%). **^{1}H NMR** ($CDCl_3$, 399.78 MHz) δ 8.44-8.40 (m, 2H), 8.10-8.06 (m, 2H), 8.06-8.01 (m, 2H), 7.59-7.43 (m, 5H), 7.43-7.38 (m, 1H), 7.12 (ddd, *J* = 8.2, 6.5, 1.8 Hz, 1H), 7.02-6.96 (m, 2H), 6.83-6.74 (m, 3H), 3.86 (s, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.53 MHz) δ 166.9, 158.8, 149.6, 143.0, 141.6, 142.2, 141.3, 134.2, 133.3, 131.8, 129.4, 129.2, 129.1, 128.4, 128.3, 126.6, 125.3, 123.6, 122.7, 111.1, 52.2. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 9/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 11.7 (major) and 16.9 (minor) min. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}N_3O_2S^+$: 452.1427; Found 452.1432. **[α]$_D^{23.7}$** = +71.8 (*c* = 1.0, $CHCl_3$). **Rf** 0.28 (hexane/AcOEt = 3/1).

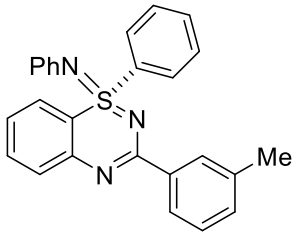


#	tR [min]	Area%
1	11.703	50.033
2	16.870	49.967

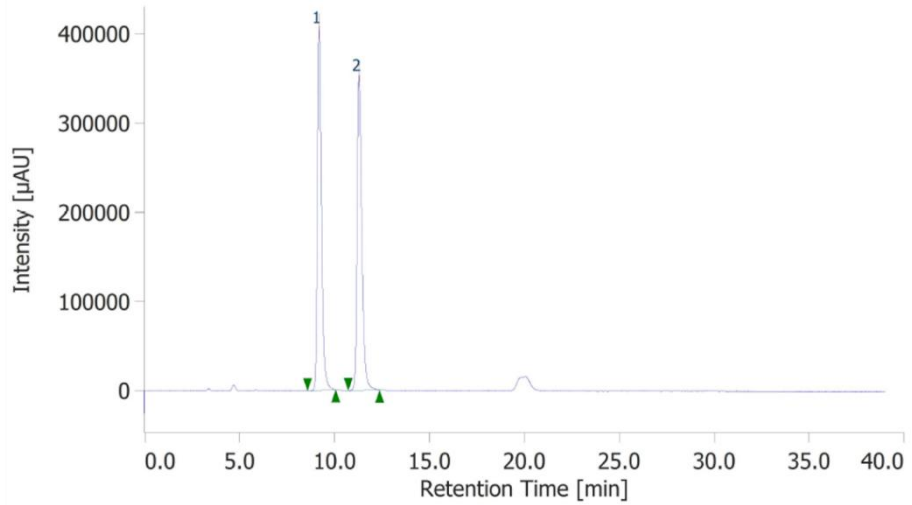


#	tR [min]	Area%
1	11.647	93.972
2	16.903	6.028

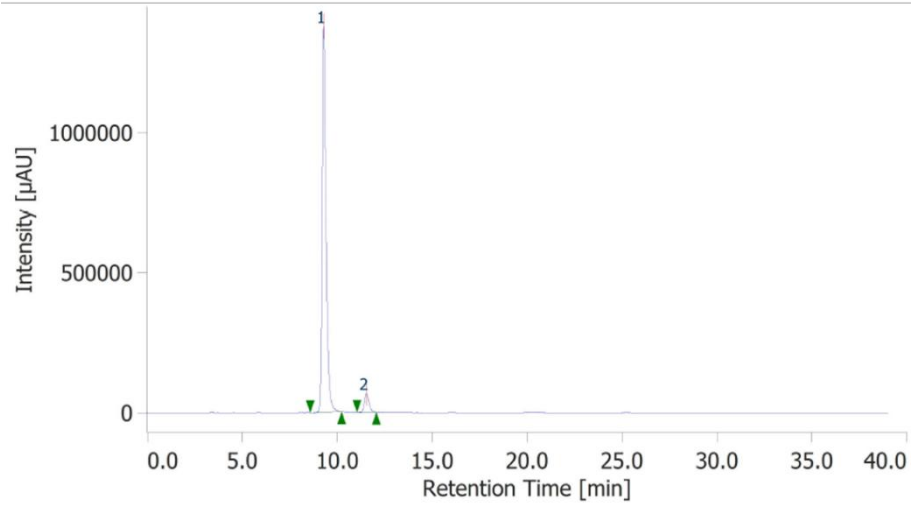
(S)-N,1-diphenyl-3-(m-tolyl)-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3ag)



General Procedure using compound **1a** (70.2 mg, 0.24 mmol) and **2g** (35.4 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/hexane = 3/2) afforded **3ag** as a colorless solid (52.8 mg, 65%).**^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.27-8.21 (m, 2H), 8.18-8.13 (m, 2H), 7.64-7.54 (m, 4H), 7.54-7.50 (m, 1H), 7.47 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.18-7.13 (m, 1H), 7.10-7.03 (m, 2H), 6.91-6.82 (m, 3H), 2.43 (s, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 160.1, 150.0, 143.3, 141.6, 137.9, 137.7, 134.1, 133.1, 131.6, 129.1, 129.0, 128.9, 128.4, 128.2, 128.1, 126.0, 125.6, 125.2, 123.5, 122.4, 110.8, 21.4 **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 9.3 (major) and 11.5 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}N_3S^+$: 408.1529; Found 408.1530. **$[\alpha]_D^{23.3}$** = +176.6 (*c* = 0.17, $CHCl_3$). **Rf** 0.45 (DCM/hexane = 3/1).

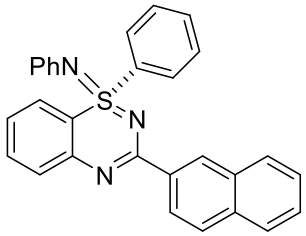


#	tR [min]	Area%
1	9.190	49.902
2	11.290	50.098

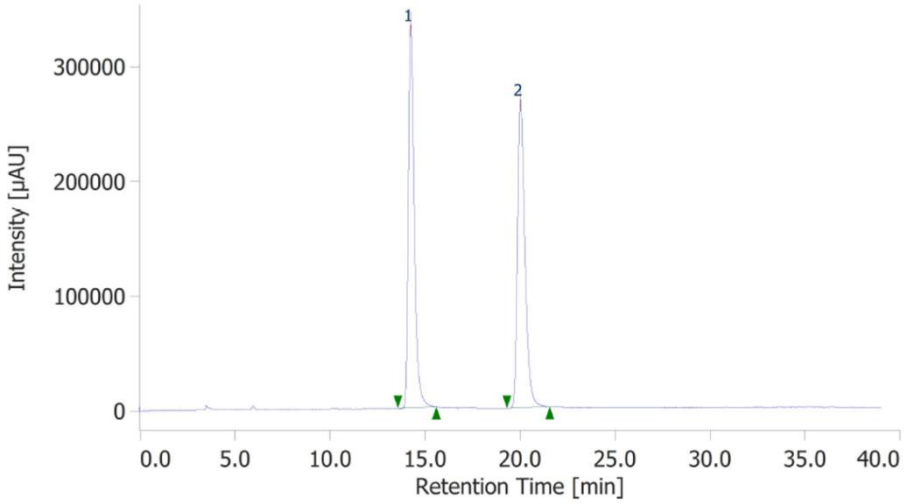


#	tR [min]	Area%
1	9.283	94.639
2	11.540	5.361

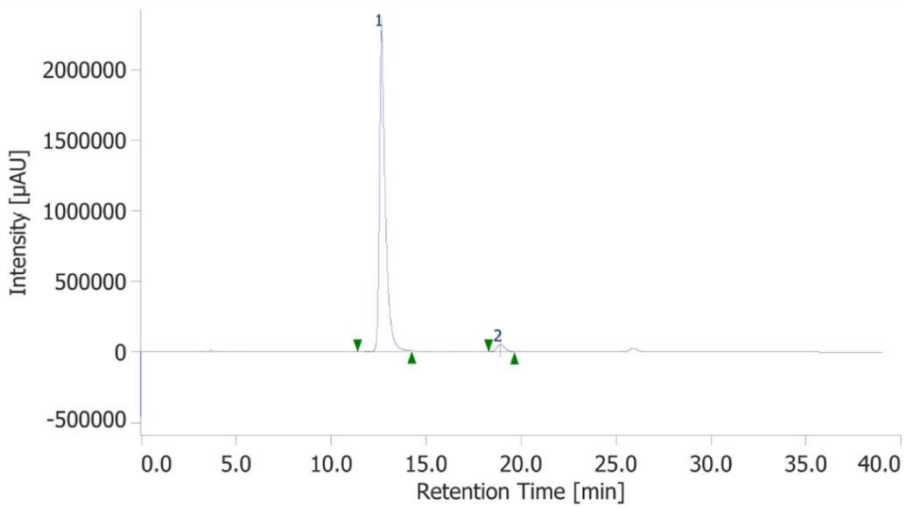
(S)-3-(naphthalen-2-yl)-N,1-diphenyl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3ah)



General Procedure using compound **1a** (70.2 mg, 0.24 mmol) and **2h** (42.6 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/hexane = 3/2) afforded **3ah** as a colorless solid (71.9 mg, 81%).**^{1}H NMR** ($CDCl_3$, 594.17 MHz) δ 8.96 (s, 1H), 8.57 (dd, *J* = 8.5, 1.7 Hz, 1H), 8.23-8.18 (m, 2H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.64-7.60 (m, 4H), 7.57-7.47 (m, 4H), 7.20-7.17 (m, 1H), 7.08-7.05 (m, 2H), 6.91-6.85 (m, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 149.41 MHz) δ 159.8, 150.0, 143.3, 141.6, 135.3, 134.8, 134.2, 133.2, 133.0, 129.2, 129.2, 129.1, 129.0, 128.5, 128.3, 127.7, 127.6, 127.1, 126.2, 126.1, 125.3, 123.6, 122.6, 111.1; one aromatic signal was missing probably due to overlapping. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 12.7 (major) and 18.9 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{22}N_3S^+$: 444.1529; Found 444.1537. **$[\alpha]_D^{23.3}$** = +51.4 (*c* = 0.16, $CHCl_3$). **Rf** 0.45 (DCM/hexane = 3/1).

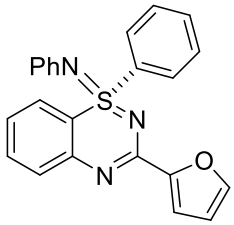


#	tR [min]	Area%
1	14.243	49.876
2	20.017	50.124

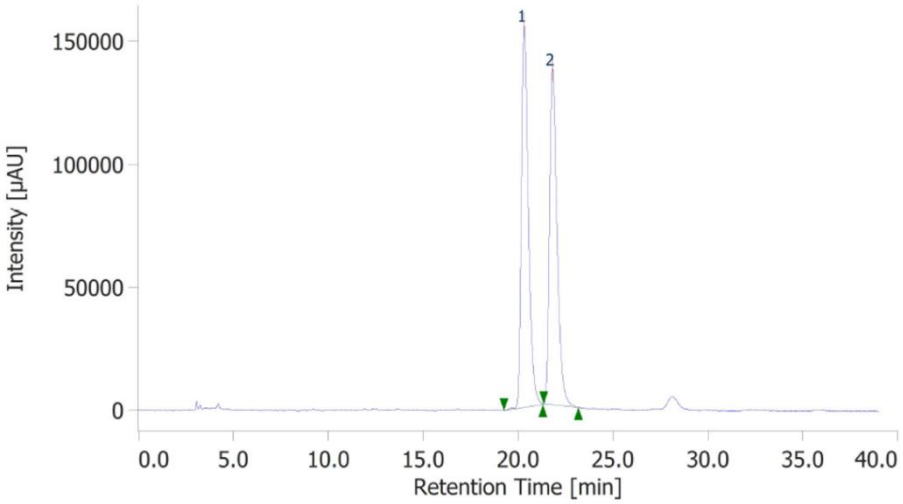


#	tR [min]	Area%
1	12.650	96.951
2	18.907	3.049

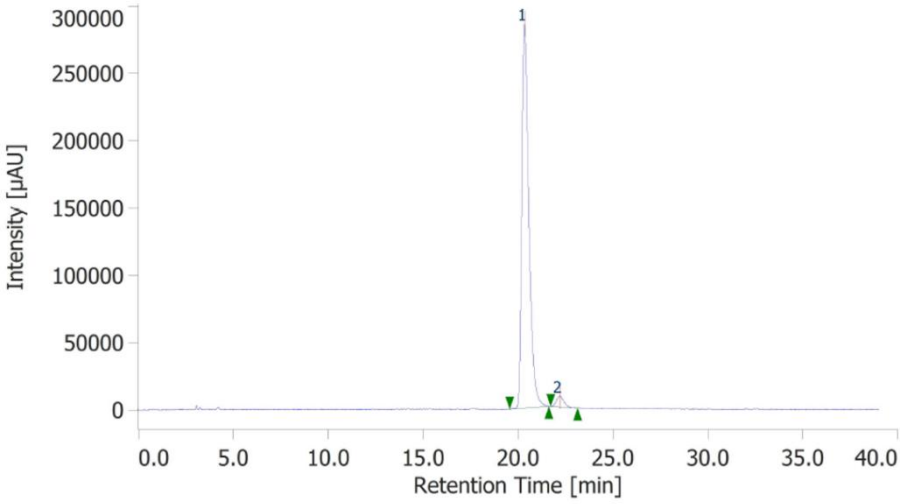
(S)-3-(furan-2-yl)-N,1-diphenyl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3ai)



General Procedure using compound **1a** (70.2 mg, 0.24 mmol) and **2i** (30.6 mg, 0.2 mmol) and purification by silica gel column chromatography (hexane/AcOEt = 6/1) afforded **3ai** as a colorless solid (39.2 mg, 51%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.20-8.12 (m, 2H), 7.65-7.56 (m, 5H), 7.54-7.48 (m, 1H), 7.47-7.42 (m, 1H), 7.26 (d, *J* = 3.4 Hz, 1H), 7.17-7.14 (m, 1H), 7.11-7.06 (m, 2H), 6.92-6.84 (m, 3H), 6.54 (dd, *J* = 3.4, 1.7 Hz, 1H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 152.5, 151.6, 149.7, 145.1, 143.0, 141.4, 134.3, 133.2, 129.2, 129.0, 128.5, 128.1, 126.1, 125.3, 123.5, 122.6, 114.4, 111.9, 111.5 **HPLC** (chiral column: DAICEL CHIRALPAK IA; solvent: hexane/2-propanol = 95/5; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 20.3 (major) and 22.2 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}N_3OS^+$: 384.1165; Found 384.1163. **$[\alpha]_D^{23.1}$** = +132.2 (*c* = 0.22, $CHCl_3$). **Rf** 0.14 (DCM/hexane = 3/1).

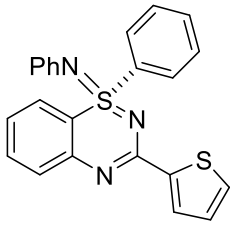


#	tR [min]	Area%
1	20.323	51.407
2	21.813	48.593

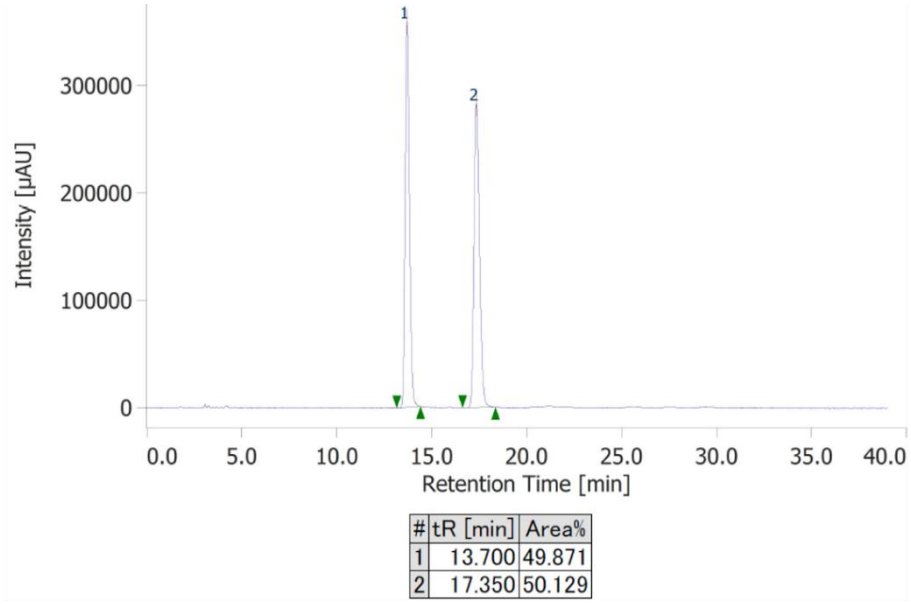


#	tR [min]	Area%
1	20.333	97.125
2	22.197	2.875

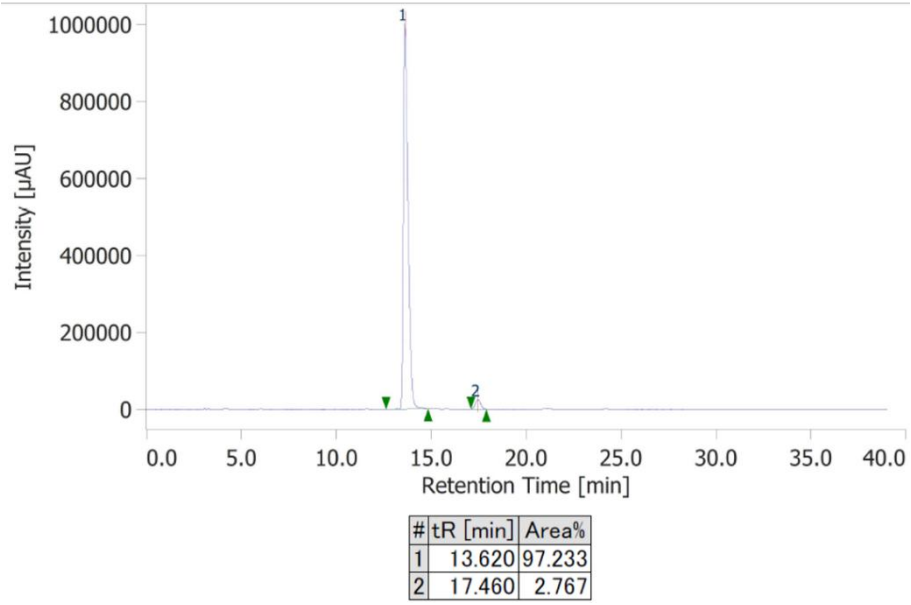
(S)-N,1-diphenyl-3-(thiophen-2-yl)-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3aj)



General Procedure using compound **1a** (70.2 mg, 0.24 mmol) and **2j** (33.8 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/hexane = 3/2) afforded **3aj** as a colorless solid (47.5 mg, 60%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.19-8.14 (m, 2H), 7.98-7.91 (m, 1H), 7.63-7.58 (m, 3H), 7.52-7.42 (m, 4H), 7.15-7.07 (m, 4H), 6.93-6.87 (m, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 156.2, 149.9, 143.9, 143.1, 141.5, 134.2, 133.2, 130.0, 129.5, 129.2, 129.0, 128.4, 127.8, 127.8, 125.8, 125.3, 123.7, 122.7, 111.2 **HPLC** (chiral column: DAICEL CHIRALPAK IA; solvent: hexane/2-propanol = 95/5; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 13.6 (major) and 17.5 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}N_3S_2^+$: 400.0937; Found 400.0926. **$[\alpha]_D^{23.2}$** = +106.8 (*c* = 0.50, $CHCl_3$). **Rf** 0.39 (DCM/hexane = 3/1).

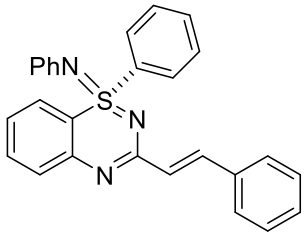


#	tR [min]	Area%
1	13.700	49.871
2	17.350	50.129

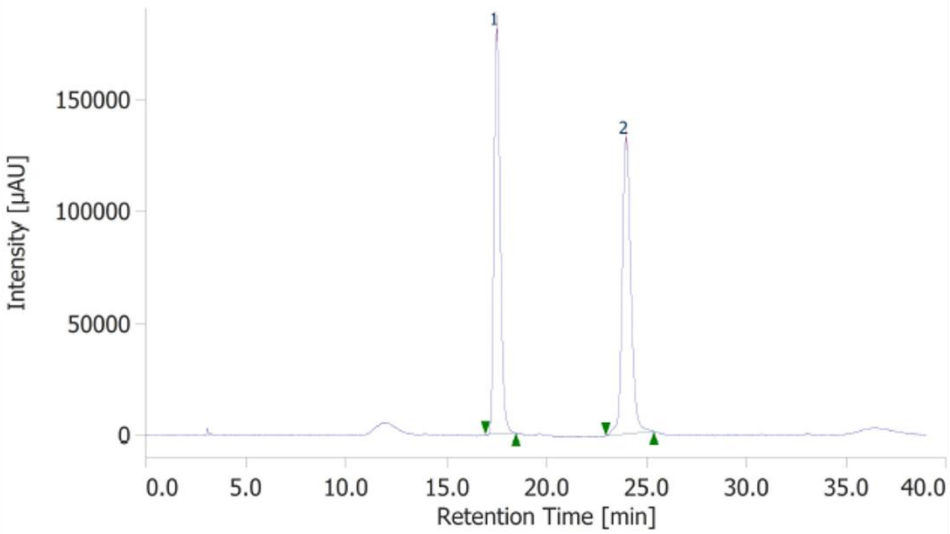


#	tR [min]	Area%
1	13.620	97.233
2	17.460	2.767

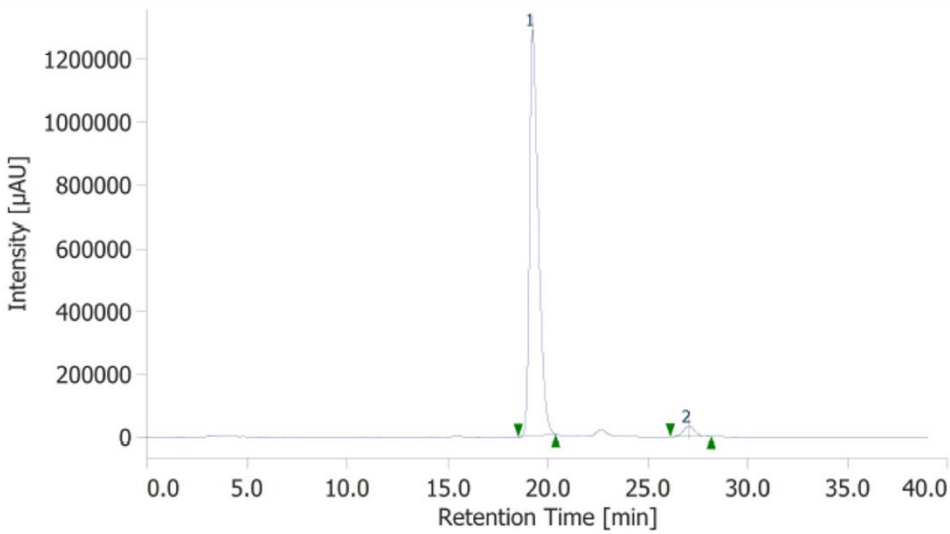
(S,E)-N,1-diphenyl-3-styryl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3ak)



General Procedure using compound **1a** (70.2 mg, 0.24 mmol) and **2k** (37.8 mg, 0.2 mmol) and purification by silica gel column chromatography (DCM/hexane = 3/1) afforded **3ak** as a colorless solid (39.1 mg, 47%). **^{1}H NMR** ($CDCl_3$, 599.67 MHz) δ 8.14 (d, *J* = 7.5 Hz, 2H), 7.89 (d, *J* = 15.8 Hz, 1H), 7.64-7.57 (m, 6H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.38-7.33 (m, 2H), 7.33-7.29 (m, 1H), 7.15 (t, *J* = 6.9 Hz, 1H), 7.12-7.06 (m, 3H), 6.91-6.85 (m, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 149.41 MHz) δ 160.2, 142.9, 141.3, 139.3, 135.7, 134.5, 133.4, 129.3, 129.2, 128.8, 128.5, 127.9, 127.0, 126.4, 125.4, 123.6, 122.8, 111.7; three aromatic signals were missing probably due to overlapping and broadened signals. **HPLC** (chiral column: DAICEL CHIRALPAK IA; solvent: hexane/2-propanol = 95/5; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 19.2 (major) and 27.1 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}N_3S^+$: 420.1529; Found 420.1538. **$[\alpha]_D^{23.1}$** = +22.9 (*c* = 0.12, $CHCl_3$). **Rf** 0.35 (DCM/hexane = 3/1).

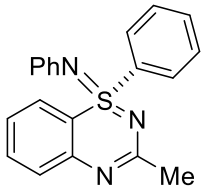


#	tR [min]	Area%
1	17.490	49.745
2	23.967	50.255

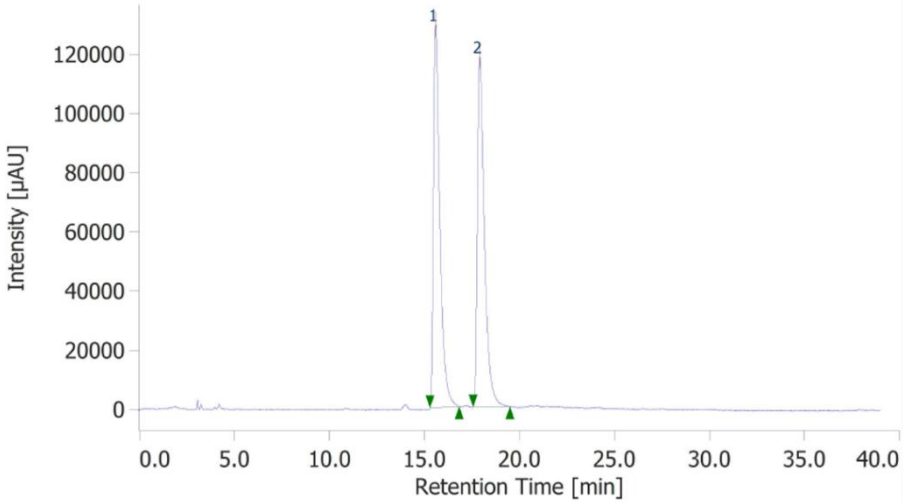


#	tR [min]	Area%
1	19.220	96.885
2	27.050	3.115

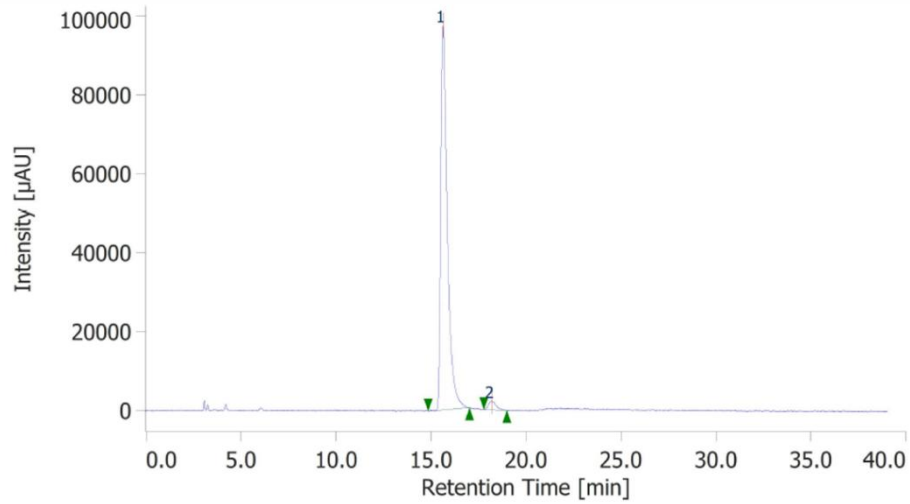
(S)-3-methyl-N,1-diphenyl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3al)



General Procedure using compound **1a** (70.2 mg, 0.24 mmol) and **2l** (20.2 µl, 0.2 mmol) and purification by silica gel column chromatography (hexane/AcOEt = 2/1) afforded **3al** as a colorless solid (45.0 mg, 68%).**^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.10 (d, *J* = 7.9 Hz, 2H), 7.64-7.59 (m, 3H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.45-7.35 (m,, 2H), 7.18-7.08 (m, 3H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 2H), 2.49 (s, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 164.0, 149.4, 143.1, 141.2, 134.2, 133.2, 129.1, 129.0, 128.3, 127.1, 125.9, 125.2, 123.5, 122.5, 110.2, 27.9 **HPLC** (chiral column: DAICEL CHIRALPAK IA; solvent: hexane/2-propanol = 95/5; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 15.6 (major) and 18.2 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}N_3S^+$: 332.1216; Found 332.1219. **$[\alpha]_D^{22.8}$** = +232.2 (*c* = 0.25, $CHCl_3$). **Rf** 0.14 (DCM/hexane = 3/1).

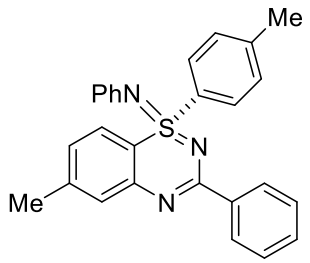


#	tR [min]	Area%
1	15.590	49.833
2	17.917	50.167

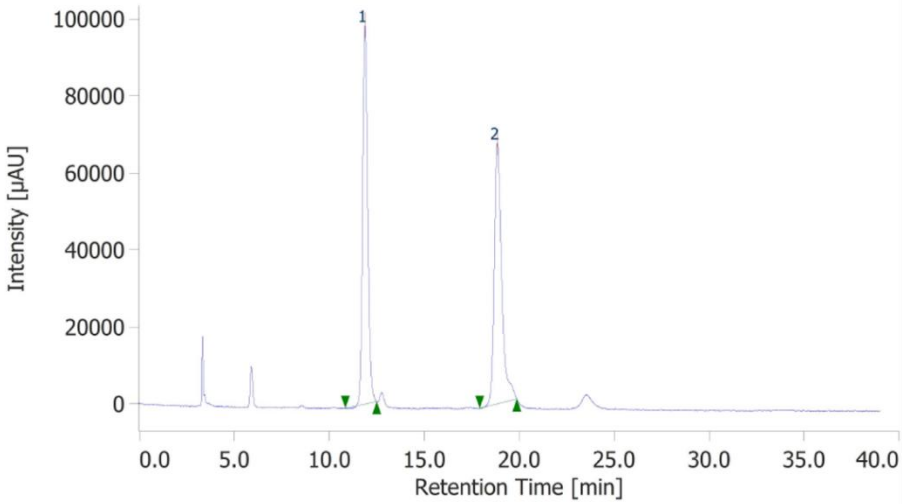


#	tR [min]	Area%
1	15.630	97.384
2	18.203	2.616

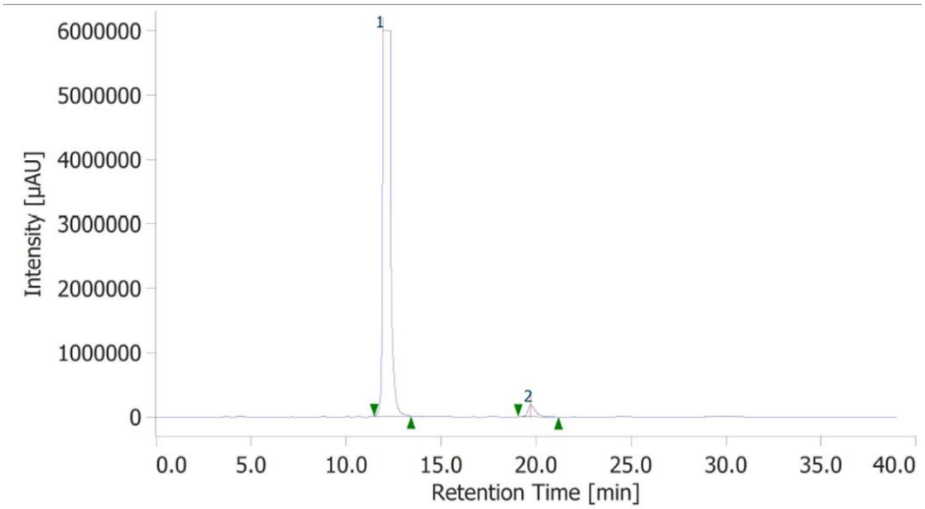
(S)-6-methyl-N,3-diphenyl-1-(p-tolyl)-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3bb)



General Procedure using compound **1b** (76.9 mg, 0.24 mmol) and **2b** (32.6 mg, 0.20 mmol) and purification by silica gel column chromatography (hexane/AcOEt = 10/1) afforded **3bb** as a colorless solid (62.3 mg, 74%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.45-8.39 (m, 2H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.51-7.42 (m, 3H), 7.40-7.33 (m, 4H), 7.09-7.03 (m, 2H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.90-6.82 (3H, m), 2.44 (s, 3H), 2.36 (s, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 159.9, 149.9, 144.9, 144.0, 143.5, 138.9, 138.1, 130.6, 129.7, 128.9, 128.3, 128.2, 128.0, 127.8, 127.5, 124.9, 123.5, 122.2, 108.3, 21.6, 21.4. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 11.9 (major) and 19.7 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}N_3S^+$: 422.1685; Found 422.1682. **$[\alpha]_D^{22.9}$** = +133.6 (*c* = 0.50, $CHCl_3$). **Rf** 0.23 (DCM/hexane = 3/1).

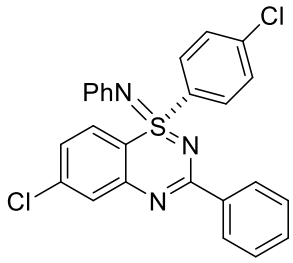


#	tR [min]	Area%
1	11.880	49.392
2	18.843	50.608

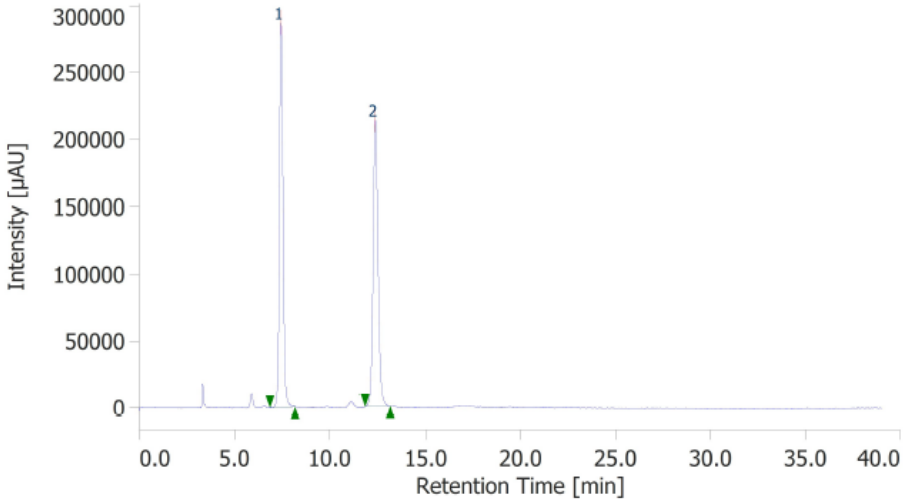


#	tR [min]	Area%
1	11.920	97.242
2	19.717	2.758

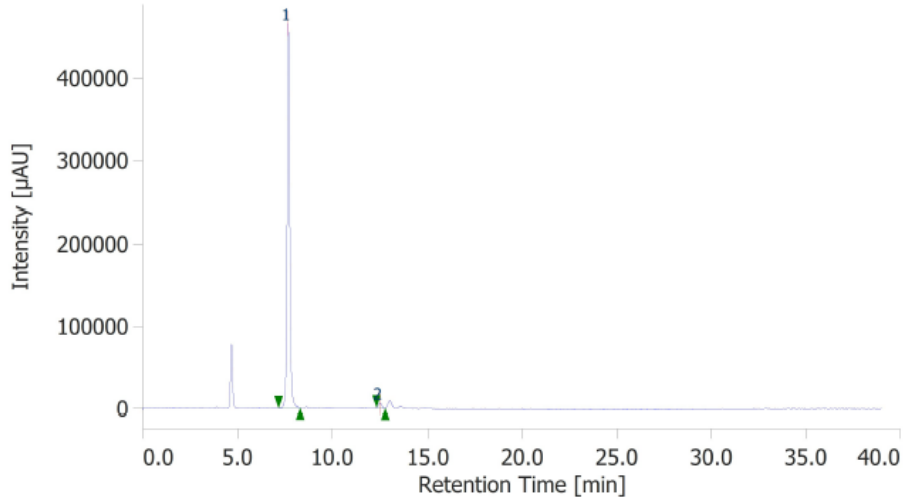
(S)-6-chloro-1-(4-chlorophenyl)-N,3-diphenyl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3cb)



General Procedure using compound **1c** (86.7 mg, 0.24 mmol) and **2b** (32.6 mg, 0.20 mmol) and purification by silica gel column chromatography (hexane/AcOEt = 40/1) afforded **3cb** as a colorless solid (73.8 mg, 80%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.43-8.38 (m, 2H), 8.09-8.04 (m, 2H), 7.58-7.55 (m, 3H), 7.53-7.49 (m, 1H), 7.49-7.45 (m, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.13 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.11-7.07 (2H, m), 6.93-6.89 (m, 1H), 6.86-6.82 (m, 2H).**^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 160.7, 151.2, 142.5, 140.3, 140.2, 139.8, 137.4, 131.2, 129.8, 129.5, 129.2, 128.5, 128.2, 127.7, 126.6, 126.4, 123.5, 123.0, 109.0. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 7.7 (major) and 12.5 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{18}Cl_2N_3S^+$: 462.0593; Found 462.0599. **$[\alpha]_D^{22.9}$** = +107.5 (*c* = 0.50, $CHCl_3$). **Rf** 0.43 (DCM/hexane = 3/1).

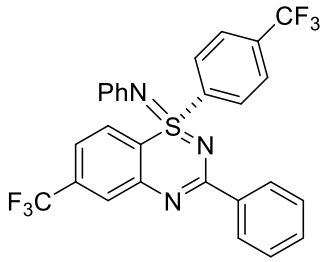


#	tR [min]	Area%
1	7.463	49.756
2	12.350	50.244

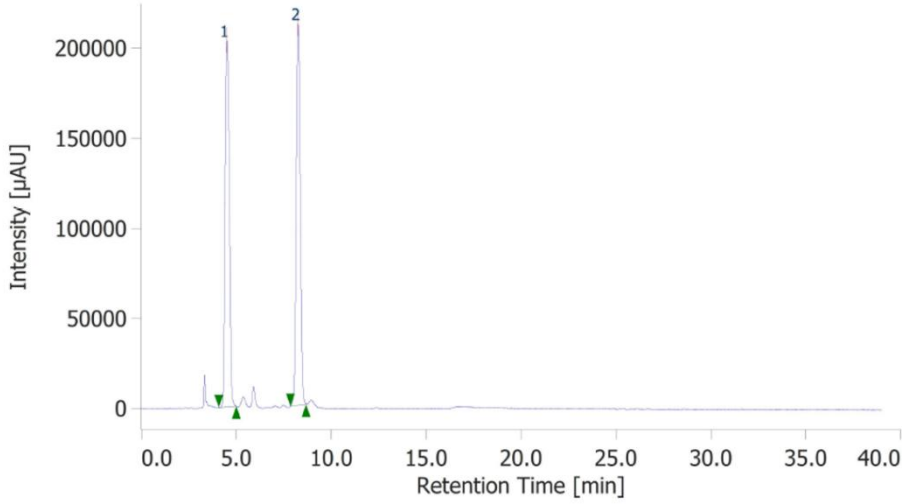


#	tR [min]	Area%
1	7.697	98.523
2	12.470	1.477

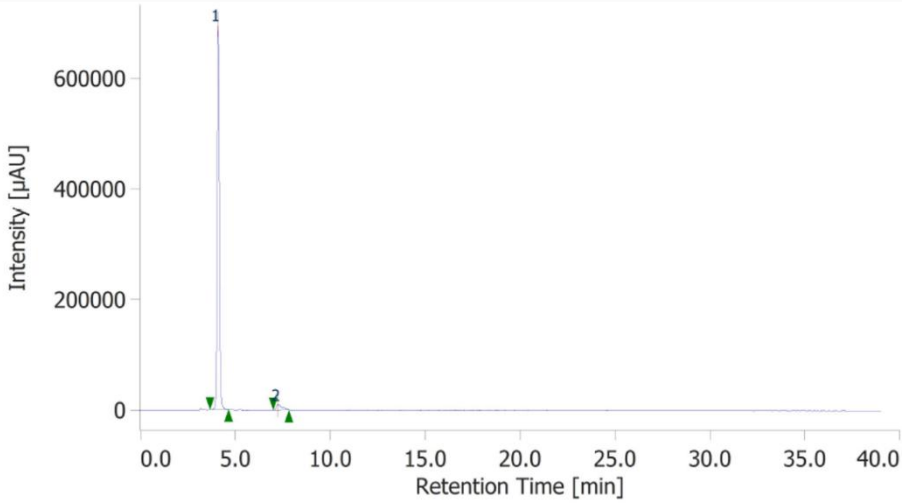
(S)-N,3-diphenyl-6-(trifluoromethyl)-1-(4-(trifluoromethyl)phenyl)-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3db)



General Procedure using compound **1d** (102.8 mg, 0.24 mmol) and **2b** (32.6 mg, 0.20 mmol) and purification by silica gel column chromatography (hexane/AcOEt = 40/1) afforded **3db** as a colorless solid (93.8 mg, 89%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.46-8.40 (m, 2H), 8.29 (d, *J* = 8.6 Hz, 2H), 7.91-7.84 (m, 3H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.55-7.51 (m, 1H), 7.51-7.46 (m, 2H), 7.38 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.14-7.09 (m, 2H), 6.96-6.92 (m, 1H), 6.89-6.84 (m, 2H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 160.9, 150.5, 144.5, 142.1, 137.1, 136.1 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 135.1 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 131.5, 129.3, 129.1, 128.6, 128.3, 126.5 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 126.2, 126.1 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 123.6, 123.4, 123.0 (q, $^1J_{C\text{-}F}$ = 273.6 Hz), 123.0 (q, $^1J_{C\text{-}F}$ = 273.6 Hz), 122.9 (q, $^3J_{C\text{-}F}$ = 3.4 Hz), 113.2. **^{19}F NMR** ($CDCl_3$, 564.67MHz) δ -63.2, -63.8. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 4.1 (major) and 7.3 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{18}F_6N_3S^+$: 530.1120; Found 530.1122. **$[\alpha]_D^{22.9}$** = +66.5 (*c* = 0.50, $CHCl_3$). **Rf** 0.43 (DCM/hexane = 3/1).

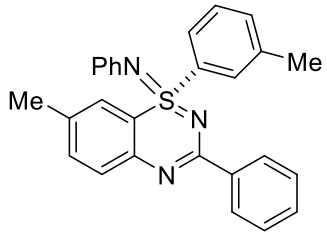


#	tR [min]	Area%
1	4.513	50.482
2	8.263	49.518

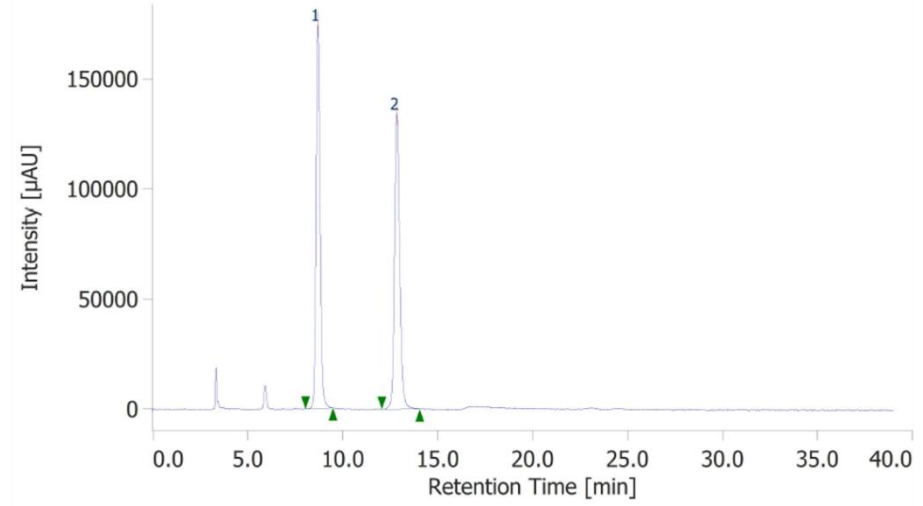


#	tR [min]	Area%
1	4.100	96.313
2	7.263	3.687

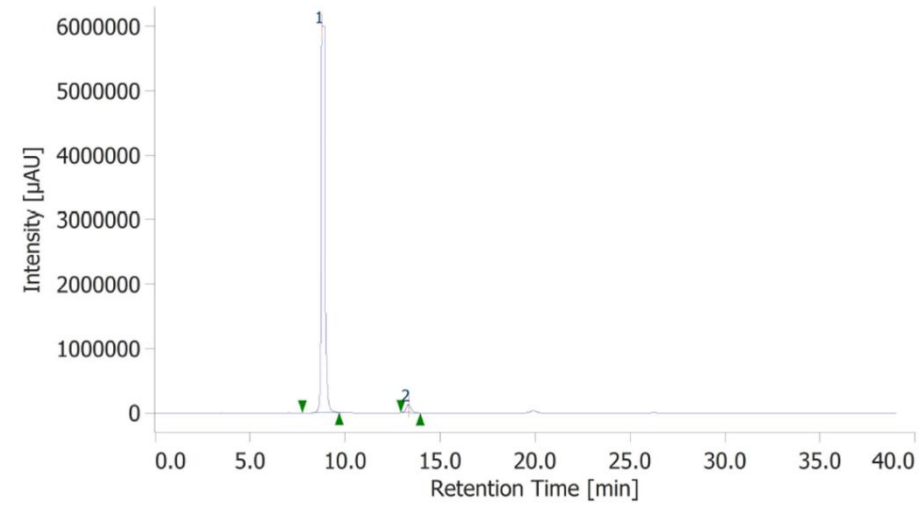
(S)-7-methyl-N,3-diphenyl-1-(m-tolyl)-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3eb)



General Procedure using compound **1e** (76.9 mg, 0.24 mmol) and **2b** (32.6 mg, 0.20 mmol) and purification by silica gel column chromatography (hexane/AcOEt = 40/1) afforded **3eb** as a colorless solid (70.6 mg, 84%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.44-8.37 (m, 2H), 7.95 (d, *J* = 7.9, 1H), 7.93 (s, 1H), 7.50-7.42 (m, 5H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.23 (s, 1H), 7.10-7.04 (m, 2H), 6.89-6.83 (m, 3H), 2.45 (s, 3H), 2.27 (s, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 159.1, 147.8, 143.4, 141.5, 139.4, 138.0, 136.2, 135.6, 133.9, 130.5, 129.0, 128.9, 128.5, 128.3, 128.0, 127.9, 125.6, 124.3, 123.4, 122.2, 110.5, 21.4, 21.0. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 8.8 (major) and 13.3 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}N_3S^+$: 422.1685; Found 422.1684. **$[\alpha]_D^{22.9}$** = +146.5 (*c* = 0.50, $CHCl_3$). **Rf** 0.30 (DCM/hexane = 3/1).

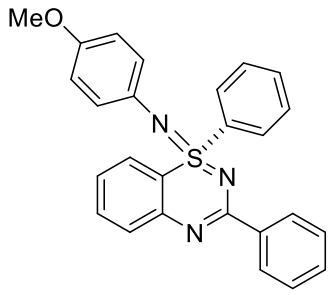


#	tR [min]	Area%
1	8.693	49.789
2	12.850	50.211

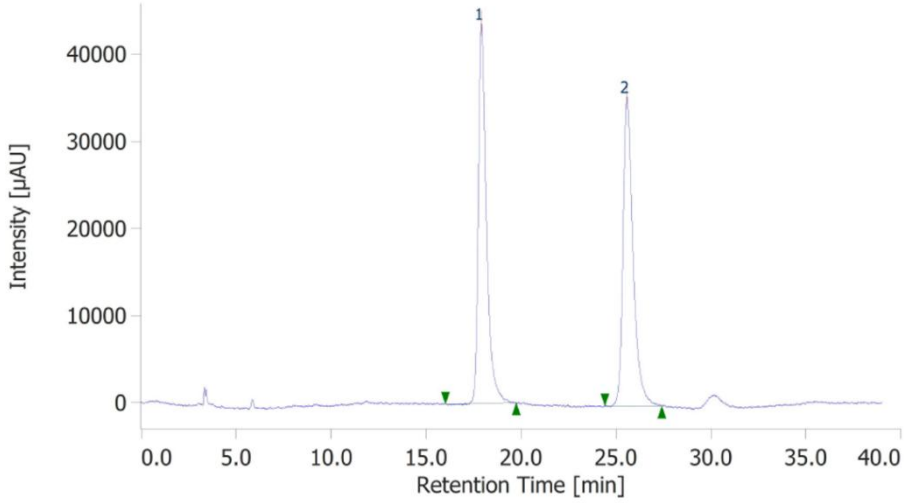


#	tR [min]	Area%
1	8.767	97.243
2	13.323	2.757

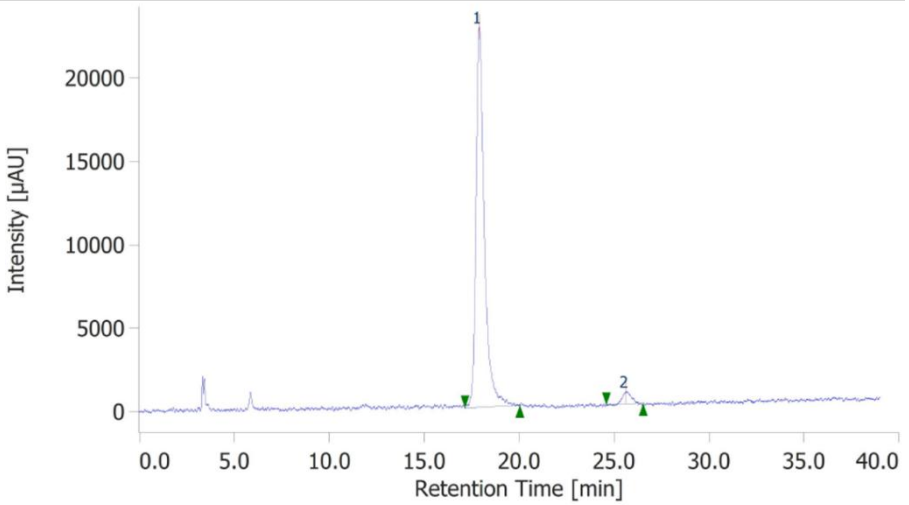
(S)-N-(4-methoxyphenyl)-1,3-diphenyl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3fb)



General Procedure using compound **1f** (77.4 mg, 0.24 mmol) and **2b** (32.6 mg, 0.20 mmol) and purification by silica gel column chromatography (hexane/DCM= 1/1) afforded **3fb** as a colorless solid (24.9 mg, 30%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ δ 8.43 (d, *J* = 5.5 Hz, 2H), 8.15 (*J* = 7.2 Hz, 2H), 7.66-7.56 (m, 3H), 7.56-7.51 (m, 2H), 7.51-7.41 (m, 4H), 7.22-7.13 (m, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 3.65 (s, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 160.0, 155.4, 150.1, 141.5, 138.1, 136.0, 134.1, 133.1, 130.8, 129.2, 128.5, 128.3, 128.2, 126.0, 125.3, 124.8, 114.4, 112.8, 111.1, 55.3. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 17.9 (major) and 25.6 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}N_3OS^+$: 424.1478; Found 424.1478. **$[\alpha]_D^{22.9}$** = +633.8 (*c* = 0.17, $CHCl_3$). **Rf** 0.13 (hexane/DCM= 1/3).

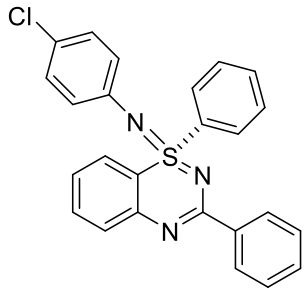


#	tR [min]	Area%
1	17.917	49.739
2	25.577	50.261

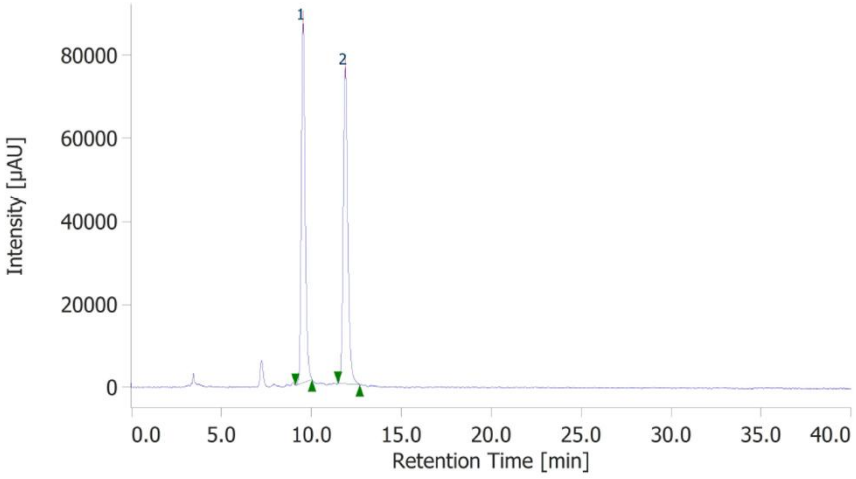


#	tR [min]	Area%
1	17.897	96.505
2	25.637	3.495

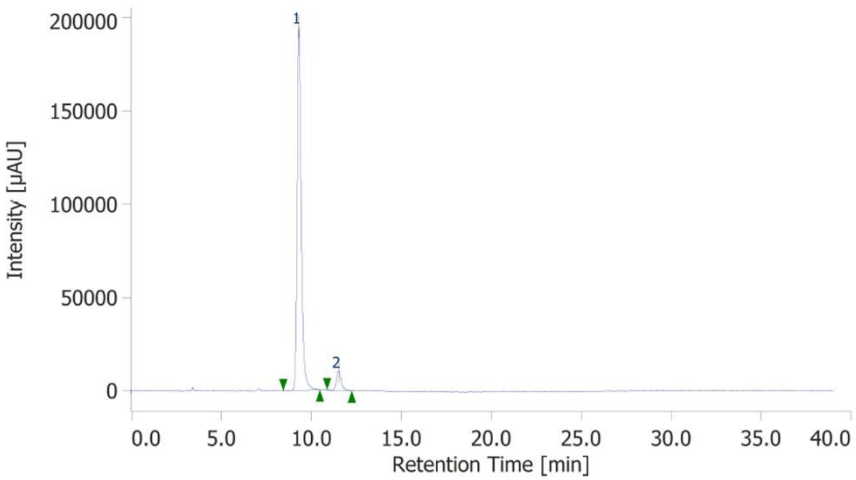
(S)-N-(4-chlorophenyl)-1,3-diphenyl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3gb)



General Procedure using compound **1g** (78.4 mg, 0.24 mmol) and **2b** (32.6 mg, 0.20 mmol) and purification by silica gel column chromatography (hexane/AcOEt = 10/1) afforded **3gb** as a colorless solid (29.7 mg, 35%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.44-8.40 (m, 2H), 8.15-8.12 (m, 2H), 7.64-7.53 (m, 5H), 7.51-7.42 (m, 4H), 7.21-7.16 (m, 1H), 7.05-6.99 (m, 2H), 6.81-6.75 (m, 2H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 160.0, 150.0, 142.0, 141.3, 137.8, 134.3, 133.3, 131.0, 129.3, 129.1, 128.4, 128.4, 128.2, 127.9, 126.2, 125.1, 124.8, 110.5; one aromatic signal was 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 254 nm): t_R = 9.3 (major) and 11.5 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}N_3SCl^+$: 428.0983; Found 428.0970. **$[\alpha]_D^{22.7}$** = +88.2 (*c* = 0.20, $CHCl_3$). **Rf** 0.45 (hexane/EtOAc = 5/1).

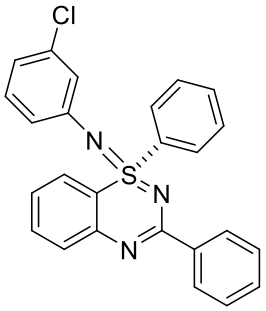


#	tR [min]	Area%
1	9.543	49.073
2	11.887	50.927

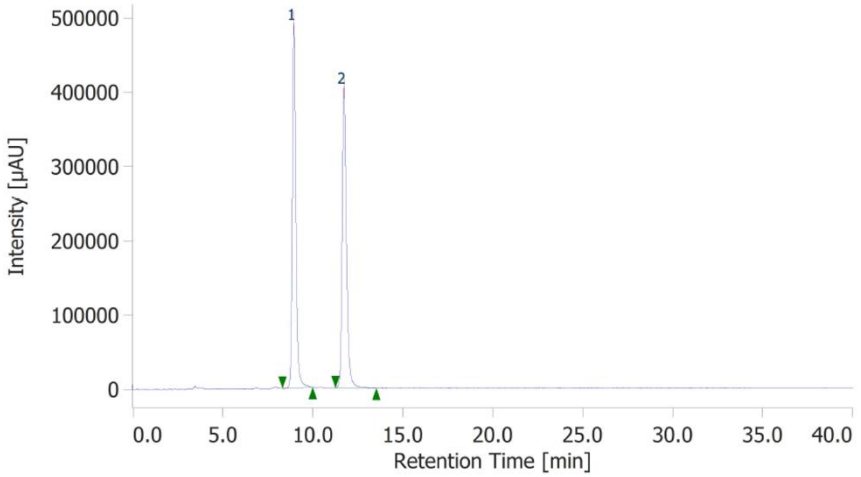


#	tR [min]	Area%
1	9.313	94.221
2	11.517	5.779

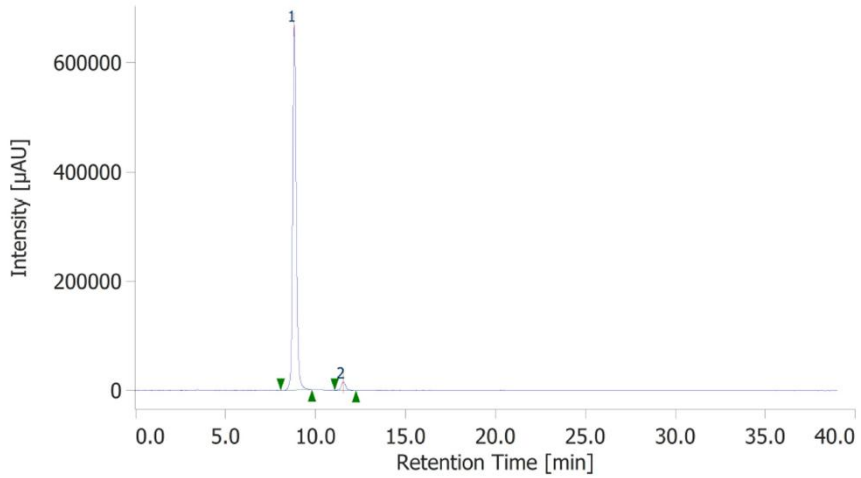
(S)-N-(3-chlorophenyl)-1,3-diphenyl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3hb)



General Procedure using compound **1h** (78.4 mg, 0.24 mmol) and **2b** (32.6 mg, 0.20 mmol) and purification by silica gel column chromatography (hexane/AcOEt = 10/1) afforded **3hb** as a colorless solid (69.1 mg, 81%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.46-8.41 (m, 2H), 8.16-8.11 (m, 2H), 7.67-7.53 (m, 5H), 7.53-7.44 (m, 4H), 7.22-7.18 (m, 1H), 7.01 (t, *J* = 2.0 Hz, 1H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.88-6.83 (m, 1H), 6.63-6.59 (m, 1H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 159.7, 149.8, 144.8, 141.3, 137.8, 134.4, 134.3, 133.3, 130.9, 129.9, 129.2, 128.4, 128.4, 128.3, 128.2, 126.3, 125.1, 124.6, 122.6, 120.8, 110.4. **HPLC** (chiral column: DAICEL CHIRALPAK IF; solvent: hexane/2-propanol = 49/1; flow rate: 1.0 mL/min; detection: at 254 nm): t_R = 8.8 (major) and 11.5 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}N_3SCl^+$: 428.0983; Found 428.0978. **$[\alpha]_D^{22.8}$** = +86.7 (*c* = 0.50, $CHCl_3$). **Rf** 0.45 (hexane/EtOAc = 5/1).

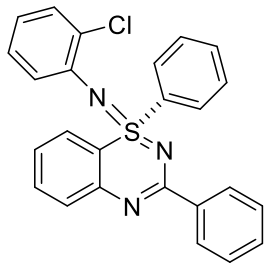


#	tR [min]	Area%
1	8.947	49.991
2	11.730	50.009

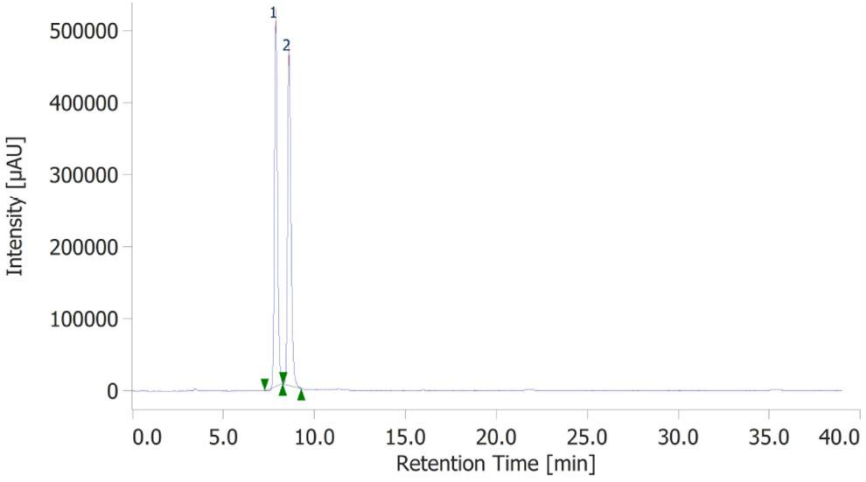


#	tR [min]	Area%
1	8.820	97.094
2	11.543	2.906

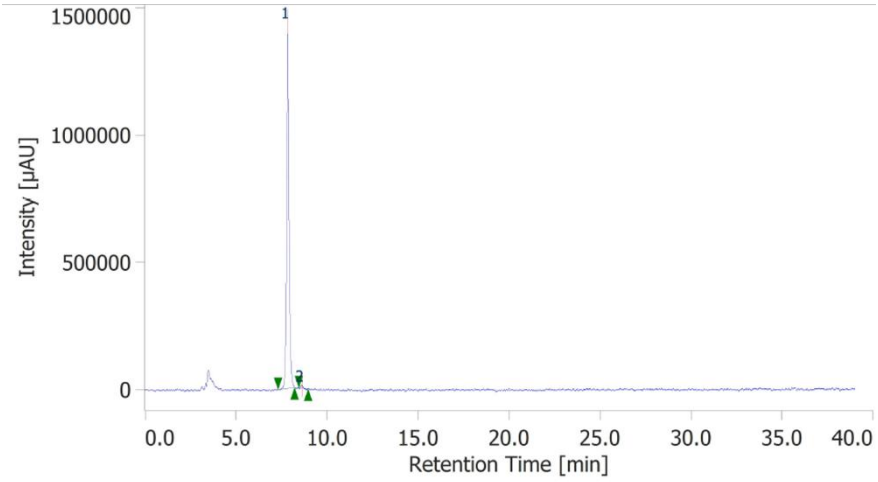
(S)-N-(2-chlorophenyl)-1,3-diphenyl-1l6-benzo[e][1,2,4]thiadiazin-1-imine (3ib)



General Procedure using compound **1i** (78.4 mg, 0.24 mmol) and **2b** (32.6 mg, 0.20 mmol) and purification by silica gel column chromatography (hexane/AcOEt = 10/1) afforded **3ib** as a colorless solid (67.3 mg, 79%). **^{1}H NMR** ($CDCl_3$, 600.17 MHz) δ 8.51-8.44 (m, 2H), 8.32-8.22 (m, 2H), 7.70-7.58 (m, 3H), 7.58-7.45 (m, 6H), 7.30 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.21-7.13 (m, 1H), 6.84 (td, *J* = 7.6, 1.5 Hz, 1H), 6.80 (td, *J* = 7.6, 1.5 Hz, 1H), 6.68 (dd, *J* = 7.9, 1.5 Hz, 1H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150.92 MHz) δ 159.5, 150.0, 141.7, 140.6, 137.8, 134.4, 133.4, 131.0, 130.0, 130.0, 129.3, 128.7, 128.5, 128.2, 127.2, 126.3, 125.3, 123.3, 122.3, 110.3; one aromatic signal was 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 254 nm): t_R = 7.8 (major) and 8.6 (minor) min. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}N_3SCl^+$: 428.0983; Found 428.0974. **$[\alpha]_D^{22.8}$** = +51.9 (*c* = 0.50, $CHCl_3$). **Rf** 0.45 (hexane/EtOAc = 5/1).



#	tR [min]	Area%
1	7.883	49.584
2	8.610	50.416



#	tR [min]	Area%
1	7.840	99.252
2	8.623	0.748

2-3. Determination of the absolute configuration of 3aa

Single crystal X-ray crystallography of 3aa

A single crystal of **3aa** suitable for X-ray diffraction analysis (XRD) was obtained by recrystallization from pentane/DCE. Measurement was performed on a RIGAKU XtaLAB Synergy-R/Cu system with 1.2 kW PhotonJet-R/Cu microfocus rotating anode using graphite monochromated CuKα radiation source (λ = 1.5418 Å) and HyPix-6000HE detector. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlisPro (Agilent Technologies, 2010). The structures were solved by direct methods with SHELXT 2018/2 and refined by full-matrix least-squares techniques against F^2 with SHELXL-2019/3 by using Olex2 software package. The non-hydrogen atoms were anisotropically refined, and hydrogen atoms were placed using AFIX instructions. The detailed crystallographic data are available as a crystallographic information file (CIF), which is available from CCDC (Deposition Number: 2423806). The ORTEP-3 program was used to draw the molecule structures. The structure and crystal data are shown in **Figure S1** and **Table S1**.

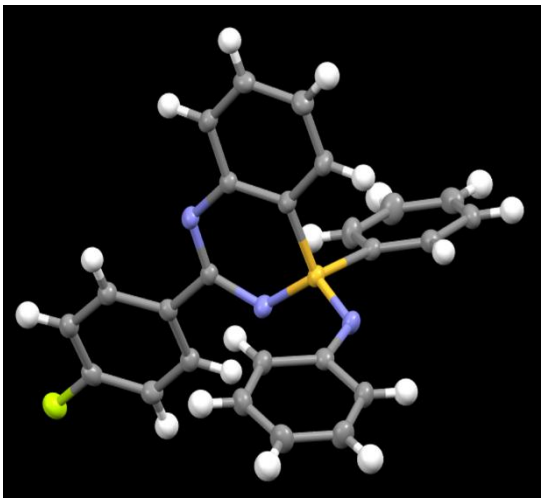


Figure S1. Structure of **3aa**

Table S1. Crystal data and structure refinement for **3aa**

Identification code	am02046_auto	
Empirical formula	C25 H18 F N3 S	
Formula weight	411.48	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 8.40678(5) Å	a= 90°.
	b = 12.62273(9) Å	b= 91.4256(5)°.
	c = 18.65018(10) Å	g = 90°.
Volume	1978.48(2) $Å^3$	
Z	4	
Density (calculated)	1.381 Mg/m^3	
Absorption coefficient	1.667 mm^{-1}	

F(000)	856
Crystal size	0.2 x 0.15 x 0.15 mm^3
Theta range for data collection	2.370 to 78.783°.
Index ranges	-10<=h<=10, -15<=k<=14, -23<=l<=23
Reflections collected	78131
Independent reflections	8270 [R(int) = 0.0403]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.70830
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8270 / 1 / 541
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0955
R indices (all data)	R1 = 0.0362, wR2 = 0.0957
Absolute structure parameter	0.023(11)
Extinction coefficient	n/a
Largest diff. peak and hole	0.720 and -0.457 $e.Å^{-3}$

3. DFT calculations and non-covalent interaction plots.

All DFT calculations and structure optimizations were performed using Gaussian 16 Rev C.02 program package[S5] unless otherwise noted.

Cp*Co(III)-catalyzed C–H activation generally proceed with an assistance of directing groups such as a imine group in sulfondiimines. We initially performed DFT calculations to elucidate a spin state in the transition state and whether N-H or N-aryl group is coordinating to the cobalt center in the transition state. We first prepared 4 transition states that possess μ^1-acetate and NH-coordinating sulfondiimine or NPh-coordinating sulfondiimine on the cobalt center (s_NH, s_NPh for the metallacycle with (*S*)-configuration, r_NH, r_NPh for the metallacycle with (*R*)-configuration). The structures were roughly optimized as the singlet and triplet states at the (U)M06L/def2-SVP[S6] level of theory with the fixed key 6 atoms (Co, C and H to be cleaved, carbonyl C and two O of the carboxylate). These structures were fully optimized to transition state structures (first-order saddle points) at the (U)M06L/def2-SVP level of theory. The vibrational calculations were performed at the optimized geometry to confirm that the obtained structures were the desired transition state structures and to calculate the correction terms for Gibbs free energies. To obtain more accurate electronic energies, single point energies with the optimized geometries were calculated at the (U)M06/def2-TZVPP[S7] level of theory with SMD implicit solvation (solvent = 2-methyl-2-propanol).[S8] The Gibbs free energies are summarized in **Table S2.** In all transition states, the singlet states were more stable than the corresponding triplet states. The singlet s_NH was the most stable, but the differences of Gibbs free energies with the singlet NPh-coordinating structures were not negligible. As all the triplet states showed significantly higher energies than the corresponding singlet states, the following calculations were performed assuming the singlet states.

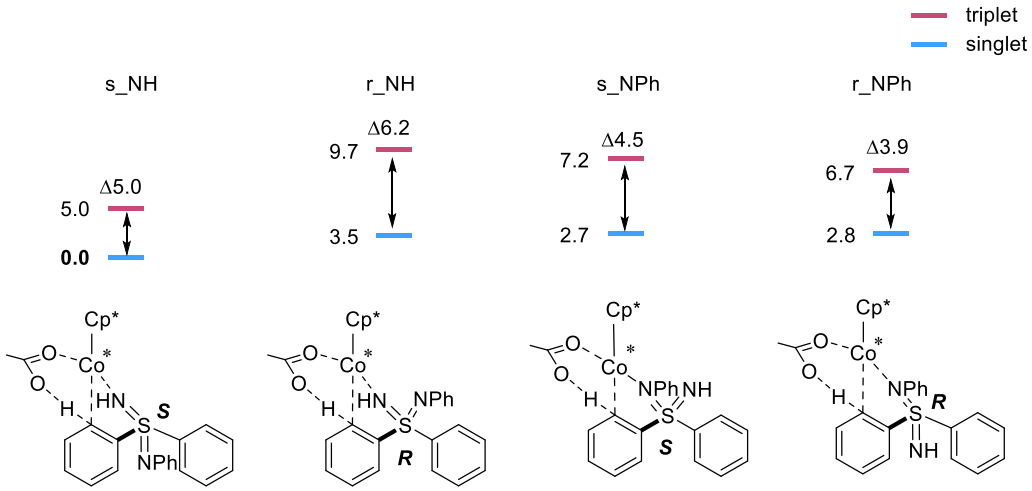


Figure S2. Comparison of transition state Gibbs energies (kcal/mol) of the singlet and triplet states

Table S2. Parameters of TS structures

	EE (M06/def2-TZVPP+SMD(*t* BuOH)) (Hartrees)	Imaginary Frequency (cm^{-1})	G correction term (Hartrees)	G (Hartrees)	Relative G to s_NH (kcal/mol)
singlet_s_NH	-3203.86426685	-1525.0895	0.500237	-3203.36403	0
singlet_r_NH	-3203.85670938	-1436.4002	0.498308	-3203.358401	3.531921
singlet_s_NPh	-3203.86157585	-1443.3729	0.501826	-3203.35975	2.685743
singlet_r_NPh	-3203.86002976	-1436.3116	0.500388	-3203.359642	2.75357
triplet_s_NH	-3203.8485254	-1473.9925	0.492401	-3203.356124	4.960749

triplet_r_NH	-3203.84283027	-1286.1958	0.494282	-3203.348548	9.714846
triplet_s_NPh	-3203.85052069	-1202.8165	0.497972	-3203.352549	7.204543
triplet_r_NPh	-3203.84832575	-1522.0098	0.494951	-3203.353375	6.686182

To reveal the key effects of **A5** on high enantioselectivity in the transition state, we carried out DFT calculation for the asymmetric reaction. We prepared eight initial structures (r1_NH_init, r1_NPh_init, r2_NH_init, r2_NPh_init for the cyclized product with (*R*)-configuration, s1_NH_init, s1_NPh_init, s2_NH_init, s2_NPh_init for the cyclized product with (*S*)-configuration shown in **Figure S3**) that possess a common key core structure near to the transition state for the C–H bond cleavage (optimized as a singlet state near to the first-order saddle point at the M06L/LANL2DZ level of theory,[S9,S10] but not completely converged).

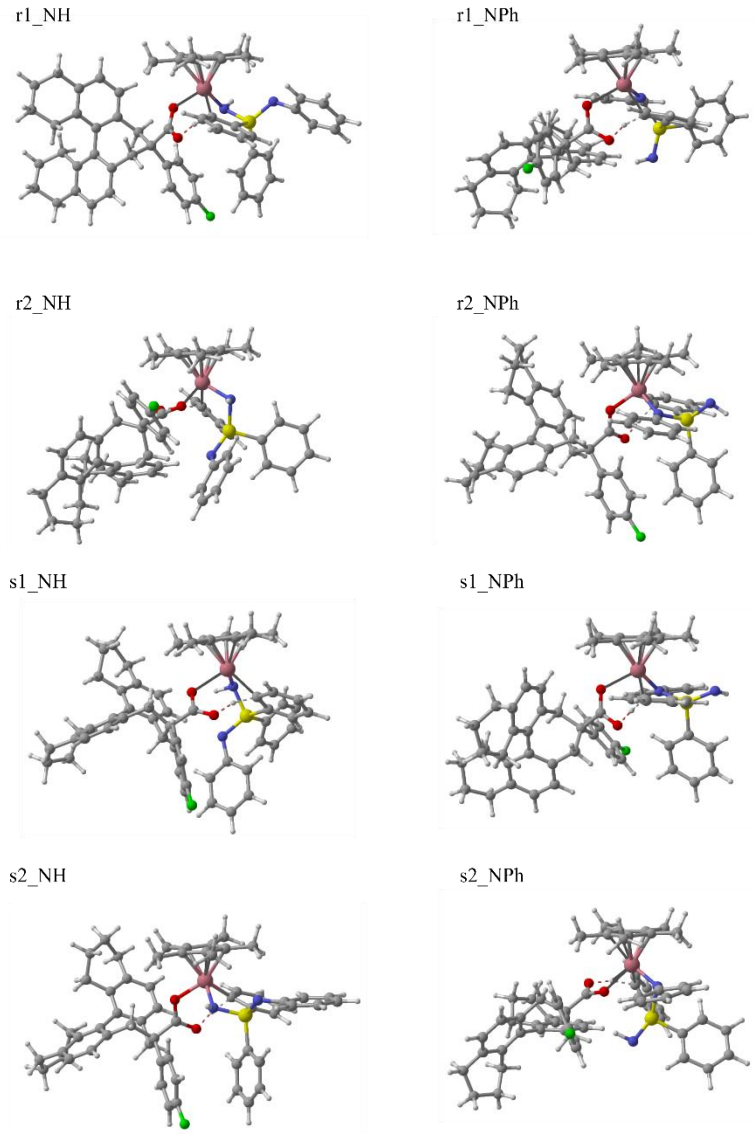


Figure S3. Initial structures for conformation searches

With these initial structures, we performed conformational searches using Grimme's crest 2.12[S11] and xtb 6.6.1[S12] programs. To keep the structures near to the desired transition state rather than local minima, key 6 atoms (Co, C and H to be cleaved, carbonyl C and two O of the carboxylate) were fixed with a force constant = 0.5. The

conformation searches were run at GFN2-xTB level with iMTD-GC algorithm, and the energy threshold was set to 10 kcal/mol for each search. Total 2391 conformers to afford the (*S*)-configuration product and 3013 conformers to afford the (*R*)-configuration product were generated. The conformers obtained from r1_NPh_init, r2_NH_init, s1_NH_init, and s2_NPh_init are 5.0 kcal/mol higher in energy than the most stable conformer obtained from s2_NH_init, and thus only the most stable conformer of each initial structure was used for further calculations. To further reduce the calculation cost, the similar conformers were summarized using cregen tool implemented in crest (ewin 6, rthr 1, ethr 2), and total 19 conformers remained. These structures were partially optimized with fixing key 6 atoms (Co, C and H to be cleaved, two O of the carboxylate) at the M06L/LANL2DZ level of theory (opt = loose, maxcycle = 20). These structures were fully optimized to transition state structures (first-order saddle points) at the M06L/def2-SVP level of theory. The vibrational calculations were performed at the optimized geometry to confirm that the obtained structures were the desired transition state structures and to calculate the correction terms for Gibbs free energies. To obtain more accurate electronic energies, single point energies with the optimized geometries were calculated at the M06/def2-TZVPP level of theory with SMD implicit solvation (solvent = 2-methyl-2-propanol). The calculated free energies of the final 19 transition state structures are summarized in **Table S3** and **S4**.

Based on the calculated free energies, s2_NH_2 was the most plausible transition state structure to give the major *S*-enantiomer (TS_{major1}), and s2_NH_1 afford the second most stable structure (TS_{major2}). s2_NH_3 had very similar structure and Gibs energy that are enough to be regarded as the same as s2_NH_1. Other structures could be negligible. r2_NPh_1 was the most stable structure to afford the minor product with (*R*)-configuration (TS_{minor}), and other structures could be negligible. Thus, we provided the discussion based on s2_NH_2 (TS_{major1}) and s2_NH_1 (TS_{major2}). r2_NPh_1 (TS_{minor}) was the most plasible transition state structures to give the minor (*R*)-enantiomer. For these three structures, IRC calculations were performed at the M06L/def2-SVP level of theory to confirm that they are the desired transition states for C–H bond cleavage. NCI plots were calculated by Multiwfn 3.7[S13] using the wavefunction files (wfx files) generated at the single point energy calculations (M06/def2-TZVPP+SMD(*t*BuOH)), and visualized by VMD 1.9.4 (**Figure 15**).[S14]

Table S3. Parameters of TS structures to afford major *S*-product

	EE (M06/def2-TZVPP+SMD (*t*BuOH)) (Hartrees)	Imaginary Frequency (cm^{-1})	G correction term (Hartrees)	G (Hartrees)	Relative G to s2_NH_2 (kcal/mol)
s1_NH	-4385.35567878	-1502.5	0.933146	-4384.42253278	4.50
s1_NPh_1	-4385.35986930	-1464.52	0.935711	-4384.42415830	3.48
s1_NPh_2	-4385.35751284	-1462.81	0.937081	-4384.42043184	5.82
s1_NPh_3	-4385.35696306	-1445.27	0.934814	-4384.42214906	4.74
s1_NPh_4	-4385.34992871	-1426.63	0.933346	-4384.41658271	8.24
s1_NPh_5	-4385.35377113	-1456.17	0.934992	-4384.41877913	6.86
s2_NH_1 (similar to s2_NH_3)	***-4385.35805015***	***-1455.31***	***0.931495***	***-4384.42655515***	***1.98***
s2_NH_2	***-4385.36412869***	***-1448.92***	***0.934421***	***-4384.42970769***	***0.00***
s2_NH_3	-4385.35805017	-1455.32	0.931495	-4384.42655517	1.98

s2_NPh	-4385.35714304	-1470.98	0.934714	-4384.42242904	4.57

Table S4. Parameters of TS structures to give minor *R*-product

	EE (M06/def2-TZVPP+SMD(*t* BuOH)) (Hartrees)	Imaginary Frequency (cm^{-1})	G correction term (Hartrees)	G (Hartrees)	Relative G to s2_NH_2 (kcal/mol)
r1_NH_1	-4385.35079584	-1487.81	0.931330	-4384.41946584	6.43
r1_NH_2	-4385.34934015	-1445.65	0.931953	-4384.41738715	7.73
r1_NH_3	-4385.34627232	-1434.68	0.931286	-4384.41498632	9.24
r1_NH_4	-4385.34419791	-1433.5	0.931336	-4384.41286191	10.57
r1_NPh	-4385.35745525	-1441.73	0.934678	-4384.42277725	4.35
r2_NH	-4385.35820841	-1509.26	0.934163	-4384.42404541	3.55
r2_NPh_1	***-4385.36036832***	***-1441.6***	***0.934436***	***-4384.42593232***	***2.37***
r2_NPh_2	-4385.35713533	-1466.75	0.934534	-4384.42260133	4.46
r2_NPh_3	-4385.35370708	-1440.37	0.934710	-4384.41899708	6.72

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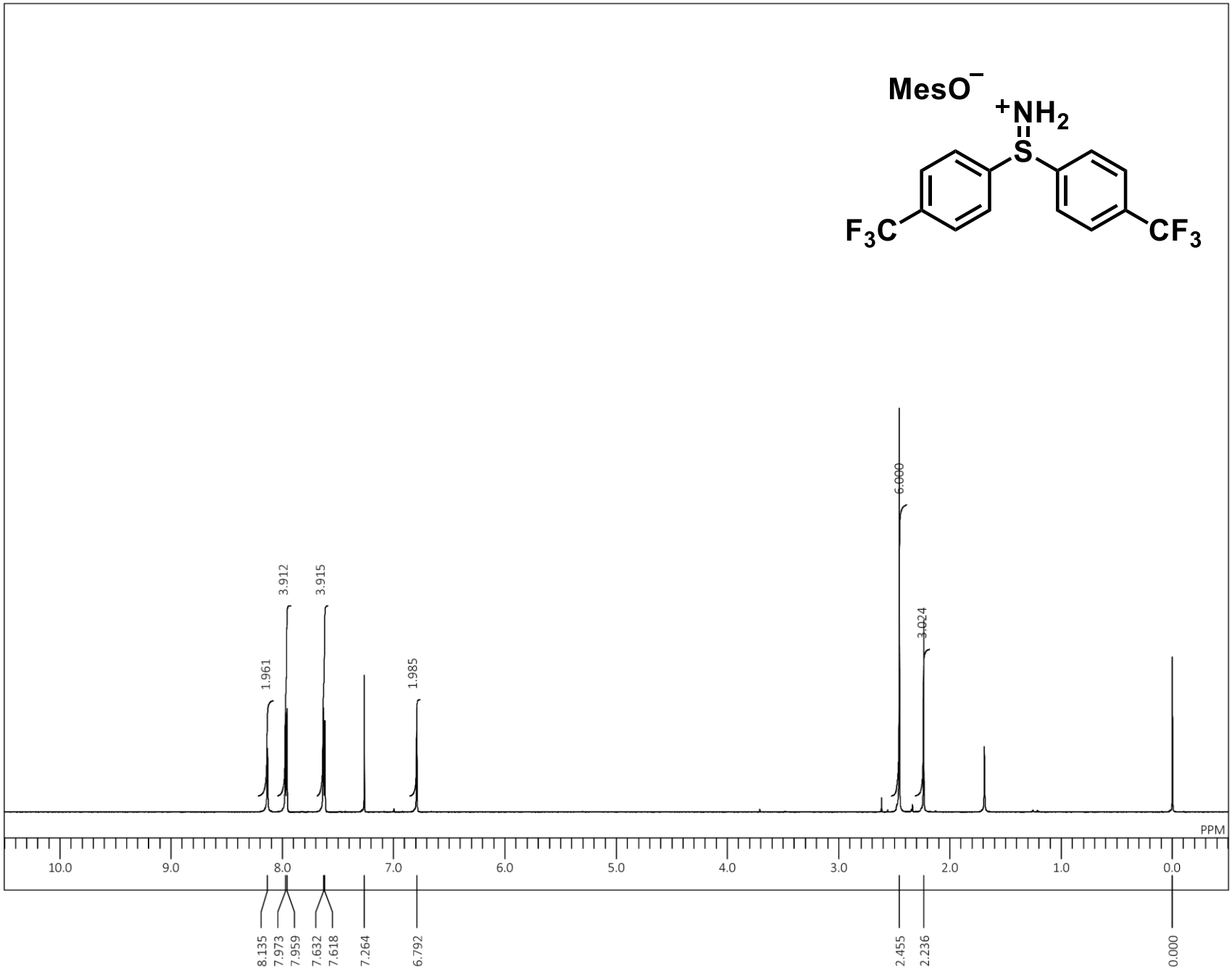
5. NMR Spectra

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of S1



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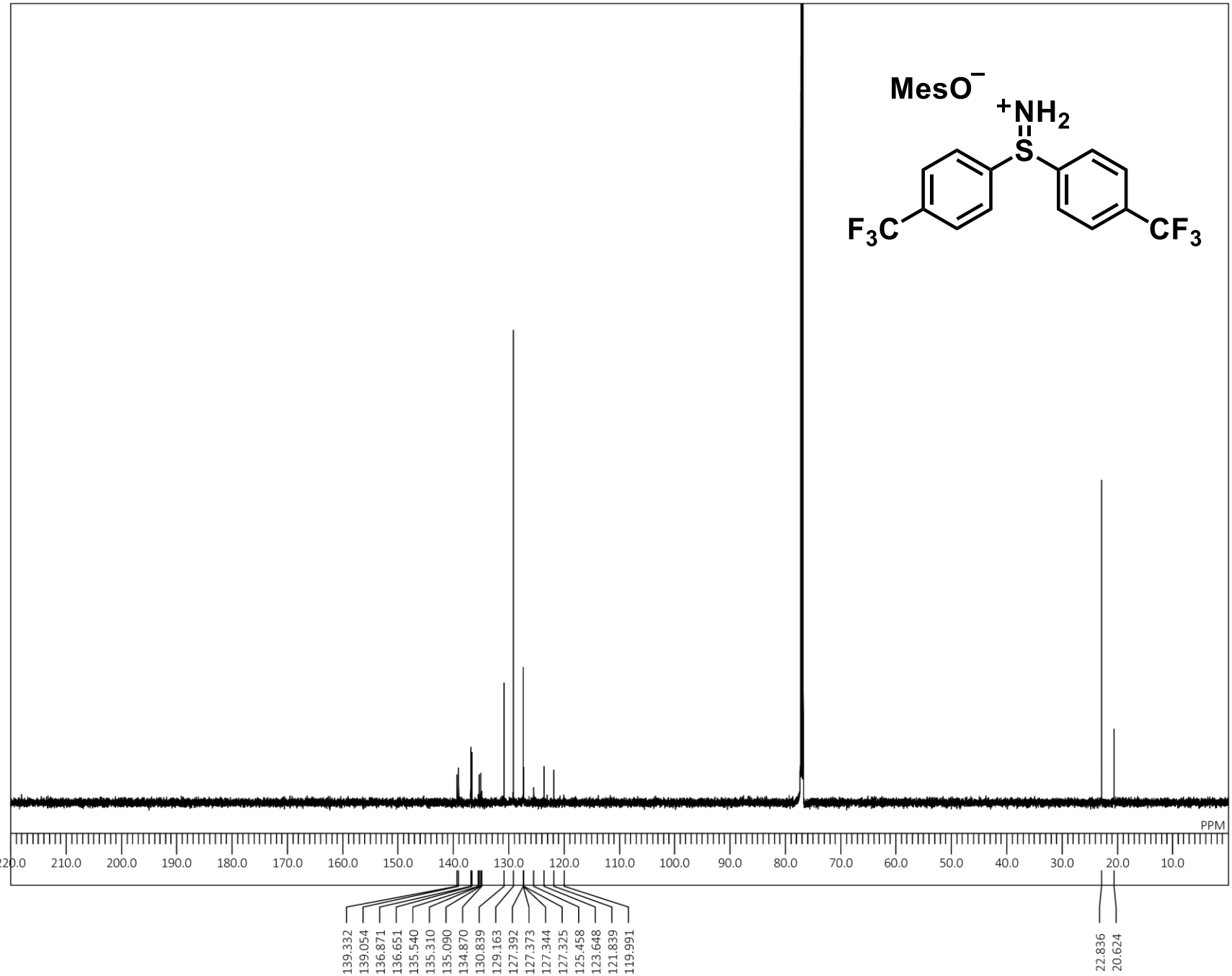
$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of S1



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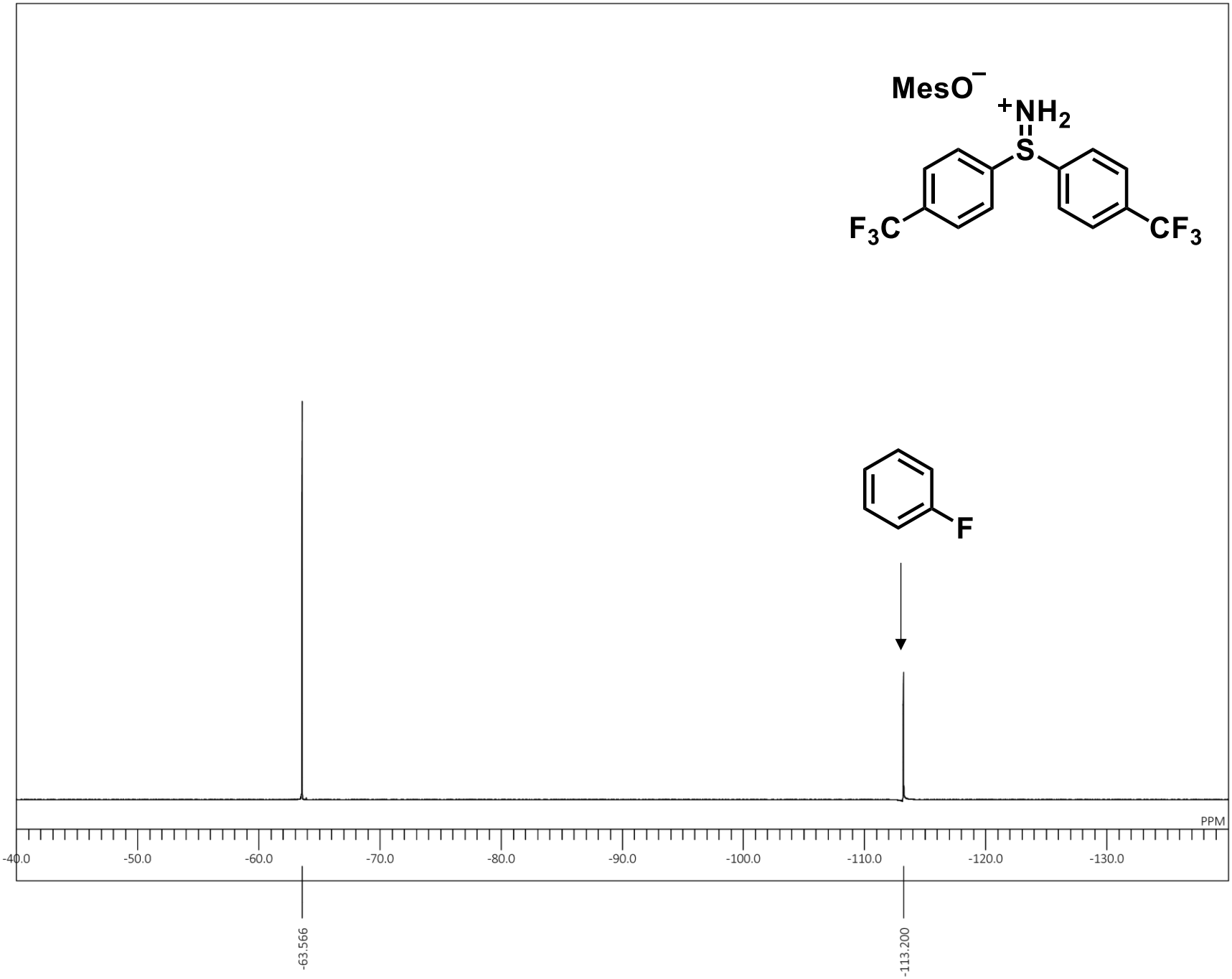
^{19}F NMR (564.67 MHz, $CDCl_3$) spectrum of S1



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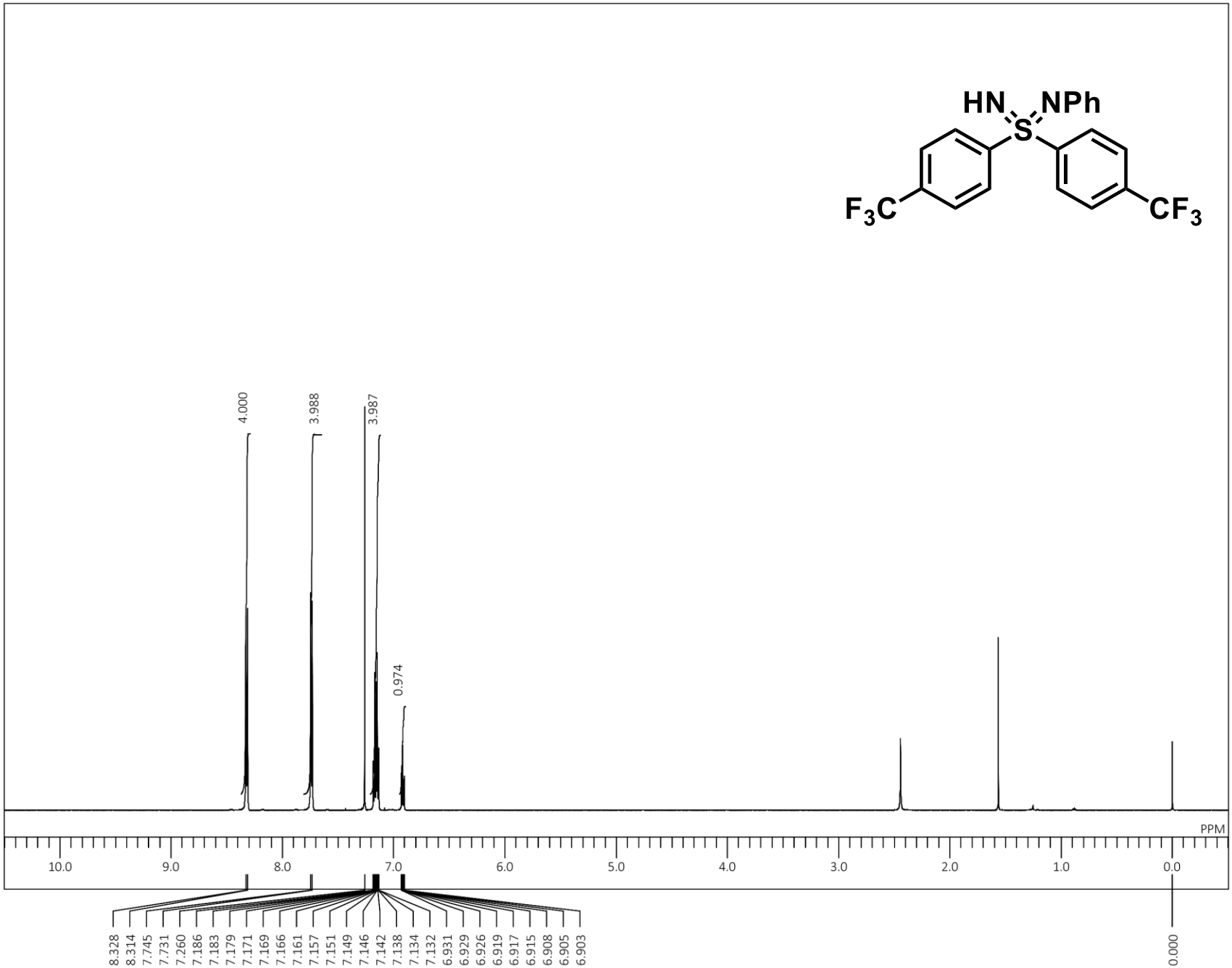
^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 1e



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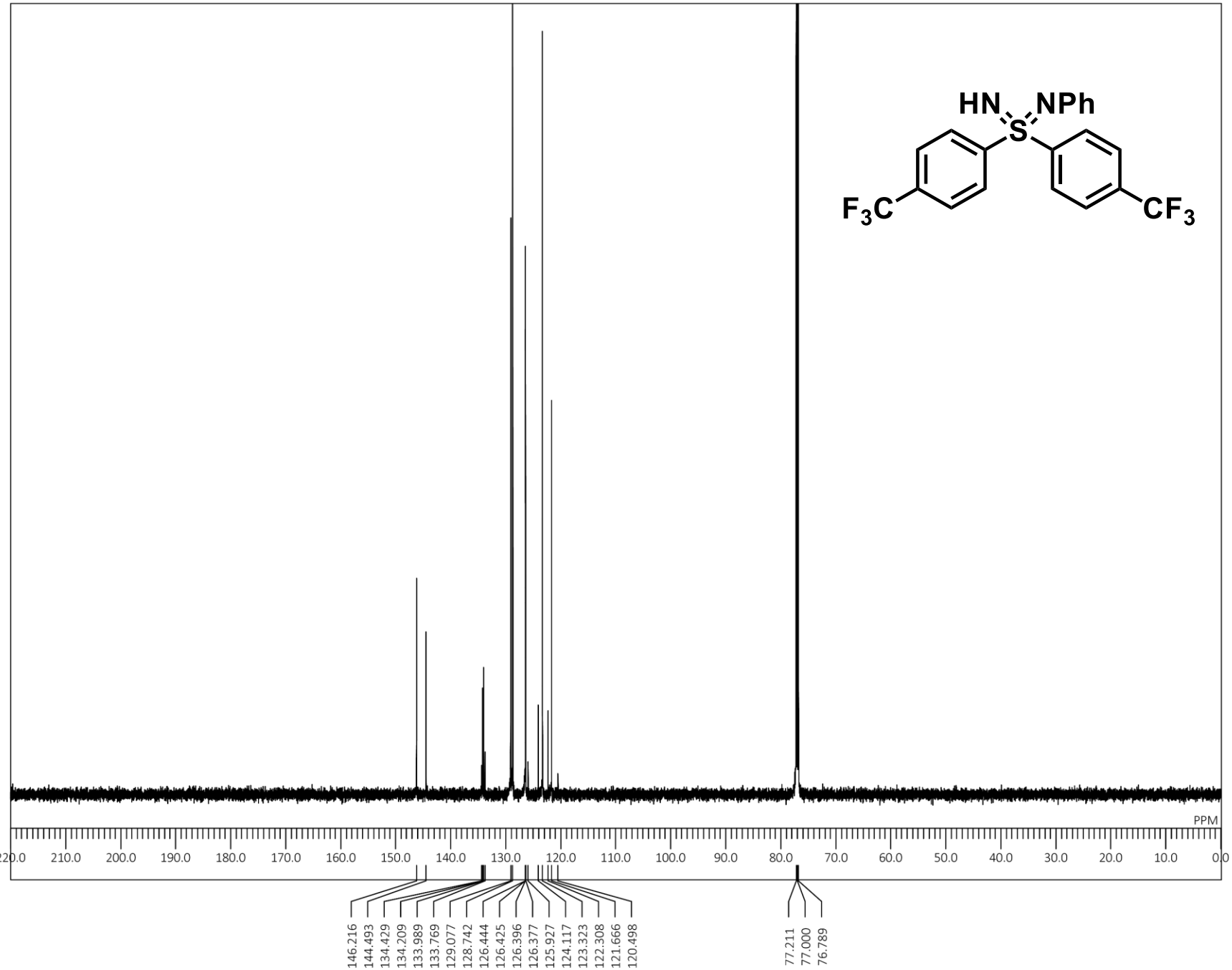
$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 1e



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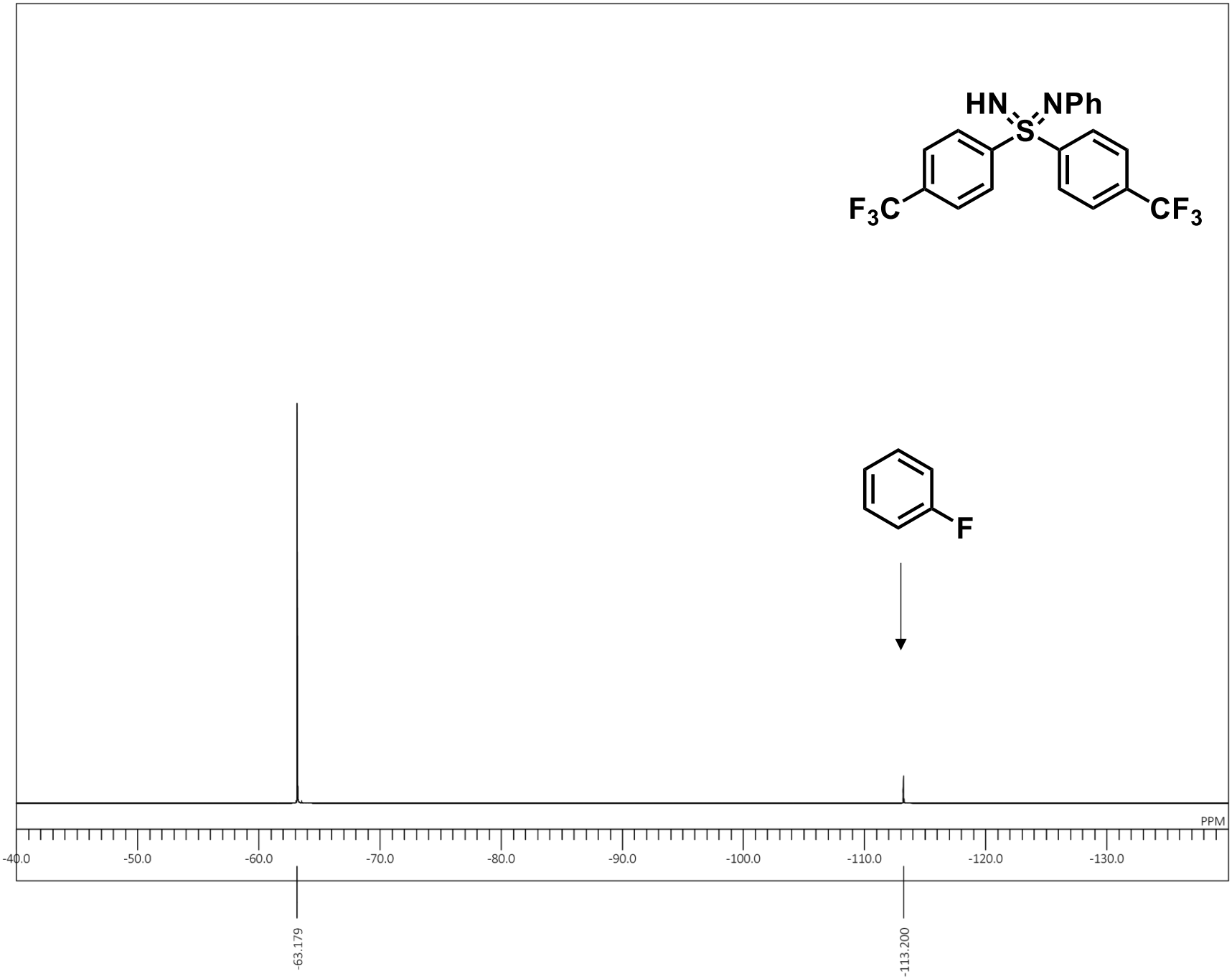
^{19}F NMR (564.67 MHz, $CDCl_3$) spectrum of 1e



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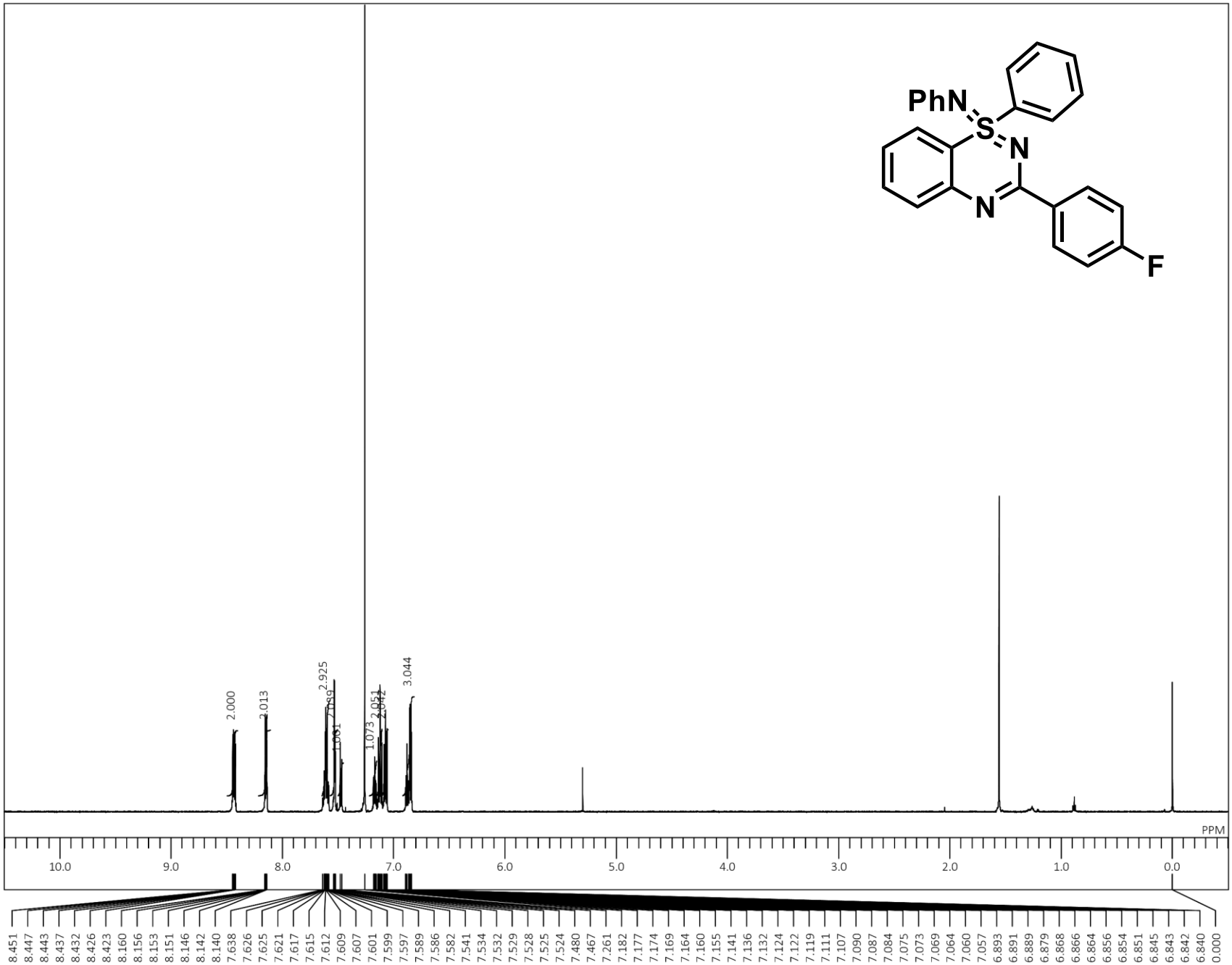
^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3aa



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RGAIN	52

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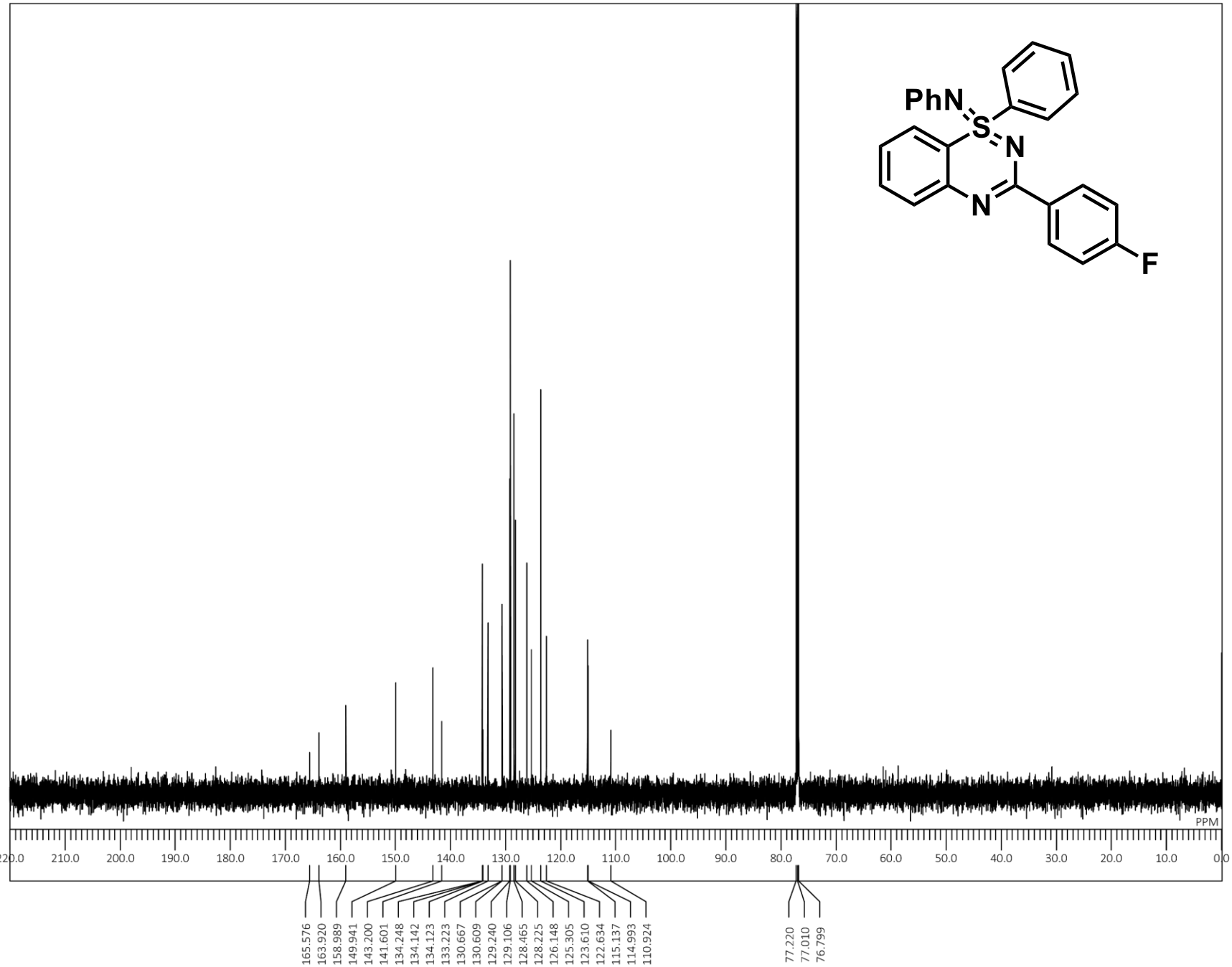
$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3aa



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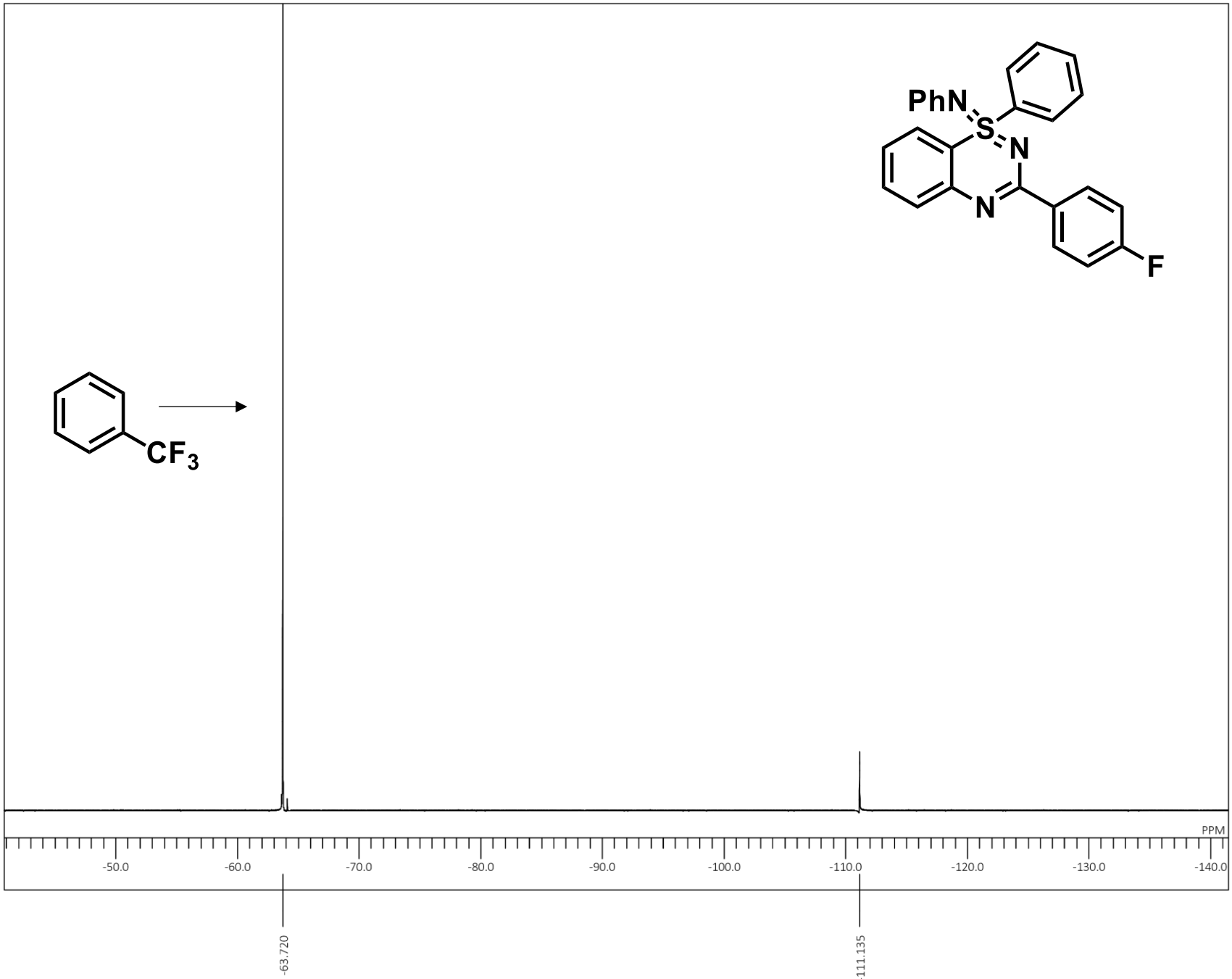
RGAIN	60

^{19}F NMR (564.67 MHz, $CDCl_3$) spectrum of 3aa



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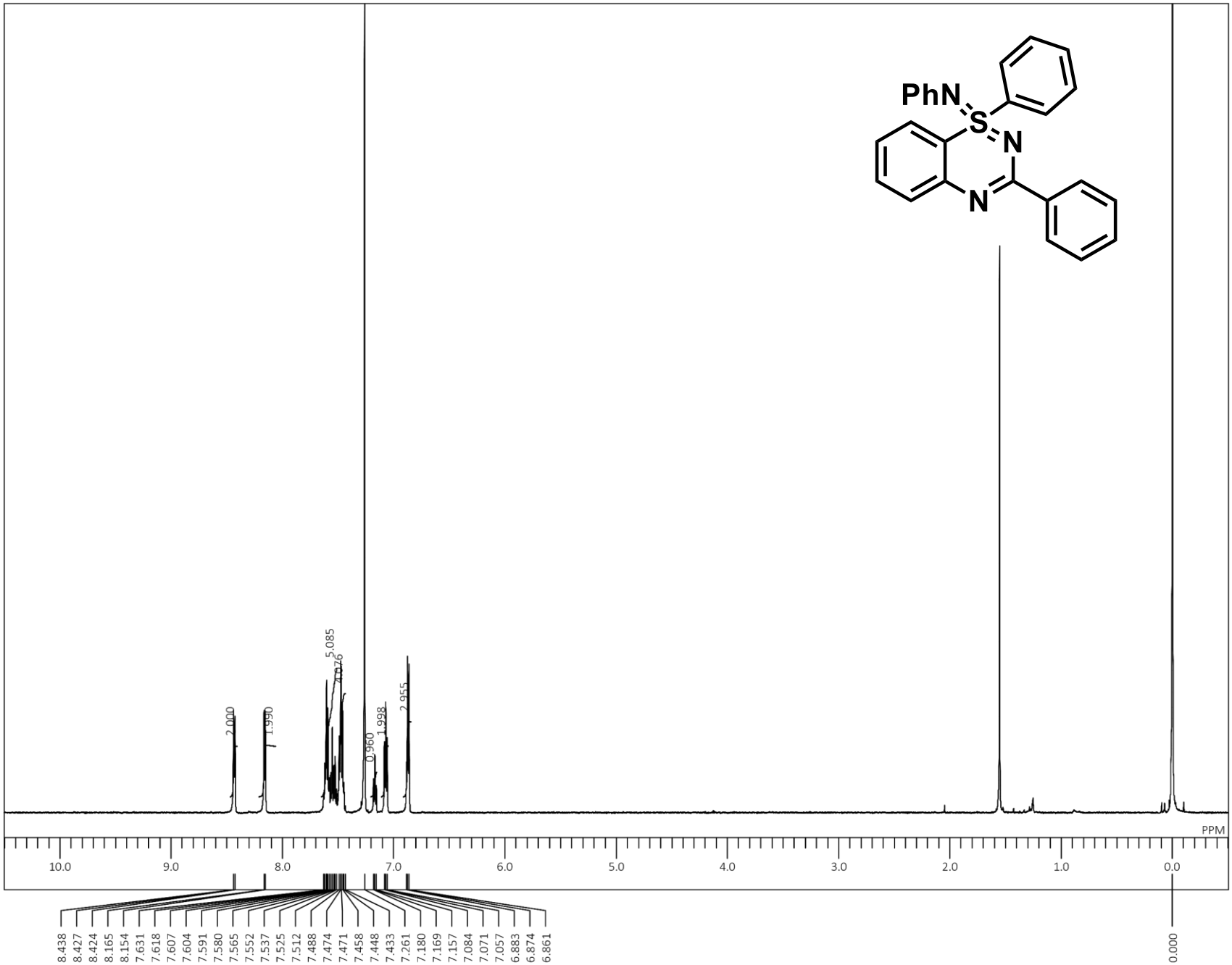
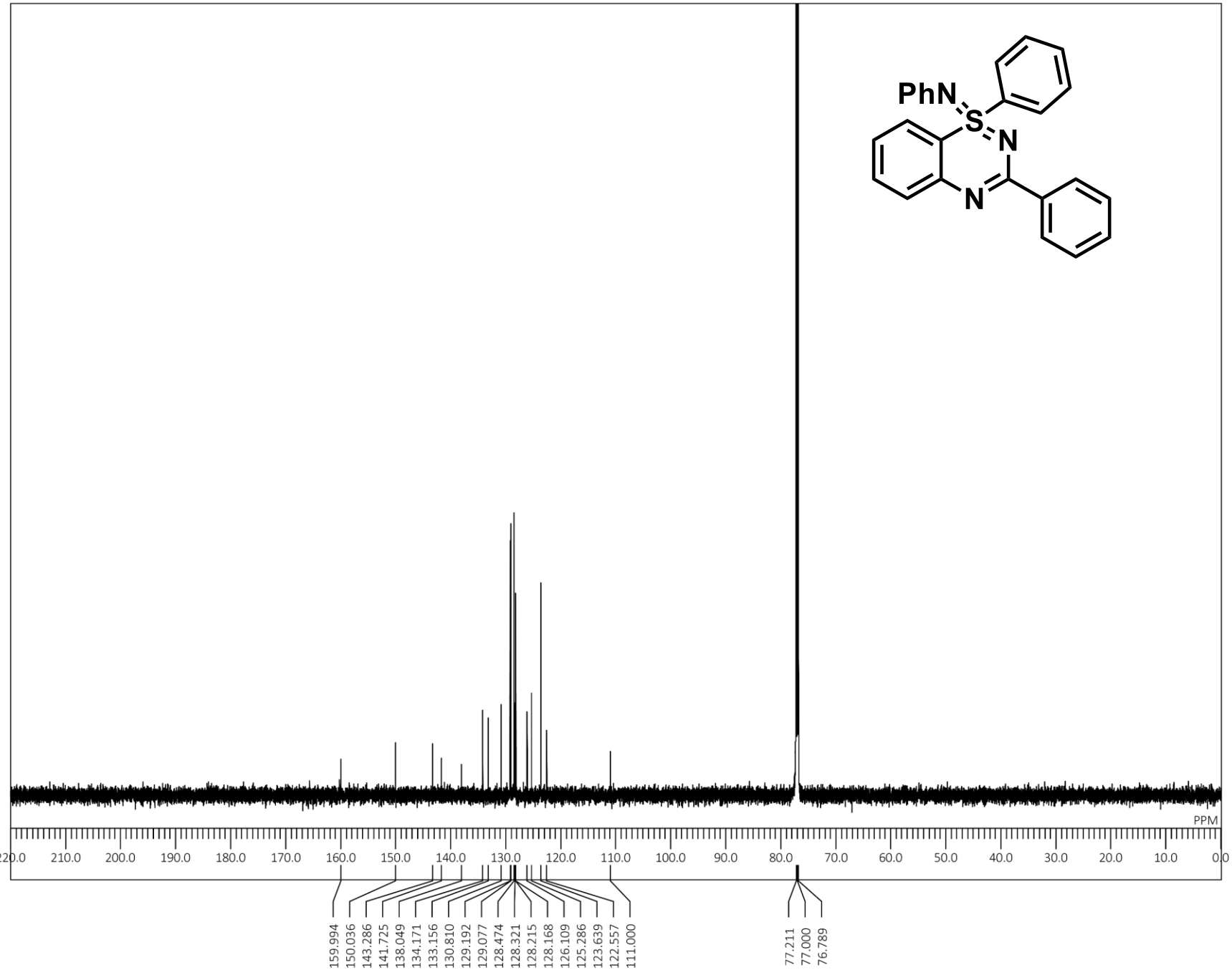
IRNUC	19F
CTEMP	20.0 c
SLVNT	CDCL3
EXREF	-63.72 ppm
BF	2.92 Hz
RGAIN	50

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3ab



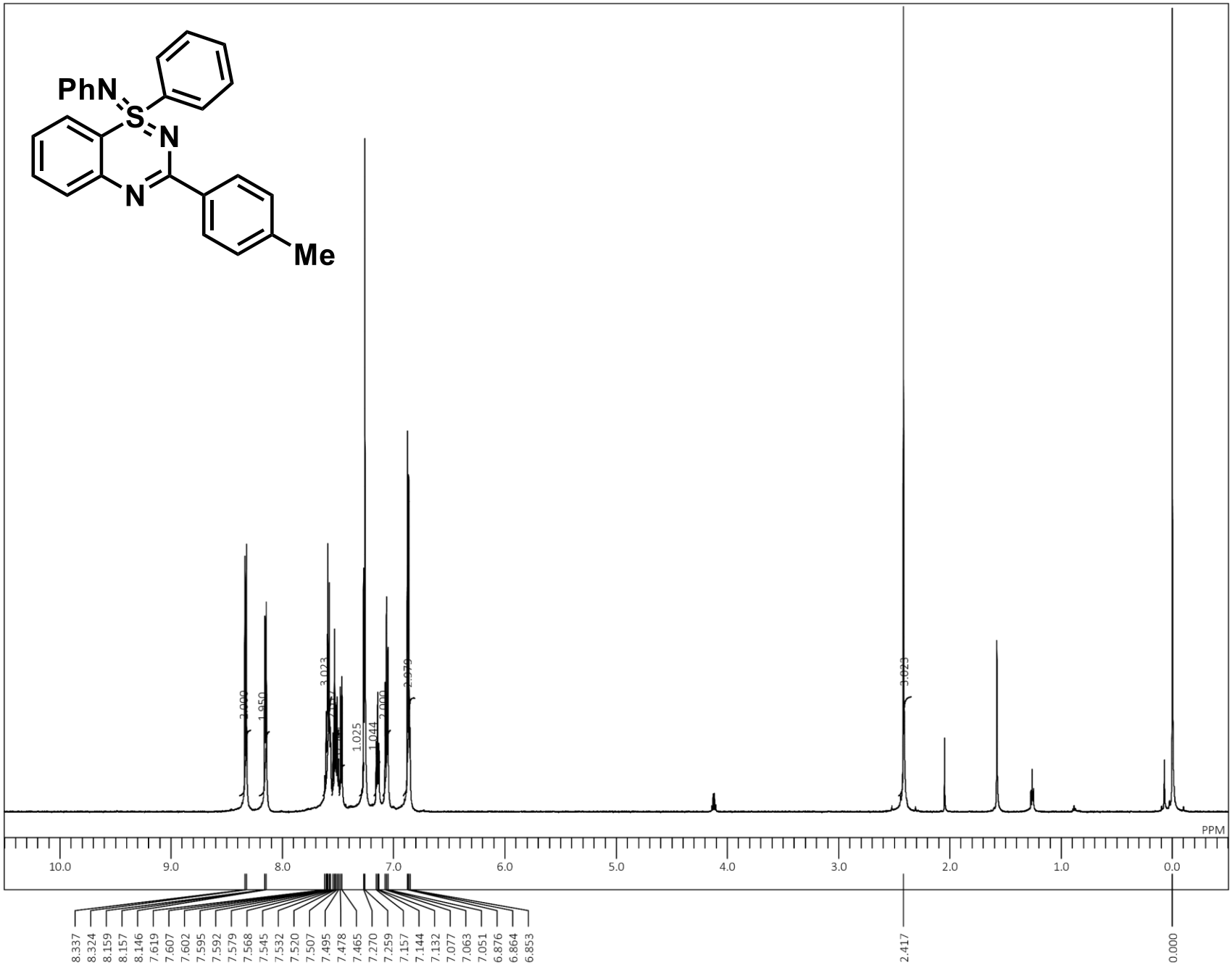
DFILE	AM_dio_pH_1H-2.als
COMNT	AM_dio_pH_1H
DATIM	2025-01-22 00:24:30
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	10.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	19.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.02 Hz
RGAIN	52

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3ab



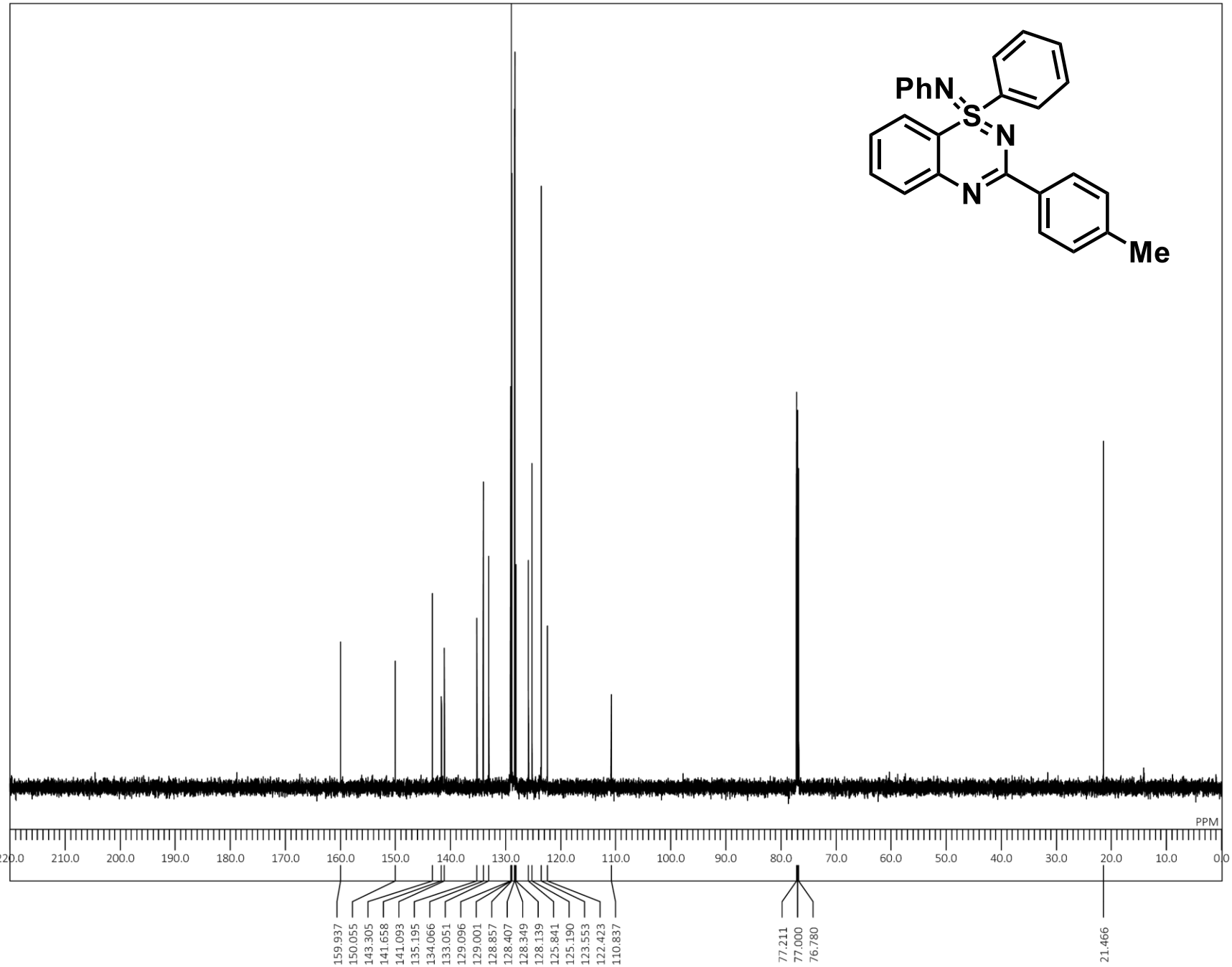
DFILE	AM03023_dio_mutikan_13C_2-1
COMNT	AM03023_dio_mutikan_13C_2
DATIM	2024-12-28 22:10:36
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	3000
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	19.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3ac



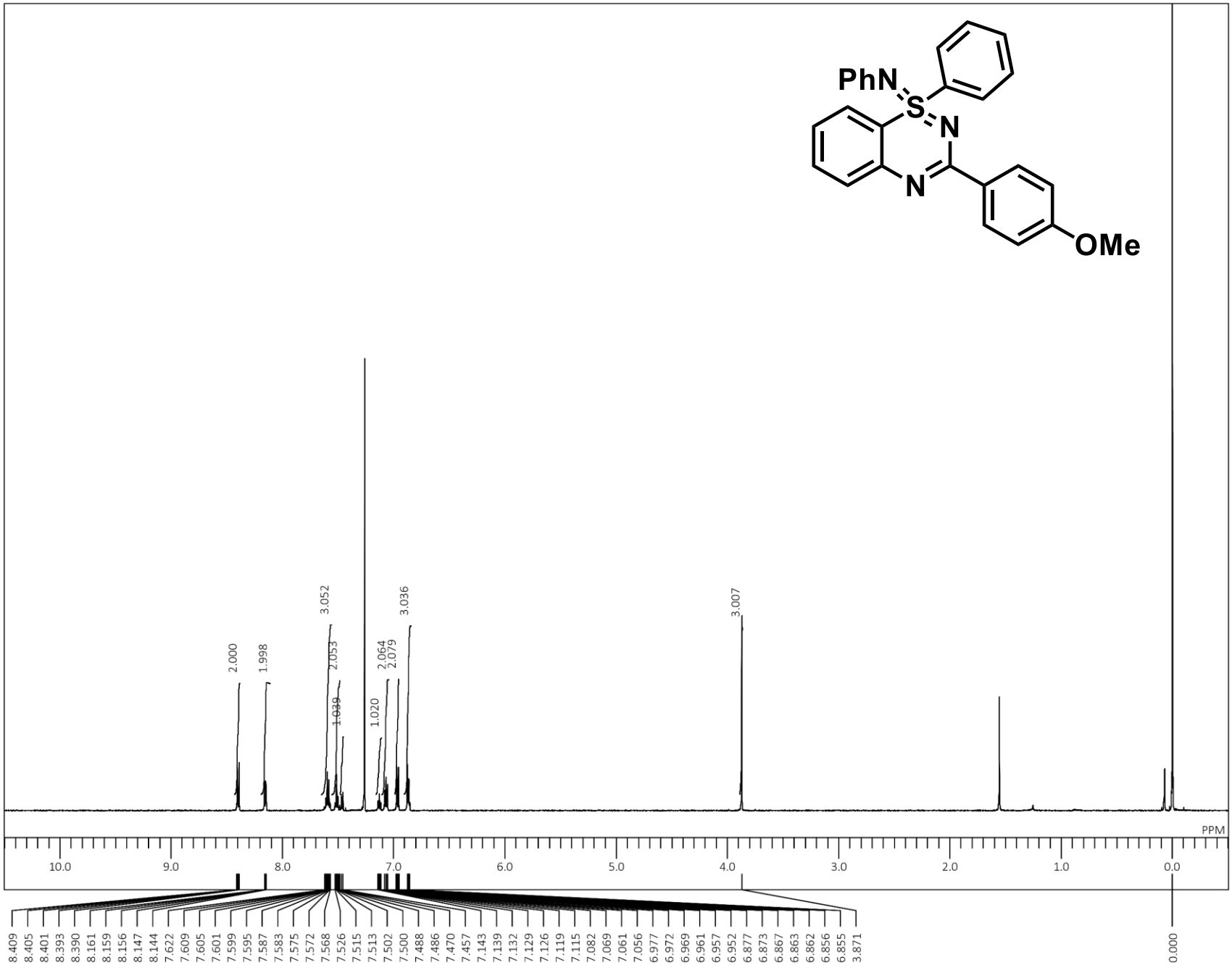
DFILE	AM_dio_pMe_1H-1.als
COMNT	AM_dio_pMe_1H
DATIM	2025-01-22 02:55:56
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	52428
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	10.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	19.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.52 Hz
RGAIN	50

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3ac



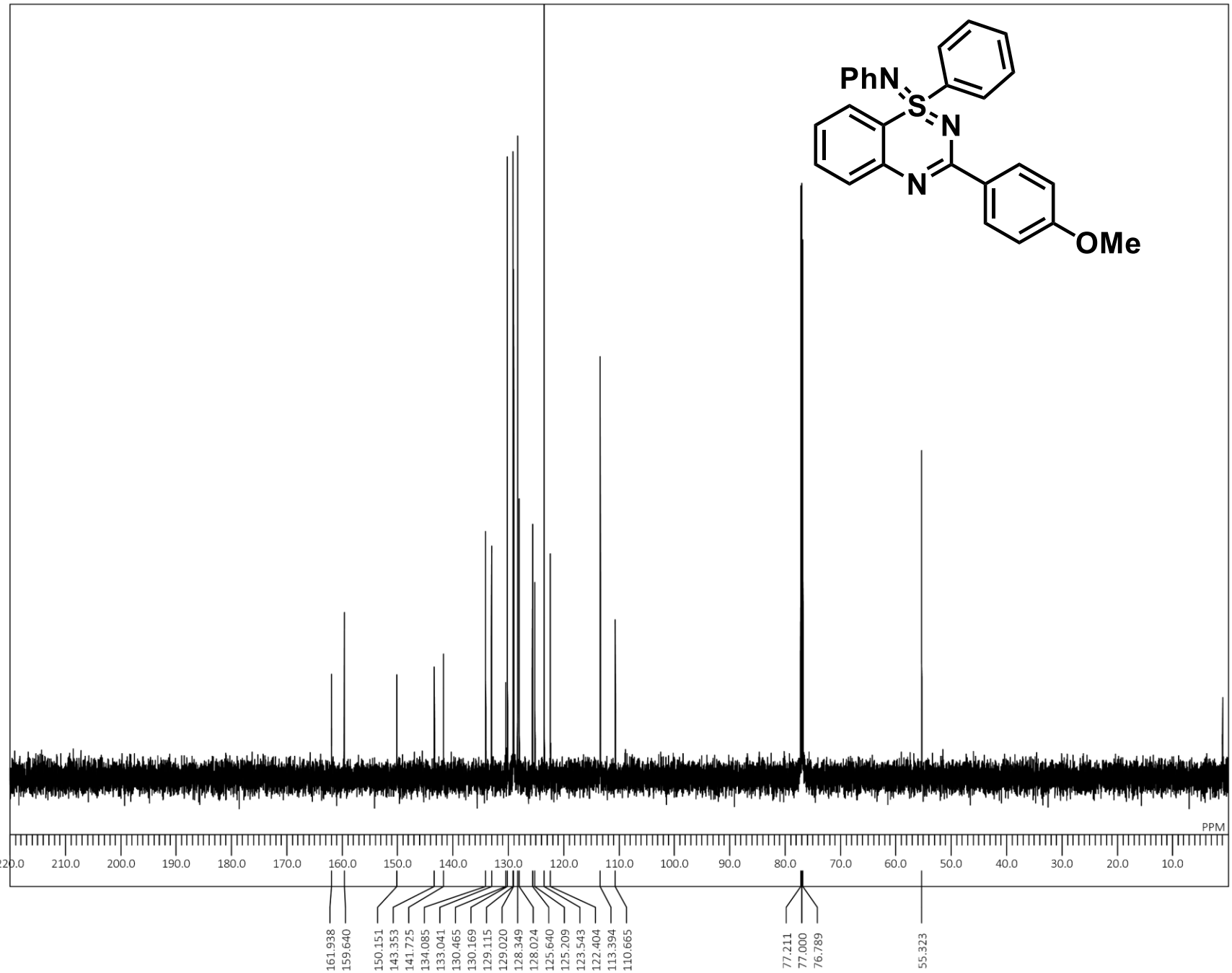
DFILE	AM03007_dio_pMe_13C-1.als
COMNT	AM03009_diox_pMe_13C
DATIM	2024-12-18 22:42:33
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	69
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	17.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3ad



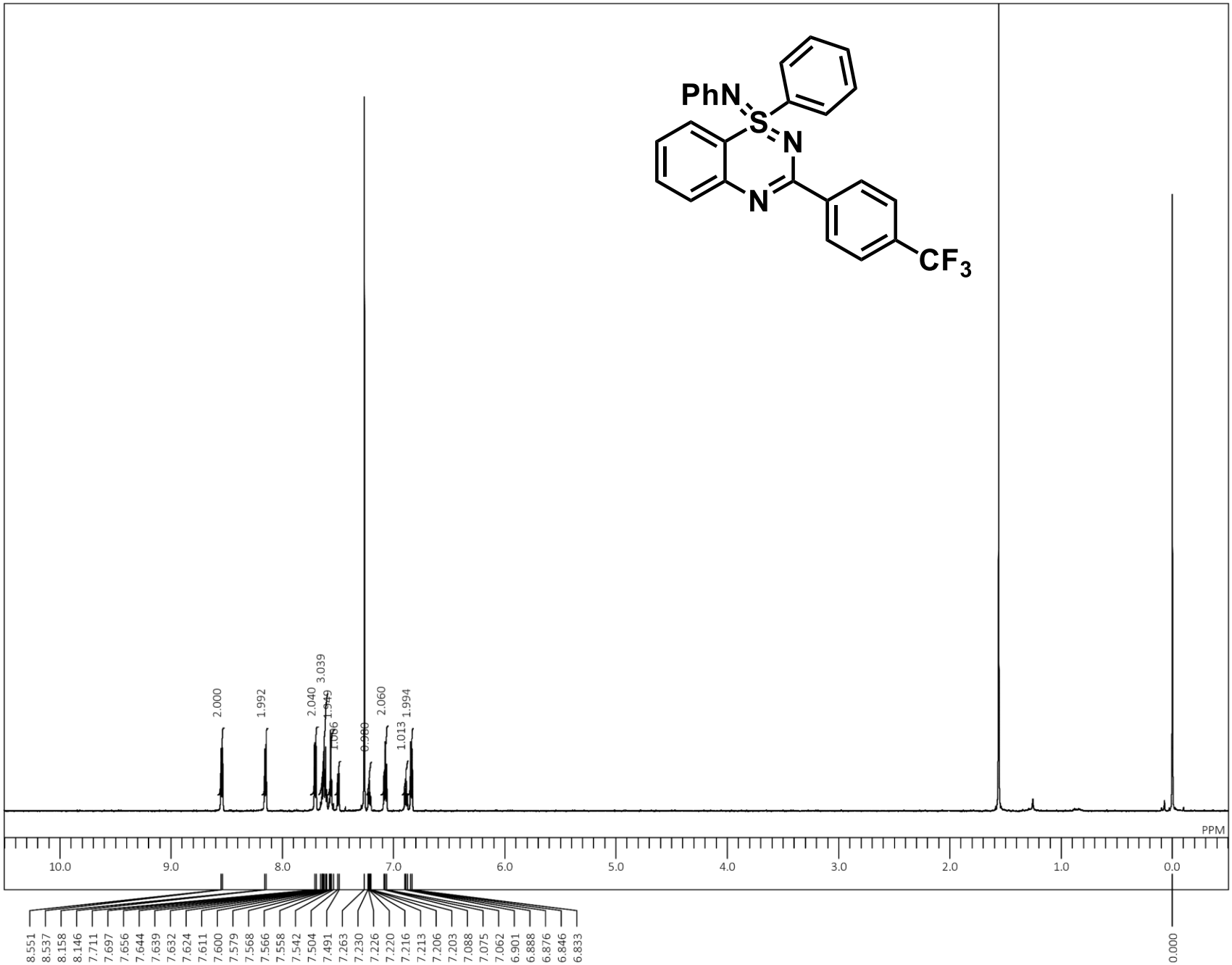
DFILE	AM_dio_pOMe_1H-1.als
COMNT	AM_dio_pOMe_1H
DATIM	2025-01-22 00:32:11
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	10.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	19.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	52

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3ad



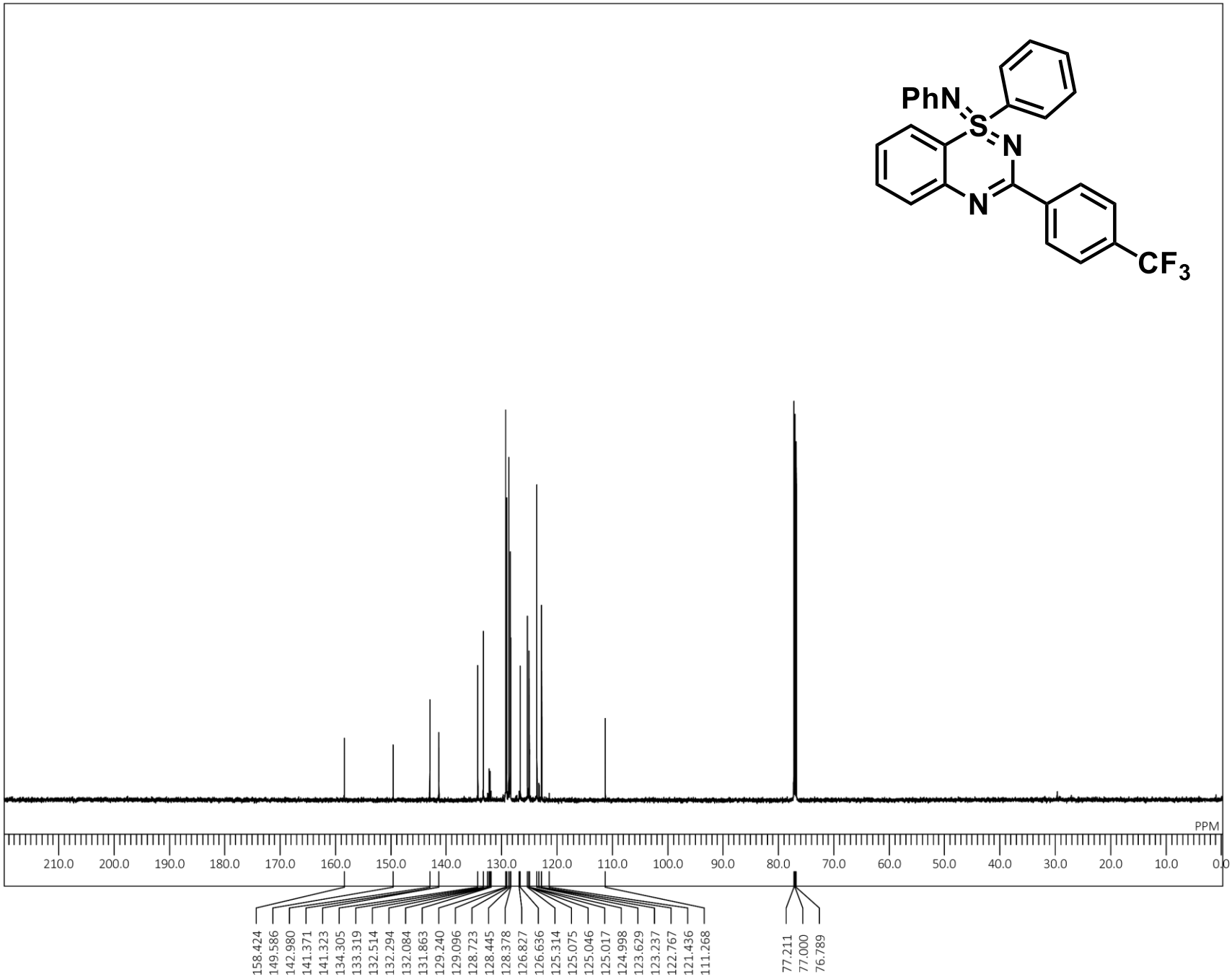
DFILE	AM03003_diox_pOMe_13C-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2024-12-18 23:57:01
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	80
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	17.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3ae



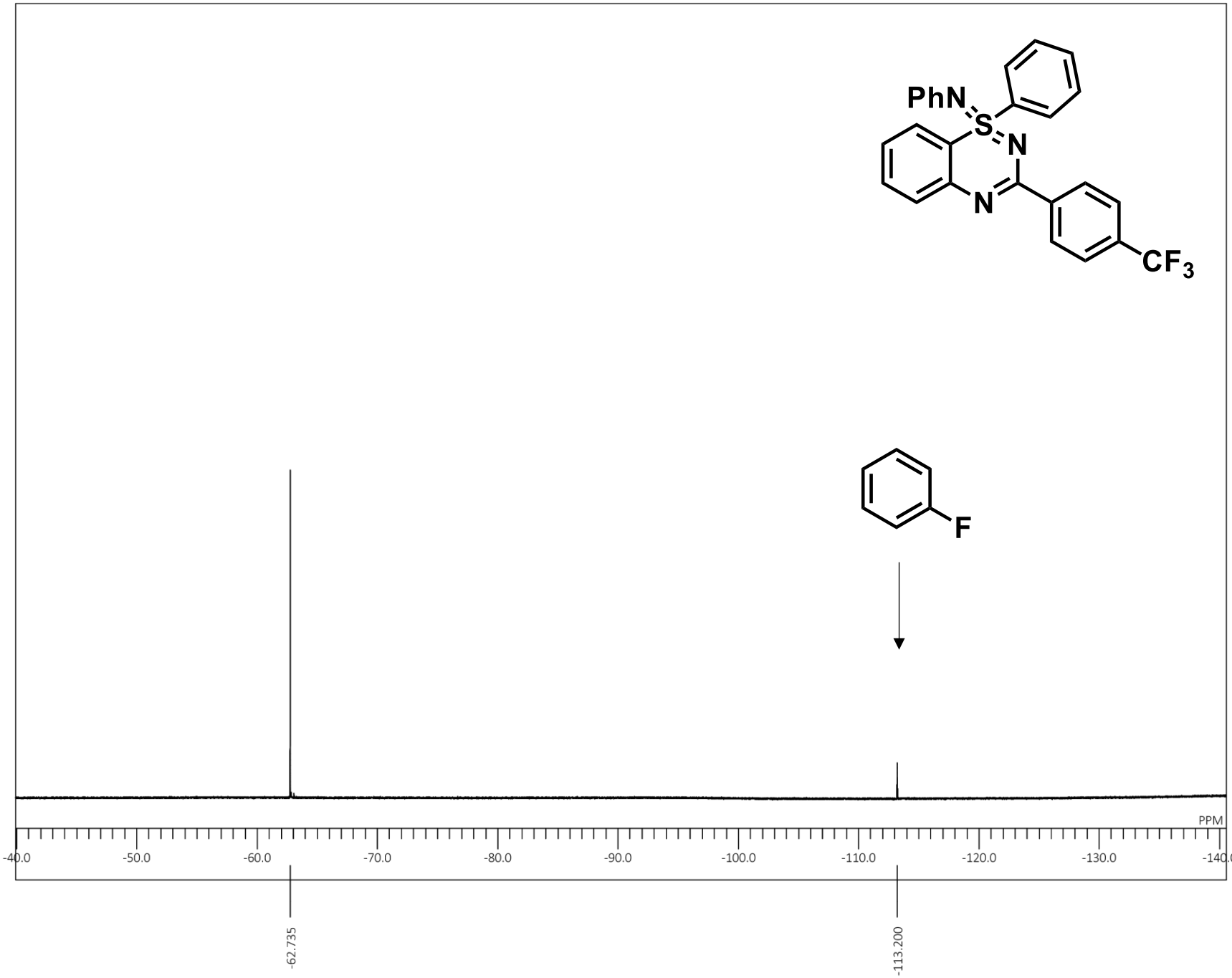
DFILE	TE02061_dio_pCF3_1H.als
COMNT	TE02061_dio_pCF3_1H
DATIM	2025-01-20 10:28:55
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	209712
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	5.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	18.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.70 Hz
RGAIN	52

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3ae



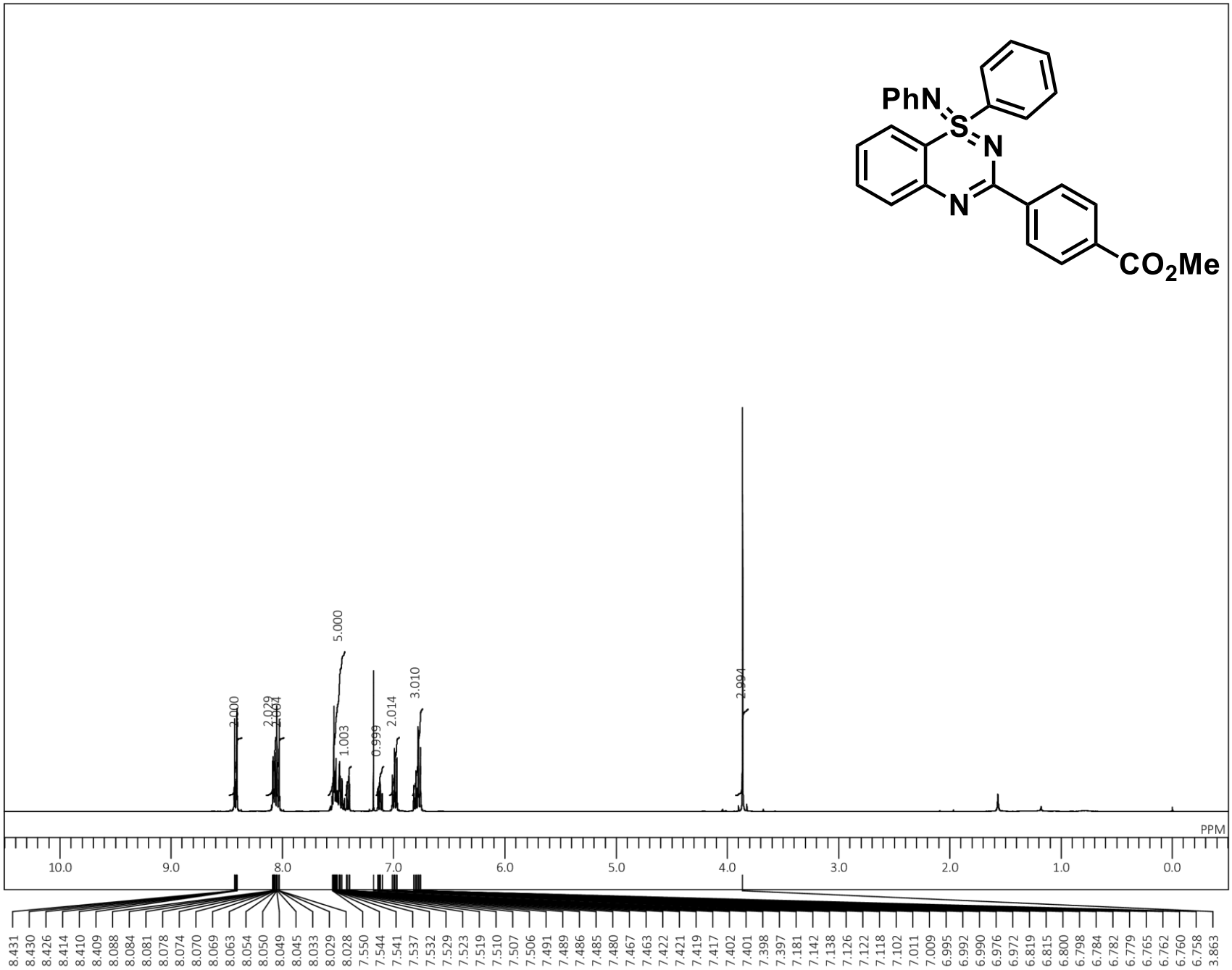
DFILE	TE02061_dio_pCF3_13C.als
COMNT	TE02061_dio_pCF3_13C
DATIM	2025-01-21 00:04:59
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	581
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.00 Hz
RGAIN	60

^{19}F NMR (564.67 MHz, $CDCl_3$) spectrum of 3ae



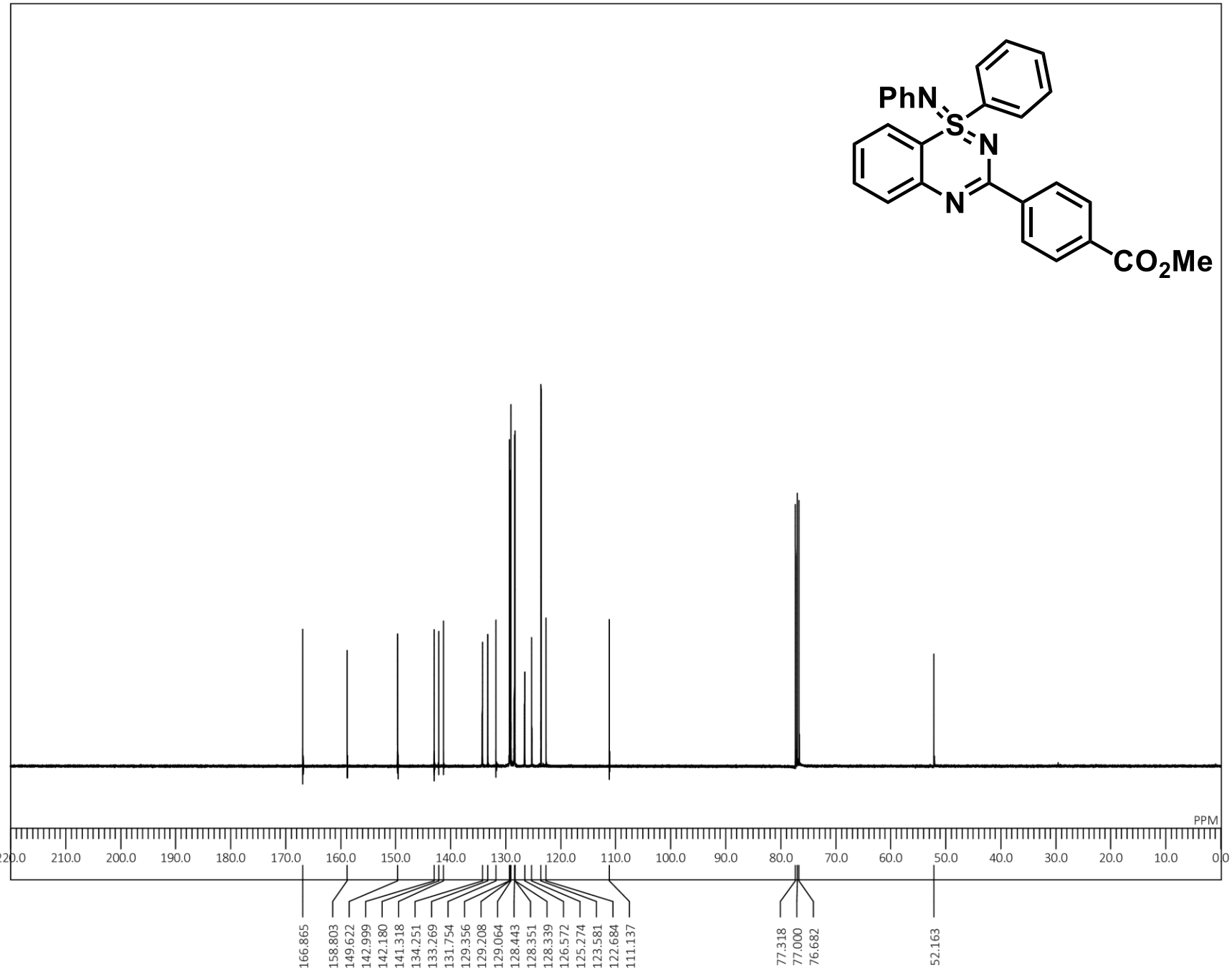
DFILE	TE02061_dio_pCF3_19F.als
COMNT	TE02061_dio_pCF3_19F
DATIM	2025-01-20 23:33:31
OBNUC	19F
EXMOD	single_pulse.ex2
OBFRQ	564.67 MHz
OBSET	5.29 KHz
OBFIN	1.21 Hz
POINT	209712
FREQU	56817.31 Hz
SCANS	8
ACQTM	0.4614 sec
PD	5.0000 sec
PW1	6.65 usec
IRNUC	19F
CTEMP	19.7 c
SLVNT	CDCL3
EXREF	-113.20 ppm
BF	1.00 Hz
RGAIN	50

^{1}H NMR (399.78 MHz, $CDCl_3$) spectrum of 3af



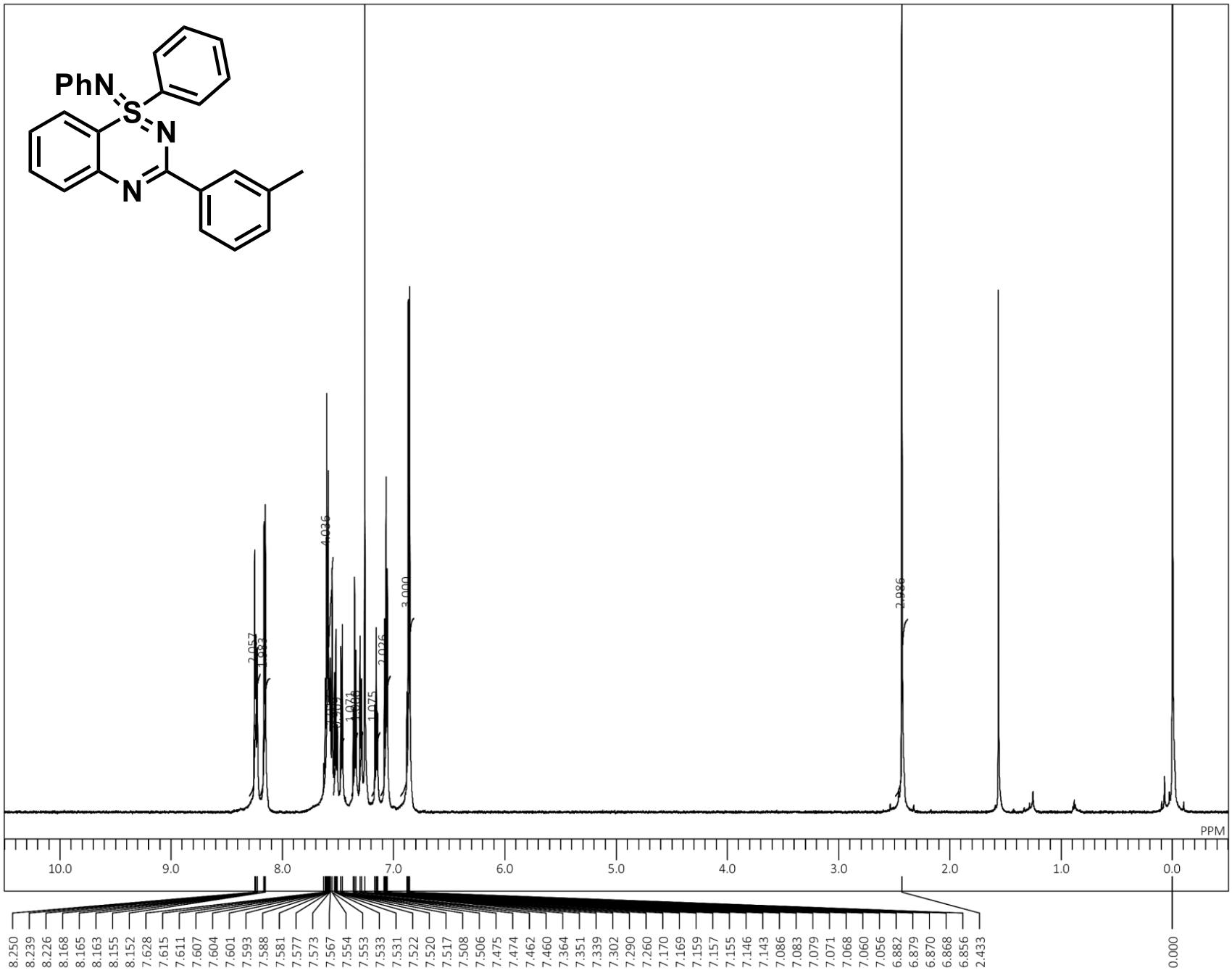
DFILE	TE02111_dio_pCO2Me_1H.als
COMNT	TE02111_dio_pCO2Me_1H
DATIM	2025-04-02 14:58:25
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	49177
FREQU	5995.20 Hz
SCANS	8
ACQTM	2.0507 sec
PD	5.0000 sec
PW1	3.45 usec
IRNUC	1H
CTEMP	19.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	56

$^{13}C\{^{1}H\}$ NMR (100.53 MHz, $CDCl_3$) spectrum of 3af



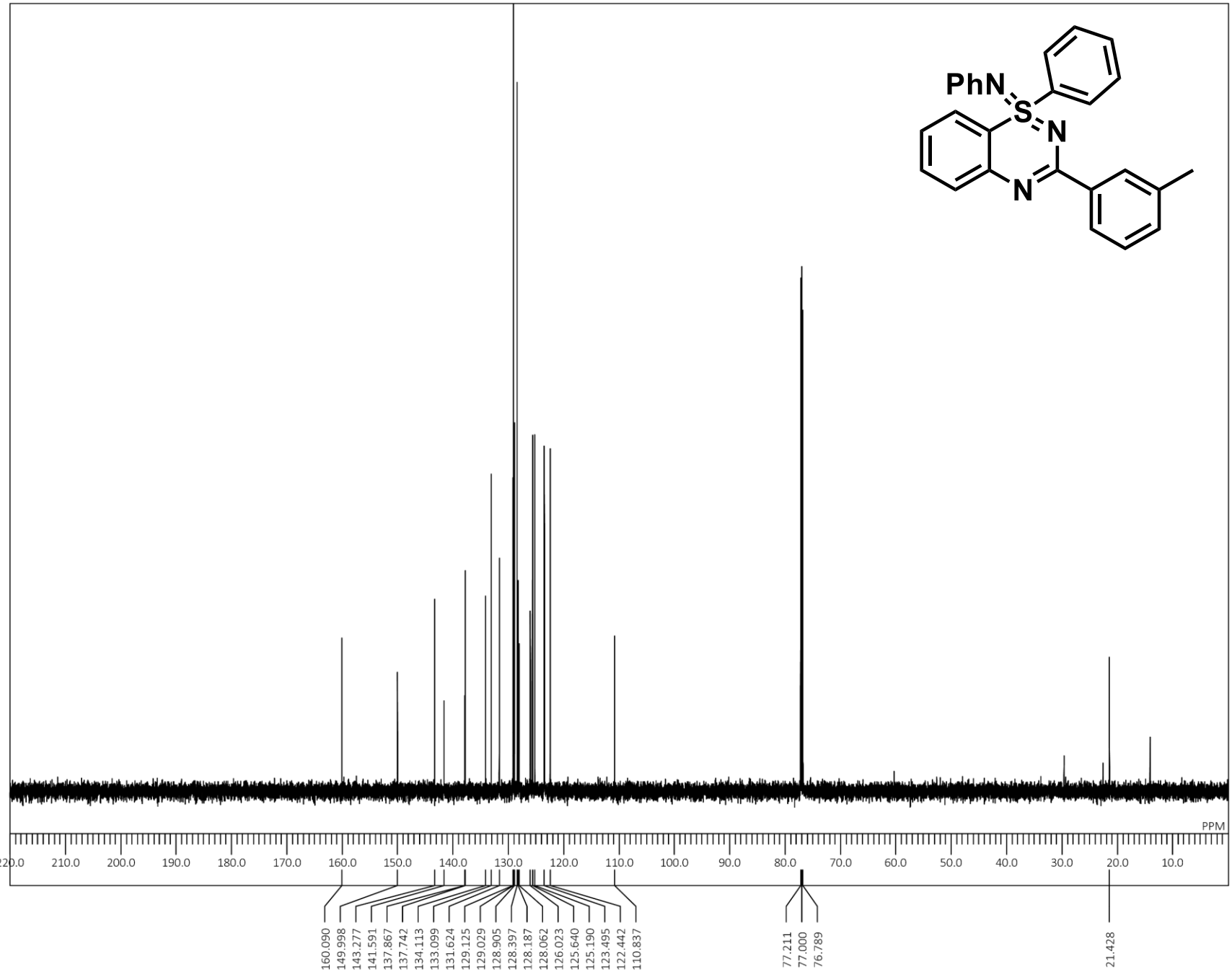
DFILE	TE02111_dio_pCO2Me_13C_deta
COMNT	TE02111_dio_pCO2Me_13C
DATIM	2025-04-02 02:04:55
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	502655
FREQU	31407.04 Hz
SCANS	5000
ACQTM	1.0003 sec
PD	2.0000 sec
PW1	3.60 usec
IRNUC	1H
CTEMP	18.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.10 Hz
RGAIN	50

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3ag



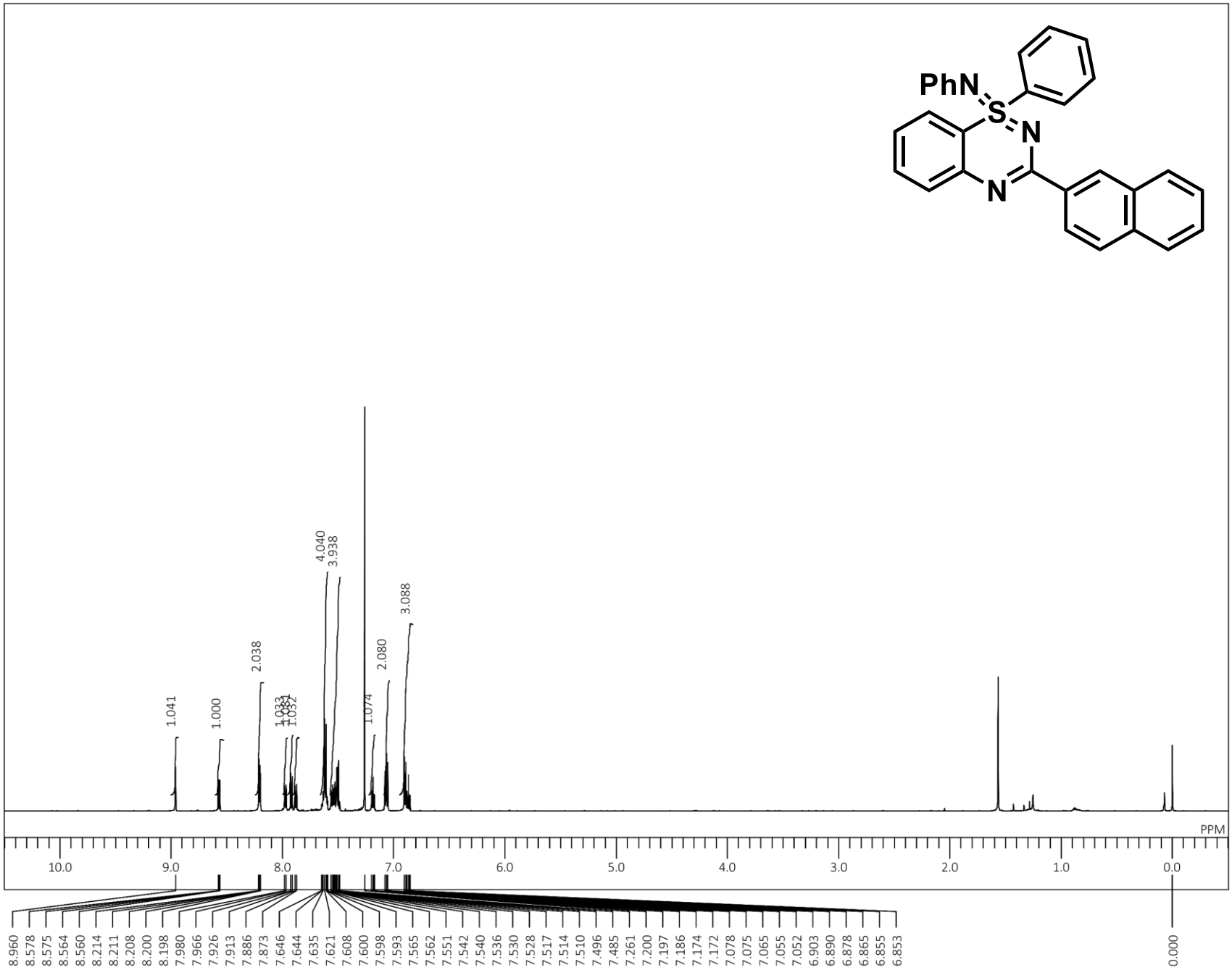
DFILE AM_dio_mMe_1H-1.als
COMNT AM_dio_mMe_1H
DATIM 2025-01-22 02:33:39
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 26214
FREQU 9008.87 Hz
SCANS 8
ACQTM 2.9098 sec
PD 10.0000 sec
PW1 7.00 usec
IRNUC 1H
CTEMP 19.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.52 Hz
RGAIN 50

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3ag



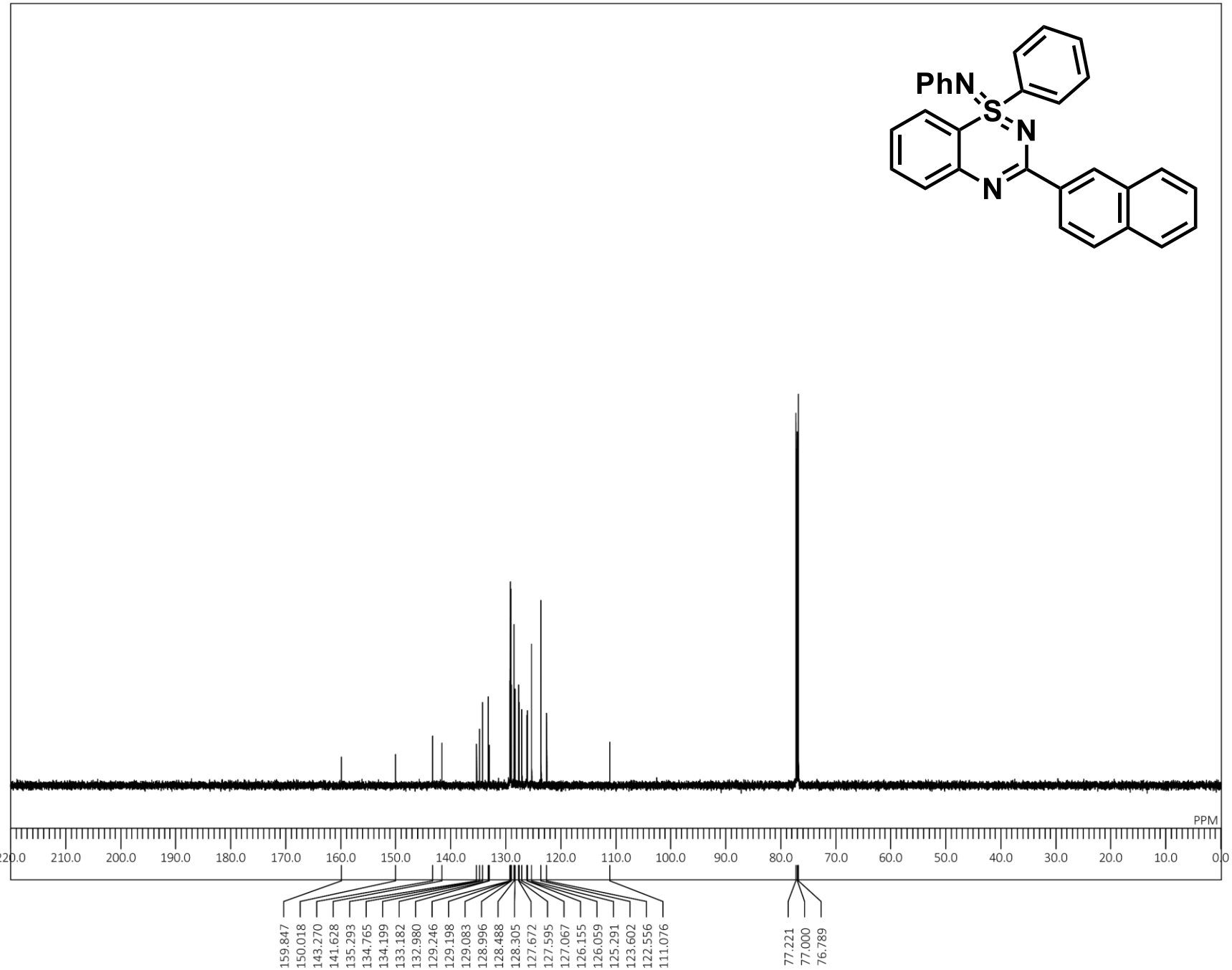
DFILE	AM03017_dio_mMe_13C-1.als
COMNT	AM03017_dio_mMe_13C
DATIM	2024-12-20 19:28:09
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	65
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	16.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

^{1}H NMR (594.17 MHz, $CDCl_3$) spectrum of 3ah



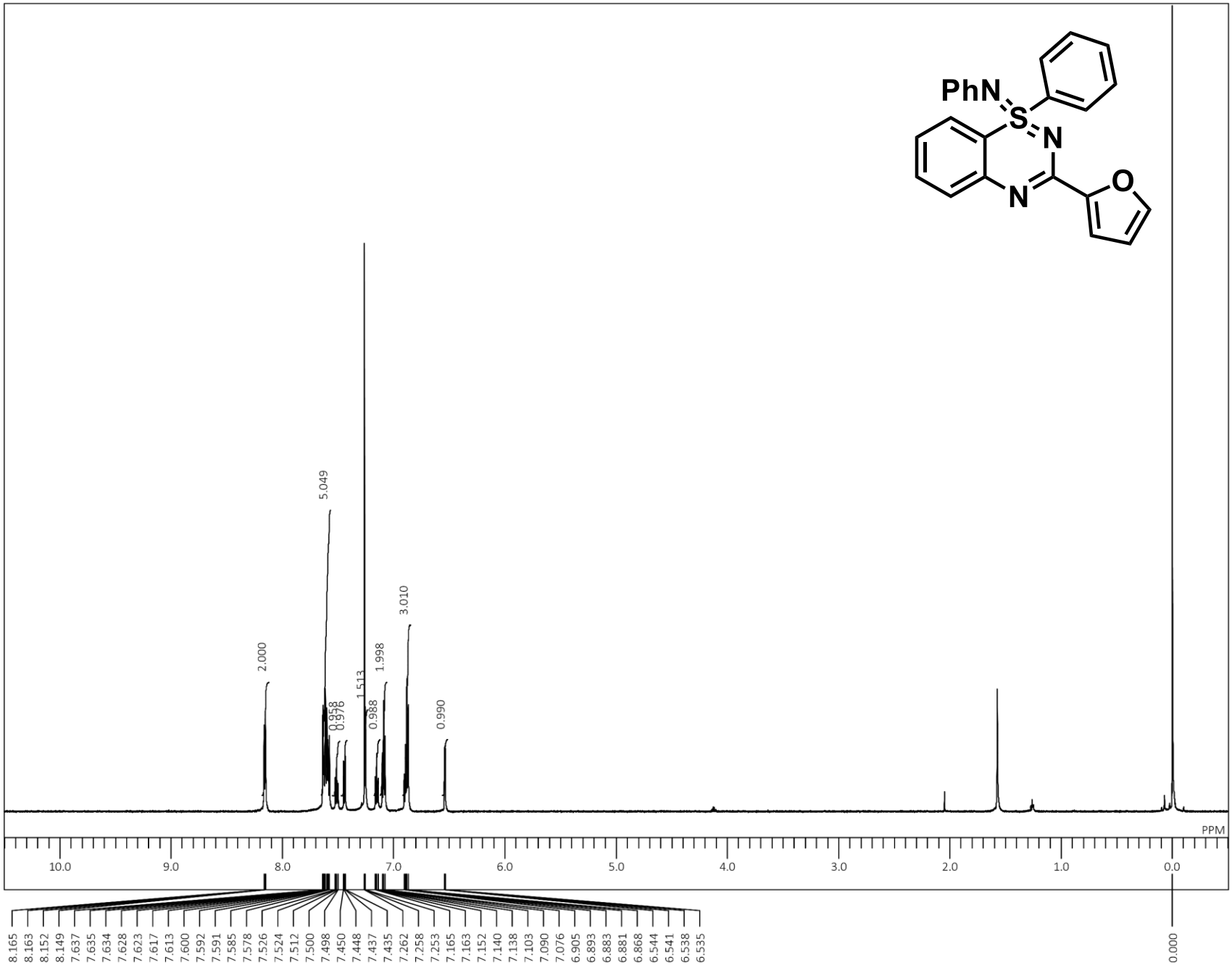
DFILE	AM_dio_naph_1H_3_Proton-1-1.
COMNT	single_pulse
DATIM	2025-02-05 17:01:01
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	594.17 MHz
OBSET	3.55 KHz
OBFIN	2.53 Hz
POINT	13107
FREQU	8912.66 Hz
SCANS	8
ACQTM	1.4706 sec
PD	5.0000 sec
PW1	7.25 usec
IRNUC	1H
CTEMP	16.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	54

$^{13}C\{^{1}H\}$ NMR (149.41 MHz, $CDCl_3$) spectrum of 3ah



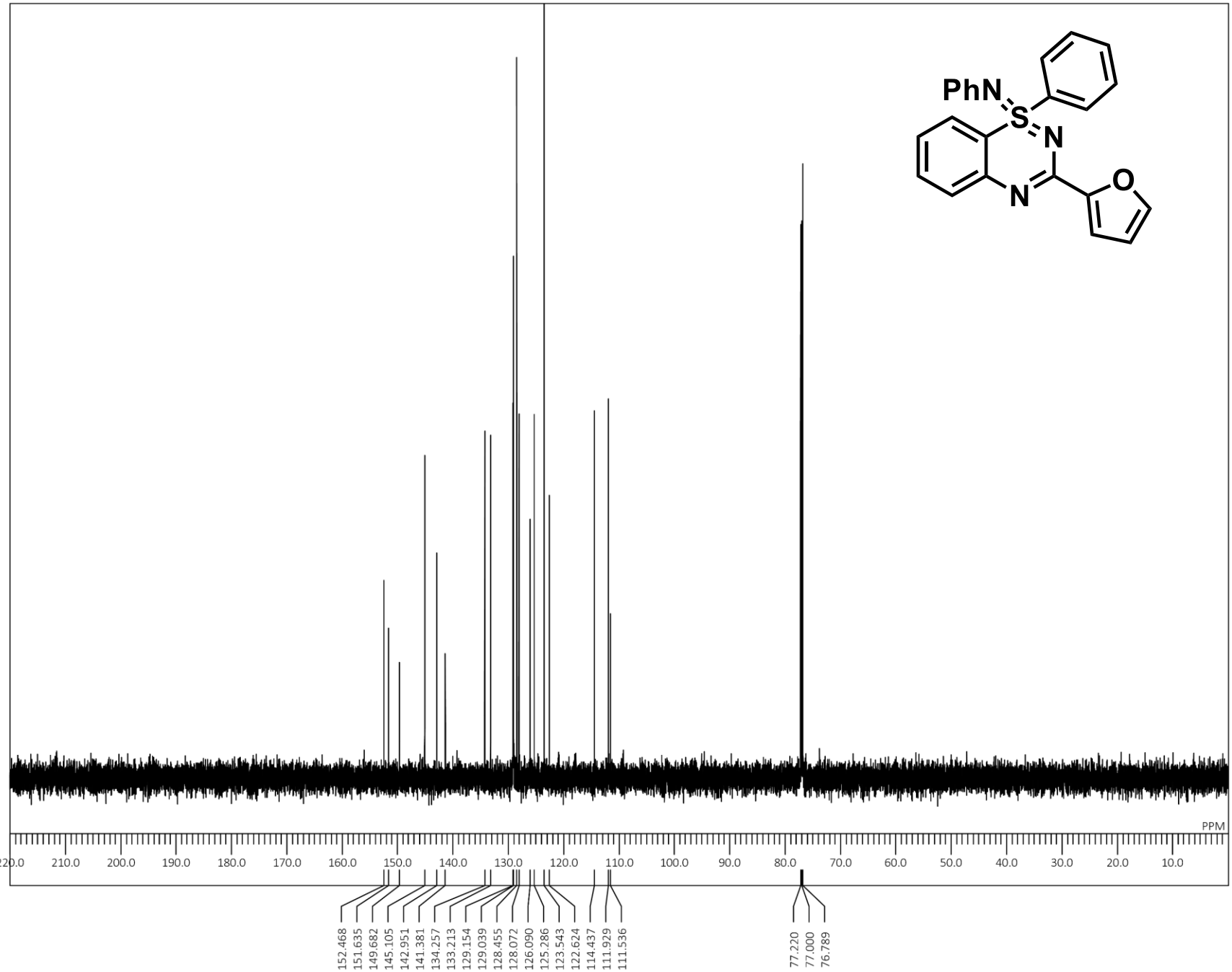
DFILE	AM_dio_naph_13C_2_Carbon-1-1
COMNT	single pulse decoupled gated NOE
DATIM	2025-02-20 15:00:23
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	149.41 MHz
OBSET	9.23 KHz
OBFIN	6.55 Hz
POINT	32767
FREQU	46992.48 Hz
SCANS	126
ACQTM	0.6973 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	16.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3ai



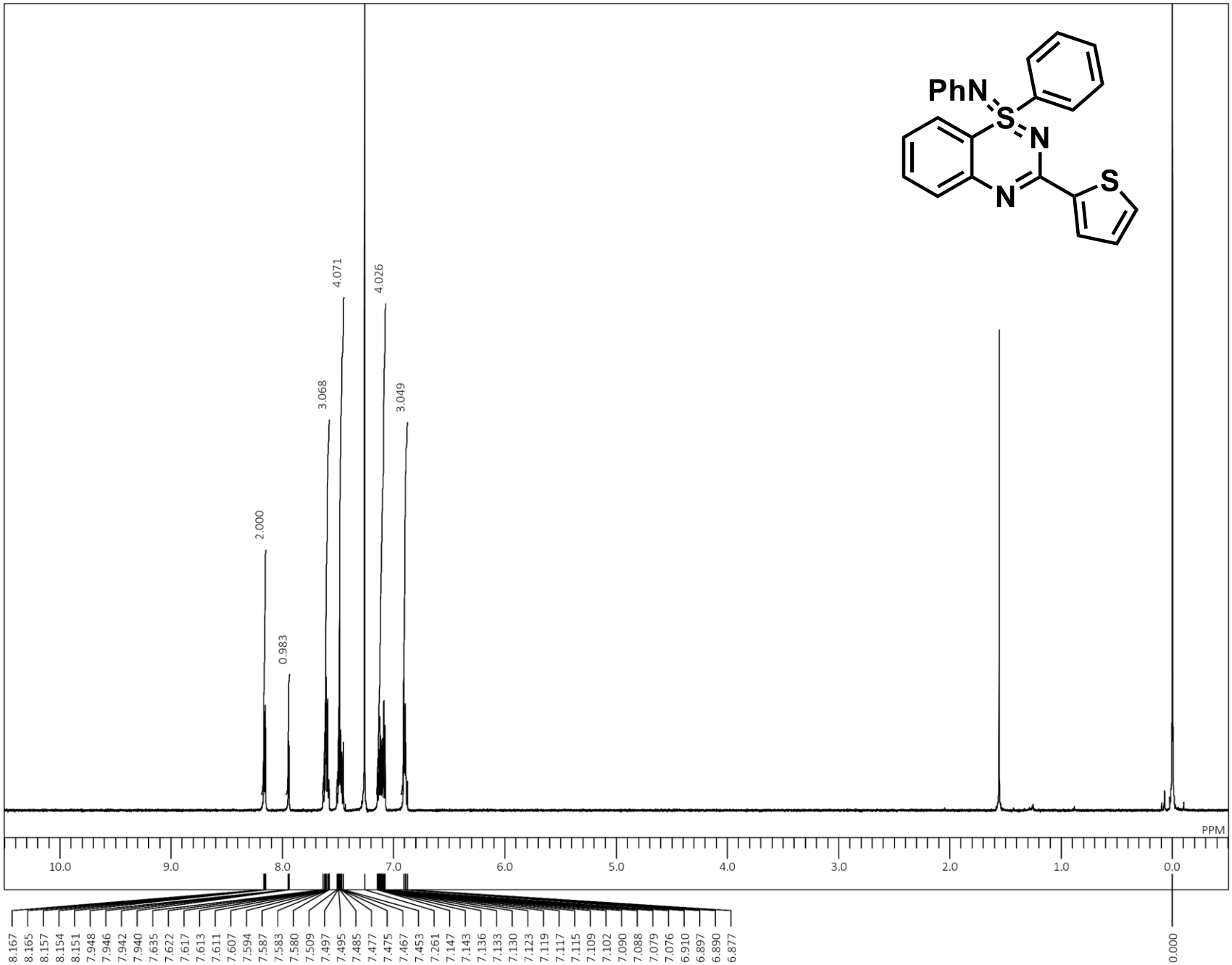
DFILE	AM_dio_furan_1H-1.als
COMNT	AM_dio_furan_1H
DATIM	2025-01-22 02:41:17
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	10.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	19.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	50

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3ai



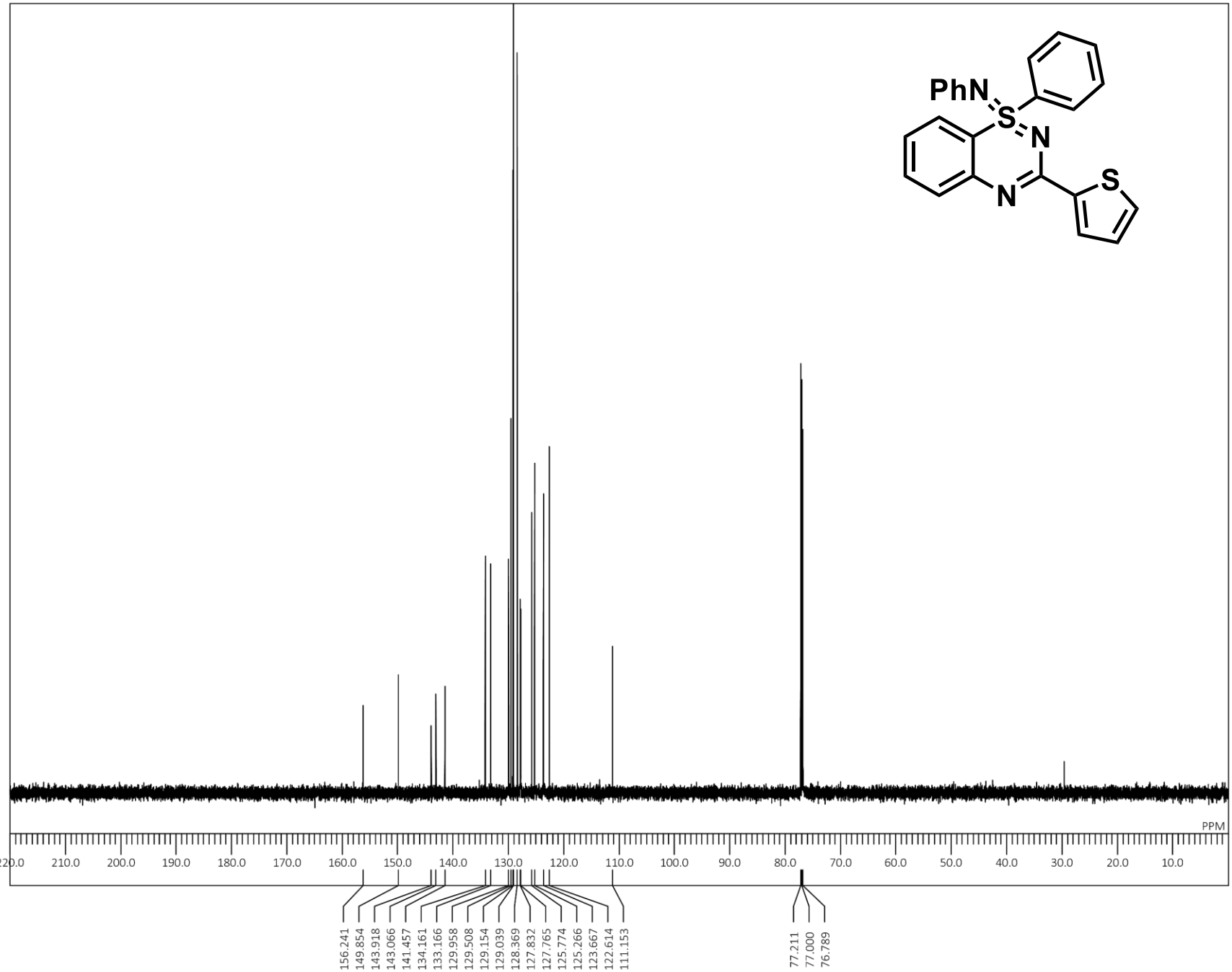
DFILE	AM03009_diox_furan_13C-1.als
COMNT	AM03007_diox_furan_13C
DATIM	2024-12-18 22:55:08
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	34
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	17.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3aj



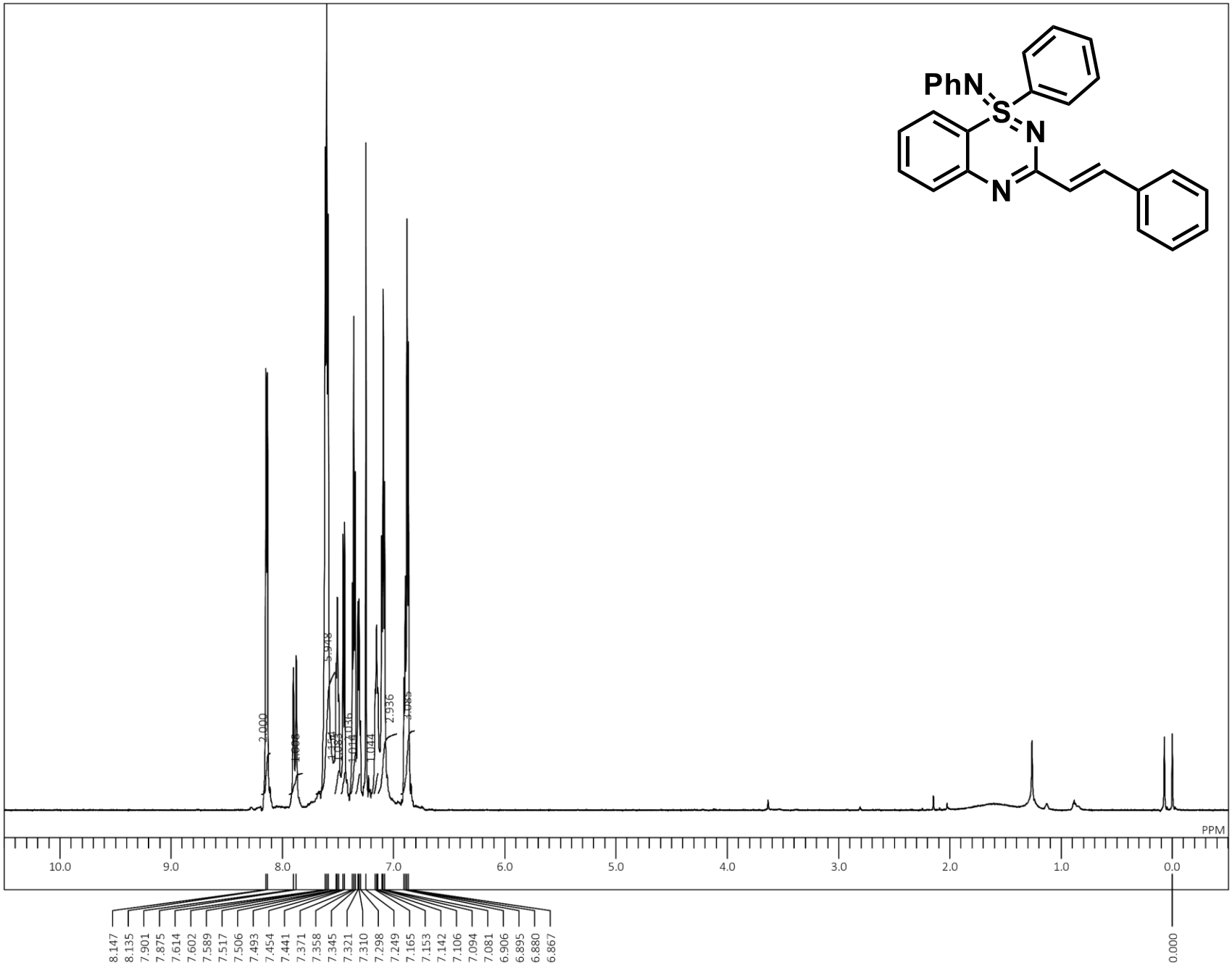
DFILE	AM_dio_thiophene_1H-1.als
COMNT	AM_dio_thiophen_1H
DATIM	2025-01-22 00:39:48
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	10.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	19.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	52

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3aj



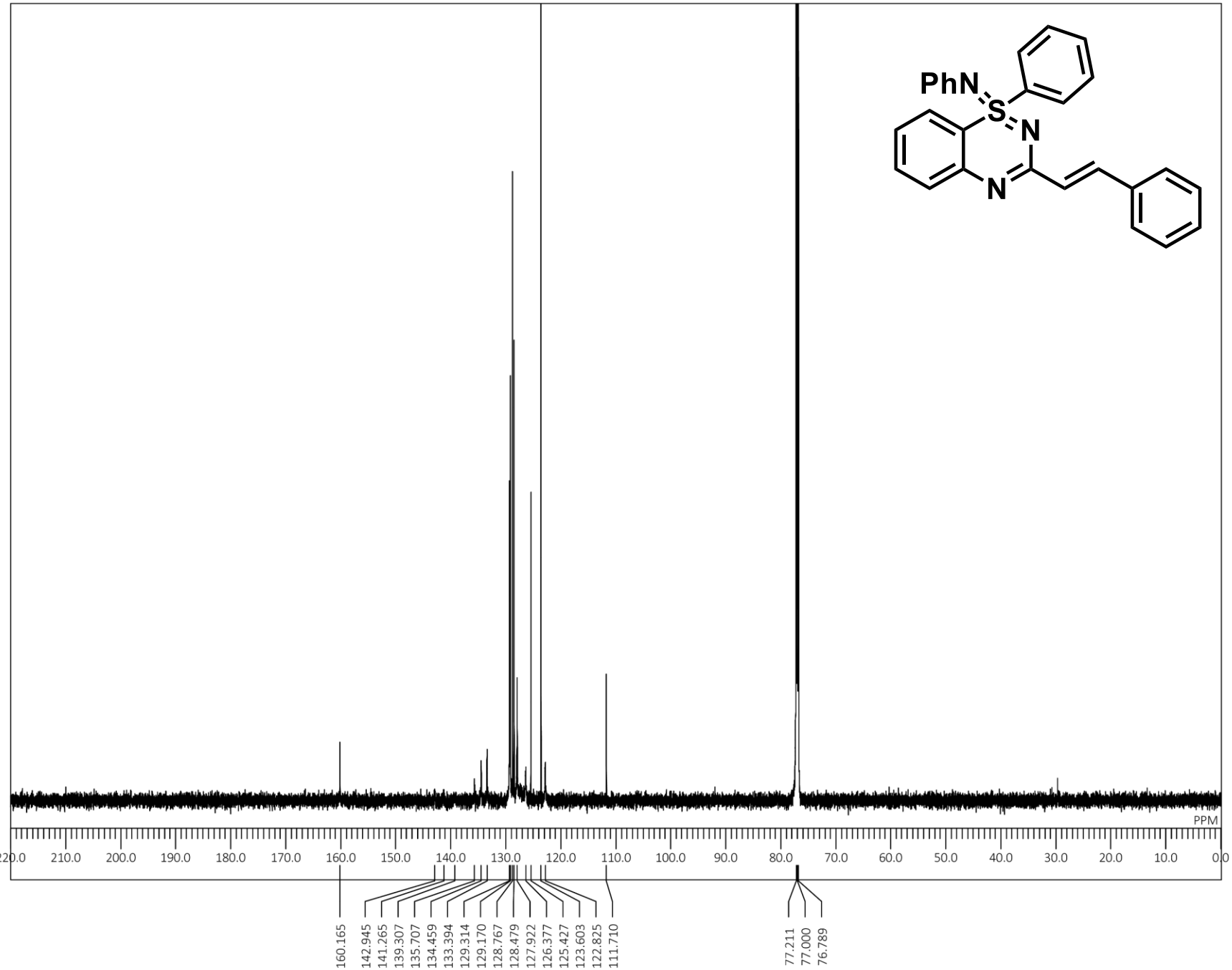
DFILE	AM03017_dio_thiophene_13C-1.als
COMNT	AM03017_dio_thiophene_13C
DATIM	2024-12-24 10:42:21
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	94
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	17.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

^{1}H NMR (599.67 MHz, $CDCl_3$) spectrum of 3ak



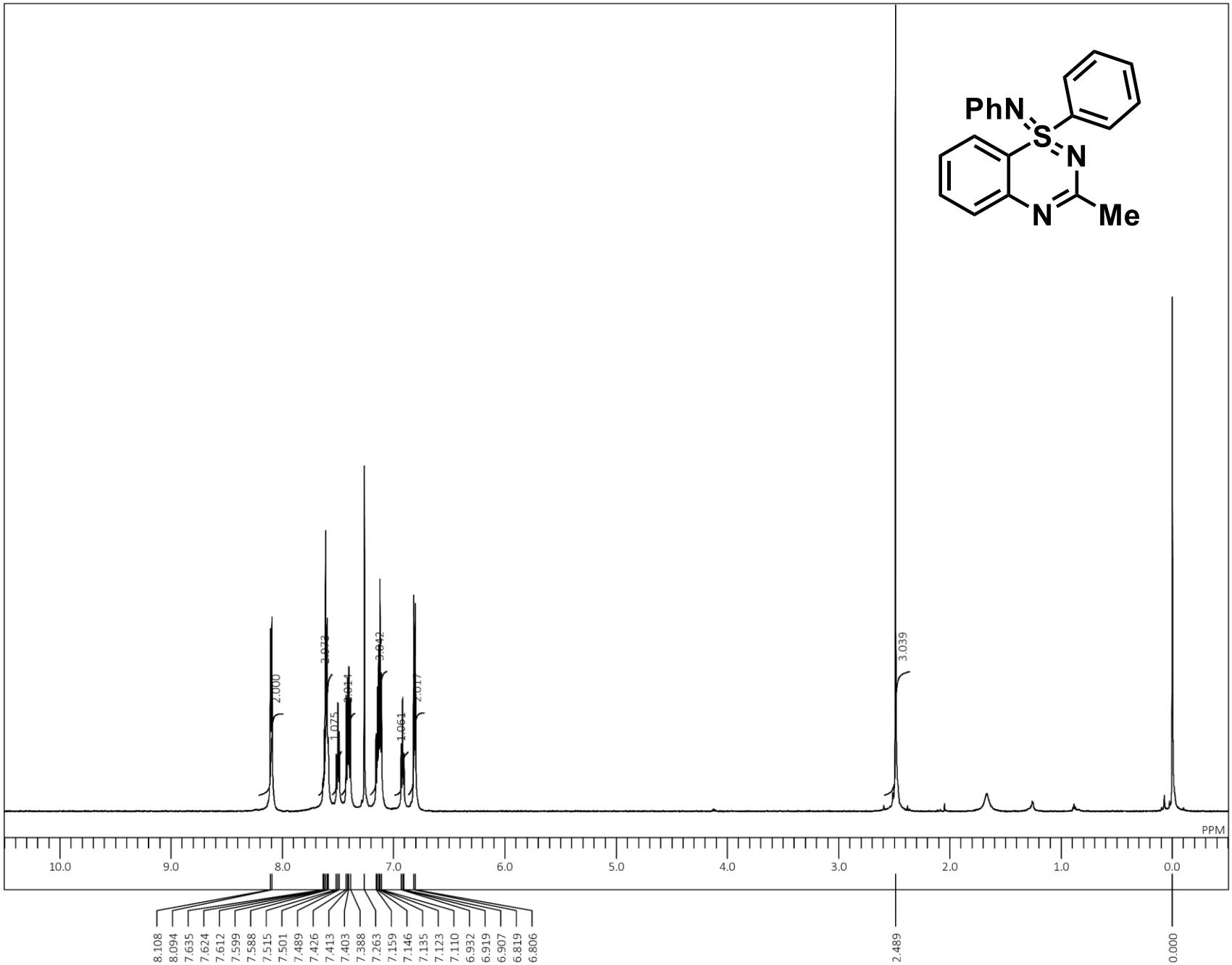
DFILE	AM_dio_cinnamyl_1H_VT_Proton-1
COMNT	single_pulse
DATIM	2025-02-18 17:05:26
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	599.67 MHz
OBSET	5.30 KHz
OBFIN	3.47 Hz
POINT	13107
FREQU	8992.81 Hz
SCANS	8
ACQTM	1.4575 sec
PD	15.0000 sec
PW1	4.00 usec
IRNUC	1H
CTEMP	50.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	46

$^{13}C\{^{1}H\}$ NMR (149.41 MHz, $CDCl_3$) spectrum of 3ak



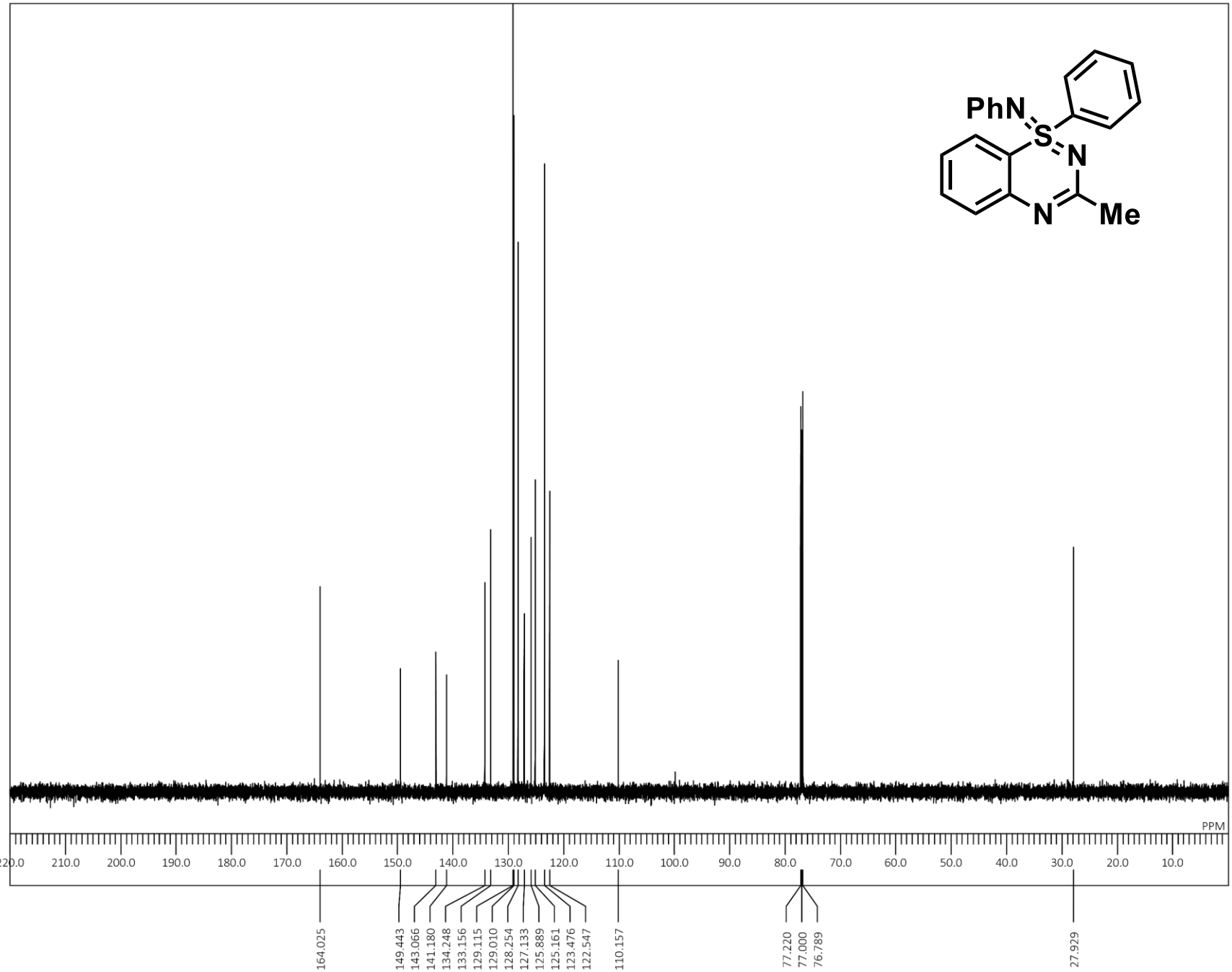
DFILE	AM_dio_cinnamyl_13C_4s_Carbo
COMNT	single pulse decoupled gated NOE
DATIM	2025-02-20 00:30:06
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	149.41 MHz
OBSET	9.23 KHz
OBFIN	6.55 Hz
POINT	26214
FREQU	37593.98 Hz
SCANS	7200
ACQTM	0.6973 sec
PD	4.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	15.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3al



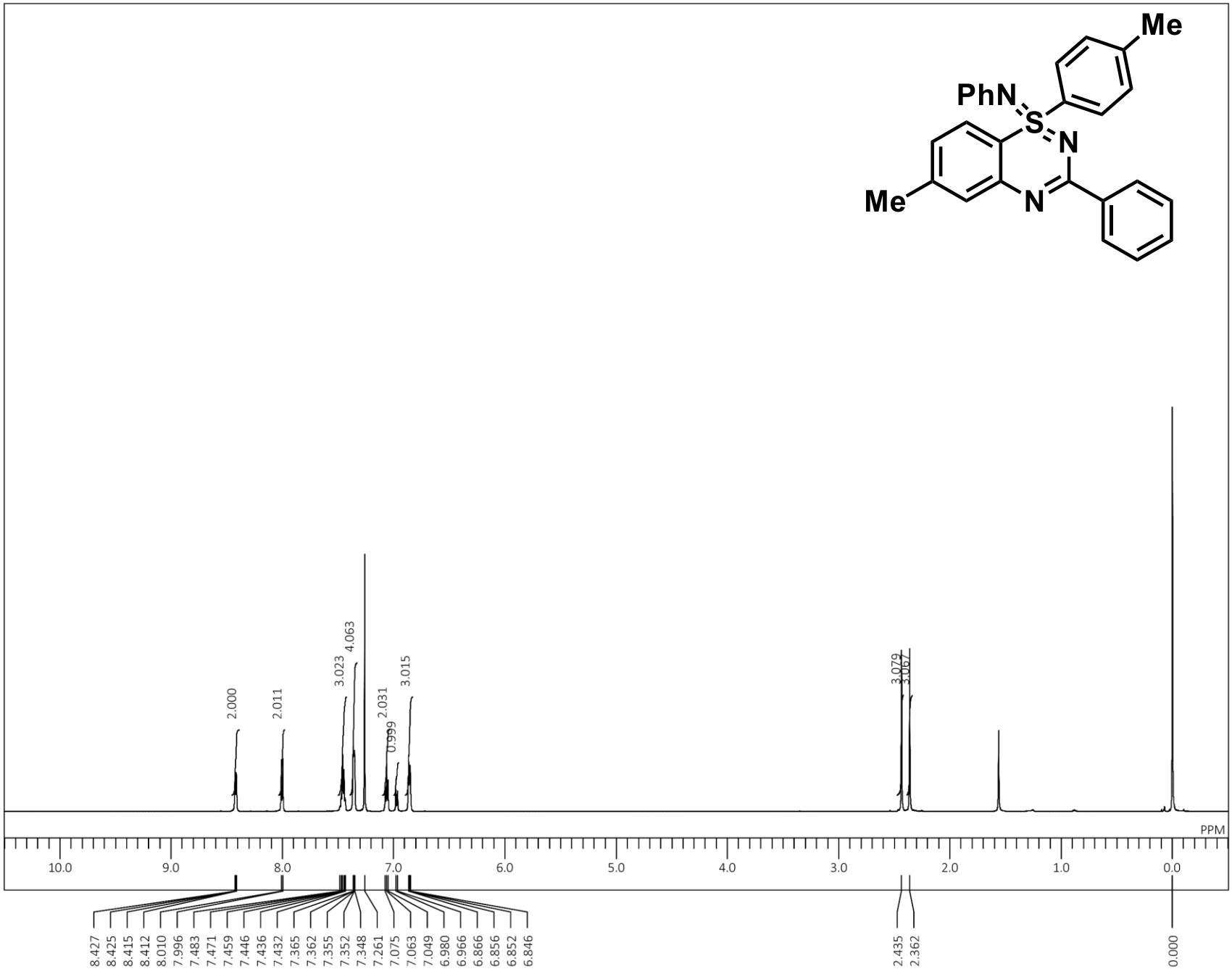
DFILE	AM_dio_Me_1H-1.als
COMNT	AM_dio_Me_1H
DATIM	2025-01-22 03:03:51
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	10.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	19.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.52 Hz
RGAIN	52

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3al



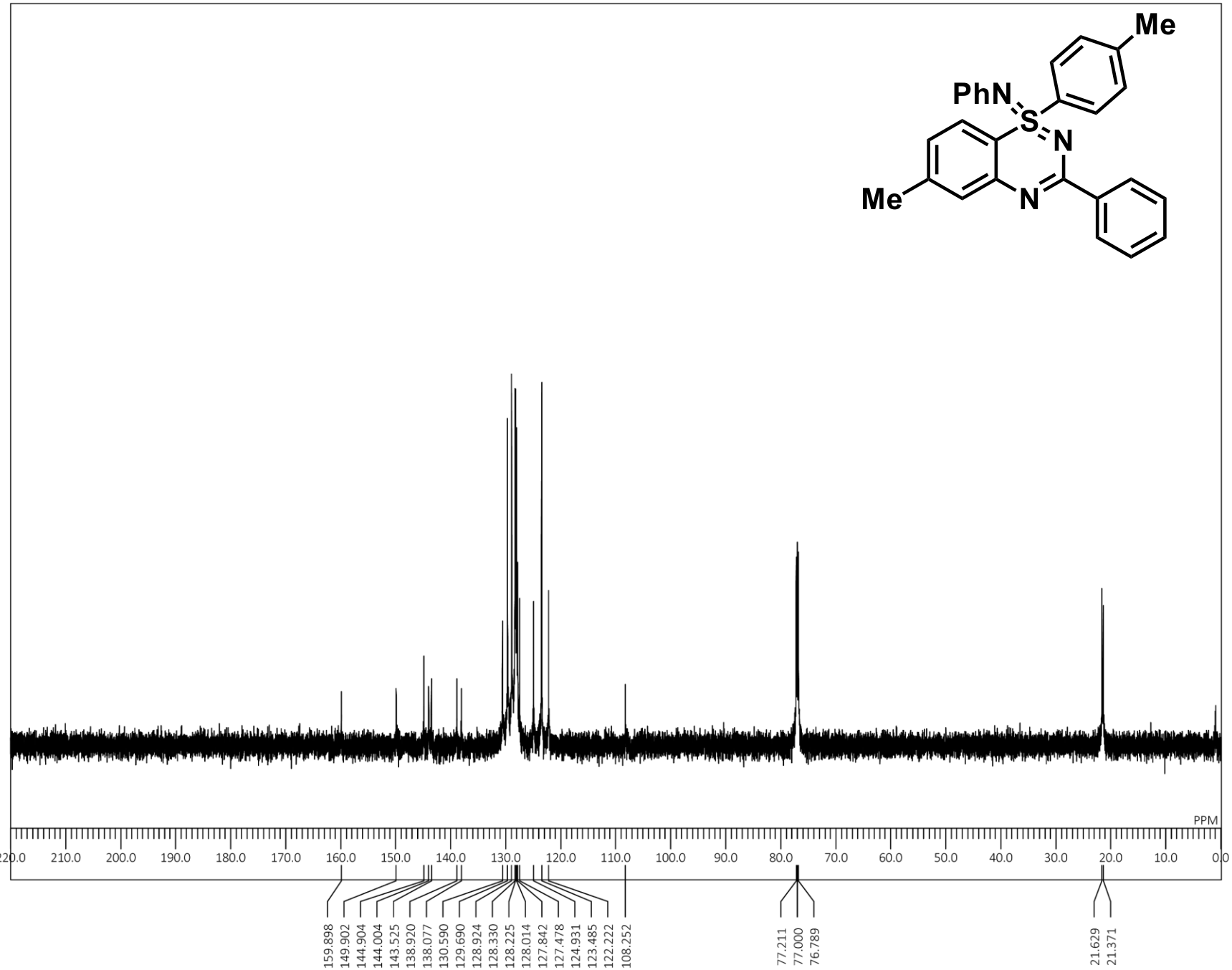
DFILE	AM03007_dio_Me_column_13C-1.a
COMNT	AM03007_dio_Me_column_13C
DATIM	2024-12-20 12:53:20
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	65
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	16.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3bb



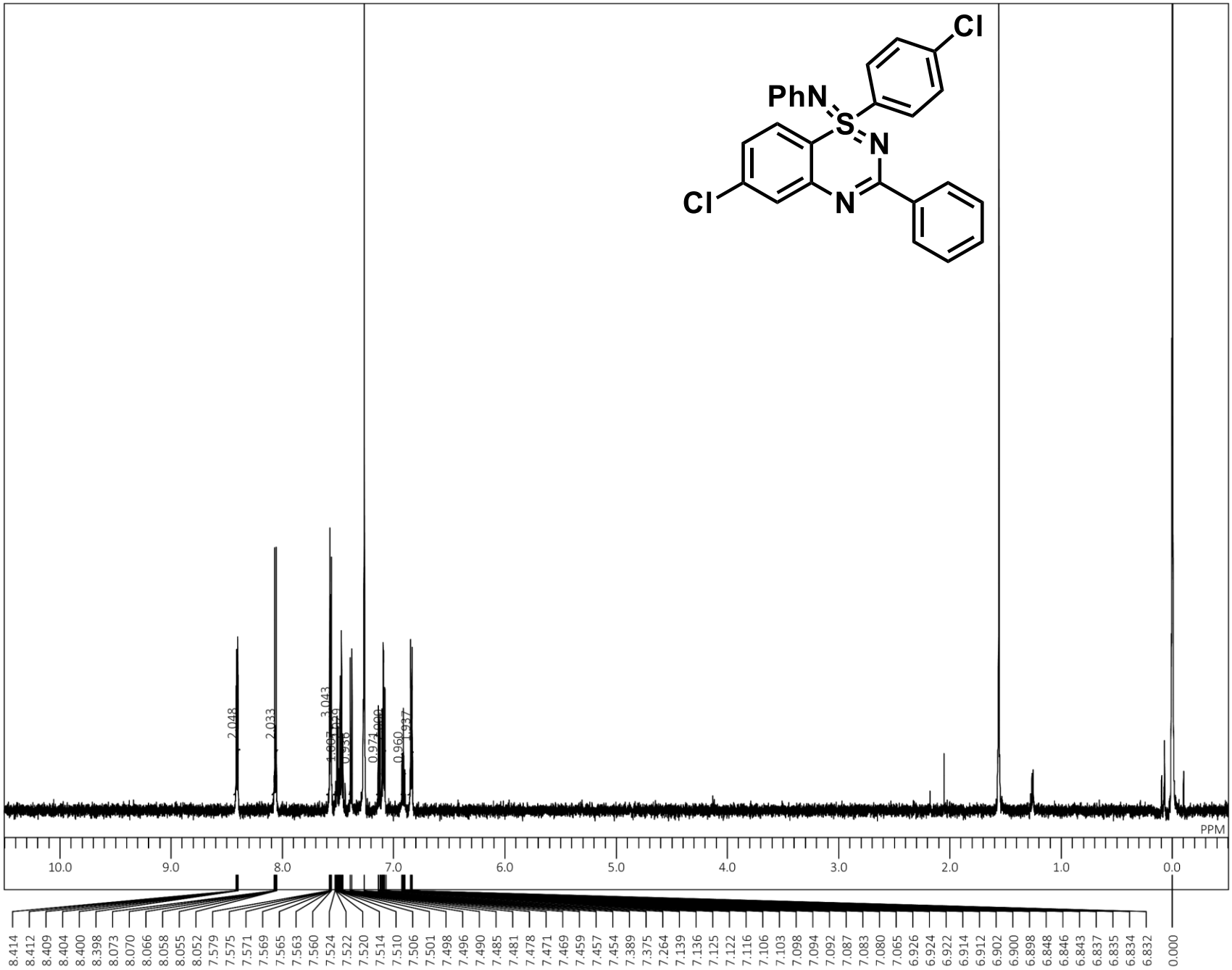
DFILE	AM_sul_pMe_1H-1.als
COMNT	AM_sul_pMe_1H
DATIM	2025-01-22 02:18:36
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	10.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	19.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.02 Hz
RGAIN	50

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3bb



DFILE	AM03009_sul_pMe_13C-1.als
COMNT	AM03009_sul_pMe_13C
DATIM	2024-12-19 00:19:49
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	316
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	17.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60

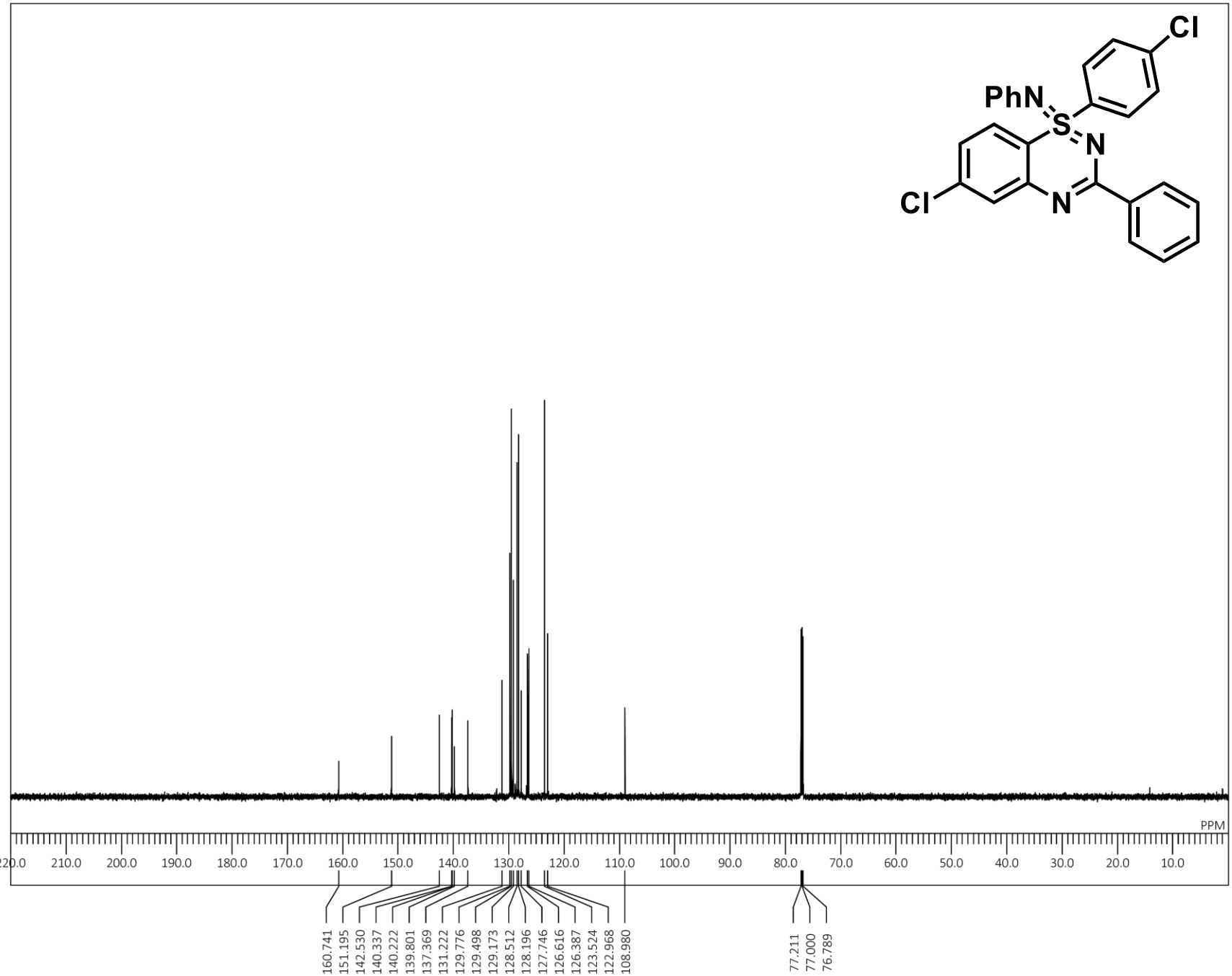
^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3cb



DFILE	AM03009_sul_pCl_1H.als
COMNT	AM03009_sul_pCl_column
DATIM	2024-12-17 12:06:43
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	5.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	16.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.02 Hz
RGAIN	52

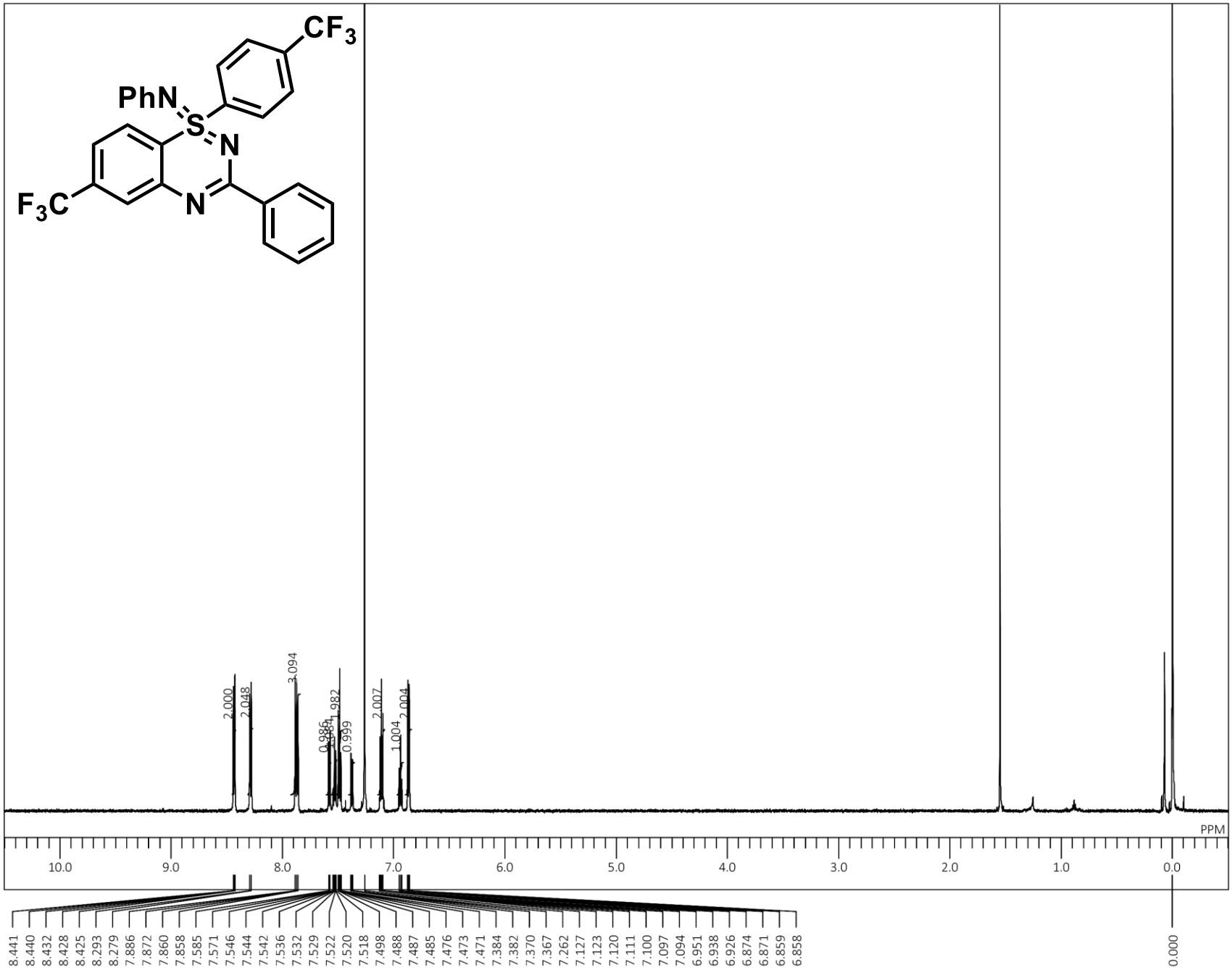
8.414 8.412 8.409 8.404 8.400 8.398 8.073 8.070 8.066 8.058 8.055 8.052 7.579 7.575 7.571 7.569 7.565 7.563 7.560 7.524 7.522 7.520 7.514 7.510 7.506 7.501 7.498 7.496 7.490 7.485 7.481 7.478 7.471 7.469 7.459 7.457 7.454 7.389 7.375 7.264 7.139 7.136 7.125 7.122 7.116 7.106 7.103 7.098 7.094 7.092 7.087 7.083 7.080 7.065 6.926 6.924 6.922 6.914 6.912 6.902 6.900 6.898 6.848 6.846 6.843 6.837 6.835 6.834 6.832 0.000

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3cb



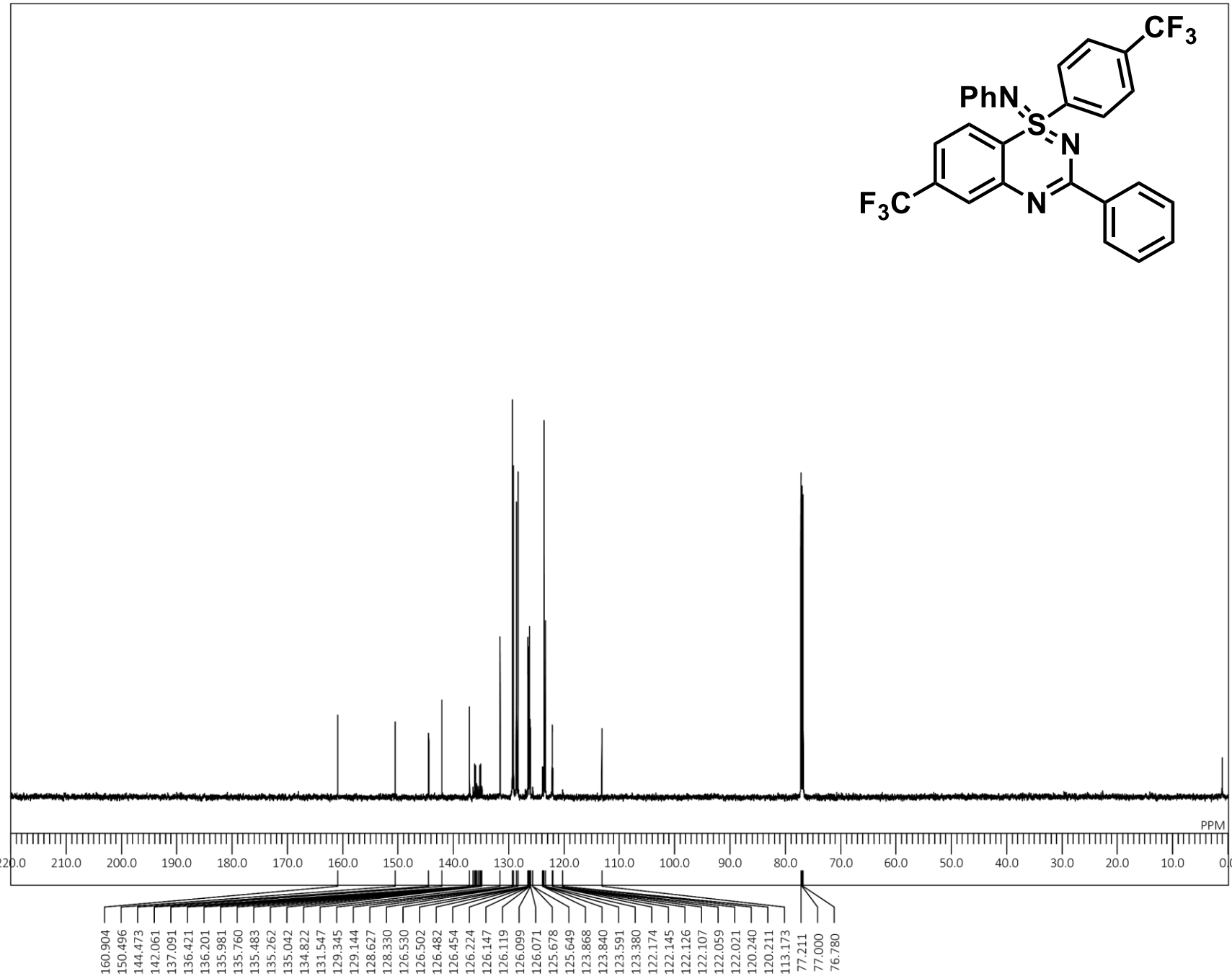
DFILE	AM03009_sul_pCl_13C-1.als
COMNT	AM03009_sul_pCl_13C
DATIM	2024-12-18 22:28:24
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	108
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	17.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3db



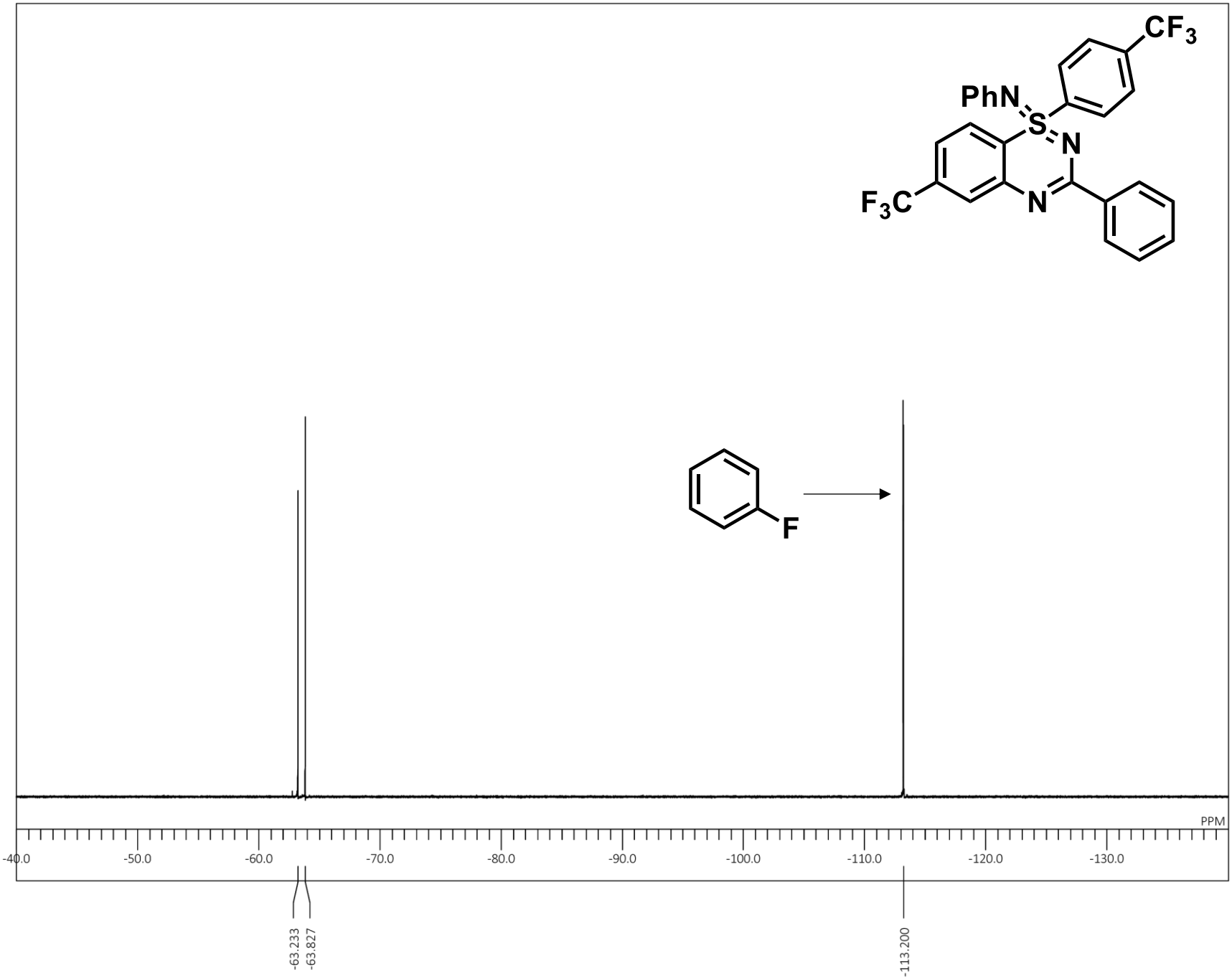
DFILE	AM_sul_pCF3_1H-3.als
COMNT	AM_sul_pCF3_1H_2
DATIM	2025-01-21 23:59:53
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	10.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	19.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.22 Hz
RGAIN	52

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3db



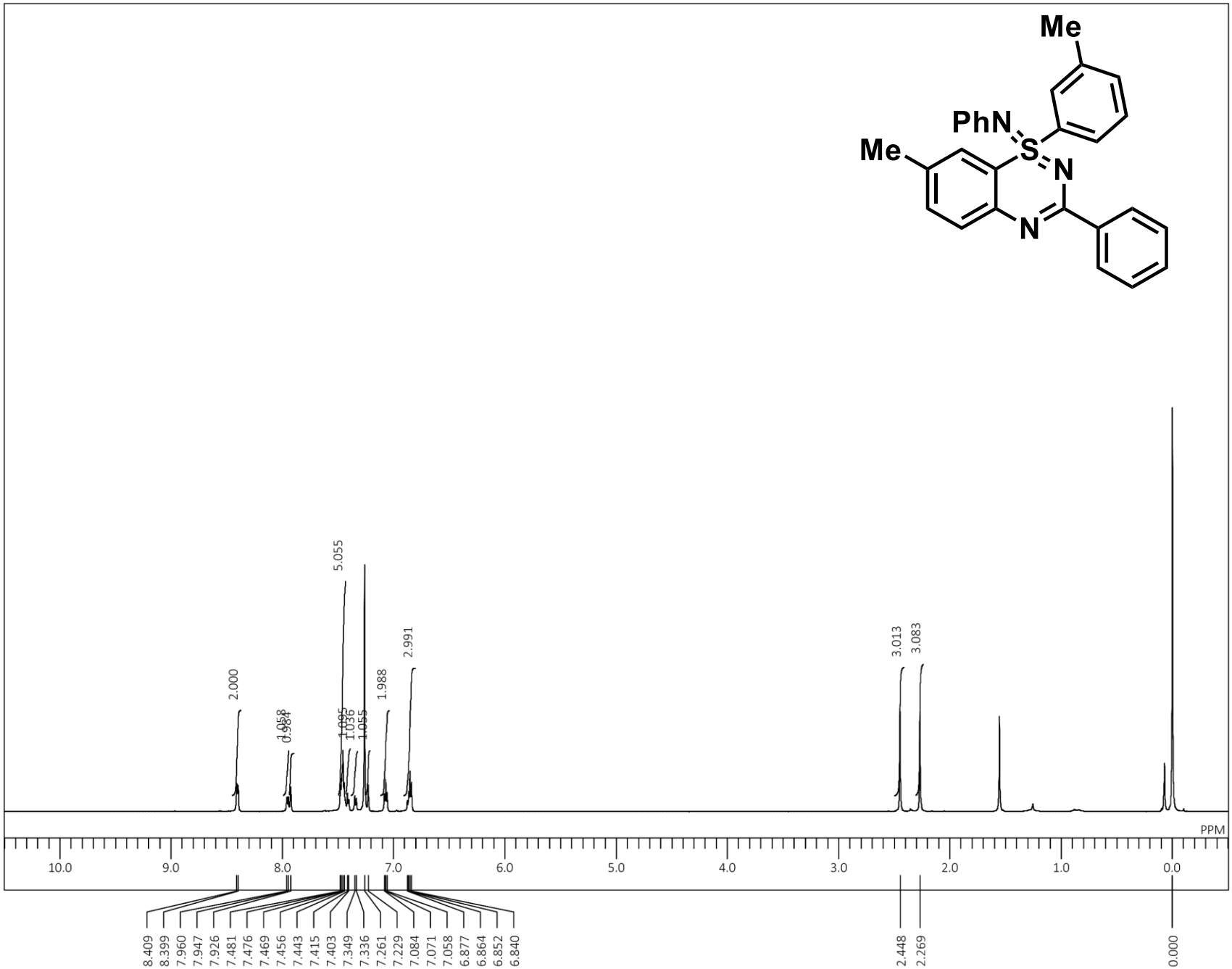
DFILE	AM03009_sul_pCF3_13C_2-1.als
COMNT	AM03009_sul_pCF3_13C_2
DATIM	2024-12-25 00:14:17
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	180
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	17.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	2.00 Hz
RGAIN	60

^{19}F NMR (564.67 MHz, $CDCl_3$) spectrum of 3db



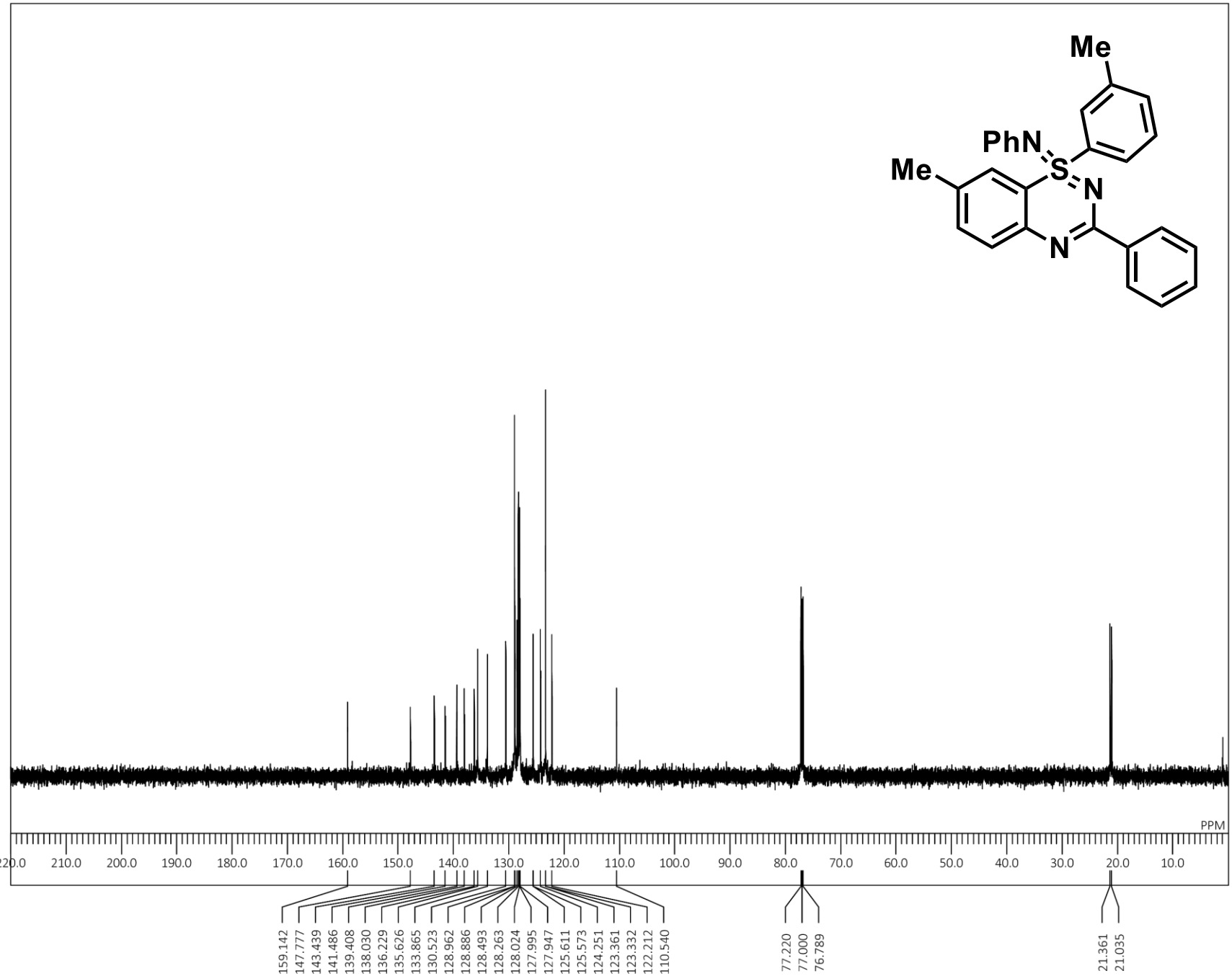
DFILE	AM_sul_pCF3_19F-1.als
COMNT	AM_sul_pCF3_19F
DATIM	2025-01-23 09:33:32
OBNUC	19F
EXMOD	single_pulse.ex2
OBFRQ	564.67 MHz
OBSET	5.29 KHz
OBFIN	1.21 Hz
POINT	26214
FREQU	56817.31 Hz
SCANS	8
ACQTM	0.4614 sec
PD	10.0000 sec
PW1	6.65 usec
IRNUC	19F
CTEMP	18.8 c
SLVNT	CDCL3
EXREF	-113.20 ppm
BF	0.02 Hz
RGAIN	52

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3eb



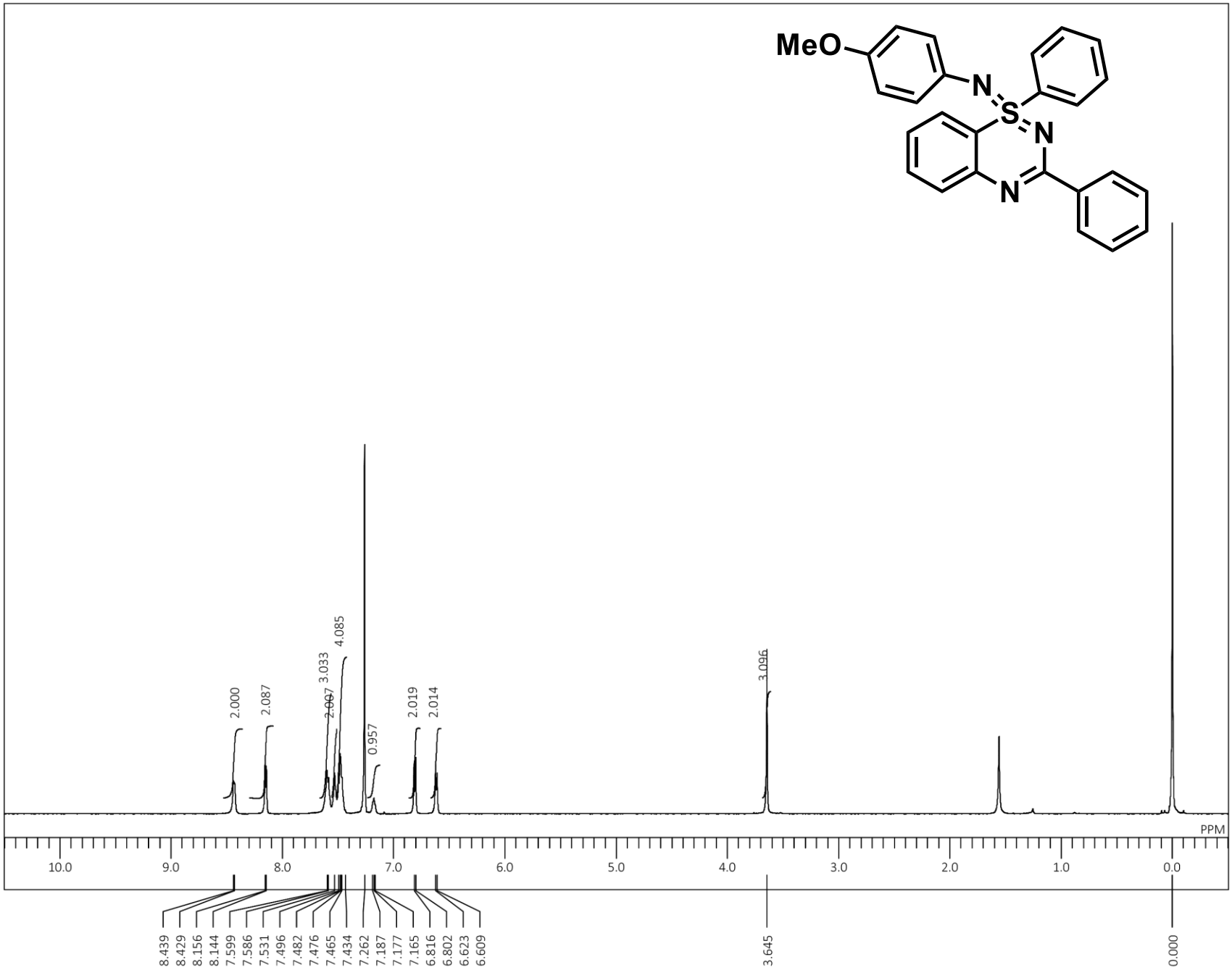
DFILE	AM_sul_mMe_1H-2.als
COMNT	AM_sul_mMe_1H
DATIM	2025-01-22 00:08:55
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	10.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	19.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	2.00 Hz
RGAIN	52

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3eb



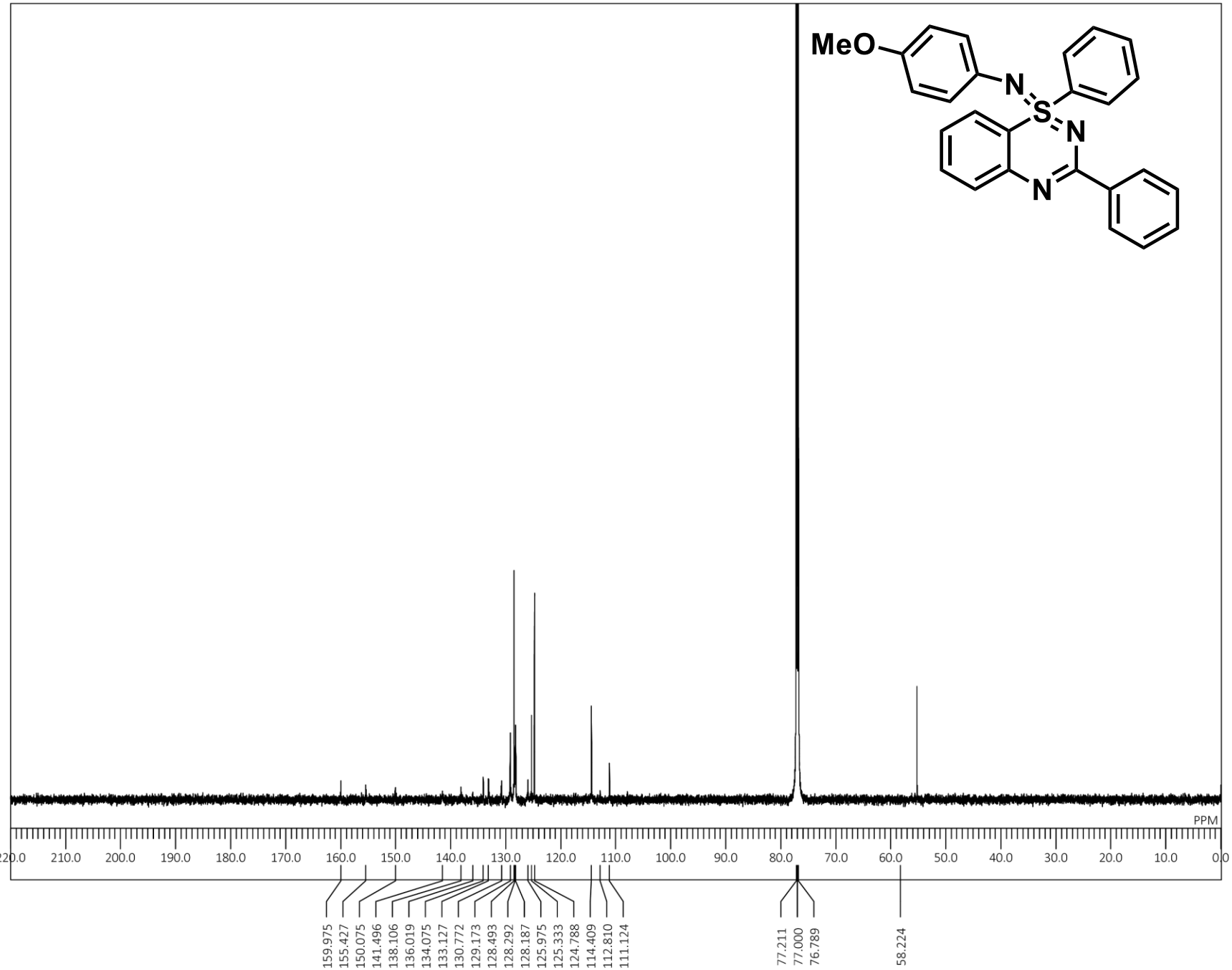
DFILE	AM03009_sul_mMe_13C-1.als
COMNT	AM03009_sul_mMe_13C
DATIM	2024-12-18 23:47:39
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	142
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	17.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.20 Hz
RGAIN	60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3fb



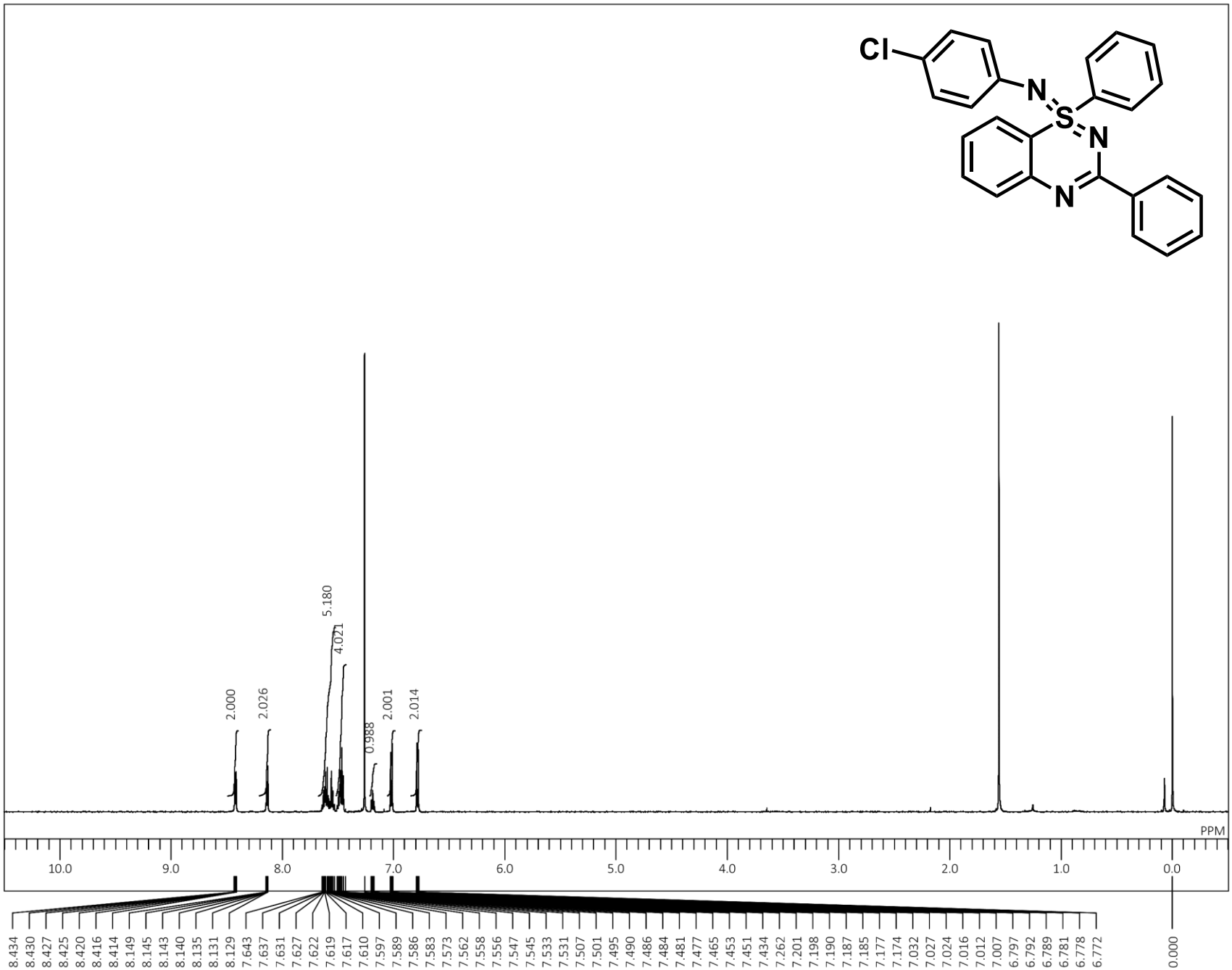
DFILE	AM_sul_NPh_pOMe_1H-2.als
COMNT	AM_sul_NPh_pOMe_1H
DATIM	2025-01-22 00:16:49
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	26214
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	10.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	19.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	2.00 Hz
RGAIN	52

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3fb



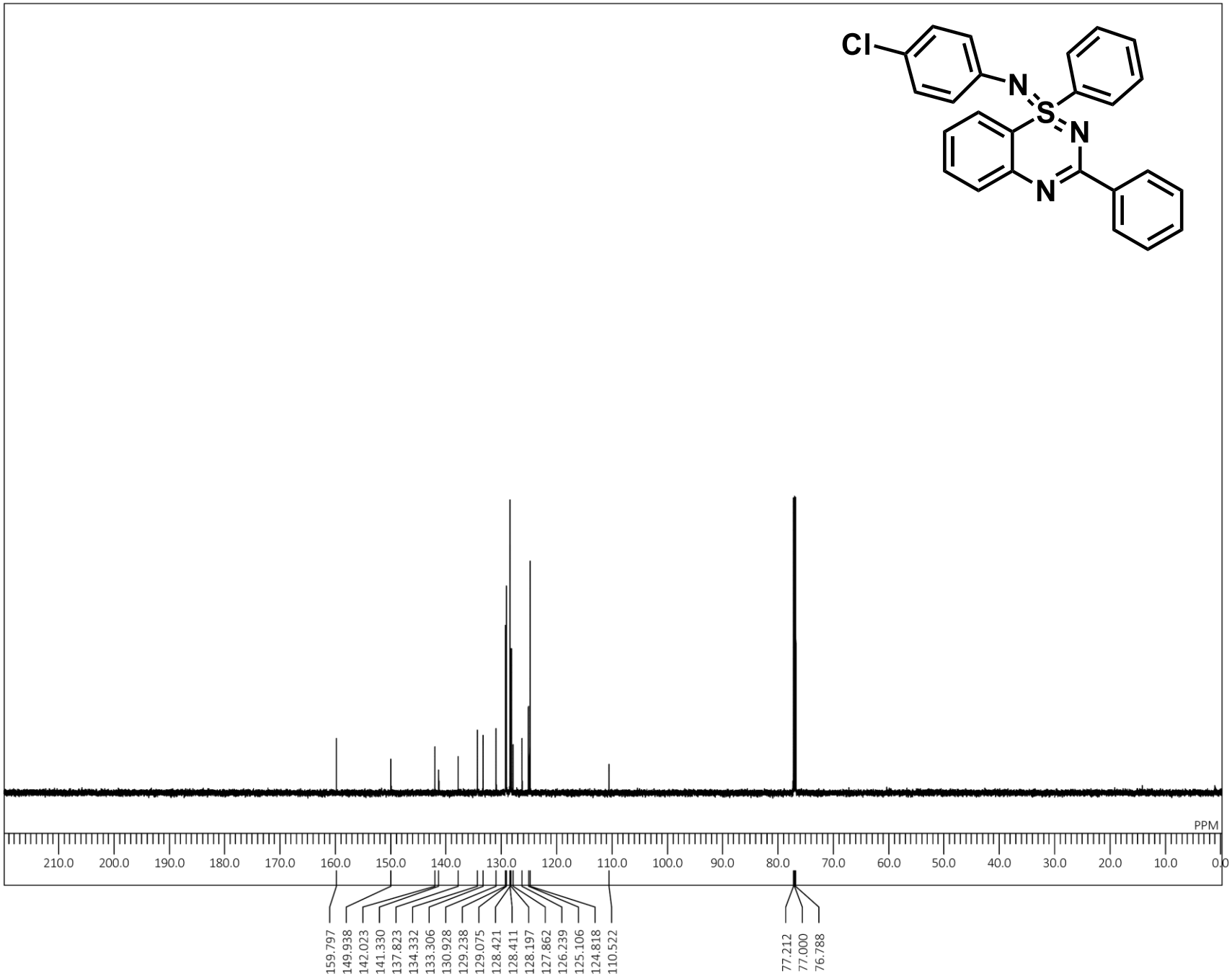
DFILE AM03021_sul_NPh_pOMe_13C-1
COMNT AM03021_sul_NPh_pOMe_13C
DATIM 2024-12-29 06:32:38
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 26214
FREQU 37878.21 Hz
SCANS 10000
ACQTM 0.6921 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 18.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.02 Hz
RGAIN 60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3gb



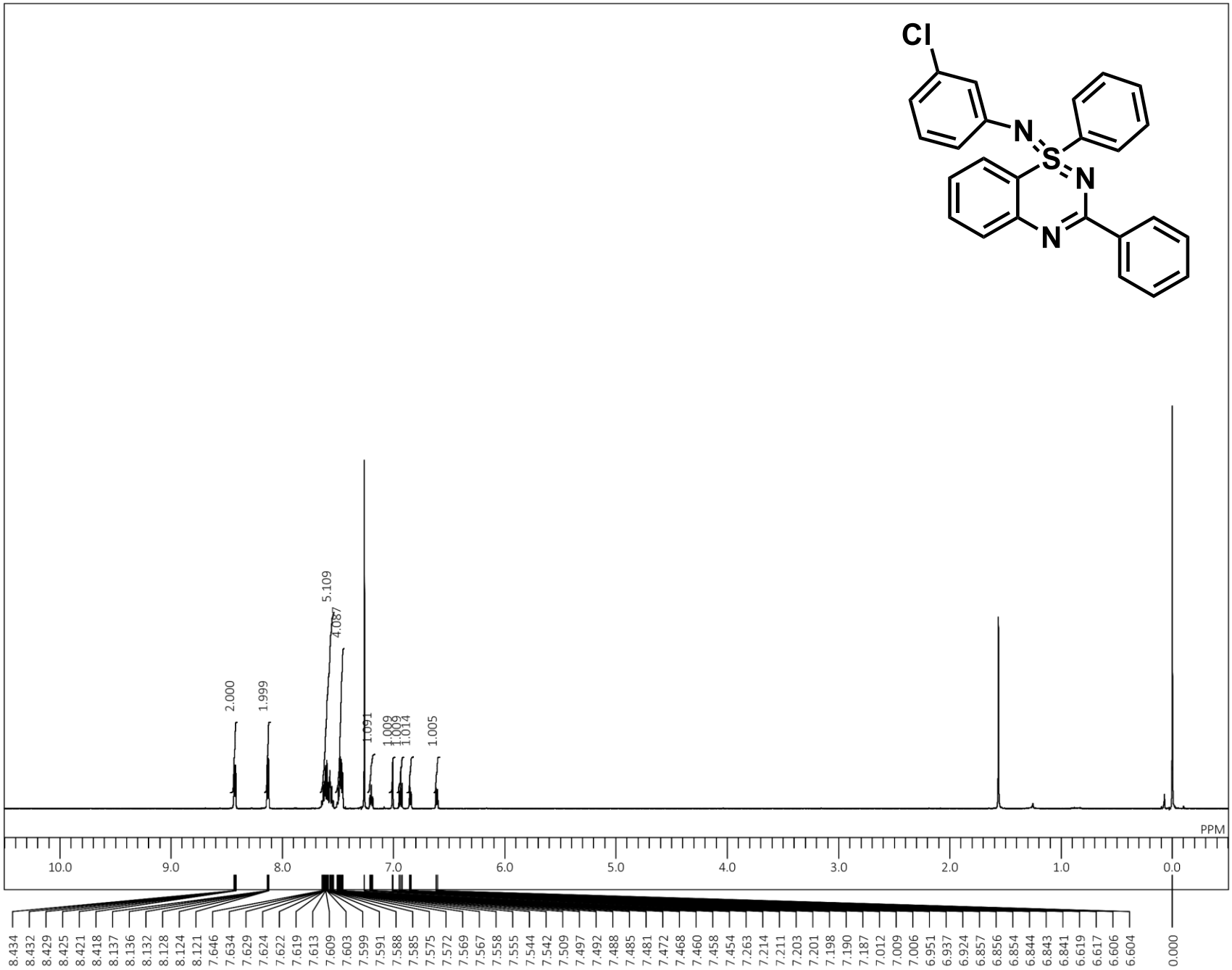
DFILE	TE02063_sul_NPh_pCl_1H.als
COMNT	TE02063_sul_NPh_pCl_1H
DATIM	2025-01-22 15:24:55
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	262144
FREQU	11261.26 Hz
SCANS	8
ACQTM	2.9098 sec
PD	5.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	20.2 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.50 Hz
RGAIN	52

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3gb



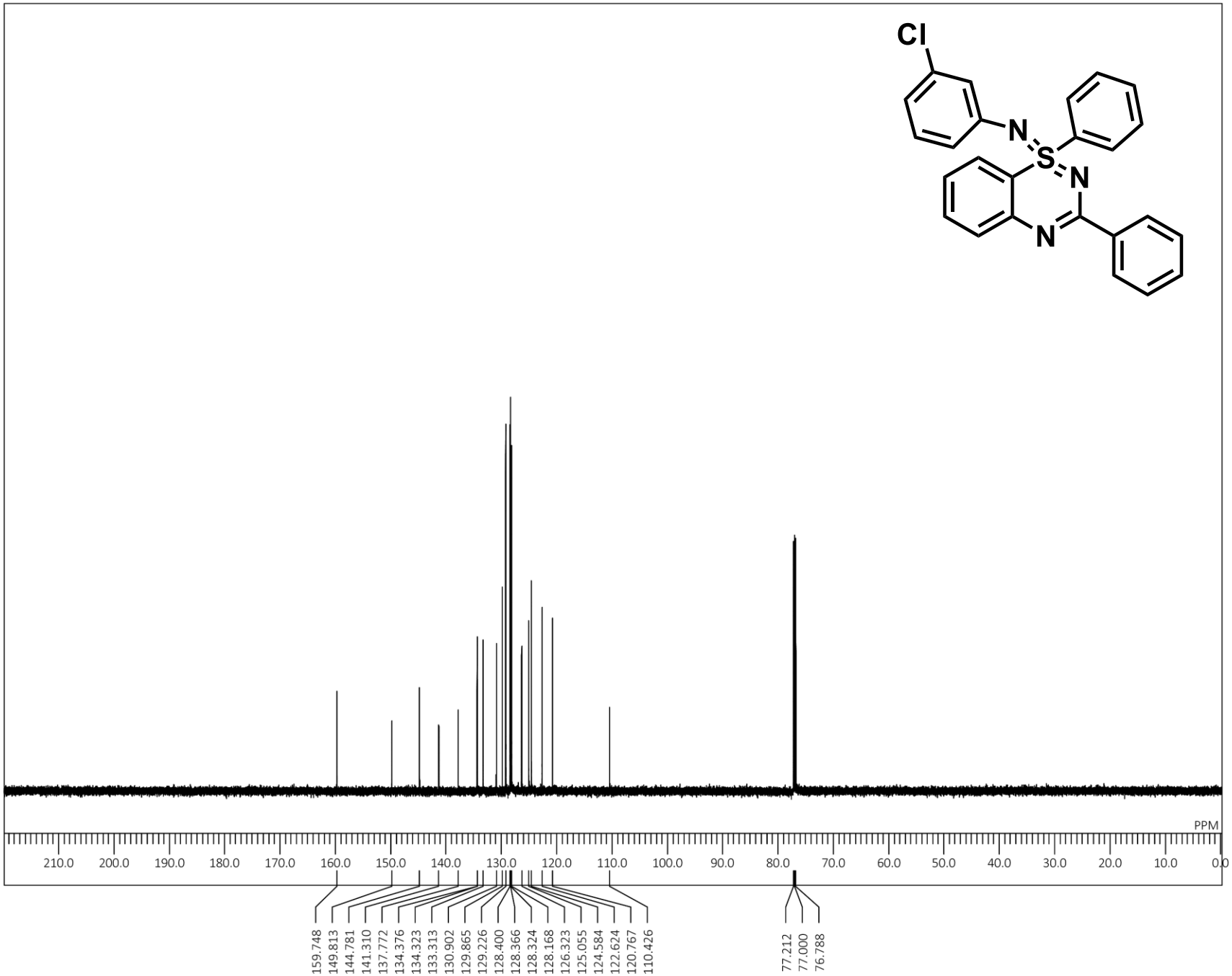
DFILE	TE02063_sul_NPh_pCl_13C.als
COMNT	TE02063_sul_NPh_pCl_13C
DATIM	2025-01-15 19:52:57
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	419424
FREQU	37878.21 Hz
SCANS	200
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.52 Hz
RGAIN	60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3hb



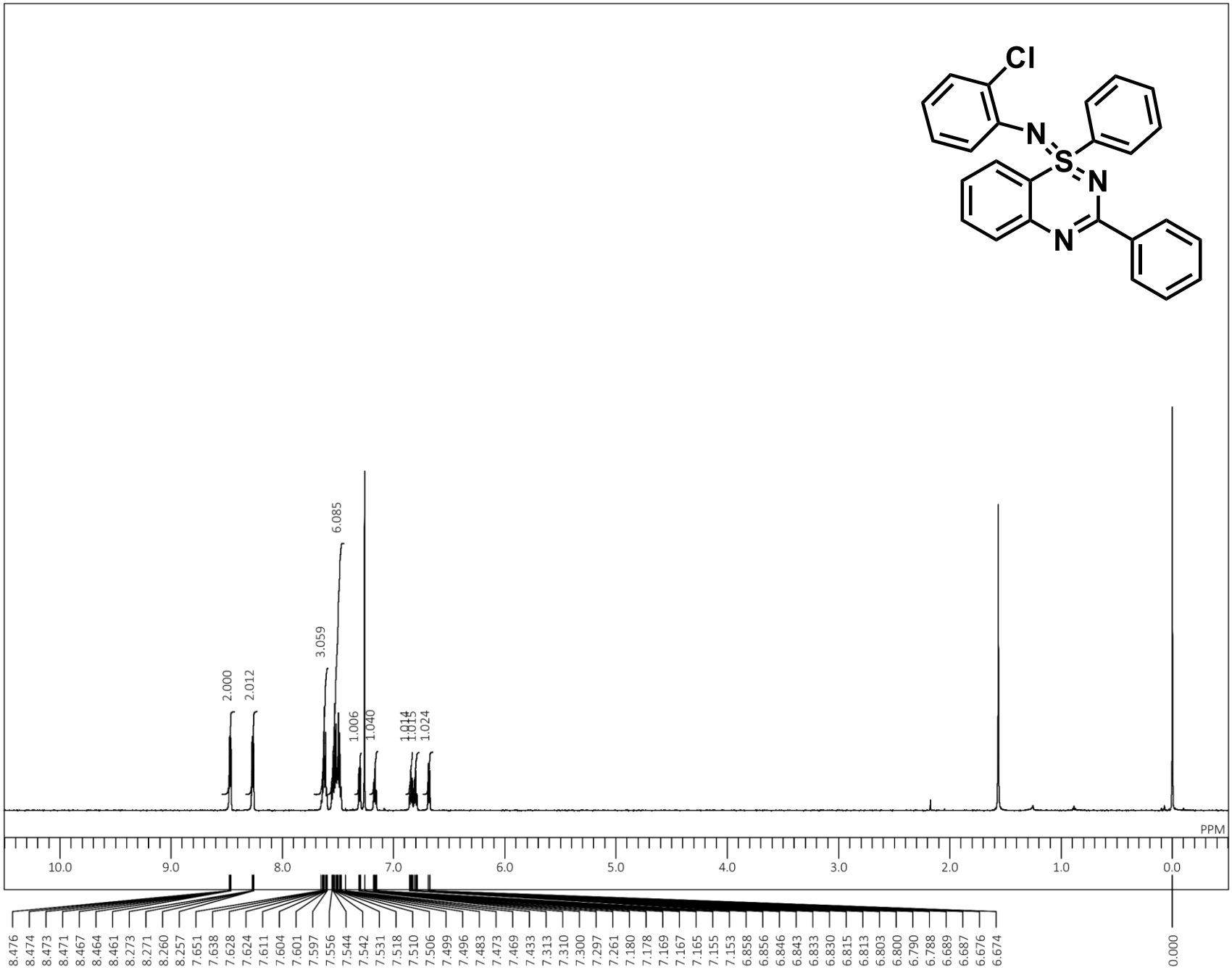
DFILE	TE02063_sul_NPh_mCl_1H.als
COMNT	TE02063_sul_NPh_mCl_1H
DATIM	2025-01-17 21:50:14
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	209712
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	5.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	17.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.50 Hz
RGAIN	54

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3hb



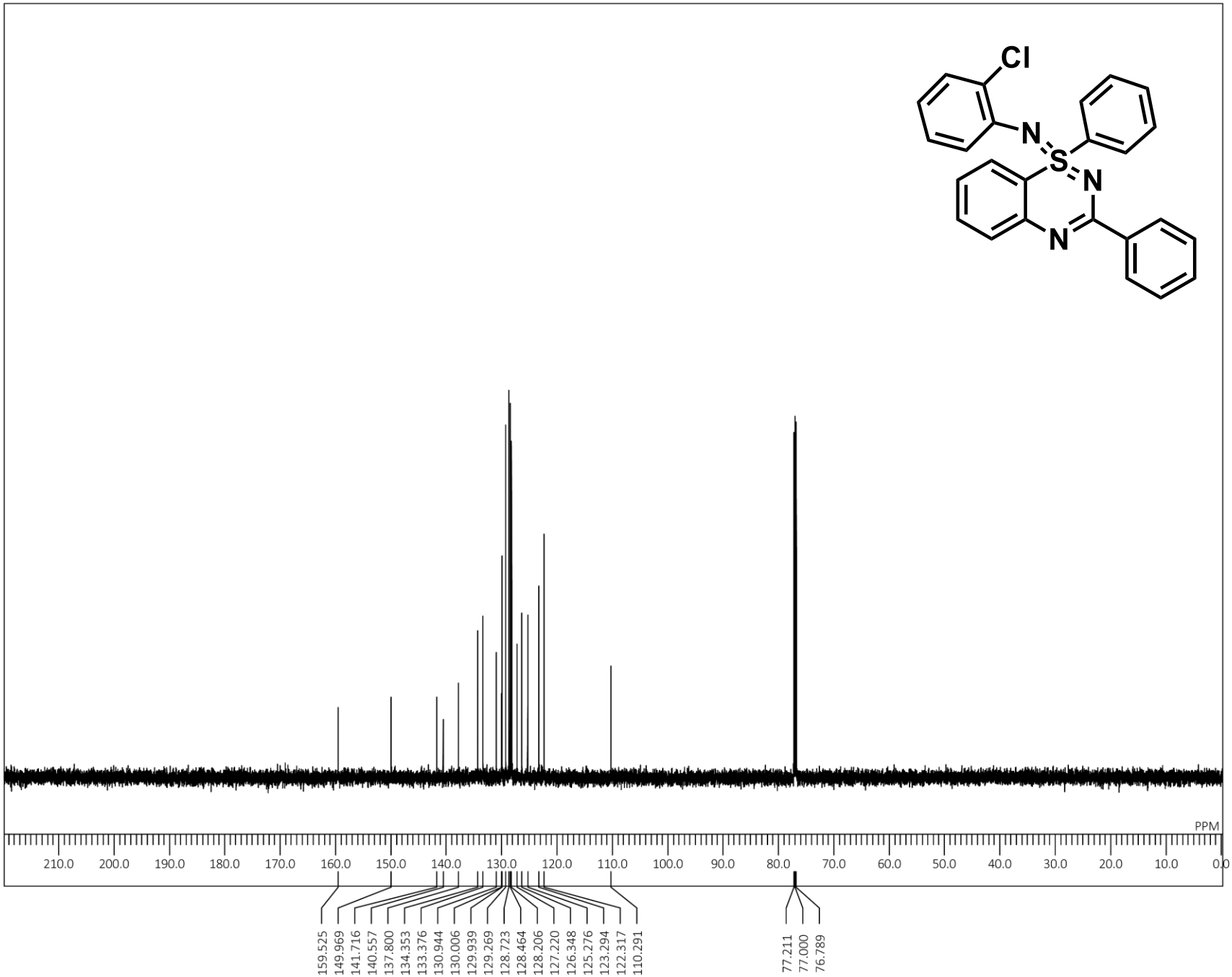
DFILE	TE02063_sul_NPh_mCl_13C.als
COMNT	TE02063_sul_NPh_mCl_13C
DATIM	2025-01-15 19:39:53
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	209712
FREQU	37878.21 Hz
SCANS	100
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	19.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

^{1}H NMR (600.17 MHz, $CDCl_3$) spectrum of 3ib



DFILE	TE02063_sul_NPh_oCl_1H.als
COMNT	TE02063_sul_NPh_oCl_1H
DATIM	2025-01-20 21:15:02
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	209712
FREQU	9008.87 Hz
SCANS	8
ACQTM	2.9098 sec
PD	5.0000 sec
PW1	7.00 usec
IRNUC	1H
CTEMP	19.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.60 Hz
RGAIN	52

$^{13}C\{^{1}H\}$ NMR (150.92 MHz, $CDCl_3$) spectrum of 3ib



DFILE	TE02063_sul_NPh_oCl_13C.als
COMNT	TE02063_sul_NPh_oCl_13C
DATIM	2025-01-15 19:30:01
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	64
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	3.83 usec
IRNUC	1H
CTEMP	18.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60