

# Supporting Information

## Enantioselective synthesis of fluorinated branched allylic compounds via Ir-catalyzed allylations of functionalized fluorinated methylene derivatives

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### Contents

#### General Experimental Details

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

All reagents were obtained from commercial sources and used without further purification. <sup>1</sup>H NMR spectra were obtained at 400 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual protio-solvent (7.26 ppm for CDCl<sub>3</sub>). <sup>13</sup>C NMR spectra were obtained at 100 MHz, and chemical shifts were recorded relative to the solvent resonance (CDCl<sub>3</sub>, 77.0 ppm). <sup>19</sup>F NMR spectra were obtained at 377 MHz. Data for NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration).

The phosphoramidite ligands<sup>[1]</sup>, substituted allylic carbonates were prepared according to the known procedures.

#### General procedure for Ir-catalyzed allylations of dimethyl 2-fluoromalonate (2a)

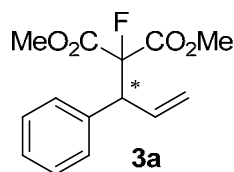
In a reaction tube equipped with a magnetic stirring bar were added in sequence allylic carbonate **1** (0.20 mmol, 1 equiv.) and a mixture of THF (2.0 mL) at room temperature under argon. To this solution were sequentially added the catalyst<sup>[2]</sup> made from both [Ir(COD)Cl]<sub>2</sub> (0.004 mmol, 2 mol%) and phosphoramidite ligand **L1** (0.008 mmol, 4 mol%) and CsF (0.40 mmol, 2 equiv.) and dimethyl 2-fluoromalonate **2a** (0.40 mmol, 2 equiv.). The reaction was vigorously stirred at room temperature for the stated time. The reaction mixture was stirring until the allylic carbonate **1** was completely consumed. The crude residue was purified by

flash column chromatography (methanol/ethyl acetate) to give the desired products **3**.

**References:**

- 1 (a) D. J. Cram, R. C. Helgeson, S. C. Peacock, L. J. Kaplan, L. A. Domeier, P. Moreau, K. Koga, J. M. Mayer, Y. Chao, M. G. Siegel, D. H. Hoffman and G. D. Y. Sogah, *J. Org. Chem.* 1978, **43**, 1930. (b) L. A. Arnold, R. Imbos, A. Mandoli, A. H. M. de Vries, R. Naasz and B. L. Feringa, *Tetrahedron* 2000, **56**, 2865.
- 2 C. A. Kiener, C. Shu, C. Incarvito and J. F. Hartwig, *J. Am. Chem. Soc.* 2003, **125**, 14272.

## Characterization Data



### Dimethyl-2-fluoro-2-(1-phenylallyl)malonate (**3a**)

Yield: 89% (23.7 mg); *ee*: 92%; colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.46 – 7.25 (m, 5H), 6.17 (dt,  $J$  = 17.2, 9.6 Hz, 1H), 5.39 – 5.13 (m, 2H), 4.41 (dd,  $J$  = 31.8, 8.9 Hz, 1H), 3.91 (s, 3H), 3.63 (s, 3H) ppm.

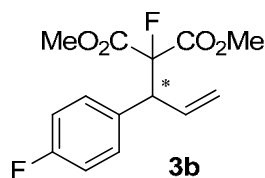
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -176.09 (s) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 165.7 (d,  $J$  = 25.8 Hz), 165.2 (d,  $J$  = 26.0 Hz), 136.5 (s), 133.7 (d,  $J$  = 4.7 Hz), 129.1 (d,  $J$  = 2.2 Hz), 128.6 (s), 127.8 (s), 119.5 (s), 97.5 (d,  $J$  = 209.5 Hz), 54.6 (s), 54.4 (s), 53.4 (d,  $J$  = 34.1 Hz).

HRMS (ESI+) calcd for  $\text{C}_{14}\text{H}_{15}\text{NaO}_4$  [ $\text{M}+\text{Na}$ ] $^+$ : 289.0846, Found: 289.0847.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL AD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 1.0 mL/min; detection wavelength = 214 nm;  $t_{\text{R}}$  = 10.318 (major), 12.242 (minor) min].  $[\alpha]_{\text{D}}^{20}$  = +28.6° (c 1.0,  $\text{CH}_3\text{OH}$ ).

IR (KBr):  $\nu$  max ( $\text{cm}^{-1}$ ) = 3091, 3078, 2955, 2878, 1729, 1645, 1590, 1505, 1460, 1428, 1360, 1037, 920, 830, 665, 531.



### Dimethyl-2-fluoro-2-(1-(4-fluorophenyl)allyl)malonate (**3b**)

Yield: 92% (26.2 mg); *ee*: 93%; colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.34 (dd,  $J$  = 7.5, 5.6 Hz, 2H), 7.04 (t,  $J$  = 8.6 Hz, 2H), 6.27 – 6.00 (m, 1H), 5.42 – 5.11 (m, 2H), 4.41 (dd,  $J$  = 31.6, 8.8 Hz, 1H), 3.90 (s, 3H), 3.65 (s, 3H) ppm.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -114.37 (s), -176.51 (s) ppm

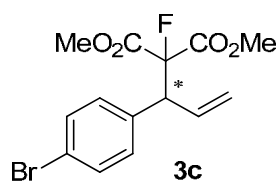
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 165.5 (d,  $J$  = 25.8 Hz), 165.1 (d,  $J$  = 25.8 Hz), 162.3 (d,  $J$  = 246.6 Hz), 133.5 (d,  $J$  = 4.6 Hz), 132.2 (d,  $J$  = 3.3 Hz), 130.8 (dd,  $J$  = 8.1, 2.4 Hz), 119.7 (s), 115.5 (d,  $J$  = 21.3 Hz), 97.4 (d,  $J$  = 209.4 Hz), 53.7 (s), 53.6 (s), 53.5 (d,  $J$  = 30.8 Hz).

HRMS (ESI+) calcd for  $\text{C}_{14}\text{H}_{14}\text{F}_2\text{NaO}_4$  [ $\text{M}+\text{Na}$ ] $^+$ : 307.0752, Found: 307.0754.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL IC (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 1.0 mL/min; detection

wavelength = 214 nm;  $t_R$  = 15.782 (major), 17.421 (minor) min].  $[\alpha]_D^{20}$  = +13.9° (c 1.0, CH<sub>3</sub>OH).

IR (KBr):  $\nu$  max (cm<sup>-1</sup>) = 3096, 3074, 2932, 2895, 1733, 1647, 1598, 1515, 1473, 1479, 1369, 1037, 922, 833, 661, 528.



Dimethyl-2-(1-(4-bromophenyl)allyl)-2-fluoromalonate (**3c**)

Yield: 87% (39.8 mg); *ee*: 94%; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.50 (dd,  $J$  = 18.6, 8.4 Hz, 2H), 7.27 (dd,  $J$  = 22.6, 8.0 Hz, 2H), 6.42 – 5.85 (m, 1H), 5.58 – 4.80 (m, 2H), 4.38 (dd,  $J$  = 31.5, 8.8 Hz, 1H), 3.90 (s, 3H), 3.66 (s, 3H).

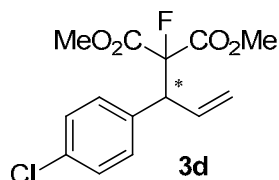
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -176.19 (s).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 165.4 (d,  $J$  = 25.8 Hz), 165.1 (d,  $J$  = 25.8 Hz), 135.5 (s), 133.2 (d,  $J$  = 4.6 Hz), 131.8 (s), 130.9 (d,  $J$  = 2.4 Hz), 122.0 (s), 119.9 (s), 97.1 (d,  $J$  = 209.7 Hz), 53.9 (s), 53.7 (s), 53.5 (d,  $J$  = 26.2 Hz).

HRMS (ESI+) calcd for C<sub>14</sub>H<sub>14</sub>BrFNaO<sub>4</sub> [M+Na]<sup>+</sup>: 366.9952, Found:366.9926.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL AD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 1.0 mL/min; detection wavelength = 214 nm;  $t_R$  = 14.202 (major), 15.608 (minor) min].  $[\alpha]_D^{20}$  = +34.4° (c 1.0, CH<sub>3</sub>OH).

IR (KBr):  $\nu$  max (cm<sup>-1</sup>) = 3037, 2956, 2930, 2845, 1760, 1470, 1239, 1156, 1076, 1048, 1015, 966, 778, 565, 519.



Dimethyl-2-(1-(4-chlorophenyl)allyl)-2-fluoromalonate (**3d**)

Yield: 92% (27.6 mg); *ee*: 99%; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.48 – 7.22 (m, 4H), 6.31 – 5.87 (m, 1H), 5.50 – 5.05 (m, 2H), 4.40 (dd,  $J$  = 31.5, 8.8 Hz, 1H), 3.90 (s, 3H), 3.66 (s, 3H).

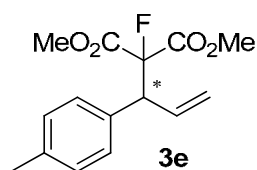
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -176.19 (s).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 165.5 (d,  $J$  = 25.8 Hz), 165.1 (d,  $J$  = 25.8 Hz), 135.0 (s), 133.8 (s), 133.2 (d,  $J$  = 4.6 Hz), 130.5 (d,  $J$  = 2.4 Hz), 128.8 (s), 119.9 (s), 97.2 (d,  $J$  = 209.5 Hz), 53.8 (s), 53.7 (s), 53.5 (d,  $J$  = 27.4 Hz).

HRMS (ESI+) calcd for C<sub>14</sub>H<sub>14</sub>ClFNaO<sub>4</sub> [M+Na]<sup>+</sup>: 323.0457, Found:323.0439.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL AD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 0.8 mL/min; detection wavelength = 214 nm;  $t_R$  = 19.145 (major), 21.535 (minor) min].  $[\alpha]_D^{20}$  = +37.1° (c 1.0, CH<sub>3</sub>OH).

IR (KBr):  $\nu$  max (cm<sup>-1</sup>) = 3025, 3007, 2977, 2945, 2862, 1759, 1685, 1489, 1252, 1089, 967, 833, 773, 511.



Dimethyl-2-fluoro-2-(1-(p-tolyl)allyl)malonate (**3e**)

Yield: 86% (24.1 mg); *ee*: 95%; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.30 – 7.05 (m, 4H), 6.33 – 5.97 (m, 1H), 5.25 (dd, *J* = 13.6, 7.2 Hz, 2H), 4.38 (dd, *J* = 31.8, 8.9 Hz, 1H), 3.88 (s, 3H), 3.64 (s, 3H), 2.36 (s, 3H).

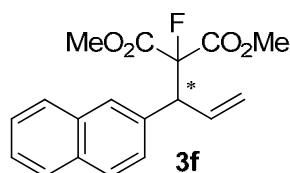
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -176.06 (s).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  165.8 (d, *J* = 25.8 Hz), 165.3 (d, *J* = 26.0 Hz), 137.5 (s), 133.9 (d, *J* = 4.7 Hz), 133.4 (s), 129.3 (s), 129.0 (d, *J* = 2.2 Hz), 119.2 (s), 97.5 (d, *J* = 209.0 Hz), 54.2 (s), 54.1 (s), 53.4 (d, *J* = 30.5 Hz), 21.1 (s).

HRMS (ESI<sup>+</sup>) calcd for C<sub>15</sub>H<sub>17</sub>FNao<sub>4</sub> [M+Na]<sup>+</sup>: 303.1003, Found:303.1001.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL IC (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 1.0 mL/min; detection wavelength = 214 nm; *t*<sub>R</sub> = 24.305 (major), 27.909 (minor) min]. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +38.8° (c 1.0, CH<sub>3</sub>OH).

IR (KBr):  $\nu$  max (cm<sup>-1</sup>) = 3093, 3069, 2948, 2883, 1732, 1650, 1589, 1511, 1463, 1458, 1363, 1052, 938, 833, 675, 527.



Dimethyl-2-fluoro-2-(1-(naphthalen-2-yl)allyl)malonate (**3f**)

Yield: 88% (27.8 mg); *ee*: 95%; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.84 (d, *J* = 6.0 Hz, 4H), 7.62 – 7.36 (m, 3H), 6.28 (dt, *J* = 17.3, 9.5 Hz, 1H), 5.48 – 5.12 (m, 2H), 4.61 (dd, *J* = 31.7, 8.7 Hz, 1H), 3.92 (s, 3H), 3.59 (s, 3H) ppm.

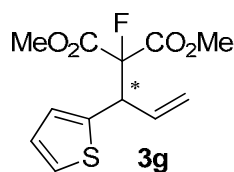
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -175.54 (s) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 165.7 (d, *J* = 25.8 Hz), 165.3 (d, *J* = 25.9 Hz), 134.1 (s), 133.7 (d, *J* = 4.6 Hz), 133.4 (s), 132.8 (s), 128.3 (s), 128.0 (s), 127.6 (s), 127.0 (d, *J* = 2.5 Hz), 126.2 (s), 119.7 (s), 97.6 (d, *J* = 209.5 Hz), 54.6 (s), 54.5 (s), 53.4 (d, *J* = 34.4 Hz).

HRMS (ESI<sup>+</sup>) calcd for C<sub>18</sub>H<sub>17</sub>FNao<sub>4</sub> [M+Na]<sup>+</sup>: 339.1003, Found: 339.0979.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL IC (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 1.0 mL/min; detection wavelength = 214 nm; *t*<sub>R</sub> = 24.202 (major), 27.438 (minor) min]. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +40.5° (c 1.0, CH<sub>3</sub>OH).

IR (KBr):  $\nu$  max (cm<sup>-1</sup>) = 3016, 2970, 2933, 2838, 1735, 1643, 1256, 1247, 1160, 769.



Dimethyl-2-fluoro-2-(1-(thiophen-2-yl)allyl)malonate (**3g**)

Yield: 94% (25.6 mg); *ee*: 97%; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.32 – 7.17 (m, 1H), 7.08 – 6.84 (m, 2H), 6.17 – 5.94 (m, 1H), 5.26 (t, *J* = 14.2 Hz, 2H), 4.70 (dd, *J* = 30.2, 9.0 Hz, 1H), 3.85 (s, 3H), 3.70 (s, 3H).

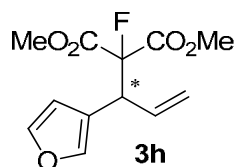
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -175.11 (s).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 165.3 (d, *J* = 22.4 Hz), 165.0 (d, *J* = 22.4 Hz), 137.8 (s), 133.3 (d, *J* = 4.4 Hz), 126.9 (s), 126.8 (d, *J* = 1.5 Hz), 125.5 (s), 119.8 (s), 97.0 (d, *J* = 209.2 Hz), 53.6 (s), 53.5 (s), 49.9 (d, *J* = 19.6 Hz).

HRMS (ESI<sup>+</sup>) calcd for C<sub>12</sub>H<sub>13</sub>FSNaO<sub>4</sub> [M+Na]<sup>+</sup>: 295.0411, Found: 295.0407.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL AD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 1.0 mL/min; detection wavelength = 214 nm; *t*<sub>R</sub> = 12.521 (major), 14.851 (minor) min]. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +12.07° (c 1.0, CH<sub>3</sub>OH).

IR (KBr):  $\nu$  max (cm<sup>-1</sup>) = 3025, 2983, 2945, 2843, 1851, 1607, 1238, 1065, 936, 800, 742, 708.



Dimethyl-2-fluoro-2-(1-(furan-3-yl)allyl)malonate (**3h**)

Yield: 93% (23.8 mg); *ee*: -97%; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.41 (d, *J* = 10.4 Hz, 2H), 6.41 (s, 1H), 6.10 – 5.87 (m, 1H), 5.27 (dd, *J* = 13.6, 7.0 Hz, 2H), 4.39 (dd, *J* = 31.2, 8.7 Hz, 1H), 3.88 (s, 3H), 3.76 (s, 3H).

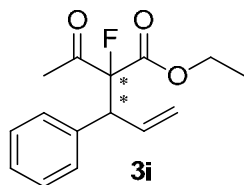
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -175.987 (s).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 165.5 (d, *J* = 8.2 Hz), 165.3 (d, *J* = 8.0 Hz), 143.1 (s), 140.6 (d, *J* = 2.0 Hz), 133.1 (d, *J* = 3.9 Hz), 120.2 (s), 119.6 (s), 110.6 (d, *J* = 1.5 Hz), 97.2 (d, *J* = 208.4 Hz), 53.5 (s), 53.4 (s), 45.9 (d, *J* = 19.7 Hz).

HRMS (ESI<sup>+</sup>) calcd for C<sub>12</sub>H<sub>13</sub>FNaO<sub>5</sub> [M+Na]<sup>+</sup>: 279.0639, Found: 279.0633.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL AD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 0.5 mL/min; detection wavelength = 214 nm; *t*<sub>R</sub> = 21.623 (minor), 22.781 (major) min]. [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +18.97° (c 1.0, CH<sub>3</sub>OH).

IR (KBr):  $\nu$  max (cm<sup>-1</sup>) = 3033, 2973, 2955, 2860, 1845, 1677, 1241, 1145, 940, 811, 747, 738.



Ethyl 2-acetyl-2-fluoro-3-phenylpent-4-enoate (**3i**)

Yield: 93% (24.6 mg); colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.41 – 7.24 (m, 10H), 6.25 – 6.11 (m, 1H), 6.11 – 5.95 (m, 0.89H), 5.27 (dd,  $J$  = 13.7, 6.8 Hz, 2H), 5.21 (dd,  $J$  = 13.6, 7.5 Hz, 1.83H), 4.51 – 4.42 (m, 1H), 4.38 (t,  $J$  = 6.1 Hz, 0.89H), 4.36 – 4.21 (m, 2H), 4.11 – 3.97 (m, 1.78H), 2.38 (d,  $J$  = 5.6 Hz, 2.72H), 1.93 (d,  $J$  = 5.6 Hz, 3H), 1.37 (t,  $J$  = 7.1 Hz, 3H), 1.04 (t,  $J$  = 7.1 Hz, 2.72H).

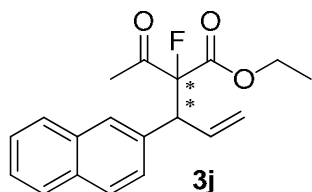
<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  = -174.87 (s), -175.47 (s).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 202.0 (d,  $J$  = 30.0 Hz), 201.6 (d,  $J$  = 29.6 Hz), 165.1 (d,  $J$  = 25.9 Hz), 164.6 (d,  $J$  = 26.1 Hz), 137.1 (s), 136.4 (s), 133.8 (d,  $J$  = 4.4 Hz), 133.8 (d,  $J$  = 5.4 Hz), 129.6 (d,  $J$  = 2.1 Hz), 129.0 (d,  $J$  = 2.5 Hz), 128.7 (s), 128.6 (s), 127.7 (s), 127.6 (s), 119.6 (s), 119.3 (s), 103.9 (d,  $J$  = 28.4 Hz), 101.9 (d,  $J$  = 29.9 Hz), 62.9 (s), 62.6 (s), 54.2 (d,  $J$  = 18.0 Hz), 54.1 (d,  $J$  = 18.1 Hz), 27.0 (s), 26.9 (s), 14.1 (s), 13.7 (s).

HRMS (ESI+) calcd for C<sub>15</sub>H<sub>17</sub>FNao<sub>3</sub> [M+Na]<sup>+</sup>: 287.1054, Found:287.1050.

$[\alpha]_D^{20}$  = +28.05° (c 1.0, CH<sub>3</sub>OH).

IR (KBr):  $\nu$  max (cm<sup>-1</sup>) = 3016, 2965, 2932, 2850, 1733, 1644, 1285, 1258, 1165, 887.



Ethyl 2-acetyl-2-fluoro-3-(naphthalen-2-yl)pent-4-enoate (**3j**)

Yield: 92% (28.9 mg); *ee*: 94%; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.78 (dd,  $J$  = 12.1, 9.3 Hz, 7.08H), 7.45 (t,  $J$  = 6.9 Hz, 5.2H), 6.33 – 6.15 (m, 1H), 6.15 – 5.99 (m, 0.8H), 5.27 (dd,  $J$  = 13.6, 8.5 Hz, 2H), 5.23 – 5.08 (m, 1.71H), 4.60 (dd,  $J$  = 8.5, 4.7 Hz, 0.88H), 4.52 (dd,  $J$  = 8.5, 4.9 Hz, 1H), 4.41 – 4.23 (m, 2H), 3.95 (qd,  $J$  = 7.1, 2.7 Hz, 1.63H), 2.38 (d,  $J$  = 5.7 Hz, 2.38H), 1.88 (d,  $J$  = 5.7 Hz, 3H), 1.35 (t,  $J$  = 7.1 Hz, 3H), 0.93 (t,  $J$  = 7.1 Hz, 2.56H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -174.46 (s), -175.00 (s).

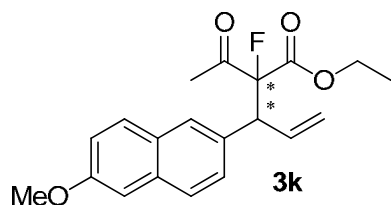
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 201.9 (d,  $J$  = 30.0 Hz), 201.6 (d,  $J$  = 30.0 Hz), 165.1 (d,  $J$  = 25.9 Hz), 164.6 (d,  $J$  = 26.1 Hz), 134.6 (s), 133.91 (s), 133.8 (d,  $J$  = 4.2 Hz), 133.7 (d,  $J$  = 5.1 Hz), 133.3 (d,  $J$  = 3.2 Hz), 132.7 (d,  $J$  = 1.2 Hz), 128.8 (s), 128.3 (s), 128.3 (s), 128.0 (d,  $J$  = 4.2 Hz), 128.0 (d,  $J$  = 3.4 Hz), 127.6 (s), 127.2 (d,  $J$  = 2.7 Hz), 127.0 (d,  $J$  = 2.6 Hz), 126.0 (s), 126.2 (s), 126.2 (s), 126.1 (s), 119.9 (s), 119.5 (s).

104.1 (d,  $J = 23.4$  Hz), 102.0 (d,  $J = 26.1$  Hz), 63.0 (s), 62.6 (s), 54.3 (d,  $J = 11.0$  Hz), 54.1 (d,  $J = 11.0$  Hz), 27.1 (s), 27.0 (s), 14.2 (s), 13.8 (s).

HRMS (ESI+) calcd for  $C_{19}H_{19}FNaO_3$   $[M+Na]^+$ : 337.1210, Found:337.1212.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL AD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 0.5 mL/min; detection wavelength = 214 nm;  $t_R = 38.875$  (major), min 53.126 (minor)].  $[\alpha]_D^{20} = +58.46^\circ$  (c 1.0,  $CH_3OH$ ).

IR (KBr):  $\nu$  max (cm<sup>-1</sup>) = 3106, 2976, 2933, 2850, 1730, 1647, 1280, 1233, 1164, 755.



Ethyl 2-acetyl-2-fluoro-3-(6-methoxynaphthalen-2-yl)pent-4-enoate (**3k**)

Yield: 80% (27.5 mg); *ee*: 97%; colorless oil.

<sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta = 7.74$  (dd,  $J = 14.9, 6.3$  Hz, 2H), 7.46 (t,  $J = 9.1$  Hz, 1H), 7.24 – 7.07 (m, 1H), 6.34 – 6.02 (m, 1H), 5.40 – 5.14 (m, 1H), 4.76 – 4.58 (m, 1H), 4.58 – 4.46 (m, 1H), 4.43 – 4.27 (m, 1H), 4.00 (d,  $J = 7.1$  Hz, 1H), 3.95 (s, 2H), 2.42 (d,  $J = 5.6$  Hz, 1H), 1.91 (d,  $J = 5.6$  Hz, 1H), 1.39 (t,  $J = 7.1$  Hz, 1H), 0.98 (t,  $J = 7.1$  Hz, 1H).

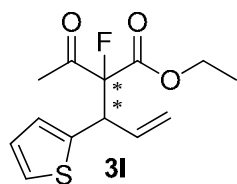
<sup>19</sup>F NMR (376 MHz,  $CDCl_3$ )  $\delta = -174.54$  (s),  $-175.11$  (s).

<sup>13</sup>C NMR (101 MHz,  $CDCl_3$ )  $\delta = 201.8$  (dd,  $J = 37.3, 29.8$  Hz), 164.9 (dd,  $J = 47.0, 26.0$  Hz), 157.9 (t,  $J = 10.3$  Hz), 135.2 (s), 134.51 (s), 134.0 (d,  $J = 4.2$  Hz), 133.9 (s), 133.8 (s), 132.2 (s), 131.5 (s), 129.6 (s), 129.6 (s), 129.4 (s), 128.8 (d,  $J = 2.2$  Hz), 128.6 (s), 127.8 (d,  $J = 2.2$  Hz), 127.7 (d,  $J = 2.5$  Hz), 127.5 (d,  $J = 2.6$  Hz), 127.2 (d,  $J = 4.1$  Hz), 127.1 (s), 126.9 (s), 124.1 (s), 121.7 (s), 119.6 (s), 119.3 (s), 119.1 (s), 119.0 (s), 105.9 (s), 105.5 (d,  $J = 5.1$  Hz), 104.3 (s), 104.0 (s), 102.2 (s), 101.9 (s), 68.7 (s), 62.9 (s), 62.6 (s), 55.4 (s), 54.9 (s), 54.1 (dd,  $J = 18.1, 9.7$  Hz), 27.0 (d,  $J = 5.2$  Hz), 14.2 (s), 13.8 (s).

HRMS (ESI+) calcd for  $C_{20}H_{21}FNaO_4$   $[M+Na]^+$ : 367.1327, Found:367.1288.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL AD-H (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 0.5 mL/min; detection wavelength = 214 nm;  $t_R = 54.457$  (minor), 49.822 (major) min].  $[\alpha]_D^{20} = +43.30^\circ$  (c 1.0,  $CH_3OH$ ).

IR (KBr):  $\nu$  max (cm<sup>-1</sup>) = 3116, 2980, 2935, 2854, 1734, 1645, 1283, 1255, 1170, 766.





Ethyl 2-acetyl-2-fluoro-3-(thiophen-2-yl)pent-4-enoate (**3l**)

Yield: 90% (24.3 mg); *ee*: 99%; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.43 – 7.15 (m, 1H), 7.11 – 6.88 (m, 2H), 6.20 – 5.80 (m, 1H), 5.34 – 5.08 (m, 2H), 4.72 (dd, *J* = 32.3, 8.8 Hz, 1H), 4.34 – 4.22 (m, 1H), 4.18 – 4.02 (m, 1H), 2.33 (d, *J* = 5.6 Hz, 1H), 2.05 (d, *J* = 5.5 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 1H).

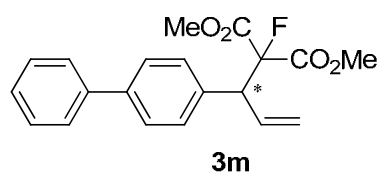
<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ = -174.68 (d, *J* = 67.5 Hz).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 201.6 (d, *J* = 29.6 Hz), 201.3 (d, *J* = 33.2 Hz), 164.6 (d, *J* = 21.5 Hz), 164.4 (d, *J* = 21.6 Hz), 138.5 (s), 137.99 (s), 133.6 (d, *J* = 4.0 Hz), 133.3 (d, *J* = 4.7 Hz), 127.1 (s), 126.8 (s), 126.8 (s), 126.6 (d, *J* = 1.7 Hz), 125.5 (s), 125.2 (s), 120.0 (s), 119.5 (s), 103.4 (d, *J* = 32.8 Hz), 101.3 (d, *J* = 33.7 Hz), 63.0 (s), 62.8 (s), 49.4 (d, *J* = 19.2 Hz), 27.0 (s), 26.8 (s), 14.1 (s), 13.8 (s).

HRMS (ESI+) calcd for C<sub>13</sub>H<sub>15</sub>FNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 293.0618, Found: 293.0614.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL IC (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 1.0 mL/min; detection wavelength = 214 nm; *t*<sub>R</sub> = 9.475 (minor), 9.143 (major) min]. [α]<sub>D</sub><sup>20</sup> = +33.30° (c 1.0, CH<sub>3</sub>OH).

IR (KBr): ν max (cm<sup>-1</sup>) = 3106, 2987, 2945, 2874, 1774, 1688, 1245, 1233, 1186, 768.



Dimethyl 2-(1-([1,1'-biphenyl]-4-yl)allyl)-2-fluoromalonate (**3m**)

Yield: 97% (1.27 g); *ee*: 95%; colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.62 (t, *J* = 8.9 Hz, 4H), 7.48 (dd, *J* = 13.9, 7.5 Hz, 4H), 7.39 (t, *J* = 7.3 Hz, 1H), 6.32 – 6.12 (m, 1H), 5.32 (t, *J* = 12.6 Hz, 2H), 4.49 (dd, *J* = 31.7, 8.9 Hz, 1H), 3.93 (s, 3H), 3.68 (s, 3H).

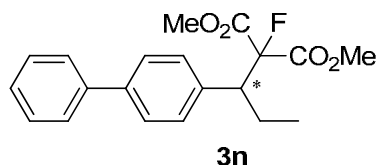
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = -175.93 (s).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 165.7 (d, *J* = 25.8 Hz), 165.3 (d, *J* = 25.9 Hz), 140.6 (d, *J* = 6.2 Hz), 135.5 (s), 133.7 (d, *J* = 4.6 Hz), 129.6 (d, *J* = 2.2 Hz), 128.8 (s), 127.5 (s), 127.3 (s), 127.1 (s), 119.7 (s), 97.5 (d, *J* = 209.3 Hz), 54.3 (s), 54.1 (s), 53.5 (d, *J* = 28.1 Hz).

HRMS (ESI+) calcd for C<sub>20</sub>H<sub>19</sub>FNaO<sub>4</sub> [M+Na]<sup>+</sup>: 365.1159, Found: 365.1151.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL IC (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 1.0 mL/min; detection wavelength = 214 nm; *t*<sub>R</sub> = 23.768 (major), 33.878 (minor) min]. [α]<sub>D</sub><sup>20</sup> = +68.87° (c 1.0, CH<sub>3</sub>OH).

IR (KBr): ν max (cm<sup>-1</sup>) = 3106, 2987, 2945, 2874, 1774, 1688, 1245, 1233, 1186, 1178, 1099, 988, 856, 807, 768.



Dimethyl 2-(1-([1,1'-biphenyl]-4-yl)propyl)-2-fluoromalonate (**3n**)

Yield: 95% (1.20 g); *ee*: 97%; colorless oil.

$\delta$  =  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.64 (d,  $J$  = 7.7 Hz, 2H), 7.59 (d,  $J$  = 7.7 Hz, 2H), 7.48 (t,  $J$  = 7.5 Hz, 2H), 7.39 (d,  $J$  = 7.4 Hz, 3H), 3.96 (s, 3H), 3.65 (dd,  $J$  = 31.1, 10.5 Hz, 1H), 3.59 (s, 3H), 2.05 – 1.87 (m, 1H), 1.84 – 1.69 (m, 1H), 0.85 (t,  $J$  = 7.3 Hz, 3H).

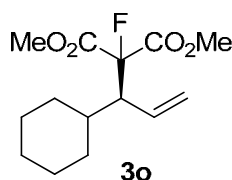
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -177.10 (s).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 166.4 (d,  $J$  = 25.7 Hz), 165.7 (d,  $J$  = 26.4 Hz), 140.6 (s), 140.4 (s), 135.8 (s), 129.9 (d,  $J$  = 1.9 Hz), 128.8 (s), 127.4 (s), 127.0 (s), 97.9 (d,  $J$  = 208.4 Hz), 53.7 (s), 53.1 (s), 51.7 (d,  $J$  = 19.2 Hz), 23.0 (d,  $J$  = 4.9 Hz), 12.1 (s).

HRMS (ESI+) calcd for  $\text{C}_{20}\text{H}_{21}\text{FNaO}_4$  [ $\text{M}+\text{Na}$ ] $^+$ : 367.1316, Found: 367.1320.

The *ee* of the product was determined by chiral HPLC [Daicel CHIRALCEL IC (0.46 cm x 25 cm); hexane/2-propanol = 98/2, flow rate = 1.0 mL/min; detection wavelength = 214 nm;  $t_{\text{R}}$  = 8.338(major), 12.147(minor) min].  $[\alpha]_{\text{D}}^{20}$  = -5.87° (c 1.0,  $\text{CH}_3\text{OH}$ ).

IR (KBr):  $\nu$  max (cm $^{-1}$ ) = 3126, 2989, 2955, 2874, 1247, 1237, 1186, 1178, 1099, 988, 819, 807, 768.



Dimethyl 2-(1-cyclohexylallyl)-2-fluoromalonate (**3o**)

Yield: 54% (14.7 mg); *ee*: 91%; Colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 5.79 (dt,  $J$  = 17.1, 10.3 Hz, 1H), 5.59 (dd,  $J$  = 15.4, 6.9 Hz, 1H), 5.42 – 5.30 (m, 1H), 5.24 (dd,  $J$  = 10.2, 1.6 Hz, 1H), 5.16 (d,  $J$  = 17.1 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 5.6H), 3.80 (s, 3H), 3.02 – 2.92 (m, 1H), 2.90 (d,  $J$  = 7.2 Hz, 1.2H), 2.84 (d,  $J$  = 7.1 Hz, 1H), 2.03 – 1.83 (m, 2H), 1.80 – 1.63 (m, 8.2H), 1.54 – 1.43 (m, 1H), 1.35 – 0.93 (m, 11H) ppm.

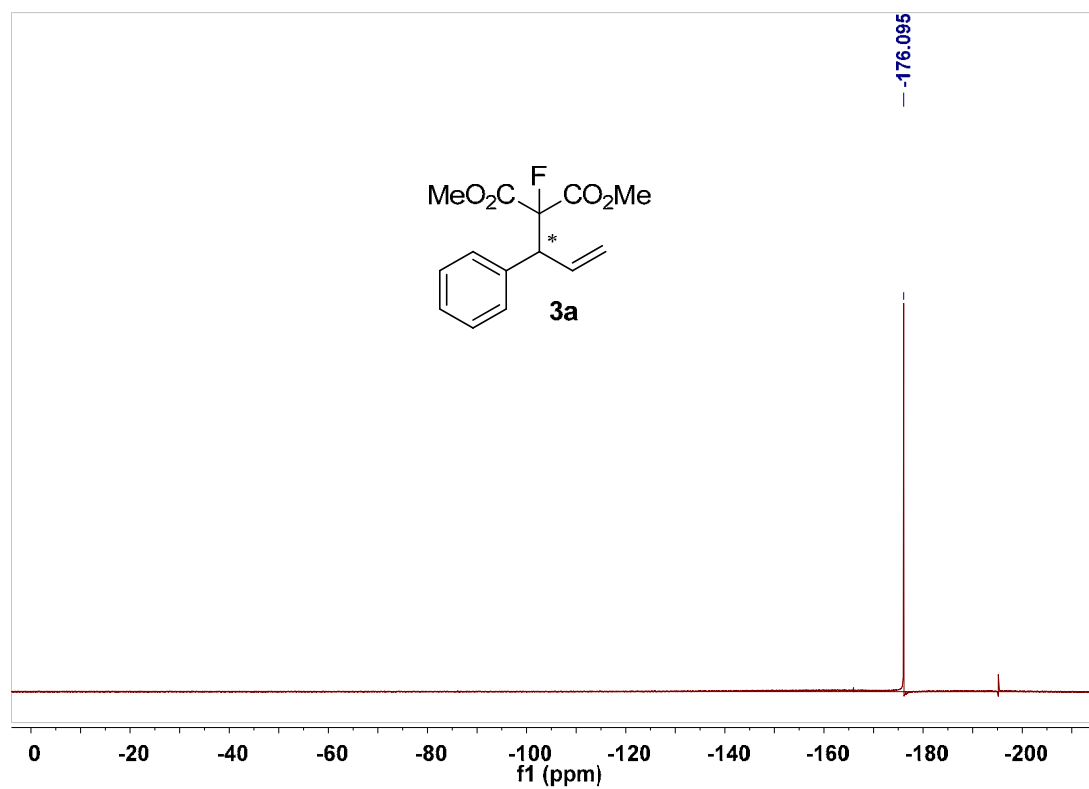
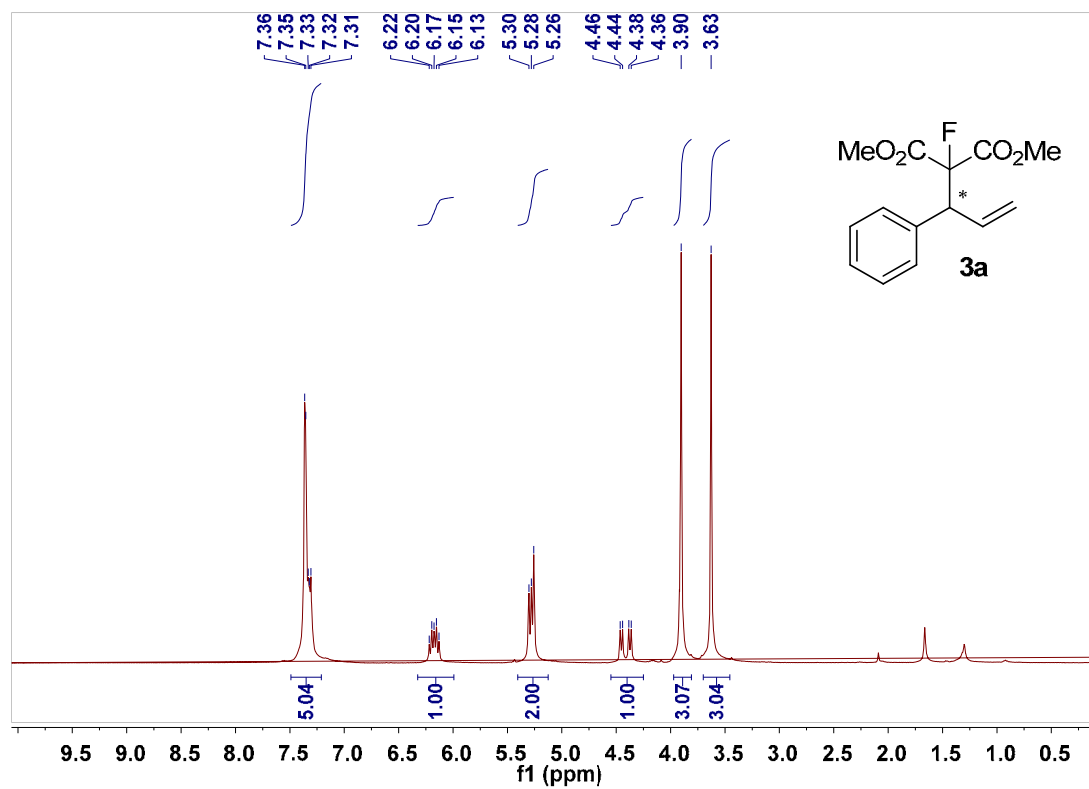
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -166.69 (s), -175.34 (s) ppm.

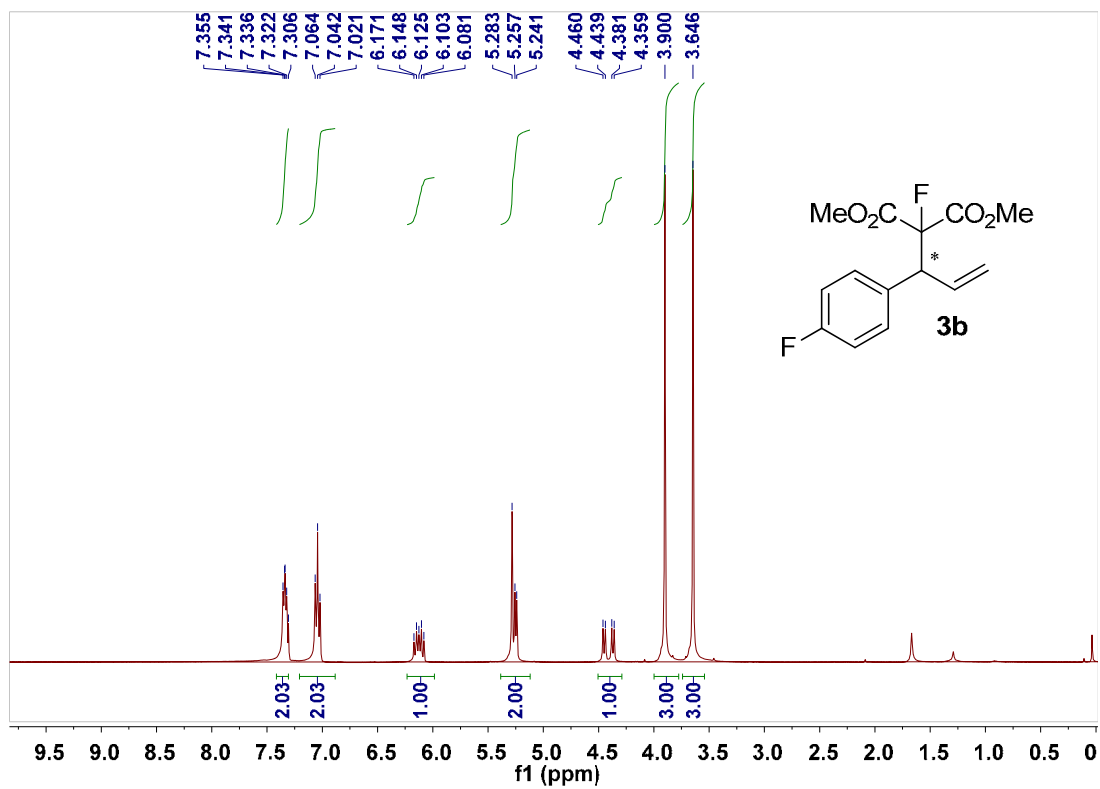
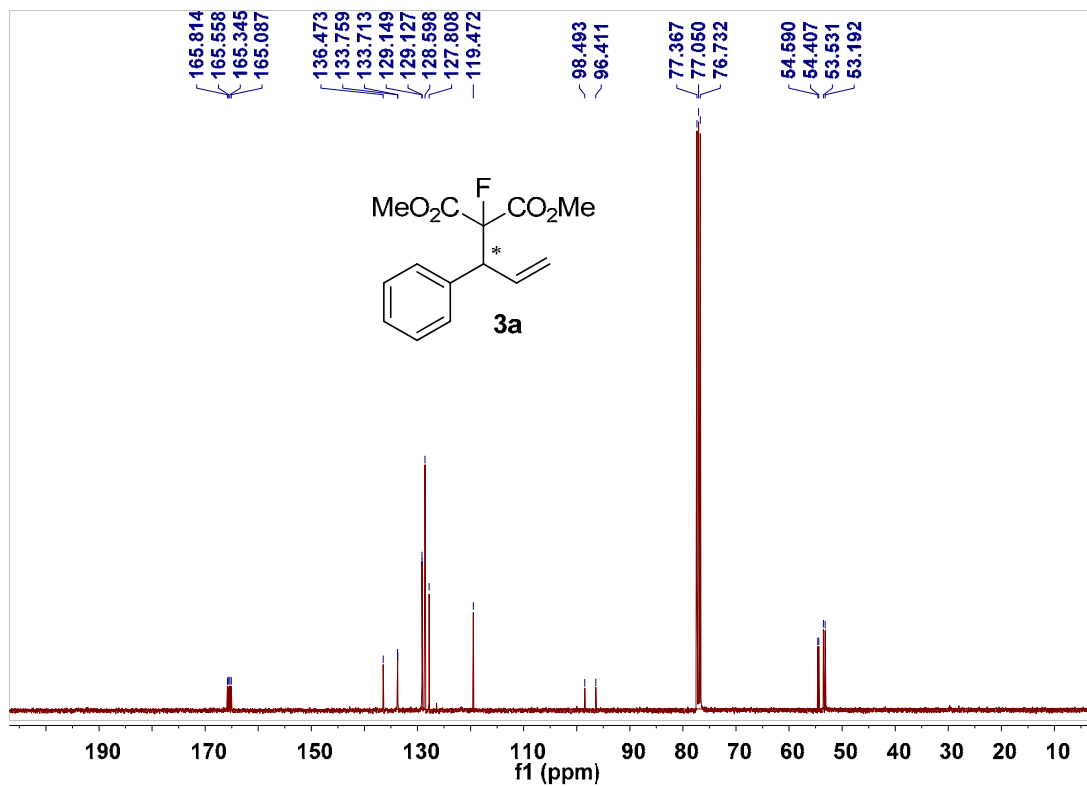
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 166.5(d,  $J$  = 26.1 Hz), 166.4(d,  $J$  = 25.6 Hz), 166.0 (s), 143.4 (s), 132.6 (d,  $J$  = 3.2 Hz), 120.5 (s), 117.7 (d,  $J$  = 2.7 Hz), 98.5 (d,  $J$  = 208.5 Hz), 94.9 (d,  $J$  = 199.4 Hz), 54.3 (d,  $J$  = 18.7 Hz), 53.4 (s), 53.2 (s), 40.7 (s), 38.7 (s), 37.9 (d,  $J$  = 21.1 Hz), 32.8 (s), 32.1 (s), 29.5 (s), 29.4 (s), 26.6 (s), 26.4 (s), 26.1 (d,  $J$  = 2.3 Hz), 25.9 (s).

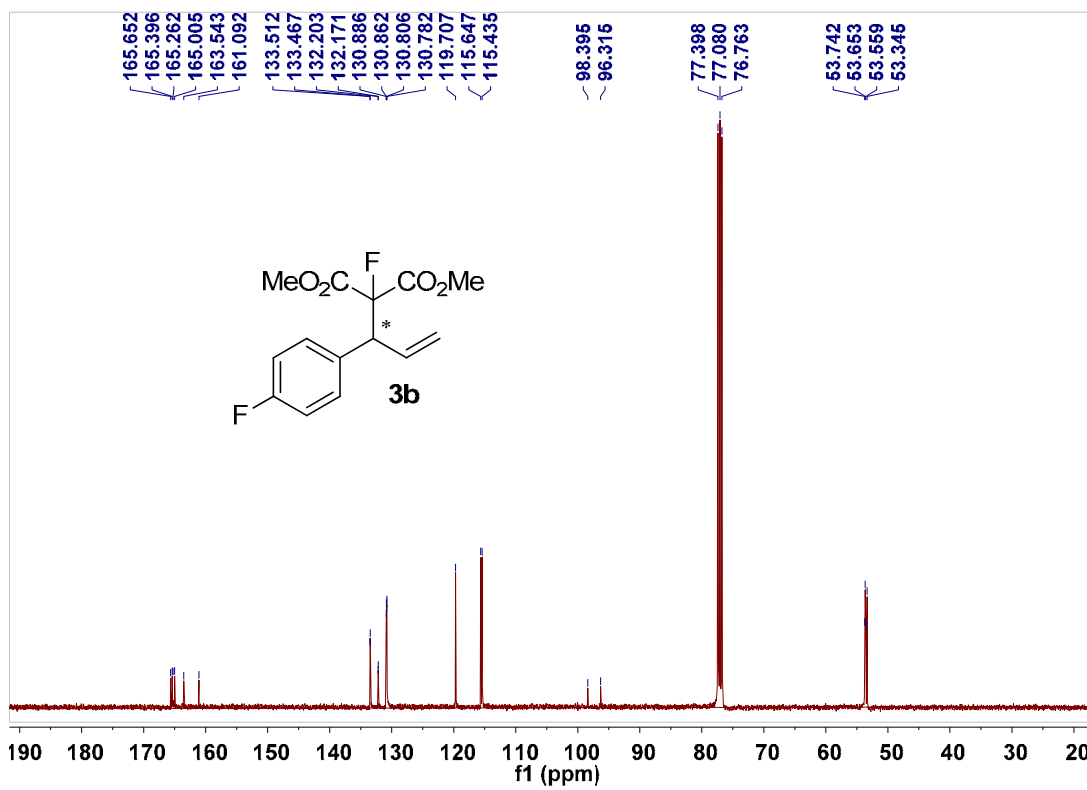
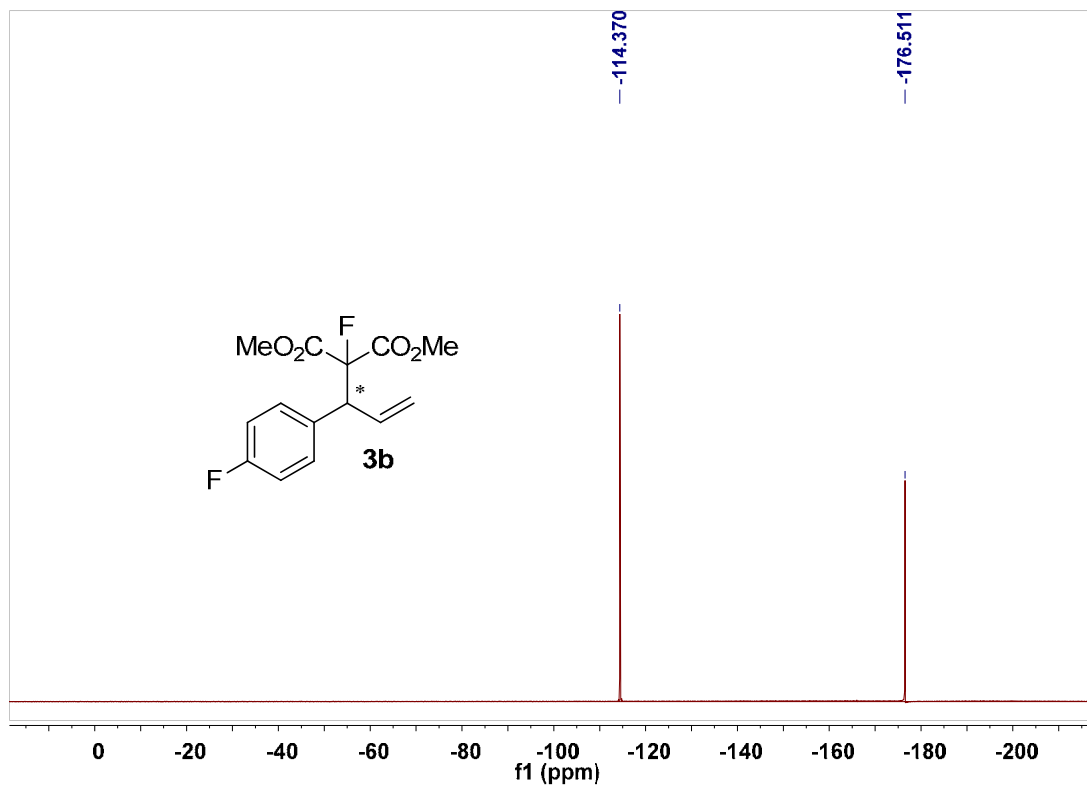
HRMS (ESI+) calcd for  $\text{C}_{14}\text{H}_{21}\text{FNaO}_4$  [ $\text{M}+\text{Na}$ ] $^+$ : 295.1316, Found: 295.1320.

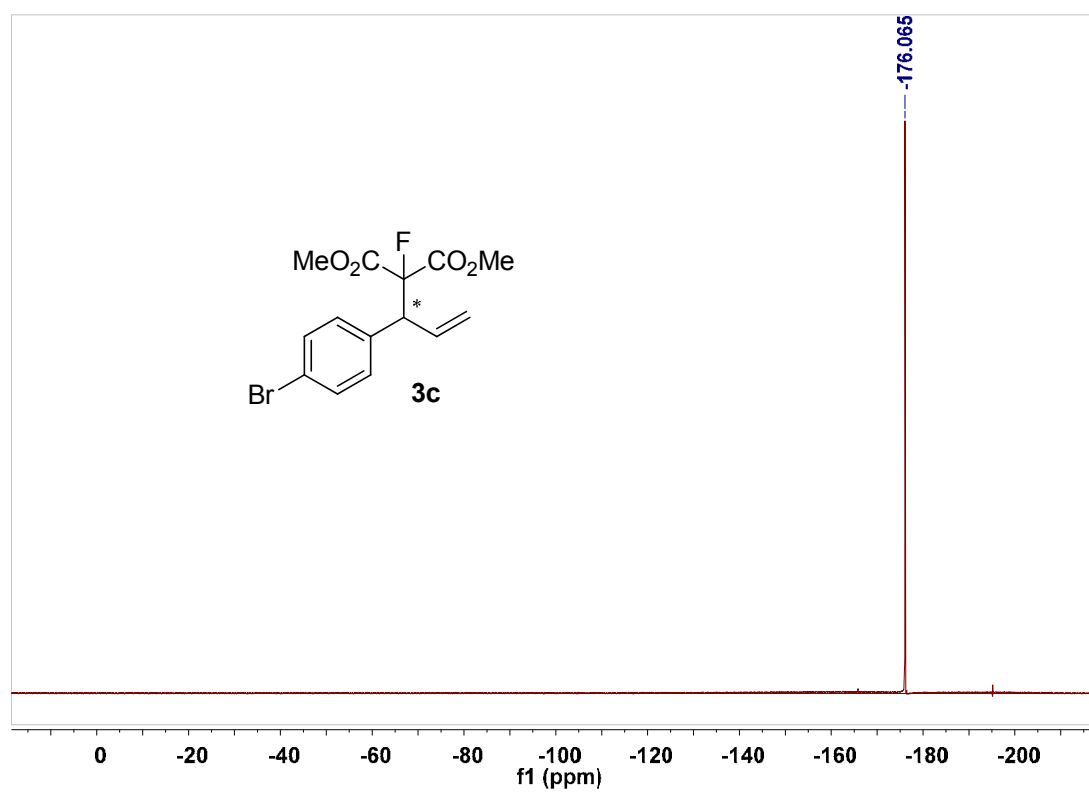
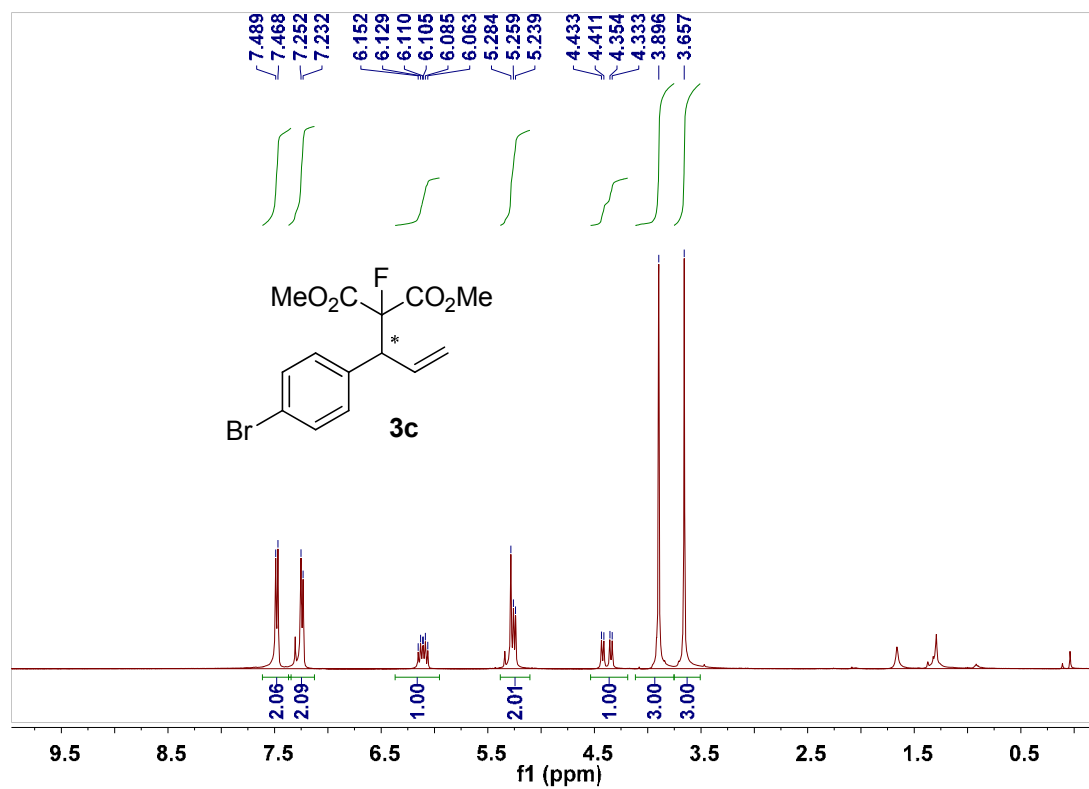
The *ee* of the product was determined by chiral HPLC. [Daicel CHIRALCEL IC (0.46 cm x 25 cm); hexane/2-propanol = 95/5, flow rate = 1.2 mL/min; detection wavelength = 214 nm;  $t_R$  = 10.203 (minor), 11.392 (major) min].  $[\alpha]_D^{20} = +23.7^\circ$  (c 1.0, CH<sub>3</sub>OH).

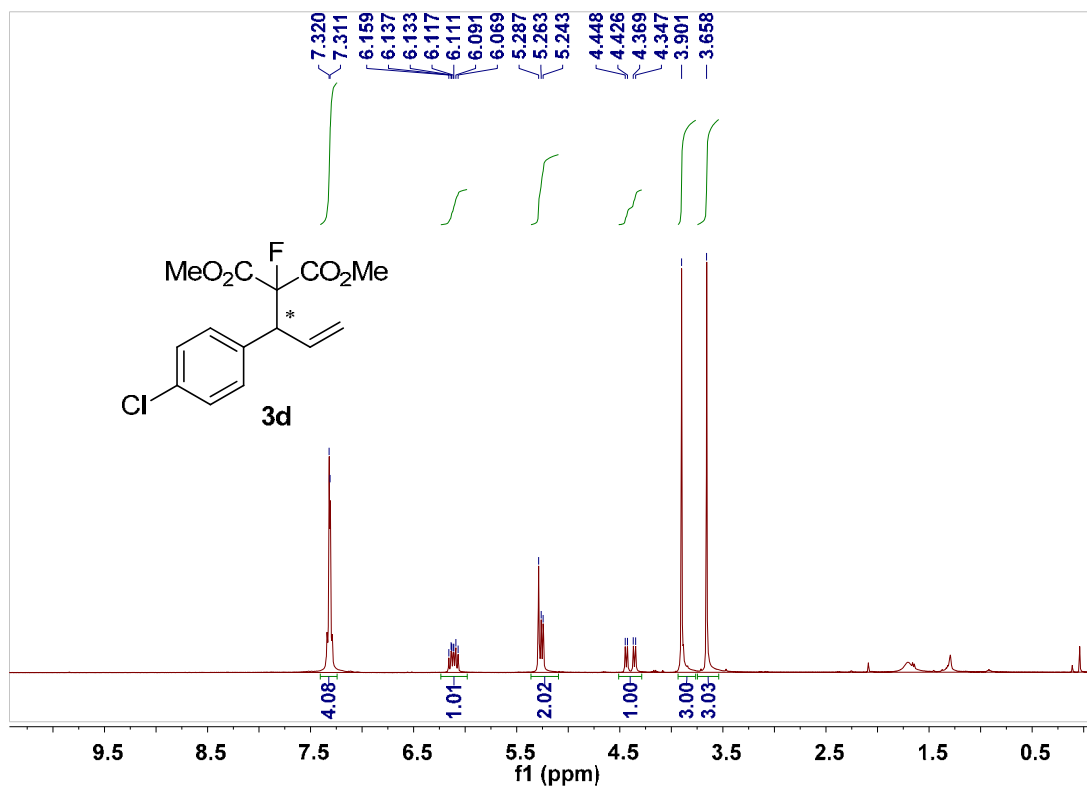
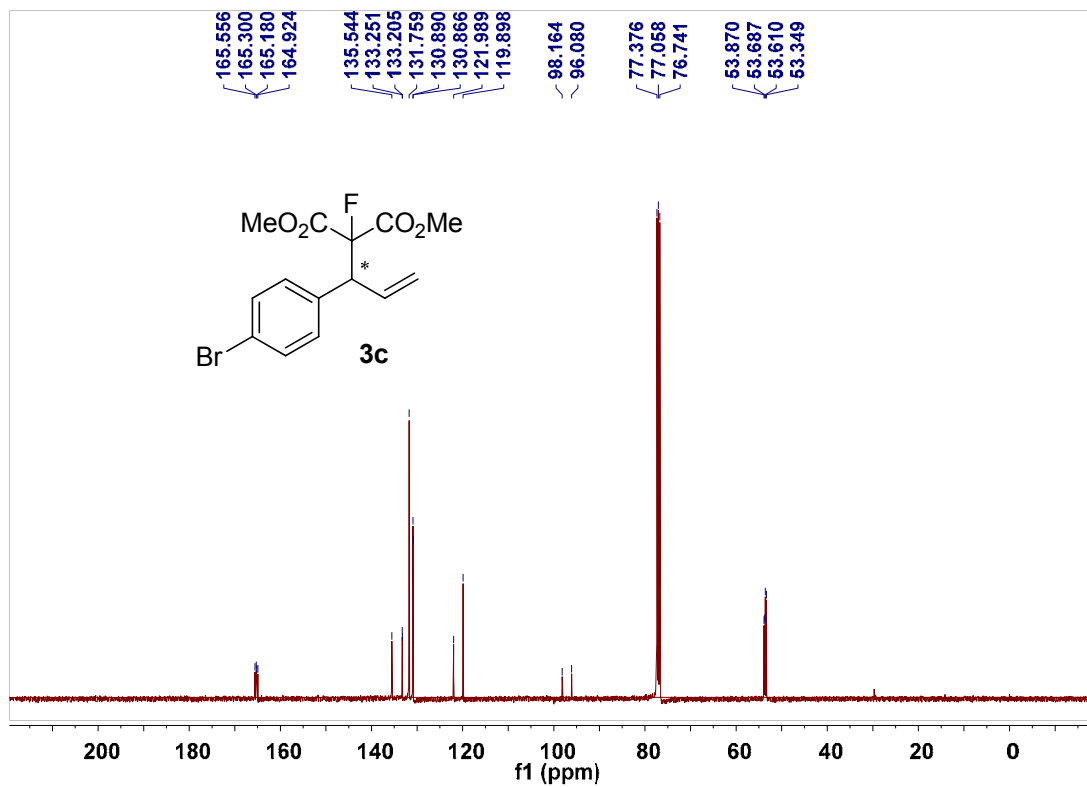
IR (KBr):  $\nu$  max (cm<sup>-1</sup>) = 3095, 3053, 2902, 2887, 2865, 2812, 1460, 1428, 1360, 1037, 920, 830, 665, 531.



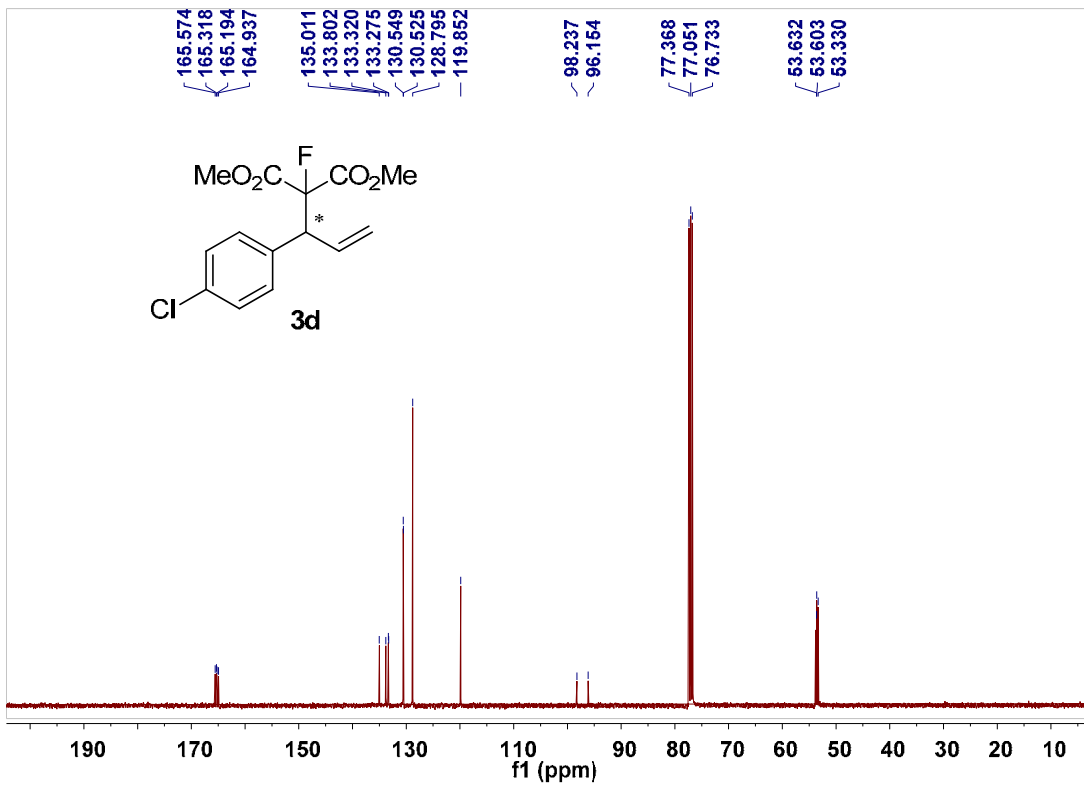
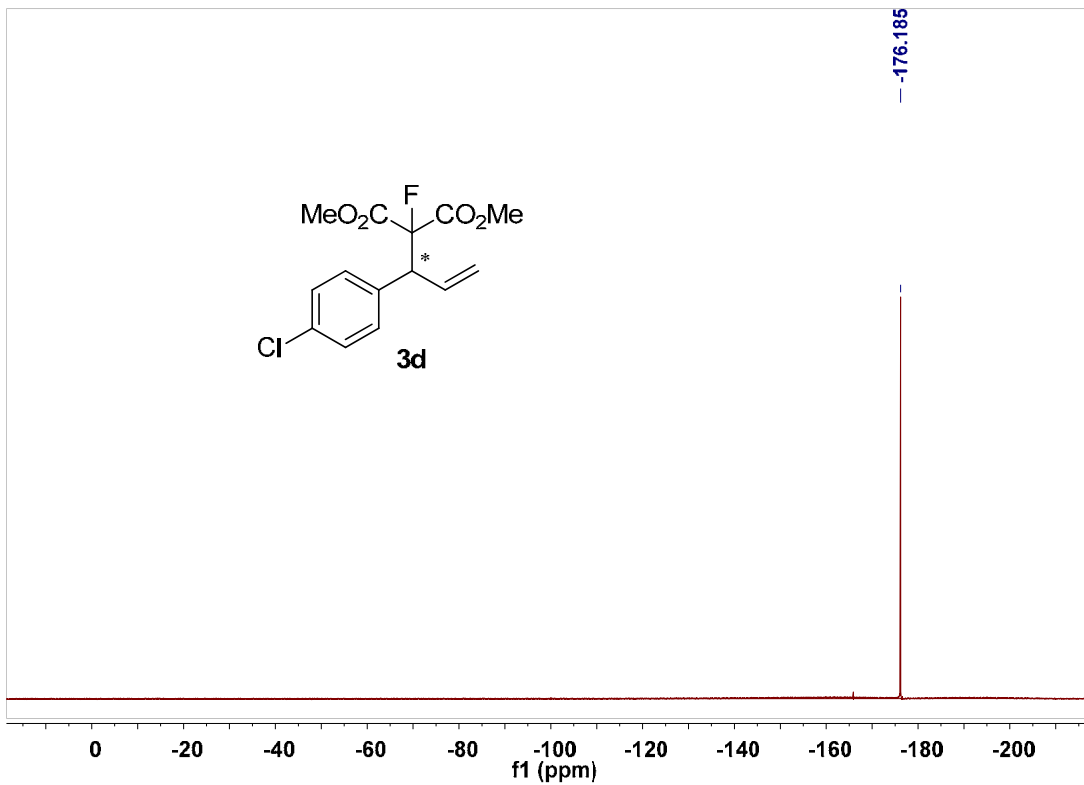


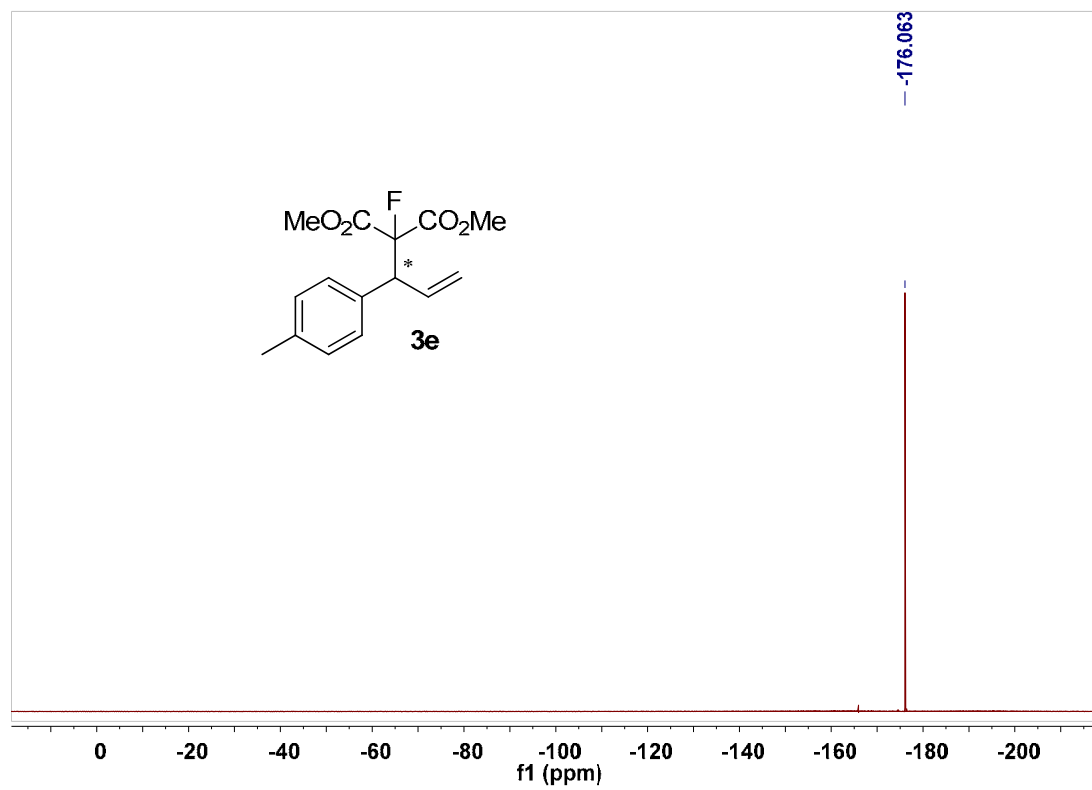
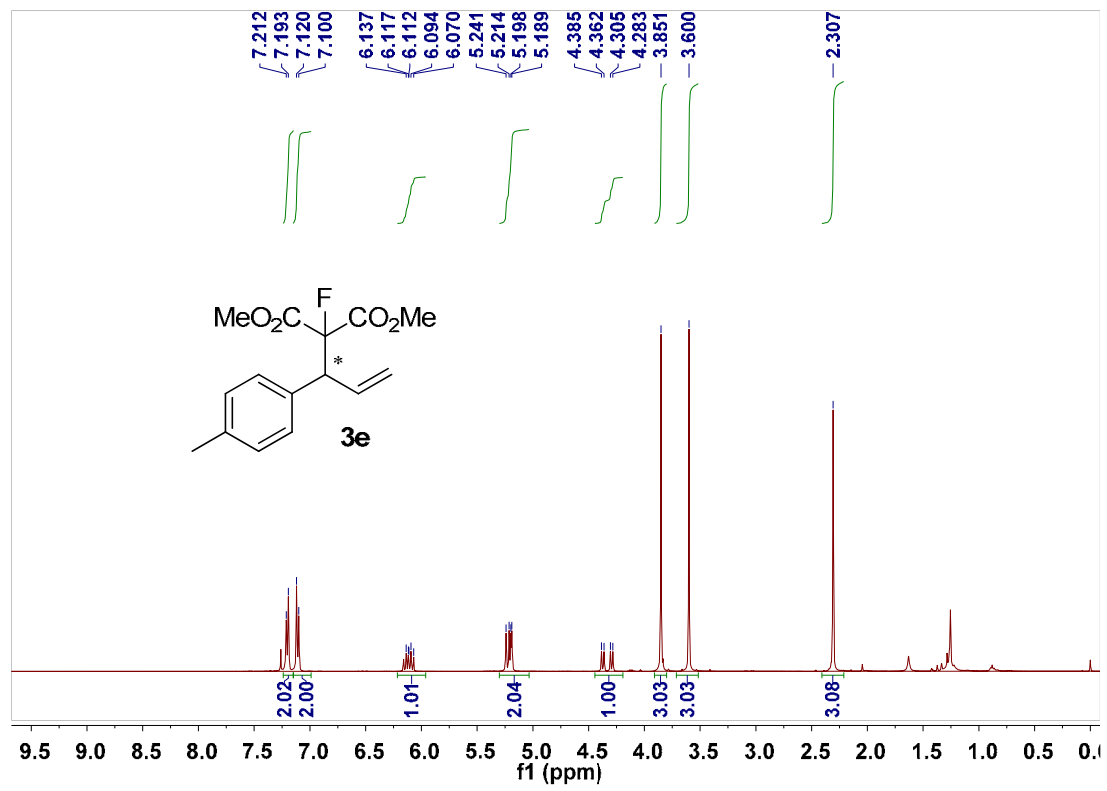


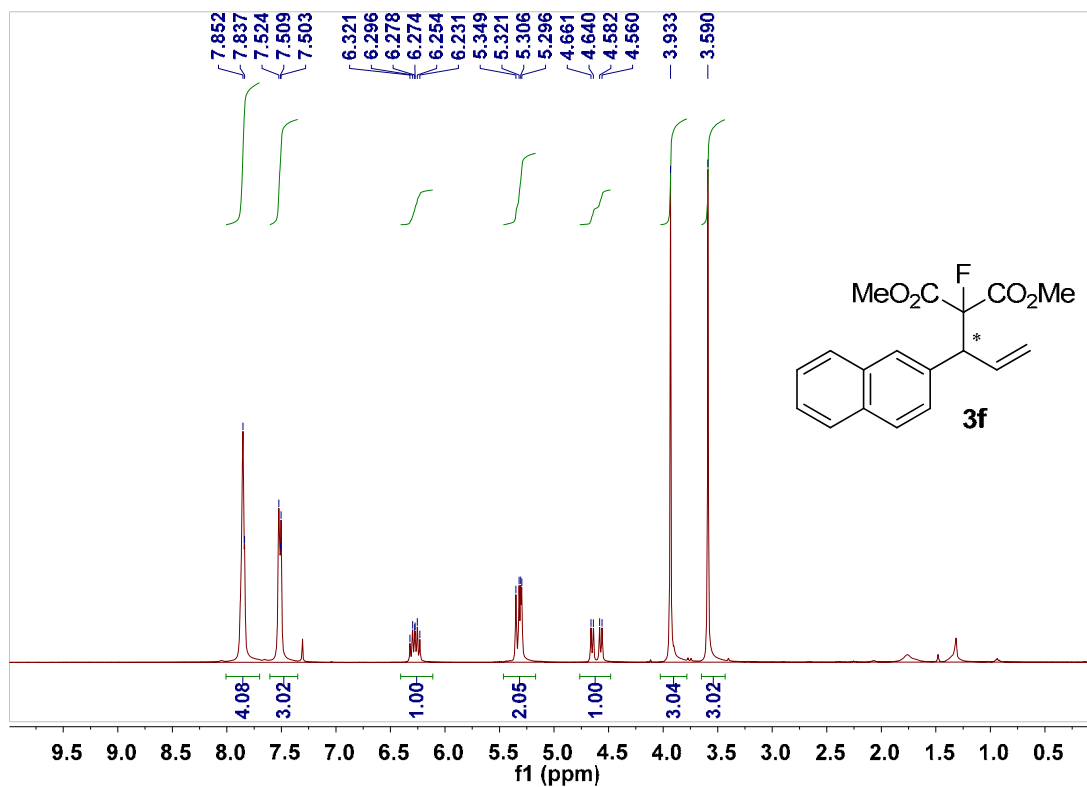
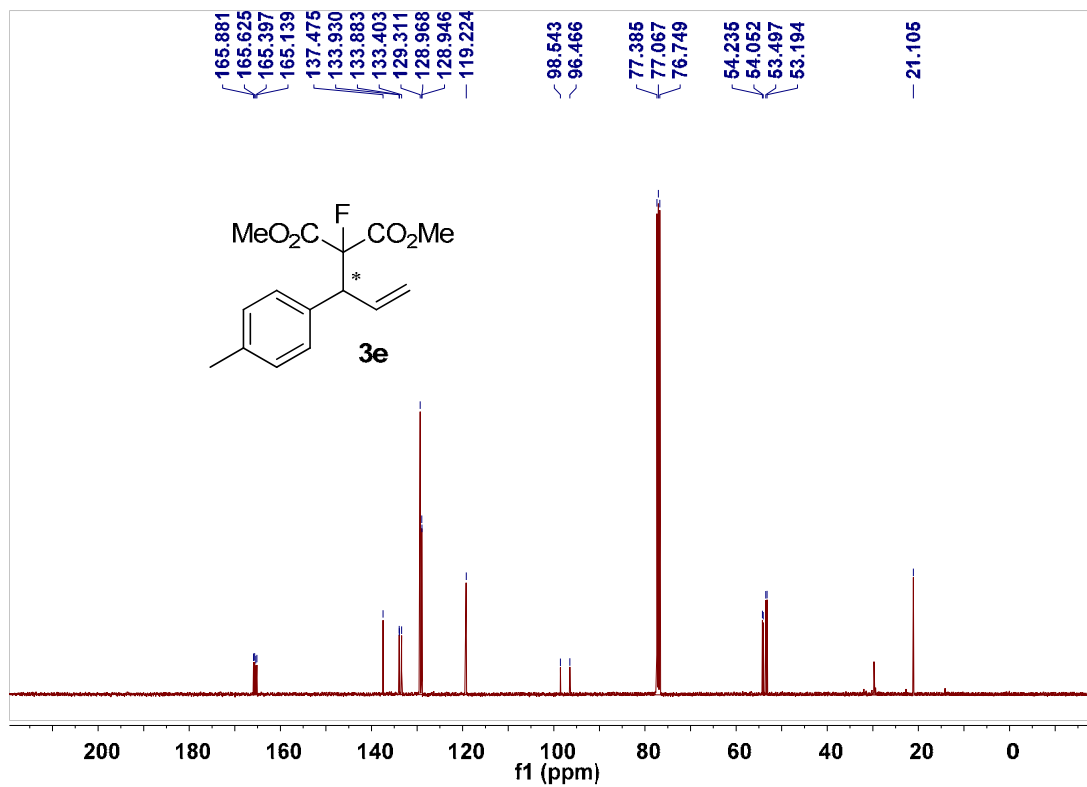


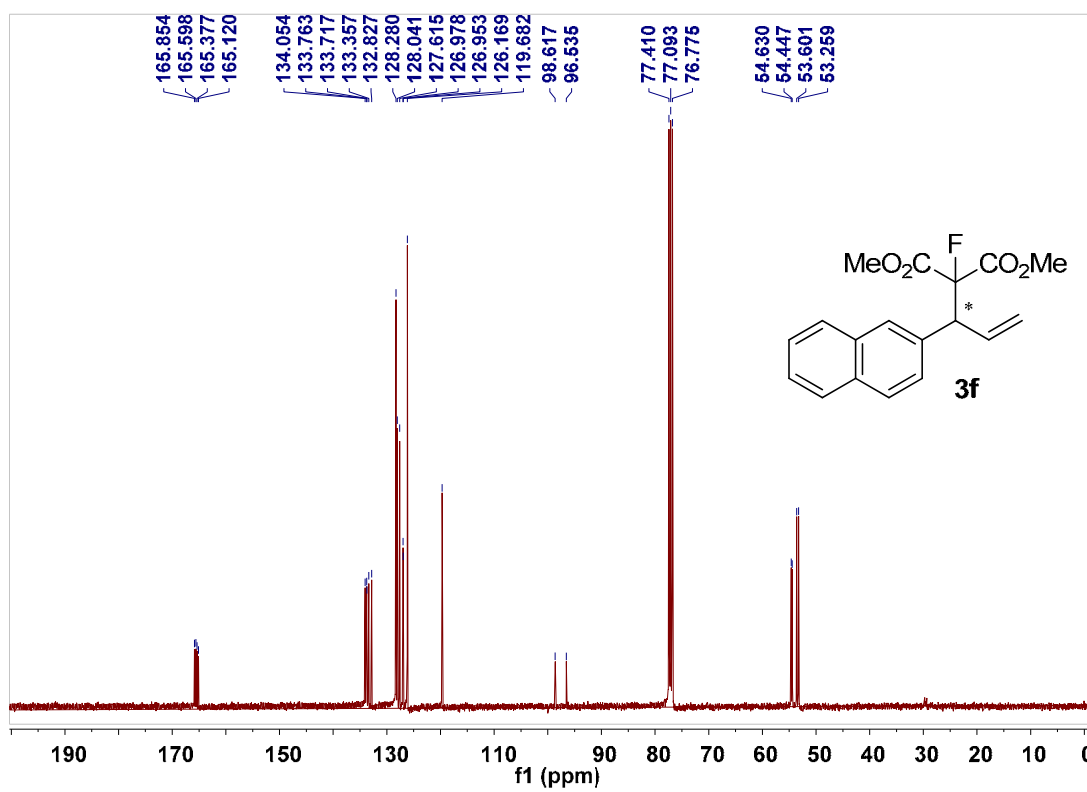
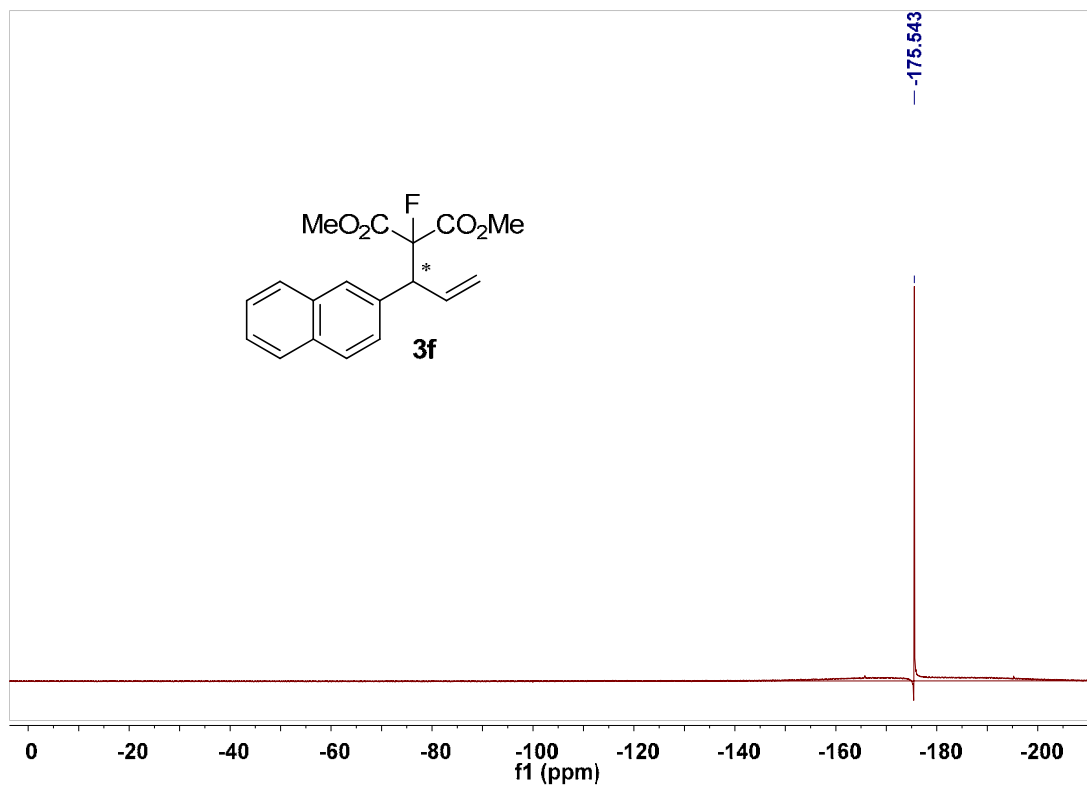


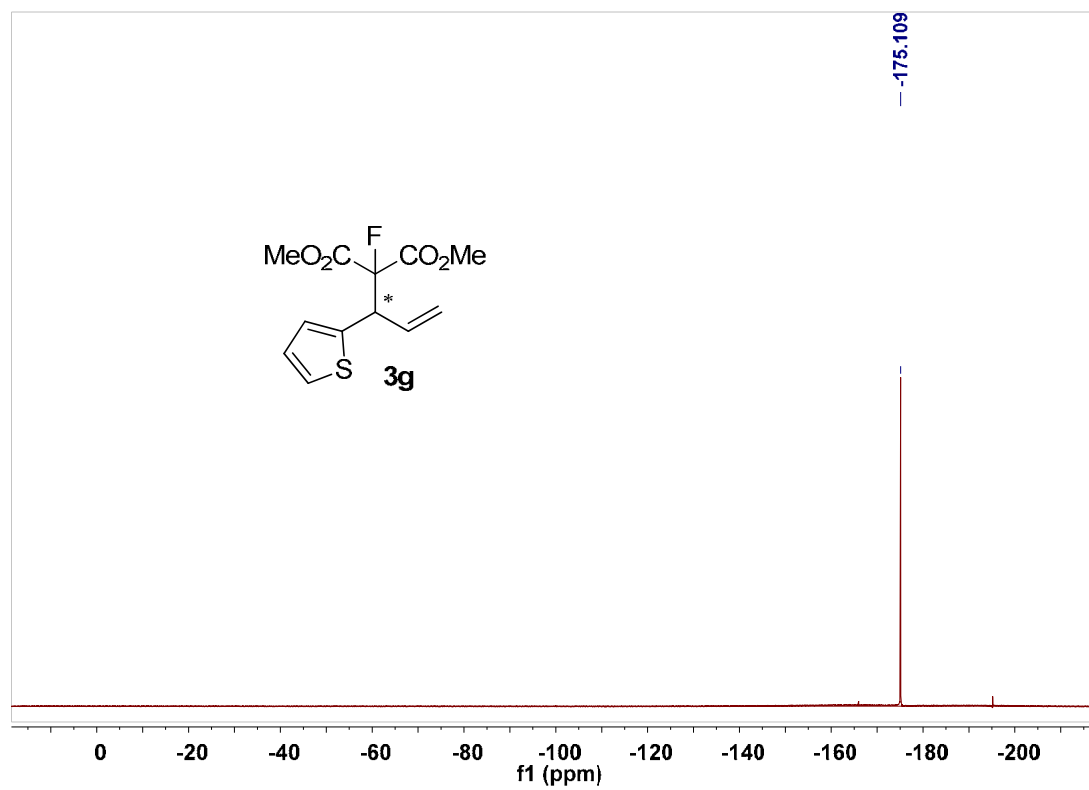
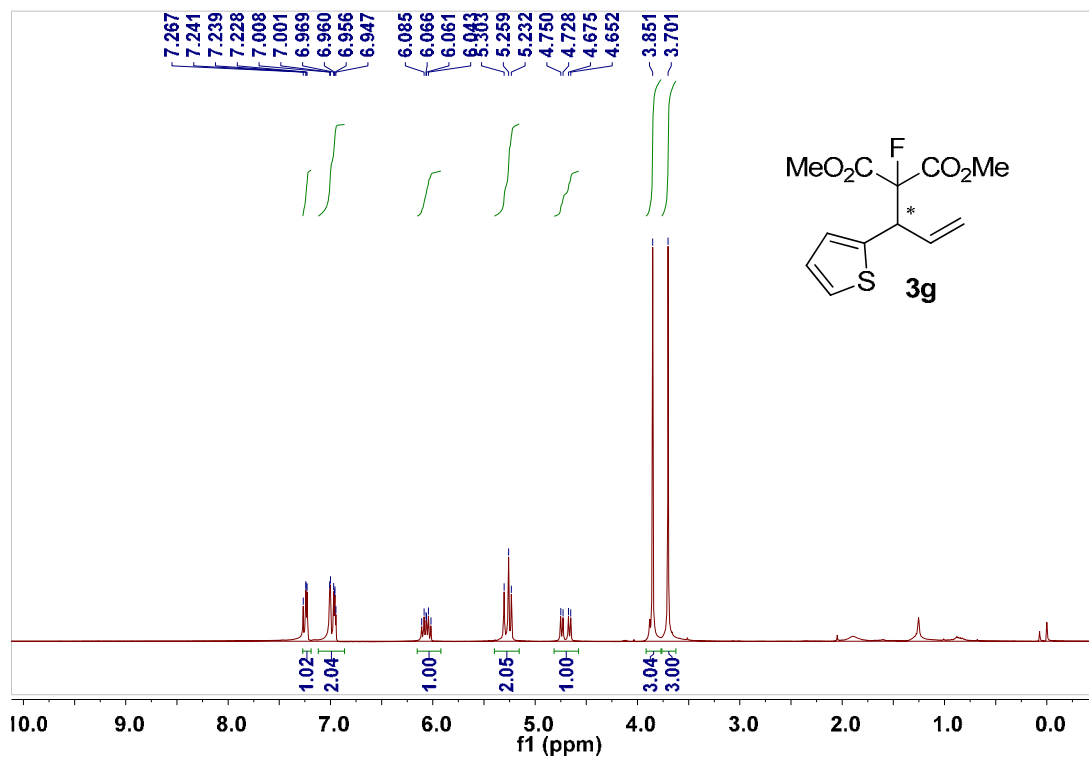


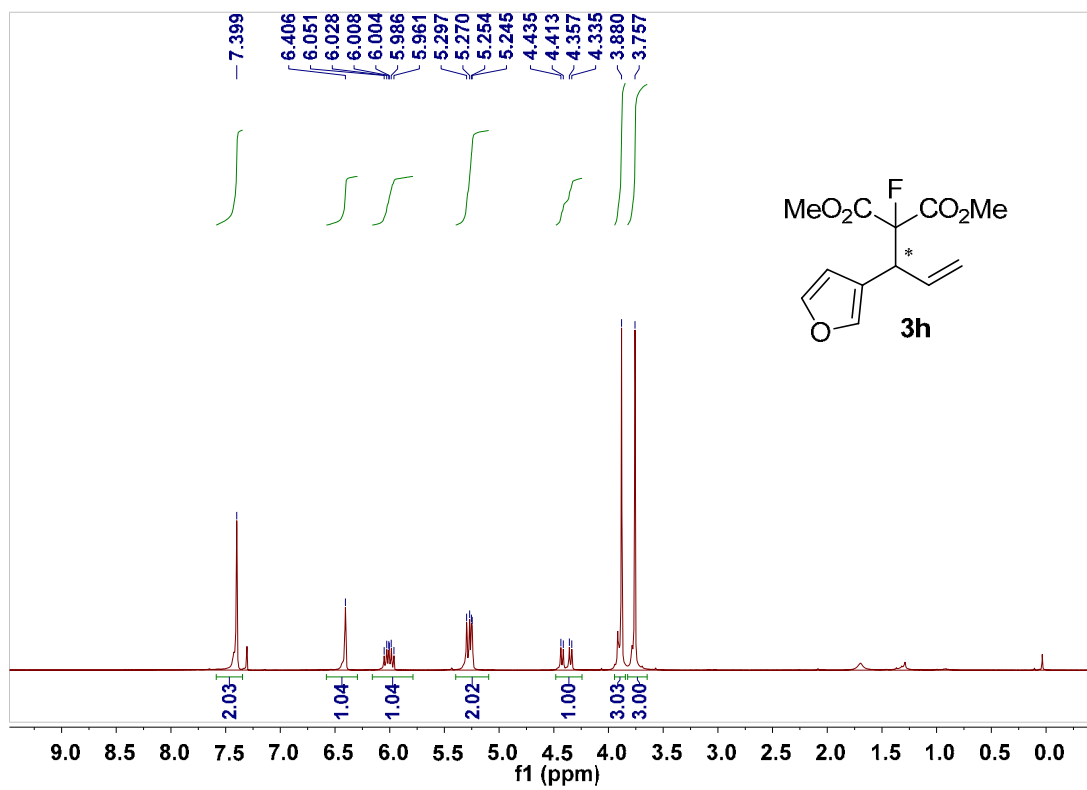
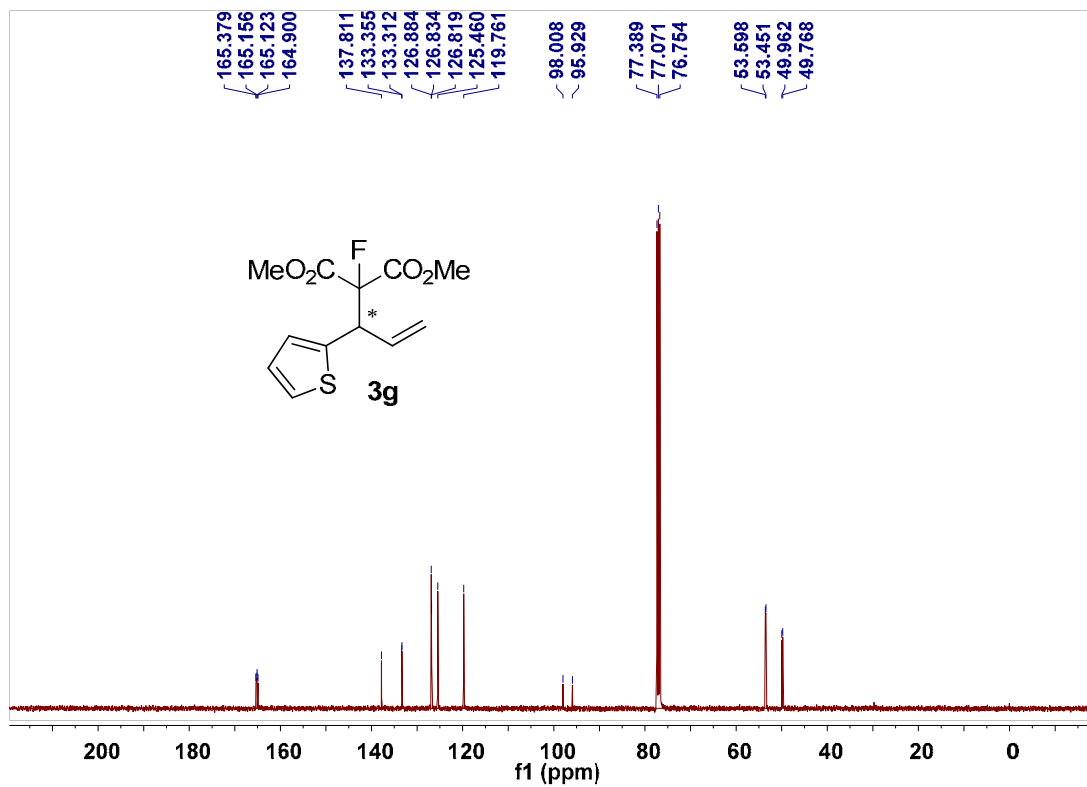


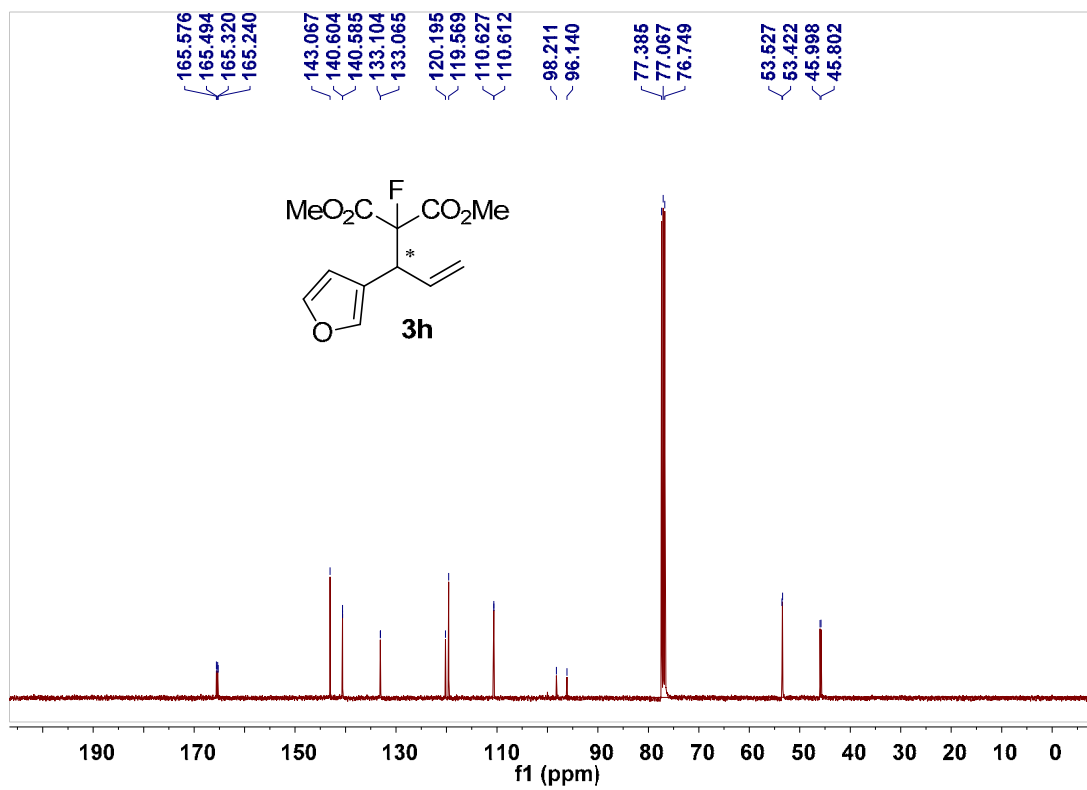
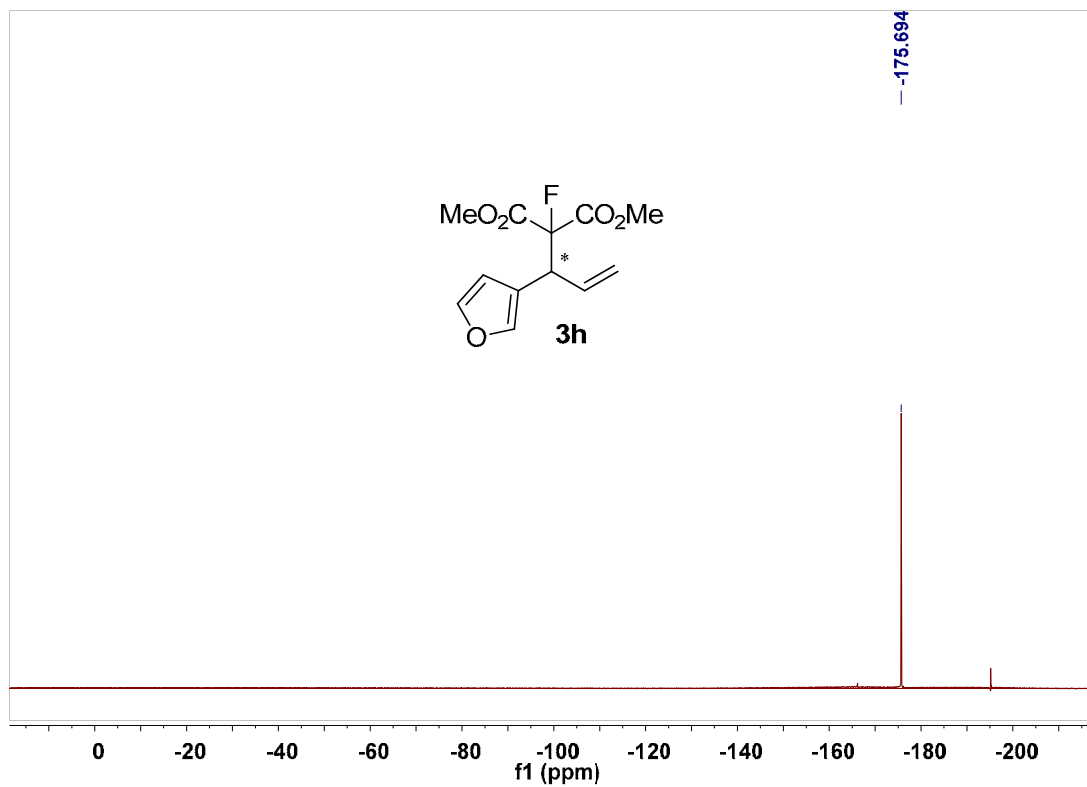


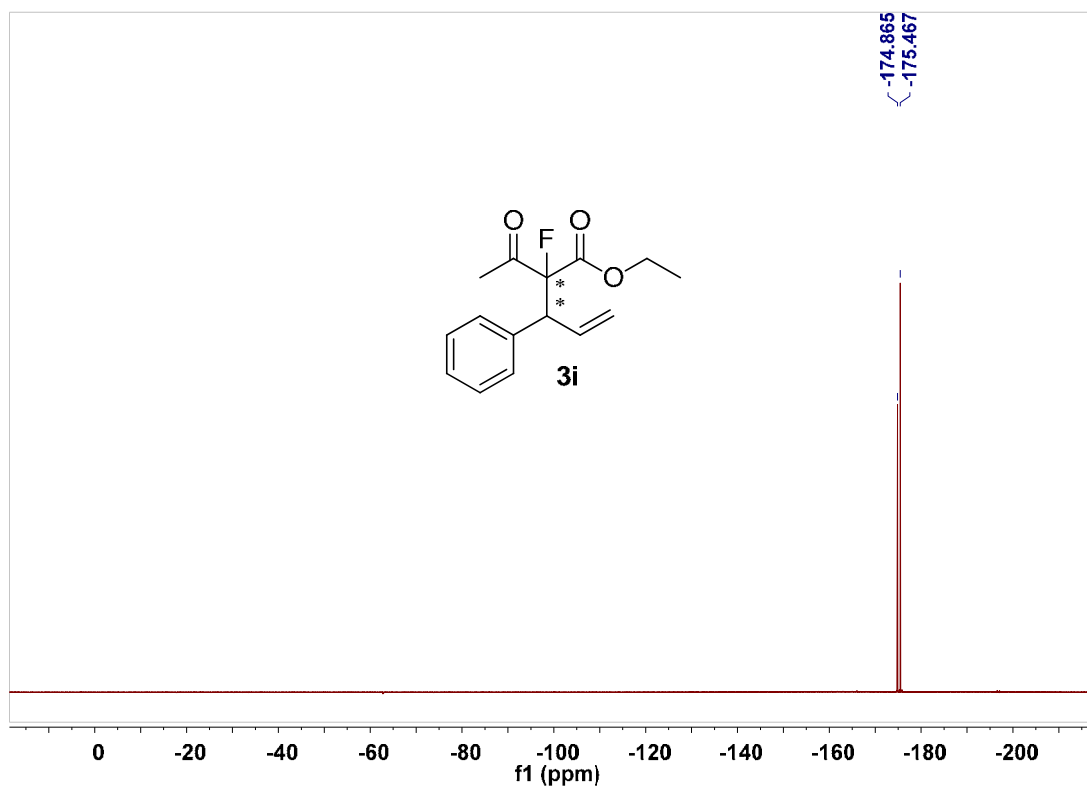
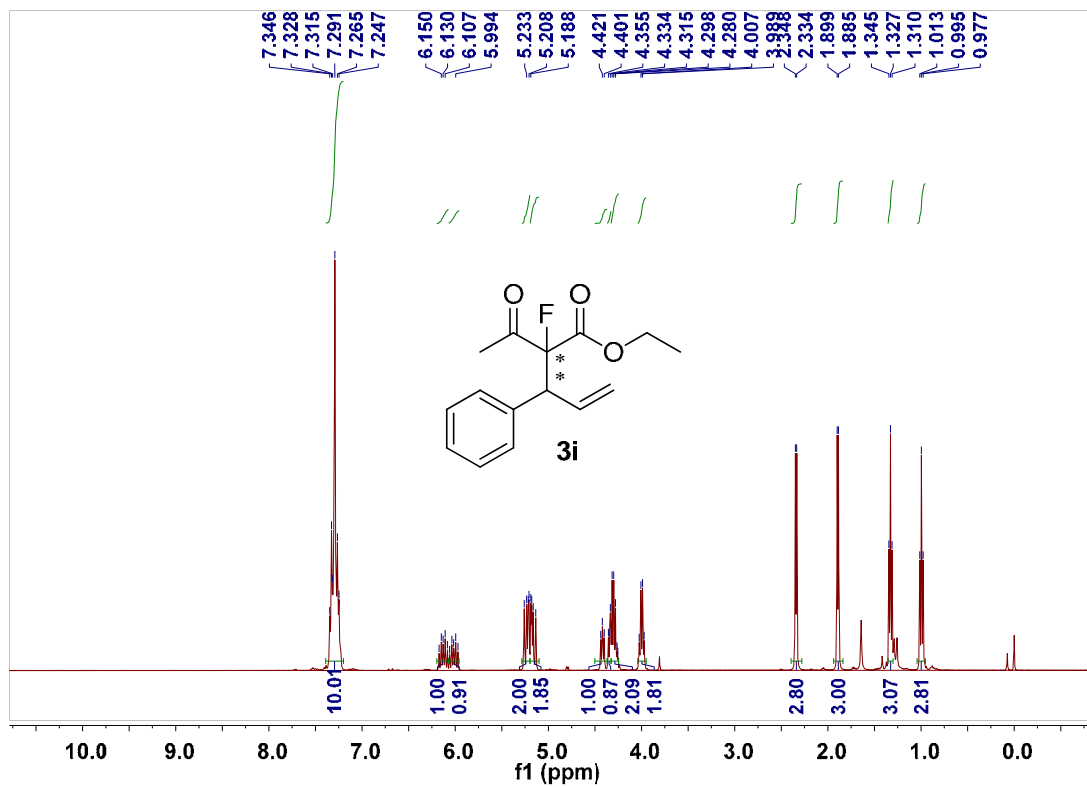




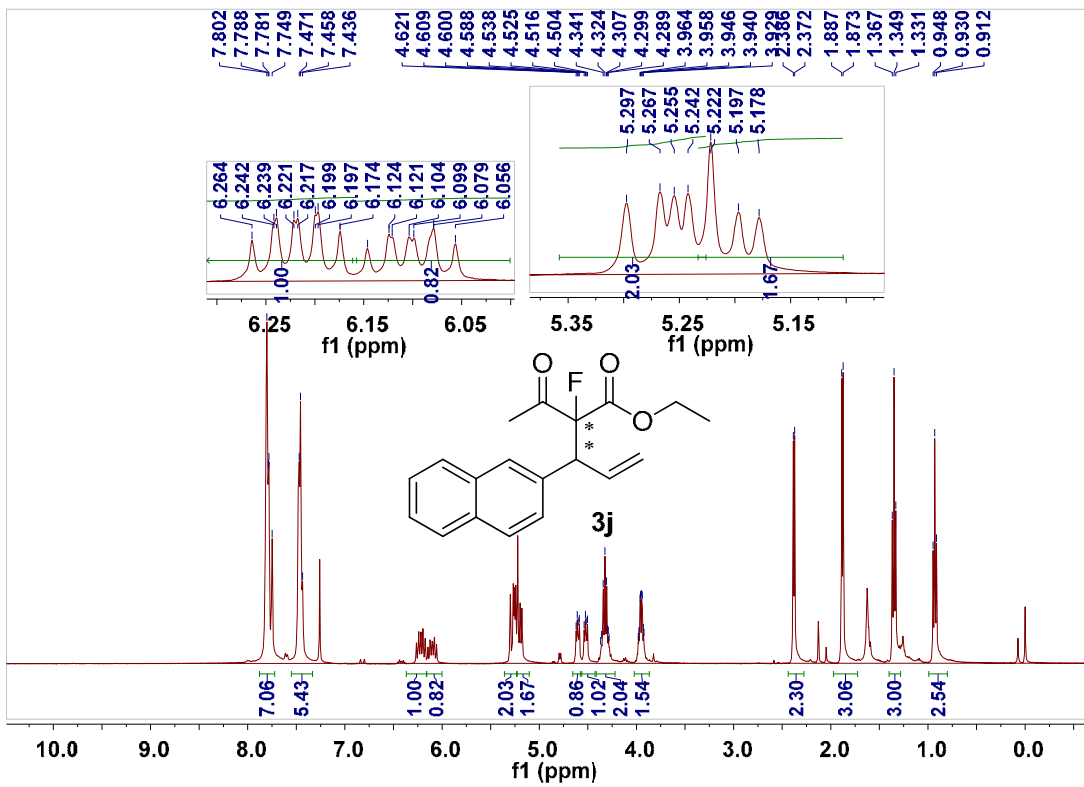
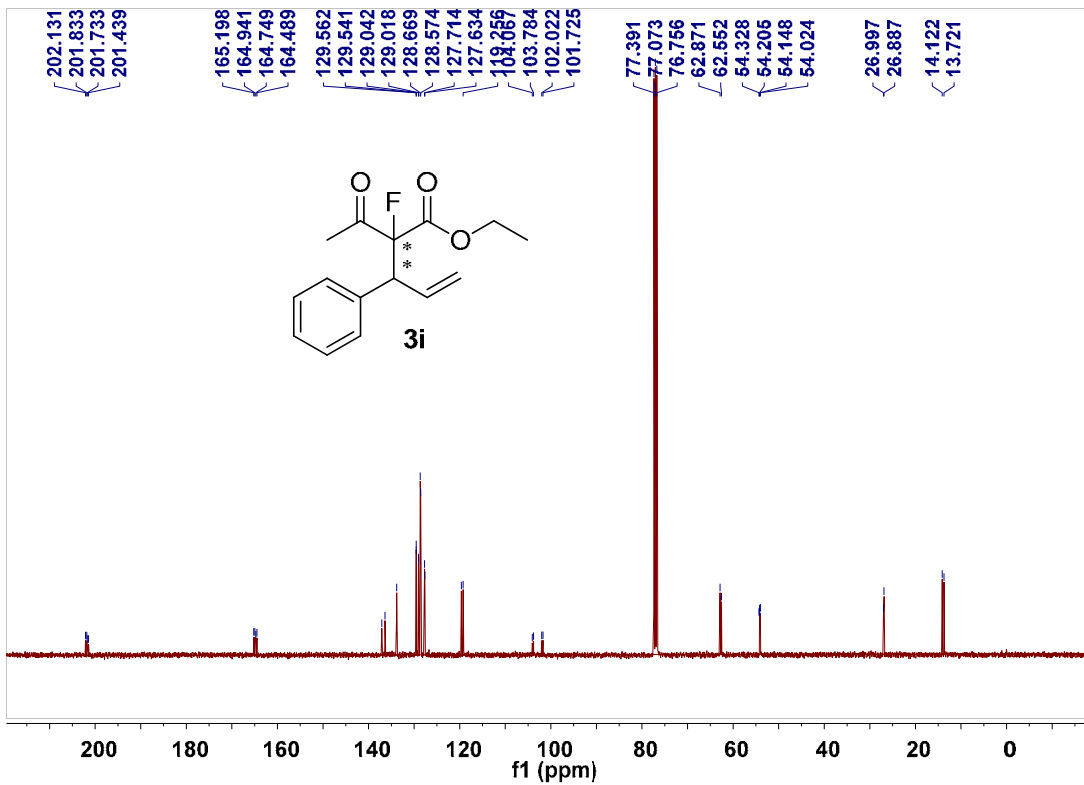


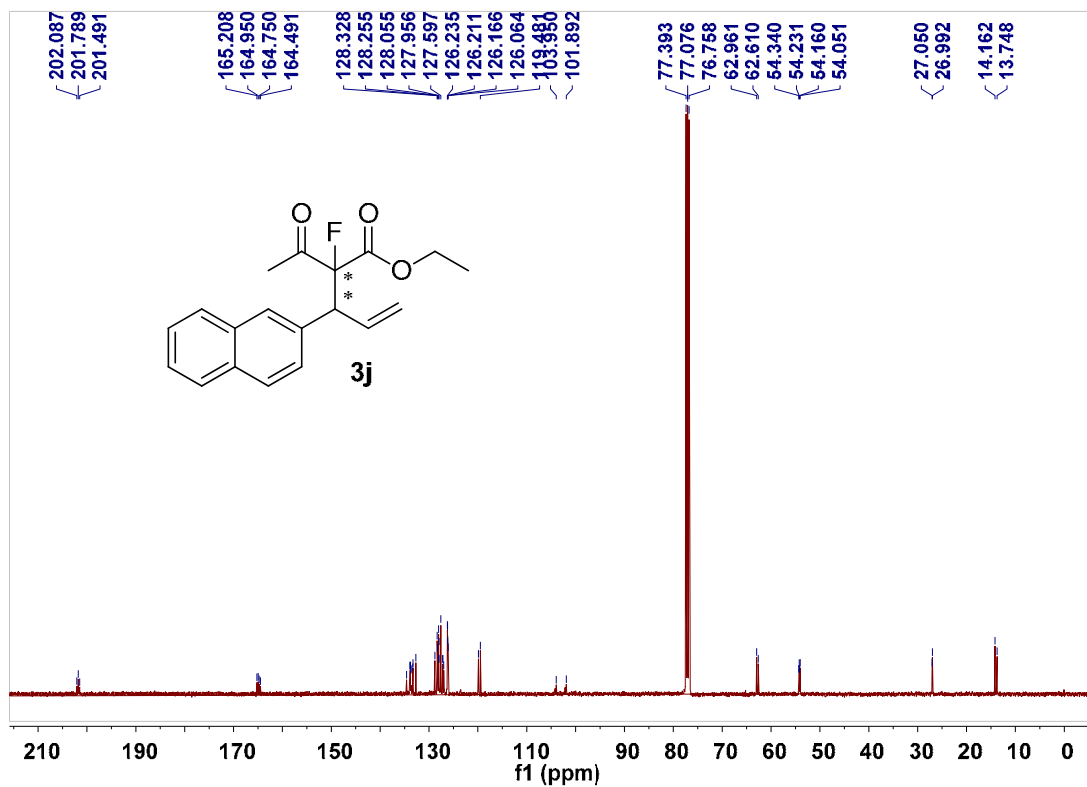
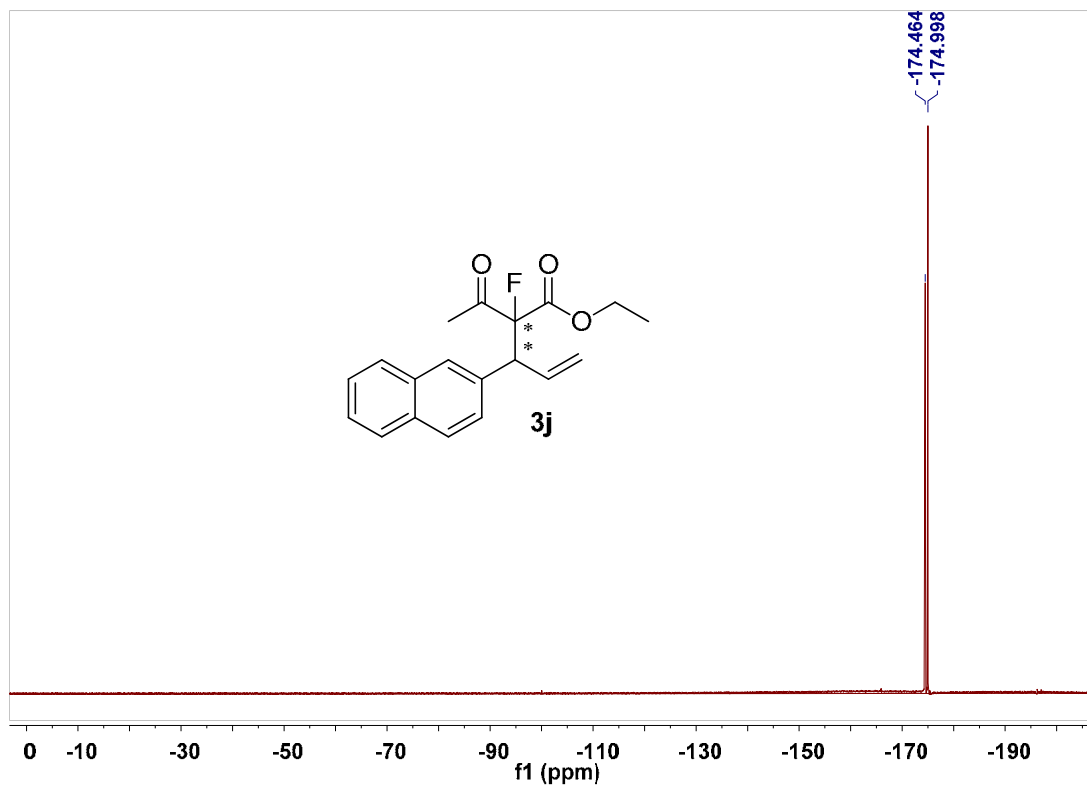


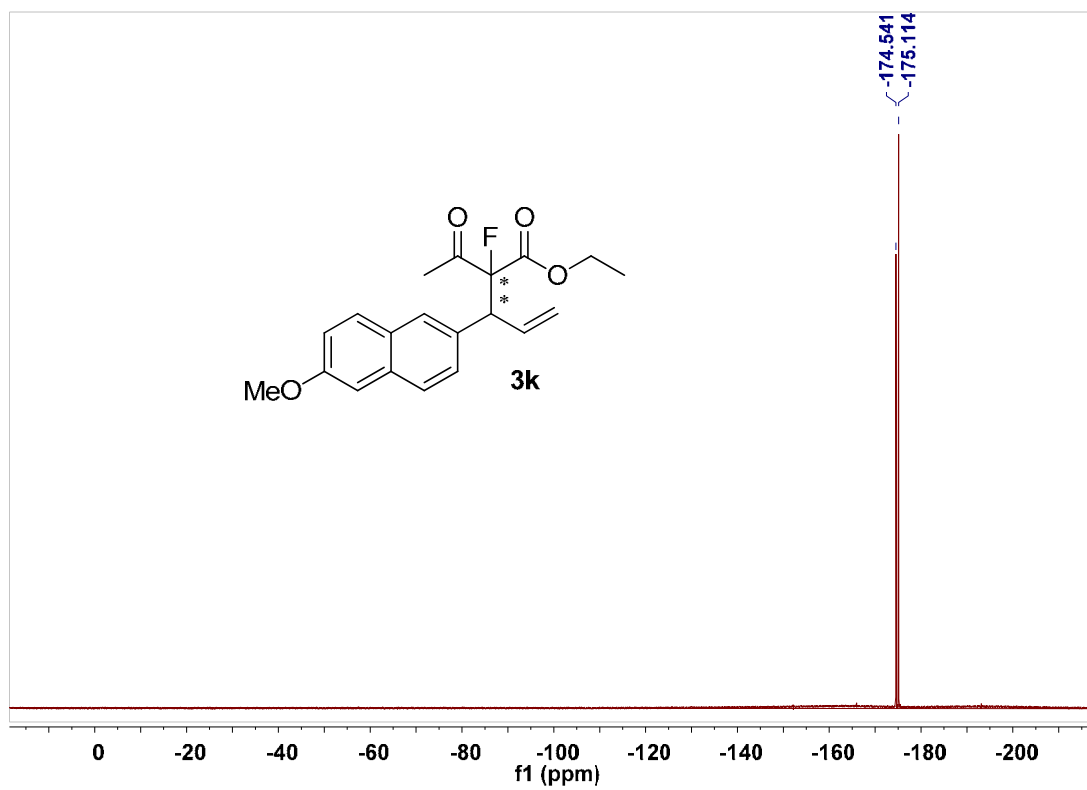
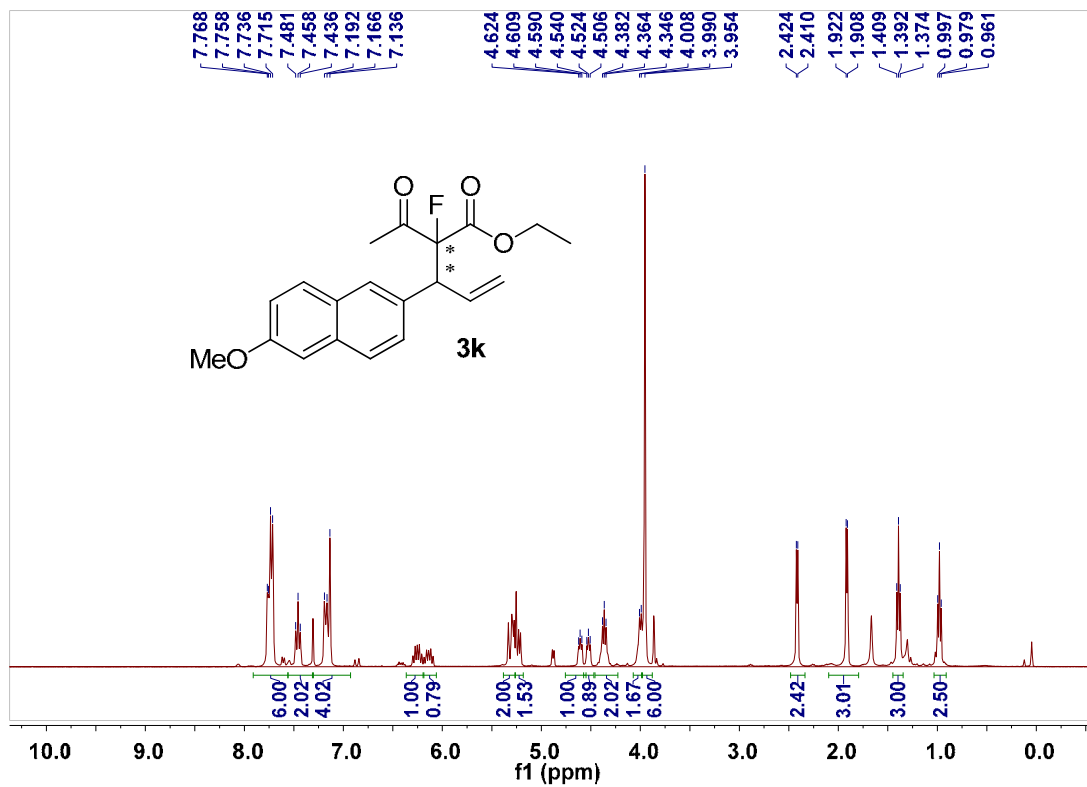


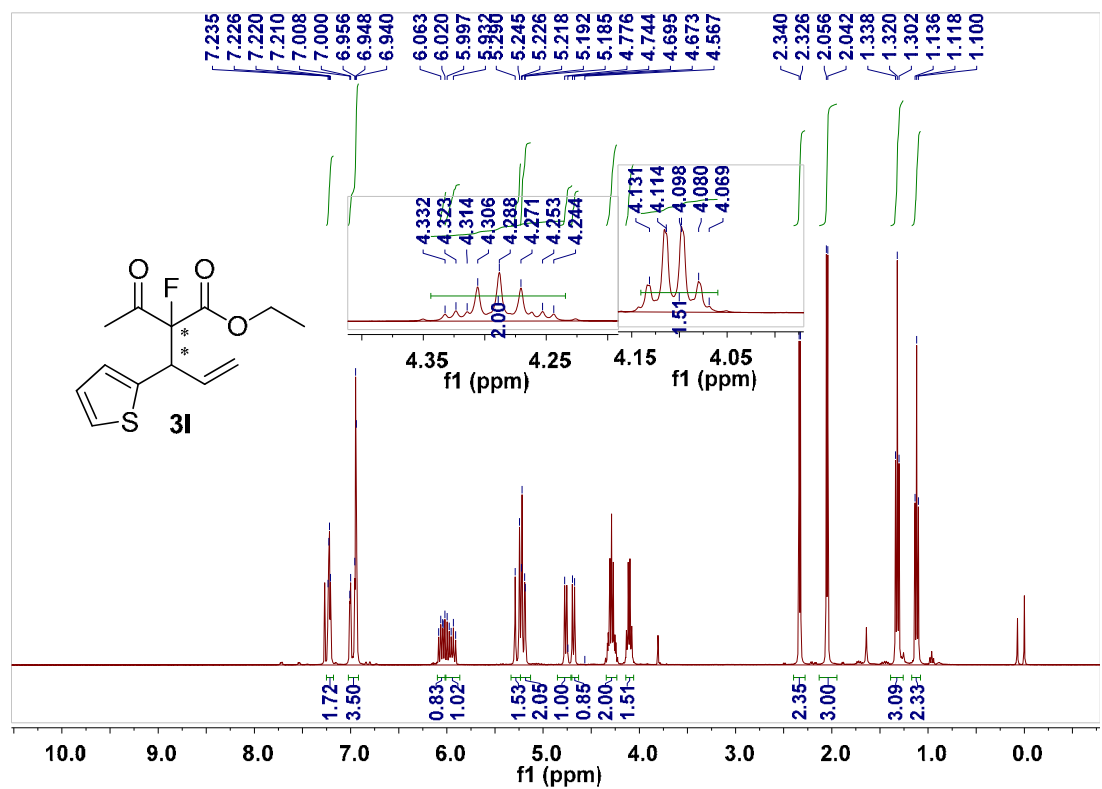
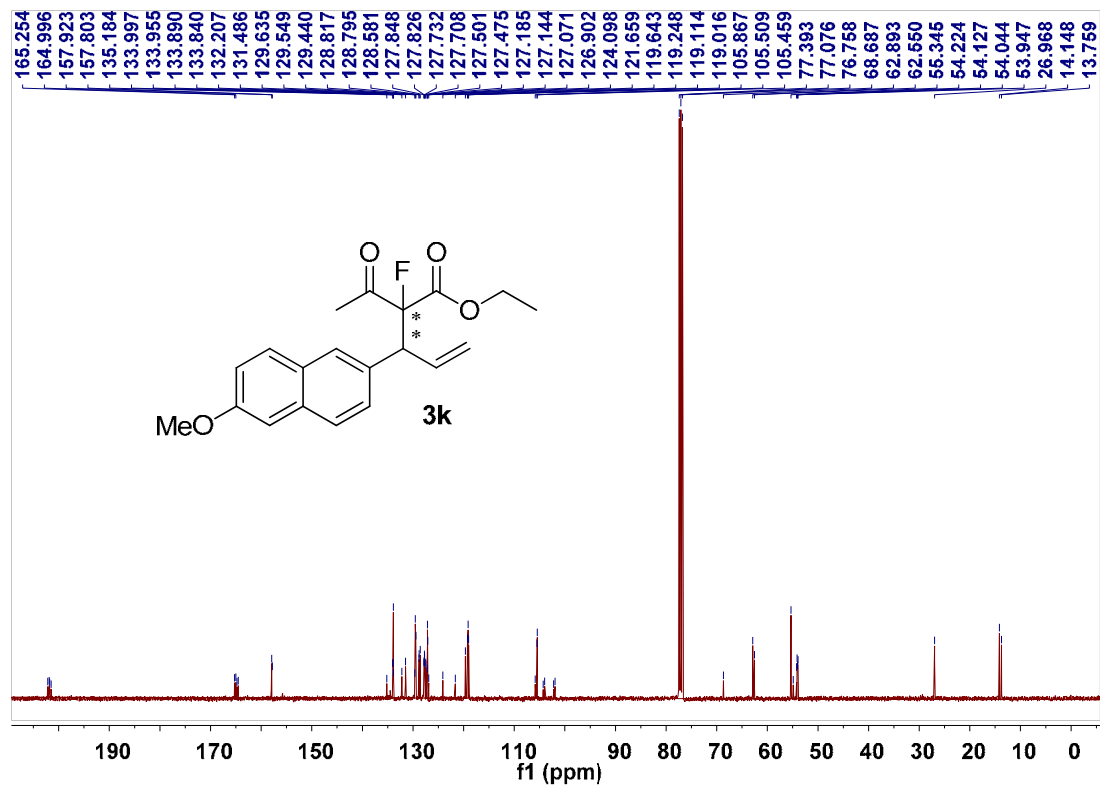


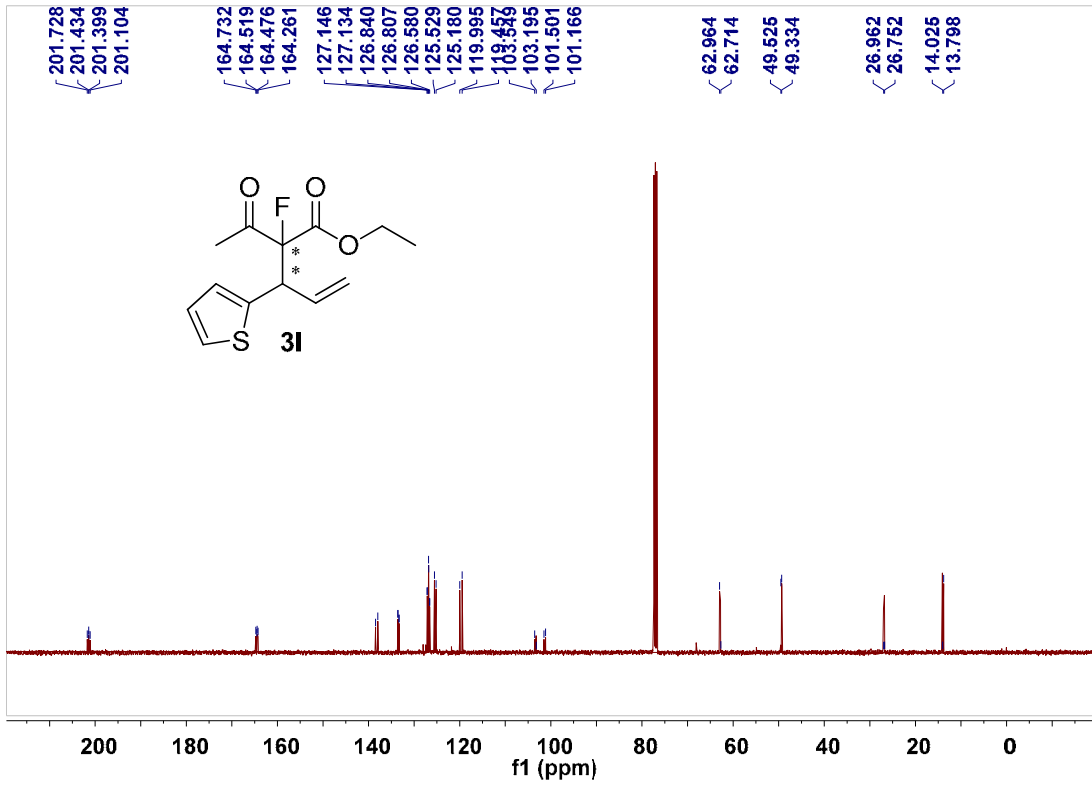
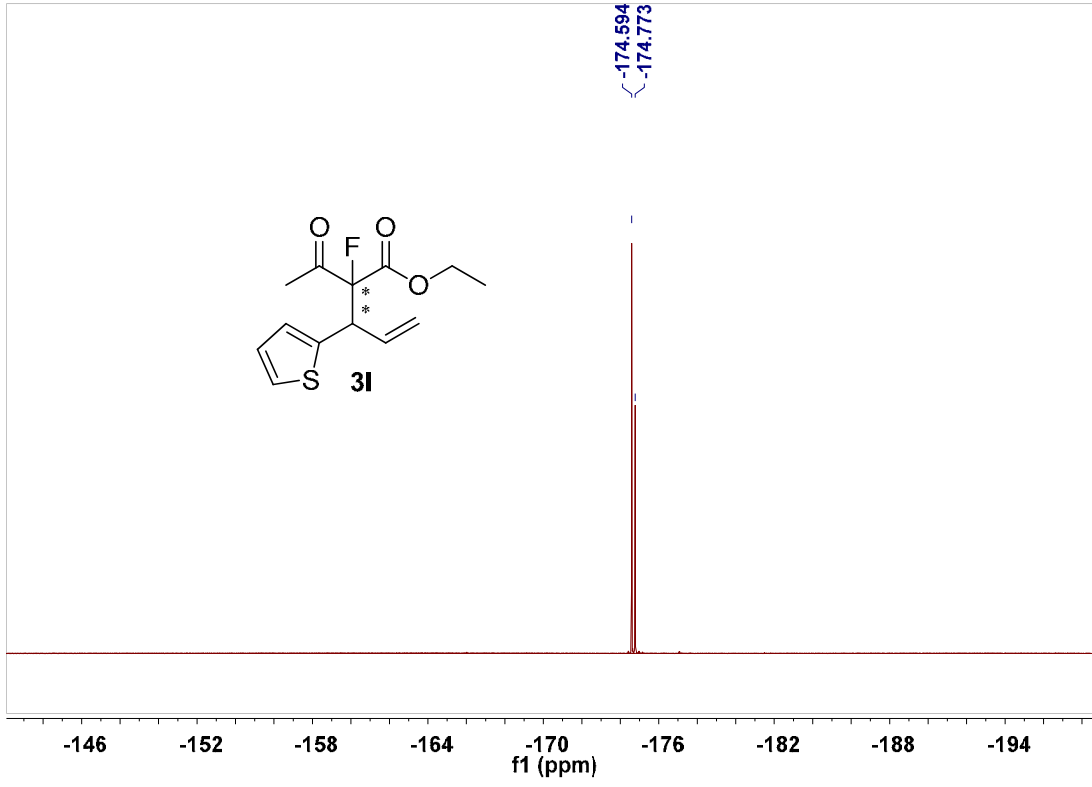


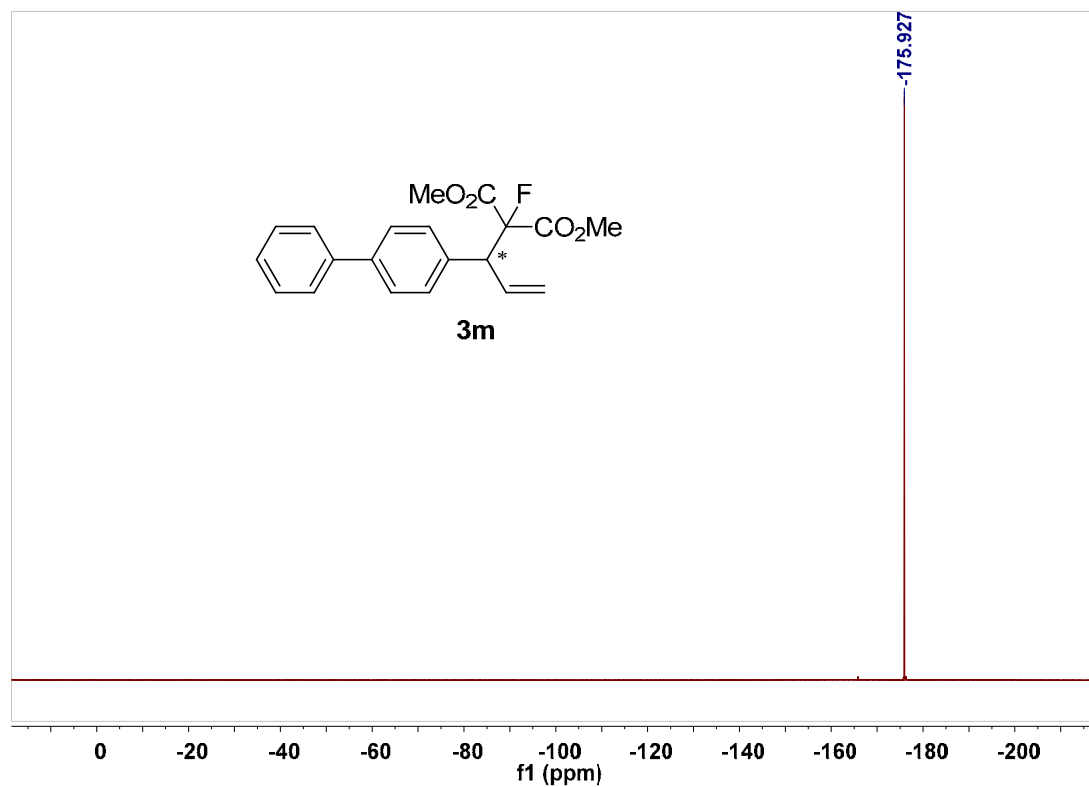
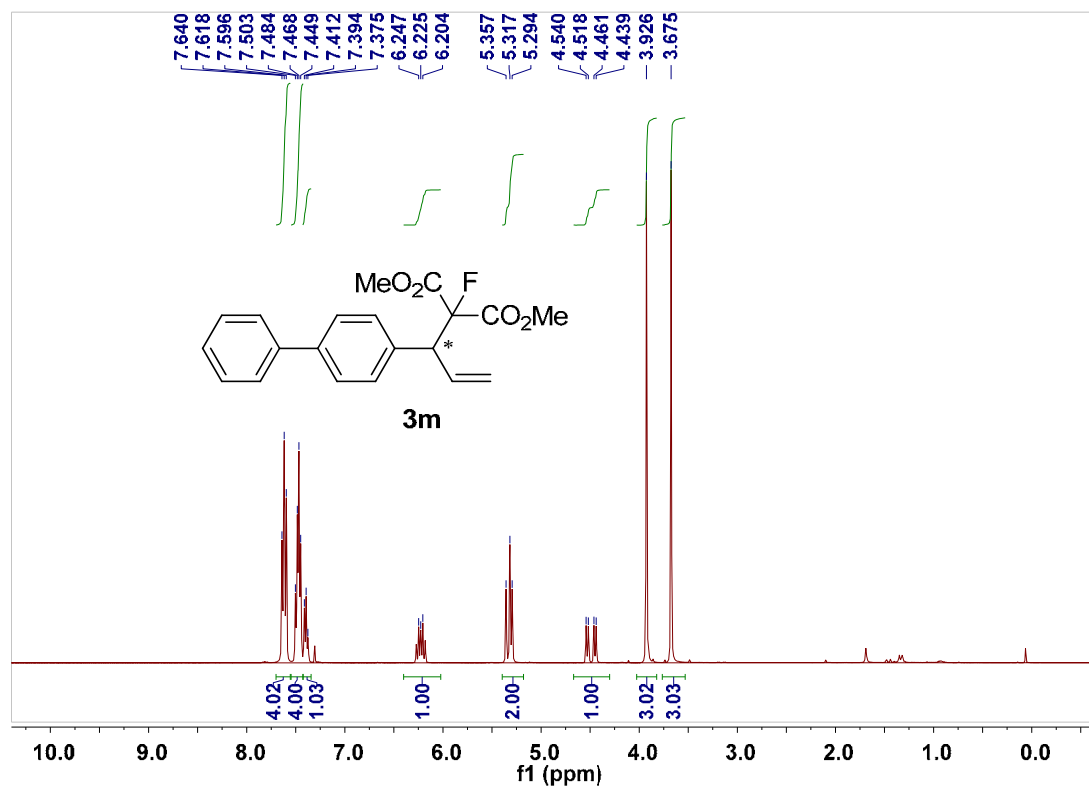


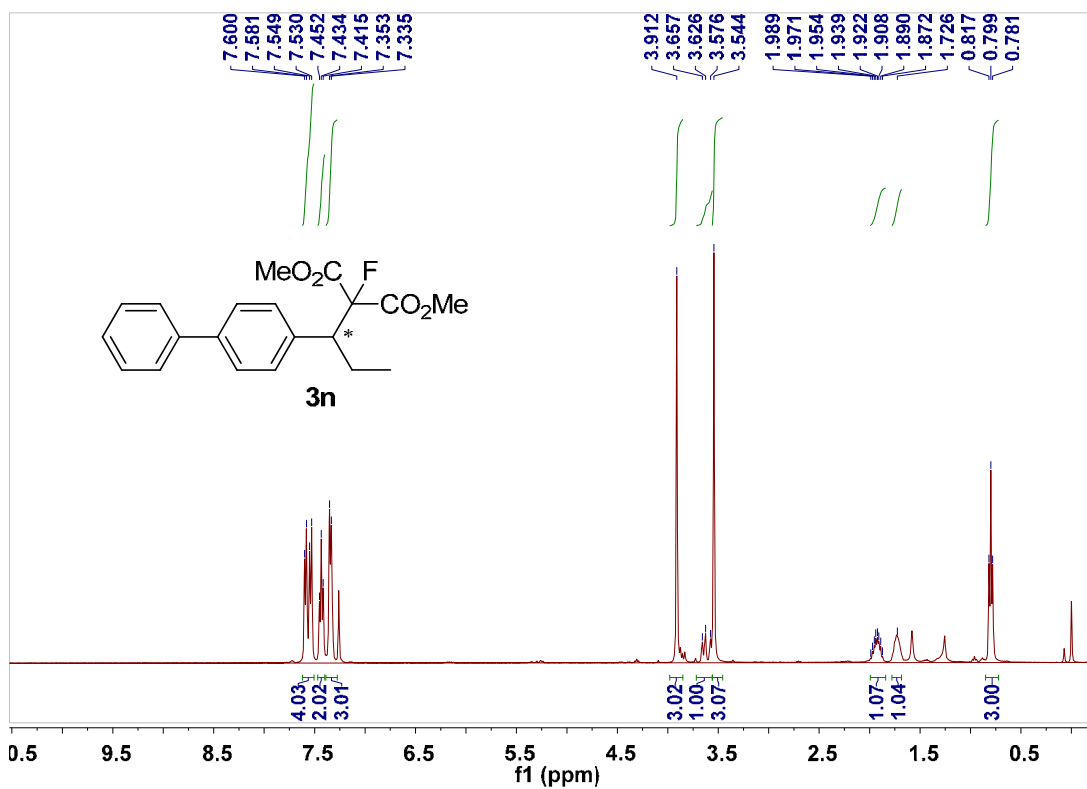
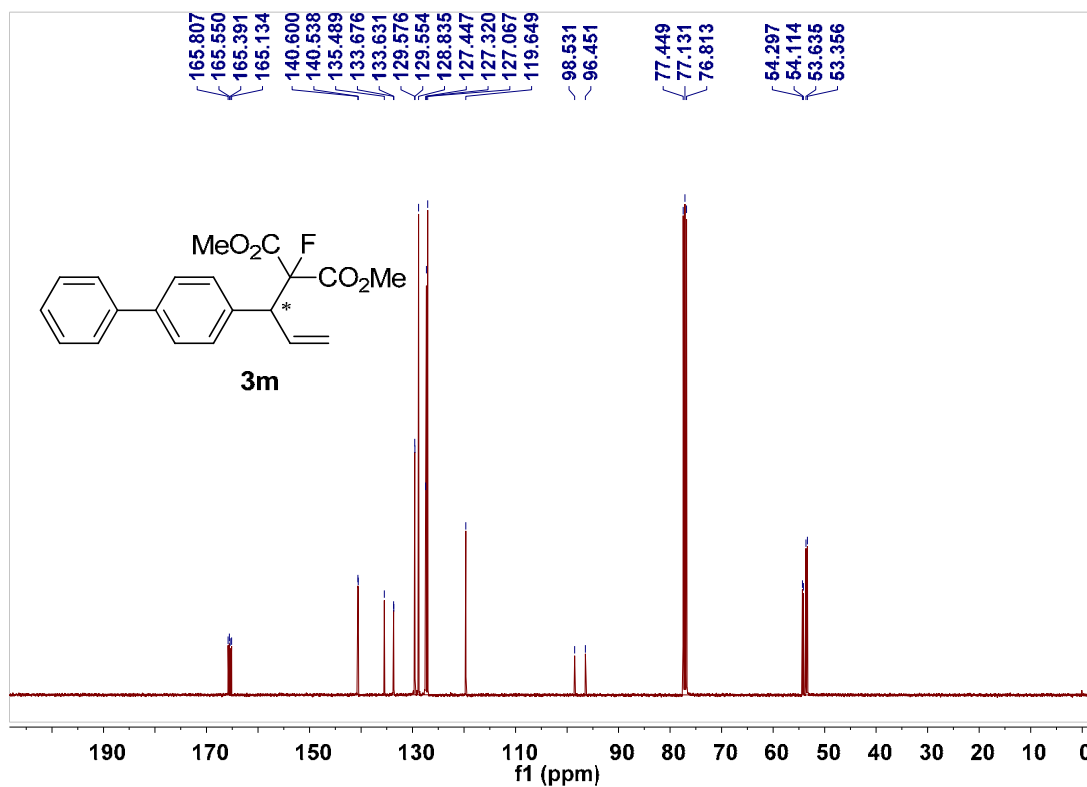


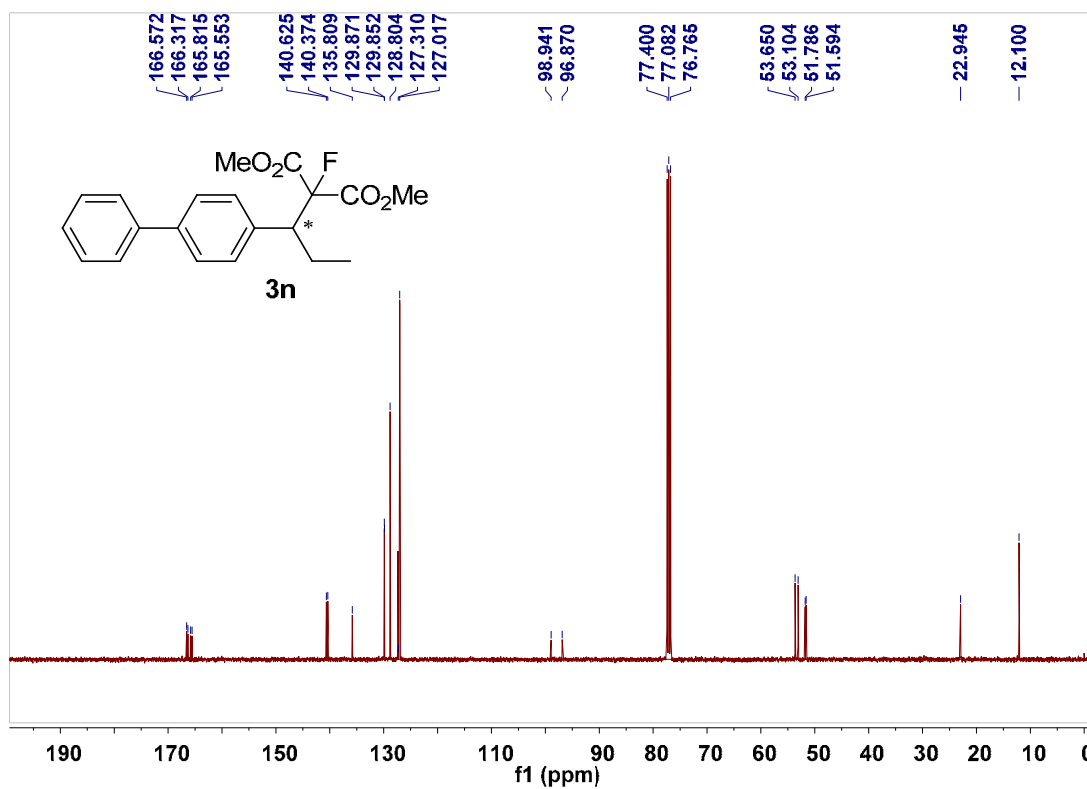
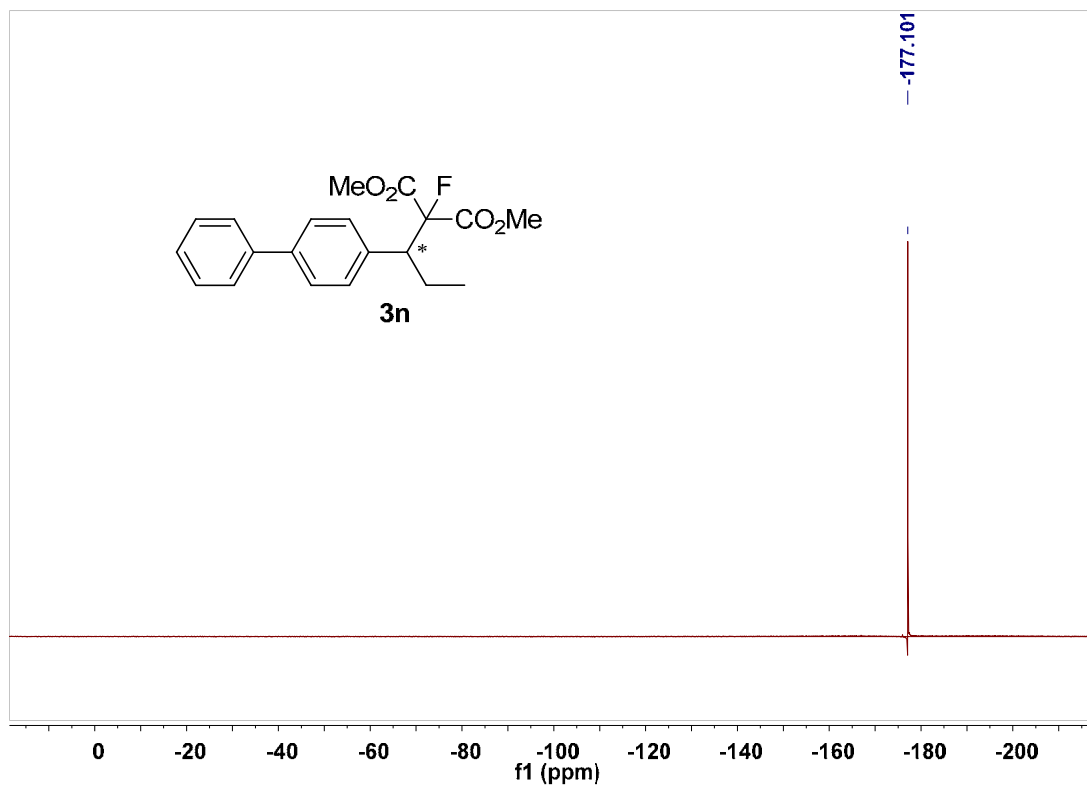




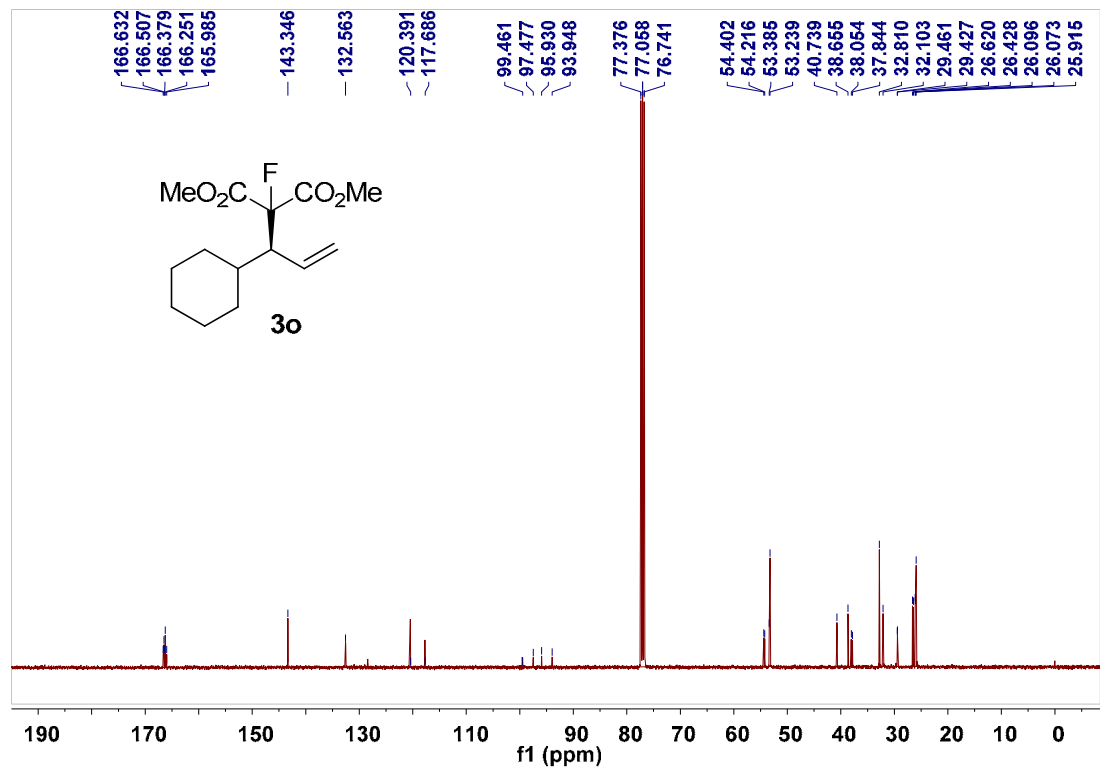
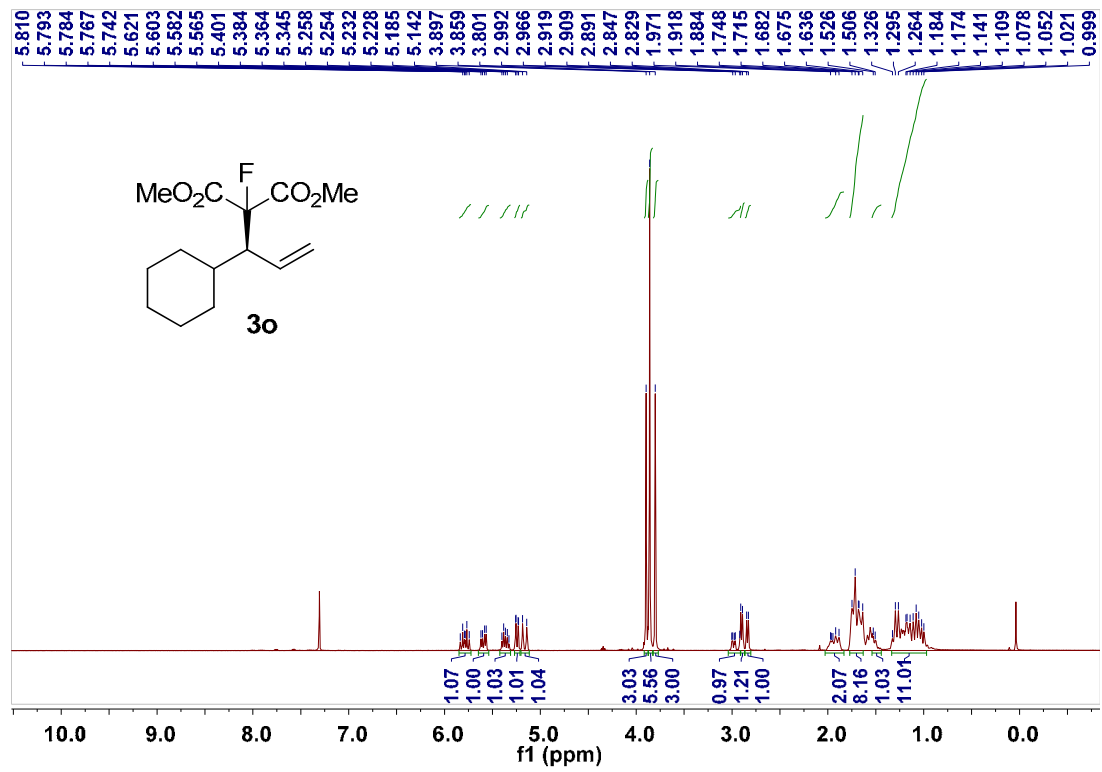


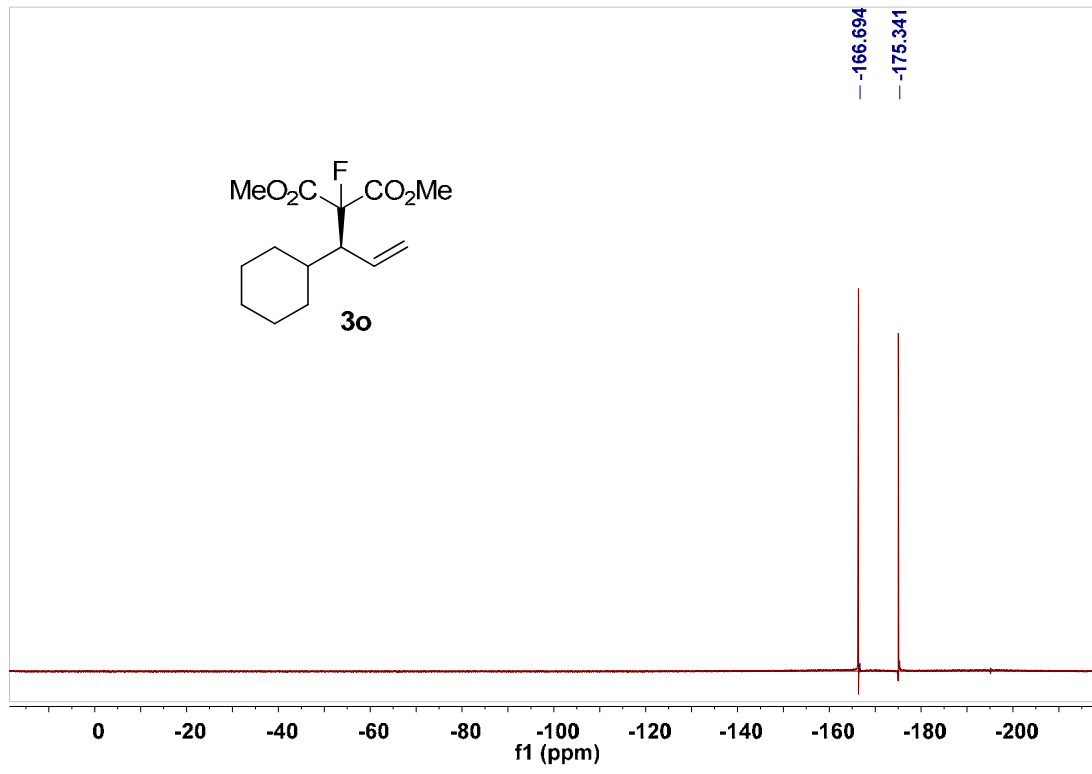
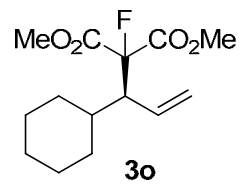




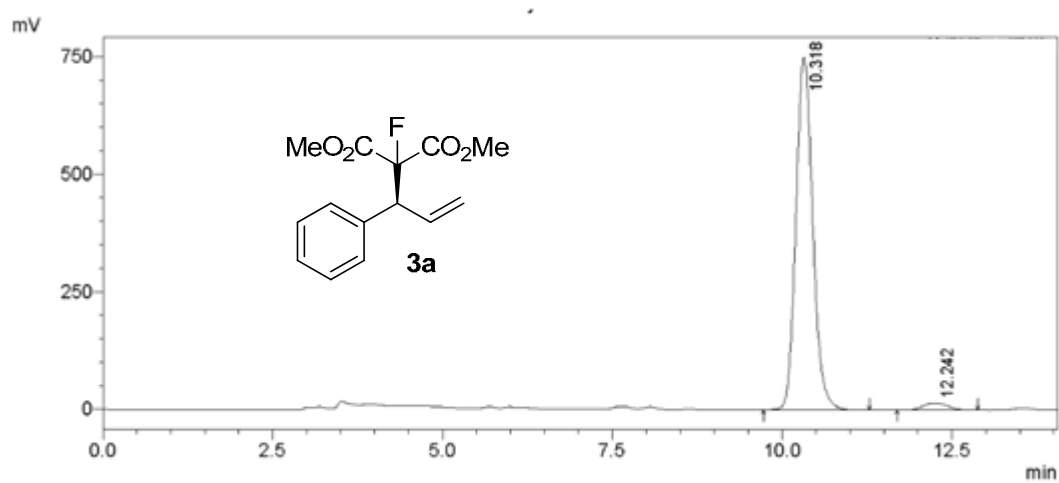






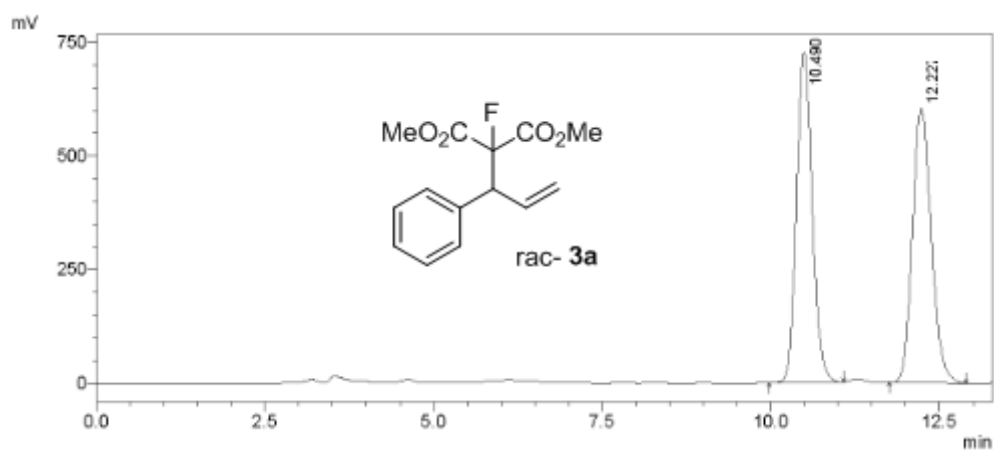


## HPLC Chromatograms



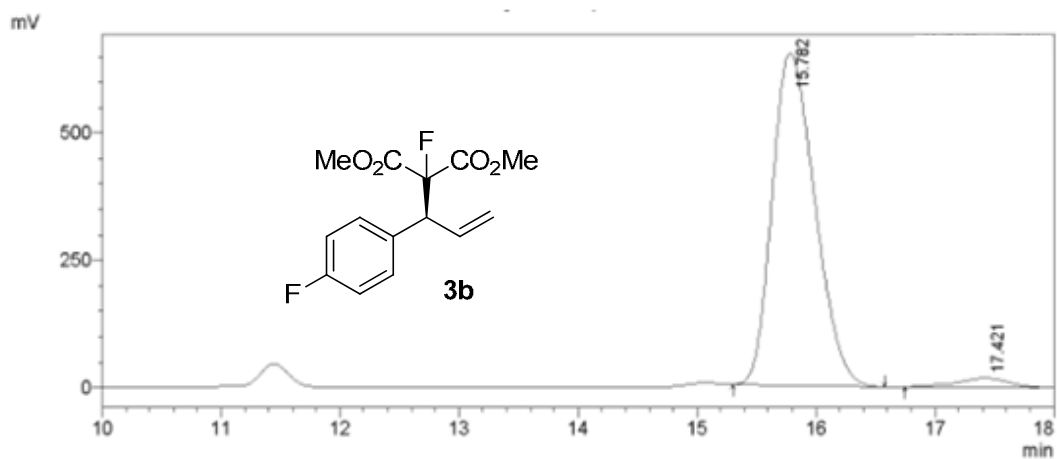
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	10.318	12970501	749435	97.043
2	12.242	395260	15271	2.957



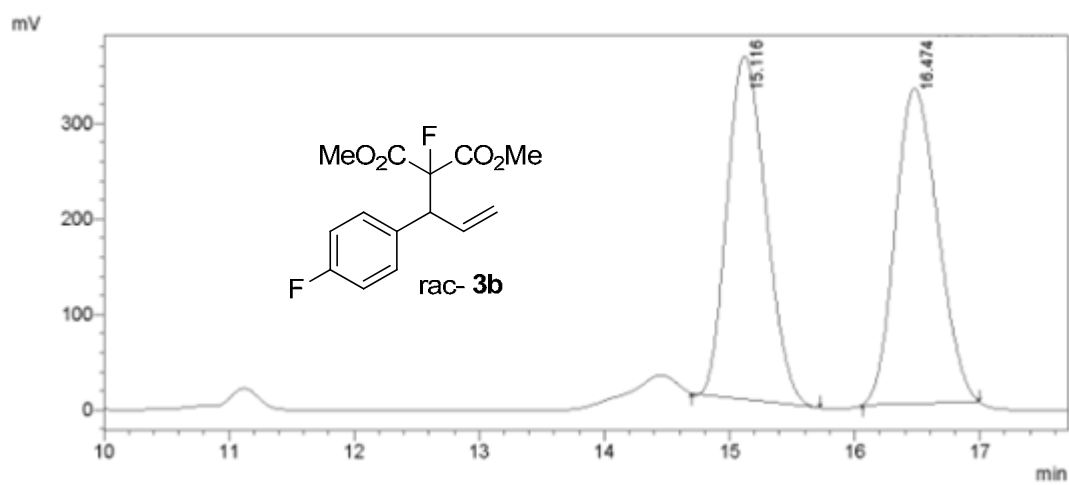
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	10.490	11776167	725470	50.105
2	12.227	11705853	603597	49.850



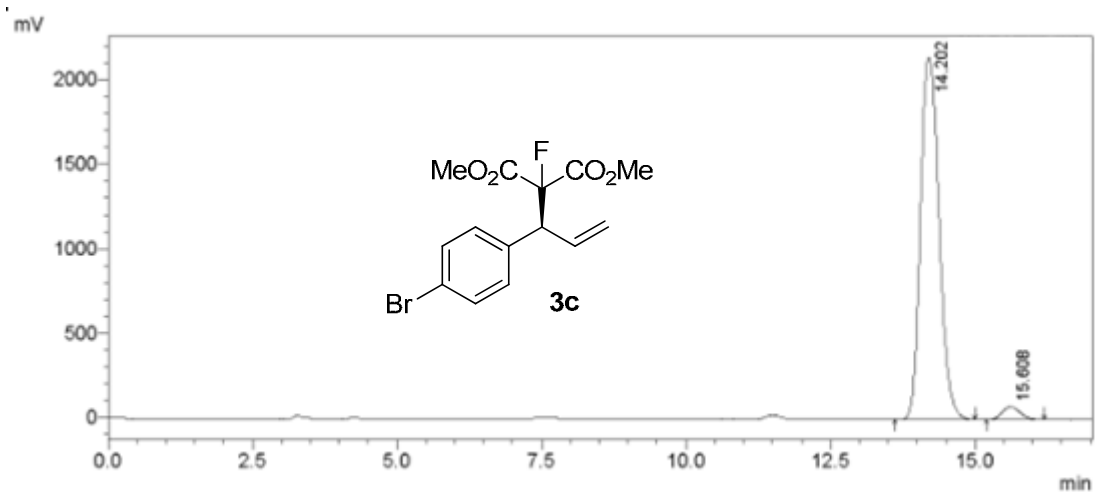
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	15.782	16360447	652661	96.699
2	17.421	558570	18357	3.301



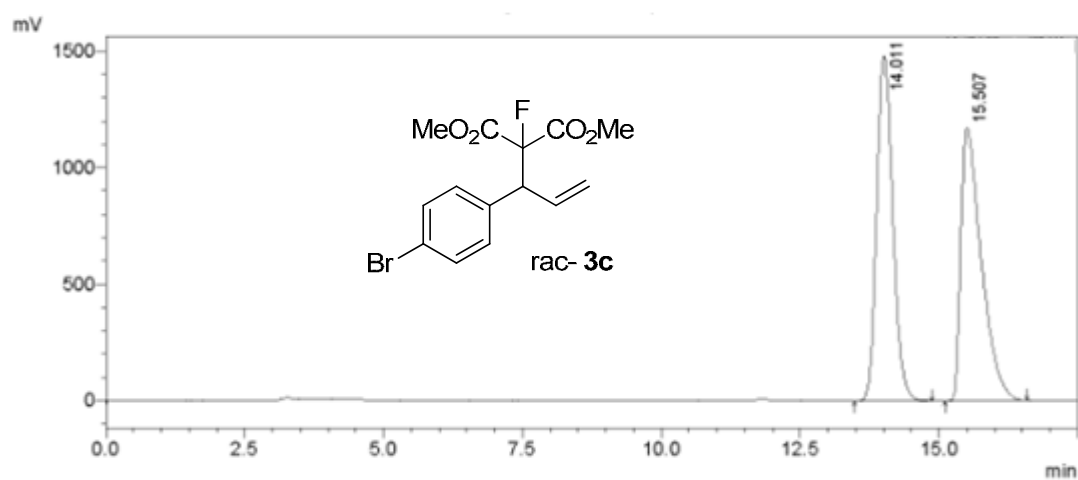
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	15.116	7780474	360127	49.902
2	16.474	7811155	329827	50.098



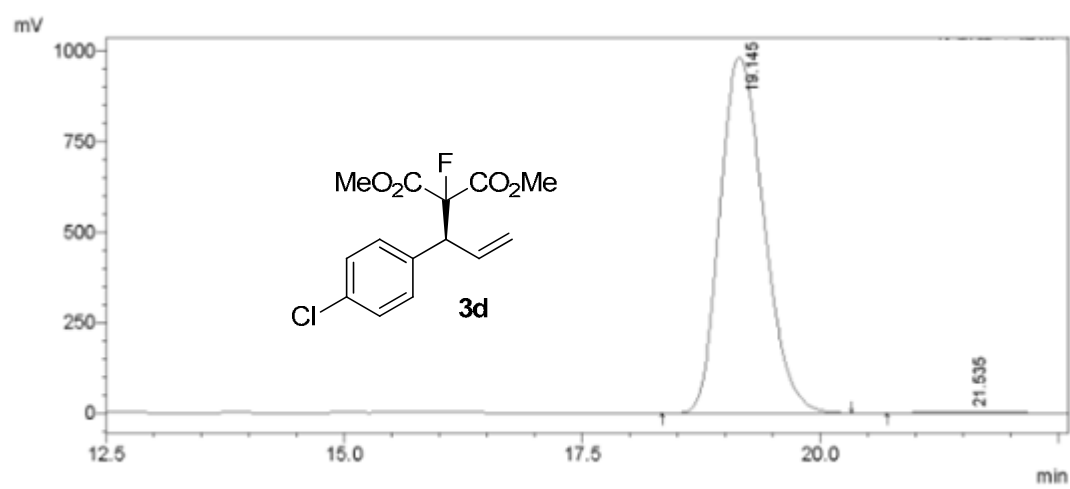
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	14.202	48134612	2142678	96.757
2	15.608	1613450	73823	3.243



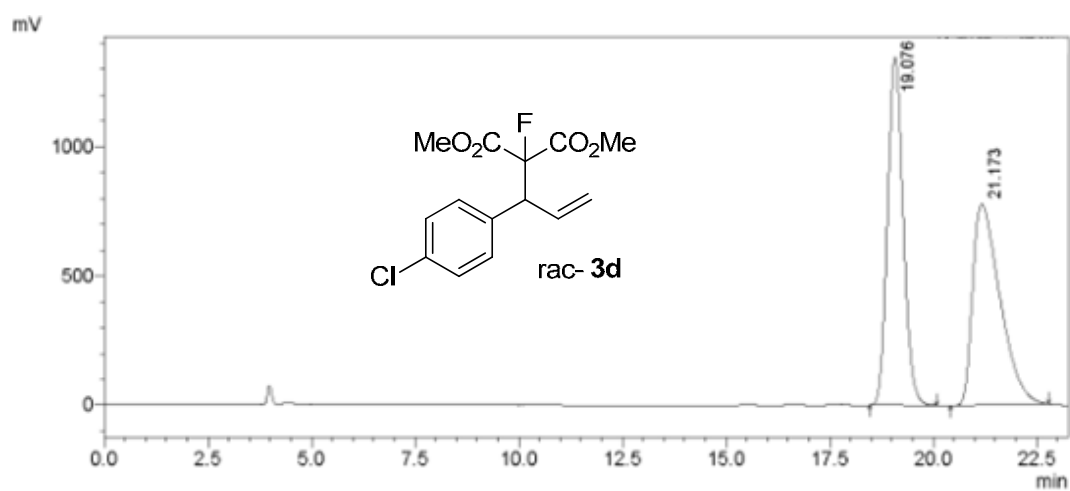
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	14.011	29860291	1479872	49.806
2	15.507	30093347	1172711	50.194



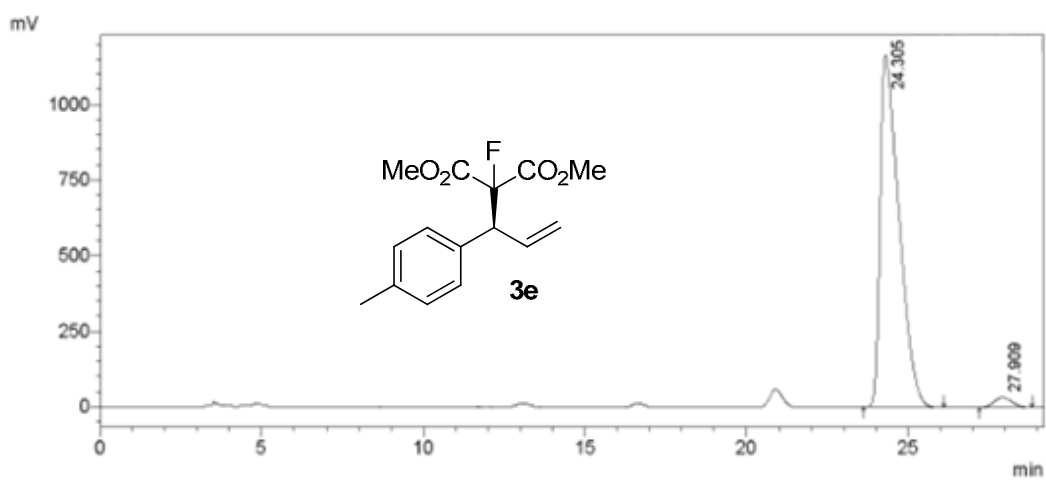
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	19.145	31667120	984485	99.461
2	21.535	171575	2345	0.539



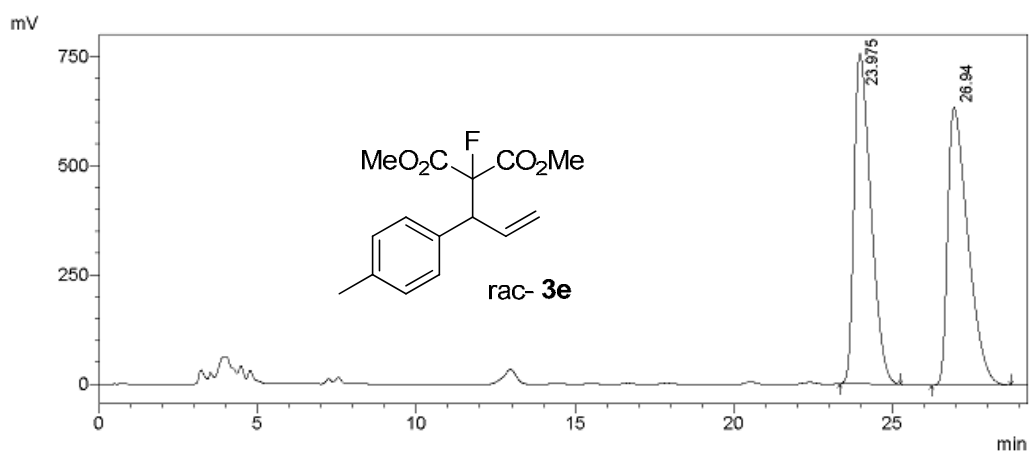
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	19.076	35621066	1347997	49.841
2	21.173	35848438	777962	50.159



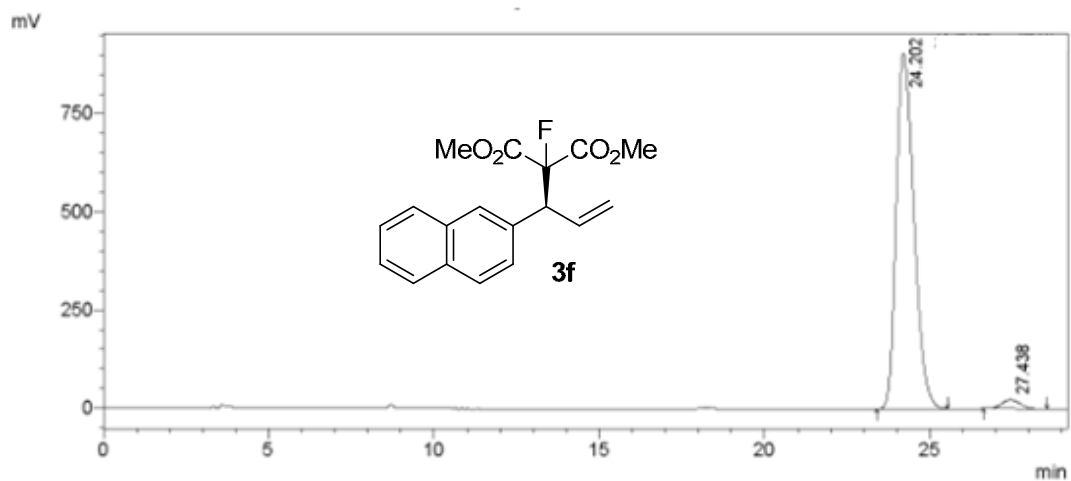
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	24.305	47342334	1163607	97.342
2	27.909	1292957	32661	2.658



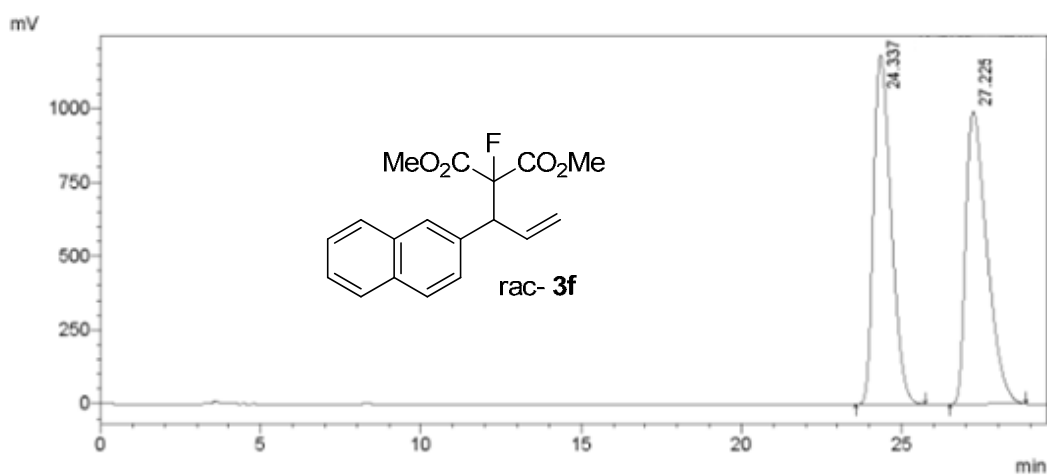
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	23.975	28025582	756879	49.805
2	26.940	28244976	635059	50.195



Ch1 214nm

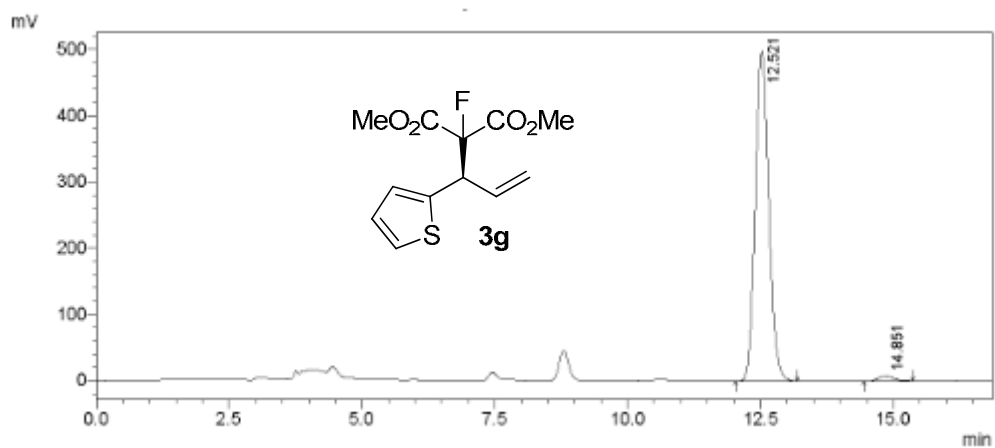
Peak#	R. Time	Area	Height	Conc. %
1	24.202	33682492	905293	97.442
2	27.438	884200	22033	2.558



Ch1 214nm

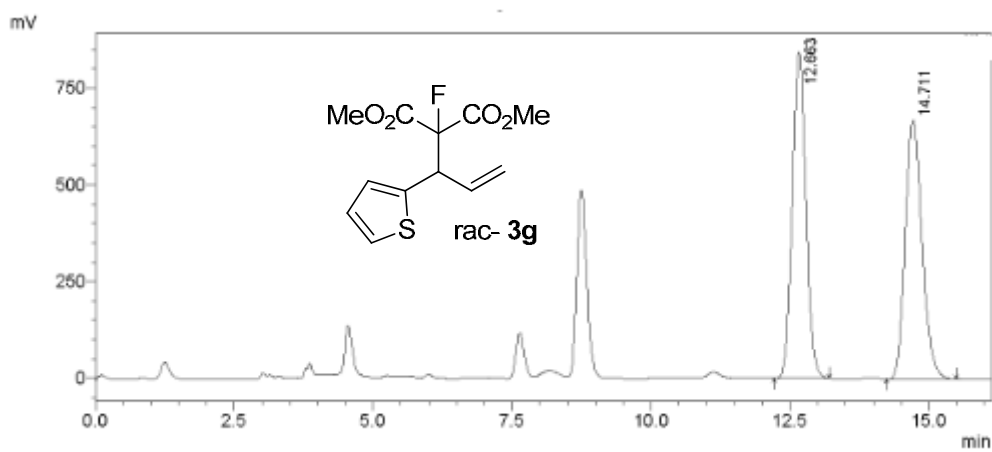
Peak#	R. Time	Area	Height	Conc. %
1	24.337	45262317	1182744	49.716
2	27.225	45780089	991612	50.284





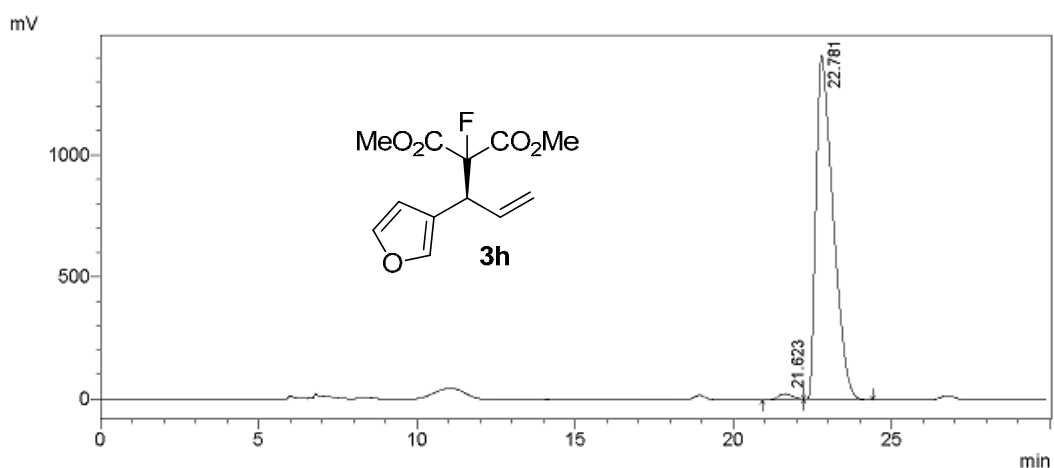
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	12.521	8822697	497808	98.212
2	14.851	160576	7981	1.788



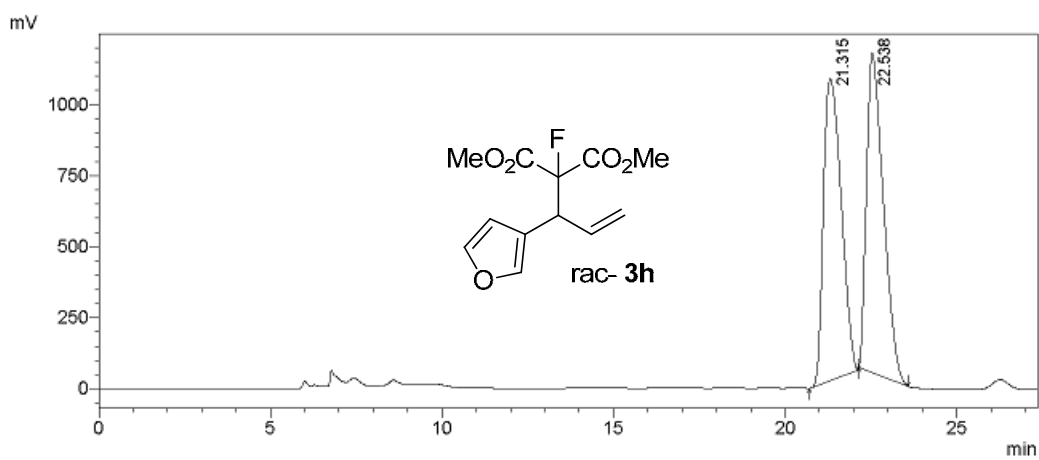
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	12.663	14423893	843322	50.456
2	14.711	14163163	668975	49.544



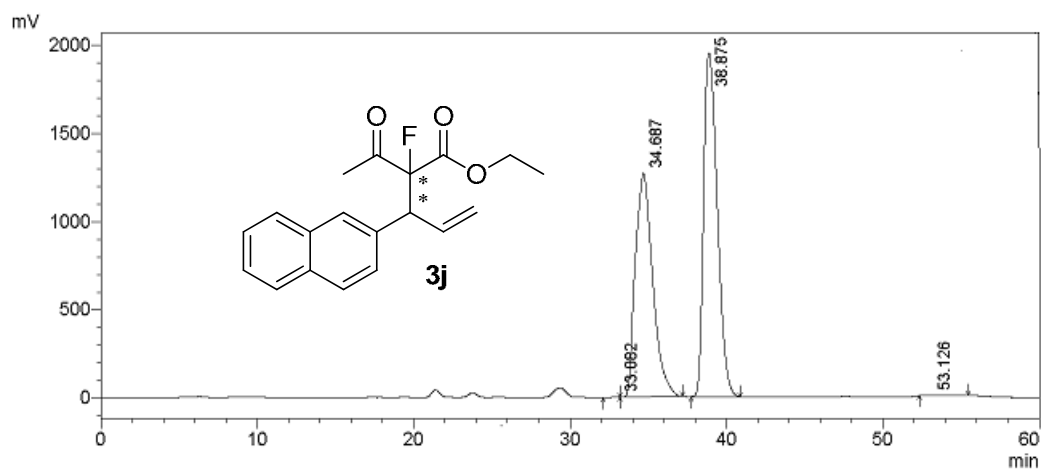
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	21.623	671940	22728	1.258
2	22.781	52724333	1411503	98.742



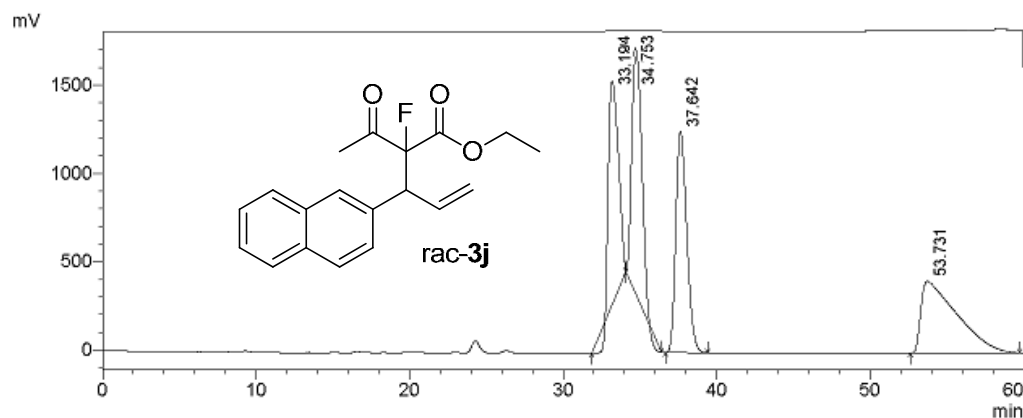
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	21.315	38158357	1061215	49.750
2	22.538	38542423	1124241	50.250



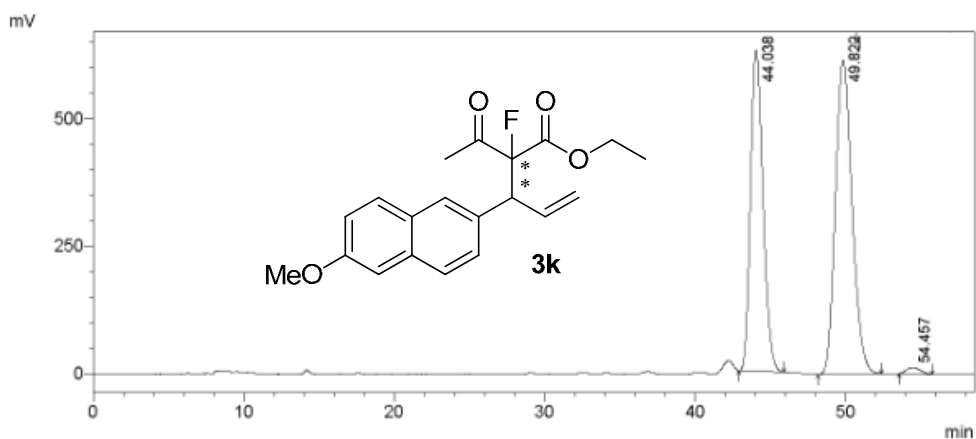
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	33.082	22350	494	0.010
2	34.678	98216151	1270026	45.286
3	38.875	118263979	1950756	54.530
4	53.126	375097	3656	0.173



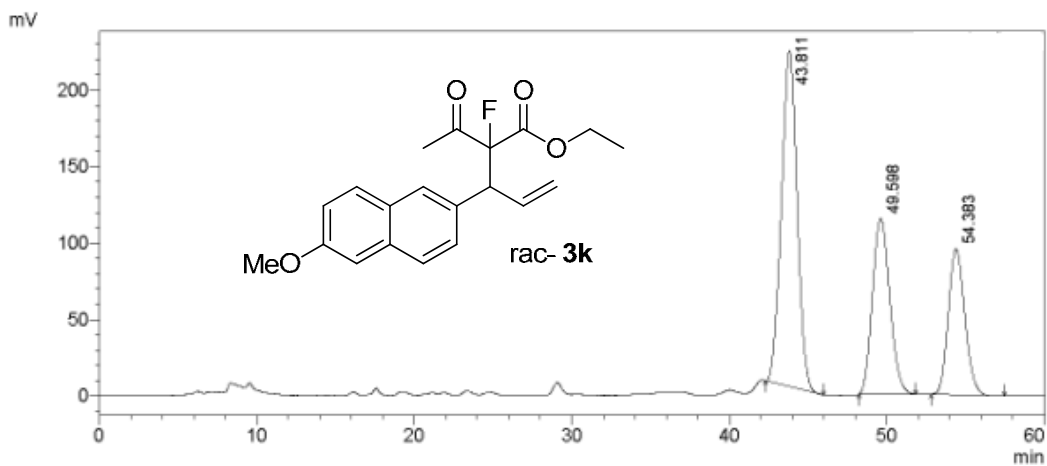
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	33.194	54083459	1267234	22.225
2	34.753	60635969	1385036	24.918
3	37.642	62403091	1252026	25.644
4	53.731	66223842	405953	27.214



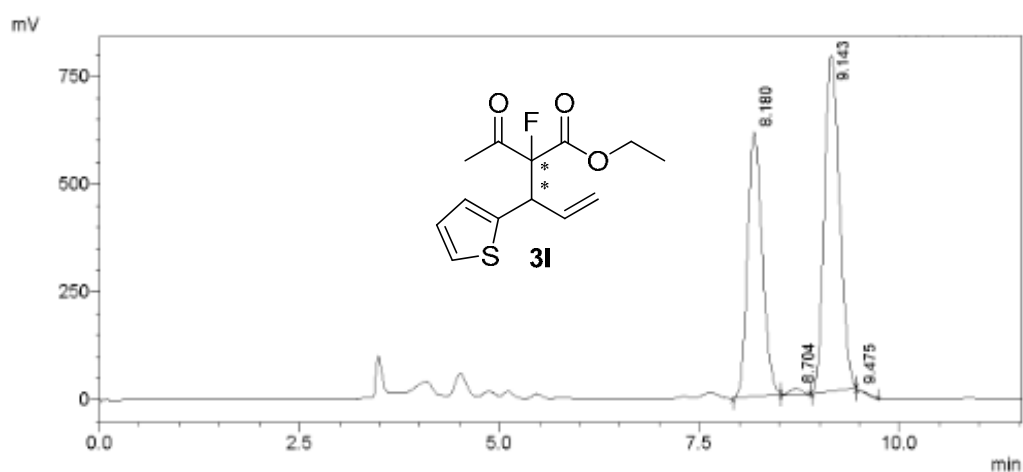
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	44.038	36538365	630472	43.054
2	49.822	47522463	615931	55.997
3	54.457	805627	12648	0.949



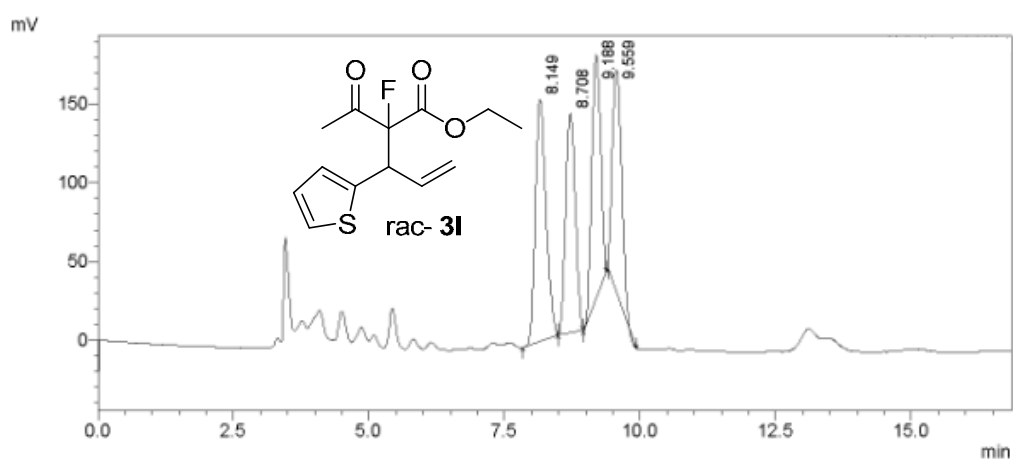
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	43.831	15206886	219402	49.122
2	49.598	8805885	114936	28.445
3	54.383	6944676	95340	22.433



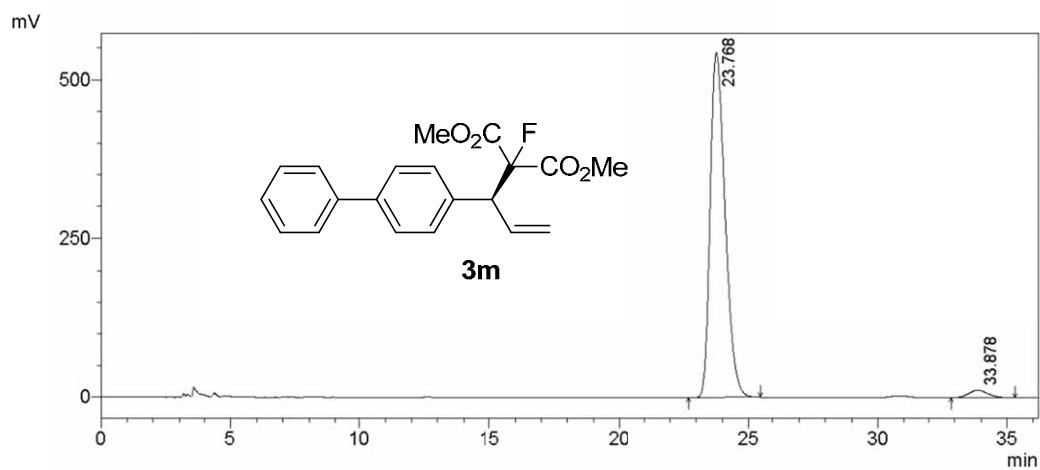
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	8.180	7830823	611273	42.625
2	8.704	171628	15142	0.934
3	9.143	10325205	776565	55.288
4	9.475	43821	1600	0.114



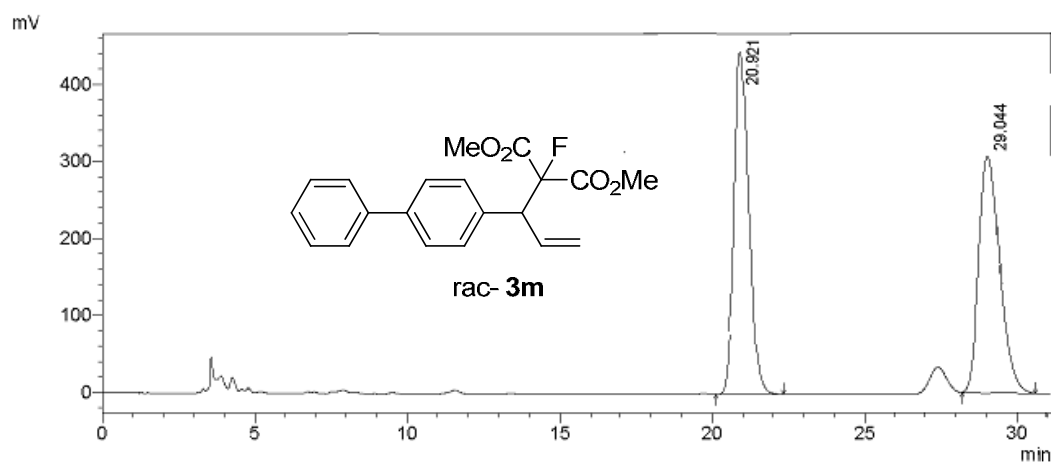
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	8.149	2090261	153912	28.719
2	8.708	1729275	139716	23.759
3	9.188	1787302	155507	24.557
4	9.559	1671461	141074	22.965



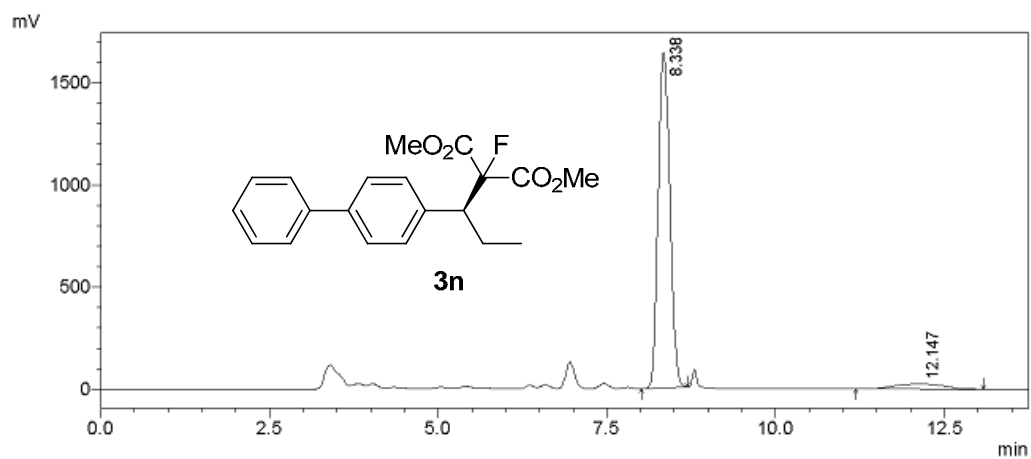
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	23.768	21584935	542634	97.197
2	33.878	622432	11905	2.803



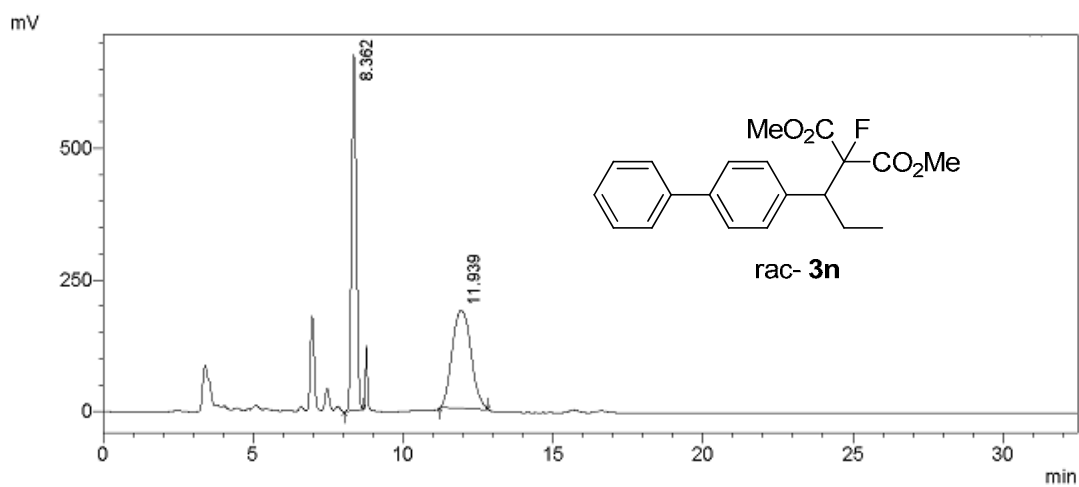
Ch1 214nm

Peak#	R. Time	Area	Height	Conc. %
1	20.921	15019985	442185	50.505
2	29.044	14719329	305823	49.495



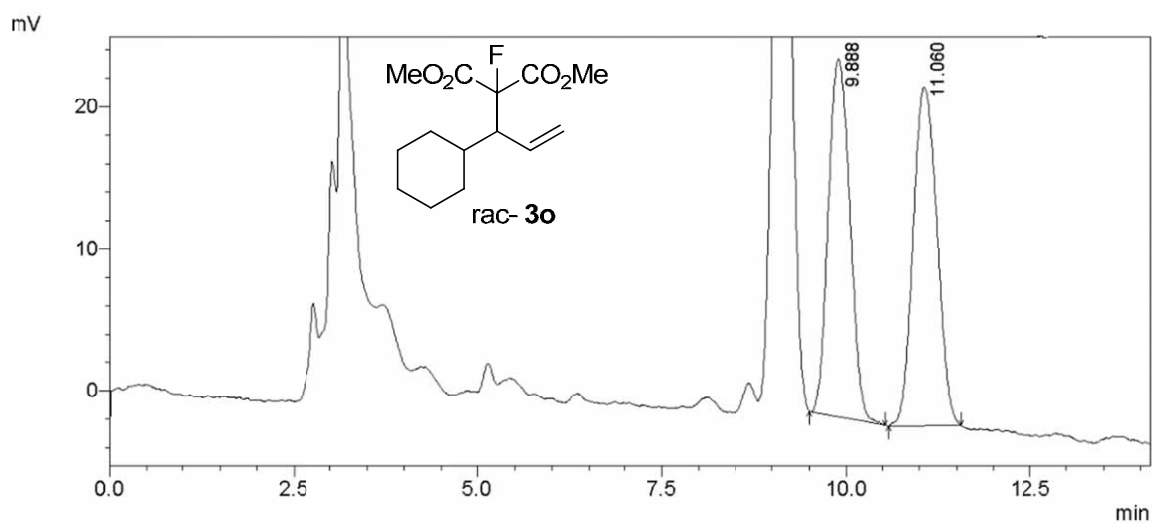
Ch1 214nm

Peak#	R. Time	Area	Height	Conc.%
1	8.338	19909783	1644479	94.421
2	12.147	1176435	23751	5.579

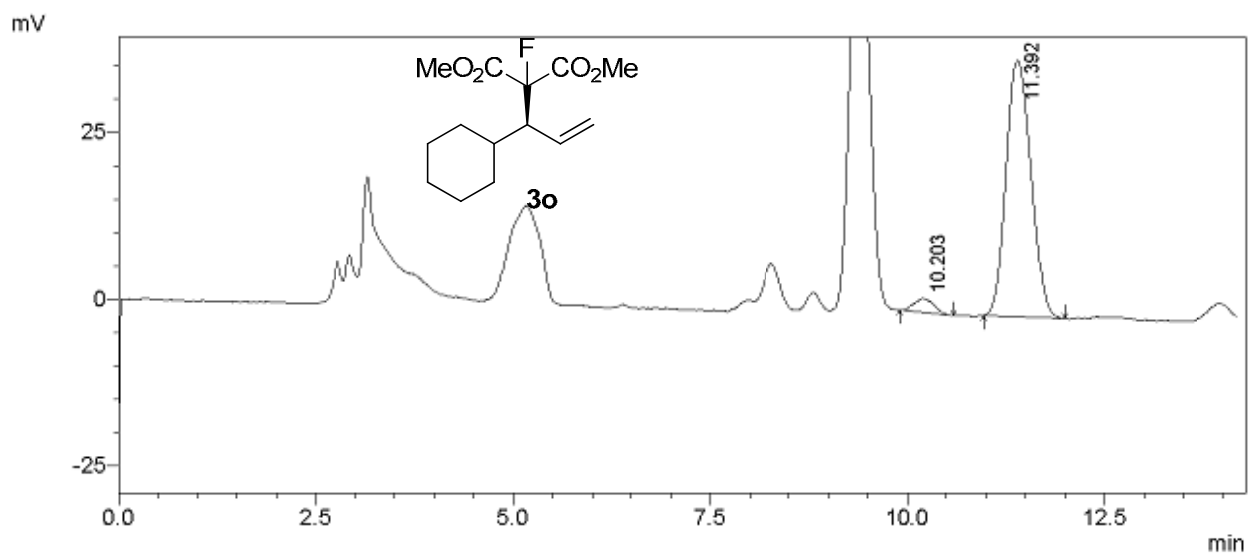


Ch1 214nm

Peak#	R. Time	Area	Height	Conc.%
1	8.362	7492305	674844	47.851
2	11.939	8165347	186148	52.149



Peak#	R. Time	Area	Height	Conc. %
1	9.888	504680	25179	48.622
2	11.060	533294	23850	51.378



Peak#	R. Time	Area	Height	Conc. %
1	10.203	37094	2073	4.240
2	11.392	837697	38408	95.760