

Supporting Information
for
Acyl Azolium Fluorides for Room Temperature Nucleophilic Aromatic Fluorination of Chloro- and Nitroarenes

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SI-1. Experimental Procedures

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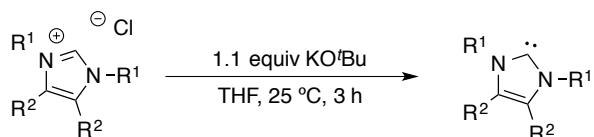
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I. General experimental

NMR spectra were recorded on a 700 MHz (699.76 MHz for ¹H; 175.95 MHz for ¹³C), 500 MHz (500.10 MHz for ¹H; 125.75 MHz for ¹³C, 470.56 MHz for ¹⁹F), or 400 MHz (400.52 MHz for ¹H; 100.71 for ¹³C; 376.87 MHz for ¹⁹F) NMR spectrometer with the residual solvent peak (CDCl₃; ¹H δ = 7.26 ppm, ¹³C δ = 77.16 ppm) used as the internal reference unless otherwise noted. Chemical shifts are reported in parts per million (ppm) (δ) relative to tetramethylsilane. Multiplicities are reported as follows: br (broad resonance), sept (septet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants (*J*) are reported in hertz. Melting points are uncorrected. All stock solutions were made using volumetric glassware. All liquid reagents were dispensed by difference from syringes. All reagents were weighed out in a nitrogen-filled drybox with exclusion of air and moisture, unless otherwise noted. All reagents were purchased from common suppliers and dried over P₂O₅ prior to use unless otherwise noted. *p*-Trifluoromethylbenzoyl fluoride was purchased from 3B Scientific and distilled under reduced pressure prior to use. The imidazolium salt required for the synthesis of **C** was purchased from Sigma Aldrich. The imidazolium salt required for the synthesis of **B** was prepared according to a literature procedure.¹ Thin layer chromatography (TLC) was performed on plates precoated with silica gel 60 F254. High resolution mass spectrometry (HRMS) was performed on a Micromass AutoSpec Ultima Magnetic sector mass spectrometer using electrospray or electron impact ionization. GCMS analysis was performed on a Shimadzu GCMS-QP2010 plus gas chromatograph mass spectrometer. The products were separated on a 30 m length by 0.25 mm id RESTEK XTI-5 column coated with a 0.25 μ m film. Helium was employed as the carrier gas, with a constant column flow of 1.5 mL/min. The injector temperature was held constant at 250 °C. The GC oven temperature program was as follows: 32 °C hold 5 min, ramp 15 °C/min to 250 °C, and hold for 1.5 min.

II. Synthesis of *N*-heterocyclic carbenes

Preparation of carbenes B and C



In a nitrogen filled glove box, the appropriate imidazolium salt (5 mmol) was dissolved in anhydrous THF (50 mL), and sublimed KO'Bu (561.1 mg, 5 mmol) was added. The reaction mixture was stirred at room temperature for 3 h. After this time, the solvent was evaporated. Anhydrous toluene was added to the residue, and the suspension was filtered through celite. The filtrate was concentrated to afford the desired compound.

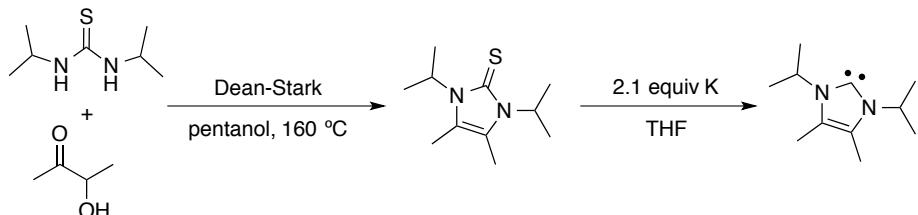
1,3-Bis(2,6-diisopropylphenyl)-4,5-dimethyl-1*H*-imidazol-3-ium-2-ide (B)

White solid (1.0 g, 47% yield). ^1H NMR (500 MHz, C_6D_6): δ 7.31 (t, $J = 7.7$ Hz, 2H), 7.21 (d, $J = 7.7$ Hz, 4H), 2.91 (sept, $J = 7.0$ Hz, 4H), 1.66 (s, 6H), 1.31 (d, $J = 7.0$ Hz, 12H), 1.19 (d, $J = 7.0$ Hz, 12H). ^{13}C NMR (125 MHz, C_6D_6): δ 217.2, 146.7, 137.4, 128.3, 123.9, 123.7, 28.8, 25.2, 23.0, 9.6.

1,3-diisopropyl-1*H*-imidazol-3-ium-2-ide (C)

Yellow oil (0.5 g, 62% yield). ^1H NMR (700 MHz, C_6D_6): δ 6.51 (s, 2H), 4.39 (sept, $J = 7.0$ Hz, 2H), 1.26 (d, $J = 7.0$ Hz). ^{13}C NMR (175 MHz, C_6D_6): δ 211.7, 115.5, 52.1, 24.2. Characterization data is consistent with that previously reported.²

Preparation of 1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-3-ium-2-ide (D)

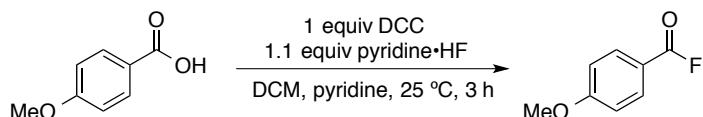


According to the procedure of Kuhn and Kratz,³ diisopropylthiourea (16.03g, 100 mmol) was dissolved in pentanol (70 mL). Acetoin (9.7 mL, 110 mmol) was added, and the flask was fitted with a Dean-Stark apparatus and reflux condenser. The reaction mixture was heated to 160 °C, until the evolution of water ceased (approximately 6 h). The solution was allowed to cool to room temperature, then placed in a freezer for 2 h. The solid was filtered and washed with cold ethanol to afford a white solid. A portion of the white solid (8.5 g, 40 mmol) was then dissolved in anhydrous THF (150 mL) in a 250 mL Schlenk flask. Potassium metal (3.3 g, 84 mmol) was added, and the flask was fitted with a

reflux condenser. The reaction mixture was heated to reflux for 24 h. After this time, the reaction mixture was taken into a nitrogen filled glove box and filtered through a glass frit. The filtrate was concentrated to afford the title compound as a pale yellow solid (5.5 g, 76% yield).

¹H NMR (700 MHz, C₆D₆): δ 3.94 (sept, *J* = 6.7 Hz, 2H), 3.31 (s, 6H), 1.50 (d, *J* = 6.7 Hz, 12H). ¹³C NMR (175 MHz, C₆D₆) δ 207.5, 121.4, 48.4, 24.7, 8.8. Characterization data is consistent with that previously reported.³

III. Synthesis of *p*-methoxybenzoyl fluoride



According to the procedure of Chen,⁴ *p*-anisic acid (3.05 g, 20 mmol) was dissolved in a solution of DCM: pyridine (60 mL: 4 mL). This mixture was then transferred via cannula to a stirred solution of DCC (4.12 g, 20 mmol) and pyridine•HF (0.6 mL of a 70% solution in pyridine, 22 mmol) in DCM (20 mL). After stirring at room temperature for 3 h, the suspension was filtered through a glass frit and the filtrate was concentrated. The resulting residue was distilled under reduced pressure to afford the title compound as a colorless oil (1.9 g, 61% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H). ¹⁹F NMR (377 MHz, CDCl₃): δ 15.8. ¹³C NMR (100 MHz, CDCl₃): δ 165.3, 157.3 (d, *J* = 337 Hz), 133.8 (d, *J* = 3.8 Hz), 116.8 (d, *J* = 61.3 Hz), 114.5, 55.7. Characterization data is consistent with that previously reported.⁵

IV. Nucleophilic aromatic substitution of aryl chlorides and nitroarenes

General Procedure A:

To a 4 mL vial equipped with a magnetic stir bar was added the appropriate aryl chloride (0.1 mmol) and NHC **D** (54 mg, 0.3 mmol). The vial was then charged with anhydrous DMF (0.5 mL), and *p*-methoxybenzoyl fluoride (45 μL, 0.3 mmol) was added. The reaction vial was capped, removed from the dry box and stirred at room temperature for 16 h.

General Procedure B:

To a 4 mL vial equipped with a magnetic stir bar was added the appropriate aryl chloride or nitroarene (0.1 mmol). The vial was charged with anhydrous DMF (0.5 mL) and *p*-methoxybenzoyl fluoride (60

μL , 0.4 mmol). Finally, **D** (54 mg, 0.3 mmol) was added in one portion, and the reaction mixture was stirred at room temperature for 16 h.

Isolation procedure 1

For compounds **5**, **6**, **7**, **8**, **9** and **3** the reaction mixture was loaded directly onto silica gel for flash column chromatography.

Isolation procedure 2

In some cases, *p*-methoxybenzoyl fluoride co-eluted with the desired product (compounds **10**, **11**, **14** and **16**), so the acyl fluoride was quenched prior to silica gel chromatography. The reaction mixtures were diluted to approximately 3 mL with DCM. TBAOH (1M aqueous solution, 0.5 mL) was then added, and the vial was capped and stirred for 1 min. The layers were then separated, and the aqueous layer was extracted with DCM. The combined organic extracts were concentrated, and the residue was purified via flash column chromatography.

Procedure for obtaining ^{19}F NMR yields

The reaction mixture was diluted to approximately 3 mL with DCM, and 1,3,5-trifluorobenzene (100 μL of a 0.5 M solution in toluene) was added as an internal standard. The reaction mixture was analyzed by ^{19}F NMR spectroscopy, and the yield was determined by relative integration of the product to the internal standard.

Isopropyl 5-fluoro-6-phenylpicolinate (**5**)

The title compound was prepared according to general procedure A and was isolated as a colorless oil using isolation procedure 1 (22.6 mg, 87% yield). Flash column chromatography was performed using a gradient elution of hexane to 10% EtOAc/90% hexanes. R_F = 0.6 (70% hexane/30% ether). ^1H NMR (400 MHz, CDCl_3): δ 8.07-8.05 (multiple peaks, 3H), 7.57 (dd, J = 10.0, 8.5 Hz, 1H), 7.51-7.44 (multiple peaks, 3H), 5.32 (sept, J = 6.2 Hz, 1H), 1.42 (d, J = 6.2 Hz, 6H). ^{19}F NMR (377 MHz, CDCl_3): δ -117.8 (d, J = 10.0 Hz). ^{13}C NMR (175 MHz, CDCl_3): δ 163.9, 159.2 (d, J = 266 Hz), 146.4 (d, J = 12 Hz), 144.6 (d, J = 5 Hz), 134.7 (d, J = 5 Hz), 129.8, 129.1 (d, J = 6 Hz), 128.6, 125.5 (d, J = 5 Hz), 124.7 (d, J = 22 Hz), 69.7, 22.0. HRMS ESI $^+$ (m/z): [M + H] $^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{FNO}_2$ 260.1081; found 260.1078. Characterization data is consistent with that previously reported.⁶

Isopropyl 6-(4-chlorophenyl)-5-fluoropicolinate (**6**)

The title compound was prepared according to general procedure A and was isolated as a white solid using isolation procedure 1 (27.0 mg, 92% yield). Flash column chromatography was performed using a gradient elution of hexane to 10% EtOAc/90% hexanes. R_F = 0.6 (70% hexane/30% ether). Mp = 76-78 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.09-8.01 (multiple peaks, 3H), 7.57 (dd, J = 10.8, 8.8 Hz,

1H), 7.46 (d, J = 8.8 Hz, 2H), 5.32 (sept, J = 6.4 Hz, 1H), 1.42 (d, J = 6.4 Hz, 6H). ^{19}F NMR (377 MHz, CDCl_3): δ -117.6 (d, J = 10.8 Hz). ^{13}C NMR (175 MHz, CDCl_3): δ 163.7, 159.2 (d, J = 266 Hz), 145.1 (d, J = 12 Hz), 144.7 (d, J = 4 Hz), 136.0, 133.1 (d, J = 5 Hz), 130.5 (d, J = 6 Hz), 128.9, 125.8 (d, J = 6 Hz), 124.9 (d, J = 22 Hz), 69.8, 22.0. HRMS ESI $^+$ (m/z): [M + H] $^+$ calcd for $\text{C}_{15}\text{H}_{14}\text{ClFNO}_2$ 294.0692; found 294.0697.

Isopropyl 5-fluoro-6-(4-methoxyphenyl)picolinate (7)

The title compound was prepared according to general procedure B and was isolated as a colourless oil using isolation procedure 1 (26.9 mg, 93% yield). Flash column chromatography was performed using a gradient elution of hexane to 20% EtOAc/80% hexanes. R_F = 0.5 (70% hexane/30% ether). ^1H NMR (400 MHz, CDCl_3): δ 8.06 (d, J = 8.4 Hz, 2H), 8.00 (dd, J = 8.4, 4.8 Hz, 1H), 7.52 (dd, J = 10.8, 8.4 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 5.31 (sept, J = 6.4 Hz, 1H), 1.42 (d, J = 6.4 Hz, 6H). ^{19}F NMR (377 MHz, CDCl_3): δ -118.0 (d, J = 10.8 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 164.0, 160.9, 159.0 (d, J = 265 Hz), 146.0 (d, J = 11 Hz), 144.4 (d, J = 5 Hz), 130.6 (d, J = 7 Hz), 127.3 (d, J = 6 Hz), 124.7 (d, J = 6 Hz), 124.5 (d, J = 22 Hz), 114.0, 69.6, 55.5, 22.0. HRMS ESI $^+$ (m/z): [M + H] $^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{FNO}_3$ 290.1187; found 290.1186.

Isopropyl 4,5-difluoro-6-phenylpicolinate (3)

The title compound was prepared according to general procedure B and was isolated as a colorless oil using isolation procedure 1 (14.4 mg, 52% yield). Flash column chromatography was performed using a gradient elution of hexane to 10% EtOAc/90% hexanes. R_F = 0.6 (70% hexane/30% ether). ^1H NMR (400 MHz, CDCl_3): δ 8.05-8.03 (multiple peaks, 2H), 7.90 (dd, J = 9.2, 5.2 Hz, 1H), 7.53-7.48 (multiple peaks, 3H), 5.31 (sept, J = 6.2 Hz, 1H), 1.42 (d, J = 6.2 Hz, 6H). ^{19}F NMR (377 MHz, CDCl_3): δ -125.2 (dd, J = 18.6, 9.2 Hz), -144.7 (dd, J = 18.6, 5.2 Hz). ^{13}C NMR (175 MHz, CDCl_3): δ 162.9 (d, J = 3.5 Hz), 156.7 (dd, J = 263, 12 Hz), 148.5 (d, J = 9 Hz), 148.0 (dd, J = 267, 10 Hz), 145.4 (t, J = 7 Hz), 133.8 (t, J = 5 Hz), 130.2, 129.0 (d, J = 6 Hz), 128.7 (d, J = 15 Hz), 113.5 (d, J = 16 Hz), 70.1, 21.8. HRMS ESI $^+$ (m/z): [M + H] $^+$ calcd for $\text{C}_{15}\text{H}_{14}\text{F}_2\text{NO}_2$ 278.0987; found 278.0993. Characterization data is consistent with that previously reported.⁶

Isopropyl 6-(4-chlorophenyl)-4,5-difluoropicolinate (8)

The title compound was prepared according to general procedure B and was isolated as a white solid using isolation procedure 1 (15.3 mg, 49% yield). Flash column chromatography was performed using a gradient elution of hexane to 10% EtOAc/90% hexanes. R_F = 0.6 (70% hexane/30% ether). M_p = 74-75 °C. ^1H NMR (500 MHz, CDCl_3): δ 8.01 (d, J = 8.5 Hz, 2H), 7.90 (dd, J = 9.0, 5.0 Hz, 1H), 7.48 (d, J = 8.5 Hz, 2H), 5.31 (sept, J = 6.3 Hz, 1H), 1.42 (d, J = 6.3 Hz, 6H). ^{19}F NMR (477 MHz, CDCl_3): δ -124.7 (dd, J = 18.5, 9.0 Hz), -144.4 (dd, J = 18.5, 5.0 Hz). ^{13}C NMR (175 MHz, CDCl_3): δ 162.8 (d, J = 2.6 Hz), 156.9 (dd, J = 264, 13 Hz), 148.2 (dd, J = 268, 11 Hz), 147.3 (d, J = 7 Hz), 145.6 (t, J

$= 7$ Hz), 136.6, 132.4 (dd, $J = 5, 4$ Hz), 130.4 (d, $J = 6$ Hz), 129.1, 113.9 (d, $J = 16$ Hz), 70.4, 22.0. HRMS ESI $^+$ (m/z): [M + H] $^+$ calcd for C₁₅H₁₃ClF₂NO₂ 312.0597; found 312.0599. Characterization data is consistent with that previously reported.⁶

Isopropyl 4,5-difluoro-6-(4-methoxyphenyl)picolinate (9)

The title compound was prepared according to general procedure A and was isolated as a colorless oil using isolation procedure 1 (24.0 mg, 78% yield). Flash column chromatography was performed using a gradient elution of hexane to 10% EtOAc/90% hexanes. $R_F = 0.5$ (70% hexane/30% ether). ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, $J = 8.8$ Hz, 2H), 7.82 (dd, $J = 9.4, 5.3$ Hz, 1H), 7.02 (d, $J = 8.8$ Hz, 1H), 5.30 (sept, $J = 6.3$ Hz, 2H), 3.88 (s, 3H), 1.42 (d, $J = 6.3$ Hz, 6H). ¹⁹F NMR (377 MHz, CDCl₃): δ -125.7 (dd, $J = 18.6, 9.4$ Hz), -145.2 (dd, $J = 18.6, 5.3$ Hz). ¹³C NMR (175 MHz, CDCl₃): δ 163.1 (d, $J = 3.3$ Hz), 161.3, 156.8 (dd, $J = 262, 13$ Hz), 148.2 (d, $J = 8$ Hz), 147.9 (dd, $J = 266, 10$ Hz), 145.3 (t, $J = 7$ Hz), 130.7 (d, $J = 6$ Hz), 126.6 (dd, $J = 5, 2.8$ Hz), 114.2, 112.9 (d, $J = 16$ Hz), 70.2, 55.5, 22.0. HRMS ESI $^+$ (m/z): [M + H] $^+$ calcd for C₁₆H₁₆F₂NO₃ 308.1093; found 308.1092. Characterization data is consistent with that previously reported.⁶

Ethyl 3-chloro-6-fluoropicolinate (10)

The title compound was prepared according to general procedure B and was isolated as a colorless oil using isolation procedure 2 (12.4 mg, 61% yield). Flash column chromatography was performed using a gradient elution of hexane to 10% EtOAc/90% hexanes. $R_F = 0.61$ (70% hexane/30% ether). ¹H NMR (400 MHz, CDCl₃): δ 7.88 (dd, $J = 8.6, 6.5$ Hz, 1H), 7.05 (dd, $J = 8.6, 3.6$ Hz, 1H), 4.47 (q, $J = 7.1$ Hz, 2H), 1.43 (t, $J = 7.1$ Hz, 3H). ¹⁹F NMR (377 MHz, CDCl₃): δ -68.0. ¹³C NMR (175 MHz, CDCl₃): δ 163.3, 160.8 (d, $J = 243$ Hz), 145.3 (d, $J = 13$ Hz), 143.9 (d, $J = 8$ Hz), 127.8 (d, $J = 5$ Hz), 113.5 (d, $J = 39$ Hz), 62.7, 14.3. HRMS ESI $^+$ (m/z): [M + H] $^+$ calcd for C₈H₈ClFNO₂ 204.0222; found 204.0217.

2-Fluoroquinoline (11)

The title compound was prepared according to general procedure A and was isolated as a colorless oil using isolation procedure 2 (12.7 mg, 86% yield). Flash column chromatography was performed using a gradient elution of hexane to 10% EtOAc/90% hexanes. $R_F = 0.6$ (70% hexane/30% ether). ¹H NMR (400 MHz, CDCl₃): δ 8.24 (t, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 8.4$ Hz, 1H), 7.73 (t, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.08 (dd, $J = 8.4, 6.4$ Hz, 1H). ¹⁹F NMR (477 MHz, CDCl₃): δ -61.8 (d, $J = 6.4$ Hz). ¹³C NMR (175 MHz, CDCl₃): δ 161.3 (d, $J = 241$ Hz), 145.9 (d, $J = 16$ Hz), 142.1 (d, $J = 10$ Hz), 130.7, 128.3 (d, $J = 1.4$ Hz), 127.7, 127.0 (d, $J = 1.4$ Hz), 126.3 (d, $J = 2.8$ Hz), 110.2 (d, $J = 42$ Hz). HRMS ESI $^+$ (m/z): [M + H] $^+$ calcd for C₉H₇FN 148.0557; found 148.0554. Characterization data is consistent with that previously reported.⁶

2-Fluorobenzonitrile (12)

The title compound was prepared following general procedure A from either the aryl chloride or the nitroarene. The reaction was analyzed by ¹⁹F NMR spectroscopy and GCMS. From the aryl chloride, the fluorinated product was formed in 26% yield as determined by ¹⁹F NMR spectroscopic analysis of the crude reaction mixture. The product showed a ¹⁹F NMR signal at -107.82 ppm in DCM (lit. -108.7 ppm in DMSO).⁷ The yield reported in the manuscript (28%) represents an average of two runs [26% (above) and 30%].

From the nitroarene, the fluorinated product was formed in 99% yield as determined by ¹⁹F NMR spectroscopic analysis of the crude reaction mixture. The yield reported in the manuscript (95%) represents an average of two runs [99% (above) and 91%].

2, 6-Difluoropyridine (13)

The title compound was prepared following general procedure A. The reaction was analyzed by ¹⁹F NMR spectroscopy and GCMS. The fluorinated product was formed in 91% yield as determined by ¹⁹F NMR spectroscopic analysis of the crude reaction mixture. The ¹⁹F NMR spectral data matched that of an authentic sample (Alfa Aesar, m, -68.91 ppm). The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 4.85 min. The yield reported in the manuscript (93%) represents an average of two runs [91% (above) and 94%].

2-Fluoro-3-chloropyridine (14)

The title compound was prepared following general procedure A. The reaction was analyzed by ¹⁹F NMR spectroscopy and GCMS. The fluorinated product was formed in 89% yield as determined by ¹⁹F NMR spectroscopic analysis of the crude reaction mixture. The product showed a ¹⁹F NMR signal at -72.73 ppm in DCM (lit. -73.03 ppm in DMSO).⁷ The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 8.94 min. The yield reported in the manuscript (92%) represents an average of two runs [89% (above) and 94%].

2-Fluoro-5-(trifluoromethyl)pyridine (15)

The title compound was prepared following general procedure B. The reaction was analyzed by ¹⁹F NMR spectroscopy and GCMS. The fluorinated product was formed in 94% yield as determined by ¹⁹F NMR spectroscopic analysis of the crude reaction mixture. The product showed ¹⁹F NMR signals at -62.71 (3F) and -63.60 (1F) ppm in DCM (lit. -60.62 (3F), -63.01 (1F) ppm in DMSO).⁷ The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 4.47 min. The yield reported in the manuscript (88%) represents an average of two runs [94% (above) and 81%].

2-Fluoropyrazine (16)

The title compound was prepared following general procedure B. The reaction was analyzed by ^{19}F NMR spectroscopy and GCMS. The fluorinated product was formed in 98% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The product showed a ^{19}F NMR signal at -81.11 ppm in DCM (lit. -80.4 ppm in DMSO).⁷ The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 3.91 min. The yield reported in the manuscript (99%) represents an average of two runs [98% (above) and 100%].

2-Fluoro-3-(trifluoromethyl)pyridine (17)

The title compound was prepared following general procedure B. The reaction was analyzed by ^{19}F NMR spectroscopy and GCMS. The fluorinated product was formed in 88% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The product showed ^{19}F NMR signals at -65.04 (3F) and -69.78 (1F) ppm in DCM (lit. -62.6 (3F), -66.3 ppm (1F) ppm in CCl_3F).⁸ The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 6.05 min. The yield reported in the manuscript (94%) represents an average of two runs [88% (above) and 100%].

2-Fluoro-5-bromopyridine (18)

The title compound was prepared following general procedure A from either the chloroarene or the nitroarene. The reaction was analyzed by ^{19}F NMR spectroscopy and GCMS. From the aryl chloride, the fluorinated product was formed in 84% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched that of an authentic sample (Oakwood Products, s, -71.69 ppm). The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 9.87 min. The yield reported in the manuscript (80%) represents an average of two runs [84% (above) and 76%].

From the nitroarene, the fluorinated product was formed in 91% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The yield reported in the manuscript (86%) represents an average of two runs [91% (above) and 81%].

2-Fluoro-5-iodopyridine (19)

The title compound was prepared following general procedure A. The reaction was analyzed by ^{19}F NMR spectroscopy and GCMS. The fluorinated product was formed in 59% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The ^{19}F NMR spectral data matched that of an authentic sample (Sigma Aldrich, m, -71.28 ppm). The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 11.37 min. The yield reported in the manuscript (47%) represents an average of two runs [59% (above) and 35%].

2-Fluoronicotinonitrile (20)

The title compound was prepared following general procedure B. The reaction was analyzed by ^{19}F NMR spectroscopy and GCMS. The fluorinated product was formed in 47% yield as determined by ^{19}F NMR spectroscopic analysis of the crude reaction mixture. The product showed a ^{19}F NMR signal at -62.95 ppm in DCM (lit. -60.0 ppm in CDCl_3).⁹ The identity of the product was further confirmed by GCMS analysis, where the product peak was observed at 10.73 min. The yield reported in the manuscript (50%) represents an average of two runs [47% (above) and 53%].

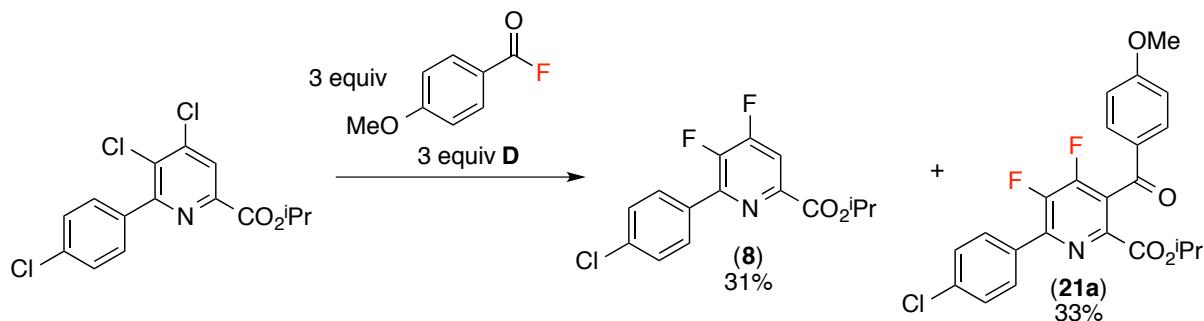
4-Fluorobenzophenone (22)

The title compound was prepared according to general procedure B from the nitrobenzene and was isolated as a white solid using isolation procedure 2 (17.2 mg, 86% yield). Flash column chromatography was performed using a gradient elution of hexane to 10% EtOAc/90% hexanes. $R_F = 0.6$ (70% hexane/30% ether). $M_p = 45\text{-}49$ °C. ^1H NMR (400 MHz, CDCl_3): δ 7.87–7.83 (multiple peaks, 2H), 7.78–7.76 (multiple peaks, 2H), 7.60 (t, $J = 7.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.16 (t, $J = 8.8$ Hz, 2H). ^{19}F NMR (377 MHz, CDCl_3): δ -106.0 . ^{13}C NMR (175 MHz, CDCl_3): δ 195.4, 165.5 (d, $J = 253$ Hz), 137.6, 133.9 (d, $J = 4$ Hz), 132.8 (d, $J = 9$ Hz), 132.6, 130.0, 128.5, 115.5 (d, $J = 22$ Hz). HRMS ESI $^+$ (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{10}\text{FO}$ 201.0710; found 201.0709. Characterization data is consistent with that previously reported.¹⁰

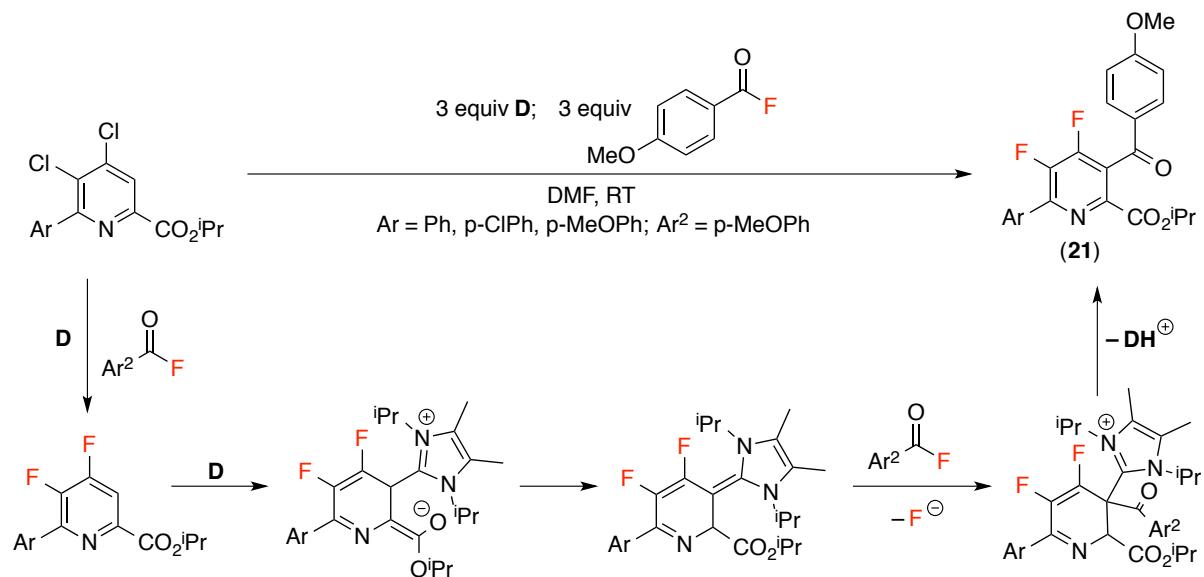
Ethyl 4-Fluorobenzoate (23)

The title compound was prepared according to general procedure B from the nitrobenzene and was isolated as a colorless oil using isolation procedure 2 (10.4 mg, 62% yield). Flash column chromatography was performed using a gradient elution of hexane to 10% EtOAc/90% hexanes. $R_F = 0.61$ (70% hexane/30% ether). ^1H NMR (400 MHz, CDCl_3): δ 8.06 (dd, $J = 8.8, 5.6$ Hz, 2H), 7.11 (t, $J = 8.8$ Hz, 2H), 4.37 (q, $J = 7.4$ Hz, 2H), 1.39 (t, $J = 7.4$ Hz, 3H). ^{19}F NMR (377 MHz, CDCl_3): δ -106.1 . ^{13}C NMR (175 MHz, CDCl_3) δ 165.9 (d, $J = 253$ Hz), 165.8, 132.2 (d, $J = 9$ Hz), 126.8 (d, $J = 3$ Hz), 115.6 (d, $J = 22$ Hz), 61.7, 14.5. HRMS EI (70 eV) (m/z): M^+ calcd for $\text{C}_9\text{H}_9\text{FO}_2$ 168.0586; found 168.0585. Characterization data is consistent with that previously reported.¹¹

V. Proposed Mechanism of Byproduct Formation



The modest yields with 4,5-dichloropicolinate substrates are due to the formation of by-product **21**. For example, when *p*-chlorophenyl picolinate was treated with 3 equiv of NHC and 3 equiv of *p*-methoxybenzoyl fluoride according to general procedure A, **21a** forms in 33% yield, as determined by ¹⁹F NMR spectroscopy of the crude reaction mixture. We propose that formation of **21** occurs via addition of **D** into the electron deficient fluorinated aromatic **8**. The resulting azolium then undergoes proton transfer to afford an extended Breslow intermediate, which can add to an equivalent of acyl azolium. Deprotonation then provides the final product.



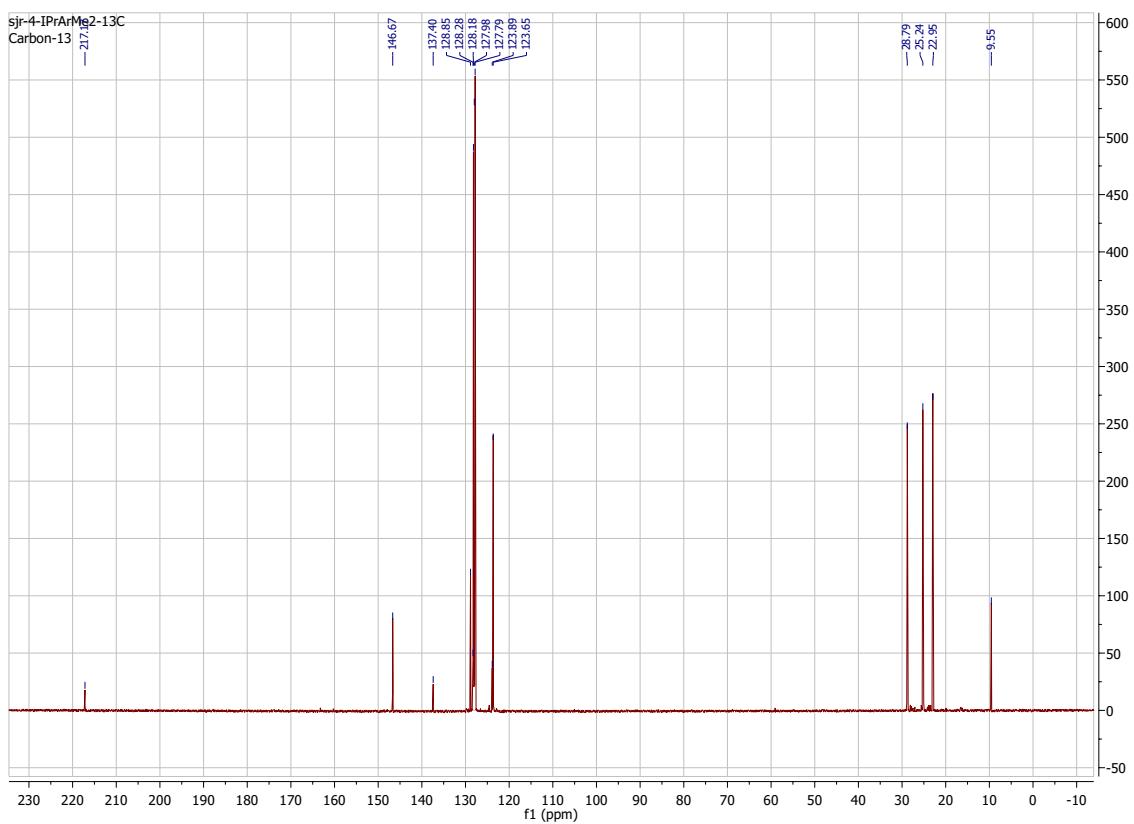
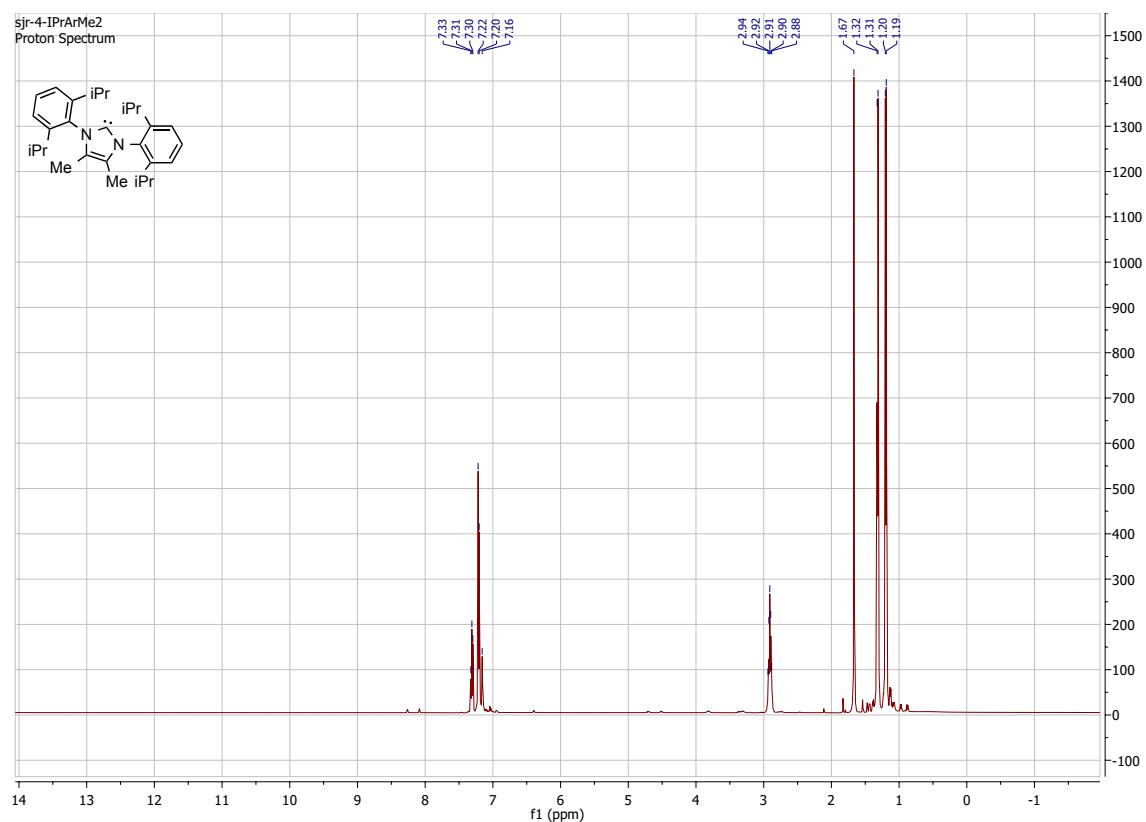
Isopropyl 6-(4-chlorophenyl)-4,5-difluoro-3-(4-methoxybenzoyl)picolinate (**21a**)

The title compound was isolated under general procedure A as a white solid (8.5 mg, 19% yield). Flash column chromatography was performed using a gradient elution of hexane to 10% EtOAc/90% hexanes. $R_F = 0.4$ (70% hexane/30% ether). $M_p = 145\text{--}148\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3): δ 8.07 (d, $J = 8.4$ Hz, 2H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 5.09 (sept, $J = 6.2$ Hz, 1H), 3.90 (s, 3H), 1.11 (d, $J = 6.2$ Hz, 6H). ^{19}F NMR (377 MHz, CDCl_3): δ -126.7 (d, $J = 19.5$ Hz), -143.4 (d, $J = 19.5$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 186.8, 164.7, 162.3 (d, $J = 3$ Hz), 154.2 (dd, $J = 264$,

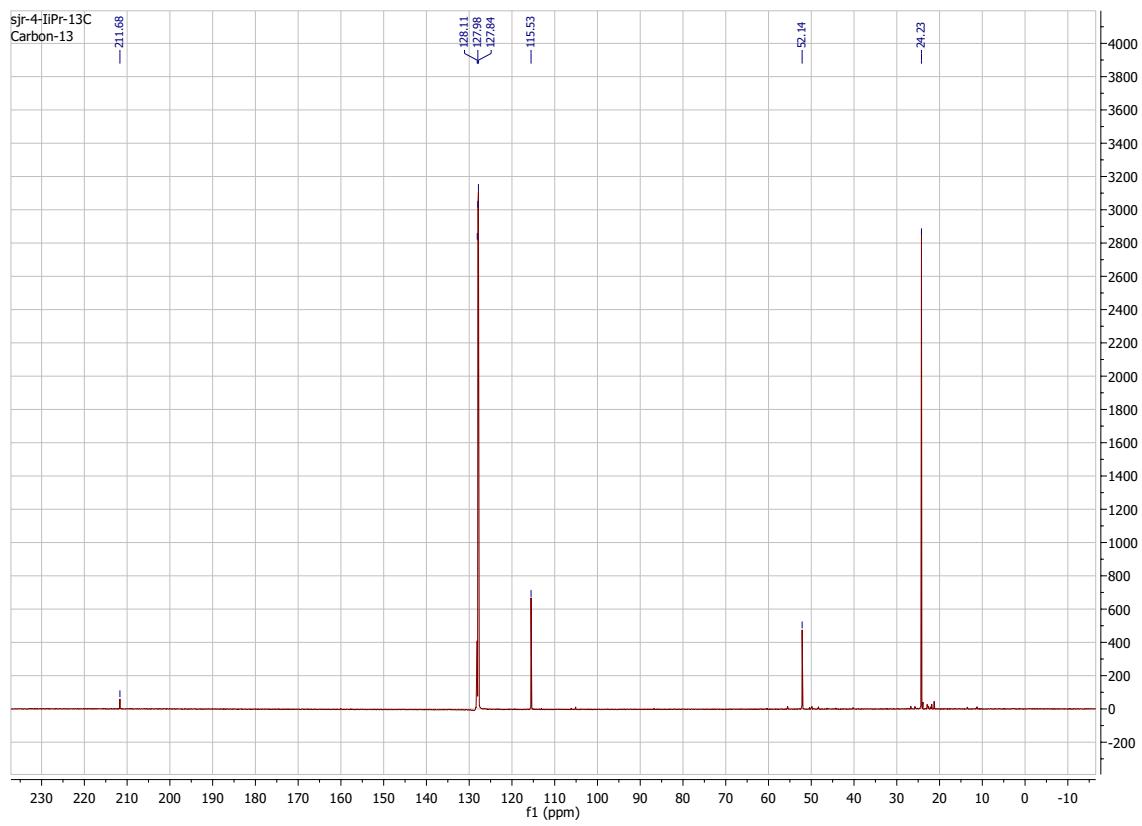
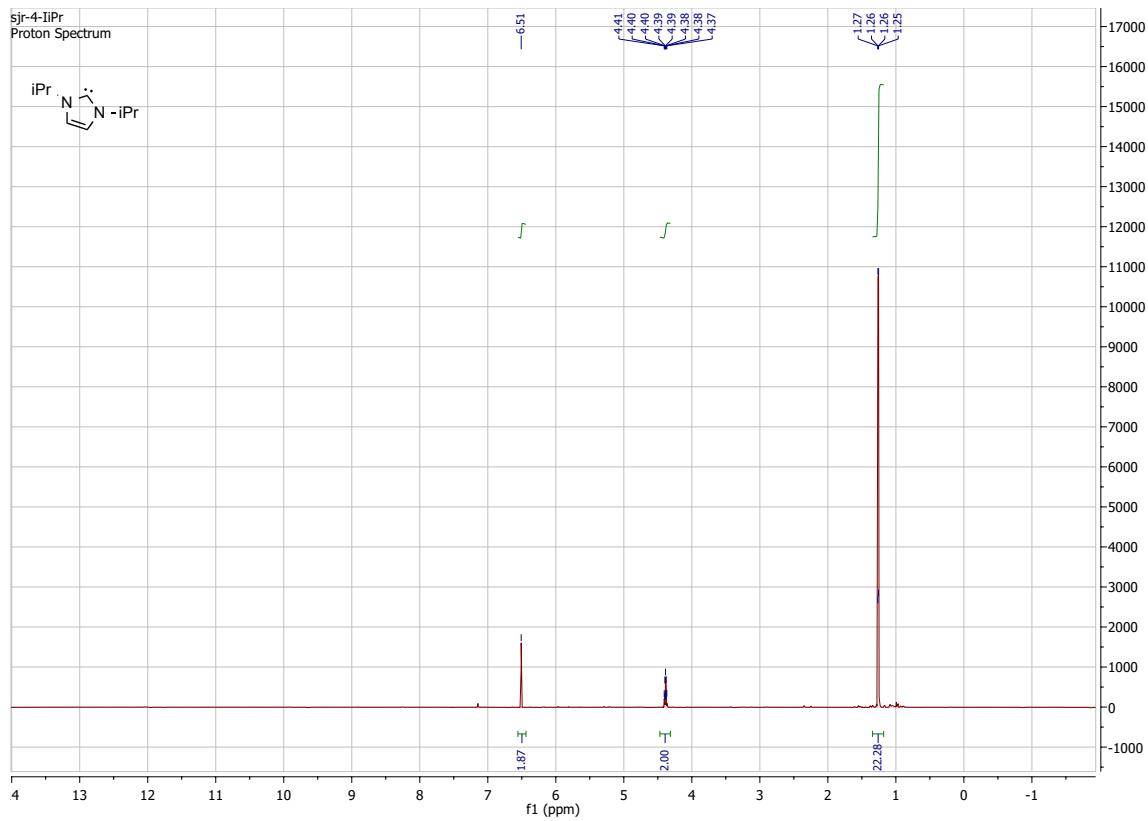
13 Hz), 147.5 (dd, J = 270, 12 Hz), 147.0 (d, J = 6 Hz), 143.3 (dd, J = 7, 4 Hz), 137.1 (d, J = 1 Hz), 132.0 (d, J = 3 Hz), 131.9, 130.5 (d, J = 7 Hz), 129.8, 129.2, 127.3 (d, J = 15 Hz), 114.5, 71.1, 55.8, 21.4. HRMS ESI⁺ (m/z): [M + H]⁺ calcd for C₂₃H₁₉ClF₂NO₄ 446.0965; found 446.0964.

VI. NMR Data

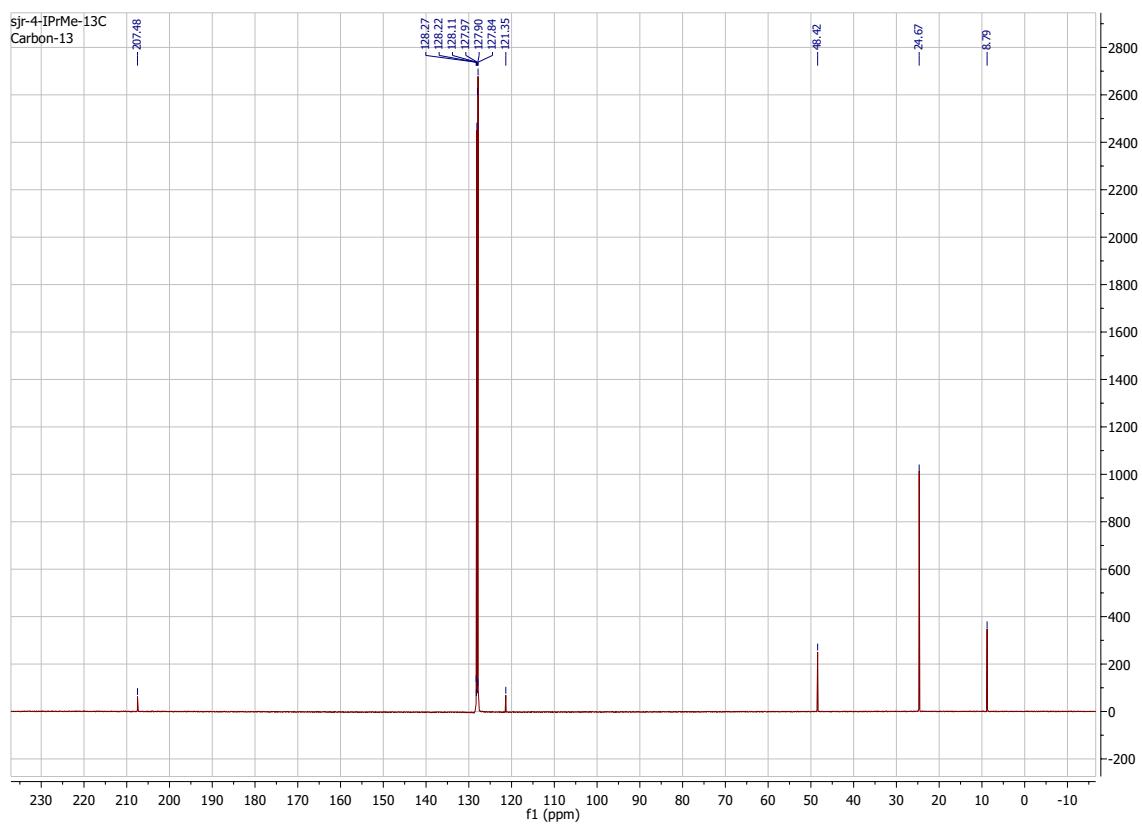
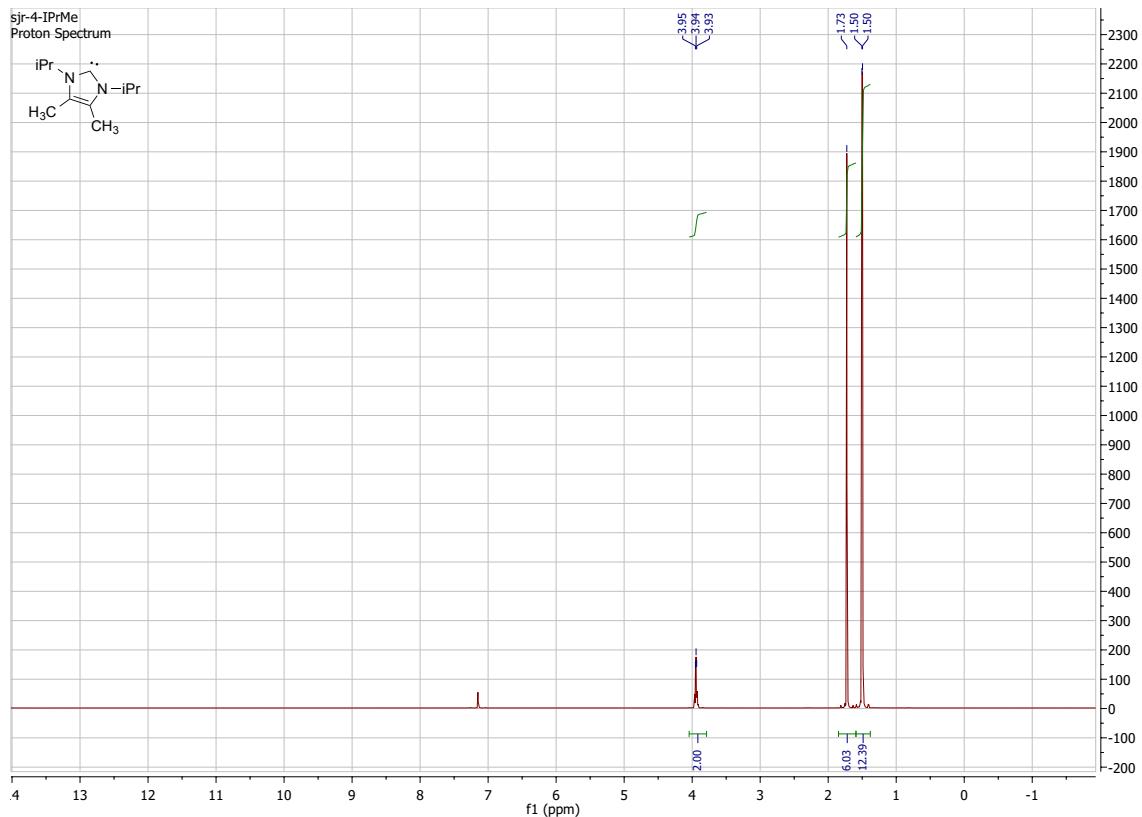
1,3-Bis(2,6-diisopropylphenyl)-4,5-dimethyl-1*H*-imidazol-3-ium-2-ide (B)



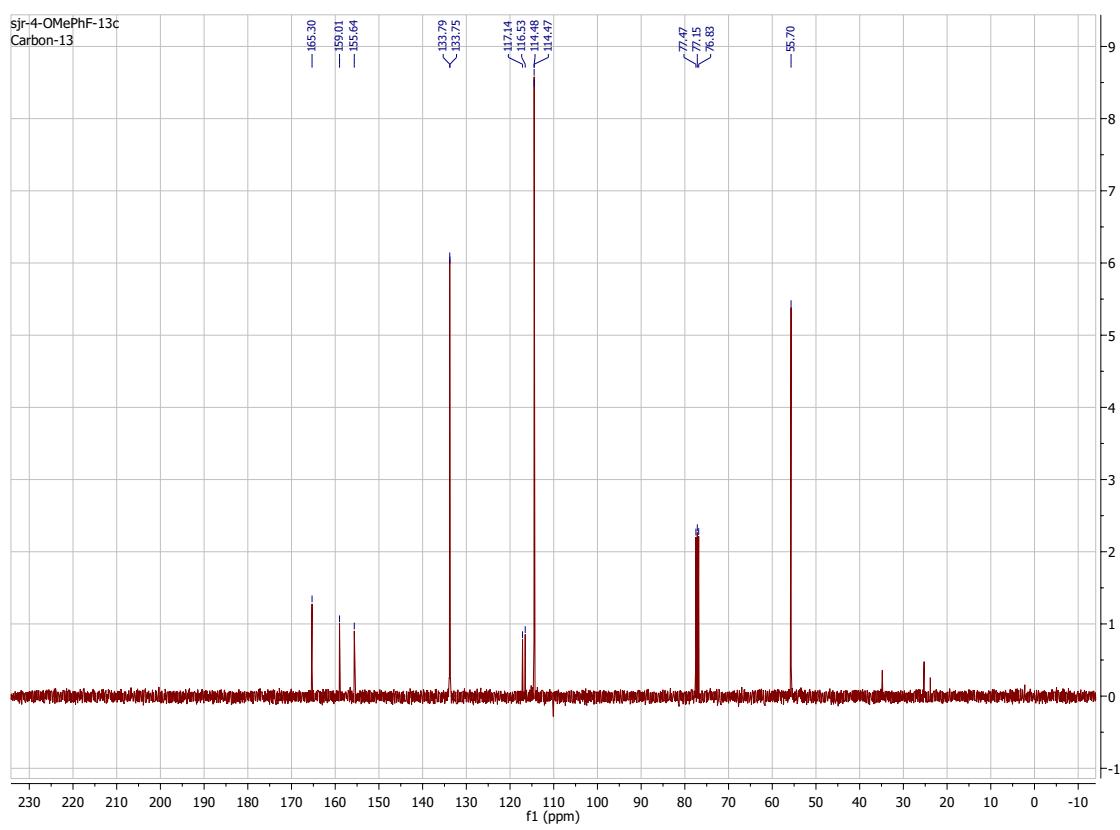
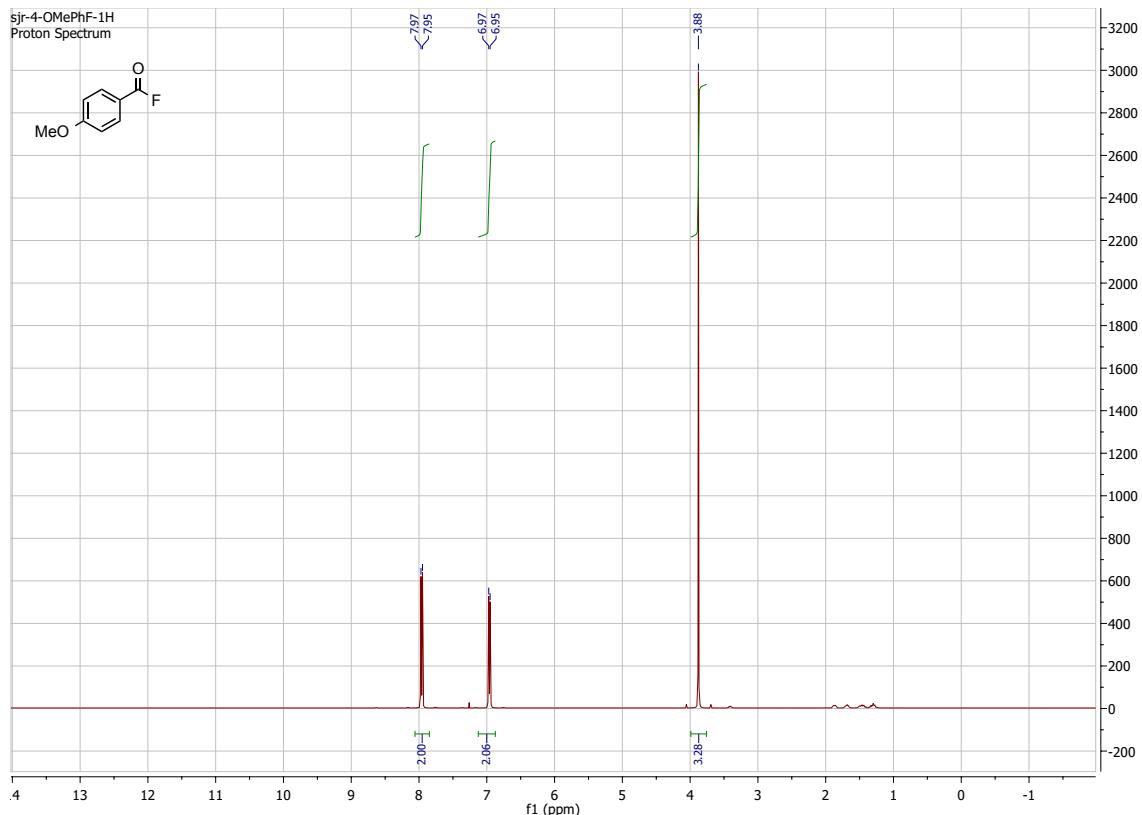
1,3-Diisopropyl-1*H*-imidazol-3-ium-2-ide (C)

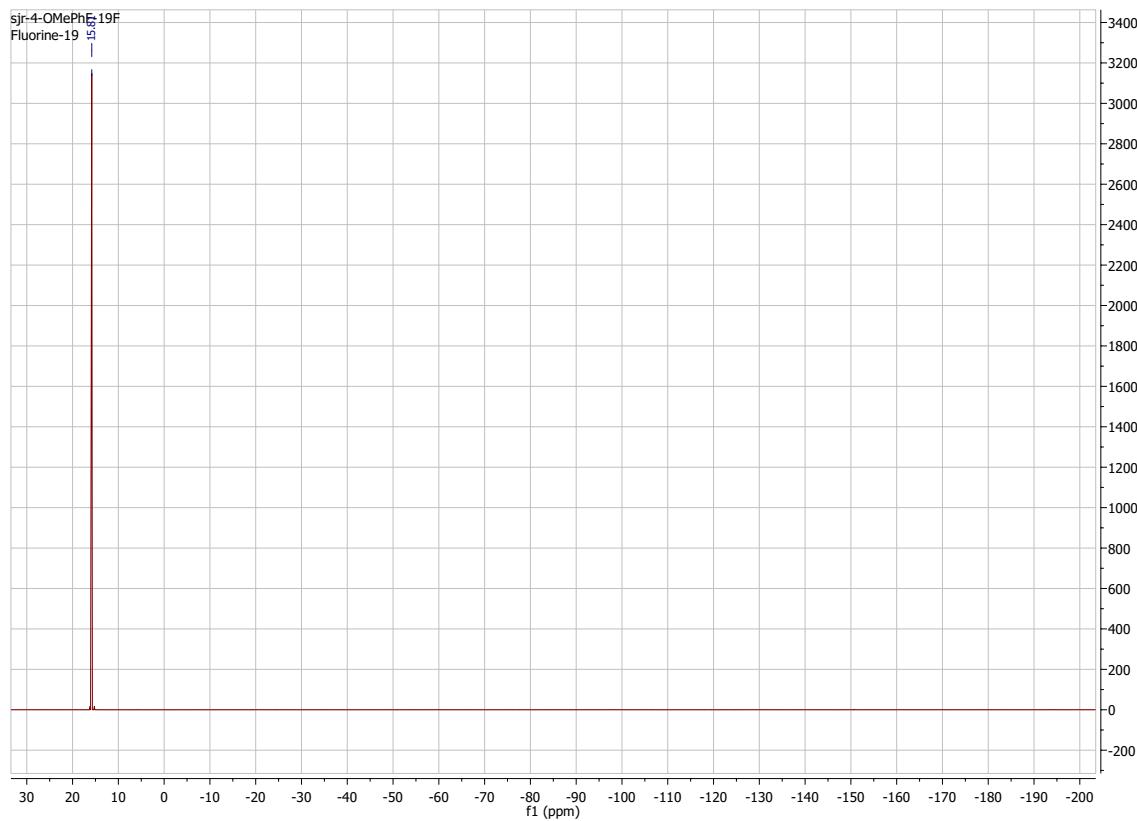


1,3-diisopropyl-4,5-dimethyl-1*H*-imidazol-3-ium-2-ide (D)

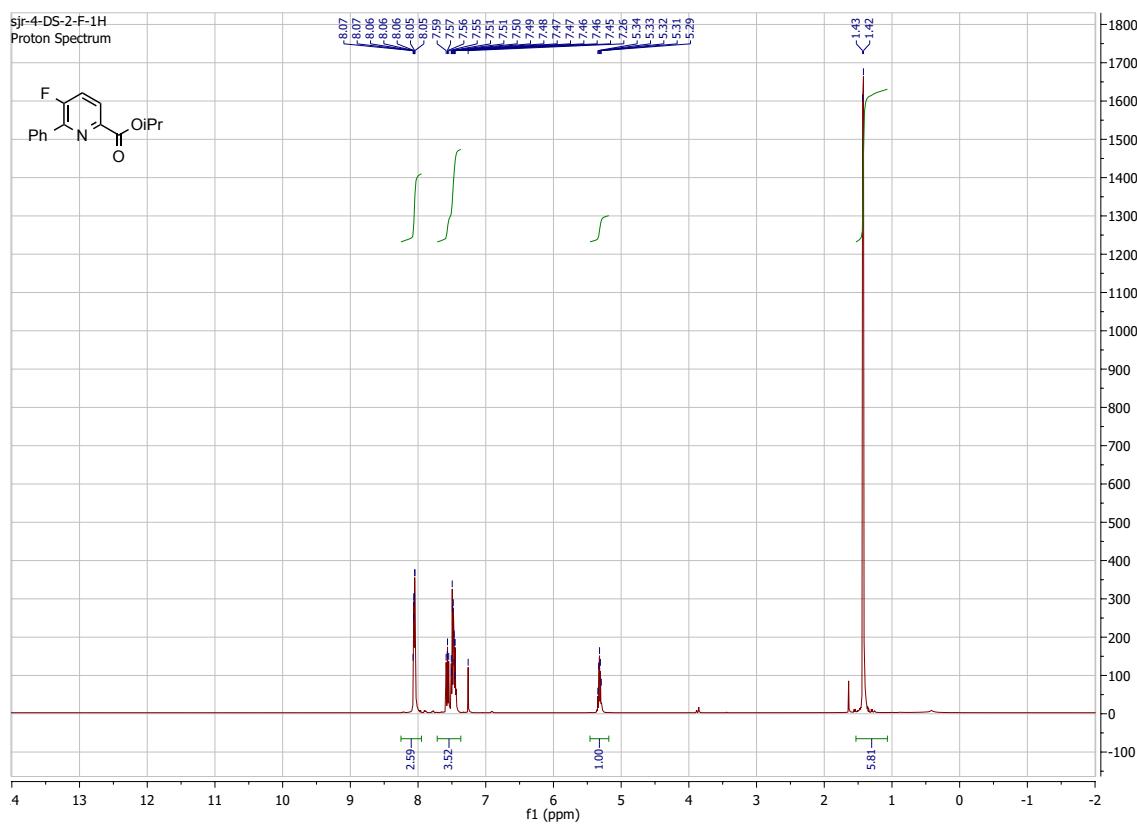


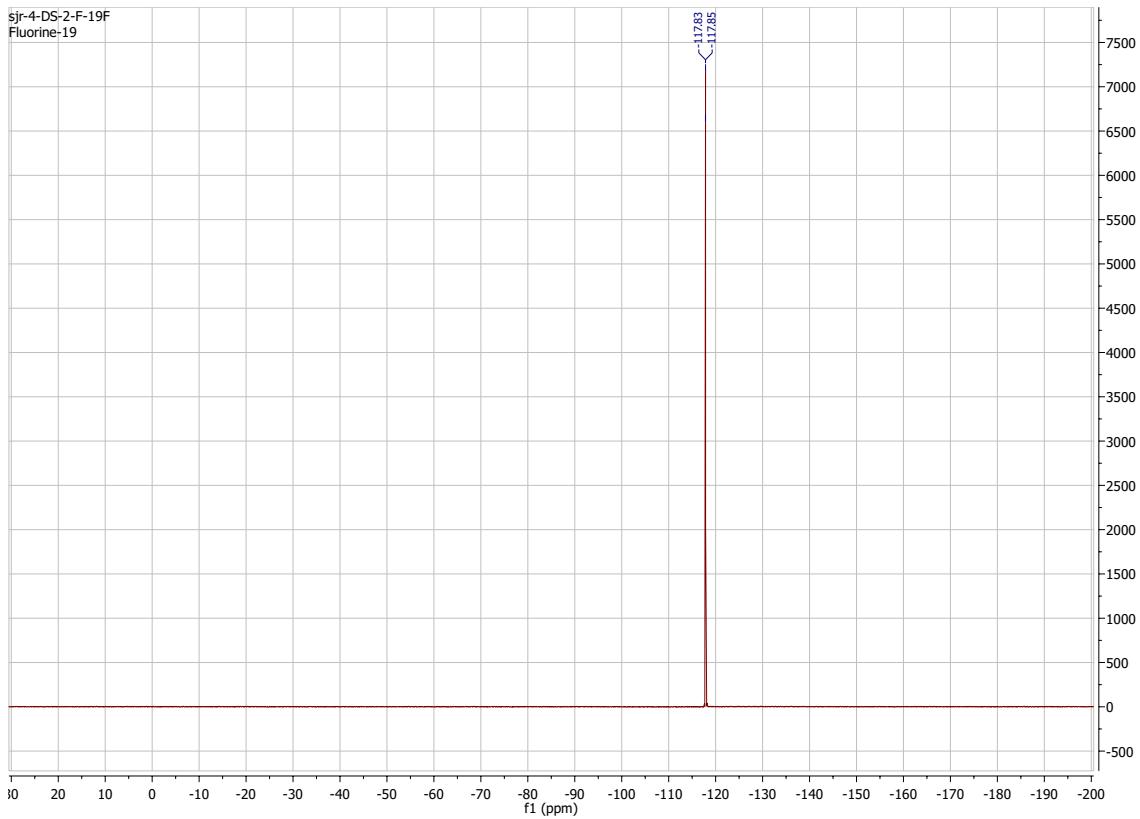
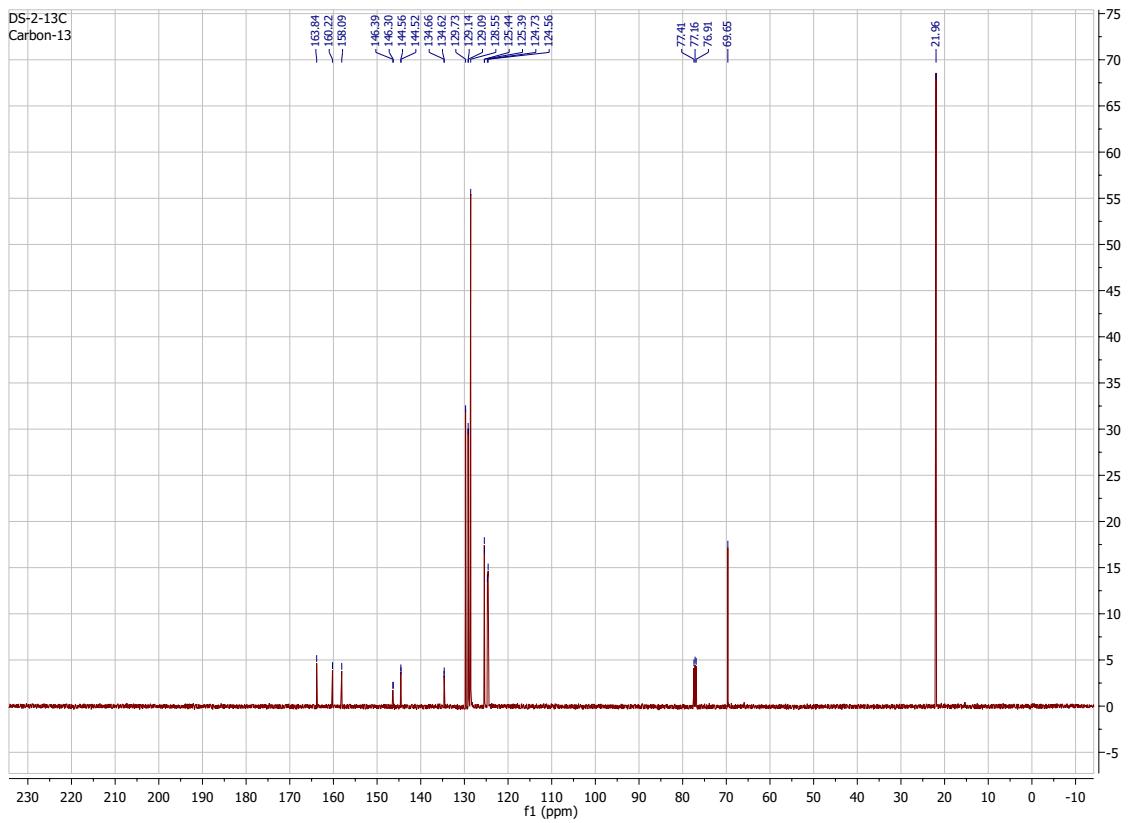
***p*-Methoxybenzoyl fluoride**



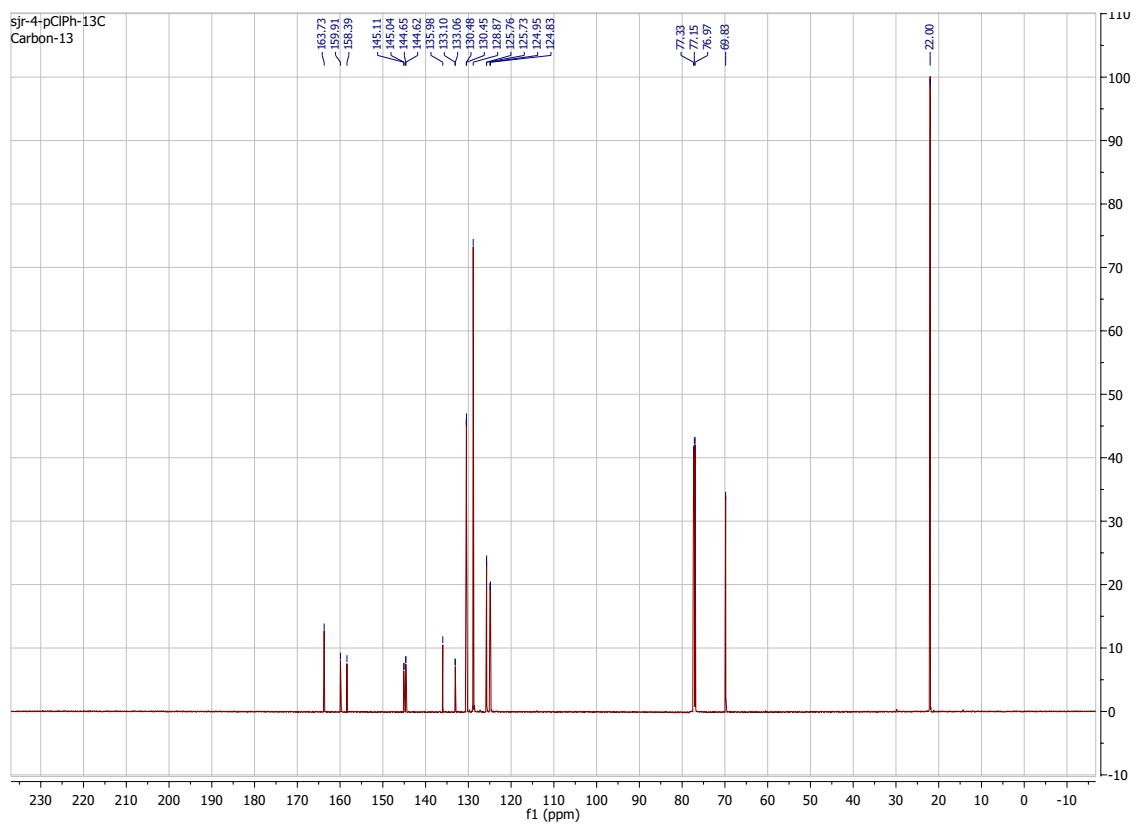
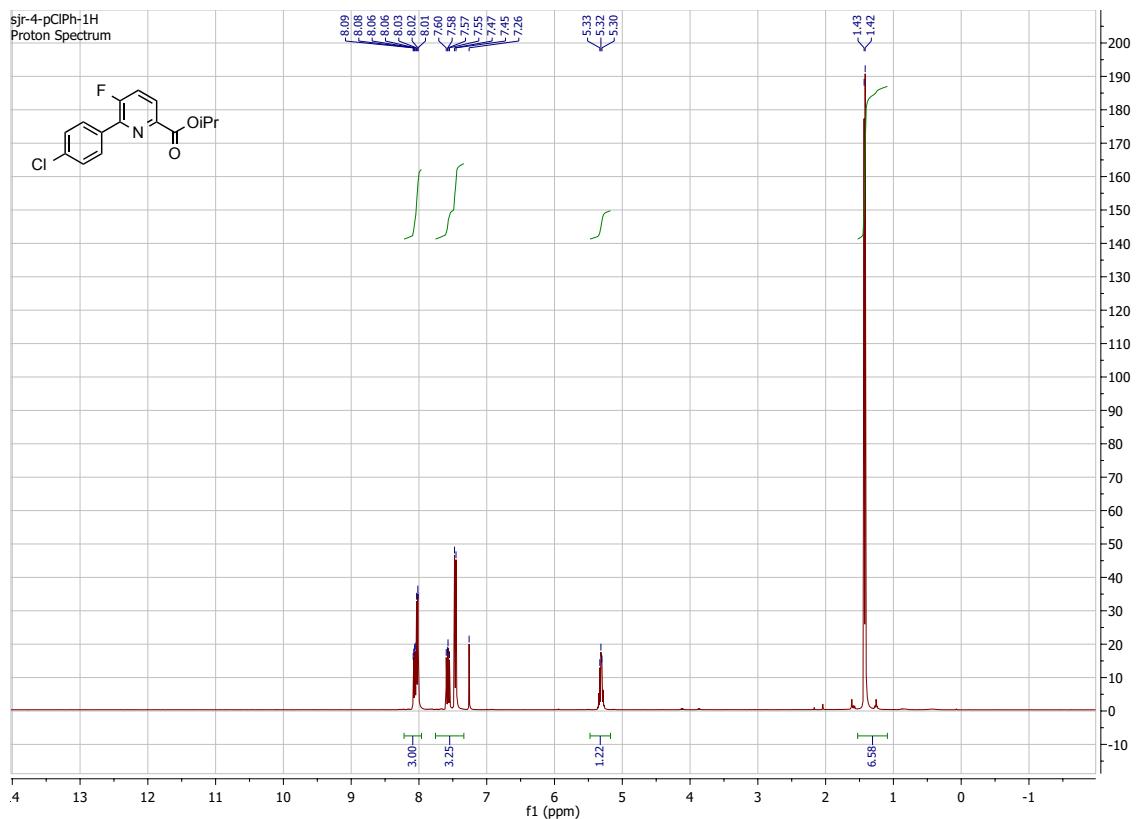


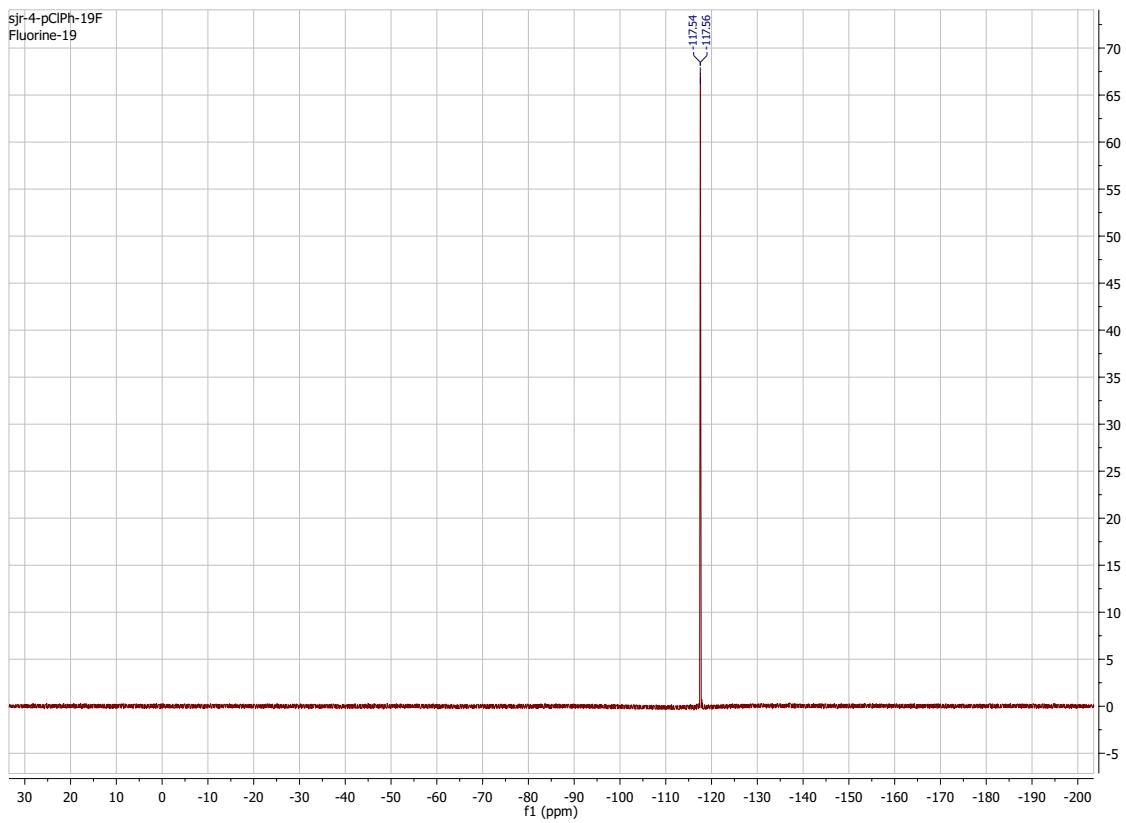
Isopropyl 5-fluoro-6-phenylpicolinate (5)



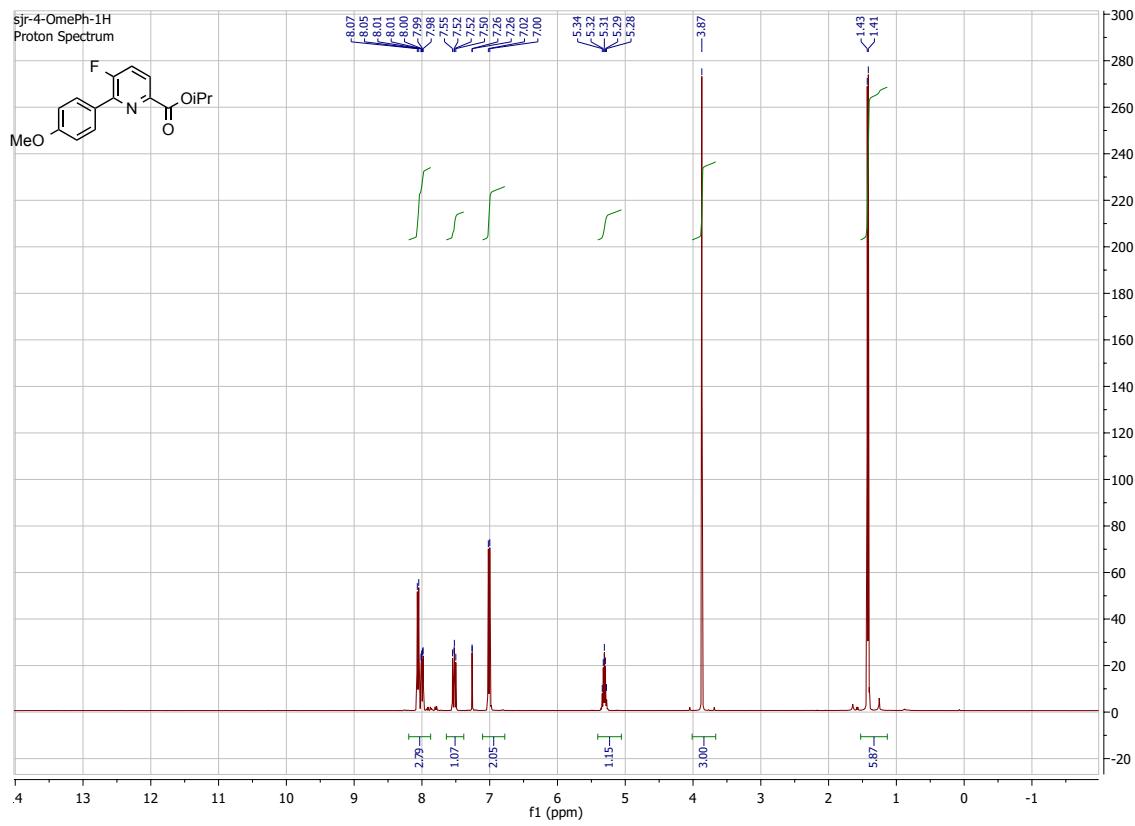


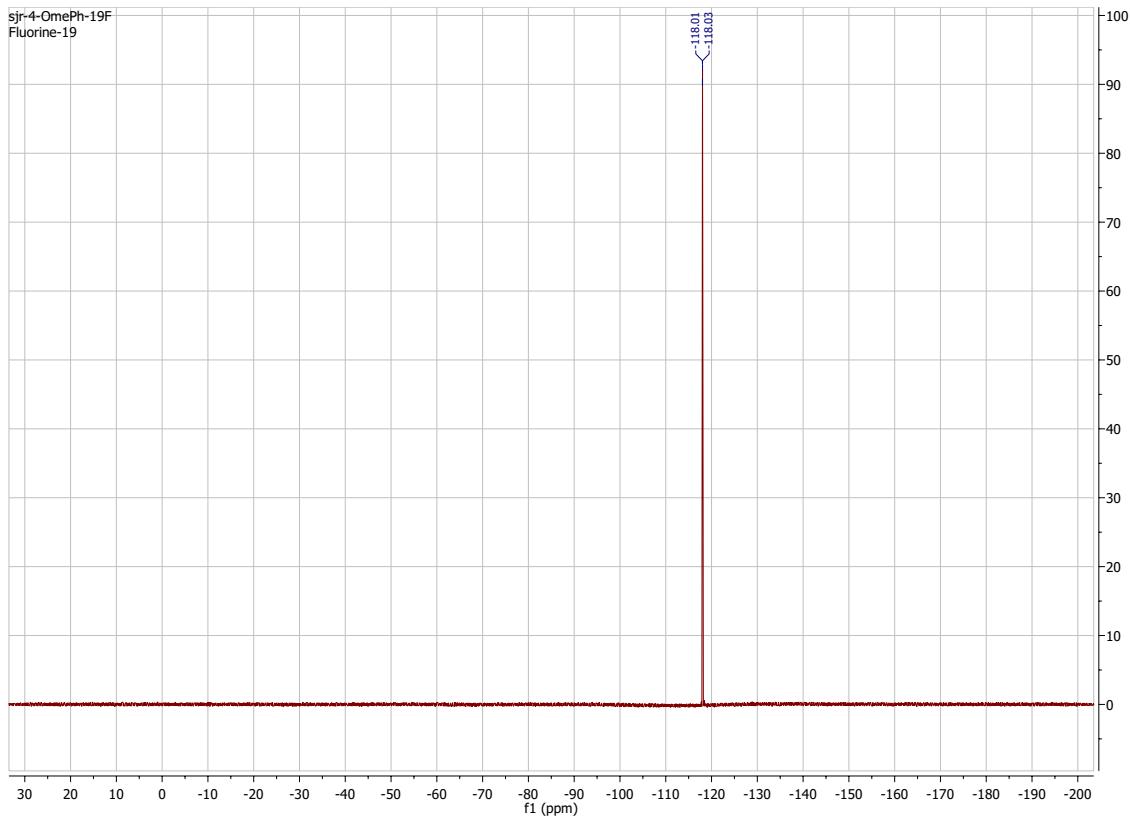
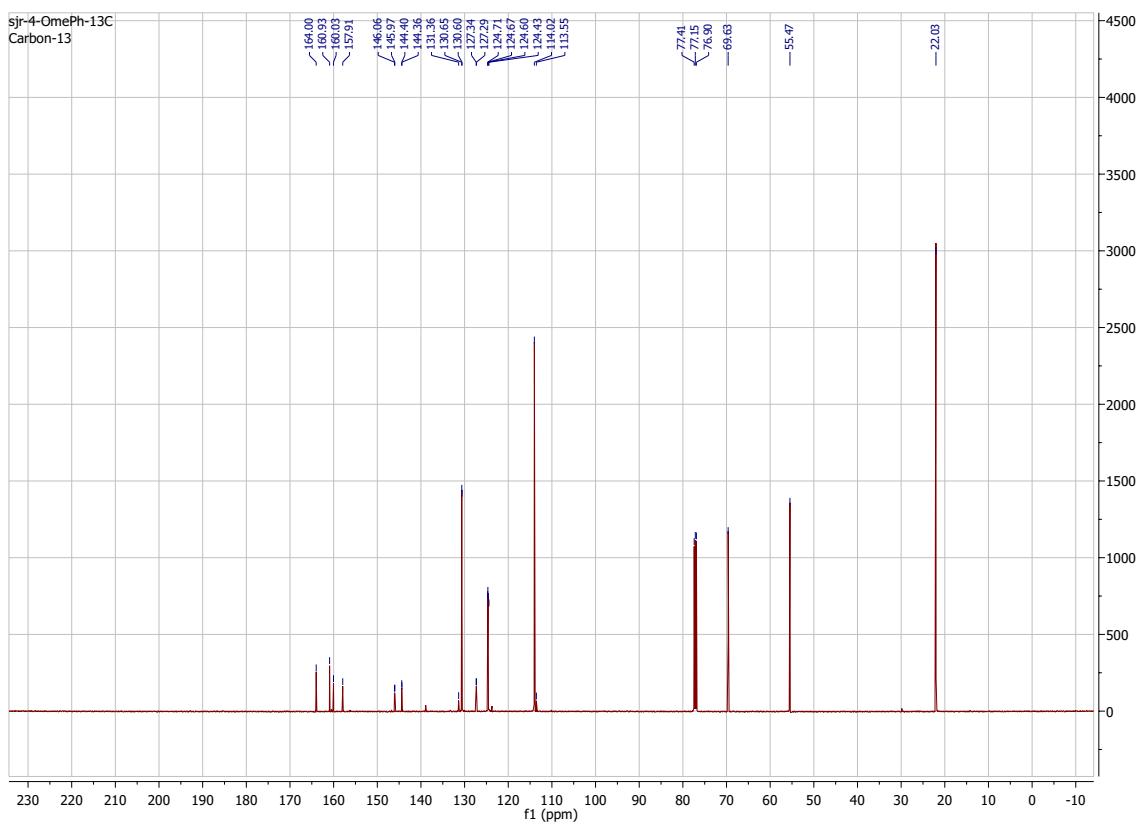
Isopropyl 6-(4-chlorophenyl)-5-fluoropicolinate (6)



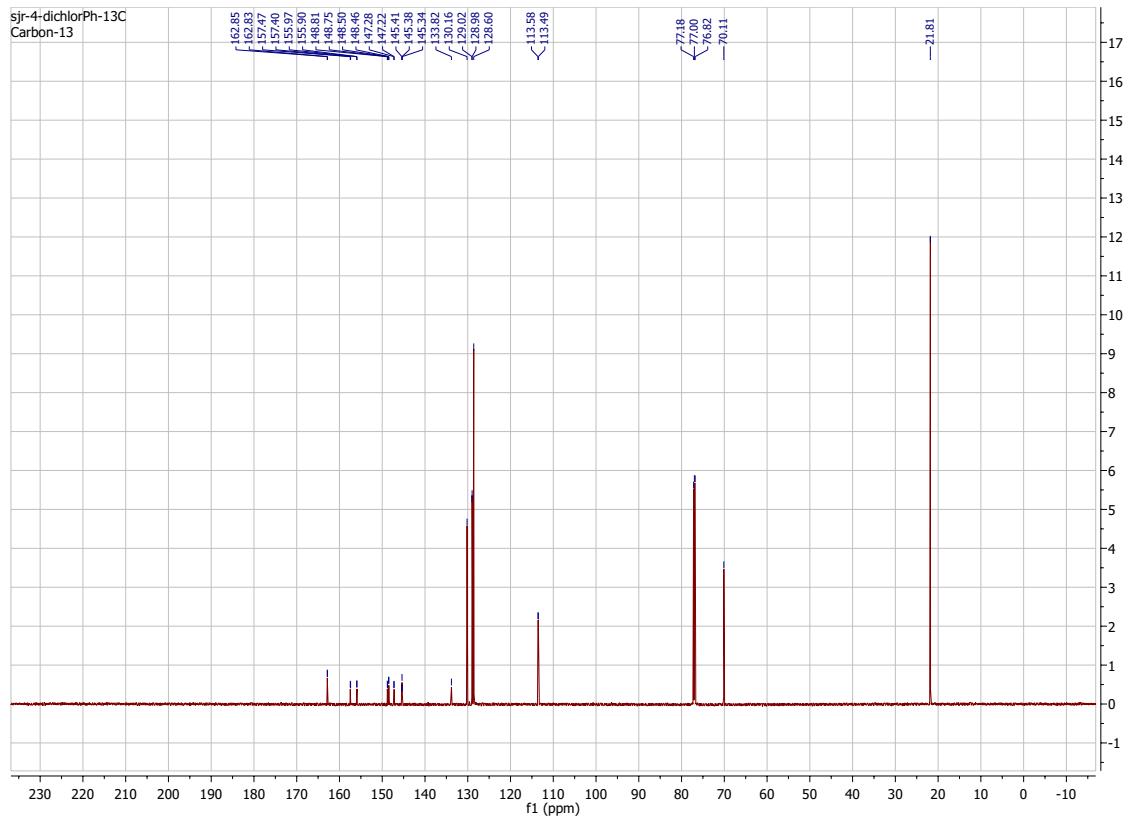
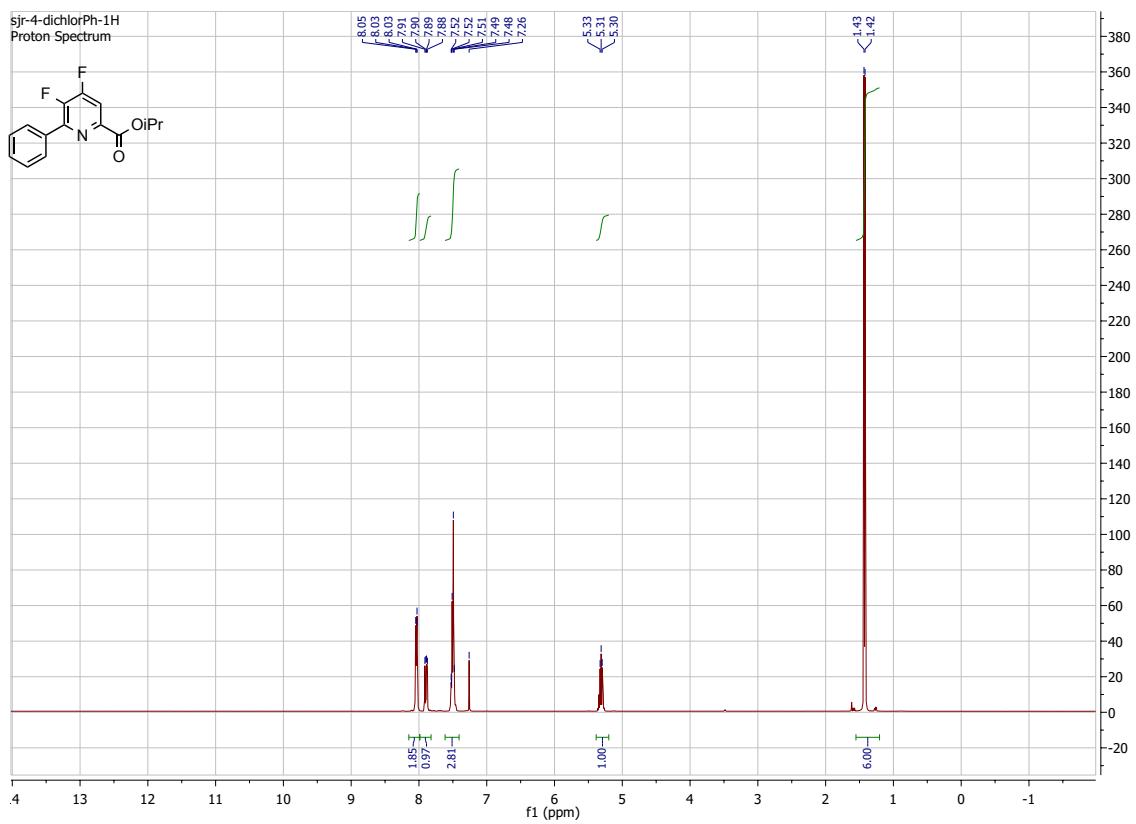


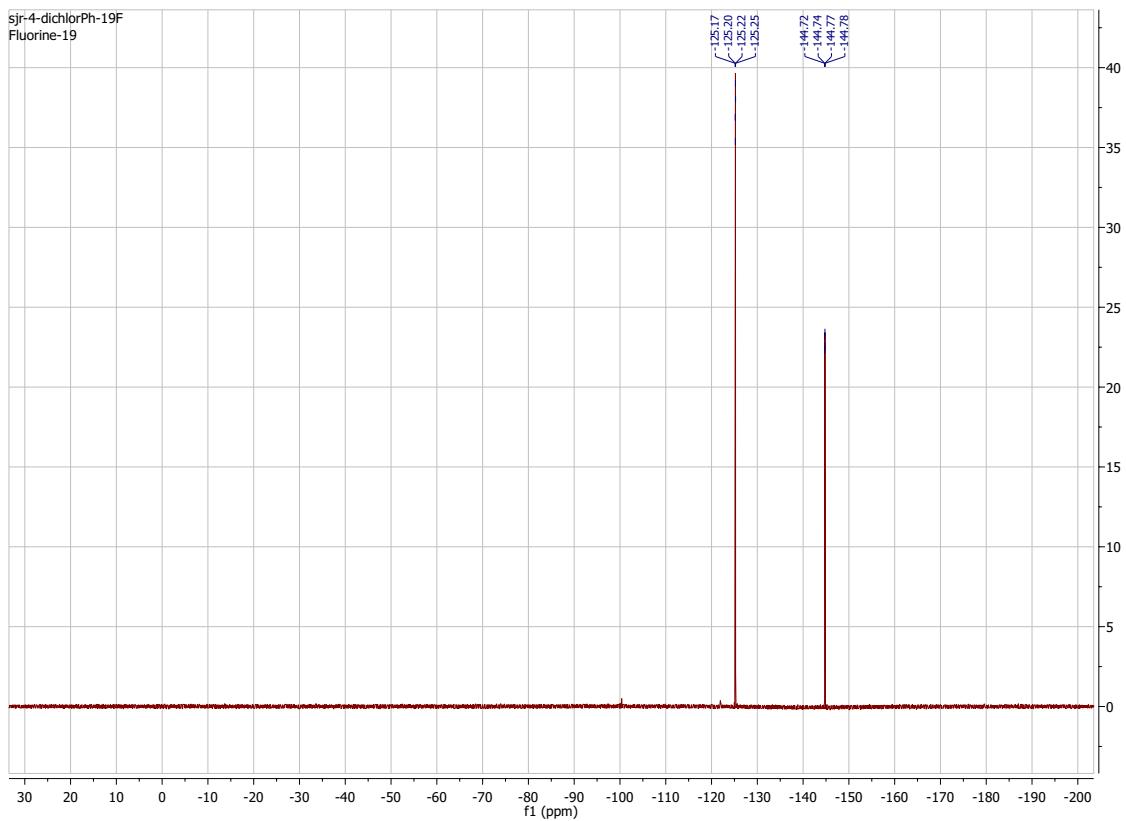
Isopropyl 4,5-difluoro-6-(4-methoxyphenyl)picolinate (7)



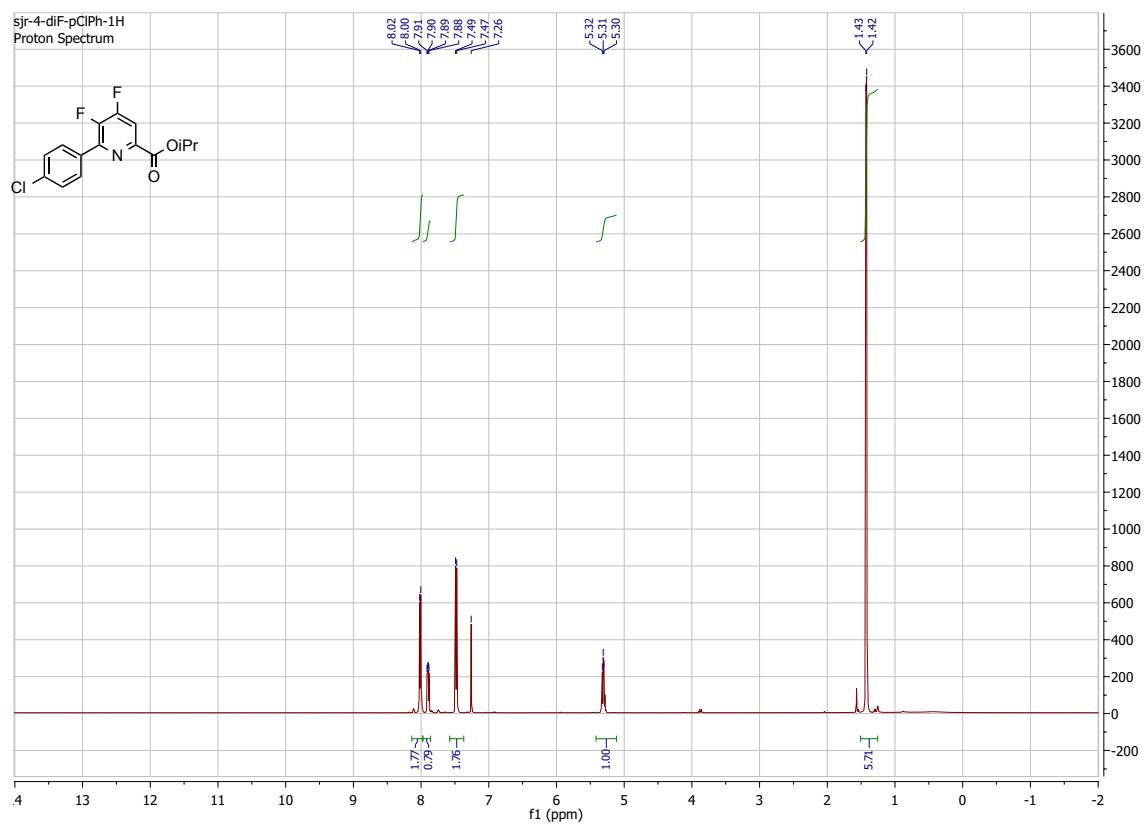


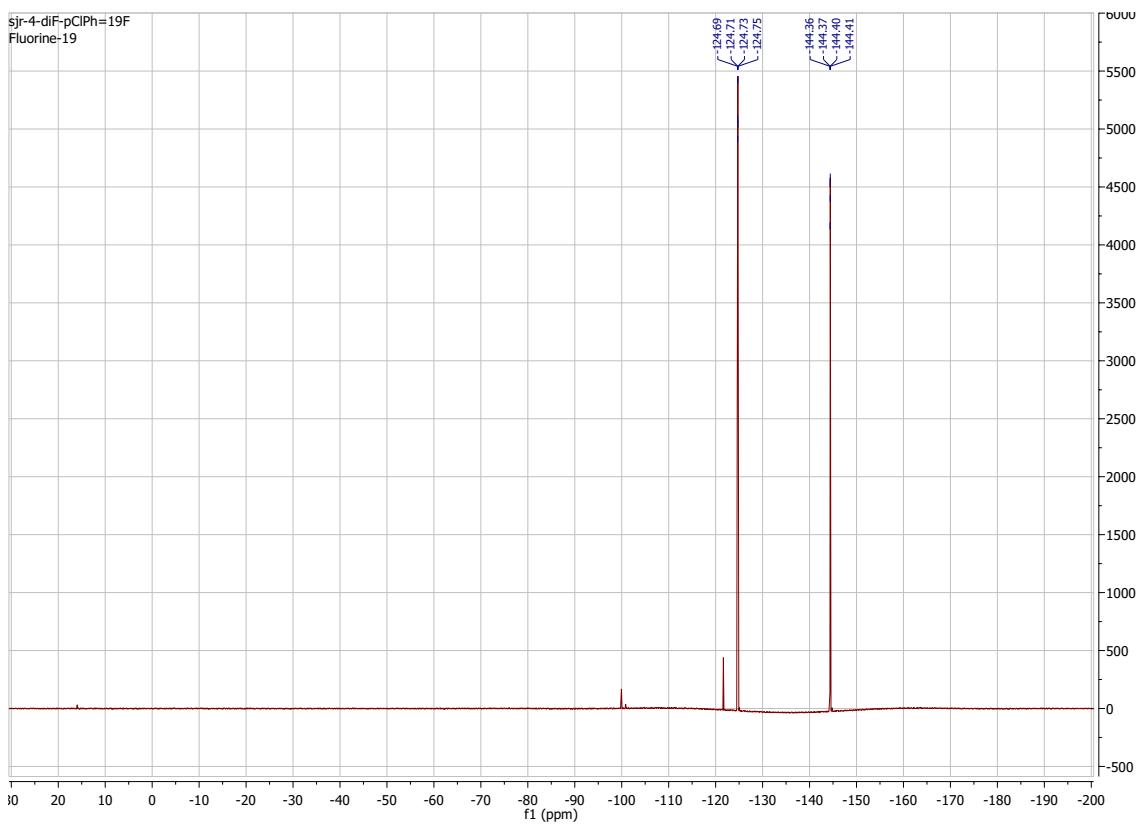
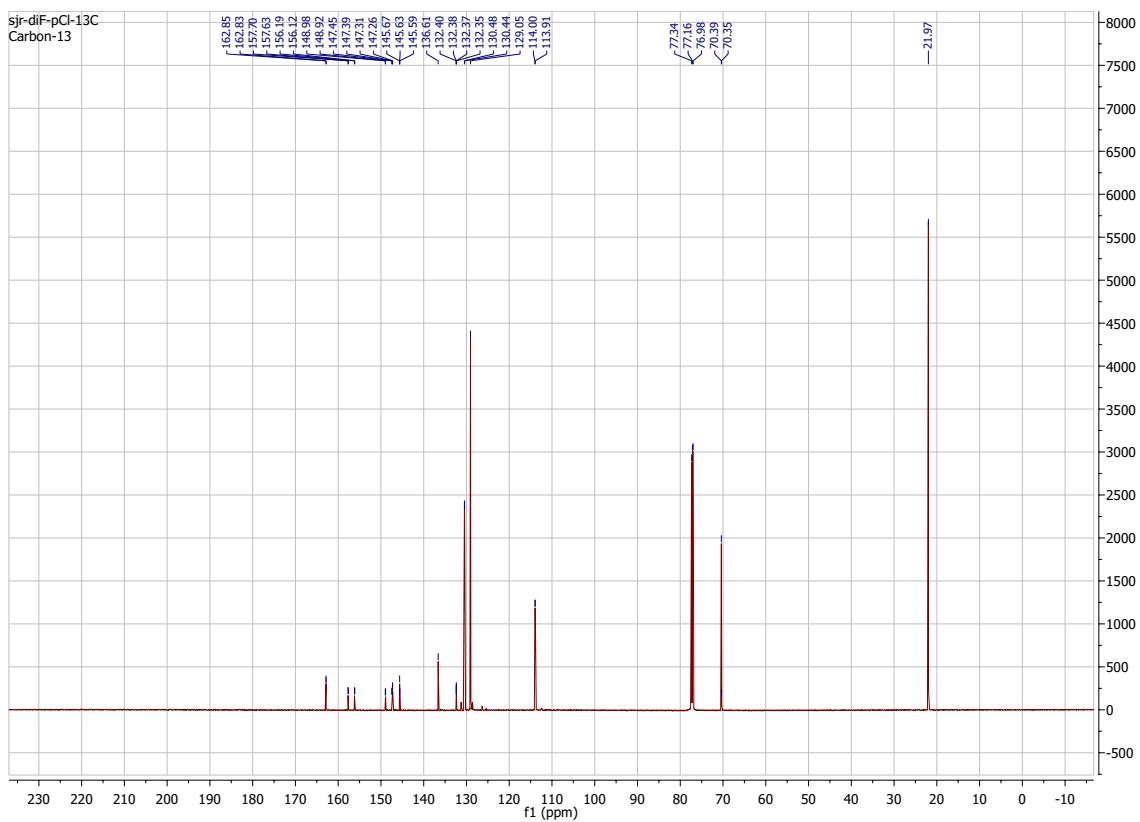
Isopropyl 4,5-difluoro-6-phenylpicolinate (3)



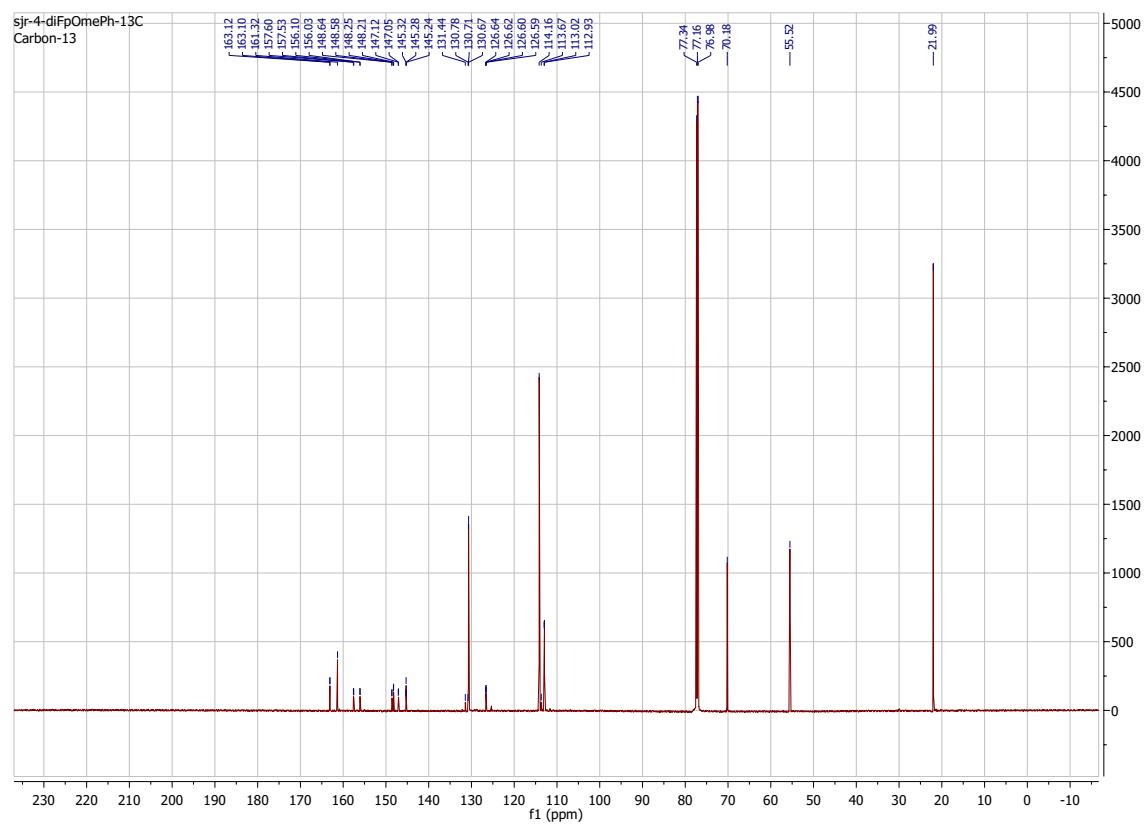
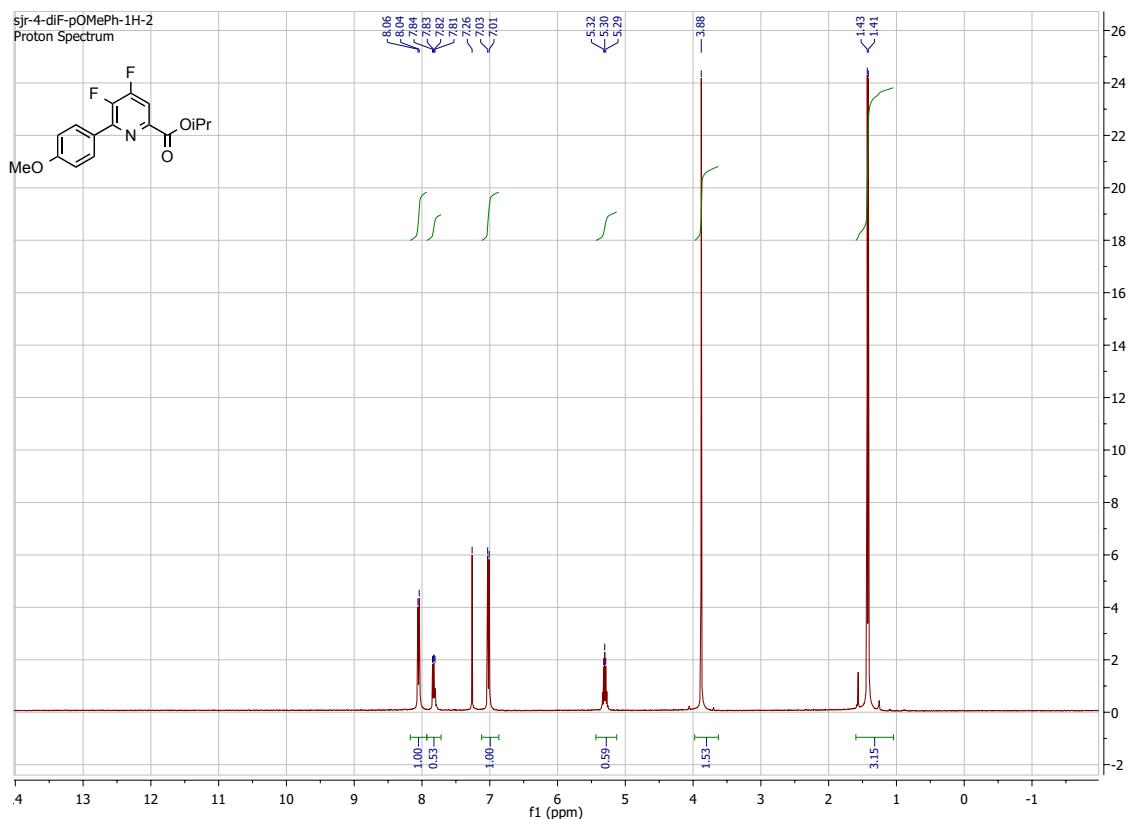


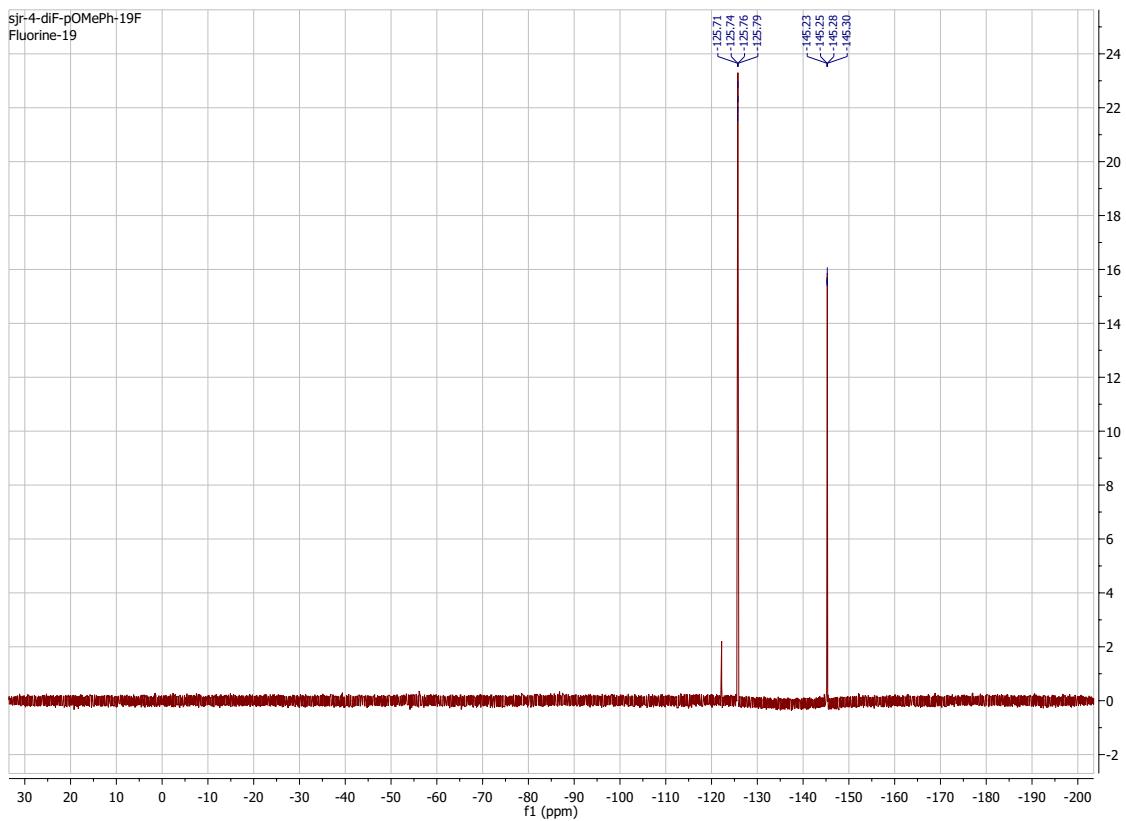
Isopropyl 6-(4-chlorophenyl)-4,5-difluoropicolinate (8)



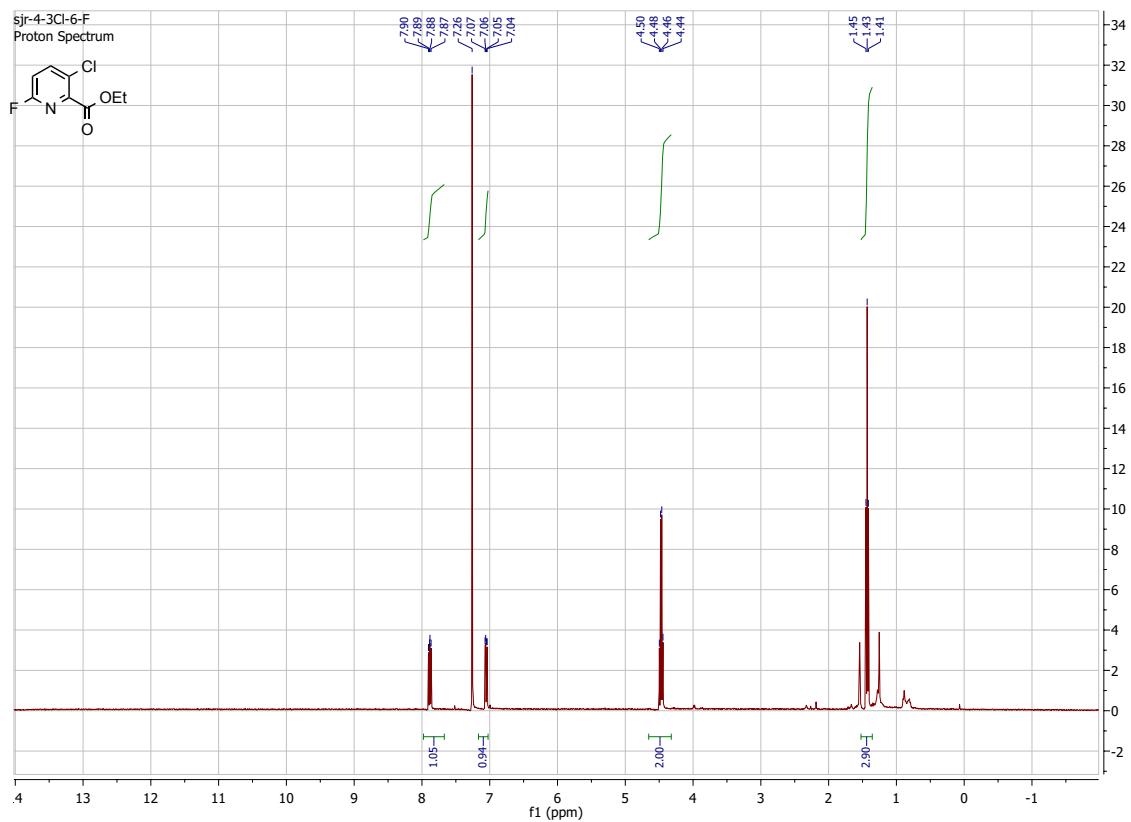


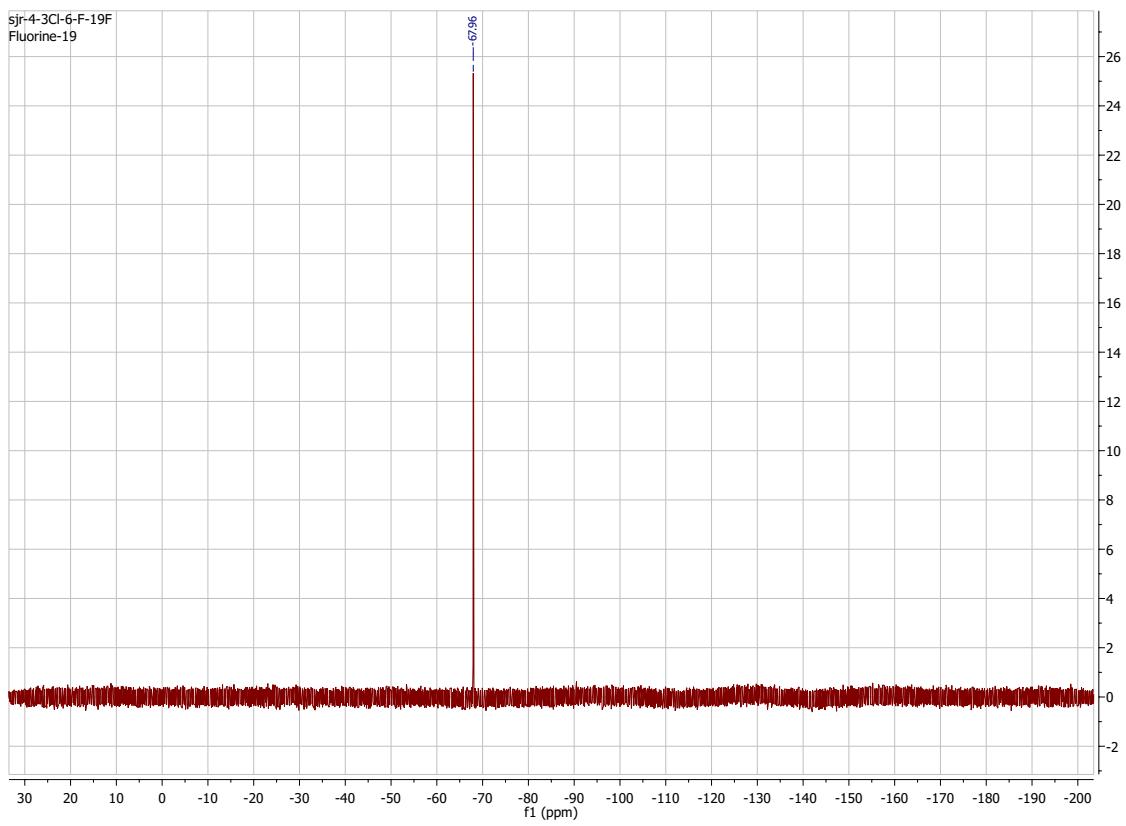
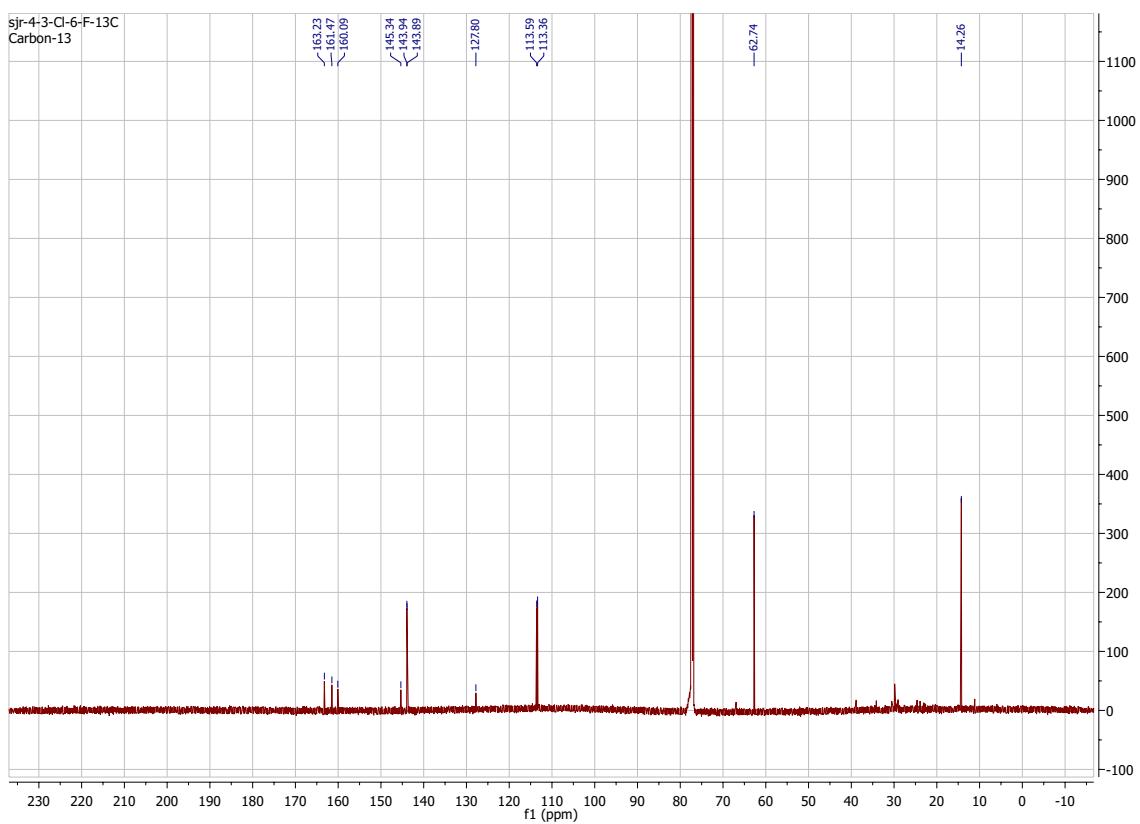
Isopropyl 4,5-difluoro-6-(4-methoxyphenyl)picolinate (9)



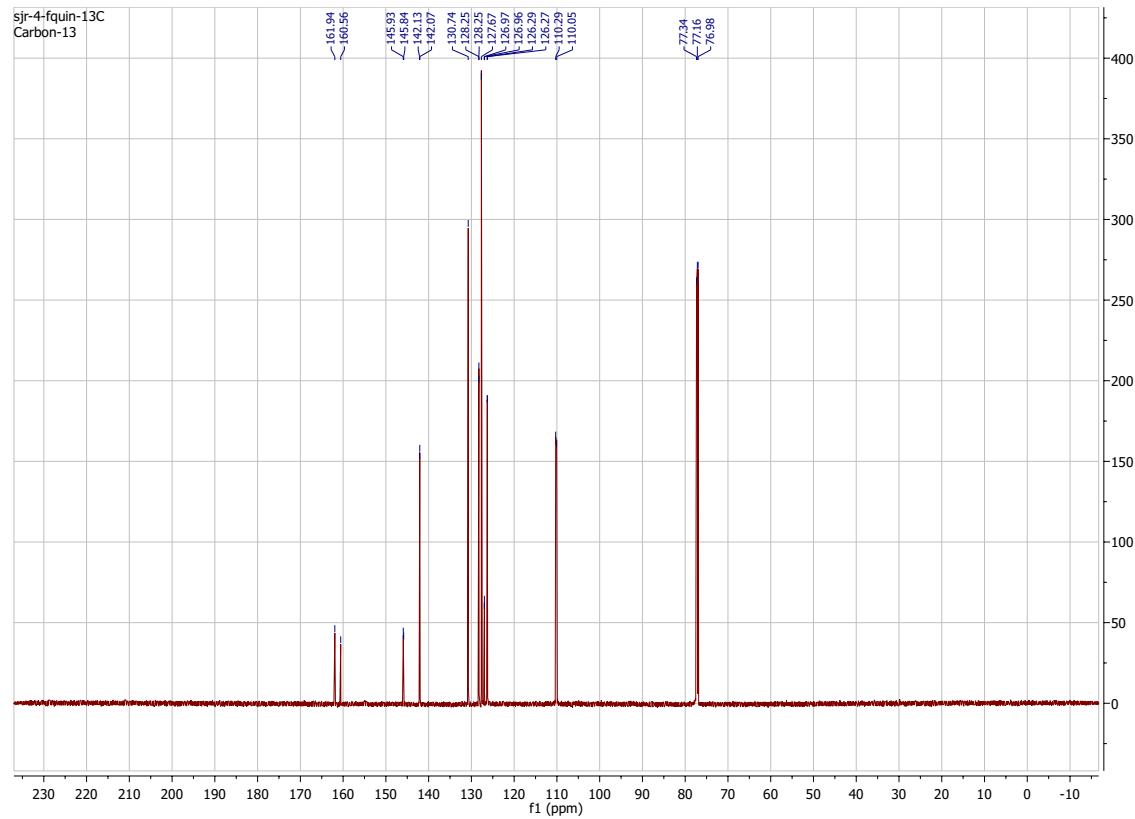
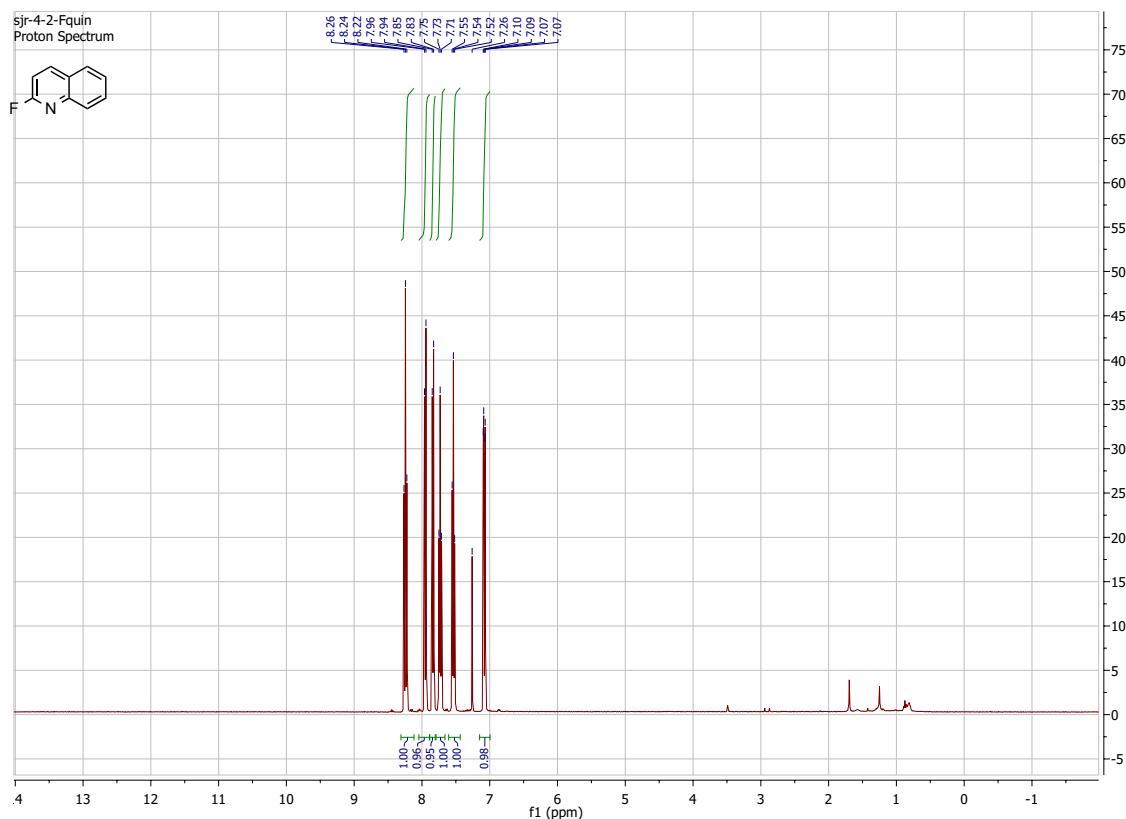


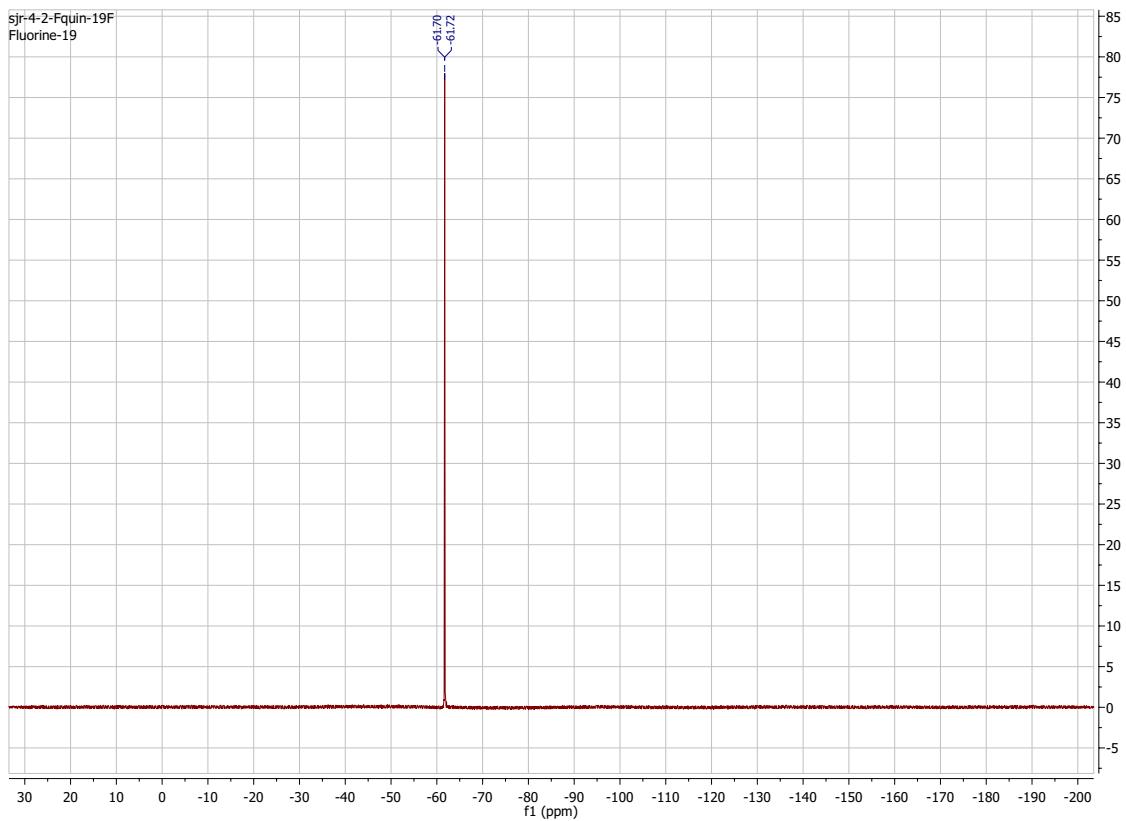
Ethyl 3-chloro-6-fluoropicolinate (10)



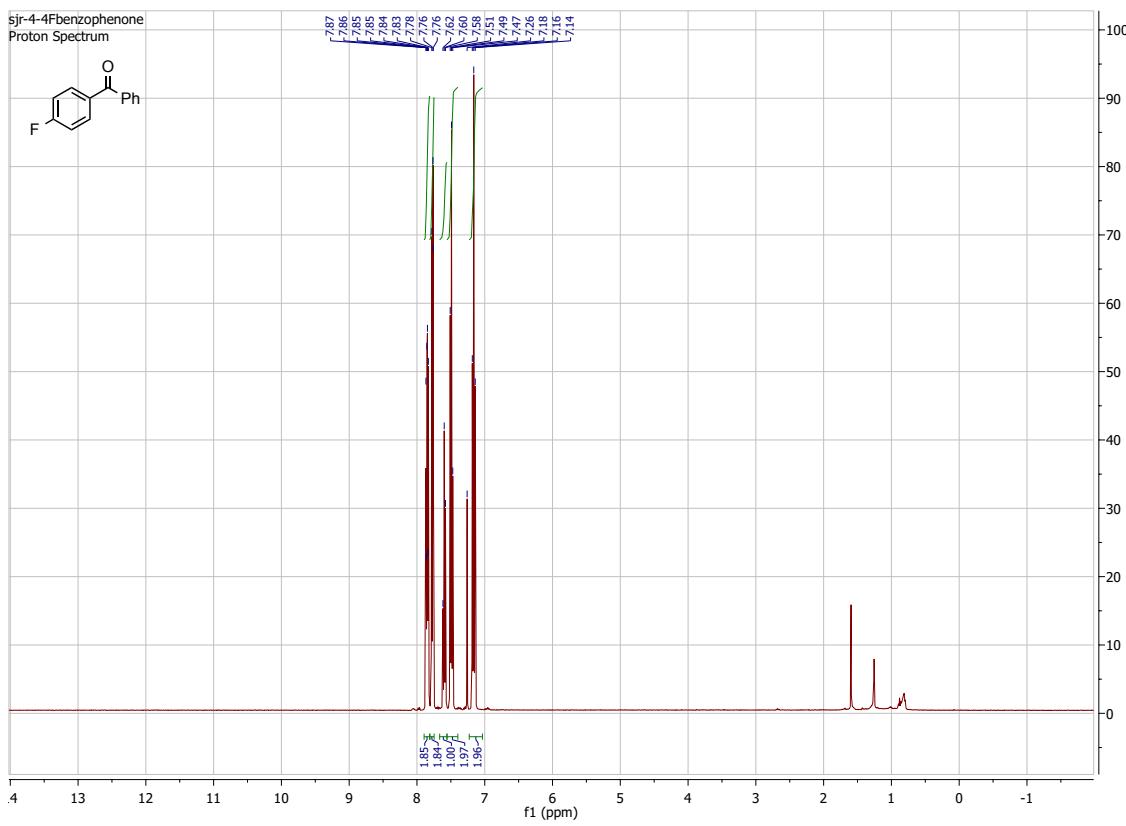


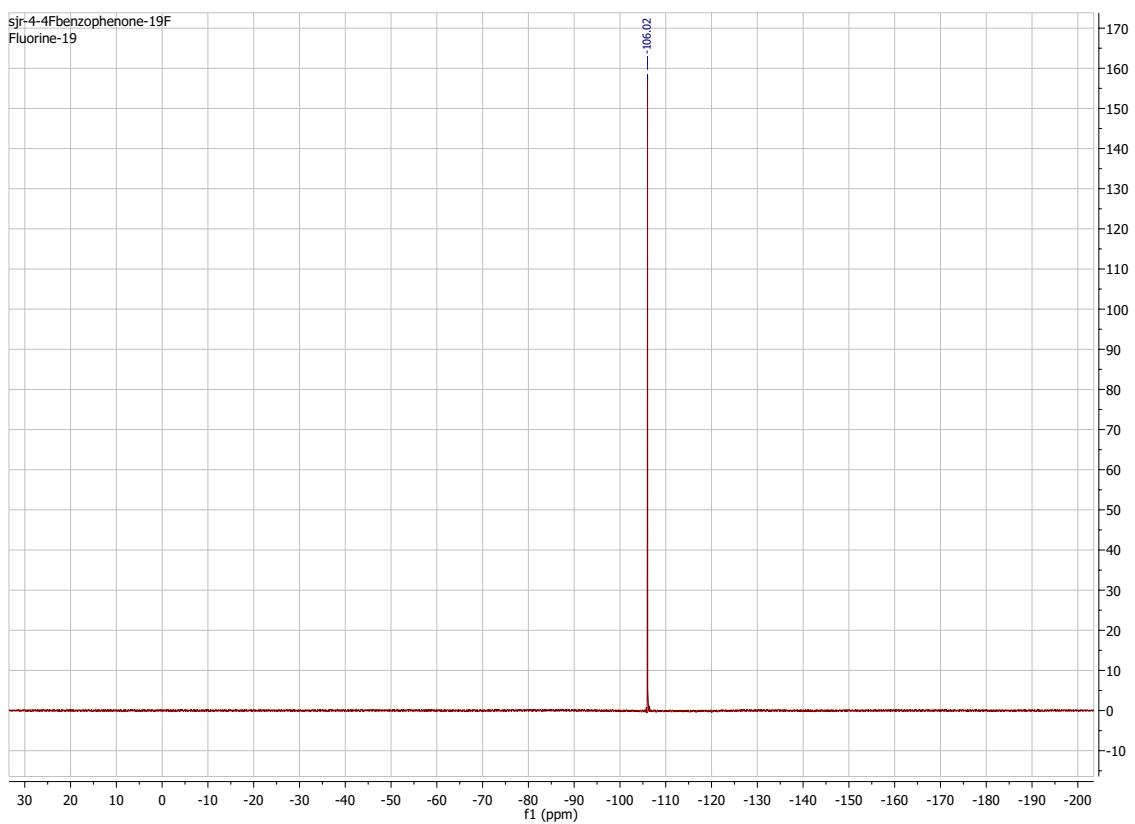
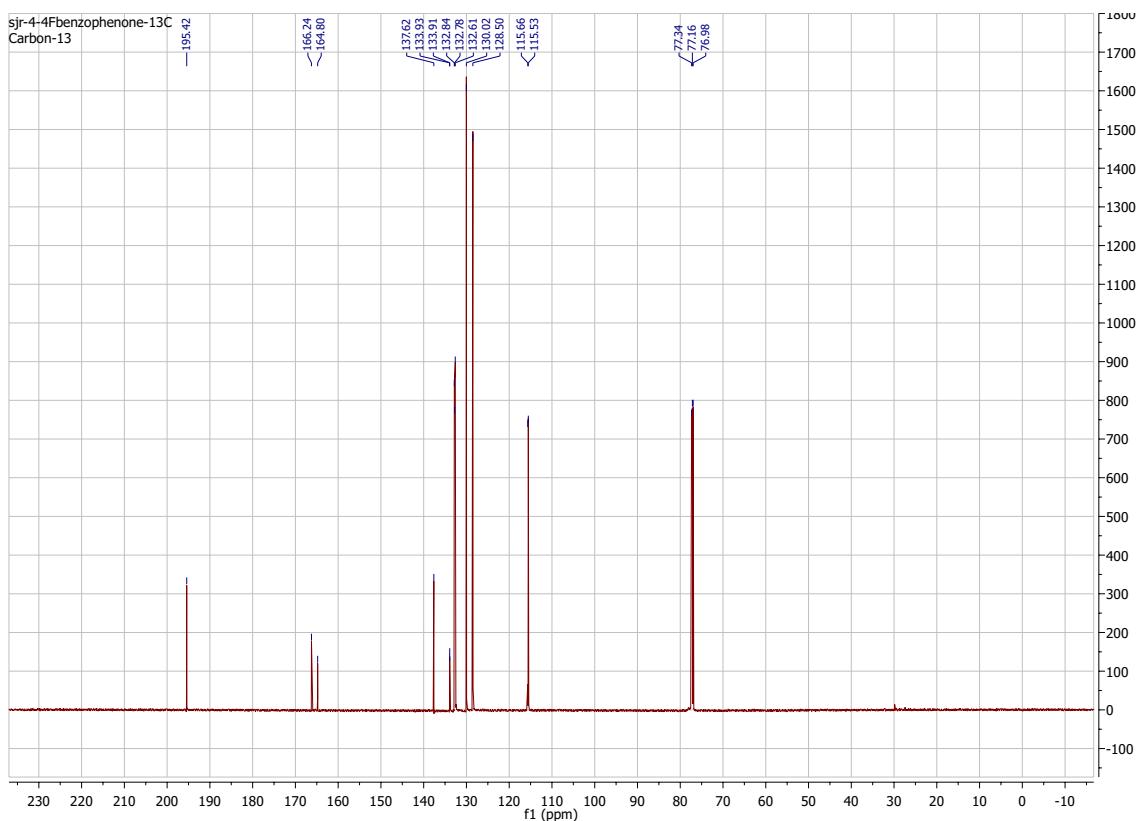
2-Fluoroquinoline (11)



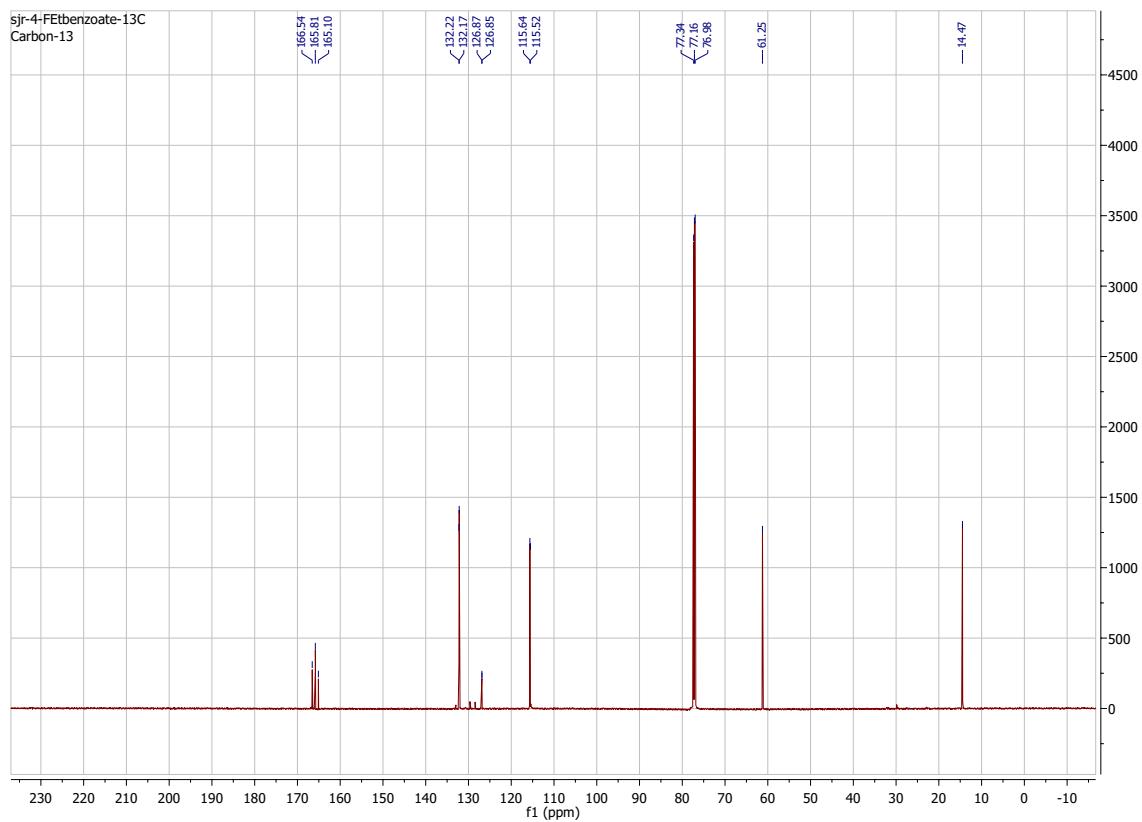
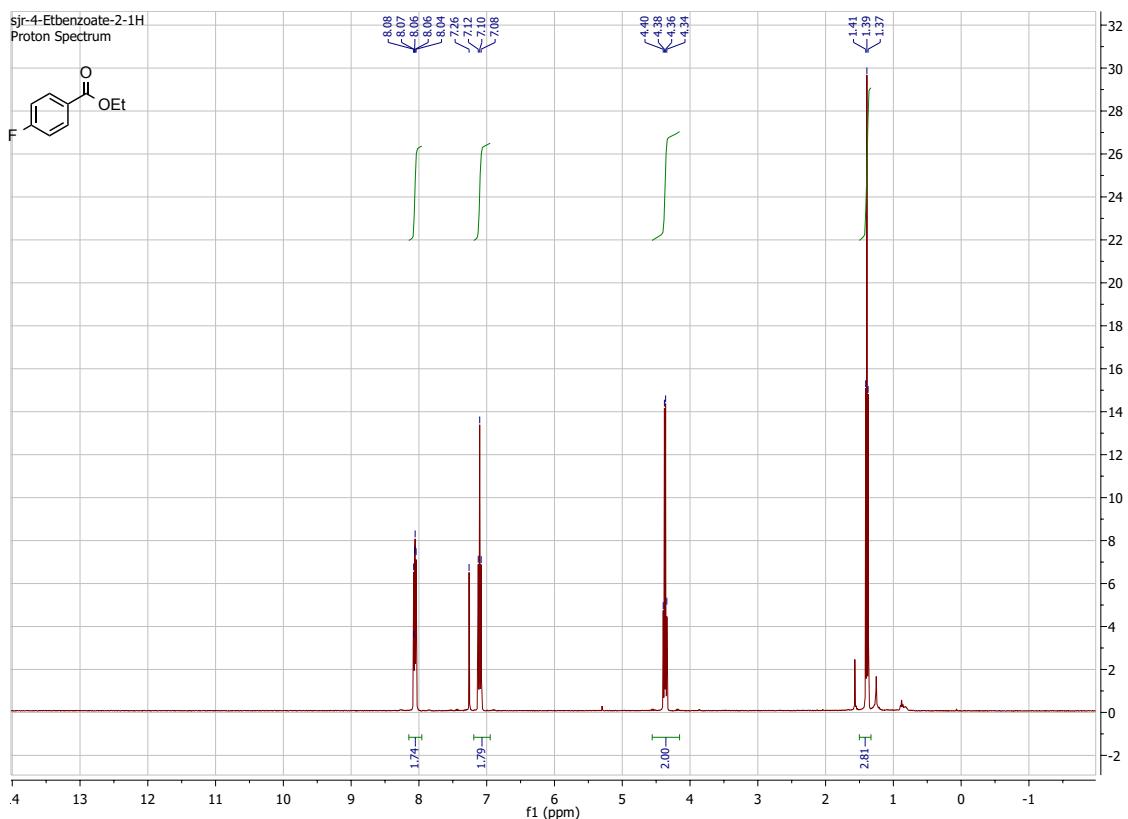


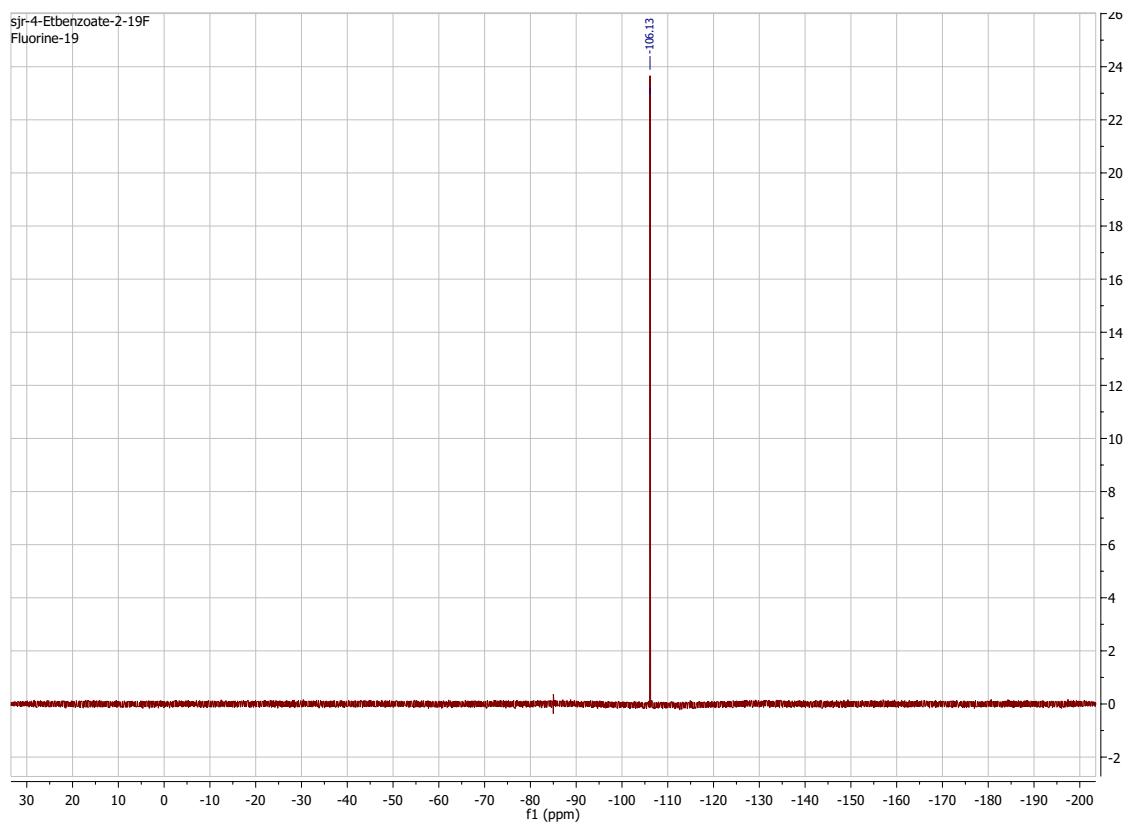
p-Fluorobenzophenone (22)



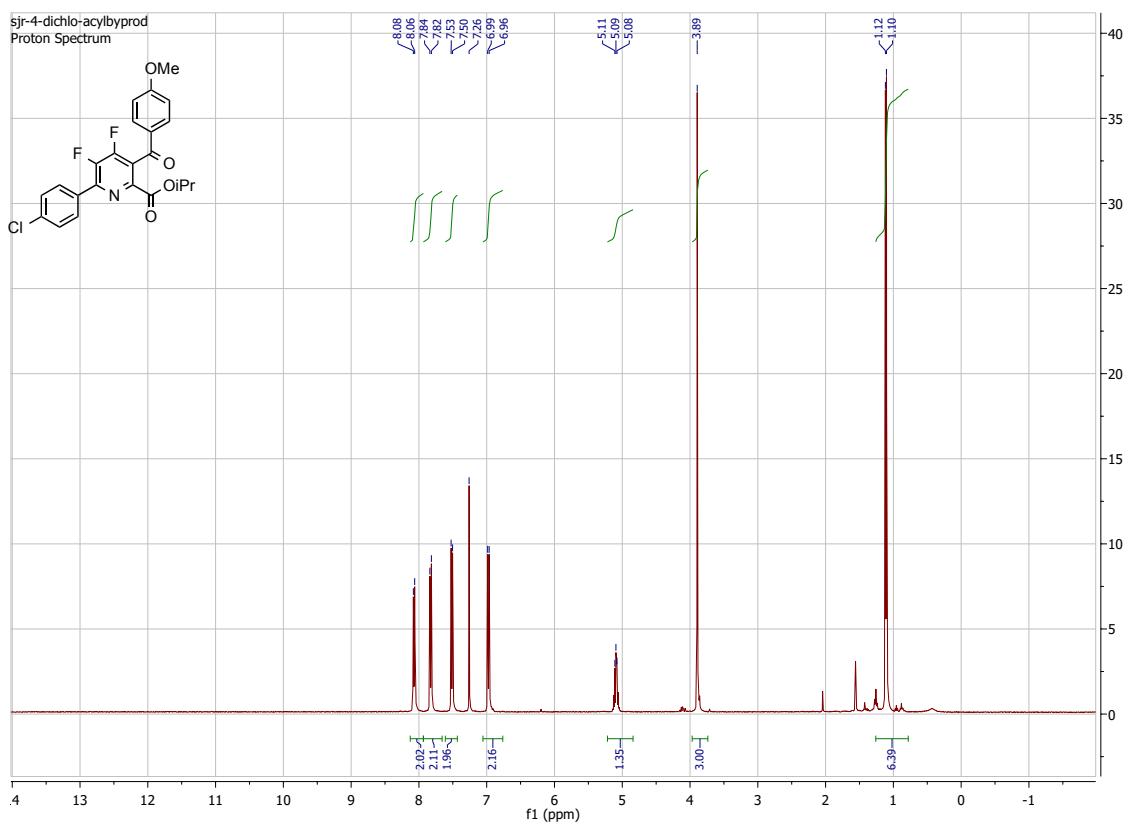


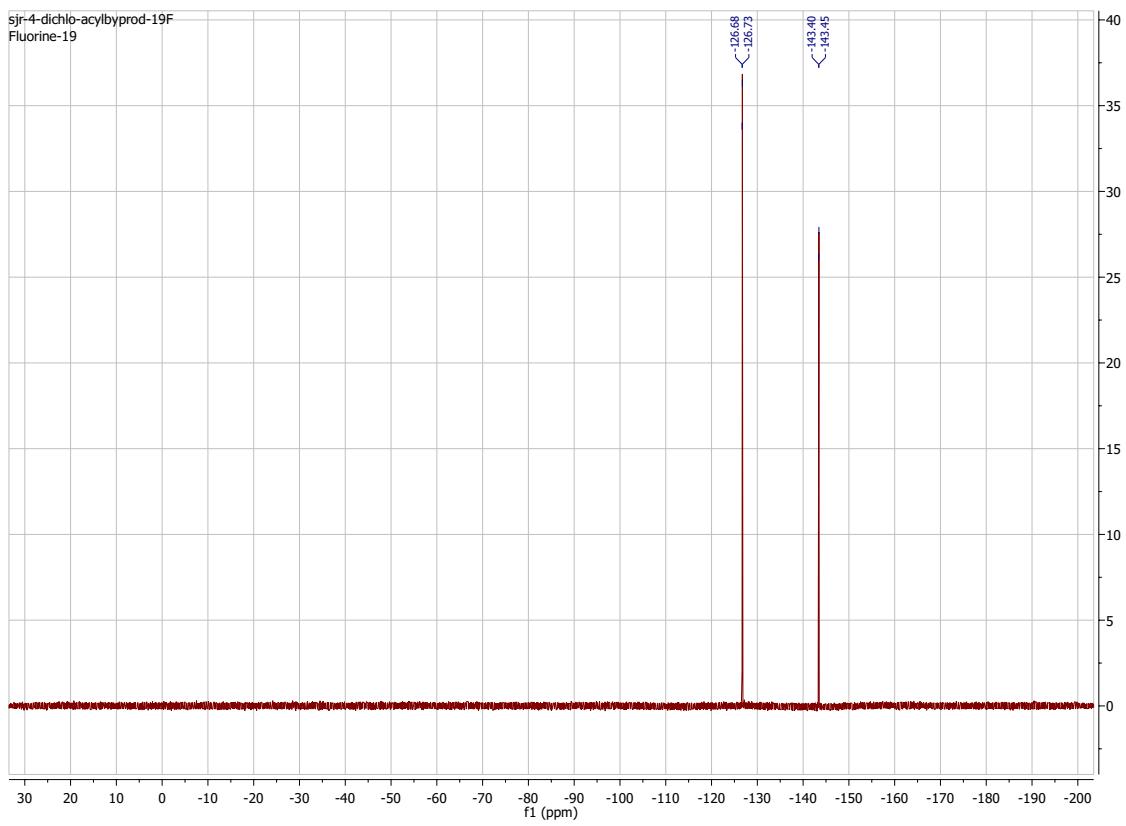
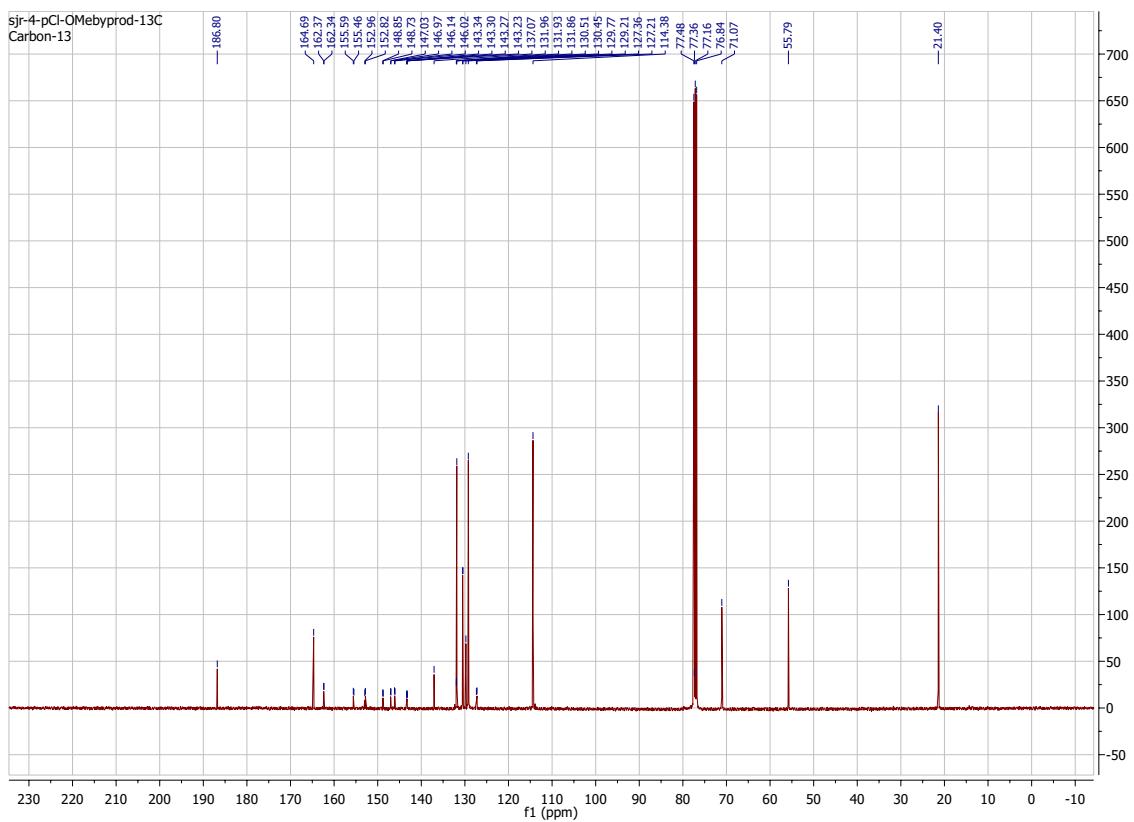
Ethyl 4-Fluorobenzoate (23)





Isopropyl 6-(4-chlorophenyl)-4,5-difluoro-3-(4-methoxybenzoyl)picolinate (21a)





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