

Enantioselective Synthesis of Functionalized Fluorinated Cyclohexenones via Robinson Annulation Catalyzed by Primary-Secondary Diamines **

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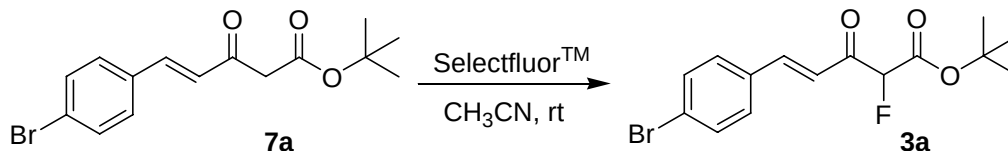
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General Information

Unless otherwise indicated, chemicals and solvents were purchased from commercial suppliers and purified by standard techniques. Flash column chromatography was performed using silica gel. For thin-layer chromatography (TLC), and compounds were visualized by irradiation with UV light or by treatment with a solution of phosphomolybdic acid in ethanol followed by heating. For NMR spectroscopy, samples were dissolved in CDCl_3 and run in room temperature. The ^1H NMR (300 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (282 MHz) were recorded on 300, 400 MHz spectrometer. All chemical shifts (δ) are given in ppm. Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad and m = multiplet) and coupling constants (Hz). Chiral analyses were done by high-performance liquid chromatography (HPLC) using chiral column. Melting points were determined on a apparatus, and are uncorrected. Optical rotations were measured using a sodium lamp ($\lambda = 589 \text{ nm}$). IR spectra were recorded on a FT-IR instrument. Mass spectra analyses were performed at 70 Ev(EI).

General Procedure for the preparation of α -fluoro- β -keto esters

(*E*)-*tert*-Butyl 5-(4-bromophenyl)-2-fluoro-3-oxopent-4-enoate **3a**



To a solution of **7a** (972 mg, 3.0 mmol) in acetonitrile (4 mL) was added SelectfluorTM (1.6 g, 4.5 mmol) at room temperature and the mixture was stirred for 10 h. Upon completion of the reaction (monitored by TLC), the solvent was removed in vacuum and the residue was mixed with 20 mL of ethyl ether, the mixture was filtered through a pad of celite. The filtrate was then concentrated under vacuum to provide a white solid. After recrystallization from petroleum ether and ethyl acetate at -10 °C, **3a** (875 mg, 85% yield) was obtained: Mp: 67-68 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, J = 15.9 Hz, 1H), 7.51 (AB, J = 28.1 Hz, 4H), 7.07 (dd, J = 2.2, 15.9 Hz, 1H), 5.31 (d, J = 49.2 Hz, 1H), 1.51 (s, 9H); ¹⁹F NMR (282 MHz, CDCl₃) δ -194.13 (d, J = 49.5 Hz, 1F); ¹³C NMR (75 MHz, CDCl₃) δ 189.3 (d, J = 21.8 Hz), 163.3 (d, J = 24.1 Hz), 144.8 (d, J = 3.2 Hz), 132.8, 132.3, 130.1, 125.8, 120.0, 91.3 (d, J = 197.6 Hz), 84.5, 27.9; IR (KBr) ν 1758, 1703, 1611 cm⁻¹; EI-MS (m/z): 342 (M⁺, 3.2%), 57 (100), 209 (75), 211 (73), 102 (54), 41 (20), 133 (13), 75 (12), 286 (12); HRMS (EI): m/z : calcd. for C₁₅H₁₆BrFO₃: 342.0267; found: 342.0266 [M]⁺.

(*E*)-*tert*-Butyl 5-(3-bromophenyl)-2-fluoro-3-oxopent-4-enoate **3b**: White solid, 69%. Mp: 75-76 °C;

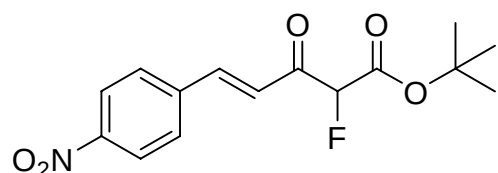
¹H NMR (300 MHz, CDCl₃) δ 7.78-7.68 (m, 2H), 7.60-7.48 (m, 2H), 7.34-7.27 (m, 1H), 7.06 (dd, J = 2.4, 16.0 Hz, 1H), 5.33 (d, J = 49.4 Hz, 1H), 1.51 (s, 9H); ¹⁹F NMR (282 MHz, CDCl₃) δ -193.50 (d, J = 49.5 Hz, 1F); ¹³C NMR (75 MHz, CDCl₃) δ 189.1 (d, J = 21.8 Hz), 163.2 (d, J = 24.3 Hz), 144.3 (d, J = 3.1 Hz), 135.9, 134.0, 131.2, 130.4, 127.4, 123.0, 120.6, 91.1 (d, J = 197.5 Hz), 84.5, 27.8; IR (KBr) ν 1751, 1805, 1561 cm⁻¹; EI-MS (m/z): 342 (M⁺, 2.1%), 209 (100), 211 (98), 57 (91), 102 (57), 41 (16), 288 (15), 286 (15), 133 (14); HRMS (EI): m/z : calcd. for C₁₅H₁₆BrFO₃: 342.0267; found: 342.0262 [M]⁺.

(*E*)-*tert*-Butyl 5-(2-bromophenyl)-2-fluoro-3-oxopent-4-enoate **3c**: White solid, 83% yield. Mp: 54-56

°C; ¹H NMR (300 MHz, CDCl₃) δ 8.19 (d, J = 16.5 Hz, 1H), 7.71-7.63 (m, 2H), 7.38-7.25 (m, 2H), 7.02 (d, J = 16.0 Hz, 1H), 5.35 (d, J = 49.7

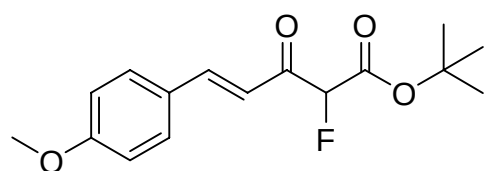
Hz, 1H), 1.51 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -193.46 (d, J = 49.5 Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 189.2 (d, J = 21.8 Hz), 163.3 (d, J = 24.2 Hz), 144.5 (d, J = 3.2 Hz), 133.9, 133.7, 132.1, 127.88, 127.79, 126.5, 122.1, 91.1 (d, J = 197.4 Hz), 84.5, 27.9; IR (KBr) ν 1756, 1702, 1608, 1562 cm^{-1} ; EI-MS (m/z): 57 (100), 209 (65), 211 (64), 102 (47), 207 (35), 41 (20), 101 (18), 263 (17); HRMS (EI): m/z : calcd. for $\text{C}_{15}\text{H}_{16}\text{BrFO}_3$: 342.0267; found: 342.0268 $[\text{M}]^+$.

(E)-tert-Butyl 2-fluoro-5-(4-nitrophenyl)-3-oxopent-4-enoate 3d: White solid, 79% yield. Mp: 124-135



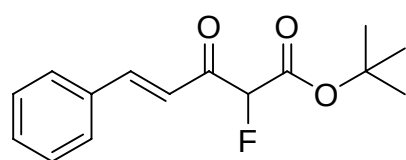
$^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 8.04 (AB, J = 55.4 Hz, 4H), 7.83 (d, J = 15.9 Hz, 1H), 7.19 (d, J = 15.9 Hz, 1H), 5.35 (d, J = 49.3 Hz, 1H), 1.52 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -193.67 (d, J = 48.5 Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 189.1 (d, J = 22.3 Hz), 163.0 (d, J = 24.0 Hz), 149.0, 142.9 (d, J = 3.2 Hz), 139.9, 129.3, 124.2, 123.1, 91.2 (d, J = 197.8 Hz), 84.8, 27.8; IR (KBr) ν 1746, 1702, 1670, 1619, 1599 cm^{-1} ; EI-MS (m/z): 309 (M^+ , 0.6%), 57 (100), 176 (66), 253 (32), 102 (21), 130 (18), 41 (16), 133 (10), 76 (8); HRMS (EI): m/z : calcd. for $\text{C}_{15}\text{H}_{16}\text{FNO}_5$: 309.1013; found: 309.1015 $[\text{M}]^+$.

(E)-tert-Butyl 2-fluoro-5-(4-methoxyphenyl)-3-oxopent-4-enoate 3e: White solid, 83% yield. Mp:



73-74 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 7.79 (d, J = 15.6 Hz, 1H), 7.57 (d, J = 8.8 Hz, 2H), 6.98-6.92 (m, 3H), 5.31 (d, J = 49.9 Hz, 1H), 3.86 (s, 3H), 1.52 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -193.63 (d, J = 49.6 Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 189.2 (d, J = 21.3 Hz), 163.7 (d, J = 24.3 Hz), 162.3, 146.2 (d, J = 3.2 Hz), 130.7, 126.6, 117.1, 114.5, 91.2 (d, J = 197.2 Hz), 84.2, 55.4, 27.9; IR (KBr) ν 1756, 1687, 1595 cm^{-1} ; EI-MS (m/z): 294 (M^+ , 4.4%), 123 (100), 247 (56), 161 (56), 95 (28), 124 (15), 246 (14), 75 (13), 109 (12); HRMS (EI): m/z : calcd. for $\text{C}_{16}\text{H}_{19}\text{FO}_4$: 294.1267; found: 294.1269 $[\text{M}]^+$.

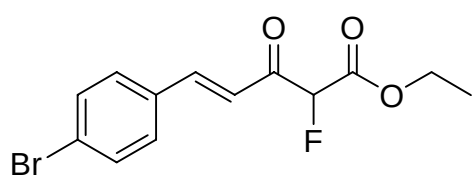
(E)-tert-Butyl 2-fluoro-3-oxo-5-phenylpent-4-enoate 3f: White solid, 73% yield. Mp: 62-63 $^{\circ}\text{C}$; ^1H



NMR (300 MHz, CDCl_3) δ 7.83 (d, J = 16.1 Hz, 1H), 7.62-7.39 (m, 5H), 7.13 (d, J = 16.0 Hz, 1H), 5.33 (d, J = 51.1 Hz, 1H), 1.51 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -193.53 (d, J = 49.5 Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 189.4 (d, J = 21.5 Hz), 163.4 (d, J = 24.2 Hz), 146.4 (d, J = 3.3 Hz), 133.9, 131.4, 129.1, 128.8, 119.5, 91.3 (d, J = 197.4 Hz), 84.4, 27.9; IR (KBr) ν 1757, 1698, 1612, 1256, 1132, 1058 cm^{-1} ; EI-MS (m/z): 264 (M^+ , 2.7%), 131 (100), 57 (34), 103 (26), 77 (15), 208 (12), 132 (10), 41 (8), 191 (6);

HRMS (EI): m/z : calcd. for $C_{15}H_{17}FO_3$: 264.1162; found: 264.1164 $[M]^+$.

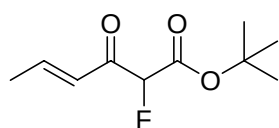
(*E*)-Ethyl-5-(4-bromophenyl)-2-fluoro-3-oxopent-4-enoate 3g: Colorless oil at room temperature, 80%.



1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, $J = 16.0$ Hz, 1H), 7.52 (AB, $J = 26.2$ Hz, 4H), 7.09 (d, $J = 16.0$ Hz, 1H), 5.42 (d, $J = 49.3$ Hz, 1H), 4.32 (q, $J = 7.4$ Hz, 2H), 1.33 (t, $J = 7.4$ Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -195.26 (d, $J = 49.8$ Hz, 1F); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 188.8 (d, $J = 21.9$ Hz), 164.3 (d, $J = 24.1$ Hz), 145.2 (d, $J = 3.2$ Hz), 132.7, 132.3, 130.1, 125.9, 119.6, 91.0 (d, $J = 198.3$ Hz), 62.7, 13.9; IR (KBr) ν 1756, 1699, 1610, 1586 cm^{-1} ; EI-MS (m/z): 314 (M^+ , 6.4%), 209 (100), 211 (96), 102 (80), 75 (15), 183 (15), 181 (15), 76 (15), 101 (13); HRMS (EI): m/z : calcd. for $C_{13}H_{12}BrFO_3$: 313.9954; found: 313.9952 $[M]^+$.

(*E*)-tert-butyl 2-fluoro-3-oxohex-4-enoate 3h: Colorless oil, quantitative. 1H NMR (300 MHz, $CDCl_3$) δ



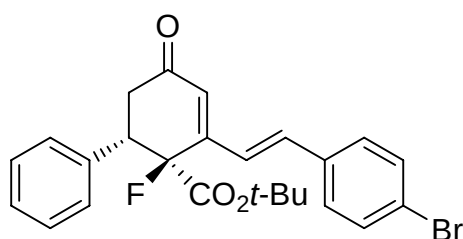
7.27-7.10 (m, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 5.30 (d, $J = 0.8$ Hz, 1H), 1.96 (d, $J = 6.9$ Hz, 3H), 1.50 (s, 9H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -193.74 (d, $J = 150.5$ Hz, 1F); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9 (d, $J = 21.2$ Hz), 163.4 (d, $J = 25.2$ Hz), 147.5, 125.8, 90.7 (d, $J = 196.7$ Hz), 84.1, 27.7, 18.6; IR (KBr) ν 1758, 1710, 1632 cm^{-1} ; EI-MS

(m/z): 202 (M^+ , 0.2%), 69 (100), 57 (63), 41 (37), 129 (14), 146 (11), 43 (7), 70 (5), 56 (5); HRMS (EI): m/z : calcd. for $C_{10}H_{15}FO_3$: 202.1005; found: 202.1008 $[M]^+$.

General Procedure for the enantioselective Robinson annulation catalyzed by primary-secondary diamine **2a**

General procedure for the Robinson annulation to give product **5a**: To a solution of **3a** (34 mg, 0.1 mmol) and **4a** (15 mg, 0.1 mmol) in 0.5 mL of chloroform, **2a** (2 mg, 0.01 mmol, 10 mol%) and 4-nitrobenzoic acid (2 mg, 0.01 mmol, 10 mol%) were added. The mixture was stirred at room temperature and monitored by TLC. After completion (20 h), the mixture was concentrated by rotary evaporation and the residue was purified by flash chromatography (ethyl acetate/petro ether: 1/10) to provide pure **5a** 38 mg, 80% yield as a white solid.

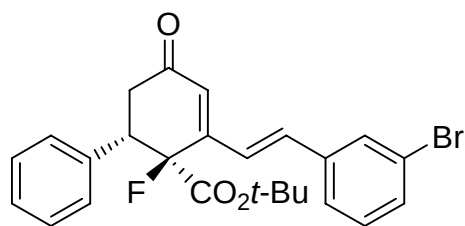
(1*S*,6*S*,*E*)-tert-butyl-2-(4-bromostyryl)-1-fluoro-4-oxo-6-phenylcyclohex-2-enecarboxylate 5a. Mp:



101-102 °C; $[\alpha]^{25}_{\text{D}} = -205.8$ ($c = 0.400$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.40 (AB, $J = 41.9$ Hz, 4H), 7.39-7.33 (m, 5H), 7.26 (d, $J = 16.5$ Hz, 1H), 6.76 (d, $J = 16.5$ Hz, 1H), 6.35 (s, 1H), 3.96-3.84 (m, 1H), 3.54-3.43 (m, 1H), 2.80-2.72 (m, 1H), 1.29 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -150.78 (d, $J = 15.9$ Hz, 1F);

^{13}C NMR (75 MHz, CDCl_3) δ 197.4 (d, $J = 2.1$ Hz), 166.0 (d, $J = 14.5$ Hz), 151.8 (d, $J = 21.1$ Hz), 137.2 (d, $J = 6.1$ Hz), 135.4 (d, $J = 0.8$ Hz), 134.8 (d, $J = 0.9$ Hz), 132.1, 128.8 (d, $J = 1.1$ Hz), 128.7, 128.5 (d, $J = 4.4$ Hz), 128.4, 128.2, 123.9 (d, $J = 1.8$ Hz), 123.6, 94.4 (d, $J = 193.5$ Hz), 84.4, 47.8 (d, $J = 21.9$ Hz), 39.2 (d, $J = 8.8$ Hz), 27.7; IR (KBr) ν 1721, 1676, 1664, 1596, 1584 cm^{-1} ; ESI-MS (m/z): 493 ($\text{M}+23$), 471 ($\text{M}+1$); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{Br}(81)\text{FO}_3$: 472.0872; found: 472.0869 $[\text{M}]^+$. HPLC separation conditions: Chiralcel AD, 20 °C, 254 nm, 9:1 hexane : *i*-PrOH, 0.8 mL/min; $t_{\text{R}} = 19.2$ min (minor enantiomer), 25.4 min (major enantiomer).

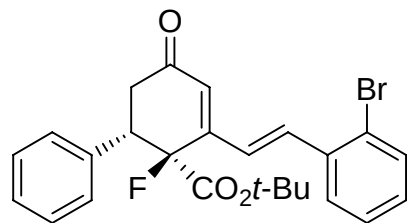
(1*S*,6*S*,*E*)-tert-butyl-2-(3-bromostyryl)-1-fluoro-4-oxo-6-phenylcyclohex-2-enecarboxylate 5b: White



solid. Mp: 132-133 °C; $[\alpha]_D^{25} = -255.2$ ($c = 1.300$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.60 (s, 1H), 7.49-7.19 (m, 9H), 6.76 (d, $J = 16.8$ Hz, 1H), 6.35 (s, 1H), 3.96-3.84 (m, 1H), 3.48 (t, $J = 14.8$ Hz, 1H), 2.82-2.69 (m, 1H), 1.30 (s, 9H); ^{19}F NMR (282 MHz,

CDCl_3) δ -150.63 (d, $J = 16.7$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 197.4 (d, $J = 2.1$ Hz), 166.0 (d, $J = 26.5$ Hz), 151.6 (d, $J = 21.2$ Hz), 138.0 (d, $J = 0.6$ Hz), 136.8 (d, $J = 7.0$ Hz), 135.4 (d, $J = 0.6$ Hz), 132.2, 130.4, 129.9, 128.9 (d, $J = 4.4$ Hz), 128.8 (d, $J = 1.1$ Hz), 128.5, 128.3, 126.1, 124.8 (d, $J = 1.9$ Hz), 123.1, 94.4 (d, $J = 194.3$ Hz), 84.4, 47.8 (d, $J = 22.0$ Hz), 39.2 (d, $J = 8.8$ Hz), 27.8; IR (KBr) ν 1756, 1666, 1616, 1590 cm^{-1} ; EI-MS (m/z): 470 (M^+ , 1.2%), 472 (1), 57 (100), 352 (30), 354 (29), 183 (19), 416 (18), 41 (17), 414 (17), 248 (12); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{BrFO}_3$: 470.0893; found: 470.0902 $[\text{M}]^+$, calcd. for $\text{C}_{25}\text{H}_{24}\text{Br}(81)\text{FO}_3$: 472.0872; found: 472.0877 $[\text{M}]^+$. HPLC separation conditions: Chiralcel ADH, 20 °C, 254 nm, 4:1 hexane : *i*-PrOH, 0.6 mL/min; $t_R = 11.4$ min (major enantiomer), 12.2 min (minor enantiomer).

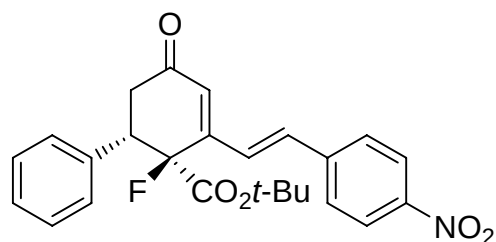
(1*S*,6*S*,*E*)-tert-butyl-2-(2-bromostyryl)-1-fluoro-4-oxo-6-phenylcyclohex-2-enecarboxylate 5c:



Colorless oil; $[\alpha]_D^{25} = -194.7$ ($c = 0.500$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.72-7.14 (m, 10H), 6.72 (d, $J = 16.5$ Hz, 1H), 6.40 (s, 1H), 3.97-3.85 (m, 1H), 3.50 (t, $J = 15.0$ Hz, 1H), 2.80-2.72 (m, 1H), 1.31 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -151.52 (d, $J = 16.3$ Hz, 1F); ^{13}C

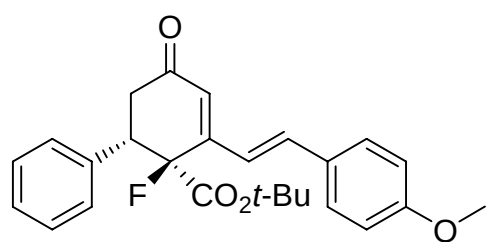
NMR (75 MHz, CDCl_3) δ 197.5 (d, $J = 2.1$ Hz), 165.9 (d, $J = 26.5$ Hz), 152.0 (d, $J = 21.2$ Hz), 136.9 (d, $J = 6.0$ Hz), 135.8 (d, $J = 0.9$ Hz), 135.4 (d, $J = 0.8$ Hz), 133.3, 130.4, 128.8(9), 128.8(8), 128.4, 128.2, 127.7, 127.0, 125.8 (d, $J = 2.0$ Hz), 125.0, 94.3 (d, $J = 194.2$ Hz), 84.4, 47.9 (d, $J = 22.0$ Hz), 39.2 (d, $J = 8.8$ Hz), 27.7; IR (film) ν 1755, 1725, 1670, 1612, 1584 cm^{-1} ; EI-MS (m/z): 470 (M^+ , 0.6%), 57 (100), 352 (33), 354 (32), 183 (25), 41 (21), 416 (20), 414 (20), 115 (13); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{BrFO}_3$: 470.0893; found: 472.0899 $[\text{M}]^+$, calcd. for $\text{C}_{25}\text{H}_{24}\text{Br}(81)\text{FO}_3$: 472.0872; found: 472.0870 $[\text{M}]^+$. HPLC separation conditions: Chiralcel AD, 20 °C, 254 nm, 9:1 hexane : *i*-PrOH, 0.7 mL/min; $t_R = 15.9$ min (major enantiomer), 18.1 min (minor enantiomer).

(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-2-(4-nitrostyryl)-4-oxo-6-phenylcyclohex-2-enecarboxylate 5d: White



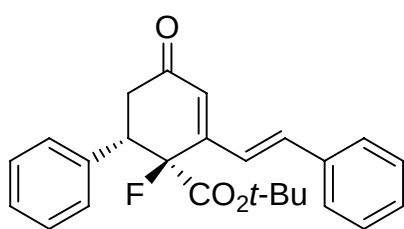
solid. Mp: 127-128 °C; $[\alpha]_D^{25} = -233.8$ ($c = 0.450$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.81 (AB, $J = 189.5$ Hz, 4H), 7.42-7.33 (m, 6H), 6.90 (d, $J = 17.1$ Hz, 1H), 6.40 (s, 1H), 3.98-3.86 (m, 1H), 3.56-3.45 (m, 1H), 2.83-2.75 (m, 1H), 1.31 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -150.95 (d, $J = 17.0$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 197.3 (d, $J = 2.2$ Hz), 165.9 (d, $J = 26.0$ Hz), 151.9 (d, $J = 21.4$ Hz), 147.8, 142.0, 135.7 (d, $J = 6.2$ Hz), 135.2, 130.0 (d, $J = 4.4$ Hz), 128.8, 128.5, 128.4, 127.8, 127.7 (d, $J = 1.3$ Hz), 124.2, 94.3 (d, $J = 193.5$ Hz), 84.6, 47.8 (d, $J = 21.9$ Hz), 39.2 (d, $J = 9.1$ Hz), 27.7; IR (KBr) ν 1730, 1676, 1597, 1519 cm^{-1} ; EI-MS (m/z): 437 (M^+ , 0.6%), 57 (100), 319 (25), 41 (24), 381 (13), 43 (8), 115 (8), 56 (8), 320 (8); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{FNO}_5$: 437.1639; found: 437.1638 $[\text{M}]^+$. HPLC separation conditions: Chiralcel ODH, 20 °C, 254 nm, 9:1 hexane : *i*-PrOH, 0.6 mL/min; $t_R = 44.4$ min (minor enantiomer), 63.0 min (major enantiomer).

(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-2-(4-methoxystyryl)-4-oxo-6-phenylcyclohex-2-enecarboxylate 5e:



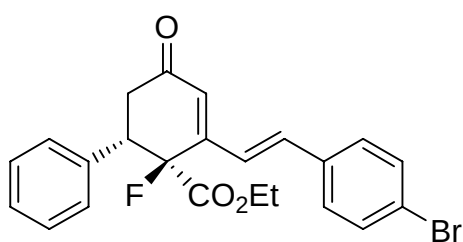
Colorless oil; $[\alpha]_D^{25} = -295.6$ ($c = 0.500$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.26 (m, 6H), 7.11 (AB, $J = 157.2$ Hz, 4H), 6.65 (d, $J = 16.4$ Hz, 1H), 6.31 (s, 1H), 3.95-3.80 (m, 1H), 3.82 (s, 3H), 3.53-3.42 (m, 1H), 2.78-2.70 (m, 1H), 1.29 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -150.58 (d, $J = 20.8$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 197.5 (d, $J = 1.7$ Hz), 166.2 (d, $J = 26.5$ Hz), 160.8, 152.5 (d, $J = 20.9$ Hz), 138.3 (d, $J = 5.9$ Hz), 135.6 (d, $J = 0.7$ Hz), 128.9, 128.8 (d, $J = 1.1$ Hz), 128.6 (d, $J = 0.9$ Hz), 128.4, 128.2, 127.1 (d, $J = 4.2$ Hz), 121.0 (d, $J = 1.8$ Hz), 114.4, 95.5 (d, $J = 193.5$ Hz), 84.2, 55.3, 47.8 (d, $J = 22.1$ Hz), 39.2 (d, $J = 9.8$ Hz), 27.7; IR (film) ν 1753, 1726, 1668, 1603, 1583, 1512 cm^{-1} ; EI-MS (m/z): 422 (M^+ , 3.8%), 84 (100), 57 (61), 86 (57), 71 (36), 55 (30), 85 (29), 311 (22), 69 (21); HRMS (EI): m/z : calcd. for $\text{C}_{26}\text{H}_{27}\text{FO}_4$: 422.1893; found: 422.1898 $[\text{M}]^+$. HPLC separation conditions: Chiralcel AD, 20 °C, 254 nm, 4:1 hexane : *i*-PrOH, 0.7 mL/min; $t_R = 16.7$ min (minor enantiomer), 22.4 min (major enantiomer).

(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-4-oxo-6-phenyl-2-styrylcyclohex-2-enecarboxylate 5f: White solid. Mp:



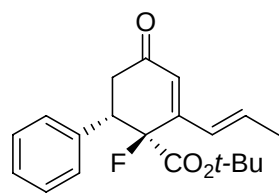
133-134 °C; $[\alpha]_D^{25} = -311.5$ ($c = 0.500$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.51-7.25 (m, 11H), 6.78 (d, $J = 16.9$ Hz, 1H), 6.35 (s, 1H), 3.96-3.84 (m, 1H), 3.49 (t, $J = 15.0$ Hz, 1H), 2.81-2.69 (m, 1H), 1.30 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -150.69 (d, $J = 16.2$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 197.5 (d, $J = 1.8$ Hz), 166.1 (d, $J = 26.4$ Hz), 152.2 (d, $J = 21.0$ Hz), 138.6 (d, $J = 5.8$ Hz), 135.9 (d, $J = 0.8$ Hz), 135.6 (d, $J = 0.6$ Hz), 129.5, 128.8 (d, $J = 1.0$ Hz), 128.4, 128.2, 128.1 (d, $J = 4.3$ Hz), 127.4, 123.3 (d, $J = 1.8$ Hz), 94.5 (d, $J = 193.6$ Hz), 84.3, 47.8 (d, $J = 22.0$ Hz), 39.2 (d, $J = 8.7$ Hz), 27.8; IR (KBr) ν 1722, 1673, 1616, 1587 cm^{-1} ; EI-MS (m/z): 392 (M^+ , 4.3%), 57 (100), 274 (44), 336 (36), 41 (26), 91 (25), 159 (20), 271 (16), 170 (15); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{25}\text{FO}_3$: 392.1788; found: 392.1793 [M] $^+$. HPLC separation conditions: Chiralcel AD, 20 °C, 254 nm, 19:1 hexane : *i*-PrOH, 0.5 mL/min; $t_R = 31.5$ min (minor enantiomer), 34.0 min (major enantiomer).

(1*S*,6*S*,*E*)-ethyl-2-(4-bromostyryl)-1-fluoro-4-oxo-6-phenylcyclohex-2-enecarboxylate 5g: Colorless



oil; $[\alpha]_D^{25} = -228.3$ ($c = 0.950$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.49-7.18 (m, 9H), 6.98 (AB, $J = 16.4$ Hz, 2H), 6.38 (s, 1H), 4.20-3.80 (m, 3H), 3.48 (t, $J = 15.9$ Hz, 1H), 2.79-2.71 (m, 1H), 1.11 (t, $J = 6.9$ Hz, 1H); ^{19}F NMR (282 MHz, CDCl_3) δ -153.46 (d, $J = 16.1$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 197.1 (d, $J = 1.8$ Hz), 167.1 (d, $J = 26.9$ Hz), 151.1 (d, $J = 21.0$ Hz), 137.1 (d, $J = 6.0$ Hz), 135.4, 134.7 (d, $J = 0.8$ Hz), 132.1, 128.8, 128.6, 128.5, 128.4(8), 128.4(0), 123.7, 123.6, 94.9 (d, $J = 193.7$ Hz), 62.6, 47.2 (d, $J = 21.7$ Hz), 39.1 (d, $J = 8.7$ Hz), 13.9; IR (film) ν 1759, 1733, 1669, 1616, 1581 cm^{-1} ; EI-MS (m/z): 442 (M^+ , 23.9%), 382 (100), 380 (98), 183 (30), 186 (27), 383 (25), 444 (24), 242 (23); HRMS (EI): m/z : calcd. for $\text{C}_{23}\text{H}_{20}\text{BrFO}_3$: 442.0580; found: 442.0578 [M] $^+$. HPLC separation conditions: Chiralcel ODH, 20 °C, 254 nm, 4:1 hexane : *i*-PrOH, 0.7 mL/min; $t_R = 30.7$ min (minor enantiomer), 38.5 min (major enantiomer).

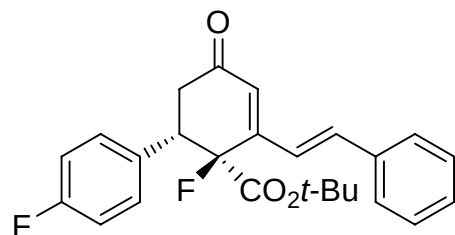
(1*S*,6*S*,*E*)-tert-butyl 1-fluoro-4-oxo-6-phenyl-2-(prop-1-enyl)cyclohex-2-enecarboxylate 5h: Colorless oil. $[\alpha]_D^{25} =$



219.5 ($c = 1.650$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.27 (m, 5H), 6.64-6.46 (m, 1H), 6.21-6.08 (m, 1H), 3.92-3.77 (t, $J = 16.0$ Hz, 2H), 2.75-2.63 (m, 1H), 1.86 (d, $J = 6.5$ Hz, 3H), 1.29 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -151.34 (d, $J = 19.9$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 197.8, 166.0 (d, $J =$

27.4 Hz), 152.5 (d, $J = 21.3$ Hz), 137.5 (d, $J = 5.5$ Hz), 135.8, 128.9, 128.4, 128.1, 126.6 (d, $J = 2.2$ Hz), 95.5 (d, $J = 192.9$ Hz), 83.9, 47.8 (d, $J = 22.0$ Hz), 39.3 (d, $J = 8.9$ Hz), 27.7, 19.5; IR (KBr) ν 1755, 1727, 1676 cm^{-1} ; EI-MS (m/z): 330 (M^+ , 0.5%), 57 (100), 274 (27), 212 (26), 69 (23), 41 (23), 230 (13), 126 (13), 229 (12); HRMS (EI): m/z : calcd. for $\text{C}_{20}\text{H}_{23}\text{FO}_3$: 330.1631; found: 330.1630 $[\text{M}]^+$. HPLC separation conditions: Chiralcel ODH, 20 $^\circ\text{C}$, 254 nm, 4:1 hexane : *i*-PrOH, 0.6 mL/min; $t_R = 9.9$ min (major enantiomer), 11.9 min (minor enantiomer).

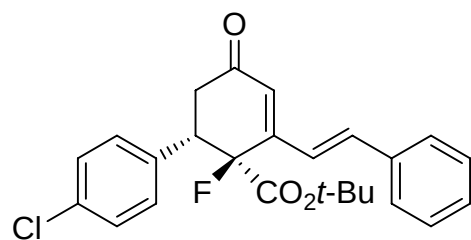
(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-6-(4-fluorophenyl)-4-oxo-2-styrylcyclohex-2-enecarboxylate 5i: White



solid. Mp: 107-108 $^\circ\text{C}$; $[\alpha]_D^{25} = -297.2$ ($c = 0.750$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.53-7.26 (m, 8H), 7.07 (t, $J = 8.5$ Hz, 1H), 6.78 (d, $J = 16.5$ Hz, 1H), 6.35 (s, 1H), 3.95-3.83 (m, 1H), 3.45 (t, $J = 14.6$ Hz, 1H), 2.80-2.66 (m, 1H), 1.31 (s, 9H); ^{19}F NMR (282

MHz, CDCl_3) δ -114.27 (s, 1F), -151.2 (d, $J = 16.6$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 197.0 (d, $J = 1.8$ Hz), 165.9 (d, $J = 26.3$ Hz), 162.0 (d, $J = 247.1$ Hz), 151.9 (d, $J = 21.8$ Hz), 138.6 (d, $J = 4.9$ Hz), 135.7, 131.3 (d, $J = 2.4$ Hz), 130.4 (d, $J = 9.7$ Hz), 129.4, 128.8, 128.0 (d, $J = 4.3$ Hz), 127.3, 123.0 (d, $J = 1.9$ Hz), 115.2 (d, $J = 20.8$ Hz), 94.3 (d, $J = 193.5$ Hz), 84.4, 47.0 (d, $J = 22.8$ Hz), 39.2 (d, $J = 8.9$ Hz), 27.7; IR (KBr) ν 1723, 1678, 1616, 1587, 1510 cm^{-1} ; EI-MS (m/z): 410 (M^+ , 5.0%), 57 (100), 354 (58), 292 (40), 289 (31), 159 (28), 170 (26), 41 (21), 309 (18); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{F}_2\text{O}_3$: 410.1694; found: 410.1700 $[\text{M}]^+$. HPLC separation conditions: Chiralcel ODH, 20 $^\circ\text{C}$, 254 nm, 4:1 hexane : *i*-PrOH, 0.7 mL/min; $t_R = 14.3$ min (minor enantiomer), 16.5 min (major enantiomer).

(1*S*,6*S*,*E*)-tert-butyl-6-(4-chlorophenyl)-1-fluoro-4-oxo-2-styrylcyclohex-2-enecarboxylate 5j:

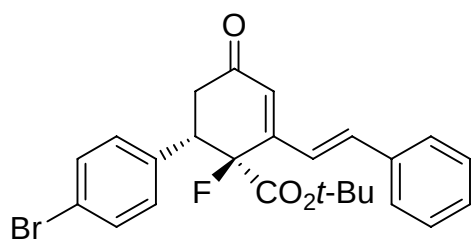


Colorless oil; $[\alpha]_D^{25} = -262.1$ ($c = 0.550$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.54-7.26 (m, 10H), 6.77 (d, $J = 16.4$ Hz, 1H), 6.35 (s, 1H), 3.93-3.81 (m, 1H), 3.43 (t, $J = 16.5$ Hz, 1H), 2.76-2.68 (m, 1H), 1.32 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ

-150.46 (d, $J = 16.6$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 196.9 (d, $J = 1.9$ Hz), 165.9 (d, $J = 26.5$ Hz),

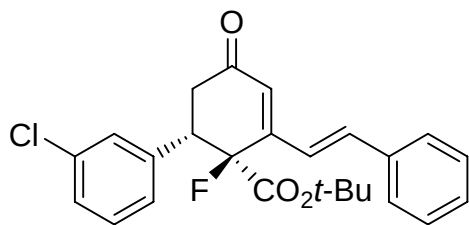
151.9 (d, $J = 21.1$ Hz), 138.7 (d, $J = 5.7$ Hz), 134.1, 134.0 (d, $J = 0.8$ Hz), 130.1 (d, $J = 1.3$ Hz), 129.5, 128.8, 128.5, 127.9 (d, $J = 4.1$ Hz), 127.3, 123.0 (d, $J = 2.0$ Hz), 94.2 (d, $J = 193.9$ Hz), 84.5, 47.2 (d, $J = 21.9$ Hz), 39.0 (d, $J = 8.8$ Hz), 27.7; IR (film) ν 1724, 1675, 1616, 1586 1494 cm^{-1} ; EI-MS (m/z): 426 (M^+ , 5.5%), 57 (100), 326 (59), 370 (52), 308 (44), 159 (38), 170 (31), 41 (31), 129 (29); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{ClFO}_3$: 426.1398; found: 426.1400 [M] $^+$. HPLC separation conditions: Chiralcel ODH, 20 $^{\circ}\text{C}$, 254 nm, 9:1 hexane : *i*-PrOH, 0.7 mL/min; $t_R = 20.6$ min (minor enantiomer), 24.0 min (major enantiomer).

(1*S*,6*S*,*E*)-tert-butyl-6-(4-bromophenyl)-1-fluoro-4-oxo-2-styrylcyclohex-2-enecarboxylate 5k:



Colorless oil; $[\alpha]_D^{25} = -241.2$ ($c = 0.650$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.21 (m, 10H), 6.77 (d, $J = 17.1$ Hz, 1H), 6.35 (s, 1H), 3.92-3.80 (m, 1H), 3.43 (t, $J = 14.4$ Hz, 1H), 2.80-2.69 (m, 1H), 1.32 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -151.21 (d, $J = 16.4$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 196.8 (d, $J = 2.1$ Hz), 165.8 (d, $J = 26.4$ Hz), 151.8 (d, $J = 21.0$ Hz), 138.6 (d, $J = 5.9$ Hz), 135.6 (d, $J = 0.8$ Hz), 131.4, 130.4 (d, $J = 1.1$ Hz), 129.5, 128.8, 127.9 (d, $J = 4.3$ Hz), 127.3, 122.9 (d, $J = 1.9$ Hz), 122.2, 123.0 (d, $J = 2.0$ Hz), 94.1 (d, $J = 193.9$ Hz), 84.5, 47.2 (d, $J = 22.0$ Hz), 38.9 (d, $J = 8.7$ Hz), 27.7; IR (film) ν 1762, 1726, 1671, 1594 cm^{-1} ; EI-MS (m/z): 470 (M^+ , 1.9%), 57(100), 159 (27), 170 (27), 416 (27), 352 (26), 41 (25), 414 (25), 354 (22); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{BrFO}_3$: 470.0893; found: 470.0887 [M] $^+$. HPLC separation conditions: Chiralcel ADH, 20 $^{\circ}\text{C}$, 254 nm, 4:1 hexane : *i*-PrOH, 0.5 mL/min; $t_R = 14.5$ min (major enantiomer), 15.7 min (minor enantiomer).

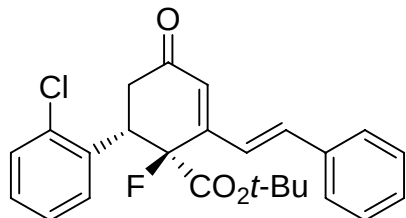
(1*S*,6*S*,*E*)-tert-butyl-6-(3-chlorophenyl)-1-fluoro-4-oxo-2-styrylcyclohex-2-enecarboxylate 5l: White



solid. Mp: 124-125 $^{\circ}\text{C}$; $[\alpha]_D^{24} = -267.6$ ($c = 0.350$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.59-7.23 (m, 10H), 6.77 (d, $J = 16.4$ Hz, 1H), 6.35 (s, 1H), 3.92-3.81 (m, 1H), 3.43 (t, $J = 16.1$ Hz, 1H), 2.81-2.67 (m, 1H), 1.33 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -154.99 (d, $J = 12.4$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 196.7 (d, $J = 2.2$ Hz), 165.9 (d, $J = 26.4$ Hz), 151.9 (d, $J = 21.1$ Hz), 138.7 (d, $J = 5.8$ Hz), 137.6 (d, $J = 1.0$ Hz), 135.7 (d, $J = 0.9$ Hz), 134.3, 129.7, 129.5, 128.9, 128.6 (d, $J = 1.1$ Hz), 128.4, 128.0 (d, $J = 4.4$ Hz), 127.5 (d, $J = 1.6$ Hz), 127.4, 123.1 123.0 (d, $J = 2.0$ Hz), 95.1 (d, $J = 194.3$ Hz), 84.7, 47.6 (d, $J = 22.1$ Hz), 39.0 (d, $J = 8.6$ Hz), 27.7;

IR (KBr) ν 1720, 1677, 1618, 1586 cm^{-1} ; EI-MS (m/z): 426 (M^+ , 2.7%), 57 (100), 308 (61), 370 (39), 326 (27), 170 (24), 41 (24), 159 (23), 310 (21); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{ClFO}_3$: 426.1398; found: 426.1397 [M] $^+$. HPLC separation conditions: Chiralcel ADH, 20 $^{\circ}\text{C}$, 254 nm, 4:1 hexane : *i*-PrOH, 0.6 mL/min; t_R = 12.1 min (minor enantiomer), 14.1 min (major enantiomer).

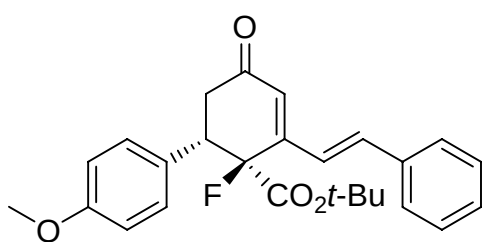
(1*S*,6*S*,*E*)-tert-butyl-6-(2-chlorophenyl)-1-fluoro-4-oxo-2-styrylcyclohex-2-enecarboxylate 5m:



White solid. Mp: 70-71 $^{\circ}\text{C}$; $[\alpha]_D^{24}$ = -316.8 (c = 0.950 in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.47-7.24 (m, 10H), 6.78 (d, J = 16.3 Hz, 1H), 6.36 (s, 1H), 3.71-3.61 (m, 1H), 3.47-3.37 (m, 1H), 2.72-2.61 (m, 1H), 1.41 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -154.54 (d, J = 12.5

Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 196.9 (d, J = 2.1 Hz), 166.4 (d, J = 26.6 Hz), 152.7 (d, J = 20.3 Hz), 138.7 (d, J = 6.1 Hz), 135.8 (d, J = 0.8 Hz), 135.7, 134.0, 130.2, 129.5, 129.2, 128.9, 128.4, 127.9 (d, J = 4.5 Hz), 127.3, 126.8, 122.8 (d, J = 1.6 Hz), 95.3 (d, J = 197.0 Hz), 84.7, 43.5 (d, J = 23.2 Hz), 40.0 (d, J = 8.7 Hz), 27.8; IR (KBr) ν 1753, 1726, 1670, 1616, 1584 cm^{-1} ; EI-MS (m/z): 426 (M^+ , 6.2%), 57 (100), 326 (77), 370 (61), 308 (52), 41 (40), 159 (38), 170 (38), 91 (36); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{ClFO}_3$: 426.1398; found: 426.1402 [M] $^+$. HPLC separation conditions: Chiralcel ADH, 20 $^{\circ}\text{C}$, 254 nm, 9:1 hexane : *i*-PrOH, 0.6 mL/min; t_R = 15.5 min (major enantiomer), 16.1 min (minor enantiomer).

(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-6-(4-methoxyphenyl)-4-oxo-2-styrylcyclohex-2-enecarboxylate 5n:

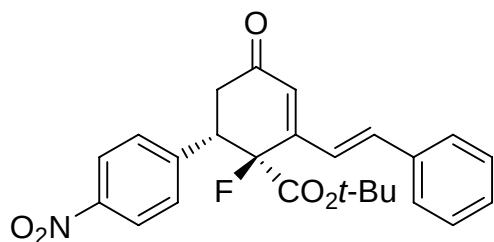


Colorless oil; $[\alpha]_D^{24}$ = -239.2 (c = 1.000 in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.51-7.25 (m, 8H), 6.90 (d, J = 8.7 Hz, 1H), 6.78 (d, J = 16.4 Hz, 1H), 6.34 (s, 1H), 3.90-3.79 (m, 4H), 3.44 (t, 15.1 Hz), 2.72 (d, J = 20.0 Hz, 1H), 1.32 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -150.69 (d, J = 15.6 Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 196.6

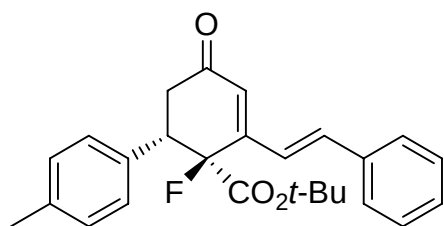
(d, J = 2.1 Hz), 165.1 (d, J = 26.7 Hz), 158.4, 151.2 (d, J = 21.2 Hz), 137.6 (d, J = 5.8 Hz), 134.9, 128.8 (d, J = 0.9 Hz), 128.5, 127.9, 127.1 (d, J = 4.3 Hz), 126.6, 126.3, 122.3 (d, J = 1.6 Hz), 112.7, 93.6 (d, J = 192.4 Hz), 83.2, 54.3, 46.1 (d, J = 22.2 Hz), 38.4 (d, J = 8.7 Hz), 26.8; IR (film) ν 1753, 1727, 1668, 1614, 1586, 1514 cm^{-1} ; EI-MS (m/z): 422 (M^+ , 5.3%), 134 (100), 57 (38), 366 (29), 304 (27), 322 (27), 174 (14), 159 (14), 135 (13); HRMS (EI): m/z : calcd. for $\text{C}_{26}\text{H}_{27}\text{FO}_4$: 422.1893; found: 422.1895 [M] $^+$. HPLC separation conditions: Chiralcel AD, 20 $^{\circ}\text{C}$, 254 nm, 9:1 hexane : *i*-PrOH, 0.8 mL/min; t_R = 26.9 min (major enantiomer), 30.1 min (minor enantiomer).

(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-6-(4-nitrophenyl)-4-oxo-2-styrylcyclohex-2-enecarboxylate**5o:**

Colorless oil; $[\alpha]_D^{23} = -203.5$ ($c = 0.850$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 8.24 (d, $J = 8.2$ Hz, 2H), 7.61-7.28 (m, 8H), 6.80 (d, $J = 16.4$ Hz, 1H), 6.39 (s, 1H), 4.09-3.97 (m, 1H), 3.50 (d, $J = 15.5$ Hz, 1H), 2.77 (d, $J = 23.2$ Hz, 1H), 1.32 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -150.61 (d, $J = 16.0$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 195.0 (d, $J = 2.0$ Hz), 164.7 (d, $J = 26.5$ Hz), 150.7 (d, $J = 20.8$ Hz), 146.7, 142.0, 137.9 (d, $J = 5.7$ Hz), 134.6, 128.9 (d, $J = 1.4$ Hz), 128.7, 127.9, 126.9 (d, $J = 4.3$ Hz), 126.4, 122.5, 121.7 (d, $J = 1.9$ Hz), 92.0 (d, $J = 194.8$ Hz), 84.0, 46.6 (d, $J = 21.8$ Hz), 37.8 (d, $J = 8.4$ Hz), 26.7; IR (film) ν 1753, 1728, 1668, 1522, 1349 cm^{-1} ; EI-MS (m/z): 437 (M^+ , 3.4%), 57 (100), 131 (54), 381 (46), 337 (34), 319 (26), 353 (25), 159 (22), 316 (22); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{24}\text{FNO}_5$: 437.1639; found: 437.1645 $[\text{M}]^+$. HPLC separation conditions: Chiralcel ODH, 20 °C, 254 nm, 9:1 hexane : *i*-PrOH, 0.6 mL/min; $t_R = 44.4$ min (minor enantiomer), 63.0 min (major enantiomer).

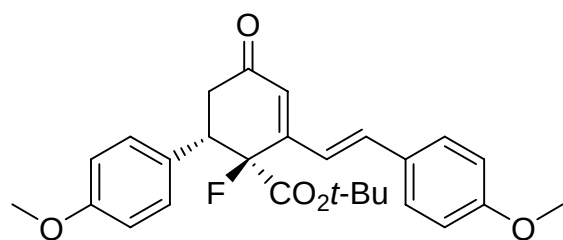
**(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-4-oxo-2-styryl-6-p-tolylcyclohex-2-enecarboxylate** **5p:**

Colorless oil; $[\alpha]_D^{24} = -295.1$ ($c = 1.450$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.50-7.42 (m, 2H), 7.39-7.11 (m, 8H), 6.77 (d, $J = 16.4$ Hz, 1H), 6.34 (s, 1H), 3.92-3.80 (m, 1H), 3.45 (t, 14.5 Hz), 2.77-2.68 (m, 1H), 2.35 (s, 3H), 1.31 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -150.73 (d, $J = 17.8$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 196.7 (d, $J = 1.8$ Hz), 165.1 (d, $J = 27.0$ Hz), 151.2 (d, $J = 21.0$ Hz), 137.6 (d, $J = 6.4$ Hz), 136.9, 134.9, 131.6, 128.5, 128.1, 127.9, 127.7, 127.1 (d, $J = 4.0$ Hz), 126.4, 122.3 (d, $J = 1.6$ Hz), 93.5 (d, $J = 192.6$ Hz), 83.2, 46.5 (d, $J = 22.3$ Hz), 38.3 (d, $J = 8.5$ Hz), 26.8, 20.1; IR (film) ν 1755, 1728, 1668, 1617, 1586 cm^{-1} ; EI-MS (m/z): 406 (M^+ , 5.4%), 288 (100), 57 (78), 306 (67), 350 (49), 158 (40), 159 (36), 41 (28), 91 (25); HRMS (EI): m/z : calcd. for $\text{C}_{26}\text{H}_{27}\text{FO}_3$: 406.1944; found: 406.1948 $[\text{M}]^+$. HPLC separation conditions: Chiralcel ODH, 20 °C, 254 nm, 9:1 hexane : *i*-PrOH, 0.6 mL/min; $t_R = 24.3$ min (major enantiomer), 27.0 min (minor enantiomer).



(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-6-(4-methoxyphenyl)-2-(4-methoxystyryl)-4-oxocyclohex-2-enecarboxylate 5q:

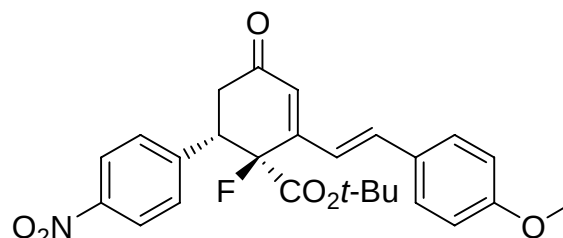
Colorless oil; $[\alpha]_D^{23} = -249.2$ ($c = 1.650$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ



7.41 (d, $J = 9.1$ Hz, 2H), 7.30-7.25 (m, 3H), 6.94-6.84 (m, 4H), 6.64 (d, $J = 16.4$ Hz, 1H), 6.30 (s, 1H), 3.89-3.75 (m, 7H), 3.42 (t, $J = 15.2$ Hz, 1H), 2.76-2.65 (m, 1H), 1.31 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -150.61 (d, $J = 16.3$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 197.6 (d, $J = 2.1$ Hz),

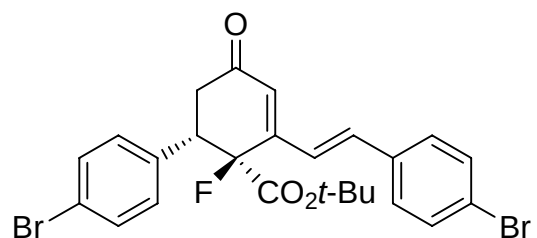
166.2 (d, $J = 26.8$ Hz), 160.8, 159.4, 152.5 (d, $J = 21.1$ Hz), 138.2 (d, $J = 5.9$ Hz), 129.8 (d, $J = 0.9$ Hz), 128.9, 128.6 (d, $J = 0.8$ Hz), 127.7 (d, $J = 0.5$ Hz), 127.1 (d, $J = 4.2$ Hz), 120.9 (d, $J = 1.7$ Hz), 114.3, 113.7, 94.6 (d, $J = 192.5$ Hz), 84.1, 55.3, 47.1 (d, $J = 22.2$ Hz), 39.4 (d, $J = 8.5$ Hz), 27.8; IR (film) ν 1753, 1727, 1668, 1614, 1586, 1514 cm^{-1} ; EI-MS (m/z): 452 (M^+ , 61.7%), 57 (100), 121 (75), 134 (70), 396 (66), 189 (65), 352 (45), 234 (45); HRMS (EI): m/z : calcd. for $\text{C}_{27}\text{H}_{29}\text{FO}_5$: 452.1999; found: 452.1998 $[\text{M}]^+$. HPLC separation conditions: Chiralcel AD, 20 $^\circ\text{C}$, 254 nm, 9:1 hexane : *i*-PrOH, 0.7 mL/min; $t_R = 24.5$ min (minor enantiomer), 32.5 min (major enantiomer).

(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-2-(4-methoxystyryl)-6-(4-nitrophenyl)-4-oxocyclohex-2-enecarboxylate 5r:



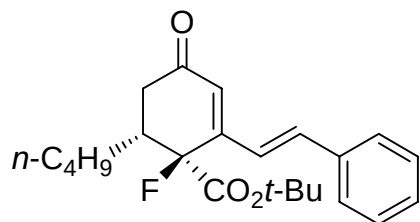
Colorless oil; $[\alpha]_D^{24} = -244.2$ ($c = 1.200$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.78 (AB, $J = 8.9$ Hz, 4H), 7.16 (AB, $J = 9.1$ Hz, 4H), 6.97 (AB, $J = 16.4$ Hz, 2H), 6.35 (s, 1H), 4.07-3.96 (m, 1H), 3.83 (s, 3H), 3.48 (t, $J = 16.6$ Hz, 1H), 2.83-2.69 (m, 1H), 1.32 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -150.40 (d, $J = 16.1$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 196.0 (d, $J = 2.0$ Hz), 165.8 (d, $J = 26.7$ Hz), 160.1, 152.1 (d, $J = 20.7$ Hz), 147.9, 143.0 (d, $J = 0.7$ Hz), 138.6 (d, $J = 5.7$ Hz), 129.9 (d, $J = 1.2$ Hz), 129.0, 128.4 (d, $J = 0.7$ Hz), 126.8 (d, $J = 4.4$ Hz), 123.4, 120.3 (d, $J = 2.0$ Hz), 114.4, 94.0 (d, $J = 194.8$ Hz), 84.9, 55.3, 47.6 (d, $J = 18.0$ Hz), 38.7 (d, $J = 8.4$ Hz), 27.7; IR (film) ν 1752, 1727, 1667, 1603, 1582, 1523, 1513 cm^{-1} ; EI-MS (m/z): 467 (M^+ , 38.9%), 57 (100), 411 (74), 367 (52), 189 (46), 234 (45), 41 (46), 121 (29); HRMS (EI): m/z : calcd. for $\text{C}_{26}\text{H}_{26}\text{FNO}_6$: 467.1744; found: 467.1747 $[\text{M}]^+$. HPLC separation conditions: Chiralcel AD, 20 $^\circ\text{C}$, 254 nm, 4:1 hexane : *i*-PrOH, 0.7 mL/min; $t_R = 28.6$ min (major enantiomer), 37.1 min (minor enantiomer).

(1*S*,6*S*,*E*)-tert-butyl-6-(4-bromophenyl)-2-(4-bromostyryl)-1-fluoro-4-oxocyclohex-2-enecarboxylate 5s: Colorless



oil; $[\alpha]_D^{25} = 98.2$ ($c = 1.250$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.54-7.47 (m, 4H), 7.36-7.20 (m, 9H), 6.75 (d, $J = 16.4$ Hz, 1H), 6.34 (s, 1H), 3.92-3.80 (m, 1H), 3.48-3.37 (m, 1H), 2.78-2.65 (m, 1H), 1.31 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -150.68 (d, $J = 16.4$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 196.7 (d, $J = 2.1$ Hz), 165.8 (d, $J = 26.5$ Hz), 151.5 (d, $J = 21.0$ Hz), 137.2 (d, $J = 6.0$ Hz), 134.6 (d, $J = 0.8$ Hz), 134.5, 132.0, 131.5, 130.4 (d, $J = 1.1$ Hz), 128.7, 128.3 (d, $J = 4.3$ Hz), 123.6 (d, $J = 1.9$ Hz), 122.3, 94.1 (d, $J = 193.7$ Hz), 84.6, 47.2 (d, $J = 22.1$ Hz), 39.0 (d, $J = 9.6$ Hz), 27.7; IR (film) ν 1731, 1665, 1581, 1488 cm^{-1} ; EI-MS (m/z): 550 ($\text{M}^+ + 2$, 3.3%), 57(100), 494 (26), 41 (17), 183 (17), 169 (15), 432 (14), 492 (13), 171 (13); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{23}\text{Br}_2\text{FO}_3$: 547.9998; found: 547.9996 $[\text{M}]^+$. HPLC separation conditions: Chiralcel AD, 20 $^\circ\text{C}$, 254 nm, 9:1 hexane : *i*-PrOH, 0.6 mL/min; $t_R = 27.2$ min (minor enantiomer), 33.0 min (major enantiomer).

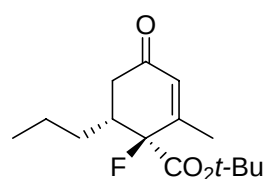
(1*S*,6*R*,*E*)-tert-butyl 6-butyl-1-fluoro-4-oxo-2-styrylcyclohex-2-enecarboxylate 5t: Colorless oil; $[\alpha]_D^{24} = -205.0$



($c = 0.900$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.55-7.27 (m, 6H), 6.74 (d, $J = 16.4$ Hz, 1H), 6.26 (s, 1H), 2.73-2.44 (m, 3H), 2.04-1.77 (m, 1H), 1.47-1.15 (m, 14H), 0.94-0.90 (m, 3H); ^{19}F NMR (282 MHz, CDCl_3) δ -153.80 (d, $J = 17.1$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ

196.5 (d, $J = 2.2$ Hz), 165.5 (d, $J = 28.4$ Hz), 151.7 (d, $J = 21.2$ Hz), 137.1 (d, $J = 5.6$ Hz), 134.9, 128.4, 127.8, 126.9 (d, $J = 4.6$ Hz), 126.4, 122.1 (d, $J = 2.6$ Hz), 93.5 (d, $J = 189.3$ Hz), 83.2, 41.7 (d, $J = 23.3$ Hz), 38.3 (d, $J = 9.9$ Hz), 28.2, 27.8, 26.9, 21.5, 12.9; IR (film) ν 1752, 1730, 1617, 1587 cm^{-1} ; EI-MS (m/z): 372 (M^+ , 8.2%), 57 (100), 316 (53), 170 (47), 197 (42), 239 (31), 41 (21), 195 (20), 91 (19); HRMS (EI): m/z : calcd. for $\text{C}_{23}\text{H}_{29}\text{FO}_3$: 372.2101; found: 372.2098 $[\text{M}]^+$. HPLC separation conditions: Chiralcel AD, 20 $^\circ\text{C}$, 254 nm, 9:1 hexane : *i*-PrOH, 0.6 mL/min; $t_R = 9.9$ min (minor enantiomer), 12.1 min (major enantiomer).

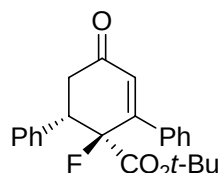
(1*S*,6*R*)-tert-butyl 1-fluoro-2-methyl-4-oxo-6-propylcyclohex-2-enecarboxylate 5u: Colorless oil. $[\alpha]_D^{25} = 204.9$



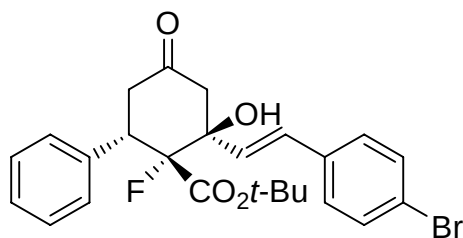
($c = 1.650$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 6.60 (s, 1H), 2.64-2.40 (m, 3H), 1.97 (s, 3H), 1.85-1.71 (m, 1H), 1.49 (s, 9H), 1.44-1.07 (m, 3H), 0.97-0.90 (m, 3H); ^{19}F NMR (282 MHz, CDCl_3) δ -157.87 (d, $J = 13.7$ Hz, 1F); ^{13}C NMR (75

MHz, CDCl₃) δ 197.2, 166.2 (d, J = 29.2 Hz), 156.1 (d, J = 24.2 Hz), 129.5 (d, J = 4.6 Hz), 95.5 (d, J = 186.0 Hz), 83.9, 42.3 (d, J = 22.7 Hz), 39.6, 32.0, 27.9, 20.0, 17.6 (d, J = 5.9 Hz), 13.9; IR (KBr) ν 1754, 1728, 1681 cm⁻¹; ESI-MS (m/z): 293 (M+23); HRMS (EI): m/z : calcd. for C₁₅H₂₃FO₃: 270.1631; found: 270.1630 [M]⁺. HPLC separation conditions: Chiralcel ODH, 20 °C, 214 nm, 9:1 hexane : *i*-PrOH, 0.7 mL/min; t_R = 8.0 min (minor enantiomer), 8.7 min (major enantiomer).

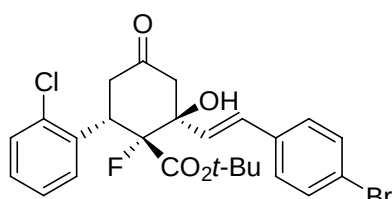
(1*S*,6*S*)-tert-butyl 1-fluoro-4-oxo-2,6-diphenylcyclohex-2-enecarboxylate 5v: Colorless oil; $[\alpha]_D^{24}$ = 125.5 (c = 0.360 in CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.52-7.18 (m, 10H), 6.42 (s, 1H), 3.97-3.85 (m, 1H), 3.48-3.36 (m, 1H), 2.76 (d, J = 17.3 Hz, 1H), 1.18 (s, 9H); ¹⁹F NMR (282 MHz, CDCl₃) δ -150.67 (d, J = 15.0 Hz, 1F); ¹³C NMR (75 MHz, CDCl₃) δ 197.3, 166.0 (d, J = 26.5 Hz), 155.6 (d, J = 22.8 Hz), 135.7, 134.6, 130.1, 129.3 (d, J = 4.5 Hz), 128.9, 128.6, 128.4, 128.3, 127.9 (d, J = 2.3 Hz), 94.5 (d, J = 194.6 Hz), 84.4, 48.7 (d, J = 22.0 Hz), 39.3 (d, J = 8.4 Hz), 27.6; IR (film) ν 1753, 1725, 1672 cm⁻¹; EI-MS (m/z): 57 (100), 266 (56), 248 (28), 265 (15), 41 (13), 267 (11), 178 (10), 133 (10); HRMS (EI): m/z : calcd. for C₂₃H₂₃FO₃: 366.1631; found: 366.1624 [M]⁺. HPLC separation conditions: Chiralcel ODH, 20 °C, 254 nm, 9:1 hexane : *i*-PrOH, 0.7 mL/min; t_R = 18.3 min (major enantiomer), 28.8 min (minor enantiomer).



(1*R*,2*S*,6*S*,*E*)-tert-butyl-2-(4-bromostyryl)-1-fluoro-2-hydroxy-4-oxo-6-phenylcyclohexanecarboxylate 6a: White solid. Mp: 146-147 °C; $[\alpha]_D^{25}$ = -40.6 (c = 0.450 in CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.52-7.22 (m, 9H), 6.60 (AB, J = 15.8 Hz, 2H), 4.20-3.93 (m, 2H), 3.10-2.89 (m, 2H), 2.71-2.44 (m, 2H), 1.05 (s, 9H); ¹⁹F NMR (282 MHz, CDCl₃) δ -178.86 (d, J = 33.1 Hz, 1F); ¹³C NMR (75 MHz, CDCl₃) δ 205.2, 169.5 (d, J = 21.5 Hz), 136.5 (d, J = 1.1 Hz), 134.8, 131.7, 129.9 (d, J = 0.8 Hz), 128.9 (d, J = 2.5 Hz), 128.8, 128.5, 128.1, 128.0, 121.9, 95.9 (d, J = 207.2 Hz), 84.6, 77.8 (d, J = 22.5 Hz), 48.0, 47.9, 44.9 (d, J = 18.8 Hz), 42.8 (d, J = 4.4 Hz), 27.4; IR (KBr) ν 3518, 1720, 1704, 1489 cm⁻¹; EI-MS (m/z): 488 (M⁺, 3.3%), 209 (100), 211 (95), 266 (54), 268 (52), 57 (38), 238 (30), 102 (29), 240 (28); HRMS (EI): m/z : calcd. for C₂₅H₂₆BrFO₄: 488.0998; found: 488.1005 [M]⁺. HPLC separation conditions: Chiralcel ODH, 20 °C, 254 nm, 9:1 hexane : *i*-PrOH, 0.8 mL/min; t_R = 12.6 min (major enantiomer), 14.8 min (minor enantiomer).

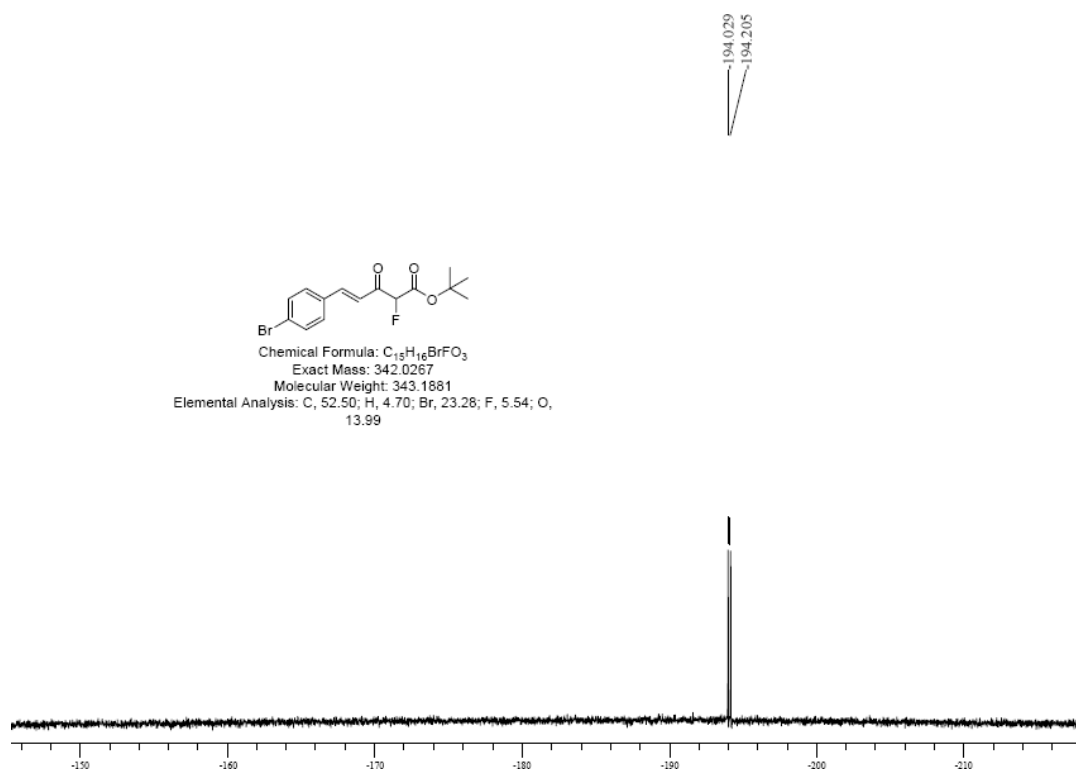
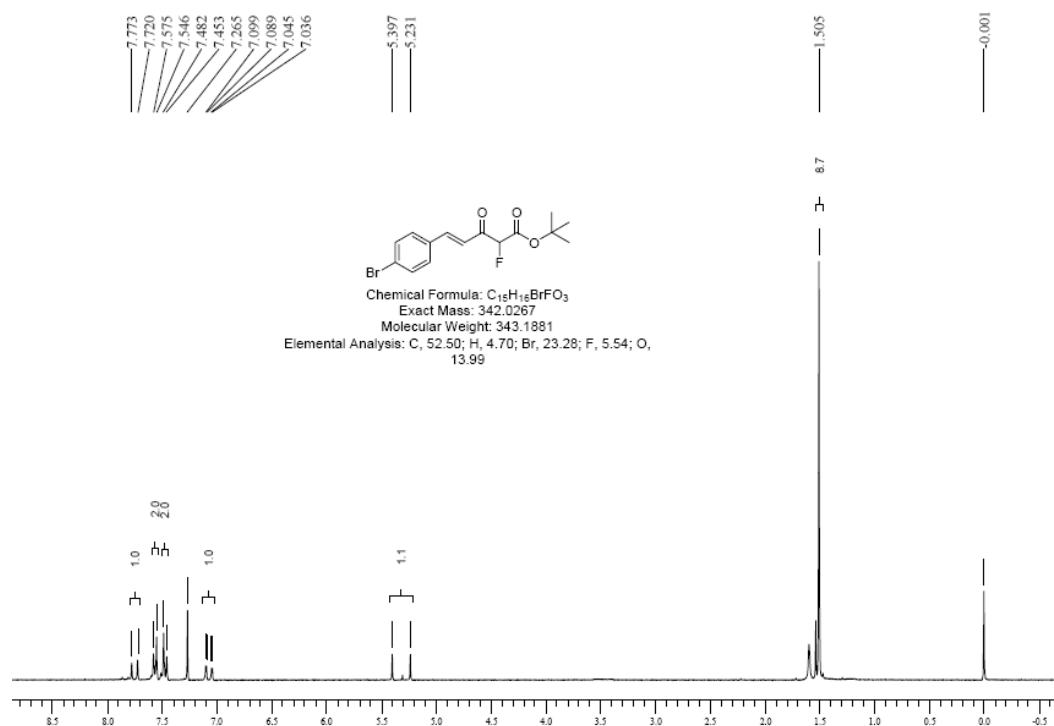


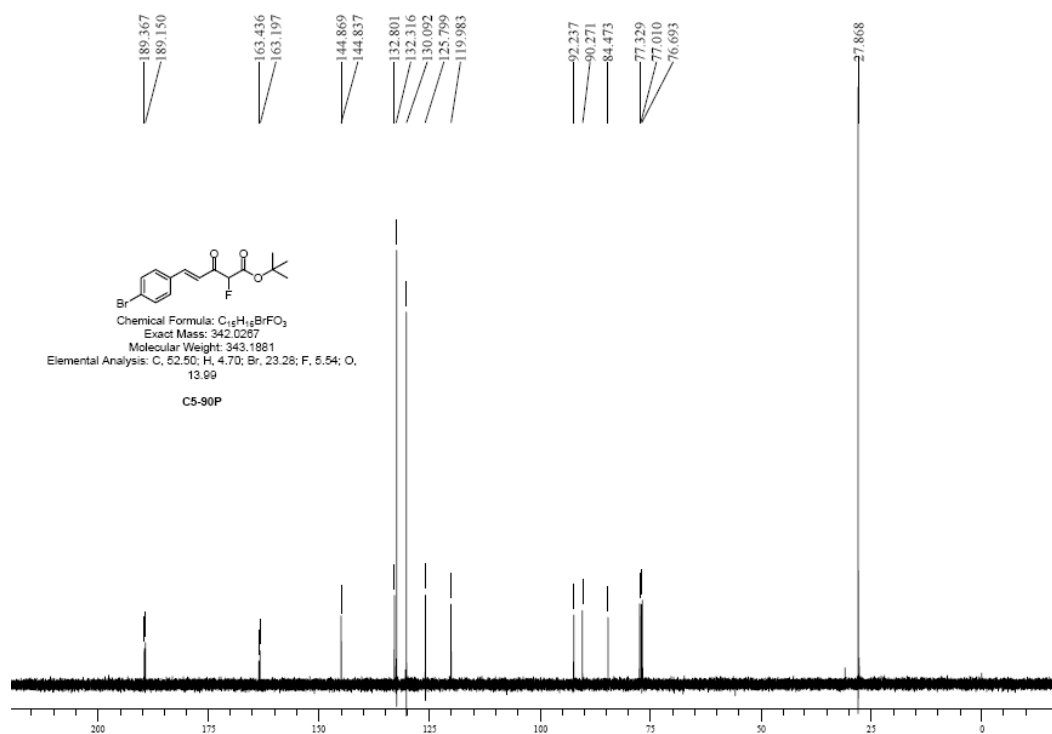
(1*R*,2*S*,6*S*,*E*)-tert-butyl-2-(4-bromostyryl)-6-(2-chlorophenyl)-1-fluoro-2-hydroxy-4-oxocyclohexane carboxylate 6m: White solid. Mp: 125-126 °C; $[\alpha]_D^{25} = 95.8$ ($c = 1.450$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.73 (d, $J = 7.7$ Hz, 1H), 7.45-7.20 (m, 8H), 6.65 (AB, $J = 16.0$ Hz, 2H), 4.95-4.77 (m, 1H), 3.98 (d, $J = 2.7$ Hz, 1H), 3.03-2.80 (m, 2H), 2.66-2.53 (m, 2H), 1.11 (s, 9H); ^{19}F NMR (282 MHz, CDCl_3) δ -177.59 (d, $J = 28.4$ Hz, 1F); ^{13}C NMR (75 MHz, CDCl_3) δ 204.7, 168.4 (d, $J = 23.6$ Hz), 135.9, 135.0, 134.6, 134.1, 130.0 (d, $J = 7.0$ Hz), 129.7, 129.1, 128.7, 128.1 (d, $J = 10.9$ Hz), 127.2, 126.7, 96.3 (d, $J = 204.9$ Hz), 84.8, 77.8, 48.4, 42.8, 42.7, 39.4 (d, $J = 18.0$ Hz), 27.4; IR (KBr) ν 3466, 2976, 1721 cm^{-1} ; EI-MS (m/z): 444 (M^+ , 0.9%), 131 (100), 188 (48), 57 (31), 160 (27), 103 (16), 41 (11), 132 (10), 77 (8); HRMS (EI): m/z : calcd. for $\text{C}_{25}\text{H}_{26}\text{ClFO}_4$: 444.1504; found: 444.1506 $[\text{M}]^+$. HPLC separation conditions: Chiralcel ADH, 20 °C, 254 nm, 4:1 hexane : *i*-PrOH, 0.7 mL/min; $t_R = 15.6$ min (major enantiomer), 16.4 min (minor enantiomer).



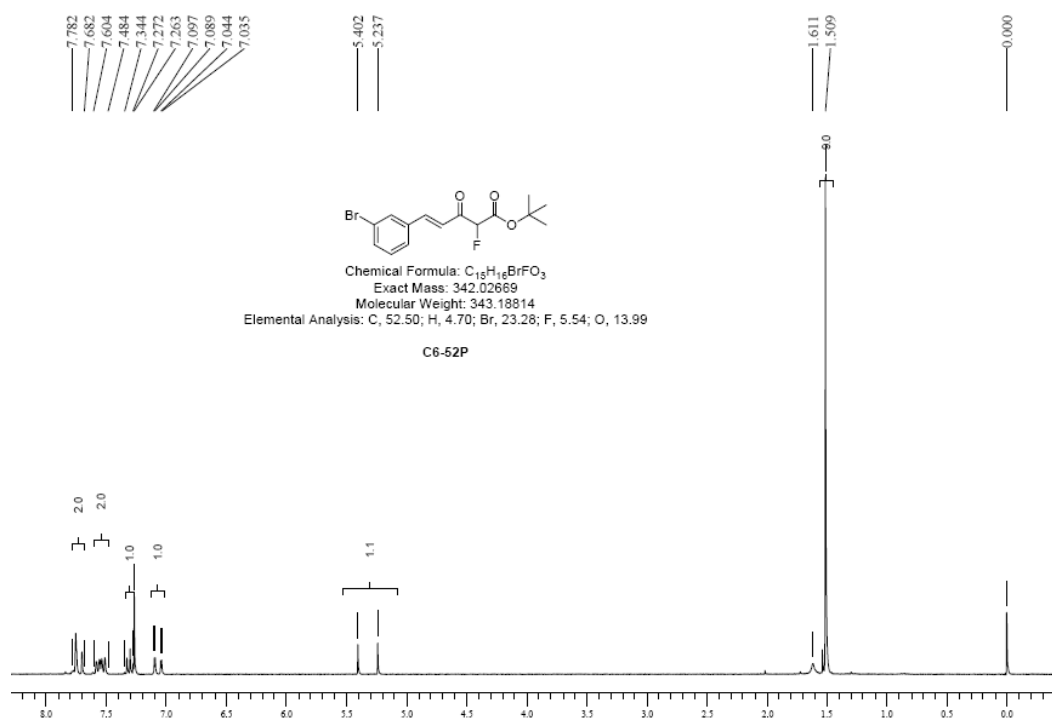
Copies of ^1H NMR, ^{19}F NMR and ^{13}C NMR

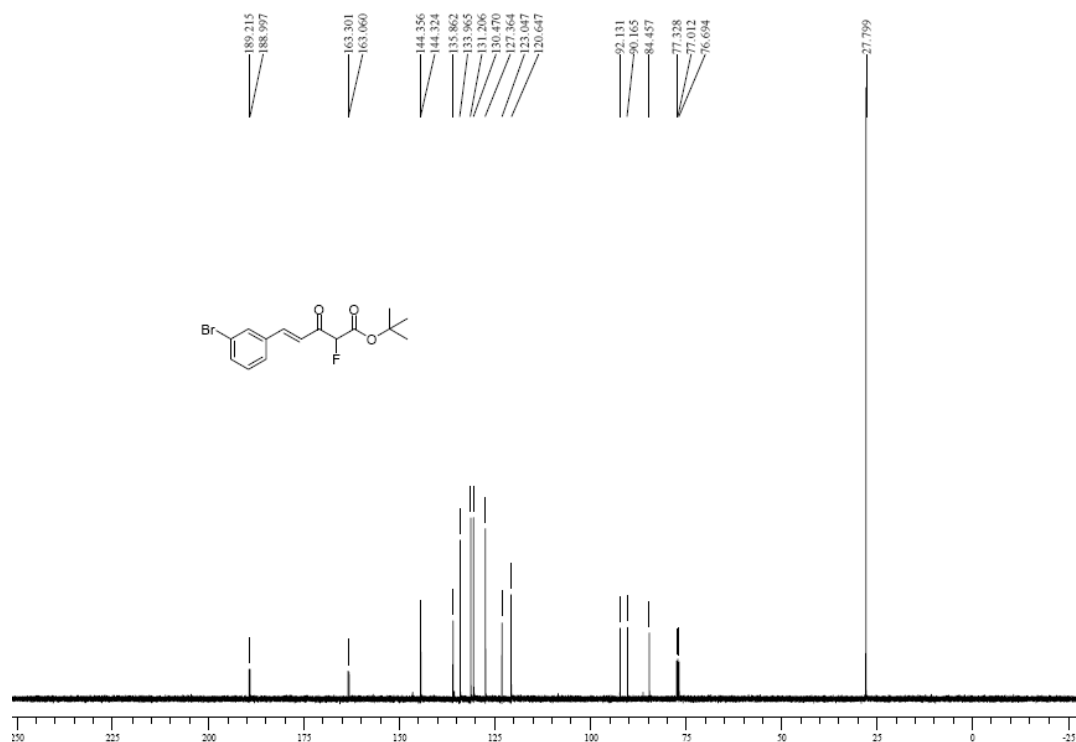
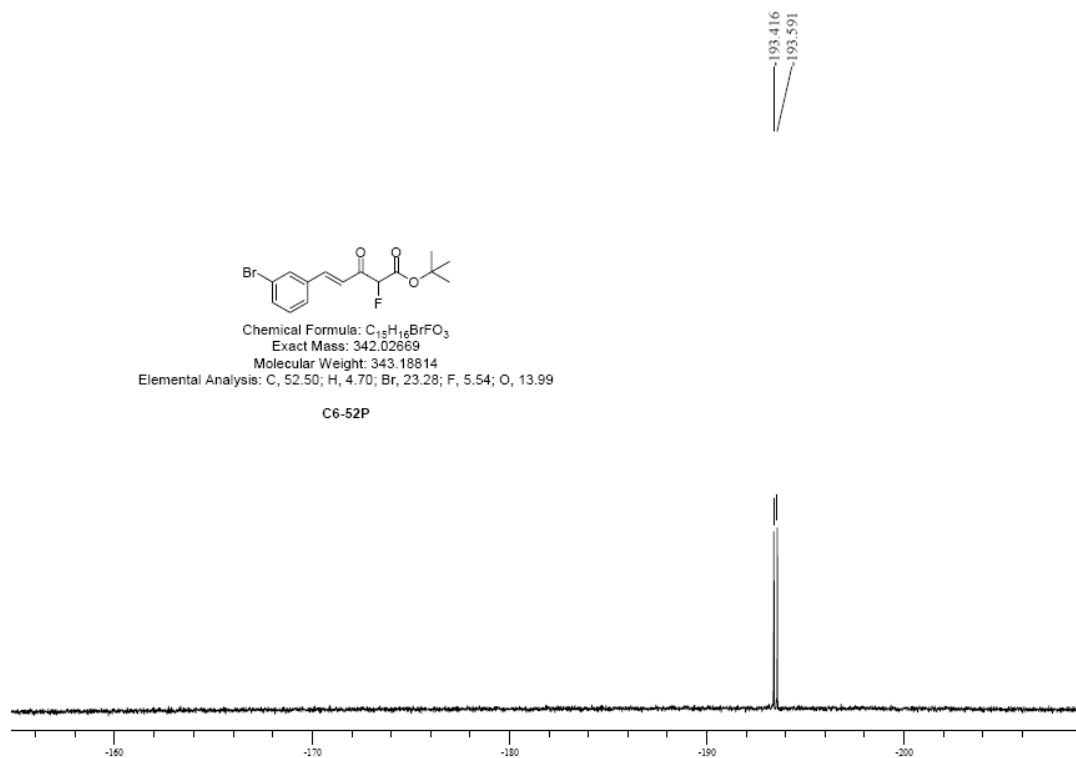
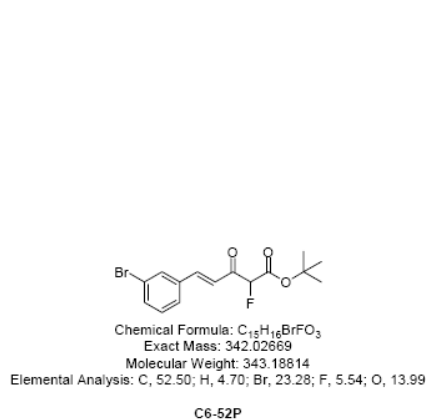
(*E*)-*tert*-Butyl 5-(4-bromophenyl)-2-fluoro-3-oxopent-4-enoate 3a



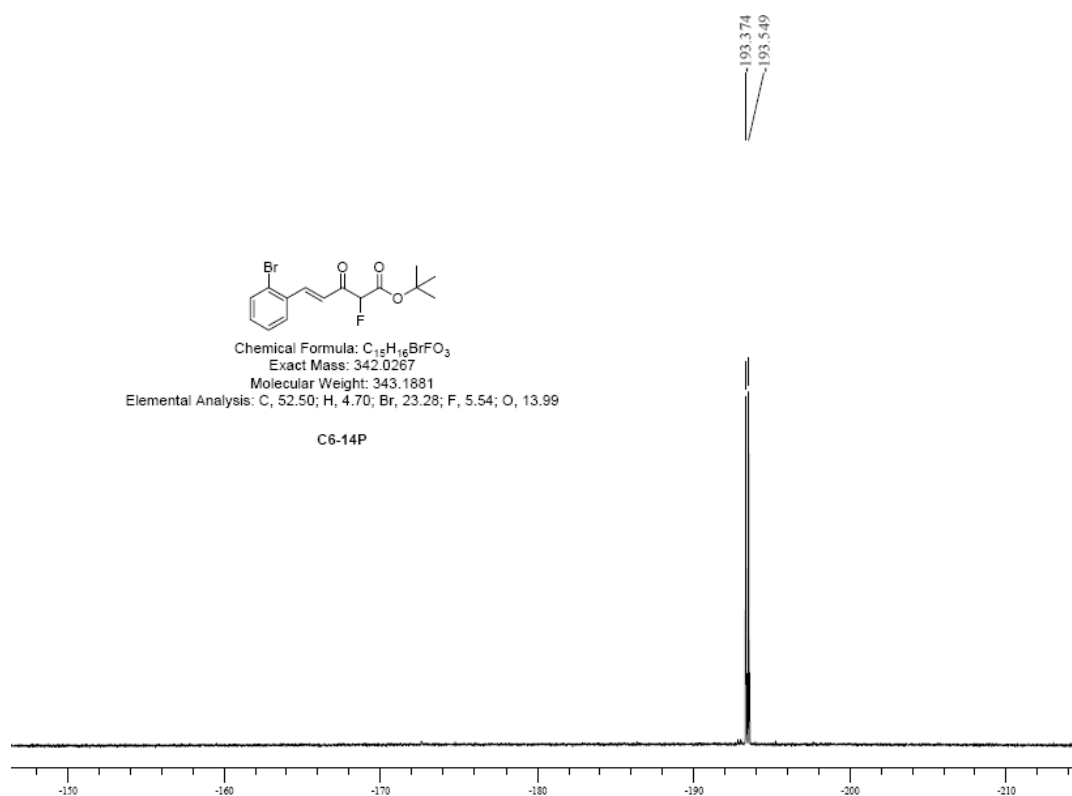
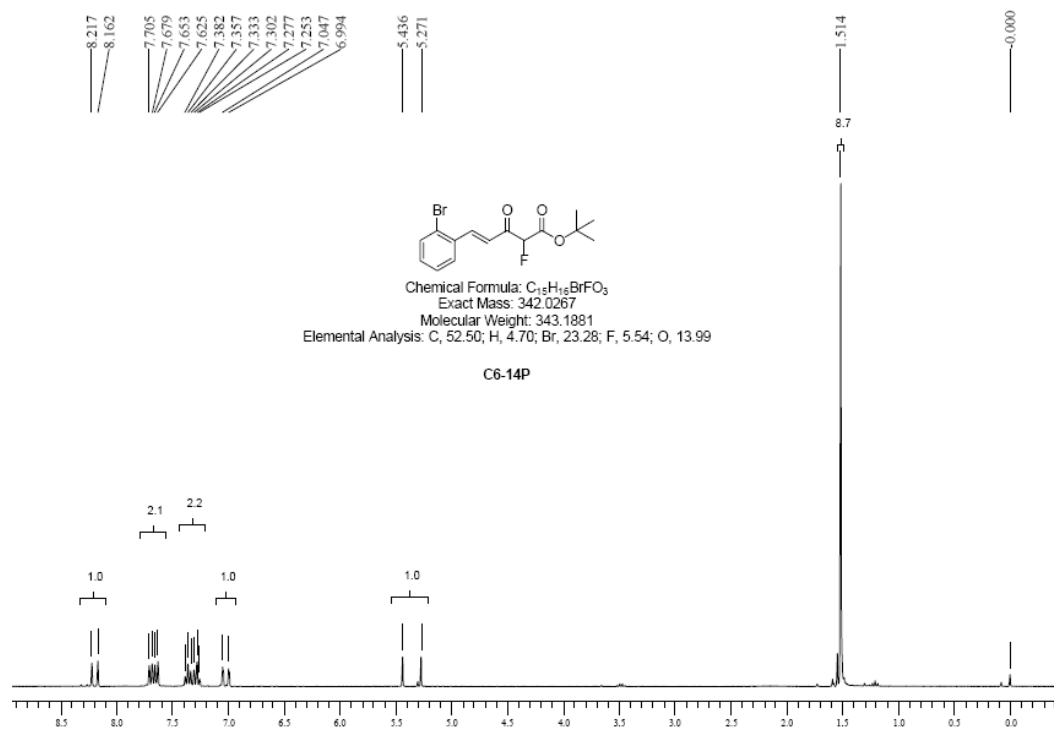


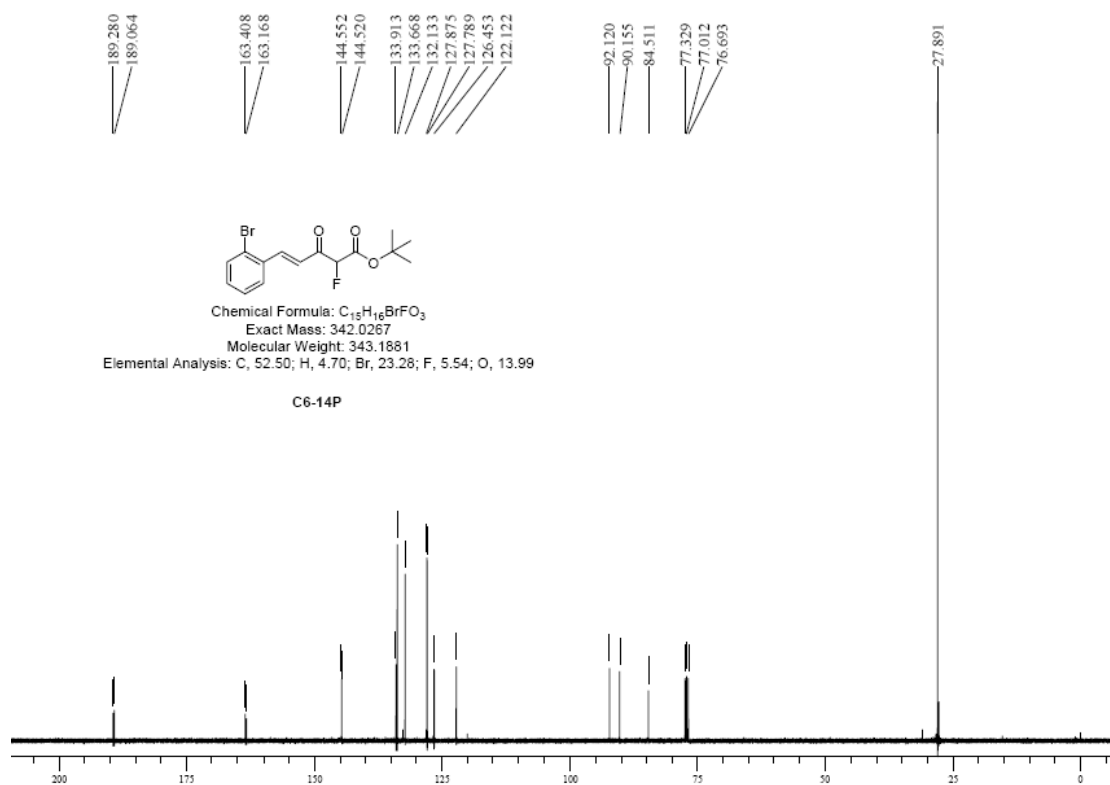
(E)-tert-Butyl 5-(3-bromophenyl)-2-fluoro-3-oxopent-4-enoate 3b



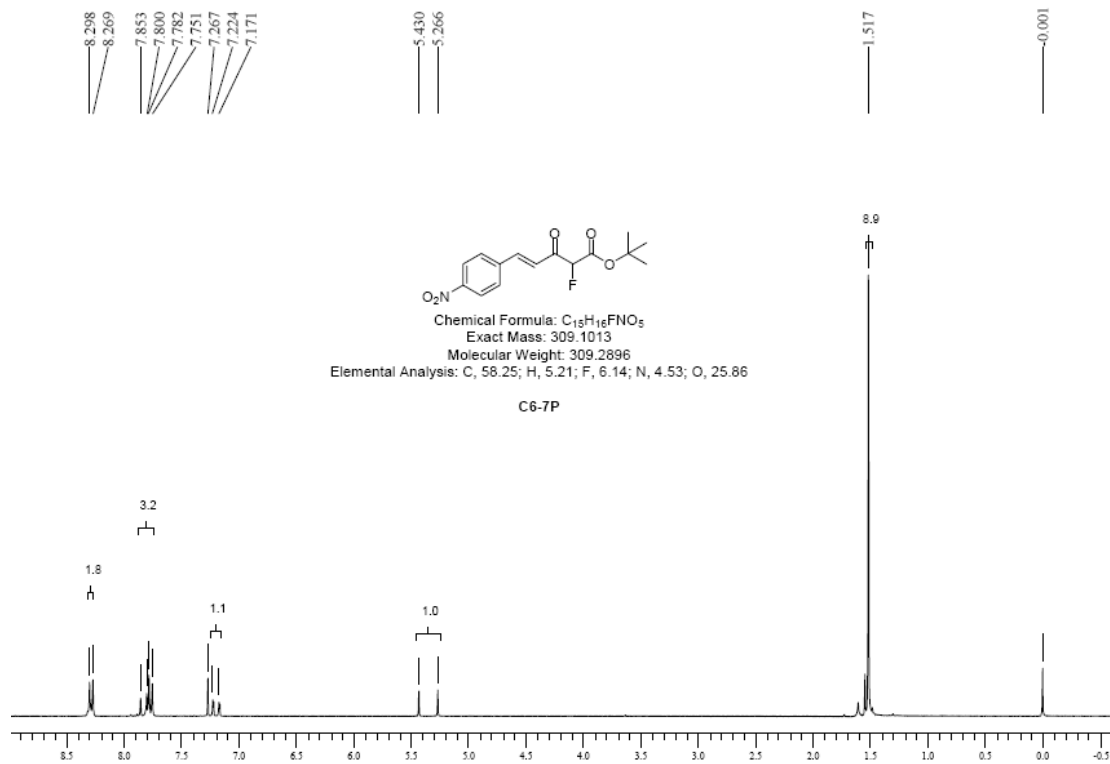


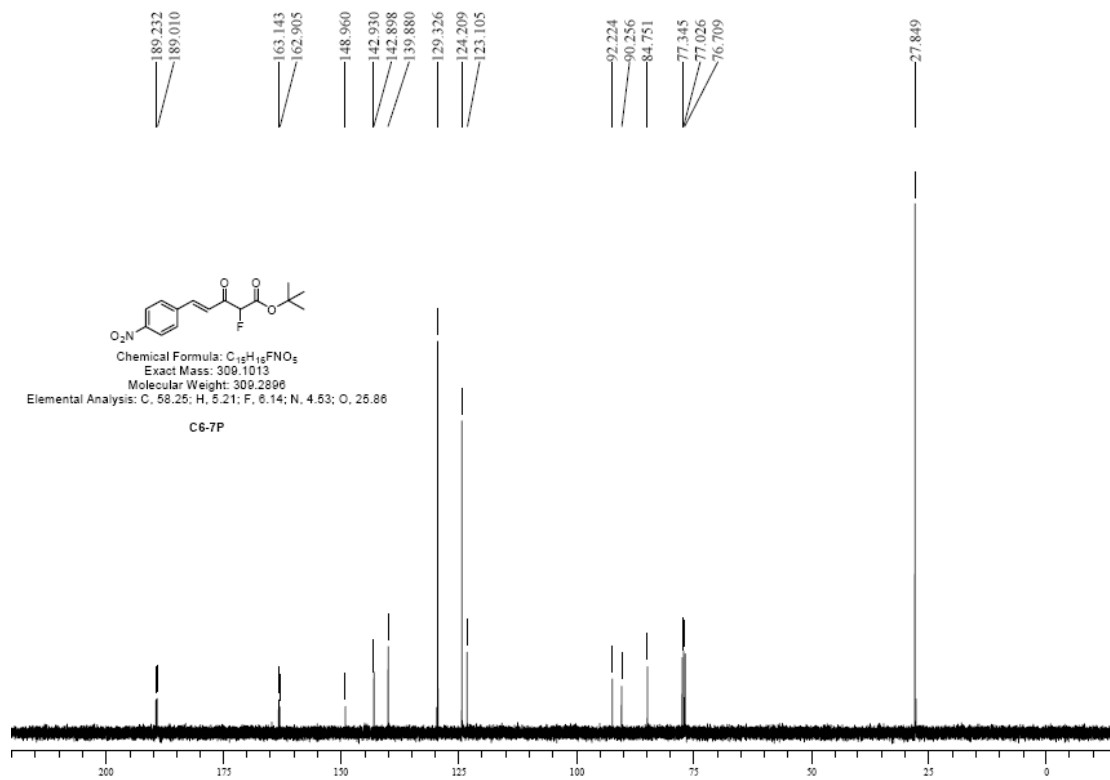
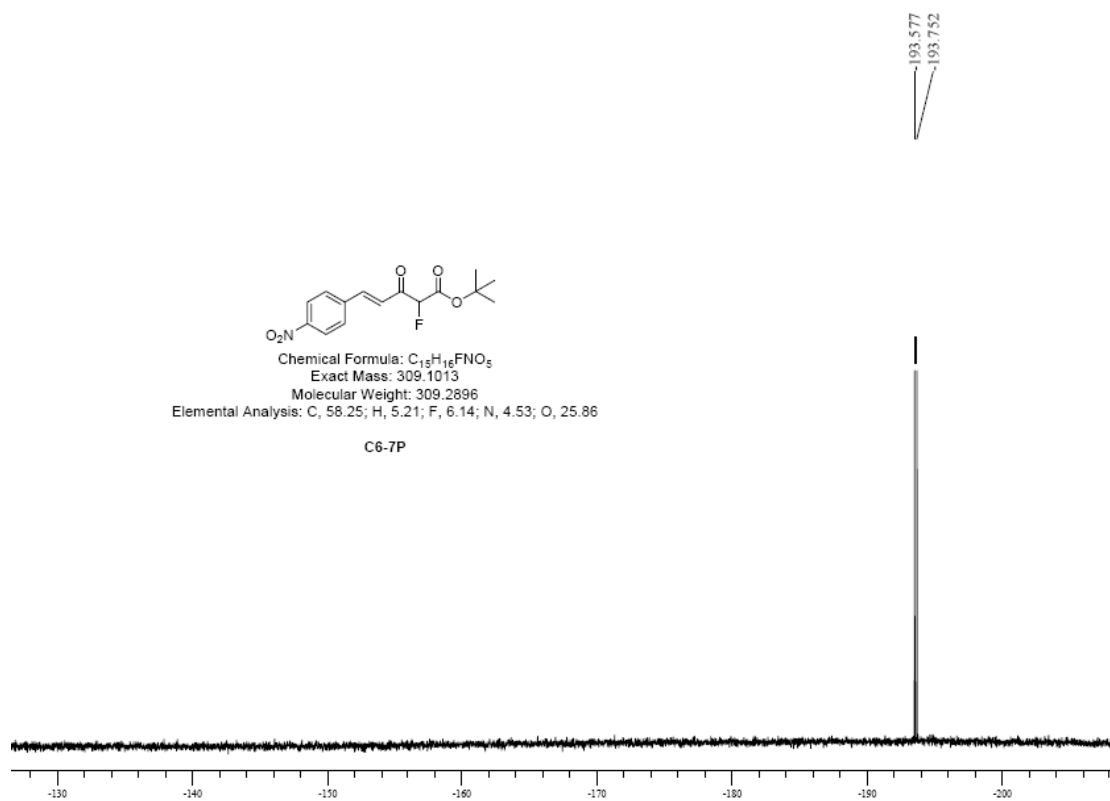
(E)-tert-Butyl 5-(2-bromophenyl)-2-fluoro-3-oxopent-4-enoate 3c



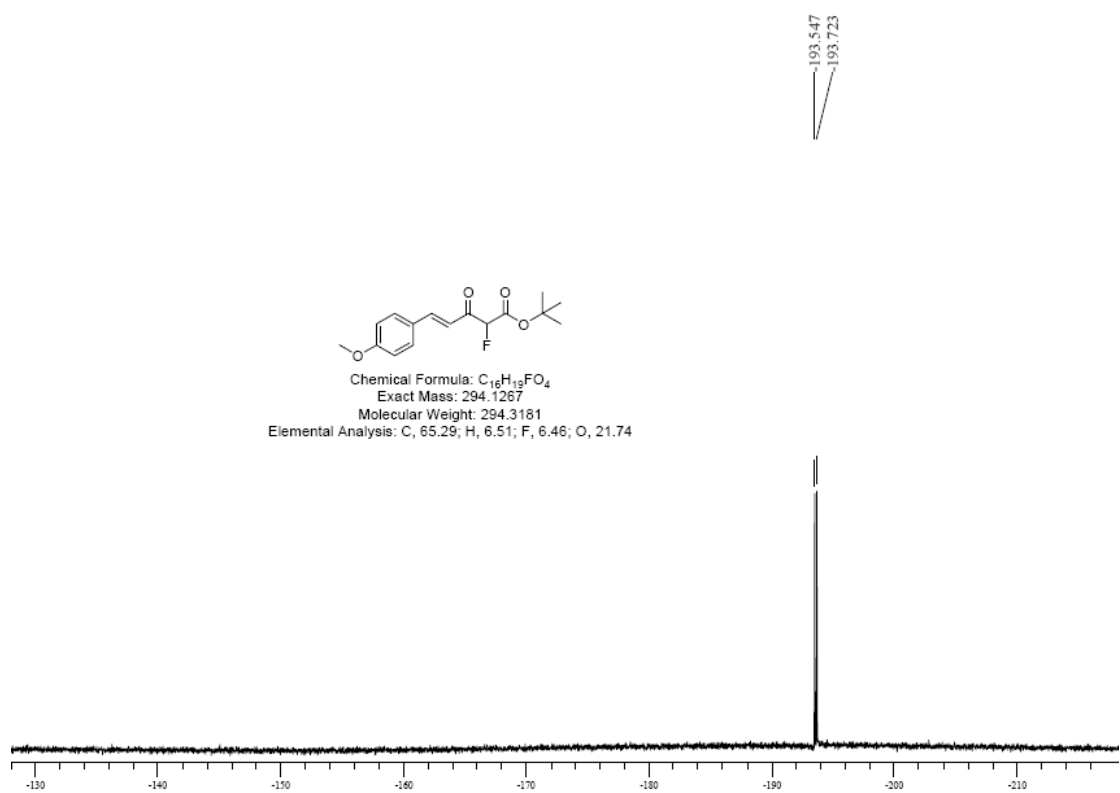
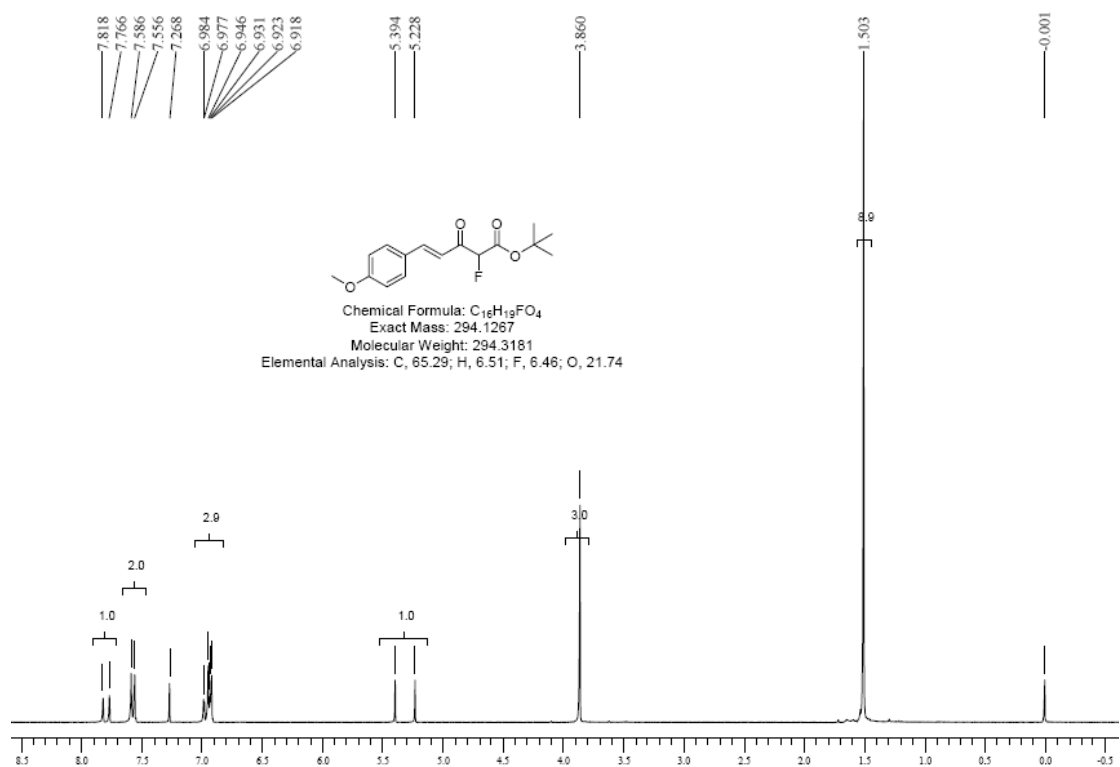


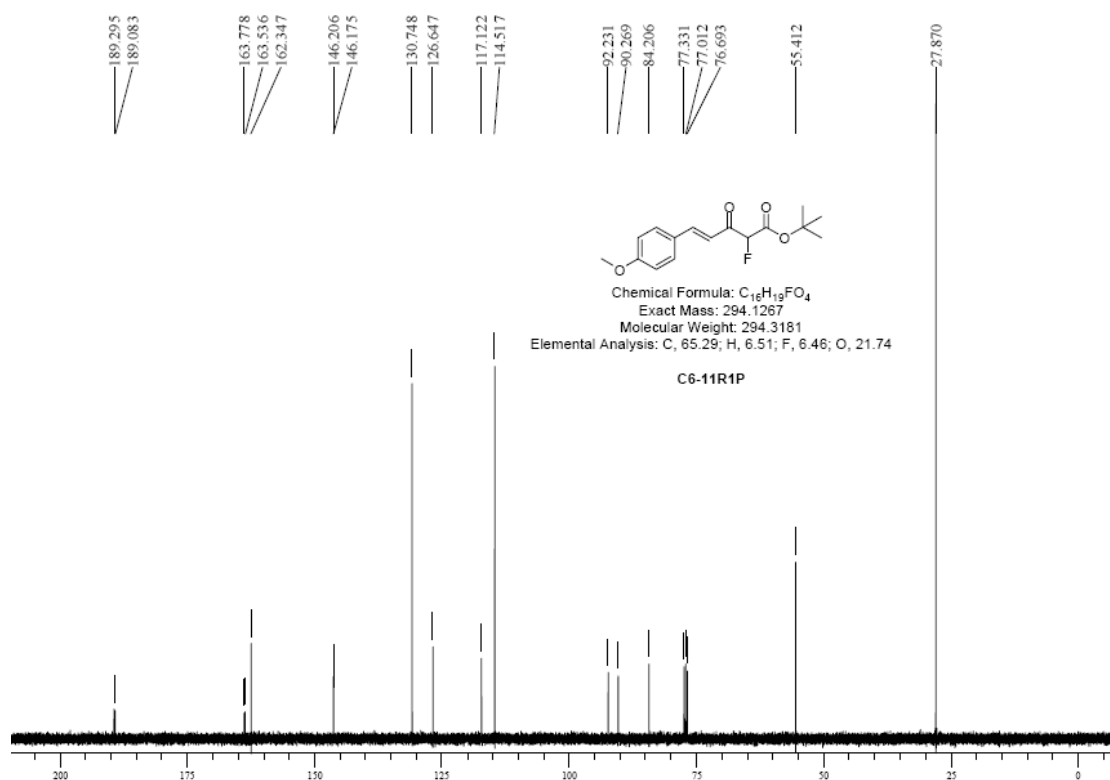
(E)-tert-Butyl 2-fluoro-5-(4-nitrophenyl)-3-oxopent-4-enoate 3d



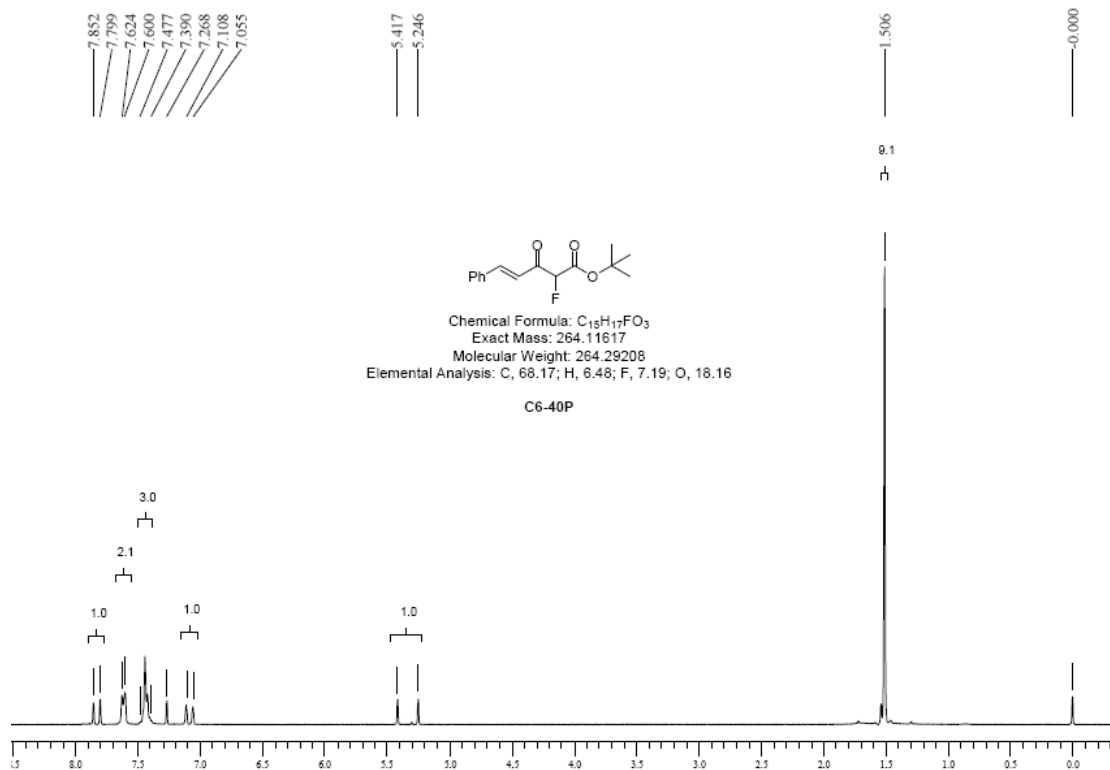


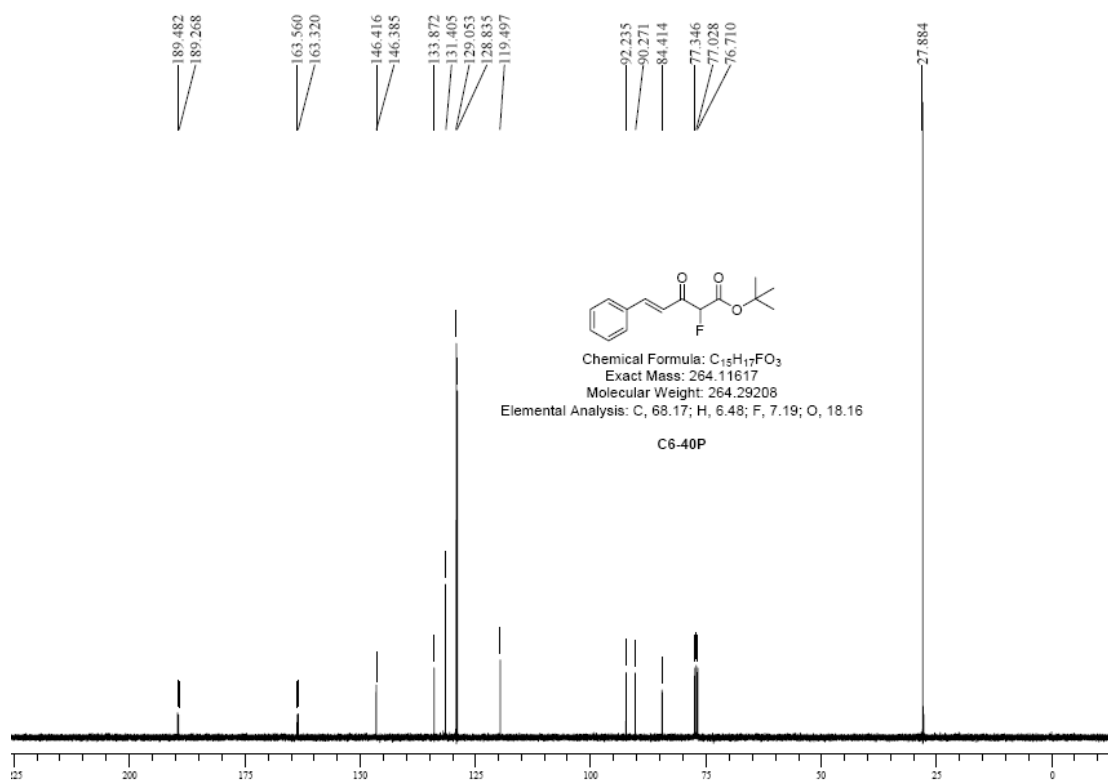
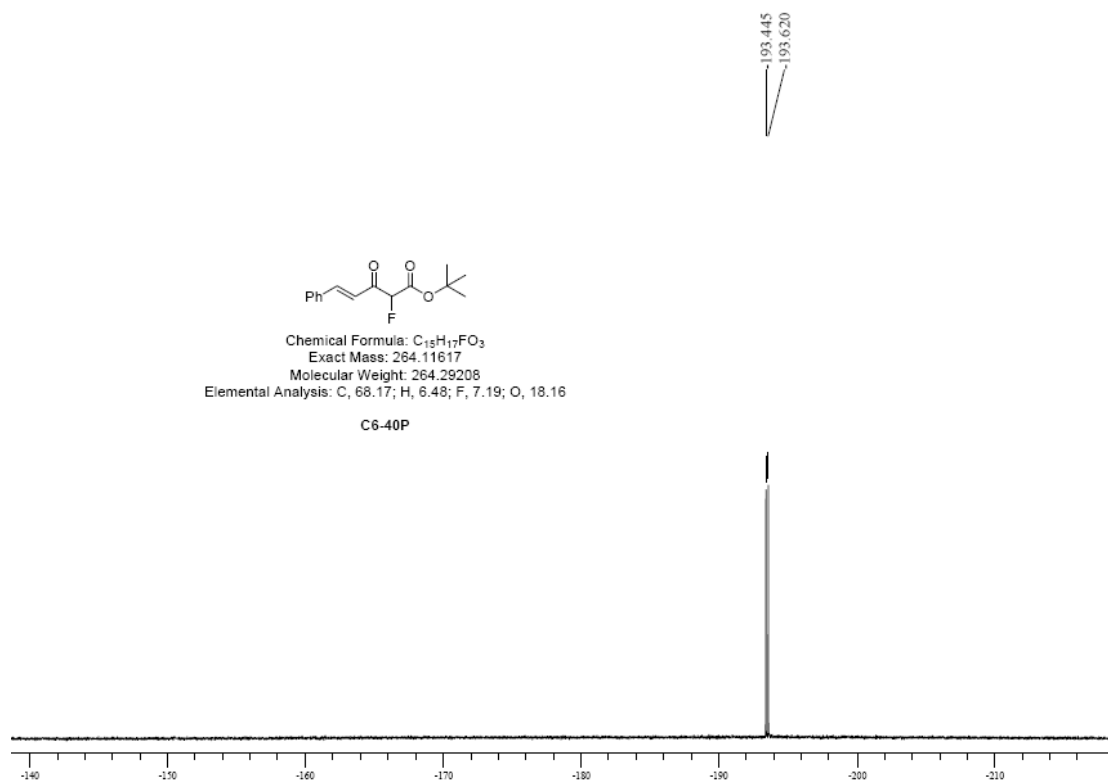
(E)-tert-Butyl 2-fluoro-5-(4-methoxyphenyl)-3-oxopent-4-enoate 3e



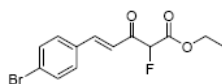


(E)-tert-Butyl 2-fluoro-3-oxo-5-phenylpent-4-enoate 3f



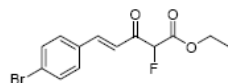
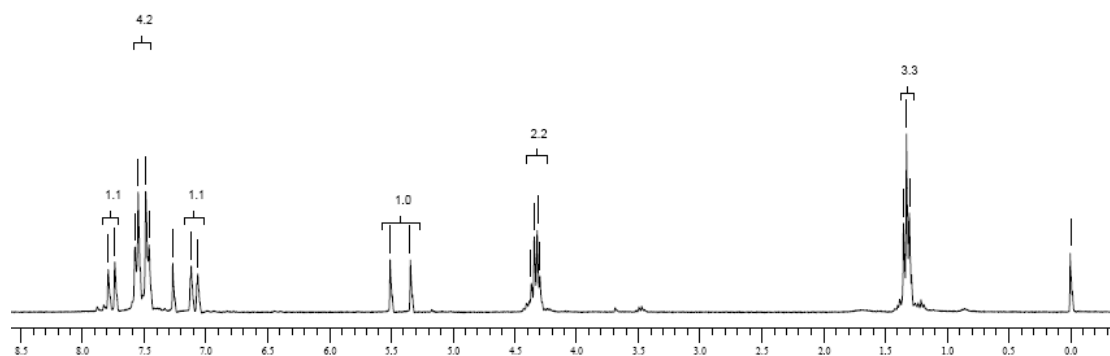


(E)-Ethyl-5-(4-bromophenyl)-2-fluoro-3-oxopent-4-enoate 3g



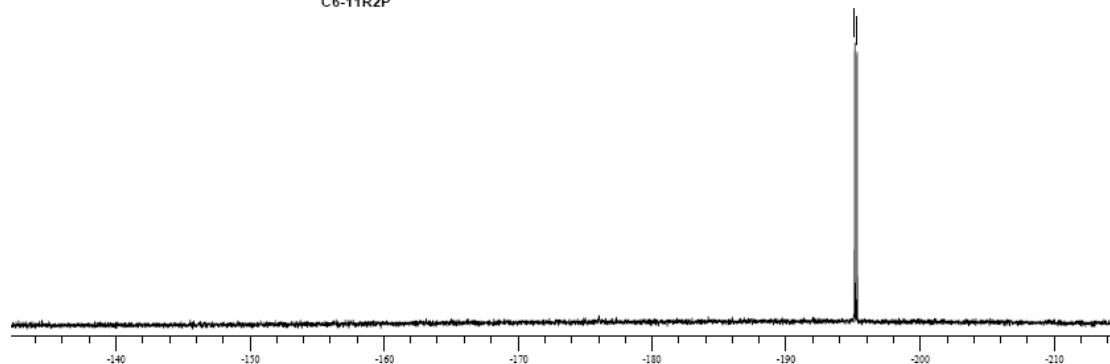
Chemical Formula: $C_{13}H_{12}BrFO_3$
 Exact Mass: 313.9954
 Molecular Weight: 315.135
 Elemental Analysis: C, 49.55; H, 3.84; Br, 25.36; F, 6.03; O, 15.23

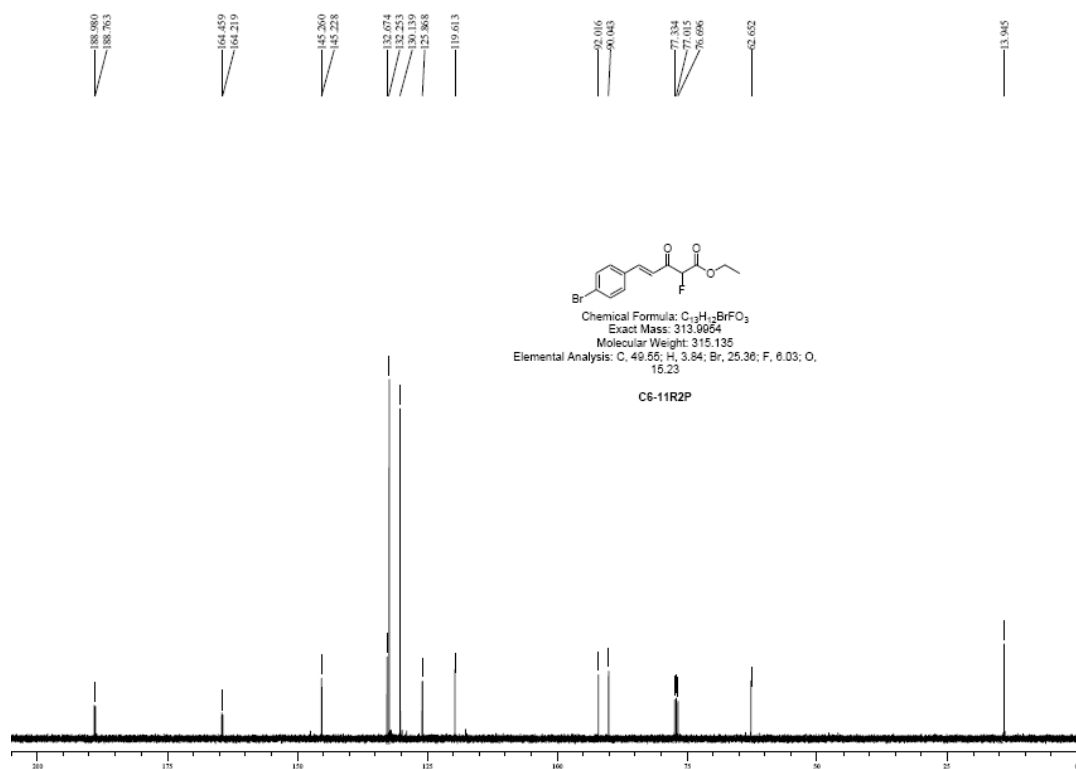
C6-11R2P



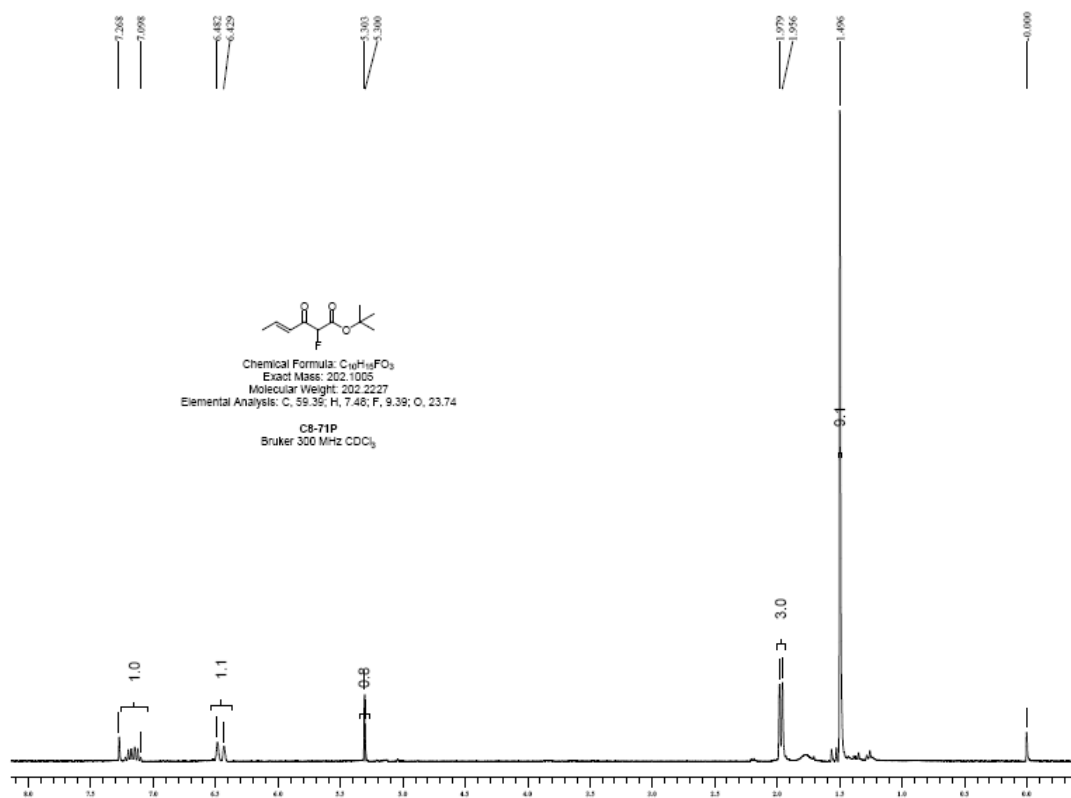
Chemical Formula: $C_{13}H_{12}BrFO_3$
 Exact Mass: 313.9954
 Molecular Weight: 315.135
 Elemental Analysis: C, 49.55; H, 3.84; Br, 25.36; F, 6.03; O, 15.23

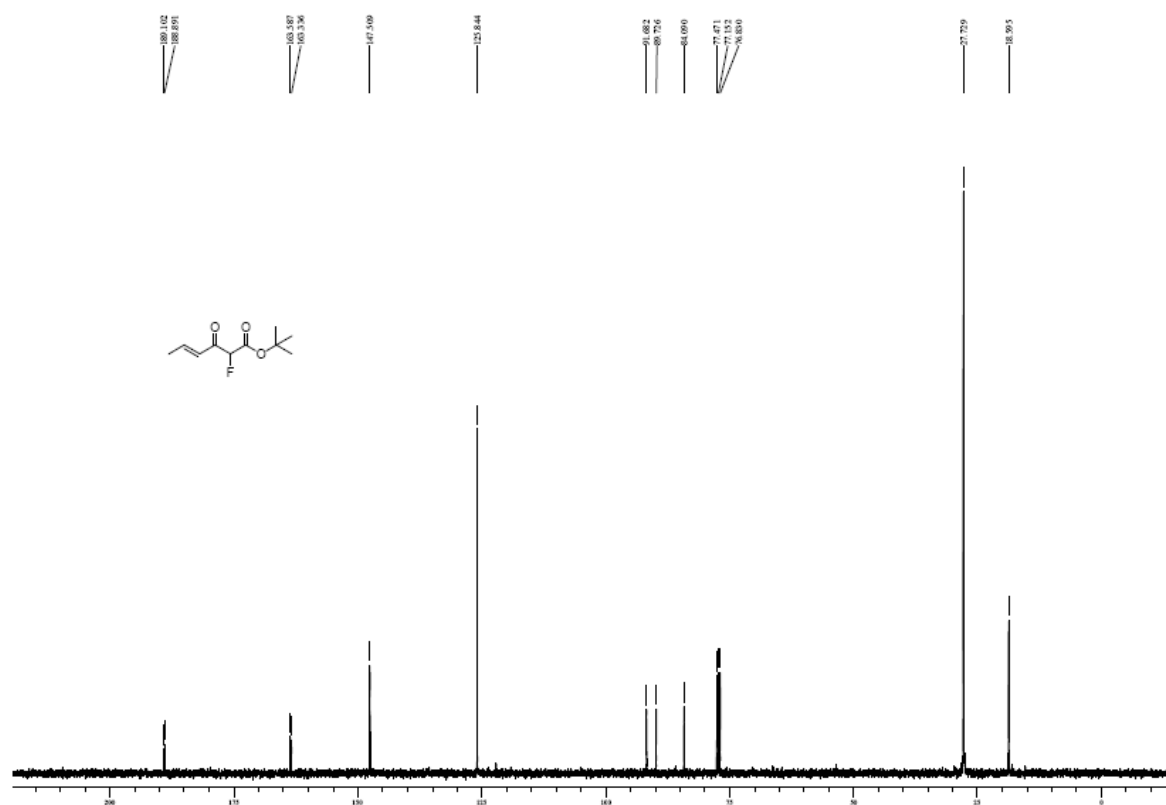
C6-11R2P



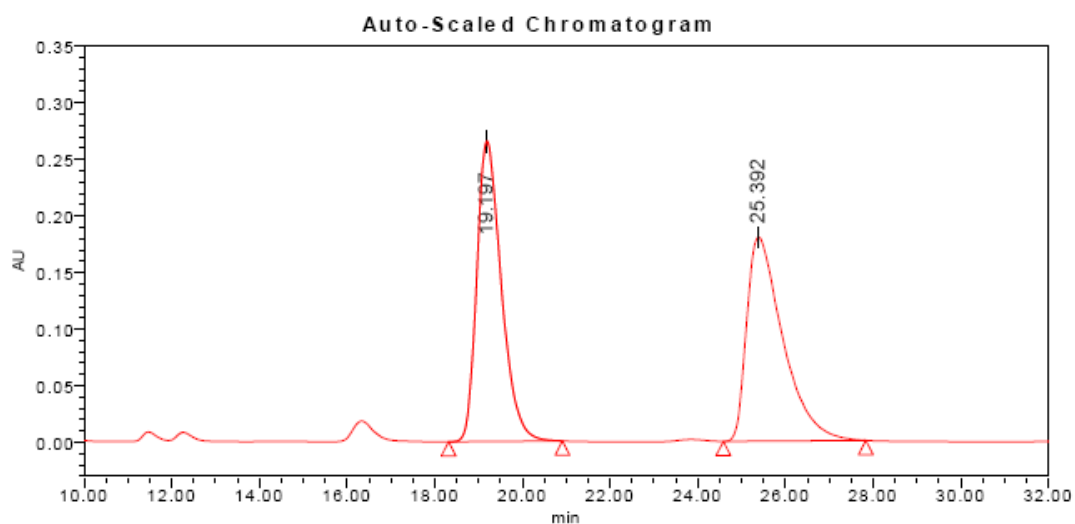


(E)-tert-butyl 2-fluoro-3-oxohex-4-enoate 3h

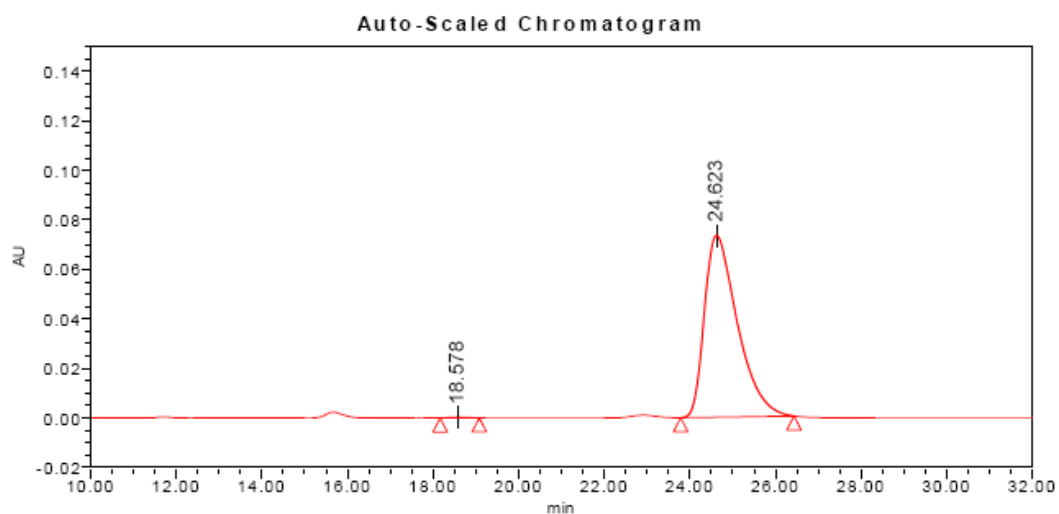




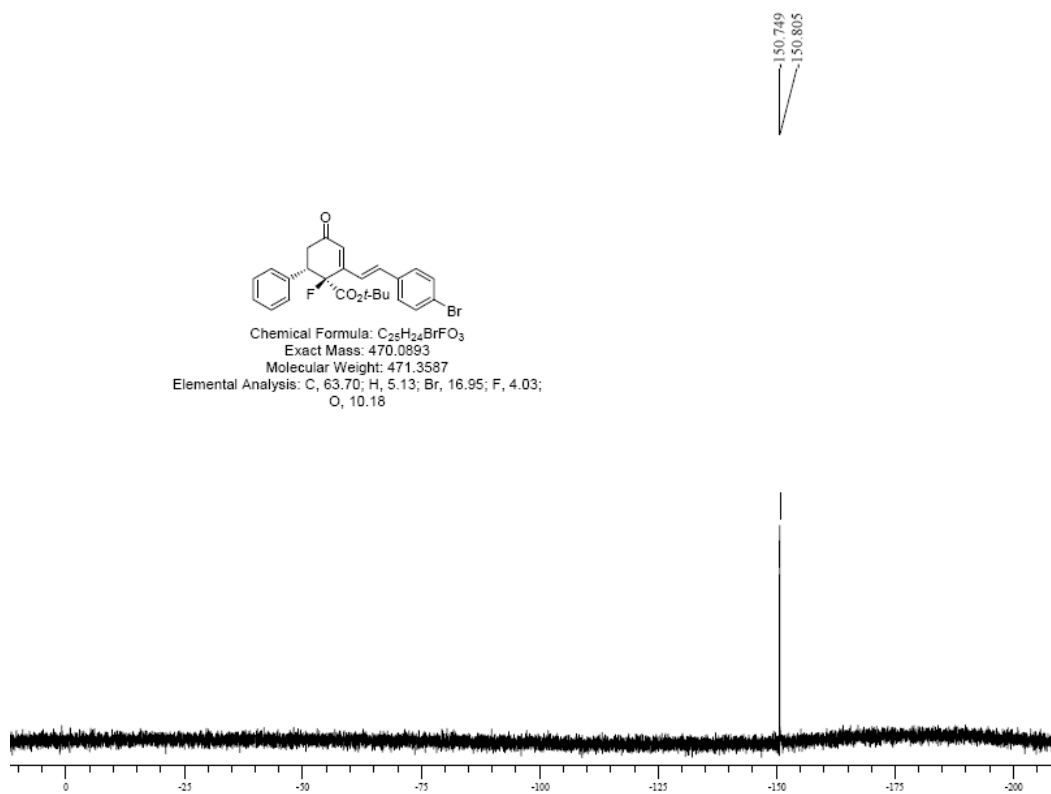
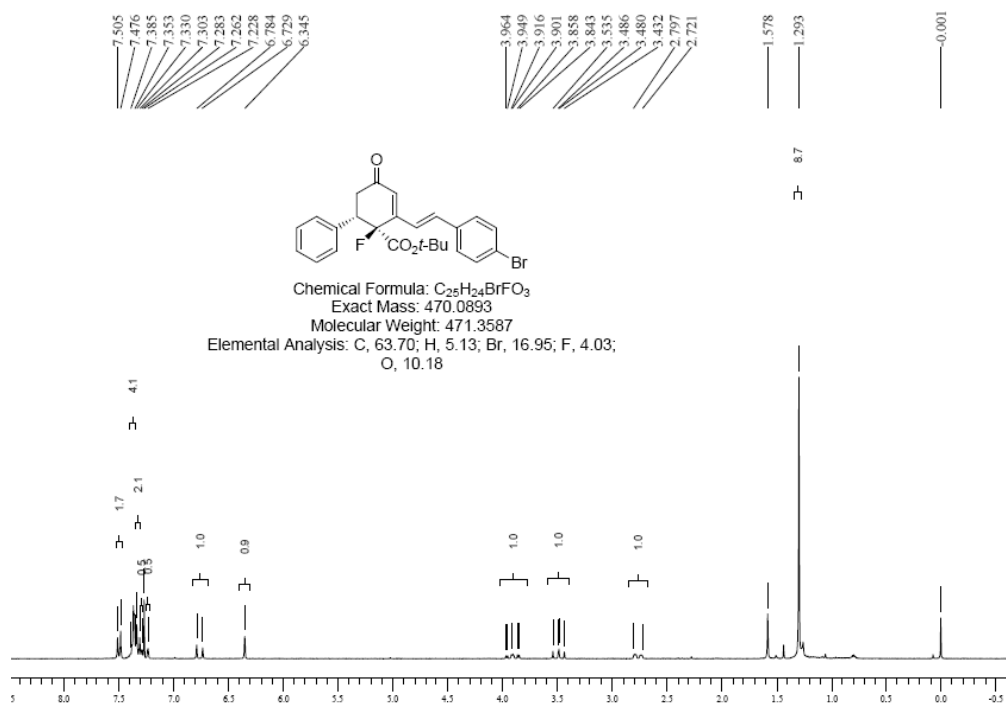
(1*S*,6*S*,*E*)-*tert*-butyl-2-(4-bromostyryl)-1-fluoro-4-oxo-6-phenylcyclohex-2-enecarboxylate 5a

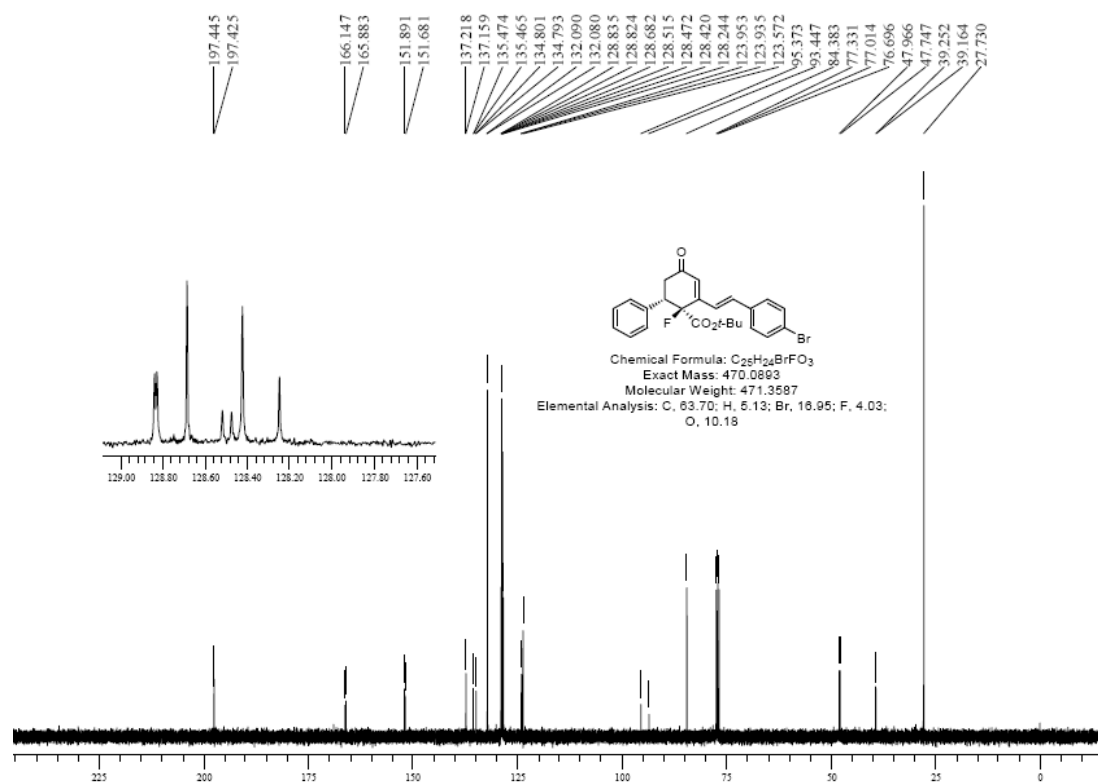


Peak Results					
	Name	RT	Area	Height	% Height
1		19.197	10315197	265303	59.55
2		25.392	10319661	180198	40.45

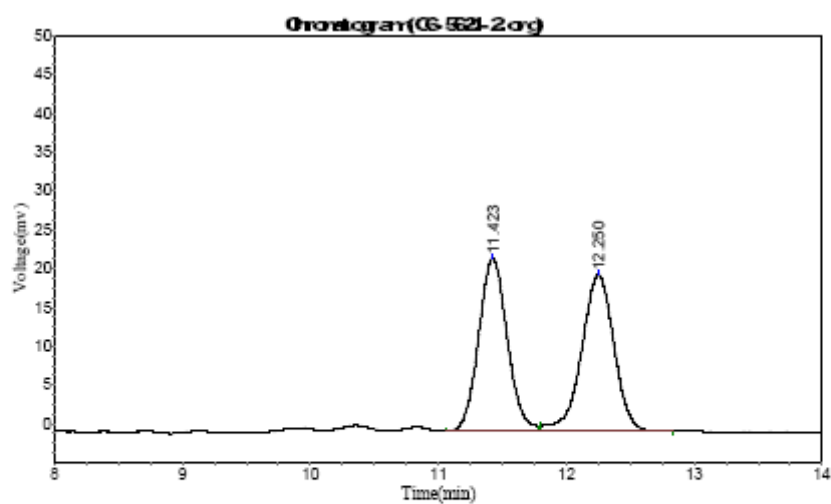


Peak Results					
	Name	RT	Area	Height	% Height
1		18.578	8599	290	0.39
2		24.623	3932290	73435	99.61



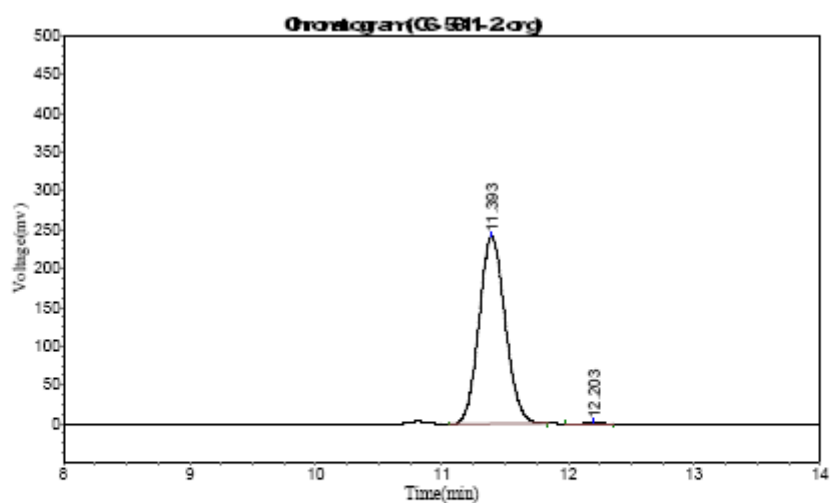


(1*S*,6*S*,*E*)-tert-butyl-2-(3-bromostyryl)-1-fluoro-4-oxo-6-phenylcyclohex-2-enecarboxylate 5b

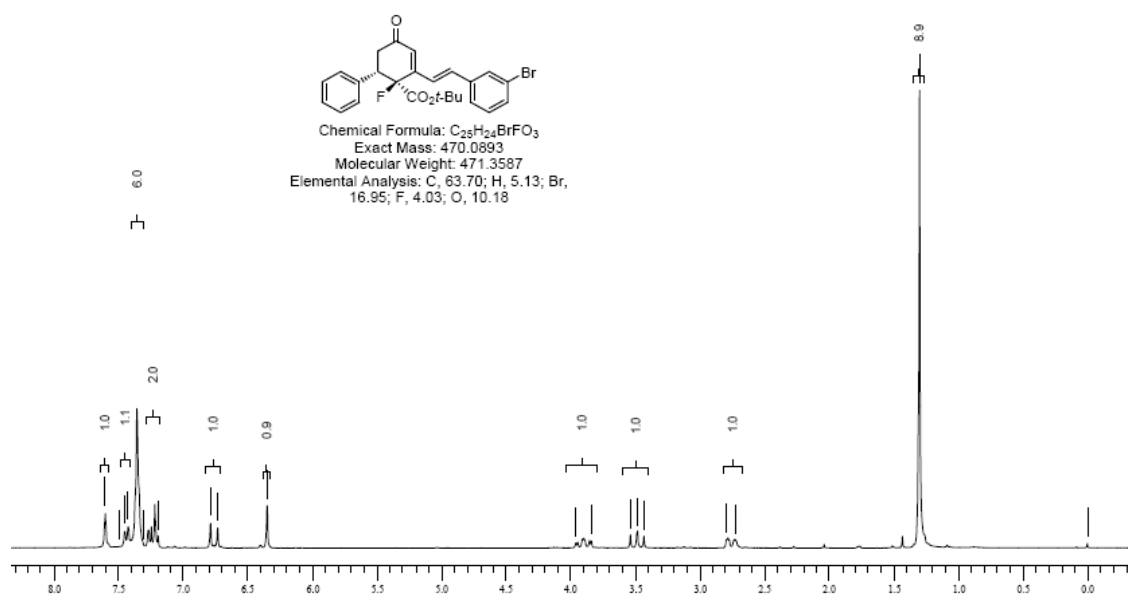


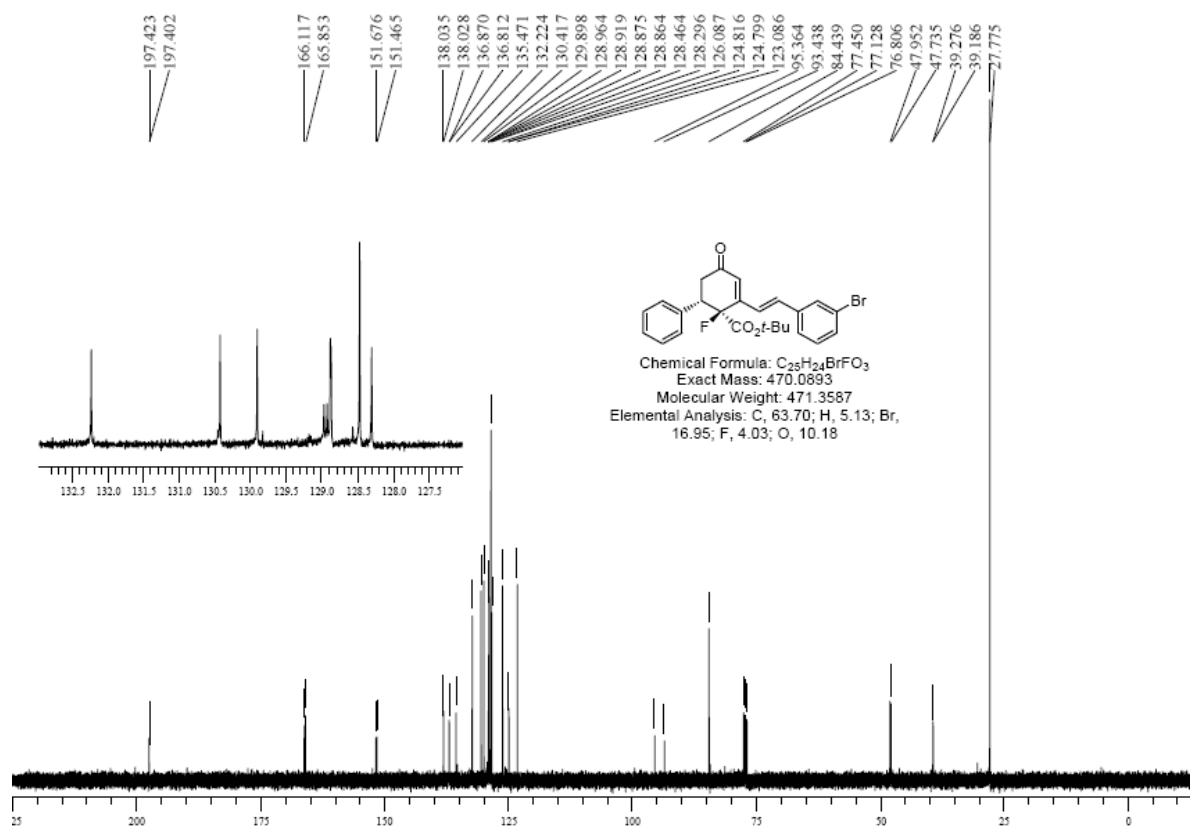
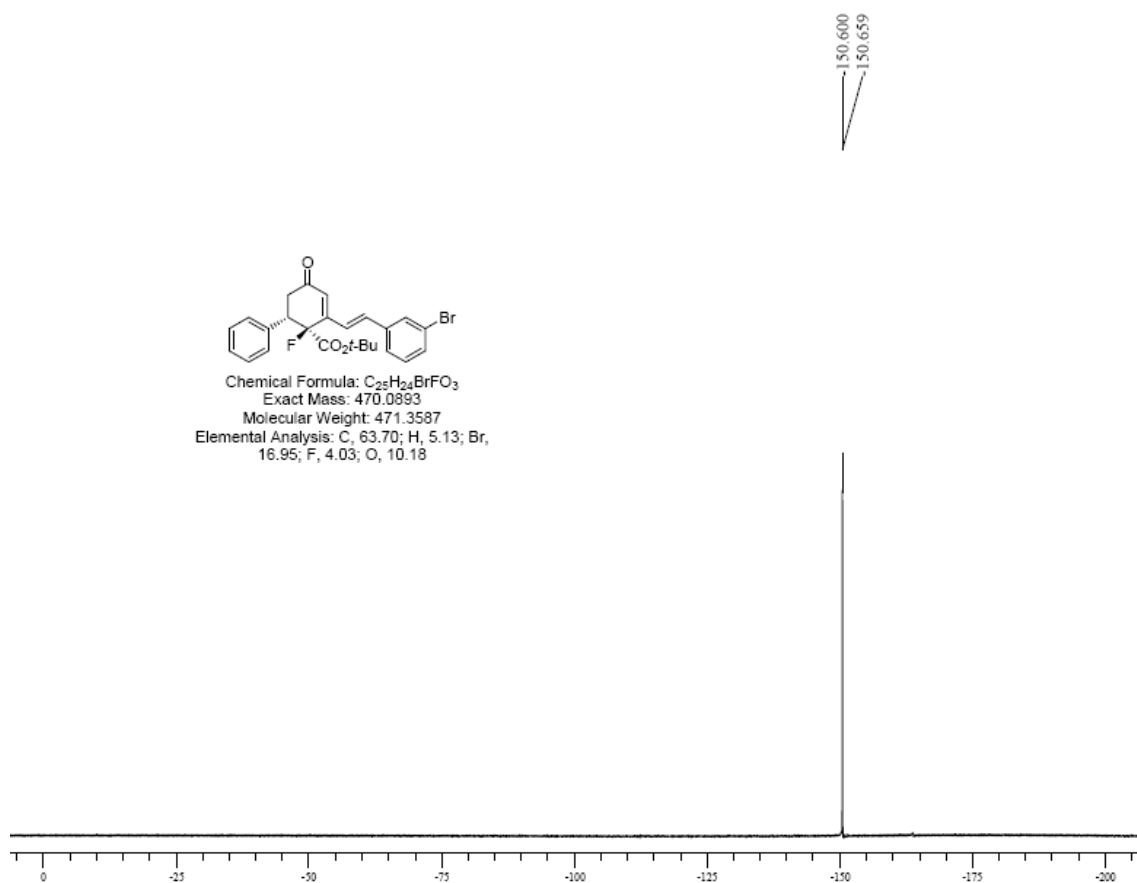
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.423	22320.941	347188.844	49.3721
2		12.250	20155.375	356020.438	50.6280
Total			42476.316	703209.281	100.0000

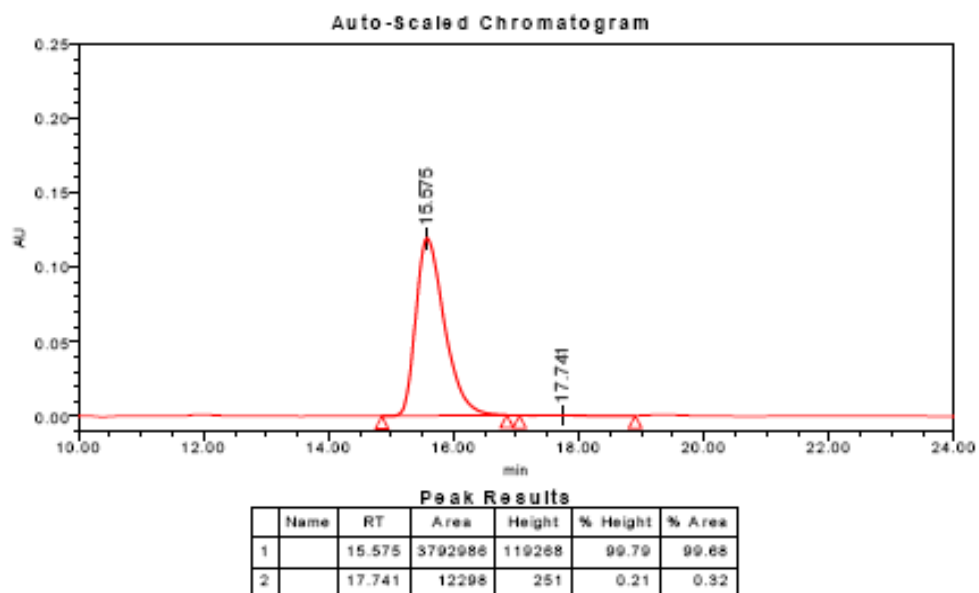
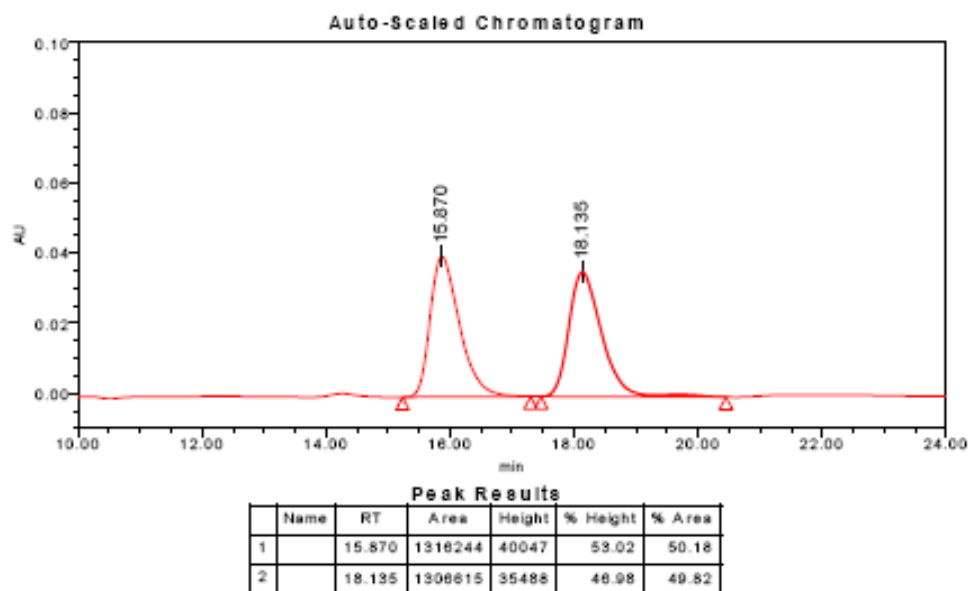


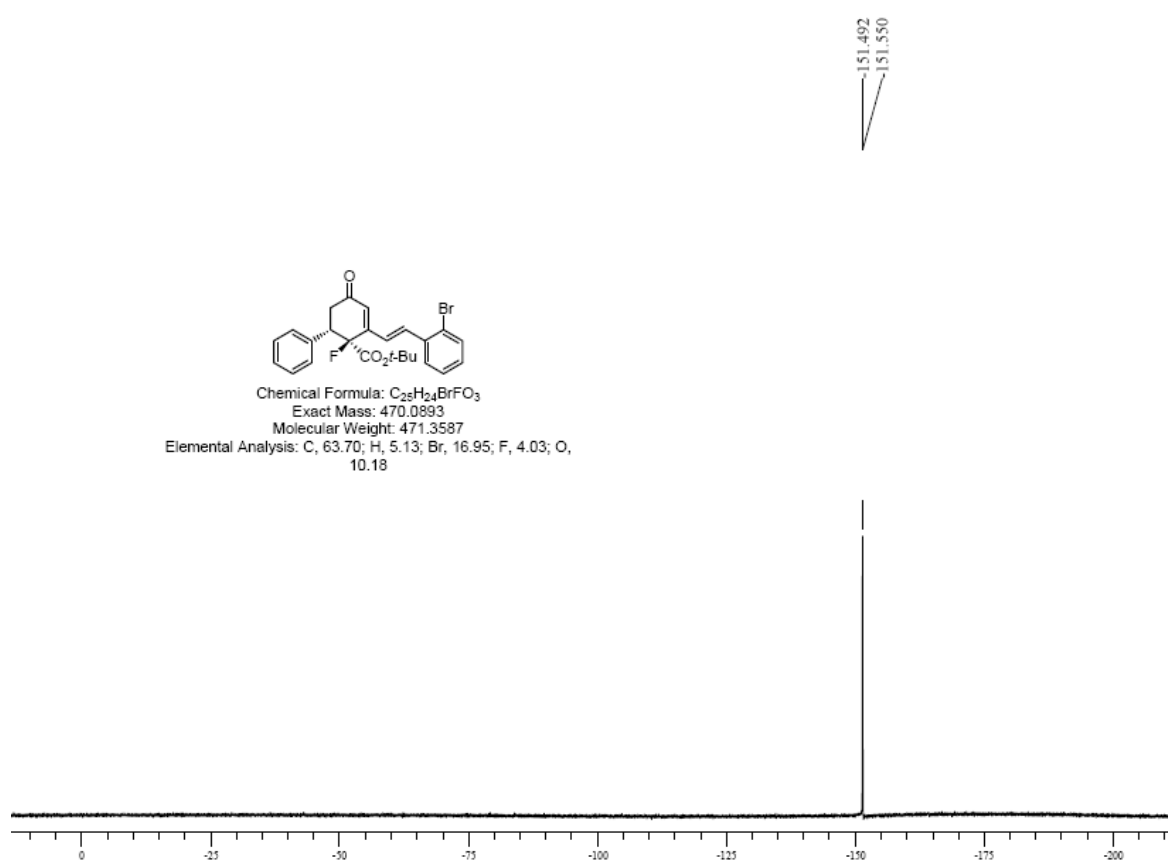
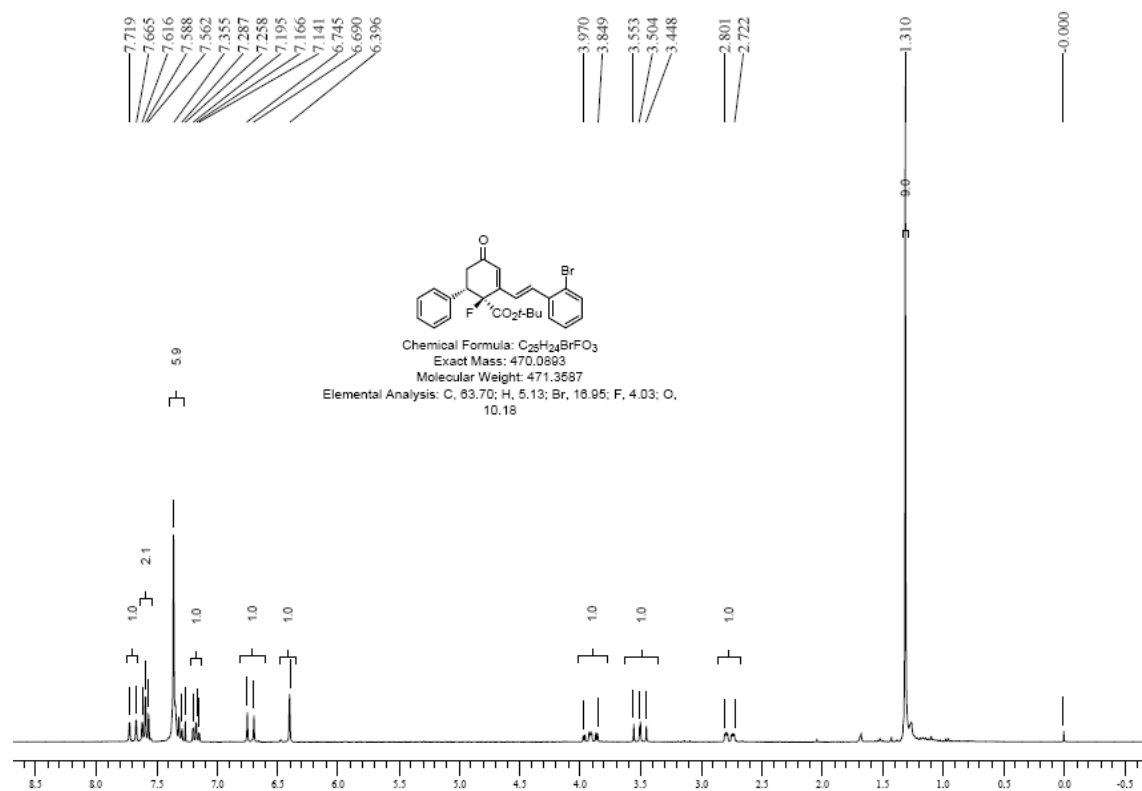
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.393	241467.953	3477432.250	99.6799
2		12.203	1115.101	11165.351	0.3201
Total			242583.054	3488597.601	100.0000

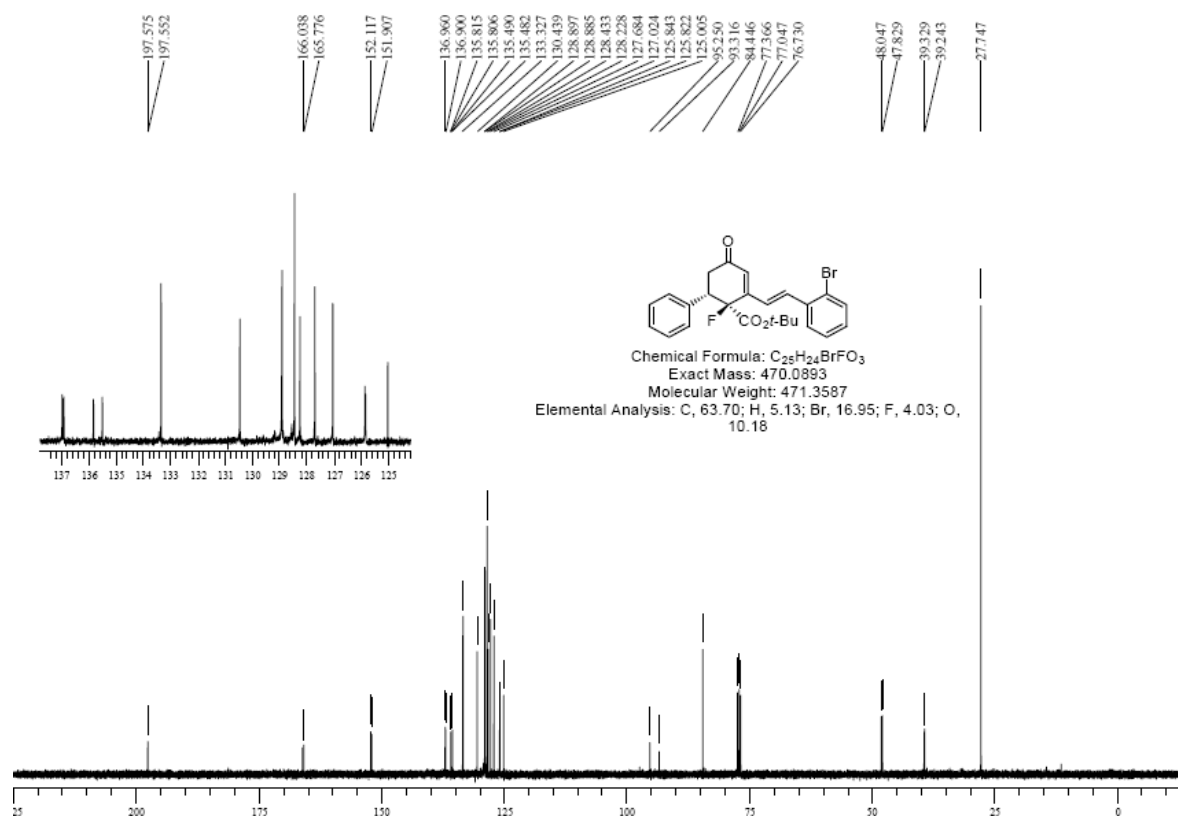




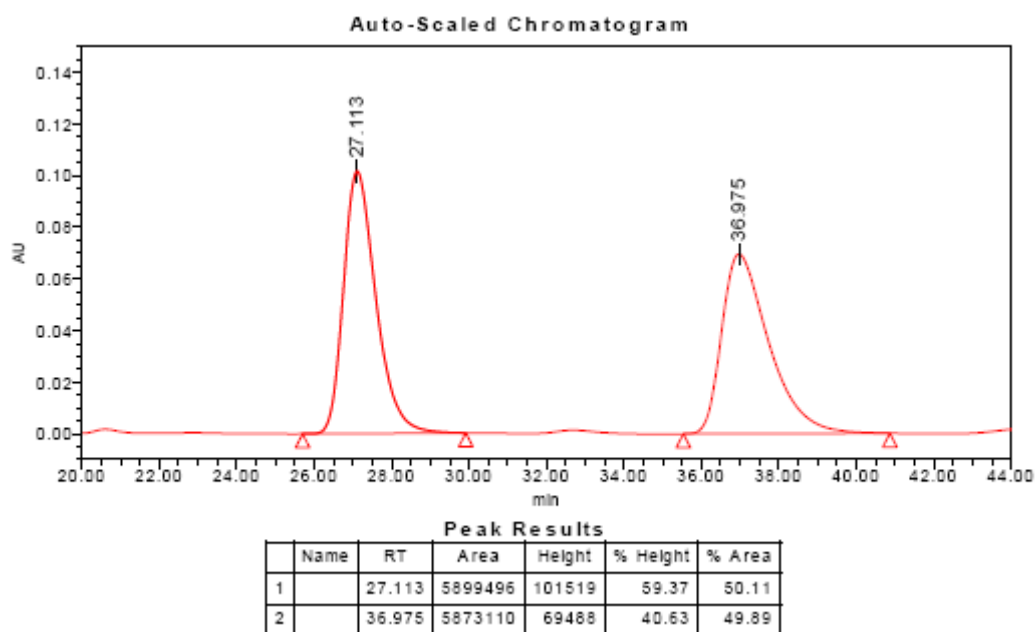
(1S,6S,E)-*tert*-butyl-2-(2-bromostyryl)-1-fluoro-4-oxo-6-phenylcyclohex-2-enecarboxylate 5c

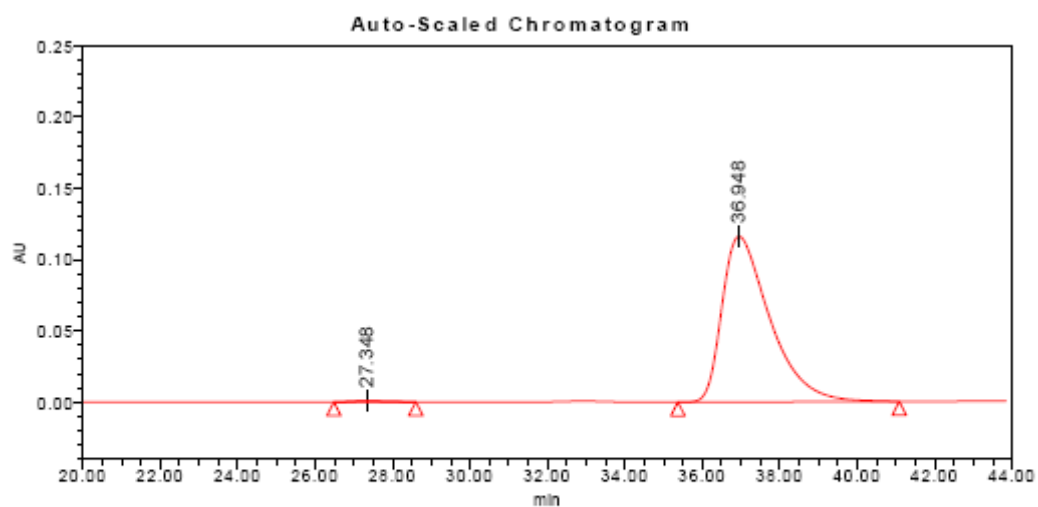






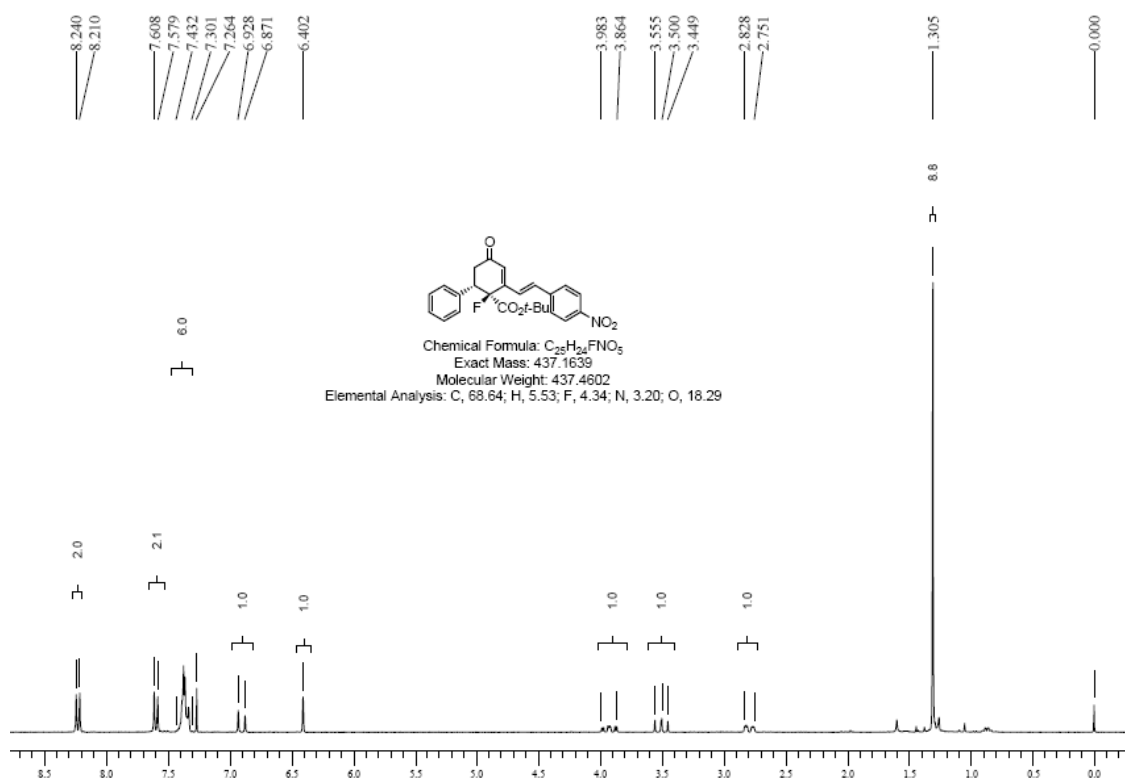
(1S,6S,E)-tert-butyl-1-fluoro-2-(4-nitrostyryl)-4-oxo-6-phenylcyclohex-2-enecarboxylate 5d

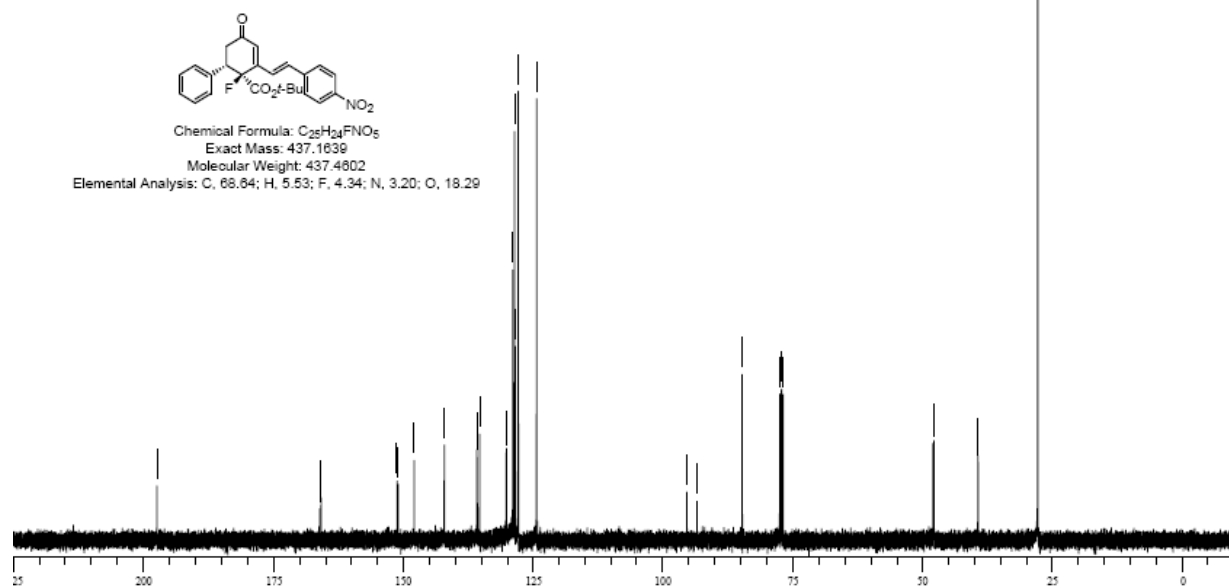
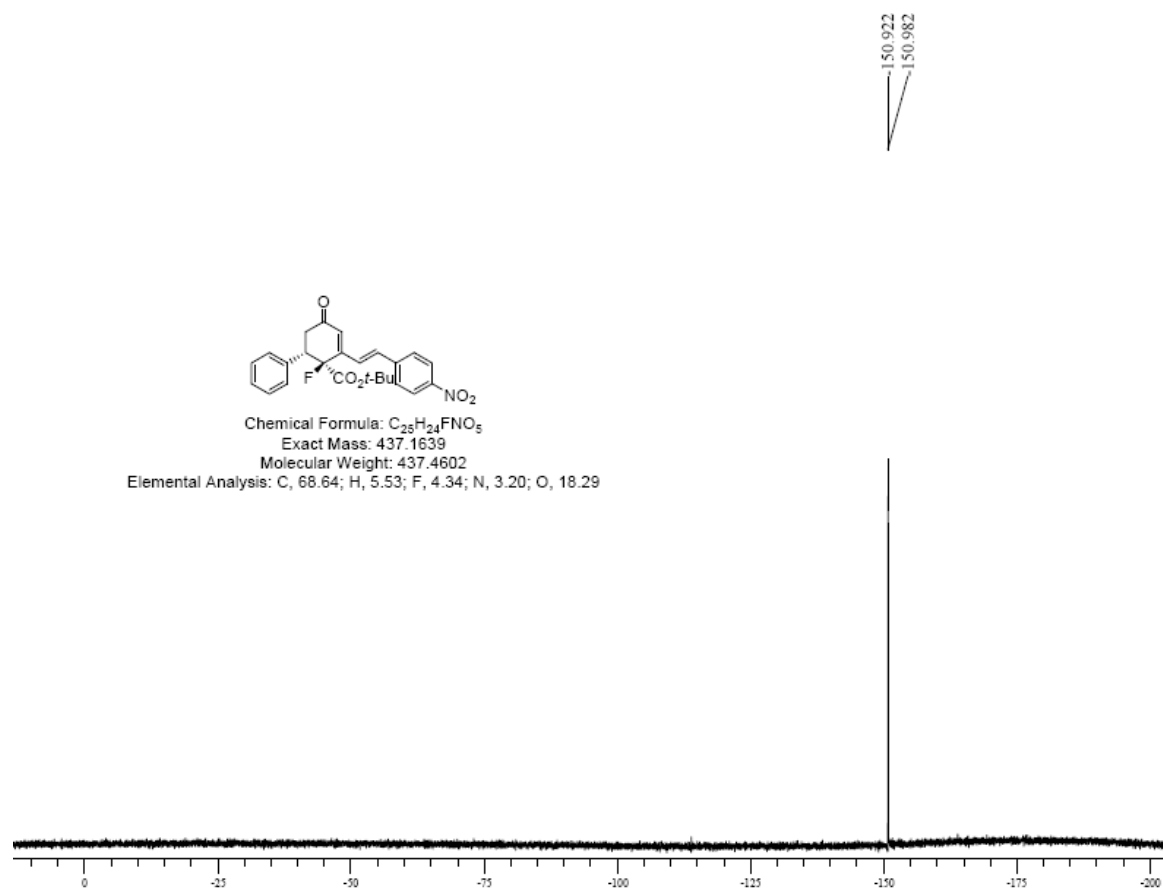




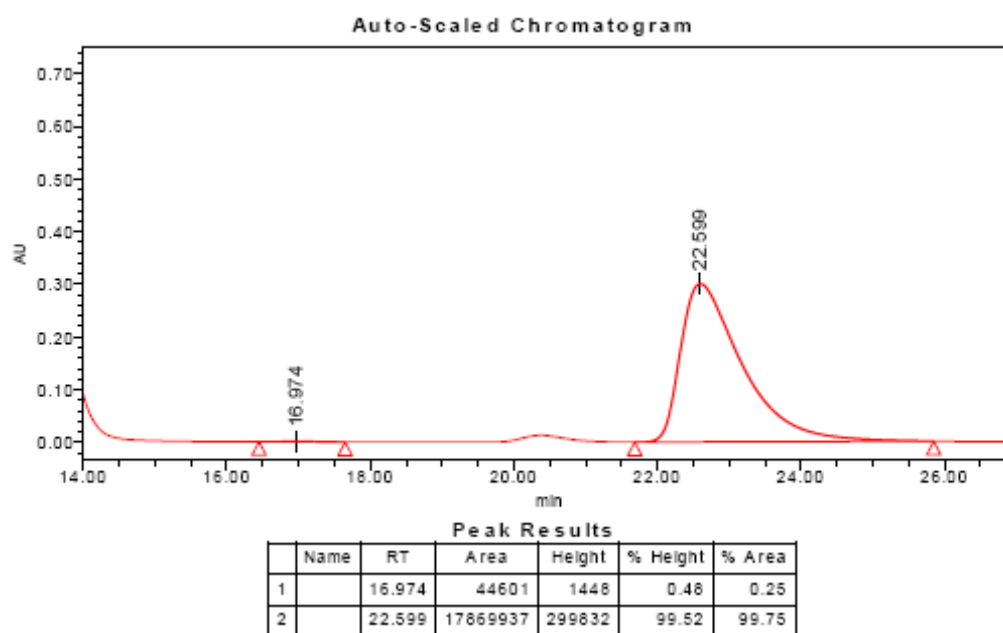
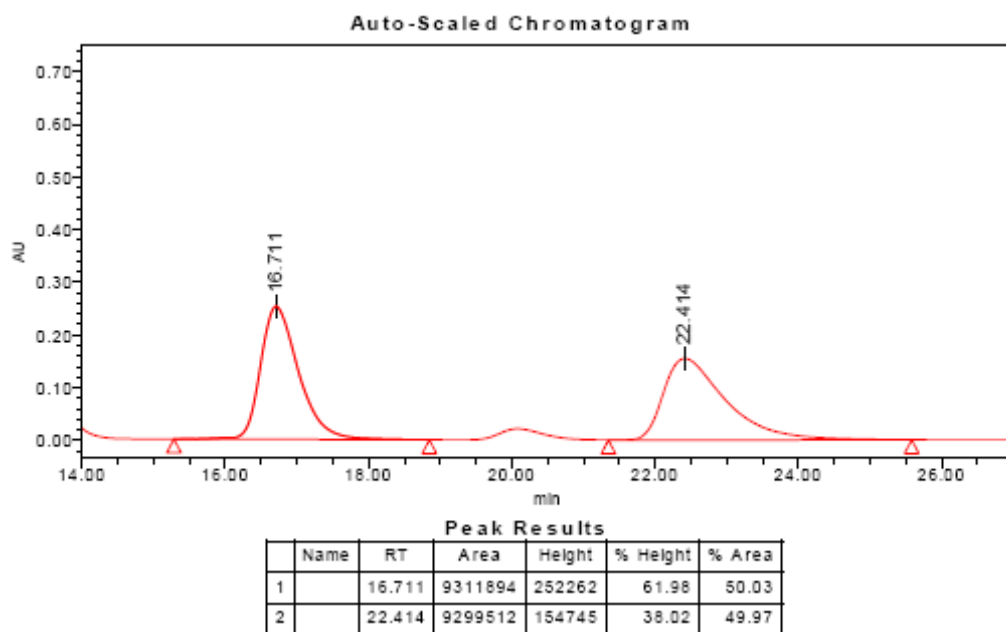
Peak Results

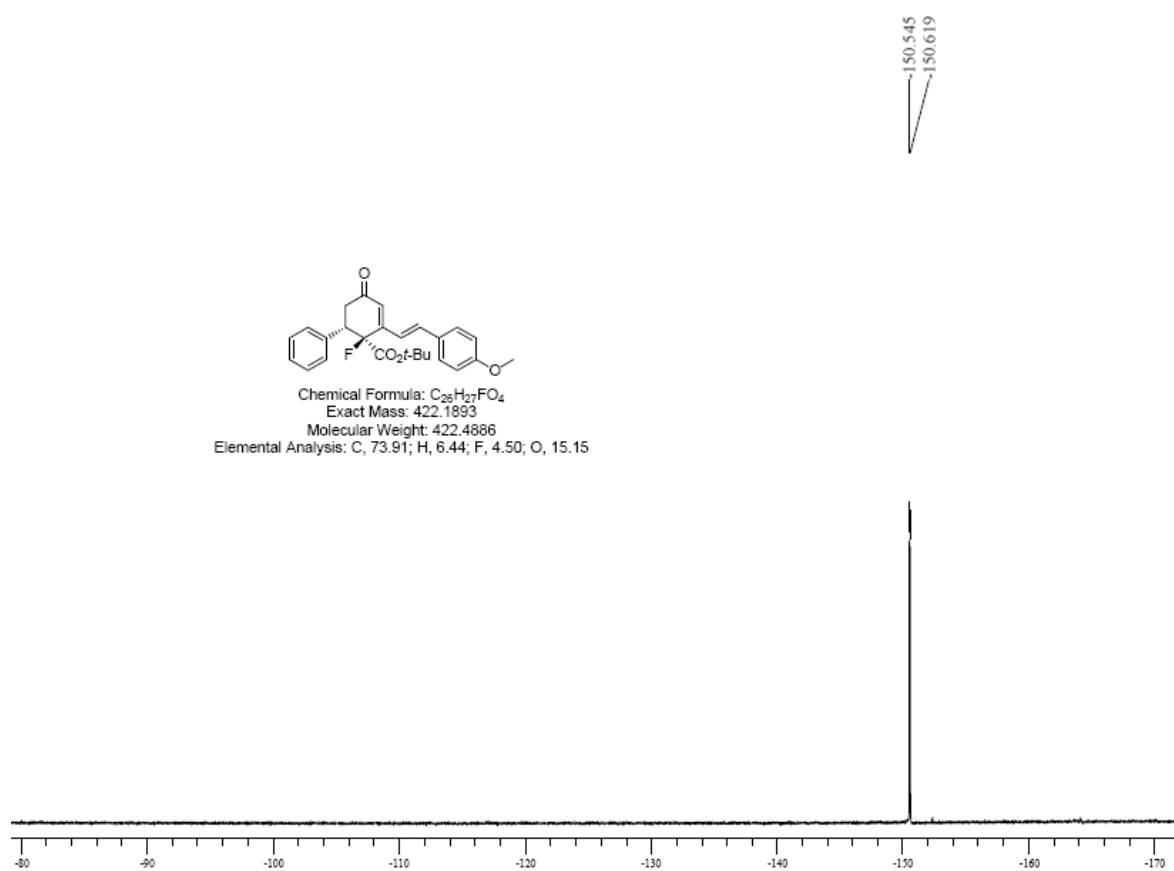
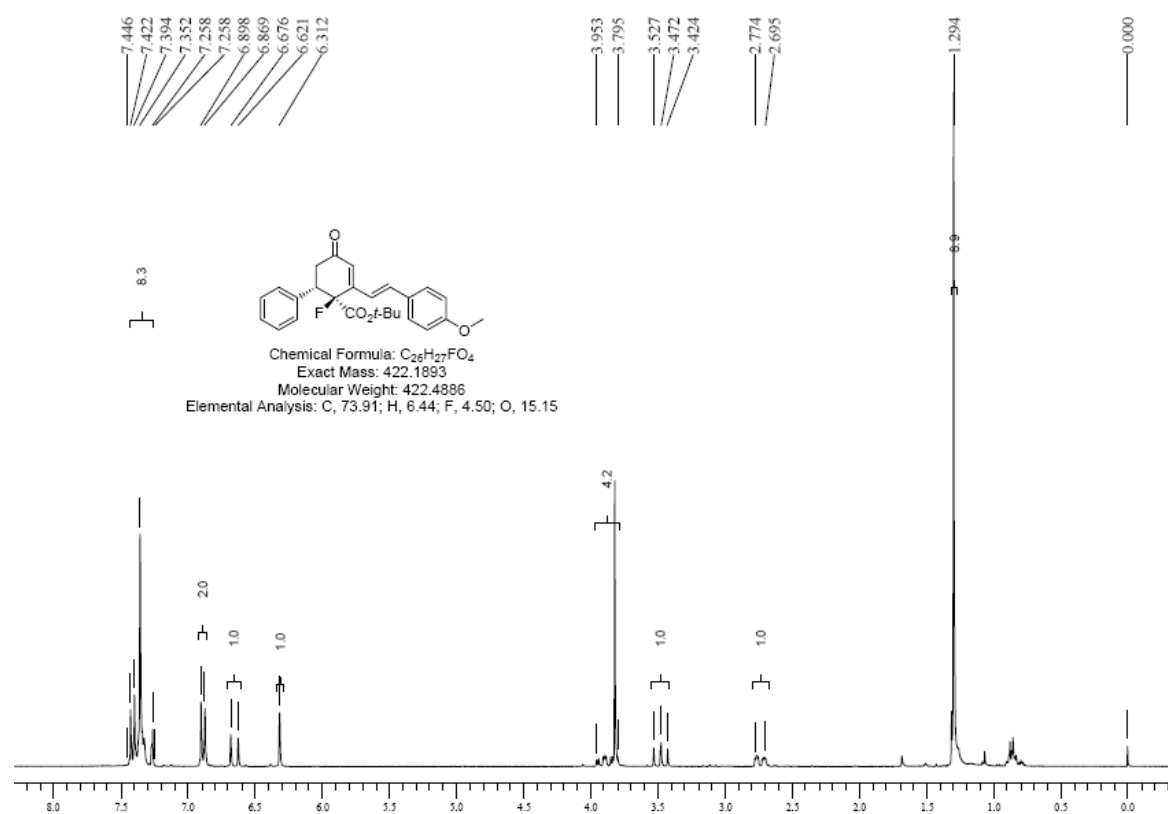
	Name	RT	Area	Height	% Height	% Area
1		27.348	39370	728	0.62	0.39
2		36.948	9976579	116158	99.38	99.61

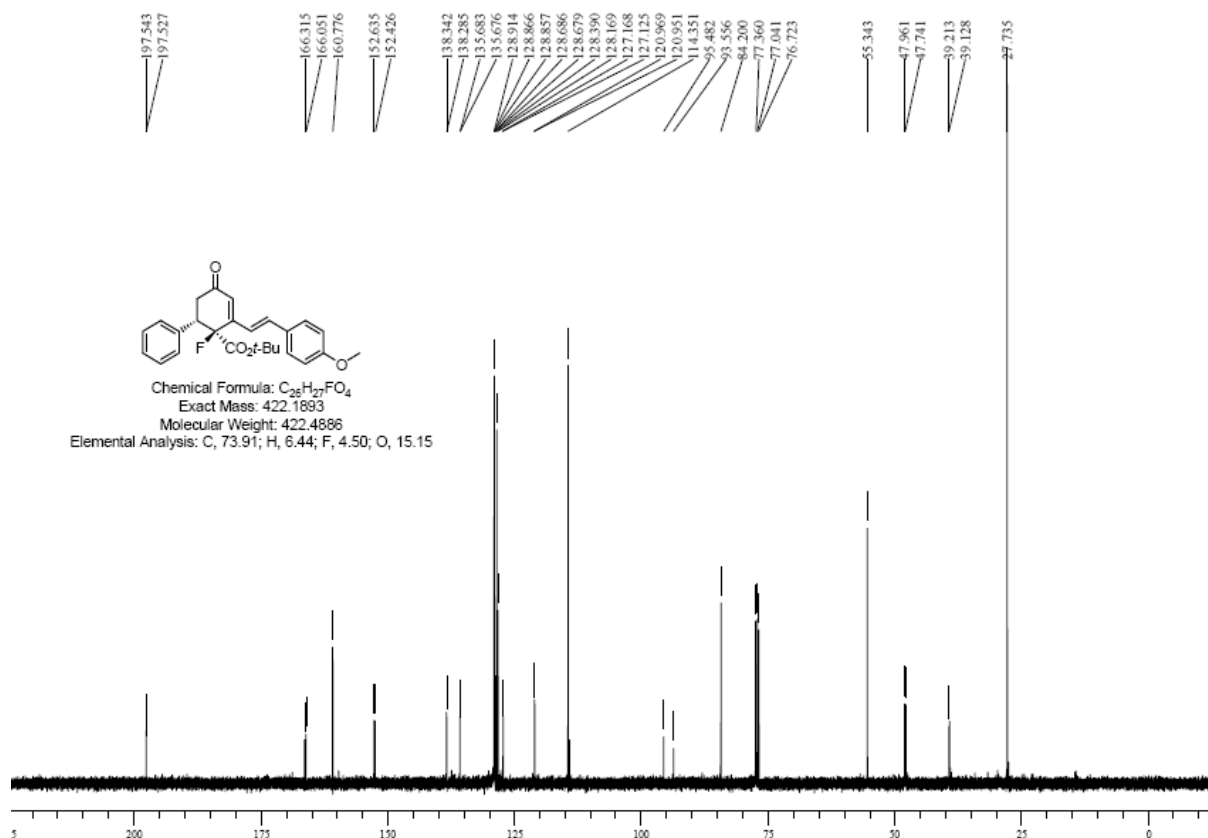




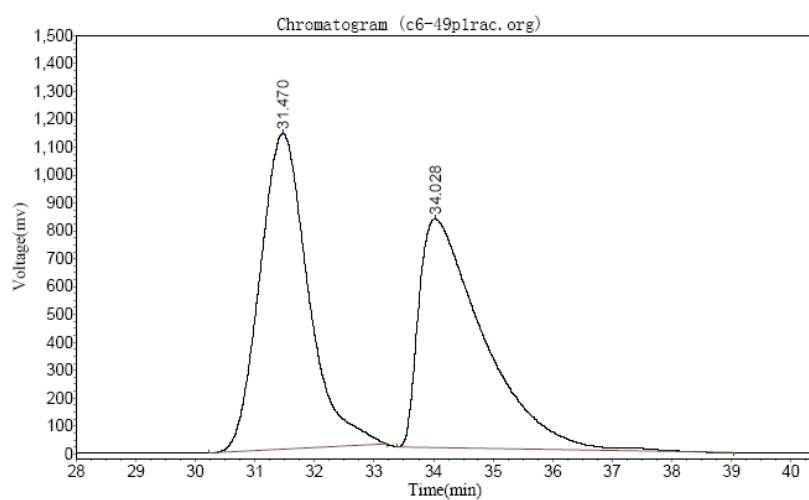
(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-2-(4-methoxystyryl)-4-oxo-6-phenylcyclohex-2-enecarboxylate 5e





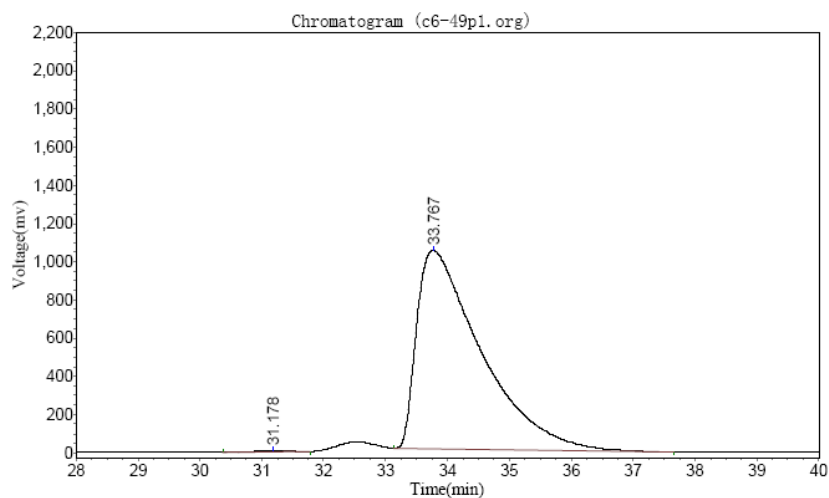


(1*S*,6*S*,*E*)-*tert*-butyl-1-fluoro-4-oxo-6-phenyl-2-styrylcyclohex-2-enecarboxylate 5f



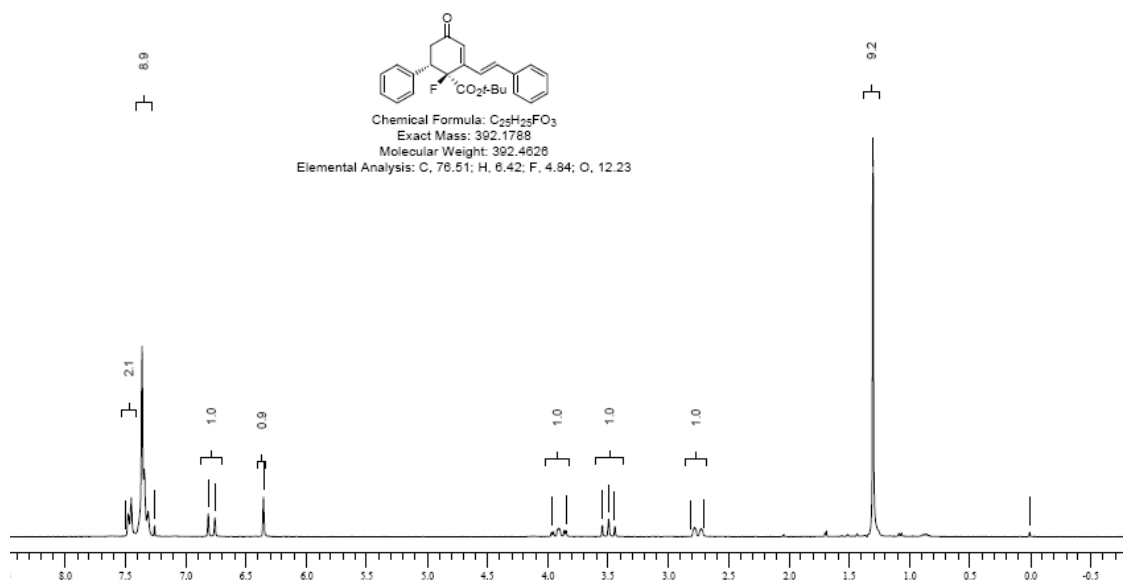
Results

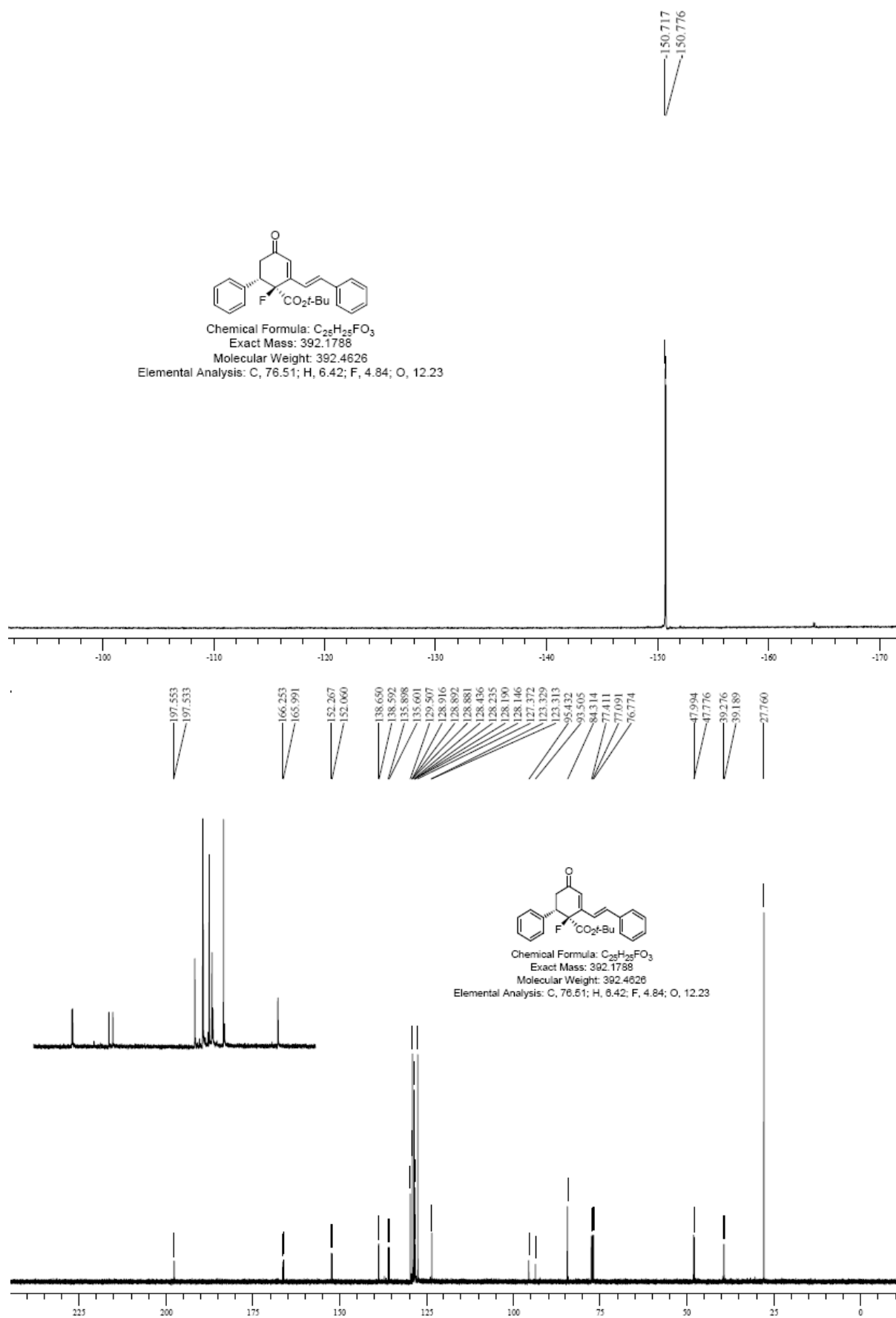
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.470	1132687.875	63817176.000	50.8709
2		34.028	820498.563	61632156.000	49.1291
Total			1953186.438	125449332.000	100.0000



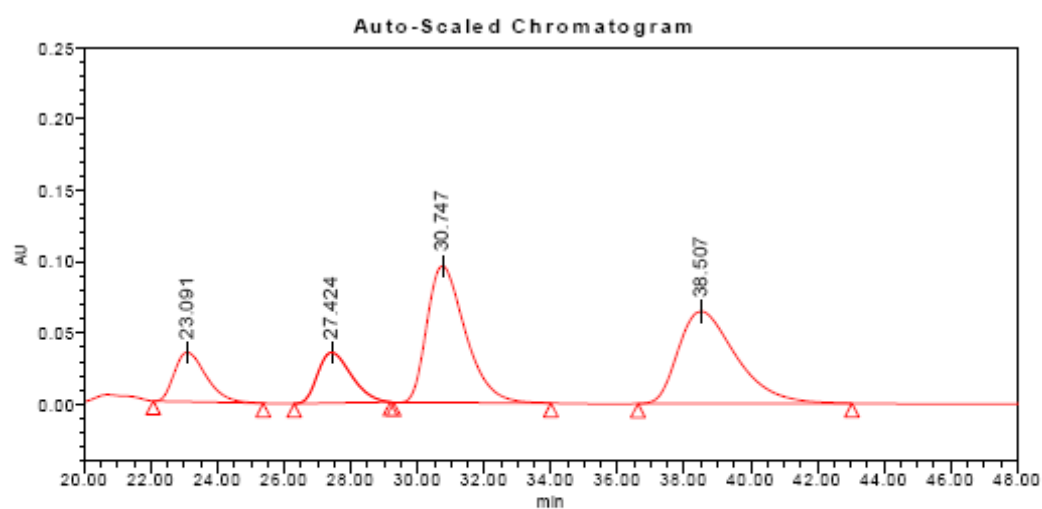
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.178	7472.119	284028.469	0.3759
2		33.767	1040033.313	75271032.000	99.6241
Total			1047505.431	75555060.469	100.0000

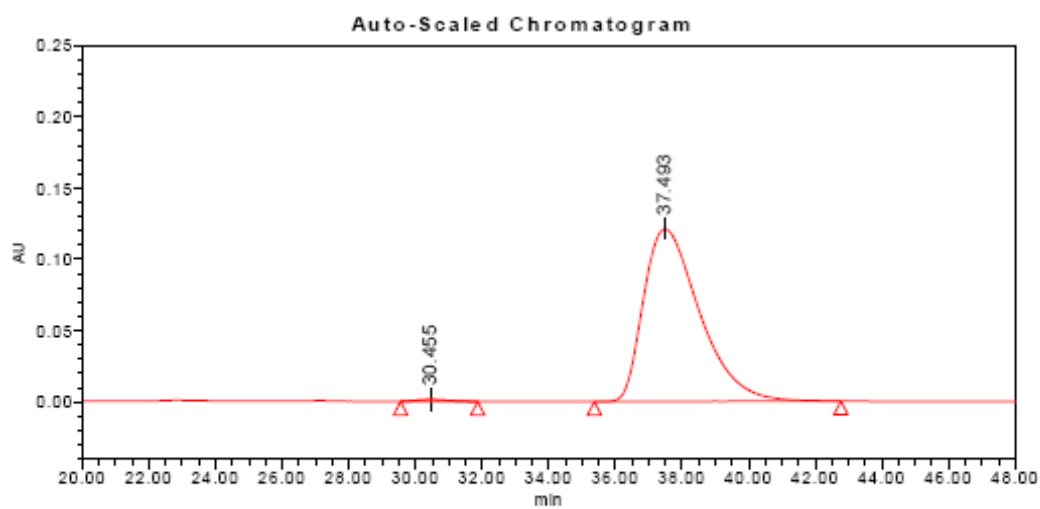




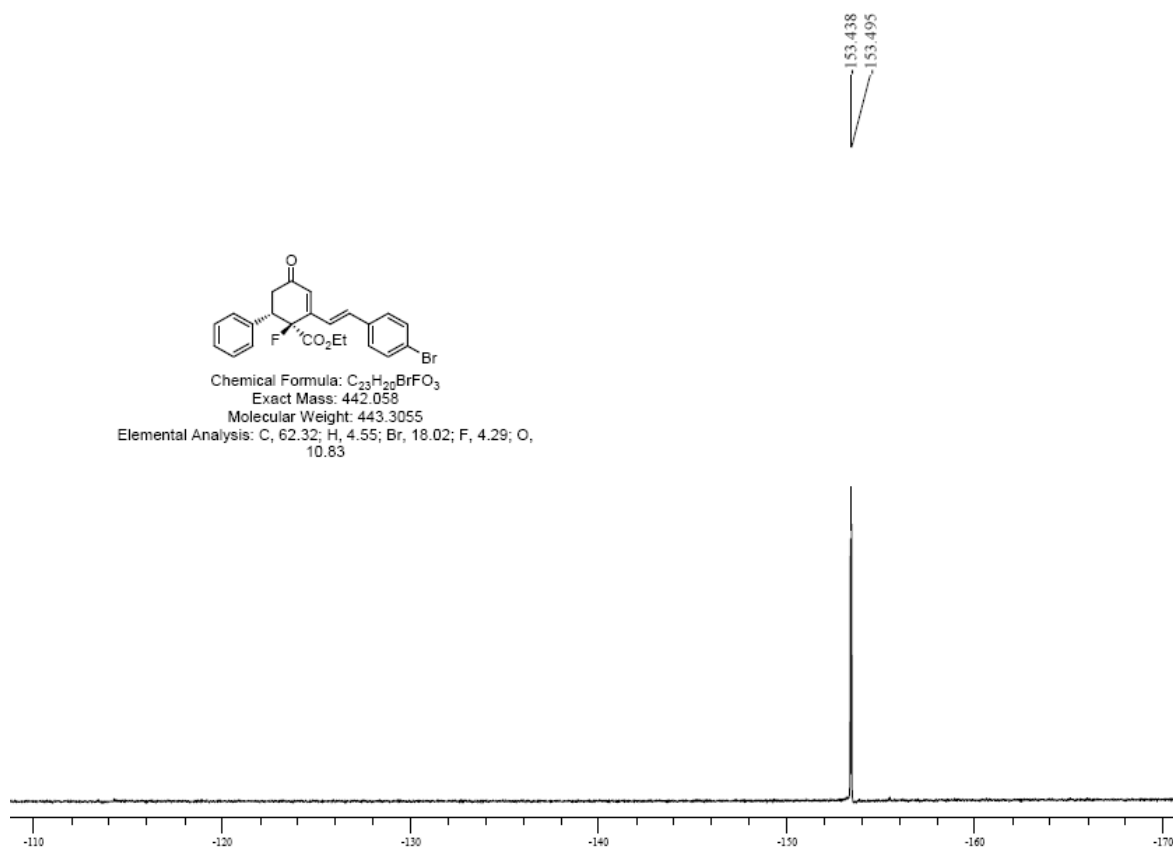
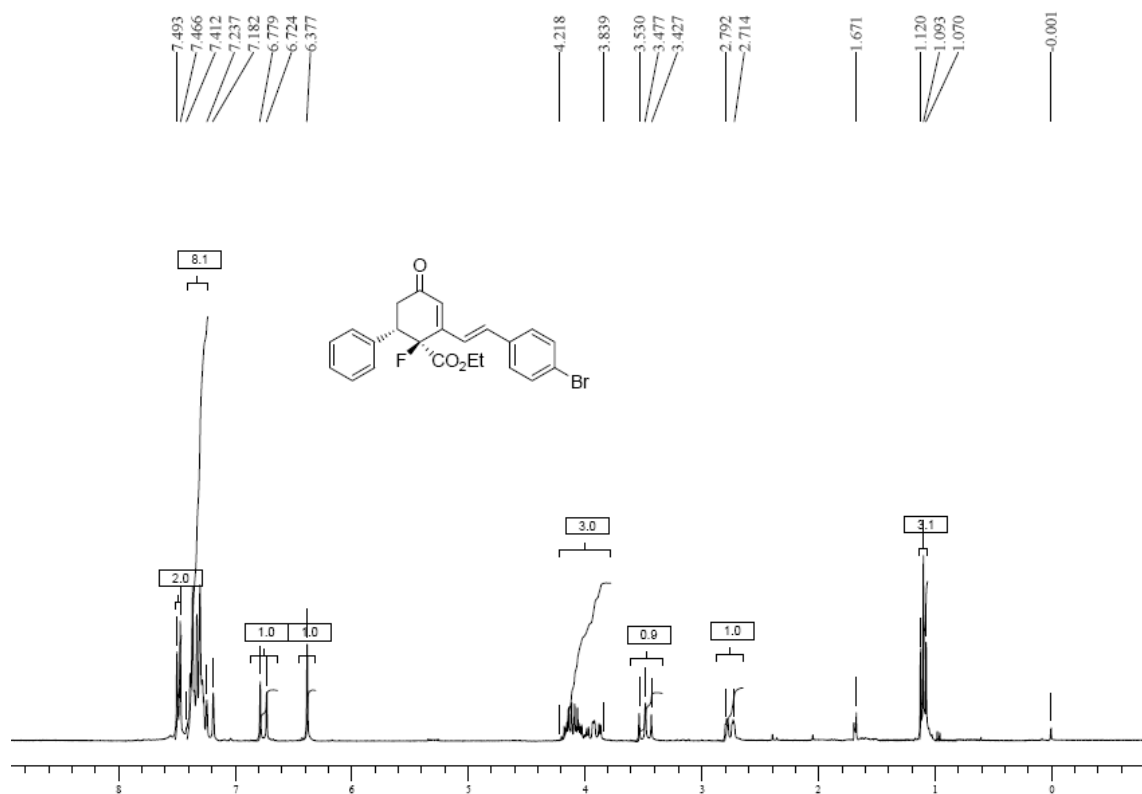
(1*S*,6*S*,*E*)-ethyl-2-(4-bromostyryl)-1-fluoro-4-oxo-6-phenylcyclohex-2-enecarboxylate 5g

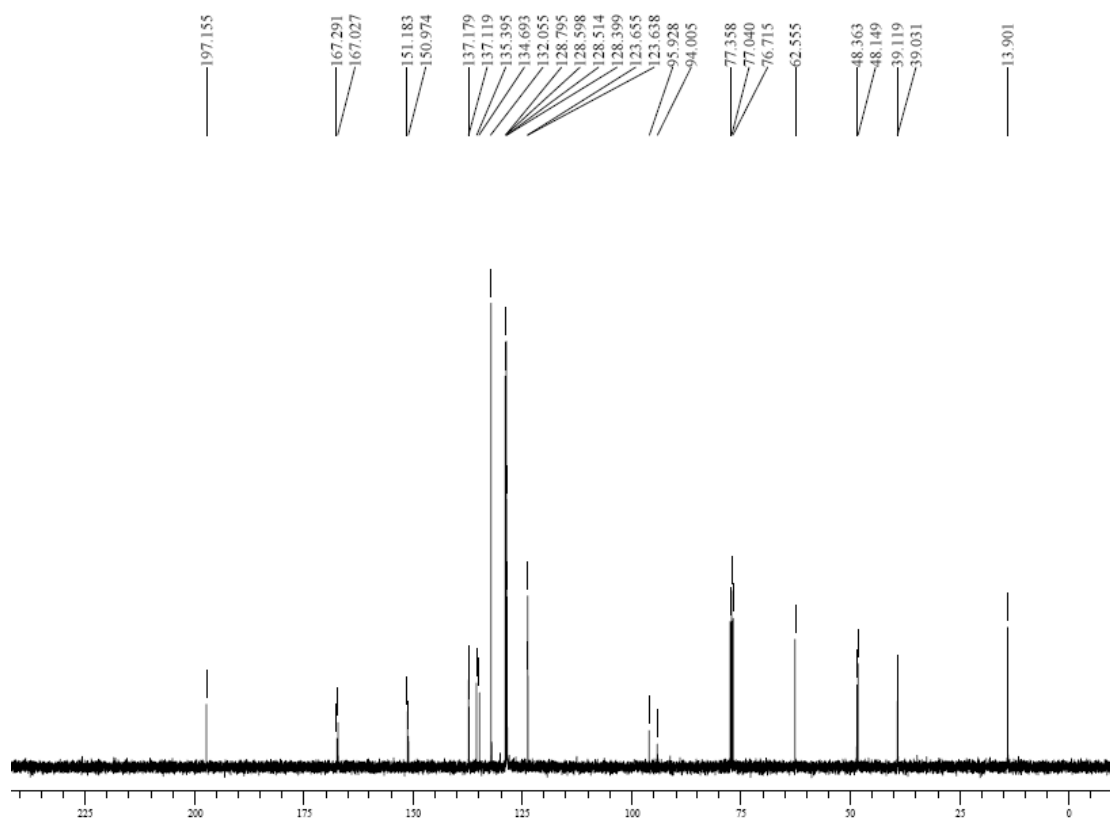


Peak Results						
	Name	RT	Area	Height	% Height	% Area
1		23.091	2290658	34666	15.03	11.34
2		27.424	2476140	35392	15.35	12.25
3		30.747	7676273	95872	41.58	37.99
4		38.507	7765299	64644	28.04	36.43

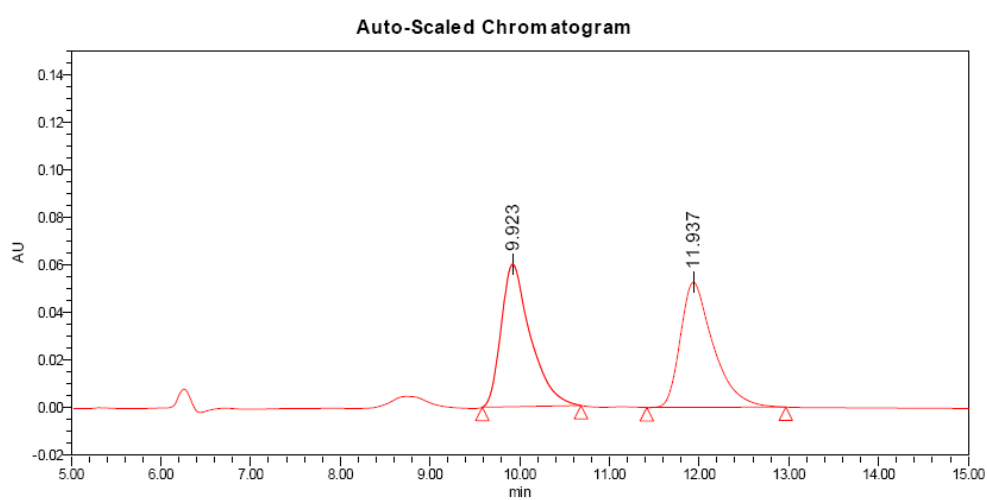


Peak Results						
	Name	RT	Area	Height	% Height	% Area
1		30.455	84760	1254	1.03	0.60
2		37.493	14145306	120980	98.97	99.40



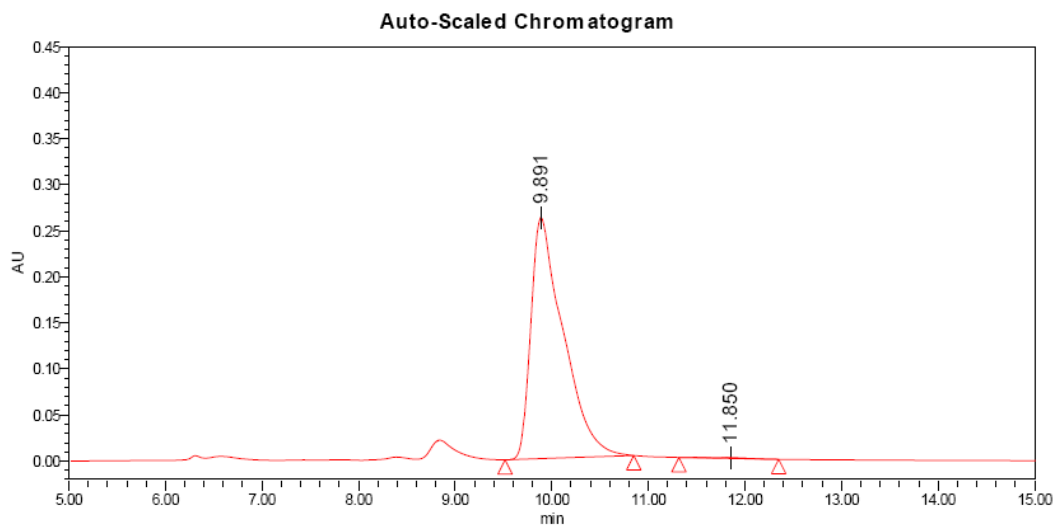


(1*S*,6*S*,*E*)-tert-butyl 1-fluoro-4-oxo-6-phenyl-2-(prop-1-enyl)cyclohex-2-enecarboxylate 5h



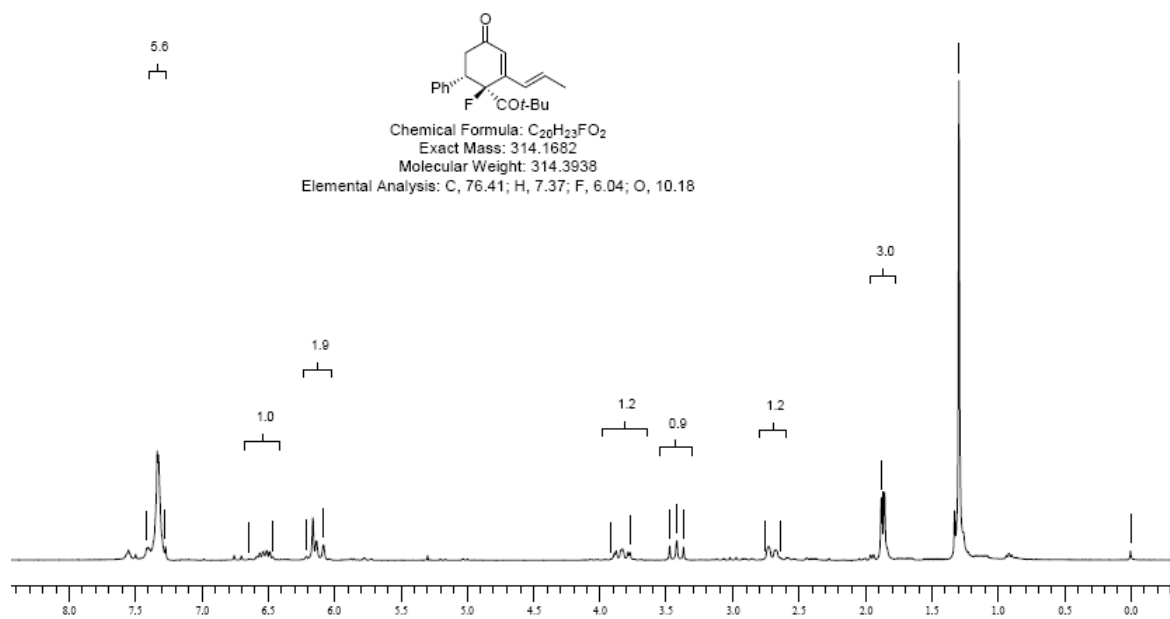
Peak Results

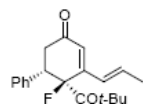
	Name	RT	Area	Height	% Height	% Area
1		9.923	1359386	59915	53.26	50.40
2		11.937	1337990	52570	46.74	49.60



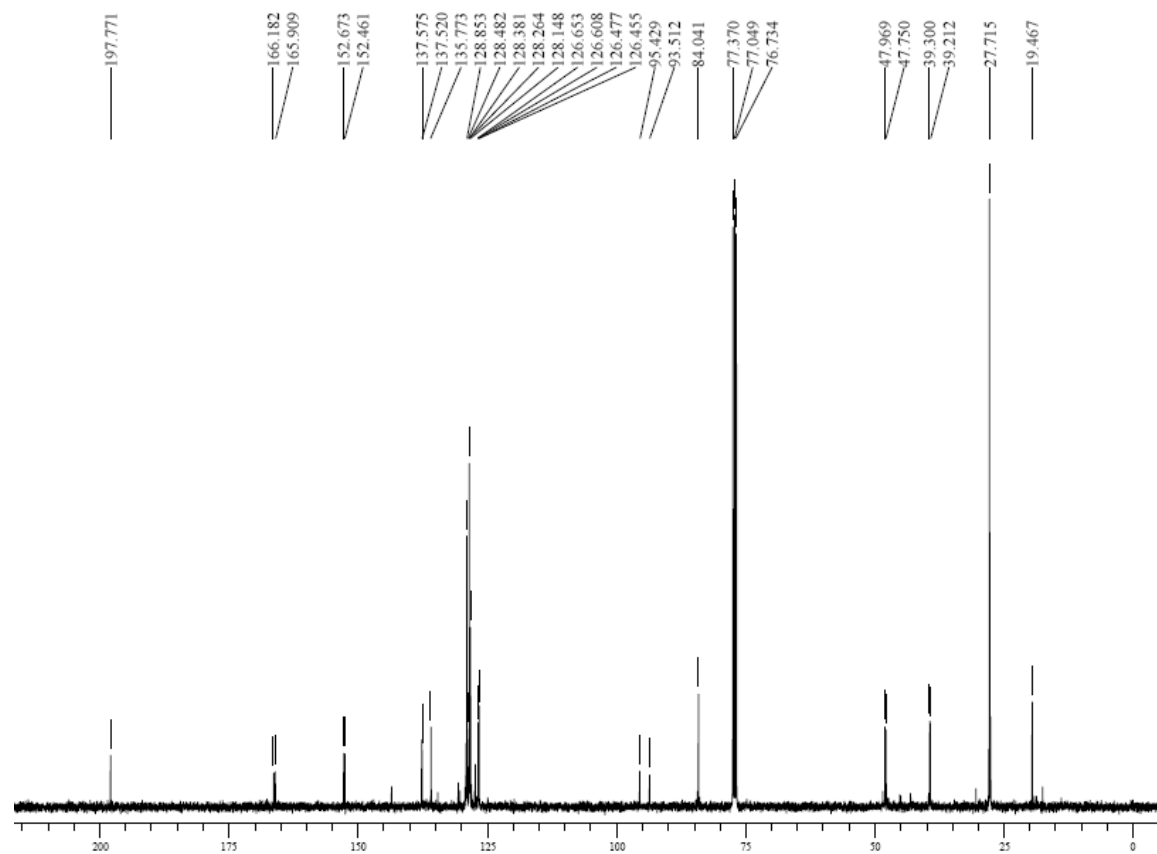
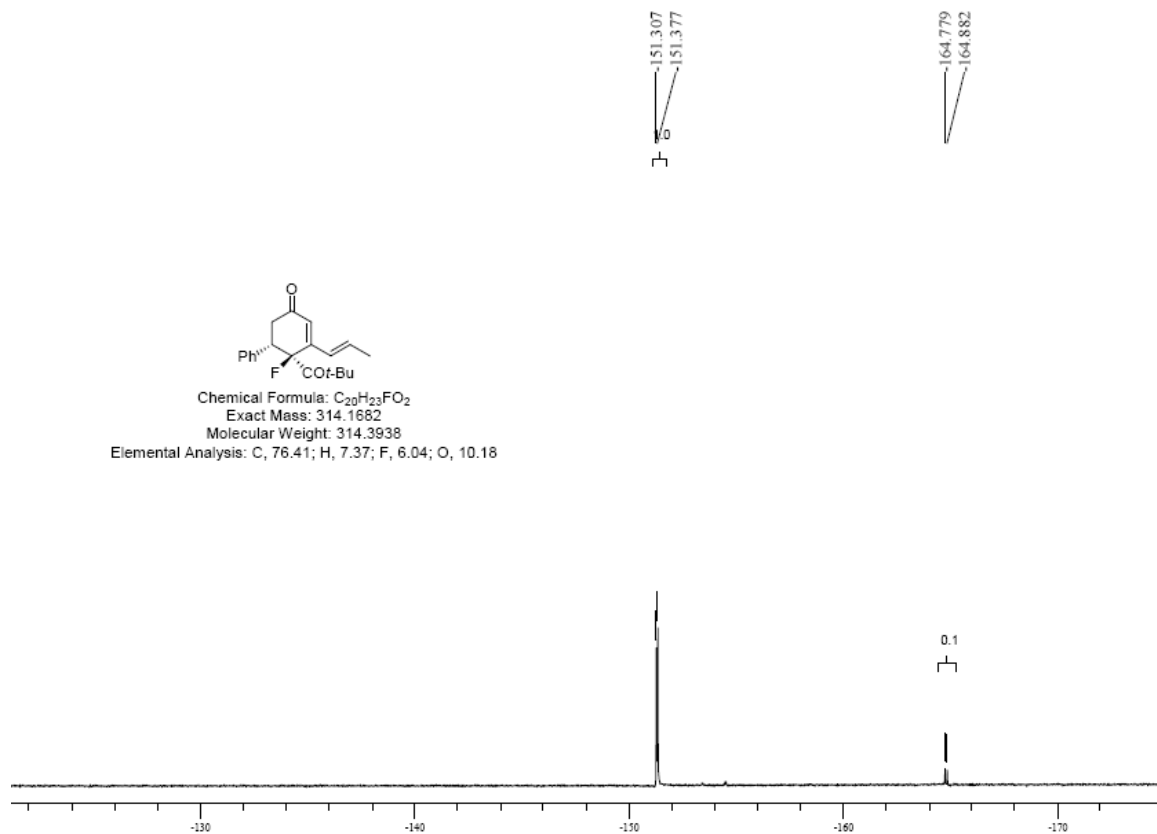
Peak Results

	Name	RT	Area	Height	% Height	% Area
1		9.891	6092562	262040	99.71	99.69
2		11.850	18850	753	0.29	0.31

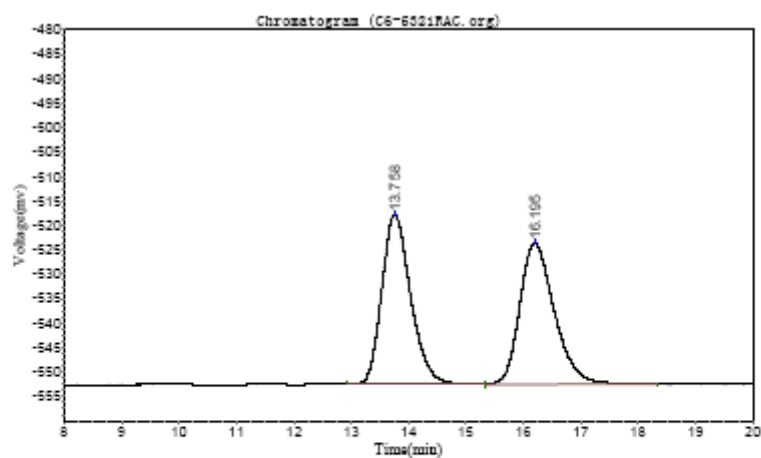




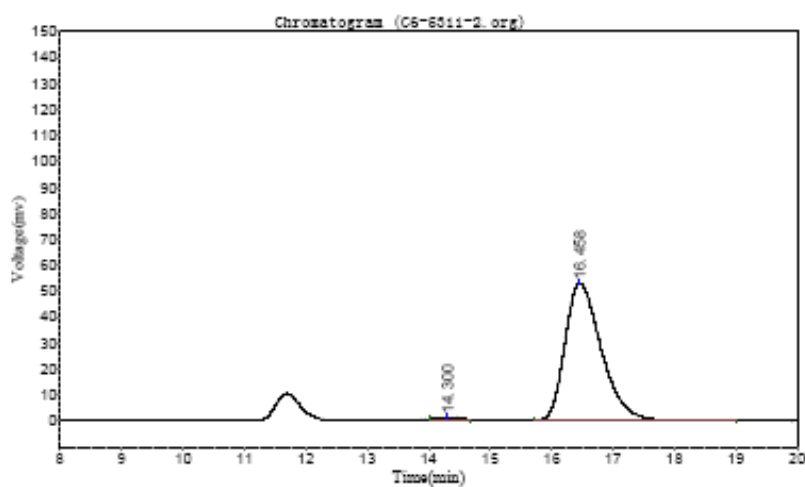
Chemical Formula: $C_{29}H_{23}FO_2$
 Exact Mass: 314.1682
 Molecular Weight: 314.3938
 Elemental Analysis: C, 76.41; H, 7.37; F, 6.04; O, 10.18



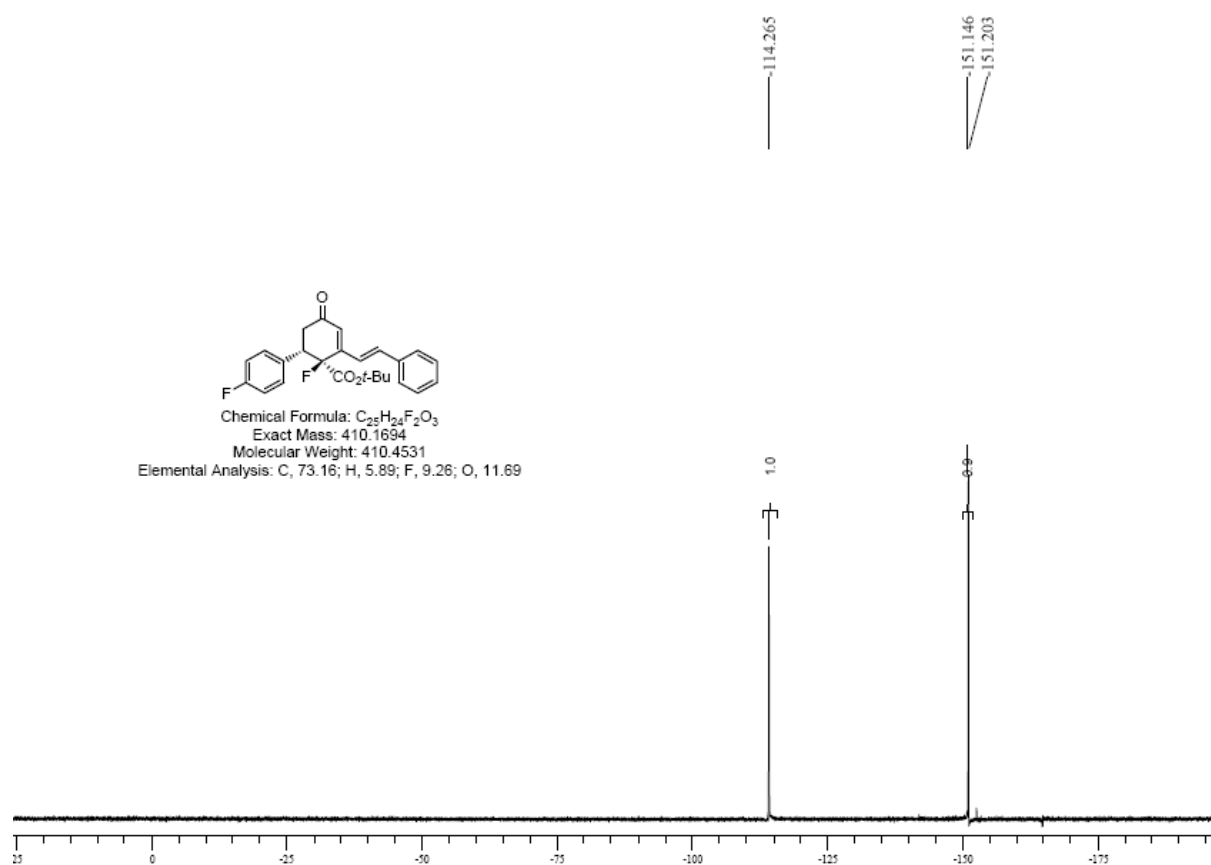
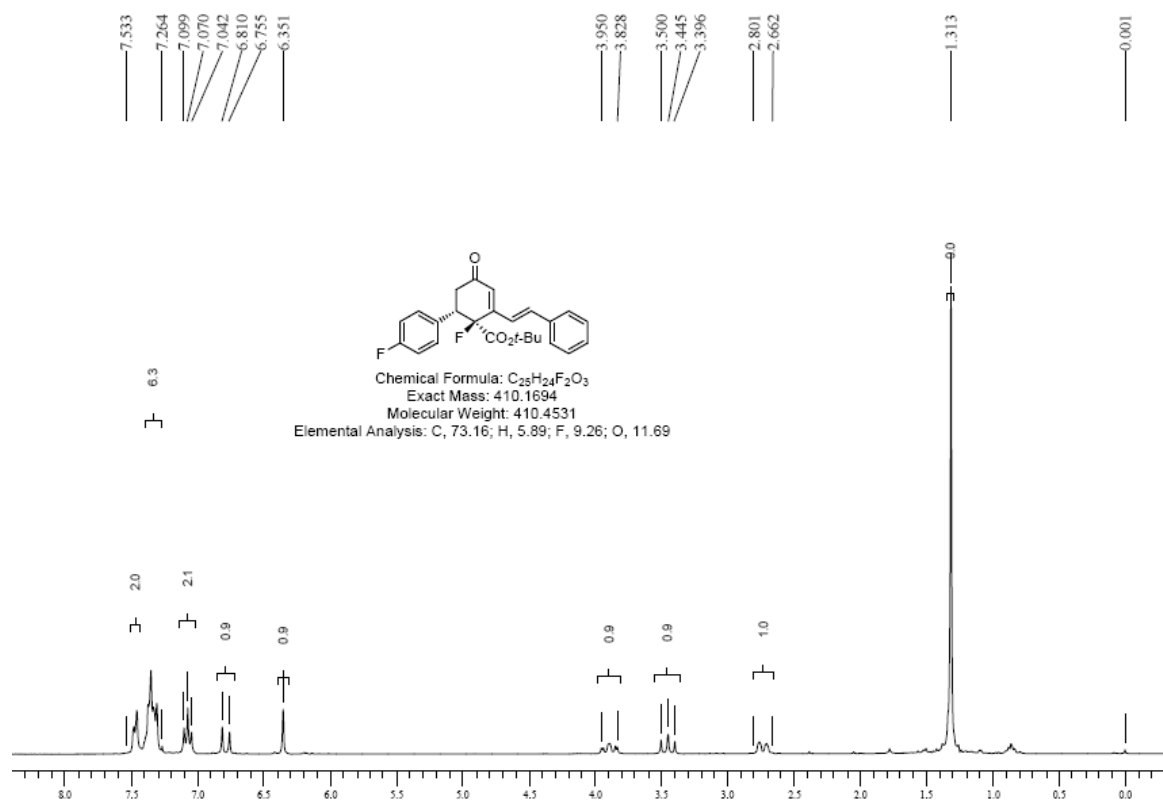
(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-6-(4-fluorophenyl)-4-oxo-2-styrylcyclohex-2-enecarboxylate 5i

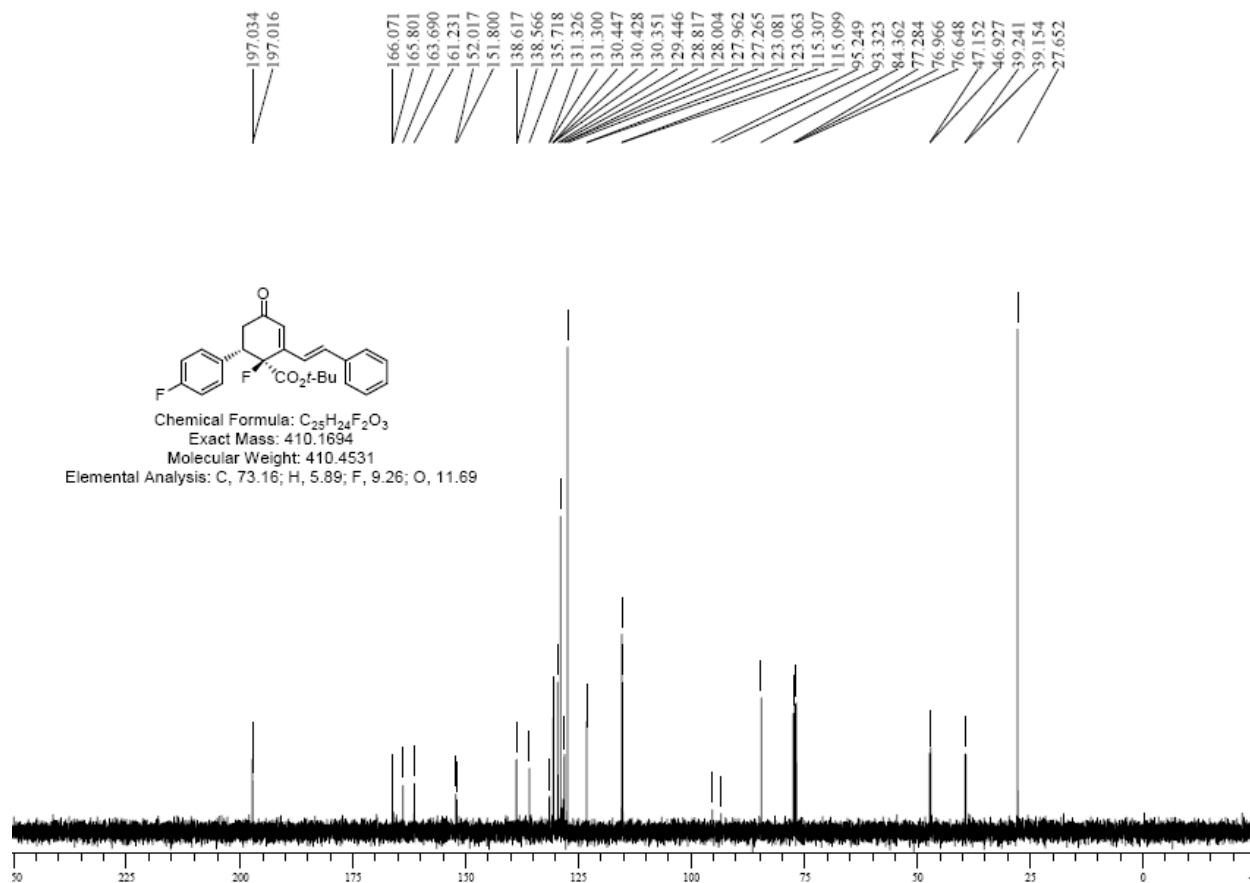


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.758	34739.410	1210419.125	50.1395
2		16.195	28935.146	1203683.125	49.8605
Total			63674.557	2414102.250	100.0000

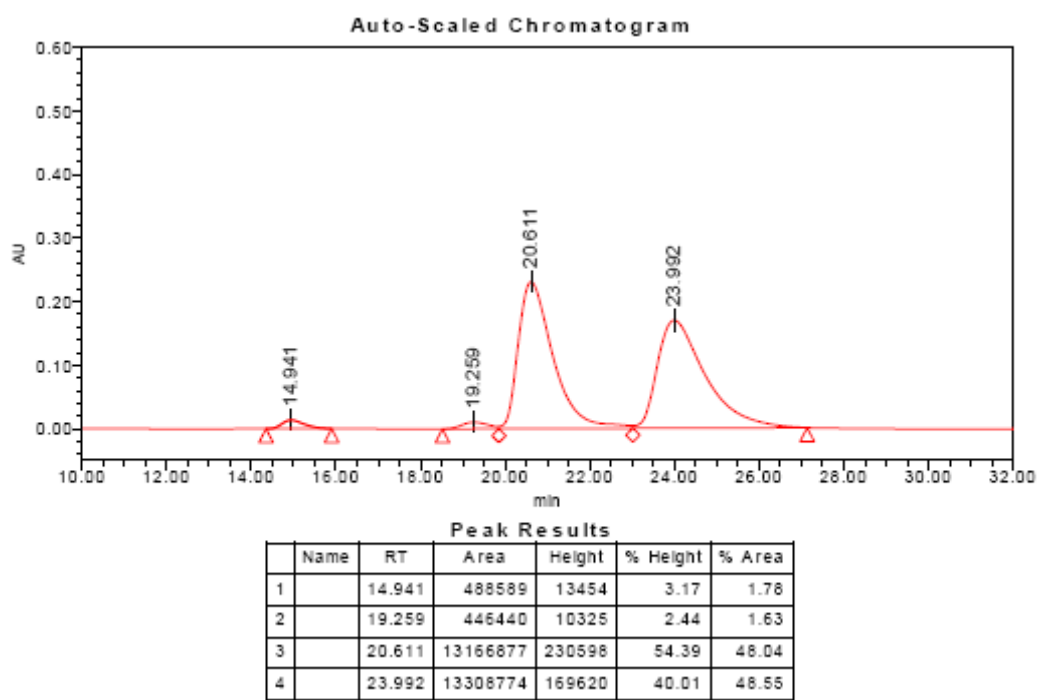


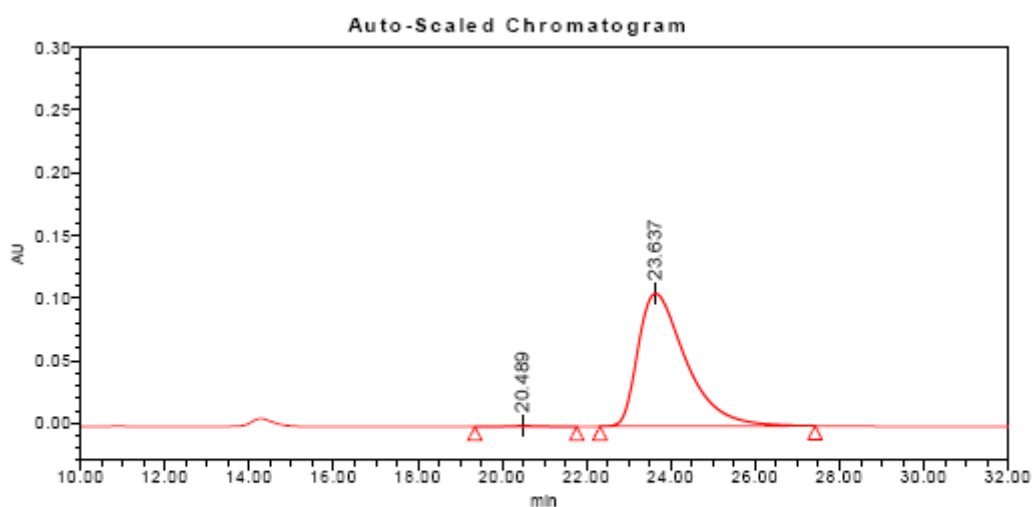
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.300	671.819	16203.450	0.7374
2		16.458	53073.414	2181055.750	99.2626
Total			53745.233	2197259.200	100.0000





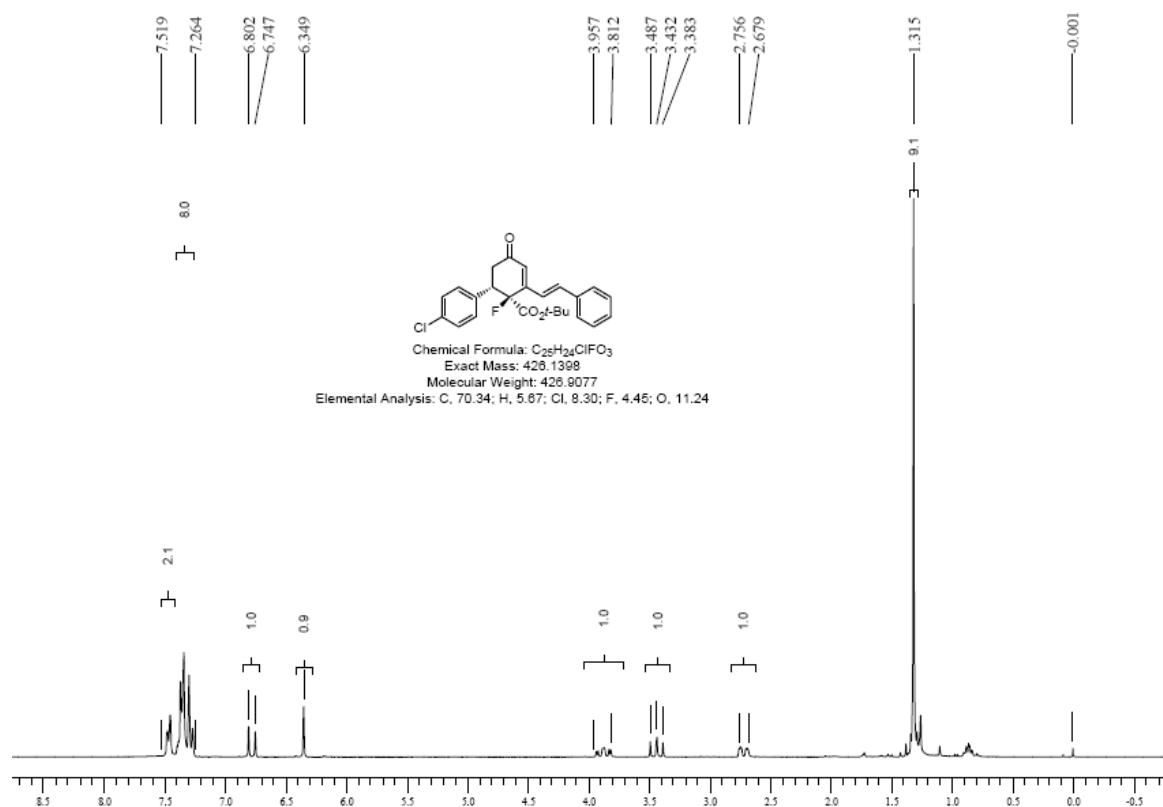
(1*S*,6*S*,*E*)-*tert*-butyl-6-(4-chlorophenyl)-1-fluoro-4-oxo-2-styrylcyclohex-2-enecarboxylate 5j

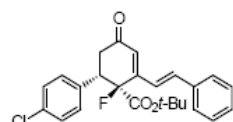




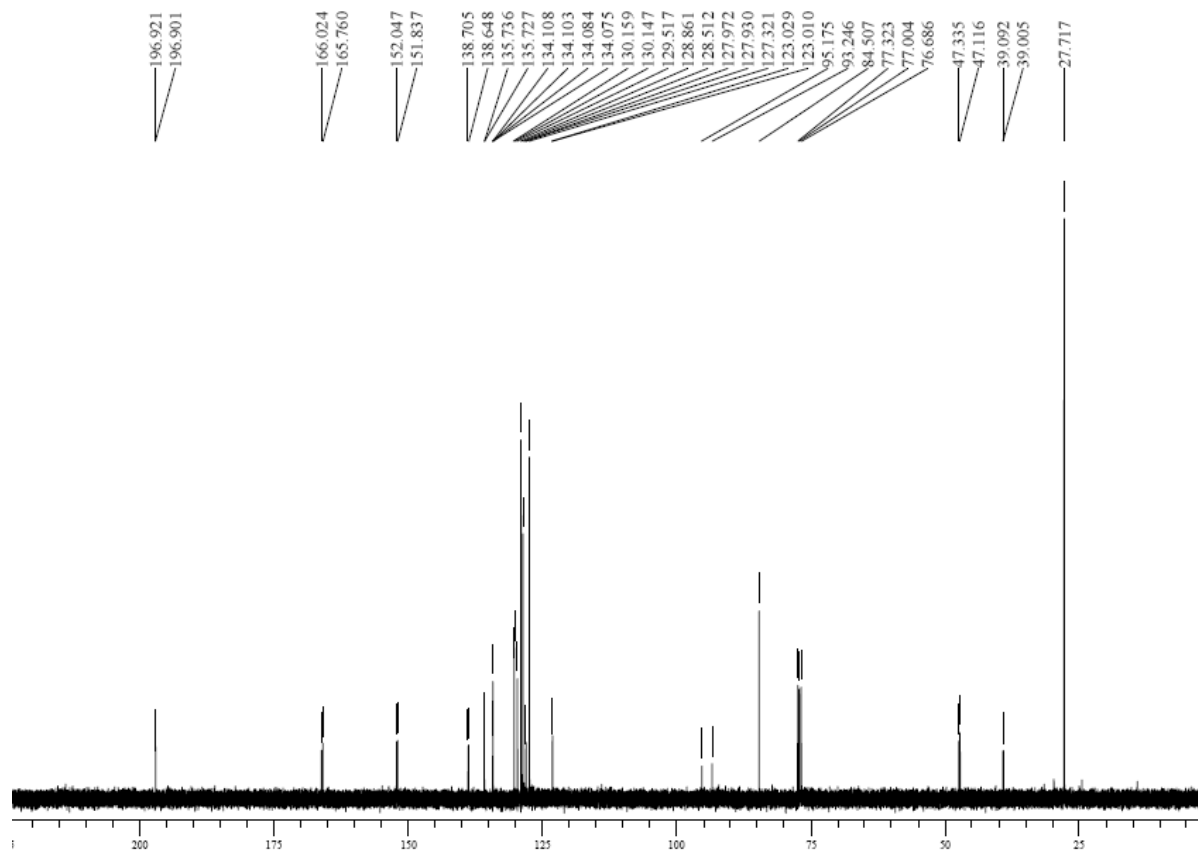
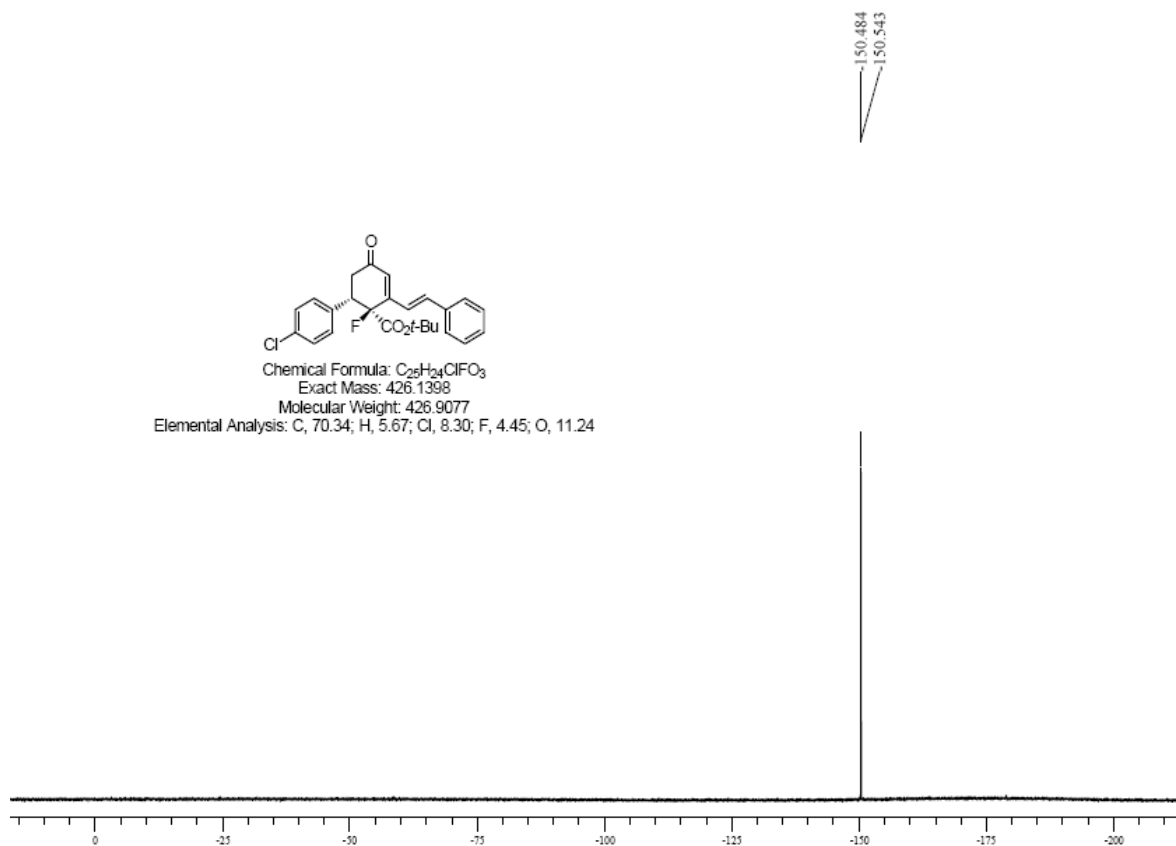
Peak Results

	Name	RT	Area	Height	% Height	% Area
1		20.489	39424	724	0.68	0.47
2		23.637	8341992	105818	99.32	99.53

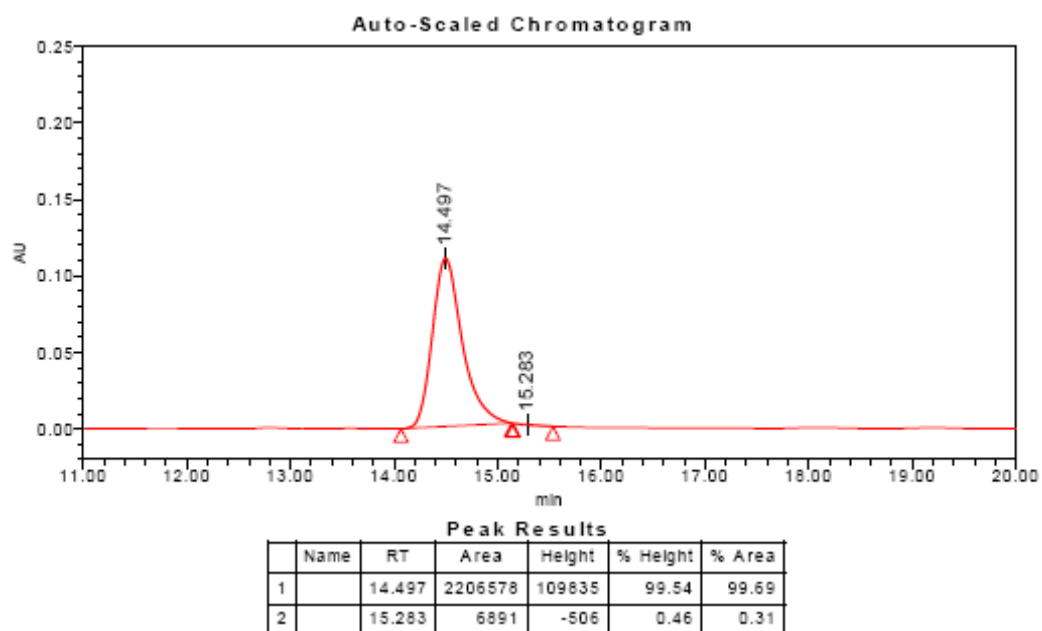
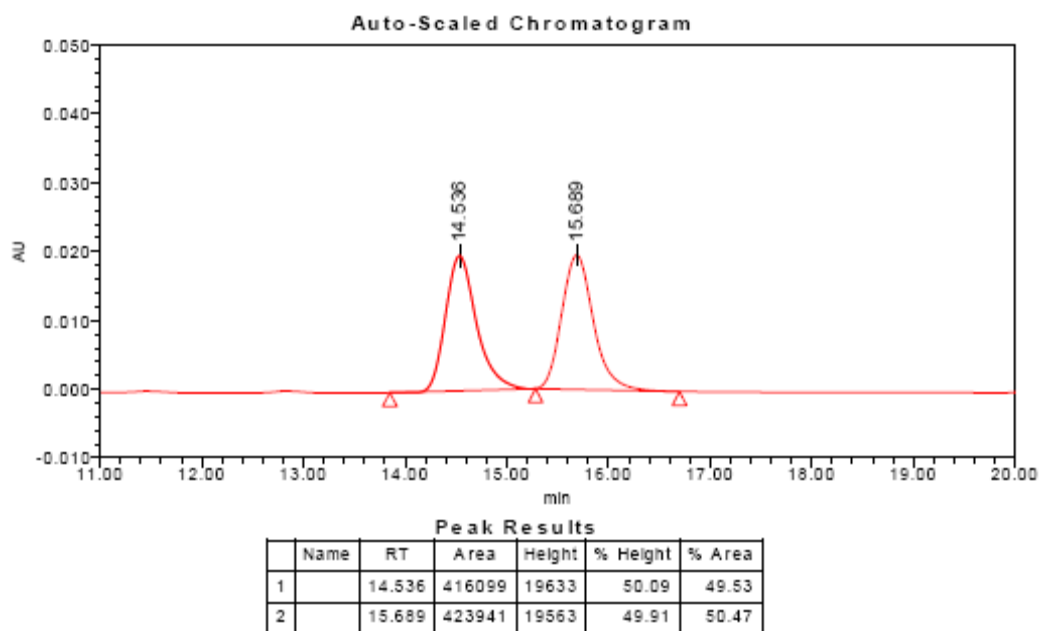


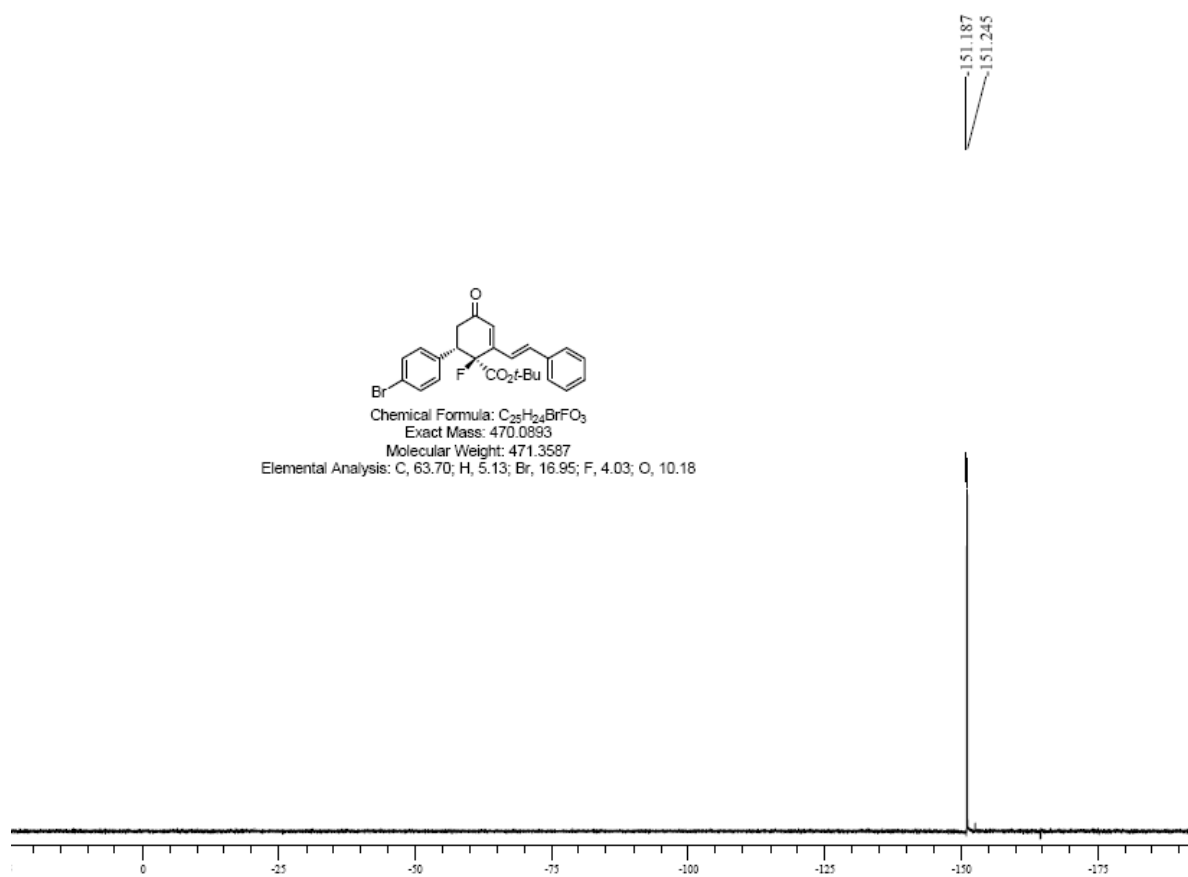
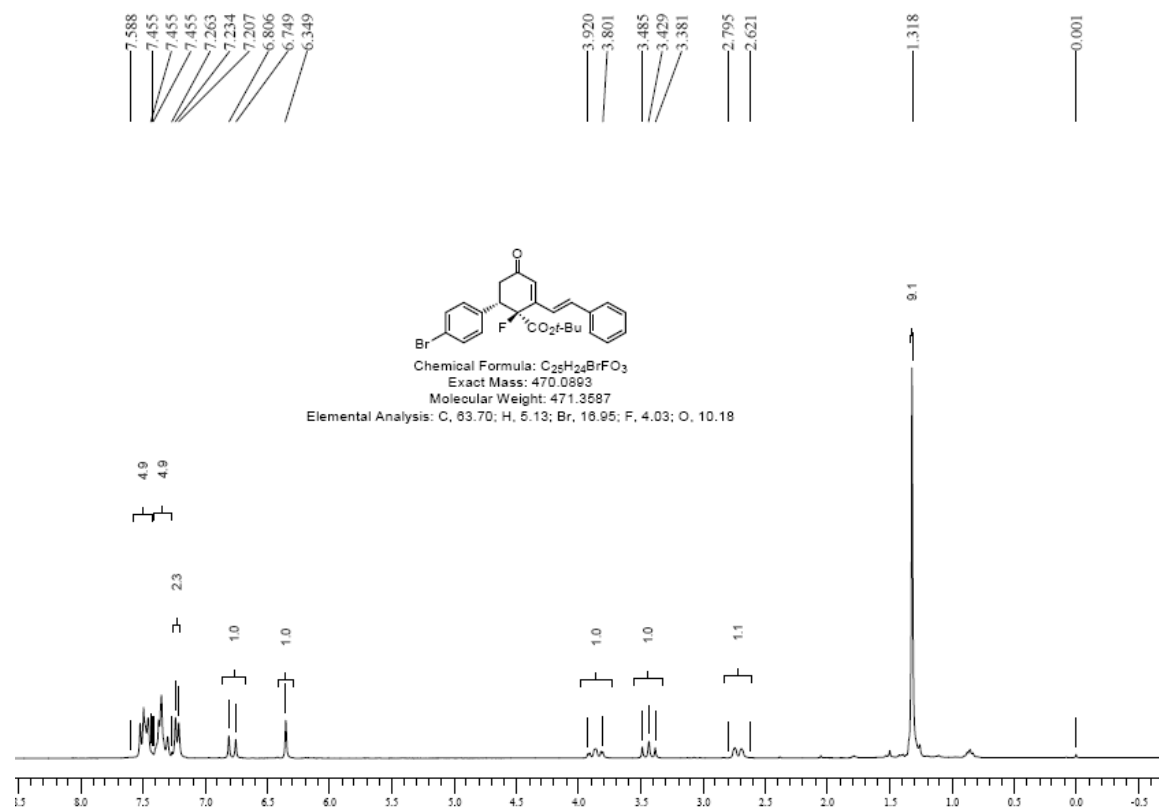


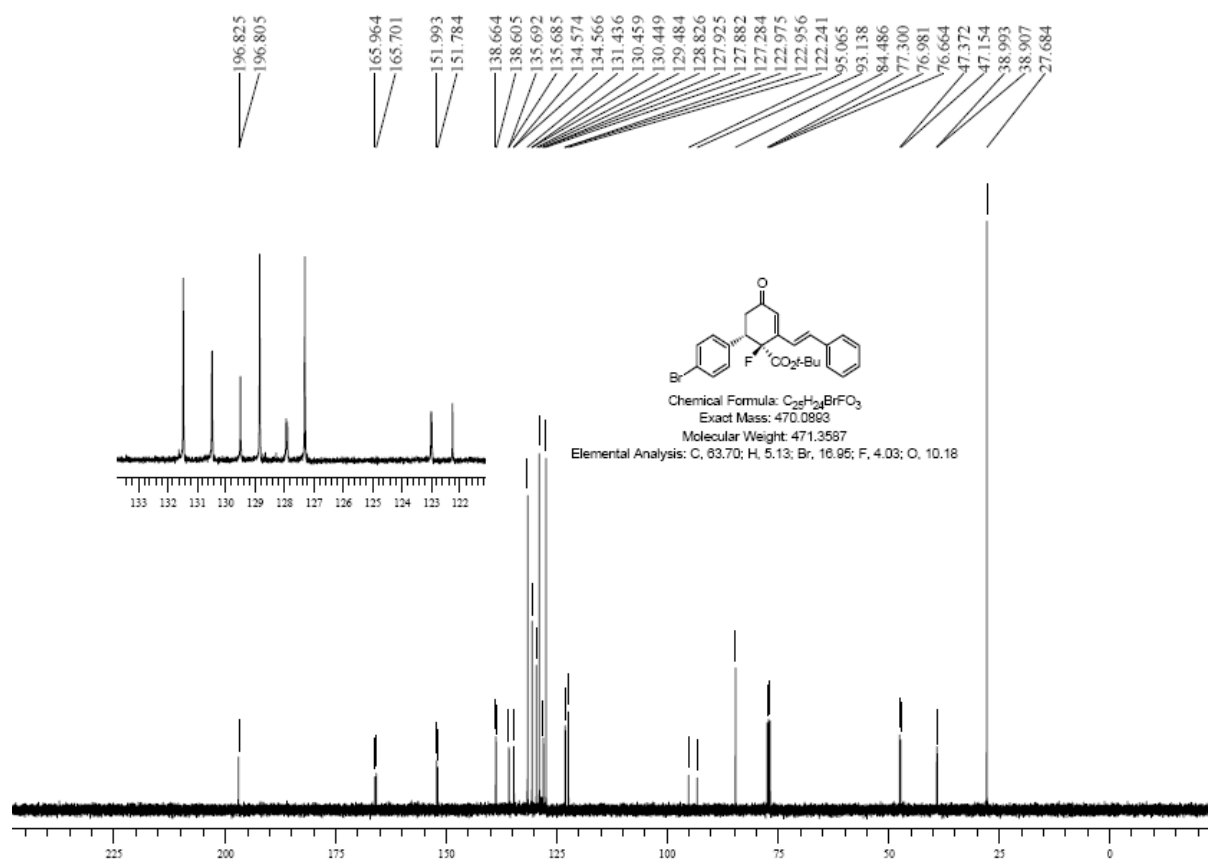
Chemical Formula: $C_{25}H_{34}ClFO_3$
 Exact Mass: 426.1398
 Molecular Weight: 426.9077
 Elemental Analysis: C, 70.34; H, 5.67; Cl, 8.30; F, 4.45; O, 11.24



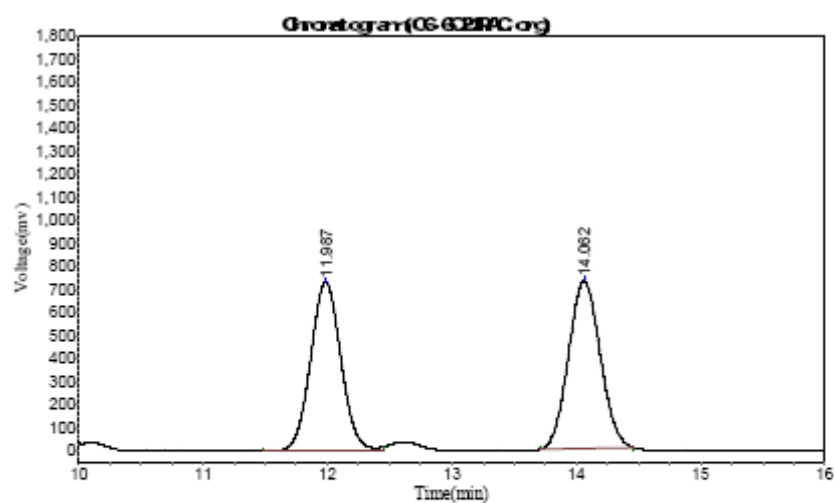
(1*S*,6*S*,*E*)-*tert*-butyl-6-(4-bromophenyl)-1-fluoro-4-oxo-2-styrylcyclohex-2-enecarboxylate 5k



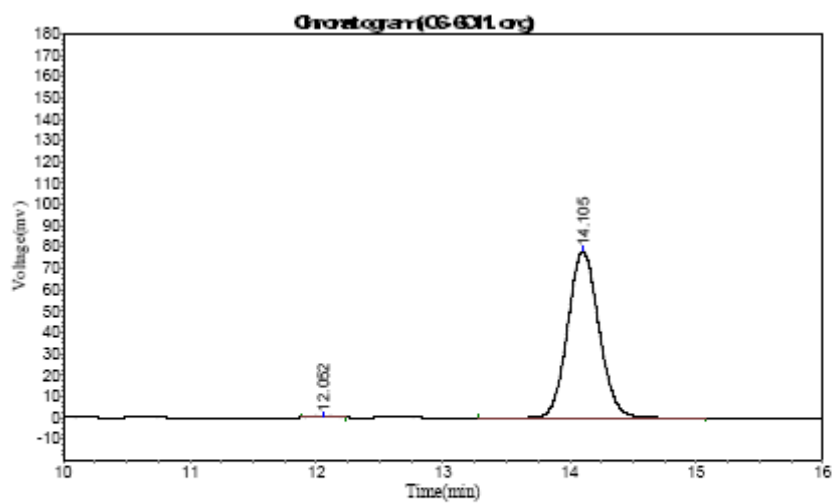




(1*S*,6*S*,*E*)-*tert*-butyl-6-(3-chlorophenyl)-1-fluoro-4-oxo-2-styrylcyclohex-2-enecarboxylate 5l

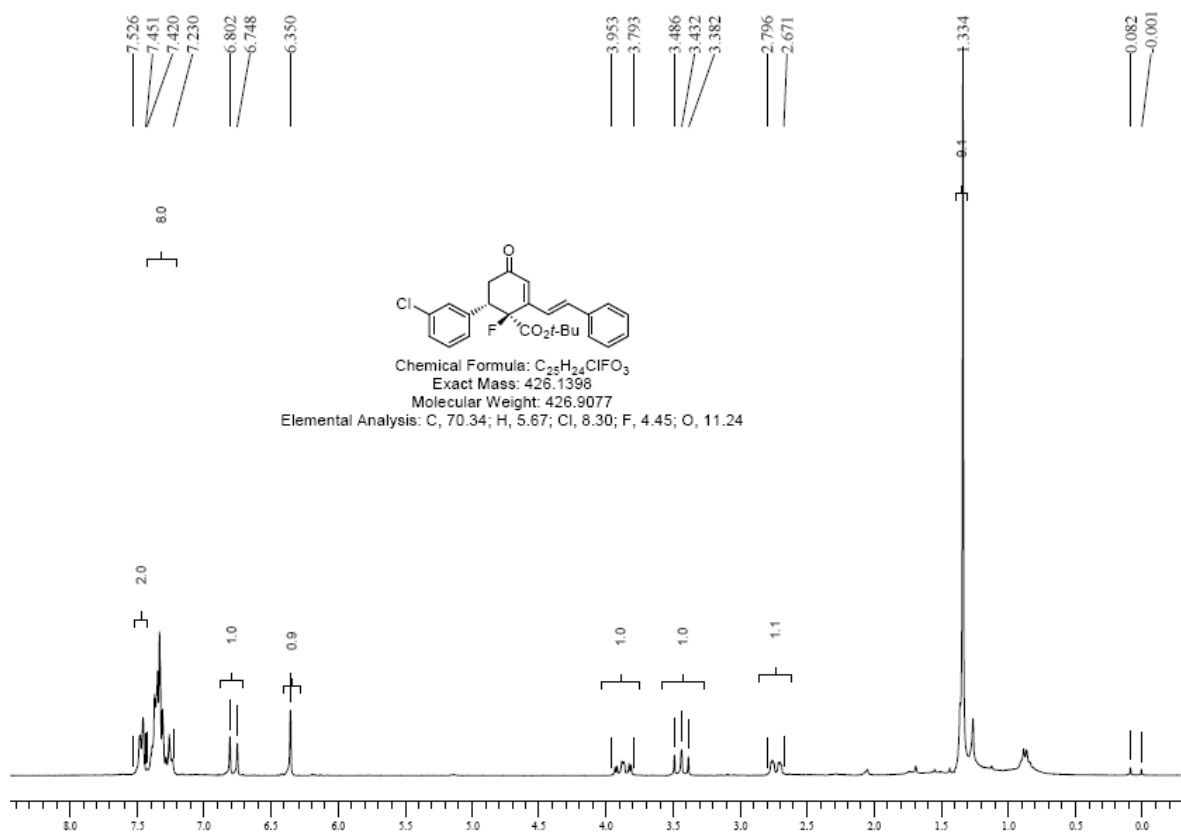


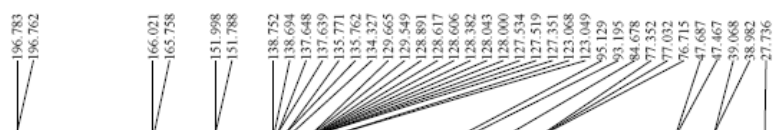
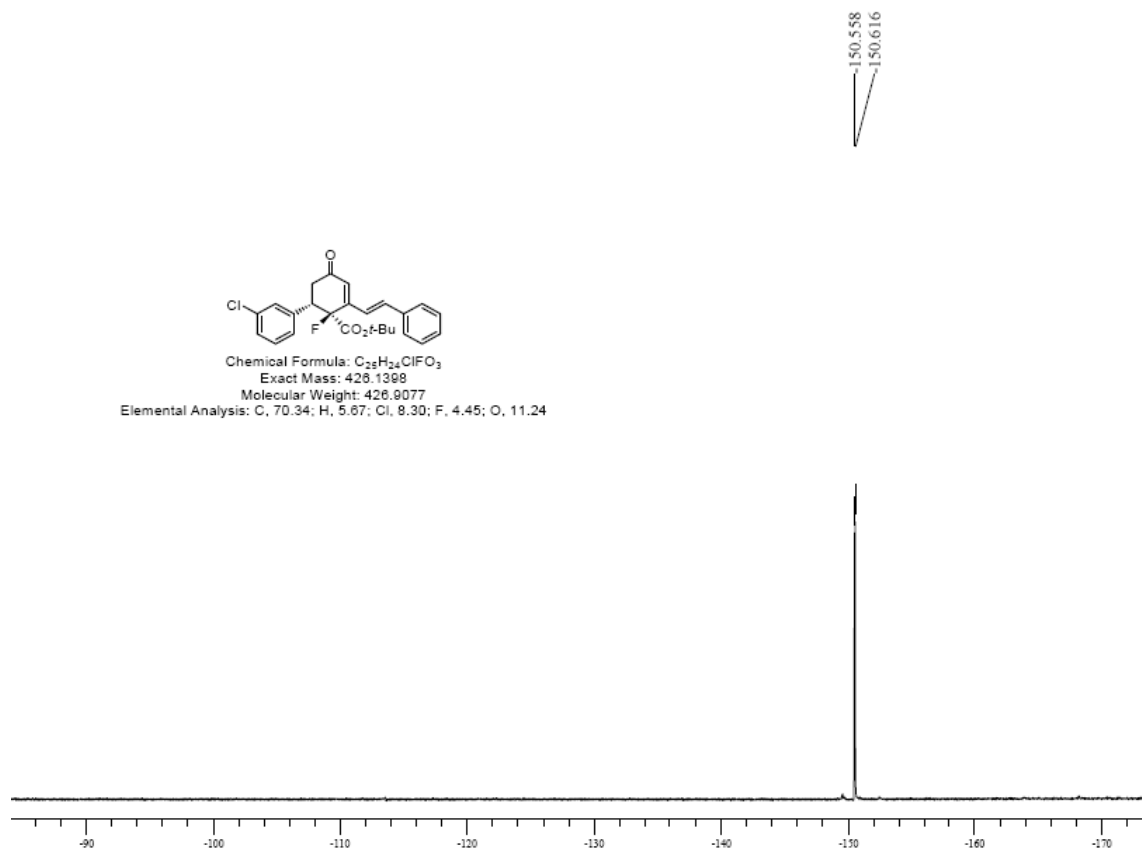
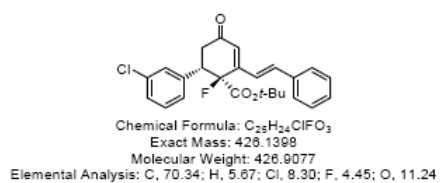
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.987	732519.875	12376575.000	48.8476
2		14.062	727858.938	12960537.000	51.1524
Total			1460378.813	25337112.000	100.0000



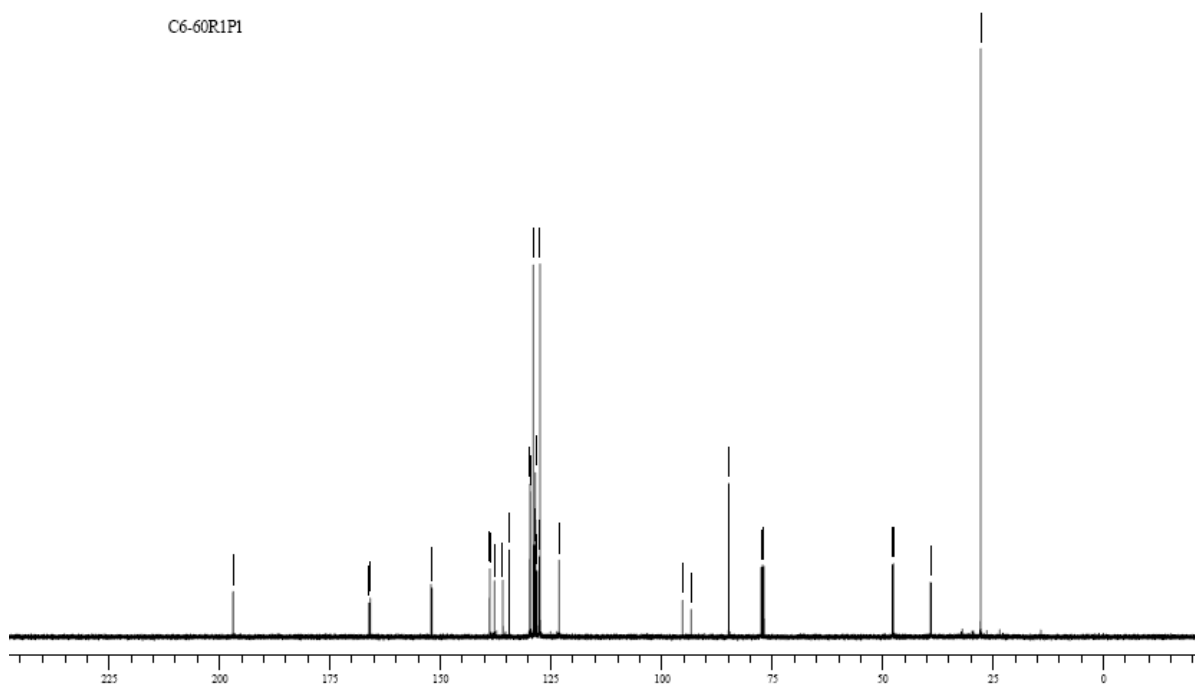
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.052	797.918	9248.500	0.6834
2		14.105	78178.539	1344128.000	99.3166
Total			78976.457	1353376.500	100.0000

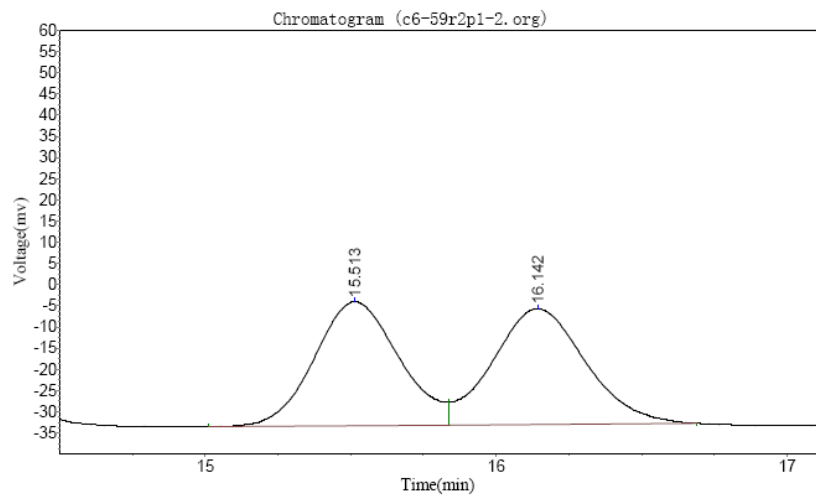




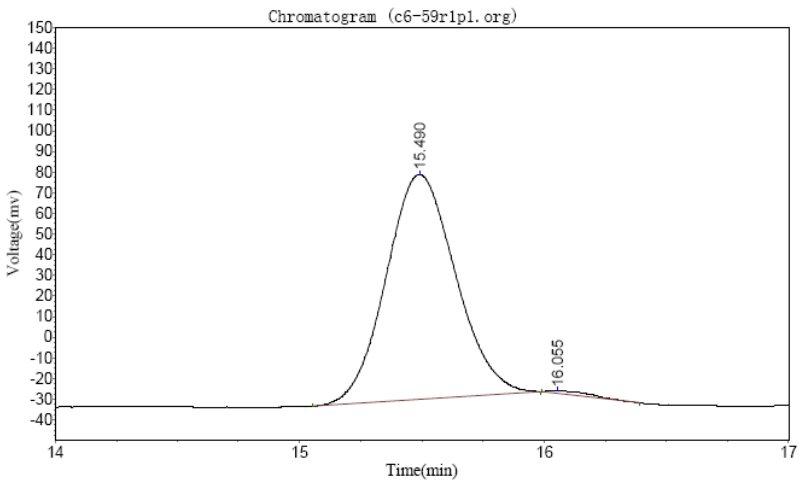
C6-60R1P1



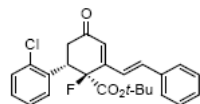
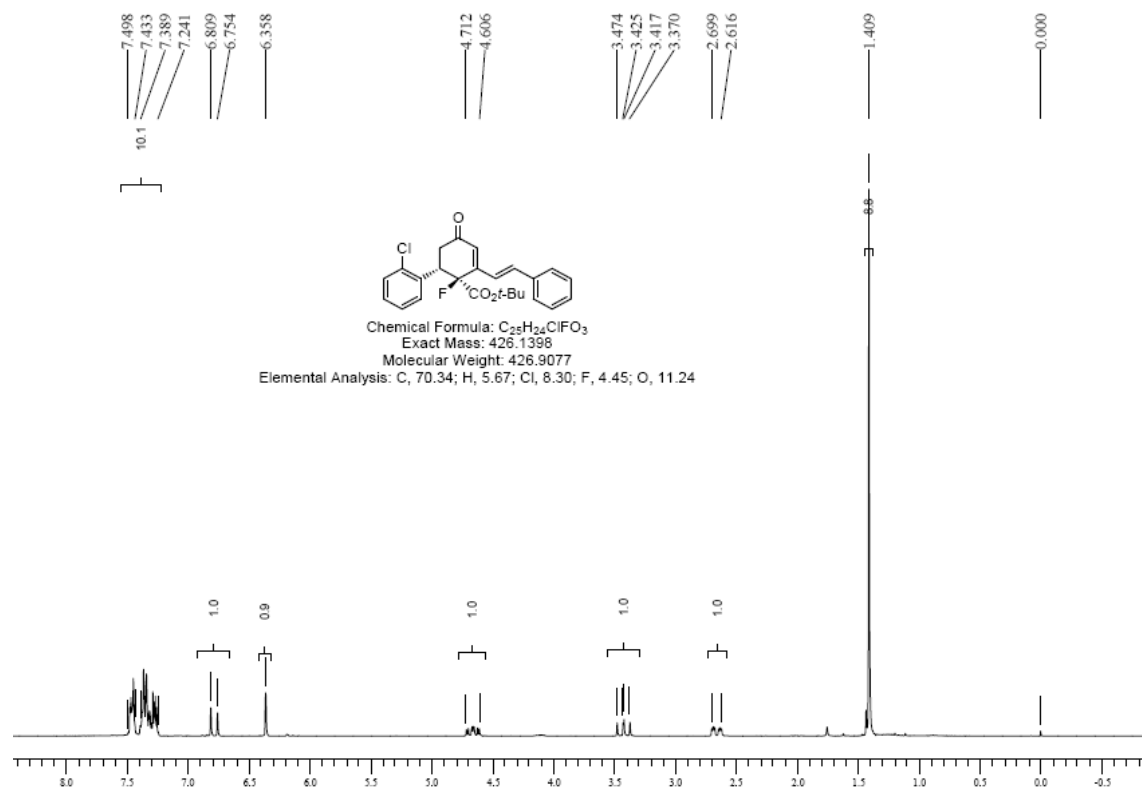
(1*S*,6*S*,*E*)-*tert*-butyl-6-(2-chlorophenyl)-1-fluoro-4-oxo-2-styrylcyclohex-2-enecar boxylate 5m



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.513	29201.096	591231.313	49.3933
2		16.142	27301.191	605755.125	50.6067
Total			56502.287	1196986.438	100.0000

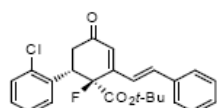
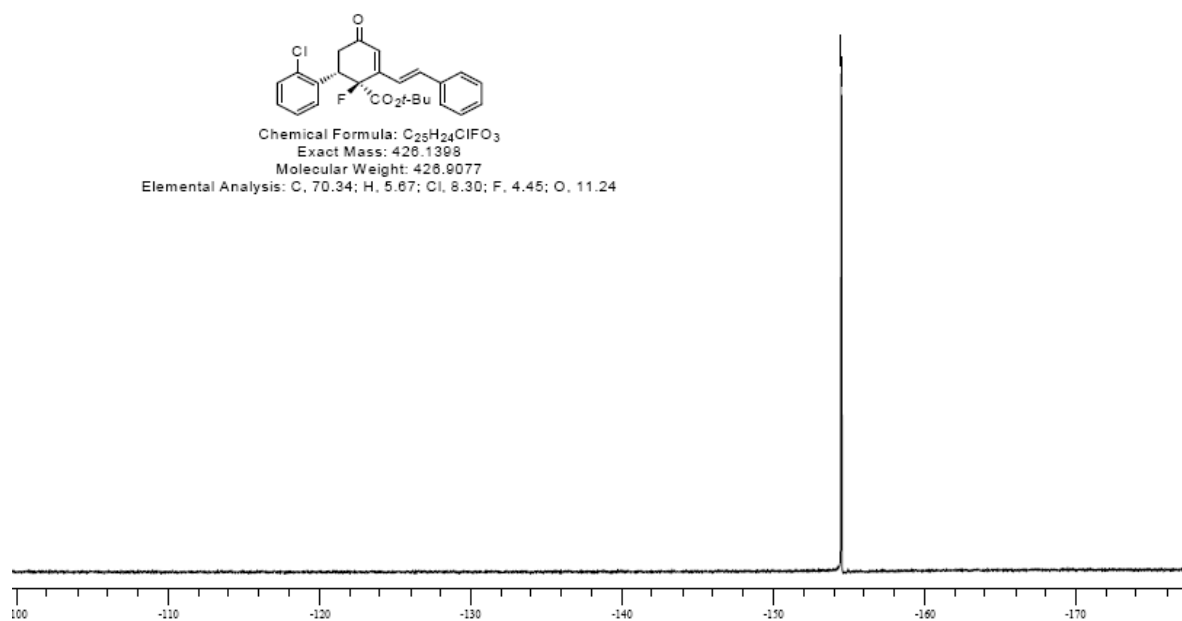


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.490	108870.578	2147534.250	99.2006
2		16.055	1026.224	17304.977	0.7994
Total			109896.802	2164839.227	100.0000

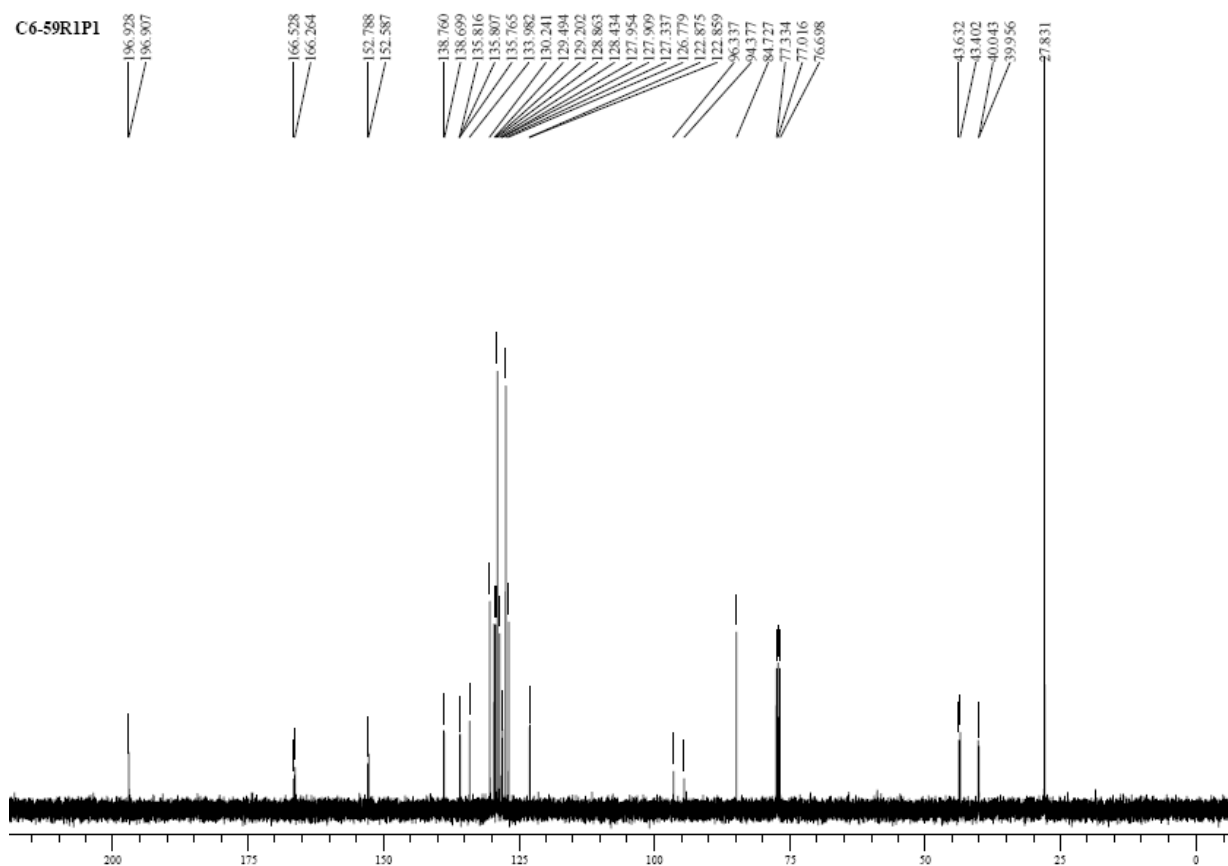


Chemical Formula: $C_{25}H_{24}ClFO_3$
 Exact Mass: 426.1398
 Molecular Weight: 426.9077
 Elemental Analysis: C, 70.34; H, 5.67; Cl, 8.30; F, 4.45; O, 11.24

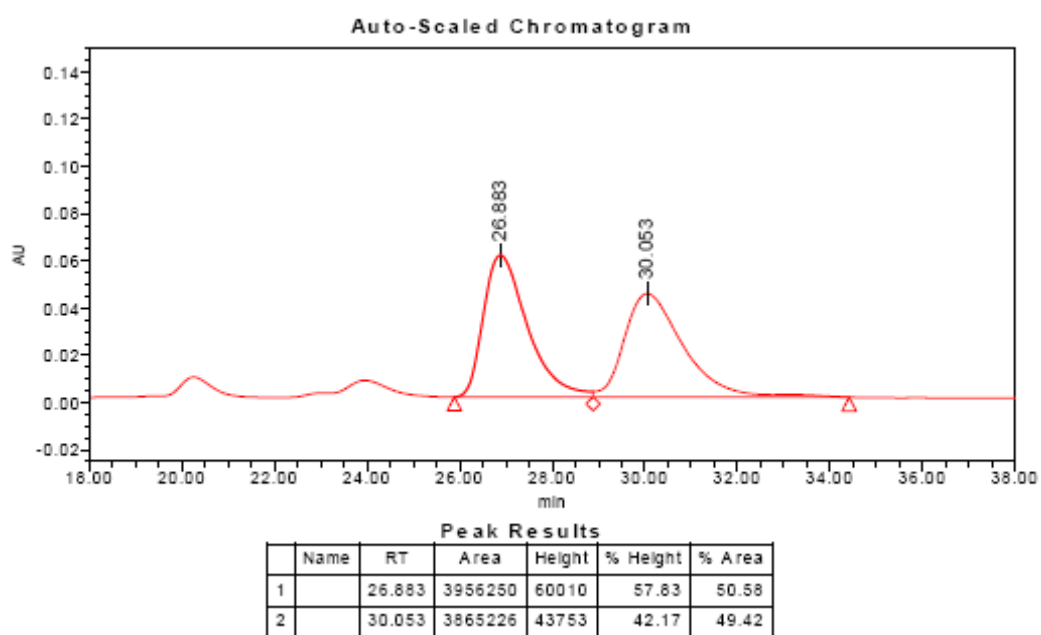
154.515
154.559

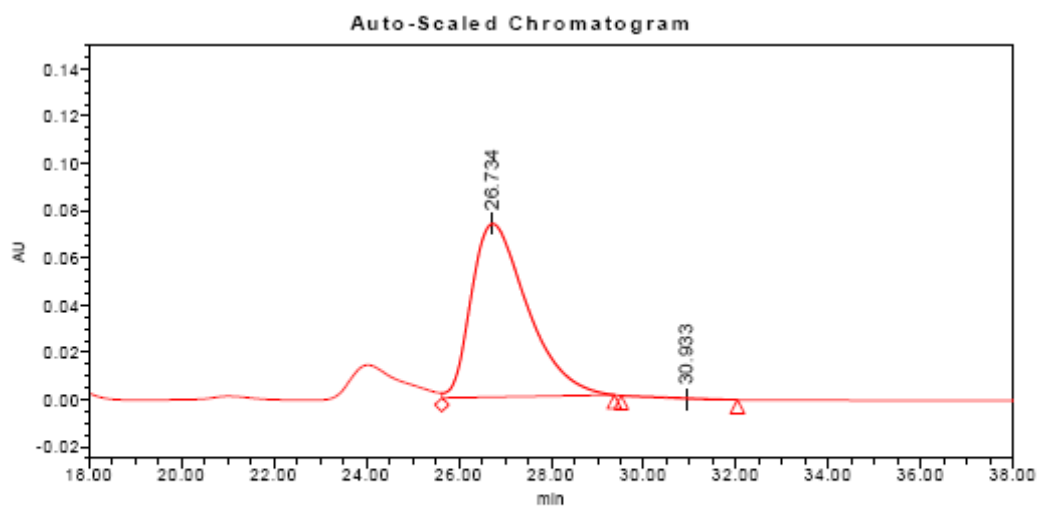


Chemical Formula: $C_{25}H_{24}ClFO_3$
 Exact Mass: 426.1398
 Molecular Weight: 426.9077
 Elemental Analysis: C, 70.34; H, 5.67; Cl, 8.30; F, 4.45; O, 11.24



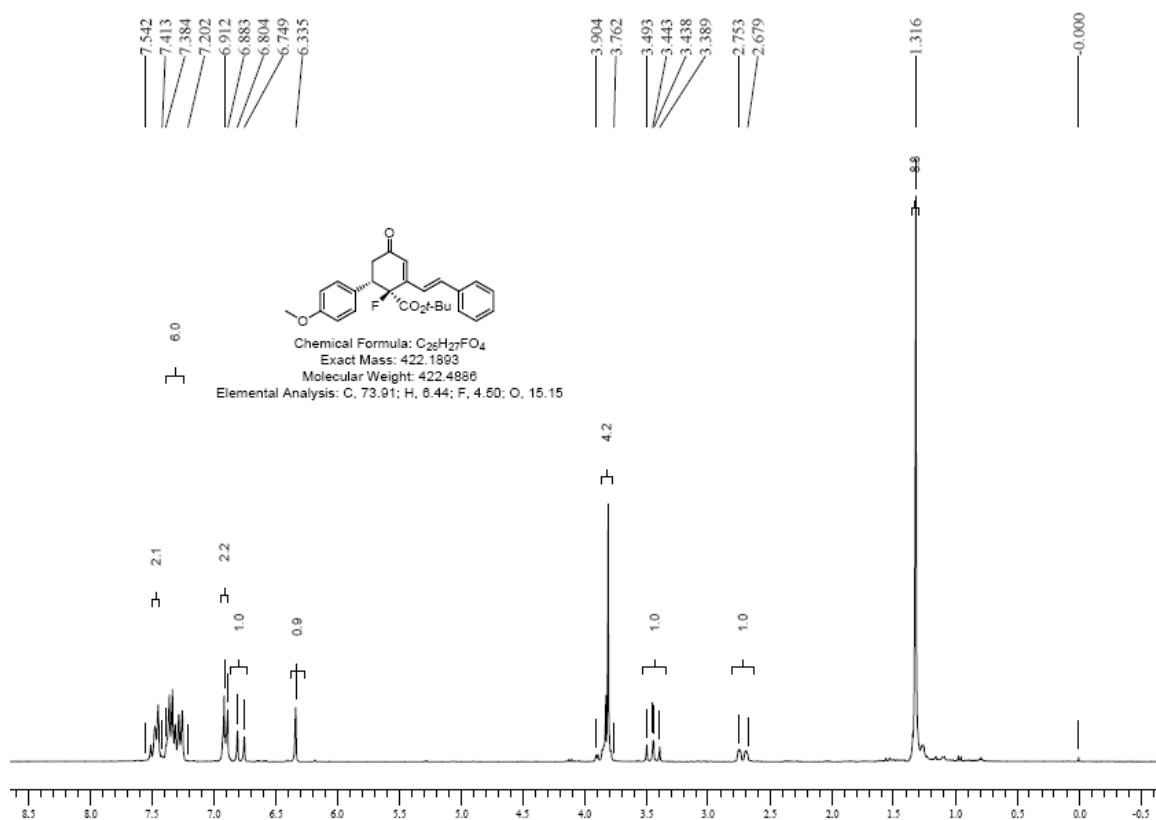
(1*S*,6*S*,*E*)-*tert*-butyl-1-fluoro-6-(4-methoxyphenyl)-4-oxo-2-styrylcyclohex-2-enec arboxylate 5n

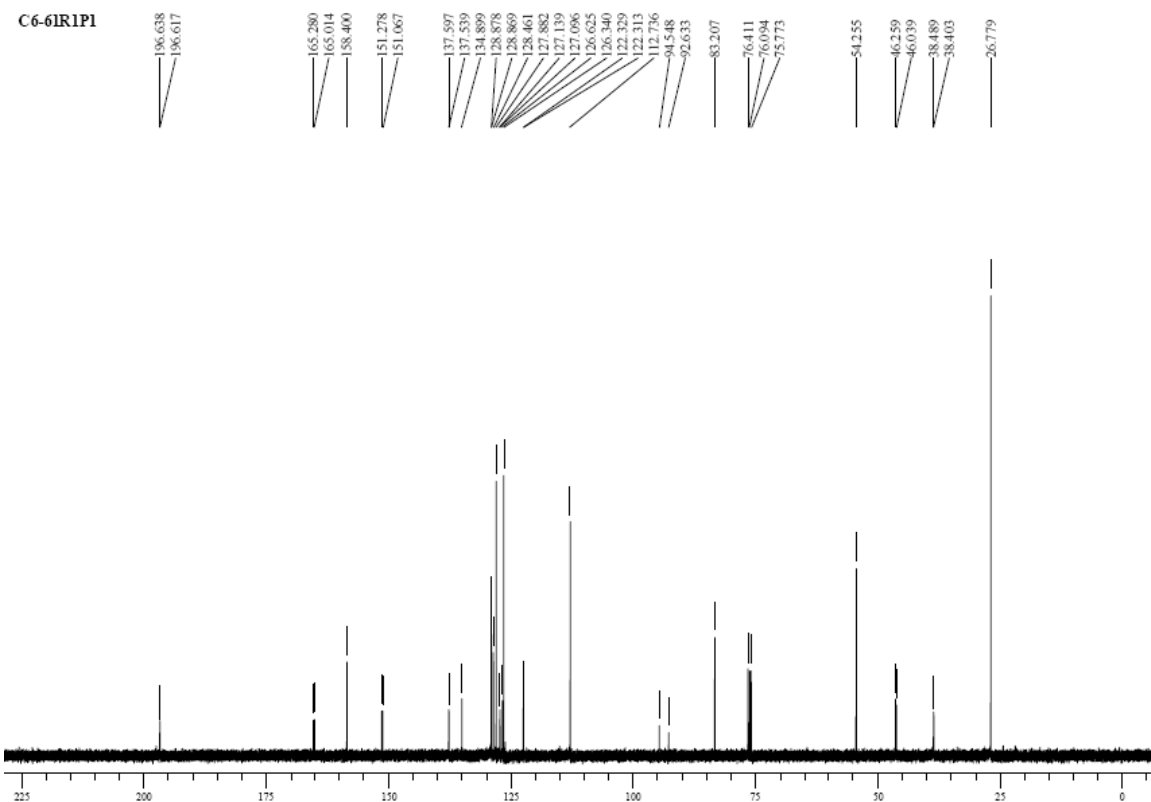
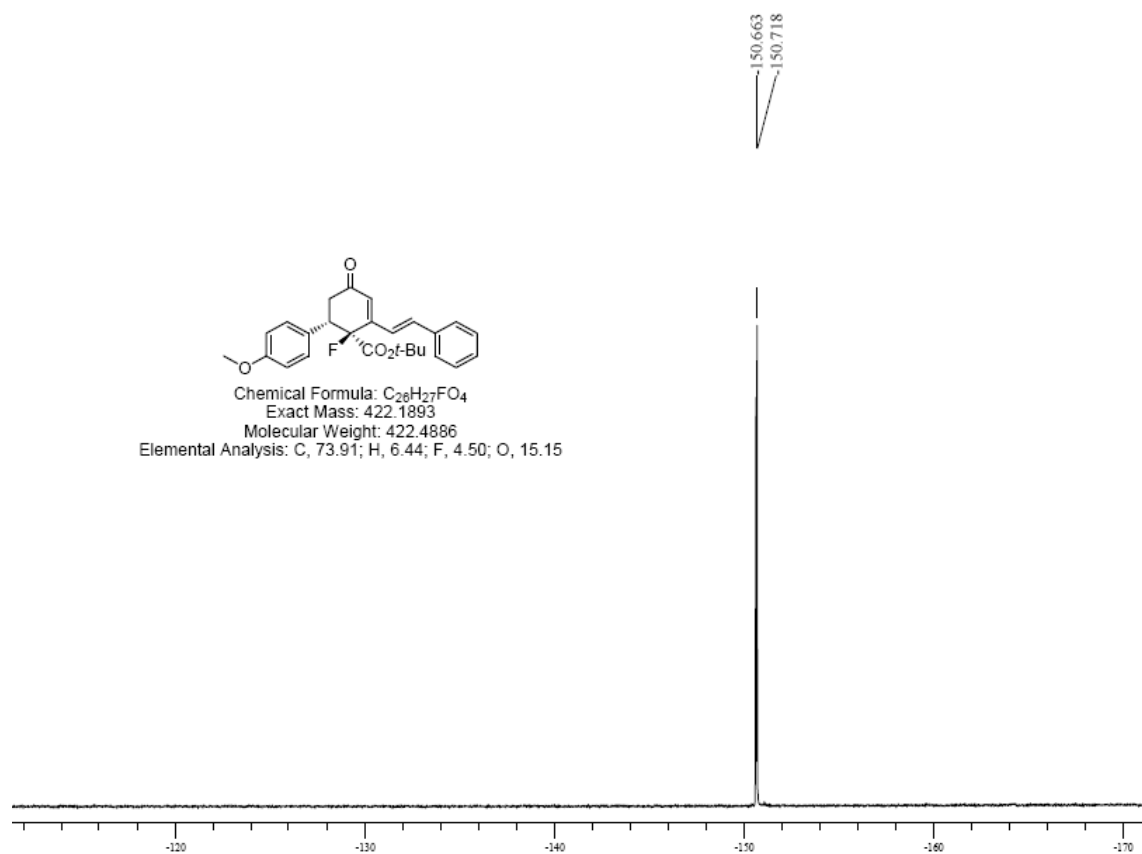




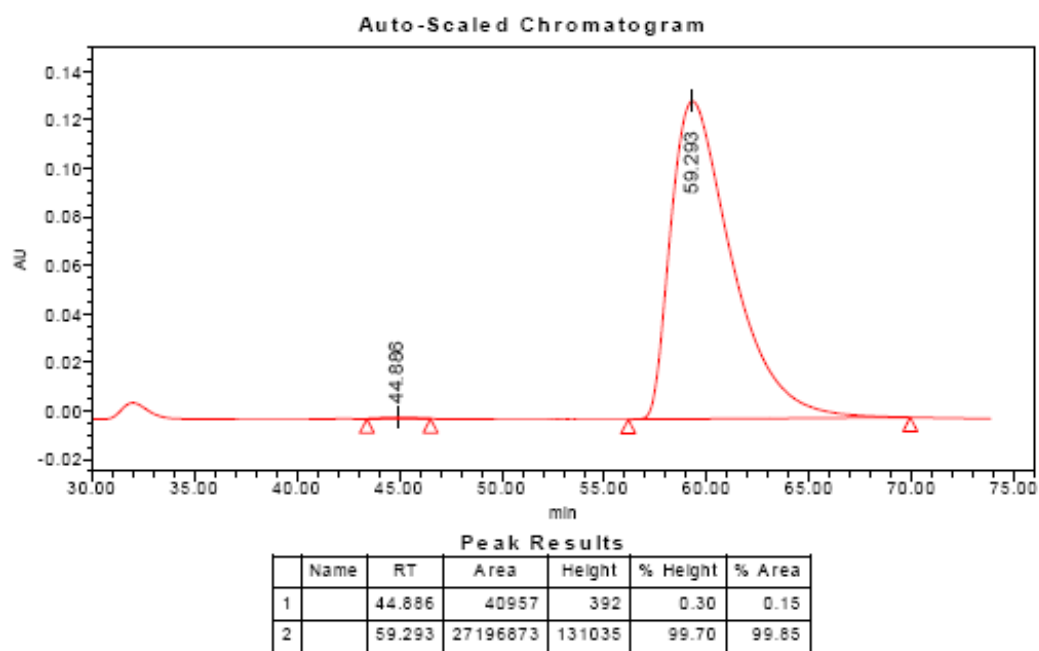
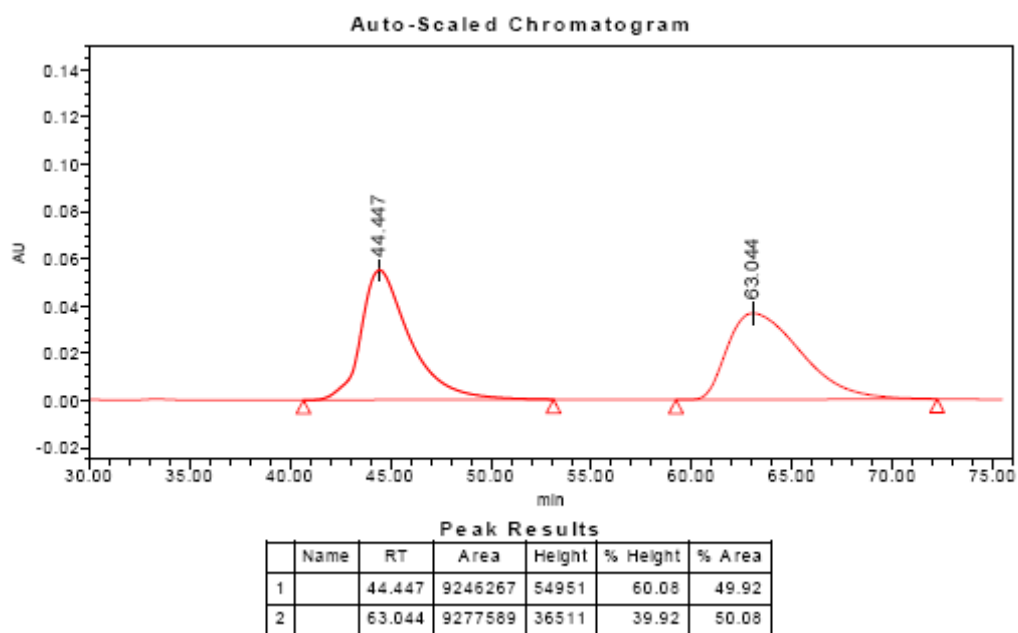
Peak Results

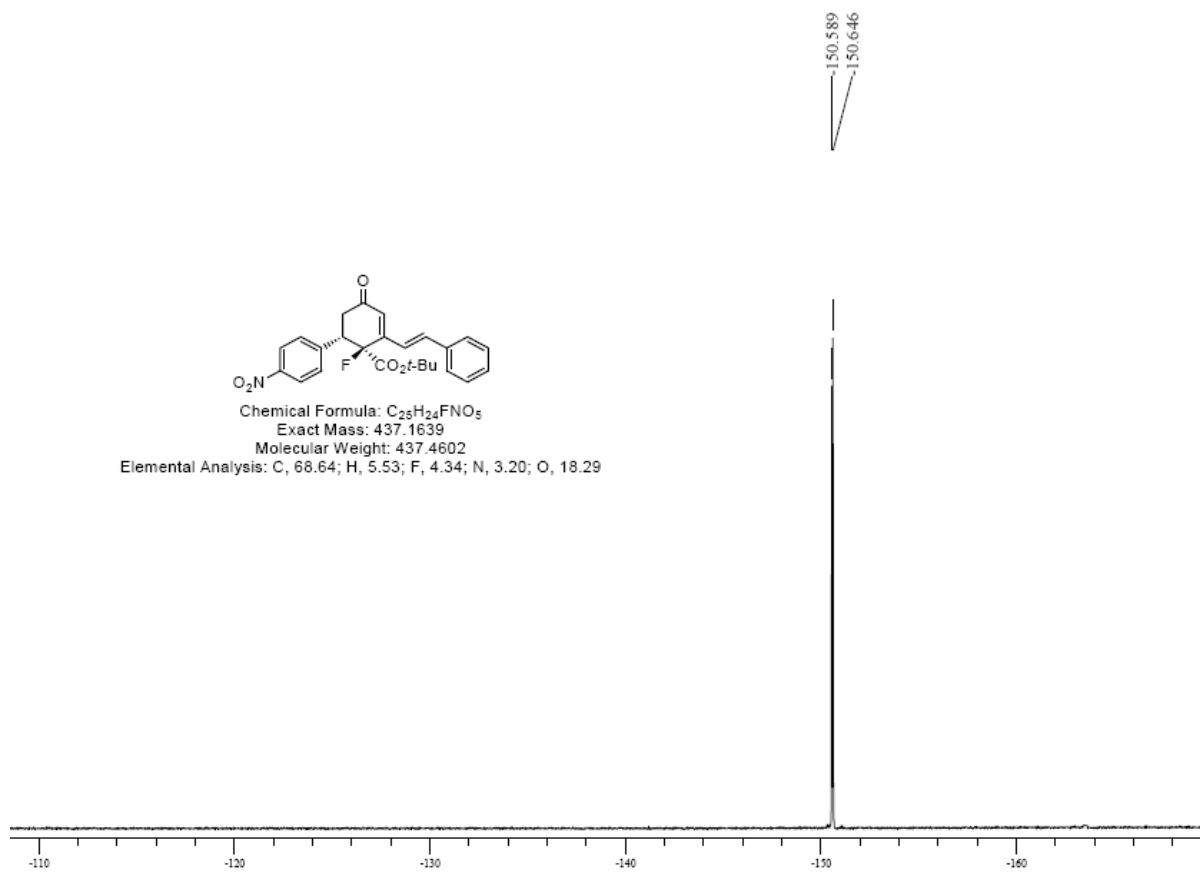
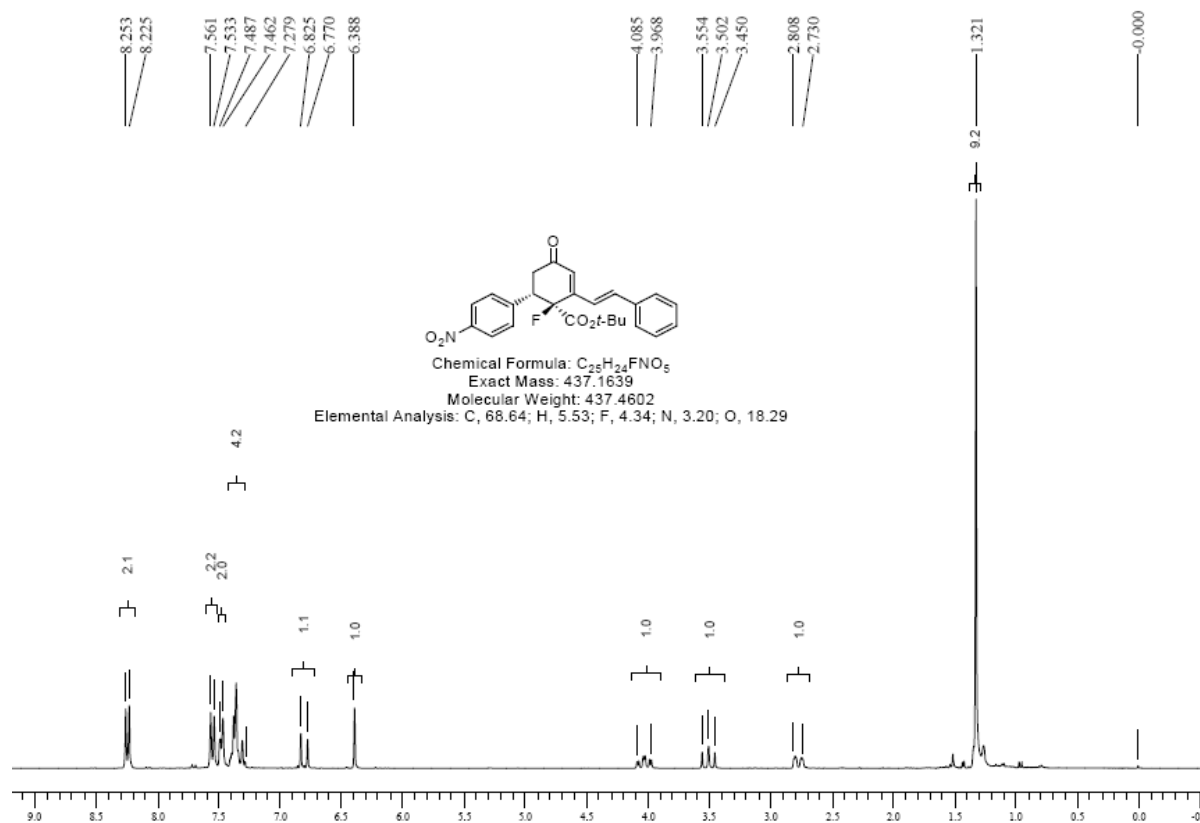
	Name	RT	Area	Height	% Height	% Area
1		26.734	6185875	73294	99.53	99.47
2		30.933	32718	-343	0.47	0.53

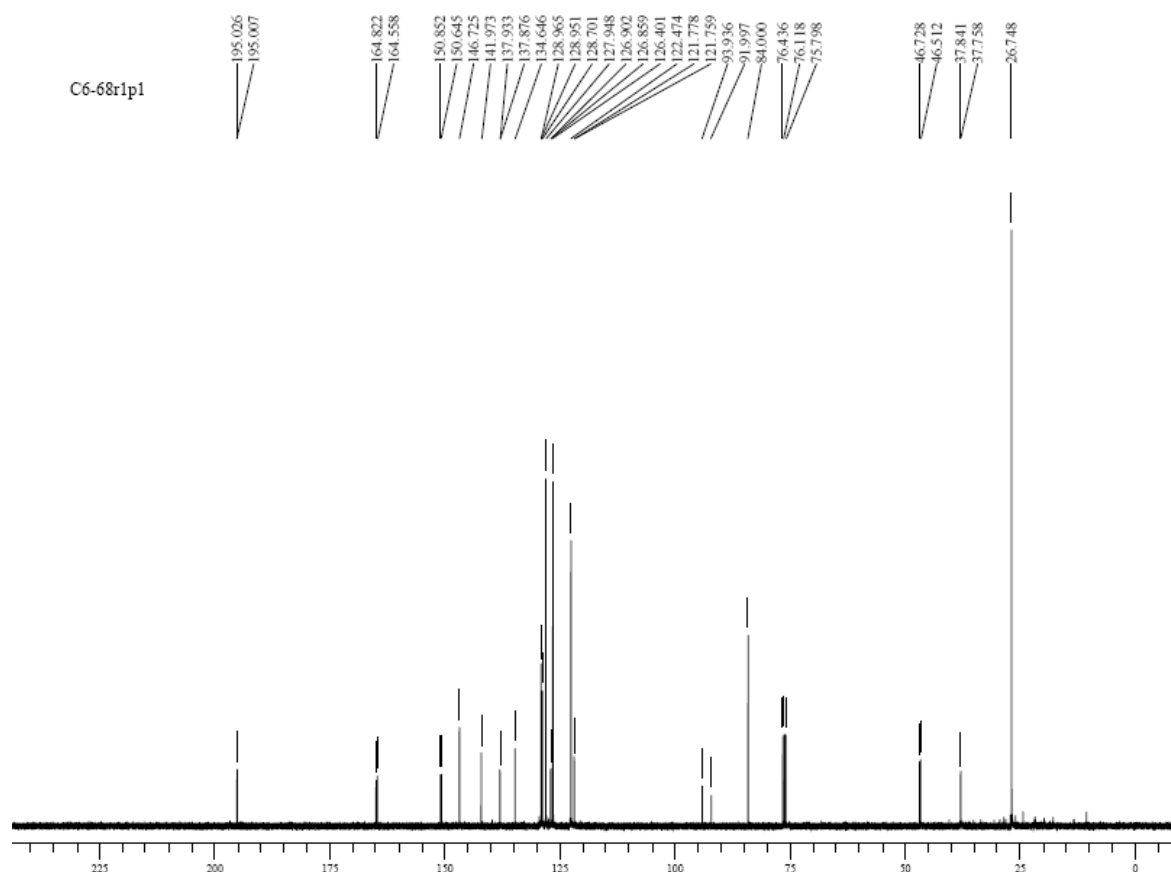




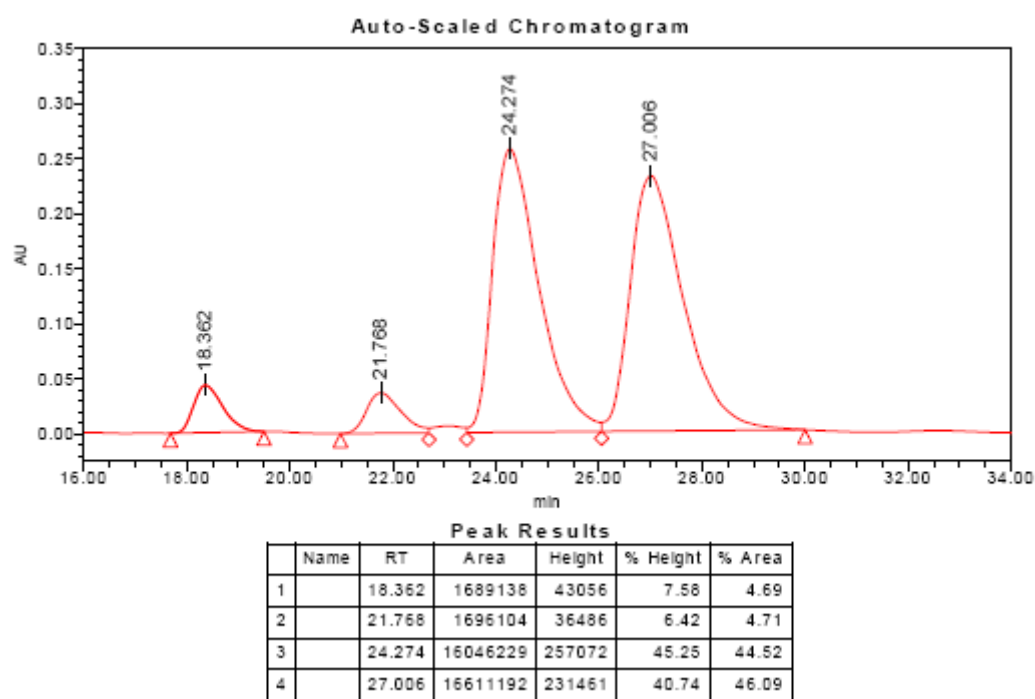
(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-6-(4-nitrophenyl)-4-oxo-2-styrylcyclohex-2-enecarboxylate 5o

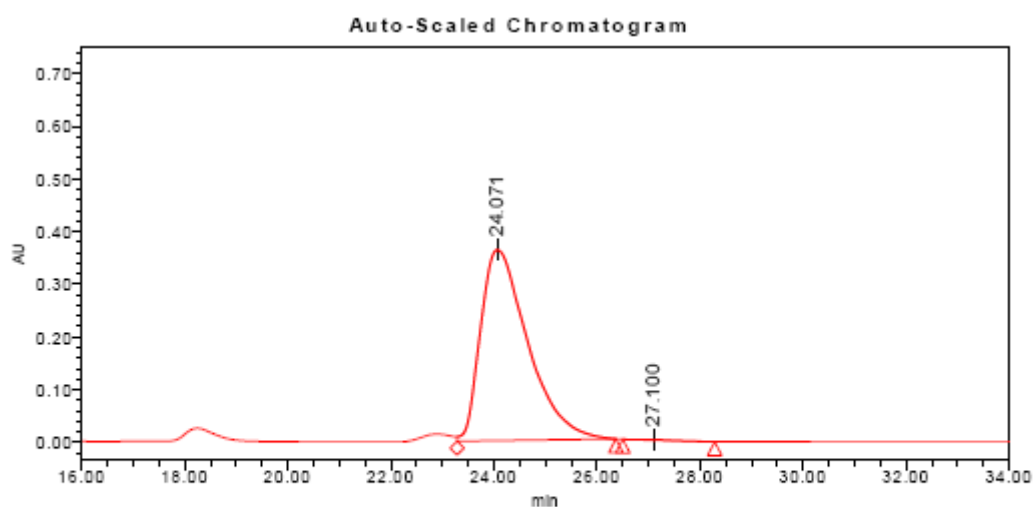






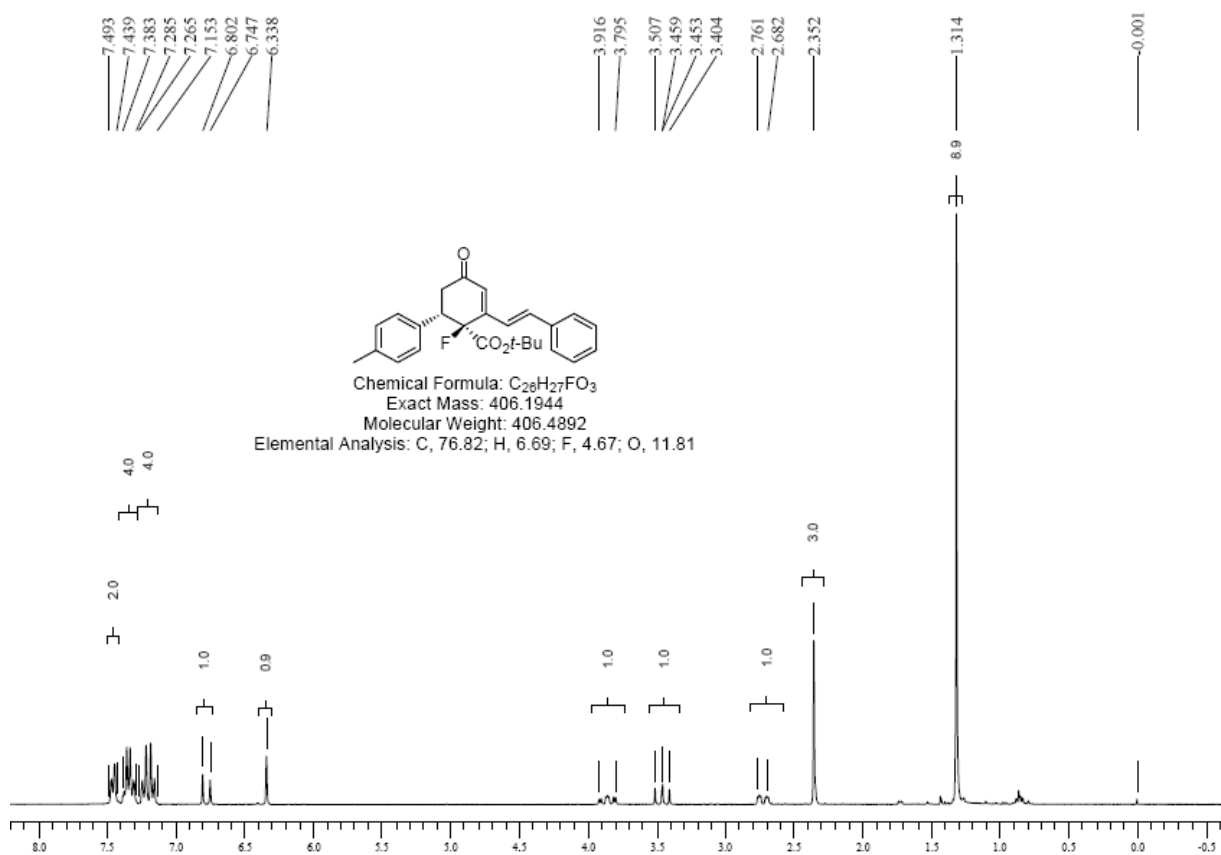
(1*S*,6*S*,*E*)-*tert*-butyl-1-fluoro-4-oxo-2-styryl-6-*p*-tolylcyclohex-2-enecarboxylate 5p

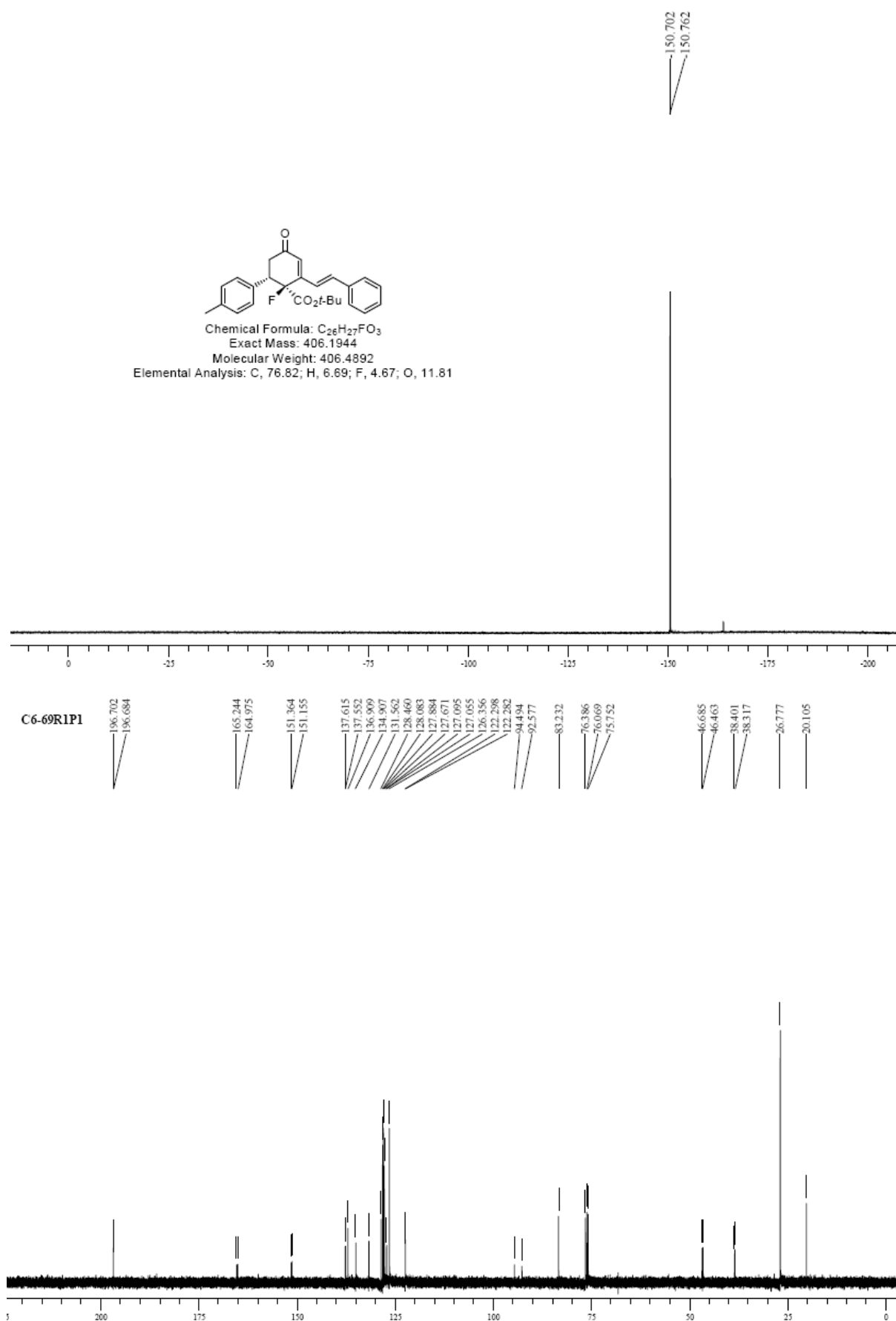




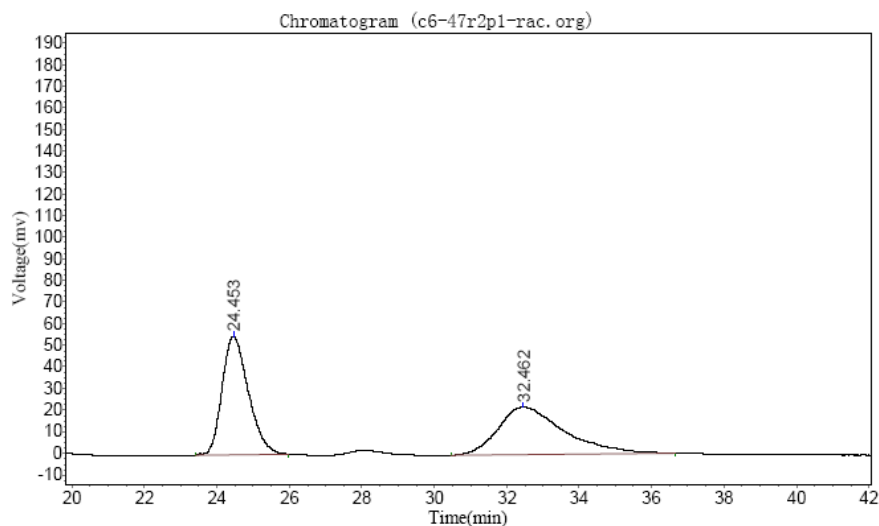
Peak Results

	Name	RT	Area	Height	% Height	% Area
1		24.071	23055563	362285	99.70	99.81
2		27.100	44615	1093	0.30	0.19

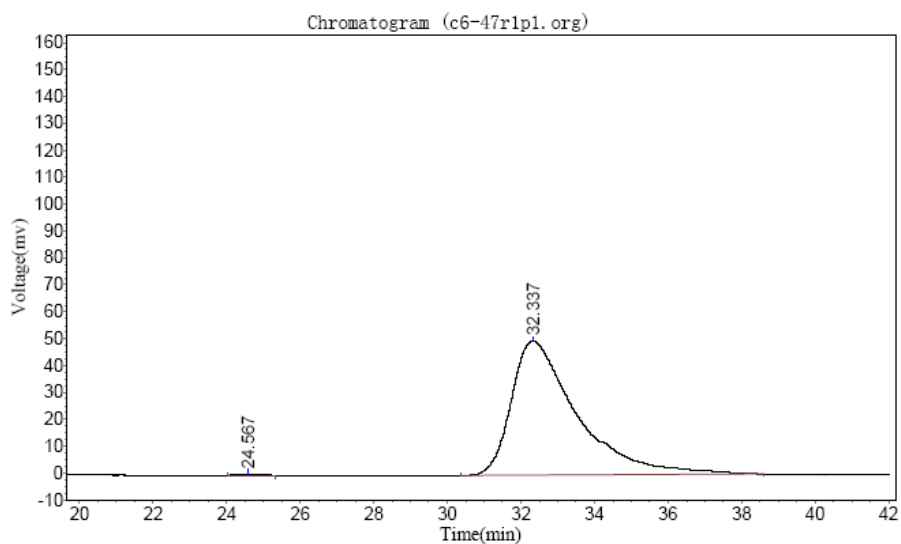




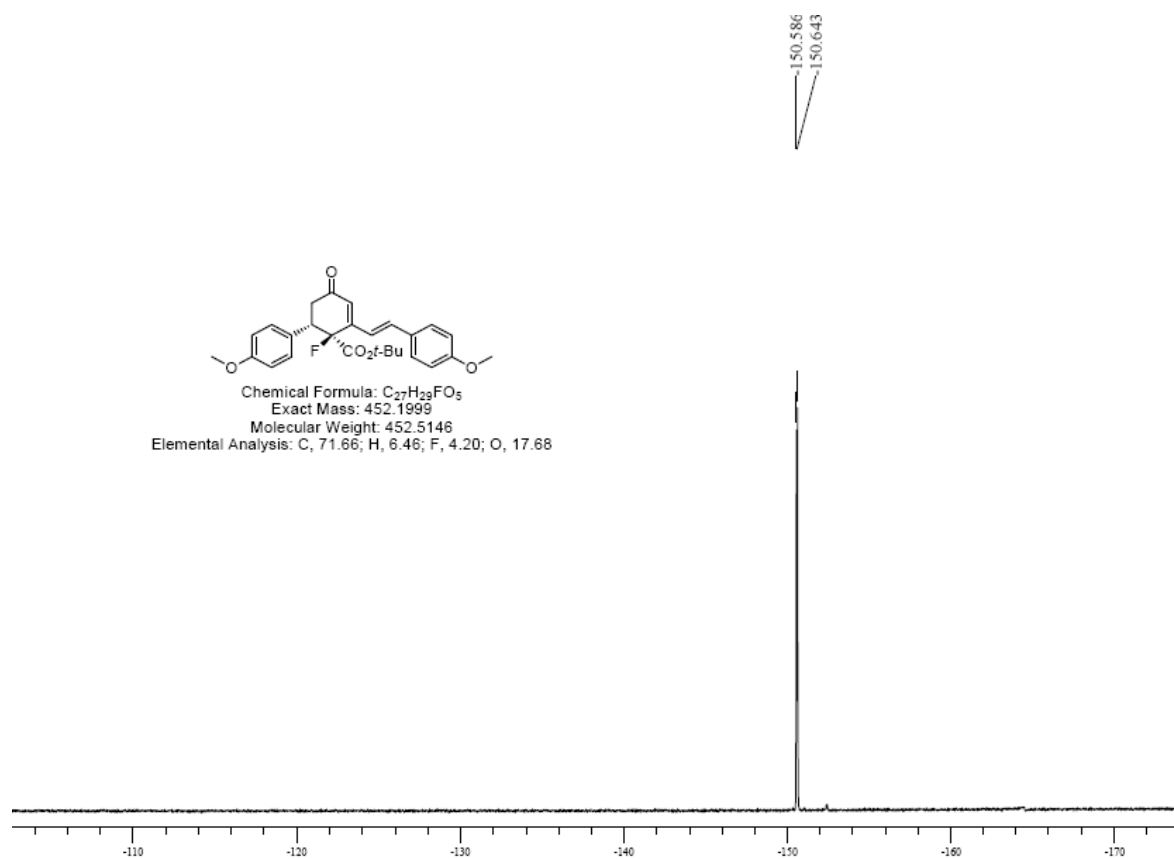
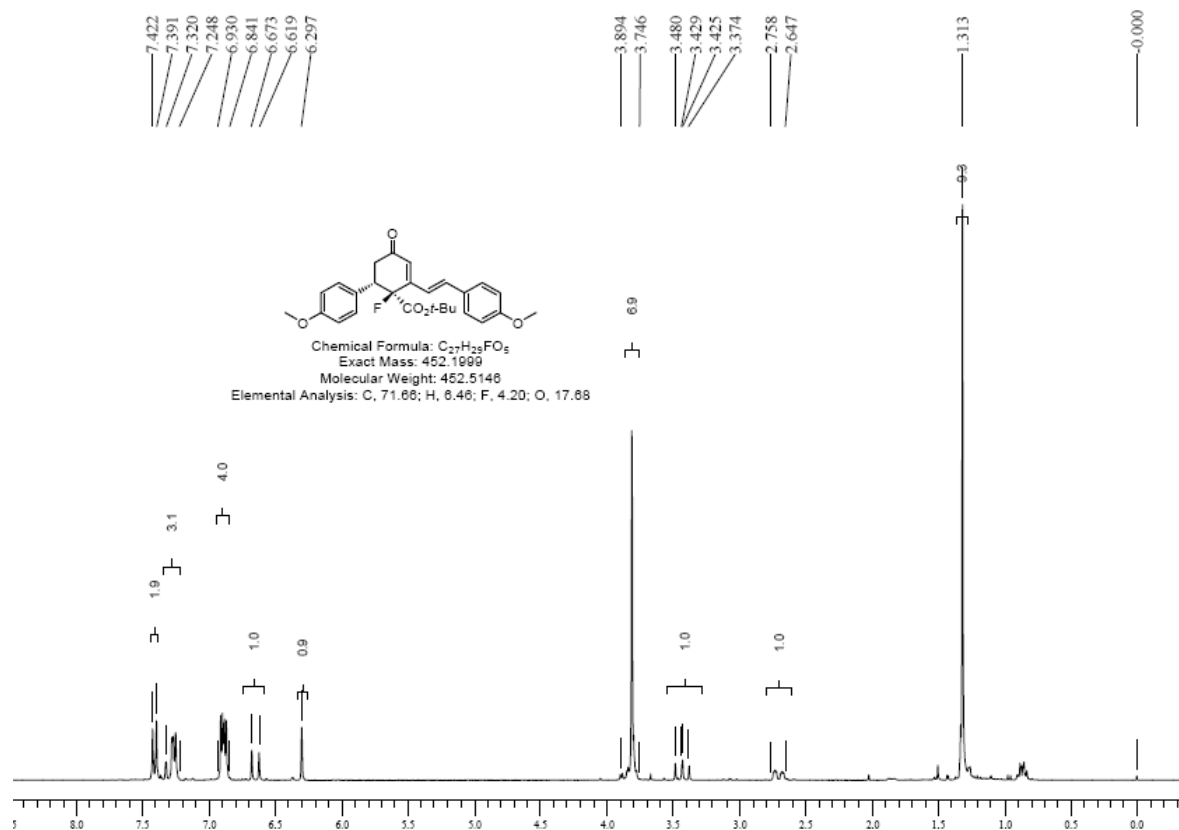
(1*S*,6*S*,*E*)-*tert*-butyl-1-fluoro-6-(4-methoxyphenyl)-2-(4-methoxystyryl)-4-oxocyclohex-2-enecarboxy
late 5q

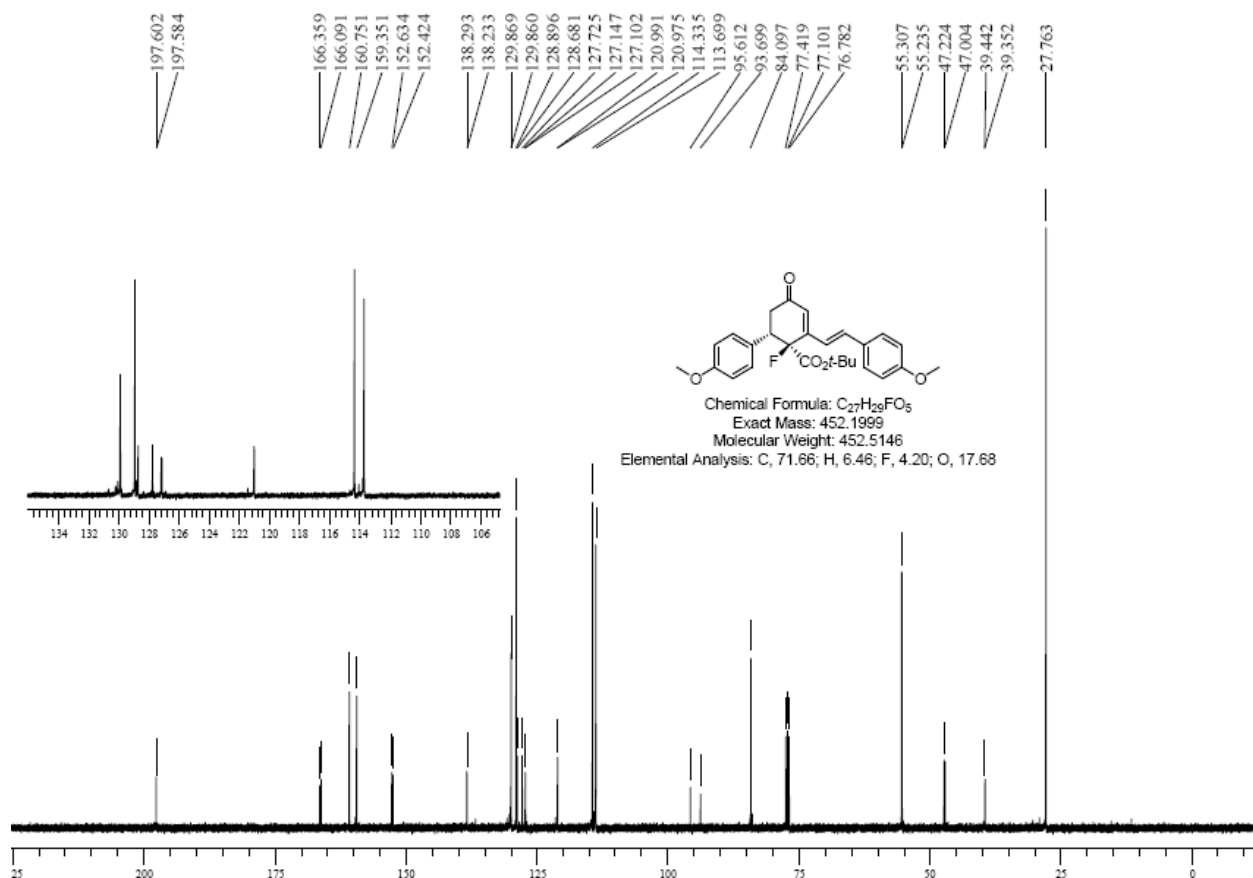


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.453	54918.527	2767952.500	49.8132
2		32.462	22067.969	2788707.000	50.1868
Total			76986.496	5556659.500	100.0000

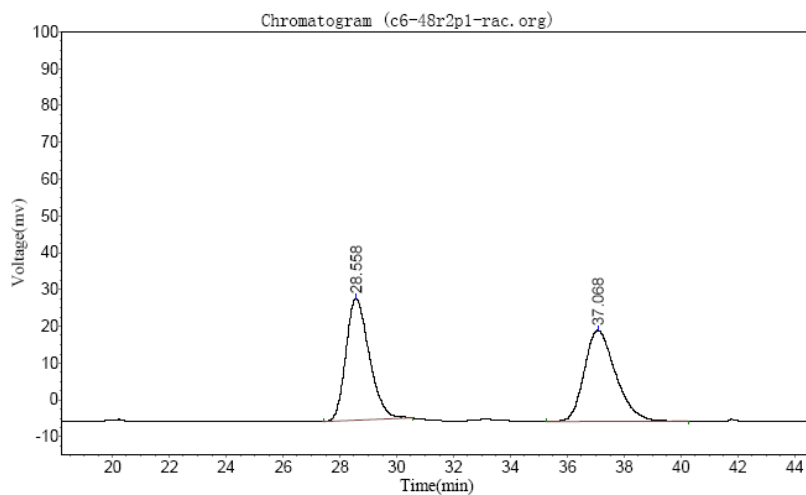


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.567	497.339	20542.404	0.3328
2		32.337	49842.074	6151939.000	99.6672
Total			50339.413	6172481.404	100.0000

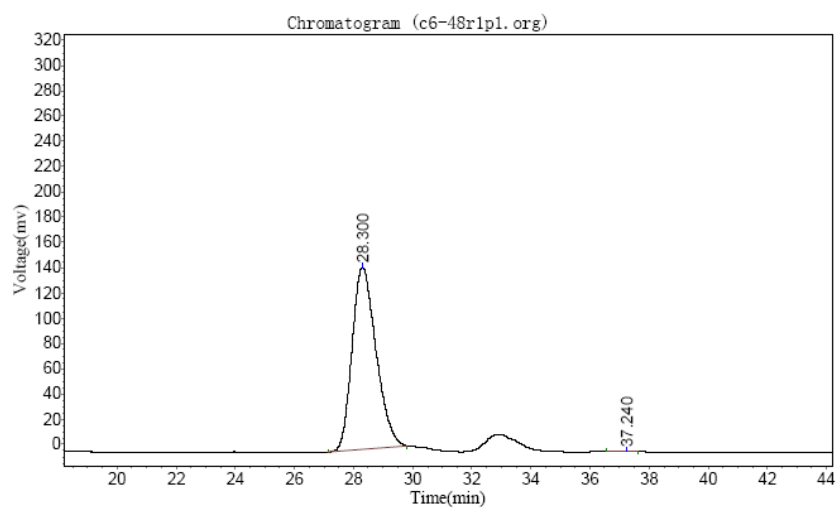




(1*S*,6*S*,*E*)-tert-butyl-1-fluoro-2-(4-methoxystyryl)-6-(4-nitrophenyl)-4-oxocyclohex-2-enecarboxylate 5r

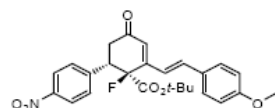
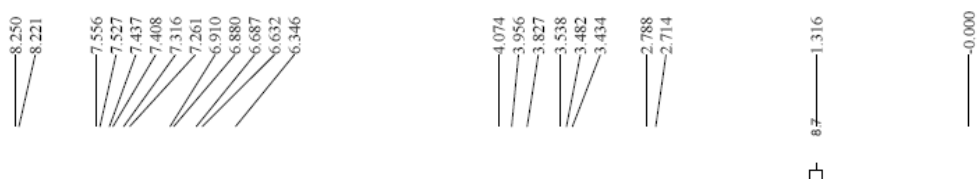


Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.558	33152.914	1879507.625	49.7327
2		37.068	24799.498	1899712.625	50.2673
Total			57952.412	3779220.250	100.0000

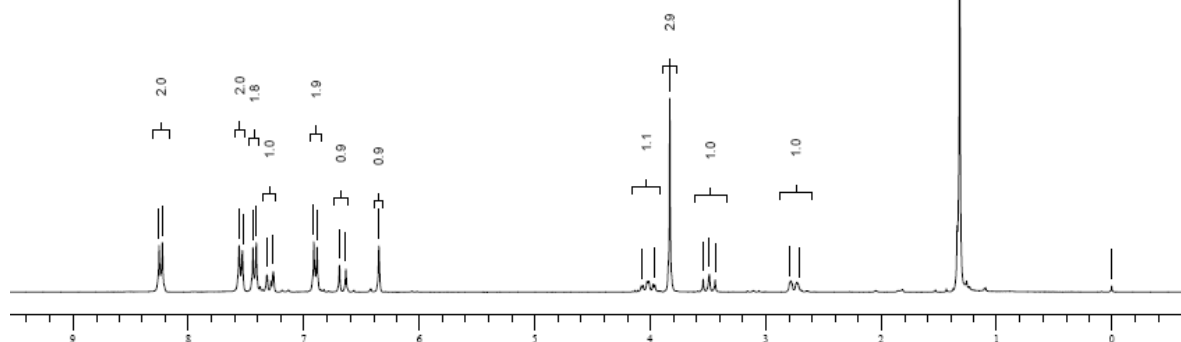


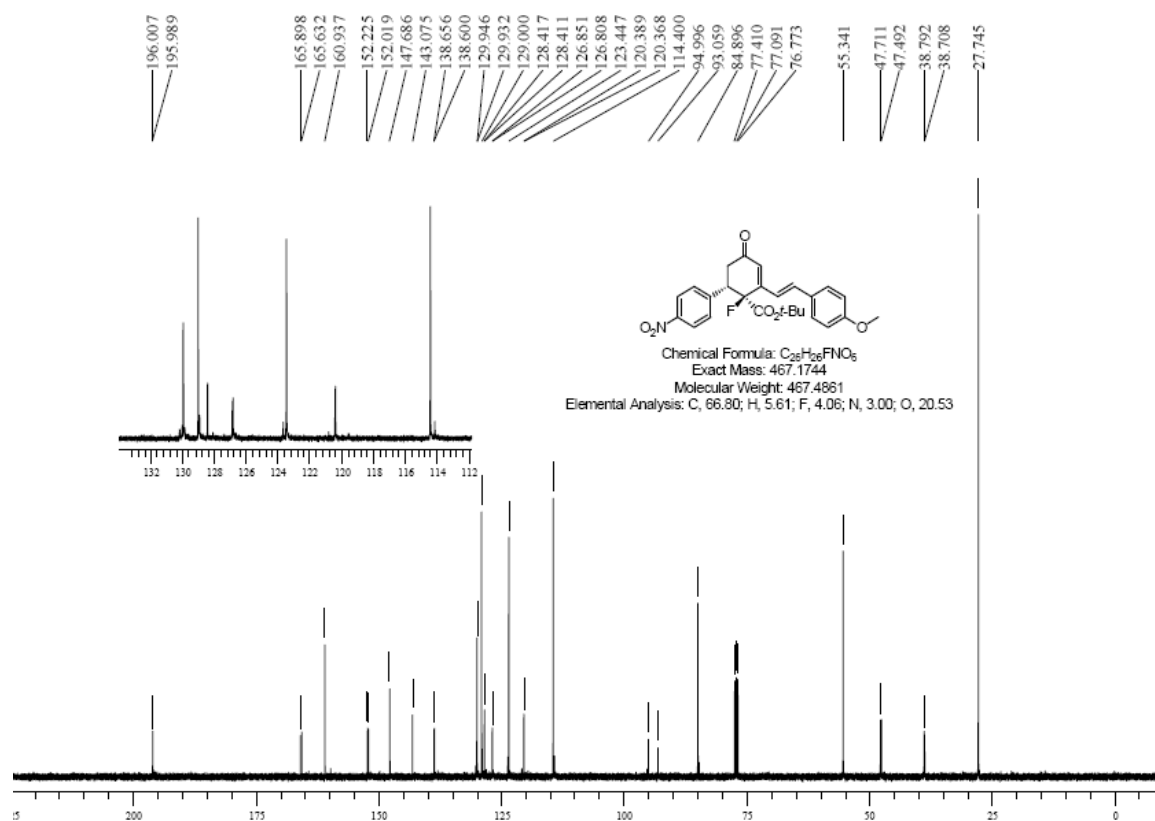
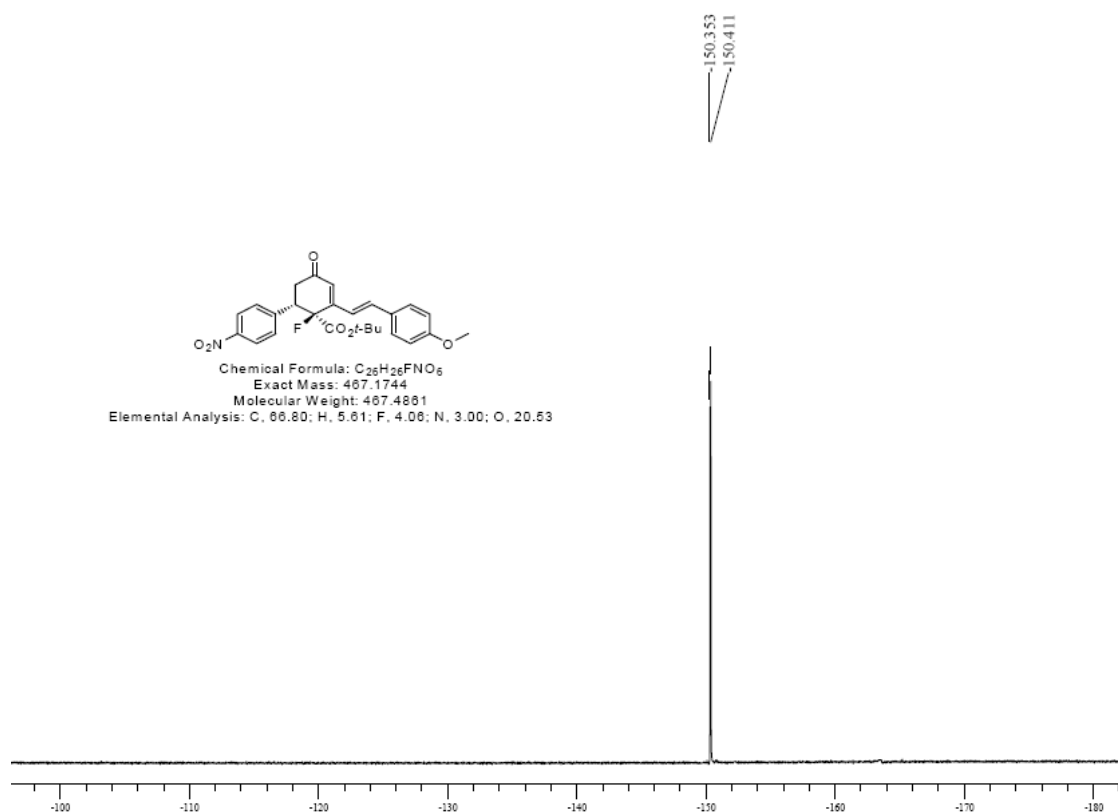
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.300	143837.859	8089020.500	99.9437
2		37.240	143.746	4557.189	0.0563
Total			143981.605	8093577.689	100.0000

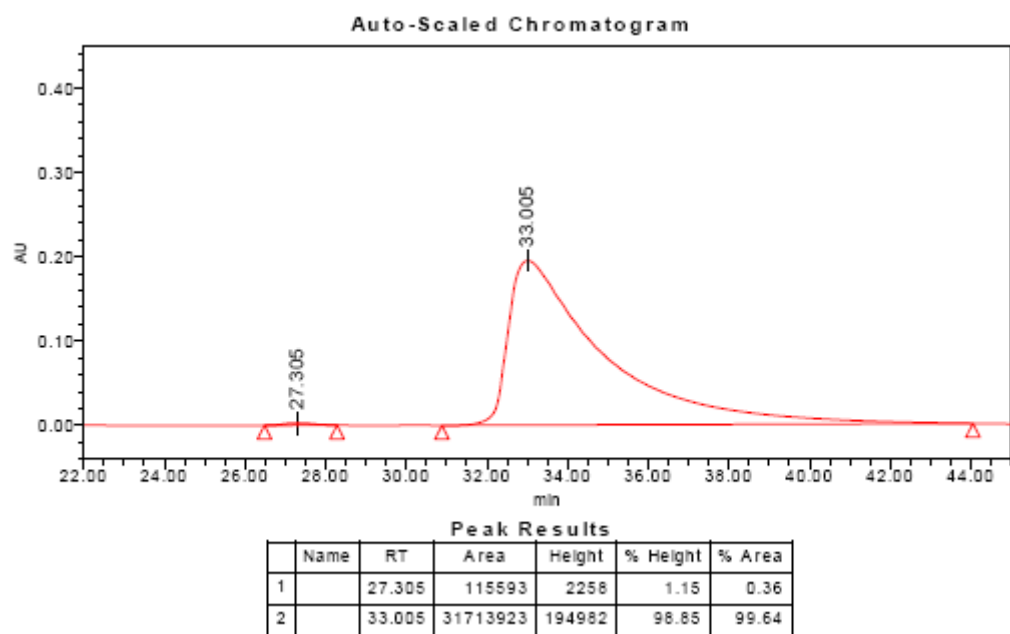
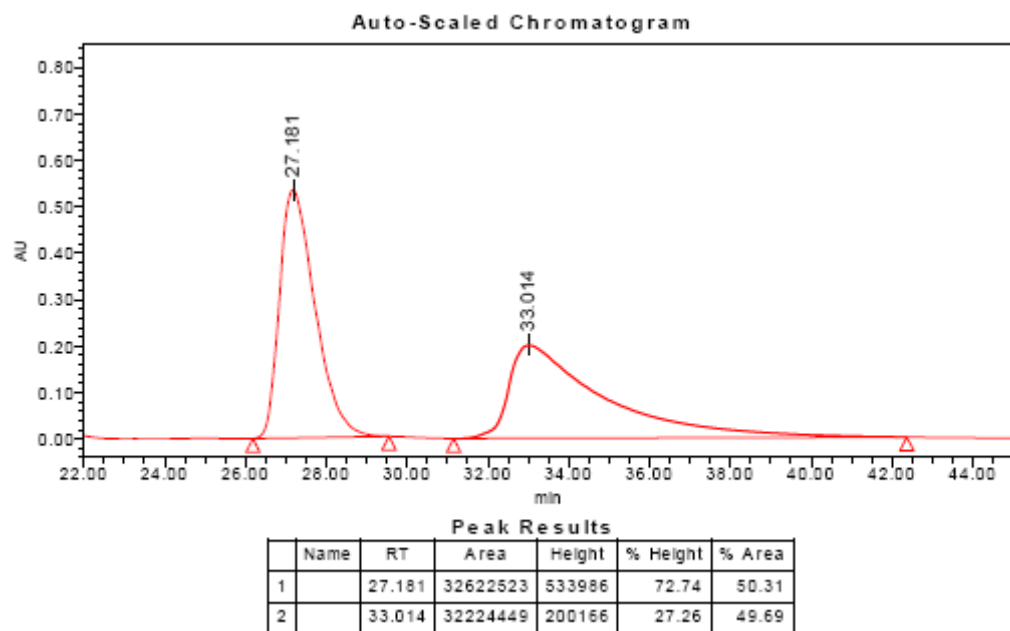


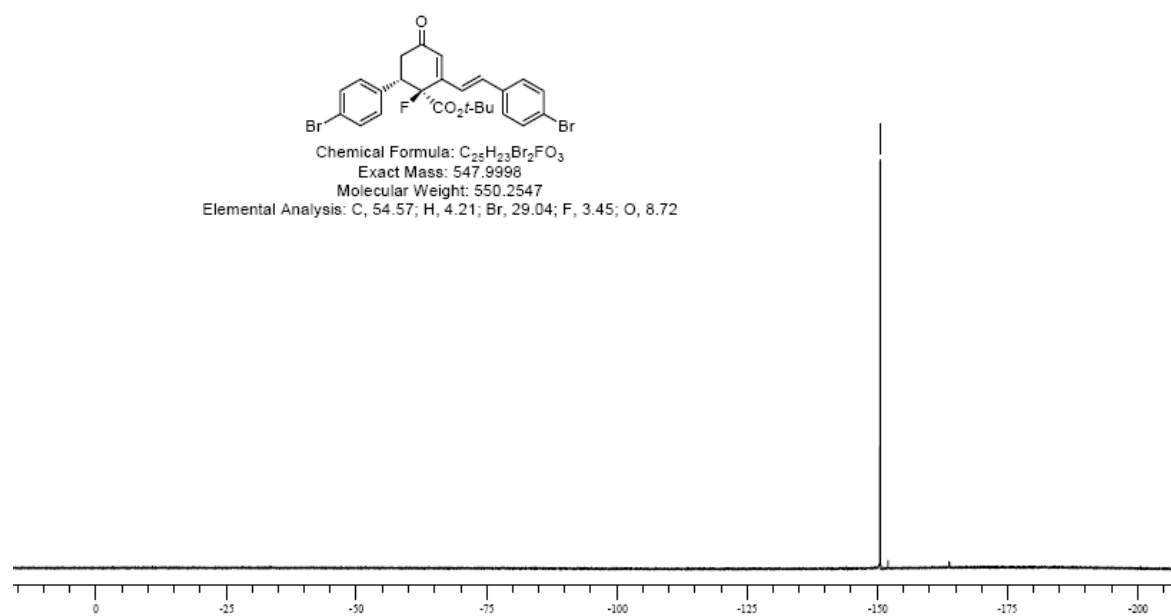
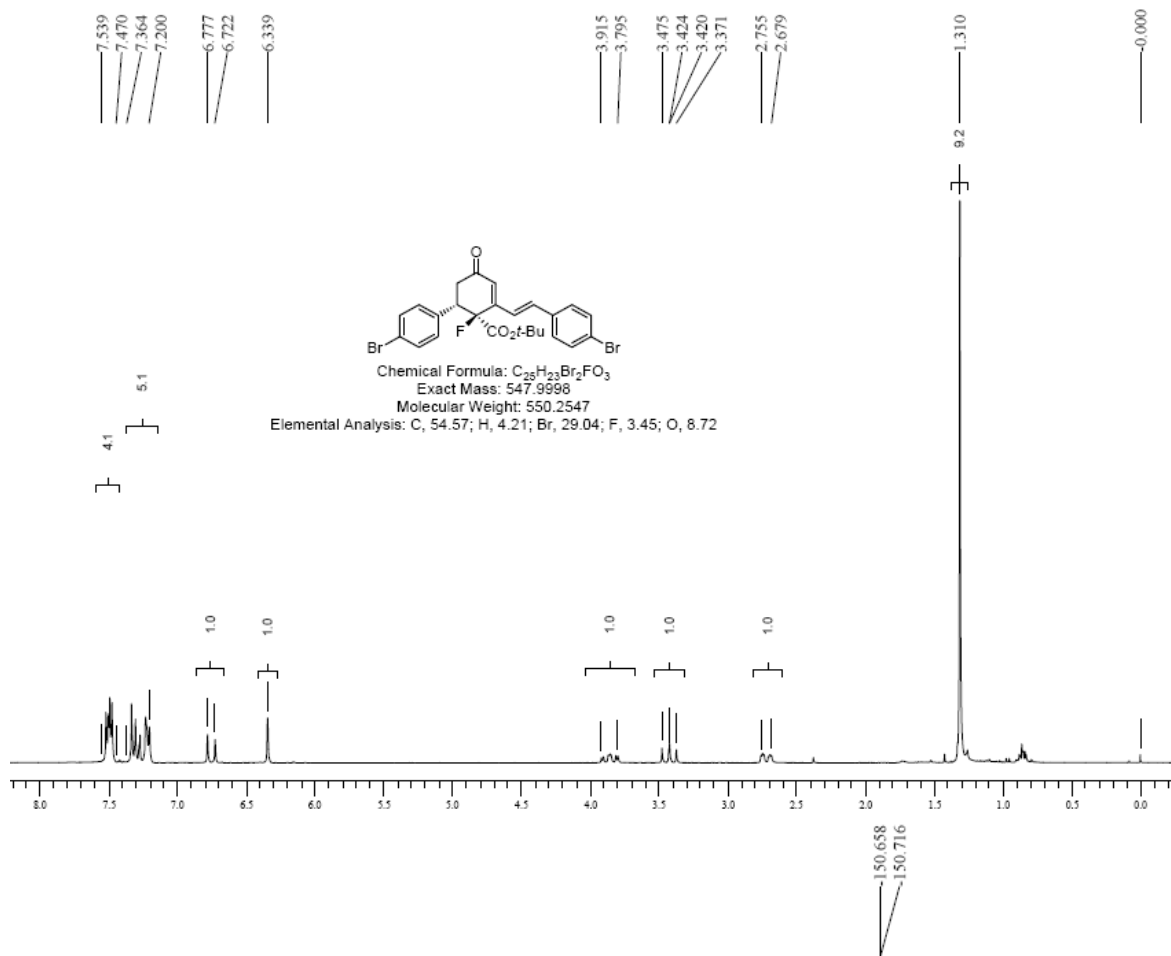
Chemical Formula: $C_{26}H_{26}FNO_6$
 Exact Mass: 467.1744
 Molecular Weight: 467.4881
 Elemental Analysis: C, 66.80; H, 5.61; F, 4.08; N, 3.00; O, 20.53

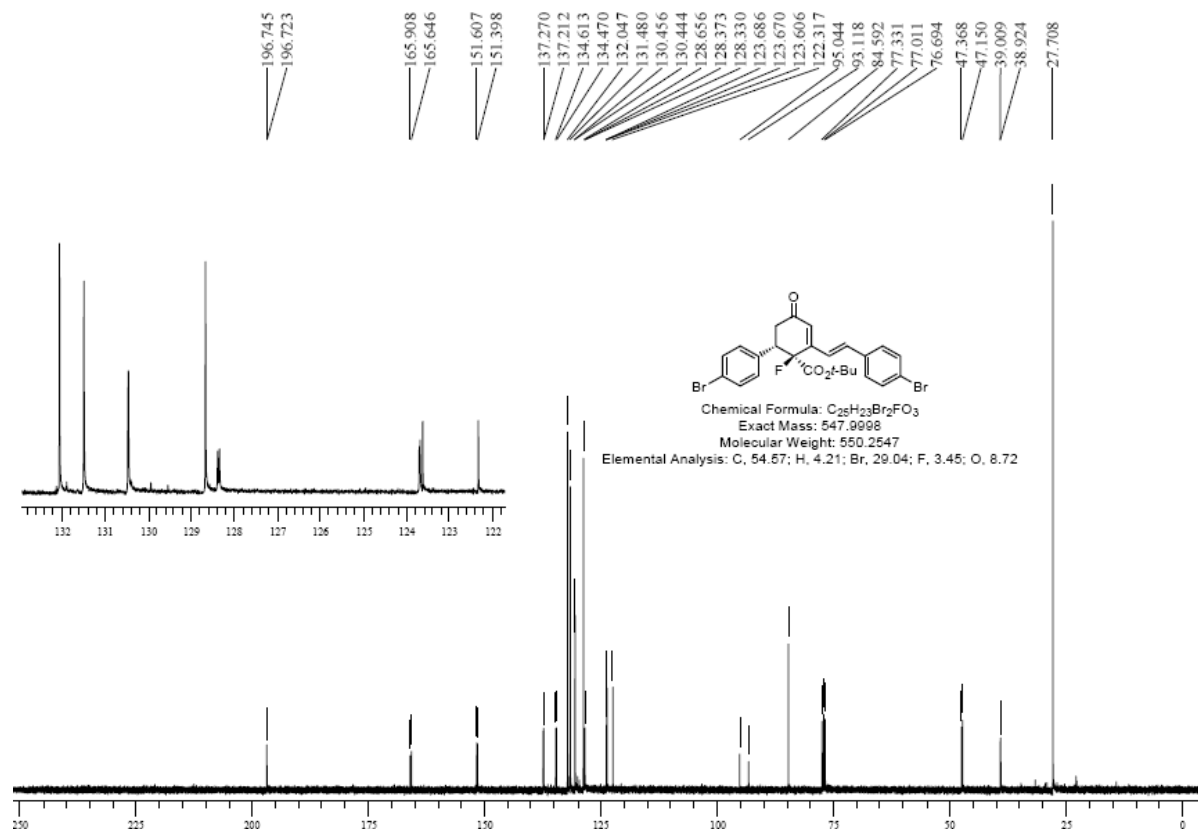




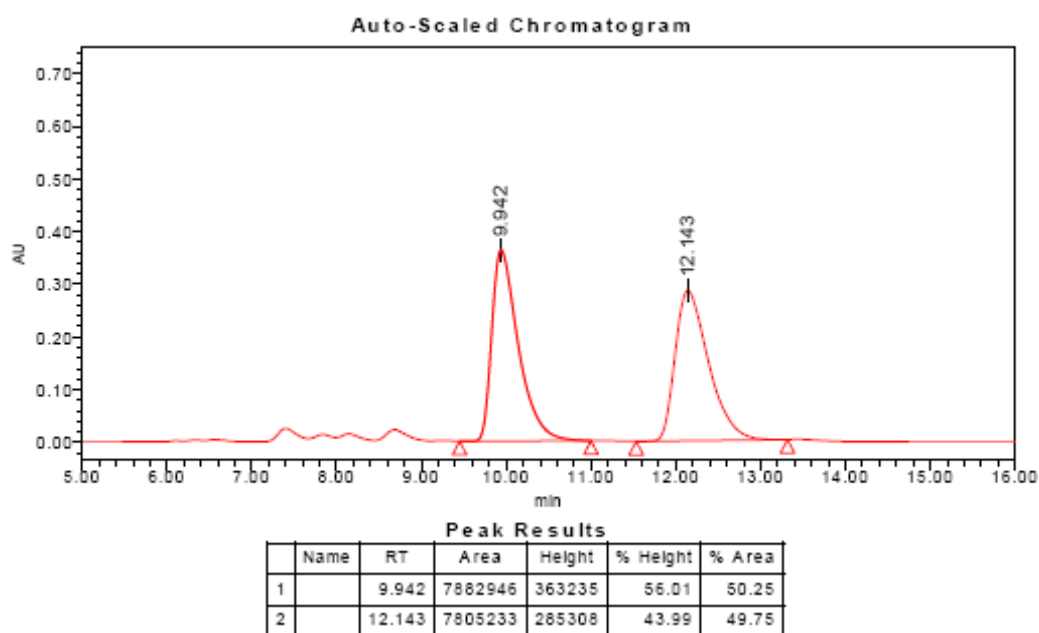
(1*S*,6*S*,*E*)-*tert*-butyl-6-(4-bromophenyl)-2-(4-bromostyryl)-1-fluoro-4-oxocyclohex-2-enecarboxylate 5s

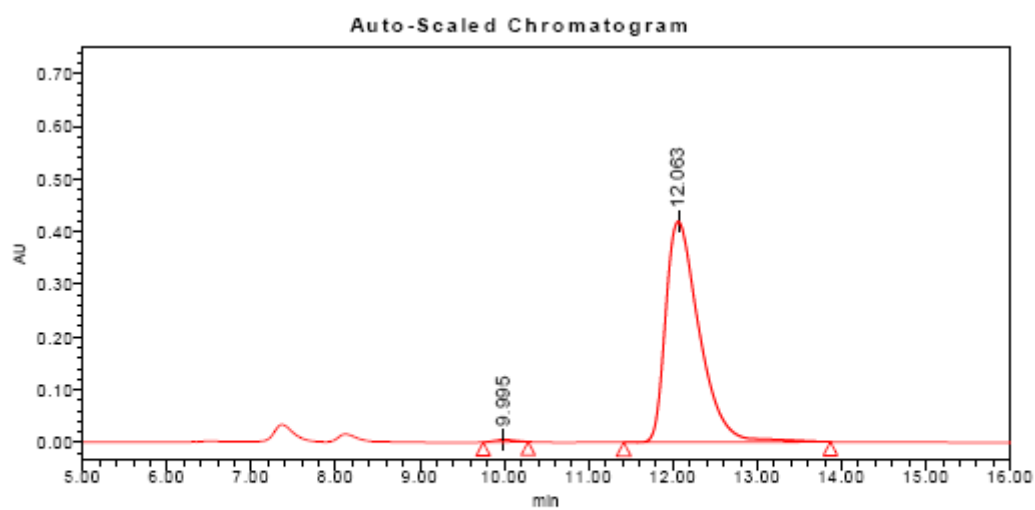






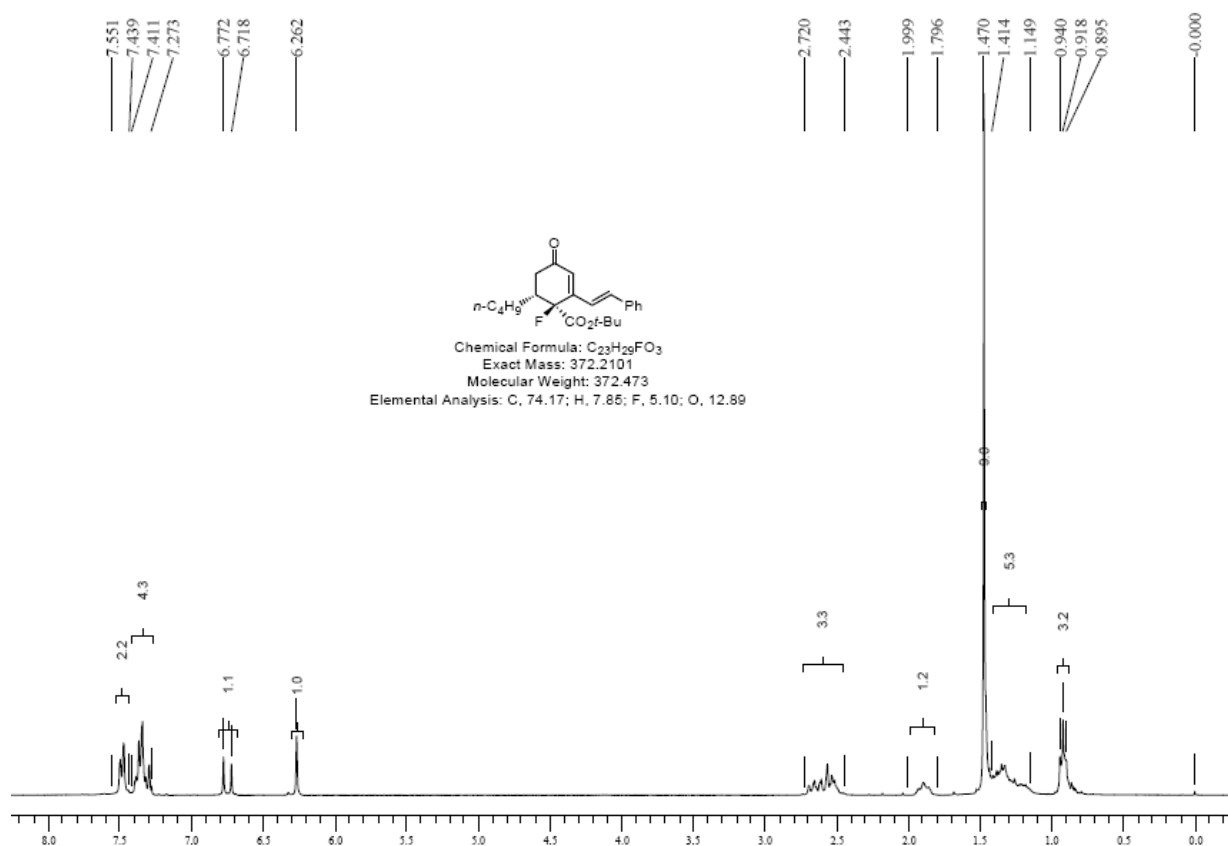
(1*S*,6*R*,*E*)-*tert*-butyl 6-butyl-1-fluoro-4-oxo-2-styrylcyclohex-2-enecarboxylate 5t

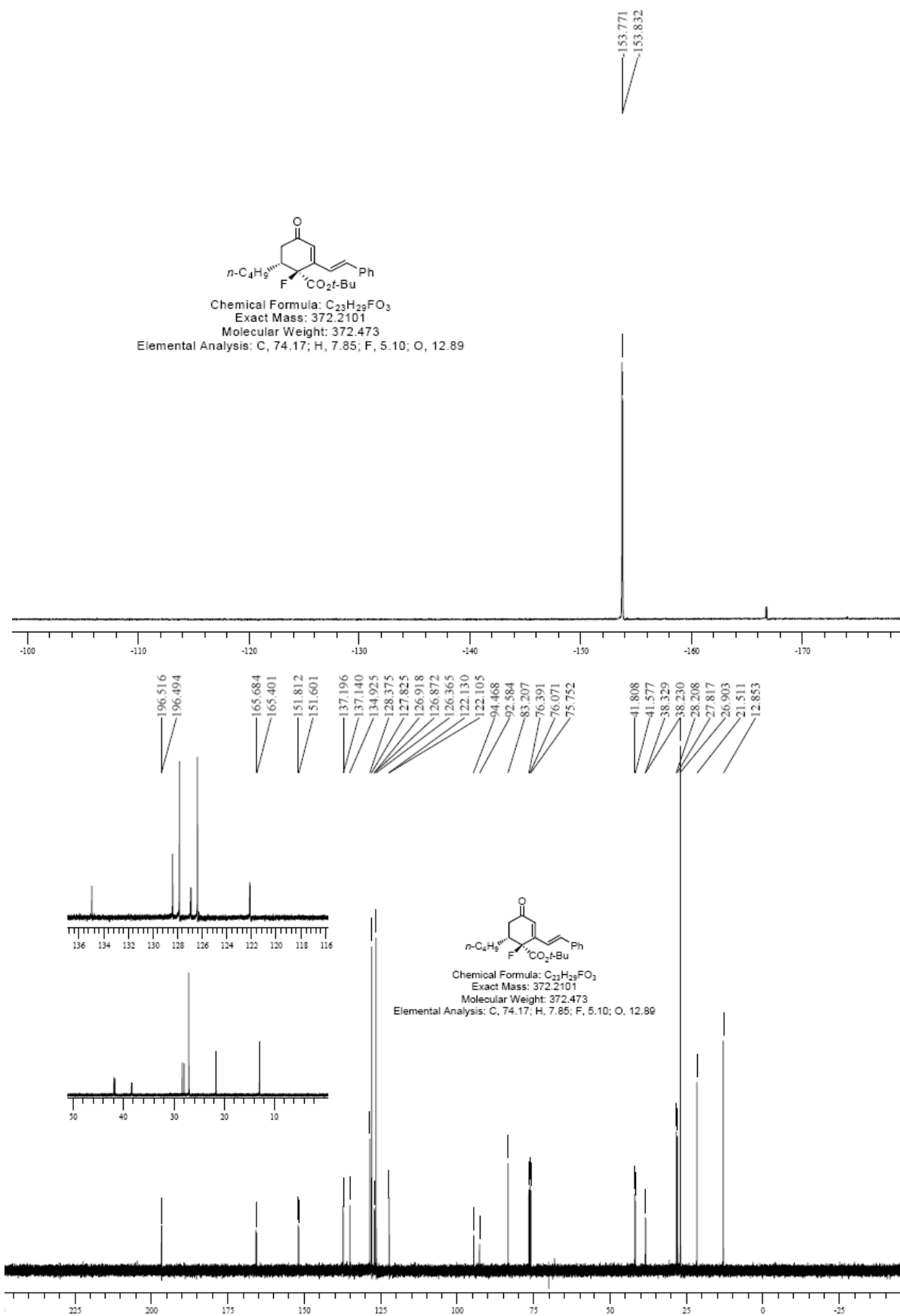




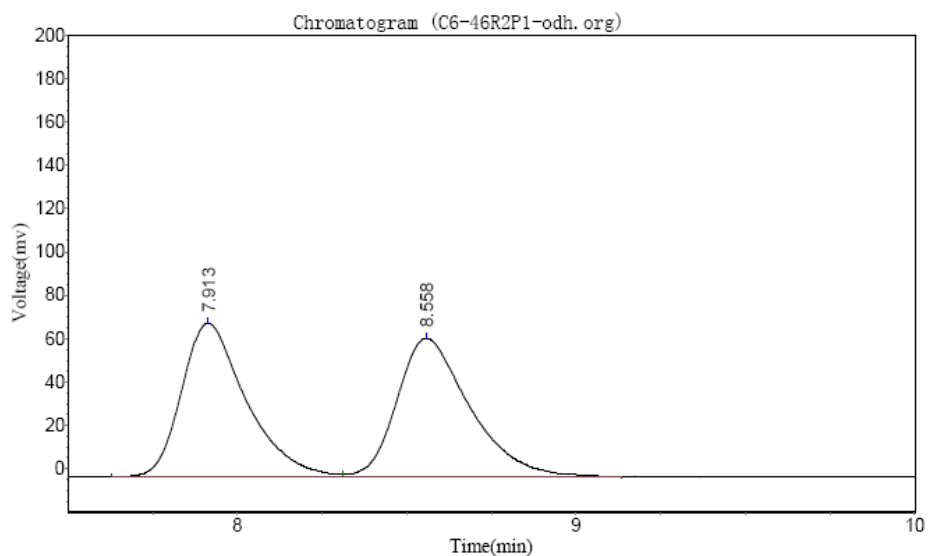
Peak Results

	Name	RT	Area	Height	% Height	% Area
1		9.995	77266	4630	1.09	0.66
2		12.063	11571997	418944	98.91	99.34



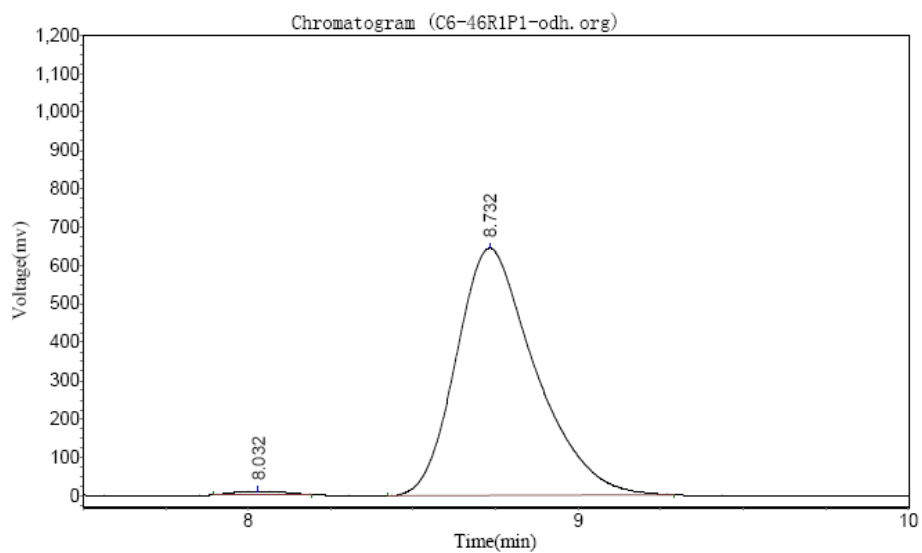


(1*S*,6*R*)-tert-butyl 1-fluoro-2-methyl-4-oxo-6-propylcyclohex-2-enecarboxylate 5u



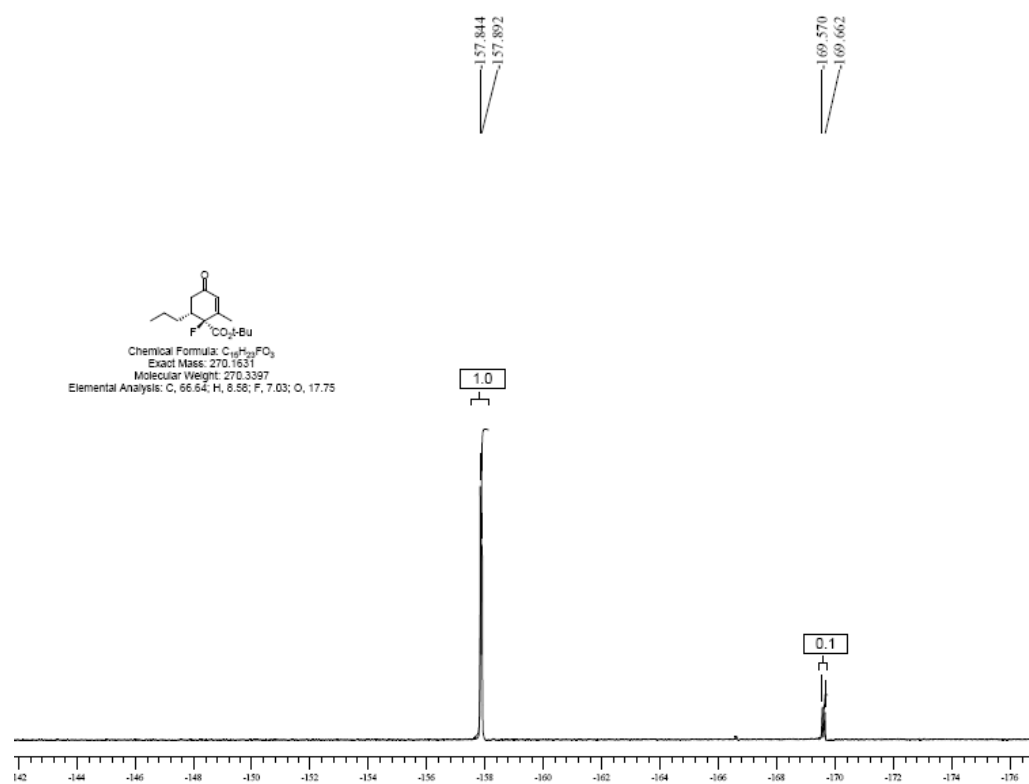
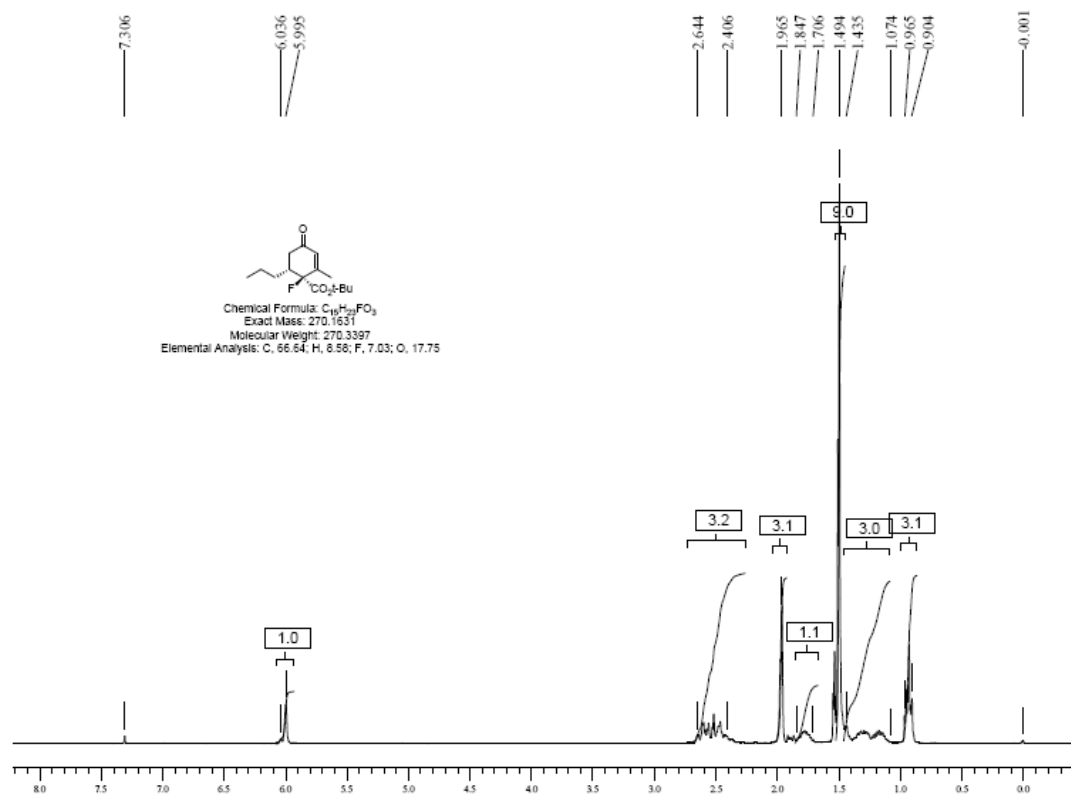
Results

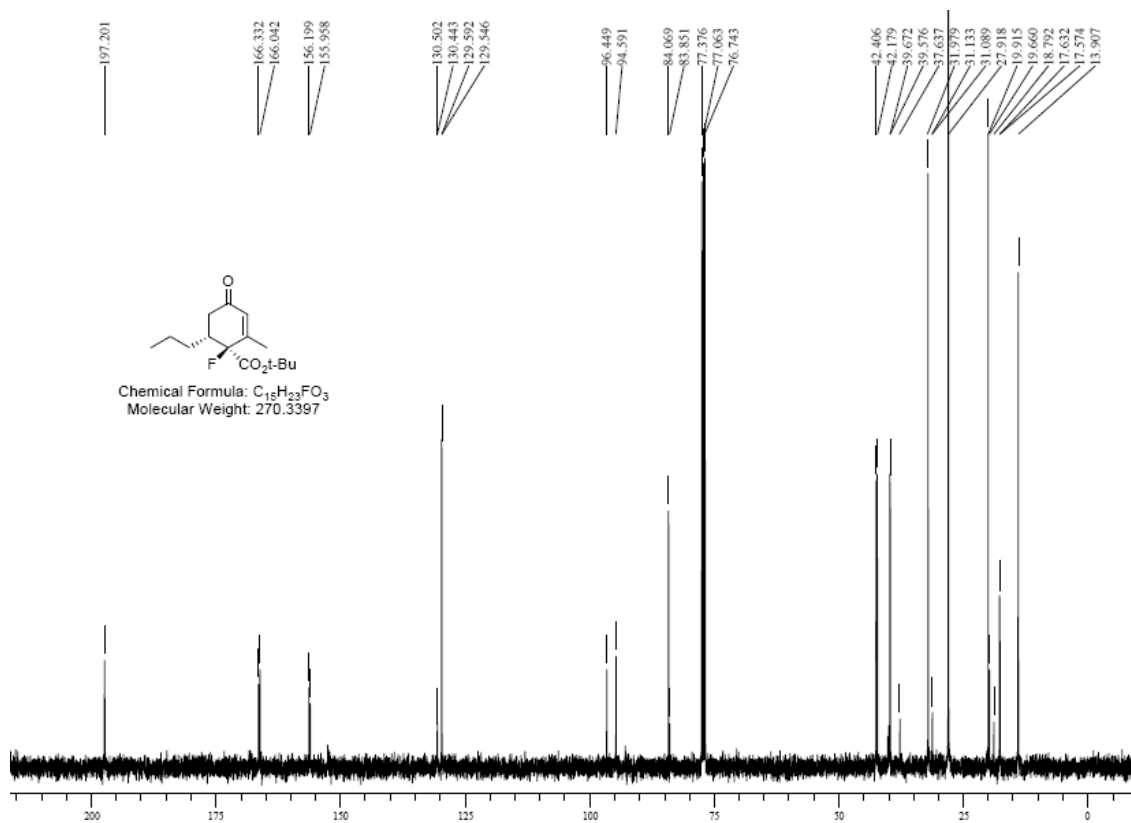
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.913	70531.195	925343.625	49.6369
2		8.558	63616.484	938881.750	50.3631
Total			134147.680	1864225.375	100.0000



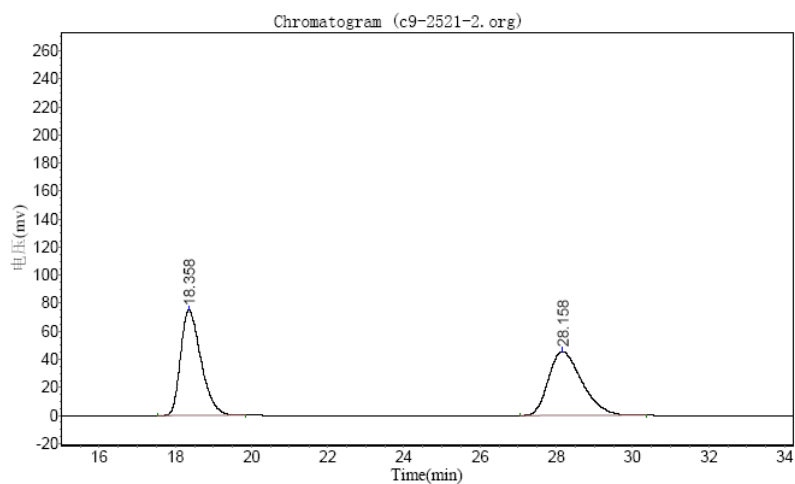
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.032	8496.436	85210.648	0.7923
2		8.732	643547.563	10670180.000	99.2077
Total			652043.998	10755390.648	100.0000

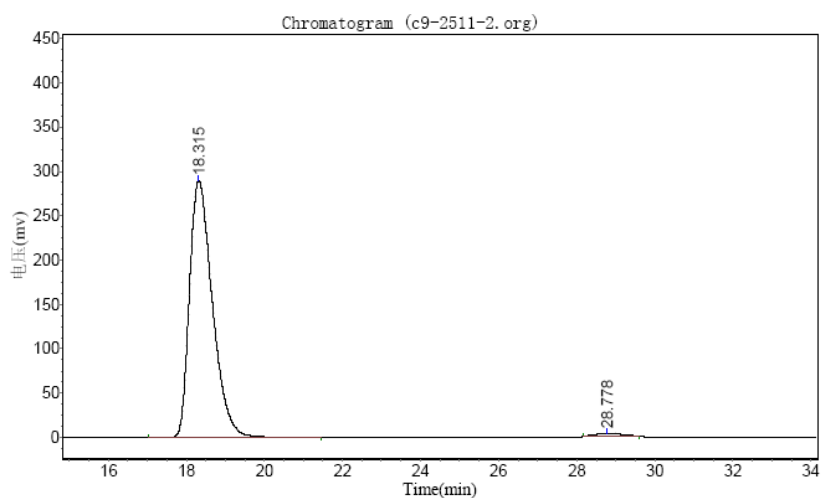




(1S,6S)-tert-butyl 1-fluoro-4-oxo-2,6-diphenylcyclohex-2-enecarboxylate 5v

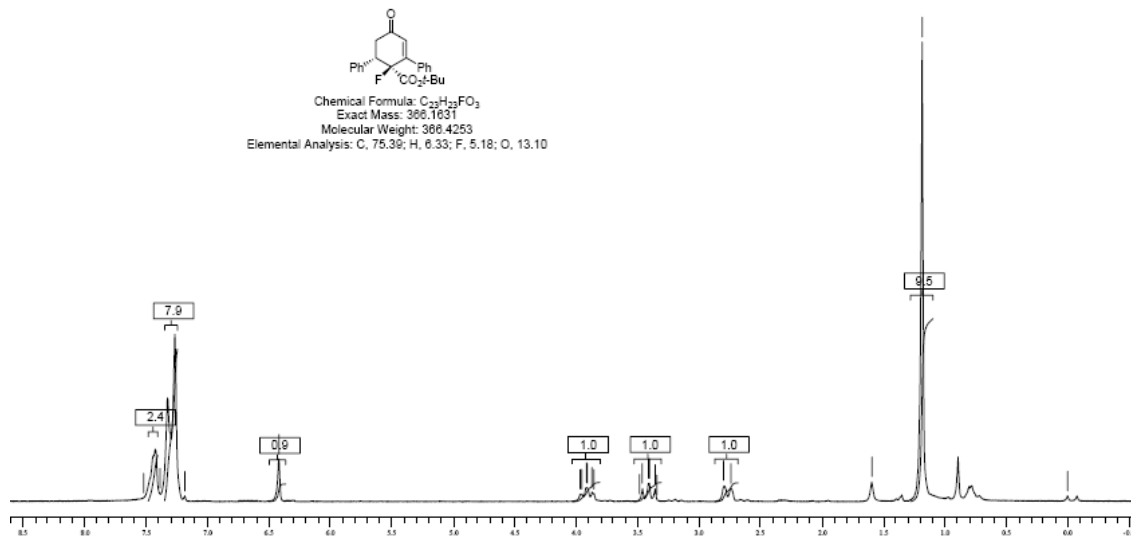
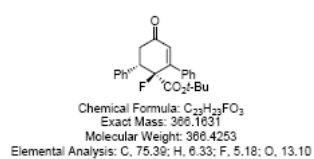


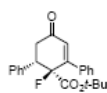
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.358	74972.750	2790486.500	50.0785
2		28.158	45532.332	2781740.500	49.9215
Total			120505.082	5572227.000	100.0000



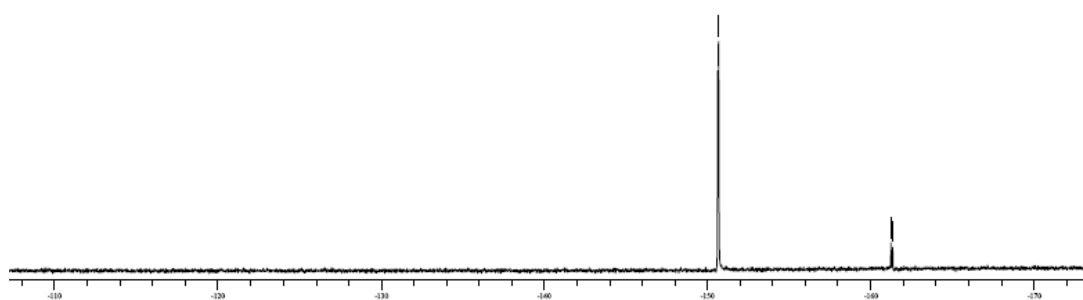
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.315	289762.969	11779767.000	98.4944
2		28.778	3679.692	180062.469	1.5056
Total			293442.660	11959829.469	100.0000

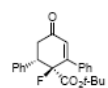
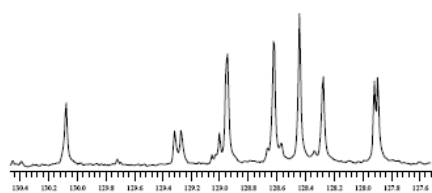




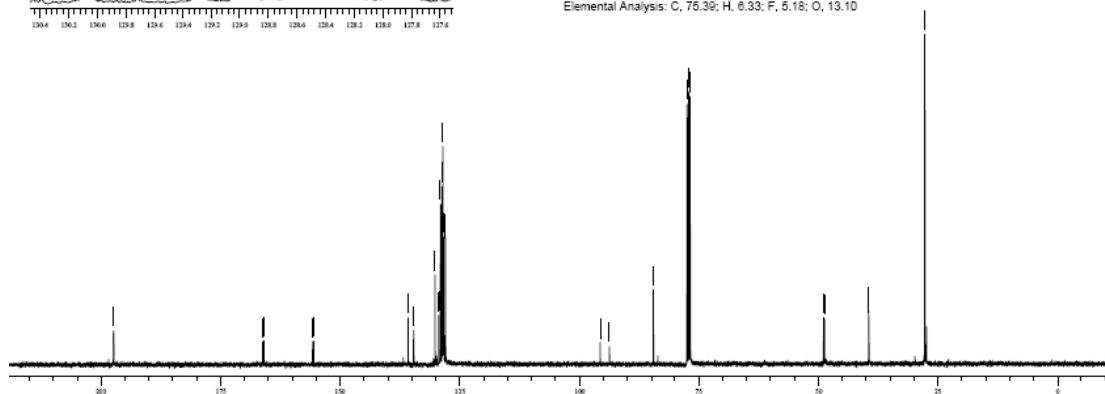
Chemical Formula: $C_{23}H_{23}FO_3$
 Exact Mass: 366.1631
 Molecular Weight: 366.4253
 Elemental Analysis: C, 75.36; H, 6.33; F, 5.18; O, 13.10



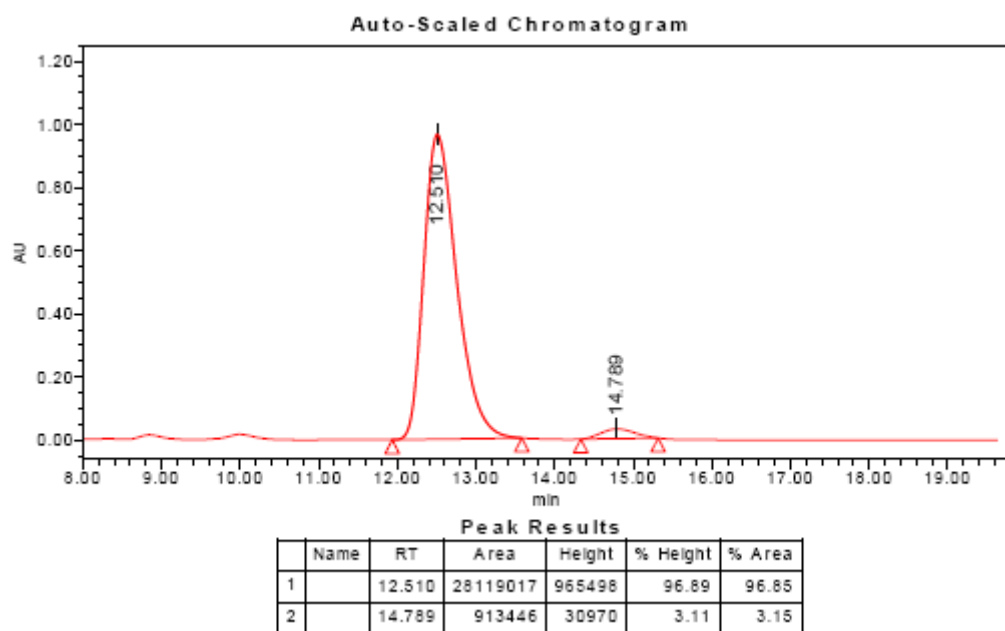
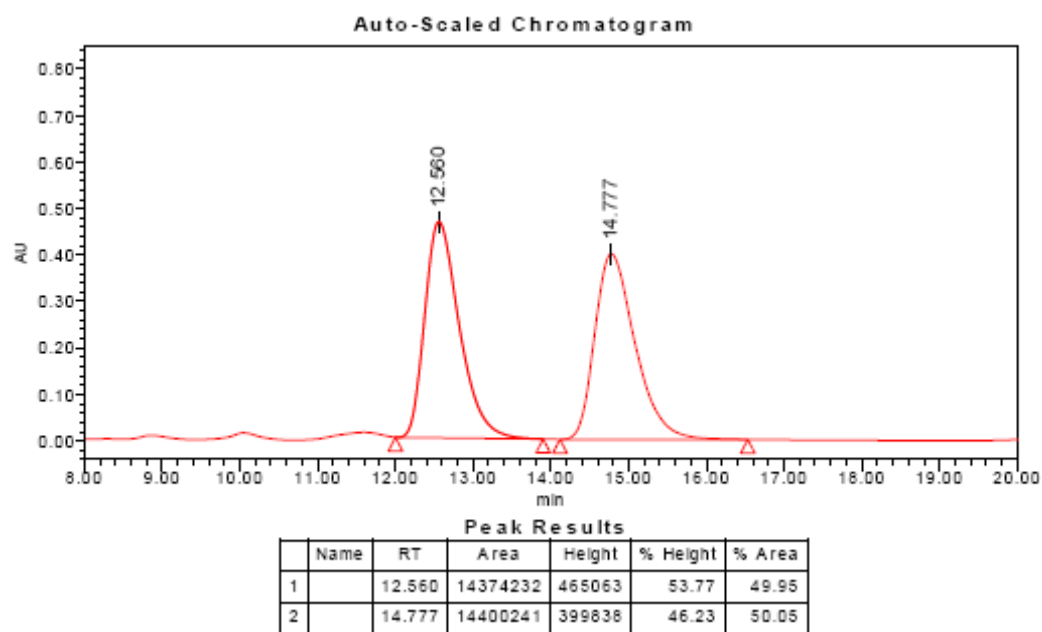
C9-2511P

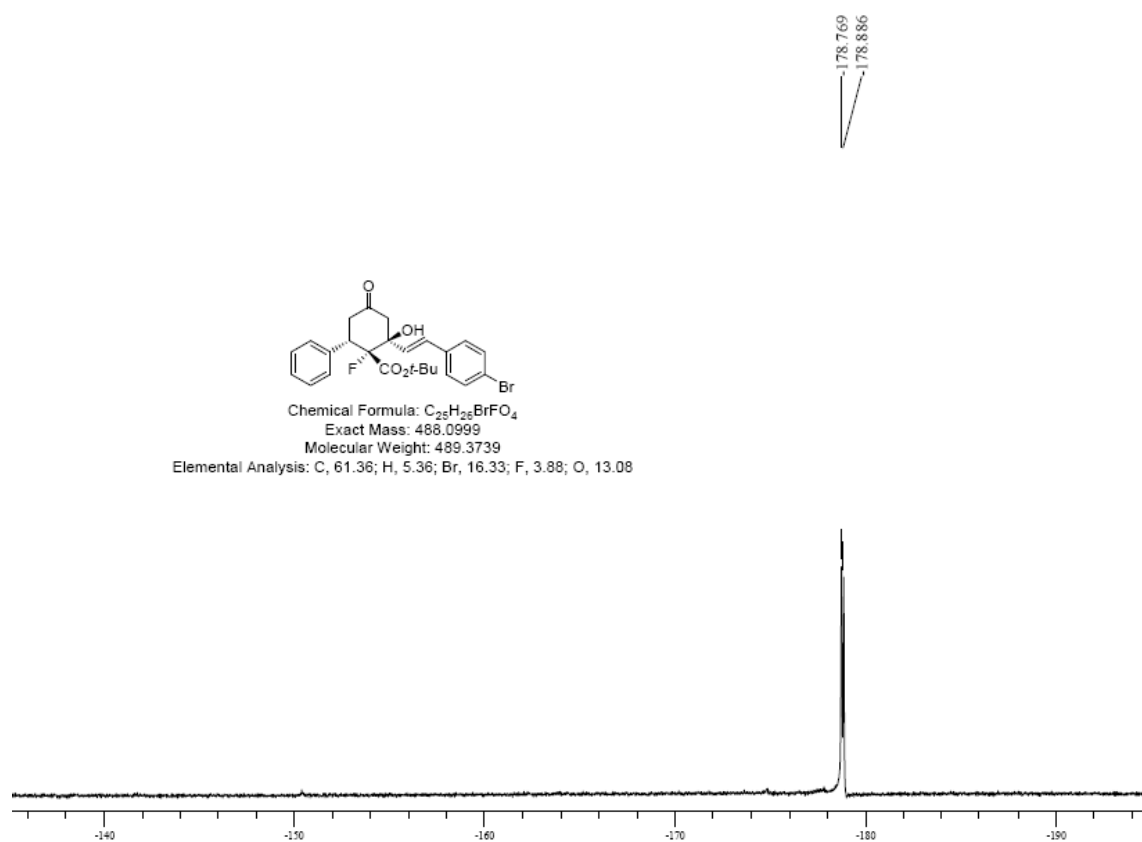
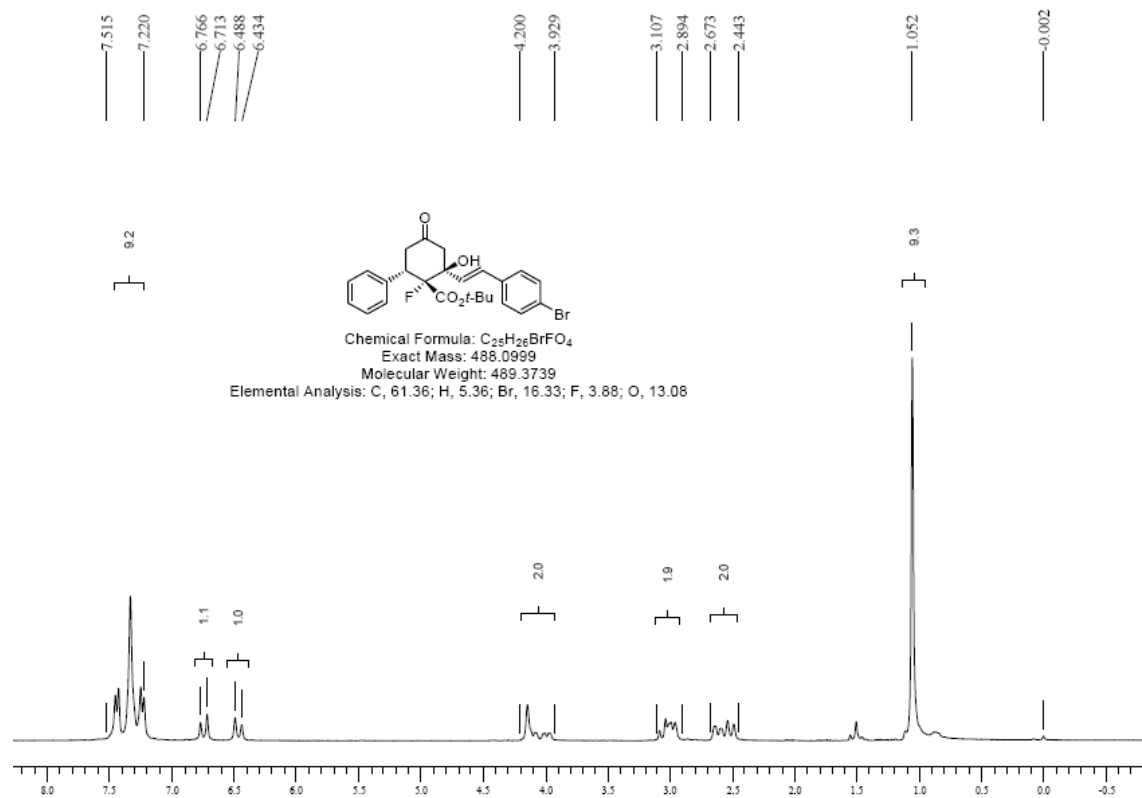


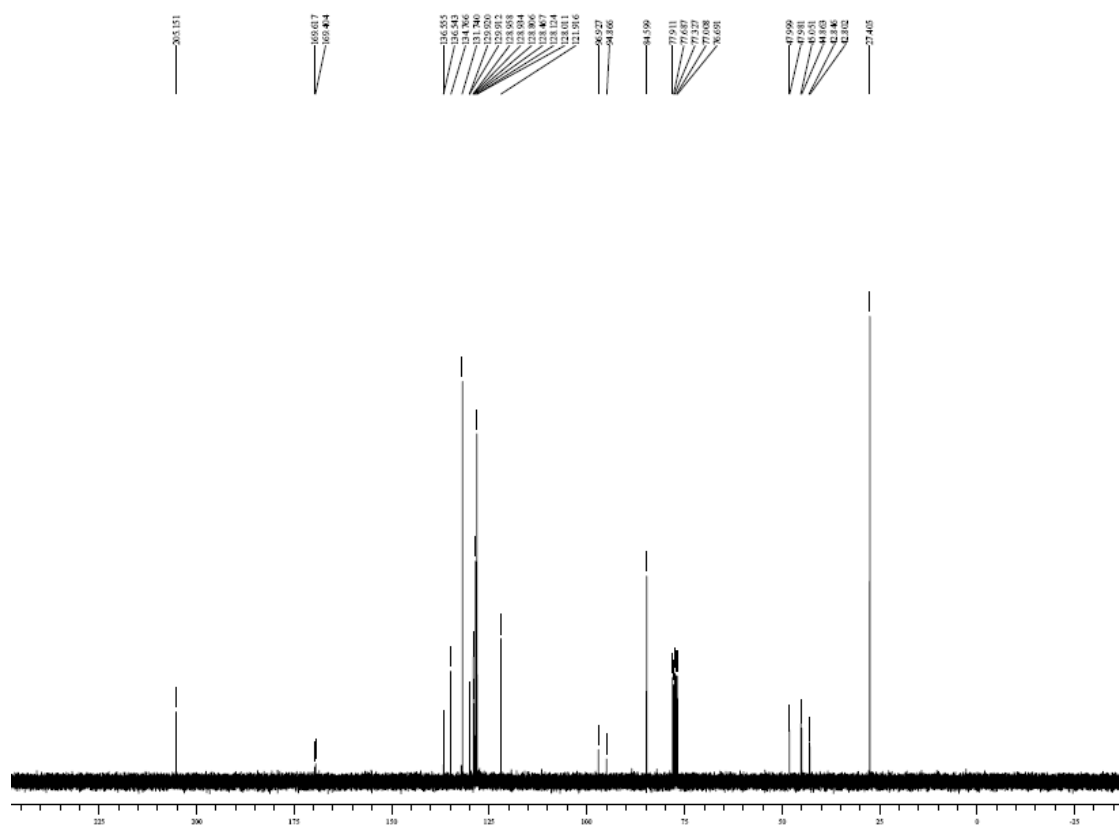
Chemical Formula: $C_{23}H_{23}FO_3$
 Exact Mass: 366.1631
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 Elemental Analysis: C, 75.36; H, 6.33; F, 5.18; O, 13.10

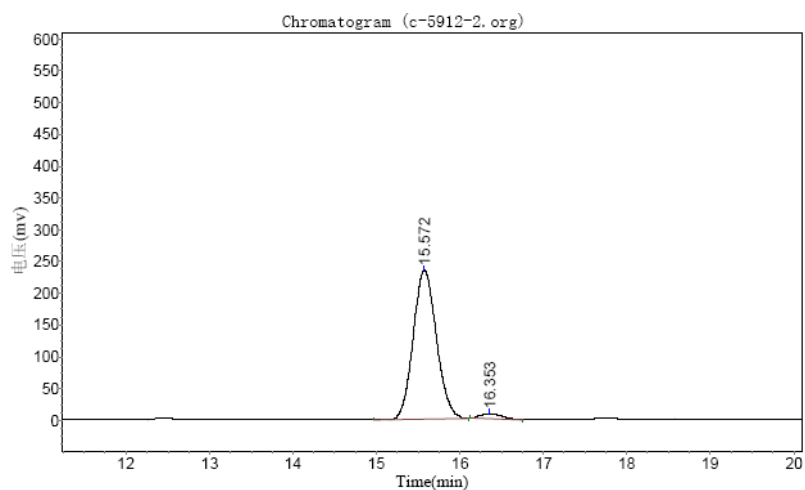


(1*R*,2*S*,6*S*,*E*)-tert-butyl-2-(4-bromostyryl)-1-fluoro-2-hydroxy-4-oxo-6-phenylcyclohexanecarboxylate 6a



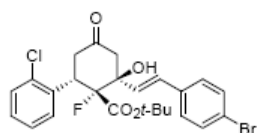






Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.572	234457.891	4521808.000	97.0977
2		16.353	7602.207	135159.297	2.9023
Total			242060.097	4656967.297	100.0000

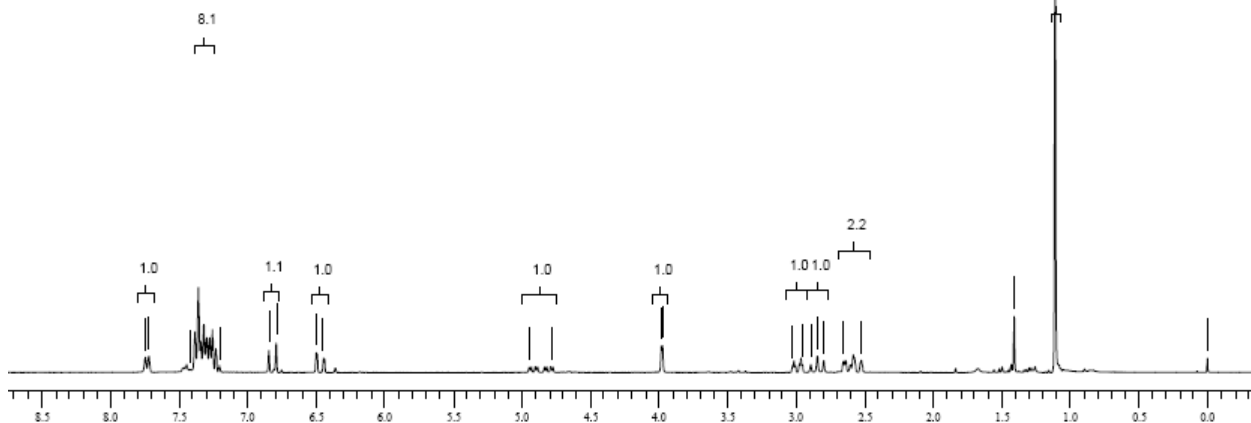


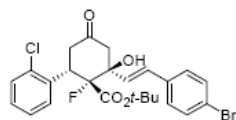
Chemical Formula: $C_{25}H_{25}BrClFO_4$

Exact Mass: 522.0609

Molecular Weight: 523.819

Elemental Analysis: C, 57.32; H, 4.81; Br, 15.25; Cl, 6.77; F, 3.63; O, 12.22

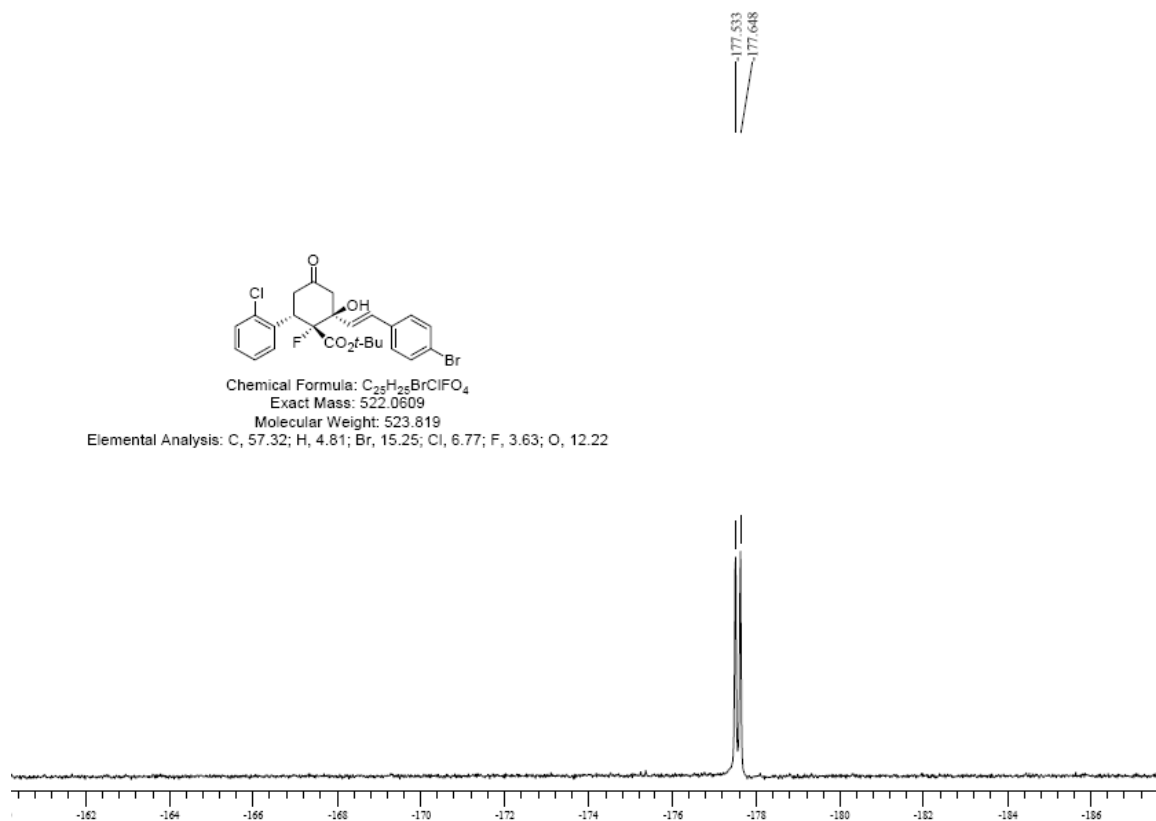




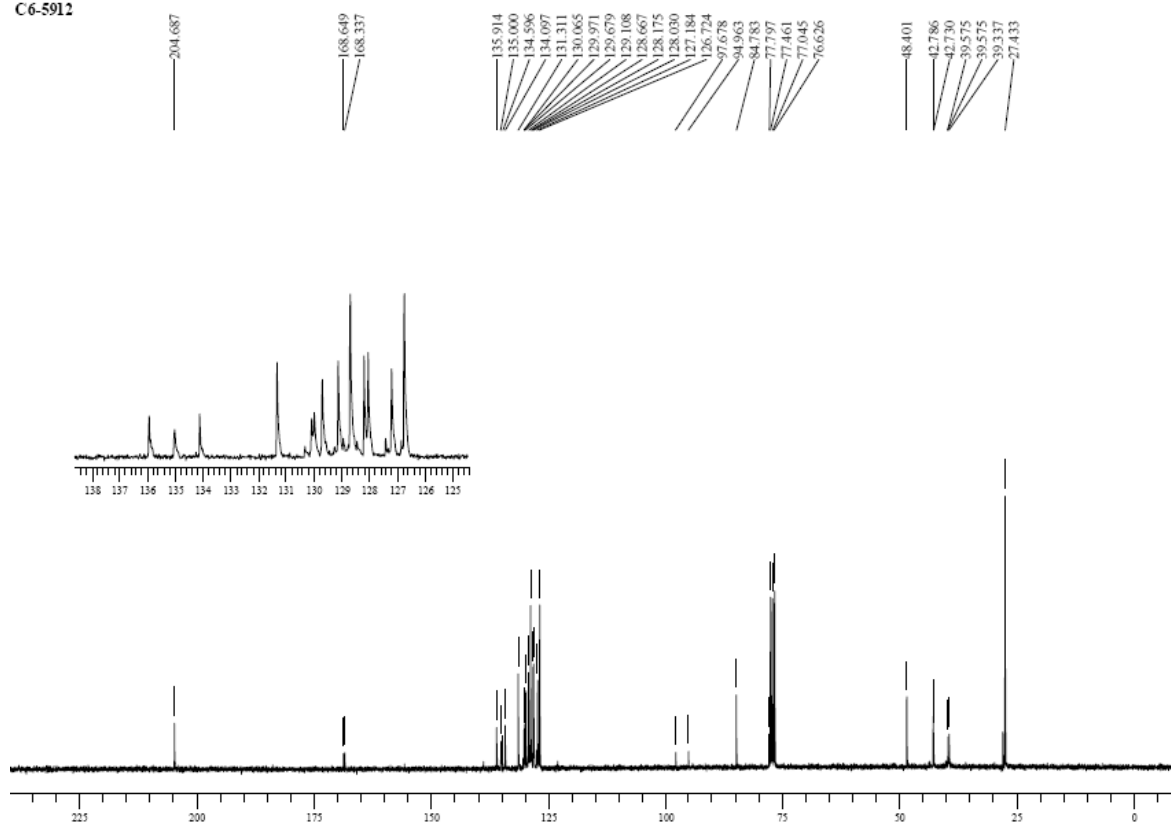
Chemical Formula: $C_{25}H_{25}BrClFO_4$
Exact Mass: 522.0609

Molecular Weight: 523.819

Elemental Analysis: C, 57.32; H, 4.81; Br, 15.25; Cl, 6.77; F, 3.63; O, 12.22

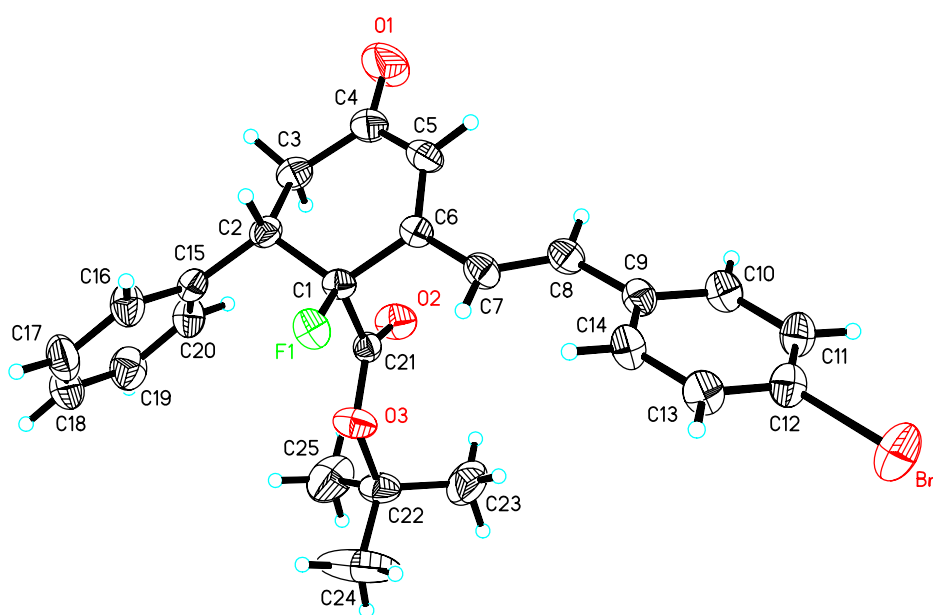
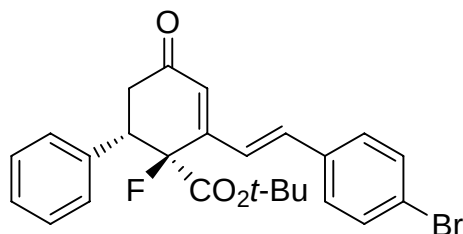


C6-5912



X-Ray Crystal structure for 5a and 6a

(1*S*,6*S*,*E*)-*tert*-butyl-2-(4-bromostyryl)-1-fluoro-4-oxo-6-phenylcyclohex-2-enecarboxylate 5a

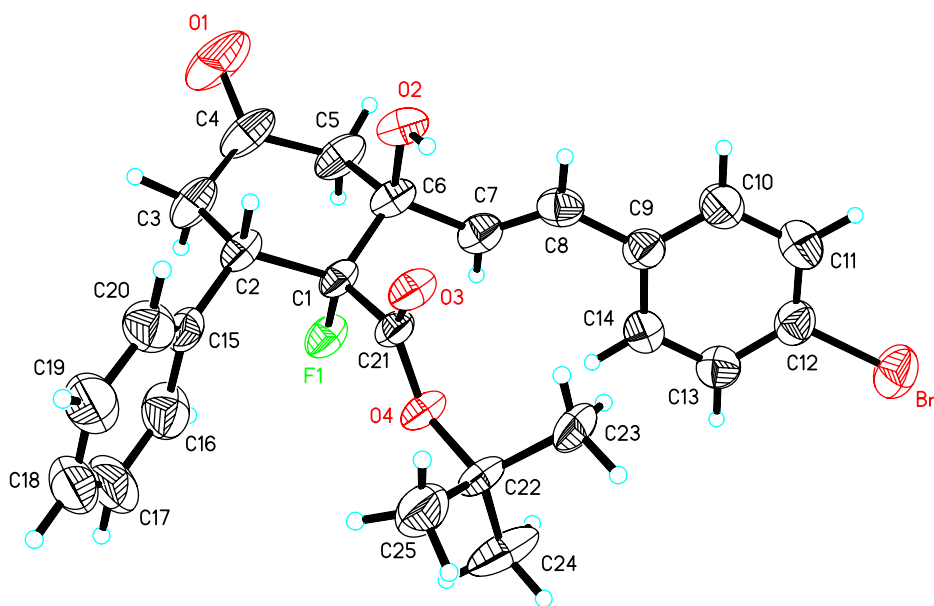
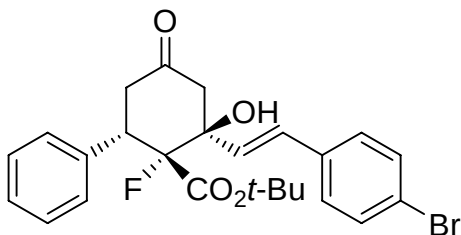


Crystal data and structure refinement for 5a.

Identification code	cd29195
Empirical formula	C ₂₅ H ₂₄ Br F O ₃
Formula weight	471.35
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 6.0261(7) Å alpha = 90 deg. b = 19.368(2) Å beta = 90 deg.

	$c = 20.028(2) \text{ \AA}$ $\gamma = 90 \text{ deg.}$
Volume	$2337.5(5) \text{ \AA}^3$
Z, Calculated density	4, 1.339 Mg/m^3
Absorption coefficient	1.788 mm^{-1}
F(000)	968
Crystal size	$0.367 \times 0.192 \times 0.180 \text{ mm}$
Theta range for data collection	$2.03 \text{ to } 26.00 \text{ deg.}$
Limiting indices	$-7 \leq h \leq 7, -23 \leq k \leq 20, -23 \leq l \leq 24$
Reflections collected / unique	12888 / 4601 [$R(\text{int}) = 0.0760$]
Completeness to $\theta = 26.00$	99.9 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.78447
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4601 / 0 / 274
Goodness-of-fit on F^2	0.832
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0443, wR2 = 0.0904$
R indices (all data)	$R1 = 0.0749, wR2 = 0.0963$
Absolute structure parameter	0.018(10)
Largest diff. peak and hole	0.358 and $-0.398 \text{ e.\AA}^{-3}$

(1*R*,2*S*,6*S*,*E*)-*tert*-butyl-2-(4-bromostyryl)-1-fluoro-2-hydroxy-4-oxo-6-phenylcyclohexanecarboxylate 6a



Crystal data and structure refinement for 6a

Identification code	cd2988
Empirical formula	C ₂₅ H ₂₆ Br F O ₄
Formula weight	489.37
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 8.7647(15) Å alpha = 90 deg. b = 7.3008(13) Å beta = 90.673(3) deg. c = 18.426(3) Å gamma = 90 deg.
Volume	1179.0(4) Å ³

Z, Calculated density	2, 1.378 Mg/m ³
Absorption coefficient	1.779 mm ⁻¹
F(000)	504
Crystal size	0.386 x 0.364 x 0.055 mm
Theta range for data collection	2.21 to 25.48 deg.
Limiting indices	-10 ≤ h ≤ 8, -8 ≤ k ≤ 8, -22 ≤ l ≤ 21
Reflections collected / unique	6219 / 3787 [R(int) = 0.0724]
Completeness to theta = 25.48	99.5 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.6534
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3787 / 1 / 284
Goodness-of-fit on F ²	0.958
Final R indices [I > 2σ(I)]	R1 = 0.0610, wR2 = 0.1590
R indices (all data)	R1 = 0.0915, wR2 = 0.1823
Absolute structure parameter	0.018(17)
Largest diff. peak and hole	0.483 and -0.429 e.Å ⁻³