

## Supporting Information

### Synthesis and characterization of a series of bis-homoleptic cycloruthenates with terdentate ligands as a family of panchromatic dyes

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**Table S1.** Crystallographic data for **1a**, **1b** and **1d**

	<b>1a</b>	<b>1b·0.2 CH<sub>2</sub>Cl<sub>2</sub></b>	<b>1d·1/2 CH<sub>2</sub>Cl<sub>2</sub></b>
empirical formula	C <sub>44</sub> H <sub>34</sub> F <sub>4</sub> N <sub>4</sub> O <sub>8</sub> Ru	C <sub>46.2</sub> H <sub>32.4</sub> F <sub>10</sub> N <sub>4</sub> O <sub>8</sub> Cl <sub>0.4</sub> Ru	C <sub>42</sub> H <sub>22</sub> F <sub>16</sub> N <sub>4</sub> O <sub>4</sub> Ru
formula weight	923.82	1076.81	1051.70
temperature, K	100.00(10)	100(2)	100(2)
wavelength (Å)	1.54184	0.68890	0.71075
crystal system	triclinic	triclinic	monoclinic
space group	P-1	P-1	P2 <sub>1</sub> /c
unit cell dimensions			
<i>a</i> (Å)	12.8716(4)	12.973(14)	13.0873(9)
<i>b</i> (Å)	13.0639(4)	13.419(15)	13.9901(10)
<i>c</i> (Å)	23.1946(7)	16.677(18)	22.8552(16)
α (deg)	101.138(3)	100.695(3)	90
β (deg)	90.227(2)	109.451(13)	91.0505(15)
γ (deg)	91.197(3)	109.473(11)	90
volume (Å <sup>3</sup> )	3825.8(2)	2433(5)	4183.9(5)
<i>Z</i>	4	2	4
density, calc <i>d</i> (g/cm <sup>3</sup> )	1.604	1.470	1.670
absorption coefficient (mm <sup>-1</sup> )	4.035	0.397	0.494
<i>F</i> (000)	1880	1084.8	2088
crystal size (mm <sup>3</sup> )	0.186 x 0.128 x 0.0733	0.050 x 0.010 x 0.010	0.34 x 0.09 x 0.01
2θ range for data collection (deg)	6.87 to 148.816	3.30-25.03	5.824-51.364
reflections collected	28056	98253	26519
independent reflections	15085	5710	7816
	[R(int) = 0.0324]	[R(int) = 0.0577]	[R(int) = 0.0989]
data/restraints/parameters	15085/39/1127	5710/0/344	7816/30/634
goodness-of-fit on <i>F</i> <sup>2</sup>	1.101	1.128	1.052
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0623 <i>wR</i> <sub>2</sub> = 0.1651	<i>R</i> <sub>1</sub> = 0.0479 <i>wR</i> <sub>2</sub> = 0.0896	<i>R</i> <sub>1</sub> = 0.0778 <i>wR</i> <sub>2</sub> = 0.2031
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0679 <i>wR</i> <sub>2</sub> = 0.1684	<i>R</i> <sub>1</sub> = 0.0635 <i>wR</i> <sub>2</sub> = 0.0958	<i>R</i> <sub>1</sub> = 0.0926 <i>wR</i> <sub>2</sub> = 0.2209
CCDC Number	1552534	1552535	1552536

Suitable crystals were selected and a dataset for **1a** was measured on an Agilent SuperNova diffractometer equipped with an Atlas detector. Datasets for **1b** and **1d** were collected by the EPSRC UK National Crystallography Service<sup>1</sup> using a Rigaku Saturn724+ detector at the Diamond Light Source Beamline I19 for **1b** and on a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator with HF Varimax optics for **1d**. All instruments were equipped with an Oxford Cryosystems Cryostream device. An absorption correction was applied using CrysAlisPro<sup>2</sup> using a numerical absorption correction based on gaussian integration over a multifaceted crystal model for **1a**. An empirical absorption correction was applied using CrystalClear-SM Expert<sup>3</sup> for **1b** and **1d**. All structures were solved by direct methods in SHELXS<sup>4</sup> and were refined by a full-matrix least-squares procedure on *F*<sup>2</sup> in SHELXL.<sup>4</sup> Apart from the disordered dichloromethane solvent molecule present at 20 % occupancy in **1b**, all non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were added at calculated positions and

refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter ( $U_{eq}$ ) of the parent atom. Figures were produced using OLEX2.<sup>5</sup>

CCDC-1552534 – CCDC-1552536 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

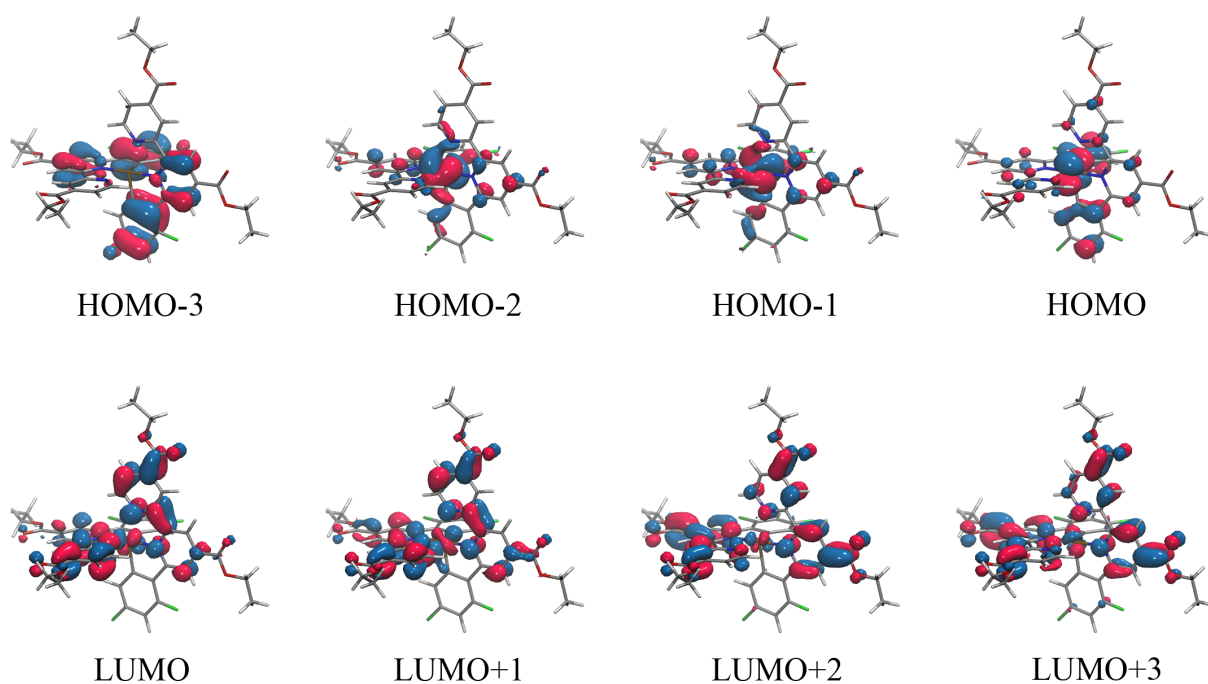
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**Theoretical calculations.** Full geometry optimizations of the different ruthenium compounds were performed in their singlet ground state with density functional theory<sup>1</sup> (DFT) using the PBE0<sup>2</sup> functional with the relativistic effective core potential and basis set LANL2DZ<sup>3</sup> for the ruthenium and the 6-311G\* basis set for the remaining atoms. No symmetry constraints were applied during the geometry optimizations. The nature of the stationary points located with DFT was further checked by computations of harmonic vibrational frequencies at the same level of theory. Absorption spectra were computed at the ground-state optimized geometry using linear-response time-dependent density functional theory<sup>4</sup> (LR-TDDFT) within the adiabatic approximation<sup>5</sup> for the first 40 singlet electronic states, with PBE0 and the aforementioned basis set and effective core potential. Condensed-phase effects were taken into account for all calculations using a self-consistent reaction-field (SCRF) model in which the solvent is implicitly represented by a dielectric continuum characterized by its relative static dielectric permittivity  $\epsilon$ . Within the different approaches that can be followed to calculate the electrostatic potential created by the polarized continuum in the cavity, we have employed the integral equation formalism of the polarizable continuum model (IEFPCM).<sup>6</sup> A relative permittivity of 8.93 was employed to simulate dichloromethane,<sup>7</sup> the solvent used in the experimental work. To facilitate the analysis of LR-

TDDFT transitions, we used Natural Transition Orbitals (NTOs)<sup>8</sup>, which are obtained through diagonalization of the transition density matrix and constitute the optimal set of orbitals to represent a given electronic transition. The open-source code NANCY\_EX-2.0 was used to compute the NTOs<sup>9</sup>. All calculations were carried out with the Gaussian 09 package<sup>7</sup> and molecular representations were produced with VMD<sup>10</sup> version 1.9.2.

**Table S2.** Selected vertical transitions for **1a** computed at the LR-TDDFT/PBE0 level of theory.

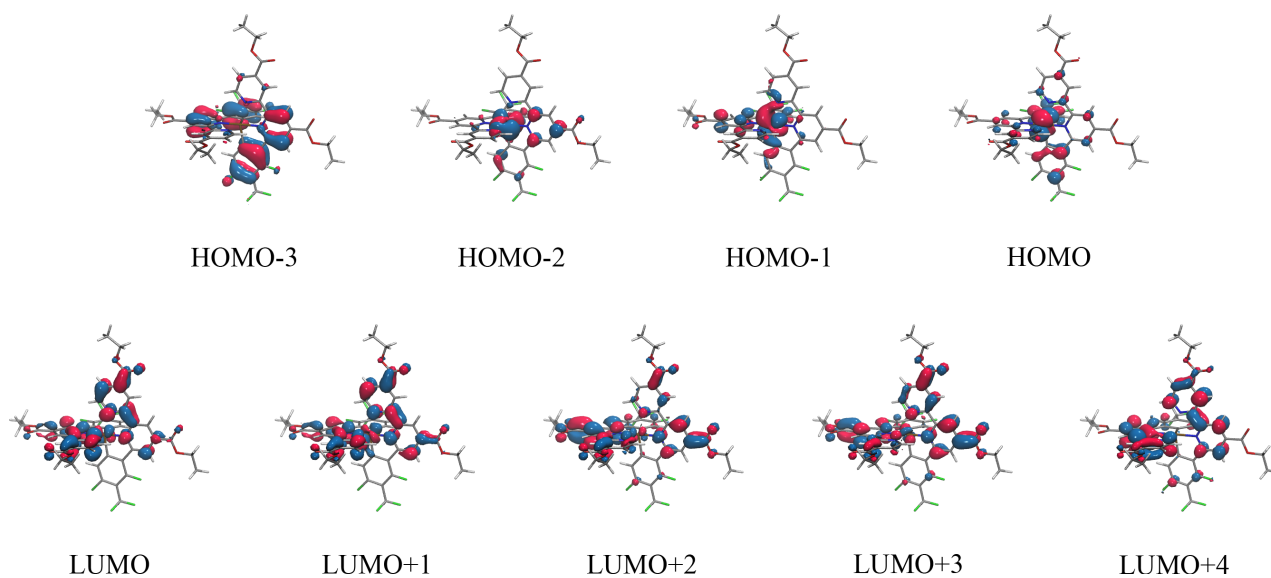
Transition	Energy (eV)	Oscillator strength	Dominant contributions
$S_0 \rightarrow S_1$	1.92	0.0216	H $\rightarrow$ L (85.3%)
$S_0 \rightarrow S_2$	1.97	0.0109	H $\rightarrow$ L+1 (84.8%)
$S_0 \rightarrow S_5$	2.30	0.2255	H-2 $\rightarrow$ L+1 (53.5%) H-1 $\rightarrow$ L (38.4%)
$S_0 \rightarrow S_7$	2.72	0.1364	H $\rightarrow$ L+2 (73.7%)
$S_0 \rightarrow S_{13}$	2.98	0.3690	H-2 $\rightarrow$ L+3 (36.3%) H-1 $\rightarrow$ L+2 (45.3%)



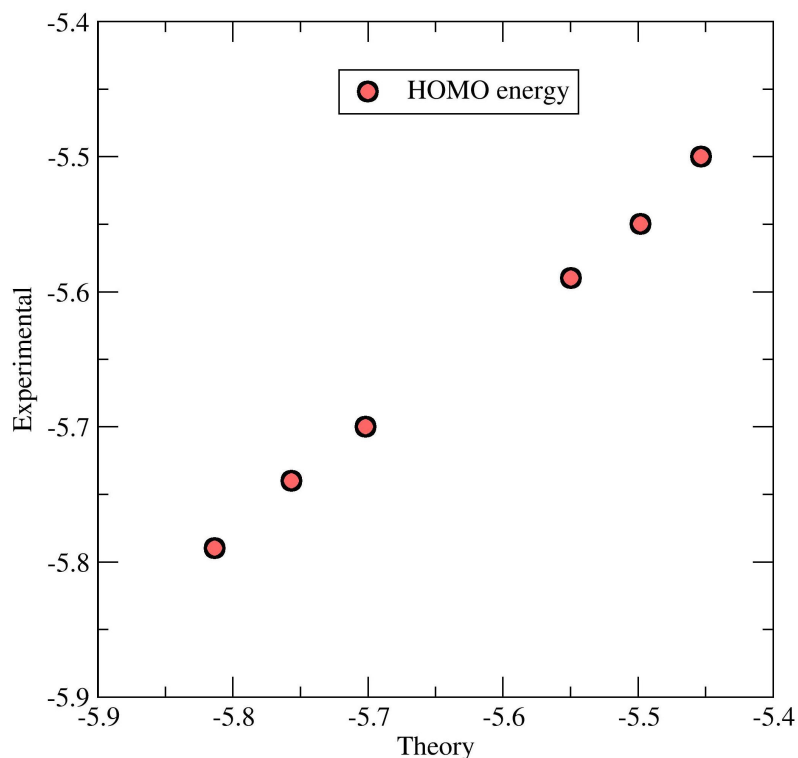
**Figure S1.** Kohn-Sham frontier molecular orbitals for **1a** (DFT/PBE0).

**Table S3.** Selected vertical transitions for **1b** computed at the LR-TDDFT/PBE0 level of theory.

Transition	Energy (eV)	Oscillator strength	Dominant contributions
$S_0 \rightarrow S_1$	2.04	0.0206	H $\rightarrow$ L (75.4%) H-1 $\rightarrow$ L+1 (14.6%)
$S_0 \rightarrow S_2$	2.11	0.0121	H $\rightarrow$ L+1 (80.1%) H-2 $\rightarrow$ L+1 (8.4%)
$S_0 \rightarrow S_5$	2.37	0.2405	H-1 $\rightarrow$ L+1 (42.5%) H-2 $\rightarrow$ L (30.0%) H-2 $\rightarrow$ L+1 (10.5%)
$S_0 \rightarrow S_7$	2.82	0.0839	H $\rightarrow$ L+2 (73.4%) H $\rightarrow$ L+4 (13.3%)
$S_0 \rightarrow S_8$	2.87	0.0991	H $\rightarrow$ L+3 (53.7%) H-2 $\rightarrow$ L+3 (18.4%)
$S_0 \rightarrow S_{12}$	3.05	0.3311	H-2 $\rightarrow$ L+2 (27.0%) H-1 $\rightarrow$ L+3 (21.9%) H-1 $\rightarrow$ L+4 (21.0%)



**Figure S2.** Kohn-Sham frontier molecular orbitals for **1b** (DFT/PBE0).



**Figure S3.** Correlation between theoretical and experimental HOMO energies for the series of complexes. Experimental values are obtained with  $E_{\text{HOMO}} = E_{\text{ox}} - 4.8$ .

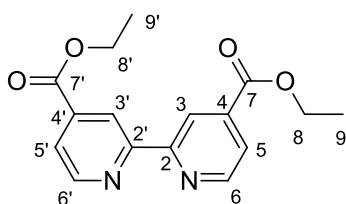
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## Synthetic procedures

### Diethyl-2,2'-bipyridine-4,4'-dicarboxylate (2a)



2,2'-Bipyridine-4,4'-dicarboxylic acid (4.00 g, 16.4 mmol) was combined with ethanol (60 mL) to form a suspension, to which was added H<sub>2</sub>SO<sub>4</sub> (98%, 10 mL) The mixture was heated to reflux at 100 °C whilst stirred, and the solid dissolved slowly to form a pink solution. The heating continued for 72 h. After cooling to rt ethanol (100 mL) was added followed by an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (20 g Na<sub>2</sub>CO<sub>3</sub> in 100 mL H<sub>2</sub>O) which was added slowly until the pH was increased to 8, causing a white precipitate and evolution of CO<sub>2</sub>. The resulting suspension was extracted with CHCl<sub>3</sub> (3 x 300 mL), the organic phases were combined and dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure to afford a white crystalline solid (3.54 g, 11.8 mmol, 72%). *R<sub>f</sub>* = 0.93 (CH<sub>2</sub>Cl<sub>2</sub>, on silica).

Mp: 159-161 °C;

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.94 (dd, *J* = 1.7, 0.9 Hz, 1H, H<sup>3,3'</sup>), 8.87 (dd, *J* = 5.0, 0.9 Hz, 1H, H<sup>6,6'</sup>), 7.91 (dd, *J* = 5.0, 1.6 Hz, 1H, H<sup>5,5'</sup>), 4.45 (q, *J* = 7.1 Hz, 4H, H<sup>8,8'</sup>), 1.43 (t, *J* = 7.1 Hz, 6H, H<sup>9,9'</sup>);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2 ( $\text{C}^{7,7'}$ ), 156.5 ( $\text{C}^{4,4'}$ ), 150.1 ( $\text{C}^{2,2'}$ ), 139.2 ( $\text{C}^{6,6'}$ ), 123.4 ( $\text{C}^{3,3'}$ ), 120.8 ( $\text{C}^{5,5'}$ ), 62.1 ( $\text{C}^{8,8'}$ ), 14.4 ( $\text{C}^{9,9'}$ );

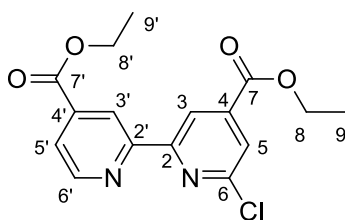
IR(film,  $\text{cm}^{-1}$ ); 2993s (C-H), 2973s (C-H), 2945s (C-H), 2930s (C-H), 2906s (C-H), 2876s (C-H), 1725s (C=O), 1597s (C=C), 1557s (C=C), 1470s (C-H), 1448 (C-H), 1398s (C-H), 1372s (C-H), 1362s (C-H), 1286s (C-O);

MS (TOF  $\text{EI}^+$ ):  $m/z$  (%): 228.1 (100), 300.1 (8)  $[\text{M}]^+$ ;

HRMS ( $\text{EI}^+$ ):  $[\text{M}]^+$  calcd. for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$ , 300.1110; found, 300.1109.

Data were in agreement with those reported in the literature.

### Diethyl-6-chloro-2,2'-bipyridine-4,4'-dicarboxylate (**4a**)



**2a** (3.40 g, 11.3 mmol, 1 eq) was dissolved in  $\text{CHCl}_3$  (70 mL), to which a solution of *m*CPBA (2.55 g, 14.8 mmol, 1.3 eq) in  $\text{CHCl}_3$  (50 mL) was added slowly at rt, producing a yellow solution. After stirring at 30 °C for 36 h the reaction mixture was washed with an aqueous solution  $\text{Na}_2\text{CO}_3$  (10 g  $\text{Na}_2\text{CO}_3$  in 100 mL  $\text{H}_2\text{O}$ ) followed by 2 x 100 mL  $\text{H}_2\text{O}$ . The organic phase was dried with  $\text{MgSO}_4$ , and the solvent removed under reduced pressure to yield 3.3 g of the crude oxide as a yellow solid. The crude oxide was then combined with  $\text{POCl}_3$  (15 mL), the mixture was stirred and heated to reflux at 120 °C and the solid dissolved to form a yellow solution. After 2.5 h the solution had turned brown. The solution was cooled to rt and the remaining  $\text{POCl}_3$  was removed by vacuum distillation at 85 °C and 10 mbar.  $\text{H}_2\text{O}$  (50 mL) was added to the remaining solid, which was extracted with  $\text{CH}_2\text{Cl}_2$  (4 x 50 mL) the organic phases were combined, and dried ( $\text{MgSO}_4$ ), and the solvent removed under reduced pressure. The remaining solid was purified by column chromatography on silica ( $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$  30:1), and washed with hexanes (5 mL) to yield a white crystalline solid (1.34 g, 4.00 mmol, 35% over 2 steps).  $R_f = 0.85$  ( $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$  9:1, on silica).

Mp: 132-134 °C;

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (dd,  $J = 1.6, 0.9$  Hz, 1H,  $\text{H}^{3'}$ ), 8.88 (d,  $J = 1.3$  Hz, 1H,  $\text{H}^3$ ), 8.85 (dd,  $J = 5.0, 0.9$  Hz, 1H,  $\text{H}^6$ ), 7.97 – 7.88 (stack, 2H,  $\text{H}^{5,5'}$ ), 4.52 – 4.40 (stack, 4H,  $\text{H}^{8,8'}$ ), 1.52 – 1.39 (stack, 6H,  $\text{H}^{9,9'}$ );

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2 ( $\text{C}^7$ ), 164.1 ( $\text{C}^{7'}$ ), 157.2 ( $\text{C}^4$ ), 155.3 ( $\text{C}^{4'}$ ), 152.0 ( $\text{C}^6$ ), 150.3 ( $\text{C}^{6'}$ ), 141.9 ( $\text{C}^2$ ), 139.3 ( $\text{C}^{2'}$ ), 124.4 ( $\text{C}^3$ ), 123.9 ( $\text{C}^{3'}$ ), 121.0 ( $\text{C}^5$ ), 119.4 ( $\text{C}^{5'}$ ), 62.4 ( $\text{C}^8$ ), 62.2 ( $\text{C}^{8'}$ ), 14.4 ( $\text{C}^9$ ), 14.4 ( $\text{C}^{9'}$ );

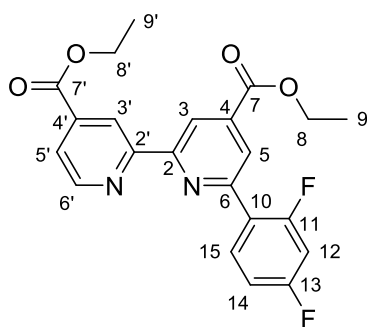
IR(film,  $\text{cm}^{-1}$ ): 3096s (C-H), 3002s (C-H), 2984s (C-H), 2945s (C-H), 2906s (C-H), 1723s (C=O), 1589s (C=C), 1552s (C=C), 1466s (C-H), 1445s (C-H), 1419s (C-H), 1394s (C-H), 1356s (C-H), 1322s (C-H), 1297s (C-O);

MS (TOF ES $^+$ ):  $m/z$  (%): 357.1 (100)  $[\text{M}+\text{Na}]^+$ ;

HRMS (ES $^+$ ):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_4\text{Na}^{35}\text{Cl}$ , 357.0618; found, 357.0633.

Data were in agreement with those reported in the literature.

### Diethyl-6-(2,4-difluorophenyl)-2,2'-bipyridine-4,4'-dicarboxylate (7a)



**4a** (800 mg, 2.39 mmol, 1 eq), 2,4-difluorophenyl boronic acid (453 mg, 2.87 mmol, 1.2 eq), and  $\text{Na}_2\text{CO}_3$  (304 mg, 2.87 mmol, 1.2 eq) were combined along with THF (50 mL) and  $\text{H}_2\text{O}$  (10 mL). The solvent was degassed with argon for 20 min. Tetrakis(triphenylphosphine)palladium(0) (138 mg 119  $\mu\text{mol}$ , 5 mol %) was then added and the mixture degassed with argon for a further 10 min before stirring under argon at 70  $^\circ\text{C}$  for 16 h. After cooling to rt the solvent was removed under reduced pressure and  $\text{CH}_2\text{Cl}_2$  (100 mL) and  $\text{H}_2\text{O}$  (50 mL) were added and the organic phase extracted. The aqueous phase was extracted with a further 2 portions of  $\text{CH}_2\text{Cl}_2$  (100 mL). The organic phases were combined and dried ( $\text{MgSO}_4$ ) and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography on silica ( $\text{CH}_2\text{Cl}_2$ : $\text{Et}_2\text{O}$  9:1) followed by a further silica column ( $\text{CH}_2\text{Cl}_2$ ), to afford a white crystalline solid (716 mg, 1.74 mmol, 73%).  $R_f$  = 0.83 ( $\text{CH}_2\text{Cl}_2$ : $\text{Et}_2\text{O}$  9:1, on silica).

Mp: 123-125  $^\circ\text{C}$

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.03 (s,  $J$  = 0.7 Hz, 1H,  $\text{H}^{3'}$ ), 8.93 (d,  $J$  = 1.3 Hz, 1H,  $\text{H}_3$ ), 8.88 (d,  $J$  = 4.9 Hz, 1H,  $\text{H}^6$ ), 8.39 (t,  $J$  = 1.5 Hz, 1H,  $\text{H}^5$ ), 8.25 (td,  $J$  = 8.8, 6.7 Hz, 1H,  $\text{H}^{15}$ ), 7.91 (dd,  $J$  = 5.0,

1.6 Hz, 1H, H<sup>5'</sup>), 7.08 (td,  $J = 8.3, 2.5$  Hz, 1H, H<sup>14</sup>), 6.98 (ddd,  $J = 11.3, 8.8, 2.5$  Hz, 1H, H<sup>12</sup>), 4.48 (stack, 4H, H<sup>8,8'</sup>), 1.46 (stack, 6H, H<sup>9,9'</sup>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.4 (s, C<sup>7</sup>), 165.3 (s, C<sup>7</sup>), 163.8 (dd,  $J = 250.1, 10.2$  Hz, C<sup>11</sup>), 161.1 (dd,  $J = 251.8, 9.9$  Hz, C<sup>13</sup>), 156.7 (s, C<sup>2</sup>), 156.44 (s, C<sup>2'</sup>), 153.1 (s, C<sup>6</sup>), 150.2 (s, C<sup>6</sup>), 140.0 (s, C<sup>4</sup>), 139.1 (s, C<sup>4'</sup>), 132.6 (dd,  $J = 9.6, 3.9$  Hz, C<sup>15</sup>), 123.8 (d,  $J = 10.7$  Hz, C<sup>5</sup>), 123.4 (s, C<sup>5'</sup>), 123.1 (dd,  $J = 11.3, 3.6$  Hz, C<sup>3'</sup>), 120.8 (s, C<sup>3</sup>), 119.4 (s, C<sup>14</sup>), 112.2 (dd,  $J = 21.1, 3.4$  Hz, C<sup>12</sup>), 104.7 (t,  $J = 26.1$  Hz, C<sup>15</sup>), 62.1 (s, C<sup>8'</sup>), 62.08 (s, C<sup>8</sup>), 14.5 (s, C<sup>9'</sup>), 14.4 (s, C<sup>9</sup>);

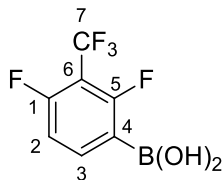
<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  -108.21 (d,  $J = 9.0$  Hz, 1F, F<sup>13</sup>), -111.70 (d,  $J = 9.0$  Hz, 1F, F<sup>11</sup>);

IR(film, cm<sup>-1</sup>): 3095s (C-H), 2987s (C-H), 2948s (C-H), 2906s (C-H), 2882s (C-H), 1731 (C=O), 1719 (C=O), 1620s (C=C), 1597 (C=C), 1560s (C=C), 1506s (C=C), 1478s (C-H), 1441s (C-H), 1382s (C-H), 1368s (C-H), 1275 (C-O);

MS (TOF ES<sup>+</sup>):  $m/z$  (%): 413.1 (100) [M+H]<sup>+</sup>;

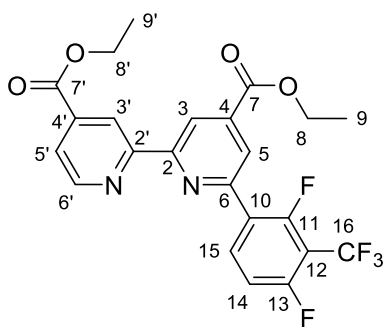
HRMS (ES<sup>+</sup>): [M+H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>F<sub>2</sub>, 413.1304; found, 413.1313.

## 2,4-Difluoro-3-(trifluoromethyl)phenyl boronic acid (B)



A 100 mL 2 neck round bottom flask fitted with addition funnel, septum and stopcock was flame dried under vacuum and filled with argon. 2,6-Difluorobenzotrifluoride (5.00 g, 27.5 mmol, 1 eq) and dry THF (50 mL) were added to the reaction vessel, and the resulting solution cooled to -78 °C. *n*BuLi (1.4 M in toluene, 25.5 mL, 35.8 mmol, 1.3 eq), was then added slowly dropwise to the stirred solution. The resulting dark red solution was stirred at -78 °C for 1 h before the addition of trimethylborate (2.28 g, 41.25 mmol, 1.3 eq). The resulting solution allowed to warm to rt turning pale yellow and was then stirred under argon for 16 h. HCl (3 M, 100 mL) was then added slowly dropwise and the solution stirred for further 1 h. The reaction mixture was then neutralised by careful addition of Na<sub>2</sub>CO<sub>3</sub> (20 g in 100 mL H<sub>2</sub>O). The organic phase was extracted and the aqueous phase extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL). The organic phases were combined dried (MgSO<sub>4</sub>) and solvent removed under reduced pressure to yield a crude brown solid (3.57 g) which was carried forward.

## Diethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2,2'-bipyridine-4,4'-dicarboxylate (7b)



**4a** (500 mg, 1.49 mmol, 1 eq), **B** (506 mg,  $\approx$ 2.24 mmol,  $\approx$ 1.5 eq), and  $\text{Na}_2\text{CO}_3$  (237 mg, 2.24 mmol, 1.5 eq) were combined along with THF (75 mL) and  $\text{H}_2\text{O}$  (15 mL). The solvent was degassed with argon for 20 min. Tetrakis(triphenylphosphine)palladium(0) (86 mg 74.4  $\mu\text{mol}$ , 5 mol %) was then added and the mixture degassed with argon for a further 10 min before stirring under argon at 70  $^\circ\text{C}$  for 16 h. After cooling to rt the solvent was removed under reduced pressure and  $\text{CH}_2\text{Cl}_2$  (50 mL) and  $\text{H}_2\text{O}$  (50 mL) were added and the organic phase extracted, dried ( $\text{MgSO}_4$ ) and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography on silica ( $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$  9:1) to afford a white crystalline solid (481 mg, 1.00 mmol, 67%).  $R_f = 0.74$  ( $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$  9:1, on silica);

Mp: 126-128  $^\circ\text{C}$ ;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.00 (dd,  $J = 1.4, 0.8$  Hz, 1H,  $\text{H}^{3'}$ ), 8.98 (d,  $J = 1.3$  Hz, 1H,  $\text{H}^3$ ), 8.88 (dd,  $J = 5.0, 0.7$  Hz, 1H,  $\text{H}^{6'}$ ), 8.44 – 8.38 (m, 1H,  $\text{H}^{15}$ ), 8.38 (dd,  $J = 2.3, 1.3$  Hz, 1H,  $\text{H}^5$ ), 7.92 (dd,  $J = 5.0, 1.6$  Hz, 1H,  $\text{H}^{5'}$ ), 7.22 (t,  $J = 9.2$  Hz, 1H,  $\text{H}^{14}$ ), 4.48 (m, 4H,  $\text{H}^{8,8'}$ ), 1.46 (m, Hz, 6H,  $\text{H}^{9,9'}$ );

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3 (s,  $\text{C}^7$ ), 165.0 (s,  $\text{C}^7$ ), 160.6 (dd,  $J = 258.0, 31.6$  Hz,  $\text{C}^{13}$ ), 158.0 (dd,  $J = 259.9, 31.2$  Hz,  $\text{C}^{11}$ ), 156.8 (s,  $\text{C}^2$ ), 156.3 (s,  $\text{C}^{2'}$ ), 151.8 (s,  $\text{C}^6$ ), 150.3 (s,  $\text{C}^6$ ), 140.2 (s,  $\text{C}^4$ ), 139.1 (s,  $\text{C}^{4'}$ ), 135.8 (dd,  $J = 10.5, 5.0$  Hz,  $\text{C}^{15}$ ), 124.5 (dd,  $J = 12.2, 3.8$  Hz,  $\text{C}^{10}$ ), 124.0 (d,  $J = 10.4$  Hz,  $\text{C}^5$ ), 123.5 (s,  $\text{C}^{5'}$ ), 120.8 (s,  $\text{C}^3$ ), 120.12 (s,  $\text{C}^{3'}$ ), 113.4 (dd,  $J = 22.3, 3.7$  Hz,  $\text{C}^{14}$ ), 62.3 (s,  $\text{C}^{8'}$ ), 62.1 (s,  $\text{C}^8$ ), 14.4 (s,  $\text{C}^{9'}$ ), 14.4 (s,  $\text{C}^9$ ). Expected signals for  $\text{C}^{12}$  (approx. 120 (tq,  $J = 30, 30$  Hz)) and  $\text{C}^{16}$  (approx. 120 (tq,  $J = 250, 10$  Hz)) not observed due to high level of splitting giving a very weak signal.  $^1\text{H}$ ,  $^{19}\text{F}$  and HRMS confirm structure is correct.

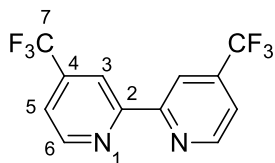
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.12 (t,  $J = 22.9$  Hz, 3F,  $\text{F}^9$ ), -108.72 (qd,  $J = 24.0, 3.2$  Hz, 1F,  $\text{F}^{13}$ ), -113.95 (qd,  $J = 22.7, 3.2$  Hz, 1F,  $\text{F}^{11}$ );

IR(film,  $\text{cm}^{-1}$ ): 3098w (C-H), 3071w (C-H), 2991s (C-H), 2944w (C-H), 2906w (C-H), 1727s (C=O), 1715s (C=O), 1626s (C=C), 1596s (C=C), 1561s (C=C), 1495s (C-H), 1470s (C-H), 1452s (C-H), 1381s (C-H), 1369s (C-H), 1317s (C-H), 1295s (C-O);

MS (TOF ES<sup>+</sup>): *m/z* (%): 480.1 (100) [M]<sup>+</sup>;

HRMS (ES<sup>+</sup>): [M]<sup>+</sup> calcd. for C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub>F<sub>5</sub>, 480.1108; found, 480.1109.

#### 4,4'-bis(trifluoromethyl)-2,2'-bipyridine (2b)



Activated zinc was prepared by washing ground zinc with 0.5 M HCl followed by water, ethanol, and Et<sub>2</sub>O; the washed zinc and tetraethylammonium iodide were dried under vacuum overnight. The activated zinc (1.09 g, 16.7 mmol, 4.5 eq) and tetraethylammonium iodide (2.22 g, 3.00 mmol, 0.9 eq) were combined with dibromobis(triphenylphosphine)-nickel(II) (2.48 g, 3.30 mmol, 1.0 eq) under argon, to which anhydrous THF (40 mL) was added. After the dark suspension was stirred at room temperature for 30 min, 2-chloro-4-(trifluoromethyl)pyridine (2.00 g, 11.1 mmol, 3.0 eq) was injected by syringe, and the reaction was stirred at 50 °C for an additional 48 h under argon. The black slurry was poured into 2 M ammonium hydroxide (120 mL), mixed with CHCl<sub>3</sub> (120 mL). The organic layer was separated, dried with anhydrous MgSO<sub>4</sub>, and evaporated under reduced pressure. The brown residue was purified by silica gel column chromatography (hexane:CH<sub>2</sub>Cl<sub>2</sub> 4:1), to afford a white powder (1.81 g, 6.19 mmol, 44%).

Mp: 78-79 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.80 (d, *J* = 5.0 Hz, 2H, H<sup>6</sup>), 8.64 (s, 2H, H<sup>3</sup>), 7.50 (dd, *J* = 5.0, 1.0 Hz, 2H, H<sup>5</sup>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.1 (s, C<sup>2</sup>), 150.3 (s, C<sup>6</sup>), 139.6 (q, *J* = 34.3 Hz, C<sup>4</sup>), 122.8 (q, *J* = 273.4 Hz, C<sup>7</sup>), 119.9 (d, *J* = 3.3 Hz, C<sup>5</sup>), 117.1 (dd, *J* = 6.9, 3.3 Hz, C<sup>3</sup>);

<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -64.94 (s, 6F, F<sup>7</sup>);

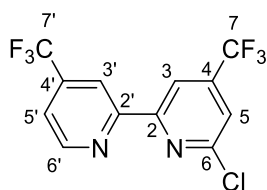
IR(film, cm<sup>-1</sup>): 3108s (C-H), 3080s (C-H), 3049 (C-H), 1608s (C=C), 1571s (C=C), 1461s (C-H), 1375s (C-H), 1319s (C-H);

MS (TOF ES<sup>+</sup>): *m/z* (%): 293.1(100) [M+H]<sup>+</sup>;

HRMS (ES<sup>+</sup>): [M+H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>7</sub>N<sub>2</sub>F<sub>6</sub>, 293.0513; found, 293.0512.

Data were in agreement with those reported in the literature.

### 6-Chloro-4,4'-bis(trifluoromethyl)-2,2'-bipyridine (4c)



**2b** (500 mg, 1.71 mmol, 1.0 eq) was dissolved in  $\text{CHCl}_3$  (20 mL), to which a solution of *m*CPBA (578 mg, 1.71 mmol, 1.0 eq), in  $\text{CHCl}_3$  (10 mL) was added slowly at rt, producing a yellow solution. After stirring at 50 °C for 16 h the reaction mixture was washed with an aqueous solution  $\text{Na}_2\text{CO}_3$  (10 g  $\text{Na}_2\text{CO}_3$  in 100 mL  $\text{H}_2\text{O}$ ) followed by 2 x 100 mL  $\text{H}_2\text{O}$ . The organic phase was dried with  $\text{MgSO}_4$ , and the solvent removed under reduced pressure to yield a yellow solid. This crude oxide was combined with  $\text{POCl}_3$  (10 mL) and the mixture was degassed with argon before being stirred and heated to reflux at 120 °C. After 1.5 h the solution was cooled to rt and the remaining  $\text{POCl}_3$  was removed by vacuum distillation at 50 °C and  $10^{-3}$  mbar.  $\text{H}_2\text{O}$  (50 mL) was added to the remaining solid, which was extracted with  $\text{CH}_2\text{Cl}_2$  (4 x 50 mL) the organic phases were combined, and dried ( $\text{MgSO}_4$ ), and the solvent removed under reduced pressure. The remaining solid was purified by column chromatography on silica (hexane: $\text{CH}_2\text{Cl}_2$  3:1), to yield a white crystalline solid (250 mg, 765  $\mu\text{mol}$ , 45%).  $R_f = 0.30$  (hexane: $\text{CH}_2\text{Cl}_2$  3:1, on silica).

Mp: 57-58 °C;

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (d,  $J = 5.0$  Hz, 1H,  $\text{H}^6$ ), 8.56 (s, 1H,  $\text{H}^{3'}$ ), 8.55 (s, 1H,  $\text{H}^3$ ), 7.51 (s, 2H,  $\text{H}^{5'}$ ,  $\text{H}^5$ )

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.72 (s,  $\text{C}^6$ ), 154.60 (s,  $\text{C}^2$ ), 152.05 (s,  $\text{C}^{2'}$ ), 150.35 (s,  $\text{C}^6$ ), 142.13 (q,  $J = 34.8$  Hz,  $\text{C}^7$ ), 139.76 (q,  $J = 34.4$  Hz,  $\text{C}^{7'}$ ), 122.37 (q,  $J = 273.6$  Hz,  $\text{C}^4$ ), 122.36 (q,  $J = 273.6$  Hz,  $\text{C}^4$ ), 120.93 (d,  $J = 3.4$  Hz,  $\text{C}^{3'}$ ), 120.39 (d,  $J = 3.3$  Hz,  $\text{C}^3$ ), 117.33 (dd,  $J = 6.7, 3.2$  Hz,  $\text{C}^5$ ), 115.78 (dd,  $J = 6.4, 3.1$  Hz,  $\text{C}^{5'}$ );

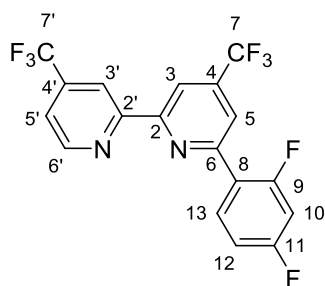
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.72 - -64.99 (m, 6F,  $\text{F}^{7,7'}$ );

IR(film,  $\text{cm}^{-1}$ ): 3106s (C-H), 3094s (C-H), 1597s (C=C), 1562s (C=C), 1478s (C=C), 1420s (C=C), 1372s (C-H), 1317s (C-H);

MS (TOF ES+):  $m/z$  (%): 293.1(100) [ $\text{M}+\text{H}$ ] $^+$ ;

HRMS (ES+): [ $\text{M}+\text{H}$ ] $^+$  calcd. for  $\text{C}_{12}\text{H}_5\text{N}_2\text{F}_6\text{Cl}$ , 326.0045; found, 326.0051.

## 6-(2,4-Difluorophenyl)-4,4'-bis(trifluoromethyl)-2,2'-bipyridine (7e)



**4c** (150 mg, 459  $\mu\text{mol}$ , 1.0 eq), 2,4-difluorophenyl boronic acid (156 mg, 689  $\mu\text{mol}$ , 1.5 eq), and  $\text{Na}_2\text{CO}_3$  (73.0 mg, 689  $\mu\text{mol}$ , 1.5 eq) were combined along with THF (25 mL) and  $\text{H}_2\text{O}$  (5 mL). The solvent was degassed with argon for 20 min. Tetrakis(triphenylphosphine)palladium(0) (26.6 mg, 23.0  $\mu\text{mol}$ , 5 mol%) was then added and the mixture degassed with argon for a further 10 min before stirring under argon at 70  $^\circ\text{C}$  for 16 h. After cooling to rt the solvent was removed under reduced pressure and  $\text{CH}_2\text{Cl}_2$  (50 mL) and  $\text{H}_2\text{O}$  (50 mL) were added and the organic phase extracted, dried ( $\text{MgSO}_4$ ) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica (hexane: $\text{CH}_2\text{Cl}_2$  3:1) to afford a white crystalline solid (201 mg, 426  $\mu\text{mol}$ , 93%).  $R_f$  = 0.25 (hexane: $\text{CH}_2\text{Cl}_2$  3:1, on silica).

Mp: 112-114  $^\circ\text{C}$ ;

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.90 (d,  $J$  = 5.0 Hz, 1H,  $\text{H}^{6'}$ ), 8.83 – 8.72 (m, 1H,  $\text{H}^3$ ), 8.69 (d,  $J$  = 0.6 Hz, 1H,  $\text{H}^{3'}$ ), 8.22 (td,  $J$  = 8.9, 6.6 Hz, 1H,  $\text{H}^{13}$ ), 8.06 (s, 1H,  $\text{H}^5$ ), 7.61 (dd,  $J$  = 5.0, 1.0 Hz, 1H,  $\text{H}^{5'}$ ), 7.18 – 7.06 (m, 1H,  $\text{H}^{12}$ ), 6.99 (ddd,  $J$  = 11.3, 8.7, 2.5 Hz, 1H,  $\text{H}^{10}$ );

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.91 (dd,  $J$  = 252.8, 12.3 Hz,  $\text{C}^{9,11}$ ), 161.04 (dd,  $J$  = 253.8, 12.0 Hz,  $\text{C}^{9,11}$ ), 156.07 (s,  $\text{C}^{2'}$ ), 155.88 (s,  $\text{C}^2$ ), 153.25 (d,  $J$  = 2.4 Hz,  $\text{C}^6$ ), 150.32 (s,  $\text{C}^{6'}$ ), 141.15 – 140.00 (m,  $\text{C}^4$ ), 139.98 – 139.01 (m,  $\text{C}^4$ ), 132.32 (dd,  $J$  = 9.7, 3.8 Hz,  $\text{C}^{13}$ ), 122.23 (d,  $J$  = 7.3 Hz,  $\text{C}^{7,7'}$ ), 127.76 – 118.19 (m,  $\text{C}^8$ ), 120.22 (dd,  $J$  = 11.2, 3.4 Hz,  $\text{C}^{5'}$ ), 119.98 (d,  $J$  = 3.4 Hz,  $\text{C}^5$ ), 117.00 (dd,  $J$  = 6.8, 3.3 Hz,  $\text{C}^3$ ), 115.82 (d,  $J$  = 3.4 Hz,  $\text{C}^{3'}$ ), 112.36 (dd,  $J$  = 21.3, 3.3 Hz,  $\text{C}^{12}$ ), 104.73 (t,  $J$  = 26.3 Hz,  $\text{C}^{10}$ );

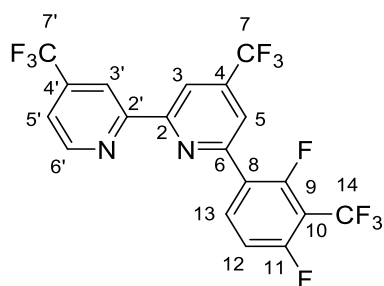
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.73 (d,  $J$  = 6.6 Hz, 3F,  $\text{F}^{7,7'}$ ), -89.06 – -109.68 (m, 1F,  $\text{F}^9$ ), -111.72 (dd,  $J$  = 20.3, 9.5 Hz, 1F,  $\text{F}^{11}$ );

IR(film,  $\text{cm}^{-1}$ ): 3094s (C-H), 3054s (C-H), 2969s (C-H), 1620s (C=C), 1608s (C=C), 1568s (C=C), 1507s (C=C), 1484s (C=C), 1443s (C=C), 1394s (C-H), 1362s (C-H);

MS (TOF ES+):  $m/z$  (%): 293.1(100) [ $\text{M}+\text{H}$ ] $^+$ ;

HRMS (ES+): [ $\text{M}+\text{H}$ ] $^+$  calcd. for  $\text{C}_{18}\text{H}_8\text{N}_2\text{F}_8$ , 404.0560; found, 404.0558.

## 6-(2,4-Difluoro-3-(trifluoromethyl)phenyl)-4,4'-bis(trifluoromethyl)-2, 2'-bipyridine (7f)



**4c** (75.0 mg, 0.23 mmol, 1.0 eq), **B** (77.8 mg, 0.34 mmol, 1.5 eq), and  $\text{Na}_2\text{CO}_3$  (73.0 mg, 689  $\mu\text{mol}$ , 1.5 eq) were combined along with THF (25 mL) and  $\text{H}_2\text{O}$  (5 mL). The solvent was degassed with argon for 20 min. Tetrakis(triphenylphosphine)palladium(0) (14.6 mg, 12.6  $\mu\text{mol}$ , 5 mol%) was then added and the mixture degassed with argon for a further 10 min before stirring under argon at 70  $^\circ\text{C}$  for 16 h. After cooling to rt the solvent was removed under reduced pressure and  $\text{CH}_2\text{Cl}_2$  (50 mL) and  $\text{H}_2\text{O}$  (50 mL) were added and the organic phase extracted, dried ( $\text{MgSO}_4$ ) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica (hexane: $\text{Et}_2\text{O}$  30:1) to afford a white crystalline solid (85.0 mg, 0.18 mmol, 86%).  $R_f$  = 0.30 (hexane: $\text{Et}_2\text{O}$  30:1, on silica).

Mp: 114-115  $^\circ\text{C}$ ;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.85 (d,  $J$  = 5.0 Hz, 1H,  $\text{H}^{6'}$ ), 8.68 (s, 1H,  $\text{H}^3$ ), 8.65 (s, 1H,  $\text{H}^{3'}$ ), 8.32 (td,  $J$  = 8.6, 6.3 Hz, 1H,  $\text{H}^{13}$ ), 8.00 (s, 1H,  $\text{H}^5$ ), 7.56 (d,  $J$  = 4.7 Hz, 1H,  $\text{H}^{5'}$ ), 7.32 – 6.79 (m, 1H,  $\text{H}^{12}$ );

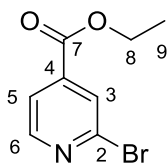
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.32 (stack,  $\text{C}^{9,11}$ ), 156.26 (s,  $\text{C}^{2'}$ ), 155.73 (s,  $\text{C}^2$ ), 152.02 (s,  $\text{C}^6$ ), 150.44 (s,  $\text{C}^{6'}$ ), 141.36 -140.08 (m,  $\text{C}^4$ ), 140.34 - 138.95 (m,  $\text{C}^{4'}$ ), 135.53 (dd,  $J$  = 10.7, 4.7 Hz,  $\text{C}^{13}$ ), 123.57 (dd,  $J$  = 11.7, 3.8 Hz,  $\text{C}^8$ ), 122.77 (q,  $J$  = 273.6,  $\text{C}^{7,7'}$ ), 120.79 - 120.34 (m,  $\text{C}^5$ ), 120.19 (d,  $J$  = 3.3 Hz,  $\text{C}^{5'}$ ), 116.98 (d,  $J$  = 3.4 Hz,  $\text{C}^3$ ), 116.58 (d,  $J$  = 3.4 Hz,  $\text{C}^{3'}$ ), 113.59 (dd,  $J$  = 22.3, 3.6 Hz,  $\text{C}^{12}$ ). Expected signals for  $\text{C}^{10}$  (approx. 120 (tq,  $J$  = 30, 30 Hz)) and  $\text{C}^{14}$  (approx. 120 (tq,  $J$  = 250, 10 Hz)) not observed due to high level of splitting giving a very weak signal;

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.17 (t, 3F,  $J$  = 23.4 Hz,  $\text{F}^{14}$ ), -64.60 – -64.72 (m, 3F,  $\text{F}^7$ ), -64.72 – -64.84 (m, 3F,  $\text{F}^{7'}$ ), -105.72-108.90 (m, 1F,  $\text{F}^9$ ), -111.54 – -116.49 (m, 1F,  $\text{F}^{11}$ );

MS (TOF ES+):  $m/z$  (%): 293.1(100) [ $\text{M}+\text{H}$ ] $^+$ ;

HRMS (ES+): [ $\text{M}+\text{H}$ ] $^+$  calcd. for  $\text{C}_{19}\text{H}_7\text{N}_2\text{F}_{11}$ , 472.0434.0045; found, 472.0451.

### Ethyl-2-bromopyridine-4-carboxylate (5)



2-Bromoisonicotinic acid (97.4%, 5.00 g, 24.0 mmol) was combined with ethanol (30 mL) to form a suspension, to which was added H<sub>2</sub>SO<sub>4</sub> (98%, 3.3 mL). The mixture was heated to reflux at 90 °C whilst stirred for 24 h. After an aqueous solution of K<sub>2</sub>CO<sub>3</sub> (20 g in 100 mL H<sub>2</sub>O) which was added slowly until the pH was increased to 7, causing a white precipitate and evolution of CO<sub>2</sub>. The resulting suspension was extracted with Et<sub>2</sub>O (3 x 300 mL), the organic phases were combined and dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure to afford a yellow oil. The crude product was purified by column chromatography on silica (hexane:Et<sub>2</sub>O 9:1) to yield a colourless oil, (3.46 g, 15. mmol, 63%). *R*<sub>f</sub> = 0.33 (hexane:Et<sub>2</sub>O 9:1, on silica).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.51 (dd, *J* = 5.0, 0.6 Hz, 1H, H<sup>6</sup>), 8.03 (dd, *J* = 1.2, 0.8 Hz, 1H, H<sup>3</sup>), 7.80 (dd, *J* = 5.0, 1.4 Hz, 1H, H<sup>5</sup>), 4.41 (q, *J* = 7.1 Hz, 2H, H<sup>8</sup>), 1.40 (t, *J* = 7.1 Hz, 3H, H<sup>9</sup>);

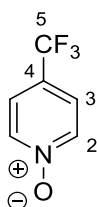
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.6 (C<sup>7</sup>), 150.9 (C<sup>6</sup>), 142.8 (C<sup>4</sup>), 140.2 (C<sup>2</sup>), 127.7 (C<sup>3</sup>), 121.9 (C<sup>5</sup>), 62.3 (C<sup>8</sup>), 14.1 (C<sup>9</sup>);

IR (film, cm<sup>-1</sup>): 3096w (C-H), 3062w (C-H), 2983s (C-H), 2934w (C-H), 2906w (C-H), 2875w (C-H), 1726s (C=O), 1588s (C=C), 1548s (C=C), 1459s (C=C) 1360s (C-O);

MS (TOF ES<sup>+</sup>): *m/z* (%): 230.0 (100) [M+H]<sup>+</sup>;

HRMS (ES<sup>+</sup>): [M+H]<sup>+</sup> calcd. For C<sub>8</sub>H<sub>9</sub>NO<sup>79</sup>Br, 229.9817; found, 229.9808.

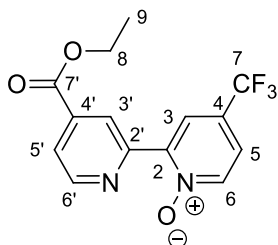
### 4-Trifluoromethylpyridine-*N*-oxide (6)



To a 100 mL round bottom flask charged with 4-(trifluoromethyl)pyridine (2.50 g, 17.0 mmol, 1 eq) and CH<sub>2</sub>Cl<sub>2</sub> (50 mL), *m*CPBA (77 %, 5.03 g, 22.4 mmol, 1.3 eq) was added slowly over 5 min. The resulting mixture was stirred at 30 °C for 16 h. The solvent was removed under reduced pressure and CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and Na<sub>2</sub>CO<sub>3</sub> solution (20 g in 100 mL H<sub>2</sub>O) were added. The organic phase

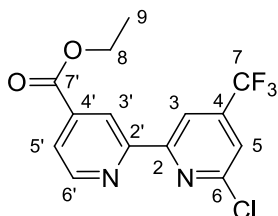
was extracted, washed with H<sub>2</sub>O (2 x 100 mL), dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure. Crude carried forward without further purification.

#### 4-(Trifluoromethyl)-4'-(ethoxycarbonyl)-2-2'-bipyridine-1-oxide (3c)



**5** (1.53g, 6.63 mmol, 1 eq), **6** (2.16 g, 13.3 mmol, 2 eq), palladium(II) acetate (74.0 mg, 401  $\mu$ mol, 5 mol %), tri-*tert*-butylphosphonium tetrafluoroborate (115 mg, 1.20 mmol, 15 mol %), potassium phosphate (2.82 g, 13.3 mmol, 2 eq) and toluene (50 ml) were combined in a 2 neck round bottom flask fitted with condenser, stop cock and magnetic stirrer. The resulting mixture was degassed with argon and heated to 110 °C and stirred for 16 h. After cooling to rt the solvent was removed under reduced pressure. CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added and extracted with H<sub>2</sub>O (50 mL). The organic phases was dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure to afford a brown solid. The crude mixture was recrystallised from CH<sub>2</sub>Cl<sub>2</sub> (10 mL) by the addition of hexane (100 mL). The precipitate was collected by vacuum filtration and dried under vacuum. The resulting crude yellow solid was carried forward without further purification.

#### Ethyl-6-chloro-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate (4b)



**3c** (2.30 g, crude) was combined with POCl<sub>3</sub> (10 mL), the mixture was degassed with argon before being stirred and heated to reflux at 120 °C. After 1.5 h the solution was cooled to rt and the remaining POCl<sub>3</sub> was removed by vacuum distillation at 50 °C and 10<sup>-3</sup> mbar. H<sub>2</sub>O (50 mL) was added to the remaining solid, which was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 50 mL) the organic phases were combined, and dried (MgSO<sub>4</sub>), and the solvent removed under reduced pressure. The

remaining solid was purified by column chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O 30:1) to yield a white crystalline solid (706 mg, 2.13 mmol, 32% over 2 steps).

Mp: 112-114 °C;

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.89 (dd, *J* = 1.5, 0.9 Hz, 1H, H<sup>3'</sup>), 8.81 (dd, *J* = 4.9, 0.8 Hz, 1H, H<sup>6'</sup>), 8.60 (d, *J* = 0.6 Hz, 1H, H<sup>3</sup>), 7.92 (dd, *J* = 4.9, 1.6 Hz, 1H, H<sup>5'</sup>), 7.57 (d, *J* = 0.6 Hz, 1H, H<sup>5</sup>), 4.46 (q, *J* = 7.1 Hz, 2H, H<sup>8</sup>), 1.44 (t, *J* = 7.1 Hz, 4H, H<sup>9</sup>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.94 (s, C<sup>7'</sup>), 157.64 (s, C<sup>2'</sup>), 154.47 (s, C<sup>2</sup>), 152.09 (s, C<sup>6</sup>), 150.29 (s, C<sup>6'</sup>), 142.10 (q, *J* = 34.6 Hz, C<sup>4</sup>), 139.40 (s, C<sup>4'</sup>), 124.26 (s, C<sup>5'</sup>), 122.27 (q, *J* = 273.9 Hz, C<sup>7</sup>), 120.96 (s, C<sup>3'</sup>), 120.63 (q, *J* = 3.4 Hz, C<sup>5</sup>), 115.85 (q, *J* = 3.3 Hz, C<sup>3</sup>), 62.18 (s, C<sup>8</sup>), 14.37 (s, C<sup>9</sup>);

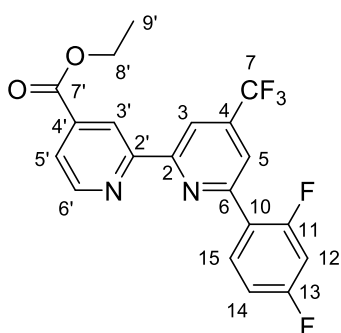
<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -64.72 (s, 3F, F<sup>7</sup>);

IR(film, cm<sup>-1</sup>): 3108s (C-H), 3084s (C-H), 3001s (C-H), 2967s (C-H), 2904s (C-H), 1724s (C=O), 1593s (C=C), 1557s (C=C), 1471s (C-H), 1419s (C-H), 1397s (C-H), 1367s (C-H), 1332s (C-H), 1298s (C-O);

MS (TOF ES<sup>+</sup>): *m/z* (%): 331.0 (100) [M+H]<sup>+</sup>;

HRMS (ES<sup>+</sup>): [M+H]<sup>+</sup> calcd. For C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>F<sub>3</sub><sup>35</sup>Cl, 331.0461; found, 331.0454.

#### Ethyl-6-(2, 4-difluorophenyl)-4-(trifluoromethyl)-2, 2'-bipyridine-4'-carboxylate (**7c**)



**4b** (116 mg, 0.90 mmol, 1.0 eq), **8** (60.0 mg, 1.08 mmol, 1.1 eq), and Na<sub>2</sub>CO<sub>3</sub> (41.0 mg, 1.08 mmol, 1.1 eq) were combined along with THF (50 mL) and H<sub>2</sub>O (10 mL). The solvent was degassed with argon for 20 min. Tetrakis(triphenylphosphine)palladium(0) (22.0 mg 45.0 μmol, 5 mol %) was then added and the mixture degassed with argon for a further 10 min before stirring under argon at 70 °C for 16 h. After cooling to rt the solvent was removed under reduced pressure and CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and H<sub>2</sub>O (50 mL) were added. The organic phase was separated and dried (MgSO<sub>4</sub>) and the solvent was removed under reduced pressure. The resulting solid was purified by column

chromatography on silica (hexane:EtOAc 9:1), to afford a white crystalline solid (205 mg, 0.53 mmol, 60%).  $R_f = 0.3$  (CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O 9:1, on silica).

Mp: 94-96 °C;

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.03 (dd,  $J = 1.5, 0.8$  Hz, 1H, H<sup>3'</sup>), 8.85 (dd,  $J = 5.0$  Hz, 1H, H<sup>6'</sup>), 8.65 (d,  $J = 0.6$  Hz, 1H, H<sup>3</sup>), 8.27 (td,  $J = 8.9, 6.6$  Hz, 1H, H<sup>12</sup>), 8.03 (s, 1H, H<sup>5</sup>), 7.92 (dd,  $J = 5.0, 1.6$  Hz, 1H, H<sup>5'</sup>), 7.13 – 7.04 (m, 1H, H<sup>14</sup>), 6.97 (ddd,  $J = 11.3, 8.7, 2.5$  Hz, 1H, H<sup>15</sup>), 4.47 (s,  $J = 7.1$  Hz, 2H, H<sup>8</sup>), 1.45 (t,  $J = 7.1$  Hz, 3H, H<sup>9</sup>);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.2 (s, C<sup>7'</sup>), 163.9 (stack, C<sup>11</sup>), 161.2 (dd,  $J = 253.6, 12.0$  Hz, C<sup>13</sup>), 156.6 (s, C<sup>2'</sup>), 155.9 (s, C<sup>2</sup>), 153.2 (d,  $J = 2.5$  Hz, C<sup>6</sup>), 150.2 (s, C<sup>6'</sup>), 140.3 (q,  $J = 33.9$  Hz, C<sup>4'</sup>), 139.2 (s, C<sup>4</sup>), 132.6 (dd,  $J = 9.7, 3.7$  Hz, C<sup>12</sup>), 123.7 (s, C<sup>5'</sup>), 123.1 (q,  $J = 273.5$  Hz, C<sup>7</sup>), 122.5 (dd,  $J = 11.0, 3.7$  Hz, C<sup>10</sup>), 120.8 (s, C<sup>3'</sup>), 120.1 -119.8 (m, C<sup>5</sup>), 115.8 (d,  $J = 3.5$  Hz, C<sup>3</sup>), 112.4 (dd,  $J = 21.2, 3.2$  Hz, C<sup>14</sup>), 104.8 (t,  $J = 26.3$  Hz, C<sup>15</sup>), 62.1 (s, C<sup>8</sup>), 14.4 (s, C<sup>9</sup>);

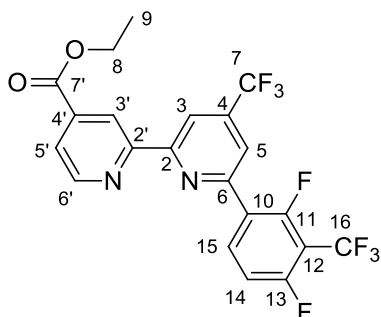
<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -64.69 (s, F<sup>7</sup>), 107.28–107.46 (m, F<sup>11</sup>), -111.66 (dd,  $J = 20.4, 9.3$  Hz, F<sup>13</sup>);

IR(film, cm<sup>-1</sup>): 3097s (C-H), 3080s (C-H), 2994s (C-H), 2951s (C-H), 2913s (C-H), 1731 (C=O), 1618s (C=C), 1597 (C=C), 1574s (C=C), 1505s (C=C), 1474s (C-H), 1443s (C-H), 1388s (C-H), 1356s (C-H), 1274 (C-O);

MS (TOF ES<sup>+</sup>):  $m/z$  (%): 431.1 (100) [M+Na]<sup>+</sup>;

HRMS (ES<sup>+</sup>): [M+H]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>NaF<sub>5</sub>, 431.0795; found, 431.0787.

### Ethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate (7d)



**4b** (150 mg, 450 μmol, 1 eq), **B** (154 mg, ≈680 μmol, ≈1.5 eq), and Na<sub>2</sub>CO<sub>3</sub> (72.1 mg, 680 μmol, 1.5 eq) were combined along with THF (20 mL) and H<sub>2</sub>O (5 mL). The solvent was degassed with argon for 20 min. Tetrakis(triphenylphosphine)palladium(0) (26.2 mg 22.7 μmol, 5 mol %) was

then added and the mixture degassed with argon for a further 10 min before stirring under argon at 70 °C for 16 h. After cooling to rt the solvent was removed under reduced pressure and CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and H<sub>2</sub>O (50 mL) were added and the organic phase extracted, dried (MgSO<sub>4</sub>) and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub> followed by hexane:Et<sub>2</sub>O 9:1) to afford a white crystalline solid (118 mg, 248 μmol, 55%). *R<sub>f</sub>* = 0.70 (CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O 9:1, on silica).

Mp: 114-116 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.01 (dd, *J* = 1.5, 0.8 Hz, 1H, H<sup>3'</sup>), 8.87 (dd, *J* = 4.9, 0.8 Hz, 1H, H<sup>6'</sup>), 8.73 (d, *J* = 0.4 Hz, 1H, H<sup>3</sup>), 8.44 (td, *J* = 8.7, 6.1 Hz, 1H, H<sup>15</sup>), 8.04 (d, *J* = 0.4 Hz, 1H, H<sup>5</sup>), 7.94 (dd, *J* = 5.0, 1.6 Hz, 1H, H<sup>5'</sup>), 7.24 (t, *J* = 9.6 Hz, 1H, H<sup>14</sup>), 4.48 (q, *J* = 7.1 Hz, 2H, H<sup>8</sup>), 1.46 (t, *J* = 7.1 Hz, 3H, H<sup>9</sup>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.19 (s, C<sup>7'</sup>), 160.78 (dd, *J* = 244.5, 4.0 Hz, C<sup>13</sup>), 158.17 (dd, *J* = 244.3, 4.5 Hz, C<sup>11</sup>), 157.07 (s, C<sup>2</sup>), 155.61 (s, C<sup>2'</sup>), 151.98 (s, C<sup>6</sup>), 150.34 (s, C<sup>6'</sup>), 140.65 (q, *J* = 34.0 Hz, C<sup>4</sup>), 139.27 (s, C<sup>4'</sup>), 135.81 (dd, *J* = 10.7, 4.9 Hz, C<sup>15</sup>), 123.91 (s, C<sup>5'</sup>), 122.95 (q, *J* = 273.8 Hz, C<sup>7</sup>), 120.78 (s, C<sup>3'</sup>), 120.20 (dd, *J* = 11.1, 3.3 Hz, C<sup>5</sup>), 116.62 (d, *J* = 3.3 Hz, C<sup>3</sup>), 113.63 (dd, *J* = 22.2, 3.7 Hz, C<sup>14</sup>), 62.20 (s, C<sub>8</sub>), 14.36 (s, C<sup>9</sup>);

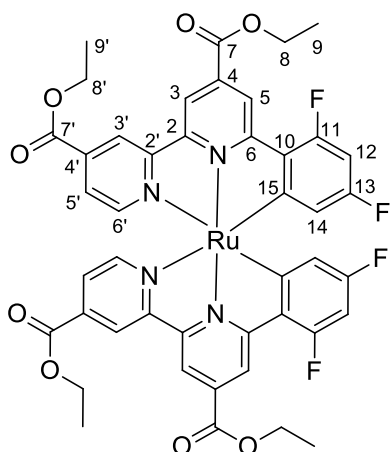
<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -56.17 (dd, *J* = 23.9, 22.8 Hz, 3F, F<sup>16</sup>), -64.69 (s, 3F, F<sup>7</sup>), -107.85 (qd, *J* = 24.0, 3.5 Hz, 1F, F<sup>11</sup>), -114.10 (qd, *J* = 22.7, 3.5 Hz, 1F, F<sup>13</sup>);

IR(film, cm<sup>-1</sup>): 3100s (C-H), 2993s (C-H), 2920s (C-H), 1734 (C=O), 1627s (C=C), 1598 (C=C), 1562s (C=C), 1495s (C=C), 1456s (C-H), 1443s (C-H), 1387s (C-H), 1358s (C-H), 1279 (C-O);

MS (TOF ES<sup>+</sup>): *m/z* (%): 477.1 (100) [M+H]<sup>+</sup>;

HRMS (ES<sup>+</sup>): [M+H]<sup>+</sup> calcd. For C<sub>21</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>F<sub>8</sub>, 477.0849; found, 477.0839.

## Ruthenium(II) bis(diethyl-6-(2,4-difluorophenyl)-2,2'-bipyridine-4,4'-dicarboxylate) (1a)



A 2 neck round bottom flask fitted with stirrer, condenser and stopcock was charged with **7a** (550 mg, 1.33 mmol, 4 eq) and  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (204 mg, 333  $\mu\text{mol}$ , 1 eq). The apparatus was filled with argon before the addition of butyronitrile (10 mL) and *N*-ethylmorpholine (2 mL). The resulting orange solution was degassed with argon for 20 min before heating and stirring at 120 °C, for 16 h under argon and reduced light. After cooling to rt solvent was removed under reduced pressure and the crude black solid was dried under high vacuum. Ethylene glycol (10 mL) was added and the resulting mixture degassed for 20 min with argon. The reaction mixture was then heated and stirred at 200 °C for 2 h under argon and reduced light. After cooling to rt, ethylene glycol was removed by vacuum distillation. The crude black mixture was combined with H<sub>2</sub>O (100 mL) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The organic phase was separated and the aqueous phase extracted with further portions of CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL). The organic phases were combined, dried (MgSO<sub>4</sub>) and solvent removed under reduced pressure. The crude product was purified by column chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O 10:0 → 9:1) to yield a black solid (400 mg, 433  $\mu\text{mol}$ , 65%). *R<sub>f</sub>* = 0.85 (CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O 9:1, on silica).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.95 (m, 2H, H<sup>5</sup>), 8.84 (d, *J* = 1.5 Hz, 2H, H<sup>3</sup>), 8.84 (d, *J* = 1.4 Hz, 2H, H<sup>3</sup>), 7.47 (dd, *J* = 5.7, 0.7 Hz, 2H, H<sup>6</sup>), 7.44 (dd, *J* = 5.7, 1.5 Hz, 2H, H<sup>5</sup>), 6.22 (td, *J* = 10.8 Hz, 2.3 Hz, 2H, H<sup>12</sup>), 5.33 (dd, *J* = 6.8, 1.9 Hz, 2H, H<sup>14</sup>), 4.64 (q, *J* = 7.1 Hz, 4H, H<sup>8</sup>), 4.43 (q, *J* = 7.1 Hz, 4H), 1.60 (t, *J* = 7.1 Hz, 6H), 1.41 (t, *J* = 7.1 Hz, 6H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  191.73 (s, C<sup>15</sup>), 165.95 (s, C<sup>7</sup>), 164.21 (s, C<sup>7</sup>), 162.45 (dd, *J* = 258.9, 11.1 Hz, C<sup>13</sup>), 161.31 (dd, *J* = 260.8, 12.5 Hz, C<sup>11</sup>), 159.34 (s, C<sup>6</sup>), 155.74 (s, C<sup>2</sup>), 150.85 (s, C<sup>2</sup>), 150.04 (s, C<sup>6</sup>), 135.38 (s, C<sup>4</sup>), 130.62 (s, C<sup>4</sup>), 127.12 (s, C<sup>10</sup>), 124.18 (s, C<sup>5</sup>), 121.71 (s, C<sup>3</sup>), 119.68 (d, *J* = 19.4 Hz, C<sup>5</sup>), 117.16 (s, C<sup>3</sup>), 114.97 (dd, *J* = 10.8, 6.1 Hz, C<sup>14</sup>), 96.54 (t, *J* = 26.5 Hz, C<sup>12</sup>), 62.37 (s, C<sup>8</sup>), 62.11 (s, C<sup>8</sup>), 14.66 (s, C<sup>9</sup>), 14.41 (s, C<sup>9</sup>);

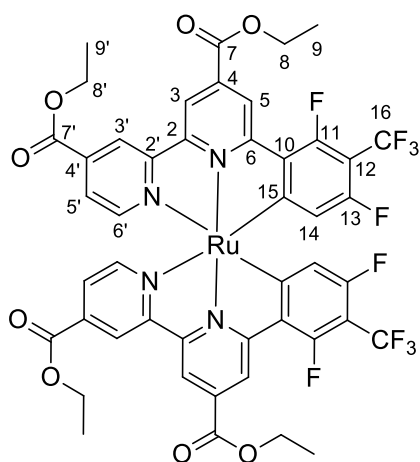
IR(film,  $\text{cm}^{-1}$ ): 3129s (C-H), 3080s (C-H), 2979s (C-H), 2937s (C-H), 2901s (C-H), 1706 (C=O), 1591s (C=C), 1555 (C=C), 1512s (C=C), 1420s (C-H), 1365s (C-H);

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -110.37 (d,  $J = 9.5$  Hz, 2F,  $\text{F}^{13}$ ), -110.41 (d,  $J = 9.3$  Hz, 2F,  $\text{F}^{11}$ );

MS (TOF  $\text{ES}^+$ ):  $m/z$  (%): 924.1 (100)  $[\text{M}+\text{H}]^+$ ;

HRMS ( $\text{ES}^+$ ):  $[\text{M}+\text{H}]^+$  calcd. For  $\text{C}_{44}\text{H}_{34}\text{N}_4\text{O}_8\text{F}_4$   $^{102}\text{Ru}$ , 924.1356; found, 924.1372.

### Ruthenium(II) bis(diethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2,2'-bipyridine-4,4'-dicarboxylate) (1b)



A 2 neck round bottom flask fitted with stirrer, condenser and stopcock was charged with **7b** (387 mg, 806  $\mu\text{mol}$ , 4 eq) and  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (123 mg, 202  $\mu\text{mol}$ , 1 eq). The apparatus evacuated and filled with argon before the addition of butyronitrile (10 mL) and *N*-ethylmorpholine (2 mL). The resulting orange solution was degassed with argon for 20 min before heating and stirring at 120  $^\circ\text{C}$ , for 16 h under argon and reduced light. After cooling to rt solvent was removed under reduced pressure and the crude black solid was dried under high vacuum. Ethylene glycol (10 mL) was added and the resulting mixture degassed for 20 min with argon. The reaction mixture was then heated and stirred at 200  $^\circ\text{C}$  for 2 h under argon and reduced light. After cooling to rt, ethylene glycol was removed by vacuum distillation. The crude black mixture was combined with  $\text{H}_2\text{O}$  (100 mL) and  $\text{CH}_2\text{Cl}_2$  (100 mL). The organic phase was separated and the aqueous phase extracted with further portions of  $\text{CH}_2\text{Cl}_2$  (3 x 100 mL). The organic phases were combined, dried ( $\text{MgSO}_4$ ) and solvent removed under reduced pressure. The crude product was purified by column chromatography on silica ( $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$  10:0  $\rightarrow$  9:1) to yield a black solid (175 mg, 161  $\mu\text{mol}$ , 65%).  $R_f = 0.89$  ( $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$  9:1, on silica).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.99 (s, 2H,  $\text{H}^5$ ), 8.89 (d,  $J = 1.2$  Hz, 2H,  $\text{H}^3$ ), 8.86 (d,  $J = 0.7$  Hz, 2H,  $\text{H}^{3'}$ ), 7.50 (dd,  $J = 5.7, 1.6$  Hz, 2H,  $\text{H}^{5'}$ ), 7.44 (d,  $J = 5.7$  Hz, 2H,  $\text{H}^6$ ), 5.45 (d,  $J = 10.0$  Hz, 2H,  $\text{H}^{14}$ ), 4.63 (q,  $J = 7.1$  Hz, 4H,  $\text{H}^8$ ), 4.43 (q,  $J = 7.1$  Hz, 4H,  $\text{H}^{8'}$ ), 1.59 (t,  $J = 7.1$  Hz, 6H,  $\text{H}^9$ ), 1.39 (t,  $J = 7.1$  Hz, 6H,  $\text{H}^{9'}$ );

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.6 (s,  $\text{C}^{15}$ ), 165.5 (s,  $\text{C}^7$ ), 163.9 (s,  $\text{C}^{7'}$ ), 159.0 (s,  $\text{C}^6$ ), 158.6 (d,  $J = 267.7$  Hz,  $\text{C}^{13}$ ), 157.7 (d,  $J = 281.0$  Hz,  $\text{C}^{11}$ ), 155.8 (s,  $\text{C}^2$ ), 151.3 (s,  $\text{C}^{2'}$ ), 150.1 (s,  $\text{C}^6$ ), 136.4 (s,  $\text{C}^4$ ), 131.64 (s,  $\text{C}^{4'}$ ), 128.2 (s,  $\text{C}^{10}$ ), 124.7 (s,  $\text{C}^{5'}$ ), 122.0 (s,  $\text{C}^{3'}$ ), 120.7 (d,  $J = 19.5$  Hz,  $\text{C}^5$ ), 118.2 (s,  $\text{C}^3$ ), 116.4 (d,  $J = 15.1$  Hz,  $\text{C}^{14}$ ) 62.58 (s,  $\text{C}^{8'}$ ), 62.40 (s,  $\text{C}^8$ ), 14.65 (s,  $\text{C}^9$ ), 14.40 (s,  $\text{C}^{9'}$ ). Expected signals for  $\text{C}^{12}$  (approx. 120 (tq,  $J = 30, 30$  Hz)) and  $\text{C}^{16}$  (approx. 120 (tq,  $J = 250, 10$  Hz)) not observed due to high level of splitting giving a very weak signal.  $^1\text{H}$ ,  $^{19}\text{F}$ , HRMS and crystal data confirm structure is correct;

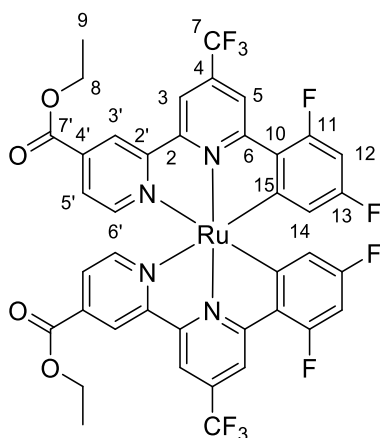
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -54.92 (t,  $J = 22.6$  Hz, 6F,  $\text{F}^{12}$ ), -113.32 (qd,  $J = 22.6, 4.1$  Hz, 2F,  $\text{F}^{13}$ ), -113.75 (qd,  $J = 22.7, 4.2$  Hz, 2F,  $\text{F}^{11}$ );

IR(film,  $\text{cm}^{-1}$ ): 3208w (C-H), 3074w (C-H), 2989s (C-H), 2957s (C-H), 2908w (C-H), 1710s (C=O), 1603s (C=C), 1535s (C=C), 1444s (C=C), 1300 (C-O);

MS (TOF  $\text{ES}^+$ ):  $m/z$  (%): 1060.1 (100)  $[\text{M}+\text{H}]^+$ ;

HRMS ( $\text{ES}^+$ ):  $[\text{M}+\text{H}]^+$  calcd. For  $\text{C}_{46}\text{H}_{32}\text{N}_4\text{O}_8\text{F}_{10}^{102}\text{Ru}$ , 1060.1104; found, 1060.1080.

### Ruthenium(II) bis(ethyl-6-(2,4-difluorophenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate) (1c)



A 2 neck round bottom flask fitted with stirrer, condenser and stopcock was charged with **7c** (33.0 mg, 81.0  $\mu\text{mol}$ , 4.0 eq) and  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (12.0 mg, 20.0  $\mu\text{mol}$ , 1.0 eq). The apparatus evacuated and filled with argon before the addition of butyronitrile (5 mL) and *N*-ethylmorpholine (0.5 mL). The resulting orange solution was degassed with argon for 20 min before heating and

stirring at 120 °C, for 16 h under argon and reduced light. After cooling to rt solvent was removed under reduced pressure and the crude black solid was dried under high vacuum. Ethylene glycol (5 mL) was added and the resulting mixture degassed for 20 min with argon. The reaction mixture was then heated and stirred at 200 °C for 2 h under argon and reduced light. After cooling to rt, ethylene glycol was removed by vacuum distillation. The crude black mixture was combined with H<sub>2</sub>O (50 mL) and CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The organic phase was separated and the aqueous phase extracted with further portions of CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL). The organic phases were combined, dried (MgSO<sub>4</sub>) and solvent removed under reduced pressure. The crude product was purified by column chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub> and then hexane:EtOAc 8:2) to yield a black solid (10.2 mg, 11.1 μmol, 27%). *R<sub>f</sub>* = 0.31 (hexane:EtOAc 8:2 on silica).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.76 (t, *J* = 1.1 Hz, 2H, H<sup>3'</sup>), 8.57 (s, 2H, H<sup>5</sup>), 8.39 (s, 2H, H<sup>3</sup>), 7.48 (d, *J* = 1.2 Hz, 4H, H<sup>5'</sup>, H<sup>6'</sup>), 6.29 – 6.13 (m, 2H, H<sub>14</sub>), 5.32 (dd, *J* = 7.8, 2.3 Hz, 2H, H<sup>12</sup>), 4.42 (q, *J* = 7.1 Hz, 4H, H<sup>8</sup>), 1.39 (t, *J* = 7.1 Hz, 6H, H<sup>9</sup>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 192.12 (s, C<sup>15</sup>), 163.90 (s, C<sup>7'</sup>), 162.64 (dd, C<sup>11</sup>), 161.32 (dd, *J* = 293.5, 9.6 Hz, C<sup>13</sup>), 154.97 (s, C<sup>2'</sup>), 151.20 (s, C<sup>2</sup>), 150.06 (s, C<sup>6'</sup>), 149.79 (s, C<sup>6</sup>), 135.24 (s, C<sup>4'</sup>), 130.96 (q, *J* = 53.8 Hz, C<sup>4</sup>), 126.65 (s, C<sup>10</sup>), 124.45 (s, C<sup>5'</sup>), 123.87 (q, C<sup>7</sup>), 121.70 (s, C<sup>3'</sup>), 115.78 (dd, *J* = 18.3, 3.5 Hz, C<sup>12</sup>), 114.92 (d, *J* = 14.9 Hz, C<sup>5</sup>), 112.85 (d, *J* = 3.0 Hz, C<sup>3</sup>), 96.55 (t, *J* = 27.1 Hz, C<sup>14</sup>), 62.32 (s, C<sup>8</sup>), 14.25 (s, C<sup>9</sup>);

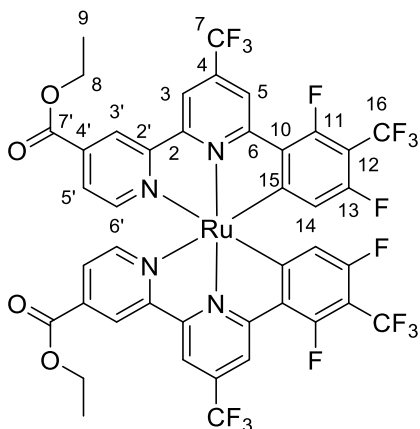
<sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ -63.04 (s, 6F, F<sup>7</sup>), -109.44 (dd, *J* = 17.5, 9.3 Hz, 2F, F<sup>11</sup>), -109.95 (t, *J* = 11.9 Hz, 2F, F<sup>13</sup>);

IR(film, cm<sup>-1</sup>): 3089s (C-H), 2989s (C-H), 2944s (C-H), 2910s (C-H), 2861s (C-H), 1713 (C=O), 1595s (C=C), 1554 (C=C), 1539s (C=C), 1431s (C-H), 1395s (C-H), 1324s (C-H), 1252 (C-O);

MS (TOF ES<sup>+</sup>): *m/z* (%): 916.6 (100) [M+H]<sup>+</sup>;

HRMS (ES<sup>+</sup>): [M+H]<sup>+</sup> calcd. for C<sub>40</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>F<sub>10</sub>, 916.0681; found, 916.0695.

**Ruthenium(II) bis(ethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2,2'-bipyridine-4'-carboxylate) (1d)**



A 2 neck round bottom flask fitted with stirrer, condenser and stopcock was charged with **7d** (50 mg, 105  $\mu\text{mol}$ , 4 eq) and  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (15.9 mg, 26  $\mu\text{mol}$ , 1 eq). The apparatus was evacuated and filled with argon before the addition of butyronitrile (10 mL) and *N*-ethylmorpholine (2 mL). The resulting orange solution was degassed with argon for 20 min before heating and stirring at 120  $^\circ\text{C}$ , for 16 h under argon and reduced light. After cooling to rt solvent was removed under reduced pressure and the crude black solid was dried under high vacuum. Ethylene glycol (10 mL) was added and the resulting mixture degassed for 20 min with argon. The reaction mixture was then heated and stirred at 200  $^\circ\text{C}$  for 2 h under argon and reduced light. The crude black mixture was combined with  $\text{H}_2\text{O}$  (100 mL) and  $\text{CH}_2\text{Cl}_2$  (100 mL). The organic phase was separated and the aqueous phase extracted with further portions of  $\text{CH}_2\text{Cl}_2$  (3 x 100 mL). The organic phases were combined, dried ( $\text{MgSO}_4$ ) and solvent removed under reduced pressure. The crude product was purified by column chromatography on silica ( $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$  10:0  $\rightarrow$  9:1) to yield a black solid (44 mg, 41.9  $\mu\text{mol}$ , 80%).  $R_f = 0.91$  ( $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$  9:1, on silica).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (s, 2H,  $\text{H}^{3'}$ ), 8.64 (s, 2H,  $\text{H}^5$ ), 8.46 (s, 2H,  $\text{H}^3$ ), 7.56 (dd,  $J = 5.7, 1.5$  Hz, 1H,  $\text{H}^{5'}$ ), 7.47 (d,  $J = 5.7$  Hz, 2H,  $\text{H}^{6'}$ ), 5.47 (d,  $J = 10.0$  Hz, 2H,  $\text{H}^{14}$ ), 4.43 (q,  $J = 7.1$  Hz, 4H,  $\text{H}^8$ ), 1.39 (t,  $J = 7.1$  Hz, 6H,  $\text{H}^9$ );

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.88 (d,  $J = 5.1$  Hz,  $\text{C}^{15}$ ), 163.69 (s,  $\text{C}^{7'}$ ), 159.69 (d,  $J = 5.9$  Hz,  $\text{C}^6$ ), 158.80 (d,  $J = 270.9$  Hz,  $\text{C}^{13}$ ), 157.95 (d,  $J = 273.2$  Hz,  $\text{C}^{11}$ ), 155.15 (s,  $\text{C}^{2'}$ ), 151.75 (s,  $\text{C}^2$ ), 150.23 (s,  $\text{C}^{6'}$ ), 136.53 (s,  $\text{C}^{4'}$ ), 132.16 (q,  $J = 34.0$  Hz,  $\text{C}^4$ ), 125.13 (s,  $\text{C}^{5'}$ ), 127.89 – 122.24 (m,  $\text{C}^{10}$ ), 122.64 (q,  $J = 272.9$  Hz,  $\text{C}^7$ ), 122.12 (s,  $\text{C}^{3'}$ ), 117.05 (d,  $J = 19.2$  Hz,  $\text{C}^5$ ), 116.52 (d,  $J = 14.7$  Hz,  $\text{C}^{14}$ ), 114.12 (s,  $\text{C}^3$ ), 62.69 (s,  $\text{C}^8$ ), 14.36 (s,  $\text{C}^9$ ). Expected signals for  $\text{C}_{12}$  (approx. 120 (tq,  $J = 30, 30$  Hz)) and  $\text{C}_{16}$  (approx. 120 (tq,  $J = 250, 10$  Hz)) not observed due to high level of splitting giving a very weak signal.  $^1\text{H}$ ,  $^{19}\text{F}$ , HRMS and crystal data confirm structure is correct;

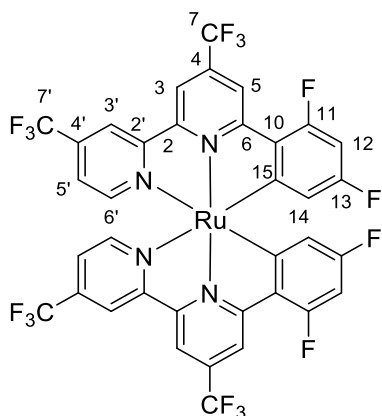
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -55.03 (t,  $J = 22.7$  Hz, 6F,  $\text{F}^{16}$ ), -63.21 (s,  $J = 6.4$  Hz, 6F,  $\text{F}^7$ ), -112.39 (qd,  $J = 22.4, 4.6$  Hz, 2F,  $\text{F}^{11}$ ), -113.26 (qd,  $J = 22.9, 4.6$  Hz, 2F,  $\text{F}^{13}$ );

IR(film,  $\text{cm}^{-1}$ ): 3129w (C-H), 3097w (C-H), 2986s (C-H), 2930s (C-H), 2867s (C-H), 1725 (C=O), 1604s (C=C), 1538(C=C), 1467w (C-H), 1432s (C-H), 1403s (C-H), 1369s (C-H), 1305s (C-H), 1241 (C-O);

MS (TOF  $\text{ES}^+$ ):  $m/z$  (%): 1052.0 (100)  $[\text{M}]^+$ ;

HRMS ( $\text{ES}^+$ ):  $[\text{M}+\text{H}]^+$  calcd. For  $\text{C}_{42}\text{H}_{22}\text{N}_4\text{O}_4\text{F}_{16}^{102}\text{Ru}$ , 1052.0429; found, 1052.0424.

### Ruthenium(II) bis(6-(2,4-difluorophenyl)-4,4'-bis(trifluoromethyl)-2,2'-bipyridine) (1e)



A 2 neck round bottom flask fitted with stirrer, condenser and stopcock was charged with **7e** (70.0 mg, 170  $\mu\text{mol}$ , 4.0 eq), and  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (26.5 mg, 42.5  $\mu\text{mol}$ , 1.0 eq). The apparatus evacuated and filled with argon before the addition of butyronitrile (5 mL) and *N*-ethylmorpholine (0.5 mL). The resulting orange solution was degassed with argon for 20 min before heating and stirring at 120  $^\circ\text{C}$ , for 16 h under argon and reduced light. After cooling to rt solvent was removed under reduced pressure and the crude black solid was dried under high vacuum. Ethylene glycol (5 mL) was added and the resulting mixture degassed for 20 min with argon. The reaction mixture was then heated and stirred at 200  $^\circ\text{C}$  for 2 h under argon and reduced light. After cooling to rt, ethylene glycol was removed by vacuum distillation. The crude black mixture was combined with  $\text{H}_2\text{O}$  (50 mL) and  $\text{CH}_2\text{Cl}_2$  (50 mL). The organic phase was separated and the aqueous phase extracted with further portions of  $\text{CH}_2\text{Cl}_2$  (3 x 50 mL). The organic phases were combined, dried ( $\text{MgSO}_4$ ) and solvent removed under reduced pressure. The crude product was purified by chromatography on silica (hexane:  $\text{CH}_2\text{Cl}_2$  3:0  $\rightarrow$  3:1) to yield a black solid (22.6 mg, 24.9  $\mu\text{mol}$ , 32%).  $R_f = 0.35$  (hexane:  $\text{CH}_2\text{Cl}_2$  3:1, on silica).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.52 (s, 2H,  $\text{H}^3$ ), 8.34 (s, 2H,  $\text{H}^{3'}$ ), 8.28 (s, 2H $^5$ ), 7.48 (d,  $J = 5.8$  Hz, 2H,  $\text{H}^6$ ), 7.09 (dd,  $J = 5.8, 1.3$  Hz, 2H,  $\text{H}^{5'}$ ), 6.16 (ddd,  $J = 12.4, 9.2, 2.3$  Hz, 2H,  $\text{H}^{12}$ ), 5.25 (dd,  $J = 7.8, 2.3$  Hz, 2H,  $\text{H}^{14}$ );

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.5 (s,  $\text{C}^{15}$ ), 162.7 (dd,  $J = 258.8, 11.1$  Hz,  $\text{C}^{11}$ ), 161.6 (dd,  $J = 260.8, 12.1$  Hz,  $\text{C}^{13}$ ), 160.1 – 159.9 (m,  $\text{C}^2$ ), 155.3 (s,  $\text{C}^{2'}$ ), 150.7 (s,  $\text{C}^6$ ), 150.6 (s,  $\text{C}^{6'}$ ), 136.8 – 134.8 (m,  $\text{C}^4$ ), 131.2 (q,  $J = 34.1$  Hz,  $\text{C}^{4'}$ ), 125.8 (q,  $J = 281.6$  Hz,  $\text{C}^7$ ), 124.4 (q,  $J = 273.0$  Hz,  $\text{C}^{7'}$ ), 121.0 (s,  $\text{C}^{10}$ ), 118.0 (s,  $\text{C}^5$ ), 116.1 (dd,  $J = 18.8, 3.1$  Hz,  $\text{C}^{12}$ ), 115.0 (dd,  $J = 14.5, 1.8$  Hz), 113.1 (d,  $J = 2.9$  Hz), 96.8 (t,  $J = 26.7$  Hz,  $\text{C}^{12}$ );

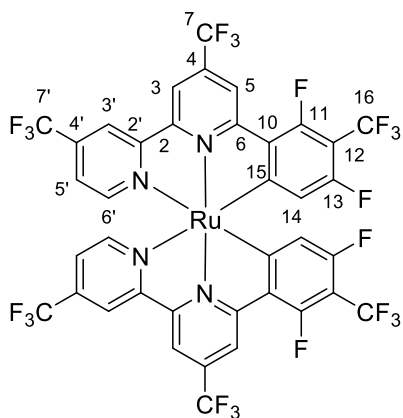
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.12 (s, 6F,  $\text{F}^7$ ), -64.39 (s, 6F,  $\text{F}^{7'}$ ), -108.89 (dd,  $J = 17.5, 9.5$  Hz, 2F,  $\text{F}^{11}$ ), -109.61 (ddd,  $J = 12.3, 10.0, 2.1$  Hz, 2F,  $\text{F}^{13}$ );

IR(film,  $\text{cm}^{-1}$ ): 3113s (C-H), 3052s (C-H), 2920s (C-H), 2851s (C-H), 1593s (C=C), 1548 (C=C), 1432s (C-H), 1393s (C-H);

MS (TOF  $\text{ES}^+$ ):  $m/z$  (%): 907.9 (100)  $[\text{M}]^+$ ;

HRMS ( $\text{ES}^+$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{36}\text{H}_{14}\text{N}_4\text{F}_{16}^{102}\text{Ru}$ , 908.0006; found, 908.0031.

### Ruthenium(II) bis(6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4,4'-bis(trifluoromethyl)-2,2'-bipyridine) (1f)



A 2 neck round bottom flask fitted with stirrer, condenser and stopcock was charged with **7f** (50.0 mg, 106  $\mu\text{mol}$ , 4.0 eq), and  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]$  (16.2 mg, 26.0  $\mu\text{mol}$ , 1.0 eq). The apparatus evacuated and filled with argon before the addition of butyronitrile (5 mL) and *N*-ethylmorpholine (0.5 mL). The resulting orange solution was degassed with argon for 20 min before heating and stirring at 120  $^\circ\text{C}$ , for 16 h under argon and reduced light. After cooling to rt solvent was removed under reduced pressure and the crude black solid was dried under high vacuum. Ethylene glycol (5 mL) was added and the resulting mixture degassed for 20 min with argon. The reaction mixture was

then heated and stirred at 200 °C for 2 h under argon and reduced light. After cooling to rt, ethylene glycol was removed by vacuum distillation. The crude black mixture was combined with H<sub>2</sub>O (50 mL) and CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The organic phase was separated and the aqueous phase extracted with further portions of CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL). The organic phases were combined, dried (MgSO<sub>4</sub>) and solvent removed under reduced pressure. The crude product was purified by chromatography on silica (hexane: CH<sub>2</sub>Cl<sub>2</sub> 3:0 → 3:1) to yield a black solid (9.3 mg, 8.91 μmol, 16%). *R<sub>f</sub>* = 0.40 (hexane: CH<sub>2</sub>Cl<sub>2</sub> 3:1, on silica).

<sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN:CDCl<sub>3</sub>, 2:1) δ 8.60 (s, 4H, H<sup>3,3'</sup>), 8.40 (s, 2H, H<sup>5</sup>), 7.44 (d, *J* = 5.4 Hz, 2H, H<sup>6</sup>), 7.11 (d, *J* = 5.5 Hz, 2H, H<sup>5'</sup>), 5.37 (d, *J* = 10.3 Hz, 2H<sup>12</sup>);

<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN:CDCl<sub>3</sub>, 2:1) δ 200.5 (s, C<sup>15</sup>), 160.3 (d, *J* = 6.4 Hz, C<sup>11</sup>), 159.5 (d, *J* = 270.3 Hz, C<sup>11</sup>), 158.6 (d, *J* = 266.1 Hz, C<sup>13</sup>), 157.0 (s, C<sup>2,2'</sup>), 153.22 (s, C<sup>6'</sup>), 152.5 (s, C<sup>6</sup>), 137.8 (q, *J* = 35.1 Hz, C<sup>4</sup>), 132.8 (q, *J* = 35.1 Hz, C<sup>4'</sup>), 129.4 (s, C<sup>5</sup>), 126.8 – 124.6 (m, C<sup>10</sup>), 125.5 – 125.3 (m, C<sup>7'</sup>), 123.1 (s, C<sup>3</sup>), 122.7 (s, C<sup>5</sup>), 120.8 (s, C<sup>5</sup>), 117.7 (s, C<sup>3</sup>), 117.1 (s, C<sup>14</sup>);

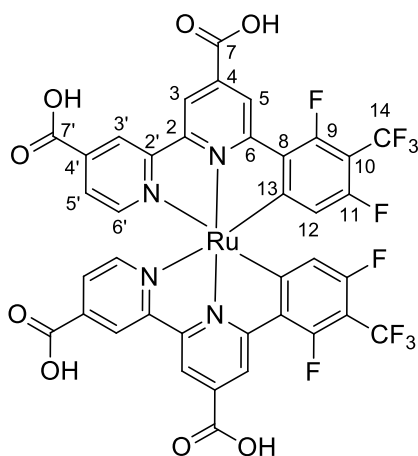
<sup>19</sup>F NMR (282 MHz, CD<sub>3</sub>CN:CDCl<sub>3</sub>, 2:1) δ -55.09 (t, *J* = 22.8 Hz, 6F, F<sup>16</sup>), -63.46 (s, 6F, F<sup>7</sup>), -64.61 (s, 6F, F<sup>7'</sup>), -114.40 (qd, *J* = 22.4, 3.9 Hz, 2F, F<sup>11</sup>), -114.73 (qd, *J* = 23.2, 3.9 Hz, 2F, F<sup>13</sup>);

IR(film, cm<sup>-1</sup>): 3219w (C-H), 3128w (C-H), 2925s (C-H), 2857s (C-H), 1607s (C=C), 1539 (C=C), 1435s (C-H), 1404s (C-H);

MS (TOF ES<sup>+</sup>): *m/z* (%): 1043.8 (100) [M]<sup>+</sup>;

HRMS (ES<sup>+</sup>): [M+H]<sup>+</sup> calcd. for C<sub>38</sub>H<sub>12</sub>N<sub>4</sub>F<sub>22</sub><sup>102</sup>Ru, 1043.9754; found, 1043.9761.

**Ruthenium(II) bis(6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2,2'-bipyridine-4,4'-dicarboxylic acid) (10)**



A 50 mL 2 neck round bottom flask fitted with condenser, stopcock and stirrer, was charged with **1b** (20.0 mg, 18.9  $\mu\text{mol}$ ). The apparatus was then evacuated and filled with argon. KOH (2M, aq, 1 mL) and acetone (5 mL) were added and the resulting mixture was degassed with argon for 20 min before heating to 60 °C and stirring for 16 h under argon and reduced light conditions. After cooling to rt the mixture was treated with HCl (1M) until a black precipitate formed. The solid was collected by filtration, washed with H<sub>2</sub>O, hexane, and CH<sub>2</sub>Cl<sub>2</sub>. After drying the filtrand was removed from the filter by dissolving in MeOH. Solvent was removed under reduced pressure to yield a black solid (15.5 mg, 16.3  $\mu\text{mol}$ , 86%).

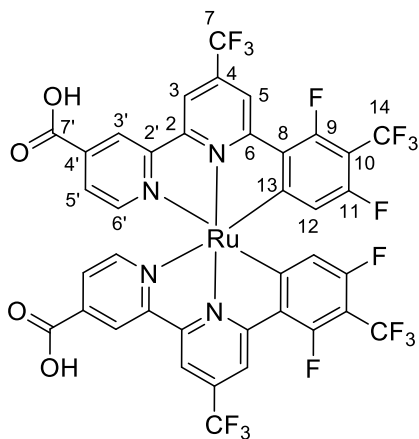
<sup>1</sup>H NMR (300 MHz, MeOD)  $\delta$  8.95 (d,  $J$  = 6.0 Hz, 2H), 8.88 (s, 1H), 7.58 (d,  $J$  = 5.7 Hz, 1H), 7.50 (d,  $J$  = 5.4 Hz, 1H), 5.45 (d,  $J$  = 10.3 Hz, 1H).

<sup>19</sup>F NMR (282 MHz, MeOD)  $\delta$  -56.17 (t,  $J$  = 22.9 Hz, 6F, F<sup>14</sup>), -116.38 (qd,  $J$  = 22.4, 2.3 Hz, 2F, F<sup>9</sup>), -116.76 (qd,  $J$  = 23.3, 2.1 Hz, 2F, F<sup>11</sup>).

MS (TOF ES<sup>-</sup>):  $m/z$  (%): 946.97 (100) [M-H]<sup>-</sup>;

HRMS (ES<sup>-</sup>): [M-H]<sup>-</sup> calcd. for C<sub>38</sub>H<sub>15</sub>N<sub>4</sub>F<sub>10</sub><sup>102</sup>Ru, 946.9774; found, 946.9769.

**Ruthenium(II) bis(6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2,2'-bipyridine-4'-carboxylic acid) (11)**



A 50 mL 2 neck round bottom flask fitted with condenser, stopcock and stirrer, was charged with **1d** (16.0 mg, 15.2  $\mu\text{mol}$ ). The apparatus was then evacuated and filled with argon. KOH (2M, aq, 1 mL) and acetone (5 mL) were added and the resulting mixture was degassed with argon for 20 min before heating to 60 °C and stirring for 16 h under argon and reduced light conditions. After cooling to rt the mixture was treated with HCl (1M) until a black precipitate formed. The solid was collected by filtration, washed with H<sub>2</sub>O, hexane, and CH<sub>2</sub>Cl<sub>2</sub>. After drying the filtrand was

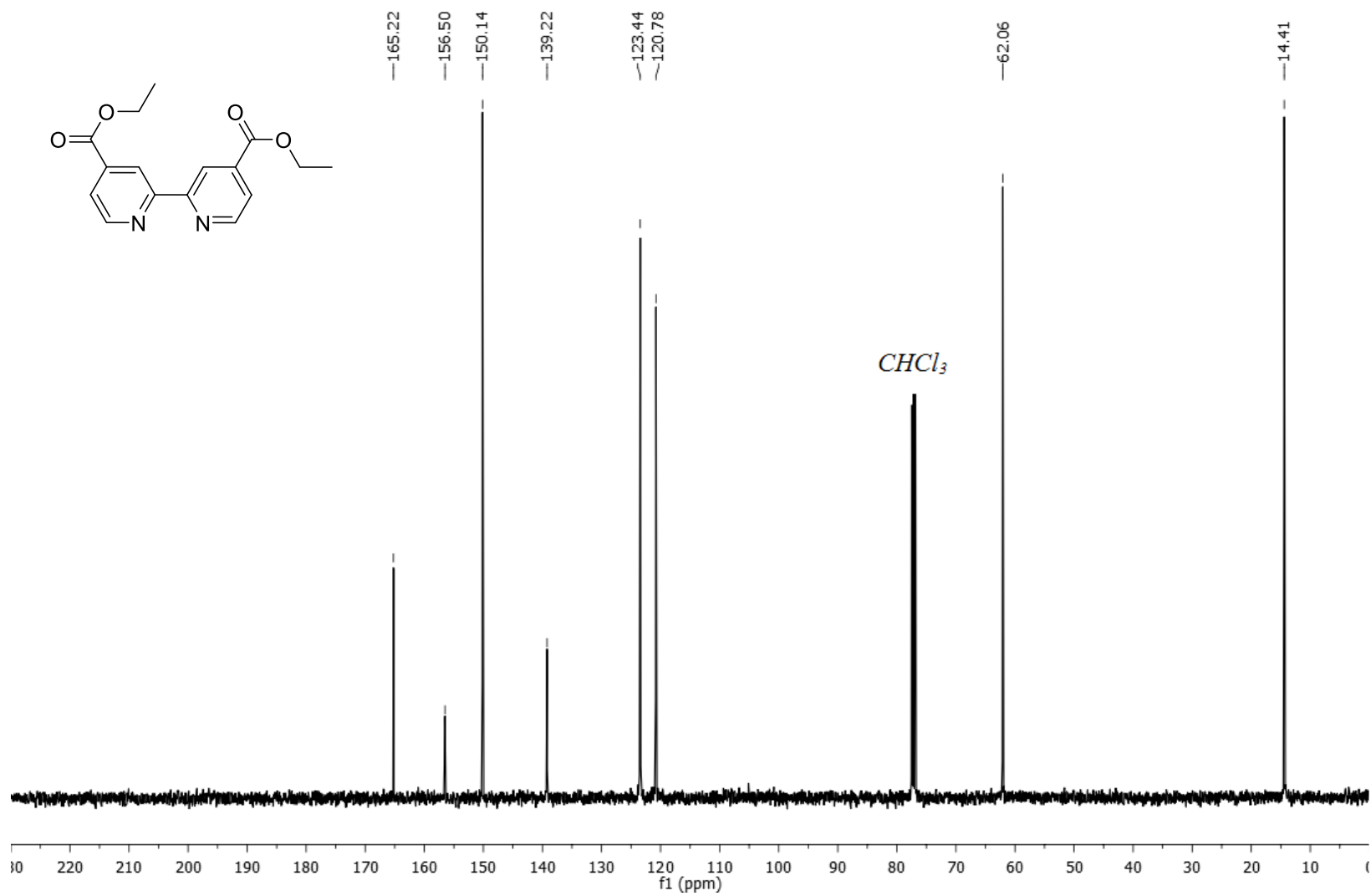
removed from the filter by dissolving in MeOH. Solvent was removed under reduced pressure to yield a black solid (12.1 mg, 12.9  $\mu\text{mol}$ , 85%).

$^1\text{H}$  NMR (300 MHz, MeOD)  $\delta$  9.27 (s, 2H, H<sup>3'</sup>), 8.90 (s, 4H, H<sup>3,5</sup>), 7.93 (d,  $J = 5.6$  Hz, 2H, H<sup>6'</sup>), 7.85 (d,  $J = 5.8$  Hz, 2H, H<sup>5'</sup>), 5.79 (d,  $J = 10.0$  Hz, 2H, H<sup>12</sup>);

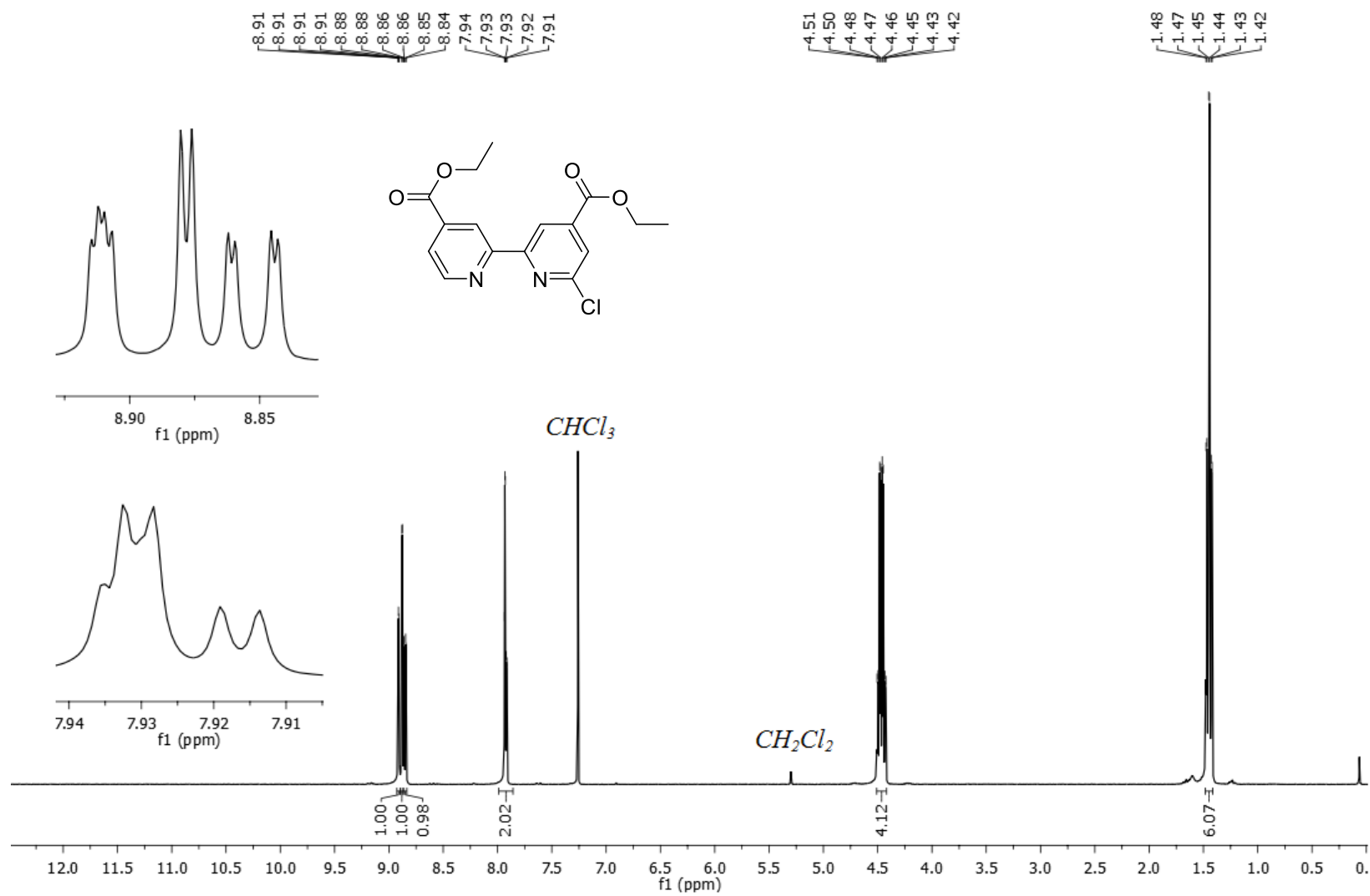
$^{19}\text{F}$  NMR (282 MHz, MeOD)  $\delta$  -55.43 (t,  $J = 22.7$  Hz, 6F, F<sup>14</sup>), -63.77 (s, 6F, F<sup>7</sup>), -113.50 (qd,  $J = 22.3, 4.1$  Hz, 2F, F<sup>9</sup>), -113.97 – -114.61 (m, 2F, F<sup>11</sup>).



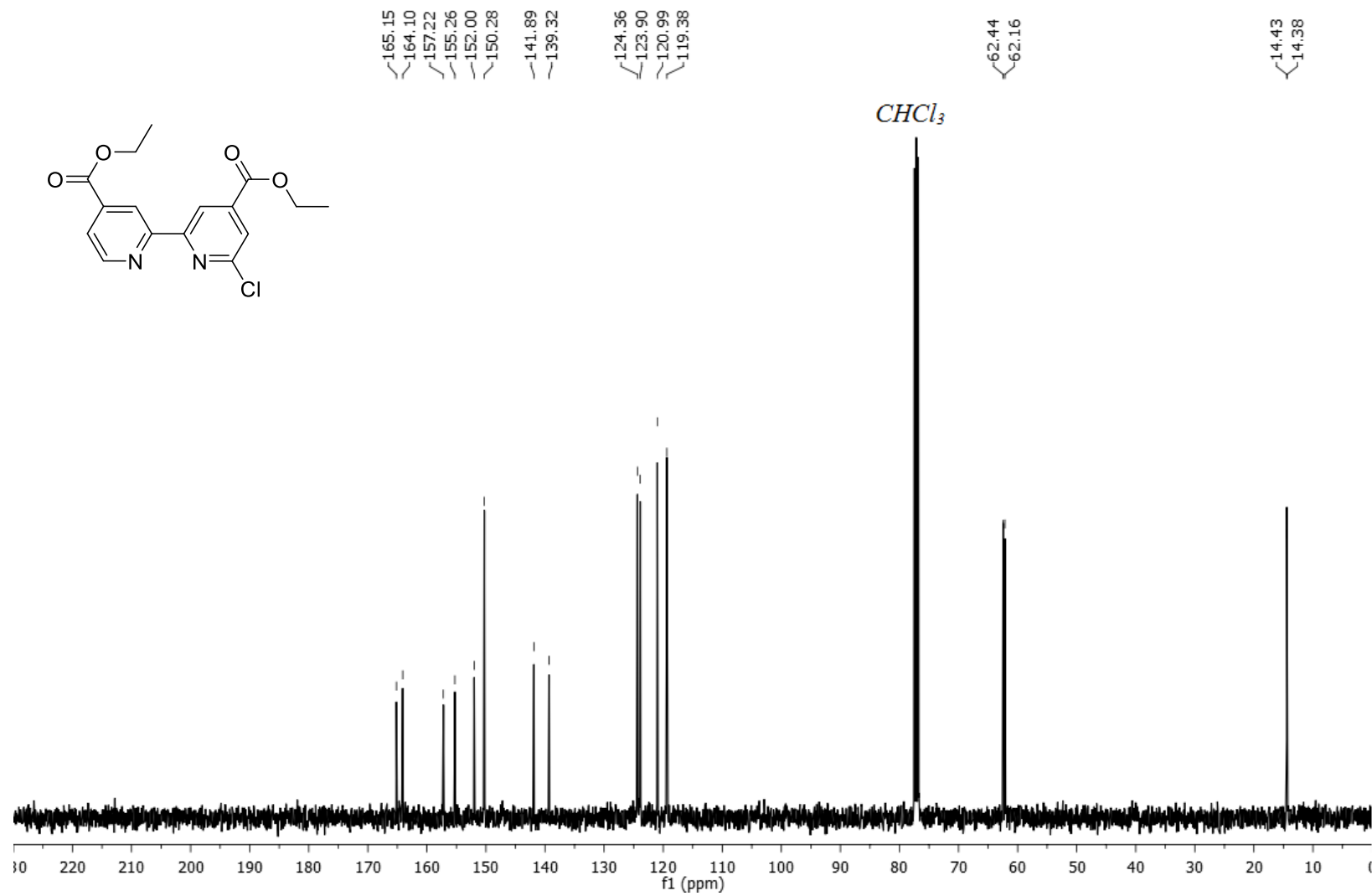
Diethyl-2,2'-bipyridine-4,4'-dicarboxylate (2a) <sup>13</sup>C NMR



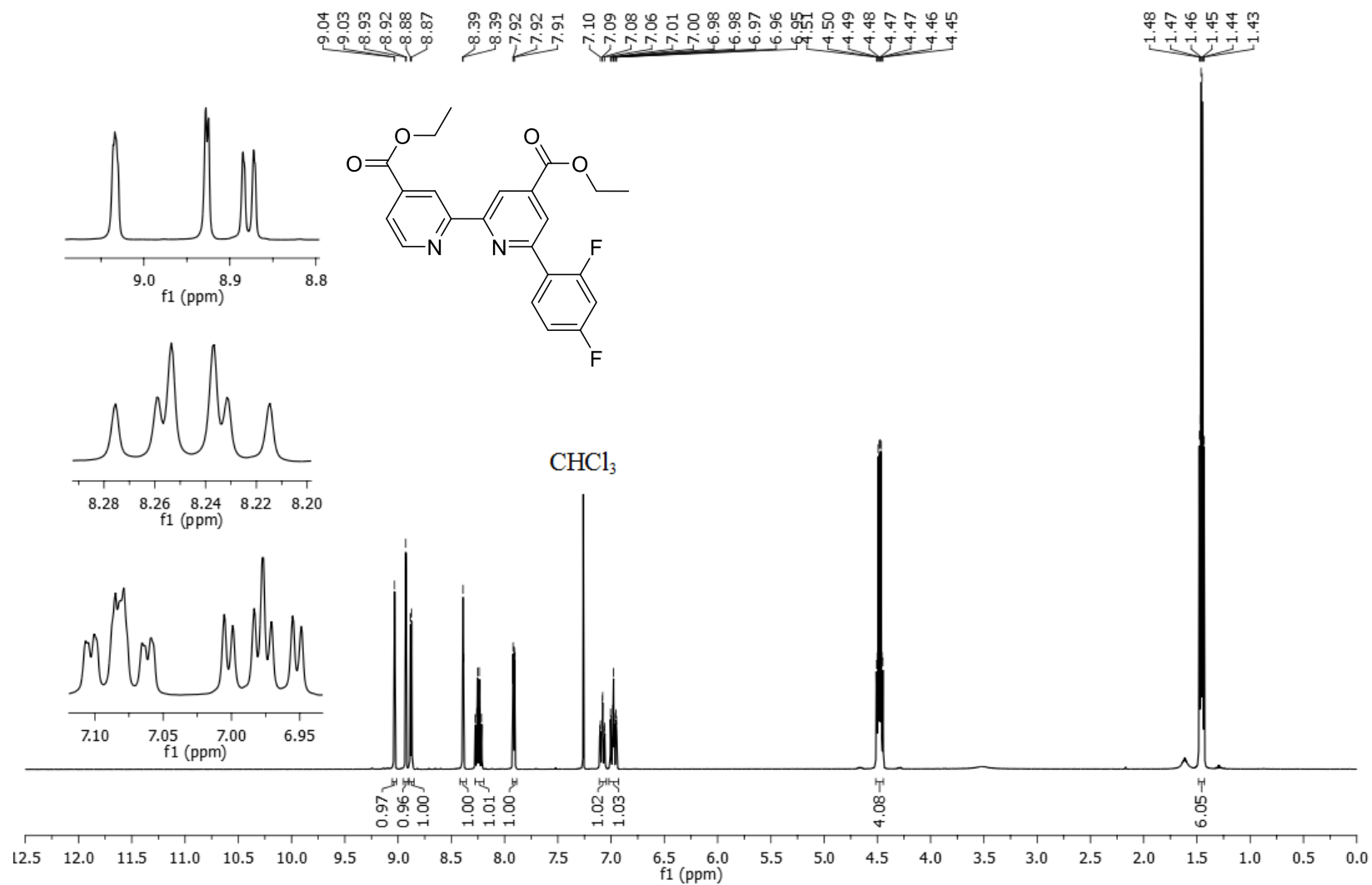
Diethyl-6-chloro-2,2'-bipyridine-4,4'-dicarboxylate (3a) <sup>1</sup>H NMR



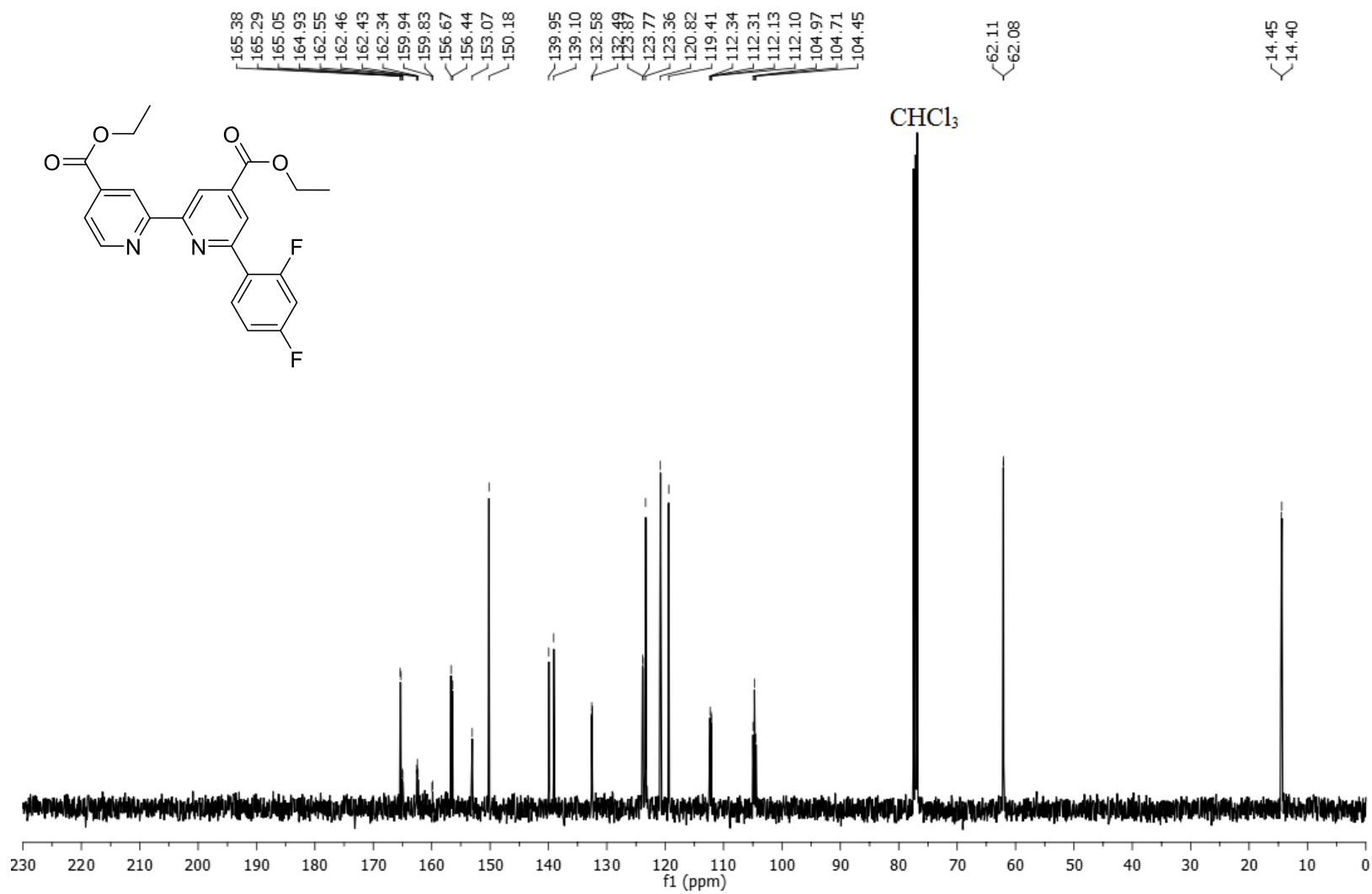
Diethyl-6-chloro-2,2'-bipyridine-4,4'-dicarboxylate (3a) <sup>13</sup>C NMR



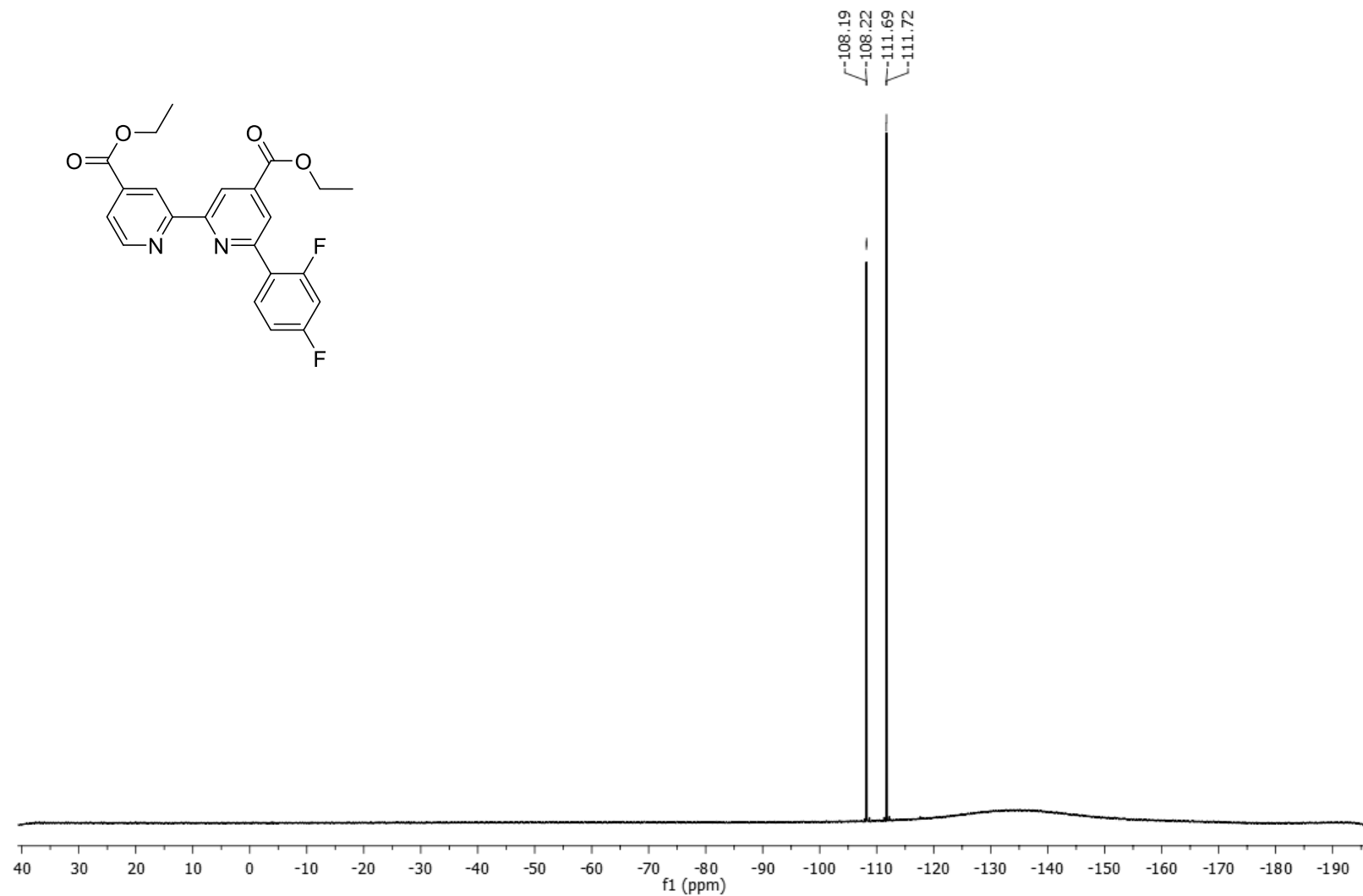
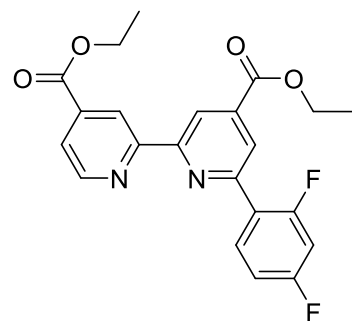
Diethyl-6-(2,4-difluorophenyl)-2,2'-bipyridine-4,4'-dicarboxylate (7a) <sup>1</sup>H NMR



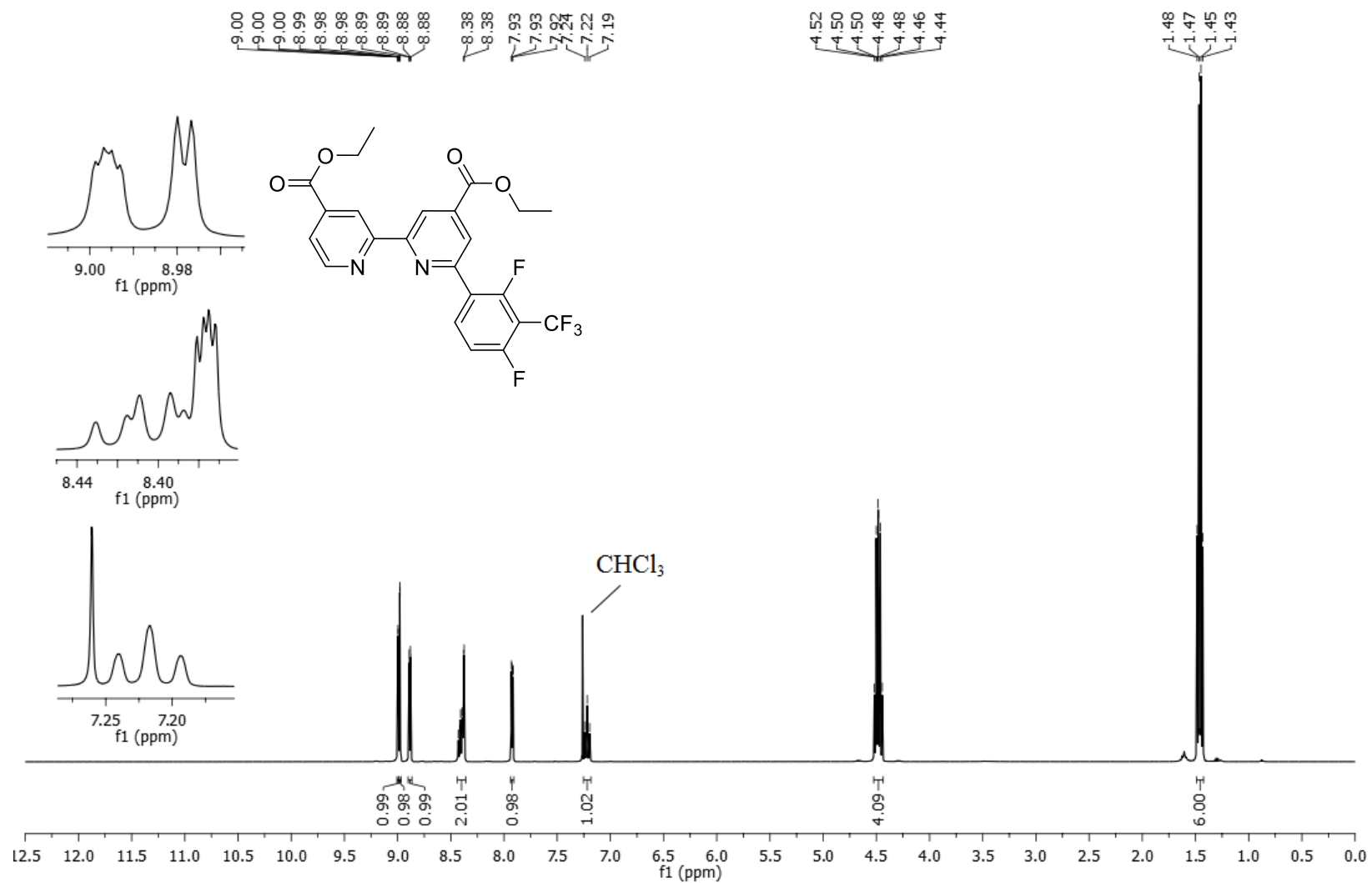
Diethyl-6-(2,4-difluorophenyl)-2,2'-bipyridine-4,4'-dicarboxylate (7a) <sup>13</sup>C NMR



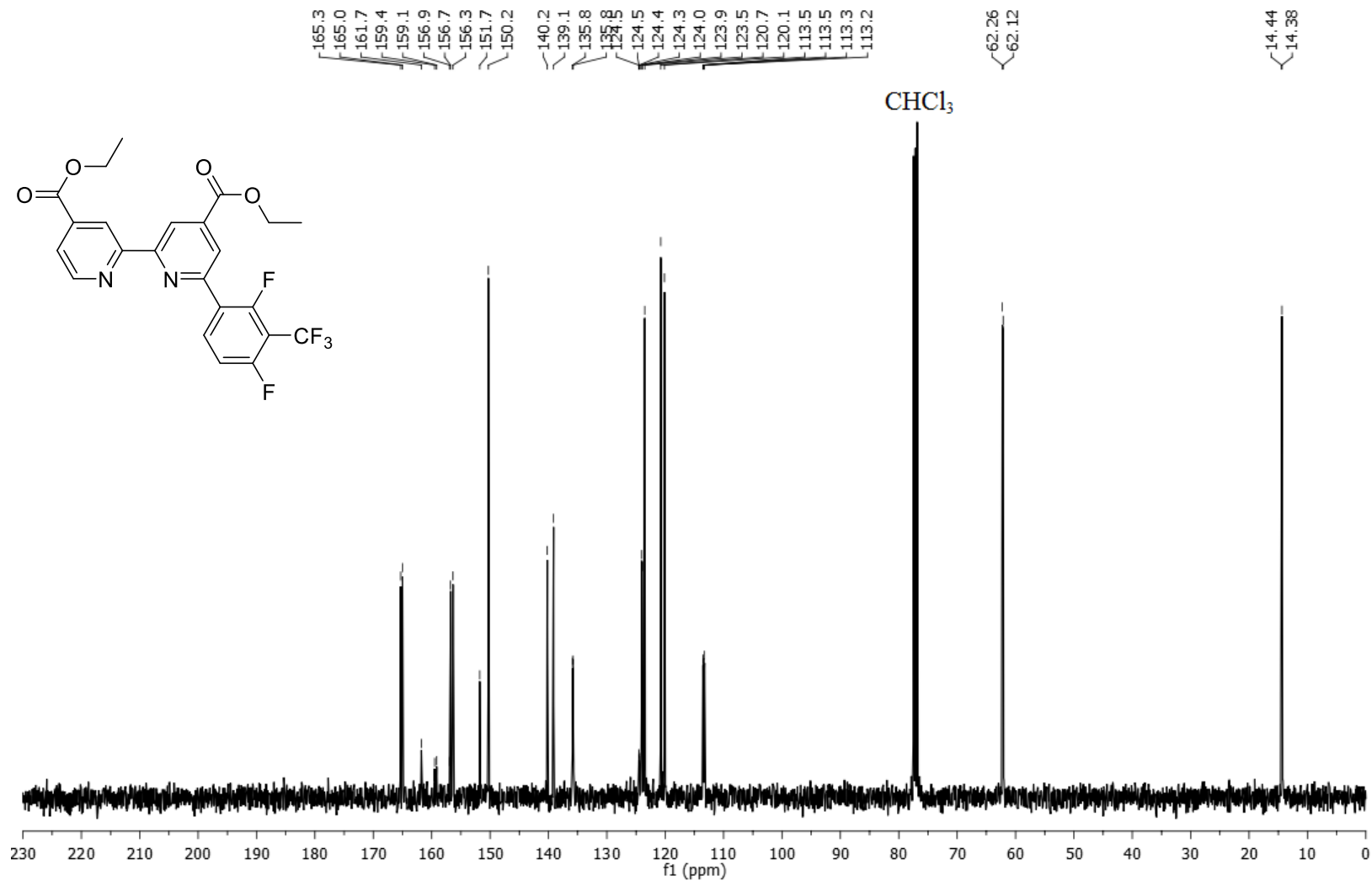
Diethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2,2'-bipyridine-4,4'-dicarboxylate (7a) <sup>19</sup>F NMR



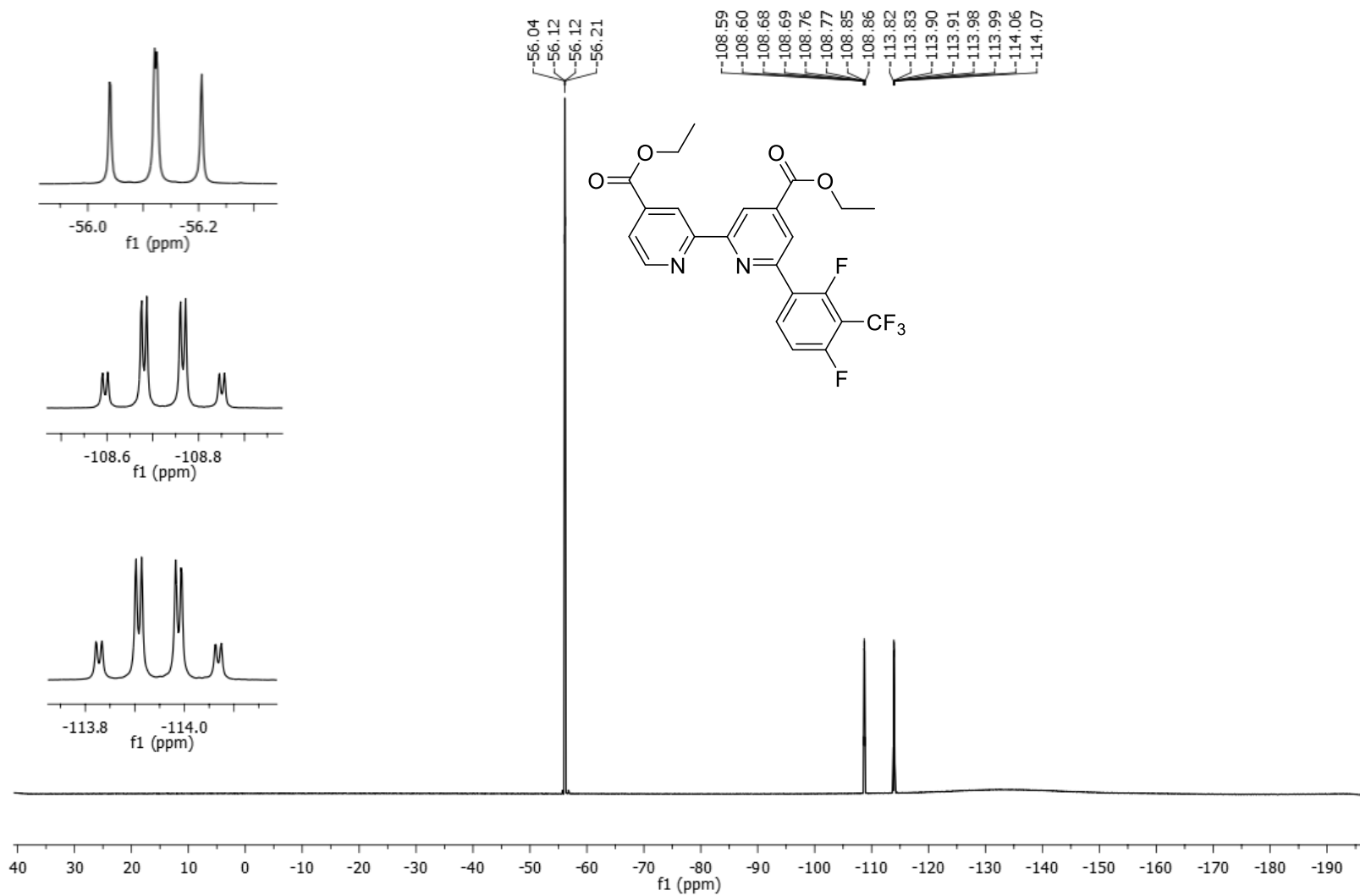
Diethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2,2'-bipyridine-4,4'-dicarboxylate (7b) <sup>1</sup>H NMR



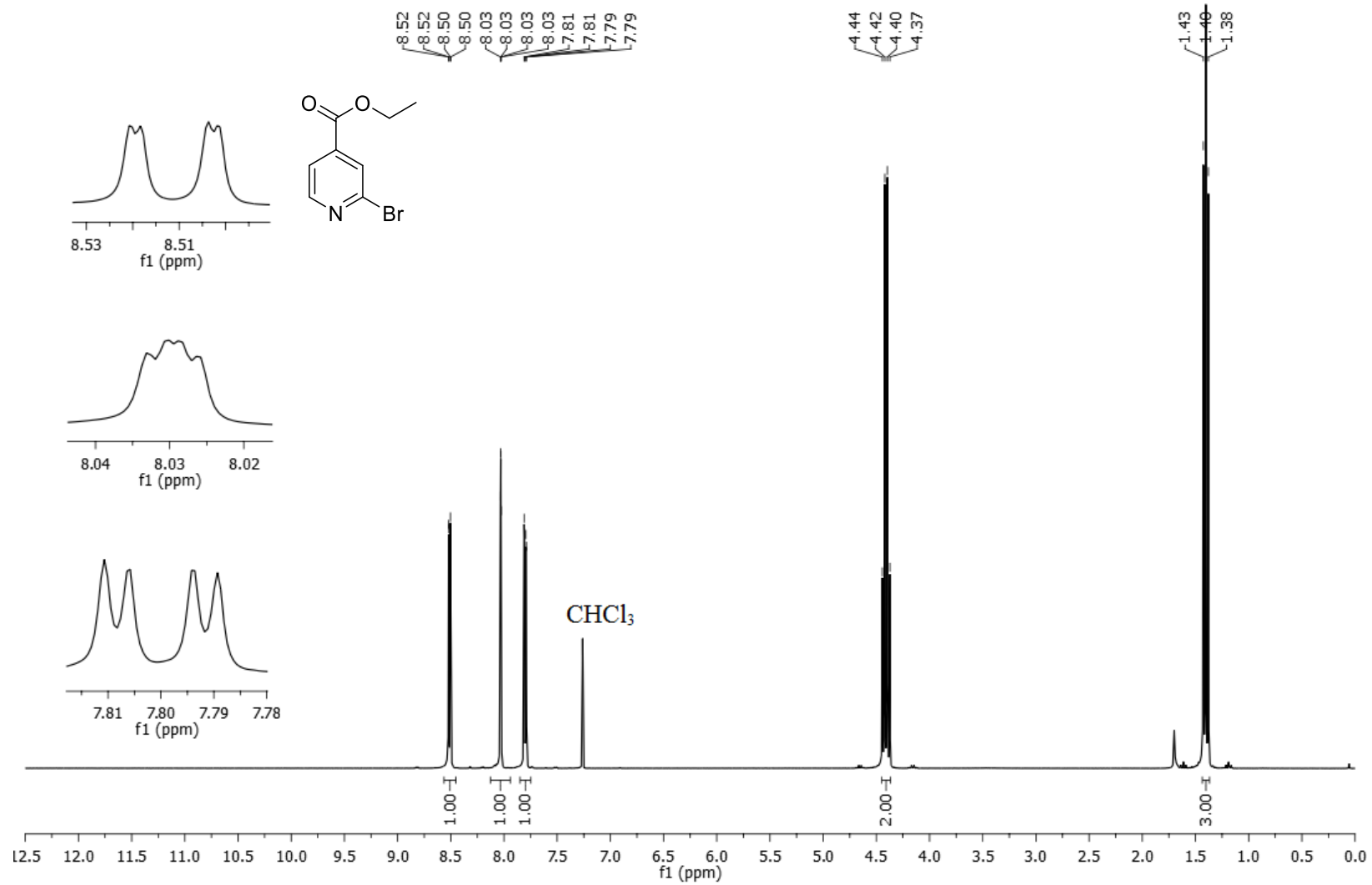
Diethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2,2'-bipyridine-4,4'-dicarboxylate (7b) <sup>13</sup>C NMR



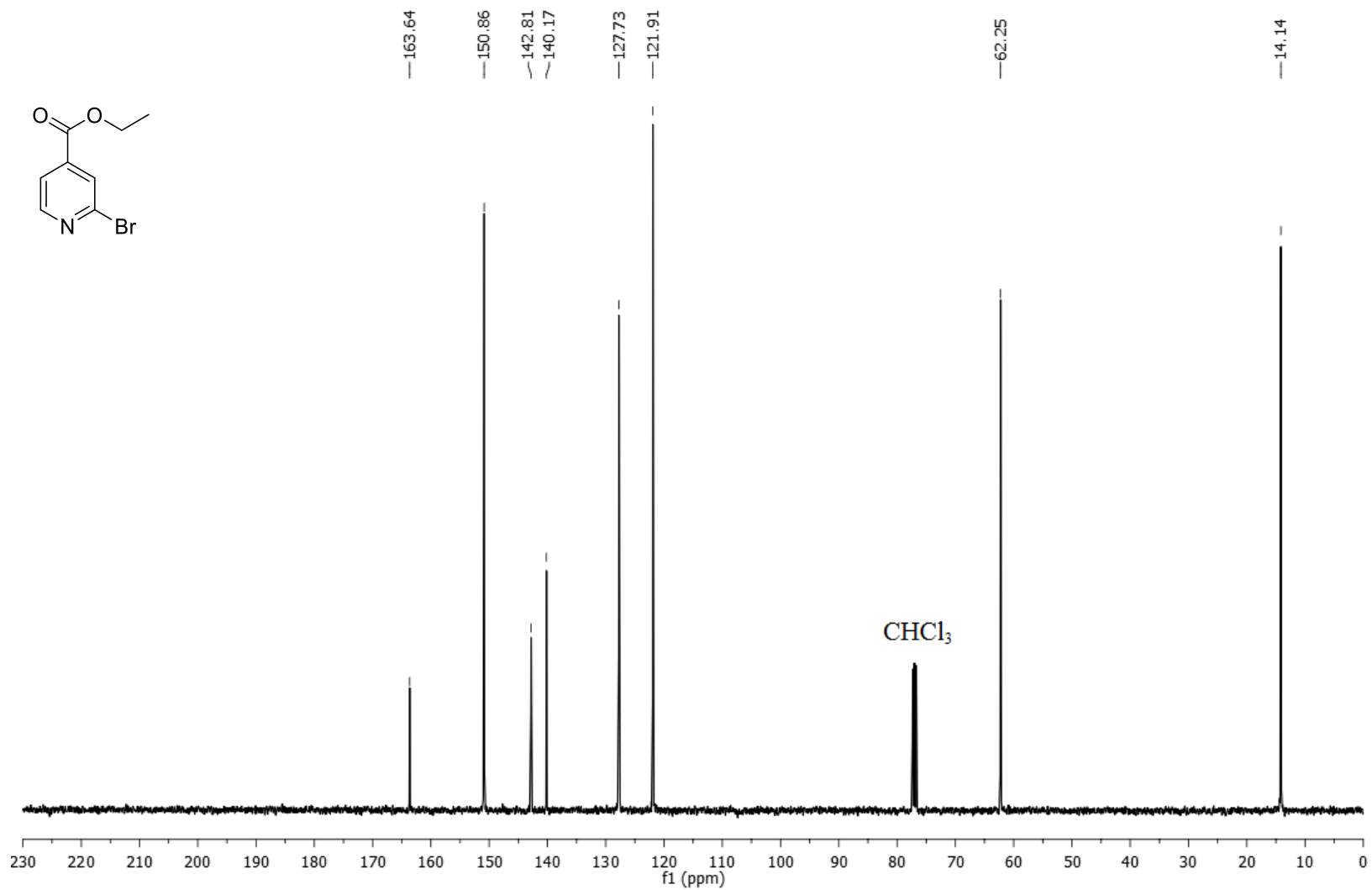
Diethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2,2'-bipyridine-4,4'-dicarboxylate (7b) <sup>19</sup>F NMR



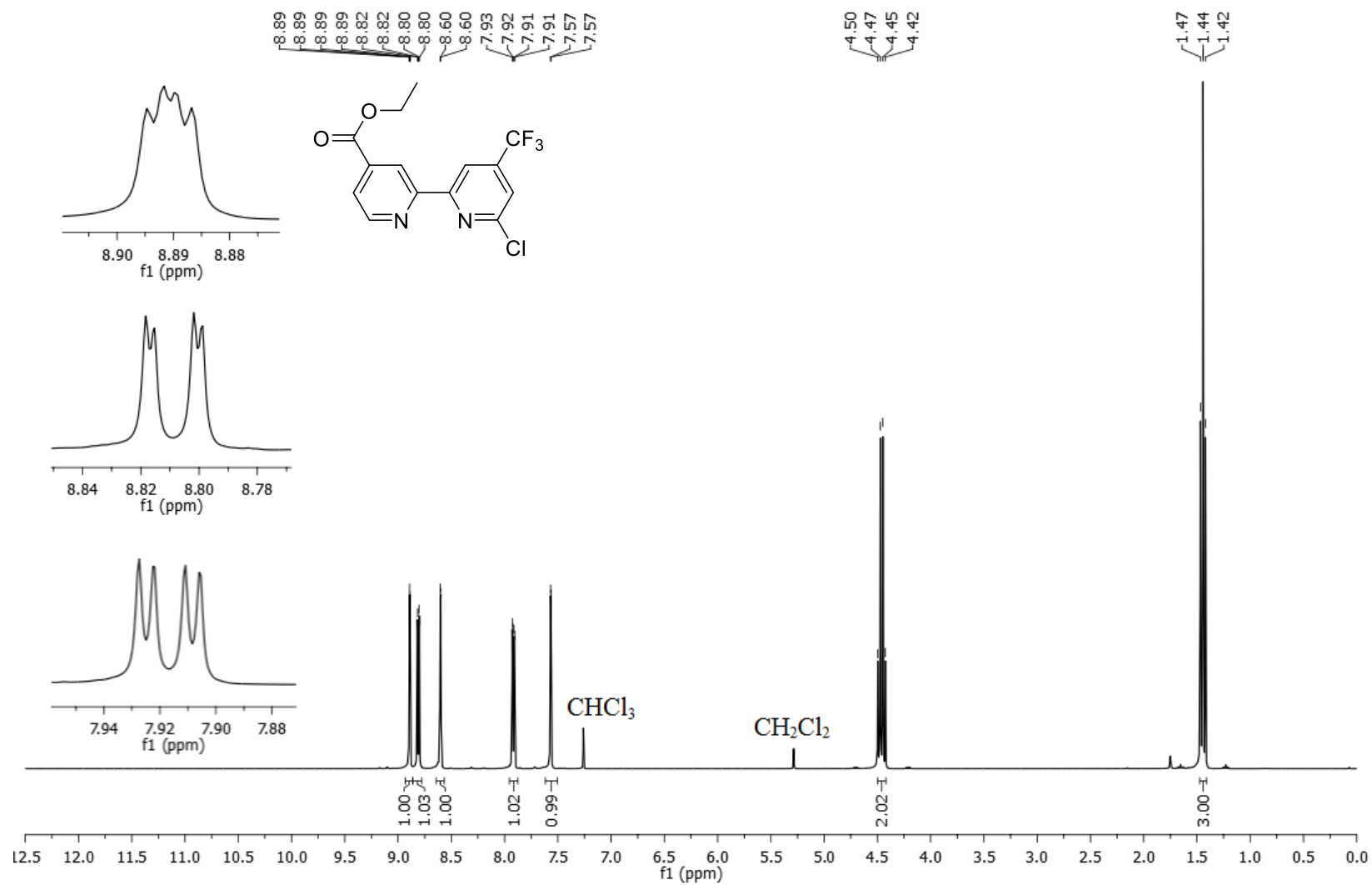
# Ethyl-2-bromopyridine-4-carboxylate (5) <sup>1</sup>H NMR



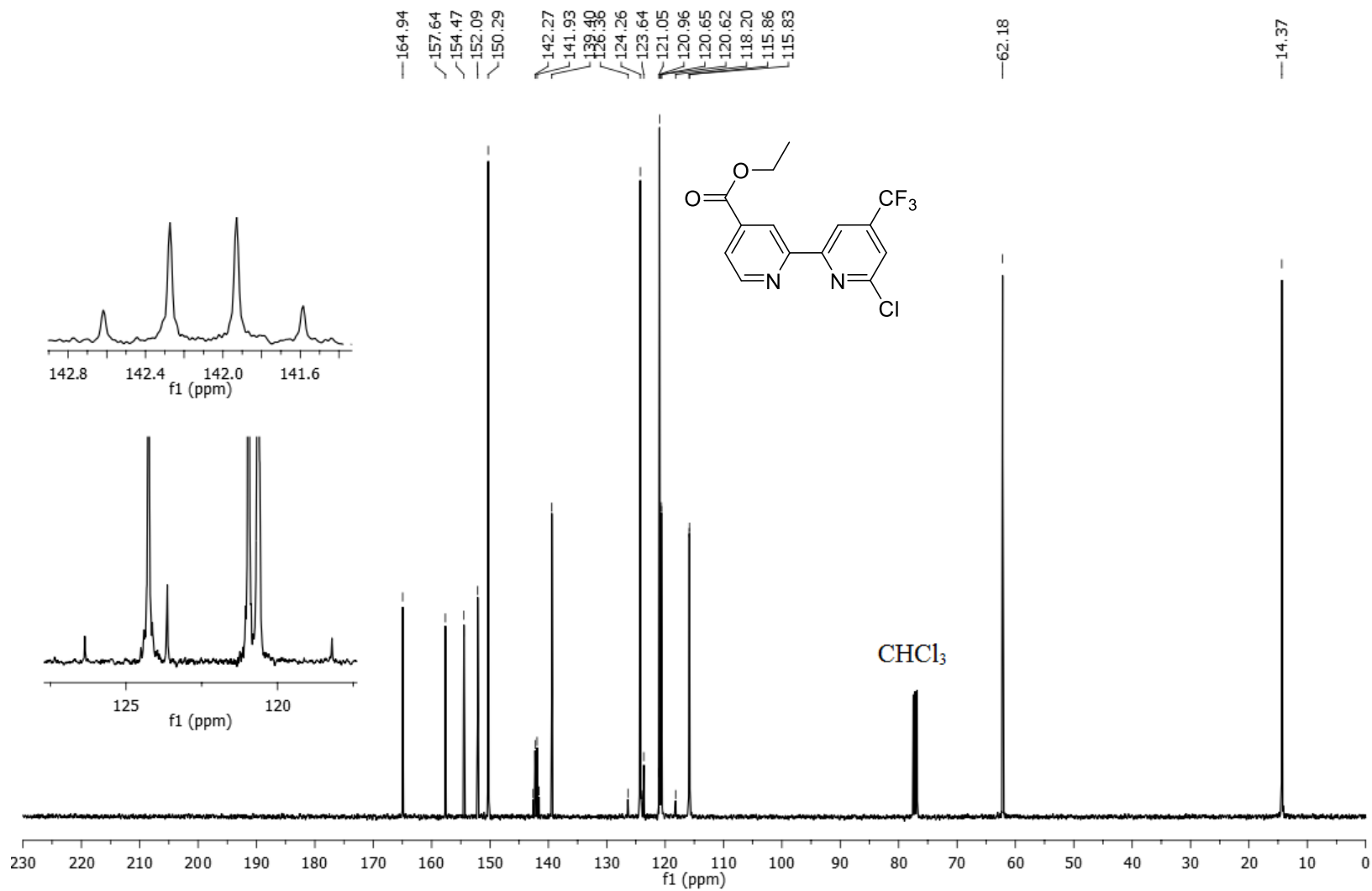
Ethyl-2-bromopyridine-4-carboxylate (5) <sup>13</sup>C NMR



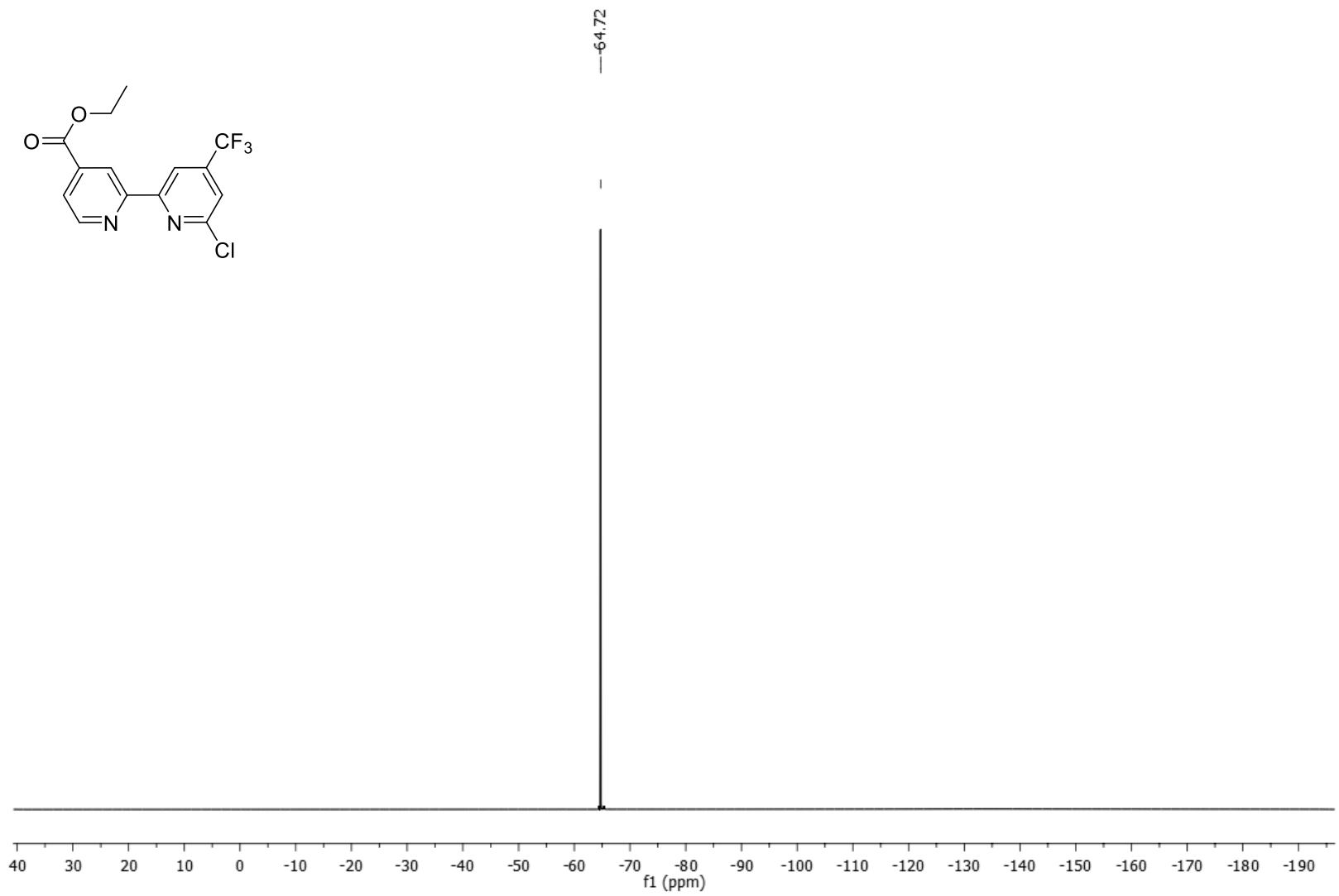
**Ethyl-6-chloro-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate (4b) <sup>1</sup>H NMR**



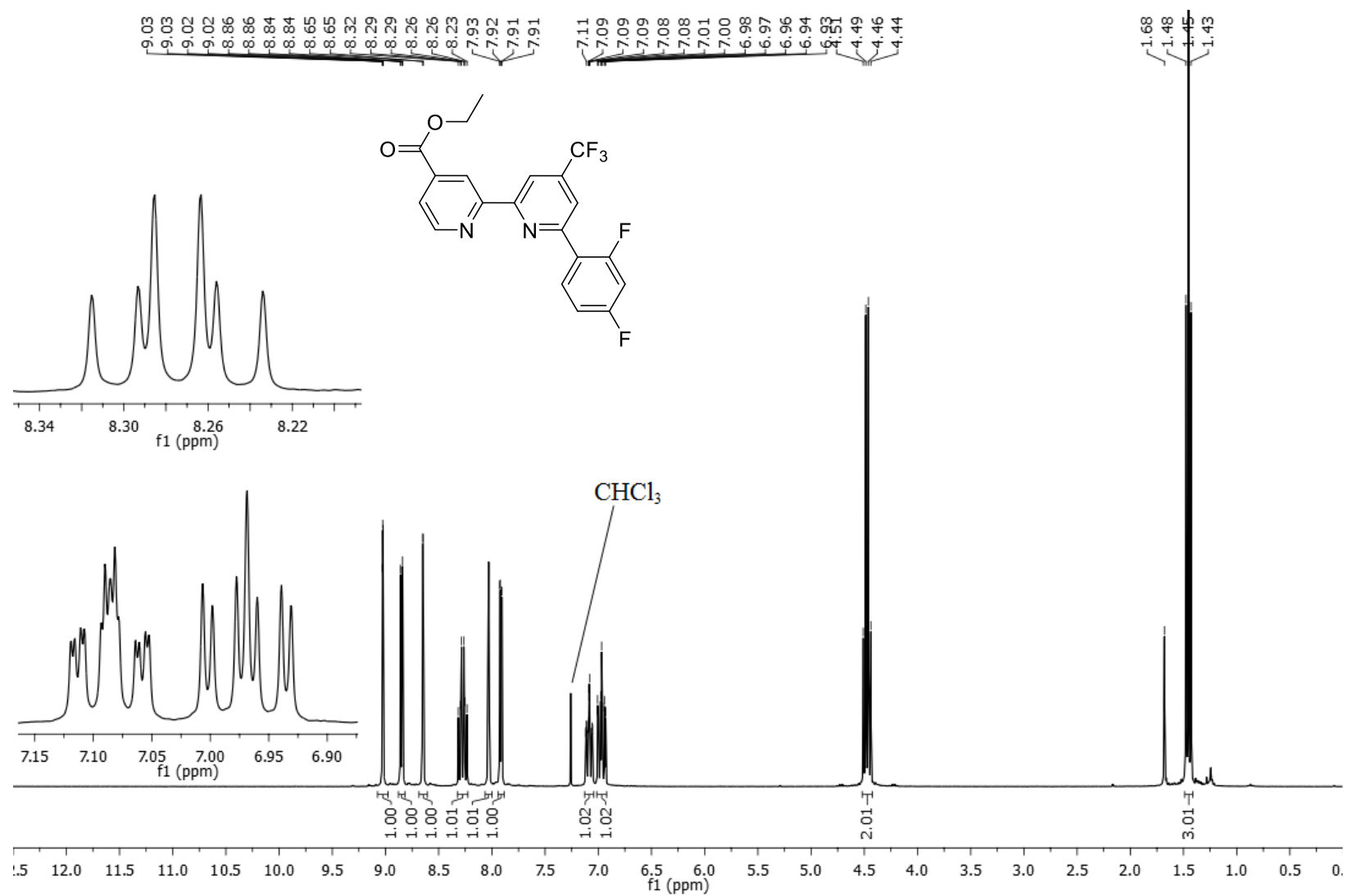
# Ethyl-6-chloro-4-(trifluoromethyl)-2,2'-bipyridine-4'-carboxylate (4b) <sup>13</sup>C NMR



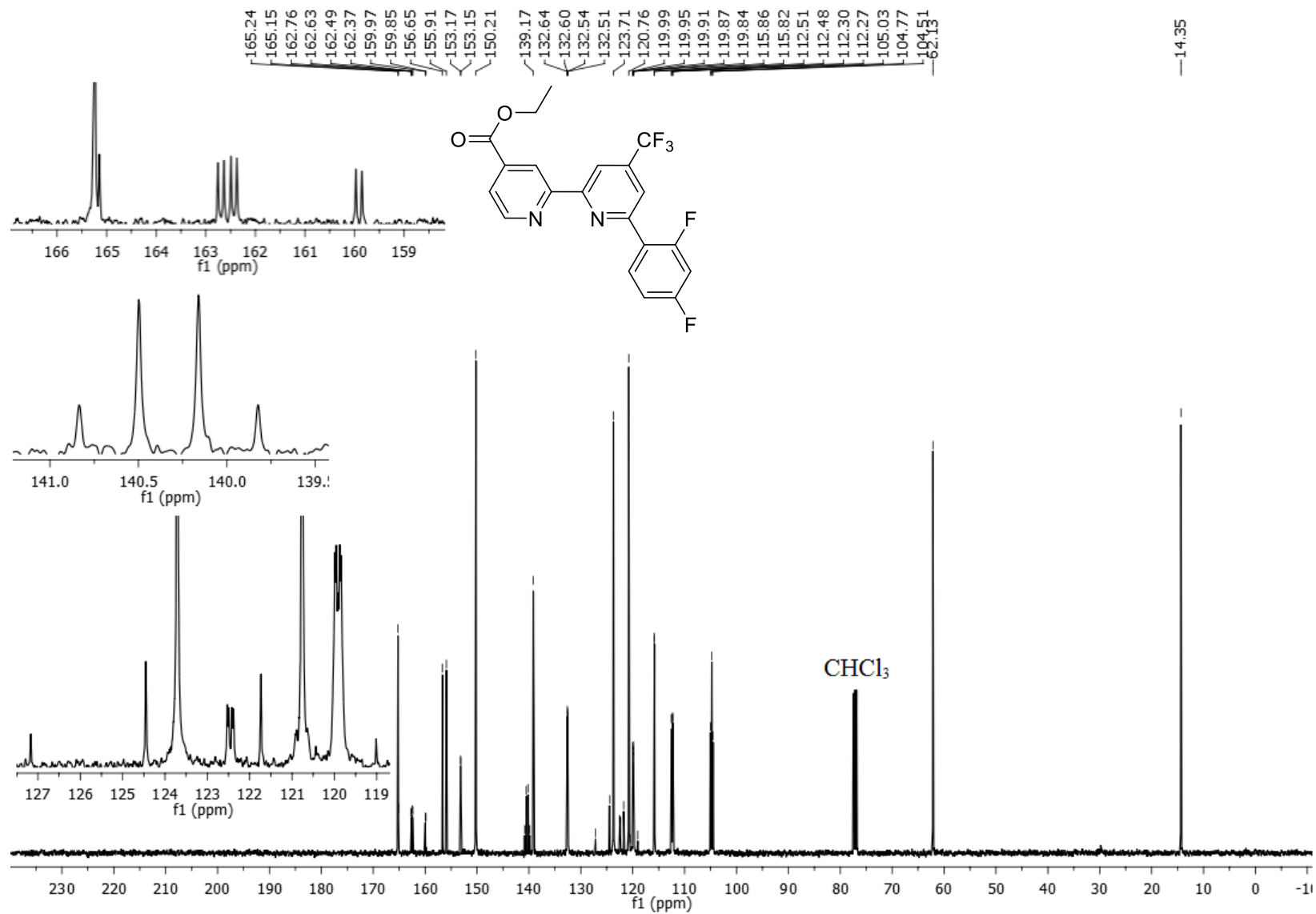
Ethyl-6-chloro-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate (4b) <sup>19</sup>F NMR



Ethyl-6-(2,4-difluorophenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate (7c) <sup>1</sup>H NMR

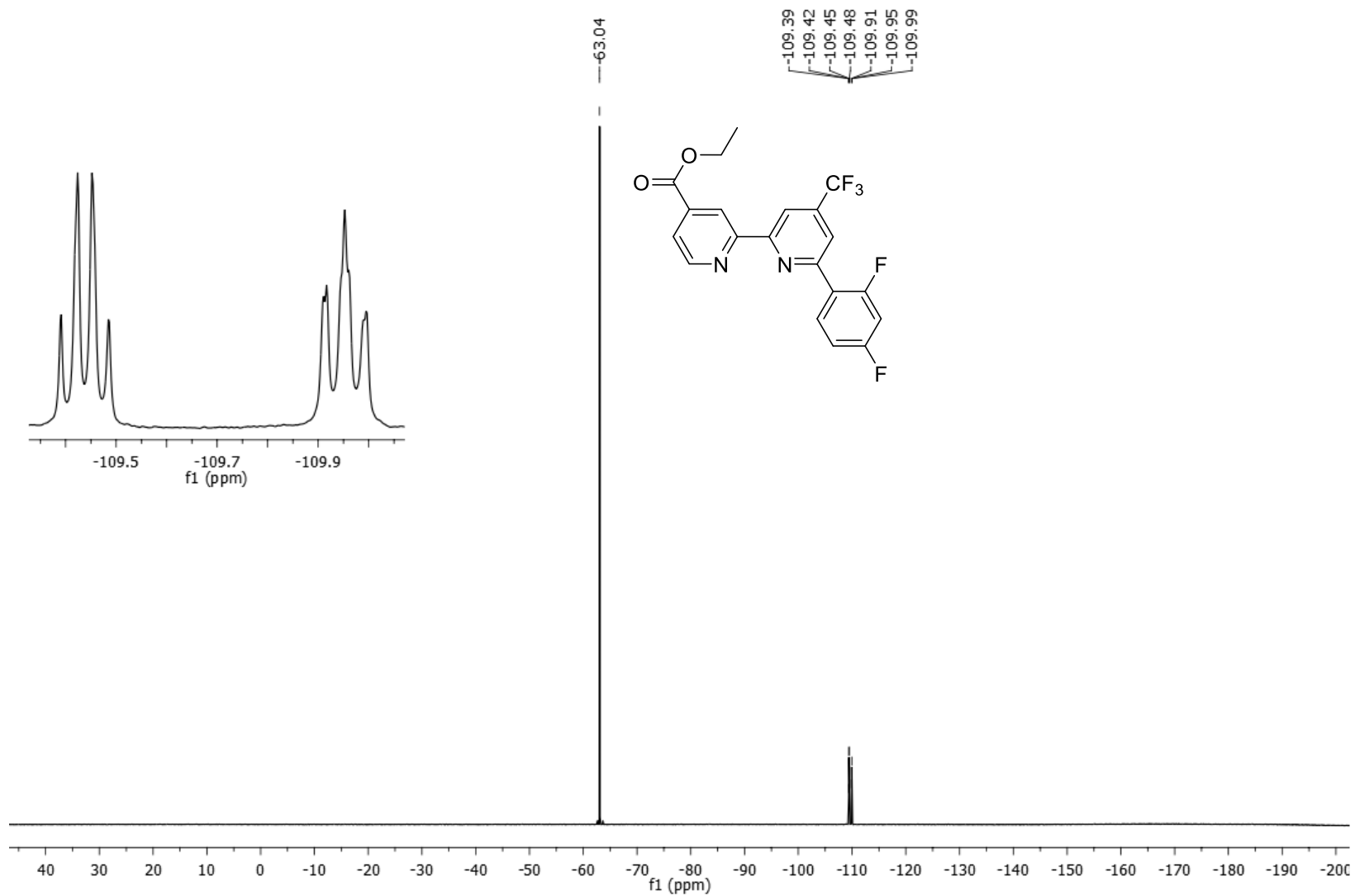


Ethyl-6-(2,4-difluorophenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate (7c) <sup>13</sup>C NMR

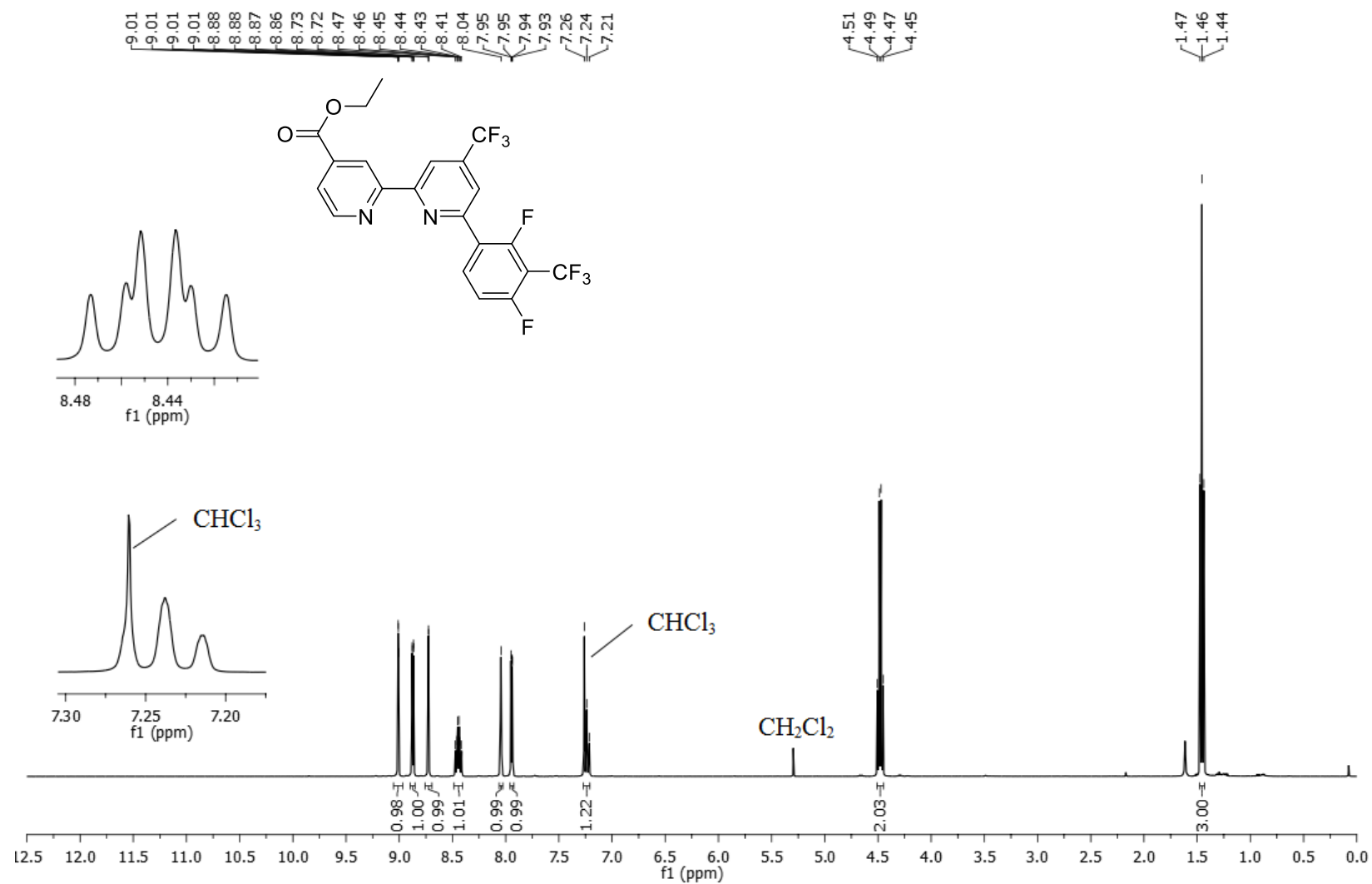


—14.35

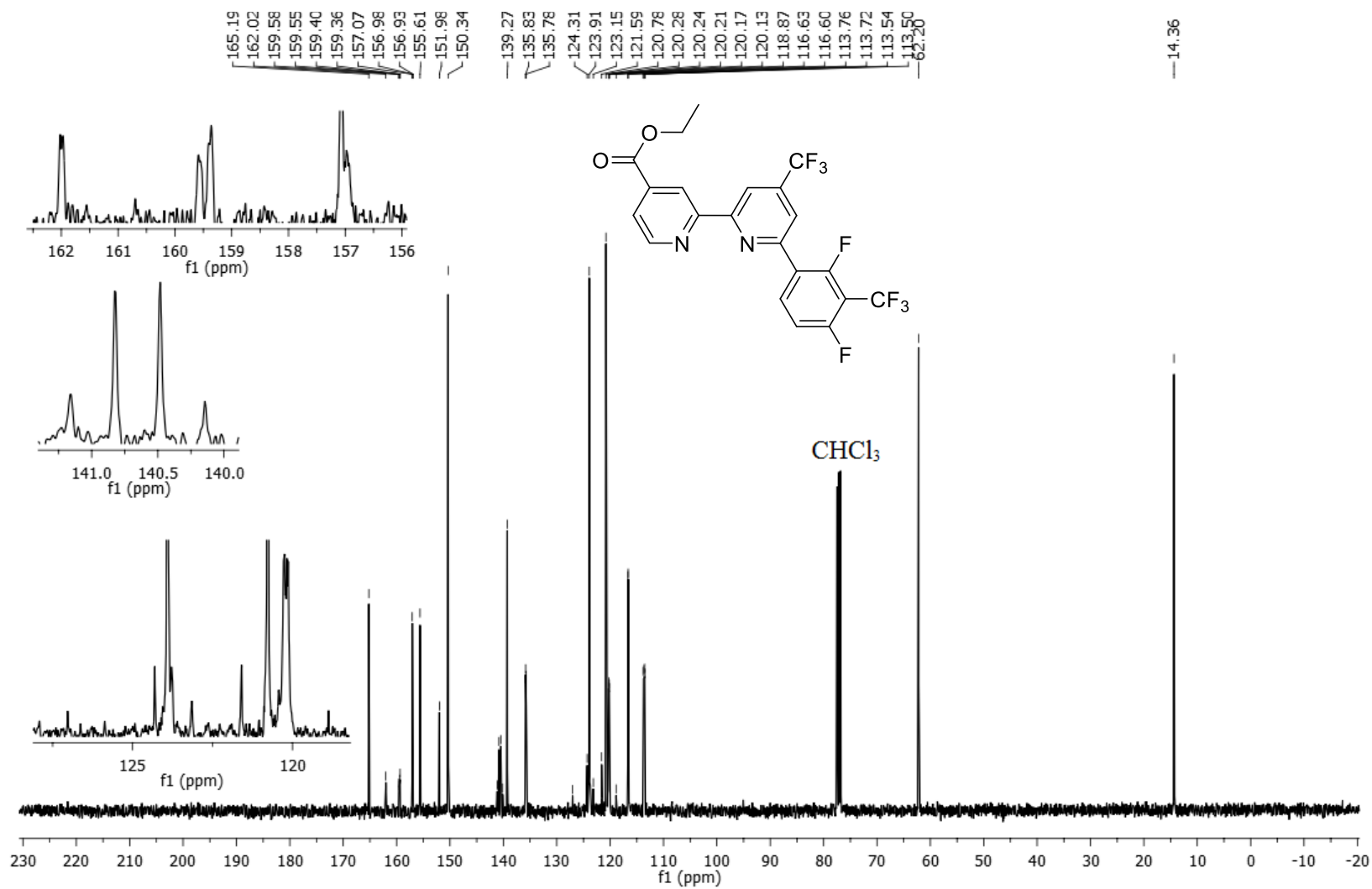
Ethyl-6-(2,4-difluorophenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate (7c) <sup>19</sup>F NMR



Ethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2,2'-bipyridine-4'-carboxylate (7d) <sup>1</sup>H NMR



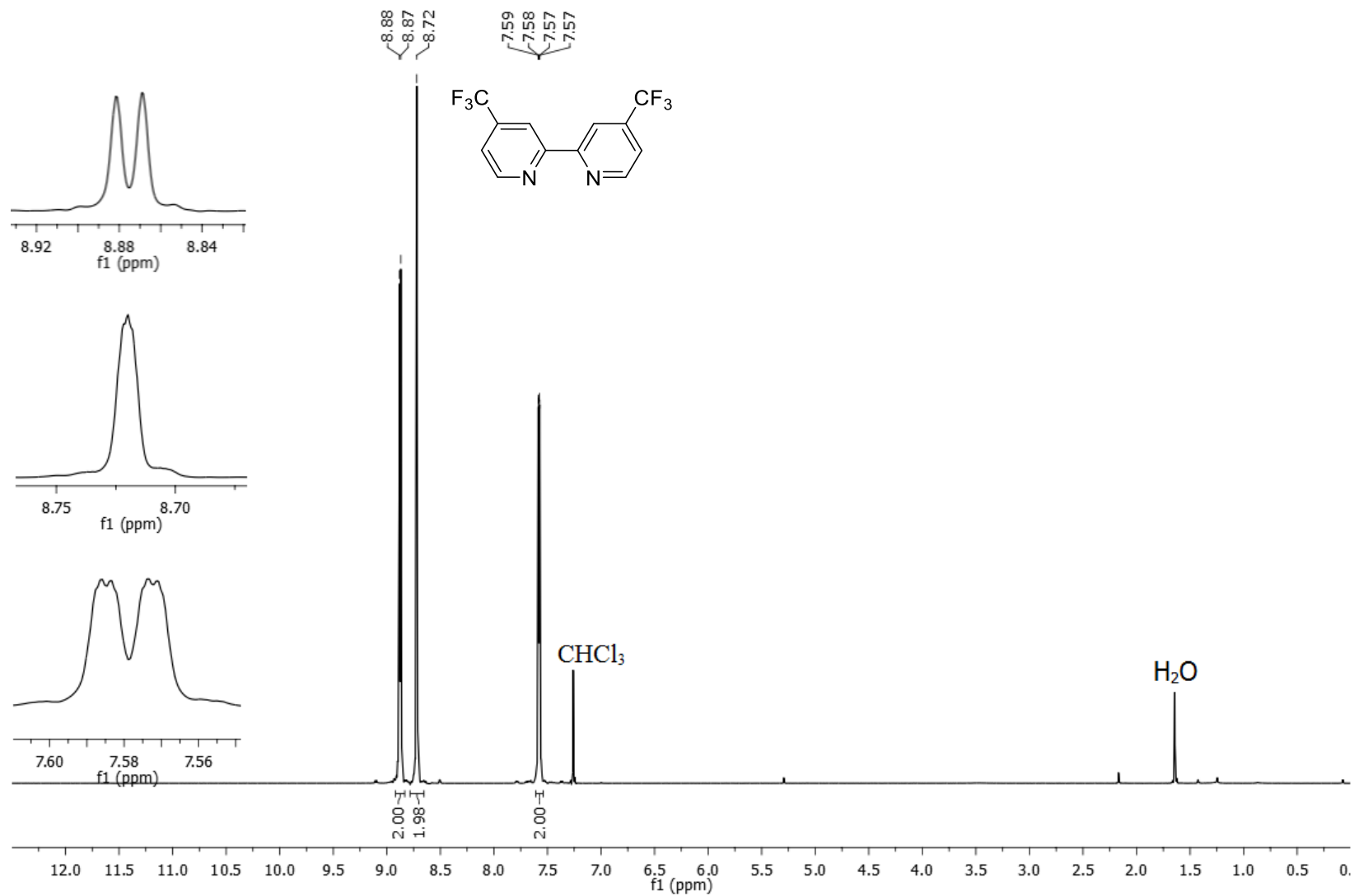
Ethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate (7d) <sup>13</sup>C NMR



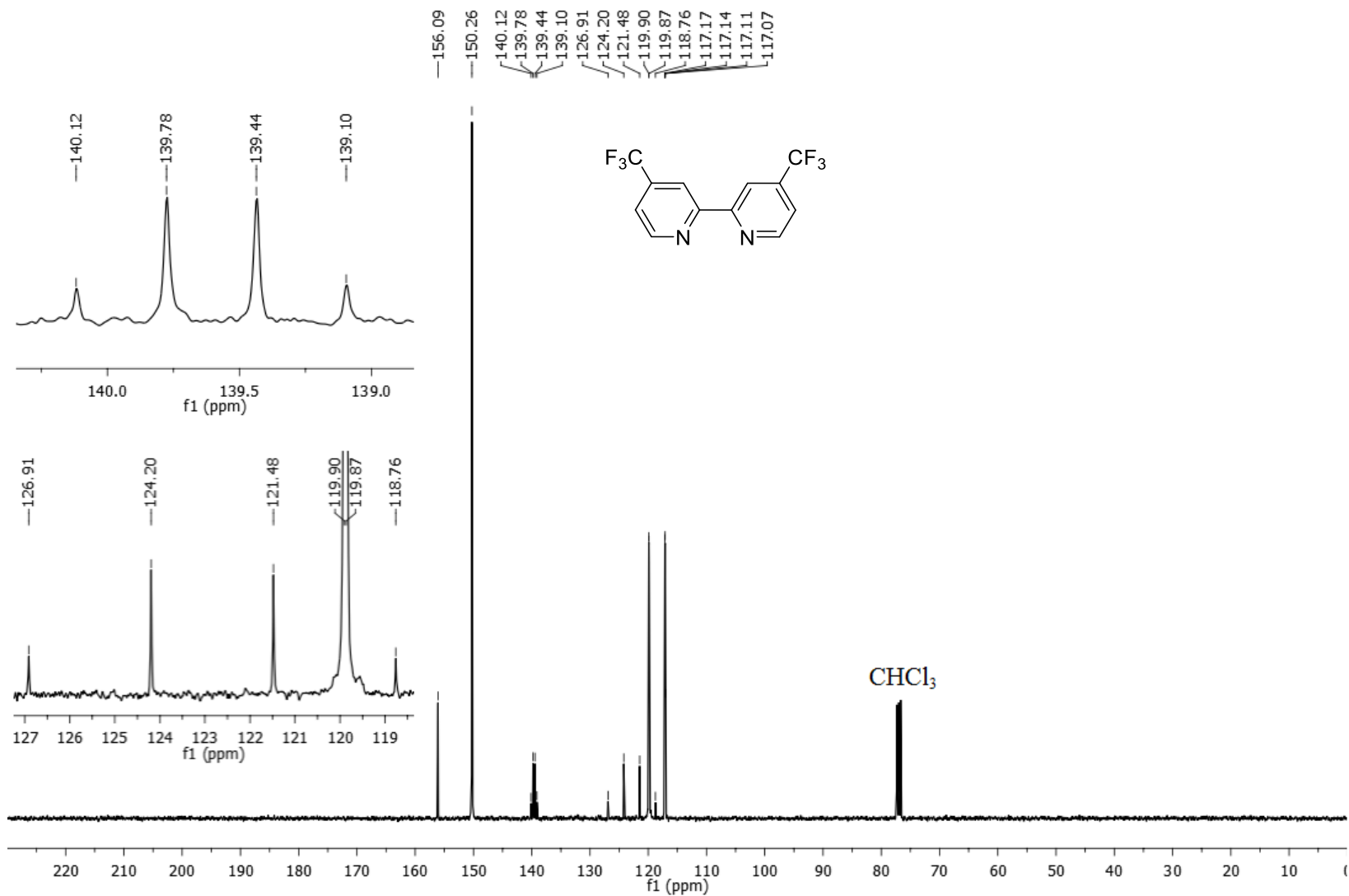
Ethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate (7d) <sup>19</sup>F NMR



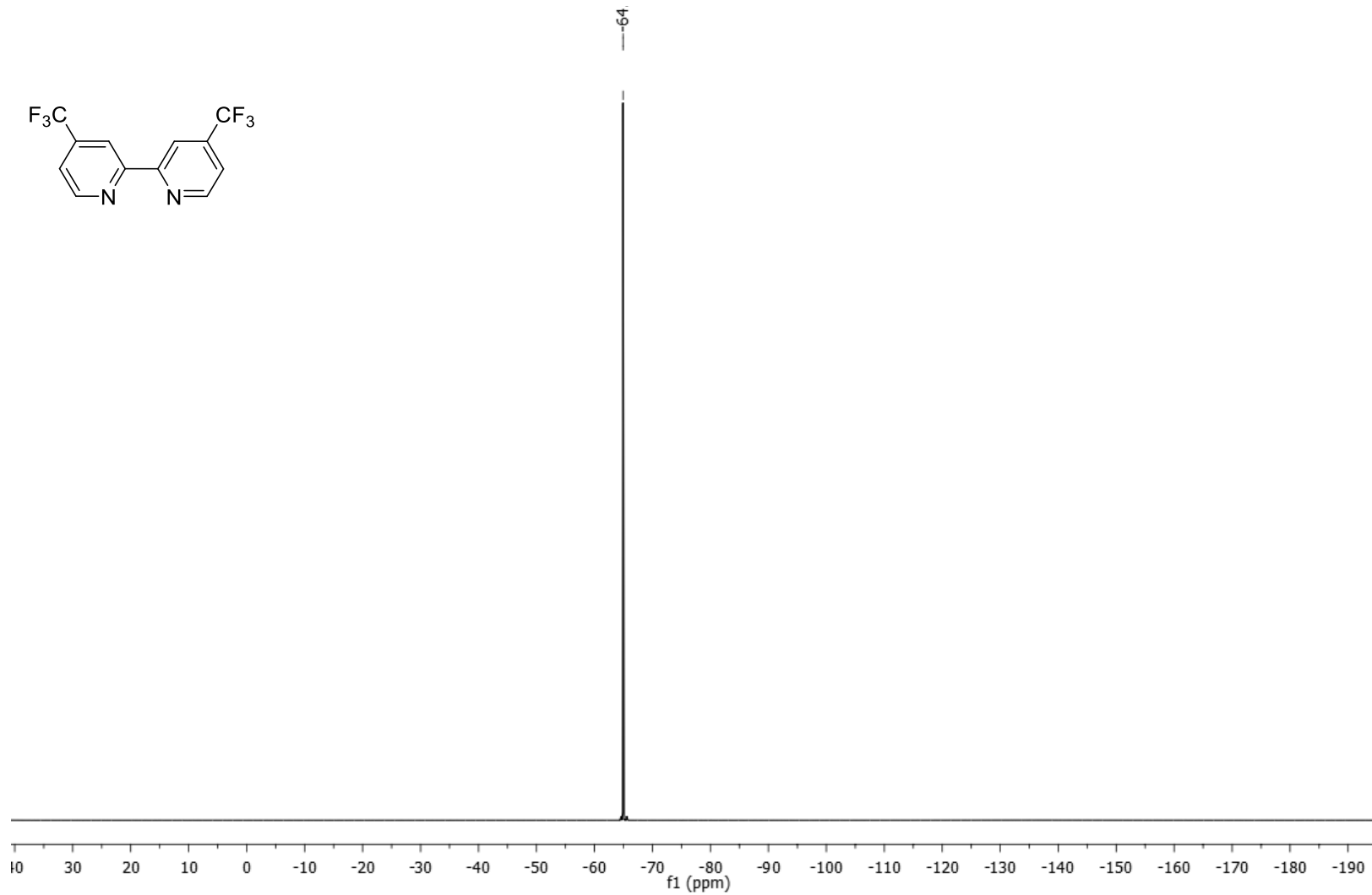
4,4'-Bis(trifluoromethyl)-2-2'-bipyridine (2b)  $^1\text{H}$  NMR



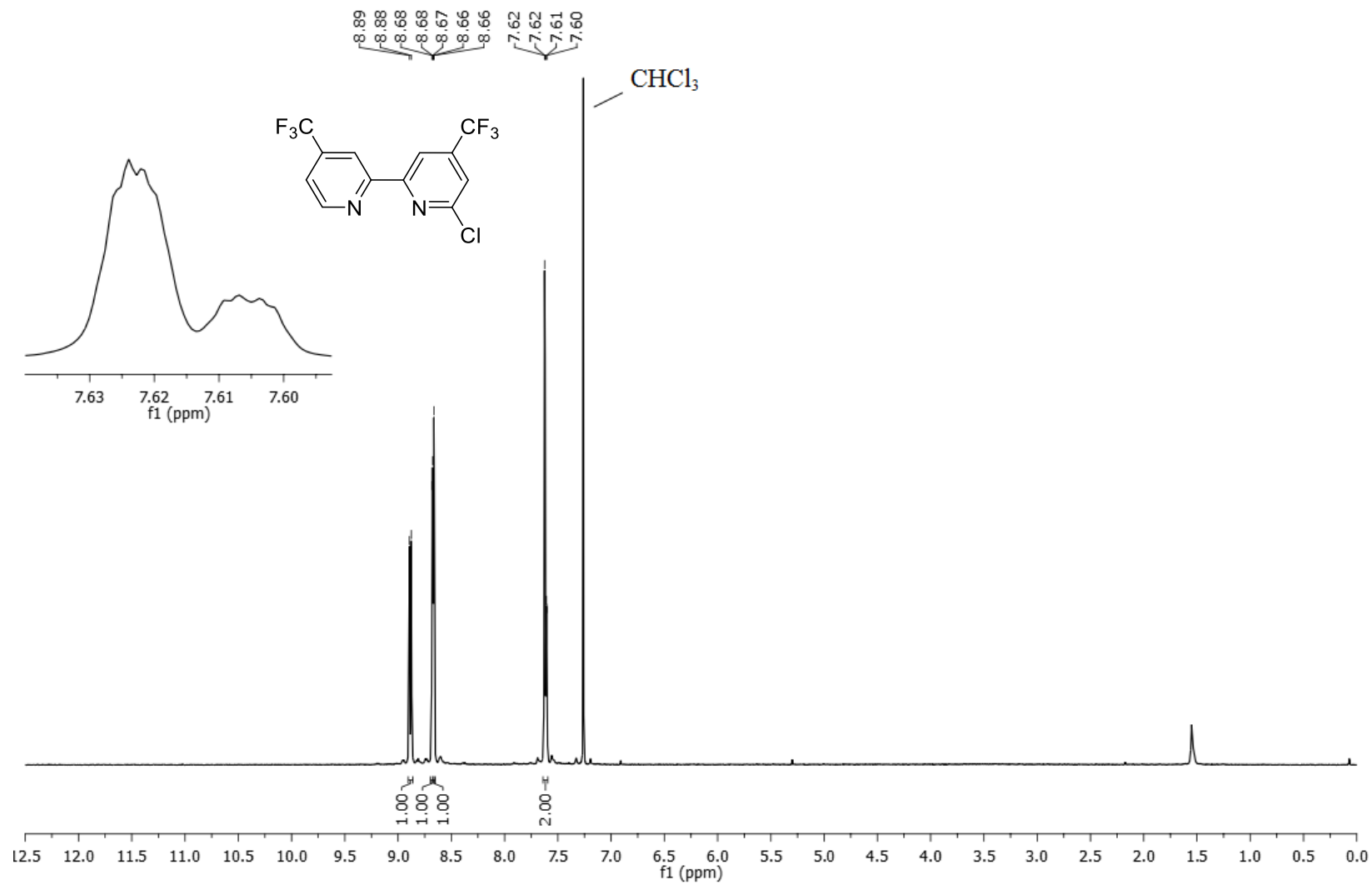
# 4,4'-Bis(trifluoromethyl)-2-2'-bipyridine (2b) <sup>13</sup>C NMR



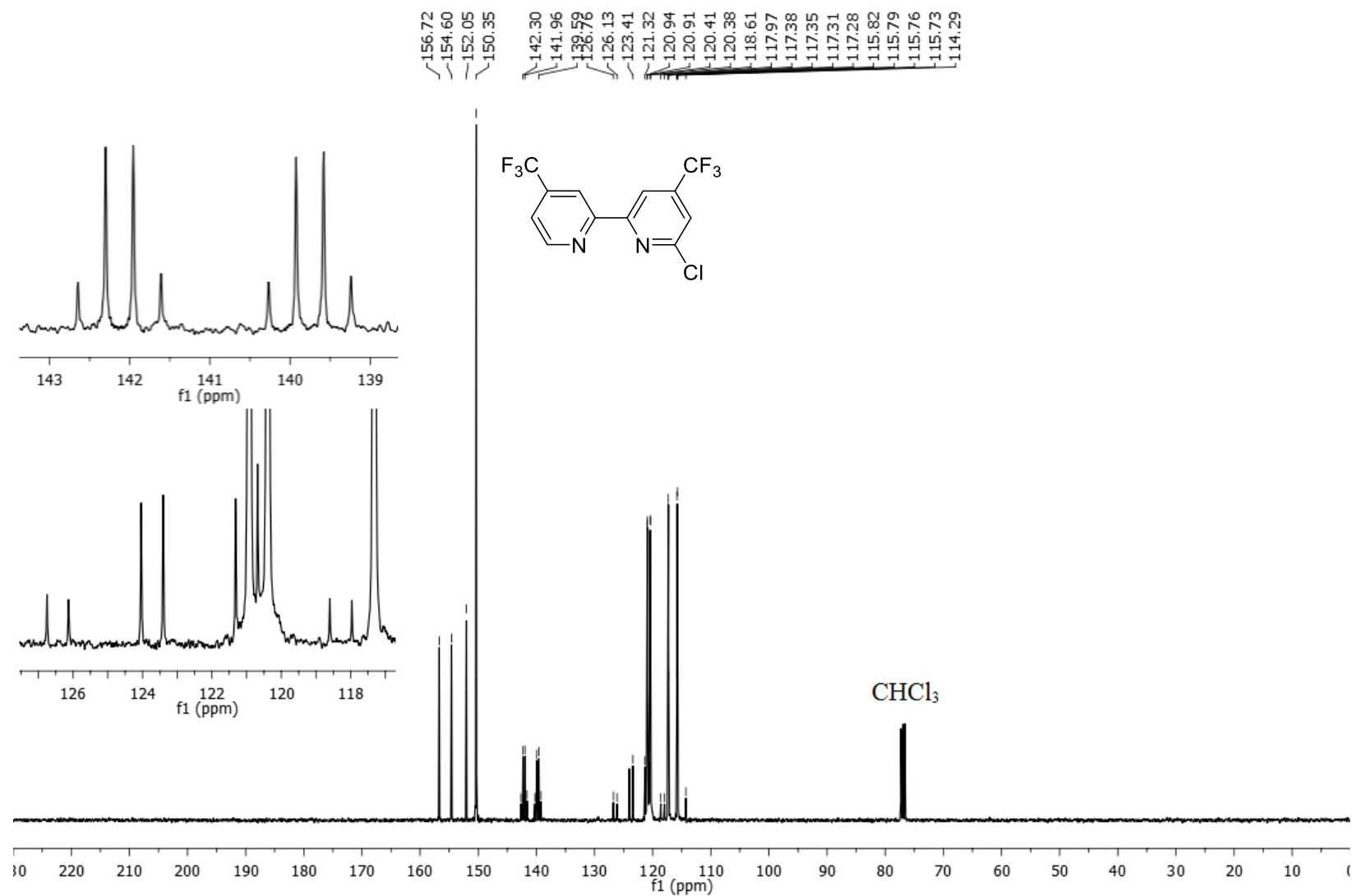
4,4'-Bis(trifluoromethyl)-2-2'-bipyridine (2b)  $^{13}\text{C}$  NMR



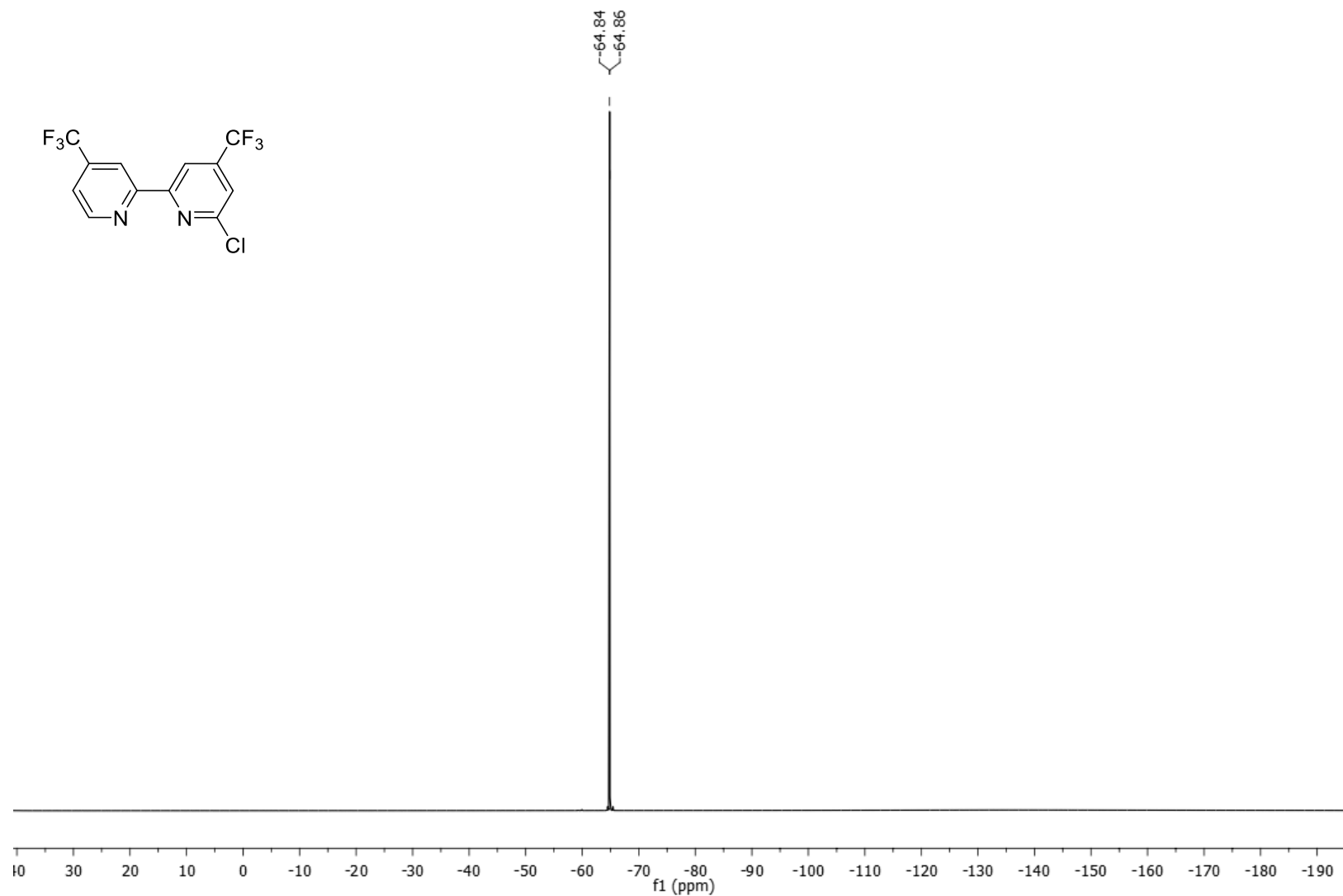
6-Chloro-4,4'-bis(trifluoromethyl)-2-2'-bipyridine (4c) <sup>1</sup>H NMR



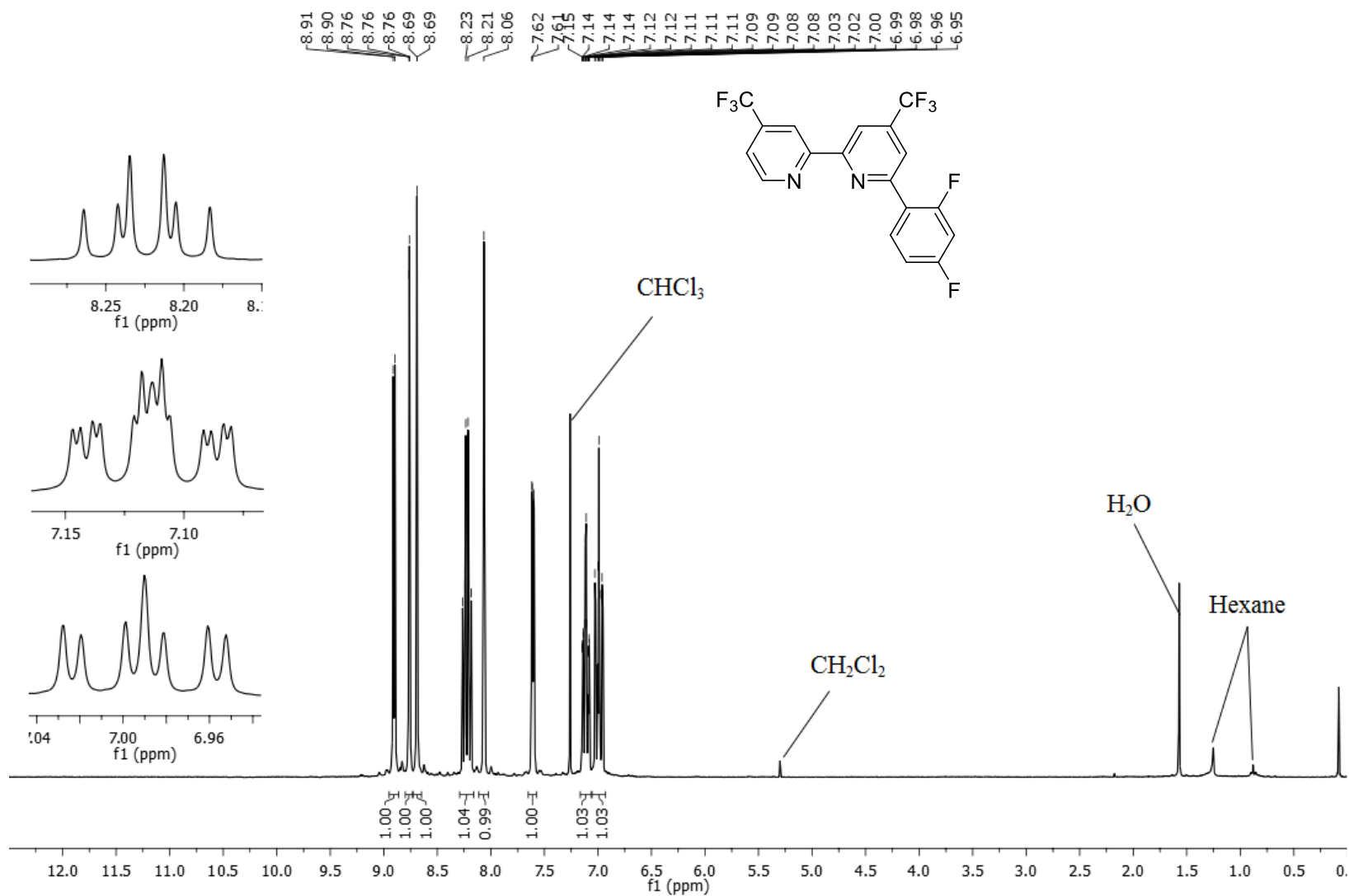
# 6-Chloro-4,4'-bis(trifluoromethyl)-2-2'-bipyridine (4c) <sup>13</sup>C NMR



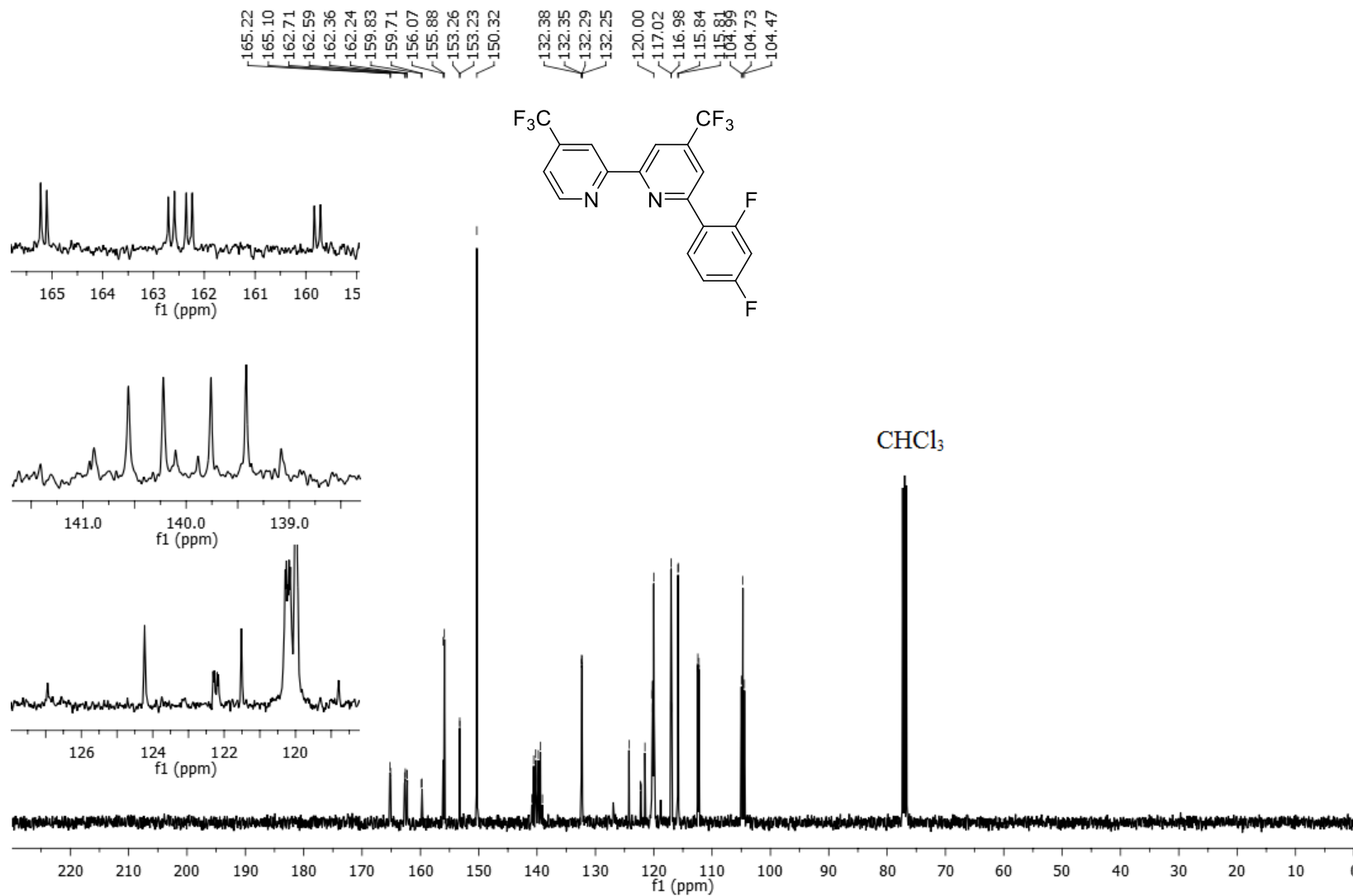
**6-Chloro-4,4'-bis(trifluoromethyl)-2,2'-bipyridine (4c) <sup>19</sup>F NMR**



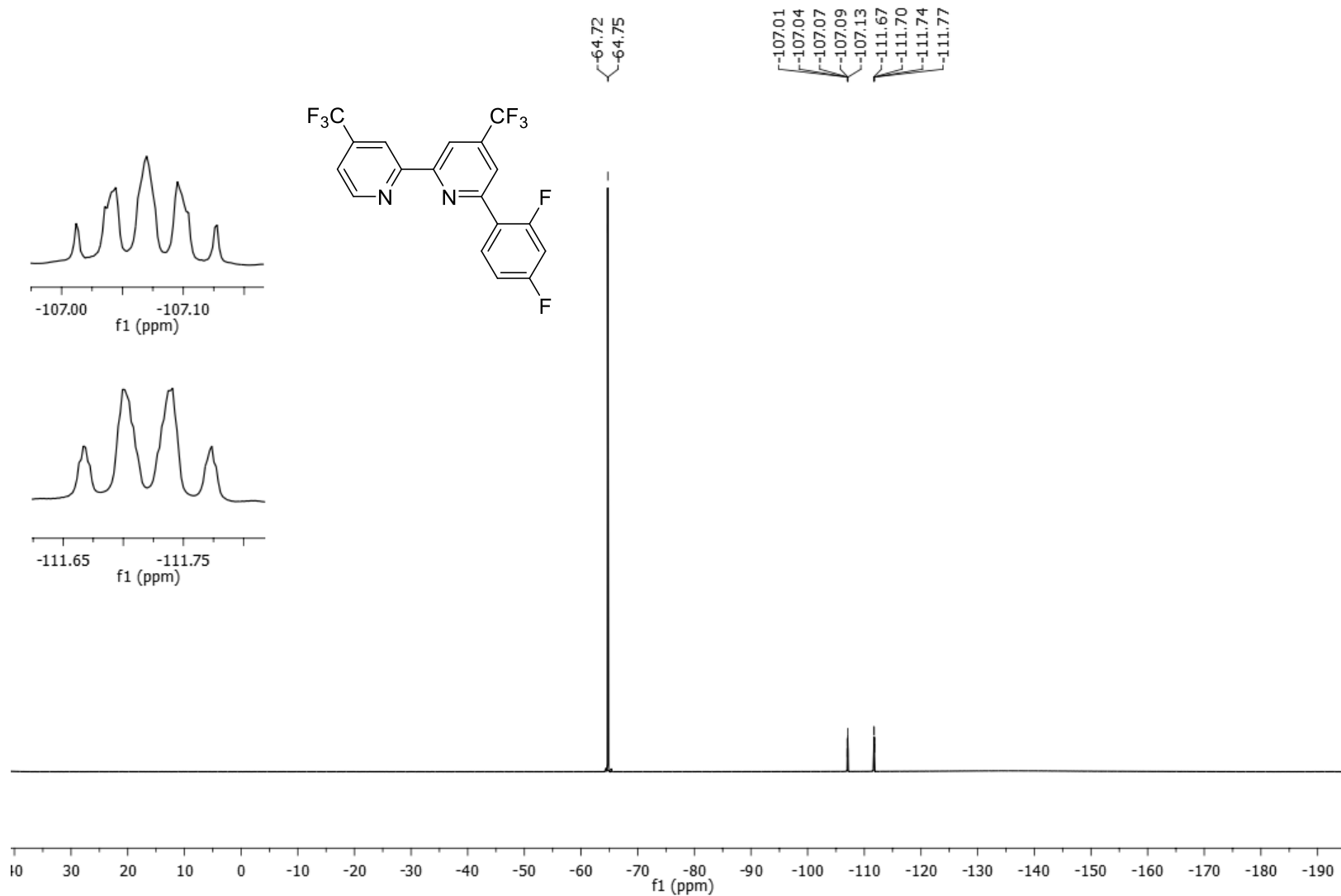
6-(2,4-Difluorophenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine (7e) <sup>1</sup>H NMR



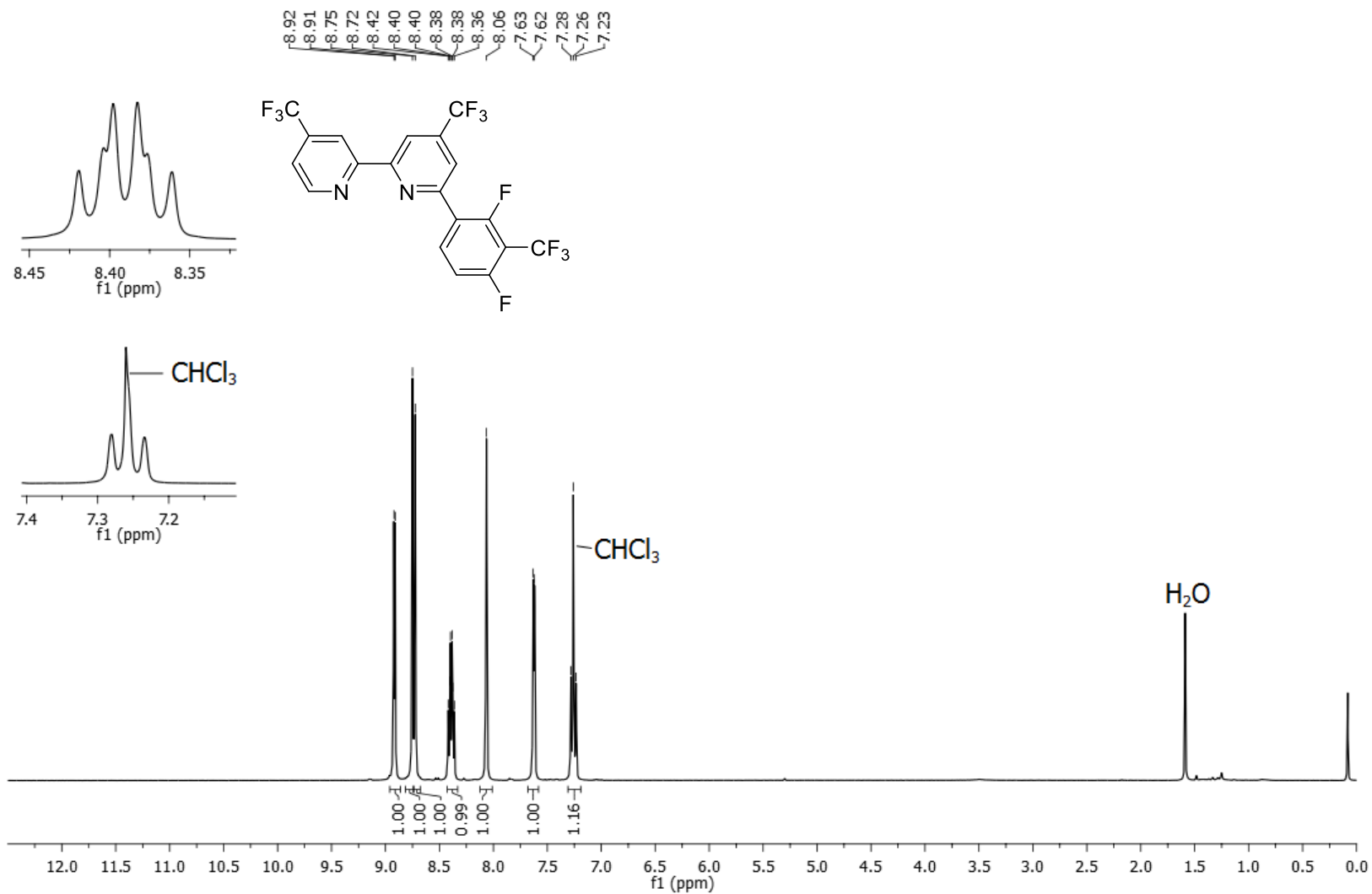
6-(2,4-Difluorophenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine (7e) <sup>13</sup>C NMR



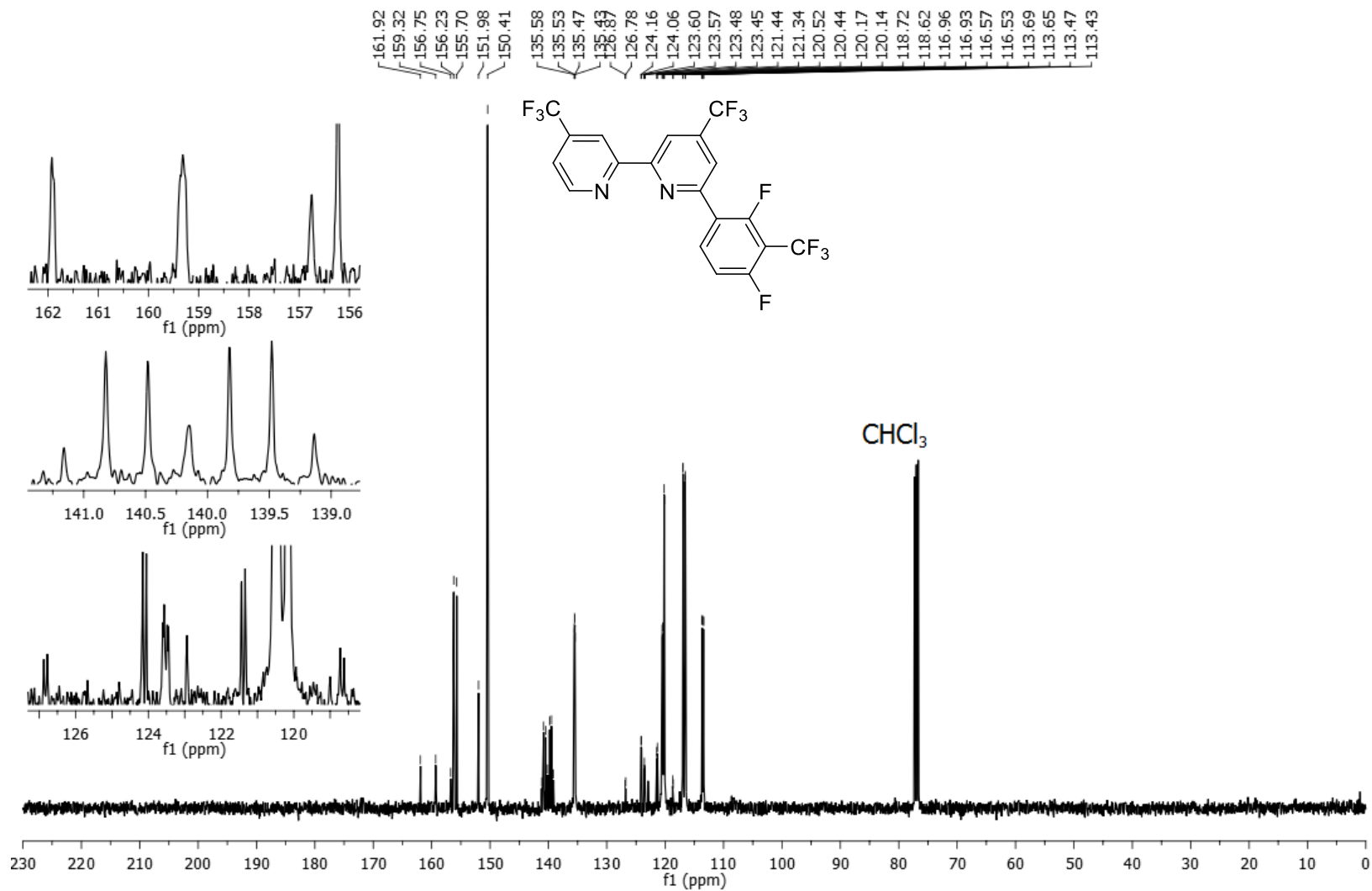
6-(2,4-Difluorophenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine (7e) <sup>19</sup>F NMR



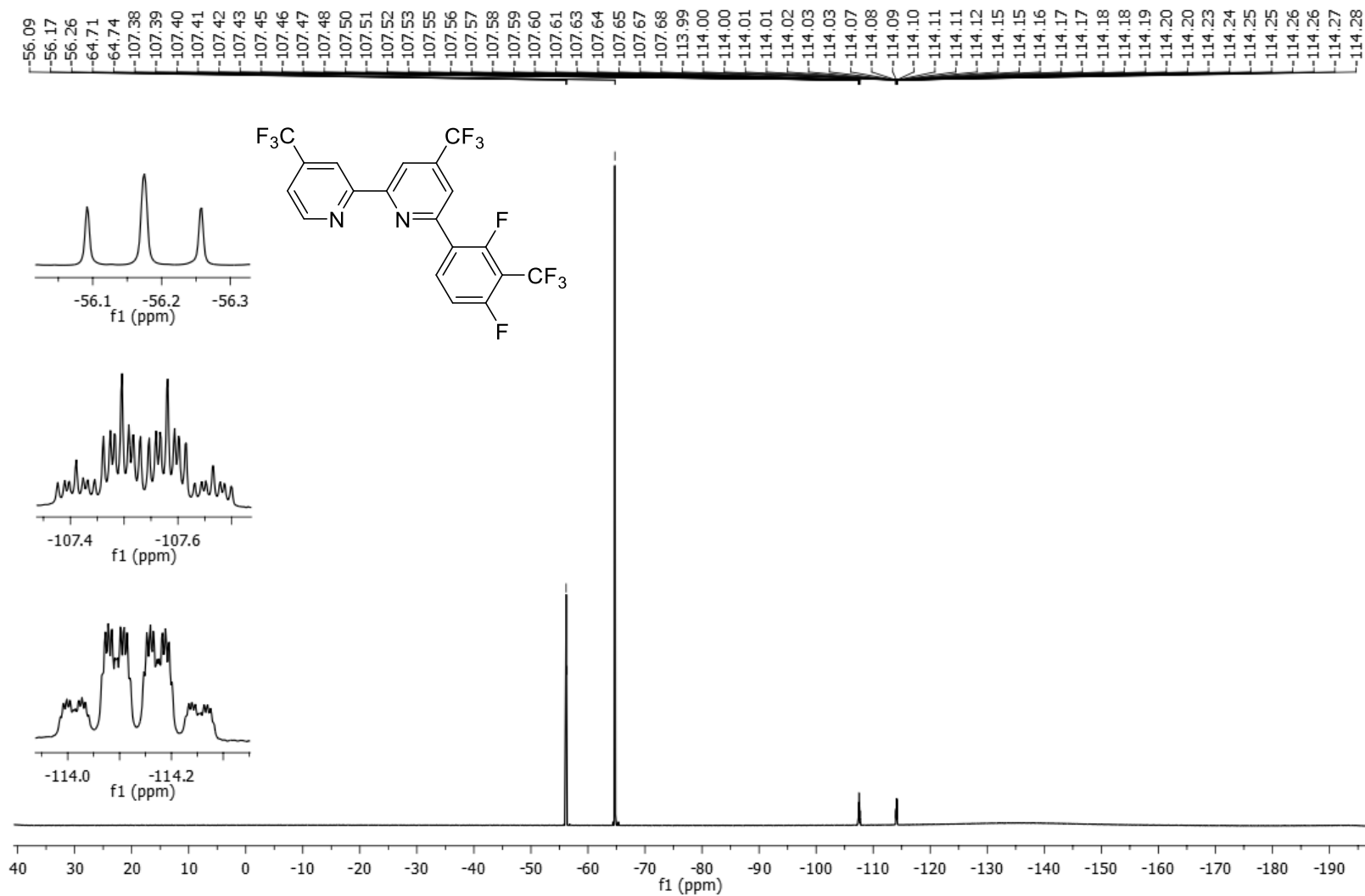
**6-(2,4-Difluoro-3-(trifluoromethyl)phenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine (7f) <sup>1</sup>H NMR**



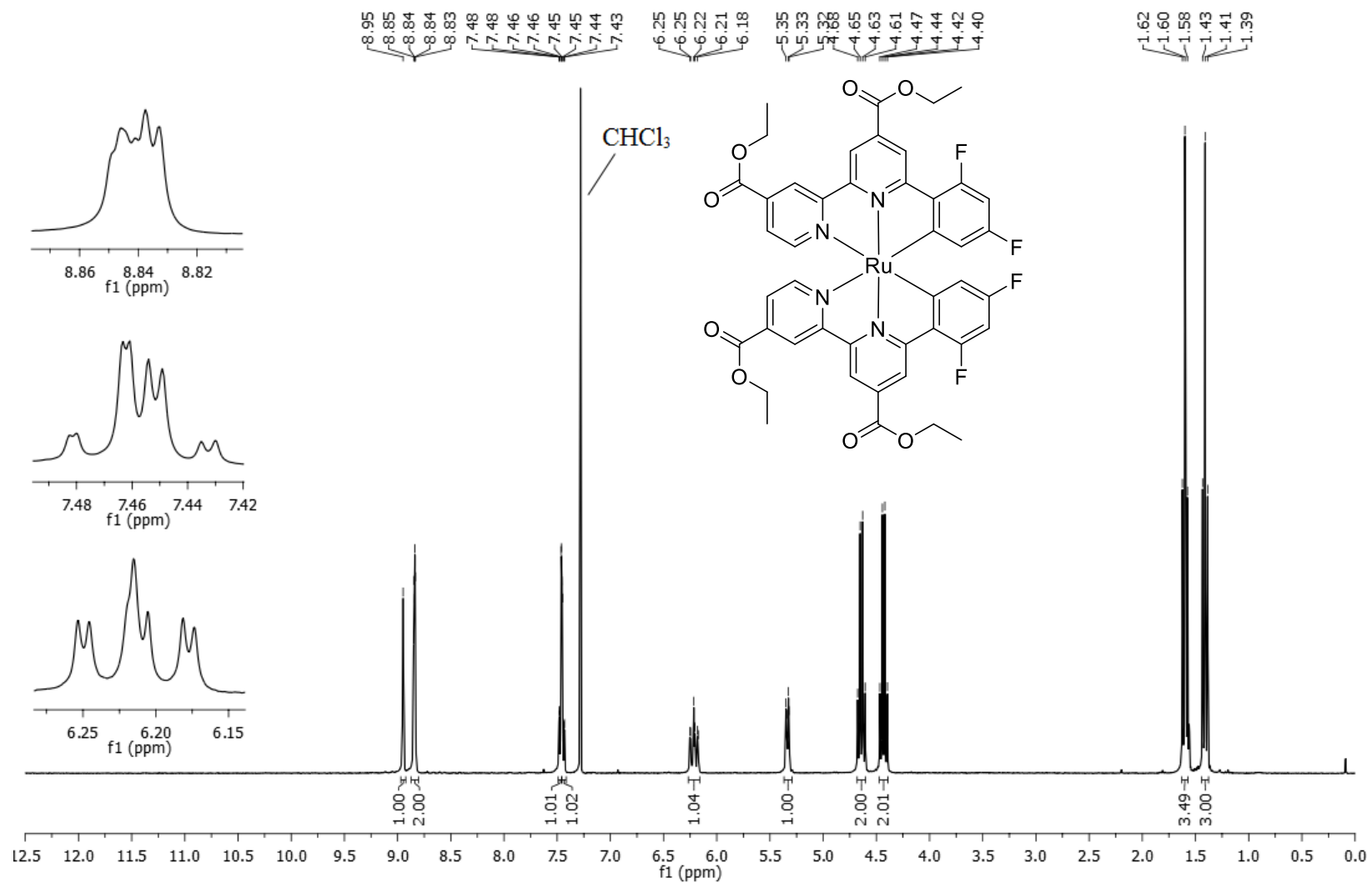
6-(2,4-Difluoro-3-(trifluoromethyl)phenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine (7f) <sup>13</sup>C NMR



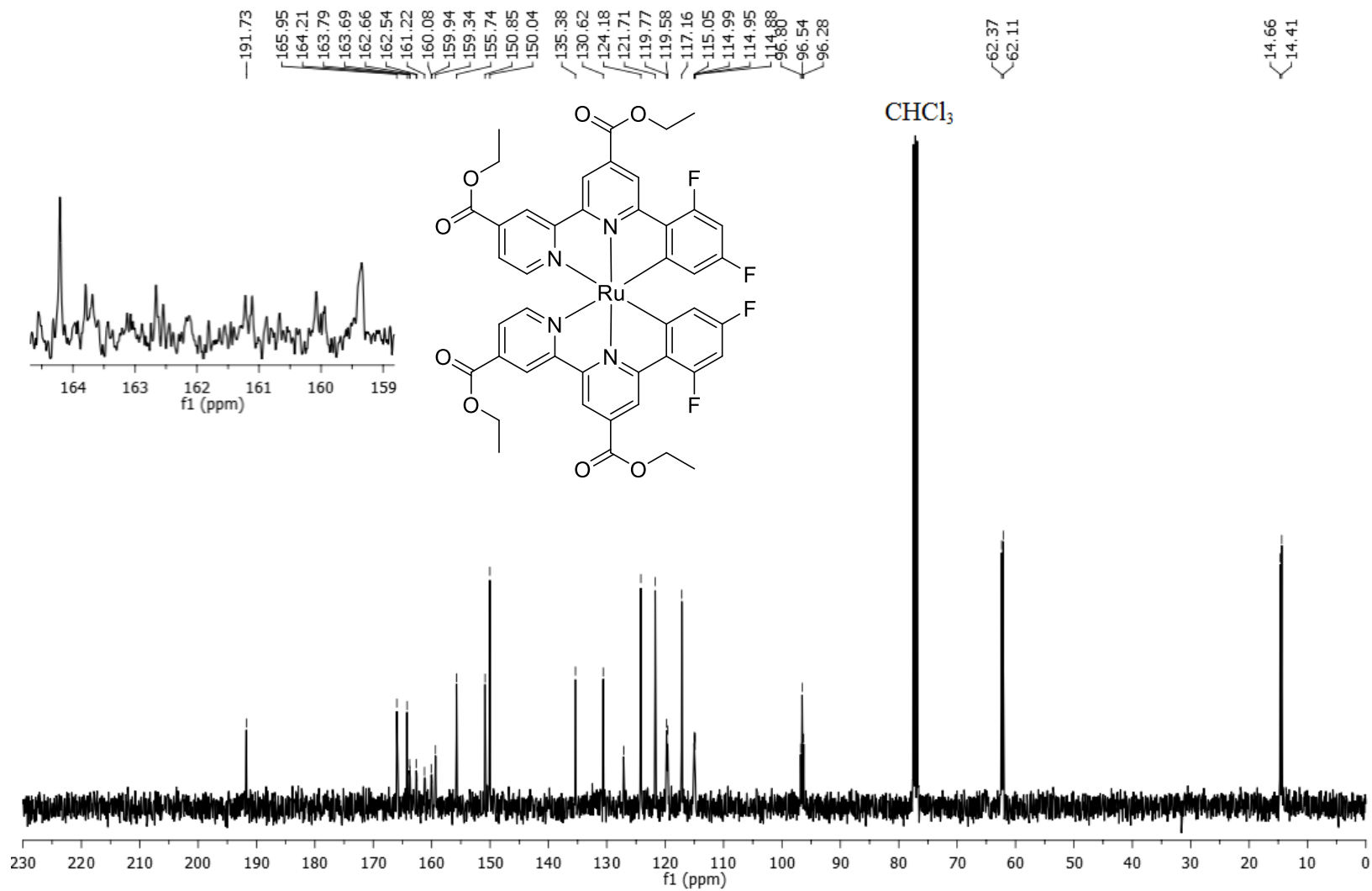
# 6-(2,4-Difluoro-3-(trifluoromethyl)phenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine (7f) <sup>19</sup>F NMR



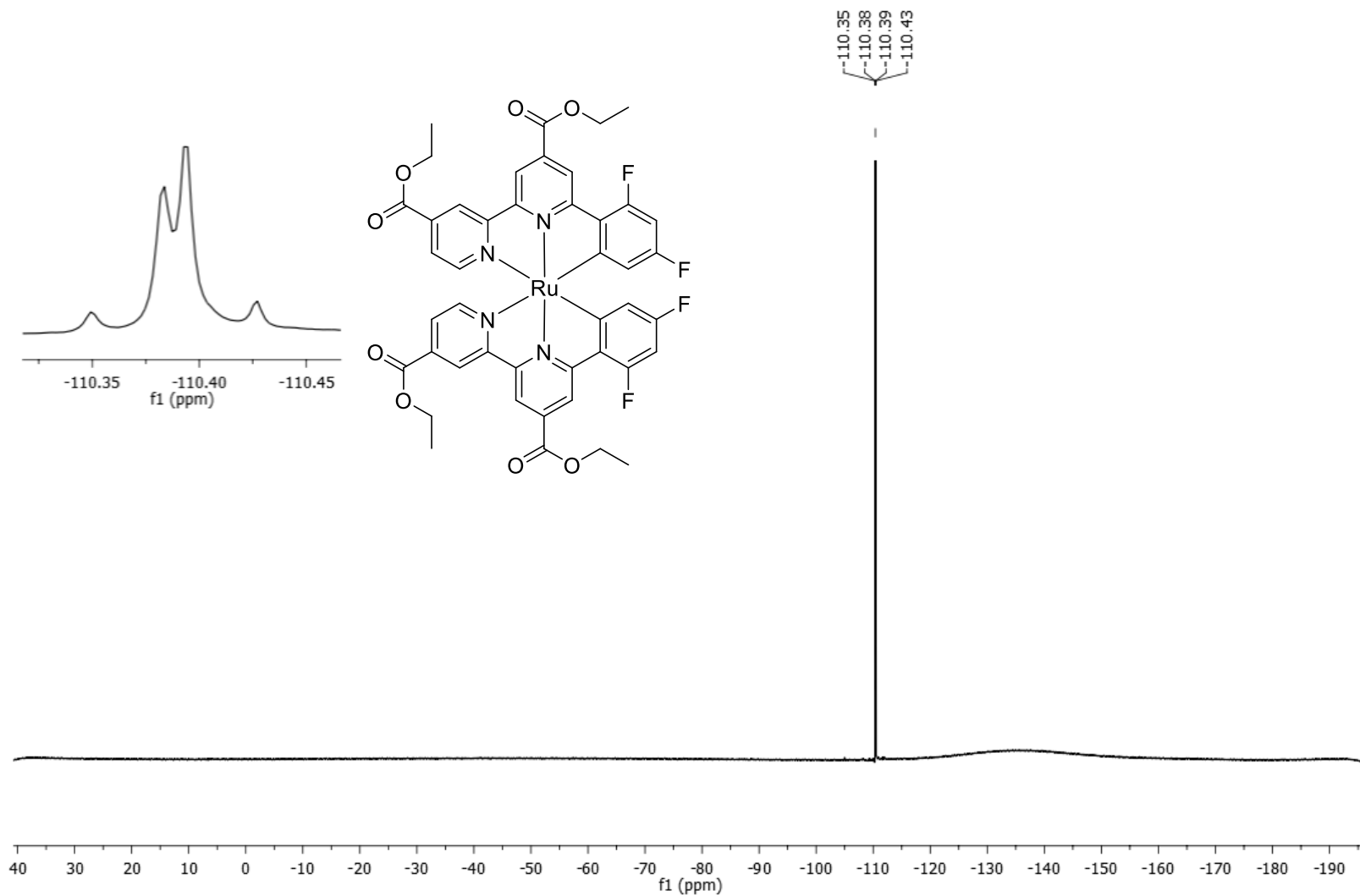
**Ruthenium(II) bis(diethyl-6-(2,4-difluorophenyl)-2-2'-bipyridine-4,4'-dicarboxylate) (1a) <sup>1</sup>H NMR**



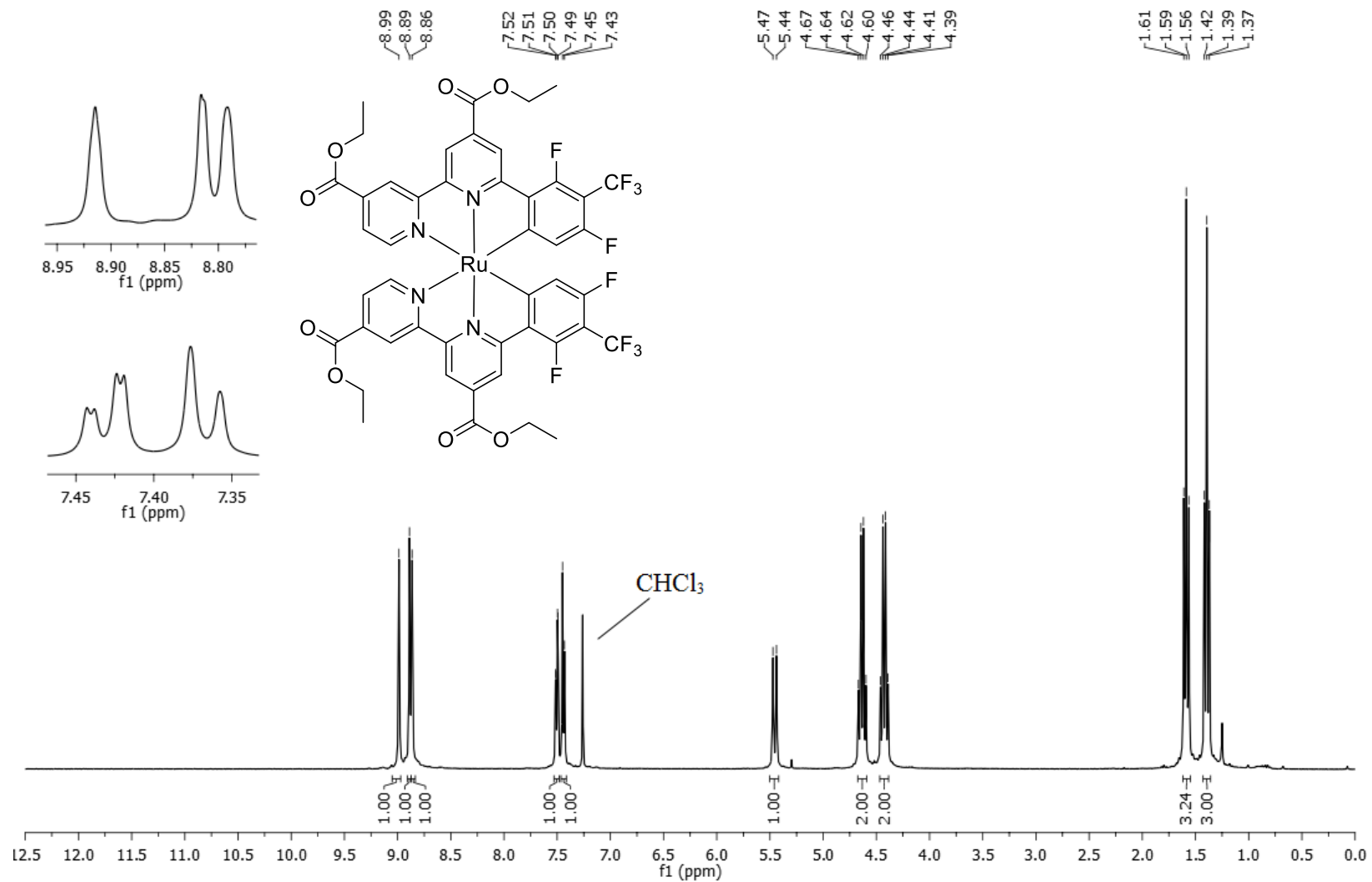
Ruthenium(II) bis(diethyl-6-(2,4-difluorophenyl)-2-2'-bipyridine-4,4'-dicarboxylate) (1a) <sup>13</sup>C NMR



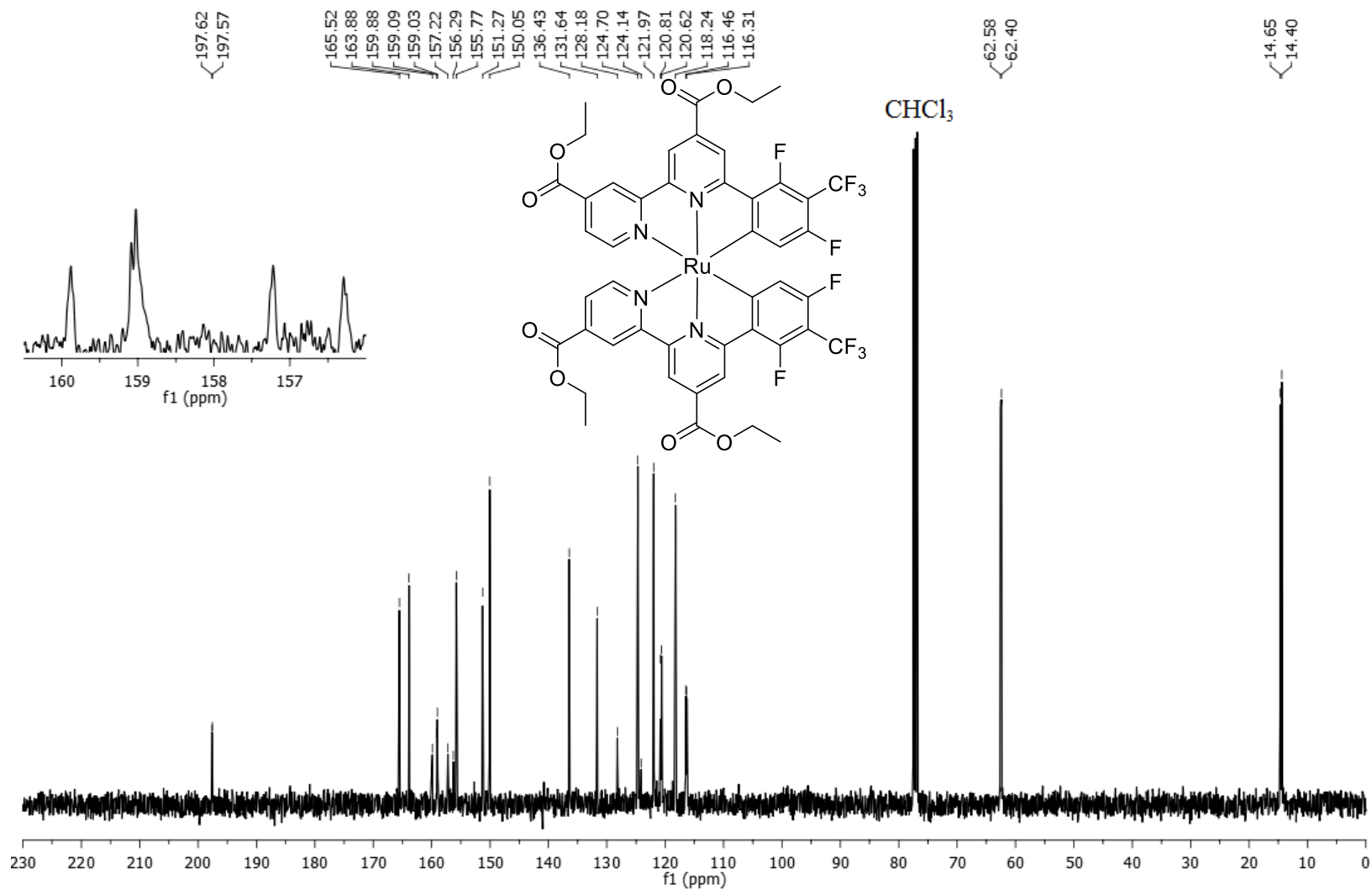
Ruthenium(II) bis(diethyl-6-(2,4-difluorophenyl)-2-2'-bipyridine-4,4'-dicarboxylate) (1a)  $^{19}\text{F}$  NMR



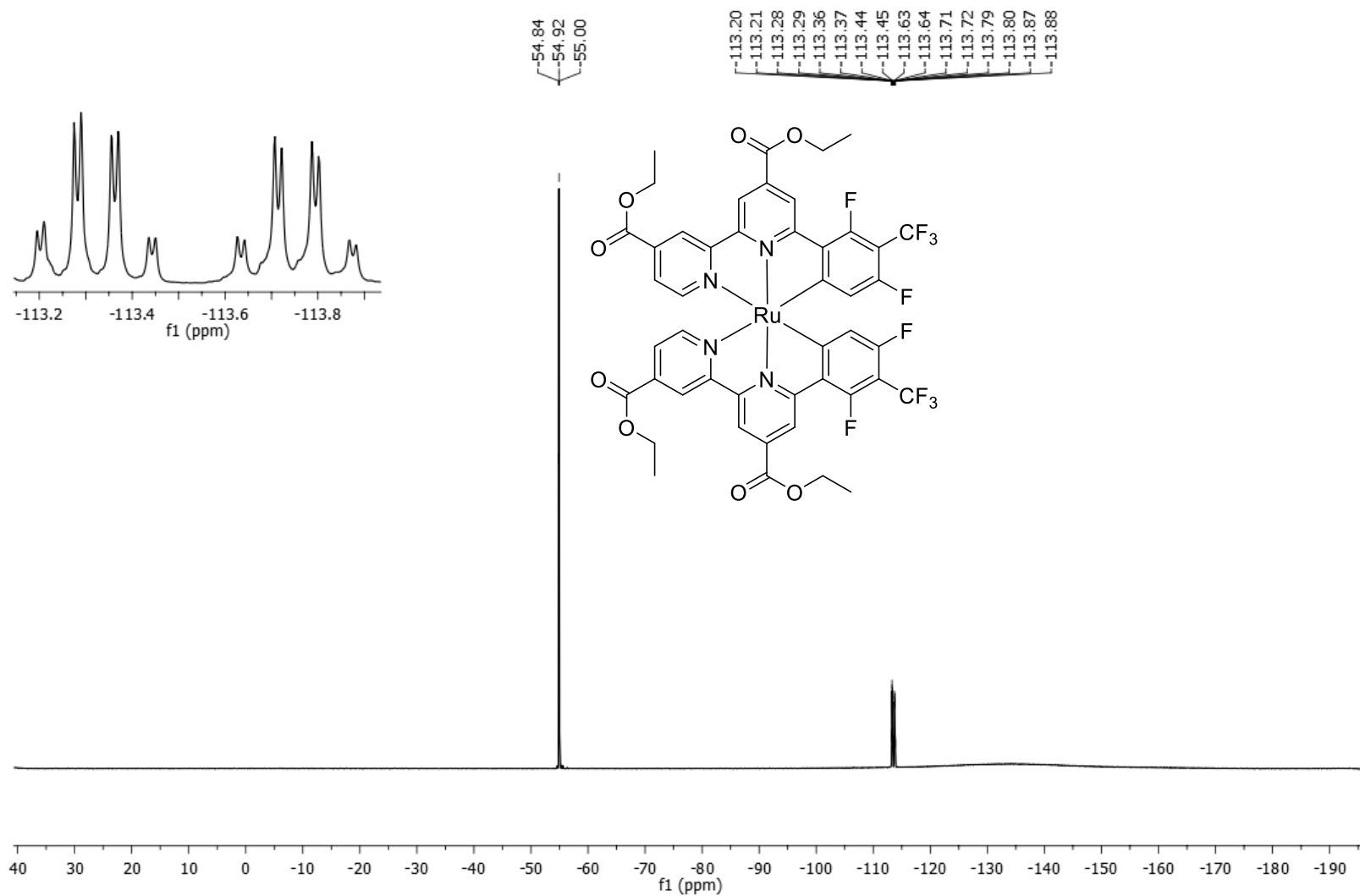
Ruthenium(II) bis(diethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2-2'-bipyridine-4,4'-dicarboxylate) (1b) <sup>1</sup>H NMR



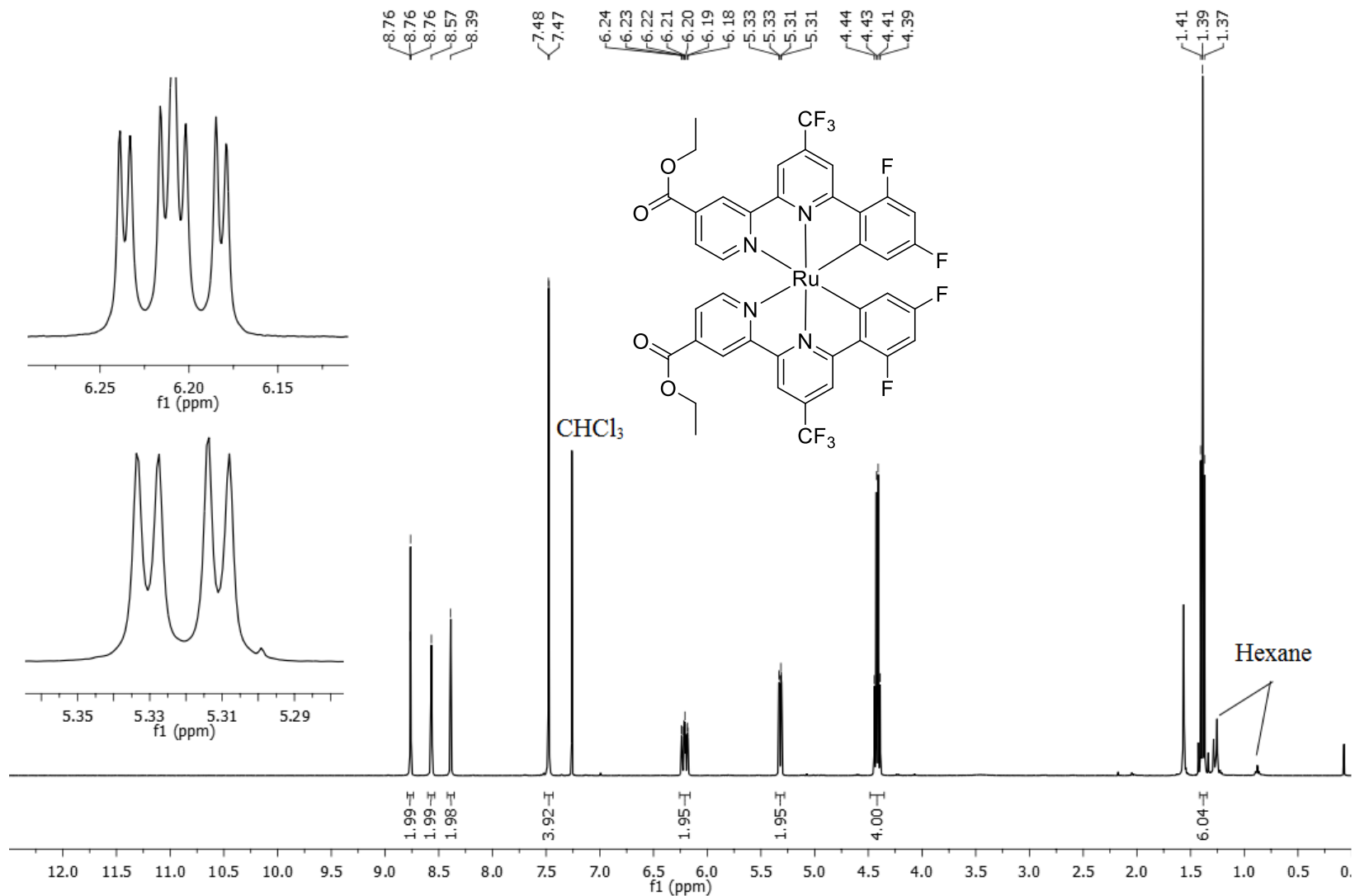
Ruthenium(II) bis(diethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2-2'-bipyridine-4,4'-dicarboxylate) (1b) <sup>13</sup>C NMR



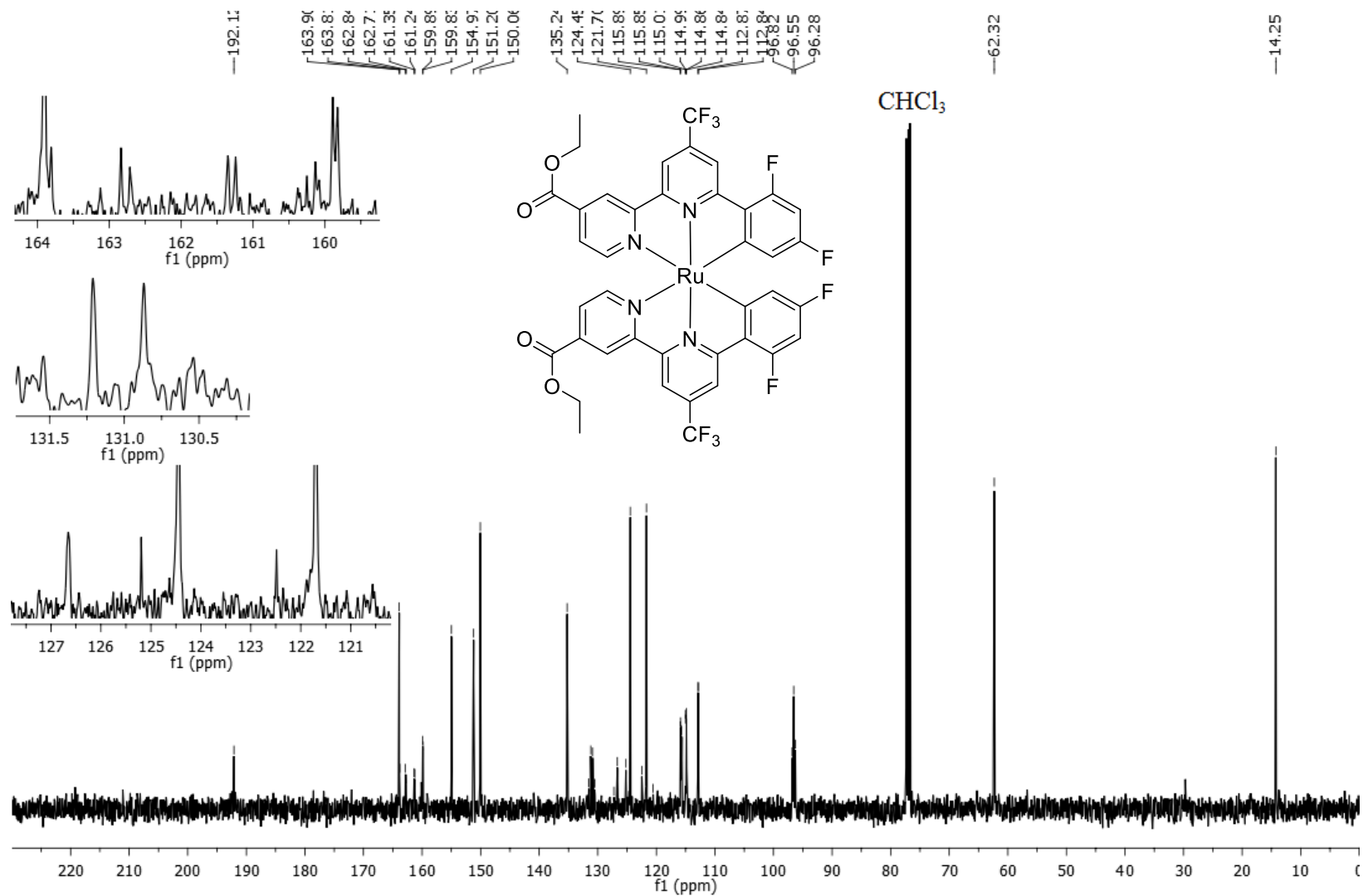
Ruthenium(II) bis(diethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2'-bipyridine-4,4'-dicarboxylate) (1b) <sup>19</sup>F NMR



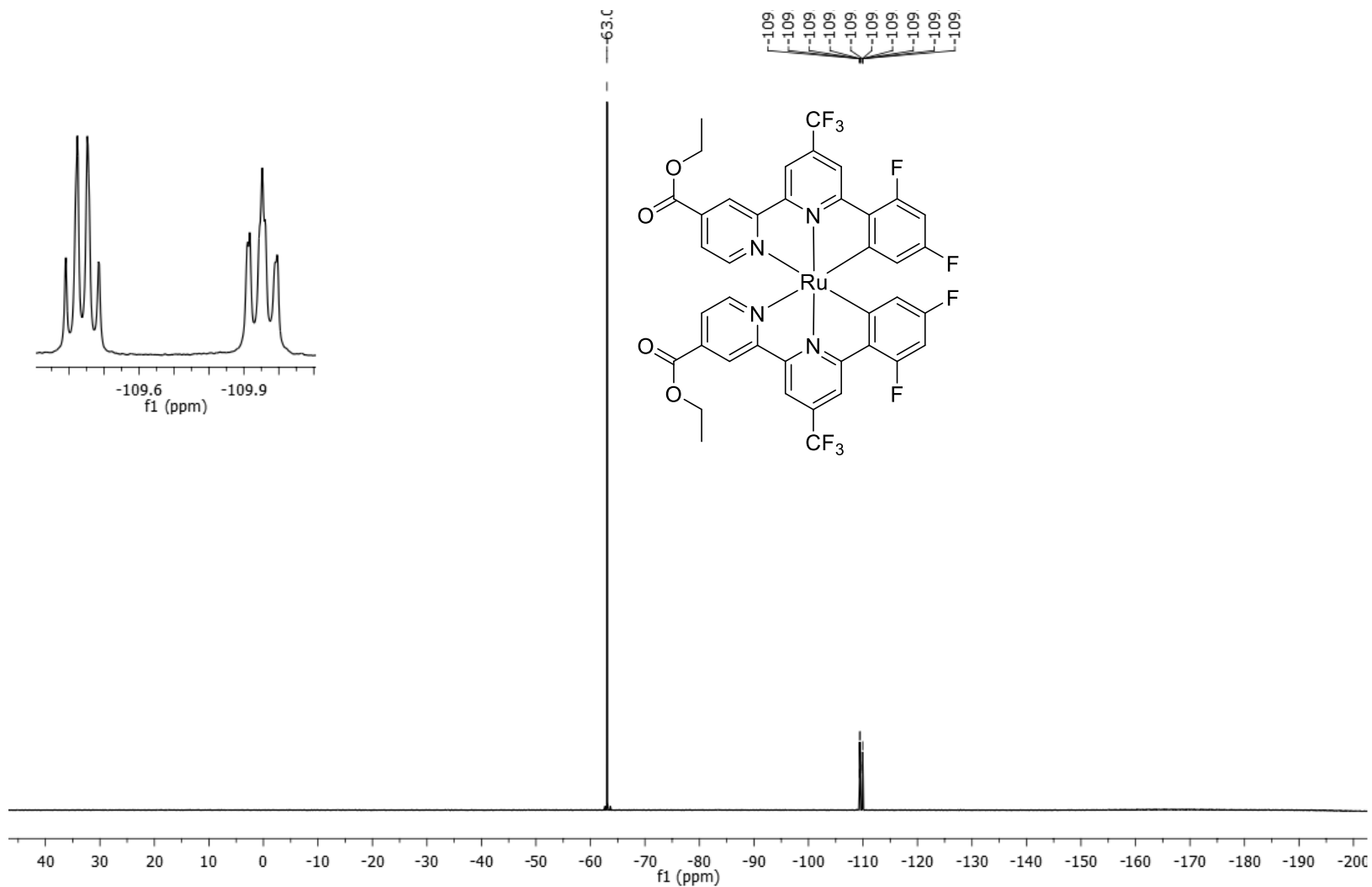
**Ruthenium(II) bis(ethyl-6-(2,4-difluorophenyl)-4-(trifluoromethyl)-2,2'-bipyridine-4'-carboxylate) (1c) <sup>1</sup>H NMR**



Ruthenium(II) bis(ethyl-6-(2,4-difluorophenyl)-4-(trifluoromethyl)-2,2'-bipyridine-4'-carboxylate) (1c) <sup>13</sup>C NMR

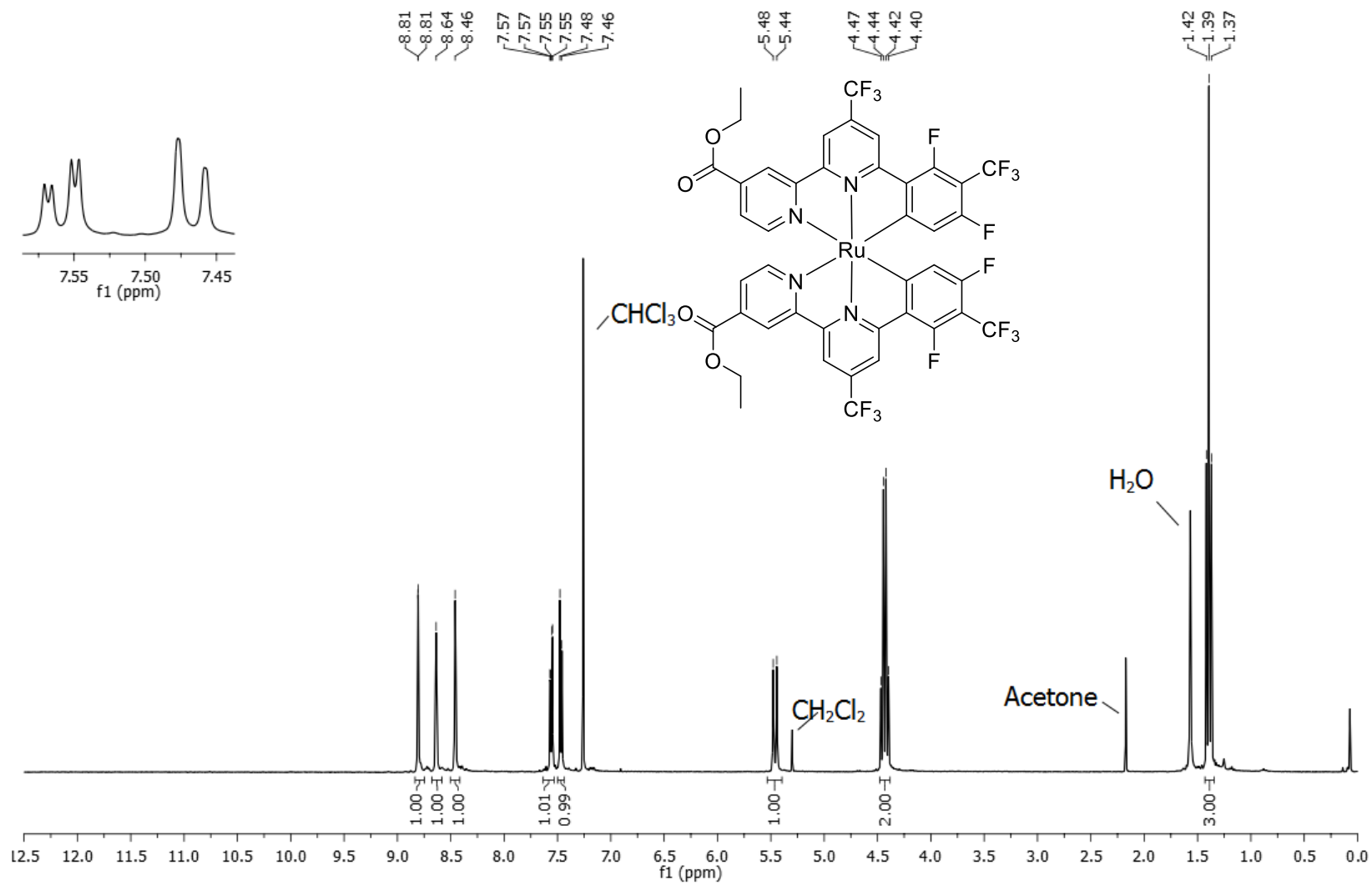


Ruthenium(II) bis(ethyl-6-(2,4-difluorophenyl)-4-(trifluoromethyl)-2'-bipyridine-4'-carboxylate) (1c) <sup>19</sup>F NMR



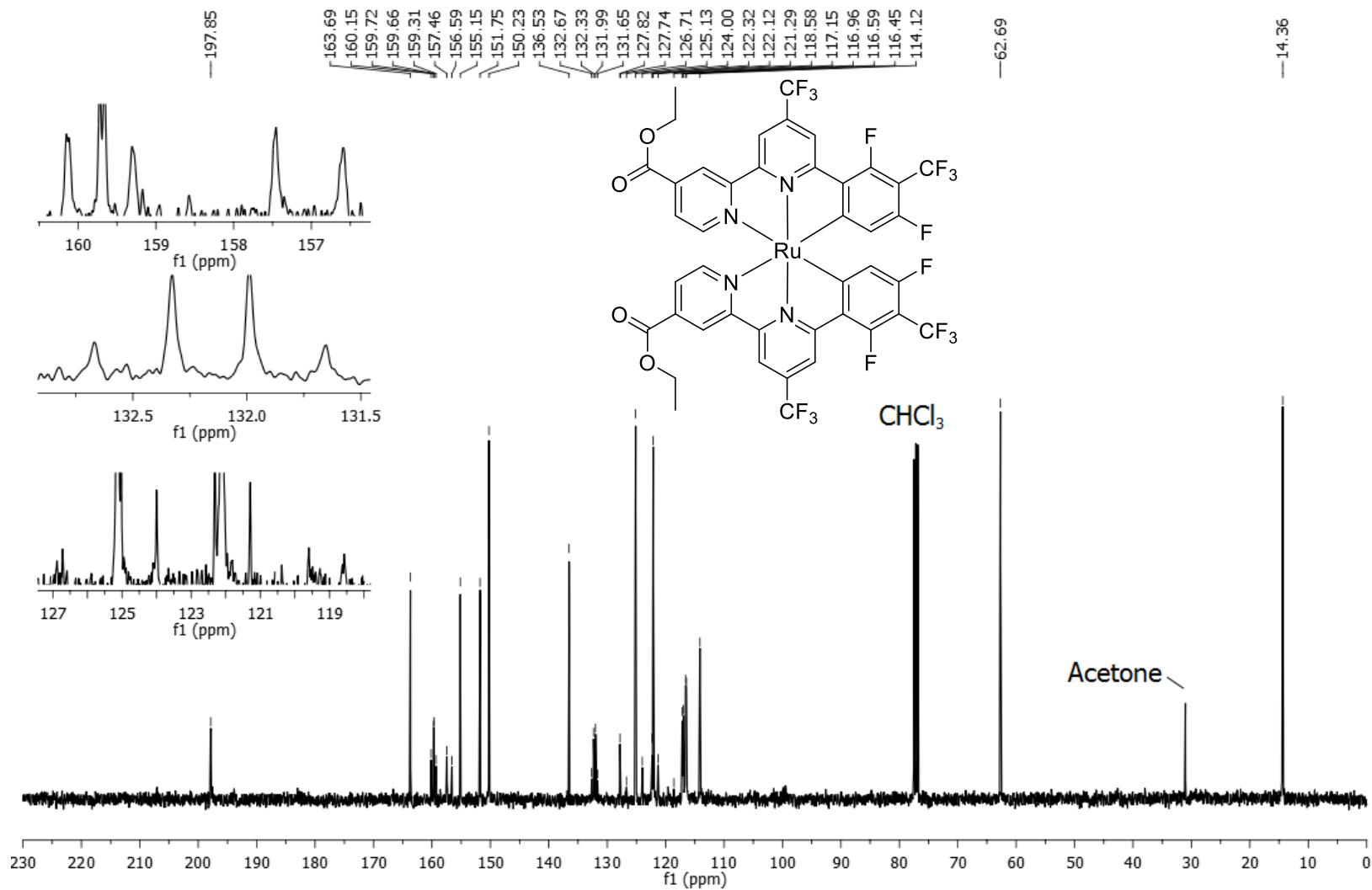
Ruthenium(II) bis(ethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2'-bipyridine-4'-carboxylate) (1d)

<sup>1</sup>H NMR



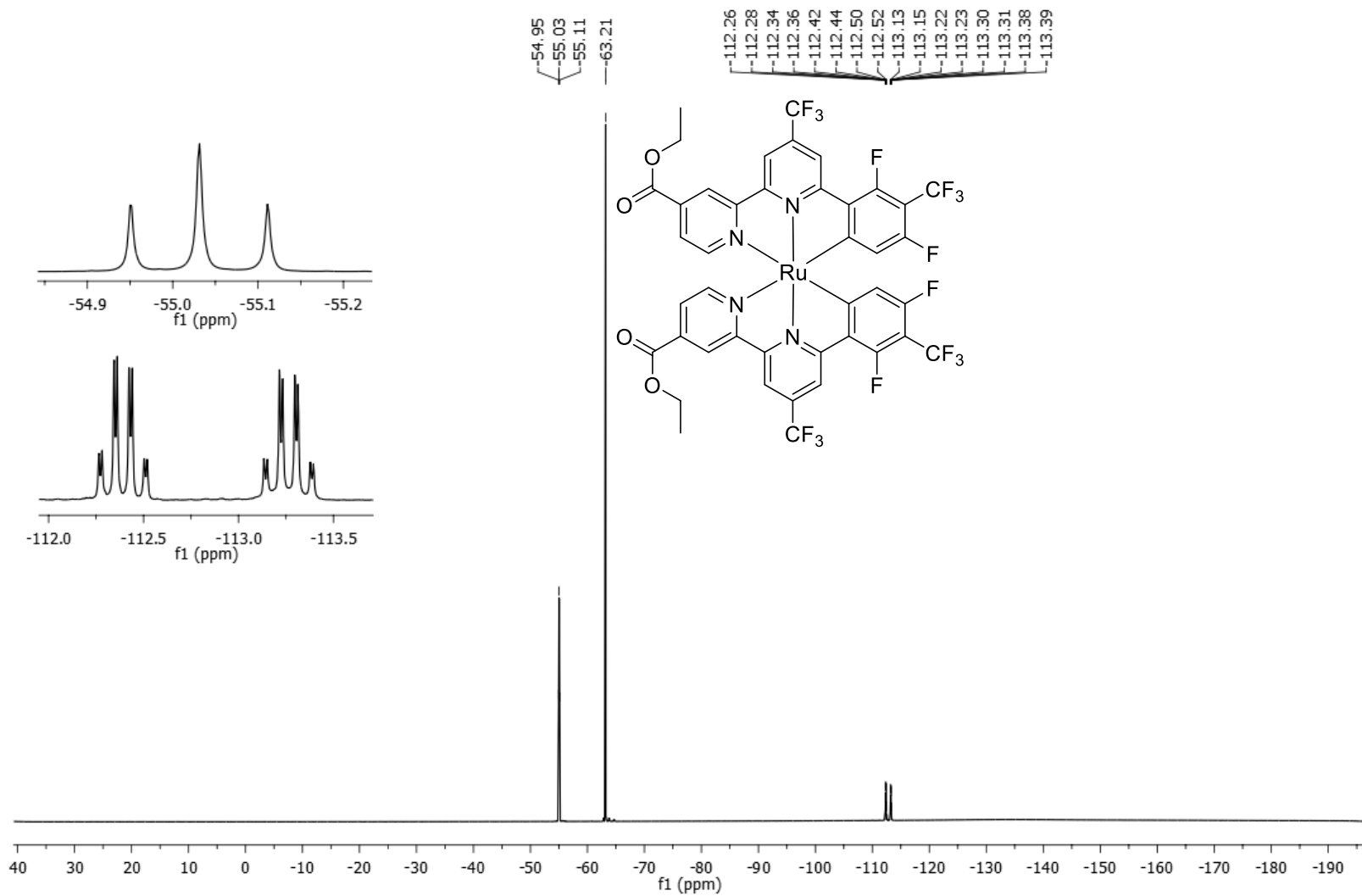
**Ruthenium(II) bis(ethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate) (1d)**

<sup>13</sup>C NMR

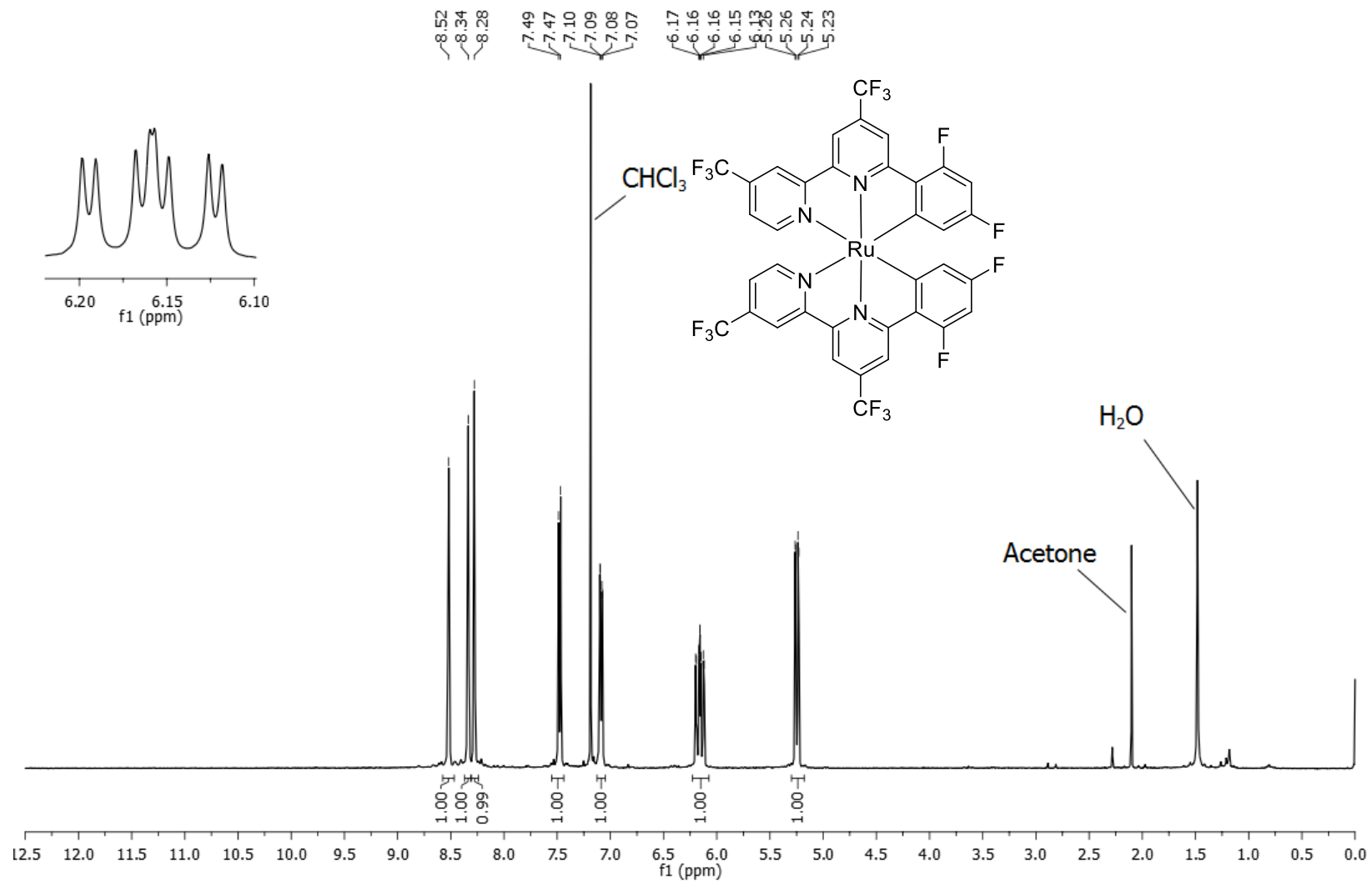


Ruthenium(II) bis(ethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2'-bipyridine-4'-carboxylate) (1d)

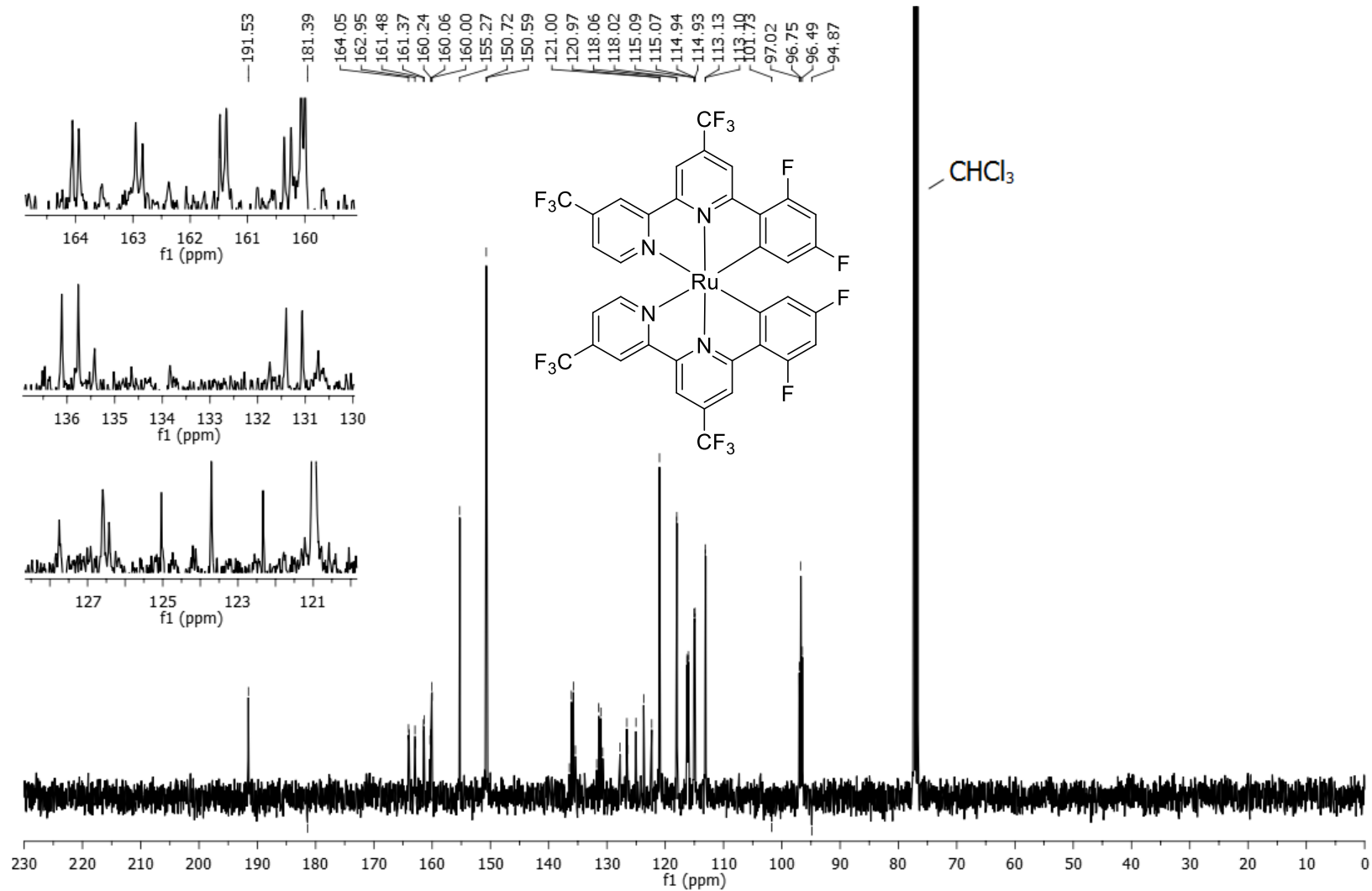
$^{19}\text{F}$  NMR



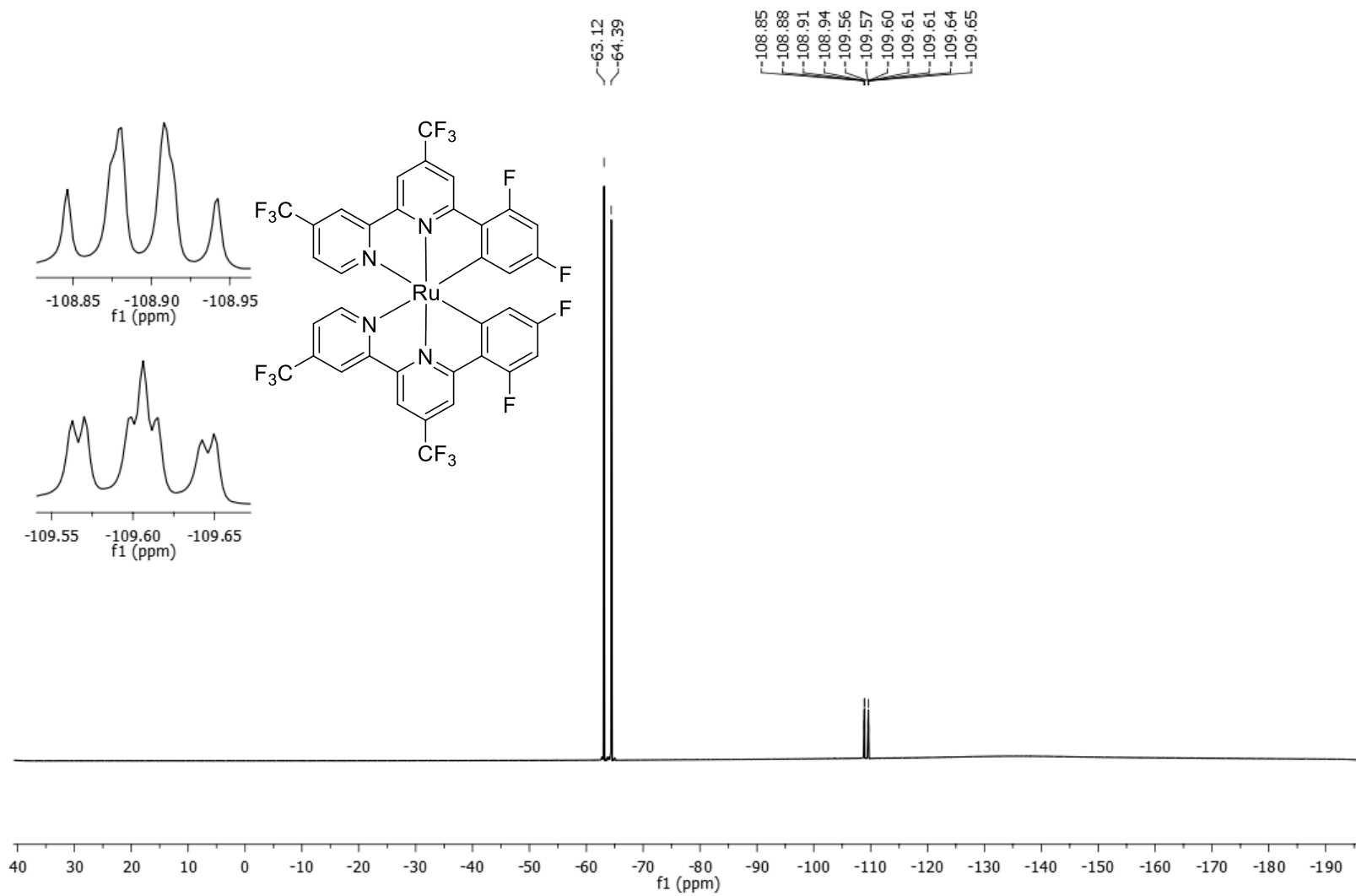
**Ruthenium(II) bis(6-(2,4-difluorophenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine) (1e) <sup>1</sup>H NMR**



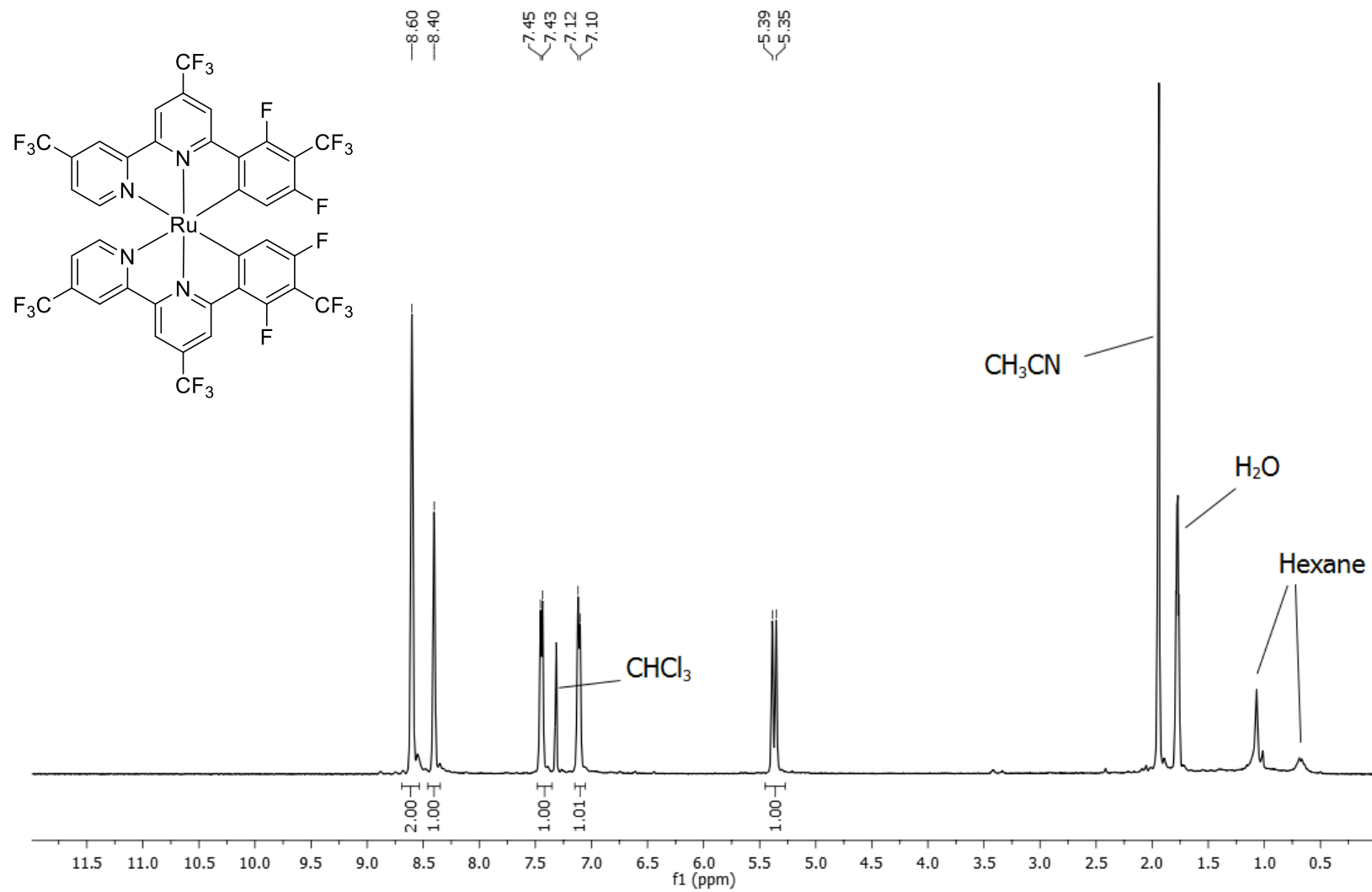
**Ruthenium(II) bis(6-(2,4-difluorophenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine) (1e)  $^{13}\text{C}$  NMR**



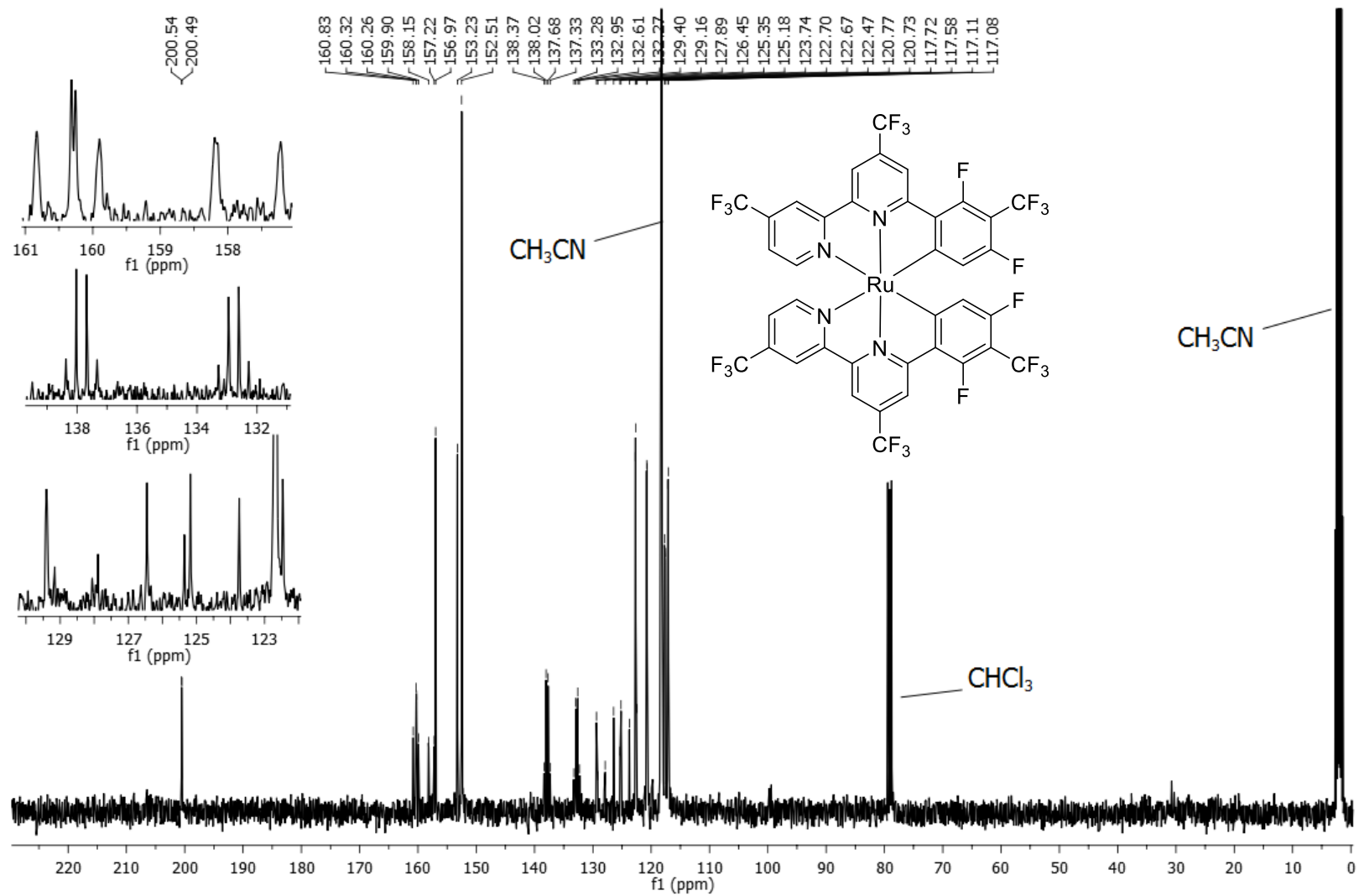
Ruthenium(II) bis(6-(2,4-difluorophenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine) (1e) <sup>19</sup>F NMR



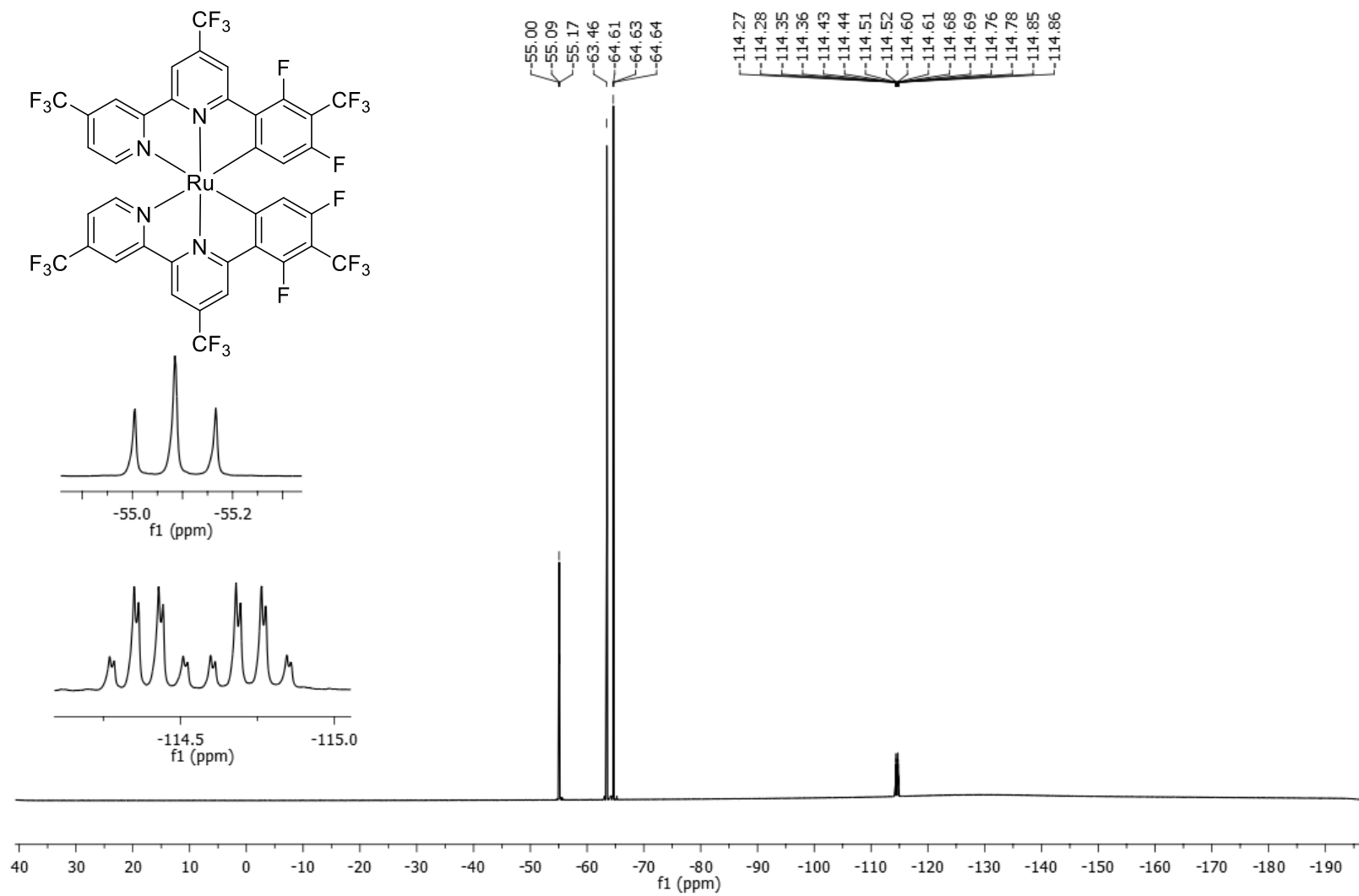
Ruthenium(II) bis(6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine) (1f) <sup>1</sup>H NMR



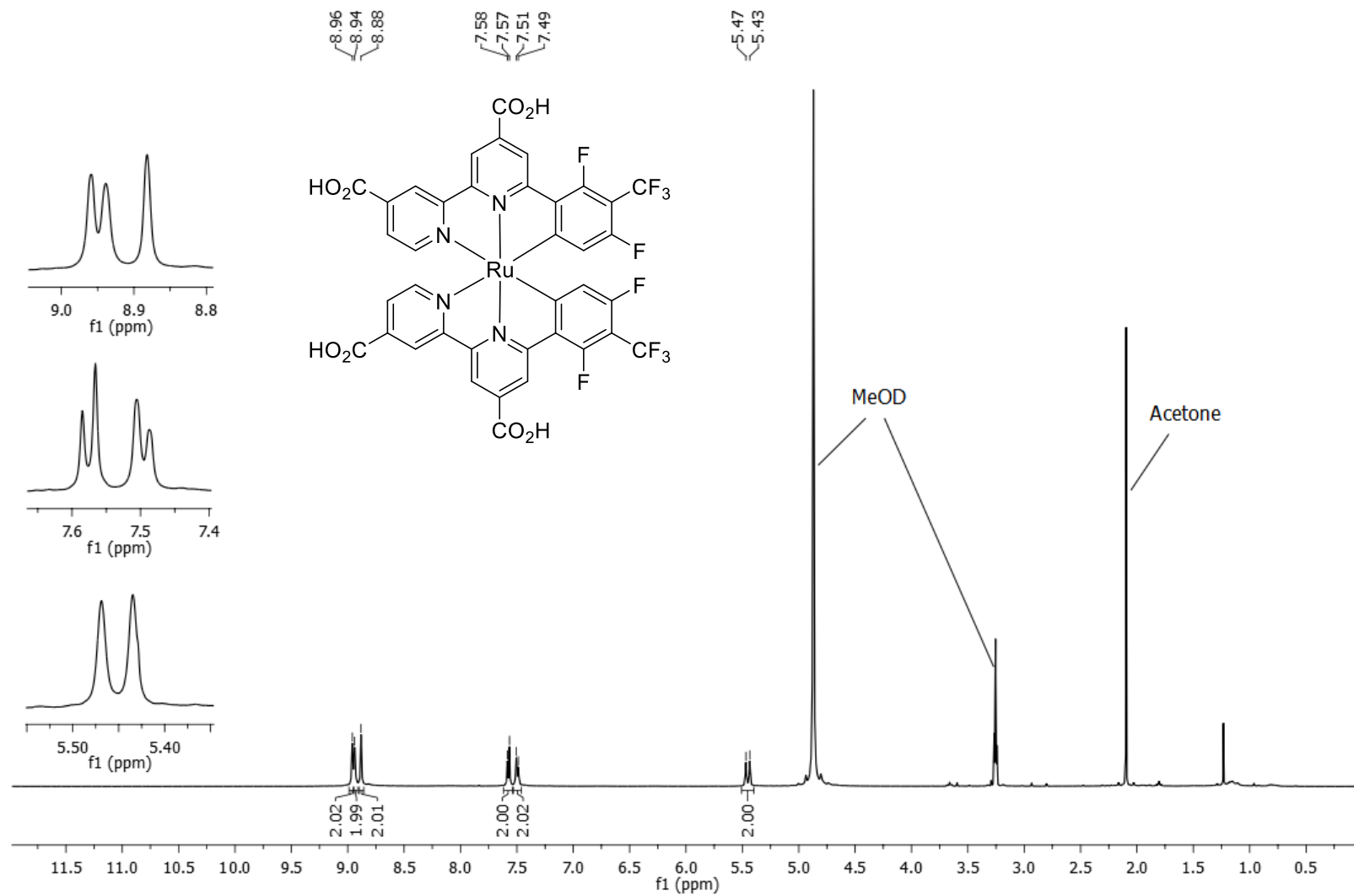
Ruthenium(II) bis(6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine) (1f) <sup>13</sup>C NMR



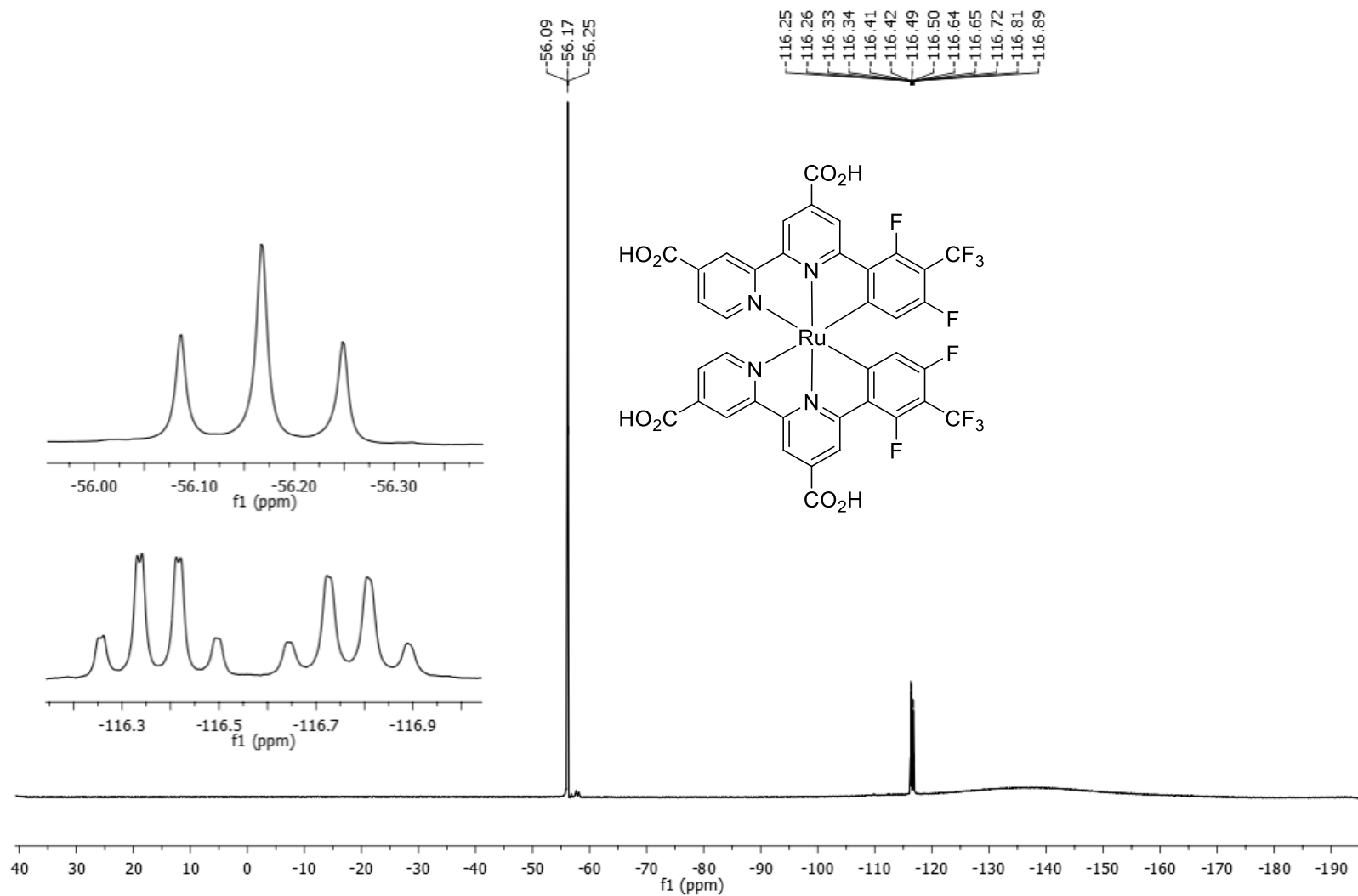
**Ruthenium(II) bis(6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4,4'-bis(trifluoromethyl)-2-2'-bipyridine) (1f)  $^{19}\text{F}$  NMR**



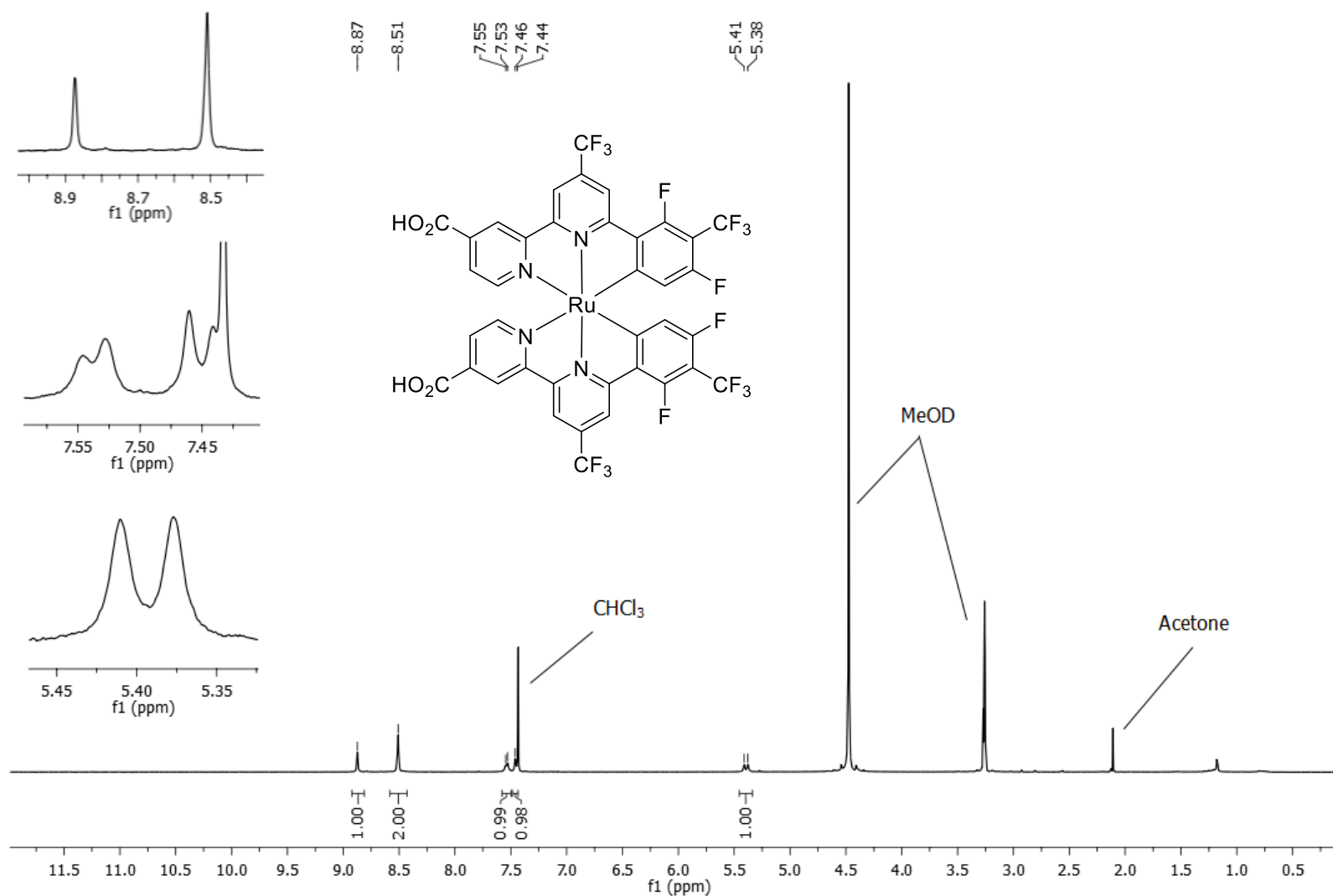
Ruthenium(II) bis(6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2-2'-bipyridine-4,4'-dicarboxylic acid) (10) <sup>1</sup>H NMR



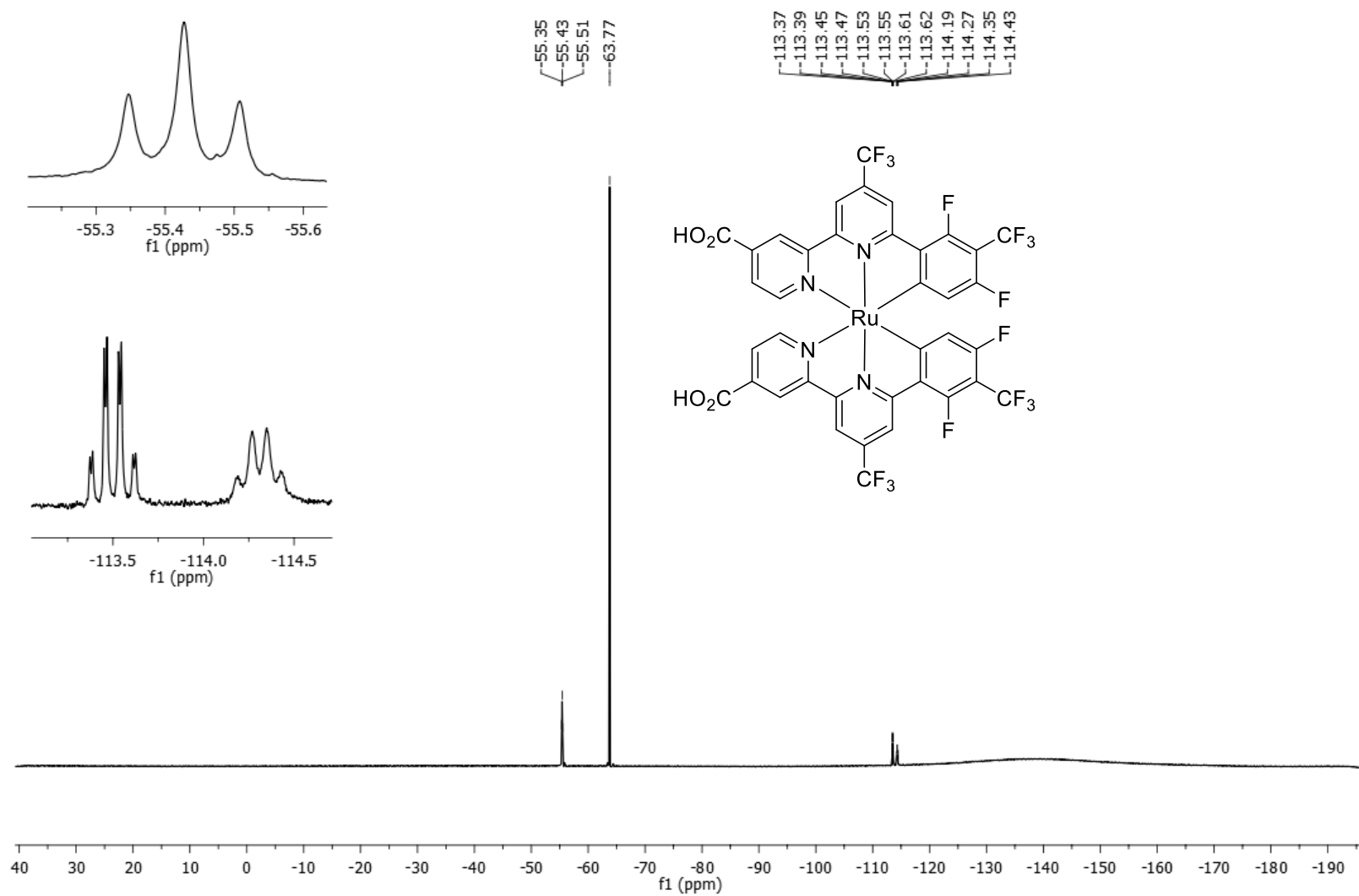
Ruthenium(II) bis(6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2-2'-bipyridine-4,4'-dicarboxylic acid) (10)  $^{19}\text{F}$  NMR



**Ruthenium(II) bis(6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylic acid) (11) <sup>1</sup>H NMR**

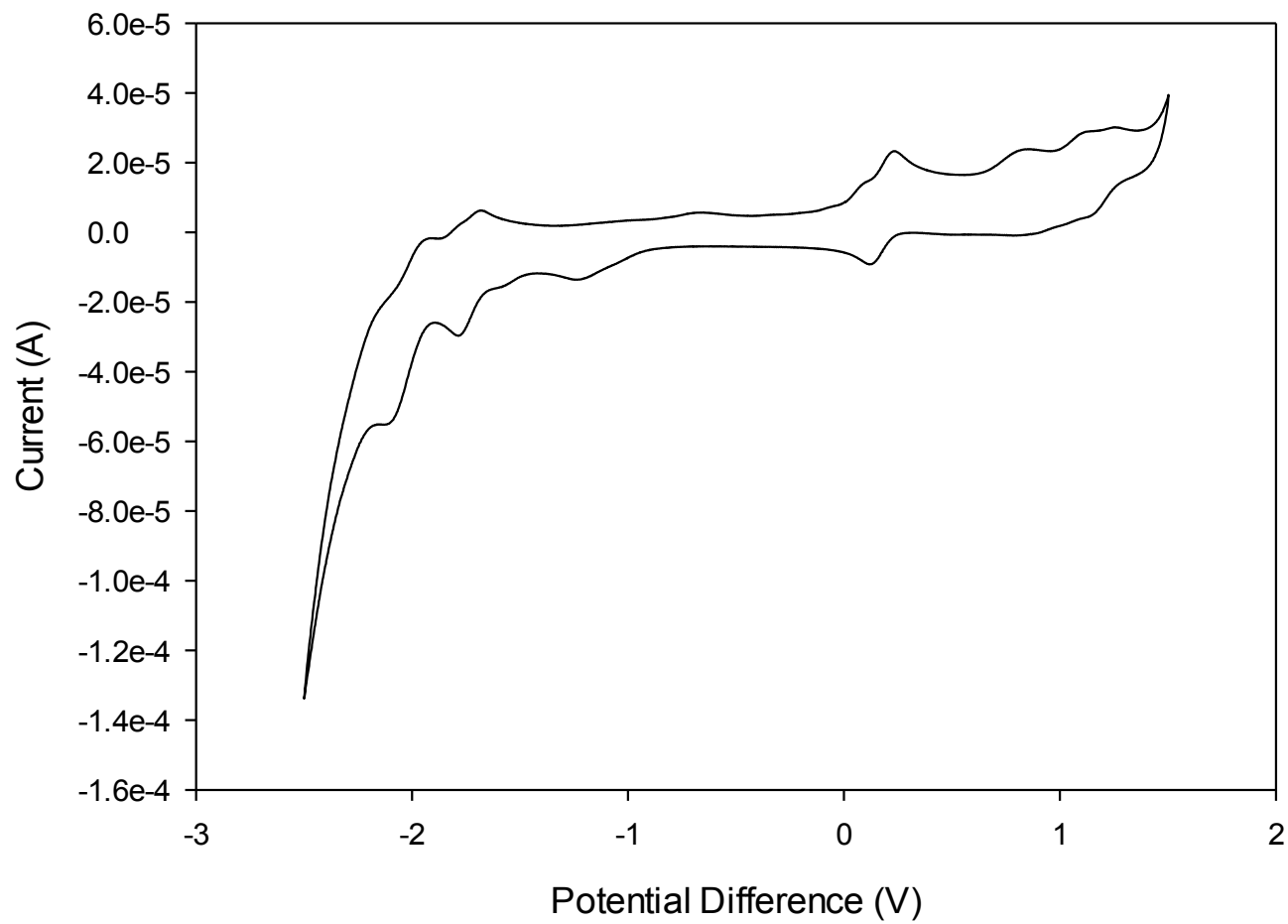


Ruthenium(II) bis(6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylic acid) (11) <sup>19</sup>F NMR

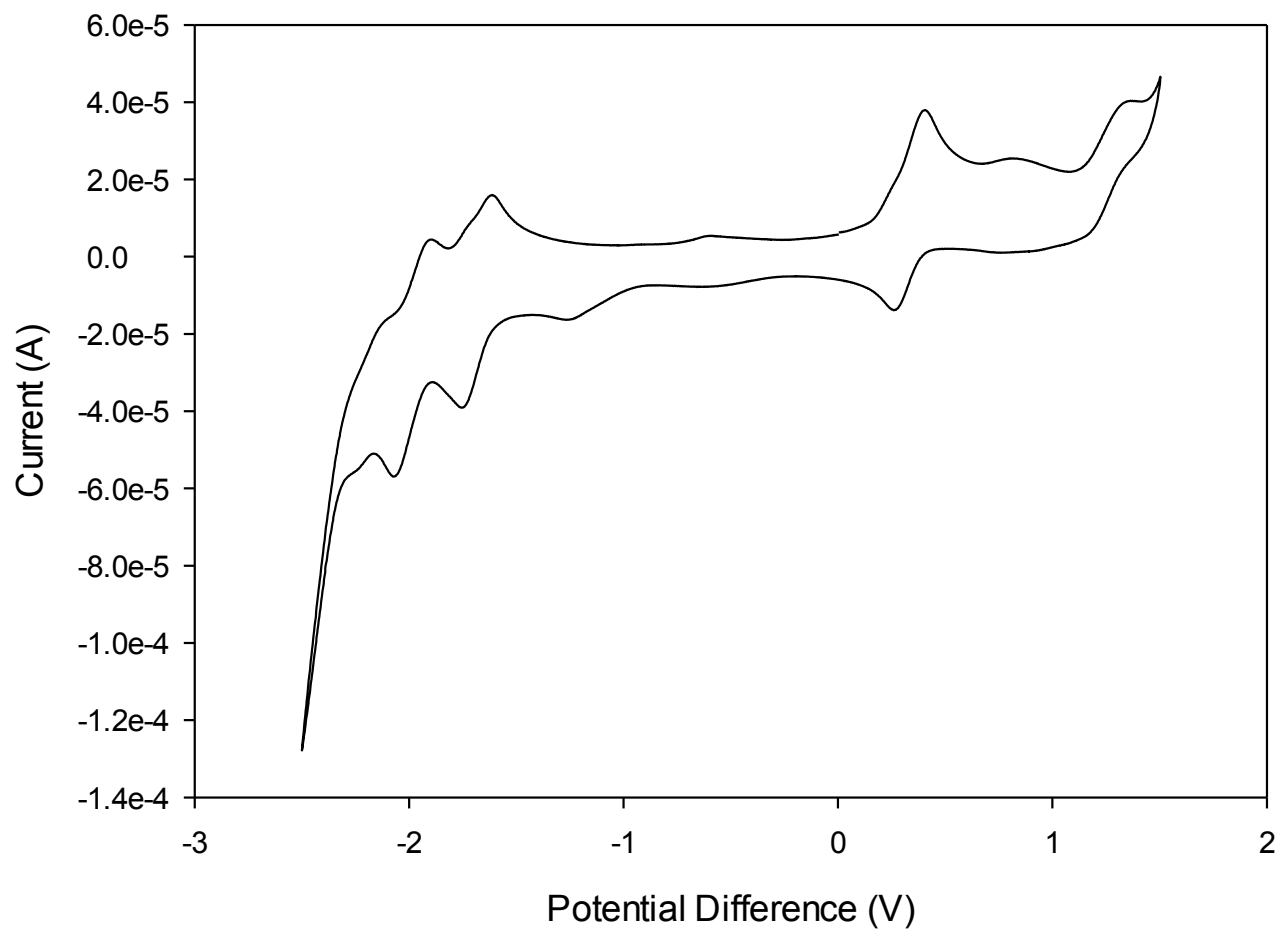


Cyclovoltammetry in dichloromethane, 100 mV/s

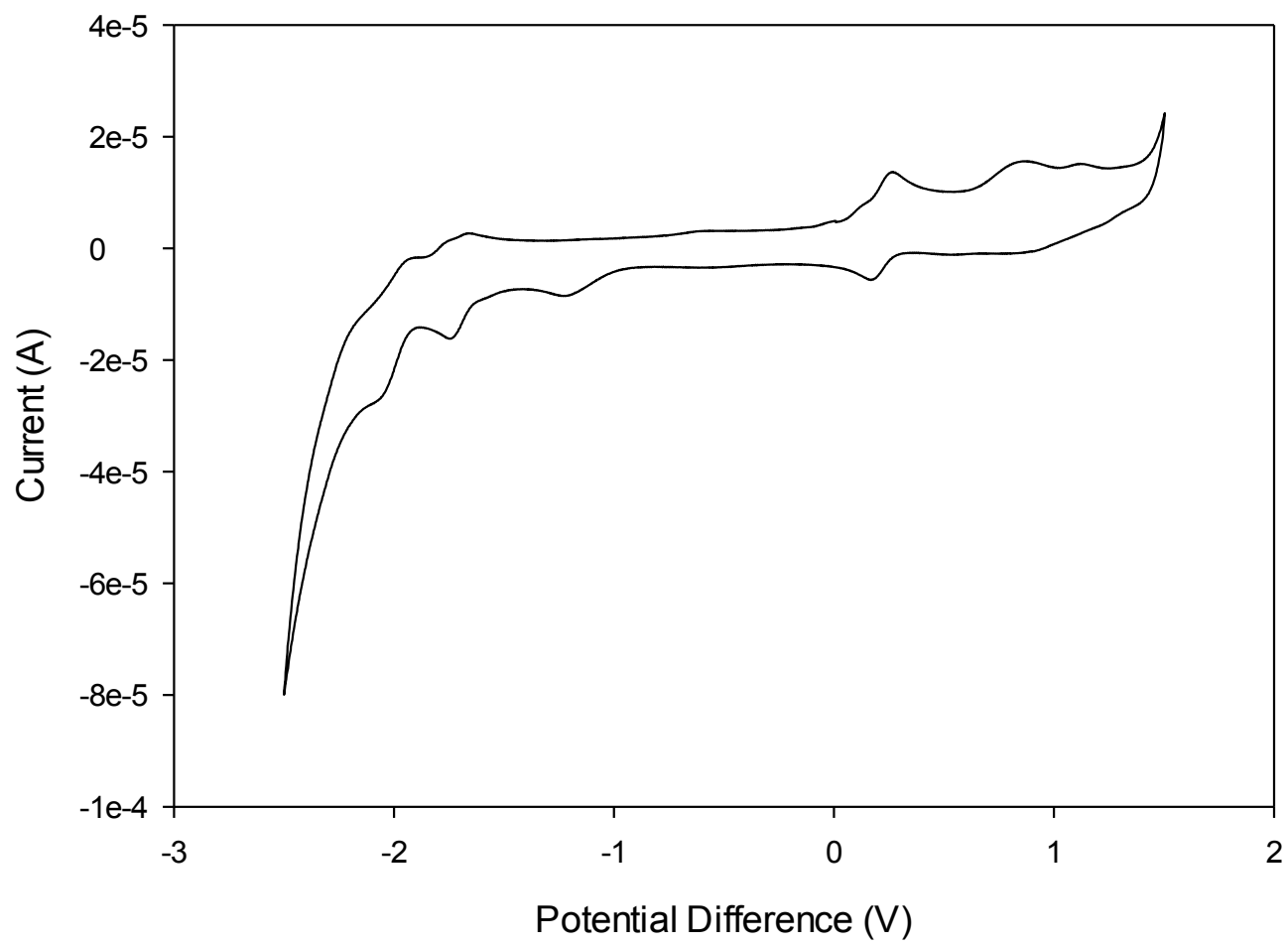
Ruthenium(II) bis(diethyl-6-(2,4-difluorophenyl)-2'-bipyridine-4,4'-dicarboxylate) (1a)



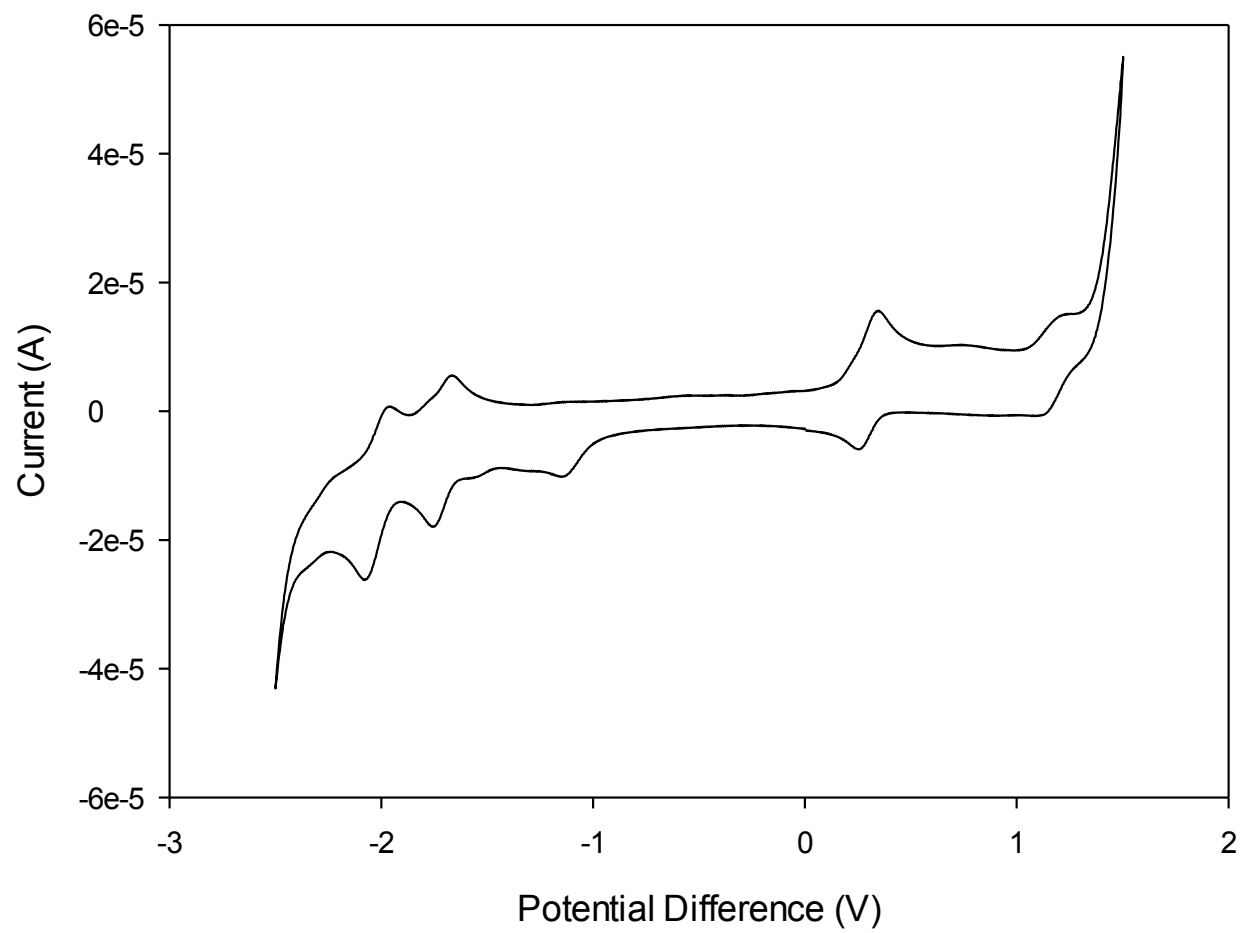
**Ruthenium(II) bis(diethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-2-2'-bipyridine-4,4'-dicarboxylate) (1b)**



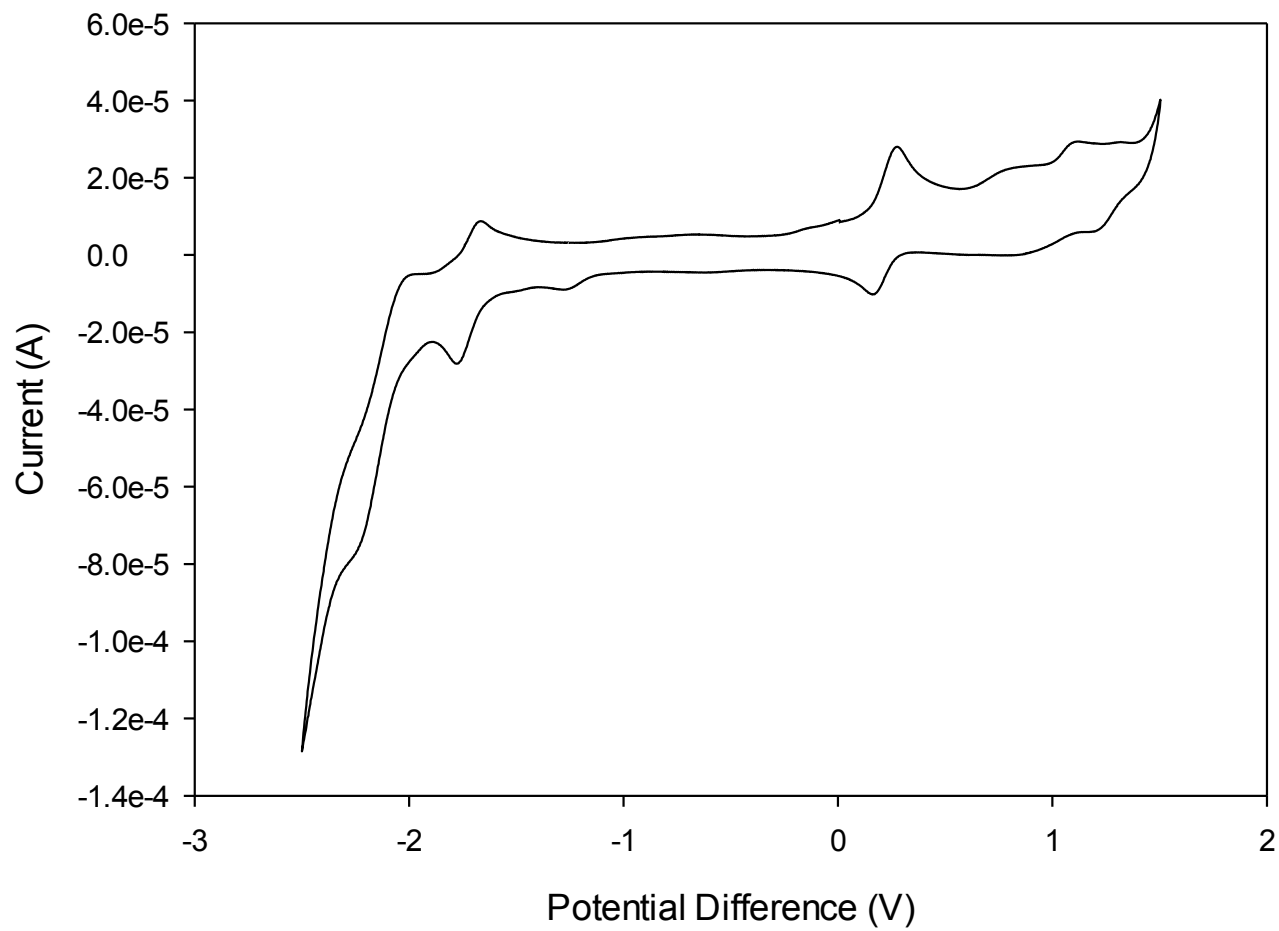
**Ruthenium(II) bis(ethyl-6-(2,4-difluorophenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate) (1c)**



**Ruthenium(II) bis(ethyl-6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4-(trifluoromethyl)-2-2'-bipyridine-4'-carboxylate) (1d)**



**Ruthenium(II) bis(6-(2,4-difluorophenyl)-4,4'-(trifluoromethyl)-2-2'-bipyridine) (1e)**



**Ruthenium(II) bis(6-(2,4-difluoro-3-(trifluoromethyl)phenyl)-4,4'-(trifluoromethyl)-2-2'-bipyridine) (1f)**

