

Supporting Information

Copper-Catalyzed Fluoroolefination of Silyl Enol Ethers and Ketones towards the Synthesis of β -Fluoroenones

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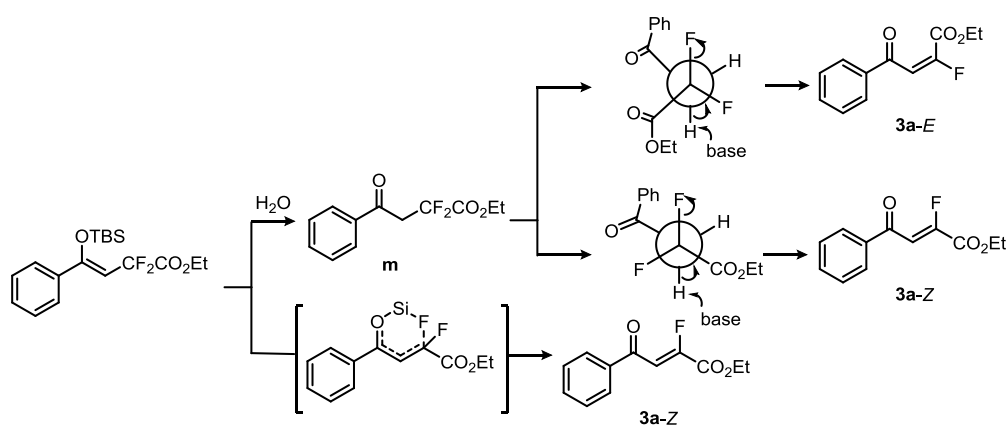
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Part 1. General information.

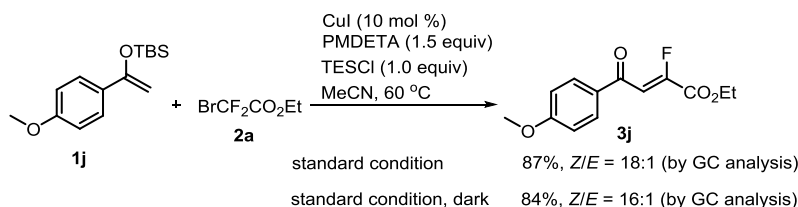
All experiments were conducted in flame-dried glassware under argon atmosphere. MeCN was dried and distilled by standard methods. PMDETA and ethyl 2-bromo-2,2-difluoroacetate were dried by activated 5 Å MS. Silyl enol ethers were prepared according to the literature procedures. Other reagents were purchased from commercial sources and used as received, unless otherwise stated. Flash chromatographic separations were carried out on 200-300 mesh silica gel. Reactions were monitored by TLC, GC 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. ¹H, ¹³C and ¹⁹F NMR spectra were recorded in CDCl₃ on a Bruker AVANCE III spectrometer. High resolution spectra (HRMS) were recorded on a QTOF mass analyzer with electrospray ionization (ESI) through a Bruker Daltonic microTOF-QII.

Part 2. Proposed reaction mechanism for the generation of Z and E products.



Scheme S1. Proposed reaction mechanism for the generation of Z and E products.

Part 3. The parallel experiments for influence of visible light.

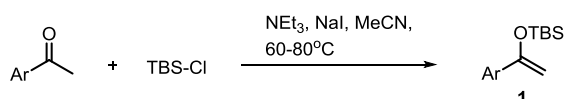


Scheme S2. The parallel experiments for influence of visible light.

The parallel experiments have been conducted to compare the yields and *Z/E* selectivities under visible light and dark conditions. Similar results were obtained which indicate that no *E/Z* isomerization occurs for our substrates under visible light.

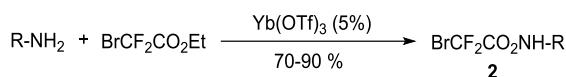
Part 4. Experimental procedures and NMR data.

General procedure for the synthesis of silyl enol ether.



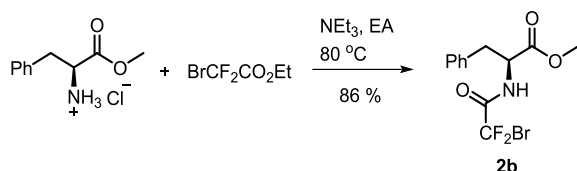
Ketone (1.7 mmol), *tert*-butylchlorodimethylsilane (3.3 mmol), and triethylamine (2.5 mmol) were placed in a round-bottom flask with acetonitrile (7 mL). Sodium iodide (2.5 mmol) in acetonitrile (3 mL) was added dropwise, and the reaction mixture was stirred for 6-8 h. Then the solvent was removed in vacuo. The resulting brown slurry was purified by column chromatography (PE/ NEt_3 = 100:2) to give silyl enol ether **1** (60-90% yield) as a colorless liquid.

General procedure for the synthesis of *gem*-difluoromethylene.^[1]



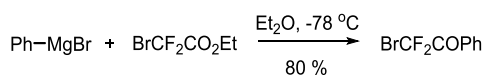
Ethyl bromodifluoroacetate (2 mL), primary amine (10 mmol), and ytterbium(III) trifluoromethanesulfonate hydrate (5 mol %) were added into a round-bottom flask. The reaction mixture was stirred at room temperature overnight. Then ethyl acetate (5 mL) was added to the reaction mixture and the resulting mixture was washed with aqueous HCl (1 M). The aqueous phase was extracted with ethyl acetate (3 x 5 mL). The collected organic phases were washed by brine and dried over anhydrous Na_2SO_4 . After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column chromatography (PE/EA = 10/1) to give the desired product **2** (70-90% yield).

The procedure for the synthesis of methyl (2-bromo-2,2-difluoroacetyl)-*L*-phenylalaninate.^[2]



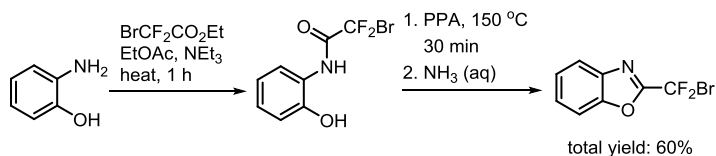
To a mixture of ammonium salt (2.16 g, 5 mmol) and ethyl acetate (20 mL) was added triethyl amine (1.4 mL) dropwise. Then ethyl bromodifluoroacetate (0.9 mL, 7 mmol) was added subsequently. After reaction mixture was stirred under 80 °C for 5 h, the mixture was poured into ethyl acetate and water. Then the aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed by brine and dried over anhydrous Na₂SO₄. After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column chromatography (PE/EA = 10/1) to give the desired product **2b** (1.44 g) in 86% yield as white solid.

The procedure for the synthesis of 2-(bromodifluoromethyl)benzo[d]oxazole.^[3]



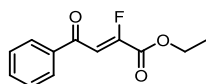
To a mixture of ethyl bromodifluoroacetate (1.02 g, 5 mmol) and diethyl ether (5 mL) was added a solution of phenylmagnesium bromide in diethyl ether (3.0 M, 1.83 mL, 5.5 mmol) at -78 °C under an argon atmosphere. After the solution was stirred at that temperature for 3 h, the mixture was quenched with aqueous HCl (3 N) and then extracted with diethyl ether. The extract was dried over anhydrous Na₂SO₄, and the solvent was removed. The residue was purified by silica gel column chromatography (PE/EA = 10/1) to give the desired product in 80% yield as colorless oil.

The procedure for the synthesis of 2-(bromodifluoromethyl)benzo[d]oxazole.^[4]



To a mixture of 2-aminophenol (1.09 g, 10 mmol), triethyl amine (1.52 mL, 11 mmol), and ethyl acetate (15 mL) was added ethyl bromodifluoroacetate (1.92g, 15 mmol). After the solution was refluxed for 1 h, the mixture was cooled to room temperature

and was washed by aqueous HCl (1 M). The organic phase was concentrated in vacuum and the crude product (2.68 g) was directly used to the next step reaction. The crude product (2.08 g) and PPA (8.04 g) were placed in a dry round-bottom flask, and the sticky reaction mixture was heated at 150 °C for 1 h. The reaction mixture was cooled to room temperature, and moderate amount of ice and concentrated ammonia (6 mL, 30% NH₃•H₂O) were added to the reaction mixture successively. The aqueous phase was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic layers were washed by brine and dried over anhydrous Na₂SO₄. After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column chromatography (PE/EA = 20/1) to give the desired product (1.48 g) in 60% total yield as colorless oil.

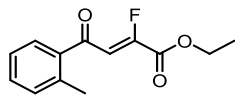


Synthesis of ethyl (Z)-2-fluoro-4-oxo-4-phenylbut-2-enoate (**3a**).^[5]

Representative Procedure I. To a mixture of CuI (19.0 mg, 0.1 mmol) and *tert*-butyldimethyl((1-phenylvinyl)oxy)silane (234 mg, 1 mmol) in MeCN (2 mL), the PMDETA (313 μL, 260 mg, 1.5 mmol) and TESCl (167.0 μL, 150.8 mg, 1.0 mmol) was added successively, and the resultant mixture was stirred for 5 min. Then ethyl 2-bromo-2,2-difluoroacetate (192 μL, 304.5 mg, 1.5 mmol) were added dropwise to the above reaction mixture and the resultant mixture was stirred at 60 °C for 14 h. Water was added to the reaction and the resultant mixture was stirred until hydrolysis completed. Then the reaction mixture was poured into ethyl acetate and water, and aqueous phase was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over anhydrous Na₂SO₄. After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column chromatography (PE/EA = 30/1) to give the desired product **3a** (200 mg) in 90% yield as yellow oil.

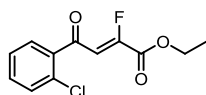
¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 30.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 188.13, 160.12 (d, *J* = 34.6 Hz), 152.08 (d, *J*

= 285.7 Hz), 136.70, 133.99, 128.93 (2C), 128.75 (2C), 112.07 (d, $J = 5.3$ Hz), 62.83, 14.05; ^{19}F NMR (376 MHz, CDCl_3) δ -110.47 (d, $J = 30.8$ Hz, 1F).



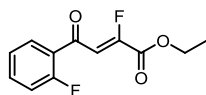
Ethyl (Z)-2-fluoro-4-oxo-4-(o-tolyl)but-2-enoate (3b).

The title compound was synthesized according to Representative Procedure I except *tert*-butyldimethyl((1-(*o*-tolyl)vinyl)oxy)silane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 75% ($Z/E = 26/1$), 177 mg, yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 7.5$ Hz, 1H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.28 (t, $J = 7.6$ Hz, 2H), 6.96 (d, $J = 31.0$ Hz, 1H), 4.36 (q, $J = 7.1$ Hz, 2H), 2.54 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.17, 160.22 (d, $J = 35.1$ Hz), 151.72 (d, $J = 284.6$ Hz), 139.00, 136.74, 132.39, 132.05, 129.92, 125.87, 114.55 (d, $J = 4.8$ Hz), 62.84, 21.12, 14.06; ^{19}F NMR (376 MHz, CDCl_3) δ -110.46 (d, $J = 30.8$ Hz, 1F). HRMS (ESI): m/z calcd. for $\text{C}_{13}\text{H}_{13}\text{FNaO}_3^+$ [$\text{M} + \text{Na}^+$]: 259.0741, found: 259.0742.



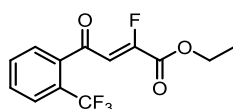
Ethyl (Z)-4-(2-chlorophenyl)-2-fluoro-4-oxobut-2-enoate (3c).

The title compound was synthesized according to Representative Procedure I except *tert*-butyl((1-(2-chlorophenyl)vinyl)oxy)dimethylsilane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 73% ($Z/E = 38/1$), 187 mg, yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.49 (m, 1H), 7.44-7.40 (m, 2H), 7.35 (m, 1H), 6.95 (d, $J = 30.0$ Hz, 1H), 4.35 (q, $J = 7.1$ Hz, 2H), 1.35 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 189.56, 160.15 (d, $J = 34.9$ Hz), 152.68 (d, $J = 289.2$ Hz), 138.32, 132.78, 131.68, 130.55, 129.82, 127.23, 114.16 (d, $J = 2.9$ Hz), 63.05, 14.11; ^{19}F NMR (376 MHz, CDCl_3) δ -108.22 (d, $J = 29.97$ Hz, 1F). HRMS (ESI): m/z calcd. for $\text{C}_{12}\text{H}_{11}\text{ClFO}_3^+$ [$\text{M} + \text{H}^+$]: 257.0375, found: 257.0371.



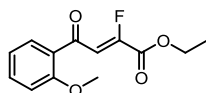
Ethyl (Z)-2-fluoro-4-(2-fluorophenyl)-4-oxobut-2-enoate (3d).

The title compound was synthesized according to Representative Procedure I except *tert*-butyl((1-(2-fluorophenyl)vinyl)oxy)dimethylsilane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 80% (*Z/E* = 27/1), 192 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (t, *J* = 7.6 Hz, 1H), 7.58 (q, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.21-7.07 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 185.69, 161.8 (d, *J* = 253.8 Hz), 160.4 (d, *J* = 34.7 Hz), 152.61 (d, *J* = 286.1 Hz), 135.55 (d, *J* = 9.0 Hz), 131.05 (d, *J* = 1.8 Hz), 126.23 (d, *J* = 11.6 Hz), 124.95 (d, *J* = 3.5 Hz), 116.90 (d, *J* = 22.9 Hz), 114.32 (dd, *J* = 6.2, 2.6 Hz), 63.10, 14.28; ¹⁹F NMR (376 MHz, CDCl₃) δ -109.87 (dd, *J* = 29.9, 5.4 Hz, 1F), -111.01- -111.16 (m, 1F). HRMS (ESI): *m/z* calcd. for C₁₂H₁₀F₂NaO₃⁺ [*M* + Na⁺]: 263.0490, found: 263.0490.



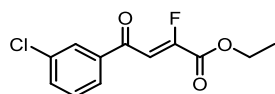
Ethyl (Z)-2-fluoro-4-oxo-4-(2-(trifluoromethyl)phenyl)but-2-enoate (3e).

The title compound was synthesized according to Representative Procedure I except *tert*-butyldimethyl((1-(2-(trifluoromethyl)phenyl)vinyl)oxy)silane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 83% (*Z/E* = 82/1), 189 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 7.0 Hz, 1H), 7.69-7.59 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 29.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 190.71, 159.83 (d, *J* = 35.1 Hz), 153.57 (d, *J* = 289.8 Hz), 138.95, 132.05, 130.83, 127.51, 127.23 (q, *J* = 32.3 Hz), 126.83 (q, *J* = 5.0 Hz), 123.56 (q, *J* = 272 Hz), 113.97 (d, *J* = 2.4 Hz), 63.13, 13.91; ¹⁹F NMR (376 MHz, CDCl₃) δ -57.97 (s, 3F), -104.95 (d, *J* = 30.0 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₃H₁₀F₄NaO₃⁺ [*M* + Na⁺]: 313.0458, found: 313.0462.



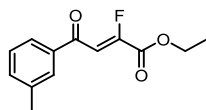
Ethyl (Z)-2-fluoro-4-(2-methoxyphenyl)-4-oxobut-2-enoate (3f).

The title compound was synthesized according to Representative Procedure I except *tert*-butyl((1-(2-methoxyphenyl)vinyl)oxy)dimethylsilane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 85% (*Z/E* = 44/1), 214 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.51-7.47 (m, 1H), 7.19 (d, *J* = 30.8 Hz, 1H), 7.01 (td, *J* = 7.5, 1.0 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 188.46, 160.80 (d, *J* = 35.0 Hz), 158.99, 151.03 (d, *J* = 285.7 Hz), 134.67, 130.76, 127.80, 120.98, 115.71 (d, *J* = 2.2 Hz), 111.78, 62.63, 55.80, 14.13; ¹⁹F NMR (376 MHz, CDCl₃) δ -113.87 (d, *J* = 31.1 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₃H₁₃FN₄O₄⁺ [M + Na⁺]: 275.0690, found: 275.0692.



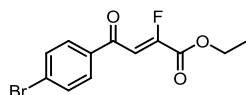
Ethyl (Z)-4-(3-chlorophenyl)-2-fluoro-4-oxo-but-2-enoate (3g).

The title compound was synthesized according to Representative Procedure I except *tert*-butyl((1-(3-chlorophenyl)vinyl)oxy)dimethylsilane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 80% (*Z/E* = 13/1), 205 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 30.3 Hz, 1H), 4.33 (q, *J* = 7.0 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 186.72, 159.86 (d, *J* = 34.8 Hz), 152.62 (d, *J* = 287.8 Hz), 138.13, 135.10, 133.84, 130.19, 128.53, 126.83, 111.25 (d, *J* = 4.7 Hz), 62.99, 14.01; ¹⁹F NMR (376 MHz, CDCl₃) δ -108.88 (d, *J* = 30.2 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₂H₁₀ClFNaO₃⁺ [M + Na⁺]: 279.0195, found: 279.0188.



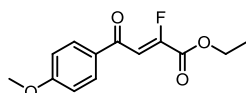
Ethyl (Z)-2-fluoro-4-oxo-4-(*m*-tolyl)but-2-enoate (3h).

The title compound was synthesized according to Representative Procedure I except *tert*-butyldimethyl((1-(*m*-tolyl)vinyl)oxy)silane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 80% (*Z/E* = 13/1), 189 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 9.0 Hz, 2H), 7.43-7.35 (m, 2H), 7.11 (d, *J* = 30.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 188.42, 160.31 (d, *J* = 34.7 Hz), 152.07 (d, *J* = 285.3 Hz), 138.87, 136.82, 134.95, 129.27, 128.81, 126.18, 112.39 (d, *J* = 5.4 Hz), 62.94, 21.41, 14.18; ¹⁹F NMR (376 MHz, CDCl₃) δ -110.94 (d, *J* = 30.8 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₃H₁₃FN₃O₃⁺ [*M* + Na⁺]: 259.0741, found: 259.0742.



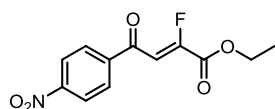
Ethyl (Z)-4-(4-bromophenyl)-2-fluoro-4-oxobut-2-enoate (3i).^[6]

The title compound was synthesized according to Representative Procedure I except ((1-(4-bromophenyl)vinyl)oxy)(*tert*-butyl)dimethylsilane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 80% (*Z/E* = 13/1), 240 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 30.6 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 187.17, 160.01 (d, *J* = 34.6 Hz), 152.45 (d, *J* = 287.0 Hz), 135.43, 132.23 (2C), 130.25 (2C), 129.44, 111.53 (d, *J* = 5.1 Hz), 63.04, 14.12; ¹⁹F NMR (376 MHz, CDCl₃) δ -109.30 (d, *J* = 30.5 Hz, 1F).



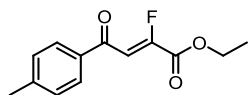
Ethyl (Z)-2-fluoro-4-(4-methoxyphenyl)-4-oxobut-2-enoate (3j).

The title compound was synthesized according to Representative Procedure I except *tert*-butyl((1-(4-methoxyphenyl)vinyl)oxy)dimethylsilane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 85% (*Z/E* = 10/1), 214 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 31.3 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 186.72, 164.45, 160.35 (d, *J* = 35.0 Hz), 151.56 (d, *J* = 283.0 Hz), 131.38 (2C), 129.79, 114.17 (2C), 112.64 (d, *J* = 6.1 Hz), 62.86, 55.68, 14.18; ¹⁹F NMR (376 MHz, CDCl₃) δ -112.05 (d, *J* = 31.3 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₃H₁₃FN₂O₄⁺ [*M* + Na⁺]: 275.0690, found: 275.0679.



Ethyl (*Z*)-2-fluoro-4-(4-nitrophenyl)-4-oxo-but-2-enoate (3k). ^[5]

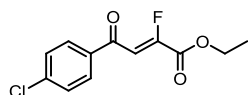
The title compound was synthesized according to Representative Procedure I except *tert*-butyldimethyl((1-(4-nitrophenyl)vinyl)oxy)silane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 45% (*Z/E* = 12/1), 120 mg, yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 8.2 Hz, 2H), 8.08 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 29.9 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 184.82, 165.68, 156.60, 150.43 (d, *J* = 290.4 Hz), 135.19 (2C), 135.01, 123.38 (2C), 90.90, 62.55, 14.00; ¹⁹F NMR (376 MHz, CDCl₃) δ -106.55 (d, *J* = 30.0 Hz, 1F).



Ethyl (*Z*)-2-fluoro-4-oxo-4-(*p*-tolyl)but-2-enoate (3l).

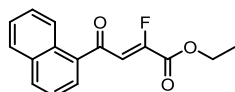
The title compound was synthesized according to Representative Procedure I except *tert*-butyldimethyl((1-(*p*-tolyl)vinyl)oxy)silane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 85% (*Z/E* = 29/1), 200 mg, yellow

oil. ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 7.8$ Hz, 2H), 7.19 (d, $J = 7.7$ Hz, 2H), 7.02 (d, $J = 31.0$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 2.32 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 187.73, 160.20 (d, $J = 35.0$ Hz), 151.82 (d, $J = 284.3$ Hz), 145.21, 134.19, 129.56 (2C), 128.93 (2C), 112.29 (d, $J = 5.4$ Hz), 62.83, 21.77, 14.08; ^{19}F NMR (376 MHz, CDCl_3) δ -111.34 (d, $J = 30.8$ Hz, 1F). HRMS (ESI): m/z calcd. for $\text{C}_{13}\text{H}_{13}\text{FNaO}_3^+$ [$\text{M} + \text{Na}^+$]: 259.0741, found: 259.0742.



Ethyl (Z)-4-(4-chlorophenyl)-2-fluoro-4-oxo-but-2-enoate (3m). ^[5]

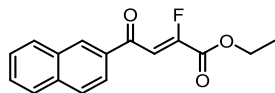
The title compound was synthesized according to Representative Procedure I except *tert*-butyl((1-(4-chlorophenyl)vinyl)oxy)dimethylsilane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 90% ($Z/E = 15/1$), 230 mg, yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 7.8$ Hz, 2H), 7.06 (d, $J = 30.6$ Hz, 1H), 4.37 (q, $J = 7.0$ Hz, 2H), 1.37 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 187.02, 160.06 (d, $J = 34.6$ Hz), 152.44 (d, $J = 286.7$ Hz), 140.66, 135.06, 130.22 (2C), 129.28 (2C), 111.64 (d, $J = 5.1$ Hz), 63.06, 14.14; ^{19}F NMR (376 MHz, CDCl_3) δ -109.39 (d, $J = 30.31$ Hz, 1F).



Ethyl (Z)-2-fluoro-4-(naphthalen-1-yl)-4-oxobut-2-enoate (3n).

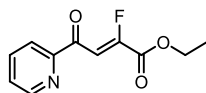
The title compound was synthesized according to Representative Procedure I except *tert*-butyldimethyl((1-(naphthalen-1-yl)vinyl)oxy)silane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 85% ($Z/E = 28/1$), 231 mg, yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.75 (d, $J = 8.6$ Hz, 1H), 8.01 (d, $J = 8.2$ Hz, 1H), 7.92-7.85 (m, 2H), 7.64-7.60 (m, 1H), 7.56-7.52 (m, 1H), 7.51-7.46 (m, 1H), 7.10 (d, $J = 30.8$ Hz, 1H), 4.36 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 190.87, 160.24 (d, $J = 35.0$ Hz), 151.81 (d, $J = 284.9$ Hz), 134.24, 134.15, 133.87, 130.29, 130.20, 128.61, 128.53, 126.79, 125.48, 124.39, 114.90 (d, $J = 4.7$ Hz), 62.88, 14.06;

^{19}F NMR (376 MHz, CDCl_3) δ -110.42 (d, J = 30.6 Hz, 1F). HRMS (ESI): m/z calcd. for $\text{C}_{16}\text{H}_{13}\text{FNaO}_3^+$ [$\text{M} + \text{Na}^+$]: 295.0741, found: 295.0744.



Ethyl (Z)-2-fluoro-4-(naphthalen-2-yl)-4-oxo-but-2-enoate (3o). ^[5]

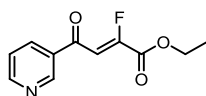
The title compound was synthesized according to Representative Procedure I except *tert*-butyldimethyl((1-(naphthalen-2-yl)vinyl)oxy)silane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 70% (Z/E = 14/1), 190 mg, yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.43 (s, 1H), 8.04-7.88 (m, 4H), 7.61 (dt, J = 23.9, 7.2 Hz, 2H), 7.28 (d, J = 30.7 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 188.13, 160.39 (d, J = 34.6 Hz), 152.22 (d, J = 285.7 Hz), 136.10, 134.16, 132.50, 131.38, 129.86, 129.22, 129.01, 128.01, 127.19, 123.81, 112.34 (d, J = 5.3 Hz), 63.05, 14.24; ^{19}F NMR (376 MHz, CDCl_3) δ -110.72 (d, J = 30.68 Hz, 1F).



Ethyl (Z)-2-fluoro-4-(pyridin-2-yl)but-2-enoate (3p).

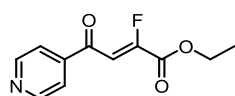
Representative Procedure II. To a mixture of CuI (19.0 mg, 0.1 mmol) and 2-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)pyridine (235 mg, 1 mmol) in MeCN (2 mL), the PMDETA (313 μL , 260 mg, 1.5 mmol) and TES-Cl (167 μL , 150.8 mg, 1.0 mmol) was added successively, and the resultant mixture was stirred for 5 min. Then ethyl 2-bromo-2,2-difluoroacetate (384 μL , 609 mg, 3 mmol) were added dropwise to the above reaction mixture and the resultant mixture was stirred at 80 $^\circ\text{C}$ for 2 h. Water was added to the reaction and the resultant mixture was stirred until hydrolysis completed. Then the reaction mixture was poured into ethyl acetate and water, and the aqueous phase was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 . After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column

chromatography (*n*-Hexane/EA =10/1) to give the desired product **3p** (183 mg) in 82% yield as yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (d, *J* = 2.88 , 1H), 8.07 (d, *J* = 7.3 Hz, 1H), 7.97 (d, *J* = 31.5 Hz, 1H), 7.86 (t, *J* = 6.7 Hz, 1H), 7.51-7.48 (m, 1H), 4.36 (q, *J* = 7.0 Hz, 1H), 1.36 (t, *J* = 7.0 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 187.53, 160.31 (d, *J* = 35.4 Hz), 153.50 (d, *J* = 289.2 Hz), 153.04, 149.17, 137.34, 127.79, 122.55, 109.56, 62.86, 14.13; ¹⁹F NMR (376 MHz, CDCl₃) δ -108.55 (d, *J* = 31.4 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₁H₁₀FNNaO₃⁺ [*M* + Na⁺]: 246.0537, found: 246.0544.



Ethyl (Z)-2-fluoro-4-oxo-4-(pyridin-3-yl)but-2-enoate (3q).

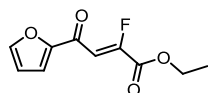
The title compound was synthesized according to Representative Procedure II except 3-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)pyridine was used instead of 2-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)pyridine. The product was purified by silica gel column chromatography (*n*-Hexane/EA = 10/1). Yield: 66%, 147 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 9.11 (s, 1H), 8.81 (d, *J* = 4.9 Hz, 1H), 8.21 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 6.5 Hz, 1H), 7.09 (d, *J* = 30.0 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 187.10, 159.91 (d, *J* = 34.7 Hz), 154.29, 153.03 (d, *J* = 287.25Hz), 150.17, 136.02, 132.30, 123.90, 111.10 (d, *J* = 4.5 Hz), 63.23, 14.17; ¹⁹F NMR (376 MHz, CDCl₃) δ -107.45 (d, *J* = 30.27 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₁H₁₀FNNaO₃⁺ [*M* + Na⁺]: 246.0537, found: 246.0544.



Ethyl (Z)-2-fluoro-4-oxo-4-(pyridin-4-yl)but-2-enoate (3r).

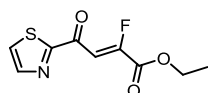
The title compound was synthesized according to Representative Procedure II except 4-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)pyridine was used instead of 2-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)pyridine. The product was purified by silica gel column chromatography (*n*-Hexane/EA = 3/1). Yield: 66%, 147 mg, brown oil. ¹H NMR (400 MHz, CDCl₃) δ 8.80 (s, 2H), 7.68 (s, 2H), 7.07 (d, *J* = 29.7 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 187.41,

159.75 (d, $J = 34.4$ Hz), 153.62 (d, $J = 289.7$ Hz), 150.91 (2C), 142.81, 121.43 (2C), 110.36, 63.25, 14.08; ^{19}F NMR (376 MHz, CDCl_3) δ -105.96 (d, $J = 29.6$ Hz, 1F). HRMS (ESI): m/z calcd. for $\text{C}_{11}\text{H}_{10}\text{FNNaO}_3^+$ [$\text{M} + \text{Na}^+$]: 246.0537, found: 246.0544.



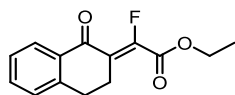
Ethyl (Z)-2-fluoro-4-(furan-2-yl)-4-oxobut-2-enoate (3s).

The title compound was synthesized according to Representative Procedure I except *tert*-butyl((1-(furan-2-yl)vinyl)oxy)dimethylsilane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 70% ($Z/E = 13/1$), 148 mg, yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.69 (s, 1H), 7.33 (d, $J = 3.2$ Hz, 1H), 7.15 (d, $J = 29.5$ Hz, 1H), 6.63-6.62 (m, 1H), 4.39 (q, $J = 7.1$ Hz, 2H), 1.40 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 174.87, 160.11 (d, $J = 34.4$ Hz), 153.14 (d, $J = 289.5$ Hz), 152.65, 147.62, 119.07, 113.07, 110.09 (d, $J = 1.8$ Hz), 62.99, 14.08; ^{19}F NMR (376 MHz, CDCl_3) δ -108.45 (d, $J = 29.7$ Hz, 1F). HRMS (ESI): m/z calcd. for $\text{C}_{10}\text{H}_{10}\text{FO}_4^+$ [$\text{M} + \text{H}^+$]: 213.0558, found: 213.0545.



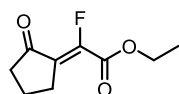
Ethyl (Z)-2-fluoro-4-oxo-4-(thiazol-2-yl)but-2-enoate (3t).

The title compound was synthesized according to Representative Procedure I except 2-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)thiazole was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 80% ($Z/E = 20/1$), 183 mg, yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (s, 1H), 7.77 (s, 1H), 7.76 (d, $J = 29.8$ 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 179.36, 167.16, 159.98 (d, $J = 35.0$ Hz), 154.17 (d, $J = 294.7$ Hz), 145.18, 127.82, 109.03, 63.15, 14.21; ^{19}F NMR (376 MHz, CDCl_3) δ -104.57 (d, $J = 29.89$ Hz, 1F). HRMS (ESI): m/z calcd. for $\text{C}_9\text{H}_8\text{FNNaO}_3\text{S}^+$ [$\text{M} + \text{Na}^+$]: 252.0101, found: 252.0093.



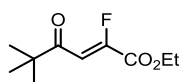
Ethyl (Z)-2-fluoro-2-(1-oxo-3,4-dihydronaphthalen-2(1H)-ylidene)acetate (3u).

The title compound was synthesized according to Representative Procedure I except *tert*-butyl((3,4-dihydronaphthalen-1-yl)oxy)dimethylsilane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 80% (*Z/E* = 3/1), 198 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.2 Hz, 1H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.07 (t, *J* = 6.4 Hz, 2H), 2.93 (td, *J* = 6.2, 5.8, 2.3 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 186.09 (d, *J* = 12.0 Hz), 161.36 (d, *J* = 36.1 Hz), 152.93 (d, *J* = 275.1 Hz), 143.31, 134.02, 132.88 (d, *J* = 4.7 Hz), 128.70, 127.77, 127.28, 120.56 (d, *J* = 13.3 Hz), 62.52, 28.36 (d, *J* = 2.2 Hz), 23.61 (d, *J* = 5.4 Hz), 13.82; ¹⁹F NMR (376 MHz, CDCl₃) δ -110.99 (s, 1F). HRMS (ESI): *m/z* calcd. for C₁₄H₁₃FNao₃⁺ [M + Na⁺]: 271.0741, found: 271.0741.



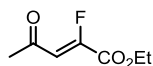
Ethyl (Z)-2-fluoro-2-(2-oxocyclopentylidene)acetate (3v).

The title compound was synthesized according to Representative Procedure I except *tert*-butyl(cyclopent-1-en-1-yloxy)dimethylsilane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 20%, 37 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 4.34 (q, *J* = 7.1 Hz, 2H), 3.10-3.05 (m, 2H), 2.40 (t, *J* = 7.9 Hz, 2H), 2.08-1.92 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 204.64, 161.24 (d, *J* = 34.5 Hz), 145.53 (d, *J* = 288.1 Hz), 125.76, 62.48, 39.52, 28.42, 20.04, 14.21; ¹⁹F NMR (376 MHz, CDCl₃) δ -115.30 (t, *J* = 4.5 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₉H₁₁FNao₃⁺ [M + Na⁺]: 209.0584, found: 209.0587.



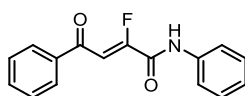
Ethyl (Z)-2-fluoro-5,5-dimethyl-4-oxohex-2-enoate (3w).

The title compound was synthesized according to Representative Procedure I except *tert*-butyl((3,3-dimethylbut-1-en-2-yl)oxy)dimethylsilane was used instead of *tert*-butyldimethyl((1-phenylvinyl)oxy)silane. The product was purified by silica gel column chromatography (PE/EA = 20/1). Yield: 35%, 71 mg, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 6.82 (d, *J* = 30.1 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.16 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 202.52, 160.34 (d, *J* = 34.7 Hz), 152.26 (d, *J* = 288.2 Hz), 110.49 (d, *J* = 3.9 Hz), 62.85, 44.53, 25.85 (3C), 14.15; ¹⁹F NMR (376 MHz, CDCl₃) δ -111.94 (d, *J* = 30.0 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₀H₁₅FNao₃⁺ [*M* + Na⁺]: 225.0897, found: 225.0897.



Ethyl (Z)-2-fluoro-4-oxo-pent-2-enoate (3x).

The title compound was synthesized according to One-pot method except acetone was used instead of acetophenone. The product was purified by silica gel column chromatography (PE/Et₂O = 20/1). Yield: 50%, 80 mg, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 6.39 (d, *J* = 33.9 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.46 (d, *J* = 3.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 195.76, 160.33 (d, *J* = 36.3 Hz), 153.25 (d, *J* = 283.7 Hz), 115.26 (d, *J* = 5.4 Hz), 63.10, 31.68 (d, *J* = 5.0 Hz), 14.16; ¹⁹F NMR (376 MHz, CDCl₃) δ -107.54 (dq, *J* = 34.0 Hz, 3.3 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₇H₉FNao₃⁺ [*M* + Na⁺]: 183.0428, found: 183.0427.

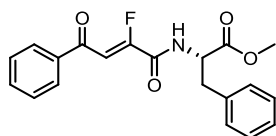


Synthesis of (Z)-2-fluoro-4-oxo-N, 4-diphenylbut-2-enamide (5a).

Representative Procedure III. To a mixture of CuI (19.0 mg, 0.1 mmol) and *tert*-butyldimethyl((1-phenylvinyl)oxy)silane (234 mg, 1 mmol) in MeCN (2 mL), the PMDETA (313 μL, 260 mg, 1.5 mmol) and TESCOI (167 μL, 150.8 mg, 1.0 mmol) was added successively, and the resultant mixture was stirred for 5 min. Then 2-bromo-2,2-difluoro-*N*-phenylacetamide (374 mg, 1.5 mmol) were added to the above reaction mixture and the resultant mixture was stirred at 70 °C for 12 h. Water

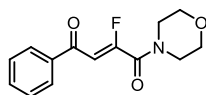
was added to the reaction and the resultant mixture was stirred until hydrolysis completed. Then the reaction mixture was poured into ethyl acetate and water, and the aqueous phase was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over anhydrous Na₂SO₄. After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column chromatography (PE/EA = 3/1) to give the desired product **5a** (145 mg) in 54% yield as yellow oil.

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.69 (s, 1H), 8.08-8.03 (m, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 2H), 7.49-7.35 (m, 3H), 7.21 (t, *J* = 7.4 Hz, 1H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 189.22, 157.98 (d, *J* = 30.4 Hz), 156.30 (d, *J* = 292.8 Hz), 138.52, 137.59, 135.00, 129.96 (2C), 129.72 (2C), 129.56 (2C), 125.78, 121.82 (2C), 110.19 (d, *J* = 3.4 Hz); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -110.71 (d, *J* = 33.9 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₆H₁₂FNNaO₂⁺ [*M* + Na⁺]: 292.0744, found: 292.0741.



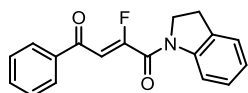
Methyl (Z)-(2-fluoro-4-oxo-4-phenylbut-2-enoyl)-L-phenylalaninate (5b).

The title compound was synthesized according to Representative Procedure III except methyl (2-bromo-2,2-difluoroacetyl)-L-phenylalaninate was used instead of 2-bromo-2,2-difluoro-*N*-phenylacetamide. The product was purified by silica gel column chromatography (PE/EA = 3/1). Yield: 56%, 198.8 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.24-7.10 (m, 3H), 7.03 (d, *J* = 7.4 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 4.88 (q, *J* = 6.6 Hz, 1H), 3.66 (s, 3H), 3.17-3.06 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 187.88, 170.94, 158.56 (d, *J* = 30.1 Hz), 154.99 (d, *J* = 294.6 Hz), 136.92, 135.19, 133.96, 129.17 (2C), 128.86 (4C), 128.72 (2C), 127.49, 108.94 (d, *J* = 3.3 Hz), 53.57, 52.69, 37.70; ¹⁹F NMR (376 MHz, CDCl₃) δ -115.59 (d, *J* = 33.3 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₂₀H₁₈FNNaO₄⁺ [*M* + Na⁺]: 378.1112, found: 378.1114.



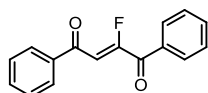
(Z)-2-fluoro-1-morpholino-4-phenylbut-2-ene-1,4-dione (5c).

The title compound was synthesized according to Representative Procedure III except 2-bromo-2,2-difluoro-1-morpholinoethan-1-one was used instead of 2-bromo-2,2-difluoro-*N*-phenylacetamide. The product was purified by silica gel column chromatography (PE/EA = 2/1). Yield: 86%, 226 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 33.8 Hz, 1H), 3.70 (s, 4H), 3.65 (s, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 187.89, 160.14 (d, *J* = 28.0 Hz), 157.68 (d, *J* = 298.4 Hz), 137.10, 133.86, 128.85 (2C), 128.68 (2C), 110.53 (d, *J* = 3.6 Hz), 66.85, 66.66, 47.07, 43.40; ¹⁹F NMR (376 MHz, CDCl₃) δ -98.75 (d, *J* = 33.6 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₄H₁₄FNNaO₃⁺ [*M* + Na⁺]: 286.0850, found: 286.0856.



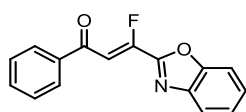
(Z)-2-fluoro-1-(indolin-1-yl)-4-phenylbut-2-ene-1,4-dione (5d).

The title compound was synthesized according to Representative Procedure III except 2-bromo-2,2-difluoro-1-(indolin-1-yl)ethan-1-one was used instead of 2-bromo-2,2-difluoro-*N*-phenylacetamide. The product was purified by silica gel column chromatography (PE/EA = 5/1). Yield: 80%, 236 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.07-8.02 (m, 1H), 7.90-7.82 (m, 2H), 7.51-7.44 (m, 1H), 7.40-7.31 (m, 2H), 7.16-7.07 (m, 3H), 6.98 (t, *J* = 7.4 Hz, 1H), 4.21-4.15 (m, 2H), 3.08 (t, *J* = 8.3 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 188.22, 158.25 (d, *J* = 29.1 Hz), 158.00 (d, *J* = 300.6 Hz), 142.46, 137.28, 133.91, 132.19, 128.93 (2C), 128.78 (2C), 127.72, 125.23 (d, *J* = 56.1 Hz), 118.28, 110.78, 49.02 (d, *J* = 14.3 Hz), 28.76; ¹⁹F NMR (376 MHz, CDCl₃) δ -103.56 (d, *J* = 32.8 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₈H₁₄FNNaO₂⁺ [*M* + Na⁺]: 318.0901, found: 318.0905.



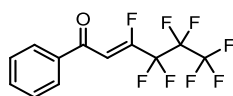
(Z)-2-fluoro-1,4-diphenylbut-2-ene-1,4-dione (5e).^[10]

The title compound was synthesized according to Representative Procedure III except 2-bromo-2,2-difluoro-1-phenylethan-1-one was used instead of 2-bromo-2,2-difluoro-*N*-phenylacetamide. The product was purified by silica gel column chromatography (PE/EA = 20/1). Yield: 60%, 152 mg, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.8 Hz, 4H), 7.69-7.59 (m, 2H), 7.54-7.49 (m, 4H), 7.08 (d, *J* = 32.3 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 188.56, 186.83 (d, *J* = 30.7 Hz), 158.80 (d, *J* = 293.8 Hz), 137.03, 134.26, 134.14, 129.88 (d, *J* = 5.0 Hz), 129.00 (4C), 128.89 (4C), 112.45 (d, *J* = 5.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -104.11 (d, *J* = 32.1 Hz, 1F).



(Z)-3-(benzo[*d*]oxazol-2-yl)-3-fluoro-1-phenylprop-2-en-1-one (5f).

The title compound was synthesized according to Representative Procedure III except 2-(bromodifluoromethyl)benzo[*d*]oxazole was used instead of 2-bromo-2,2-difluoro-*N*-phenylacetamide. The product was purified by silica gel column chromatography (PE/EA = 10/1). Yield: 60%, 160 mg, yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.48-7.43 (m, 2H), 7.38 (d, *J* = 31.5 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 187.38, 155.16 (d, *J* = 36.0 Hz), 152.39 (d, *J* = 274.4 Hz), 150.84, 141.31, 137.38, 133.96, 129.00 (2C), 128.76 (2C), 127.59, 125.85, 121.41, 111.32, 108.36 (d, *J* = 2.8 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -111.02 (d, *J* = 31.4 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₆H₁₀FNNaO₂⁺ [*M* + Na⁺]: 290.0588, found: 290.0594.

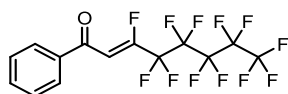


Synthesis of (Z)-3,4,4,5,5,6,6,6-octafluoro-1-phenylhex-2-en-1-one (5g).^[7]

Representative Procedure IV. To a mixture of CuI (19.0 mg, 0.1 mmol) and *tert*-butyldimethyl((1-phenylvinyl)oxy)silane (234 mg, 1 mmol) in MeCN (2 mL), the PMDETA (313 μL, 260 mg, 1.5 mmol) and TESCOI (167 μL, 150.8 mg, 1.0 mmol)

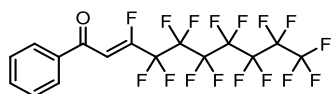
was added successively, and the resultant mixture was stirred for 5 min. Then 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (344 μ L, 692 mg, 2 mmol) were added dropwise to the above reaction mixture and the resultant mixture was stirred at 80 $^{\circ}$ C for 6 h. Water was added to the reaction and the resultant mixture was stirred until hydrolysis completed. Then the reaction mixture was poured into ethyl acetate and water, and the aqueous phase was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 . After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column chromatography (PE/EA = 30/1) to give the desired product **5g** (207 mg) in 65% yield as yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 7.8 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 6.75 (d, J = 31.7 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 186.43, 151.65 (dt, J = 285.3, 29.5 Hz), 136.34, 134.56, 129.16, 128.89, 110.81 (d, J = 3.8 Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -80.70 (t, J = 8.7 Hz), -112.21 – -112.50 (m), -119.33 – -119.44 (m), -126.98 – -127.04 (m).



(Z)-3,4,4,5,5,6,6,7,7,8,8,8-dodecafluoro-1-phenyloct-2-en-1-one (5h). ^[8]

The title compound was synthesized according to Representative Procedure IV except 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane was used instead of 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane. The product was purified by silica gel column chromatography (PE/EA = 30/1). Yield: 70%, 293 mg, yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 7.7 Hz, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 6.76 (d, J = 31.7 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 186.45, 151.84 (dt, J = 285.8, 29.6 Hz), 136.36, 134.57, 129.17 (2C), 128.90 (2C), 110.82 (d, J = 3.9 Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -80.83 – -80.87 (m, 3F), -111.98 – -112.16 (m, 1F), -118.30 – -118.42 (m, 2F), -122.68 – -122.85 (m, 4F), -126.17 – -126.28 (m, 2F).

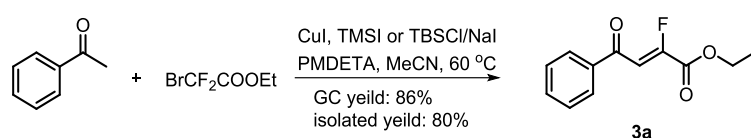


(Z)-3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-hexadecafluoro-1-phenyldec-2-en-1-one (5i).

[5]

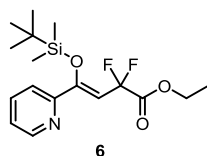
The title compound was synthesized according to Representative Procedure IV except 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-8-iodooctane was used instead of 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane. The product was purified by silica gel column chromatography (PE/EA = 30/1). Yield: 80%, 414 mg, white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 6.76 (d, *J* = 31.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 186.45, 151.89 (dt, *J* = 284.9, 29.3 Hz), 136.38, 134.54, 129.15, 128.89, 110.81 (d, *J* = 3.8 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -81.04 (t, *J* = 9.9 Hz, 3F), -112.07 – -112.29 (m, 1F), -118.35 – -118.48 (m, 2F), -121.88 (2F), -122.10 (2F), -122.64 (2F), -122.89 (2F), -126.26 – -126.38 (m, 2F).

Part 5. The representative procedure for one-pot method.



To a mixture of CuI (19.0 mg, 0.1 mmol), acetophenone (117 μL, 120.2 mg, 1 mmol) and PMDETA (313 μL, 260 mg, 1.5 mmol) in MeCN (2.0 mL), the TMSI (213.5 μL, 300.1 mg, 1.5 mmol) or TBSCl (1.5 mmol)/NaI (1.5 mmol) was added, and the resultant mixture was stirred for 2 min. Then ethyl 2-bromo-2,2-difluoroacetate (320 μL, 507.5 mg, 2.5 mmol) were added dropwise to the above reaction mixture. The resultant mixture was stirred at 60 °C for 15 h. Water was added to the reaction and the resultant mixture was stirred until hydrolysis completed. Then the reaction mixture was poured into ethyl acetate and water, and the aqueous phase was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over anhydrous Na₂SO₄. After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column chromatography (PE/EA = 10/1) to give the desired product **3a** (178 mg) in 80% yield as yellow oil.

Part 6. Isolated intermediate (6) of this reaction.

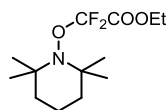


Ethyl

(Z)-4-((*tert*-butyldimethylsilyloxy)-2,2-difluoro-4-(pyridin-2-yl)but-3-enoate (6).

The title compound was synthesized according to Representative Procedure II without hydrolysis process. The product was purified by silica gel column chromatography (*n*-Hexane/EA = 10/1). Yield: 90%, 321 mg, yellow oil.

^1H NMR (400 MHz, DCCl_3) δ 8.54 (d, $J = 4.5$ Hz, 1H), 7.67 (t, $J = 7.7$ Hz, 1H), 7.50 (d, $J = 7.9$ Hz, 1H), 7.26-7.22 (m, 1H), 5.81 (t, $J = 12.8$ Hz, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H), 0.93 (s, 9H), 0.00 (s, 6H). ^{13}C NMR (100 MHz, DCCl_3) δ 164.03 (t, $J = 35.0$ Hz), 156.48 (t, $J = 7.9$ Hz), 154.57, 149.02, 136.51, 124.14, 121.39, 112.76 (t, $J = 246.2$ Hz), 103.40 (t, $J = 26.3$ Hz), 62.79, 25.90, 18.65, 14.06, -3.60. ^{19}F NMR (376 MHz, DCCl_3) δ -96.50 (d, $J = 12.8$ Hz, 2F). HRMS (ESI): m/z calcd. for $\text{C}_{17}\text{H}_{25}\text{F}_2\text{NNaO}_3\text{Si}^+$ [$\text{M} + \text{Na}^+$]: 380.1464, found: 380.1470.



Part 7. TEMPO experiment.

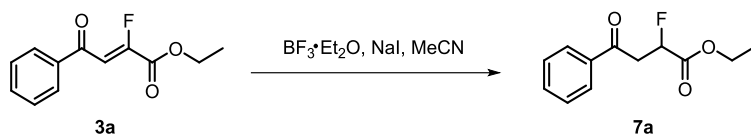
Ethyl 2,2-difluoro-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetate

This reaction was run according to Representative Procedure I, meanwhile the TEMPO (1.5 equiv) was added as radical scavenger. The product was purified by silica gel column chromatography (PE/EA = 20/1). Yield: 25%, 70 mg, yellow oil.

^1H NMR (400 MHz, DCCl_3) δ 4.34 (q, $J = 7.2$ Hz, 2H), 1.58-1.53 (m, 6H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.18-1.15 (m, 12H). ^{13}C NMR (100 MHz, DCCl_3) δ 160.94 (t, $J = 42.6$ Hz), 115.74 (t, $J = 271.4$ Hz), 63.22, 61.61 (2C), 40.43 (2C), 33.63 (t, $J = 4.3$ Hz, 2C), 20.97 (2C), 17.13, 14.13. ^{19}F NMR (376 MHz, DCCl_3) δ -73.48 (1F).

Part 8. Derivatization of 3a-Z.

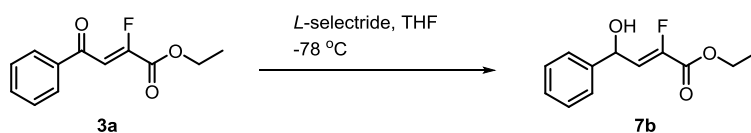
The procedure ^[11] for the synthesis of ethyl 2-fluoro-4-oxo-4-phenylbutanoate (**7a**).



To a stirred solution of ethyl (Z)-2-fluoro-4-oxo-4-phenylbut-2-enoate (111 mg, 0.5 mmol) and sodium iodide (233 mg, 1.25 mmol) in dry MeCN (5 mL) at 0 °C, the boron trifluoride etherate (154 μL , 178 mg, 1.25 mmol) was added. The reaction mixture was stirred at this temperature until reaction completed. Then the reaction mixture was poured into cold water, and aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 . After filtration, the filtrate was concentrated in vacuum and the residue was purified by silica gel column chromatography (PE/EA = 10/1) to give the desired product **7a** (82 mg) in 73% yield as yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 7.6$ Hz, 2H), 7.51 (t, $J = 7.3$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 2H), 5.52-5.35 (m, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 3.63-3.39 (m, 2H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.61 (d, $J = 1.9$ Hz), 169.50 (d, $J = 22.8$ Hz), 136.22, 133.81, 128.84 (2C), 128.24 (2C), 84.98 (d, $J = 185.2$ Hz), 61.97, 40.85 (d, $J = 22.1$ Hz), 14.14; ^{19}F NMR (376 MHz, CDCl_3) δ -191.26 (m, 1F). HRMS (ESI): m/z calcd. for $\text{C}_{12}\text{H}_{13}\text{FNaO}_3^+$ [$\text{M} + \text{Na}^+$]: 247.0741, found: 247.0746.

The procedure ^[12] for the synthesis of ethyl (Z)-2-fluoro-4-hydroxy-4-phenylbut-2-enoate (**7b**).



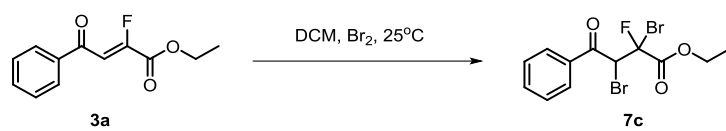
To the stirred solution of ethyl (Z)-2-fluoro-4-oxo-4-phenylbut-2-enoate (111 mg, 0.5 mmol) in THF (5 mL) at -78 °C, the *L*-selectride in THF (1 M) was added dropwise. Then the reaction mixture was stirred at -78 °C until reaction completed. The reaction mixture quenched by cold water slowly. Then the mixture was poured into ethyl

acetate (5 mL) and water (5 mL). The aqueous phase was extracted by ethyl acetate (3 x 10 mL). The combined layer was dried by anhydrous Na₂SO₄. After filtration, the filtrate was concentrated in vacuum and residue was purified by silica gel column chromatography (PE/EA = 5/1) to give desired product **7b** (202 mg) in 90% yield as yellow oil.

¹H NMR (400MHz, CDCl₃) δ 7.45-7.32 (m, 5H), 6.35 (dd, *J* = 32.3, 9.0 Hz, 1H), 5.78 (d, *J* = 8.9 Hz, 1H), 4.31-4.26 (m, 2H), 2.47 (s, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.60 (d, *J* = 35.5 Hz), 147.29 (d, *J* = 260.5 Hz), 141.47, 128.94 (2C), 128.42, 126.02 (2C), 121.57 (d, *J* = 8.9 Hz), 67.66 (d, *J* = 3.7 Hz), 62.11, 14.19. ¹⁹F NMR (376MHz, CDCl₃) δ -127.02 (d, *J* = 32.5 Hz). HRMS (ESI): *m/z* calcd. for C₁₂H₁₃FN₃⁺ [M + Na⁺]: 247.0741, found: 247.0732.

The procedure for the synthesis of ethyl

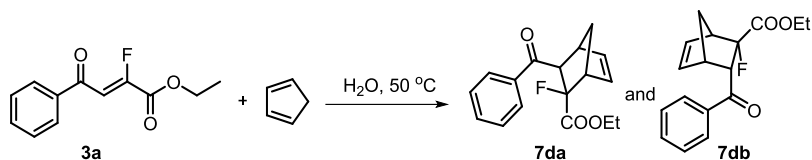
2,3-dibromo-2-fluoro-4-oxo-4-phenylbutanoate (**7c**).^[12]



To a stirred solution of ethyl (*Z*)-2-fluoro-4-oxo-4-phenylbut-2-enoate (111 mg, 0.5 mmol) in CH₂Cl₂ (5 mL) at room temperature, the bromine (30 μL, 94.8 mg, 0.6 mmol) was added. The reaction mixture was stirred until reaction completed. Then the mixture was concentrated in vacuum and residue was purified by silica gel column chromatography (PE/EA = 10/1) to give the desired product **7c** (365 mg) in 96% yield (dr = 31/1) as yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 5.89 (d, *J* = 19.0 Hz, 1H), 4.38-4.30 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 190.18 (d, *J* = 2.3 Hz), 164.31 (d, *J* = 26.3 Hz), 134.58, 133.31, 129.08 (2C), 128.98 (2C), 94.37 (d, *J* = 281.4 Hz), 63.82, 52.57 (d, *J* = 17.9 Hz), 13.74. ¹⁹F NMR (376 MHz, CDCl₃) δ -121.03 (d, *J* = 19.0 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₂H₁₁Br₂FN₃⁺ [M + Na⁺]: 402.8951, found: 402.8946.

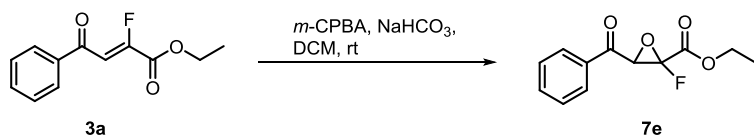
The procedure for D-A reaction product (**7d**).^[13]



To a stirred solution of ethyl (*Z*)-2-fluoro-4-oxo-4-phenylbut-2-enoate (111 mg, 0.5 mmol) in H₂O (2 mL) at room temperature, the cyclopenta-1,3-diene (82 μL, 66.05 mg, 1 mmol) was added. The reaction mixture was stirred at 50 °C until reaction completed. The reaction mixture was concentrated in vacuum and residue was purified by silica gel column chromatography (PE/EA = 20/1) to give the desired product **7d** (endo/exo = 1:1) (130 mg) in 90% yield as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.53-7.49 (m, 2H), 7.44-7.37 (m, 4H), 6.94 (s, 1H), 6.47 (s, 1H), 6.04 (s, 1H), 6.00 (s, 1H), 4.61 (d, *J* = 14.7 Hz, 1H), 4.37-4.34 (m, 2H), 4.30-4.21 (m, 2H), 4.07 (d, *J* = 16.7 Hz, 1H), 3.32 (s, 1H), 3.24 (s, 1H), 3.13 (s, 1H), 2.40 (d, *J* = 9.1 Hz, 1H), 1.88 (s, 2H), 1.58 (s, 1H), 1.34-1.26 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 197.09 (d, *J* = 10.0 Hz), 196.44 (d, *J* = 7.1 Hz), 172.25 (d, *J* = 27.7 Hz), 169.99 (d, *J* = 26.6 Hz), 141.88 (d, *J* = 2.8 Hz), 141.17 (d, *J* = 1.9 Hz), 138.23, 137.87, 133.20, 133.10, 133.08, 133.01, 129.53, 129.47, 128.65, 128.24, 127.94, 102.50, 101.42, 100.45, 99.39, 62.51, 62.21, 58.44, 58.24, 53.78, 53.58, 53.38, 53.16, 52.60, 52.36, 48.37, 46.12, 45.14, 44.83, 14.27, 14.21. ¹⁹F NMR (376 MHz, CDCl₃) δ -162.25 (d, *J* = 16.3 Hz, 1F), -165.65 (d, *J* = 14.9 Hz, 1F). HRMS (ESI): *m/z* calcd. for C₁₇H₁₇FNao₃⁺ [*M* + Na⁺]: 311.1054, found: 311.1051.

The procedure for the synthesis of ethyl 3-benzoyl-2-fluorooxirane-2-carboxylate (7e).



To a stirred solution of *m*-CPBA (104 mg, 0.5 mmol) and NaHCO₃ (42 mg, 0.5 mmol) in CH₂Cl₂ (2 mL) at room temperature, the ethyl (*Z*)-2-fluoro-4-oxo-4-phenylbut-2-enoate (111 mg, 0.5 mmol) was added. The reaction mixture was stirred until reaction completed. The reaction mixture was

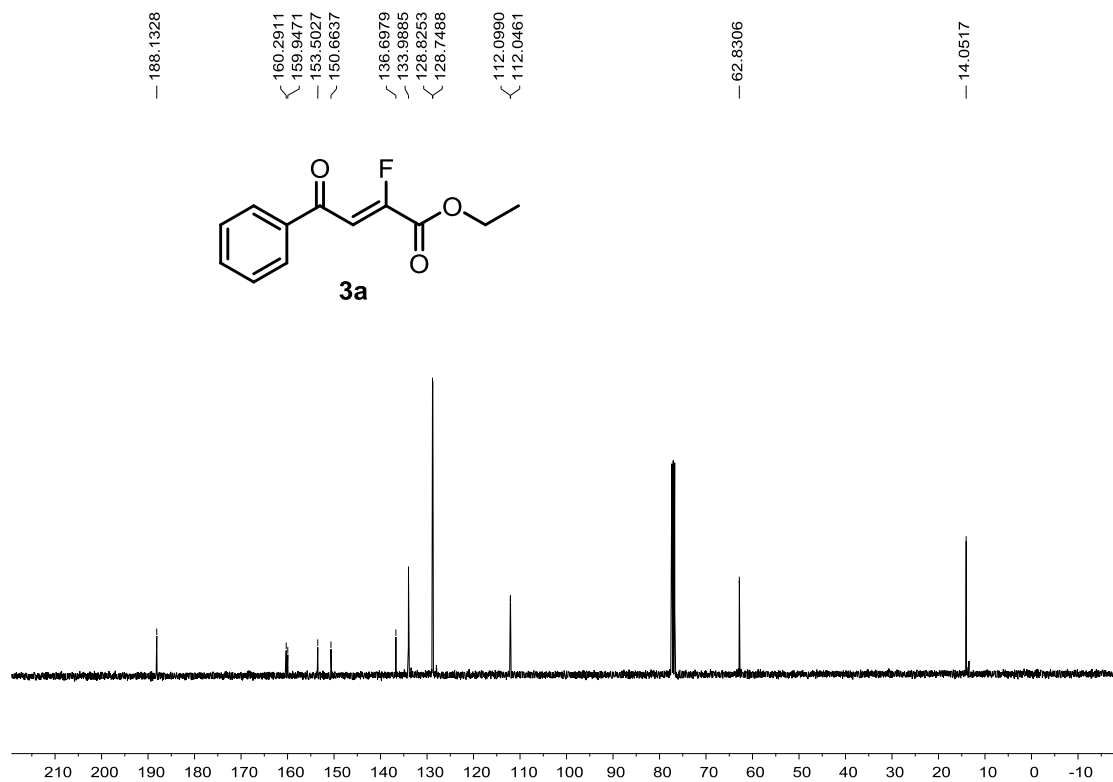
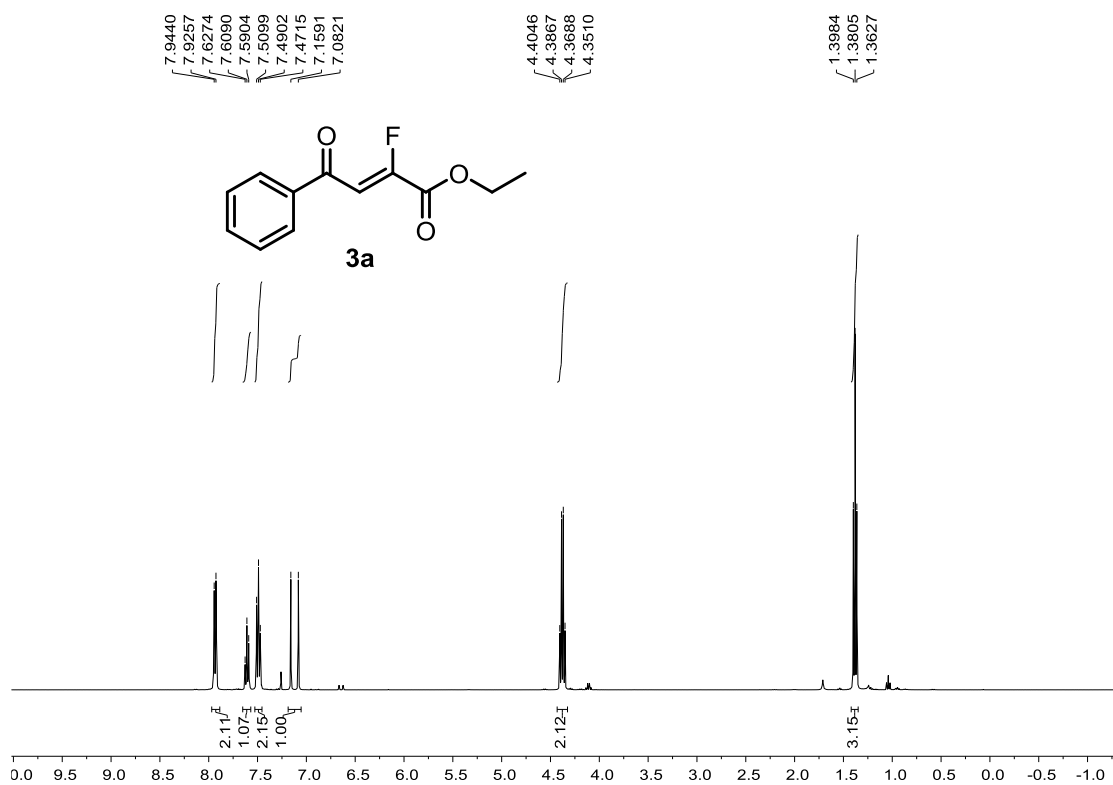
concentrated in vacuum and residue was purified by silica gel column chromatography (PE/EA = 10/1) to give the desired product **7e** (89 mg) in 75% yield (dr = 26/1) as thin yellow oil.

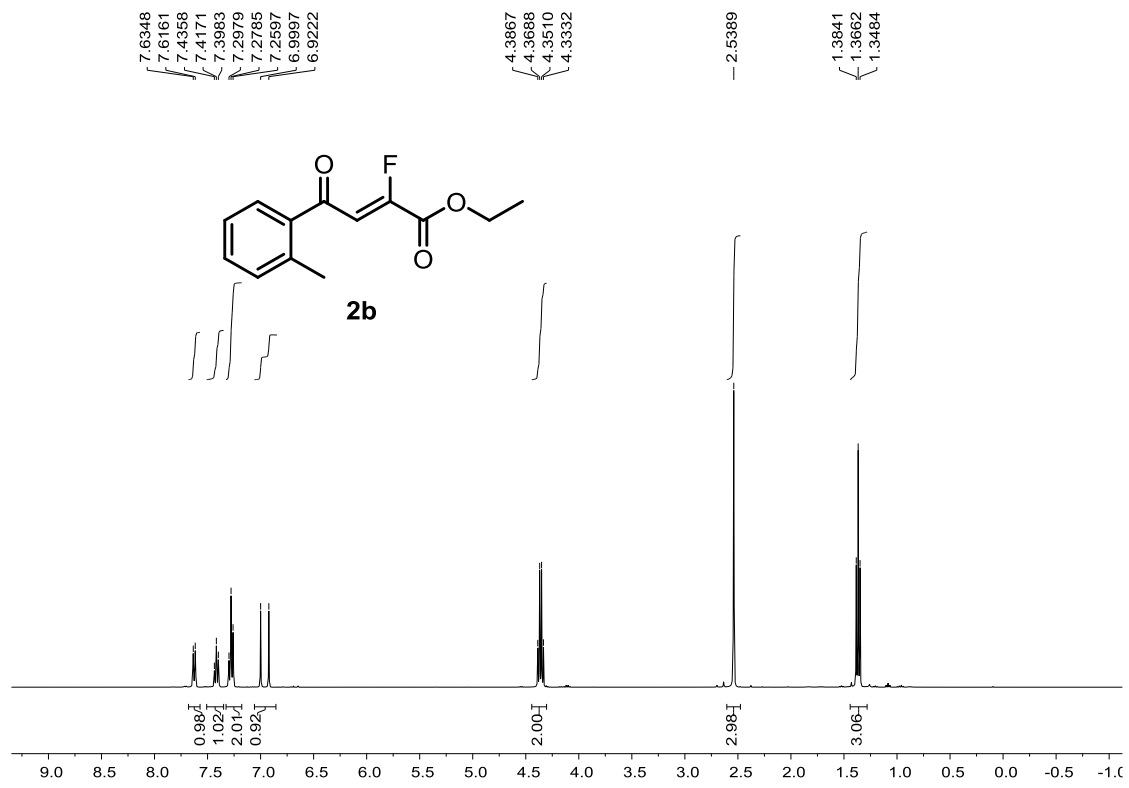
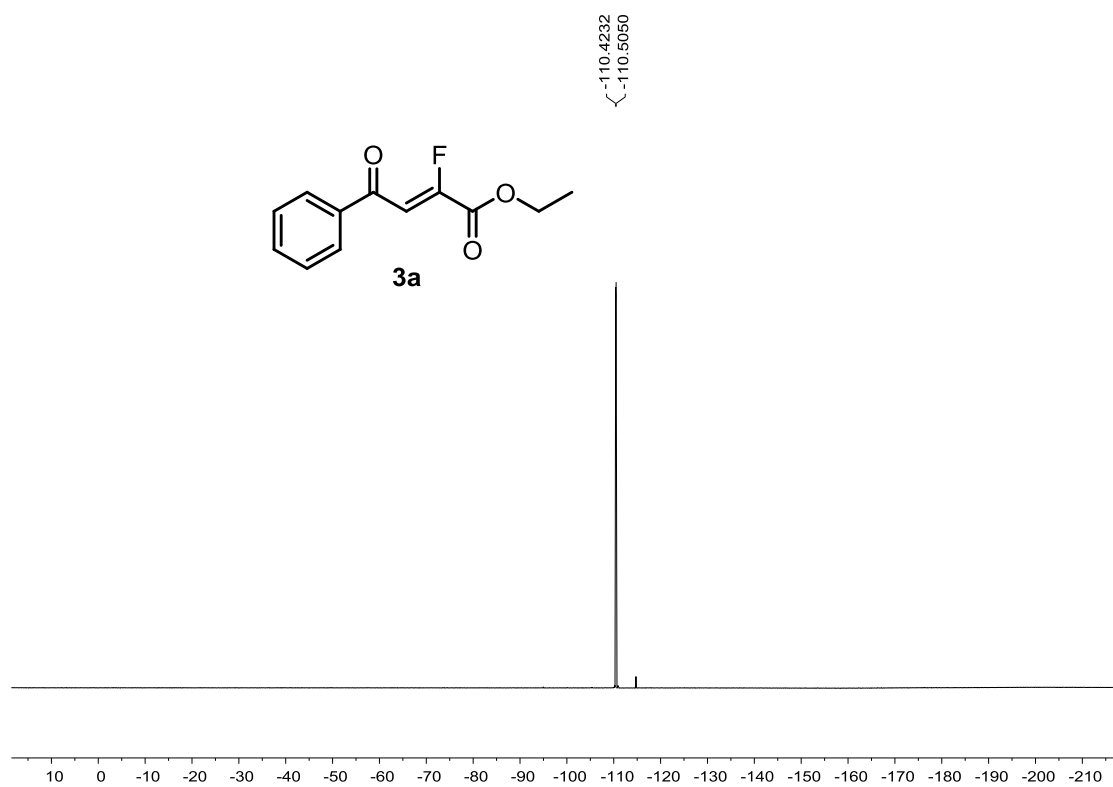
^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 7.6$ Hz, 2H), 7.70 (t, $J = 7.4$ Hz, 1H), 7.57 (t, $J = 7.3$ Hz, 2H), 4.67 (s, 1H), 4.46 (q, $J = 6.9$ Hz, 2H), 1.44 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 187.54 (d, $J = 4.6$ Hz), 162.45 (d, $J = 39.6$ Hz), 134.74, 129.11, 128.73, 89.12 (d, $J = 284.4$ Hz), 63.92, 60.29 (d, $J = 19.4$ Hz), 14.04. ^{19}F NMR (376 MHz, CDCl_3) δ -158.30 (s, 1F). HRMS (ESI): m/z calcd. for $\text{C}_{12}\text{H}_{11}\text{FNaO}_4^+ [\text{M} + \text{Na}^+]$: 261.0534, found: 261.0541.

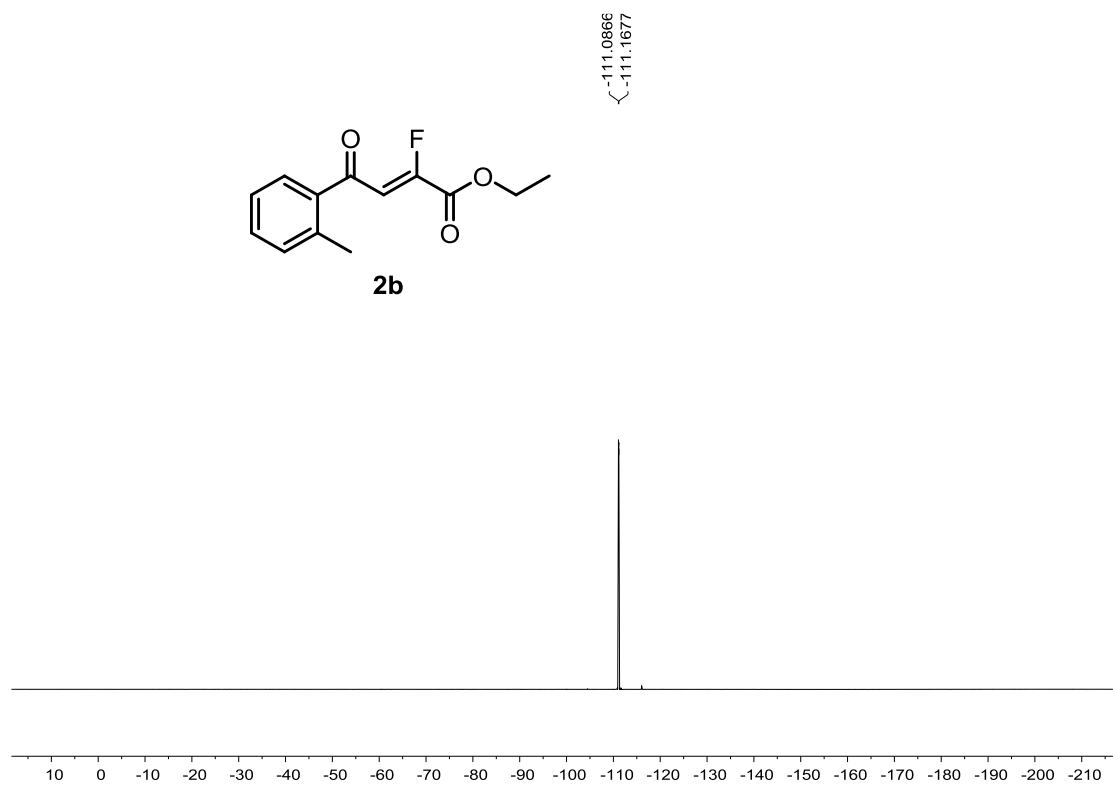
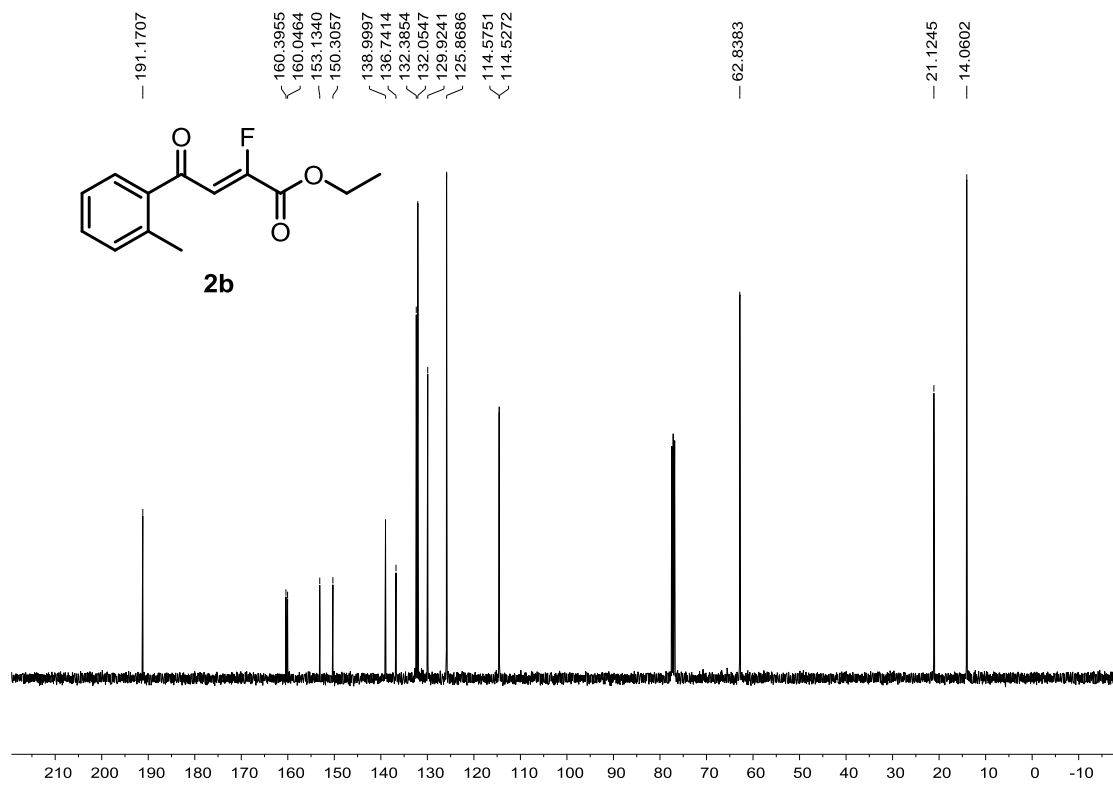
Part 9. References.

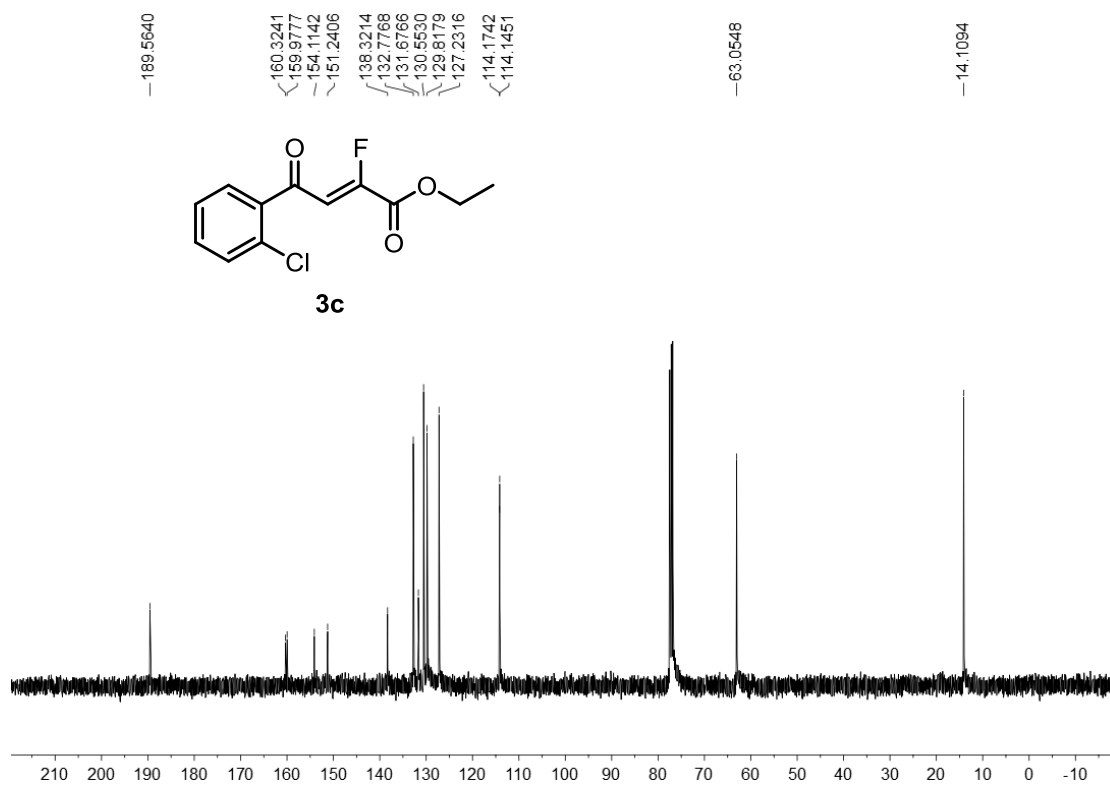
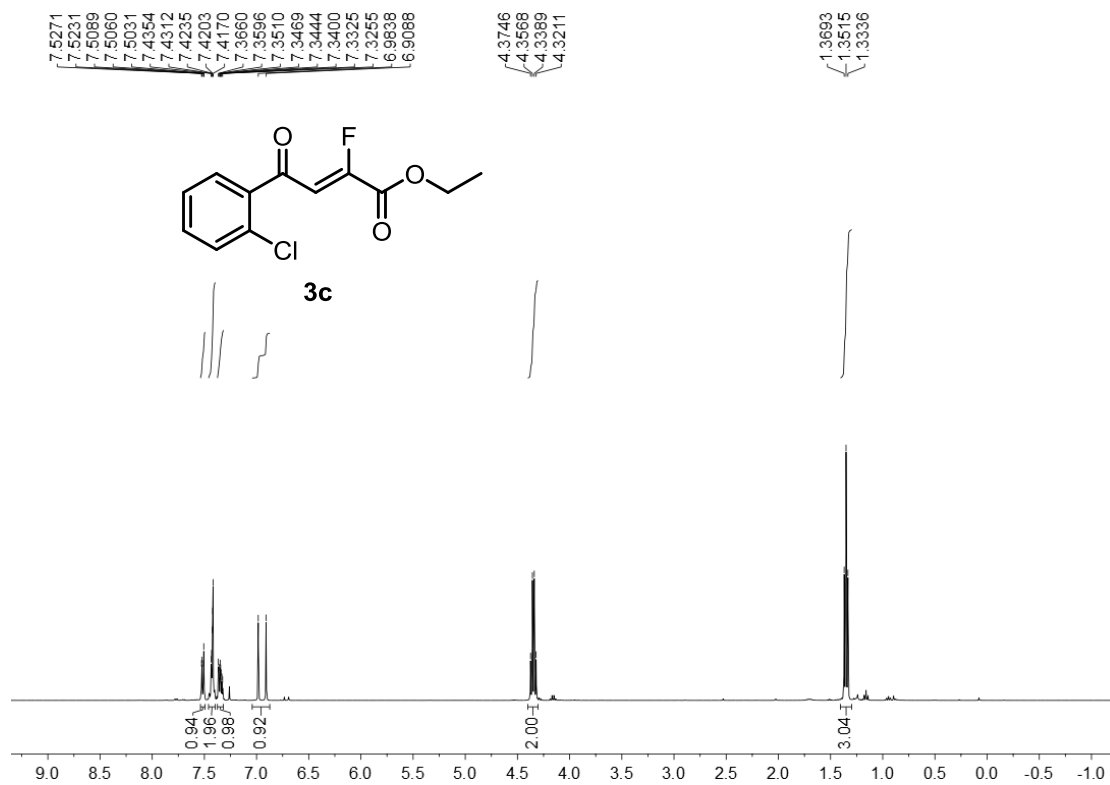
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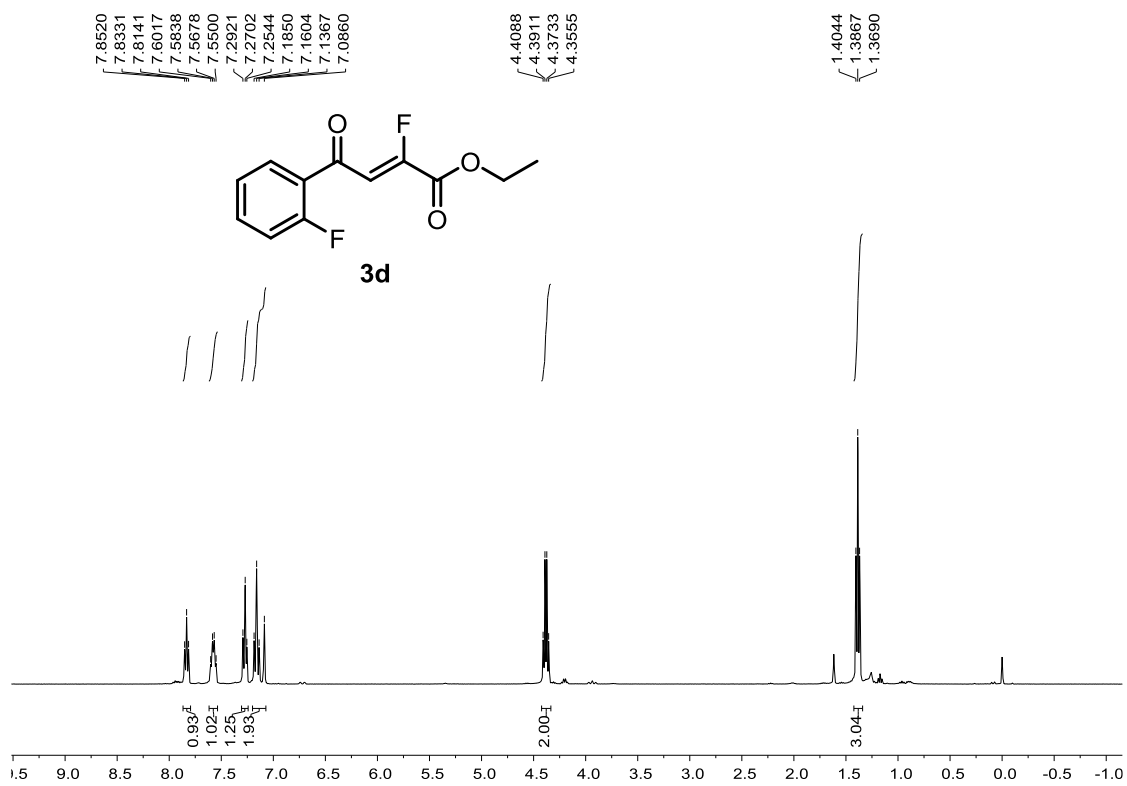
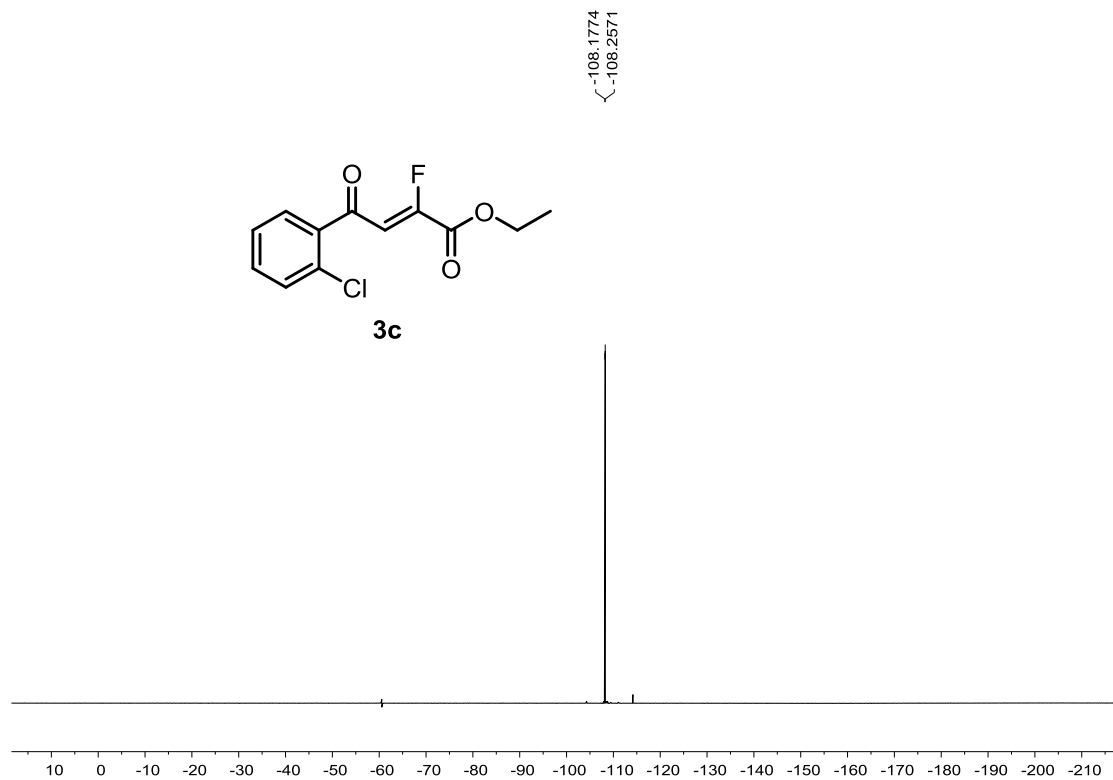
Part 10. ^1H , ^{13}C , and ^{19}F NMR spectra.

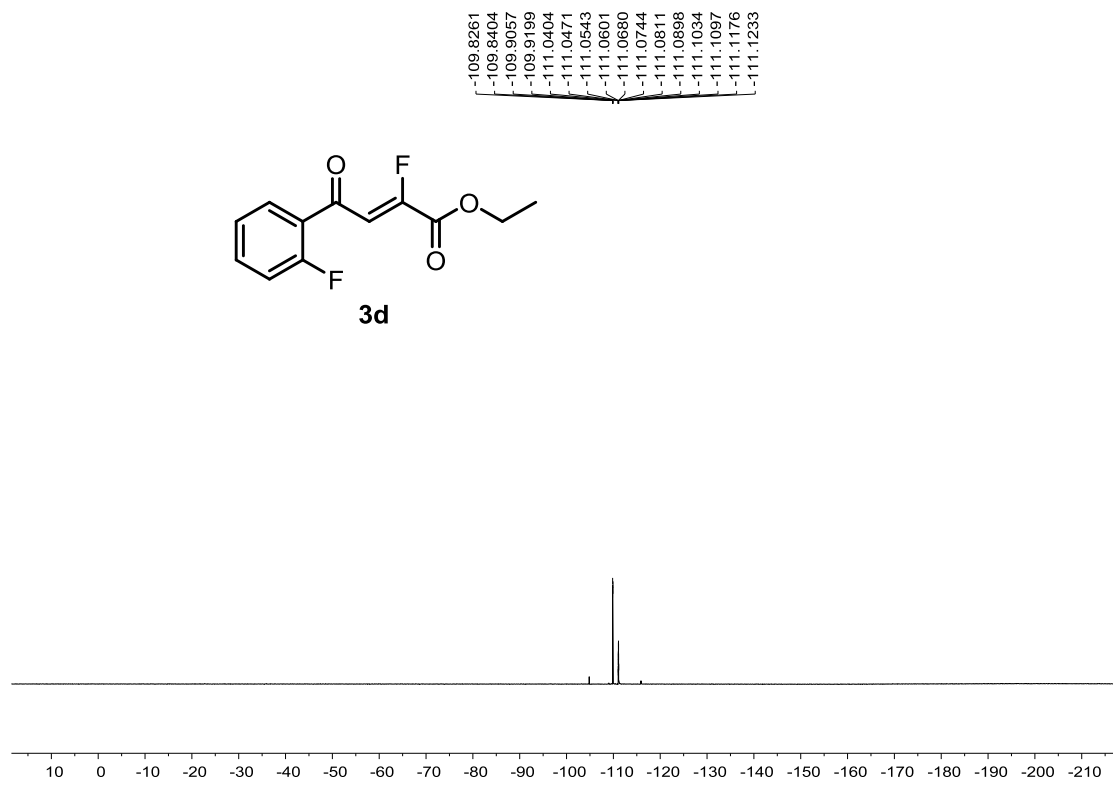
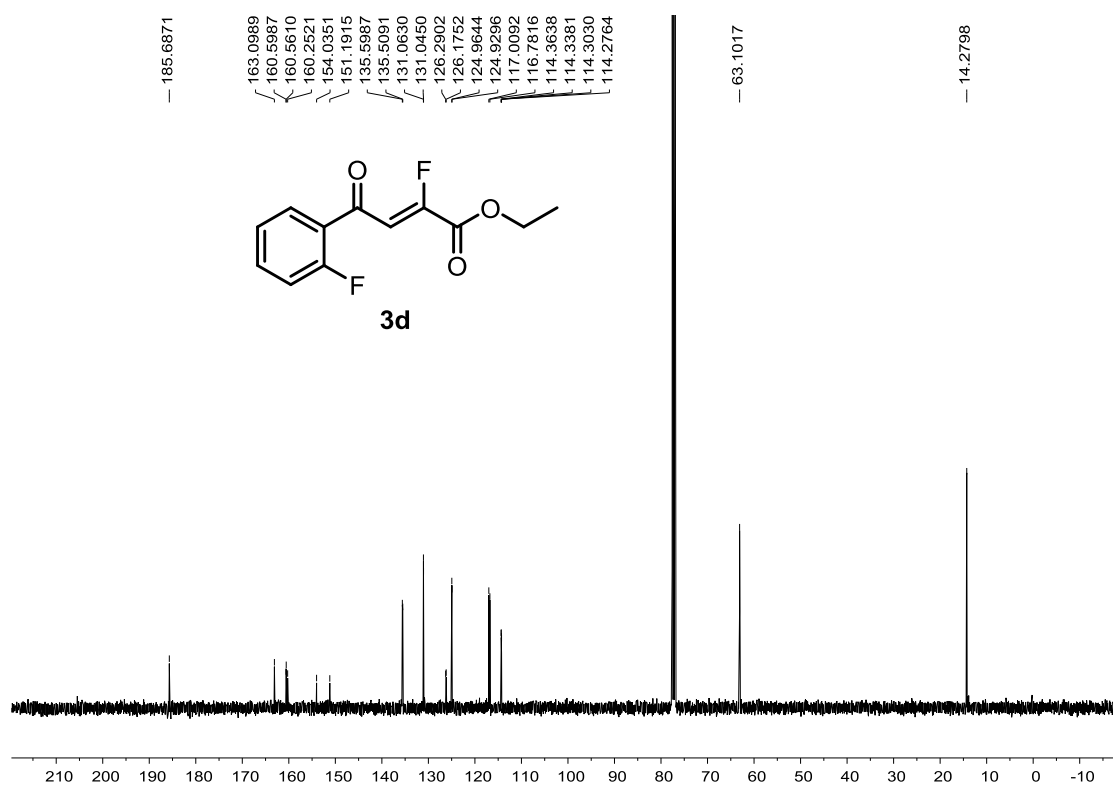


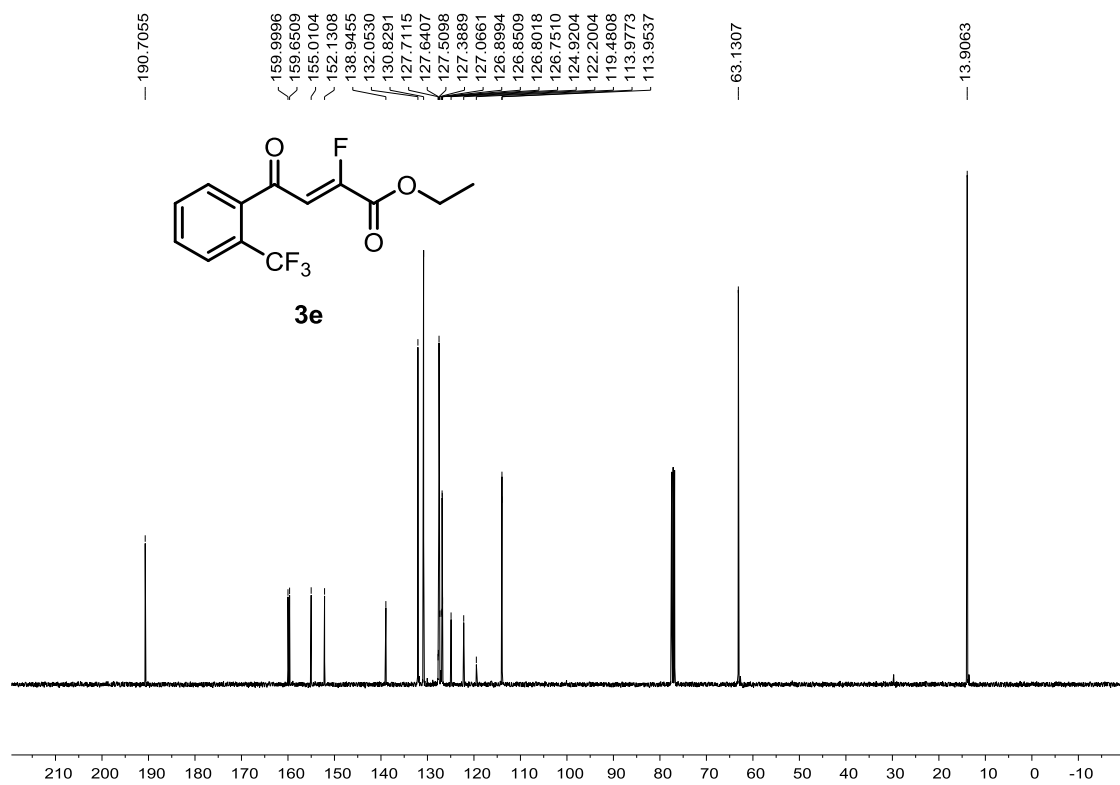
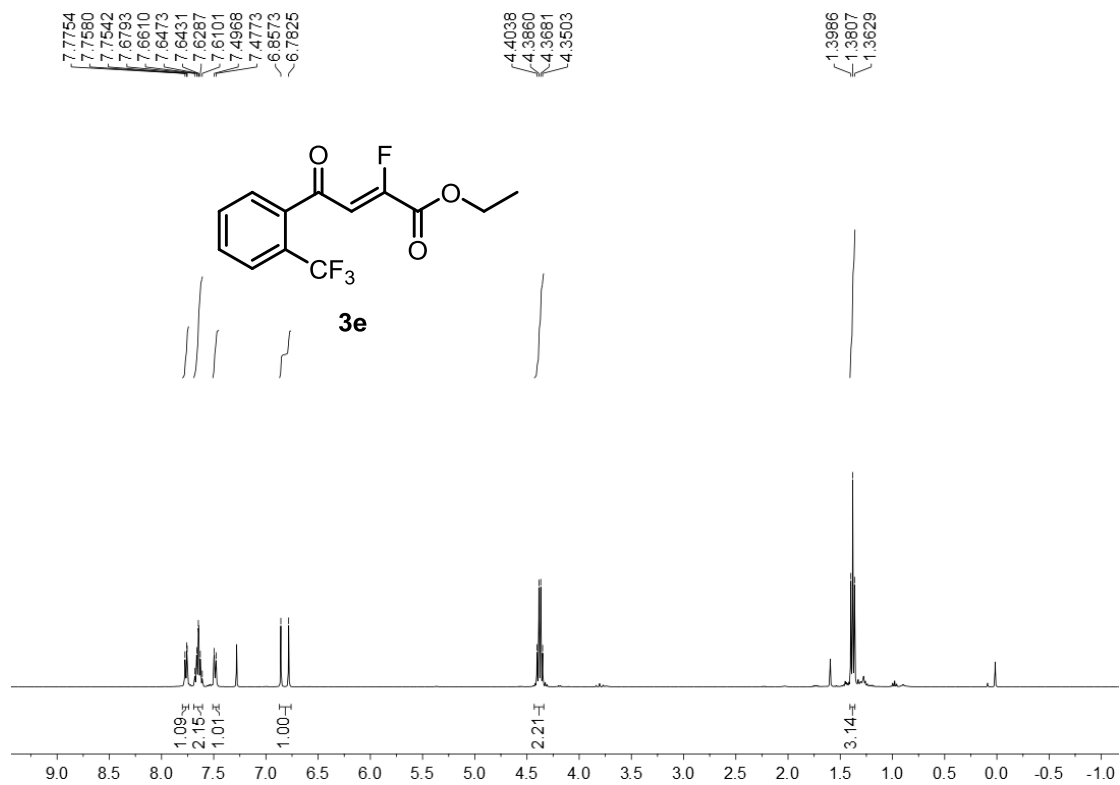


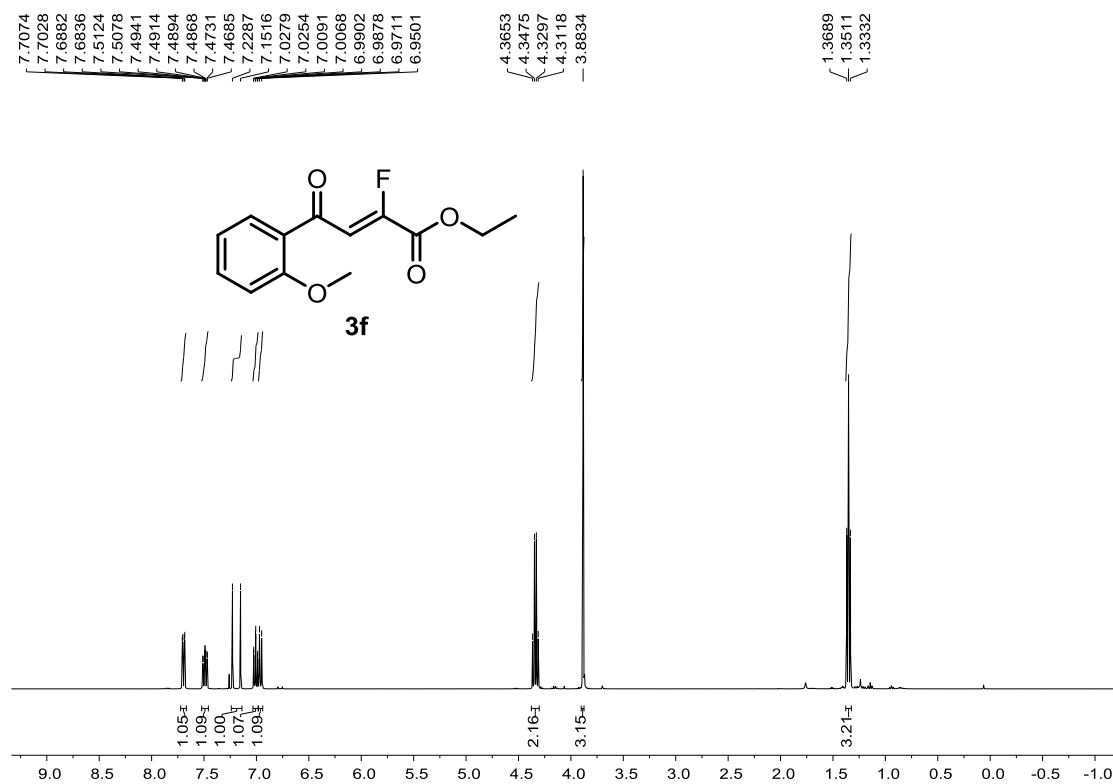
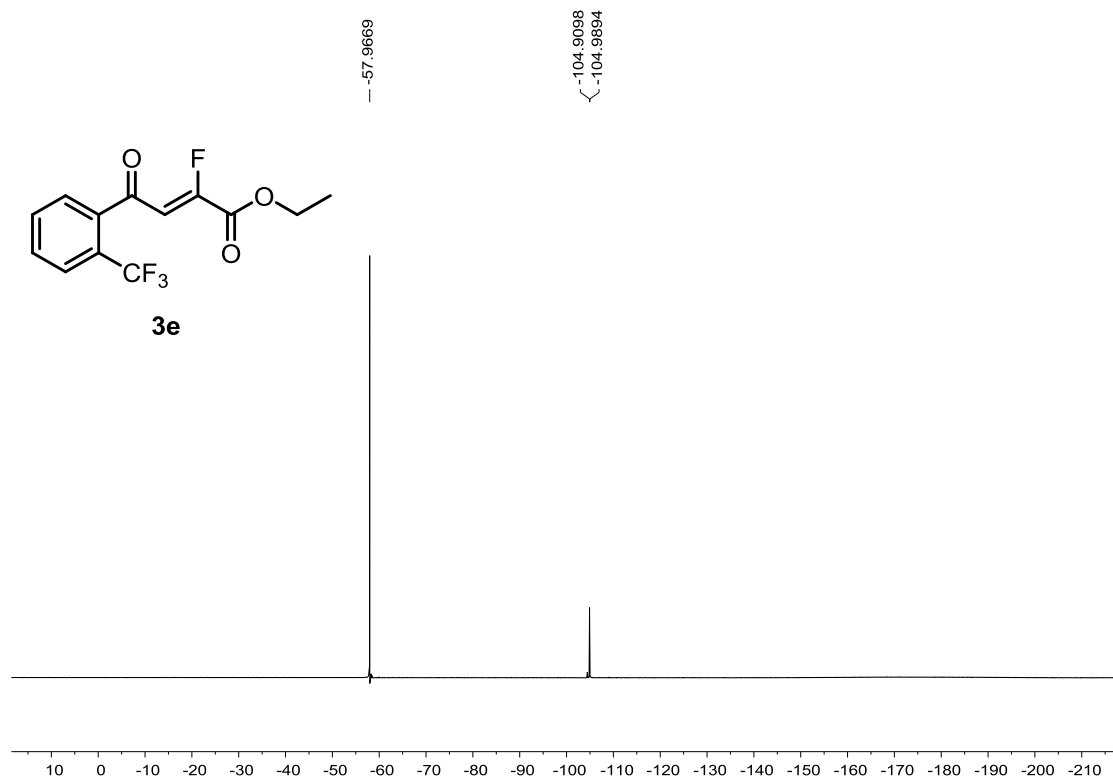


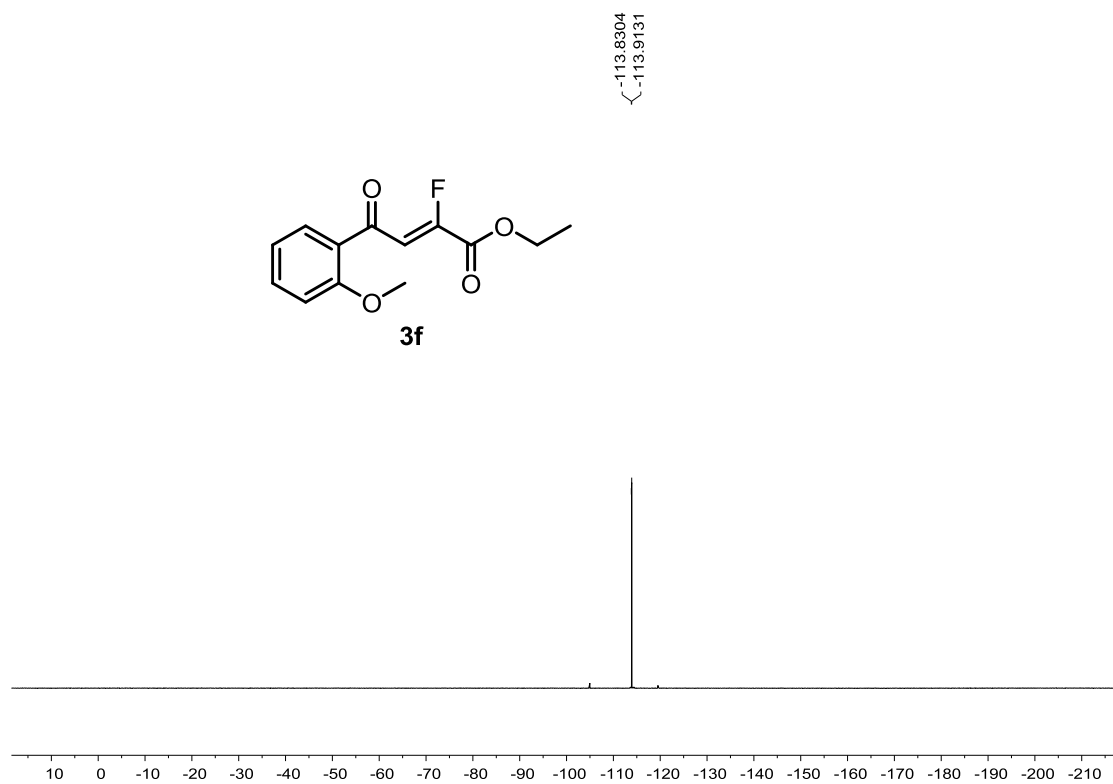
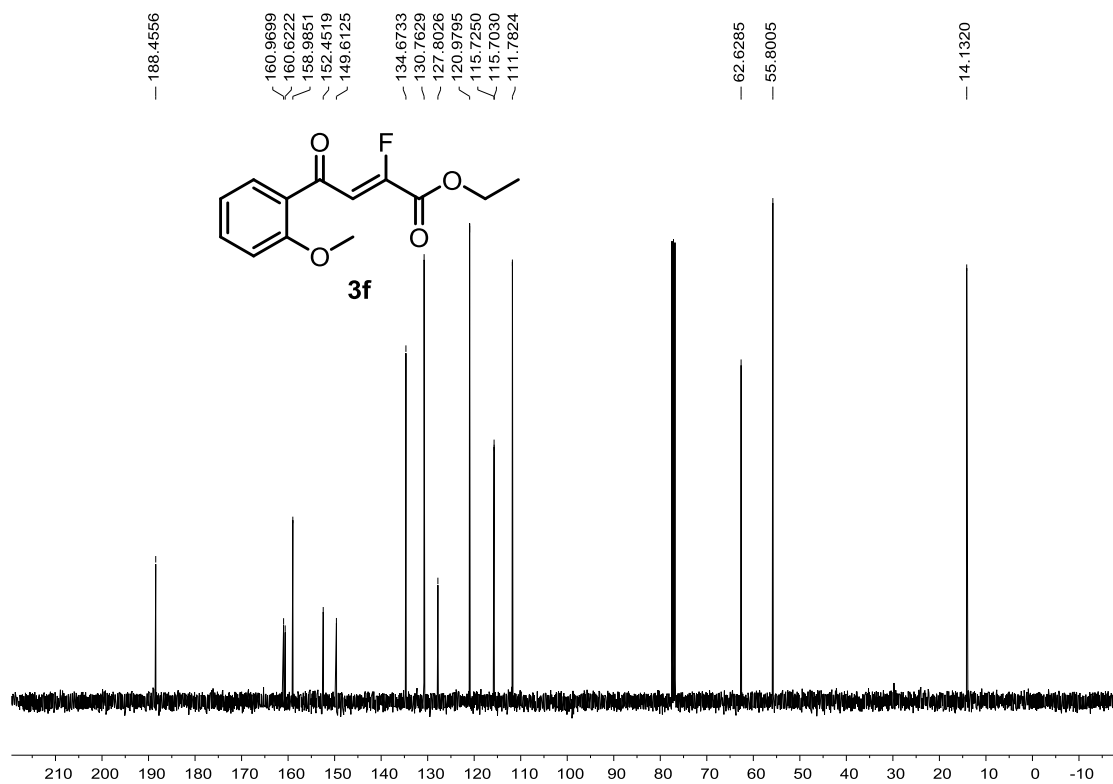


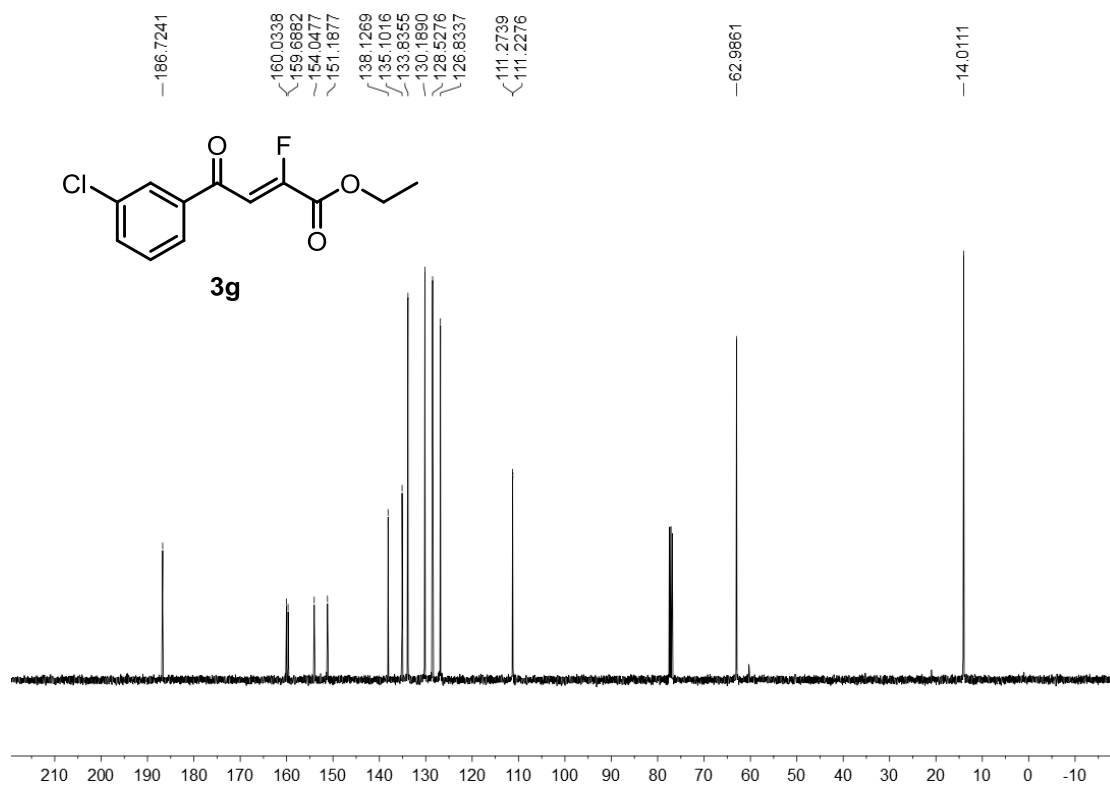
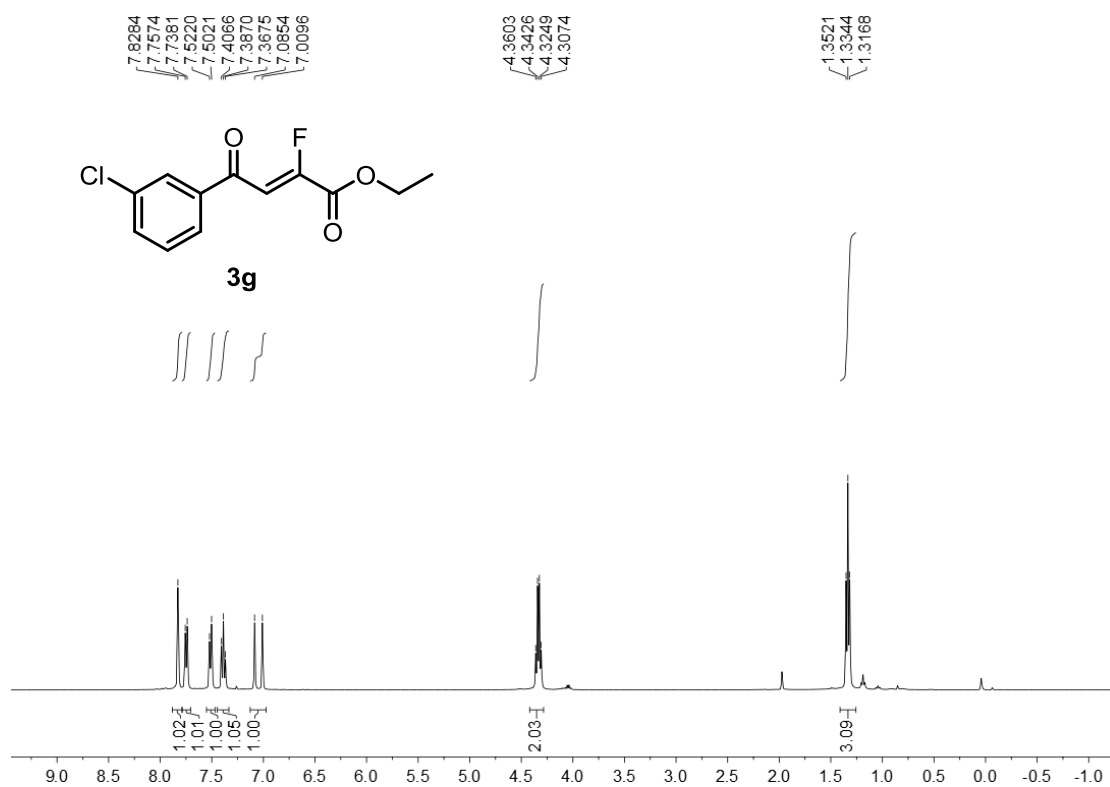


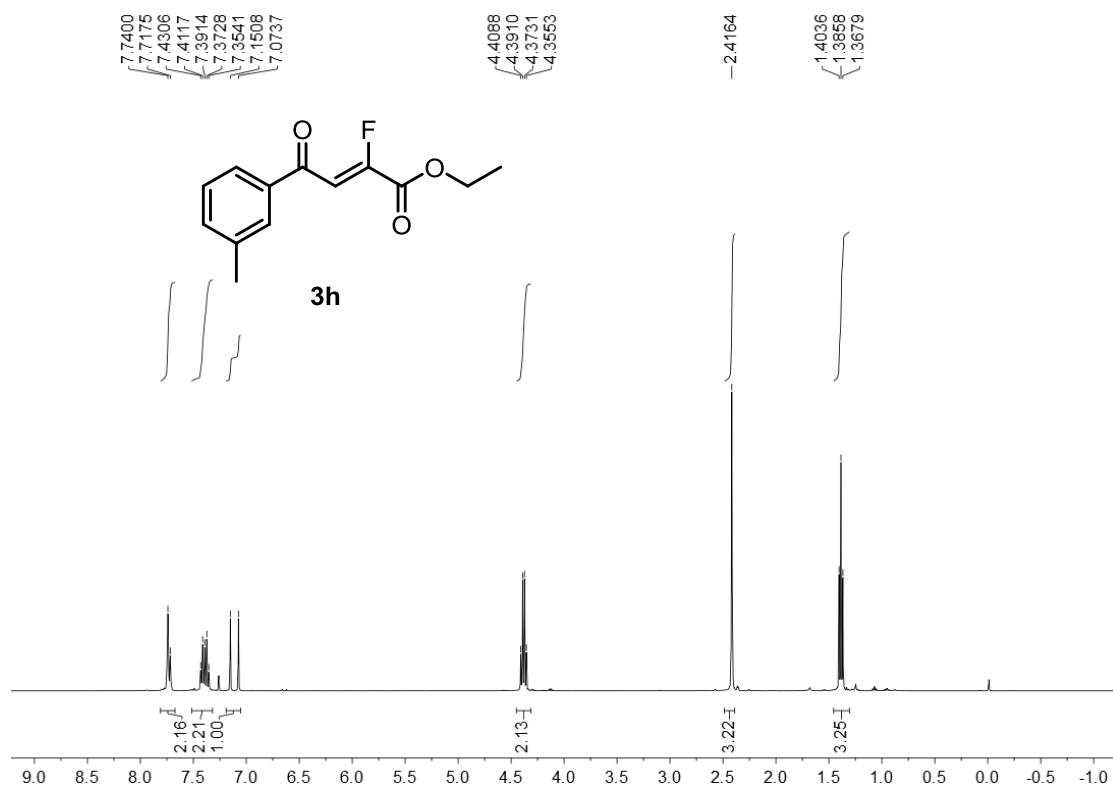
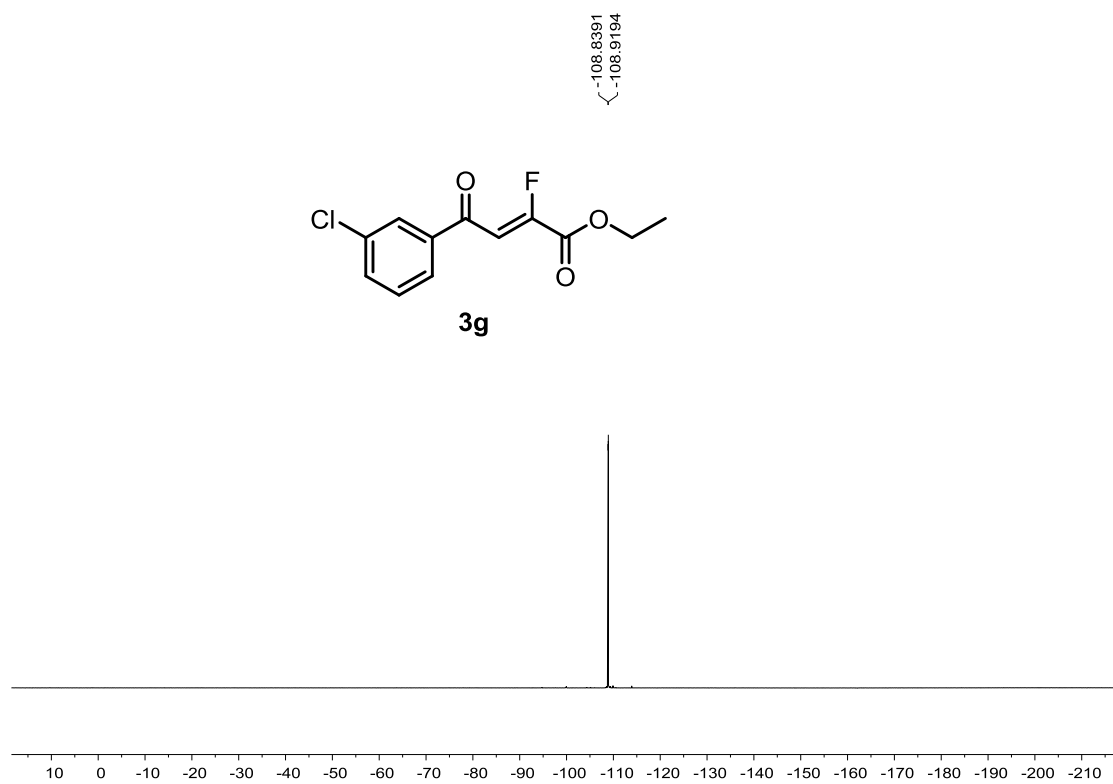


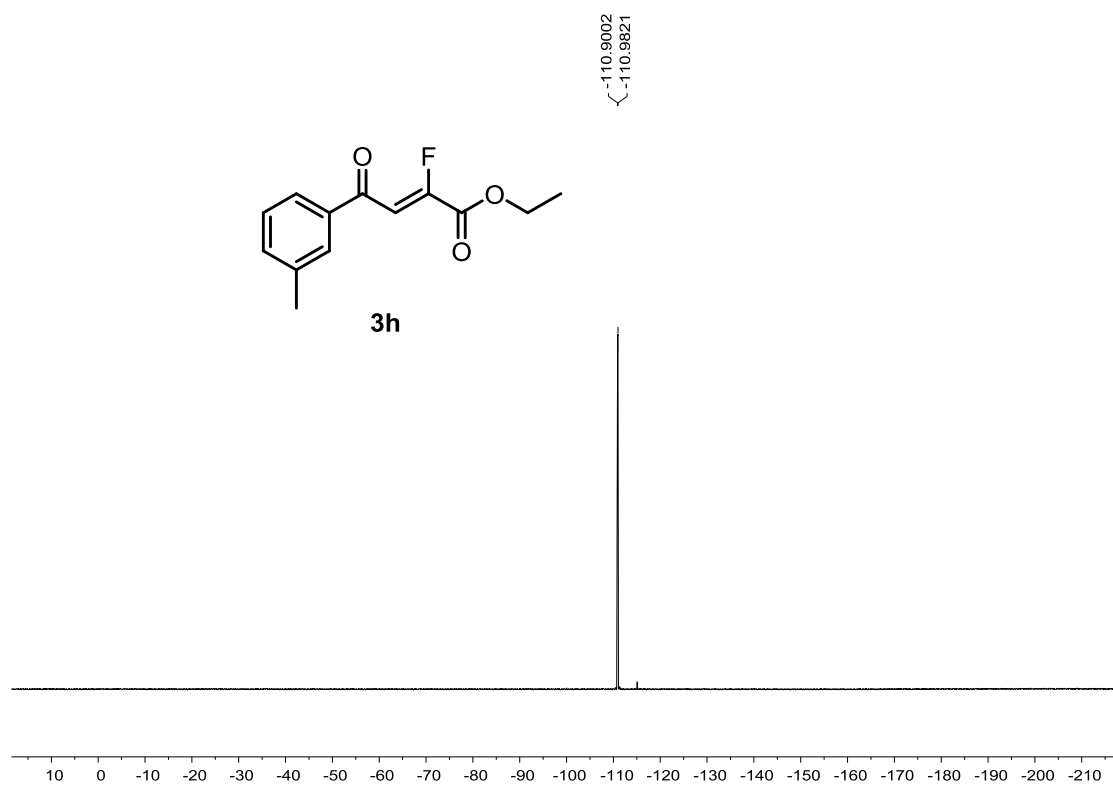
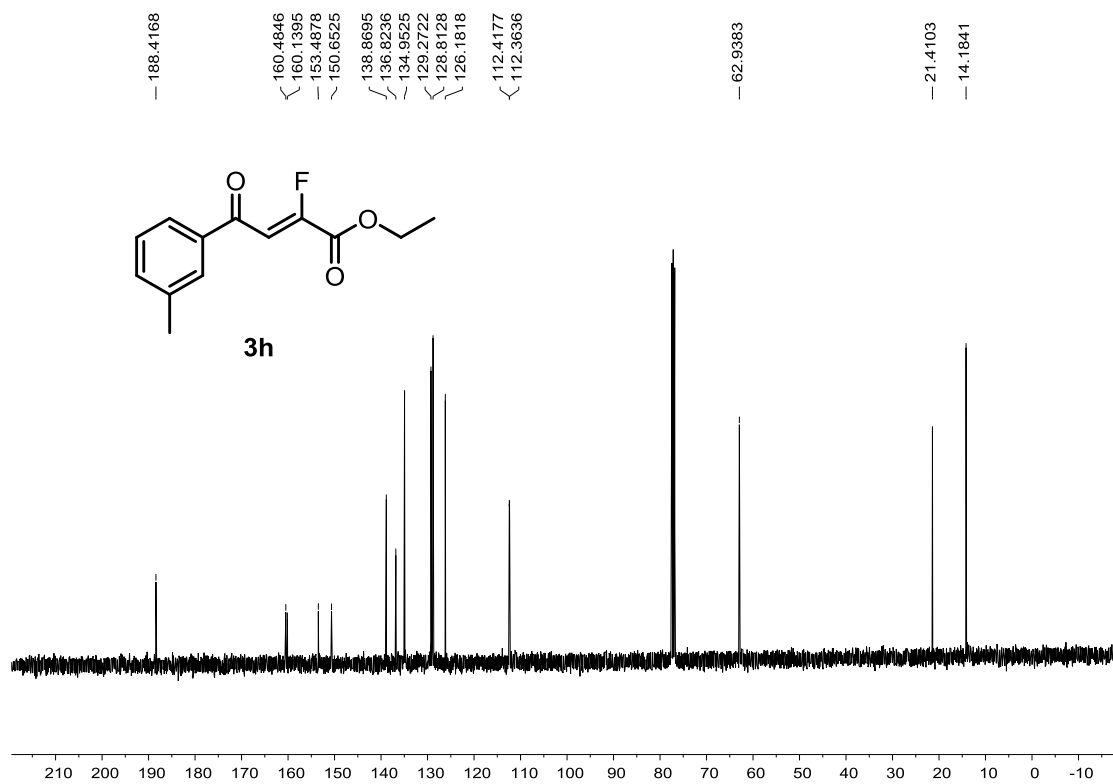


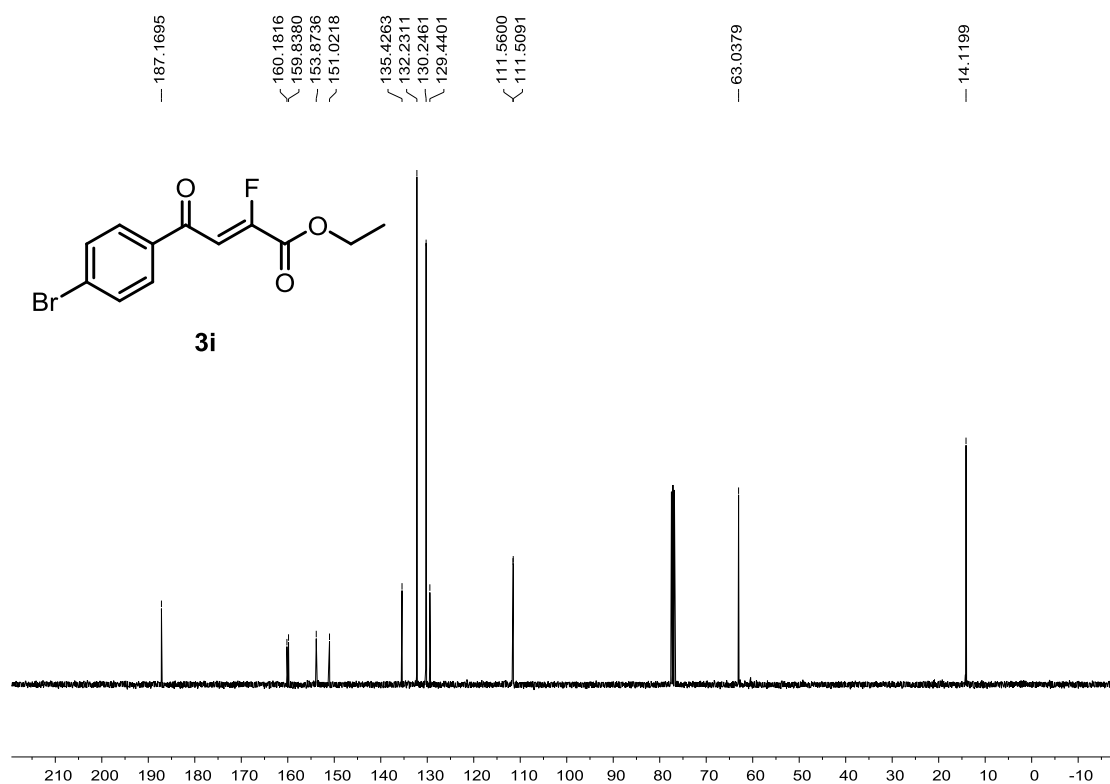
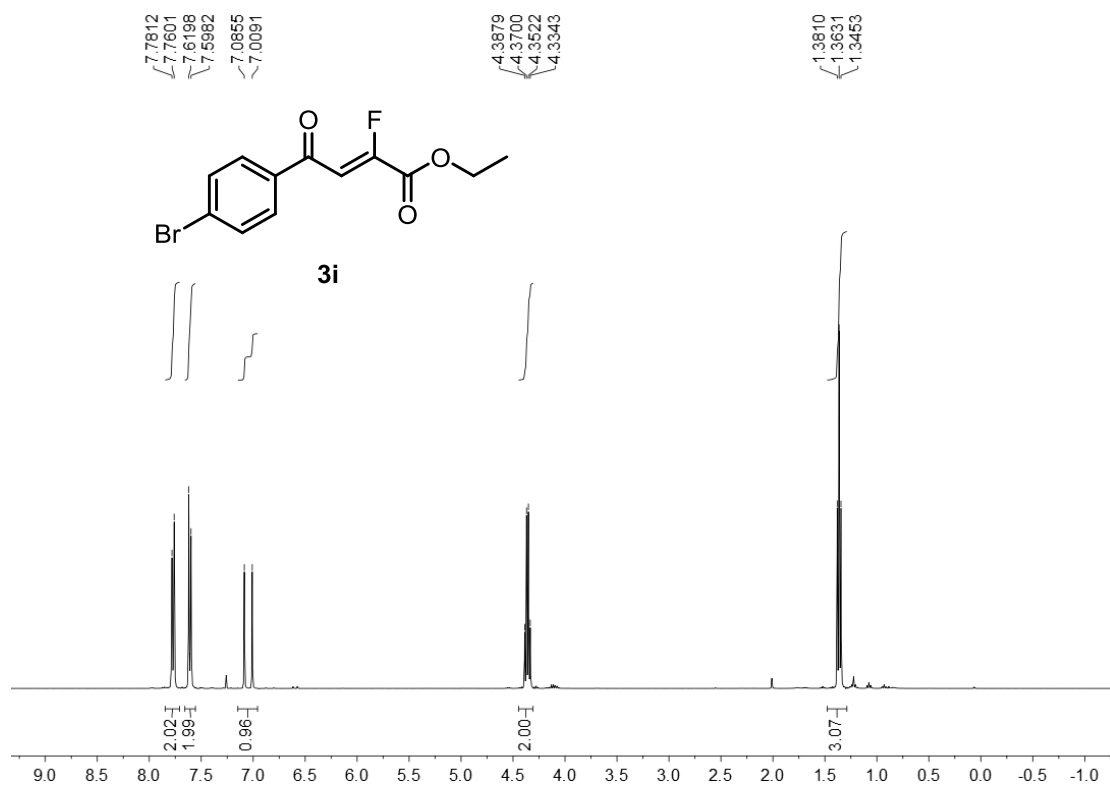


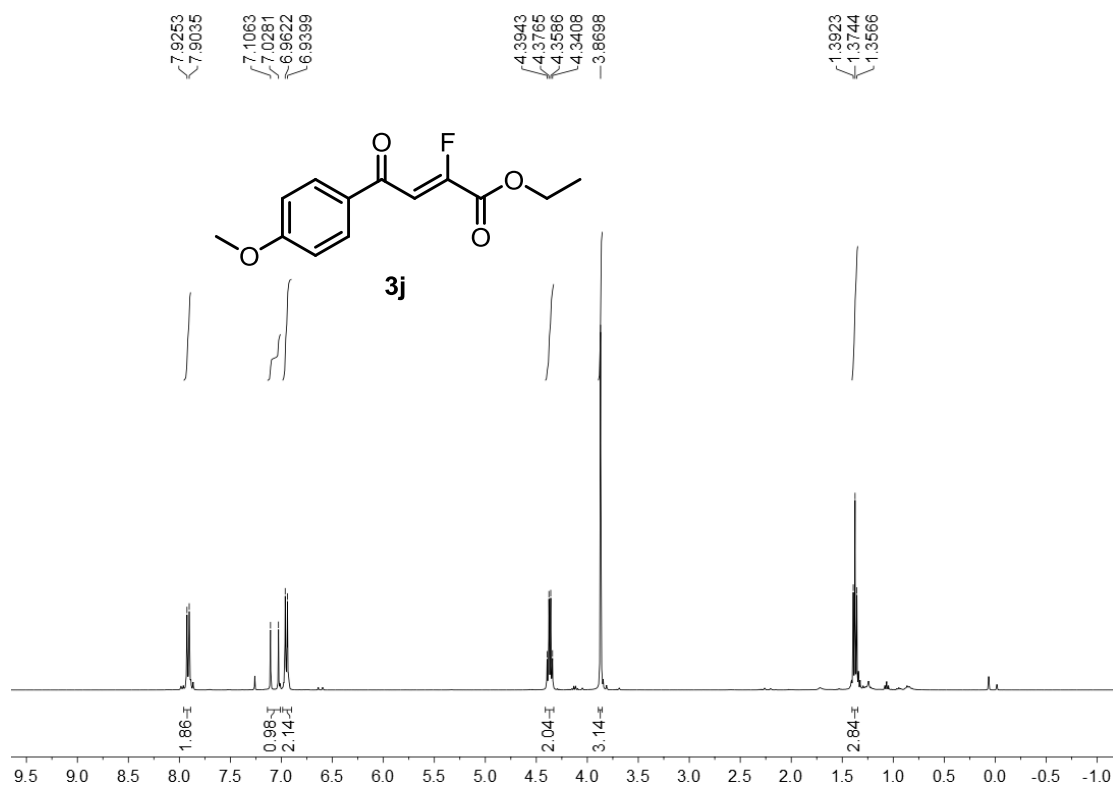
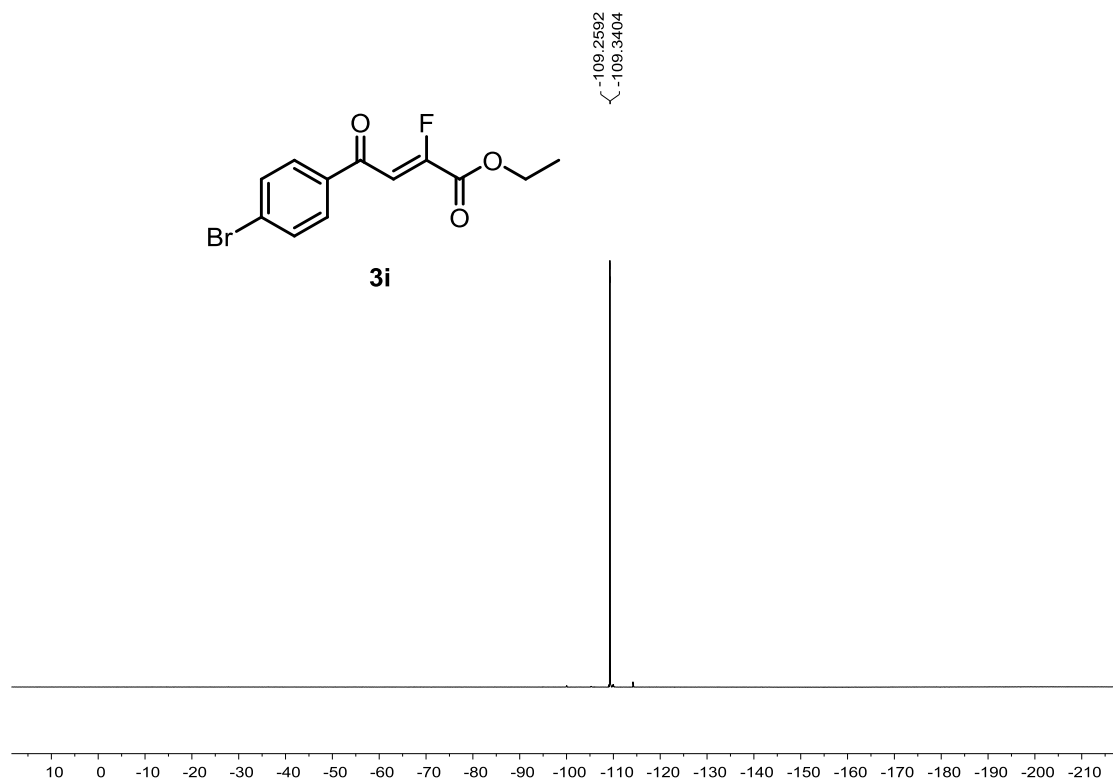


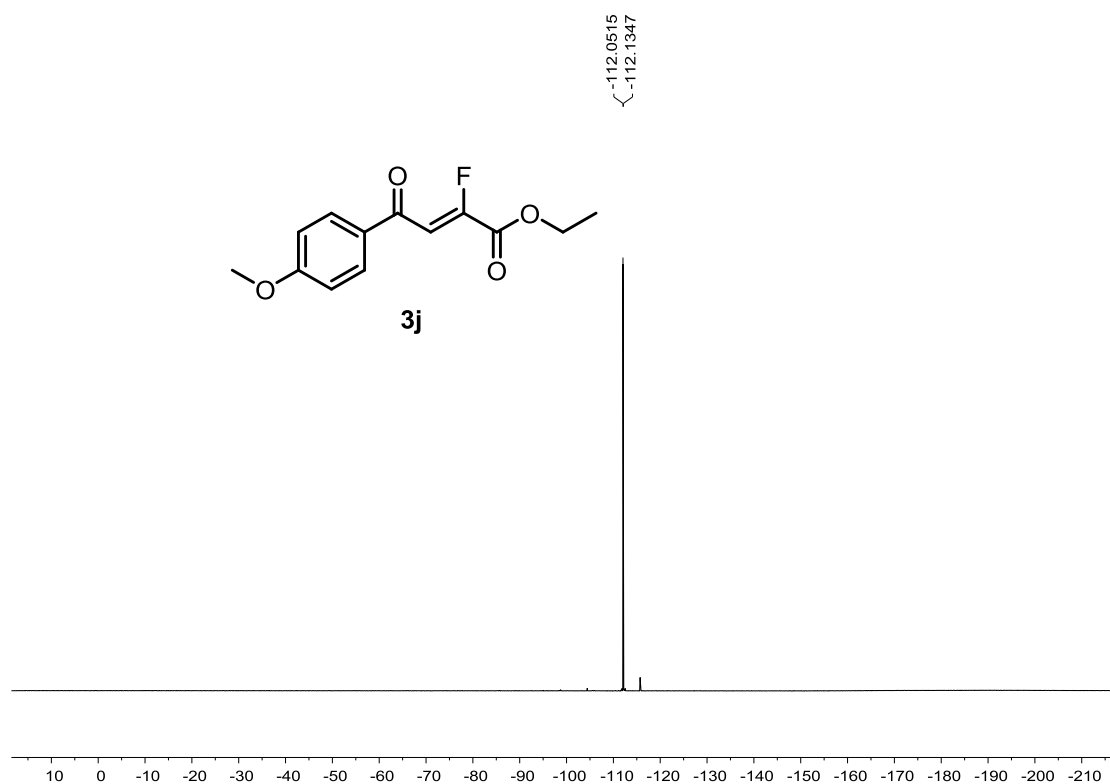
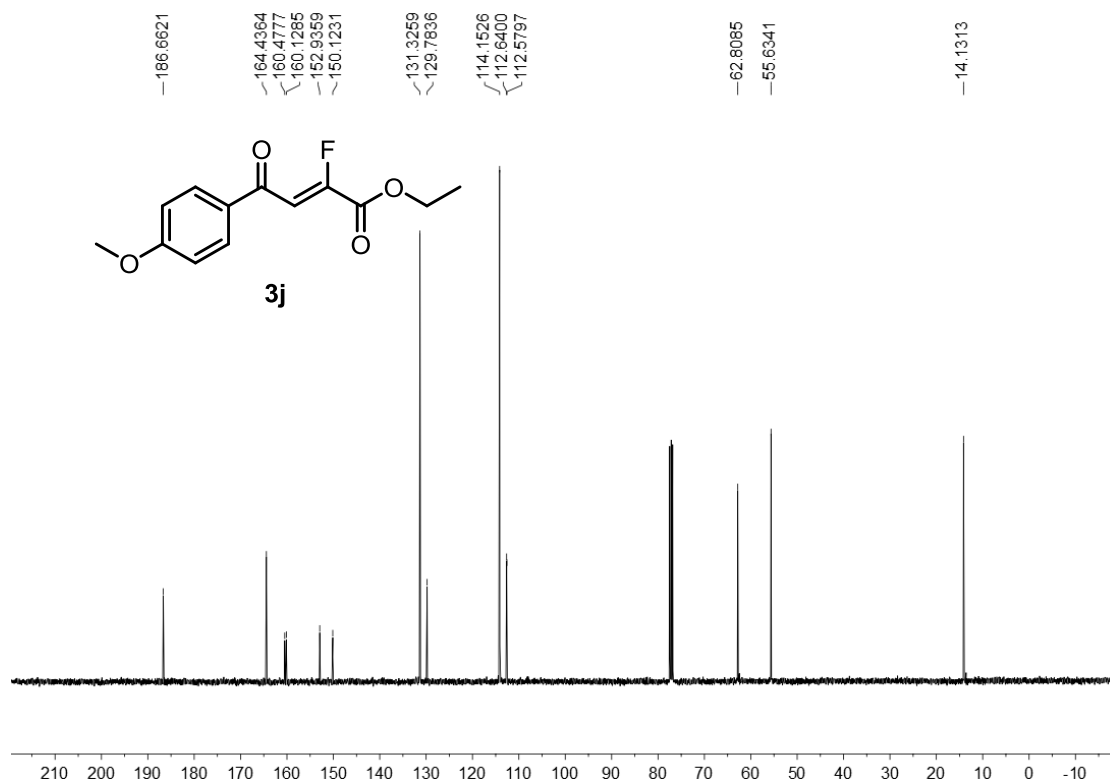


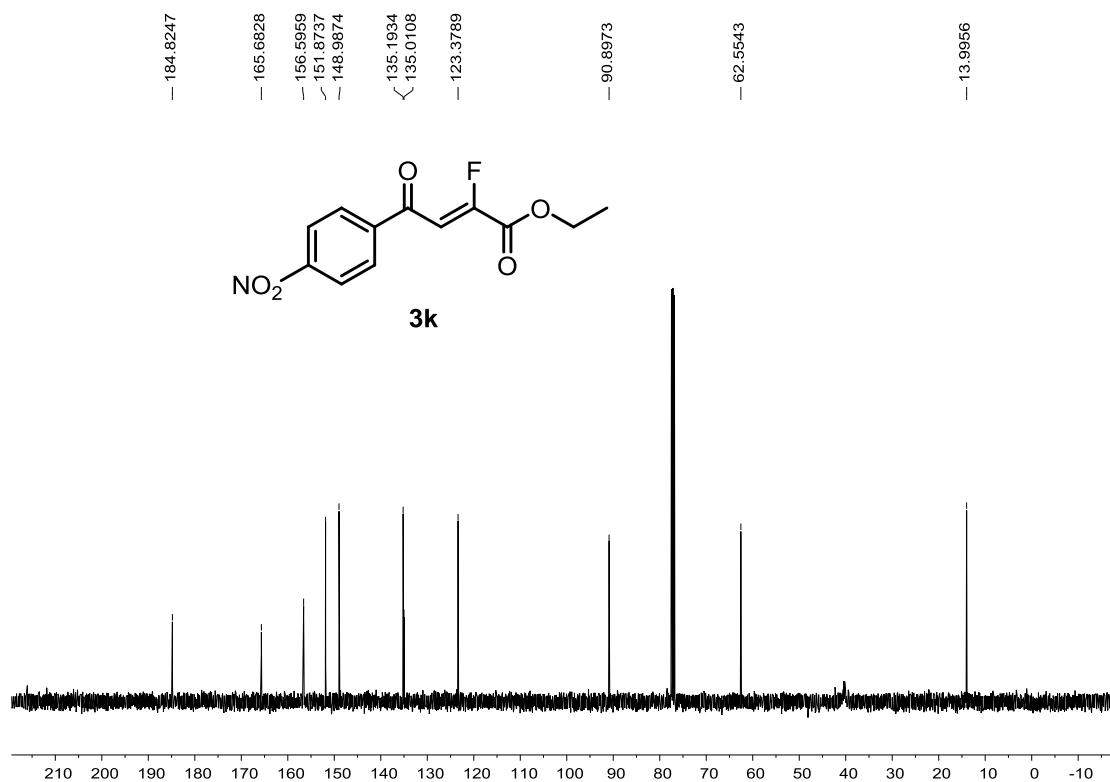
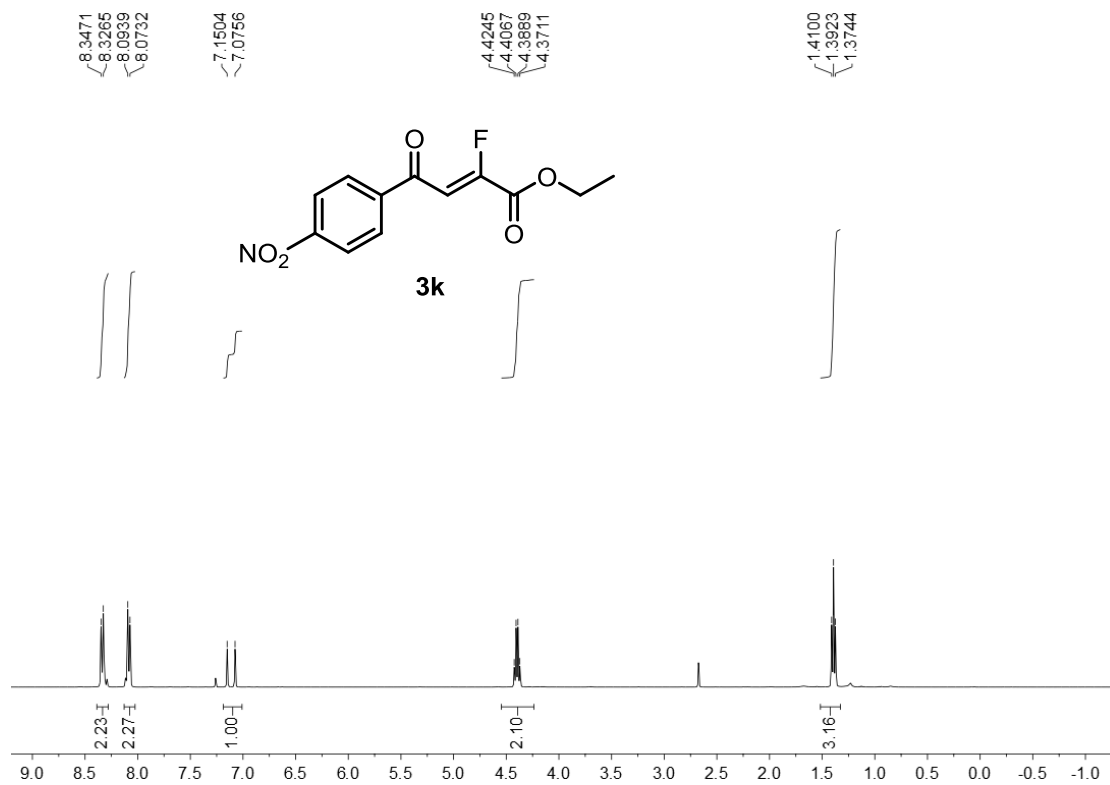


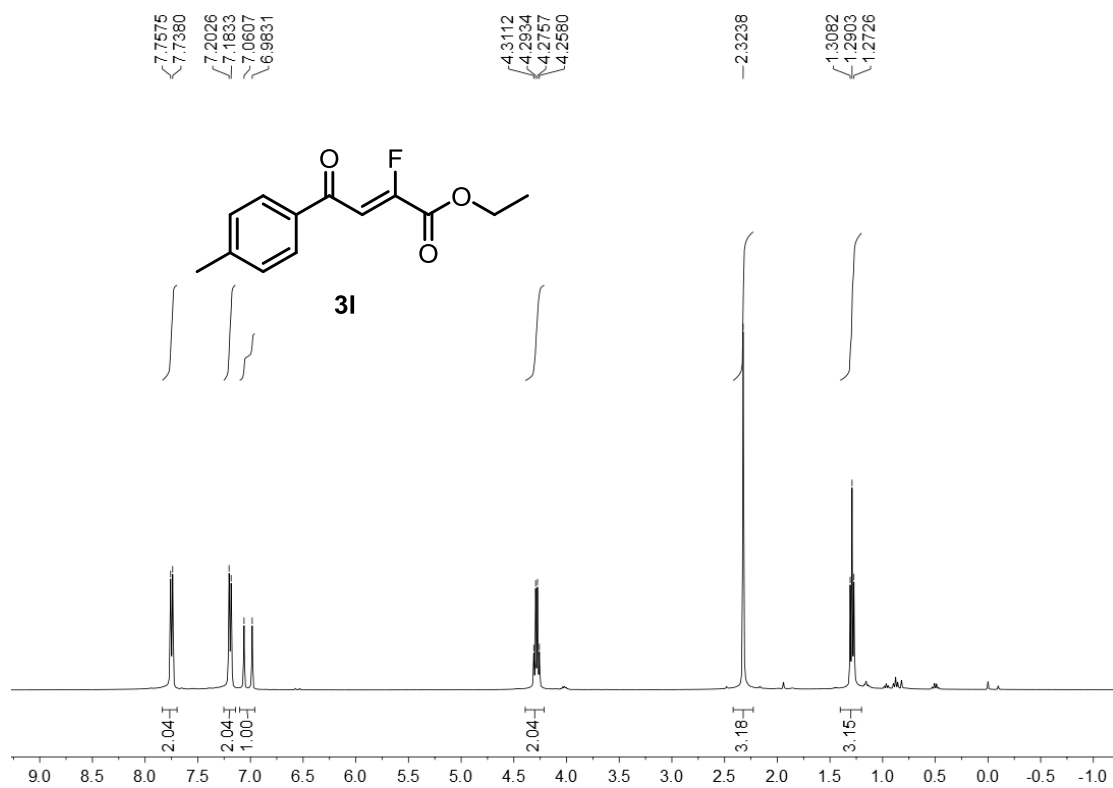
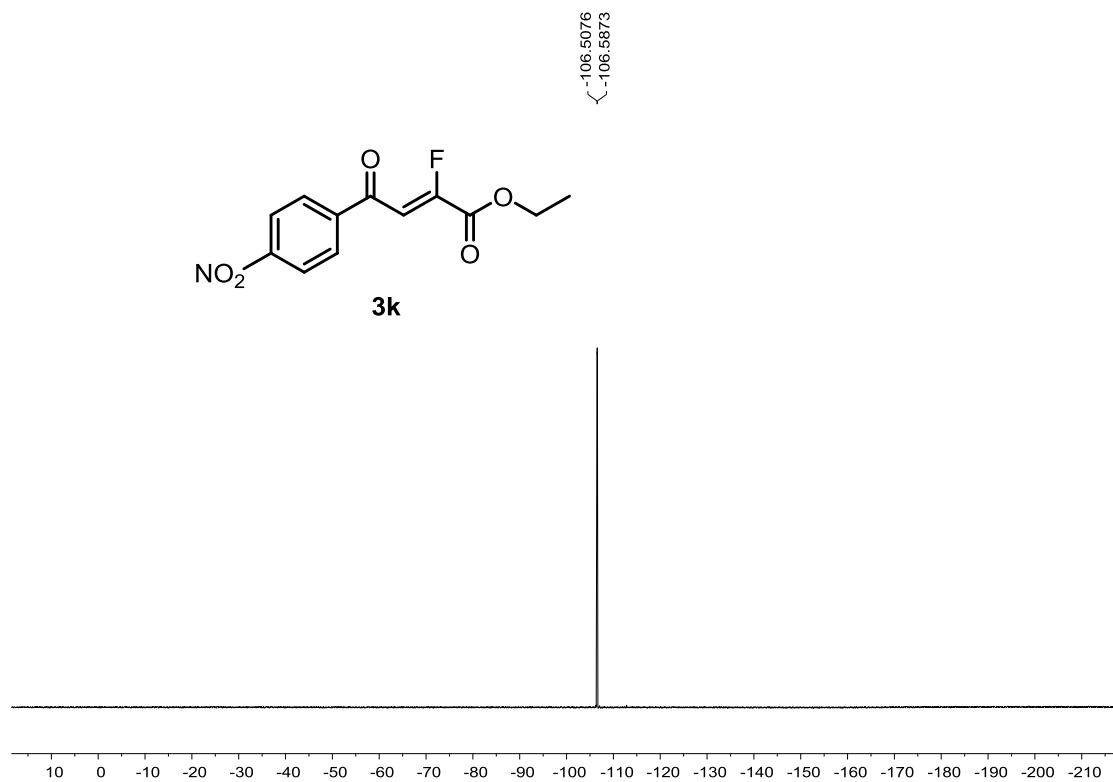


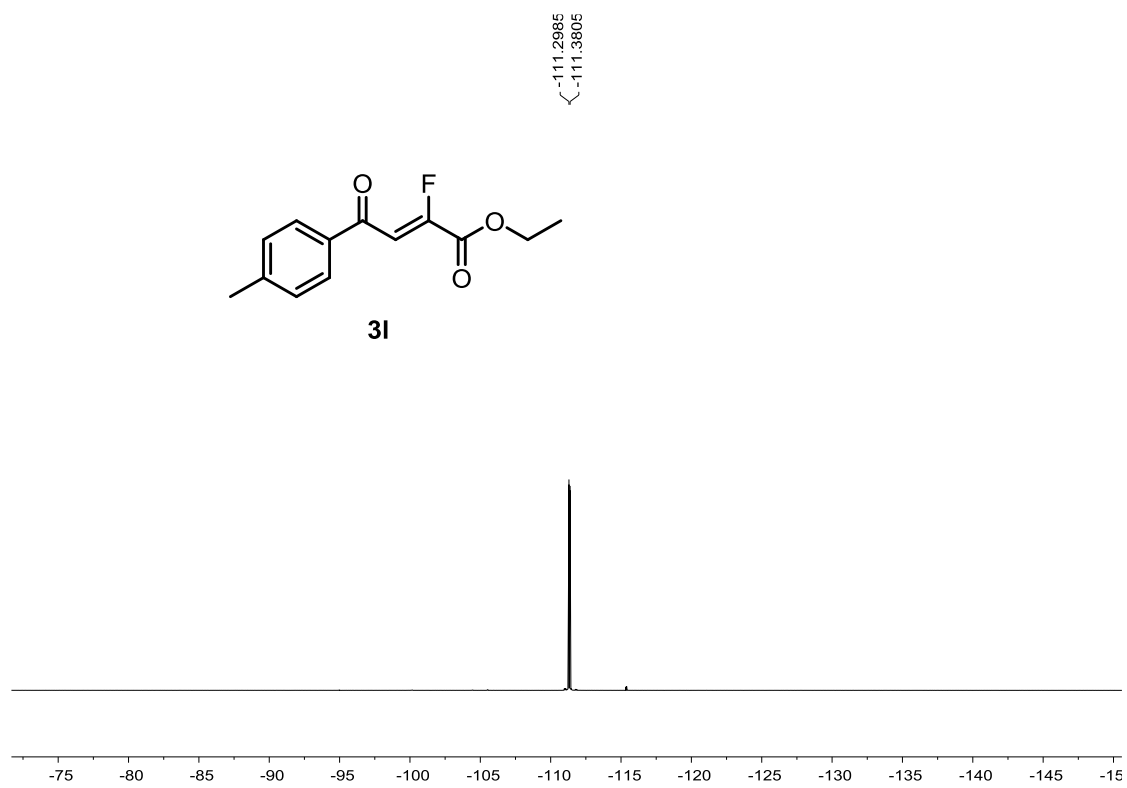
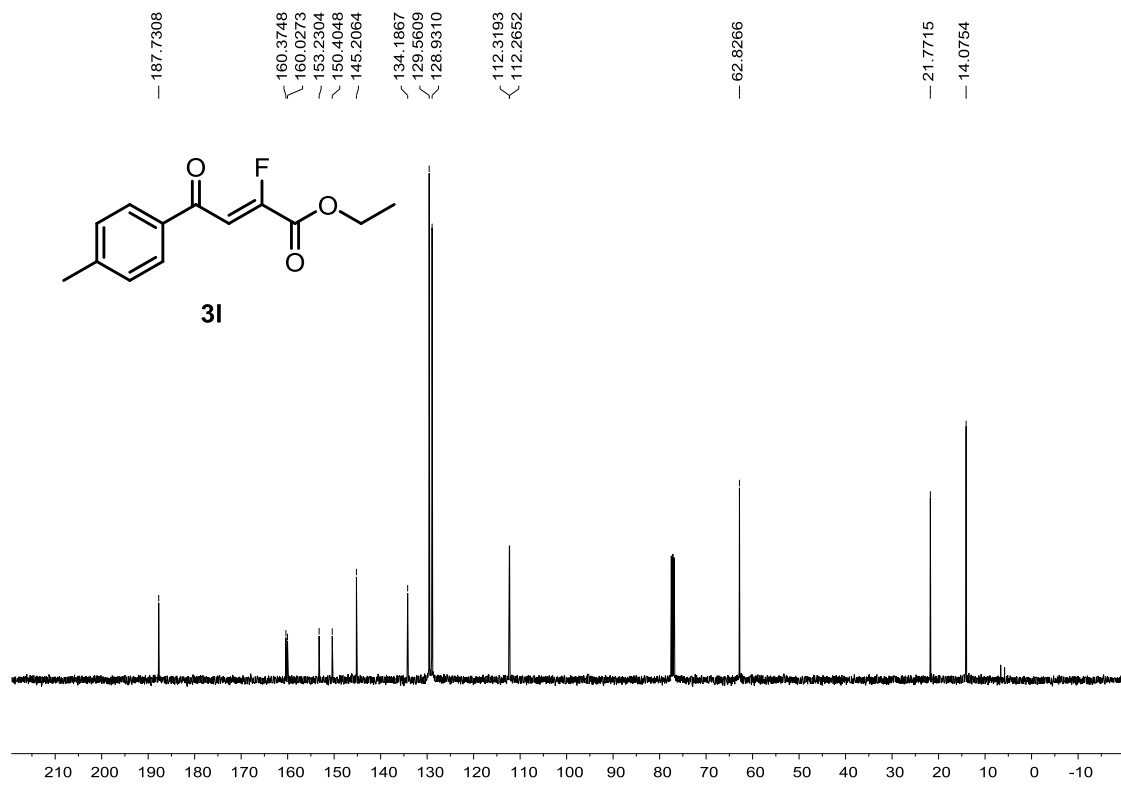


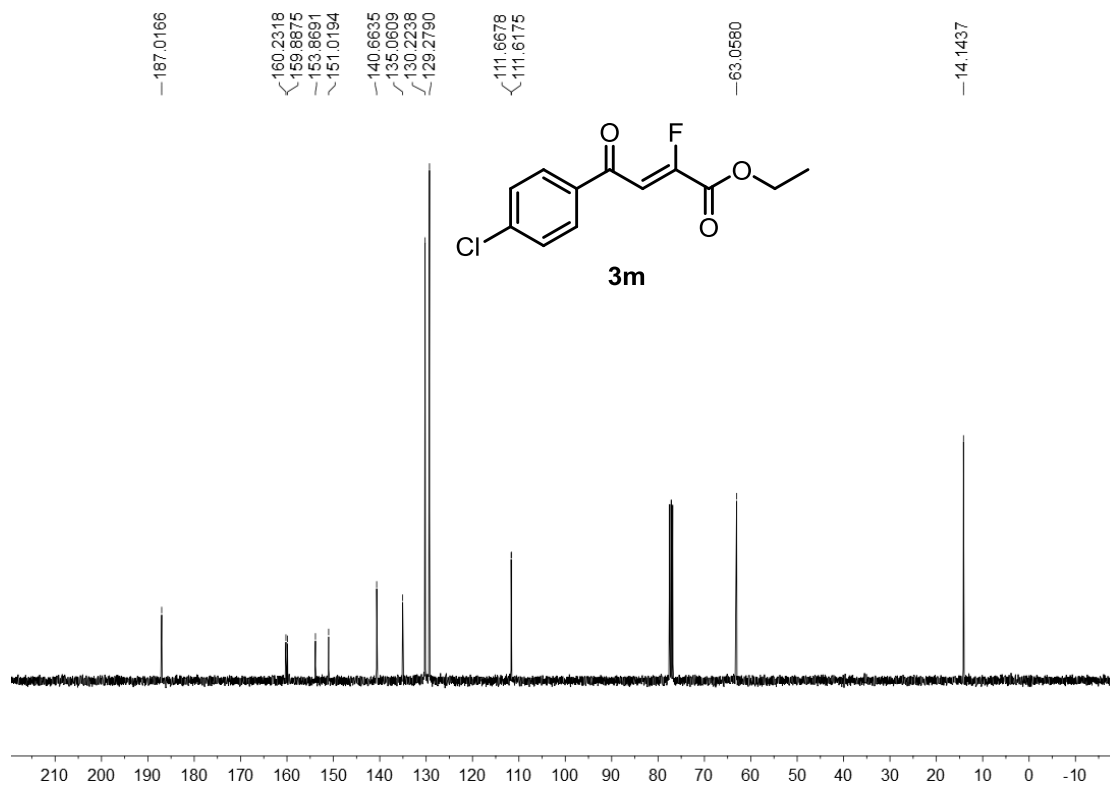
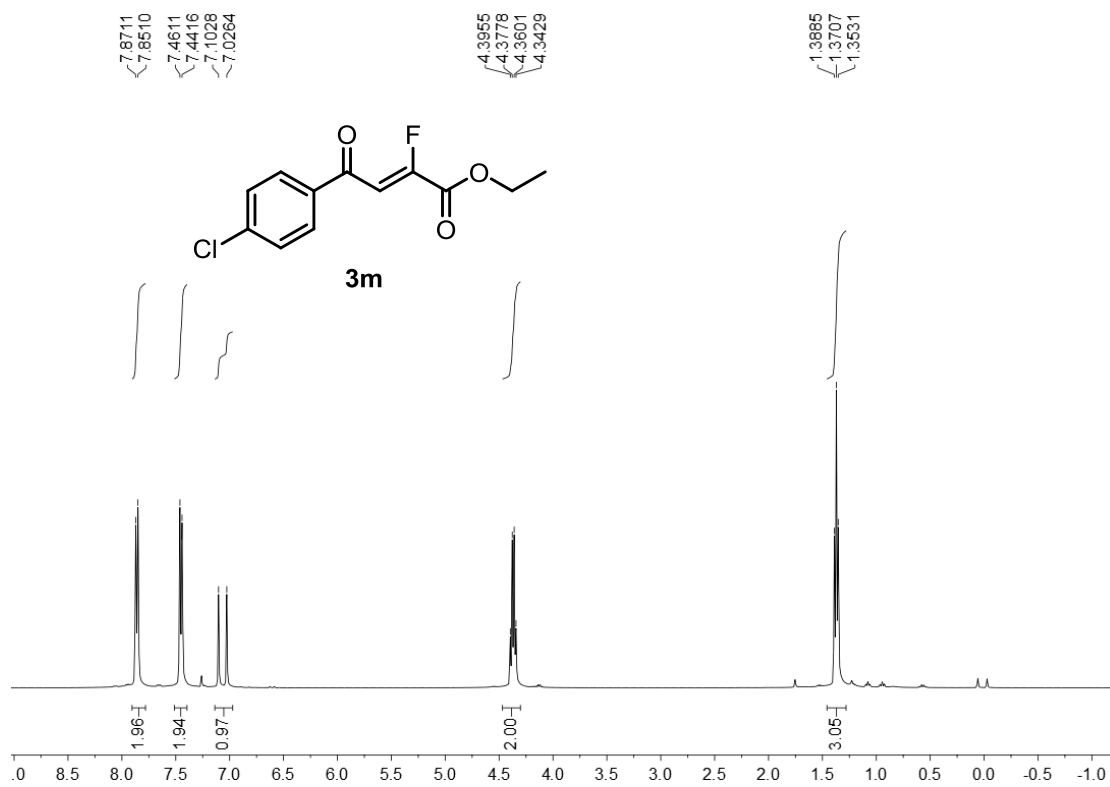


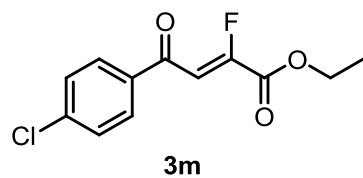




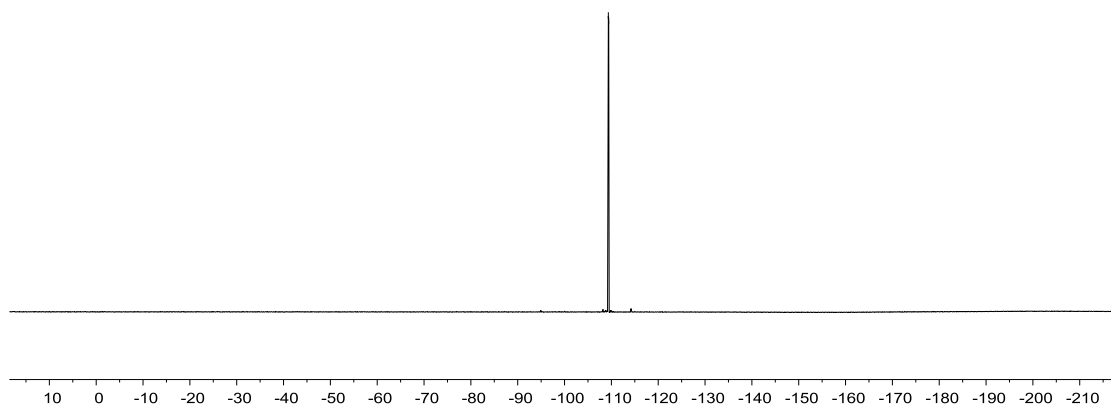




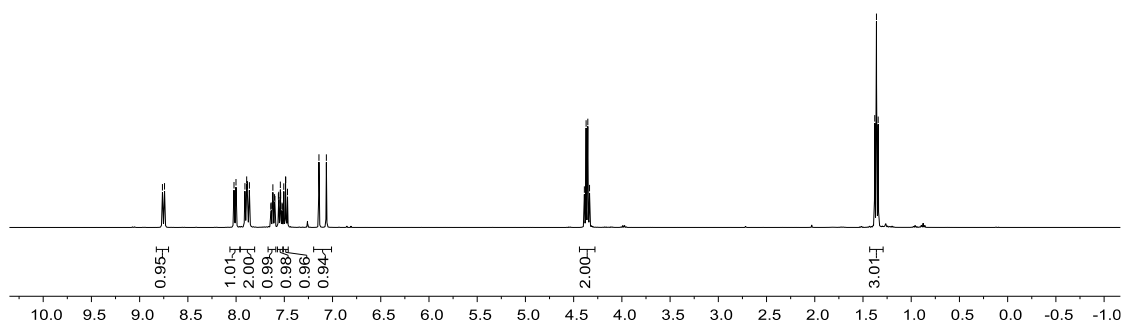
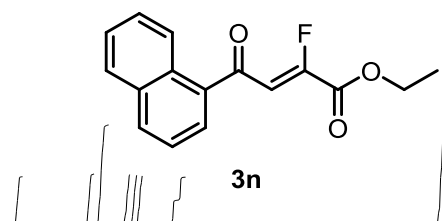




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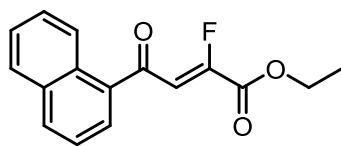


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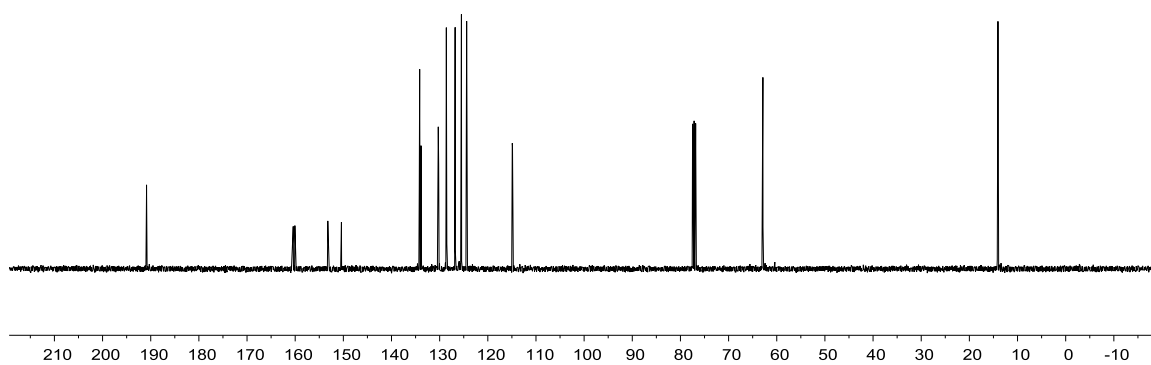
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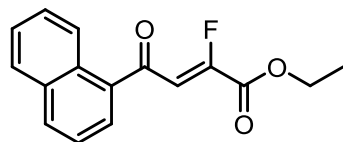
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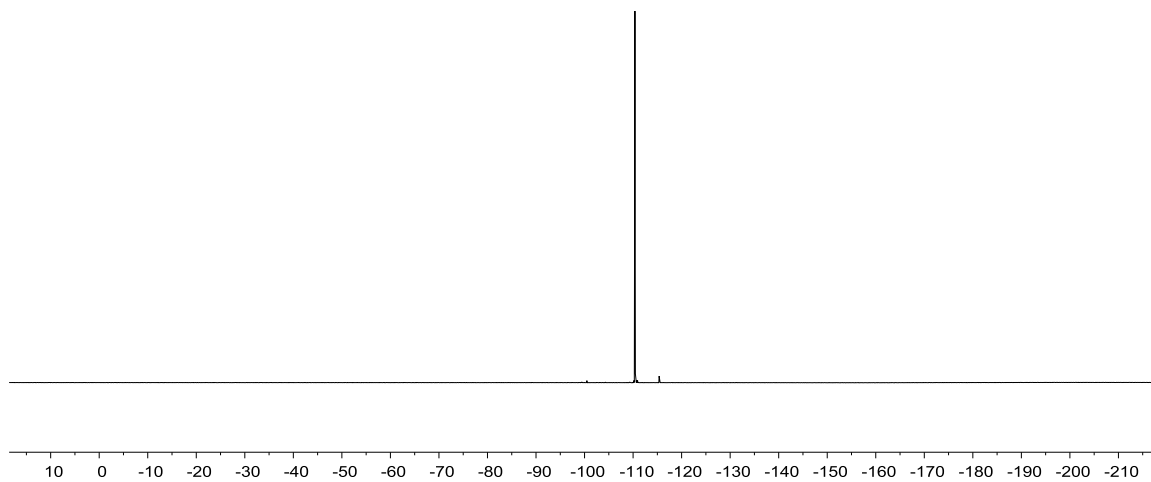
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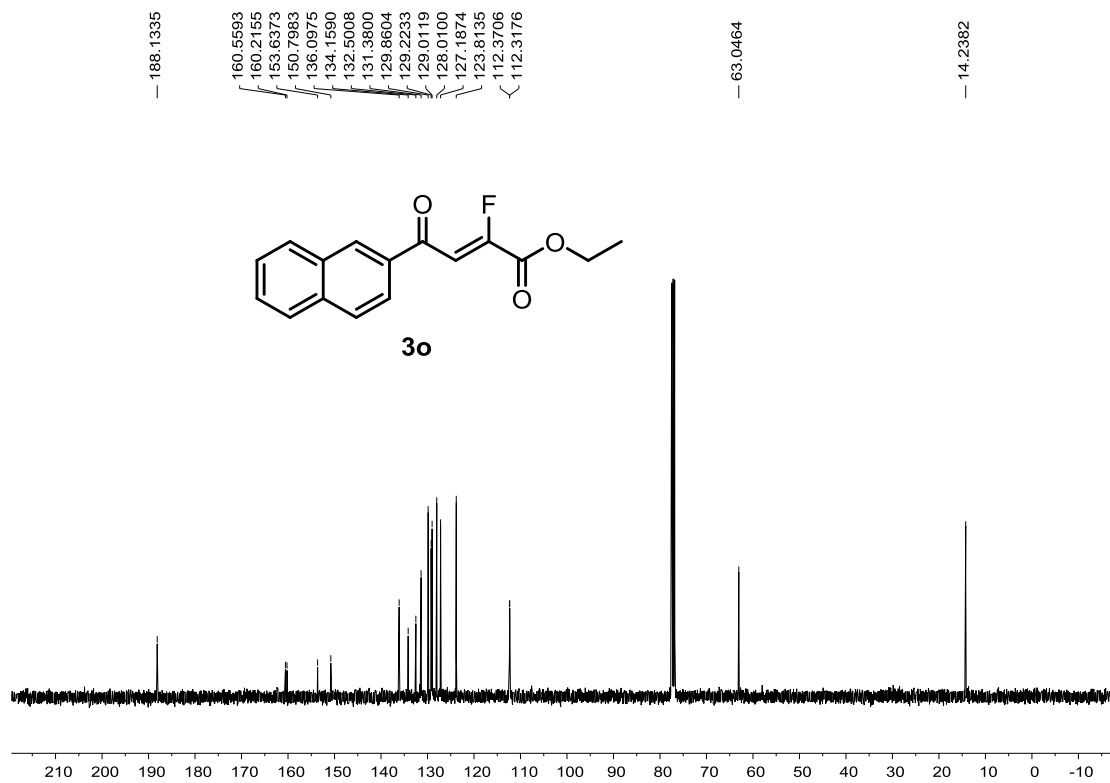
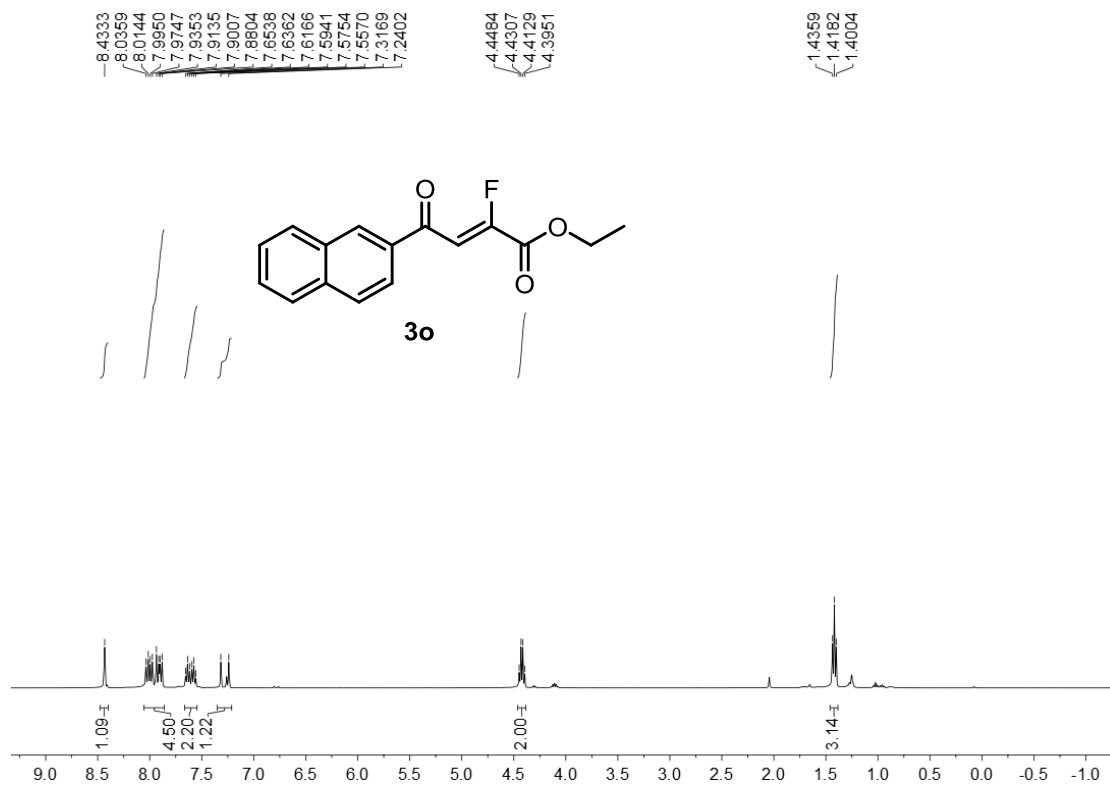


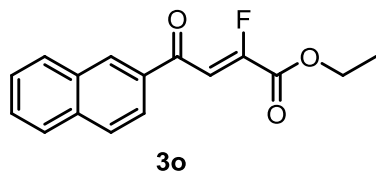
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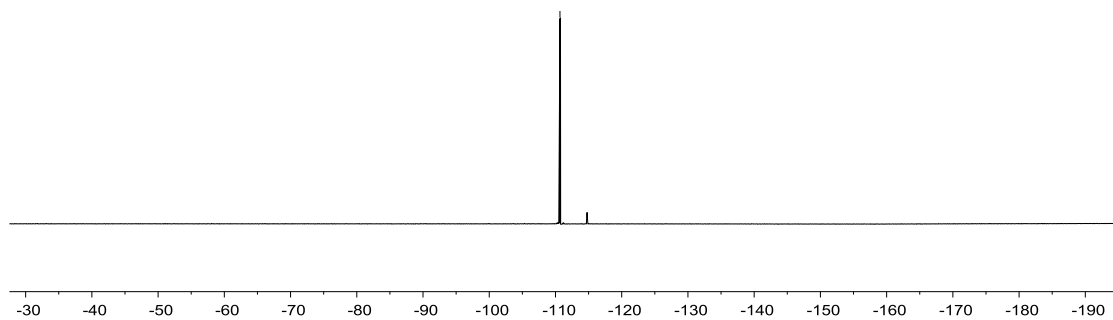
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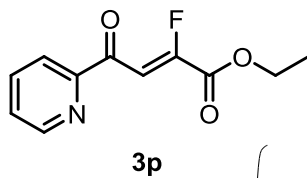
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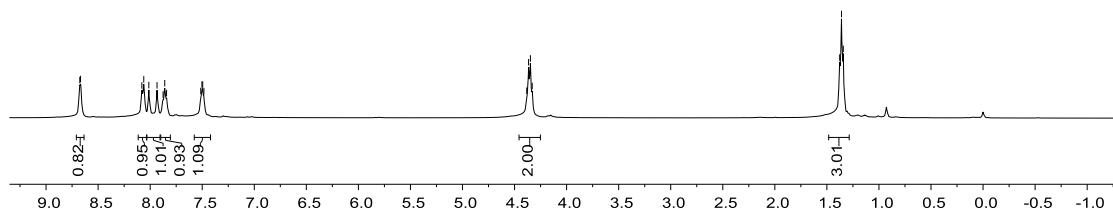
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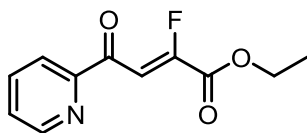
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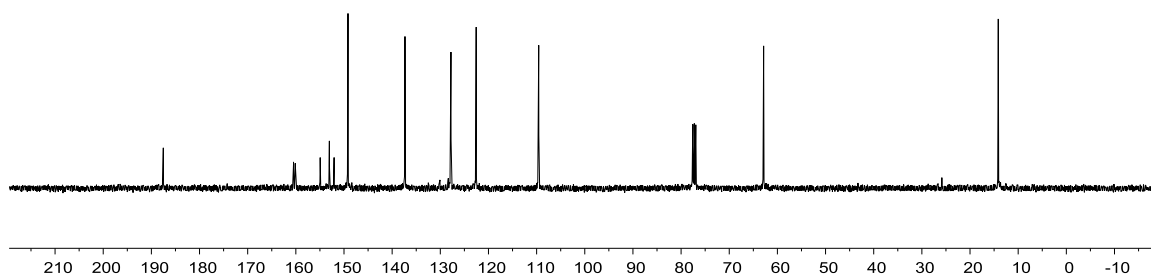
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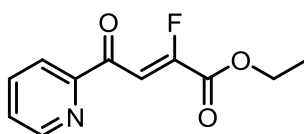
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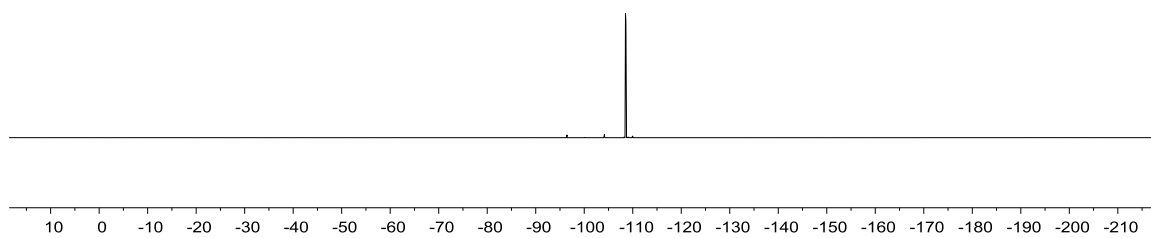
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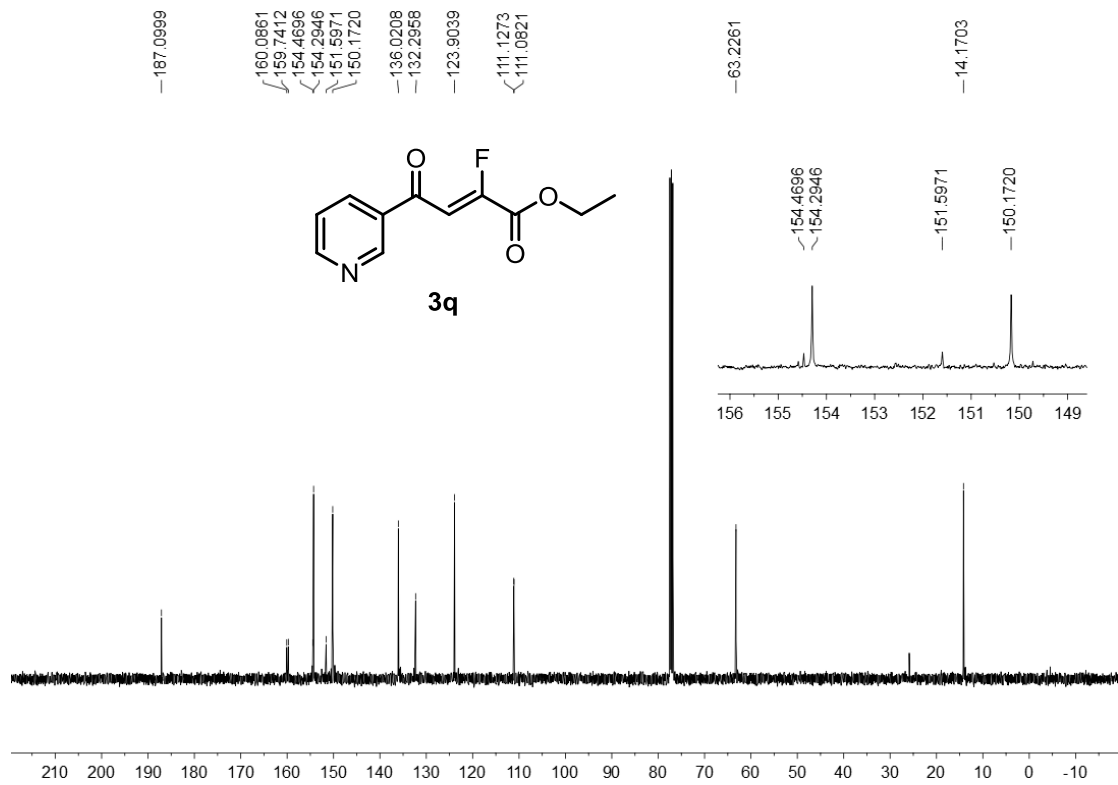
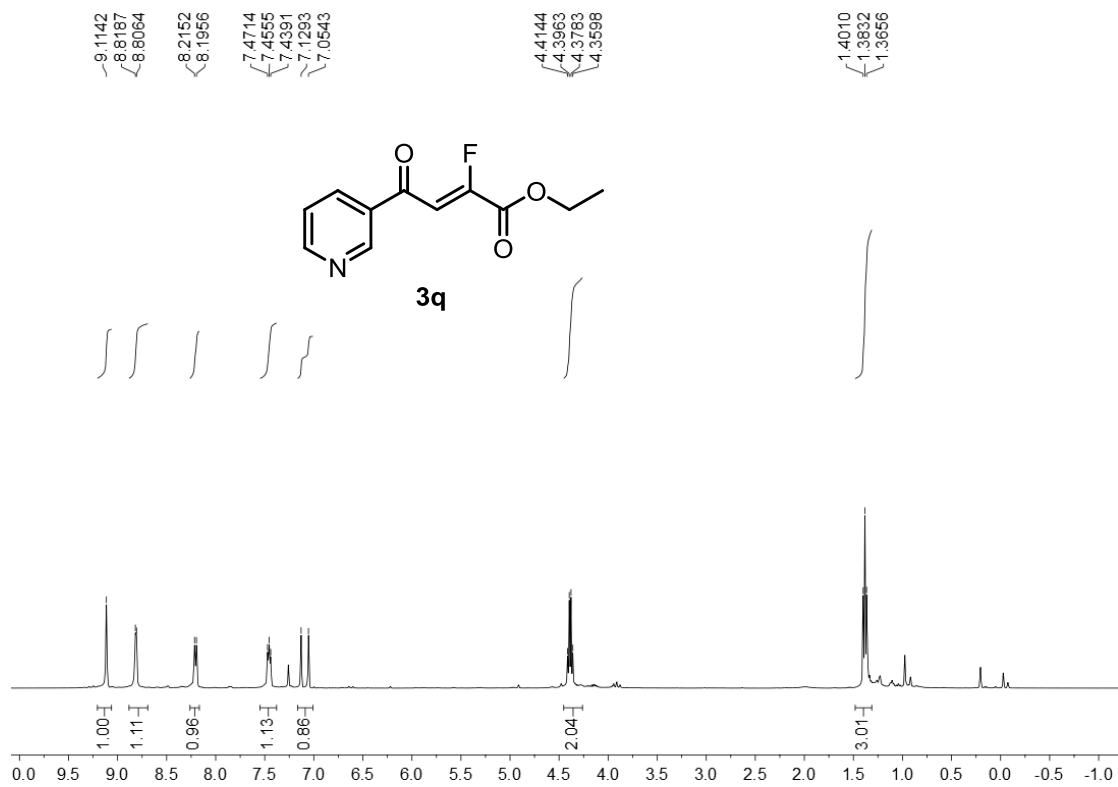


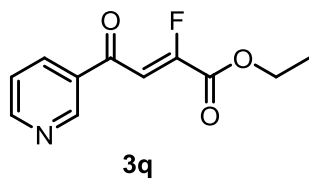
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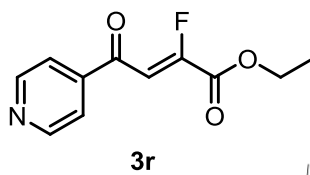
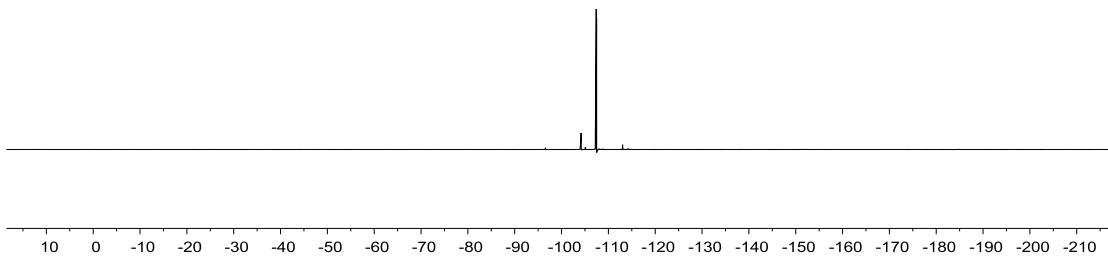
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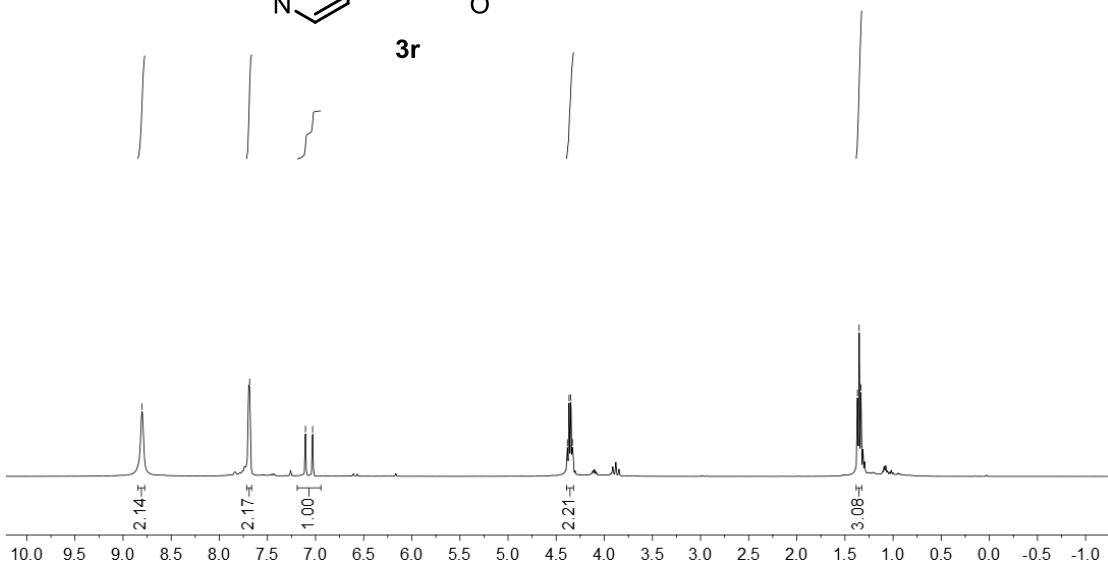


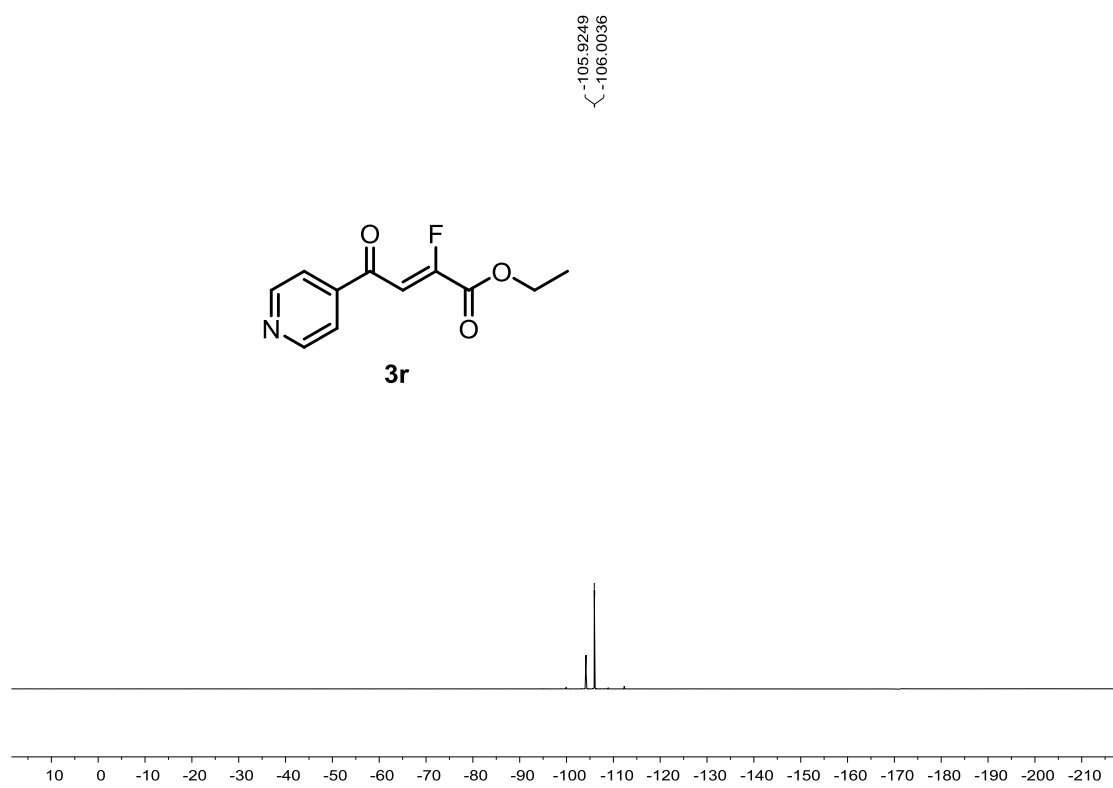
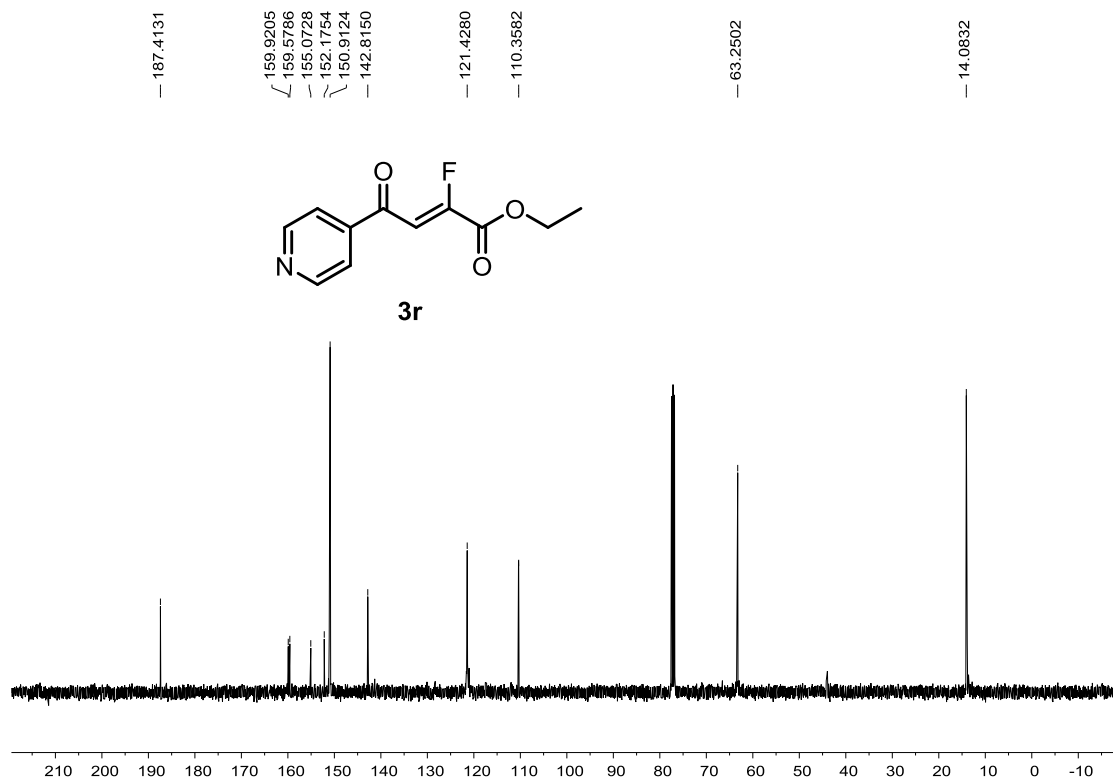


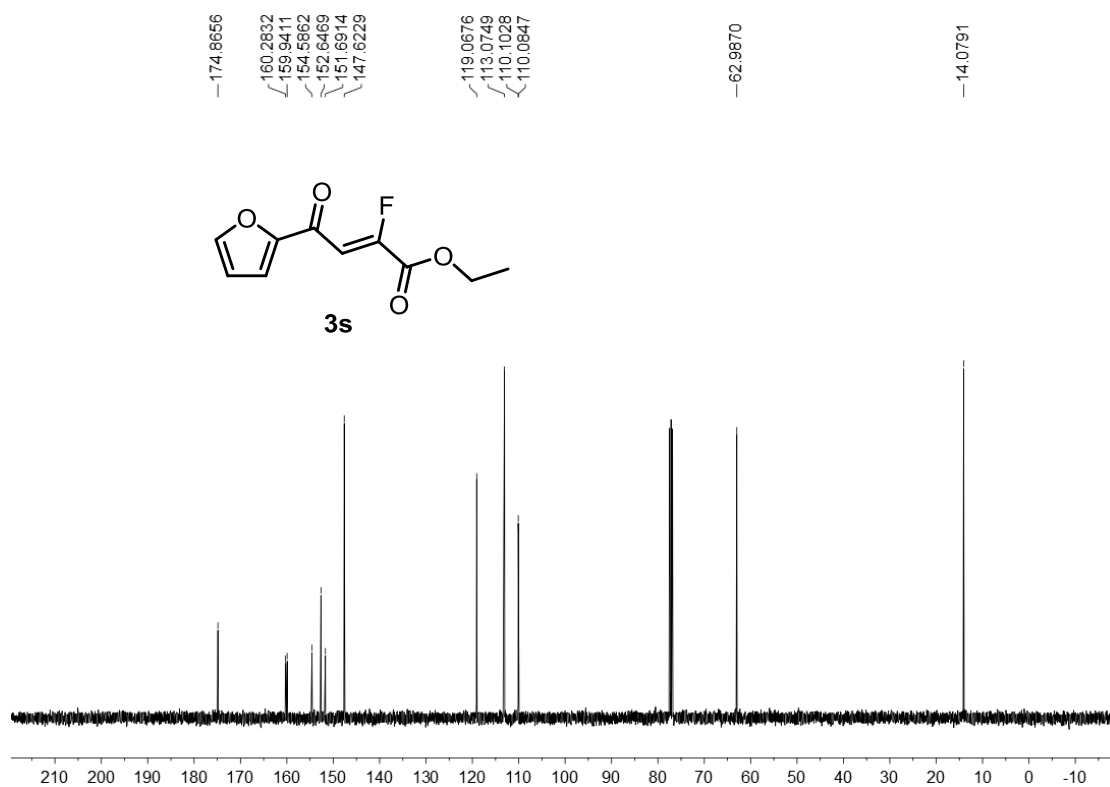
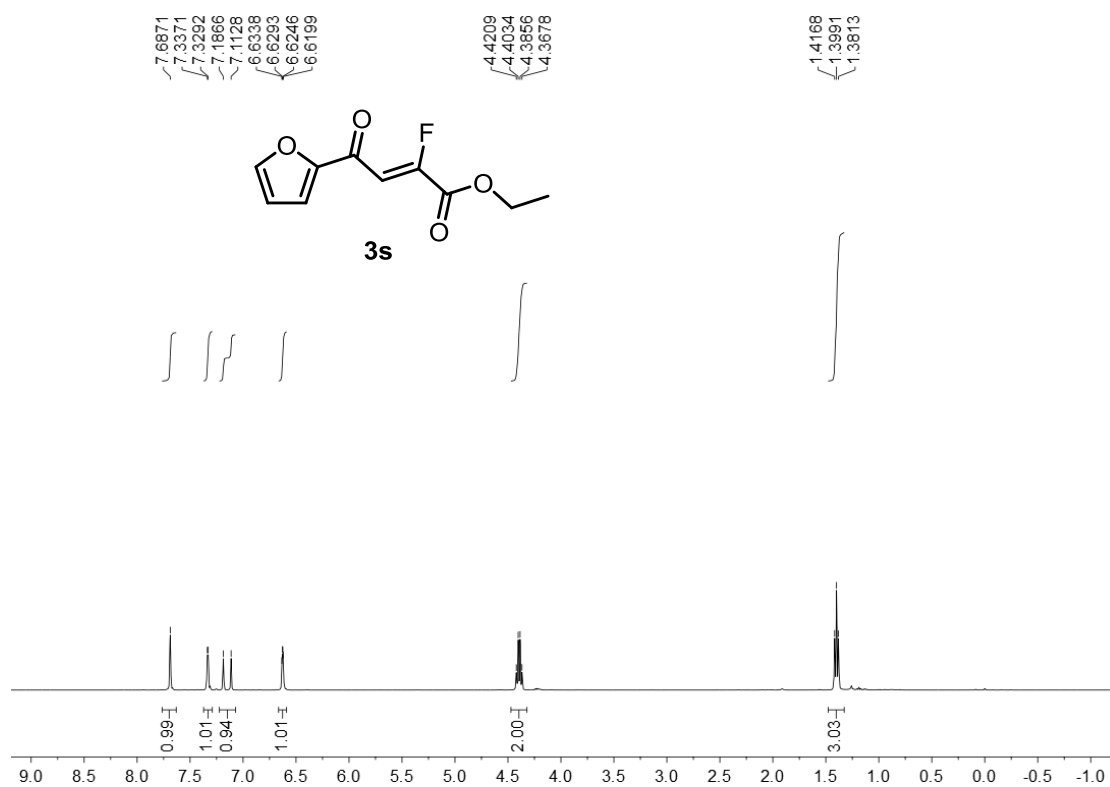
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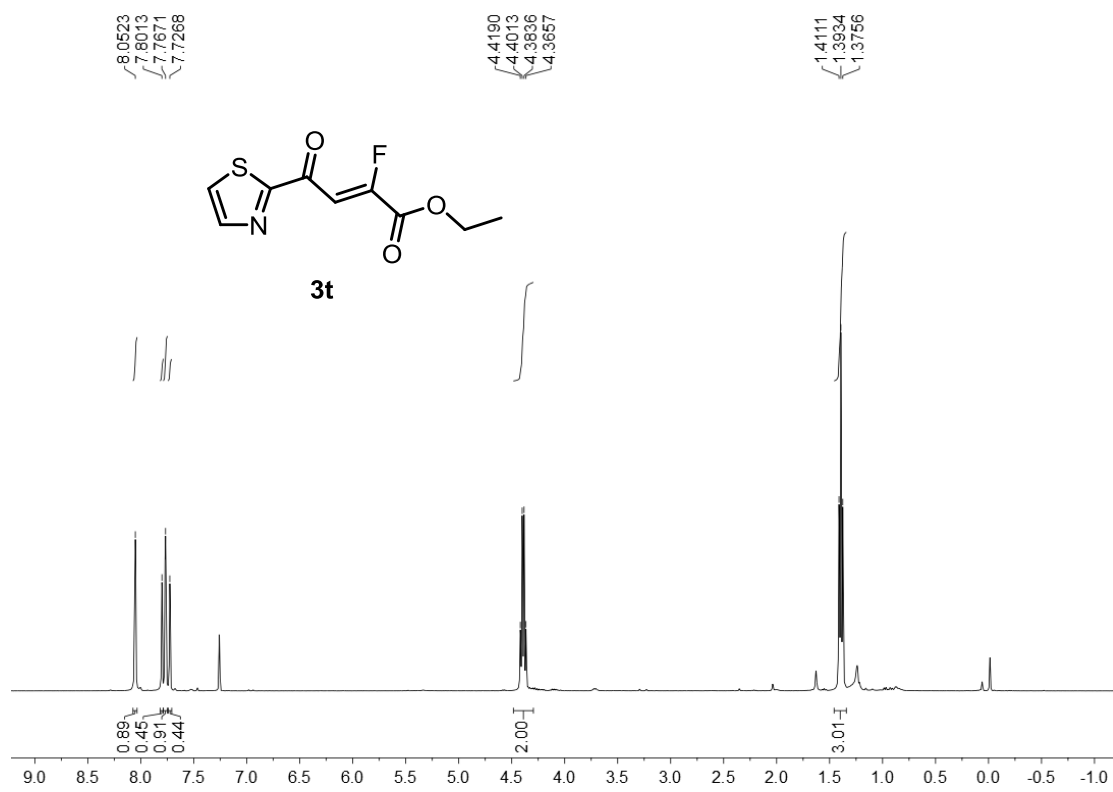
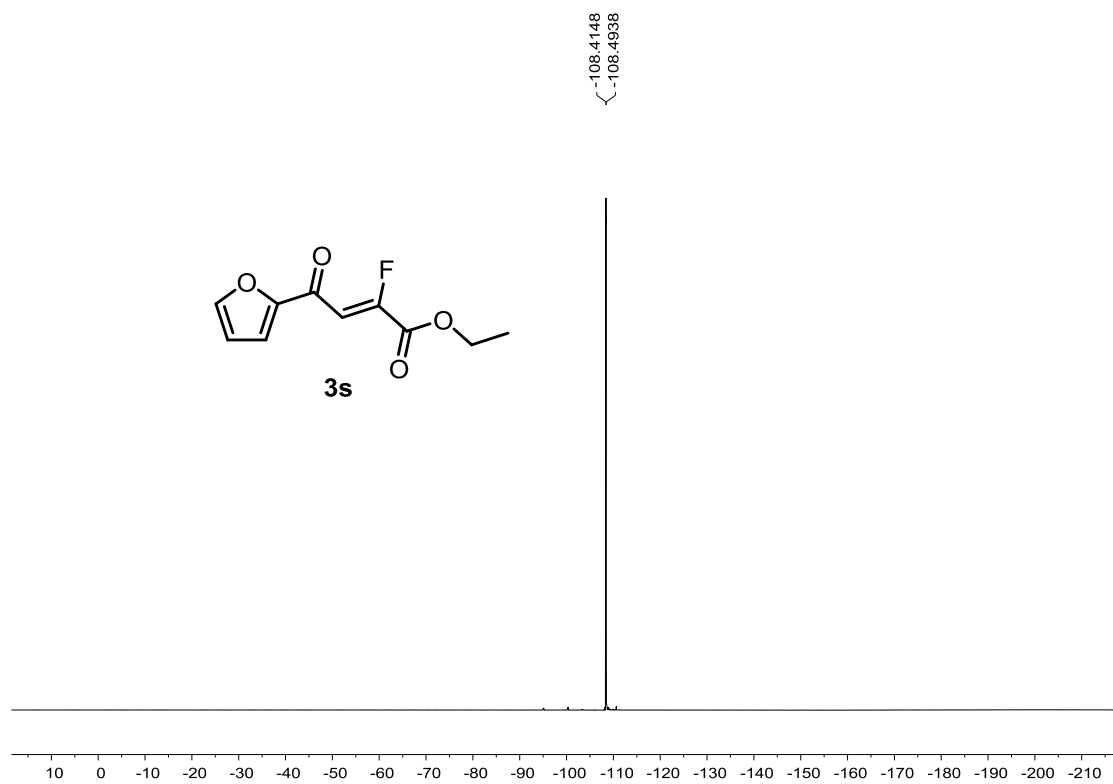


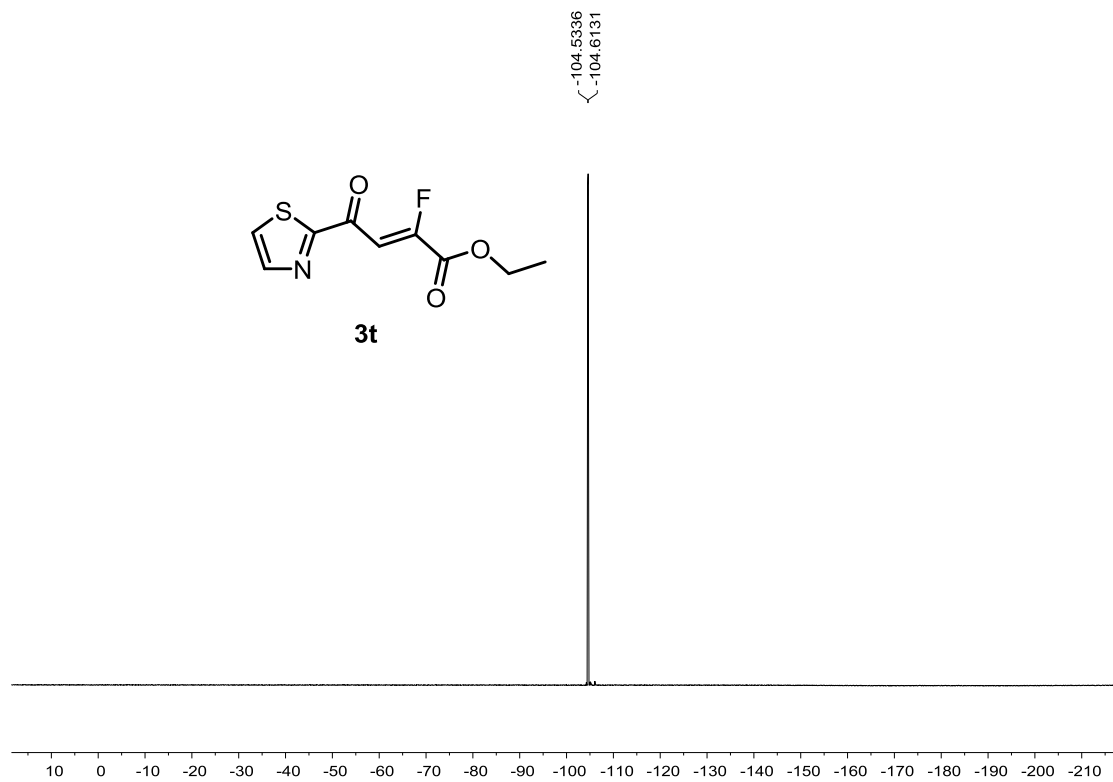
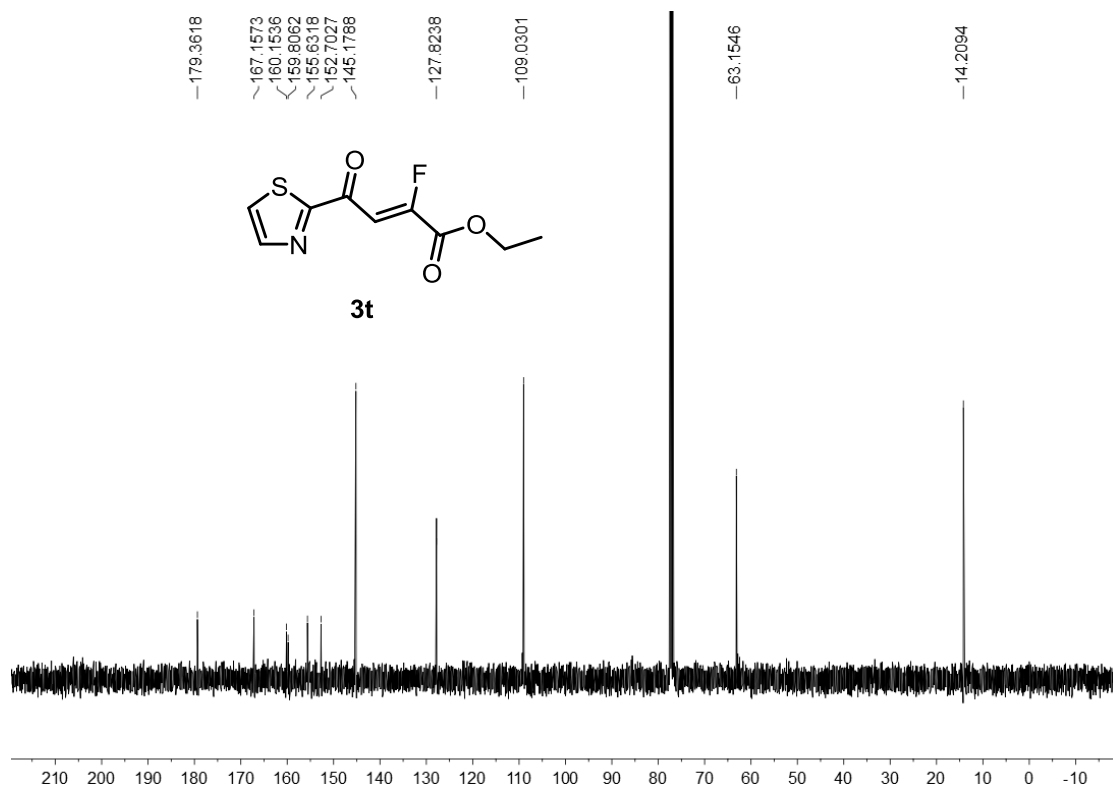
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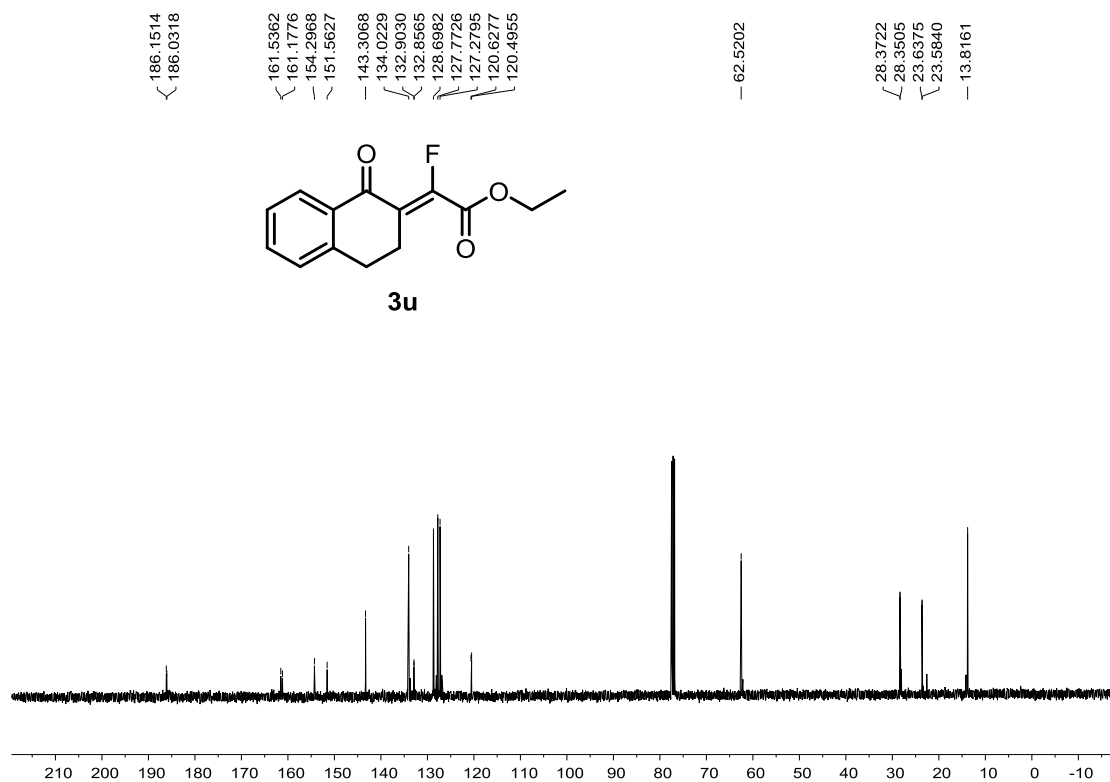
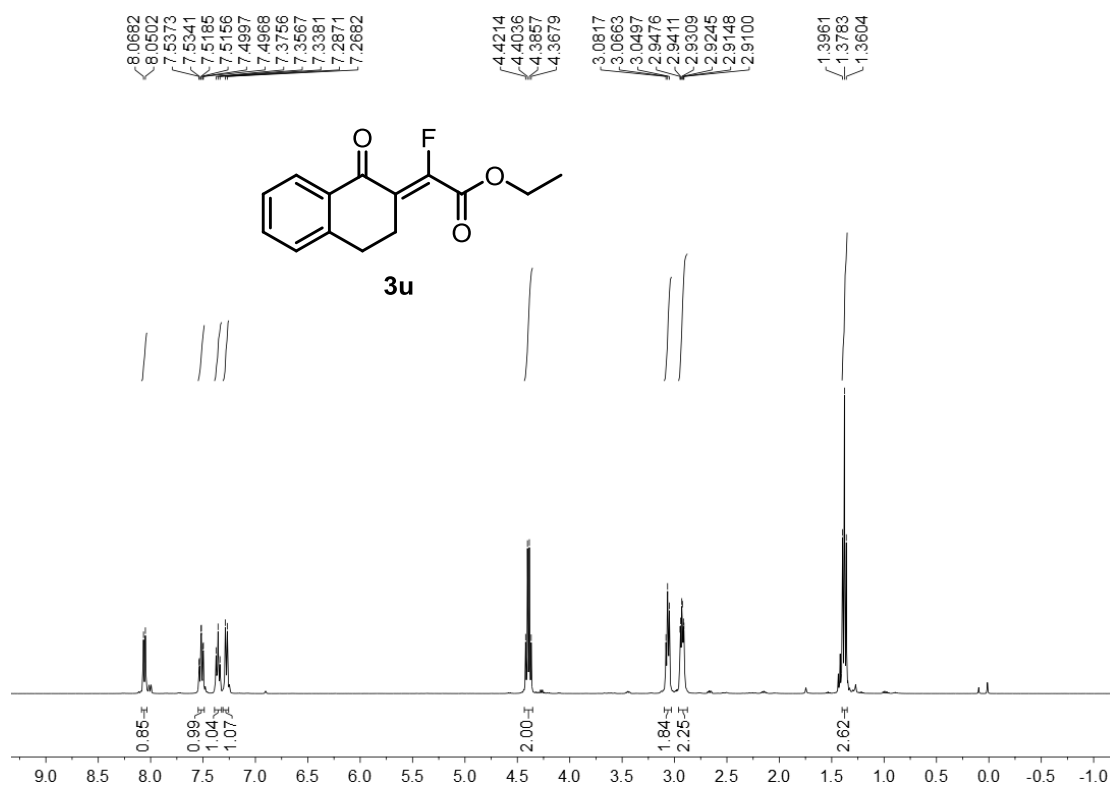


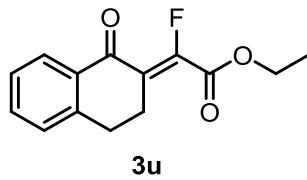




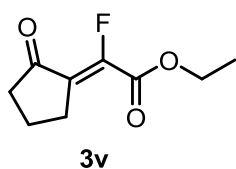
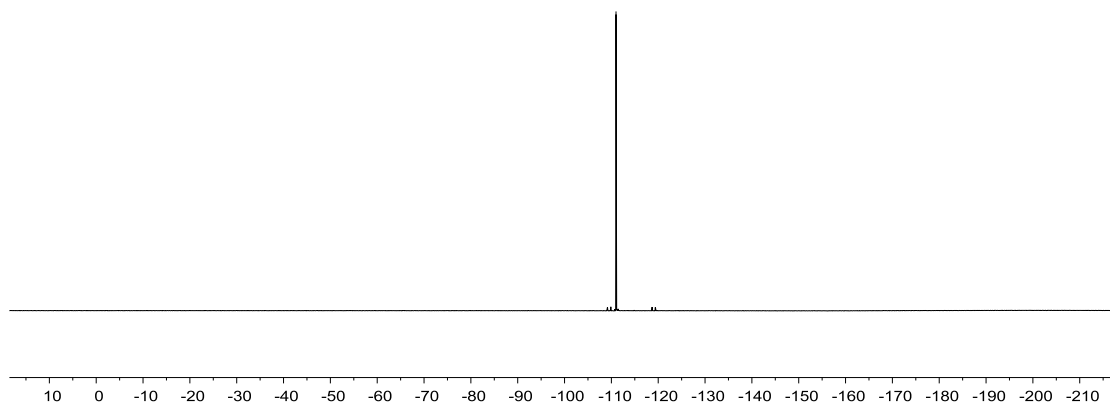




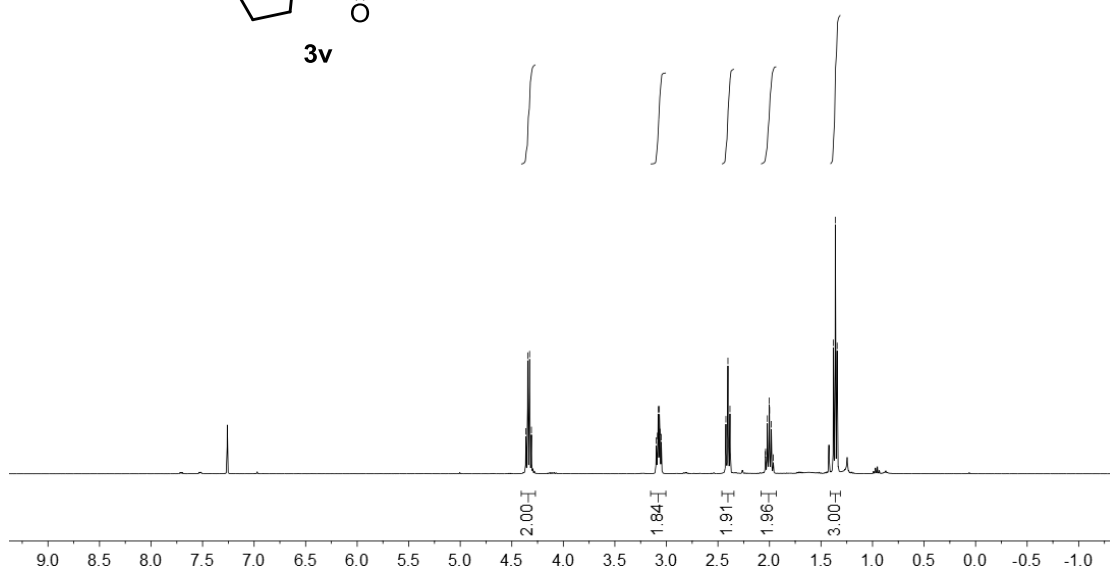


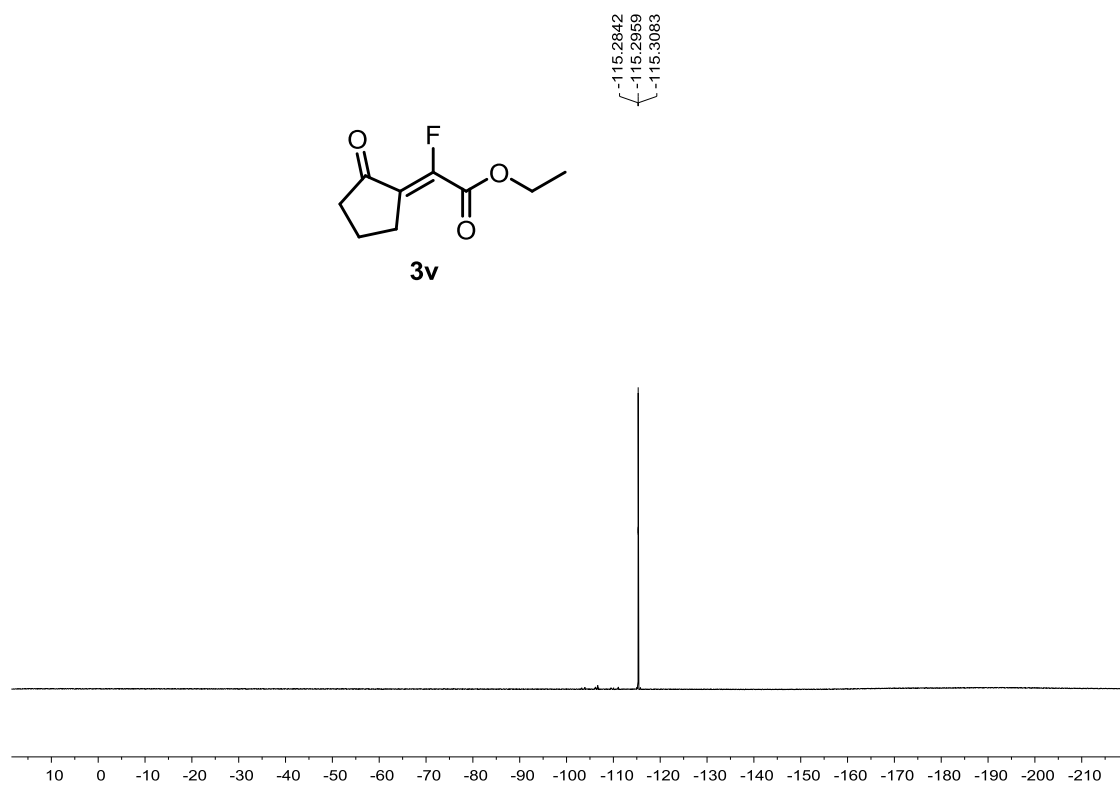
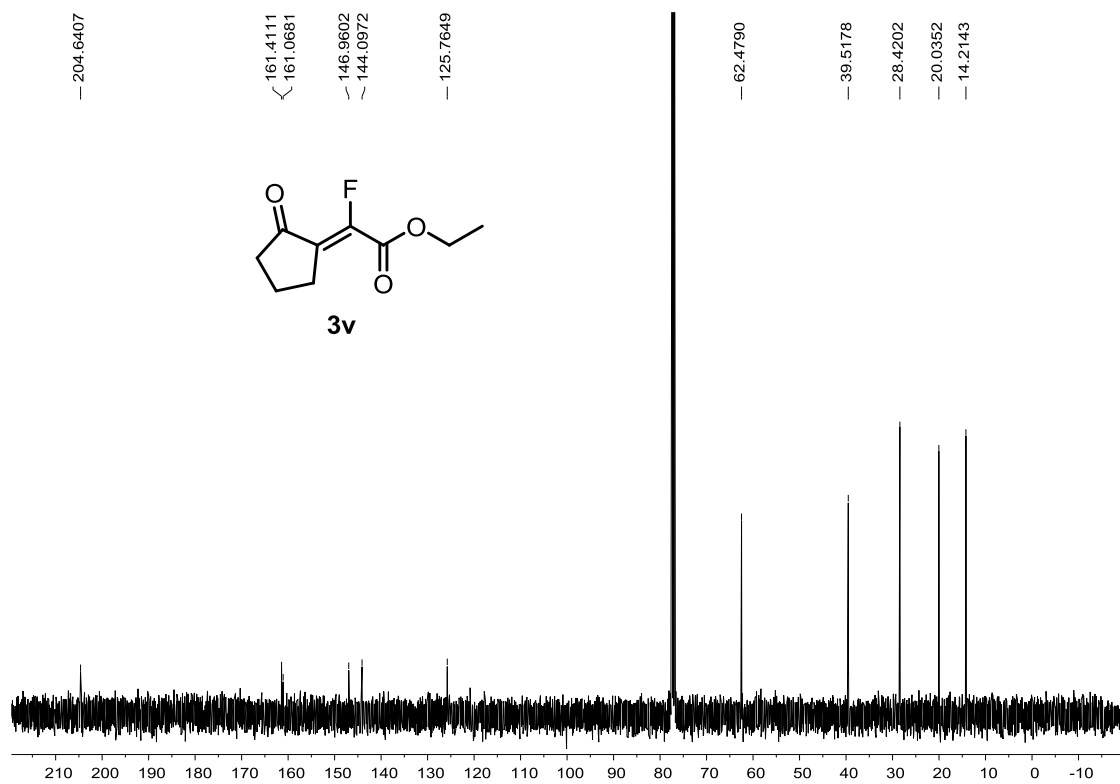


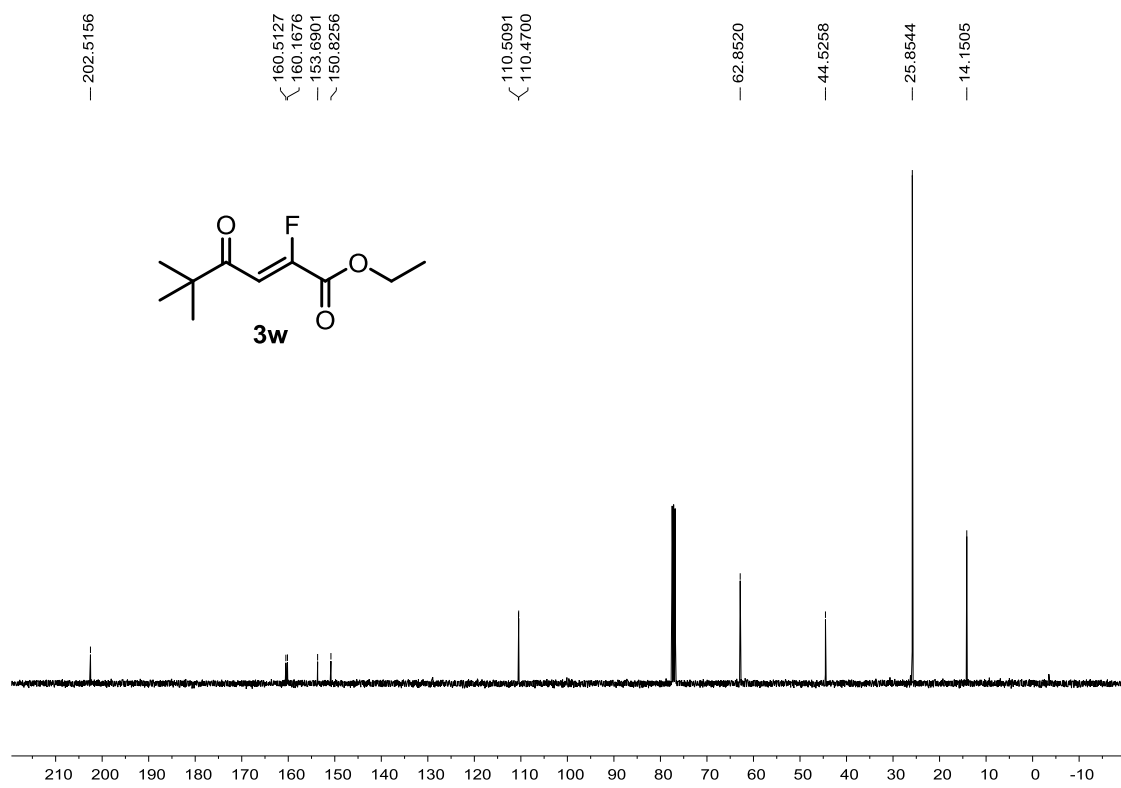
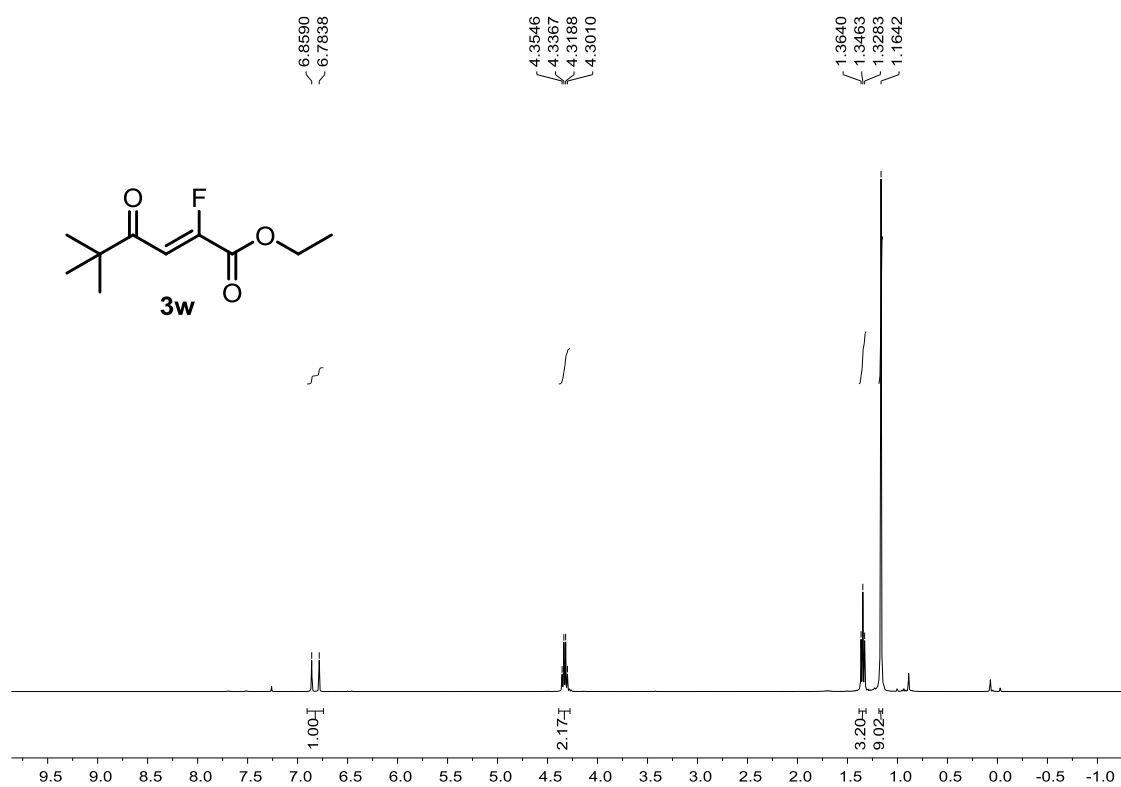
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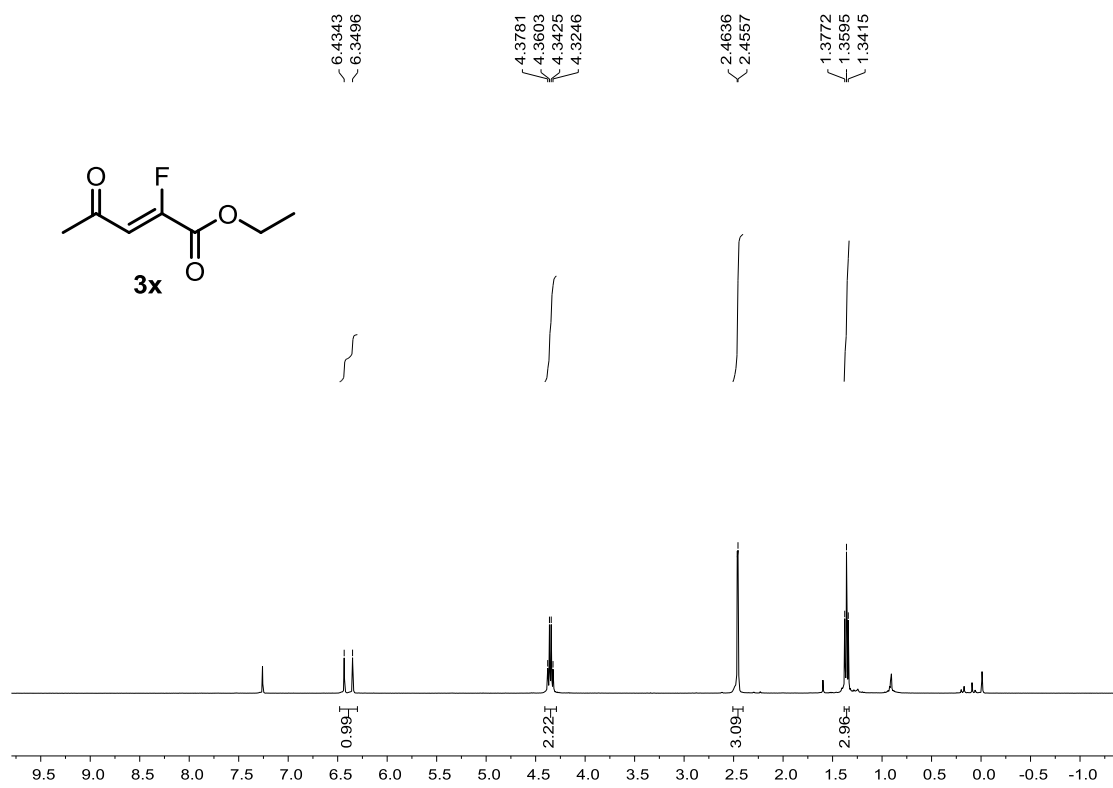
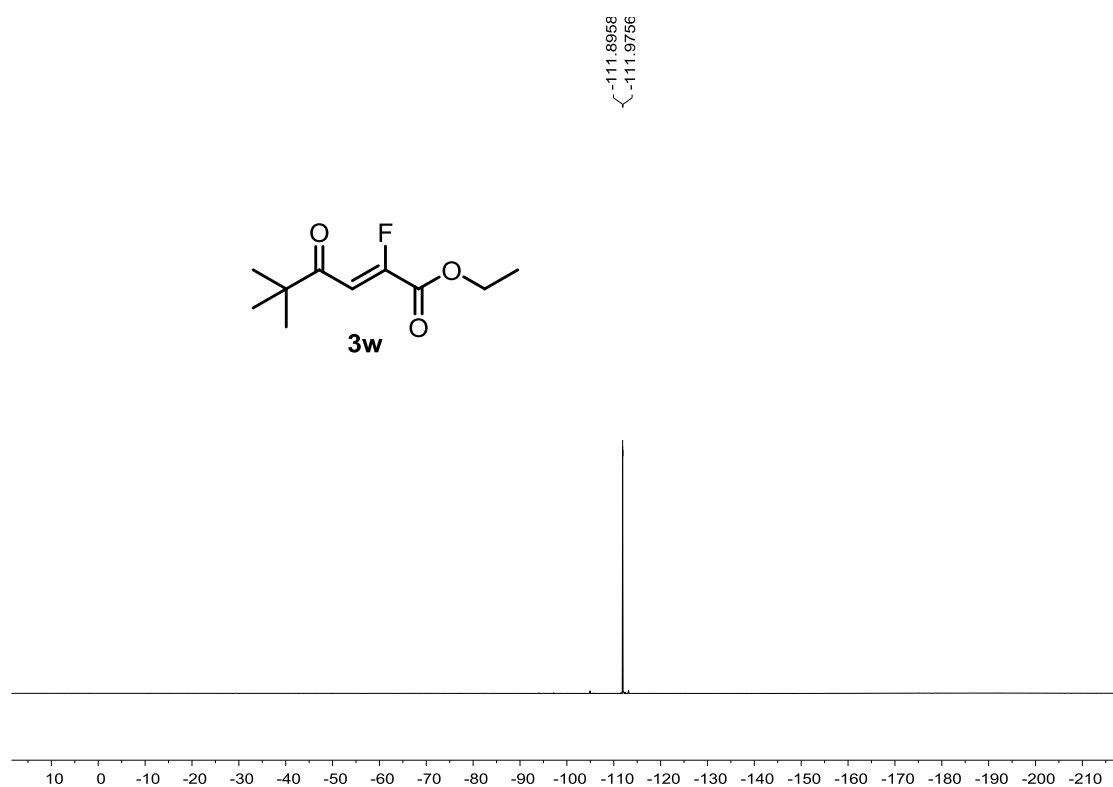


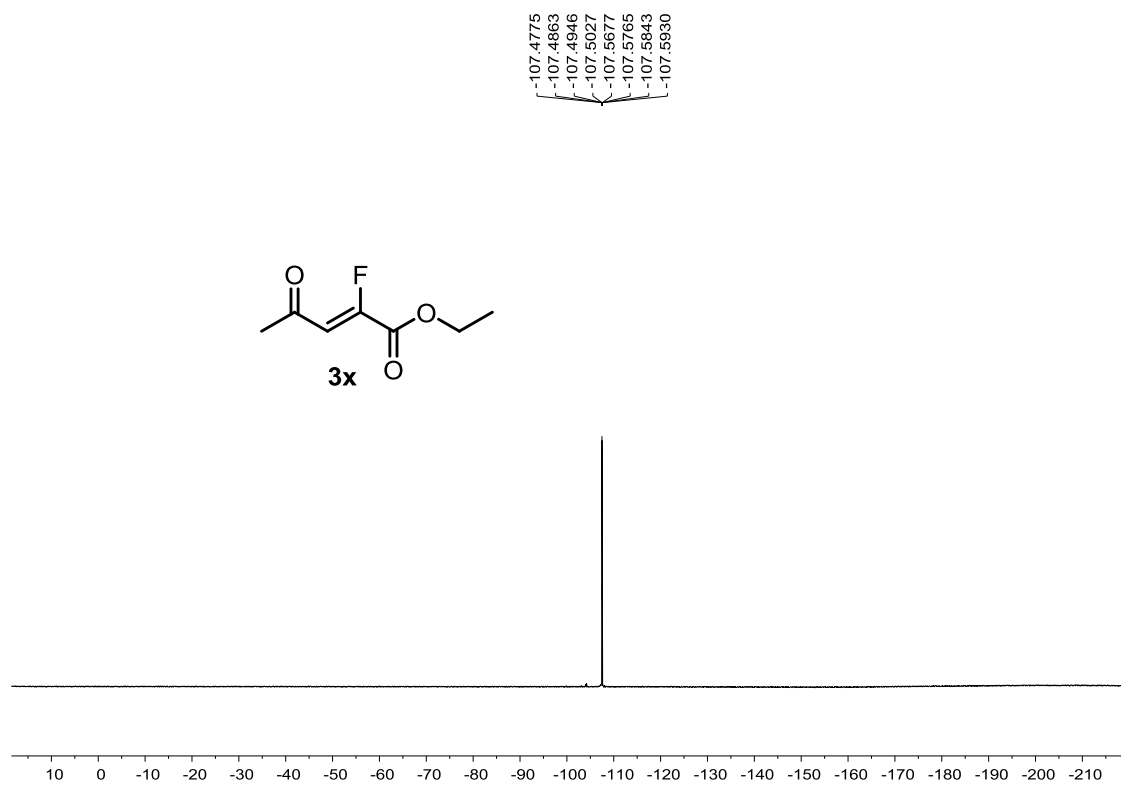
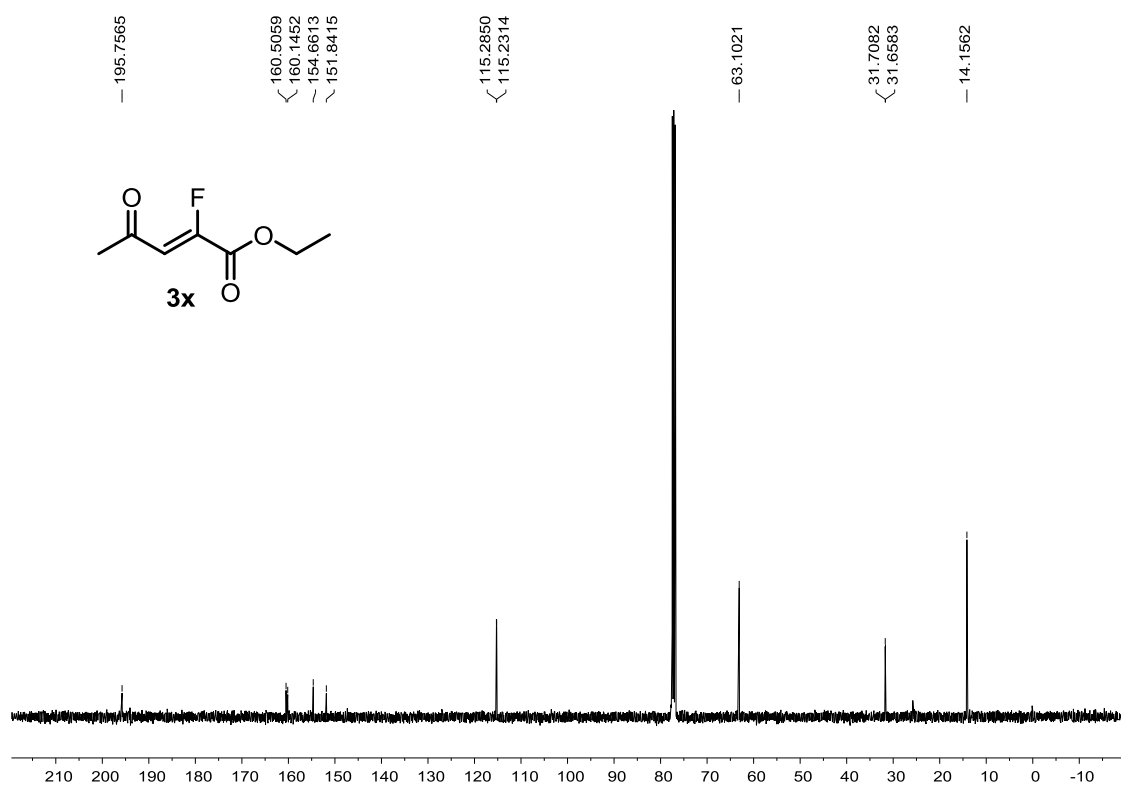
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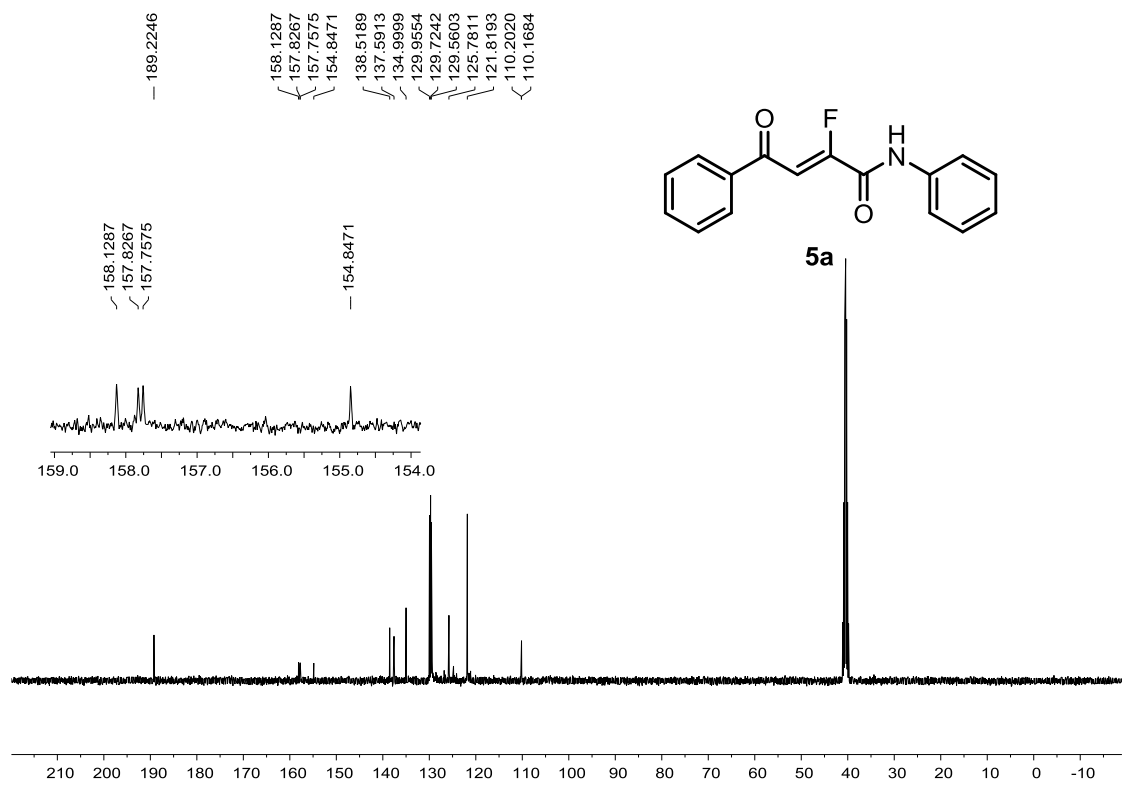
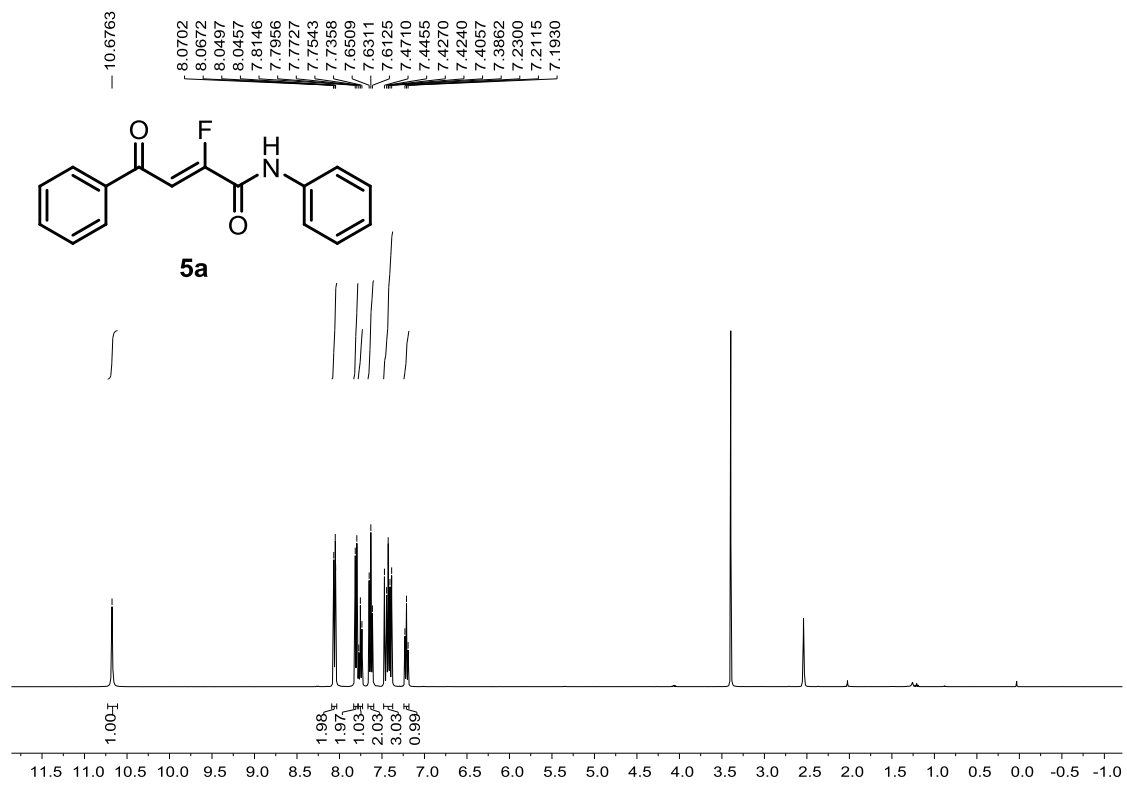


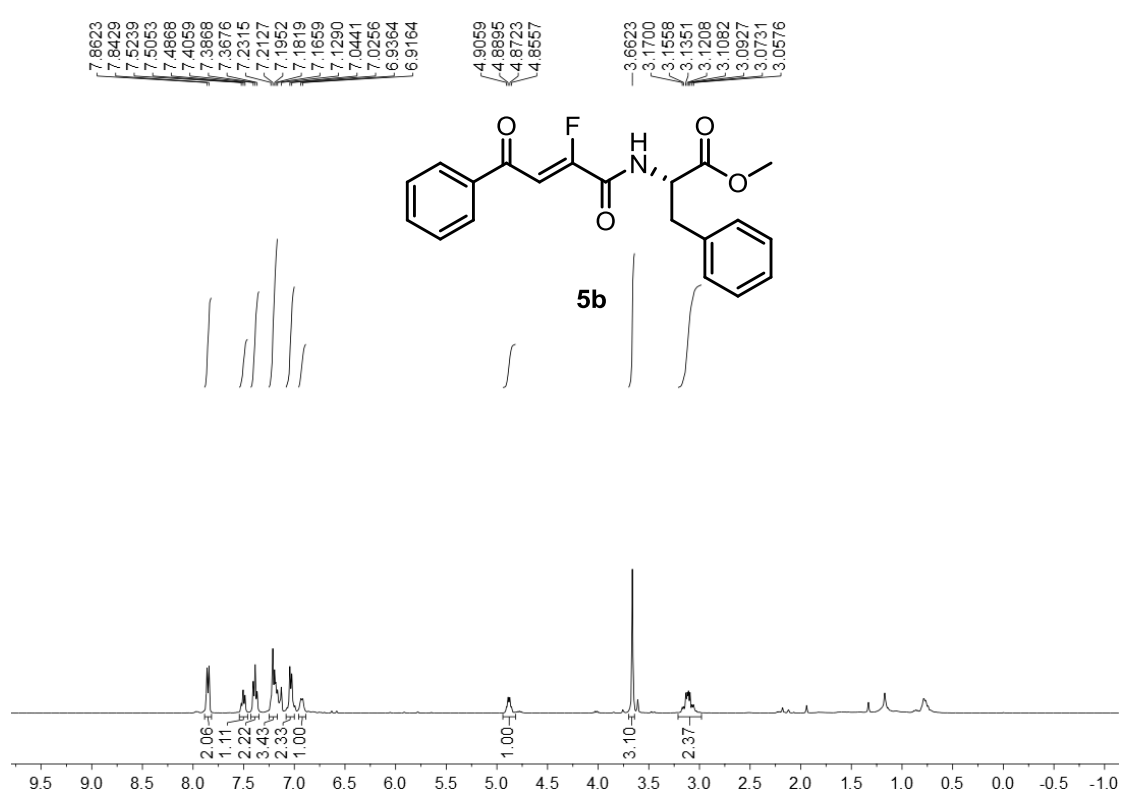
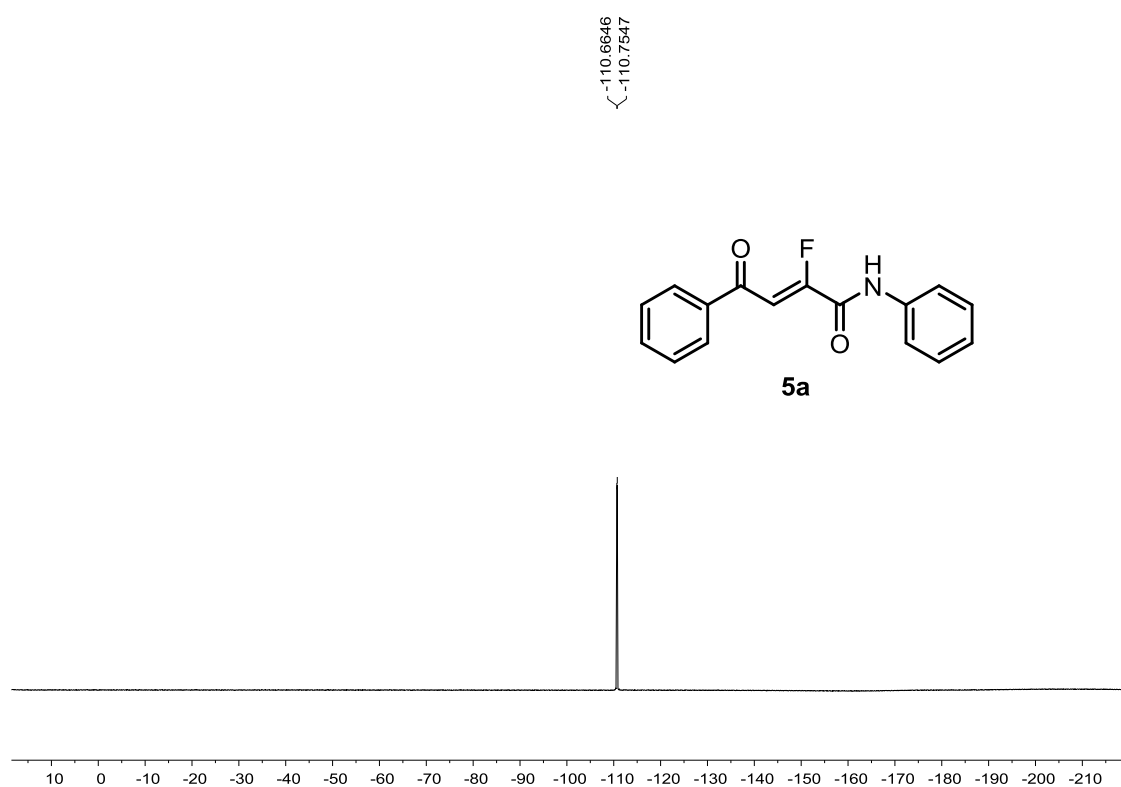


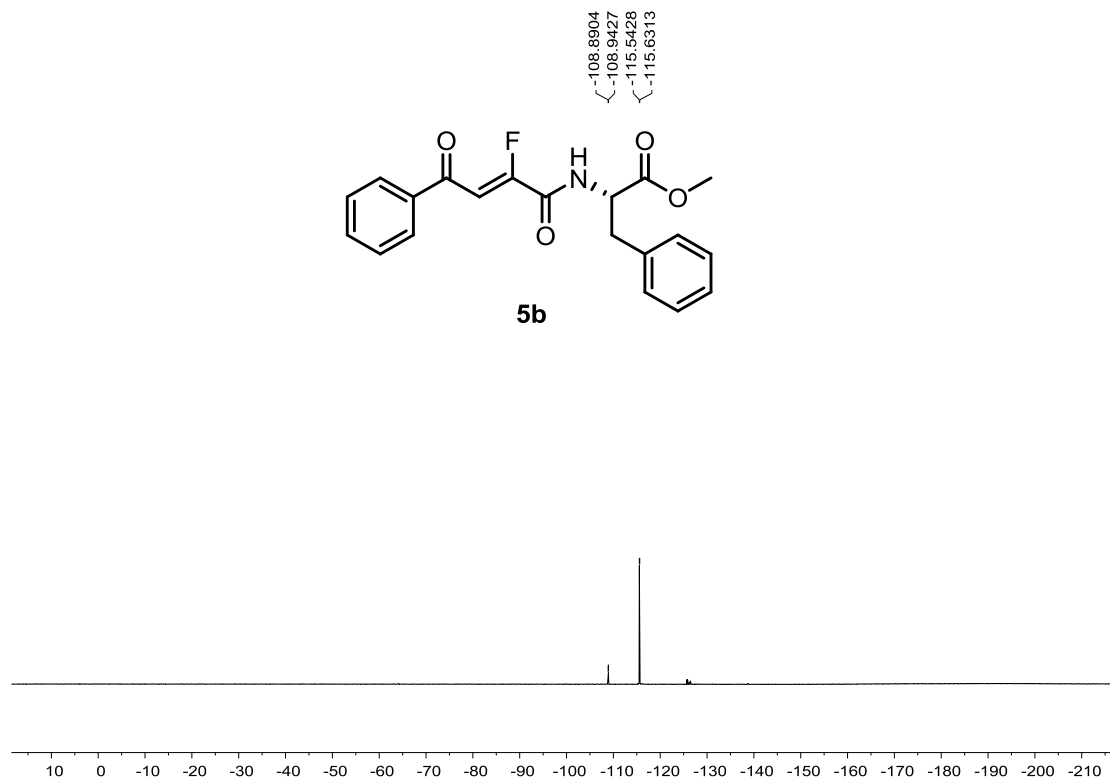
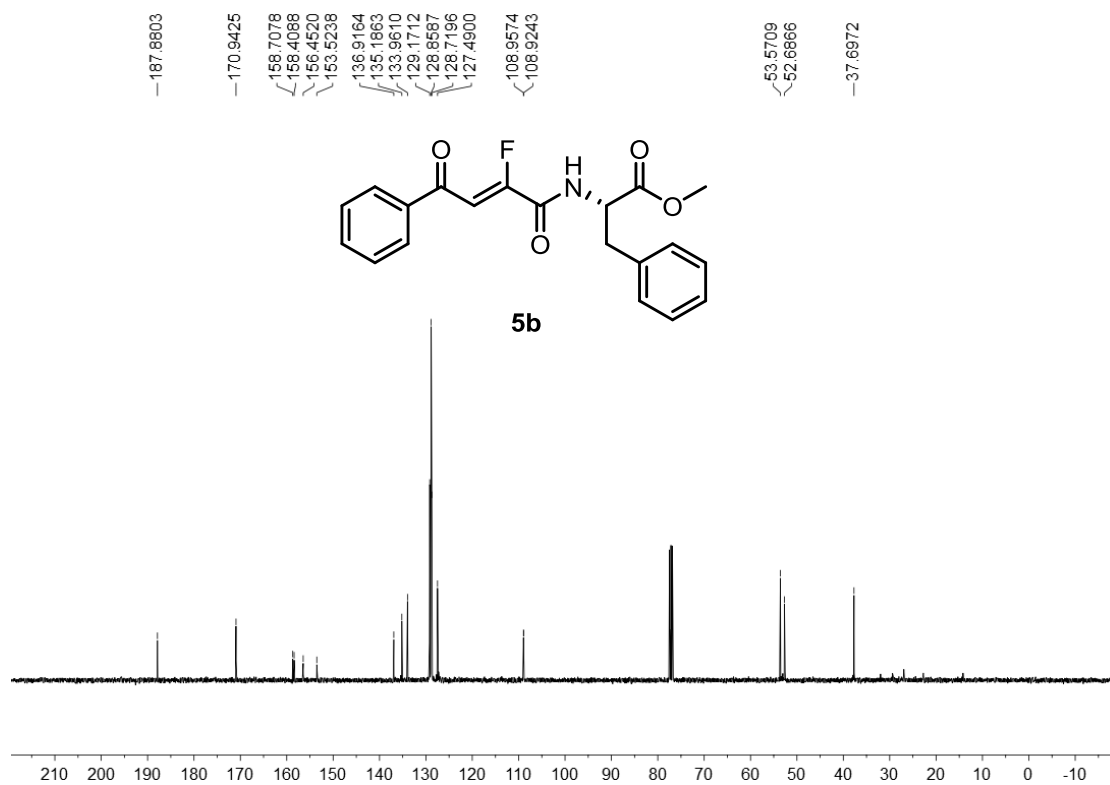


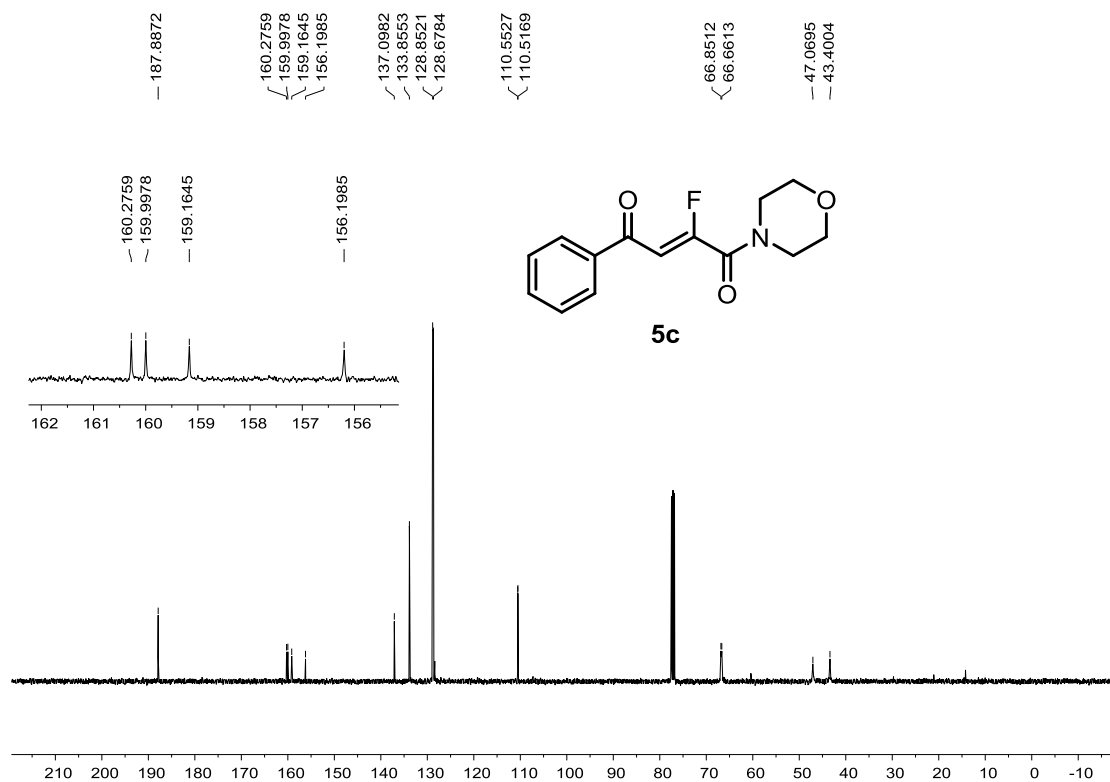
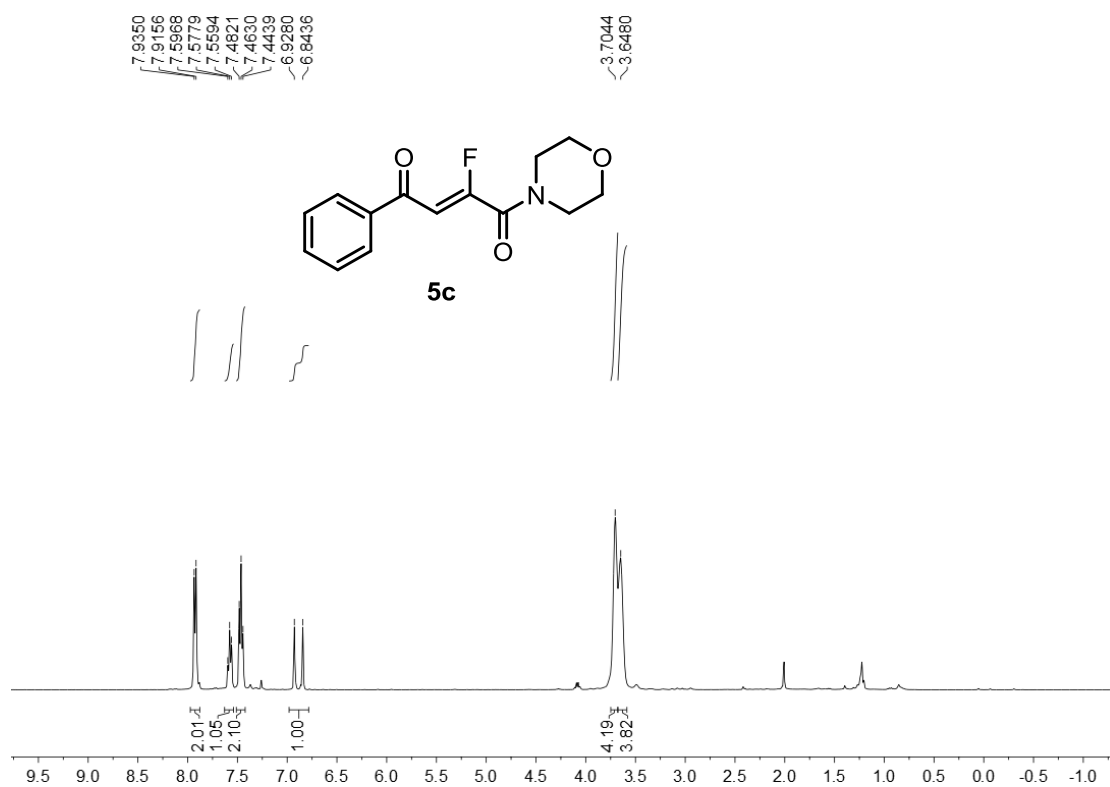


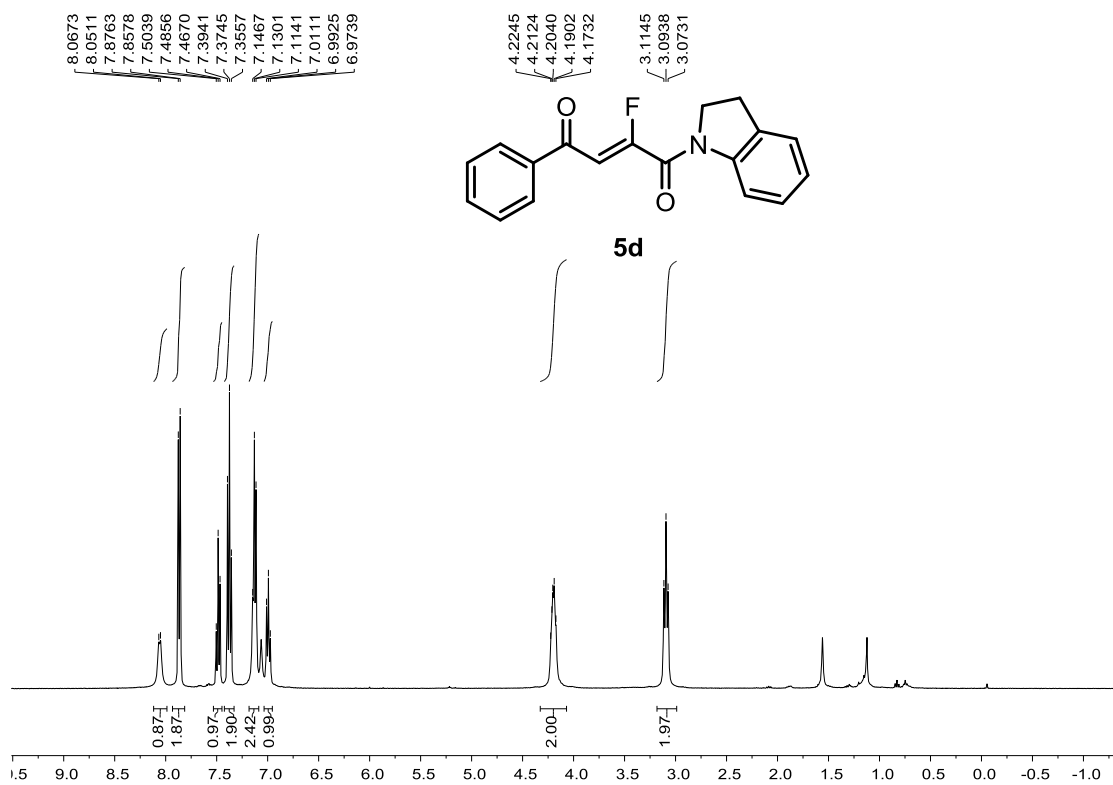
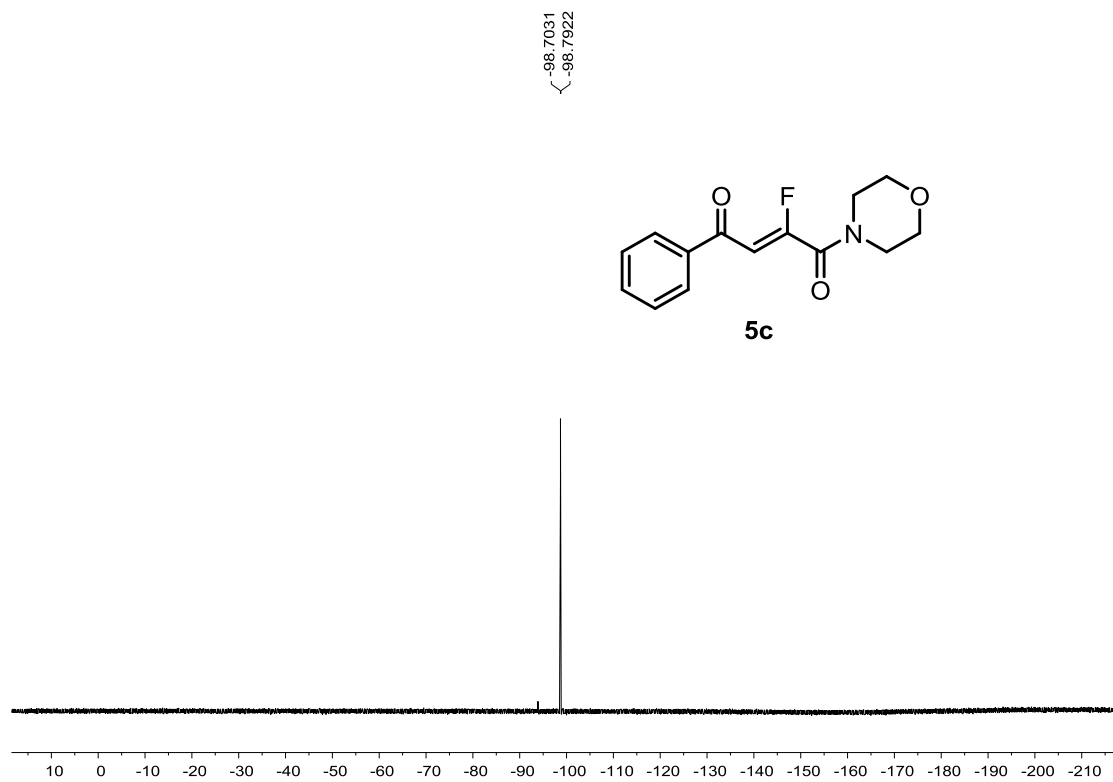


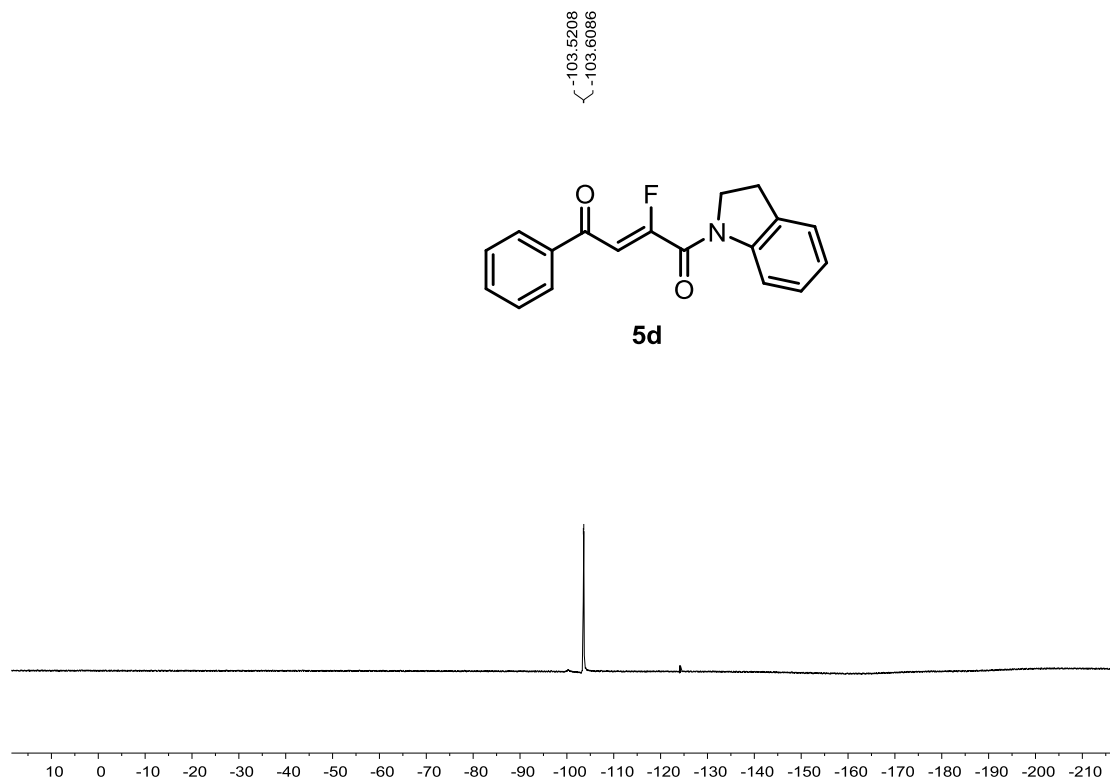
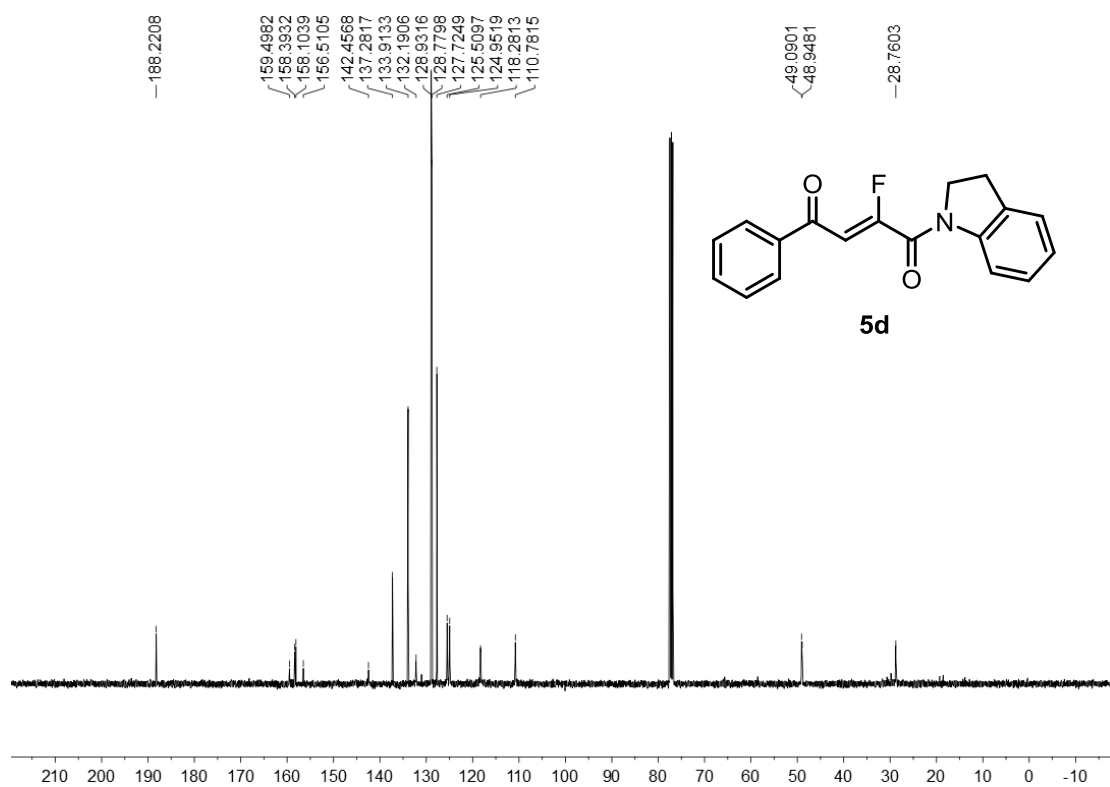




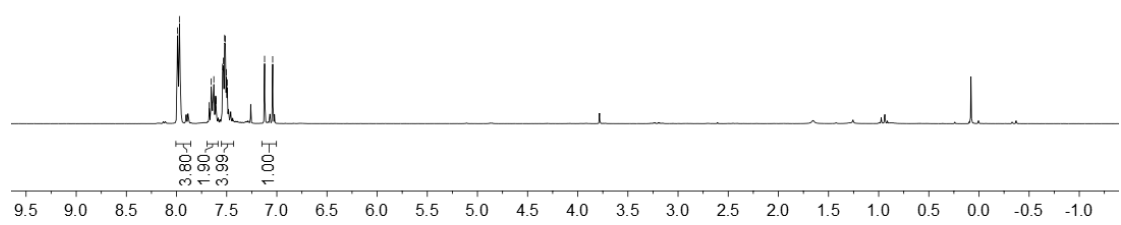
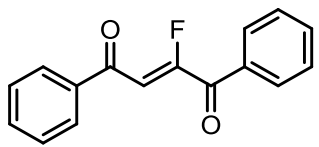




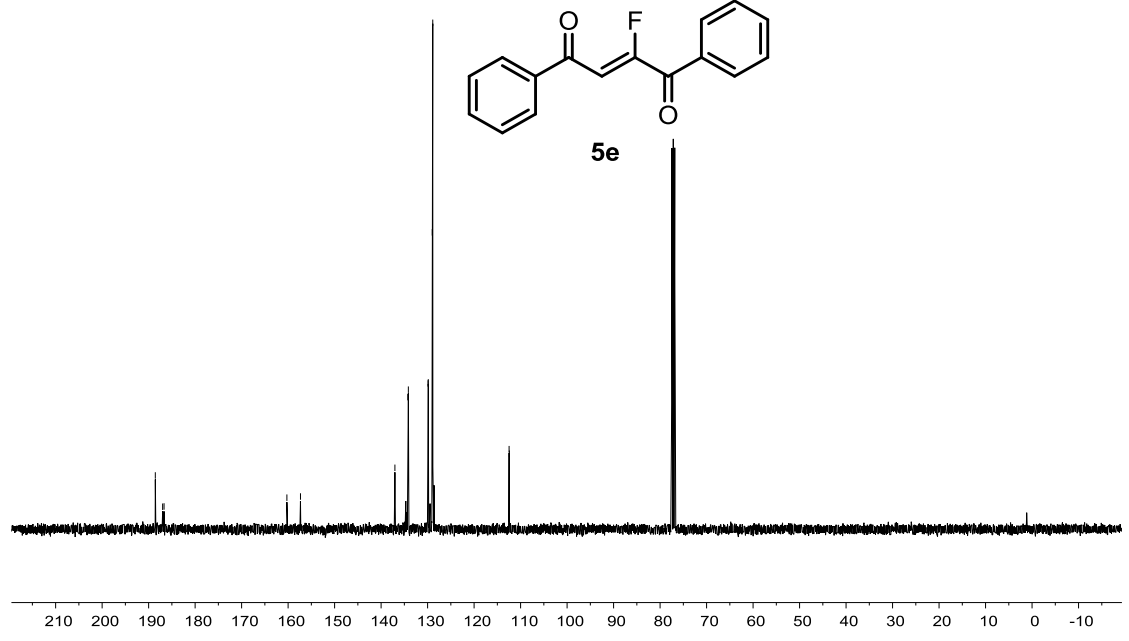
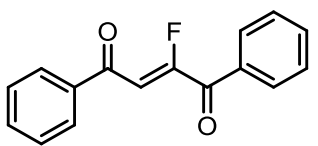


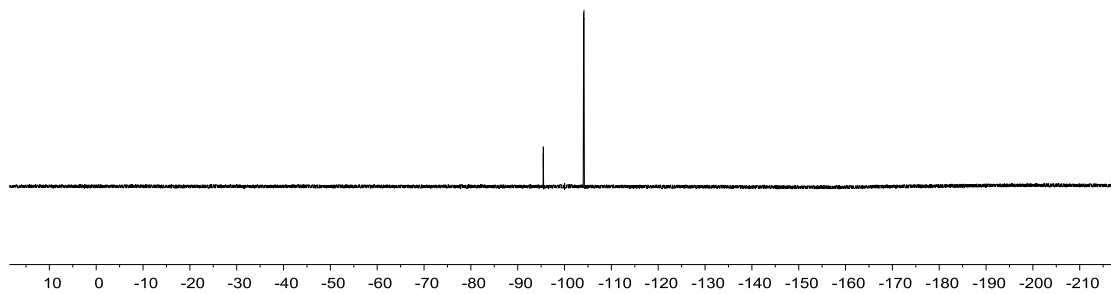
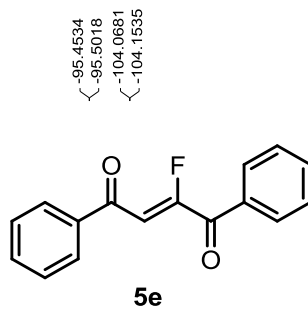


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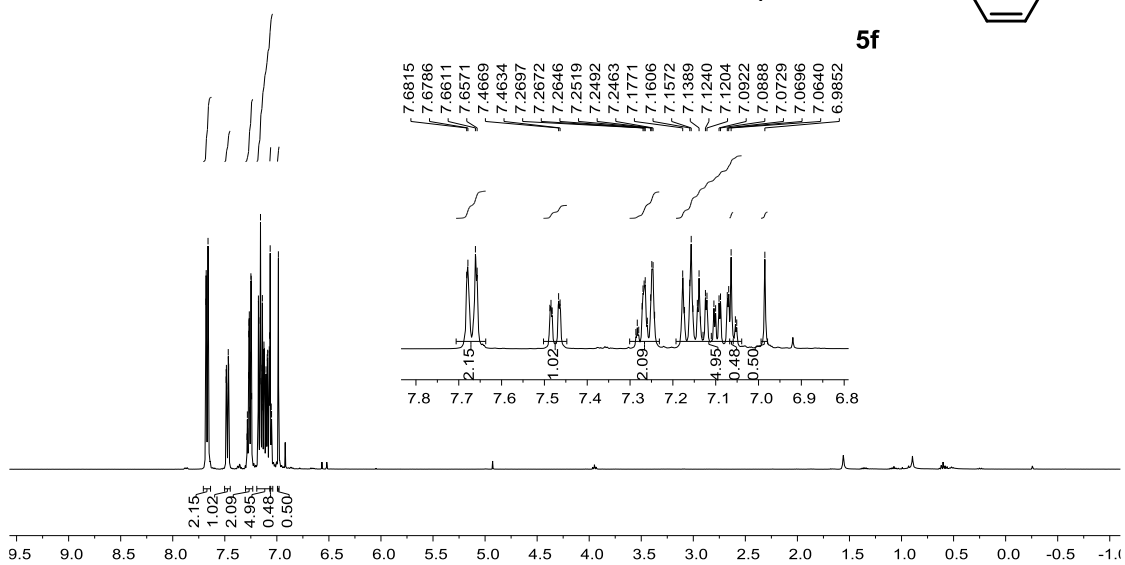
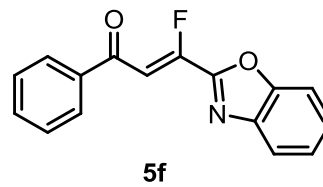


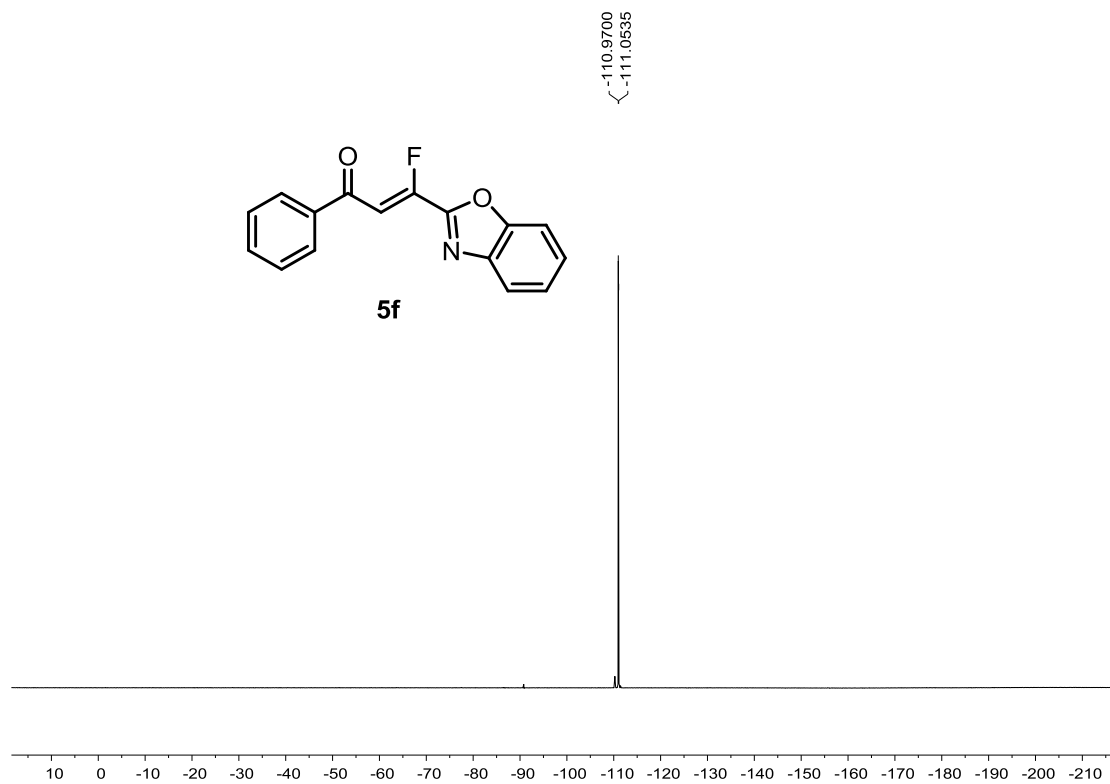
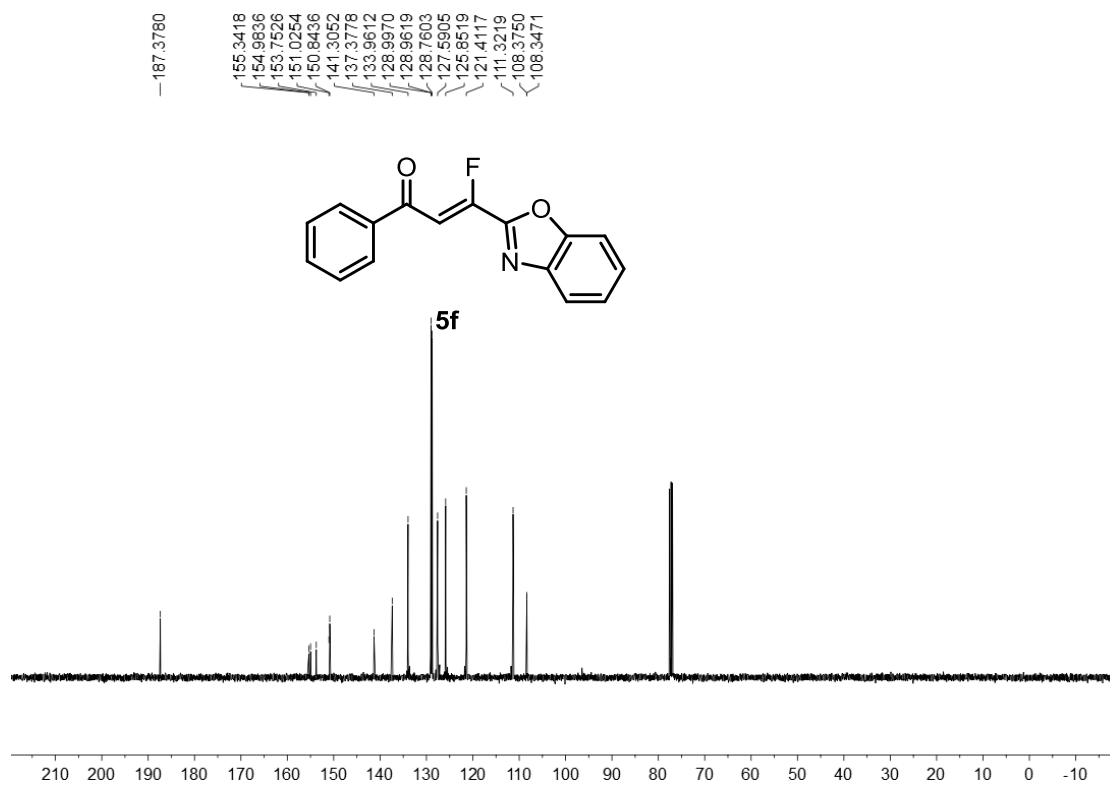
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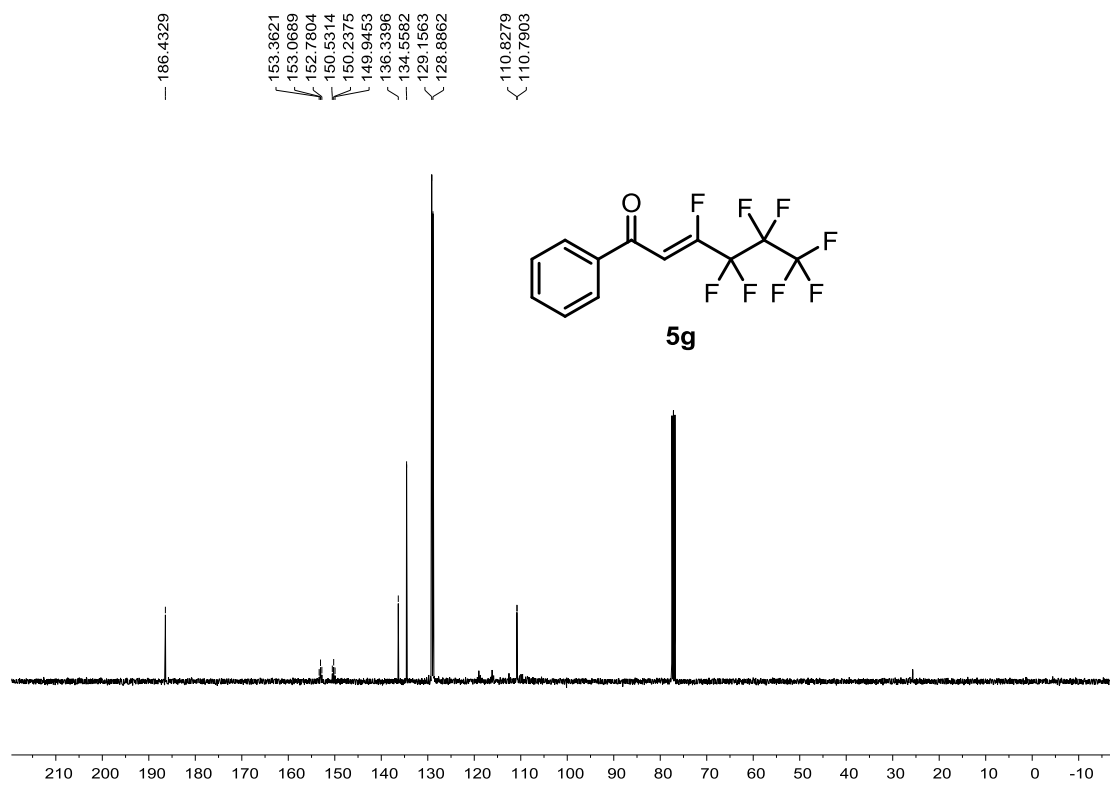
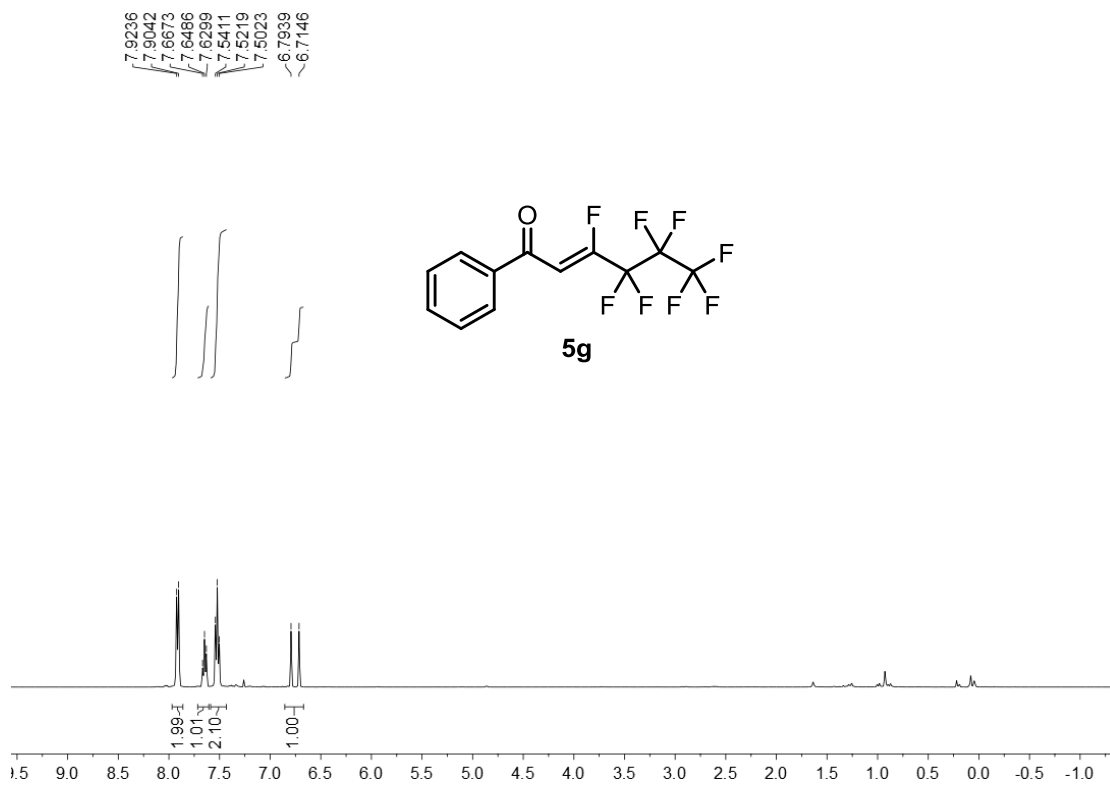


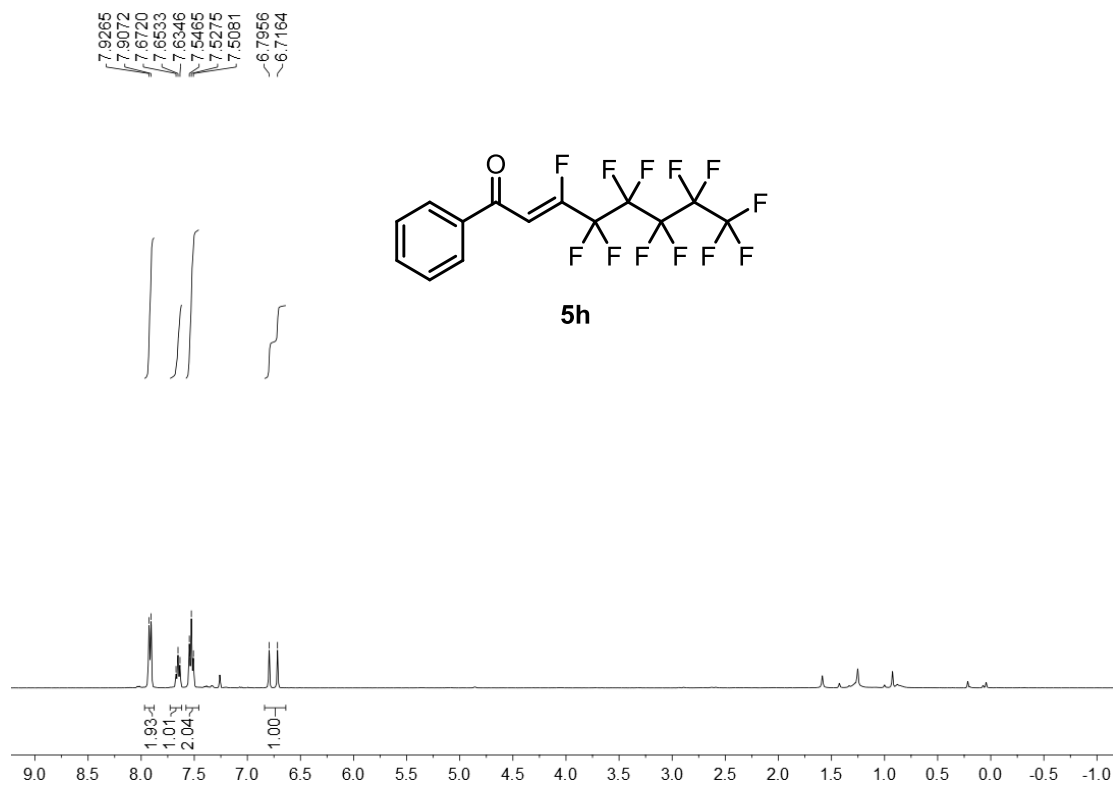
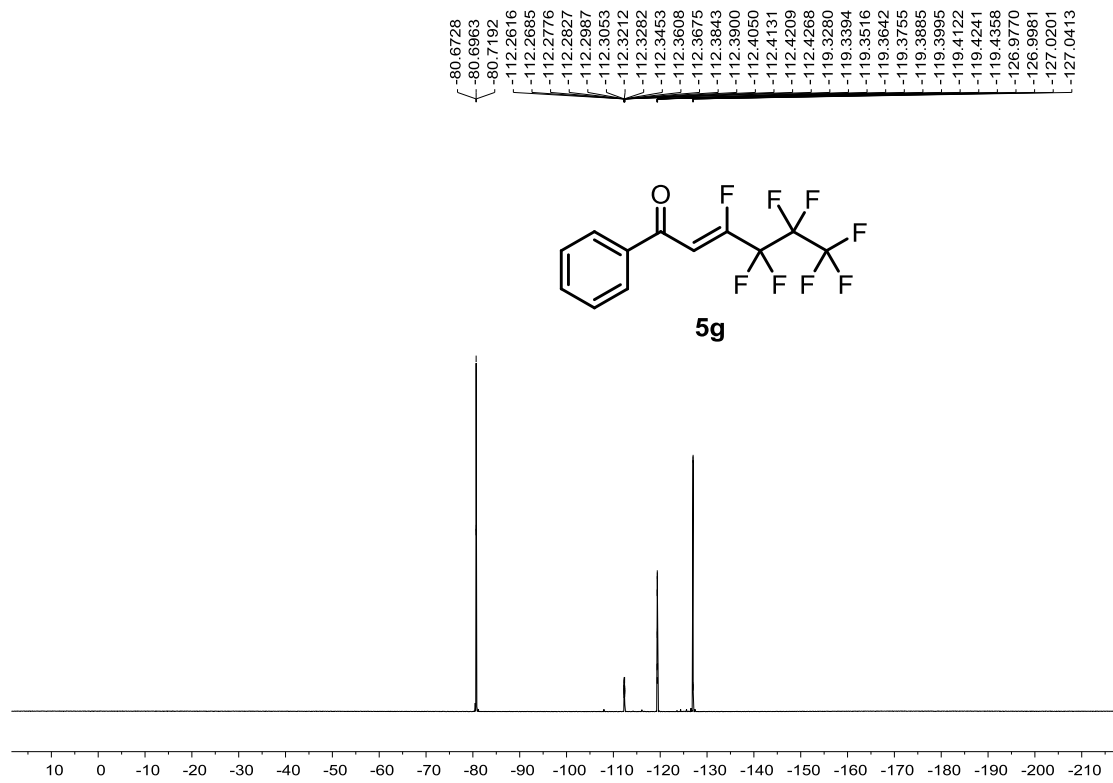


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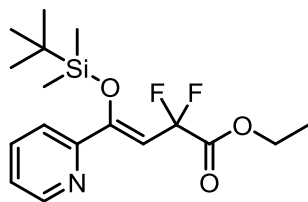
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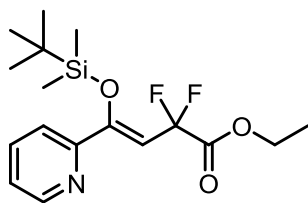
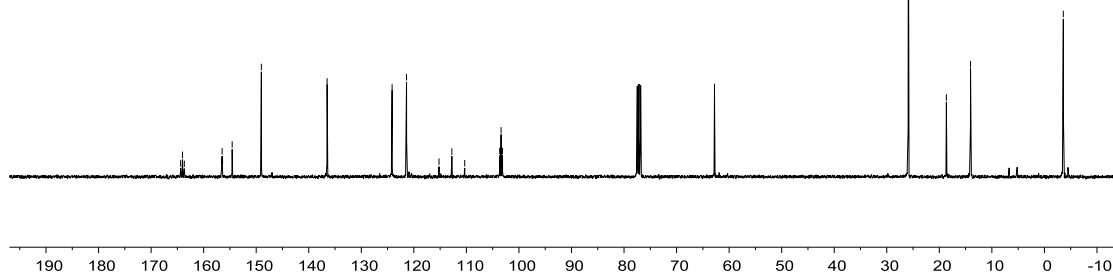
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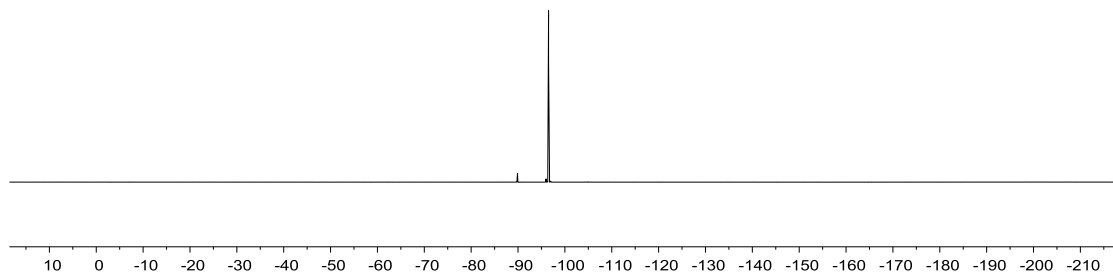


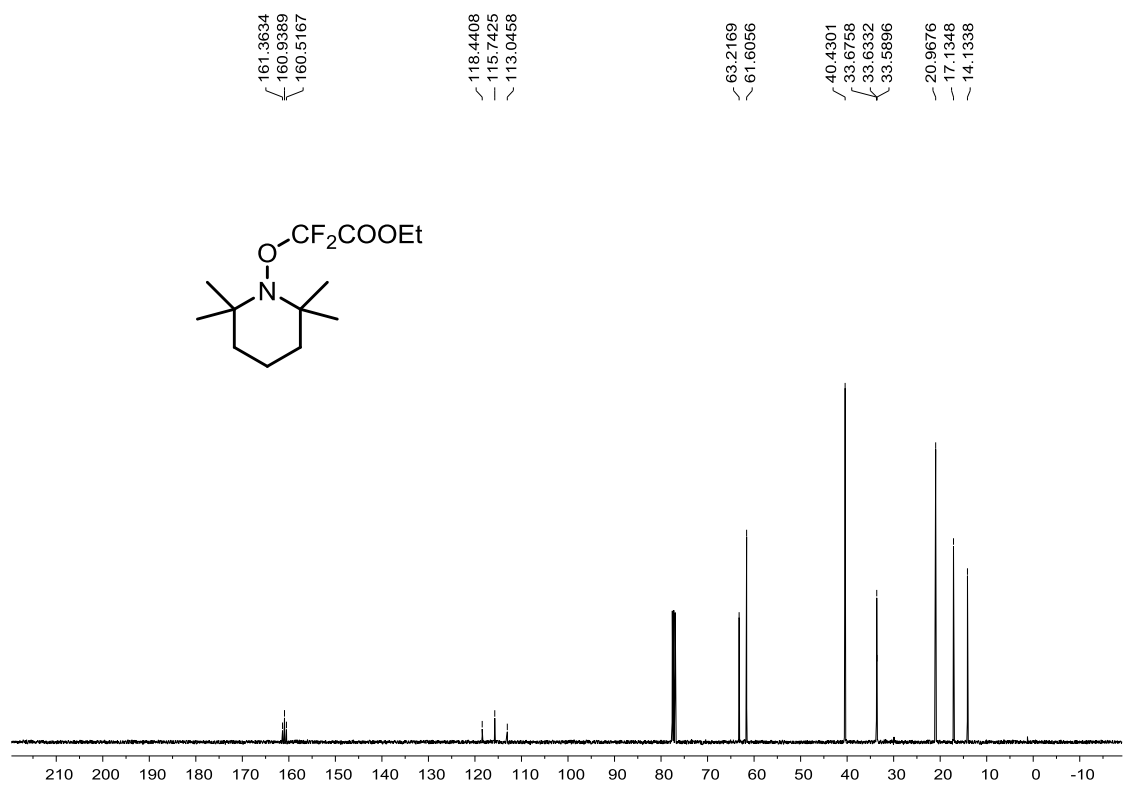
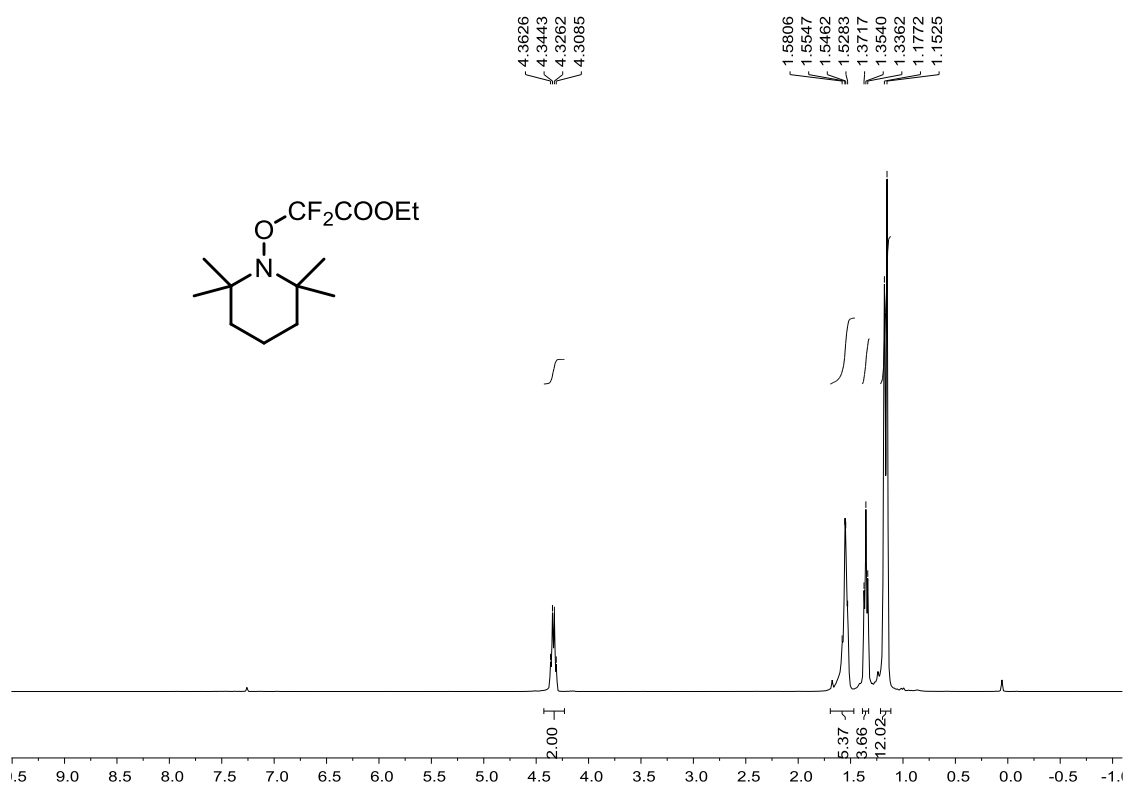
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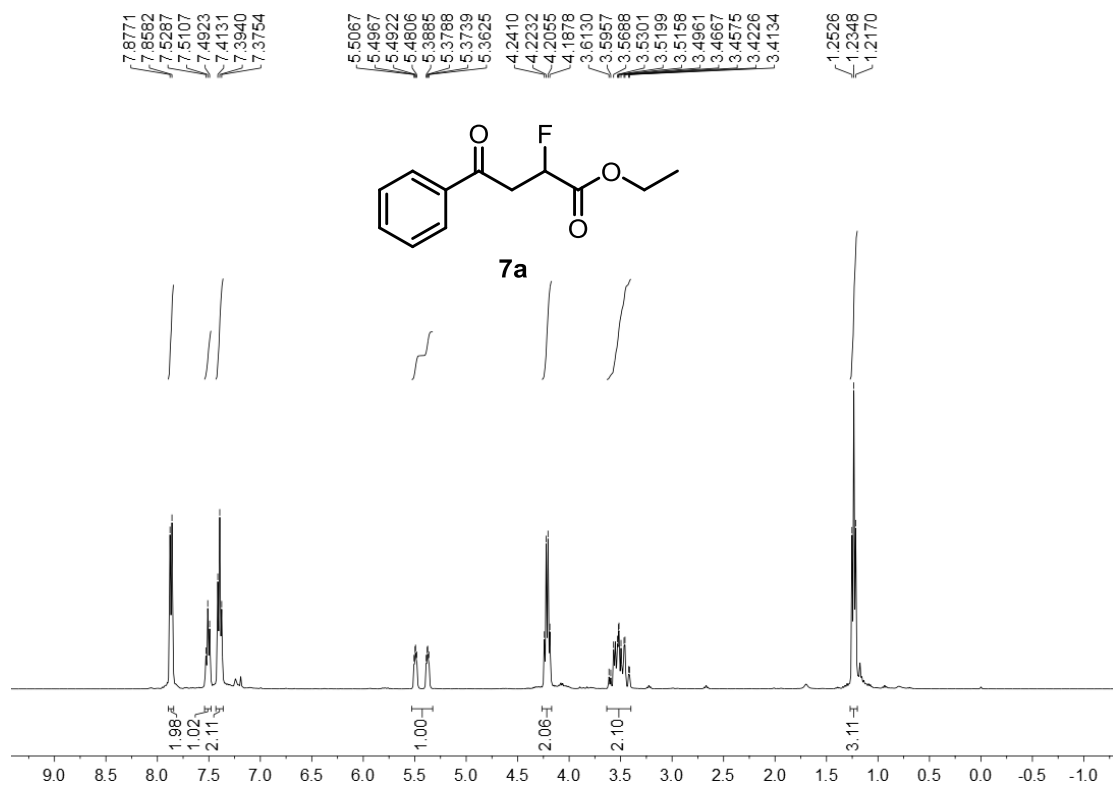
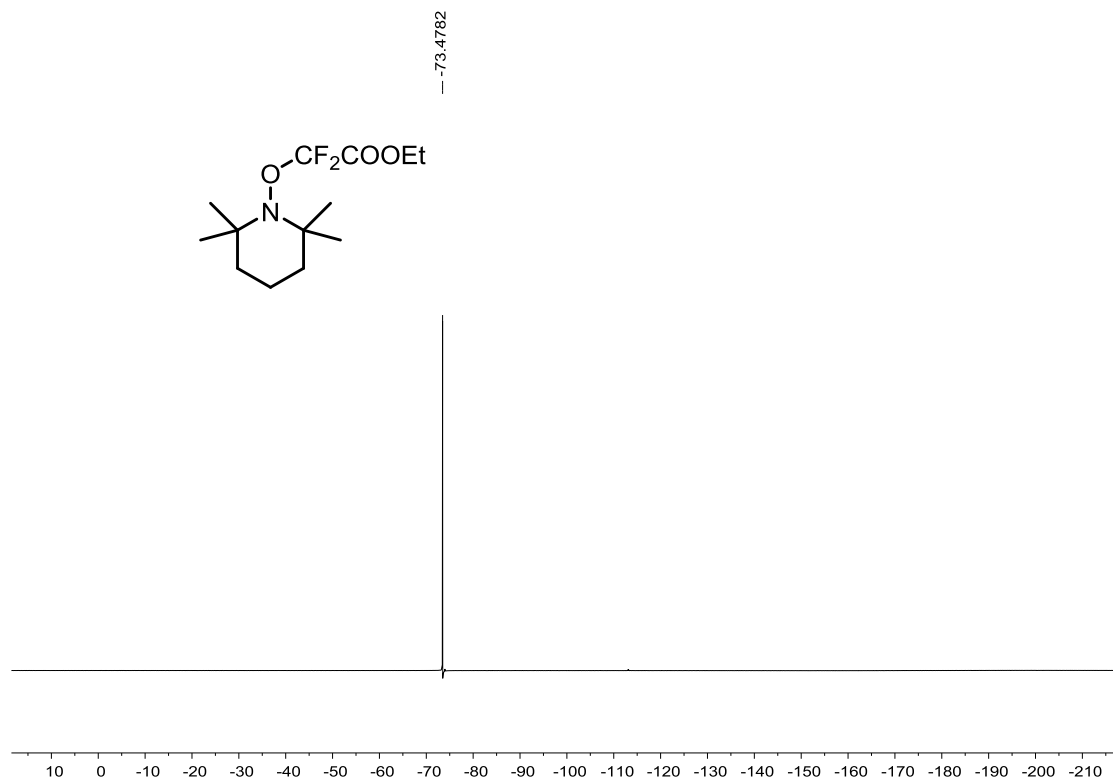


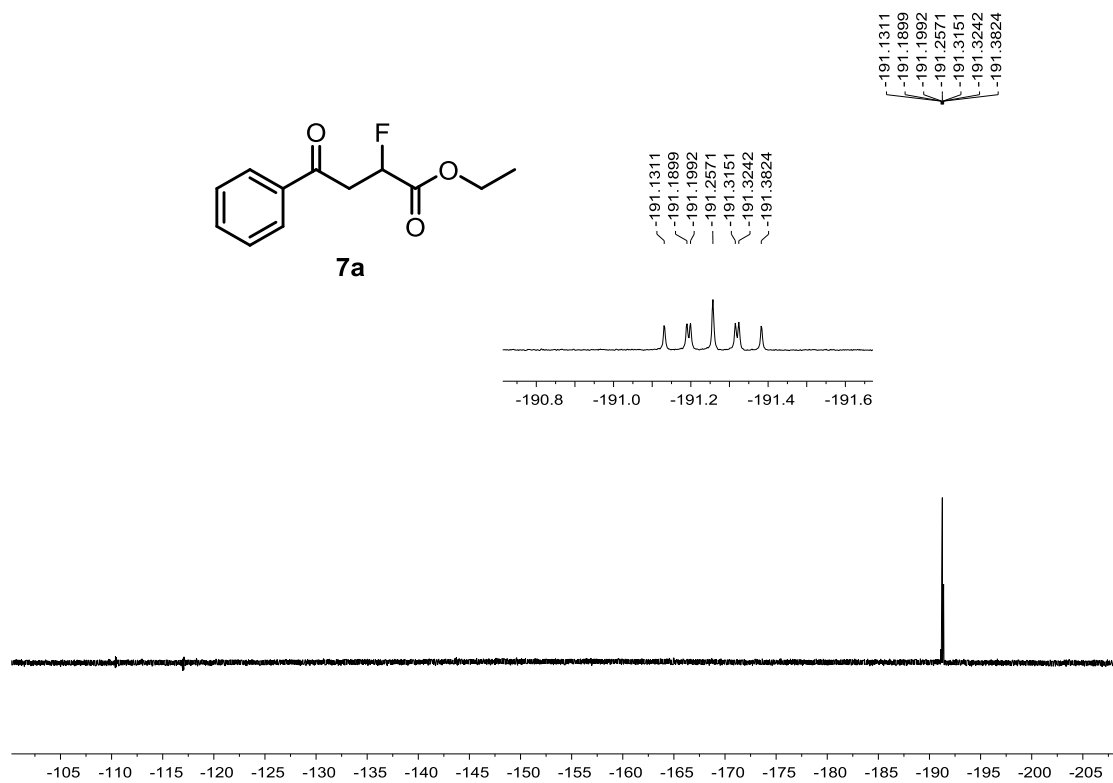
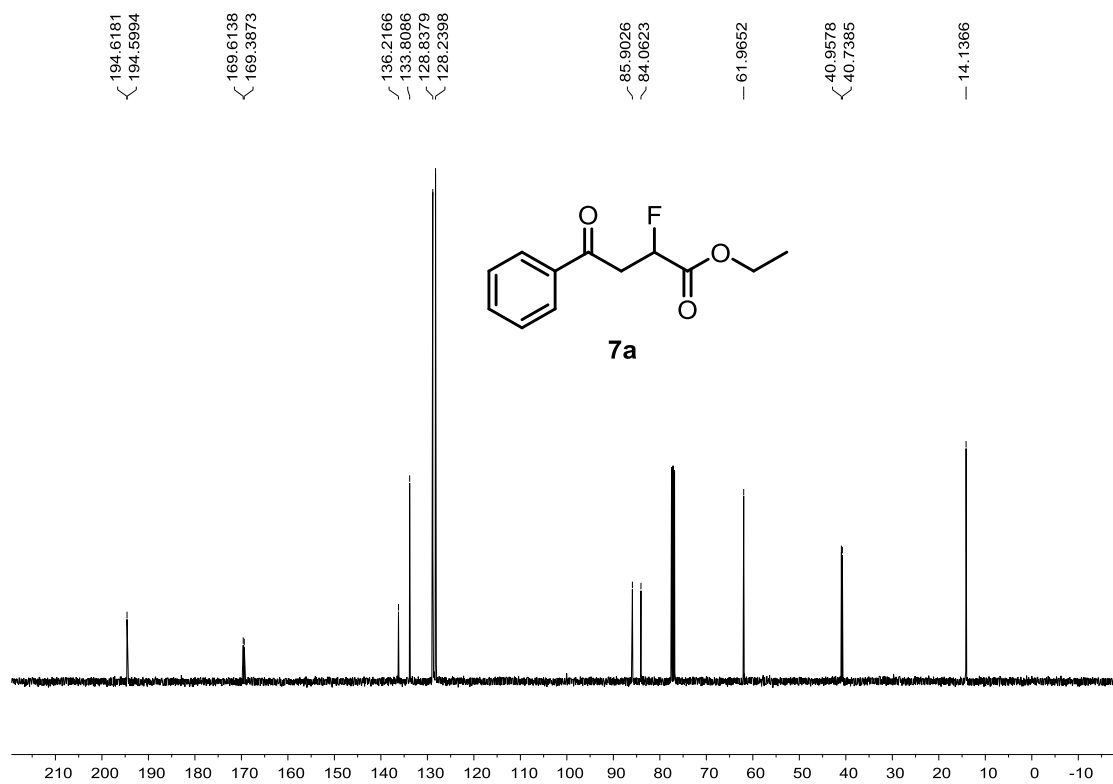
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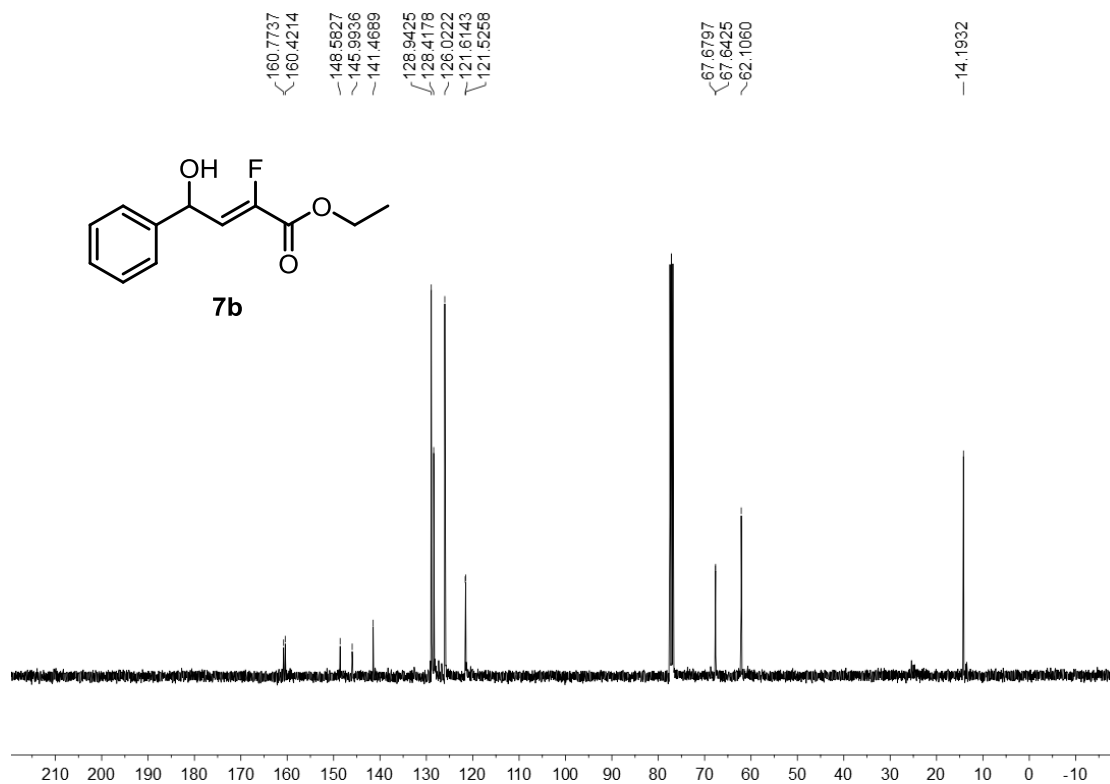
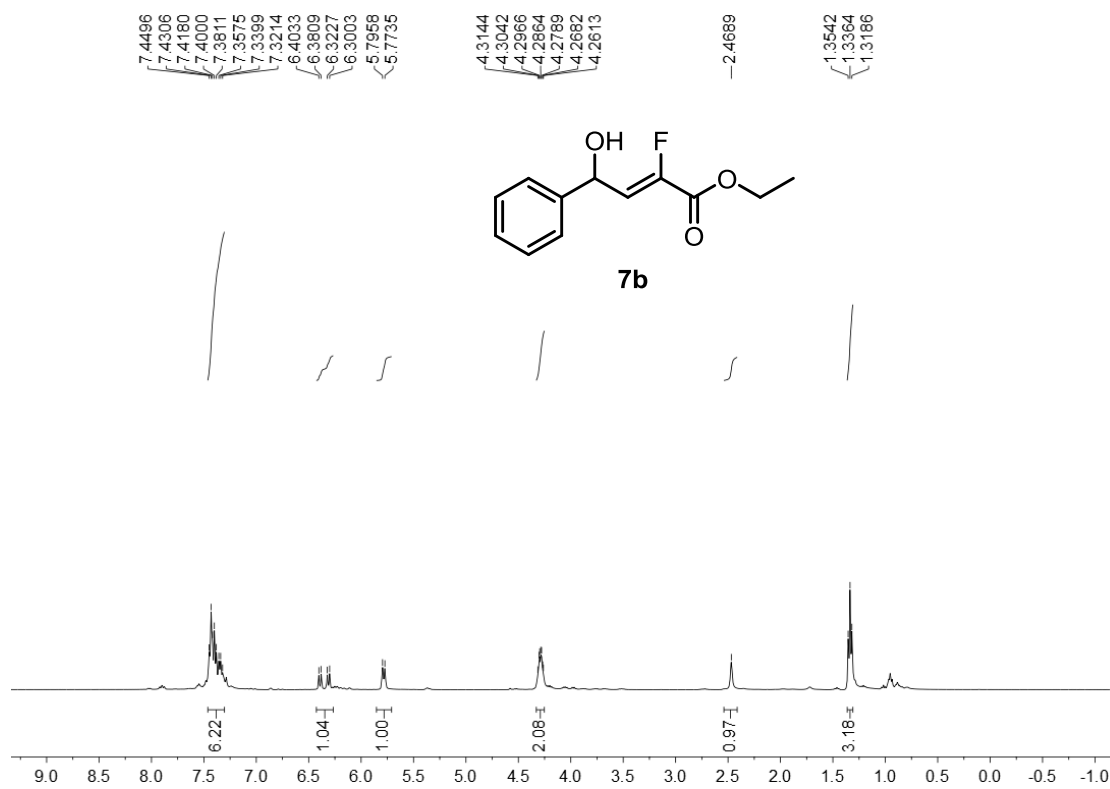
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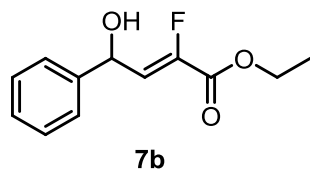




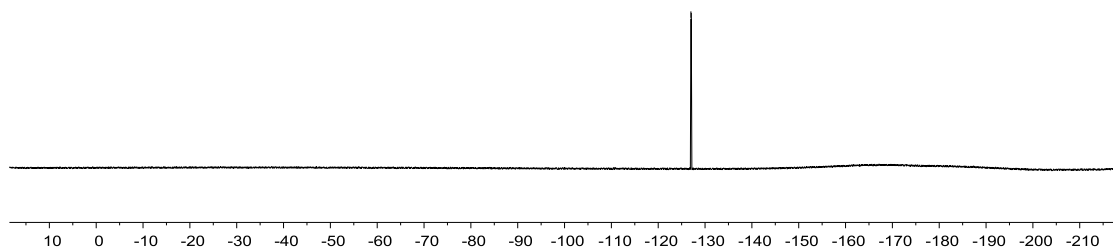








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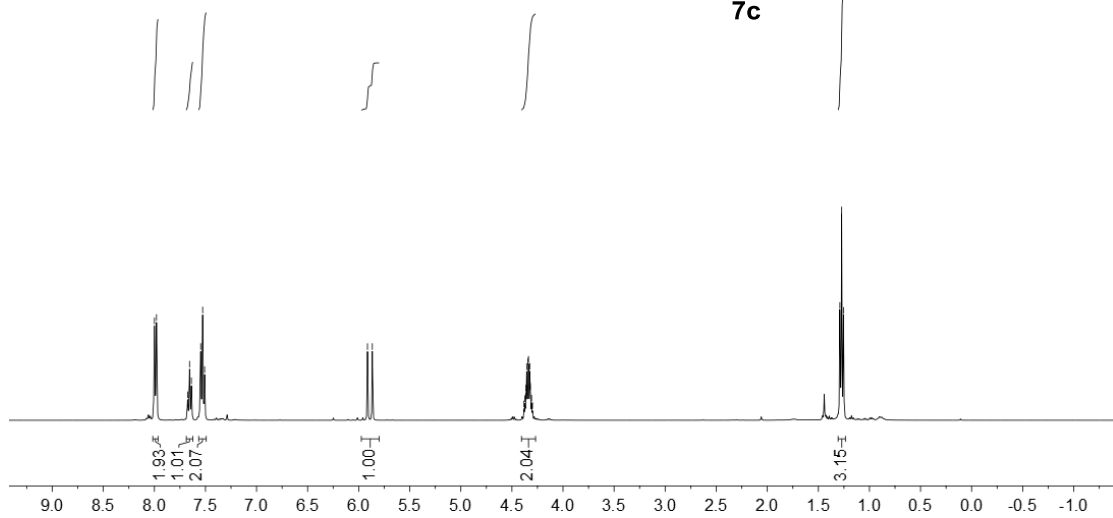
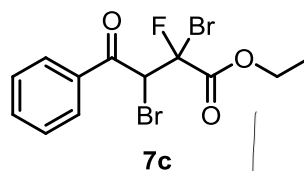


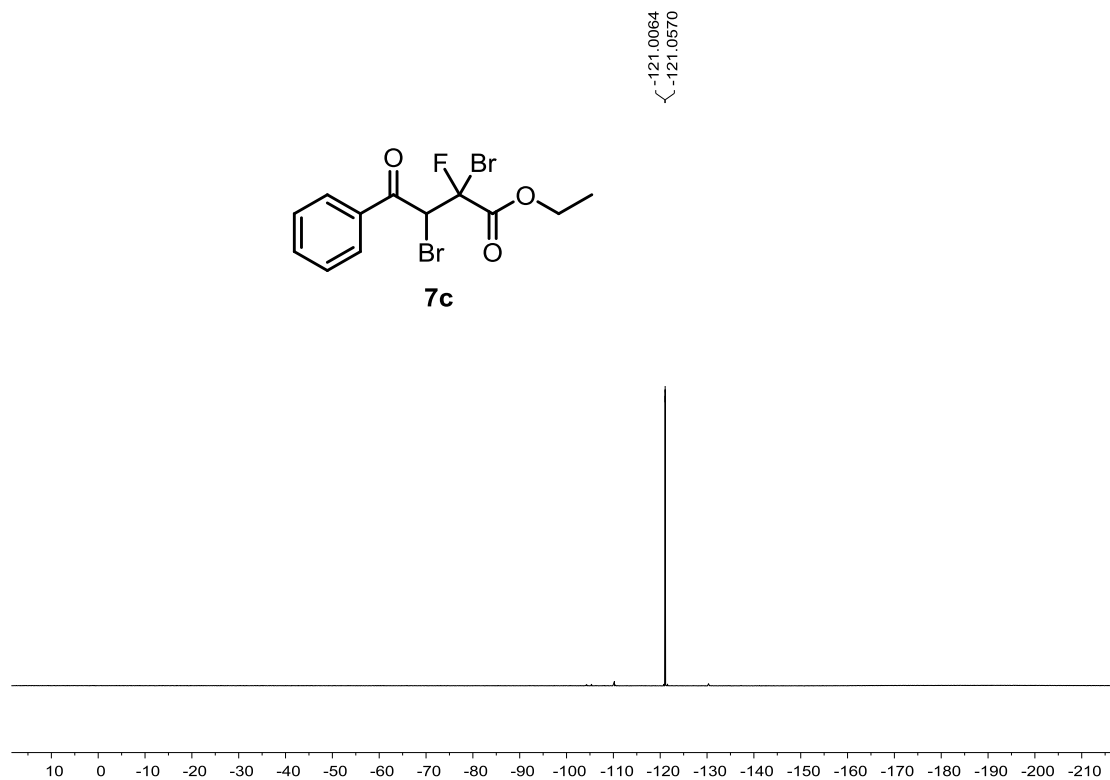
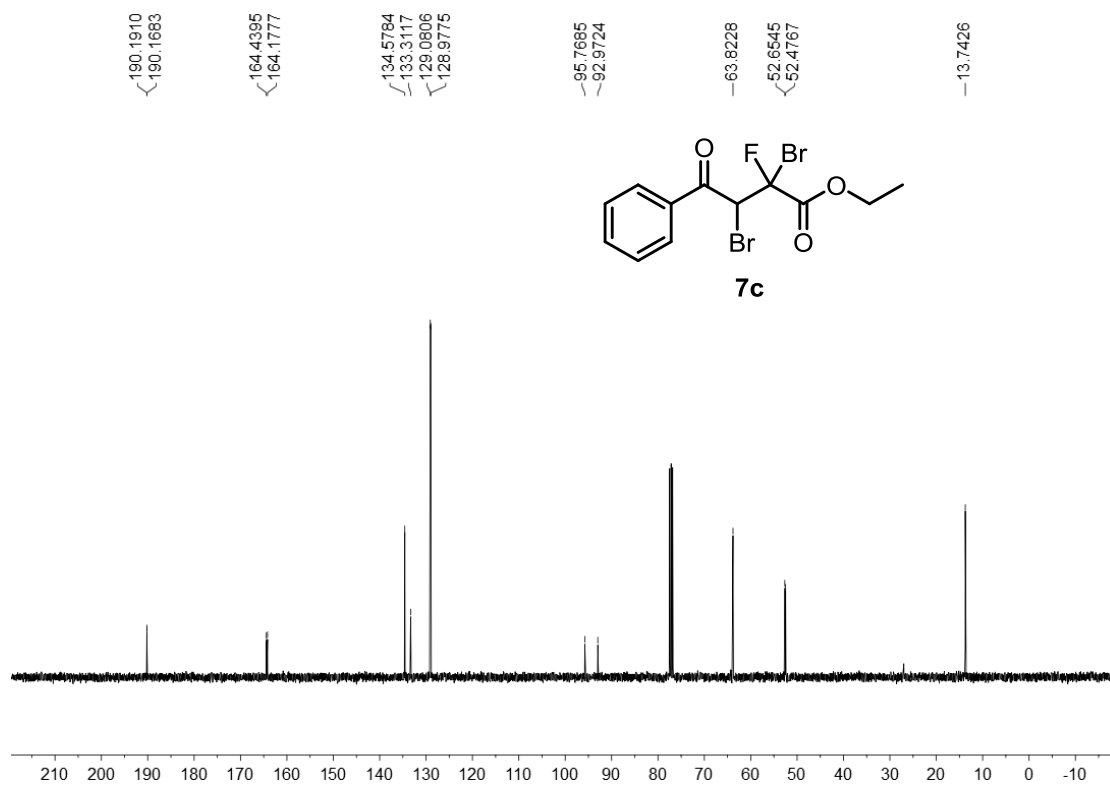
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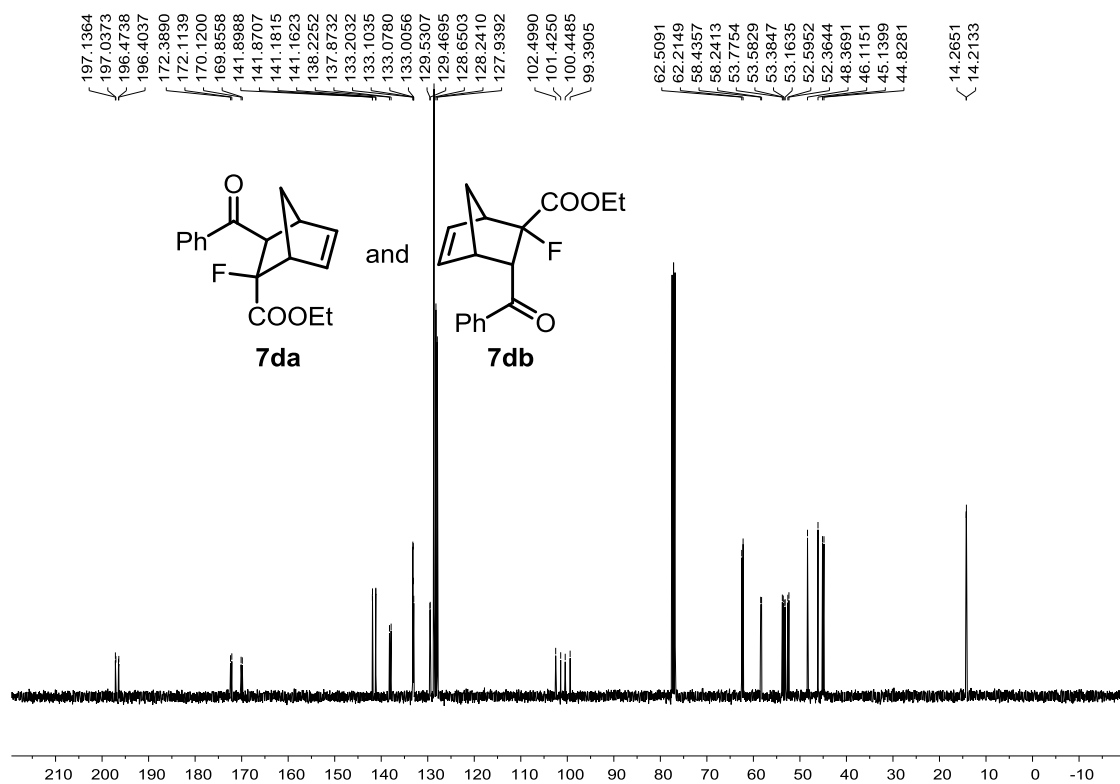
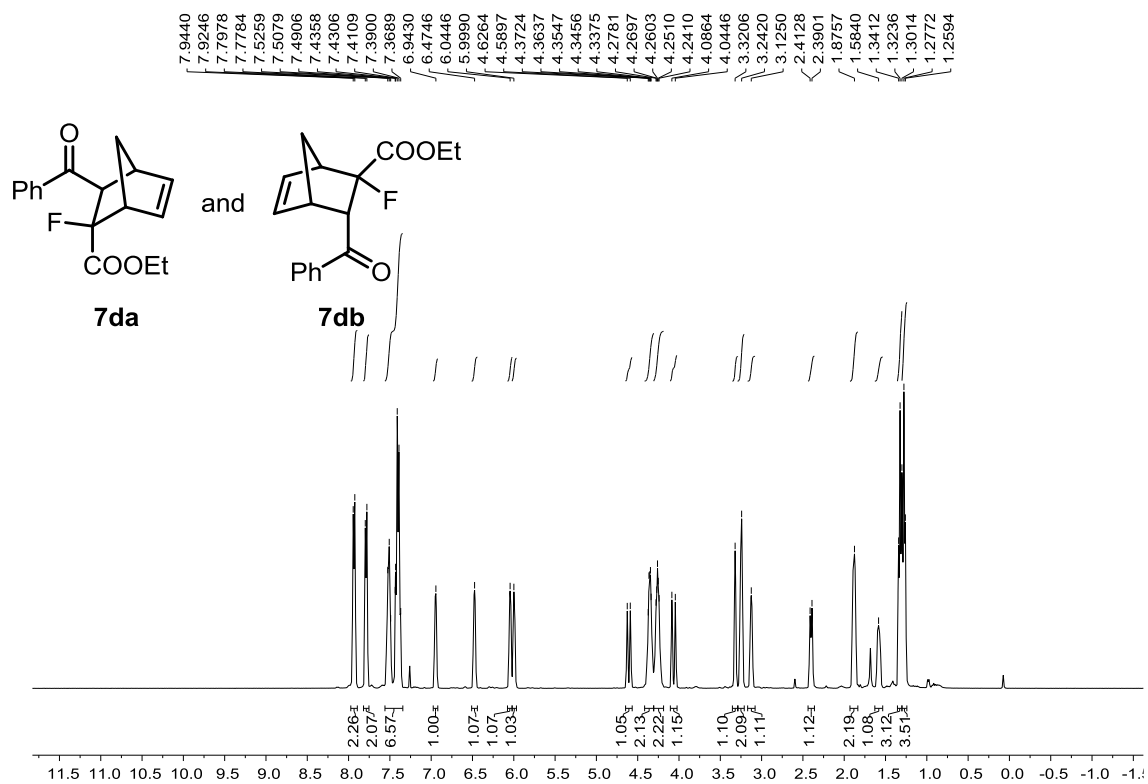
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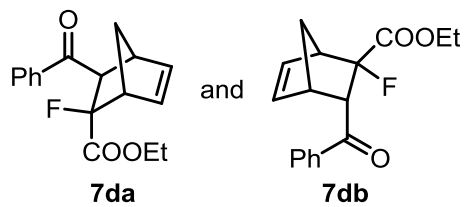
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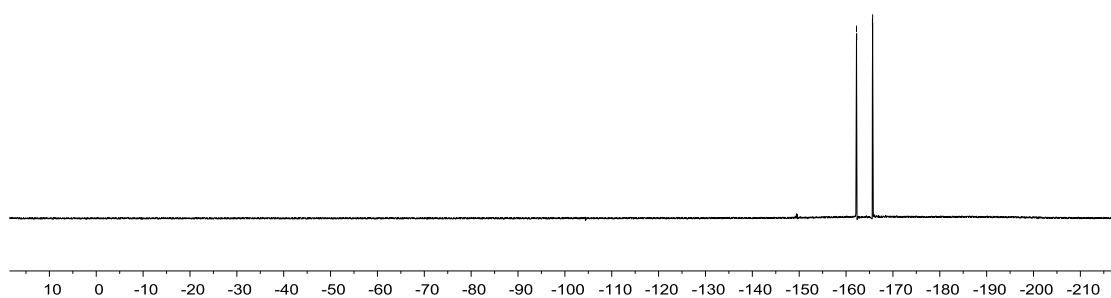








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