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Electronic Supplementary Information (ESI)

Pyridine tetrafluoro-λ^6-sulfanyl chlorides: Spontaneous addition to alkynes and alkenes in the presence or absence of photo-irradiation

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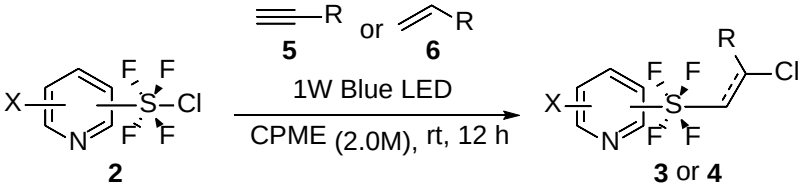
Contents

General information

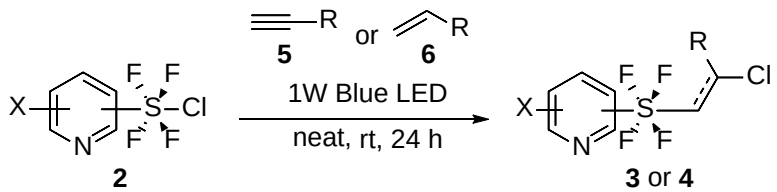
All reactions were performed in oven-dried 2 mL vial unless otherwise mentioned. All reagents were weighed out under N_2 atmosphere in a glove box. Solvents were transferred via syringe and were introduced into the reaction vessels. All the reactions were monitored by thin-layer chromatography (TLC) or ^{19}F NMR. Products were purified by column chromatography carried out on columns packed with silica gel (60N spherical neutral size 40-50 µm). The ^{1}H NMR (300 MHz) and ^{19}F NMR (282 MHz) spectra were recorded for solution in $CDCl_3$ on a Varian Mercury 300. ^{13}C NMR (126 MHz) spectra were recorded on Avance 500. Chemical shifts (δ) are expressed in ppm downfield from TMS (δ = 0.00 ppm), C_6F_6 [δ = −162.2 ppm ($CDCl_3$)], and $CHCl_3$ (δ = 77.16 ppm) as an internal standard for ^{1}H, ^{19}F and ^{13}C NMR respectively. High resolution mass spectrometry (HRMS) was recorded on a Waters, GCT Premier (EI-MS) with a TOF analyser and Waters Synapt G2 HDMS (ESI-MS). The wave numbers (ν˜) of recorded IR-signals are quoted in cm^{-1} on a JASCO FT/IR-4100 spectrometer. Melting points were recorded on a BUCHI M-565. Chemicals were purchased and used without further purification unless otherwise noted. Solvents DCM, Et_2O, Toluene, Hexane, $CHCl_3$, THF, 1,4-Dioxane, TBME, CPME were dried and distilled before use.

General Procedure 1: Synthesis of pyridine-*trans*-SF_4-alkynes 3 or pyridine-SF_4-alkanes 4 in CPME



An oven-dried 2 mL vial equipped with a magnetic stirrer bar was charged with pyridine-SF_4Cl **2** (0.2 mmol, 1.0 equiv) and an appropriate alkyne **5** or alkene **6** (0.22 mmol, 1.1 equiv) in CPME (0.1 mL) in the glove box. The closed vial was removed from the glove box. The reaction mixture was irradiated by the 1W blue LED light and stirred at room temperature for 12 h. The reaction mixture was concentrated to give the crude product, which was purified by column chromatography on silica gel eluting with *n*-Hexane/AcOEt to give the product **3** or **4**.

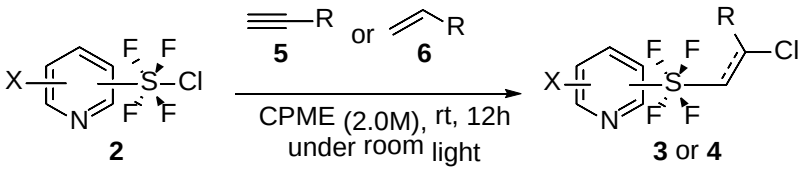
General Procedure 2: Synthesis of pyridine-SF_4-alkenes 3 or pyridine-SF_4-alkanes 4 under neat condition (without solvent)



An oven-dried 2 mL vial equipped with a magnetic stirrer bar was charged with pyridine-SF_4Cl **2** (0.2 mmol, 1.0 equiv) and an appropriate alkyne **5** or alkene **6** (0.22 mmol, 1.1 equiv) in the

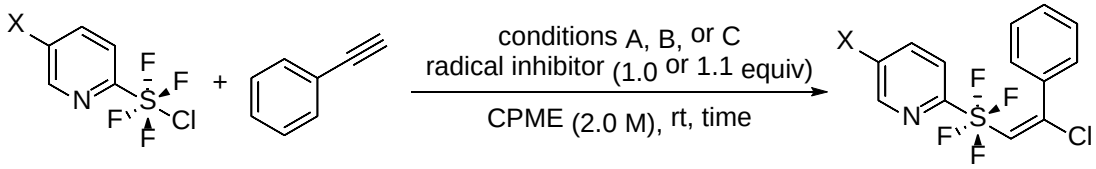
glove box. The closed vial was removed from the glove box. The reaction mixture was irradiated by the 1W blue LED light and stirred at room temperature for 24 h. The reaction mixture was concentrated to give the crude product, which was checked by ^{19}F NMR to calculate the yield using C_6H_5F as an internal standard. The crude product was purified by column chromatography on silica gel eluting with *n*-Hexane/AcOEt to give the product **3** or **4**.

General Procedure 3: Synthesis of pyridine-SF_4-alkenes 3 or pyridine-SF_4-alkanes 4 under regular laboratory room light



An oven-dried 2 mL vial equipped with a magnetic stirrer bar was charged with pyridine-SF_4Cl **2** (0.2 mmol, 1.0 equiv) and an appropriate alkyne **5** or alkene **6** (0.22 mmol, 1.1 equiv) in CPME (0.1 mL) in the glove box. The closed vial was removed from the glove box. The reaction mixture was stirred at room temperature for 12 h under regular laboratory room light. The reaction mixture was concentrated to give the crude product. The yield was calculated by ^{19}F NMR using C_6H_5F as an internal standard.

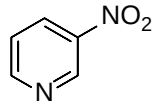
General Procedure 4: Mechanistic investigations (Reaction of 2 with 5a in the presence of radical inhibitor)



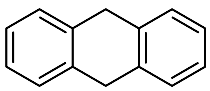
2a: X = Br
2b: X = H
2c: X = NO_2

5a

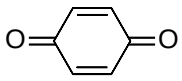
radical inhibitor



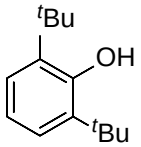
3-nitropyridine
(1.0 equiv)



DHA
(1.1 equiv)



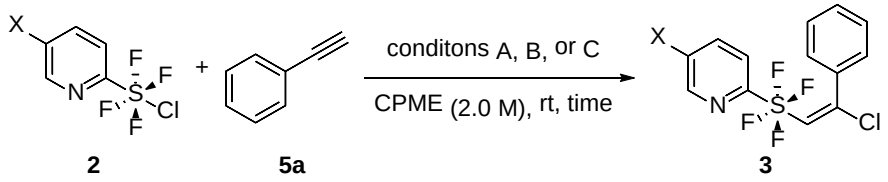
p-benzoquinone
(1.1 equiv)



2,6-di-*tert*-butylphenol
(1.1 equiv)

An oven-dried 2 mL vial equipped with a magnetic stirrer bar was charged with pyridine-SF_4Cl **2** (0.1 mmol, 1.0 equiv) and alkyne **5a** (0.11 mol, 1.1 equiv) in CPME (0.05 mL) followed by the addition of a radical inhibitor (see above scheme) in the glove box. The closed vial was removed from the glove box. The reaction mixture was irradiated by the 1W blue LED light and stirred at room temperature for 12 h. The reaction progress was monitored by ^{19}F NMR. After complete conversion, the yield was checked by ^{19}F NMR of crude reaction mixture using $PhCF_3$ as an internal standard.

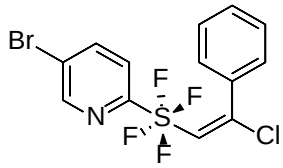
General Procedure 5:Time-dependent analysis of the addition of 2 to 5a under three different conditions



2 **5a** **3**

A NMR tube was charged with pyridine-SF_4Cl **2** (0.5 mmol, 1.0 equiv) and alkyne **5a** (0.55 mol, 1.1 equiv) in CPME (0.25 mL) in the glove box. The closed tube was removed from the glove box. The reaction mixture was stirred at room temperature under condition A: irradiation with the 1W blue LED light, condition B: in regular room light, or condition C: in the dark. The conversion and yield were calculated by each integration of substrate and product by ^{19}F NMR (Spinsolve®, Magritek) with regular intervals. After complete conversion, the yield was checked by ^{19}F NMR of crude reaction mixture using $PhCF_3$ or C_6H_5F as an internal standard.

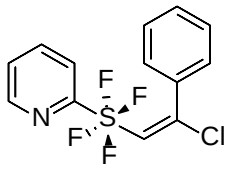
(*E*)-5-Bromo-2-((2-chloro-2-phenylvinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3aa)[1]



White solid. 91% yield (74.0 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5a** (0.22 mmol, 22.5 mg) for 12 h or 78% yield (62.9 mg) according to general procedure 2. HRMS (ESI): *m/z* calcd for $C_{13}H_9BrClF_4NNaS$ $[M+Na]^+$: 423.9161, found 423.9160. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 1.9 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.47–7.32 (m, 5H), 7.26–7.14 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.01 (d, *J* = 8.5 Hz, 4F).

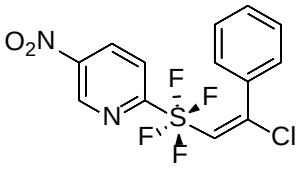
Gram scale synthesis: according to general procedure 1, pyridine-SF_4Cl **2a** (3.33 mmol, 1.0 equiv) and alkyne **5a** (3.66 mmol, 1.1 equiv) in CPME (1.67 mL) gave the product **3aa** (1.18 g, 88%).

(*E*)-2-((2-Chloro-2-phenylvinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ba)[1]



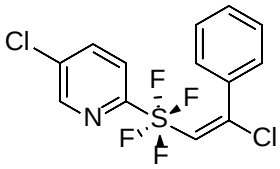
Colorless oil. 90% yield (58.3 mg) according to general procedure 1 with **2b** (0.2 mmol, 44.3 mg) and **5a** (0.22 mmol, 22.5 mg) for 12 h or 74% yield (47.7 mg) according to general procedure 2. HRMS (ESI): *m/z* calcd for $C_{13}H_{10}ClF_4NNaS$ $[M+Na]^+$: 346.0056 found: 346.0060. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 4.2 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.49–7.40 (m, 2H), 7.40–7.30 (m, 3H), 7.23 (quint, *J* = 8.3 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 60.28 (d, *J* = 5.9 Hz, 4F).

(*E*)-5-Nitro-2-((2-chloro-2-phenylvinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ca)[1]



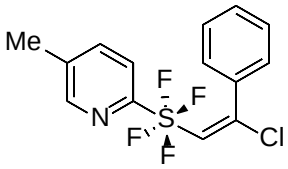
White solid. 80% yield (59.0 mg) according to general procedure 1 with **2c** (0.2 mmol, 53.3 mg) and **5a** (0.22 mmol, 22.5 mg) for 12 h. HRMS (EI): *m/z* calcd for $C_{13}H_9ClF_4N_2O_2S$ $[M]^+$: 368.0009 found: 368.0015. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.25 (d, *J* = 2.6 Hz, 1H), 8.54 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.48–7.33 (m, 5H), 7.21 (quint, *J* = 8.3 Hz, 1H), ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.14 (d, *J* = 8.7 Hz, 4F).

(*E*)-5-Chloro-2-((2-chloro-2-phenylvinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3da)[1]



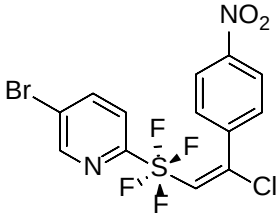
White solid. 88% yield (62.9 mg) according to general procedure 1 with **2d** (0.2 mmol, 51.2 mg) and **5a** (0.22 mmol, 22.5 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{13}H_9Cl_2F_4NNaS$ $[M+Na]^+$: 379.96m67, found 379.9669. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 2.6 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.48–7.33 (m, 5H), 7.26–7.13 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.19 (d, *J* = 8.1 Hz, 4F).

(*E*)-5-Methyl-2-((2-chloro-2-phenylvinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ea)[1]



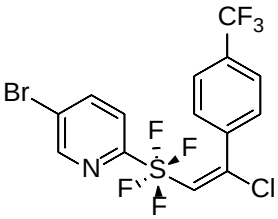
White solid. 84% yield (57.0 mg) according to general procedure 1 with **2e** (0.2 mmol, 47.1 mg) and **5a** (0.22 mmol, 22.5 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{14}H_{12}ClF_4NNaS$ $[M+Na]^+$: 360.0213 found: 360.0208. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (s, 1H), 7.57–7.41 (m, 3H), 7.40–7.31 (m, 2H), 7.29–7.15 (m, 1H), 2.31 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 60.33 (d, *J* = 7.9 Hz, 4F).

(*E*)-5-Bromo-2-((2-chloro-2-(4-nitrophenyl)vinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ab)[1]



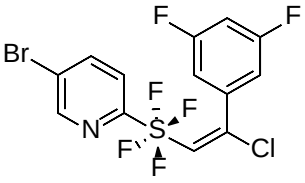
Yellow solid. 39% yield (34.8 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5b** (0.22 mmol, 32.4 mg) for 24 h. HRMS (ESI): *m/z* calcd for $C_{13}H_8BrClF_4N_2NaO_2S$ $[M+Na]^+$: 468.9012 found: 468.8994. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 2.4 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.26 (quint, *J* = 7.9 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.34 (d, *J* = 8.0 Hz, 4F).

(*E*)-5-Bromo-2-((2-chloro-2-(4-(trifluoromethyl)phenyl)vinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ac)[1]



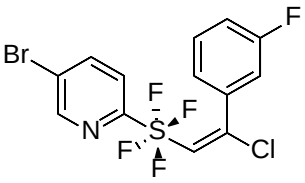
White solid. 44% yield (41.0 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5c** (0.22 mmol, 37.4 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{14}H_8NF_7NaSClBr$ $[M+Na]^+$: 491.9035 found: 491.9034. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 2.2 Hz, 1H), 7.90 (d, *J* = 9.5 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.24 (quint, *J* = 8.2 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.23 (d, *J* = 8.4 Hz, 4F), −63.42 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.14 (quint, *J* = 31.0 Hz), 148.36, 143.85 (quint, *J* = 29.4 Hz), 140.91, 140.37, 137.54 (quint, *J* = 7.7 Hz), 131.41 (q, *J* = 32.7 Hz), 128.68, 125.35 (q, *J* = 3.8 Hz), 123.84 (q, *J* = 271.9 Hz), 122.75, 122.71 (quint, *J* = 4.5 Hz). IR (KBr): 3082, 3057, 1643, 1446, 1325, 1130, 850, 760, 633, 530 cm^{-1}. m.p.: 103.6–104.9 °C. (CH_2Cl_2/pentane).

(*E*)-5-Bromo-2-((2-chloro-2-(3,5-difluorophenyl)vinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ad)[1]



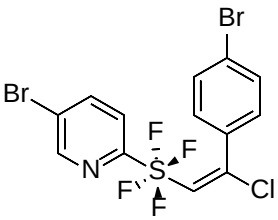
Light-yellow solid. 53% yield (46.2 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5d** (0.22 mmol, 30.4 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{13}H_8BrF_4NNaS$ $[M+Na]^+$: 459.8973 found: 459.8969. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 1.9 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 7.20 (quint, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 5.4 Hz, 2H), 6.90–6.76 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.10 (d, *J* = 8.3 Hz, 4F), -109.30 (dd, *J* = 8.5 Hz, 2F).

(*E*)-5-Bromo-2-((2-chloro-2-(3-fluorophenyl)vinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ae)[1]



Light-yellow solid. 73% yield (61.4 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5e** (0.22 mmol, 26.4 mg) for 12 h or 61% yield (51.3 mg) according to general procedure 2. HRMS (ESI): *m/z* calcd for $C_{13}H_8BrClF_5NNaS$ $[M+Na]^+$: 441.9067 found: 441.9058. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 1.8 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.40–7.29 (m, 1H), 7.28–7.12 (m, 3H), 7.12–7.01 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.08 (d, *J* = 8.1 Hz, 4F), −112.93 (dd, *J* = 14.3, 8.5 Hz, 1F).

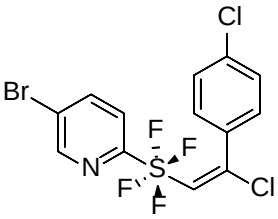
(*E*)-5-Bromo-2-((2-chloro-2-(4-bromophenyl)vinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3af)



White solid. 70% yield (68.1 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5f** (0.22 mmol, 39.8 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{13}H_8NF_4NaSClBr_2$ $[M+Na]^+$: 501.8267 found: 501.8271. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 2.0 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.57 –7.45 (m, 3H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.20 (quint, *J* = 8.2 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ =

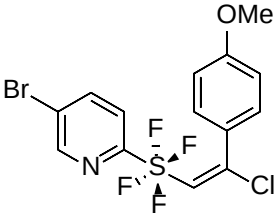
61.13 (d, *J* = 8.1 Hz, 4F). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.22 (quint, *J* = 31.1 Hz), 148.29, 143.48 (quint, *J* = 29.1 Hz), 140.84, 138.13 (quint, *J* = 7.6 Hz), 135.69, 131.52, 129.82, 123.91, 122.89, 122.72 (quint, *J* = 4.4 Hz). IR (KBr): 3078, 3055, 1639, 1446, 1005, 908, 841, 766, 634, 532 cm^{-1}. m.p.: 97.5–99.0 °C. (CH_2Cl_2/pentane)

(*E*)-5-Bromo-2-((2-chloro-2-(4-chlorophenyl)vinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ag)



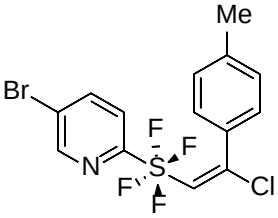
White solid. 78% yield (68.2 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5g** (0.22 mmol, 30.0 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{13}H_8NF_4NaSCl_2Br$ $[M+Na]^+$: 456.8772 found: 456.8760. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 2.0 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.36 (br s, 4H), 7.20 (quint, *J* = 8.2 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.11 (d, *J* = 8.3 Hz, 4F) ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.20 (quint, *J* = 31.1 Hz), 148.24, 143.47 (quint, *J* = 29.0 Hz), 140.80, 138.11 (quint, *J* = 7.7 Hz), 135.56, 135.16, 129.59, 128.53, 122.84, 122.68 (quint, *J* = 4.3 Hz). IR (KBr): 3086, 3055, 1639, 1446, 1007, 914, 843, 766, 638, 530 cm^{-1}. m.p.: 99.0–100.2 °C. (CH_2Cl_2/pentane).

(*E*)-5-Bromo-2-((2-chloro-2-(4-methoxyphenyl)vinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ah)[1]



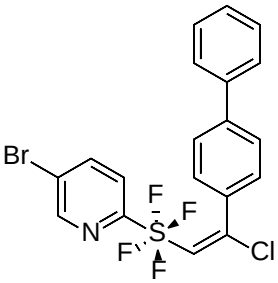
White solid. 93% yield (80.9 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5h** (0.22 mmol, 29.1 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{14}H_{11}BrClF_4NNaOS$ $[M+Na]^+$: 453.9267 found:453.9261. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 2.1 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.17 (quint, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 60.87 (d, *J* = 8.2 Hz, 4F).

(*E*)-5-Bromo-2-((2-chloro-2-(*p*-tolyl)vinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ai)[1]



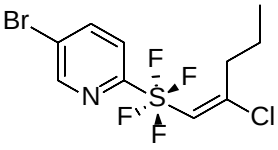
White solid. 83% yield (69.2 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5i** (0.22 mmol, 25.6 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{14}H_{11}BrClF_4NNaS$ $[M+Na]^+$: 437.9318 found: 437.9316. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.23–7.11 (m, 3H), 2.35 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 60.98 (d, *J* = 8.1 Hz, 4F).

(*E*)-2-((2-([1,1'-biphenyl]-4-yl)-2-chlorovinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3aj)[1]



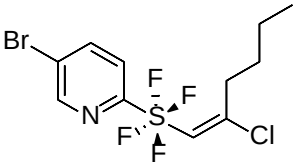
White solid. 89% yield (85.1 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5j** (0.22 mmol, 39.2 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{19}H_{13}NF_4NaSClBr$ $[M+Na]^+$: 499.9474 found: 499.9481. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.65–7.55 (m, 4H), 7.54–7.48 (m, 3H), 7.48–7.40 (m, 2H), 7.39–7.32 (m, 1H), 7.23 (quint, *J* = 8.5 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.14 (d, *J* = 8.5 Hz, 4F). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.39 (quint, *J* = 31.4 Hz), 148.24, 143.03 (quint, *J* = 28.8 Hz), 142.21, 140.79, 140.22, 139.30 (quint, *J* = 7.6 Hz), 135.64, 128.94, 128.65, 127.88, 127.25, 126.87, 122.79 (quint, *J* = 4.4 Hz), 122.79. IR (KBr): 3097, 3051, 1635, 1007, 912, 849, 756, 631, 530 cm^{-1}. m.p.: 92.2–93.5 °C. (CH_2Cl_2/pentane).

(*E*)-5-Bromo-2-((2-chloropent-1-en-1-yl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ak)[1]



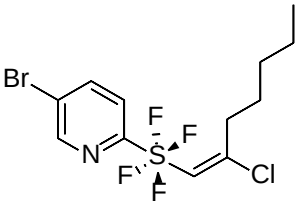
White solid. 79% yield (58.3 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5k** (0.22 mmol, 15.0 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{10}H_{11}BrClF_4NNaS$ $[M+Na]^+$: 389.9318 found: 389.9319. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 2.0 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 6.87 (quint, *J* = 8.8 Hz, 1H), 2.77 (t, *J* = 7.2 Hz, 2H), 1.80–1.62 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 59.21 (d, *J* = 8.6 Hz, 4F).

(*E*)-5-Bromo-2-((2-chlorohex-1-en-1-yl)tetrafluoro-λ^6-sulfaneyl)pyridine (3al)[1]



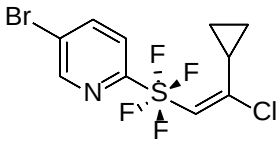
White solid. 71% yield (54.5 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5l** (0.22 mmol, 18.1 mg) for 12 h or 70% yield (53.4 mg) according to general procedure 2. HRMS (ESI): *m/z* calcd for $C_{11}H_{13}BrClF_4NNaS$ $[M+Na]^+$: 403.9474 found: 403.9474. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.59 (d, *J* = 2.4 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 6.86 (quint, *J* = 8.9 Hz, 1H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.74–1.56 (m, 2H), 1.47–1.31 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 59.03 (d, *J* = 8.6 Hz, 4F).

(*E*)-5-Bromo-2-((2-chlorohept-1-en-1-yl)tetrafluoro-λ^6-sulfaneyl)pyridine (3am)[1]



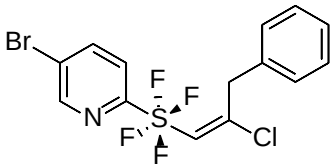
White solid. 72% yield (57.3 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5m** (0.22 mmol, 21.2 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{12}H_{15}BrClF_4NNaS$ $[M+Na]^+$: 417.9631 found: 417.9629. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 2.3 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 6.86 (quint, *J* = 8.8 Hz, 1H), 2.78 (t, *J* = 7.7 Hz, 2H), 1.77–1.59 (m, 2H), 1.45–1.30 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 59.08 (d, *J* = 8.8 Hz, 4F).

(*E*)-5-Bromo-2-((2-chloro-2-cyclopropylvinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3an)[1]



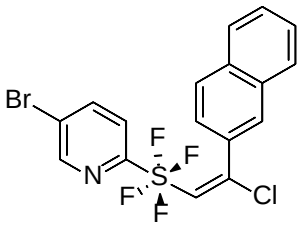
White solid. 84% yield (61.6 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5n** (0.22 mmol, 14.5 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{10}H_9BrClF_4NNaS$ $[M+Na]^+$: 387.9161 found: 387.9166. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 6.95 (quint, *J* = 9.1 Hz, 1H), 2.66 (brs, 1H), 1.13–1.05 (m, 2H), 0.97–0.87 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 60.56 (d, *J* = 8.4 Hz, 4F).

(*E*)-5-Bromo-2-((2-chloro-3-phenylprop-1-en-1-yl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ao)[1]



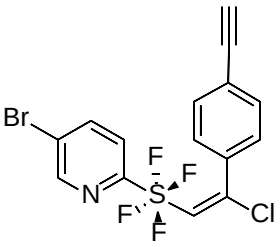
White solid. 58% yield (48.0 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5o** (0.22 mmol, 25.6 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{14}H_{11}BrClF_4NNaS$ $[M+Na]^+$: 437.9318 found: 437.9305. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.59 (d, *J* = 1.8 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.41–7.23 (m, 5H), 7.00 (quint, *J* = 8.6 Hz, 1H), 4.16 (s, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 59.83 (d, *J* = 8.4 Hz, 4F).

(*E*)-5-Bromo-2-((2-chloro-2-cyclopropylvinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ap)



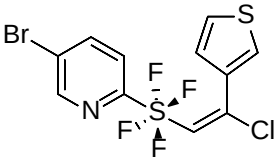
White solid. 72% yield (65.4 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5p** (0.22 mmol, 33.5 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{17}H_{11}NF4NaSClBr$ $[M+Na]^+$: 473.9318 found: 473.9312. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 2.1 Hz, 1H), 7.92 (s, 1H), 7.88–7.72(m, 4H), 7.57–7.43 (m, 3H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.28 (quint, *J* = 8.1 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.15 (d, *J* = 8.6 Hz, 4F). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.30 (quint, *J* = 31.3 Hz), 148.14, 143.16 (quint, *J* = 28.9 Hz), 140.68, 139.53 (quint, *J* = 7.7 Hz), 134.00, 133.34, 132.52, 128.66, 128.05, 127.97, 127.82, 127.27, 126.69, 125.27, 122.70 (quint, *J* = 4.7 Hz), 122.70. IR (KBr): 3078, 3057, 1448, 1005, 920, 845, 825, 754, 744, 630 cm^{-1}. m.p.: 84.8–86.2 °C. (CH_2Cl_2/pentane).

(*E*)-5-Bromo-2-((2-chloro-2-(4-ethynylphenyl)vinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3aq)[1]



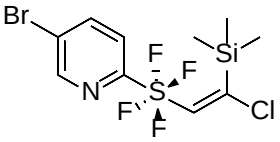
White solid. 78% yield (66.4 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5q** (0.22 mmol, 27.8 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{15}H_9BrClF_4NNaS$ $[M+Na]^+$: 447.9161 found: 447.9164. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.55–7.46 (m, 3H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.20 (quint, *J* = 7.9 Hz, 1H), 3.12 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.13 (d, *J* = 8.1 Hz, 4F).

(*E*)-5-Bromo-2-((2-chloro-2-(thiophen-3-yl)vinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3ar)[1]



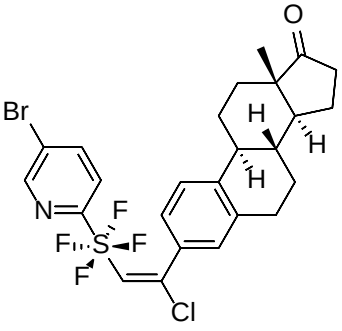
Light-brown solid. 81% yield (66.5 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5r** (0.22 mmol, 23.8 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{11}H_7BrClF_4NNaS_2$ $[M+Na]^+$: 429.8726 found: 429.8677. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 2.4 Hz, 1H), 7.91 (d, *J* = 8.7 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.32–7.27 (m, 1H), 7.24 (d, *J* = 4.9 Hz, 1H), 7.16 (quint, *J* = 8.4 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 59.64 (d, *J* = 8.7 Hz, 4F).

(*E*)-5-Bromo-2-((2-chloro-2-(trimethylsilyl)vinyl)tetrafluoro-λ^6-sulfaneyl)pyridine (3as)[1]



Light-yellow solid. 75% yield (59.8 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5s** (0.22 mmol, 21.6 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{10}H_{13}BrClF_4NNaSSi$ $[M+Na]^+$: 419.9244 found: 419.9245. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 2.4 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.49 (quint, *J* = 9.2 Hz, 1H), 0.35 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 60.28 (d, *J* = 5.9 Hz, 4F).

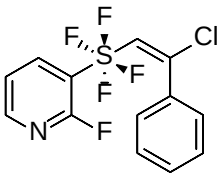
(8*R*,9*S*,13*S*,14*S*)-3-((*E*)-2-((5-Bromopyridin-2-yl)tetrafluoro-λ^6-sulfaneyl)-1-chlorovinyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (3at)



Colorless amorphous. 70% yield (80.9 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **5t** (0.22 mmol, 61.2 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{25}H_{25}NOF_4NaSClBr$ $[M+Na]^+$: 600.0363 found: 600.0363. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 2.3 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.24–7.10 (m, 3H), 2.97–2.85 (m, 2H), 2.58–2.22 (m, 3H), 2.22–1.91(m, 4H), 1.73–1.38 (m, 6H), 0.90 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 61.08 (d, *J* = 8.3 Hz, 4F). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 220.98, 168.49 (quint, *J* = 31.5 Hz), 148.25,

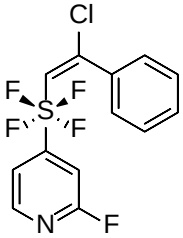
142.57 (quint, *J* = 28.8 Hz), 141.23, 140.81, 139.74 (quint, *J* = 7.7 Hz), 136.47, 134.25, 128.55, 125.46, 125.18, 122.89 (quint, *J* = 4.4 Hz), 122.77, 50.61, 48.06, 44.52, 37.90, 35.97, 31.64, 29.38, 26.46, 25.58, 21.70, 13.96. IR (KBr): 3091, 2933, 2868, 1738, 1637, 1448, 1005, 833, 764, 631 cm^{-1}.

(*E*)-3-((2-Chloro-2-phenylvinyl)tetrafluoro-λ⁶-sulfaneyl)-2-fluoropyridine (3fa)[1]



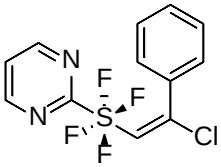
Light-brown oil. 80% yield (54.3 mg) according to general procedure 1 with **2f** (0.2 mmol, 47.9 mg) and **5a** (0.22 mmol, 22.5 mg) for 12 h. HRMS (EI): *m/z* calcd for $C_{13}H_9ClF_5NS$ $[M]^+$: 341.0064 found: 341.0069. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 4.7 Hz, 1H), 8.06–8.00 (m, 1H), 7.48–7.35 (m, 5H), 7.24–7.09 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 74.99 (dd, *J* = 22.2, 8.3 Hz, 4F), −60.13–−60.47 (m, 1F).

(*E*)-4-((2-Chloro-2-phenylvinyl)tetrafluoro-λ⁶-sulfaneyl)-2-fluoropyridine (3ga)[1]



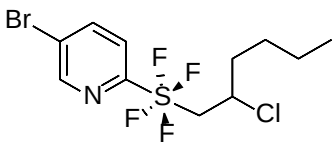
Light-brown oil. 61% yield (41.9 mg) according to general procedure 1 with **2g** (0.2 mmol, 47.9 mg) and **5a** (0.22 mmol, 22.5 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{13}H_{10}ClF_5NS$ $[M+H]^+$: 342.0143 found: 342.0140. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 5.6 Hz, 1H), 7.47–7.34 (m, 6H), 7.22–7.09 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 69.42 (d, *J* = 8.4 Hz, 4F), −65.28 (s, 1F).

((*E*)-2-((2-Chloro-2-phenylvinyl)tetrafluoro-λ⁶-sulfaneyl)pyrimidine (3ha)



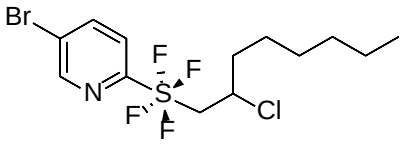
White solid. 77% yield (49.8 mg) according to general procedure 1 with **2h** (0.2 mmol, 44.5 mg) and **5a** (0.22 mmol, 22.5 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{12}H_9N_2F_4NaSCl$ $[M+Na]^+$: 347.0009 found: 347.0008. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 4.7 Hz, 2H), 7.50–7.43 (m, 2H), 7.42–7.32 (m, 4H), 7.31–7.18 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 55.44 (s, 4F). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.78 (quint, *J* = 35.9 Hz), 158.41, 142.31 (quint, *J* = 35.9 Hz), 139.67 (quint, *J* = 7.6 Hz), 136.84, 129.42, 128.19, 128.14, 122.79. IR (KBr): 3095, 1649, 1562, 1448, 1387, 906, 837, 768, 625, 596 cm^{-1}. m.p.: 100.2–100.9 °C (CH_2Cl_2/pentane).

5-Bromo-2-((2-chlorohexyl)tetrafluoro-λ⁶-sulfaneyl)pyridine (4aa)[1]



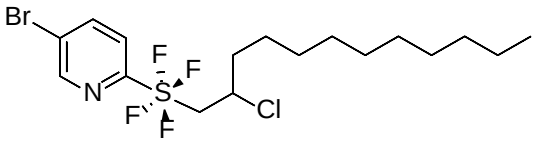
Colorless oil. 84% yield (64.4mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **6a** (0.22 mmol, 18.5 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{11}H_{15}BrClF_4NNaS$ $[M+Na]^+$: 405.9631 found: 405.9626. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (s, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 4.60–4.52 (m, 1H), 4.38–4.14 (m, 2H), 2.22–2.02 (m, 1H), 1.91–1.71 (m, 1H), 1.70–1.25 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 57.49 (t, *J* = 8.9 Hz, 4F).

5-Bromo-2-((2-chlorooctyl)tetrafluoro-λ⁶-sulfaneyl)pyridine (4ab)[1]



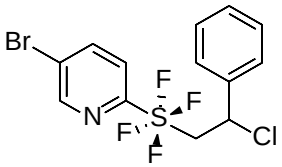
Colorless oil. 90% yield (73.9 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **6b** (0.22 mmol, 24.7 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{13}H_{19}BrClF_4NNaS$ $[M+Na]^+$: 433.9944 found: 433.9945. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 2.4 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 4.60–4.52 (m, 1H), 4.36–4.13 (m, 2H), 2.14–2.03 (m, 1H), 1.85–1.73 (m, 1H), 1.63–1.59 (m, 2H), 1.38–1.26 (m, 6H), 0.91–0.87 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 57.50 (t, *J* = 8.5 Hz, 4F).

5-Bromo-2-((2-chlorododecyl)tetrafluoro-λ⁶-sulfaneyl)pyridine (4ac)[1]



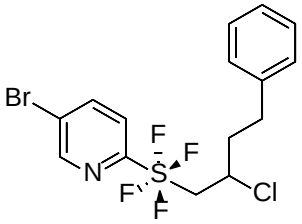
Colorless oil. 89% yield (83.3 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **6c** (0.22 mmol, 37.0 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{17}H_{27}BrClF_4NNaS$ $[M+Na]^+$: 490.0570 found: 490.0556. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.56 (s, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 1H), 4.60–4.52 (m, 1H), 4.38–4.13 (m, 2H), 2.14–2.03 (m, 1H), 1.85–1.73 (m, 1H), 1.63–1.47 (m, 2H), 1.37–1.15 (m, 14H), 0.90–0.86 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 57.49 (t, *J* = 8.9 Hz, 4F).

5-Bromo-2-((2-chloro-2-phenylethyl)tetrafluoro-λ⁶-sulfaneyl)pyridine (4ad)[1]



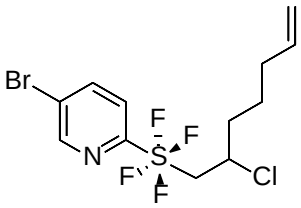
White solid. 86% yield (69.6 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **6d** (0.22 mmol, 22.9 mg) for 12 h or 81% yield (65.6 mg) according to general procedure 2. HRMS (ESI): *m/z* calcd for $C_{13}H_{11}BrClF_4NNaS$ $[M+Na]^+$: 425.9318 found: 425.9321. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 2.3 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.46 (d, *J* = 6.9 Hz, 2H), 7.43–7.31 (m, 3H), 5.57 (t, *J* = 6.7 Hz, 1H), 4.61 (h, *J* = 8.2 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 57.93 (t, *J* = 8.0 Hz, 4F).

5-Bromo-2-((2-chloro-4-phenylbutyl)tetrafluoro-λ⁶-sulfaneyl)pyridine (4ae)[1]



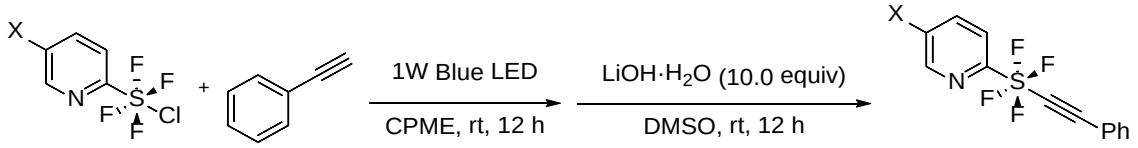
White solid. 95% yield (82.0 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **6e** (0.22 mmol, 29.1 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{15}H_{15}BrClF_4NNaS$ $[M+Na]^+$: 453.9631 found: 453.9623. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.54 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.32–7.18 (m, 5H), 4.56–4.48 (m, 1H), 4.44–4.12 (m, 2H), 3.02–2.92 (m, 1H), 2.85–2.75 (m, 1H), 2.48–2.39 (m, 1H), 2.14–2.02 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 57.75 (t, *J* = 8.2 Hz, 4F).

5-Bromo-2-((2-chlorohept-6-en-1-yl)tetrafluoro-λ^6-sulfaneyl)pyridine (4af)[1]



White solid. 67% yield (53.1 mg) according to general procedure 1 with **2a** (0.2 mmol, 60.1 mg) and **6f** (0.22 mmol, 21.2 mg) for 12 h. HRMS (ESI): *m/z* calcd for $C_{12}H_{15}BrClF_4NNaS$ [M+Na]$^+$: 417.9631 found: 417.9635. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 2.4 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 1H), 5.90–5.74 (m, 1H), 5.13–4.95 (m, 2H), 4.64–4.53 (m, 1H), 4.43–4.11 (m, 2H), 2.23–2.03 (m, 5H), 1.89–1.68 (m, 2H), 1.66–1.51 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 57.51 (t, *J* = 8.3 Hz 4F).

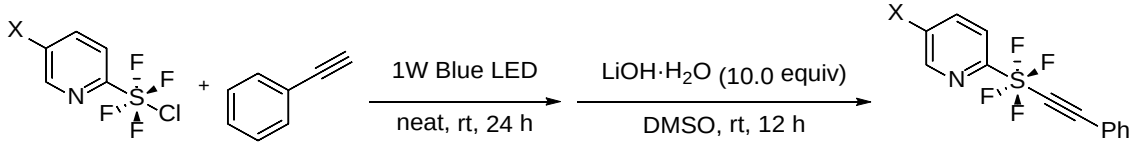
General Procedure 6: One-pot synthesis of pyridine-SF_4-alkynes 7



2 **5a** **7**

An oven-dried 10 mL vial equipped with a magnetic stirrer bar was charged with pyridine-SF_4Cl **2** (0.5 mmol, 1.0 equiv) and alkyne **5a** (0.55 mmol, 1.1 equiv) in CPME (0.25 mL) in the glove box. The closed vial was removed from the glove box. The reaction mixture was irradiated by the 1W blue LED light and stirred at room temperature for 12 h. Then, DMSO (2.5 mL) was added to the reaction mixture via syringe, followed by lithium hydroxide monohydrate (10.0 equiv) and the mixture was stirred at room temperature for 12 h. The reaction mixture was poured into ice-water and extracted with Et_2O. The organic phase was dried with Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with *n*-Hexane/AcOEt to give the product **7**.

General Procedure 7: One-pot synthesis of pyridine-SF_4-alkynes 7 (without solvent for radical addition)

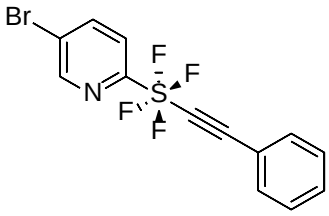


2 **5a** **7**

An oven-dried 10 mL vial equipped with a magnetic stirrer bar was charged with pyridine-SF_4Cl **2** (0.5 mmol, 1.0 equiv) and alkyne **5a** (0.55 mmol, 1.1 equiv) in the glove box. The closed vial was removed from the glove box. The reaction mixture were irradiated by 1W blue LED light and stirred at room temperature for 24 h. Then, DMSO (2.5 mL) was added to the reaction mixture via syringe, followed by lithium hydroxide monohydrate (209.8 mg, 10.0 equiv) and stirred at room temperature for 12 h. The reaction mixture was poured into ice-water and extracted with Et_2O. The organic phase was dried with Na_2SO_4 and concentrated

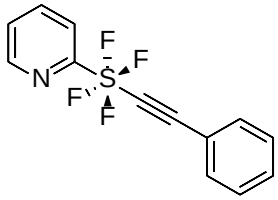
in vacuo. The crude was purified by column chromatography on silica gel eluting with *n*-Hexane/AcOEt to give the product **7**.

5-Bromo-2-(tetrafluoro(phenylethynyl)-λ^6-sulfaneyl)pyridine (7a)[2]



Light-yellow solid. 87% yield (159.5 mg) according to general procedure 7 with **2a** (0.5 mmol) and **5a** (0.55 mmol) or 81% yield (116.0 mg) according to general procedure 8. HRMS (ESI): *m*/*z* calcd for $C_{13}H_8NF_4NaSBr$ $[M]^+$: 387.9395 found: 387.9387. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 2.3 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 6.6 Hz, 2H), 7.52–7.32 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 77.55 (s, 4F).

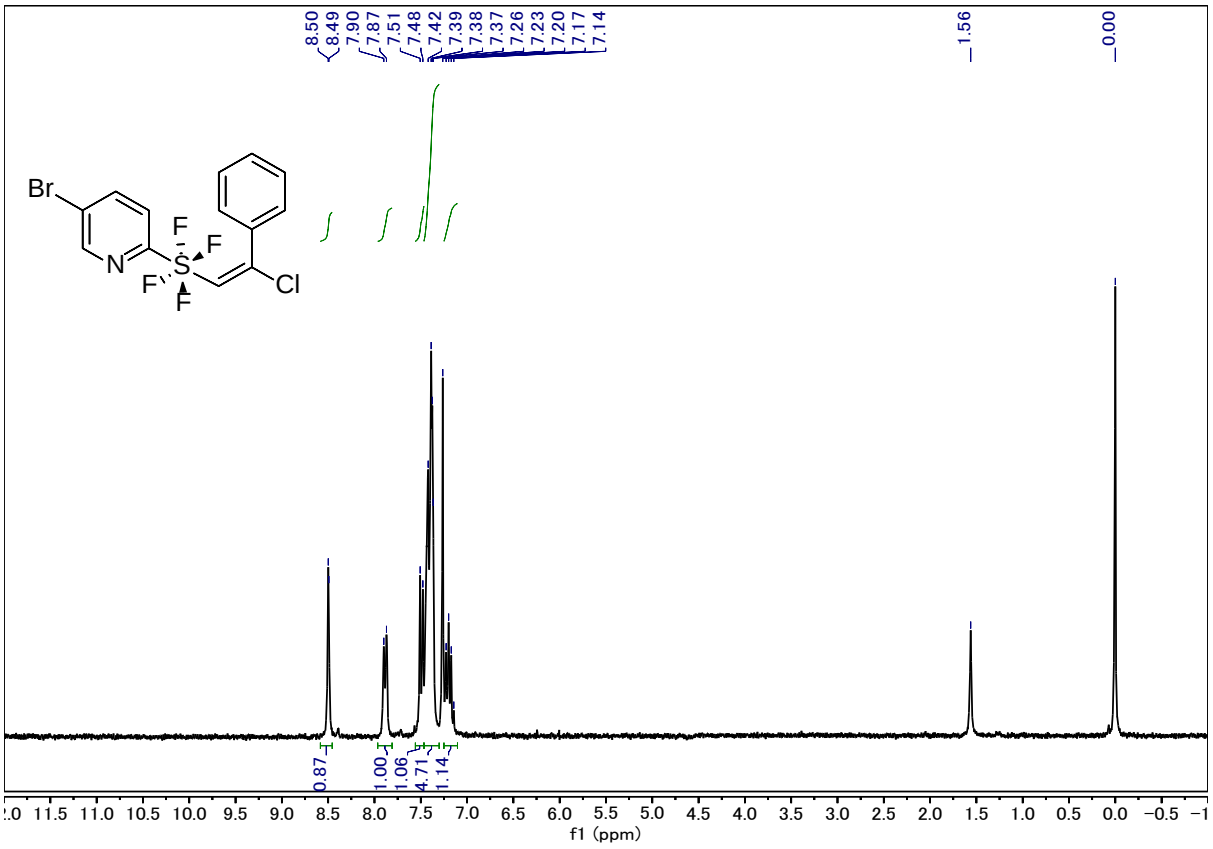
2-(Tetrafluoro(phenylethynyl)-λ^6-sulfaneyl)pyridine (7e)[2]



Light-yellow solid. 80% yield (146.0 mg) according to general procedure 7 with **2b** (0.5 mmol) and **5a** (0.55 mmol) or 70% yield (100.9 mg) according to general procedure 8. HRMS (ESI): *m*/*z* calcd for $C_{13}H_9NF_4NaS$ $[M]^+$: 310.0290 found: 310.0289. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 4.7 Hz, 1H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 7.0 Hz, 2H), 7.52–7.31 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = 76.34 (s, 4F).

References

1. P. Das, M. Takada, E. Tokunaga, N. Saito and N. Shibata, *Org. Chem. Front.*, 2018, **5**, 719–724.
2. P. Das, K. Niina, T. Hiromura. E. Tokunaga, N. Saito and N. Shibata, *Chem. Sci.*, 2018, **9**, 4931–4936.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7.48
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7.39
7.38
7.37
7.26
7.23
7.20
7.17
7.14
1.56
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Br
N
S
F
F
F
F
Cl
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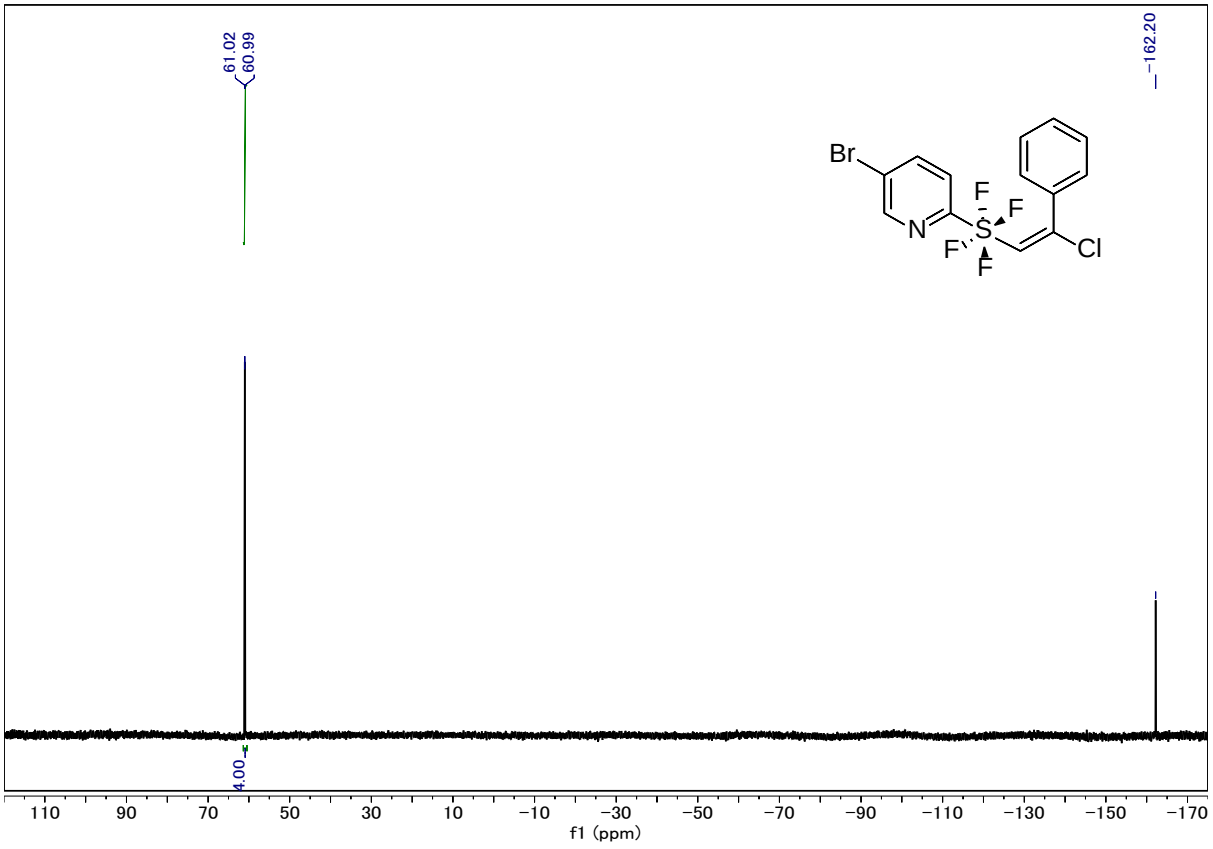
1.14
f1 (ppm)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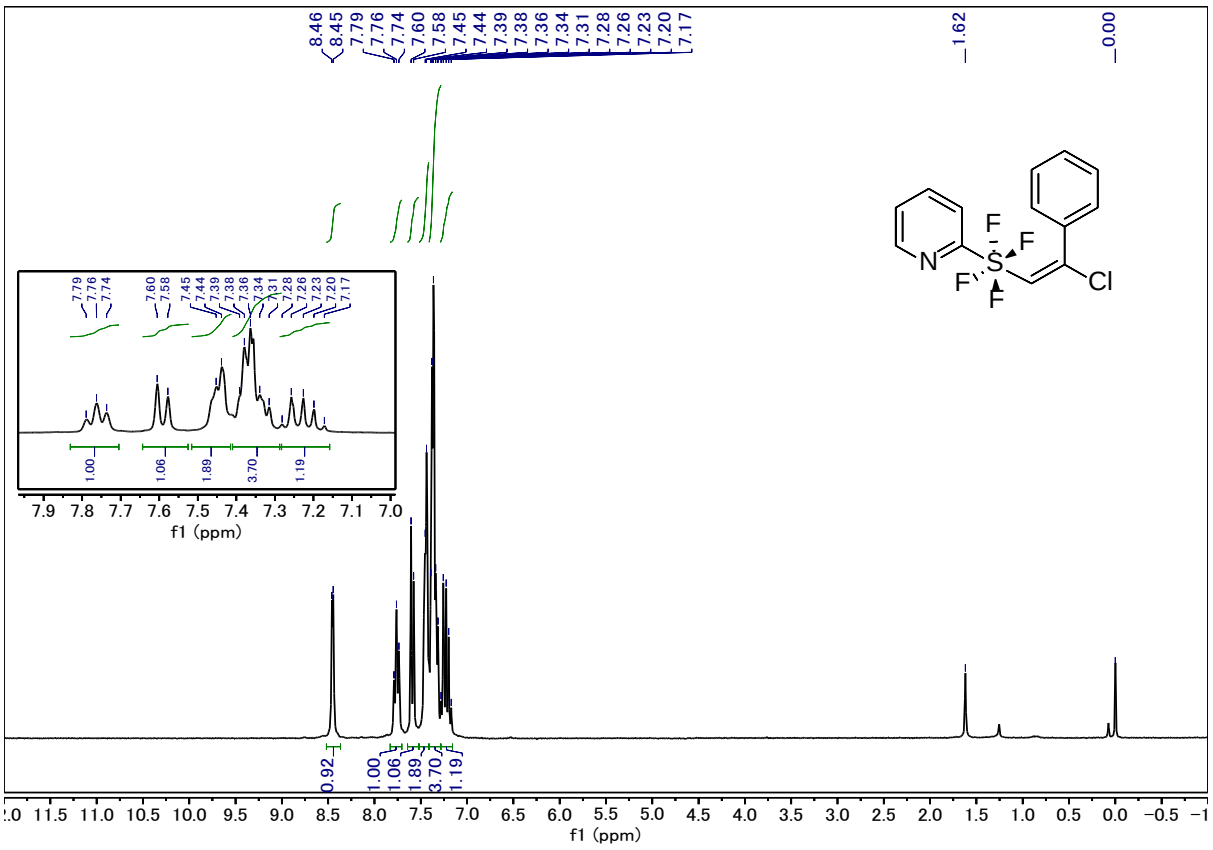
S
F
F
F
F
Cl
4.00
f1 (ppm)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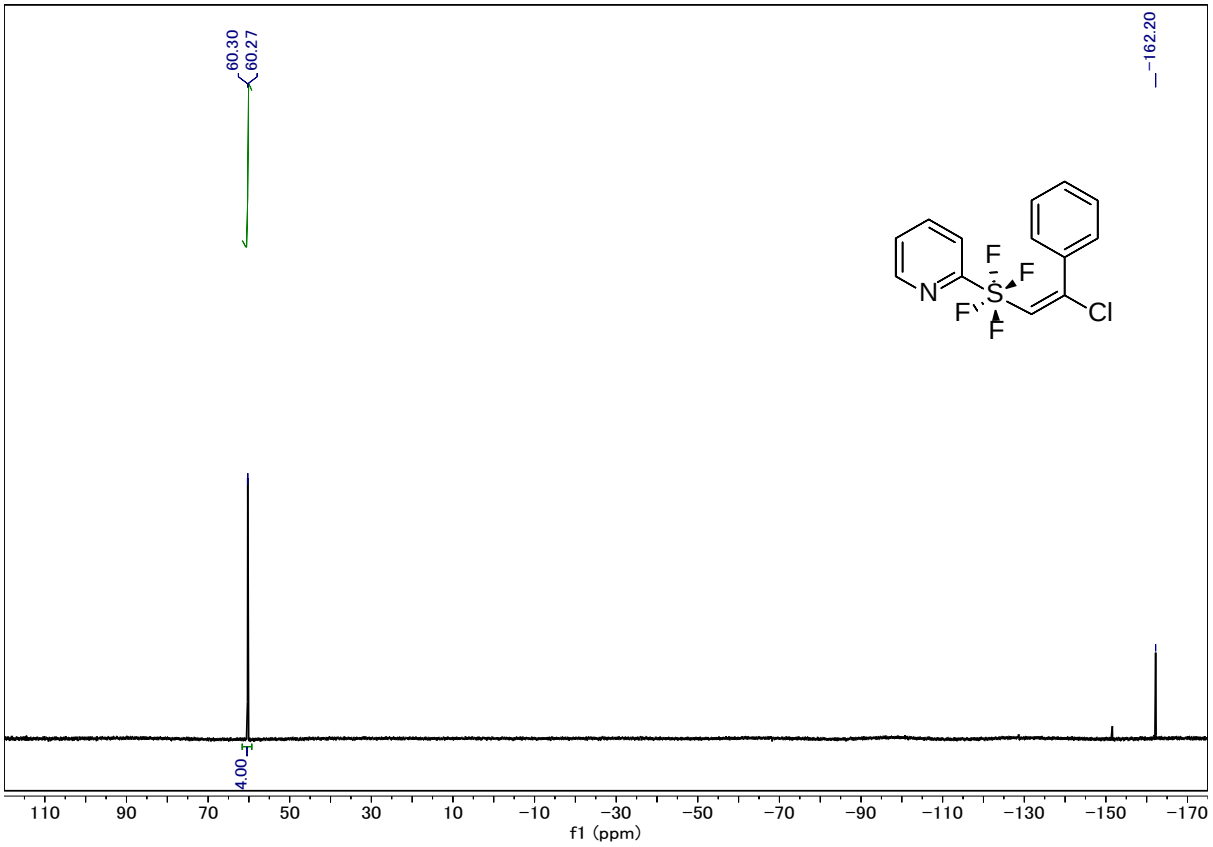
7.28
7.26
7.23
7.20
7.17
1.62
0.00
F
F
N
S
F
F
Cl
1.00
1.06
1.89
3.70
1.19
f1 (ppm)
0.92
1.00
1.06
1.89
3.70
1.19
f1 (ppm)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F
N
S
F
F
Cl
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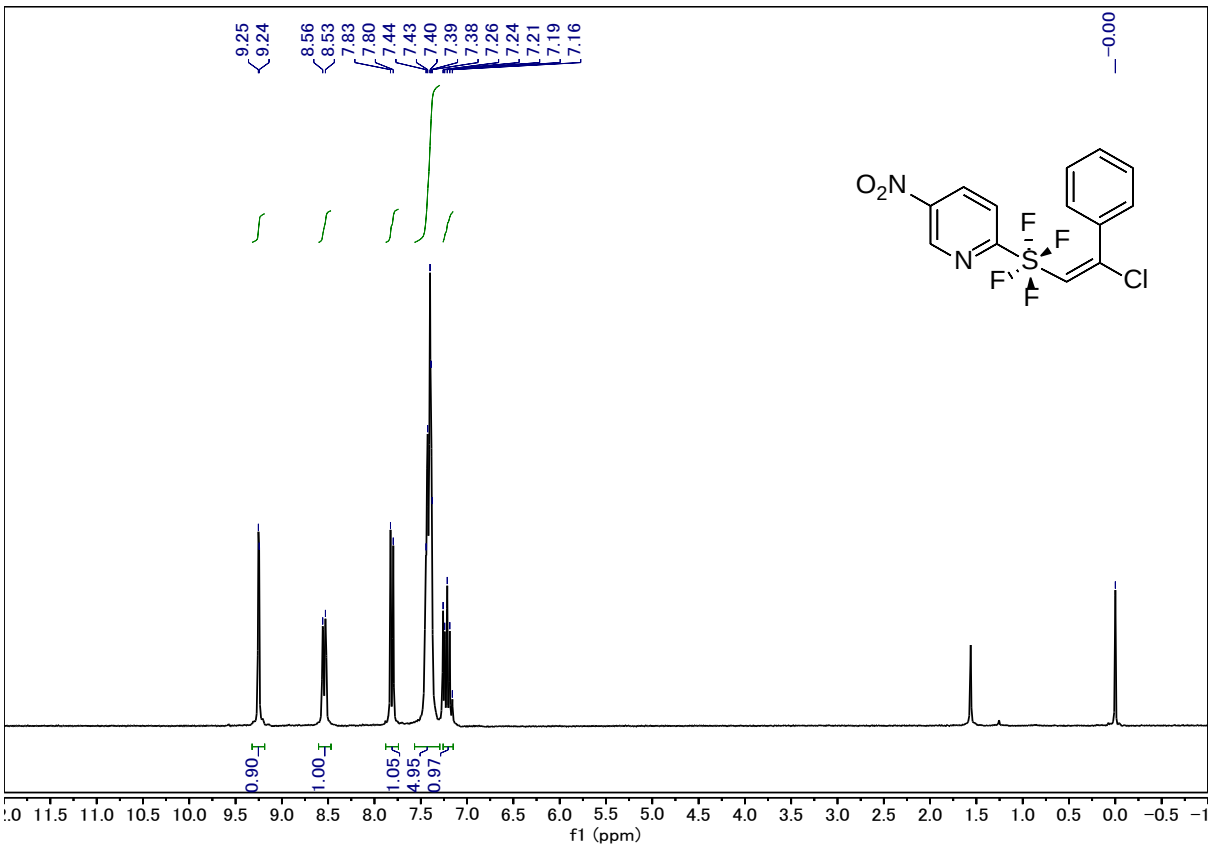
f1 (ppm)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7.24
7.21
7.19
7.16
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S
F
F
F
Cl
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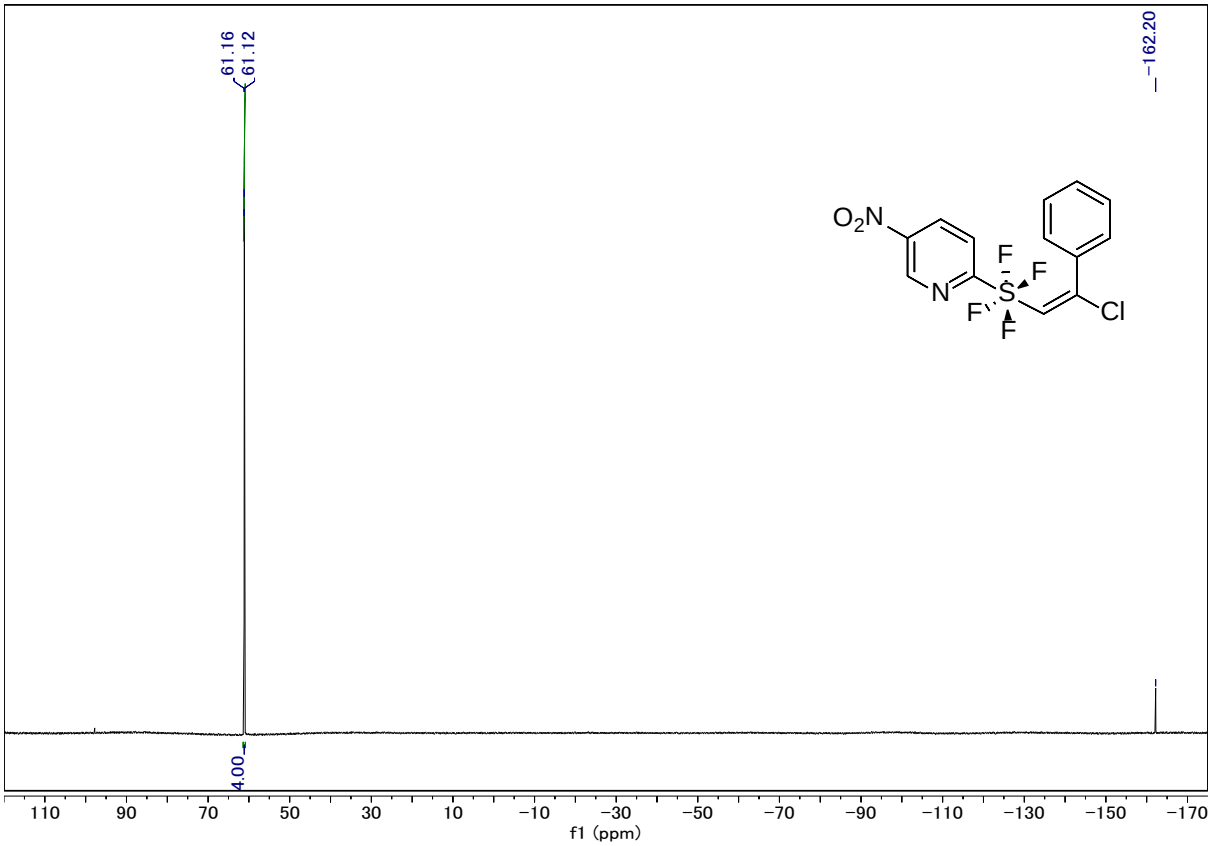
0.97
f1 (ppm)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N
S
F
F
Cl
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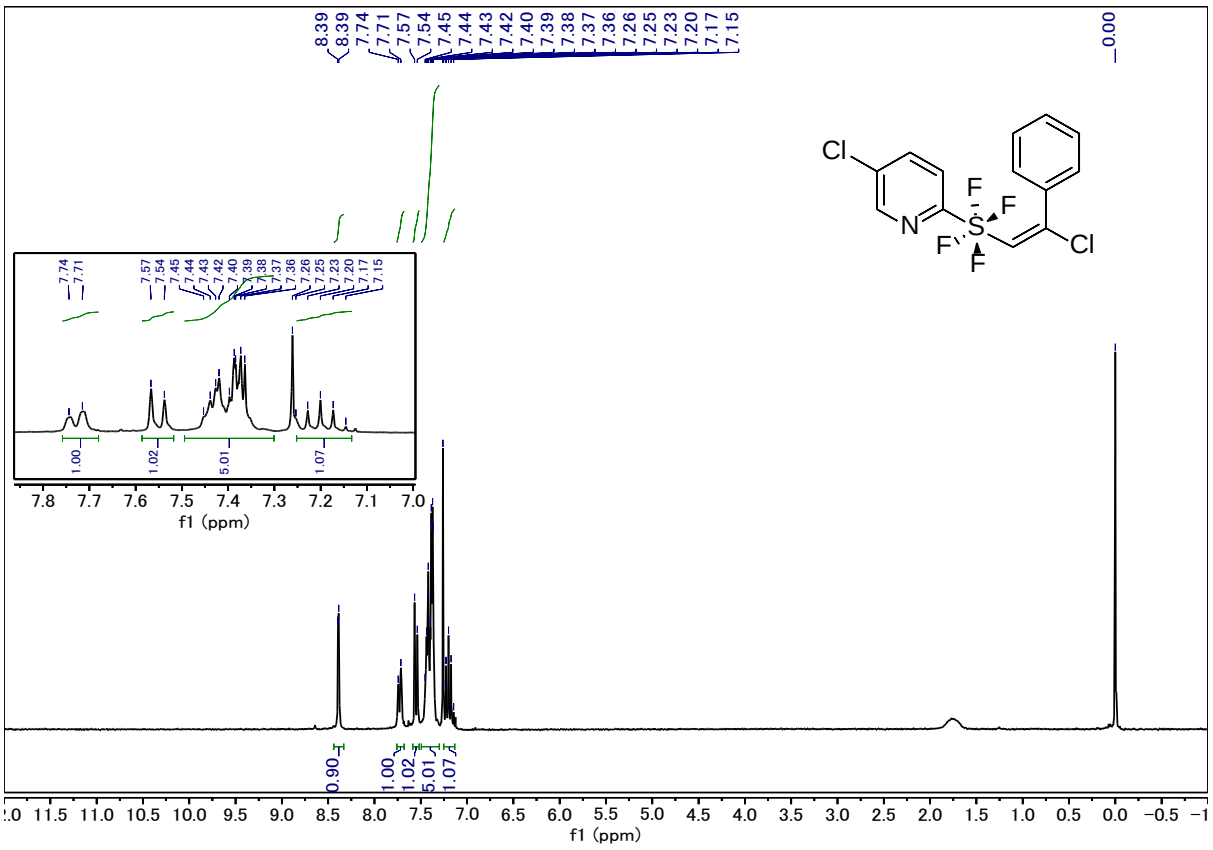
f1 (ppm)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F
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F
F
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f1 (ppm)
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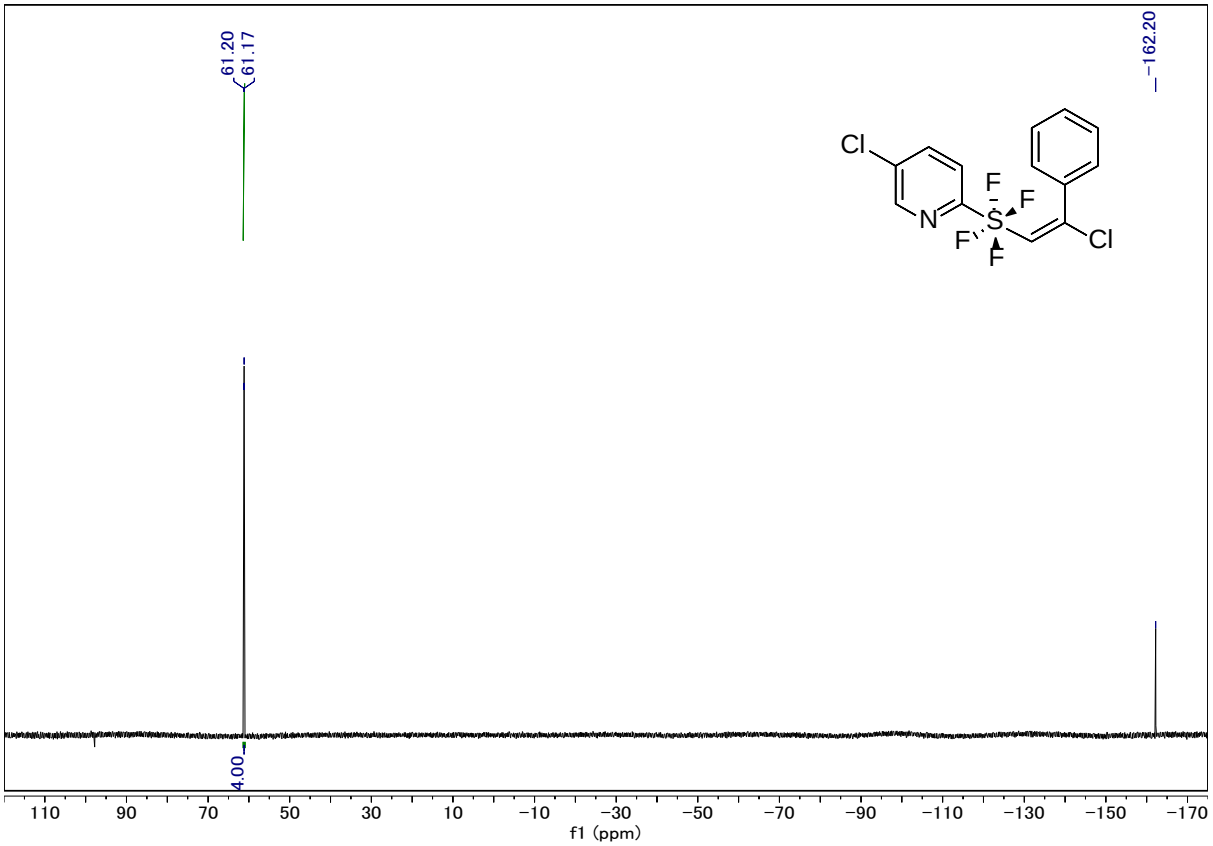
1.07
f1 (ppm)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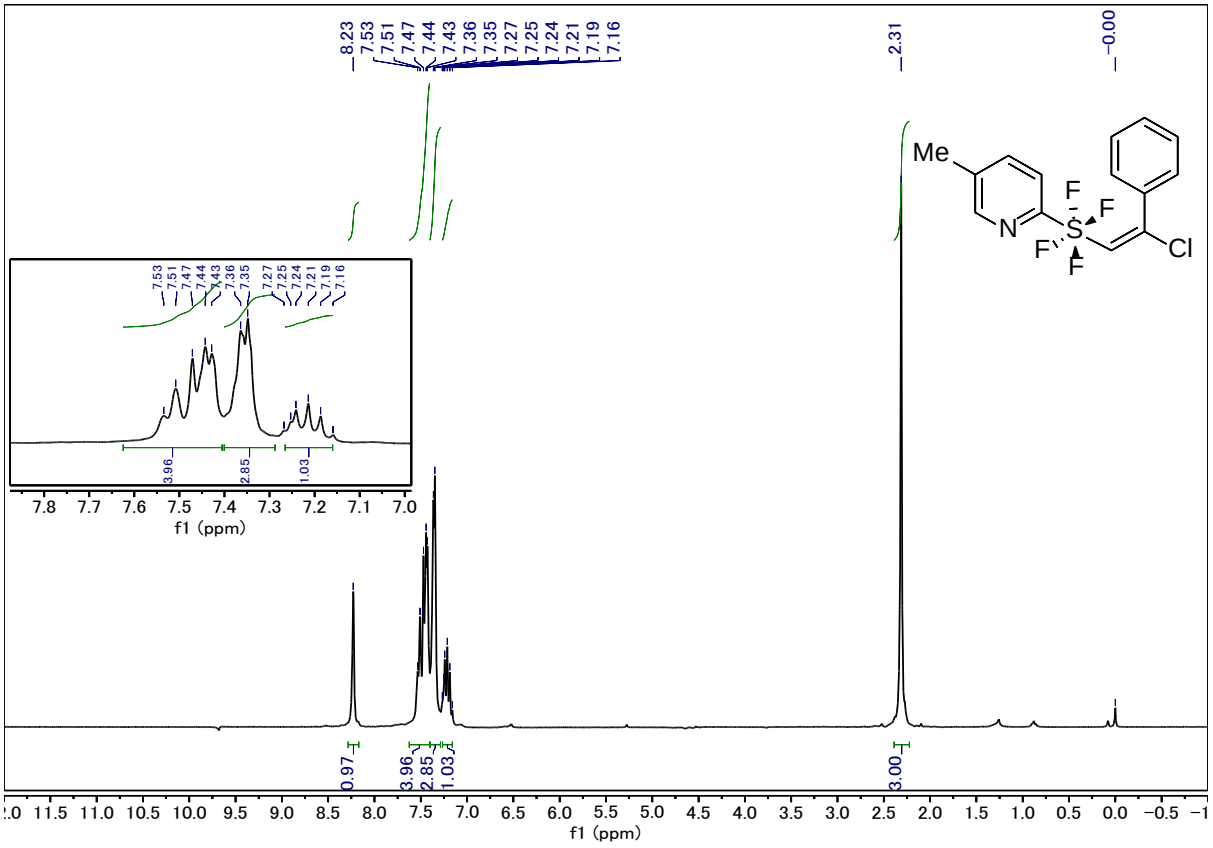
Cl
F
F
N
S
F
F
Cl
4.00
f1 (ppm)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N
S
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Cl
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f1 (ppm)
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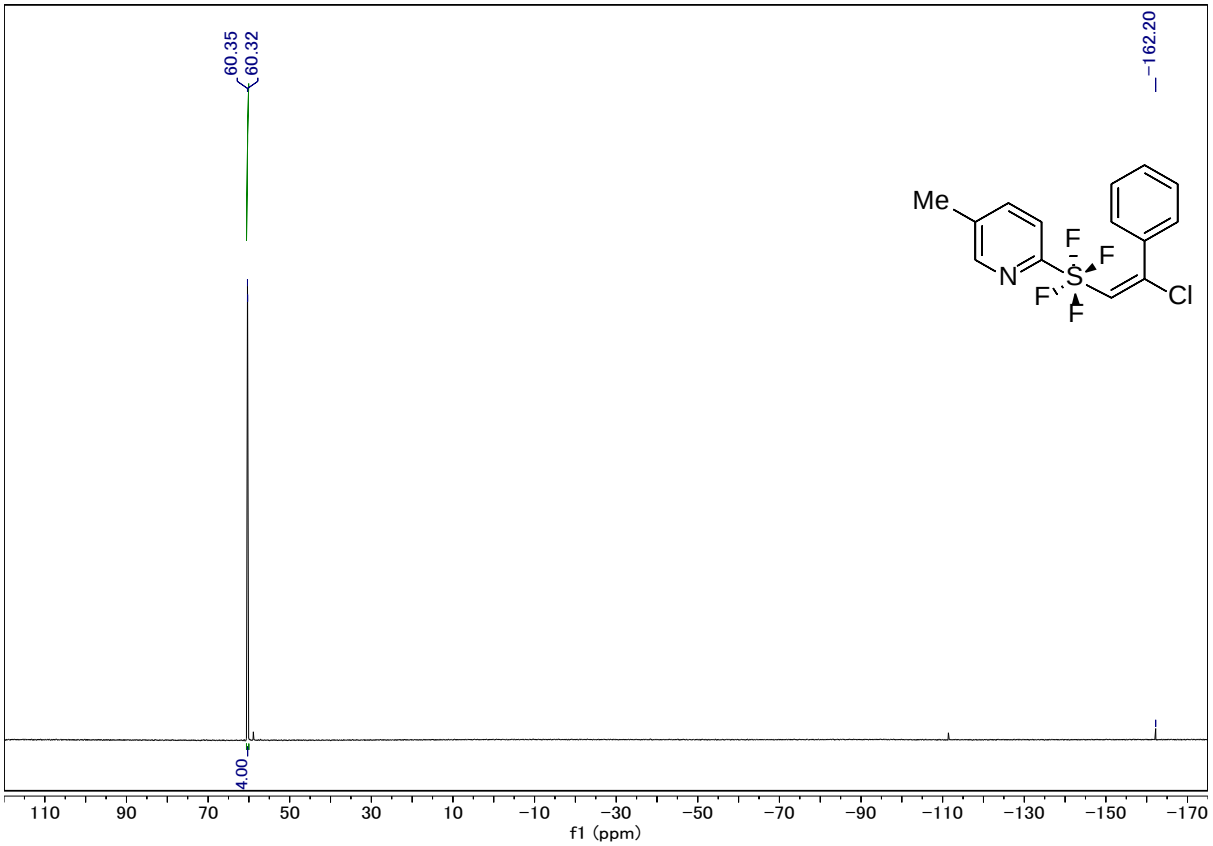
2.85
1.03
3.00
f1 (ppm)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60.32
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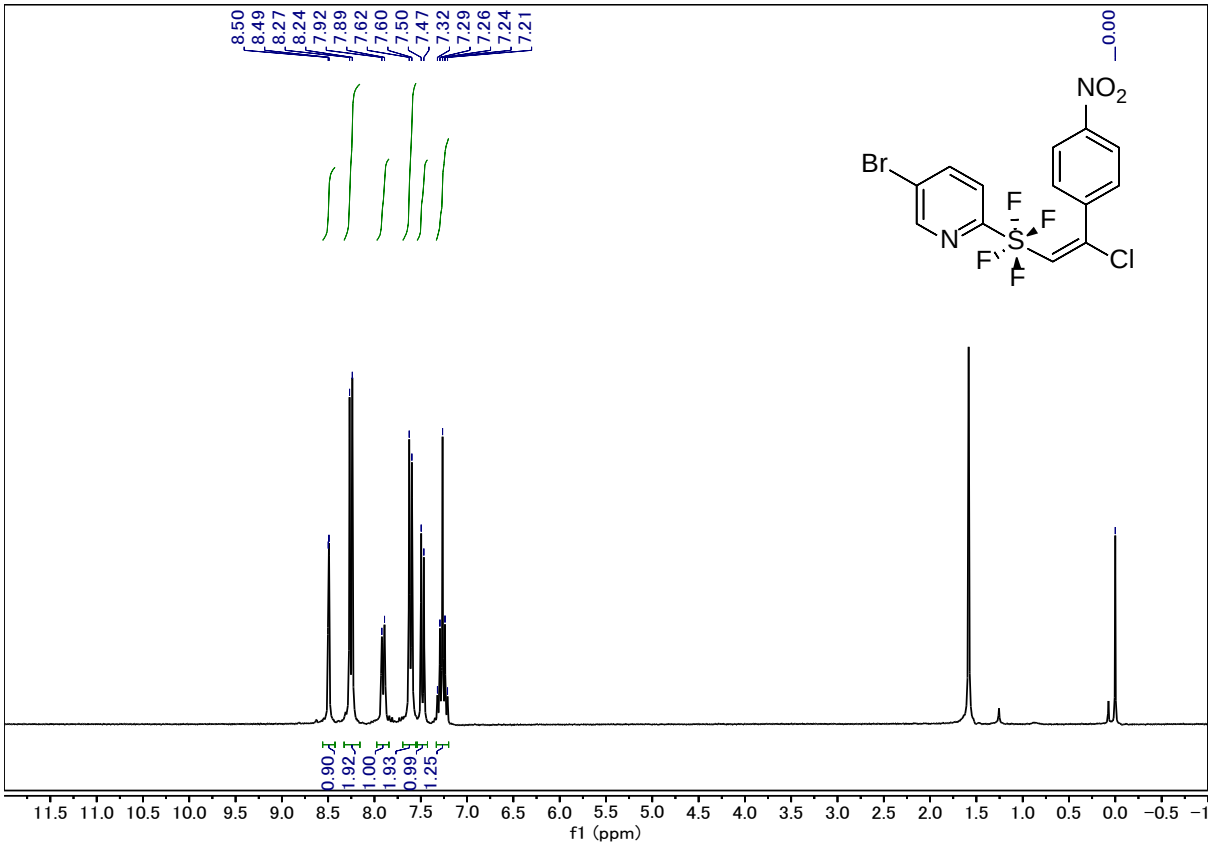
Me
F
F
N
S
F
F
Cl
4.00
f1 (ppm)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NO2
Br
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F
N
S
F
F
Cl
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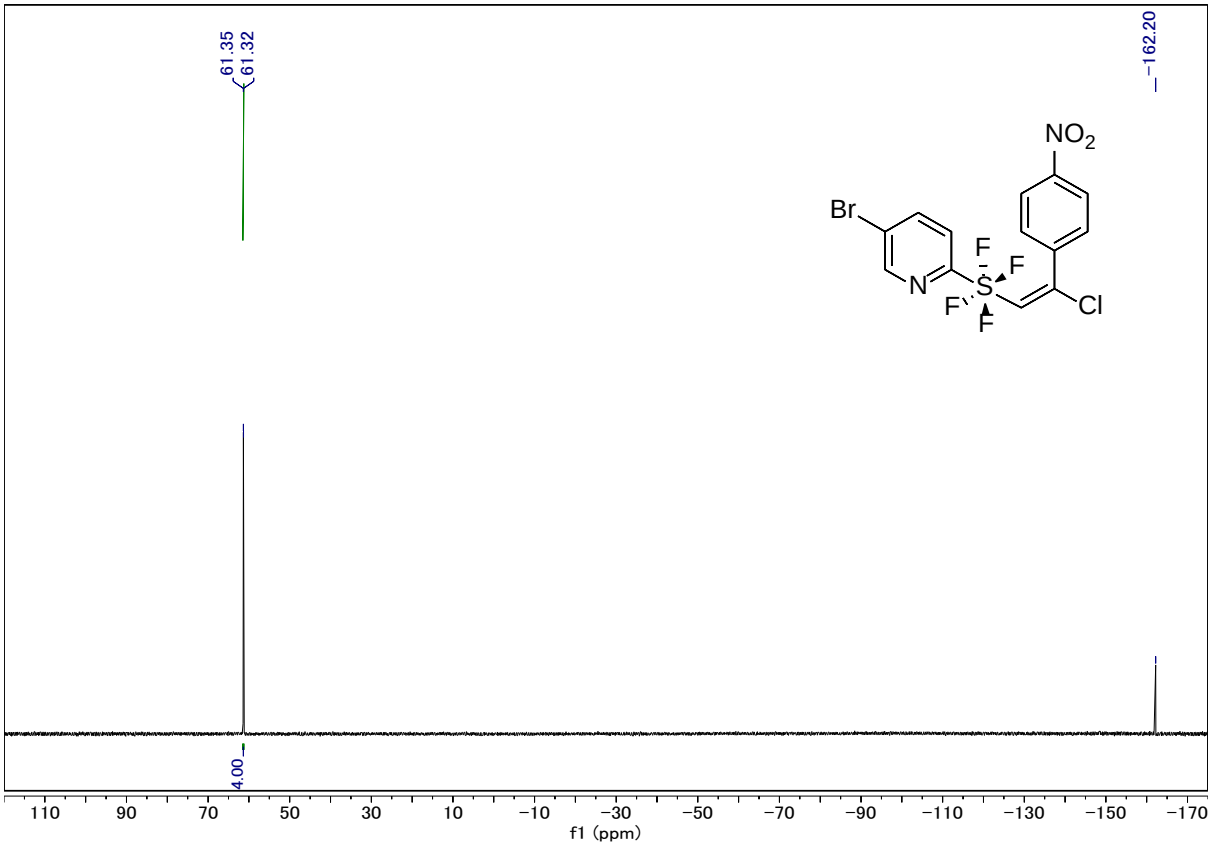
1.00
1.93
0.99
1.25
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)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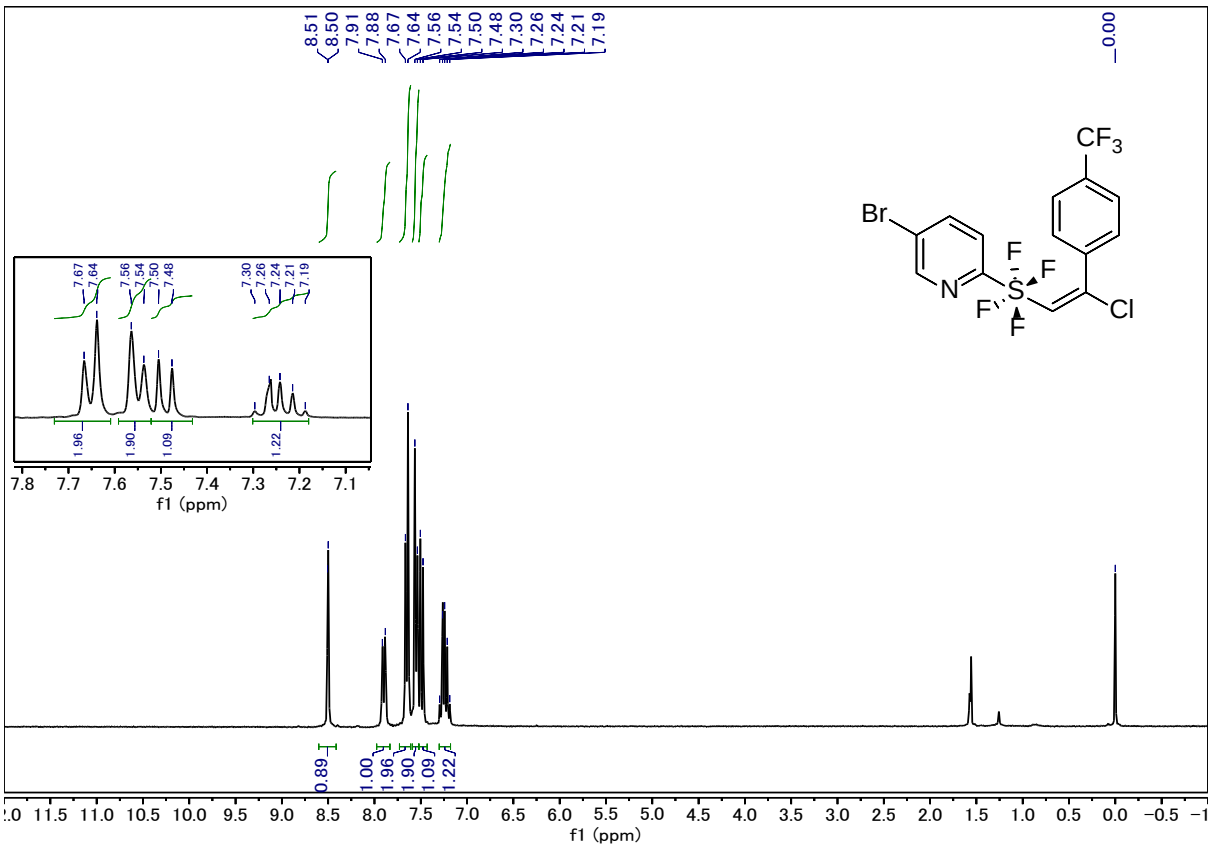
f1 (ppm)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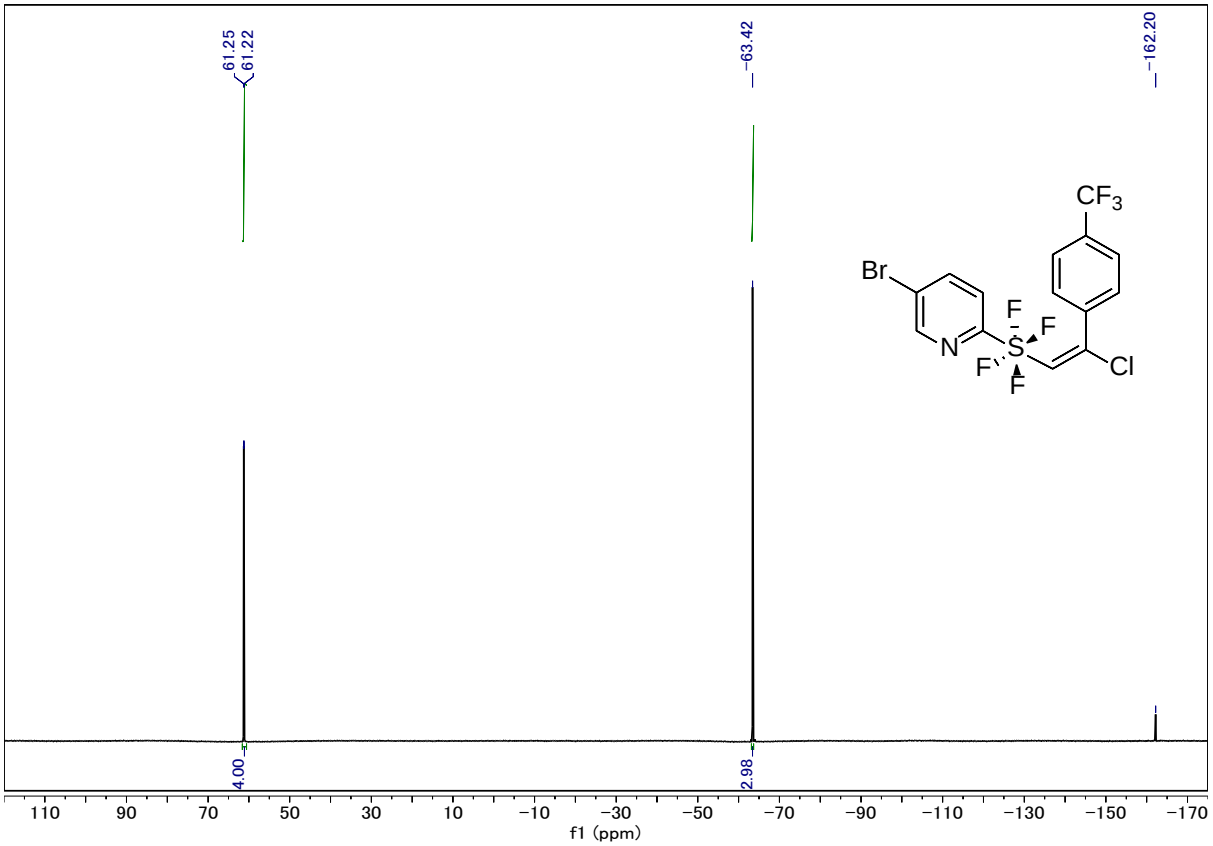
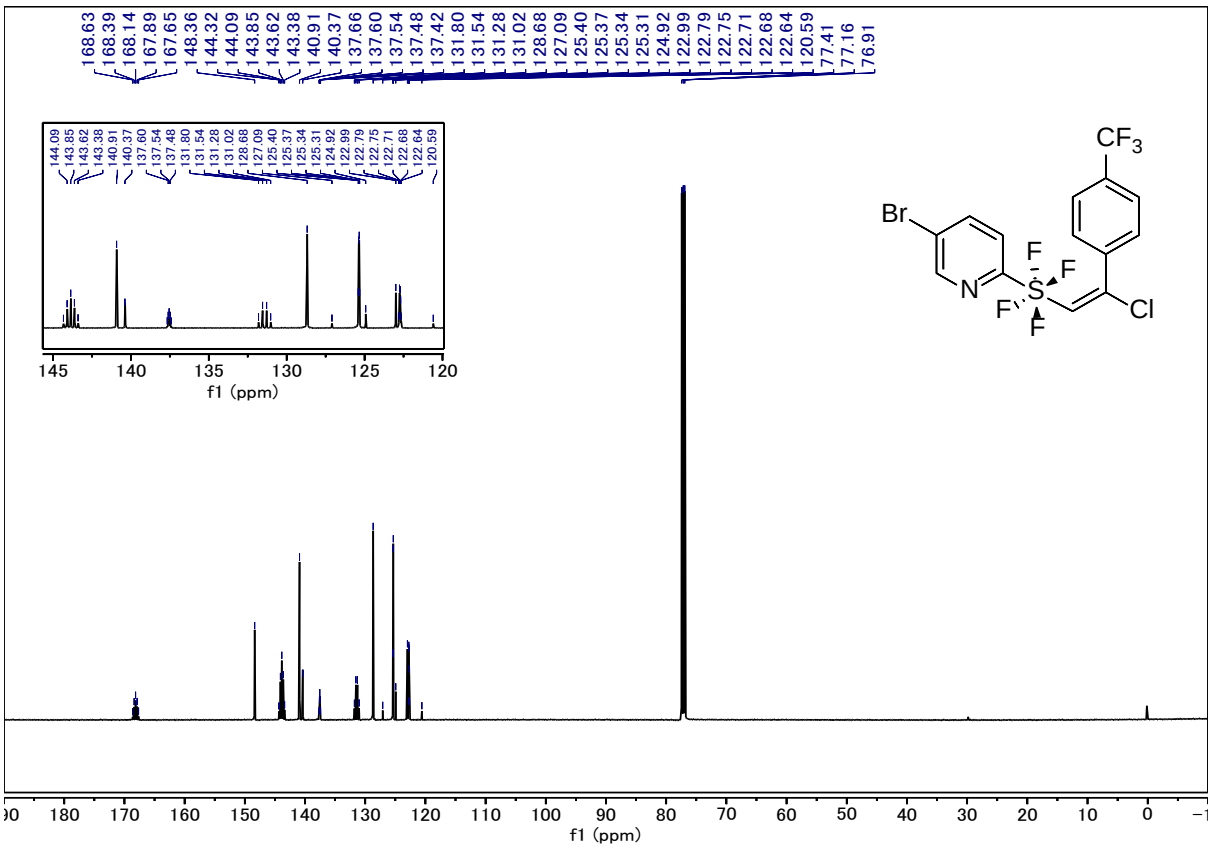
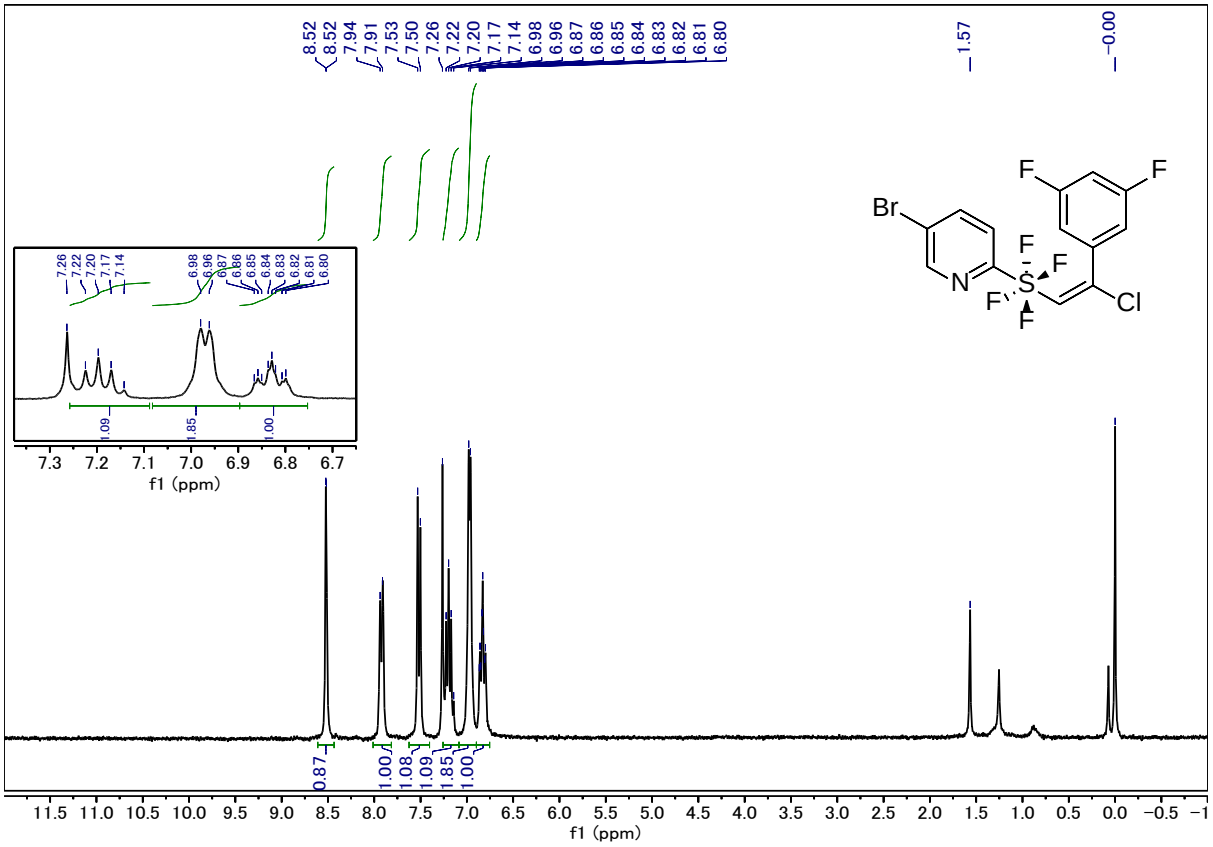
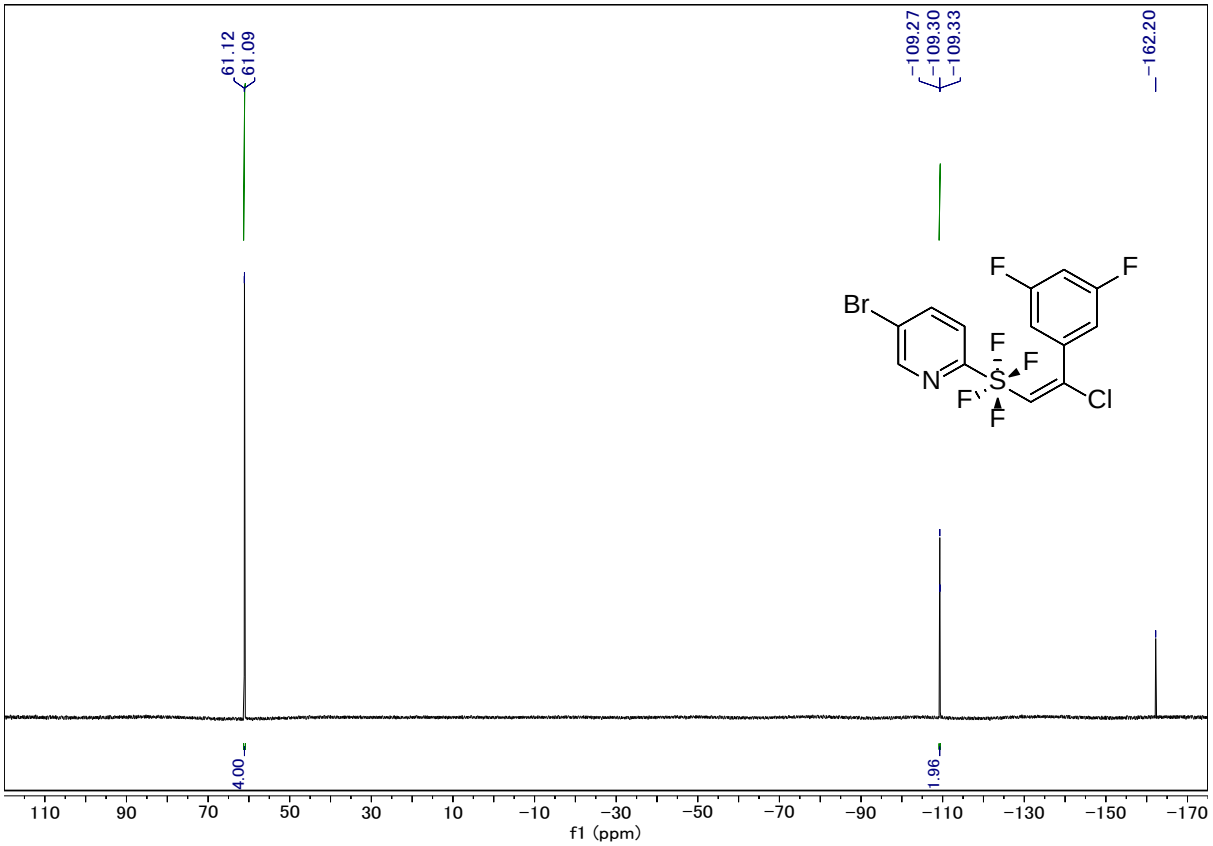
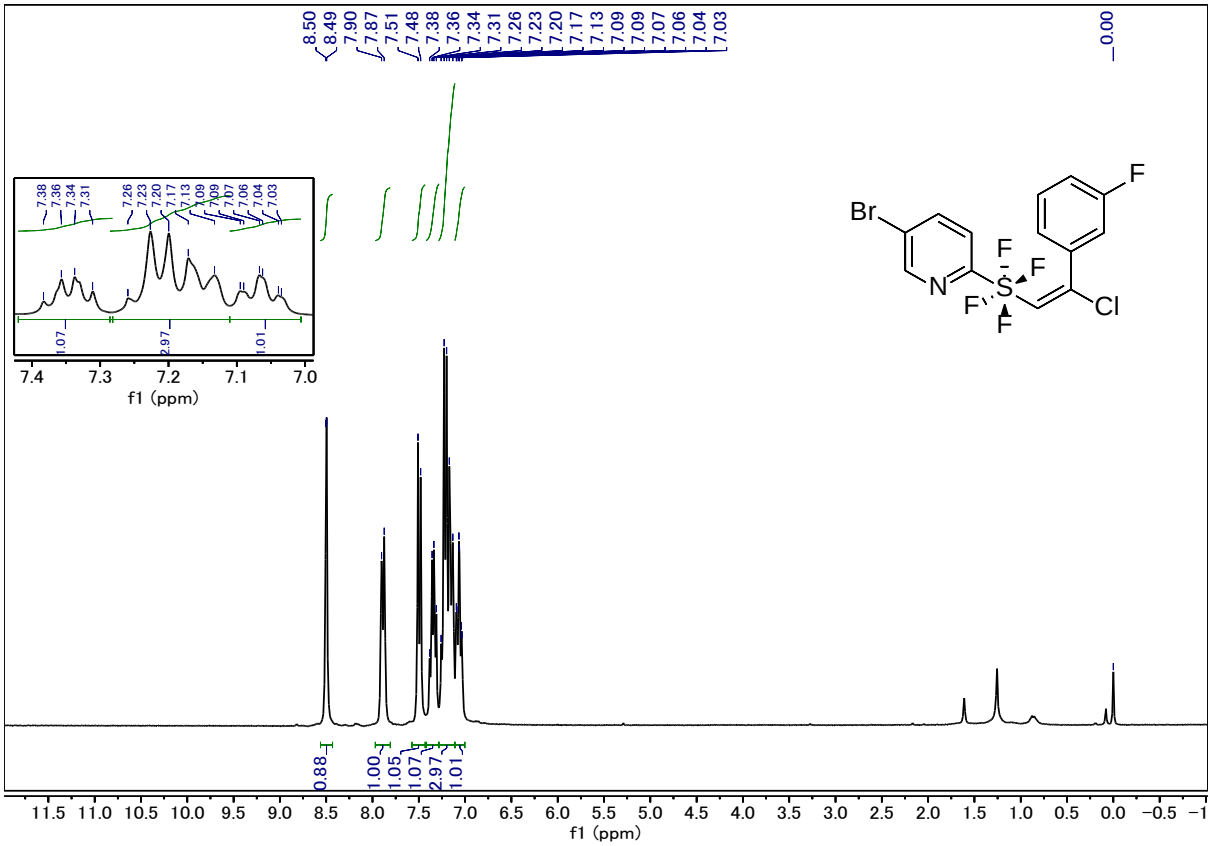
Br
N
F
F
F
F
S
Cl
1.96
1.90
1.09
1.22
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
0.89
1.00
1.96
1.90
1.09
1.22
f1 (ppm)

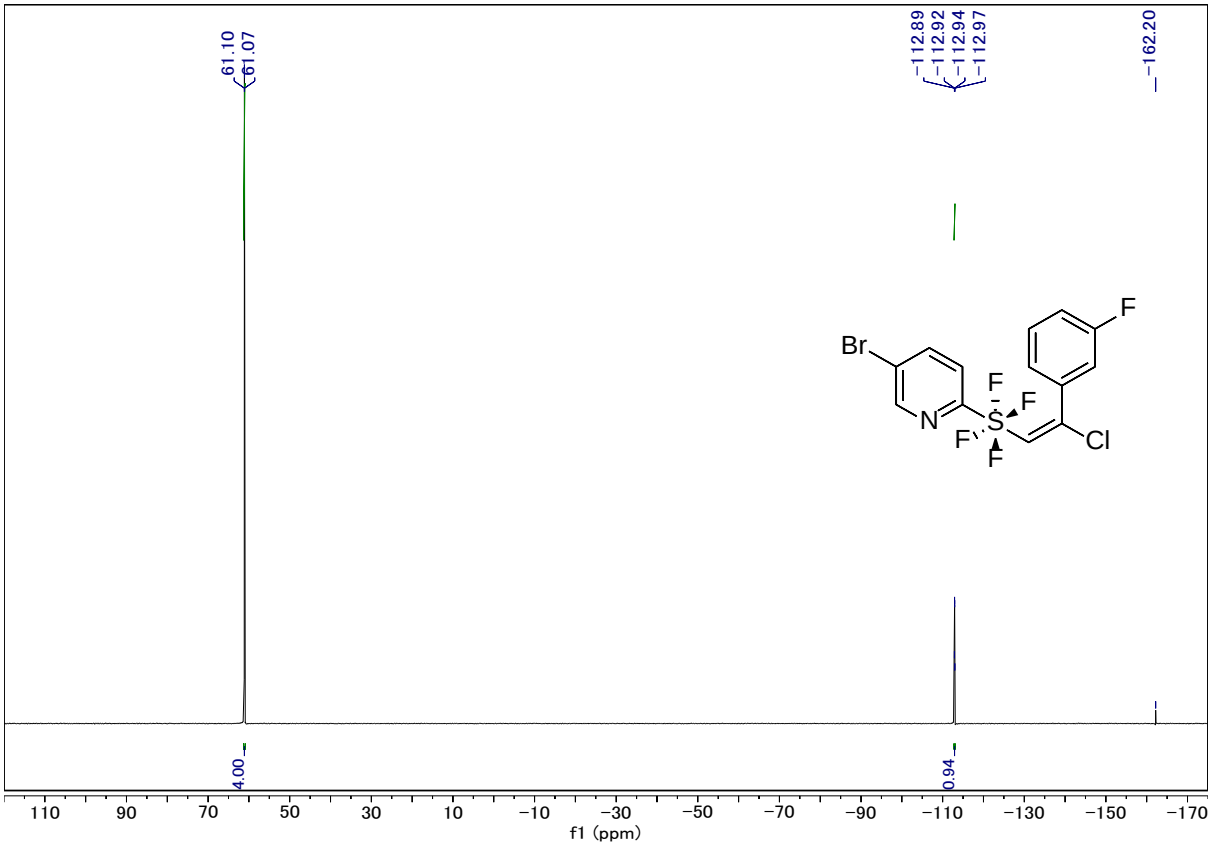

61.25
61.22
-63.42
-162.20
CF3
Br
N
F
F
F
F
S
Cl
4.00
2.98
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)

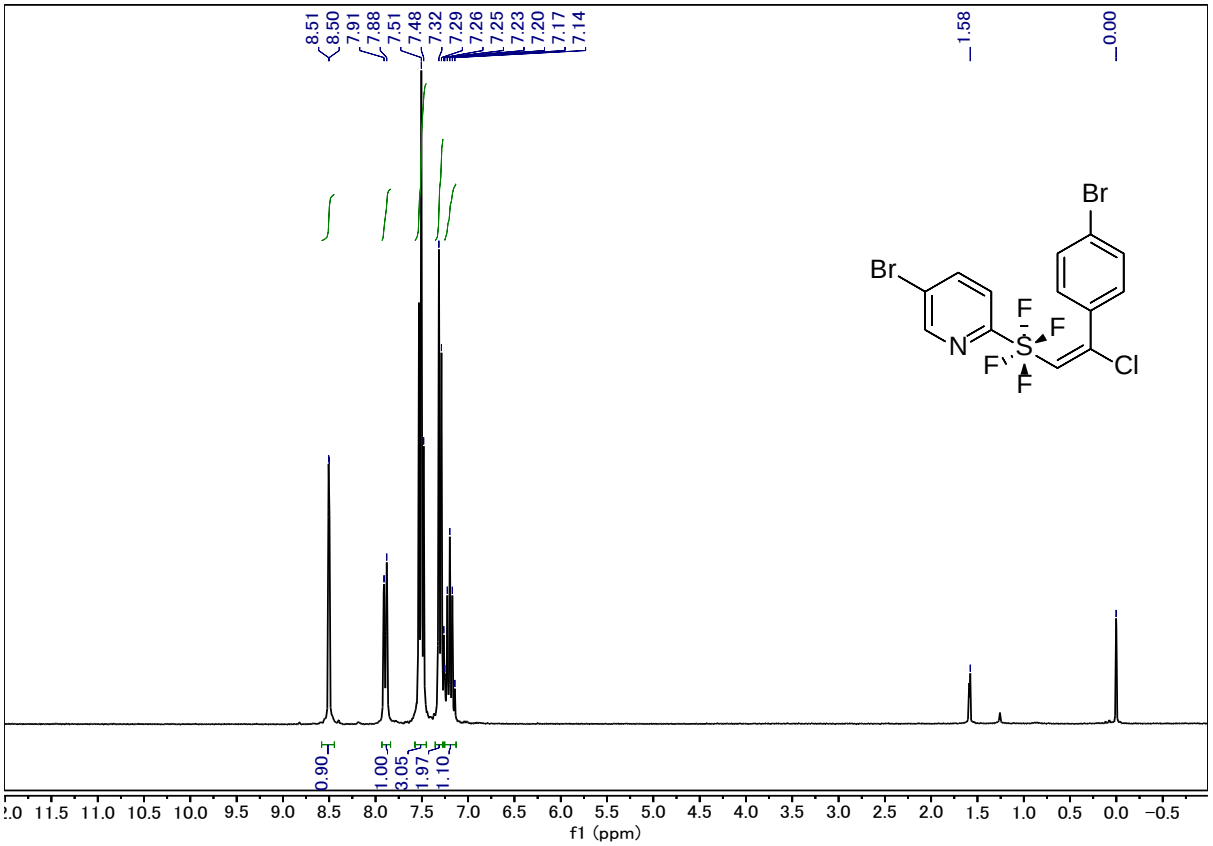

168.63
168.39
168.14
167.89
167.65
148.36
144.32
144.09
143.85
143.62
143.38
140.91
140.37
137.66
137.60
137.54
137.48
137.42
131.80
131.54
131.28
131.02
128.68
127.09
125.40
125.37
125.34
125.31
124.92
122.99
122.79
122.75
122.71
122.68
122.64
120.59
77.41
77.16
76.91
CF3
Br
N
S
F
Cl
f1 (ppm)

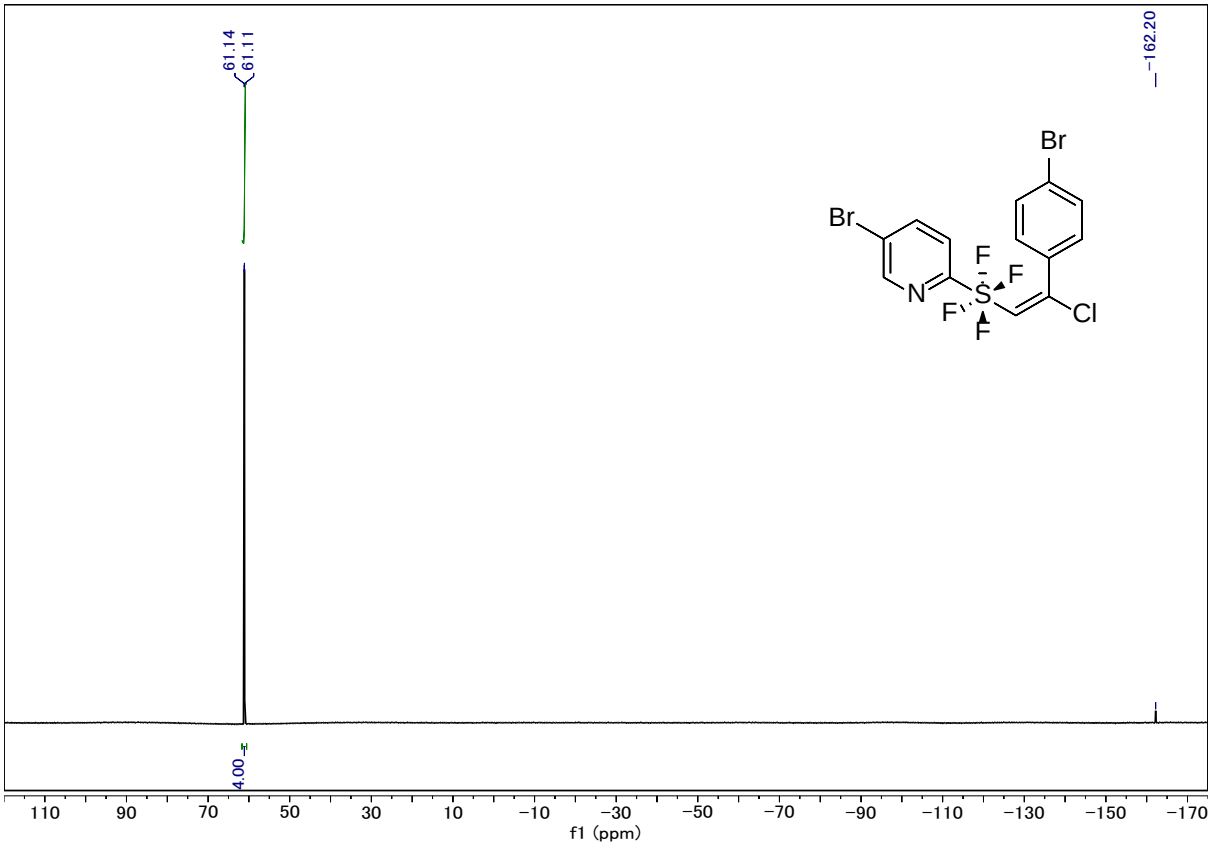

8.52
8.52
7.94
7.91
7.53
7.50
7.26
7.22
7.20
7.17
7.14
6.98
6.96
6.87
6.86
6.85
6.84
6.83
6.82
6.81
6.80
1.57
0.00
Br
N
S
F
Cl
0.87
1.00
1.08
1.09
1.85
1.00
f1 (ppm)

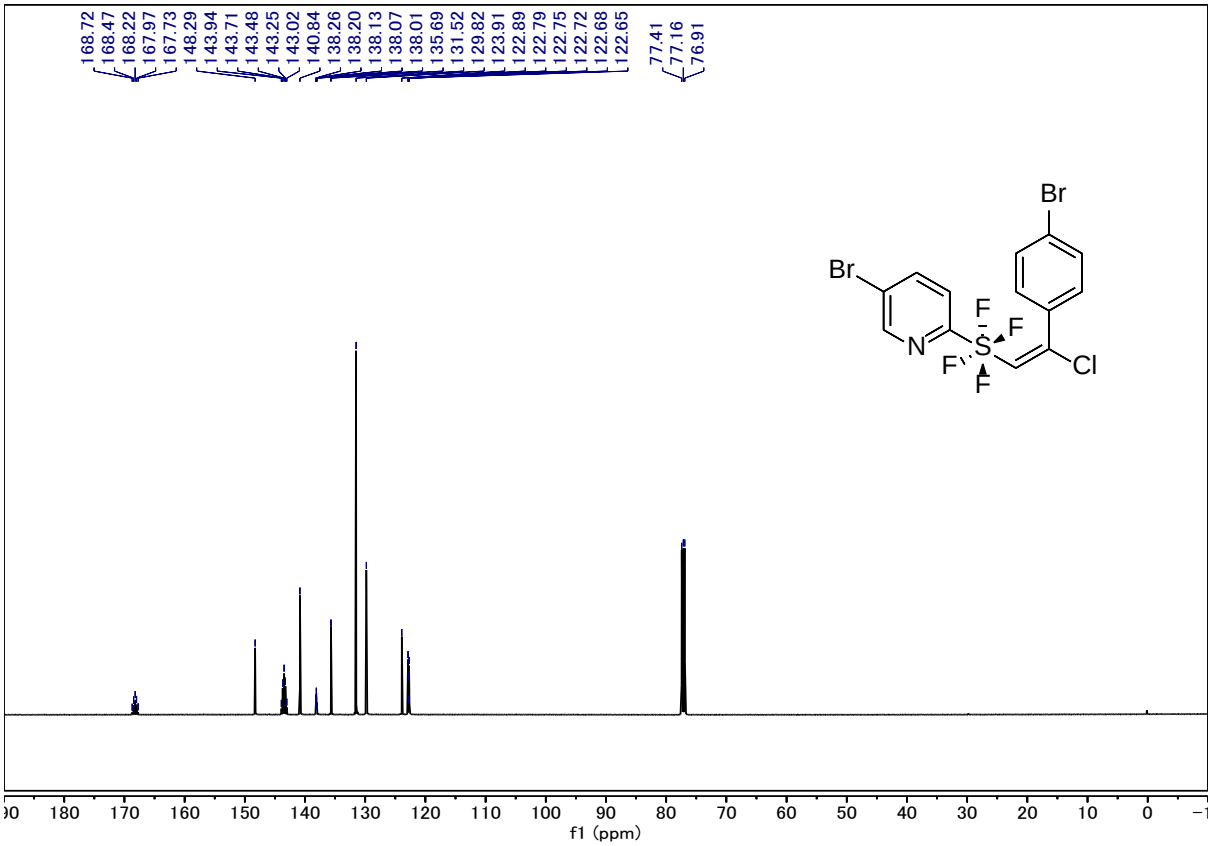

61.12
61.09
-109.27
-109.30
-109.33
-162.20
Br
N
S
F
Cl
4.00
1.96
f1 (ppm)

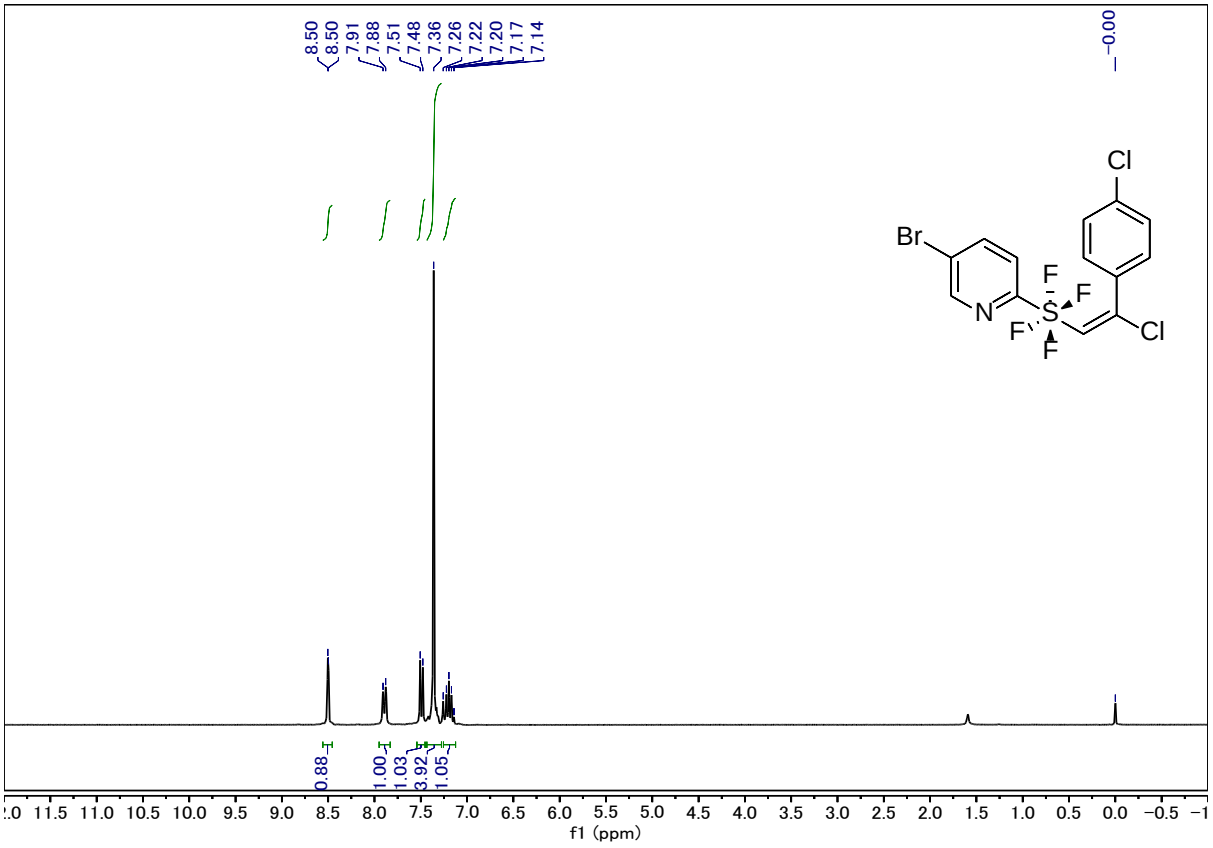

8.50
8.49
7.90
7.87
7.51
7.48
7.38
7.36
7.34
7.31
7.26
7.23
7.20
7.17
7.13
7.09
7.09
7.07
7.06
7.04
7.03
0.00
Br
N
S
F
Cl
0.88
1.00
1.05
1.07
2.97
1.01
f1 (ppm)

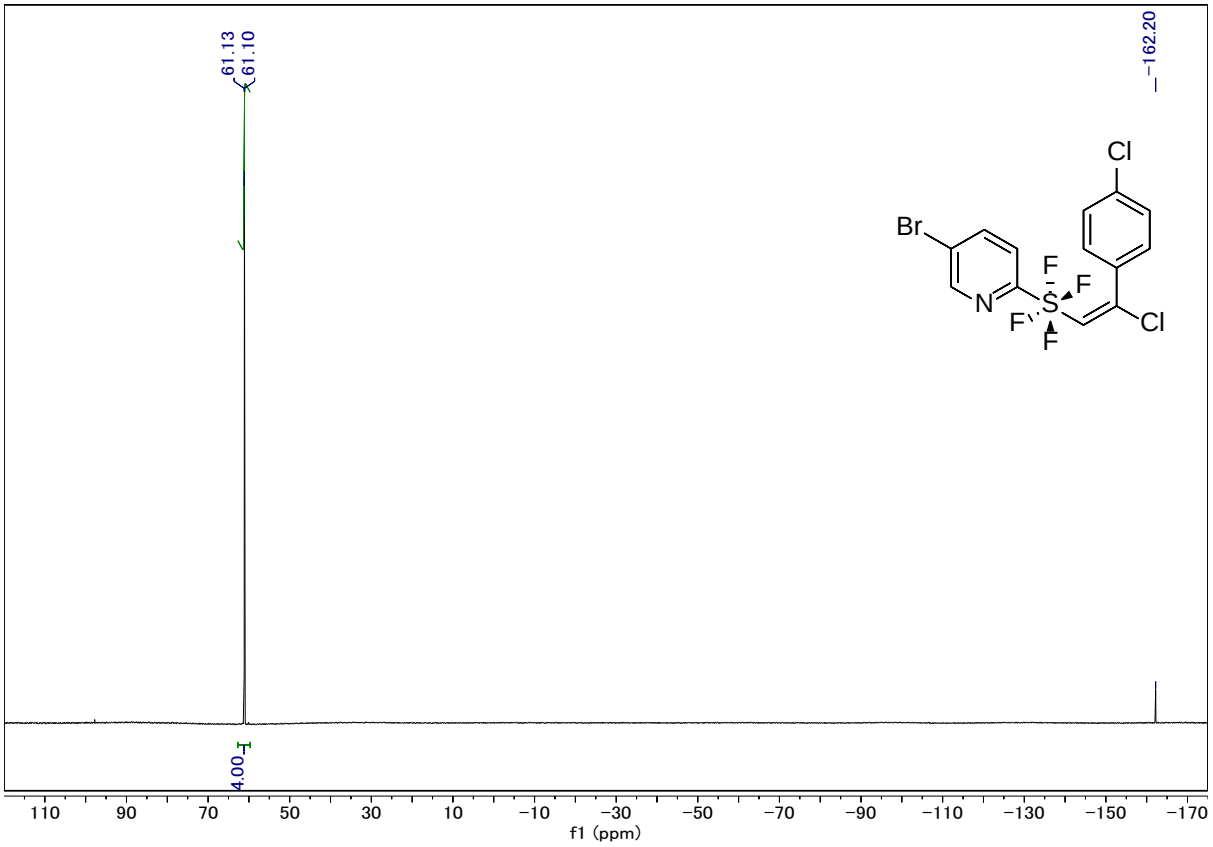

61.10
61.07
-112.89
-112.92
-112.94
-112.97
-162.20
Br
F
N
S
F
F
F
F
Cl
4.00
0.94
f1 (ppm)

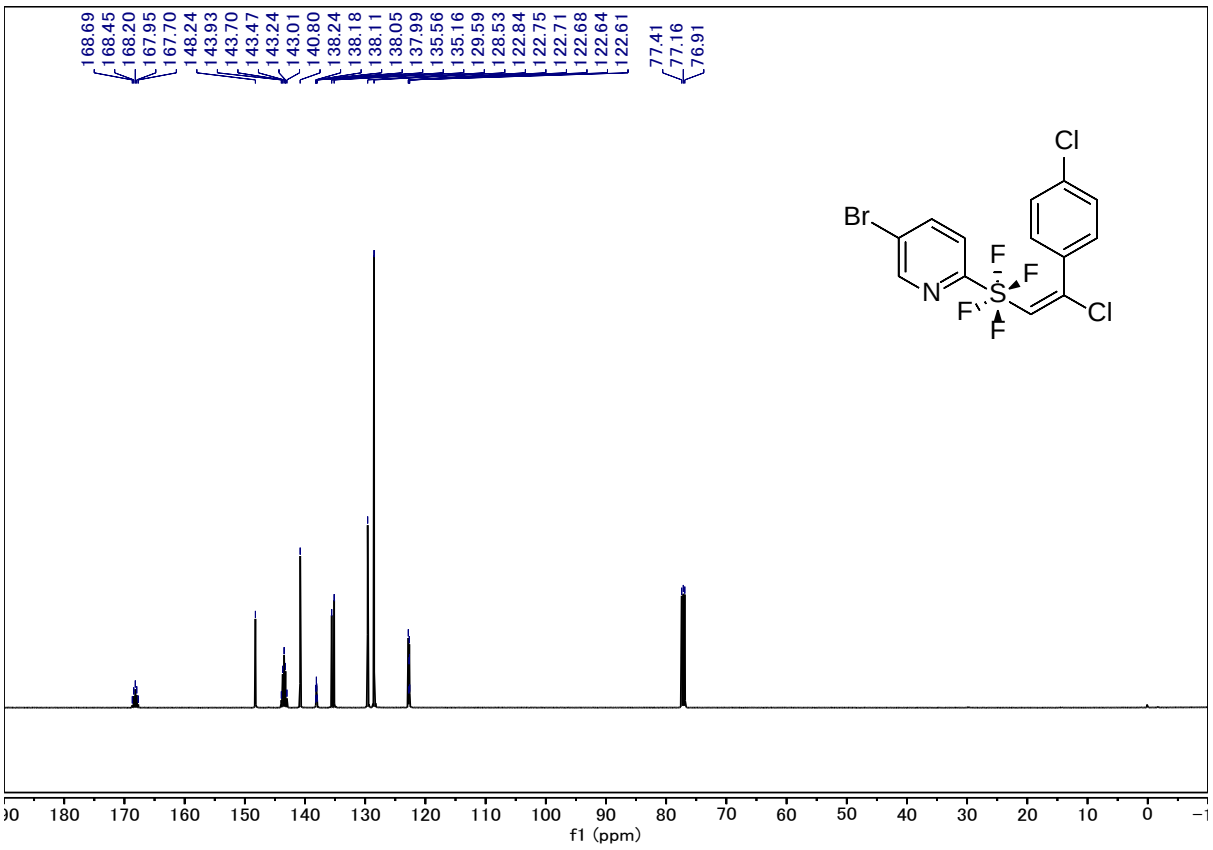

8.51
8.50
7.91
7.88
7.51
7.48
7.32
7.29
7.26
7.25
7.23
7.20
7.17
7.14
1.58
0.00
Br
Br
N
S
F
F
F
F
Cl
0.90
1.00
3.05
1.97
1.10
f1 (ppm)

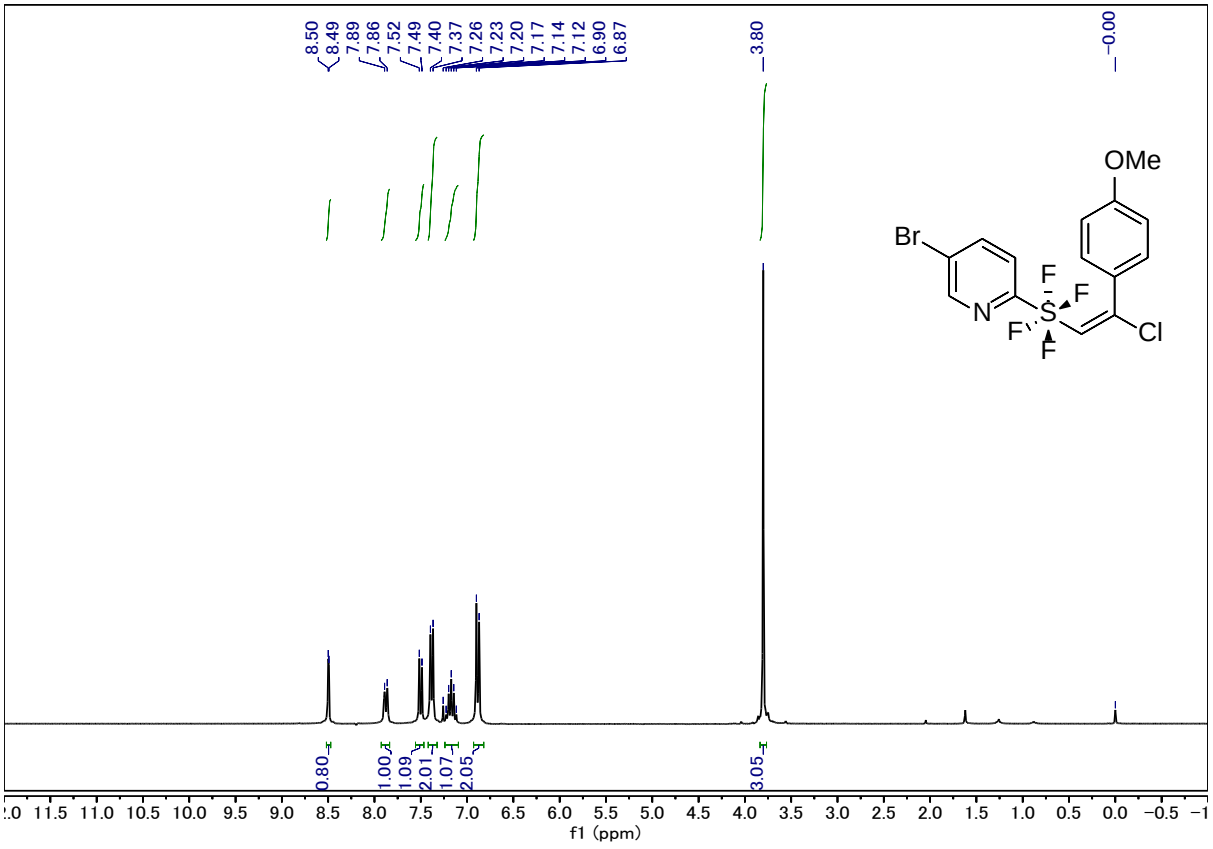

61.14
61.11
−162.20
Br
Br
N
S
F
F
F
F
Cl
4.00
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
f1 (ppm)

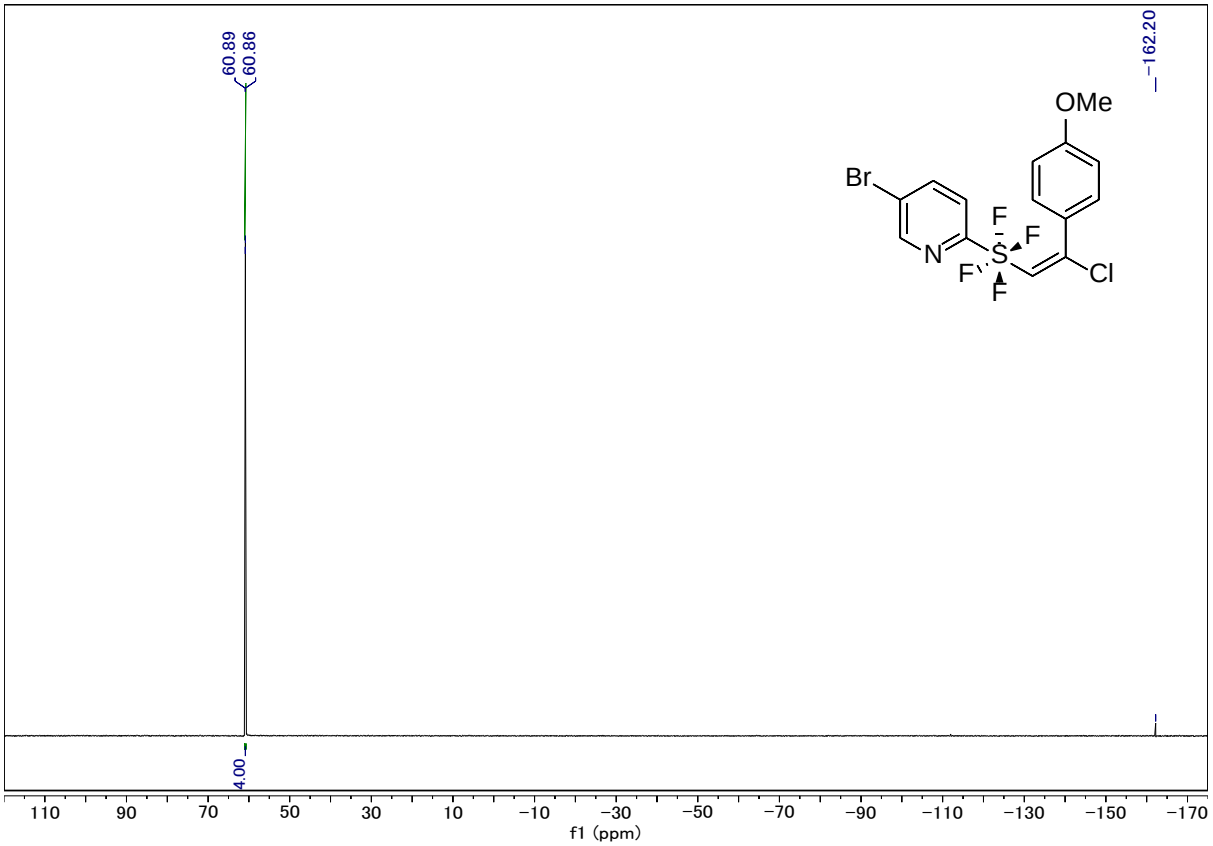

168.72
168.47
168.22
167.97
167.73
148.29
143.94
143.71
143.48
143.25
143.02
140.84
138.26
138.20
138.13
138.07
138.01
135.69
131.52
129.82
123.91
122.89
122.79
122.75
122.72
122.68
122.65
77.41
77.16
76.91
Br
Br
N
S
F
F
F
F
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

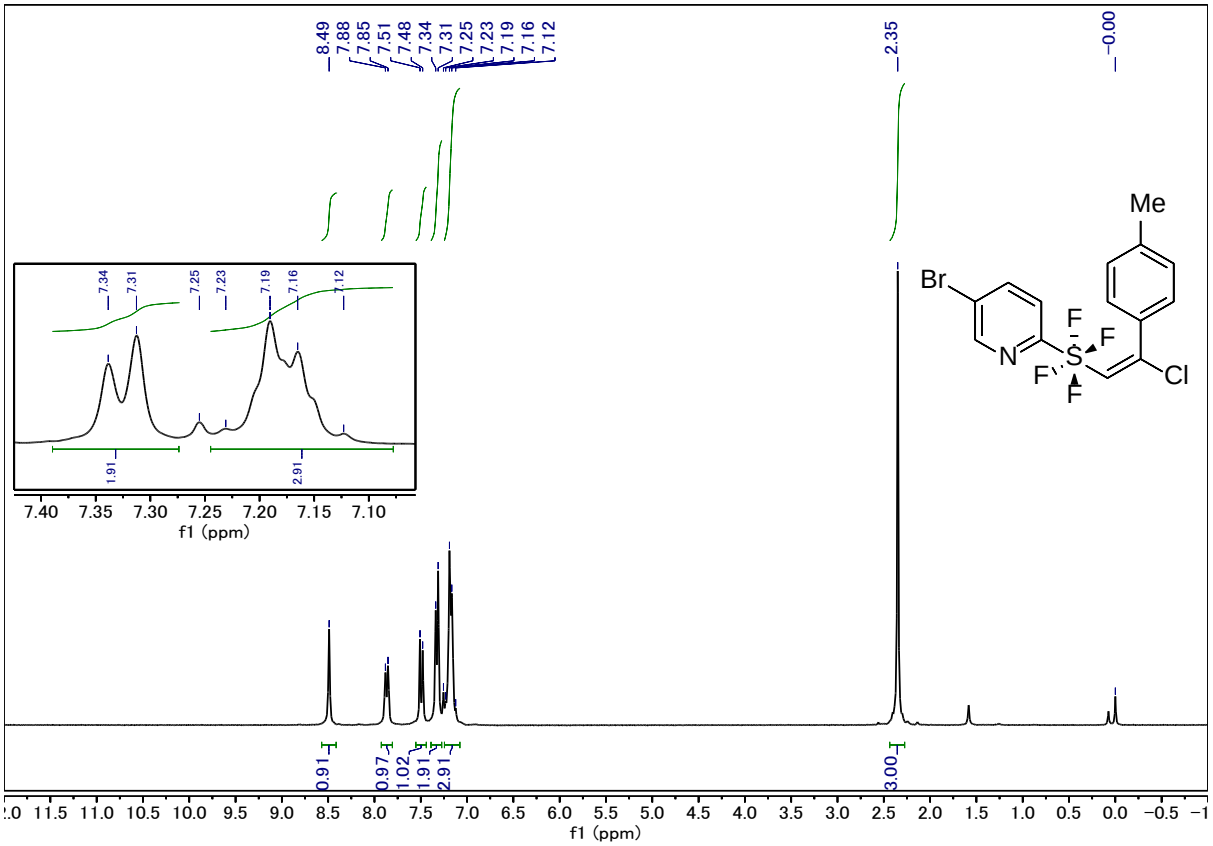

8.50
8.50
7.91
7.88
7.51
7.48
7.36
7.26
7.22
7.20
7.17
7.14
0.00
Cl
Br
F
F
F
F
S
N
Cl
0.88
1.00
1.03
3.92
1.05
f1 (ppm)

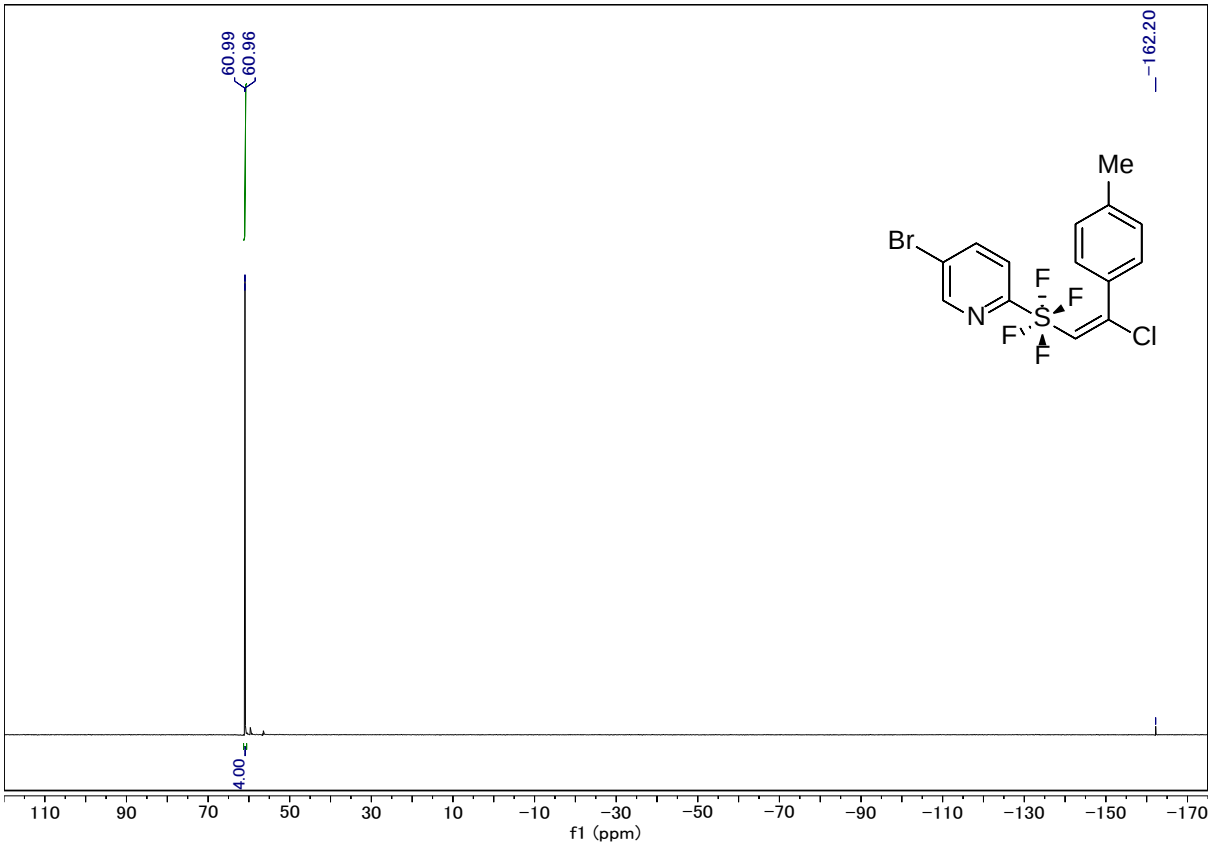

61.13
61.10
-162.20
Cl
Br
F
F
F
F
S
N
Cl
4.00
f1 (ppm)

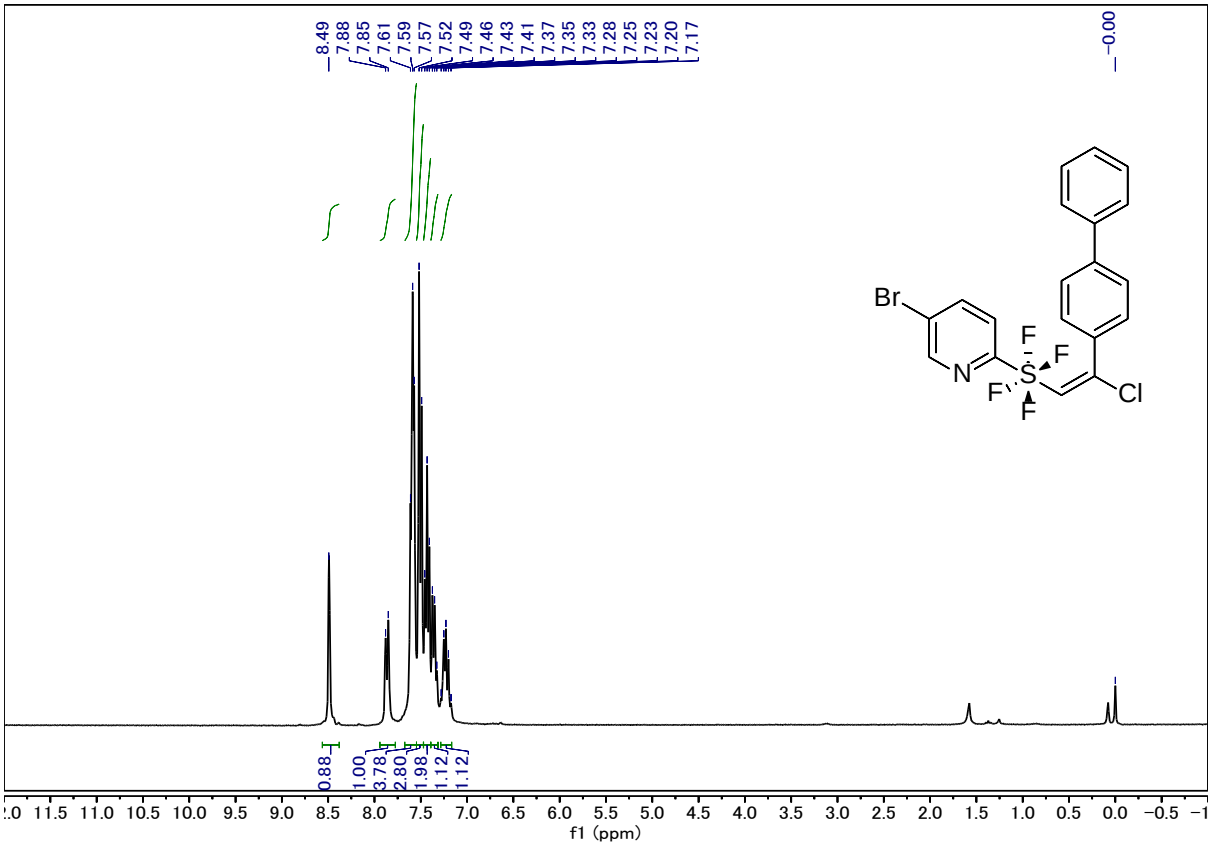

168.69
168.45
168.20
167.95
167.70
148.24
143.93
143.70
143.47
143.24
143.01
140.80
138.24
138.18
138.11
138.05
137.99
135.56
135.16
129.59
128.53
122.84
122.75
122.71
122.68
122.64
122.61
77.41
77.16
76.91
Cl
Br
F
F
N
S
F
F
Cl
f1 (ppm)

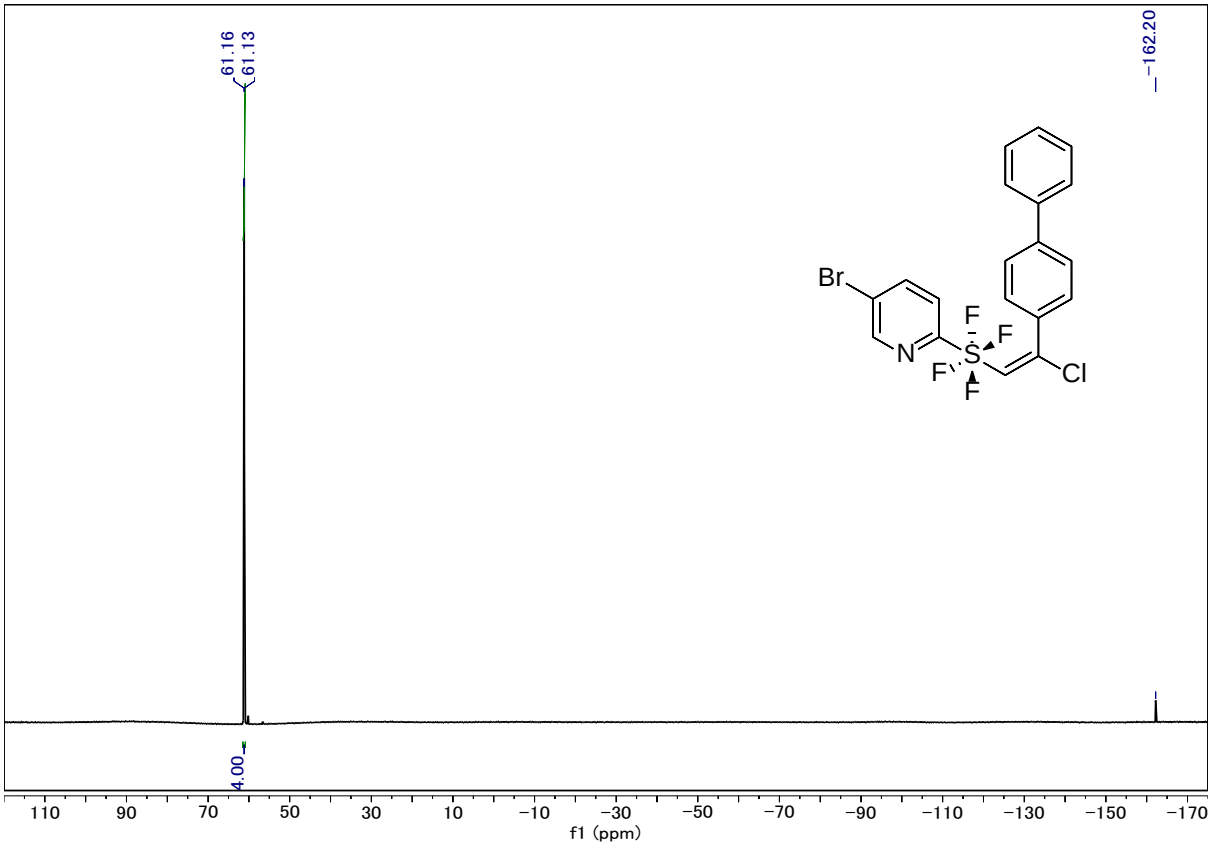

8.50
8.49
7.89
7.86
7.52
7.49
7.40
7.37
7.26
7.23
7.20
7.17
7.14
7.12
6.90
6.87
3.80
0.00
OMe
Br
F
F
N
S
F
F
Cl
0.80
1.00
1.09
2.01
1.07
2.05
3.05
f1 (ppm)

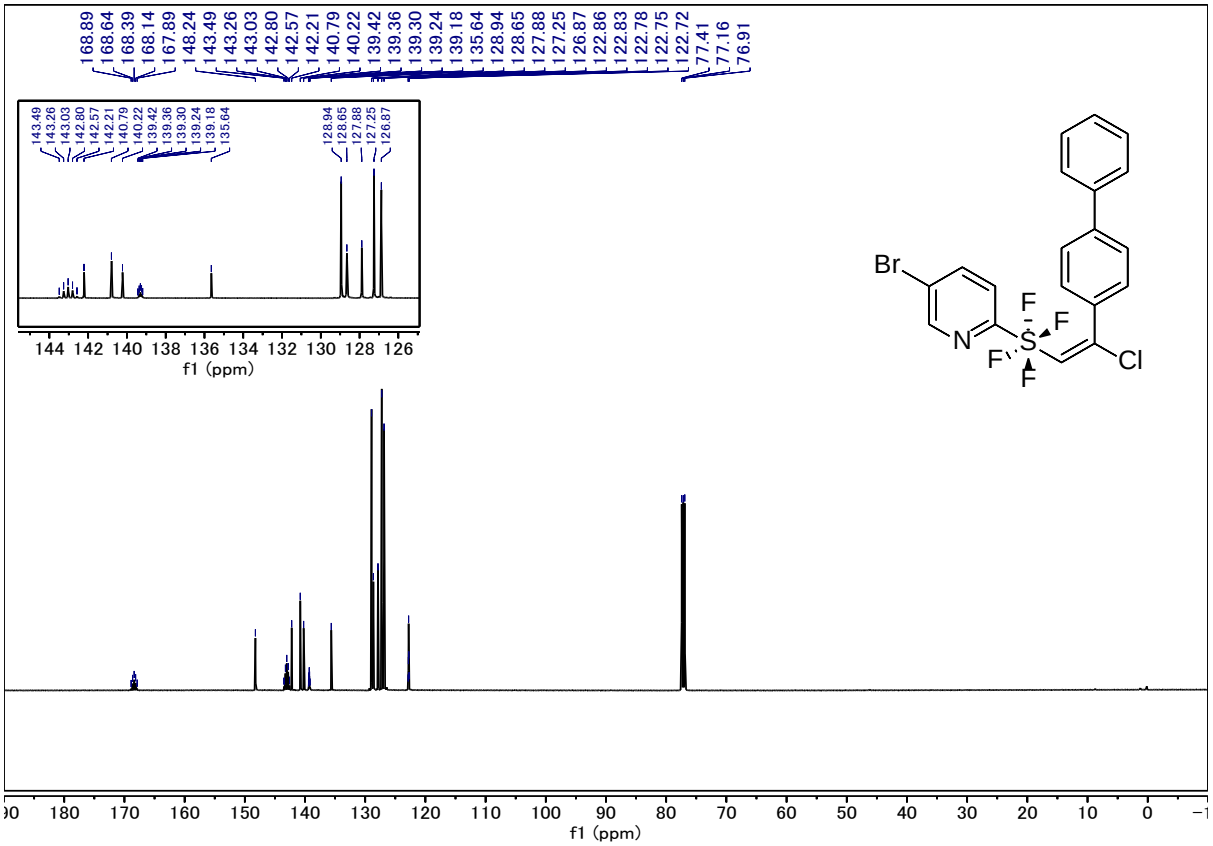

60.89
60.86
−162.20
OMe
Br
F
F
N
S
F
F
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)

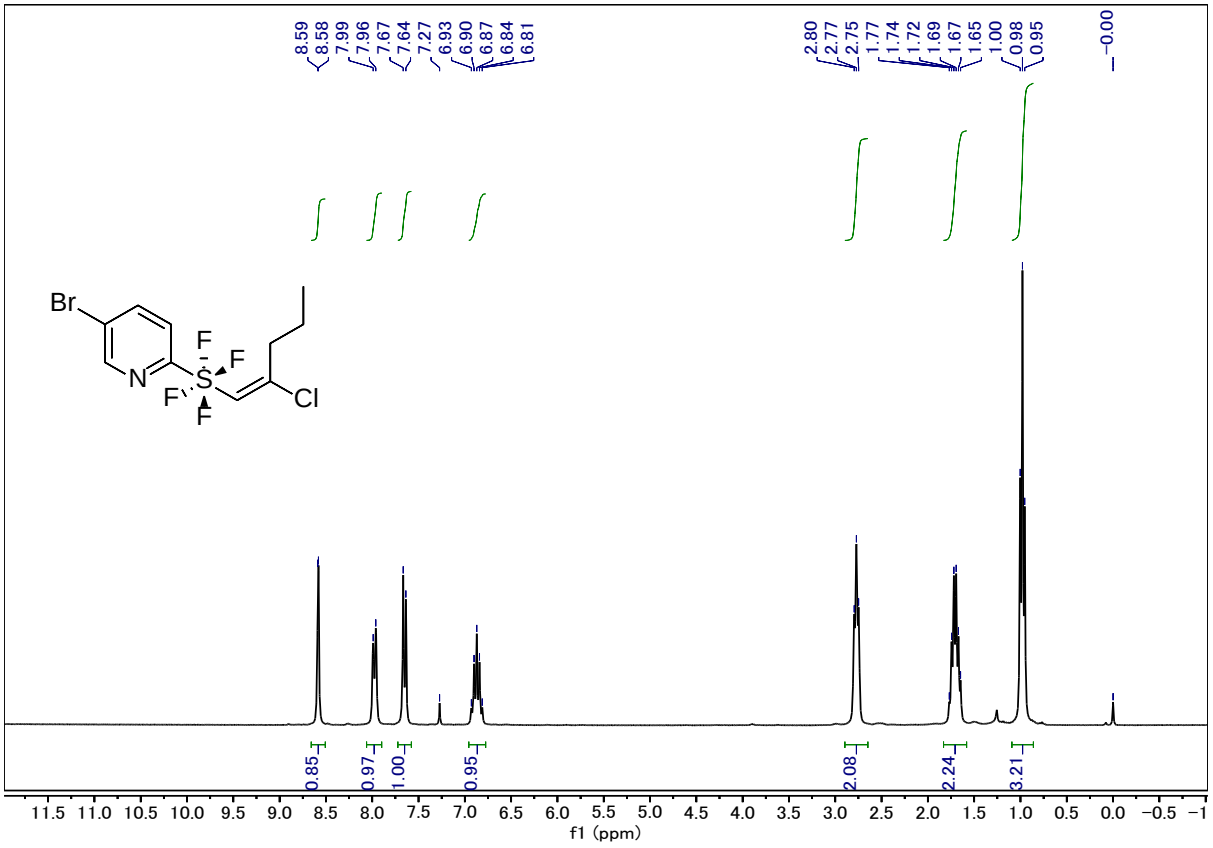

8.49
7.88
7.85
7.51
7.48
7.34
7.31
7.25
7.23
7.19
7.16
7.12
2.35
0.00
Me
Br
F
F
N
S
F
F
Cl
7.34
7.31
7.25
7.23
7.19
7.16
7.12
1.91
2.91
7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
0.91
0.97
1.02
1.91
2.91
3.00
f1 (ppm)


60.99
60.96
−162.20
Me
Br
F
F
N
S
F
F
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)


8.49
7.88
7.85
7.61
7.59
7.57
7.52
7.49
7.46
7.43
7.41
7.37
7.35
7.33
7.28
7.25
7.23
7.20
7.17
−0.00
Br
F
F
N
S
F
F
Cl
0.88
1.00
3.78
2.80
1.98
1.12
1.12
f1 (ppm)


61.16
61.13
−162.20
Br
N
F
F
S
F
F
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)


168.89
168.64
168.39
168.14
167.89
148.24
143.49
143.26
143.03
142.80
142.57
142.21
140.79
140.22
139.42
139.36
139.30
139.24
139.18
135.64
128.94
128.65
127.88
127.25
126.87
122.86
122.83
122.78
122.75
122.72
77.41
77.16
76.91
144 142 140 138 136 134 132 130 128 126
f1 (ppm)
Br
N
F
F
S
F
F
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.59
8.58
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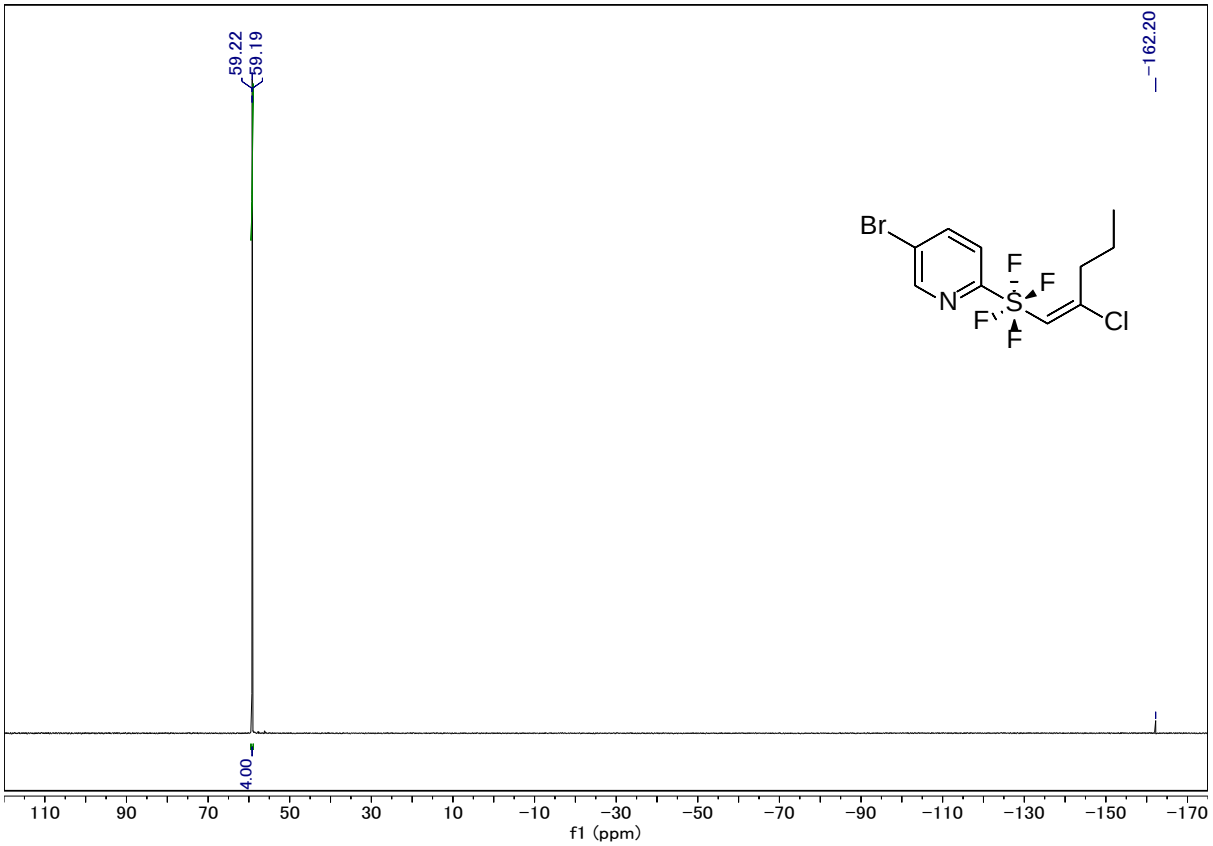
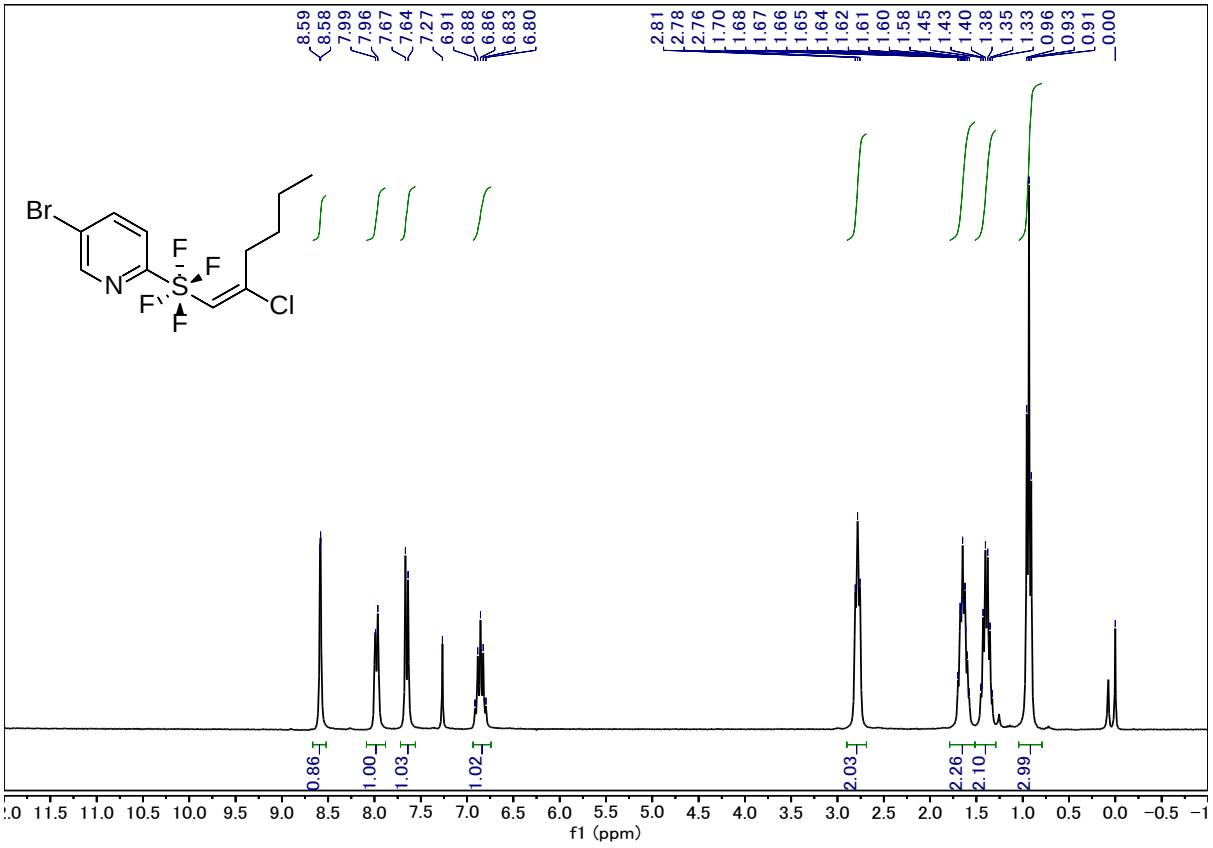
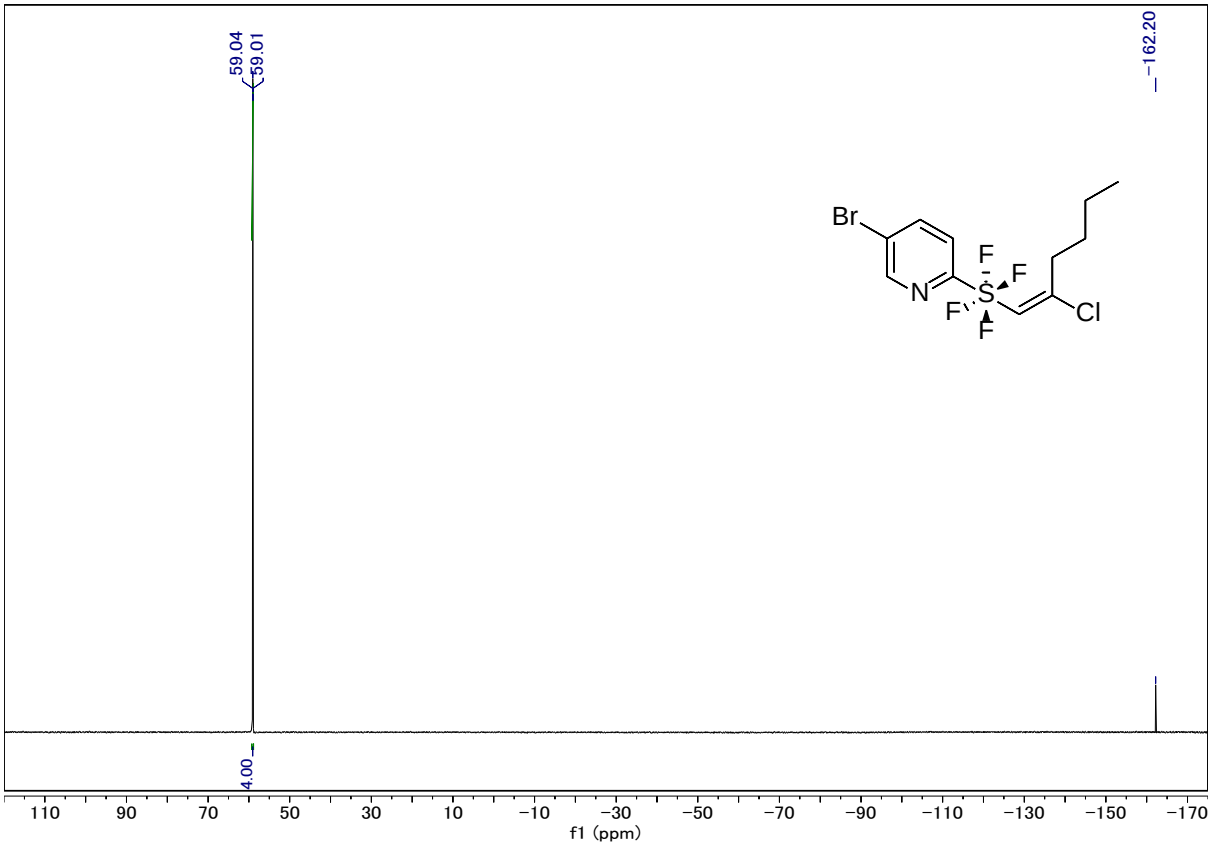
7.67
7.64
7.27
6.93
6.90
6.87
6.84
6.81
2.80
2.77
2.75
1.77
1.74
1.72
1.69
1.67
1.65
1.00
0.98
0.95
0.00
Br
N
F
F
F
S
F
Cl
0.85
0.97
1.00
0.95
2.08
2.24
3.21
f1 (ppm)


59.22
59.19
-162.20
Br
N
F
F
F
S
F
Cl
4.00
f1 (ppm)


8.59
8.58
7.99
7.96
7.67
7.64
7.27
6.91
6.88
6.86
6.83
6.80
2.81
2.78
2.76
1.70
1.68
1.67
1.66
1.65
1.64
1.62
1.61
1.60
1.58
1.45
1.43
1.40
1.38
1.35
1.33
0.96
0.93
0.91
0.00
Br
N
F
F
F
F
S
Cl
0.86
1.00
1.03
1.02
2.03
2.26
2.10
2.99
f1 (ppm)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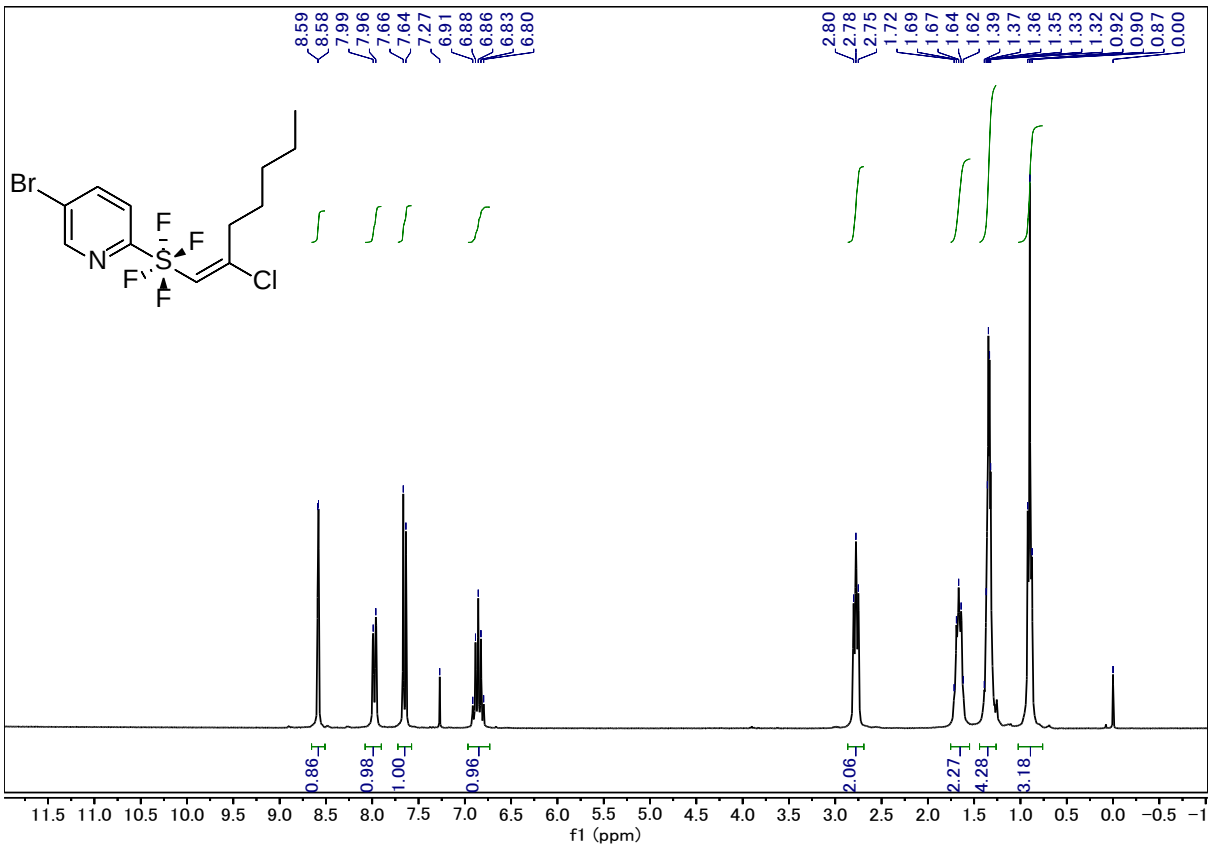
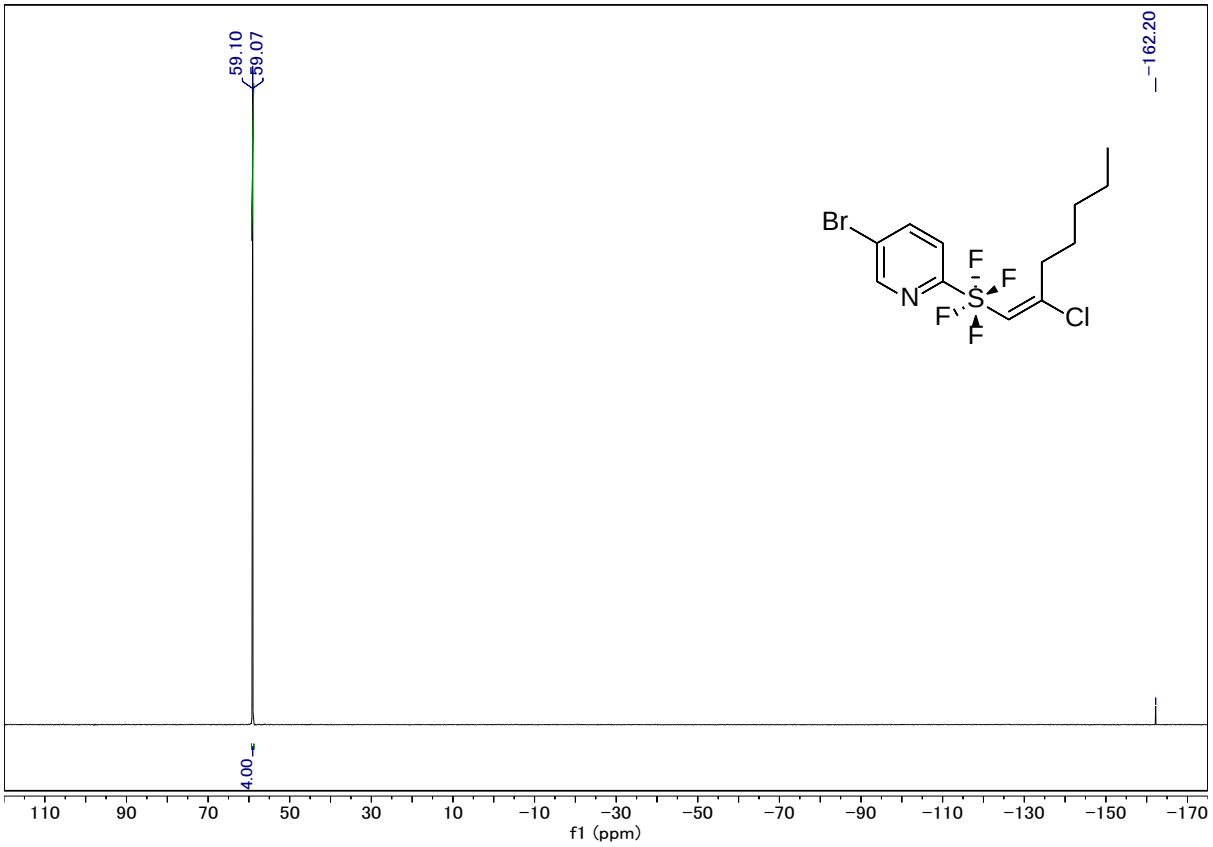
59.01
−162.20
Br
N
F
F
F
F
S
Cl
4.00
f1 (ppm)


8.59
8.58
7.99
7.96
7.66
7.64
7.27
6.91
6.88
6.86
6.83
6.80
2.80
2.78
2.75
1.72
1.69
1.67
1.64
1.62
1.39
1.37
1.36
1.35
1.33
1.32
0.92
0.90
0.87
0.00
Br
N
F
F
F
F
S
Cl
0.86
0.98
1.00
0.96
2.06
2.27
4.28
3.18
f1 (ppm)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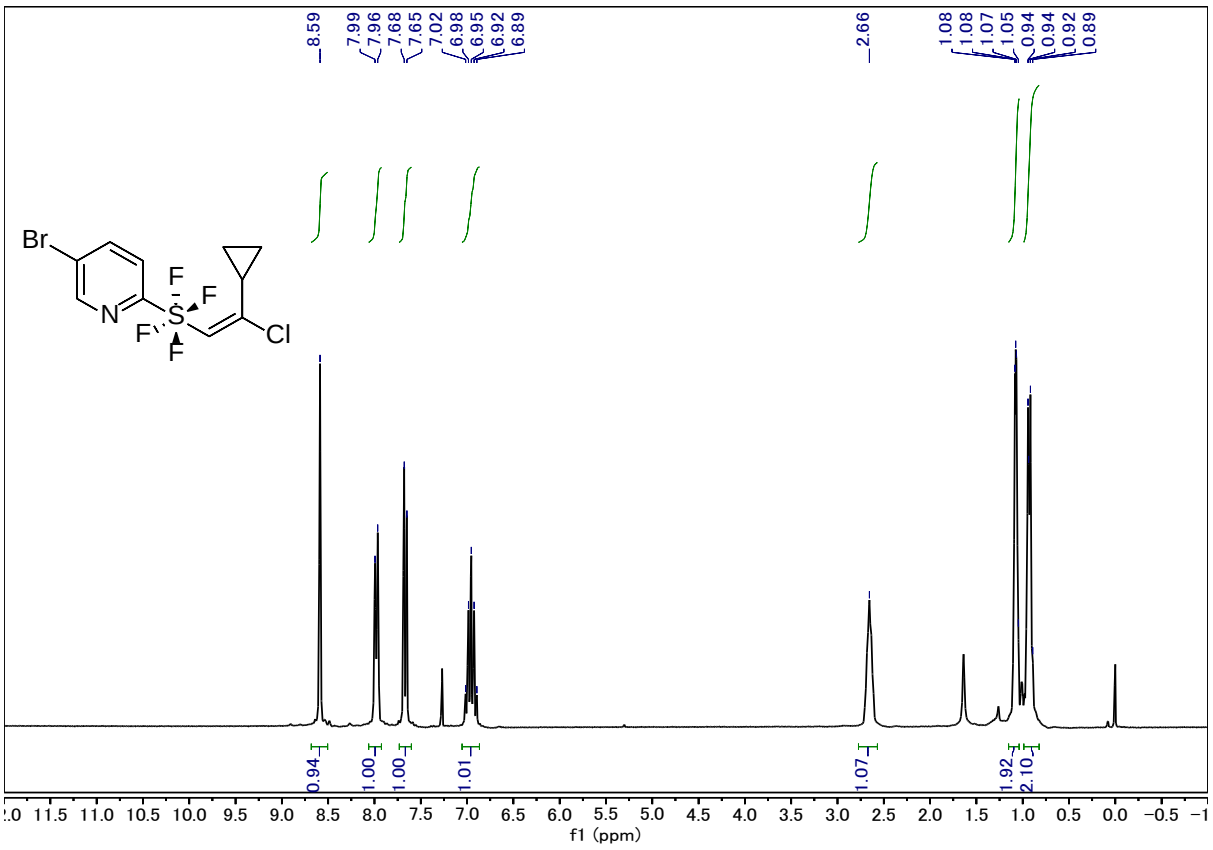
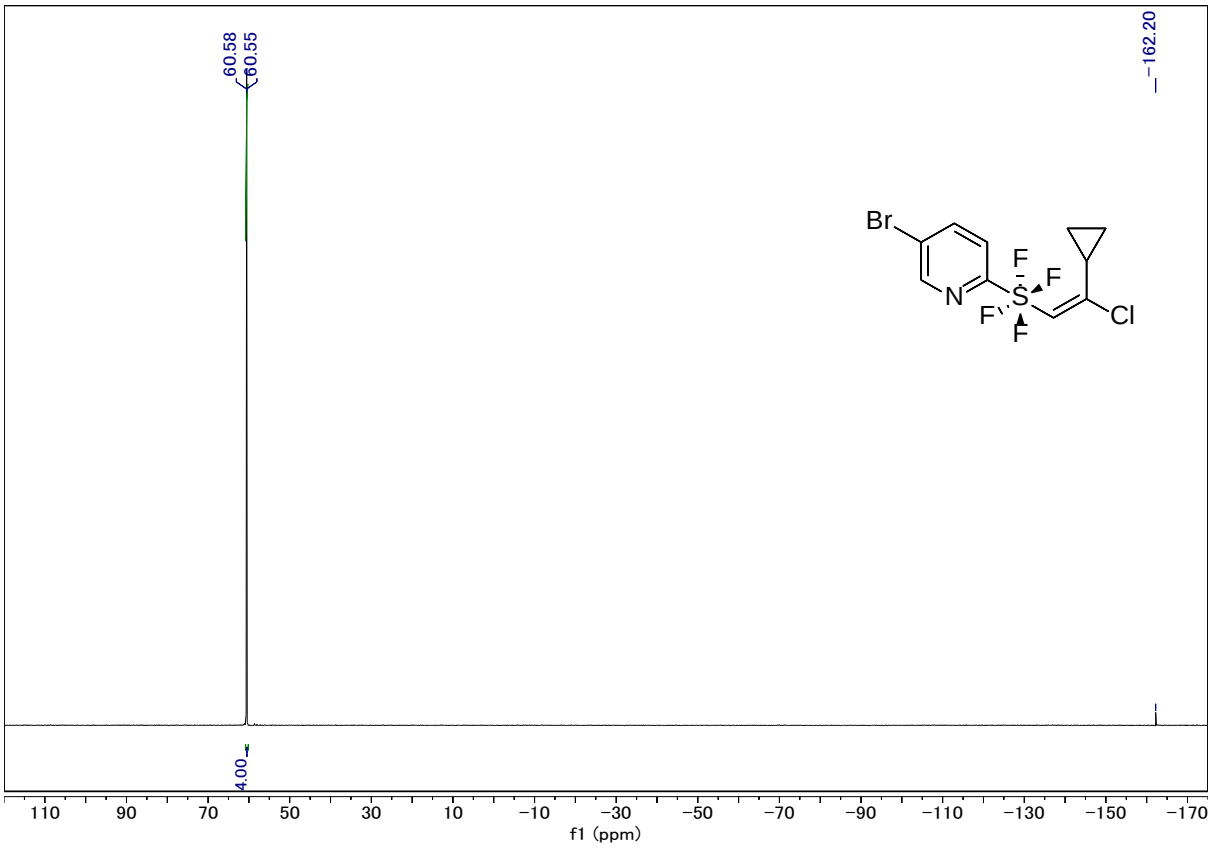
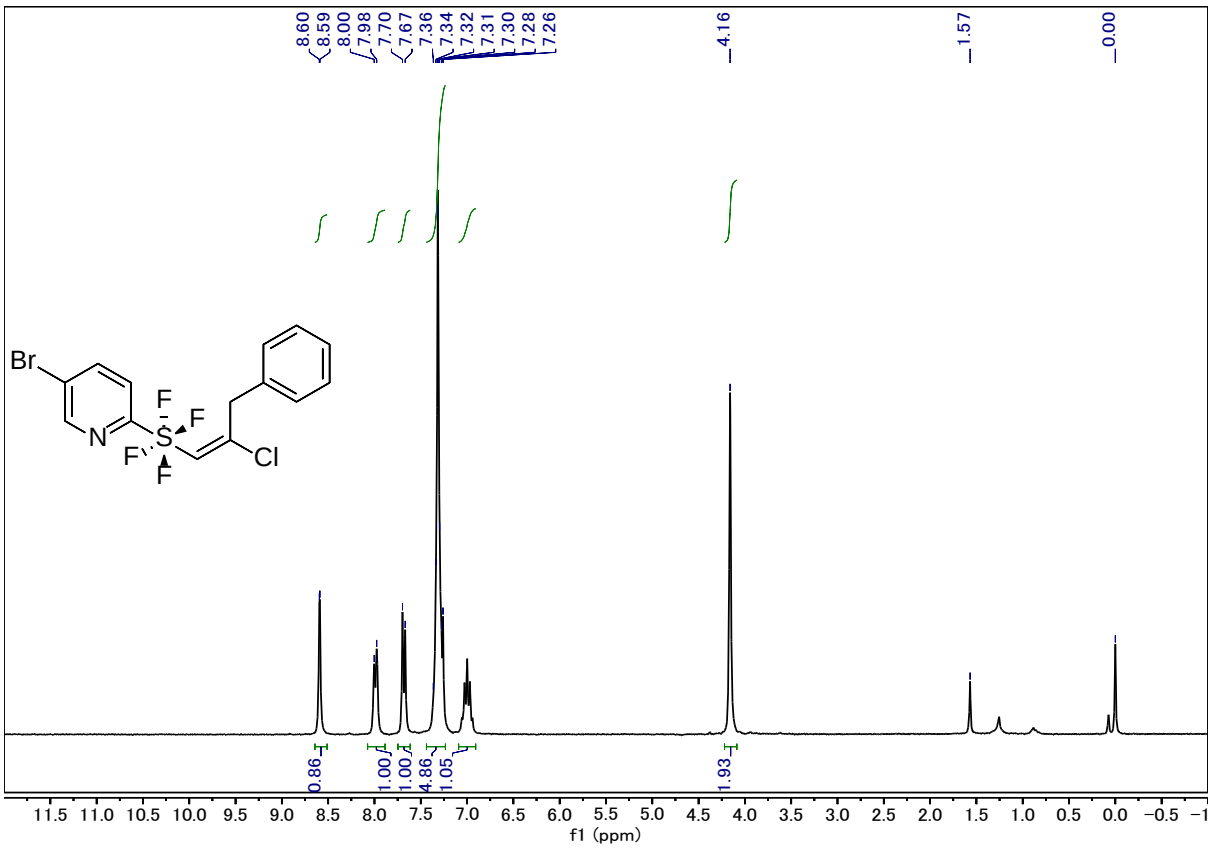
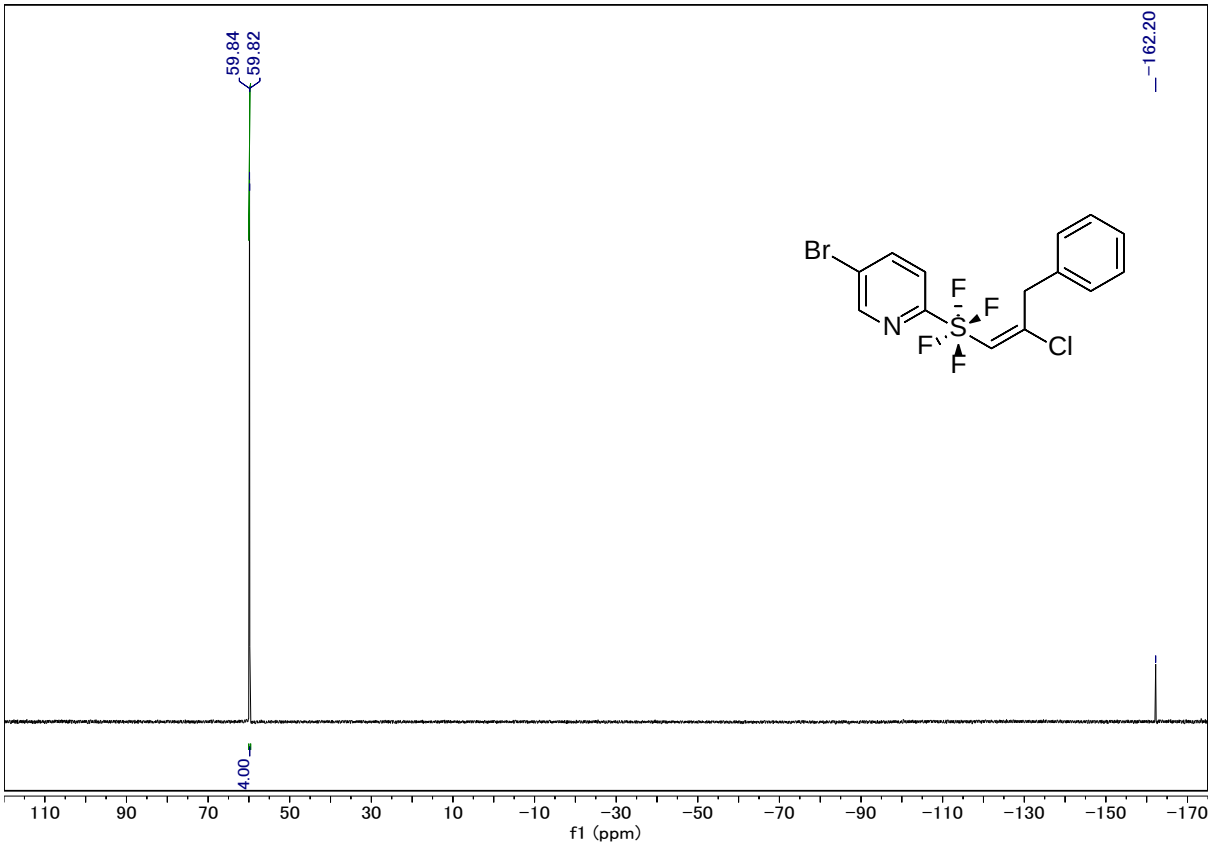
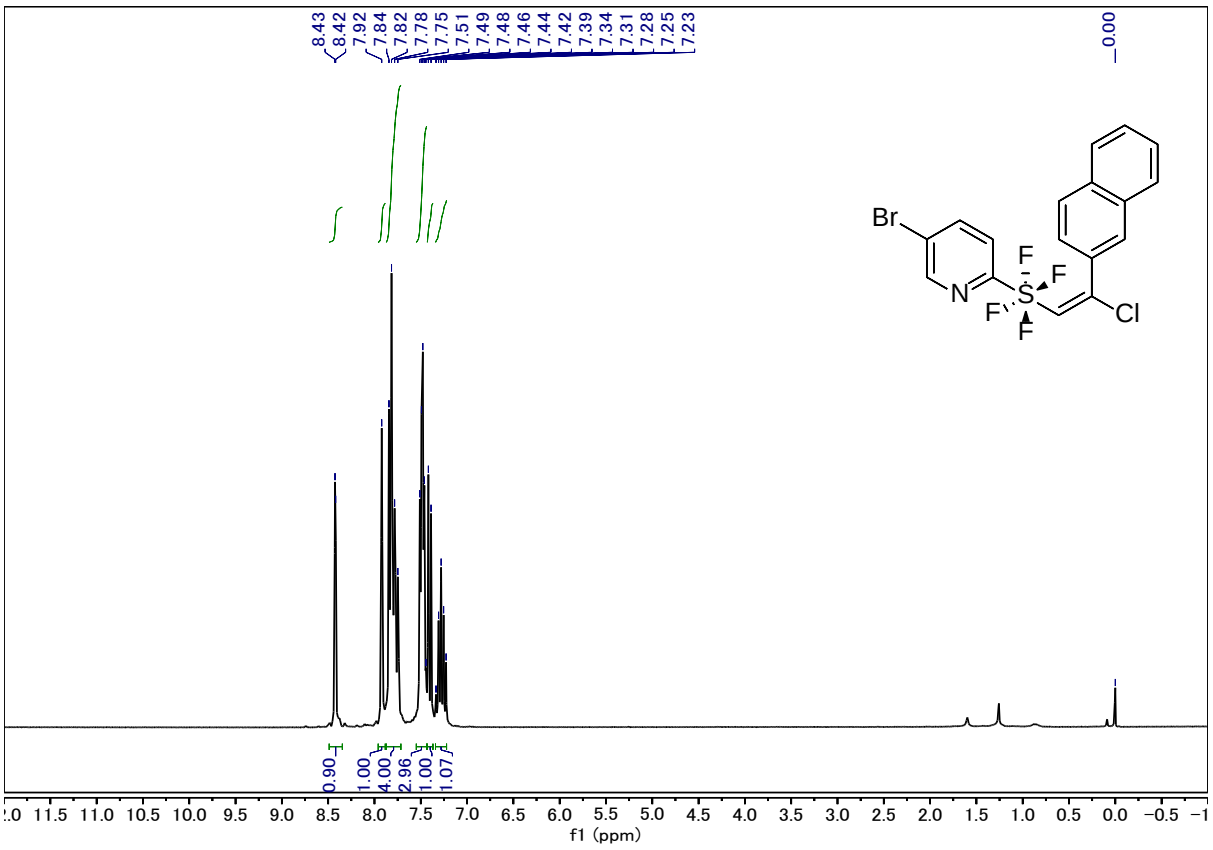
Br
N
F
F
F
F
S
Cl
4.00
f1 (ppm)


8.59
7.99
7.96
7.68
7.65
7.02
6.98
6.95
6.92
6.89
2.66
1.08
1.08
1.07
1.05
0.94
0.94
0.92
0.89
Br
N
F
F
S
F
F
Cl
0.94
1.00
1.00
1.01
1.07
1.92
2.10
f1 (ppm)


60.58
60.55
-162.20
Br
N
F
F
S
F
F
Cl
4.00
f1 (ppm)


8.60
8.59
8.00
7.98
7.70
7.67
7.36
7.34
7.32
7.31
7.30
7.28
7.26
4.16
1.57
0.00
Br
F
F
N
S
F
F
Cl
0.86
1.00
1.00
4.86
1.05
1.93
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)


59.84
59.82
−162.20
Br
F
F
N
S
F
F
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)


8.43
8.42
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7.82
7.78
7.75
7.51
7.49
7.48
7.46
7.44
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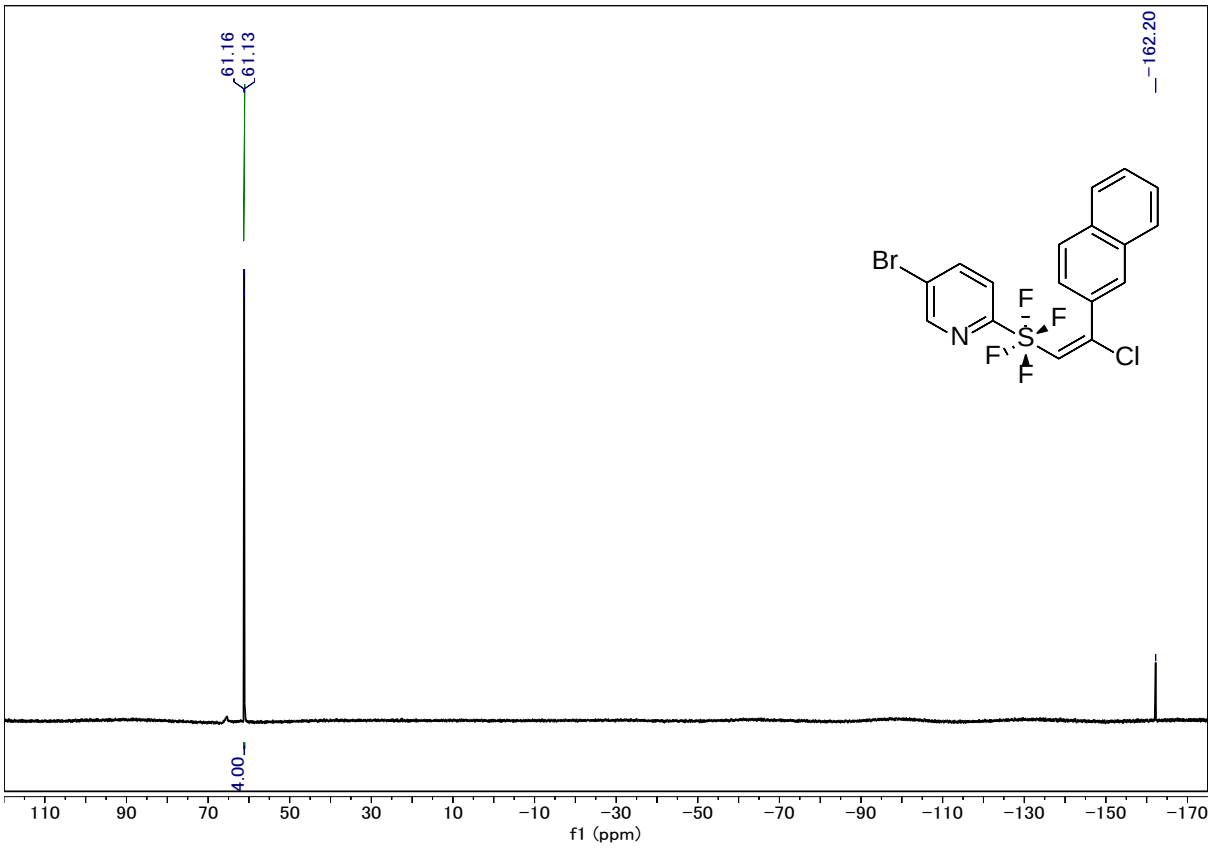
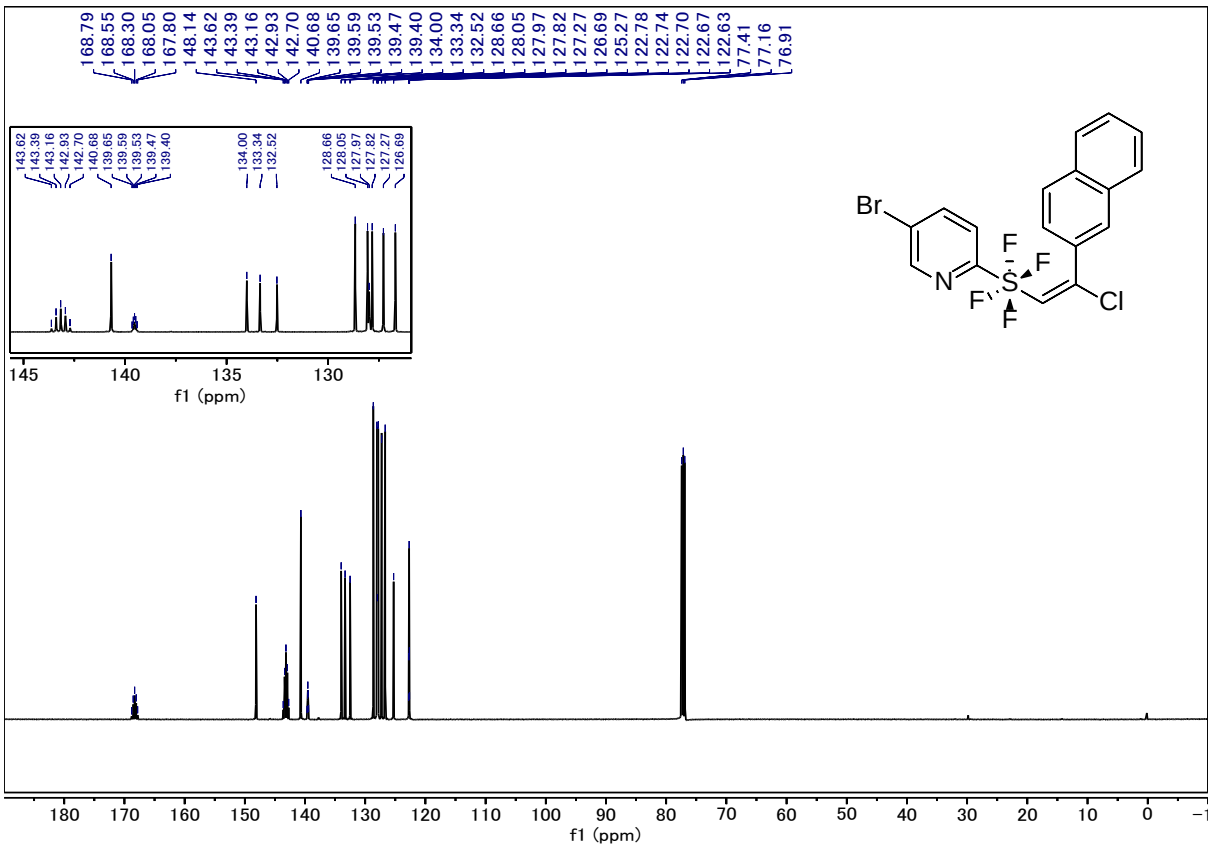
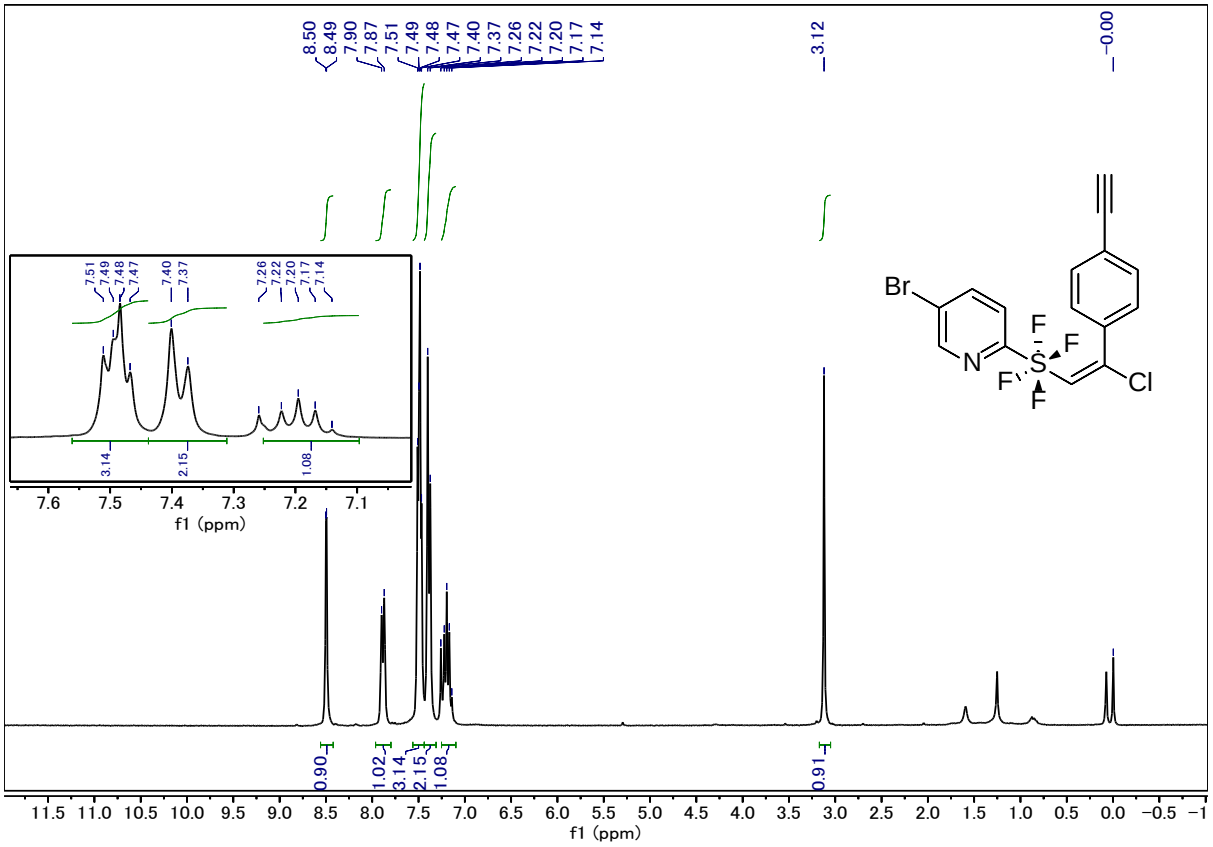
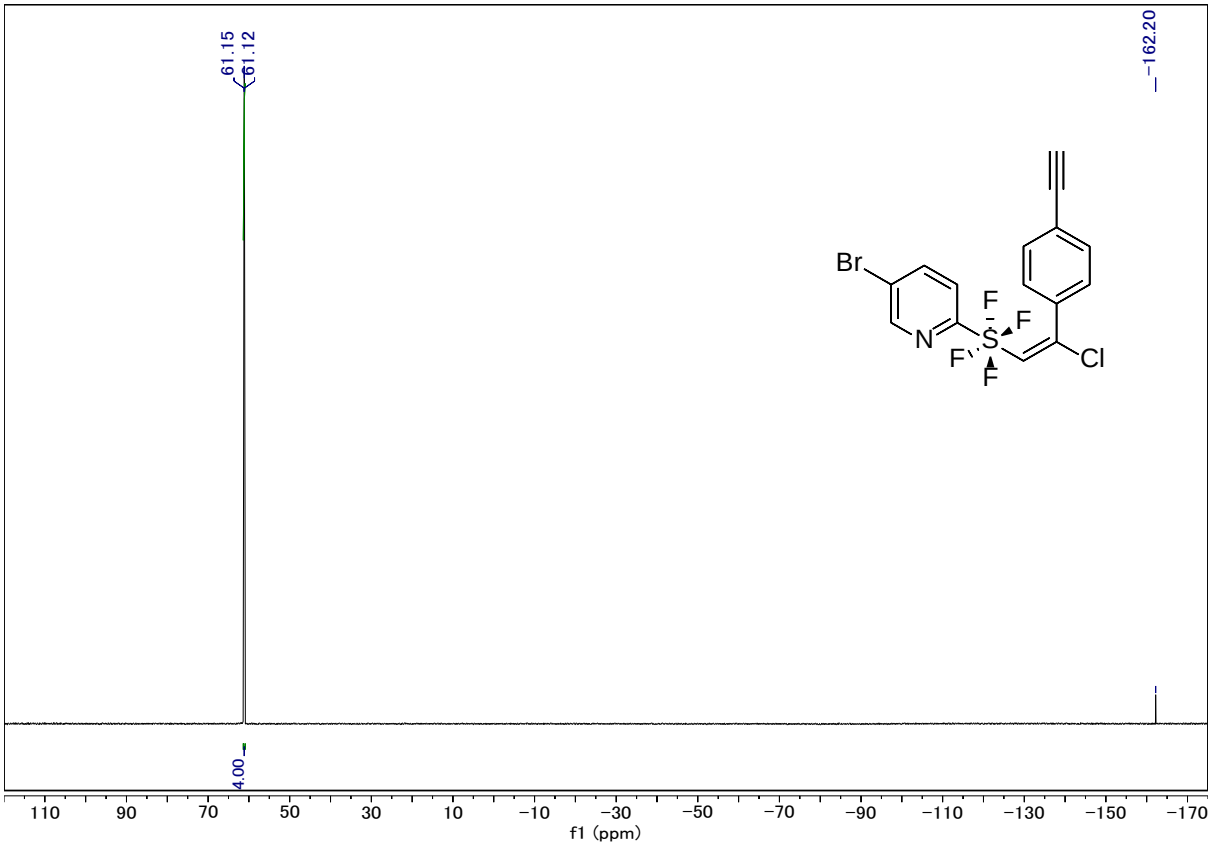
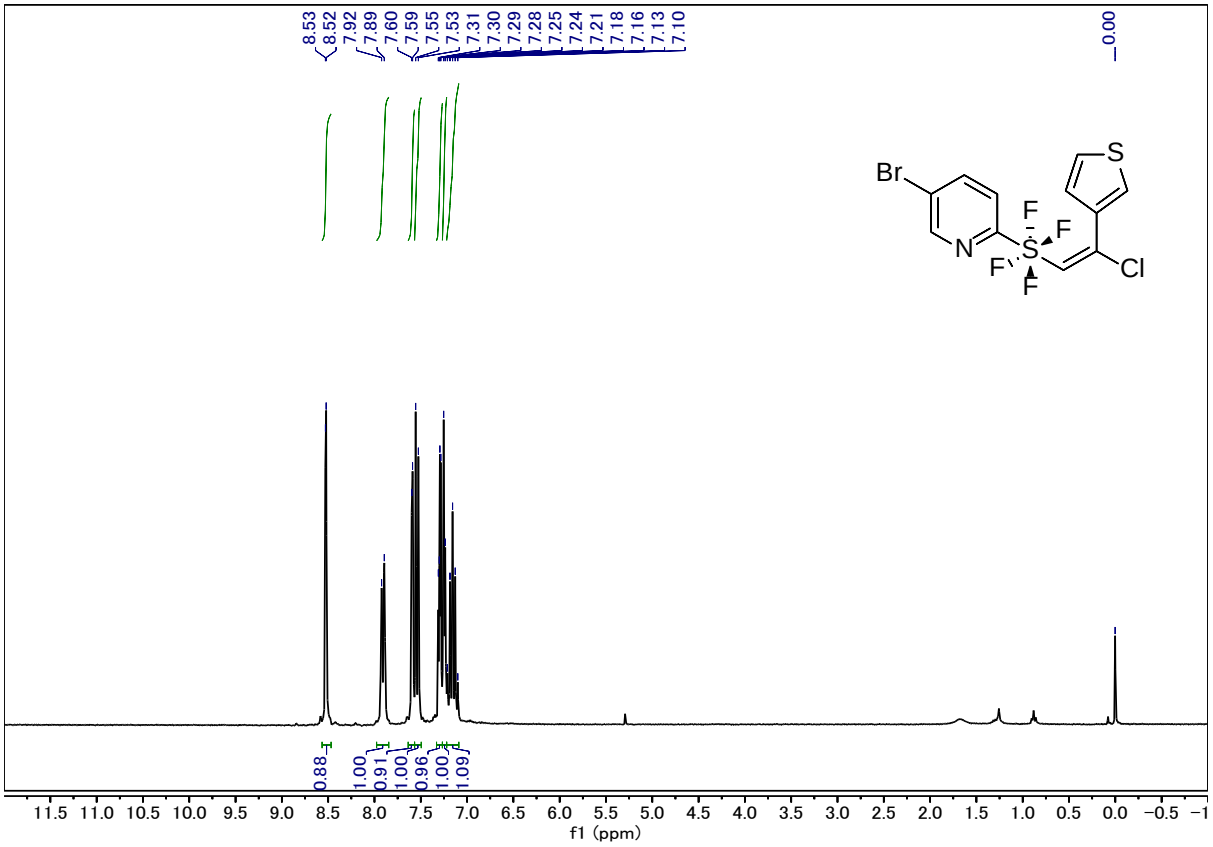
7.39
7.34
7.31
7.28
7.25
7.23
0.00
Br
N
F
F
S
F
F
Cl
0.90
1.00
4.00
2.96
1.00
1.07
f1 (ppm)

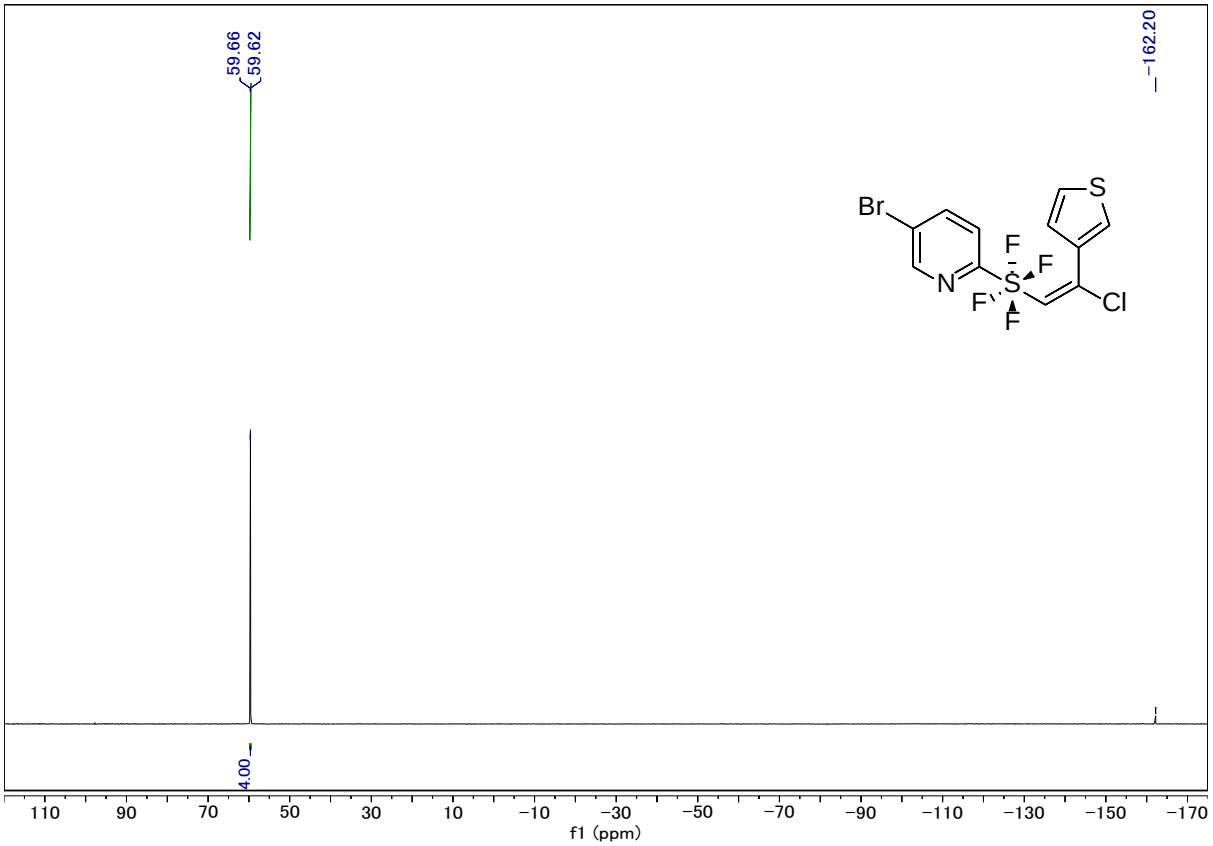

61.16
61.13
-162.20
Br
N
F
F
S
F
F
Cl
4.00
f1 (ppm)

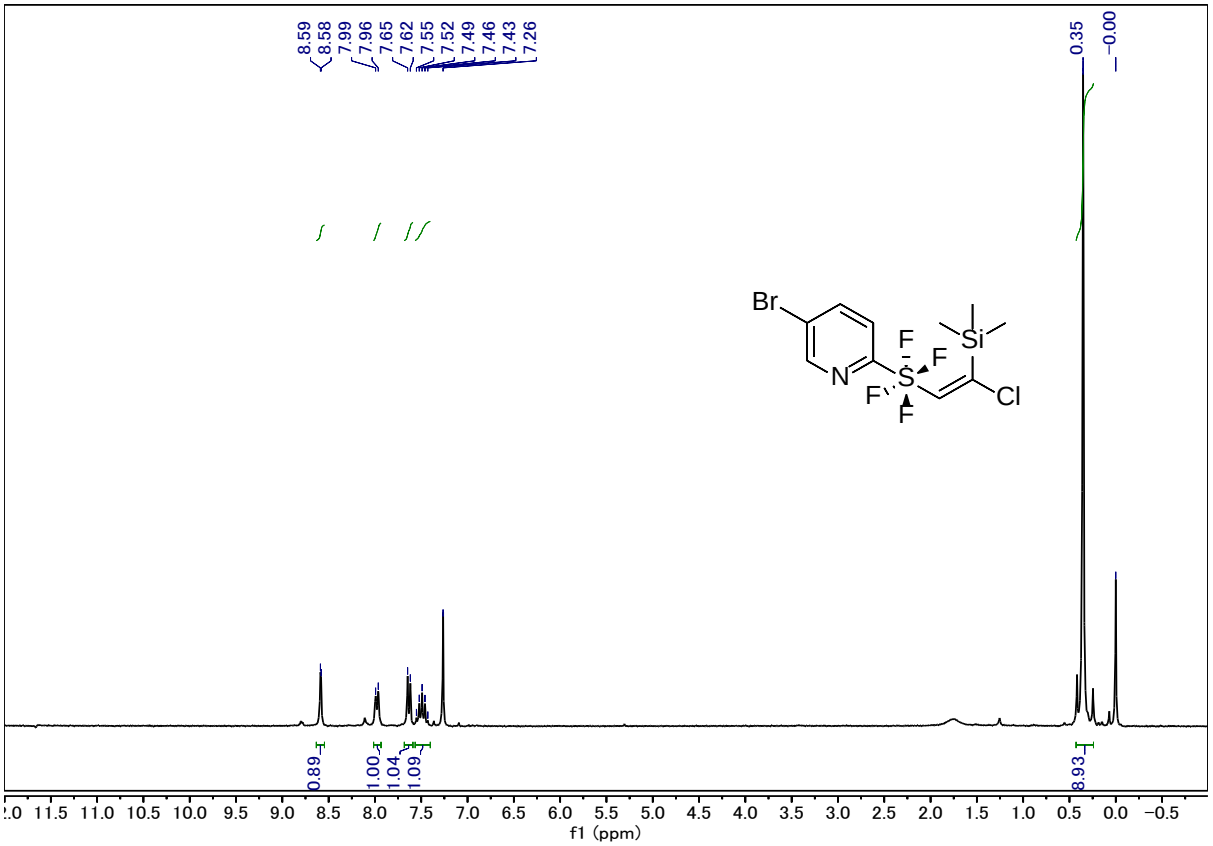

168.79
168.55
168.30
168.05
167.80
148.14
143.62
143.39
143.16
142.93
142.70
140.68
139.65
139.59
139.53
139.47
139.40
134.00
133.34
132.52
128.66
128.05
127.97
127.82
127.27
126.69
125.27
122.78
122.74
122.70
122.67
122.63
77.41
77.16
76.91
Br
N
S
F
F
F
F
Cl
f1 (ppm)

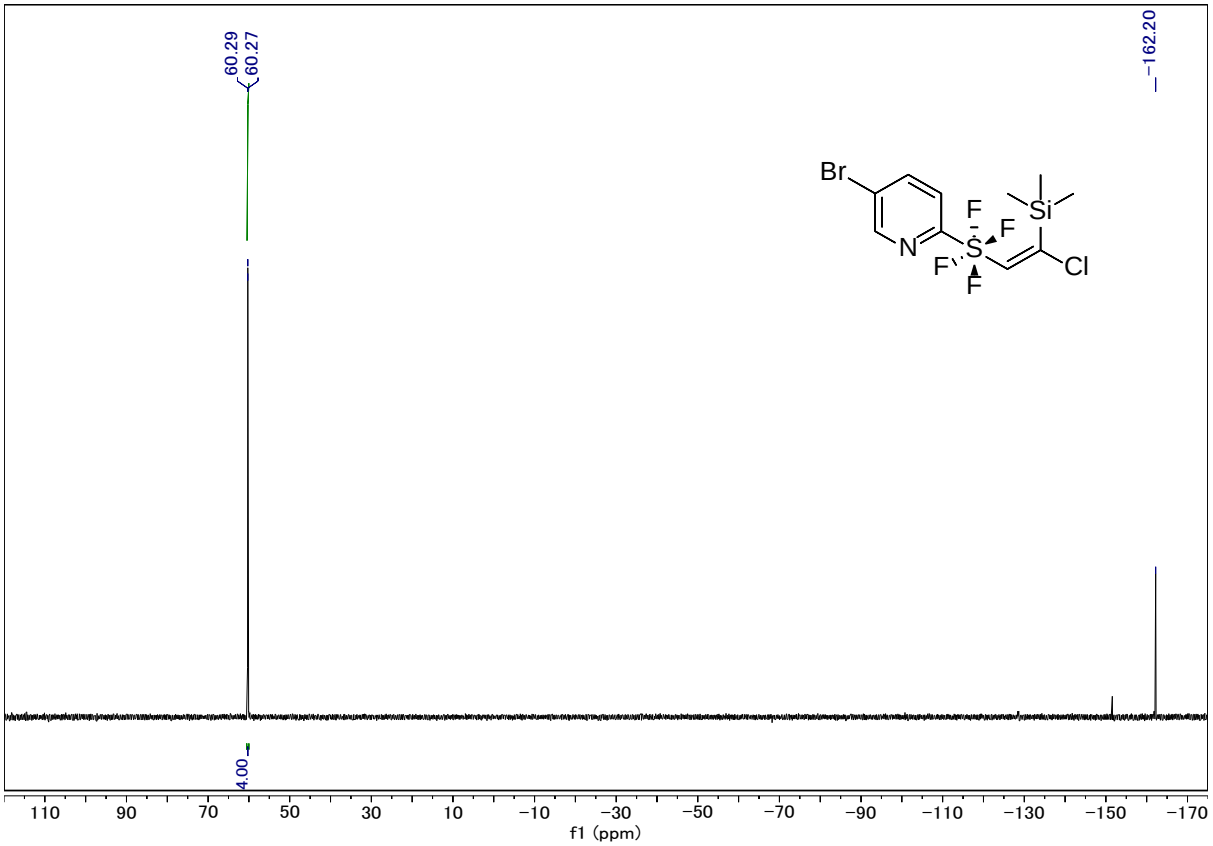

8.50
8.49
7.90
7.87
7.51
7.49
7.48
7.47
7.40
7.37
7.26
7.22
7.20
7.17
7.14
3.12
0.00
Br
N
S
F
F
F
F
Cl
0.90
1.02
3.14
2.15
1.08
0.91
f1 (ppm)

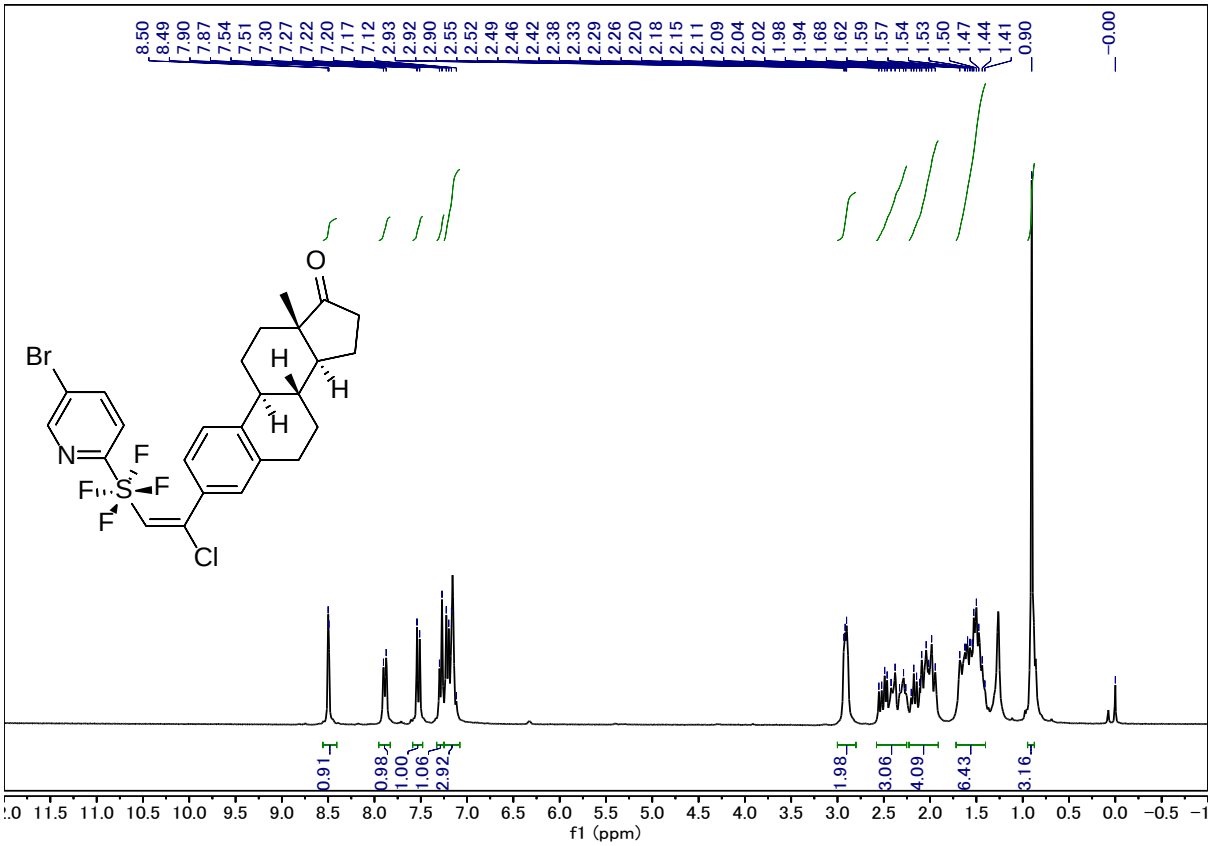

61.15
61.12
−162.20
Br
F
F
N
S
F
F
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)

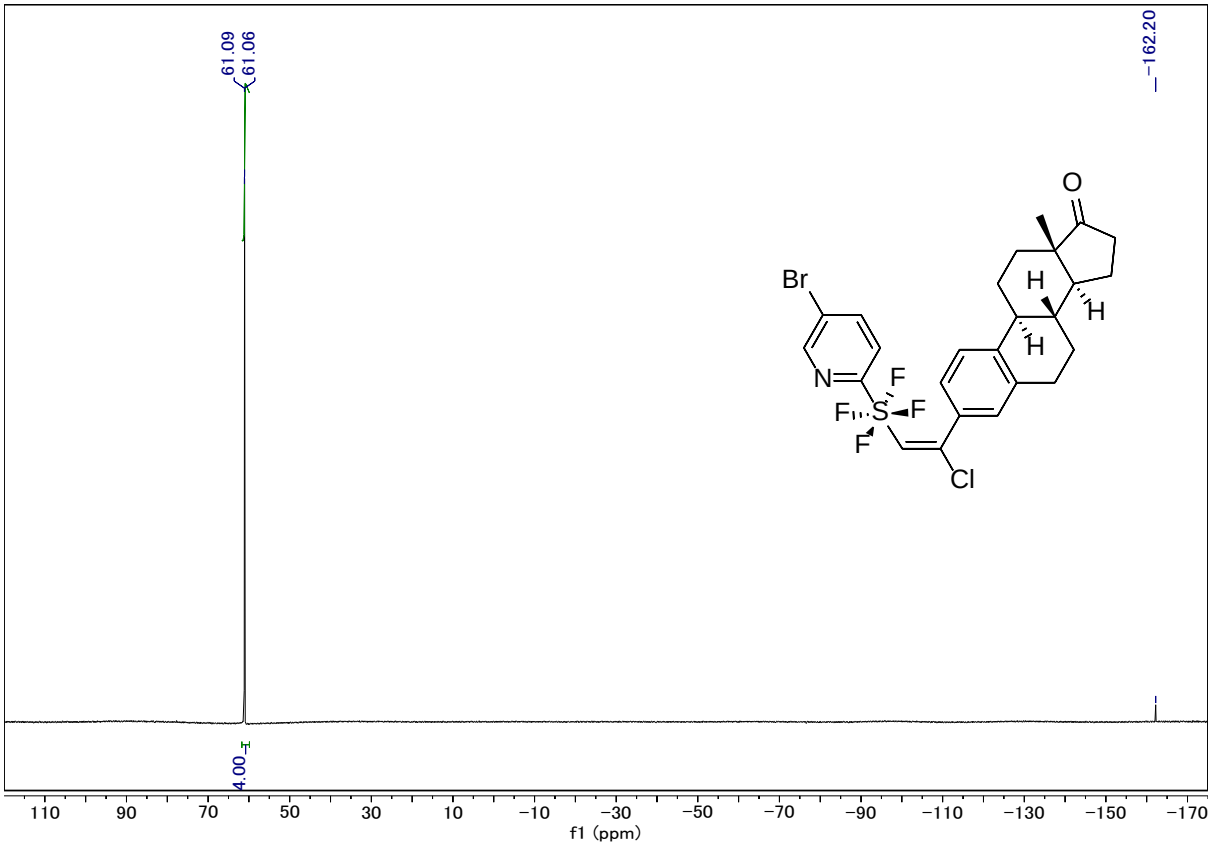

8.53
8.52
7.92
7.89
7.60
7.59
7.55
7.53
7.31
7.30
7.29
7.28
7.25
7.24
7.21
7.18
7.16
7.13
7.10
0.00
Br
S
F
F
N
S
F
F
Cl
0.88
1.00
0.91
1.00
0.96
1.00
1.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

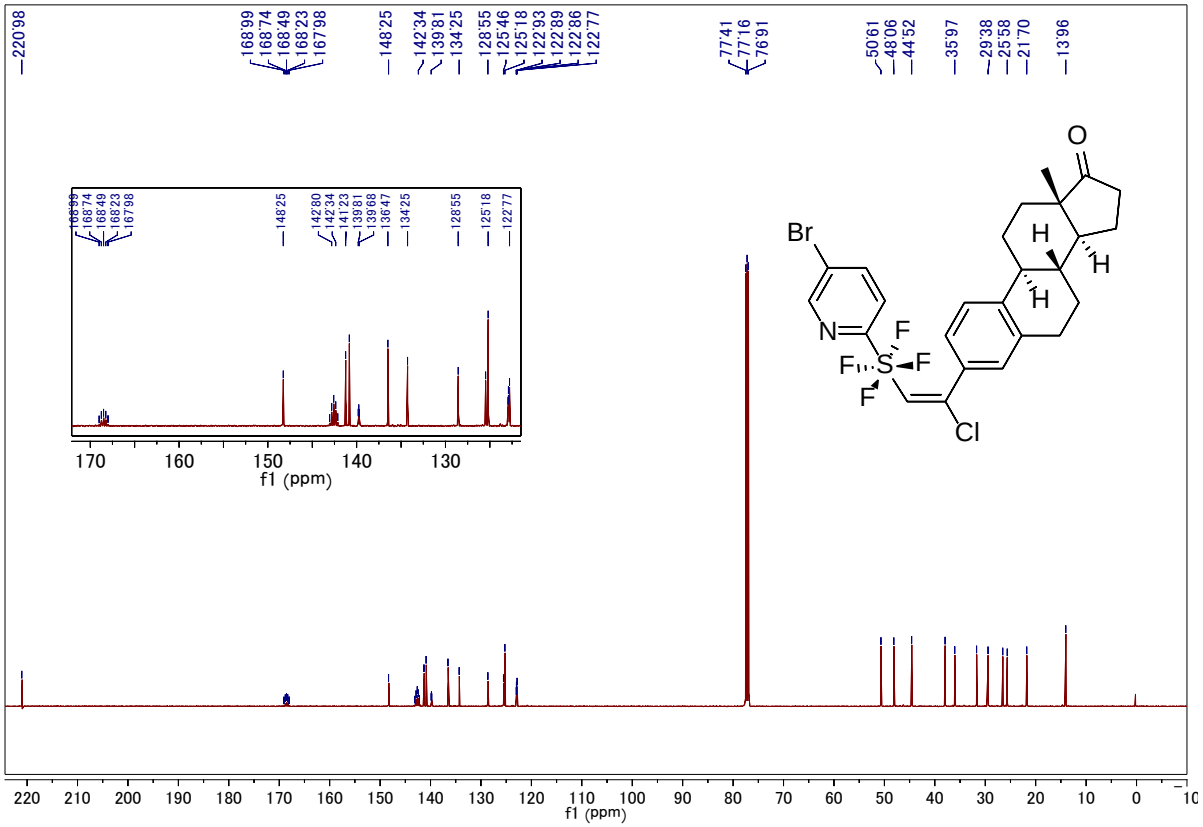

59.66
59.62
−162.20
Br
S
F
F
N
S
F
F
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)

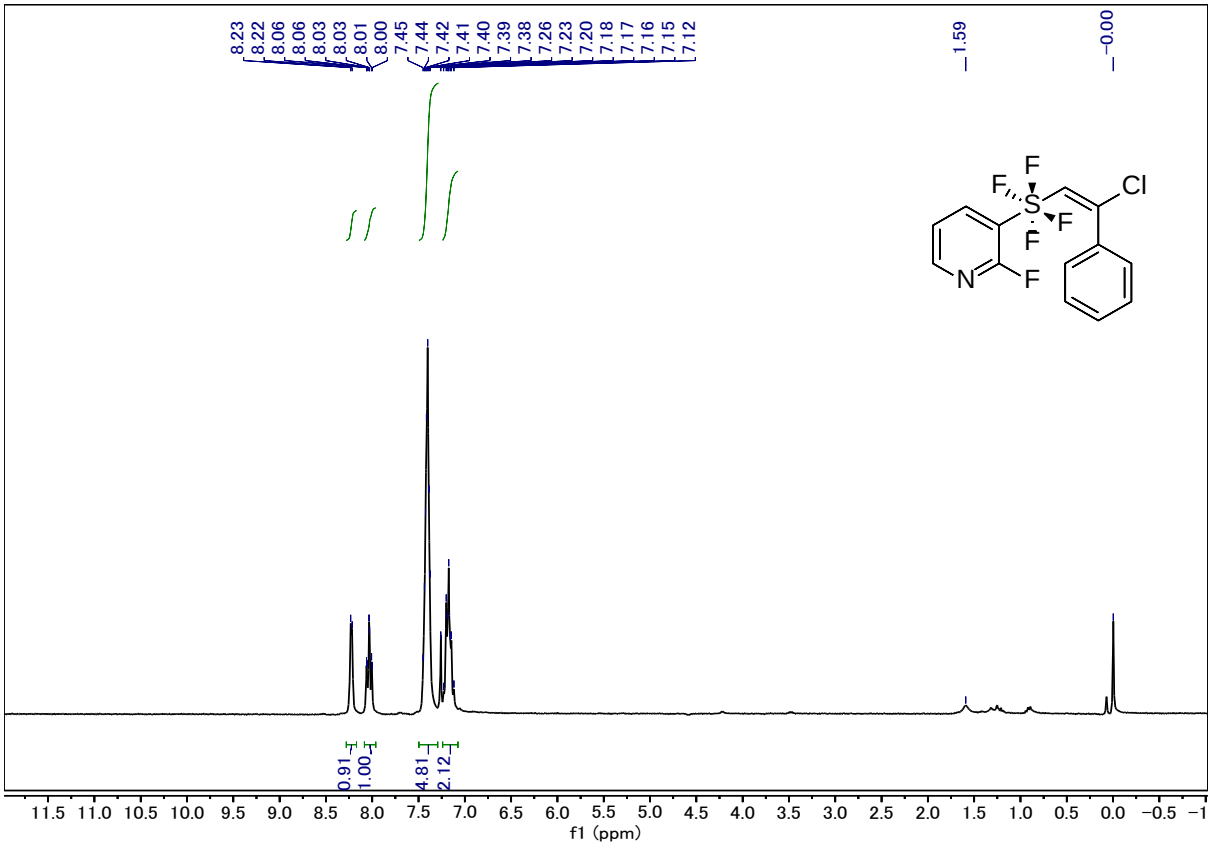

8.59
8.58
7.99
7.96
7.65
7.62
7.55
7.52
7.49
7.46
7.43
7.26
0.35
−0.00
Br
Si
F
F
N
S
F
F
Cl
0.89
1.00
1.04
1.09
8.93
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

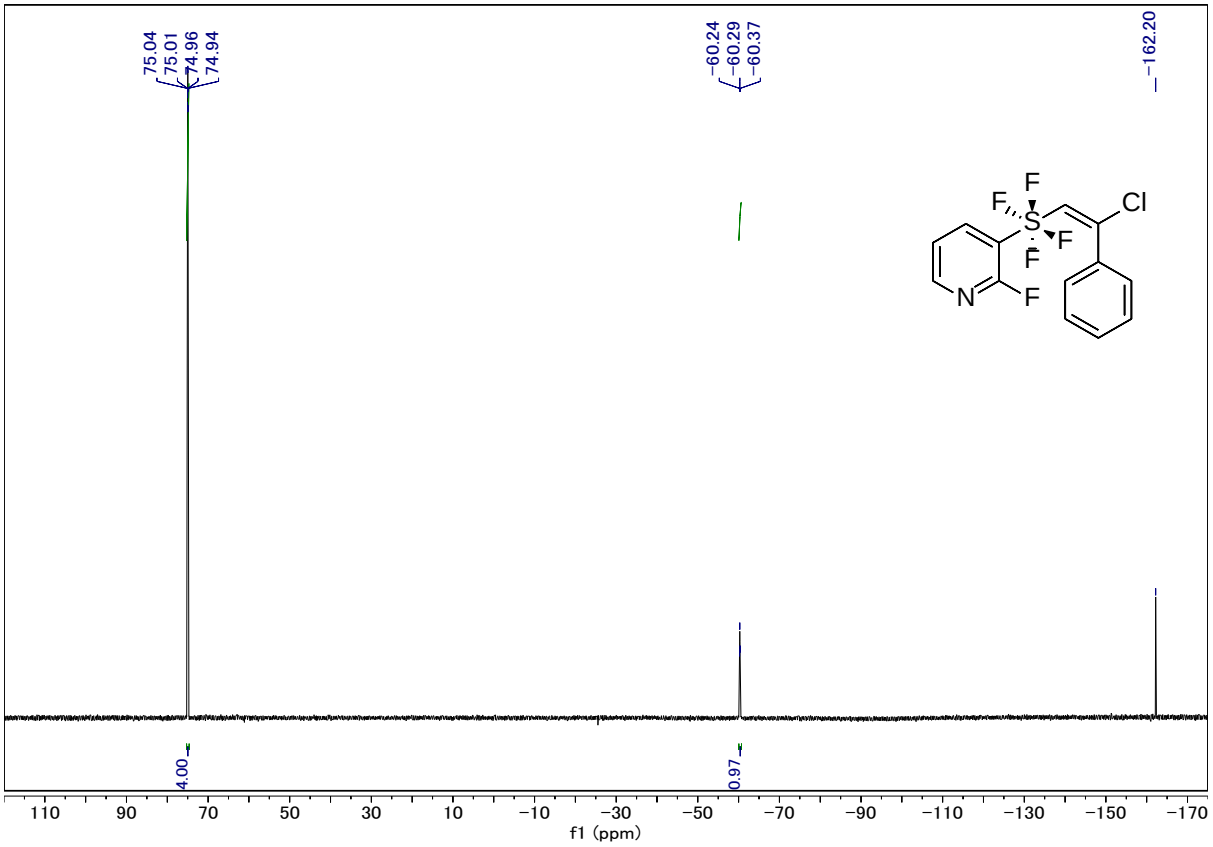

60.29
60.27
−162.20
Br
F
F
Si
N
S
F
F
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)

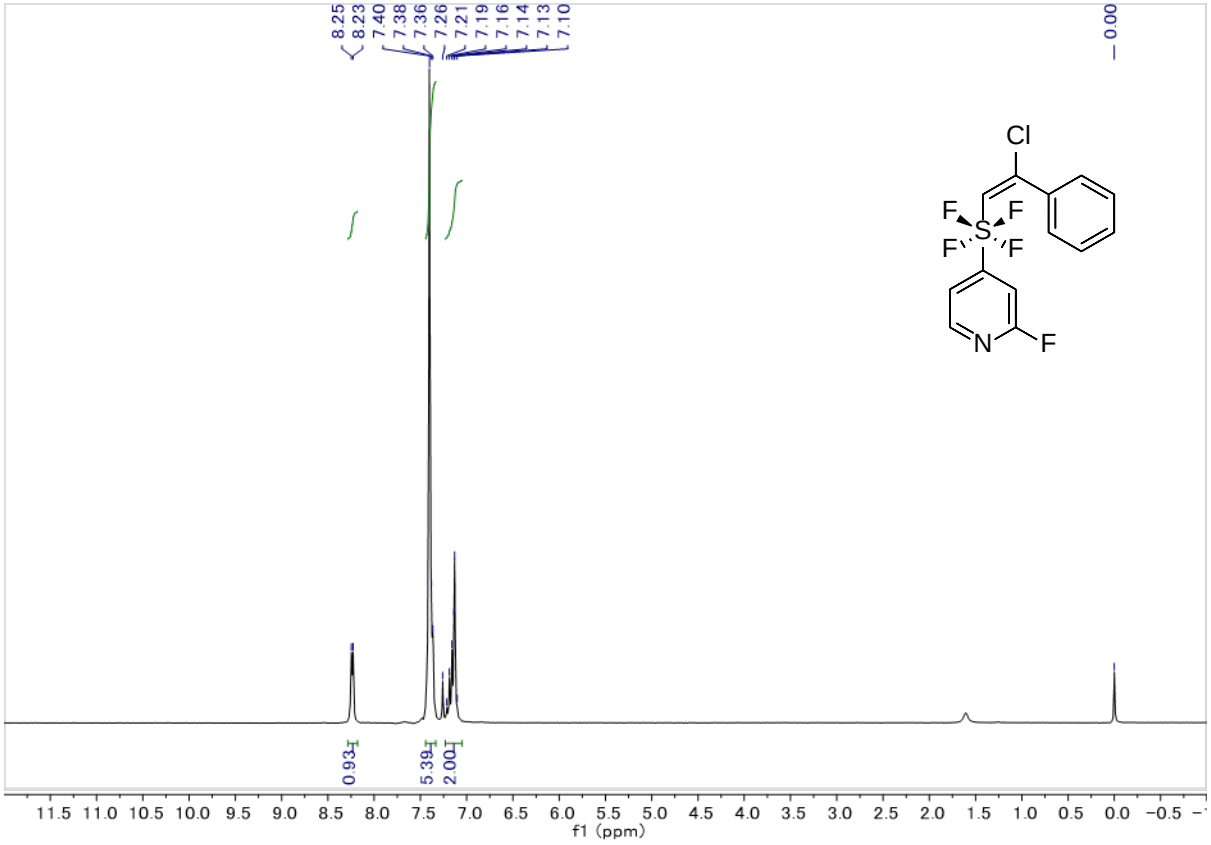

8.50 8.49 7.90 7.87 7.54 7.51 7.30 7.27 7.22 7.20 7.17 7.12 2.93 2.92 2.90 2.55 2.52 2.49 2.46 2.42 2.38 2.33 2.29 2.26 2.20 2.18 2.15 2.11 2.09 2.04 2.02 1.98 1.94 1.68 1.62 1.59 1.57 1.54 1.53 1.50 1.47 1.44 1.41 0.90
−0.00
O
H
H
H
Br
N
F
F
S
F
F
Cl
0.91
0.98
1.00
1.06
2.92
1.98
3.06
4.09
6.43
3.16
f1 (ppm)

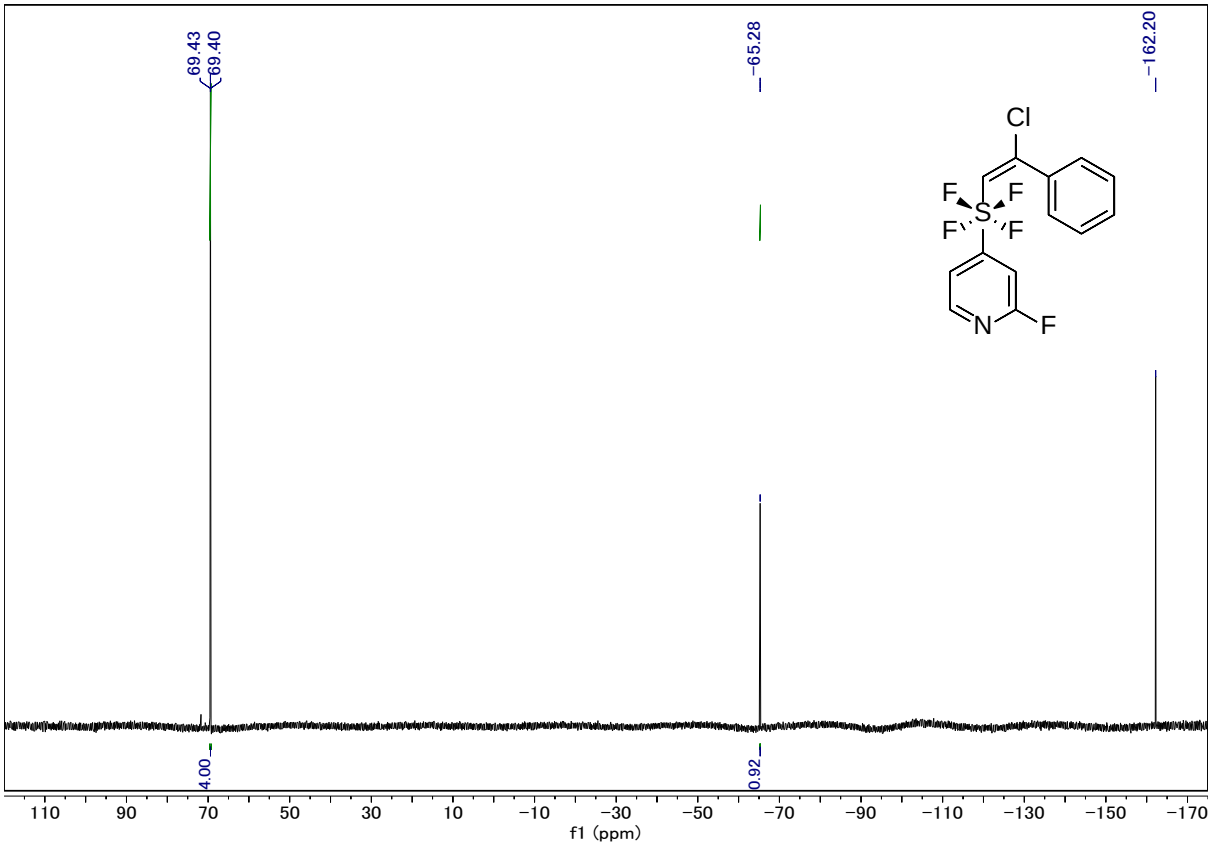

61.09
61.06
-162.20
4.00
110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)
O
Br
H
H
H
N
F
F
S
F
F
Cl

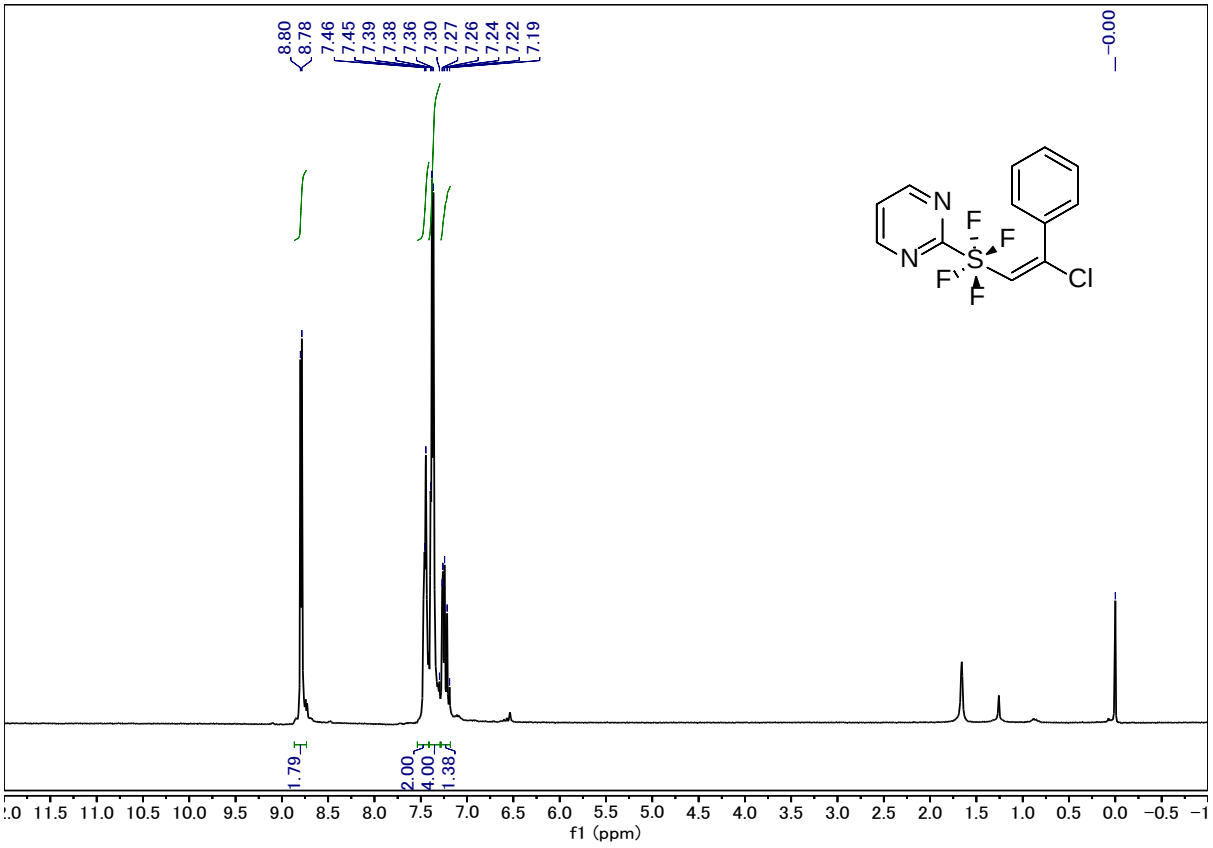

220.98
168.99
168.74
168.49
168.23
167.98
148.25
142.34
139.81
134.25
128.55
125.46
125.18
122.93
122.89
122.86
122.77
77.41
77.16
76.91
50.61
48.06
44.52
35.97
29.38
25.58
21.70
13.96
170 160 150 140 130
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
Br
H
H
H
N
F
F
S
F
F
Cl

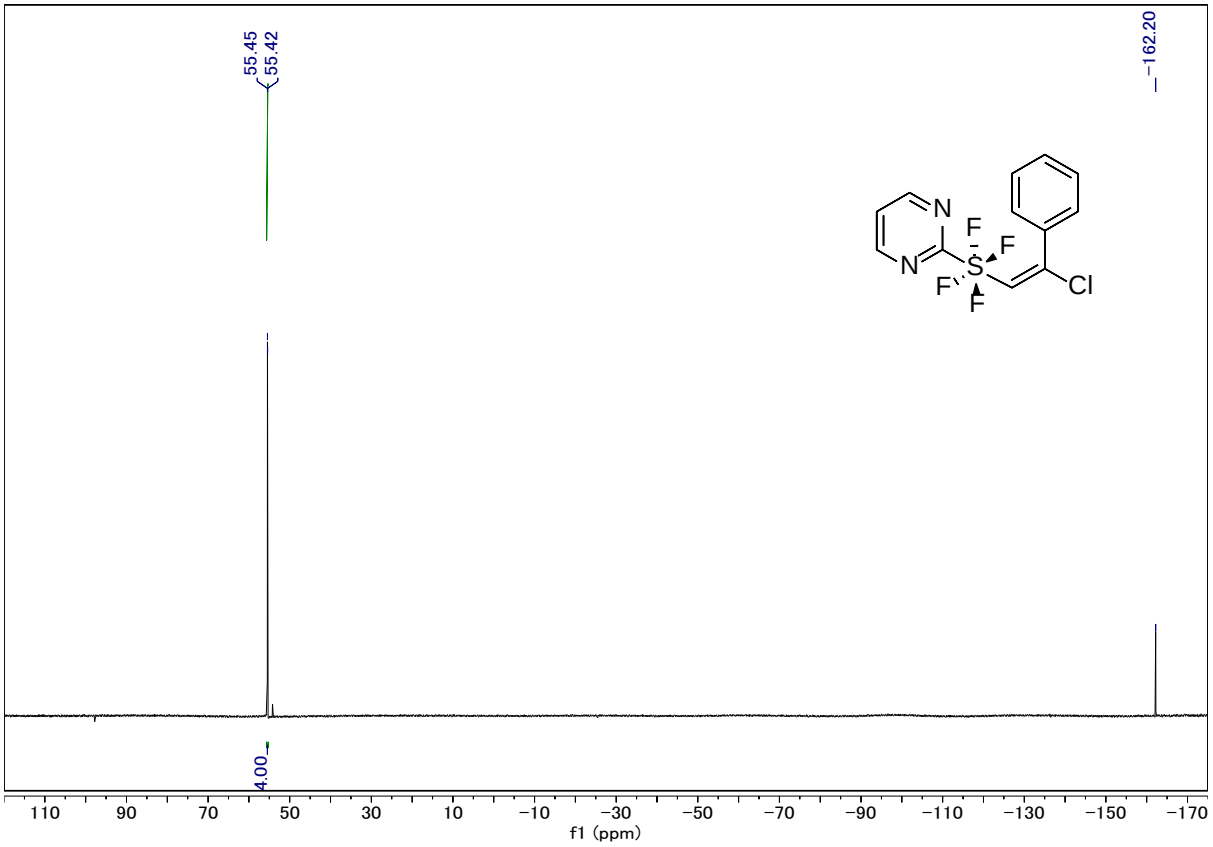

8.23
8.22
8.06
8.06
8.03
8.03
8.01
8.00
7.45
7.44
7.42
7.41
7.40
7.39
7.38
7.26
7.23
7.20
7.18
7.17
7.16
7.15
7.12
1.59
0.00
F
F
S
F
F
Cl
N
F
0.91
1.00
4.81
2.12
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

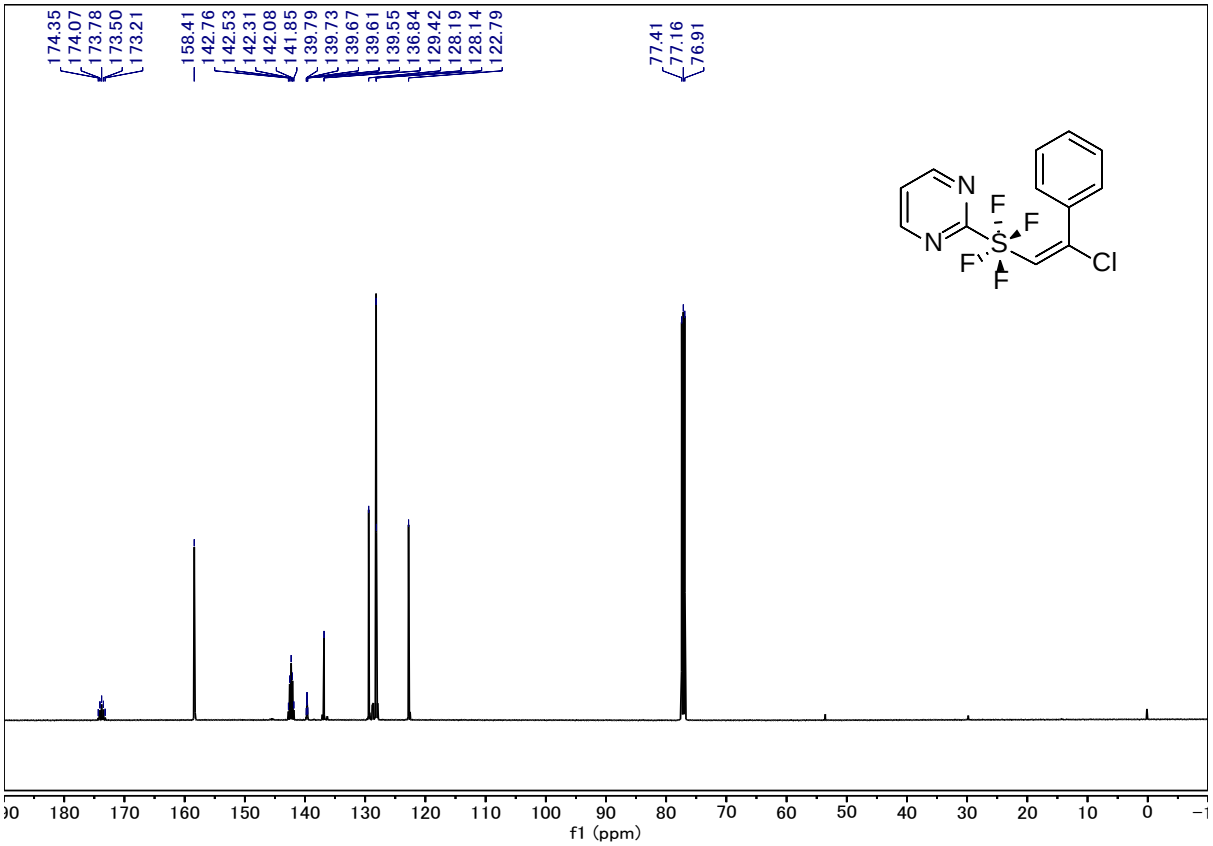

75.04
75.01
74.96
74.94
−60.24
−60.29
−60.37
−162.20
F
F
S
F
F
Cl
N
F
4.00
0.97
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)

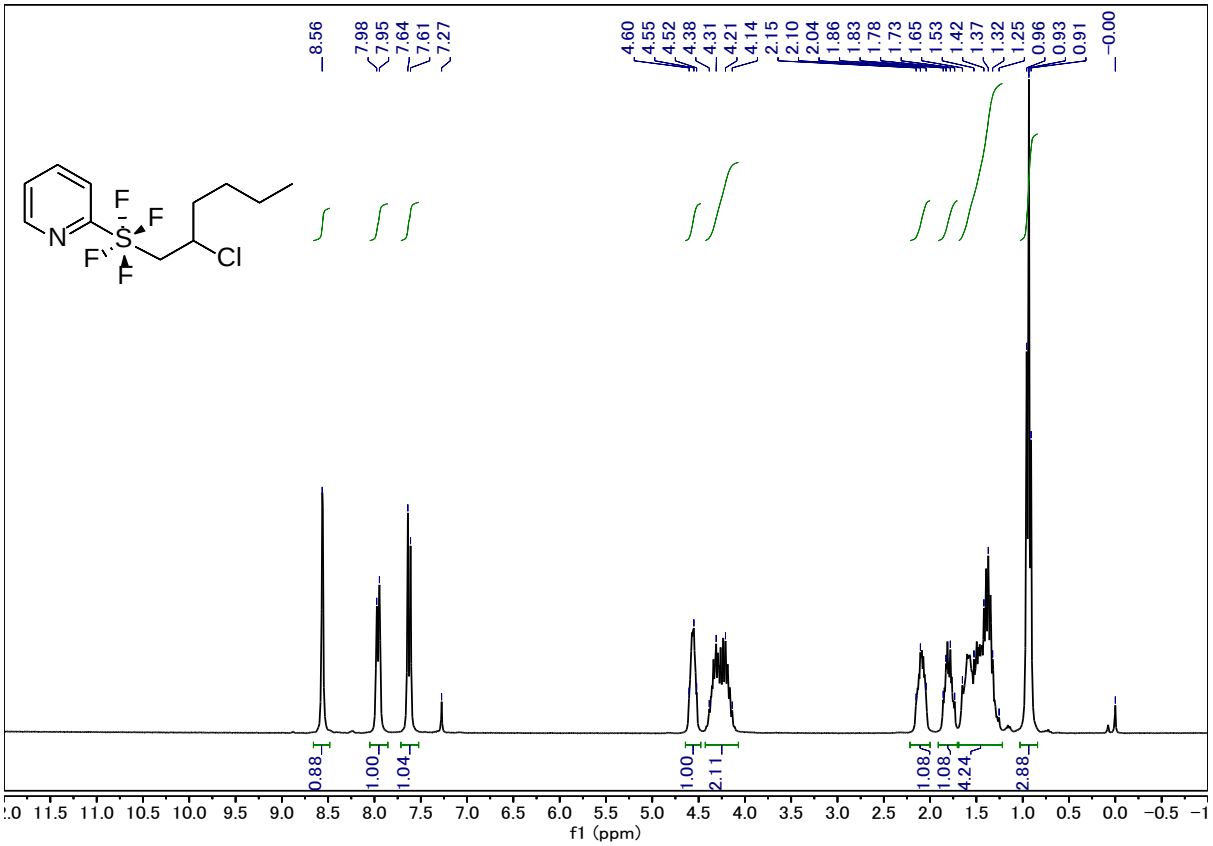

8.25
8.23
7.40
7.38
7.36
7.26
7.21
7.19
7.16
7.14
7.13
7.10
0.00
0.93
5.39
2.00
Cl
F
F
S
F
F
N
F
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

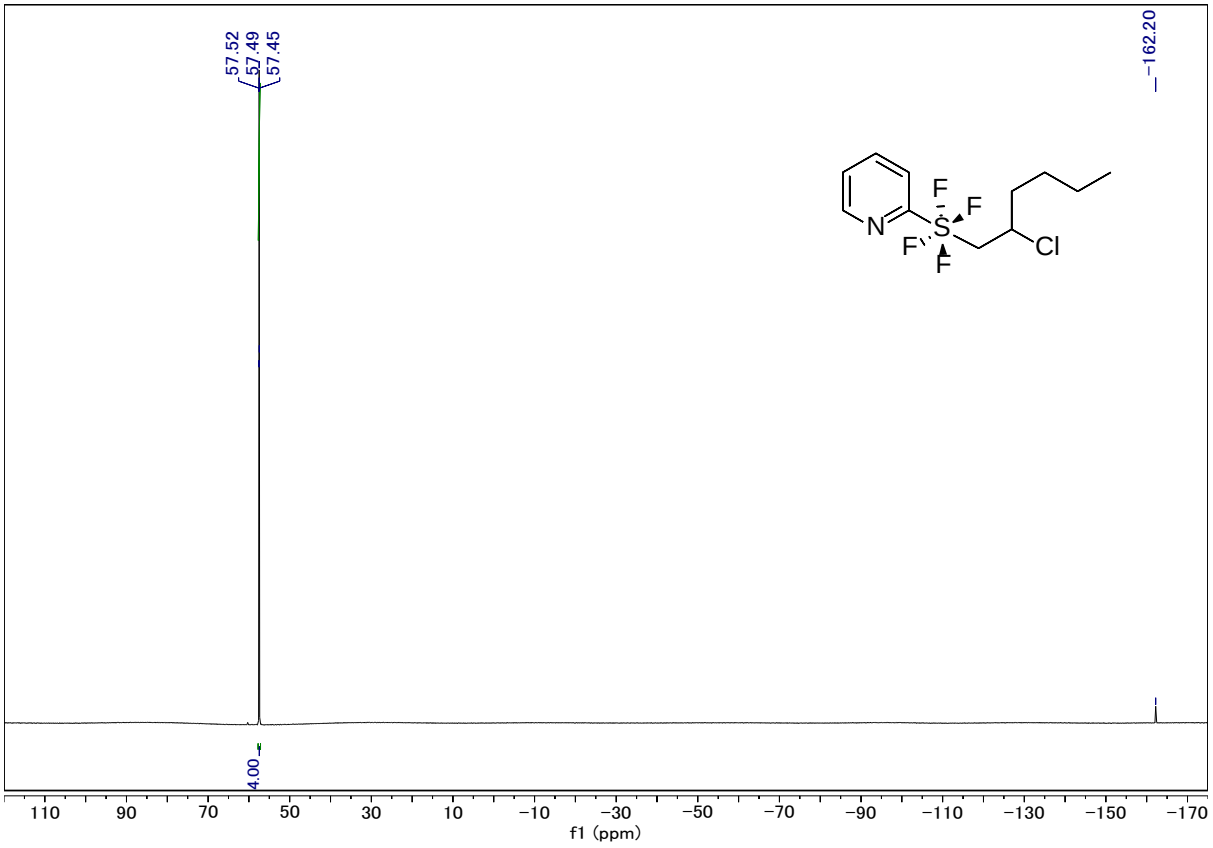

69.43
69.40
−65.28
−162.20
Cl
F
F
S
F
F
N
F
4.00
0.92
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)

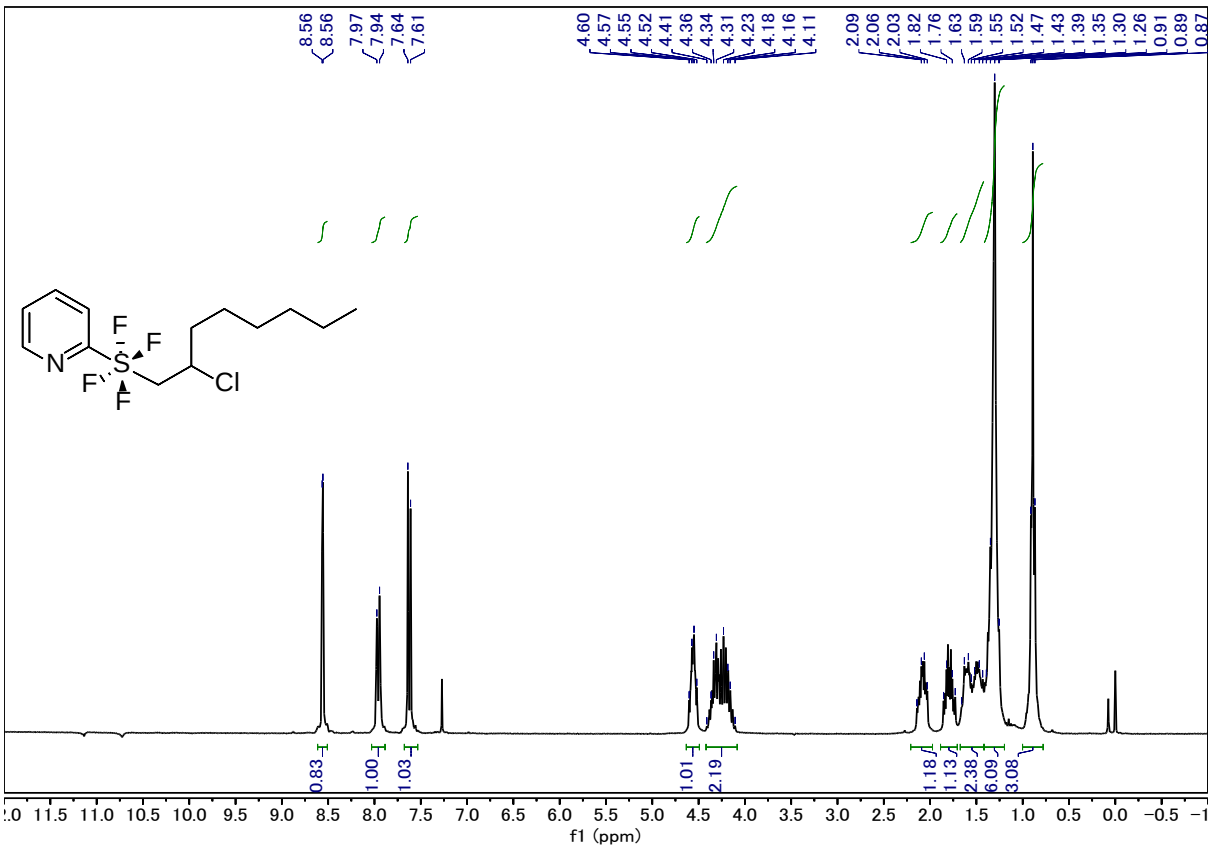

8.80
8.78
7.46
7.45
7.39
7.38
7.36
7.30
7.27
7.26
7.24
7.22
7.19
0.00
1.79
2.00
4.00
1.38
f1 (ppm)

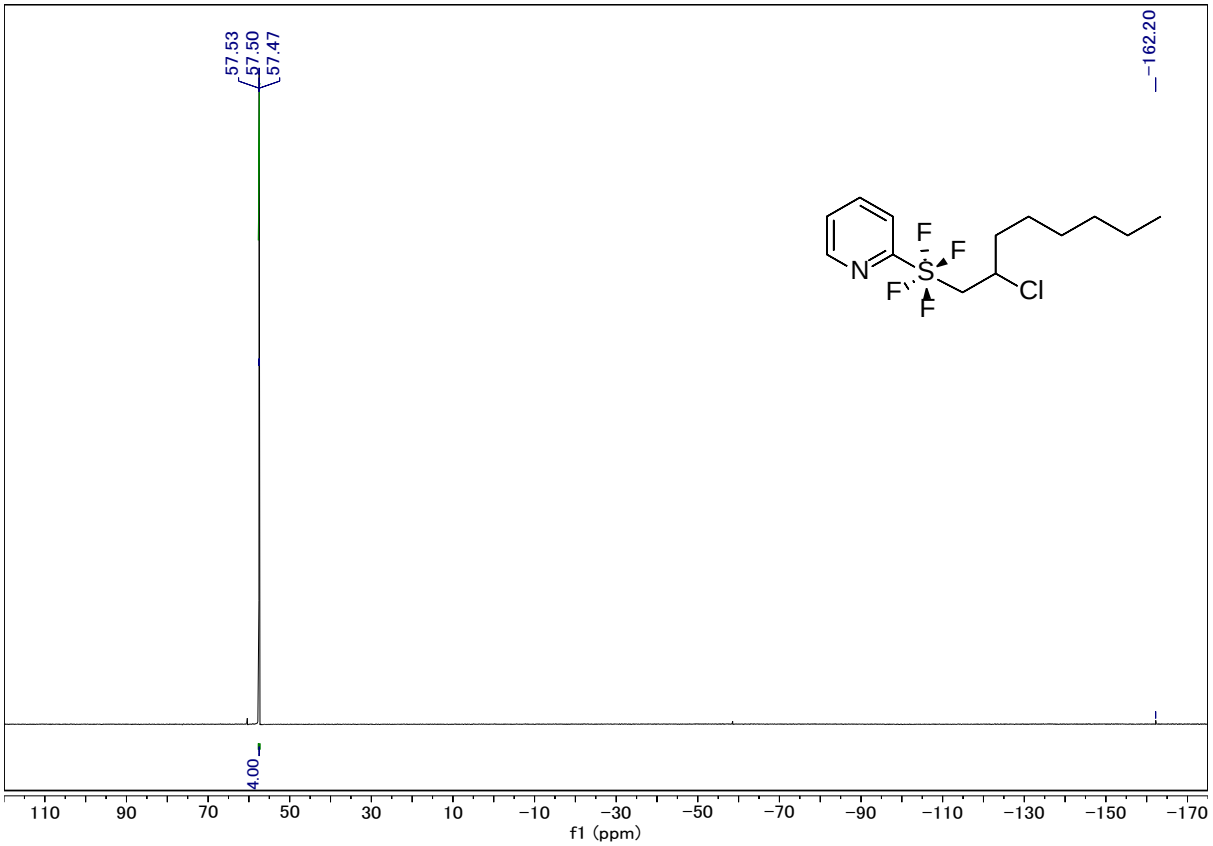

55.45
55.42
162.20
4.00
f1 (ppm)

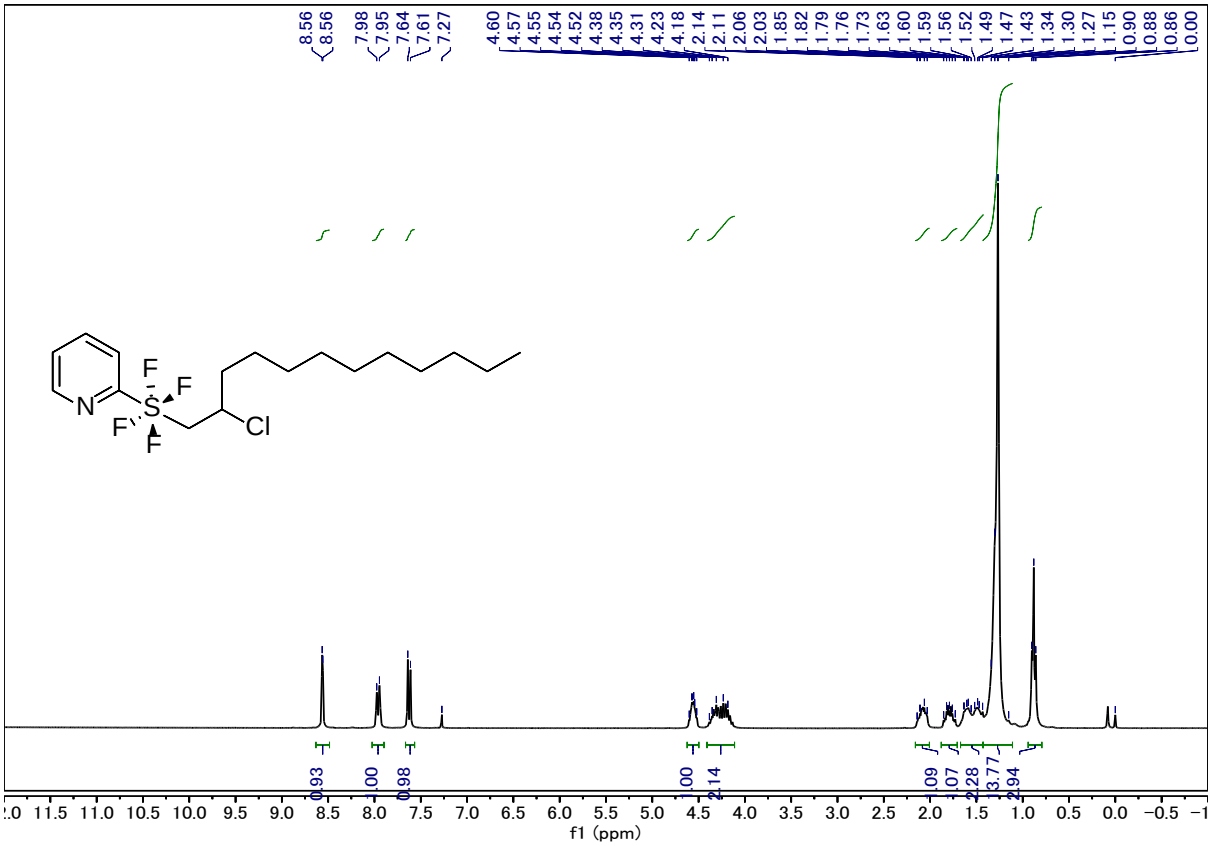

174.35
174.07
173.78
173.50
173.21
158.41
142.76
142.53
142.31
142.08
141.85
139.79
139.73
139.67
139.61
139.55
136.84
129.42
128.19
128.14
122.79
77.41
77.16
76.91
N
N
F
F
S
F
F
Cl
f1 (ppm)

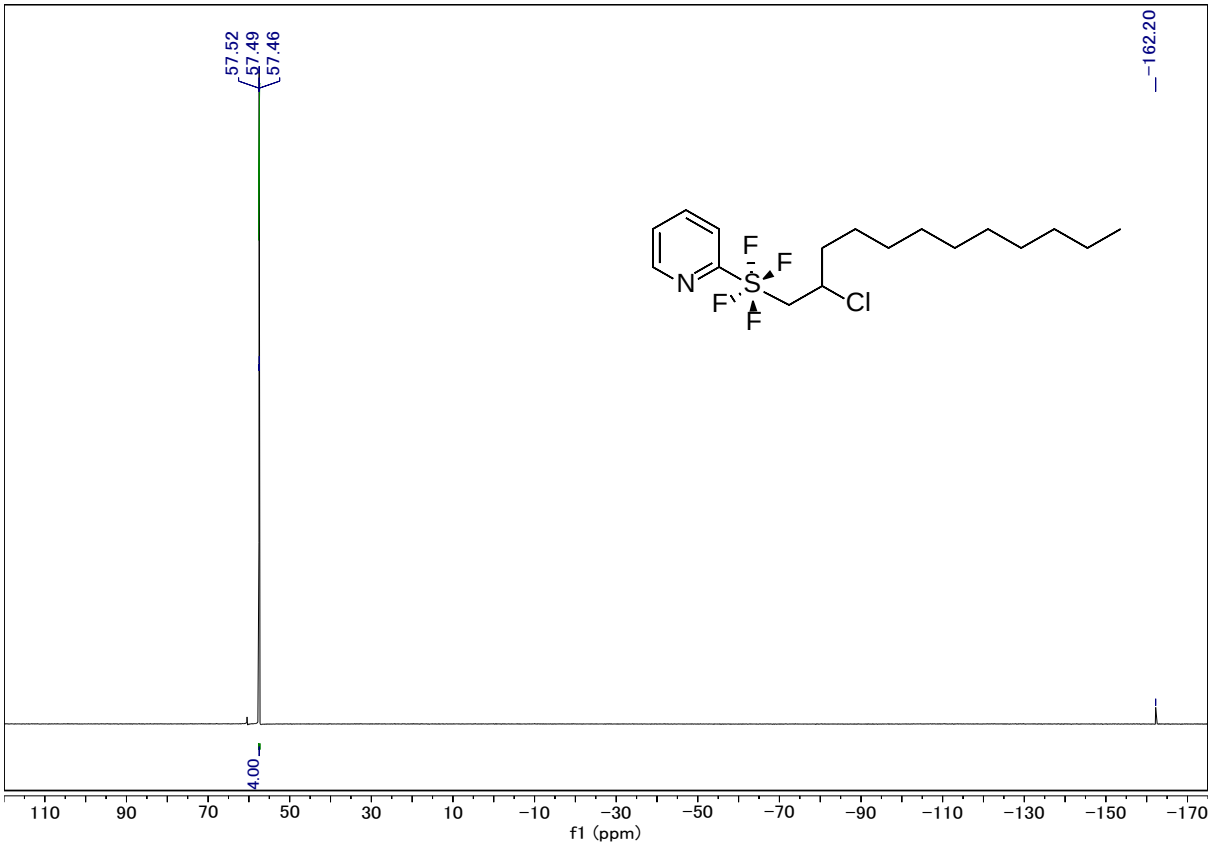

8.56
7.98
7.95
7.64
7.61
7.27
4.60
4.55
4.52
4.38
4.31
4.21
4.14
2.15
2.10
2.04
1.86
1.83
1.78
1.73
1.65
1.53
1.42
1.37
1.32
1.25
0.96
0.93
0.91
0.00
N
F
F
S
F
F
Cl
0.88
1.00
1.04
1.00
2.11
1.08
1.08
4.24
2.88
f1 (ppm)

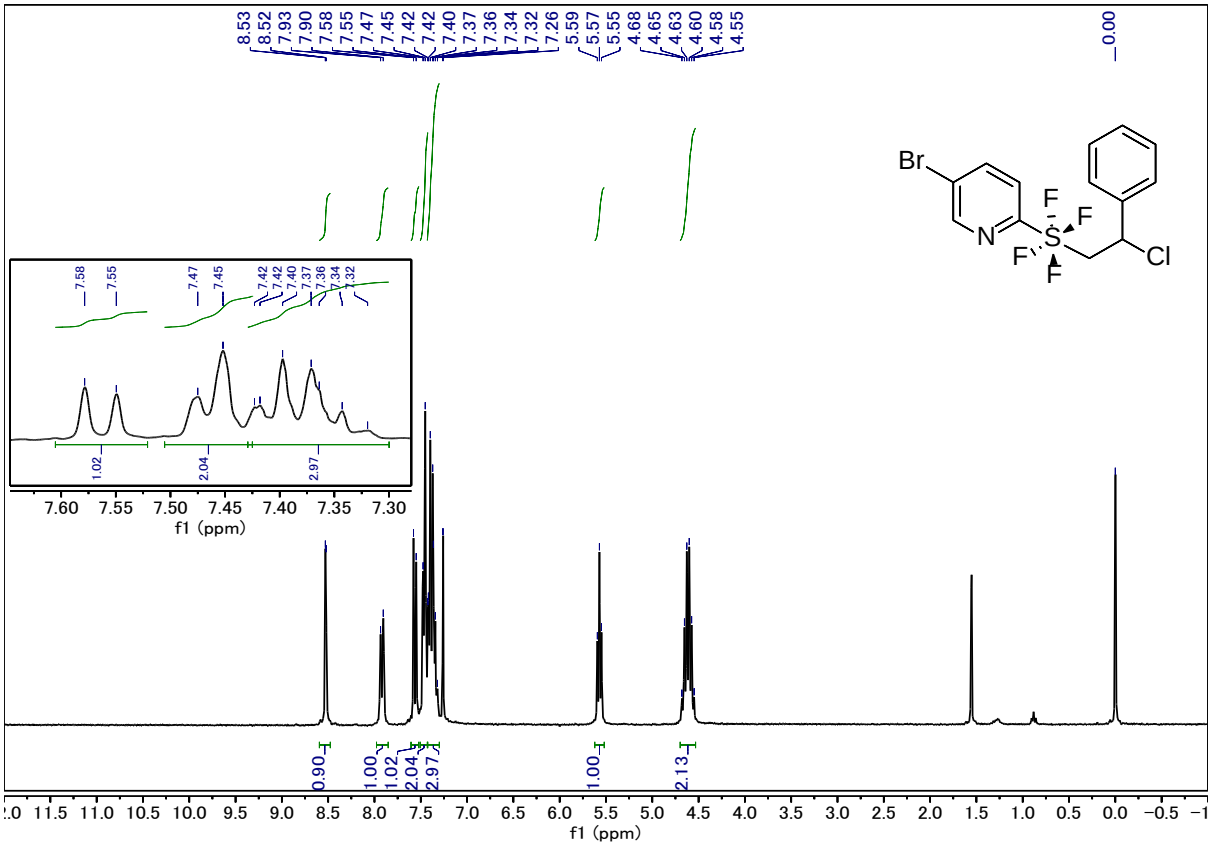

57.52
57.49
57.45
−162.20
F
F
F
F
S
N
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)

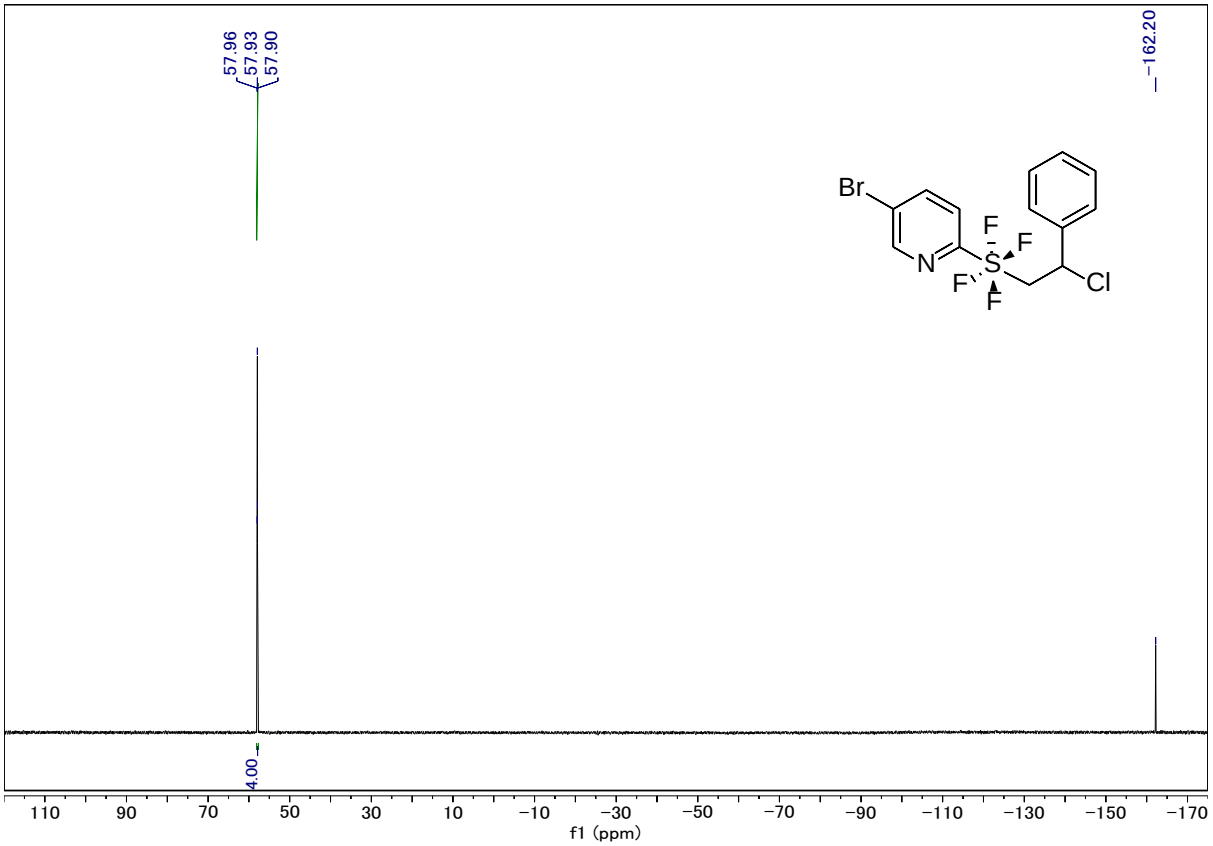

8.56
8.56
7.97
7.94
7.64
7.61
4.60
4.57
4.55
4.52
4.41
4.36
4.34
4.31
4.23
4.18
4.16
4.11
2.09
2.06
2.03
1.82
1.76
1.63
1.59
1.55
1.52
1.47
1.43
1.39
1.35
1.30
1.26
0.91
0.89
0.87
F
F
F
F
S
N
Cl
0.83
1.00
1.03
1.01
2.19
1.18
1.13
2.38
6.09
3.08
f1 (ppm)

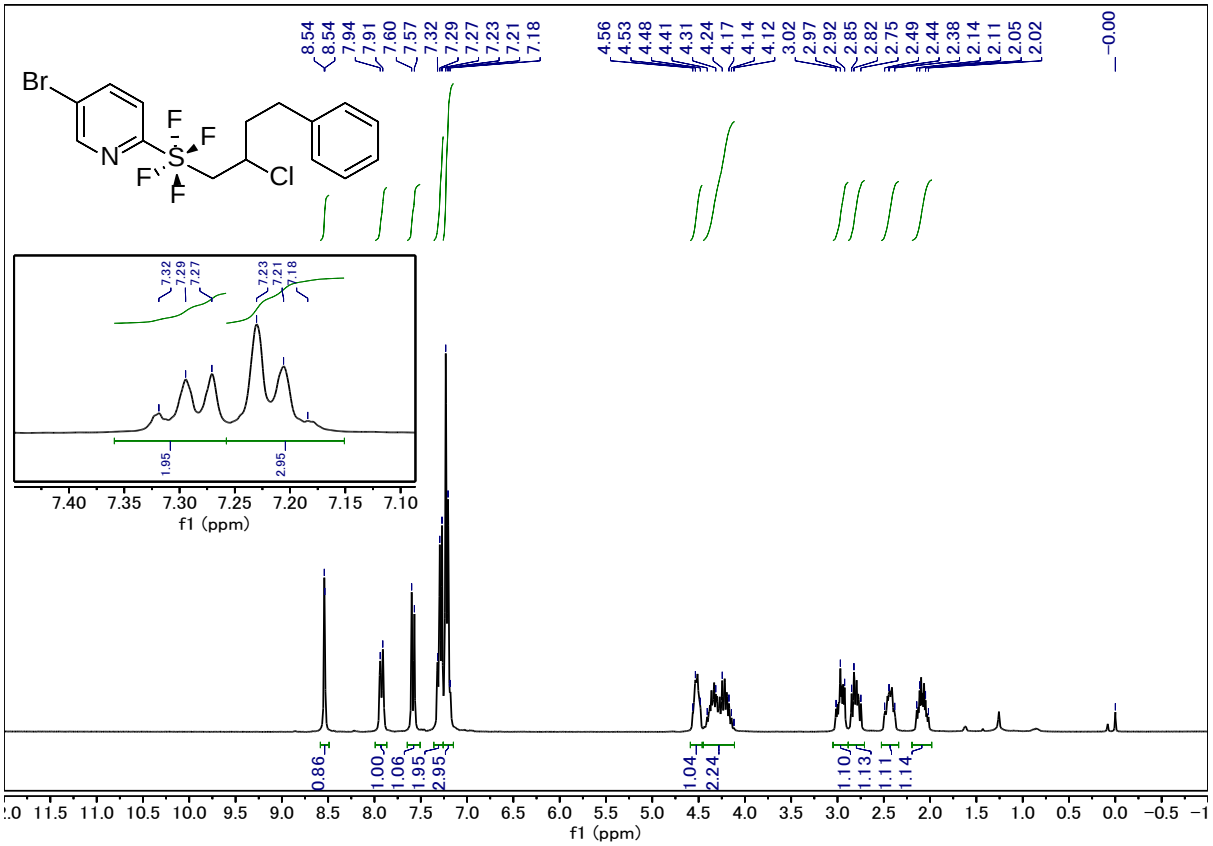

57.53
57.50
57.47
−162.20
F
F
F
F
S
N
Cl
4.00
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
f1 (ppm)

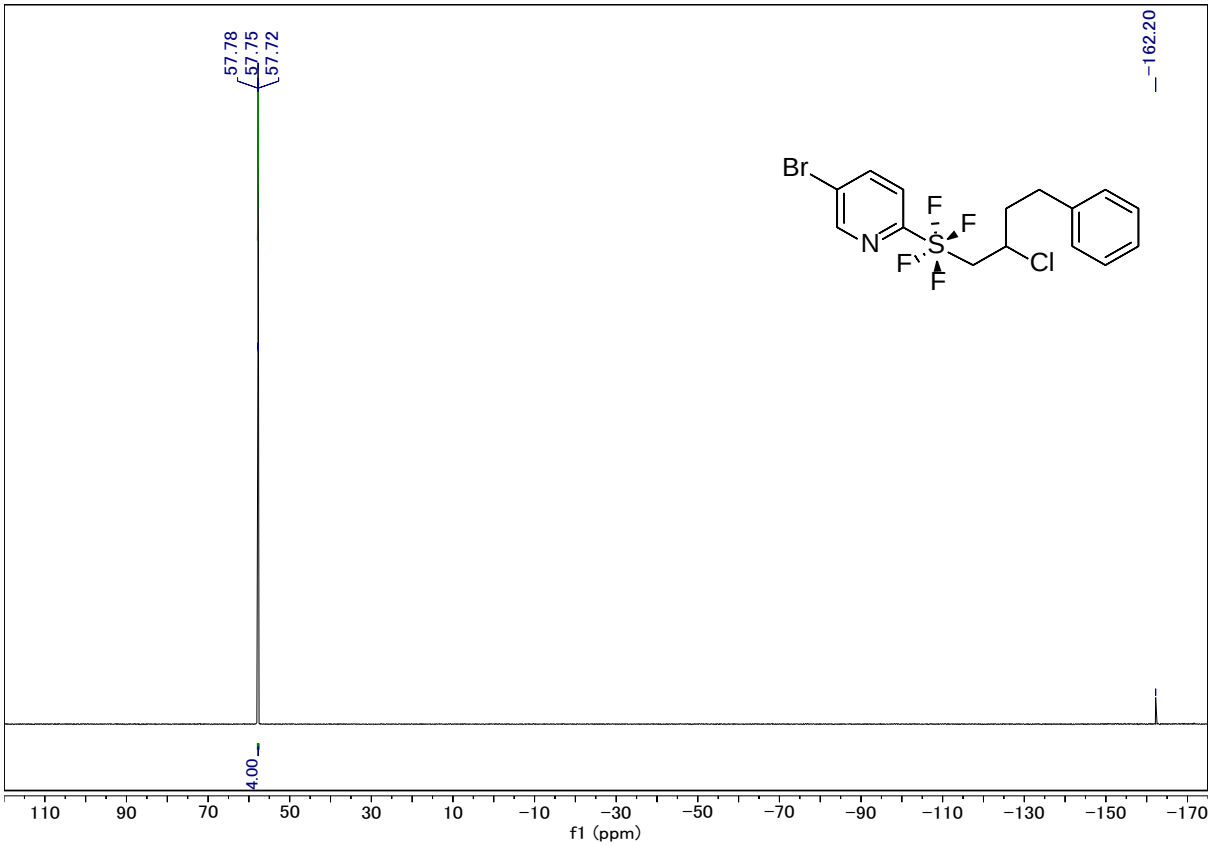

8.56
8.56
7.98
7.95
7.64
7.61
7.27
4.60
4.57
4.55
4.54
4.52
4.38
4.35
4.31
4.23
4.18
2.14
2.11
2.06
2.03
1.85
1.82
1.79
1.76
1.73
1.63
1.60
1.59
1.56
1.52
1.49
1.47
1.43
1.34
1.30
1.27
1.15
0.90
0.88
0.86
0.00
F
F
F
F
S
N
Cl
0.93
1.00
0.98
1.00
2.14
1.09
1.07
2.28
3.77
2.94
f1 (ppm)

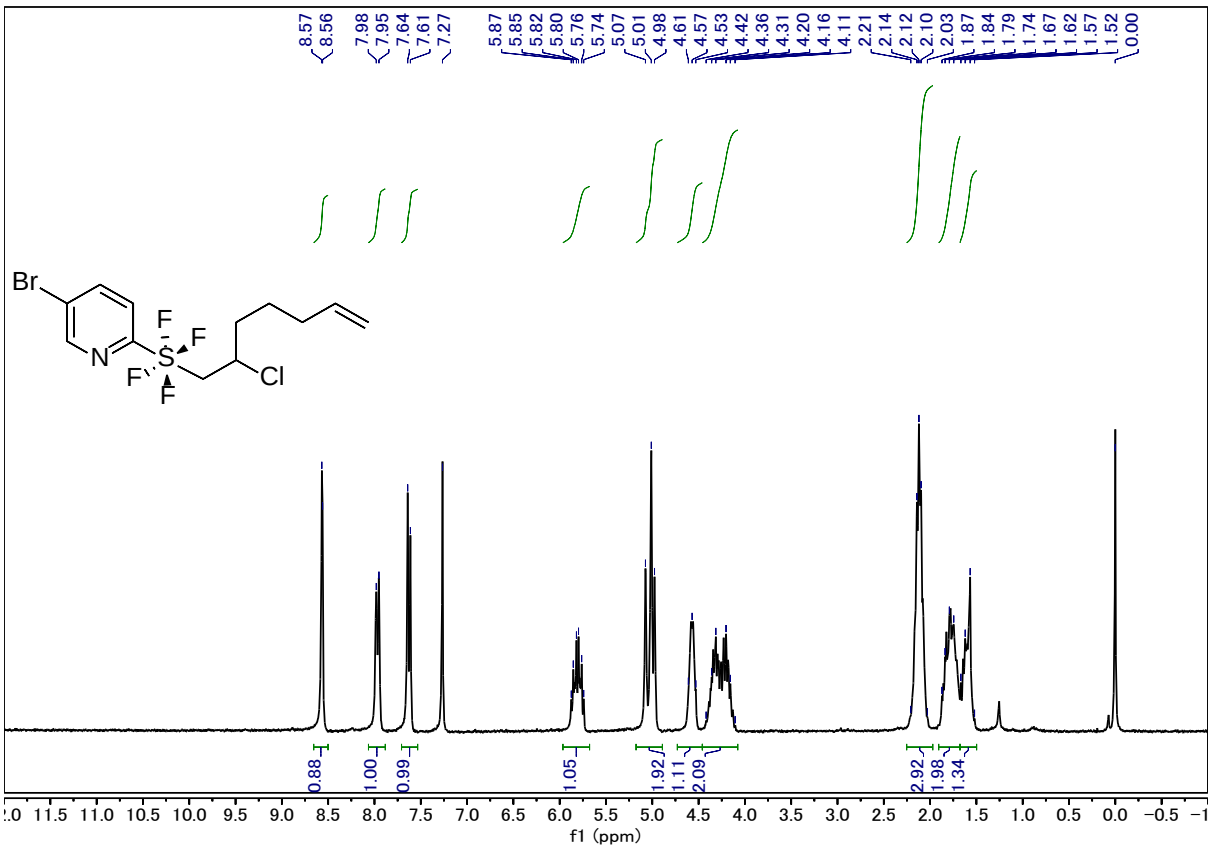

57.52
57.49
57.46
−162.20
F
F
N
S
F
F
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)

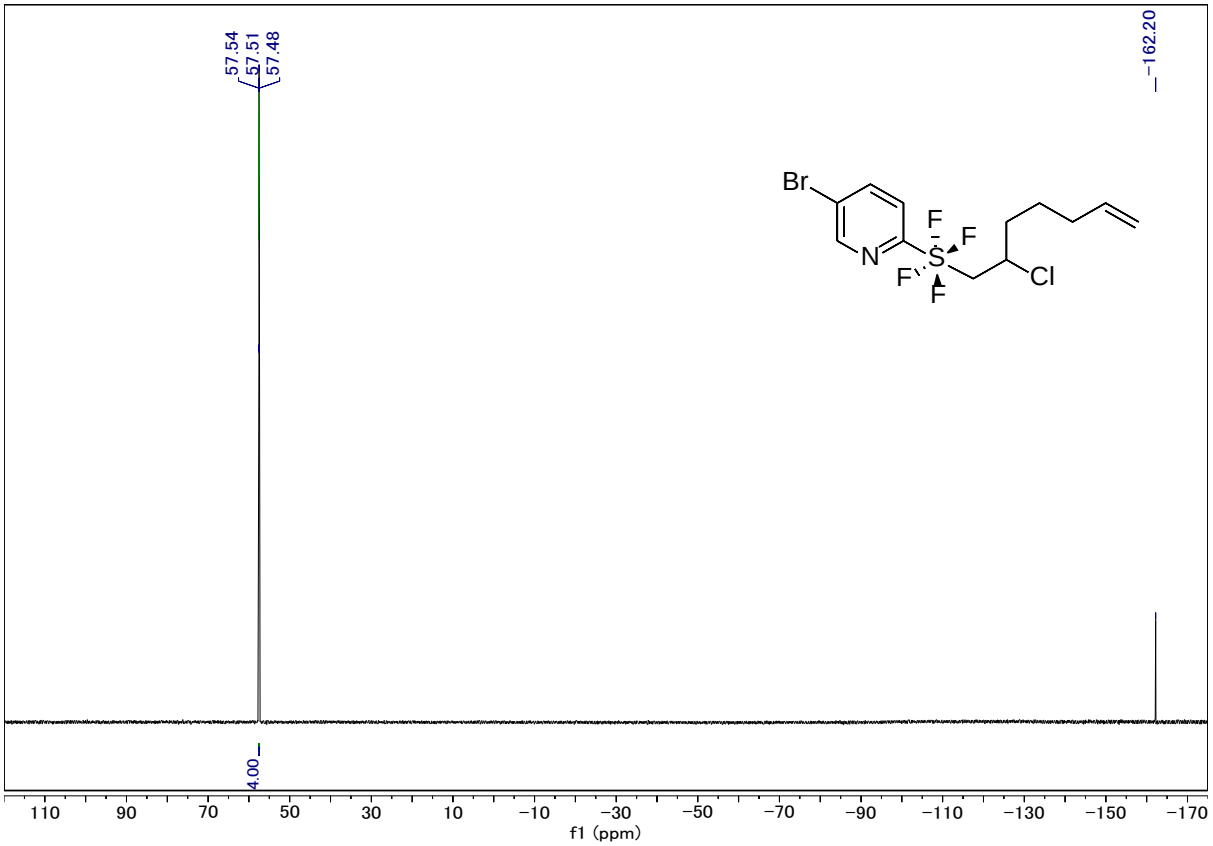

8.53
8.52
7.93
7.90
7.58
7.55
7.47
7.45
7.42
7.42
7.40
7.37
7.36
7.34
7.32
7.26
5.59
5.57
5.55
4.68
4.65
4.63
4.60
4.58
4.55
0.00
Br
N
F
F
S
F
F
Cl
1.02
2.04
2.97
7.60 7.55 7.50 7.45 7.40 7.35 7.30
f1 (ppm)
0.90
1.00
1.02
2.04
2.97
1.00
2.13
f1 (ppm)

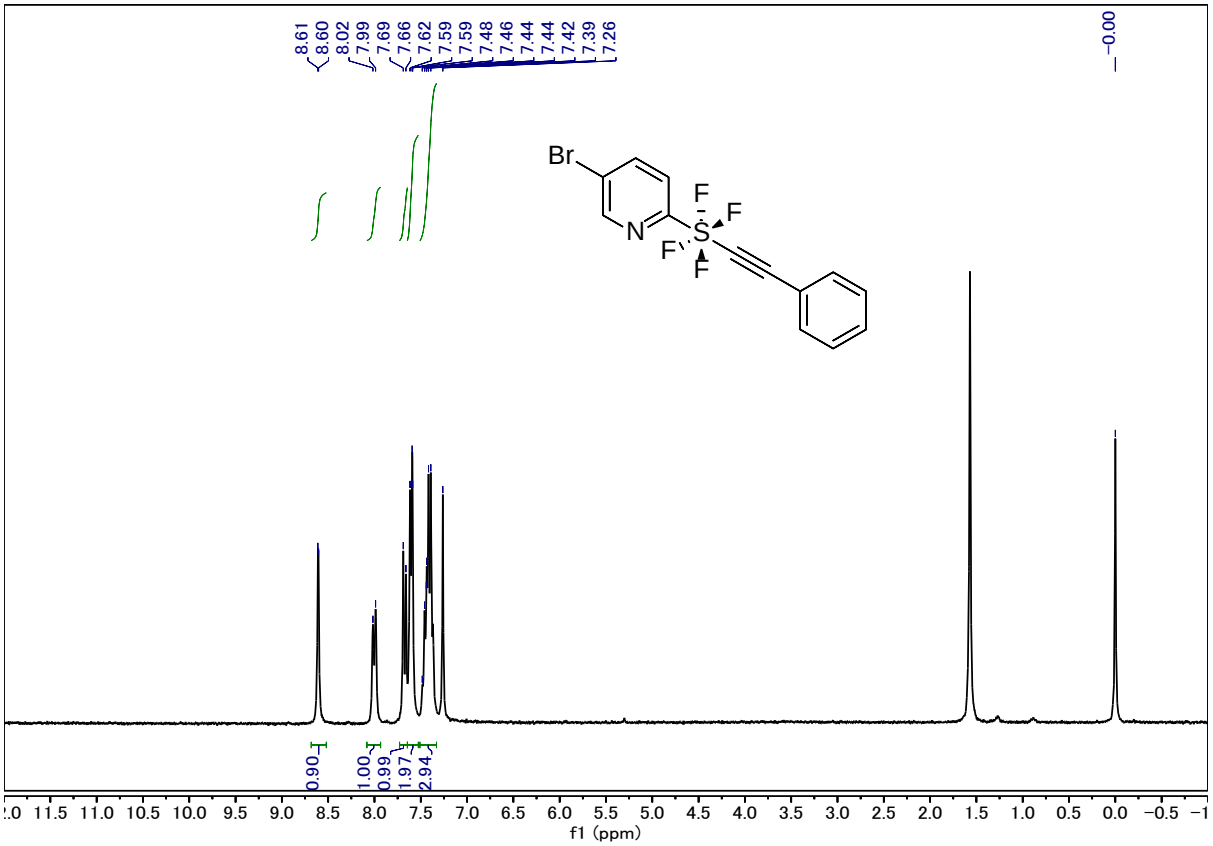

57.96
57.93
57.90
−162.20
Br
F
F
N
S
F
F
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)

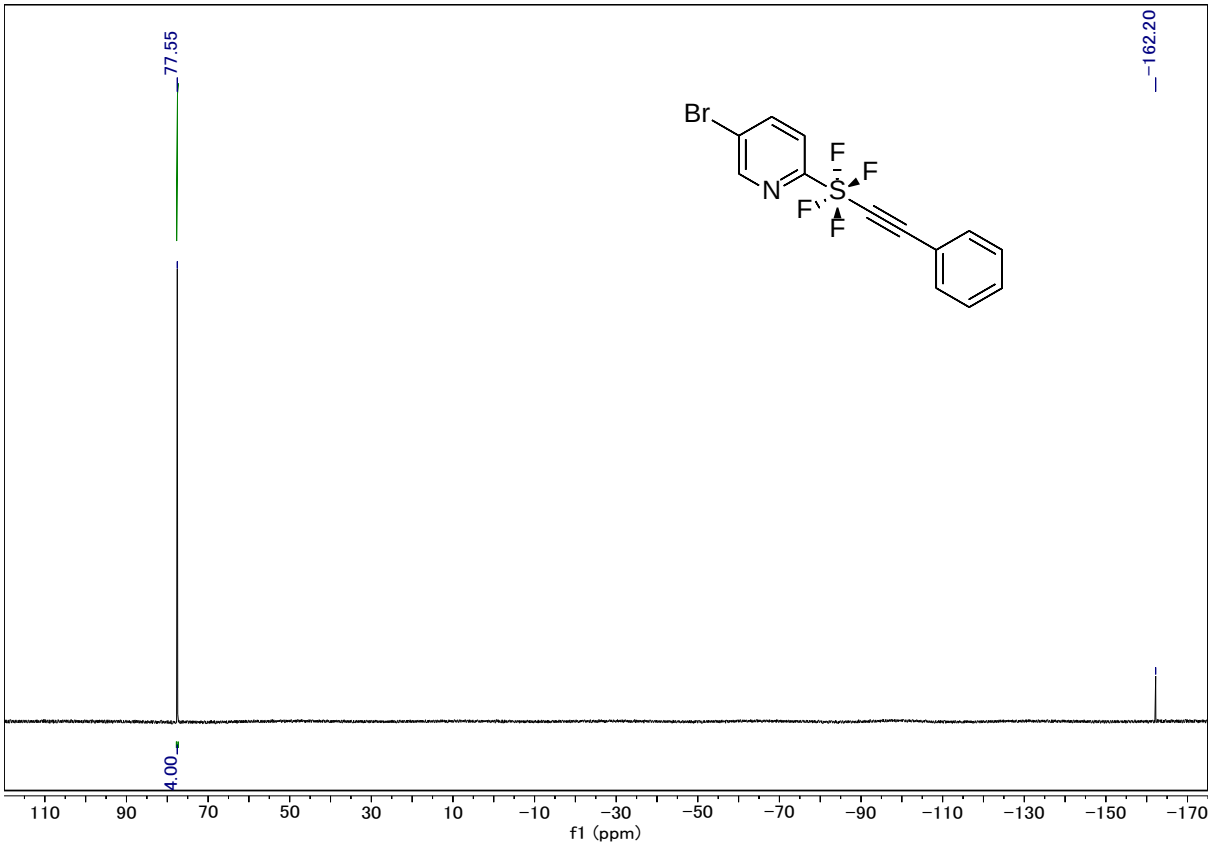

8.54 8.54 7.94 7.91 7.60 7.57 7.32 7.29 7.27 7.23 7.21 7.18
4.56 4.53 4.48 4.41 4.31 4.24 4.17 4.14 4.12 3.02 2.97 2.92 2.85 2.82 2.75 2.49 2.44 2.38 2.14 2.11 2.05 2.02
−0.00
Br
F
F
N
S
F
F
Cl
7.32 7.29 7.27 7.23 7.21 7.18
1.95 2.95
7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
0.86 1.00 1.06 1.95 2.95 1.04 2.24 1.10 1.13 1.11 1.14
f1 (ppm)

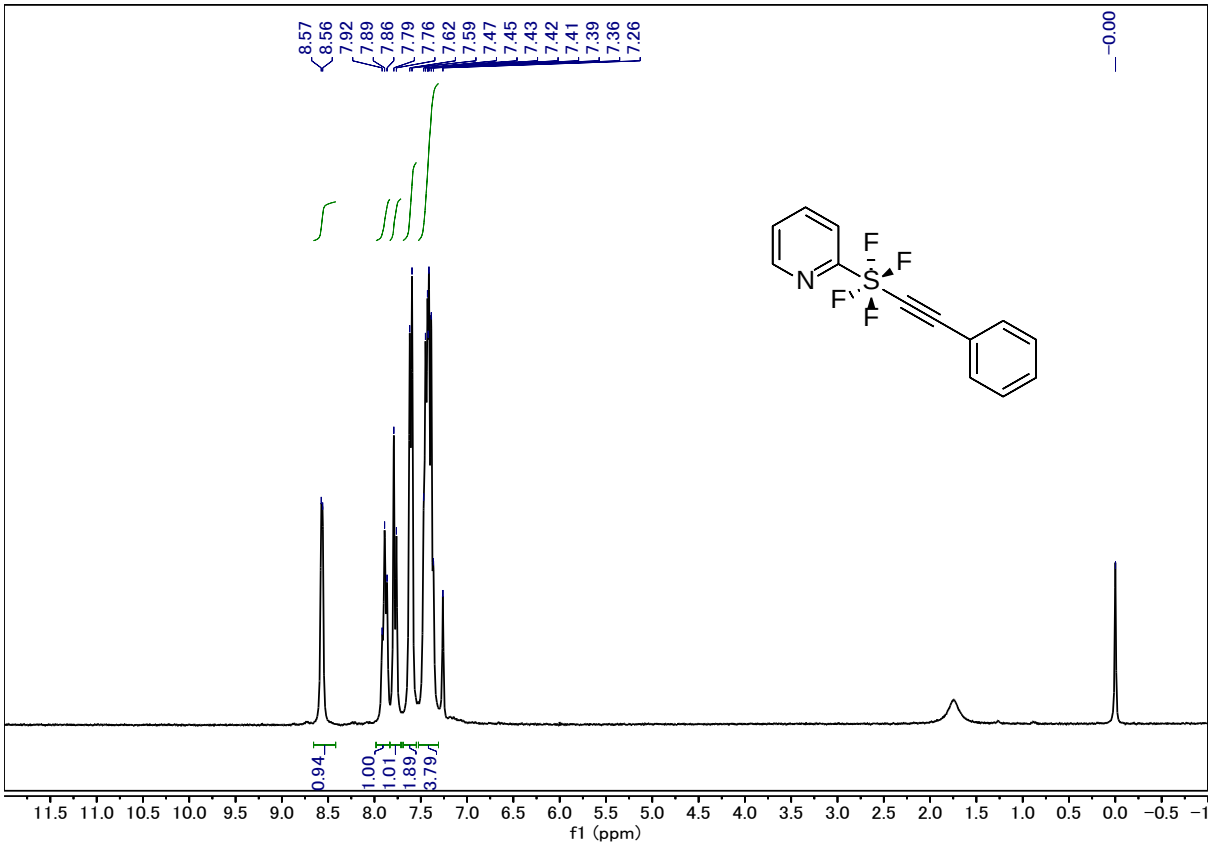

57.78
57.75
57.72
−162.20
Br
F
F
N
S
F
F
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)

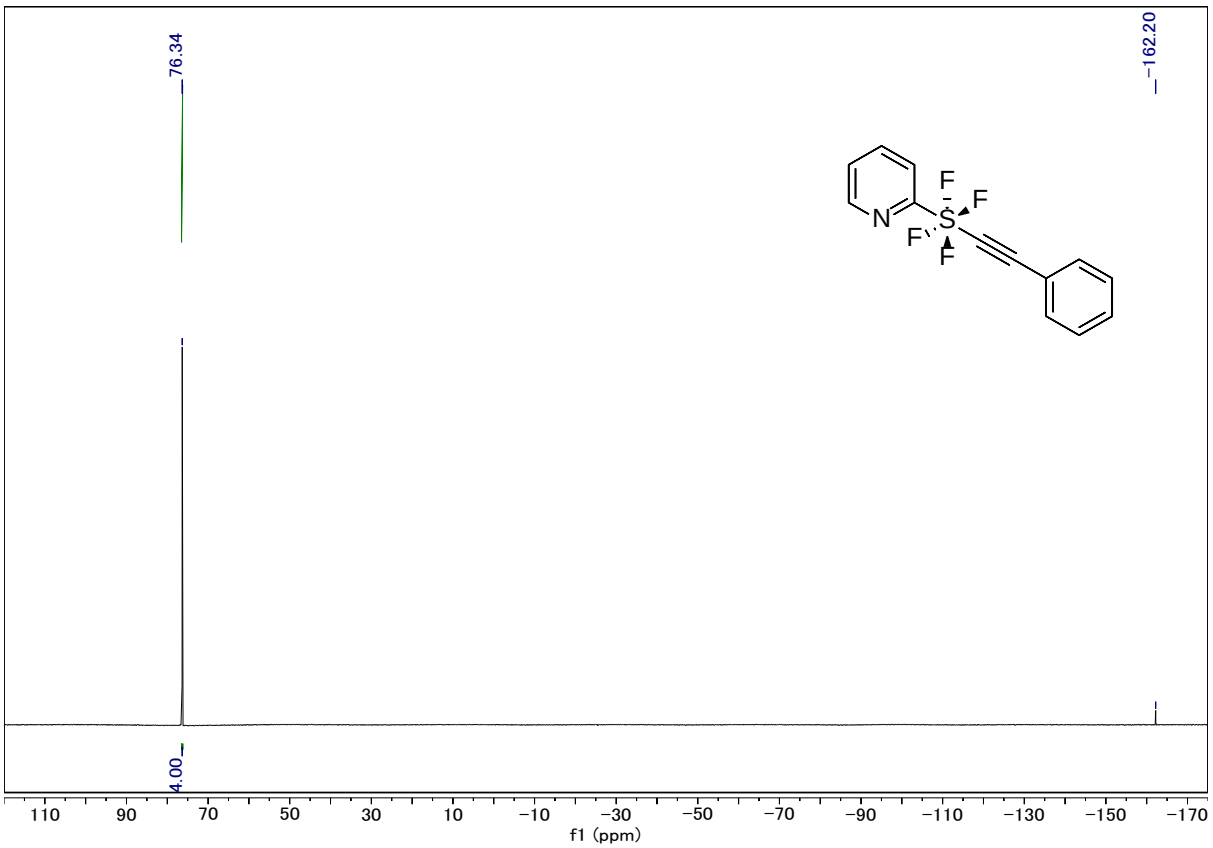

8.57
8.56
7.98
7.95
7.64
7.61
7.27
5.87
5.85
5.82
5.80
5.76
5.74
5.07
5.01
4.98
4.61
4.57
4.53
4.42
4.36
4.31
4.20
4.16
4.11
2.21
2.14
2.12
2.10
2.03
1.87
1.84
1.79
1.74
1.67
1.62
1.57
1.52
0.00
Br
F
F
N
S
F
F
Cl
0.88
1.00
0.99
1.05
1.92
1.11
2.09
2.92
1.98
1.34
f1 (ppm)


57.54
57.51
57.48
−162.20
Br
F
F
N
S
F
F
Cl
4.00
110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm)


8.61
8.60
8.02
7.99
7.69
7.66
7.62
7.59
7.59
7.48
7.46
7.44
7.44
7.42
7.39
7.26
−0.00
Br
F
F
N
S
F
F
0.90
1.00
0.99
1.97
2.94
f1 (ppm)


77.55
-162.20
Br
F
F
N
S
F
F
4.00
110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)


8.57
8.56
7.92
7.89
7.86
7.79
7.76
7.62
7.59
7.47
7.45
7.43
7.42
7.41
7.39
7.36
7.26
0.00
F
F
N
S
F
F
0.94
1.00
1.01
1.89
3.79
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


76.34
−162.20
4.00
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
f1 (ppm)
N
S
F
F
F
F