Supporting Information

for

Synthesis of enones, pyrazolines and pyrrolines with *gem*-difluoroalkyl side chains

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Experimental details, NMR analysis and characterization data of new compounds

*Note: all compounds **2** and **4**–**12** are prepared in racemic form only*.

General Methods

All reagents were obtained commercially and used without further purification. All reactions were carried out under a nitrogen atmosphere and dry conditions. The solvents used were freshly distilled under anhydrous conditions, unless otherwise specified. The reaction mixtures were magnetically stirred with Teflon stirring bars, and the temperatures were measured externally. Reactions that required anhydrous conditions were carried out by using oven dried (120 °C, 24 h) glassware. Yields refer to chromatographically and spectroscopically (^{1}H, ^{13}C, and ^{19}F NMR) homogeneous materials. Reactions were monitored by ^{19}F NMR and by thin-layer chromatography (TLC), carried out on 0.25 mm Merck silica gel plates (60 F254) with detection by UV light or staining with *p*-anisaldehyde. The eluents used were mixtures of pentane (Pent) and ether (Et_2O). Acros silica gel (60, particle size 0.040–0.063 mm) was used for column chromatography. Nuclear magnetic resonance (NMR) spectra have been recorded with Bruker Avance 500, 400 and 300 spectrometers. ^{1}H NMR spectra: δ (H) are given in ppm relative to tetramethylsilane (TMS), using [δ (C*H*Cl_3) = 7.26 ppm] as internal reference. ^{13}C NMR spectra: δ (C) are given in ppm relative to TMS, using [δ (*C*DCl_3) = 77.0 ppm] as internal reference. ^{19}F NMR spectra: δ (F) are given in ppm relative to C*F*Cl_3 = 0.0 ppm as external reference. Multiplicities were designated as singlet (s), doublet (d), triplet (t), quadruplet (q), quintuplet (qt), multiplet (m) or br (broad). Mass spectral analyses have been performed at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO) in Rennes (France).

1. General procedure for the synthesis of difluoropropargylic alcohols (2)

To a solution of propargylic *gem*-difluoro intermediate **1** (1 equiv) in anhydrous THF (2 ml per mmol) cooled at −78 °C, was added, dropwise under nitrogen, a solution of *n*-BuLi in hexanes (1.2 equiv). The mixture was stirred for 1 h at $T \leq -40$ °C. Then the aldehyde (1.2 equiv) in anhydrous THF (1 ml per mmol) was added at −78 °C and the resulting solution was allowed to warm to room temperature over 2 h. The mixture was treated with saturated ammonium chloride solution and extracted with ether (3 x 10 ml). The combined organic phases were washed with water, dried over $MgSO_4$ and concentrated in vacuo. The crude product is purified by chromatography on silica gel, using a mixture of ether/pentane as eluent.

1.1. Synthesis of 4,4-difluoro-1-phenyl-tridec-2-yn-1-ol ((±)-2a)

The reaction was performed with **1** (990 mg, 4.90 mmol) and benzaldehyde (0.6 ml, 9.8 mmol), according to the general procedure. After purification by chromatography on silica gel, propargylic alcohol **2a** was obtained as a yellow oil (1.30 g, 82% yield). $\mathbf{R}_f$ = 0.38 (Et_2O/pentane 1/9). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.54-7.41 (m, 2H); 7.38-7.27 (m, 3H); 5.47 (t, 1H, $^5J_{HF}$ = 3.9 Hz); 2.19 (bs, 1H); 2.13-1.97 (m, 2H); 1.60-1.52 (m, 2H); 1.30-1.27 (m, 12H); 0.89 (t, 3H, *J* = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 139.0 (t, $^5J_{CF}$ = 1.4 Hz); 128.9 (2C); 126.6 (2C); 114.9 (t, $^1J_{CF}$ = 232.8 Hz); 86.3 (t, $^3J_{CF}$ = 6.7 Hz); 79.7 (t, $^2J_{CF}$ = 41.2 Hz); 64.3 (t, $^4J_{CF}$ = 1.9 Hz); 39.5 (t, $^2J_{CF}$ = 25.7 Hz); 31.9; 29.4; 29.32; 29.26; 28.9; 22.7 (t, $^3J_{CF}$ = 3.5 Hz); 22.7; 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -83.10 (td, J_{FH} = 15.0 Hz, 3.9 Hz). HRMS (ESI) calcd for $C_{19}H_{26}F_2O^{79}BrNa$: $[M+Na]^+$: *m/z* 331.19518. Found*: m/z* 331.1953 (1ppm).

1.2. Synthesis of 4,4-difluoro-1-(pyridine-3-yl)-tridec-2-yn-1-ol ((±)-2b)

The reaction was performed with **1** (400 mg, 1.29 mmol) and 3-pyridinecarboxaldehyde (0.22 ml, 2.38 mmol), according to the general procedure. After purification by chromatography on silica gel, propargylic alcohol **2b** was obtained as a yellow oil (472 mg, 78% yield). $\mathbf{R}_f$ = 0.29 (Et_2O/pentane 7/3). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 8.66 (s, 1H); 8.54 (d, 1H, *J* = 4.4 Hz); 7.92 (d, 1H, *J* = 7.4 Hz); 7.38 (dd, 1H, *J* = 7.4 Hz, *J* = 4.4 Hz) ; 5.62 (t, 1H, $^5J_{HF}$ = 3.8 Hz); 3.80 (bs, 1H); 2.13-1.92 (m, 2H); 1.61-1.43 (m, 2H); 1.16-1.45 (m, 12H); 0.88 (t, H_1, *J* = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 148.6; 147.3; 136.3; 135.2; 123.9; 114.8 (t, $^1J_{CF}$ = 232.9 Hz); 86.1 (t, $^3J_{CF}$ = 6.8 Hz); 79.6 (t, $^2J_{CF}$ = 41.2 Hz); 61.3; 39.1 (t, $^2J_{CF}$ = 25.7 Hz); 31.8; 29.4; 29.3; 29.2; 28.9; 22.7 (t, $^3J_{CF}$ = 3.4 Hz); 22.7; 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -83.23 (td, J_{FH} = 15.3 Hz, 3.8 Hz). HRMS (ESI) calcd for $C_{22}H_{32}NOF_2{}^{79}BrNa$: $[M+Na]^+$: *m/z* 332.18019. Found*: m/z* 332.1812 (3 ppm).

1.3. Synthesis of 4,4-difluoro-1-(furane-2-yl)-tridec-2-yn-1-ol ((±)-2c)

The reaction was performed with **1** (400 mg, 1.29 mmol) and furane-2-carbaldehyde (0.2 ml, 2.38 mmol), according to the general procedure. After purification by chromatography on silica gel, propargylic alcohol **2c** was obtained as a yellow oil (463 mg, 79% yield). $\mathbf{R}_f$ = 0.46 (Et_2O/pentane 2/8). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.44 (dd, 1H, *J* = 1.8 Hz, *J* = 0.8

Hz); 6.47 (dt, 1H, J = 3.3 Hz, J = 0.7 Hz); 6.38 (dd, 1H, J = 3.3 Hz, J = 1.8 Hz); 5.54 (t, 1H, $^5J_{HF}$ = 3.8 Hz); 2.47 (bs, 1H); 2.19-1.98 (m, 2H); 1.61-1.42 (m, 2H); 1.15-1.34 (m, 12H); 0.88 (t, H_1, J = 6.3 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 151.4 (t, $^5J_{CF}$ = 2.0 Hz); 143.4; 114.8 (t, $^1J_{CF}$ = 233.1 Hz); 110.6; 108.4; 83.9 (t, $^3J_{CF}$ = 6.7 Hz); 78.8 (t, $^2J_{CF}$ = 41.4 Hz); 57.8 (t, $^4J_{CF}$ = 1.8 Hz); 39.1 (t, $^2J_{CF}$ = 25.6 Hz); 31.8; 29.4; 29.30; 29.2; 28.9; 22.7 (t, $^3J_{CF}$ = 3.5 Hz); 22.7; 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -83.51 (td, J_{FH} = 15.2 Hz, 3.8 Hz). HRMS (ESI) calcd for $C_{17}H_{24}O_2F_2{}^{79}BrNa$: $[M + Na]^+$: *m/z* 321.16421. Found*: m/z* 321.1641 (0 ppm).

1.4. Synthesis of 4,4-difluoro-1-(thiophene-2-yl)-tridec-2-yn-1-ol ((±)-2d)

The reaction was performed with **1** (877 mg, 4.34 mmol) and thiophene-2-carbaldehyde (0.47 ml, 5.21 mmol), according to the general procedure. After purification by chromatography on silica gel, propargylic alcohol **2d** was obtained as a yellow oil (966 mg, 71% yield). $\mathbf{R_f}$ = 0.43 (Et_2O/pentane 2/8). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.24 (dd, 1H, J = 5.1 Hz, J = 1.2 Hz); 7.18 (dt, 1H, J = 3.4 Hz, 0.9 Hz); 6.38 (dd, 1H, J = 5.1 Hz, J = 3.4 Hz); 5.62 (bs, 1H); 2.72 (bs, 1H); 2.18-1.84 (m, 2H); 1.61-1.42 (m, 2H); 1.37-1.17 (m, 12H); 0.83 (t, H_1, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 142.7 (t, $^5J_{CF}$ = 1.7 Hz); 126.9; 126.6; 126.1; 114.9 (t, $^1J_{CF}$ = 233.2 Hz); 85.6 (t, $^3J_{CF}$ = 6.7 Hz); 79.1 (t, $^2J_{CF}$ = 41.4 Hz); 59.9 (t, $^4J_{CF}$ = 1.8 Hz); 39.1 (t, $^2J_{CF}$ = 25.6 Hz); 31.9; 29.4; 29.33; 29.27; 29.0; 22.7 (t, $^3J_{CF}$ = 3.8 Hz); 22.7; 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -83.45 (td, J_{FH} = 15.0 Hz, 3.8 Hz). HRMS (ESI) calcd for $C_{17}H_{24}OF_2S^{79}BrNa$: $[M +Na]^+$: m/z 377.14136. Found: m/z 337.1416 (1 ppm).

1.5. Synthesis of 1-(4-bromophenyl)-4,4-difluoro-tridec-2-yn-1-ol ((±)-2e)

The reaction was performed with **1** (400 mg, 1.98 mmol) and 4-bromobenzaldehyde (0.44 mg, 2.376 mmol), according to the general procedure. After purification by chromatography on silica gel, propargylic alcohol **2e** was obtained as a yellow oil (614 mg, 81% yield). $\mathbf{R_f}$ = 0.34 (Et_2O/pentane 1/9). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.41-7.32 (m, 2H); 7.25-7.16 (m, 2H); 5.28 (t, 1H, $^5J_{HF}$ = 3.7 Hz); 2.46 (bs, 1H); 2.02-1.88 (m, 2H); 1.50-1.35 (m, 2H); 1.29-1.11 (m, 12H); 0.80 (t, H_1, J = 6.4 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 138.0; 131.9; 128.3; 122.9; 114.8 (t, $^1J_{CF}$ = 233.0 Hz); 85.8 (t, $^3J_{CF}$ = 6.7 Hz); 79.9 (t, $^2J_{CF}$ = 41.3 Hz); 63.4 (t, $^4J_{CF}$ = 1.8 Hz); 39.1 (t, $^2J_{CF}$ = 25.7 Hz); 32.0; 29.43; 29.35; 29.30; 28.9; 22.7 (t, $^3J_{CF}$ = 3.5 Hz); 22.7; 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -83.25 (td, J_{FH} = 15.1 Hz, 3.7

Hz). HRMS (ESI) calcd for $C_{19}H_{25}OF_2Br^{79}BrNa$: $[M+Na]^+$: *m/z* 409.09545. Found*: m/z* 409.0951 (2 ppm).

2. General procedure for the synthesis of *gem*-difluoroenones (3)

The difluoropropargylic alcohol **2** (1 equiv) was dissolved in THF (2 ml per mmol), then DBU (1.5 equiv) was added, and stirred at 35 °C for the appropriate time (monitored by ^{19}F NMR). After completion of the reaction, the mixture was neutralized with a saturated solution of NH_4Cl. After extraction with diethyl ether, the organic phases were washed with water, dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by chromatography on silica gel, using ether/pentane as eluent.

2.1. Synthesis of 4,4-difluoro-1-phenyl-tridec-2-en-1-one (3a)

The reaction was performed with **2a** (920 mg, 2.99 mmol) according to the general procedure. After 6 h, ^{19}F NMR showed 100% conversion, and there were two enones, *cis* and *trans* (1/100). After purification by flash chromatography on silica gel, the enone **3a** was isolated as a yellow oil (570 mg, 62%). $\mathbf{R_f}$ = 0.30 (Et_2O/pentane 2/98). ^1H NMR ($CDCl_3$, 400 MHz), δ ppm: 8.02-7.94 (m, 2H); 7.66-7.57 (m, 1H); 7.55-7.46 (m, 2H); 7.31 (dt, 1H, J = 15.6 Hz, $^4J_{HF}$ = 2.3 Hz); 6.85 (dt, 1H, J = 15.6 Hz, $^3J_{HF}$ = 11.6 Hz); 2.08-1.91 (m, 2H); 1.51-1.43 (m, 2H); 1.41-1.17 (m, 12H); 0.88 (t, 3H, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz), δ ppm: 189.3; 138.9 (t, $^2J_{CF}$ = 27.3 Hz); 133.6; 136.9; 128.8 (2C); 128.7 (2C); 127.40 (t, $^3J_{CF}$ = 7.5 Hz); 121.3 (t, $^1J_{CF}$ = 239.9 Hz); 37.3 (t, $^2J_{CF}$ = 25.7 Hz); 31.8; 29.4; 29.3; 29.2 (2C); 22.7; 22.2 (t, $^3J_{CF}$ = 4.1 Hz); 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -98.36 (tdd, J_{FH} = 16.0 Hz, 11.6 Hz, 2.3Hz). HRMS (ESI) calcd for $C_{19}H_{26}F_2O^{79}BrNa$: $[M+Na]^+$: *m/z* 331.19518. Found*: m/z* 331.1952 (0ppm).

2.2. Synthesis of 4,4-difluoro-1-(pyridine-3-yl)-tridec-1-en-one (3b)

The reaction was performed with **2b** (386 mg, 1.25 mmol) according to the general procedure. After 30 min, ^{19}F NMR showed 100% conversion, and that a single product is formed. After purification by flash chromatography on silica gel, the enone **3b** was isolated as a sticky syrup (225 mg, 62%). $\mathbf{R_f}$ = 0.26 (Et_2O/pentane 3/7). ^1H NMR ($CDCl_3$, 300 MHz), δ ppm: 9.16 (dd, 1H, J = 2.1 Hz, J = 0.5 Hz); 8.80 (dd, 1H, J = 4.8 Hz, J = 1.6 Hz); 8.23 (ddd,

1H, *J* = 7.9 Hz, *J* = 2.1 Hz, *J* = 1.6 Hz); 7.44 (ddd, 1H, *J* = 7.9 Hz, *J* = 4.8 Hz, *J* = 0.5 Hz); 7.26 (dt, 1H, *J* = 15.5 Hz, $^{4}J_{HF}$ = 2.3 Hz); 6.88 (dt, 1H, *J* = 15.5 Hz, $^{3}J_{HF}$ = 11.9 Hz); 2.06-1.90 (m, 2H); 1.51-1.40 (m, 2H); 1.39-1.12 (m, 12H); 0.85 (t, 3H, *J* = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 188.0; 153.8; 149.9; 140.0 (t, $^{2}J_{CF}$ = 27.5 Hz); 135.9; 132.1; 126.6 (t, $^{3}J_{CF}$ = 7.5 Hz); 123.7; 121.0 (t, $^{1}J_{CF}$ = 239.9 Hz); 37.1 (t, $^{2}J_{CF}$ = 25.6 Hz); 31.8; 29.3; 29.2; 29.1 (2C); 22.6; 22.1 (t, $^{3}J_{CF}$ = 4.1 Hz); 14.0. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -98.63 (td, J_{FH} = 15.4 Hz, 11.9 Hz). HRMS (ESI) calcd for $C_{18}H_{25}NOF_2{}^{79}BrNa$: $[M+Na]^+$: *m/z* 332.18019 Found*: m/z* 332.1814 (4 ppm).

2.3. Synthesis of 4,4-difluoro-1-(furane-2-yl)-tridec-2-en-1-one (3c)

The reaction was performed with **2c** (386 mg, 1.25 mmol) according to the general procedure. After 40 min, ^{19}F NMR showed 100% conversion, and there were two enones, *cis* and *trans* (1/100). After purification by flash chromatography on silica gel, the enone **3c** was isolated as yellow oil (138 mg, 63%). $\mathbf{R_f}$ = 0.31 (Et_2O/pentane 5/95). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.67 (dd, 1H, *J* = 1.7 Hz, *J* = 0.7 Hz); 7.33 (dd, 1H, *J* = 3.7 Hz, *J* = 0.7 Hz); 7.18 (dt, 1H, *J* = 15.6 Hz, $^{4}J_{HF}$ = 2.2 Hz); 6.92 (dt, 1H, *J* = 15.6 Hz, $^{3}J_{HF}$ = 11.5 Hz); 6.59 (dd, 1H, *J* = 3.6 Hz, *J* = 1.7 Hz); 2.08-1.85 (m, 2H); 1.55-1.39 (m, 2H); 1.35-1.14 (m, 12H); 0.85 (t, 3H, *J* = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 176.7; 152.9; 147.4; 138.4 (t, $^{2}J_{CF}$ = 27.5 Hz); 126.7 (t, $^{3}J_{CF}$ = 7.6 Hz); 121.2 (t, $^{1}J_{CF}$ = 239.7 Hz); 119.0; 112.8; 37.24 (t, $^{2}J_{CF}$ = 25.7 Hz); 31.82; 29.37; 29.3; 29.2 (2C); 22.6; 22.1 (t, C_8, $^{3}J_{CF}$ = 4.1 Hz); 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -98.48 (tdd, J_{FH} = 16.1 Hz, 11.5 Hz, 2.1 Hz). HRMS (ESI) calcd for $C_{17}H_{24}O_2F_2{}^{79}BrNa$: $[M+Na]^+$: *m/z* 321.16421. Found*: m/z* 321.1640 (1 ppm).

2.4. Synthesis of 4,4-difluoro-1-(thiophene-2-yl)-tridec-2-en-1-one (3d)

The reaction was performed with **2d** (730 mg, 2.32 mmol) according to the general procedure. After 1 h, ^{19}F NMR showed 100% conversion, and there were two enones, *cis* and *trans* (1/100). After purification by flash chromatography on silica gel, the enone **3c** was isolated as a yellow oil (437 mg, 60%). $\mathbf{R_f}$ = 0.24 (Et_2O/pentane 2/98). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.83 (dd, 1H, *J* = 3.9 Hz, *J* = 1.1 Hz); 7.73 (dd, 1H, *J* = 5.0 Hz, *J* = 1.1 Hz); 7.19 (dt, 1H, *J* = 15.4 Hz, $^{4}J_{HF}$ = 2.3 Hz); 7.18 (dd, 1H, *J* = 5.0 Hz, *J* = 3.9 Hz); 6.89 (dt, 1H, *J* = 15.4 Hz, $^{3}J_{HF}$ = 11.6 Hz); 2.09-1.90 (m, 2H); 1.52-1.43 (m, 2H); 1.38-1.18 (m, 12H); 0.87

(t, 3H, J = 6.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 181.0; 144.4; 138.4 (t, $^2J_{CF}$ = 27.2 Hz); 135.2; 133.0; 128.5; 127.1 (t, $^3J_{CF}$ = 7.5 Hz); 121.2 (t, $^1J_{CF}$ = 239.7 Hz); 37.3 (t, $^2J_{CF}$ = 25.7 Hz); 31.8; 29.4; 29.3; 29.2 (2C); 22.7; 22.1 (t, $^3J_{CF}$ = 4.1 Hz); 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -98.45 (tdd, J_{FH} = 16.1 Hz, 11.6 Hz, 2.3 Hz). HRMS (ESI) calcd for $C_{17}H_{24}OF_2S^{79}BrNa$: $[M+Na]^+$: *m/z* 377.14136. Found*: m/z* 337.1418 (1 ppm).

2.5. Synthesis of 1-(4-bromophenyl)-4,4-difluoro-tridec-2-en-1-one (3e)

The reaction was performed with **2e** (332 mg, 1.07 mmol) according to the general procedure. After 1 h, ^{19}F NMR showed 100% conversion, and there were two enones, *cis* and *trans* (1/100). After purification by flash chromatography on silica gel, the enone **3c** was isolated as a sticky syrup (203 mg, 61%). $\mathbf{R_f}$ = 0.31 (pentane). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.86-7.62 (m, 4H); 7.26 (dt, 1H , J = 15.5 Hz, $^4J_{HF}$ = 2.3 Hz); 6.86 (dt, 1H, J = 15.5 Hz, $^3J_{HF}$ = 11.5 Hz); 2.07-1.89 (m, 2H); 1.53-1,41 (m, 2H, H_8); 1.40-1.2 (m, 12H); 0.87 (t, 3H, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 188.2; 139.5 (t, $^2J_{CF}$ = 27.3 Hz); 135.60; 132.2 (2C); 130.2 (2C); 128.9; 126.8 (t, $^3J_{CF}$ = 7.5 Hz); 121.1(t, $^1J_{CF}$ = 239.8 Hz); 37.3 (t, $^2J_{CF}$ = 25.7 Hz); 31.9; 29.4; 29.3; 29.2 (2C); 22.7; 22.2 (t, $^3J_{CF}$ = 4.1 Hz); 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -98.47 (td, J_{FH} = 16.1 Hz, 11.5 Hz, 2.3 Hz). HRMS (ESI) calcd for $C_{19}H_{25}OF_2Br^{79}BrNa$: $[M+Na]^+$: *m/z* 409.09545. Found*: m/z* 409.0952 (1 ppm).

3. General procedure for the synthesis of pyrazolines (4)

The enone **3** (1 equiv) was dissolved in ethanol (2 ml per 1 mmol), then methylhydrazine (4 equiv) was added. The reaction mixture was stirred at 40 °C for the appropriate time (monitored by ^{19}F NMR). After evaporation of ethanol, the crude product was crystallized and the pyrazoline **4** was purified by chromatography on silica gel, using ether/pentane as eluent.

3.1. Synthesis of 5-(1,1-difluorodecyl)-1-methyl-3-phenyl-4,5-dihydro-1H-pyrazole ((±)-4a)

The reaction was performed with **3a** (100 mg, 0.33 mmol) according to the general procedure. After 11.5 h, ^{19}F NMR monitoring showed the absence of starting material. After purification by flash chromatography on silica gel, the pyrazoline **4a** was isolated as a sticky syrup (90 mg, 85%). $\mathbf{R_f}$ = 0.47 ((Et_2O/pentane 1/9). ^{1}H NMR ($CDCl_3$, 400 MHz), δ ppm: 7.72-7.62 (m, 2H); 7.34-7.33 (m, 3H); 3.54 (dddd, 1H, $^3J_{HF}$ = 11.7 Hz, J = 11.6 Hz, J = 11.6

Hz, $^{3}J_{HF}$ = 7.4 Hz); 3.36 (dd, 1H, *J* = 16.8 Hz, *J* = 11.6 Hz); 3.07 (dd, 1H, *J* = 16.8 Hz, *J* = 11.6 Hz); 2.99 (s, 3H); 2.05-1.82 (m, 2H); 1.62-1.54 (m, 2H); 1.38-1.22 (m, 12H); 0.89 (t, 3H, *J* = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz); δ ppm: 149.3; 132.1; 128.9; 128.8 (2C); 127.1 (2C); 124.7 (t, $^{1}J_{CF}$ = 251.9 Hz); 71.19 (dd, $^{2}J_{CF}$ = 27.5 Hz, $^{2}J_{CF}$ = 26.6 Hz); 43.9; 35.8 (dd, $^{3}J_{CF}$ = 5.3 Hz, $^{3}J_{CF}$ = 2.0 Hz); 33.0 (t, $^{2}J_{CF}$ = 24.2 Hz); 31.9; 29.43; 29.40; 29.3; 22.7; 22.2 (t, $^{3}J_{CF}$ = 4.2 Hz); 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -102.11(dddd, J_{FF} = 250.6Hz, J_{FH} = 20.8 Hz, 15.6 Hz, 11.7 Hz); -104.33 (dddd, J_{FF} = 250.6 Hz, J_{FH} = 22.1 Hz, 16.5 Hz, 7.4 Hz). HRMS (ESI) calcd for $C_{20}H_{30}F_2N_2{}^{79}BrNa$: $[M+Na]^+$: *m*/z 359.22747. Found*: m/z* 359.2274 (0 ppm).

3.2. Synthesis 3-[5-(1,1-difluorodecyl)-1-methyl-4,5-dihydro-1*H*-pyrazole-3-yl]-pyridine ((±)-4b)

The reaction was performed with **3b** (100 mg, 0.29 mmol) according to the general procedure. After 2.5 h, ^{19}F NMR monitoring showed the absence of starting material. After purification by flash chromatography on silica gel, the pyrazoline **4b** was isolated as yellow crystals (88 mg, 79%). Mp: 51-53 °C. $\mathbf{R_f}$ = 0.44 (Et_2O/pentane 5/5). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 8.72 (s, 1H); 8.50 (d, 1H, *J* = 3.8 Hz); 7.93 (dt, 1H, *J* = 8.0 Hz, *J* = 1.6 Hz); 7.23 (dd, 1H, *J* = 8.0 Hz, *J* = 3.8 Hz); 3.51 (dddd, 1H, *J* = 11.9 Hz, *J* = 11.7 Hz, $^{3}J_{HF}$ = 11.7 Hz, $^{3}J_{HF}$ = 6.6 Hz); 3.26 (dd, 1H, *J* = 16.9 Hz, *J* = 11.7 Hz); 2.94 (dd, 1H, *J* = 16.9 Hz, *J* = 11.9 Hz); 2.93 (s, 3H); 2.03-1.66 (m, 2H); 1.56-1.41 (m, 2H); 1.34-1.09 (m, 12H); 0.80 (t, 3H, *J* = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 149.6; 147.1; 146.1; 132.8; 128.2; 124.36 (t, C_{10}, $^{1}J_{CF}$ = 242.8 Hz); 123.4; 71.1 (dd, $^{2}J_{CF}$ = 27.9 Hz, $^{2}J_{CF}$ = 27.2 Hz); 43.67 (t, *J* = 1.5 Hz); 35.2 (dd, $^{3}J_{CF}$ = 5.1 Hz, $^{3}J_{CF}$ = 2.6 Hz); 32.90 (t, $^{2}J_{CF}$ = 24.3 Hz); 31.2; 29.39 (2C); 29.36 ; 29.2; 22.6; 21.1 (t, $^{3}J_{CF}$ = 4.0 Hz) ; 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -102.55 (ddt, J_{FF} = 250.7 Hz, J_{FH} = 26.5 Hz, 11.7 Hz); -104.54 (dddd, J_{FF} = 250.7 Hz, J_{FH} = 26.3 Hz, 10.4 Hz, 6.6 Hz). HRMS (ESI) calcd for $C_{19}H_{29}F_2N_3{}^{79}BrNa$: $[M+H]^+$: *m/z* 338.24078. Found*: m/z* 338.2408 (0 ppm).

3.3. Synthesis of 5-(1,1-difluorodecyl)-3-furan-2-yl-1-methyl-4,5-dihydro-1*H*-pyrazole ((±)-4c)

The reaction was performed with **3c** (58 mg, 0.17 mmol) according to the general procedure. After 2 h 35 min, ^{19}F NMR monitoring showed the absence of starting material. After purification by flash chromatography on silica gel, the pyrazoline **4c** was isolated as white

crystals (54 mg, 81%). Mp: 68-70 °C. $\mathbf{R_f}$ = 0.31 (Et_2O/pentane 1/9). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.44 (dd, 1H, , *J* = 1.8 Hz, 0.7 Hz); 6.52 (dd, 1H, *J* = 3.4 Hz, *J* = 0.7 Hz); 6.43 (dd, 1H, *J* = 3.4 Hz, *J* = 1.8 Hz); 3.50 (dddd, 1H, *J* = 11.9 Hz, $^3J_{HF}$ = 11,9 Hz, *J* = 11.8 Hz , $^3J_{HF}$ = 6.2 Hz); 3.24 (dd, 1H, *J* = 16.9 Hz, *J* = 11.9 Hz); 3.00 (dd, 1H, *J* = 16.9 Hz, *J* = 12.1 Hz); 2.87 (s, 3H); 2.02-1.77 (m, 2H); 1.61-1.49 (m, 2H); 1.39-1.19 (m, 12H); 0.85 (t, 3H, *J* = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz), δ ppm: 147.5; 143.5; 141.3; 124.5 (t, $^1J_{CF}$ = 242.8 Hz); 111.5; 109.8; 123.4; 71.9 (dd, $^2J_{CF}$ = 28.5 Hz, $^2J_{CF}$ = 27.5 Hz); 43.9; 35.7 (dd, $^3J_{CF}$ = 5.4 Hz, $^3J_{CF}$ = 2.1 Hz); 32.9 (t, $^2J_{CF}$ = 24.3 Hz); 31.9; 29.43 (2C); 29.39; 29.2; 22.7; 21.1 (t, $^3J_{CF}$ = 4.0 Hz); 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -102.05 (ddt, J_{FF} = 251.6 Hz, J_{FH} = 27.3 Hz, 11.9 Hz); -104.17 (dddd, J_{FF} = 251.6 Hz, J_{FH} = 25.8 Hz, 11.6 Hz, 6.2 Hz). HRMS (ESI) calcd for $C_{18}H_{28}F_2N_2O^{79}BrNa$: $[M+Na]^+$: *m/z* 349.20674. Found*: m/z* 349.2067 (0 ppm).

3.4. Synthesis of 5-(1,1-difluorodecyl)-1-methyl-3-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrazole ((±)-4d)

The reaction was performed with **3d** (155 mg, 0.45 mmol) according to the general procedure. After 4 h 35 min, ^{19}F NMR monitoring showed the absence of starting material. After purification by flash chromatography on silica gel, the pyrazoline **4d** was isolated as white crystals (137 mg, 82%). Mp: 67-69 °C. $\mathbf{R_f}$ = 0.29 (Et_2O/pentane 5/95). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.28 (dd, 1H, *J* = 5.0 Hz, 1.2 Hz); 7.06 (dd, 1H, *J* = 3.6 Hz, *J* = 1.2 Hz); 7.00 (dd, 1H, *J* = 5.0 Hz, *J* = 3.6 Hz); 3.52 (dddd, 1H, *J* = 11.9 Hz, *J* = 11.5 Hz, $^3J_{HF}$ = 11.5 Hz, $^3J_{HF}$ = 6.7 Hz); 3.31 (dd, 1H, *J* = 16.7 Hz, *J* = 11.5 Hz); 3.05 (dd, 1H, *J* = 16.7 Hz, *J* = 11.9 Hz); 2.89 (s, 3H); 2.09-1.76 (m, 2H); 1.65-1.49 (m, 2H); 1.43-1.23 (m, 12H); 0.88 (t, 3H, *J* = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 145.1; 135.8; 127.2; 126.8; 126.3; 124.5 (t, $^1J_{CF}$ = 242.6 Hz); 71.6 (dd, $^2J_{CF}$ = 28.5 Hz, $^2J_{CF}$ = 27.6 Hz); 43.8 (t, ^3J = 1.4 Hz); 36.5 (dd, $^3J_{CF}$ = 5.4 Hz, $^3J_{CF}$ = 2.4 Hz); 32.8 (t, $^2J_{CF}$ = 24.2 Hz); 31.2; 29.37 (2C); 29.34; 29.2; 22.6; 21.0 (t, $^3J_{CF}$ = 4.0 Hz); 14.0. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -101.92 (ddt, J_{FF} = 250.9 Hz, J_{FH} = 27.9 Hz, 11.5 Hz); -104.21 (dddd, J_{FF} = 250.9 Hz, J_{FH} = 27.5 Hz, 11.2 Hz, 6.7 Hz). HRMS (ESI) calcd for $C_{18}H_{28}F_2N_2S^{79}BrNa$: $[M+Na]^+$: *m/z* 365.18390. Found*: m/z* 365.1849 (3 ppm).

3.5. Synthesis of 3-(4-bromophenyl)-5-(1,1-difluorodecyl)-1-methyl-4,5-dihydro-1*H*-pyrazole ((±)-4e)

The reaction was performed with **3e** (75 mg, 0.18 mmol) according to the general procedure. After 2.5 h, ^{19}F NMR monitoring showed the absence of starting material. After purification by flash chromatography on silica gel, the pyrazoline **4e** was isolated as a sticky syrup (74 mg, 86%). $\mathbf{R}_f$ = 0.43 (Et_2O/pentane 5/95). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.47 (s, 4H); 3.55 (dddd, 1H, J = 12.0 Hz, J = 11.8 Hz, $^3J_{HF}$ = 11.8 Hz, $^3J_{HF}$ = 6.6 Hz); 3.29 (dd, 1H, J = 16.9 Hz, J = 11.8 Hz); 3.00 (dd, 1H, J = 16.9 Hz, J = 12.0 Hz); 2.99 (s, 3H,) ; 2.08-1.75 (m, 2H); 1.64-1.49 (m, 2H); 1.43-1.18 (m, 12H); 0.88 (t, 3H, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 148.0; 131.7 (2C); 131.1; 127.7 (2C); 124.5 (t, $^1J_{CF}$ = 242.6 Hz); 123.0; 71.3 (dd, $^2J_{CF}$ = 28.5 Hz, $^2J_{CF}$ = 27.5 Hz); 43.8 (t, 1.4 Hz); 35.6 (dd, $^3J_{CF}$ = 5.1 Hz, $^3J_{CF}$ = 2.5 Hz); 33.1 (t, $^2J_{CF}$ = 24.3 Hz); 31.9; 29.5 (2C); 29.4; 29.3; 22.7; 21.1 (t, $^3J_{CF}$ = 3.9 Hz); 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -102.23 (ddt, J_{FF} = 250.8 Hz, J_{FH} = 26.9 Hz, 11.8 Hz); -104.38 (dddd, J_{FF} = 250.8 Hz, J_{FH} = 27.3 Hz, 11.5 Hz, 6.6 Hz). HRMS (ESI) calcd for $C_{20}H_{29}F_2N_2Br^{79}BrNa$: $[M+Na]^+$: m/z 437.13799. Found: m/z 437.1382 (0 ppm).

4. General procedure for the synthesis of pyrrolines (6)

To a solution of *gem*-difluoroenone **3** (1 equiv) and Schiff base **5** (1 equiv) in CH_2Cl_2 (1.5 ml per mmol) cooled to 5 °C was added DBU (0.5 equiv). After stirring at 25 °C for the appropriate time (monitored by ^{19}F NMR), HCl (12 N, 1.5 equiv) was added and the mixture was stirred at 25 °C for the time *t* (monitored by ^{19}F NMR). Then water was added and the mixture was extracted with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated in vacuo. The crude residue was then purified by flash chromatography over silica gel.

4.1. Synthesis of 3-(1,1-difluorodecyl)-5-phenyl-3,4-dihydro-2*H*-pyrrole-2-carboxylic acid ethyl ester ((±)-6a)

The reaction was performed from **3a** (400 mg, 1.29 mmol) according to the general procedure. After purification by chromatography on silica gel, pyrroline **6a** was obtained as beige crystals (378 mg, 74% yield). Mp: 66-68 °C. $\mathbf{R}_f$ = 0.31 (Et_2O/pentane 2/8). ^1H NMR (C_6D_6, 300 MHz), δ ppm: 7.85-7.75 (dd, 2H, J = 7.7 Hz, J = 1.4 Hz); 7.11-7.03 (m, 3H); 5.23 (dt, 1H, J = 6.5 Hz, $^4J_{HF}$ = 1.7 Hz); 4.41-3.94 (m, 2H); 3.51-3.29 (m, 1H); 2.92 (ddd, 1H, J = 17.4 Hz, J = 7.2 Hz, $^4J_{HF}$ = 1.7 Hz); 2.82 (ddd, 1H, J = 17.4 Hz, J = 10.0 Hz, $^4J_{HF}$ = 2.3 Hz); 1.73-1.62 (m, 2H); 1.56-1.43 (m, 2H); 1.33-1.12 (m, 12H); 0.96 (t, 3H, J = 7.1 Hz), 0.91 (t, 3H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 174.1; 171.8; 133.2; 131.2; 128.4 (2C); 128.0 (2C); 124,4 (t, $^1J_{CF}$ = 243,1 Hz); 75.5 (dd, $^3J_{CF}$ = 4.0 Hz, $^3J_{CF}$ = 2.7 Hz); 61.6; 46.1 (t, $^2J_{CF}$ = 25.1 Hz); 36.7 (dd, $^3J_{CF}$ = 5.0 Hz, $^3J_{CF}$ = 2.7 Hz); 35.3 (t, $^2J_{CF}$ = 25.1 Hz); 31.8; 29.4; 29.32; 29.27; 29.2; 22.6; 21.8 (t, $^3J_{CF}$ = 4.3 Hz); 14.11; 14.05. ^{19}F NMR (C_6D_6, 282 MHz), δ ppm: -103.05 (dq, 1F, J_{FF} = 244.1 Hz, J_{FH} = 16.5 Hz); -104,8 (dq, 1F, J_{FF} = 244.1 Hz, J_{FH} = 16.2 Hz). HRMS (ESI) calcd for $C_{23}H_{33}F_2NO_2{}^{79}BrNa$: $[M+Na]^+$: *m/z* 416.23771. Found: *m/z* 416.2370 (2 ppm).

4.2. Synthesis of 3-(1,1-Difluorodecyl)-5-(pyridin-3-yl)-3,4-dihydro-2*H*-pyrrole-2-carboxylic acid ethyl ester ((±)-6b)

The reaction was performed from **3b** (205 mg, 0.66 mmol) according to the general procedure. After purification by chromatography on silica gel, pyrroline **6b** was obtained as

white crystals (191 mg, 73% yield). Mp: 43-45 °C. $\mathbf{R}_f$ = 0.32 (Et_2O/pentane 7/3). ^{1}H NMR (C_6D_6, 300 MHz), δ ppm: 8.91 (d, 1H, *J* = 1.2 Hz); 8.46 (dd, 1H, *J* = 4.6 Hz, *J* = 1.2 Hz); 7.94 (dt, 1H, *J* = 8,0 Hz, *J* = 1.8 Hz); 6.61 (ddd, 1H, *J* = 8,0 Hz, *J* = 4.6 Hz, *J* = 0.6 Hz); 5.19 (dt, 1H, *J* = 6.5 Hz, $^4J_{HF}$ = 1.7 Hz); 4.10-3.94 (m, 2H); 3.45-3.21 (m, 1H); 2.74 (ddd, 1H, *J* = 17.5 Hz, *J* = 7.2 Hz, $^4J_{HF}$ = 1.7 Hz); 2.63 (ddd, 1H , *J* = 17.5 Hz, *J* = 10.0 Hz, $^4J_{HF}$ = 2.4 Hz); 1.75-1.59 (m, 2H); 1.54-1.45 (m, 2H); 1.28-1.13 (m, 12H); 0.96 (t, 3H, *J* = 7.1 Hz), 0.92 (t, 3H, *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 171.9; 171.5; 152.0; 149.3; 135.1; 129.0; 127.5; 124,3 (t, $^1J_{CF}$ = 243,3 Hz); 123.5; 75.6 (dd, $^3J_{CF}$ = 4.2 Hz, $^3J_{CF}$ = 2.8 Hz); 61.8; 46.1 (t, $^2J_{CF}$ = 25.3 Hz); 36.6 (dd, $^3J_{CF}$ = 5.2 Hz, $^3J_{CF}$ = 2.7 Hz); 35.7 (t, $^2J_{CF}$ = 24.8 Hz); 31.8; 29.4; 29.34; 29.30; 29.2; 22.6; 21.8 (t, $^3J_{CF}$ = 3.9 Hz); 14.1; 14.0. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -103.55 (dq, 1F, J_{FF} = 244.4 Hz, J_{FH} = 17.8 Hz); -105,86 (dq, 1F, J_{FF} = 244.5 Hz, J_{FH} = 15.5 Hz). HRMS (ESI) calcd for $C_{22}H_{32}F_2N_2O_2{}^{79}BrNa$: $[M+Na]^+$: *m/z* 417.23295. Found*: m/z* 417.2328 (0 ppm).

4.3. Synthesis of 3-(1,1-difluorodecyl)-5-(furan-2-yl)-3,4-dihydro-2*H*-pyrrole-2-carboxylic acid ethyl ester ((±)-6c)

The reaction was performed from **3c** (236 mg, 0.79 mmol) according to the general procedure. After purification by chromatography on silica gel, pyrroline **6c** was obtained as beige crystals (227 mg, 75% yield). Mp: 64-66 °C. $\mathbf{R}_f$ = 0.28 (Et_2O/pentane 3/7). ^{1}H NMR (C_6D_6, 300 MHz), δ ppm: 6.96 (d, 1H, *J* = 1.5 Hz); 6.74 (d, 1H, *J* = 3.5 Hz); 5.94 (dd, 1H, *J* = 3.5 Hz, *J* = 1.5 Hz); 5.21 (dt, 1H, *J* = 6.3 Hz, $^4J_{HF}$ = 1.9 Hz); 4.07-3.91 (m, 2H); 3.43-3.21 (m, 1H); 2.95 (ddd, 1H, *J* = 17.7 Hz, *J* = 7.4 Hz, $^4J_{HF}$ = 1.8 Hz); 2.86 (ddd, 1H , *J* = 17.7 Hz, *J* = 9.9 Hz, $^4J_{HF}$ = 2.1 Hz); 1.74-1.56 (m, 2H); 1.52-1.38 (m, 2H); 1.34-1.08 (m, 12H); 0.94 (t, 3H, *J* = 7.2 Hz), 0.91 (t, 3H, *J* = 6.9 Hz). ^{13}C NMR (C_6D_6, 75 MHz), δ ppm: 171.7; 164.4; 150.0; 144.5; 124,8 (t, $^1J_{CF}$ = 243,0 Hz); 113.3; 111.8; 76.3 (dd, $^3J_{CF}$ = 3.7 Hz, $^3J_{CF}$ = 2.9 Hz); 61.3; 46.2 (t, $^2J_{CF}$ = 25.3 Hz); 36.9 (dd, $^3J_{CF}$ = 4.9 Hz, $^3J_{CF}$ = 3.0 Hz); 35.9 (t, $^2J_{CF}$ = 25.1 Hz); 32.1; 29.7; 29.6; 29.5; 29.4; 22.9; 22.1 (t, $^3J_{CF}$ = 4.2 Hz); 14.2; 13.9. ^{19}F NMR (C_6D_6, 282 MHz), δ ppm: -103.43 (dq, 1F, J_{FF} = 244.3 Hz, J_{FH} = 16.4 Hz); -104,57 (dq, 1F, J_{FF} = 244.3 Hz, J_{FH} = 15.9 Hz). HRMS (ESI) calcd for $C_{21}H_{31}F_2NO_3{}^{79}BrNa$: $[M+Na]^+$: *m/z* 406.21697. Found*: m/z* 406.2168 (0 ppm).

4.4. Synthesis of 3-(1,1-difluorodecyl)-5-(thiophen-2-yl)-3,4-dihydro-2*H*-pyrrole-2-carboxylic acid ethyl ester ((±)-6d)

The reaction was performed from **3d** (250 mg, 0.79 mmol) according to the general procedure. After purification by chromatography on silica gel, pyrroline **6d** was obtained as white crystals (235 mg, 74% yield). Mp: 67-69 °C. $\mathbf{R_f}$ = 0.24 (Et_2O/pentane 2/8). ^{1}H NMR (C_6D_6, 400 MHz), δ ppm: 6.87 (dd, 1H, *J* = 3.6 Hz, *J* = 0.8 Hz); 6.81 (dd, 1H, *J* = 4.9 Hz, *J* = 0.8 Hz); 6.59 (dd, 1H, *J* = 4.9 Hz, *J* = 3.6 Hz); 5.14 (dt, 1H, *J* = 6.4 Hz, $^4J_{HF}$ = 1.4 Hz); 4.08-3.92 (m, 2H); 3.49-3.29 (m, 1H); 2.91 (ddd, 1H, *J* = 17.2 Hz, *J* = 7.1 Hz, $^4J_{HF}$ = 1.5 Hz); 2.80 (ddd, 1H , *J* = 17.2 Hz, *J* = 10.1 Hz, $^4J_{HF}$ = 2.2 Hz); 1.73-1.61 (m, 2H); 1.55-1.42 (m, 2H); 1.32-1.09 (m, 12H); 0.93 (t, 3H, *J* = 7.2 Hz), 0.88 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR (C_6D_6, 75 MHz), δ ppm: 171.8; 168.2; 150.0; 138.7; 130.4; 130.3; 127.3; 124.9 (t, $^1J_{CF}$ = 243,0 Hz); 76.0 (dd, $^3J_{CF}$ = 4.2 Hz, $^3J_{CF}$ = 1.2 Hz); 61.5; 47.0 (t, $^2J_{CF}$ = 25.3 Hz); 37.4 (dd, $^3J_{CF}$ = 4.9 Hz, $^3J_{CF}$ = 1.9 Hz); 36.0 (t, $^2J_{CF}$ = 25.1 Hz); 32.2; 29.8; 29.71; 29.66; 29.59; 23.1; 22.2 (t, $^3J_{CF}$ = 4.2 Hz); 14.3; 14.0. ^{19}F NMR (C_6D_6, 282 MHz), δ ppm: -102.73 (dq, 1F, J_{FF} = 244.3 Hz, J_{FH} = 16.8 Hz); -104,8 (dq, 1F, J_{FF} = 244.3 Hz, J_{FH} = 16.1 Hz). HRMS (ESI) calcd for $C_{21}H_{31}F_2NO_2S^{79}BrNa$: $[M+Na]^+$: m/z 422.19413. Found: m/z 422.1927 (3 ppm).

4.5. Synthesis of 5-(4-bromophenyl)-3-(1,1-difluorodecyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylic acid ethyl ester ((±)-6e)

The reaction was performed from **3e** (380 mg, 0.98 mmol) according to the general procedure. After purification by chromatography on silica gel, pyrroline **6e** was obtained as white crystals (363 mg, 78% yield). Mp: 45-47 °C. $\mathbf{R_f}$ = 0.29 (Et_2O/pentane 1/9). ^{1}H NMR (C_6D_6, 400 MHz), δ ppm: 7.40 (d, 1H, *J* = 8.6 Hz, *J* = 1.9 Hz); 7.17 (dd, 1H, *J* = 8.6 Hz, *J* = 1.6 Hz); 5.16 (dt, 1H, *J* = 6.5 Hz, $^4J_{HF}$ = 1.7 Hz); 4.09-3.95 (m, 2H); 3.48-3.21 (m, 1H); 2.78 (ddd, 1H, *J* = 17.4 Hz, *J* = 7.3 Hz, $^4J_{HF}$ = 1.5 Hz); 2.65 (ddd, 1H , *J* = 17.4 Hz, *J* = 10.1 Hz, $^4J_{HF}$ = 2.3 Hz); 1.76-1.64 (m, 2H); 1.57-1.45 (m, 2H); 1.34-1.14 (m, 12H); 0.91 (t, 3H, *J* = 7.1 Hz), 0.86 (t, 3H, *J* = 6.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 173.2; 171.7; 132.1; 131.8 (2C); 129.6 (2C); 125.9; 124.4 (t, $^1J_{CF}$ = 243.2 Hz); 75.6 (dd, $^3J_{CF}$ = 4.1 Hz, $^3J_{CF}$ = 2.6 Hz); 61.8; 46.2 (t, $^2J_{CF}$ = 25.2 Hz); 36.7 (dd, $^3J_{CF}$ = 5.1 Hz, $^3J_{CF}$ = 2.6 Hz); 35.7 (t, $^2J_{CF}$ = 24.9 Hz); 31.9; 29.4; 29.39; 29.34; 29.28; 22.7; 21.9 (t, $^3J_{CF}$ = 4.1 Hz); 14.2; 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -103.48 (dq, 1F, J_{FF} = 244.5 Hz , J_{FH} = 13.6 Hz); -105.73 (dq, 1F, J_{FF} = 244.5 Hz, J_{FH} = 15.6 Hz). HRMS (ESI) calcd for $C_{23}H_{32}F_2NO_2Br^{79}BrNa$: $[M+Na]^+$: m/z 494.14822. Found: *m/z* 494.1483 (0 ppm).

5. General procedure for the Suzuki–Miyaura reaction

A solution of brominated derivates **4e** or **6e** (1 equiv), phenylboronic acid (2 equiv), palladium dichlorobistriphenylphosphine (5 mol %) and potassium carbonate (2 equiv) in a 5/1 mixture of dioxane and water (1 ml per 0.1 mmol) was stirred at 90 °C for 24 h. After addition of $MgSO_4$ and filtration, the residues were washed with ether and the solution concentated in vacuo. The crude residue was then purified by flash chromatography on silica gel.

5.1. Synthesis of 3-biphenyl-4-yl-5(1,1-difluorodecyl)-1-methyl-4,5-dihydro-1*H*-pyrazole ((±)-7e)

The reaction was performed from **4e** (78 mg, 0.19 mmol) according to the general procedure. After purification by chromatography on silica gel, the product **7e** was isolated as a sticky syrup (64 mg, 82% yield). $\mathbf{R_f}$ = 0.31 (Et_2O/pentane 5/95). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.72-7.67(m, 2H); 7.64-7.57(m, 4H); 7.49-7.34 (m, 3H); 3.54 (dddd, 1H, J = 12.0 Hz, J = 11.7 Hz, $^3J_{HF}$ = 11.7 Hz, $^3J_{HF}$ = 6.6 Hz); 3.29 (dd, 1H, J = 16.9 Hz, J = 11.7 Hz); 3.02 (dd, 1H, J = 16.9 Hz, J = 12.0 Hz); 3.00 (s, 3H,) ; 2.09-1.74 (m, 2H); 1.63-1.51 (m, 2H); 1.43-1.18 (m, 12H); 0.87 (t, 3H, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 149.3; 141.7; 140.3; 130.8; 128.82 (2C); 127.6; 127.2 (2C); 127.0 (2C); 126.4 (2C); 124.5 (t, $^1J_{CF}$ = 242.8 Hz); 71.1 (dd, $^2J_{CF}$ = 28.4 Hz, $^2J_{CF}$ = 27.4 Hz); 44.0; 35.8 (dd, $^3J_{CF}$ = 5.1 Hz, $^3J_{CF}$ = 2.1 Hz); 33.0 (t, $^2J_{CF}$ = 24.4 Hz); 31.8; 29.43 (2C); 29.40; 29.3; 22.7; 21.1 (t, $^3J_{CF}$ = 4.1 Hz); 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -102.13 (ddt, J_{FF} = 250.5 Hz, J_{FH} = 26.8 Hz, 11.7 Hz); -104.33 (dddd, J_{FF} = 250.5 Hz, J_{FH} = 27.2 Hz, 11.5 Hz, 6.6 Hz). HRMS (ESI) calcd for $C_{26}H_{34}F_2N_2{}^{79}BrNa$: $[M+Na]^+$: 435.25878. m/z Found: 435.2584 (1 ppm).

5.2. Synthesis of 5-biphenyl-4-yl-3-(1,1-difluorodecyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylic acid ethyl ester (±)-10e

The reaction was performed from **6e** (67 mg, 0.14 mmol) according to the general procedure. After purification by chromatography on silica gel, the product **10e** was isolated as a sticky syrup (52 mg, 78% yield). $\mathbf{R_f}$ = 0.35 (Et_2O/pentane 2/8). ^{1}H NMR (C_6D_6, 300 MHz), δ ppm: 7.88-7.79 (m, 2H); 7.43-7.34 (m, 4H); 7.24-7.16 (m, 3H); 5.28 (dt, 1H, J = 6.4 Hz, $^4J_{HF}$ = 1.5 Hz); 4.06-3.92 (m, 2H); 3.55-3.32 (m, 1H); 3.01 (ddd, 1H, J = 17.4 Hz, J = 7.3 Hz, $^4J_{HF}$ = 1.6

Hz); 2.88 (ddd, 1H , J = 17.4 Hz, J = 10.1 Hz, $^{4}J_{HF}$ = 2.3 Hz); 1.84-1.63 (m, 2H); 1.61-1.48 (m, 2H); 1.36-1.12 (m, 12H); 0.99 (t, 3H, J = 7.1 Hz), 0.92 (t, 3H, J = 7.0 Hz). ^{13}C NMR (C_6D_6, 75 MHz), δ ppm: 173.3; 172.1; 144.0; 140.7; 132.9; 129.2 (2C); 129.1(2C); 127.3 (2C); 127,2 (2C); 125.1 (t, $^{1}J_{CF}$ = 242,9 Hz); 76.4 (dd, $^{3}J_{CF}$ = 3.7 Hz, $^{3}J_{CF}$ = 2.7 Hz); 61.5; 46.8 (t, $^{2}J_{CF}$ = 24.8 Hz); 36.9 (dd, ^{3}J = 4.6 Hz, $^{3}J_{CF}$ = 2.7 Hz); 35.1 (t, $^{2}J_{CF}$ = 25.1 Hz); 32.2; 29.84; 29.75; 29.68; 29.65; 23.1; 22.3 (t, $^{3}J_{CF}$ = 4.3 Hz); 14.3; 14.1. ^{19}F NMR (C_6D_6, 282 MHz), δ ppm: -102.9 (dq, 1F, J_{FF} = 243.8 Hz, J_{FH} = 16.7 Hz); -104.8 (dq, 1F, J_{FF} = 243.8 Hz, J_{FH} = 16.2 Hz). HRMS (ESI) calcd for $C_{29}H_{37}F_2NO_2{}^{79}BrNa$: $[M+Na]^+$: m/z 492.26901. Found: *m/z* 492.2682 (2 ppm).

6. General procedure for the Heck reaction

Et_3N (1 ml per 0.1 mmol) was first degassed by bubbling argon for 10 min. Then were added successively: bromo-compound **4e** or **6e** (1 equiv), palladium acetate (10 mol %), tri-*o*-tolylphosphine (0.2 equiv) and methyl acrylate (3.2 equiv). The reaction mixture was stirred under argon at 100 °C for 12 h. After addition of ether, the reaction mixture was washed with water and the aqueous phase was extracted with ether. The combined organic phases were dried ($MgSO_4$), filtered and concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel.

6.1. Synthesis of 3-{4-[5-(1,1-difluorodecyl)-1-methyl-4,5-dihydro-1*H*-pyrazol-3-yl]-phenyl}-acrylic acid methyl ester ((±)-8e)

The reaction was performed from **4e** (111 mg, 0.27 mmol) according to the general procedure. After purification by chromatography on silica gel, the product **8e** was isolated as a sticky syrup (81 mg, 72% yield). $\mathbf{R}_f$ = 0.30 (Et_2O/pentane 1/9). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.67 (d, 1H, J = 16.1 Hz); 7.61 (d, 2H, J = 8.4 Hz); 7.50 (d, 2H, J = 8.4 Hz); 6.45 (d, 1H, J = 16.1 Hz); 3.80 (s, 3H); 3.58 (dddd, 1H, J = 12.0 Hz, $^{3}J_{HF}$ = 11.9 Hz, J = 11.7 Hz, $^{3}J_{HF}$ = 6.5 Hz); 3.33 (dd, 1H, J = 16.8 Hz, J = 11.7 Hz); 3.02 (dd, 1H, J = 16.8 Hz, J = 12.0 Hz); 3.01 (s, 3H,) ; 2.08-1.76 (m, 2H); 1.63-1.50 (m, 2H); 1.39-1.17 (m, 12H); 0.88 (t, 3H, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 167.3; 148.1; 144.0; 134.6; 133.9; 128.2 (2C); 126.2 (2C); 124.5 (t, $^{1}J_{CF}$ = 242.6 Hz); 118.0; 71.2 (t, $^{2}J_{CF}$ = 28.8 Hz); 51.7; 43.7; 35.5 (dd, $^{3}J_{CF}$ = 5.0 Hz, $^{3}J_{CF}$ = 2.3 Hz); 33.0 (t, $^{2}J_{CF}$ = 24.3 Hz); 31.8; 29.41 (2C); 29.37; 29.2; 22.6; 21.1 (t, $^{3}J_{CF}$ = 4.0 Hz); 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -102.22 (ddt, J_{FF} = 250.5 Hz, J_{FH} =

27.0 Hz, 11.9 Hz); -104.34 (dddd, J_{FF} = 250.9 Hz, J_{FH} = 26.7 Hz, 12.2 Hz, 6.5 Hz). HRMS (ESI) calcd for $C_{24}H_{34}F_2N_2O_2Na$: $[M+Na]^+$: m/z 443.24860. Found: m/z 443.2787 (0 ppm).

6.2. Synthesis of 3-(1,1-difluorodecyl)-5-[4-(2-methoxycarbonyl-vinyl)-phenyl]-3,4-dihydro-2*H*-pyrrole-2-carboxylic acid ethyl ester ((±)-11e)

The reaction was performed from **6e** (124 mg, 0.26 mmol) according to the general procedure. After purification by chromatography on silica gel, the product **11e** was isolated as a sticky syrup (80 mg, 64% yield). $\mathbf{R}_f$ = 0.14 (Et_2O/pentane 2/8). ^{1}H NMR (C_6D_6, 300 MHz), δ ppm: 7.70 (d, 1H, *J* = 16.1 Hz); 7.62 (d, 2H, *J* = 8.3 Hz); 7.00 (d, 2H, *J* = 8.3 Hz); 6.37 (d, 1H, *J* = 16.1 Hz); 5.23 (dt, 1H, *J* = 6.4 Hz, $^4J_{HF}$ = 1.8 Hz); 4.12-3.94 (m, 2H); 3.48 (s, H); 3.47-3.29 (m, 1H); 2.83 (ddd, 1H, *J* = 17.4 Hz, *J* = 7.3 Hz, $^4J_{HF}$ = 1.6 Hz); 2.65 (ddd, 1H , *J* = 17.4 Hz, *J* = 10.1 Hz, $^4J_{HF}$ = 2.3 Hz); 1.80-1.62 (m, 2H); 1.60-1.45 (m, 2H); 1.31-1.13 (m, 12H); 0.98 (t, 3H, *J* = 7.1 Hz), 0.92 (t, 3H, *J* = 6.5 Hz). ^{13}C NMR (C_6D_6, 75 MHz), δ ppm: 173.0; 171.9; 166.7; 143.8; 137.1; 135.1; 128.8 (2C); 128.2; 124.4 (t, $^1J_{CF}$ = 242.7 Hz); 119.6; 75.4 (dd, $^3J_{CF}$ = 4.2 Hz, $^3J_{CF}$ = 2.7 Hz); 61.6; 51.3; 46.7 (t, $^2J_{CF}$ = 25.4 Hz); 36.8 (dd, $^3J_{CF}$ = 5.0 Hz, $^3J_{CF}$ = 2.7 Hz); 36.1 (t, $^2J_{CF}$ = 25.0 Hz); 32.2; 29.8; 29.73; 29.67; 29.6; 23.1; 22.3 (t, $^3J_{CF}$ = 4.0 Hz); 14.3; 14.1. ^{19}F NMR (C_6D_6, 282 MHz), δ ppm: -102.90 (dq, 1F, J_{FF} = 244.3 Hz, J_{FH} = 16.2 Hz); -105.0 (dq, 1F, J_{FF} = 244.3 Hz, J_{FH} = 16.8 Hz). HRMS (ESI) calcd for $C_{27}H_{37}F_2NO_4Na$: $[M+Na]^+$: m/z 500.25883. Found: *m/z* 500.2590 (0 ppm).

7. General procedure for the Sonogashira reaction

Dioxane (1 ml per 0.1 mmol) was first degassed by bubbling argon. Then were added successively: bromo-compound (**4e** or **6e**) (1 equiv), palladium dichlorobistriphenylphosphine (5 mol %), copper iodide (2.5 mol %), potassium carbonate (2 equiv) and ethynylbenzene (1 equiv). The reaction mixture was stirred under argon at 90 °C for 2 d. After addition of ether the reaction mixture was washed with water, the aqueous phase was extracted with ether. The combined organic phases were dried ($MgSO_4$), filtered and concentrated in vacuo. The crude residue was then purified by flash chromatography on silica gel.

7.1. Synthesis of 5-(1,1-difluorodecyl)-1-methyl-3-(4-phenylethynyl-phenyl)-4,5-dihydro-1*H*-pyrazole ((±)-9e)

The reaction was performed from **4e** (100 mg, 0.26 mmol) according to the general procedure. After purification by chromatography on silica gel, the product **9e** was isolated as

a sticky syrup (78 mg, 74% yield). $\mathbf{R}_f$ = 0.29 (Et_2O/pentane 5/95). ^{1}H NMR ($CDCl_3$, 300 MHz), δ ppm: 7.67-7.53 (m, 6H); 7.42-7.36 (m, 3H); 3.61 (dddd, 1H, J = 12.0 Hz, $^3J_{HF}$ = 11.8 Hz; J = 11.7 Hz, $^3J_{HF}$ = 6.4 Hz); 3.29 (dd, 1H, J = 16.8 Hz, J = 11.7 Hz); 3.00 (dd, 1H, J = 16.8 Hz, J = 12.0 Hz); 3.04 (s, 3H,) ; 2.15-1.81 (m, 2H); 1.63-1.58 (m, 2H); 1.41-1.24 (m, 12H); 0.91 (t, 3H, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 148.4; 131.9; 131.7 (2C); 131.6 (2C); 128.4 (2C); 125,9 (2C); 125.3; 124.6 (t, $^1J_{CF}$ = 242.7 Hz); 123.6; 123.1; 90.9; 89.3; 71.3 (dd, $^2J_{CF}$ = 28.6 Hz, J_{CF} = 27.4 Hz); 43.8; 35.5 (dd, $^3J_{CF}$ = 5.1 Hz, J_{CF} = 2.3 Hz); 33.0 (t, $^2J_{CF}$ = 24.5 Hz); 31.9; 29.43 (2C); 29.40; 29.3; 22.7; 21.1 (t, $^3J_{CF}$ = 4.1 Hz); 14.1. ^{19}F NMR ($CDCl_3$, 282 MHz), δ ppm: -102.23 (ddt, J_{FF} = 250.8Hz, J_{FH} = 26.9 Hz, 11.8 Hz); -104.38 (dddd, J_{FF} = 250.8 Hz, J_{FH} = 27.3 Hz, 11.5 Hz, 6.4 Hz). HRMS (ESI) calcd for $C_{28}H_{34}F_2N_2{}^{79}BrNa$: $[M+Na]^+$: m/z 459.2583. Found: m/z 459.25877 (0 ppm).

7.2. Synthesis of 3-(1,1-difluorodecyl)-5-(4-phenylethynyl-phenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylic acid ethyl ester ((±)-12e)

The reaction was performed from **6e** (100 mg, 0.21 mmol) according to the general procedure. After purification by chromatography on silica gel, the product **12e** was isolated as a sticky syrup (73 mg, 70% yield). $\mathbf{R}_f$ = 0.21 (Et_2O/pentane 1/9). ^{1}H NMR (C_6D_6, 400 MHz), δ ppm: 7.69-7.61 (m, 2H); 7.55-7.49 (m, 2H); 7.46-7.40 (2H); 7.1-6.8 (3H); 5.22 (dt, 1H, J = 6.5 Hz, $^4J_{HF}$ = 1.6 Hz); 4.13-3.97 (m, 2H); 3.49-3.32 (m, 1H); 2.85 (ddd, 1H, J = 17.4 Hz, J = 7.4 Hz, $^4J_{HF}$ = 1.6 Hz); 2.71 (ddd, 1H , J = 17.4 Hz, J = 10.2 Hz, $^4J_{HF}$ = 2.3Hz); 1.77-1.64 (m, 2H); 1.57-1.47 (m, 2H); 1.29-1.15 (m, 12H); 0.99 (t, 3H, J = 7.1 Hz), 0.92 (t, 3H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz), δ ppm: 172.7; 171.6; 133.3; 131.7 (2C); 131.6 (2C); 128.4 (2C); 128.3 (2C); 126.1; 124.7 (t, $^1J_{CF}$ = 242,9 Hz); 92.0; 89.6; 76.1; 61.3; 46.2 (t, $^2J_{CF}$ = 25.1 Hz); 36.5 (dd, ^3J = 5.0 Hz, $^3J_{CF}$ = 2.0 Hz); 35.9 (t, $^2J_{CF}$ = 25.1 Hz); 32.0; 29.6; 29.5; 29.4; 22. 8; 21.0 (t, $^3J_{CF}$ = 3.9 Hz); 14.1; 13.8. ^{19}F NMR (C_6D_6, 282 MHz), δ ppm: -102.91 (dq, 1F, J_{FF} = 243.9 Hz, J_{FH} = 16.5 Hz); -104.75 (dq, 1F, J_{FF} = 243.9 Hz, J_{FH} = 16.1 Hz). HRMS (ESI) calcd for $C_{31}H_{37}F_2NO_2{}^{79}BrNa$: $[M+Na]^+$: m/z 516.26901 . Found: m/z 516.2689 (0 ppm).

8. Analysis of $^{19}F/^{1}H$ HOESY 2D-NMR spectrum of (±)-6a

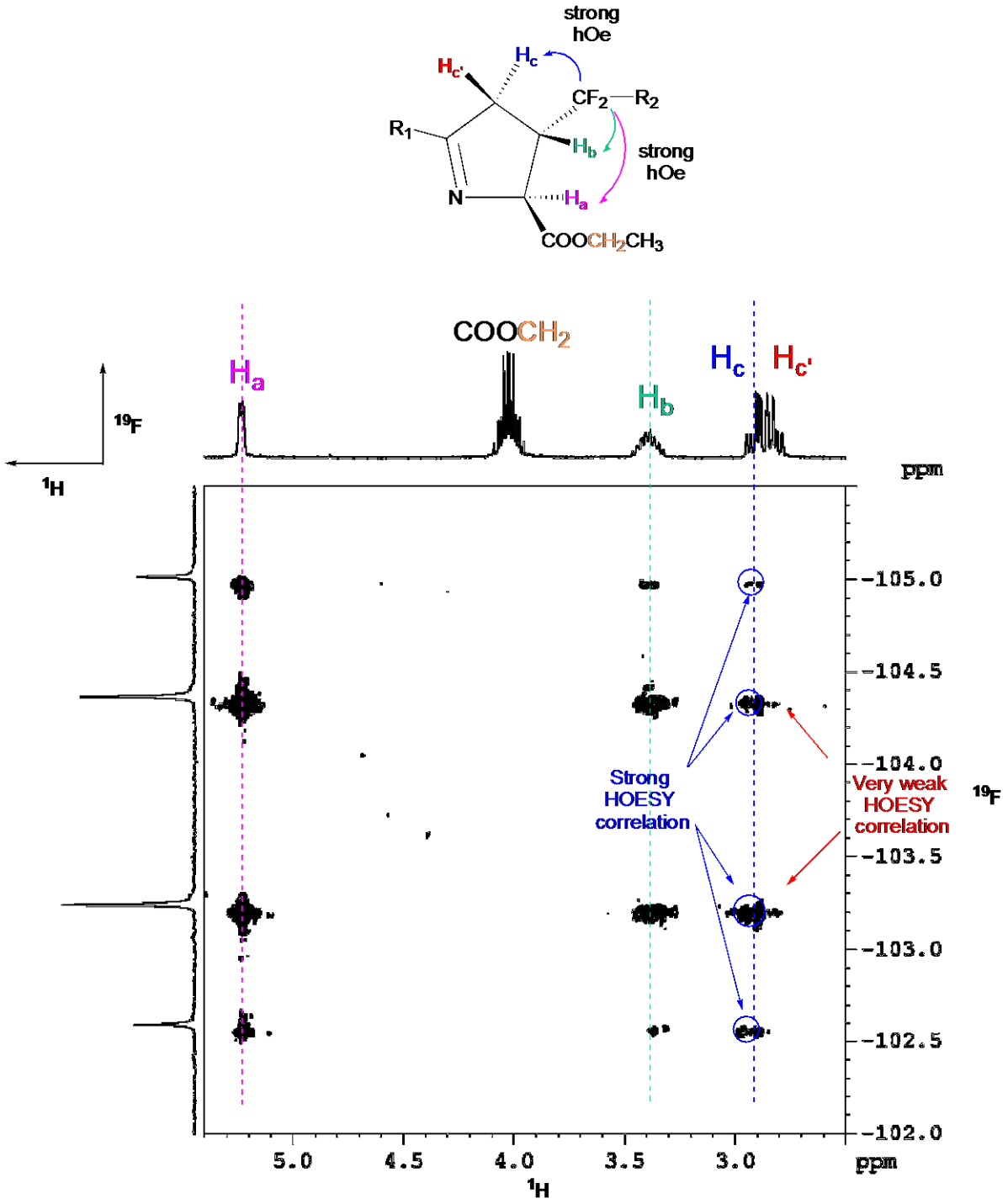
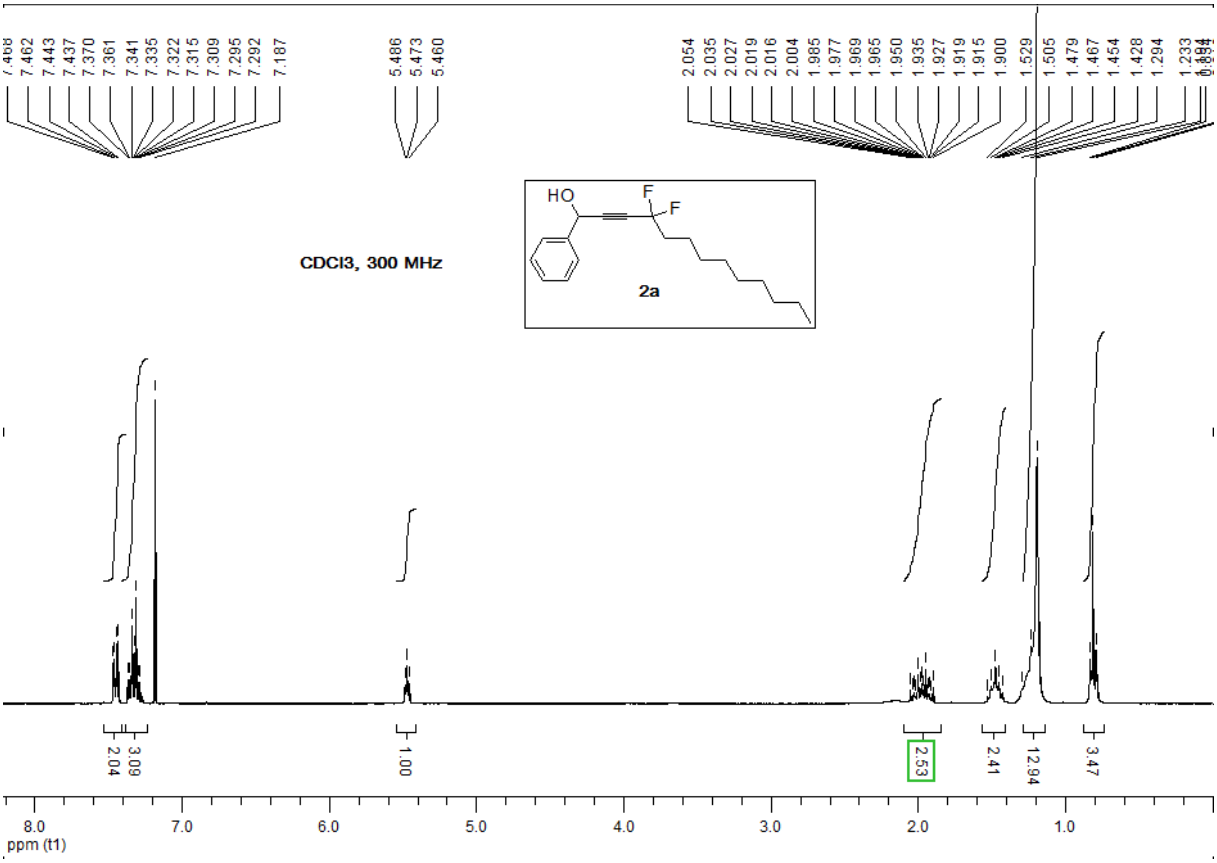
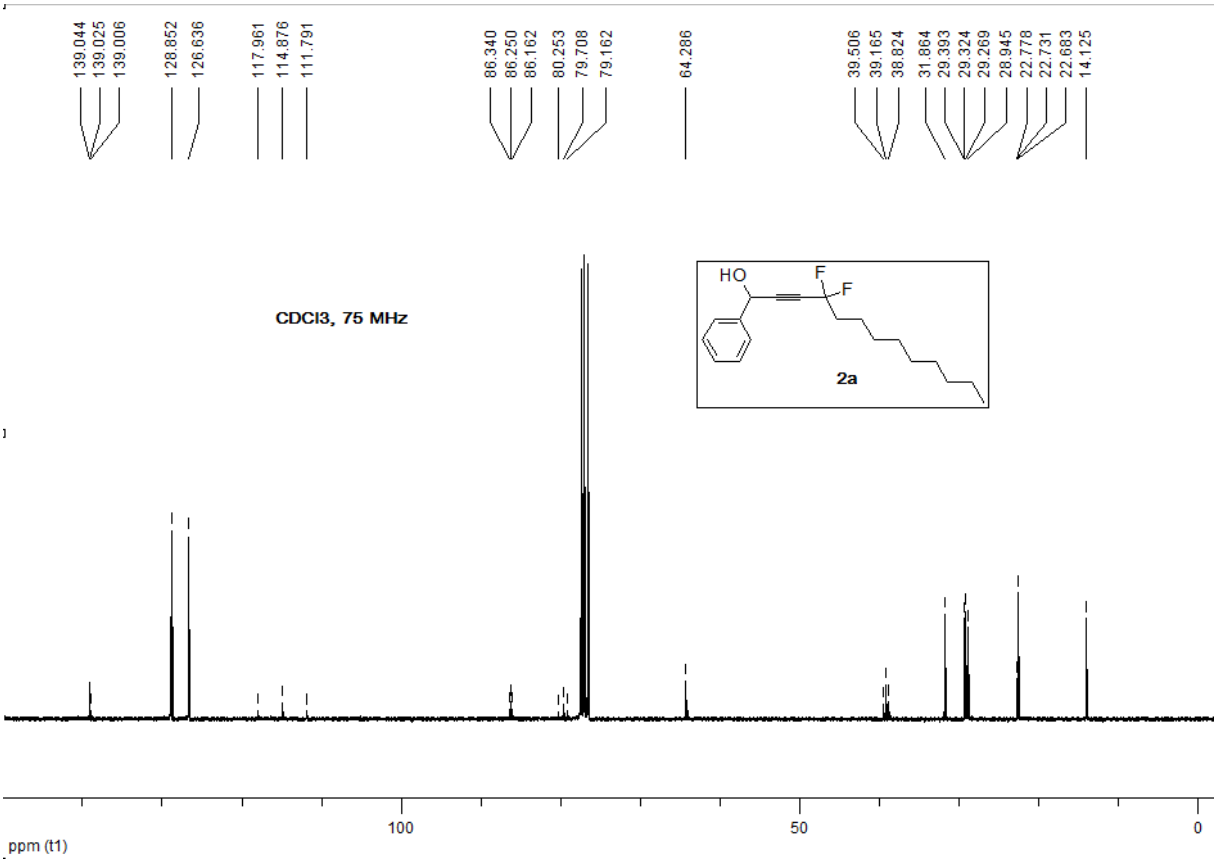
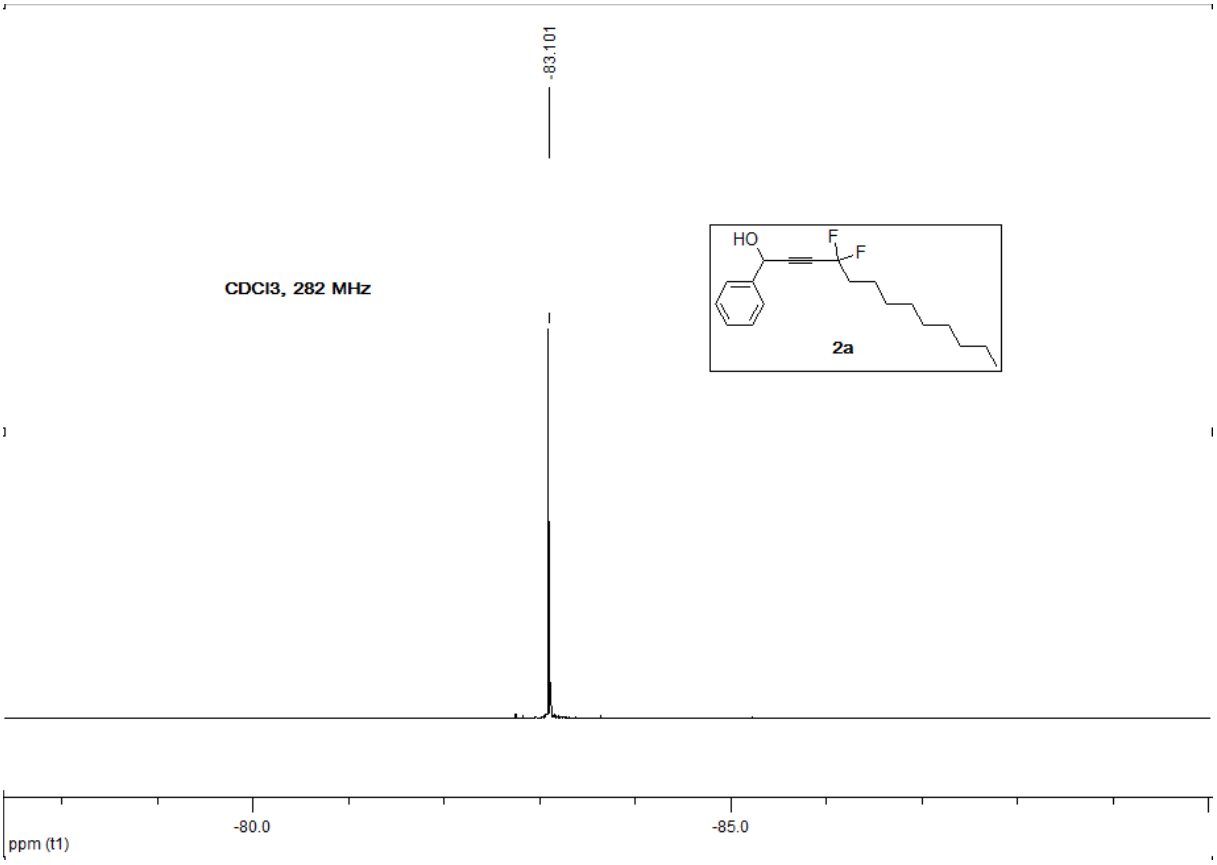


Figure S-1: Pulse gradient $^{19}F/^{1}H$ HOESY 2D-NMR spectrum of **(±)-6a** in C_6D_6 recorded at 300 K and 9.4 T (Bruker avance I NMR spectrometer equipped with a QXO probe, ($\nu(^{19}F)$ = 376,5 MHz/$\nu(^{1}H)$ = 400.1 MHz) and 300 K. The map was recorded using a 2D matrix of 4096(t_1) × 256(t_2) data points, and then zero-filled to 4096(t_1) × 1024(t_2) data points. The mixing time was set up at 800 ms. 16 scans were added per t_1 increment. Exponential filtering (LB = 5 Hz) was applied in both spectral dimensions. The F_1 and F_2 projections displayed correspond to ^{19}F-{^{1}H} and ^{1}H 1D spectra, respectively.

9. Library of ^{1}H, ^{13}C-{^{1}H},^{19}F-{^{1}H} and ^{19}F 1D-NMR spectra



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HO
F
F
2a
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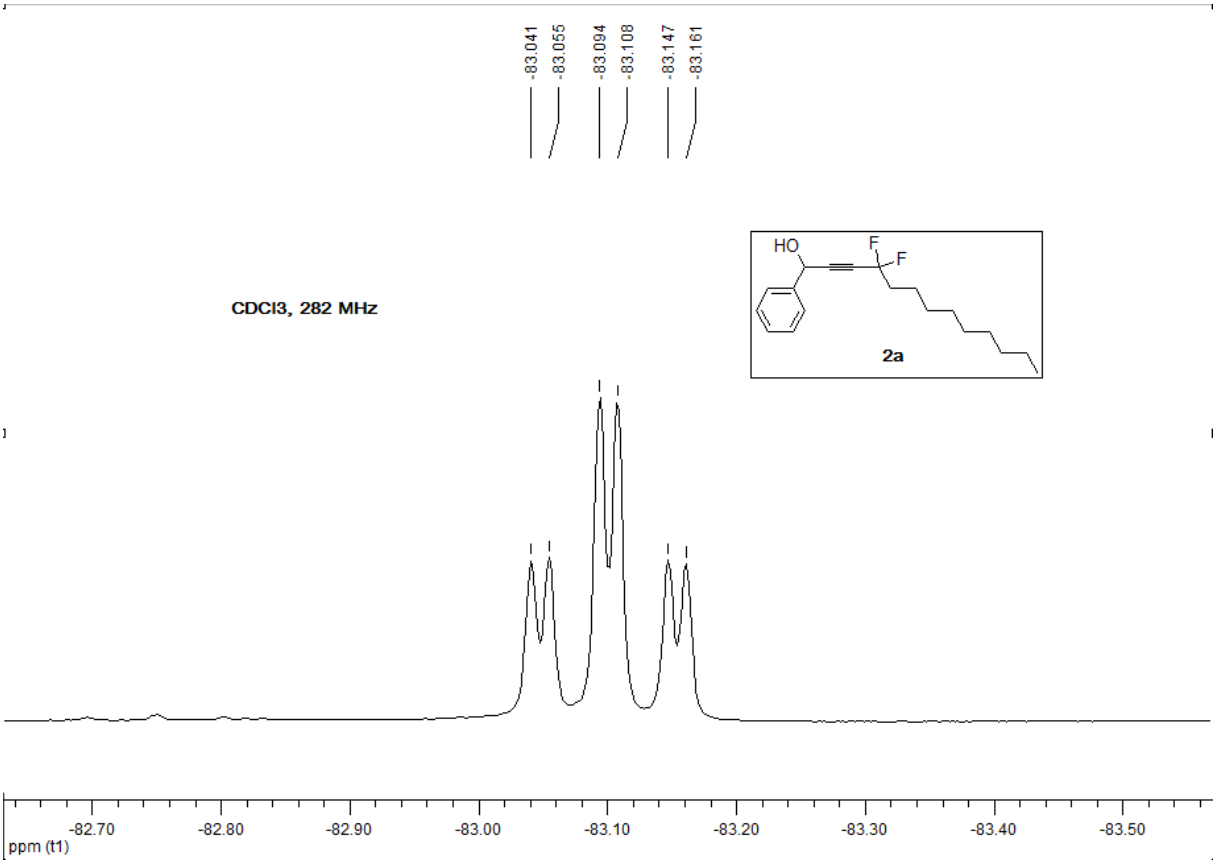
-85.0
ppm (t1)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-83.108
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-83.161
CDCl3, 282 MHz
HO
F
F
2a
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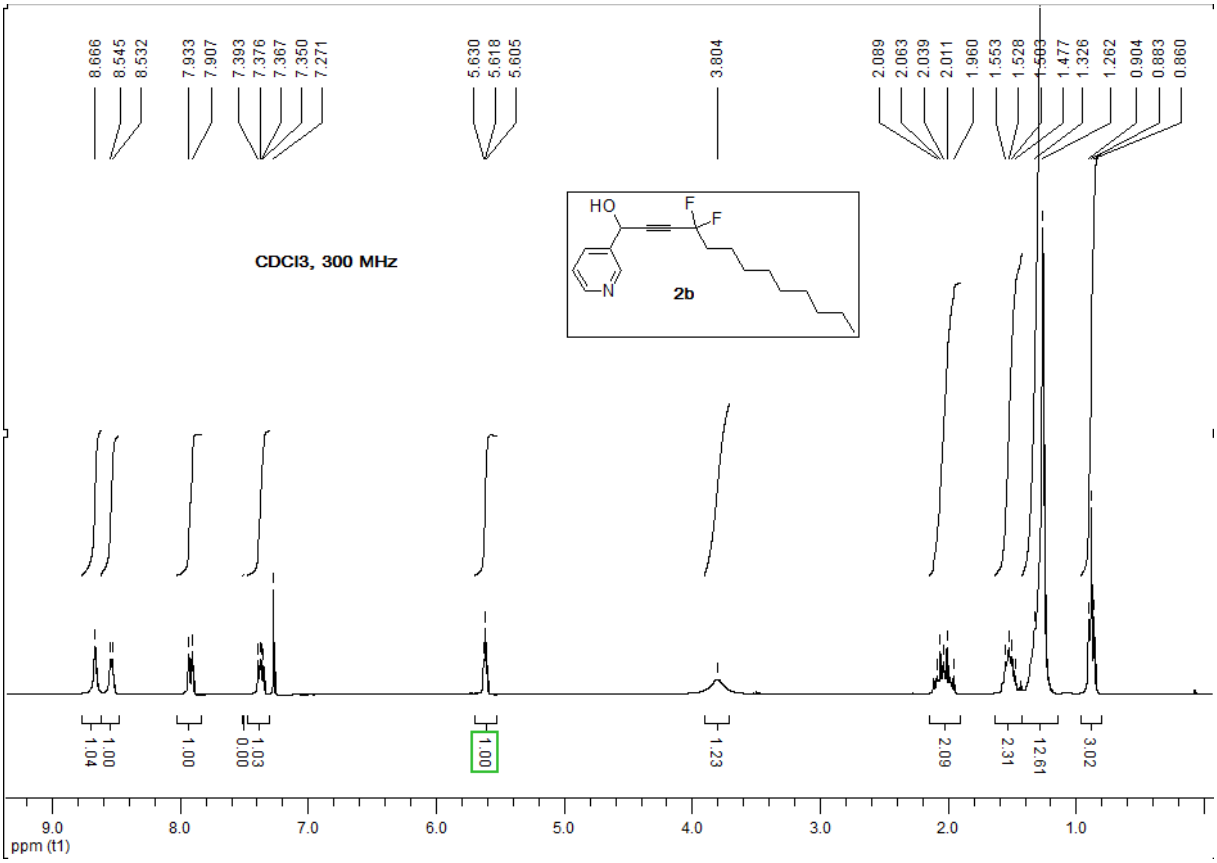
-82.80
-82.90
-83.00
-83.10
-83.20
-83.30
-83.40
-83.50
ppm (t1)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7.367
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7.271
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3.804
2.089
2.063
2.039
2.011
1.960
1.553
1.528
1.503
1.477
1.326
1.262
0.904
0.883
0.860
CDCl3, 300 MHz
HO
F
F
N
2b
1.04
1.00
1.00
1.03
0.00
1.00
1.23
2.09
2.31
12.61
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6.0
5.0
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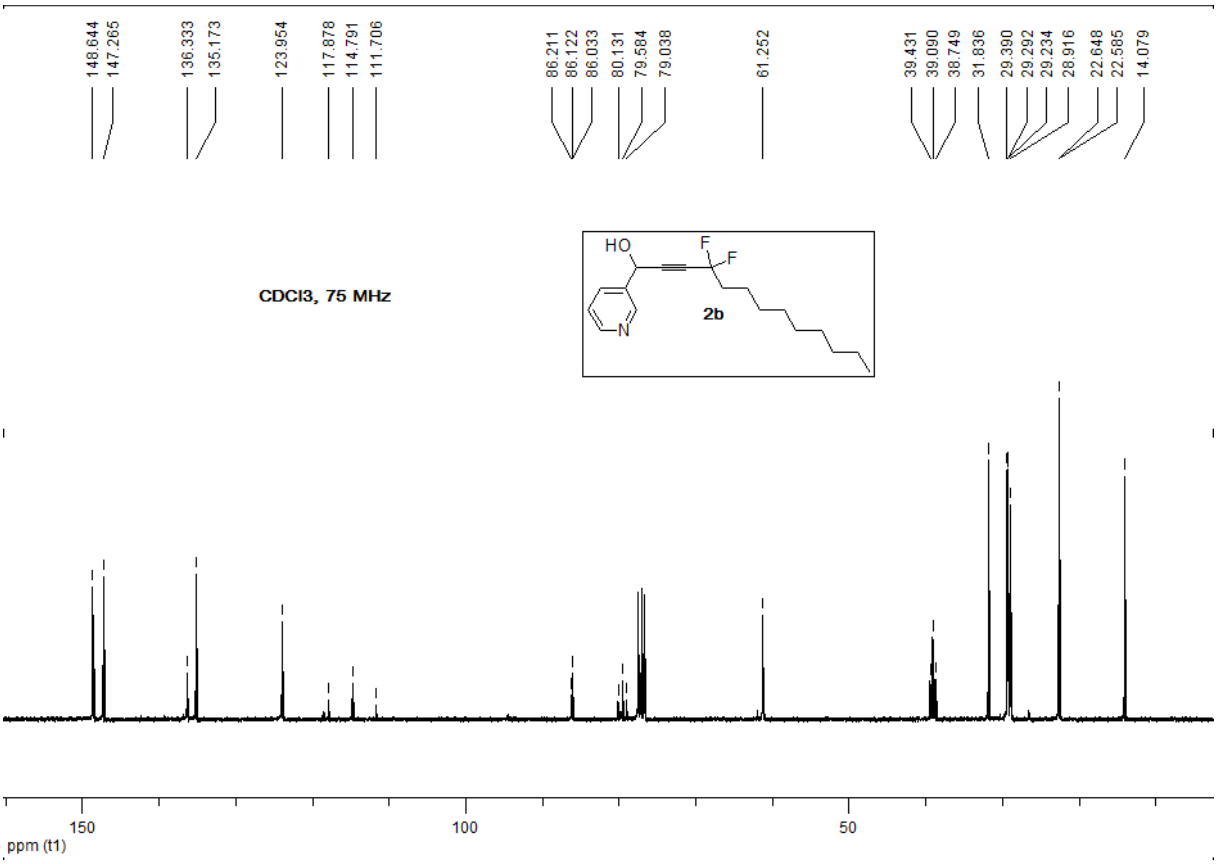
3.0
2.0
1.0
ppm (t1)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61.252
39.431
39.090
38.749
31.836
29.390
29.292
29.234
28.916
22.648
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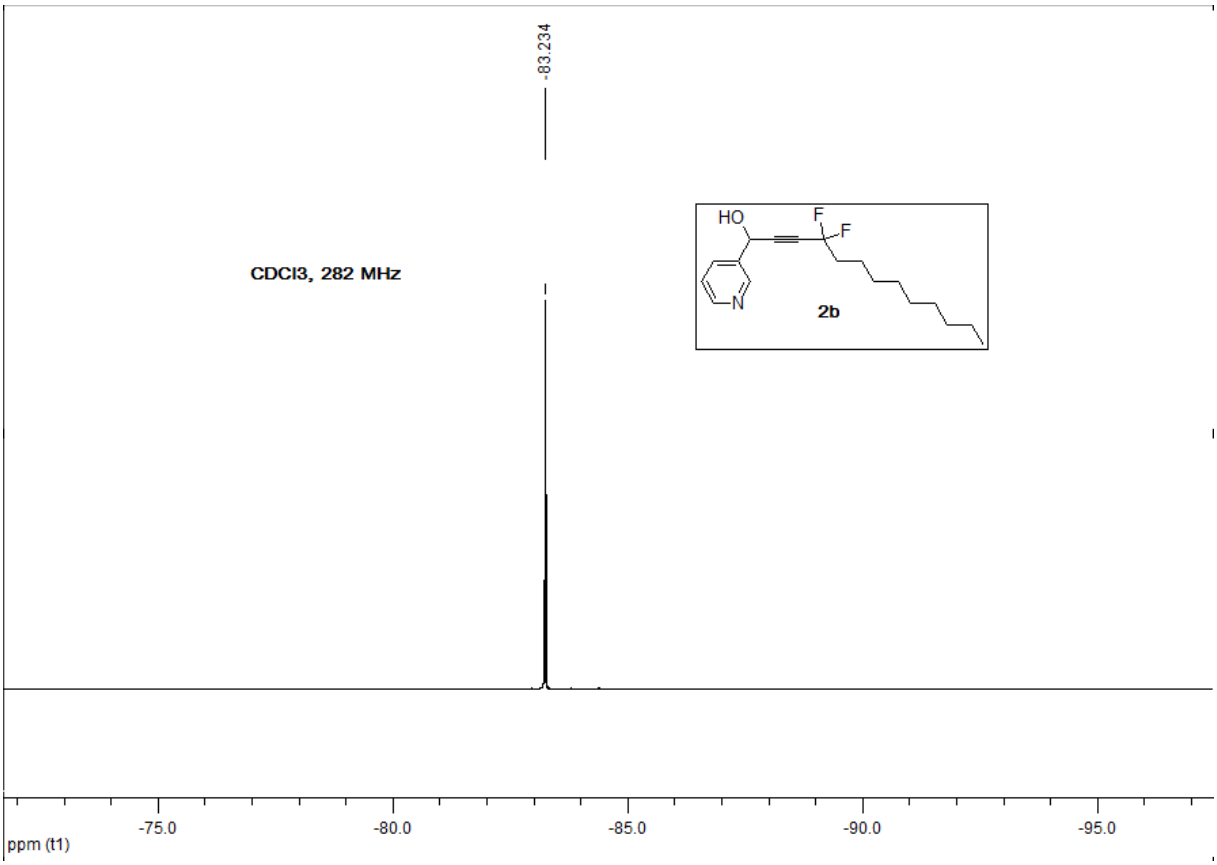
HO
F
F
N
2b
150
100
50
ppm (t1)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N
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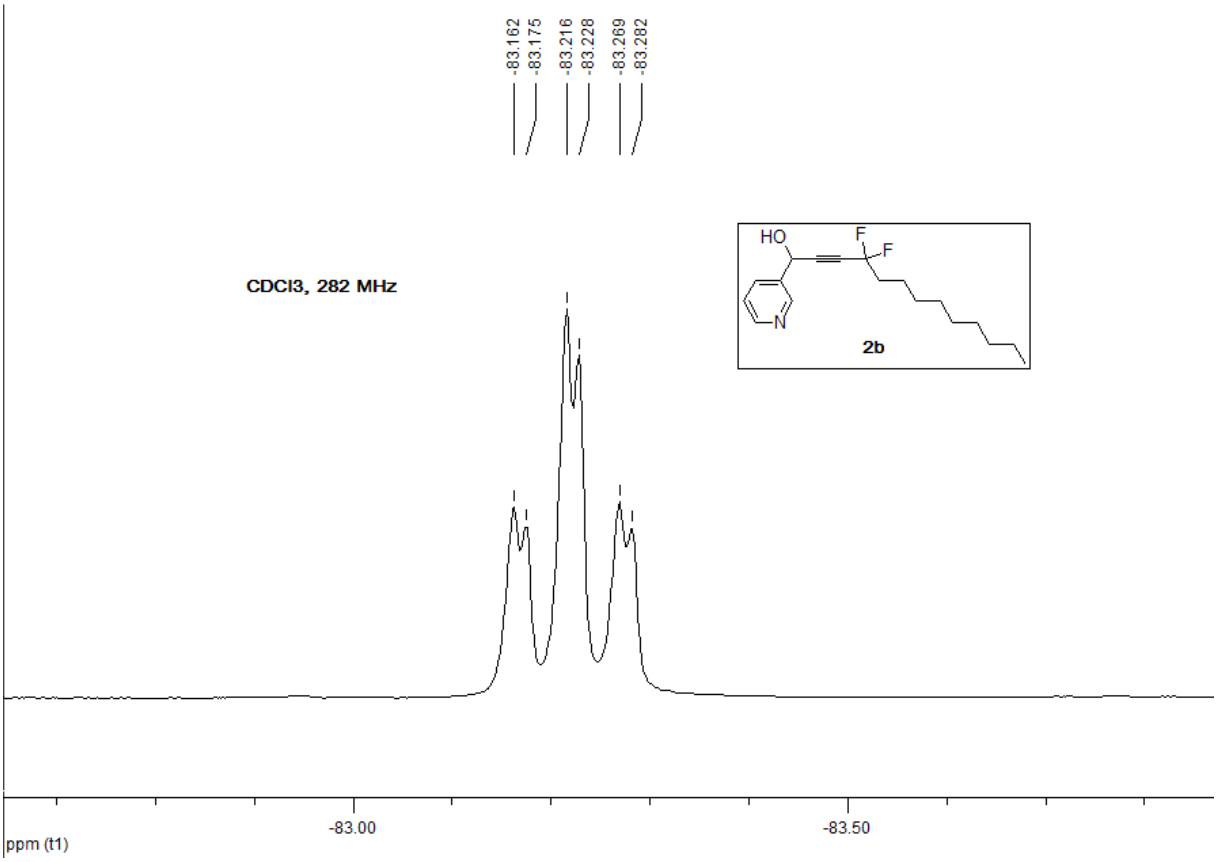
ppm (t1)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N
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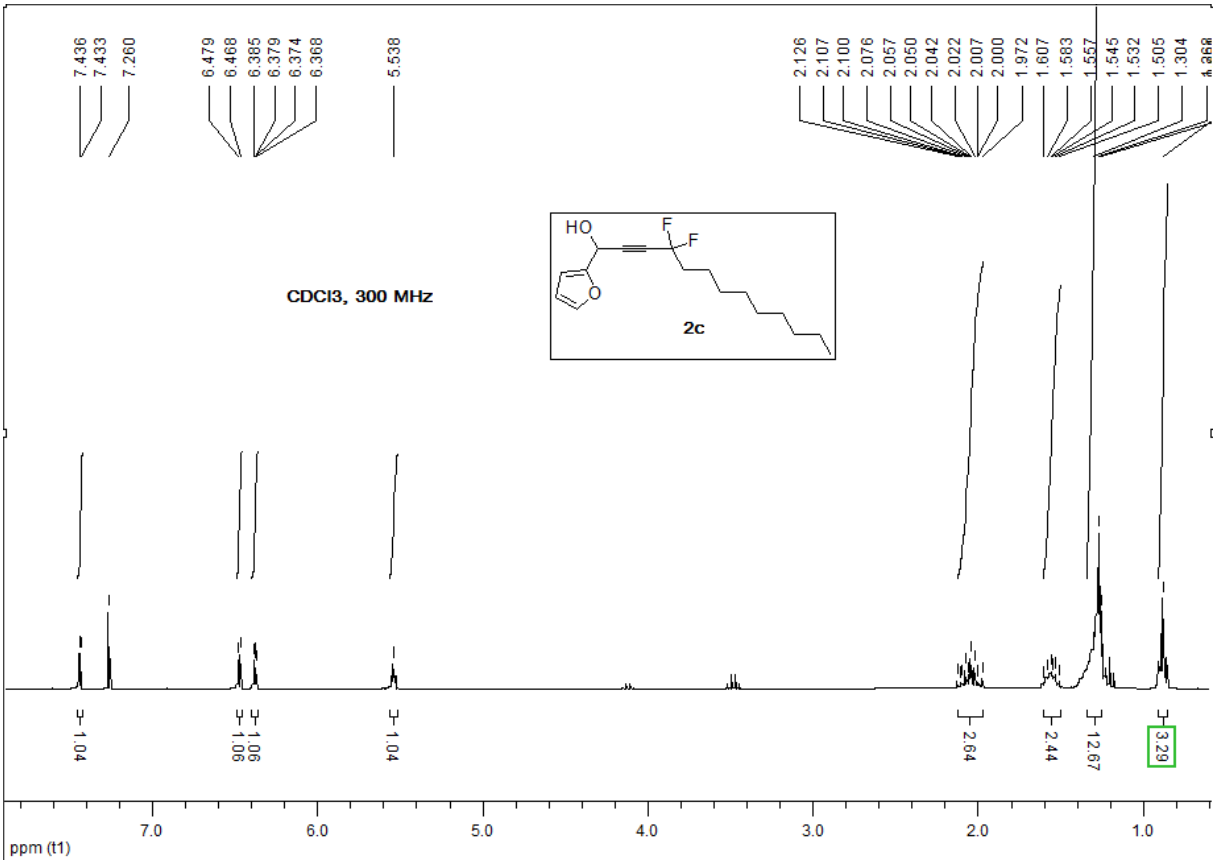
ppm (t1)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2.022
2.007
2.000
1.972
1.607
1.583
1.557
1.545
1.532
1.505
1.304
CDCl3, 300 MHz
HO
F
F
O
2c
1.04
1.06
1.06
1.04
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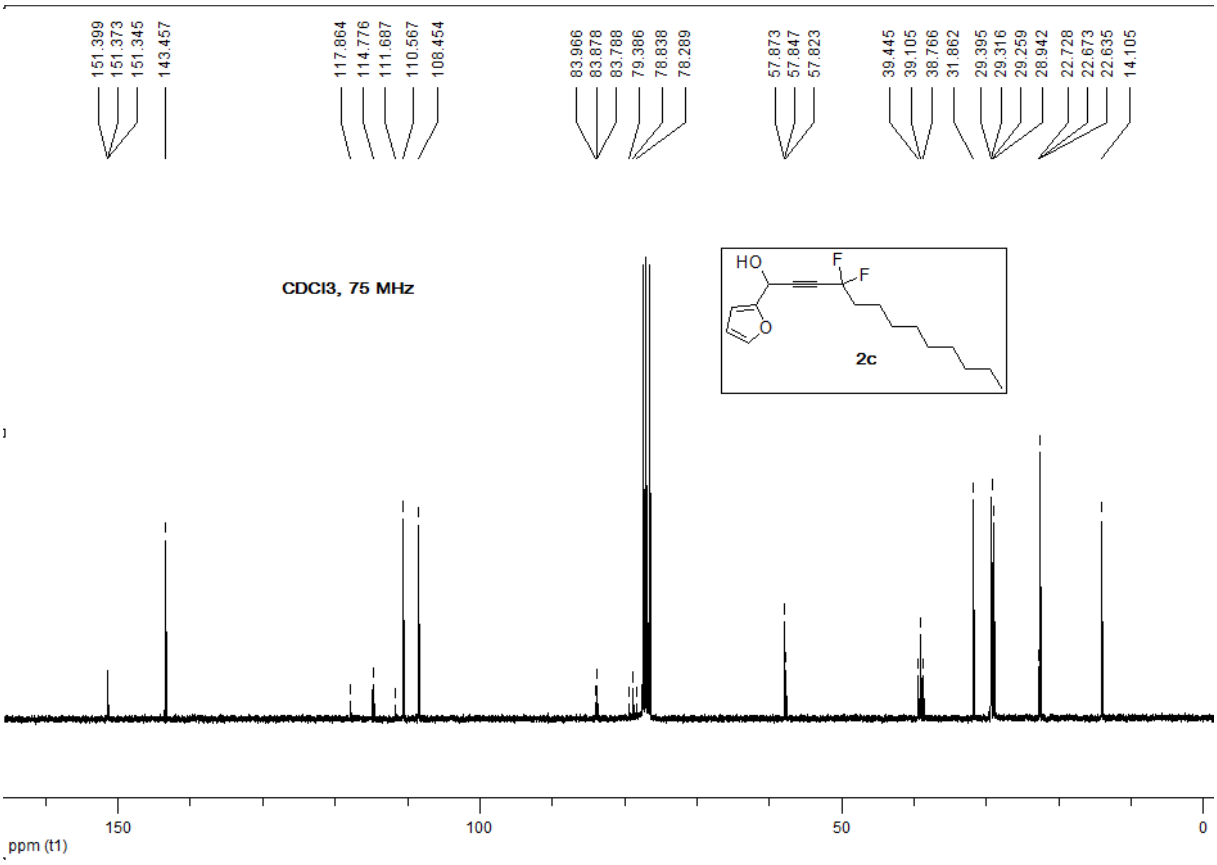
3.0
2.0
1.0
ppm (t1)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57.847
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39.445
39.105
38.766
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29.395
29.316
29.259
28.942
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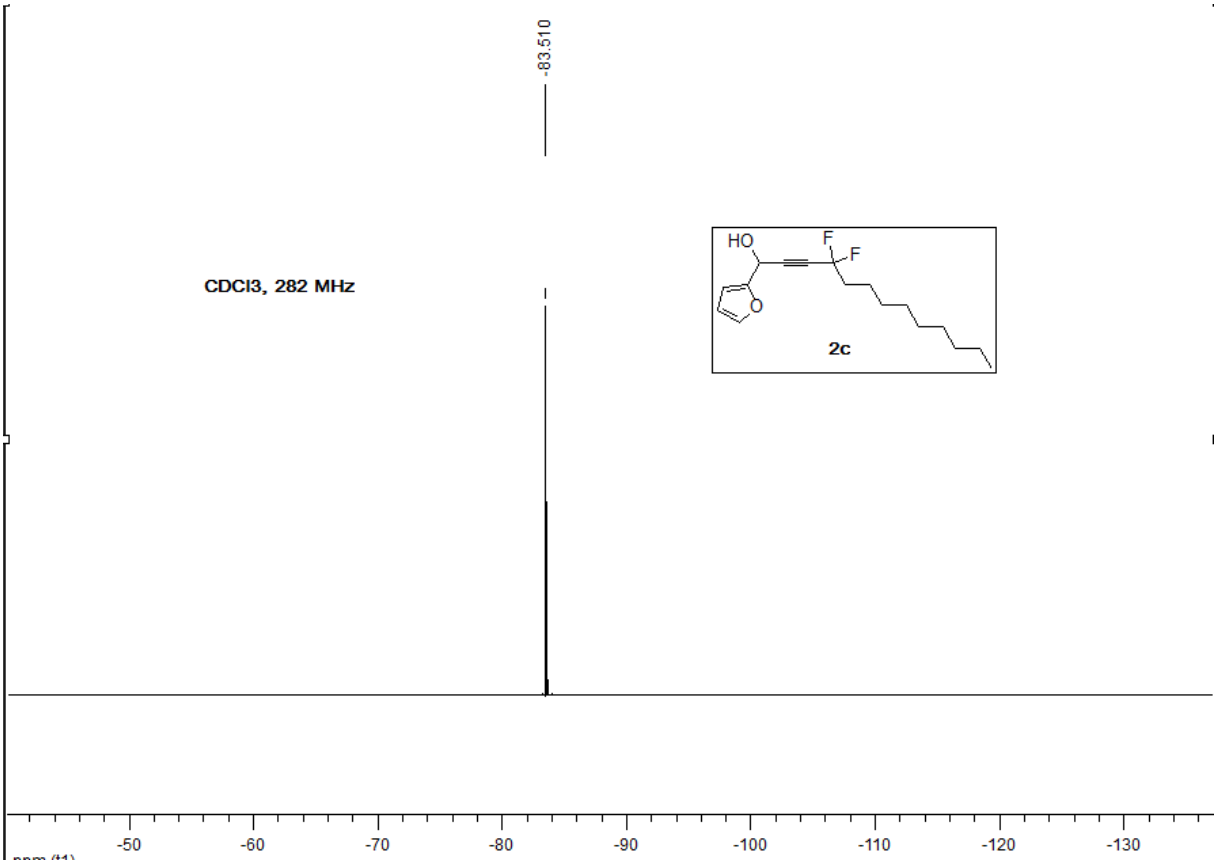
HO
F
F
O
2c
150
100
50
0
ppm (t1)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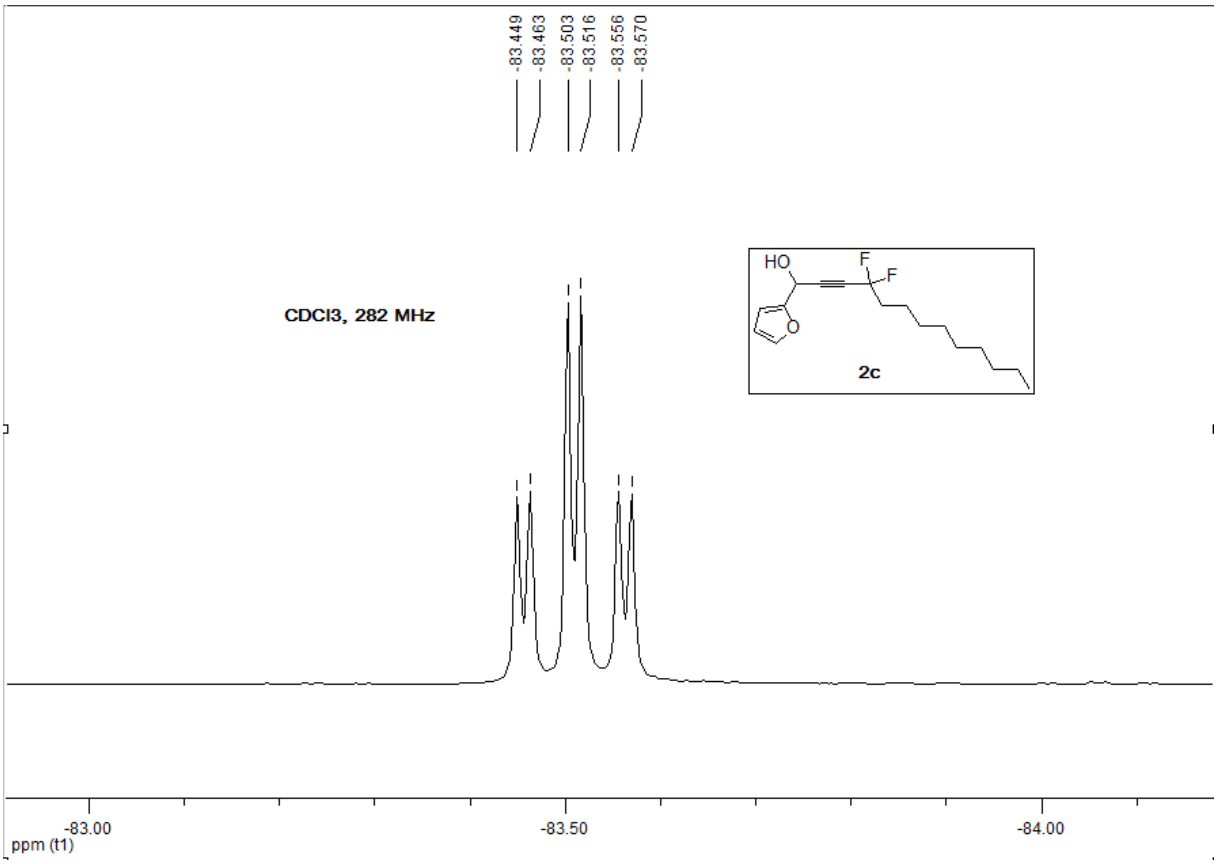
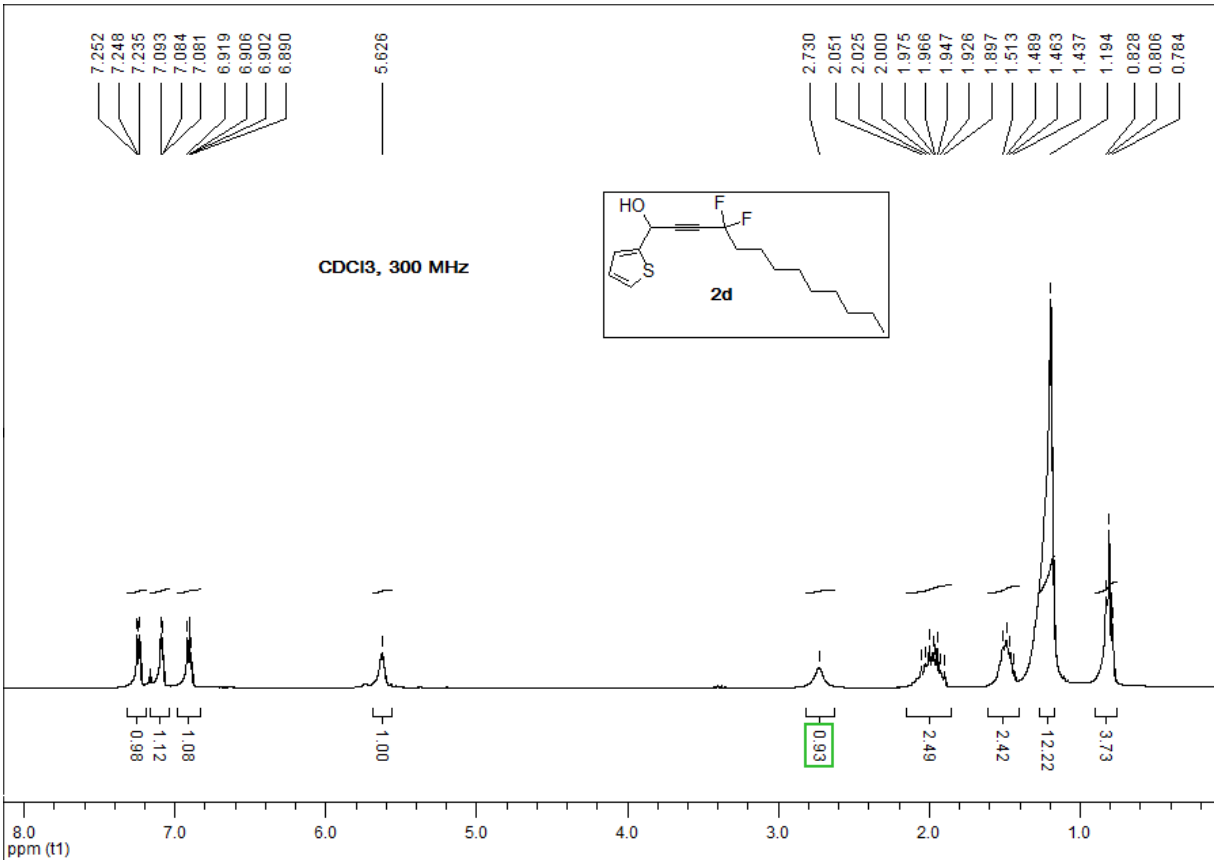
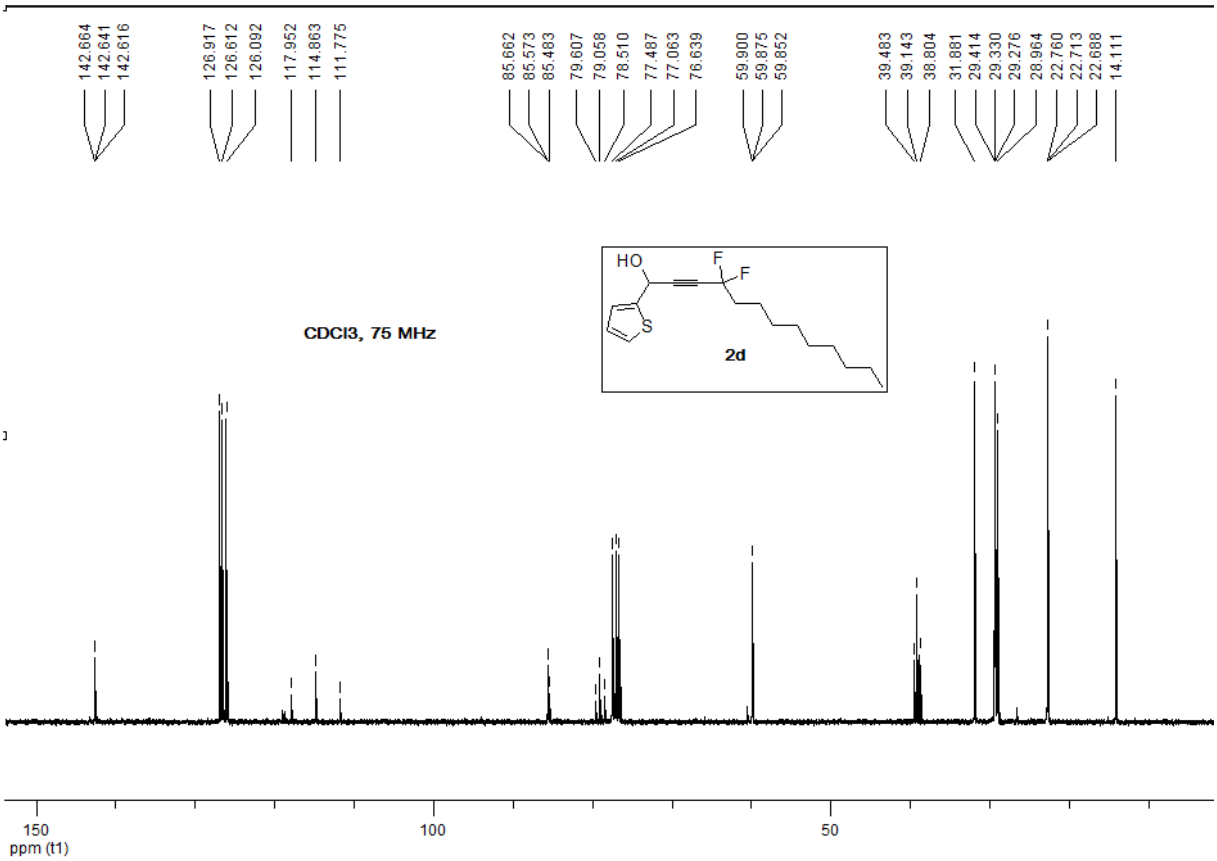
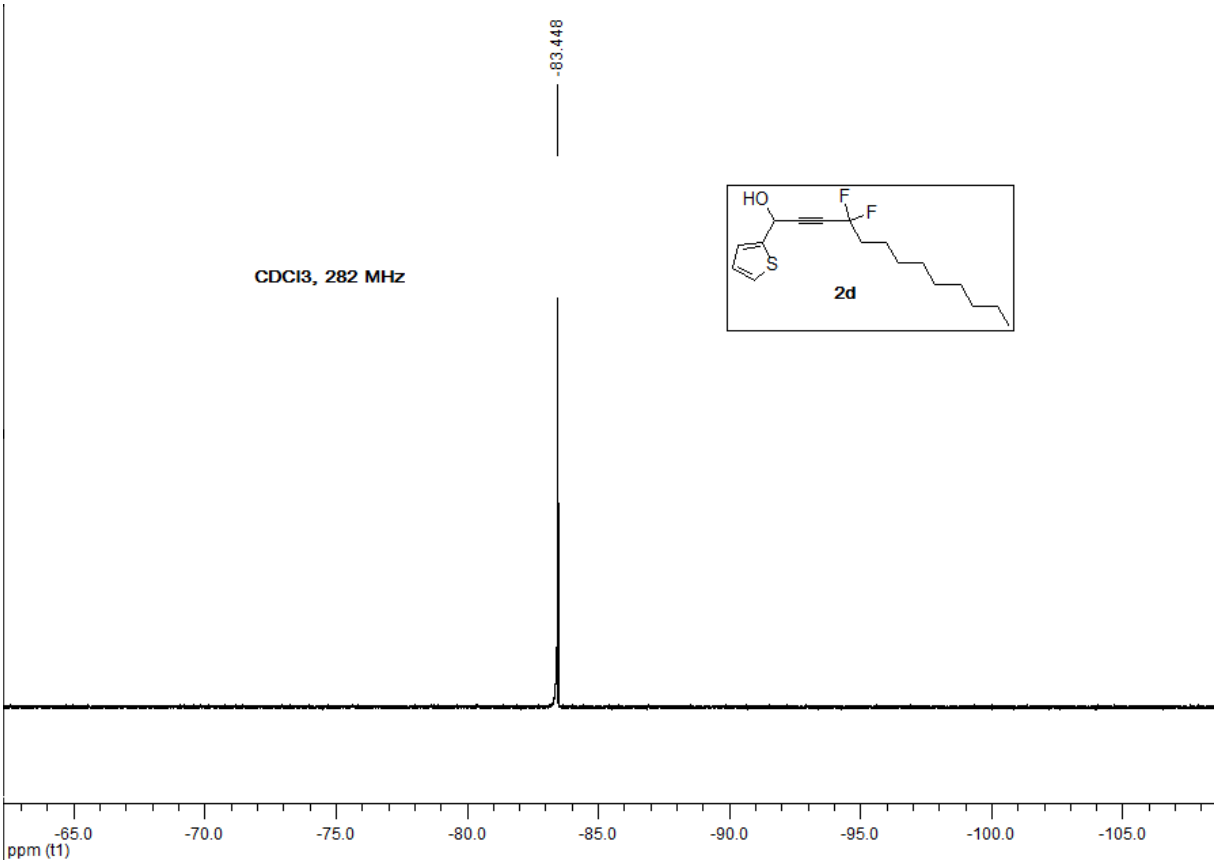
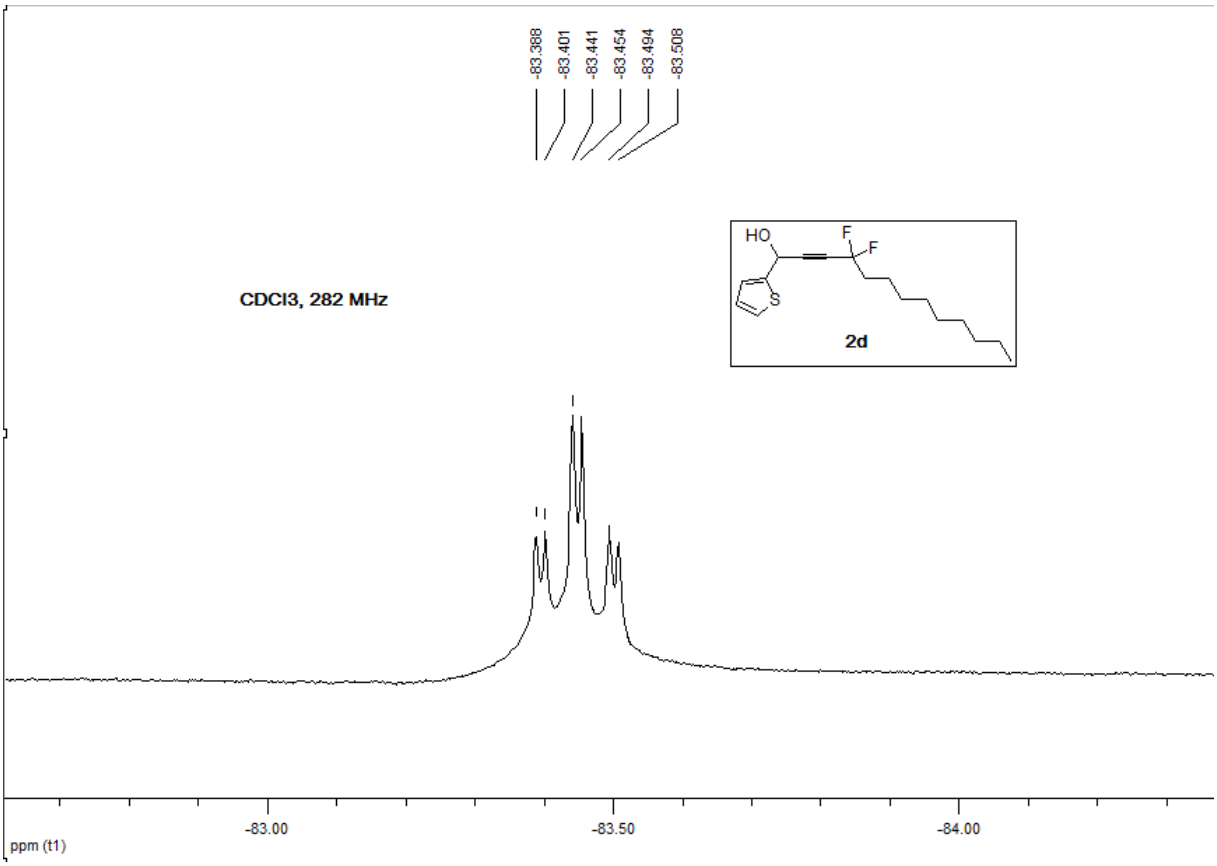
CDCl3, 282 MHz
HO
F
F
O
2c
-50
-60
-70
-80
-90
-100
-110
-120
-130

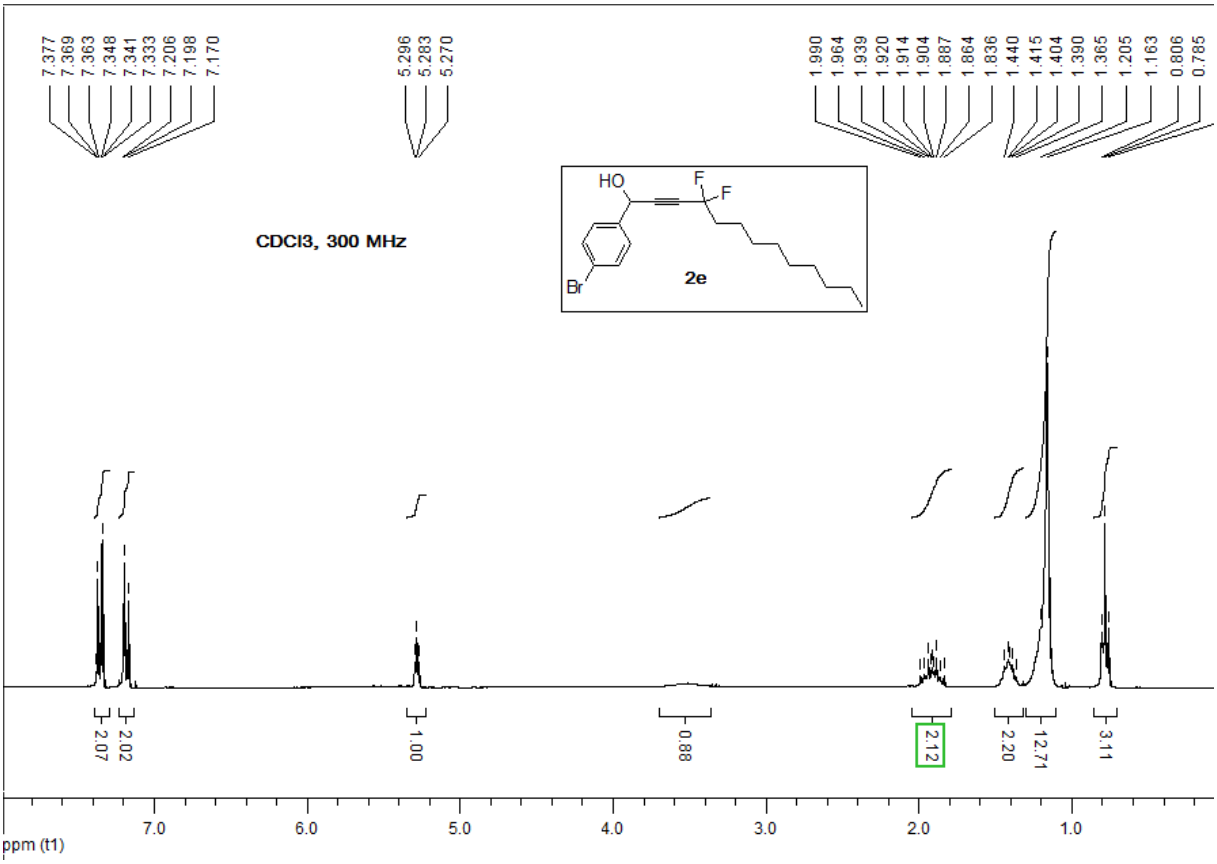

-83.449
-83.463
-83.503
-83.516
-83.556
-83.570
CDCl3, 282 MHz
HO
F
F
O
2c
-83.00
-83.50
-84.00
ppm (t1)

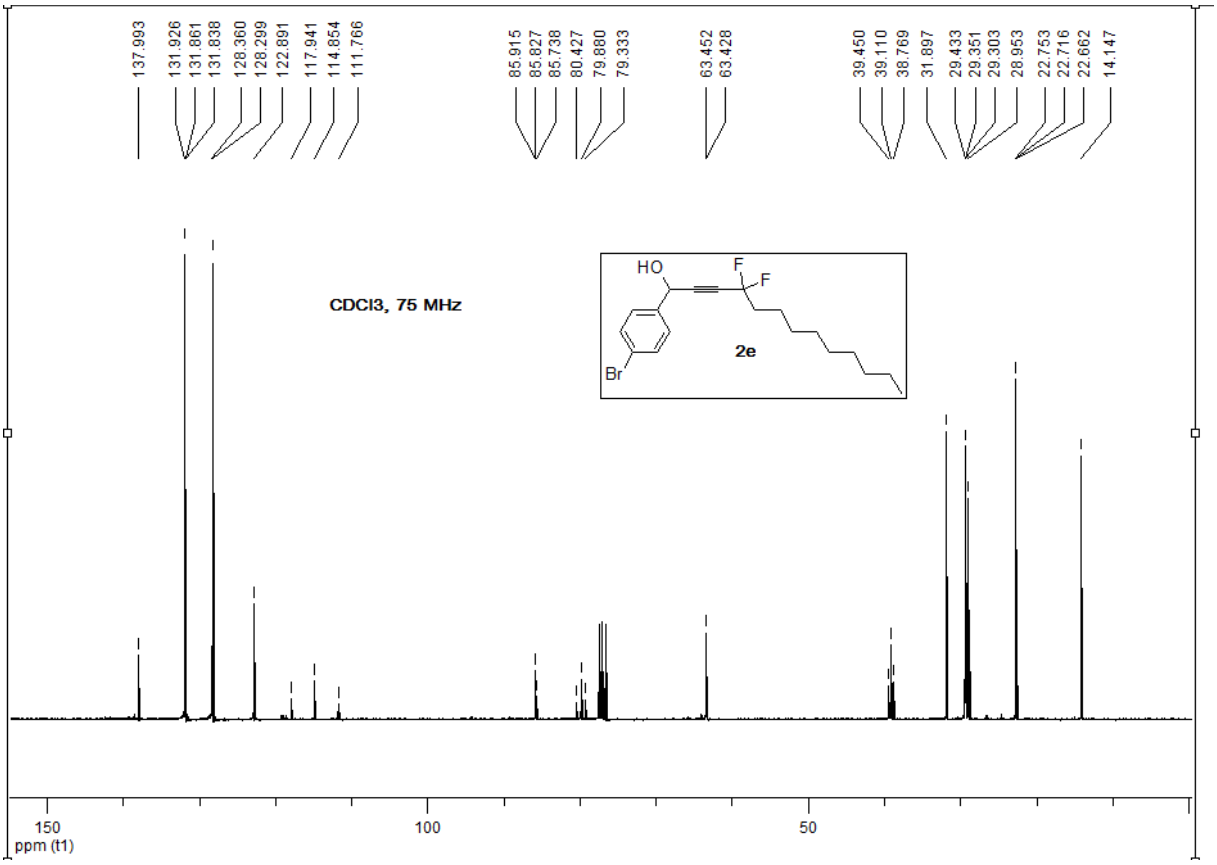

7.252
7.248
7.235
7.093
7.084
7.081
6.919
6.906
6.902
6.890
5.626
2.730
2.051
2.025
2.000
1.975
1.966
1.947
1.926
1.897
1.513
1.489
1.463
1.437
1.194
0.828
0.806
0.784
CDCl3, 300 MHz
HO
F
F
S
2d
0.98
1.12
1.08
1.00
0.93
2.49
2.42
12.22
3.73
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

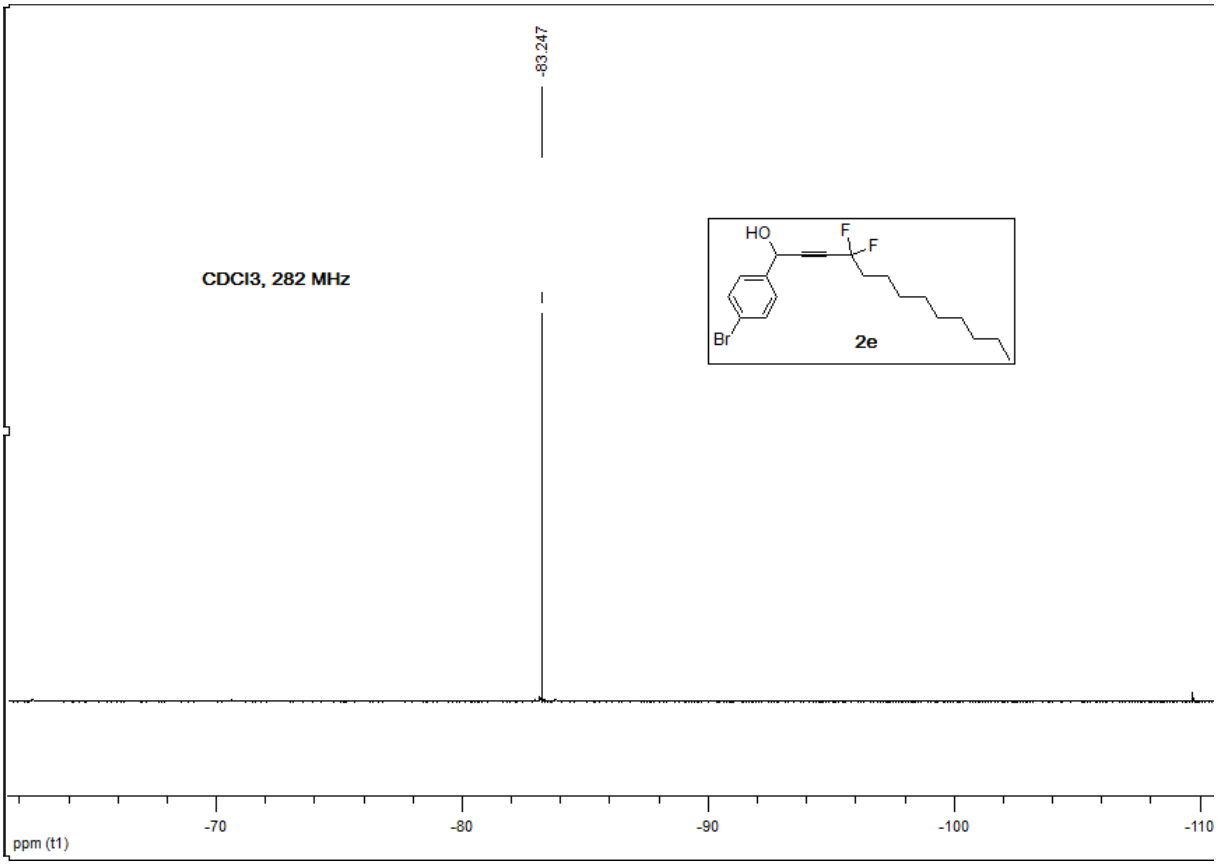

142.664
142.641
142.616
126.917
126.612
126.092
117.952
114.863
111.775
85.662
85.573
85.483
79.607
79.058
78.510
77.487
77.063
76.639
59.900
59.875
59.852
39.483
39.143
38.804
31.881
29.414
29.330
29.276
28.964
22.760
22.713
22.688
14.111
CDCl3, 75 MHz
HO
F
F
S
2d
150
100
50
ppm (t1)

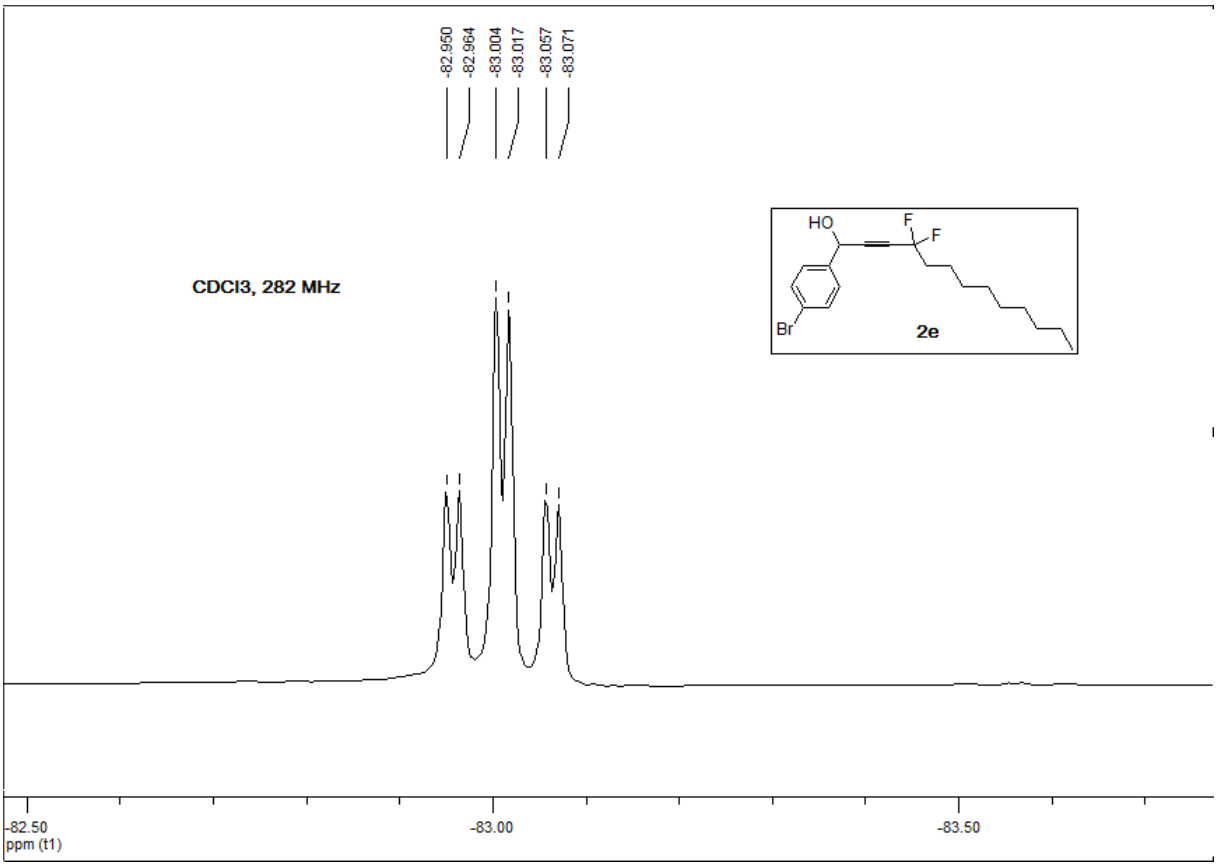

-83.448
CDCl3, 282 MHz
HO
F
F
S
2d
-65.0
-70.0
-75.0
-80.0
-85.0
-90.0
-95.0
-100.0
-105.0
ppm (t1)

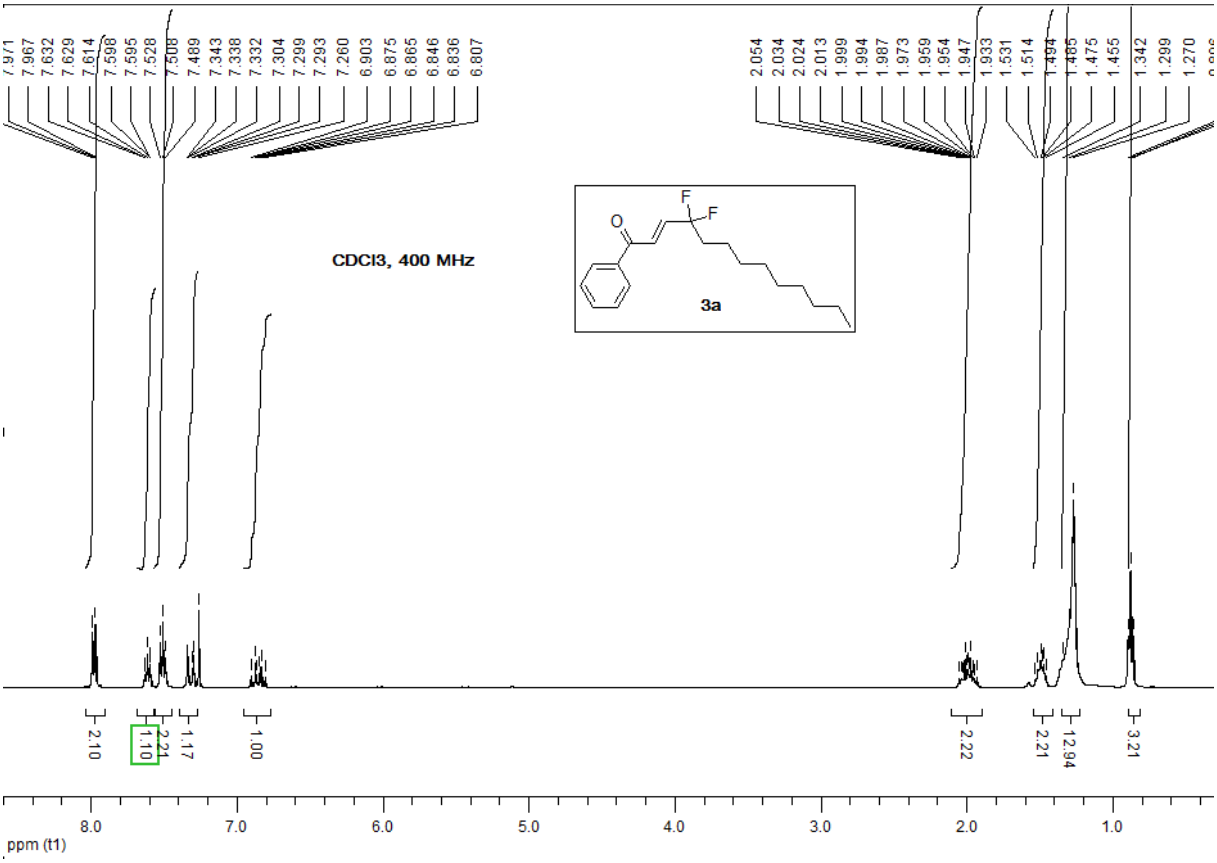

-83.388
-83.401
-83.441
-83.454
-83.494
-83.508
CDCl3, 282 MHz
HO
F
F
S
2d
-83.00
-83.50
-84.00
ppm (t1)

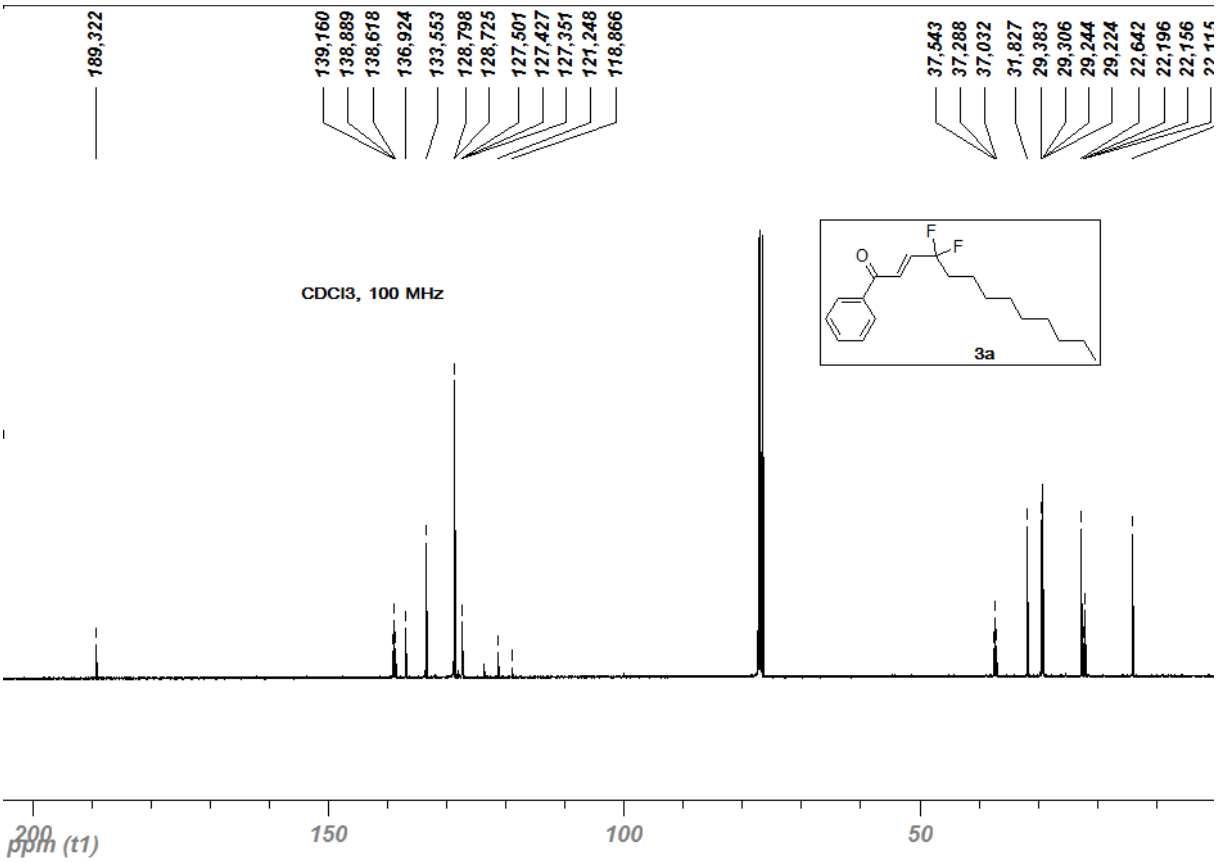

7.377
7.369
7.363
7.348
7.341
7.333
7.206
7.198
7.170
5.296
5.283
5.270
1.990
1.964
1.939
1.920
1.914
1.904
1.887
1.864
1.836
1.440
1.415
1.404
1.390
1.365
1.205
1.163
0.806
0.785
CDCl3, 300 MHz
HO
F
F
Br
2e
2.07
2.02
1.00
0.88
2.12
2.20
12.71
3.11
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

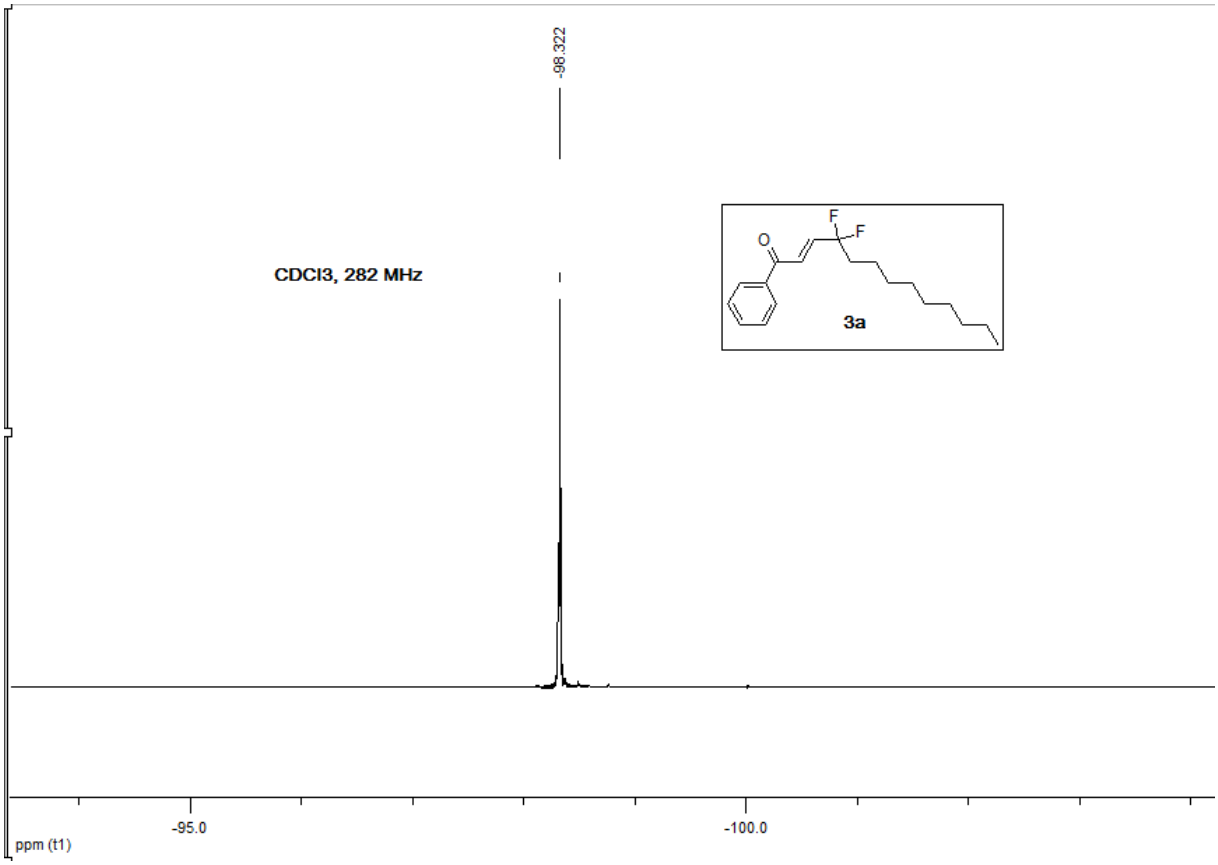

137.993
131.926
131.861
131.838
128.360
128.299
122.891
117.941
114.854
111.766
85.915
85.827
85.738
80.427
79.880
79.333
63.452
63.428
39.450
39.110
38.769
31.897
29.433
29.351
29.303
28.953
22.753
22.716
22.662
14.147
CDCl3, 75 MHz
HO
F
F
Br
2e
150
100
50
ppm (t1)

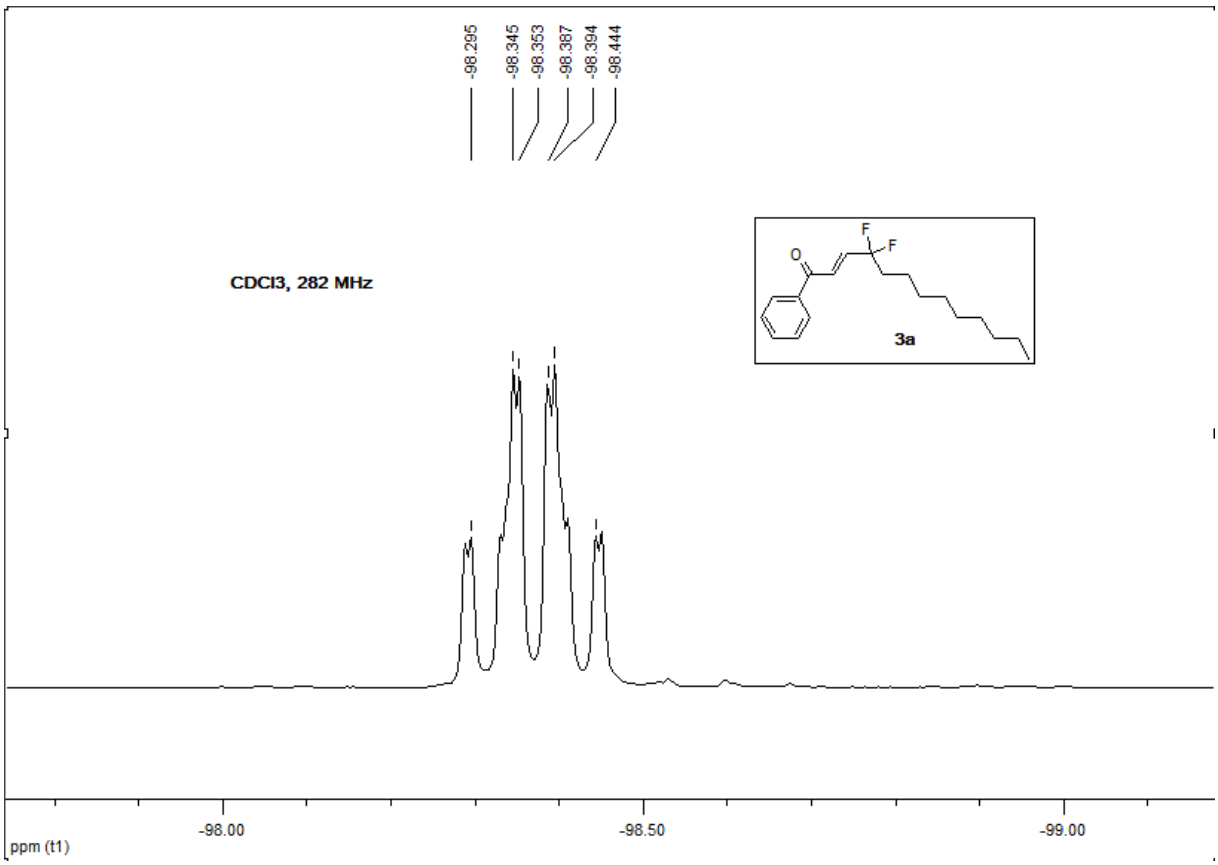

-83.247
CDCl3, 282 MHz
HO
F
F
Br
2e
-70
-80
-90
-100
-110
ppm (t1)

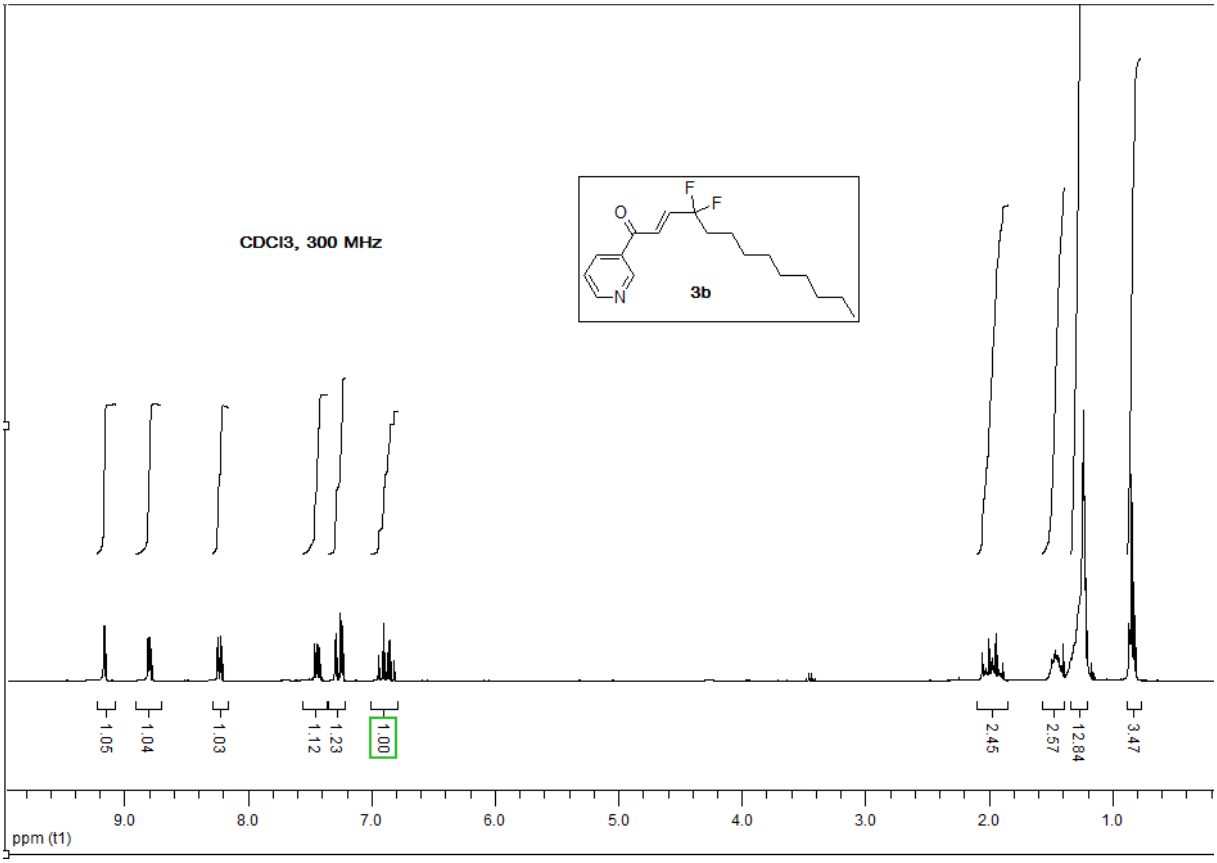

-82.950
-82.964
-83.004
-83.017
-83.057
-83.071
CDCl3, 282 MHz
HO
F
F
Br
2e
-82.50
-83.00
-83.50
ppm (t1)

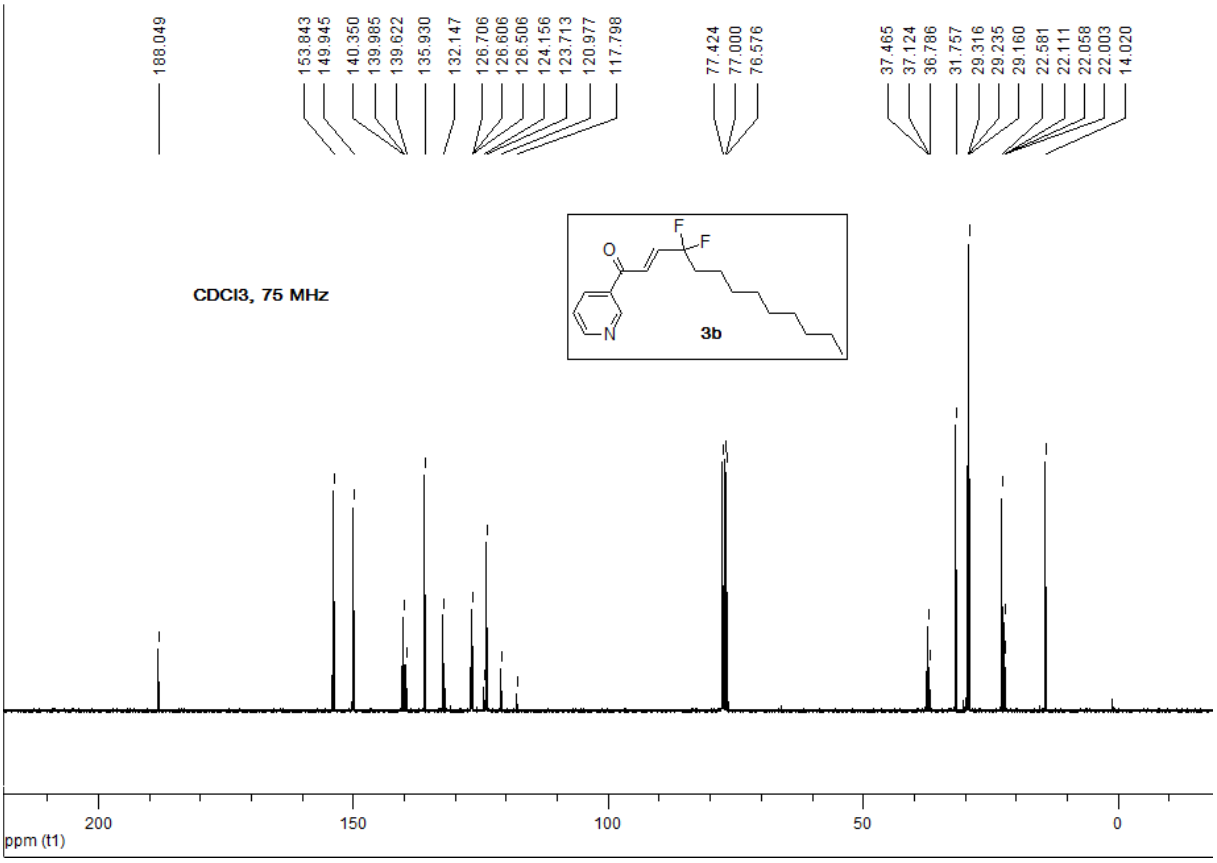

7.967
7.632
7.629
7.614
7.598
7.595
7.528
7.508
7.489
7.343
7.338
7.332
7.304
7.299
7.293
7.260
6.903
6.875
6.865
6.846
6.836
6.807
2.054
2.034
2.024
2.013
1.999
1.994
1.987
1.973
1.959
1.954
1.947
1.933
1.531
1.514
1.494
1.485
1.475
1.455
1.342
1.299
1.270
CDCl3, 400 MHz
F
F
O
3a
2.10
1.10
2.21
1.17
1.00
2.22
2.21
12.94
3.21
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

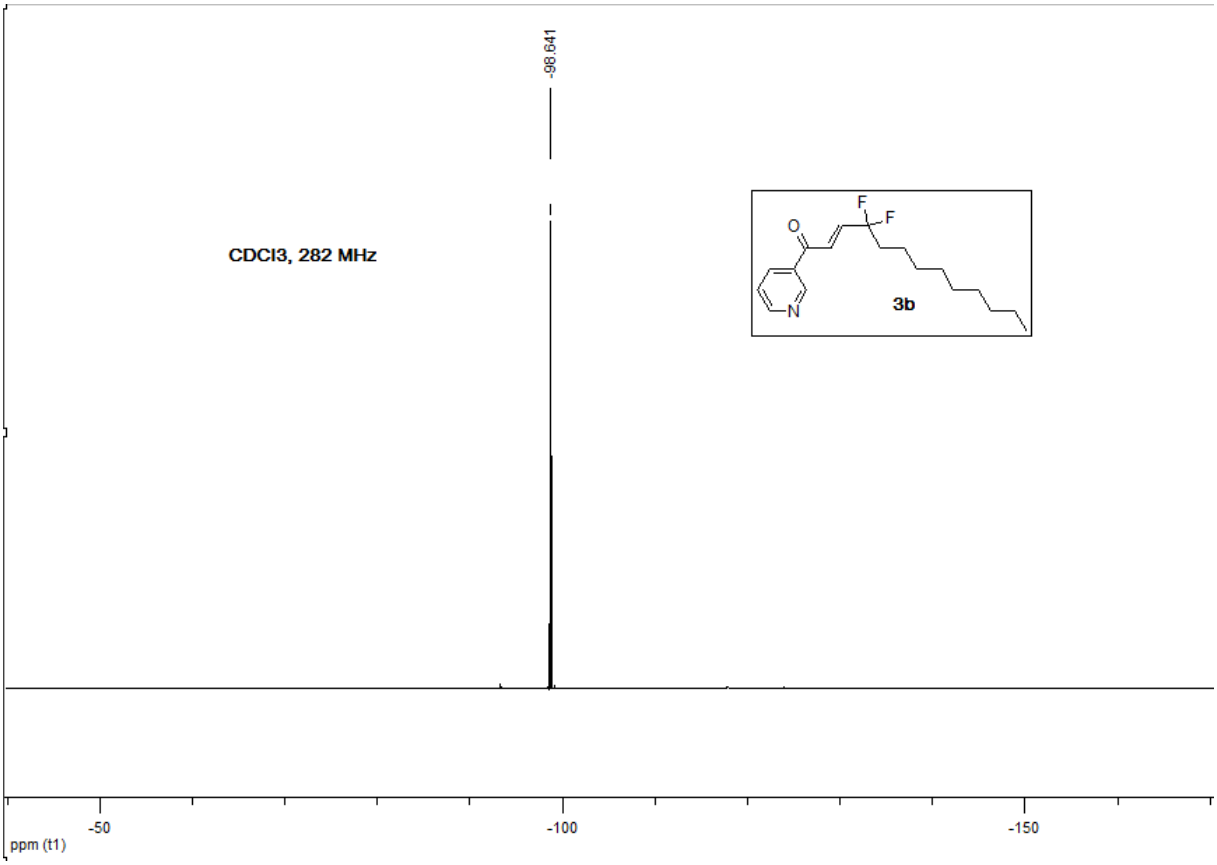

189,322
139,160
138,889
138,618
136,924
133,553
128,798
128,725
127,501
127,427
127,351
121,248
118,866
37,543
37,288
37,032
31,827
29,383
29,306
29,244
29,224
22,642
22,196
22,156
CDCl3, 100 MHz
F
F
O
3a
200
150
100
50
ppm (t1)

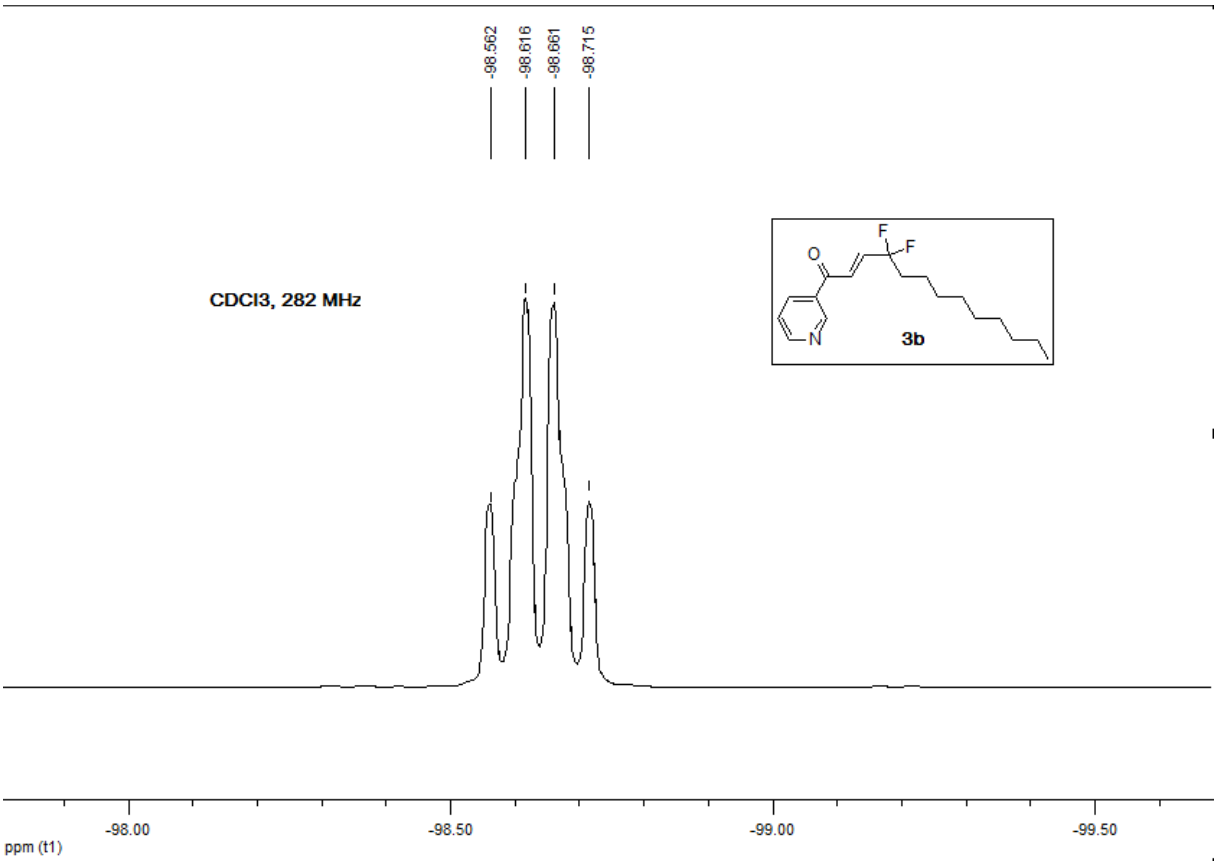

-98.322
CDCl3, 282 MHz
F
F
O
3a
-95.0
-100.0
ppm (t1)

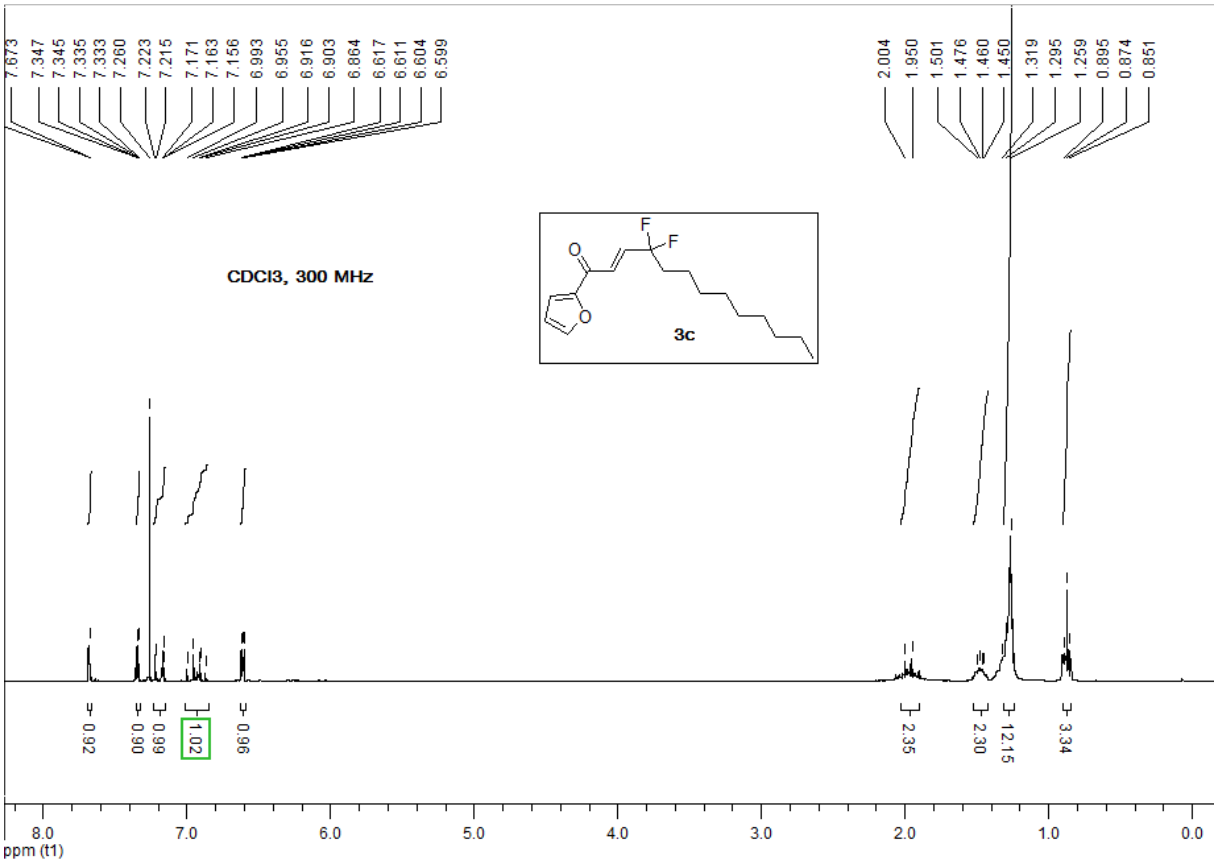

-98.295
-98.345
-98.353
-98.387
-98.394
-98.444
CDCl3, 282 MHz
F
F
O
3a
-98.00
-98.50
-99.00
ppm (t1)

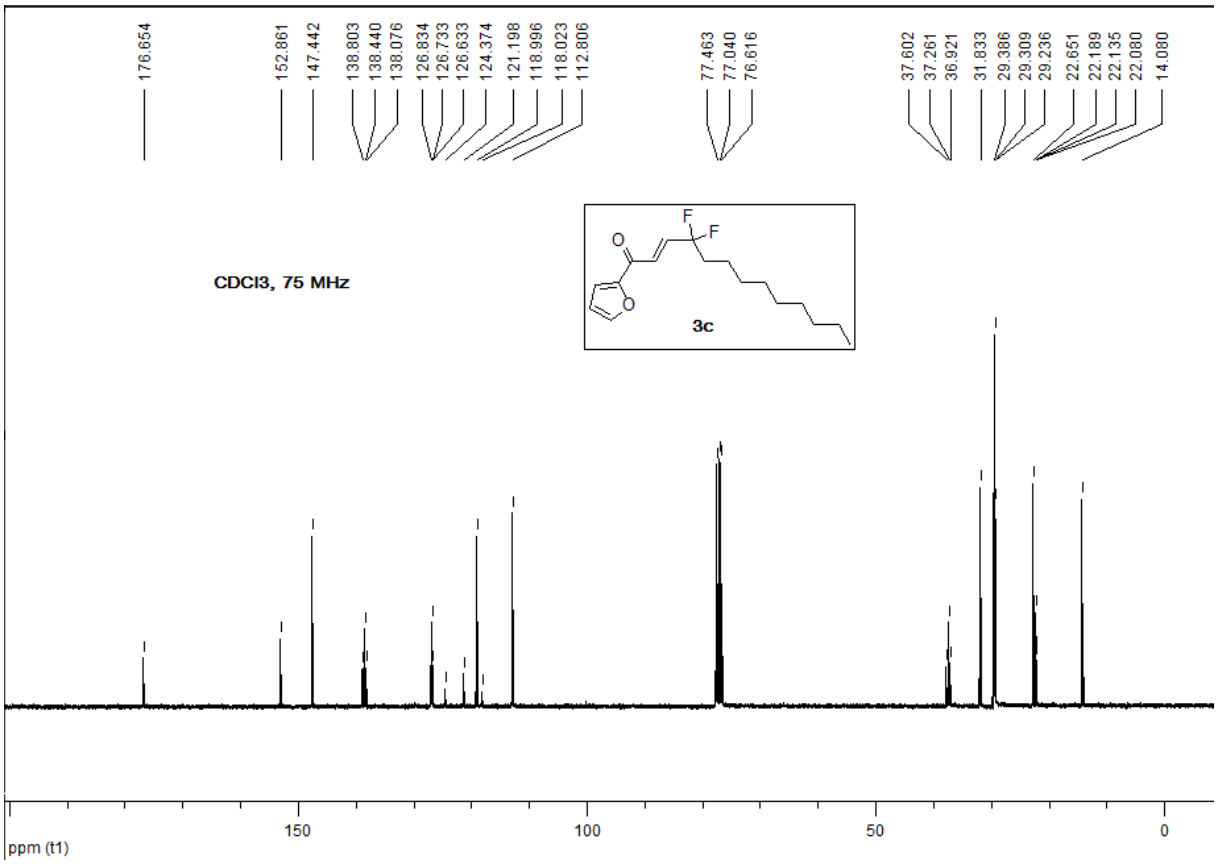

CDCl3, 300 MHz
3b
1.05
1.04
1.03
1.12
1.23
1.00
2.45
2.57
12.84
3.47
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

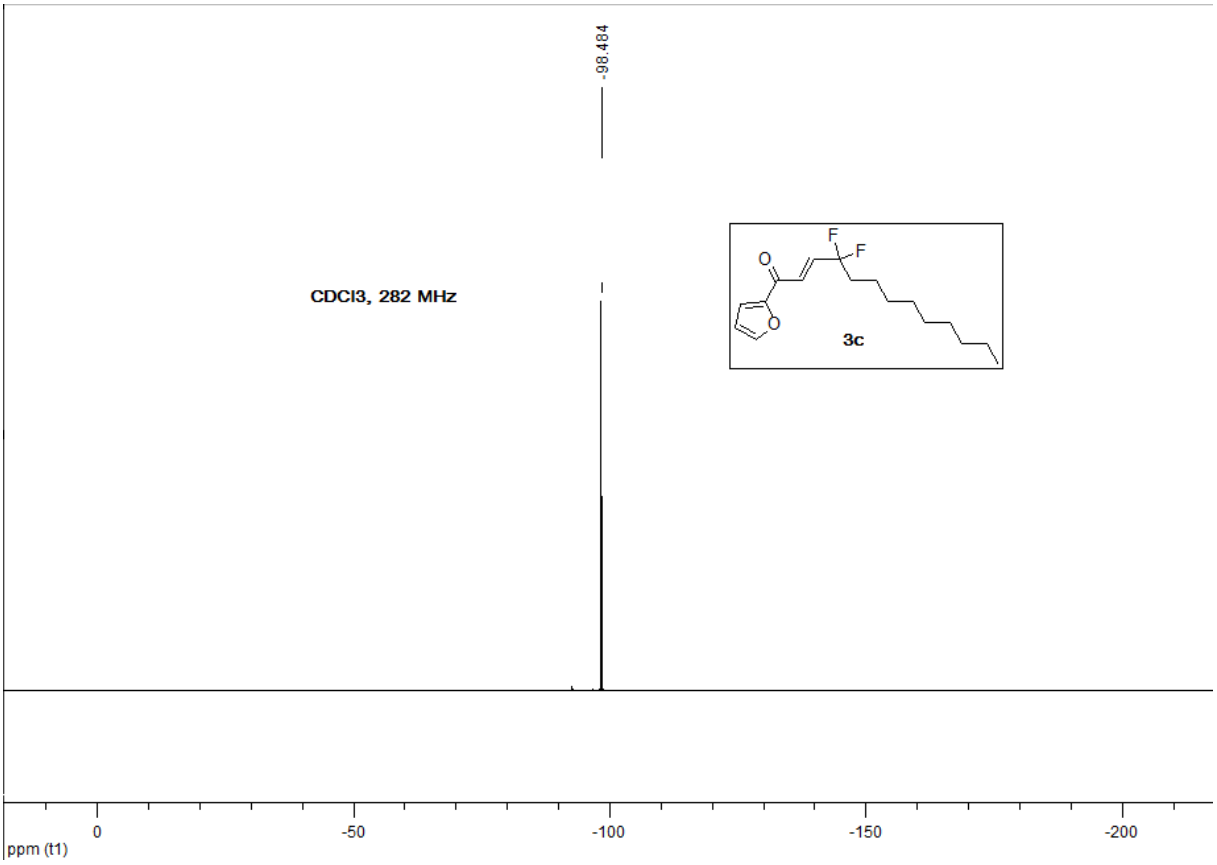

188.049
153.843
149.945
140.350
139.985
139.622
135.930
132.147
126.706
126.606
126.506
124.156
123.713
120.977
117.798
77.424
77.000
76.576
37.465
37.124
36.786
31.757
29.316
29.235
29.160
22.581
22.111
22.058
22.003
14.020
CDCl3, 75 MHz
3b
200
150
100
50
0
ppm (t1)

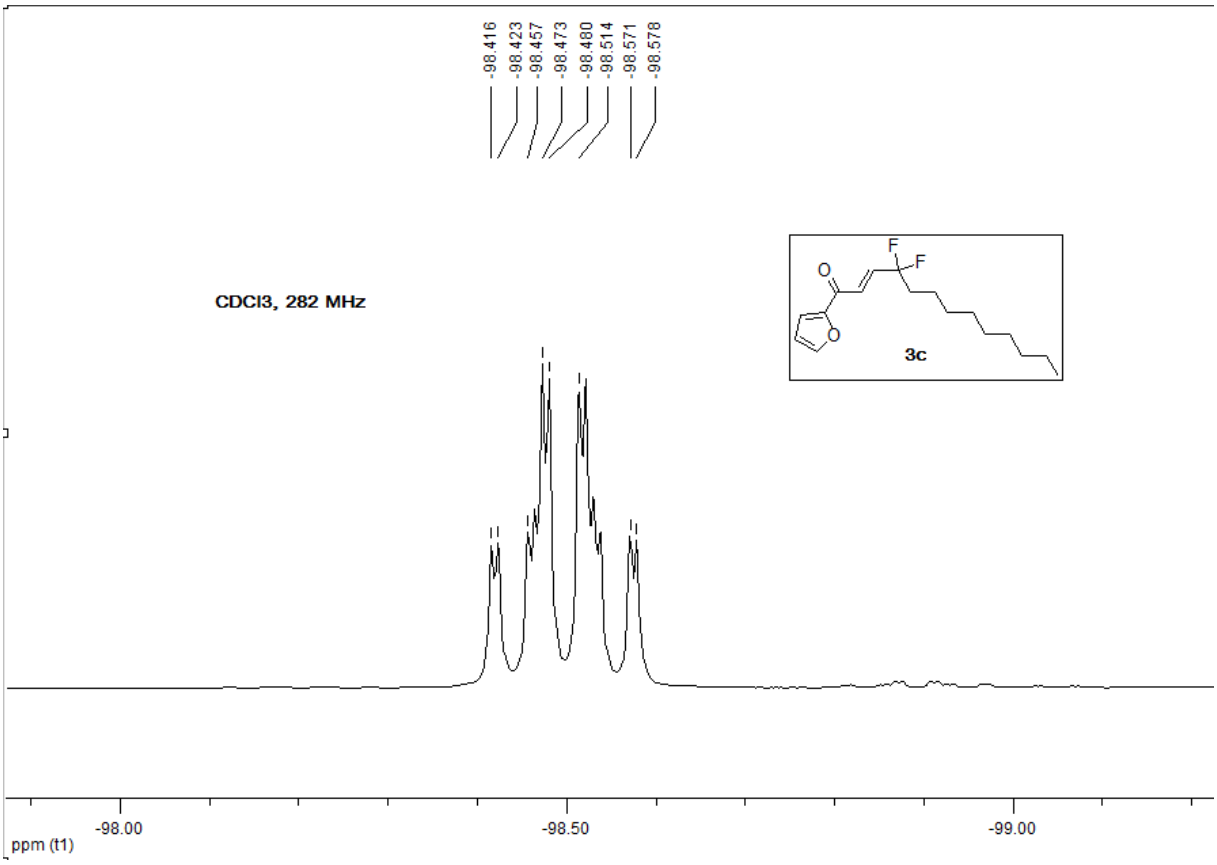

-98.641
CDCl3, 282 MHz
F
F
O
N
3b
-50
-100
-150
ppm (t1)

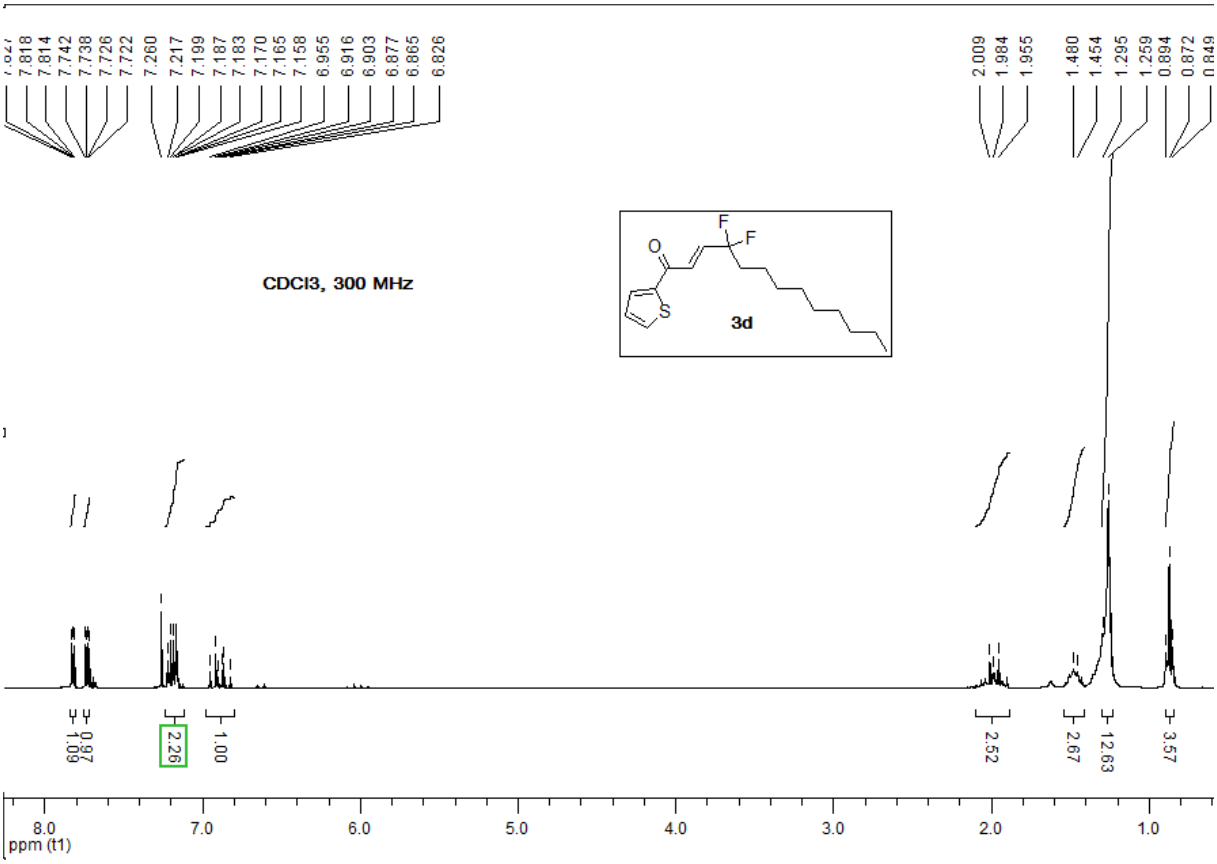

-98.562
-98.616
-98.661
-98.715
CDCl3, 282 MHz
F
F
O
N
3b
-98.00
-98.50
-99.00
-99.50
ppm (t1)

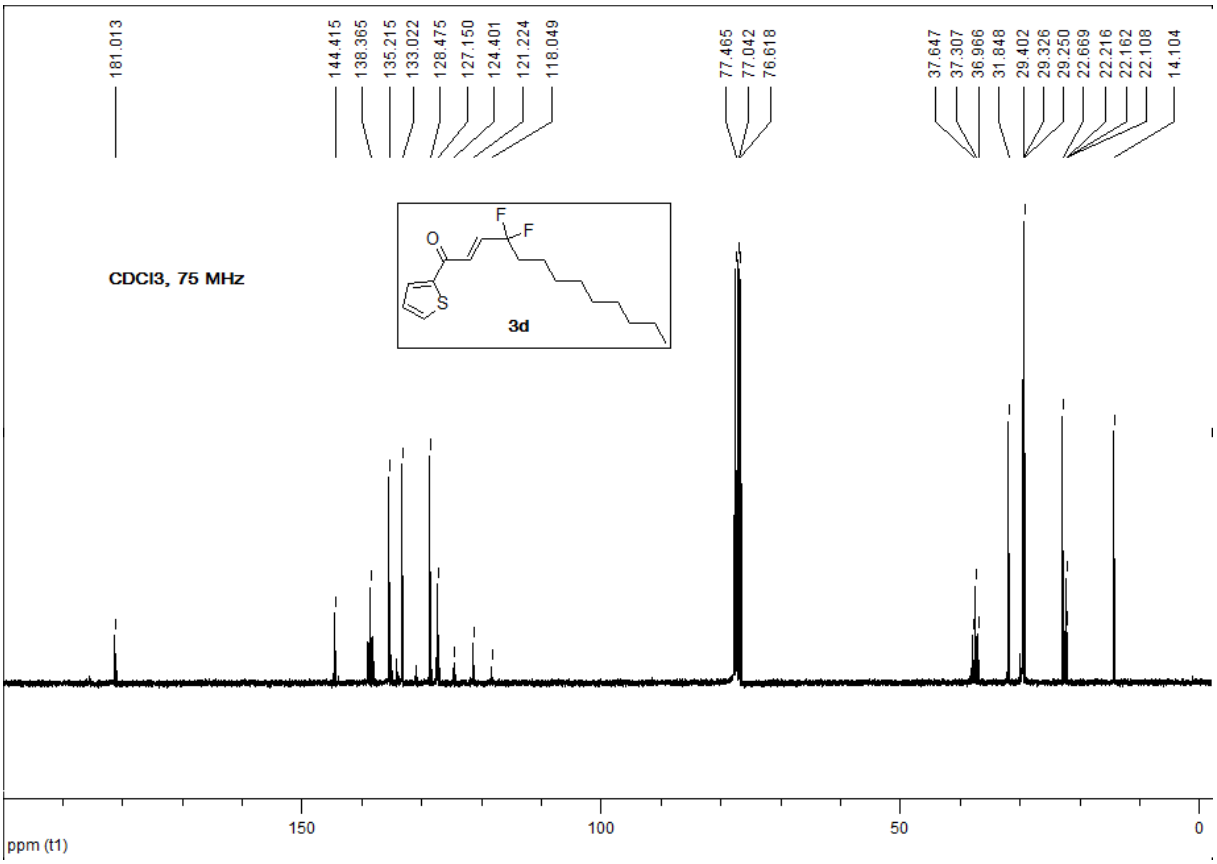

7.673
7.347
7.345
7.335
7.333
7.260
7.223
7.215
7.171
7.163
7.156
6.993
6.955
6.916
6.903
6.864
6.617
6.611
6.604
6.599
2.004
1.950
1.501
1.476
1.460
1.450
1.319
1.295
1.259
0.895
0.874
0.851
CDCl3, 300 MHz
F
F
O
O
3c
0.92
0.90
0.99
1.02
0.96
2.35
2.30
12.15
3.34
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

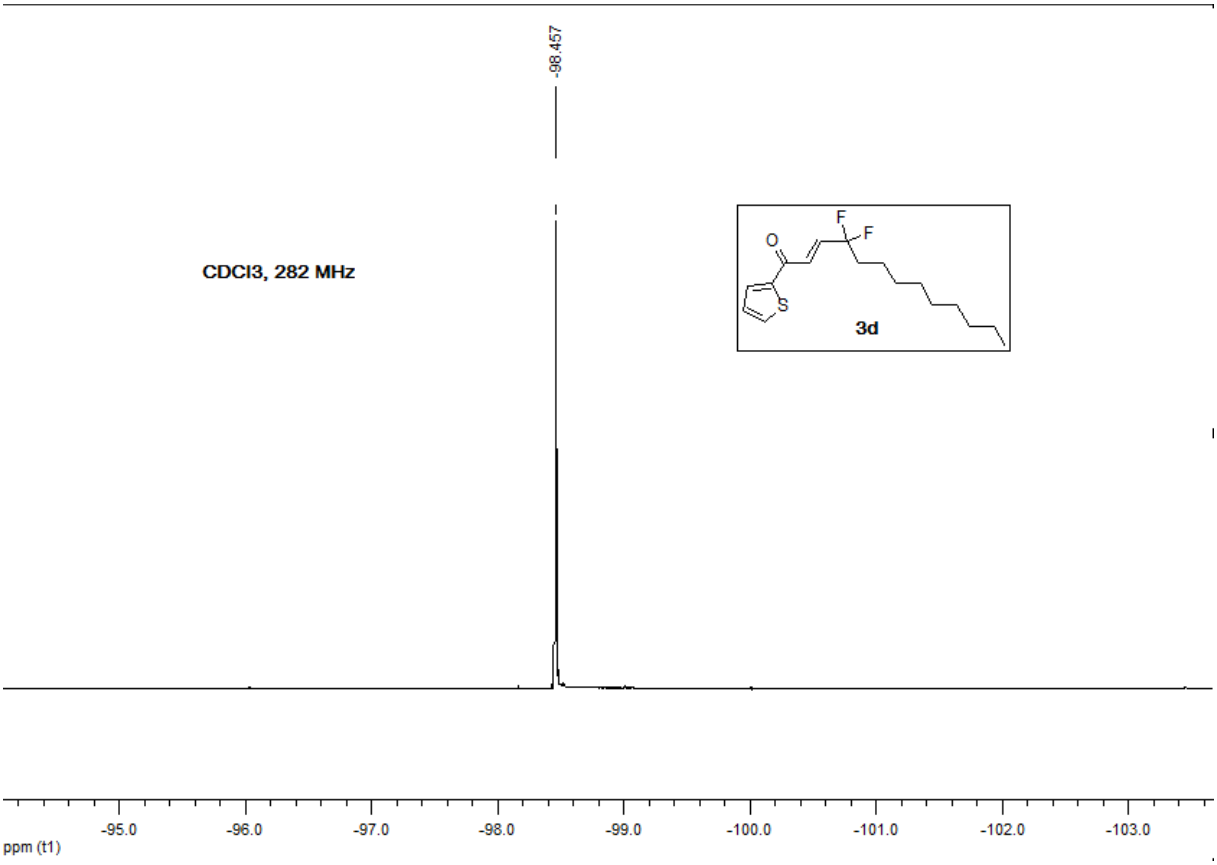

176.654
152.861
147.442
138.803
138.440
138.076
126.834
126.733
126.633
124.374
121.198
118.996
118.023
112.806
77.463
77.040
76.616
37.602
37.261
36.921
31.833
29.386
29.309
29.236
22.651
22.189
22.135
22.080
14.080
CDCl3, 75 MHz
F
F
O
O
3c
150
100
50
0
ppm (t1)

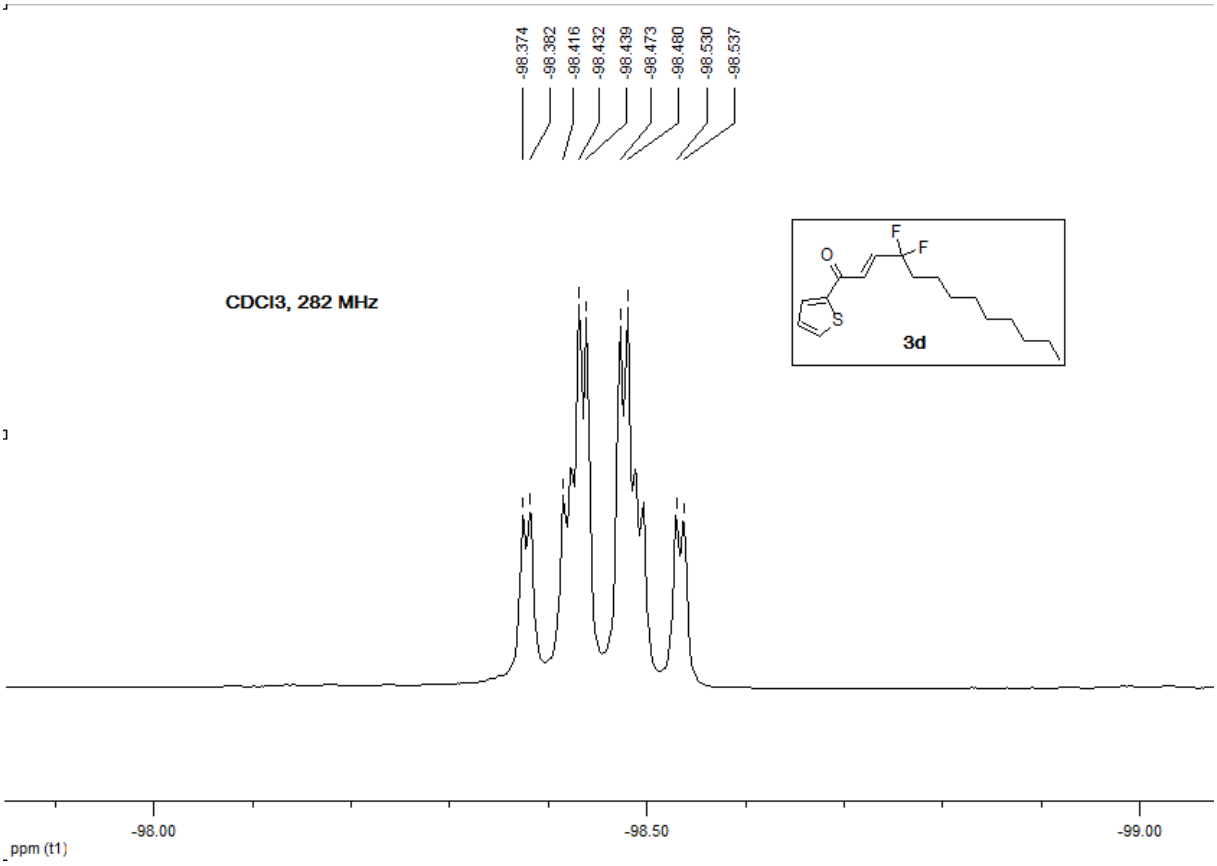

-98.484
CDCl3, 282 MHz
F
F
O
O
3c
0
-50
-100
-150
-200
ppm (t1)

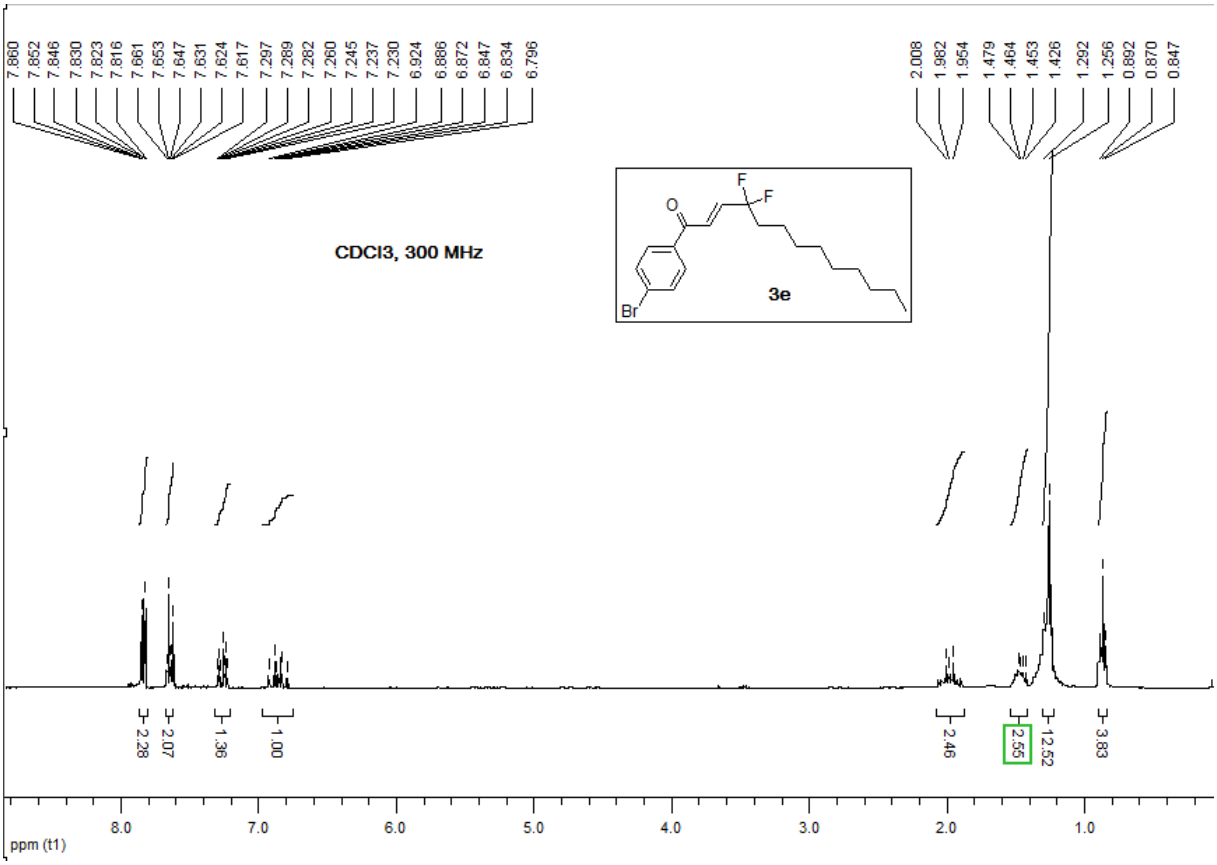

-98.416
-98.423
-98.457
-98.473
-98.480
-98.514
-98.571
-98.578
CDCl3, 282 MHz
F
F
O
O
3c
-98.00
-98.50
-99.00
ppm (t1)

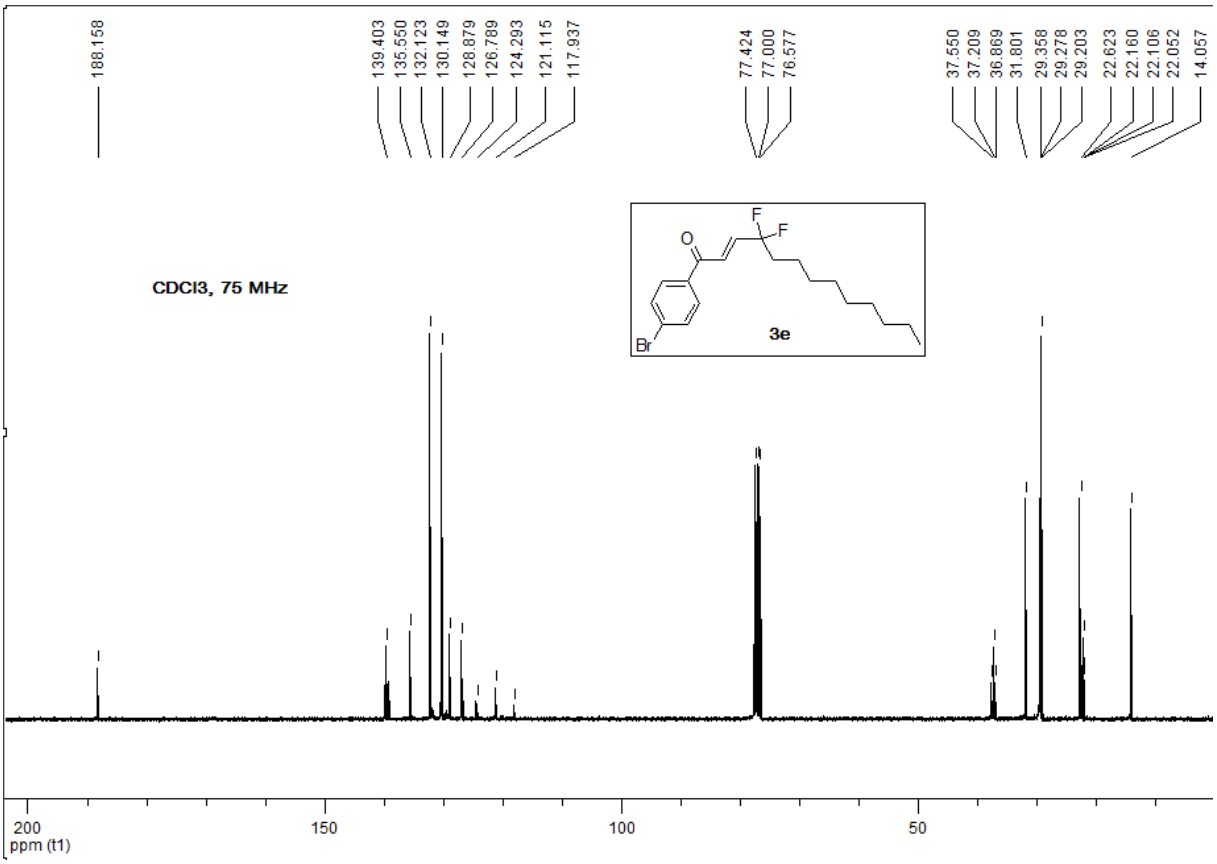

7.818
7.814
7.742
7.738
7.726
7.722
7.260
7.217
7.199
7.187
7.183
7.170
7.165
7.158
6.955
6.916
6.903
6.877
6.865
6.826
2.009
1.984
1.955
1.480
1.454
1.295
1.259
0.894
0.872
0.849
CDCl3, 300 MHz
3d
1.07
2.26
1.00
2.52
2.97
12.63
3.57
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

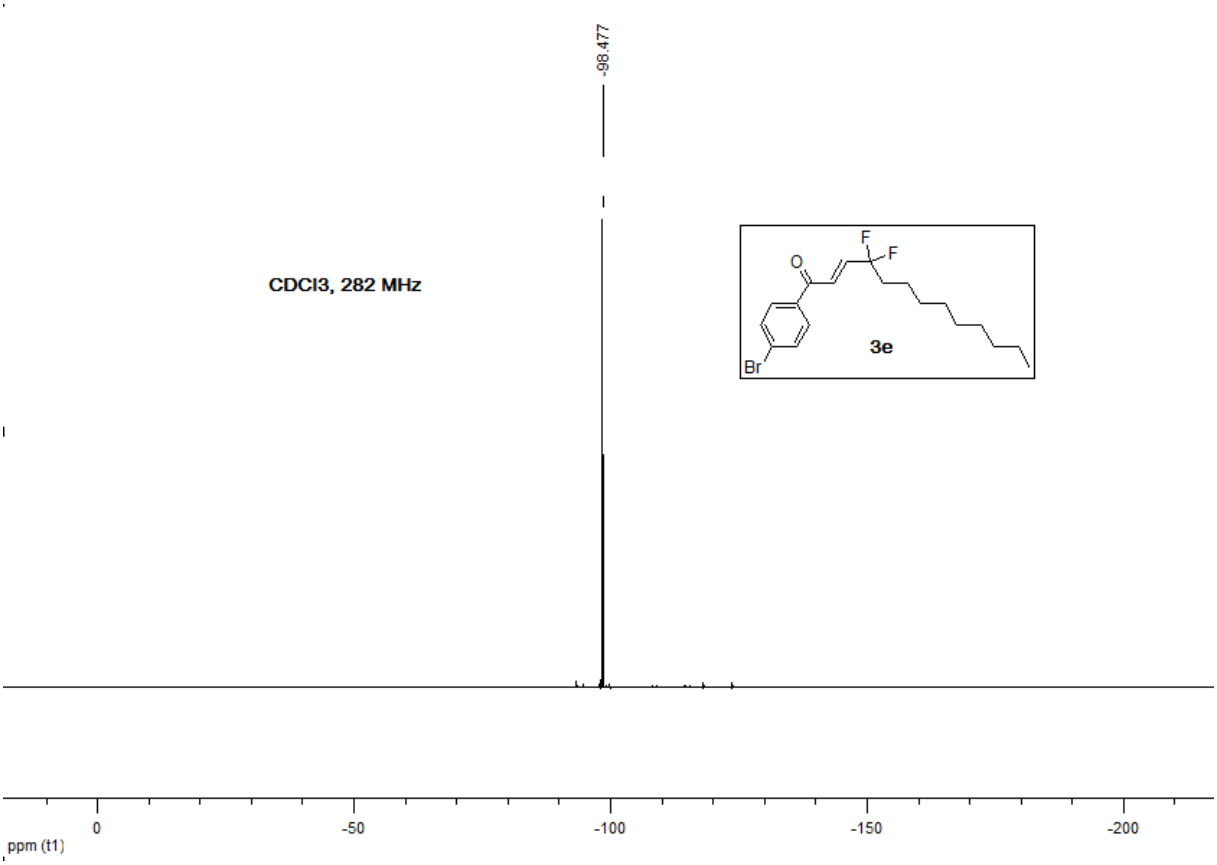

181.013
144.415
138.365
135.215
133.022
128.475
127.150
124.401
121.224
118.049
77.465
77.042
76.618
37.647
37.307
36.966
31.848
29.402
29.326
29.250
22.669
22.216
22.162
22.108
14.104
CDCl3, 75 MHz
3d
150
100
50
0
ppm (t1)

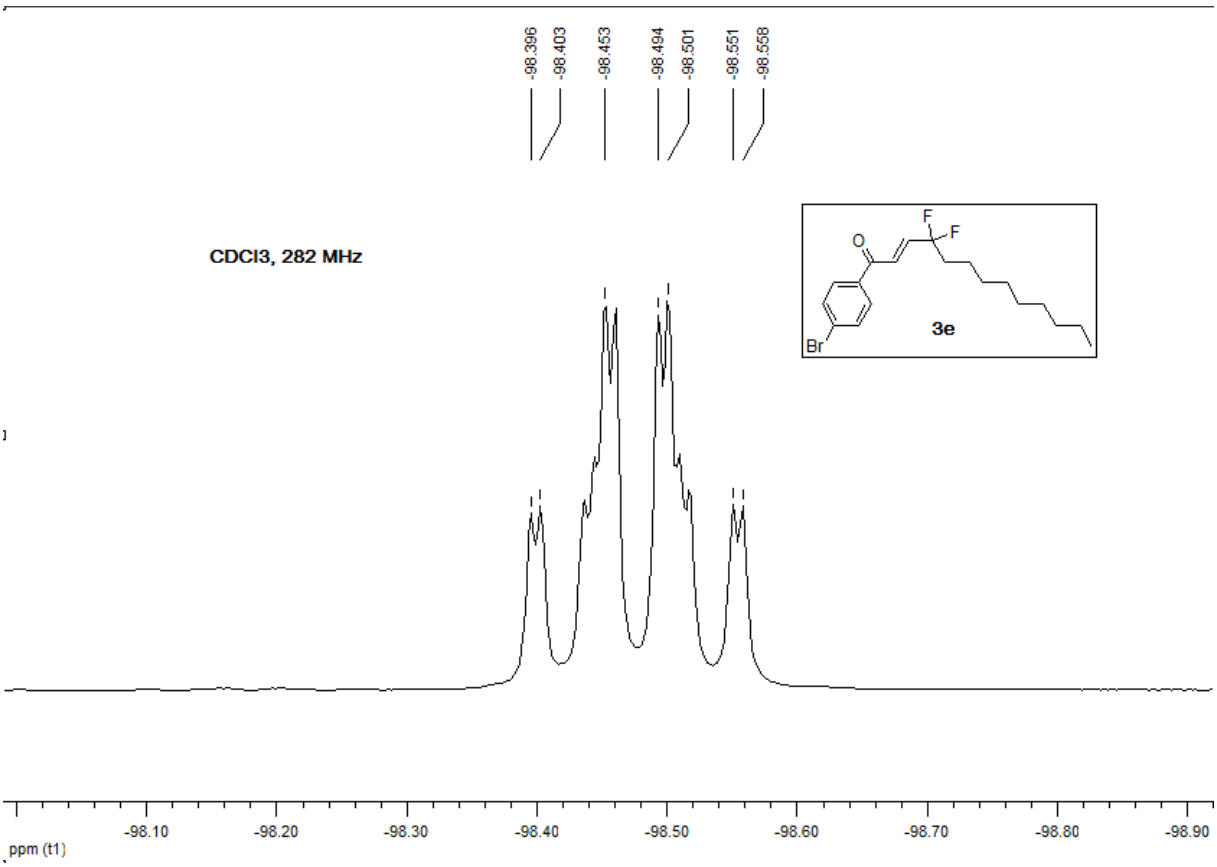

-98.457
CDCl3, 282 MHz
F
F
O
S
3d
-95.0
-96.0
-97.0
-98.0
-99.0
-100.0
-101.0
-102.0
-103.0
ppm (t1)

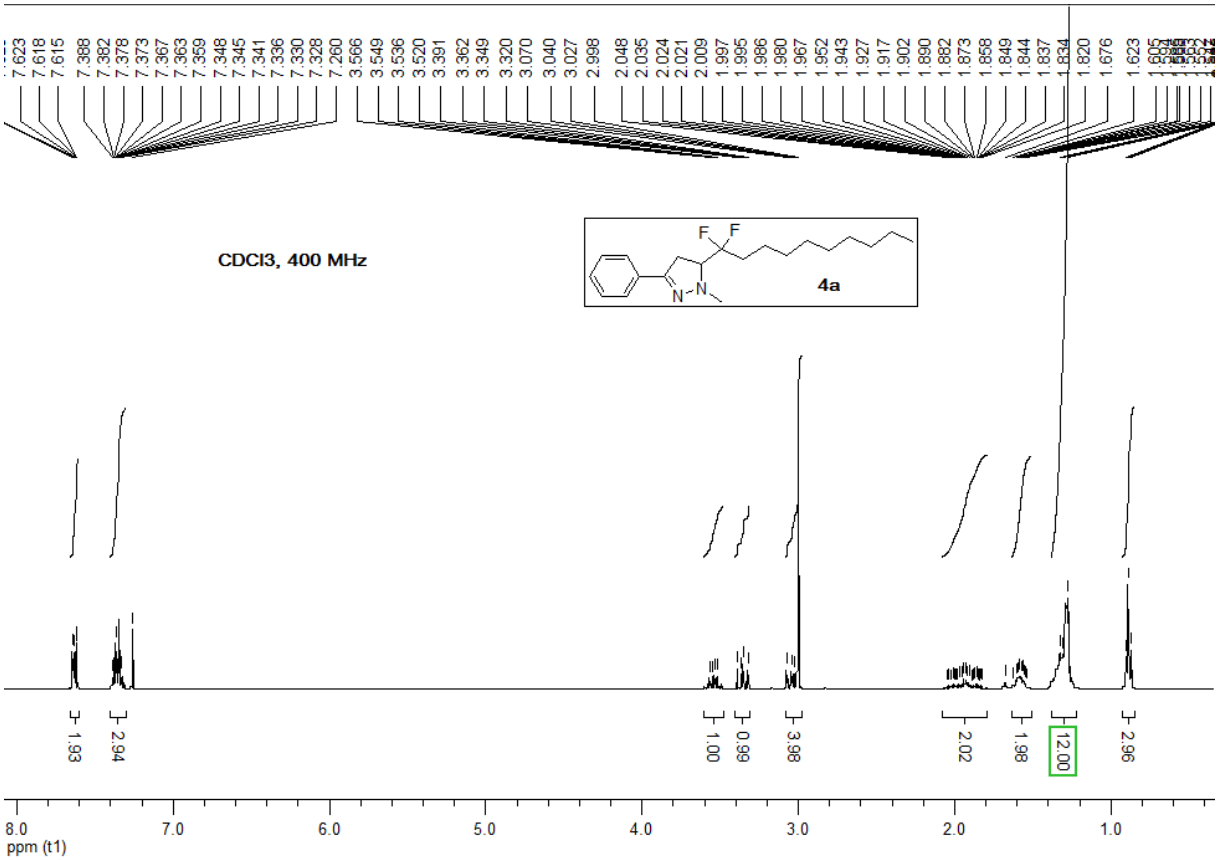

-98.374
-98.382
-98.416
-98.432
-98.439
-98.473
-98.480
-98.530
-98.537
CDCl3, 282 MHz
F
F
O
S
3d
-98.00
-98.50
-99.00
ppm (t1)

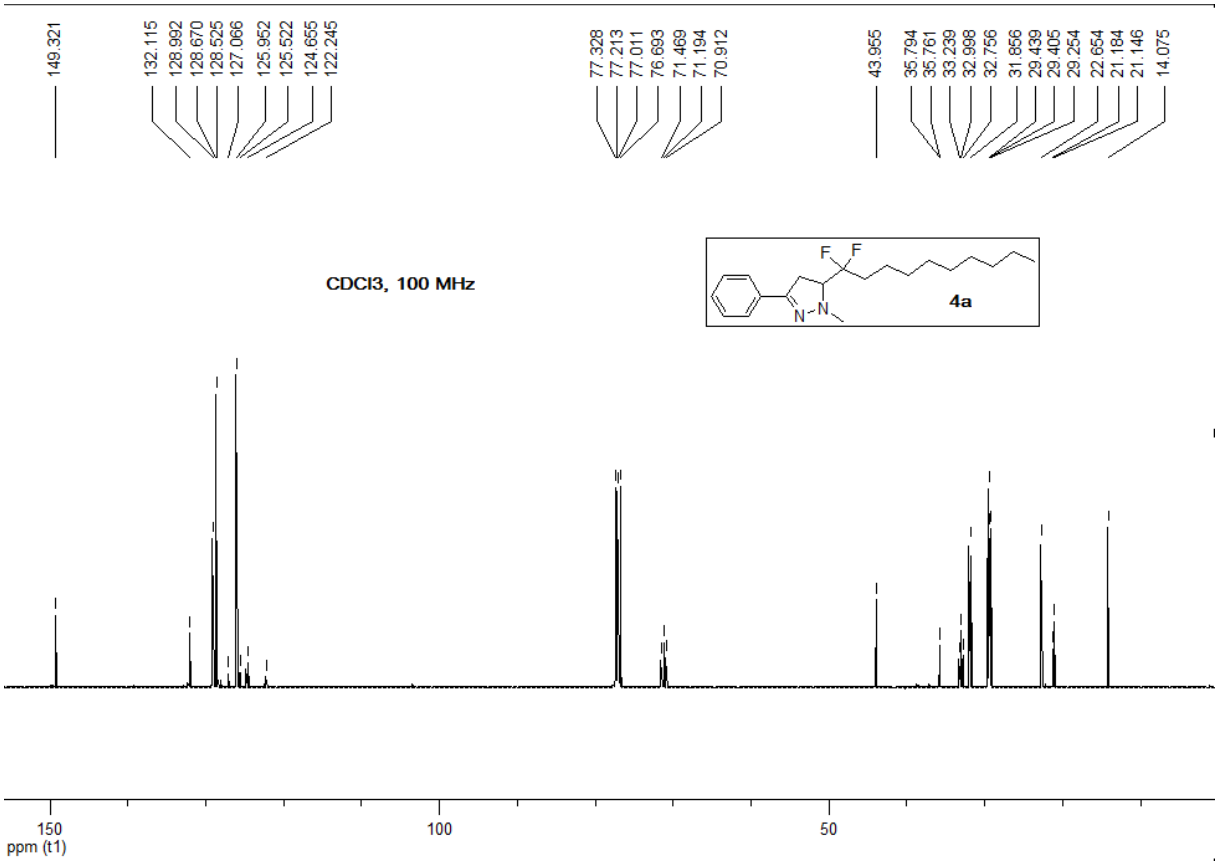

7.860
7.852
7.846
7.830
7.823
7.816
7.661
7.653
7.647
7.631
7.624
7.617
7.297
7.289
7.282
7.260
7.245
7.237
7.230
6.924
6.886
6.872
6.847
6.834
6.796
2.008
1.982
1.954
1.479
1.464
1.453
1.426
1.292
1.256
0.892
0.870
0.847
CDCl3, 300 MHz
3e
2.28
2.07
1.36
1.00
2.46
2.55
12.52
3.83
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

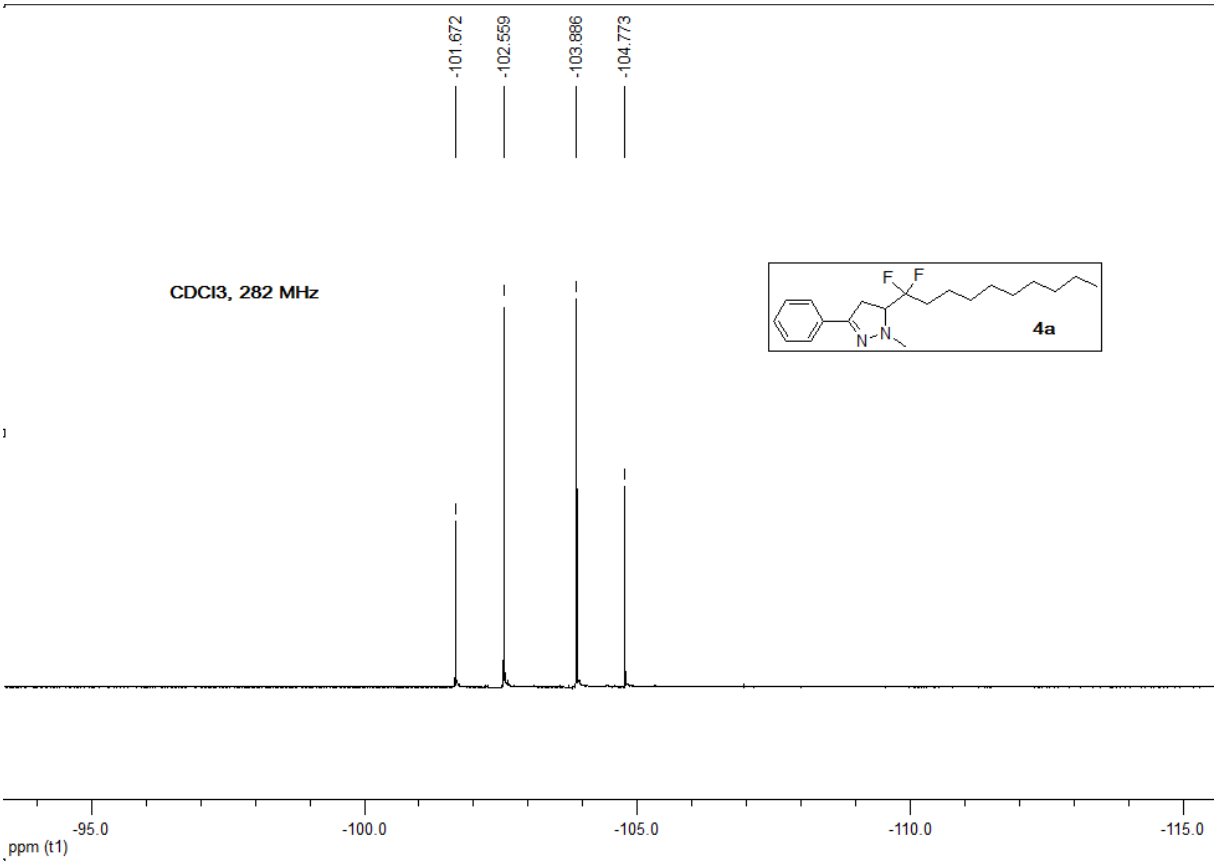

188.158
139.403
135.550
132.123
130.149
128.879
126.789
124.293
121.115
117.937
77.424
77.000
76.577
37.550
37.209
36.869
31.801
29.358
29.278
29.203
22.623
22.160
22.106
22.052
14.057
CDCl3, 75 MHz
3e
200
150
100
50
ppm (t1)

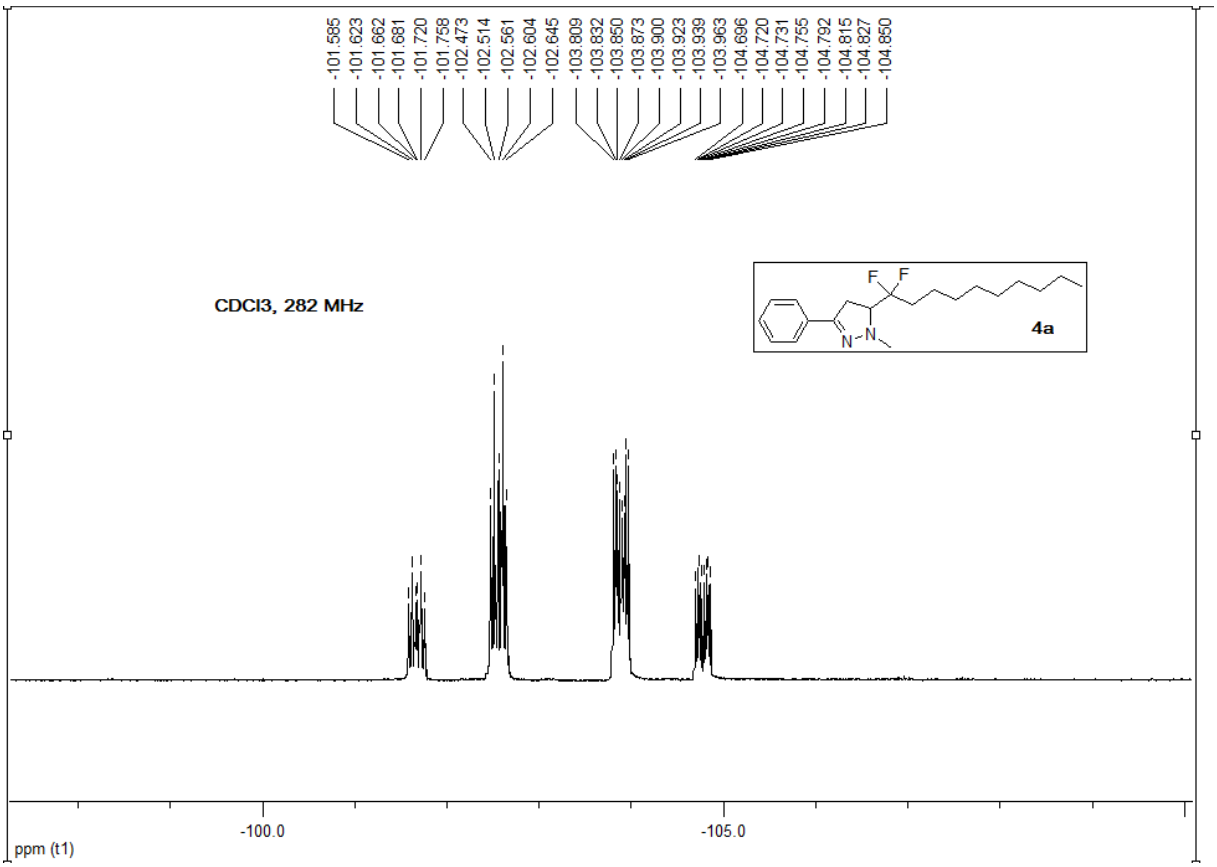

-98.477
CDCl3, 282 MHz
F
F
O
Br
3e
0
-50
-100
-150
-200
ppm (t1)

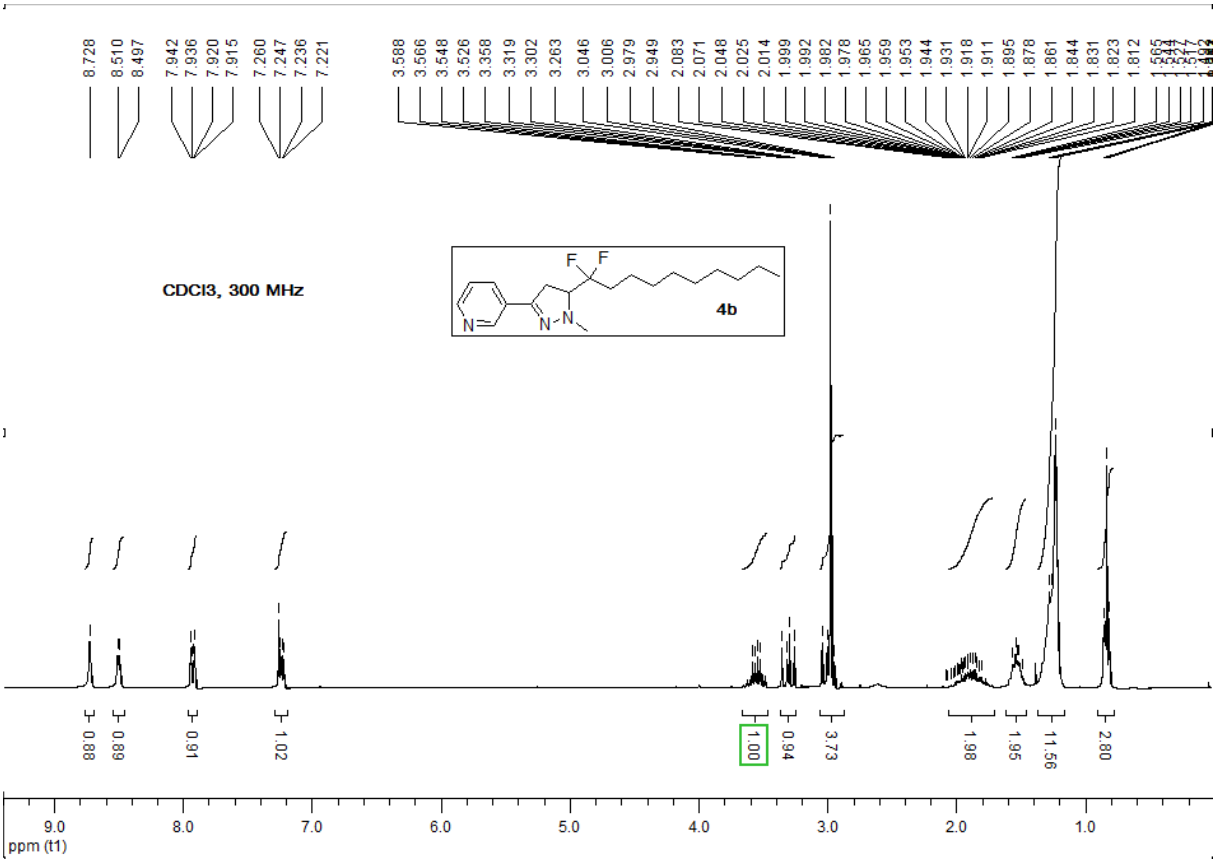

-98.396
-98.403
-98.453
-98.494
-98.501
-98.551
-98.558
CDCl3, 282 MHz
F
F
O
Br
3e
-98.10
-98.20
-98.30
-98.40
-98.50
-98.60
-98.70
-98.80
-98.90
ppm (t1)

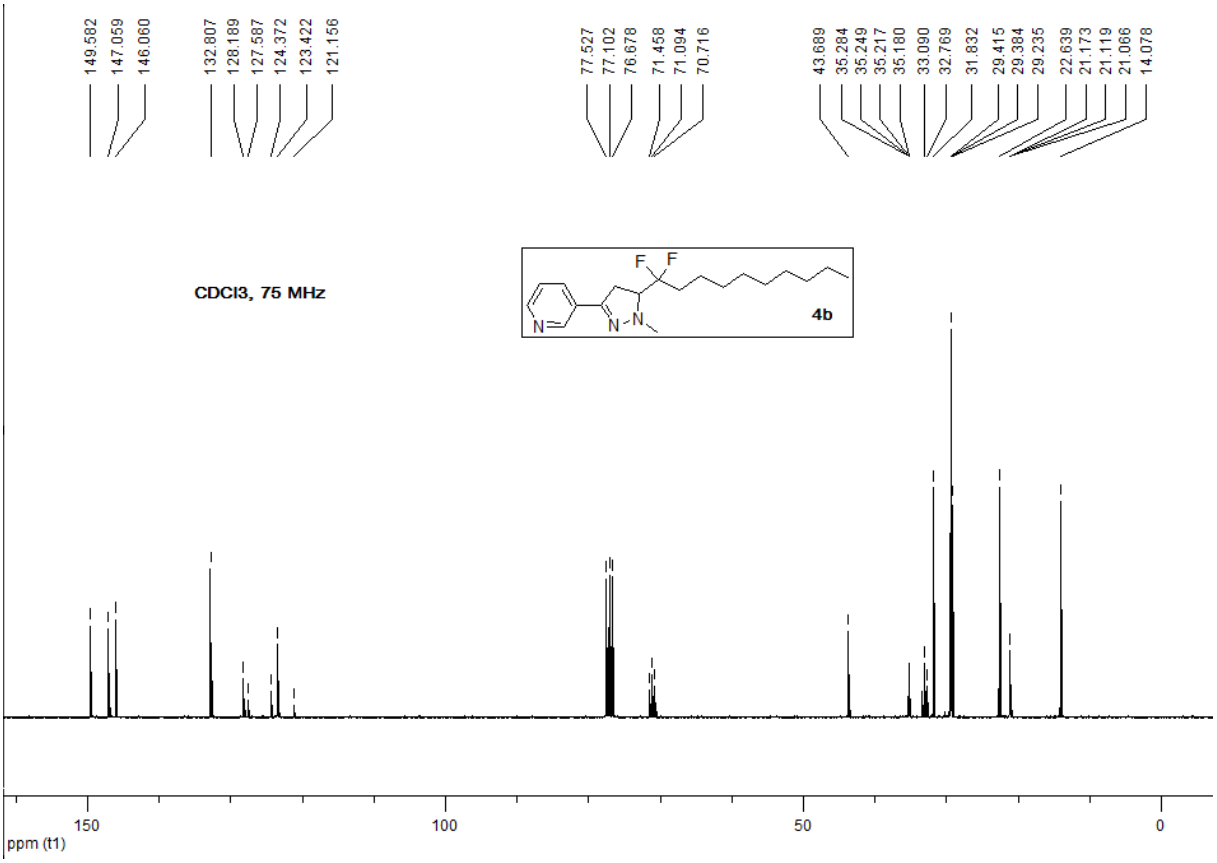

7.623
7.618
7.615
7.388
7.382
7.378
7.373
7.367
7.363
7.359
7.348
7.345
7.341
7.336
7.330
7.328
7.260
3.566
3.549
3.536
3.520
3.391
3.362
3.349
3.320
3.070
3.040
3.027
2.998
2.048
2.035
2.024
2.021
2.009
1.997
1.995
1.986
1.980
1.967
1.952
1.943
1.927
1.917
1.902
1.890
1.882
1.873
1.858
1.849
1.844
1.837
1.834
1.820
1.676
1.623
CDCl3, 400 MHz
F
F
N
N
4a
1.93
2.94
1.00
0.99
3.98
2.02
1.98
12.00
2.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

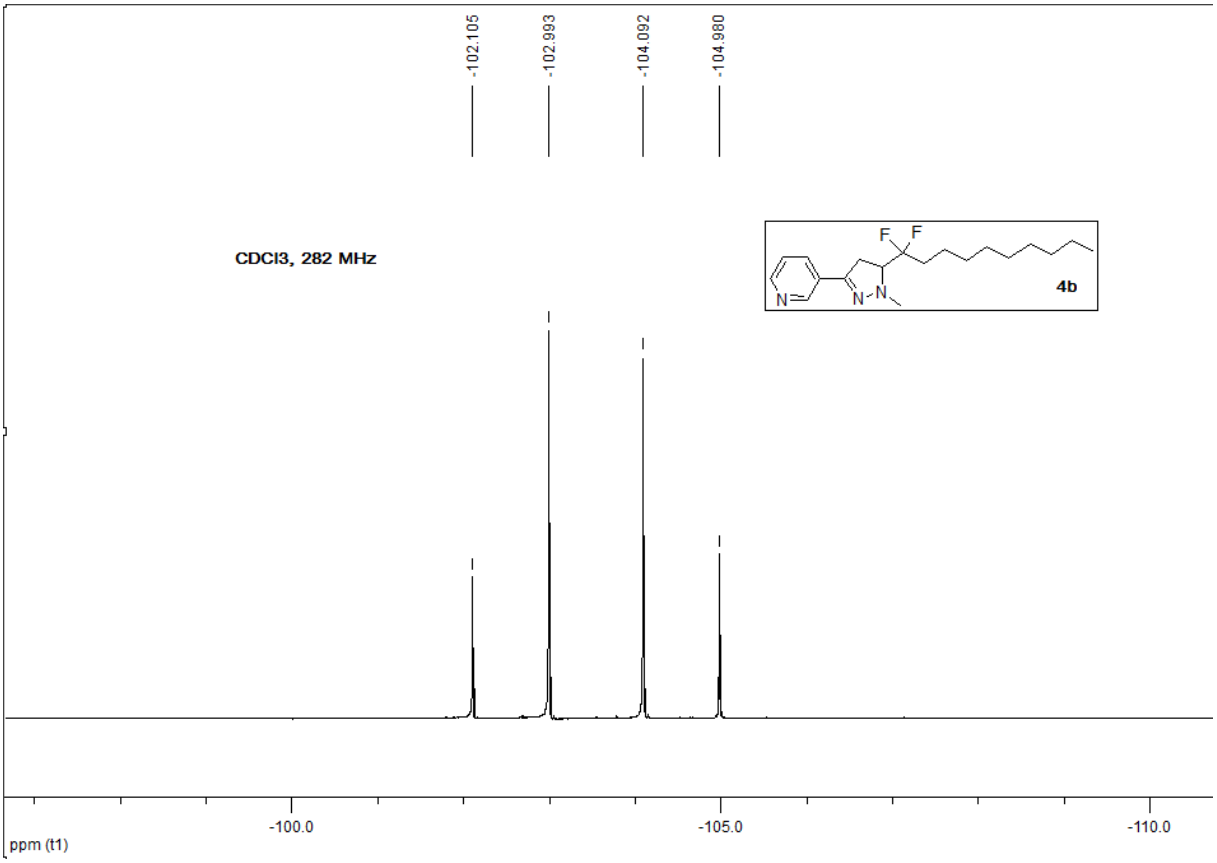

149.321
132.115
128.992
128.670
128.525
127.066
125.952
125.522
124.655
122.245
77.328
77.213
77.011
76.693
71.469
71.194
70.912
43.955
35.794
35.761
33.239
32.998
32.756
31.856
29.439
29.405
29.254
22.654
21.184
21.146
14.075
CDCl3, 100 MHz
F
F
N
N
4a
150
100
50
ppm (t1)

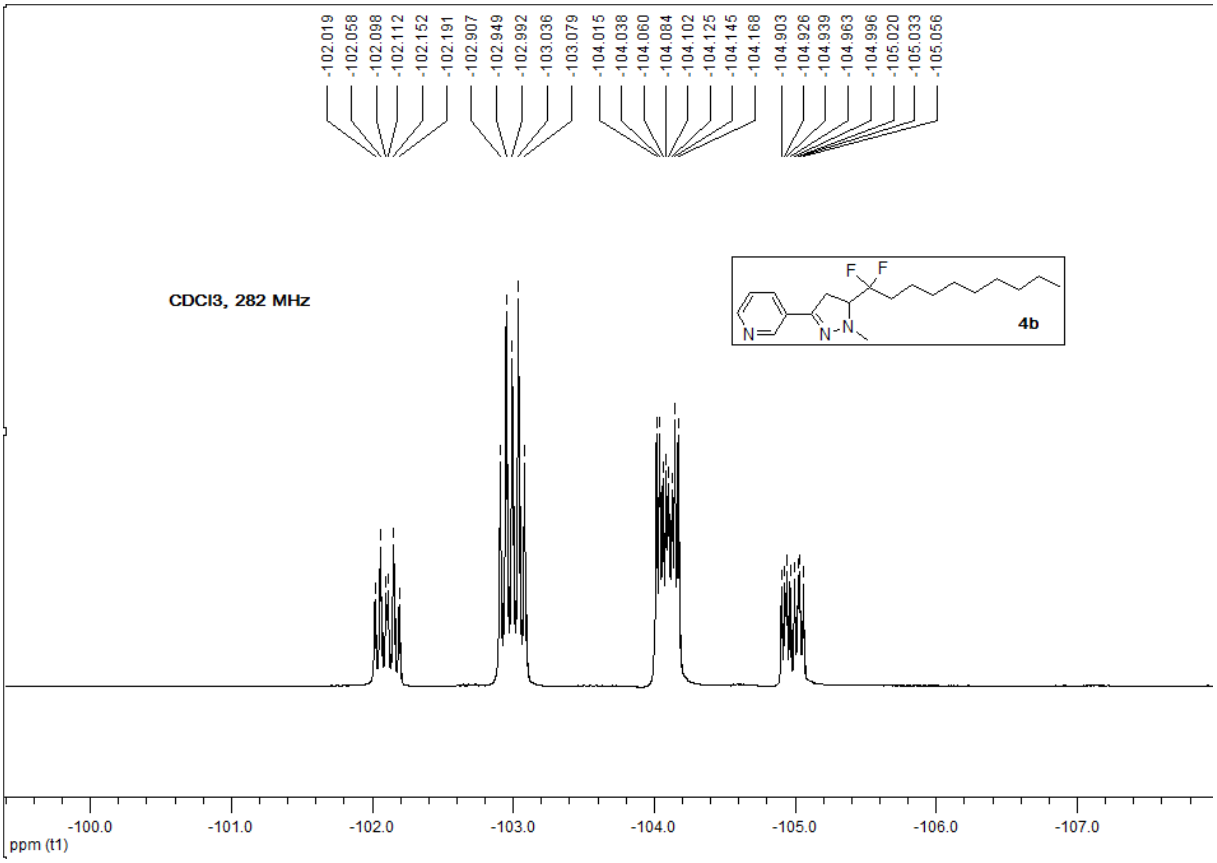

-101.672
-102.559
-103.886
-104.773
CDCl3, 282 MHz
F
F
N
N
4a
-95.0
-100.0
-105.0
-110.0
-115.0
ppm (t1)

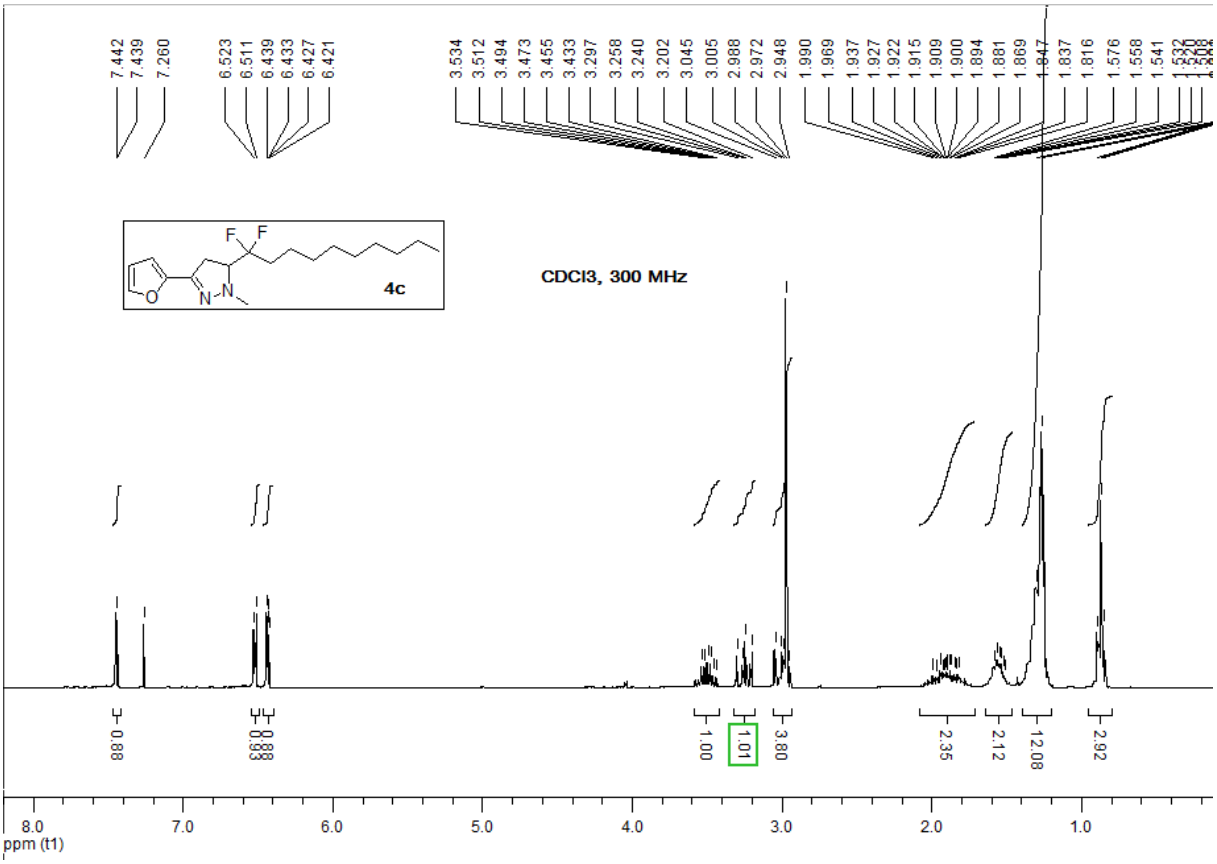

-101.585
-101.623
-101.662
-101.681
-101.720
-101.758
-102.473
-102.514
-102.561
-102.604
-102.645
-103.809
-103.832
-103.850
-103.873
-103.900
-103.923
-103.939
-103.963
-104.696
-104.720
-104.731
-104.755
-104.792
-104.815
-104.827
-104.850
CDCl3, 282 MHz
F
F
N
N
4a
-100.0
-105.0
ppm (t1)

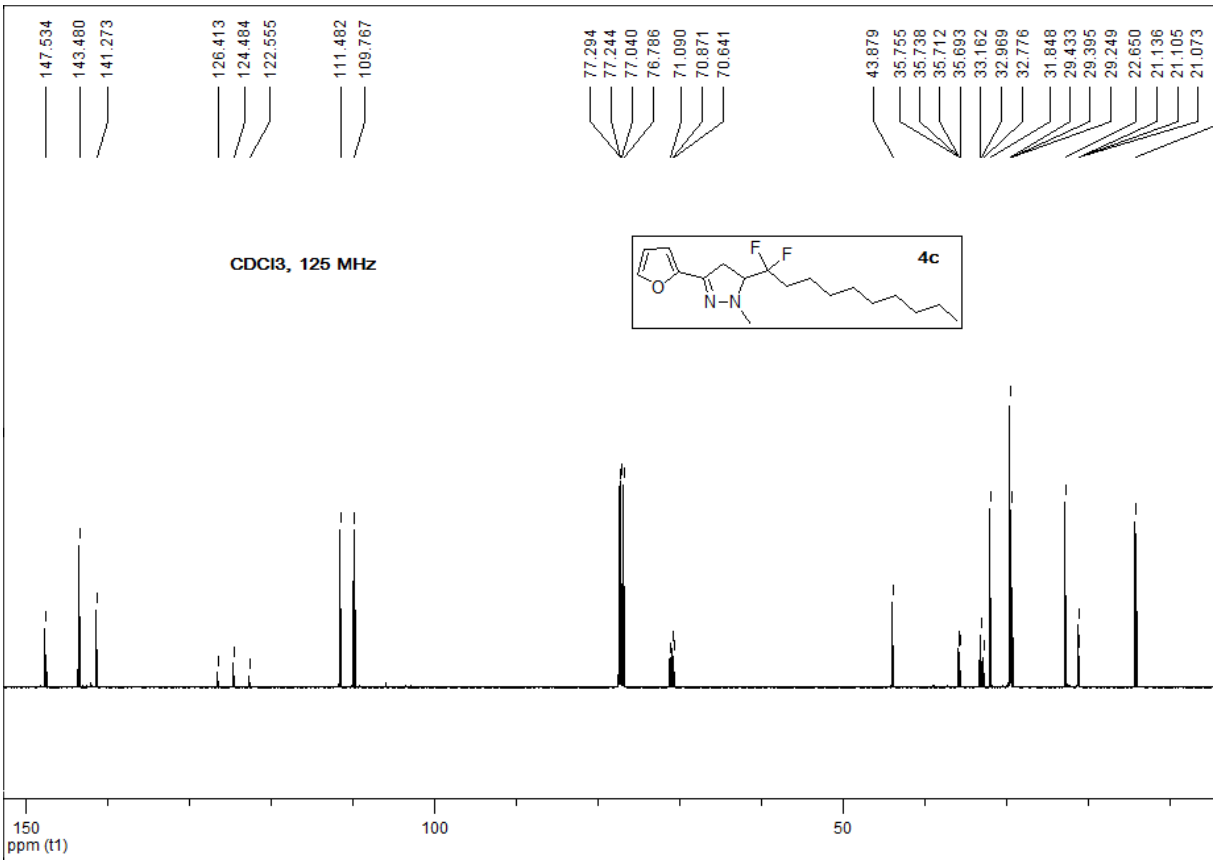

8.728
8.510
8.497
7.942
7.936
7.920
7.915
7.260
7.247
7.236
7.221
3.588
3.566
3.548
3.526
3.358
3.319
3.302
3.263
3.046
3.006
2.979
2.949
2.083
2.071
2.048
2.025
2.014
1.999
1.992
1.982
1.978
1.965
1.959
1.953
1.944
1.931
1.918
1.911
1.895
1.878
1.861
1.844
1.831
1.823
1.812
CDCl3, 300 MHz
F
F
N
N
4b
0.88
0.89
0.91
1.02
1.00
0.94
3.73
1.98
1.95
11.56
2.80
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

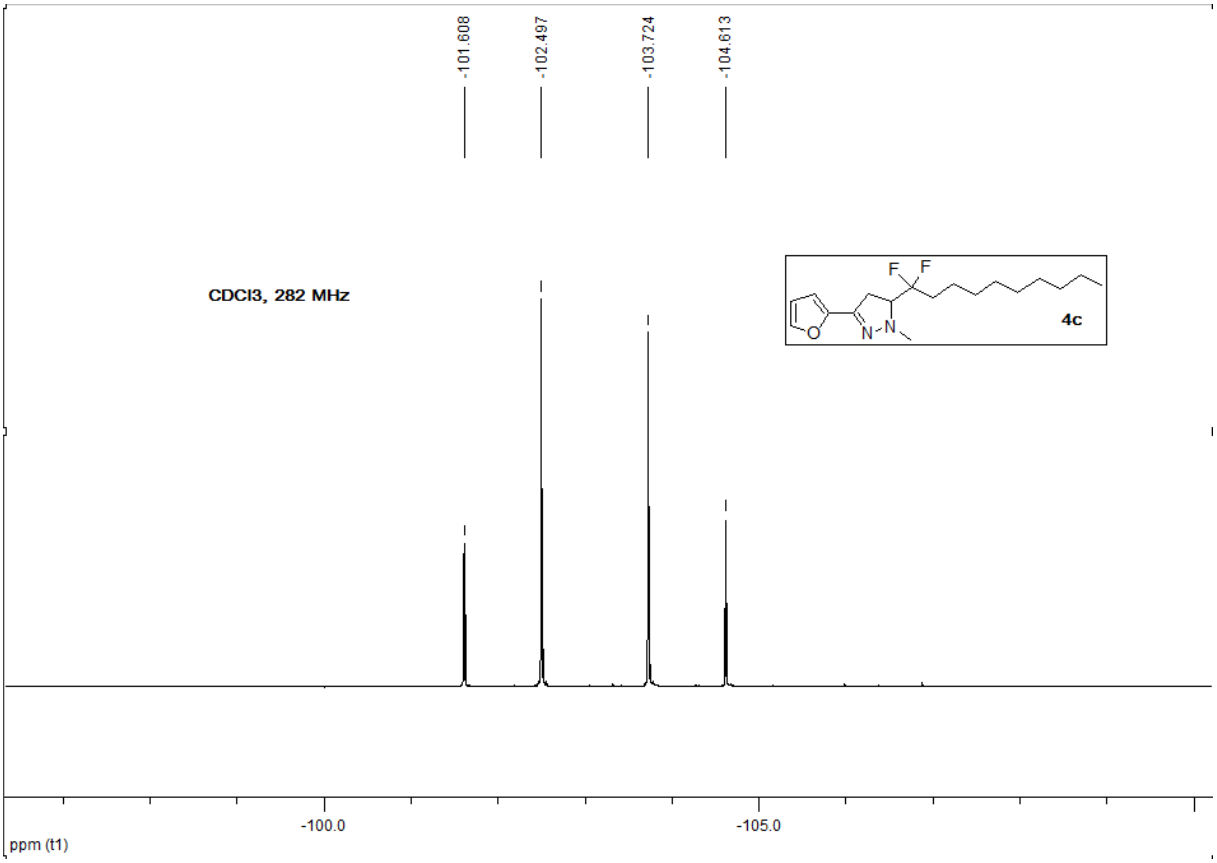

149.582
147.059
146.060
132.807
128.189
127.587
124.372
123.422
121.156
77.527
77.102
76.678
71.458
71.094
70.716
43.689
35.284
35.249
35.217
35.180
33.090
32.769
31.832
29.415
29.384
29.235
22.639
21.173
21.119
21.066
14.078
CDCl3, 75 MHz
F
F
N
N
4b
150
100
50
0
ppm (t1)

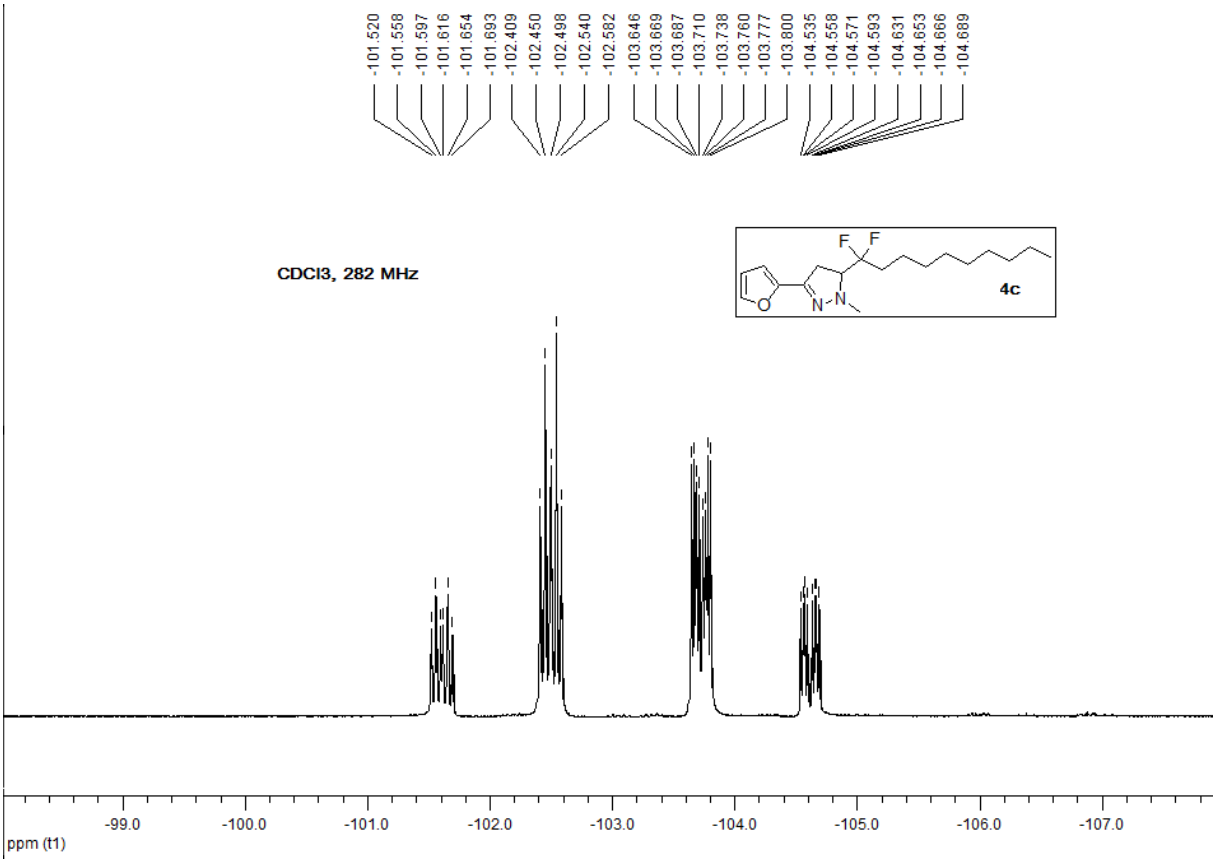

-102.105
-102.993
-104.092
-104.980
CDCl3, 282 MHz
F
F
N
N
N
4b
-100.0
-105.0
-110.0
ppm (t1)

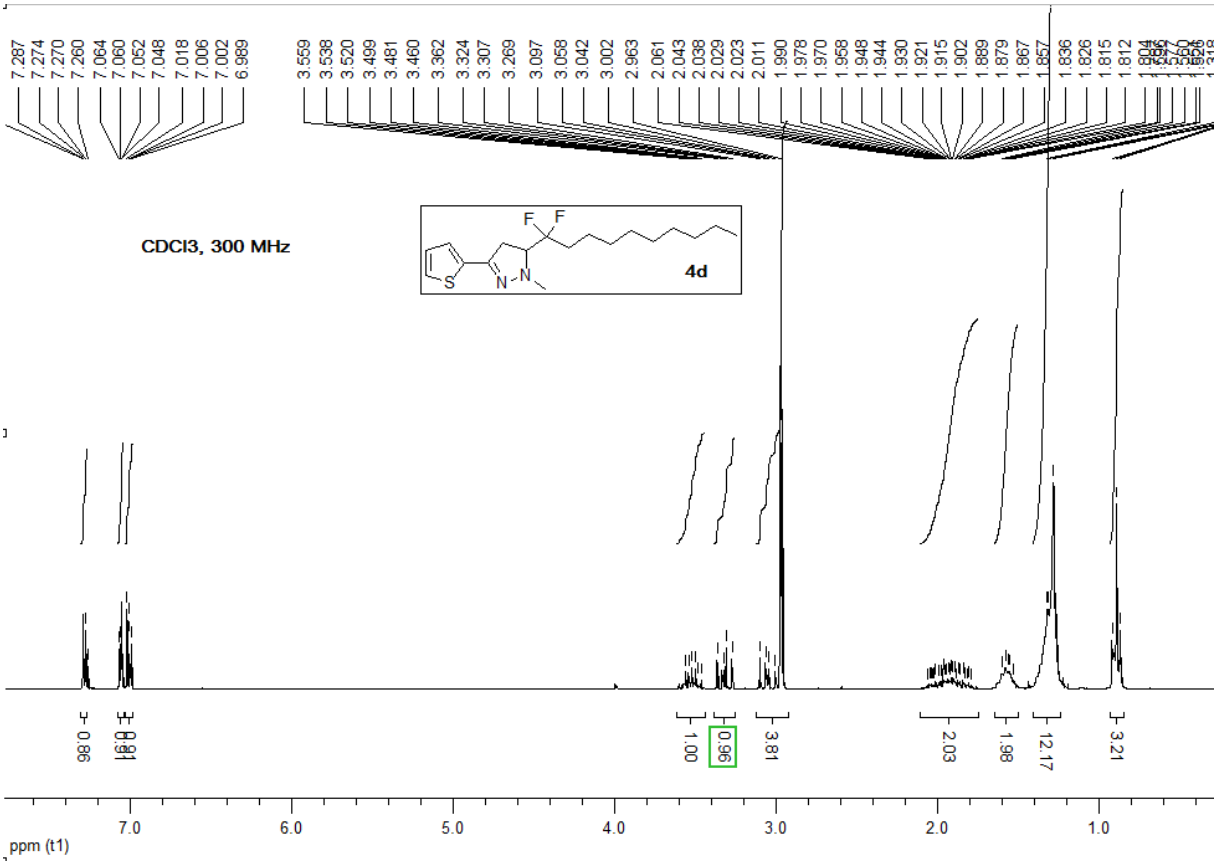

-102.019
-102.058
-102.098
-102.112
-102.152
-102.191
-102.907
-102.949
-102.992
-103.036
-103.079
-104.015
-104.038
-104.060
-104.084
-104.102
-104.125
-104.145
-104.168
-104.903
-104.926
-104.939
-104.963
-104.996
-105.020
-105.033
-105.056
CDCl3, 282 MHz
F
F
N
N
N
4b
-100.0
-101.0
-102.0
-103.0
-104.0
-105.0
-106.0
-107.0
ppm (t1)

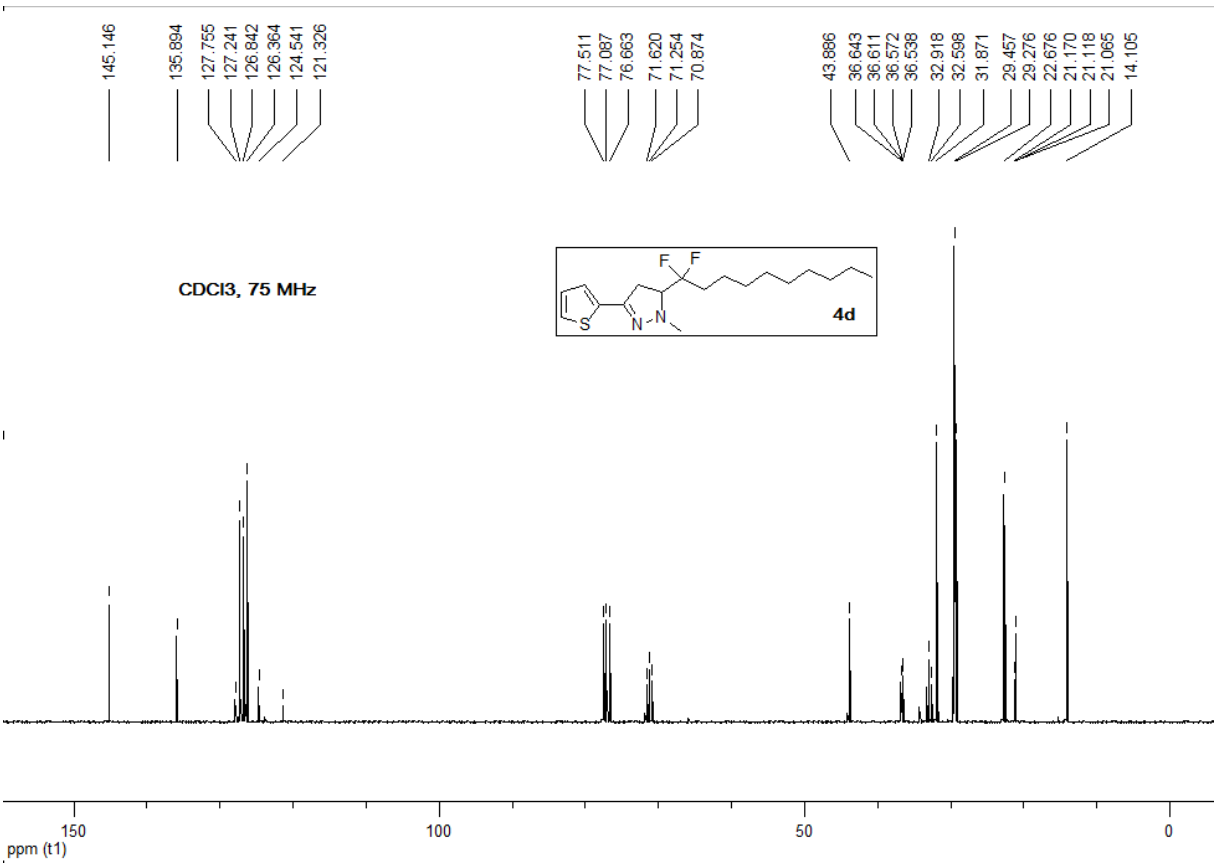

7.442
7.439
7.260
6.523
6.511
6.439
6.433
6.427
6.421
3.534
3.512
3.494
3.473
3.455
3.433
3.297
3.258
3.240
3.202
3.045
3.005
2.988
2.972
2.948
1.990
1.969
1.937
1.927
1.922
1.915
1.909
1.900
1.894
1.881
1.869
1.847
1.837
1.816
1.576
1.558
1.541
F
F
O
N
N
4c
CDCl3, 300 MHz
0.88
0.93
0.88
1.00
1.01
3.80
2.35
2.12
12.08
2.92
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

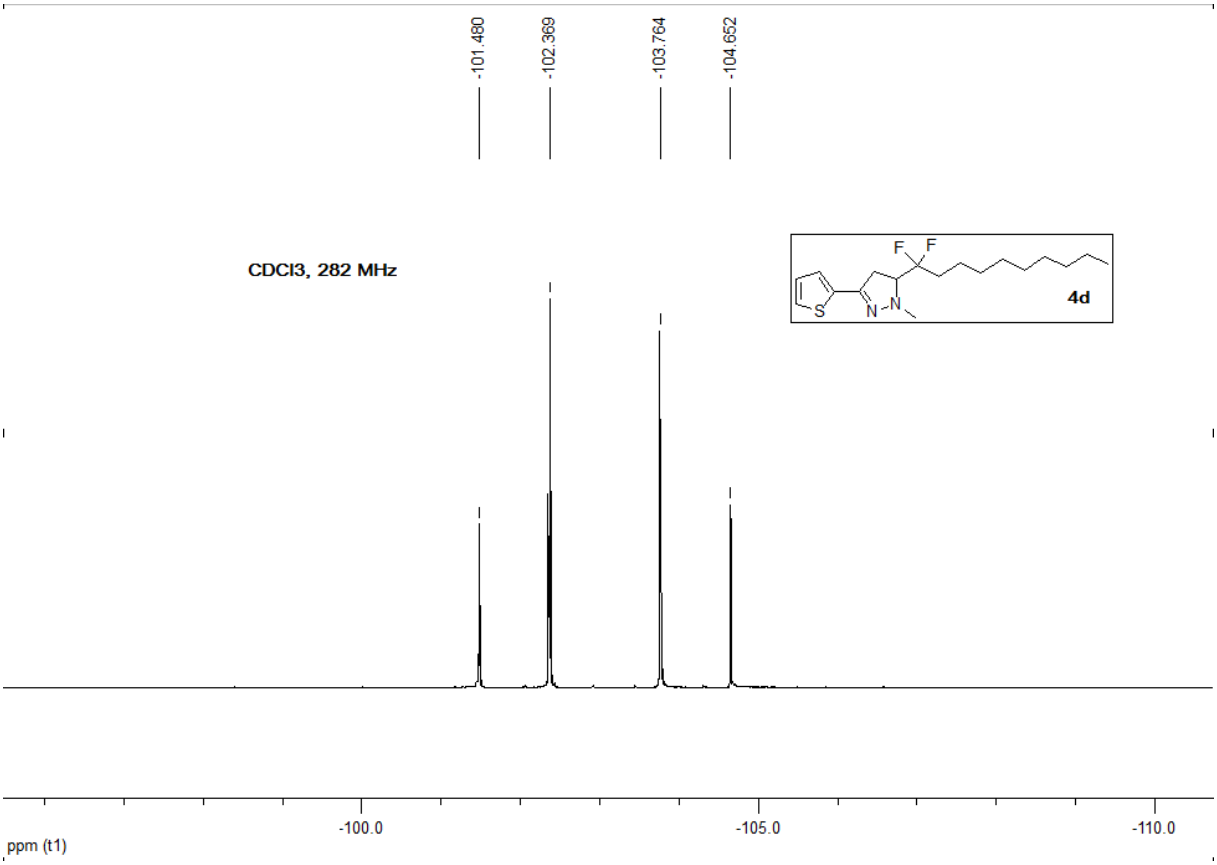

147.534
143.480
141.273
126.413
124.484
122.555
111.482
109.767
77.294
77.244
77.040
76.786
71.090
70.871
70.641
43.879
35.755
35.738
35.712
35.693
33.162
32.969
32.776
31.848
29.433
29.395
29.249
22.650
21.136
21.105
21.073
CDCl3, 125 MHz
F
F
O
N
N
4c
150
100
50
ppm (t1)

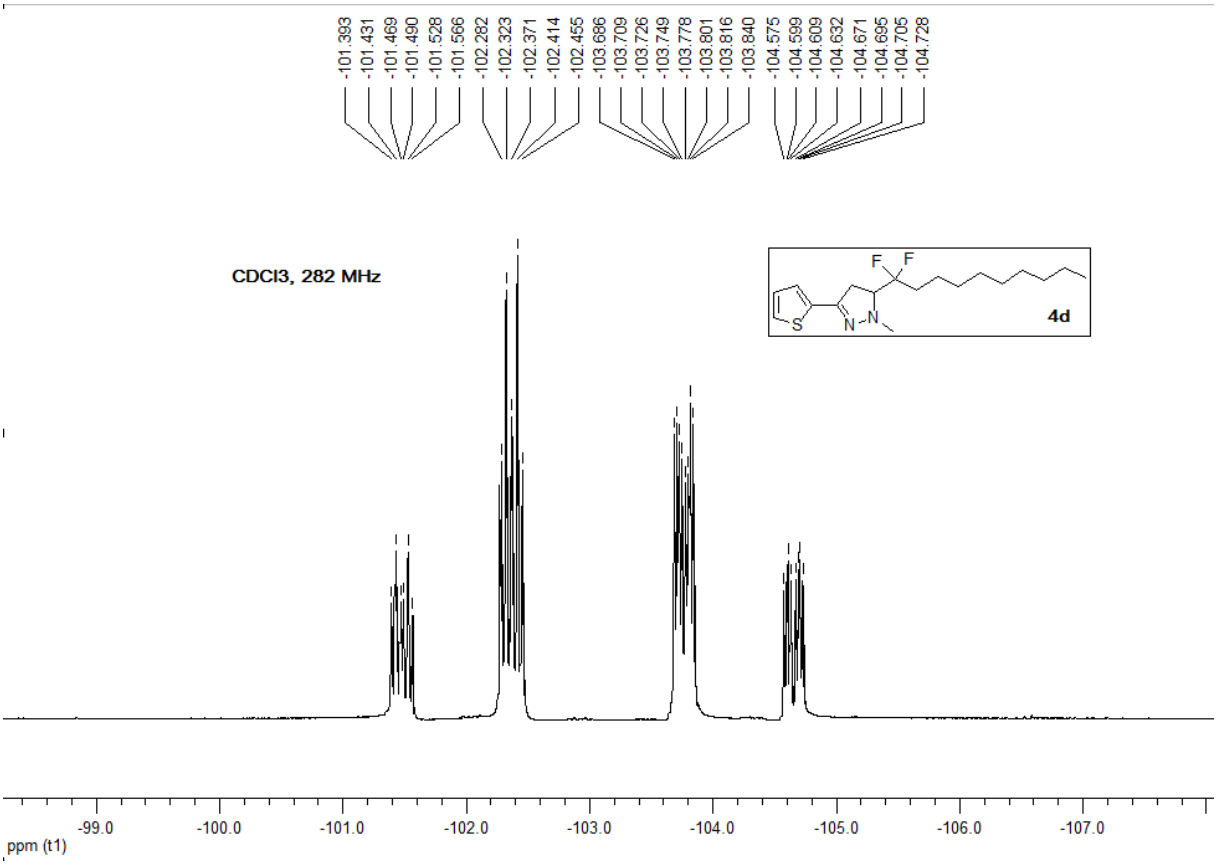

-101.608
-102.497
-103.724
-104.613
CDCl3, 282 MHz
F
F
O
N
N
4c
-100.0
-105.0
ppm (t1)

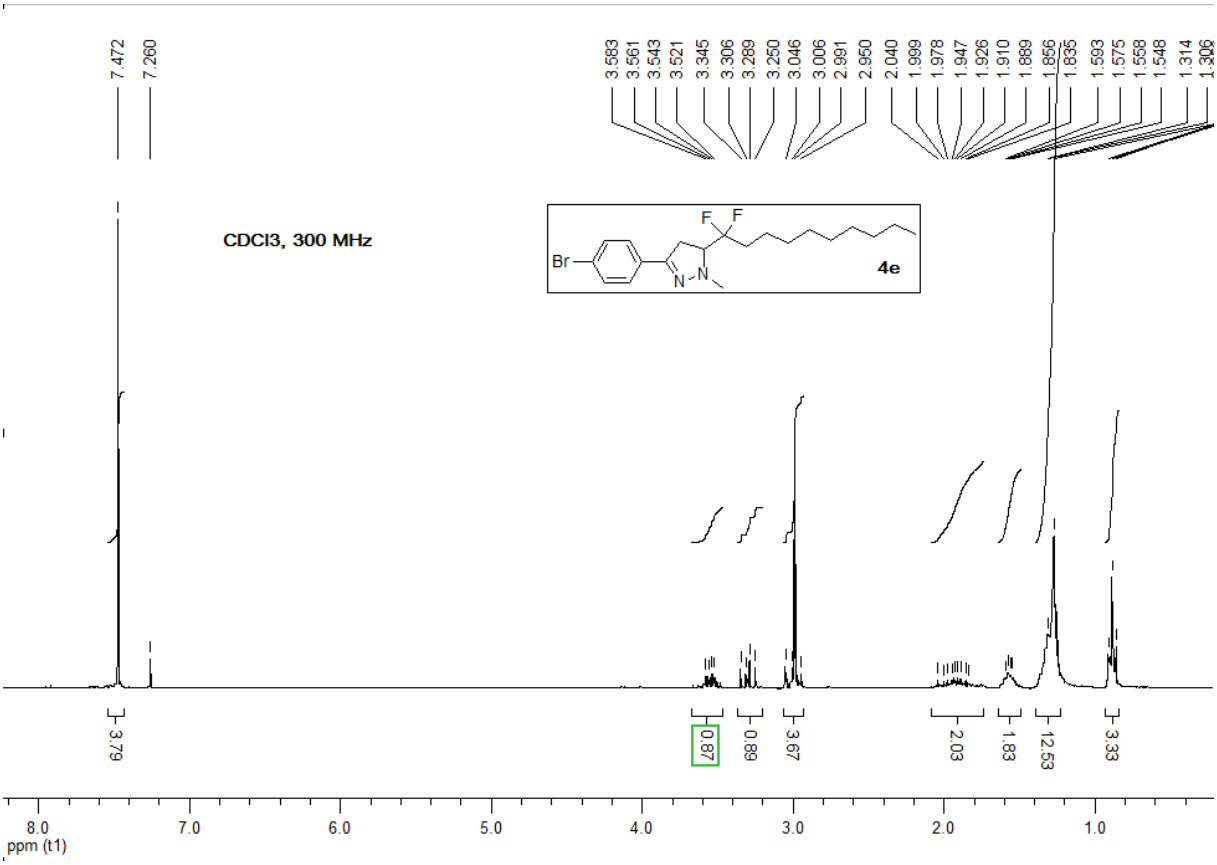

-101.520
-101.558
-101.597
-101.616
-101.654
-101.693
-102.409
-102.450
-102.498
-102.540
-102.582
-103.646
-103.669
-103.687
-103.710
-103.738
-103.760
-103.777
-103.800
-104.535
-104.558
-104.571
-104.593
-104.631
-104.653
-104.666
-104.689
CDCl3, 282 MHz
F
F
O
N
N
4c
-99.0
-100.0
-101.0
-102.0
-103.0
-104.0
-105.0
-106.0
-107.0
ppm (t1)

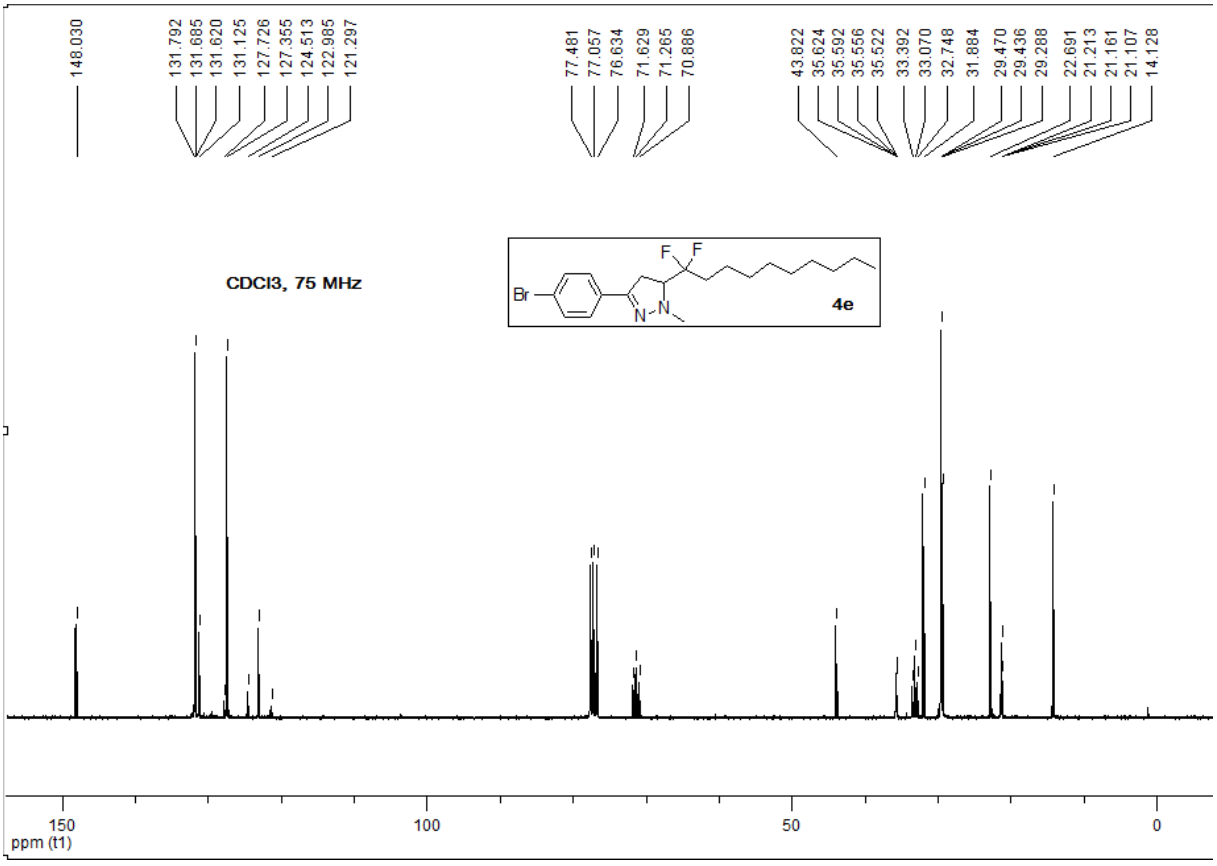

CDCl3, 300 MHz
4d
F F
S
N N
7.287 7.274 7.270 7.260 7.064 7.060 7.052 7.048 7.018 7.006 7.002 6.989
3.559 3.538 3.520 3.499 3.481 3.460 3.362 3.324 3.307 3.269 3.097 3.058 3.042 3.002 2.963 2.061 2.043 2.038 2.029 2.023 2.011 1.990 1.978 1.970 1.958 1.948 1.944 1.930 1.921 1.915 1.902 1.889 1.879 1.867 1.857 1.836 1.826 1.815 1.812
0.86 0.91 1.00 0.96 3.81 2.03 1.98 12.17 3.21
7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm (t1)

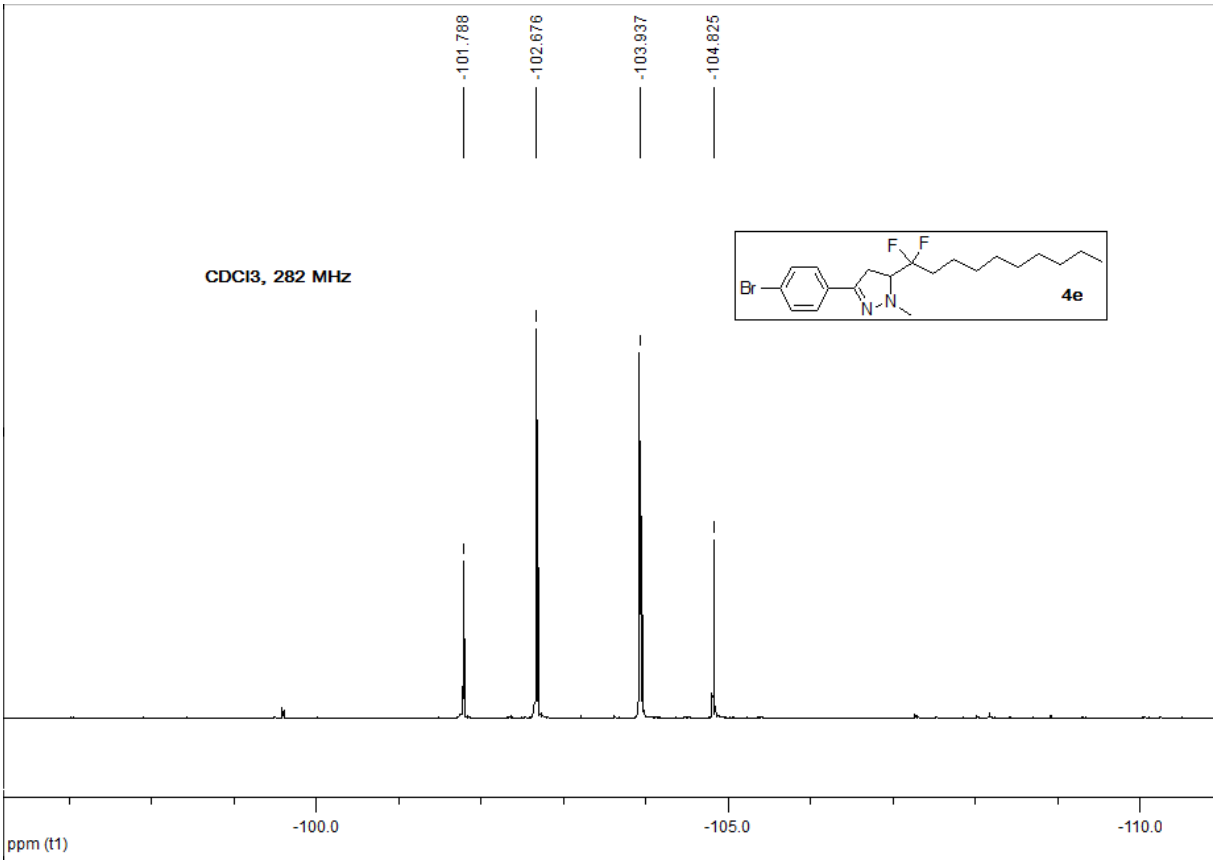

CDCl3, 75 MHz
4d
F F
S
N N
145.146 135.894 127.755 127.241 126.842 126.364 124.541 121.326
77.511 77.087 76.663 71.620 71.254 70.874
43.886 36.643 36.611 36.572 36.538 32.918 32.598 31.871 29.457 29.276 22.676 21.170 21.118 21.065 14.105
150 100 50 0
ppm (t1)

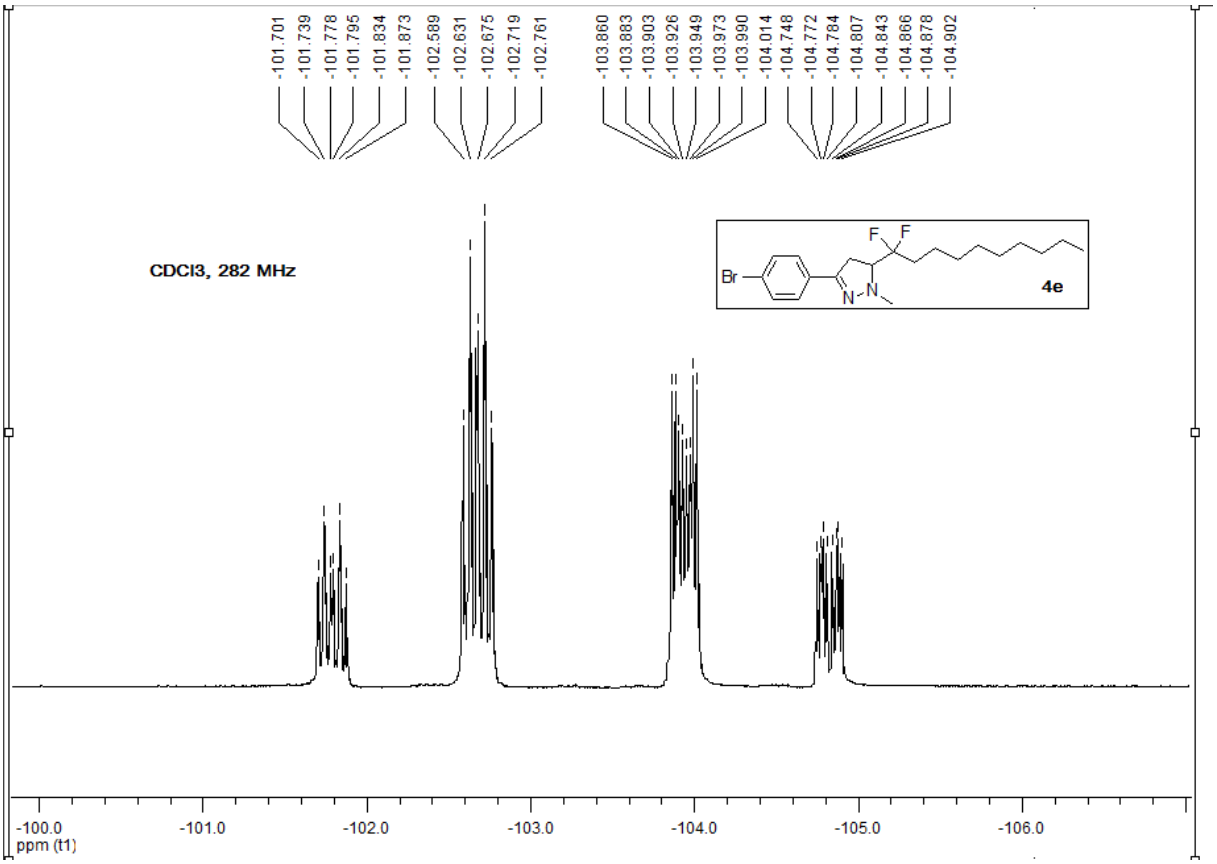

-101.480
-102.369
-103.764
-104.652
CDCl3, 282 MHz
F
F
S
N
N
4d
-100.0
-105.0
-110.0
ppm (t1)

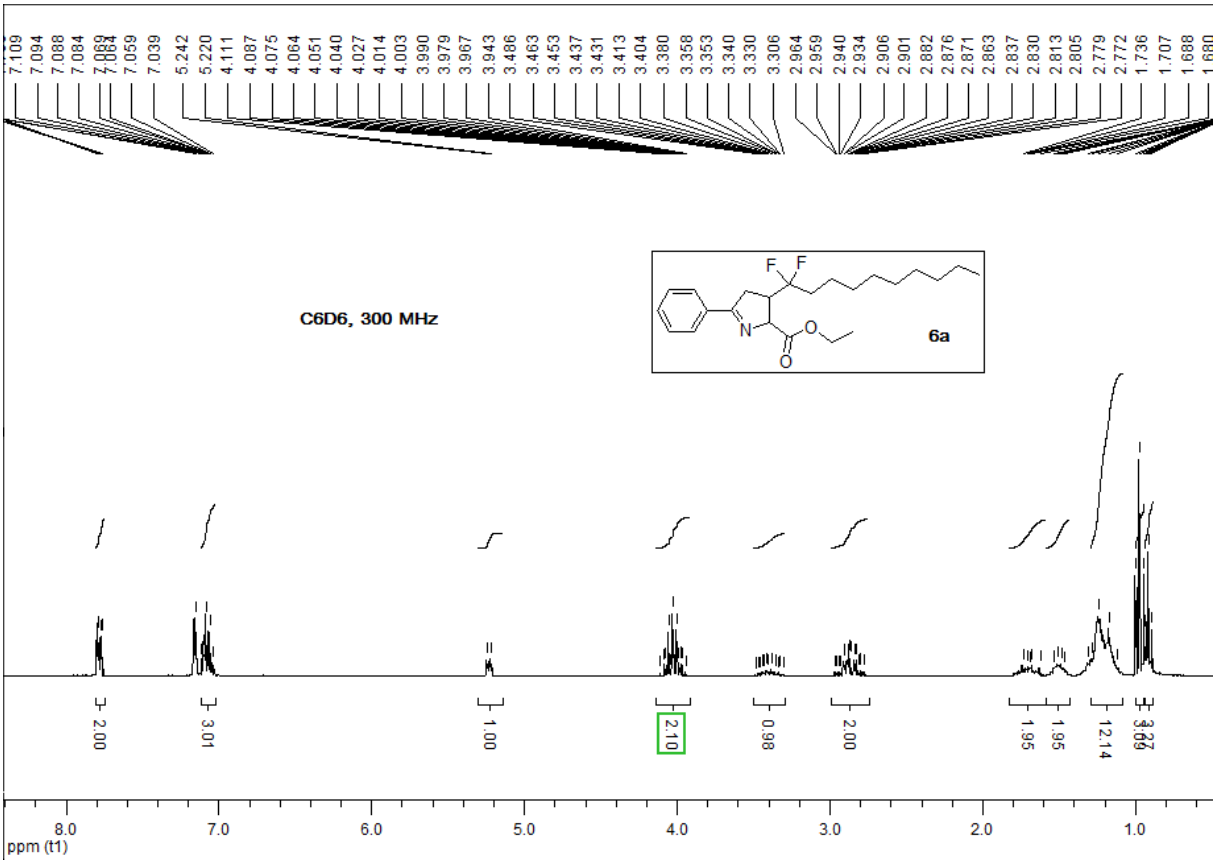

-101.393
-101.431
-101.469
-101.490
-101.528
-101.566
-102.282
-102.323
-102.371
-102.414
-102.455
-103.686
-103.709
-103.726
-103.749
-103.778
-103.801
-103.816
-103.840
-104.575
-104.599
-104.609
-104.632
-104.671
-104.695
-104.705
-104.728
CDCl3, 282 MHz
F
F
S
N
N
4d
-99.0
-100.0
-101.0
-102.0
-103.0
-104.0
-105.0
-106.0
-107.0
ppm (t1)

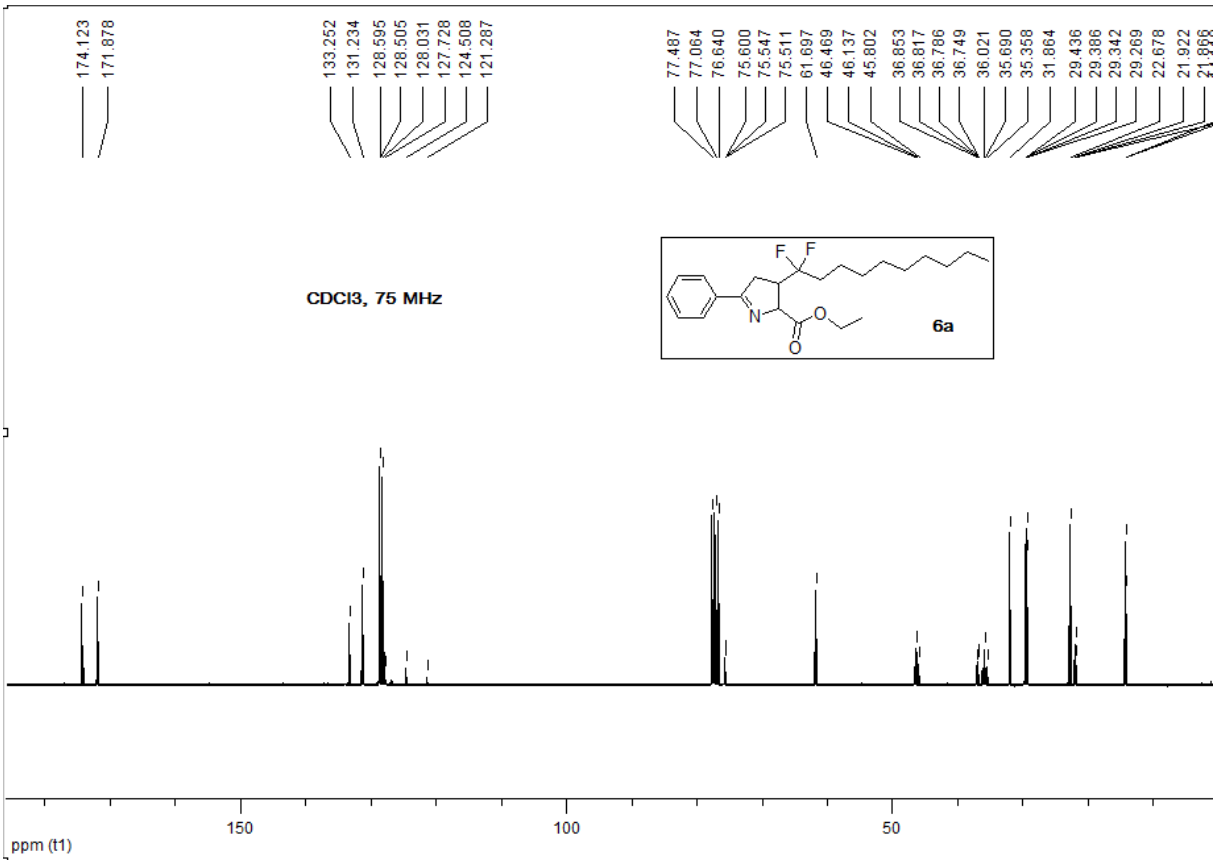

7.472
7.260
3.583
3.561
3.543
3.521
3.345
3.306
3.289
3.250
3.046
3.006
2.991
2.950
2.040
1.999
1.978
1.947
1.926
1.910
1.889
1.856
1.835
1.593
1.575
1.558
1.548
1.314
1.306
CDCl3, 300 MHz
F
F
Br
N
N
4e
3.79
0.87
0.89
3.67
2.03
1.83
12.53
3.33
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

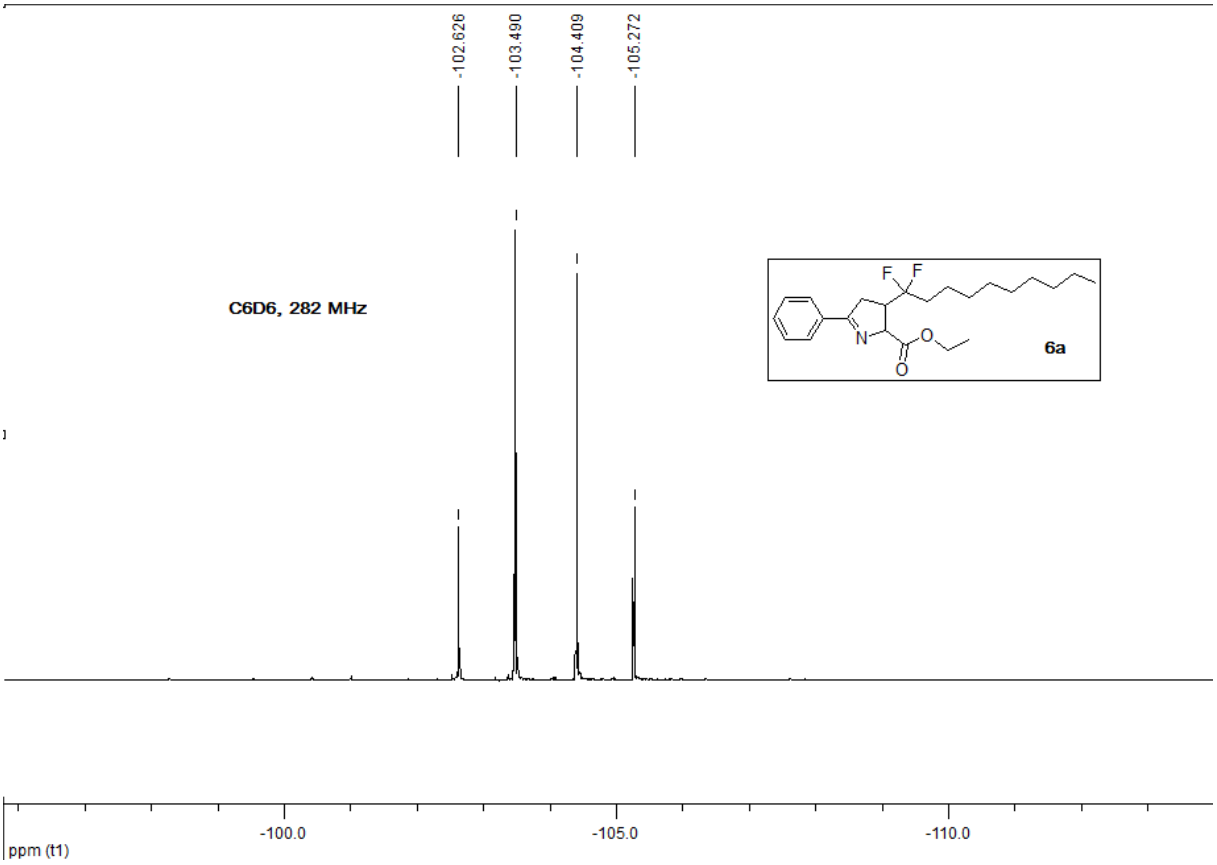

148.030
131.792
131.685
131.620
131.125
127.726
127.355
124.513
122.985
121.297
77.481
77.057
76.634
71.629
71.265
70.886
43.822
35.624
35.592
35.556
35.522
33.392
33.070
32.748
31.884
29.470
29.436
29.288
22.691
21.213
21.161
21.107
14.128
CDCl3, 75 MHz
F
F
Br
N
N
4e
150
100
50
0
ppm (t1)

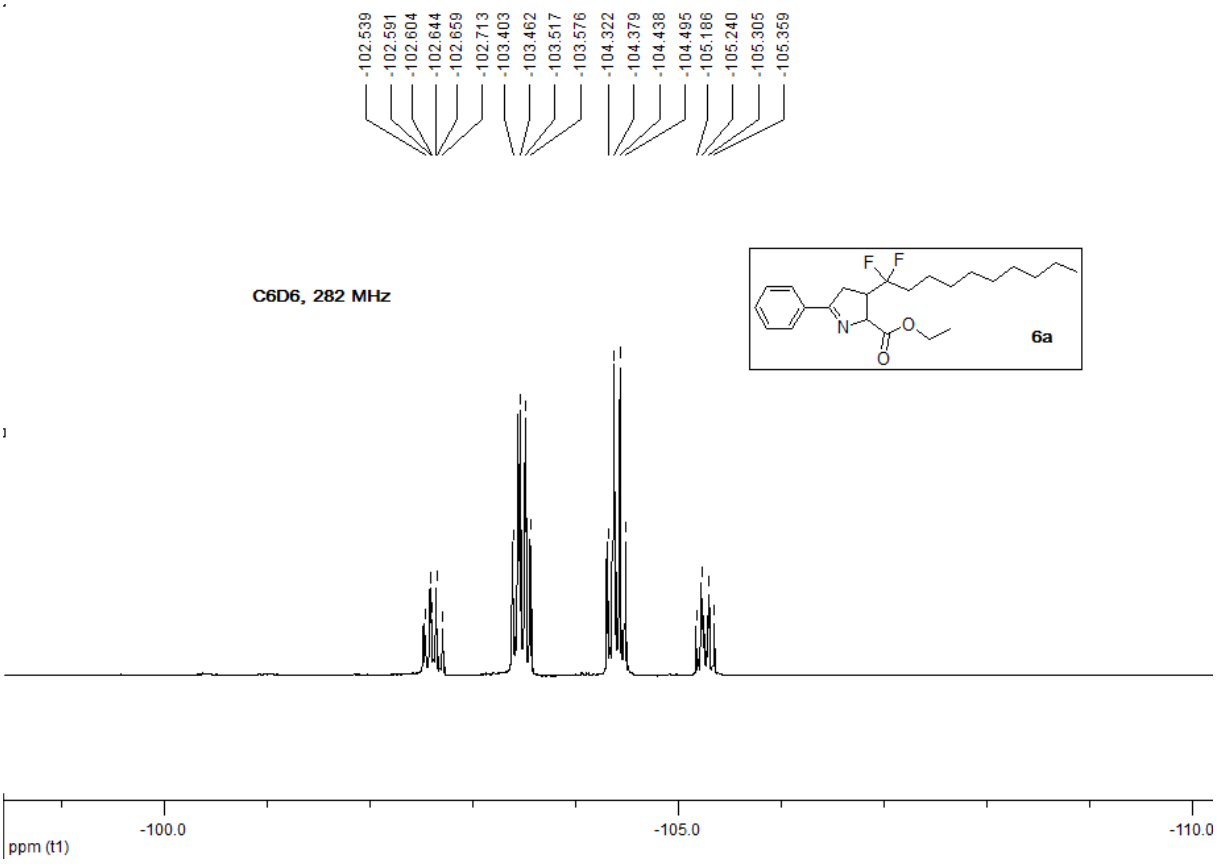

-101.788
-102.676
-103.937
-104.825
CDCl3, 282 MHz
F
F
Br
N
N
4e
-100.0
-105.0
-110.0
ppm (t1)

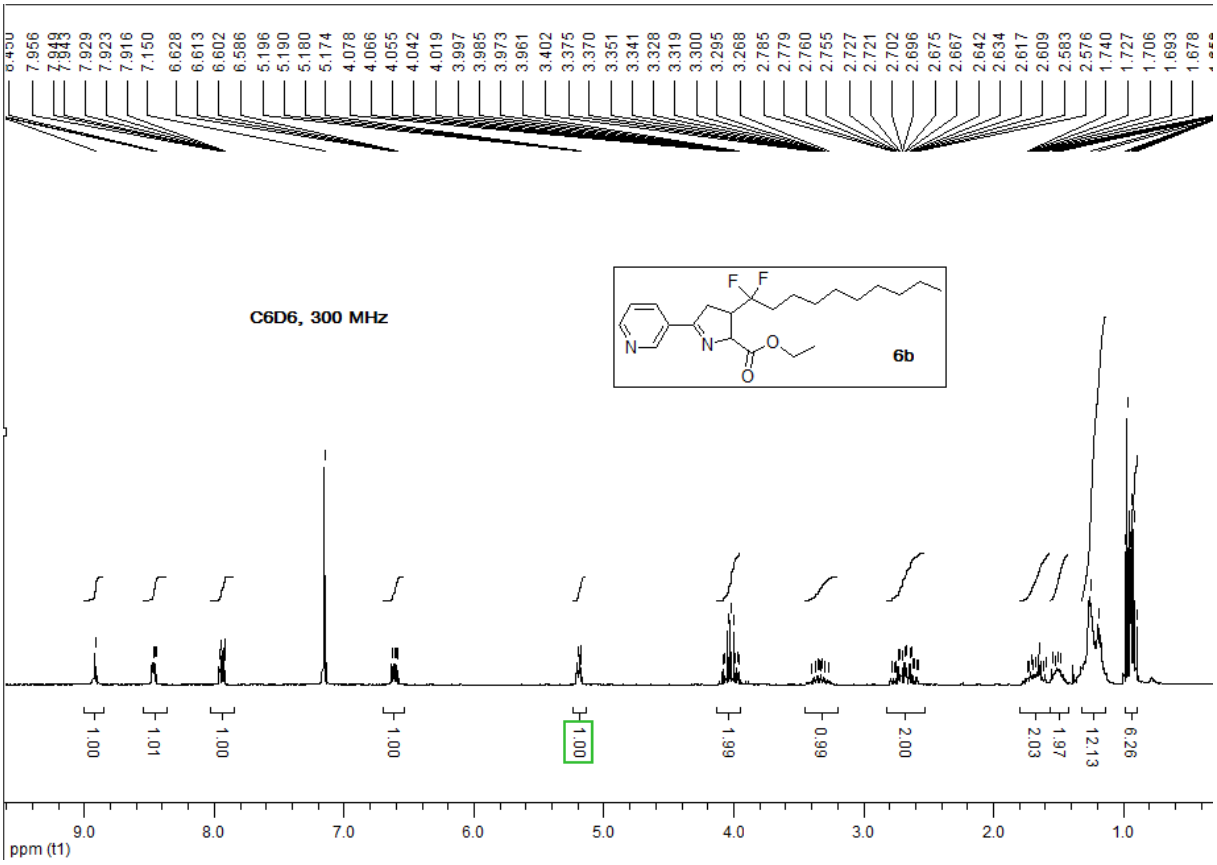

-101.701
-101.739
-101.778
-101.795
-101.834
-101.873
-102.589
-102.631
-102.675
-102.719
-102.761
-103.860
-103.883
-103.903
-103.926
-103.949
-103.973
-103.990
-104.014
-104.748
-104.772
-104.784
-104.807
-104.843
-104.866
-104.878
-104.902
CDCl3, 282 MHz
F
F
Br
N
N
4e
-100.0
-101.0
-102.0
-103.0
-104.0
-105.0
-106.0
ppm (t1)

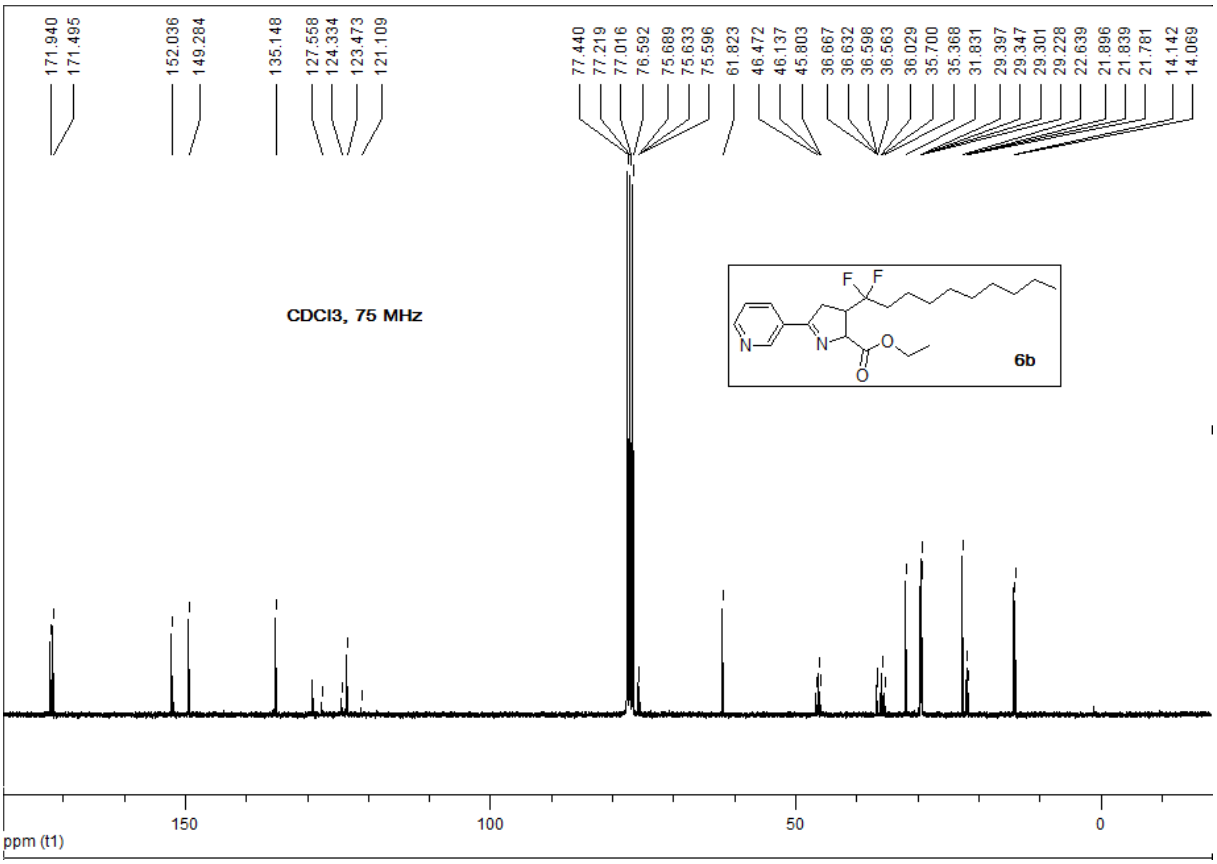

C6D6, 300 MHz
6a
ppm (t1)

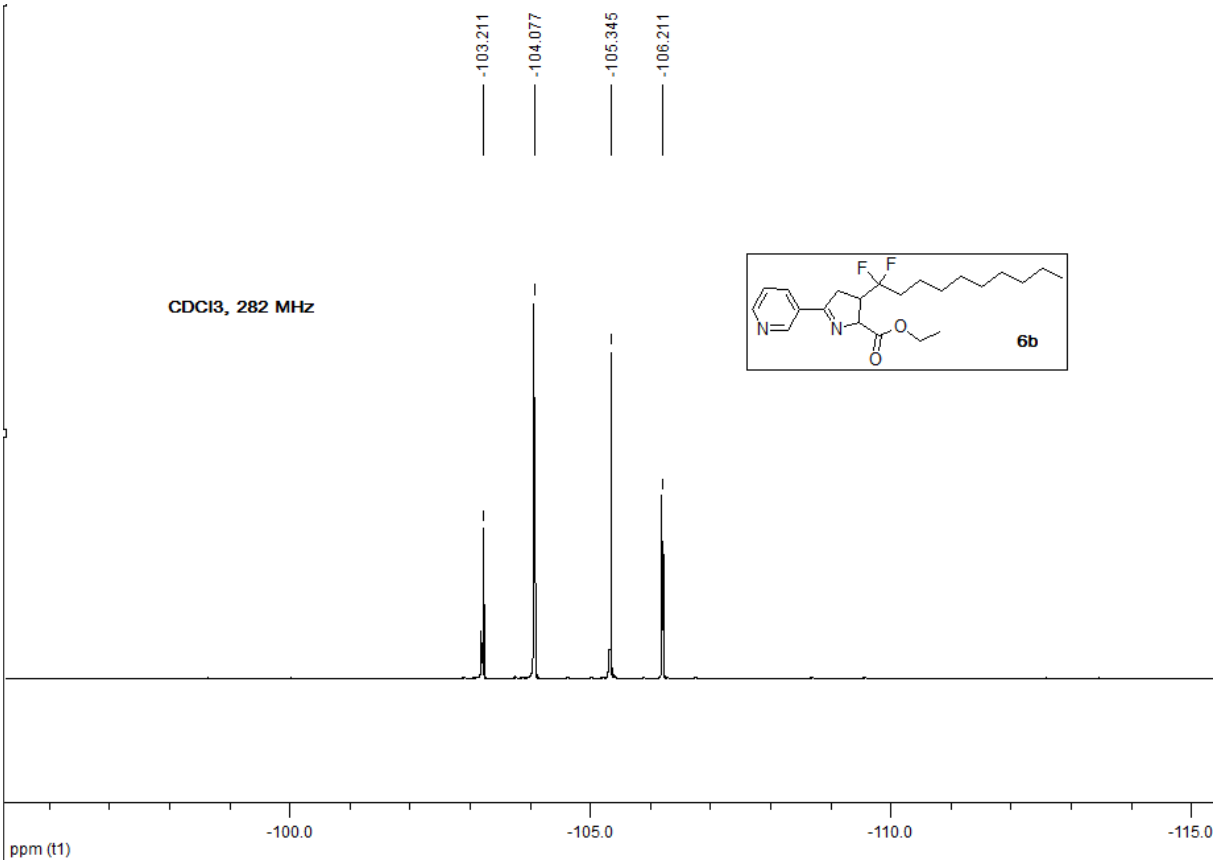

CDCl3, 75 MHz
6a
ppm (t1)

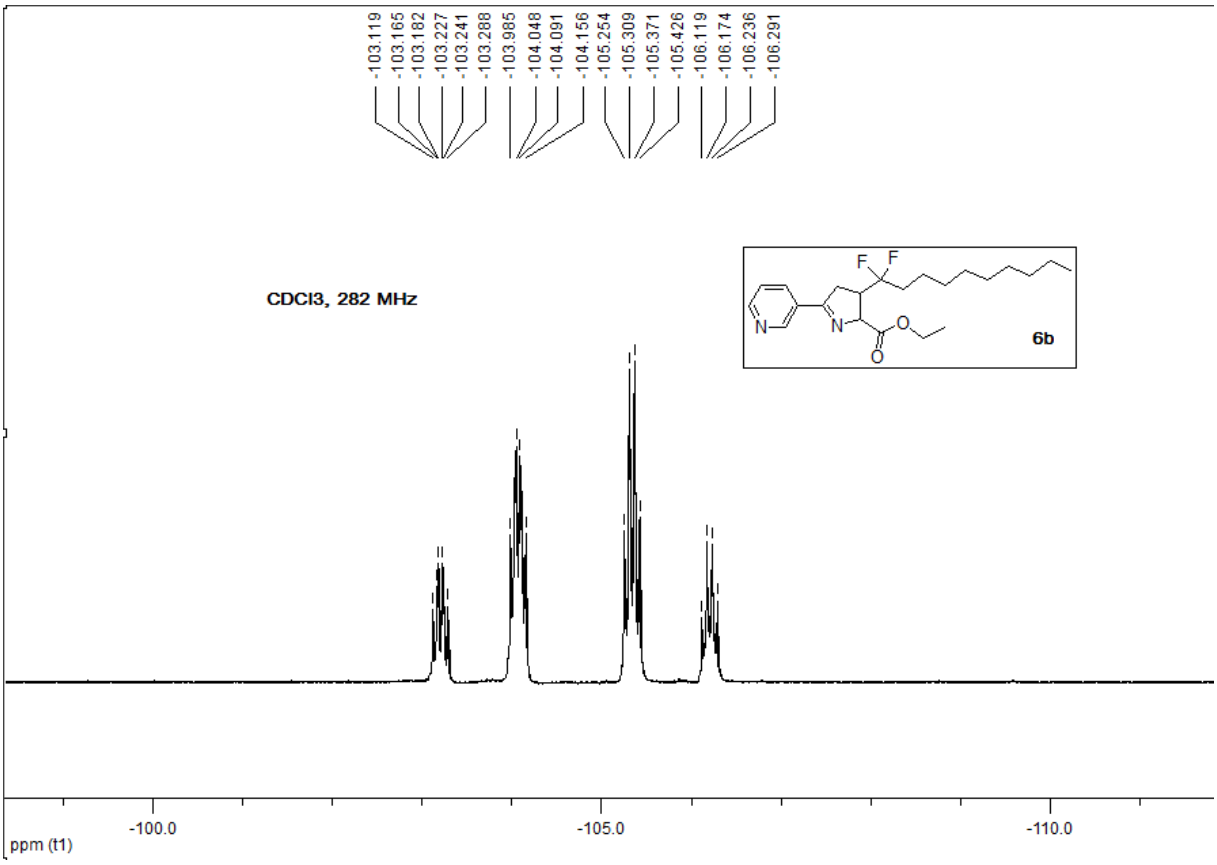

-102.626
-103.490
-104.409
-105.272
C6D6, 282 MHz
F
F
N
O
O
6a
-100.0
-105.0
-110.0
ppm (t1)

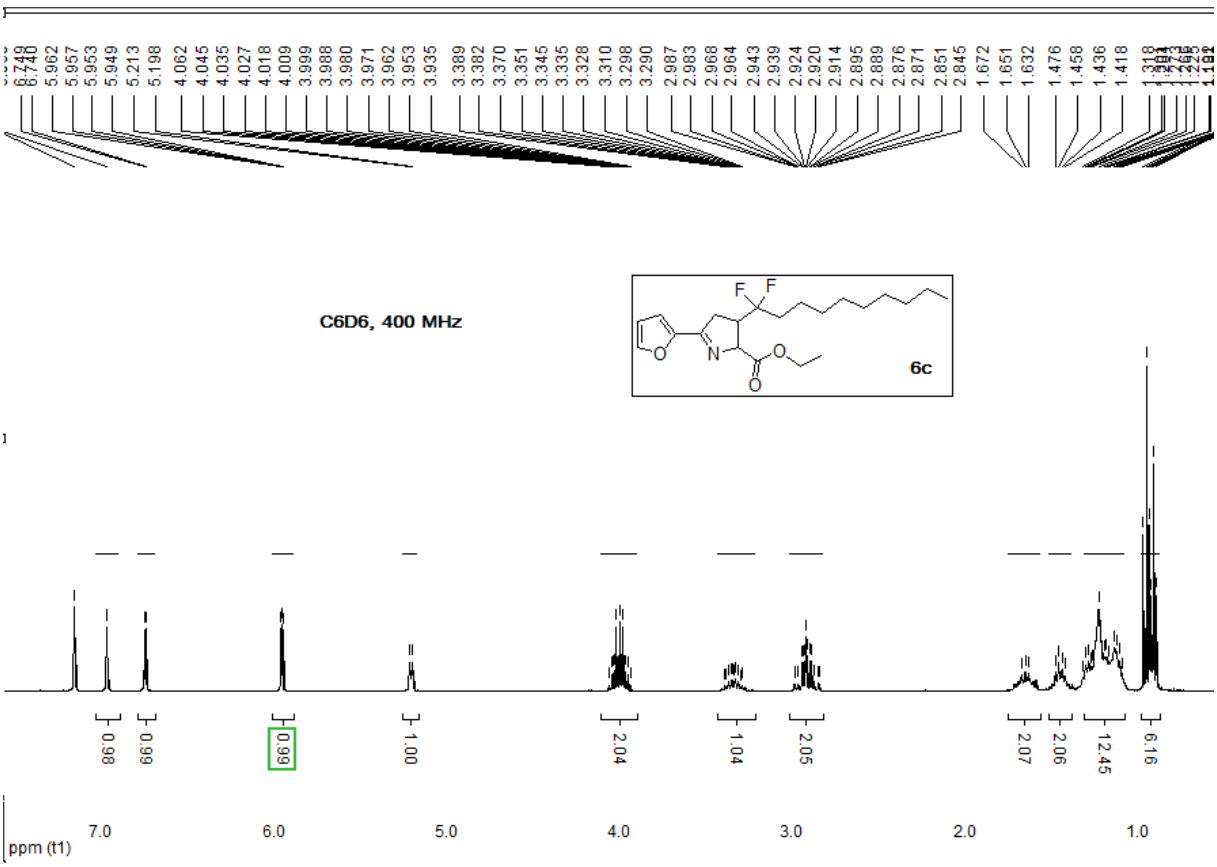

-102.539
-102.591
-102.604
-102.644
-102.659
-102.713
-103.403
-103.462
-103.517
-103.576
-104.322
-104.379
-104.438
-104.495
-105.186
-105.240
-105.305
-105.359
C6D6, 282 MHz
F
F
N
O
O
6a
-100.0
-105.0
-110.0
ppm (t1)

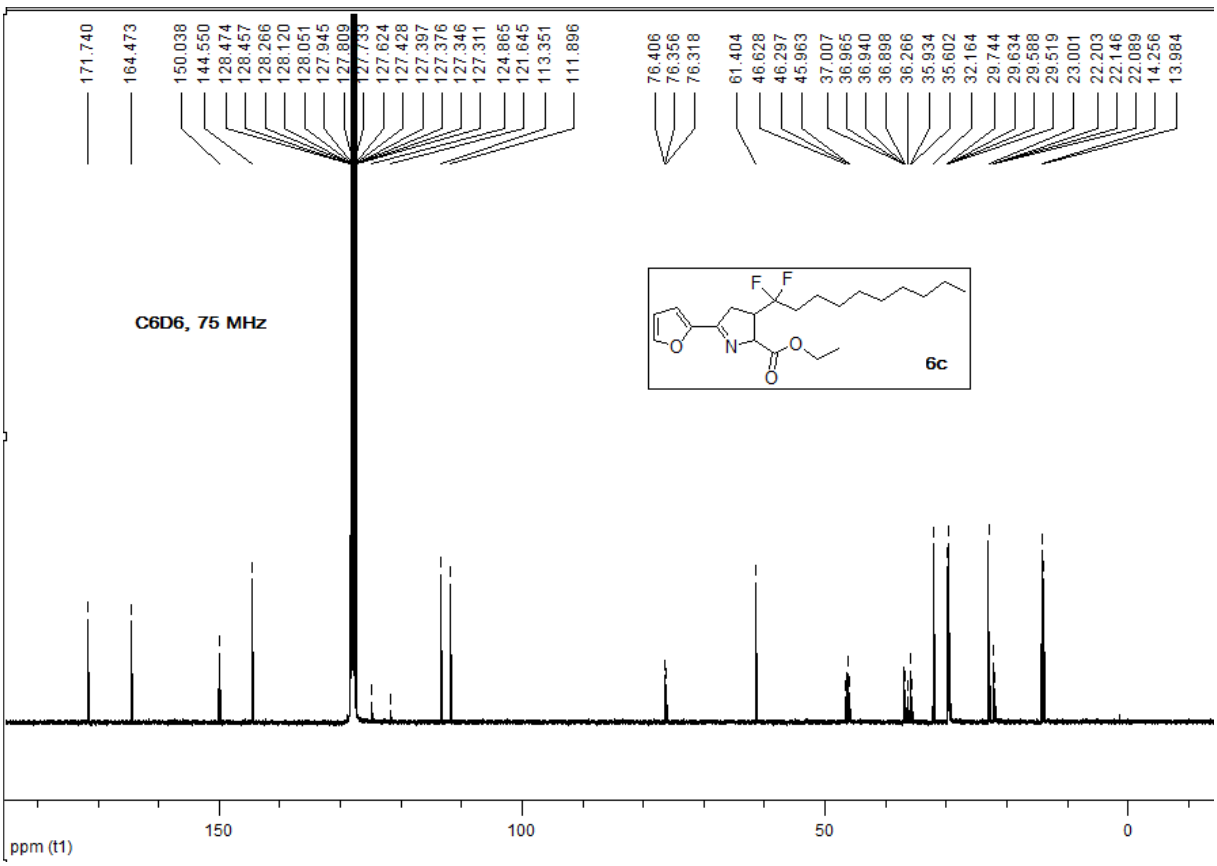

C6D6, 300 MHz
6b
ppm (t1)

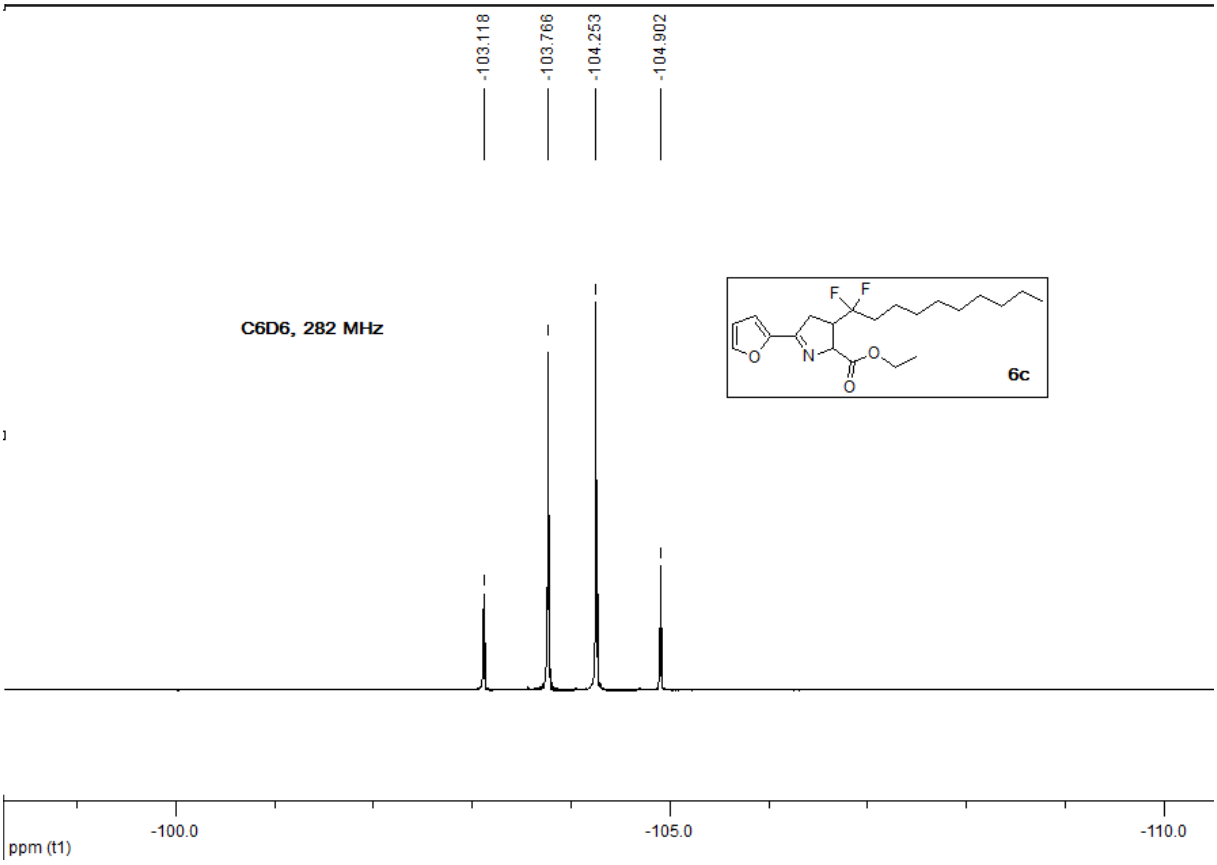

CDCl3, 75 MHz
6b
ppm (t1)

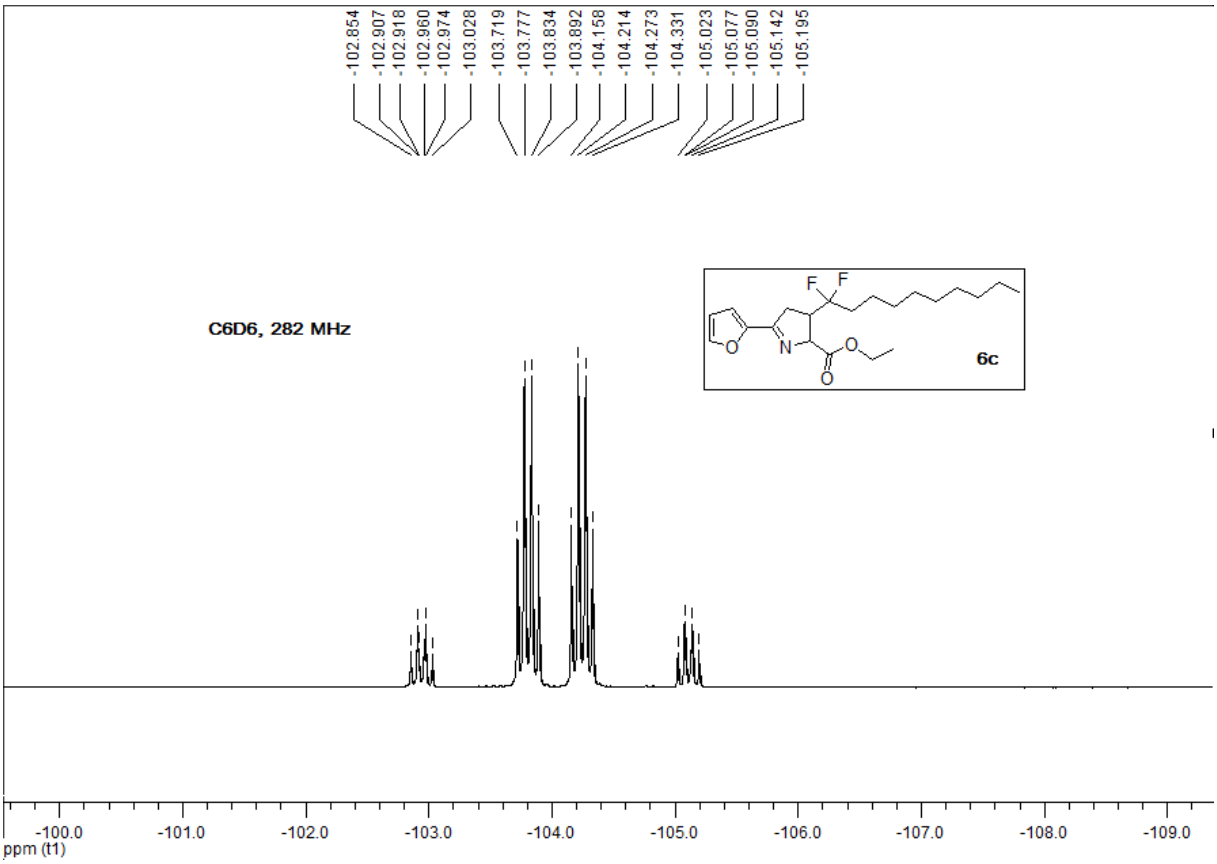

-103.211
-104.077
-105.345
-106.211
CDCl3, 282 MHz
F
F
N
N
O
O
6b
-100.0
-105.0
-110.0
-115.0
ppm (t1)

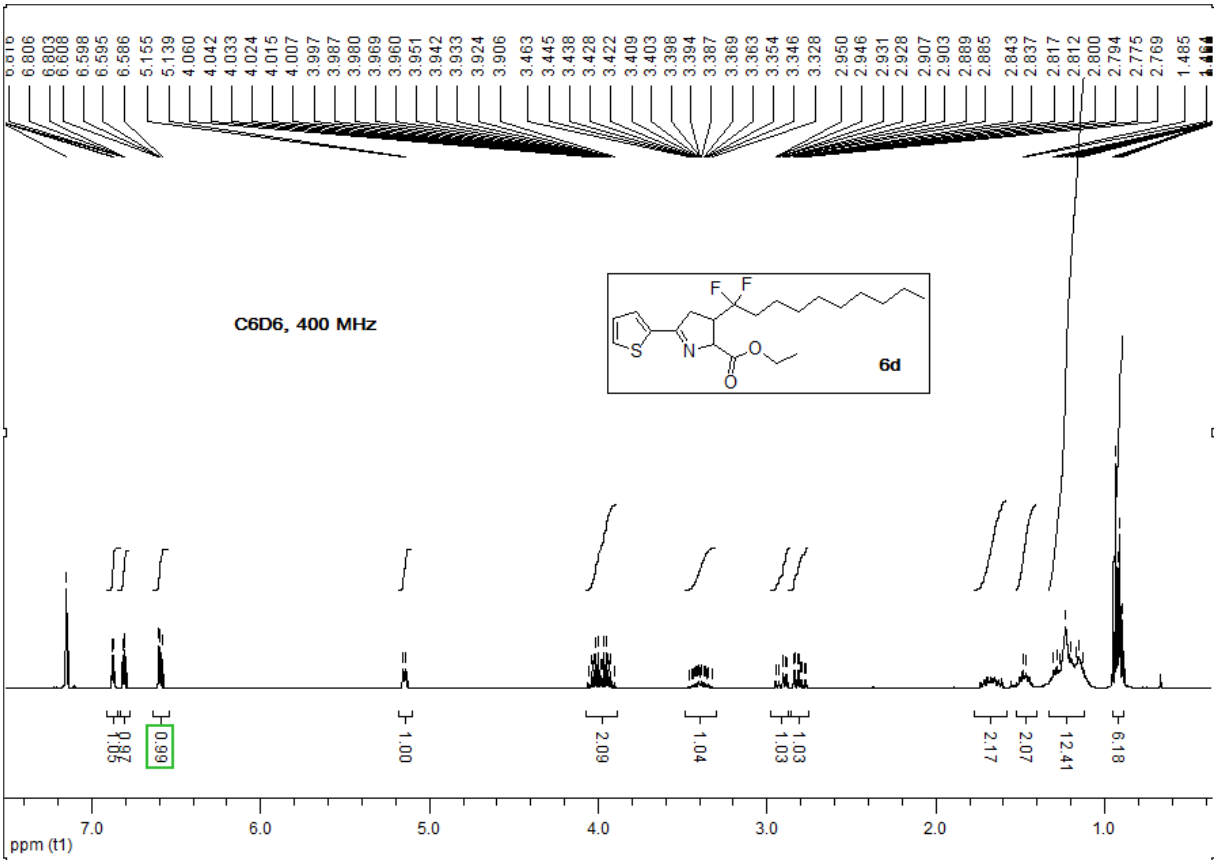

-103.119
-103.165
-103.182
-103.227
-103.241
-103.288
-103.985
-104.048
-104.091
-104.156
-105.254
-105.309
-105.371
-105.426
-106.119
-106.174
-106.236
-106.291
CDCl3, 282 MHz
F
F
N
N
O
O
6b
-100.0
-105.0
-110.0
ppm (t1)

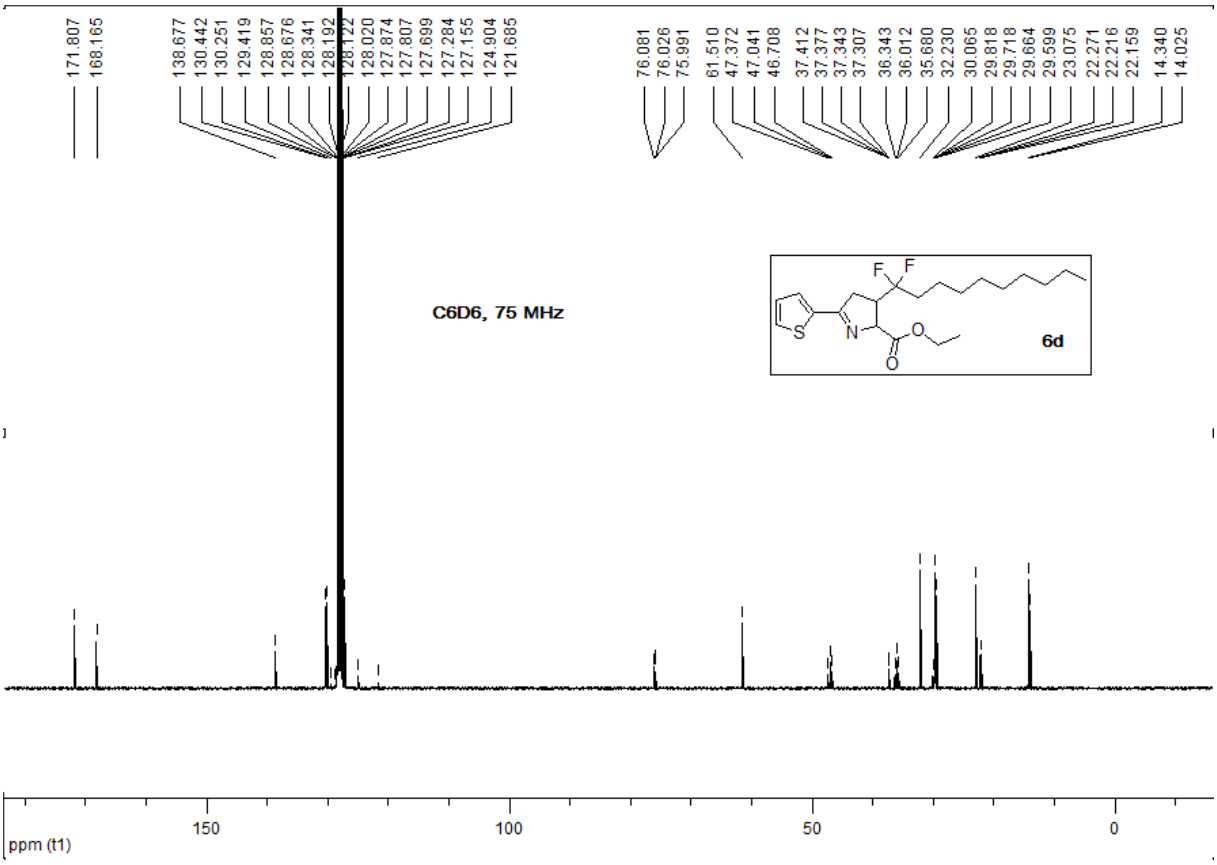

C6D6, 400 MHz
6c
0.98
0.99
0.99
1.00
2.04
1.04
2.05
2.07
2.06
12.45
9.16
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

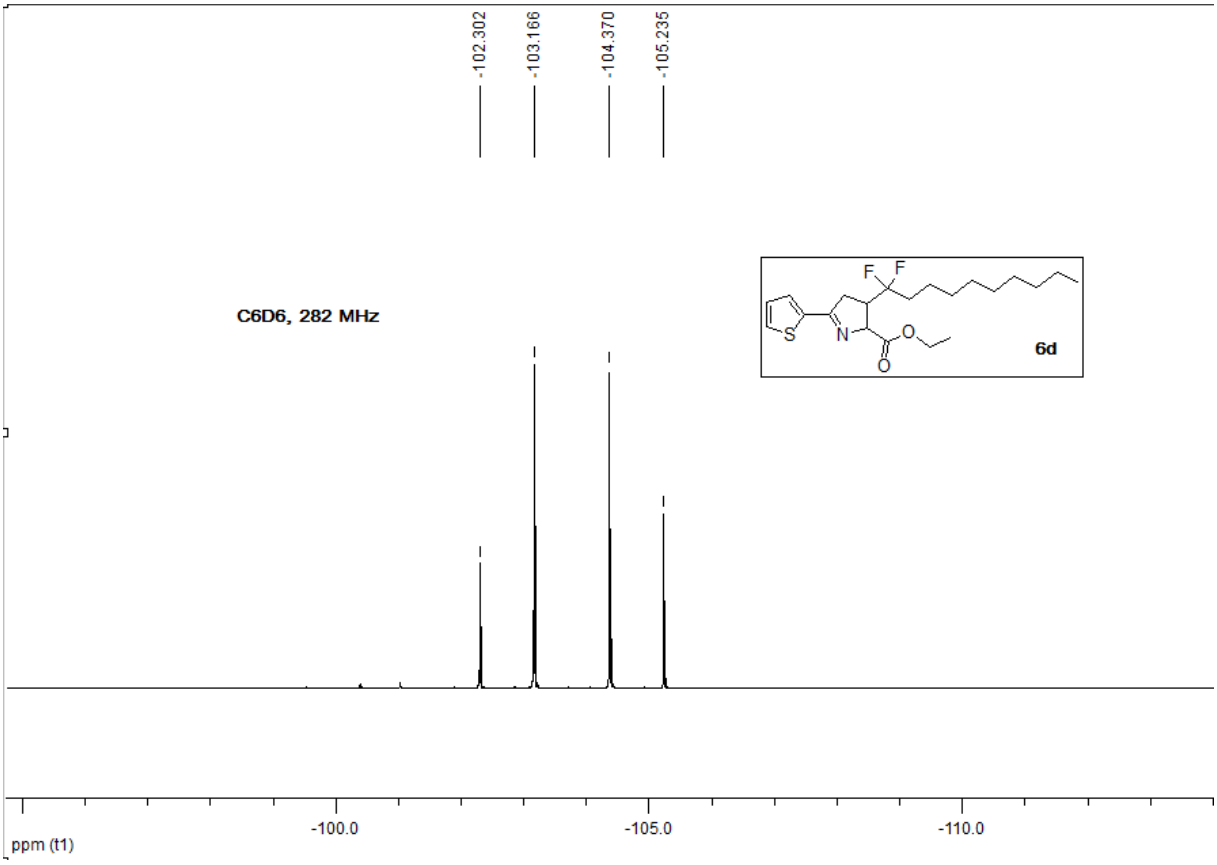

C6D6, 75 MHz
6c
171.740
164.473
150.038
144.550
128.474
128.457
128.266
128.120
128.051
127.945
127.809
127.733
127.624
127.428
127.397
127.376
127.346
127.311
124.865
121.645
113.351
111.896
76.406
76.356
76.318
61.404
46.628
46.297
45.963
37.007
36.965
36.940
36.898
36.266
35.934
35.602
32.164
29.744
29.634
29.588
29.519
23.001
22.203
22.146
22.089
14.256
13.984
150
100
50
0
ppm (t1)

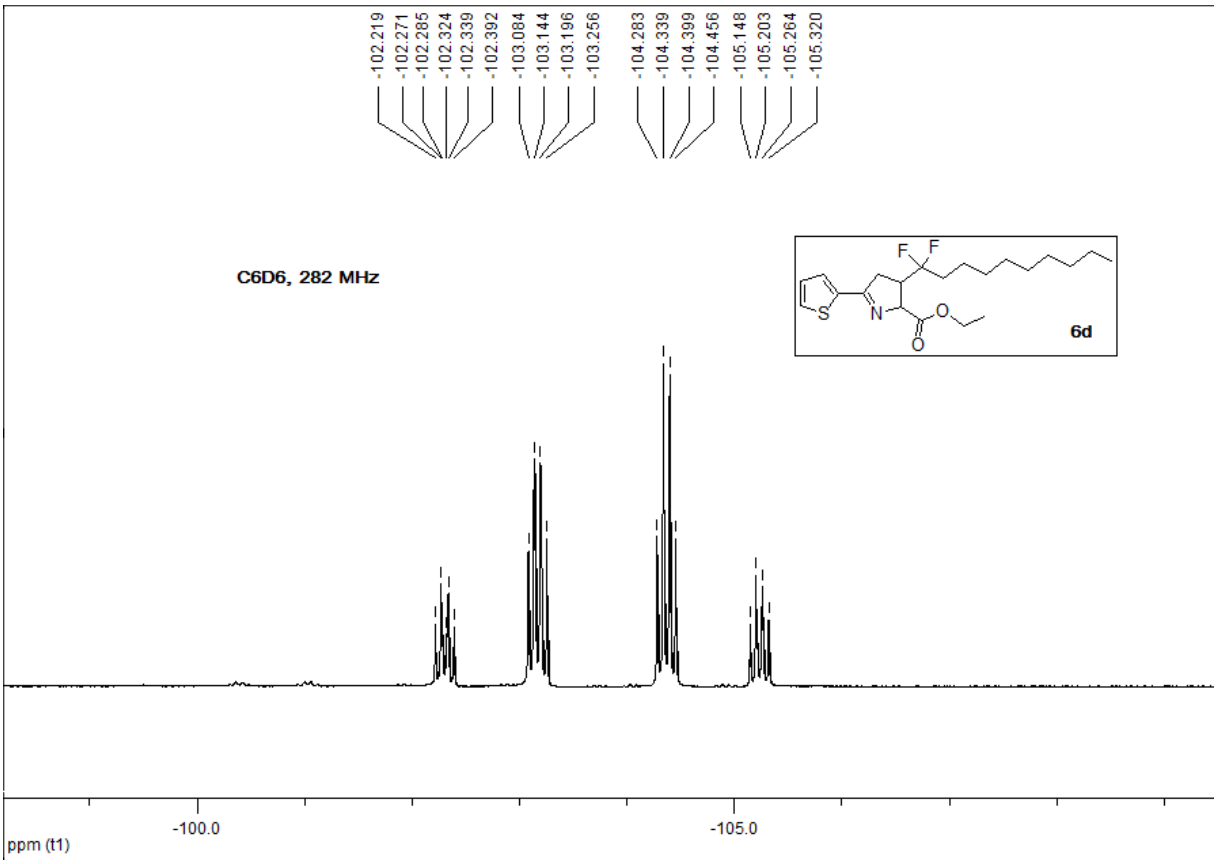

-103.118
-103.766
-104.253
-104.902
C6D6, 282 MHz
F
F
O
N
O
O
6c
-100.0
-105.0
-110.0
ppm (t1)

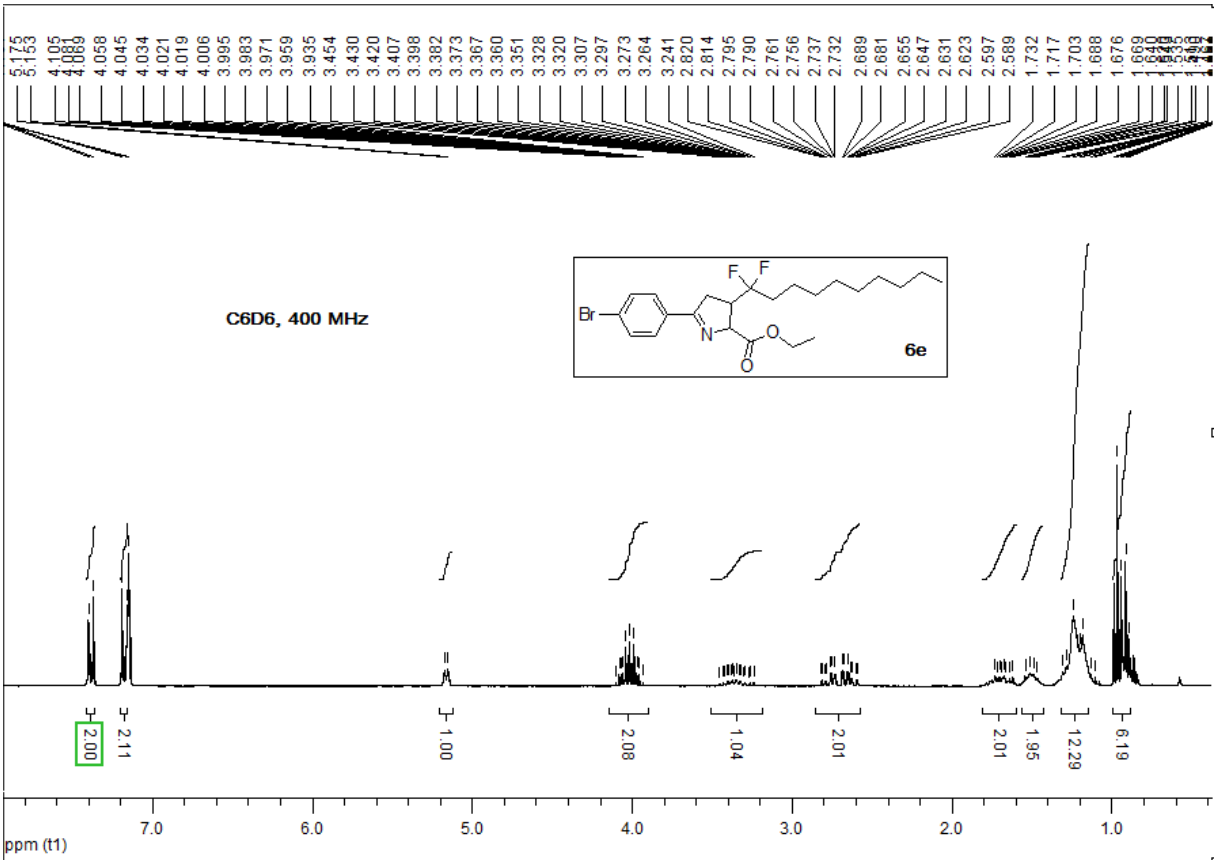

-102.854
-102.907
-102.918
-102.960
-102.974
-103.028
-103.719
-103.777
-103.834
-103.892
-104.158
-104.214
-104.273
-104.331
-105.023
-105.077
-105.090
-105.142
-105.195
C6D6, 282 MHz
F
F
O
N
O
O
6c
-100.0
-101.0
-102.0
-103.0
-104.0
-105.0
-106.0
-107.0
-108.0
-109.0
ppm (t1)

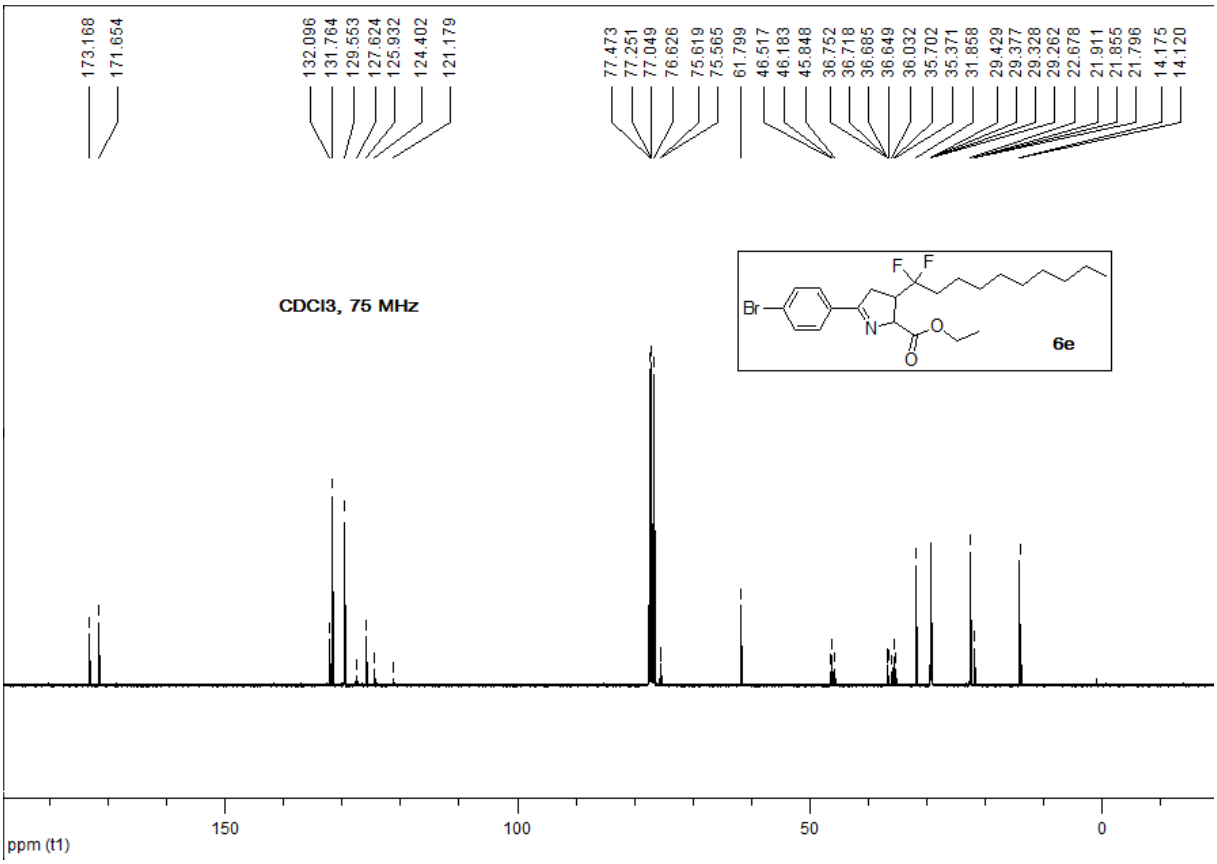

C6D6, 400 MHz
6d
ppm (t1)

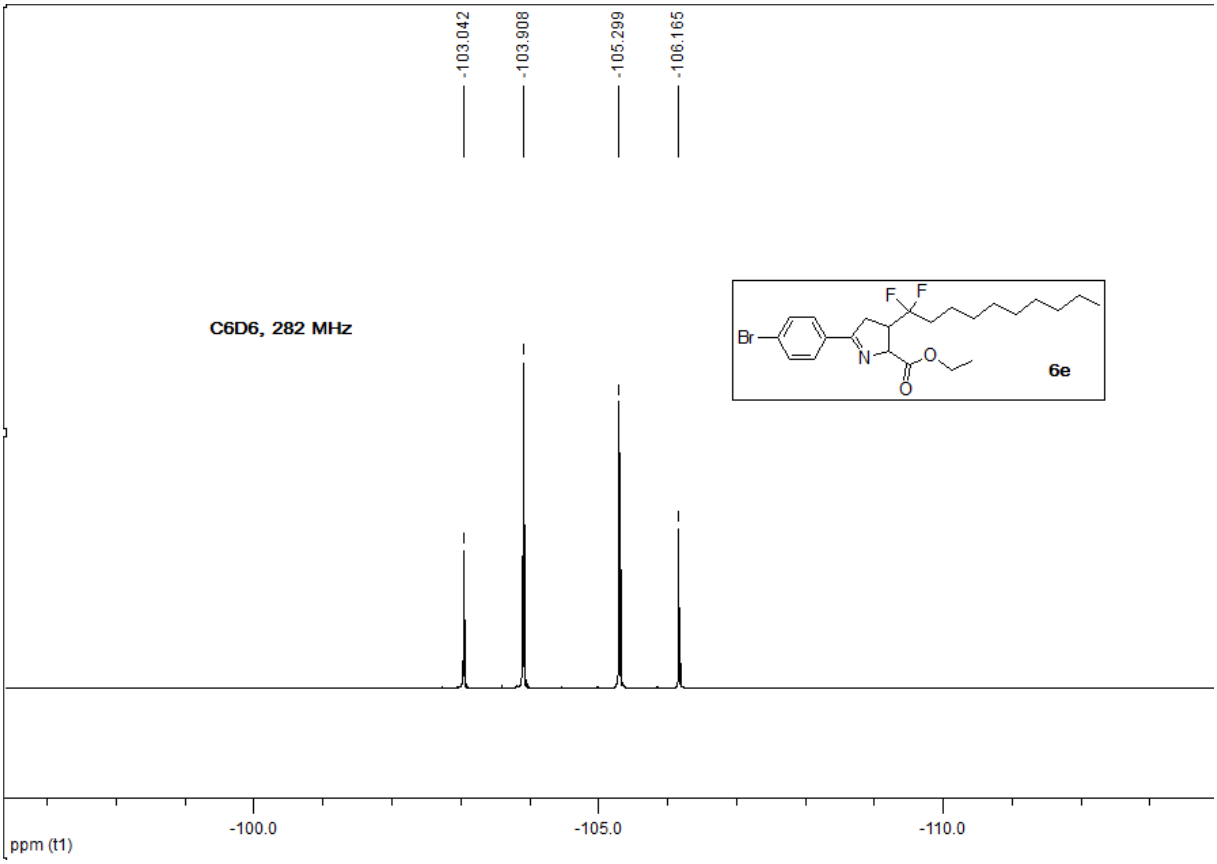

C6D6, 75 MHz
6d
ppm (t1)

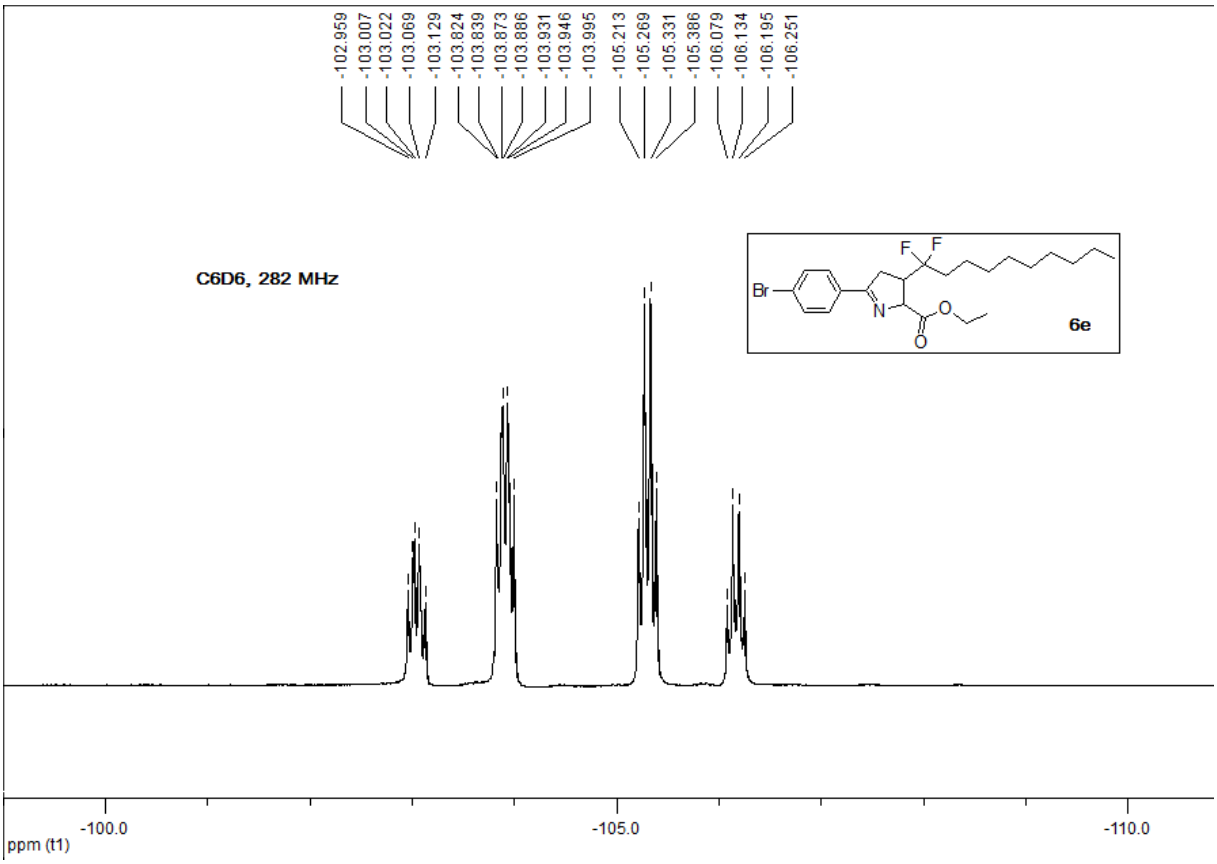

-102.302
-103.166
-104.370
-105.235
C6D6, 282 MHz
F
F
S
N
O
O
6d
-100.0
-105.0
-110.0
ppm (t1)

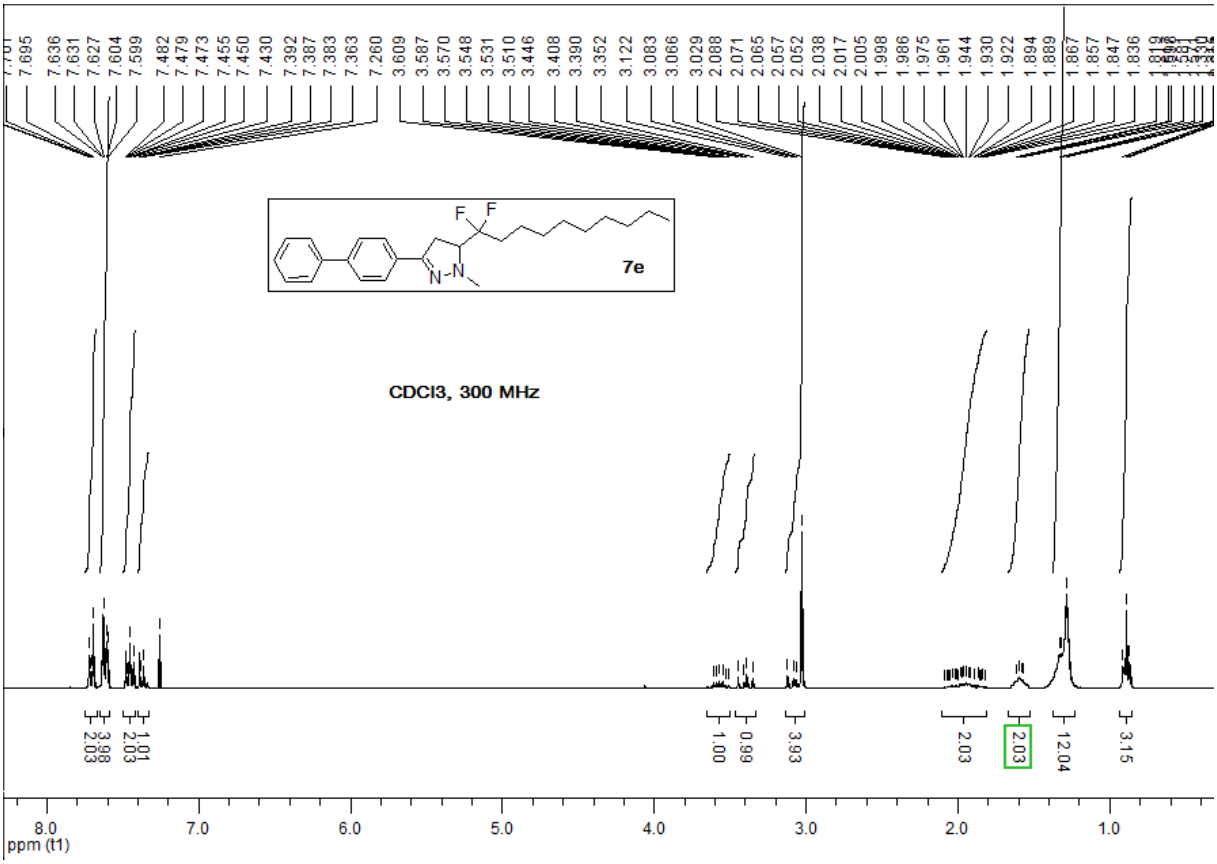

-102.219
-102.271
-102.285
-102.324
-102.339
-102.392
-103.084
-103.144
-103.196
-103.256
-104.283
-104.339
-104.399
-104.456
-105.148
-105.203
-105.264
-105.320
C6D6, 282 MHz
F
F
S
N
O
O
6d
-100.0
-105.0
ppm (t1)

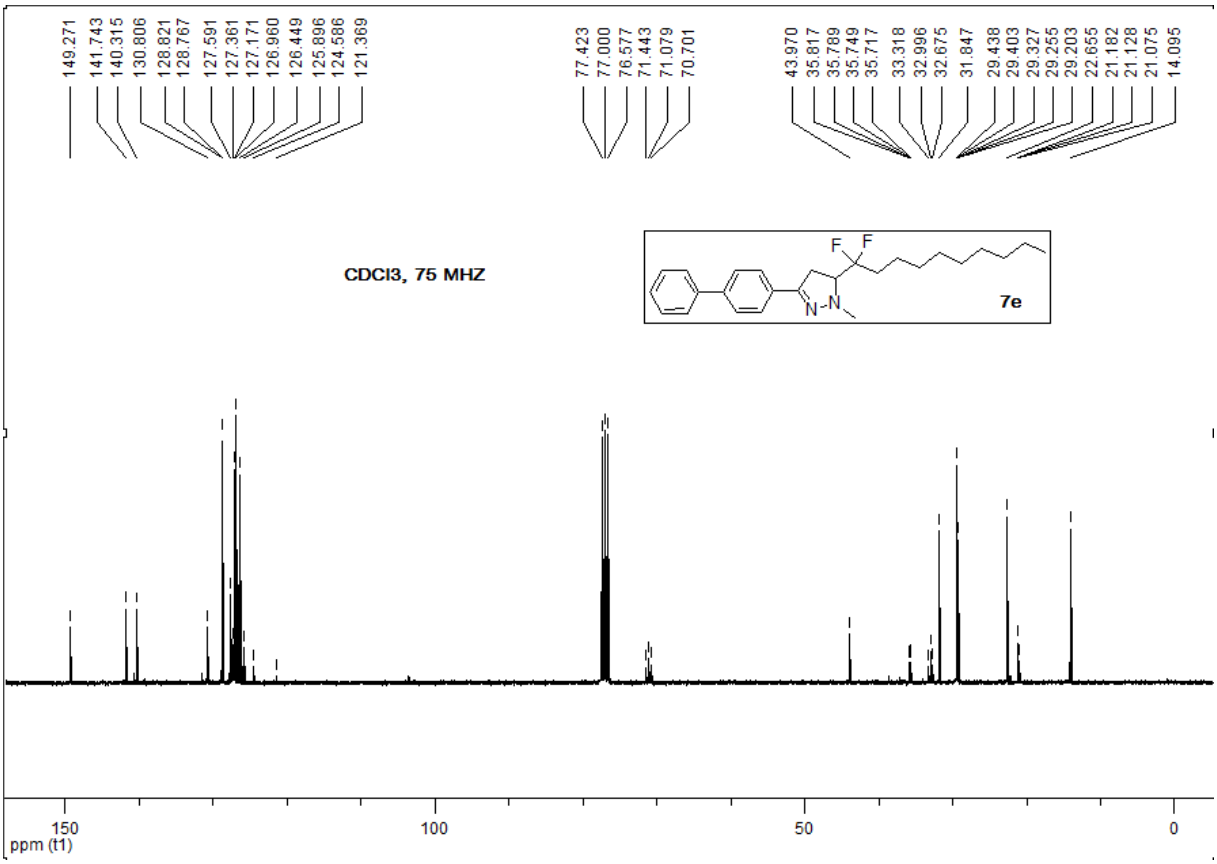

C6D6, 400 MHz
6e
Br
F
F
N
O
O
2.00
2.11
1.00
2.08
1.04
2.01
2.01
1.95
12.29
6.19
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

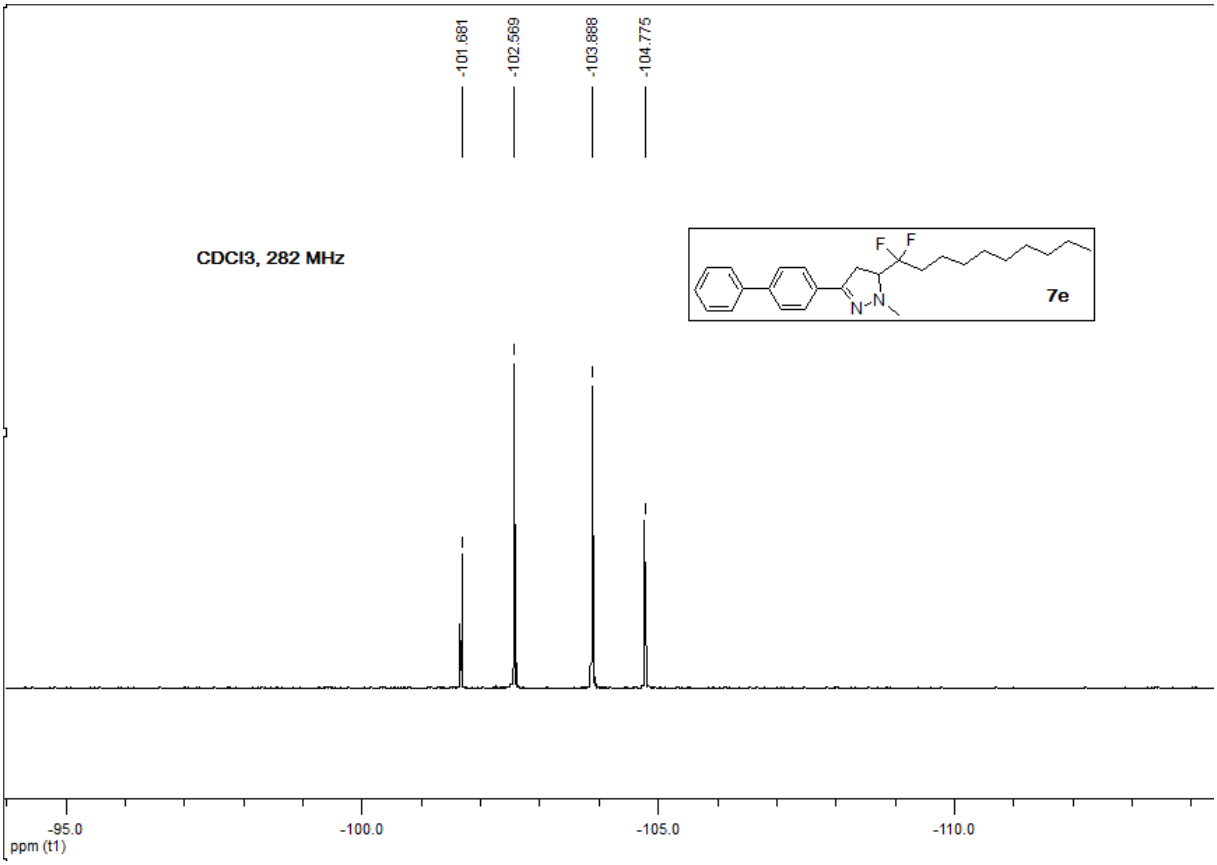

CDCl3, 75 MHz
6e
Br
F
F
N
O
O
173.168
171.654
132.096
131.764
129.553
127.624
125.932
124.402
121.179
77.473
77.251
77.049
76.626
75.619
75.565
61.799
46.517
46.183
45.848
36.752
36.718
36.685
36.649
36.032
35.702
35.371
31.858
29.429
29.377
29.328
29.262
22.678
21.911
21.855
21.796
14.175
14.120
150
100
50
0
ppm (t1)

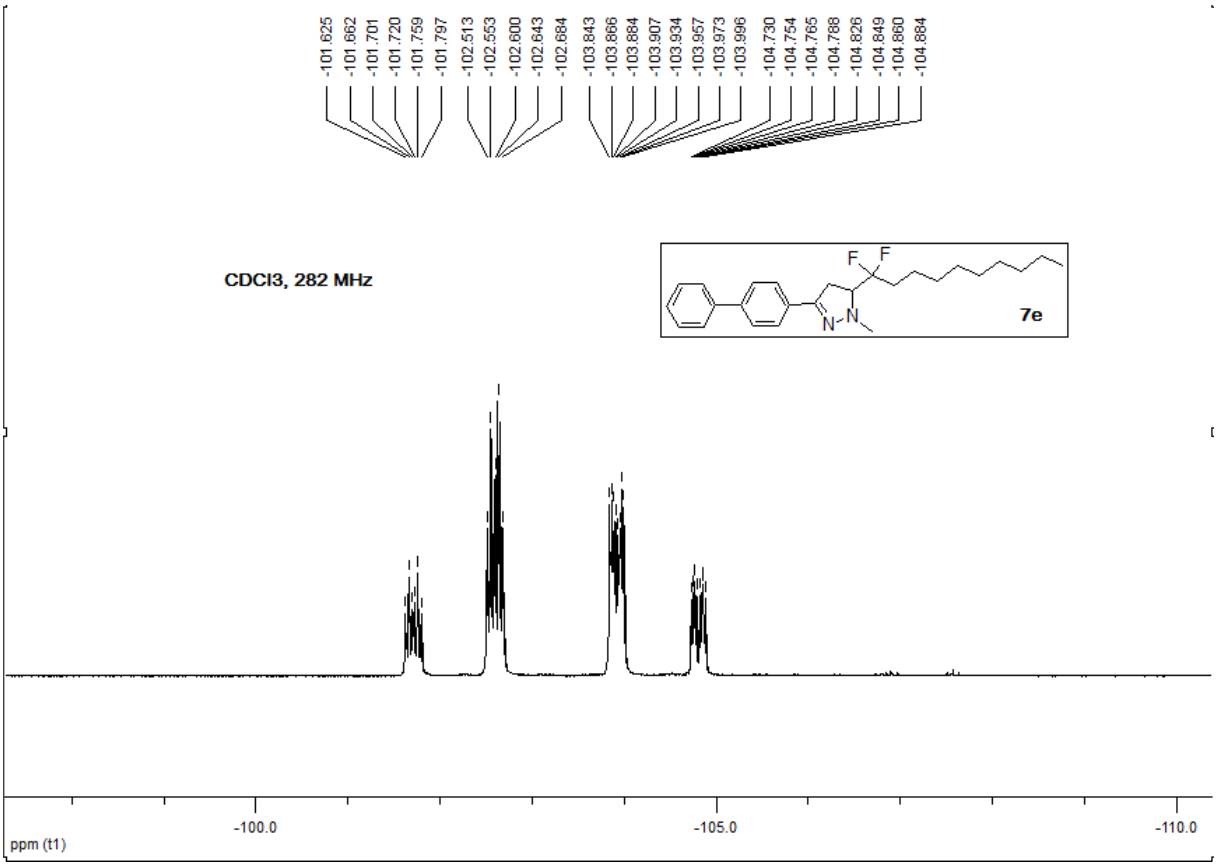

-103.042
-103.908
-105.299
-106.165
C6D6, 282 MHz
F
F
Br
N
O
O
6e
-100.0
-105.0
-110.0
ppm (t1)

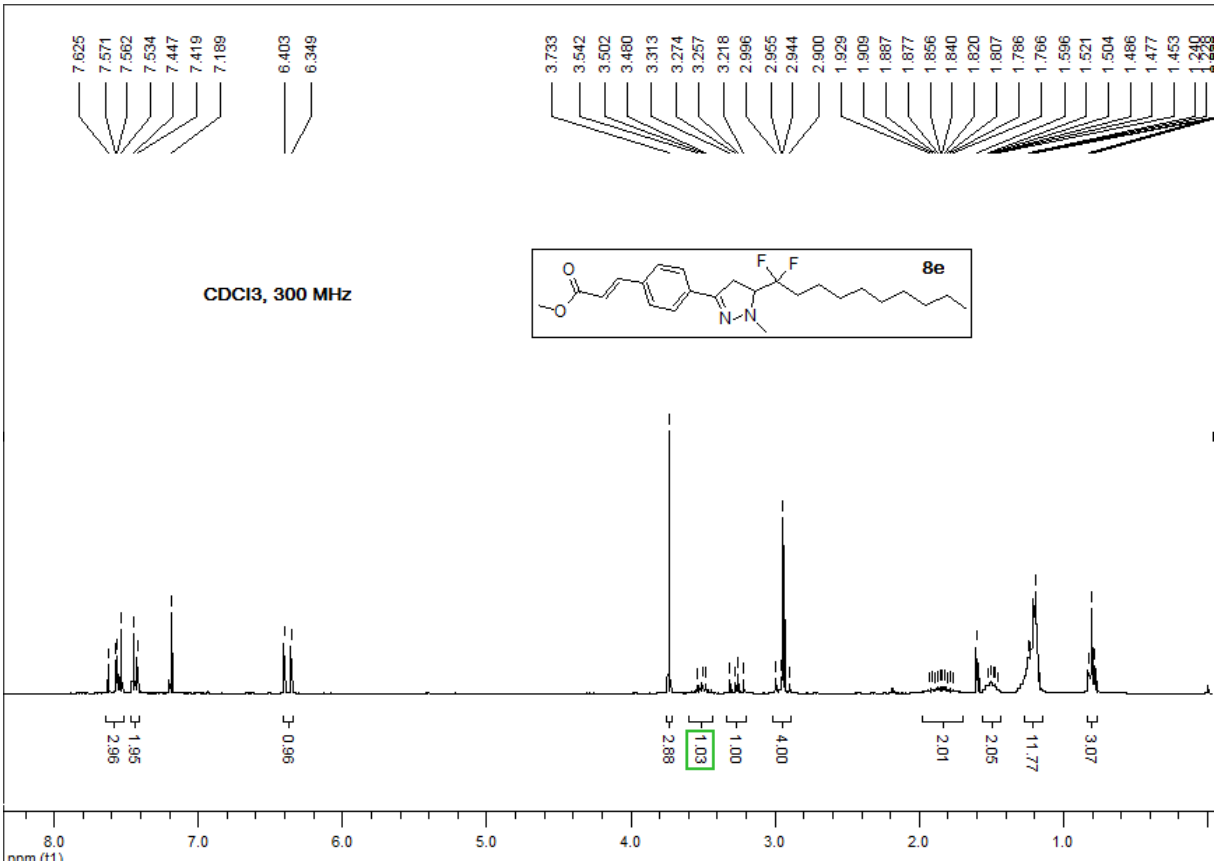

-102.959
-103.007
-103.022
-103.069
-103.129
-103.824
-103.839
-103.873
-103.886
-103.931
-103.946
-103.995
-105.213
-105.269
-105.331
-105.386
-106.079
-106.134
-106.195
-106.251
C6D6, 282 MHz
F
F
Br
N
O
O
6e
-100.0
-105.0
-110.0
ppm (t1)

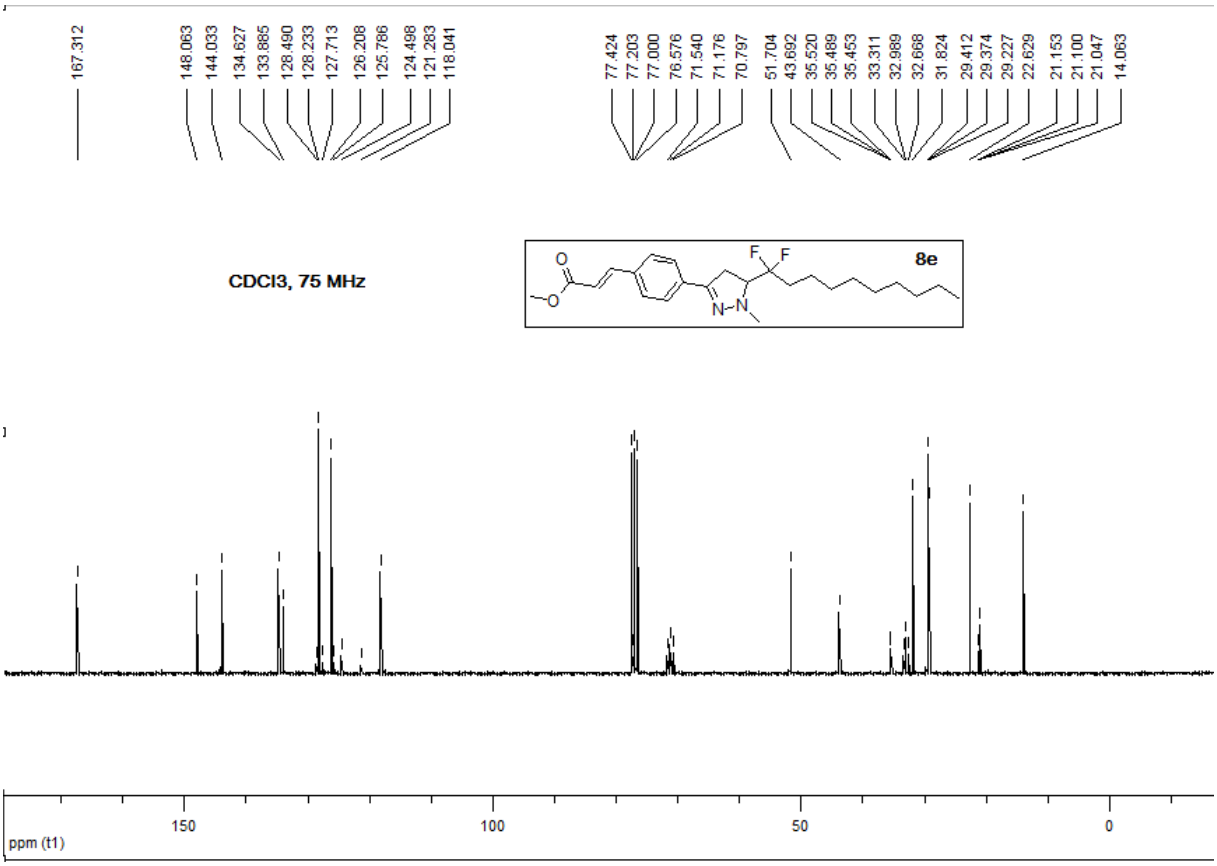

7.695
7.636
7.631
7.627
7.604
7.599
7.482
7.479
7.473
7.455
7.450
7.430
7.392
7.387
7.383
7.363
7.260
3.609
3.587
3.570
3.548
3.531
3.510
3.446
3.408
3.390
3.352
3.122
3.083
3.066
3.029
2.088
2.071
2.065
2.057
2.052
2.038
2.017
2.005
1.998
1.986
1.975
1.961
1.944
1.930
1.922
1.894
1.889
1.867
1.857
1.847
1.836
F
F
N-N
7e
CDCl3, 300 MHz
2.03
3.98
1.03
1.00
0.99
3.93
2.03
2.03
1.04
3.15
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

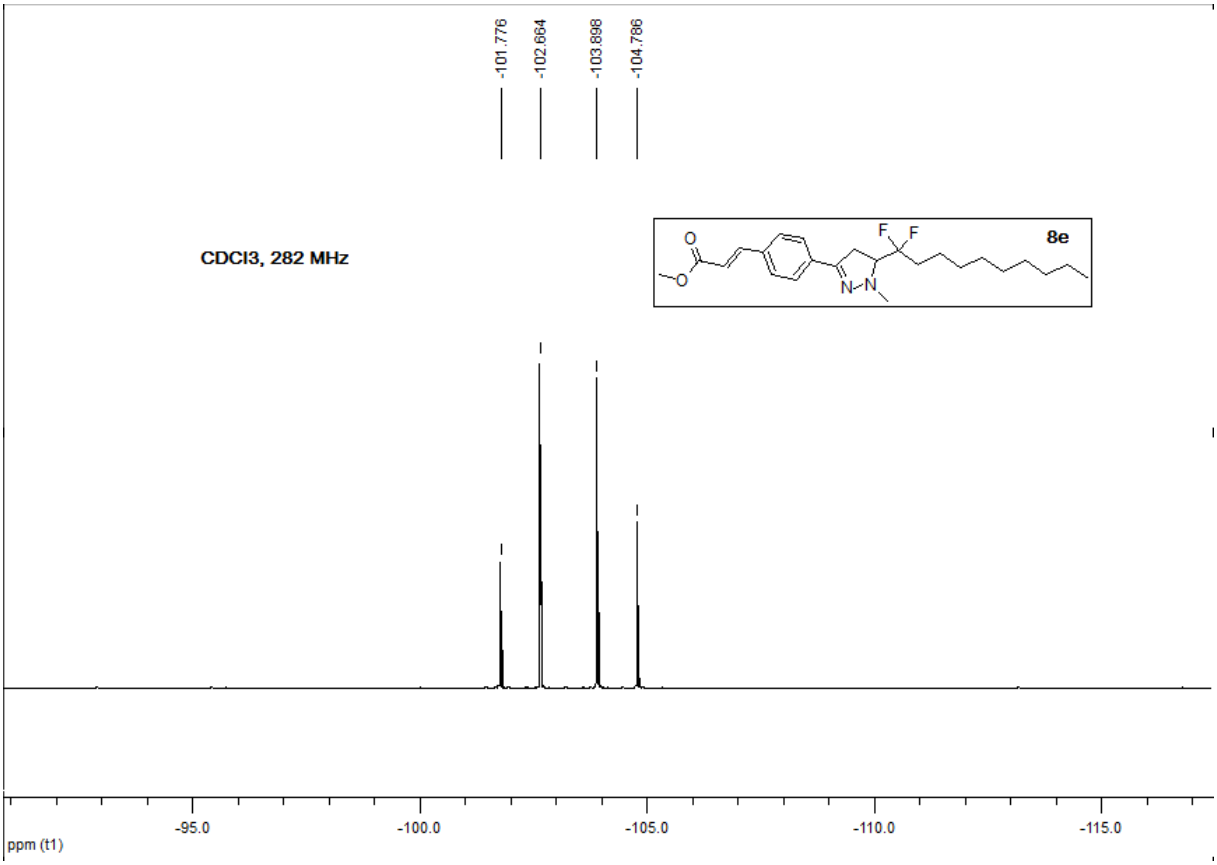

149.271
141.743
140.315
130.806
128.821
128.767
127.591
127.361
127.171
126.960
126.449
125.896
124.586
121.369
77.423
77.000
76.577
71.443
71.079
70.701
43.970
35.817
35.789
35.749
35.717
33.318
32.996
32.675
31.847
29.438
29.403
29.327
29.255
29.203
22.655
21.182
21.128
21.075
14.095
CDCl3, 75 MHZ
F
F
N-N
7e
150
100
50
0
ppm (t1)

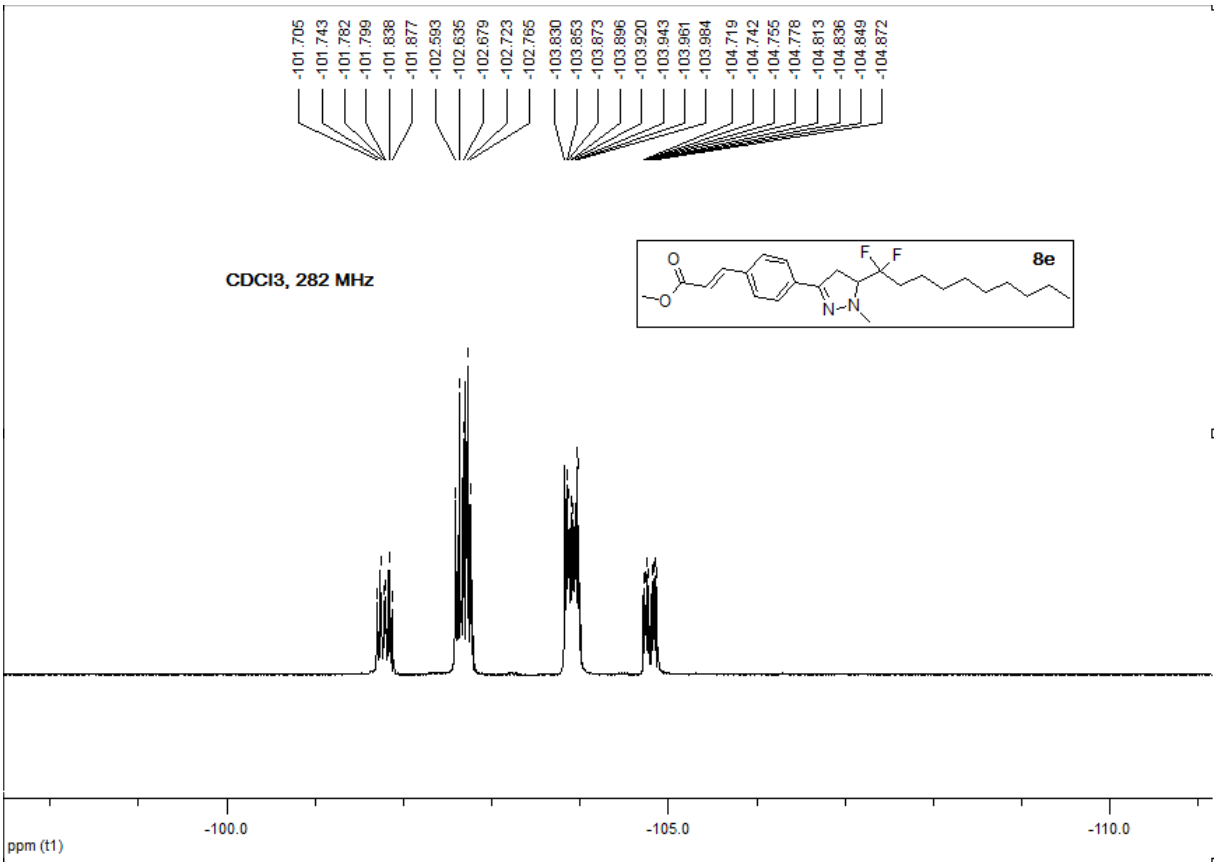

-101.681
-102.569
-103.888
-104.775
CDCl3, 282 MHz
F
F
N
N
7e
-95.0
-100.0
-105.0
-110.0
ppm (t1)

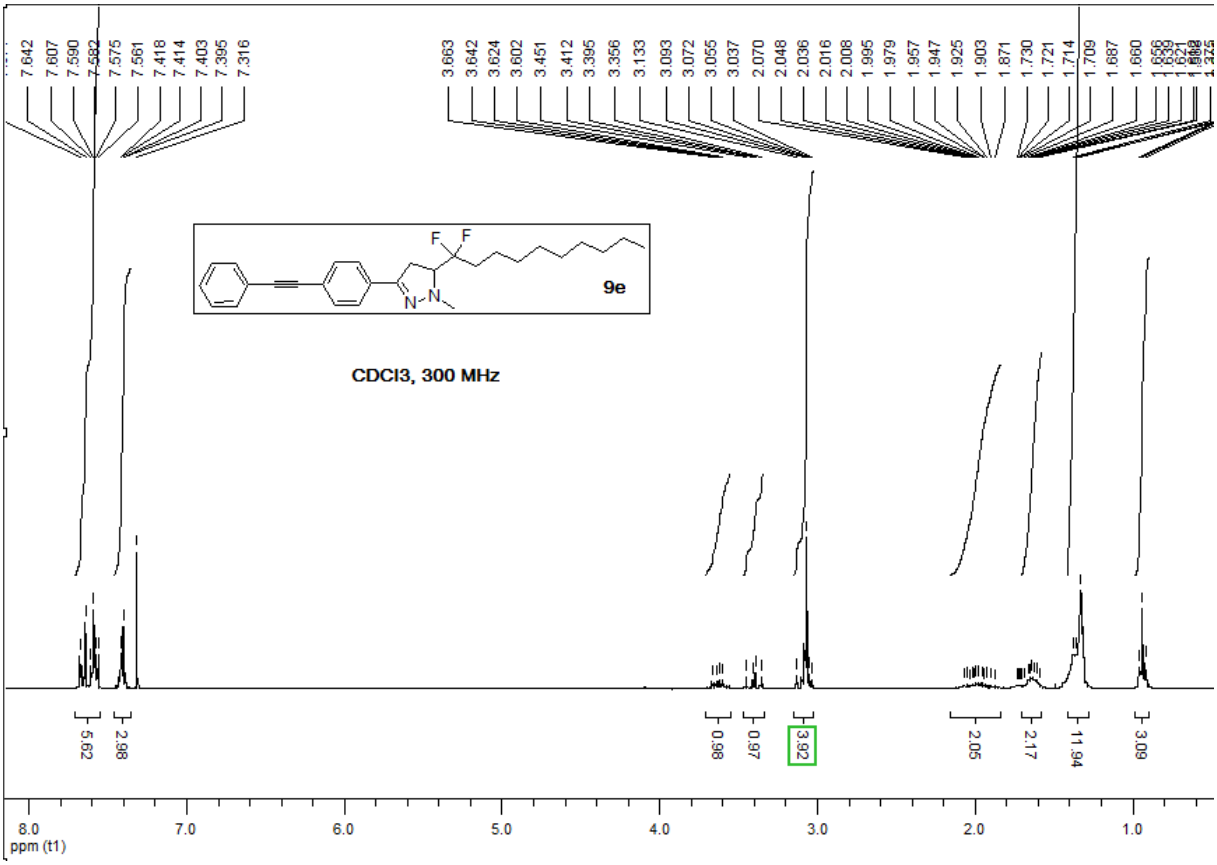

-101.625
-101.662
-101.701
-101.720
-101.759
-101.797
-102.513
-102.553
-102.600
-102.643
-102.684
-103.843
-103.866
-103.884
-103.907
-103.934
-103.957
-103.973
-103.996
-104.730
-104.754
-104.765
-104.788
-104.826
-104.849
-104.860
-104.884
CDCl3, 282 MHz
F
F
N
N
7e
-100.0
-105.0
-110.0
ppm (t1)

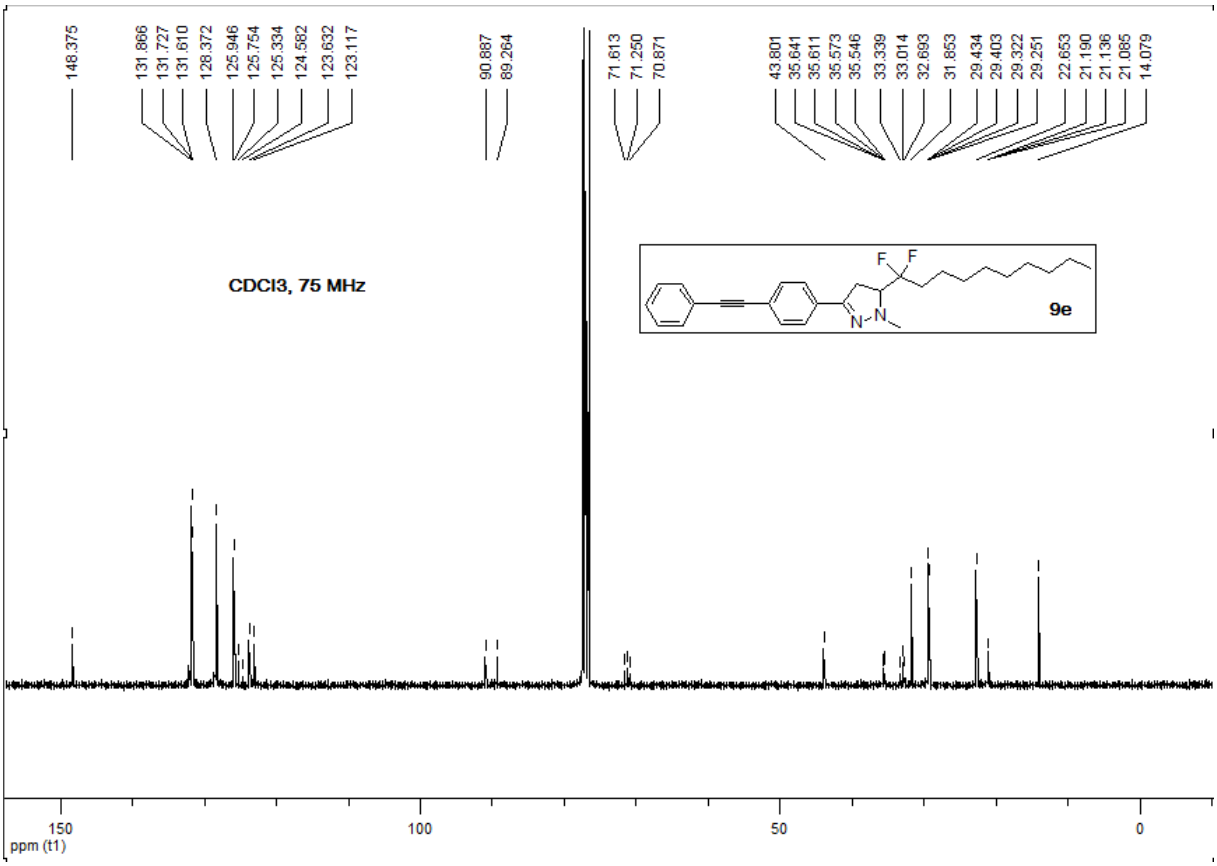

7.625
7.571
7.562
7.534
7.447
7.419
7.189
6.403
6.349
3.733
3.542
3.502
3.480
3.313
3.274
3.257
3.218
2.996
2.955
2.944
2.900
1.929
1.909
1.887
1.877
1.856
1.840
1.820
1.807
1.786
1.766
1.596
1.521
1.504
1.486
1.477
1.453
CDCl3, 300 MHz
8e
1.96
2.96
0.96
2.88
1.03
1.00
4.00
2.01
2.05
11.77
3.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

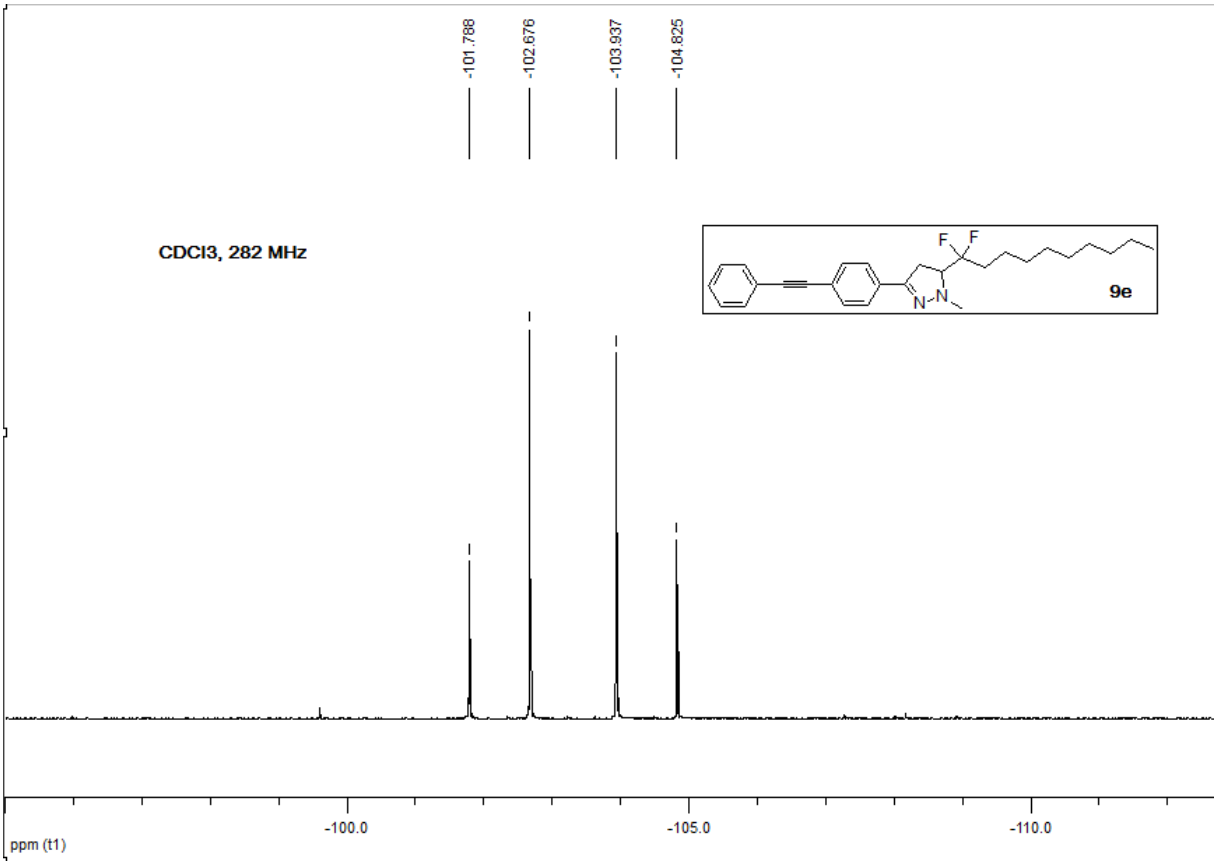

167.312
148.063
144.033
134.627
133.865
128.490
128.233
127.713
126.208
125.786
124.498
121.283
118.041
77.424
77.203
77.000
76.576
71.540
71.176
70.797
51.704
43.692
35.520
35.489
35.453
33.311
32.989
32.668
31.824
29.412
29.374
29.227
22.629
21.153
21.100
21.047
14.063
CDCl3, 75 MHz
8e
150
100
50
0
ppm (t1)

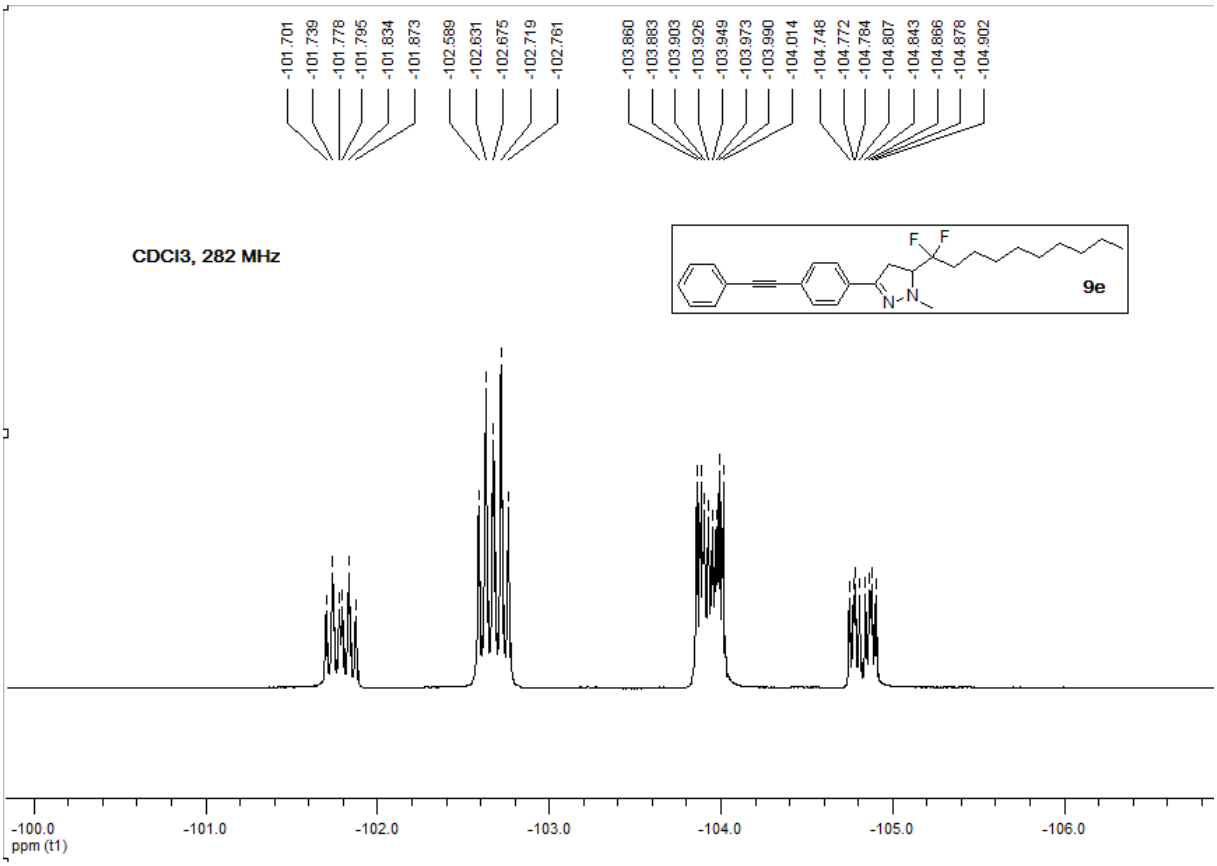

-101.776
-102.664
-103.898
-104.786
CDCl3, 282 MHz
8e
-95.0
-100.0
-105.0
-110.0
-115.0
ppm (t1)

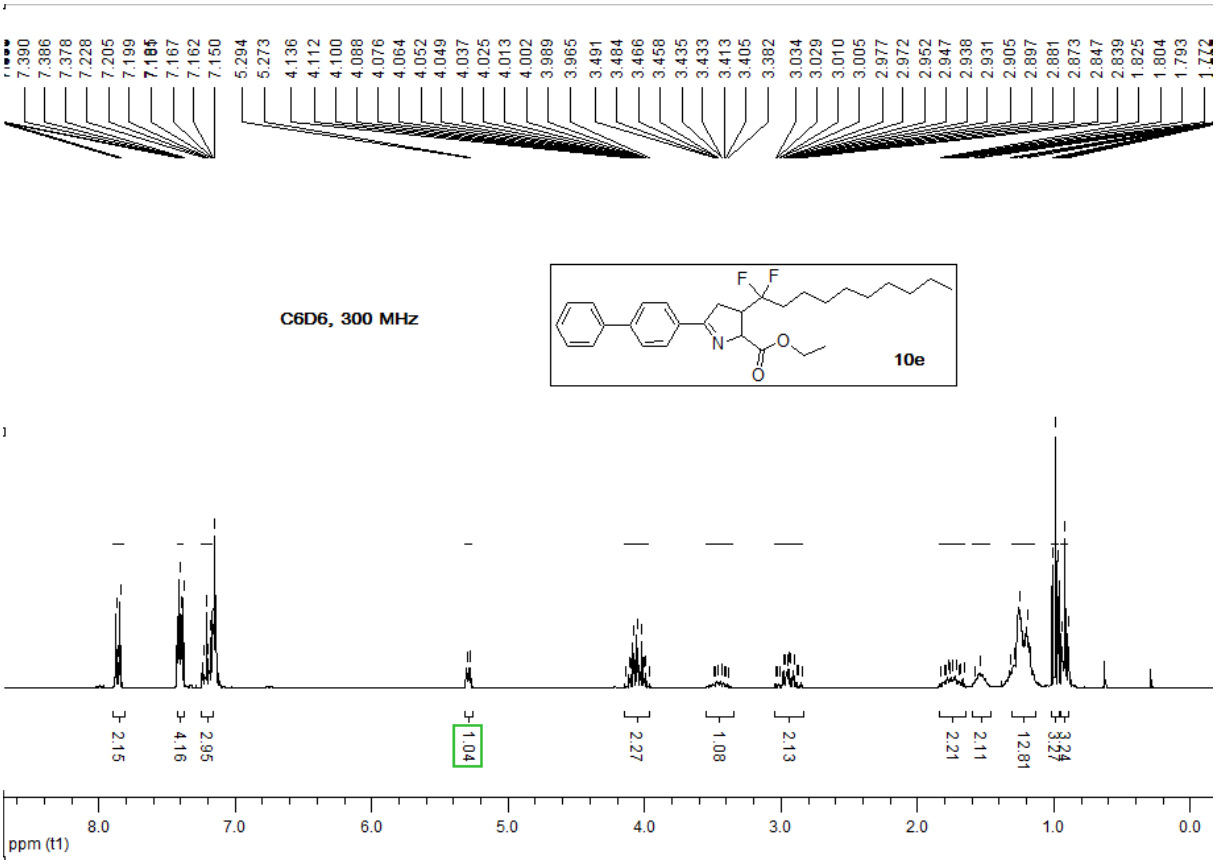

-101.705
-101.743
-101.782
-101.799
-101.838
-101.877
-102.593
-102.635
-102.679
-102.723
-102.765
-103.830
-103.853
-103.873
-103.896
-103.920
-103.943
-103.961
-103.984
-104.719
-104.742
-104.755
-104.778
-104.813
-104.836
-104.849
-104.872
CDCl3, 282 MHz
8e
-100.0
-105.0
-110.0
ppm (t1)

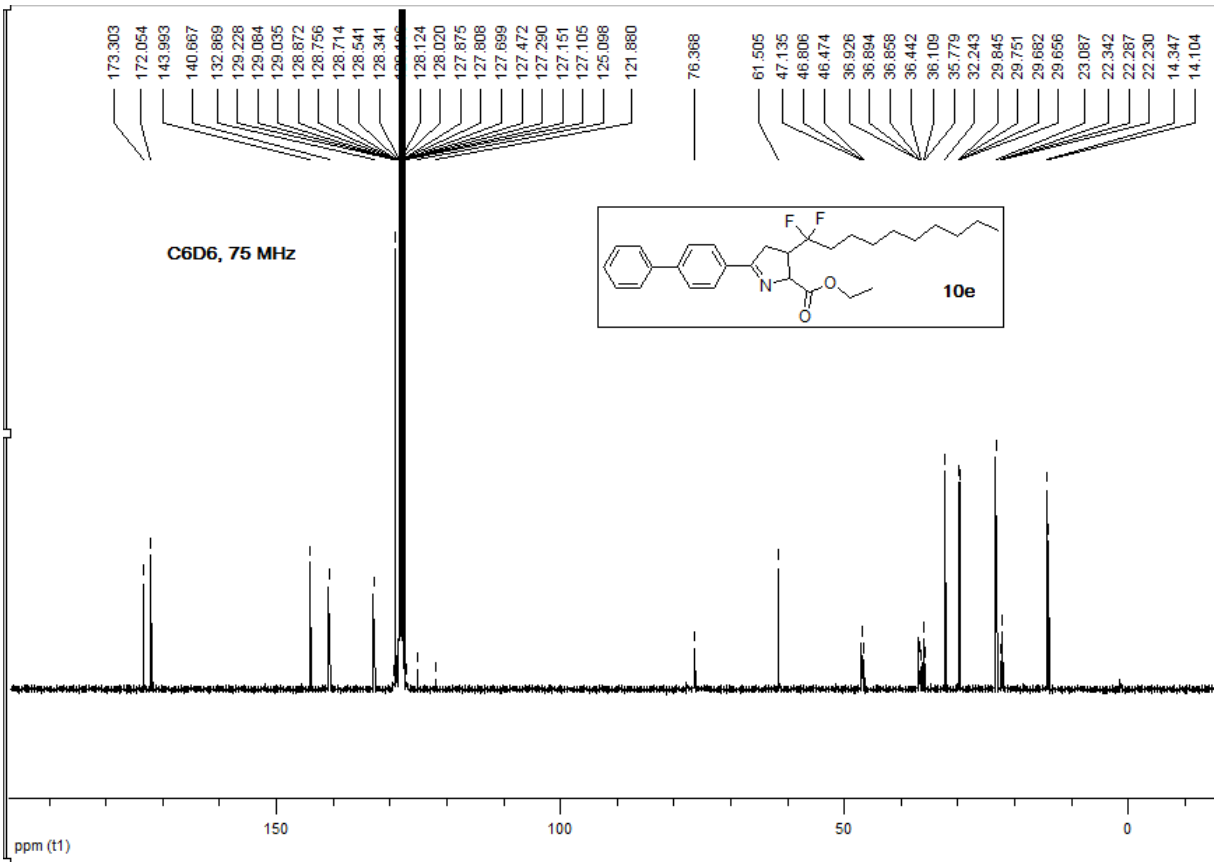

7.642
7.607
7.590
7.582
7.575
7.561
7.418
7.414
7.403
7.395
7.316
3.663
3.642
3.624
3.602
3.451
3.412
3.395
3.356
3.133
3.093
3.072
3.055
3.037
2.070
2.048
2.036
2.016
2.008
1.995
1.979
1.957
1.947
1.925
1.903
1.871
1.730
1.721
1.714
1.709
1.687
1.660
F
F
N
N
9e
CDCl3, 300 MHz
5.62
2.98
0.98
0.97
3.92
2.05
2.17
11.94
3.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

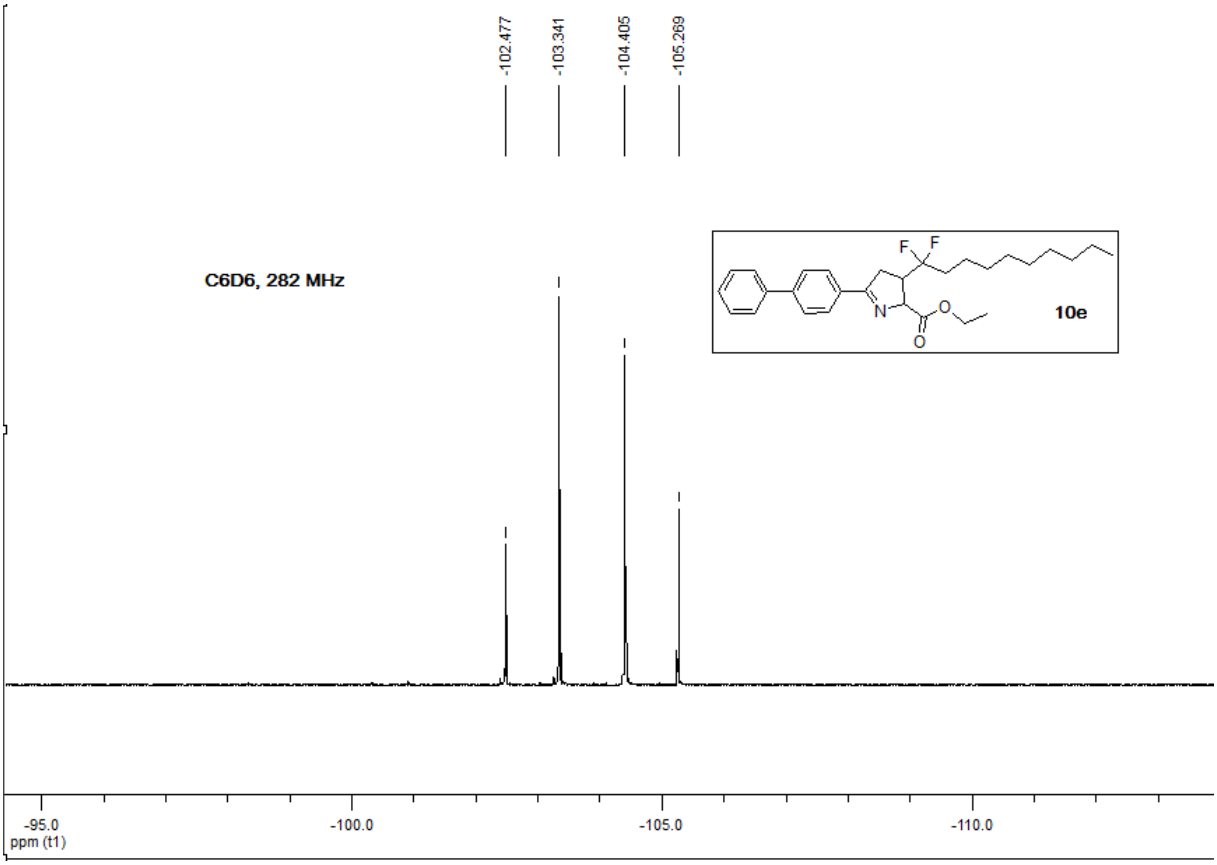

148.375
131.866
131.727
131.610
128.372
125.946
125.754
125.334
124.582
123.632
123.117
90.887
89.264
71.613
71.250
70.871
43.801
35.641
35.611
35.573
35.546
33.339
33.014
32.693
31.853
29.434
29.403
29.322
29.251
22.653
21.190
21.136
21.085
14.079
CDCl3, 75 MHz
F
F
N
N
9e
150
100
50
0
ppm (t1)

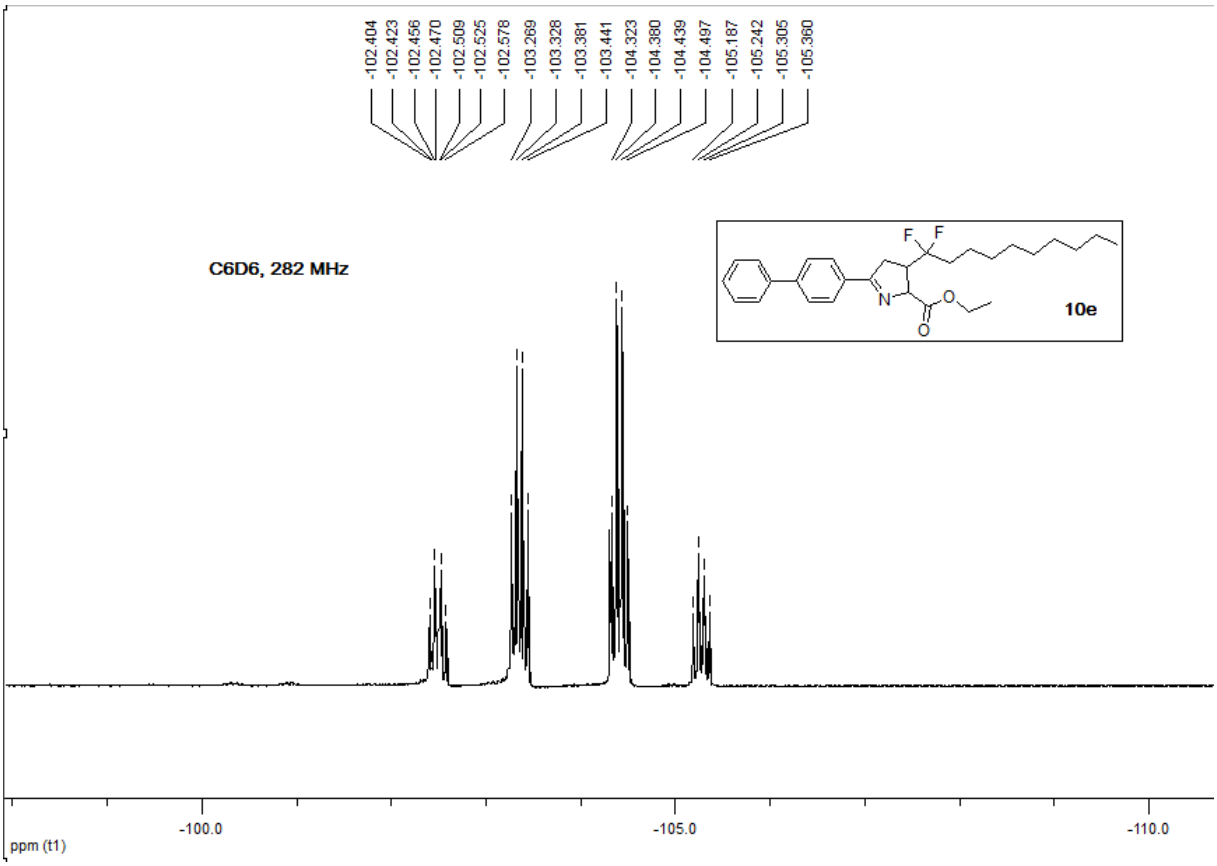

-101.788
-102.676
-103.937
-104.825
CDCl3, 282 MHz
F
F
N
N
9e
-100.0
-105.0
-110.0
ppm (t1)

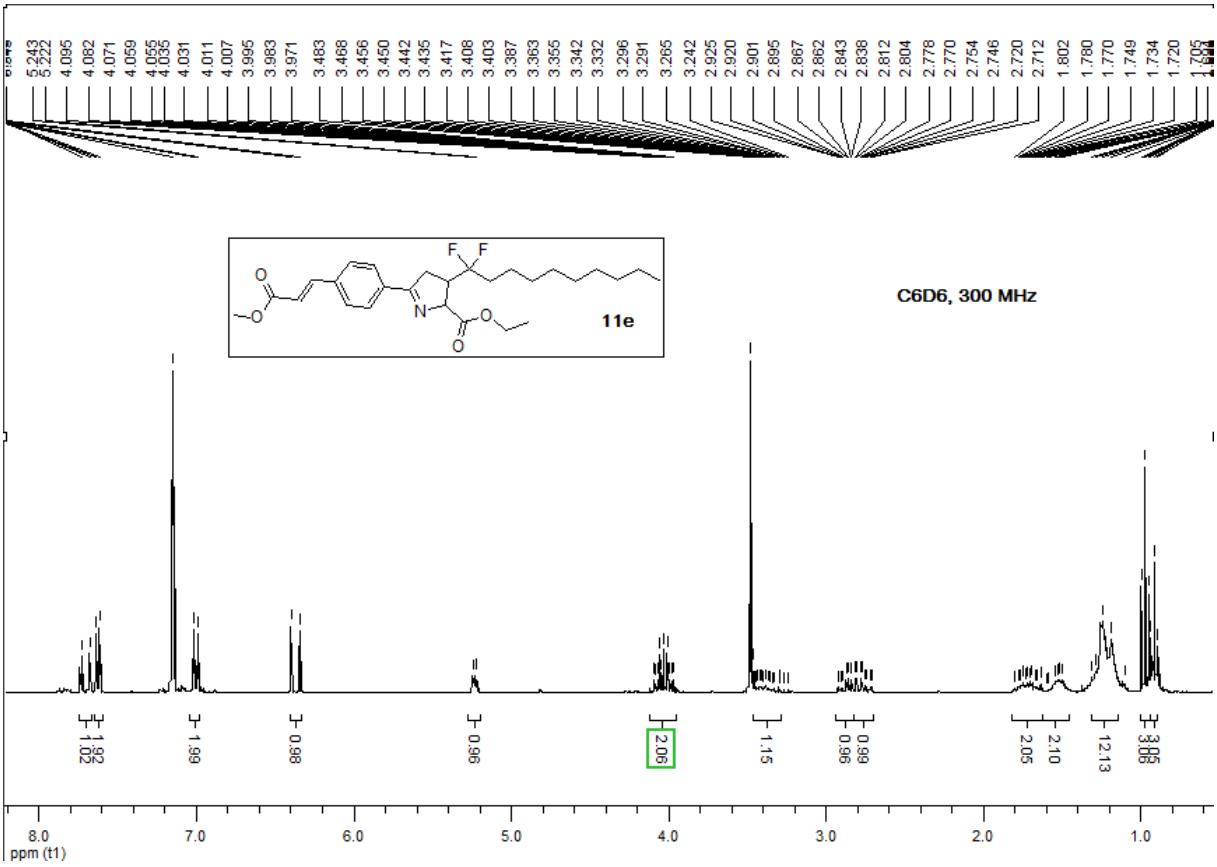

-101.701
-101.739
-101.778
-101.795
-101.834
-101.873
-102.589
-102.631
-102.675
-102.719
-102.761
-103.860
-103.883
-103.903
-103.926
-103.949
-103.973
-103.990
-104.014
-104.748
-104.772
-104.784
-104.807
-104.843
-104.866
-104.878
-104.902
CDCl3, 282 MHz
F
F
N
N
9e
-100.0
-101.0
-102.0
-103.0
-104.0
-105.0
-106.0
ppm (t1)

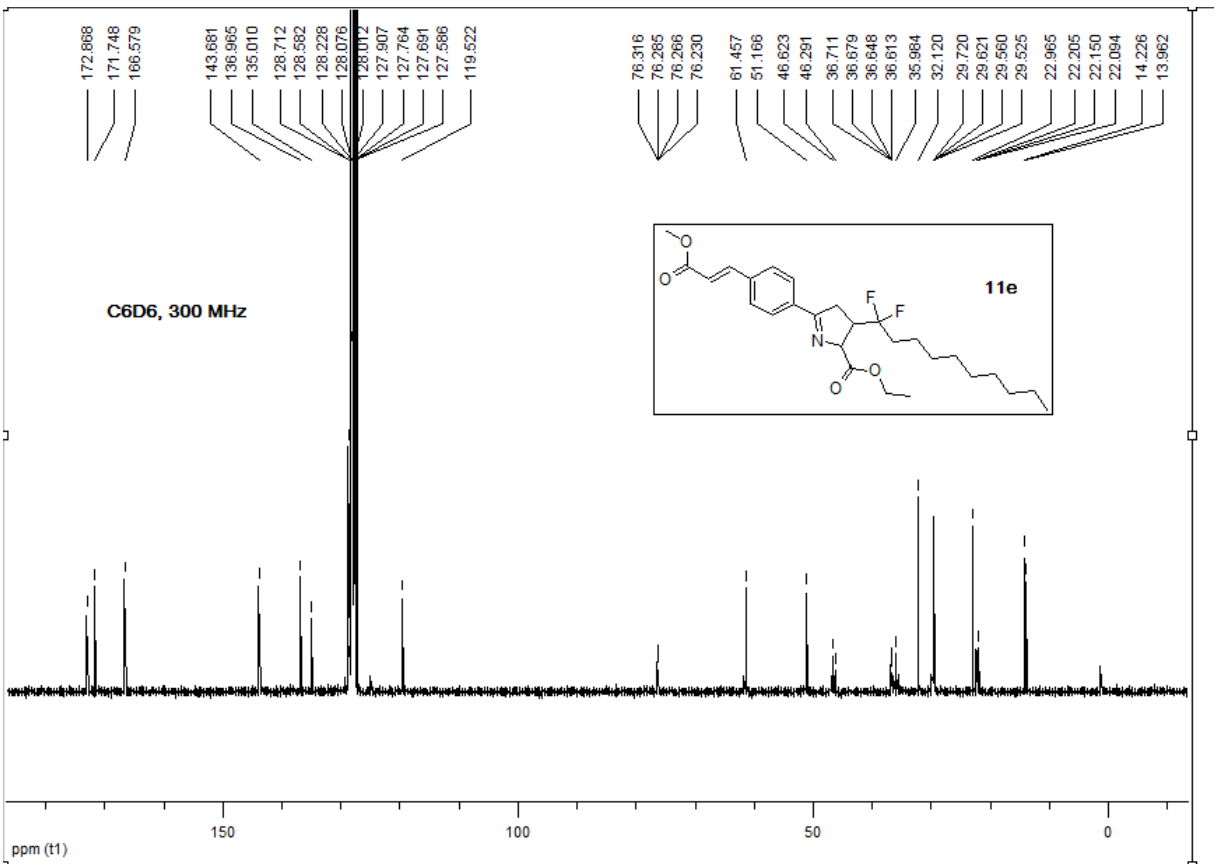

7.390
7.386
7.378
7.228
7.205
7.199
7.167
7.162
7.150
5.294
5.273
4.136
4.112
4.100
4.088
4.076
4.064
4.052
4.049
4.037
4.025
4.013
4.002
3.989
3.965
3.491
3.484
3.466
3.458
3.435
3.433
3.413
3.405
3.382
3.034
3.029
3.010
3.005
2.977
2.972
2.952
2.947
2.938
2.931
2.905
2.897
2.881
2.873
2.847
2.839
1.825
1.804
1.793
C6D6, 300 MHz
F
F
N
O
O
10e
2.15
4.16
2.95
1.04
2.27
1.08
2.13
2.21
2.11
12.81
3.24
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

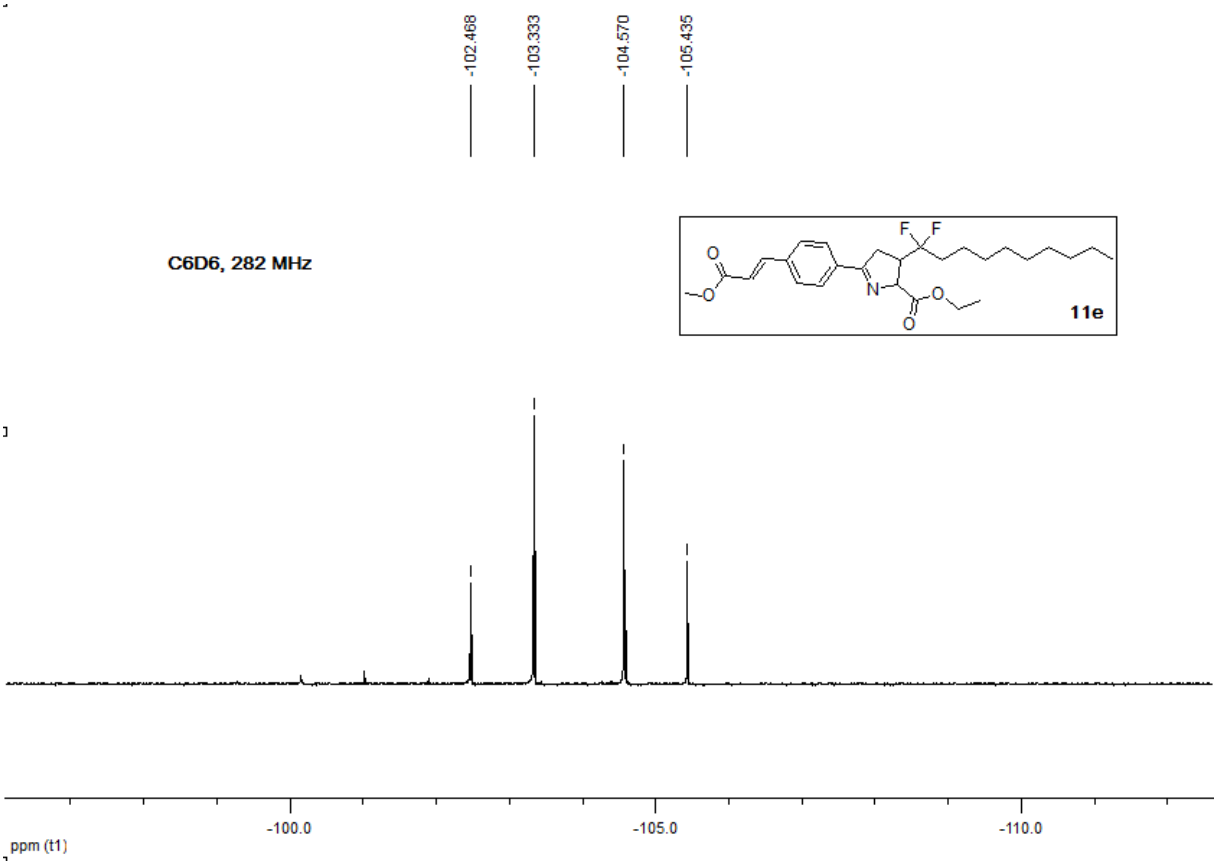

173.303
172.054
143.993
140.667
132.869
129.228
129.084
129.035
128.872
128.756
128.714
128.541
128.341
128.124
128.020
127.875
127.808
127.699
127.472
127.290
127.151
127.105
125.098
121.880
76.368
61.505
47.135
46.806
46.474
36.926
36.894
36.858
36.442
36.109
35.779
32.243
29.845
29.751
29.682
29.656
23.087
22.342
22.287
22.230
14.347
14.104
C6D6, 75 MHz
F
F
N
O
O
10e
150
100
50
0
ppm (t1)

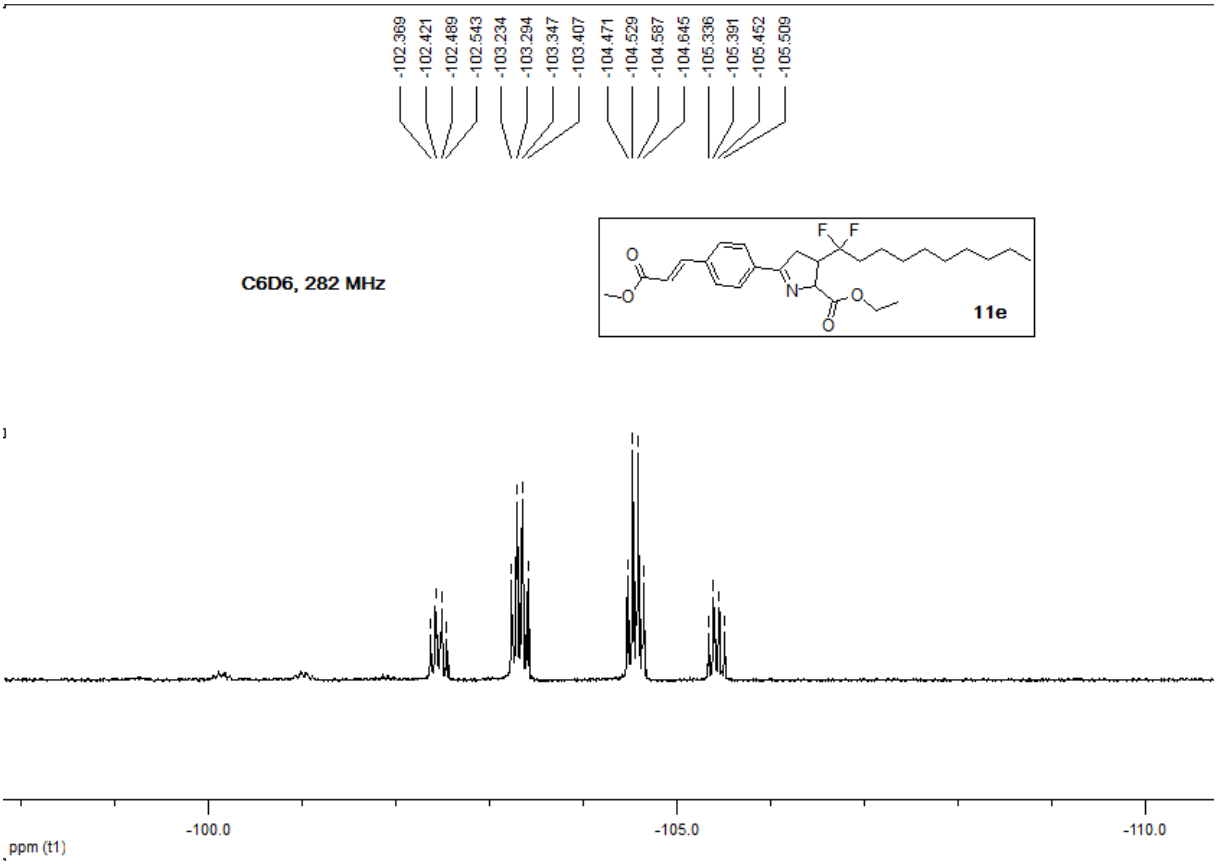

-102.477
-103.341
-104.405
-105.269
C6D6, 282 MHz
F
F
N
O
O
10e
-95.0
-100.0
-105.0
-110.0
ppm (t1)

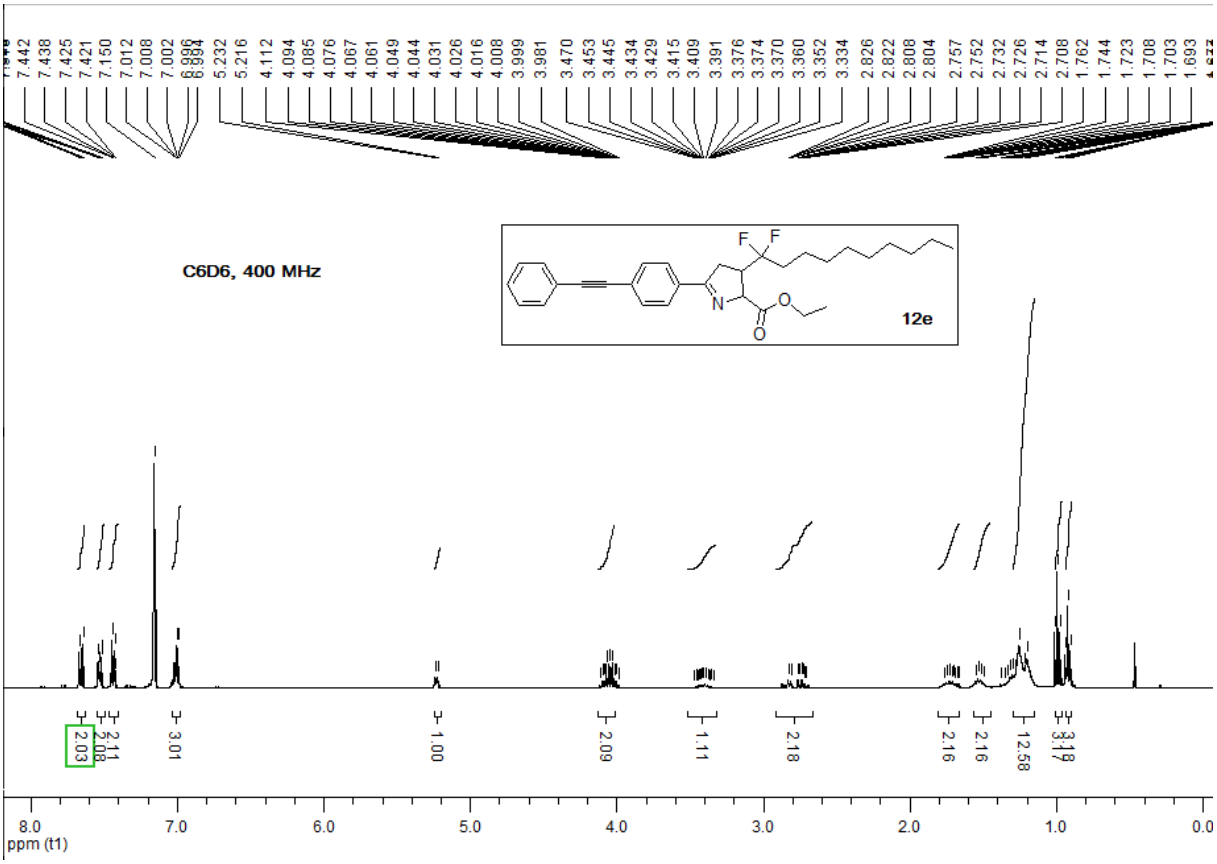

-102.404
-102.423
-102.456
-102.470
-102.509
-102.525
-102.578
-103.269
-103.326
-103.381
-103.441
-104.323
-104.380
-104.439
-104.497
-105.187
-105.242
-105.305
-105.360
C6D6, 282 MHz
F
F
N
O
O
10e
-100.0
-105.0
-110.0
ppm (t1)

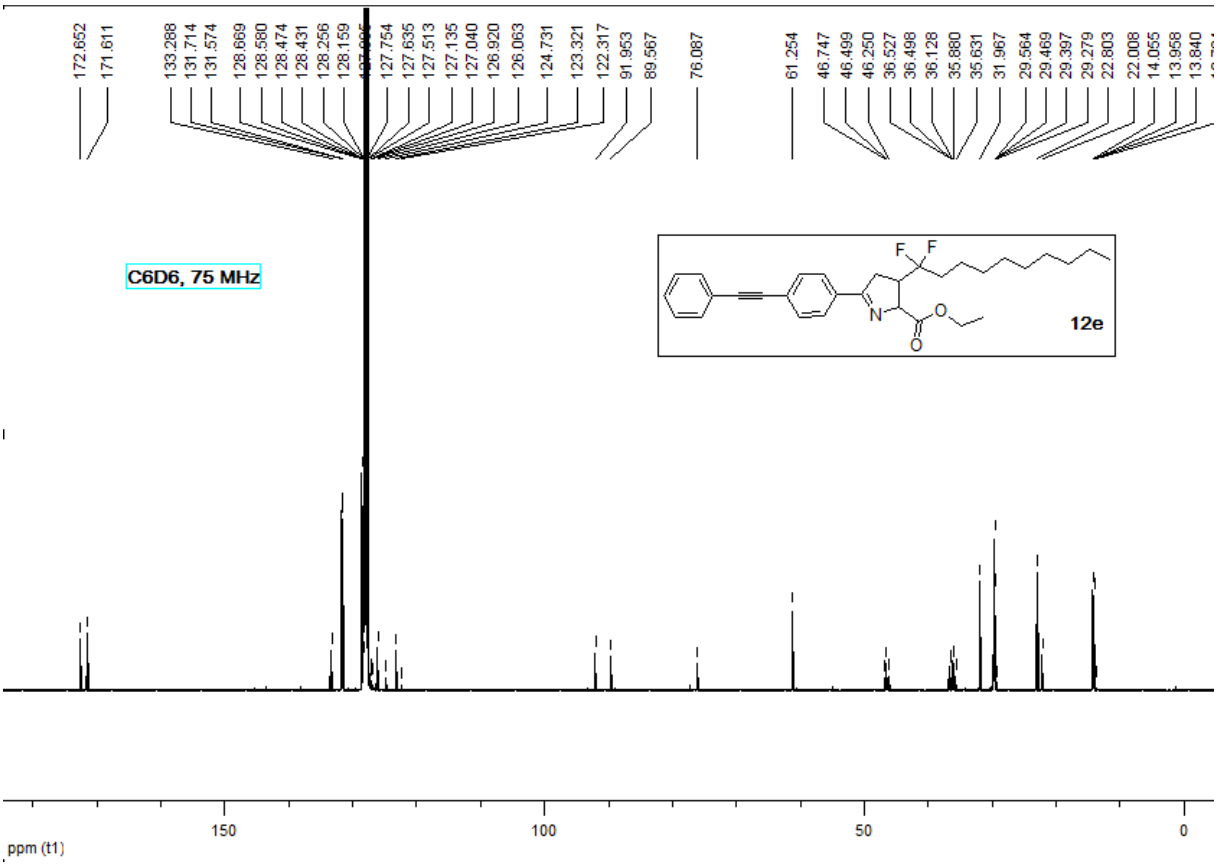

C6D6, 300 MHz
11e
ppm (t1)

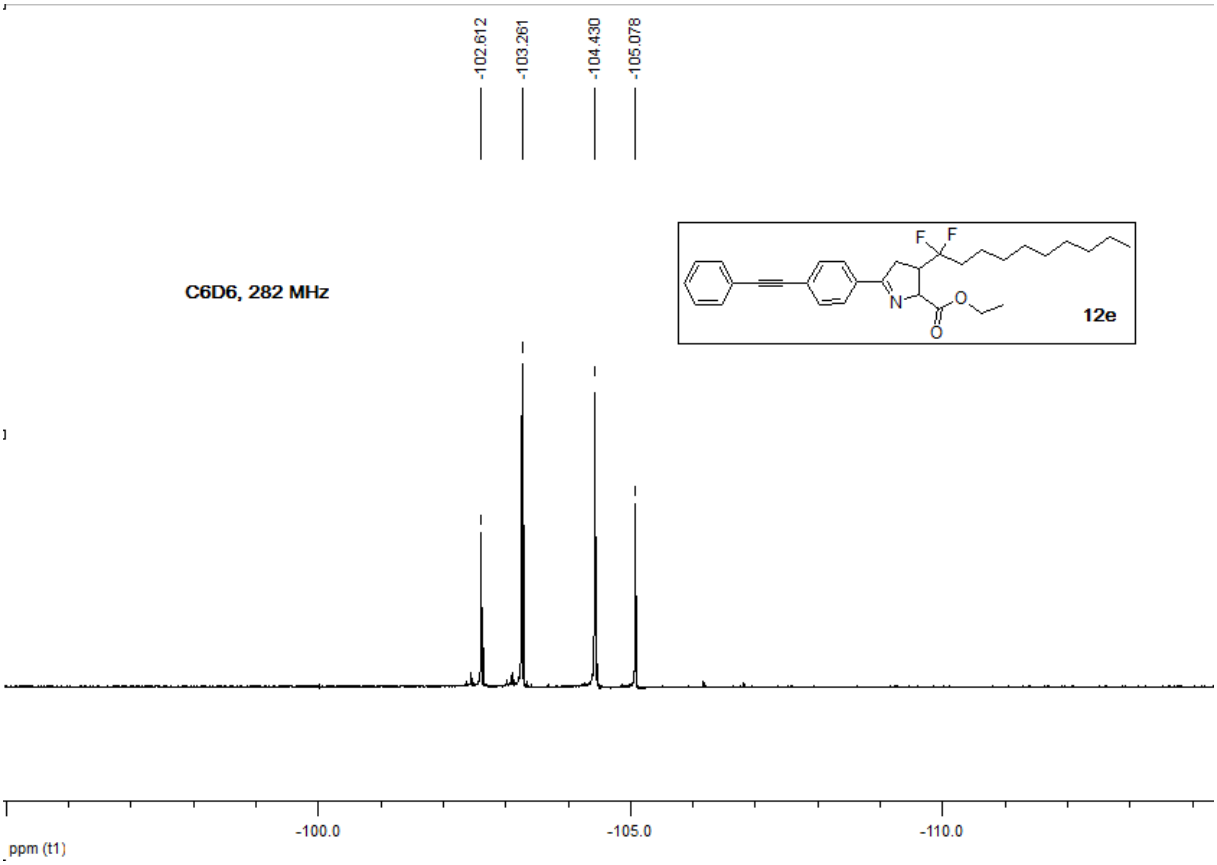

C6D6, 300 MHz
11e
ppm (t1)

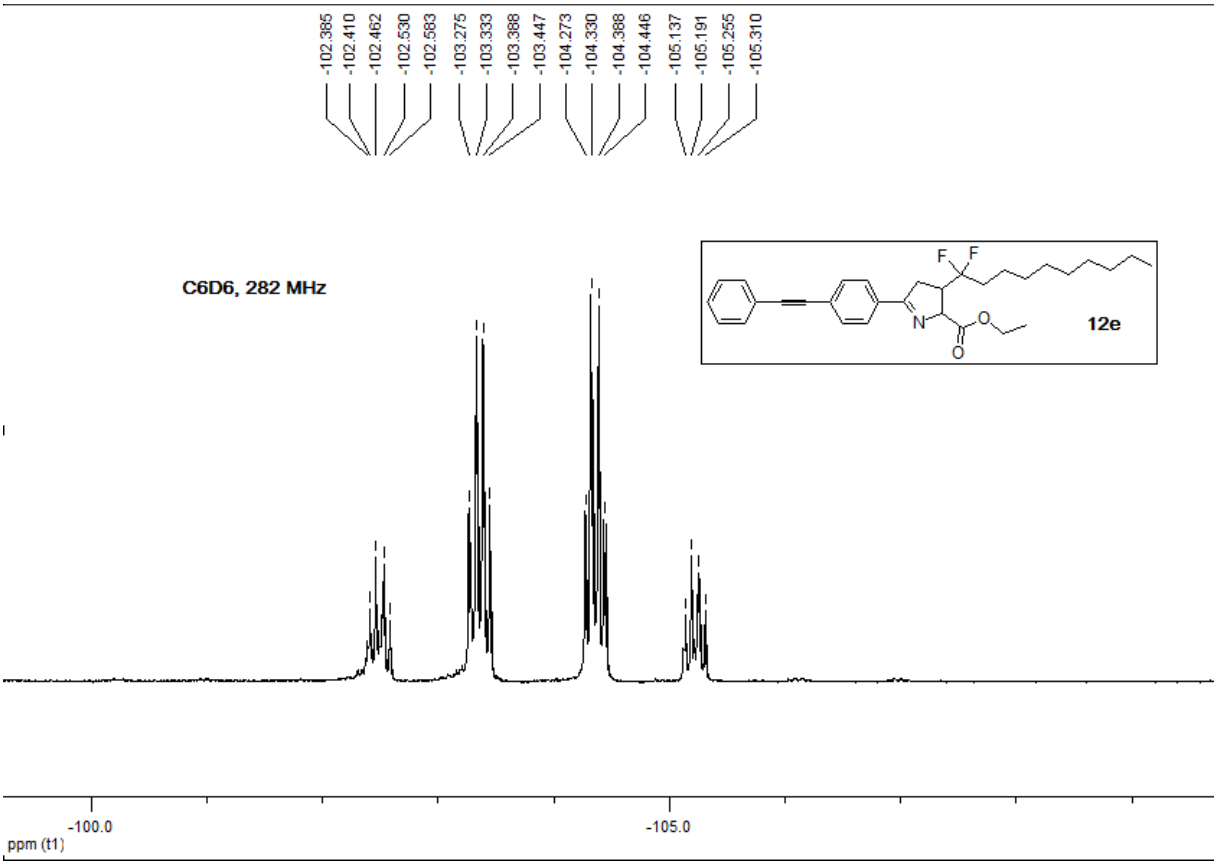

-102.468
-103.333
-104.570
-105.435
C6D6, 282 MHz
F
F
O
O
N
O
O
11e
-100.0
-105.0
-110.0
ppm (t1)


-102.369
-102.421
-102.489
-102.543
-103.234
-103.294
-103.347
-103.407
-104.471
-104.529
-104.587
-104.645
-105.336
-105.391
-105.452
-105.509
C6D6, 282 MHz
F
F
O
O
N
O
O
11e
-100.0
-105.0
-110.0
ppm (t1)


C6D6, 400 MHz
12e
F
F
N
O
O
ppm (t1)


C6D6, 75 MHz
12e
F
F
N
O
O
ppm (t1)


-102.612
-103.261
-104.430
-105.078
C6D6, 282 MHz
F
F
N
O
O
12e
-100.0
-105.0
-110.0
ppm (t1)


-102.385
-102.410
-102.462
-102.530
-102.583
-103.275
-103.333
-103.388
-103.447
-104.273
-104.330
-104.388
-104.446
-105.137
-105.191
-105.255
-105.310
C6D6, 282 MHz
F
F
N
O
O
12e
-100.0
-105.0
ppm (t1)