

Supporting Information

for

Pyridine-promoted dediazonation of aryldiazonium tetrafluoroborates: Application to the synthesis of SF₅-substituted phenylboronic esters and iodobenzenes

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Experimental part

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General information

NMR spectra were recorded at 25 °C in CD₂Cl₂, CDCl₃, [D₆]acetone, [D₆]DMSO or CD₃CN on a Bruker Avance 400 MHz or 600 MHz instruments. Chemical shifts (δ) are reported in ppm and coupling constants (J) are given in Hertz and referenced to residual signals of solvents or internal standards: CD₂Cl₂ δ_{H} = 5.32, δ_{C} = 53.80; [D₆]acetone δ_{H} = 2.05, δ_{C} = 29.84; [D₆]DMSO δ_{H} = 2.50, δ_{C} = 39.52; CD₃CN δ_{H} = 1.94, δ_{C} = 1.32; Me₄Si δ_{H} = 0.00; CFCl₃ δ_{F} = 0.0; BF₃·OEt₂ (capillary) δ_{F} = -153.0, δ_{B} = 0.0. ¹³C and ¹⁹F NMR spectra were ¹H decoupled. Due to low intensity some aromatic quaternary carbons were not observed in the ¹³C NMR. GC–MS spectra were recorded on an Agilent 7890A gas chromatograph coupled with a 5975C quadrupole mass-selective electron impact (EI) detector (70 eV). High-resolution mass spectra (HRMS) were recorded on an Agilent 7890A gas chromatograph coupled with a Waters GCT Premier orthogonal acceleration time-of-flight detector using chemical (CI) ionizations or LTQ Orbitrap XL instrument using electrospray (ESI) ionization. Elemental analyses were obtained using a Perkin–Elmer PE 2400 Series II CHNS. Infrared spectra were measured on a FTIR instrument. Purification of the products was performed by flash chromatography using silica gel 60. Dry solvents if used were obtained the following way: Et₂O and THF were freshly distilled over

Na/benzophenone, MeCN was distilled over P₂O₅ and kept over activated 4 Å molecular sieves. Commercial 90% *t*-butyl nitrite was used.

Synthesis of aryldiazonium tetrafluoroborates **3**

1. General procedure 1

To a stirred solution of **1** (18.3 mmol) in dry Et₂O (30 mL) BF₃·OEt₂ (5.46 g, 38.4 mmol, 2.1 equiv) was added and the resulting solution was cooled to -20 °C. *t*-BuONO (2.03 g, 20.0 mmol, 1.1 equiv) in dry Et₂O (6 mL) was added over 5 min and the reaction mixture was warmed to rt over 30 min. EtOH (10 mL) was added, the precipitate was filtered and washed with EtOH (2 × 5 mL) and Et₂O (2 × 5 mL). If the solid on the filter changed the color from white to yellow within minutes, washing was repeated. Traces of solvent were removed under reduced pressure providing pure **3**.

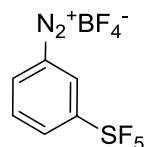
2. General procedure 2

To a stirred solution of **1** (22.8 mmol) in CH₂Cl₂ (65 mL) BF₃·OEt₂ (6.81 g, 47.9 mmol, 2.1 equiv) was added. After stirring for 5 min, dry THF (10 mL) was added to give clear solution followed by cooling to -20 °C. *t*-Butyl nitrite (2.94 g, 22.8 mmol, 1.0 equiv) in CH₂Cl₂ (7 mL) was added and the reaction mixture was warmed to 0 °C over 30 min. The formed precipitate was filtered, washed with Et₂O (25 mL) and dried under reduced pressure affording pure **3**.

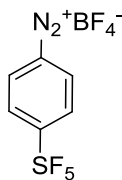
3. General procedure 3

A mixture of aqueous HF (2.08 g, 104 mmol, 17.2 equiv), H₃BO₃ (2.29 g, 26.0 mmol, 4.3 equiv) and water (5 mL) was added to **1** (6.0 mmol). After 5 min of stirring at rt, NaNO₂ (765 mg, 11.1 mmol, 1.9 equiv) was added in few portions over 3 min. After 15 minutes, the formed precipitate was filtered, washed with Et₂O (5 mL), suspended in MeCN (10 mL), filtered and dissolved in MeCN (4 mL). After addition of

Et₂O, the formed precipitate was filtered and dried under reduced pressure affording pure **3**.

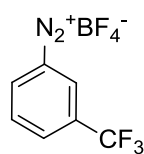


3a: Prepared according to the general procedure 1 starting from **1a** (4.00 g, 18.3 mmol), BF₃·OEt₂ (5.46 g, 38.4 mmol, 2.1 equiv) and *t*-BuONO (2.03 g, 20.0 mmol, 1.1 equiv) affording **3a** as a white solid (5.51 g, 95% yield): FT-IR (film): $\nu_{\max}$ (cm⁻¹) = 3097, 1589, 2299 (N₂⁺), 1574, 1476, 1437, 1300, 1054 (BF₄⁻), 1037 (BF₄⁻), 864, 851 (SF); ¹H NMR (400 MHz, CD₃CN): δ = 8.14 (t, ³J_{H,H} = 8.5, 1H), 8.66 (ddd, ³J_{H,H} = 8.6, ⁴J = 2.0, ⁴J = 1.0, 1H), 8.74 (dd, ³J_{H,H} = 8.6, ⁴J_{H,H} = 1.5, 1H), 9.03 (t, ⁴J_{H,H} = 2.0, 1H); ¹H NMR (400 MHz, [D₆]acetone): δ = 8.37 (t, ³J_{H,H} = 8.5, 1H), 8.87 (ddd, ³J_{H,H} = 8.5, ⁴J_{H,H} = 2.3, 0.9, 1H), 9.11 (dd, ³J_{H,H} = 8.3, ⁴J_{H,H} = 1.3, 1H), 9.43 (t, ⁴J_{H,H} = 2.0, 1H); ¹¹B NMR (128 MHz, CD₃CN): δ = -0.6 (s); ¹³C NMR (101 MHz, CD₃CN): δ = 117.7, 131.8 (quint, ³J_{C,F} = 5.3), 134.3, 136.9, 139.8 (quint, ³J_{C,F} = 4.6), 153.7–154.6 (m); ¹⁹F NMR (377 MHz, [D₆]acetone): δ = -149.3 (s), 63.3 (d, ²J_{F,F} = 150.3, 4F), 78.7–80.5 (m, 1F); Elem. anal.: Calc. for C₆H₄BF₉N₂S: C, 22.66; H, 1.27; F, 57.77; N, 8.81; S, 10.08. Found: C, 22.58; H, 1.15; F, 57.60; N, 8.75; S, 10.43.

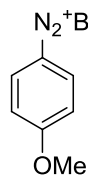


3b: Prepared according to the general procedure 1 starting from **1b** (6.00 g, 27.4 mmol), BF₃·OEt₂ (8.1 g, 57.5 mmol, 2.1 equiv) and *t*-BuONO (3.10 g, 30.1 mmol, 1.1 equiv) affording **3b** as a white solid (8.08 g, 93% yield). Also prepared according to the general procedure 2 starting from **1a** (5.00 g, 22.8 mmol), BF₃·OEt₂ (6.81 g, 47.9 mmol, 2.1 equiv) and *t*-BuONO (2.90 g, 22.8 mmol, 1.0 equiv) affording **3b** as a white solid (6.22 g, 86% yield): FT-IR (film): $\nu_{\max}$ (cm⁻¹) = 3119, 3070, 3031, 3014, 2986, 2304 (N₂⁺), 1573, 1470, 1412, 1303, 1124, 1054 (BF₄⁻), 842 (SF); ¹H NMR (400 MHz, CD₃CN): δ = 8.34–8.38 (m, 2H),

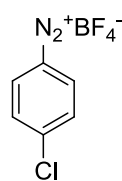
8.71–8.74 (m, 2H); ^1H NMR (400 MHz, $[\text{D}_6]\text{acetone}$): δ = 8.61–8.65 (m, 2H), 9.09–9.11 (m, 2H); ^{11}B NMR (128 MHz, $[\text{D}_6]\text{acetone}$): δ = –0.3 (s); ^{13}C NMR (101 MHz, CD_3CN): δ = 120.3, 130.7 (quint, $^3J_{\text{C,F}}$ = 4.8), 134.9, 161.8 (quint, $^2J_{\text{C,F}}$ = 20.5); ^{19}F NMR (377 MHz, CD_3CN): δ = –149.5 (s), 62.2 (d, $^2J_{\text{F,F}}$ = 149.4, 4F), 78.3–79.9 (m, 1F); ^{19}F NMR (377 MHz, $[\text{D}_6]\text{acetone}$): δ = –149.2 (s), 62.2 (d, $^2J_{\text{F,F}}$ = 149.7, 4F), 78.6–80.3 (m, 1F); HRMS (ESI $^+$): m/z = Calc. for $\text{C}_6\text{H}_4\text{N}_2\text{F}_5\text{S}$, 231.00099; Found, 231.00094; Elem. anal.: Calc. for $\text{C}_6\text{H}_4\text{BF}_9\text{N}_2\text{S}$: C, 22.66; H, 1.27; F, 57.77; N, 8.81; S, 10.08. Found: C, 22.58; H, 1.07; F, 57.48; N, 8.84; S, 10.63.



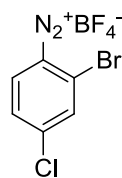
3c: Prepared according to general procedure 2 starting from **1c** (644 mg, 4.0 mmol), $\text{BF}_3\cdot\text{OEt}_2$ (1.20 g, 8.4 mmol, 2.1 equiv) and $t\text{-BuONO}$ (453 mg, 4.4 mmol, 1.1 equiv) affording **3c** as a white solid (940 mg, 90% yield): ^1H NMR (400 MHz, CD_3CN): δ = 8.15 (t, $^3J_{\text{H,H}}$ = 8.2, 1H), 8.53 (d, $^3J_{\text{H,H}}$ = 8.3, 1H), 8.76 (d, $^3J_{\text{H,H}}$ = 8.6, 1H), 8.85 (s, 1H); ^{13}C NMR (101 MHz, CD_3CN): δ = 117.7, 123.0 (q, $^1J_{\text{C,F}}$ = 272.9), 130.9 (q, $^3J_{\text{C,F}}$ = 4.2), 133.8 (q, $^2J_{\text{C,F}}$ = 36.0), 134.2, 137.1, 139.4 (q, $^3J_{\text{C,F}}$ = 3.4); ^{19}F NMR (376 MHz, CD_3CN): δ = –149.7 (s), –62.8 (s). Elem. anal.: Calc. for $\text{C}_7\text{H}_4\text{BF}_7\text{N}_2$: C, 32.35; H, 1.55; N, 10.78. Found: C, 32.42; H, 1.50; N, 10.92.



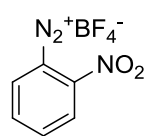
3d:^[1] Prepared according to general procedure 3 starting from **1d** (738 mg, 6.0 mmol), HBF_4 (3.17 g, 36.0 mmol, 6.0 equiv), NaNO_2 (765 mg, 11.1 mmol, 1.9 equiv) and water (5 mL) affording **3d** as a pale violet solid (988 mg, 74% yield): ^1H NMR (400 MHz, CD_3CN): δ = 4.05 (s, 3H), 7.32–7.36 (m, 2H), 8.40–8.44 (m, 2H); ^{13}C NMR (101 MHz, CD_3CN): δ = 58.5, 102.8, 118.9, 136.8, 171.3; ^{19}F NMR (376 MHz, $[\text{D}_6]\text{acetone}$): δ = –150.1 (s).



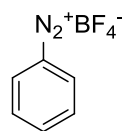
3e:^[2] Prepared according to general procedure 3 starting from **1e** (762 mg, 6.0 mmol), HBF_4 (3.17 g, 36.0 mmol, 6.0 equiv), NaNO_2 (765 mg, 11.1 mmol, 1.9 equiv) and water (3 mL) affording **3e** as a white solid (1.06 g, 78% yield): ^1H NMR (400 MHz, CD_3CN): δ = 7.91–7.95 (m, 2H), 8.45–8.50 (m, 2H); ^{13}C NMR (101 MHz, CD_3CN): δ = 133.3, 134.9, 150.1; ^{19}F NMR (376 MHz, CD_3CN): δ = –150.0 (s).



3f: Prepared according to general procedure 2 starting from **1f** (824 mg, 4.0 mmol), $\text{BF}_3\cdot\text{OEt}_2$ (1.20 g, 8.4 mmol, 2.1 equiv) and $t\text{-BuONO}$ (453 mg, 4.4 mmol, 1.1 equiv) affording **3f** as a white solid (1.14 g, 93% yield): ^1H NMR (400 MHz, CD_3CN): δ = 7.92 (dd, $^3J_{\text{H,H}}$ = 9.1, $^4J_{\text{H,H}}$ = 2.0, 1H), 8.25 (d, $^4J_{\text{H,H}}$ = 2.0, 1H), 8.55 (d, $^3J_{\text{H,H}}$ = 9.1, 1H); ^{13}C NMR (101 MHz, CD_3CN): δ = 127.2, 132.6, 136.8, 137.2, 151.0; ^{19}F NMR (376 MHz, CD_3CN): δ = –150.1 (s). Elem. anal.: Calc. for $\text{C}_6\text{H}_3\text{BBrClF}_4\text{N}_2$: C, 23.61; H, 0.99; N, 9.18. Found: C, 23.90; H, 1.02; N, 9.32.

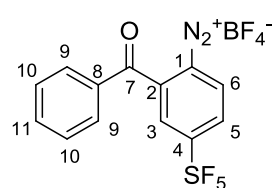


3g:^[1] Prepared according to general procedure 2 starting from **1g** (552 mg, 4.0 mmol), $\text{BF}_3\cdot\text{OEt}_2$ (1.20 g, 2.1 equiv, 8.4 mmol) and $t\text{-BuONO}$ (453 mg, 4.4 mmol, 1.1 equiv) affording **3g** as a white solid (898 mg, 95% yield): ^1H NMR (400 MHz, CD_3CN): δ = 8.30–8.35 (m, 1H), 8.49–8.53 (m, 1H), 8.70 (dd, $^3J_{\text{H,H}}$ = 8.5, $^4J_{\text{H,H}}$ = 1.1, 1H), 8.88 (dd, $^3J_{\text{H,H}}$ = 8.2, $^3J_{\text{H,H}}$ = 1.4, 1H); ^{13}C NMR (101 MHz, CD_3CN): δ = 129.7, 137.9, 138.0, 144.4; ^{19}F NMR (376 MHz, CD_3CN): δ = –150.2 (s).



3h: Prepared according to general procedure 3 starting from aniline (**1h**) (10.0 g, 108 mmol), HBF_4 (57 g, 648 mmol, 6.0 equiv), NaNO_2 (11.2 g, 162 mmol, 1.5 equiv) and water (20 mL) affording **3h** as a white solid turning pink (4.91 g,

23% yield): ^1H NMR (400 MHz, CD_3CN): δ = 7.90–7.94 (m, 2H), 8.25 (tt, $^3J_{\text{H,H}}$ = 7.7, $^4J_{\text{H,H}}$ = 1.2, 1H), 8.49–8.51 (m, 2H); ^{13}C NMR (126 MHz, CD_3CN): δ = 115.7, 132.8, 133.4, 142.9; ^{19}F NMR (470 MHz, CD_3CN): δ = -150.3 (s); Elem. anal.: Calc. for $\text{C}_6\text{H}_5\text{BF}_4\text{N}_2$: C, 37.55; H, 2.63; B, 5.63; F, 39.60; N, 14.60. Found: C, 37.69; H, 2.71; N, 14.69.



3i: Prepared according to general procedure 2 starting from **1i** (969 mg, 3.0 mmol), $\text{BF}_3\cdot\text{OEt}_2$ (894 mg, 6.3 mmol, 2.1 equiv) and *t*-BuONO (309 mg, 3.3 mmol, 1.1 equiv) affording **3i** as a white solid (859 mg, 97% yield): FT-IR (film): ν_{max} (cm^{-1}) = 3069, 3024, 2300 (N_2^+), 1673 (CO), 1597, 1582, 1450, 1395, 1317, 1308, 1290, 1258, 1058 (BF_4^-), 1036 (BF_4^-), 952, 845 (SF); ^1H NMR (500 MHz, CD_3CN): δ = 7.65–7.69 (m, 2H, C10H), 7.82–7.86 (m, 1H, C11H), 7.91–7.93 (m, 2H, C9H), 8.48 (d, $^4J_{\text{H,H}}$ = 2.2, 1H, C3H), 8.62 (dd, $^3J_{\text{H,H}}$ = 9.0, $^4J_{\text{H,H}}$ = 2.3, 1H, C5H), 9.02 (d, $^3J_{\text{H,H}}$ = 8.9, 1H, C6H); ^{11}B NMR (160 MHz, CD_3CN): δ = -0.6 (br s); ^{13}C NMR (126 MHz, CD_3CN): δ = 119.7 (C1), 130.3 (C10), 131.8 (C9), 132.8 (quint, $^3J_{\text{C,F}}$ = 4.7, C3), 133.6 (quint, $^3J_{\text{C,F}}$ = 4.7, C5), 134.6 (C8), 136.4 (C11), 138.1 (C6), 140.8 (C2), 160.5 (quint, $^2J_{\text{C,F}}$ = 21.4, C4), 189.7 (C7); ^{19}F NMR (377 MHz, CD_3CN): δ = -150.7 (s), 62.6 (d, $^2J_{\text{F,F}}$ = 149.7, 4F), 77.3–79.0 (m, 1F); HRMS (ESI $^+$): m/z = Calc. for $\text{C}_{13}\text{H}_8\text{F}_5\text{N}_2\text{OS}$ [M] $^+$, 335.02720; Found, 335.02733.

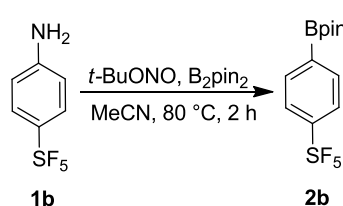
Synthesis of arylboronates 2

1. From anilines **1**^[3]

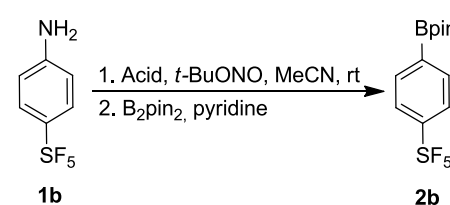


A mixture of **1a** (219 mg, 1.0 mmol), B_2pin_2 (279 mg, 1.1 mmol, 1.1 equiv), *t*-BuONO (155

mg, 1.5 mmol, 1.5 equiv), dibenzoyl peroxide (BPO) (2 mg, 0.02 mmol, 2 mol%) in MeCN (3 mL) was stirred at rt for 2 h. The solvent was removed under reduced pressure. Purification by column chromatography ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$, 5:5:90) afforded **2a** as a brown solid (240 mg, 70% yield).



A mixture of **1b** (219 mg, 1.0 mmol), B_2pin_2 (279 mg, 1.1 mmol, 1.1 equiv), *t*-BuONO (155 mg, 1.5 mmol, 1.5 equiv) and MeCN (3 mL) was stirred and heated to 80 °C for 2 h. The solvent was removed under reduced pressure. Purification by column chromatography ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$, 5:5:90) afforded **2b** as a brown solid (180 mg, 55% yield, 82% purity according to ^1H NMR).

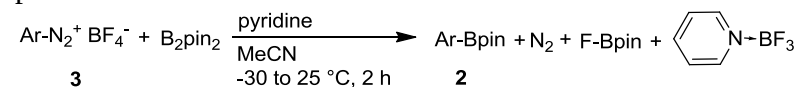


To a stirred mixture of **1b** (219 mg, 1.0 mmol) and *p*TsOH $\cdot\text{H}_2\text{O}$ (190 mg, 1.0 mmol, 1 equiv) in MeCN (3 mL), *t*-BuONO (103 mg, 1.0 mmol, 1.0 equiv) in MeCN (1 mL) was added over 1 min. After 10 min of stirring at rt B_2pin_2 (254 mg, 1.0 mmol, 1.0 equiv) was added at once followed by addition of pyridine (125 mg, 1.6 mmol, 1.6 equiv) over 45 min. The mixture was stirred overnight followed by removal of solvent under reduced pressure and column chromatography ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$, 5:5:90) to afford **2b** as a pale yellow solid (167 mg, 51%).

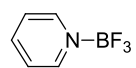
To a stirred solution of **1b** (219 mg, 1.0 mmol) in MeCN (1.0 mL) at 0 °C, 33% HBF_4 (450 mg, 1.7 equiv) in MeCN (1.0 mL) was added. The mixture was stirred for 5 min followed by addition of *t*-BuONO (107 mg, 1.05 mmol, 1.05 equiv) in MeCN (1.0 mL). After 15 min stirring B_2pin_2 (254 mg, 1.0 mmol, 1.0 equiv) in MeCN (1.0 mL) was

added and the reaction mixture was transferred to a $-25\text{ }^{\circ}\text{C}$ bath. Pyridine (330 μL , 4.0 mmol, 4.0 equiv) in MeCN (1.0 mL) was added over ca. 30 s and the mixture was allowed to warm to rt over 1 h. Solvent was removed under reduced pressure. Solution of 1M HCl (10 mL) was added to the crude product mixture, extraction with Et₂O (2 $\times$ 10 mL), washing the combined organic phase with water (10 mL), brine (10 mL) and drying (MgSO₄), followed by column chromatography (CH₂Cl₂/Et₂O/hexane, 5:5:90) afforded **2b** as a pale yellow solid (266 mg, 81%). The same procedure using 35% HCl (177 mg, 1.7 equiv) provided **2b** as a pale yellow solid (257 mg, 78%).

2. From aryldiazonium tetrafluoroborates **3** using pyridine, General procedure

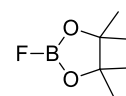


3 (1 mmol), B₂pin₂ (254 mg, 1 mmol, 1 equiv) and MeCN (2 mL) were mixed and cooled to $-30\text{ }^{\circ}\text{C}$. Pyridine (0.33 mL, 4 mmol, 4 equiv) was added to the stirred solution over half a minute and the mixture was slowly warmed to rt over 2 h. Solvent was removed under reduced pressure and the residue was dissolved in a minimum amount of MeCN. Pyridine trifluoroborate complex precipitated upon addition of Et₂O and was filtered, washed with Et₂O and dried under reduced pressure. The filtrate was concentrated and purified by column chromatography (Et₂O/CH₂Cl₂/hexane, 5:5:90) affording the desired arylboronate **2**. Side products, pyridine-BF₃ complex and 2-fluoro-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (F-Bpin), were observed by ¹¹B and ¹⁹F NMR of the crude reaction mixture and compared with authentic samples.

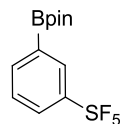


Prepared independently by mixing BF₃·OEt₂ (30 mg, 0.21 mmol), pyridine (17 mg, 0.21 mmol, 1.0 equiv) and Et₂O

(0.5 mL), solvent removal under reduced pressure and addition of CD₃CN: ¹¹B NMR (128 MHz, CD₃CN): δ = 1.0 (q, ²J_{BF} = 10.4); ¹⁹F NMR (376 MHz, CD₃CN): δ = -150.1 to -149.9 (m).

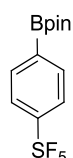


Prepared independently by a modified literature procedure^[4] by slow addition of *n*-BuLi (2.5 M, 0.80 mL, 2.0 mmol, 2.0 equiv) to a solution of pinacol (118 mg, 1.0 mmol) in dry THF (3 mL) causing precipitation of the bislithium salt of pinacol. BF₃·OEt₂ (156 mg, 1.1 mmol, 1.1 equiv) in dry THF (1 mL) was added dropwise and the mixture was stirred for 15 min. Solvent was removed under reduced pressure, and CD₃CN was added: ¹¹B NMR (128 MHz, CDCl₃): δ = 23.0 (br s) (4.2^[5], ca. 1.2^[6]); ¹⁹F NMR (376 MHz, CD₃CN): δ = -151.5 (s) (-152.5^[6]).

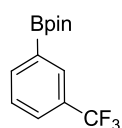


2a: Prepared according to the general procedure from **3a** (318 mg, 1.0 mmol), B₂pin₂ (254 mg, 1.0 mmol, 1 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4 equiv) affording **2a** as a white solid (265 mg, 80% yield): *R*_f = 0.55 (Et₂O/CH₂Cl₂/hexane, 5:5:90); mp = 72–74 $^{\circ}\text{C}$ (MeOH); FT-IR (film): ν_{max} (cm⁻¹) = 3007, 2988, 2973, 2934, 1603, 1484, 1460, 1424, 1437, 1374, 1356, 1350, 1335, 1272, 1214, 1169, 1146 (BO), 1101, 1082, 916, 845 (SF), 838, 599; ¹H NMR (400 MHz, CDCl₃): δ = 1.35 (s, 12H), 7.46 (t, ³J_{H,H} = 7.8, 1H), 7.82 (ddd, ³J_{H,H} = 8.3, ⁴J_{H,H} = 2.4, 1.1, 1H), 7.90–7.95 (m, 1H), 8.17 (d, ⁴J_{H,H} = 2.2, 1H); ¹¹B NMR (128 MHz, CDCl₃): δ = 30.1 (br s); ¹³C NMR (101 MHz, CDCl₃): δ = 24.8, 84.5, 128.2, 128.4 (quint, ³J_{C,F} = 4.7), 131.7 (quint, ³J_{C,F} = 4.5), 137.8, 153.7 (quint, ²J_{C,F} = 16.6); ¹⁹F NMR (377 MHz, CDCl₃): δ = 62.2 (d, ²J_{F,F} = 149.7, 4F), 83.3–85.0 (m, 1F); MS (EI⁺): *m/z* (%) = 315 (82) [M - Me]⁺, 314 (20), 231 (89), 230 (22), 180 (15), 179 (14), 131 (47), 104 (18), 103 (23), 85 (27), 77 (14), 59 (32), 58 (44), 57 (23), 43 (100), 42 (48),

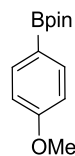
41 (43), 39 (16); HRMS (Cl^+): m/z = Calc. for $\text{C}_{12}\text{H}_{17}\text{BF}_5\text{O}_2\text{S}$ [$\text{M} + \text{H}$] $^+$, 331.0962; Found, 331.0974.



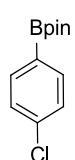
2b: Prepared according to the general procedure from **3b** (954 mg, 3.0 mmol), B_2pin_2 (762 mg, 3.0 mmol, 1.0 equiv), MeCN (6 mL) and pyridine (1.0 mL, 12.0 mmol, 4.0 equiv) affording **2b** as a white solid (760 mg, 77% yield): R_f = 0.44 ($\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2/\text{hexane}$, 5:5:90); mp = 85–89 °C (MeOH); FT-IR (film): ν_{max} (cm^{-1}) = 3001, 2977, 2925, 1602, 1400, 1374, 1366, 1336, 1275, 1213, 1169, 1145 (BO), 1083, 1019, 839 (SF), 595; ^1H NMR (400 MHz, CDCl_3): δ = 1.35 (s, 12H), 7.72–7.74 (m, 2H), 7.87–7.90 (m, 2H); ^{11}B NMR (128 MHz, CDCl_3): δ = 30.0 (br s); ^{13}C NMR (101 MHz, CDCl_3) δ = 24.8, 84.4, 125.0 (quint, $^3J_{\text{C,F}}$ = 4.6), 135.1, 156.1 (quint, $^2J_{\text{C,F}}$ = 17.6); ^{19}F NMR (377 MHz, CDCl_3): δ = 61.7 (d, $^2J_{\text{F,F}}$ = 149.7, 4F), 82.8–84.5 (m, 1F); MS (EI^+): m/z (%) = 316 (14), 315 (100) [$\text{M} - \text{Me}$] $^+$, 314 (24), 245 (11), 244 (88), 231 (62), 230 (15), 104 (11), 103 (10), 85 (18), 59 (20), 58 (28), 57 (15), 43 (39), 42 (31), 41 (28), 39 (10); HRMS (Cl^+): m/z = Calc. for $\text{C}_{12}\text{H}_{17}\text{BF}_5\text{O}_2\text{S}$ [$\text{M} + \text{H}$] $^+$, 331.0962; Found, 331.0959.



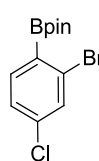
2c:^[7] Prepared according to the general procedure from **3c** (260 mg, 1.0 mmol), B_2pin_2 (254 mg, 1.0 mmol, 1.0 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **2c** as a yellow liquid which slowly solidified (215 mg, 64% yield); R_f = 0.45 ($\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2/\text{hexane}$, 5:5:90); ^1H NMR (400 MHz, CDCl_3): δ = 1.35 (s, 12H), 7.48 (t, $^3J_{\text{H,H}}$ = 7.6, 1H), 7.66–7.73 (m, 1H), 7.98 (d, $^3J_{\text{H,H}}$ = 7.3, 1H), 8.07 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 24.9, 84.3, 124.3 (q, $^1J_{\text{C,F}}$ = 272.2), 127.8 (q, $^3J_{\text{C,F}}$ = 3.7), 128.0, 130.0 (q, $^2J_{\text{F,C}}$ = 32.0), 131.3 (q, $^3J_{\text{F,C}}$ = 3.7), 138.0 (q, $^5J_{\text{F,C}}$ = 1.5 Hz); ^{19}F NMR (376 MHz, CDCl_3): δ = -63.1 (s).



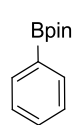
2d:^[5] Prepared according to the general procedure from **3d** (222 mg, 1.0 mmol), B_2pin_2 (254 mg, 1.0 mmol, 1.0 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **2d** as a yellow liquid (148 mg, 64% yield); R_f = 0.45 ($\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2/\text{hexane}$, 5:5:90); ^1H NMR (400 MHz, CDCl_3): δ = 1.33 (s, 12H), 3.82 (s, 3H), 6.87–6.92 (m, 2H), 7.73–7.78 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ = 24.8, 55.1, 83.5, 113.3, 136.5, 162.1.



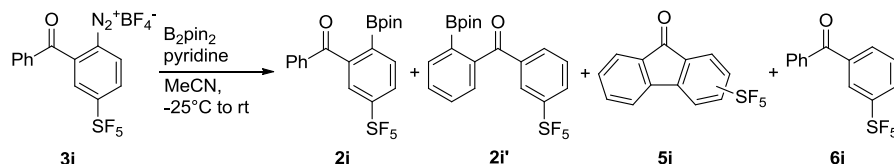
2e:^[6] Prepared according to the general procedure from **3e** (226 mg, 1.0 mmol), B_2pin_2 (254 mg, 1.0 mmol, 1.0 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **2e** as a yellow liquid which slowly solidifies (129 mg, 54% yield); R_f = 0.69 ($\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2/\text{hexane}$, 5:5:90); ^1H NMR (400 MHz, CDCl_3) δ = 1.34 (s, 12H), 7.32–7.35 (m, 2H), 7.71–7.74 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ = 24.8, 84.0, 128.0, 136.1, 137.5.



2f:^[8] Prepared according to the general procedure from **3f** (305 mg, 1.0 mmol), B_2pin_2 (254 mg, 1.0 mmol, 1.0 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **2f** as a yellow liquid (92 mg, 30% yield); R_f = 0.65 ($\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2/\text{hexane}$, 5:5:90); FT-IR (film): ν_{max} (cm^{-1}) 3086, 3056, 1580, 1543, 1472, 1380, 1372, 1344, 1320 (B-O), 1273, 1253, 1214, 1167, 1146 (B-O), 1104, 1029, 962, 858; ^1H NMR (400 MHz, CDCl_3): δ = 1.37 (s, 12H), 7.26 (dd, $^3J_{\text{H,H}}$ = 8.1, $^4J_{\text{H,H}}$ = 1.8, 1H), 7.56 (d, $^3J_{\text{H,H}}$ = 8.1, 1H), 7.57 (d, $^4J_{\text{H,H}}$ = 2.0, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 24.8, 84.4, 126.7, 128.4, 132.5, 137.2, 137.4; MS (EI^+): m/z (%) = 318 (19) [M] $^+$, 303 (24) [$\text{M} - \text{Me}$] $^+$, 239 (34), 238 (21), 237 (100), 236 (25), 221 (23), 219 (89), 218 (47), 217 (73), 216 (33), 197 (25), 195 (74), 137 (20), 85 (29), 43 (41), 41 (36); HRMS (Cl^+): m/z = Calc. for $\text{C}_{12}\text{H}_{17}\text{BBrClO}_2$ [$\text{M} + \text{H}$] $^+$, 317.0115; Found, 317.0116.



2h.^[9] Prepared according to the general procedure from **3h** (192 mg, 1.0 mmol), B₂pin₂ (254 mg, 1.0 mmol, 1.0 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **2h** as a pale yellow liquid which solidifies (110 mg, 54%); *R*_f = 0.43 (Et₂O/CH₂Cl₂/hexane, 5:5:90); ¹H NMR (400 MHz, CDCl₃): δ = 1.34 (s, 12H), 7.34–7.38 (m, 2H), 7.43–7.47 (m, 1H), 7.80–7.82 (m, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 24.8, 83.7, 127.7, 131.2, 134.7.



Borylation of 3i: **3i** (380 mg, 0.9 mmol) was subjected to borylation according to the general procedure with B₂pin₂ (229 mg, 0.9 mmol, 1.0 equiv), MeCN (2 mL) and pyridine (0.30 mL, 3.64 mmol, 4.0 equiv) affording a mixture of unreacted B₂pin₂ and products **2i**, **2i'**, **5i** and **6i** in 16:31:28:25 ratio (GCMS, Figures S11-S17). B₂pin₂: MS (EI⁺): *m/z* (%) = 239 (38) [M - Me]⁺, 238 (18), 113 (10), 85 (25), 84 (100) [C₆H₁₂]⁺, 83 (44), 69 (26), 59 (11), 57 (10), 55 (14), 43 (23), 42 (11), 41 (30), 39 (10); **2i**: MS (EI⁺): *m/z* (%) = 419 (13) [M - Me]⁺, 377 (19), 376 (100), 375 (28), 336 (13), 335 (79), 334 (18), 105 (7) [PhCO]⁺, 77 (9) [Ph]⁺; **2i'**: MS (EI⁺): *m/z* (%) = 419 (10) [M - Me]⁺, 377 (20), 376 (100), 375 (28), 336 (11), 335 (70), 334 (18), 207 (12), 164 (8); **5i** isomer 1: MS (EI⁺): *m/z* (%) = 307 (15) [M + 1]⁺, 306 (100) [M]⁺, 198 (36), 179 (28) [M - SF₅]⁺, 170 (25), 169 (9), 151 (56), 150 (35); **5i** isomer 2: MS (EI⁺): *m/z* (%) = 307 (16) [M + 1]⁺, 306 (100) [M]⁺, 199 (14), 198 (96), 179 (10) [M - SF₅]⁺, 170 (35), 169 (8), 151 (40), 150 (39), 85 (10), 75 (10); **6i**: MS (EI⁺): *m/z* (%) = 308 (53) [M]⁺, 231 (28) [M - Ph]⁺, 181 (10) [M - SF₅]⁺, 105 (100) [PhCO]⁺, 95 (10), 77 (41) [Ph]⁺, 76 (13), 75 (12), 51 (12).

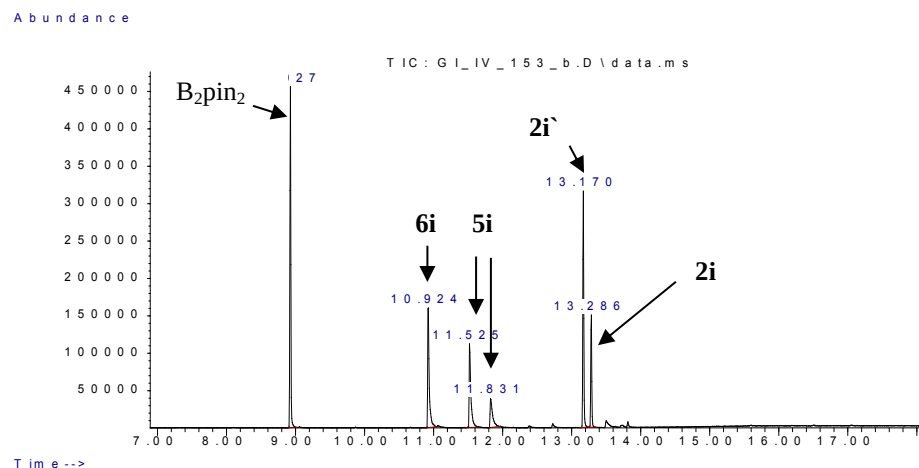


Figure S1: GC chromatogram of the crude product mixture of borylation of **3i**.

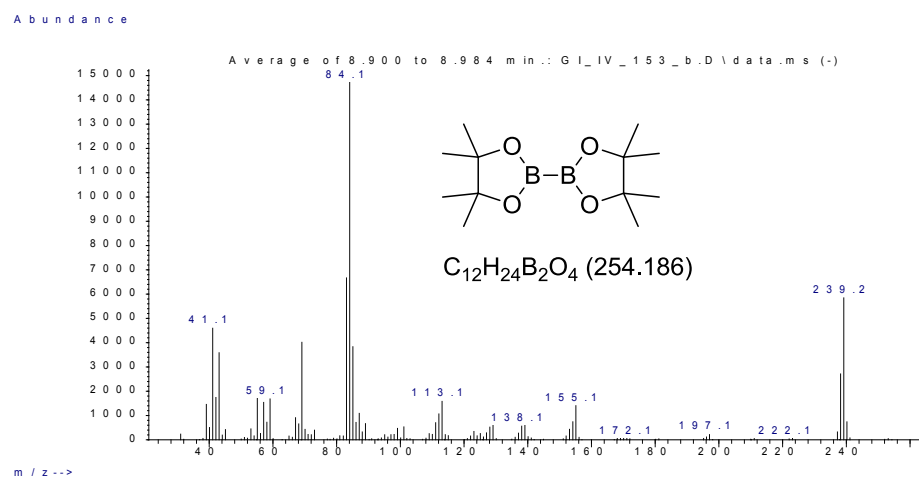


Figure S2: MS (EI⁺) spectrum of B₂pin₂.

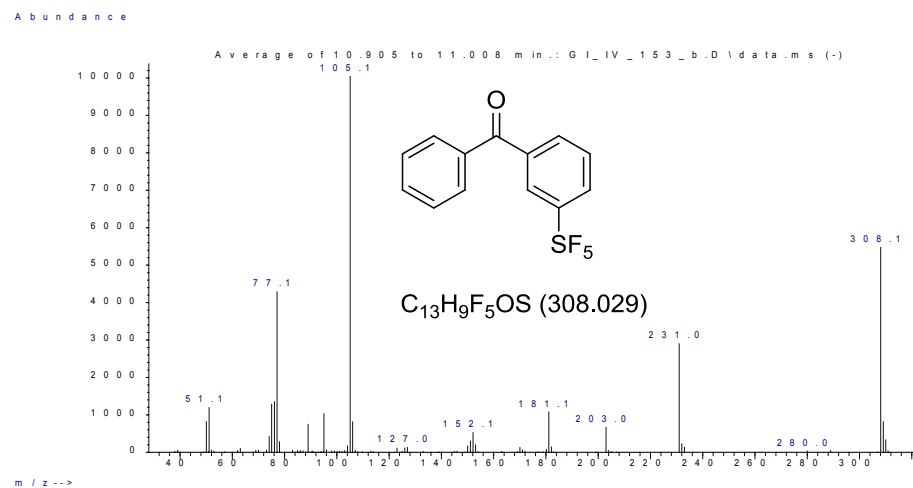


Figure S3: MS (EI^+) spectrum of **6i**.

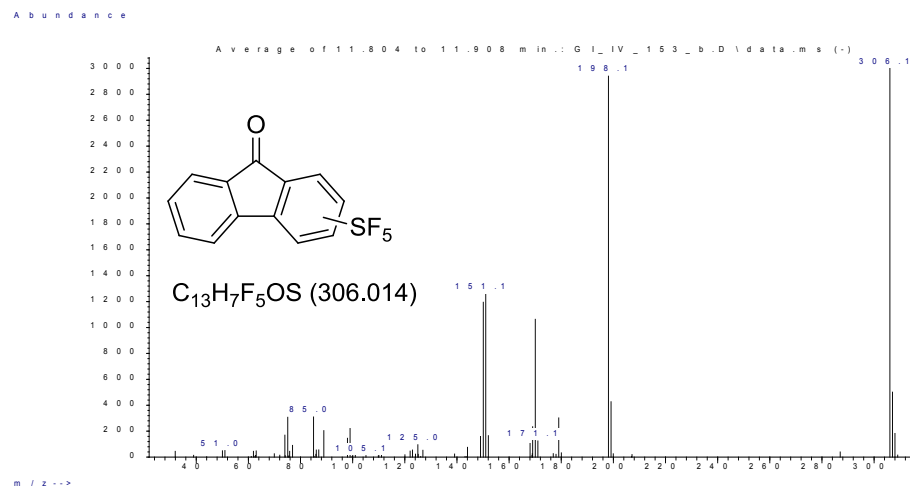


Figure S5: MS (EI^+) spectrum of **5a** isomer 2.

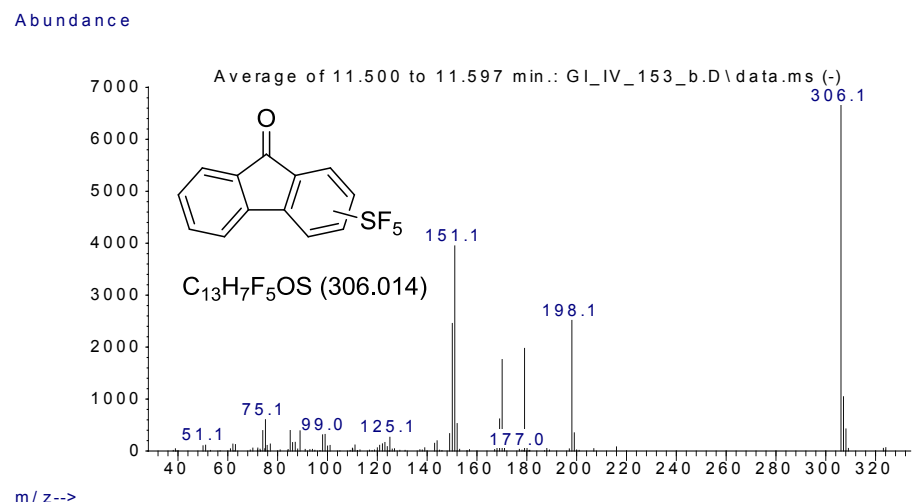


Figure S4: MS (EI^+) spectrum of **5a** isomer 1.

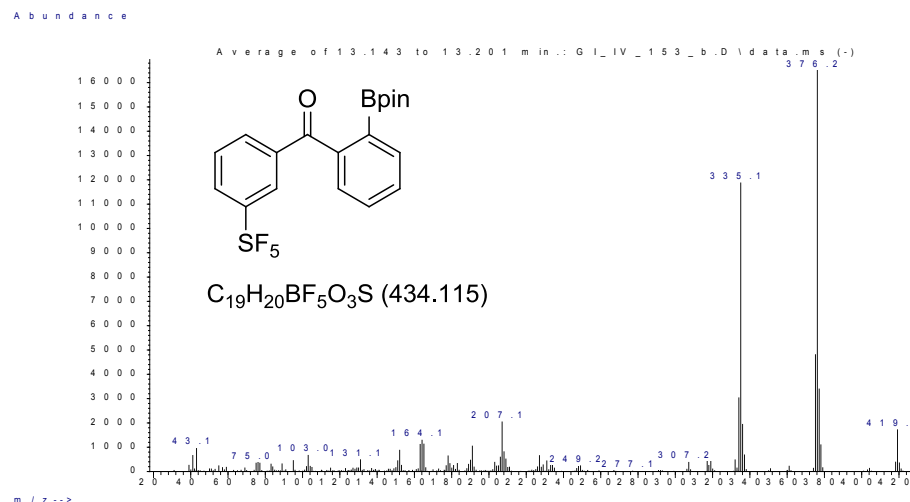


Figure S6: MS (EI^+) spectrum of **2i'**.

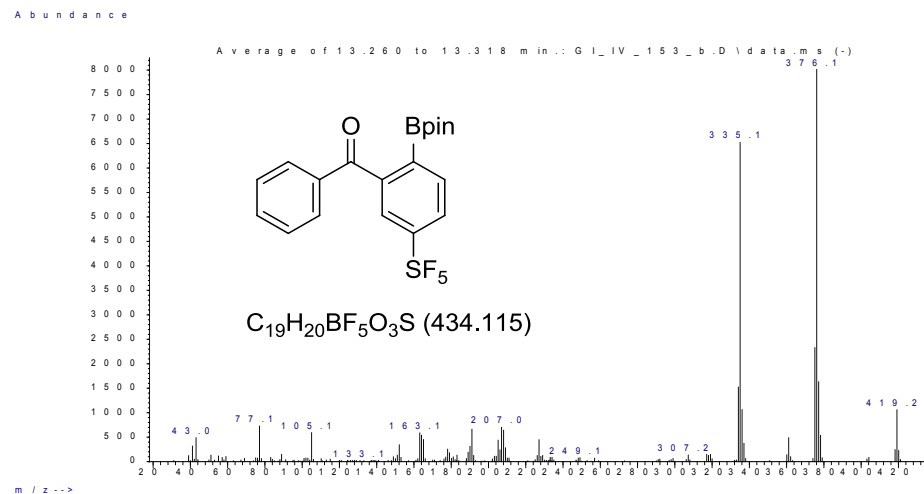
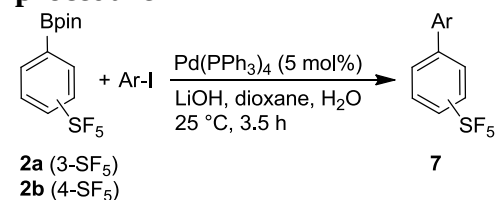


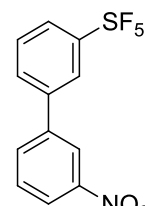
Figure S7: MS (EI⁺) spectrum of **2i**.

Synthesis of biaryls **7** by the Suzuki coupling reaction, General procedure

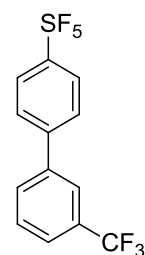


To a mixture of **2a** or **2b** (165 mg, 0.5 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol, 5 mol %), ArI (0.55 mmol, 1.1 equiv) in dry 1,4-dioxane (2 mL), a solution of LiOH·H₂O (84 mg, 2 mmol,

4 equiv) in water (1 mL) was added. The reaction mixture was stirred under argon at 50 °C for 3.5 h followed by addition of water (10 mL). Extraction into Et₂O (3 × 10 mL), drying (MgSO₄) and solvent removal under reduced pressure provided crude product which was purified by column chromatography.

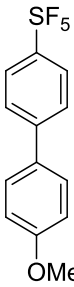


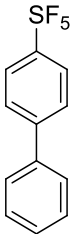
7ah: Prepared according to the general procedure from **2a** (165 mg, 0.5 mmol) and 3-nitroiodobenzene (137 mg, 0.55 mmol, 1.1 equiv) affording **7ah** as a white solid (89 mg, 55% yield): *R*_f = 0.13 (CH₂Cl₂/hexane, 10:90); mp = 72–75 °C; FT-IR (film): *ν*_{max} (cm⁻¹) = 3092, 1600, 1532 (N=O), 1495, 1472, 1349 (N=O), 1117, 839 (SF), 738 (N=O), 597; ¹H NMR (400 MHz, CDCl₃): δ = 7.60–7.70 (m, 2H), 7.77–7.79 (m, 1H), 7.82–7.85 (m, 1H), 7.90–7.93 (m, 1H), 7.98–7.99 (m, 1H), 8.27–8.30 (m, 1H), 8.44–8.45 (m, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 122.1, 123.0, 124.8 (quint, ³*J*_{C,F} = 4.6), 125.9 (quint, ³*J*_{C,F} = 4.8), 129.6, 130.2, 130.3, 133.2, 139.8, 141.1, 148.8, 154.7 (quint, ²*J*_{C,F} = 17.6); ¹⁹F NMR (377 MHz, CDCl₃): δ = 62.3 (d, ²*J*_{F,F} = 149.7, 4F), 82.4–84.1 (m, 1F); MS (EI⁺): *m/z* (%) = 326 (10), 325 (72) [M]⁺, 295 (10), 170 (28), 153 (13), 152 (100), 151 (26), 150 (14); HRMS (CI⁺): *m/z* = Calc. for C₁₂H₉F₅NO₂S [M + H]⁺, 326.0274; Found, 326.0278.



7bc: Prepared according to the general procedure from **2b** (165 mg, 0.50 mmol) and 3-(trifluoromethyl)iodobenzene (150 mg, 0.55 mmol, 1.1 equiv) affording **7bc** as a white solid (92 mg, 53% yield): *R*_f = 0.39 (hexane); mp = 66–68 °C; FT-IR (film): *ν*_{max} (cm⁻¹) = 1602, 1486, 1446, 1439, 1399, 1337, 1262, 1170, 1131, 1102, 1077, 1038, 847 (SF), 837 (SF), 649, 598; ¹H NMR (400 MHz, CDCl₃): δ = 7.58–7.69 (m, 4H), 7.75–7.76 (m, 1H), 7.82 (br s, 1H), 7.84–7.87 (m, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 125.3 (q, ¹*J*_{C,F} = 272.3), 124.1 (q, ³*J*_{C,F} = 3.7), 125.1 (q, ³*J*_{C,F} = 3.7), 126.7 (quint, ³*J*_{C,F} = 4.6), 127.4, 129.6, 130.6, 131.6 (quint, ²*J*_{C,F} = 32.0), 139.9, 143.0, 153.5 (quint, ²*J*_{C,F} = 17.6); ¹⁹F NMR (377 MHz, CDCl₃): δ = -63.2 (s, 3F), 62.5 (d, ²*J*_{F,F} = 149.7, 4F), 82.8–84.5 (m, 1F); MS (EI⁺): *m/z* (%) = 349 (15), 348 (100) [M]⁺, 329 (17), 241 (14), 240 (99), 221 (13), 219 (15),

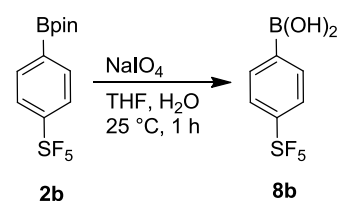
201 (34), 171(11), 170 (24), 152 (27), 151 (13).; HRMS (Cl^+): m/z = Calc. for $\text{C}_{13}\text{H}_9\text{F}_8\text{S}$ [$\text{M} + \text{H}$] $^+$, 349.0297; Found, 349.0298.

 **7bd**: Prepared according to the general procedure from **2b** (165 mg, 0.5 mmol) and 4-(methoxy)iodobenzene (129 mg, 0.55 mmol, 1.1 equiv) affording **7bd** as a white solid (80 mg, 52% yield); R_f = 0.17 (hexane); mp = 122–125 °C; FT-IR (film): ν_{max} (cm^{-1}) = 3067, 3030, 2979, 2949, 2850 (CH_3), 1610, 1582, 1528, 1493, 1461, 1445 (OCH_3), 1397, 1314, 1298, 1261, 1184, 1115, 1037, 846 (SF), 838, 820, 581; ^1H NMR (400 MHz, CDCl_3): δ = 3.85 (s, 3H), 6.97–7.01 (m, 2H), 7.49–7.53 (m, 2H), 7.57–7.60 (m, 2H), 7.74–7.80 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ = 55.3, 114.5, 126.3 (quint, $^3J_{\text{C,F}}$ = 4.6), 126.6, 128.4, 131.4, 144.1, 152.3 (quint, $^2J_{\text{C,F}}$ = 16.8), 160.1; ^{19}F NMR (377 MHz, CDCl_3): δ = 62.8 (d, $^2J_{\text{F,F}}$ = 149.7, 4F), 83.7–85.5 (m, 1F); MS (EI^+): m/z (%) = 311 (15), 310 (100) [M] $^+$, 295 (9), 187 (24), 159 (26), 140 (10), 139 (26), 133 (12); HRMS (Cl^+): m/z = Calc. for $\text{C}_{13}\text{H}_{12}\text{F}_5\text{OS}$ [$\text{M} + \text{H}$] $^+$, 311.0529; Found, 311.0533.

 **7bh**:^[10] Prepared according to the general procedure from **2b** (165 mg, 0.50 mmol) and iodobenzene (74 μL , 0.55 mmol, 1.1 equiv) affording **7bh** as a white solid (82 mg, 58% yield); R_f = 0.56 (hexane); FT-IR (film): ν_{max} (cm^{-1}) = 3080, 3032, 1569, 1485, 1450, 1400, 841 (SF), 766, 721, 695, 586; ^1H NMR (400 MHz, CDCl_3): δ = 7.38–7.49 (m, 3H), 7.56–7.58 (m, 2H), 7.63–7.65 (m, 2H), 7.80–7.82 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ = 126.4 (quint, $^3J_{\text{C,F}}$ = 4.6), 127.2, 127.3, 128.4, 129.0, 139.1, 144.5, 152.9 (quint, $^2J_{\text{C,F}}$ = 17.6); ^{19}F NMR (377 MHz, CDCl_3): δ = 62.7 (d, $^2J_{\text{F,F}}$ = 150.3, 4F), 83.4–85.1 (m, 1F); HRMS (Cl^+): m/z = Calc. for $\text{C}_{12}\text{H}_{10}\text{F}_5\text{S}$ [$\text{M} + \text{H}$] $^+$, 281.0423; Found 281.0417.

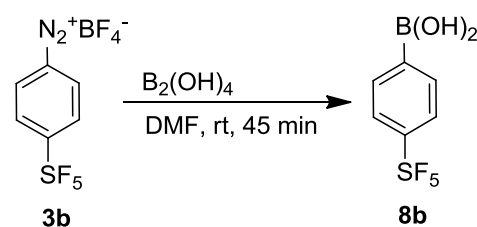
Synthesis of 4-(pentafluorosulfanyl)phenylboronic acid (**8b**)

1. From boronic ester **2b**



8b: **2b** (330 mg, 1 mmol), THF (4 mL) and water (1 mL) were stirred at rt for 5 min. NaIO_4 (642 mg, 3.0 mmol, 3.0 equiv) was added in one portion. After stirring for additional 30 min, 1 M HCl (0.7 mL) was added and the mixture was left stirring overnight, followed by removal of solvent under reduced pressure, addition of water (15 mL), extraction with Et_2O (3×10 mL), drying (MgSO_4), and solvent removal under reduced pressure. The resulting pale orange solid was sonicated for 10 min. with hexane (1 mL) and the hexane was carefully removed. Sonication with hexane was repeated twice and drying under reduced pressure at 30 °C provided a mixture of **8b** and 5% of its anhydride (trimer) as white solid (212 mg, 85% yield): mp > 250 °C (subl.); FT-IR (film): ν_{max} (cm^{-1}) = 1604, 1573, 1404, 1367, 1351, 1317, 1307, 1104, 1079, 1019, 842 (SF), 826, 598; ^1H NMR (400 MHz, CD_3CN): δ = 6.25 (s, 2H), 7.81 (d, $^3J_{\text{H,H}}$ = 8.6, 2H), 7.92 (d, $^3J_{\text{H,H}}$ = 8.2, 2H); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): δ = 7.89 (d, $^3J_{\text{H,H}}$ = 8.6, 2H), 8.05 (d, $^3J_{\text{H,H}}$ = 8.1, 2H); ^{11}B NMR (128 MHz, $[\text{D}_6]\text{DMSO}$): δ = 28.7 (br s); ^{13}C NMR (101 MHz, $[\text{D}_6]\text{DMSO}$): δ = 124.6–124.8 (m), 134.2, 142.8–143.4 (m), 153.7–154.4 (m); ^{19}F NMR (377 MHz, CD_3CN): δ = 63.0 (d, $^2J_{\text{F,F}}$ = 147.0, 4F), 84.7–86.4 (m, 1F); HRMS (ESI^+): m/z = Calc. for $\text{C}_6\text{H}_5\text{BF}_5\text{O}_2\text{S}$ [$\text{M} - \text{H}$] $^-$, 247.00290; Found, 247.00273. Anhydride (trimer) of **8b** (5%): ^1H NMR (400 MHz, CD_3CN) δ = 8.02 (d, $^3J_{\text{H,H}}$ = 8.5, 2H), 8.41 (d, $^3J_{\text{H,H}}$ = 8.0, 2H); ^{13}C NMR (101 MHz, $[\text{D}_6]\text{DMSO}$) δ = 124.4–124.6 (m), 134.9; ^{19}F NMR (377 MHz, CD_3CN) δ = 62.8 (d, $^2J_{\text{F,F}}$ = 147, 4F), 84.0–85.7 (m, 1F).

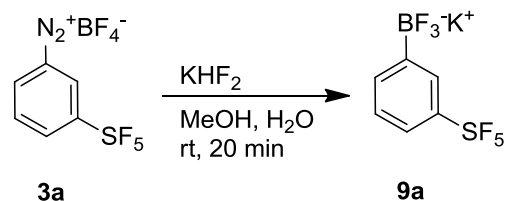
2. From diazonium salt **3b**^[11]



To a solution of $\text{B}_2(\text{OH})_4$ (180 mg, 2.0 mmol, 2.0 equiv) in DMF (4 mL), **3b** (318 mg, 1.0 mmol) was added portion-wise. The mixture was stirred for 45 min followed by addition of water (10 mL) and brine (4 mL),

extraction of the product into EtOAc (3 × 10 mL). Combined organic phase was washed with brine (4 mL), water (2 × 4 mL) and brine (4 mL), dried (MgSO_4) and solvent was removed under reduced pressure. Column chromatography (EtOAc/hexane, 60:40 to 100:0) afforded **8b** as a mixture with estimated yield 25%, based on ^{19}F NMR.

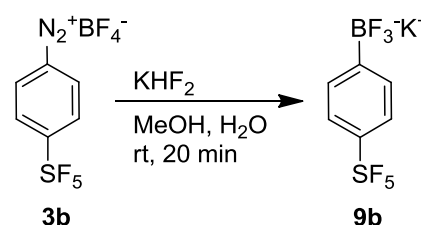
Synthesis of potassium (pentafluorosulfanyl)phenyltrifluoroborates **9**



9a: A solution of KHF_2 (780 mg, 10.0 mmol, 5 equiv) in water (3.6 mL) was added at rt to a solution of **3a** (660 mg, 2 mmol) in MeOH (8 mL). After stirring for 20 min,

solvents were removed under reduced pressure (1 mm Hg, 70 °C, 5 min). The residuum was dissolved in MeCN (5 mL), filtered and the solid was washed with MeCN (2 × 2.5 mL). The filtrate was concentrated under reduced pressure and dissolved in EtOAc (1 mL). The product precipitated upon addition of CH_2Cl_2 (15 mL). Filtration, washing with CH_2Cl_2 (5 mL) and drying the solid under reduced pressure afforded **9a** as a white solid (520 mg, 84% yield): mp = 224–240 °C; FT-IR (film): ν_{max} (cm^{-1}) = 3064, 3021, 1713, 1702, 1598,

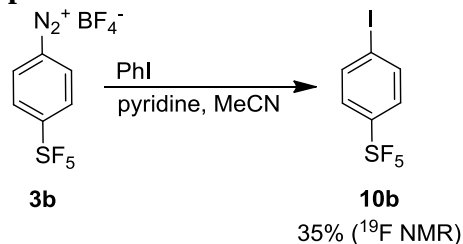
1479, 1412, 1371, 1233, 1219, 1112, 1099, 1002 (BF), 987 (BF), 899, 834 (SF); ^1H NMR (400 MHz, $[\text{D}_6]$ acetone) δ = 7.32 (t, $^3J_{\text{H,H}}$ = 7.7, 1H), 7.53 (ddd, $^3J_{\text{H,H}}$ = 8.2, $^4J_{\text{H,H}}$ = 2.5, 1.0, 1H), 7.68 (d, $^3J_{\text{H,H}}$ = 7.1, 1H), 7.90 (d, $^4J_{\text{H,H}}$ = 2.1, 1H); ^{11}B NMR (128 MHz, $[\text{D}_6]$ acetone) δ = 3.7 (quint, $^1J_{\text{B,F}}$ = 50.0); ^{13}C NMR (101 MHz, $[\text{D}_6]$ acetone) δ = 123.5 (quint, $^3J_{\text{C,F}}$ = 4.6), 127.9, 128.9–129.2 (m), 136.0; ^{19}F NMR (377 MHz, $[\text{D}_6]$ acetone) δ = -143.1 to -142.1 (m, 3F), 63.4 (d, $^2J_{\text{F,F}}$ = 147.4, 4F), 87.6–89.2 (m, 1F); Elem. anal.: Calc. for $\text{C}_6\text{H}_4\text{BF}_8\text{KS}$: C, 23.24, H, 1.30; S, 10.34%; Found: C, 23.27; H, 1.41; S, 10.44.



9b: A solution of KHF_2 (780 mg, 10 mmol, 5 equiv) in water (3.6 mL) was added at rt to a solution of **3b** (660 mg, 2 mmol) in MeOH (8 mL). After stirring for 20 min, solvents were removed under reduced pressure (1 mm Hg, 70 °C, 5 min).

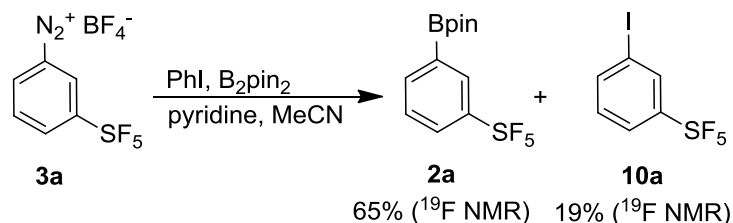
The residue was dissolved in MeCN (10 mL) and filtered. The filtrate was concentrated under reduced pressure and dissolved in MeCN (5 mL). The product precipitated upon addition of CH_2Cl_2 (25 mL). Filtration, washing with CH_2Cl_2 (5 mL) and drying the solid under reduced pressure afforded **9b** as a white solid (579 mg, 93%): mp >220 °C (decomp.); FT-IR (film): ν_{max} (cm^{-1}) = 3097, 3055, 3037, 1714, 1389, 1371, 1234, 1225, 1024 (BF), 972 (BF), 922, 842 (SF), 819; ^1H (400 MHz, $[\text{D}_6]$ acetone): δ = 7.56–7.66 (m, 4H); ^{11}B NMR (128 MHz, $[\text{D}_6]$ acetone) δ = 3.7 (br s); ^{13}C NMR (101 MHz, $[\text{D}_6]$ acetone) δ = 124.3 (quint, $^3J_{\text{C,F}}$ = 4.6), 132.8, 152.4–153.1 (m); ^{19}F NMR (377 MHz, $[\text{D}_6]$ acetone): δ = -142.8 to -142.1 (m, 3F), 63.7 (d, $^2J_{\text{F,F}}$ = 147.4, 4F), 87.6–89.1 (m, 1F); Elem. anal.: Calc. for $\text{C}_6\text{H}_4\text{BF}_8\text{KS}$: C, 23.24, H, 1.30; S, 10.34%; Found: C, 23.07; H, 1.58; S, 9.87.

Trapping experiment, pyridine-promoted dediazonation in the presence of iodobenzene



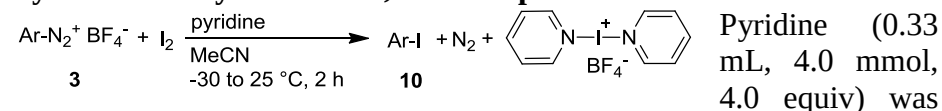
To a solution of **3b** (159 mg, 0.5 mmol) and PhI (408 mg, 2 mmol, 4 equiv) in MeCN (2 mL) cooled to $-20\text{ }^{\circ}\text{C}$, pyridine (330 μL , 4.0 mmol, 4.0 equiv) was added dropwise. The mixture was slowly warmed to rt over 1.5 h and 4-nitro(pentafluorosulfanyl)benzene (0.5 mmol) was added as an internal standard. The yield was calculated based on ^{19}F NMR spectroscopy.

Competitive experiment, pyridine-promoted dediazonation-borylation vs. -iodination in the presence of B_2pin_2 and iodobenzene



3a (318 mg, 1.0 mmol), B_2pin_2 (254 mg, 1 mmol, 1 equiv), PhI (204 mg, 1 mmol, 1 equiv) and MeCN (2 mL) were mixed and cooled to $-30\text{ }^{\circ}\text{C}$. Pyridine (0.33 mL, 4 mmol, 4 equiv) was added to the stirred solution over half a minute and the mixture was slowly warmed to rt over 2 h. 4-Nitro(pentafluorosulfanyl)benzene (0.5 mmol) was then added as an internal standard and the yield was calculated based on ^{19}F NMR spectroscopy.

Synthesis of aryl iodides **10**, General procedure

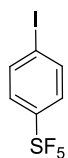


Pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) was added over half a minute to a mixture of **3** (1.0 mmol), I_2 (279 mg, 1.1 mmol, 1.1 equiv) and MeCN (2 mL) cooled to $-30\text{ }^{\circ}\text{C}$. The reaction mixture was warmed to rt over 2 h, solvent was removed under reduced pressure, Et_2O (20 mL) was added. The ether phase was washed with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (1 M, 5 mL), brine (5 mL), dried (MgSO_4), and solvent was removed under reduced pressure. Purification by column chromatography afforded **10**.

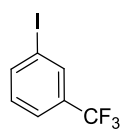
Bis(pyridine)iodonium tetrafluoroborate:^[12] isolated as a pale brown solid by the addition of Et_2O to the MeCN solution of the crude reaction mixture, filtration and drying under reduced pressure: ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.53–7.69 (m, 4H), 8.22 (tt, $^3J_{\text{HH}}$ = 7.6, $^4J_{\text{HH}}$ = 1.5, 2H), 8.70–8.82 (m, 4H); ^{11}B NMR (128 MHz, CD_2Cl_2): δ = -1.3 (s); ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 128.4, 142.5, 149.9; ^{19}F NMR (376 MHz, CD_2Cl_2): δ = -152.3 (d, $^1J_{\text{BF}}$ = 1.7); HRMS (ESI $^+$): m/z = Calc. for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{I}$ [M] $^+$, 284.98832; Found, 284.98846.

10a:^[10] Prepared according to the general procedure from **3a** (318 mg, 1.0 mmol), I_2 (279 mg, 1.1 mmol, 1.1 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **10a** as a colorless liquid (278 mg, 84% yield): R_f = 0.76 (hexane); ^1H NMR (400 MHz, CDCl_3): δ = 7.21 (tt, $^3J_{\text{H,H}}$ = 8.0, $^5J_{\text{H,H}}$ = 0.8, 1H), 7.74 (ddd, $^3J_{\text{H,H}}$ = 8.3, $^4J_{\text{H,H}}$ = 2.1, 0.8, 1H), 7.83–7.88 (m, 1H), 8.08 (t, $^4J_{\text{H,H}}$ = 1.9, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 93.1, 125.2 (quint, $^3J_{\text{C,F}}$ = 4.7), 130.3, 134.7 (quint, $^3J_{\text{C,F}}$ = 4.7),

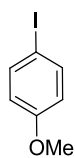
140.6; ^{19}F NMR (377 MHz, CDCl_3) δ = 62.3 (d, $^2J_{\text{F,F}}$ = 150.3, 4F), 81.8–83.4 (m, 1F).



10b:^[10] Prepared according to the general procedure from **3b** (318 mg, 1.0 mmol), I_2 (279 mg, 1.1 mmol, 1.1 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **10b** as a colorless solid (279 mg, 85% yield), or on 2 mmol scale (580 mg, 88% yield), or on 1 mmol scale using collidine (0.67 mL, 4 mmol, 4 equiv) instead of pyridine (269 mg, 82% yield): R_f = 0.76 (hexane); ^1H NMR (400 MHz, CDCl_3): δ = 7.46–7.49 (m, 2H), 7.80–7.83 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ = 98.2, 127.5 (quint, $^3J_{\text{C,F}}$ = 4.8), 137.9; ^{19}F NMR (377 MHz, CDCl_3) δ = 62.3 (d, $^2J_{\text{F,F}}$ = 150.3, 4F), 82.2–83.8 (m, 1F).

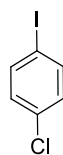


10c:^[13] Prepared according to the general procedure from **3c** (260 mg, 1.0 mmol), I_2 (279 mg, 1.1 mmol, 1.1 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **10c** as a colorless liquid (142 mg, 52% yield), or on 1 mmol scale using collidine (0.67 mL, 4 mmol, 4 equiv) instead of pyridine (162 mg, 60% yield): R_f = 0.73 (hexane); ^1H NMR (400 MHz, CDCl_3): δ = 7.20–7.24 (m, 1H), 7.58–7.60 (m, 1H), 7.88–7.90 (m, 1H), 7.96–7.96 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 93.8, 122.9 (q, $^1J_{\text{F,C}}$ = 273), 124.5 (q, $^3J_{\text{F,C}}$ = 3.9), 130.4, 132.4 (q, $^2J_{\text{F,C}}$ = 32.9), 134.3 (q, $^3J_{\text{F,C}}$ = 3.7), 140.9 (q, $^5J_{\text{F,C}}$ = 1.5); ^{19}F NMR (376 MHz, CDCl_3): δ = -63.4 (s).

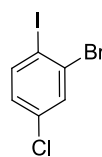


10d:^[14] Prepared according to the general procedure from **3d** (222 mg, 1.0 mmol), I_2 (279 mg, 1.1 mmol, 1.1 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **10d** as a white solid (20 mg, 9% yield), or using collidine (0.67 mL, 4 mmol, 4 equiv) instead of pyridine (26 mg, 11%

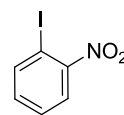
yield): R_f = 0.30 (hexane); ^1H NMR (400 MHz, CDCl_3): δ = 3.77 (s, 3H), 6.66–6.69 (m, 2H), 7.53–7.57 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ = 55.3, 82.6, 116.3, 138.1, 159.4.



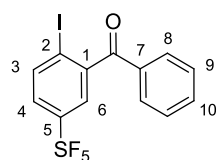
10e:^[13] Prepared according to the general procedure from **3e** (226 mg, 1.0 mmol), I_2 (279 mg, 1.1 mmol, 1.1 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **10e** as a white solid (110 mg, 46% yield): R_f = 0.77 (hexane); ^1H NMR (400 MHz, CDCl_3): δ = 7.07–7.10 (m, 2H), 7.59–7.63 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3): δ = 91.1, 130.5, 134.2, 138.7.



10f:^[15] Prepared according to the general procedure from **3f** (305 mg, 1.0 mmol), I_2 (279 mg, 1.1 mmol, 1.1 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **10f** as a colorless liquid (198 mg, 63% yield): R_f = 0.85 (hexane); ^1H NMR (400 MHz, CDCl_3): δ = 6.99 (dd, $^3J_{\text{H,H}}$ = 8.5, $^4J_{\text{H,H}}$ = 2.4, 1H), 7.62 (d, $^4J_{\text{H,H}}$ = 2.4, 1H), 7.76 (d, $^3J_{\text{H,H}}$ = 8.5, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 98.6, 128.8, 130.4, 132.4, 135.0, 140.8.

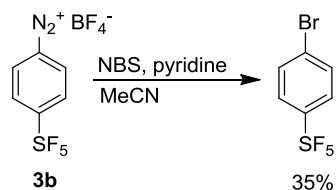


10g:^[16] Prepared according to the general procedure from **3g** (237 mg, 1.0 mmol), I_2 (279 mg, 1.1 mmol, 1.1 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **10g** as a yellow liquid (222 mg, 89% yield): R_f = 0.29 (EtOAc/hexane, 5:95); ^1H NMR (400 MHz, CDCl_3): δ = 7.26–7.30 (m, 1H), 7.48–7.52 (m, 1H), 7.85 (dd, $^3J_{\text{H,H}}$ = 8.1, $^4J_{\text{H,H}}$ = 1.6, 1H), 8.04 (dd, $^3J_{\text{H,H}}$ = 7.8, $^4J_{\text{H,H}}$ = 1.4, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ = 86.2, 125.4, 129.0, 133.3, 141.9.



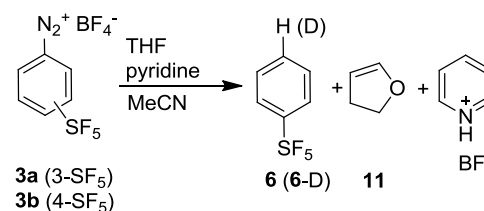
10i: Prepared according to the general procedure from **3i** (422 mg, 1.0 mmol), I₂ (279 mg, 1.1 mmol, 1.1 equiv), MeCN (2 mL) and pyridine (0.33 mL, 4.0 mmol, 4.0 equiv) affording **10i** as a white solid (398 mg, 92% yield): *R*_f = 0.27 (Et₂O/hexane, 20:80); mp = 107–110 °C; FT-IR (film): ν_{max} (cm⁻¹) = 3091, 3072, 3007, 1668 (C=O), 1595, 1584, 1458, 145, 1392, 1315, 1292, 1258, 1170, 1022, 842 (SF); ¹H NMR (400 MHz, CDCl₃): δ = 7.49–7.53 (m, 2H, C9H), 7.56 (dd, ³*J*_{H,H} = 8.6, ⁴*J*_{H,H} = 2.5, 1H, C4H), 7.63–7.69 (m, 2H, C6H, C10H), 7.79–7.83 (m, 2H, C8H), 8.05 (d, ³*J*_{H,H} = 8.8, 1H; C3H); ¹³C NMR (101 MHz, CDCl₃): δ = 96.4 (C2), 125.6 (quint, ³*J*_{C,F} = 4.6, C6), 128.0 (quint, ³*J*_{C,F} = 4.7, C4), 129.0, 130.4, 134.4 (C10), 134.6 (C7), 140.3 (C3), 145.1 (C1), 153.5 (quint, ²*J*_{C,F} = 18.3, C5), 195.2 (CO); ¹⁹F NMR (377 MHz, CDCl₃): δ = 62.5 (d, ²*J*_{F,F} = 150.9, 4F), 81.1–82.8 (m, 1F); MS (EI⁺): *m/z* (%) = 435 (15), 434 (100) [M]⁺, 357 (32) [M - Ph]⁺, 152 (11), 105 (91), 94 (10), 77 (43), 75 (14), 51 (11); HRMS (ESI⁺): *m/z* = Calc. for C₁₃H₈F₅INaOS [M + Na]⁺, 456.91529; Found, 456.91527.

Synthesis of 1-bromo-4-(pentafluorosulfonyl)benzene



To a mixture of **3b** (318 mg, 1 mmol) and NBS (178 mg, 1 mmol, 1 equiv) in MeCN (2 mL), pyridine (0.33 mL, 4 mmol, 4 equiv) was added at rt and the reaction was stirred overnight. Solvent was removed under reduced pressure, water (10 mL) was added and product was extracted into Et₂O (3 × 10 mL). Combined organic phase was washed with 1 M HCl (5 mL), brine (5 mL), dried (MgSO₄), and solvent was removed under reduced pressure. Column chromatography (hexane) provided product as a colorless liquid (99 mg, 35% yield). Characterization corresponds to literature.^[17]

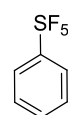
Synthesis of (pentafluorosulfonyl)benzenes **6** by hydrodediazotization of aryldiazonium tetrafluoroborates, General procedure



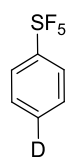
A solution of **3** (159 mg, 0.5 mmol) in THF (0.50 mL) and MeCN (2 mL) was cooled to -25 °C and pyridine (165 μ L, 2.0 mmol, 4.0 equiv) as added over half a minute. The reaction mixture was warmed to rt over 2 h. 4-Nitro(pentafluorosulfonyl)benzene (ca 0.5 mmol) was then added as an internal standard and the yield was calculated based on ¹⁹F NMR. Side products dihydrofuran (**11**) was observed by GCMS: MS (EI⁺): *m/z* (%) = 70 (100), 69 (52), 42 (25), 41(85), 40 (23), 39 (73), 38 (13) and pyridinium tetrafluoroborate by ¹¹B and ¹⁹F NMR.



Prepared independently by mixing H₃BO₃ (248 mg, 4.0 mmol, 1 equiv) with aqueous 40% HF (800 mg, 16.0 mmol, 4 equiv) followed by addition of pyridine (411 mg, 5.2 mmol, 1.3 equiv) ^{BF₄⁻} at rt. Addition of MeCN (4 mL), MeOH (1 mL) and Et₂O (25 mL) filtration and drying the solid under reduced pressure provided product as white solid (528 mg, 60% yield): ¹¹B NMR (128 MHz, CD₃CN): δ = -0.5 (s); ¹⁹F NMR (376 MHz, CD₃CN): δ = -150.2 (s).



6: Prepared according to the general procedure from **3a** (159 mg, 0.5 mmol), THF (0.50 mL), MeCN (2 mL) and pyridine (165 μ L, 2.0 mmol, 4.0 equiv) in 75% ¹⁹F NMR yield: ¹⁹F NMR (377 MHz, CDCl₃): δ 63.2 (d, ²*J*_{F,F} = 147.7, 4F), 85.0–86.6 (m, 1F); MS (EI⁺): *m/z* (%) = 204 (71), 96 (94), 89(22), 77 (100), 74 (10), 70 (10), 51 (44), 50 (23); or from **3b** (159 mg, 0.5 mmol), THF (0.50 mL), MeCN (2 mL) and pyridine (165 μ L, 2.0 mmol, 4.0 equiv) in 70% ¹⁹F NMR yield.



6-D: Prepared according to the general procedure from **3b** (159 mg, 0.5 mmol), [D₈]THF (0.50 mL), MeCN (2 mL) and pyridine (165 μ L, 2.0 mmol, 4.0 equiv) in 48% ¹⁹F NMR yield and 77-82% deuterium enrichment determined by GCMS; ¹⁹F (377 MHz, CDCl₃): δ = 63.2 (d, ²J_{F,F} = 148.0, 4F), 85.0–86.6 (m, 1F); MS (EI⁺): *m/z* (%) (**6** + **6-D**) = 205 (100), 204 (22), 127 (11), 97 (99), 96 (25), 89 (30), 78 (100), 77 (28), 52 (24), 51 (33), 50 (18).

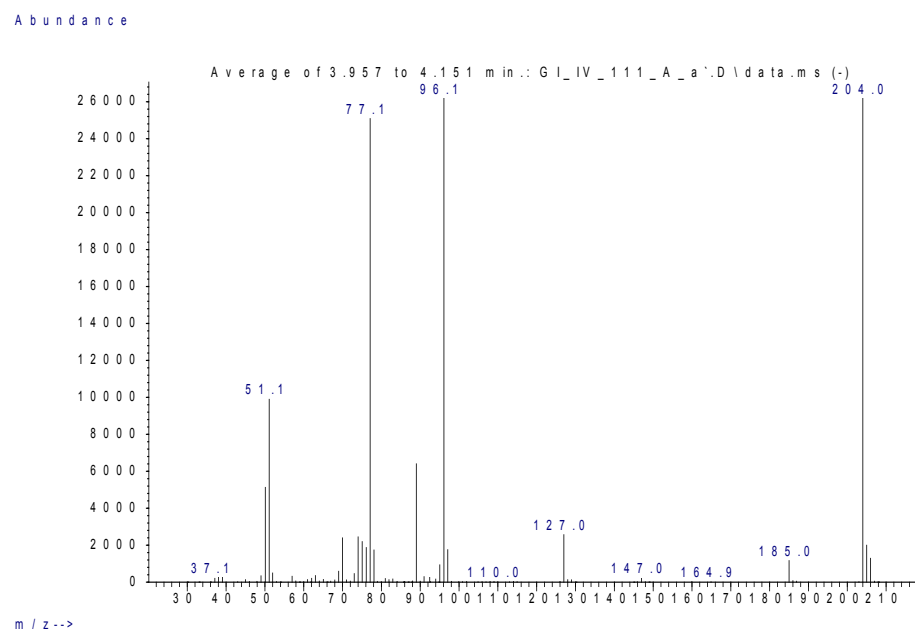


Figure S8: MS (EI⁺) spectrum of **6**.

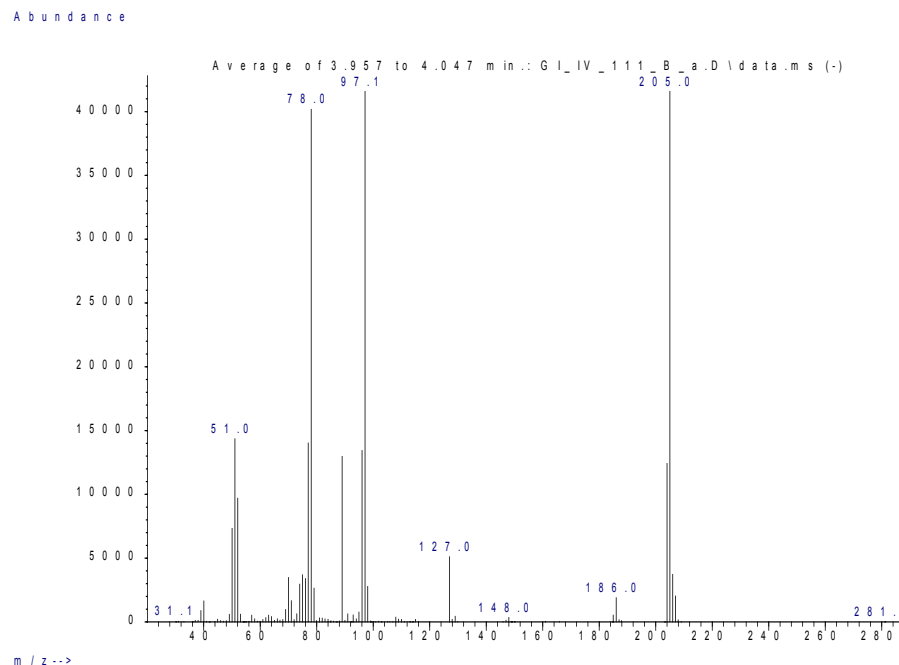


Figure S9: MS (EI⁺) spectrum of a mixture of **6** and **6-D** in ca 20:80 ratio.

KIE experiment

A solution of **3b** (159 mg, 0.5 mmol) in a mixture THF (0.25 mL), [D₈]THF (0.25 mL) and MeCN (2 mL) was cooled to −25 °C. Pyridine (165 μ L, 2.0 mmol, 4.0 equiv) was added over half a minute and the reaction mixture was warmed to rt over 2 h. 4-Nitro(pentafluorosulfonyl)benzene (0.5 mmol) was then added as an internal standard and the yield was calculated based on ¹⁹F NMR. A mixture of **6** and **6-D** formed in 62% ¹⁹F NMR yield and **6**:**6-D** ratio of 5.5 (determined by GC–MS, Figures S10 and S11).

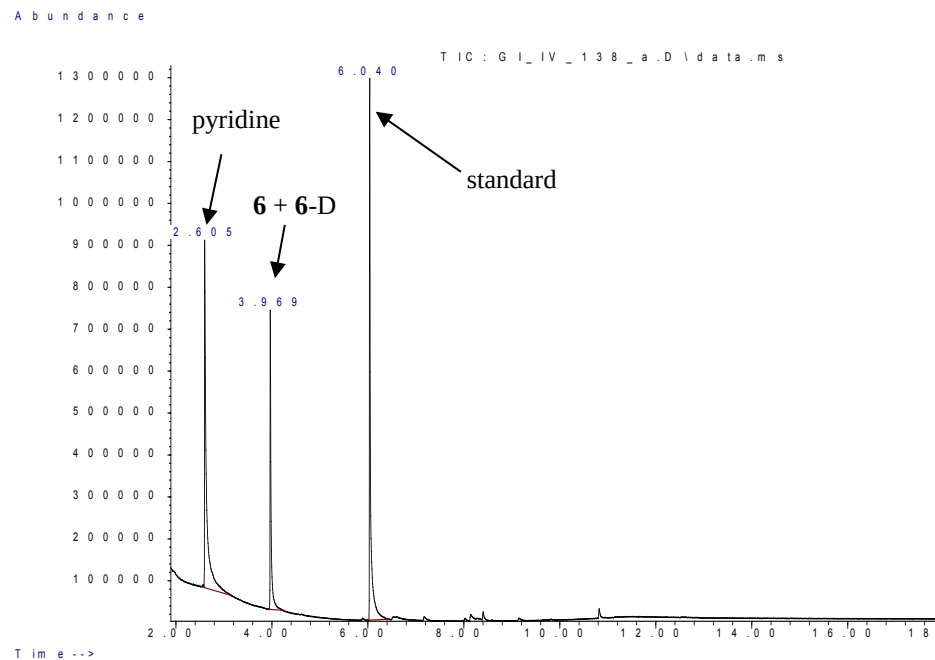


Figure S10: GC chromatogram of the crude product mixture after the KIE experiment.

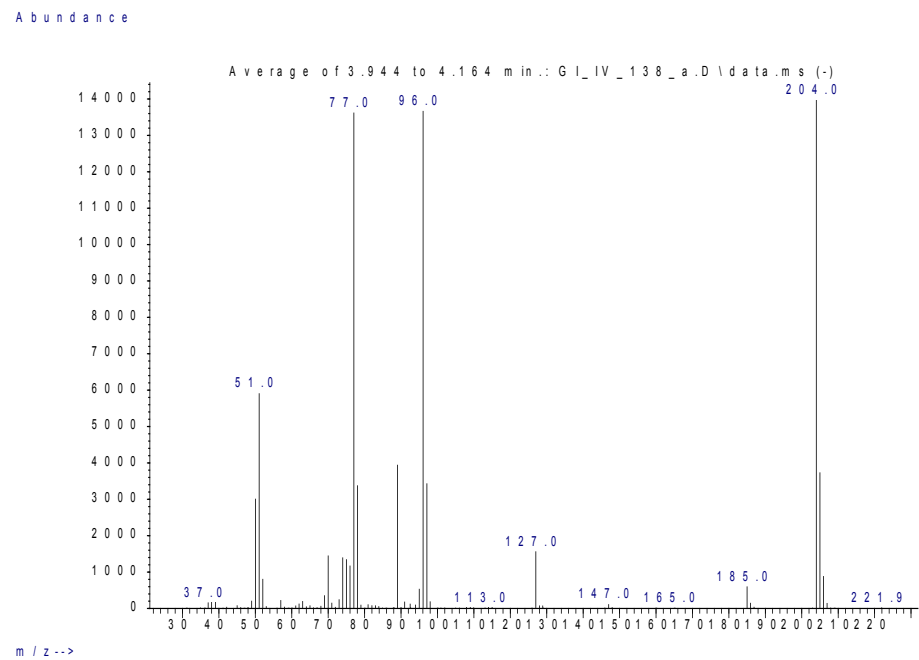
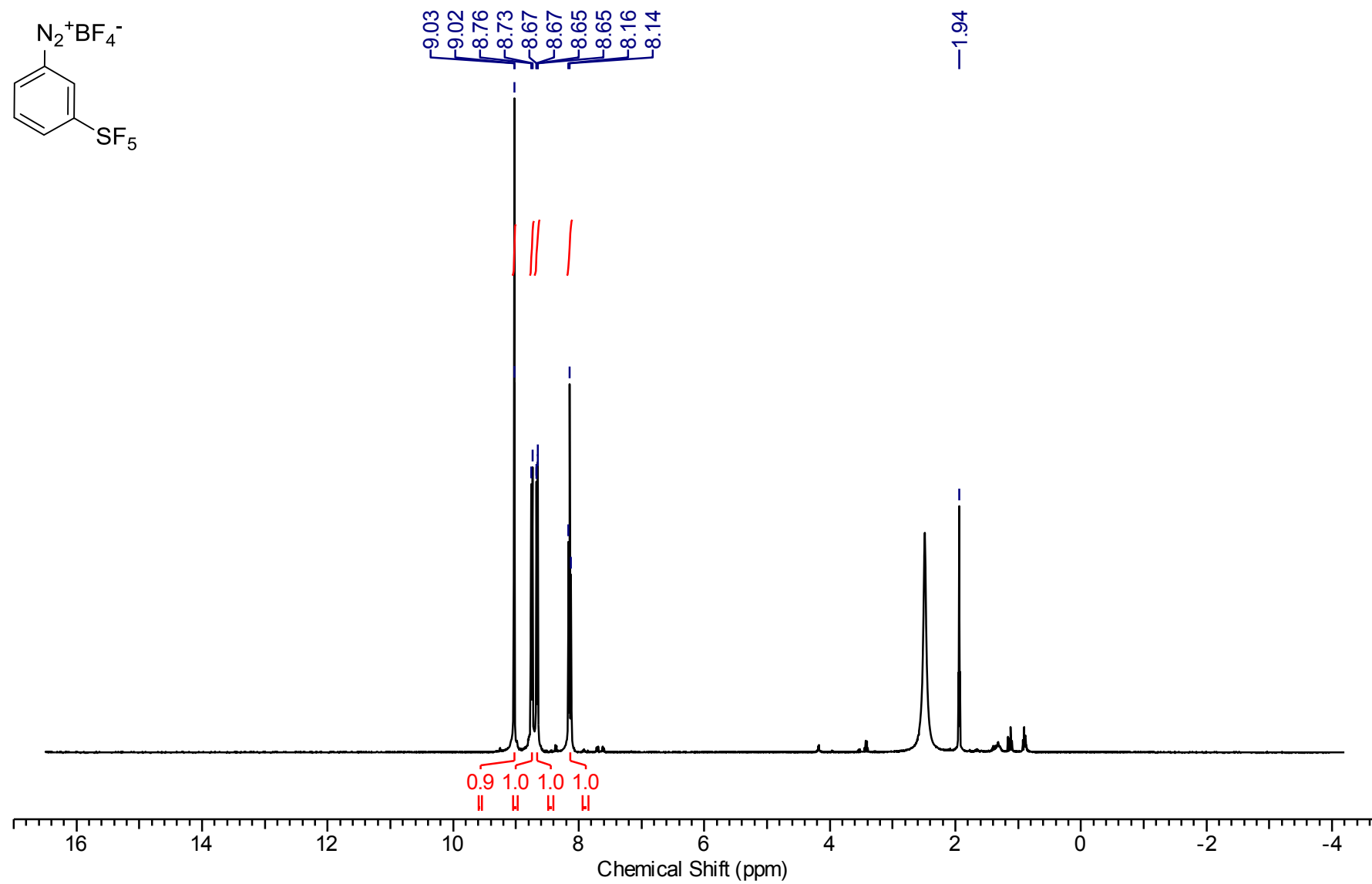
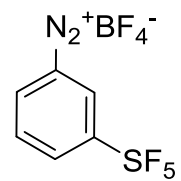
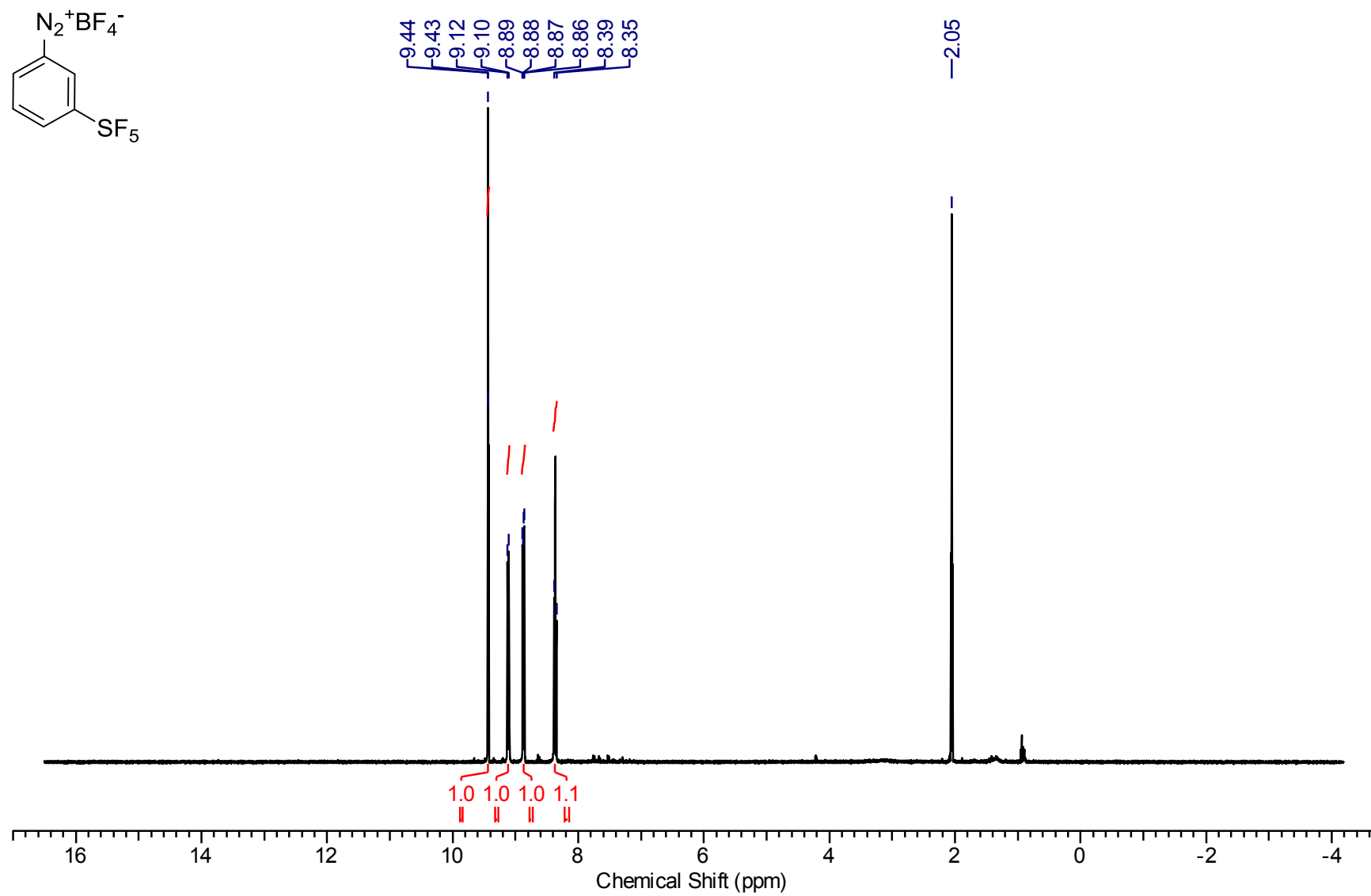


Figure S11: MS (EI^+) spectrum of a mixture of **6** + **6-D**.

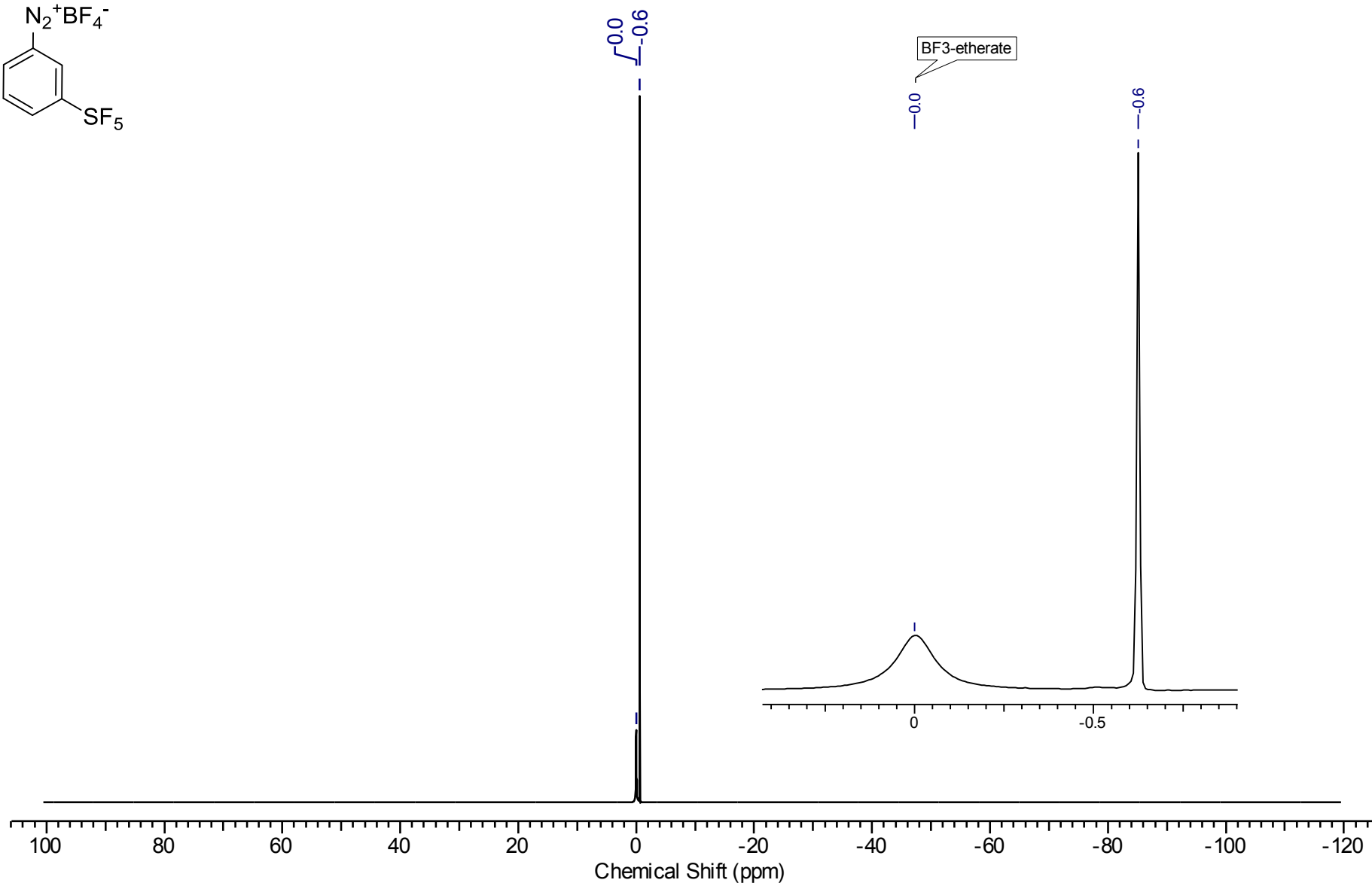
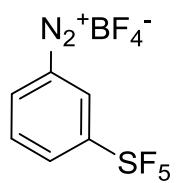
3a: ^1H NMR (400 MHz, CD_3CN)



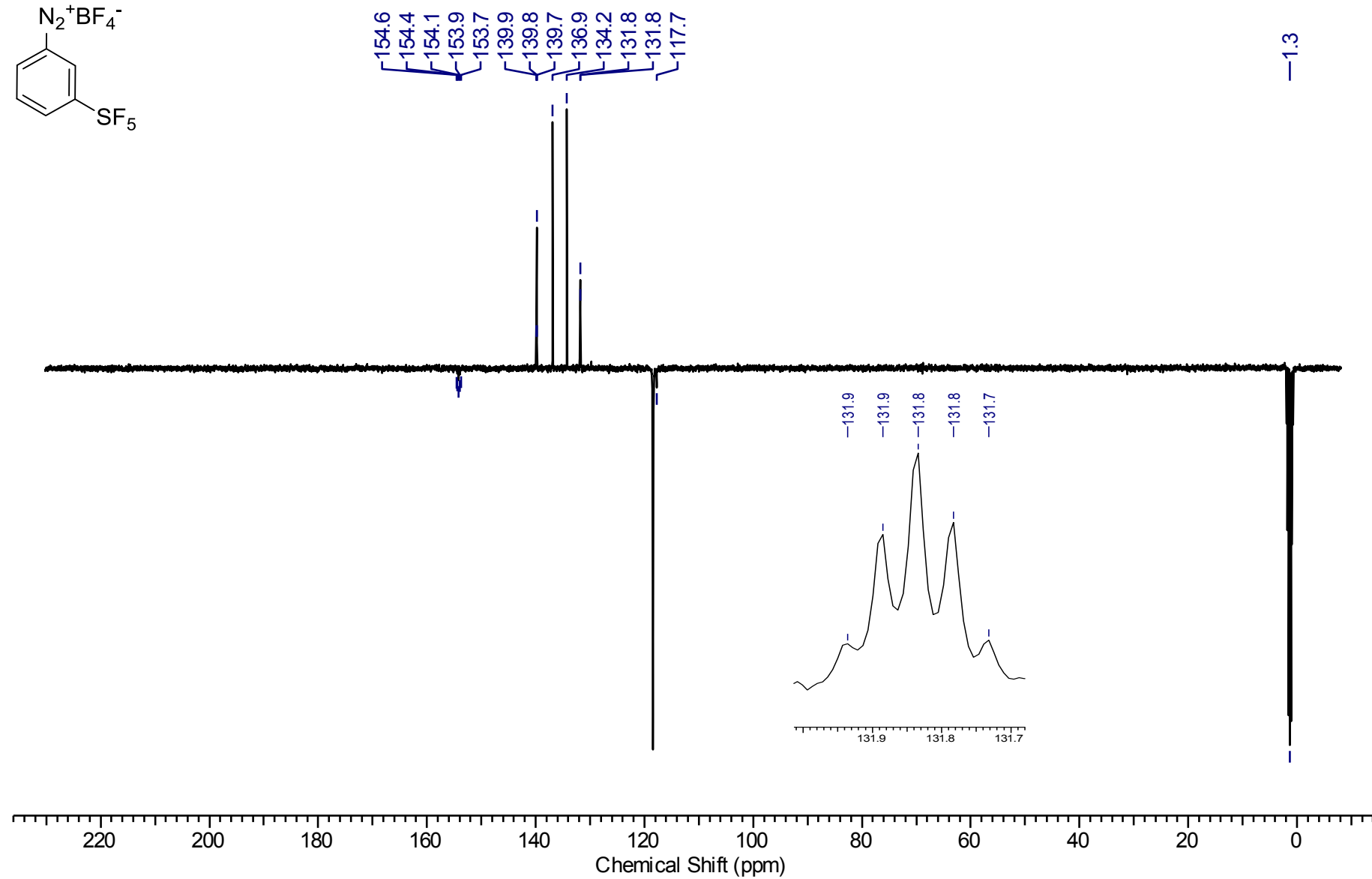
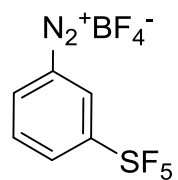
3a: ^1H NMR (400 MHz, $[\text{D}_6]$ acetone)



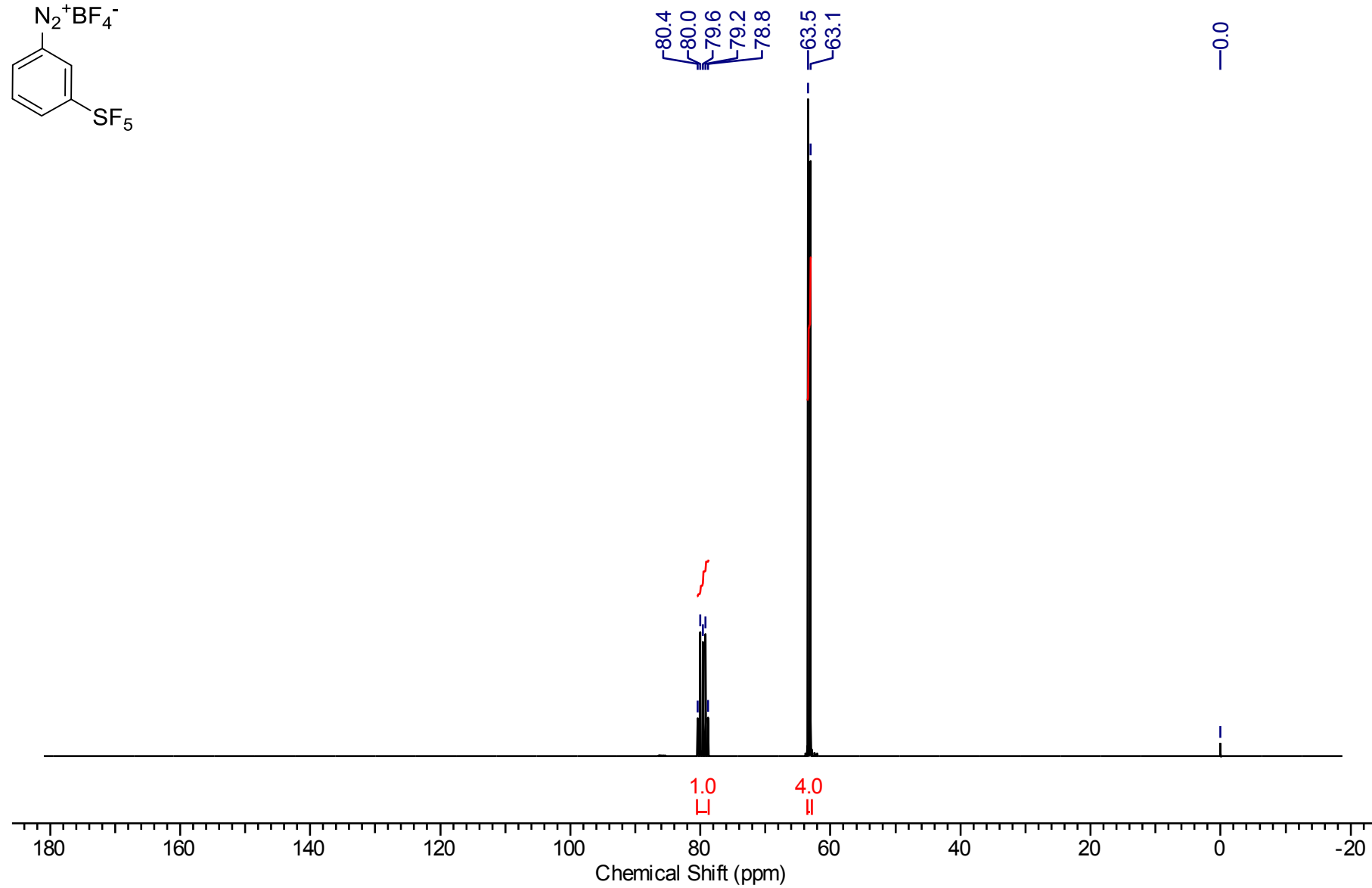
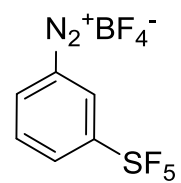
3a: ^{11}B NMR (128 MHz, CD_3CN)



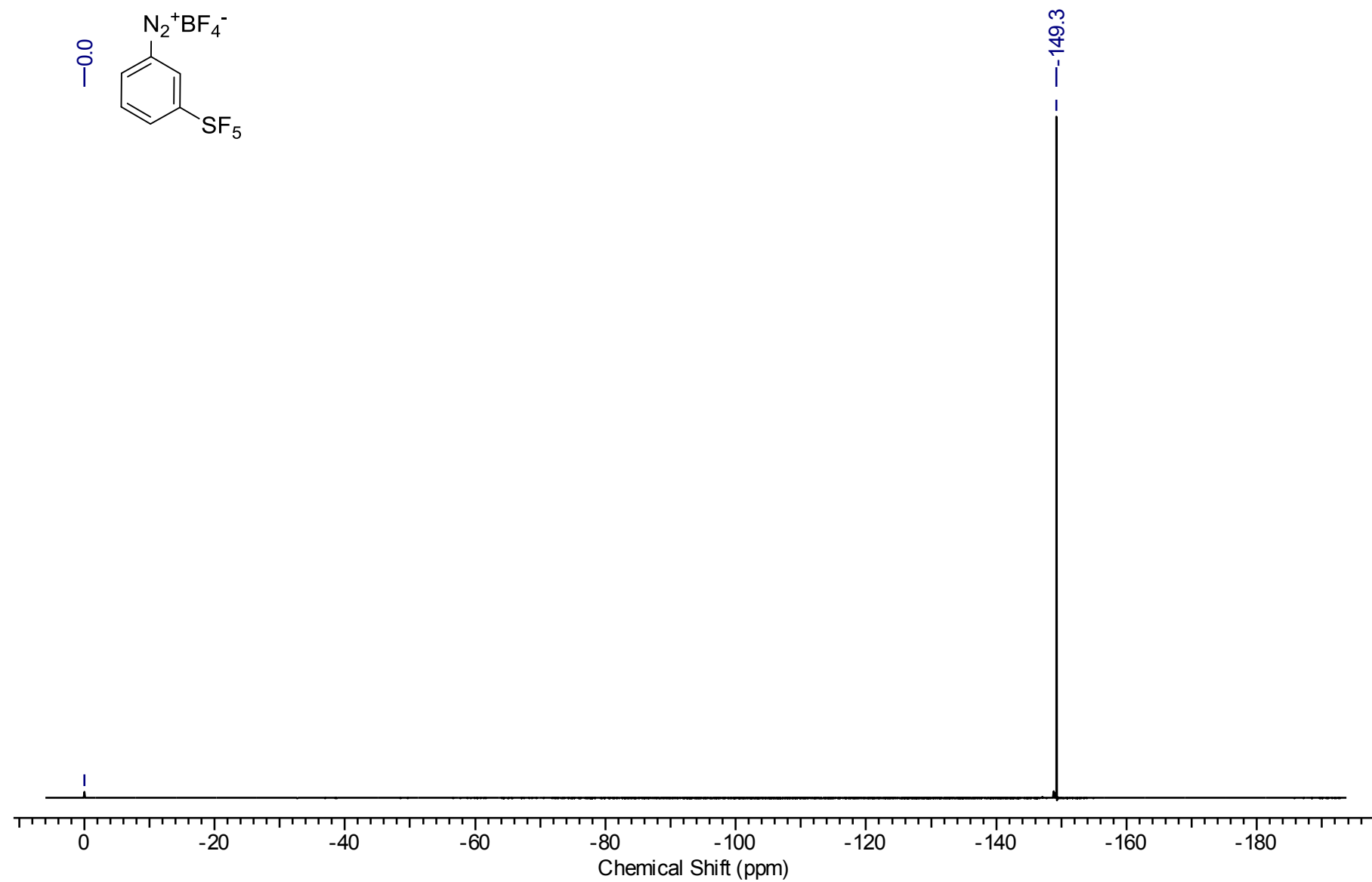
3a: ^{13}C NMR (101 MHz, CD_3CN)



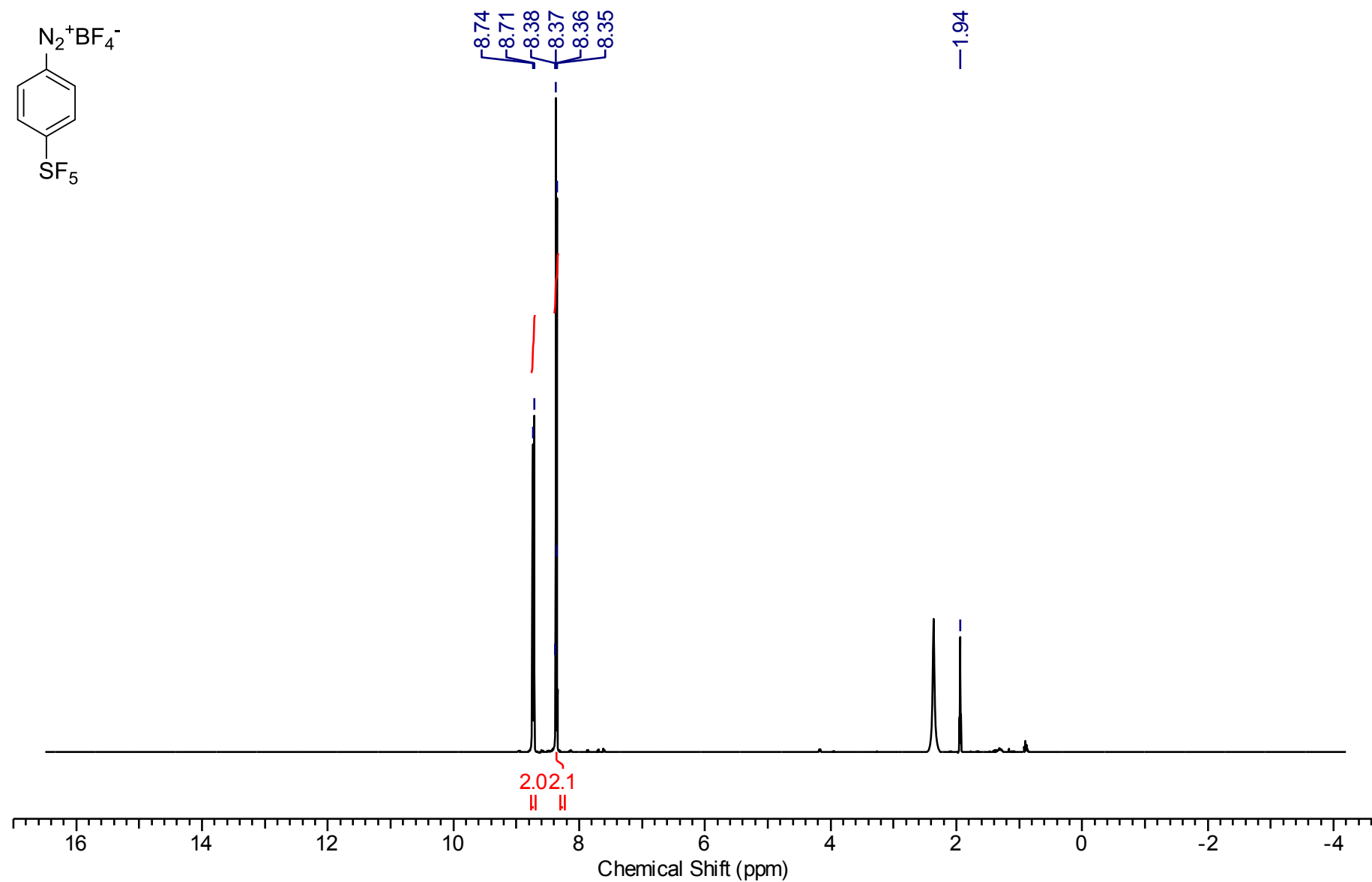
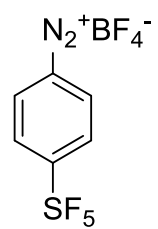
3a: ^{19}F NMR (377 MHz, $[\text{D}_6]\text{acetone}$)



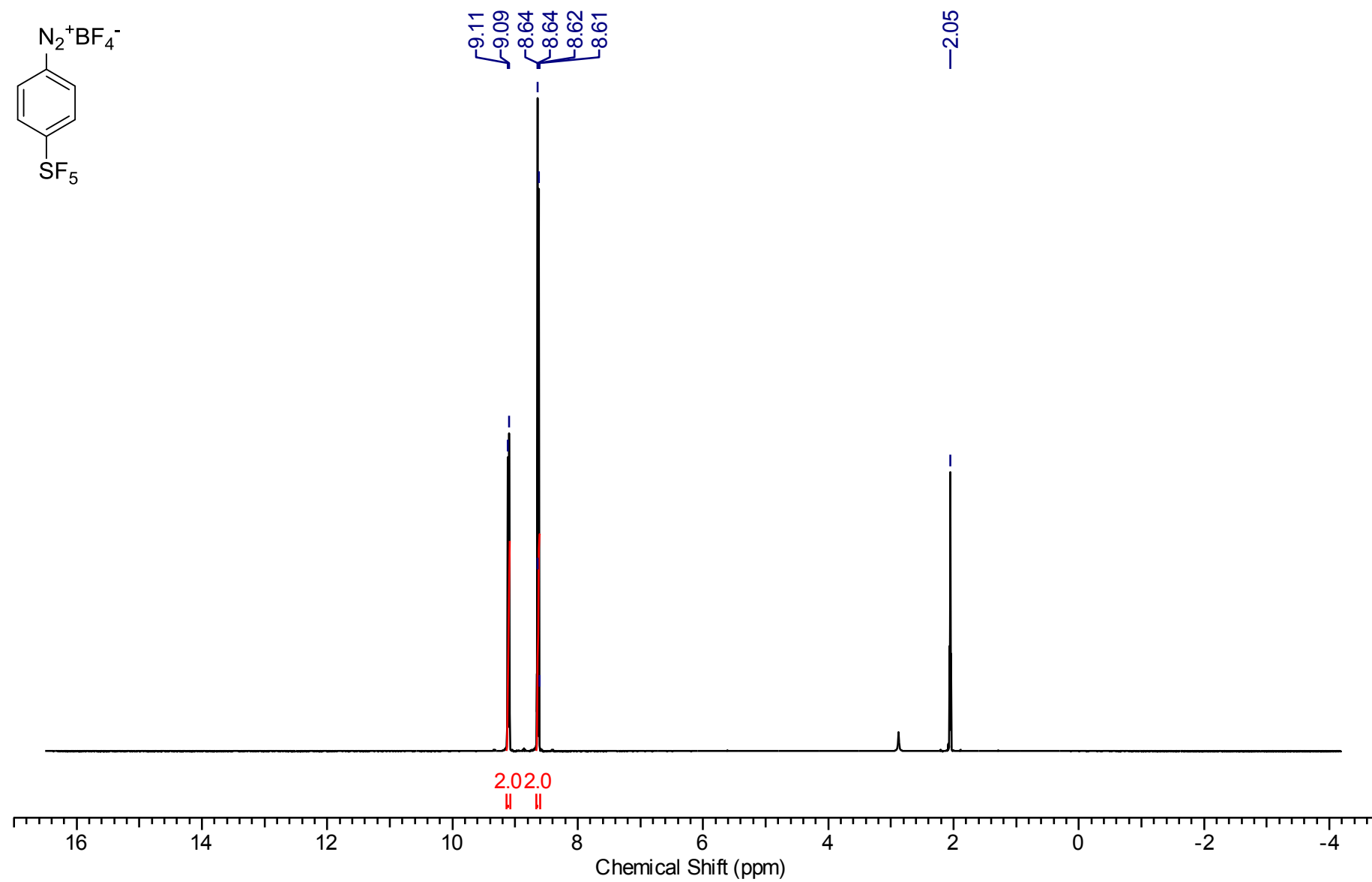
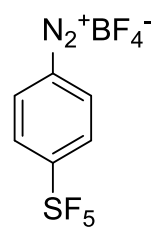
3a: ^{19}F NMR (377 MHz, $[\text{D}_6]\text{acetone}$)



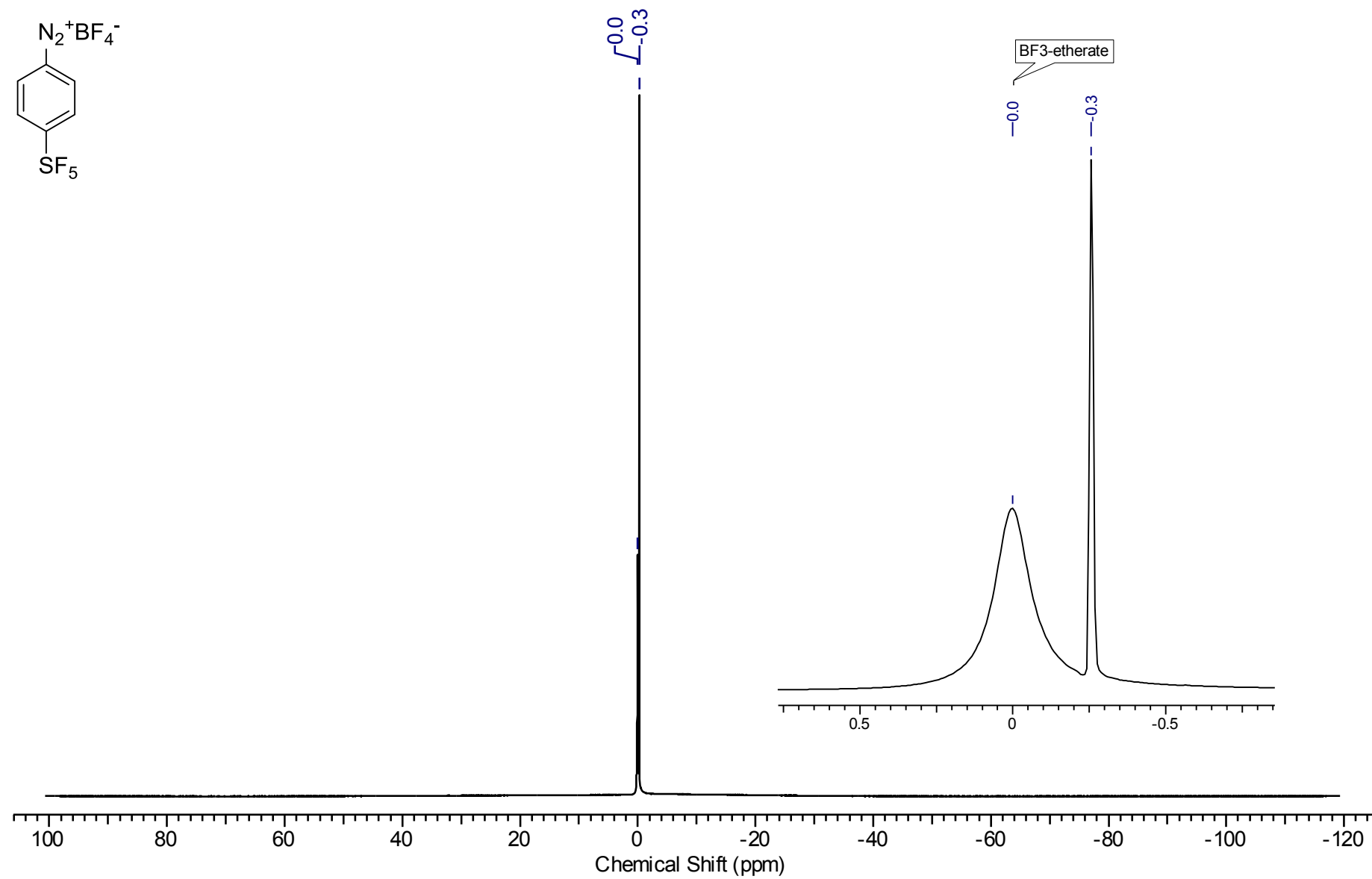
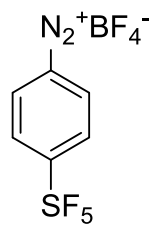
3b: ^1H NMR (400 MHz, CD_3CN)



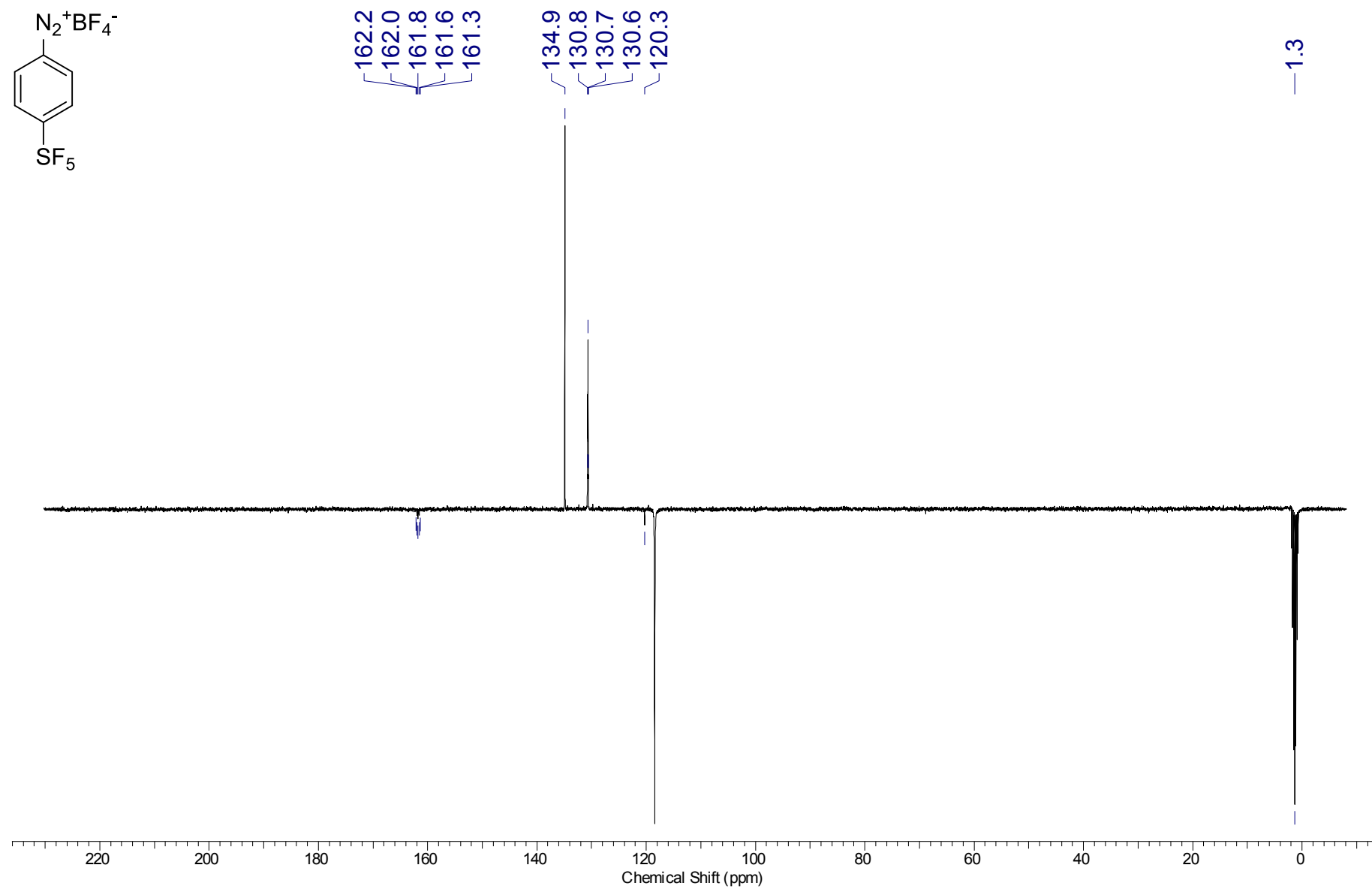
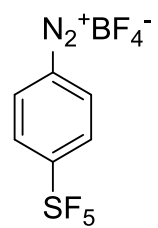
3b: ^1H NMR (400 MHz, $[\text{D}_6]$ acetone)



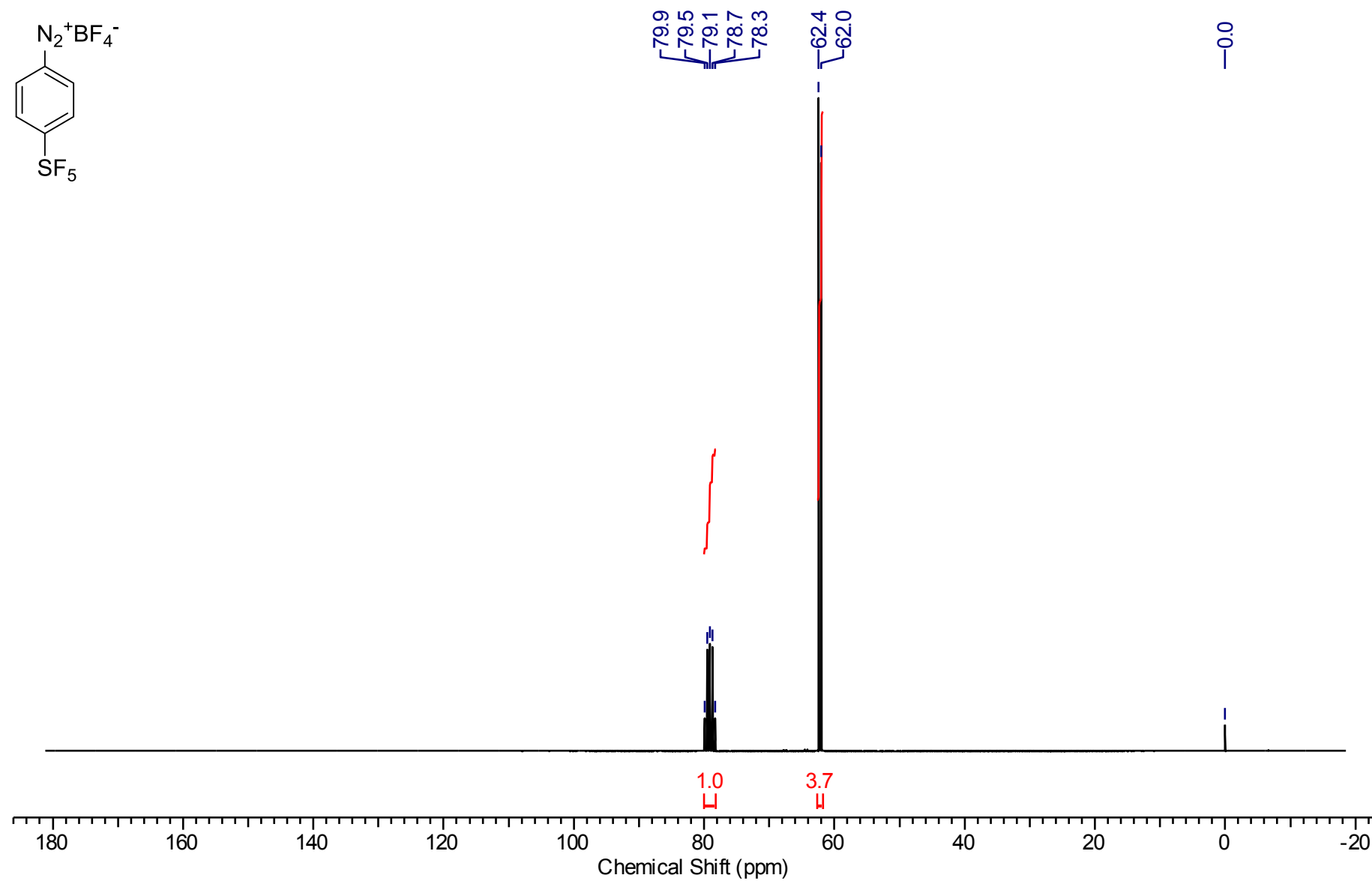
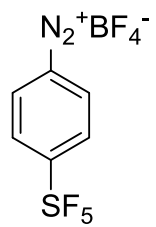
3b: ^{11}B NMR (128 MHz, $[\text{D}_6]\text{acetone}$)



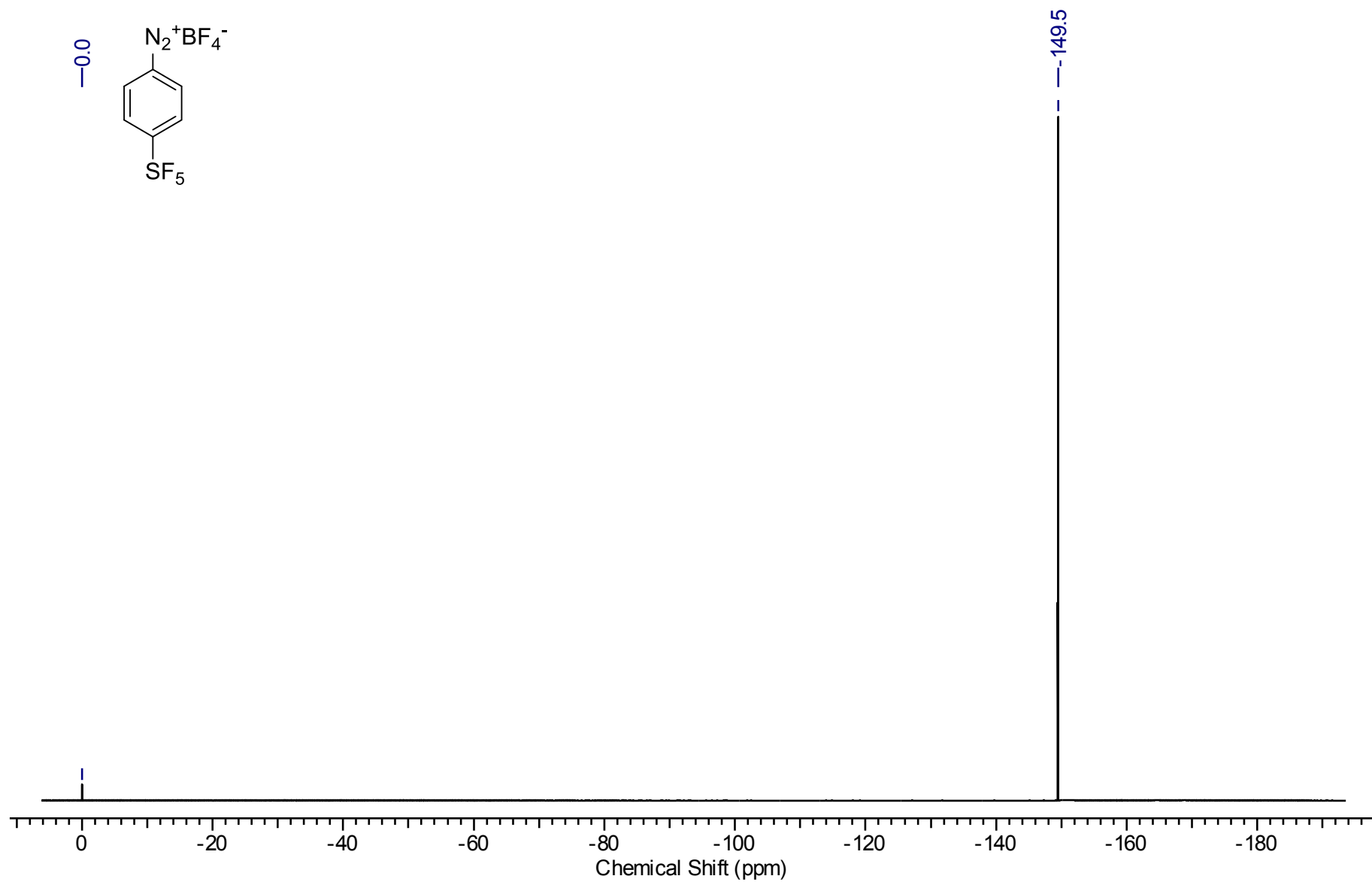
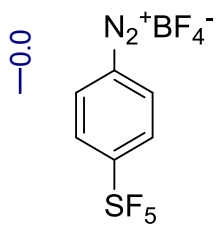
3b: ^{13}C NMR (101 MHz, CD_3CN)



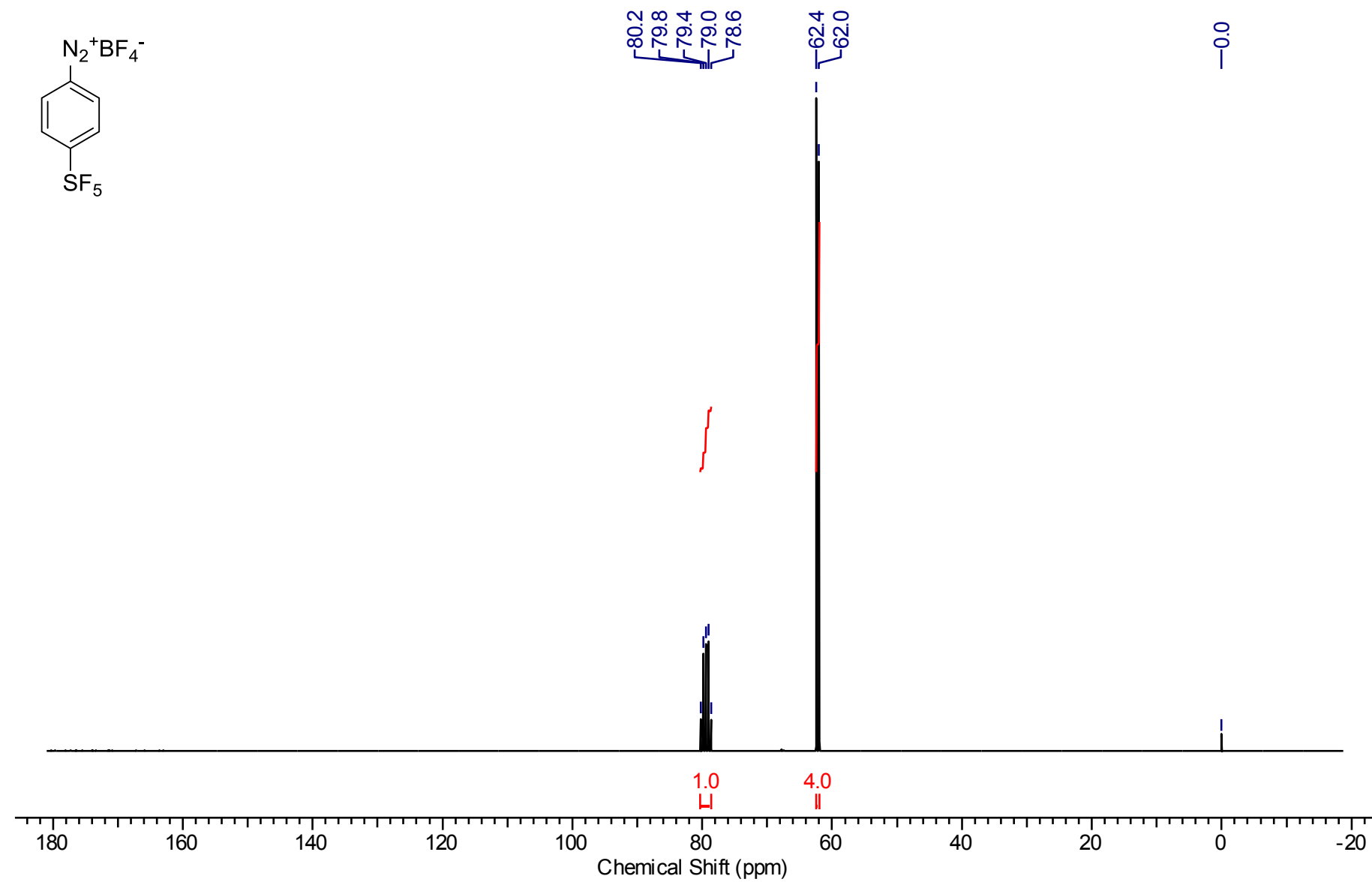
3b: ^{19}F NMR (377 MHz, CD_3CN)



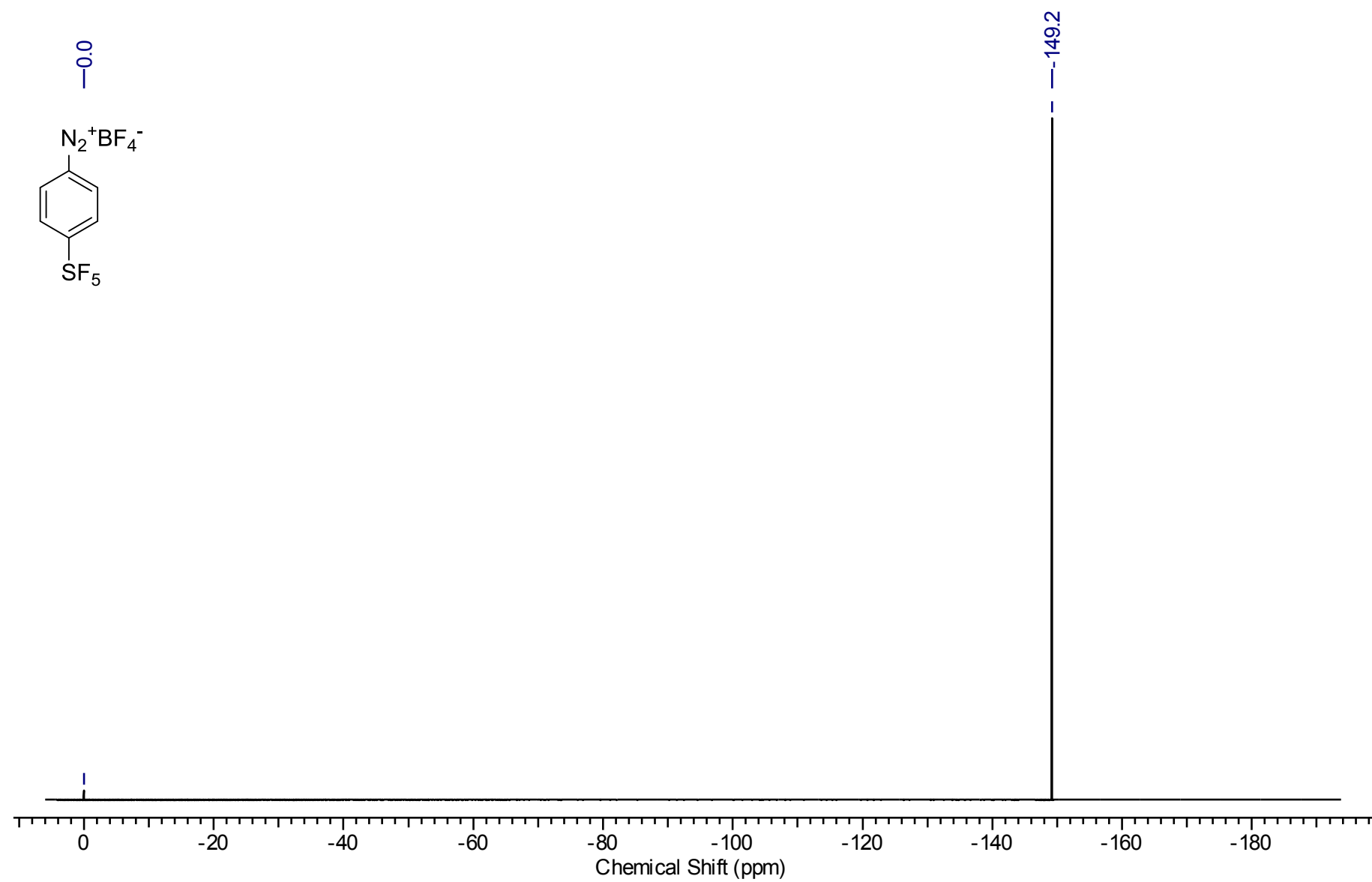
3b: ^{19}F NMR (377 MHz, CD_3CN)



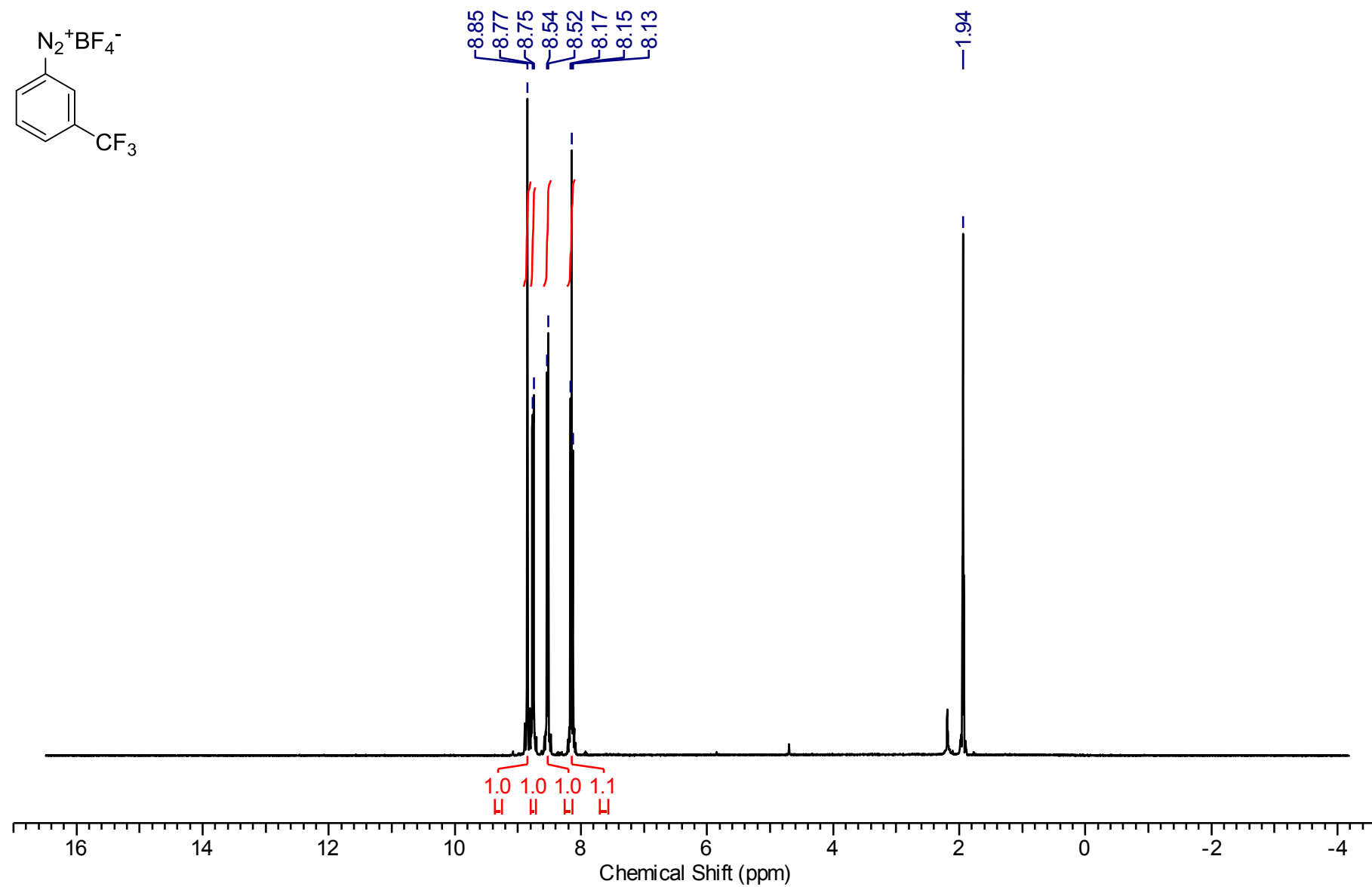
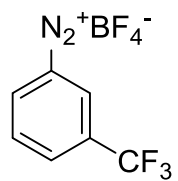
3b: ^{19}F NMR (377 MHz, $[\text{D}_6]\text{acetone}$)



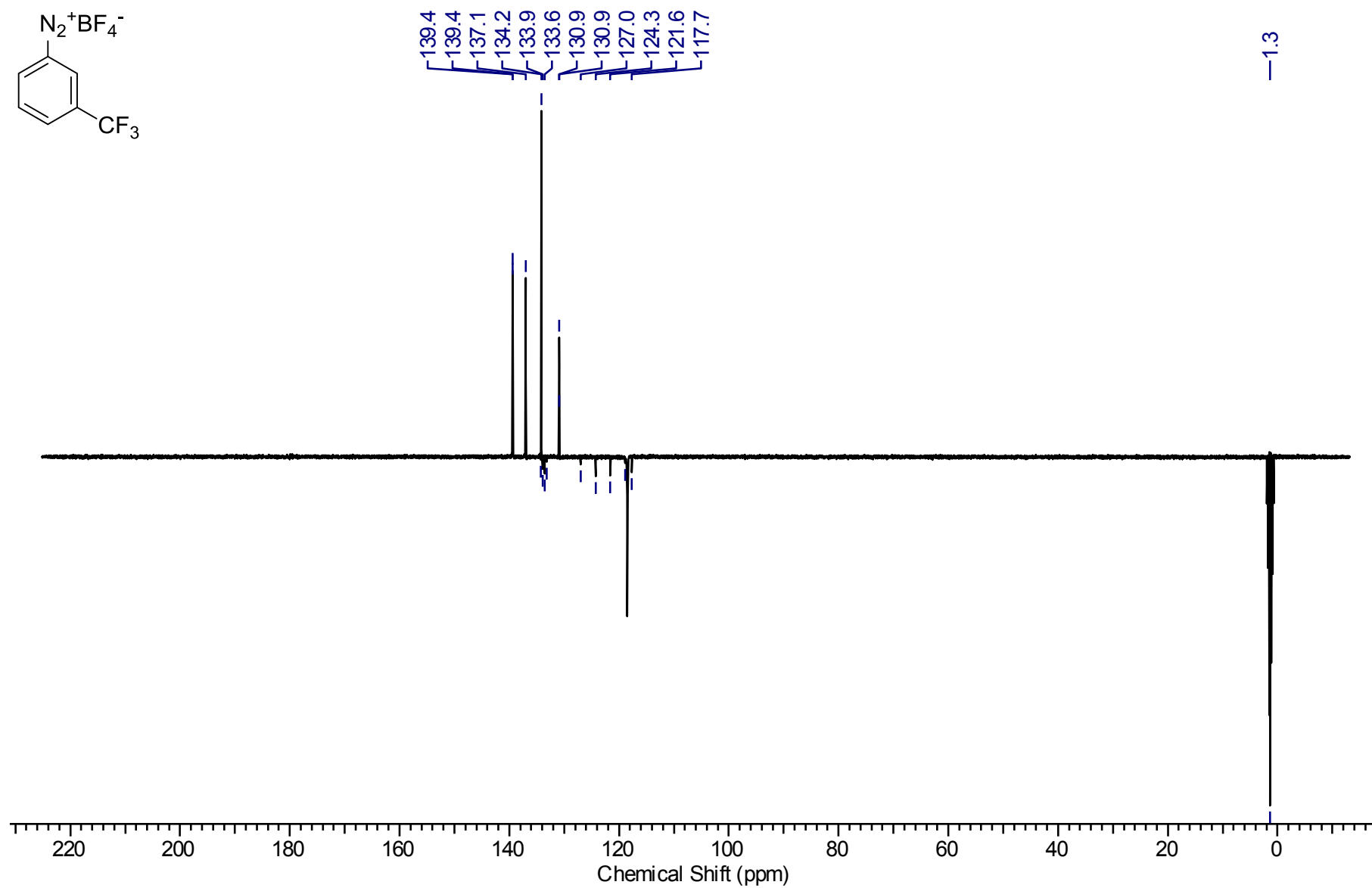
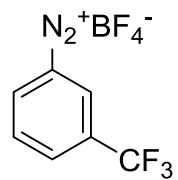
3b: ^{19}F NMR (376 MHz, $[\text{D}_6]\text{acetone}$)



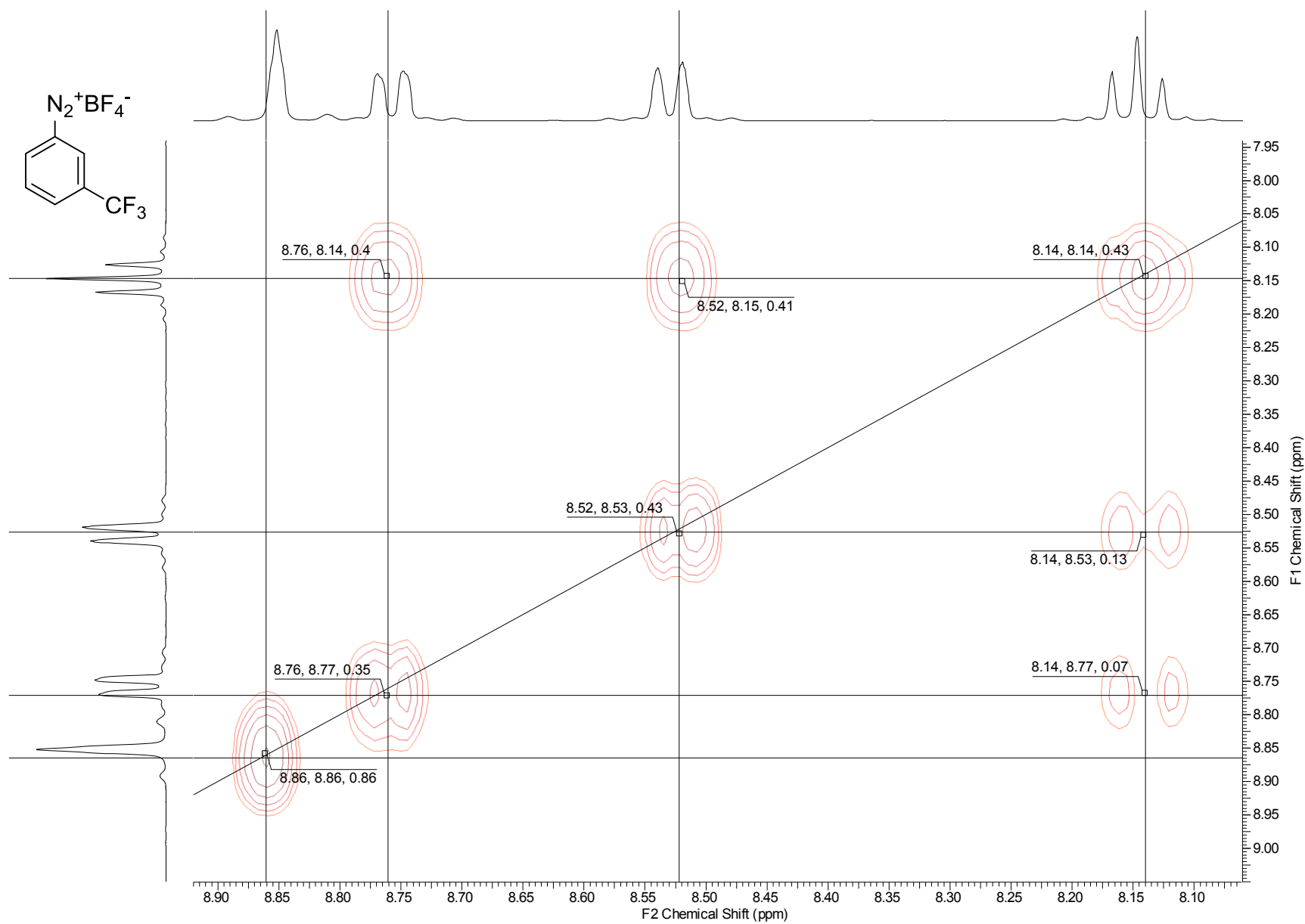
3c: ^1H NMR (400 MHz, CD_3CN)



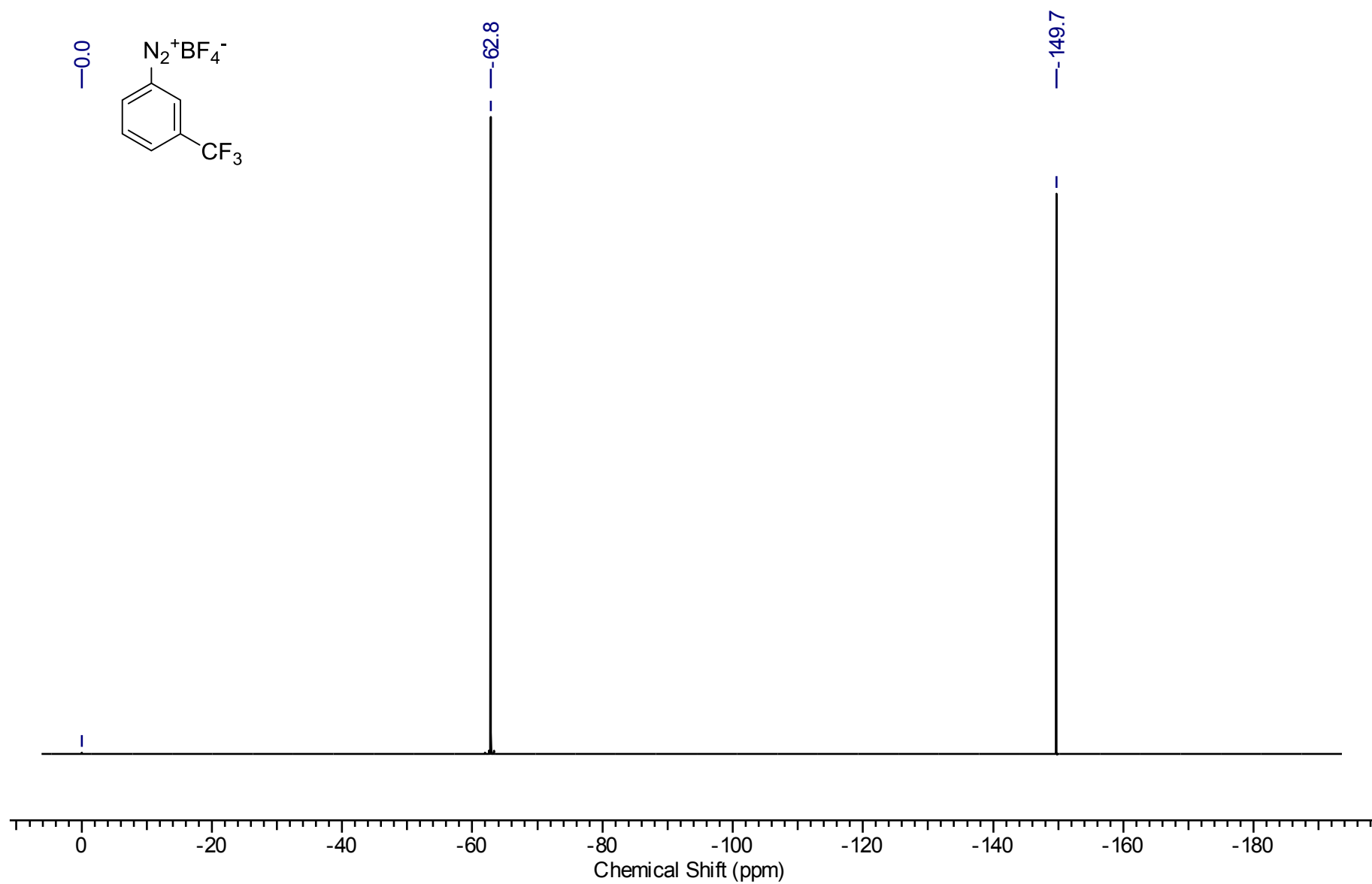
3c: ^{13}C NMR (101 MHz, CD_3CN)



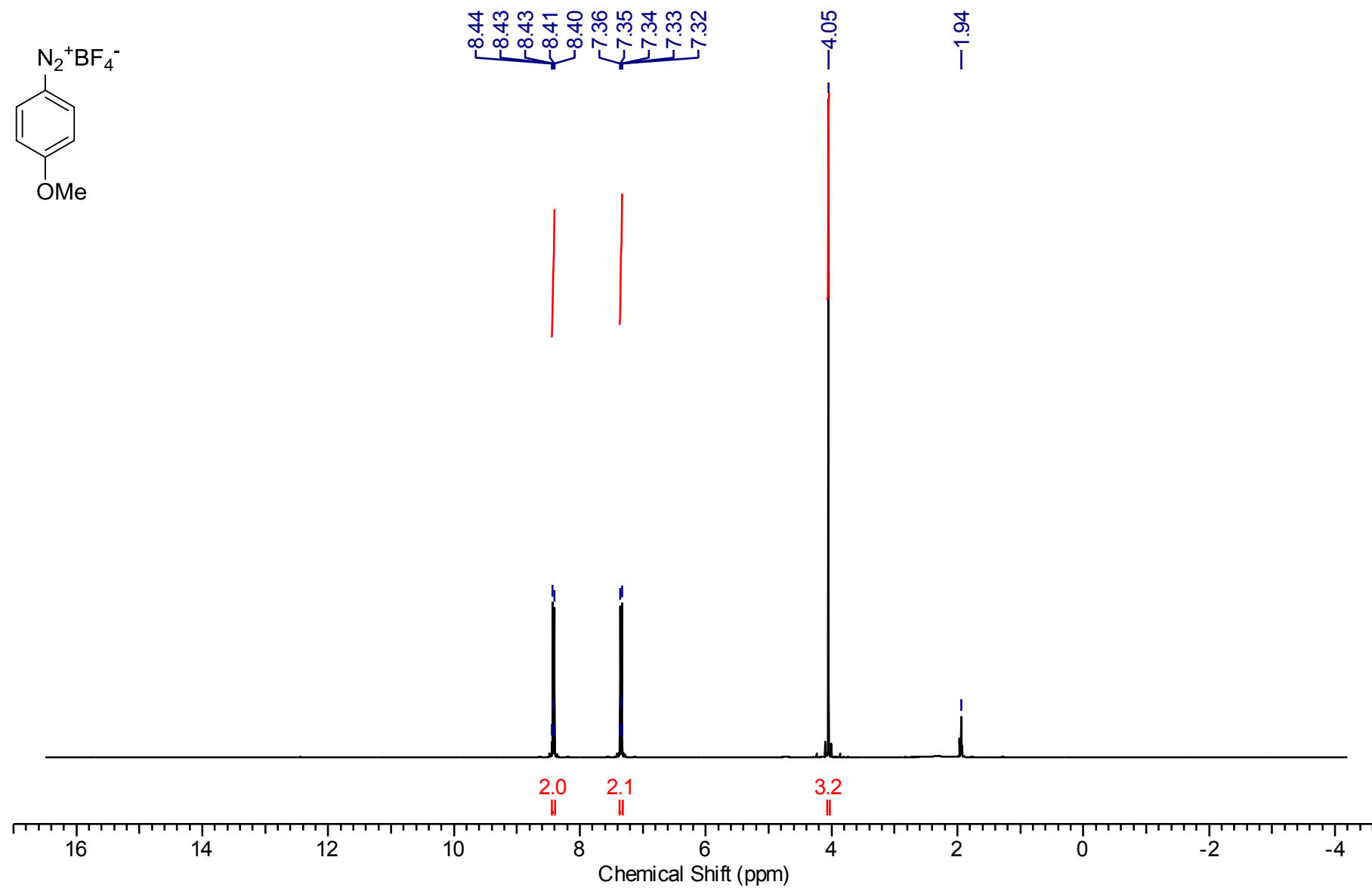
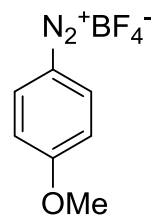
3c: ^1H - ^1H COSY NMR



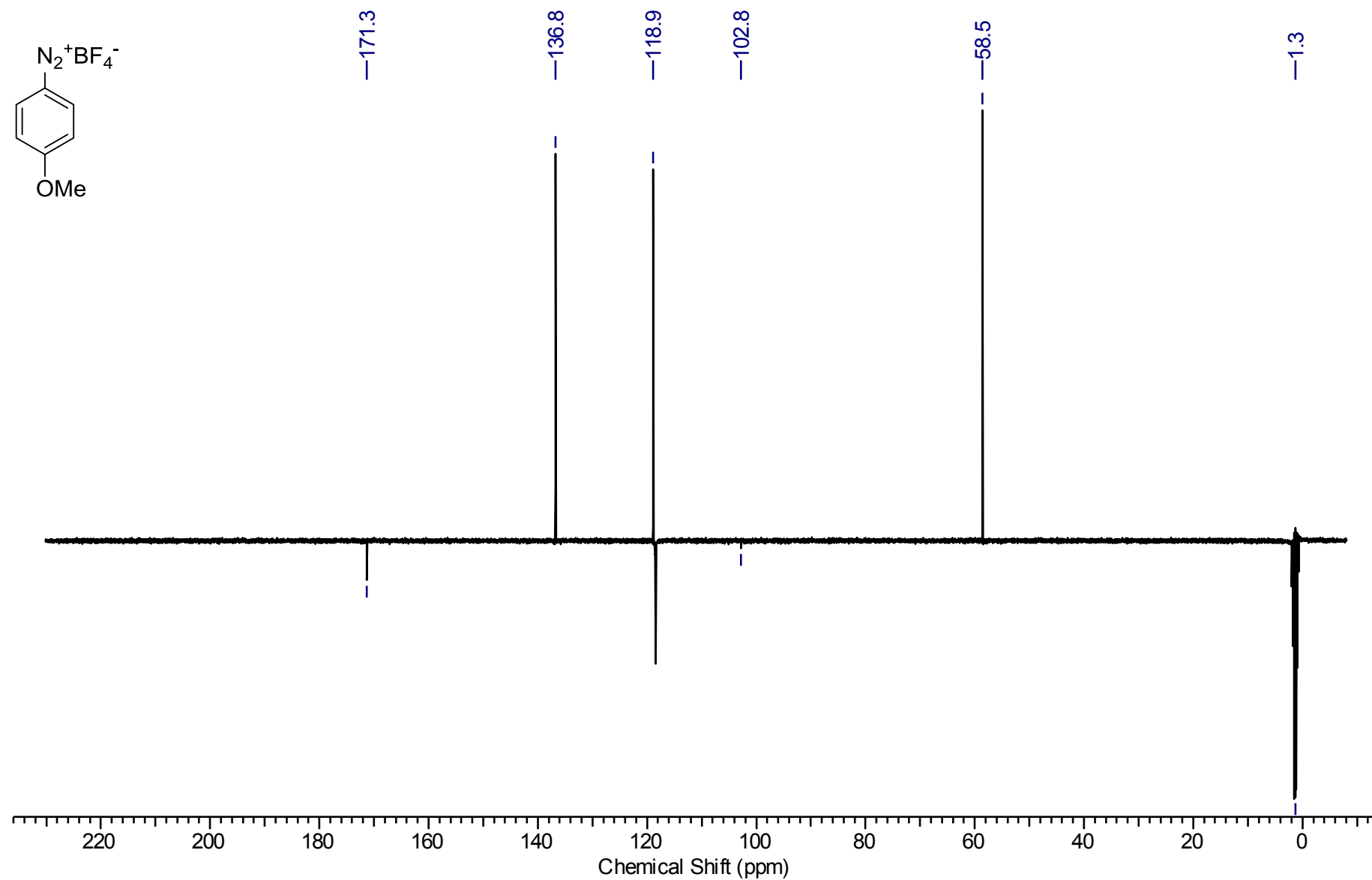
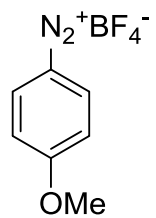
3c: ^{19}F NMR (376 MHz, CD_3CN)



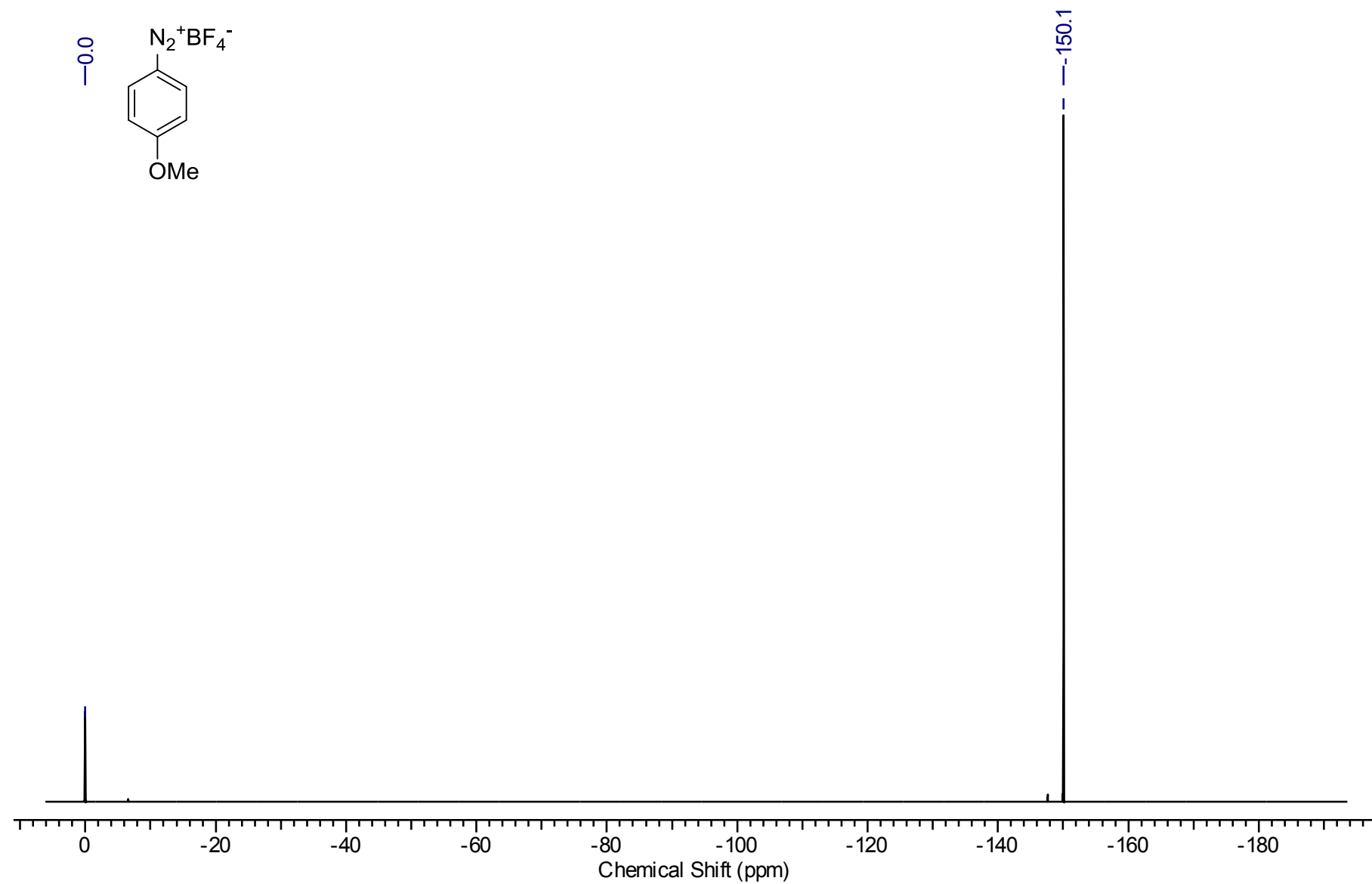
3d: ^1H NMR (400 MHz, CD_3CN)



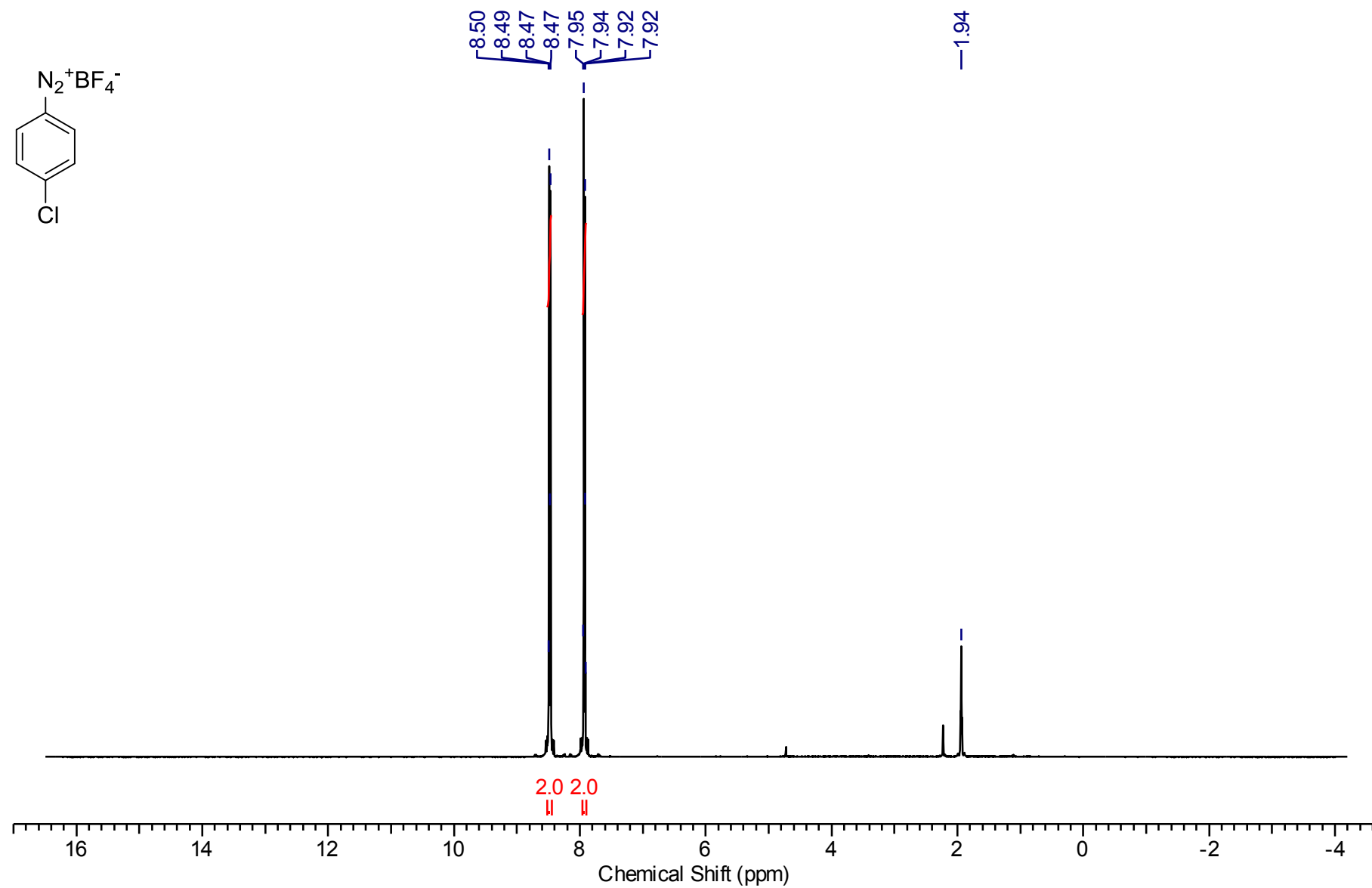
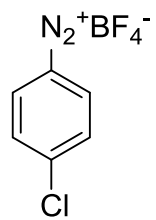
3d: ^{13}C NMR (101 MHz, CD_3CN)



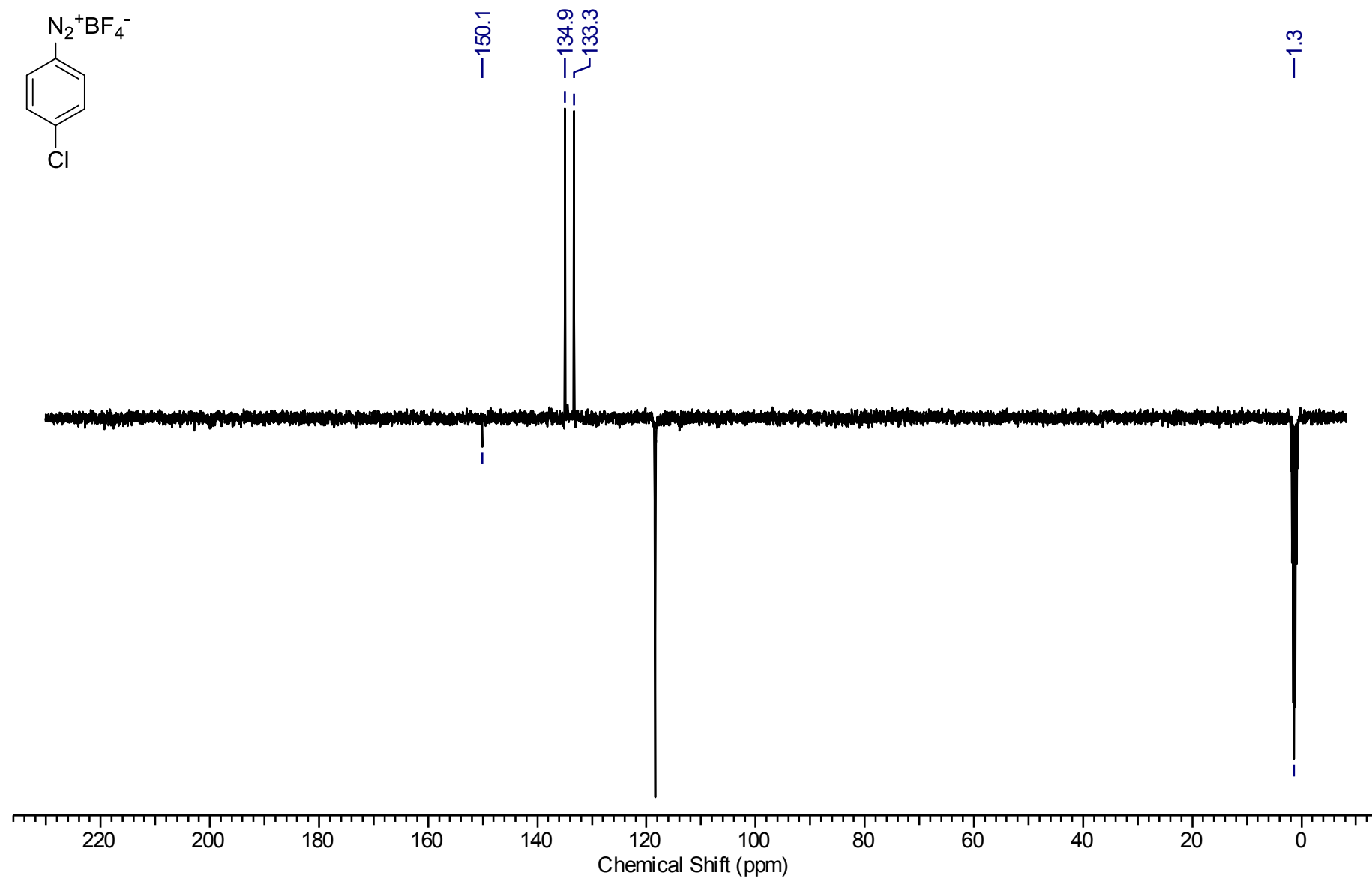
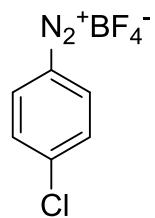
3d: ^{19}F NMR (376 MHz, $[\text{D}_6]\text{acetone}$)



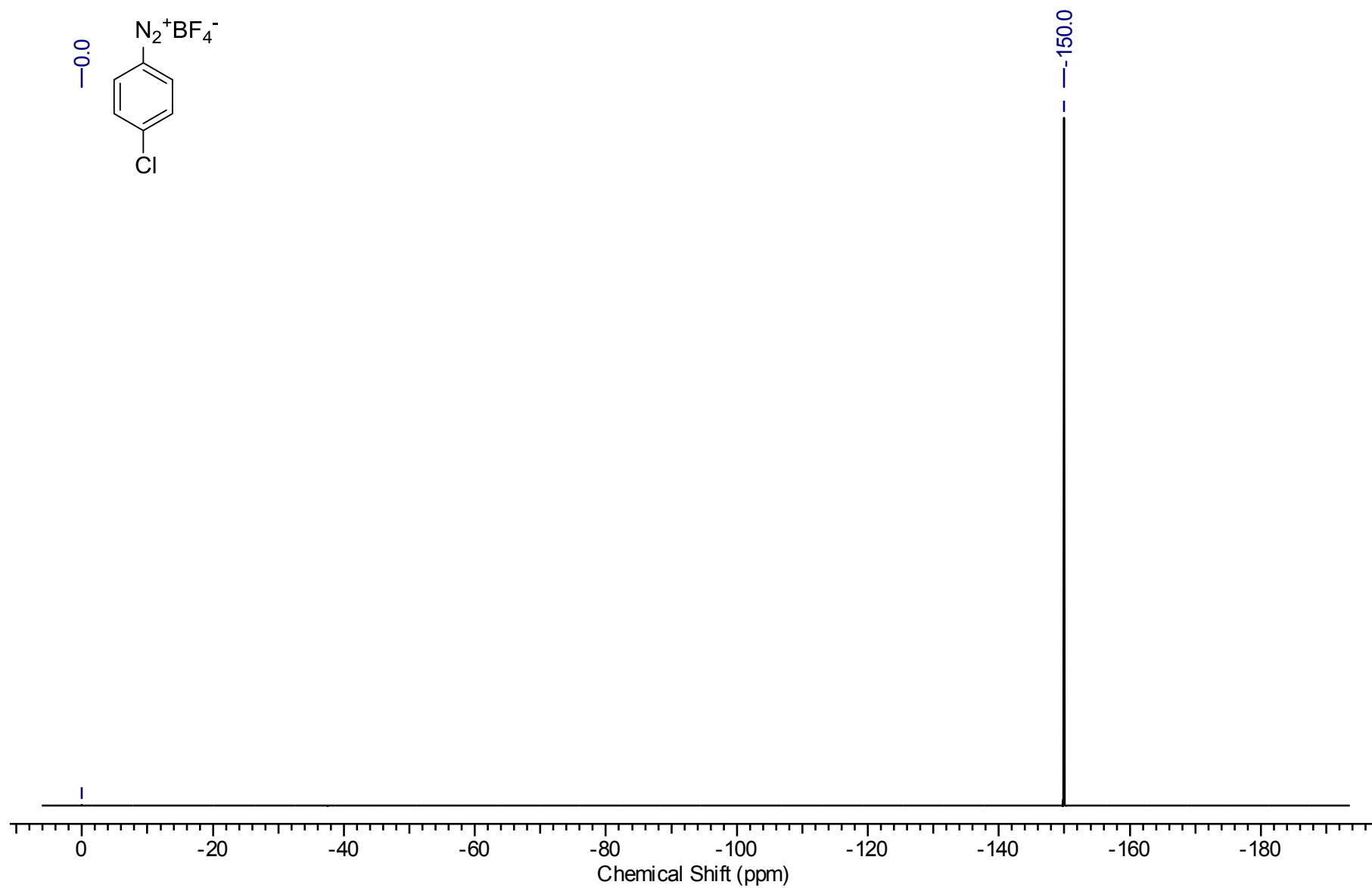
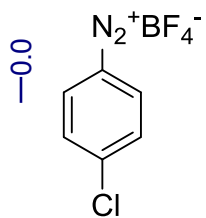
3e: ^1H NMR (400 MHz, CD_3CN)



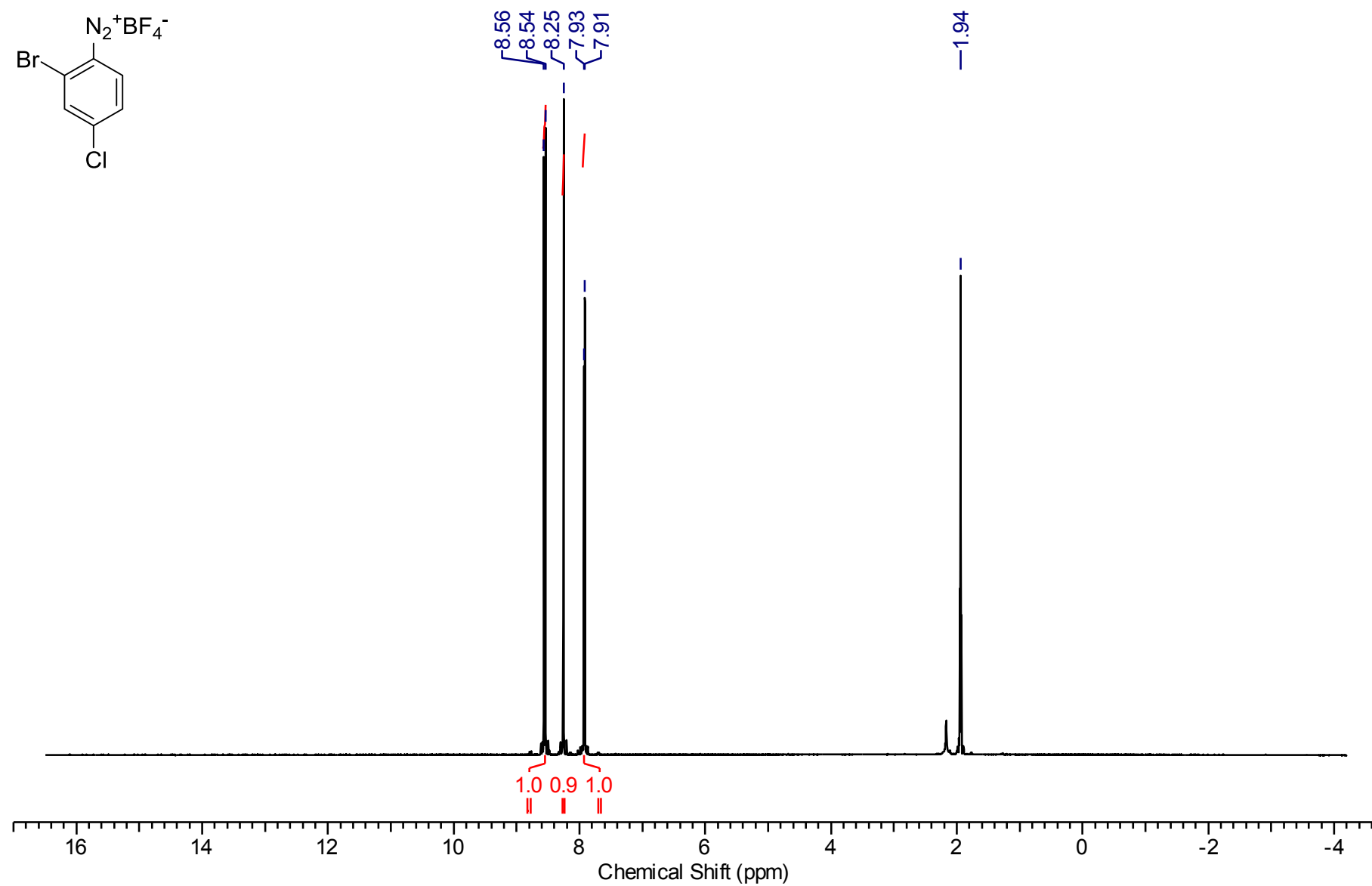
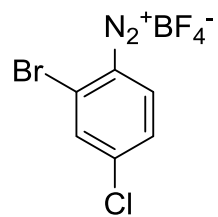
3e: ^{13}C NMR (101 MHz, CD_3CN)



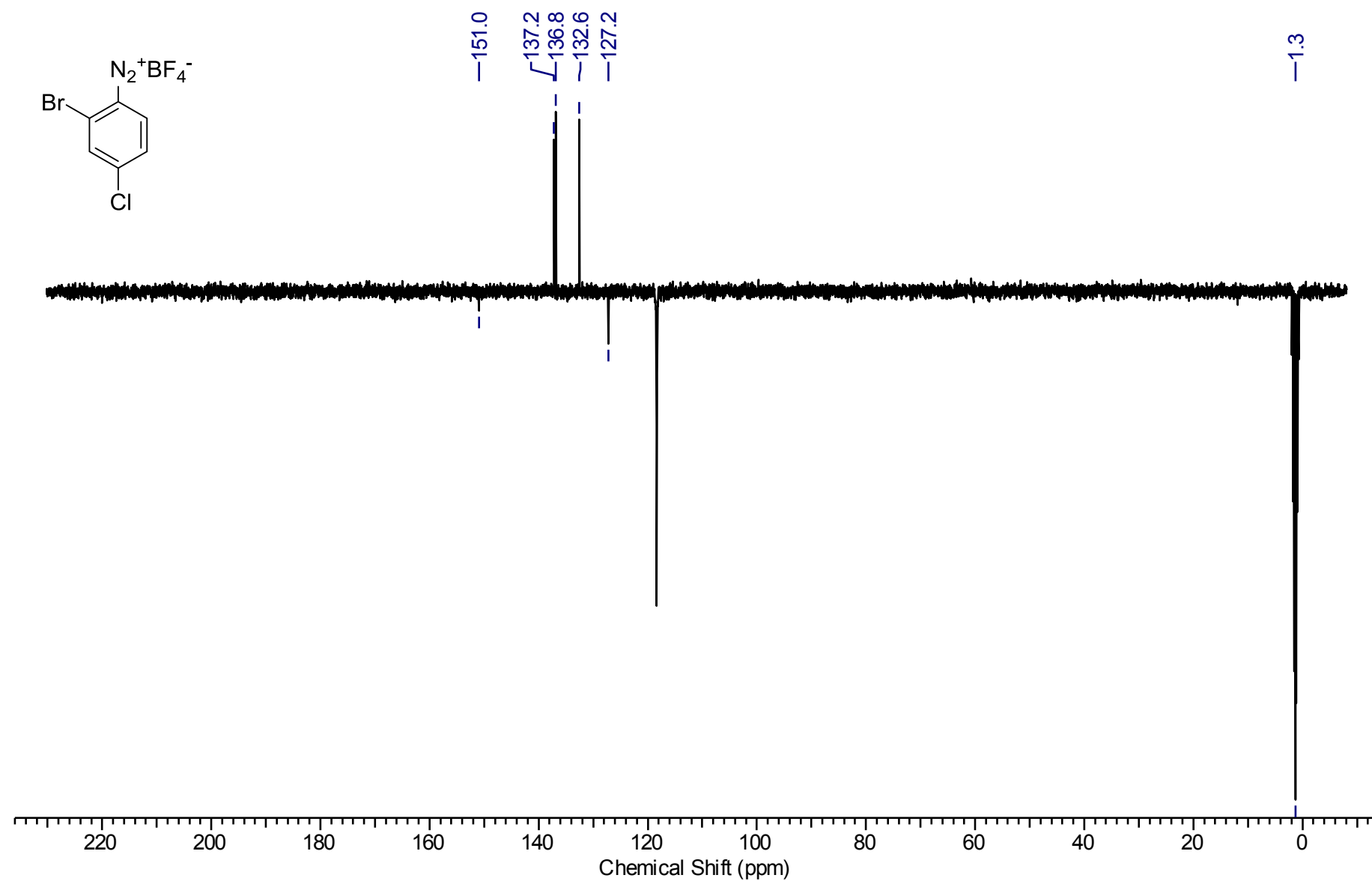
3e: ^{19}F NMR (376 MHz, CD_3CN)



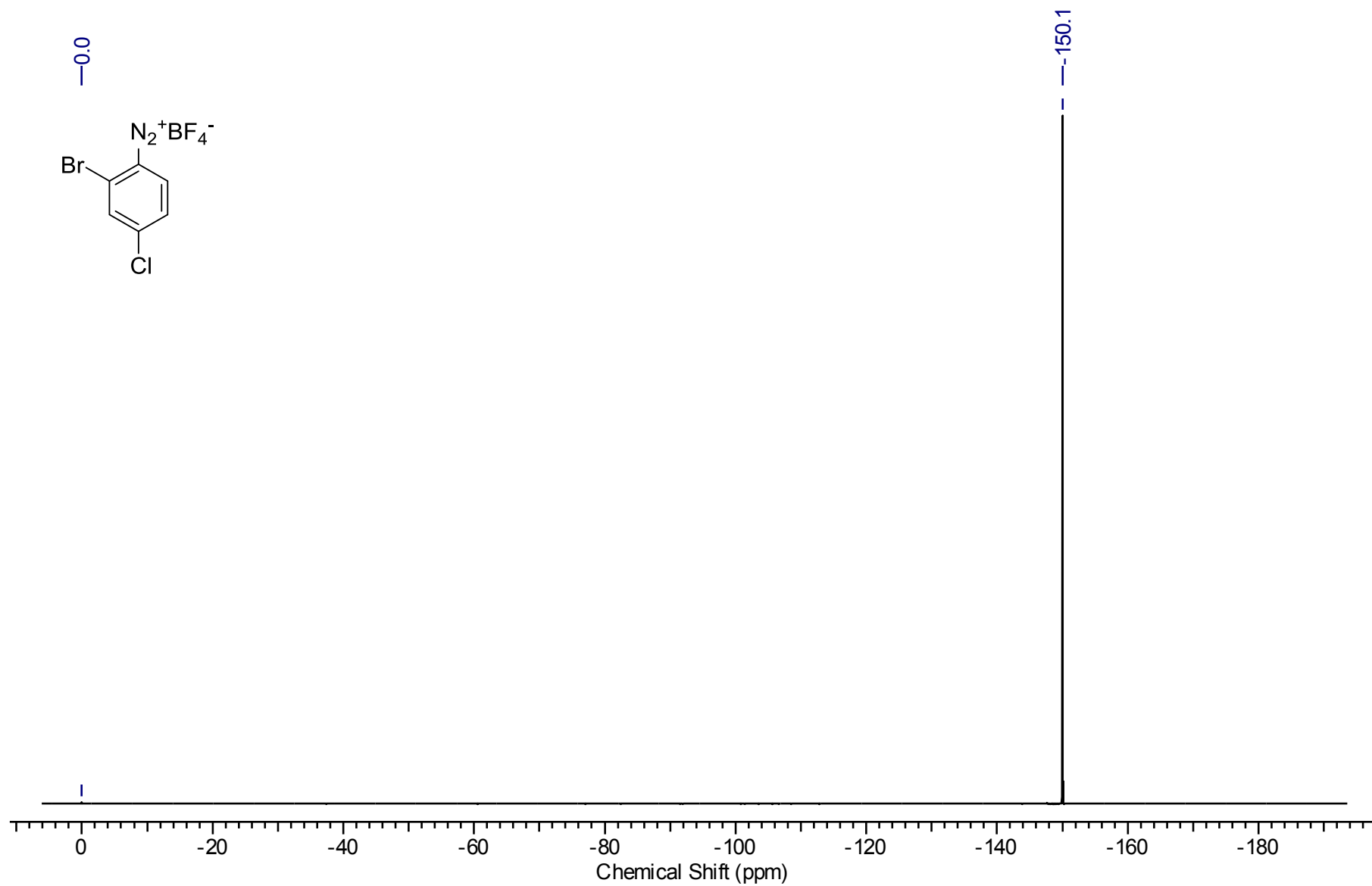
3f: ^1H NMR (400 MHz, CD_3CN)



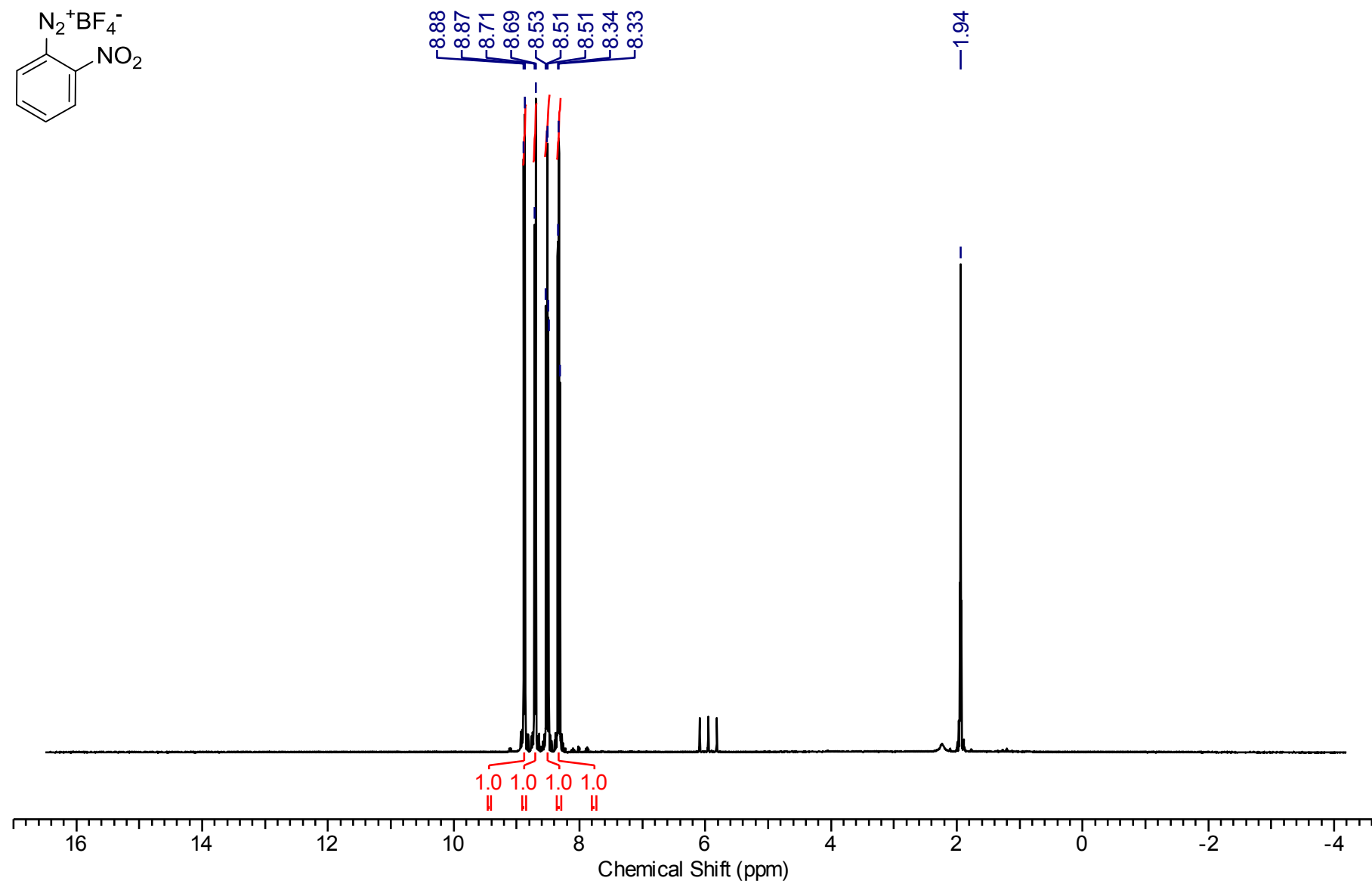
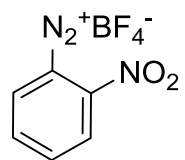
3f: ^{13}C NMR (101 MHz, CD_3CN)



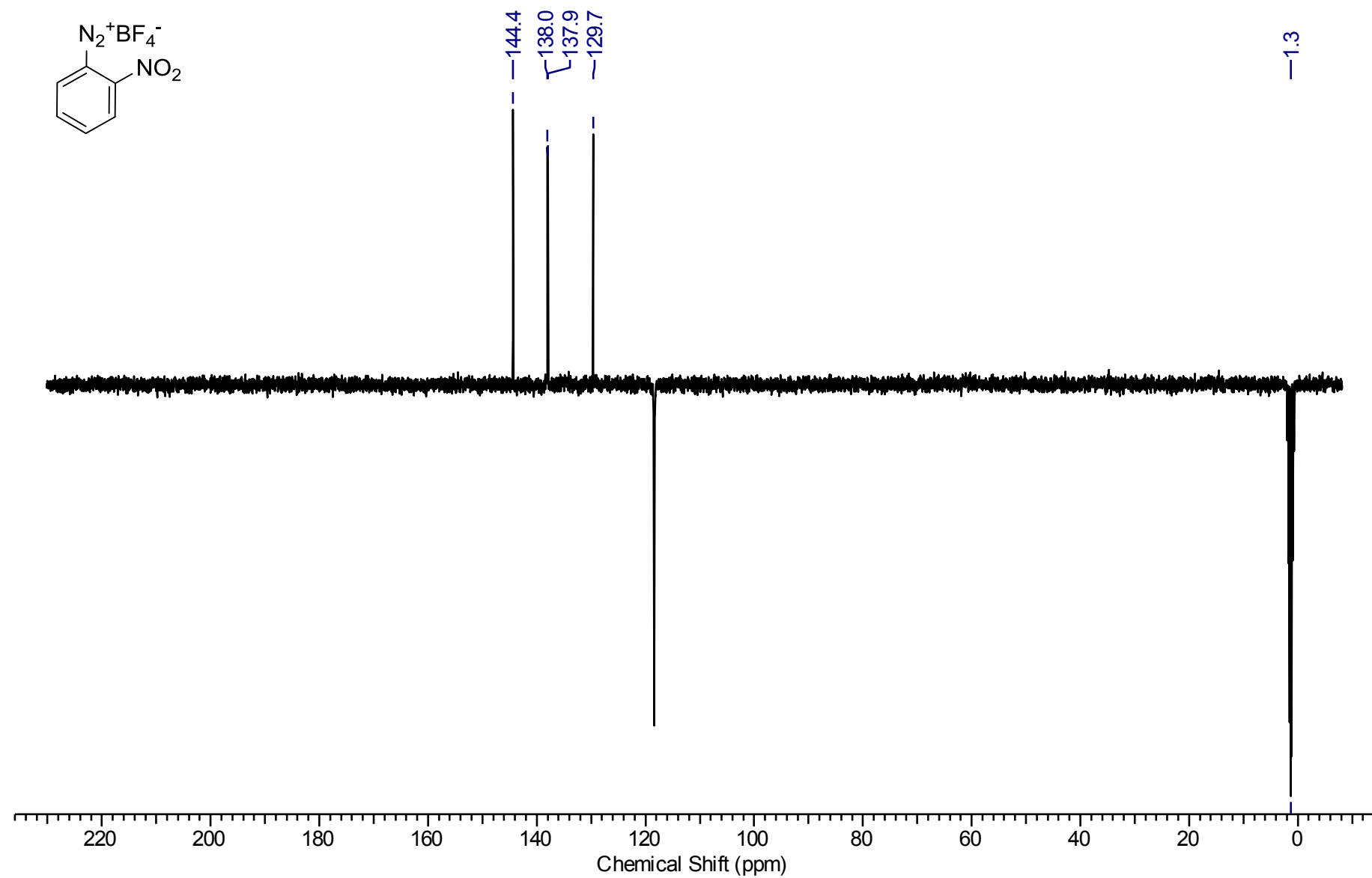
3f: ^{19}F NMR (376 MHz, CD_3CN)



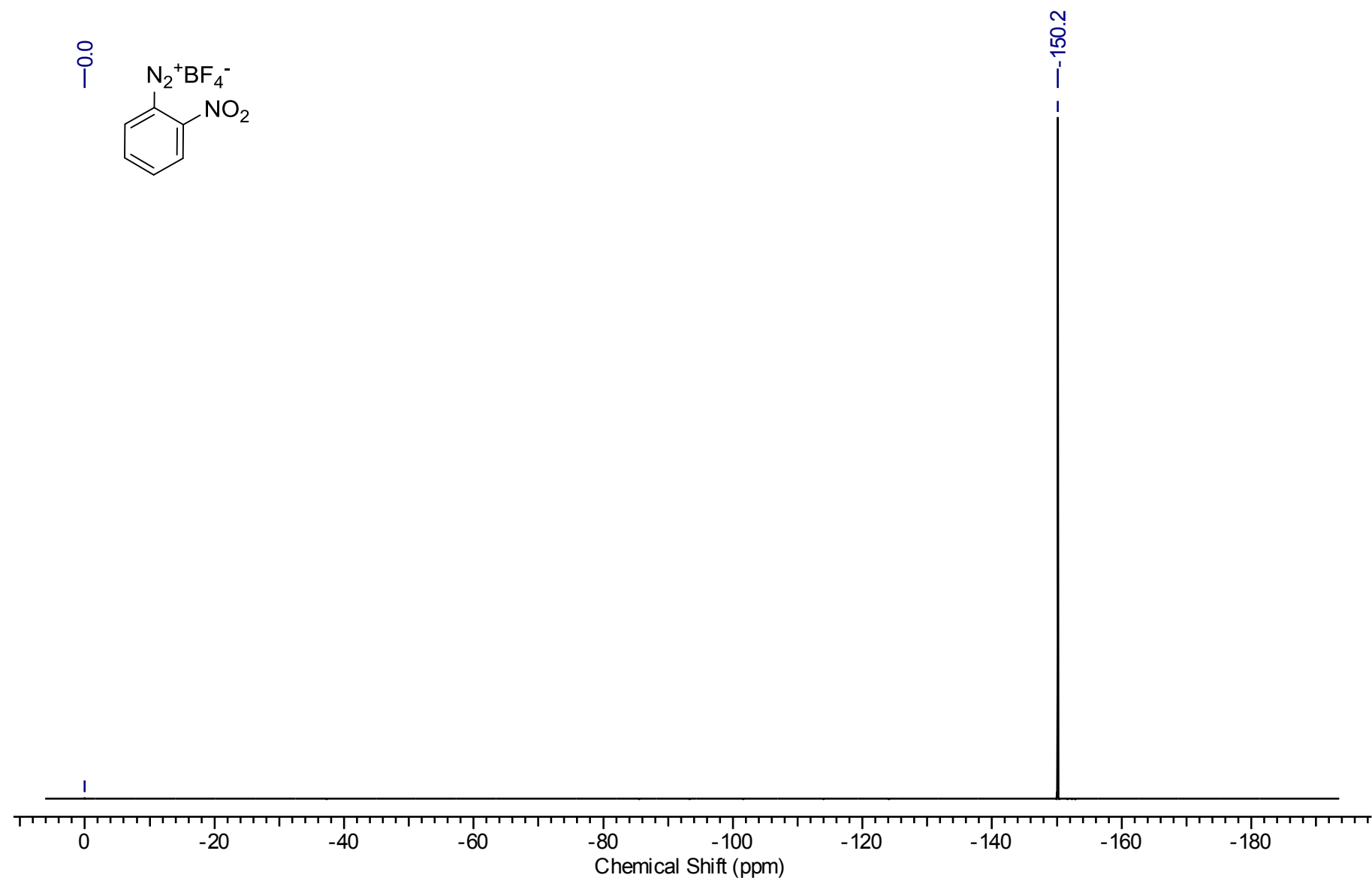
3g: ^1H NMR (400 MHz, CD_3CN)



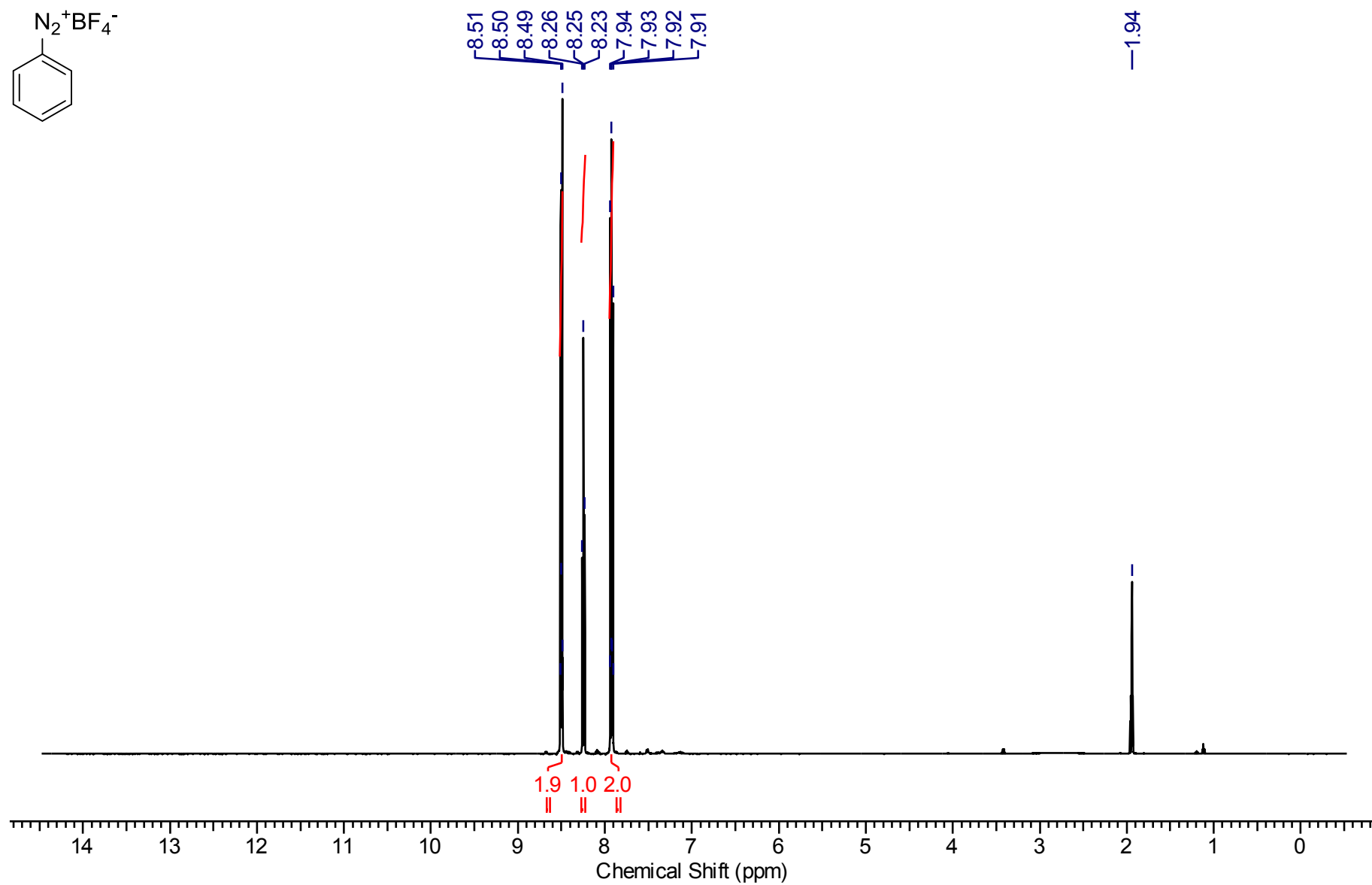
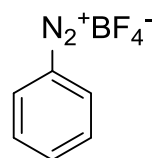
3g: ^{13}C NMR (101 MHz, CD_3CN)



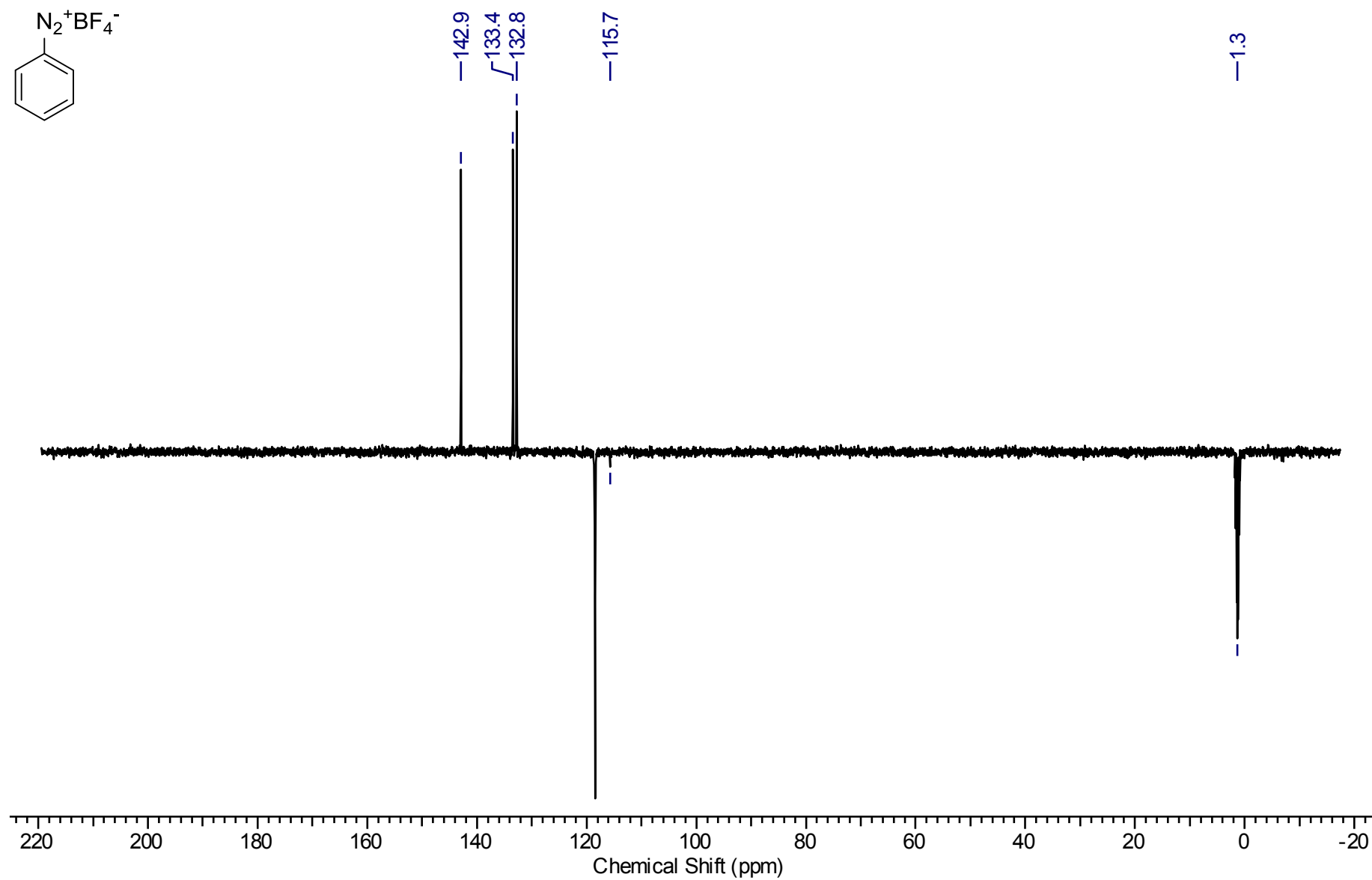
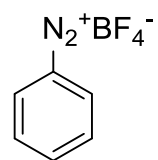
3g: ^{19}F NMR (376 MHz, CD_3CN)



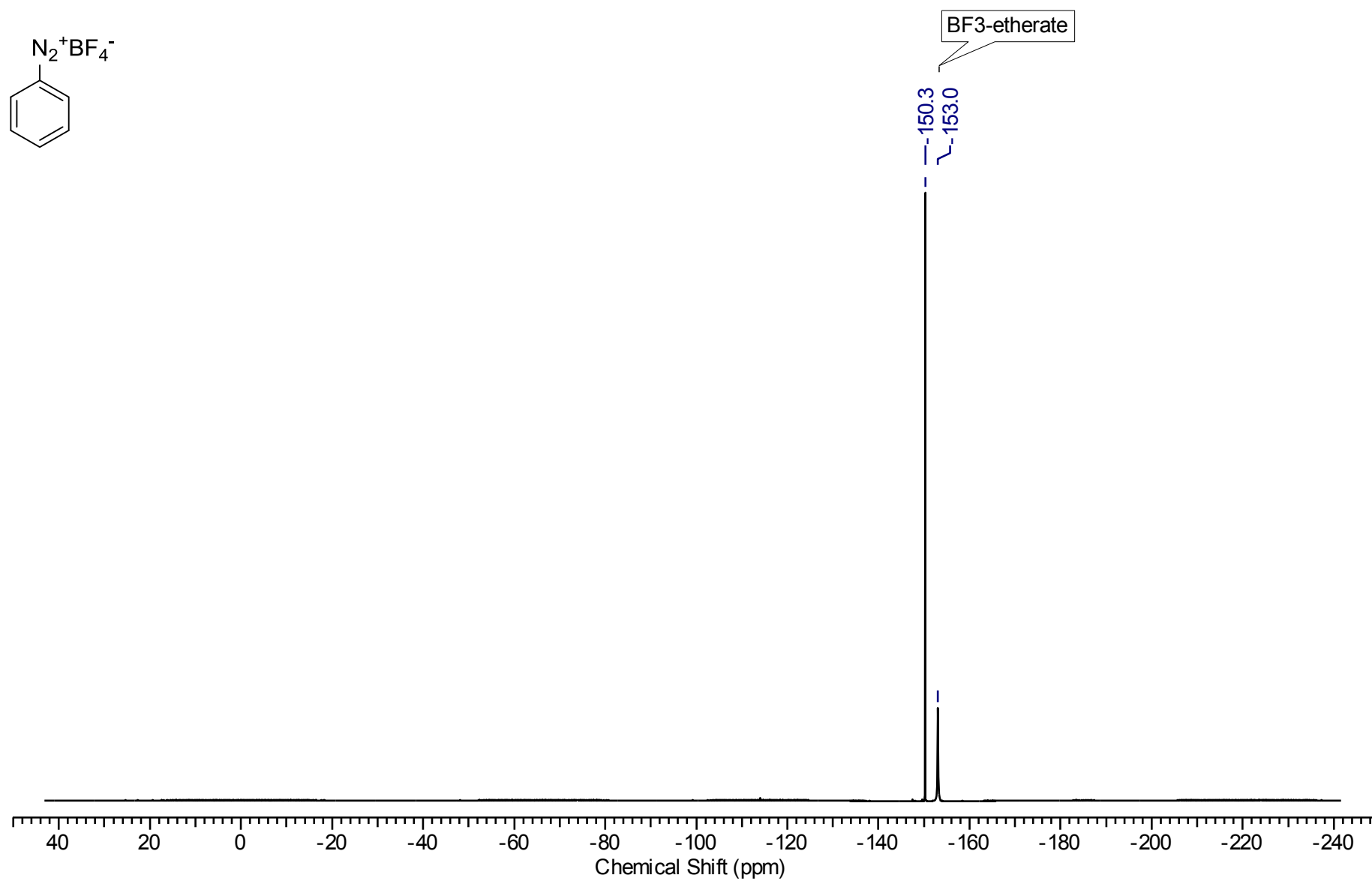
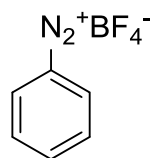
3h: ^1H NMR (400 MHz, CD_3CN)



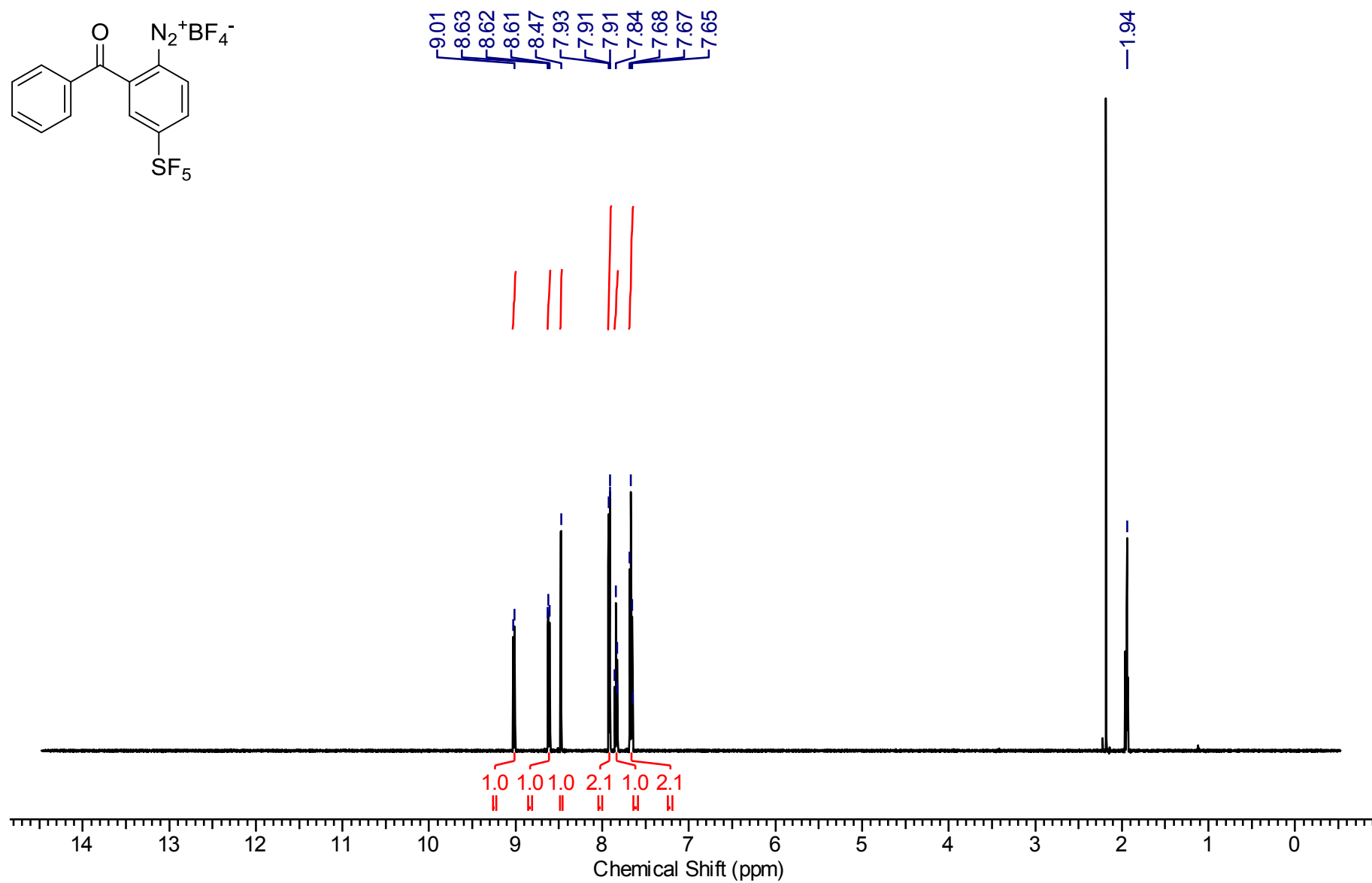
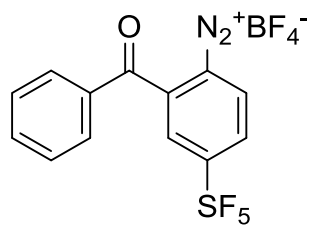
3h: ^{13}C NMR (126 MHz, CD_3CN)



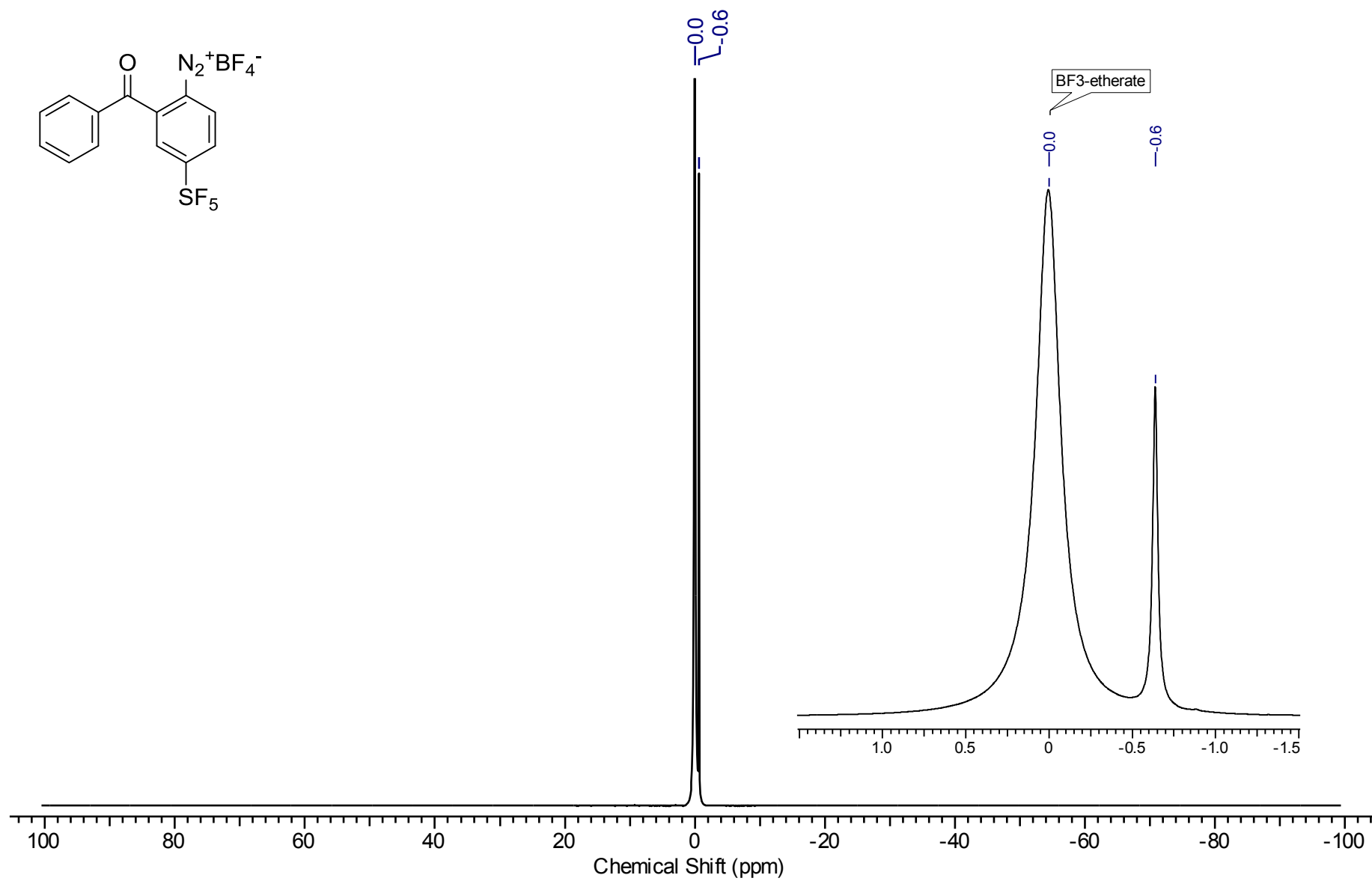
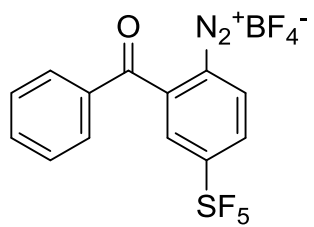
3h: ^{19}F NMR (470 MHz, CD_3CN)



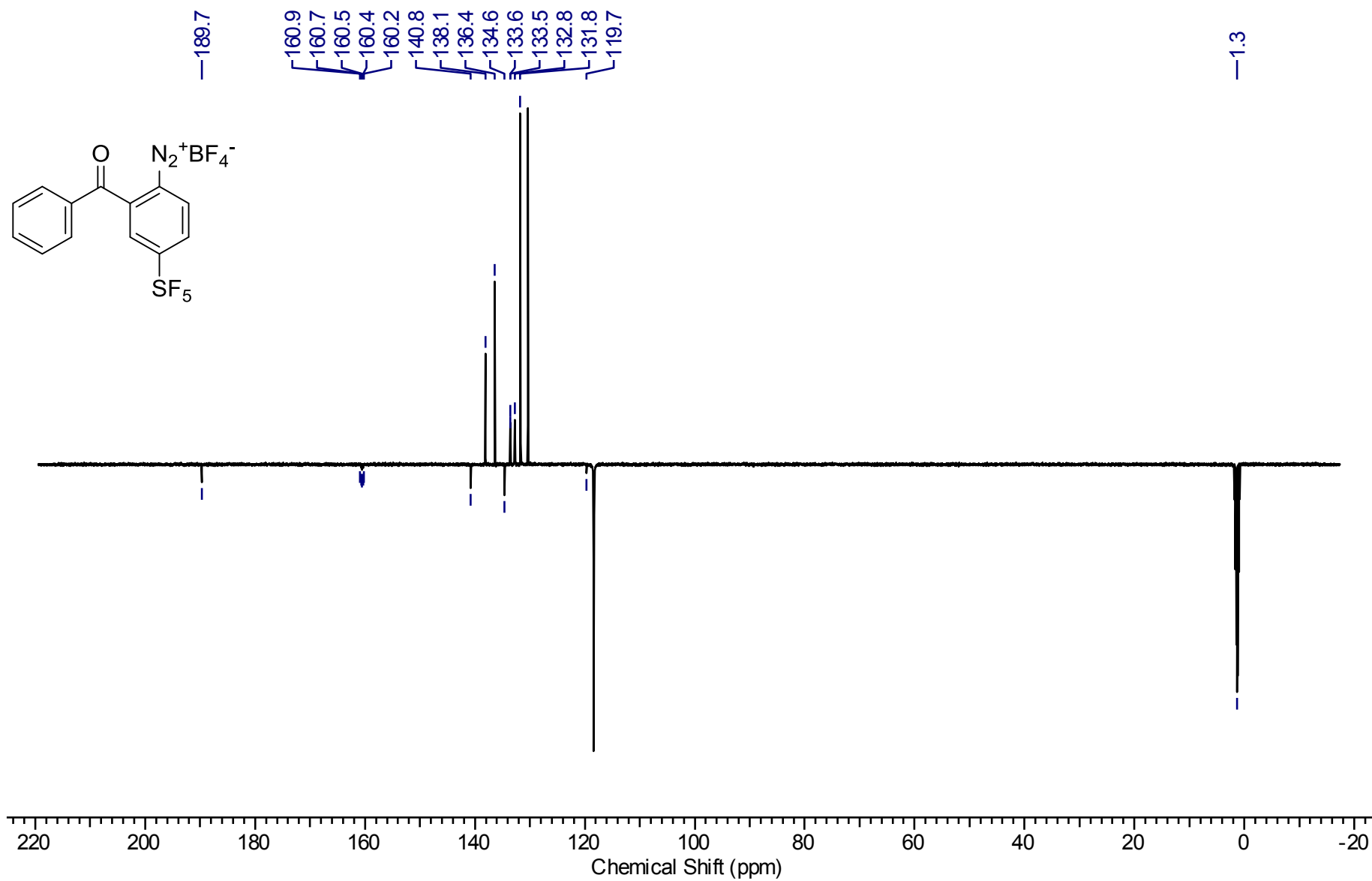
3i: ^1H NMR (500 MHz, CD_3CN)



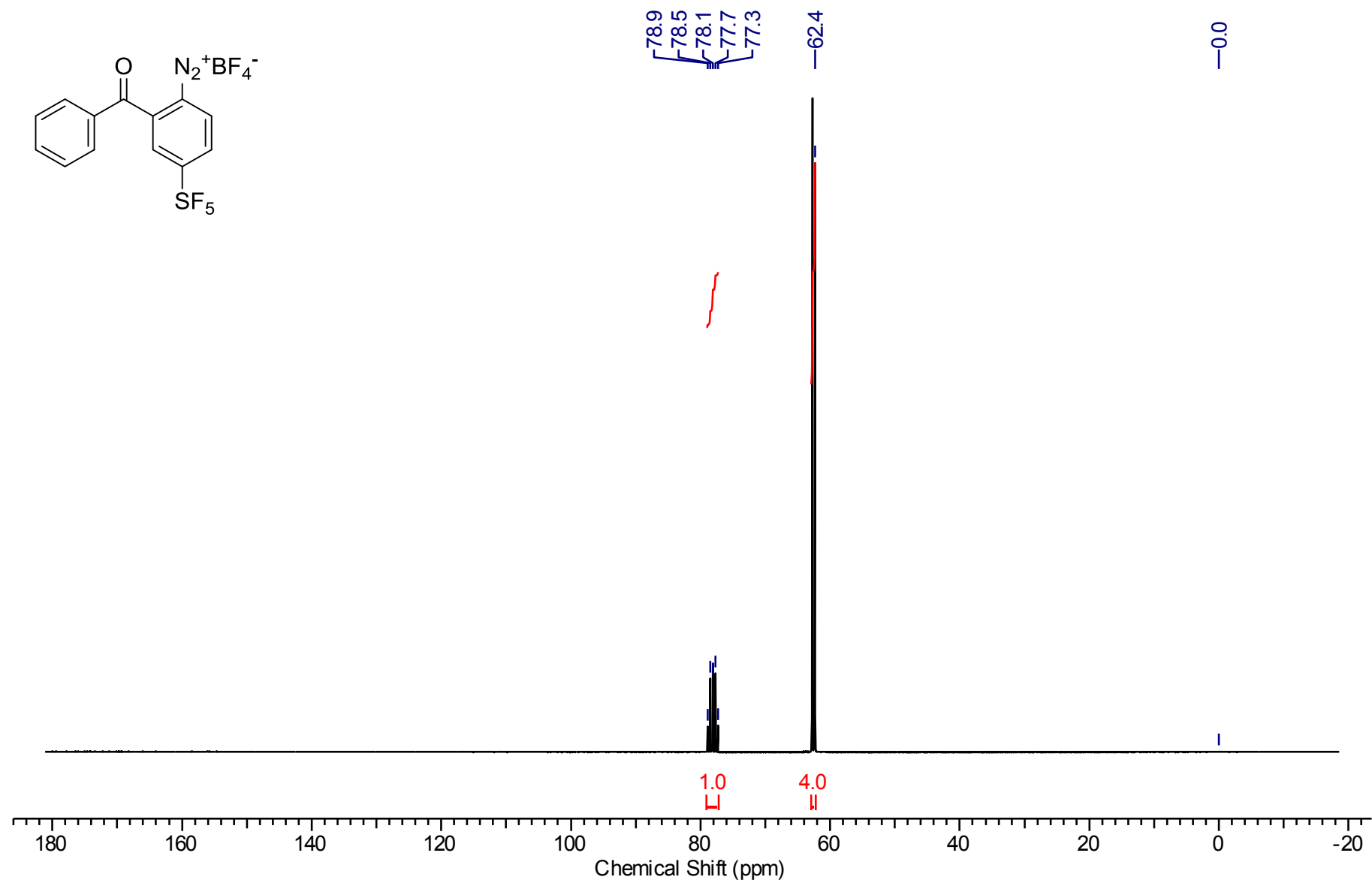
3i: ^{11}B NMR (160 MHz, CD_3CN)



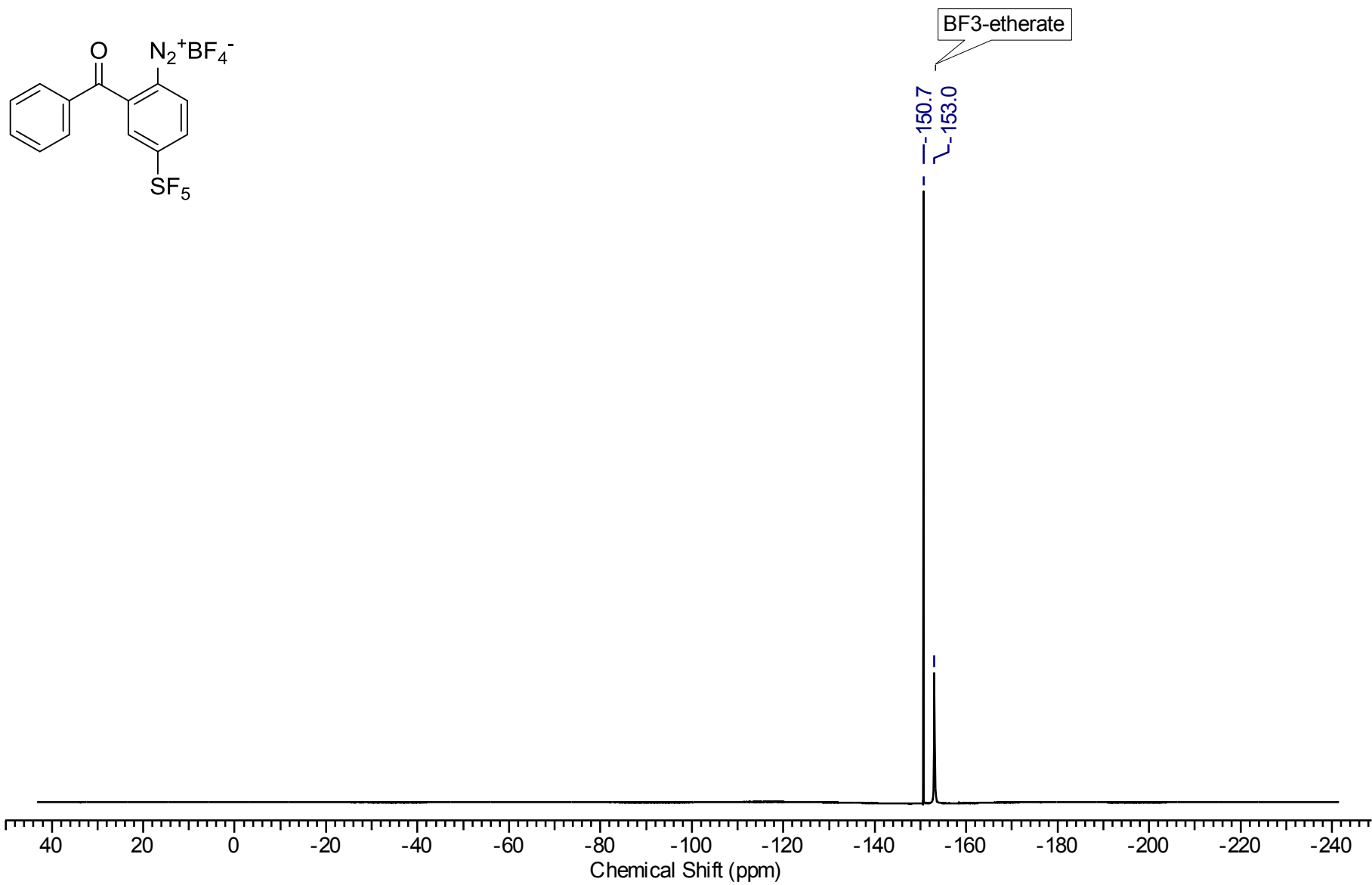
3i: ^{13}C NMR (126 MHz, CD_3CN)



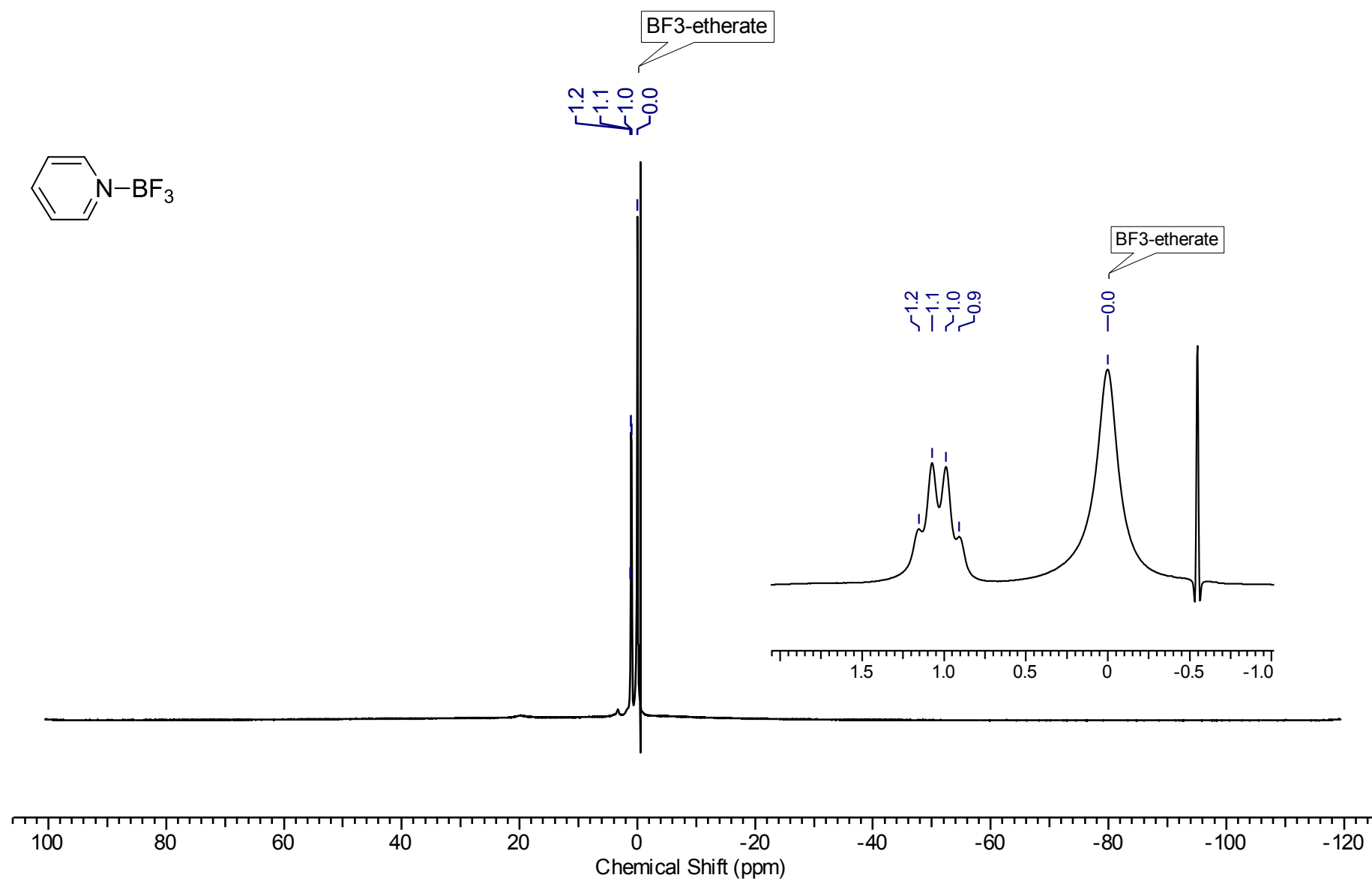
3i: ^{19}F NMR (377 MHz, CD_3CN)



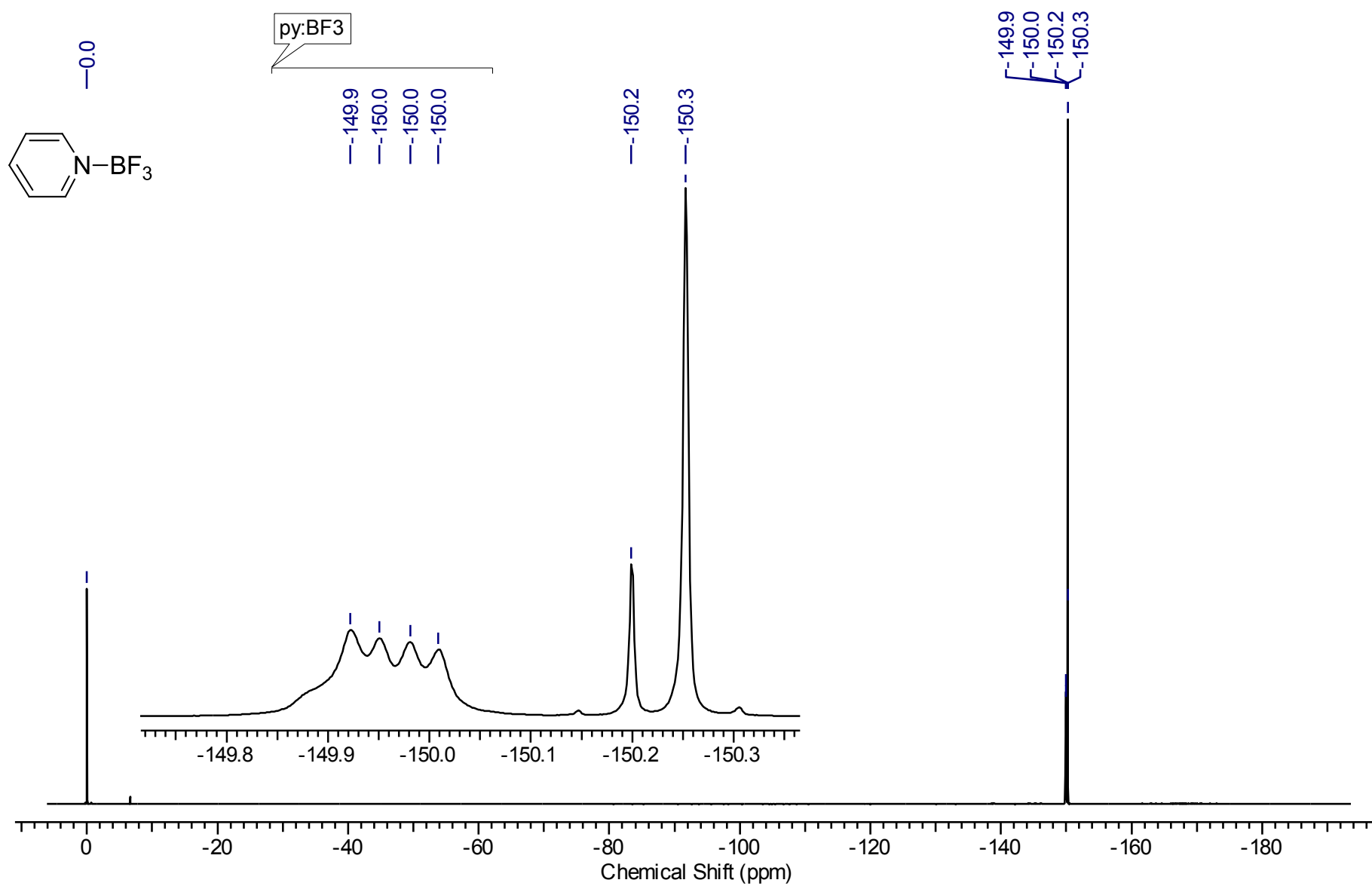
3i: ^{19}F NMR (377 MHz, CD_3CN)



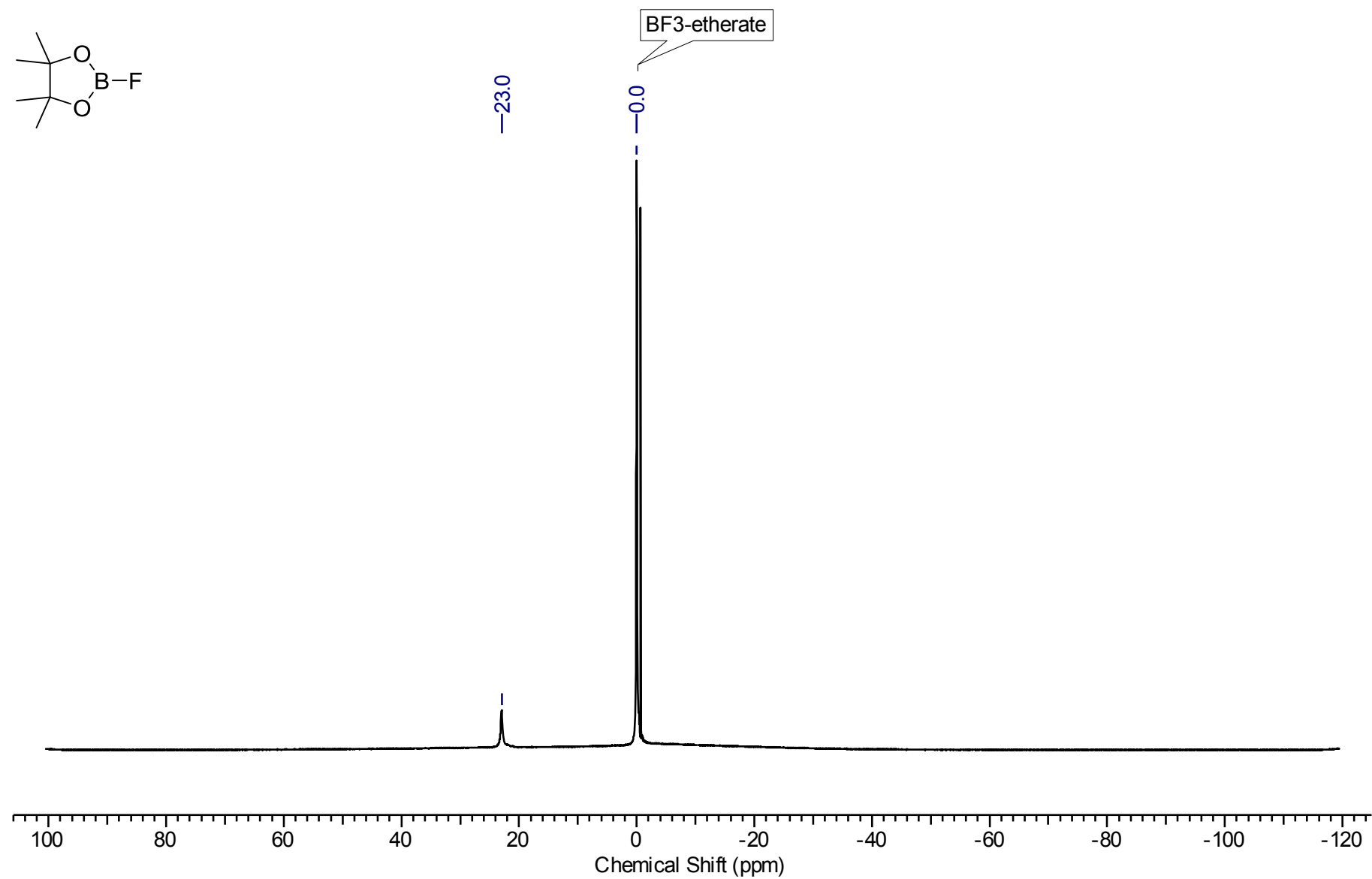
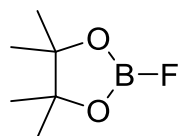
pyridine-BF₃ complex: ¹¹B NMR (128 MHz, CD₃CN)



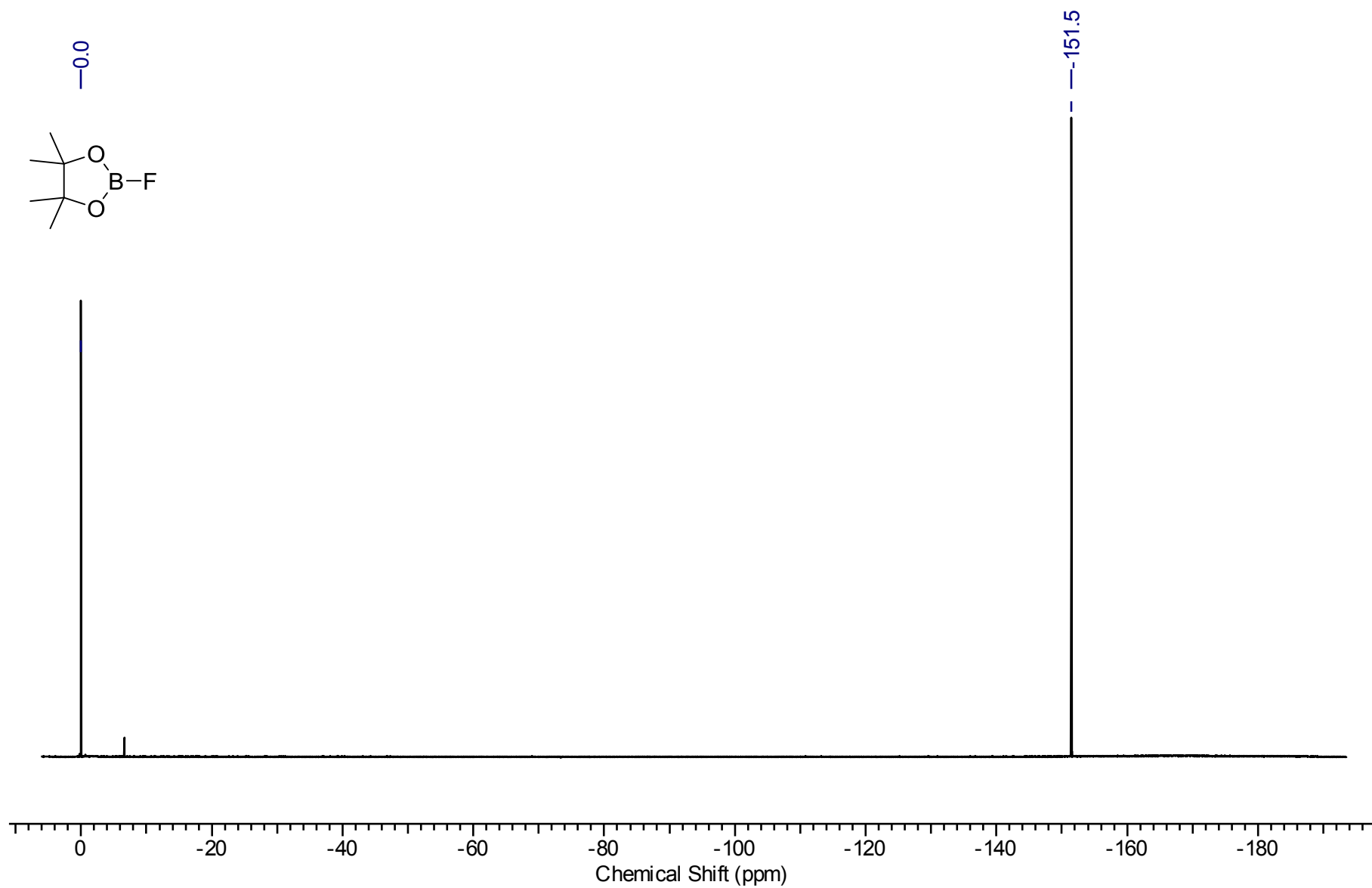
pyridine-BF₃ complex: ¹⁹F NMR (376 MHz, CD₃CN)



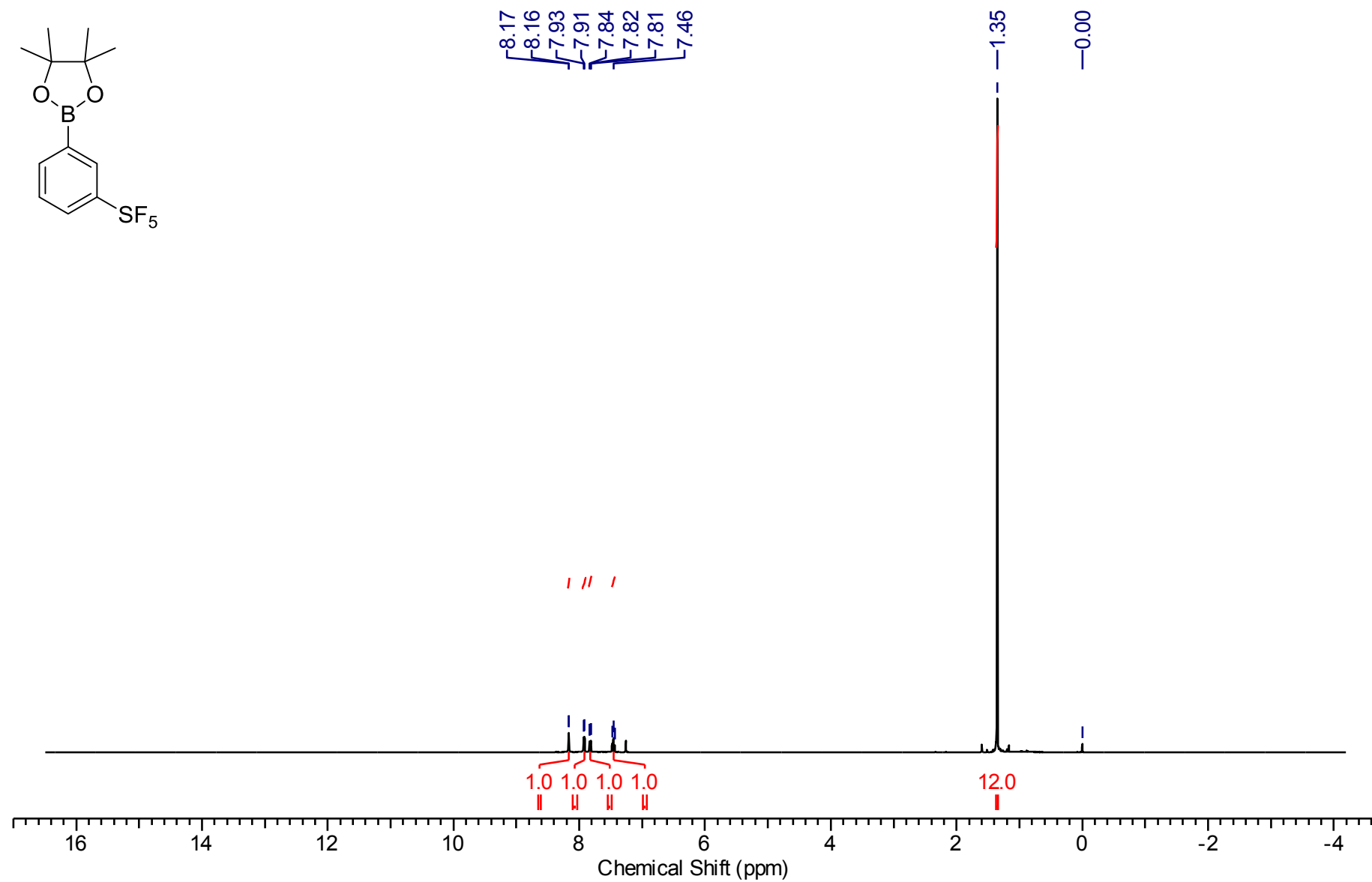
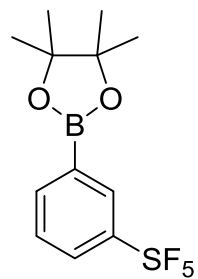
F-Bpin: ^{11}B NMR (128 MHz, CD_3CN)



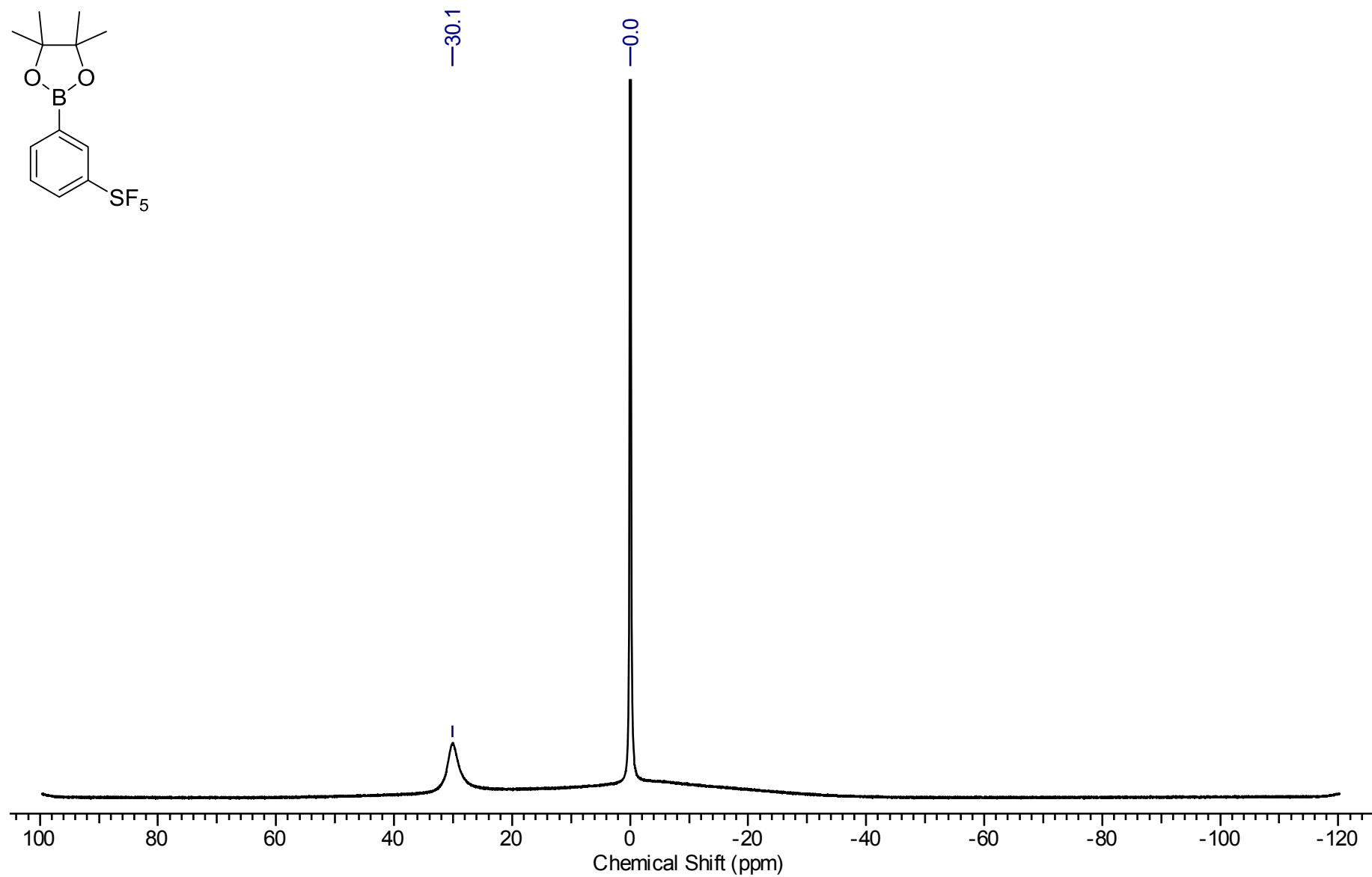
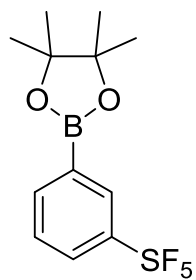
F-Bpin: ^{19}F NMR (376 MHz, CD_3CN)



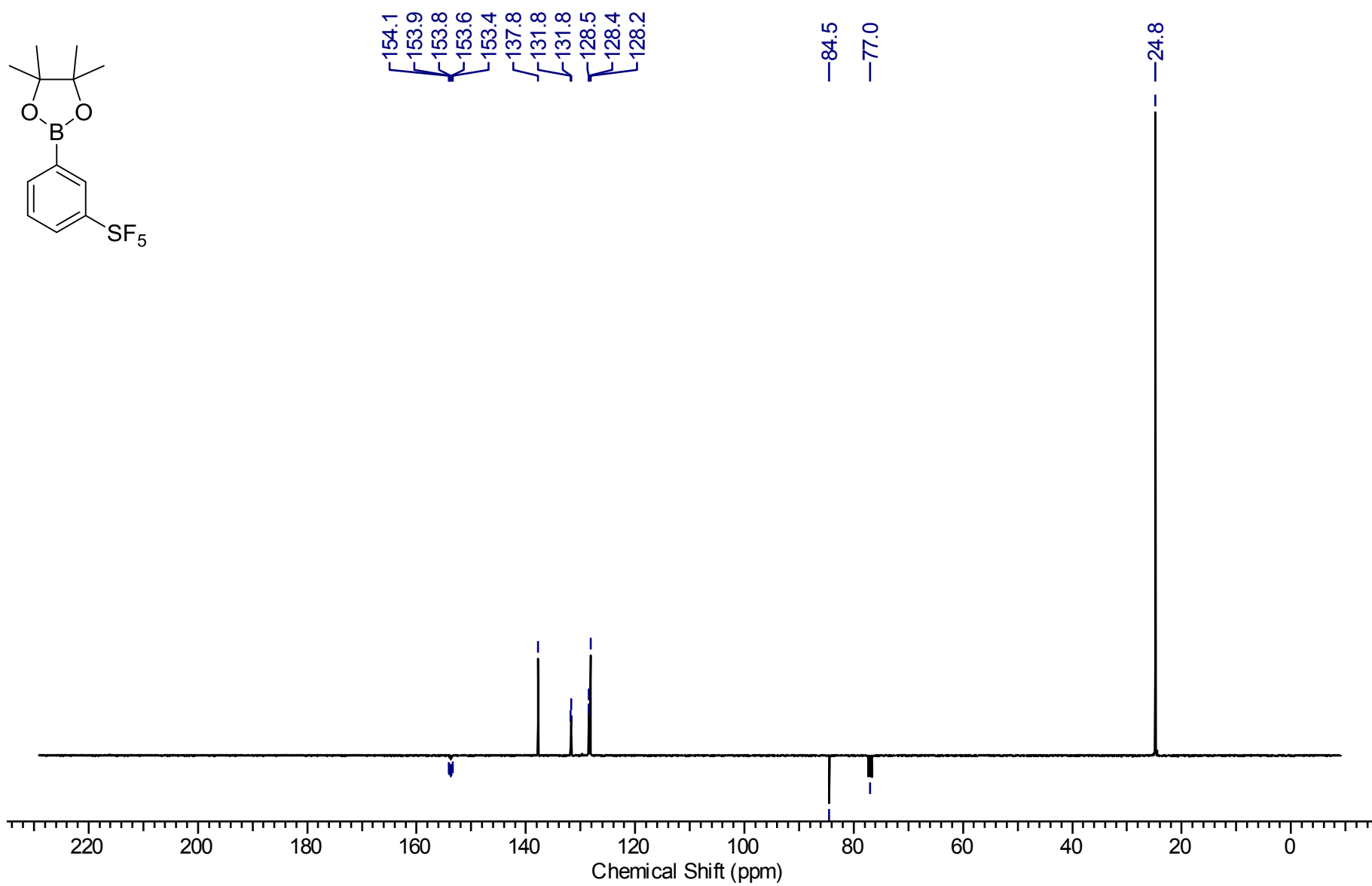
2a: ^1H NMR (400 MHz, CDCl_3)



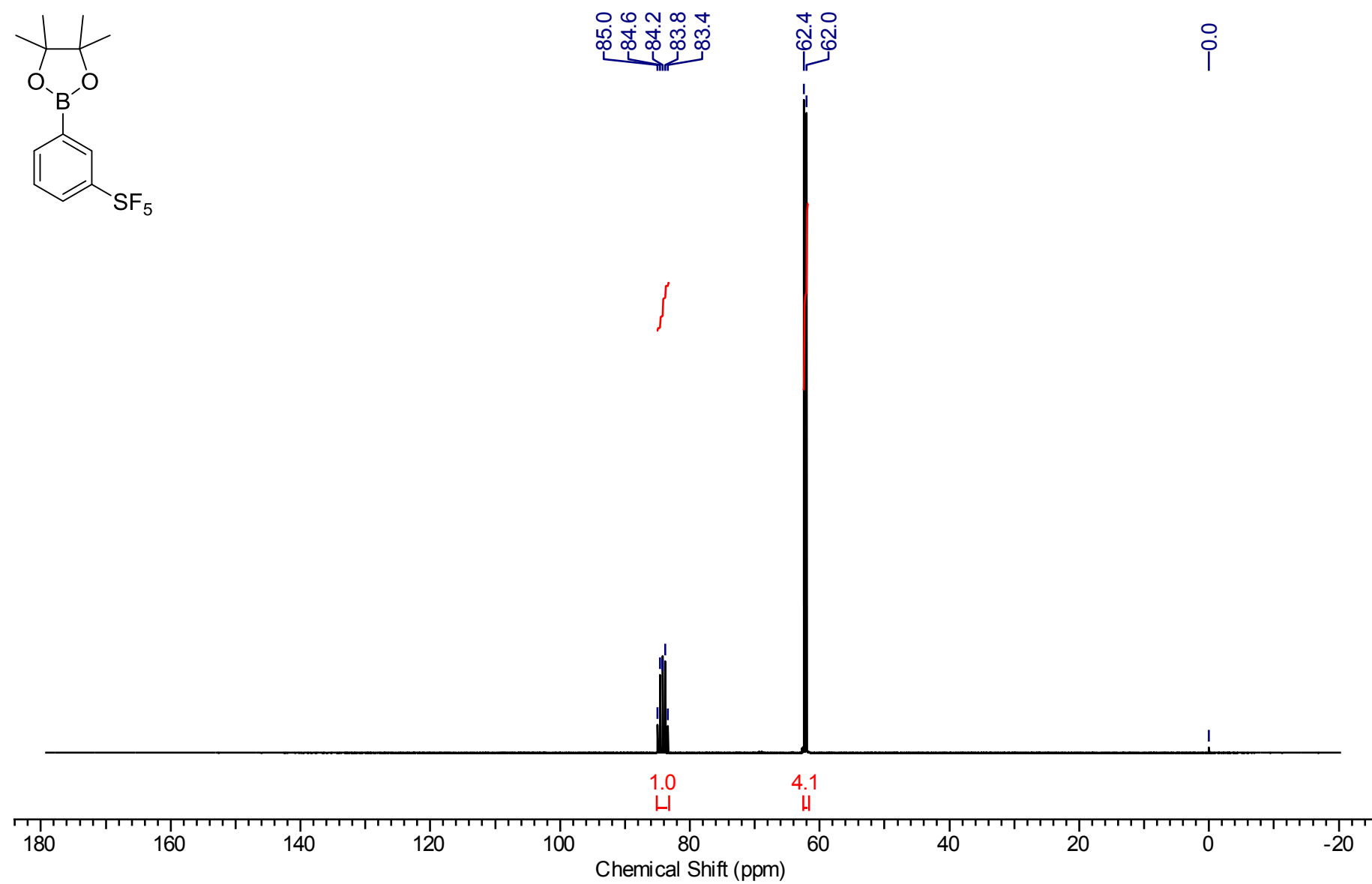
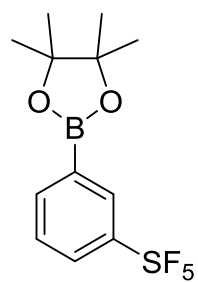
2a: ^{11}B NMR (128 MHz, CDCl_3)



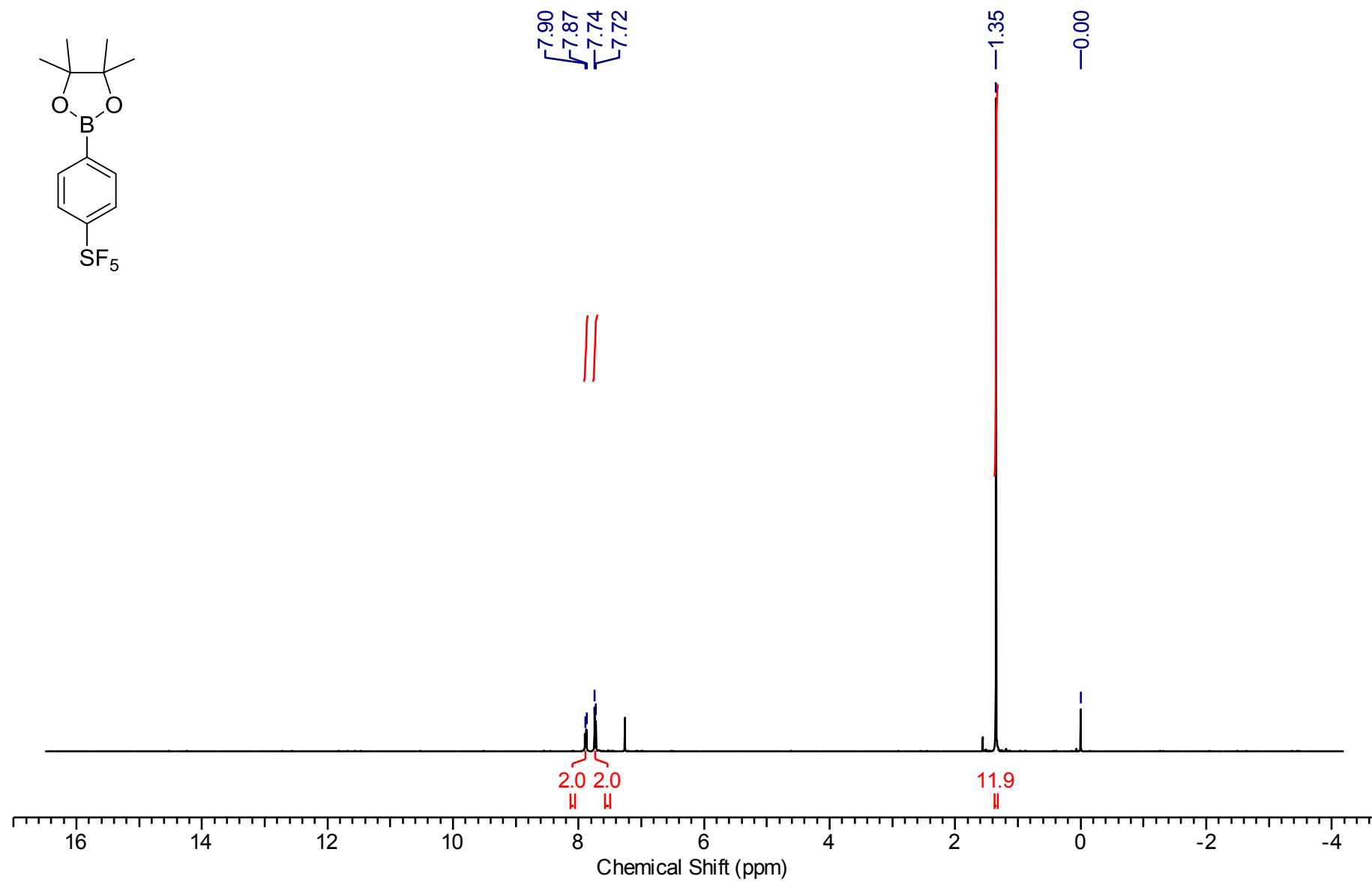
2a: ^{13}C NMR (101 MHz, CDCl_3)



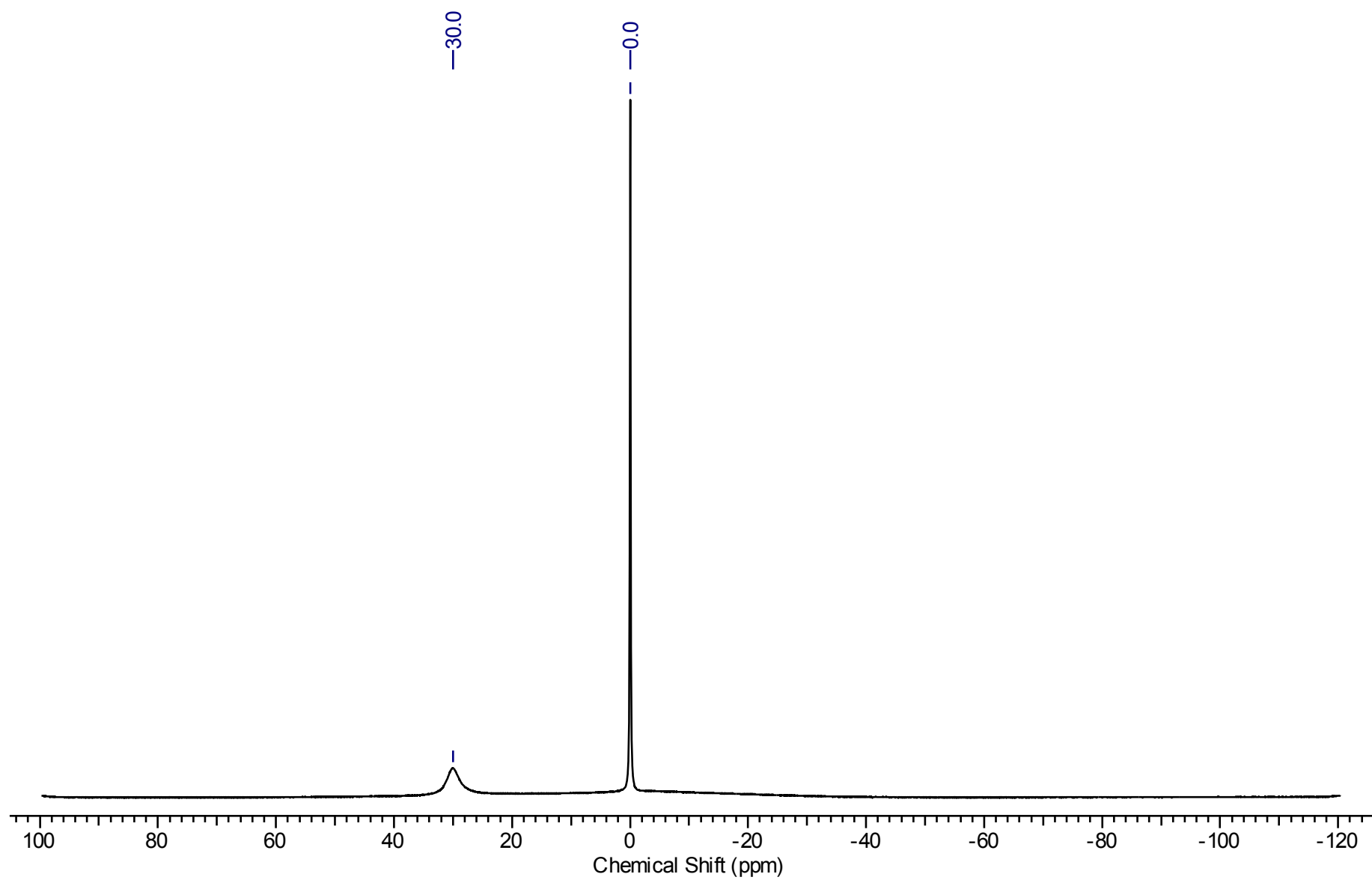
2a: ^{19}F NMR (377 MHz, CDCl_3)



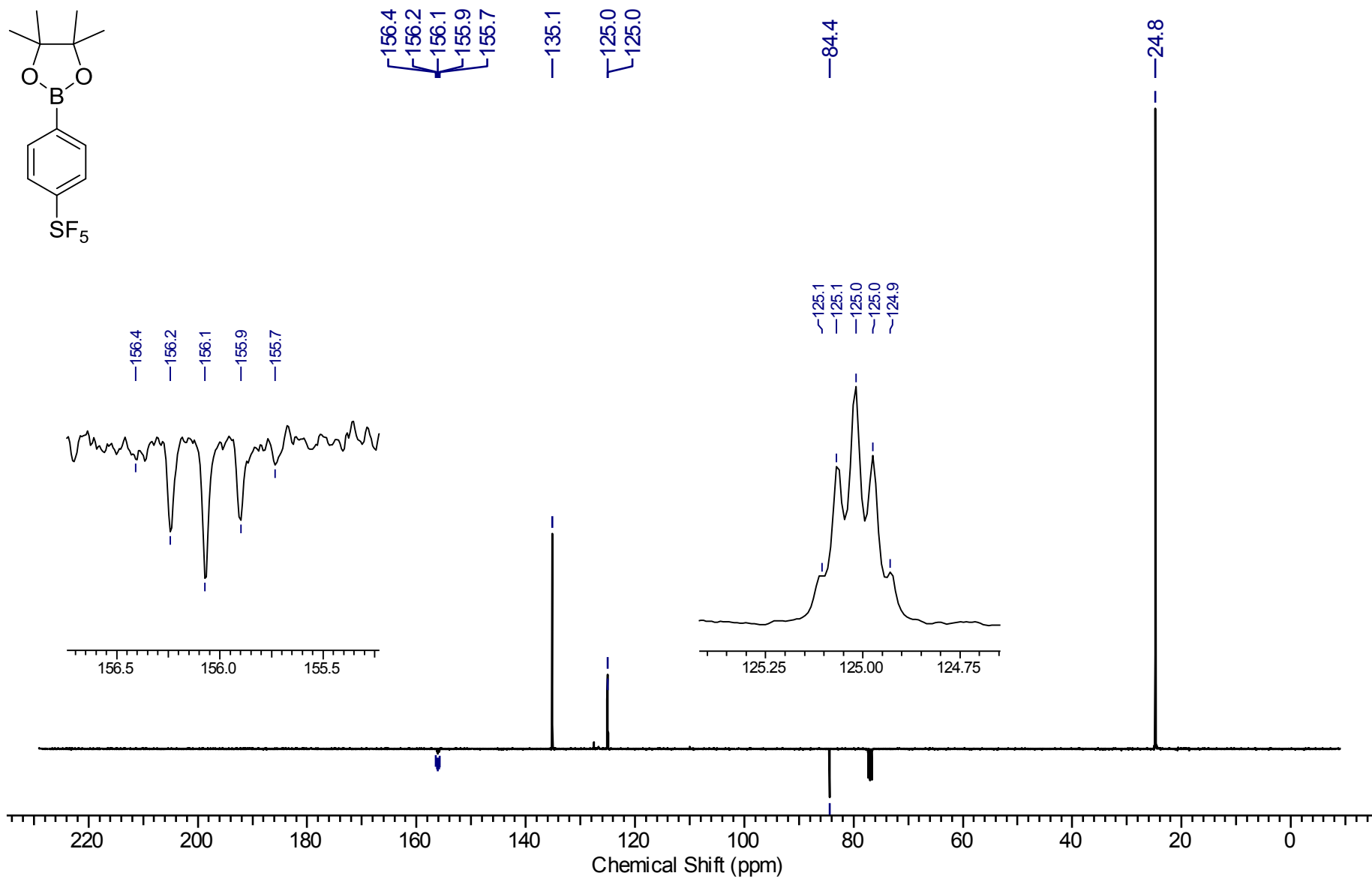
2b: ^1H NMR (400 MHz, CDCl_3)



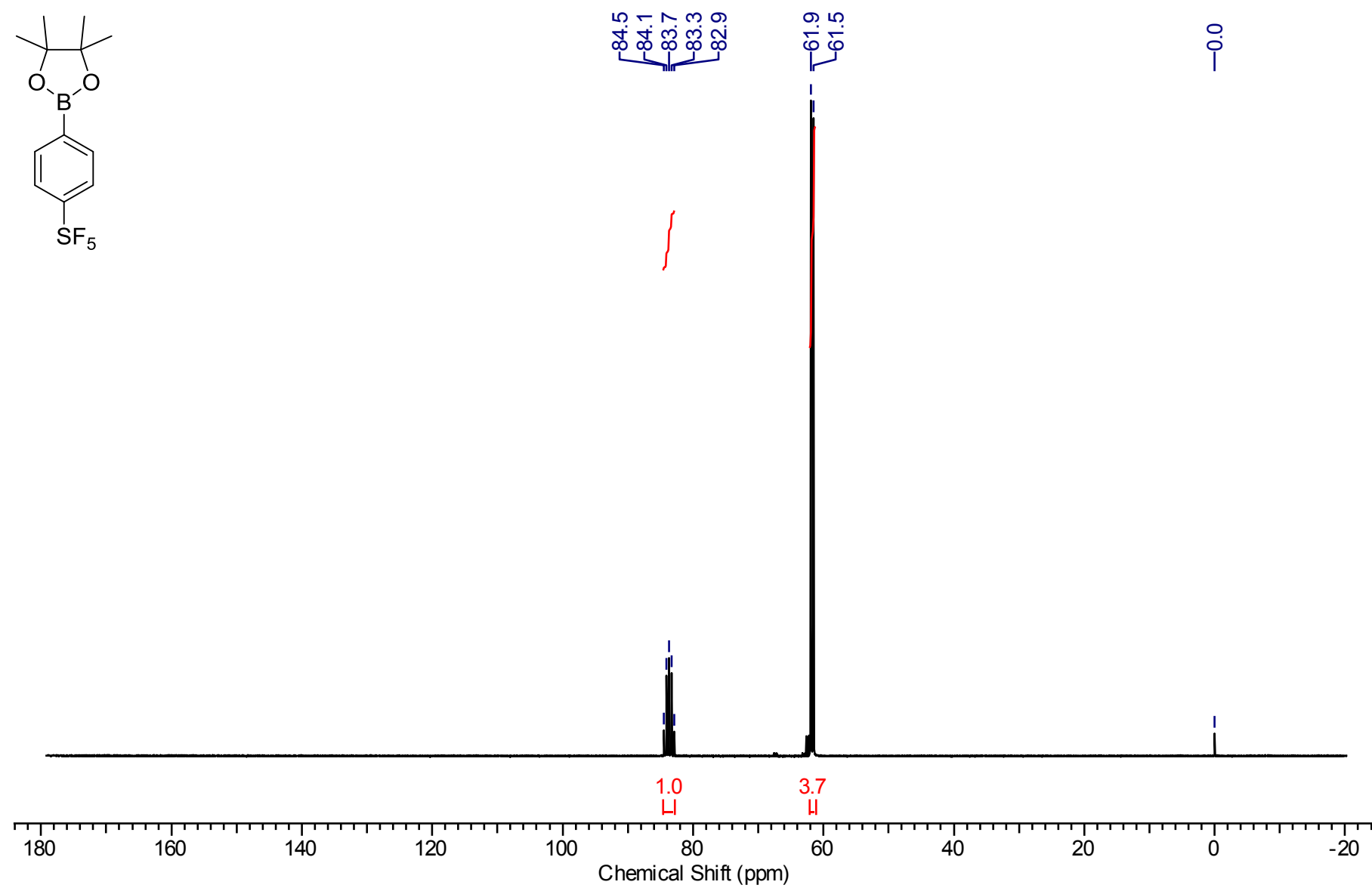
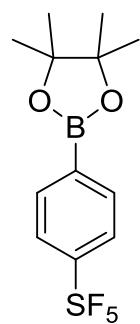
2b: ^{11}B NMR (128 MHz, CDCl_3)



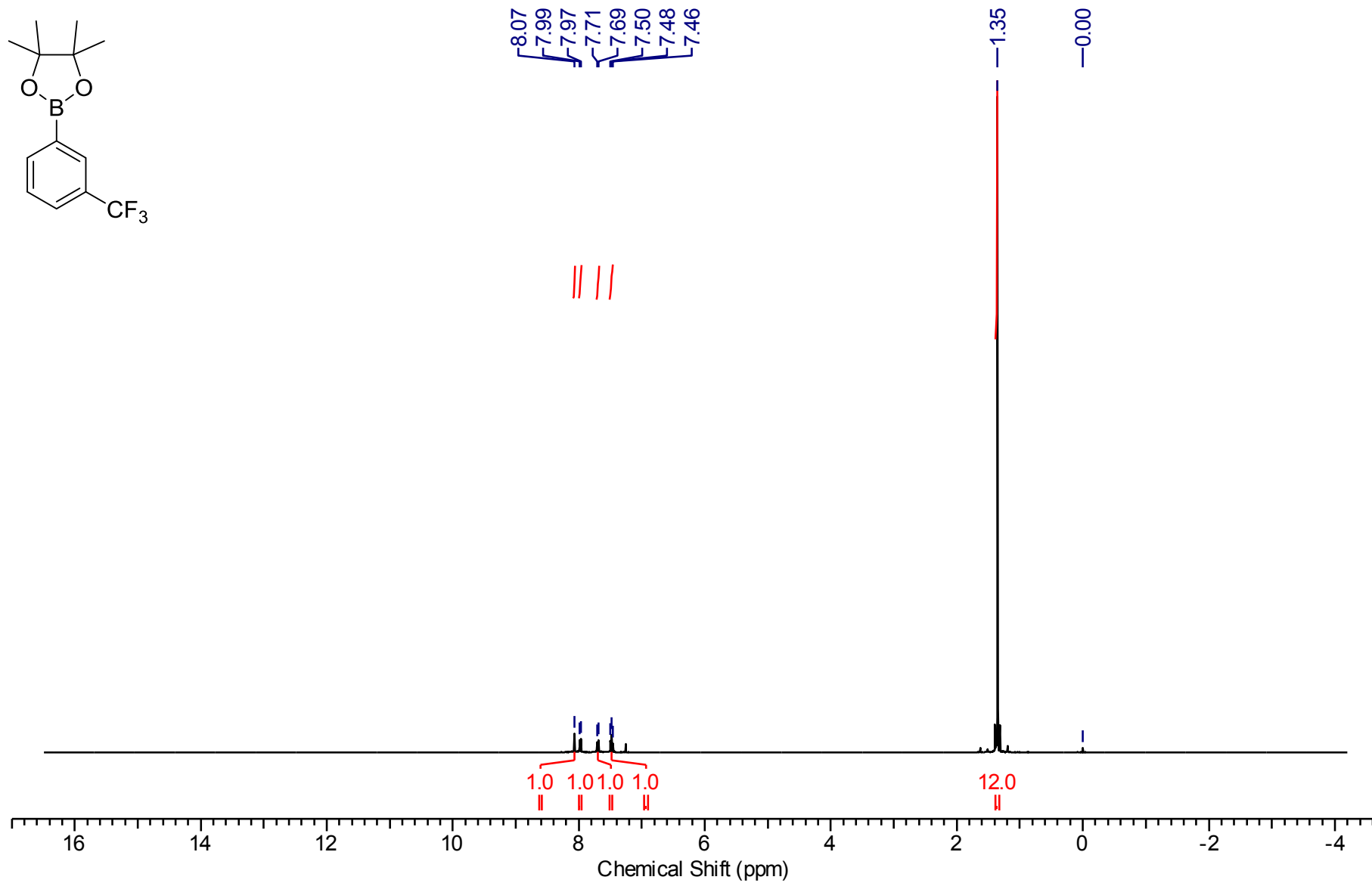
2b: ^{13}C NMR (101 MHz, CDCl_3)



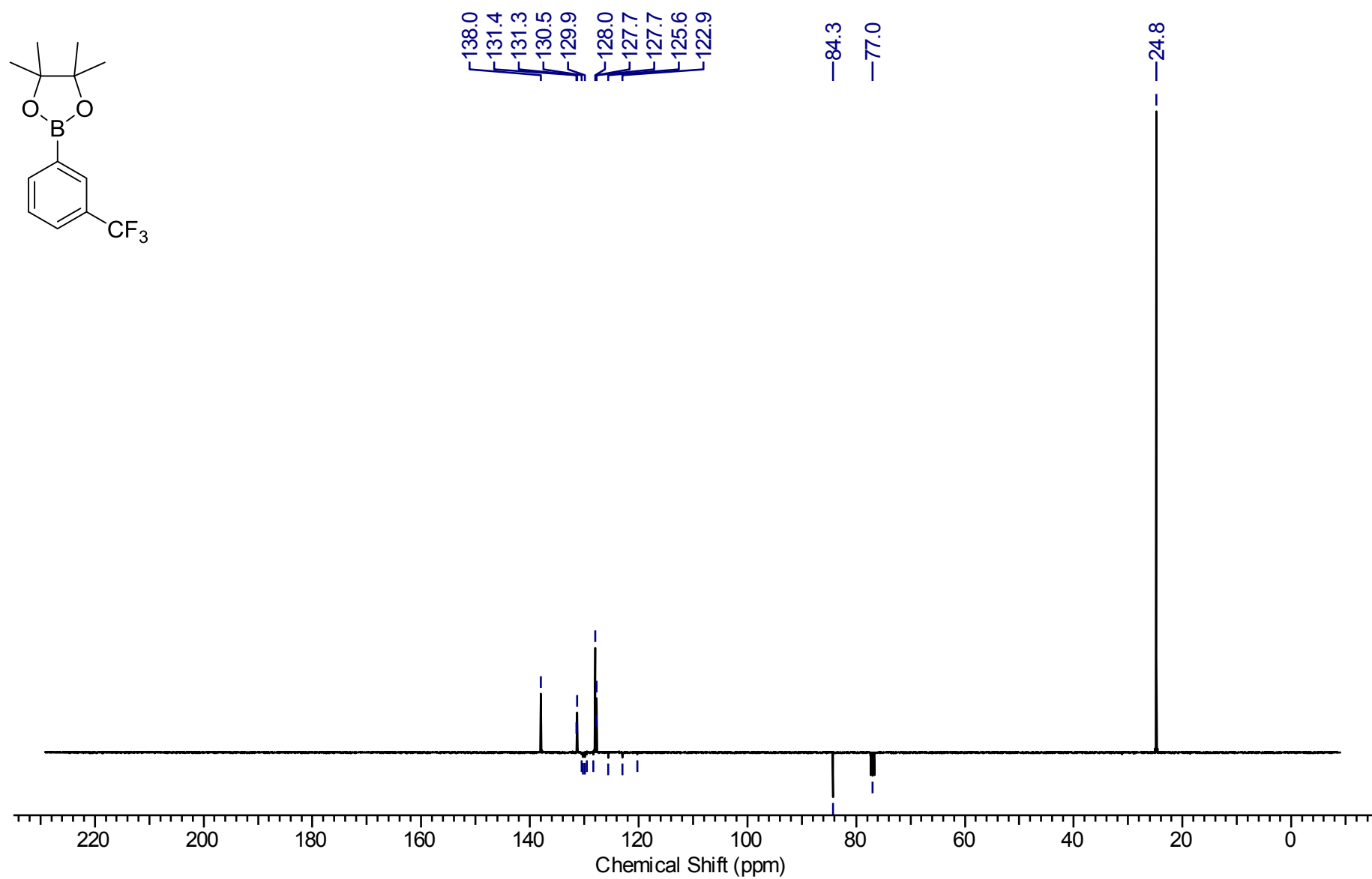
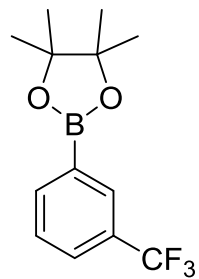
2b: ^{19}F NMR (377 MHz, CDCl_3)



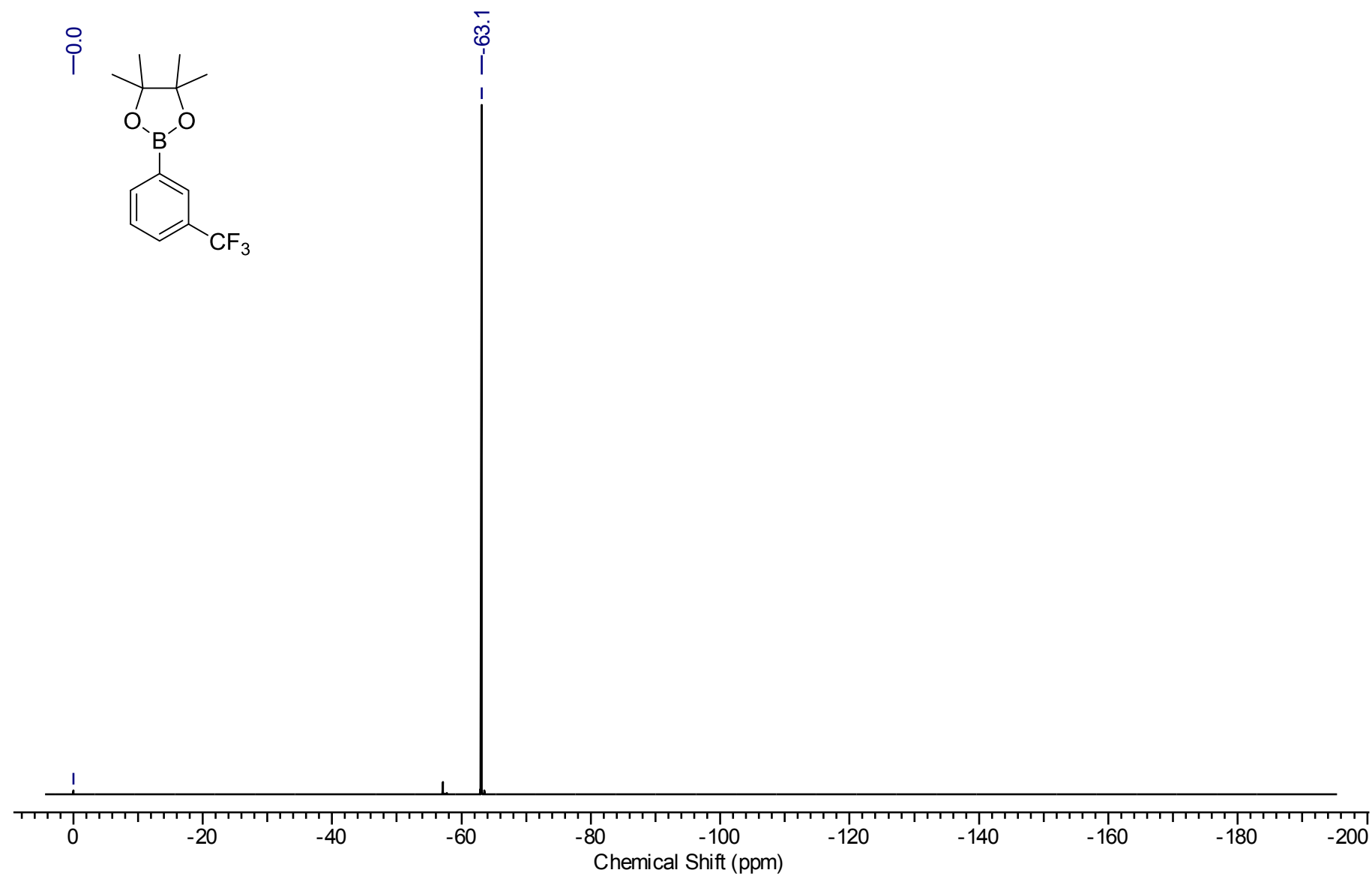
2c: ^1H NMR (400 MHz, CDCl_3)



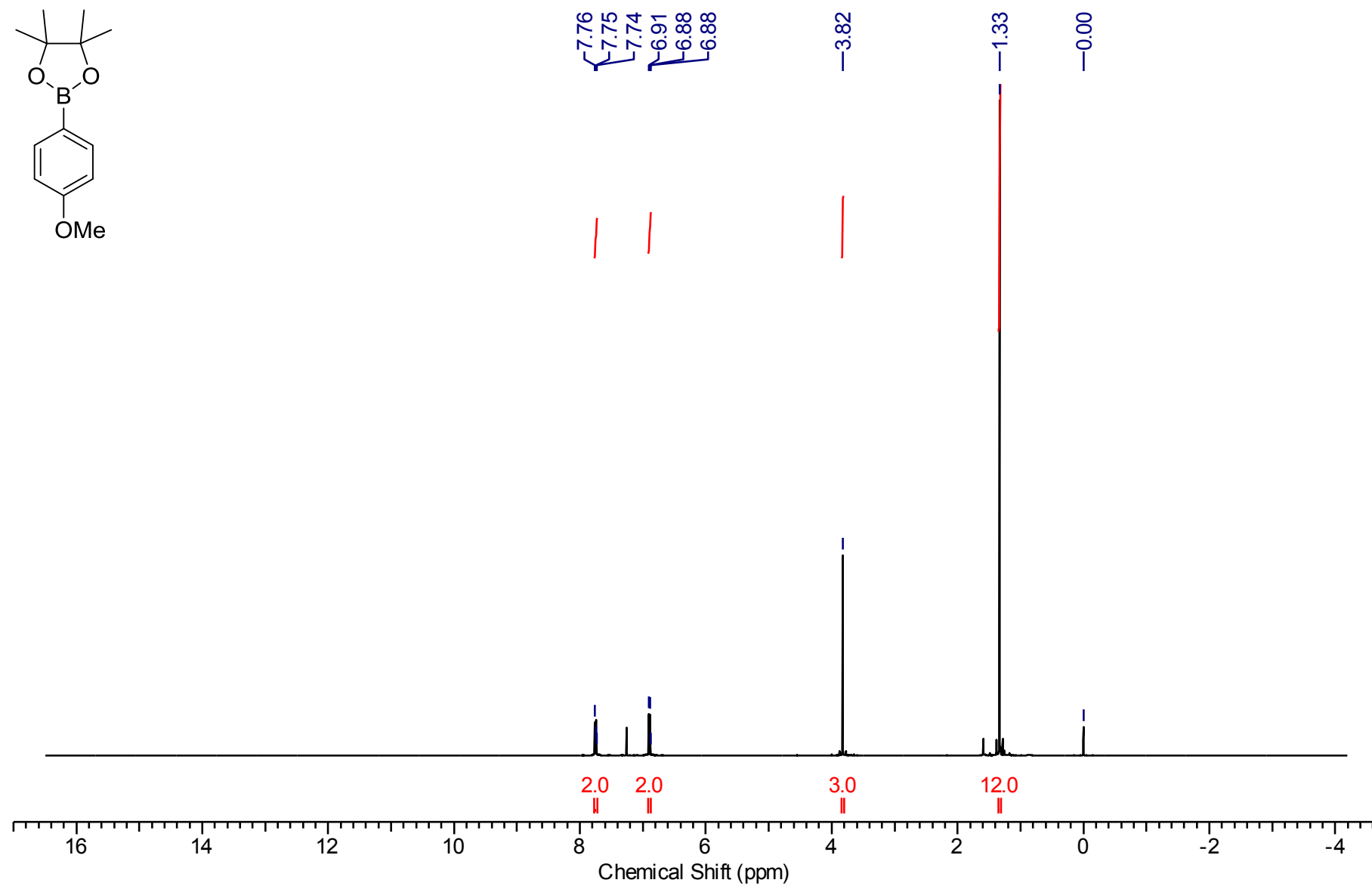
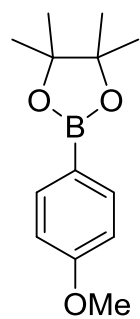
2c: ^{13}C NMR (101 MHz, CDCl_3)



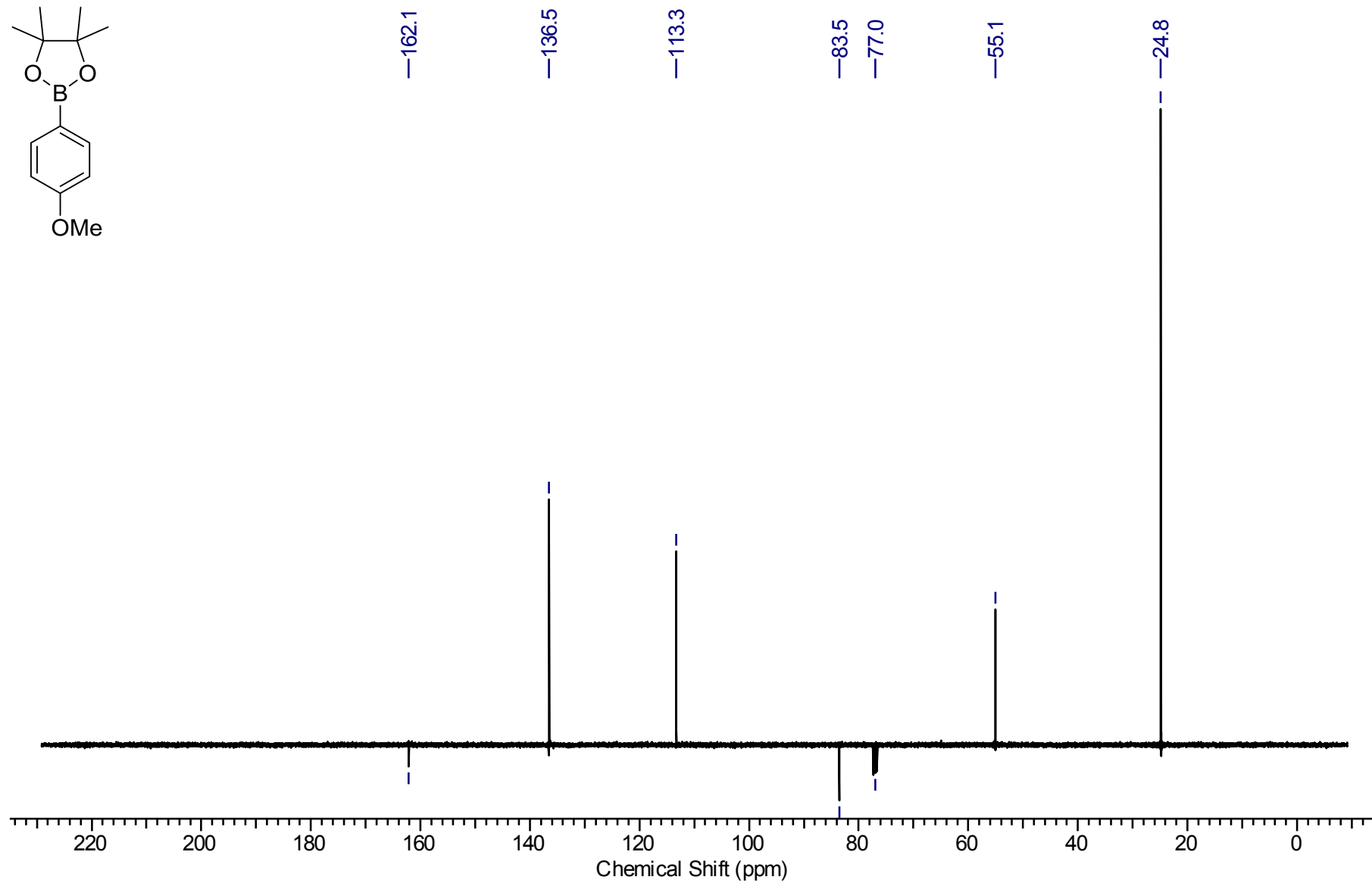
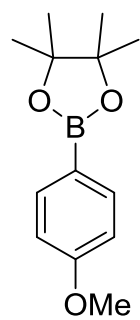
2c: ^{19}F NMR (376 MHz, CDCl_3)



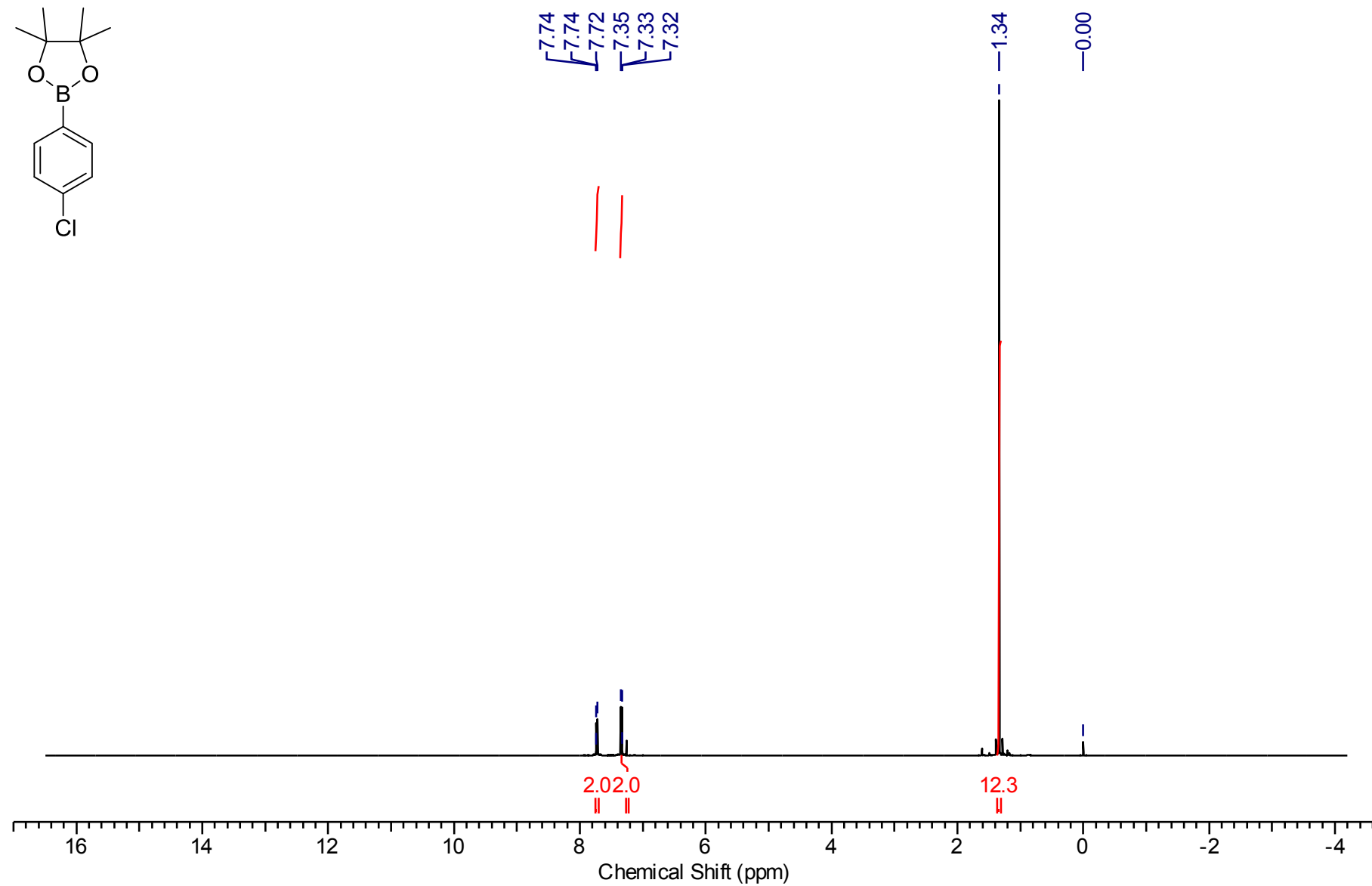
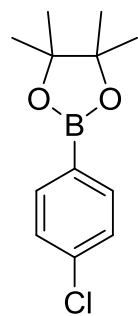
2d: ^1H NMR (400 MHz, CDCl_3)



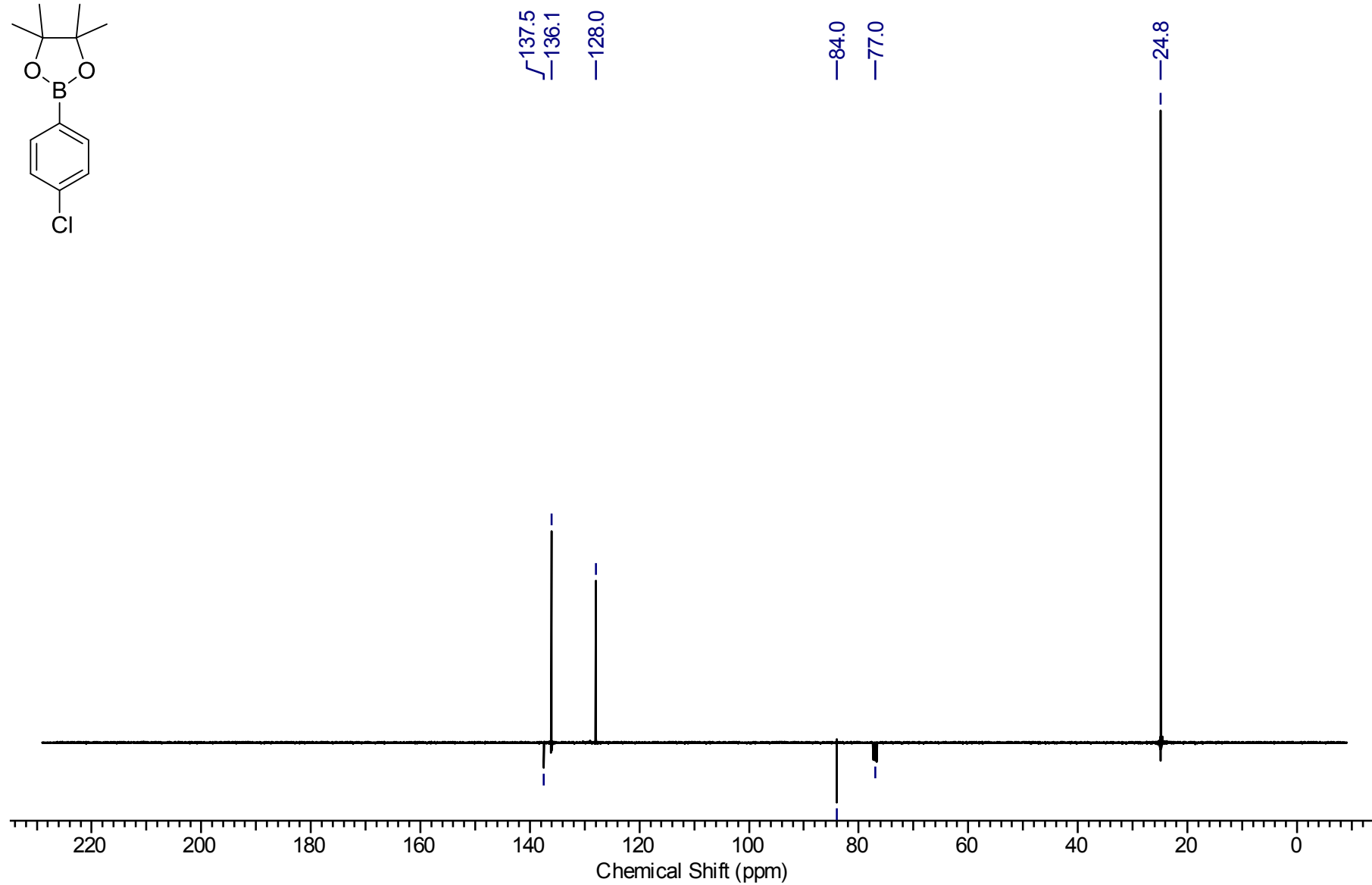
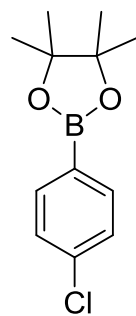
2d: ^{13}C NMR (101 MHz, CDCl_3)



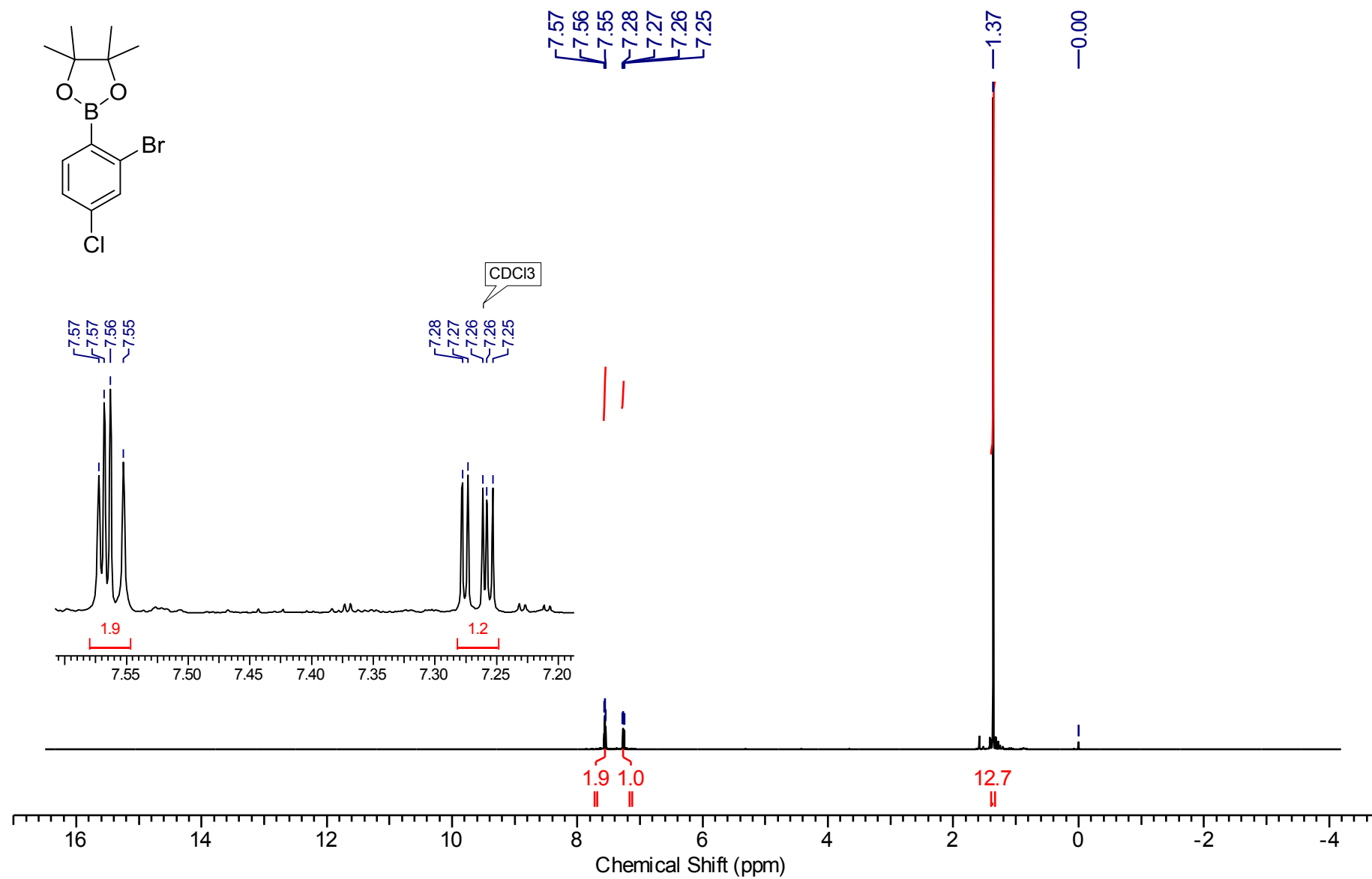
2e: ^1H NMR (400 MHz, CDCl_3)



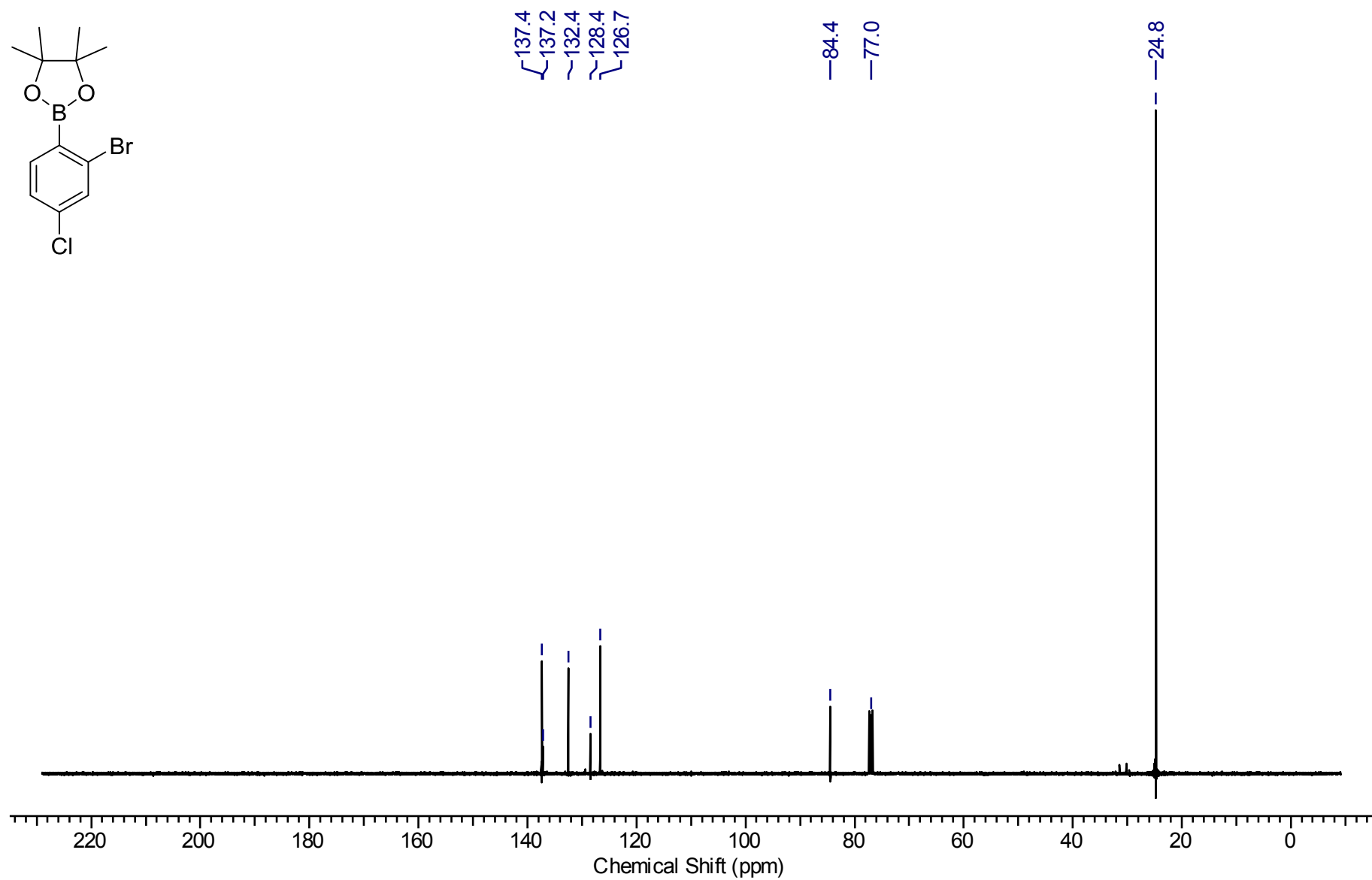
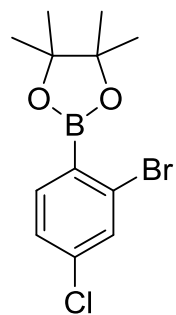
2e: ^{13}C NMR (101 MHz, CDCl_3)



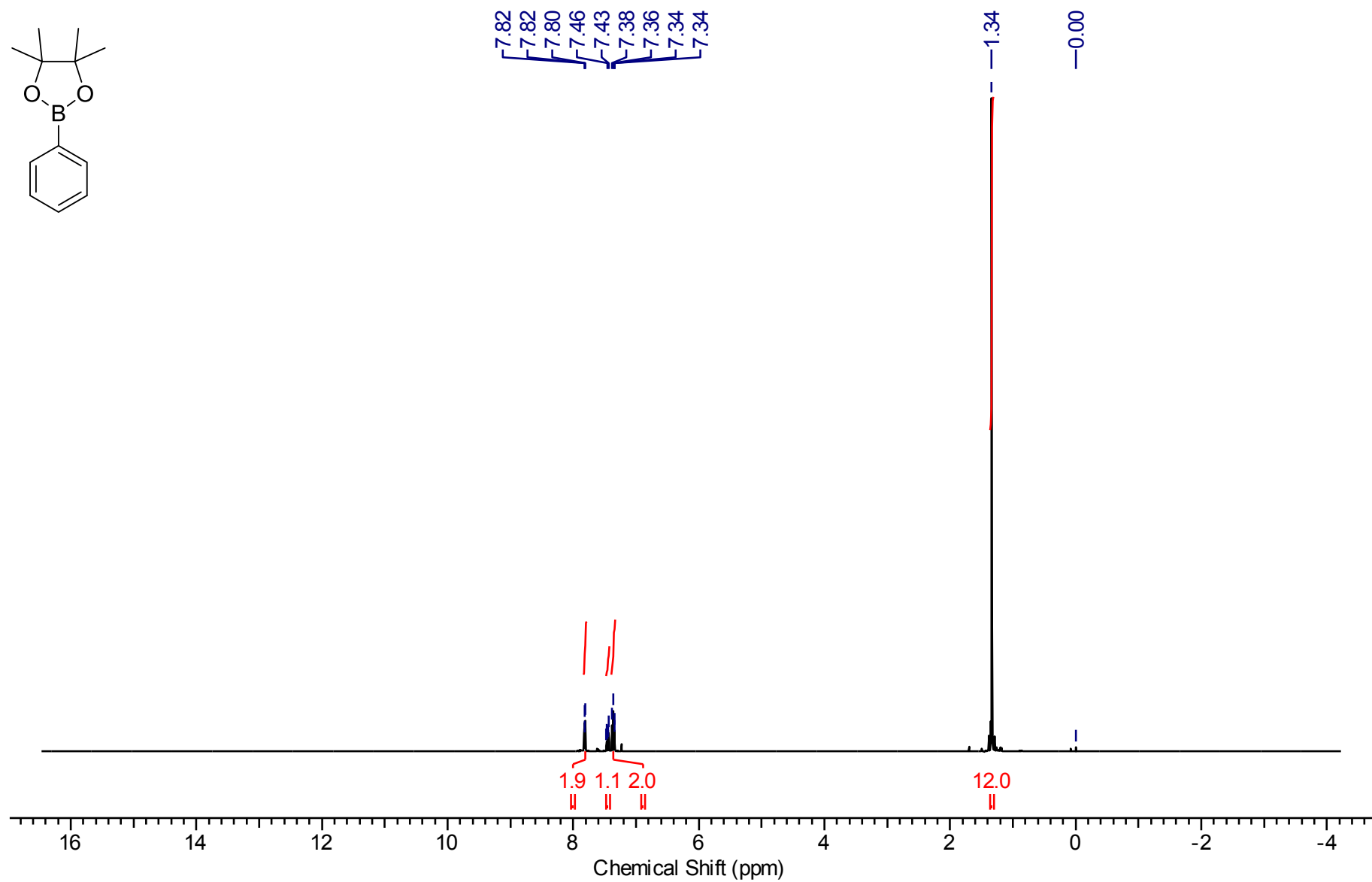
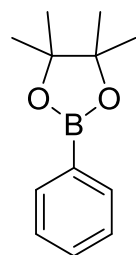
2f: ^1H NMR (400 MHz, CDCl_3)



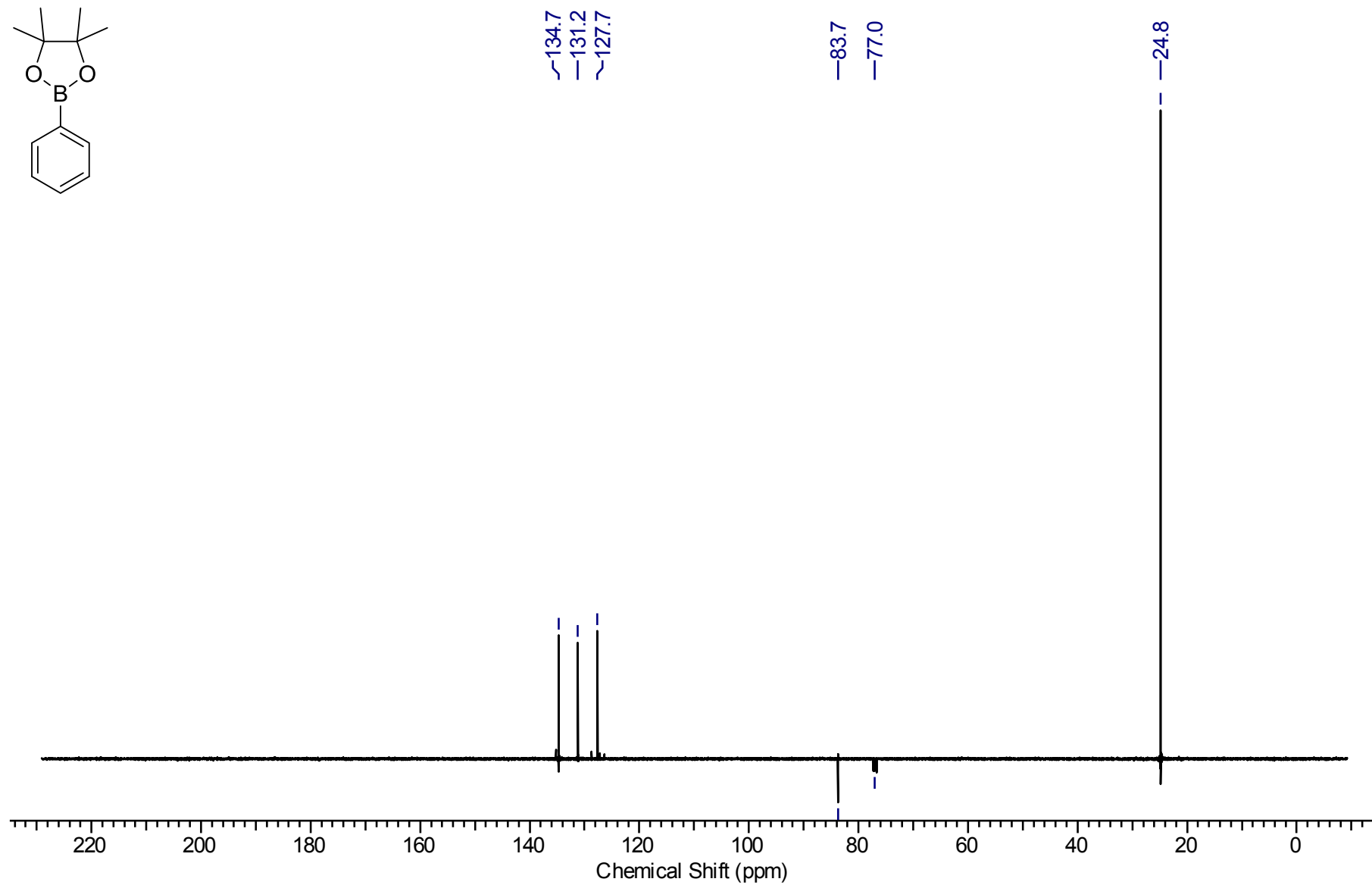
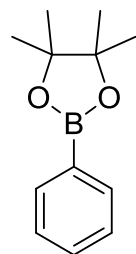
2f: ^{13}C NMR (101 MHz, CDCl_3)



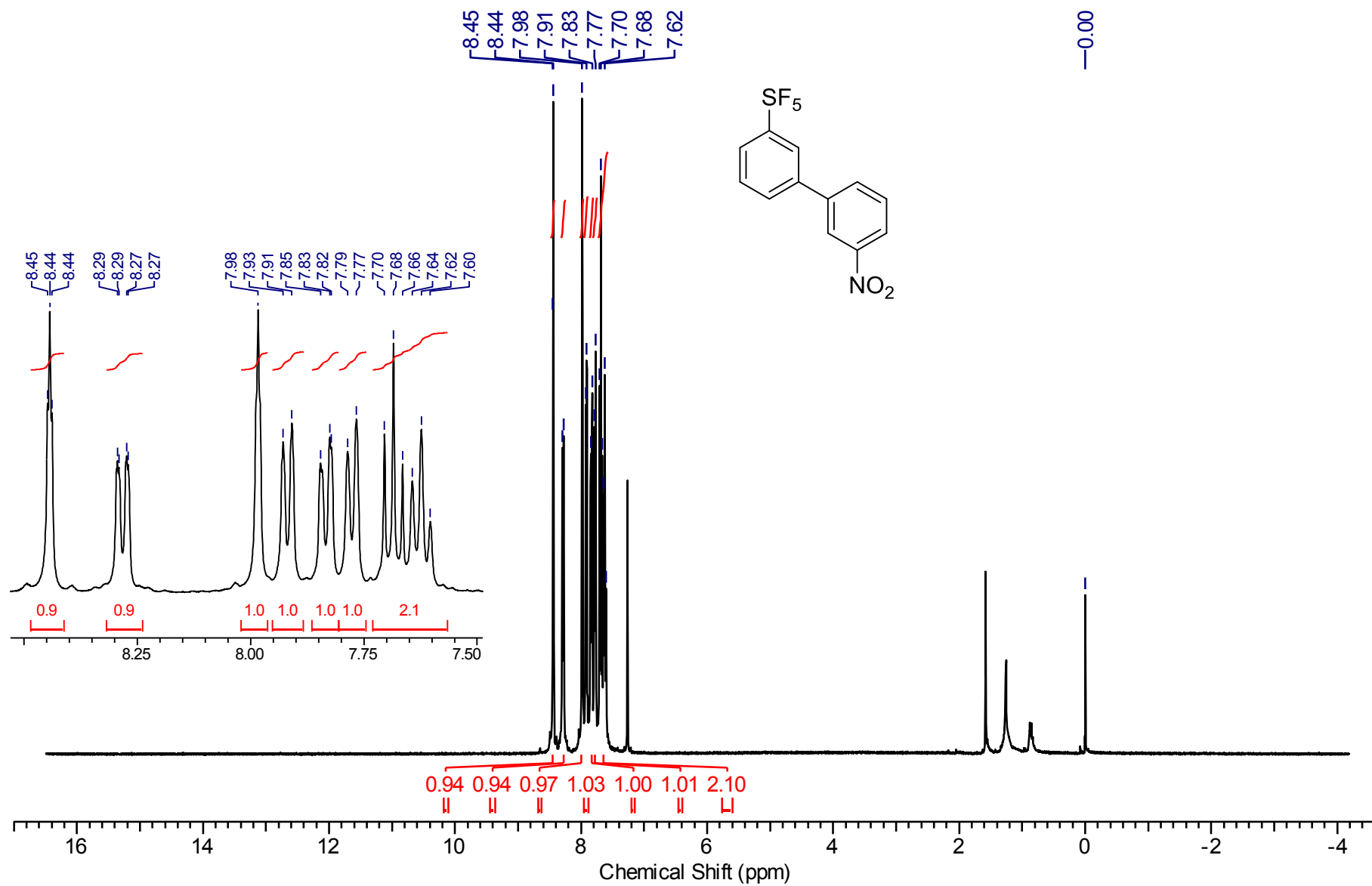
2h: ^1H NMR (400 MHz, CDCl_3)



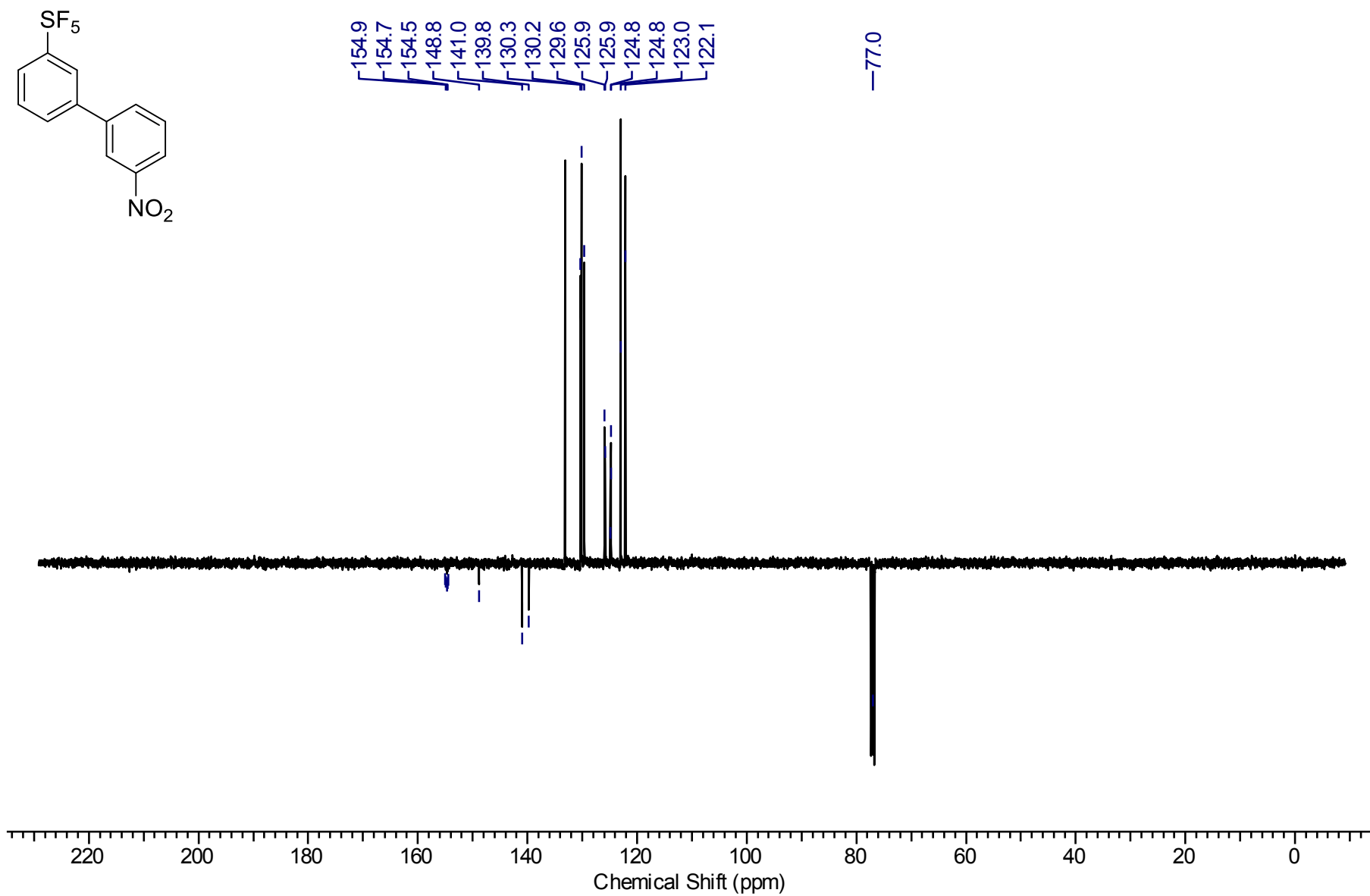
2h: ^{13}C NMR (101 MHz, CDCl_3)



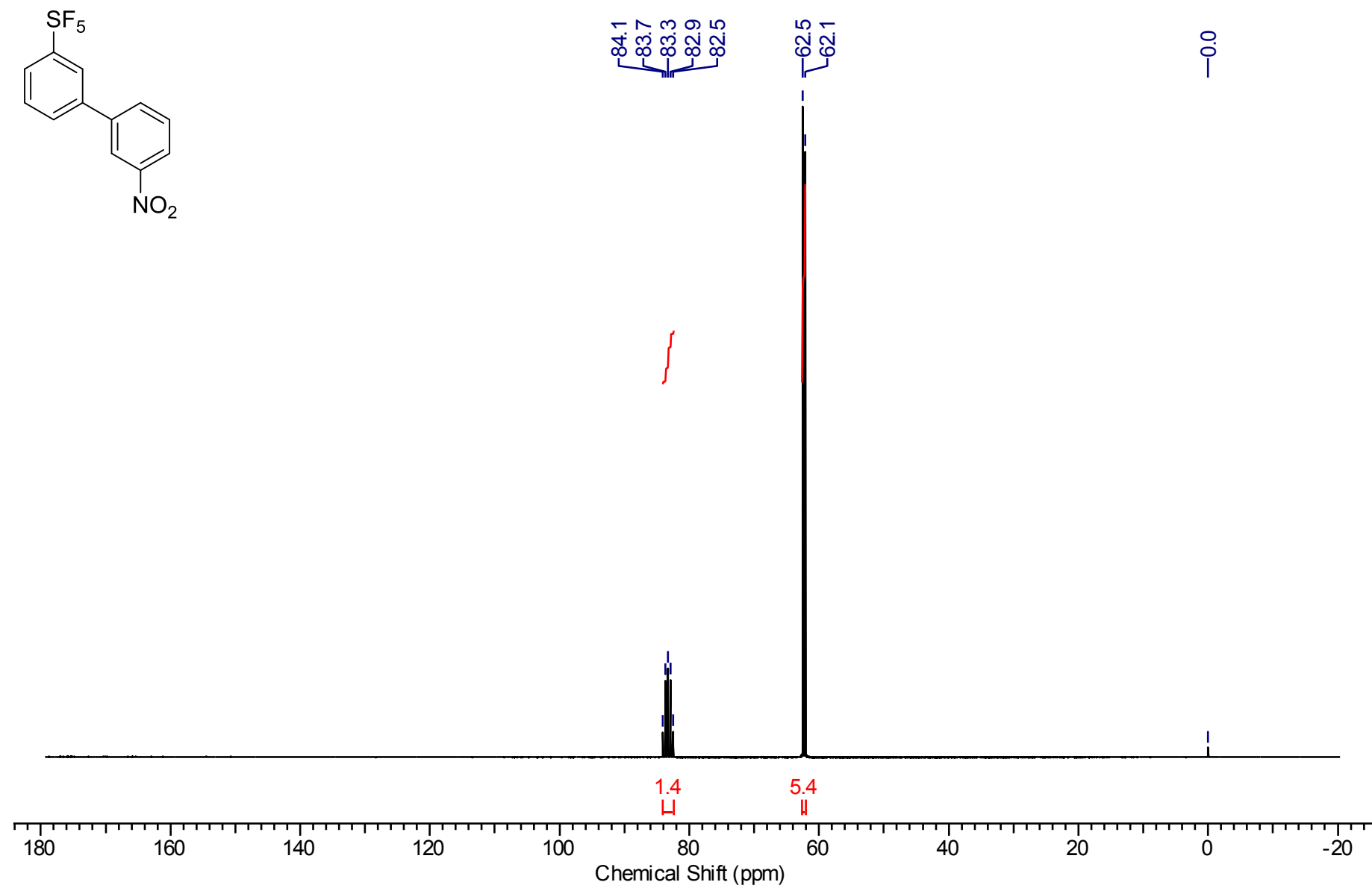
7ah: ^1H NMR (400 MHz, CDCl_3)



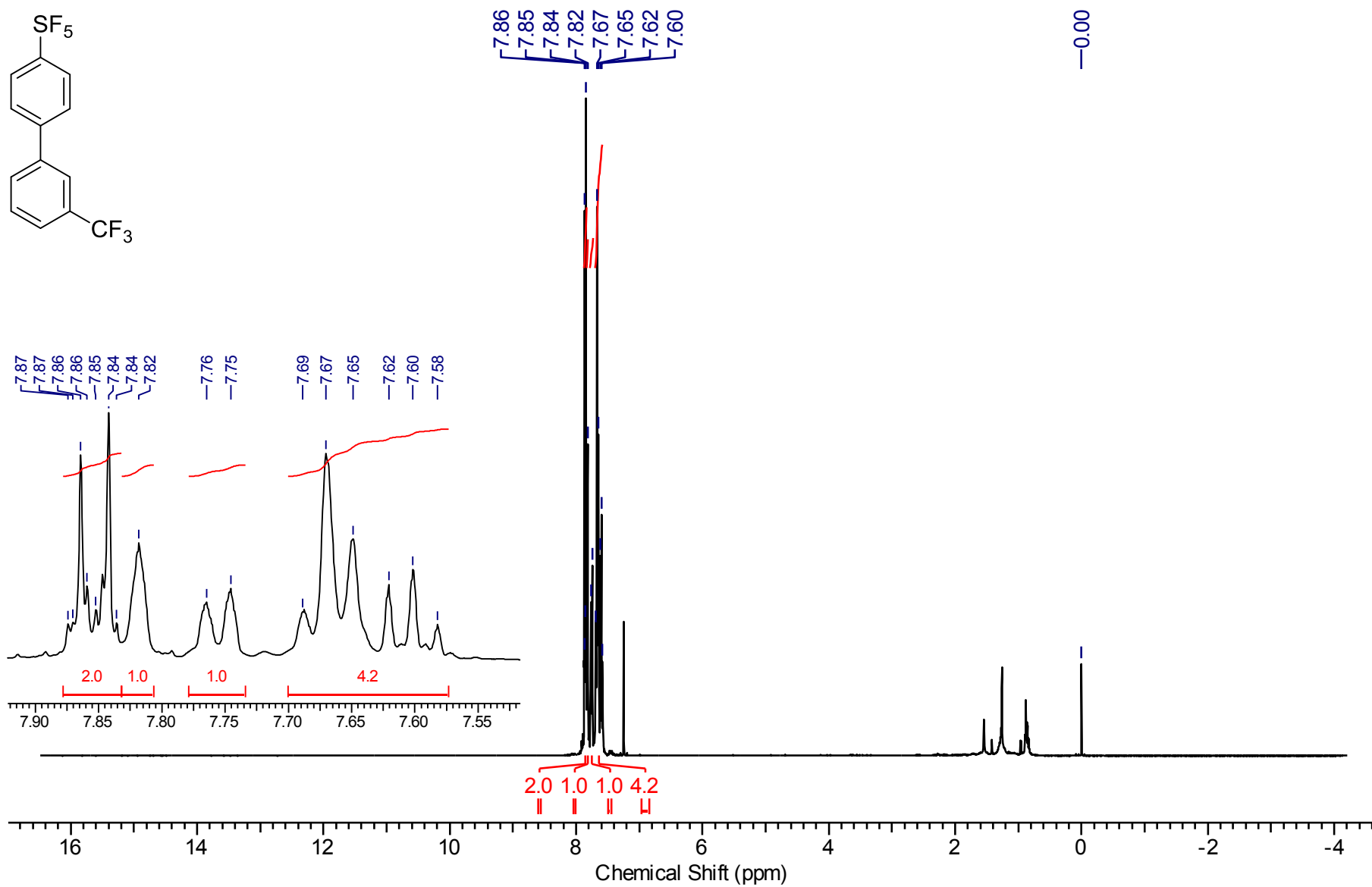
7ah: ^{13}C NMR (101 MHz, CDCl_3)



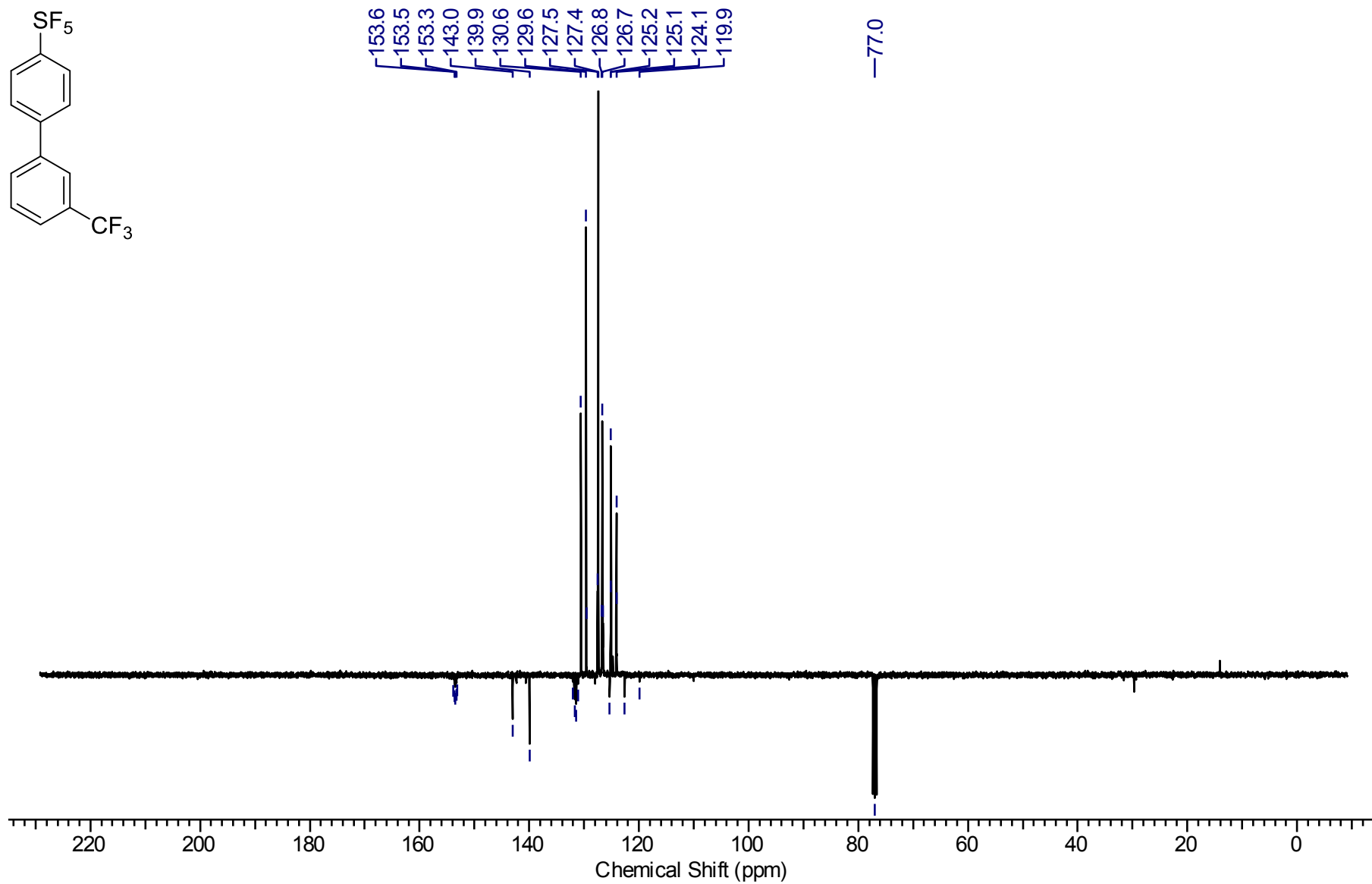
7ah: ^{19}F NMR (377 MHz, CDCl_3)



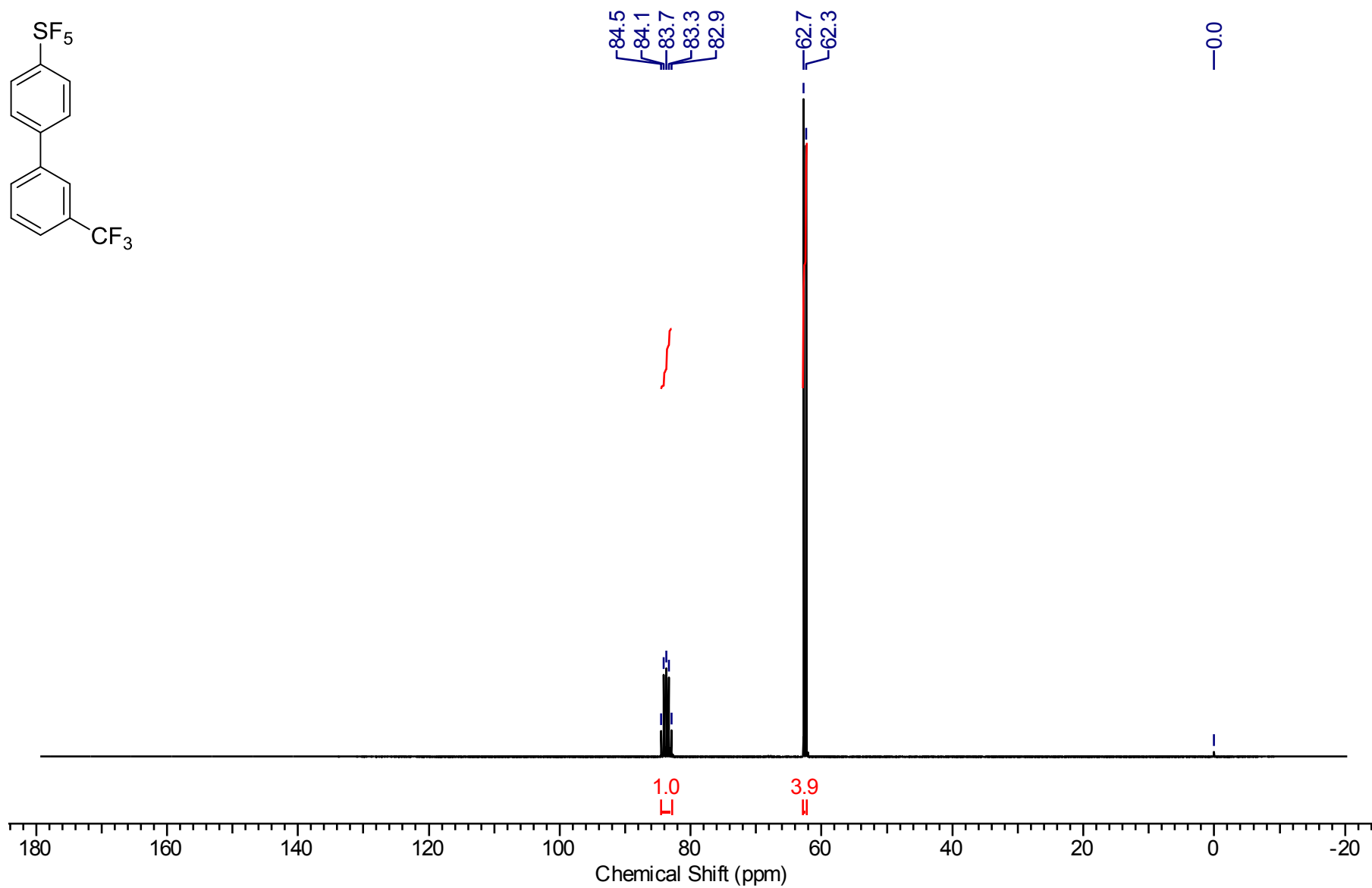
7bc: ^1H NMR (400 MHz, CDCl_3)



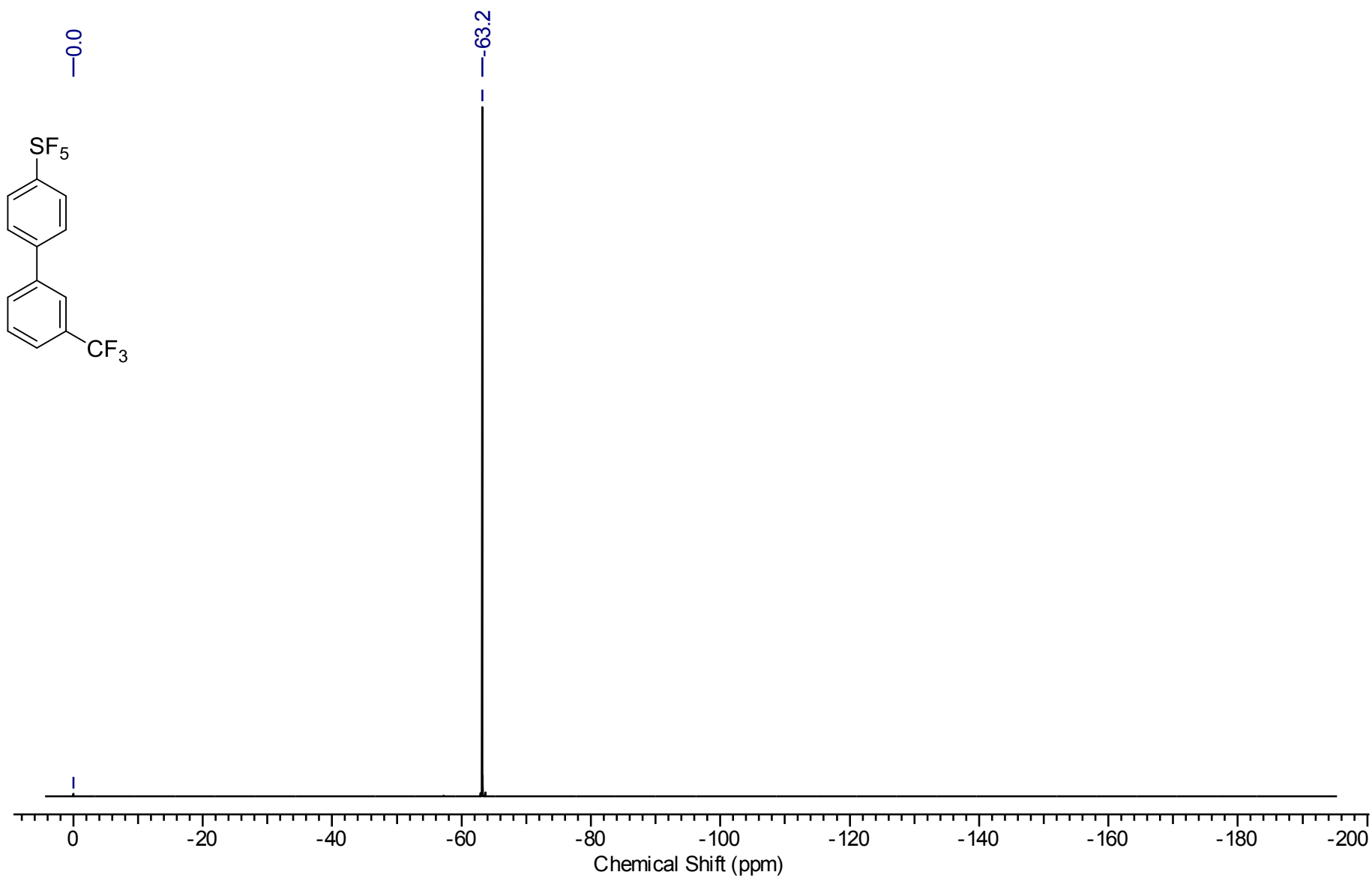
7bc: ^{13}C NMR (101 MHz, CDCl_3)



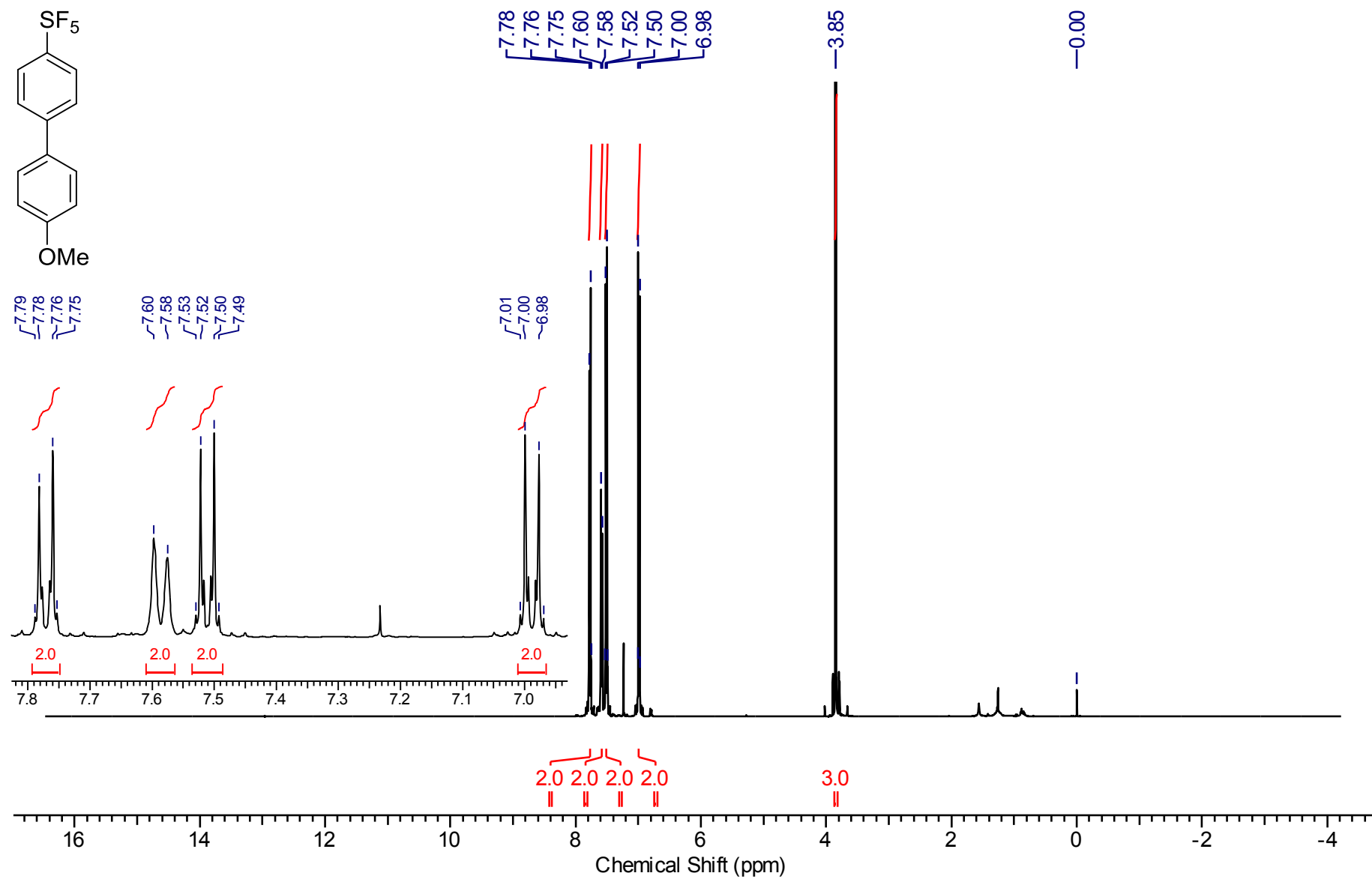
7bc: ^{19}F NMR (377 MHz, CDCl_3)



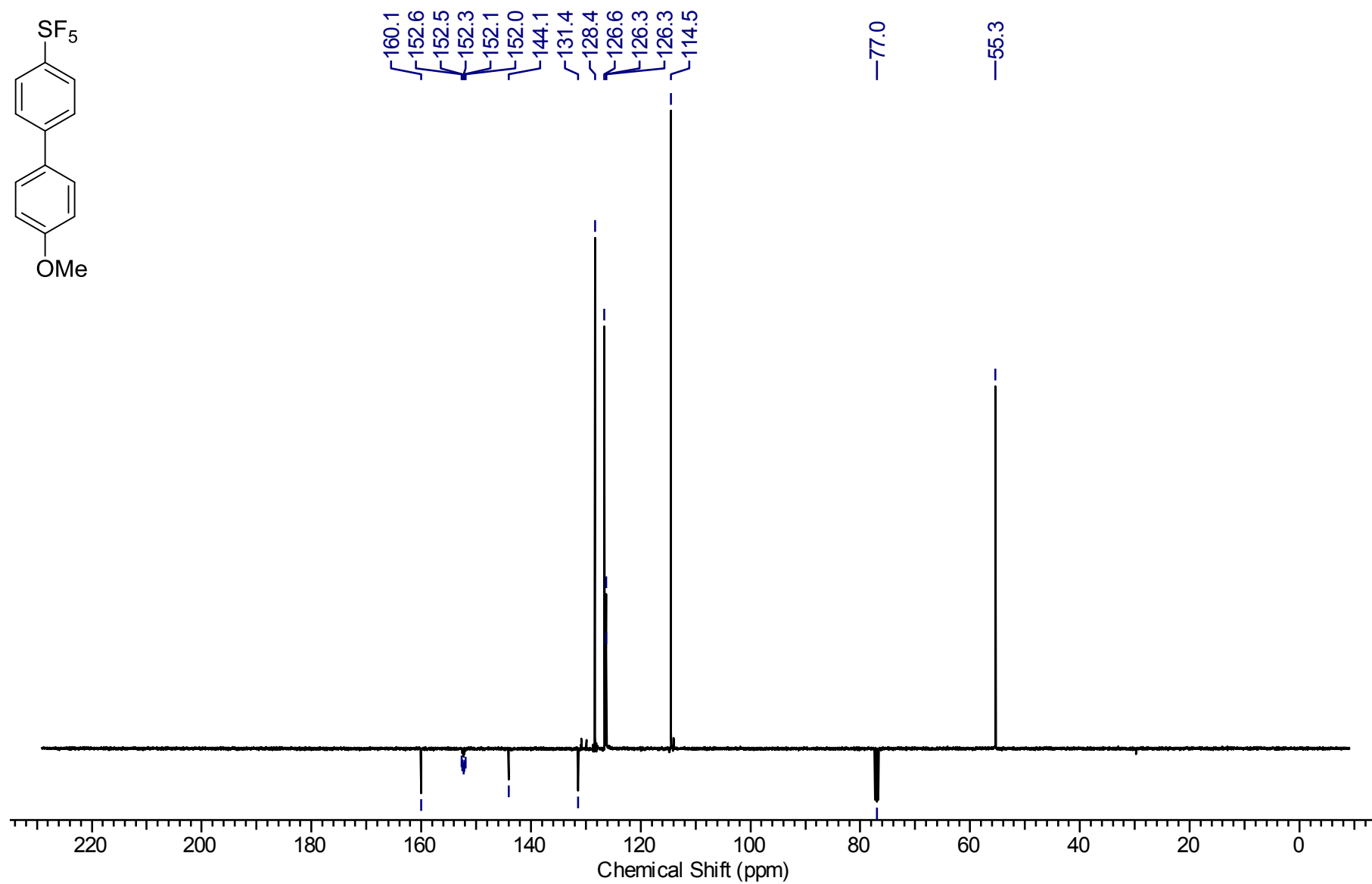
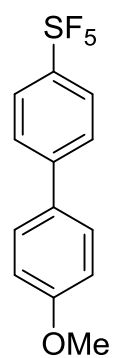
7bc: ^{19}F NMR (377 MHz, CDCl_3)



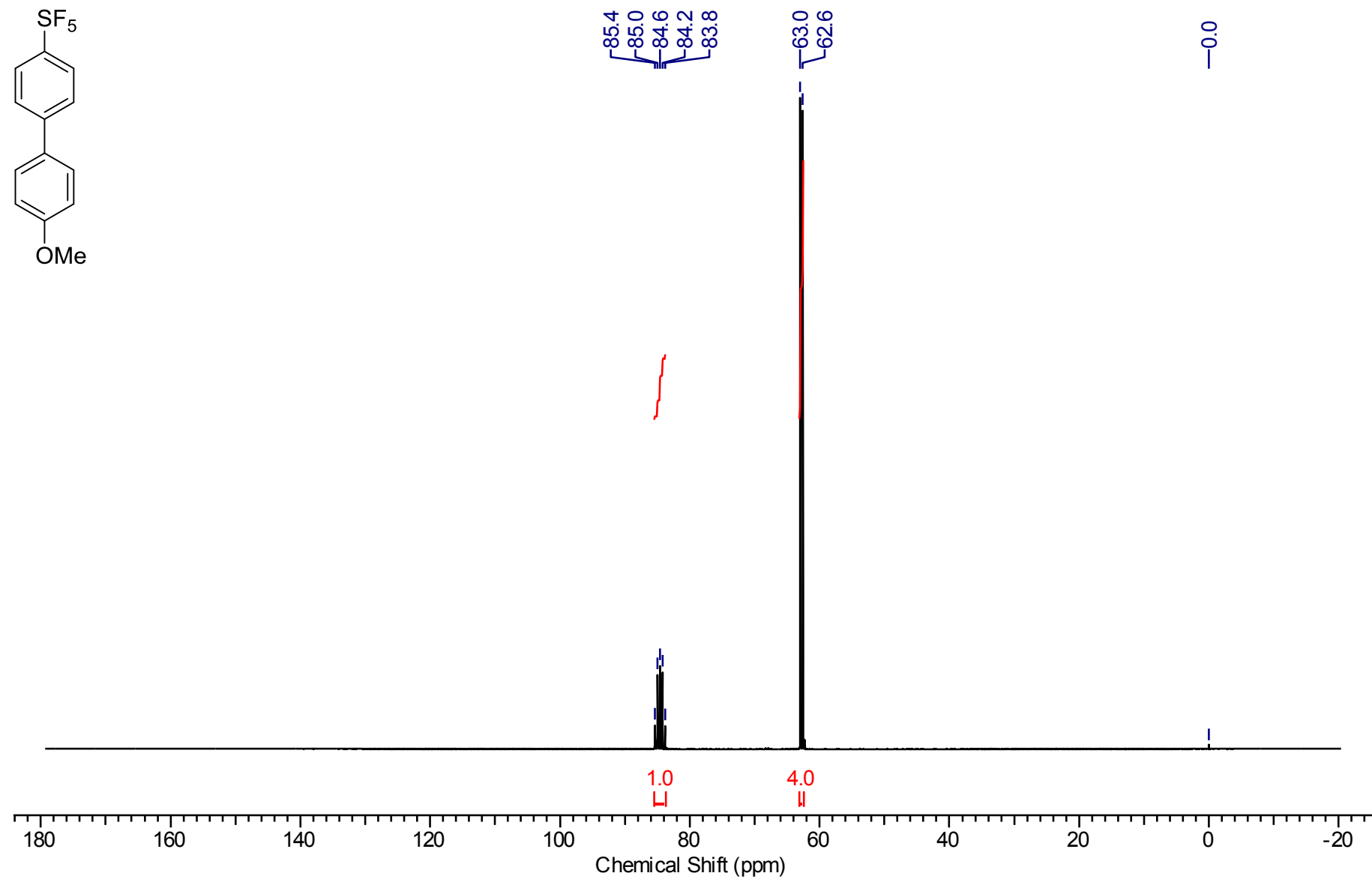
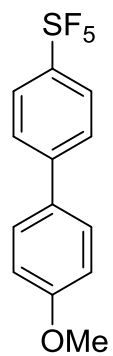
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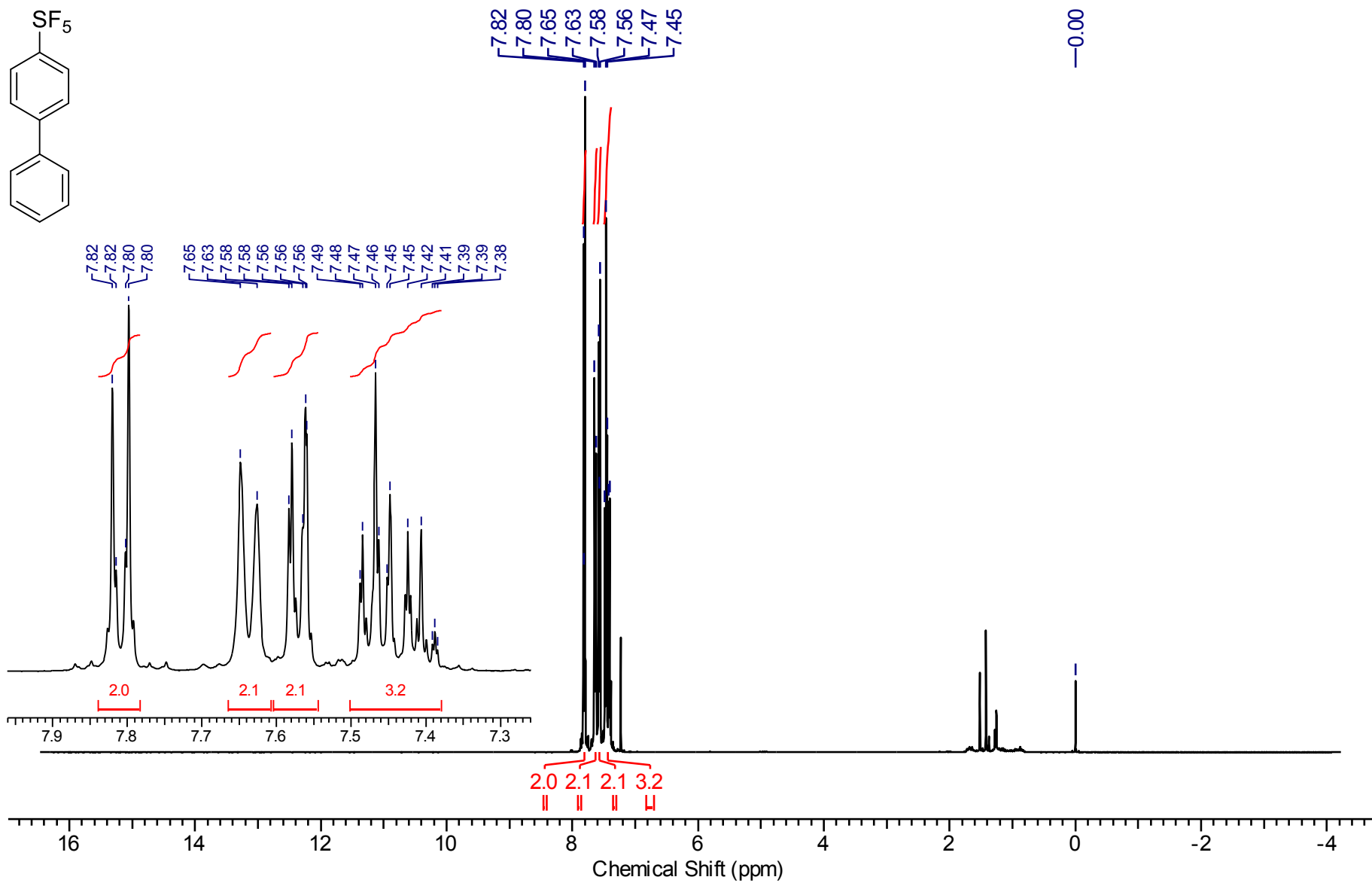
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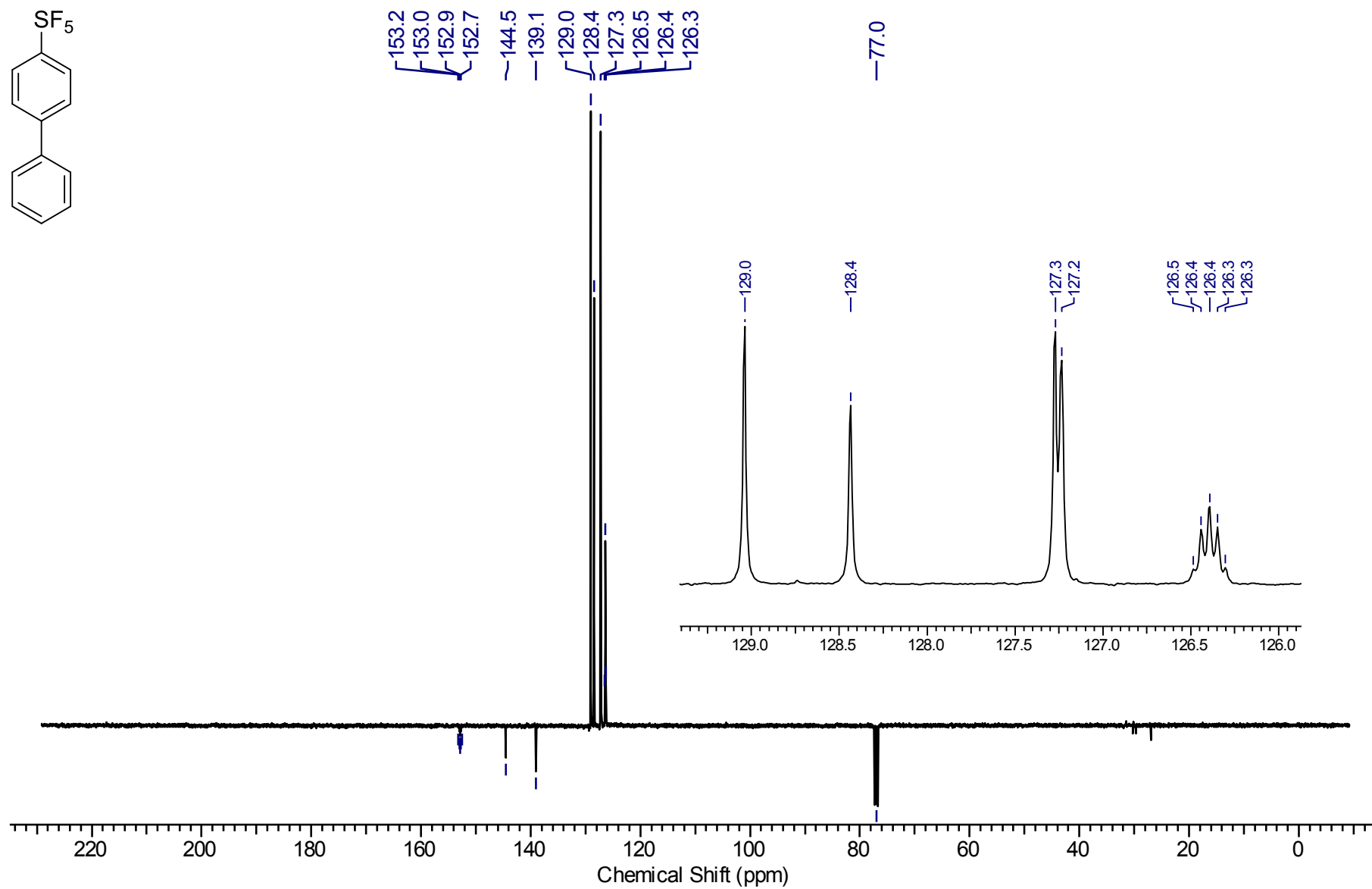
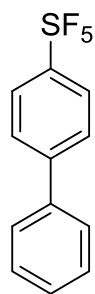
7bd: ^{19}F NMR (377 MHz, CDCl_3)



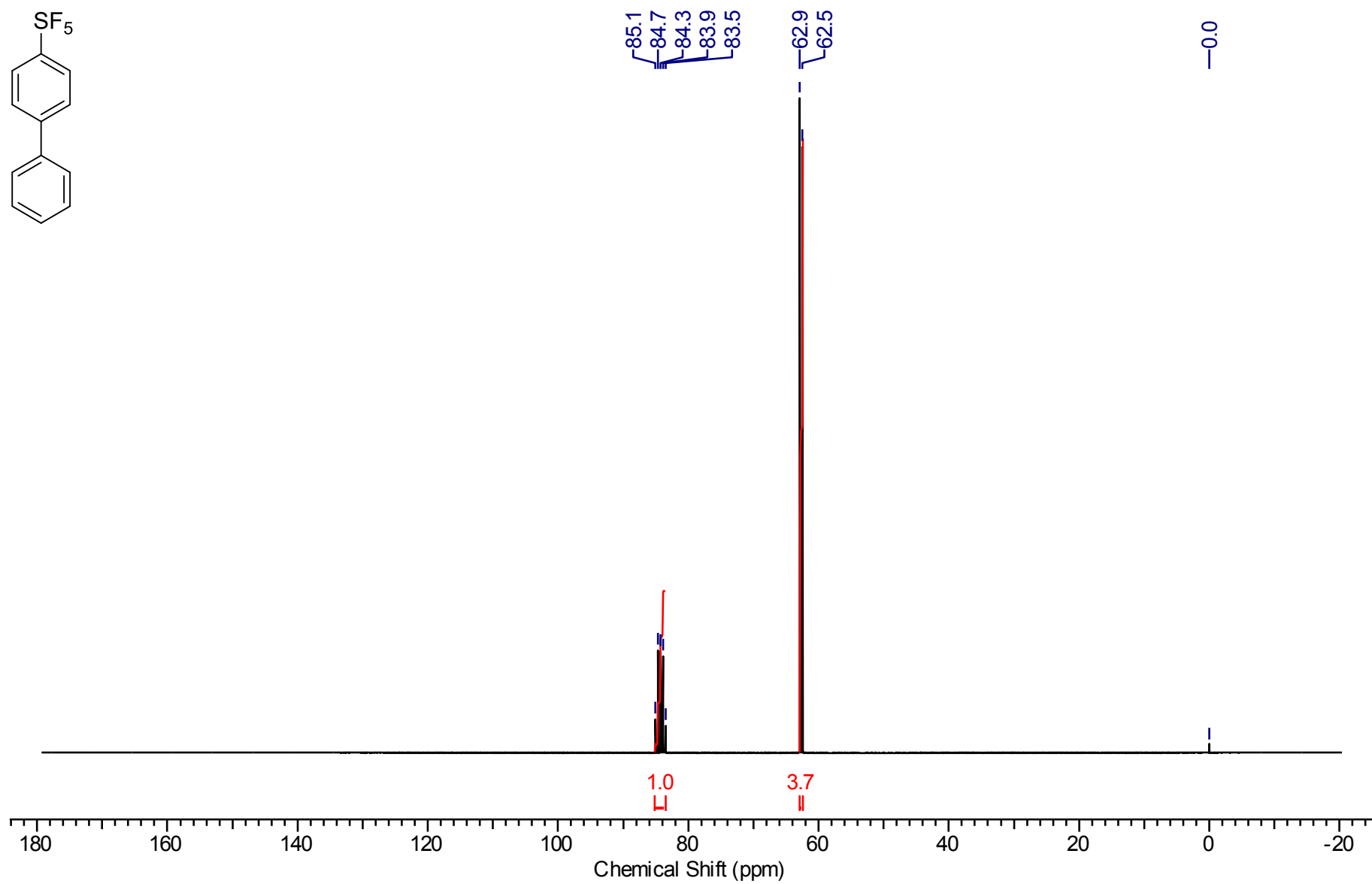
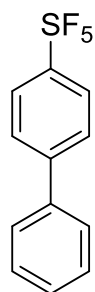
7bh: ^1H NMR (400 MHz, CDCl_3)



7bh: ^{13}C NMR (101 MHz, CDCl_3)

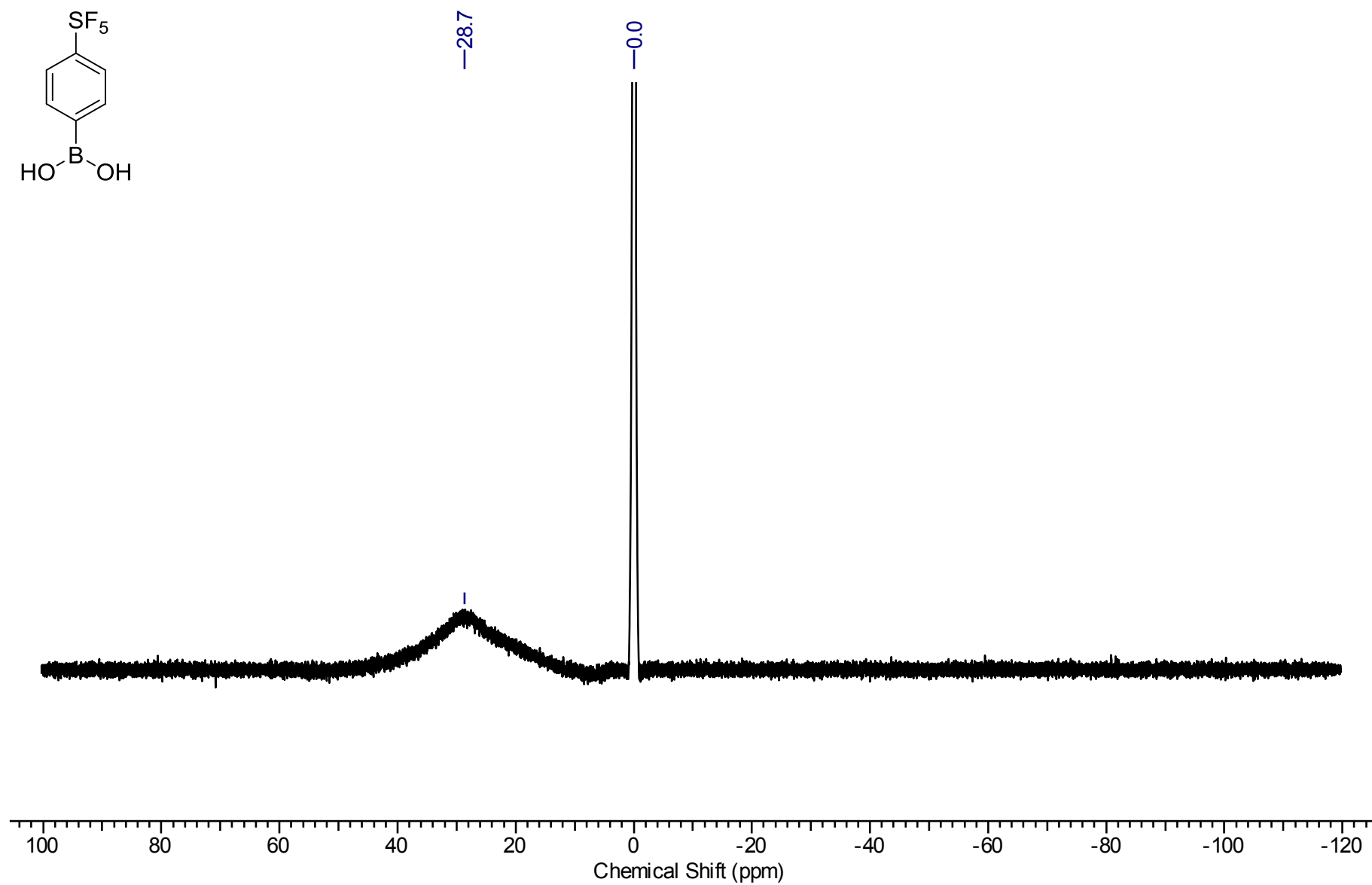
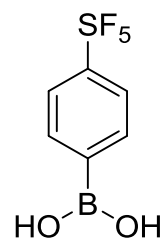


7bh: ^{19}F NMR (377 MHz, CDCl_3)

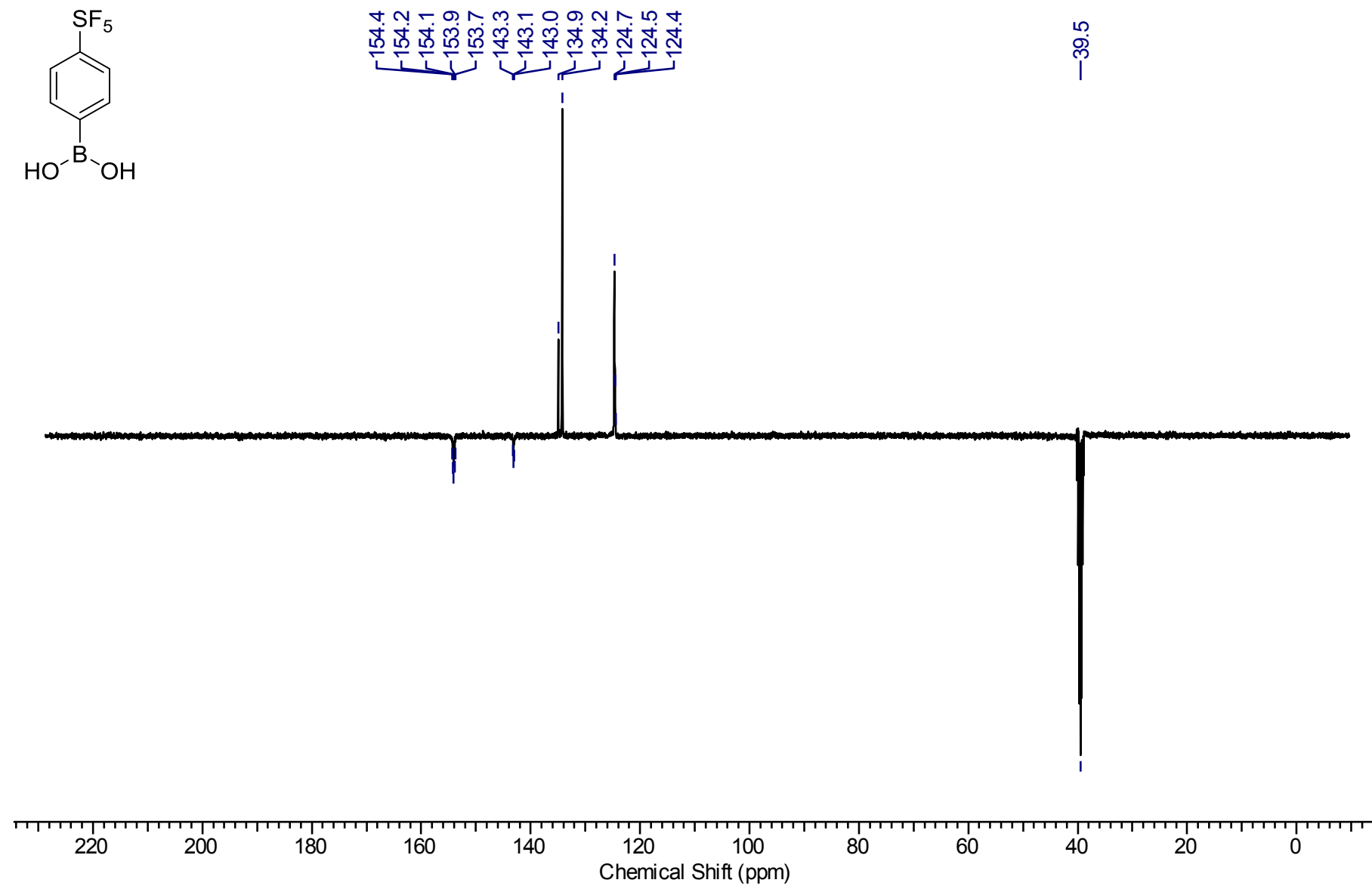


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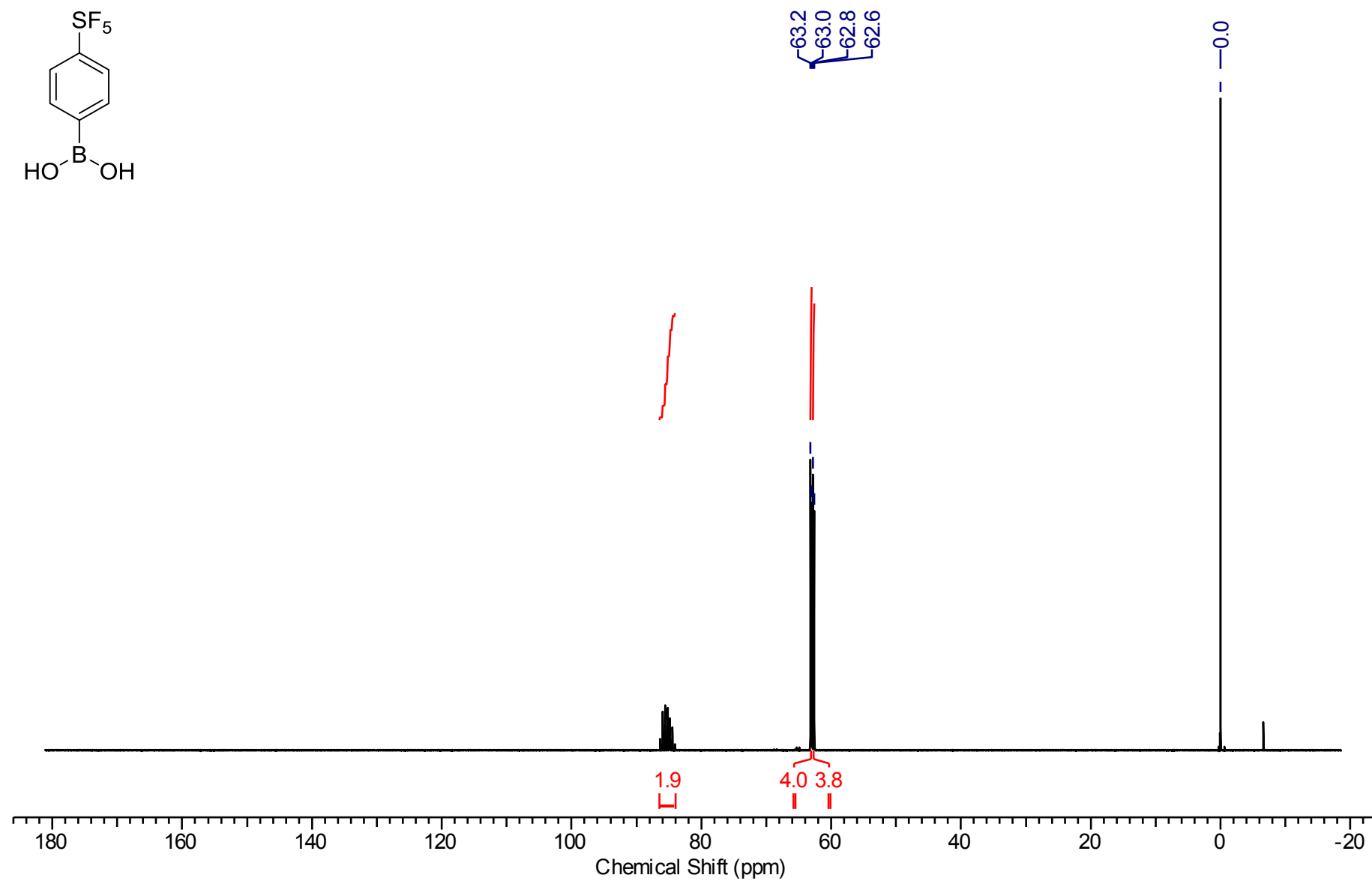
8b: ^{11}B NMR (128 MHz, $[\text{D}_6]\text{DMSO}$)



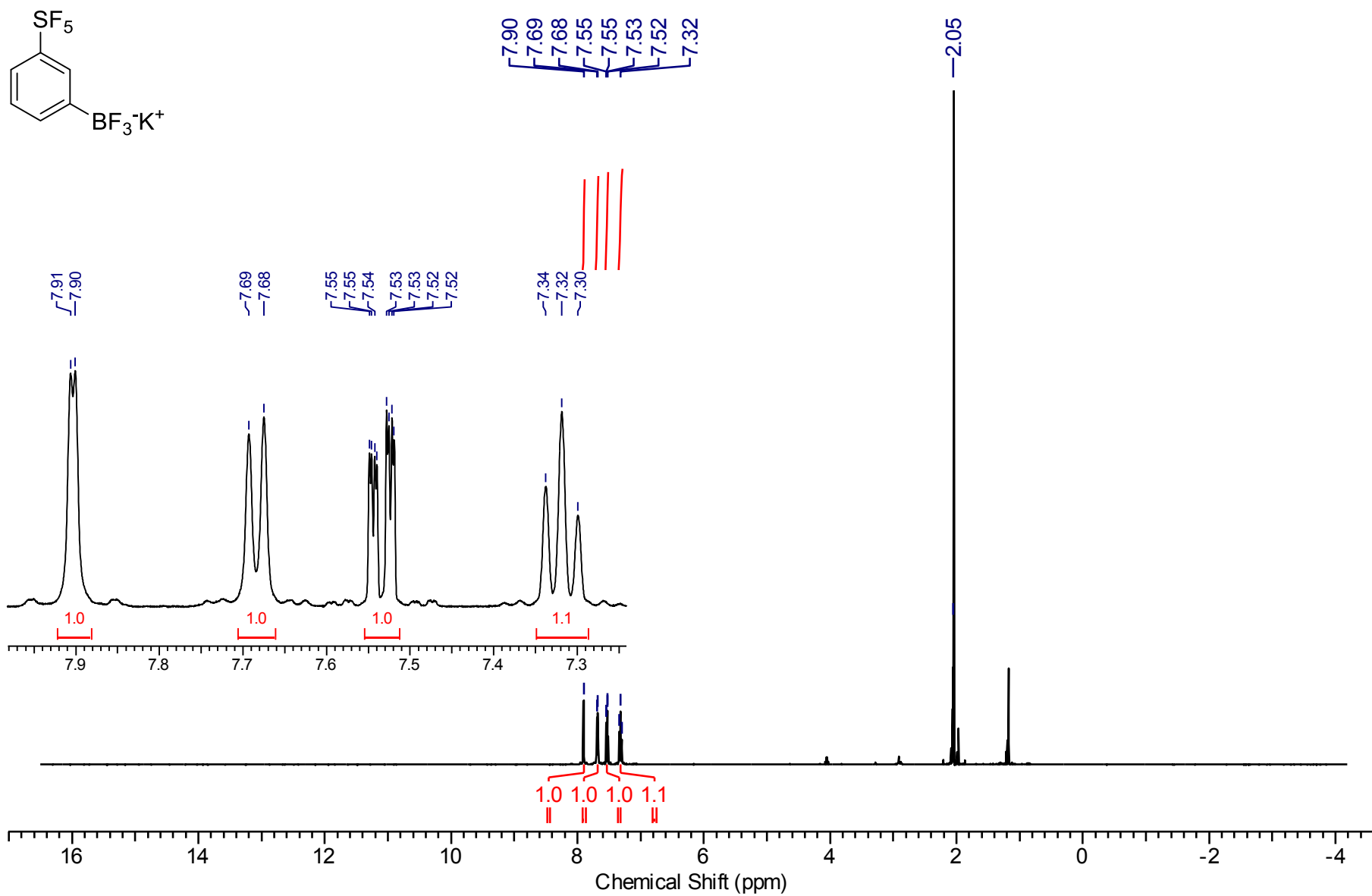
8b: ^{13}C NMR (101 MHz, $[\text{D}_6]\text{DMSO}$)



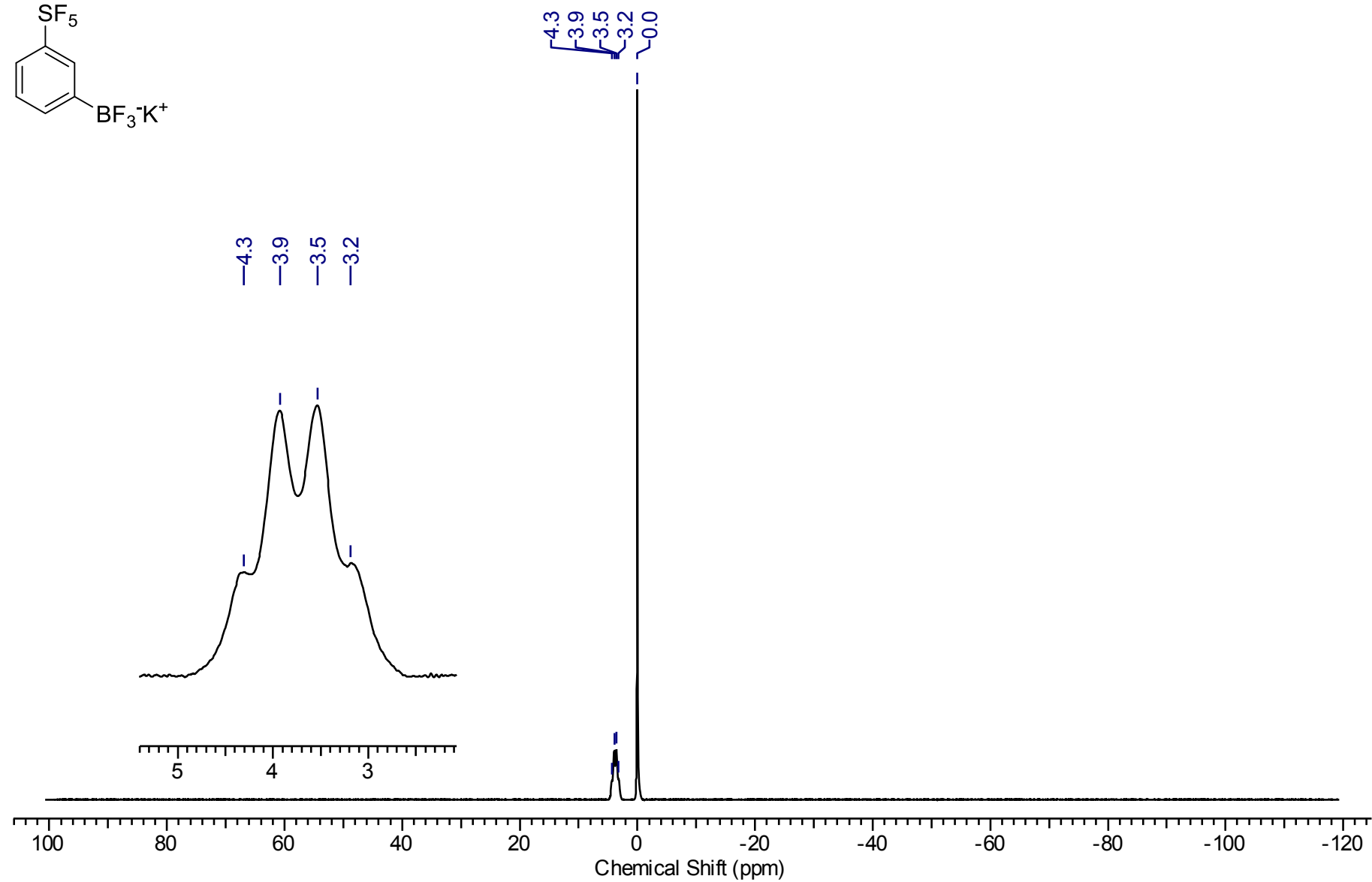
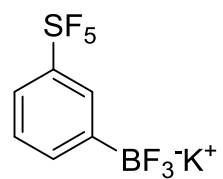
8b: ^{19}F NMR (377 MHz, CD_3CN)



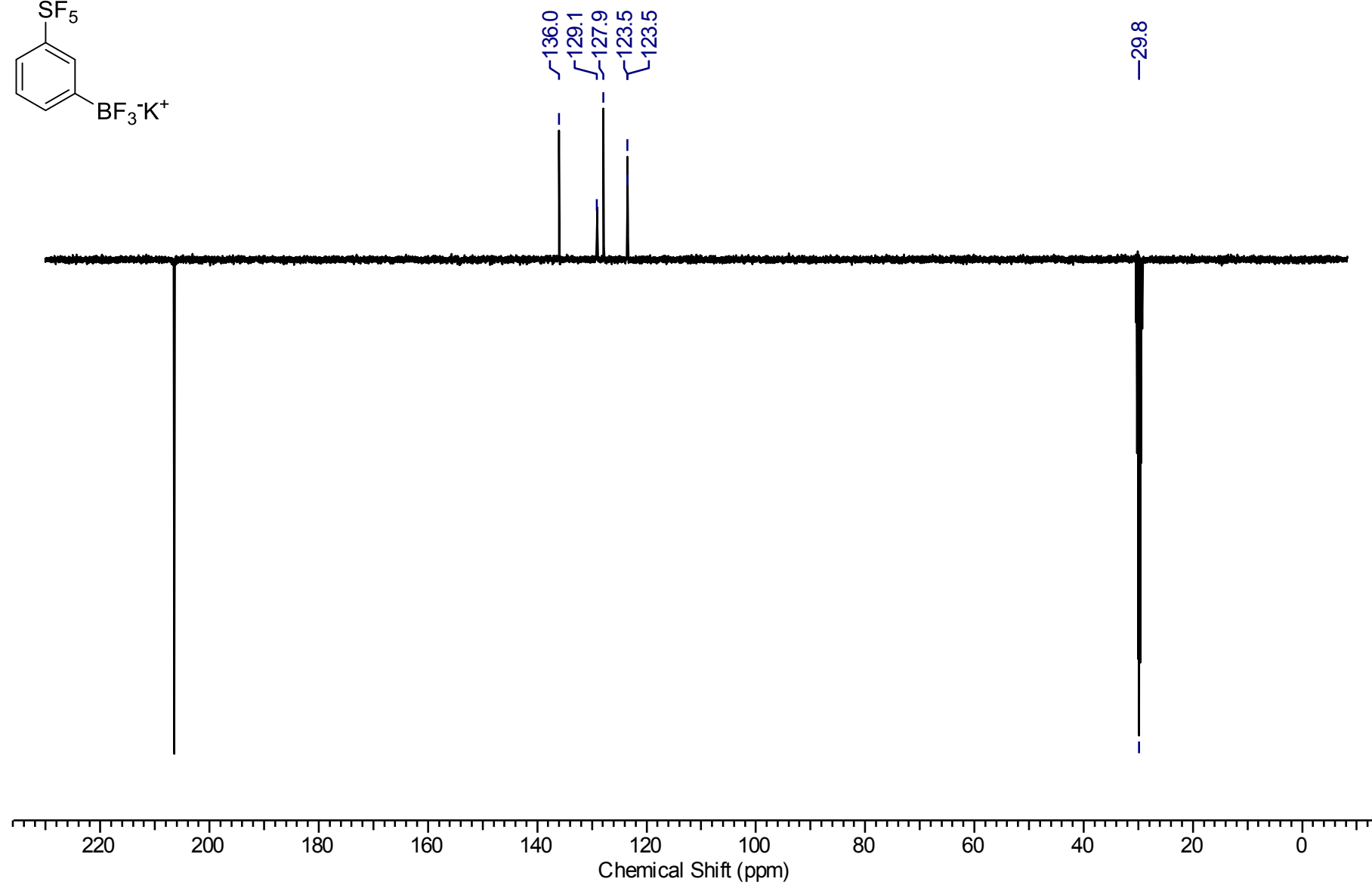
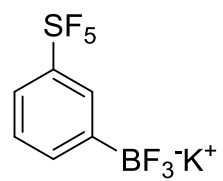
9a: ^1H NMR (400 MHz, $[\text{D}_6]\text{acetone}$)



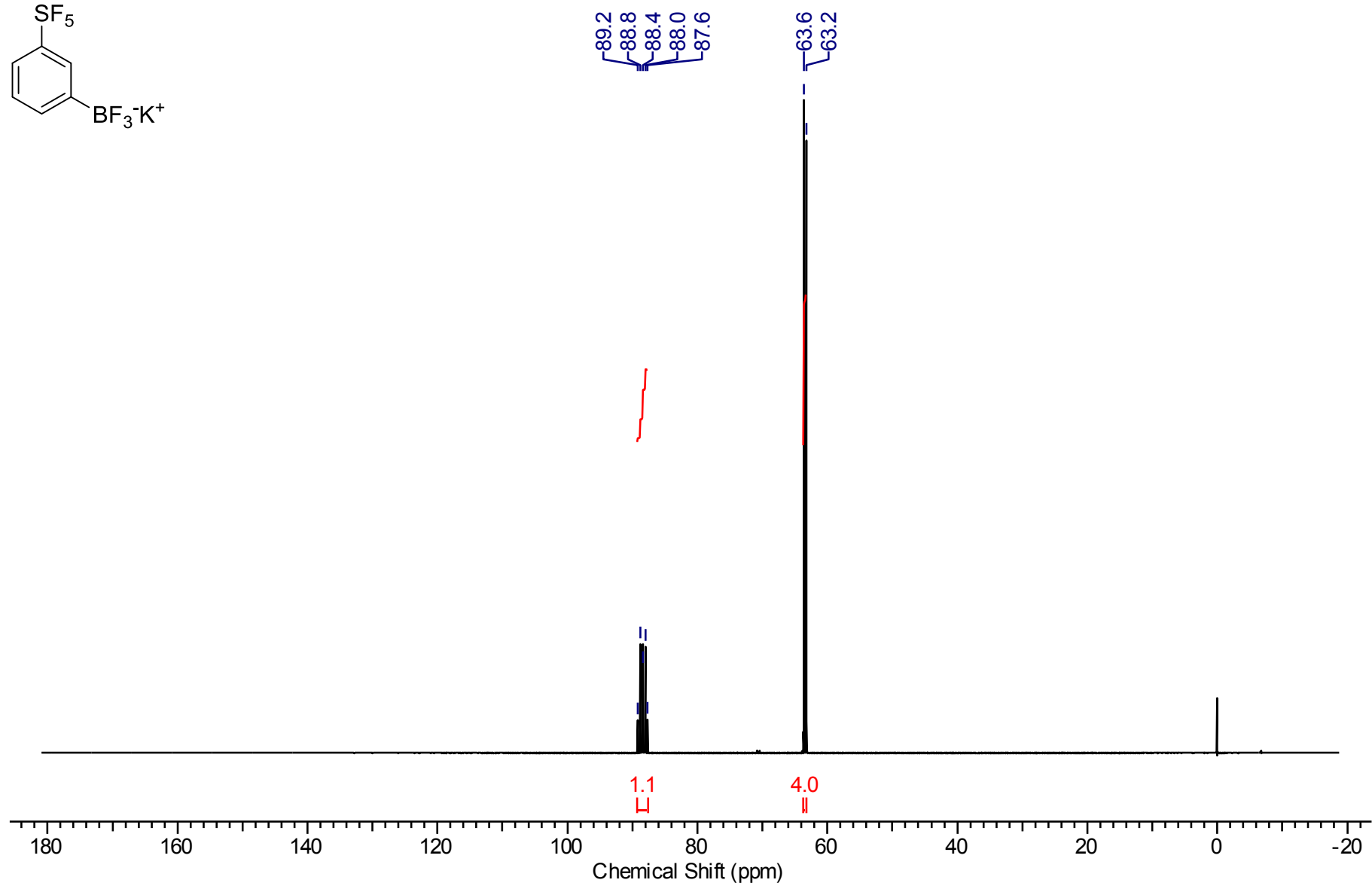
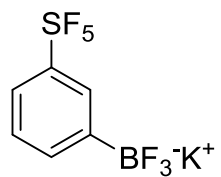
9a: ^{11}B NMR (128 MHz, $[\text{D}_6]\text{acetone}$)



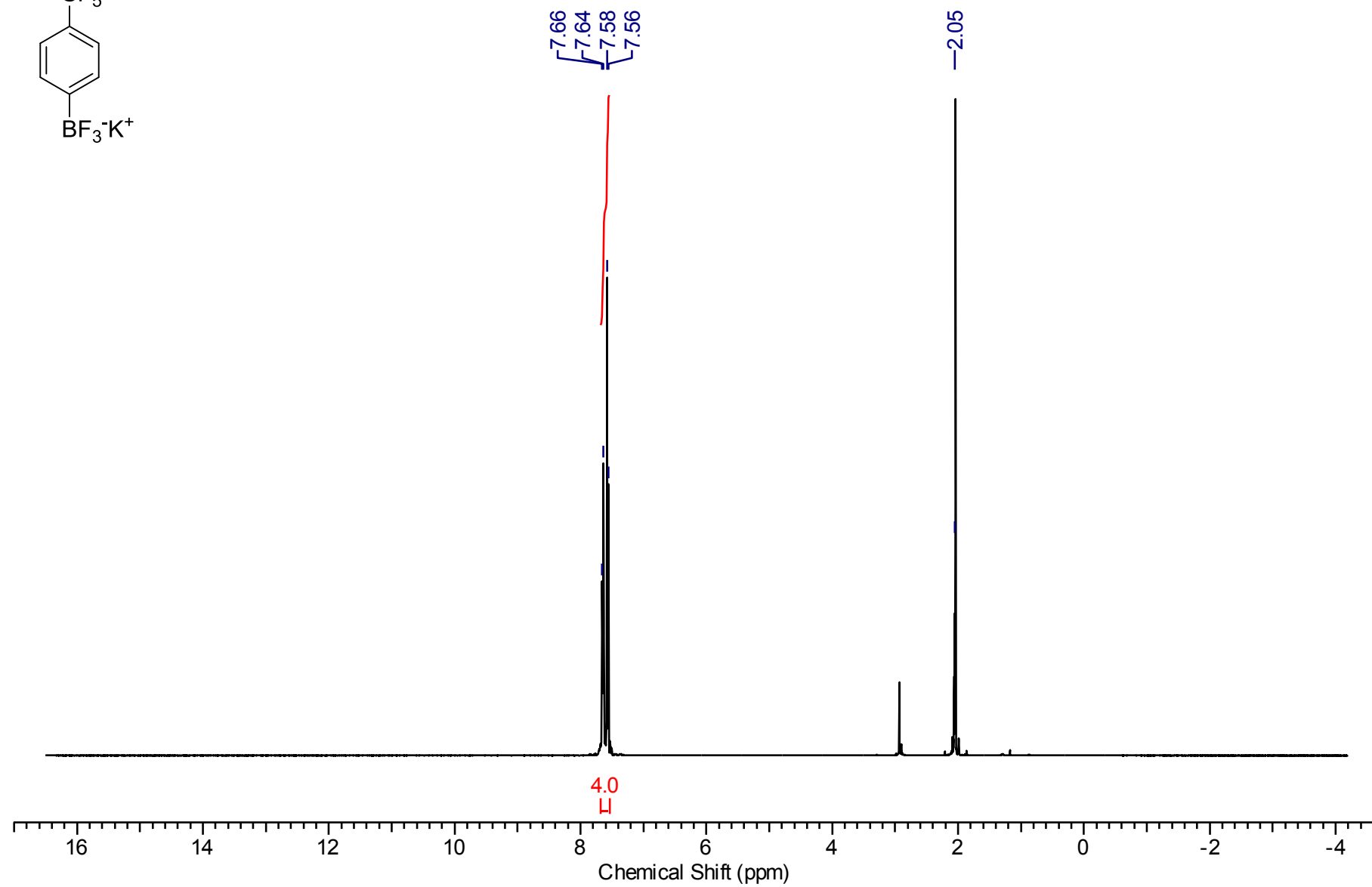
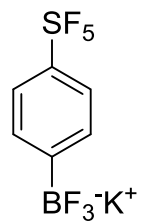
9a: ^{13}C NMR (101 MHz, $[\text{D}_6]\text{acetone}$)



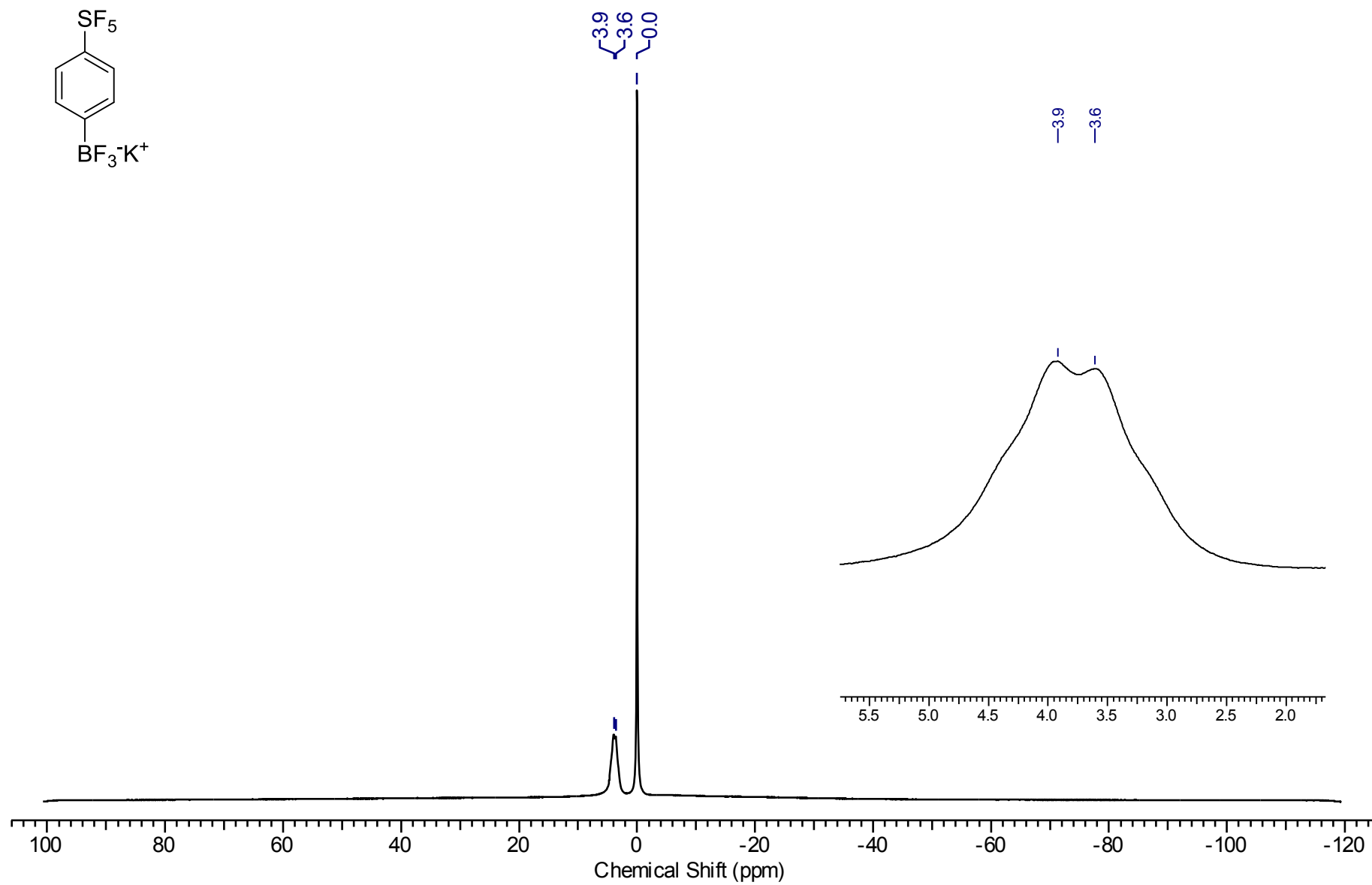
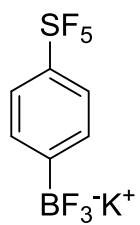
9a: ^{19}F NMR (377 MHz, $[\text{D}_6]\text{acetone}$)



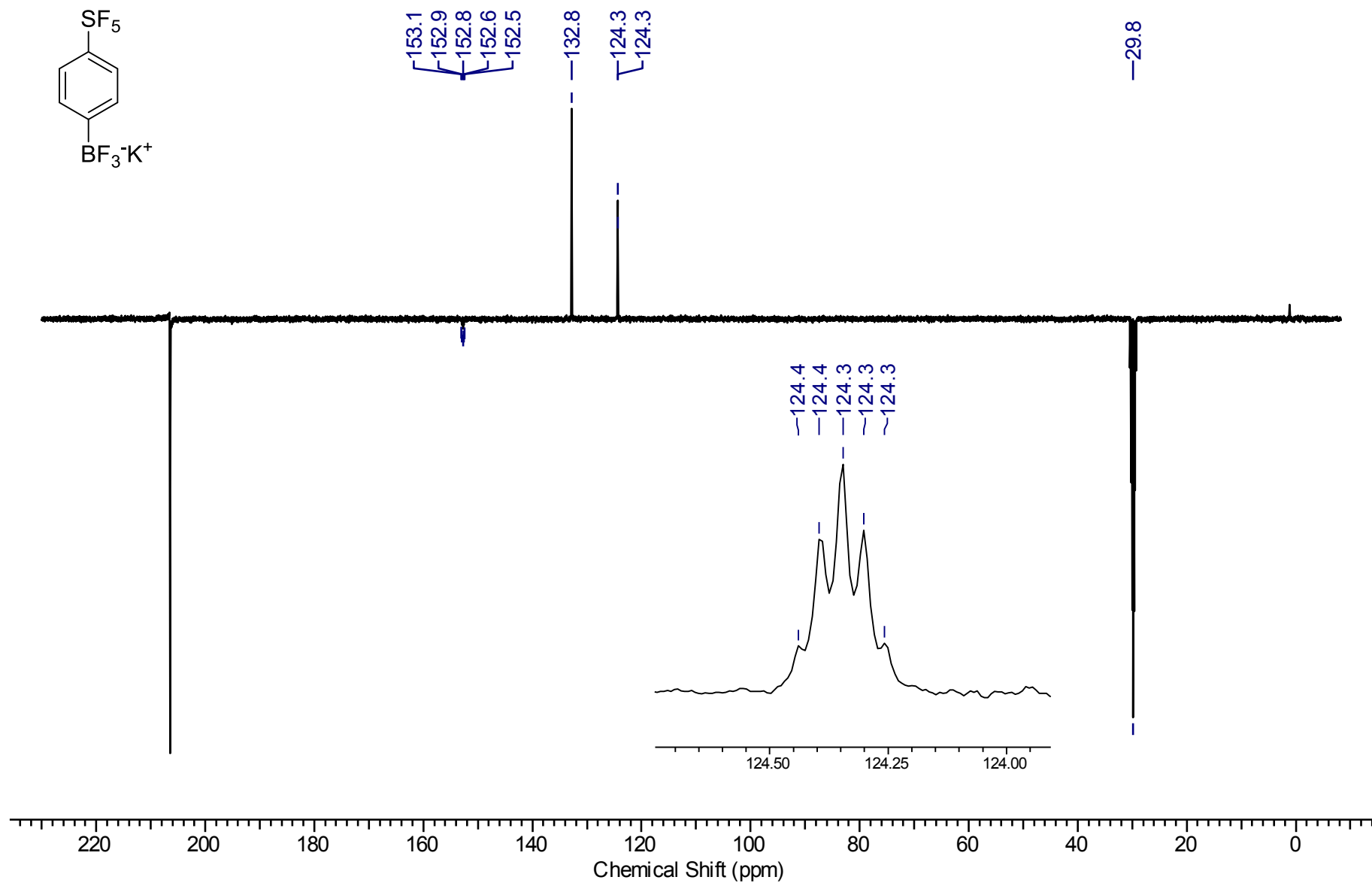
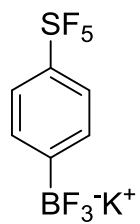
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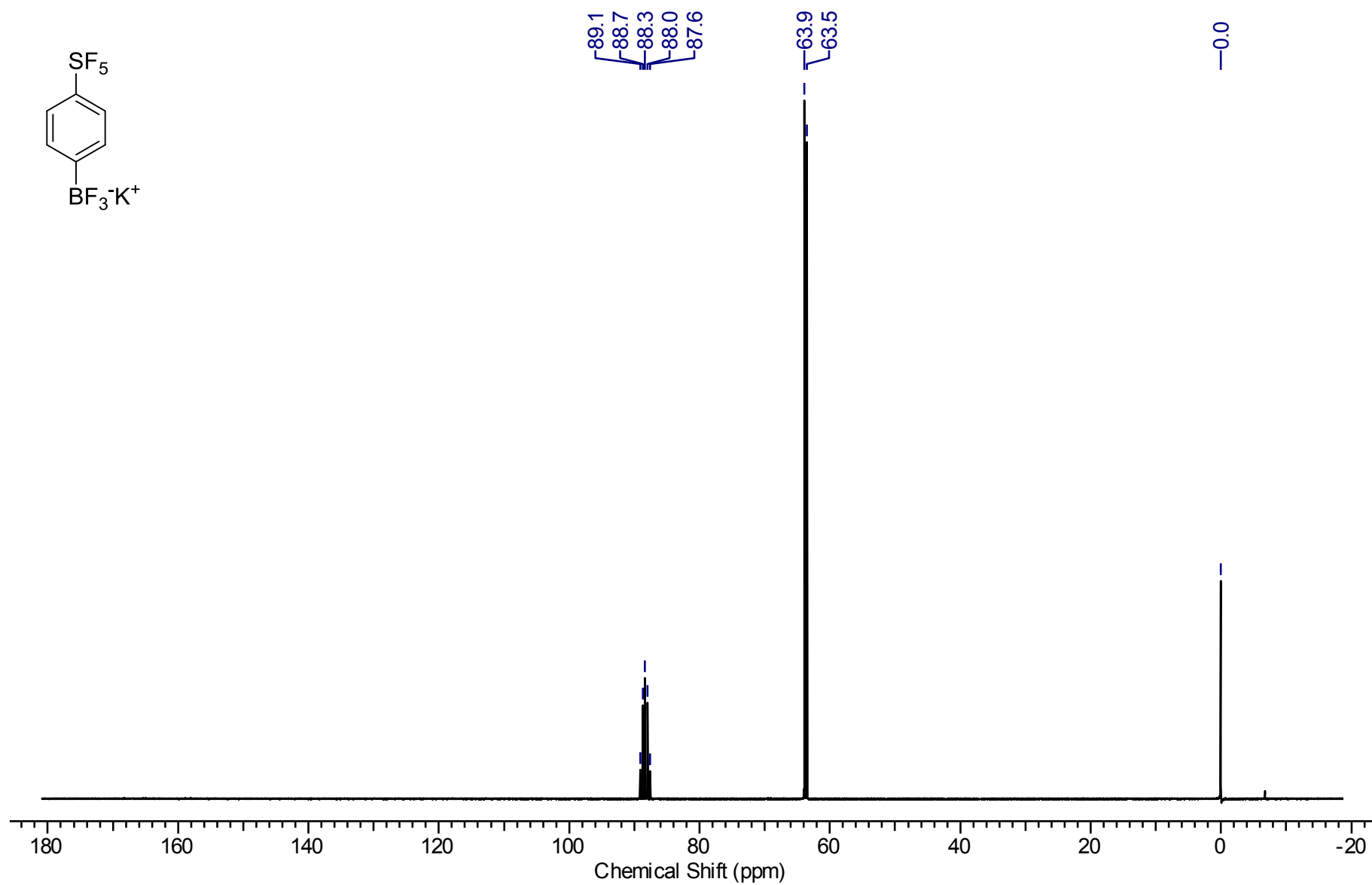
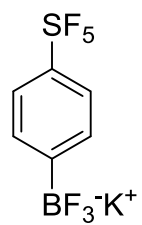
9b: ^{11}B NMR (128 MHz, $[\text{D}_6]\text{acetone}$)



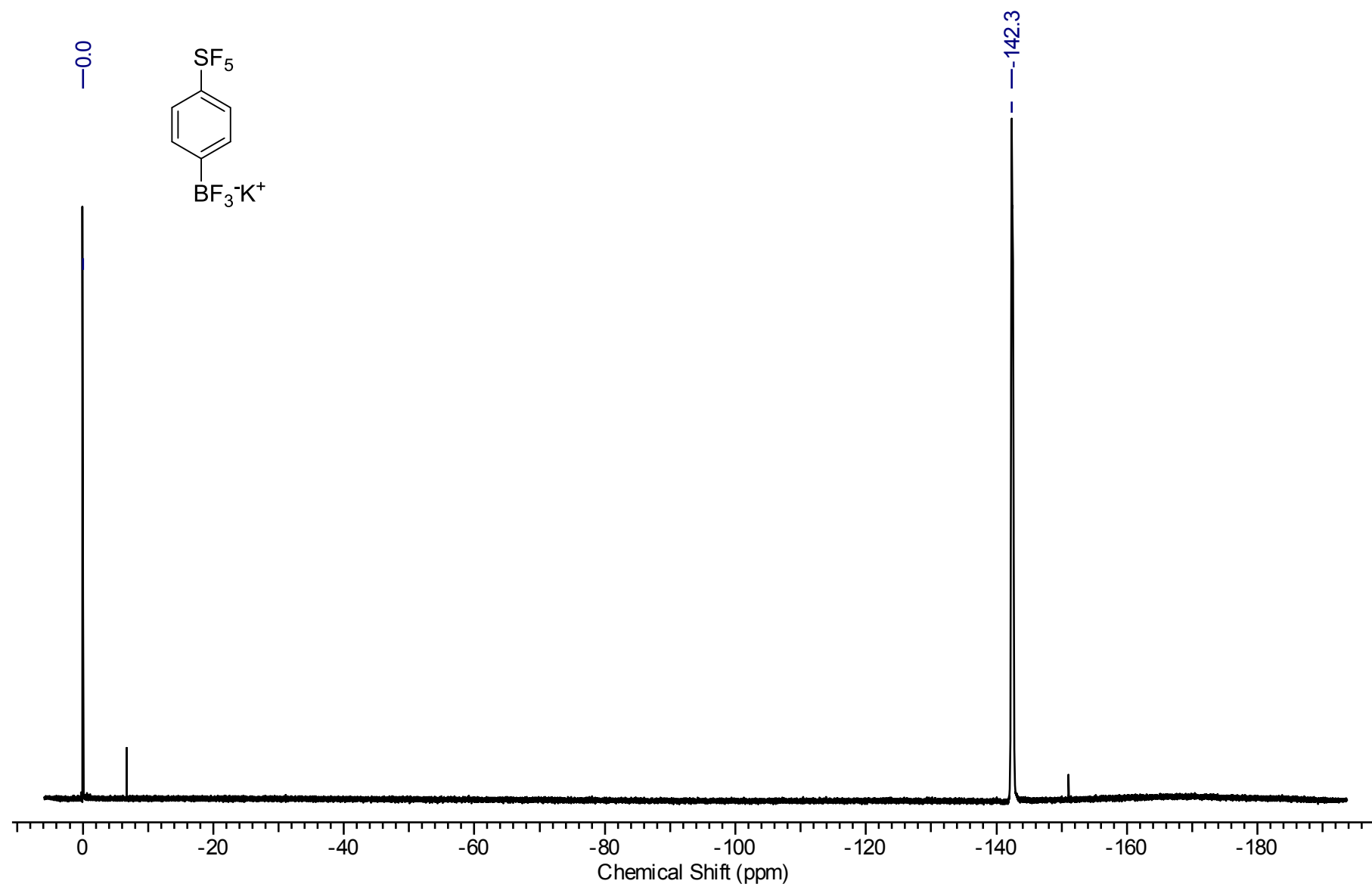
9b: ^{13}C NMR (101 MHz, $[\text{D}_6]\text{acetone}$)



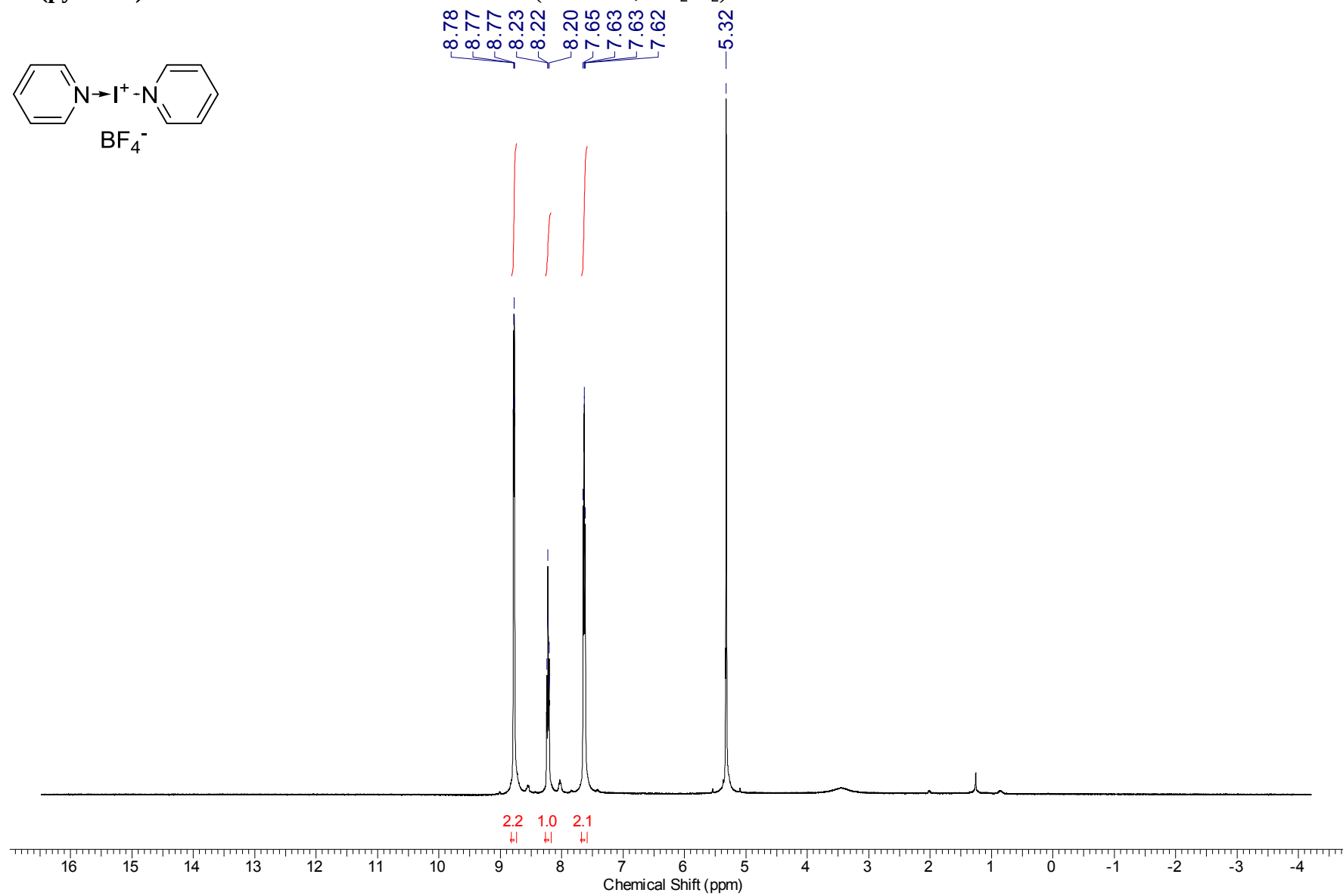
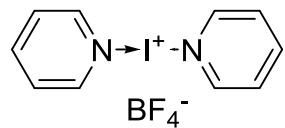
9b: ^{19}F NMR (377 MHz, $[\text{D}_6]\text{acetone}$)



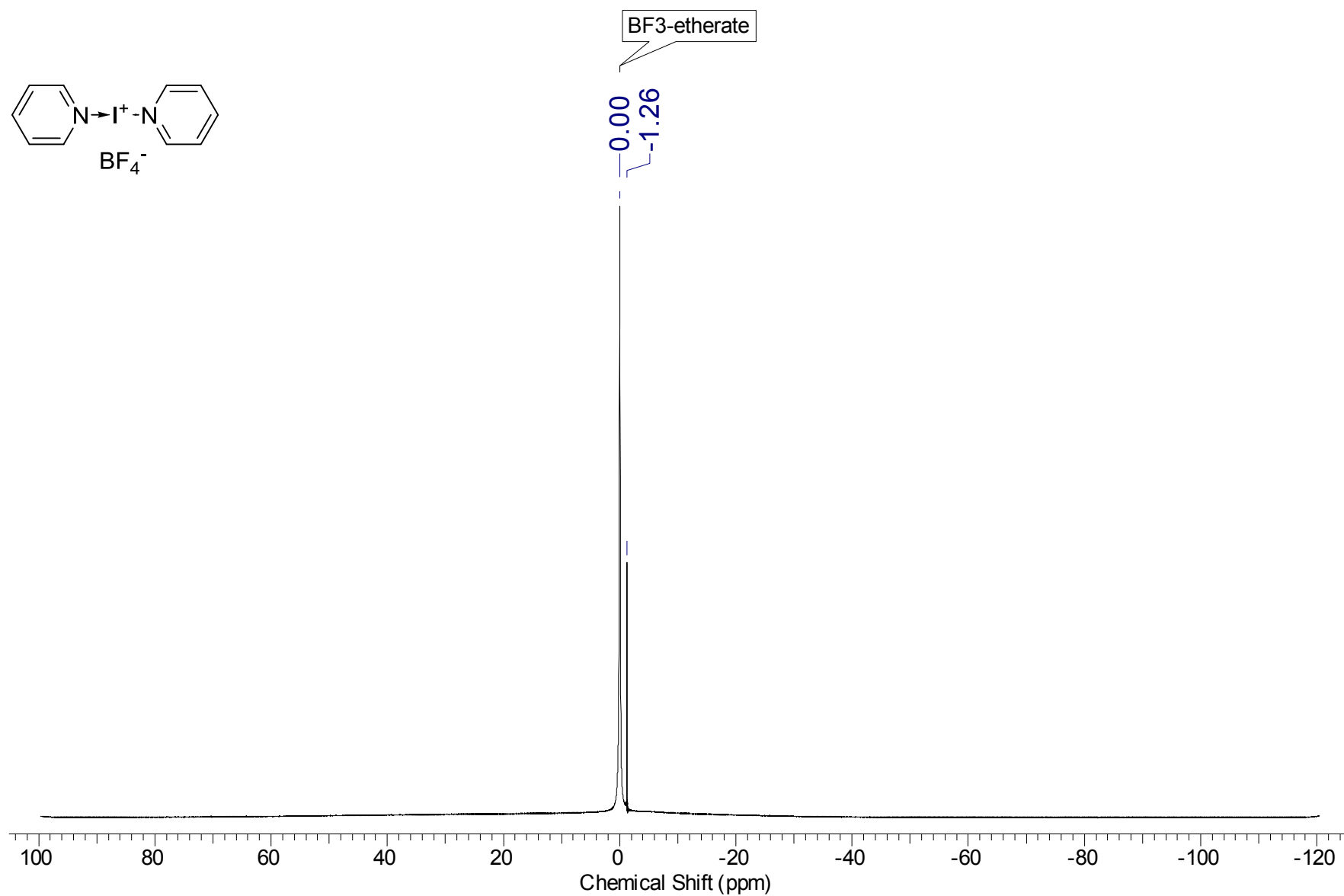
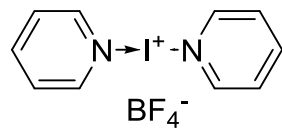
9b: ^{19}F NMR (376 MHz, $[\text{D}_6]\text{acetone}$)



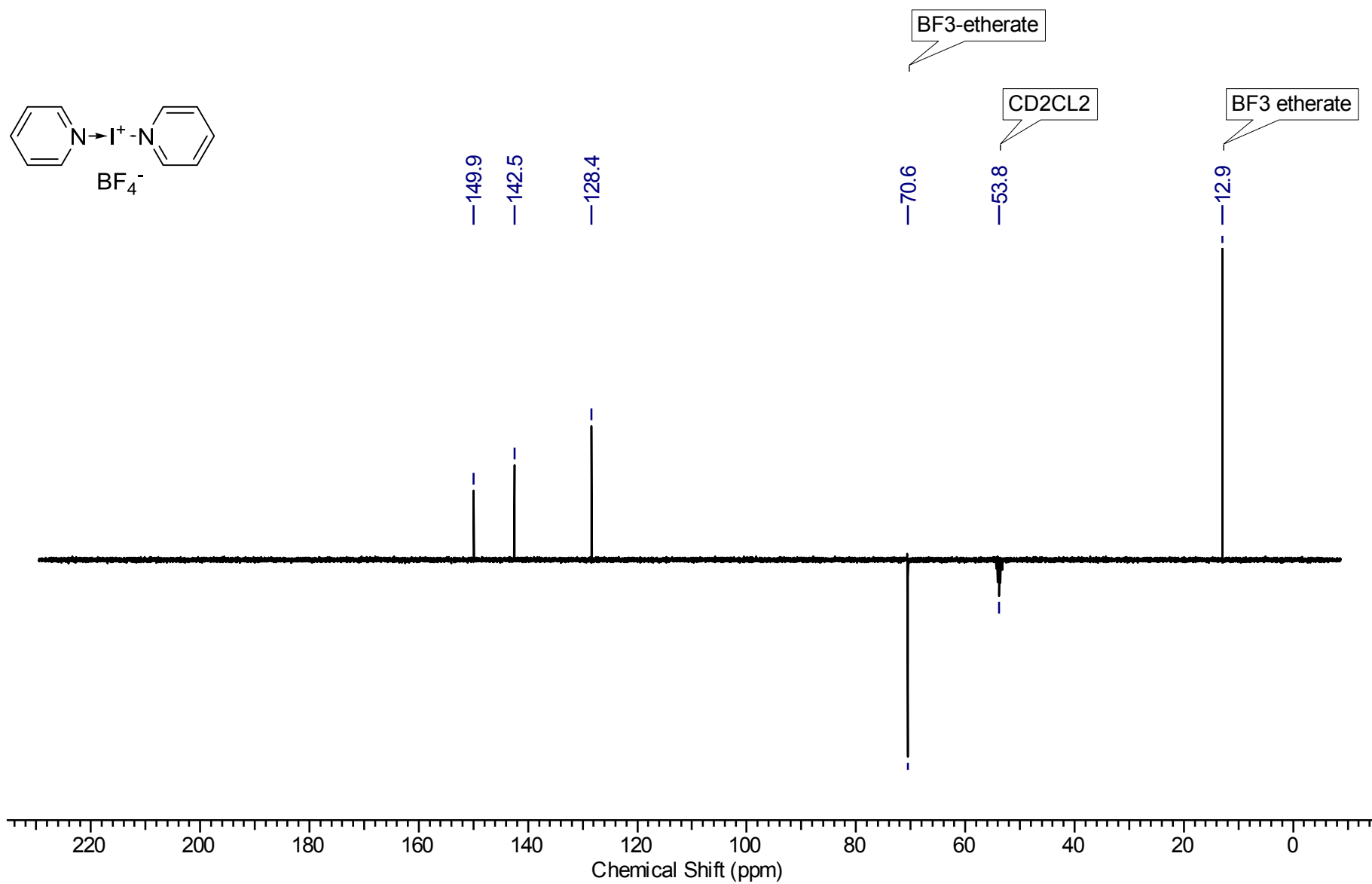
Bis(pyridine)iodonium tetrafluoroborate: ^1H NMR (400 MHz, CD_2Cl_2)



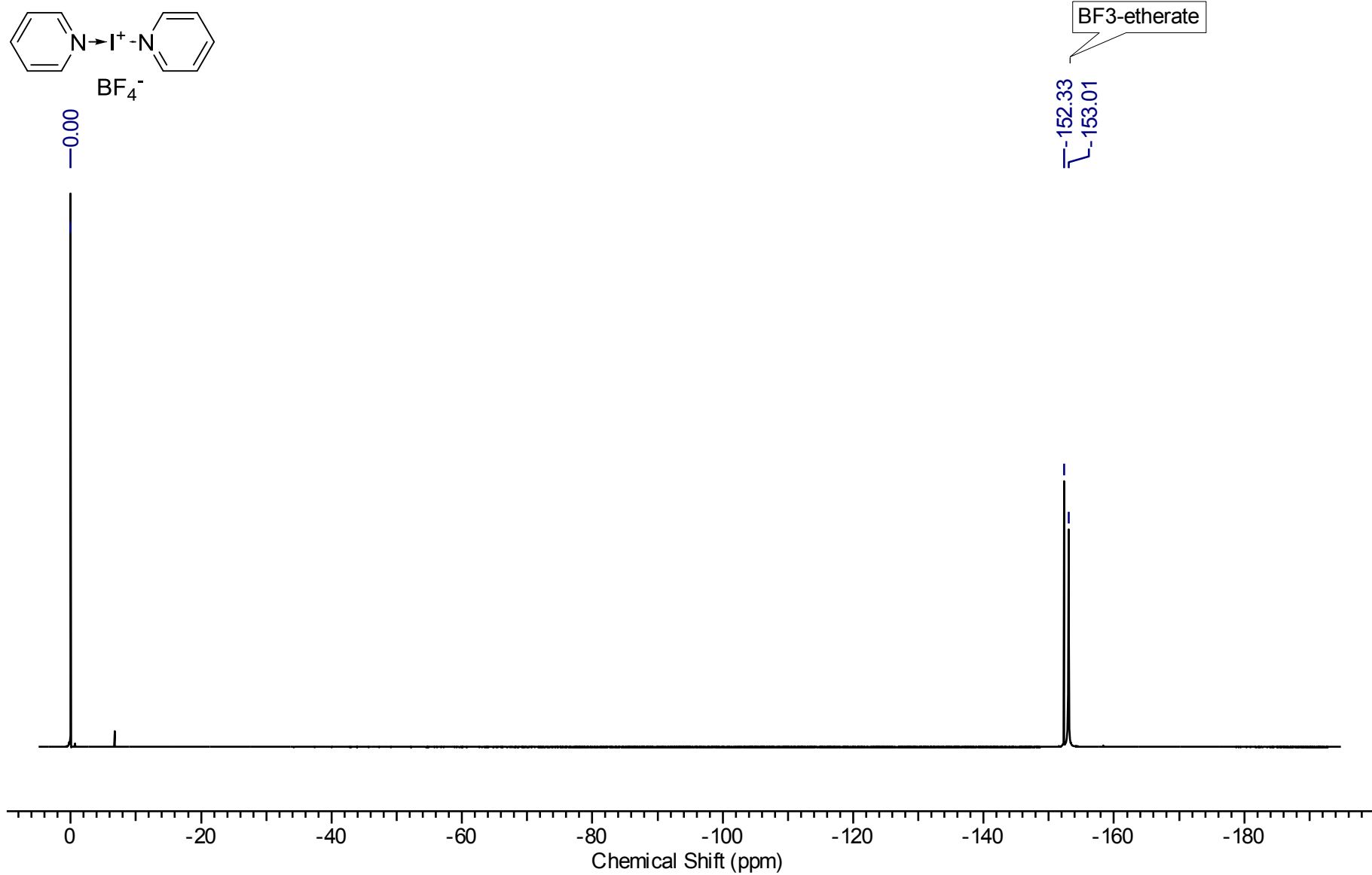
Bis(pyridine)iodonium tetrafluoroborate: ^{11}B NMR (128 MHz, CD_2Cl_2)



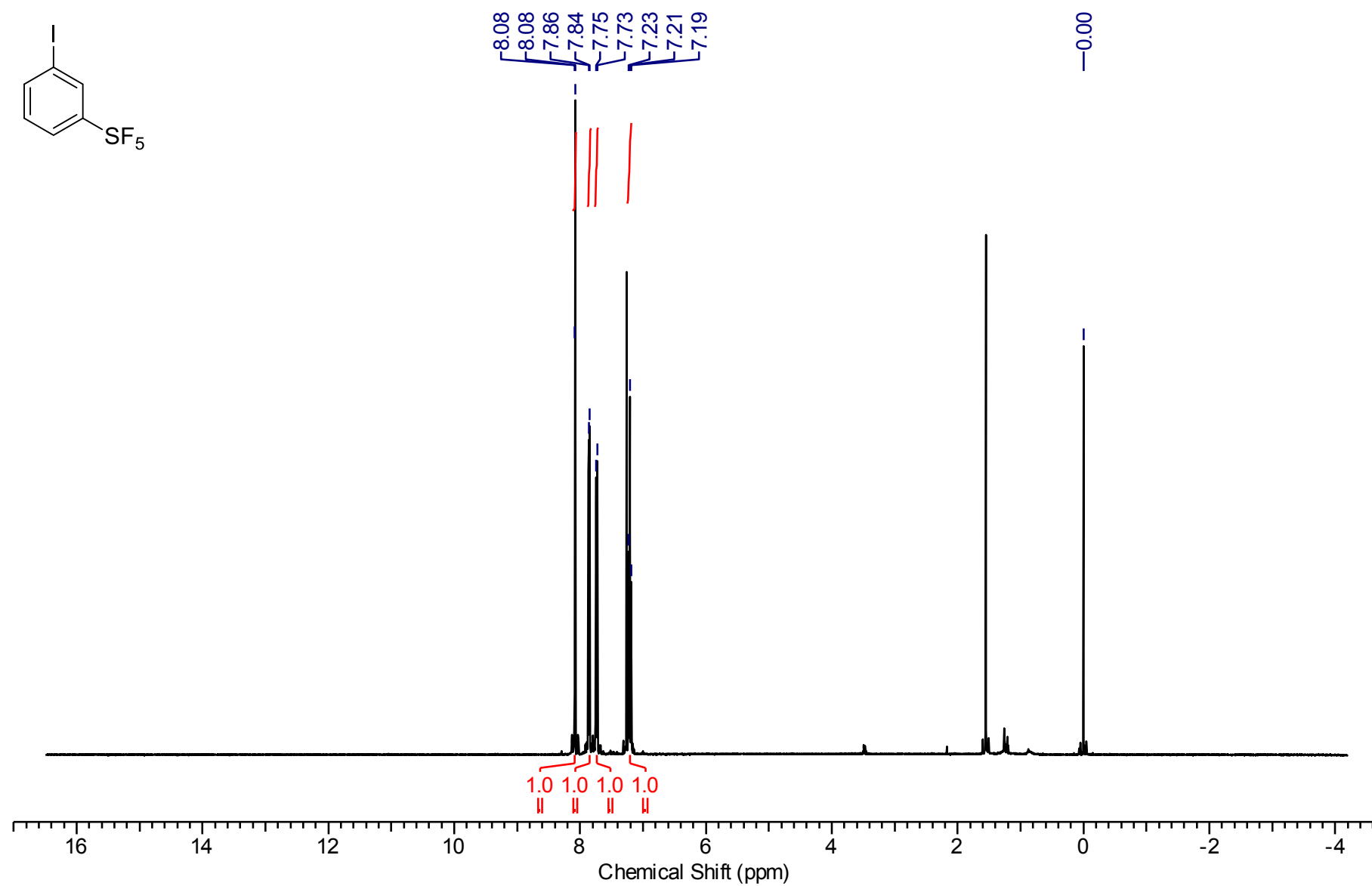
Bis(pyridine)iodonium tetrafluoroborate: ^{13}C NMR (101 MHz, CD_2Cl_2)



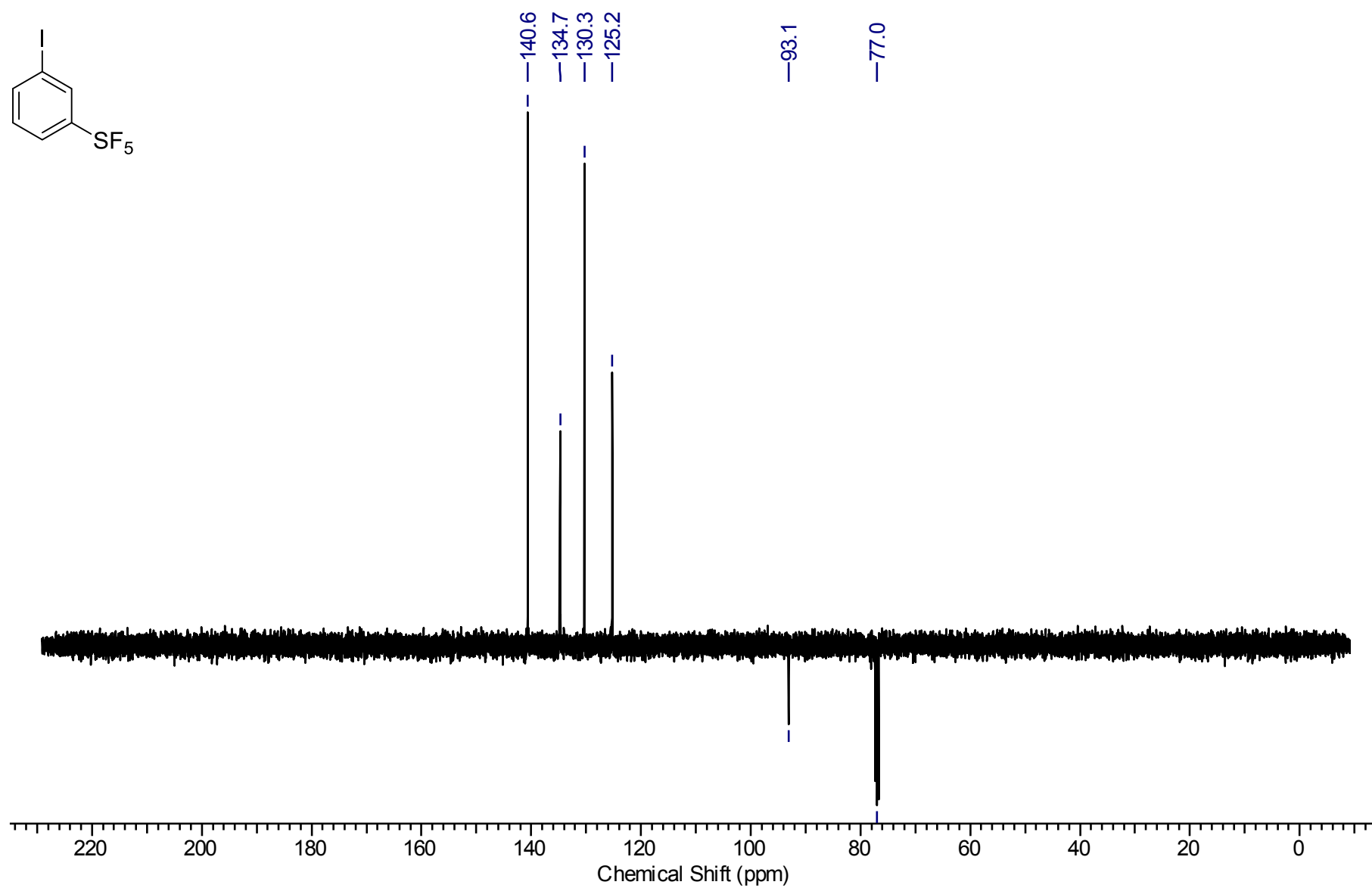
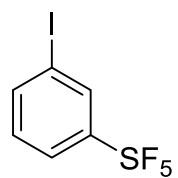
Bis(pyridine)iodonium tetrafluoroborate: ^{19}F NMR (376 MHz, CD_2Cl_2)



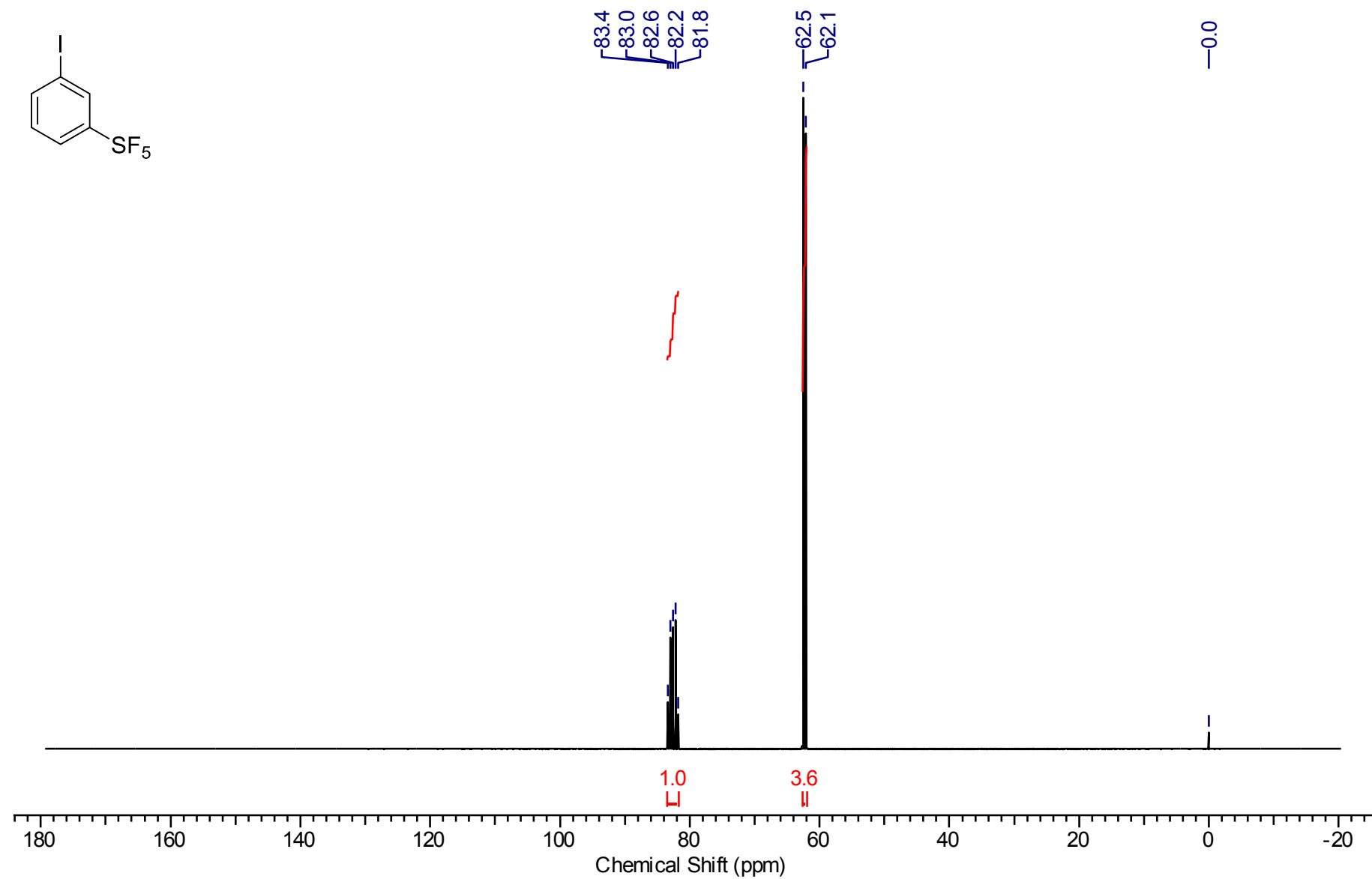
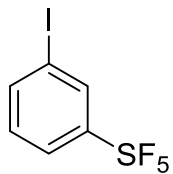
10a: ^1H NMR (400 MHz, CDCl_3)



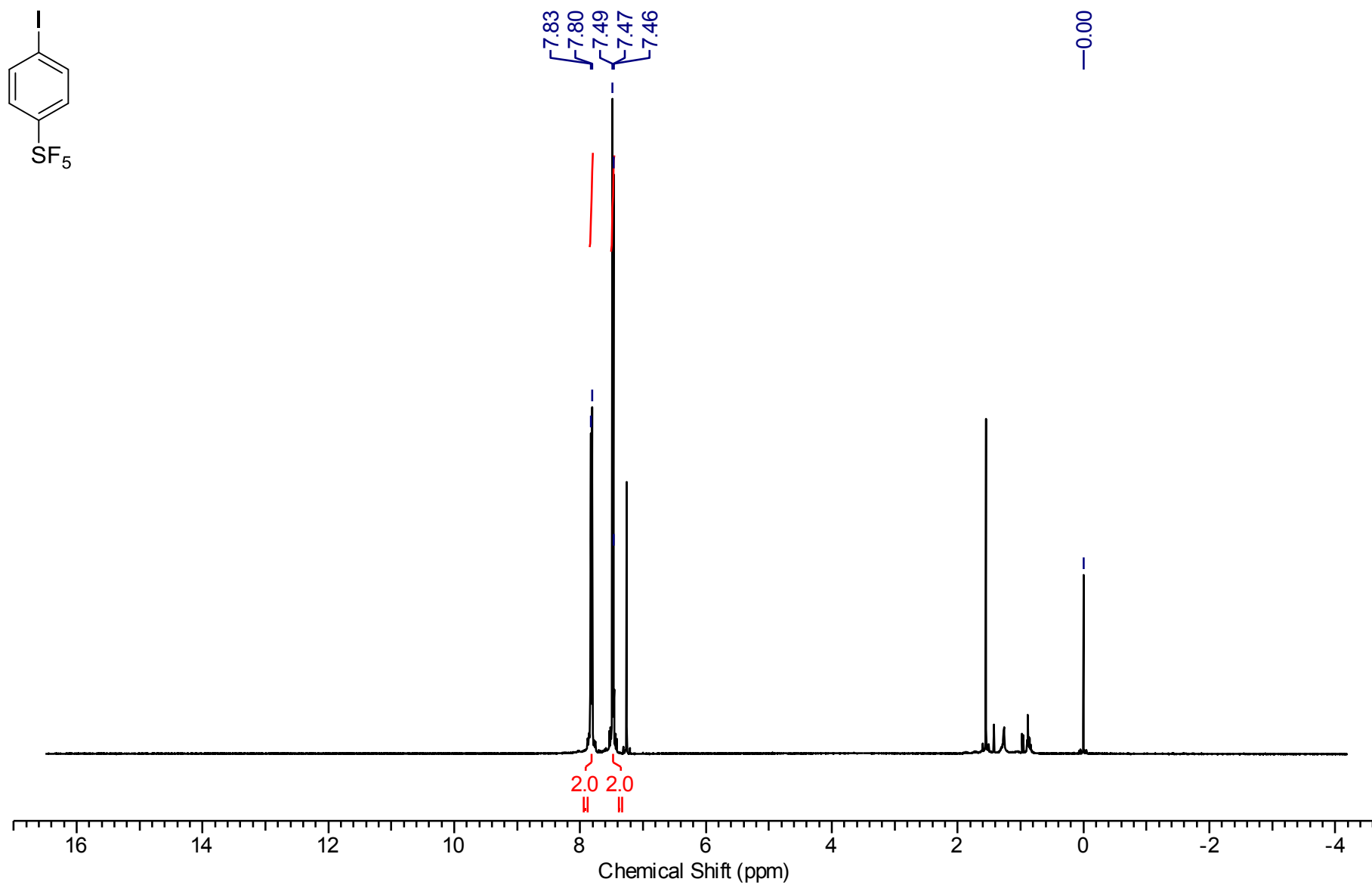
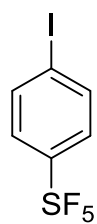
10a: ^{13}C NMR (101 MHz, CDCl_3)



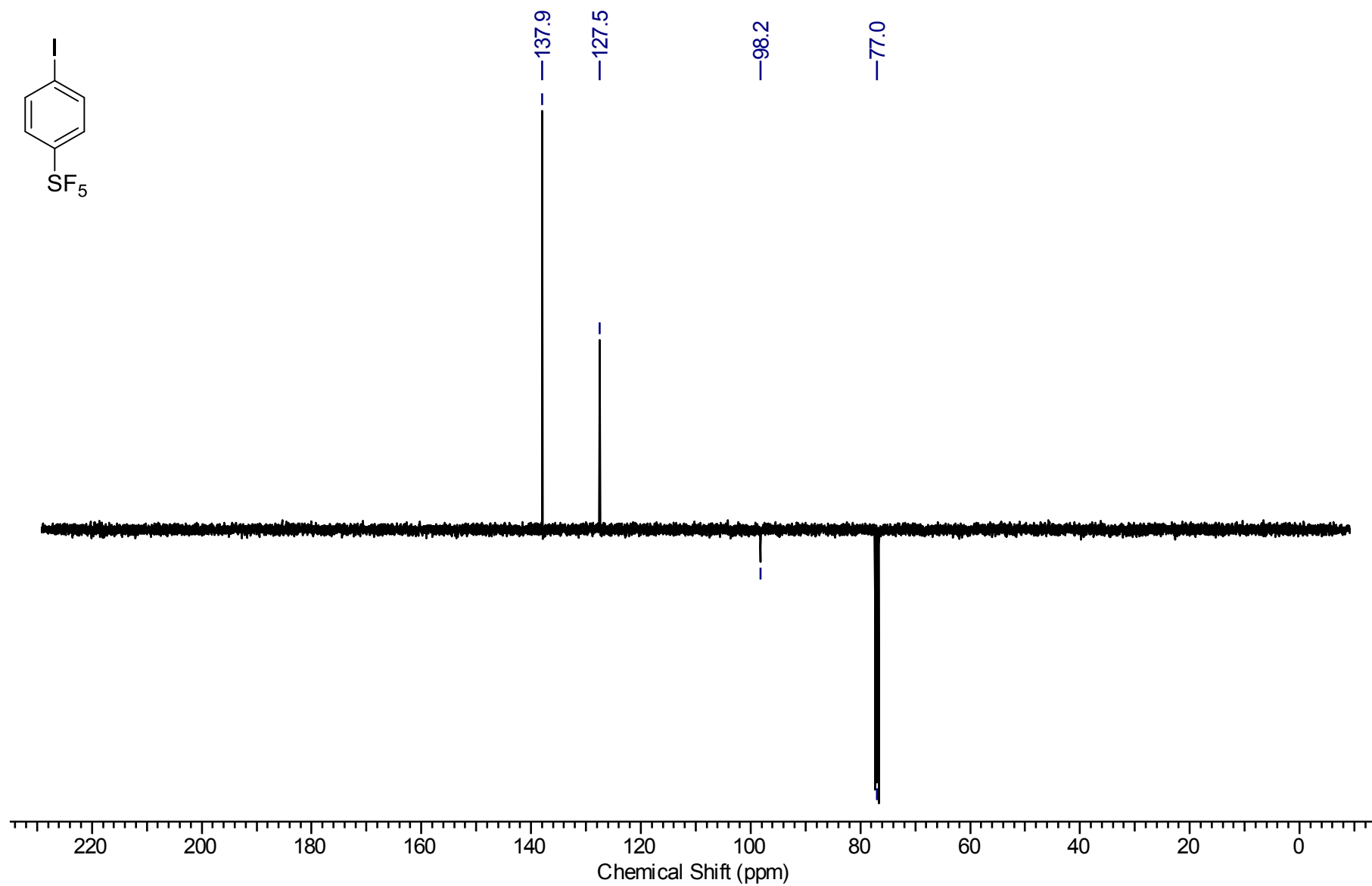
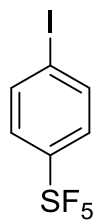
10a: ^{19}F NMR (377 MHz, CDCl_3)



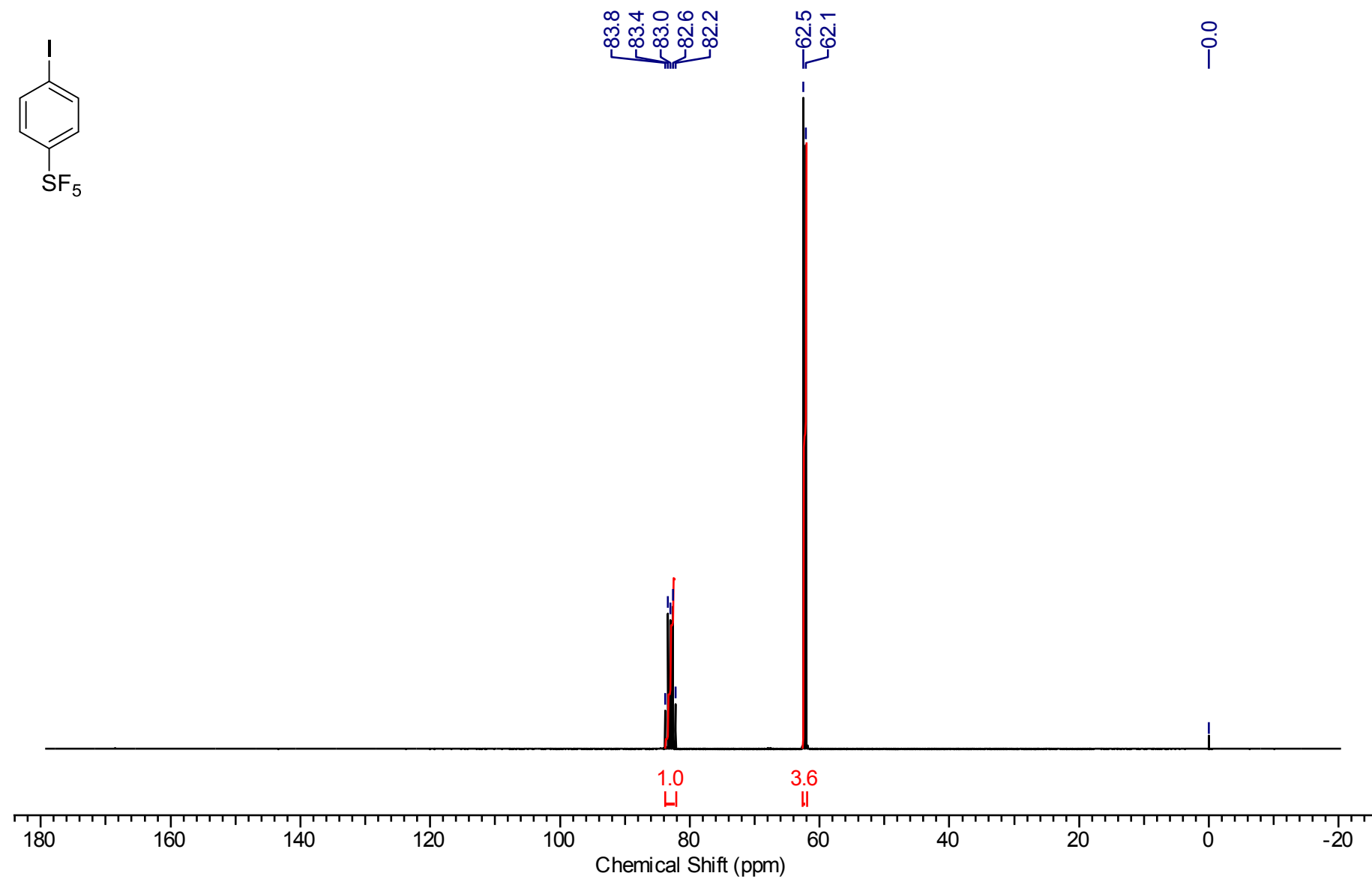
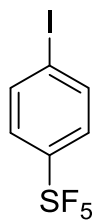
10b: ^1H NMR (400 MHz, CDCl_3)



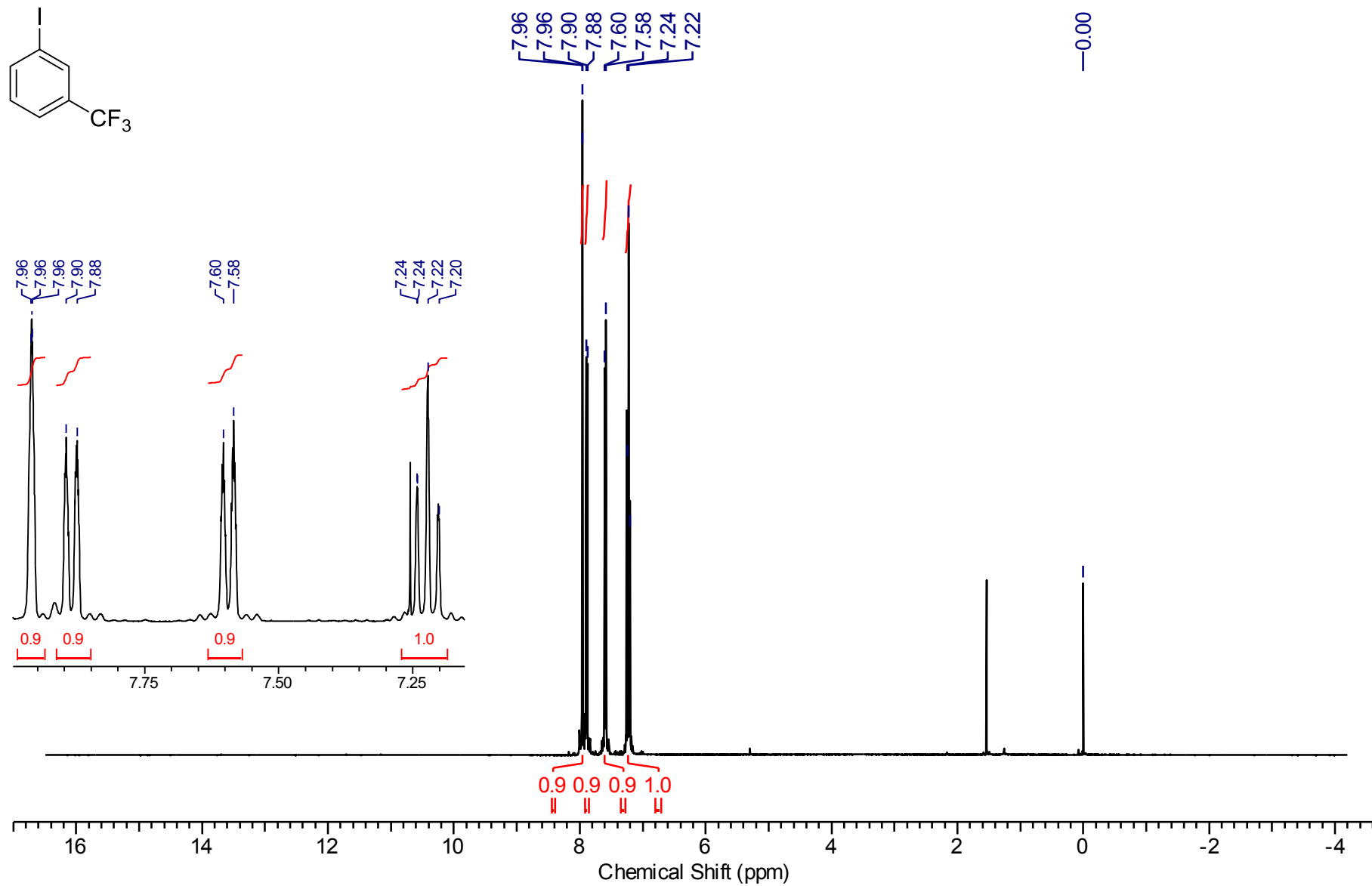
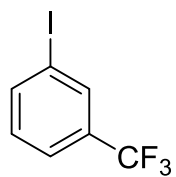
10b: ^{13}C NMR (101 MHz, CDCl_3)



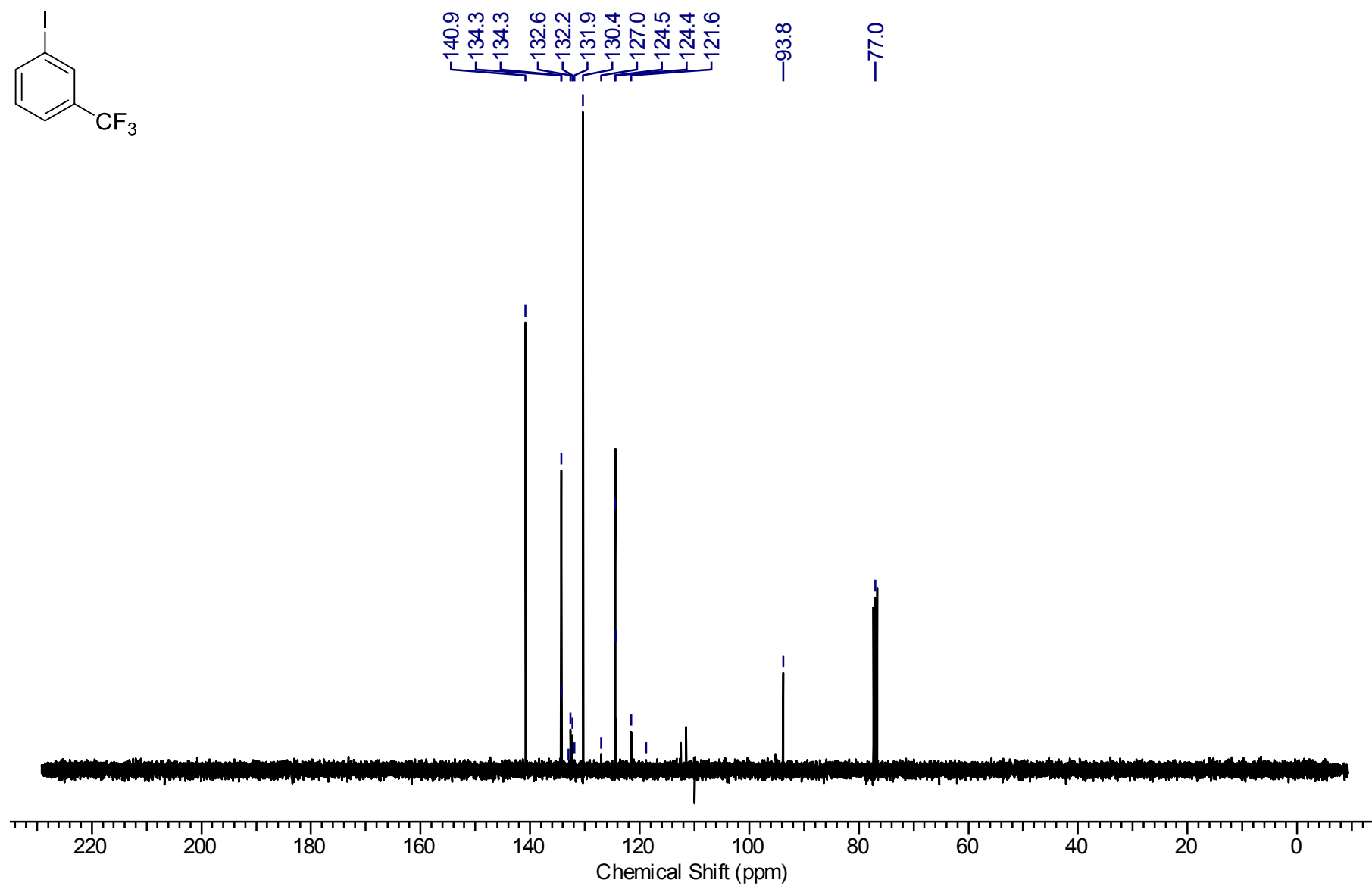
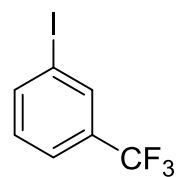
10b: ^{19}F NMR (377 MHz, CDCl_3)



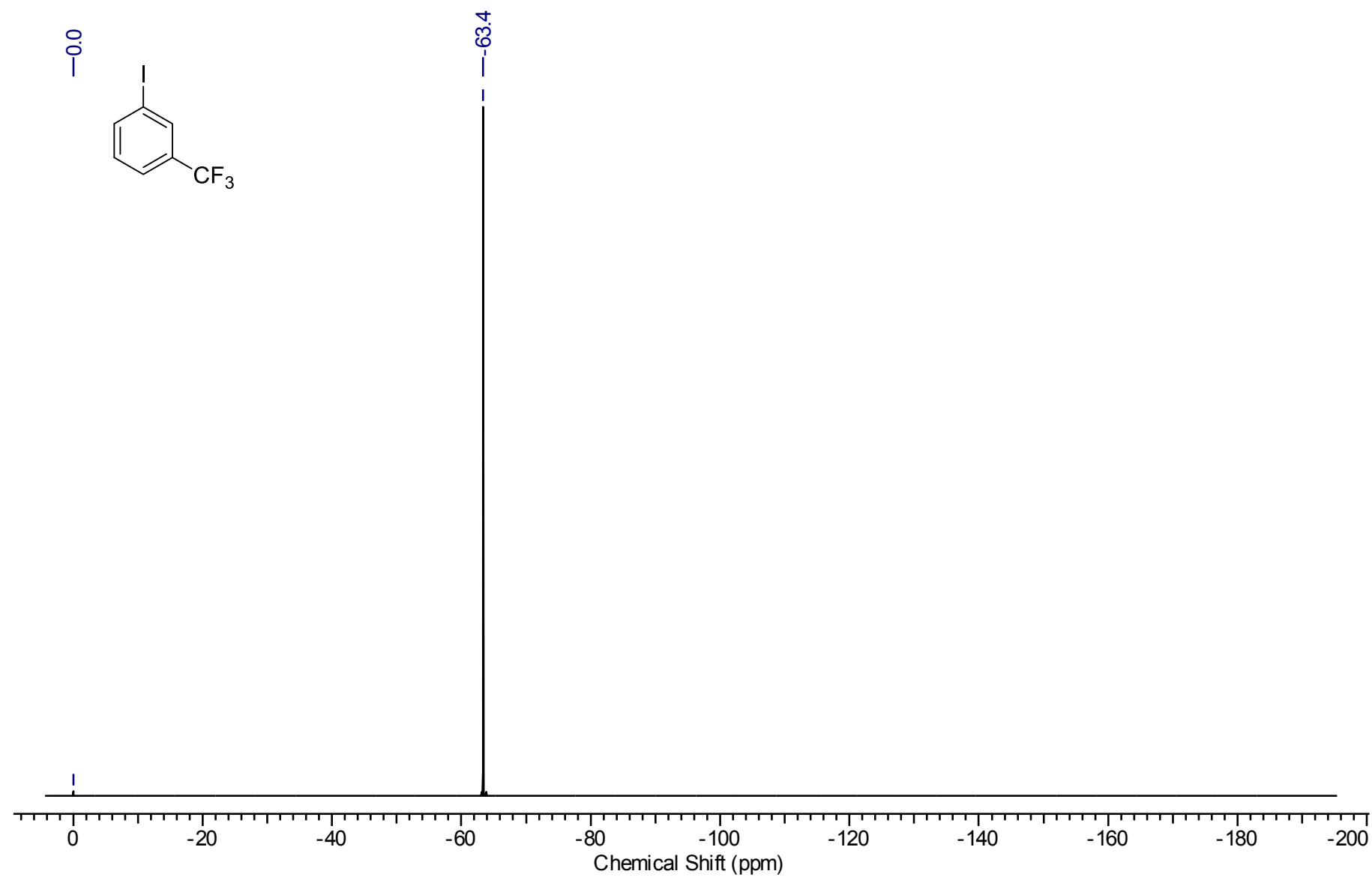
10c: ^1H NMR (400 MHz, CDCl_3)



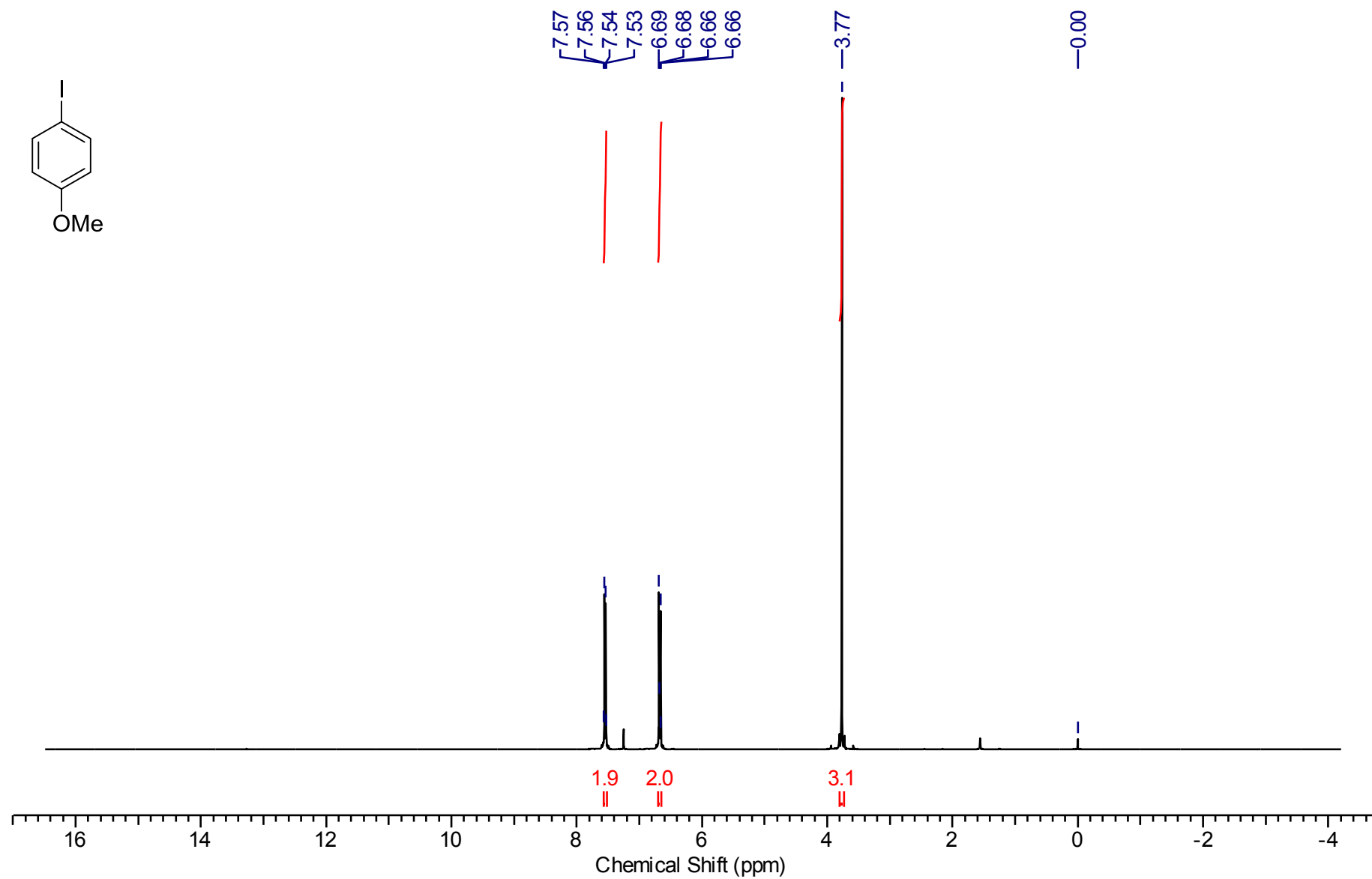
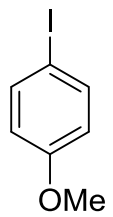
10c: ^{13}C NMR (101 MHz, CDCl_3)



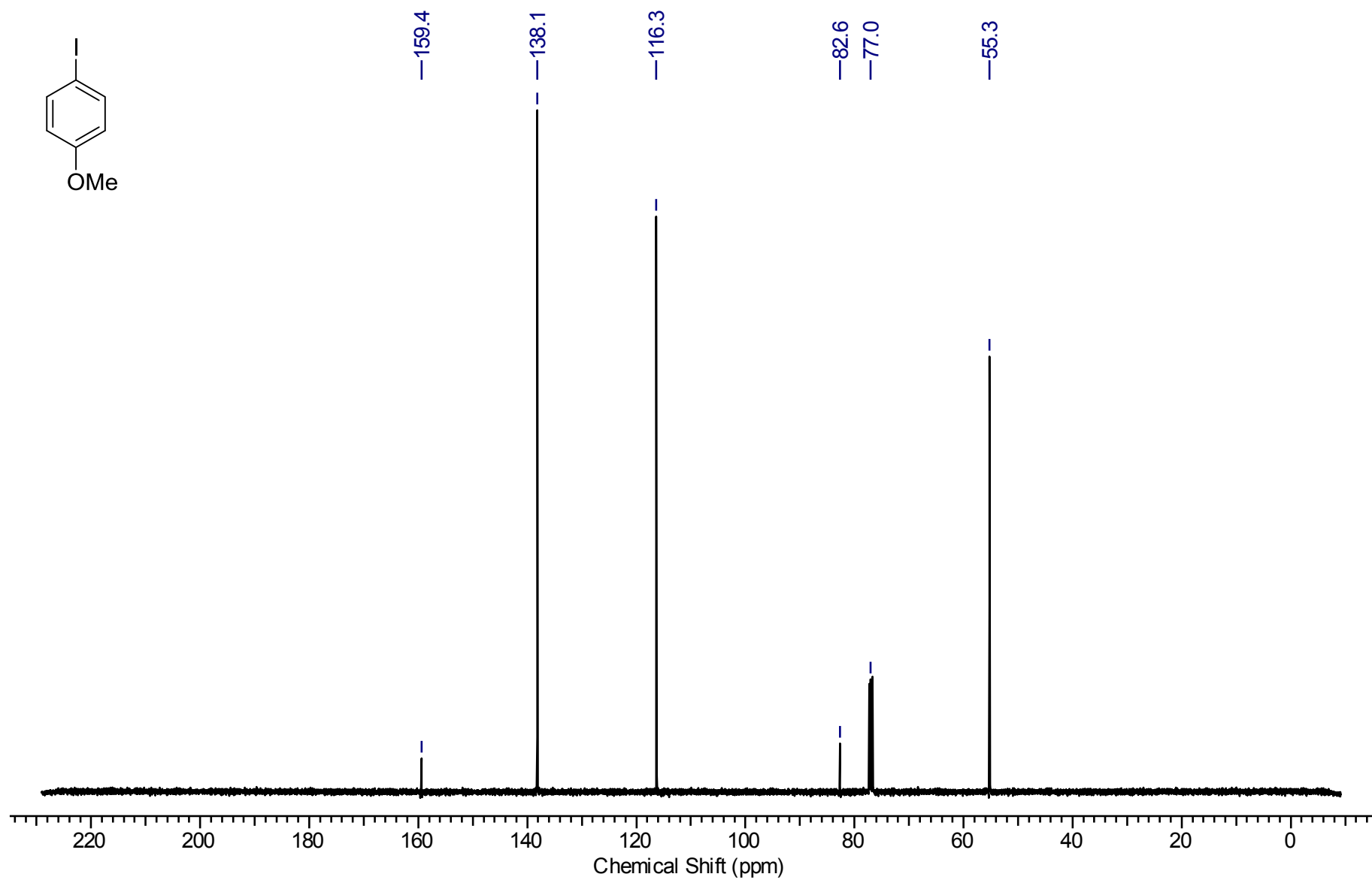
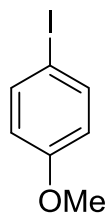
10c: ^{19}F NMR (376 MHz, CDCl_3)



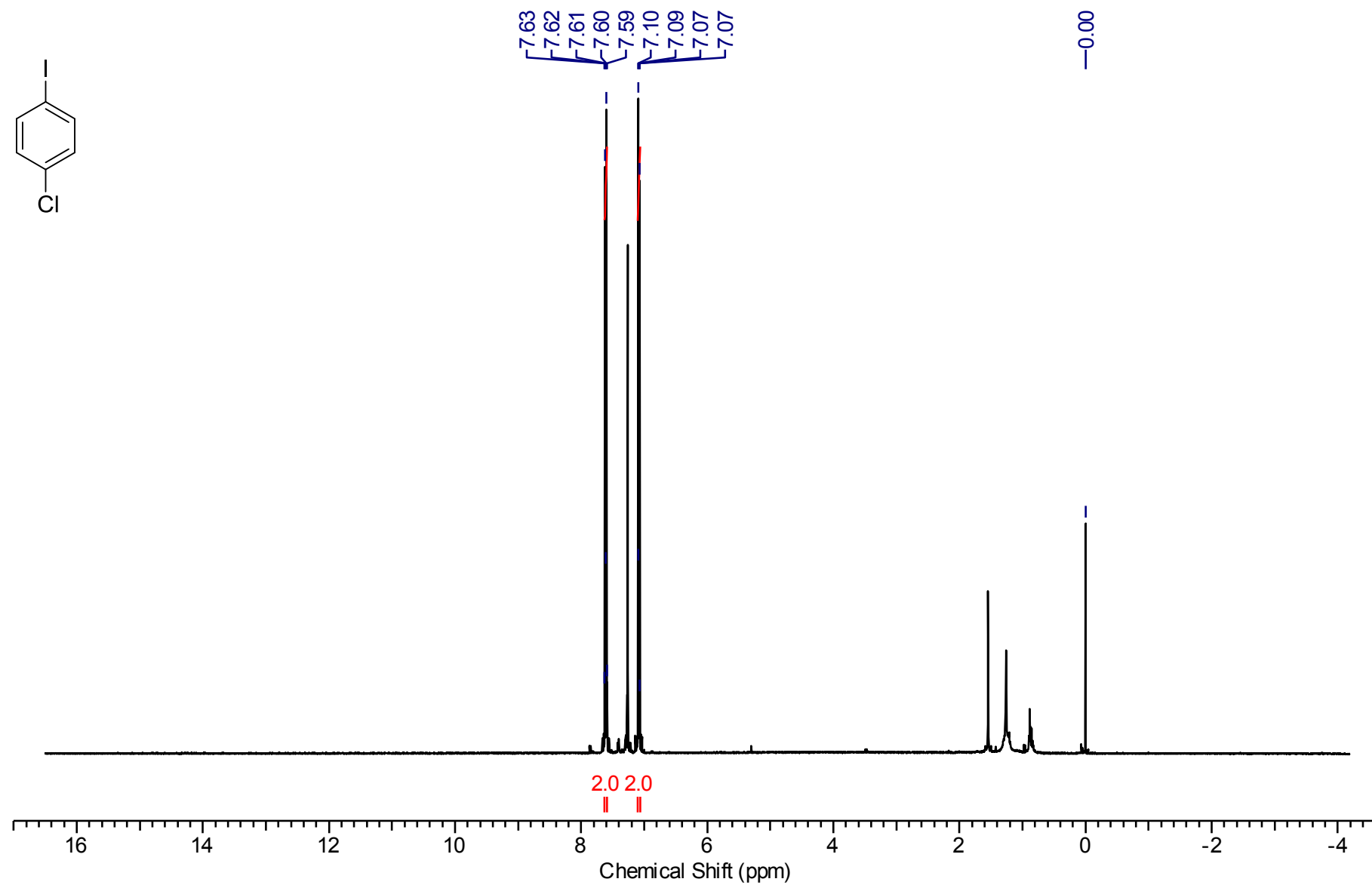
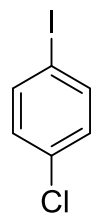
10d: ^1H NMR (400 MHz, CDCl_3)



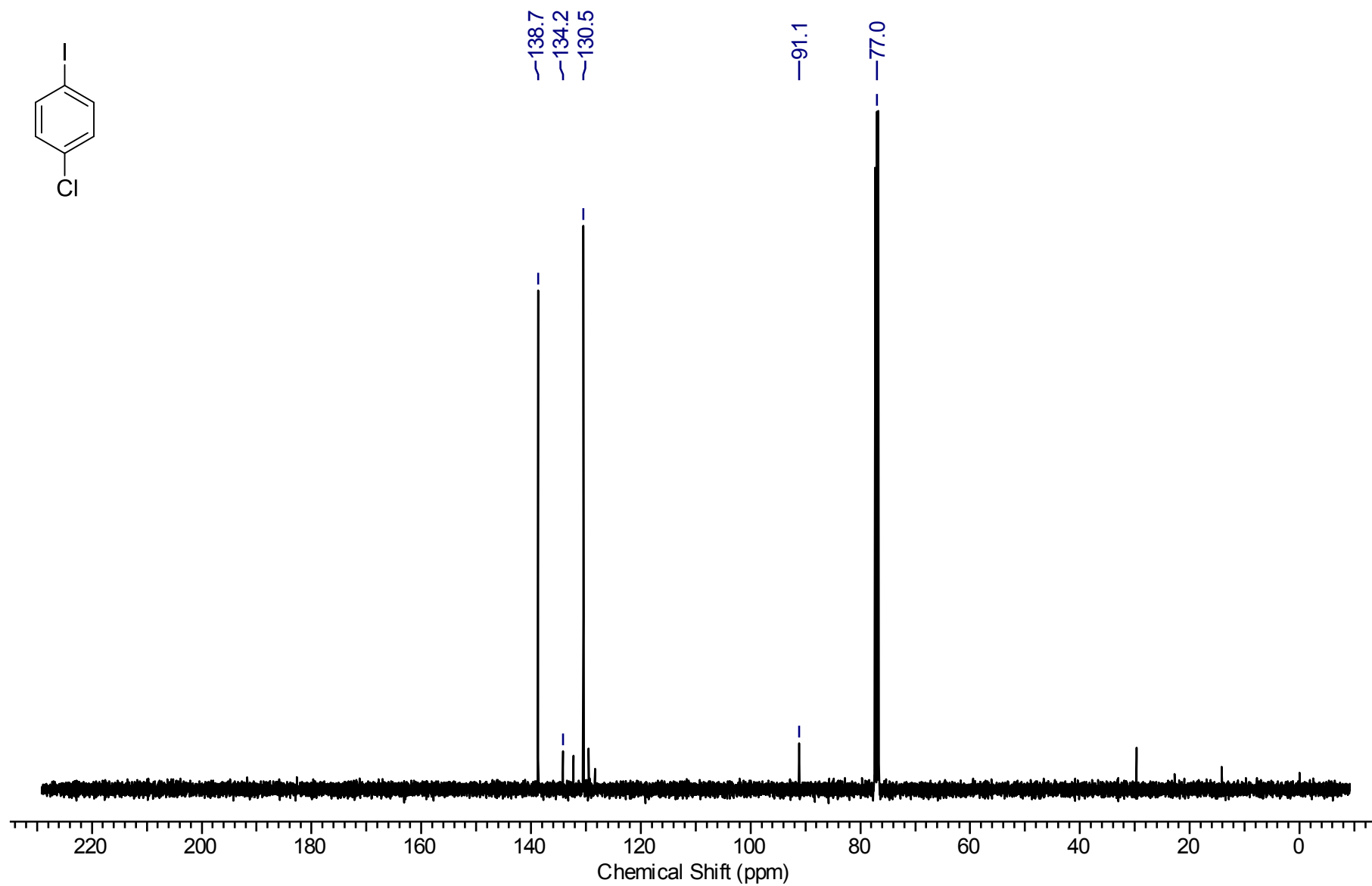
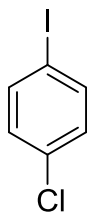
10d: ^{13}C NMR (101 MHz, CDCl_3)



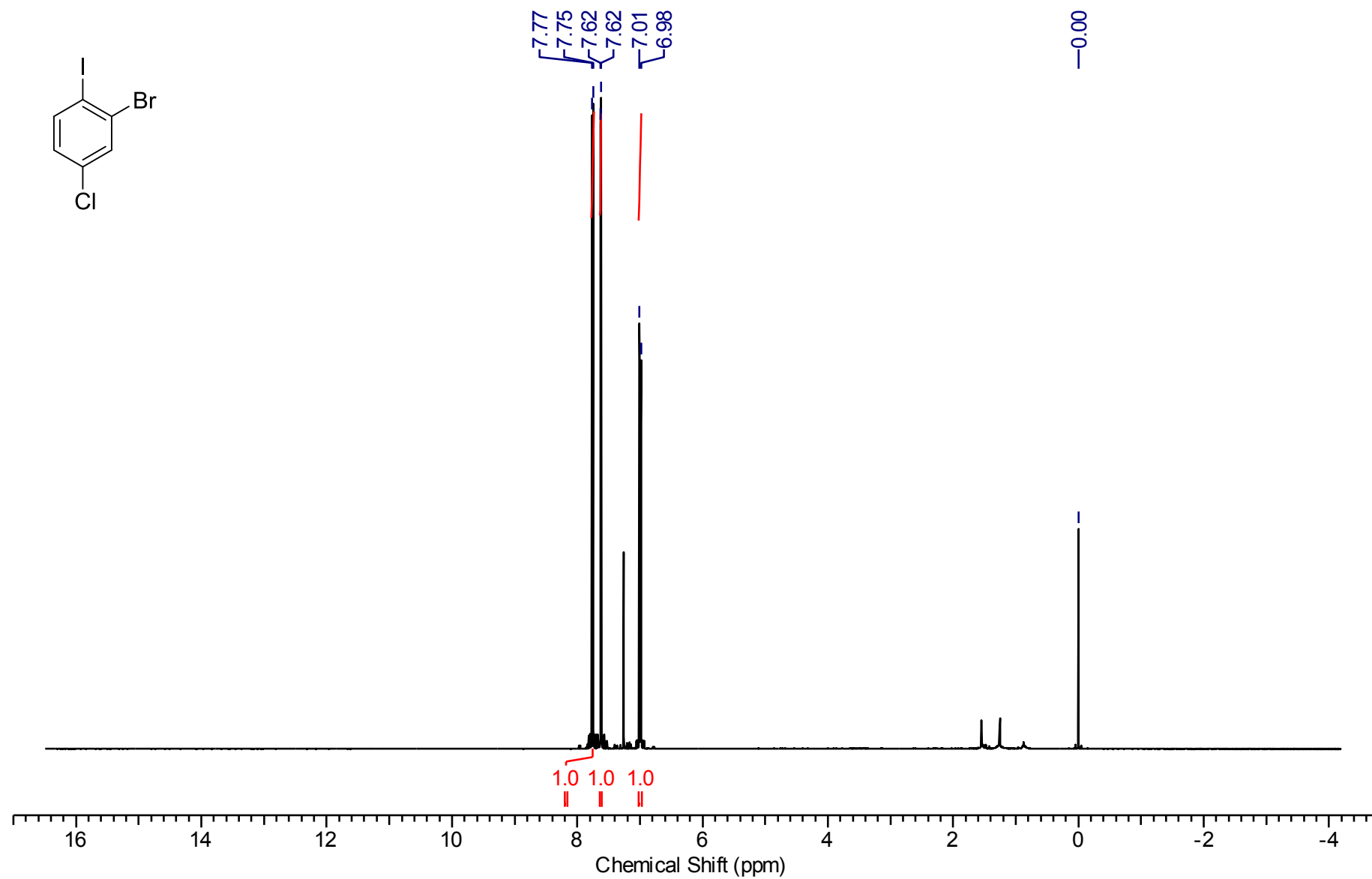
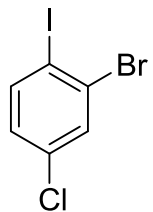
10e: ^1H NMR (400 MHz, CDCl_3)



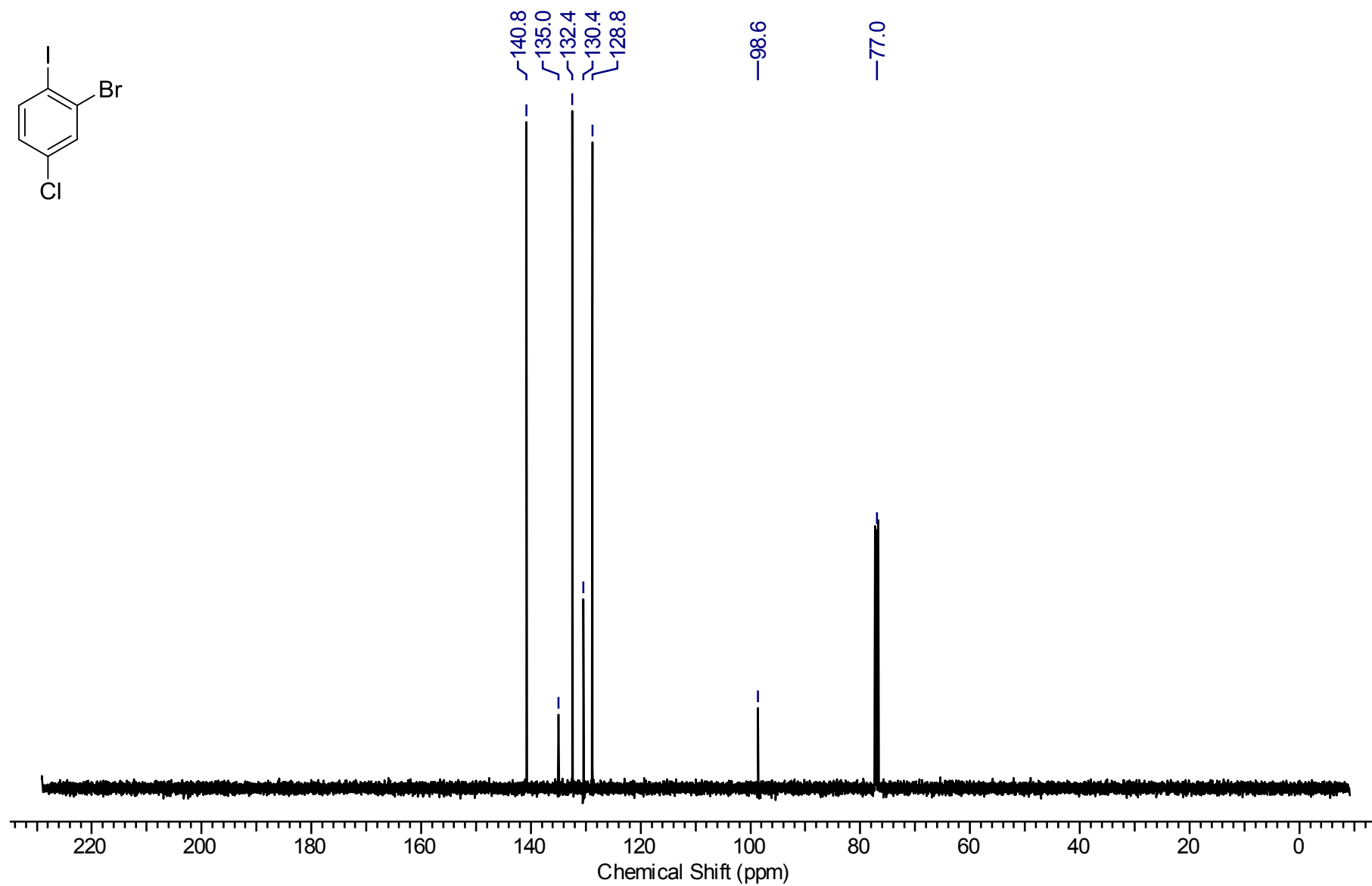
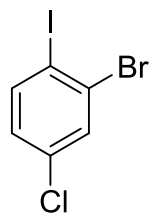
10e: ^{13}C NMR (101 MHz, CDCl_3)



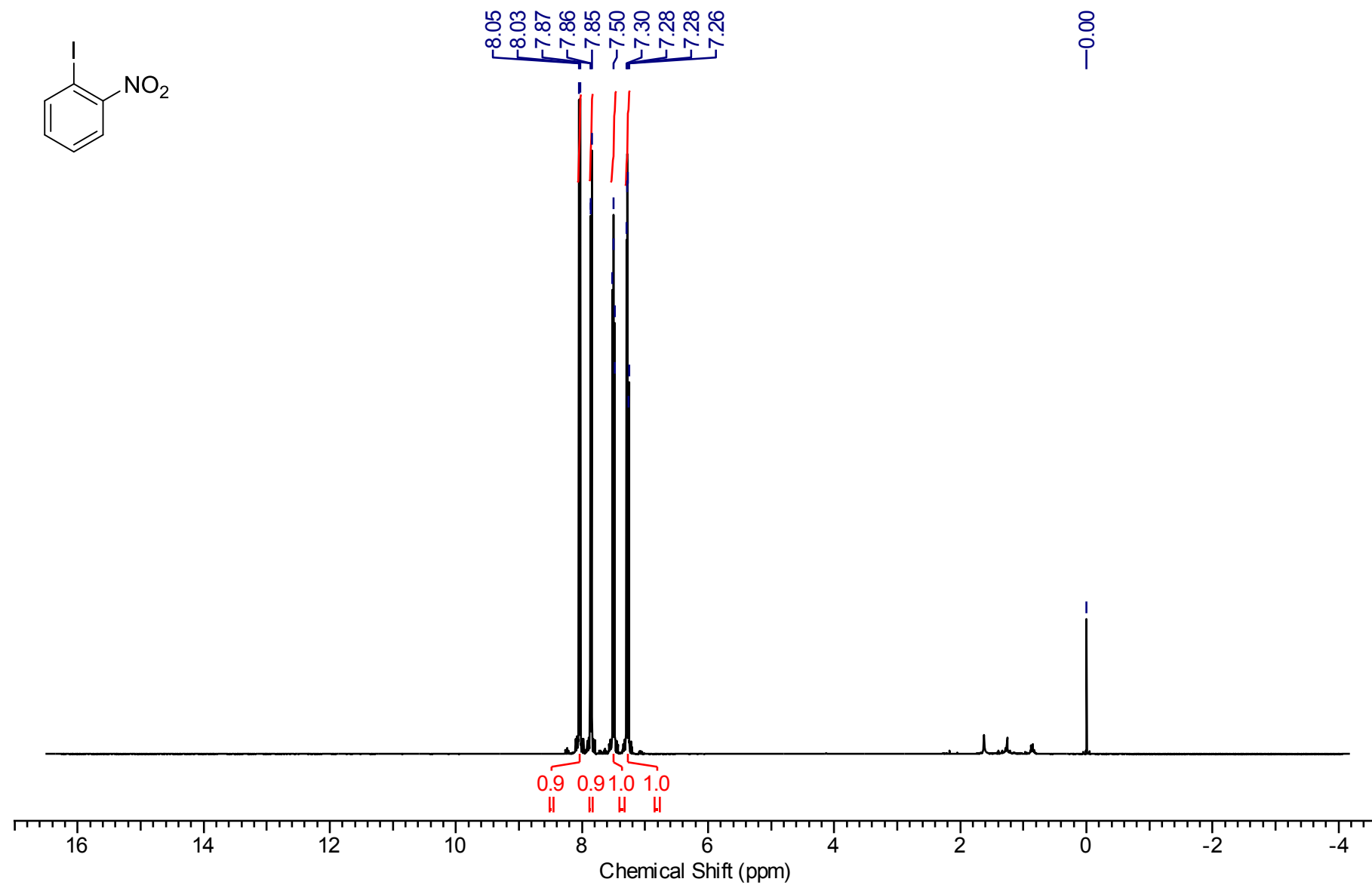
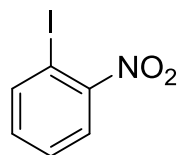
10f: ^1H NMR (400 MHz, CDCl_3)



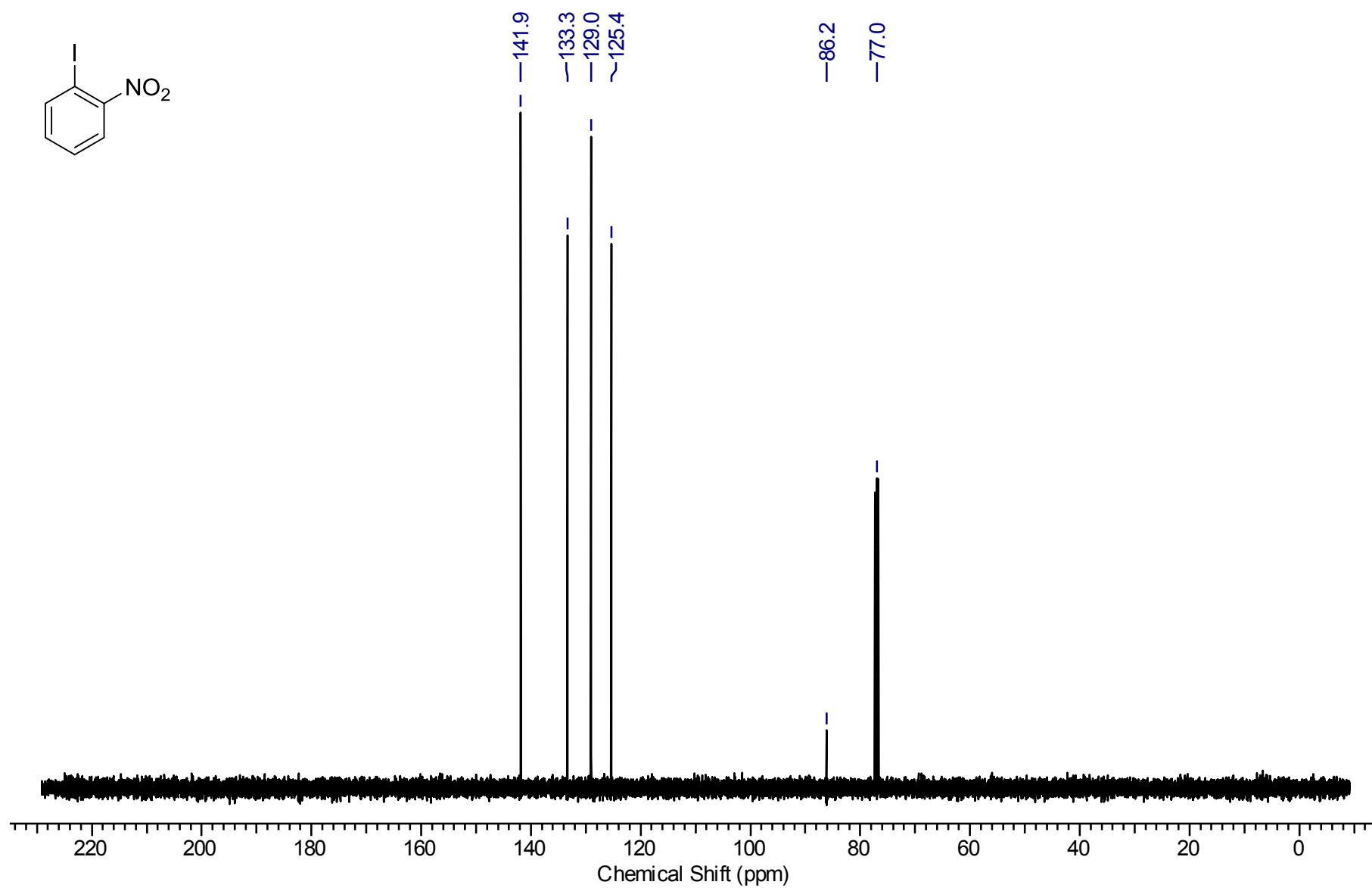
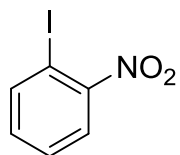
10f: ^{13}C NMR (101 MHz, CDCl_3)



10g: ^1H NMR (400 MHz, CDCl_3)



10g: ^{13}C NMR (101 MHz, CDCl_3)

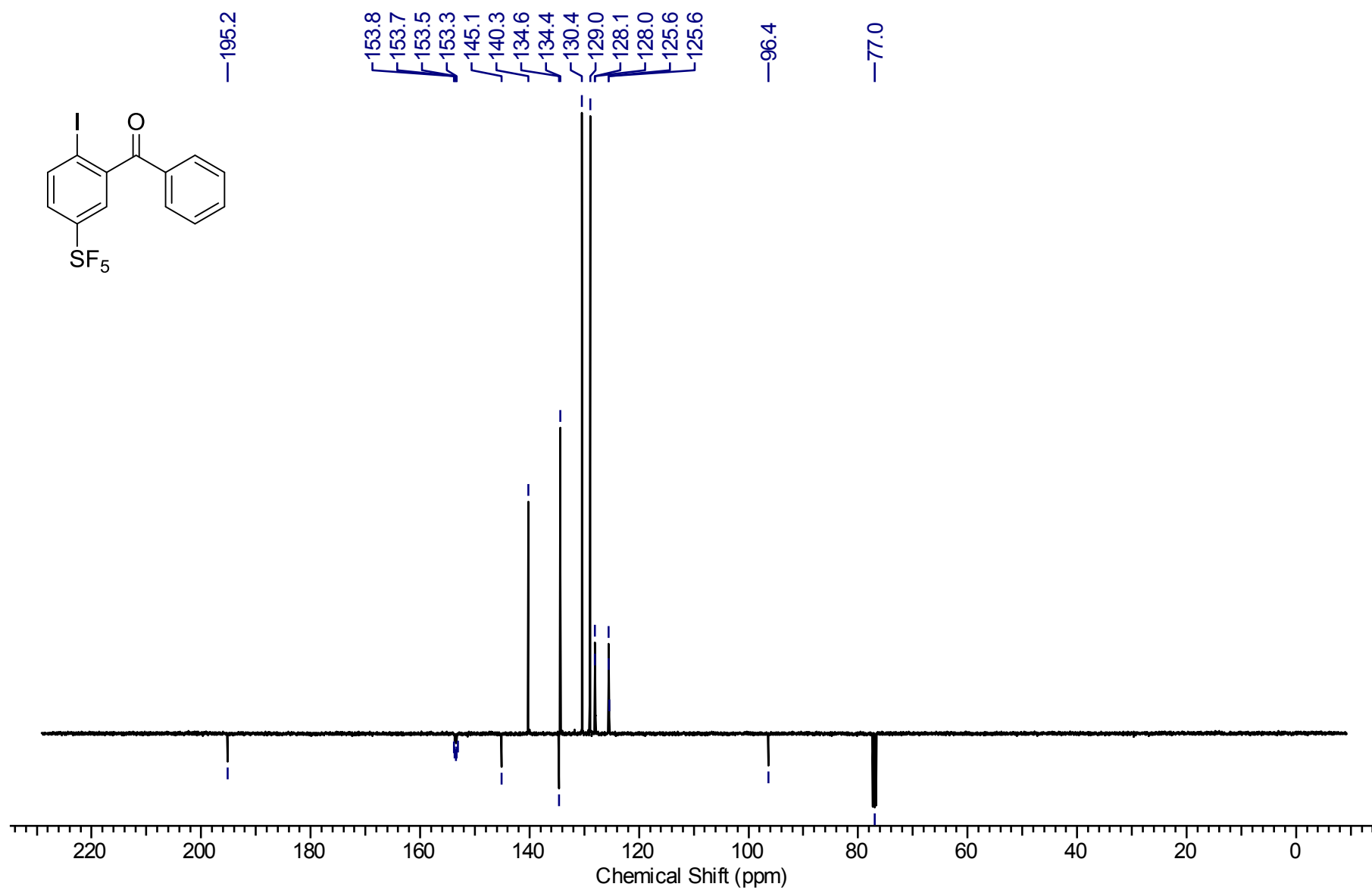


O=C(c1ccccc1)c2ccc(I)cc2

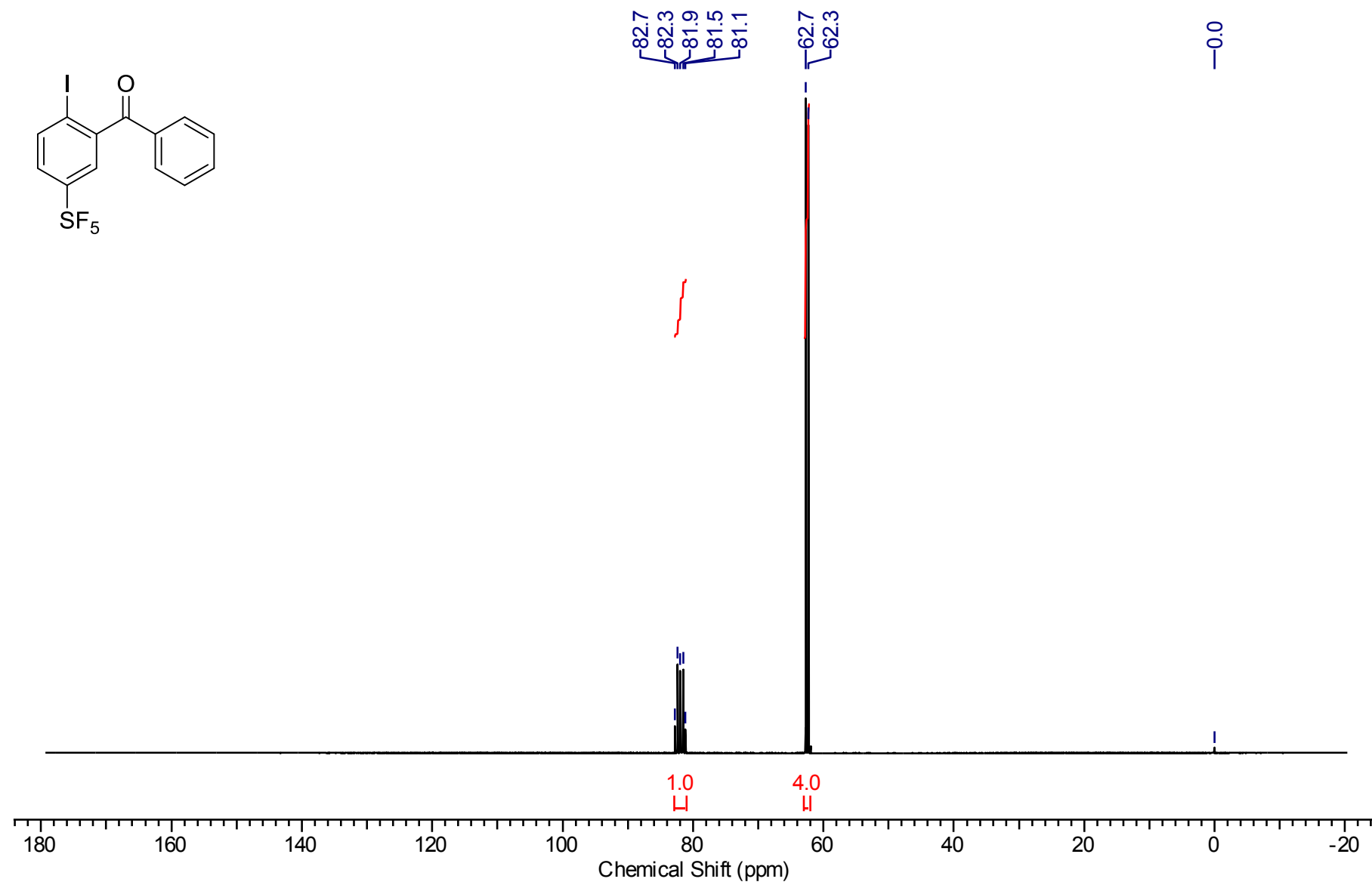
Chemical Shift (ppm): 8.06, 8.04, 7.82, 7.82, 7.80, 7.79, 7.68, 7.67, 7.66, 7.66, 7.64, 7.58, 7.57, 7.55, 7.53, 7.51, 7.51, 7.49, 0.00

Integration: 1.0, 2.0, 2.0, 1.1, 2.1

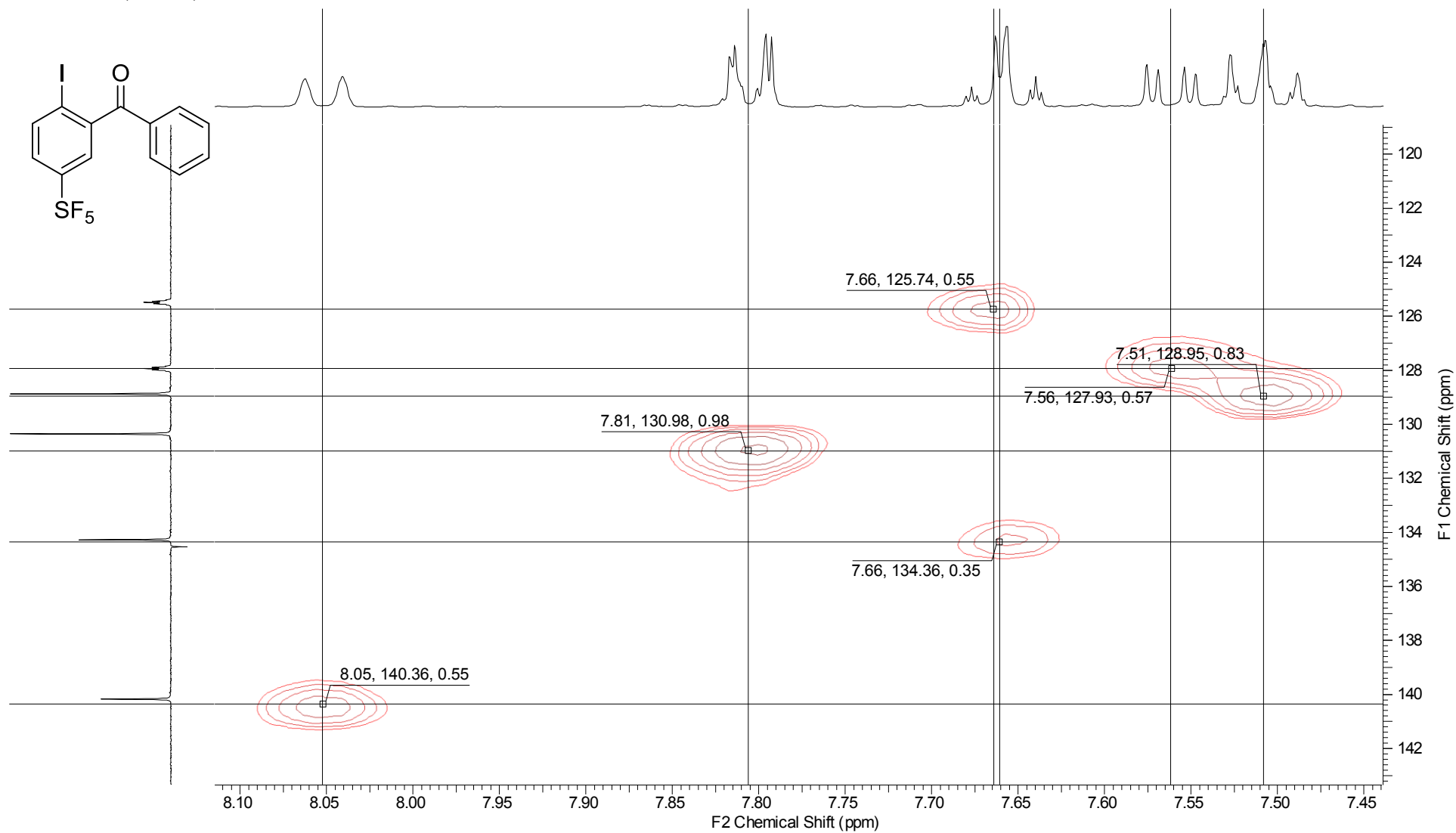
10i: ^{13}C NMR (101 MHz, CDCl_3)



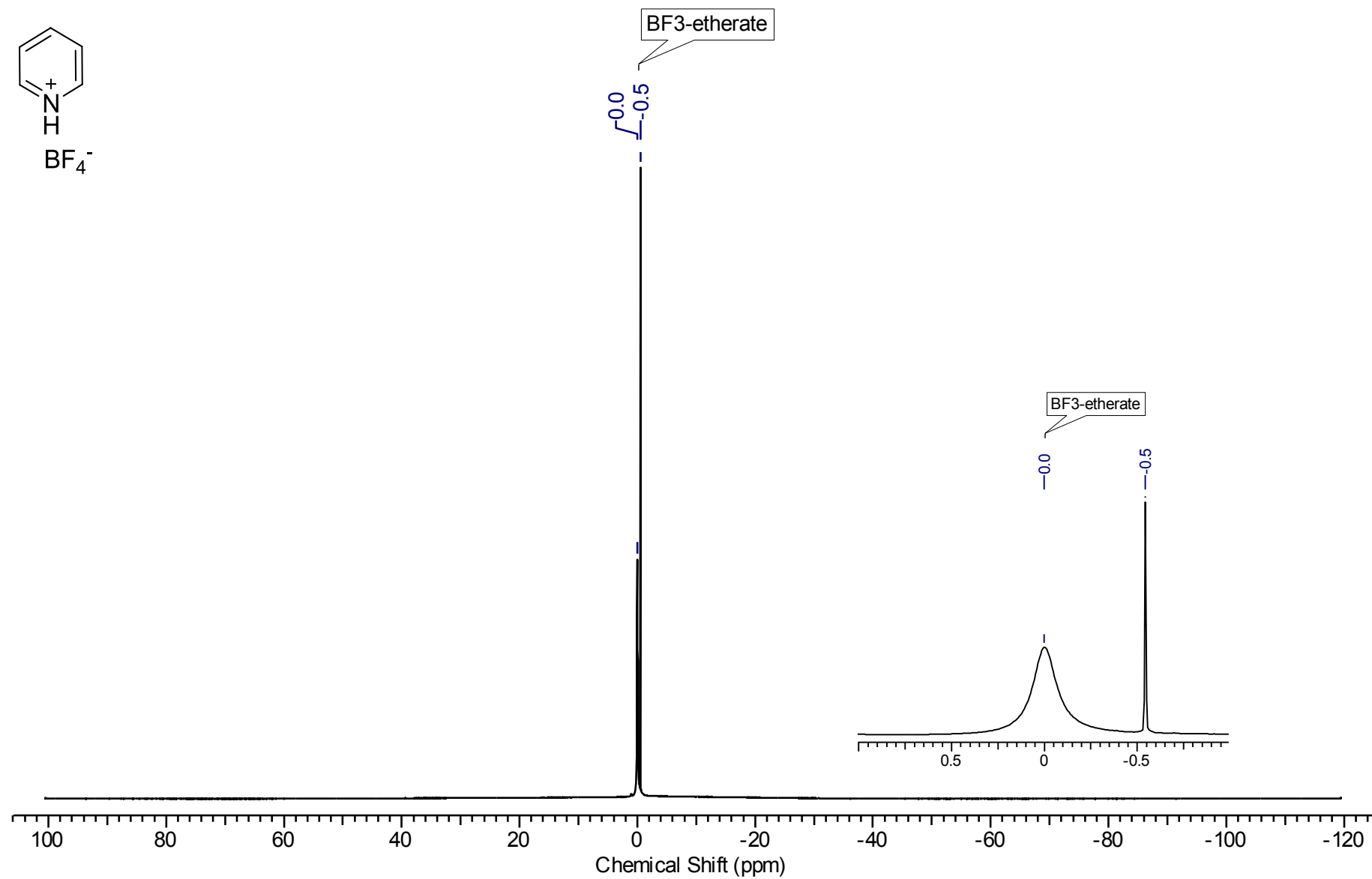
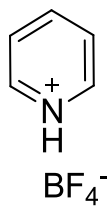
10i: ^{19}F NMR (377 MHz, CDCl_3)



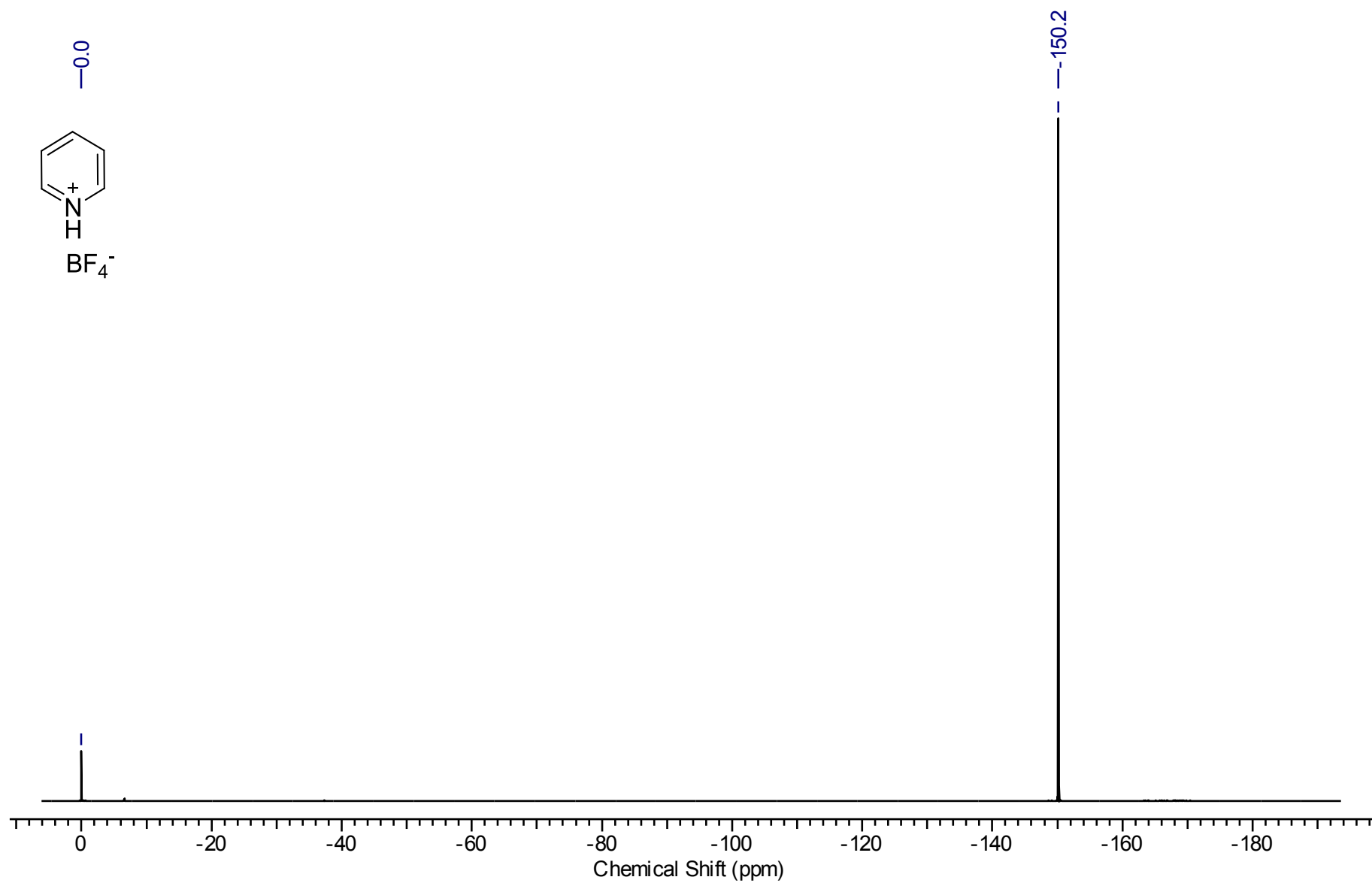
10i: HSQC (CDCl₃)



Pyridinium tetrafluoroborate: ^{11}B NMR (128 MHz, CD_3CN)



Pyridinium tetrafluoroborate: ^{19}F NMR (376 MHz, CD_3CN)



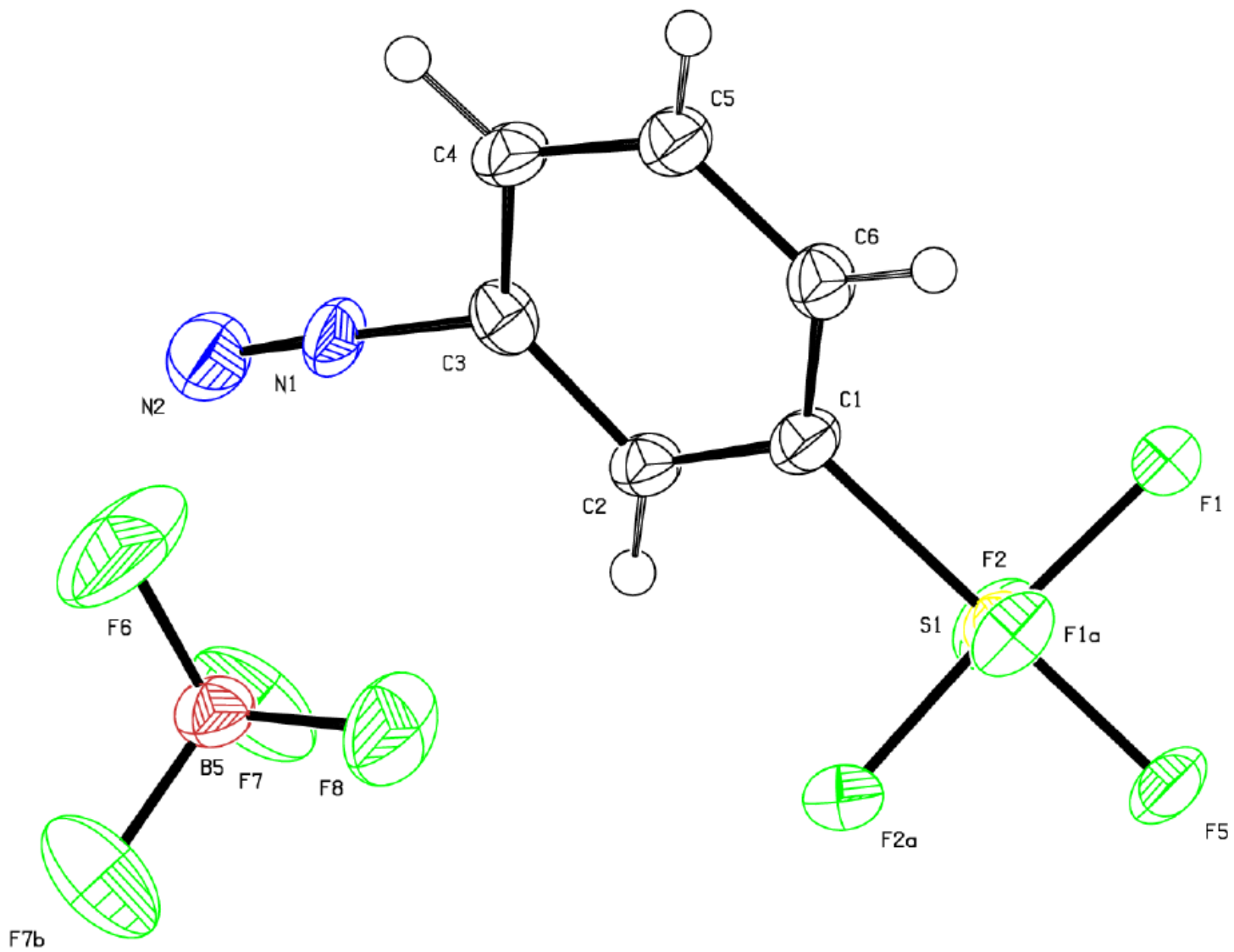


Figure S12: X-ray crystal structure of (3-pentafluorosulfanyl)benzenediazonium tetrafluoroborate (**3a**). Thermal ellipsoids are drawn at the 50% probability level.

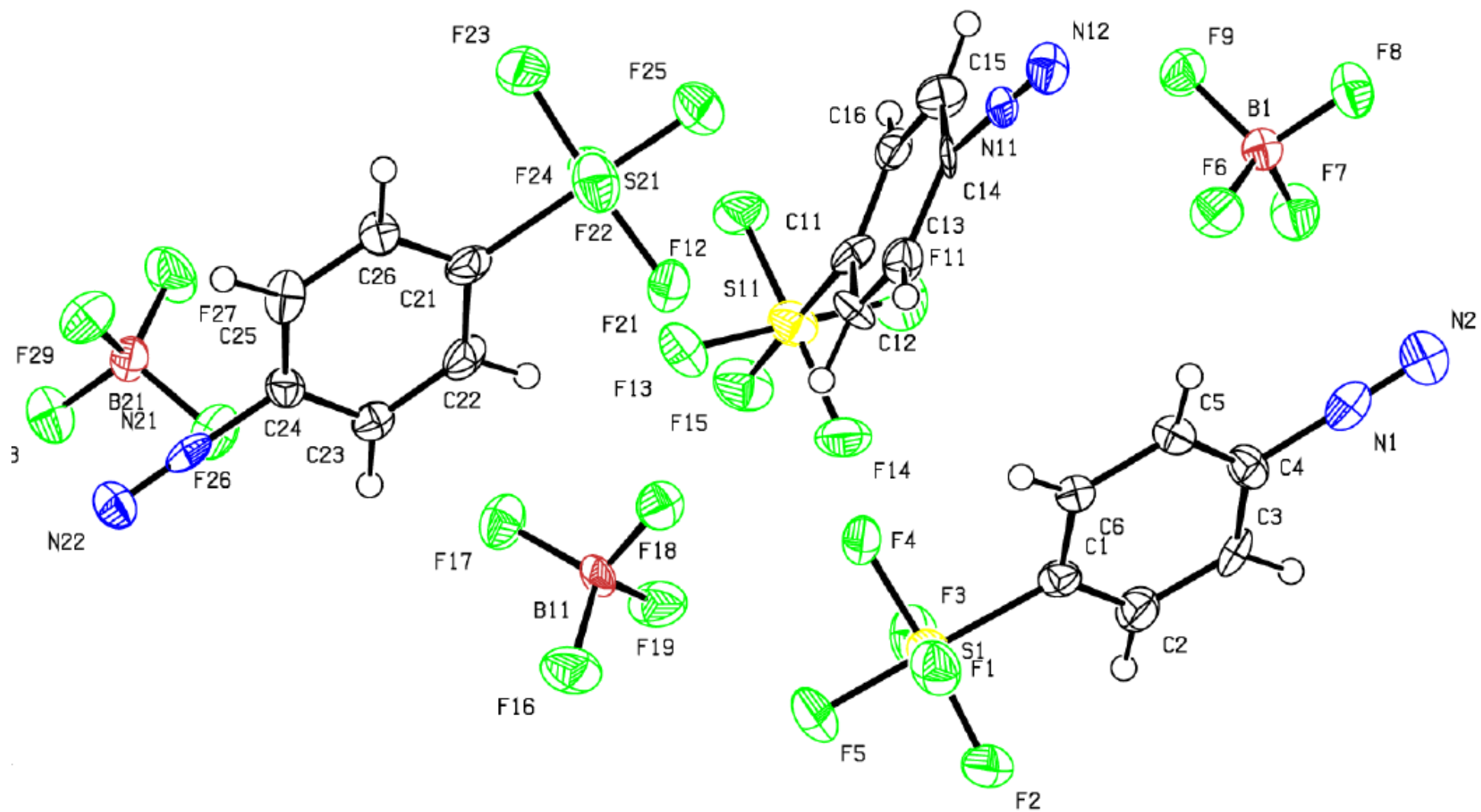


Figure S13: X-ray crystal structure of (4-pentafluorosulfonyl)benzenediazonium tetrafluoroborate (**3b**). Thermal ellipsoids are drawn at the 50% probability level.

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