

## Supporting Information

### High *Trans* Kinetic Selectivity in Ruthenium-based Olefin Cross Metathesis Through Stereoretention

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### Table of Contents

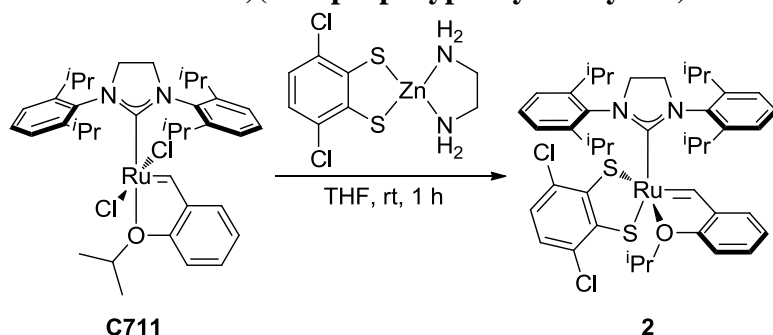
General Experimental Procedure and Reagent Availability .....	S3
Preparation of <b>2</b> .....	S3
ORTEP diagram of <b>2</b> .....	S4
Preparation of <i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -bis(2-fluoro-6-methylphenyl)oxalamide .....	S4
Preparation of 1,3-bis(2-fluoro-6-methylphenyl)-4,5-dihydro-1 <i>H</i> -imidazol-3-ium chloride .....	S4
Preparation of <b>C829</b> .....	S5
Preparation of <b>3</b> .....	S6
Preparation of <i>N,N</i> -bis(2,6-difluorophenyl)formimidamide .....	S7
Preparation of 1,3-bis(2,6-difluorophenyl)-4,4-dimethyl-4,5-dihydro-1 <i>H</i> -imidazol-3-ium tetrafluoroborate ...	S7
Preparation of <b>C642</b> .....	S8
Preparation of <b>4</b> .....	S8
Experimental Details for Table 1: Self Metathesis of 5-Tetradecene .....	S9
Experimental Details for Table 2: Self Metathesis of Methyl Oleate .....	S9
Experimental Details for Table 2, Entry 1 .....	S9
Experimental Details for Table 2, Entry 7 .....	S10
Experimental Details for Table 3: Cross Metathesis of 4-Octene and 1,4-Diacetoxy-2-Butene .....	S10
Experimental Details for Table 3, Entry 1 .....	S11
Experimental Details for Table 3, Entry 3 .....	S11
Experimental Details for Table 4: Cross Metathesis of <i>trans</i> -4-Octene and <i>trans</i> -1,4-Diacetoxy-2-Butene ..	S11
Experimental Details for Table 5: Cross Metathesis of 1-Decene and 4-Octene.....	S11
GC Methods.....	S12
References.....	S13
Figure S1. <sup>1</sup> H NMR of <b>2</b> .....	S14
Figure S2. <sup>13</sup> C NMR of <b>2</b> .....	S15
Figure S3. <sup>1</sup> H NMR of <i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -bis(2-fluoro-6-methylphenyl)oxalamide .....	S16
Figure S4. <sup>13</sup> C NMR of <i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -bis(2-fluoro-6-methylphenyl)oxalamide .....	S17
Figure S5. <sup>19</sup> F NMR of <i>N</i> <sup>1</sup> , <i>N</i> <sup>2</sup> -bis(2-fluoro-6-methylphenyl)oxalamide .....	S18

Figure S6. $^1\text{H}$ NMR of 1,3-bis(2-fluoro-6-methylphenyl)-4,5-dihydro-1 <i>H</i> -imidazol-3-ium chloride.....	S19
Figure S7. $^{13}\text{C}$ NMR of 1,3-bis(2-fluoro-6-methylphenyl)-4,5-dihydro-1 <i>H</i> -imidazol-3-ium chloride.....	S20
Figure S8. $^{19}\text{F}$ NMR of 1,3-bis(2-fluoro-6-methylphenyl)-4,5-dihydro-1 <i>H</i> -imidazol-3-ium chloride .....	S21
Figure S9. $^1\text{H}$ NMR of <b>C829</b> .....	S22
Figure S10. $^{31}\text{P}$ NMR of <b>C829</b> .....	S23
Figure S11. $^{19}\text{F}$ NMR of <b>C829</b> .....	S24
Figure S12. $^1\text{H}$ NMR of <b>3</b> .....	S25
Figure S13. $^{19}\text{F}$ NMR of <b>3</b> .....	S26
Figure S14. $^1\text{H}$ NMR of <i>N,N'</i> -bis(2,6-difluorophenyl)formimidamide .....	S27
Figure S15. $^{19}\text{F}$ NMR of <i>N,N'</i> -bis(2,6-difluorophenyl)formimidamide .....	S28
Figure S16. $^1\text{H}$ NMR of 1,3-bis(2,6-difluorophenyl)-4,4-dimethyl-4,5-dihydro-1 <i>H</i> -imidazol-3-ium tetrafluoroborate.....	S29
Figure S17. $^{13}\text{C}$ NMR of 1,3-bis(2,6-difluorophenyl)-4,4-dimethyl-4,5-dihydro-1 <i>H</i> -imidazol-3-ium tetrafluoroborate.....	S30
Figure S18. $^{19}\text{F}$ NMR of 1,3-bis(2,6-difluorophenyl)-4,4-dimethyl-4,5-dihydro-1 <i>H</i> -imidazol-3-ium tetrafluoroborate.....	S31
Figure S19. $^1\text{H}$ NMR of <b>C642</b> .....	S32
Figure S20. $^{19}\text{F}$ NMR of <b>C642</b> .....	S33
Figure S21. $^1\text{H}$ NMR of <b>4</b> .....	S34
Figure S22. $^1\text{H}$ NMR of <b>4</b> .....	S35
Figure S23. $^1\text{H}$ NMR of Methyl <i>cis</i> -9-octadecenoate .....	S36
Figure S24. $^{13}\text{C}$ NMR of Methyl <i>cis</i> -9-octadecenoate .....	S37
Figure S25. $^1\text{H}$ NMR of ( <i>Z</i> )-octadec-9-ene.....	S38
Figure S26. $^{13}\text{C}$ NMR of ( <i>Z</i> )-octadec-9-ene .....	S39
Figure S27. $^1\text{H}$ NMR of ( <i>Z</i> )-dimethyl octadec-9-enedioate.....	S40
Figure S28. $^{13}\text{C}$ NMR of ( <i>Z</i> )-dimethyl octadec-9-enedioate .....	S41
Figure S29. $^1\text{H}$ NMR of Methyl <i>trans</i> -9-octadecenoate .....	S42
Figure S30. $^{13}\text{C}$ NMR of Methyl <i>trans</i> -9-octadecenoate .....	S43
Figure S31. $^1\text{H}$ NMR of ( <i>E</i> )-octadec-9-ene .....	S44
Figure S32. $^{13}\text{C}$ NMR of ( <i>E</i> )-octadec-9-ene .....	S45
Figure S33. $^1\text{H}$ NMR of ( <i>E</i> )-dimethyl octadec-9-enedioate.....	S46
Figure S34. $^{13}\text{C}$ NMR of ( <i>E</i> )-dimethyl octadec-9-enedioate .....	S47
Figure S35. $^1\text{H}$ NMR of ( <i>Z</i> )-hex-2-en-1-yl-acetate.....	S48
Figure S36. $^{13}\text{C}$ NMR of ( <i>Z</i> )-hex-2-en-1-yl-acetate .....	S49
Figure S37. $^1\text{H}$ NMR of ( <i>E</i> )-hex-2-en-1-yl-acetate.....	S50
Figure S38. $^{13}\text{C}$ NMR of ( <i>E</i> )-hex-2-en-1-yl-acetate .....	S51

## General Experimental Procedure and Reagent Availability

All manipulations were carried out under an inert atmosphere using an argon-filled glovebox or standard Schlenk techniques. All glassware was oven dried prior to use. All solvents were anhydrous grade. All reagents, unless specified, were obtained from commercial sources and used without further purification.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{19}\text{F}\{^{13}\text{C}\}$  NMR spectra were obtained at 400, 101, 162 and 376 MHz respectively.  $^1\text{H}$  NMR spectra were recorded relative to residual protio-solvent.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded relative to the solvent resonance.  $^{31}\text{P}\{^1\text{H}\}$  and  $^{19}\text{F}\{^{13}\text{C}\}$  NMR spectra were recorded relative to external standards (85% phosphoric acid and trifluoroacetic acid). **1**<sup>1</sup> and *trans*-1,4-diacetoxy-2-butene<sup>2</sup> were prepared as previously published. Preparations of *N,N'*-bis(2,6-difluorophenyl)formimidamide<sup>3</sup> and 1,3-bis(2,6-difluorophenyl)-4,4-dimethyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate<sup>4</sup> have been detailed in the literature but are included for completeness.

### Preparation of **2** [(1,3-bis-(2,6-diisopropylphenyl)-2-imidazolidinylidene)(3,6-dichloro-1,2-benzenedithiolato)(*o*-isopropoxyphenylmethylene)ruthenium]

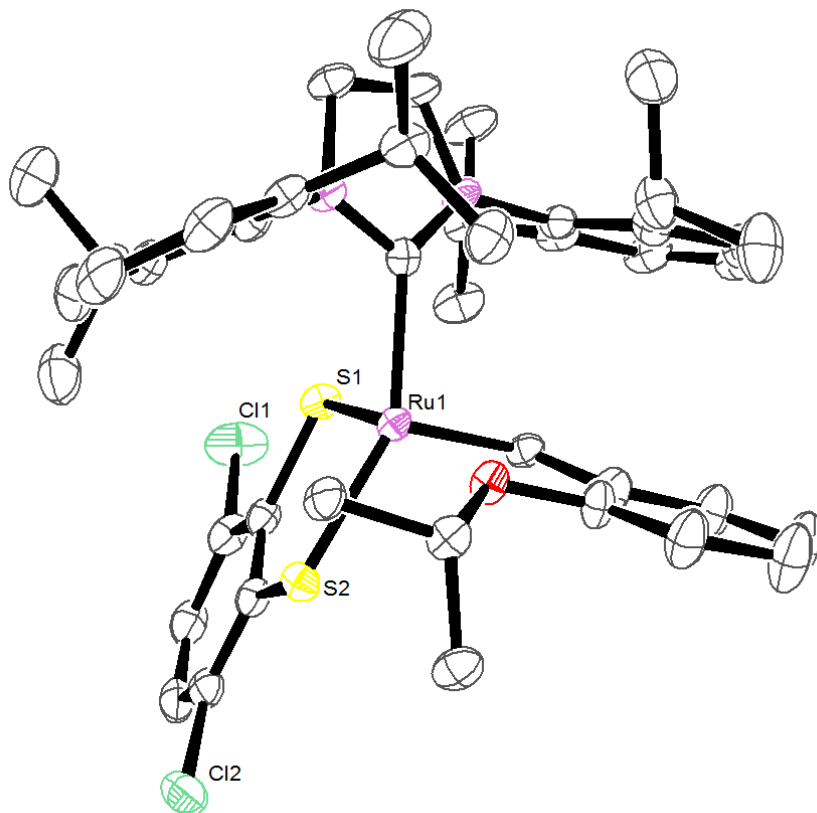


In an argon filled glovebox, a 40 mL scintillation vial equipped with a magnetic stirbar was charged with **C711** (0.500 g, 0.703 mmol), (3,6-dichlorobenzene-1,2-dithiolato)(ethylenediamine)zinc(II) (0.259 g, 0.774 mmol), and 15 mL THF. The resulting suspension was stirred for 6 hours at room temperature then devolatilized. The resulting residue was redissolved in a minimal amount of dichloromethane, filtered through a pad of celite, devolatilized and recrystallized from dichloromethane/diethyl ether at -35 °C. The red/brown crystals were isolated by filtration then dried in vacuo to afford **2** (0.462 g, 77.4% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  14.52 (s, 1H), 7.52-7.34 (m, 4H), 7.31 (d,  $J$  = 6.8 Hz, 1H), 7.20 (d,  $J$  = 6.4 Hz, 1H), 6.97-6.86 (m, 2H), 6.82 (t,  $J$  = 7.3 Hz, 2H), 6.74 (d,  $J$  = 7.0 Hz, 1H), 6.55 (d,  $J$  = 6.3 Hz, 1H), 4.97 (hept,  $J$  = 5.6 Hz, 1H), 4.36 (dd,  $J$  = 20.2, 10.5 Hz, 1H), 4.18 (dd,  $J$  = 19.1, 9.4 Hz, 1H), 4.02 (dd,  $J$  = 17.6, 9.5 Hz, 1H), 3.96-3.80 (m, 3H), 3.21 – 2.99 (m, 1H), 2.54-2.34 (m, 1H), 1.91 (d,  $J$  = 5.5 Hz, 3H), 1.43 (d,  $J$  = 5.8 Hz, 3H), 1.38 (d,  $J$  = 5.9 Hz, 3H), 1.20-1.35 (m, 6H), 1.00-1.10 (m, 6H), 0.94 (d,  $J$  = 5.9 Hz, 3H), 0.54 (d,  $J$  = 5.6 Hz, 3H), 0.04 (d,  $J$  = 5.4 Hz, 3H).

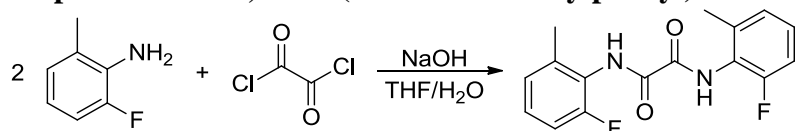
$^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  260.6 (d,  $J$  = 9.5 Hz), 220.3, 156.0, 153.8, 149.6, 148.9, 147.3, 145.7, 143.1, 141.9, 138.8, 136.1, 131.4, 130.6, 130.1, 129.2, 129.1, 126.0, 126.0, 125.6, 125.4, 124.5, 123.5, 122.9, 121.9, 115.0, 76.5, 54.4, 54.4, 30.1, 29.5, 29.1, 28.8, 27.5, 27.3, 26.7, 26.1, 26.1, 24.2, 23.4, 21.9, 21.2, 20.4.

HRMS (FAB<sup>+</sup>):  $[\text{M}]^+$   $\text{C}_{43}\text{H}_{52}\text{Cl}_2\text{N}_2\text{ORuS}_2$  Calculated – 848.1942, Found – 848.1960



**ORTEP diagram of 2**

**Preparation of  $N^1,N^2$ -bis(2-fluoro-6-methylphenyl)oxalamide**



To a 500 mL round bottom flask equipped with a magnetic stirbar was added 2-methyl-6-fluoroaniline (15.0 mL, 130 mmol), tetrahydrofuran /water (1:1, 200 mL), sodium hydroxide (5.19 g, 130 mmol), and triethylamine (0.90 mL, 6.5 mmol). The suspension was stirred vigorously at 0 °C and oxalyl chloride (6.58 mL, 77.8 mmol) was added dropwise. After complete addition the reaction was stirred for 1 hour while warming to ambient temperature. The resulting solid was isolated by filtration, washed with 1M HCl (50 mL), water (3 x 50 mL), and diethyl ether (2 x 50 mL) then dried in vacuo to afford  $N^1,N^2$ -bis(2-fluoro-6-methylphenyl)oxalamide (7.05 g, 35.7% yield).

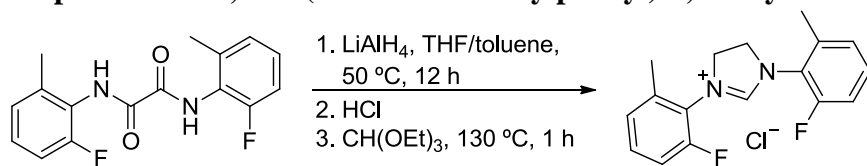
$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.52 (s, 2H), 7.32-7.24 (m, 2H), 7.19-7.11 (m, 4H), 2.24 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ ) (peak list)  $\delta$  158.8, 158.7, 156.4, 137.8, 137.8, 128.4, 128.3, 125.9, 125.8, 123.1, 123.0, 113.4, 113.2, 17.6, 17.6.

$^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ ) (peak list)  $\delta$  -120.22, -120.23, -120.24, -120.26.

HRMS (FAB+):  $[\text{M}+\text{H}]^+$   $\text{C}_{16}\text{H}_{15}\text{F}_2\text{N}_2\text{O}_2$  Calculated – 305.1102, Found – 305.1090

### Preparation of 1,3-bis(2-fluoro-6-methylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride



In an argon filled glovebox, lithium aluminum hydride (3.74 g, 98.6 mmol) and tetrahydrofuran/toluene (1:1, 100 mL) were combined in a 500 mL round bottom flask equipped with a magnetic stirbar. *N*<sup>1</sup>,*N*<sup>2</sup>-bis(2-fluoro-6-methylphenyl)oxalamide (6.00 g, 19.7 mmol) was subsequently added to the suspension in small portions with stirring. The reaction was sealed, removed from the glovebox, fitted with a reflux condenser and heated to 50 °C under argon for 12 h. After cooling to ambient temperature the reaction was quenched by slowly adding water (3.8 mL), followed by aqueous sodium hydroxide (15 wt%, 3.8 mL), then an additional portion of water (11.4 mL). The reaction was stirred rapidly for 2 hours then decanted away from solid residues and dried over magnesium sulfate. Filtration through a pad of celite afforded a clear solution which was combined with a hydrochloric acid (2.0 M in ether, 30 mL, 60 mmol). The resulting precipitate was isolated by filtration then combined with triethyl orthoformate (30 mL) and heated to 130 °C for 1 hour. After cooling the reaction to ambient temperature, the precipitate was isolated by filtration, washed with diethyl ether (2 x 25 mL), hexanes (2 x 50 mL), then dried in vacuo to afford 1,3-bis(2-fluoro-6-methylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (4.56 g, 71.7% yield)

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.63 (s, 1H), 7.55-7.47 (m, 2H), 7.38 (t, *J* = 9.2 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 4.57 (s, 4H), 2.48 (s, 6H).

<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) (peak list) δ 161.6, 158.7, 156.2, 137.9, 131.5, 131.4, 127.2, 127.1, 122.5, 122.3, 114.4, 114.2, 51.8, 51.8, 17.1, 17.1.

<sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) (peak list) δ -122.06, -122.08, -122.09, -122.10.

HRMS (FAB<sup>+</sup>): [M]<sup>+</sup> C<sub>17</sub>H<sub>17</sub>F<sub>2</sub>N<sub>2</sub> Calculated – 287.1360, Found – 287.1367

### Preparation of **C829** [(1,3-Bis(2-fluoro-6-methylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium]



In an argon filled glovebox, **C823** (0.676 g, 0.822 mmol), 1,3-bis(2-fluoro-6-methylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (0.500 g, 1.64 mmol) and toluene (50 mL) were combined in a 250 mL round bottom flask equipped with a magnetic stirbar. A solution of potassium bis(trimethylsilyl)amide (0.328 g, 1.64 mmol) in toluene (20 mL) was subsequently added and the solution stirred at ambient temperature for 2 hours. All volatiles were subsequently removed in vacuo. The resulting residue was redissolved in dichloromethane (10 mL), filtered through a pad of celite, and devolatilized. The crude product was triturated with hexanes (2 x 20 mL) then recrystallized from toluene/hexanes at ambient temperature. The red/brown crystalline complex was isolated by filtration and dried in vacuo to afford **C829** (0.454 g, 66.7% yield)

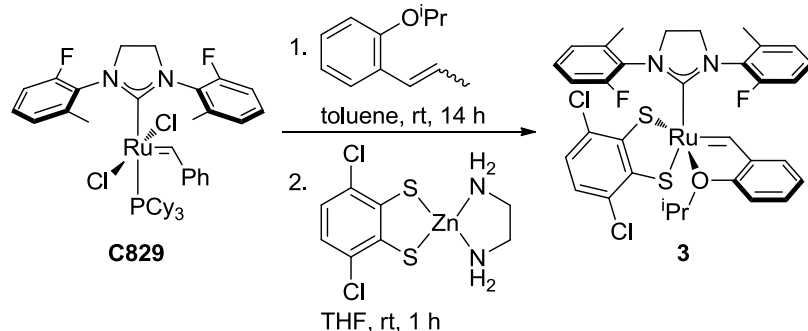
$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  19.28 (s, 1H), 9.4-8.0 (br s 1H), 7.41-7.30 (m, 2 H), 7.20 (d,  $J$  = 7.6 Hz, 1H), 7.16-7.04 (m, 3H), 6.90-5.80 (br s, 3H), 6.72-6.62 (m, 1H), 4.22-3.75 (m, 4H), 2.75 (pseudo d,  $J$  = 16.5 Hz, 3H), 2.55-2.05 (br s, 3H), 2.11 (pseudo dd,  $J$  = 22.7, 11.9 Hz, 3H), 1.65-1.23 (m, 15H), 1.10-0.72 (m, 15H).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  28.5 (s).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ ) (peak list)  $\delta$  -110.7 (br s), -111.7 (br s), -119.7 (br s), -120.4.

HRMS (FAB $^+$ ):  $[\text{M}]^+$   $\text{C}_{42}\text{H}_{55}\text{Cl}_2\text{F}_2\text{N}_2\text{PRu}$  Calculated – 828.2492, Found – 828.2493.

**Preparation of 3 [(1,3-bis-(2-fluoro-6-methylphenyl)-2-imidazolidinylidene)(3,6-dichloro-1,2-benzenedithiolato)(o-isopropoxyphenylmethylene)ruthenium]**



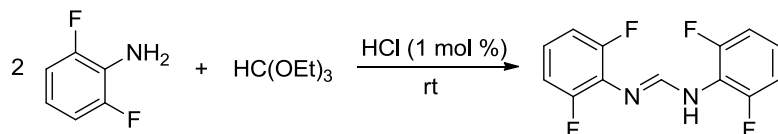
In an argon filled glovebox, **C829** (0.300 g, 0.362 mmol), 1-isopropoxy-2-(prop-1-en-1-yl)benzene (0.638 g, 3.62 mmol) and toluene (10 mL) were combined in a 40 mL scintillation vial equipped with a magnetic stirbar. The reaction was stirred at ambient temperature for 14 hours then directly adsorbed onto silica gel. Purification by column chromatography (silica gel, 2 to 6 % gradient of ethyl acetate / hexanes) afforded 0.190 g (90% pure by NMR spectroscopy) of crude intermediate. The impure intermediate was subsequently combined with (3,6-dichlorobenzene-1,2-dithiolato)(ethylenediamine)zinc(II) (0.115 g, 0.345 mmol) and tetrahydrofuran (5 mL) in a 20 mL scintillation vial equipped with a magnetic stirbar. After 4 hours of stirring at ambient temperature, all volatiles were removed, the residue redissolved in dichloromethane, filtered through celite, devolatilized and recrystallized from dichloromethane/diethyl ether at -35 °C. The resulting yellow/brown crystals were isolated by filtration, washed with cold diethyl ether (2 x 5 mL) then dried in vacuo to afford **3** (0.116 g, 35.7% yield)

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) [three conformers in solution, 8:25:67]  $\delta$  14.42 (s, 0.08H), 14.39 (s, 0.25H), 14.36 (s, 0.67H), 7.37-7.27 (m, 1H), 7.26-7.02 (m, 2.7H), 7.02-6.62 (m, 7.3H), 6.41 (s, 0.4H), 6.10 (t,  $J$  = 9.0 Hz, 0.6H), 5.47-5.38 (m, 1H), 4.13-3.86 (m, 4H), 2.61-2.40 (m, 5H), 1.85-1.65 (m, 7H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ ) (peak list) -118.7 (br s), -119.6 (br s), -120.4 (br s), -123.8 - -123.9 (m).

HRMS (FAB $^+$ ):  $[\text{M}]^+$   $\text{C}_{33}\text{H}_{30}\text{Cl}^{37}\text{ClF}_2\text{N}_2\text{ORuS}_2$  Calculated – 746.0159, Found – 746.0132

### Preparation of *N,N'*-bis(2,6-difluorophenyl)formimidamide

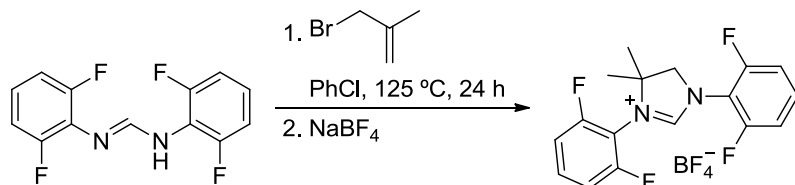


To a 100 mL round bottom flask equipped with a magnetic stirbar was added 2,6-difluoroaniline (10.0 mL, 95.9 mmol) and triethyl orthoformate (8.11 mL, 48.8 mmol). To the stirring solution was added hydrochloric acid (0.040 mL, 12 M, 0.48 mmol) and the reaction stirred at ambient temperature for 10 minutes. The reaction solidified and was subsequently sonicated for an additional 10 minutes. The resulting precipitate was subsequently isolated by filtration, washed with hexanes (2 x 30 mL) then dried in vacuo to afford *N,N'*-bis(2,6-difluorophenyl)formimidamide (8.47 g, 67.9% yield).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.47 (br s, 1H), 8.03 (s, 1H), 7.10 (br s, 6H).

<sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ -117.1 (br s, 1F), -125.3 (br s, 3F).

### Preparation of 1,3-bis(2,6-difluorophenyl)-4,4-dimethyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate



To a 250 mL round bottom flask equipped with a magnetic stirbar was added *N,N'*-bis(2,6-difluorophenyl)formimidamide (4.00 g, 14.9 mmol), 3-bromo-2-methylpropene (1.65 mL, 16.4 mmol), and chlorobenzene (120 mL). The reaction was heated to 125 °C for 24 h. After cooling the resulting precipitate was isolated by filtration and washed with diethyl ether (2 x 20 mL). The crude product was then partitioned between dichloromethane and an aqueous sodium tetrafluoroborate solution (100 mL, 1:1, 2.0 g NaBF<sub>4</sub>/50 mL). The organic layer was separated, dried over magnesium sulfate, filtered through celite and all volatiles were removed by rotary evaporation. The resulting residue was recrystallized from dichloromethane/diethyl ether to afford 1,3-bis(2,6-difluorophenyl)-4,4-dimethyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (3.25 g, 53.1% yield).

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 9.59 (s, 1H), 7.79 (m, 1H), 7.70-7.60 (m, 1H), 7.55-7.42 (m, 4H), 4.55 (s, 2H), 1.54 (s, 6H).

<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) (peak list) δ 161.6, 159.9, 159.8, 157.7, 157.7, 157.3, 157.3, 155.2, 155.2, 133.9, 133.8, 133.7, 131.7, 131.6, 131.5, 113.3, 113.3, 113.2, 113.2, 113.2, 113.2, 113.1, 113.1, 113.0, 113.0, 113.0, 109.4, 109.3, 109.1, 71.5, 62.5, 62.5, 62.5, 40.2, 39.9, 39.7, 39.5, 39.3, 39.1, 38.9, 24.5.

<sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) (peak list) -116.4 (pseudo triplet, *J* = 7.9 Hz, 2F), -119.8 (pseudo triplet, *J* = 8.3 Hz, 2F), -148.3 (s, 4F).

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 16.76 (s, 1H), 7.59-7.54 (m, 1H), 7.53-7.41 (m, 2H), 7.17-7.07 (m, 5H), 6.98-6.90 (m, 2H), 5.07-4.96 (sept, *J* = 6.2 Hz, 1H), 4.06 (s, 2H), 1.49 (s, 3H), 1.48 (s, 3H), 1.42 (d, *J* = 6.1 Hz, 6H).

HRMS (FAB+):  $[M]^+$   $C_{27}H_{26}Cl_2F_4N_2ORu$  Calculated – 642.0402, Found – 642.0421

Chemical reaction scheme showing the conversion of C642 to complex 4. C642 is a ruthenium complex with a 1,1'-bis(2,4,6-trifluorophenyl)imidazolidine ligand, a 1,1'-bis(2,4,6-trichlorophenyl)ferrocene ligand, and an isopropoxyphenyl ligand. It reacts with a zinc complex of 1,1'-bis(2,4,6-trichlorophenyl)-2,2'-bithiophene and 1,2-ethanedithiol in THF at room temperature for 1 hour to form complex 4, where the ferrocene ligand is replaced by the bithiophene ligand.

S8



and recrystallized from dichloromethane/diethyl ether at -35 °C. The resulting yellow/brown crystals were washed with cold diethyl ether (2 x 3 mL) then dried in vacuo to afford **4** (0.128 g, 70.2% yield).

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) [two conformers in solution, 40:60] δ 14.52 br s (0.4H), 14.43 (br s, 0.6H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.05-6.67 (m, 9H), 6.13 (br s, 1H), 5.42 (br s, 1H), 3.94 (br q, *J* = 8.0 Hz, 1.2H), 3.78 (br s, 0.8H), 1.88-1.74 (m, 6H), 1.50-1.28 (m, 6H).

<sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>) (peak list) δ -100.7, -108.5 (broad), -111.9, -113.1, -115.2 (broad), -116.7, -117.9, -121.8.

HRMS (FAB+): [M]<sup>+</sup> C<sub>33</sub>H<sub>28</sub>Cl<sup>37</sup>ClF<sub>4</sub>N<sub>2</sub>ORuS<sub>2</sub> Calculated – 781.9971, Found – 781.9982

### Table 1: Self-Metathesis of 5-Tetradecene

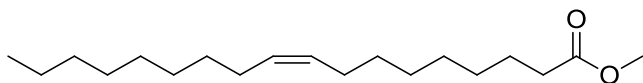
In an argon filled glovebox, a 20 mL scintillation vial equipped with a magnetic stirbar was charged with C765 (4.5 mg, 0.0059 mmol) and tetrahydrofuran (1 mL). 5-tetradecene (*cis* or *trans*) (0.150 mL, 0.588 mmol) was subsequently added, the vial sealed and heated to 40 °C for 2 hours. Yields and stereoselectivities were determined by gas chromatography (method 1).

### Table 2: Self-Metathesis of Methyl Oleate

In an argon filled glovebox, a 20 mL scintillation vial equipped with a magnetic stirbar was charged with either C765 (0.5-7.5 mol %) or C849z (0.01 mol %) and tetrahydrofuran (1 mL). Methyl-9-octadecenoate (*cis* or *trans*) (0.150 mL, 0.442 mmol) was subsequently added, the vial sealed and stirred at ambient temperature. Reactions were sampled at appropriate time intervals and yields/stereoselectivities were determined by gas chromatography (method 2).

#### Table 2, Entry 1 [isolated yield]:

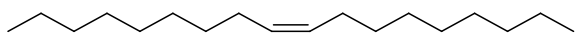
In an argon filled glovebox, a 20 mL scintillation vial equipped with a magnetic stirbar was charged with C849z (0.8 mg, 0.09 μmol, 0.01 mol %) and tetrahydrofuran (2 mL). Methyl *cis*-9-octadecenoate (0.300 mL, 0.88 mmol) was subsequently added, the vial sealed and stirred at ambient temperature for 2 hours. The reaction was directly adsorbed onto silica gel and purified by column chromatography eluting with a gradient of 0→5% ethyl acetate in hexanes. All three reaction products were isolated as colorless oils.



Methyl *cis*-9-octadecenoate: 132.3 mg, 50.7% yield

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.38-5.26 (m, 2H), 3.64 (s, 3H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.04-1.93 (m, 4H), 1.66-1.53 (m, 2H), 1.37-1.20 (m, 20H), 0.86 (t, *J* = 6.7 Hz, 3H).

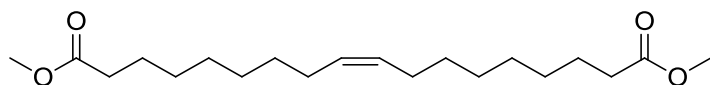
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.3, 130.1, 129.8, 51.5, 34.2, 32.0, 29.9, 29.8, 29.6, 29.4, 29.4, 29.3, 29.2, 29.2, 27.3, 27.3, 25.1, 22.8, 14.2.



(*Z*)-octadec-9-ene: 53.6 mg, 24.1% yield

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.46-5.27 (m, 2H), 2.02 (dd, *J* = 12.1, 6.4 Hz, 4H), 1.40-1.22 (m, 24H), 0.89 (t, *J* = 6.8 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 130.1, 32.1, 30.0, 29.7, 29.5, 29.5, 27.4, 22.9, 14.3.



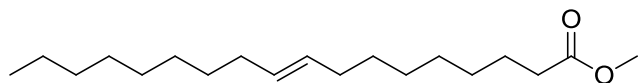
(Z)-dimethyl octadec-9-enedioate: 73.2 mg, 24.4% yield

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.37-5.22 (m, 2H), 3.63 (s, 6H), 2.27 (t,  $J = 7.5$  Hz, 4H), 2.04-1.91 (m, 4H), 1.65-1.51 (m, 4H), 1.35-1.22 (m, 16H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 129.9, 51.5, 34.2, 29.7, 29.2, 29.2, 29.2, 27.2, 25.0.

**Table 2, Entry 7 [isolated yield]:**

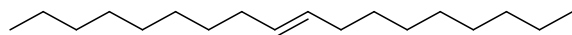
In an argon filled glovebox, a 20 mL scintillation vial equipped with a magnetic stirbar was charged with C765 (50.7 mg, 0.0663 mmol, 7.5 mol %) and tetrahydrofuran (2 mL). Methyl *trans*-9-octadecenoate (0.300 mL, 0.884 mmol) was subsequently added, the vial sealed and stirred at ambient temperature for 20 hours. The reaction was directly adsorbed onto silica gel and purified by column chromatography eluting with a gradient of 0→5% ethyl acetate in hexanes. All three reaction products were isolated as colorless oils.



Methyl *trans*-9-octadecenoate: 132.0 mg, 50.6% yield

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.45-5.27 (m, 2H), 3.63 (s, 3H), 2.27 (t,  $J = 7.5$  Hz, 2H), 1.99-1.89 (m, 4H), 1.68-1.51 (m, 2H), 1.34-1.19 (m, 20H), 0.86 (t,  $J = 6.7$  Hz, 3H).

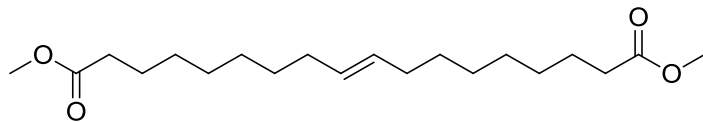
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 130.5, 130.3, 51.4, 34.2, 32.7, 32.7, 32.0, 29.8, 29.7, 29.6, 29.4, 29.3, 29.2, 29.2, 29.0, 25.1, 22.8, 14.2.



(E)-octadec-9-ene: 53.8 mg, 24.2% yield

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.46-5.33 (m, 1H), 1.97 (dd,  $J = 10.7, 5.9$  Hz, 4H), 1.40-1.13 (m, 24H), 0.89 (t,  $J = 6.8$  Hz, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  130.5, 32.8, 32.1, 29.9, 29.7, 29.5, 29.4, 22.9, 14.3.



(E)-dimethyl octadec-9-enedioate: 72.6 mg, 24.2% yield

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.41-5.27 (m, 2H), 3.63 (s, 6H), 2.27 (t,  $J = 7.5$  Hz, 4H), 1.98-1.88 (m, 4H), 1.65-1.50 (m, 4H), 1.34-1.21 (m, 16H).

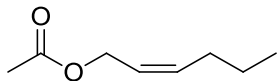
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 130.4, 51.5, 34.2, 32.6, 29.6, 29.2, 29.2, 29.0, 25.0.

**Table 3: Cross Metathesis of 4-Octene and 1,4-Diacetoxy-2-Butene**

In an argon filled glovebox, a 20 mL scintillation vial equipped with a magnetic stirbar was charged with catalyst and tetrahydrofuran (0.50 mL). 4-Octene (0.100 mL, 0.64 mmol) and 1,4-diacetoxy-2-butene (0.406 mL, 2.55 mmol) were subsequently added, the vial sealed and stirred at ambient temperature. Reactions were sampled at appropriate time intervals and yields/stereoselectivities were determined by gas chromatography (method 2).

**Table 3, Entry 1 [isolated yield]:**

In an argon filled glovebox, a 20 mL scintillation vial equipped with a magnetic stirbar was charged with C765 (14.6 mg, 0.0191 mmol, 3 mol %) and tetrahydrofuran (0.5 mL). *Cis*-4-octene (0.100 mL, 0.636 mmol) and *cis*-1,4-diacetoxy-2-butene (0.406 mL, 2.55 mmol) were subsequently added, the vial sealed and stirred at ambient temperature for 5 hours. The reaction was directly adsorbed onto silica gel and purified by column chromatography eluting with a gradient of 0→5% ethyl acetate in hexanes to afford (*Z*)-hex-2-en-1-yl acetate (74.6 mg, 0.525 mmol, 82.5% yield) as a colorless oil.

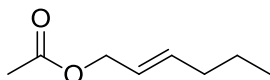


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.69-5.44 (m, 2H), 4.59 (d, *J* = 6.8 Hz, 2H), 2.11-1.96 (m, 5H), 1.44-1.32 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.0, 135.2, 123.6, 60.5, 29.6, 22.6, 21.0, 13.7.

**Table 3, Entry 3 [isolated yield]:**

In an argon filled glovebox, a 20 mL scintillation vial equipped with a magnetic stirbar was charged with C765 (36.5 mg, 0.0477 mmol, 7.5 mol %) and tetrahydrofuran (0.5 mL). *Trans*-4-octene (0.100 mL, 0.636 mmol) and *trans*-1,4-diacetoxy-2-butene (0.406 mL, 2.55 mmol) were subsequently added, the vial sealed and stirred at ambient temperature for 5 hours. The reaction was directly adsorbed onto silica gel and purified by column chromatography eluting with a gradient of 0→5% ethyl acetate in hexanes to afford (*E*)-hex-2-en-1-yl acetate (22.8 mg, 0.160 mmol, 25.2% yield) as a colorless oil.



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.81-5.52 (m, 2H), 4.50 (d, *J* = 6.7 Hz, 2H), 2.09-1.95 (m, 5H), 1.45-1.35 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.0, 135.3, 123.5, 66.7, 35.6, 22.7, 21.1, 13.7.

**Table 4: Cross Metathesis of *trans*-4-Octene and *trans*-1,4-Diacetoxy-2-Butene**

In an argon filled glovebox, a 4 mL scintillation vial equipped with a magnetic stirbar was charged with catalyst and tetrahydrofuran (1 mL). *Trans*-4-octene (0.050 mL, 0.32 mmol) and *trans*-1,4-diacetoxy-2-butene (0.203 mL, 1.27 mmol) were subsequently added, the vial sealed and stirred at ambient temperature. Reactions were sampled at appropriate time intervals and yields/stereoselectivities were determined by gas chromatography (method 2).

**Table 5: Cross Metathesis of 1-Decene and 4-Octene**

In an argon filled glovebox, a 4 mL scintillation vial equipped with a magnetic stirbar was charged with catalyst and tetrahydrofuran (2 mL). 4-Octene (*cis* or *trans*) (0.125 mL, 0.79 mmol) and 1-decene (0.050 mL, 0.26 mmol) were subsequently added, the vial sealed and stirred at ambient temperature. Reactions were sampled at appropriate time intervals and yields/stereoselectivities were determined by gas chromatography (method 1).

## GC Methods

Volatile products were analyzed using an Agilent 6850 gas chromatography (GC) instrument with a flame ionization detector (FID). The following conditions and equipment were used:

### Method 1

Column: DB-225, 30m x 0.25mm (ID) x 0.25µm film thickness.

Manufacturer: Agilent

GC and column conditions: Injector temperature: 220 °C, Detector temperature: 220 °C

Oven temperature: Starting temperature: 35 °C, hold time: 0.5 minutes.

Ramp rate 10 °C/min to 130 °C, hold time: 0 minutes.

Ramp rate 20 °C/min to 220 °C, hold time: 5 minutes.

Carrier gas: Helium

Mean gas velocity: 25 cm/sec

Split ratio: 20:1

### Method 2

Column: HP-5, 30m x 0.25mm (ID) x 0.25µm film thickness.

Manufacturer: Agilent

GC and column conditions: Injector temperature: 250 °C, Detector temperature: 280 °C

Oven temperature: Starting temperature: 100 °C, hold time: 1 minute

Ramp rate 10 °C/min to 270 °C, hold time: 12 minutes.

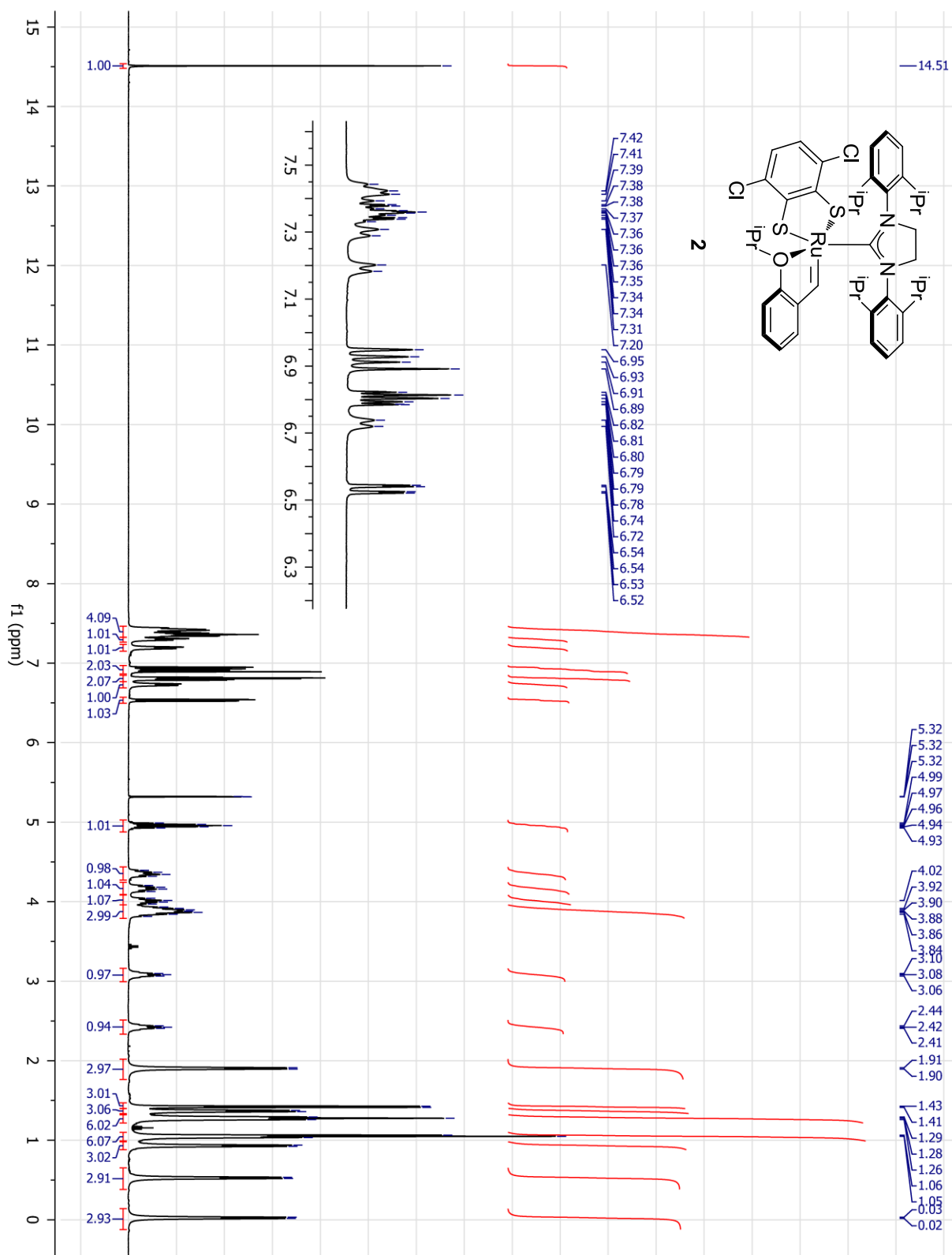
Carrier gas: Helium

Average velocity: 30 cm/sec

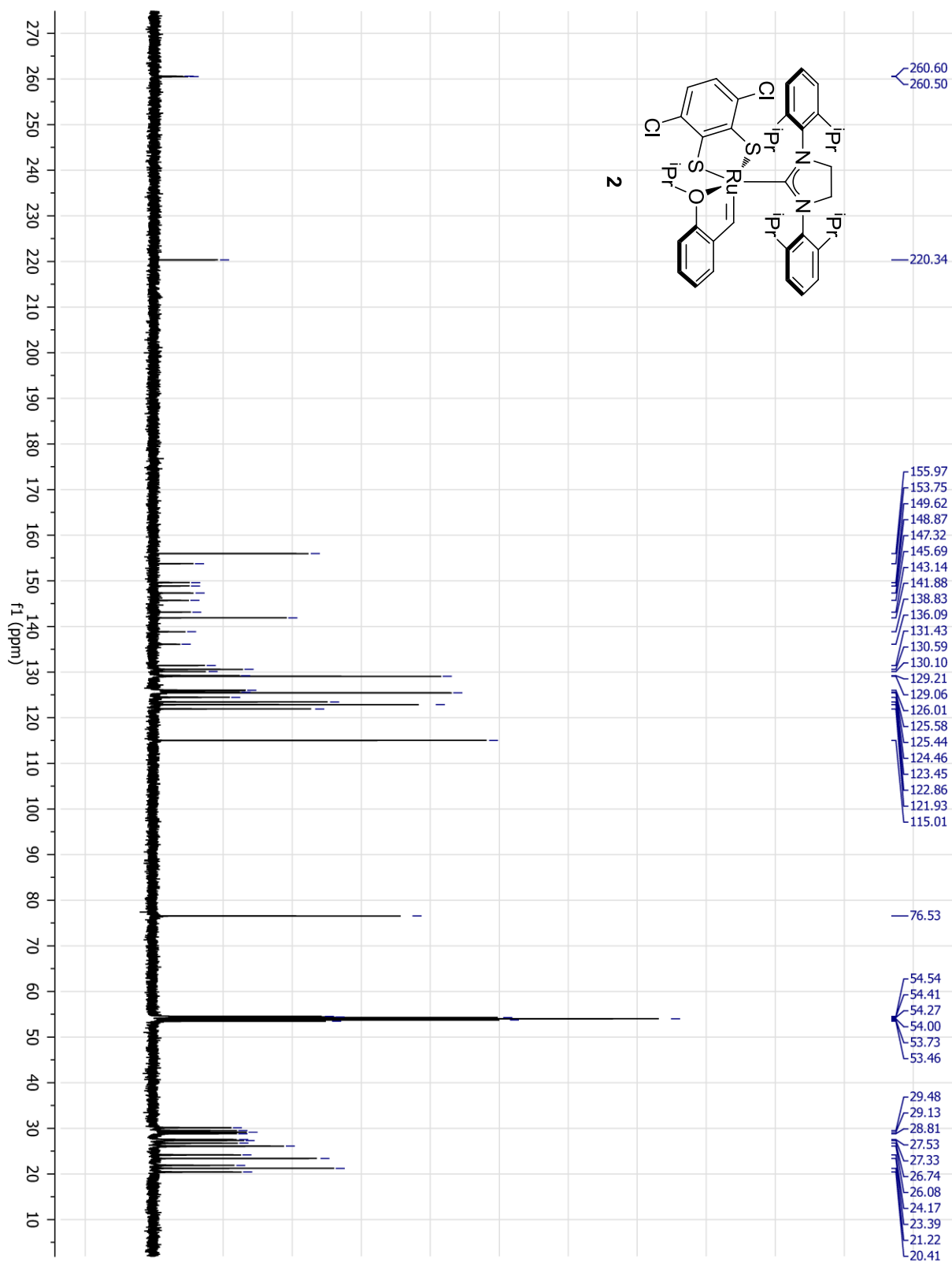
Split ratio: 40.8:1

## References

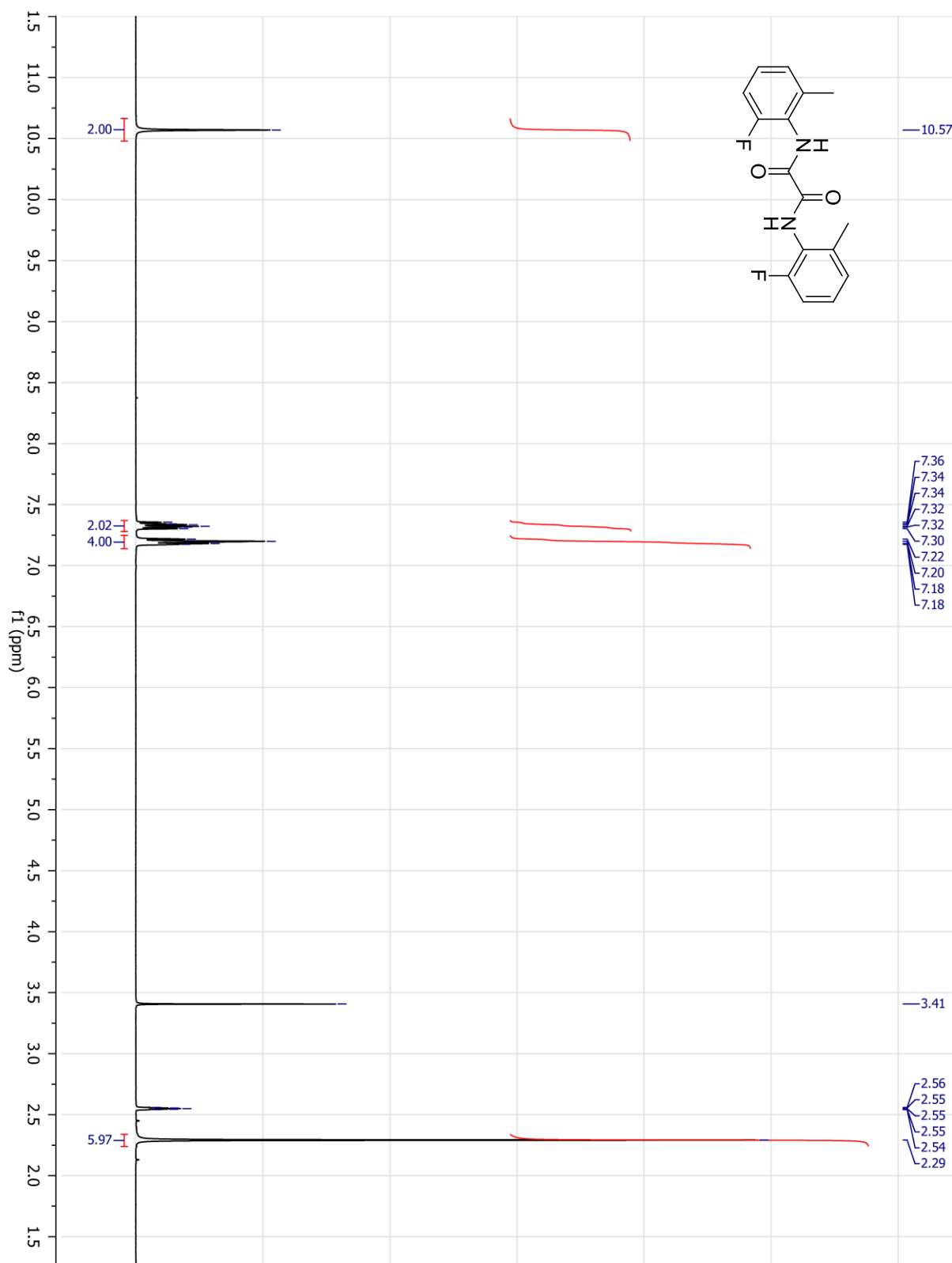
1. Koh, M. J.; Khan, R. K. M.; Torker, S.; Yu, M.; Mikus, M. S.; Hoveyda, A. H. *Nature* **2015**, *517*, 181.
2. Rodriguez, R. A.; Steed D. B.; Kawamata, Y.; Su, S.; Smith, P. A.; Steed, T. C.; Romesberg, F. E.; Baran, P. S. *J. Am. Chem. Soc.* **2014**, *136*, 15403.
3. Hobbs, M. G.; Knapp, C. J.; Welsh, P. T.; Borau-Garcia, J.; Ziegler, T.; Roesler, R. *Chem. Eur. J.* **2010**, *16*, 14520.
4. Jazzar, R.; Bourg, J. B.; Dewhurst, R. D.; Donnadieu, B.; Bertrand, G. *J. Org. Chem.* **2007**, *72*, 3492.



**Figure S1.** <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of **2**

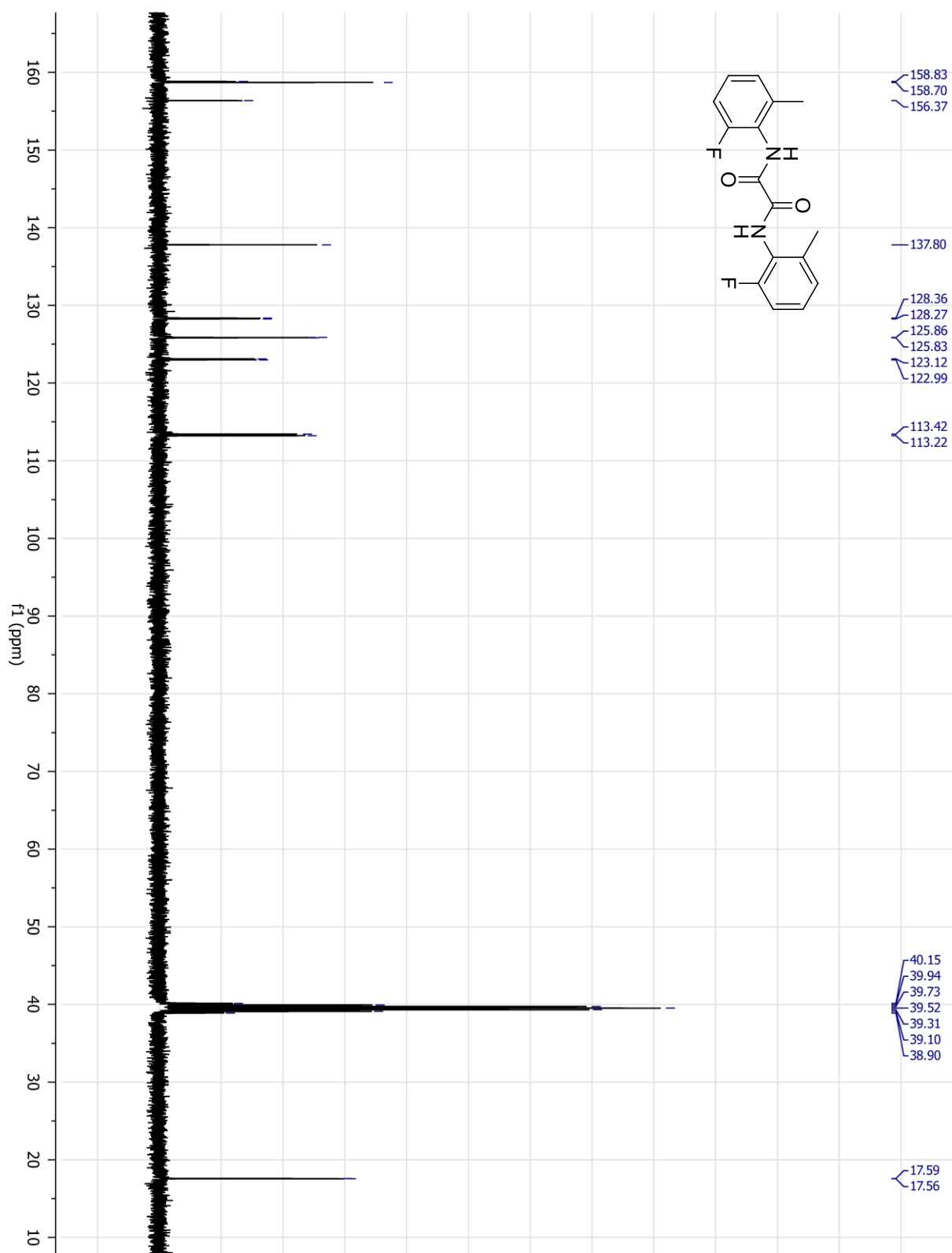


**Figure S2.** <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of **2**

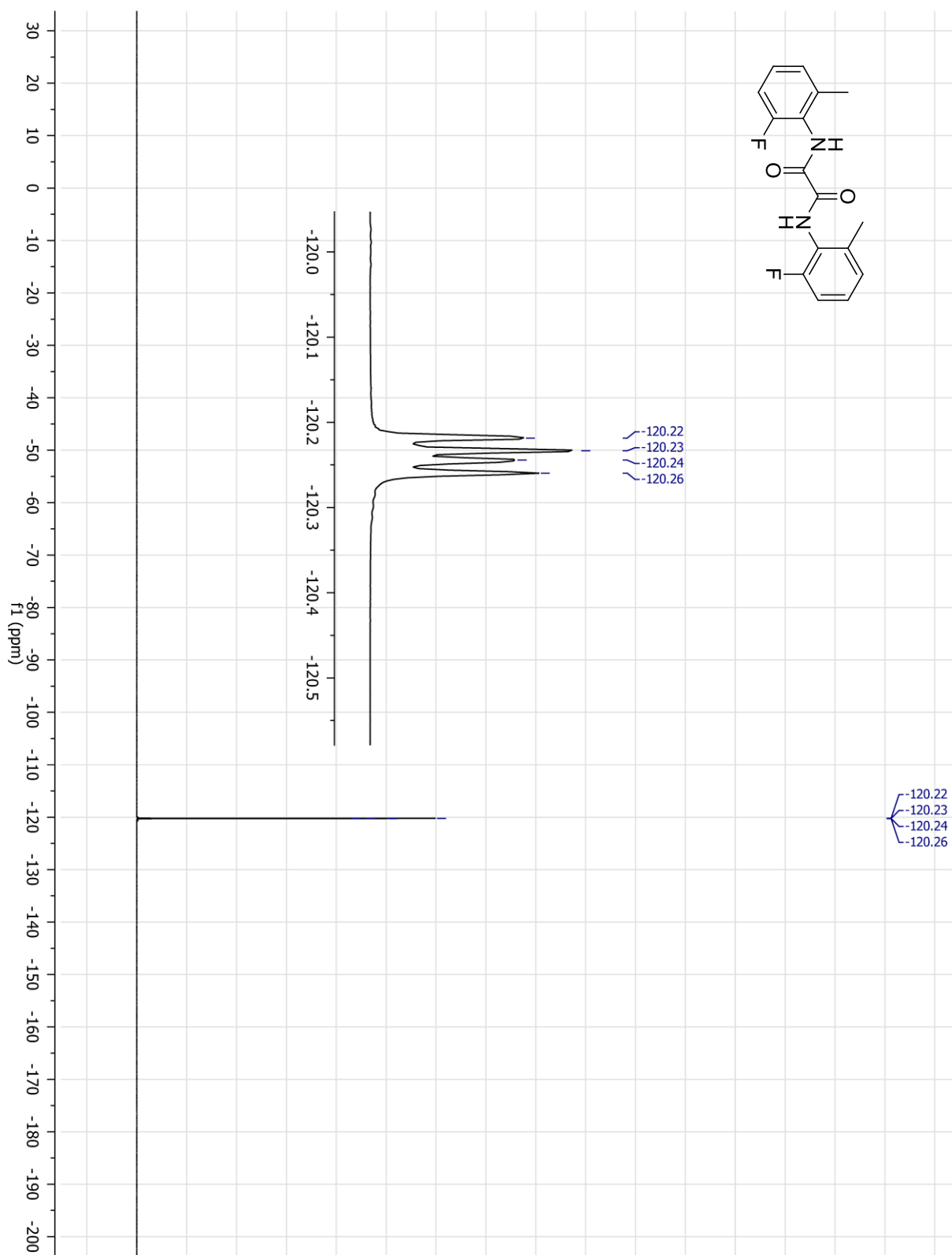


**Figure S3.** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of *N*<sup>1</sup>,*N*<sup>2</sup>-bis(2-fluoro-6-methylphenyl)oxalamide

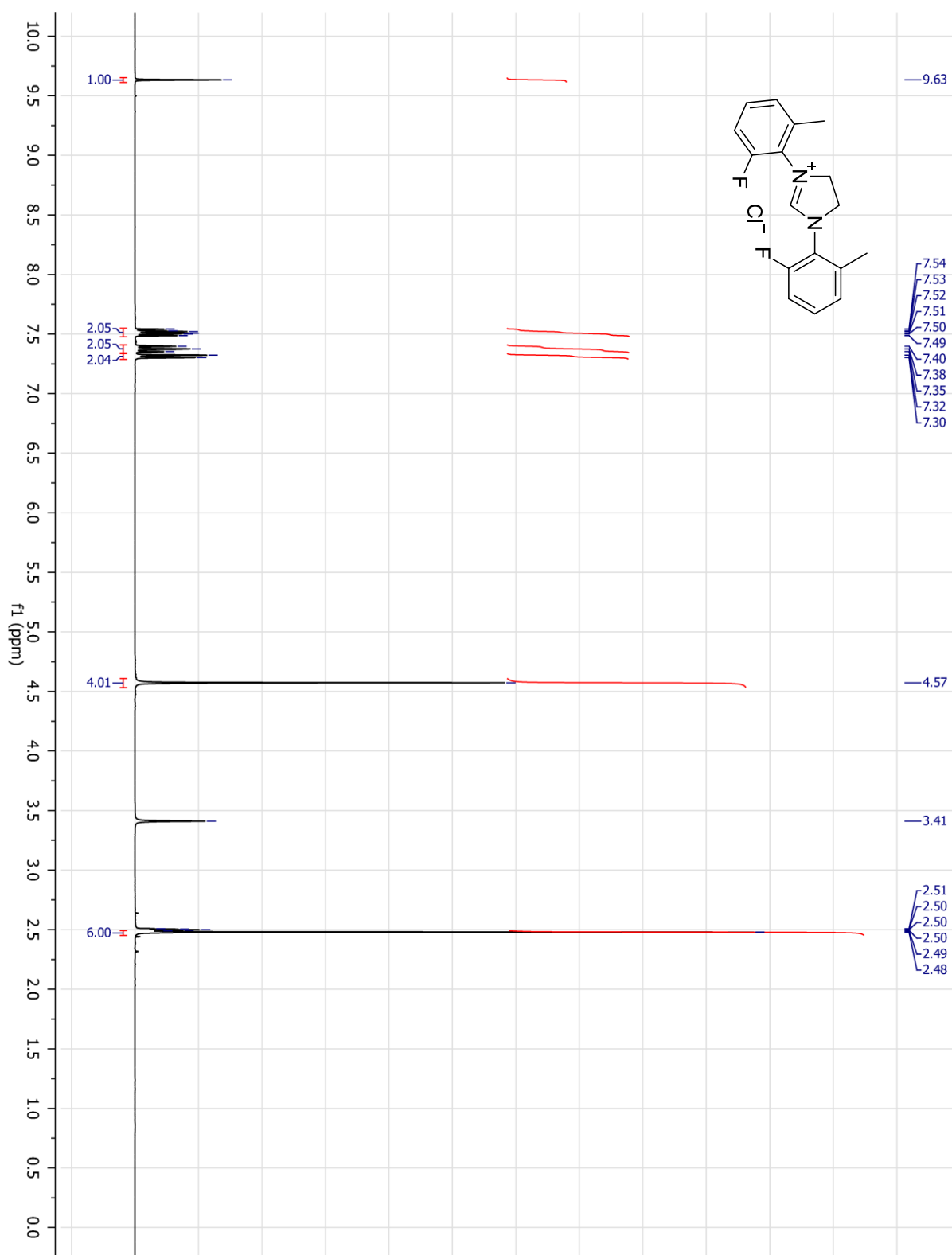




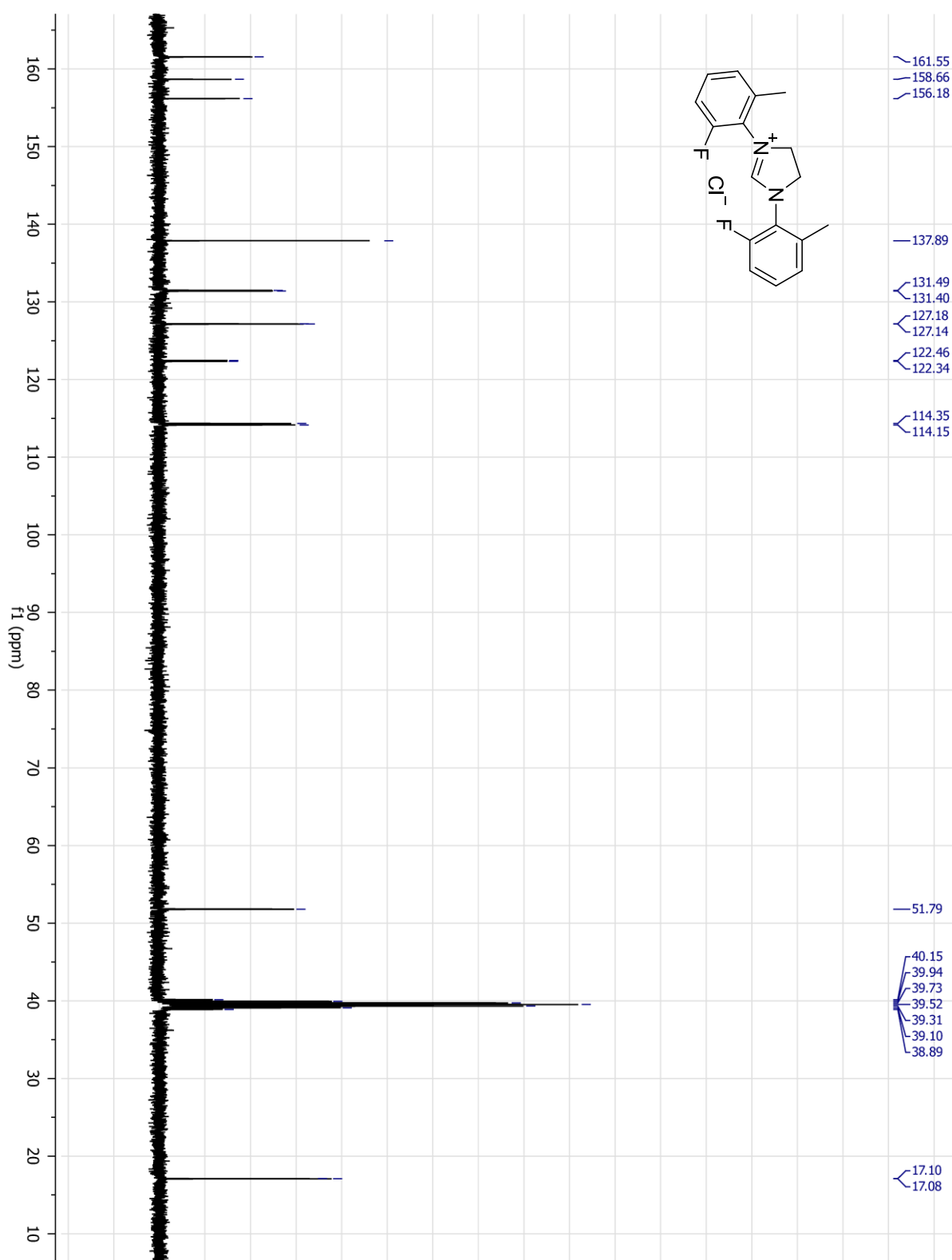
**Figure S4.** <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) of *N*<sup>1</sup>,*N*<sup>2</sup>-bis(2-fluoro-6-methylphenyl)oxalamide



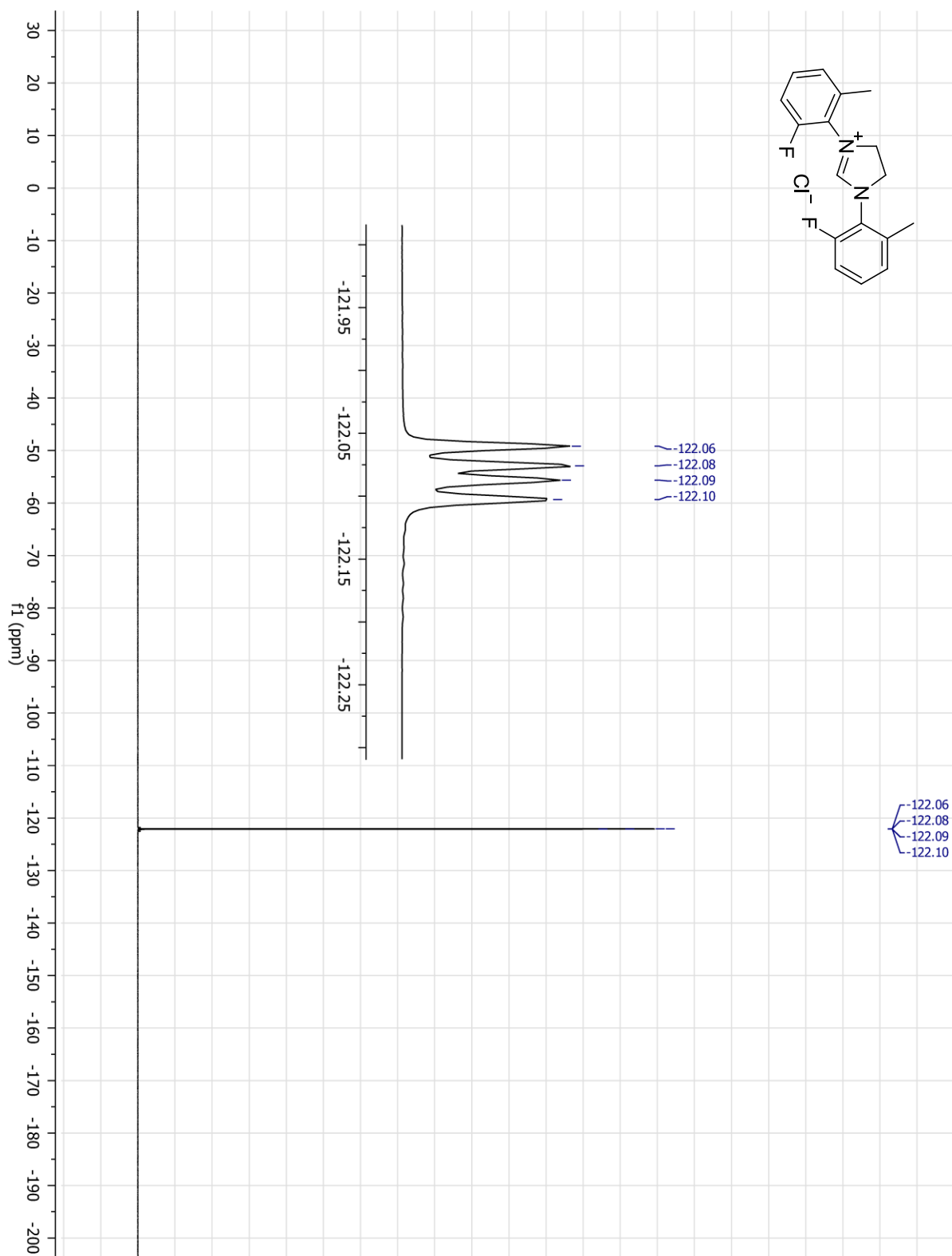
**Figure S5.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-d}_6$ ) of  $N^1,N^2$ -bis(2-fluoro-6-methylphenyl)oxalamide



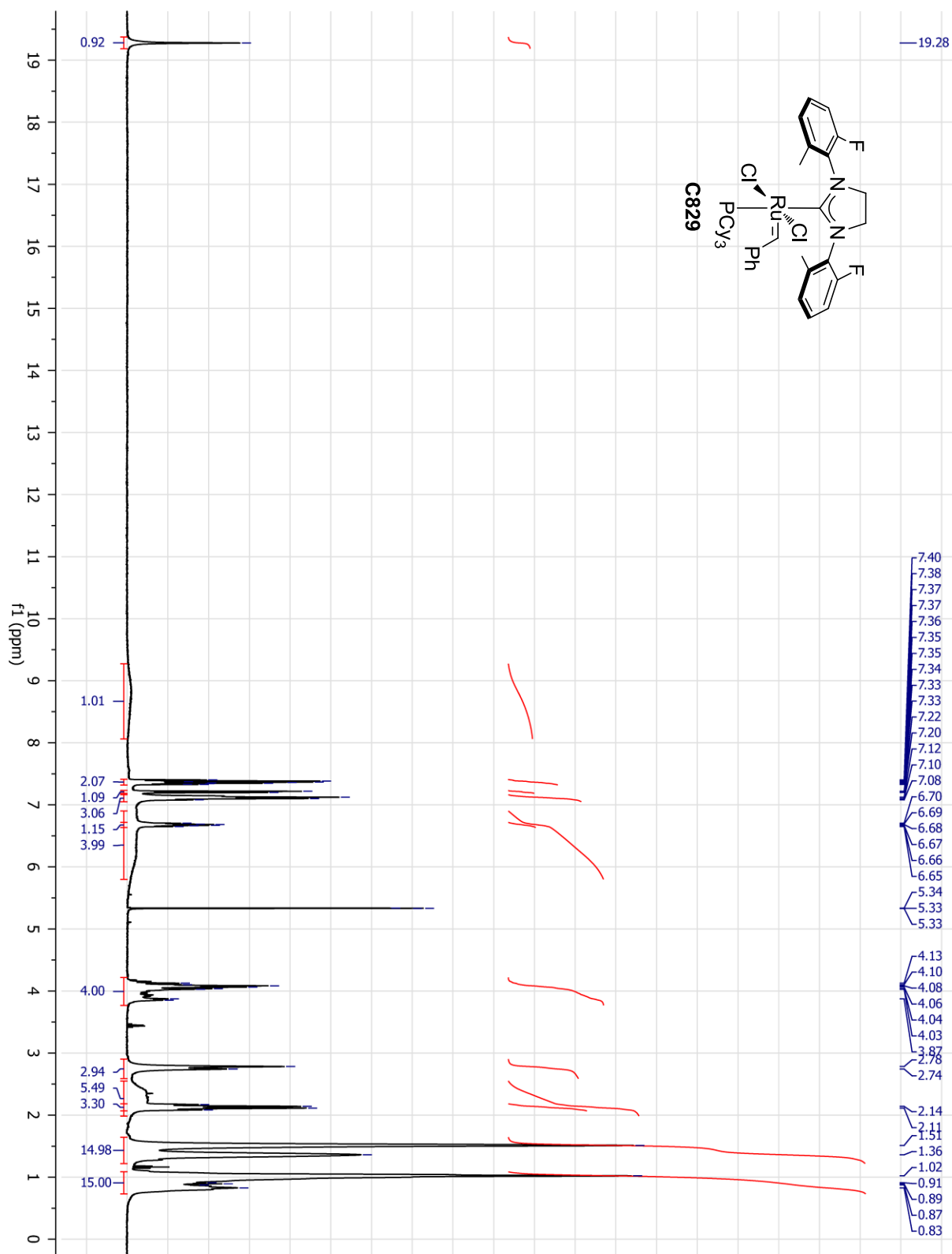
**Figure S6.**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) of 1,3-bis(2-fluoro-6-methylphenyl)-4,5-dihydro-1H-imidazol-3-ium chloride



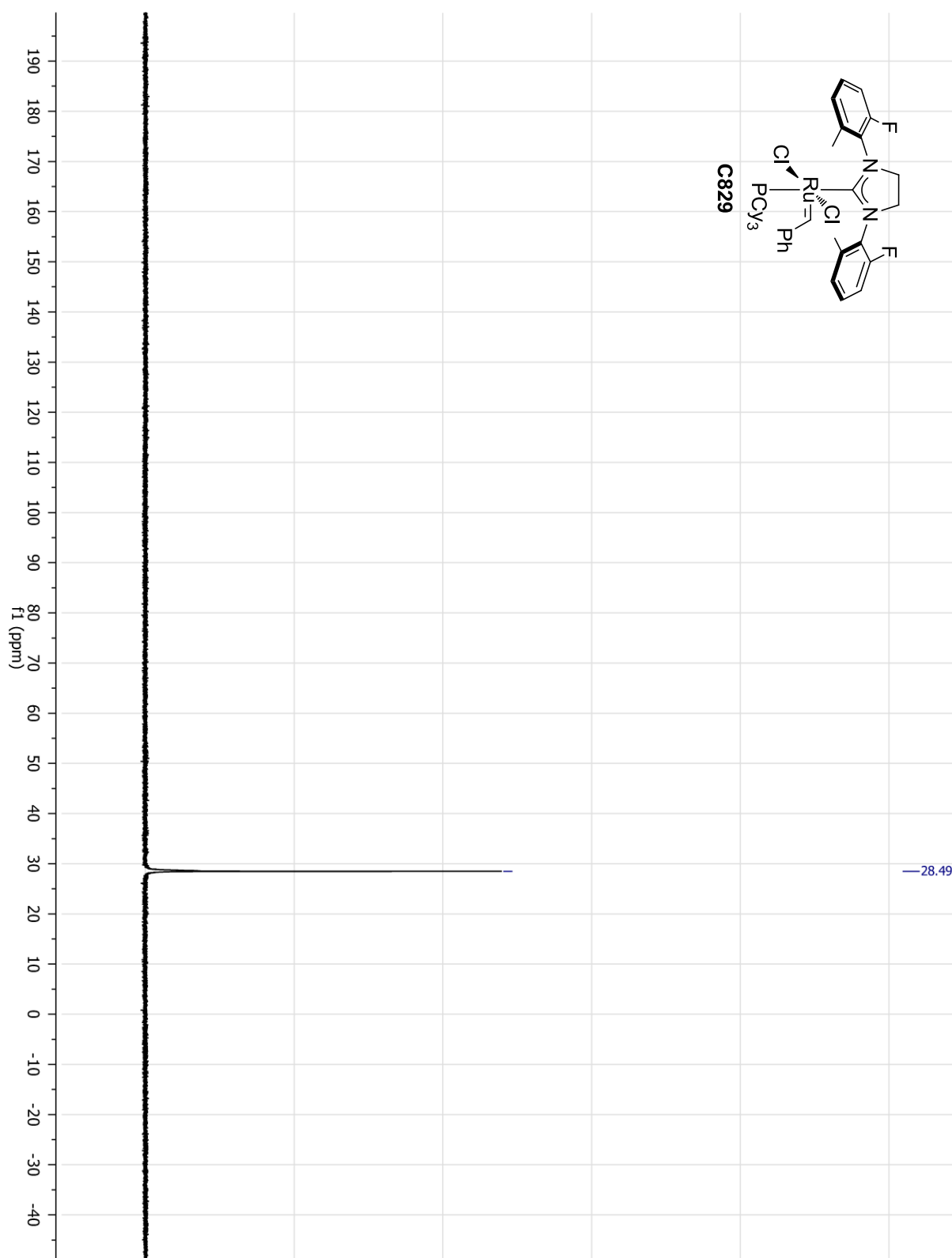
**Figure S7.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-d}_6$ ) of 1,3-bis(2-fluoro-6-methylphenyl)-4,5-dihydro-1H-imidazol-3-ium chloride



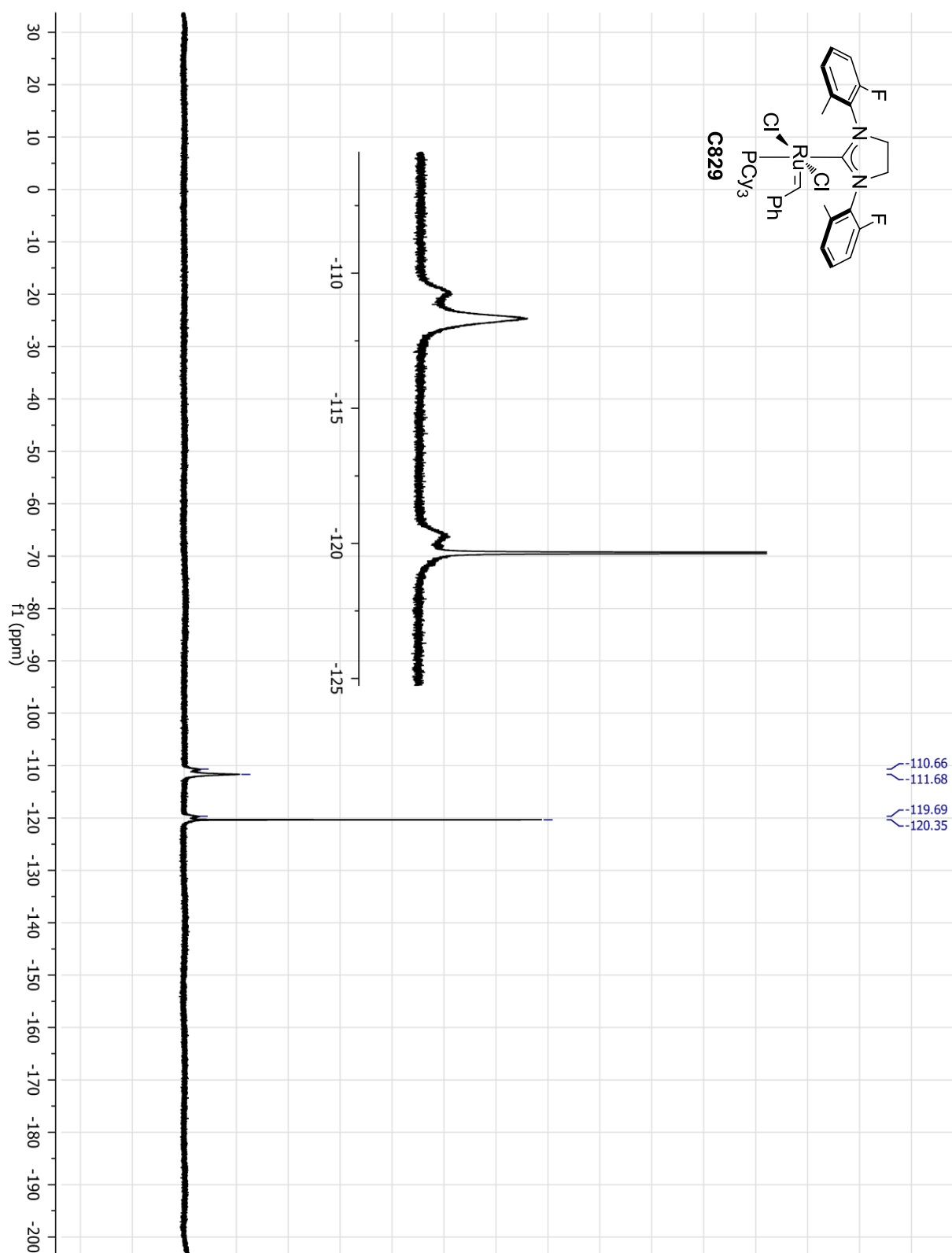
**Figure S8.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-d}_6$ ) of 1,3-bis(2-fluoro-6-methylphenyl)-4,5-dihydro-1H-imidazol-3-ium chloride



**Figure S9.** <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of **C829**

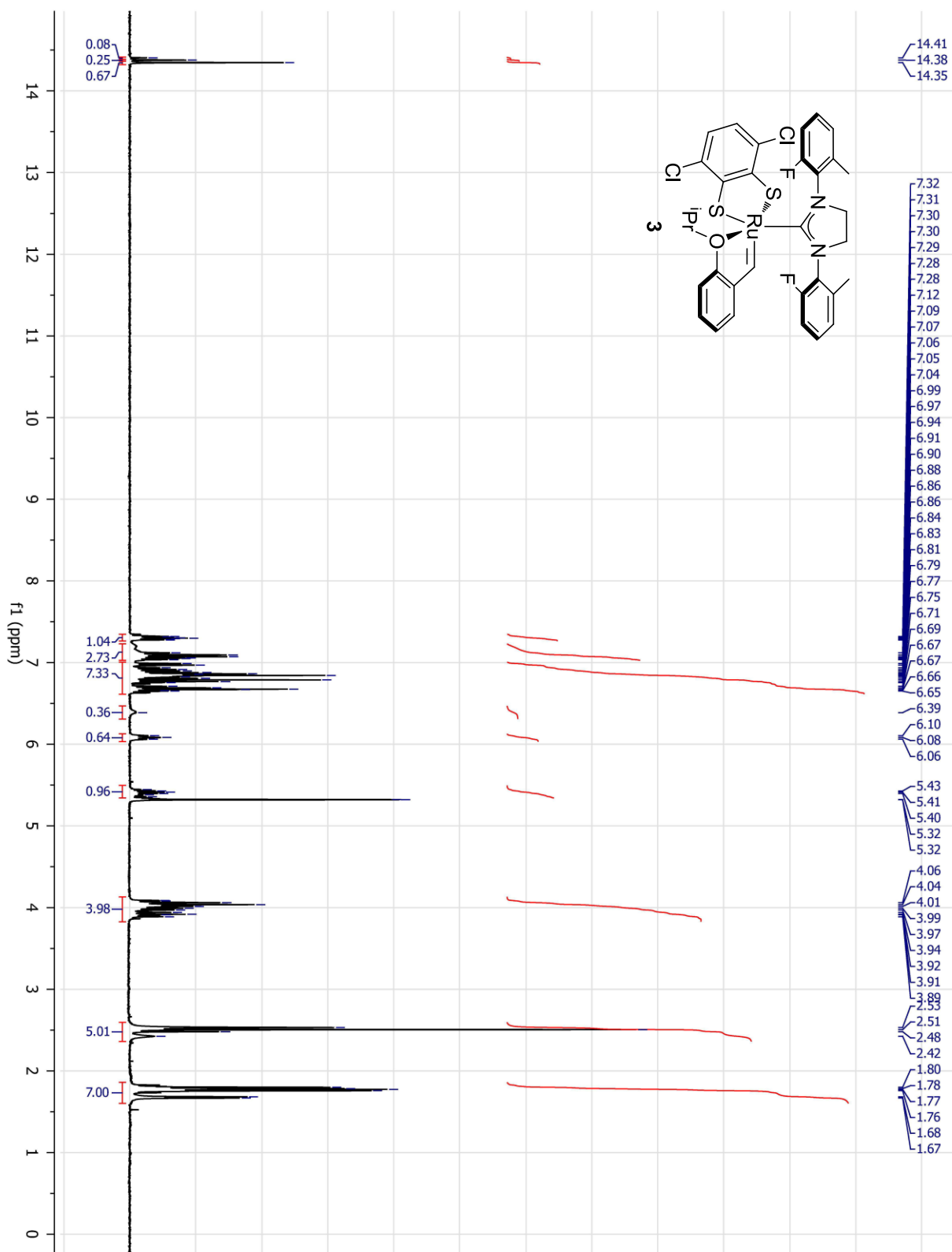


**Figure S10.**  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **C829**

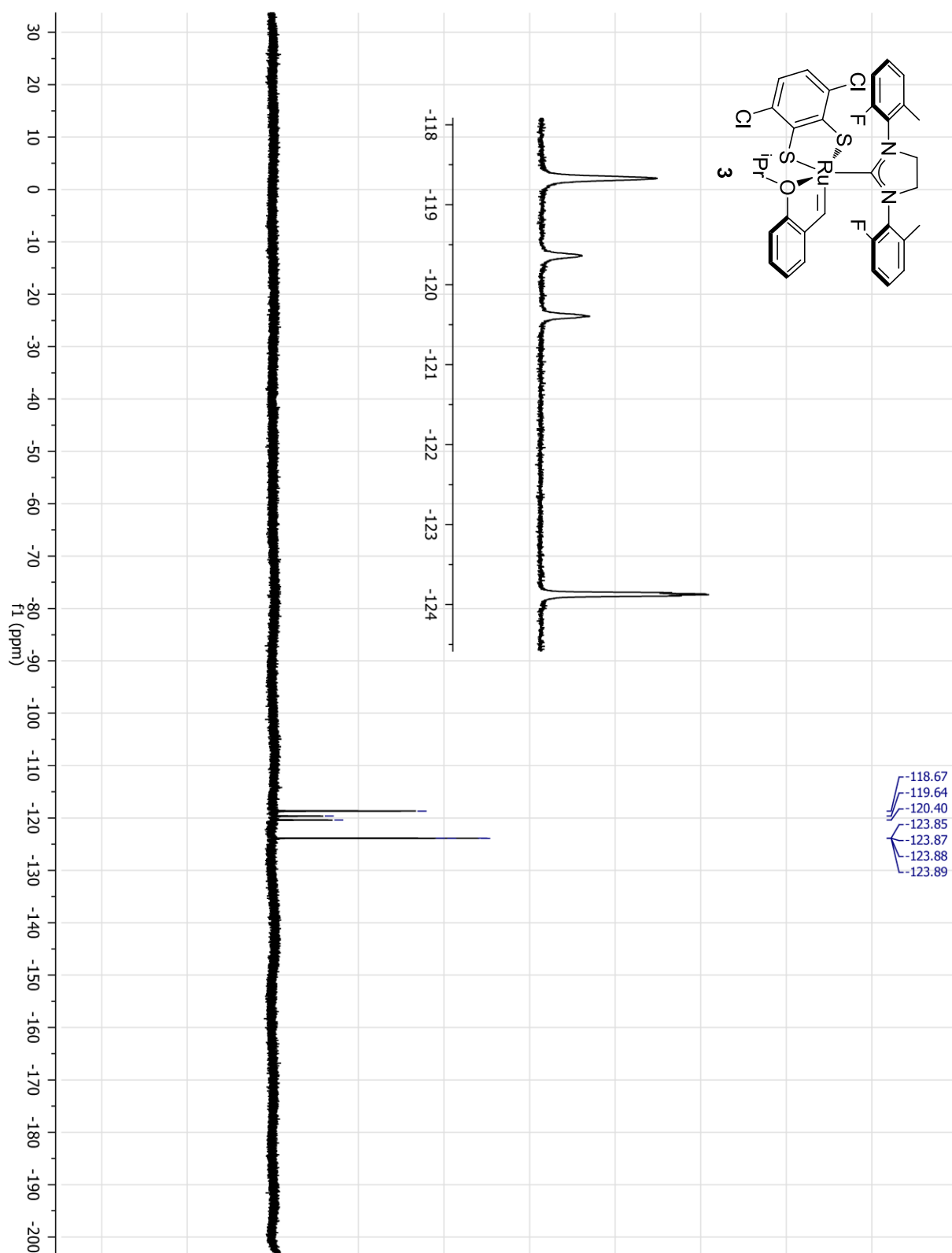


**Figure S11.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **C829**

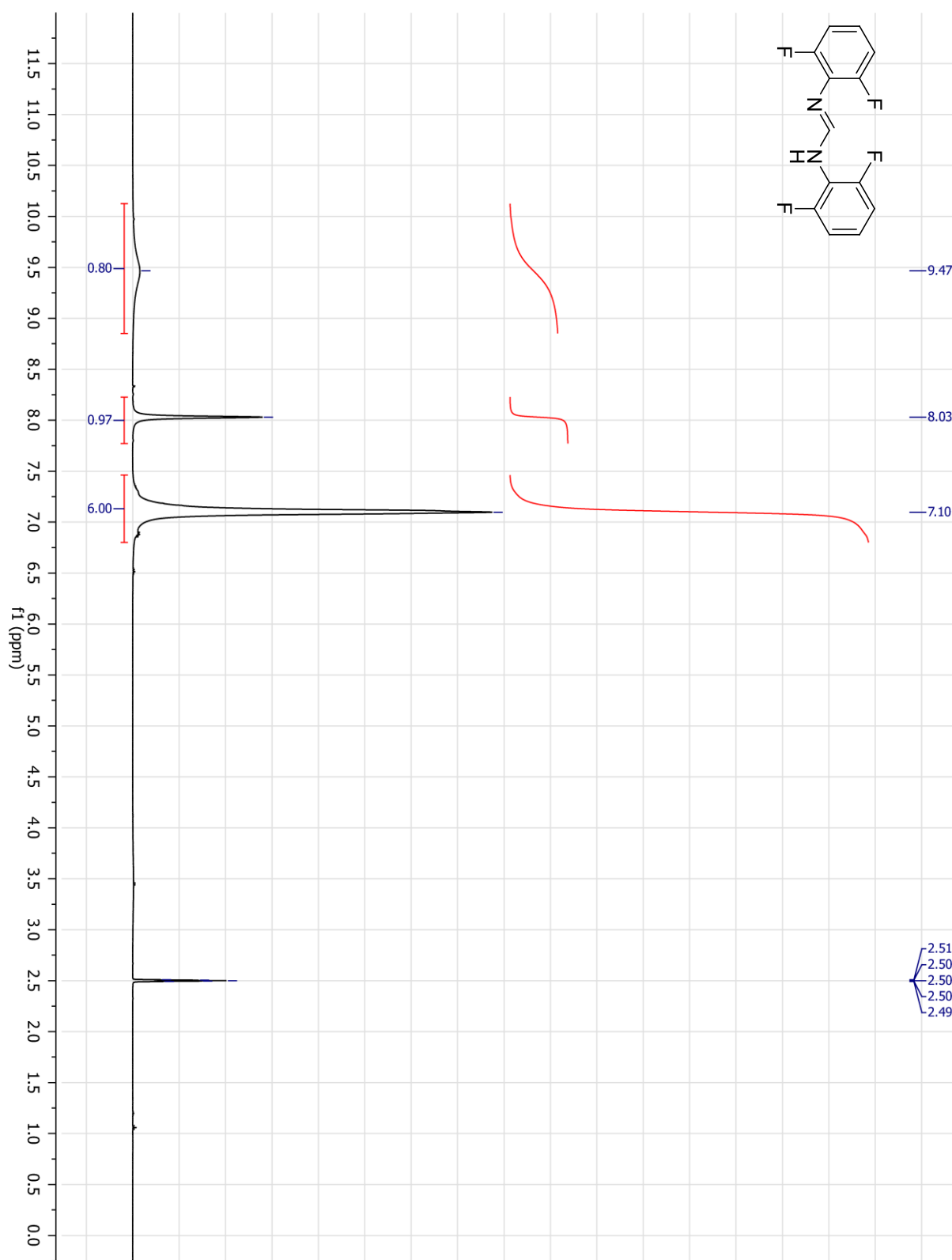




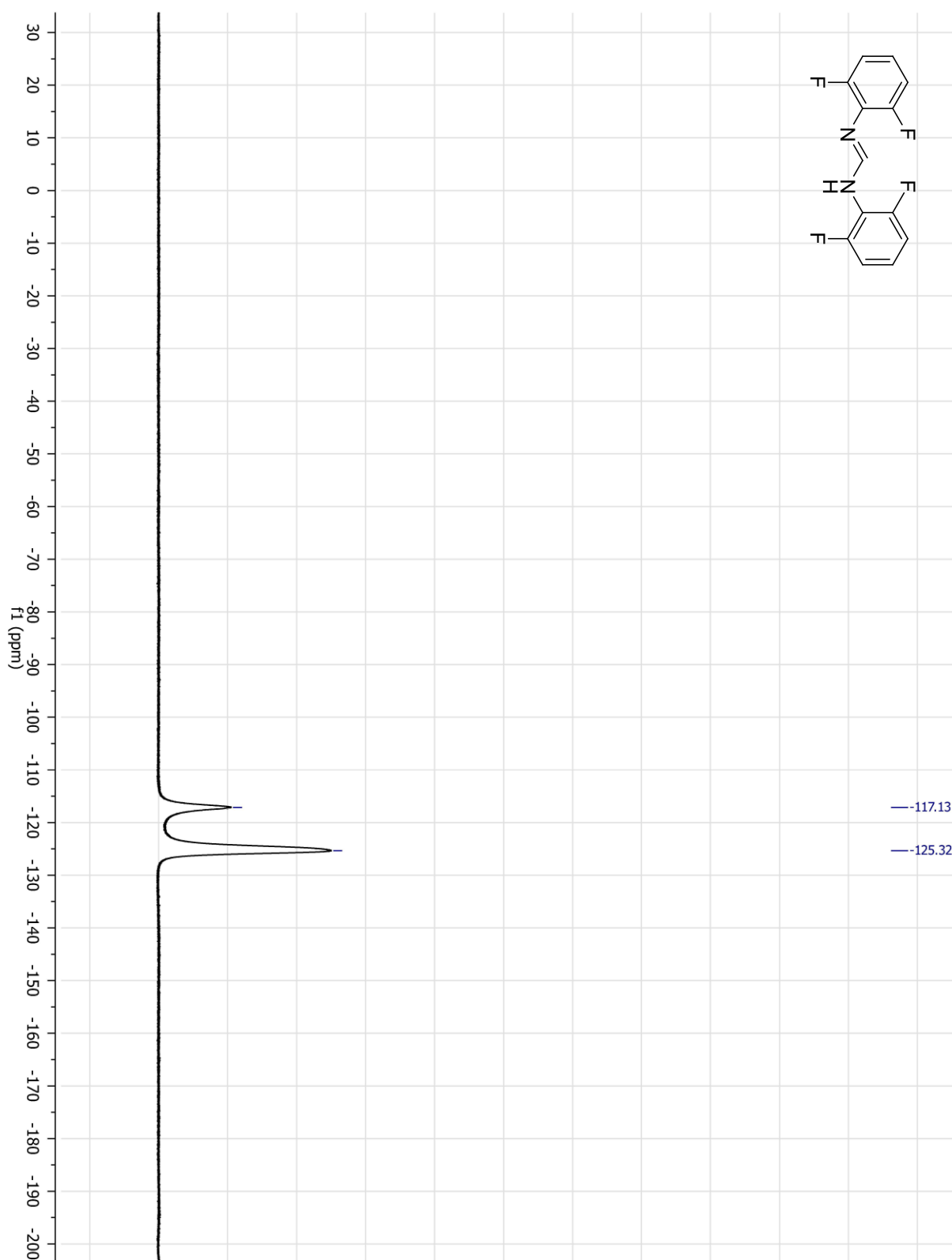
**Figure S12.**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **3**



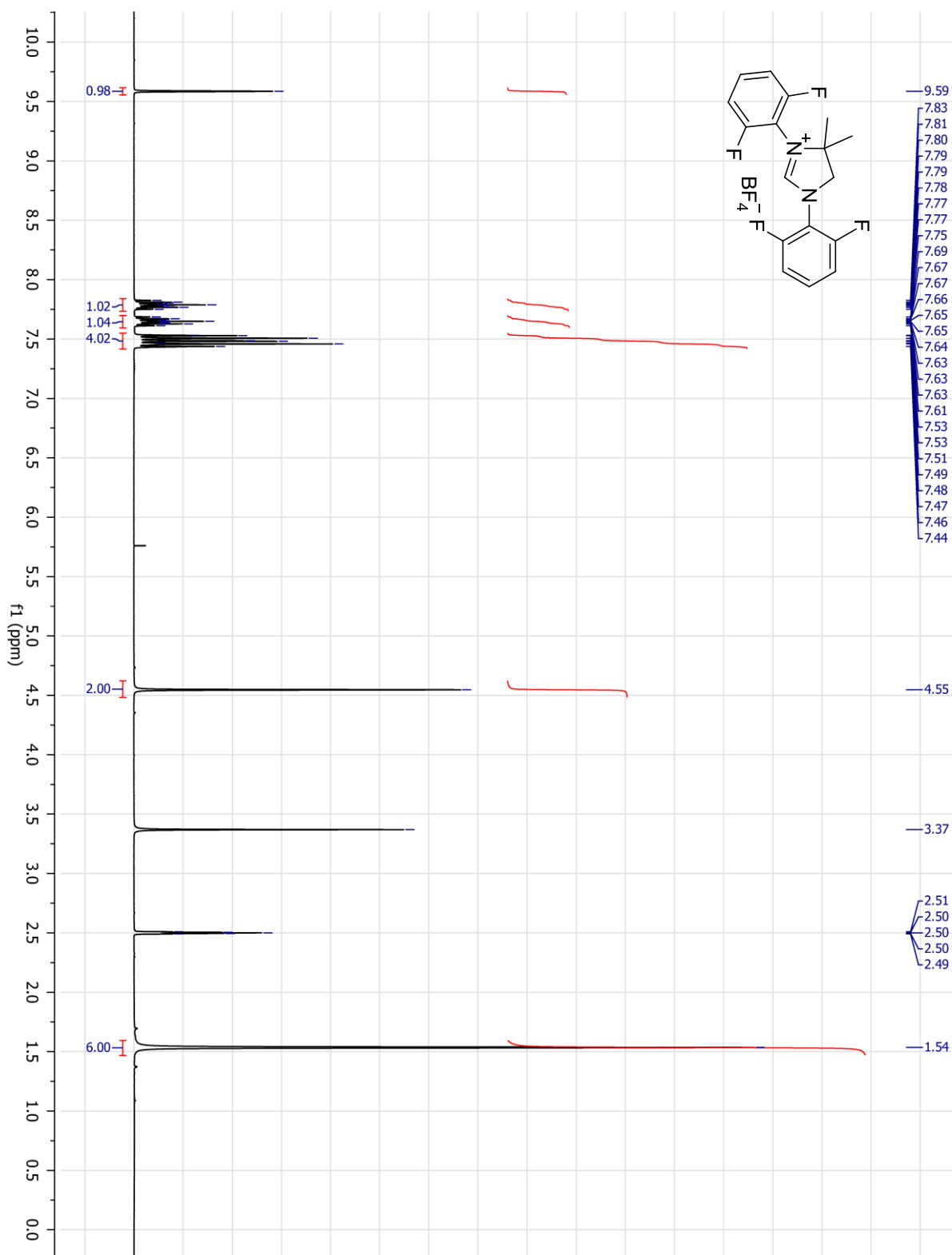
**Figure S13.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **3**



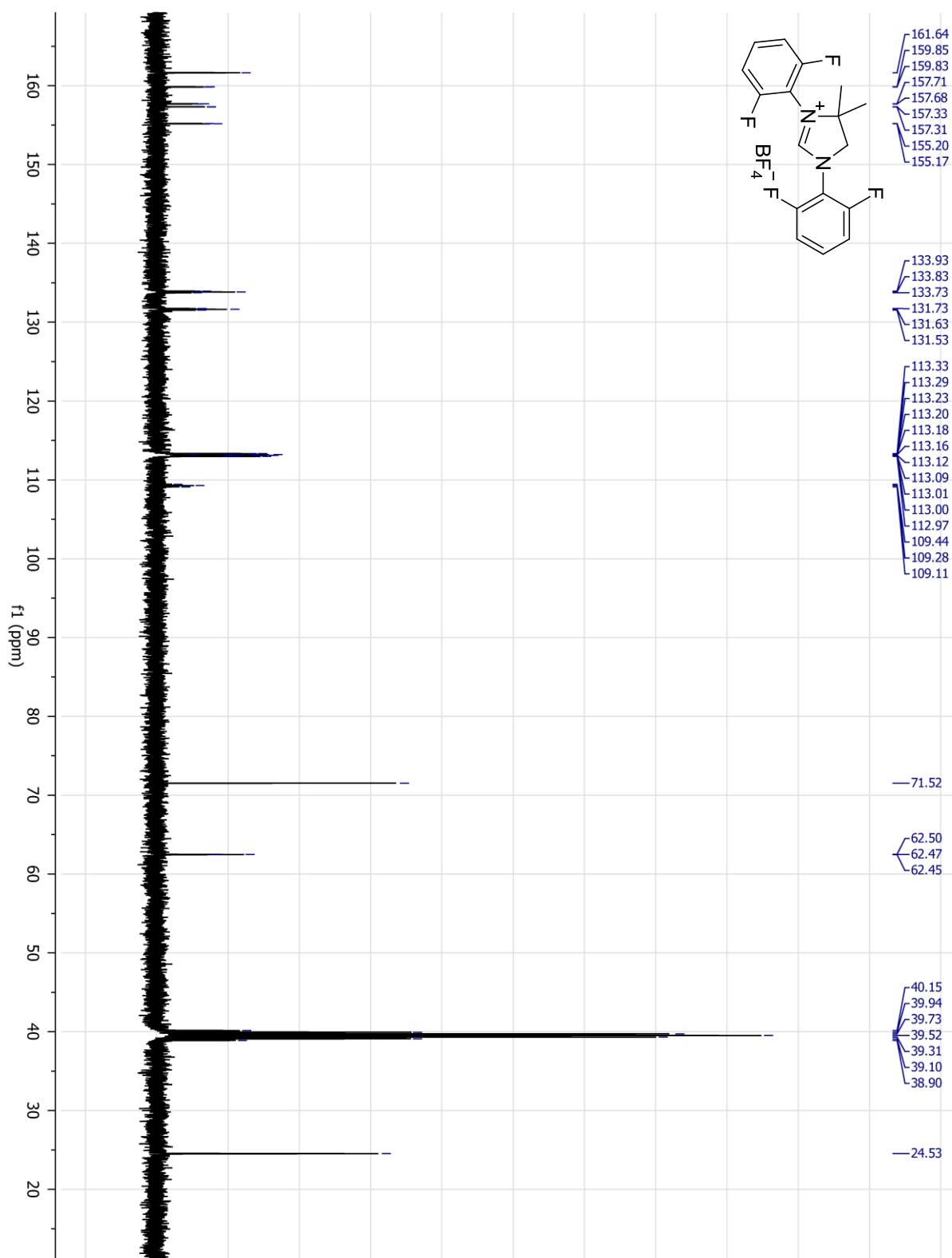
**Figure S14.**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) of *N,N'*-bis(2,6-difluorophenyl)formimidamide



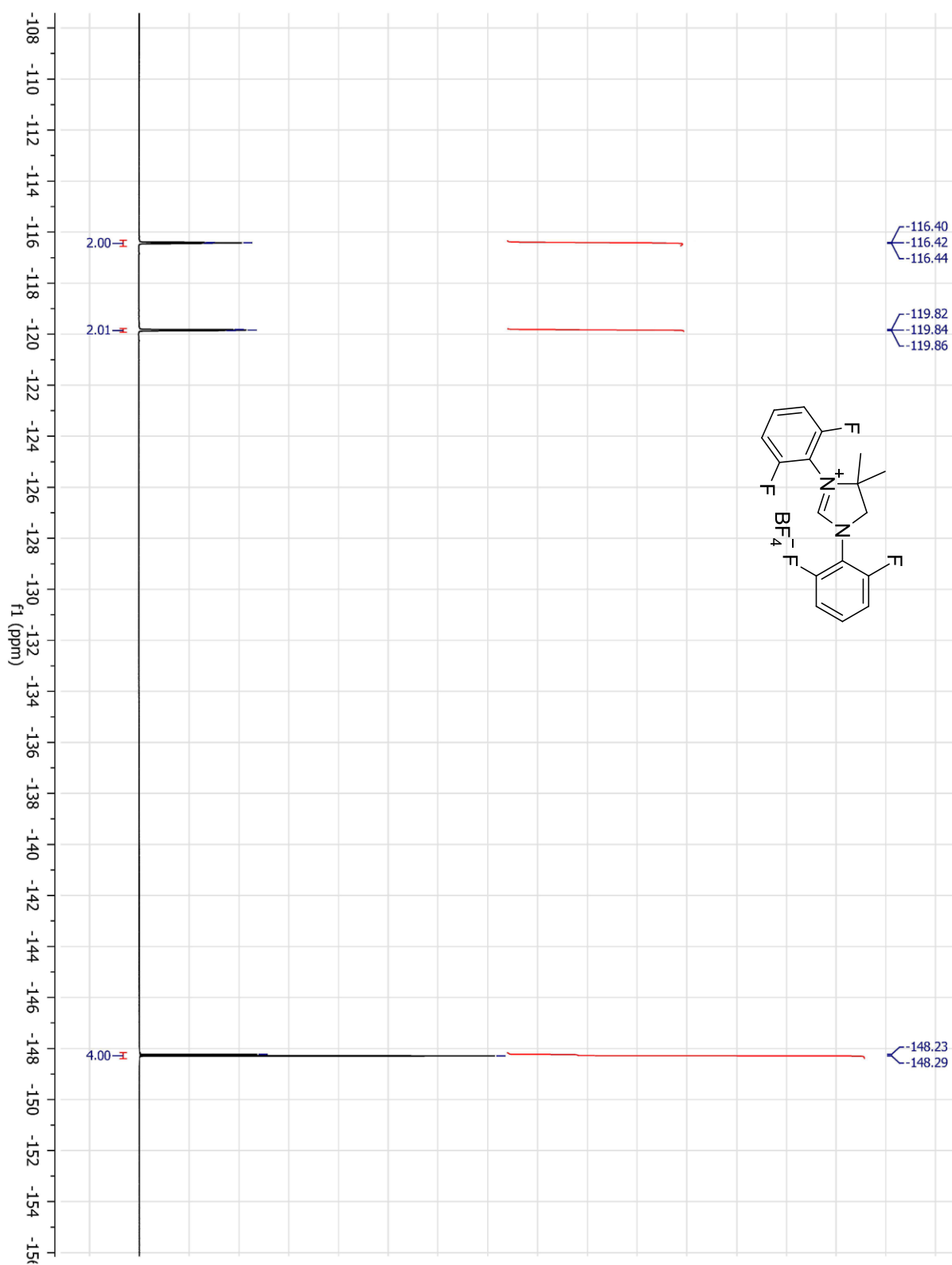
**Figure S15.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-d}_6$ ) of *N,N'*-bis(2,6-difluorophenyl)formimidamide



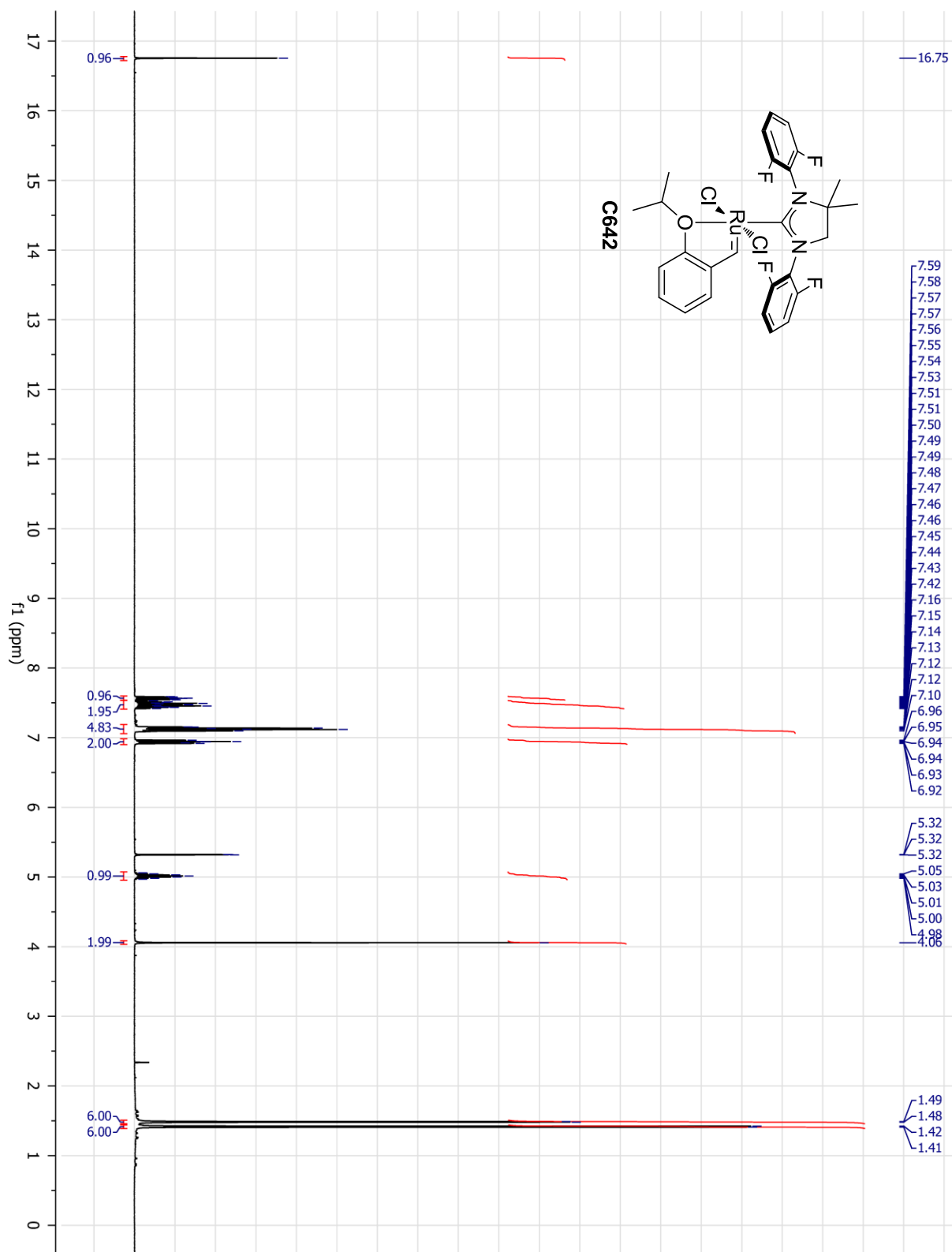
**Figure S16.** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) of 1,3-bis(2,6-difluorophenyl)-4,4-dimethyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate



**Figure S17.** <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) of 1,3-bis(2,6-difluorophenyl)-4,4-dimethyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate

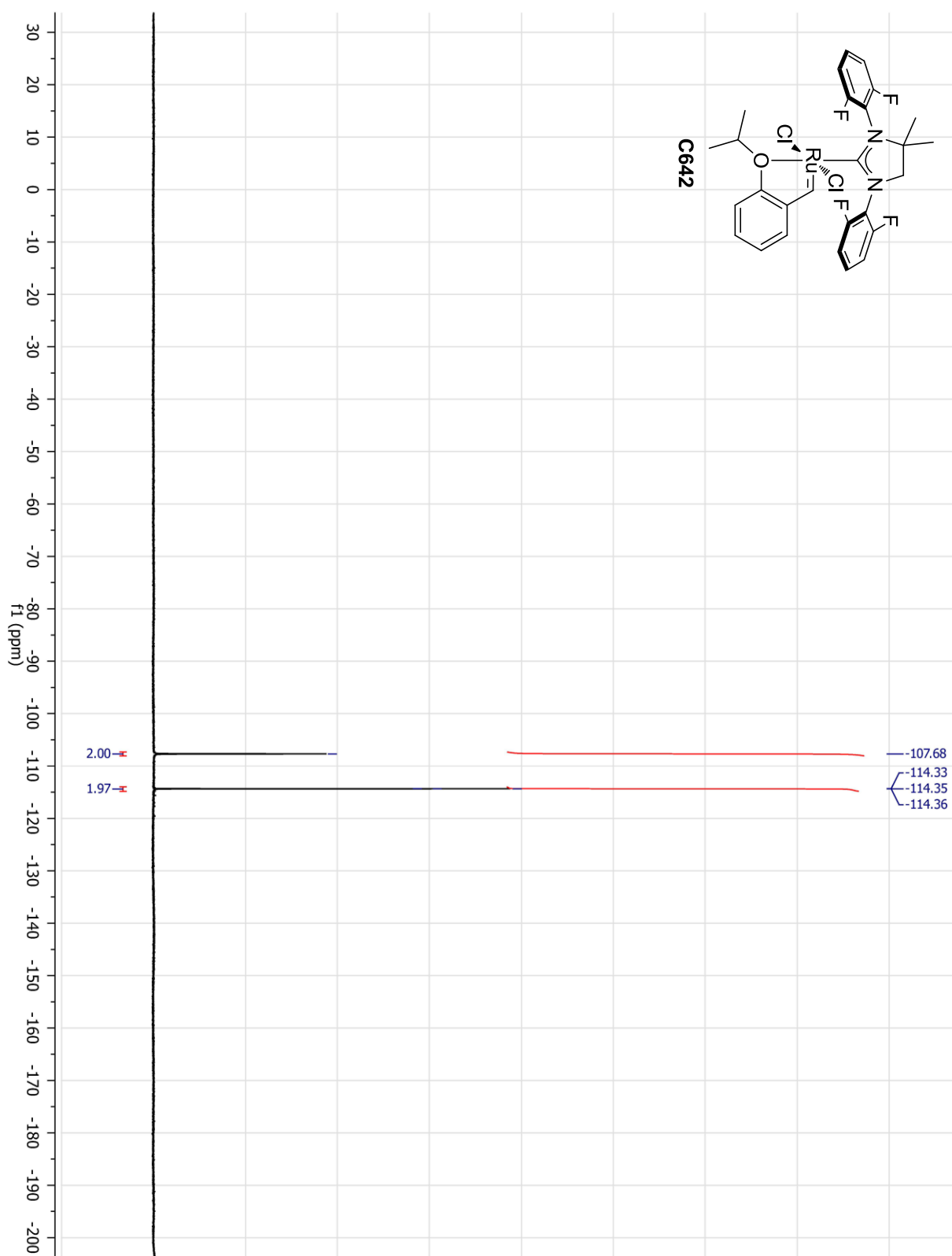


**Figure S18.** <sup>19</sup>F NMR (376 MHz, DMSO-d<sub>6</sub>) of 1,3-bis(2,6-difluorophenyl)-4,4-dimethyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate

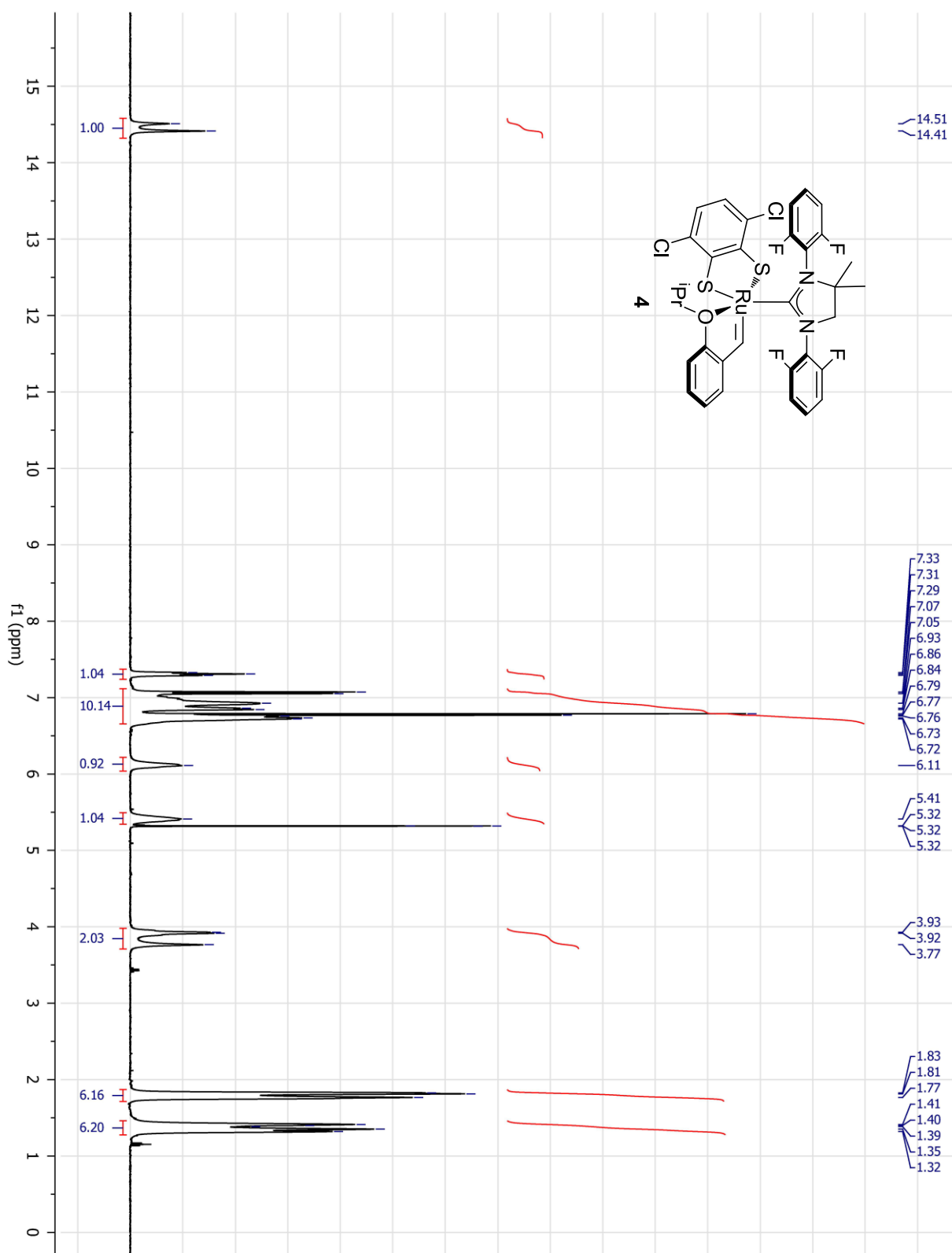


**Figure S19.** <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of **C642**

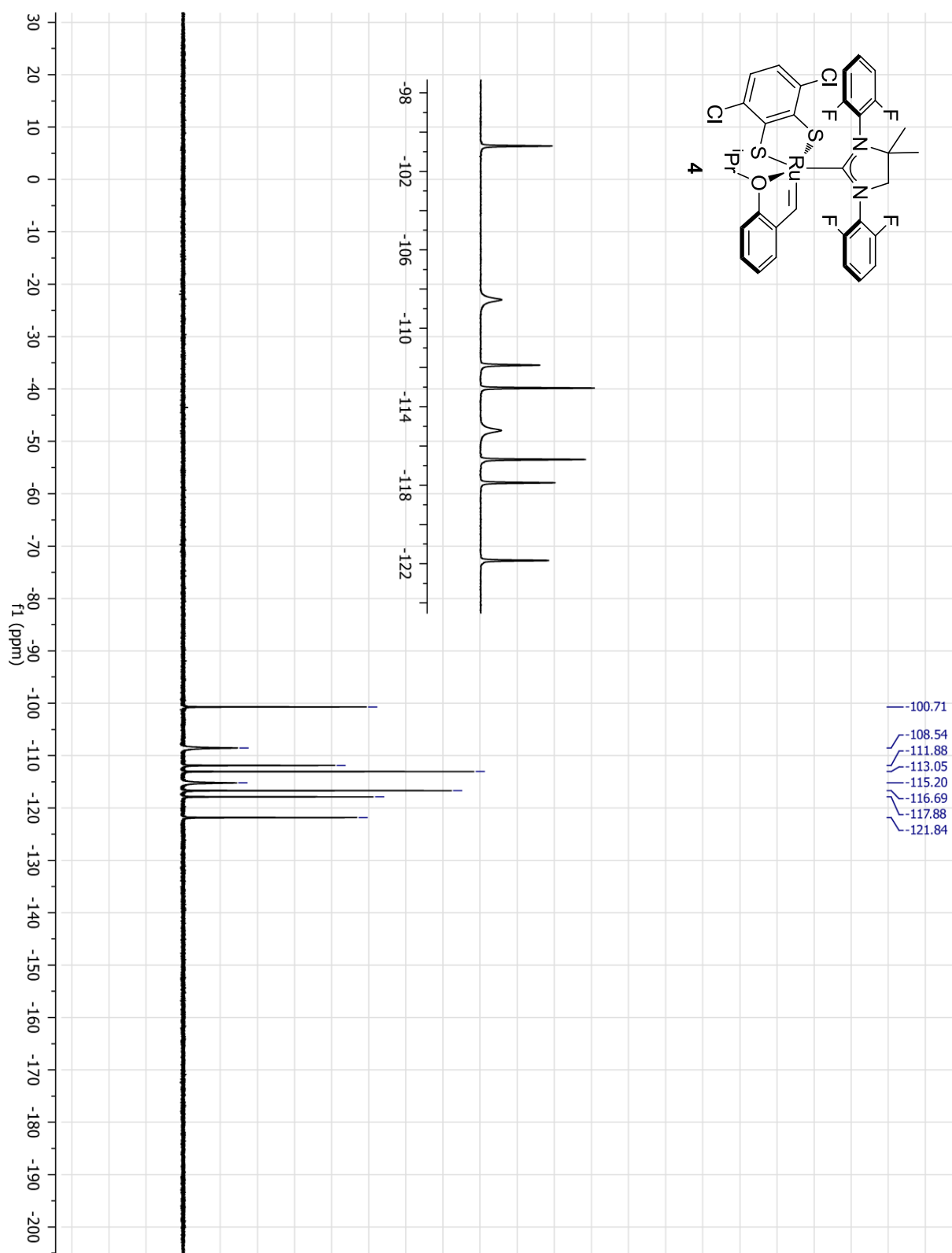




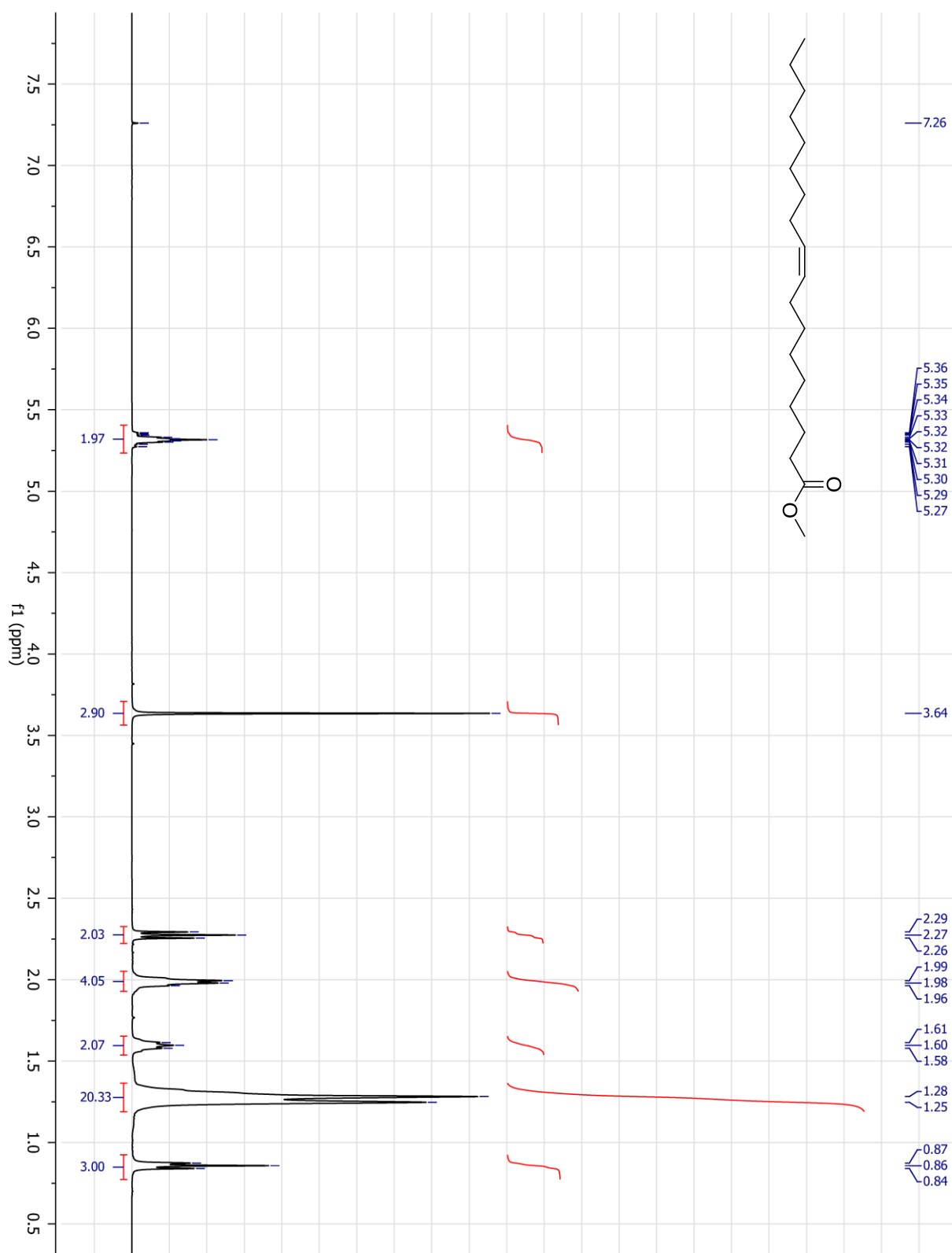
**Figure S20.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ ) of C642



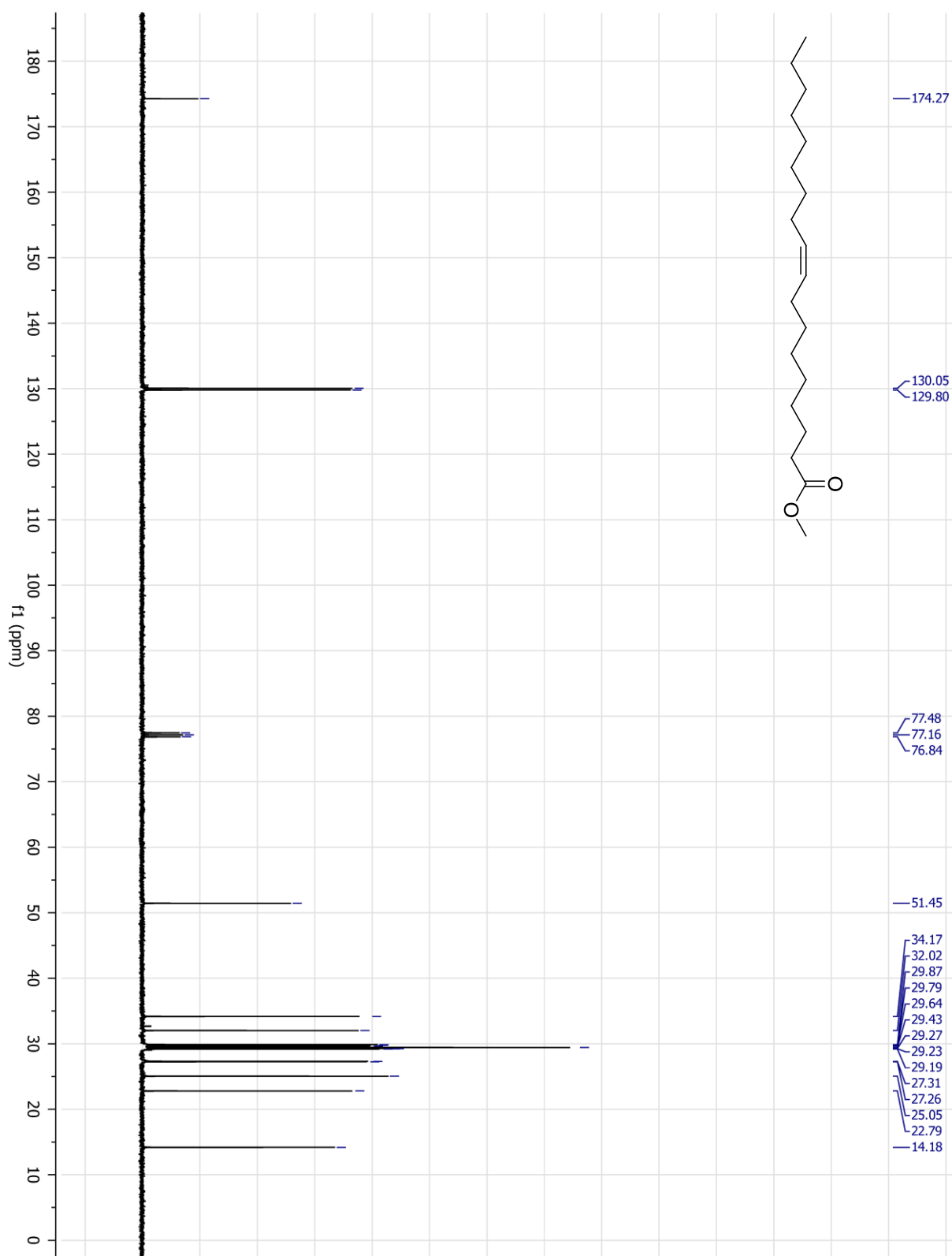
**Figure S21.**  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **4**



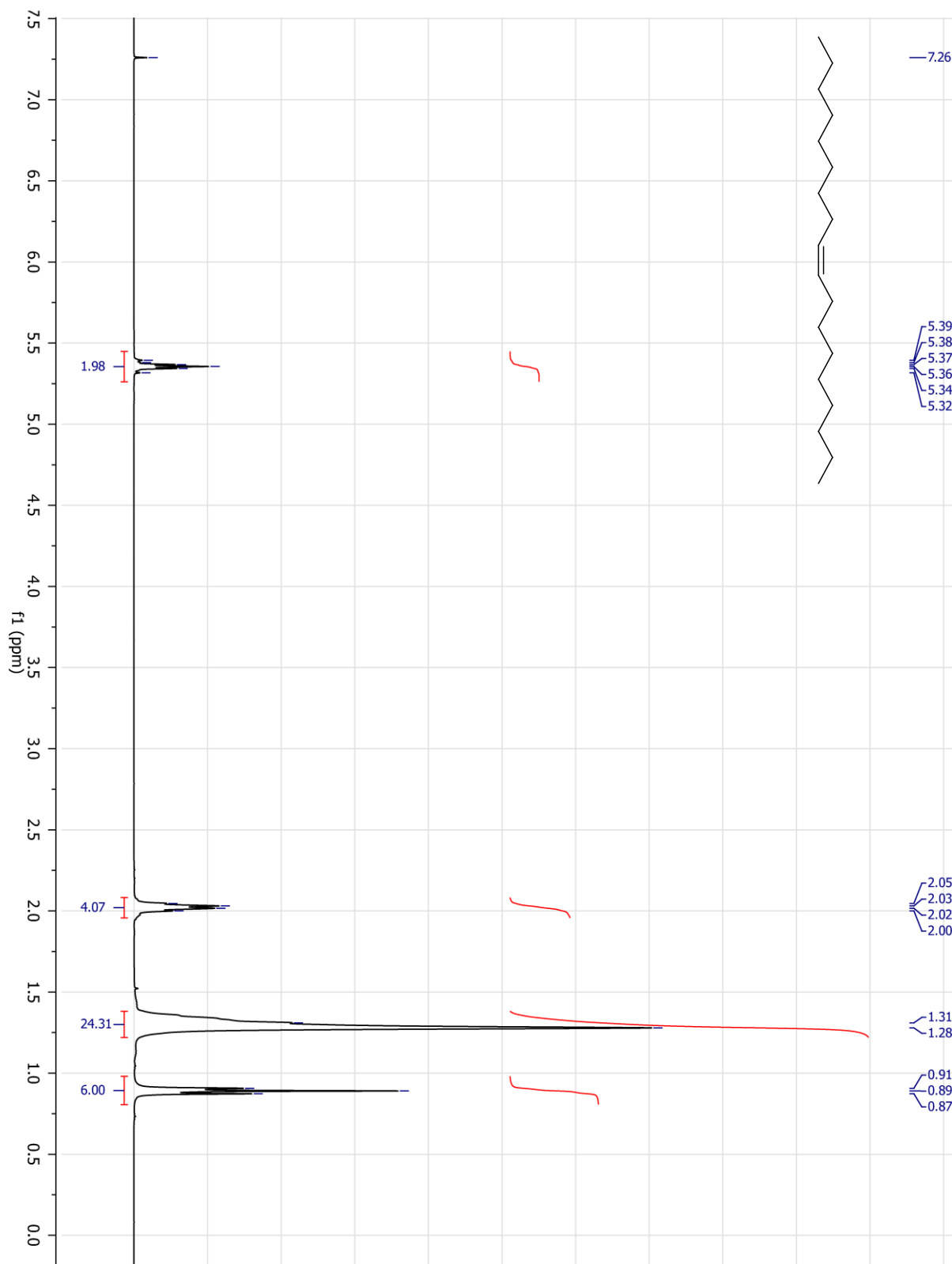
**Figure S22.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **4**



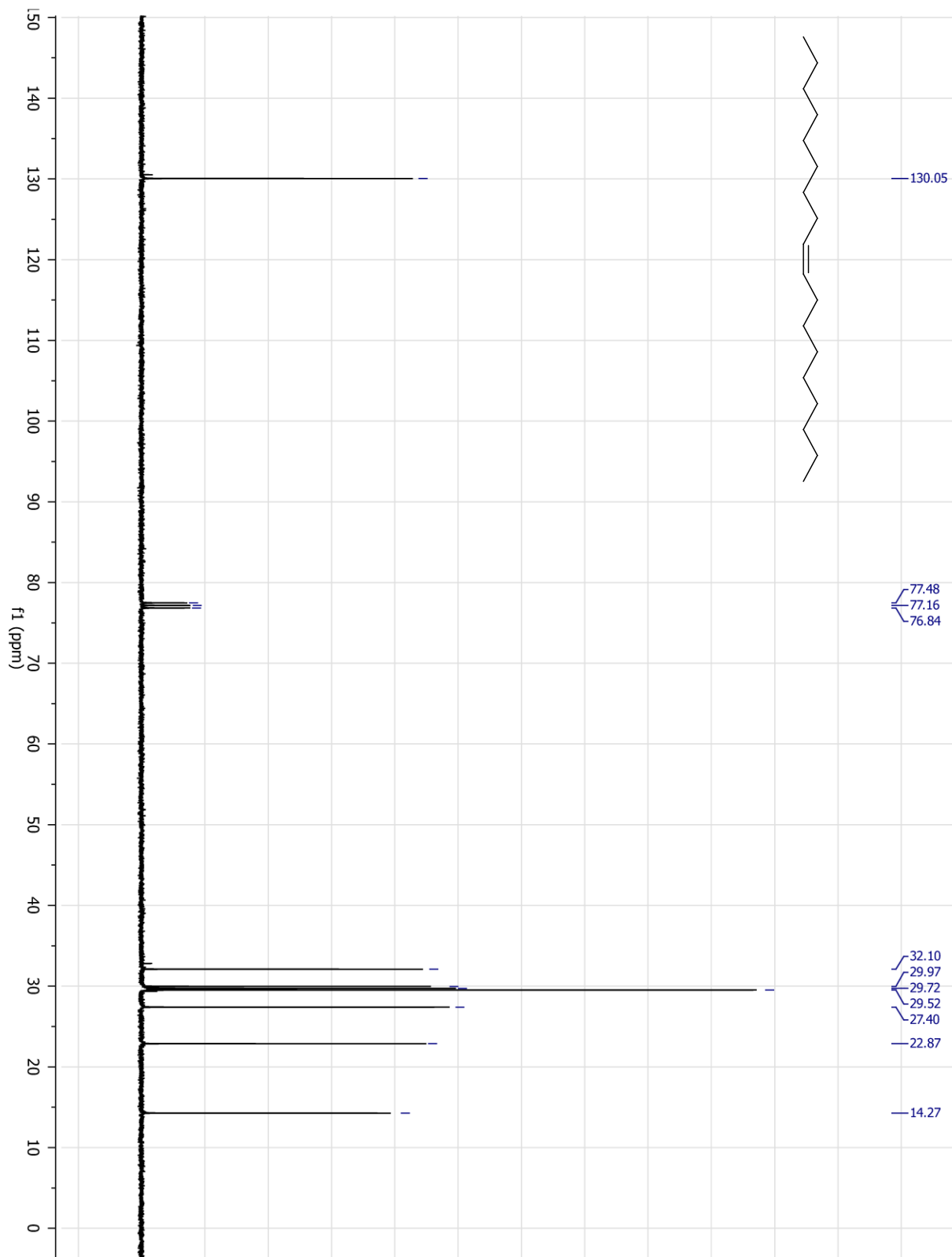
**Figure S23.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of Methyl *cis*-9-octadecenoate



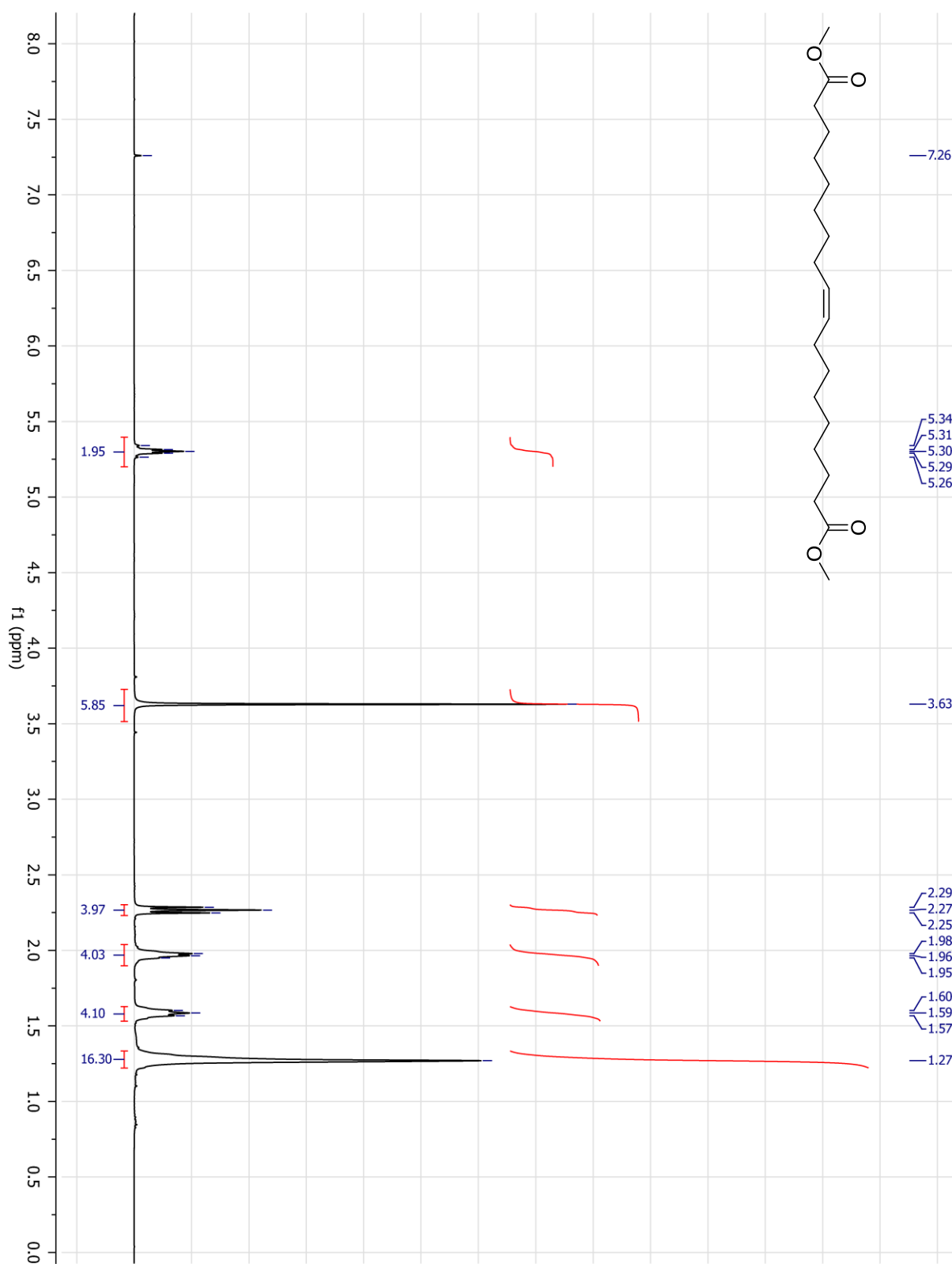
**Figure S24.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of Methyl *cis*-9-octadecenoate



**Figure S25.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of (Z)-octadec-9-ene

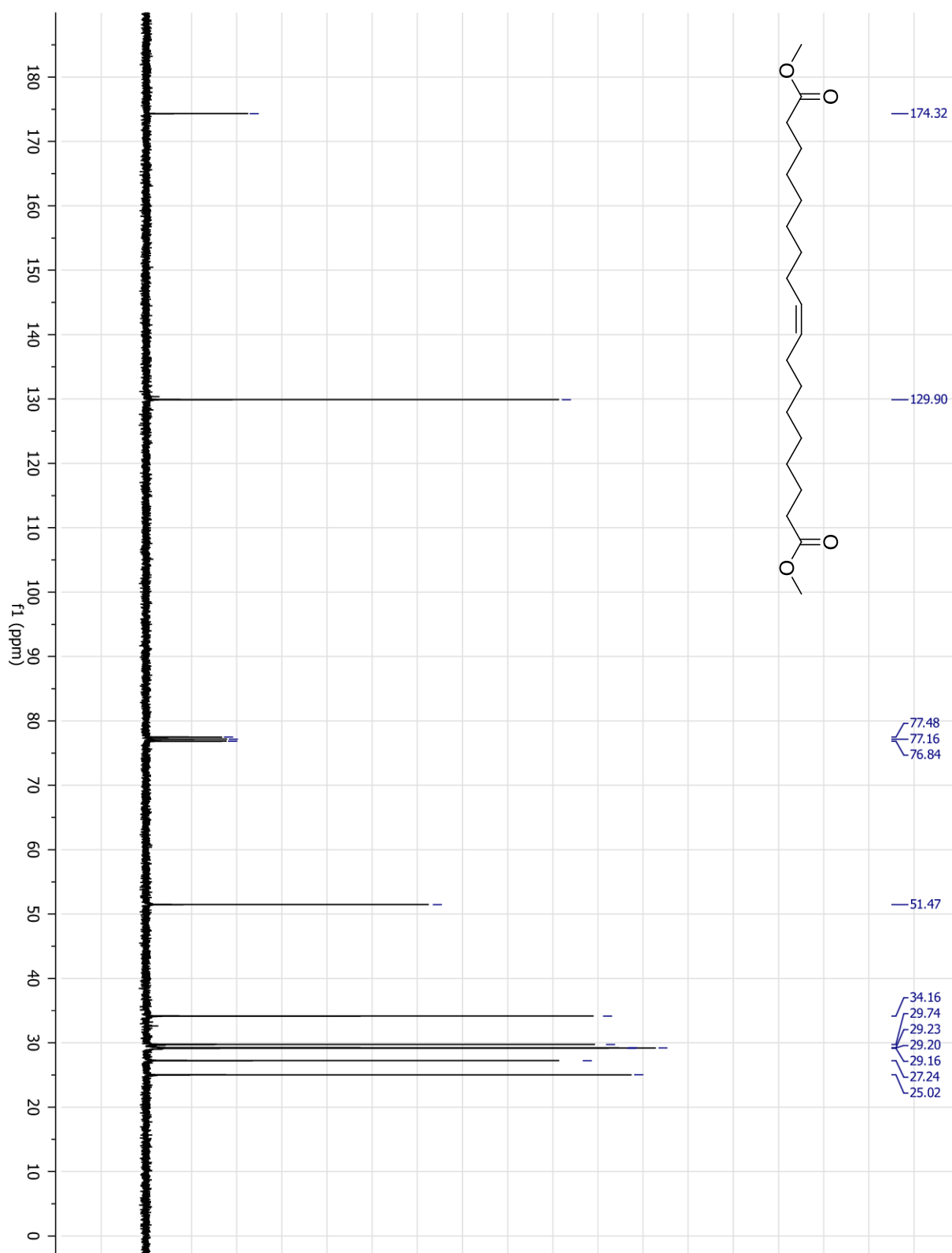


**Figure S26.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of (Z)-octadec-9-ene

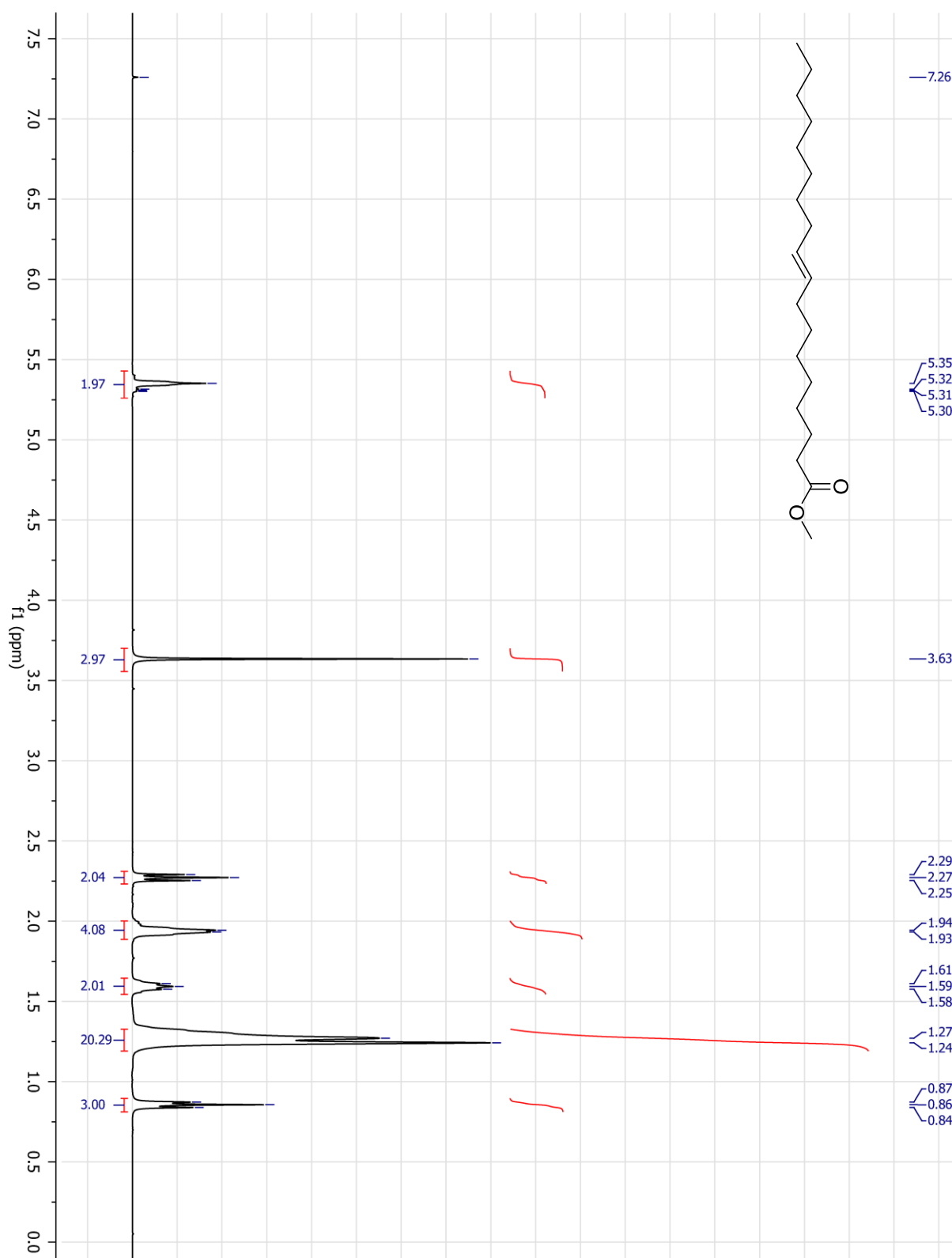


**Figure S27.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of (Z)-dimethyl octadec-9-enedioate

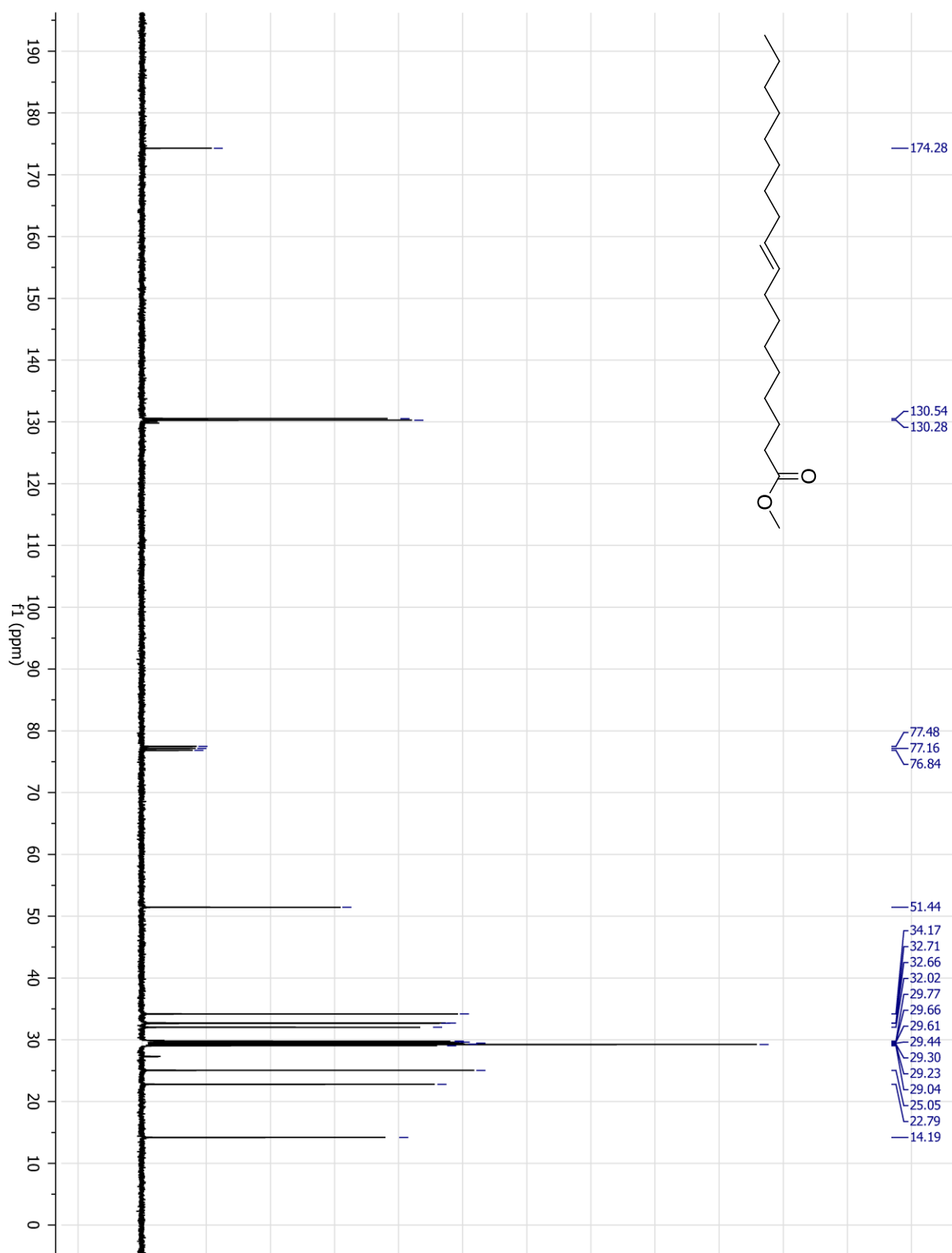




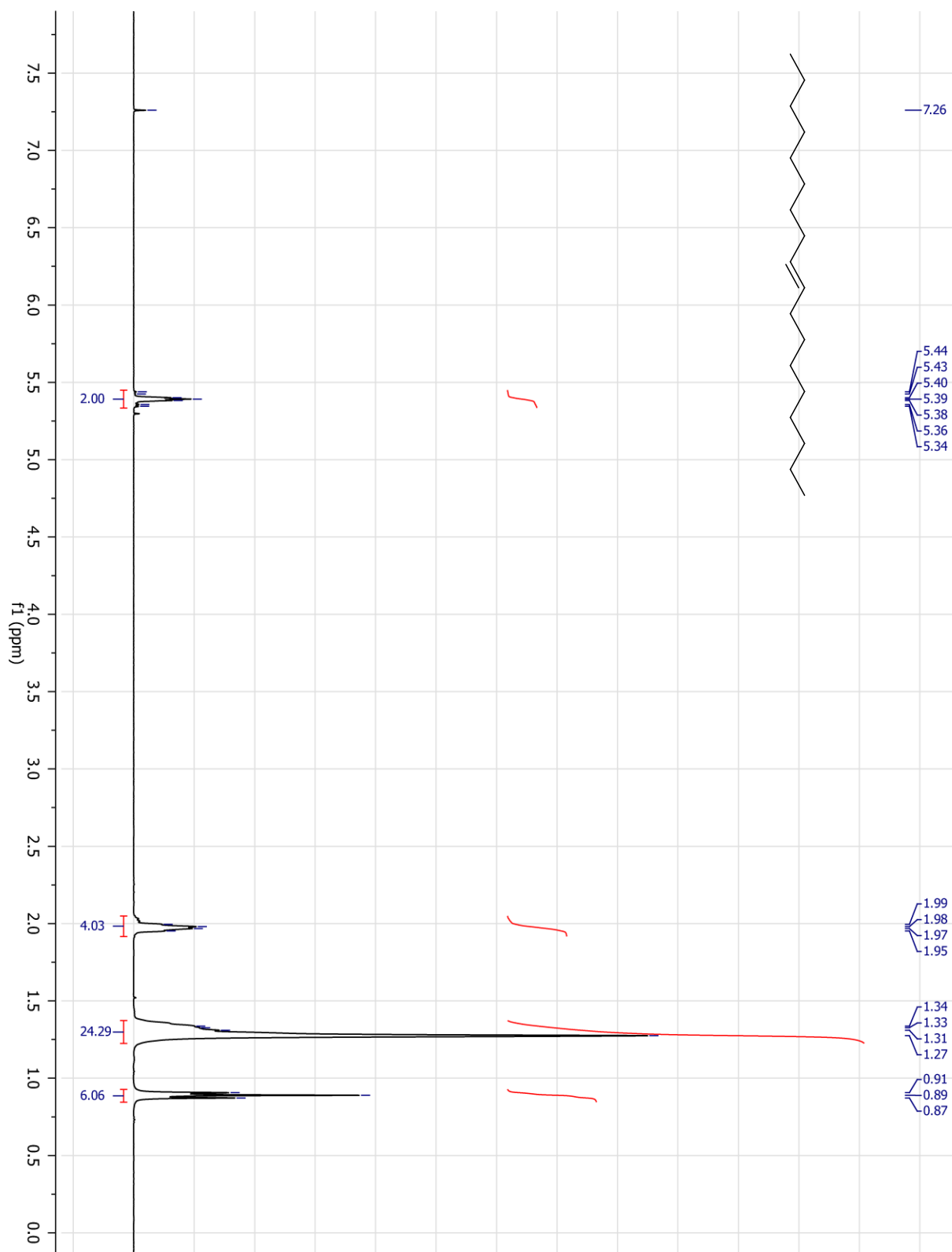
**Figure S28.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of (Z)-dimethyl octadec-9-enedioate



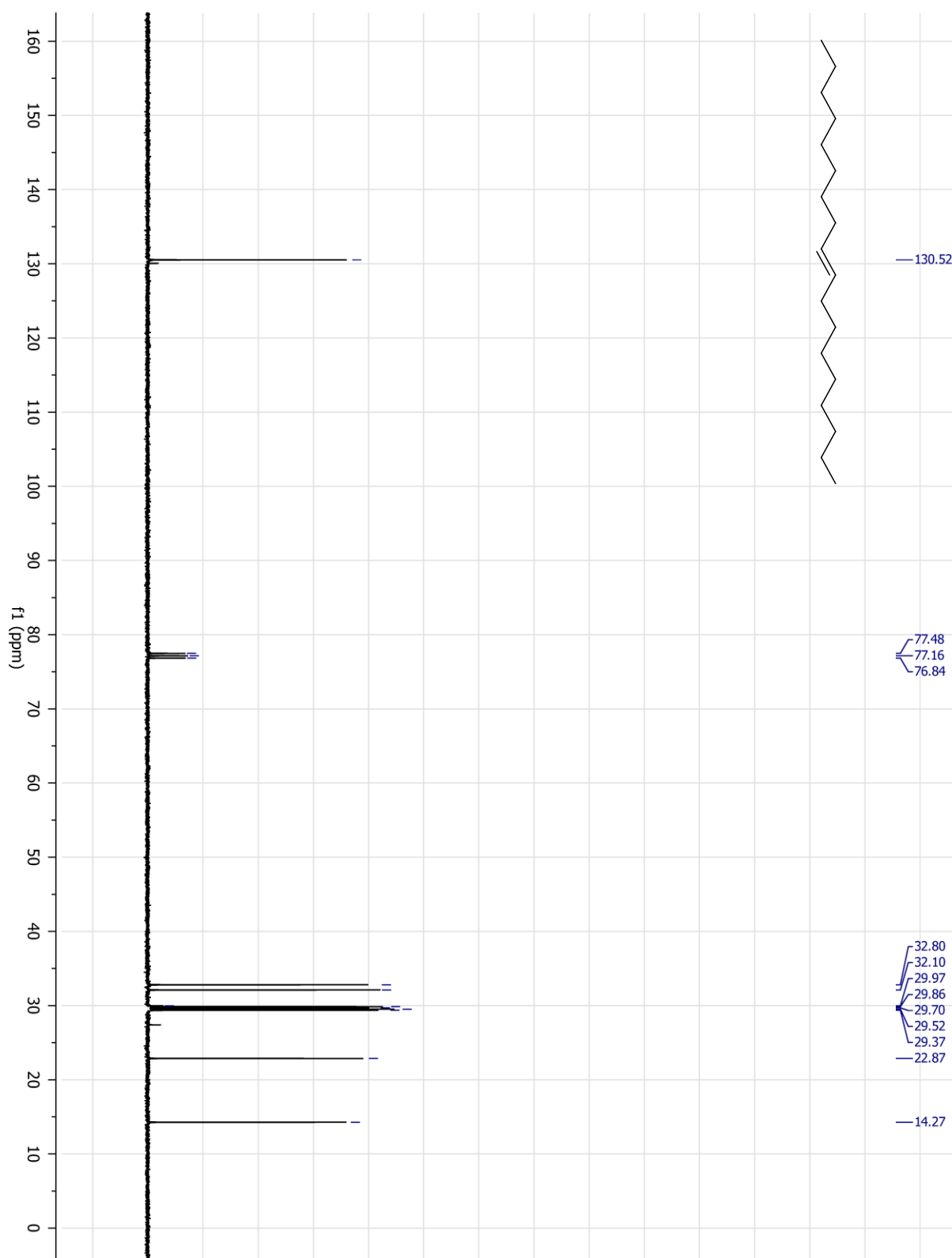
**Figure S29.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of Methyl *trans*-9-octadecenoate



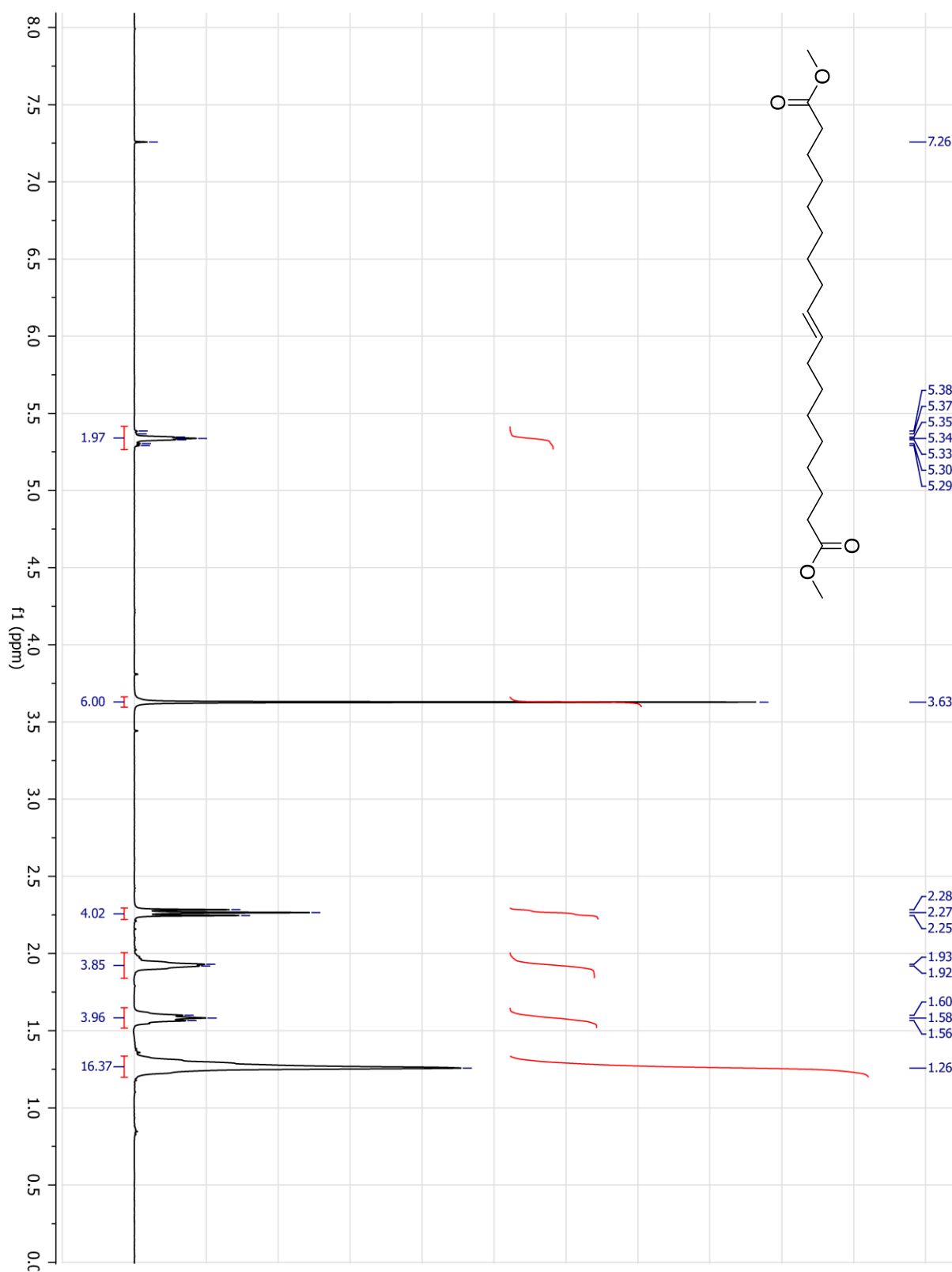
**Figure S30.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of Methyl *trans*-9-octadecenoate



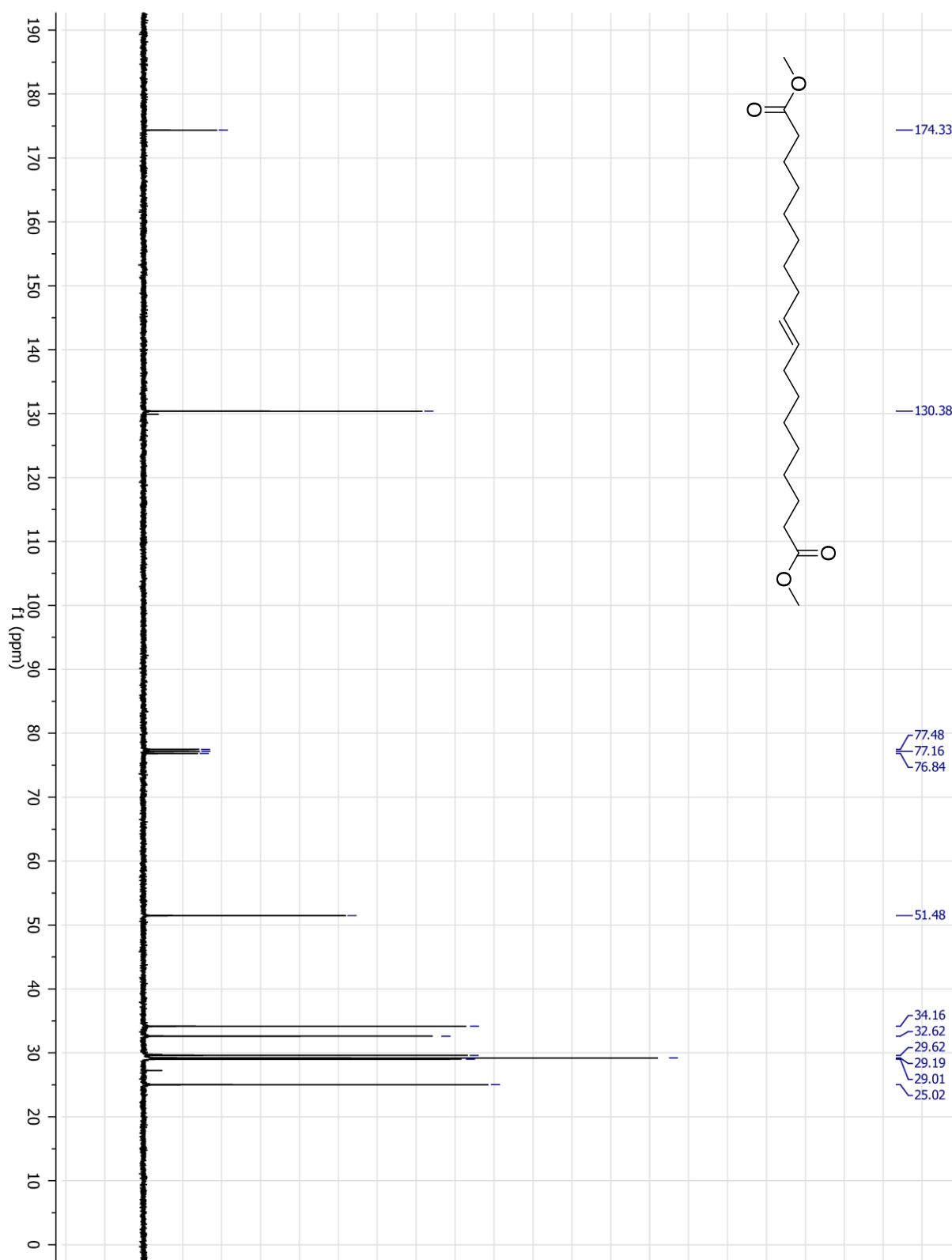
**Figure S31.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of *(E)*-octadec-9-ene



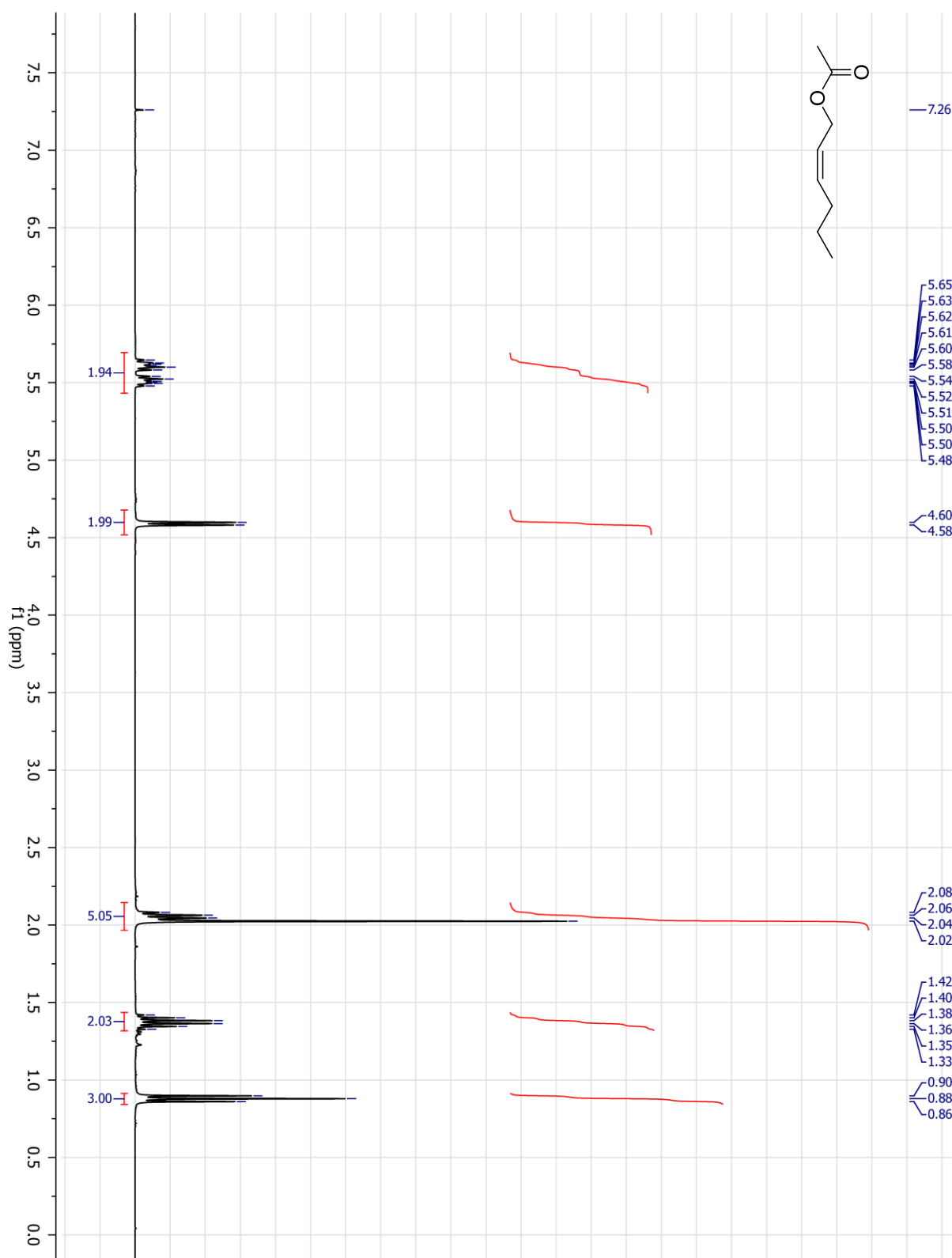
**Figure S32.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of (*E*)-octadec-9-ene



**Figure S33.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of *(E)*-dimethyl octadec-9-enedioate

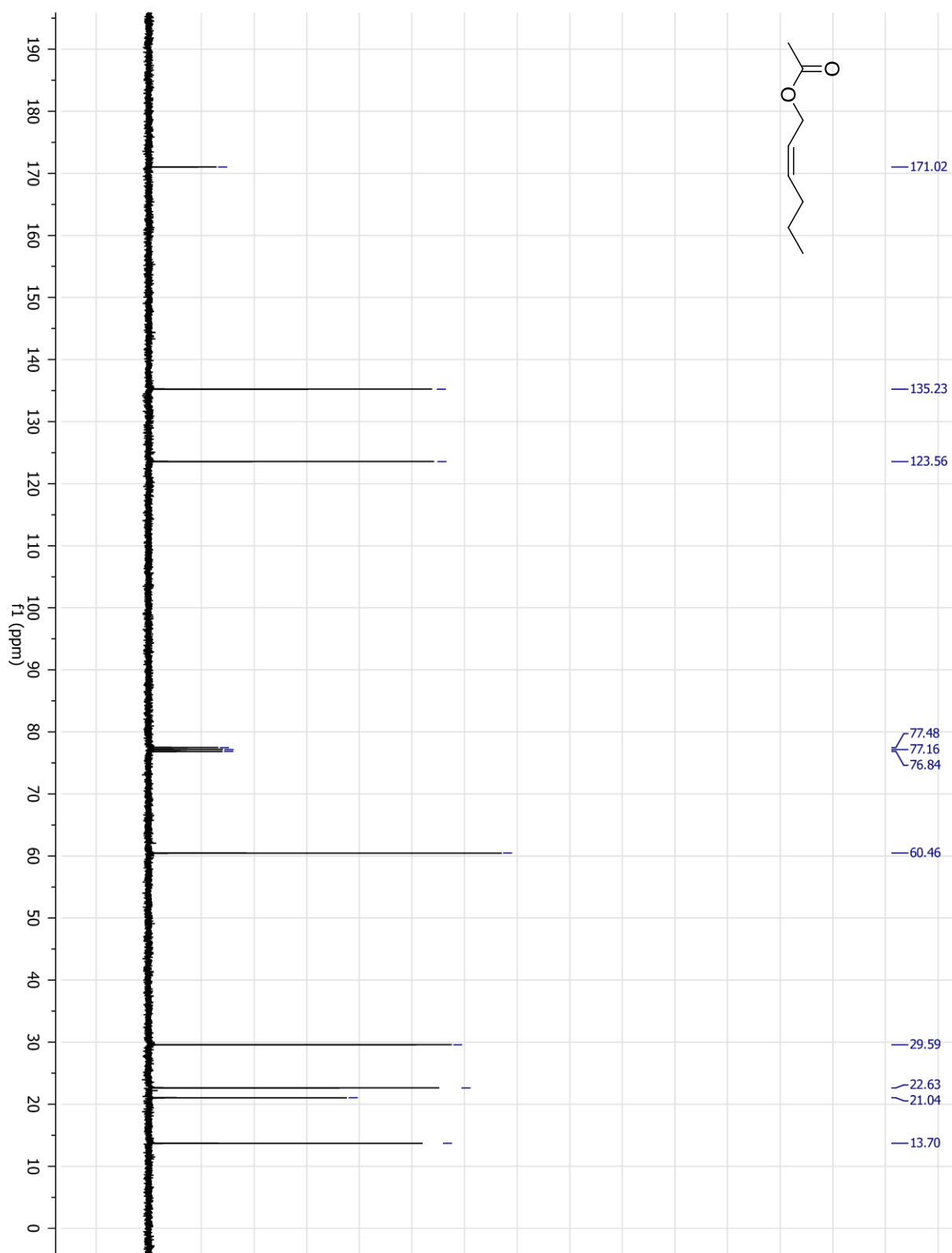


**Figure S34.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of (*E*)-dimethyl octadec-9-enedioate

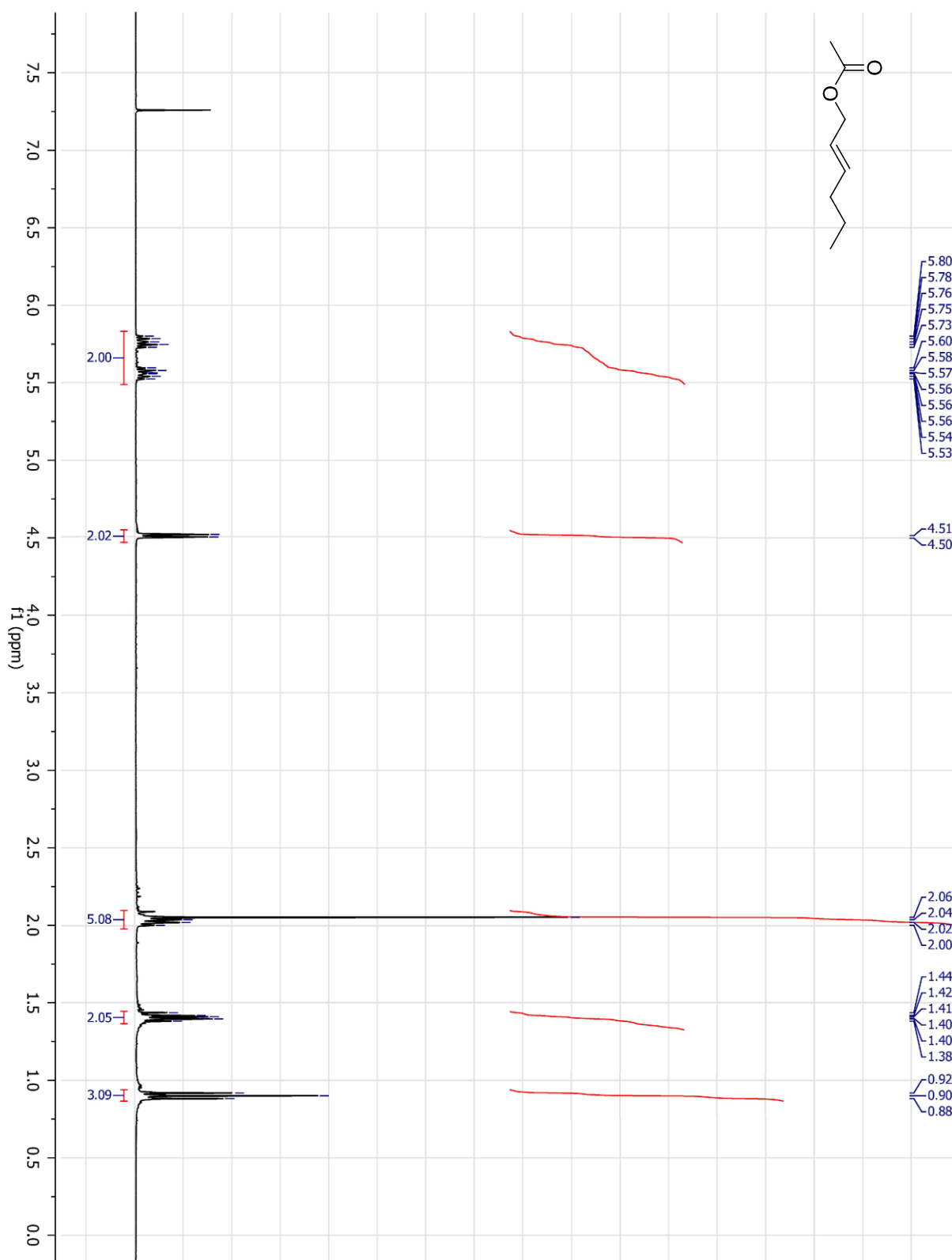


**Figure S35.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of (Z)-hex-2-en-1-yl acetate

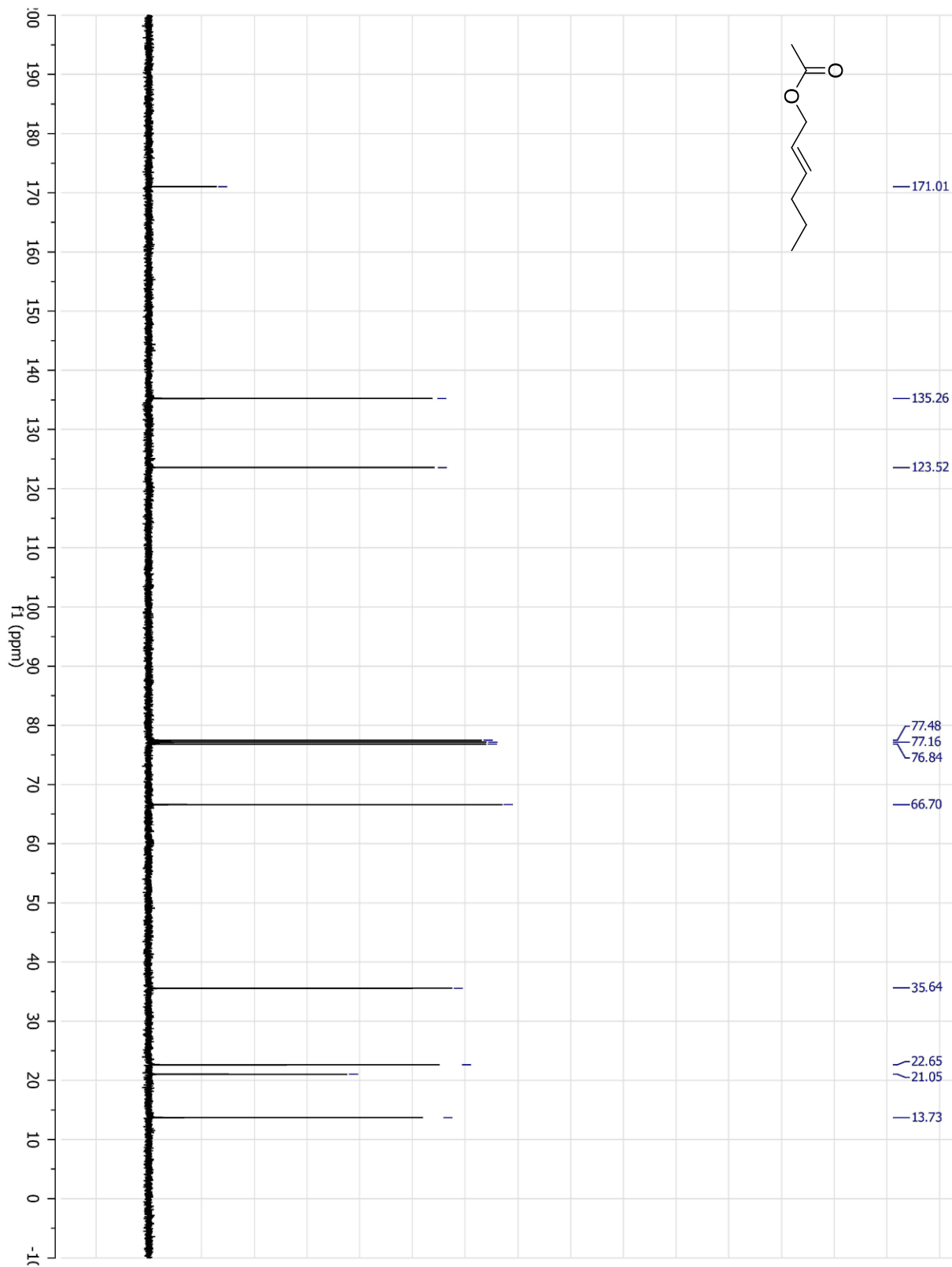




**Figure S36.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of (Z)-hex-2-en-1-yl acetate



**Figure S37.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of *(E)*-hex-2-en-1-yl acetate



**Figure S38.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of (*E*)-hex-2-en-1-yl acetate