Supporting Information

Copper-Mediated Regioselective Hydrodifluoroalkylation of Alkynes

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General Information

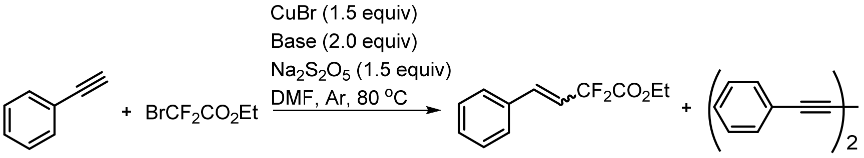
Flash chromatographic separations were carried out on 200-300 mesh silica gel. Reactions were monitored by TLC, GC, or HPLC analysis of reaction aliquots. GC analysis was performed on an Agilent 7890 Gas Chromatography using a HP-5 capillary column (30 m × 0.32 mm, 0.5 μm film) with appropriate hydrocarbons as internal standards. HPLC analysis was performed on an Agilent 1260 Liquid Chromatography using a ZORBAX SB-C18 column (4.6 × 150 mm, 5-micron). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE III spectrometer. ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0 or at the signal of a residual protonated solvent: $CDCl_3$ δ 7.26. ^{13}C NMR chemical shifts were determined relative to $CDCl_3$ δ 77.16. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, t = triplet, td = triplet of doublets, q = quartet, m = multiplet, br = broad. High resolution spectra (HRMS) were recorded on a QTOF mass analyzer with electrospray ionization (ESI) through a Bruker Daltonicmior OTOF-QII. integration value. All reagents were weighed and handled in air, and refilled with an inert atmosphere of Ar at r.t. Petroleum ether (PE) used refers to the hydrocarbon mixture with a boiling range of 60–90 °C.

General Procedure:

Hydrodifluoroalkylation of Alkynes with Functionalized Difluoromethyl Bromides

To a mixture of CuBr (0.75 mmol, 1.5 equiv) and $Na_2S_2O_5$ (0.75 mmol, 1.5 equiv) in 25 mL of Schlenk tube under Ar atmosphere, were added DMF (5 mL), TMEDA (1.0 mmol, 2.0 equiv), functionalized difluoromethyl bromide (0.75 mmol, 1.5 equiv) and alkyne (0.5 mmol. 1.0 equiv) successively. The reaction mixture was heated to 80 °C (oil bath). After stirring for 6-8 h, the reaction was cooled to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and filtered with a pad of celite. The filtrate was concentrated in vacuum and then purified with silica gel chromatography to give the desired product.

Table S1. The Effects of the Base on the Reaction of Hydrodifluoroalkylation of Alkynes[*a*]

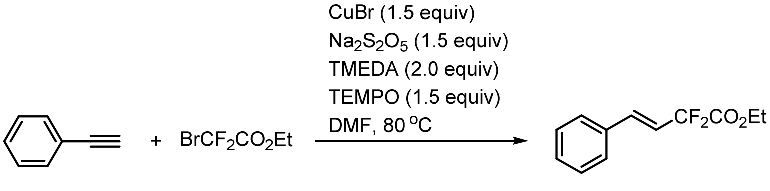


Entry	Base	yield[b] (%)	
		3a (*E*/*Z*)	**4**
1	none	6 (>99:1)	0
2	Et_3N	6 (>99:1)	0
3	bpy	66 (1:2)	0
4	PMDETA	19 (10:1)	0
5	TMPDA	32 (20:1)	0

[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **2a** (0.45 mmol, 1.5 equiv), CuBr (0.45 mmol, 1.5 equiv), Base (0.6 mmol, 2.0 equiv), $Na_2S_2O_5$ (0.45 mmol, 1.5 equiv), DMF (3 mL), 80 °C, under argon.

Mechanistic Studies:

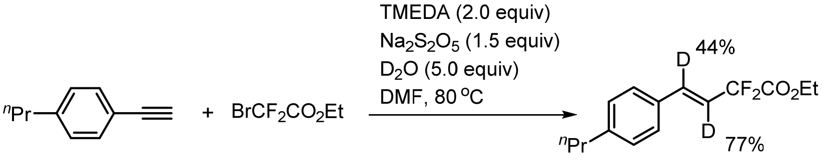
1. Radical Trapping Experiment with TEMPO



1a **2a** **3a**, not detected

To a mixture of CuBr (0.75 mmol, 1.5 equiv), $Na_2S_2O_5$ (0.75 mmol, 1.5 equiv) and TEMPO (0.75 mmol, 1.5 equiv) in 25 mL of Schlenk tube under Ar atmosphere, were added DMF (5 mL), TMEDA (1.0 mmol, 2.0 equiv), ethyl bromodifluoroacetate **2a** (0.75 mmol, 1.5 equiv) and phenylacetylene **1a** (0.5 mmol. 1.0 equiv) successively. The reaction mixture was heated to 80 °C (oil bath). After stirring for 6 hours, the reaction was cooled to room temperature. No desired product **3a** was detected by crude ^{19}F NMR.

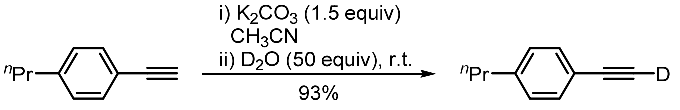
2. Deuterium-Labeling Experiment



1c **2a** **3c-D**

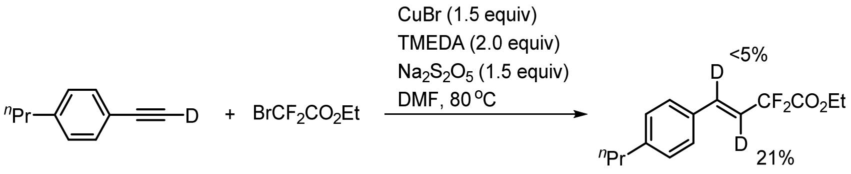
To a mixture of CuBr (0.75 mmol, 1.5 equiv) and $Na_2S_2O_5$ (0.75 mmol, 1.5 equiv) in 25 mL of Schlenk tube under Ar atmosphers, were added DMF (5 mL), TMEDA (1.0 mmol, 2.0 equiv), D_2O (2.5 mmol, 5.0 equiv), ethyl bromodifluoroacetate **2a** (0.75 mmol, 1.5 equiv) and phenylacetylene **1c**

(0.5 mmol. 1.0 equiv) successively. The reaction mixture was heated to 80 °C (oil bath). After stirring for 6 hours, the reaction was cooled to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and filtered with a pad of celite. The filtrate was concentrated in vacuum and then purified with silica gel chromatography to give the product **3c-D**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.05 (s, 1H), 6.31 – 6.22 (m, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.60 (t, J = 7.6 Hz 2H), 1.67 – 1.59 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (t, J = 35.2 Hz), 144.8, 136.7 (d, J = 7.2 Hz), 131.8, 129.1, 127.5, 118.2 – 117.4 (m), 113.0 (t, J = 249.2 Hz), 63.2, 38.0, 24.5, 14.1, 13.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.00 (dd, J = 11.4, 1.8 Hz, 2F), -103.02 (d, J = 11.4 Hz, 2F), -103.13 (s, 2F).



1c **1c-D**

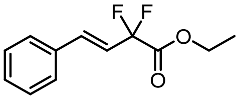
A flame dried 10 mL round bottomed flask was charged with 4-propylphenylacetylene (1.0 mmol, 1.0 equiv) and potassium carbonate (1.5 mmol, 1.5 equiv) in CH_3CN (4 mL). This was allowed to stir under an atmosphere of N_2 for 30 minutes. To this D_2O (1 mL, ~50 equiv) was added and left to stir for 1 hour. The reaction mixture was diluted with DCM (10 mL) and transferred to a separating funnel. The organic layer was dried over anhydrous Na_2SO_4 and filtered with a pad of celite. The filtrate was concentrated and then purified with silica gel chromatography to give the product **1c-D**.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 HZ, 2H), 7.15 (d, J = 8.0 HZ, 2H), 2.60 (t, J = 7.6 HZ, 2H), 1.70 – 1.60 (m, 2H), 0.95 (t, J = 7.3 HZ, 3H).



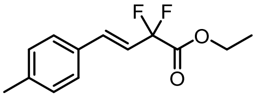
1c-D **2a** **3c-D**

To a mixture of CuBr (0.75 mmol, 1.5 equiv) and $Na_2S_2O_5$ (0.75 mmol, 1.5 equiv) in 25 mL of Schlenk tube under Ar atmosphers, were added DMF (5 mL), TMEDA (1.0 mmol, 2.0 equiv), ethyl bromodifluoroacetate **2a** (0.75 mmol, 1.5 equiv) and deuterated 4-propylphenylethylene **1c-D** (0.5 mmol. 1.0 equiv) successively. The reaction mixture was heated to 80 °C (oil bath). After stirring for 6 hours, the reaction was cooled to room temperature. The reaction mixture was diluted with ethyl acetate and then washed with saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and filtered with a pad of celite. The filtrate was concentrated in vacuum and then purified with silica gel chromatography to give the product **3c-D**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.06 (dt, J = 16.2, 2.4 Hz, 1H), 6.26 (dt, J = 16.2, 11.5 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.60 (t, J = 7.6 Hz 2H), 1.69 – 1.60 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (t, J = 35.2 Hz), 144.8, 136.9 (t, J = 9.5 Hz), 131.8, 129.1, 127.5, 118.0 (t, J = 24.4 Hz), 113.0 (t, J = 249.2 Hz), 63.2, 38.0, 24.5, 14.1, 13.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.00 (dd, J = 11.5, 2.4 Hz, 2F), -103.13 (s, 2F).

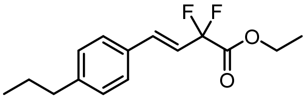
Characterization Data



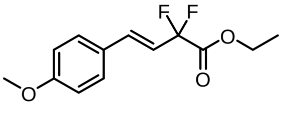
Ethyl (*E*)-2,2-difluoro-4-phenyl-3-butenoate (**3a**, *E*/*Z* = 62:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 50:1) as colorless oil (96 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.41 – 7.36 (m, 3H), 7.09 (dt, J = 16.3, 2.5 Hz, 1H), 6.32 (dt, J = 16.3, 11.4 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0 (t, J = 34.7 Hz), 137.0 (t, J = 9.5 Hz), 134.3, 129.8, 129.0, 127.6, 119.0 (t, J = 25.3 Hz), 112.9 (t, J = 249.0 Hz), 63.2, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.20 (dd, J = 11.4, 2.4 Hz, 2F).



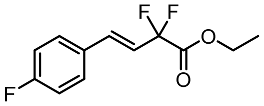
Ethyl (*E*)-2,2-difluoro-4-(*p*-tolyl)-3-butenoate (**3b**, *E/Z* > 99:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 50:1) as colorless oil (97 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.06 (dt, J = 16.2, 2.4 Hz, 1H), 6.26 (dt, J = 16.2, 11.5 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.37 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (t, J = 35.3 Hz), 140.0, 136.9 (t, J = 9.5 Hz), 131.5, 129.7, 127.5, 117.9 (t, J = 25.2 Hz), 113.0 (t, J = 249.3 Hz), 63.2, 21.4, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.93 (dd, J = 11.5, 2.2 Hz, 2F).



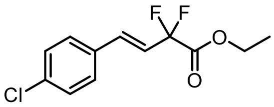
Ethyl (*E*)-2,2-difluoro-4-(4-propylphenyl)-3-butenoate (**3c**, *E*/*Z* = 50:1).[3] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 50:1) as colorless oil (111 mg, 83% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz,2H), 7.06 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.26 (dt, *J* = 16.2, 11.5 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.60 (t, *J* = 7.6 Hz 2H), 1.69 – 1.60 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 164.2 (t, *J* = 35.2 Hz), 144.8, 136.9 (t, *J* = 9.5 Hz), 131.8, 129.1, 127.5, 118.0 (t, *J* = 24.4 Hz), 113.0 (t, *J* = 249.2 Hz), 63.2, 38.0, 24.5, 14.1, 13.9; ^{19}F NMR (377 MHz, CDCl$_3$) δ -102.99 (dd, *J* = 11.5, 2.4 Hz, 2F).



Ethyl (*E*)-2,2-difluoro-4-(4-methoxyphenyl)-3-butenoate (**3d**, *E*/*Z* = 30:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 35:1) as colorless oil (88 mg, 69% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, *J* = 8.7 Hz, 2 H), 7.02 (dt, *J* = 16.2, 2.4 Hz, 1 H), 6.89 (d, *J* = 8.7 Hz, 2 H), 6.16 (dt, *J* = 16.2, 11.5 Hz, 1 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 3.82 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 164.2 (t, *J* = 35.4 Hz), 160.9, 136.4 (t, *J* = 9.5 Hz), 129.0, 127.0, 116.5 (t, *J* = 25.8 Hz), 114.4, 113.1 (t, *J* = 249.2 Hz), 63.1, 55.5, 14.1; ^{19}F NMR (377 MHz, CDCl$_3$) δ -102.63 (dd, *J* = 11.5, 2.4 Hz, 2F).

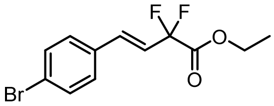


Ethyl (*E*)-2,2-difluoro-4-(4-fluorophenyl)-3-butenoate (**3e**, *E*/*Z* > 99:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 40:1) as colorless oil (92 mg, 75% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.08 – 7.02 (m, 3H), 6.23 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 164.0 (t, *J* = 35.0 Hz), 163.7 (d, *J* = 251.0 Hz), 135.8 (t, *J* = 9.5 Hz), 130.5 (d, *J* = 3.5 Hz), 129.4 (d, *J* = 8.4 Hz), 118.7 (t, *J* = 24.5 Hz), 116.1 (d, *J* = 22.0 Hz), 112.8 (t, *J* = 249.5 Hz), 63.3, 14.1; ^{19}F NMR (377 MHz, CDCl$_3$) δ -103.18 (dd, *J* = 11.3, 2.0 Hz, 2F), -110.86 – -110.93 (m, 1F).

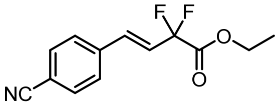


Ethyl (*E*)-2,2-difluoro-4-(4-chlorophenyl)-3-butenoate (**3f**, *E*/*Z* = 16:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 50:1) as colorless oil (91 mg, 70% yield).

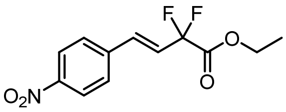
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 16.2 Hz, 1H), 6.28 (dt, *J* = 16.2, 11.4 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.9 (t, *J* = 34.8 Hz), 135.7 (t, *J* = 9.5 Hz), 135.6, 132.7, 129.2, 128.8, 119.5 (t, *J* = 24.7 Hz), 112.7 (t, *J* = 249.8 Hz), 63.3, 14.1; ^{19}F NMR (377 MHz, CDCl$_3$) δ -103.31 (dd, *J* = 11.3, 2.4 Hz, 2F).



Ethyl (*E*)-2,2-difluoro-4-(4-bromophenyl)-3-butenoate (**3g**, *E/Z* = 12:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 50:1) as colorless oil (95 mg, 62% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 16.2 Hz, 1H), 6.30 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.9 (t, *J* = 34.7 Hz), 135.8 (t, *J* = 9.5 Hz), 133.1, 132.2, 129.0, 123.9, 119.6 (t, *J* = 25.1 Hz), 112.6 (t, *J* = 249.8 Hz), 63.4, 14.1; ^{19}F NMR (377 MHz, CDCl$_3$) δ -103.36 (dd, *J* = 11.3, 2.4 Hz, 2F).

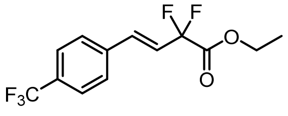


Ethyl (*E*)-2,2-difluoro-4-(4-cyanophenyl)-3-butenoate (**3h**, *E/Z* = 2:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1) as colorless oil (82 mg, 65% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 16.2 Hz, 1H), 6.41 (dt, *J* = 16.2, 11.2 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.5 (*J* = 34.6 Hz), 138.4, 135.1 (t, *J* = 9.5 Hz), 132.7, 128.1, 122.6 (t, *J* = 25.3 Hz), 118.4, 113.1, 112.2(t, *J* = 250.3 Hz), 63.5, 14.0; ^{19}F NMR (377 MHz, CDCl$_3$) δ -103.82 (dd, *J* = 11.2, 2.4 Hz, 2F). *Z*-isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 12.7 Hz, 1H), 6.03 – 5.93 (m, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (377 MHz, CDCl$_3$) δ -96.26 (dd, *J* = 13.7, 1.8 Hz, 2F).

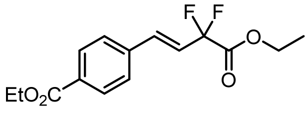


Ethyl (*E*)-2,2-difluoro-4-(4-nitrophenyl)-3-butenoate (**3i**, *E/Z* = 1.6:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1) as yellow solid (46 mg, 34% yield).

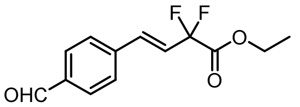
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.23 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 16.2 Hz, 1H), 6.46 (dt, *J* = 16.2, 11.4 Hz, 1H), 4.36 (q, *J* = 6.8 Hz, 2H), 1.37 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.5 (*J* = 34.2 Hz), 148.3, 140.3, 134.6 (t, *J* = 9.5 Hz), 128.4, 124.3, 123.3 (t, *J* = 25.3 Hz), 112.2 (t, *J* = 250.4 Hz), 63.6, 14.1; ^{19}F NMR (377 MHz, CDCl$_3$) δ -103.93 (dd, *J* = 11.2, 2.2 Hz, 2F). *Z*-isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.19 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 12.6 Hz, 1H), 6.07 – 5.97 (m, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 1.24(t, *J* = 7.0 Hz, 3H); ^{19}F NMR (377 MHz, CDCl$_3$) δ -96.62 (dd, *J* = 13.8, 1.7 Hz, 2F).



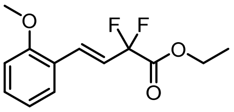
Ethyl (*E*)-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)-3-butenoate (**3j**, *E/Z* = 2:1).[2] The product was purified with silica gel cnhromatography (Petroleum ether/EtOAc = 60:1) as colorless oil (88 mg, 60% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 16.2 Hz, 1H), 6.40 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.8 (*J* = 34.6 Hz), 137.7, 135.5 (t, *J* = 9.3 Hz), 131.5 (q, *J* = 32.8 Hz), 127.8, 126.0 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 273.2 Hz), 121.7 (t, *J* = 25.2 Hz), 112.5 (t, *J* = 250.1 Hz), 63.4, 14.1; ^{19}F NMR (377 MHz, CDCl$_3$) δ -62.84 (s, 3F), -103.73 (dd, *J* = 11.3, 1.6 Hz, 2F). *Z*-isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 12.7 Hz, 1H), 6.02 – 5.92 (m, 1H), 4.12(q, *J* = 7.1 Hz, 2H), 1.19(t, *J* = 7.1 Hz, 3H); ^{19}F NMR (377 MHz, CDCl$_3$) δ -62.84 (s, 3F), -95.56 (dd, *J* = 13.6, 0.9 Hz, 2F).



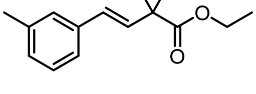
Ethyl (*E*)-4-(4-ethoxy-3,3-difluoro-4-oxobut-1-en-1-yl)benzoate (**3k**, *E/Z*= 5:1). The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1) as pale yellow oil (79 mg, 53% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.11 (dt, *J* = 16.2, 2.3 Hz, 1H), 6.40 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.49 – 4.26 (m, 4H), 1.47 – 1.31 (m, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.1, 163.8 (*J* = 34.6 Hz), 138.3, 135.9 (t, *J* = 9.4 Hz), 131.4, 130.2, 127.5, 121.2 (t, *J* = 25.3 Hz), 112.5(t, *J* = 249.9 Hz), 63.4, 61.3, 14.4, 14.1; ^{19}F NMR (377 MHz, CDCl$_3$) δ -103.58 (dd, *J* = 11.2, 2.4 Hz, 2F); HRMS (ESI): *m/z* calcd. for $C_{15}H_{16}F_2NaO_4^+$ [M + Na]$^+$: 321.0909, found: 321.0909. *Z*-isomer: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 12.7 Hz, 1H), 5.99 – 5.90 (m, 1H), 4.49 – 4.26 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.47 – 1.31 (m, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.17 (dd, *J* = 13.4, 1.3 Hz, 2F).



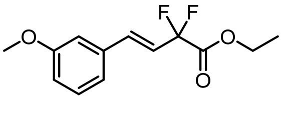
Ethyl (*E*)-2,2-difluoro-4-(4-formylphenyl)-3-butenoate (**3l**, *E/Z*= 4:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1) as pale yellow solid (60 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.13 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.44 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 163.7 (*J* = 35.4 Hz), 139.9, 137.0, 135.7 (t, *J* = 9.4 Hz), 130.3, 128.1, 122.3 (t, *J* = 25.1 Hz), 112.4(t, *J* = 250.1 Hz), 63.5, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.71 (dd, *J* = 11.3, 2.4 Hz, 2F). *Z*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 12.7 Hz, 1H), 6.04 – 5.94 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.64 (dd, *J* = 13.6, 1.5 Hz, 2F).



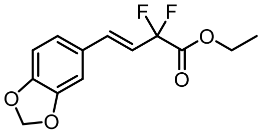
Ethyl (*E*)-2,2-difluoro-4-(2-methoxyphenyl)-3-butenoate (**3m**, *E/Z* > 99:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 35:1) as colorless oil (80 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.38 (dt, *J* = 16.4, 2.5 Hz, 1H), 7.35 – 7.30 (m, 1H), 6.98 – 6.90 (m, 2H), 6.42 (dt, *J* = 16.4, 11.5 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (t, *J* = 35.2 Hz), 157.9, 132.4 (t, *J* = 9.9 Hz), 130.9, 128.5, 123.2, 120.8, 119.5 (t, *J* = 24.8 Hz), 113.2 (t, *J* = 248.1 Hz), 111.2, 63.1, 55.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.86 (dd, *J* = 11.5, 2.5 Hz, 2F).



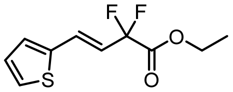
Ethyl (*E*)-2,2-difluoro-4-(m-tolyl)-3-butenoate (**3n**, *E/Z* = 33:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 50:1) as colorless oil (87 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 3H), 7.20 – 7.19 (m, 1H), 7.08 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.32 (dt, J = 16.2, 11.4 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (t, J = 34.9 Hz), 138.6, 137.1 (t, J = 9.4 Hz), 134.2, 130.6, 128.9, 128.2, 124.8, 118.8 (t, J = 25.1 Hz), 112.9 (t, J = 248.5 Hz), 63.2 , 21.4 , 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.11 (dd, J = 11.8, 3.0 Hz, 2F).



Ethyl (*E*)-2,2-difluoro-4-(3-methoxyphenyl)-3-butenoate (**3o**, *E/Z* = 70:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 35:1) as colorless oil (91 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 8.0 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.97 – 6.96 (m, 1H), 6.91 (dd, J = 8.0, 2.4 Hz, 1H), 6.30 (dt, J = 16.2, 11.4 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0 (J = 34.9 Hz), 160.1, 136.9 (t, J = 9.4 Hz), 135.6, 130.0, 120.2, 119.3 (t, J = 25.0 Hz), 115.5, 112.8 (t, J = 249.6 Hz), 112.7, 63.3, 55.4, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.24 (dd, J = 11.4, 2.5 Hz, 2F).

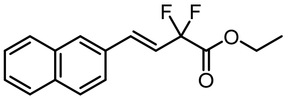


Ethyl (*E*)-2,2-difluoro-4-(1,3-benzodioxol-5-yl)-3-butenoate (**3p**, *E/Z* > 99:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 30:1) as colorless oil (90 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.95 (m, 2H), 6.90 (dd, J = 8.0, 1.1 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.12 (dt, J = 16.1, 11.4 Hz, 1H), 5.98 (s, 2H), 4.34 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (t, J = 34.9 Hz), 149.1, 148.4, 136.6 (t, J = 9.6 Hz), 128.6, 123.3, 117.0 (t, J = 25.4 Hz), 113.0 (t, J = 248.4 Hz), 108.6, 106.3, 101.6, 63.2, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.73 (dd, J = 11.5, 2.3 Hz, 2F).

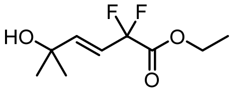


Ethyl (*E*)-2,2-difluoro-4-(thiophen-2-yl)-3-butenoate (**3s**, *E/Z* > 99:1).[2] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 50:1) as colorless oil (84 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 5.0 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.02 (dd, J = 5.0, 3.7 Hz, 1H), 6.12 (dt, J = 15.9, 11.5 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (J = 35.2 Hz), 139.1, 129.9 (t, J = 10.0 Hz), 129.5, 128.0, 127.4, 117.8 (t, J =

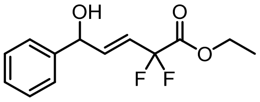
25.1 Hz), 112.6 (t, J = 248.6 Hz), 63.3, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.93 (dd, J = 11.5, 2.2 Hz, 2F).



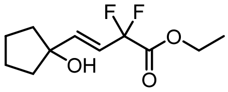
Ethyl (*E*)-2,2-difluoro-(4-naphthalen-2-yl)-3-butenoate (**3r**, *E/Z* = 29:1).[3] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 50:1) as white solid (101 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.82 (m, 4H), 7.61 (dd, J = 8.7, 1.3 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.26 (dt, J = 16.2, 2.4 Hz, 1H), 6.44 (dt, J = 16.2, 11.4 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (t, J = 35.0 Hz), 137.1 (t, J = 9.5 Hz), 134.0, 133.4, 131.7, 128.9, 128.8, 128.5, 127.9, 127.1, 126.8, 123.4, 119.2 (t, J = 24.7 Hz), 113.0 (t, J = 248.6 Hz), 63.3, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.97 (dd, J = 11.4, 2.4 Hz, 2F).



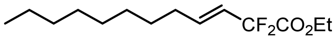
Ethyl (*E*)-2,2-difluoro-5-hydroxy-5-methyl-3-hexenoate (**3s**, *E/Z* > 99:1). The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 8:1) as pale yellow oil (64 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (dt, J = 15.8, 2.4 Hz, 1H), 5.90 (dt, J = 15.8, 11.3 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.84 (s, 1H), 1.35 – 1.31 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (t, J = 34.3 Hz), 146.3 (t, J = 8.2 Hz), 118.2 (t, J = 25.9 Hz), 112.7 (t, J = 247.9 Hz), 70.6, 63.1, 29.5, 14.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.36 (dd, J = 11.3, 2.4 Hz, 2F); HRMS (ESI): *m/z* calcd. for $C_9H_{14}F_2NaO_3^+$ $[M + Na]^+$: 231.0803, found: 231.0804.



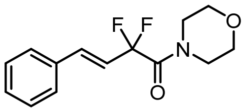
Ethyl (*E*)-2,2-difluoro-5-hydroxy-5-phenyl-3-pentenoate (**3t**, *E/Z* > 99:1). The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 8:1) as pale yellow oil (82 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 5H), 6.48 – 6.42 (m, 1H), 6.16 – 6.06 (m, 1H), 5.33 (s, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.10 (s, 1H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (t, J = 34.6 Hz), 141.0, 140.3 (t, J = 8.4 Hz), 129.0, 128.6, 126.7, 120.6 (t, J = 25.4 Hz), 112.5 (t, J = 248.2 Hz), 73.2, 63.2, 14.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -103.56 (ddt, J = 23.8, 11.4, 2.6 Hz, 2F); HRMS (ESI): *m/z* calcd. for $C_{13}H_{14}F_2NaO_3^+$ $[M + Na]^+$: 279.0803, found: 279.0813.



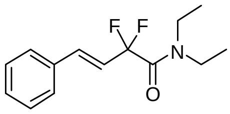
Ethyl (*E*)-2,2-difluoro-4-(1-hydroxycyclopentyl)-3-butenoate (**3u**, *E/Z* > 99:1). The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 8:1) as pale yellow oil (69 mg, 59% yield). ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.34 (dt, *J* = 15.7, 2.2 Hz, 1H), 5.93 (dt, *J* = 15.7, 11.5 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.91 (br, 1H), 1.86 – 1.84 (m, 2H), 1.73 – 1.60 (m, 6H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 164.2 (t, *J* = 34.8 Hz), 145.2 (t, *J* = 8.1 Hz), 118.4 (t, *J* = 25.0 Hz), 112.8 (t, *J* = 247.9 Hz), 81.5, 63.1, 40.6, 23.9, 14.0; ^{19}F NMR (565 MHz, CDCl$_3$) δ -103.10 (dd, *J* = 11.5, 2.2 Hz, 2F); HRMS (ESI): *m/z* calcd. for $C_{11}H_{16}F_2NaO_3^+$ [M + Na]$^+$: 257.0960, found: 257.0960.



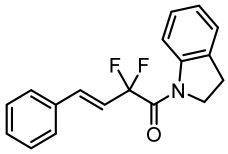
Ethyl (*E*)-2,2-difluoro-3-dodecenoate (**3v**, *E/Z* = 19:1).[4] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 60:1) as colorless oil (147 mg, 56% yield). ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.29 – 6.24 (m, 1H), 5.69 – 5.63 (m, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.15 – 2.11 (m, 2H), 1.42 – 1.39 (m, 2H), 1.34 (t, *J* = 7.1 Hz,3H), 1.31 – 1.26 (m, 11H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 163.3 (t, *J* = 34.7 Hz), 139.2 (t, *J* = 9.0 Hz), 120.1 (t, *J* = 25.0 Hz), 111.5 (t, *J* = 247.5 Hz), 62.0, 31.0, 31.0, 28.5, 28.3, 28.2, 27.3, 21.8, 13.2, 13.1; ^{19}F NMR (565 MHz, CDCl$_3$) δ -102.96 – -102.99 (m, 2F).



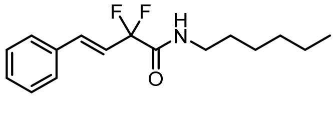
(*E*)-2,2-Difluoro-1-morpholino-4-phenylbut-3-en-1-one (**5a**, *E/Z* = 50:1).[5] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 6:1) as colorless oil (104 mg, 78% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 – 7.44 (m, 2H), 7.38 – 7.33 (m, 3H), 7.00 (dt, *J* = 16.3, 2.7 Hz, 1H), 6.45 (dt, *J* = 16.3, 11.1 Hz, 1H), 3.72 – 3.68 (m, 8H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 162.0 (t, *J* = 30.4 Hz), 135.8 (t, *J* = 9.8 Hz), 134.2, 129.6, 128.9, 127.5, 120.0 (t, *J* = 24.4 Hz), 115.3 (t, *J* = 249.3 Hz), 66.8, 66.7, 46.7 (t, *J* = 5.2 Hz), 43.5; ^{19}F NMR (377 MHz, CDCl$_3$) δ -95.09 (dd, *J* = 11.1, 2.2 Hz, 2F).



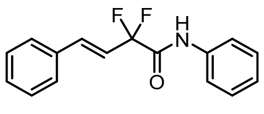
(*E*)-*N*,*N*-Diethyl-2,2-difluoro-4-phenyl-3-butenamide (**5b**, *E/Z* = 50:1).[5] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1) as colorless oil (94 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.38 – 7.32 (m, 3H), 6.98 (dt, *J* = 16.3, 2.7 Hz, 1H), 6.47 (dt, *J* = 16.3, 10.8 Hz, 1H), 3.51 – 3.40 (m, 4H), 1.24 – 1.17 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (t, *J* = 30.1 Hz), 135.3 (t, *J* = 9.7 Hz), 134.5, 129.5, 128.9, 127.5, 120.7 (t, *J* = 24.8 Hz), 115.4 (t, *J* = 249.1 Hz), 42.2 (t, *J* = 5.0 Hz), 41.6, 14.3, 12.4; ^{19}F NMR (377 MHz, $CDCl_3$) δ -95.67 (d, *J* = 10.8 Hz, 2F).



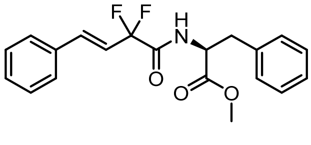
(*E*)-2,2-Difluoro-1-(indolin-1-yl)-4-phenyl-3-buten-1-one (**5c**, *E/Z* = 10:1).[4] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1) as yellow oil (105 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.46 (m, 2H), 7.39 – 7.34 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.05 (m, 2H), 6.51 (dt, *J* = 16.3, 11.1 Hz, 1H), 4.31 (t, *J* = 8.3 Hz, 2H), 3.18 (t, *J* = 8.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (t, *J* = 31.5 Hz), 142.7, 136.2 (t, *J* = 9.7 Hz), 134.3, 131.7, 129.7, 128.9, 127.7, 127.6, 125.3, 124.8, 119.7 (t, *J* = 24.8 Hz), 118.1, 115.1 (t, *J* = 249.8 Hz), 48.2 (t, *J* = 6.3 Hz), 28.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -98.78 (d, *J* = 11.1 Hz, 2F).



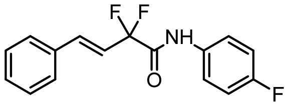
(*E*)-2,2-Difluoro-*N*-hexyl-4-phenyl-3-butenamide (**5d**, *E/Z* = 45:1). The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 10:1) as white solid (103 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 6.6 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.06 (d, *J* = 16.2 Hz, 1H), 6.43 – 6.33 (m, 2H), 3.34 (q, *J* = 6.0 Hz, 2H), 1.60 – 1.53 (m, 2H), 1.31 (br, 6H), 0.91 – 0.87 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (*J* = 29.9 Hz), 136.5 (t, *J* = 9.7 Hz), 134.4, 129.6, 128.9, 127.6, 119.3 (t, *J* = 25.3 Hz), 114.5 (t, *J* = 249.5 Hz), 39.8, 31.5, 29.3, 26.6, 22.6, 14.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ -102.50 (d, *J* = 10.9 Hz, 2F). HRMS (ESI): *m/z* calcd. for $C_{16}H_{21}F_2NNaO^+$ $[M + Na]^+$: 304.1483, found: 304.1486.



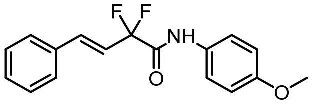
(*E*)-2,2-Difluoro-*N*,4-diphenylbut-3-enamide (**5e**, *E/Z* = 32:1).[5] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 15:1) as pale yellow solid (95 mg, 70% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.36 (m, 7H), 7.22 – 7.13 (m, 2H), 6.50 – 6.40 (m, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 161.8 (*J* = 30.6 Hz), 137.0 (t, *J* = 9.5 Hz), 136.1, 134.1, 129.7, 129.3, 128.9, 127.5, 125.7, 120.3, 118.7 (t, *J* = 25.0 Hz), 114.4 (t, *J* = 250.9 Hz); ^{19}F NMR (377 MHz, CDCl$_3$) δ -102.00 (d, *J* = 11.5 Hz, 2F).



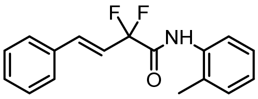
Methyl (*E*)-(2,2-Difluoro-4-phenylbut-3-enoyl)-*L*-phenylalaninate (**5f**, *E/Z* = 30:1).[3] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 8:1) as colorless oil (125 mg, 70% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.42 (m, 2H), 7.40 – 7.35 (m, 3H), 7.28 – 7.23 (m, 3H), 7.11 – 7.09 (m, 2H), 7.03 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.31 (dt, *J* = 16.2, 11.4 Hz, 1H), 4.95 – 4.90 (m, 1H), 3.77 (s, 3H), 3.22 (ddd, *J* = 40.1, 13.9, 5.6 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.0, 163.5 (t, *J* = 31.2 Hz), 136.8 (t, *J* = 9.6 Hz), 135.2, 134.2, 129.6, 129.3, 128.9, 128.7, 127.5, 127.4, 118.9 (t, *J* = 25.2 Hz), 114.2 (t, *J* = 249.7 Hz), 53.3, 52.7, 37.6; ^{19}F NMR (377 MHz, CDCl$_3$) δ -102.03 (d, *J* = 11.4 Hz, 2F).



(*E*)-2,2-Difluoro-*N*-(4-fluorophenyl)-4-phenyl-3-butenamide (**5g**, *E/Z* = 42:1). The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1) as pale yellow solid (113 mg, 78% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.21 (s, 1H), 7.59 – 7.56 (m, 2H), 7.45 – 7.43 (m, 2H), 7.39 – 7.35 (m, 3H), 7.13 (dt, *J* = 16.2, 2.5 Hz, 1H), 7.07 – 7.03 (m, 2H), 6.42 (dt, *J* = 16.2, 11.5 Hz, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 161.9 (t, *J* = 30.8 Hz), 160.2 (d, *J* = 245.4 Hz)., 137.2 (t, *J* = 9.6 Hz), 134.1, 132.2 (d, *J* = 3.0 Hz), 129.8, 129.0, 127.6, 122.4 (d, *J* = 8.1 Hz), 118.6 (t, *J* = 24.9 Hz), 116.1 (d, *J* = 22.7 Hz), 114.5 (t, *J* = 250.9 Hz); ^{19}F NMR (377 MHz, CDCl$_3$) δ ^{19}F NMR (376 MHz, CDCl$_3$) δ -101.99 (d, *J* = 11.3 Hz, 2F), -115.87 – -115.92 (m, 1F). HRMS (ESI): *m/z* calcd. for $C_{16}H_{12}F_3NaNO+$ [M + Na]$^+$: 314.0763, found: 314.0774.



(*E*)-2,2-difluoro-*N*-(4-methoxyphenyl)-4-phenyl-3-butenamide (**5h**, *E/Z* = 38:1).[5] The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 8:1) as white solid (95 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.53 – 7.49 (m, 2H), 7.46 – 7.44 (m, 2H), 7.39 – 7.34 (m, 3H), 7.14 (dt, *J* = 16.2, 2.5 Hz, 1H), 6.91 – 6.87 (m, 2H), 6.44 (dt, *J* = 16.2, 11.5 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6 (t, *J* = 30.4 Hz), 157.4, 137.0 (t, *J* = 9.5 Hz), 134.3, 129.7, 129.2, 128.9, 127.6, 122.1, 118.9 (t, *J* = 25.1 Hz), 114.5 (t, *J* = 250.8 Hz), 114.5, 55.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -101.95 (dt, *J* = 11.5, 2.5 Hz, 2F).



(*E*)-2,2-Difluoro-4-phenyl-*N*-(o-tolyl)-3-butenamide (**5i**, *E/Z* = 45:1). The product was purified with silica gel chromatography (Petroleum ether/EtOAc = 20:1) as yellow oil (118 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.43 (m, 2H), 7.37 – 7.32 (m, 3H), 7.24 – 7.19 (m, 2H), 7.17 – 7.10 (m, 2H), 6.44 (dt, *J* = 16.2, 11.5 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (t, *J* = 30.4 Hz), 137.0 (t, *J* = 9.6 Hz), 134.2, 133.9, 130.8, 129.8, 129.6, 128.9, 127.6, 127.1, 126.4, 123.0, 118.9 (t, *J* = 25.1 Hz), 114.7 (t, *J* = 250.8 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -101.79 (dt, *J* = 11.5, 2.5 Hz, 2F). HRMS (ESI): *m/z* calcd. for $C_{17}H_{15}F_2NaNO^+$ $[M + Na]^+$: 310.1014, found: 310.1021.

References

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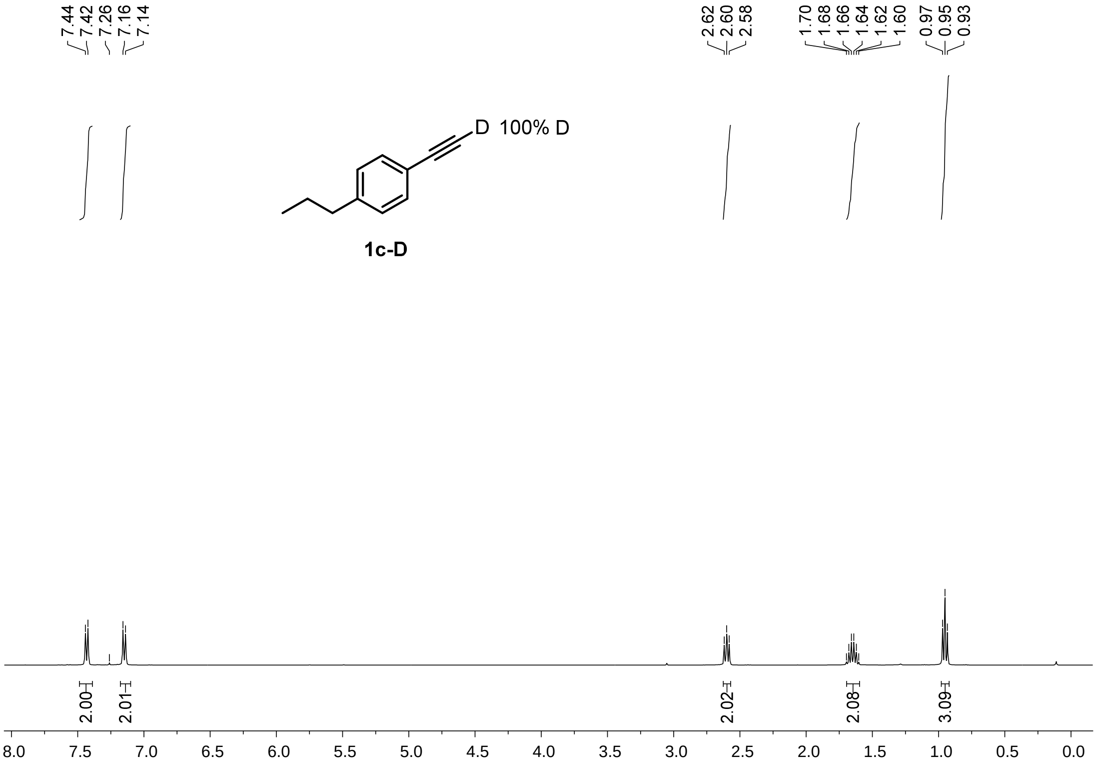
2. G. Li, T. Wang, F. Fei, Y.-M. Su, Y. Li, Q. Lan, X.-S. Wang, *Angew. Chem. Int. Ed.,* 2016, **55**, 3491.
3. M. Ke, Q. Feng, K. Yang, Q. Song, *Org. Chem. Front.*, 2016, **3**, 150.
4. X. Wang, S. Zhao, J. Liu, D. Zhu, M. Guo, X. Tang, G. Wang, *Org. Lett.*, 2017, **19**, 4187.
5. J. Zhu, W. Zhang, L. Zhang, J. Liu, J. Zheng, J. Hu, *J. Org. Chem.*, 2010, **75**, 5505.

^{1}H, ^{13}C, and ^{19}F NMR Spectra



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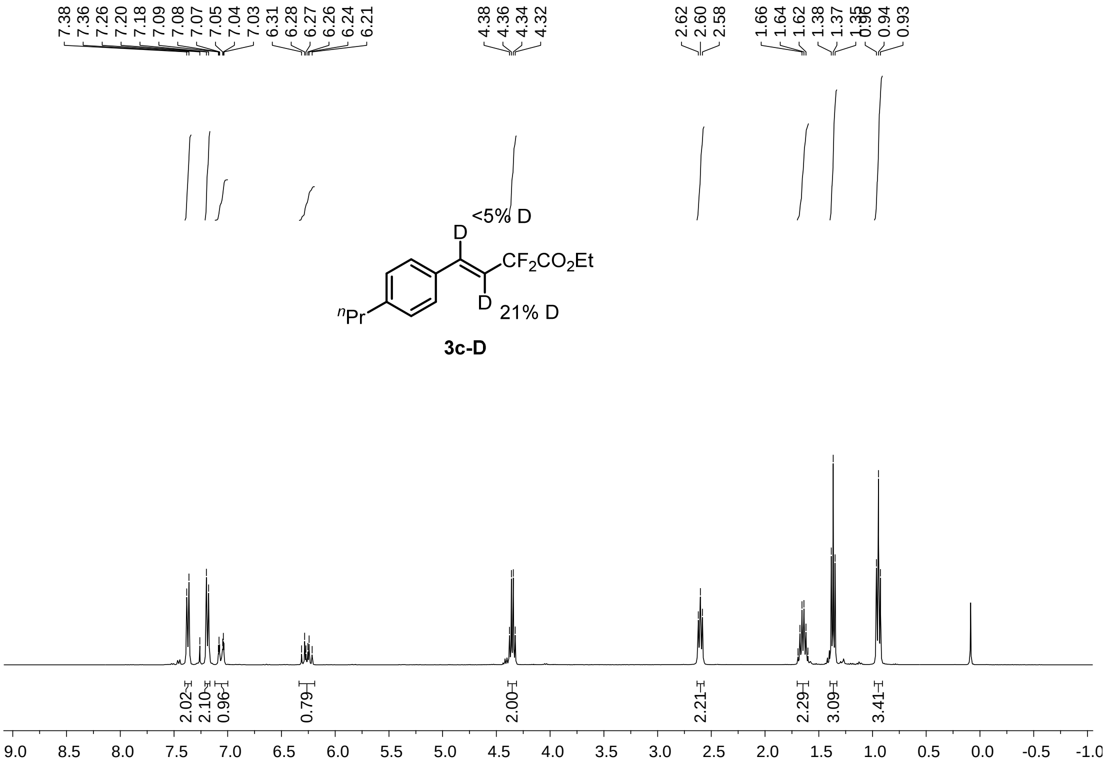

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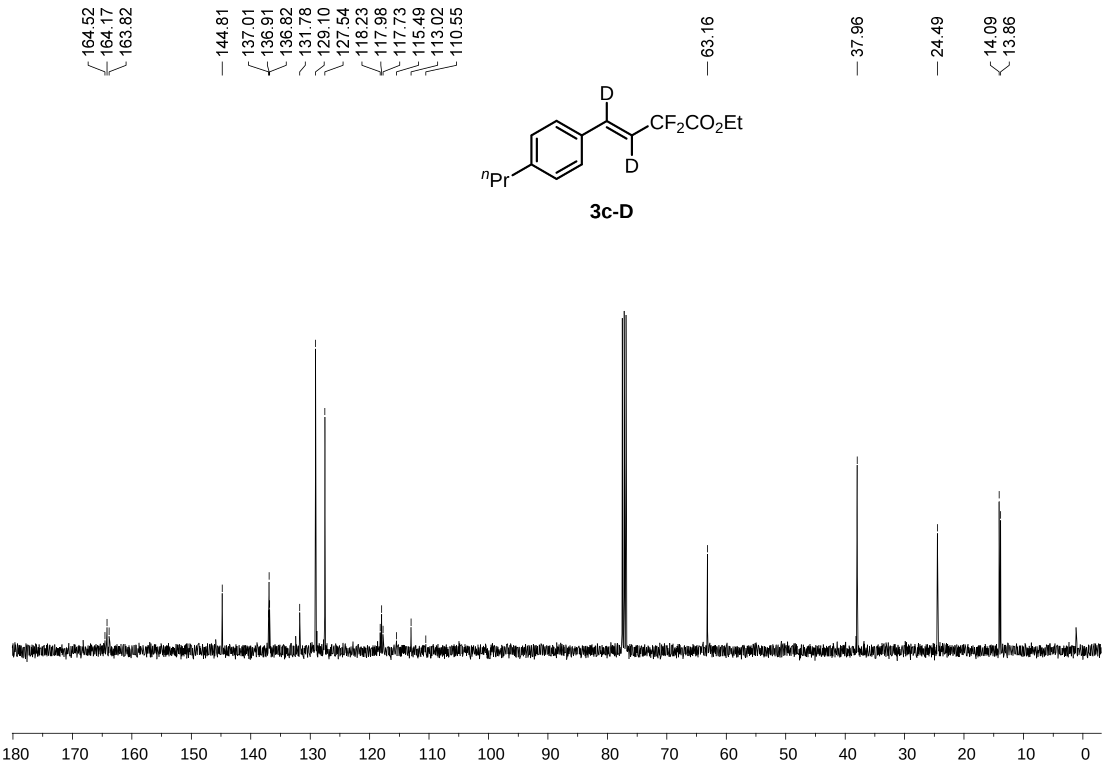
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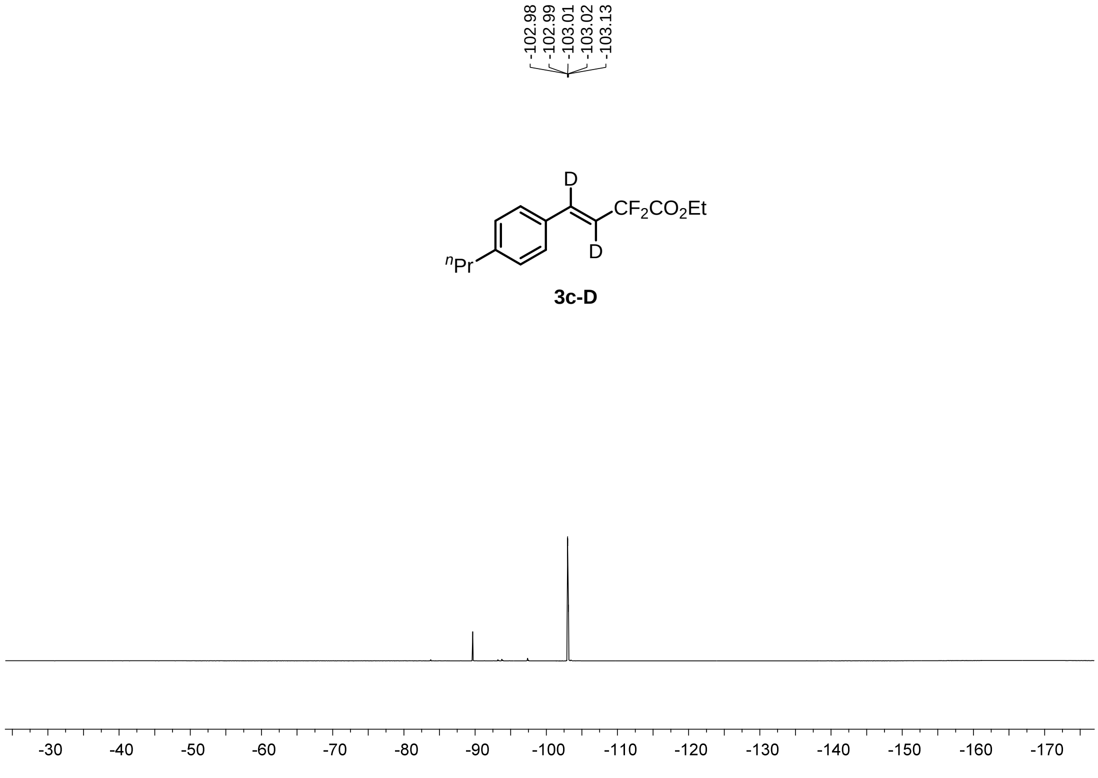
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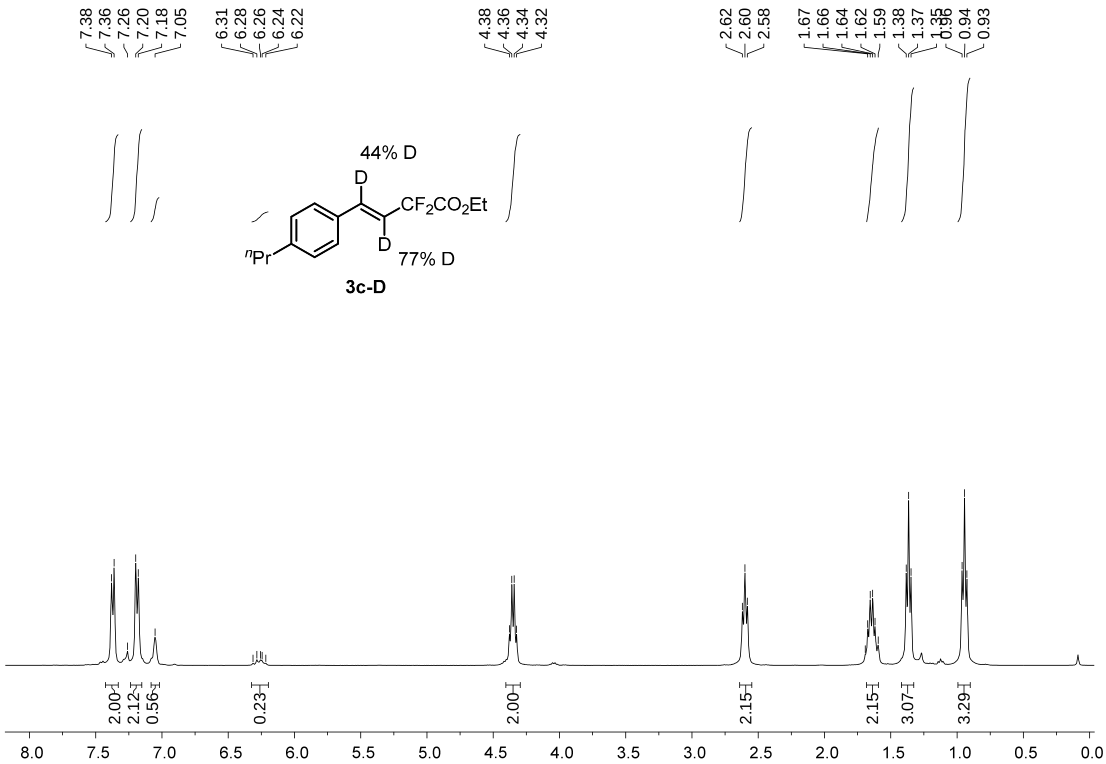
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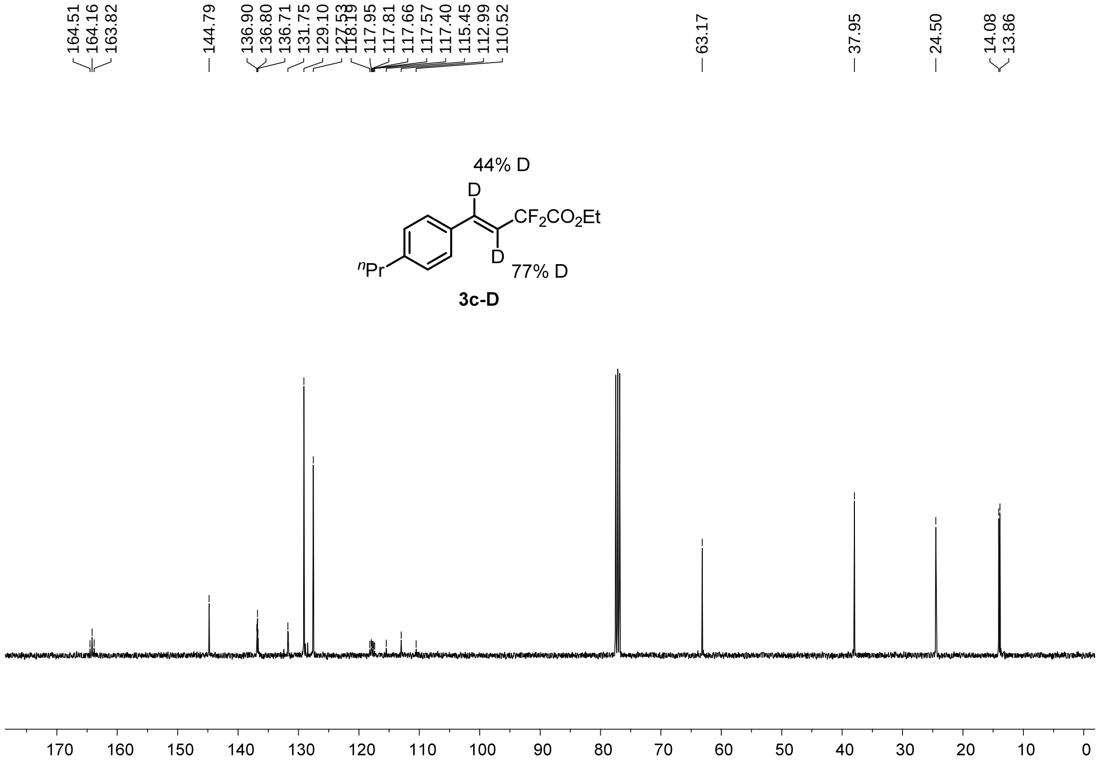
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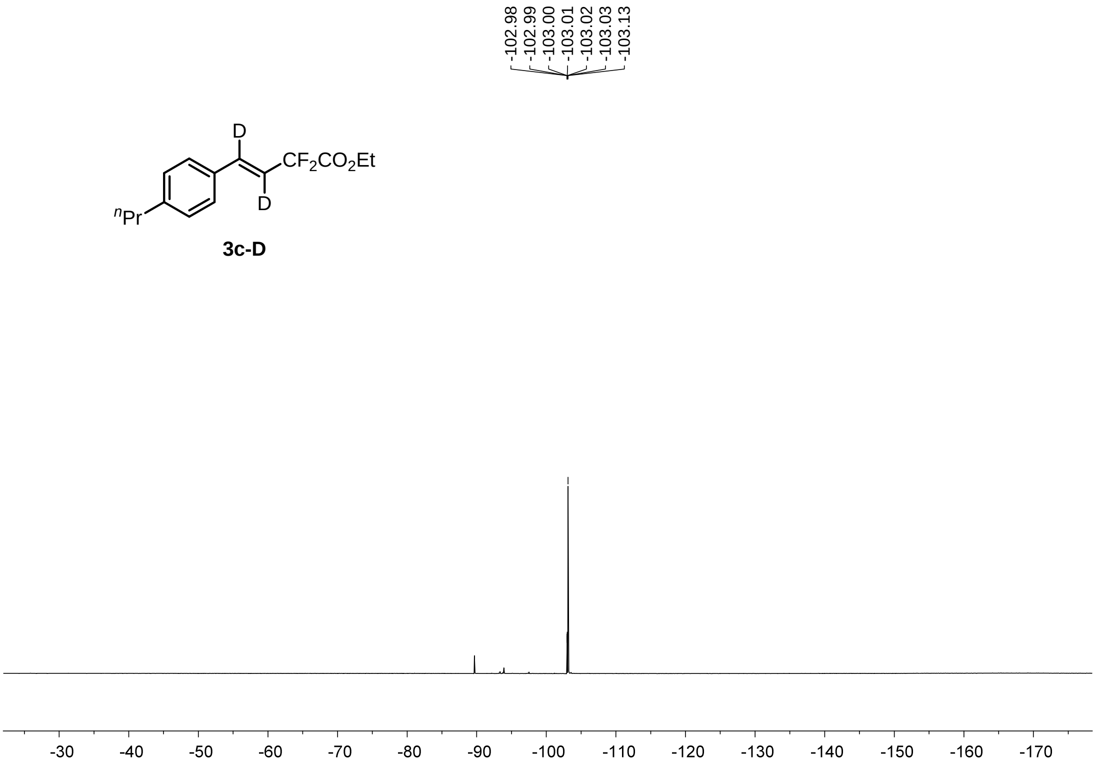
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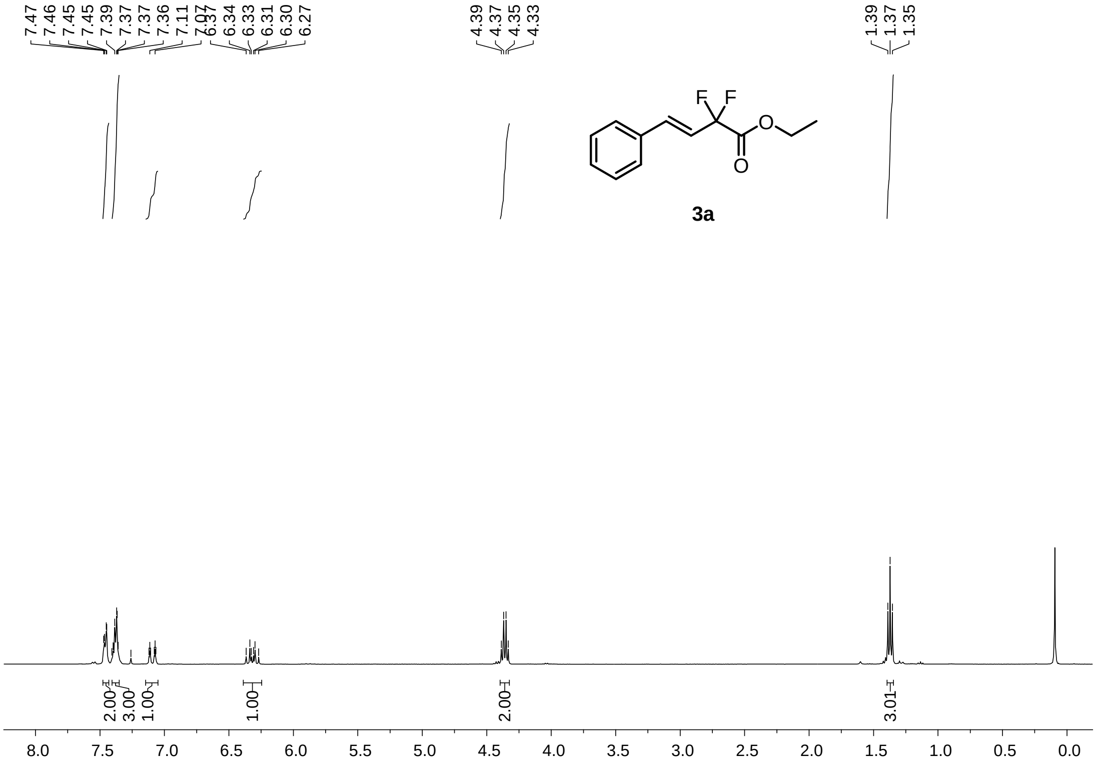
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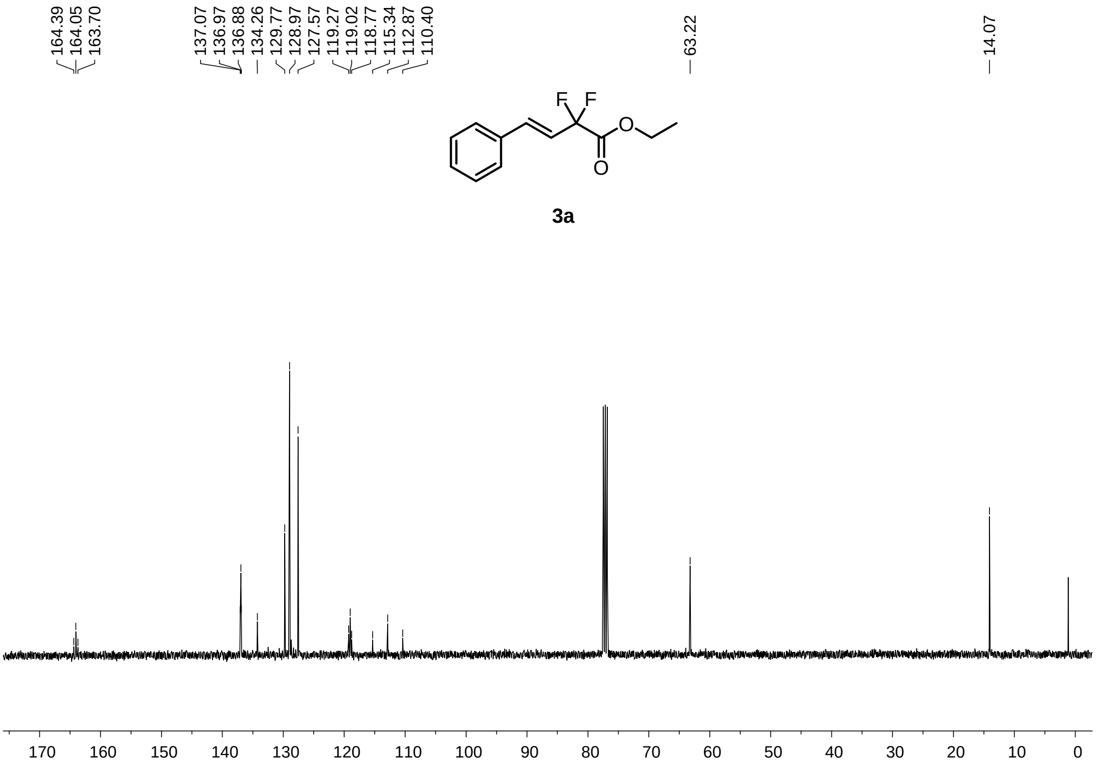
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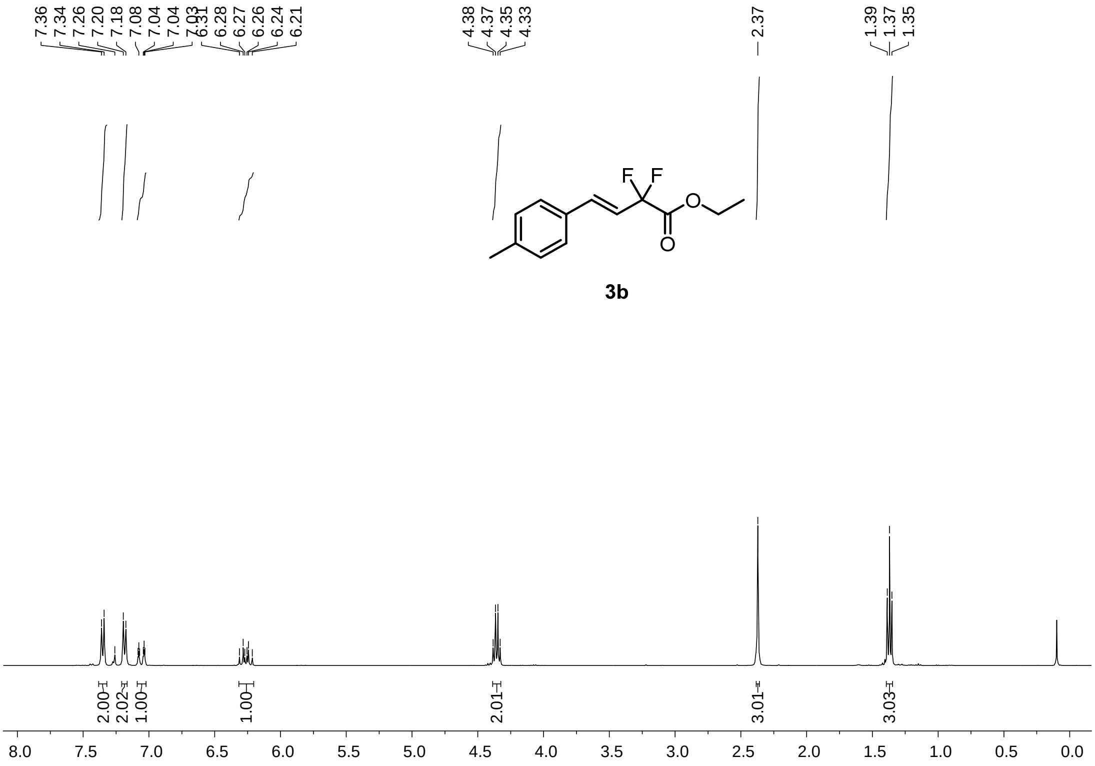
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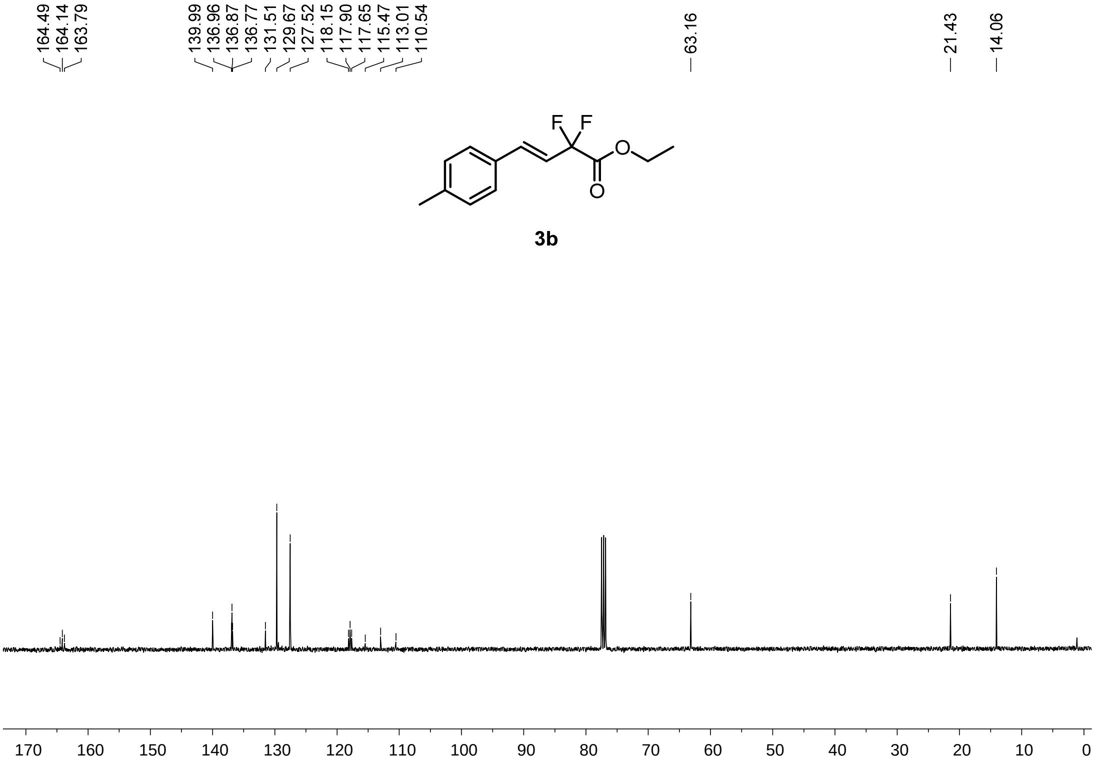
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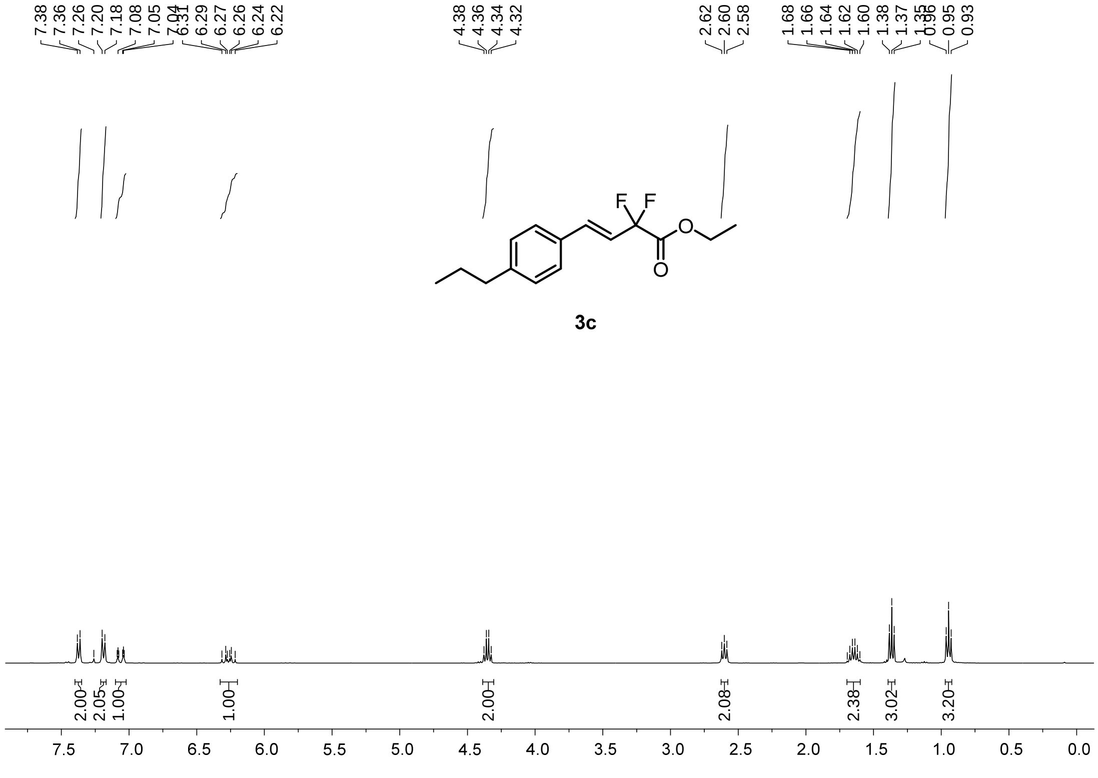
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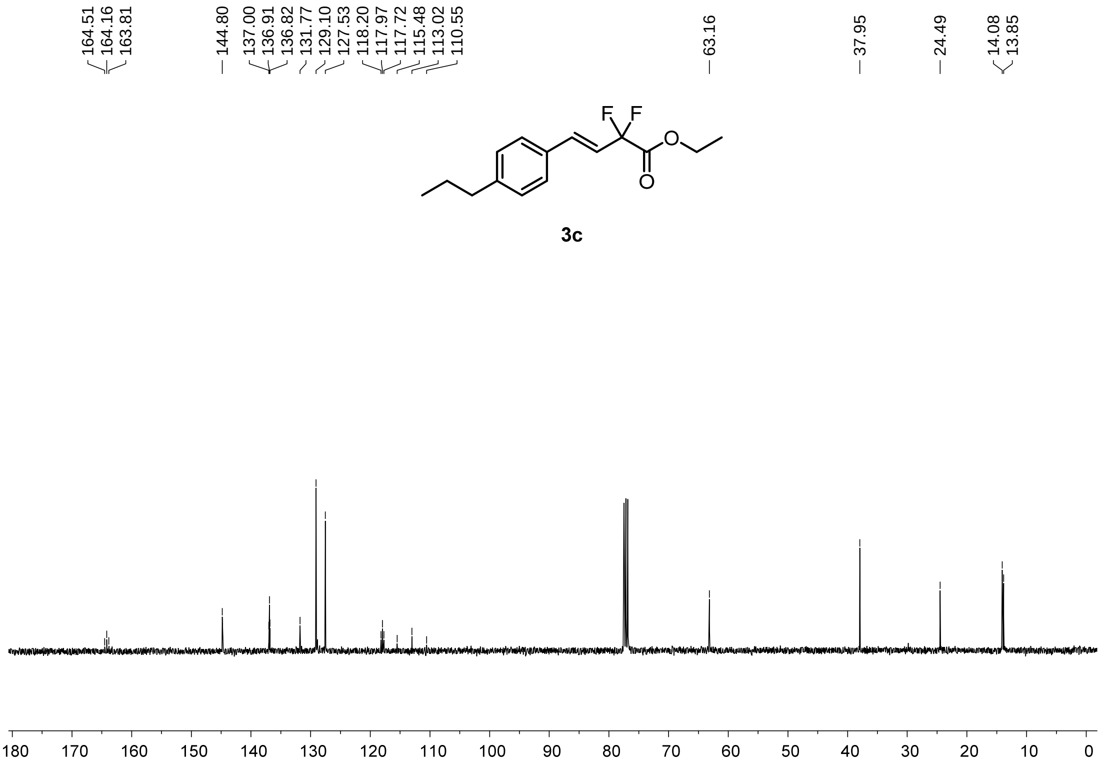
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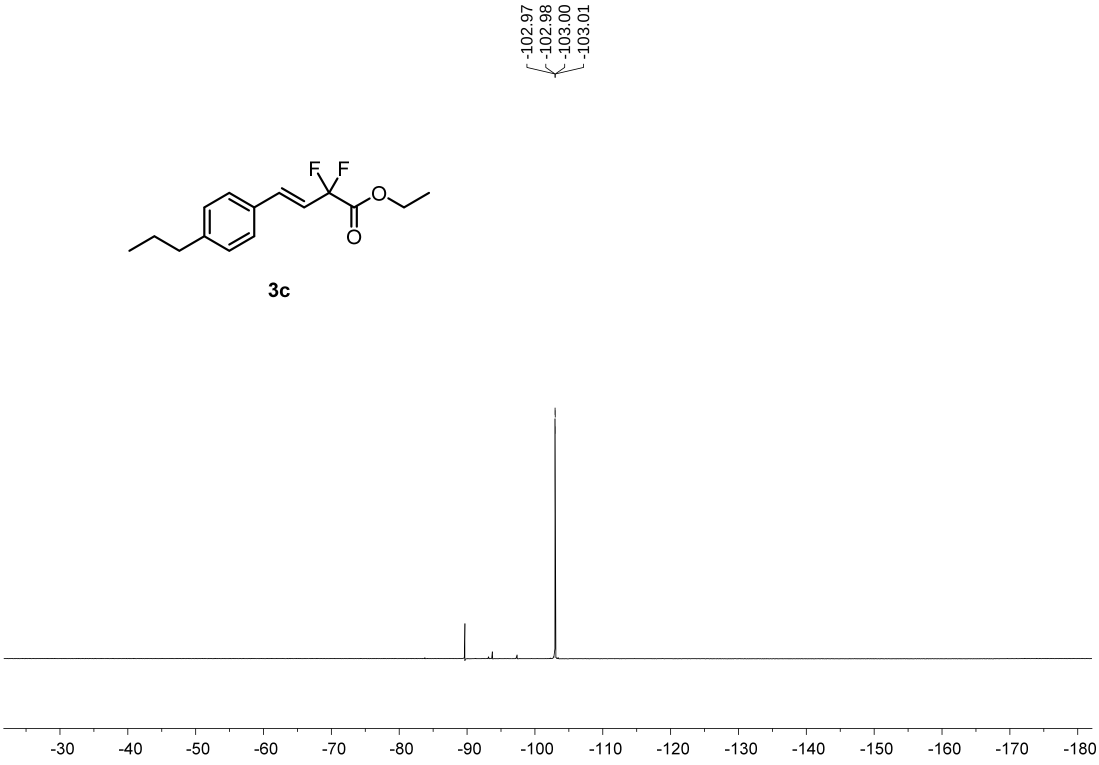
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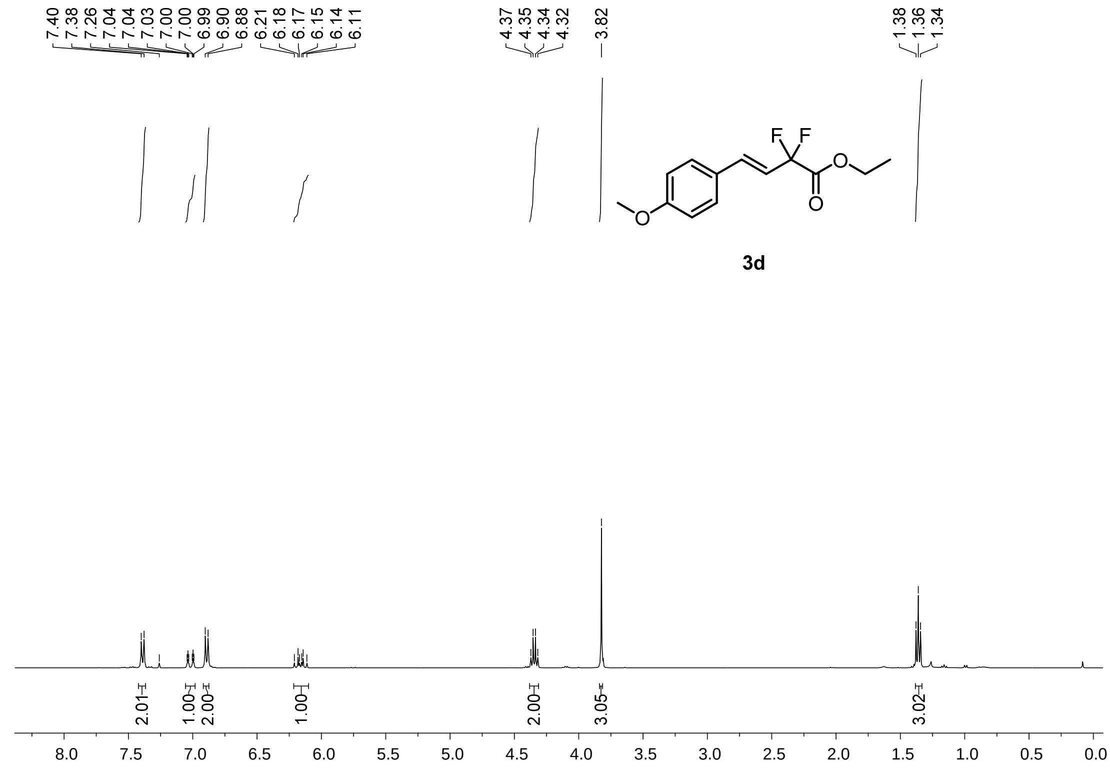
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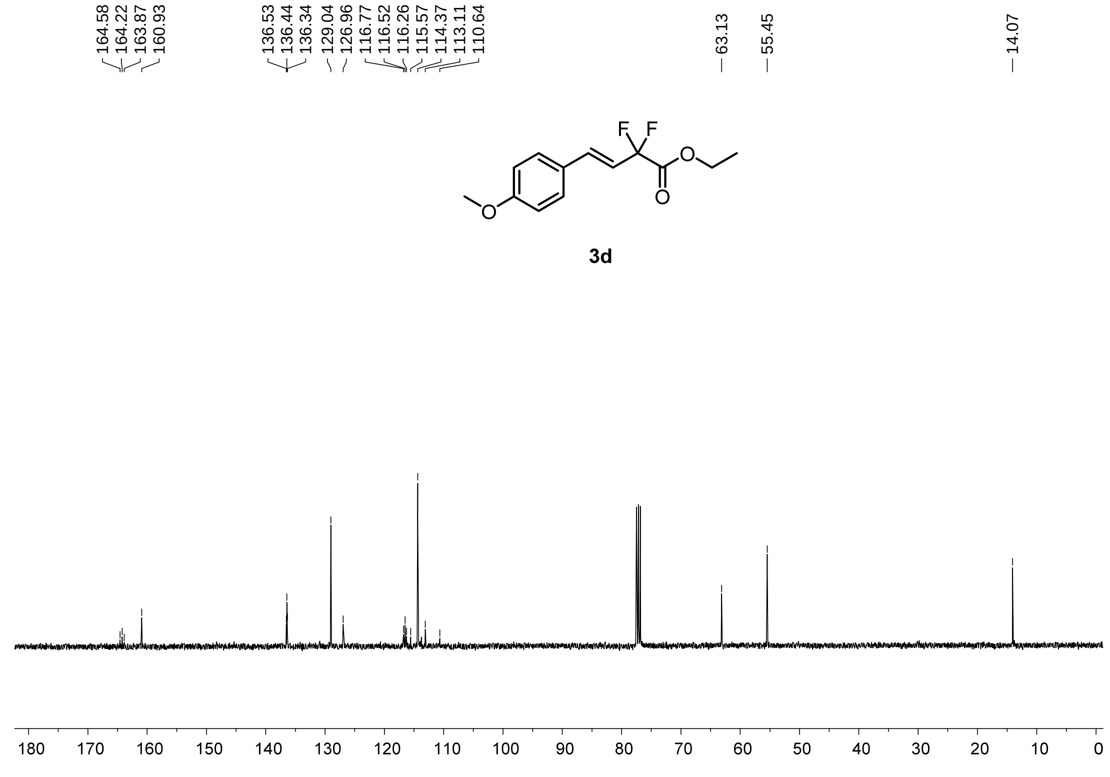
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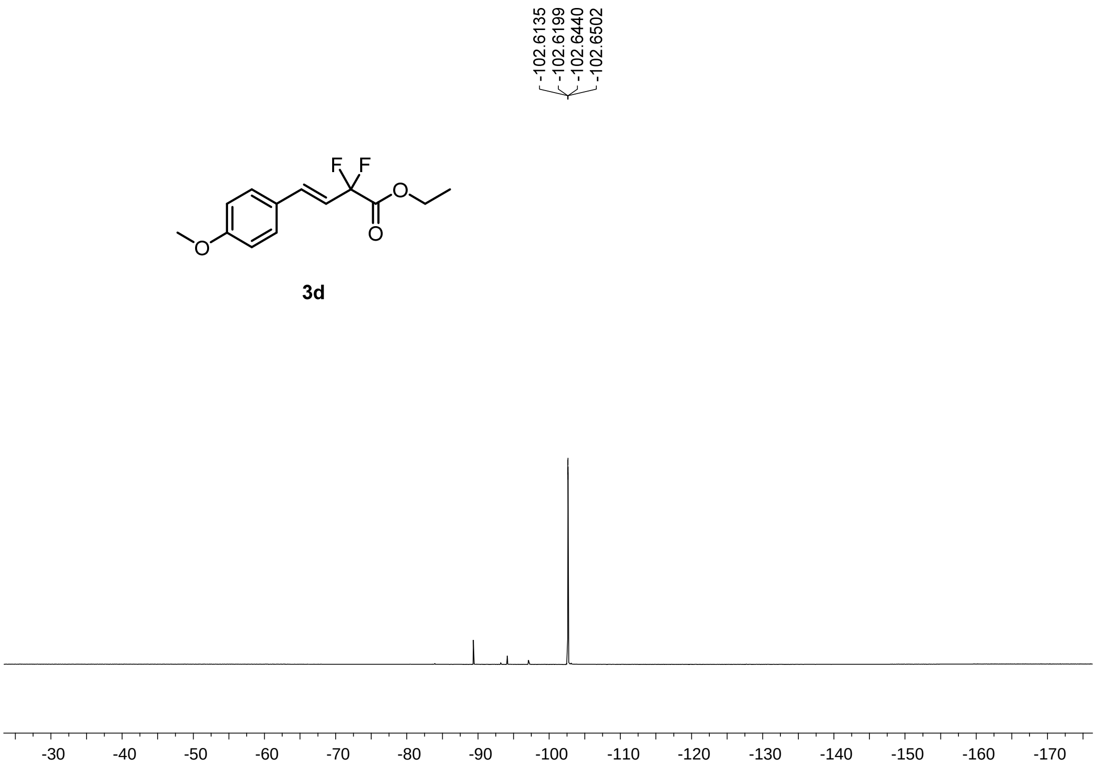
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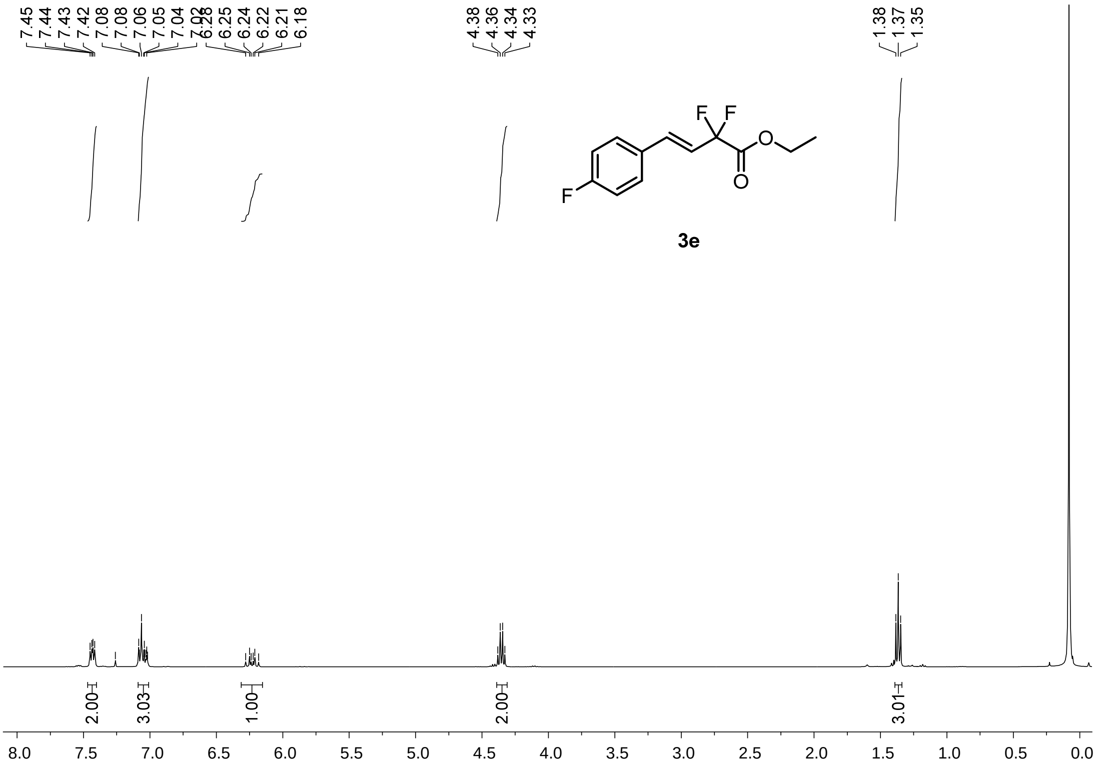
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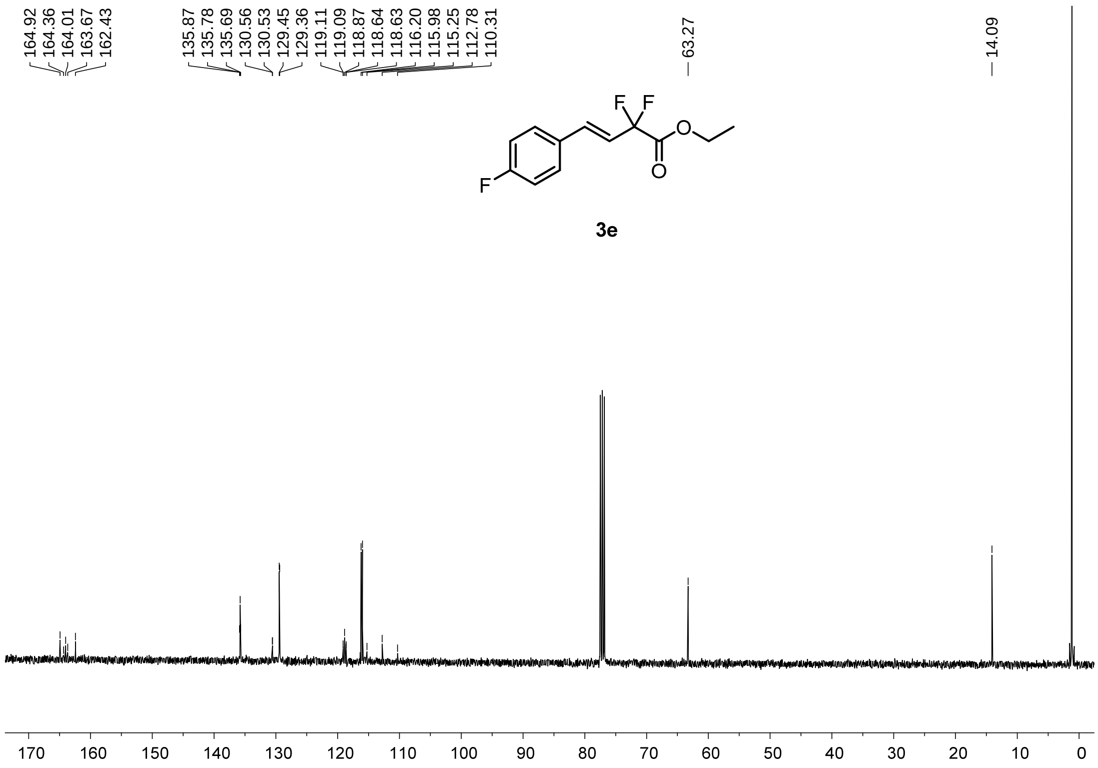
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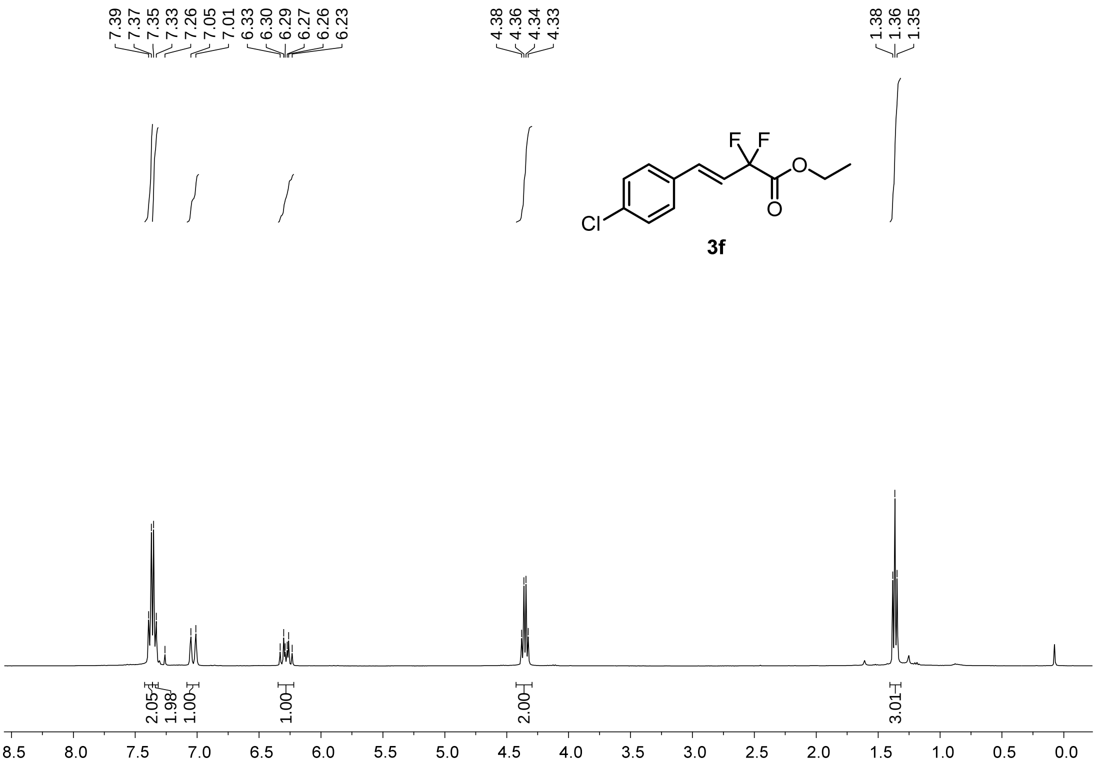
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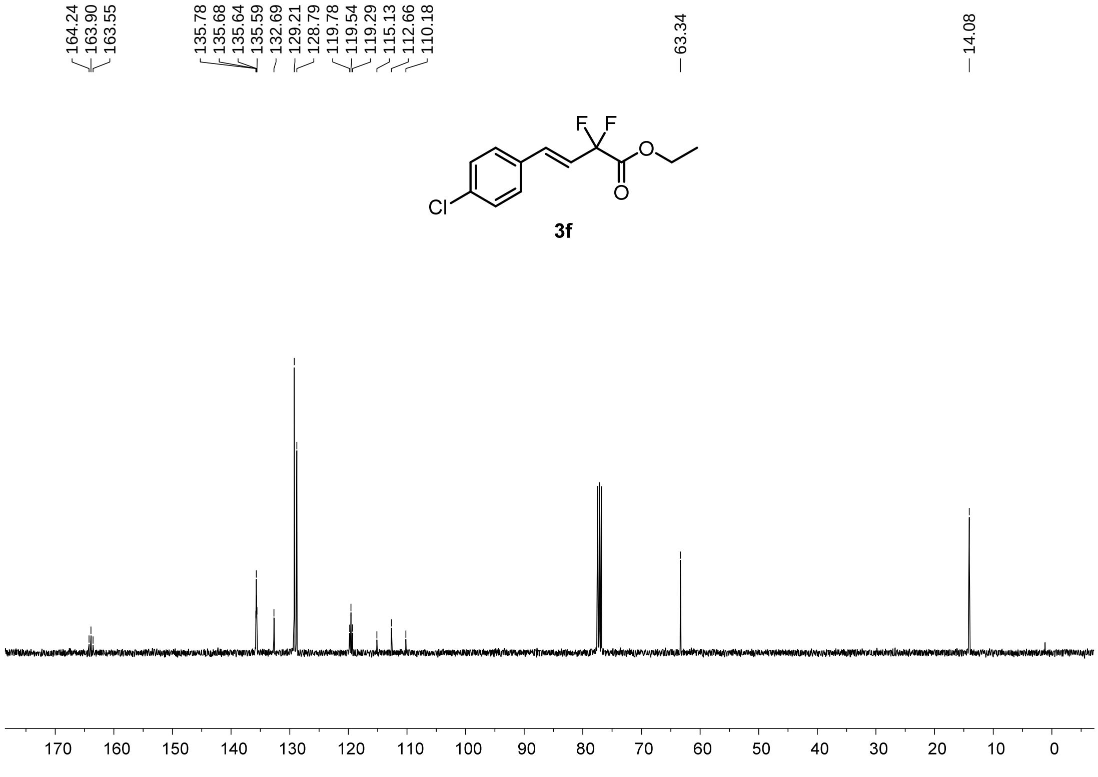
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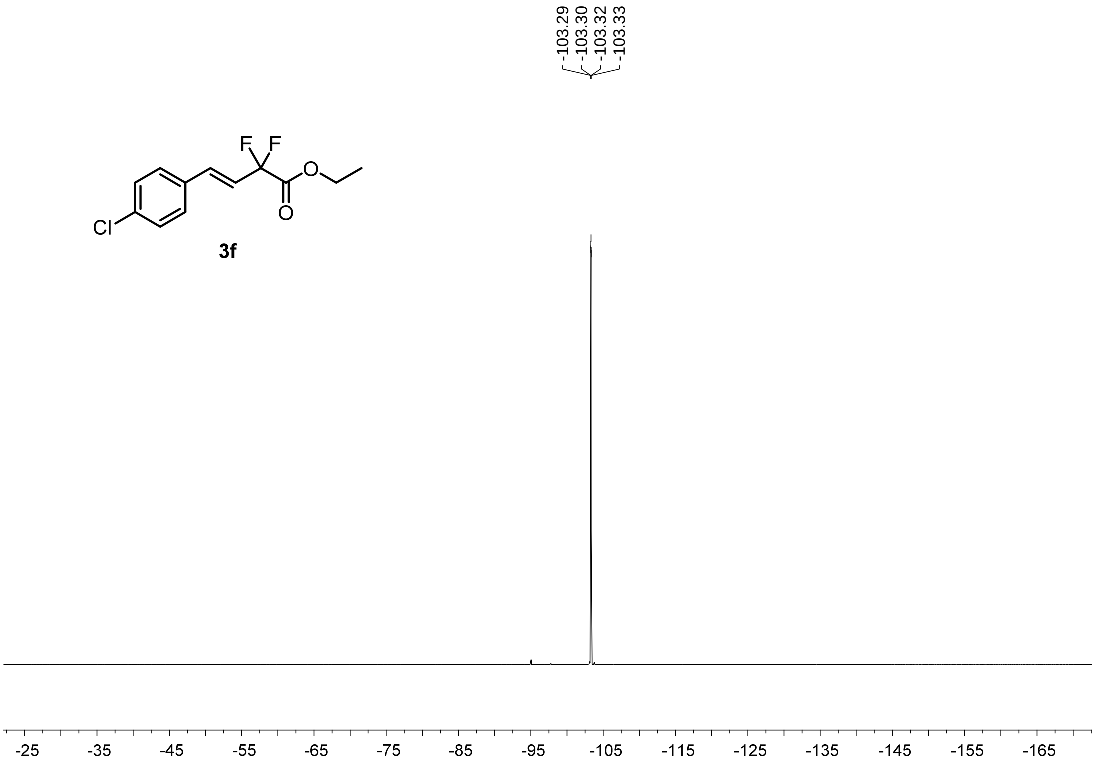
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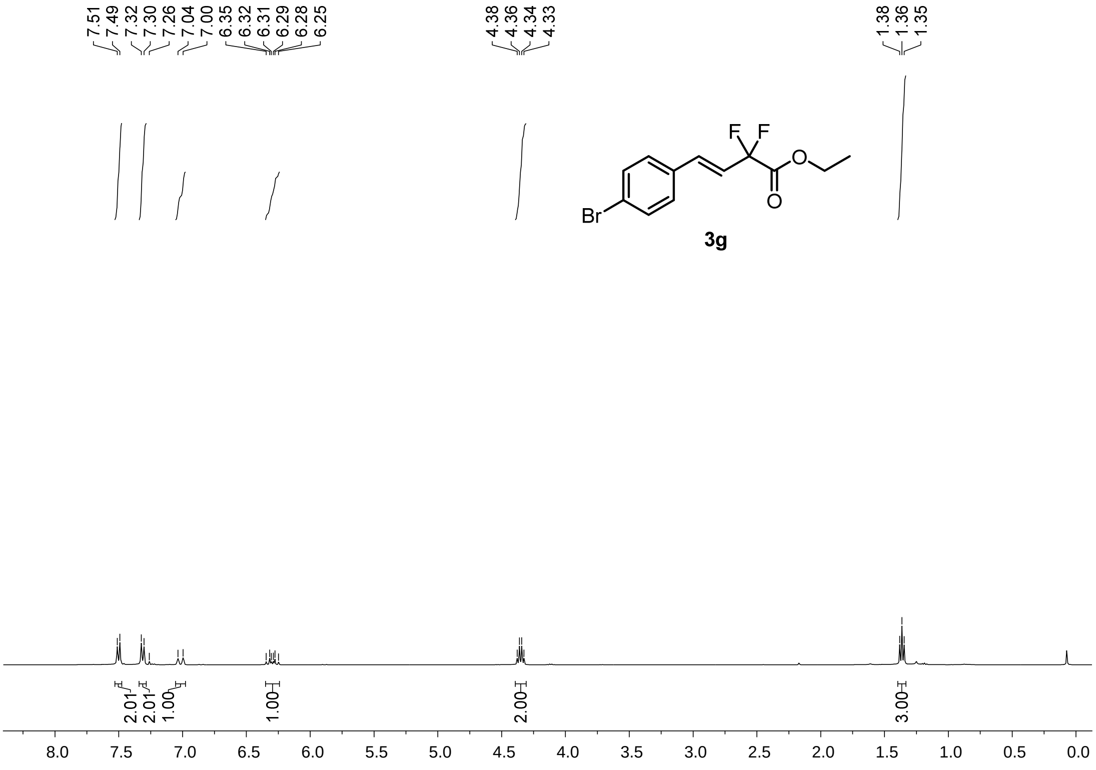
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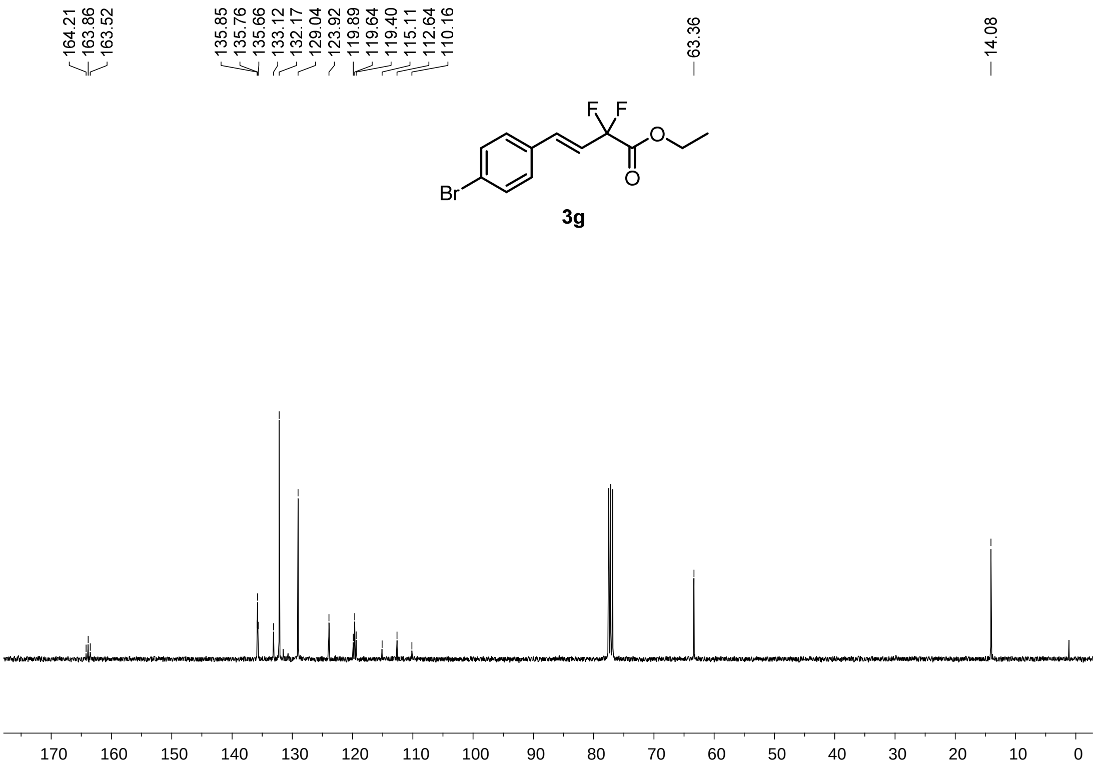
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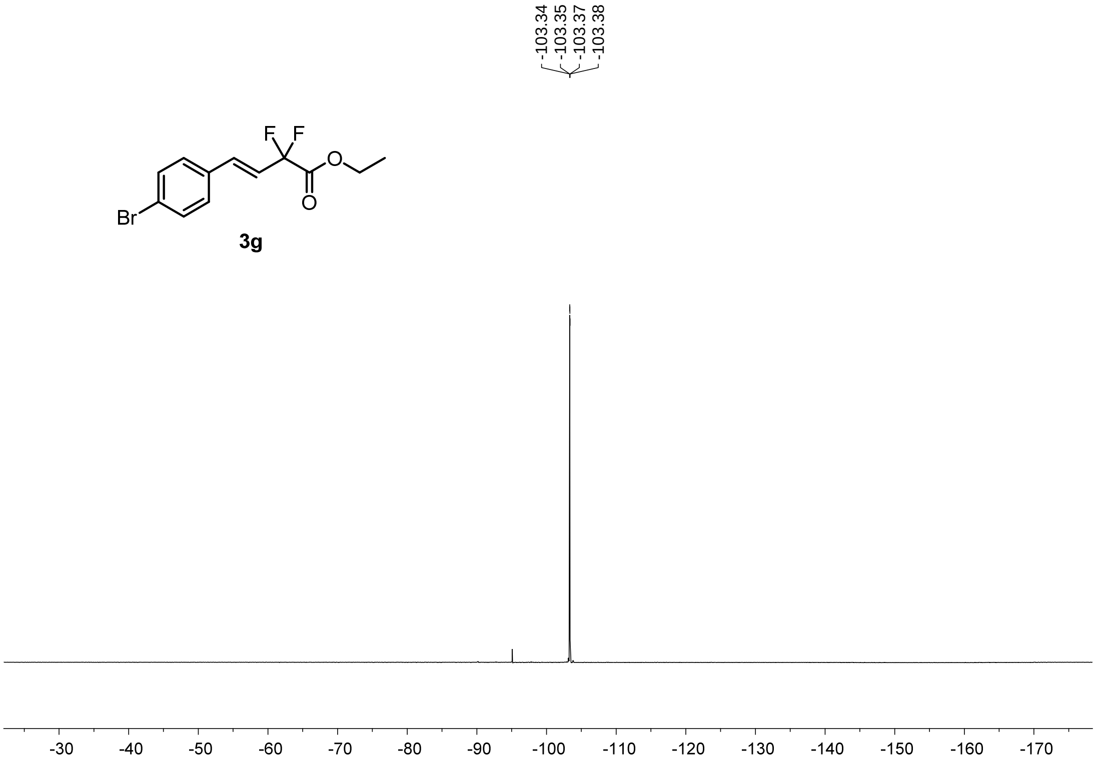
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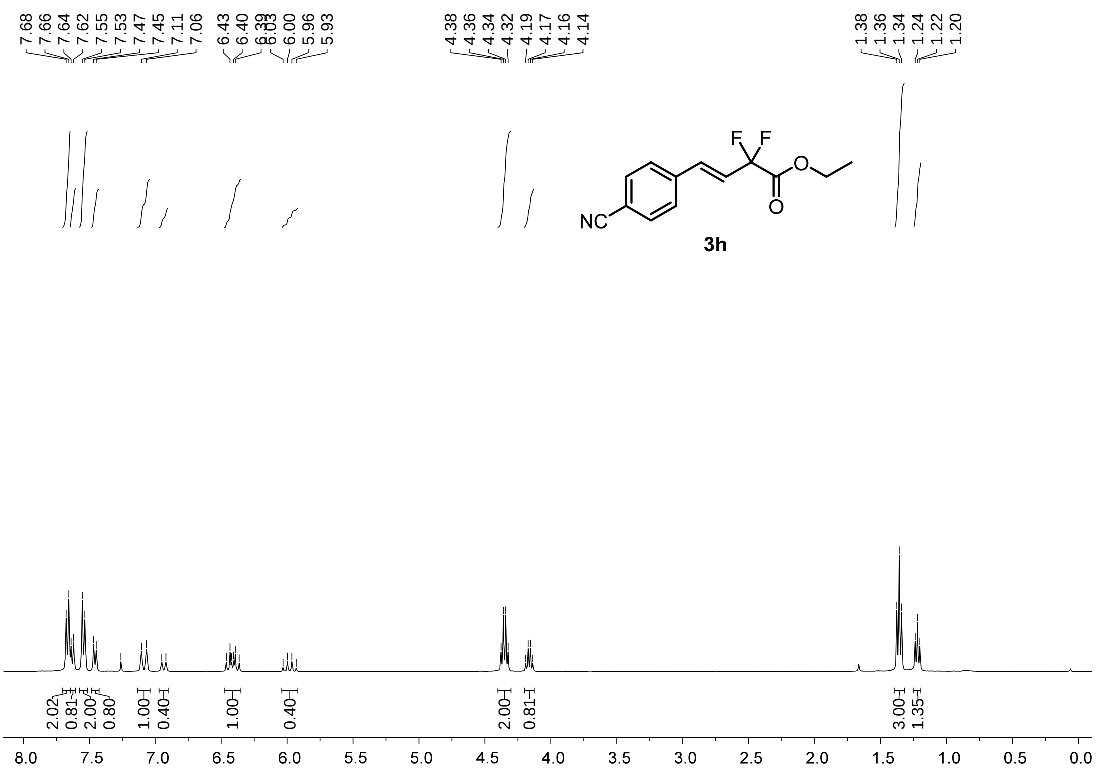
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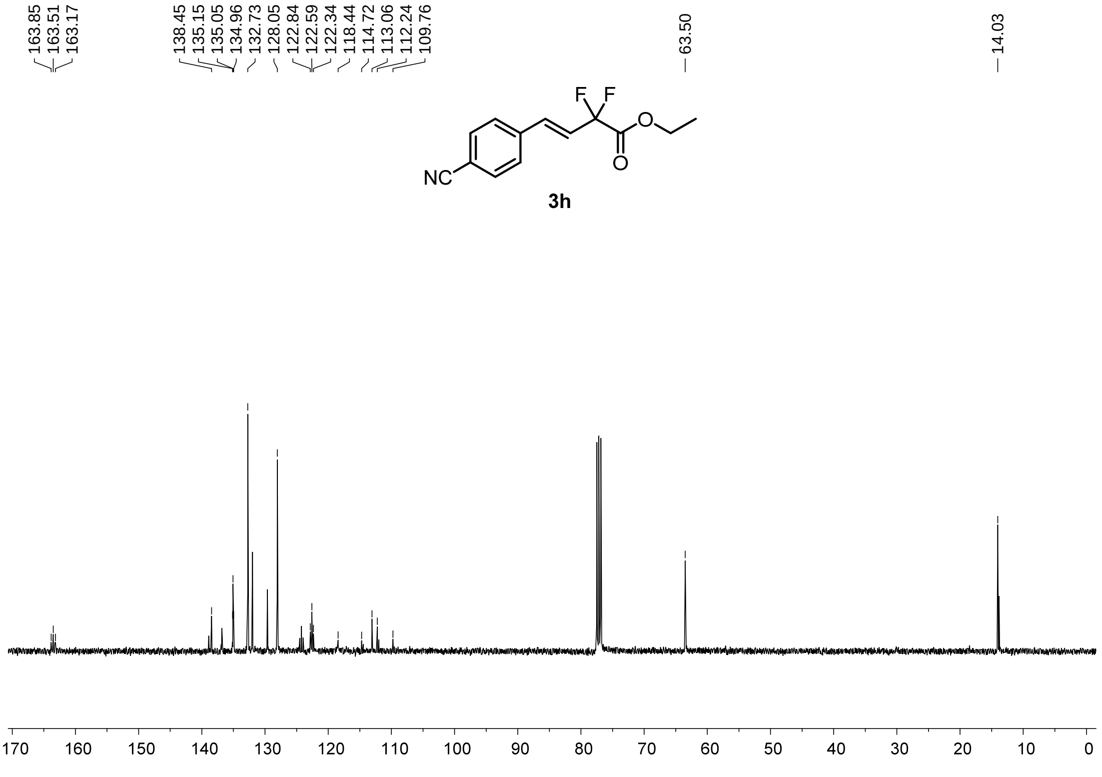
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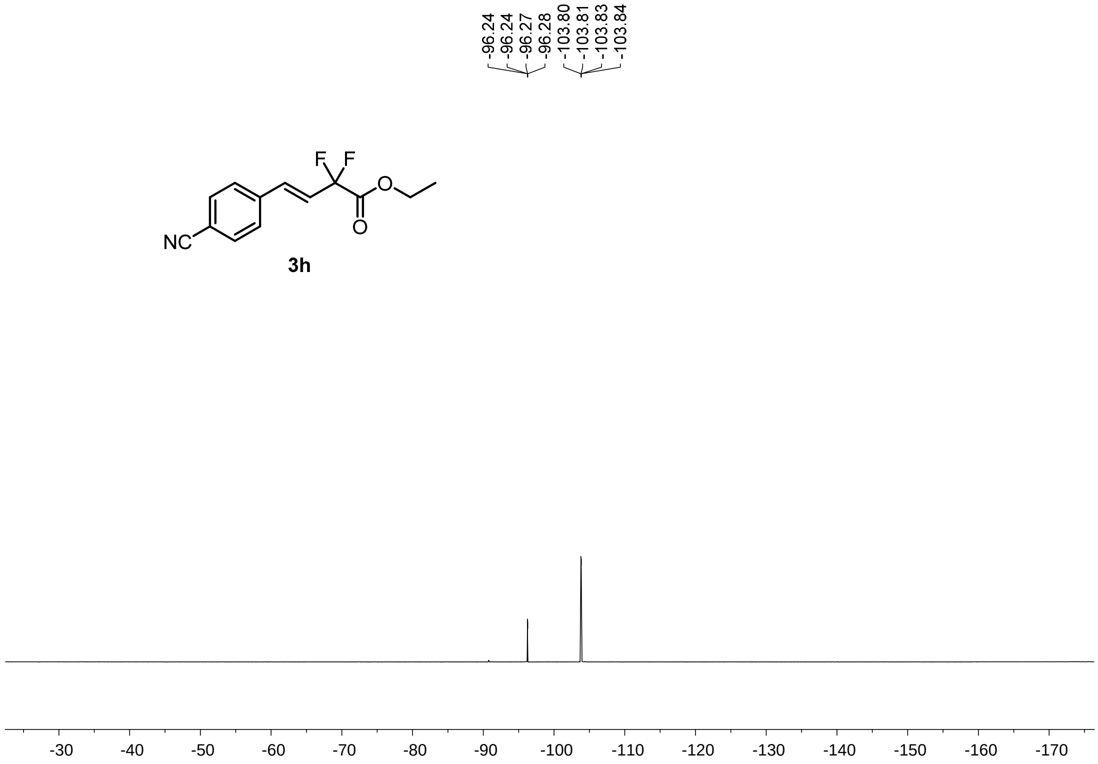
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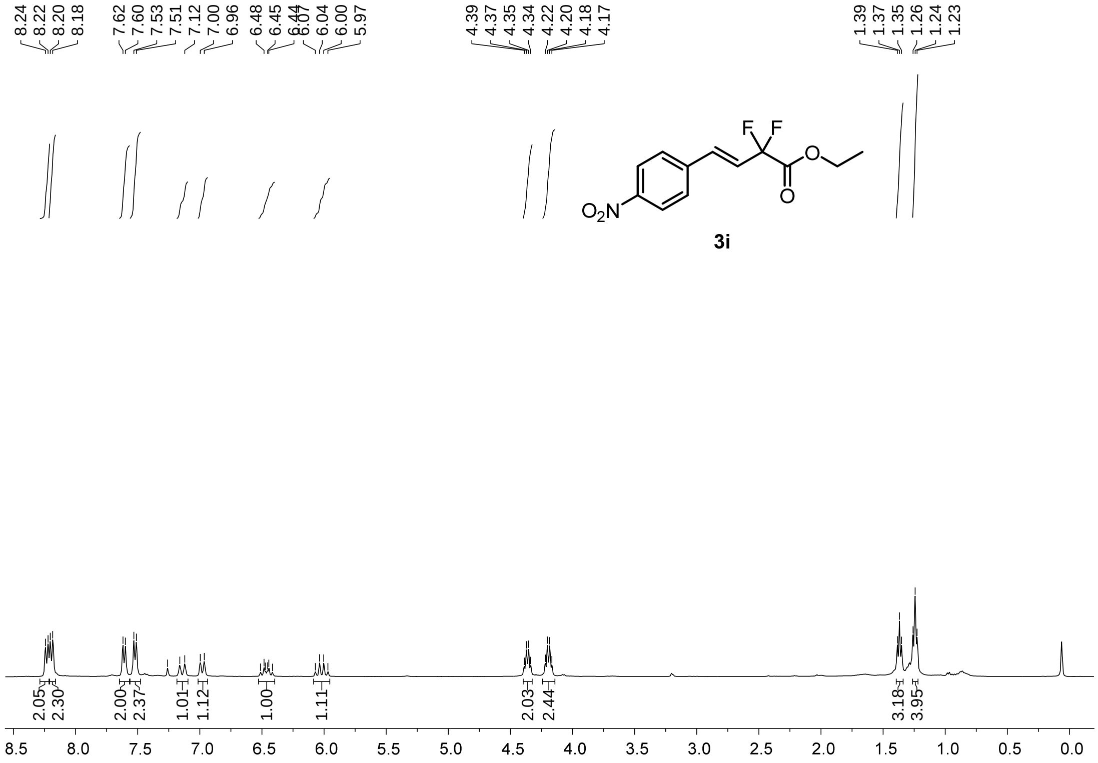
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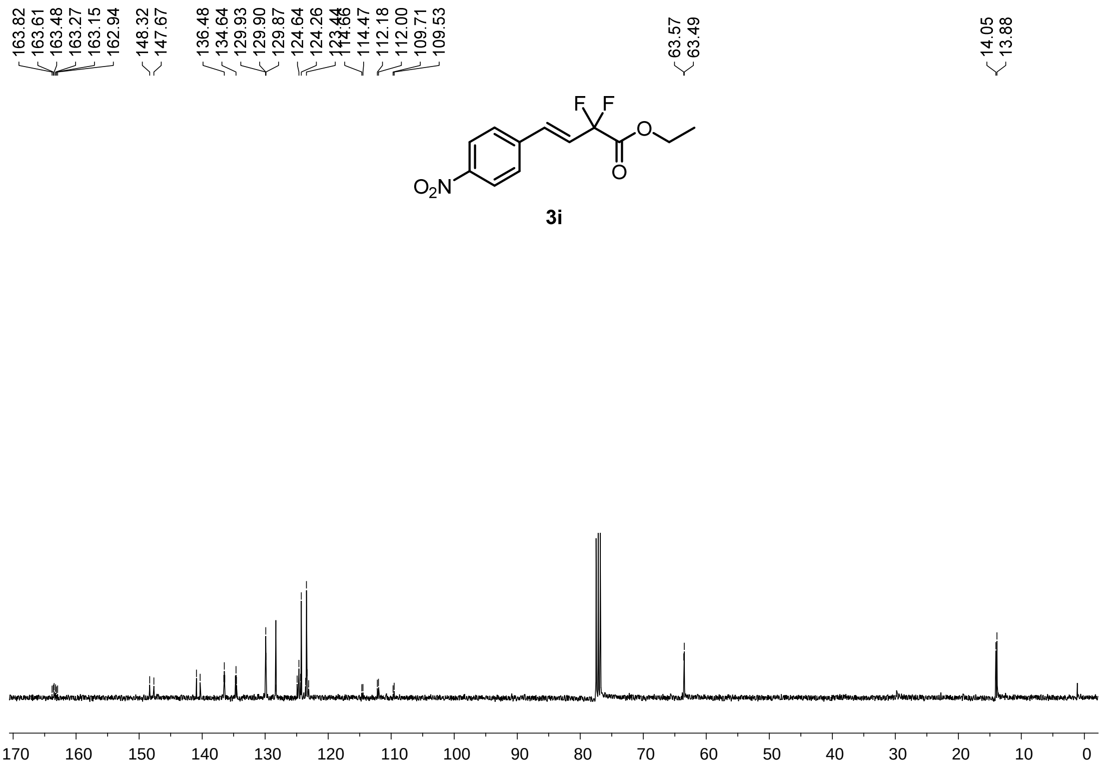
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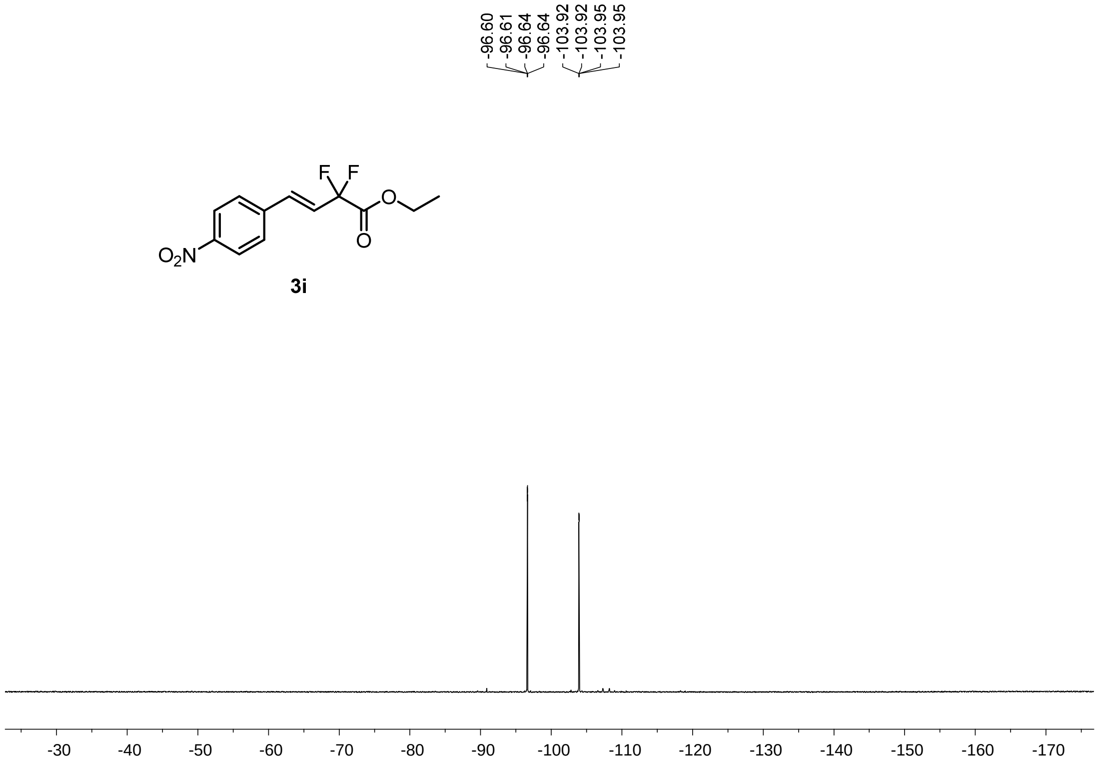
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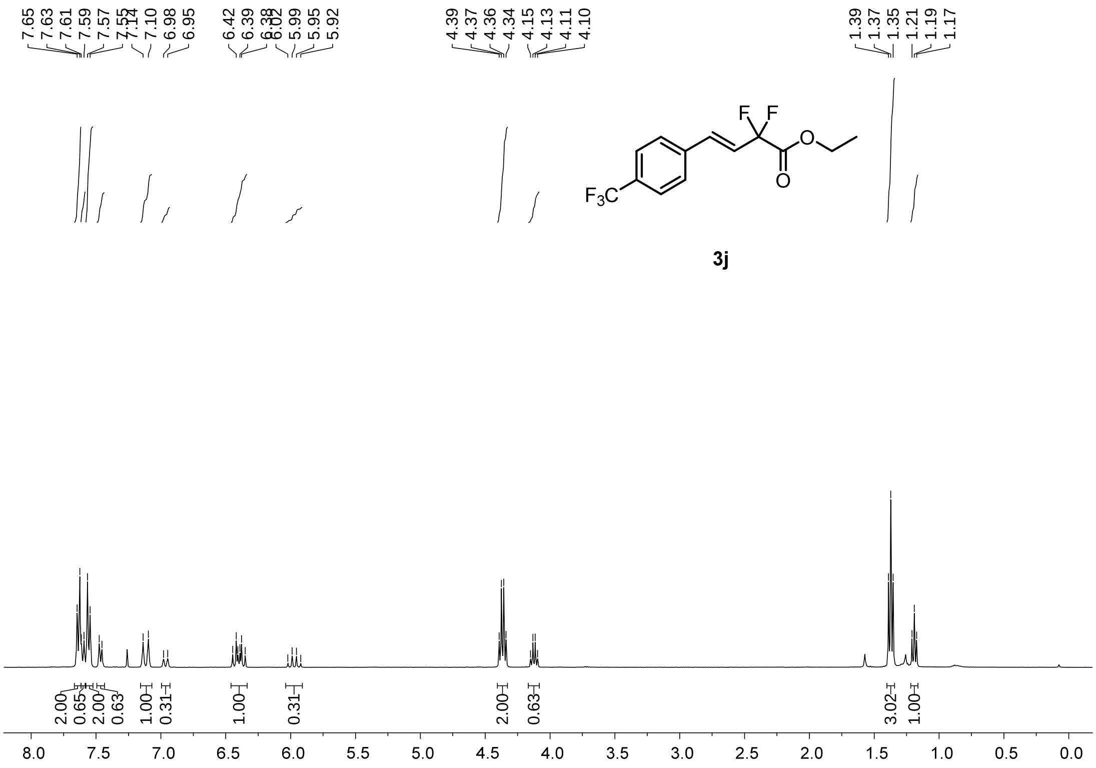
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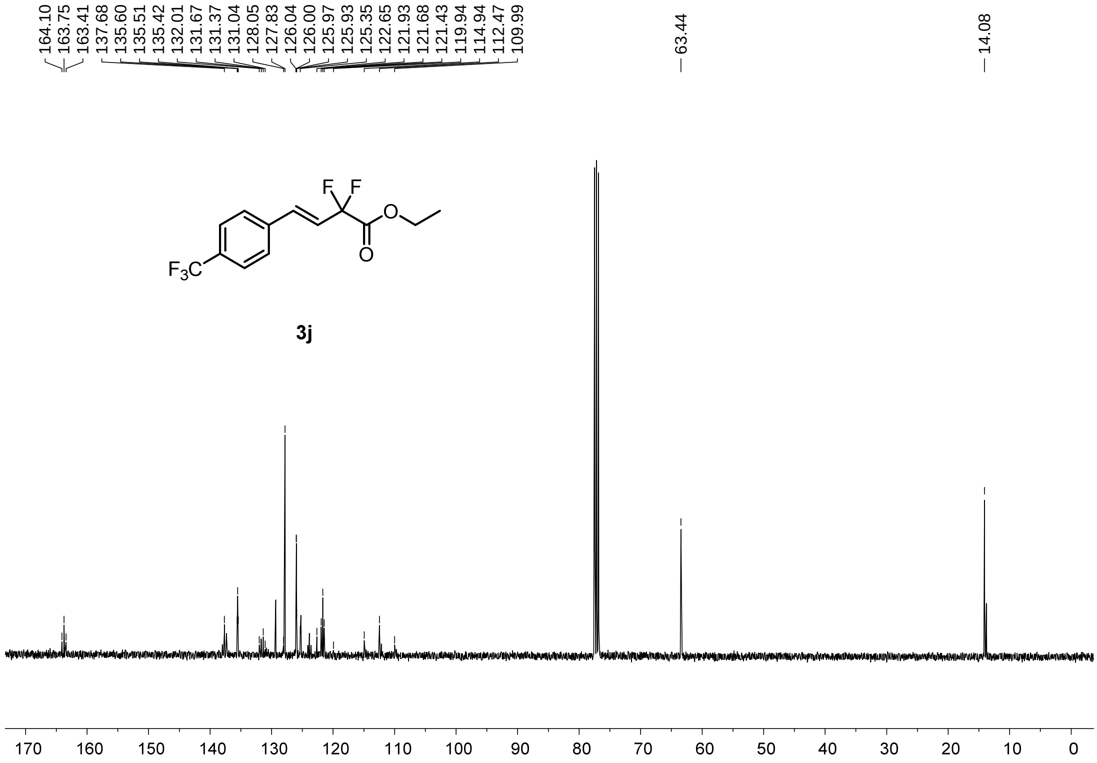
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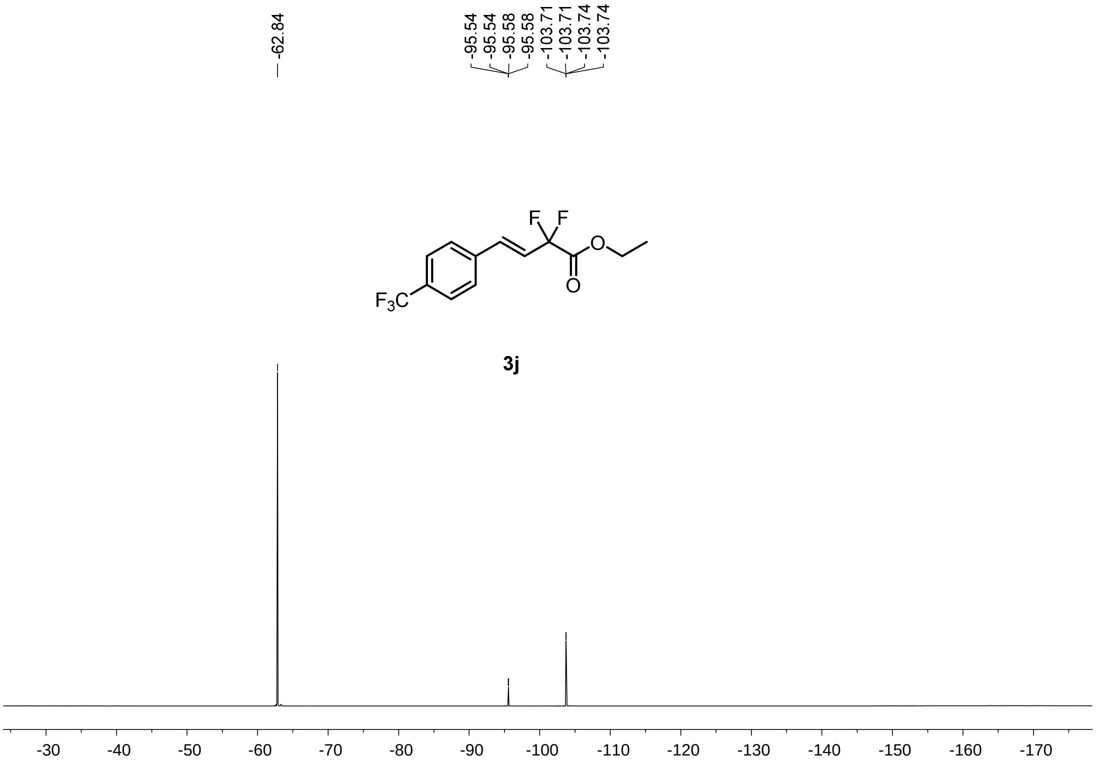
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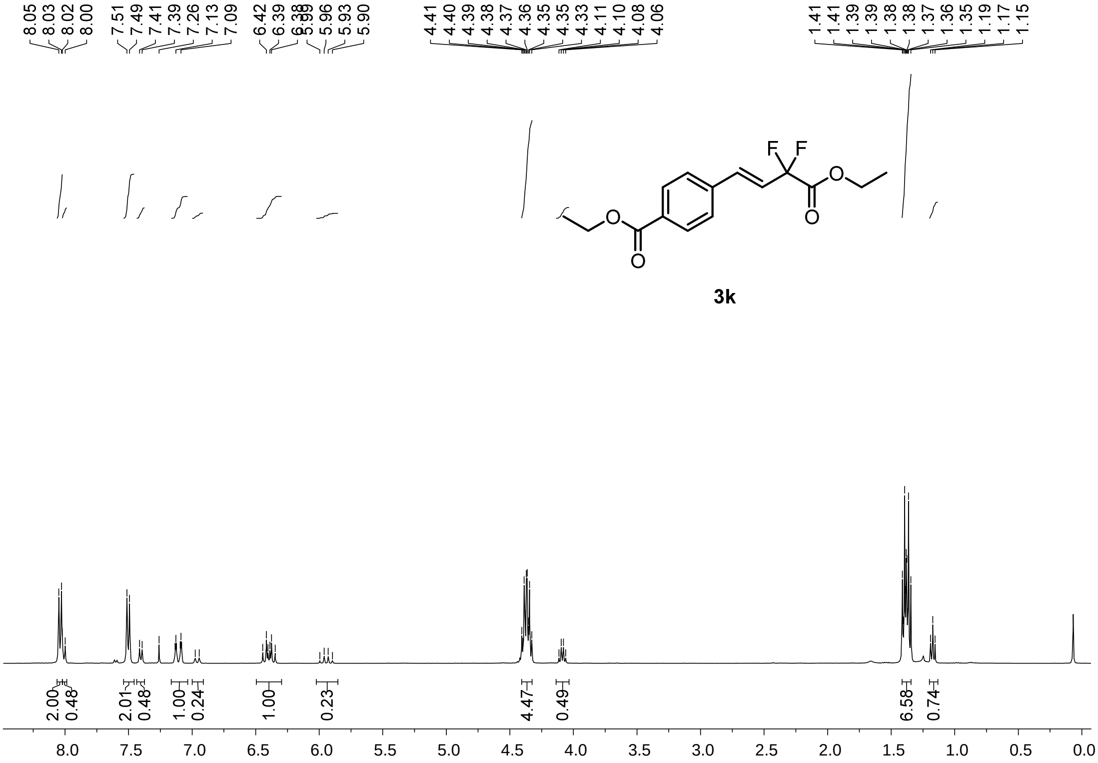
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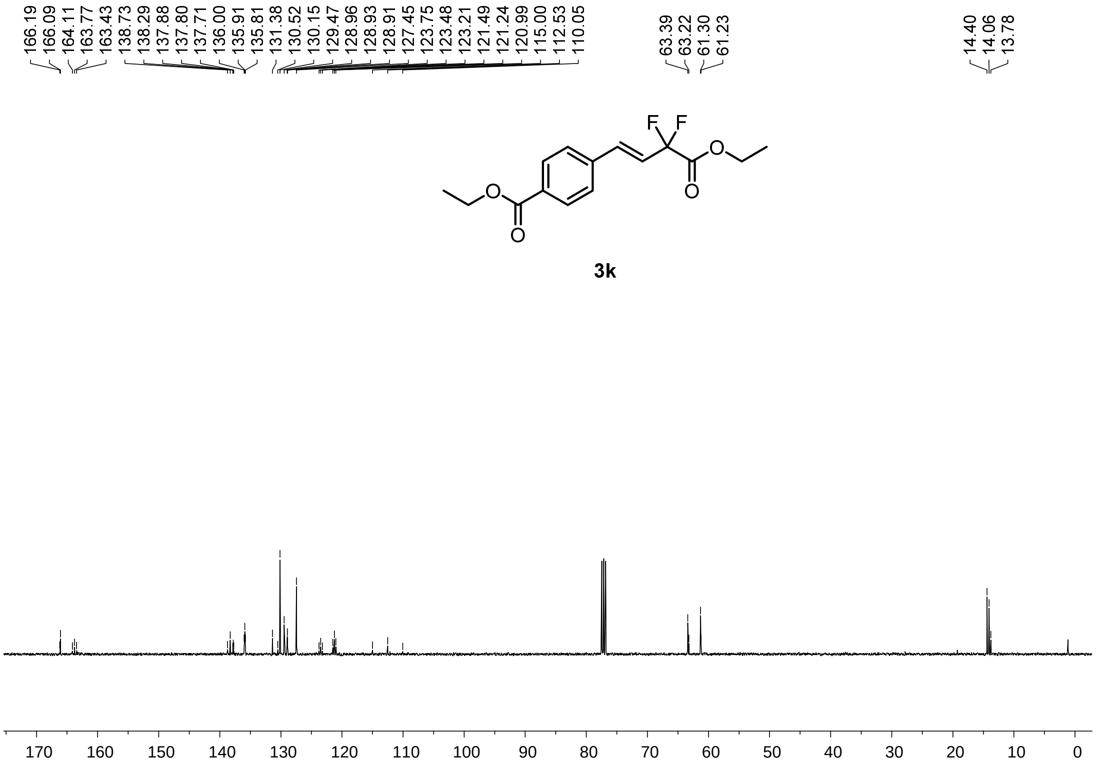
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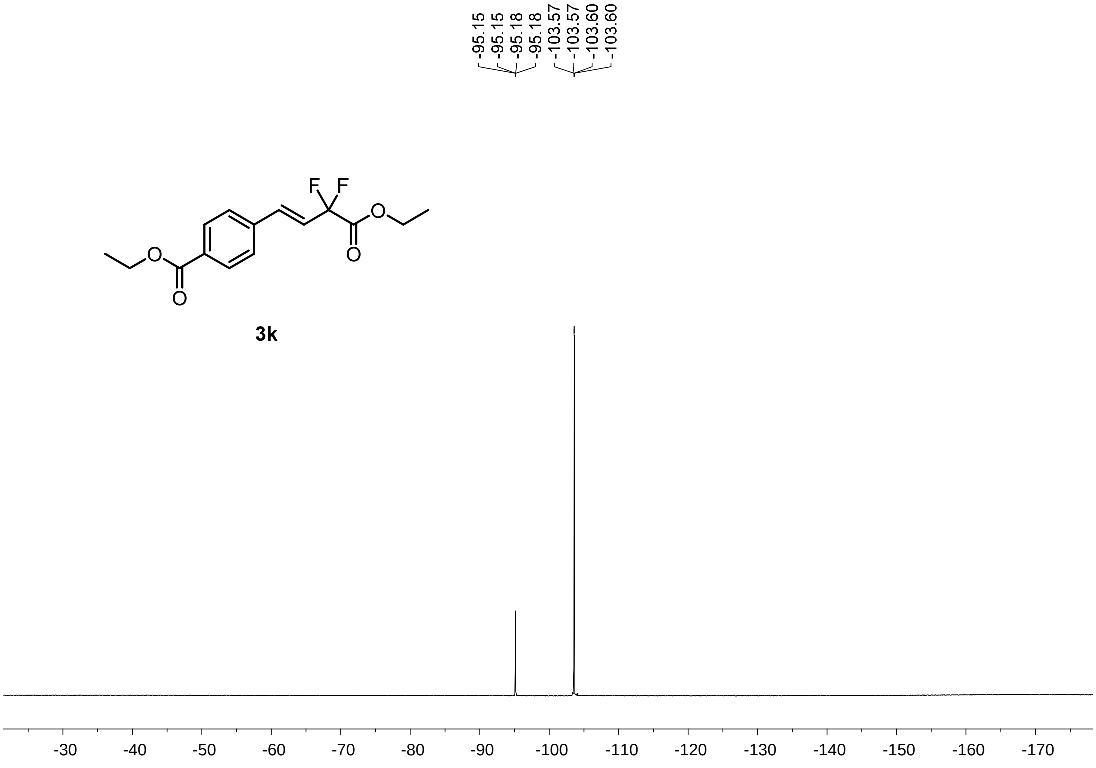
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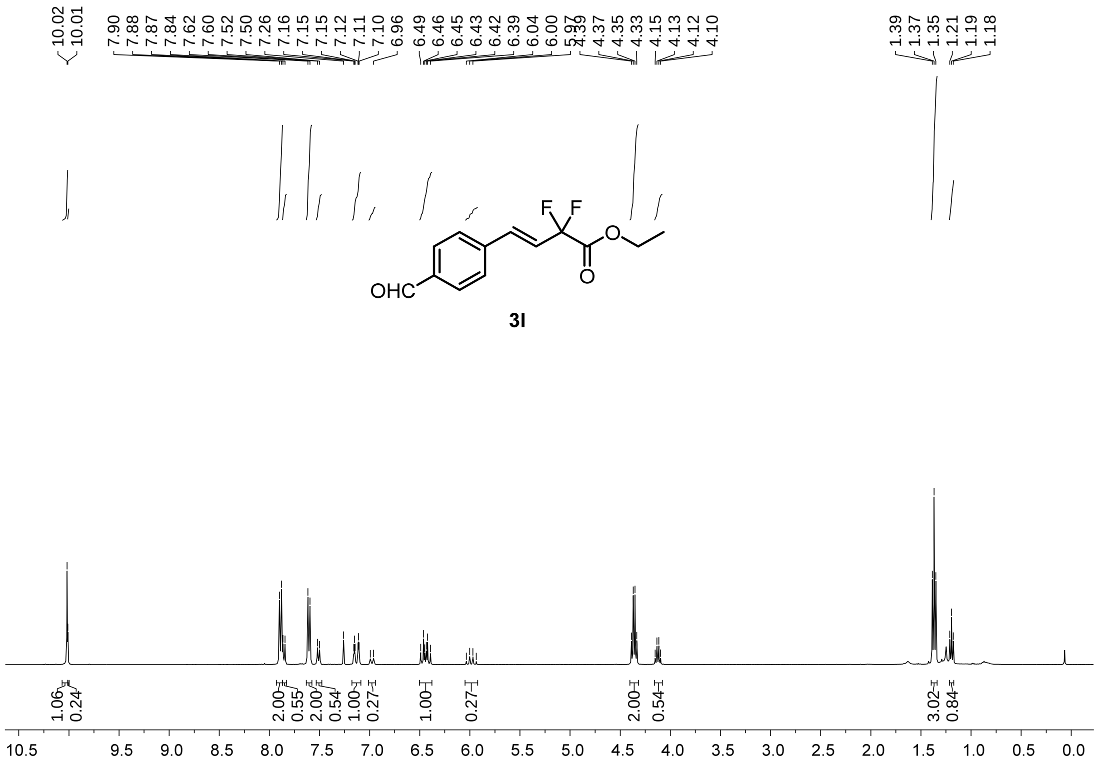
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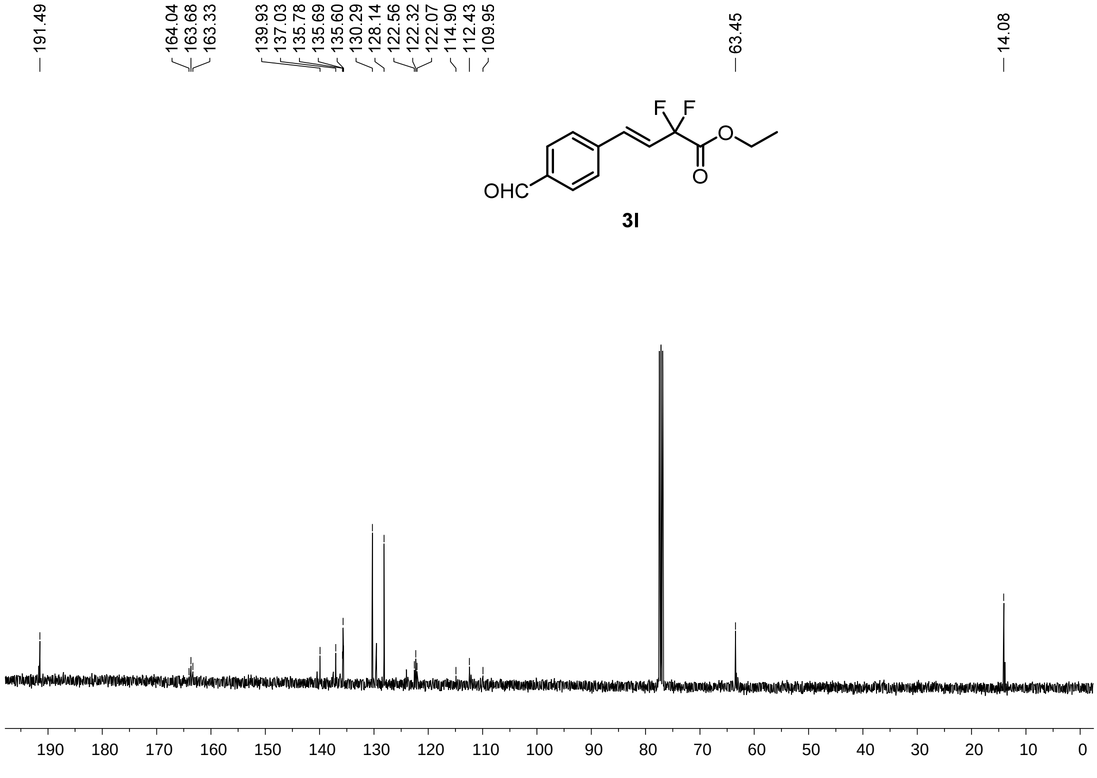
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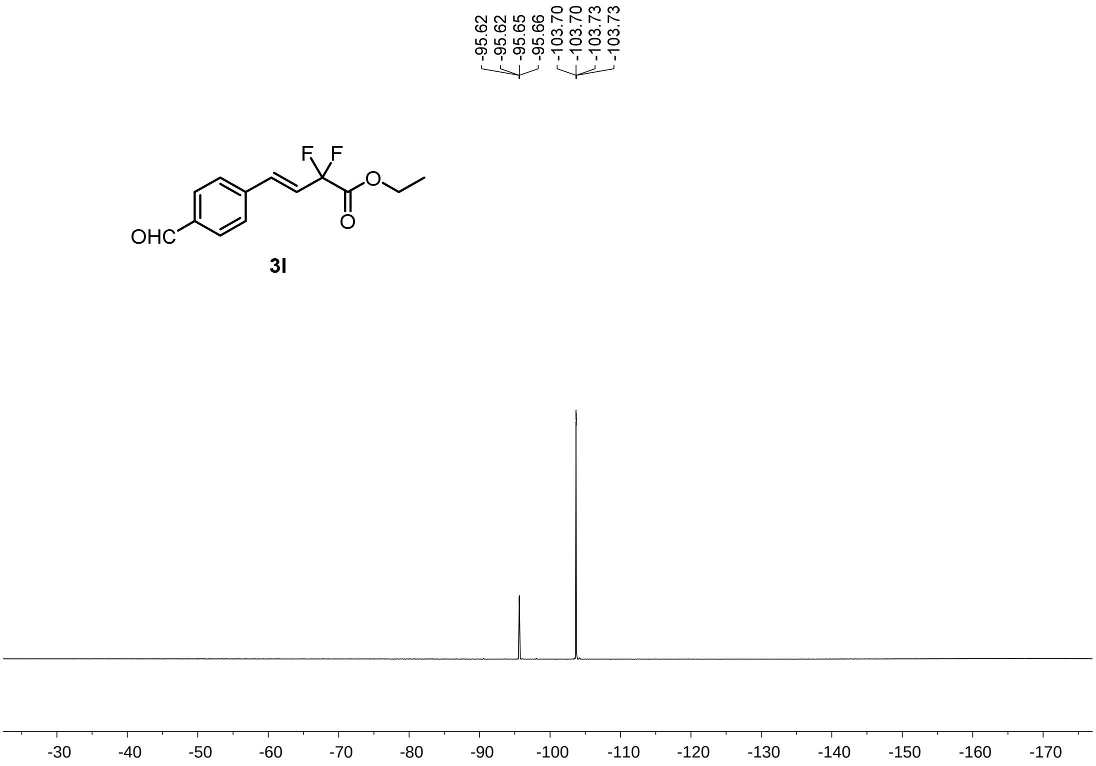

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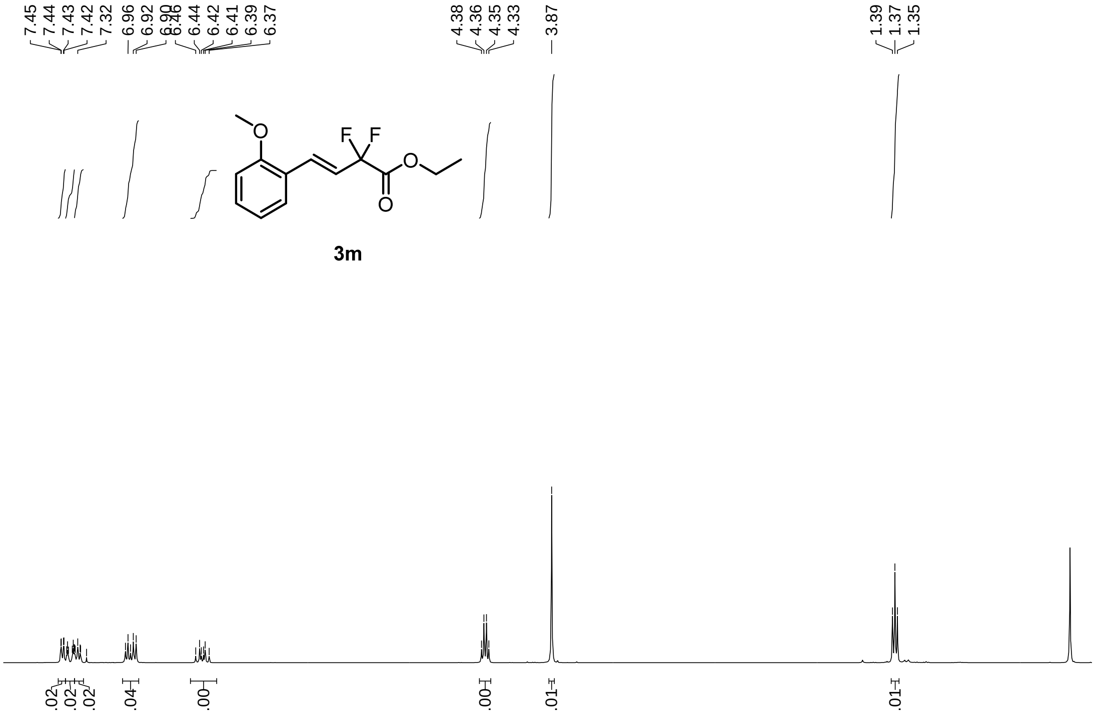

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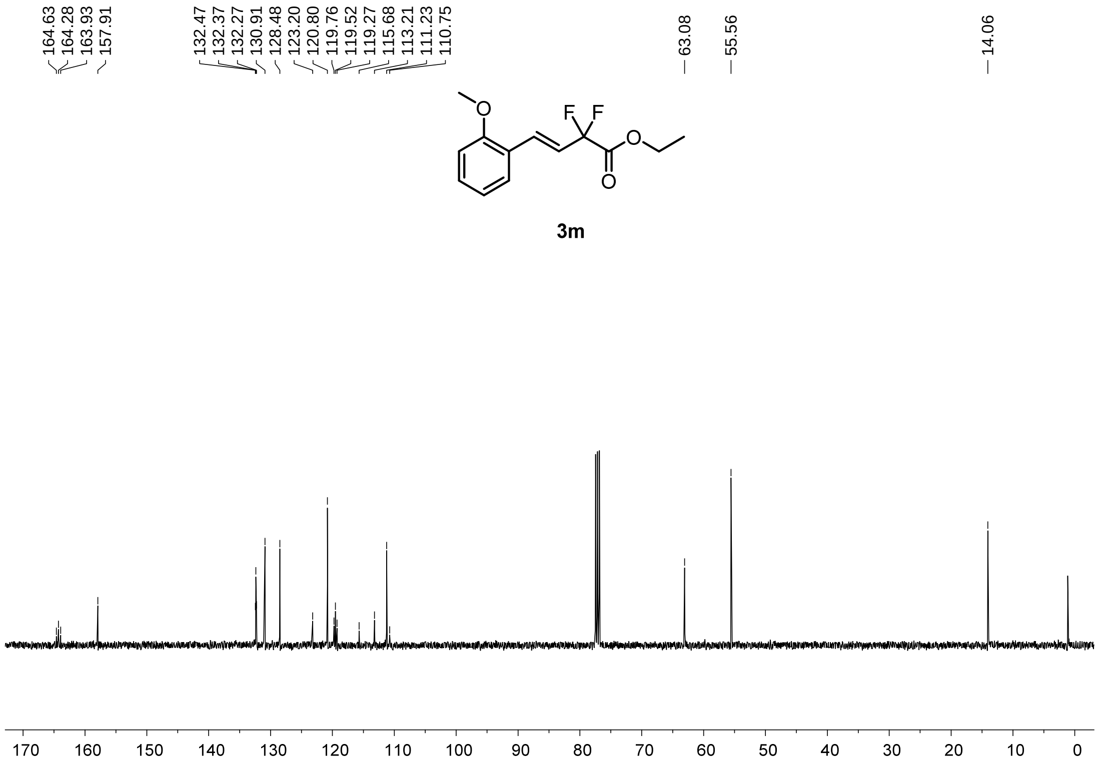
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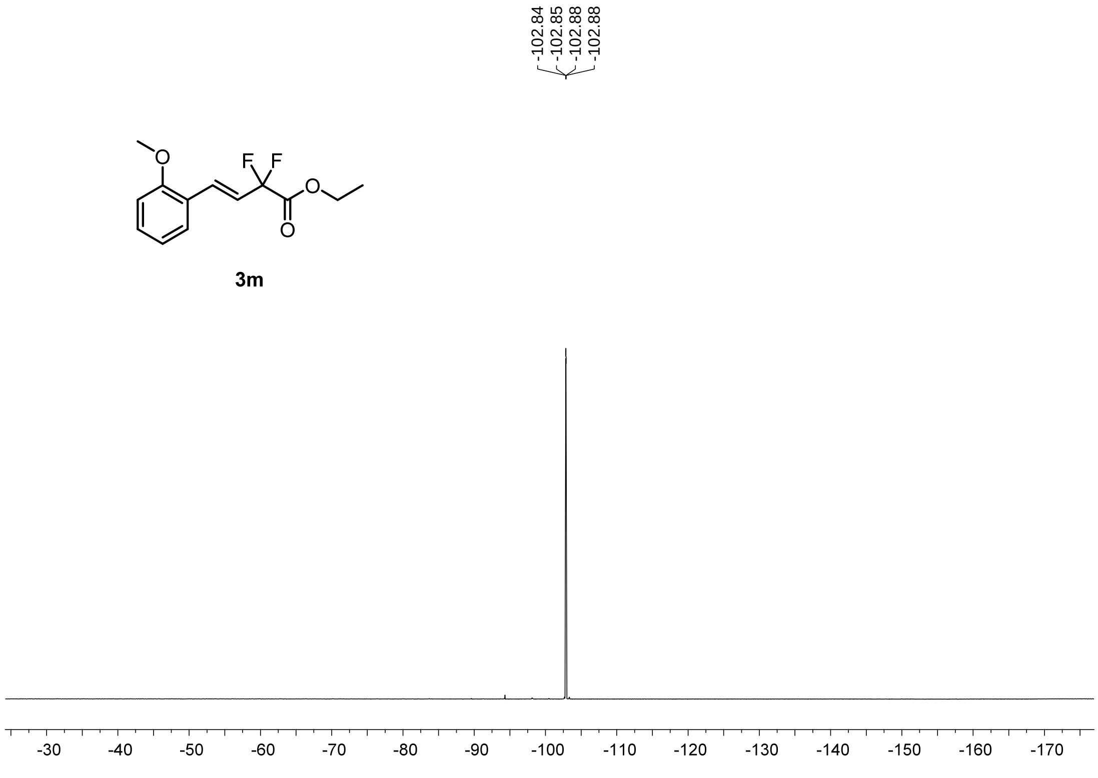
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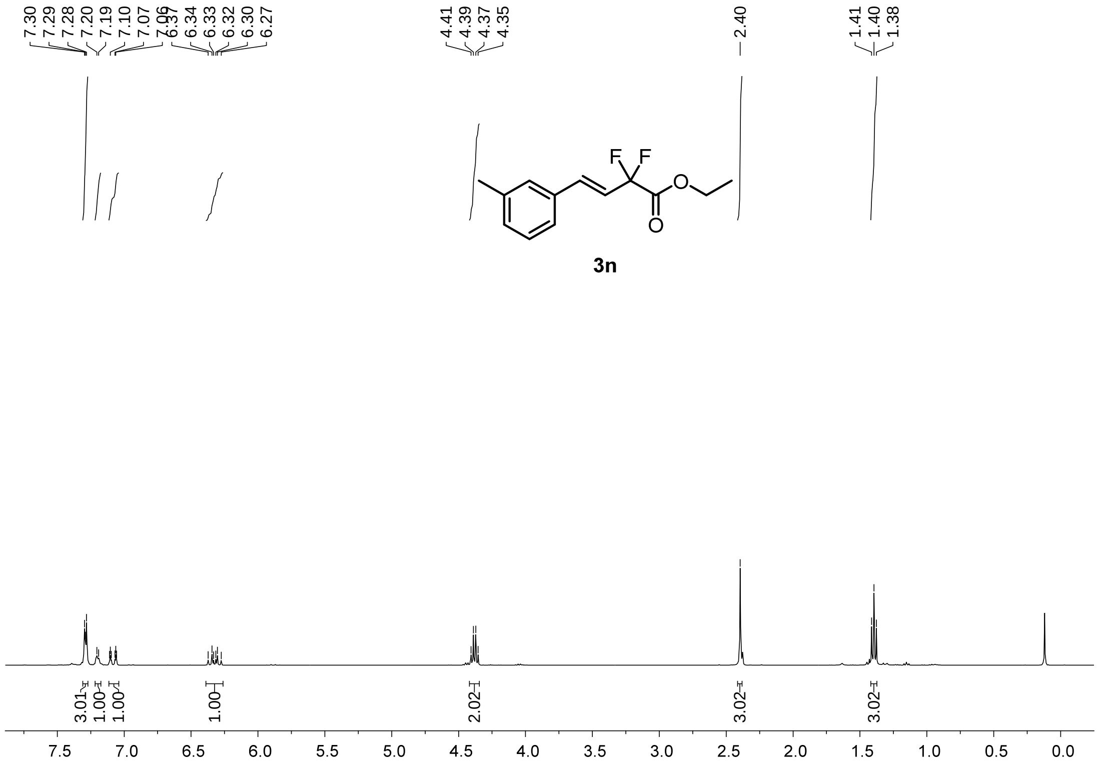
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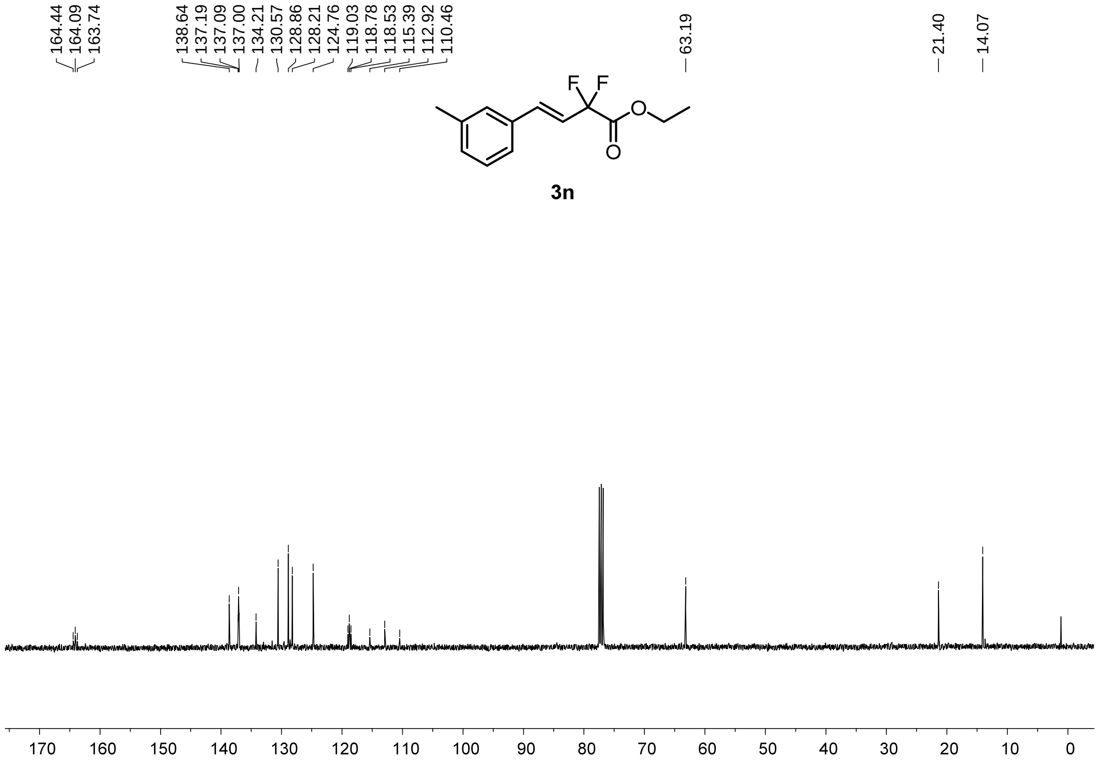
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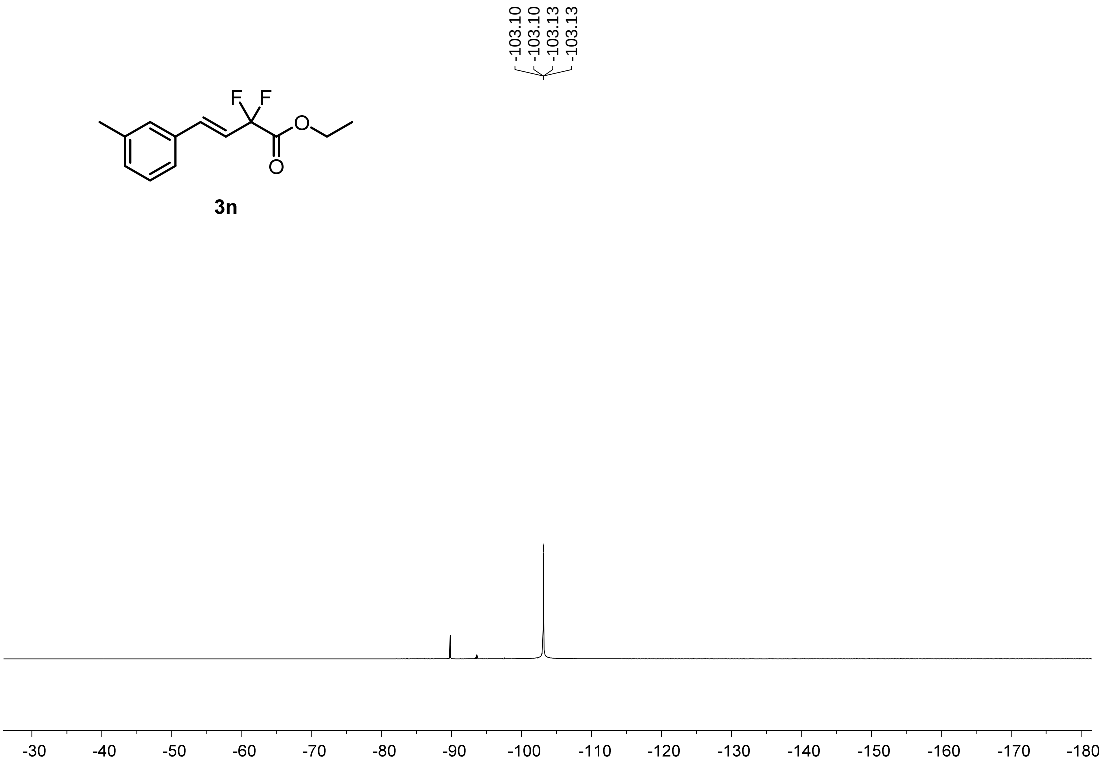

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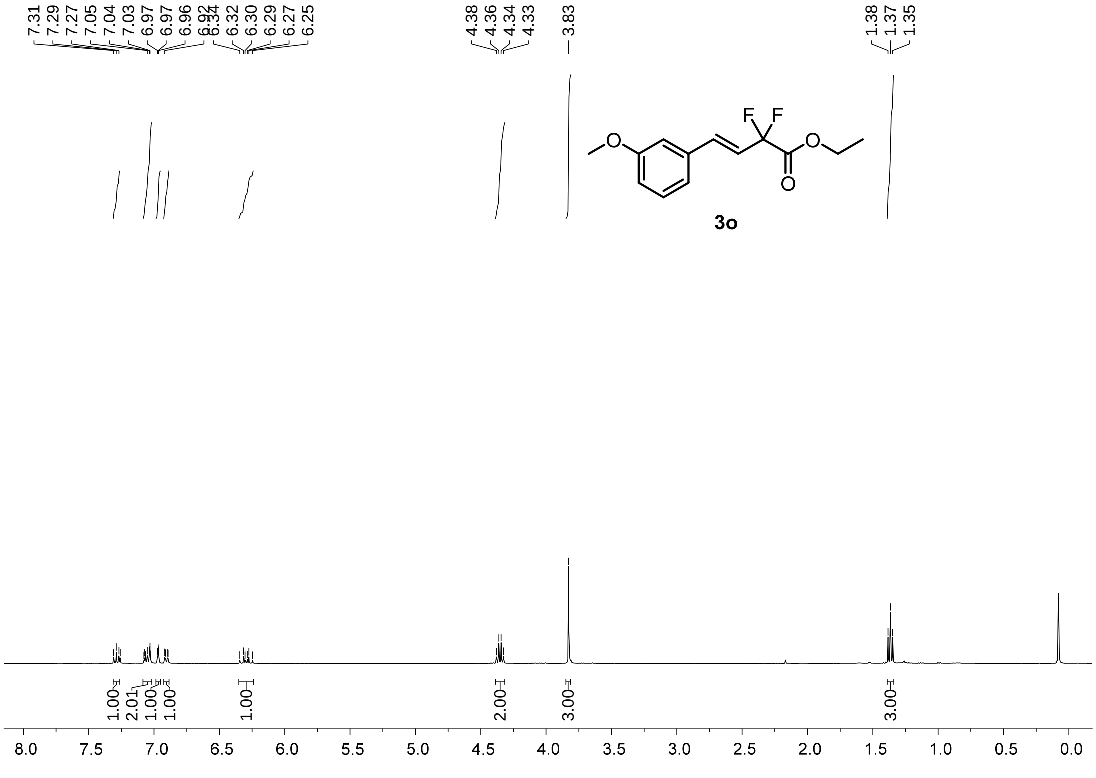

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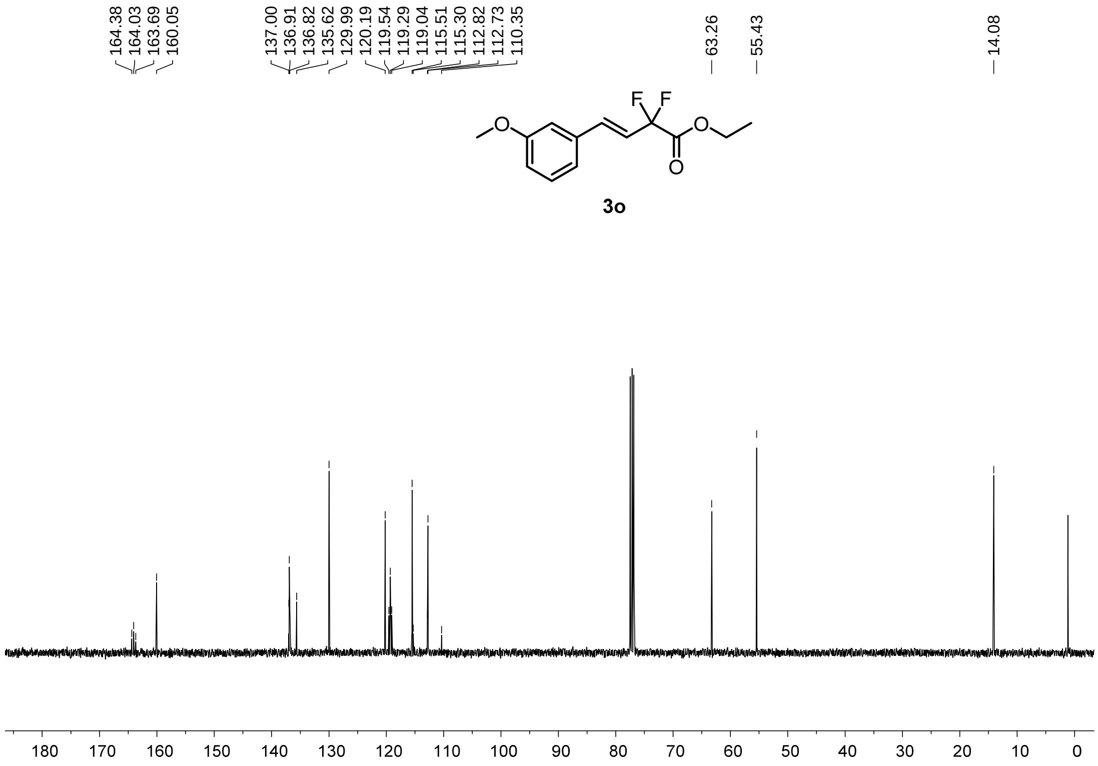
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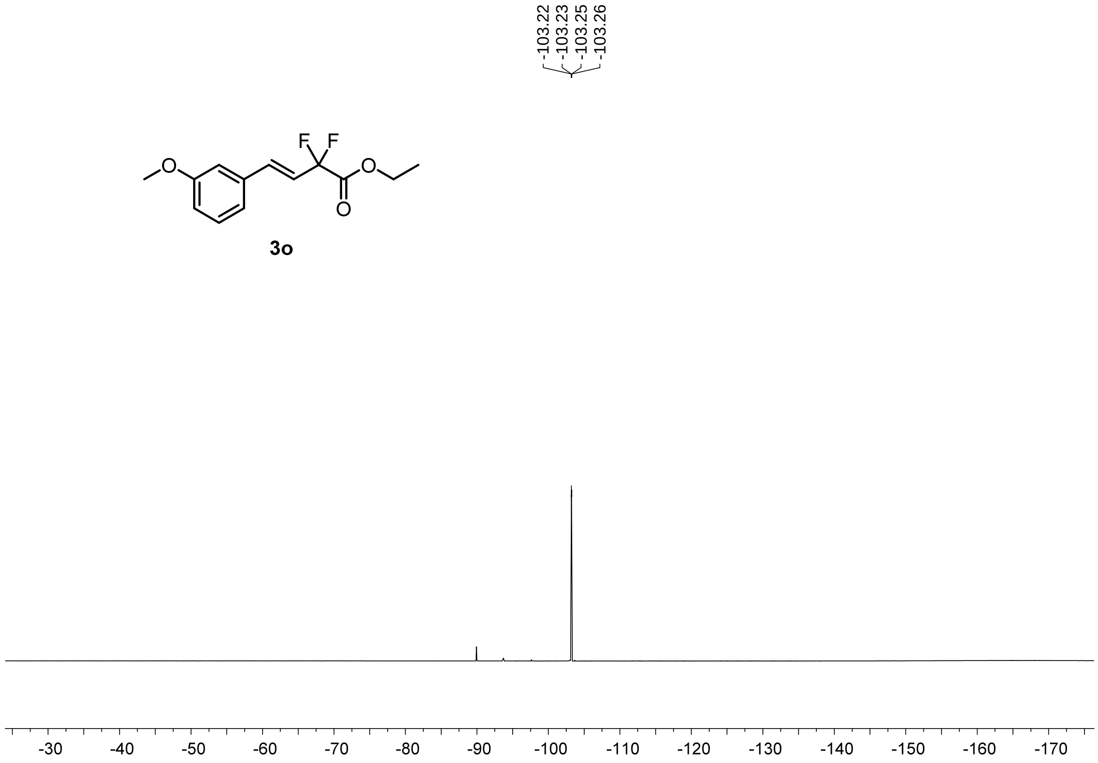
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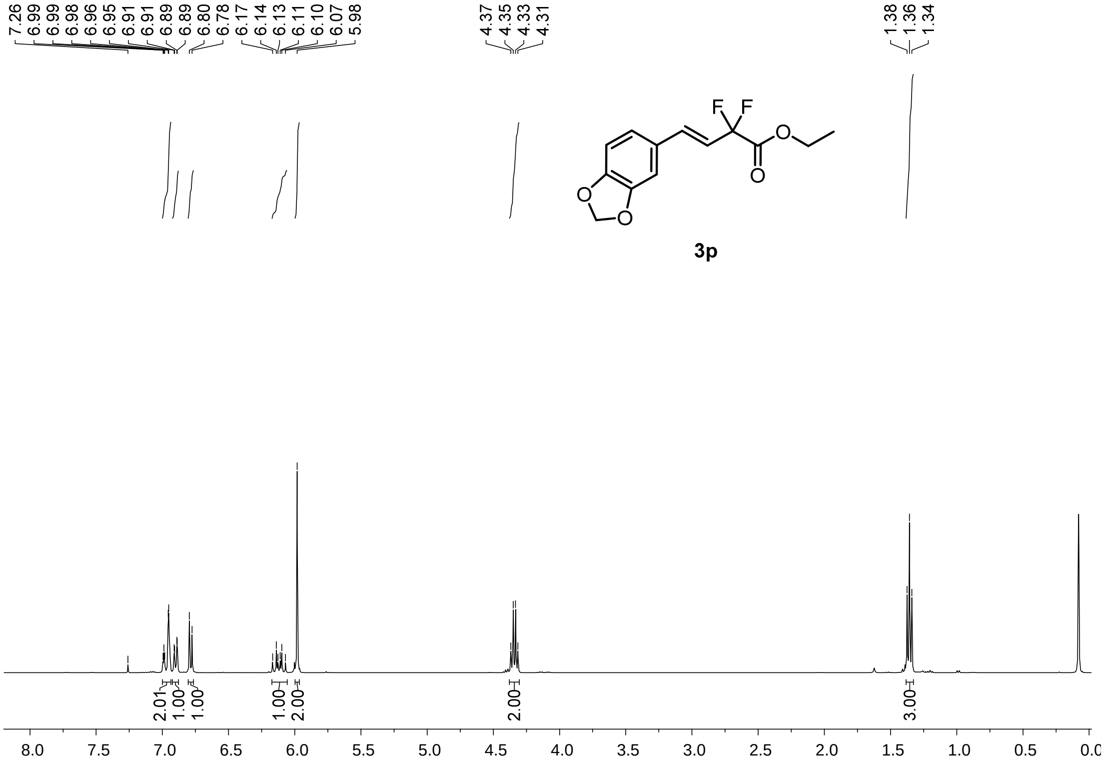
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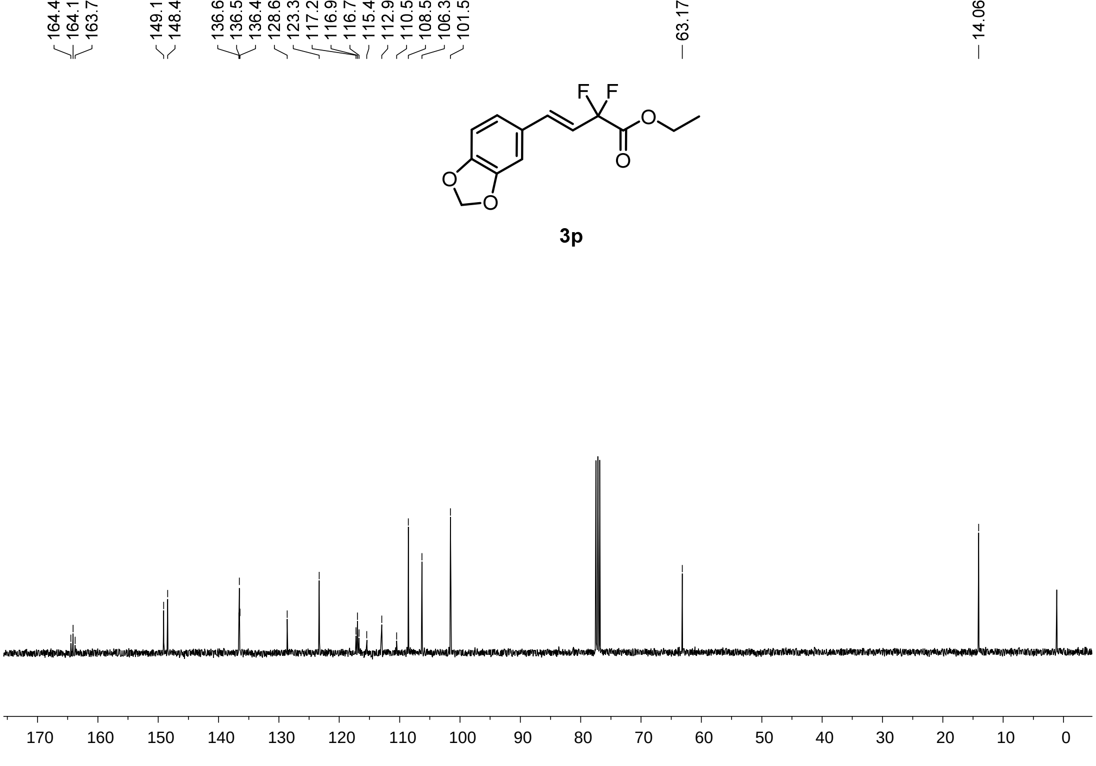
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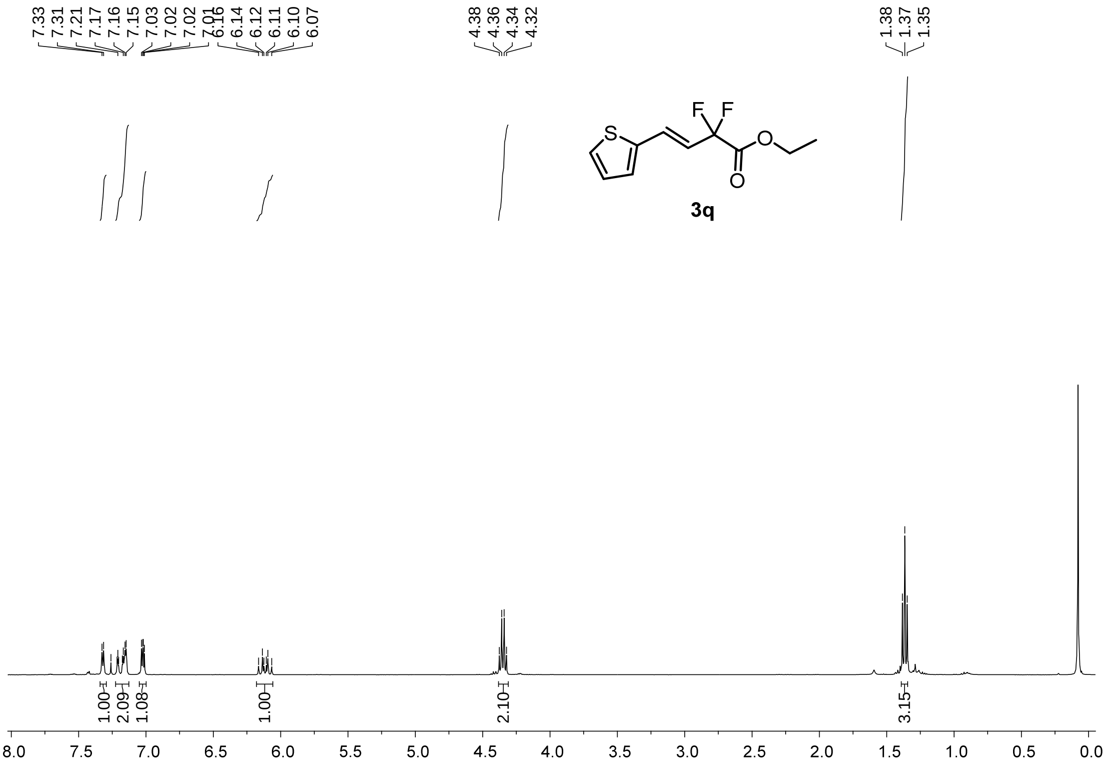
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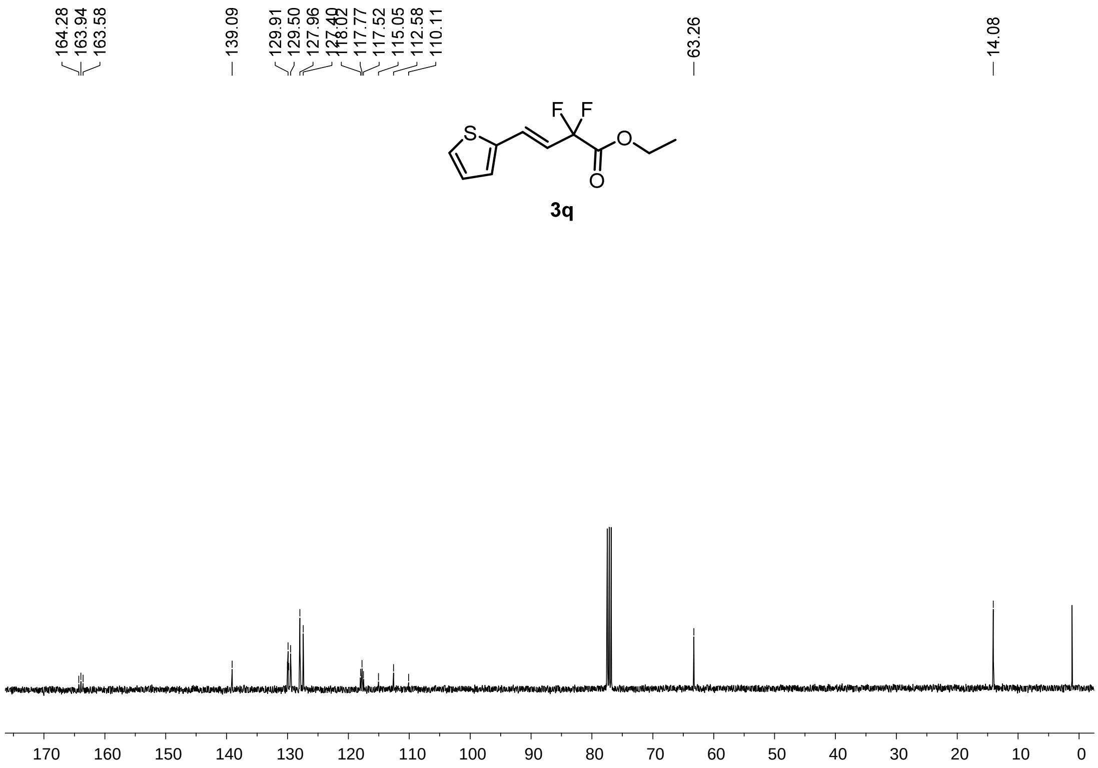
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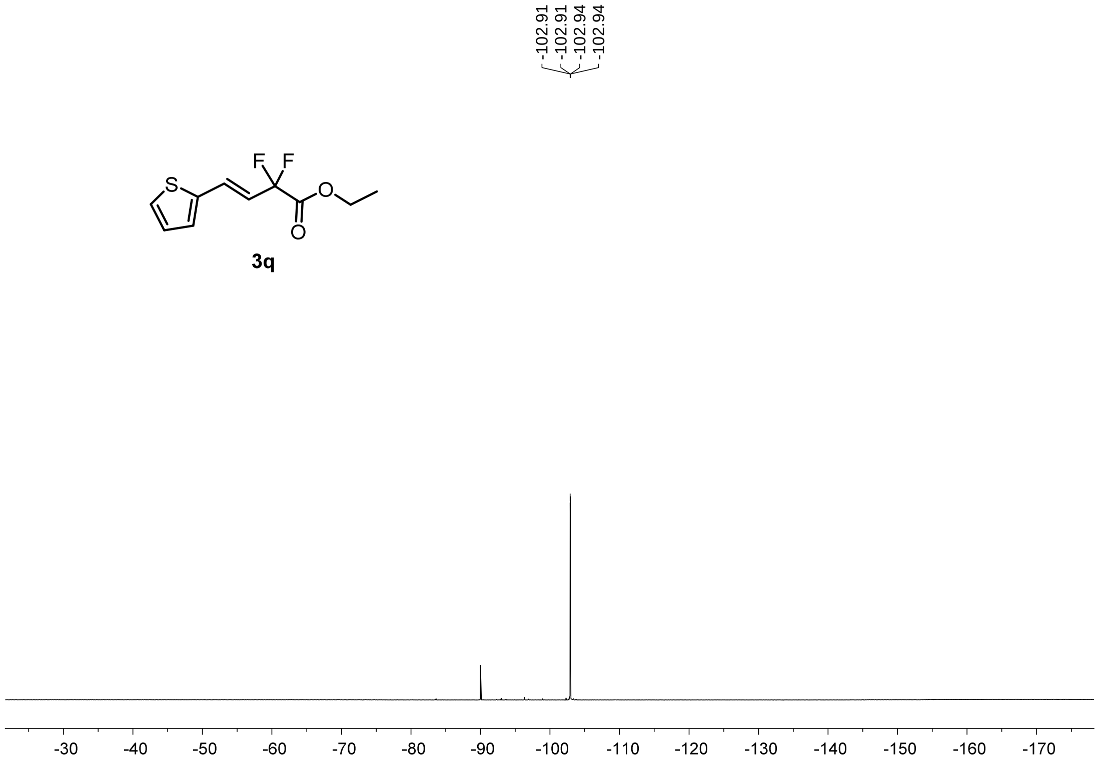
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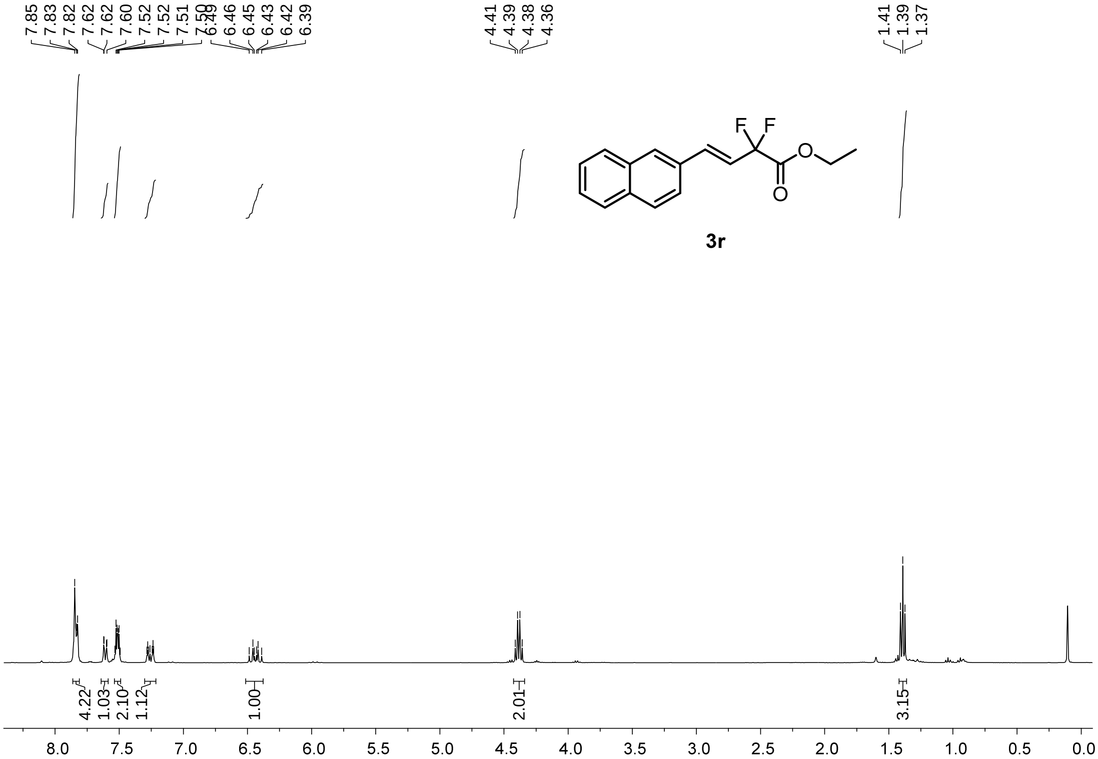
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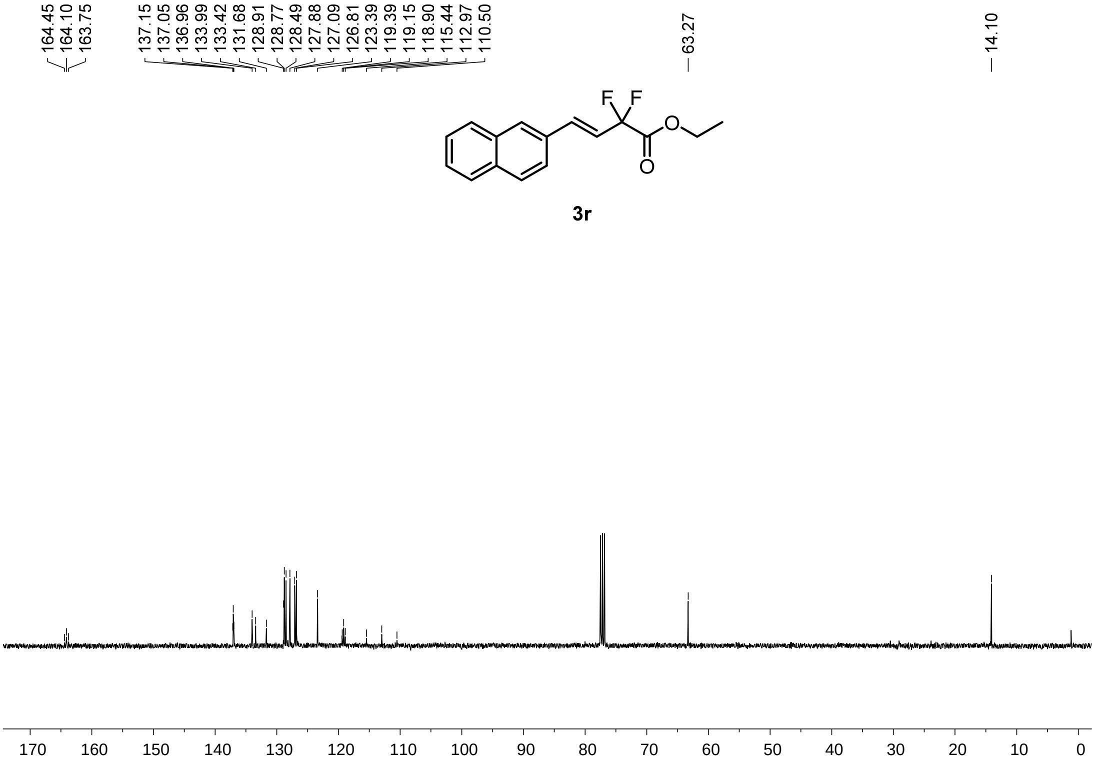
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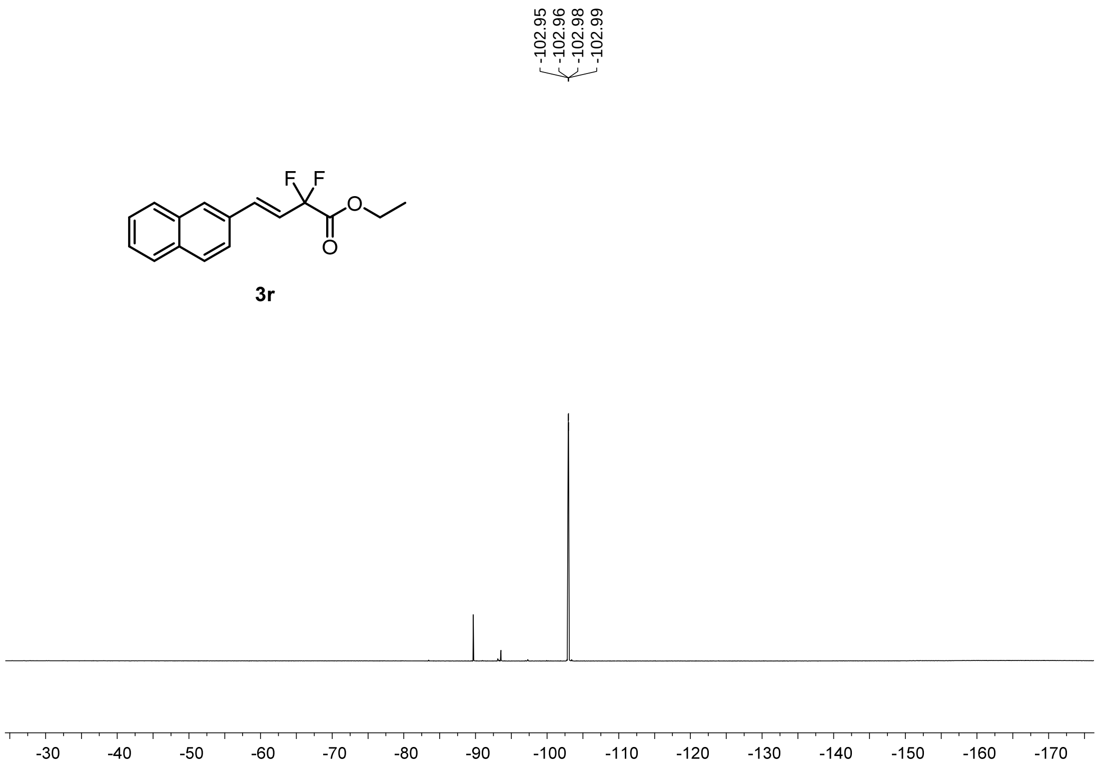
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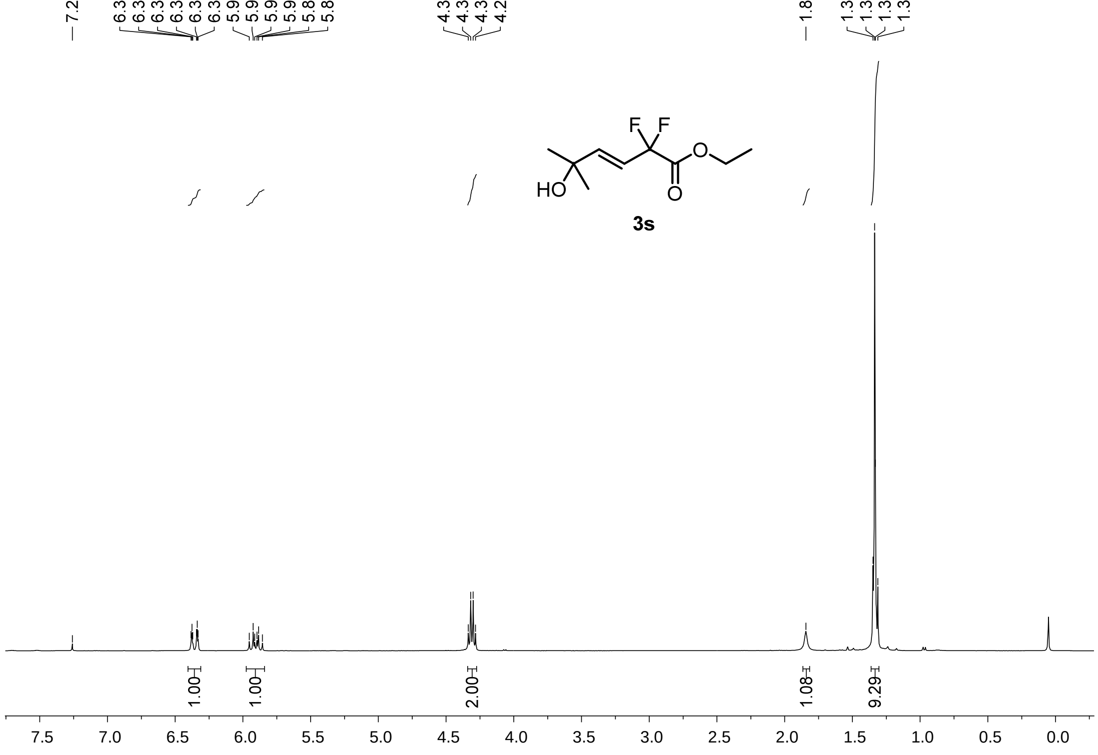
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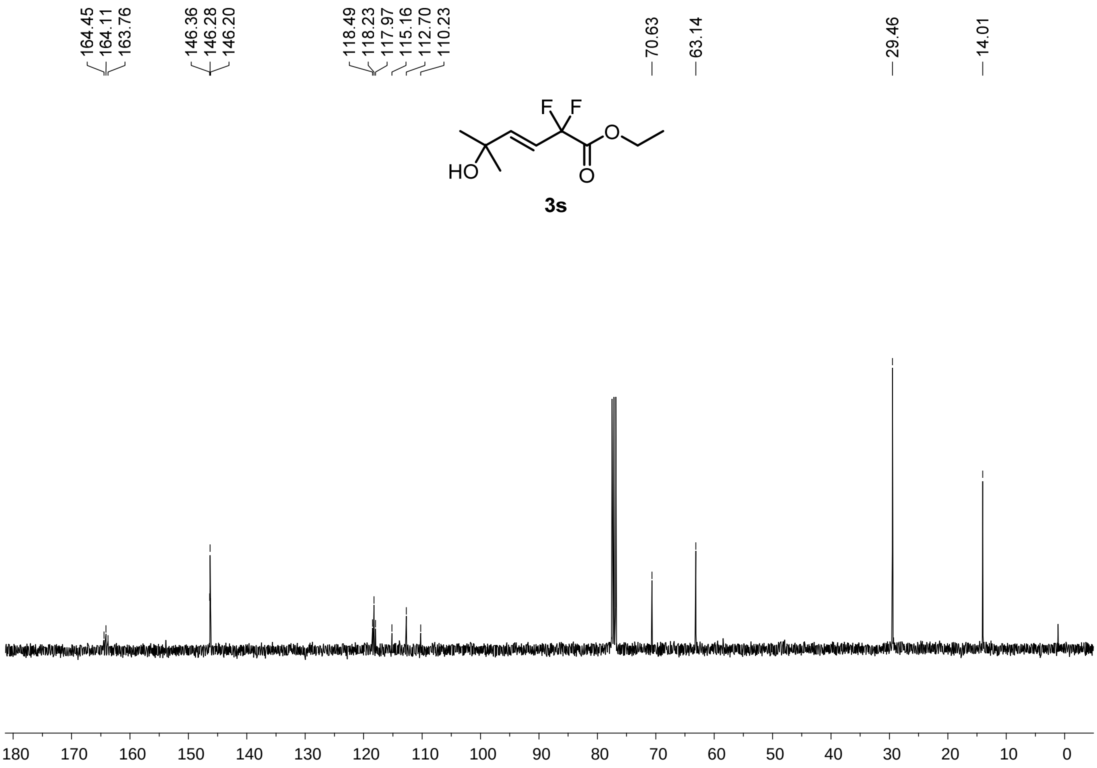
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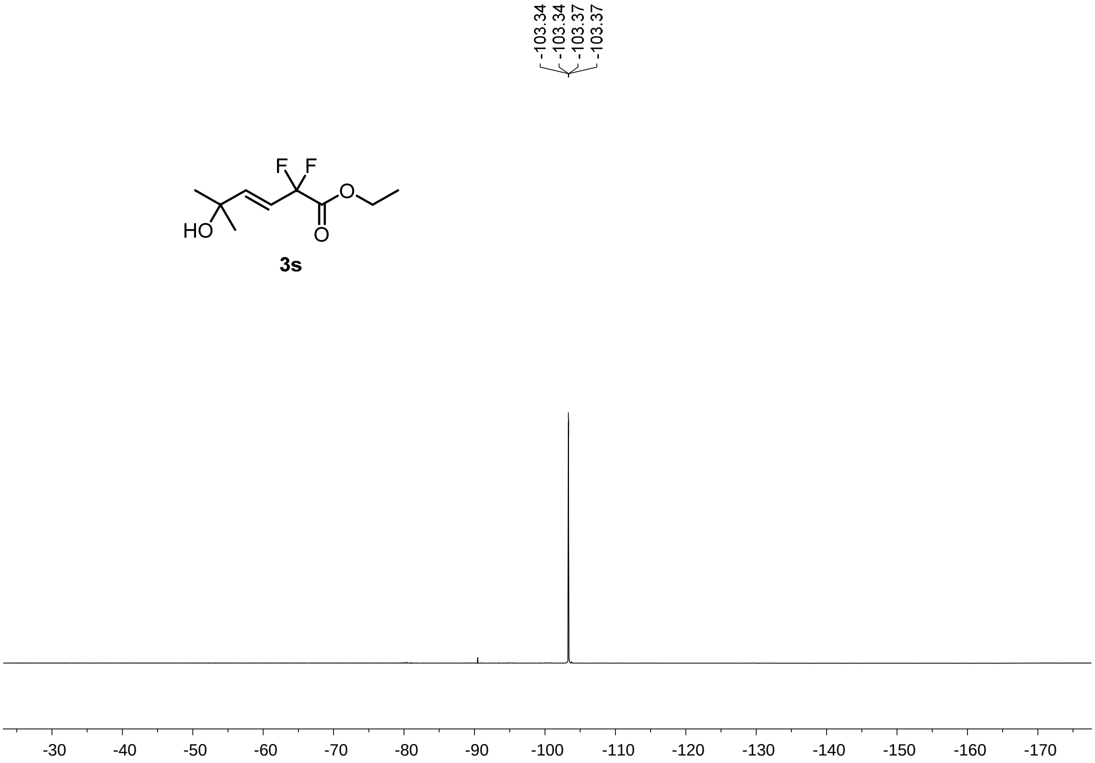
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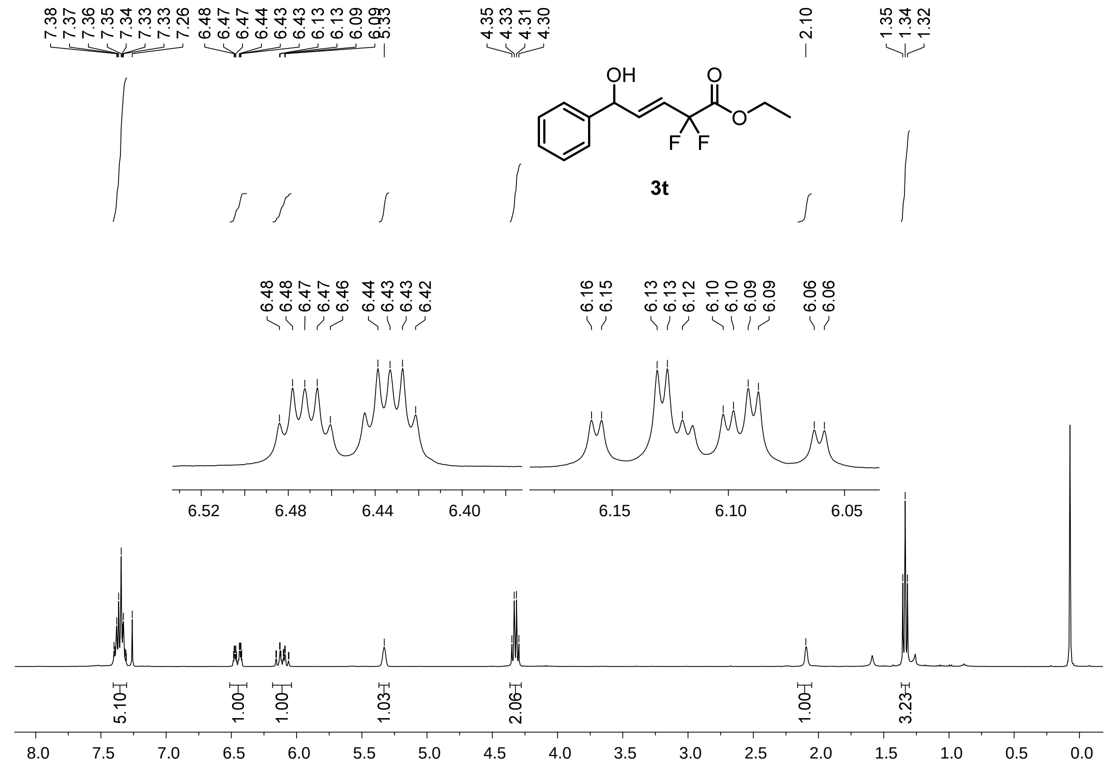
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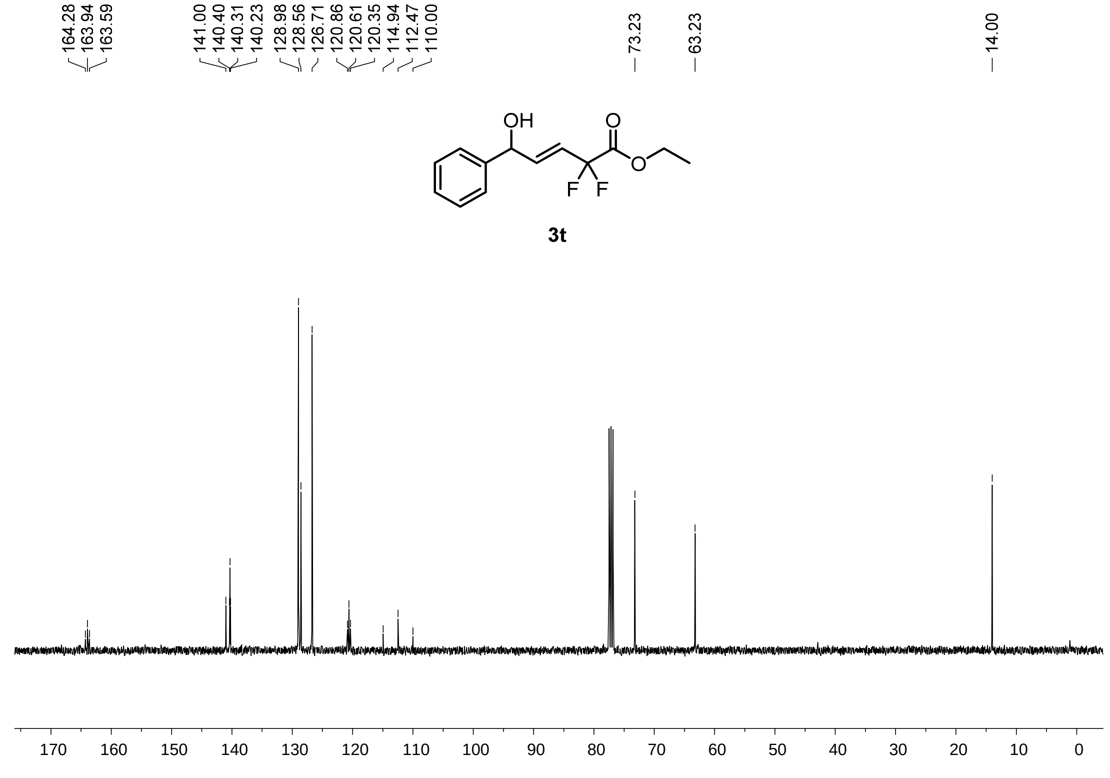
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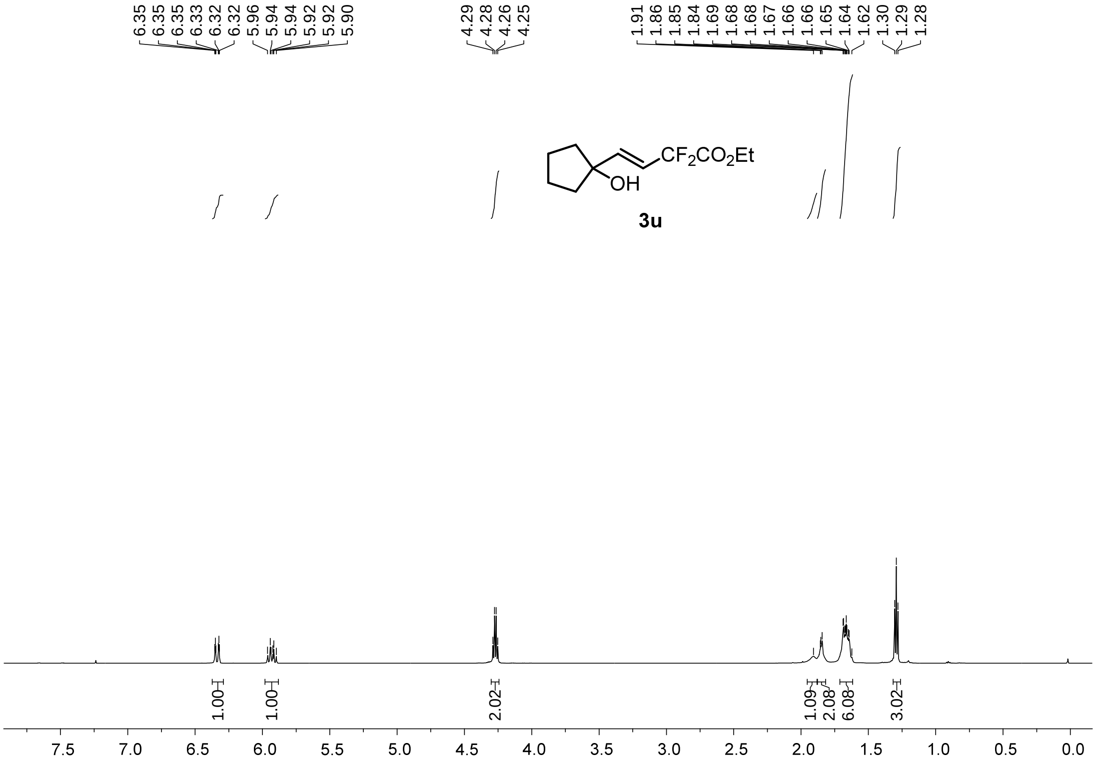
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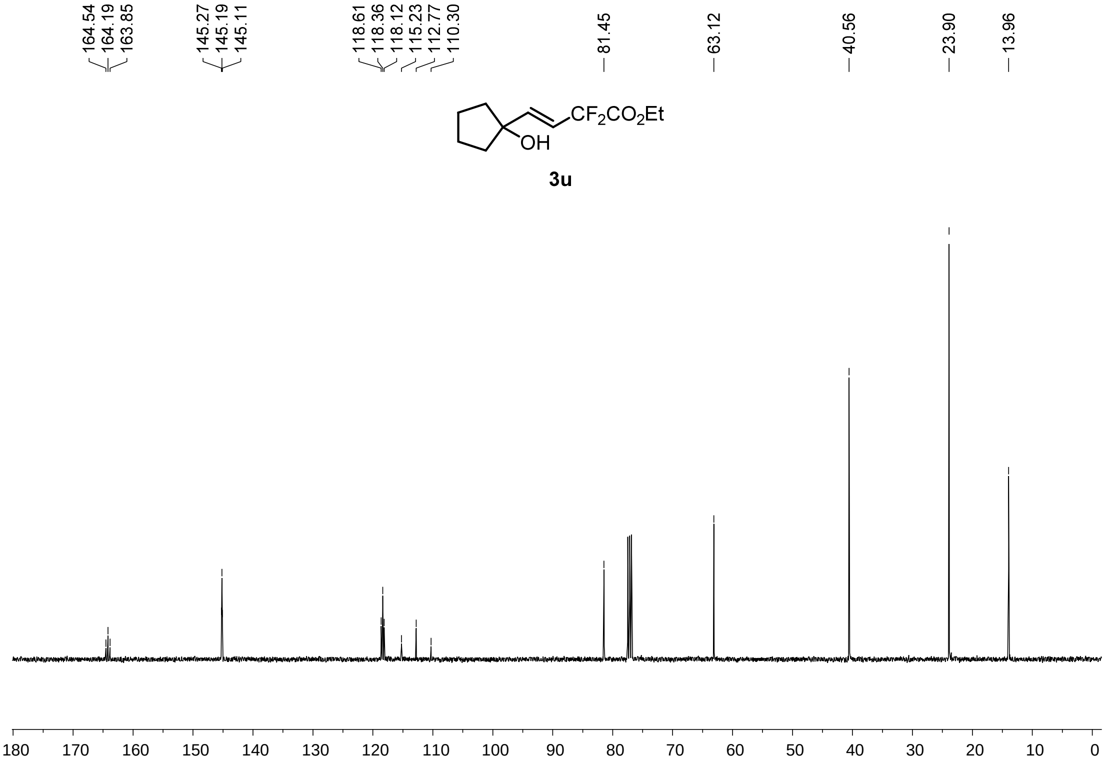
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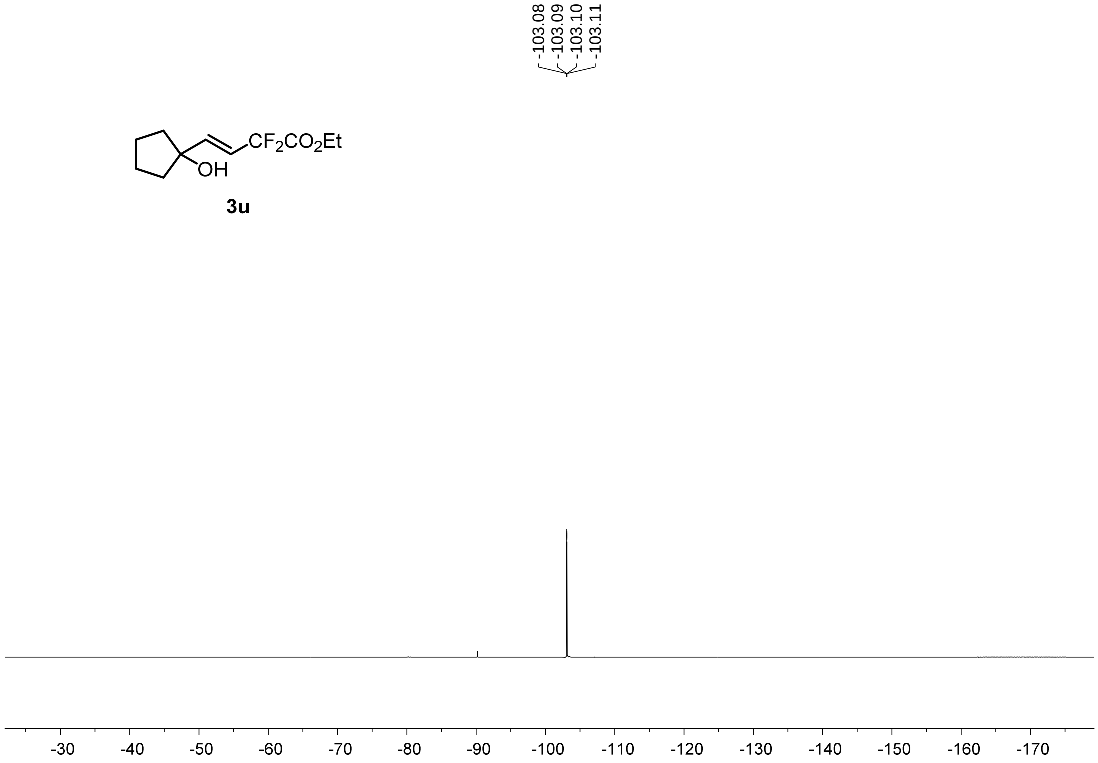
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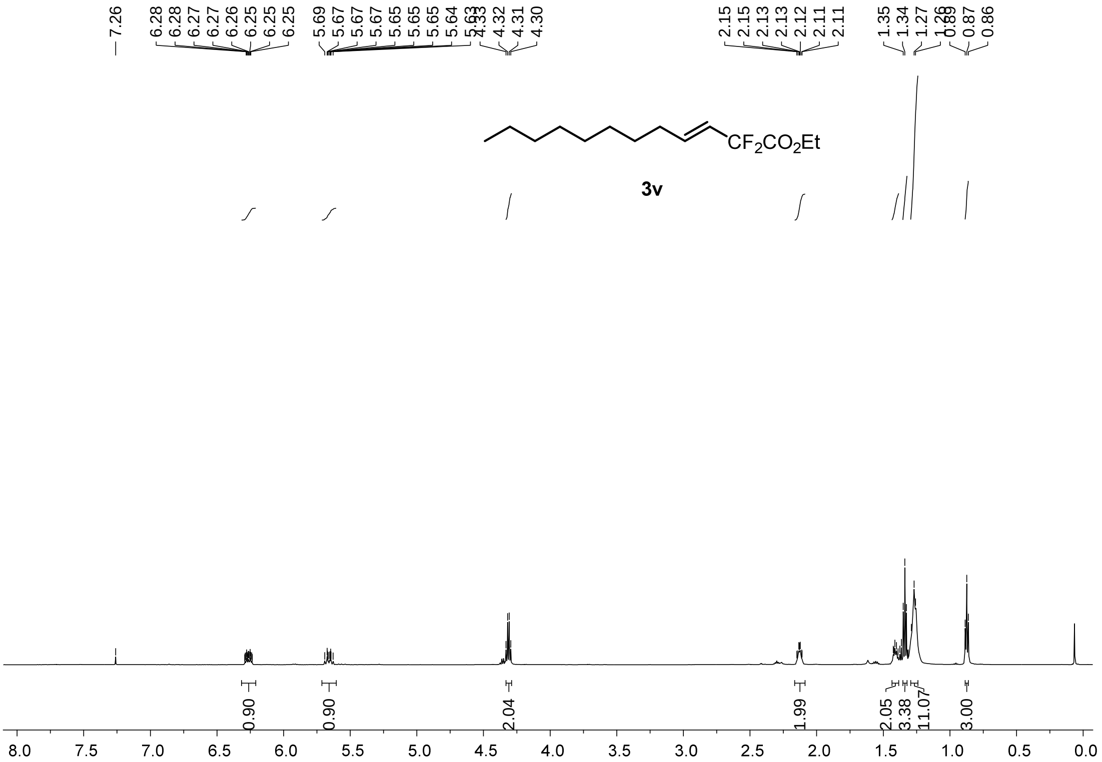
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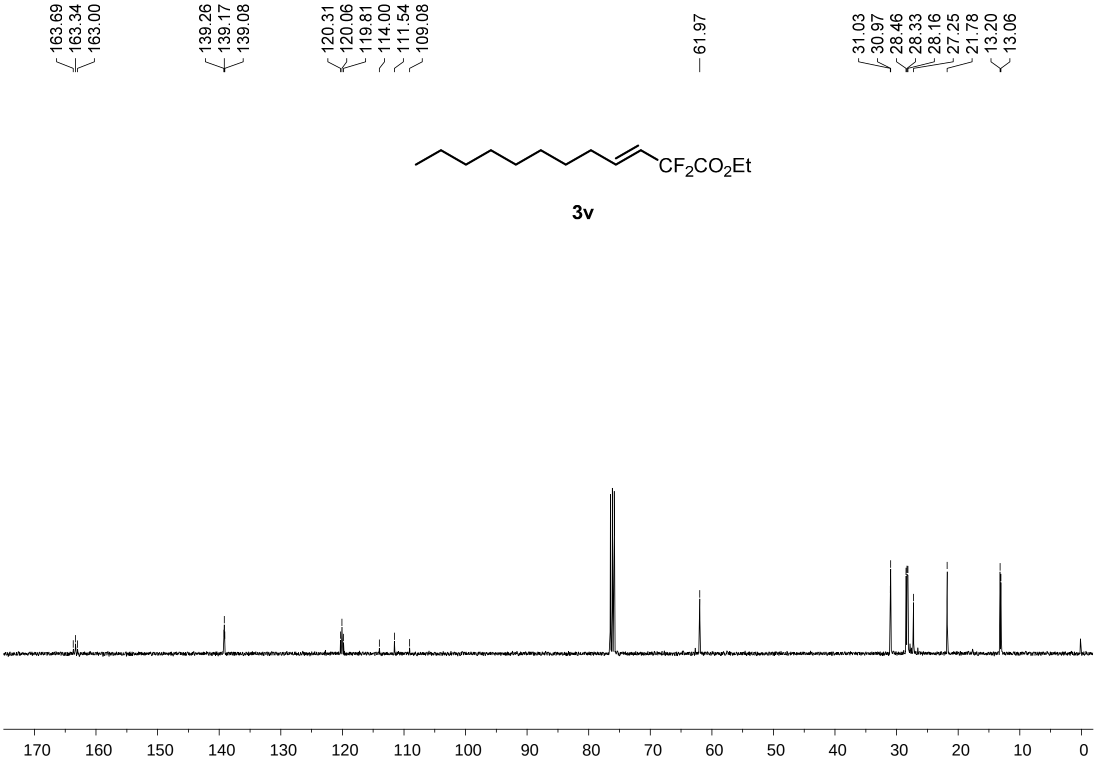
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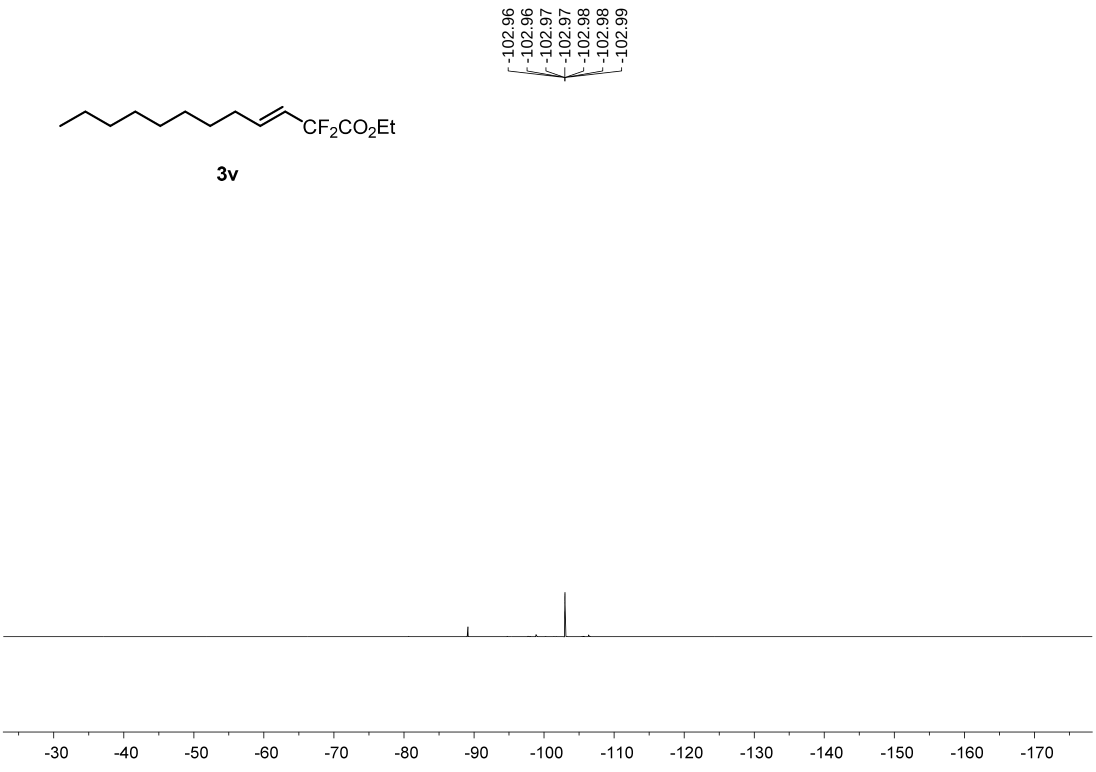
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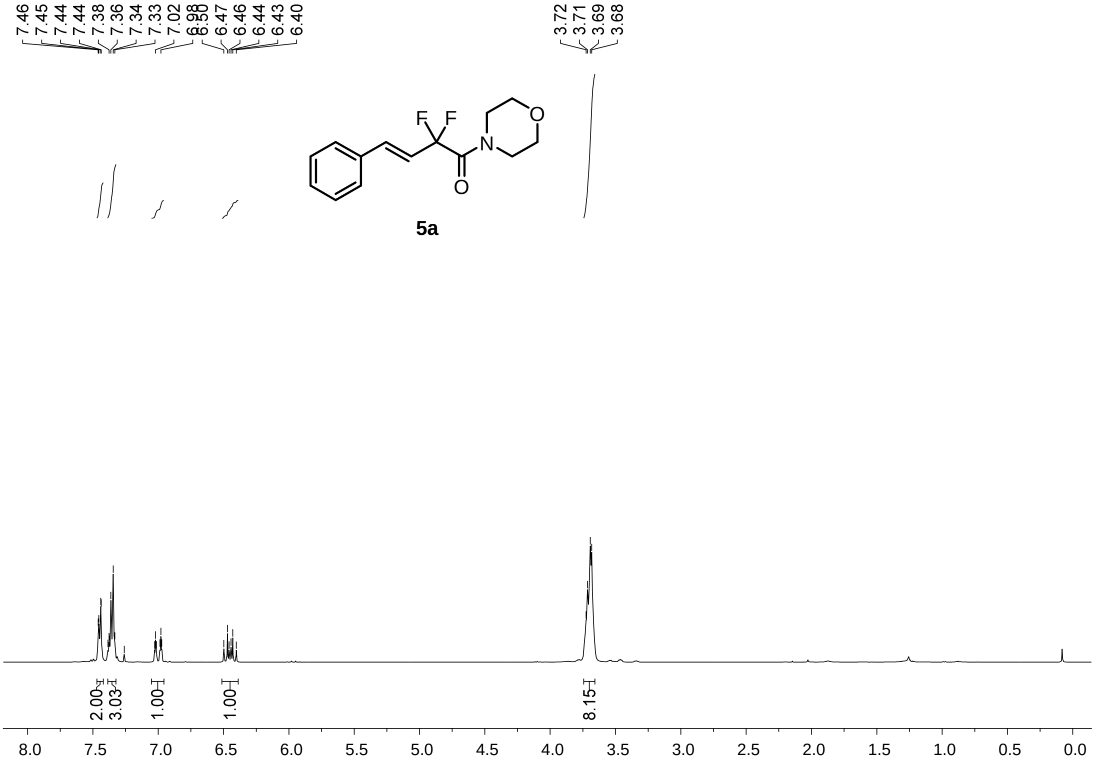
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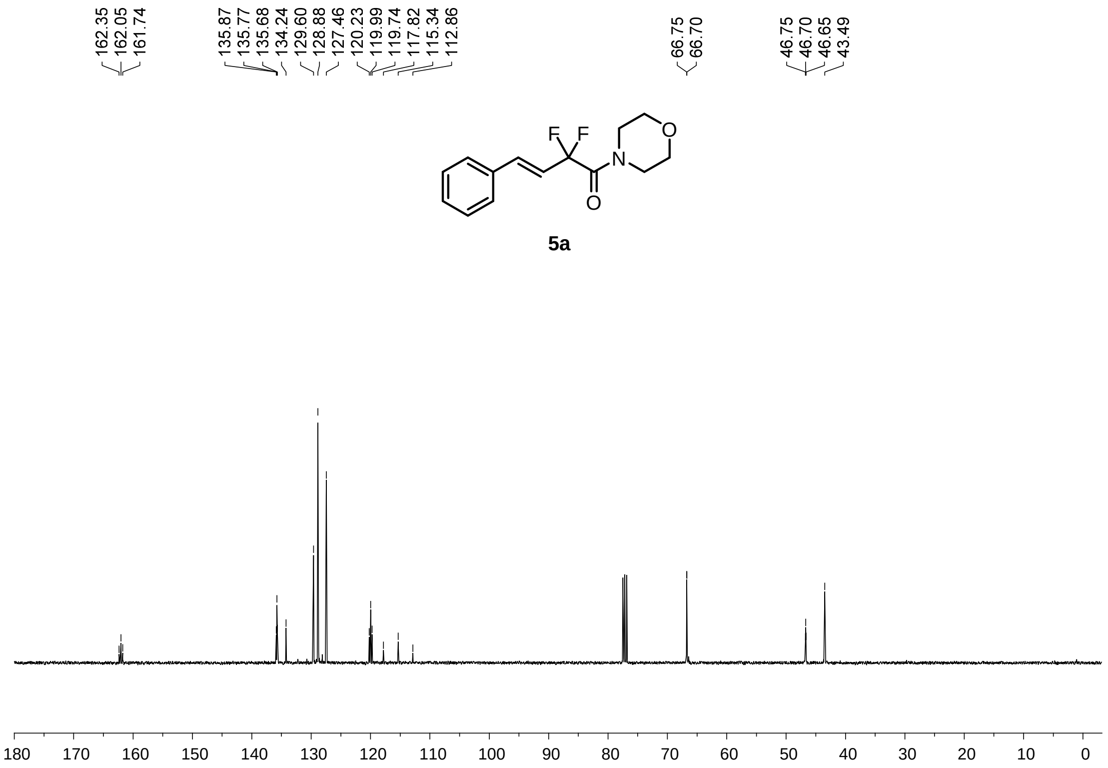
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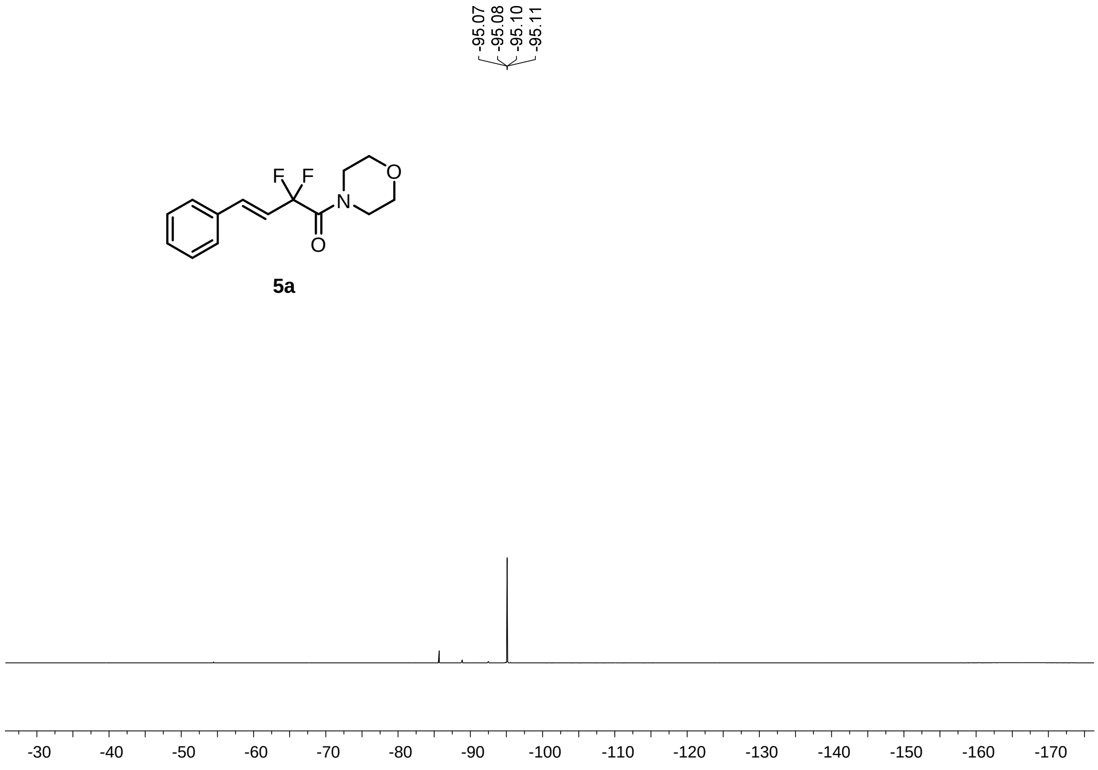
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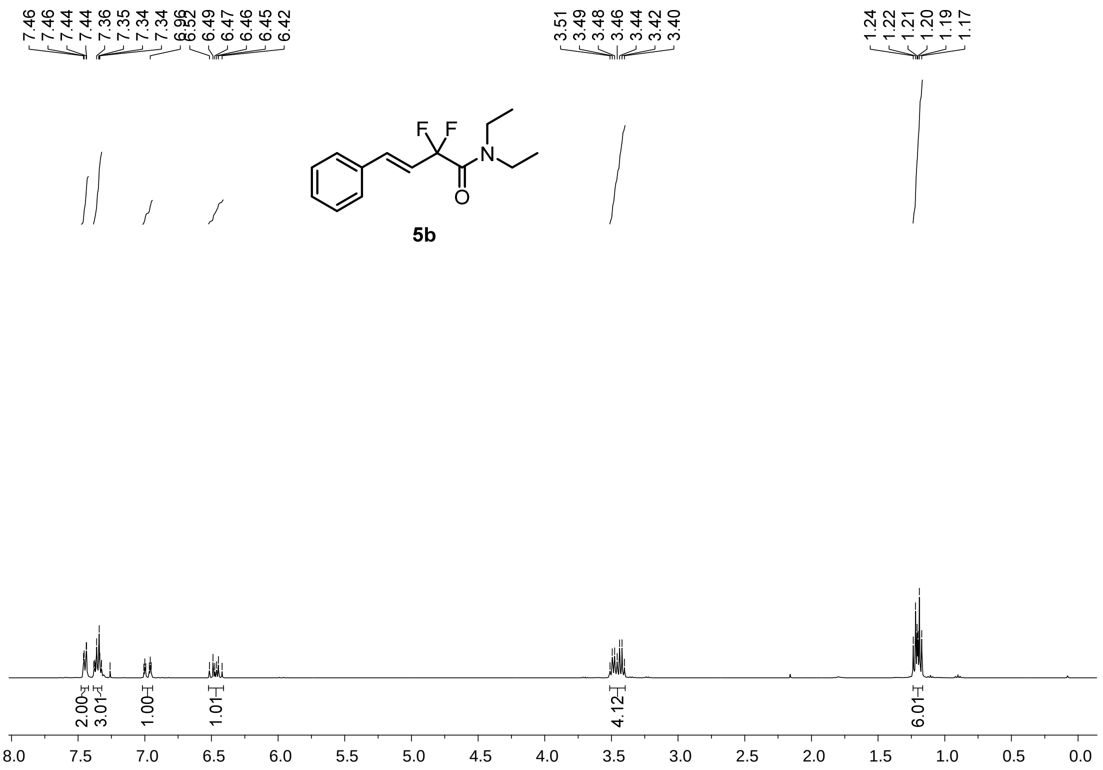
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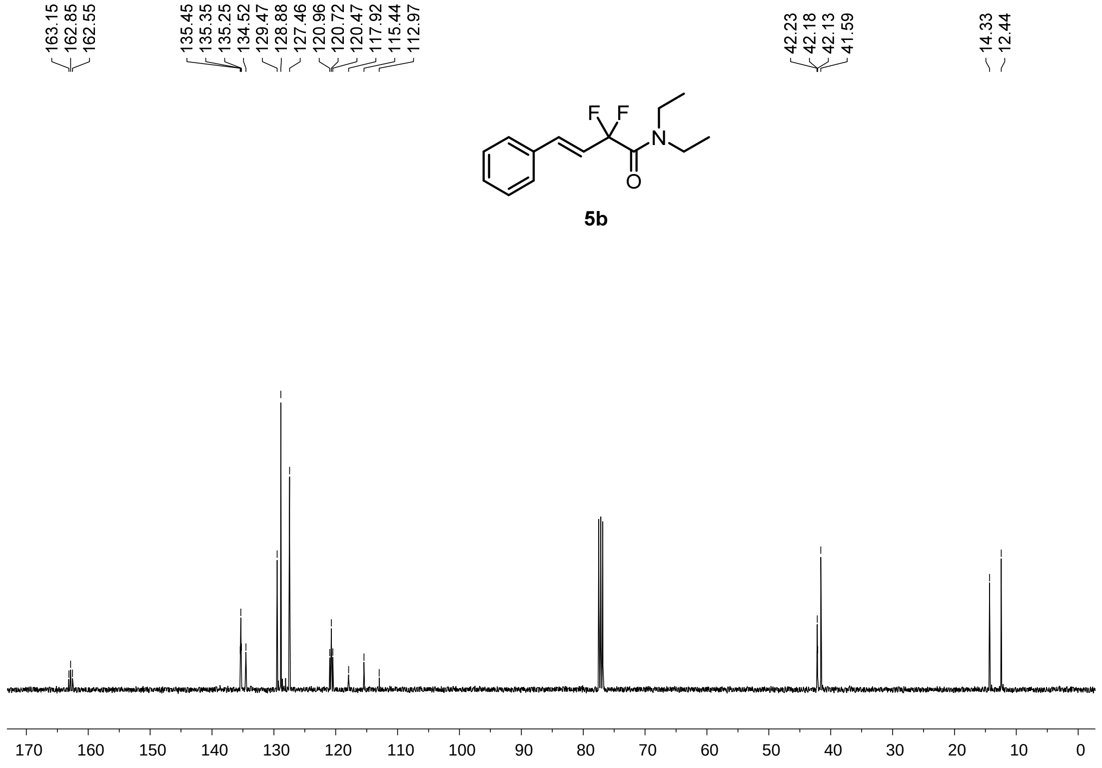
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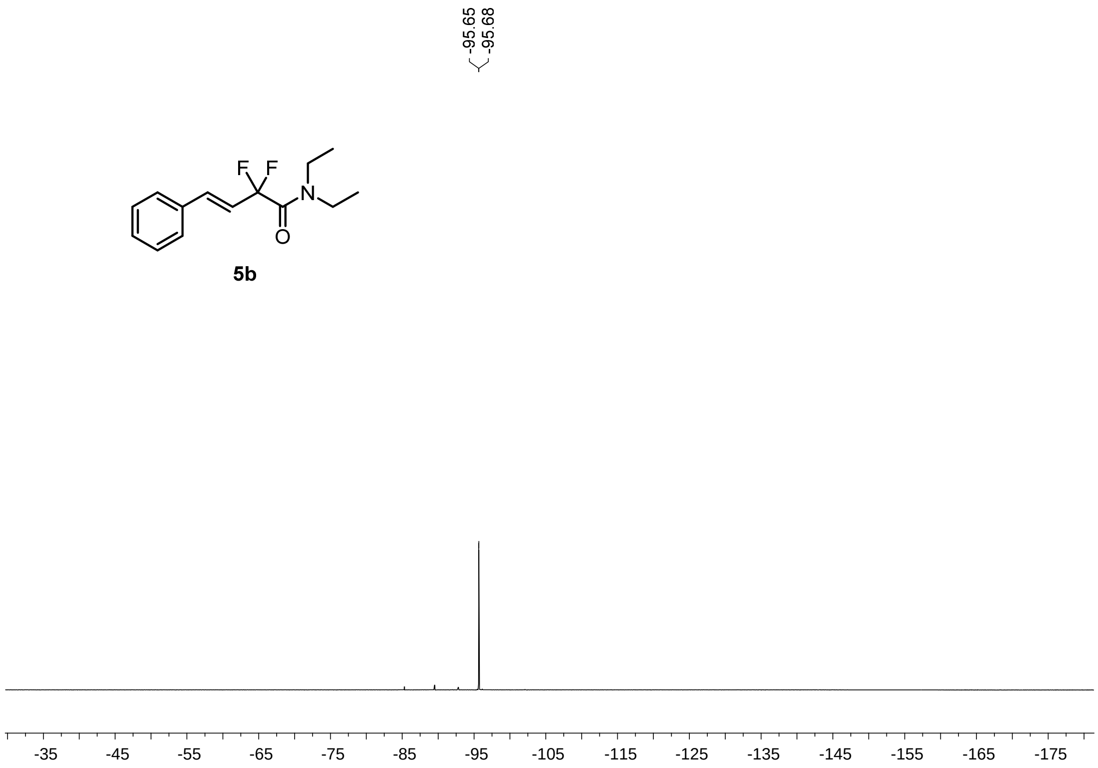
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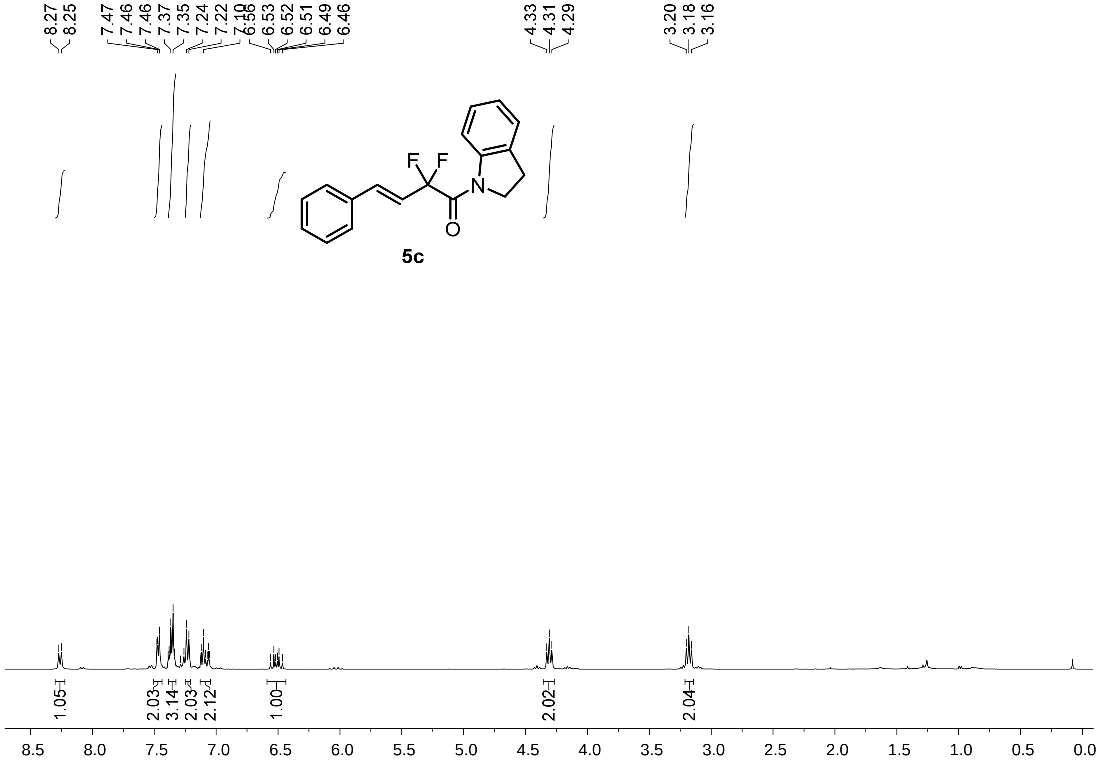
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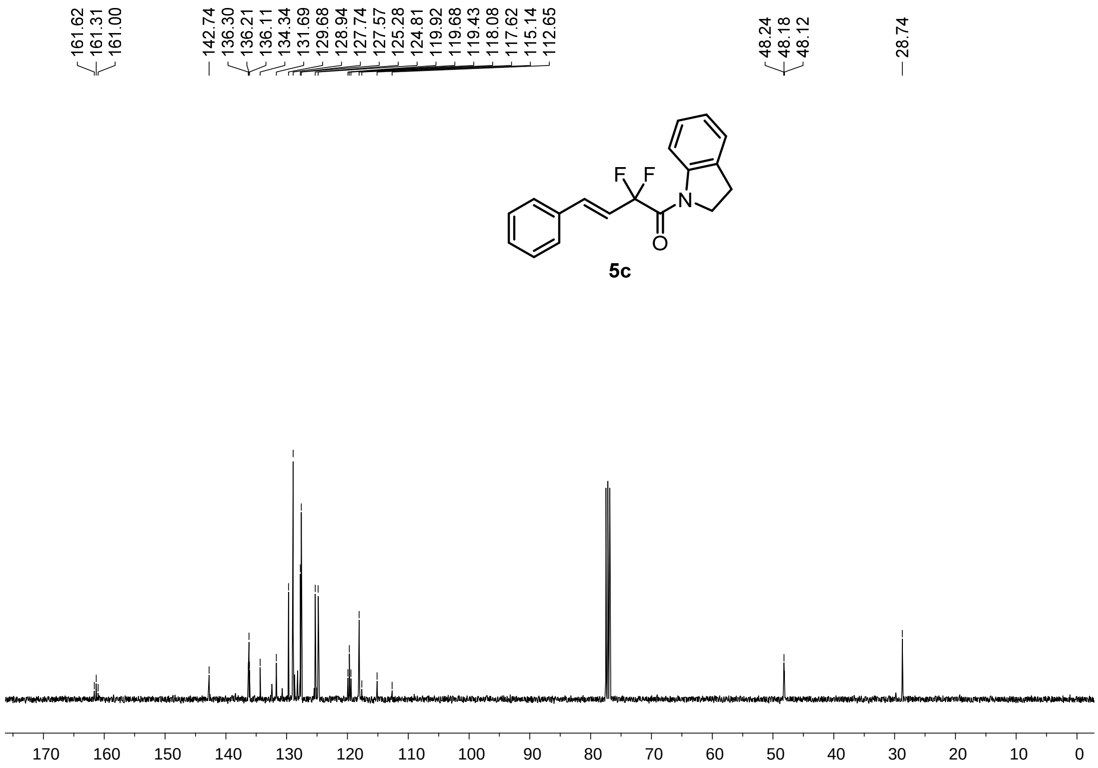
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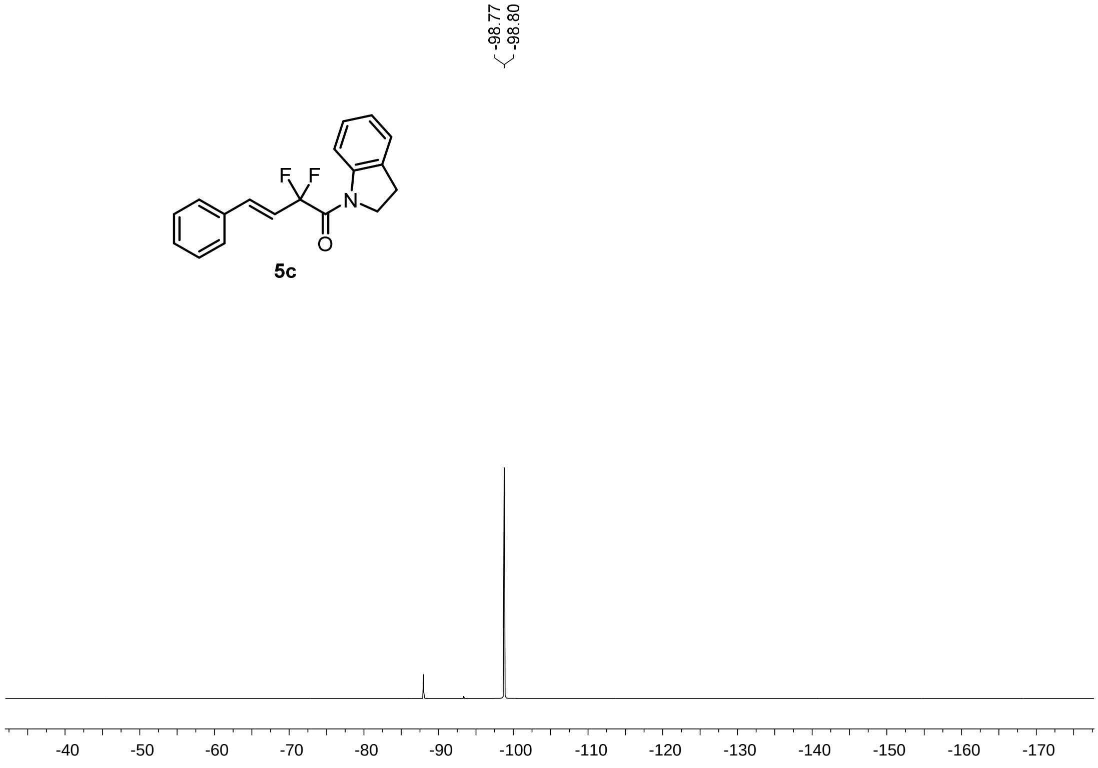
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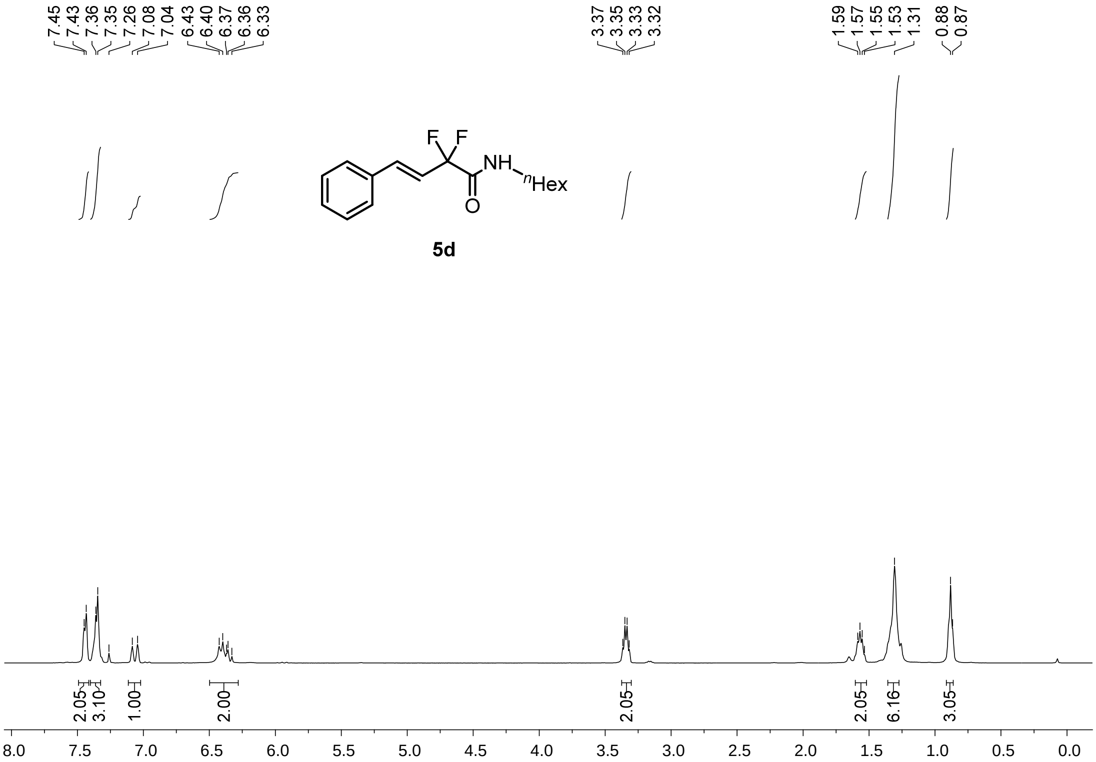
5c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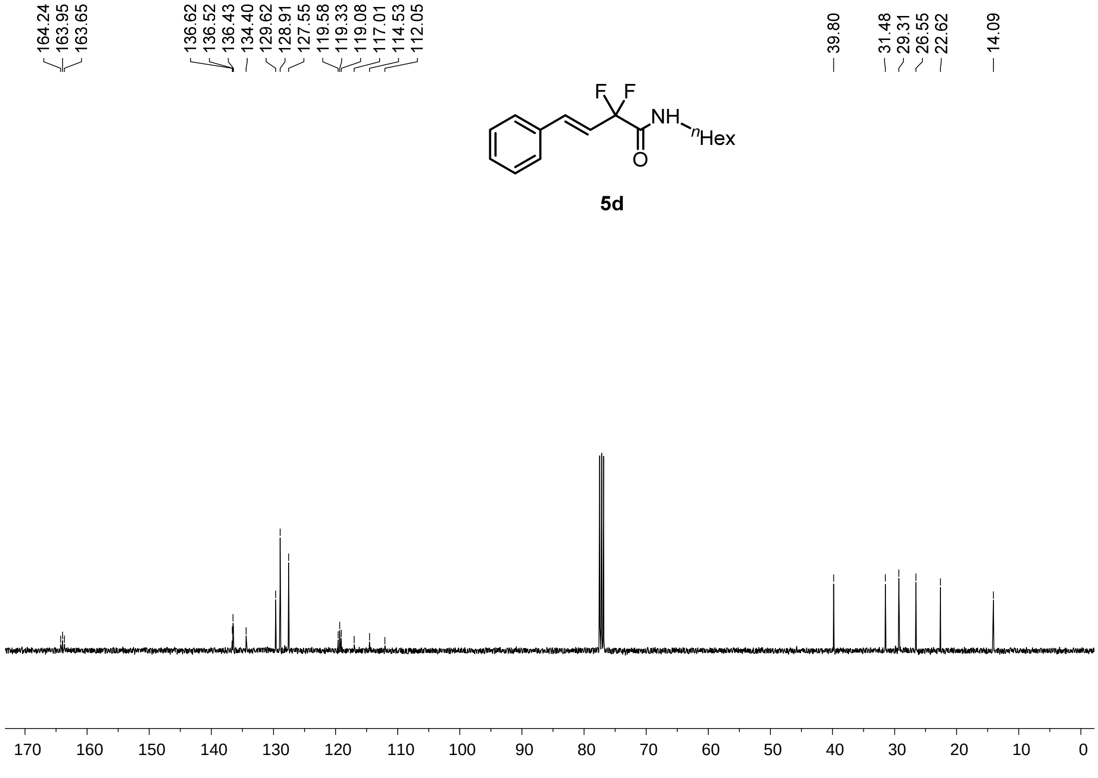
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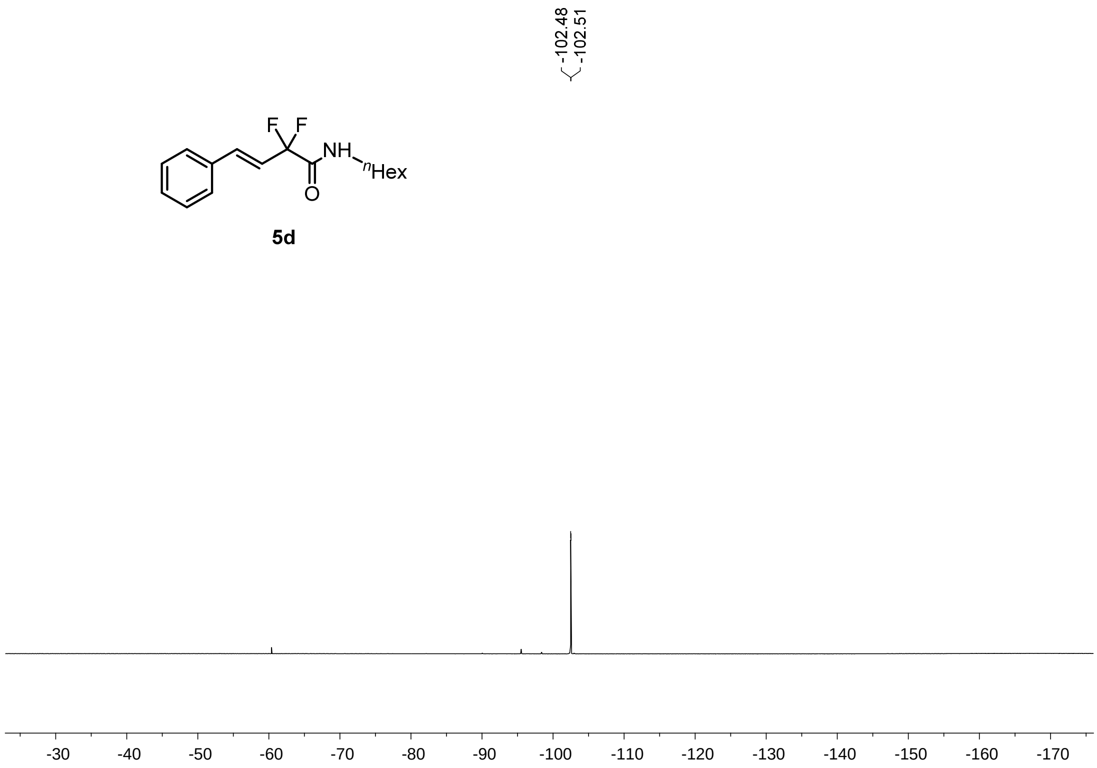
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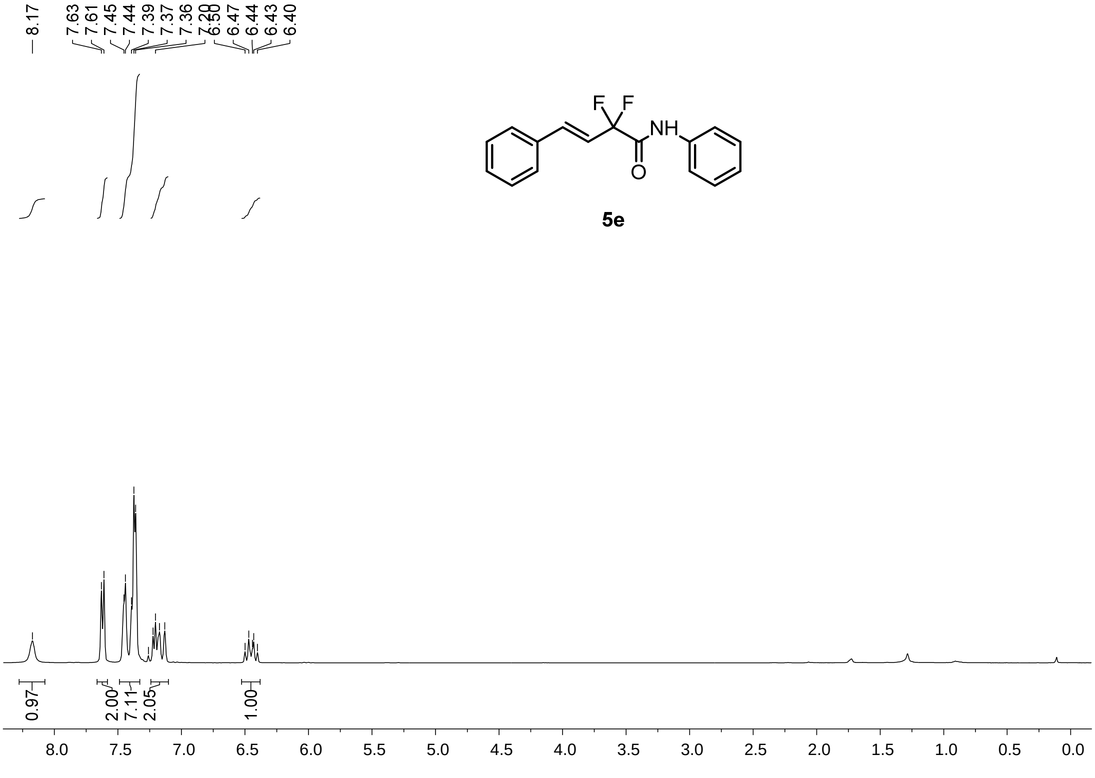
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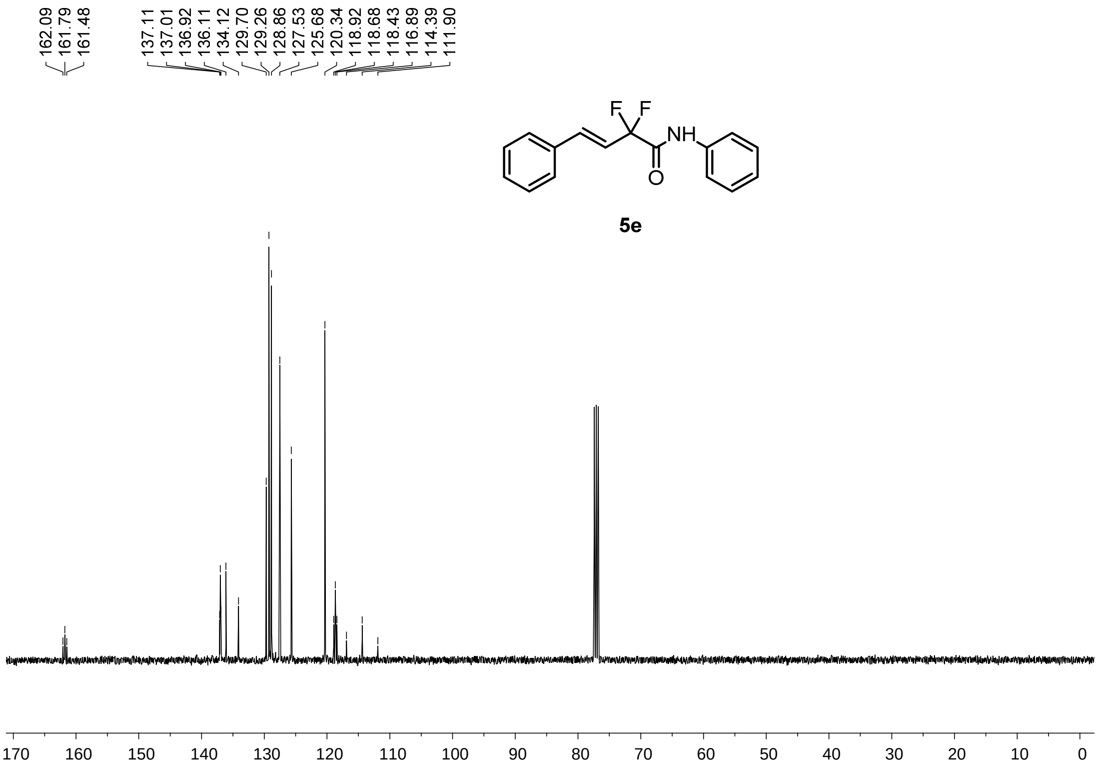
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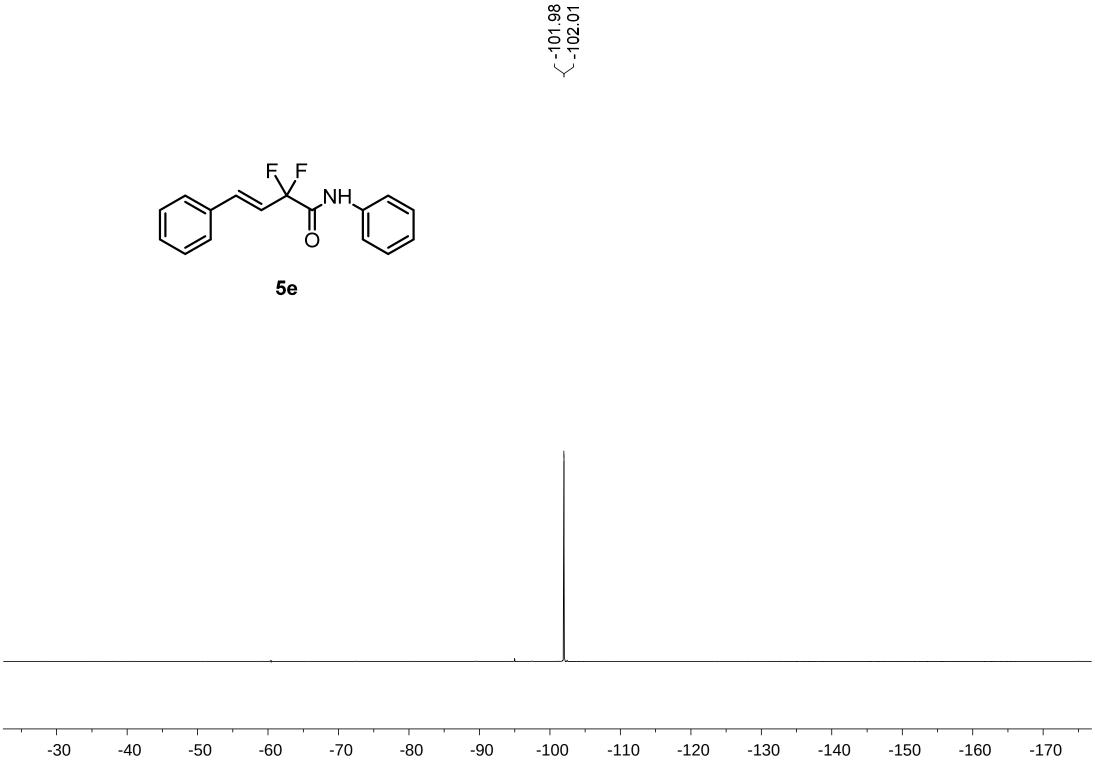
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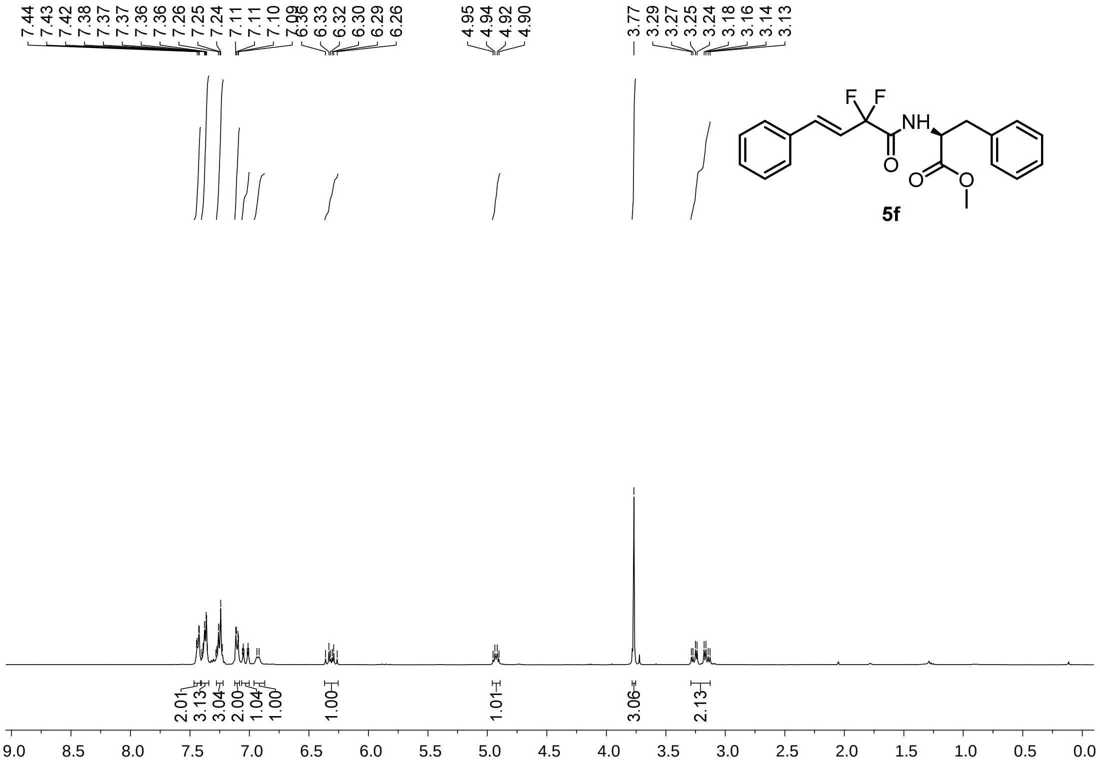
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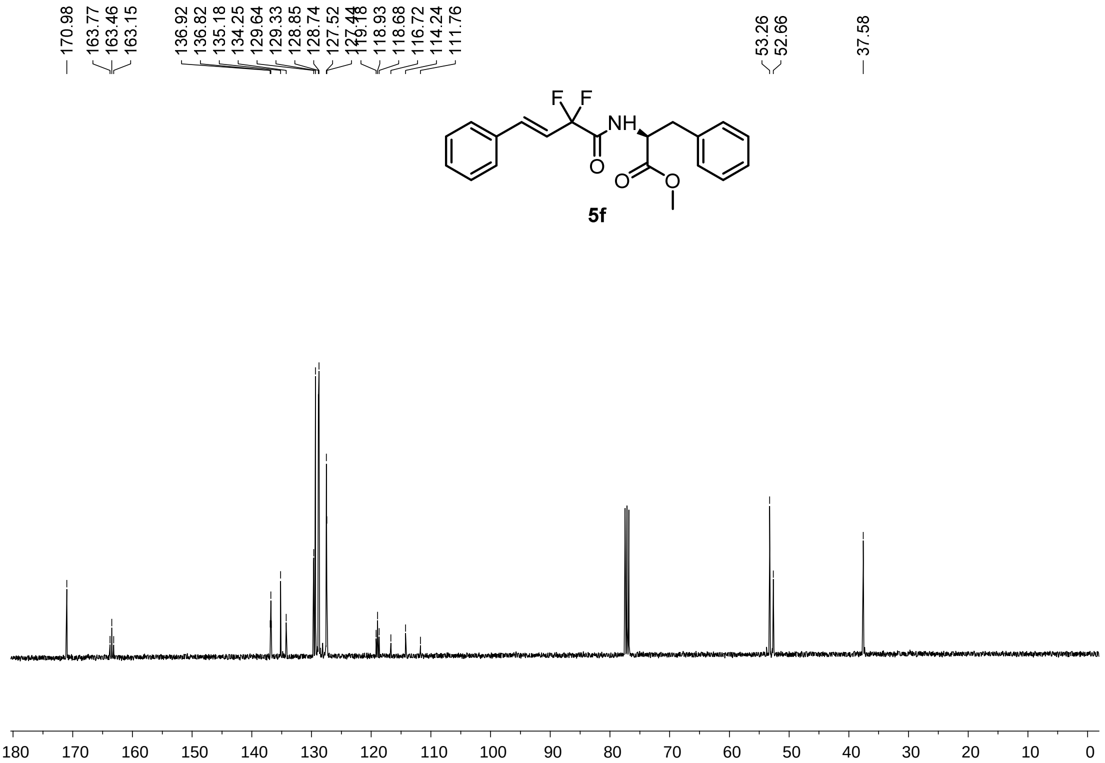
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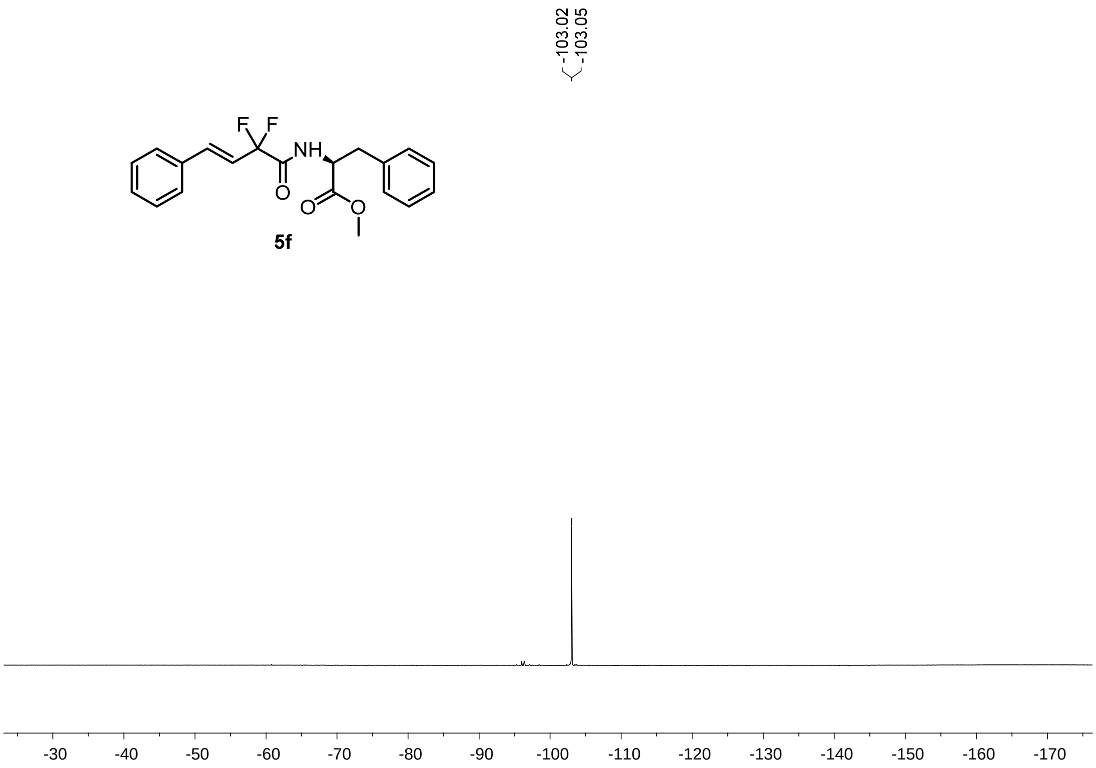
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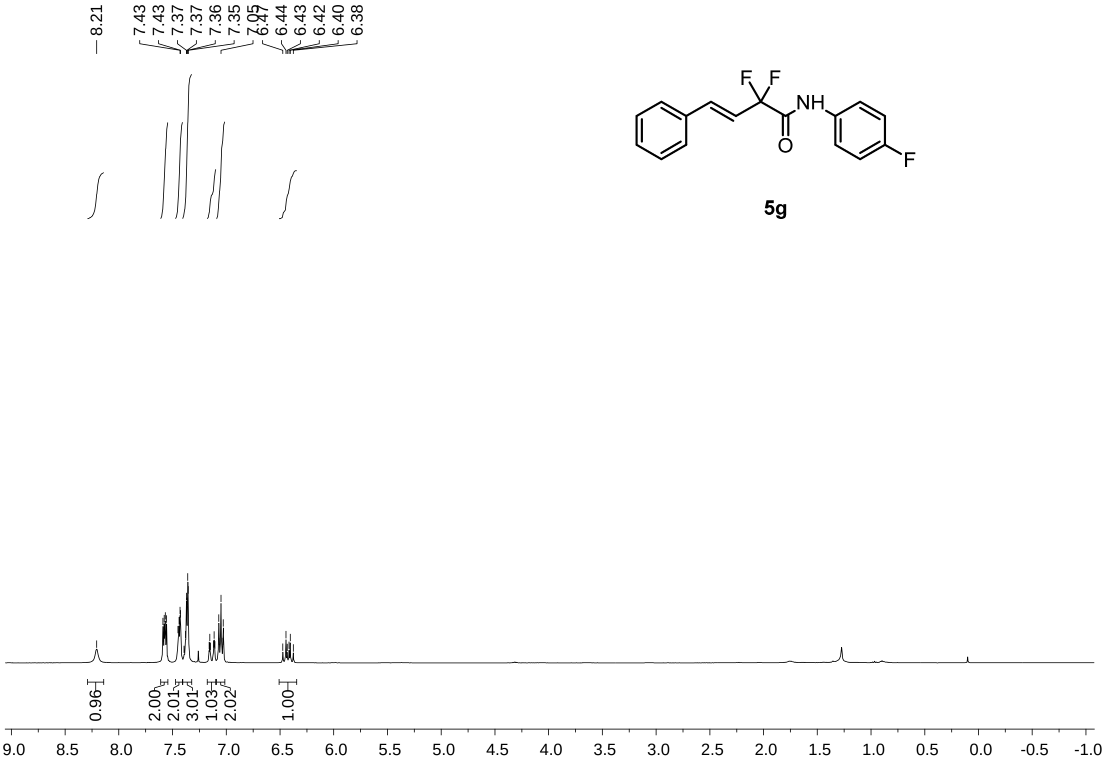
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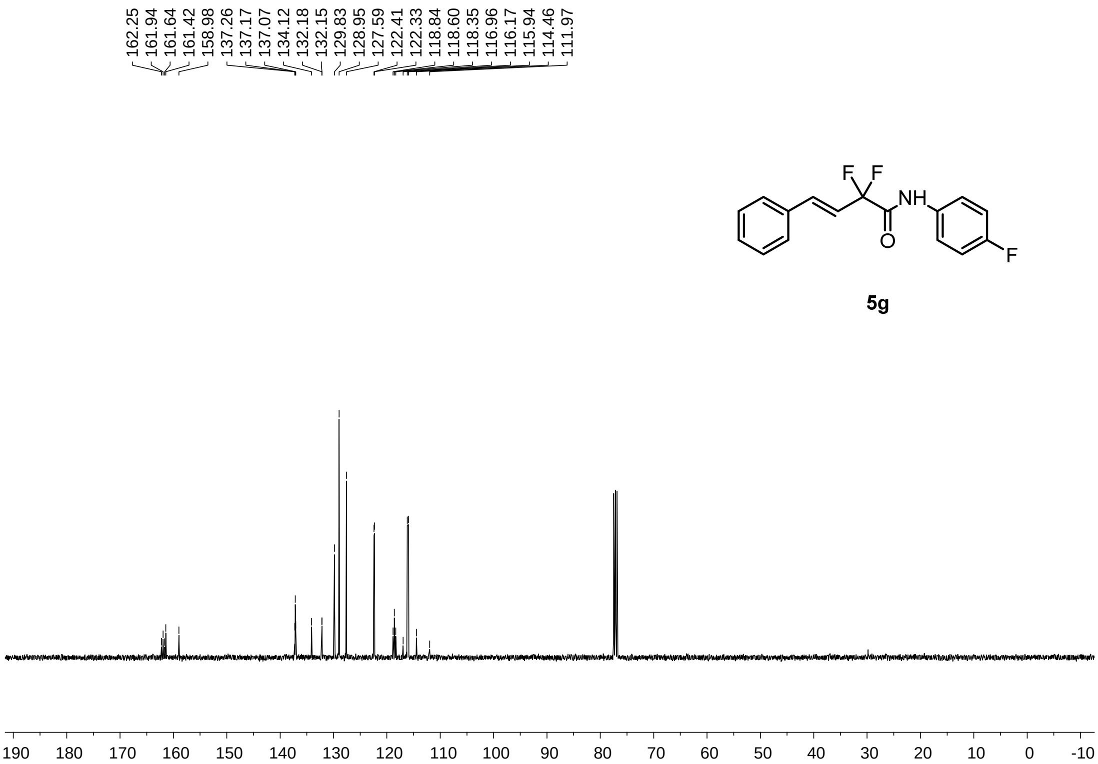
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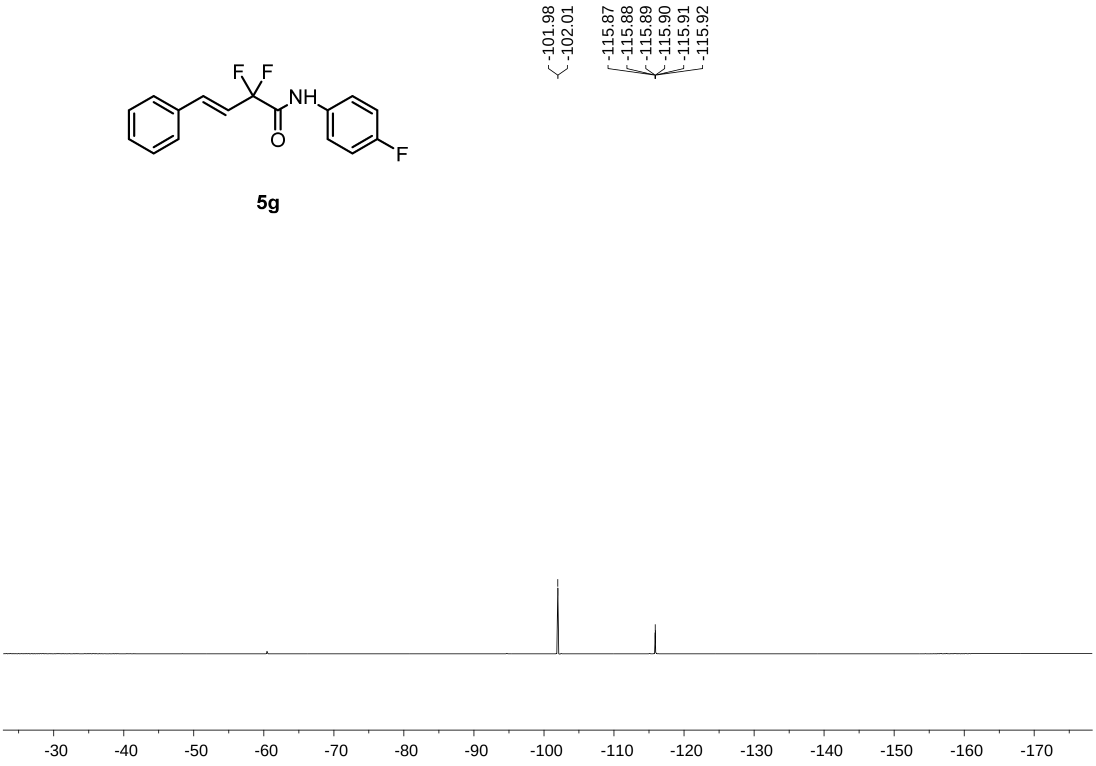
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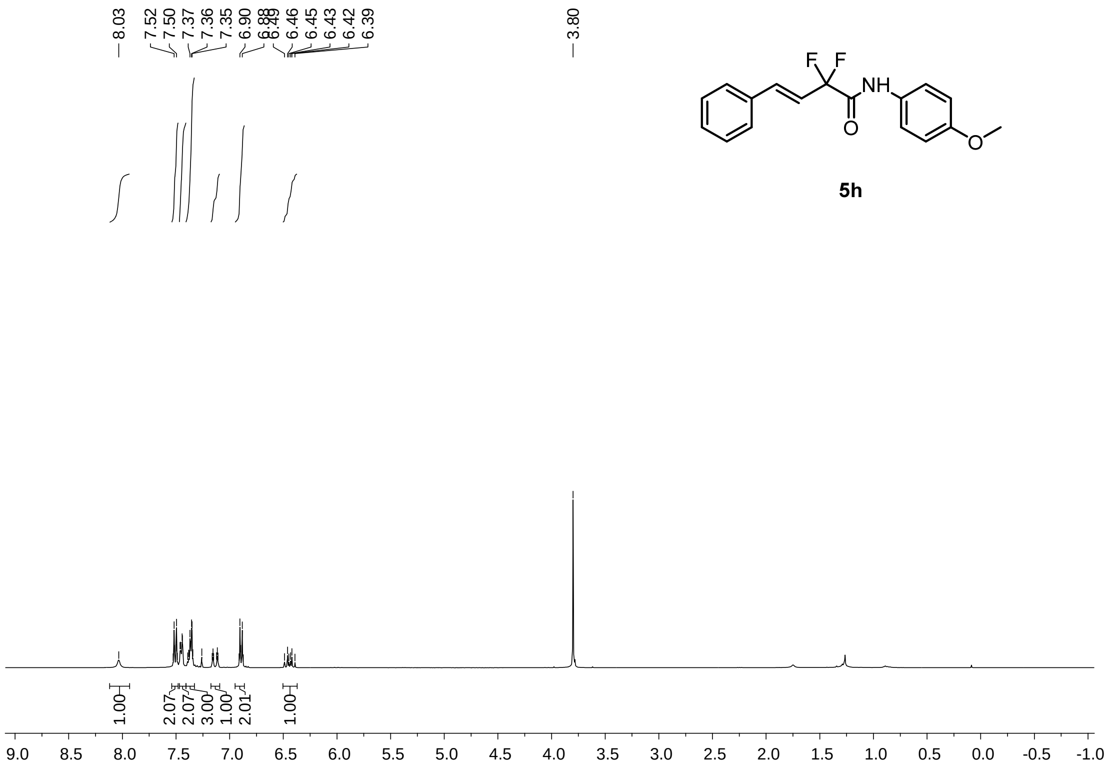
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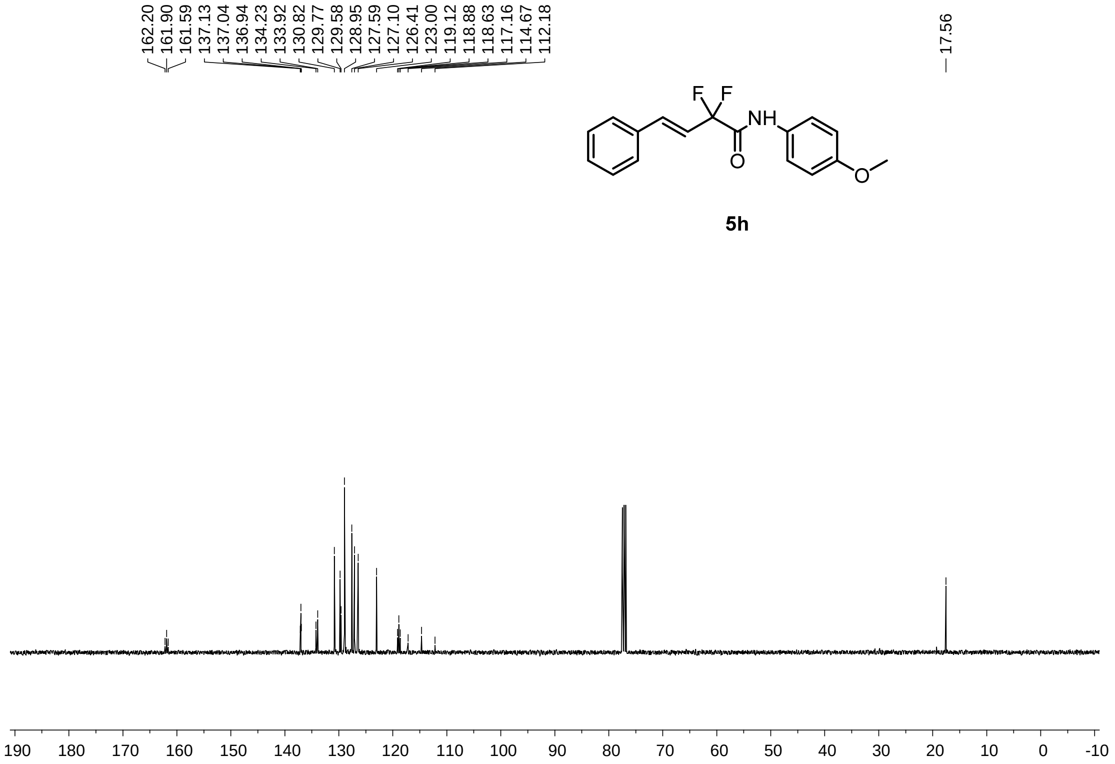
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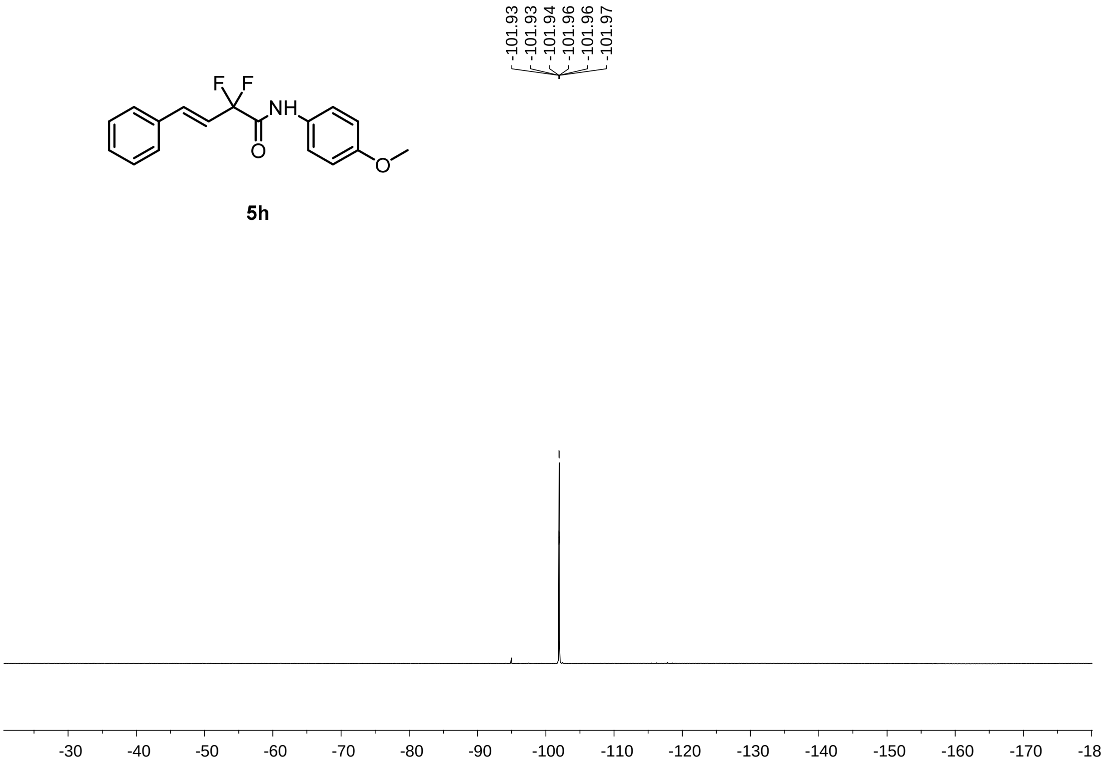

5h

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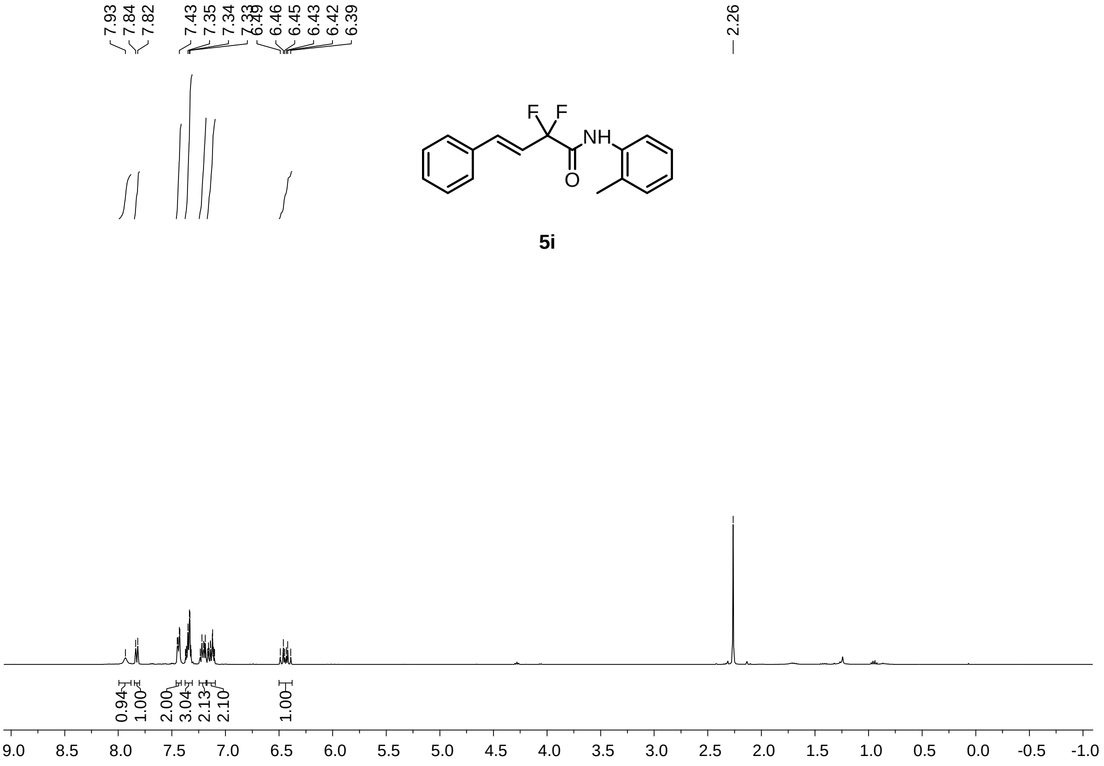

5i

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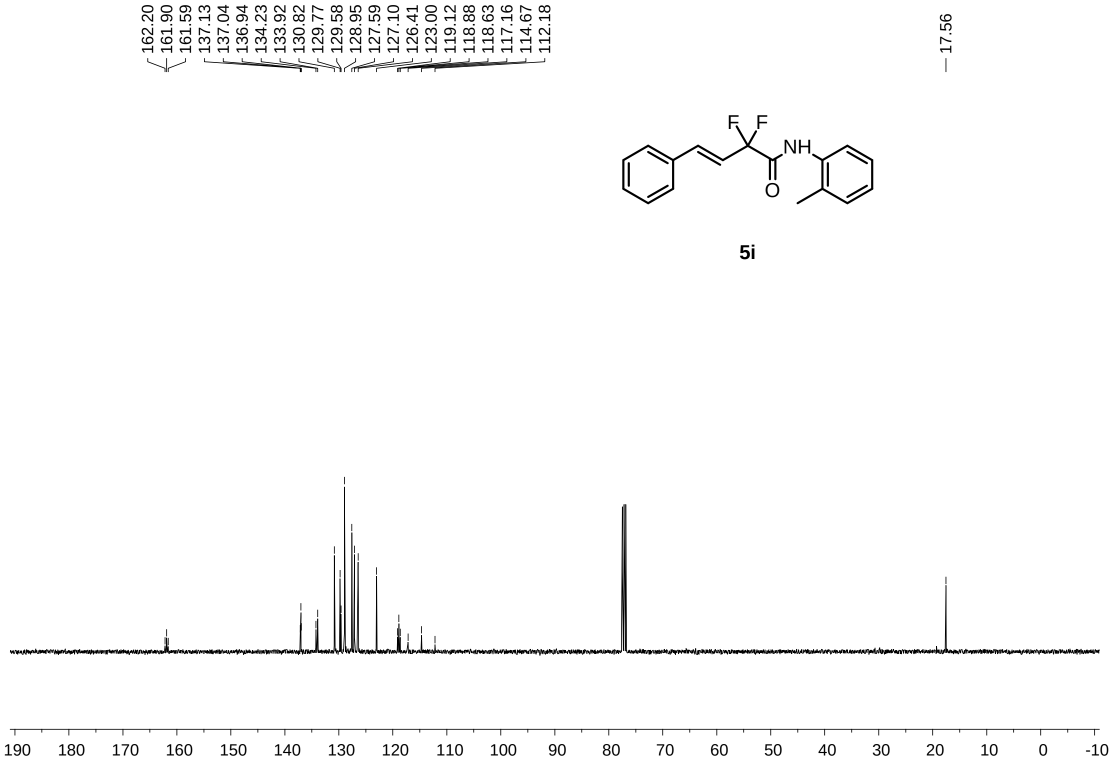
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5i


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5i