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Electronic Supplementary Information

Photoredox 1,2-Dicarbofunctionalization of Unactivated Alkenes via Tandem Radical Difluoroalkylation and Alknyl Migration

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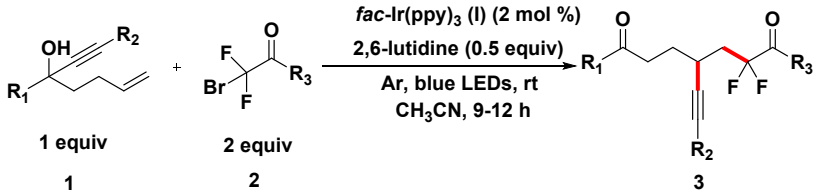
1. General information

All reactions were carried out under argon atmosphere with dry solvents in Schlenk-tube unless otherwise noted. Dry solvents were purchased from J&K®. All other reagents were purchased from commercial sources and used as received. The luminescence quenching experiment was taken using a F-7000 FL Spectrophotometer (Hitachi, Japan). Thin layer chromatography (TLC) was performed on silica coated glass plates (GF 254) with detection by UV (λ = 254 and 366 nm). Flash chromatography was performed on silica (200-300 mesh) with the indicated eluent mixtures. ^{1}H NMR, ^{13}C NMR spectra and ^{19}F NMR spectra were recorded on Bruker AVANCE 400 spectrometer. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. The configuration of product **3** were determined by NMR spectra (^{1}H, ^{13}C, ^{19}F NMR). High resolution mass spectra were gained using an Agilent 6210 Series TOF LC-MS equipped with electrospray ionization (ESI) probe operating in positive ion mode.

The substrates alkynyl-substituted tertiary alcohols **1** were prepared by the addition of freshly prepared alkynyllithium to the precursor ketones referring to the reported procedures. [1-2]

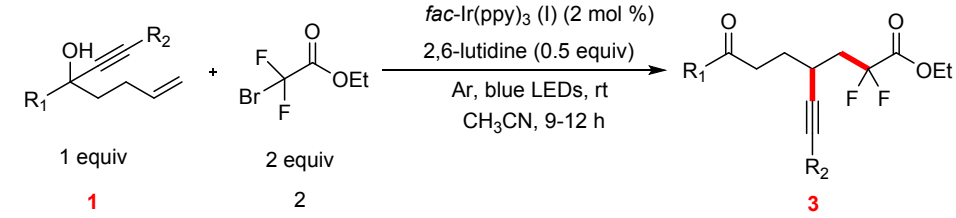
2. General procedure for alkynyl migration of corresponding

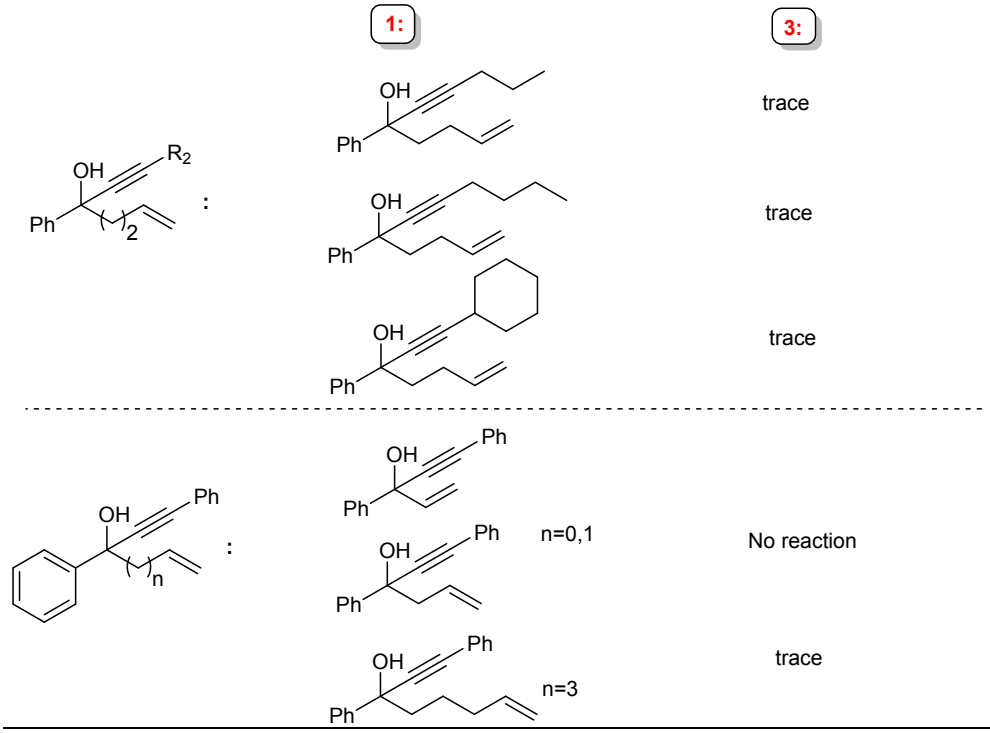
substrates



In a 10 mL oven-dried Schlenk tube equipped with a stirring bar, alkyne-substituted tertiary alcohol **1** (0.2 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (0.004 mmol, 2 mol %), bromodifluoro reagents **2** (0.4 mmol, 2.0 equiv), 2,6-lutidine (0.1 mmol, 0.5 equiv) and anhydrous MeCN (2.0 mL) were successively added. The resulting reaction mixture was subjected to evacuation/flushing with argon for three times under -78 ^{o}C. Then it was allowed to warm to room temperature and irradiated with 3 W blue LEDs until the starting material was fully consumed (monitored by TLC). Removing the solvent in vacuo, the resulting residues were purified by preparative thin layer chromatography (PTLC; PE/EA) to afford the desired akynyl migration product **3.**

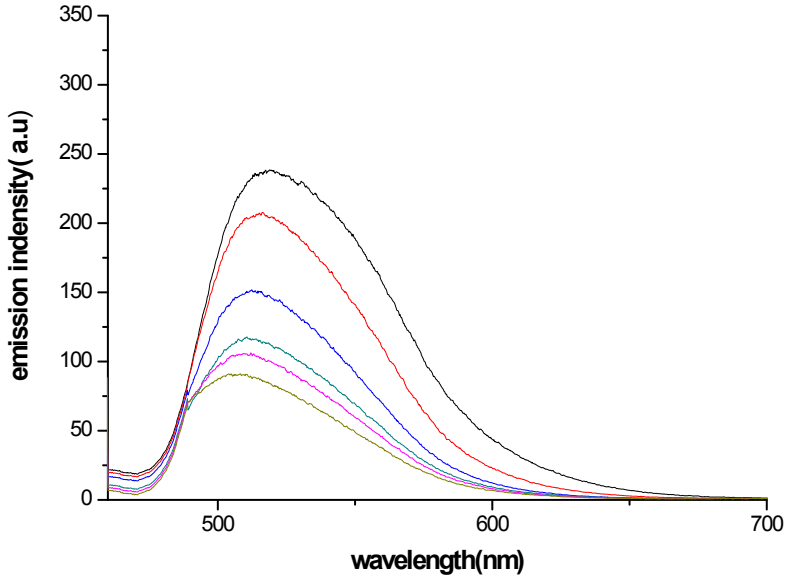
■ Addition: other unsatisfactory examples

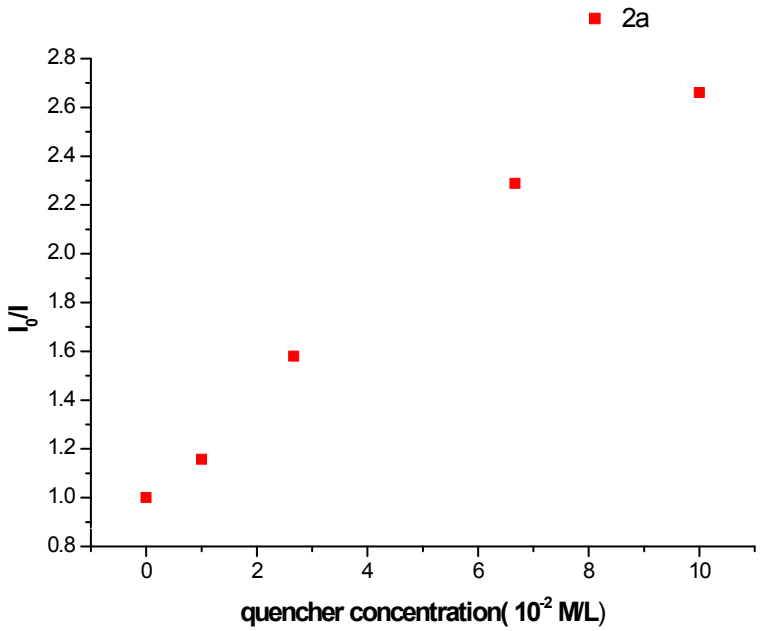




3. Stern-Volmer plot (Luminescence quenching experiment)

The luminescence quenching experiment was taken using a F-7000 FL Spectrophotometer (Hitachi, Japan). The experiments were carried out in 3 x 10-5 mol/L of *fac*-Irppy$_3$ in anhydrous CH_3CN at 25 ℃. The excitation wavelength was 375 nm and the emission intensity was collected at 516 nm. The concentrations of quencher (bromodifluoroacetate) in anhydrous CH_3CN were 0 mol/L, 1.00 x 10^{-2} mol/L, 2.7 x 10^{-2} mol/L, 6.7 x 10^{-2} mol/L, 1.00 x 10^{-1} mol/L.

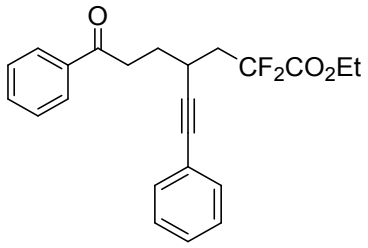




Luminescence quenching of *fac*-Irppy$_3$ by bromodifluoroacetate

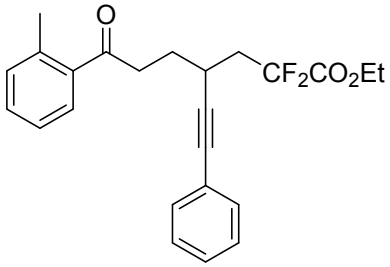
4. Characterization of the products 3

ethyl 2,2-difluoro-7-oxo-7-phenyl-4-(phenylethynyl)heptanoate (**3a**)
(prepared according to the general procedure described above by using **1a** and **2a** as substrates.)



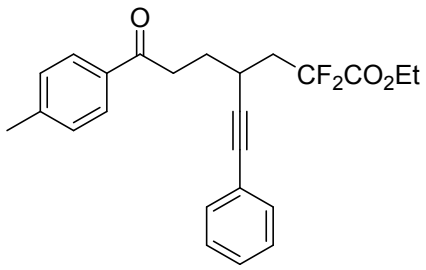
Yellow oil, yield 69%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.97 (m, 2H), 7.59 – 7.53 (m, 1H), 7.48 – 7.43 (m, 2H), 7.39 – 7.35 (m, 2H), 7.30 – 7.27 (m, 3H), 4.23 (d, *J* = 7.2 Hz, 2H), 3.29 – 3.20 (m, 2H), 3.05 (hept, *J* = 4.8 Hz, 1H), 2.63 – 2.47 (m, 1H), 2.35 (m,1H), 2.20 – 2.09 (m, 1H), 2.04 – 1.91 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.2, 163.9 (t, *J* = 32.3 Hz), 136.8, 133.2, 131.6, 128.6, 128.3, 128.2, 128.1, 123.0, 115.4 (t, *J* = 249.2 Hz), 89.5, 83.7, 63.0, 40.0 (t, *J* = 23.2 Hz), 36.0, 29.7, 25.8, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.1 (d, *J* = 262.8 Hz), -106.7 (d, *J* = 262.8 Hz). HRMS (ESI) calcd for $C_{23}H_{22}F_2O_3Na$ [M+Na]$^{+}$: 407.1429, found: 407.1426.

ethyl 2,2-difluoro-7-oxo-4-(phenylethynyl)-7-(o-tolyl)heptanoate (**3b**)
(prepared according to the general procedure described above by using **1b** and **2a** as substrates.)



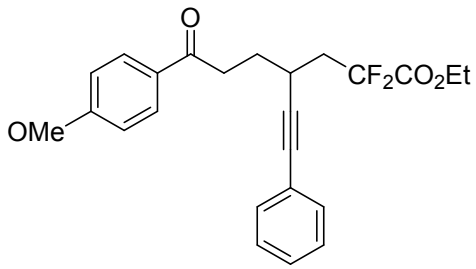
Yellow oil, yield 59%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.67 (m, 1H), 7.39 – 7.34 (m, 3H), 7.29 – 7.23 (m, 5H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.21 – 3.14 (m, 2H), 3.04 (hept, *J* =4.7 Hz, 1H), 2.63 – 2.45 (m, 4H), 2.34 (qd, *J* = 14.6, 4.7 Hz, 1H), 2.19 – 2.06 (m, 1H), 1.99 – 1.87 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.3, 163.9 (t, *J* = 32.5 Hz), 138.1, 137.8, 132.0, 131.6, 131.4, 128.5, 128.3, 128.1, 125.7, 123.0, 115.4 (t, *J* = 247.9 Hz), 89.5, 83.7, 63.0, 40.0 (t, *J* = 23.2 Hz), 38.8, 29.7, 25.7, 21.4, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.1 (d, *J* = 262.7 Hz), -106.8 (d, *J* = 262.7 Hz). HRMS (ESI) calcd for $C_{24}H_{24}F_2O_3Na$ [M+Na]$^{+}$: 421.1586, found: 421.1579.

ethyl 2,2-difluoro-7-oxo-4-(phenylethynyl)-7-(p-tolyl)heptanoate (**3c**)
(prepared according to the general procedure described above by using **1c** and **2a** as substrates.)



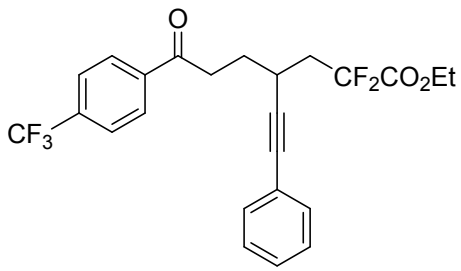
Yellow oil, yield 59%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.31 – 7.22 (m, 5H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.25 – 3.19 (m, 2H), 3.04 (hept, *J* =4.7 Hz, 1H), 2.63 – 2.47 (m, 1H), 2.42 – 2.28 (m, 4H), 2.19 – 2.07 (m, 1H), 2.03 – 1.89 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.9, 163.9 (t, *J* = 32.3 Hz), 144.0, 134.3, 131.6, 129.3, 128.2 (t, *J* = 6.5 Hz), 123.0, 115.4 (t, *J* = 248.0 Hz), 89.6, 83.6, 63.0, 40.0 (t, *J* = 23.2 Hz), 35.9, 29.8, 25.8, 21.7, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.1 (d, *J* = 262.7 Hz), -106.7 (d, *J* = 262.7 Hz). HRMS (ESI) calcd for $C_{24}H_{24}F_2O_3Na$ [M+Na]$^+$: 421.1586, found: 421.1583.

ethyl 2,2-difluoro-7-(4-methoxyphenyl)-7-oxo-4-(phenylethynyl)heptanoate (**3d**)
(prepared according to the general procedure described above by using **1d** and **2a** as substrates.)



Faint yellow oil, 57% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.93 (m, 2H), 7.38 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.28 (dd, *J* = 5.1, 1.8 Hz, 3H), 6.97 – 6.90 (m, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 3.28 – 3.11 (m, 2H), 3.04 (hept, *J* =4.8 Hz, 1H), 2.64 – 2.45 (m, 1H), 2.35 (qd, *J* = 14.6, 4.6 Hz, 1H), 2.19 – 2.08 (m, 1H), 2.01 – 1.88 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.8, 163.9 (t, *J* = 33.0 Hz), 163.5, 131.6, 130.3, 128.3, 128.1, 123.0, 115.4 (t, *J* = 251.9 Hz), 113.8, 89.6, 83.6, 63.0, 55.5, 40.0 (t, *J* = 23.4 Hz), 35.6, 29.9, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.1 (d, *J* = 262.6 Hz), -106.8 (d, *J* = 262.6 Hz). HRMS (ESI) calcd for $C_{24}H_{24}F_2O_4Na$ [M+Na]$^+$: 437.1535, found: 437.1531.

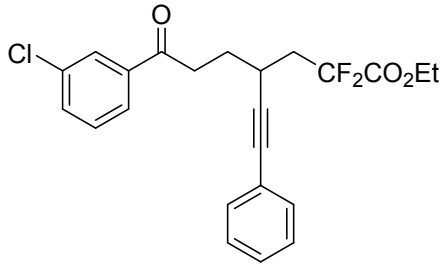
ethyl 2,2-difluoro-7-oxo-4-(phenylethynyl)-7-(4-(trifluoromethyl)phenyl)heptanoate (**3e**)
(prepared according to the general procedure described above by using **1e** and **2a** as substrates.)



Orange yellow oil, yield 64%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.24 (m, 3H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.35 – 3.19 (m,

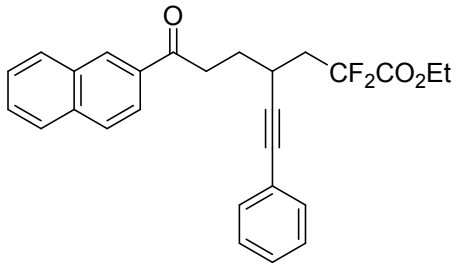
2H), 3.06 (hept, *J* = 4.8 Hz, 1H), 2.64 – 2.48 (m, 1H), 2.36 (qd, *J* = 14.8, 4.8 Hz, 1H), 2.22 – 2.13 (m, 1H), 2.04 – 1.93 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.9 (t, *J* = 32.5 Hz), 139.4, 134.4 (q, *J* = 32.6 Hz), 131.6, 128.4, 128.3, 128.3, 125.7, 125.7, 122.8, 115.3 (t, *J* = 249.6 Hz), 89.3, 83.9, 63.0, 40.0 (t, *J* = 23.3 Hz), 36.3, 29.4, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.1, -101.2 (d, *J* = 262.9 Hz), -106.8 (d, *J* = 262.9 Hz). HRMS (ESI) calcd for $C_{24}H_{21}F_5O_3Na$ $[M+Na]^+$: 475.1303, found: 475.1295.

ethyl 7-(3-chlorophenyl)-2,2-difluoro-7-oxo-4-(phenylethynyl)heptanoate (**3f**)
(prepared according to the general procedure described above by using **1f** and **2a** as substrates.)



Faint yellow oil, yield 54%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.30 – 7.26 (m, 3H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.25 – 3.17 (m, 2H), 3.04 (hept, *J* = 4.8 Hz, 1H), 2.64 – 2.47 (m, 1H), 2.35 (qd, *J* = 14.6, 4.8 Hz, 1H), 2.20 – 2.10 (m, 1H), 2.02 – 1.91 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.9, 163.9 (t, *J* = 32.4 Hz), 138.3, 135.0, 133.1, 131.6, 130.0, 128.3, 128.2, 126.2, 122.9, 115.3 (t, *J* = 249.5 Hz), 89.3, 83.8, 63.0, 40.0 (t, *J* = 23.2 Hz), 36.1, 29.5, 25.7, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.1 (d, *J* = 262.9 Hz), -106.7 (d, *J* = 263.0 Hz). HRMS (ESI) calcd for $C_{23}H_{21}ClF_2O_3Na$ $[M+Na]^+$: 441.1039, found: 441.1043.

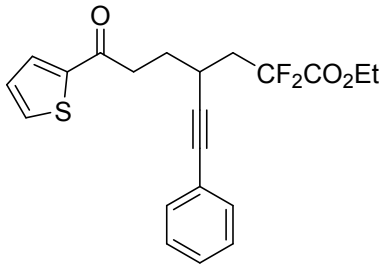
ethyl 2,2-difluoro-7-(naphthalen-2-yl)-7-oxo-4-(phenylethynyl)heptanoate (**3g**)
(prepared according to the general procedure described above by using **1g** and **2a** as substrates.)



Yellow oil, yield 56%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.40 – 7.37 (m, 2H), 7.30 – 7.25 (m, 3H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.42 – 3.35 (m, 2H), 3.09 (hept, *J* = 4.8 Hz, 1H), 2.66 – 2.50 (m, 1H), 2.38 (qd, *J* = 14.5, 4.7 Hz, 1H), 2.25 – 2.16 (m, 1H), 2.08 – 1.98 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.2, 163.9 (t, *J* = 32.1 Hz), 135.6, 134.1, 132.5, 131.6, 129.8, 129.6, 128.5, 128.5, 128.3, 128.2, 127.8, 126.8, 123.8, 115.4 (t, *J* = 249.4 Hz), 89.6, 83.7, 63.0, 40.0 (t, *J* = 23.2 Hz), 36.0, 29.9, 13.8. ^{19}F NMR (376 MHz, Chloroform-d) δ -101.1 (d, J = 262.7 Hz), -106.8 (d, J = 262.8 Hz). HRMS (ESI) calcd for $C_{27}H_{24}F_2O_3Na$ $[M+Na]^+$: 457.1586, found: 457.1580.

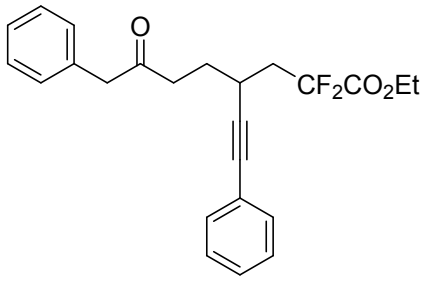
ethyl 2,2-difluoro-7-oxo-4-(phenylethynyl)-7-(thiophen-2-yl)heptanoate (**3h**)

(prepared according to the general procedure described above by using **1h** and **2a** as substrates.)



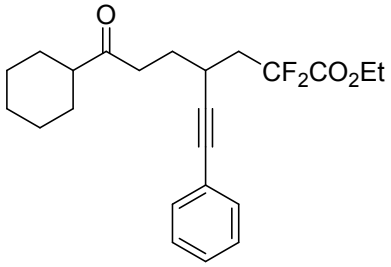
Yellow oil, yield 45%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.63 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.32 – 7.24 (m, 3H), 7.12 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.24 – 3.16 (m, 3H), 3.03 (hept, *J* = 4.8 Hz, 1H), 2.62 – 2.47 (m, 1H), 2.34 (qd, *J* = 14.6, 4.7 Hz, 1H), 2.21 – 2.09 (m, 1H), 2.02 – 1.91 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.2, 163.9 (t, *J* = 32.4 Hz), 144.1, 133.7, 132.0, 131.6, 128.3, 128.2, 128.1, 122.9, 115.3 (t, *J* = 249.0 Hz), 89.4, 83.8, 63.0, 39.9 (t, *J* = 23.2 Hz), 36.7, 29.8, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.1 (d, *J* = 262.9 Hz), -106.7 (d, *J* = 262.5 Hz). HRMS (ESI) calcd for $C_{21}H_{20}F_2O_3SNa$ $[M+Na]^+$: 413.0993, found: 413.0997.

ethyl 2,2-difluoro-7-oxo-8-phenyl-4-(phenylethynyl)octanoate (**3i**)
(prepared according to the general procedure described above by using **1i** and **2a** as substrates.)



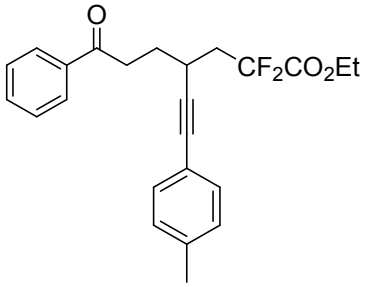
Yellow oil, 20 % yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.24 (m, 8H), 7.21 – 7.18 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 2H), 2.89 (hept, *J* = 4.8 Hz, 1H), 2.81 – 2.63 (m, 2H), 2.55 – 2.36 (m, 1H), 2.24 (qd, *J* = 14.6, 4.7 Hz, 1H), 1.98 – 1.88 (m, 1H), 1.81 – 1.70 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 207.4, 163.9 (t, *J* = 32.5 Hz), 134.1, 131.6, 129.4, 128.8, 128.2, 128.2, 127.1, 122.9, 115.3 (t, *J*=248.0 Hz), 89.3, 83.6, 63.0, 50.3, 39.8 (t, *J* = 23.3 Hz), 39.2, 29.0, 25.5, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.2 (d, *J* = 262.8 Hz), -106.8 (d, *J* = 262.8 Hz). HRMS (ESI) calcd for $C_{24}H_{24}F_2O_3Na$ $[M+Na]^+$: 421.1586, found: 421.1592.

ethyl 7-cyclohexyl-2,2-difluoro-7-oxo-4-(phenylethynyl)heptanoate (**3j**)
(prepared according to the general procedure described above by using **1j** and **2a** as substrates.)



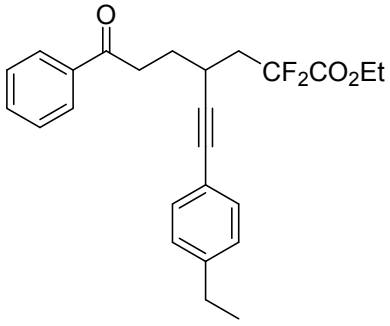
Faint yellow oil, 65% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.33 – 7.28 (m, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.92 (hept, *J* = 4.8Hz, 1H), 2.70 (t, *J* = 7.3 Hz, 2H), 2.58 – 2.43 (m, 1H), 2.41 – 2.21 (m, 2H), 2.00 – 1.90 (m, 1H), 1.87 – 1.72 (m, 5H), 1.68 – 1.64 (m, 1H), 1.39 – 1.16 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.1, 163.9 (t, *J* = 32.4 Hz), 131.6, 128.3, 128.1, 123.1, 115.3 (t, *J* = 249.4 Hz), 89.5, 83.5, 63.0, 51.0, 39.9 (t, *J* = 23.3 Hz), 37.8, 29.1, 28.6, 28.5, 25.8, 25.7, 25.6, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.1 (d, *J* = 262.8 Hz), -106.9 (d, *J* = 262.8 Hz). HRMS (ESI) calcd for $C_{23}H_{28}F_2O_3Na$ $[M+Na]^+$: 413.1899, found: 413.1897.

ethyl 2,2-difluoro-7-oxo-7-phenyl-4-(p-tolylethynyl)heptanoate (**3k**)
(prepared according to the general procedure described above by using **1k** and **2a** as substrates.)



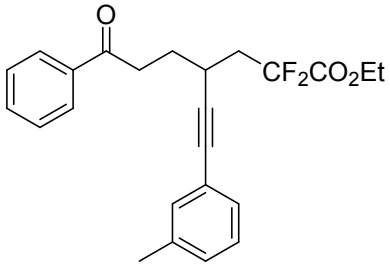
Colorless oil, yield 57%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.96 (m, 2H), 7.59 – 7.53 (m, 1H), 7.50 – 7.41 (m, 2H), 7.30 – 7.23 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.29 – 3.20 (m, 2H), 3.03 (hept, *J* = 4.8 Hz, 1H), 2.63 – 2.46 (m, 1H), 2.40 – 2.28 (m, 4H), 2.19 – 2.09 (m, 1H), 2.01 – 1.90 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.3, 163.9 (t, *J* = 32.4 Hz), 138.2, 136.8, 133.1, 131.5, 129.0, 128.6, 128.1, 119.9, 115.4 (t, *J* = 246.1 Hz), 88.7, 83.8, 63.0, 40.0 (t, *J* = 23.0 Hz), 36.0, 29.7, 25.8, 21.4, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.0 (d, *J* = 262.6 Hz), -106.8 (d, *J* = 262.7 Hz). HRMS (ESI) calcd for $C_{24}H_{24}F_2O_3Na$ $[M+Na]^+$: 421.1586, found: 421.1581.

ethyl 4-((4-ethylphenyl)ethynyl)-2,2-difluoro-7-oxo-7-phenylheptanoate (**3l**)
(prepared according to the general procedure described above by using **1l** and **2a** as substrates.)



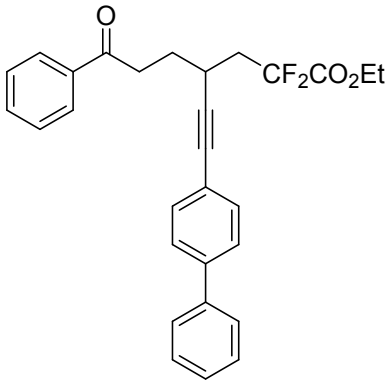
Yellow oil, yield 67%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.97 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 – 7.42 (m, 2H), 7.31 – 7.24 (m, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.32 – 3.17 (m, 2H), 3.03 (hept, *J* = 4.7 Hz, 1H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.59 – 2.47 (m, 1H), 2.34 (qd, *J* = 14.6, 4.7 Hz, 1H), 2.21 – 2.09 (m, 1H), 2.01 – 1.90 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.3, 163.9 (t, *J* = 32.4 Hz), 144.5, 136.8, 133.1, 131.6, 128.6, 128.1, 127.8, 120.1, 115.4 (t, *J* = 244.0 Hz), 88.7, 83.8, 63.0, 40.1 (t, *J* = 23.3 Hz), 36.0, 29.7, 28.8, 25.9, 15.4, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.0 (d, *J* = 262.5 Hz), -106.8 (d, *J* = 262.5 Hz). HRMS (ESI) calcd for $C_{25}H_{26}F_2O_3Na$ $[M+Na]^+$: 435.1742, found: 435.1737.

ethyl 2,2-difluoro-7-oxo-7-phenyl-4-(m-tolylethynyl)heptanoate (**3m**)
(prepared according to the general procedure described above by using **1m** and **2a** as substrates.)



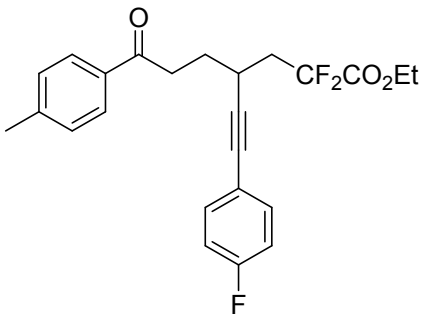
Orange yellow oil, 57% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.95 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.15 (m, 3H), 7.11 – 7.05 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.33 – 3.16 (m, 2H), 3.04 (hept, *J* = 4.8 Hz, 1H), 2.62 – 2.46 (m, 1H), 2.41 – 2.28 (m, 4H), 2.19 – 2.10 (m, 1H), 2.01 – 1.90 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.3, 163.9 (t, *J* = 32.4 Hz), 137.9, 136.8, 133.2, 132.2, 129.0, 128.6, 128.2, 128.1, 122.8, 115.4 (t, *J* = 249.9 Hz), 89.1, 83.8, 63.0, 40.0 (t, *J* = 23.2 Hz), 36.0, 29.7, 25.8, 21.2, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.1 (d, *J* = 262.5 Hz), -106.7 (d, *J* = 262.5 Hz). HRMS (ESI) calcd for $C_{24}H_{24}F_2O_3Na$ $[M+Na]^+$: 421.1586, found: 421.1585.

ethyl 4-([1,1'-biphenyl]-4-ylethynyl)-2,2-difluoro-7-oxo-7-phenylheptanoate (**3n**)
(prepared according to the general procedure described above by using **1n** and **2a** as substrates.)



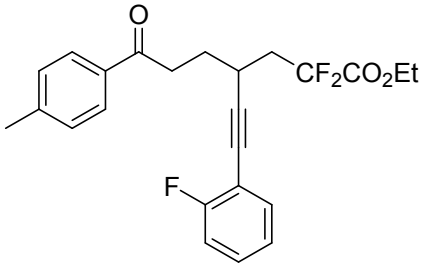
Yellow oil, yield 53%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.96 (m, 2H), 7.59 – 7.50 (m, 5H), 7.48 – 7.41 (m, 6H), 7.37 – 7.32 (m, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.30 – 3.18 (m, 2H), 3.07 (hept, *J* = 4.8 Hz, 1H), 2.66 – 2.48 (m, 1H), 2.37 (qd, *J* = 14.5, 4.6 Hz, 1H), 2.21 – 2.10 (m, 1H), 2.05 – 1.93 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.2, 163.9 (t, *J* = 32.5 Hz), 140.9, 140.3, 136.8, 133.2, 132.0, 128.9, 128.7, 128.1, 127.7, 127.0, 126.9, 121.9, 115.4 (t, *J* = 249.9 Hz), 90.2, 83.6, 63.1, 40.0 (t, *J* = 23.2 Hz), 36.0, 29.7, 25.9, 13.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.1 (d, *J* = 262.4 Hz), -106.7 (d, *J* = 262.7 Hz). HRMS (ESI) calcd for $C_{29}H_{26}F_2O_3Na$ $[M+Na]^+$: 483.1742, found: 483.1750.

ethyl 2,2-difluoro-4-((4-fluorophenyl)ethynyl)-7-oxo-7-(p-tolyl)heptanoate (**3o**)
(prepared according to the general procedure described above by using **1o** and **2a** as substrates.)



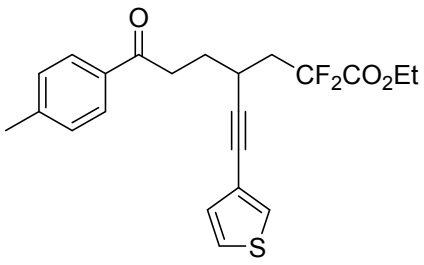
Yellow oil, 56% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.02 – 6.93 (m, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.26 – 3.15 (m, 2H), 3.03 (hept, *J* = 4.8 Hz, 1H), 2.62 – 2.44 (m, 1H), 2.42 – 2.27 (m, 4H), 2.19 – 2.07 (m, 1H), 2.01 – 1.90 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.8, 163.9 (t, *J* = 32.3 Hz), 162.9 (d, *J* = 247.5 Hz), 144.0, 134.3, 133.4 (d, *J* = 8.3 Hz), 129.3, 128.2, 119.1 (d, *J* = 3.2 Hz), 115.5 (d, *J* = 22.0 Hz), 115.3 (t, *J* = 243.6 Hz), 89.3, 82.5, 63.0, 39.9 (t, *J* = 23.2 Hz), 35.8, 29.7, 25.8, 21.6, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.3 (d, *J* = 262.9 Hz), -106.6 (d, *J* = 262.9 Hz), -111.2 (s). HRMS (ESI) calcd for $C_{24}H_{23}F_3O_3Na$ [M+Na]$^{+}$: 439.1492, found: 439.1485.

ethyl 2,2-difluoro-4-((2-fluorophenyl)ethynyl)-7-oxo-7-(p-tolyl)heptanoate (**3p**)
(prepared according to the general procedure described above by using **1p** and **2a** as substrates.)



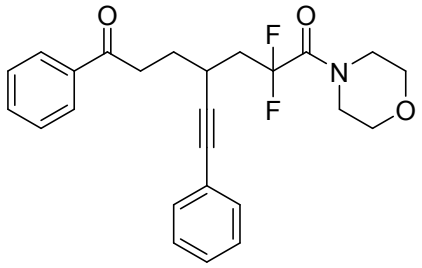
Yellow oil, 48% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.35 (m, 1H), 7.31 – 7.23 (m, 3H), 7.09 – 7.01 (m, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.34 – 3.18 (m, 2H), 3.09 (hept, *J* = 4.8 Hz, 1H), 2.65 – 2.48 (m, 1H), 2.44 – 2.30 (m, 4H), 2.23 – 2.10 (m, 1H), 2.02 – 1.90 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.0, 164.0 (t, *J* = 16.2 Hz), 163.5, 161.5, 143.9, 134.3, 133.5, 129.8 (d, *J* = 7.9 Hz), 129.3, 128.2, 123.9 (d, *J* = 3.5 Hz), 115.4 (d, *J* = 21.1 Hz), 115.3 (t, *J* = 247.3 Hz), 111.5 (d, *J* = 15.7 Hz), 95.1, 63.0, 39.8 (t, *J* = 23.2 Hz), 35.8, 29.7, 26.0, 21.6, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.7 (d, *J* = 262.8 Hz), -106.3 (d, *J* = 262.7 Hz), -110.5 (s). HRMS (ESI) calcd for $C_{24}H_{23}F_3O_3Na$ [M+Na]$^{+}$: 439.1492, found: 439.1482.

ethyl 2,2-difluoro-7-oxo-4-(thiophen-3-ylethynyl)-7-(p-tolyl)heptanoate (**3q**)
(prepared according to the general procedure described above by using **1q** and **2a** as substrates.)



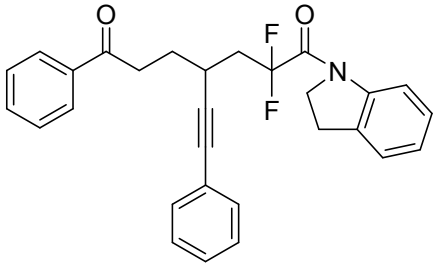
Yellow oil, 33% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.36 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.27 – 7.22 (m, 3H), 7.04 (dd, *J* = 5.0, 1.1 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.28 – 3.12 (m, 2H), 3.01 (hept, *J* = 4.7 Hz, 1H), 2.61 – 2.45 (m, 1H), 2.43 – 2.27 (m, 4H), 2.17 – 2.07 (m, 1H), 2.00 – 1.89 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.9, 163.9 (t, *J* = 32.3 Hz), 144.0, 134.3, 129.8, 129.3, 128.4, 128.2, 122.0, 115.4 (t, *J* = 251.8 Hz), 89.1, 78.7, 63.0, 39.9 (t, *J* = 23.3 Hz), 35.8, 29.7, 25.8, 21.7, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.1 (d, *J* = 262.7 Hz), -106.9 (d, *J* = 262.7 Hz). HRMS (ESI) calcd for $C_{22}H_{22}F_2O_3SNa$ $[M+Na]^+$: 427.1150, found: 427.1157.

2,2-difluoro-1-morpholino-7-phenyl-4-(phenylethynyl)heptane-1,7-dione (**3s**)
(prepared according to the general procedure described above by using **1a** and **2b** as substrates.)



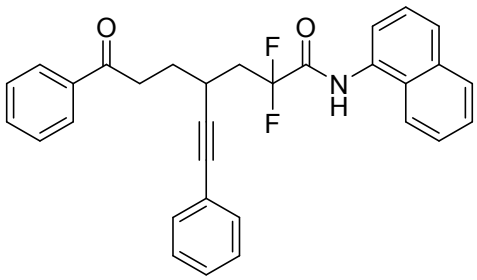
Colorless oil, yield 36%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.98 (m, 2H), 7.59 – 7.53 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.30 – 7.25 (m, 3H), 3.79 – 3.61 (m, 8H), 3.35 – 3.23 (m, 2H), 3.22 – 3.11 (m, 1H), 2.68 – 2.41 (m, 2H), 2.24 – 2.14 (m, 1H), 2.04 – 1.94 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.5, 161.8 (t, *J* = 28.9 Hz), 136.9, 133.1, 131.6, 128.6, 128.2, 128.1, 128.0, 123.3, 118.8 (t, *J* = 255.8 Hz), 90.9, 82.8, 66.7 (d, *J* = 9.0 Hz), 46.6, 43.4, 39.9 (t, *J* = 22.0 Hz), 36.1, 29.8, 25.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -97.6 (d, *J* = 282.3 Hz), -98.9 (d, *J* = 282.1 Hz). HRMS (ESI) calcd for $C_{25}H_{25}F_2NO_3H$ $[M+H]^+$: 426.1875, found: 426.1872.

2,2-difluoro-1-(indolin-1-yl)-7-phenyl-4-(phenylethynyl)heptane-1,7-dione (**3t**)
(prepared according to the general procedure described above by using **1a** and **2c** as substrates.)



Brown oil, yield 36%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 7.9 Hz, 1H), 8.03 – 7.98 (m, 2H), 7.59 – 7.53 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.25 – 7.18 (m, 5H), 7.13 – 7.04 (m, 1H), 4.37 (t, *J* = 8.3 Hz, 2H), 3.33 – 3.25 (m, 2H), 3.23 – 3.14 (m, 3H), 2.80 – 2.46 (m, 2H), 2.28 – 2.17 (m, 1H), 2.10 – 1.95 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.5, 161.2 (t, *J* = 30.0 Hz), 142.7, 136.9, 133.1, 131.7, 131.6, 128.6, 128.2, 127.9, 127.5, 125.1, 124.7, 123.2, 118.5 (t, *J* = 255.9 Hz), 118.0, 90.6, 83.0, 48.0, 39.6 (t, *J* = 22.5 Hz), 36.1, 29.8, 28.7, 25.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.3 (s). HRMS (ESI) calcd for $C_{29}H_{25}F_2NO_2Na$ $[M+Na]^+$: 480.1746, found: 480.1738.

2,2-difluoro-N-(naphthalen-1-yl)-7-oxo-7-phenyl-4-(phenylethynyl)heptanamide (**3u**)
(prepared according to the general procedure described above by using **1a** and **2d** as substrates.)



Khaki oil, 34% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 8.01 – 7.92 (m, 3H), 7.89 – 7.77 (m, 2H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.52 – 7.35 (m, 5H), 7.27 – 7.20 (m, 3H), 7.22 – 7.16 (m, 1H), 7.18 – 7.09 (m, 2H), 3.30 – 3.20 (m, 2H), 3.15 (hept, *J* = 4.8 Hz, 1H), 2.84 – 2.65 (m, 1H), 2.63 – 2.47 (m, 1H), 2.30 – 2.13 (m, 1H), 2.07 – 1.95 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.3, 162.3 (t, *J* = 28.1 Hz), 136.8, 134.0, 133.2, 131.6, 130.3, 128.8, 128.6, 128.1, 128.0, 126.7, 126.7, 126.2, 125.5, 122.8, 120.8, 120.1, 117.9 (t, *J* = 255.7 Hz), 89.5, 84.0, 39.1 (t, *J* = 22.8 Hz), 35.9, 29.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -100.7 (d, *J* = 257.4 Hz), -104.1 (d, *J* = 257.4 Hz). HRMS (ESI) calcd for $C_{31}H_{25}F_2NO_2Na$ $[M+Na]^+$: 504.1746, found: 504.1741.

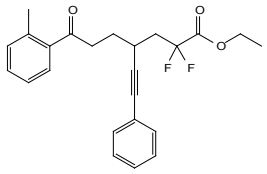
5. References

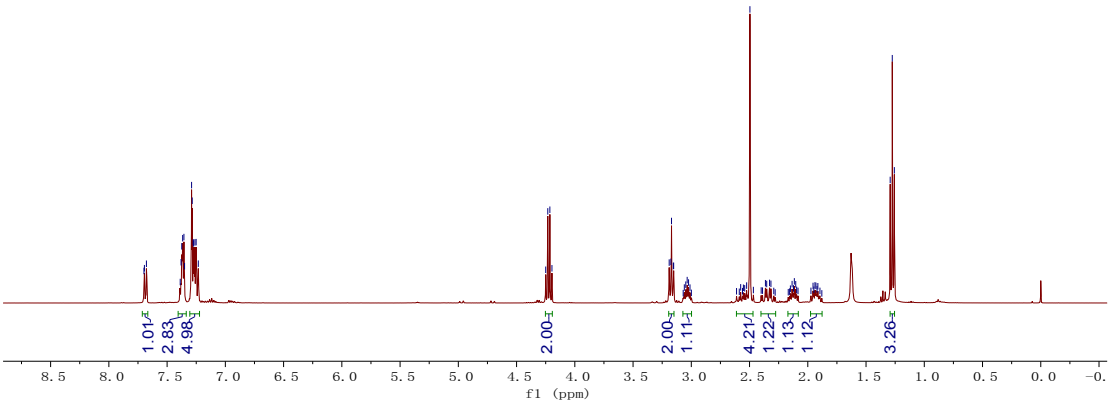
[1] Denis V. Gribkov, Kai C. Hultzsch, and Frank Hampel, *J. Am. Chem. Soc.*, **2006**, *128*, 3748–3759.
[2] Weidong Raoa and Philip Wai Hong Chan, *Org. Biomol. Chem.*, **2010**, *8*, 4016-4025

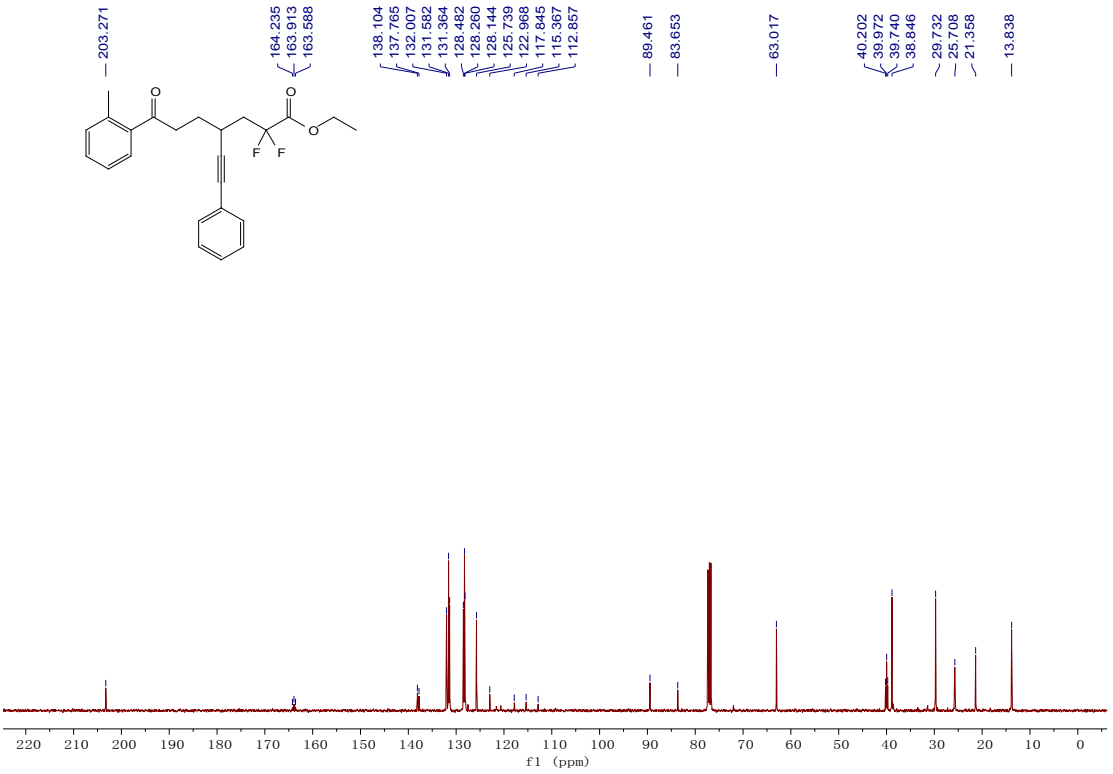
^{1}H, ^{13}C, and ^{19}F NMR spectra

ethyl 2,2-difluoro-7-oxo-7-phenyl-4-(phenylethynyl)heptanoate (**3a**)

ethyl 2,2-difluoro-7-oxo-4-(phenylethynyl)-7-(o-tolyl)heptanoate (**3b**)



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164.235
163.913
163.588
138.104
137.765
132.007
131.582
131.364
128.482
128.260
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125.739
122.968
117.845
115.367
112.857
89.461
83.653
63.017
40.202
39.972
39.740
38.846
29.732
25.708
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O
O
F
F
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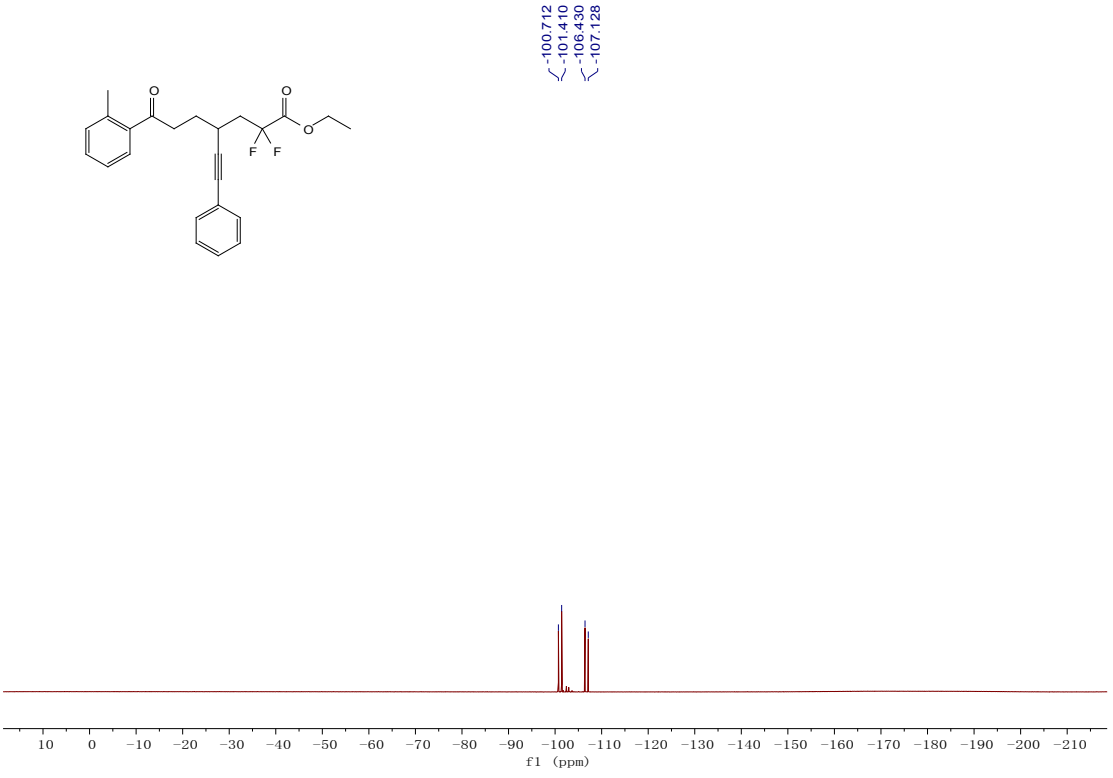
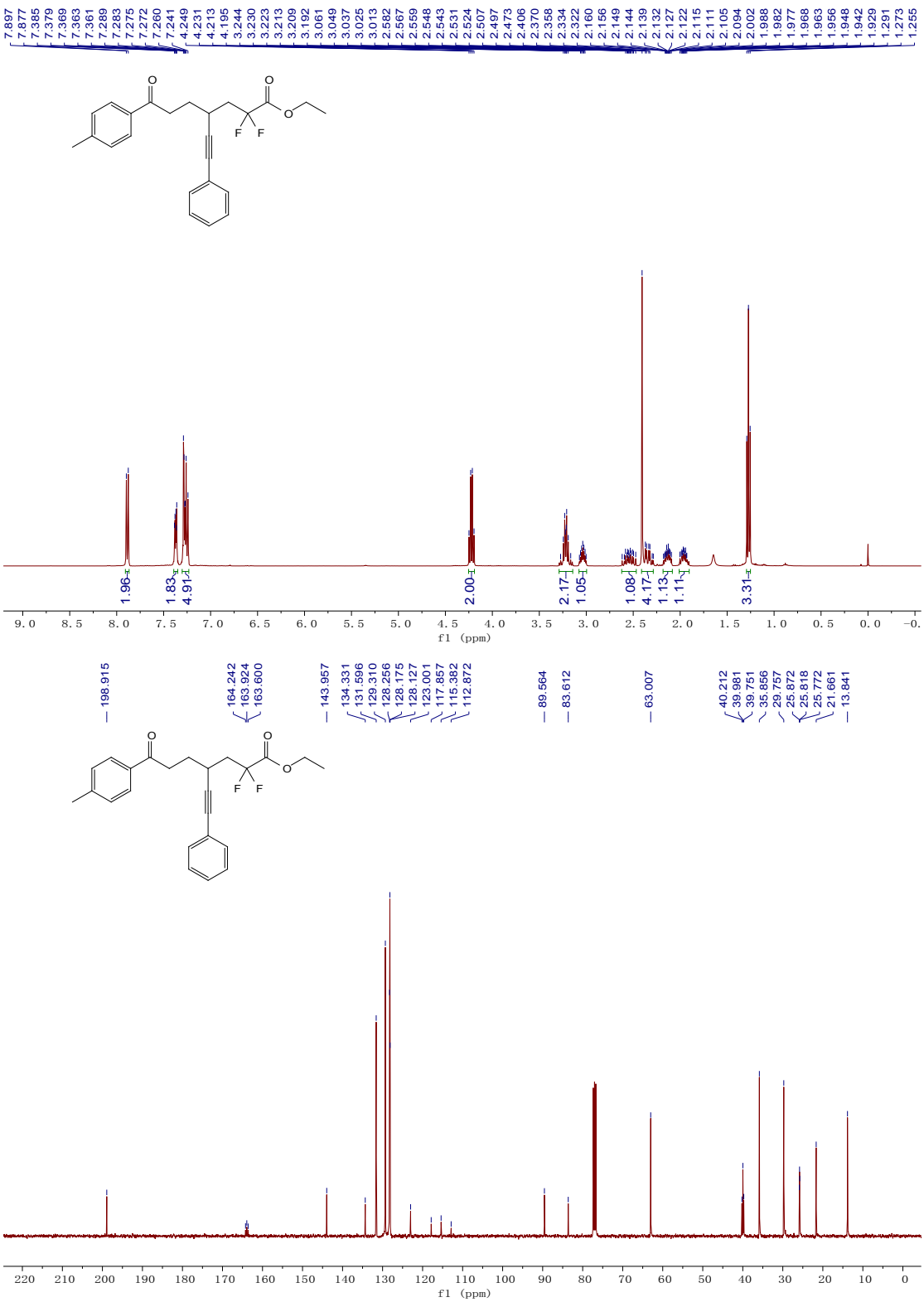
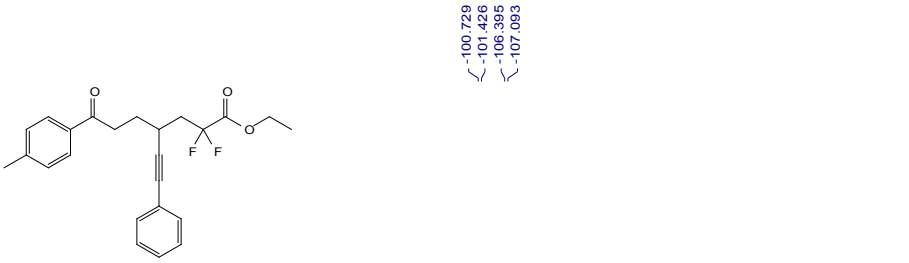
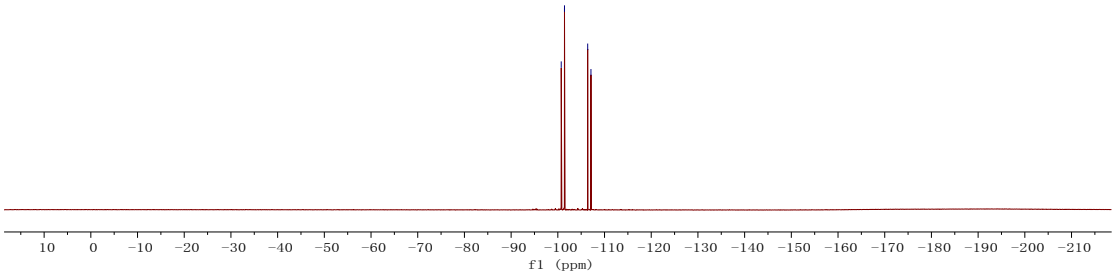
f1 (ppm)


-100.712
-101.410
-106.430
-107.128
O
O
O
F
F
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

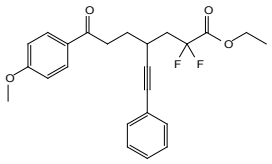
ethyl 2,2-difluoro-7-oxo-4-(phenylethynyl)-7-(p-tolyl)heptanoate (**3c**)

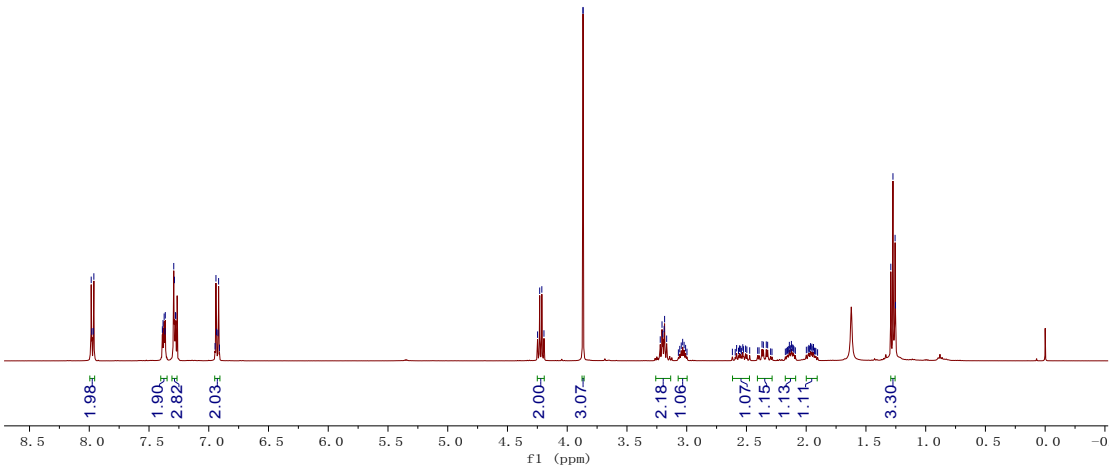


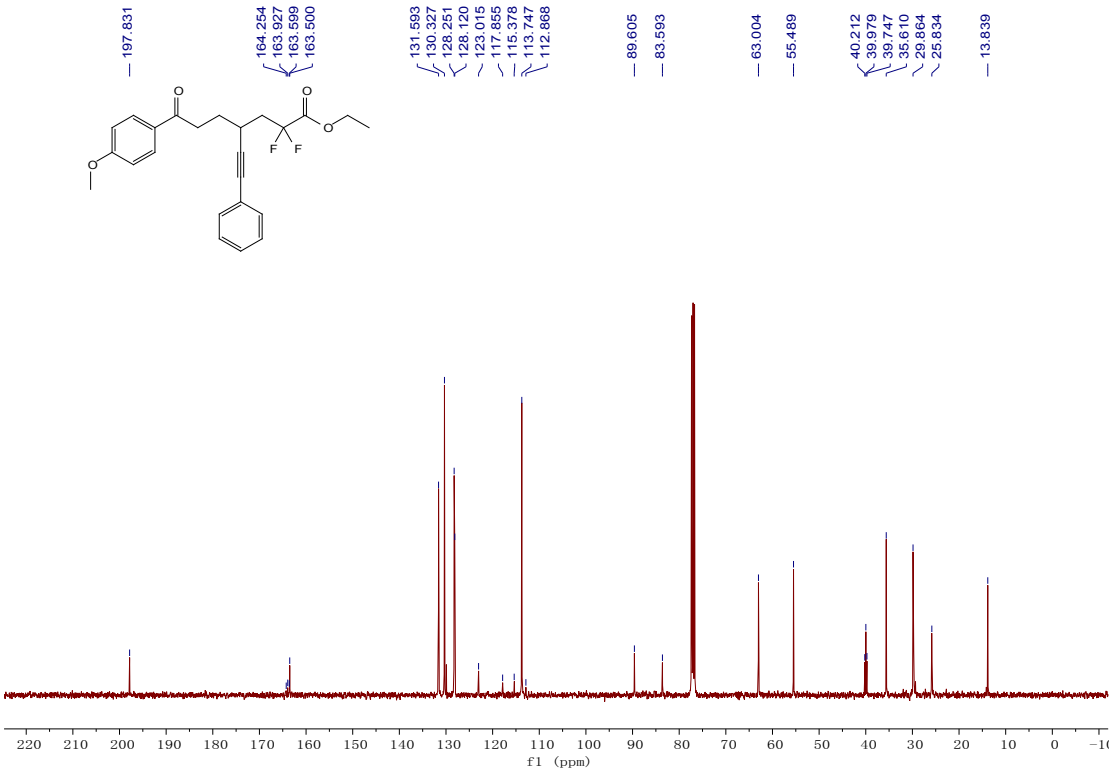


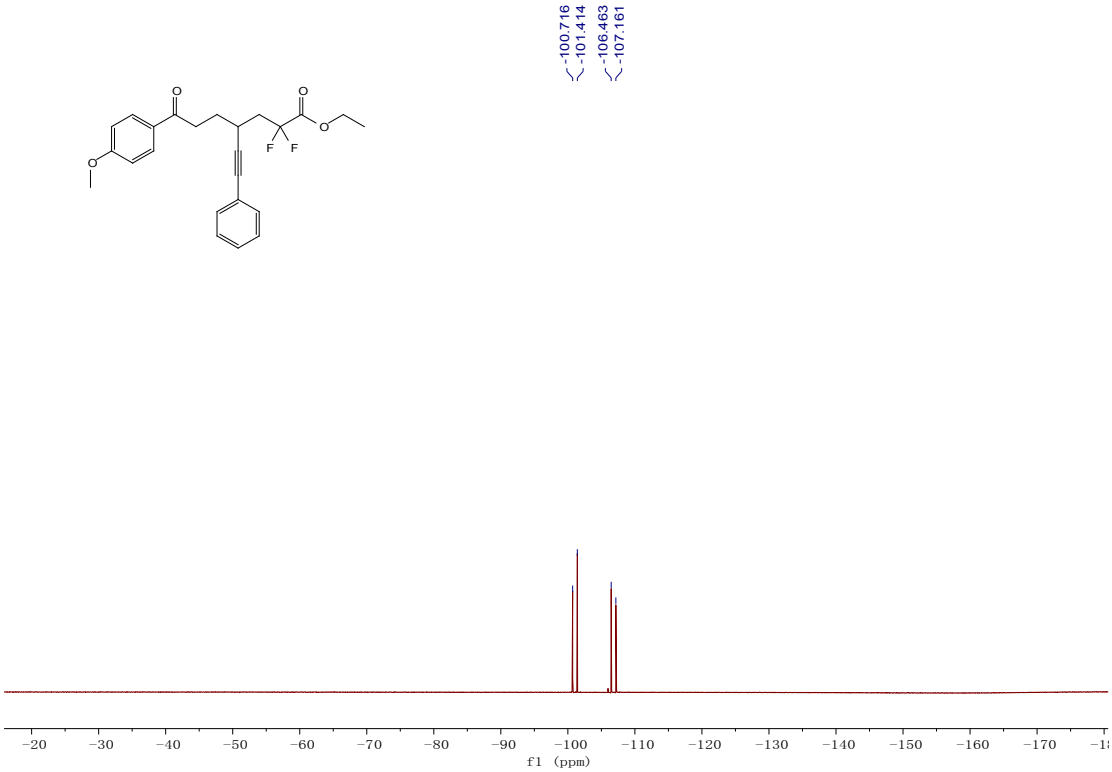


ethyl 2,2-difluoro-7-(4-methoxyphenyl)-7-oxo-4-(phenylethynyl)heptanoate (**3d**)

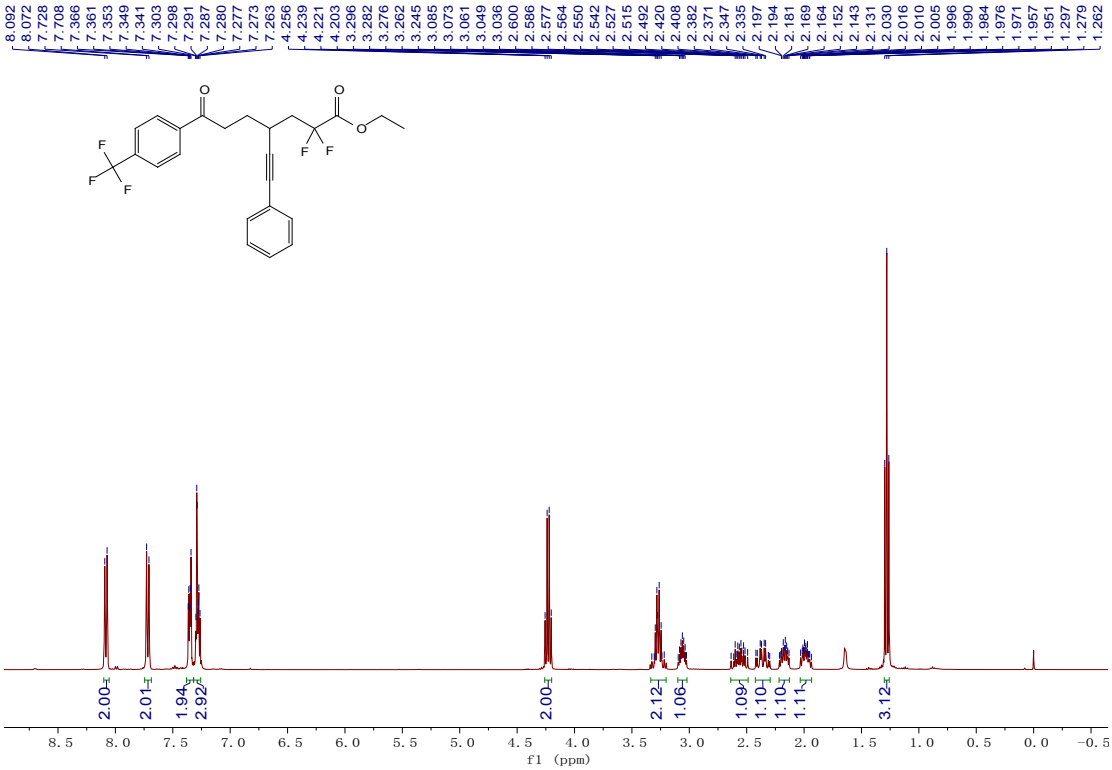


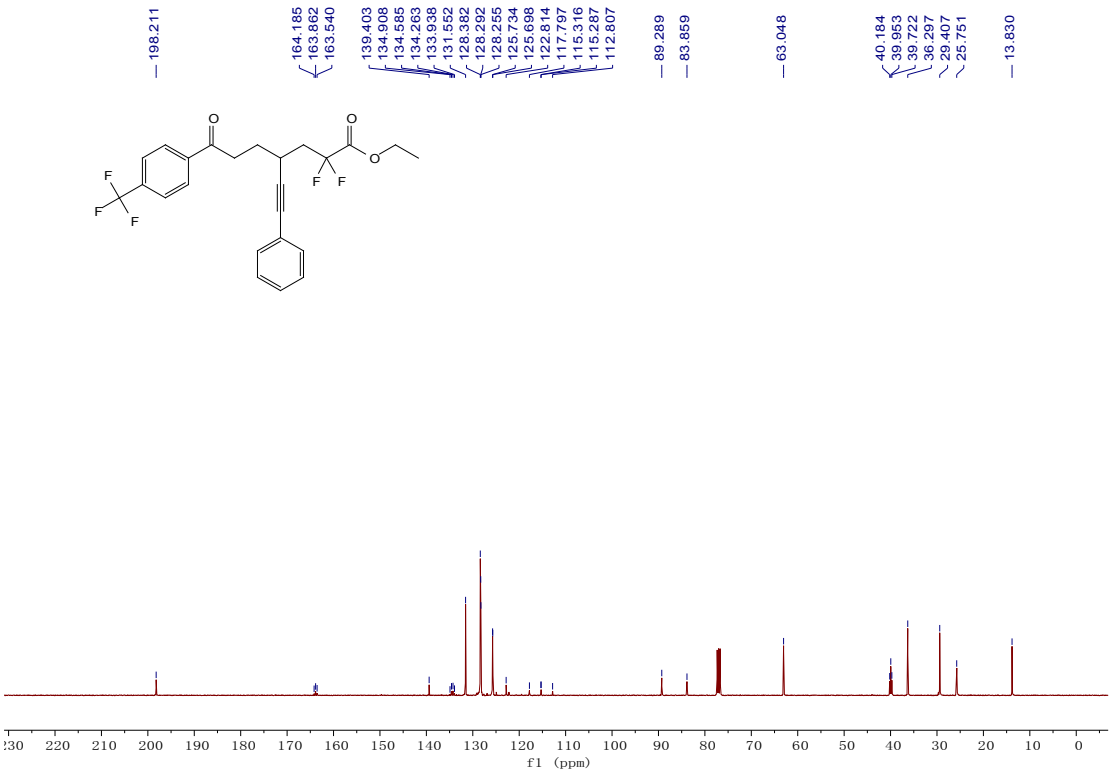


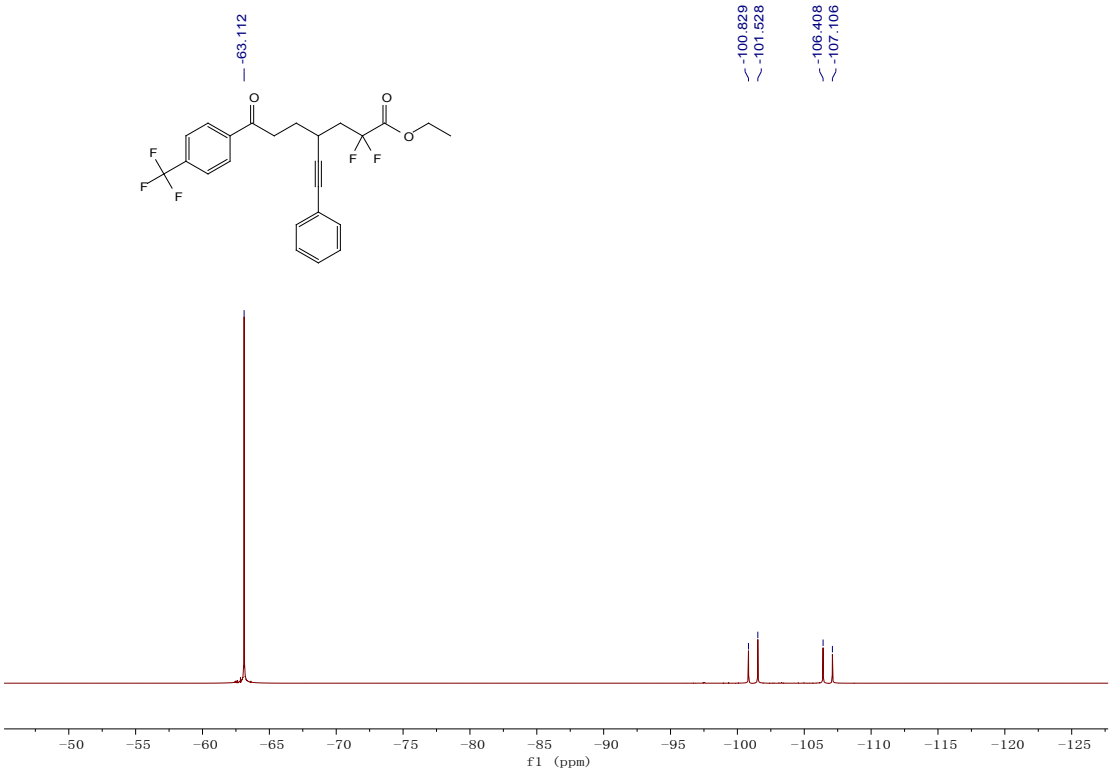

197.831
164.254
163.927
163.599
163.500
131.593
130.327
128.251
128.120
123.015
117.855
115.378
113.747
112.868
89.605
83.593
63.004
55.489
40.212
39.979
39.747
35.610
29.864
25.834
13.839
O
O
O
O
F
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)


-100.716
-101.414
-106.463
-107.161
O
O
O
O
F
F
−20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −1
f1 (ppm)

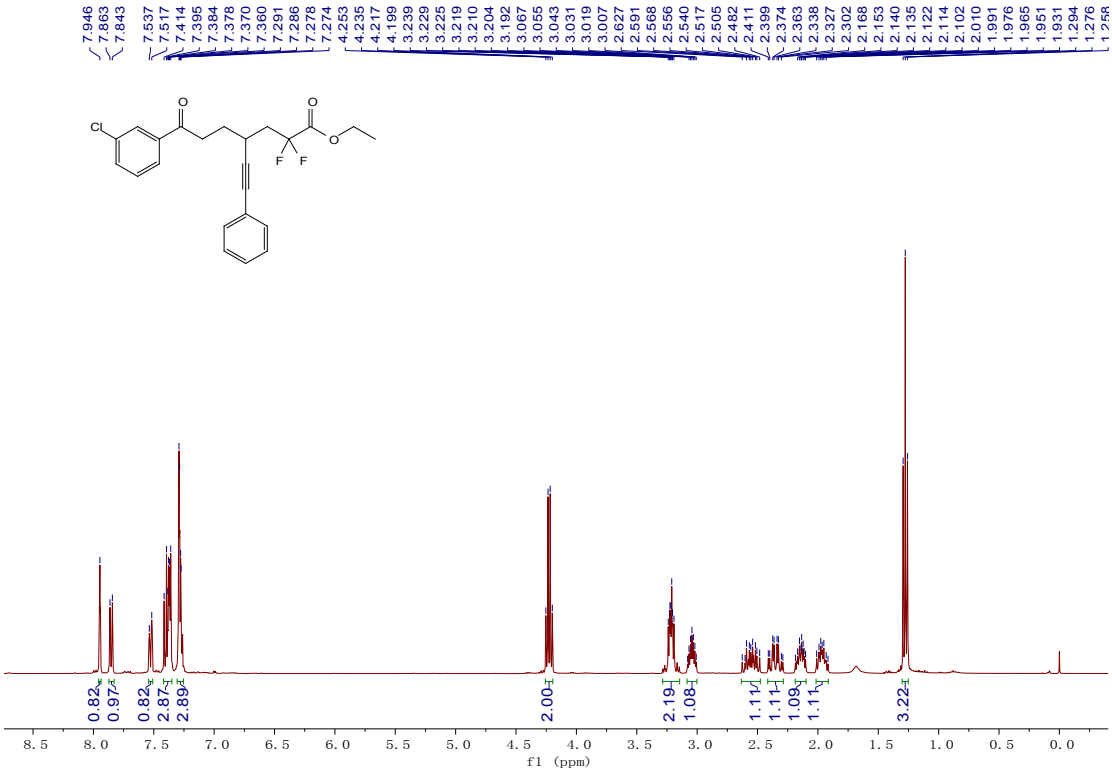
ethyl 2,2-difluoro-7-oxo-4-(phenylethynyl)-7-(4-(trifluoromethyl)phenyl)heptanoate (**3e**)

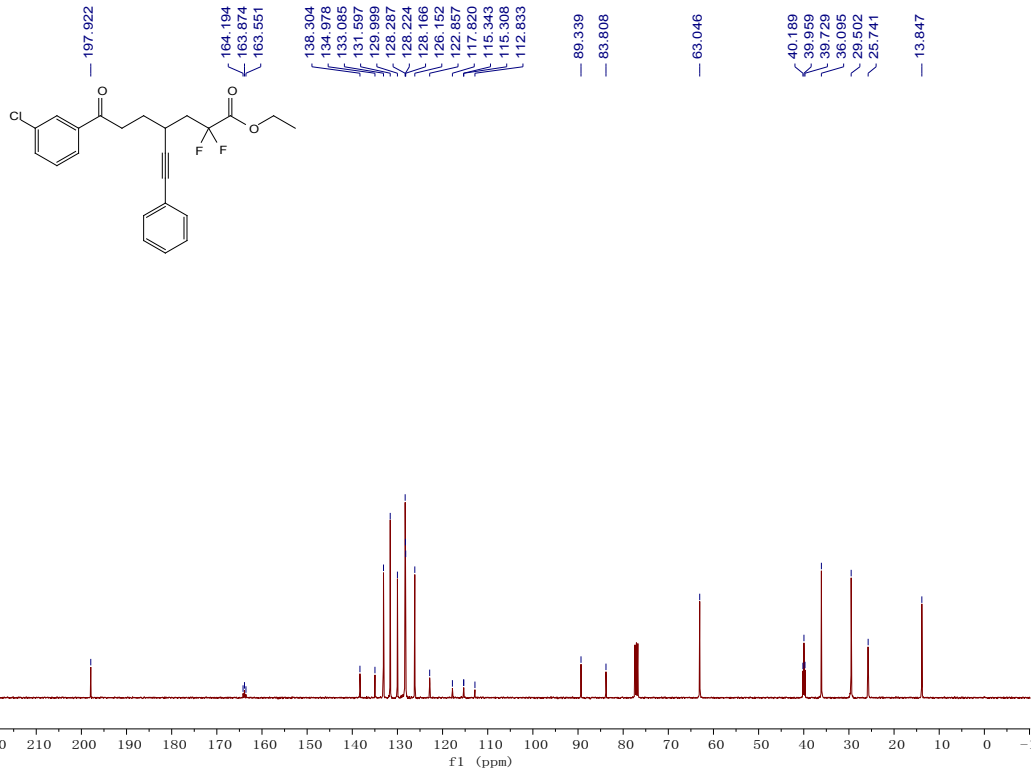


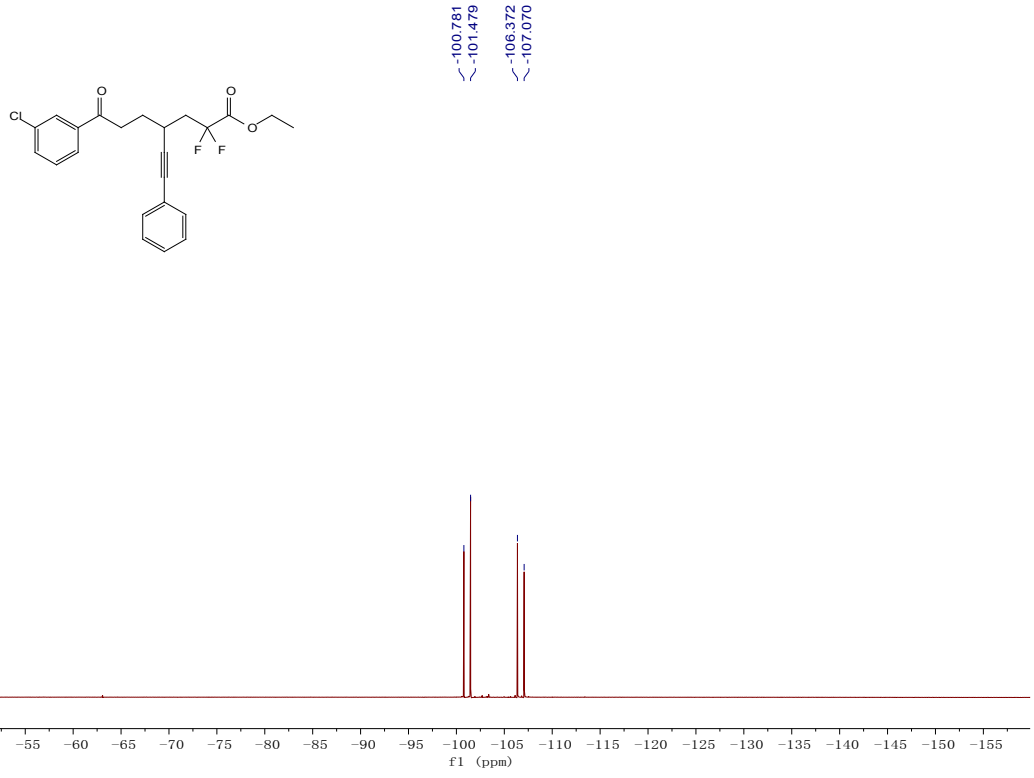




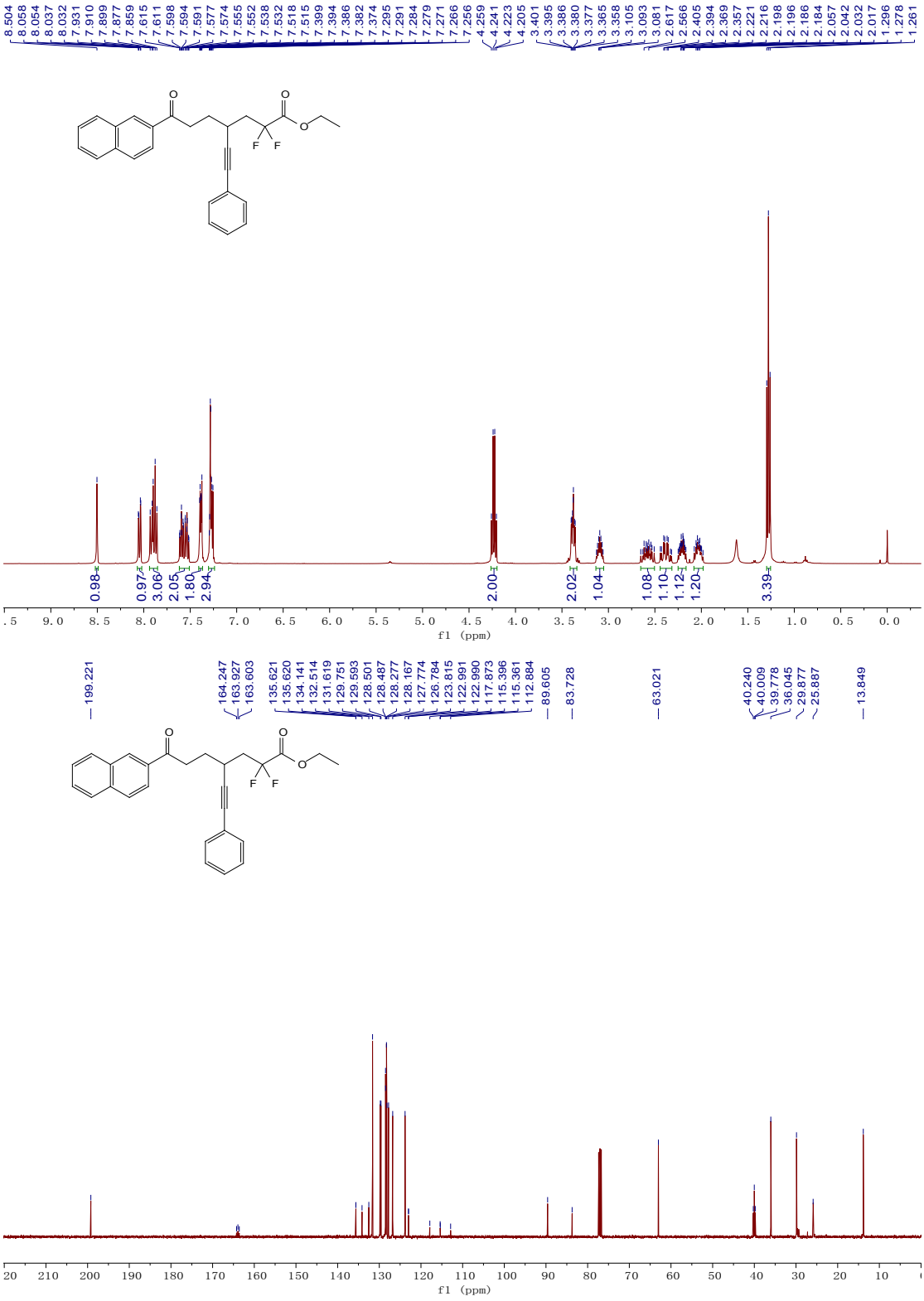
ethyl 7-(3-chlorophenyl)-2,2-difluoro-7-oxo-4-(phenylethynyl)heptanoate (**3f**)

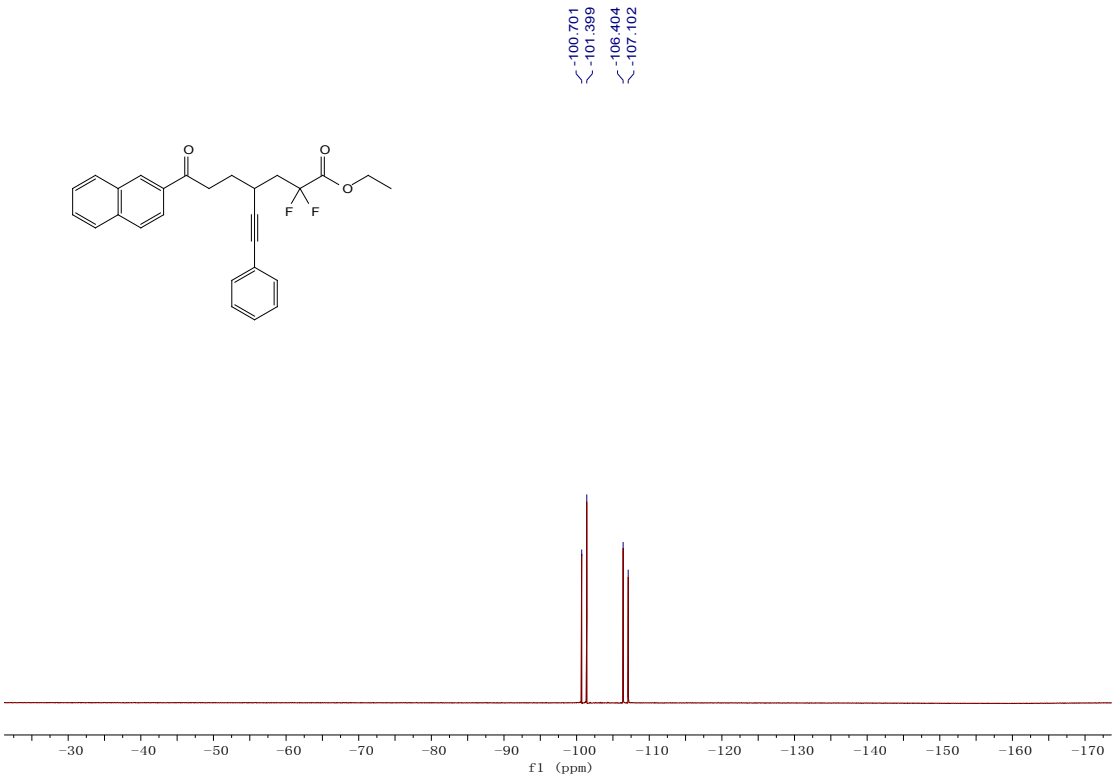



197.922
164.194
163.874
163.551
138.304
134.978
133.085
131.597
129.999
128.287
128.224
128.166
126.152
122.857
117.820
115.343
115.308
112.833
89.339
83.808
63.046
40.189
39.959
39.729
36.095
29.502
25.741
13.847
Cl
O
O
O
F
F
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

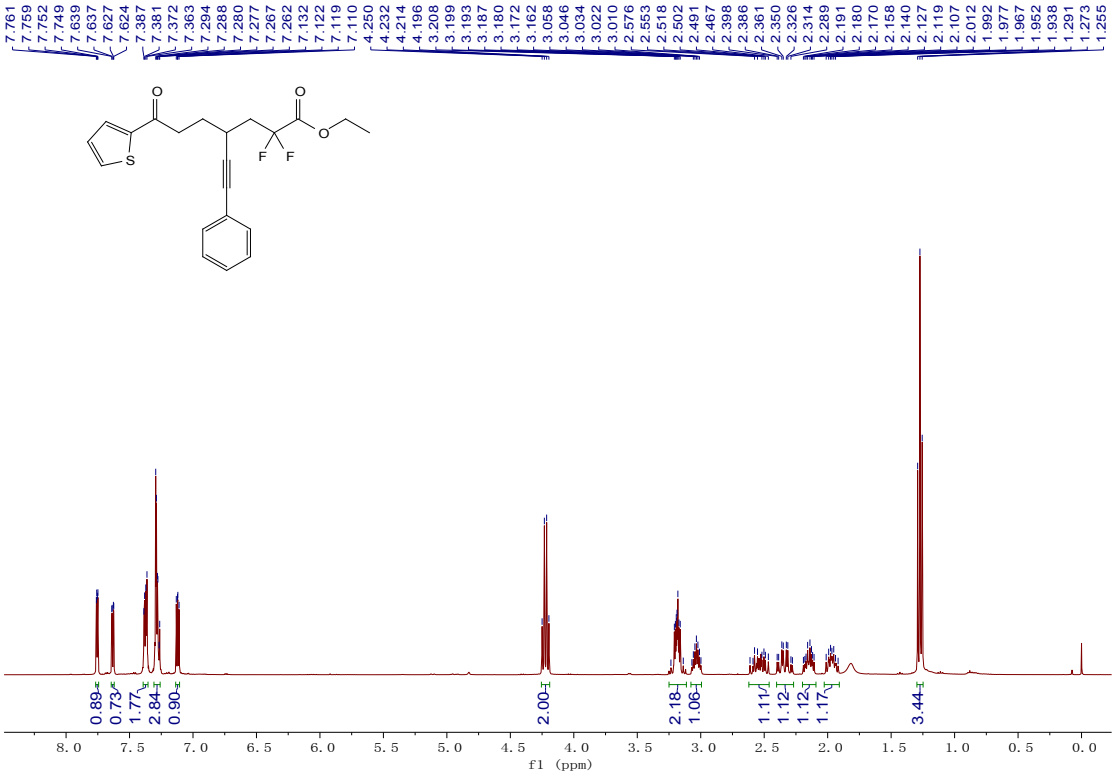

-100.781
-101.479
-106.372
-107.070
Cl
O
O
O
F
F
45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
f1 (ppm)

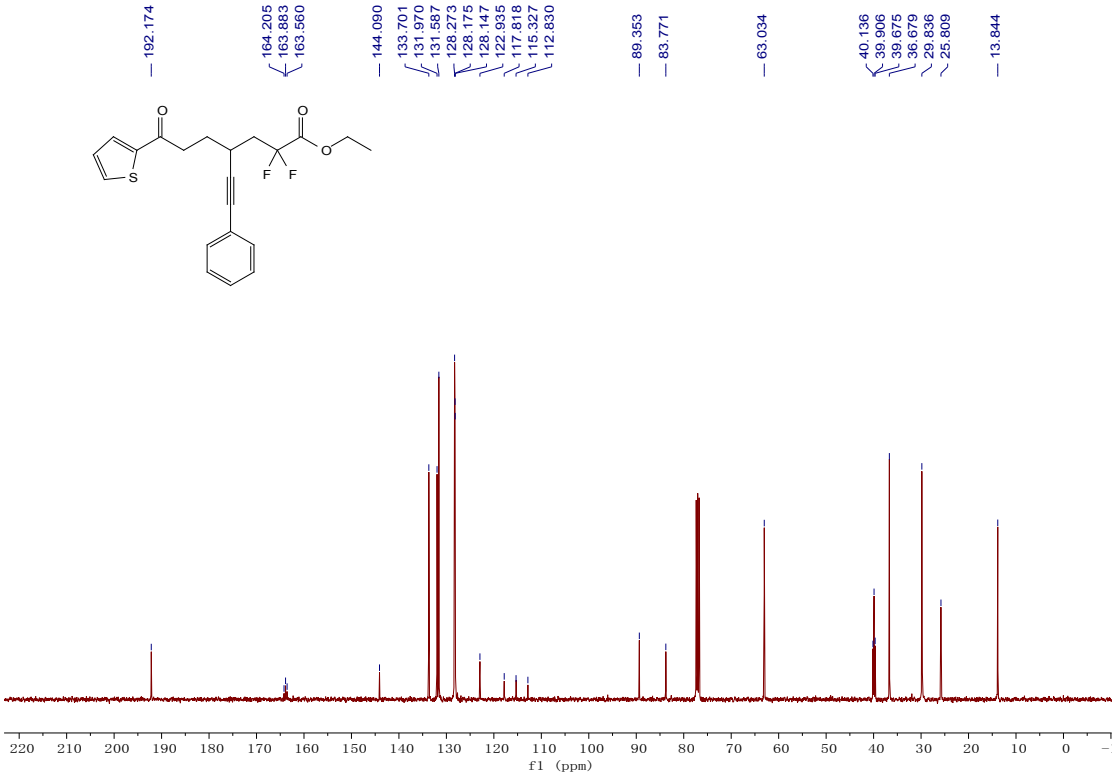
ethyl 2,2-difluoro-7-(naphthalen-2-yl)-7-oxo-4-(phenylethynyl)heptanoate (**3g**)





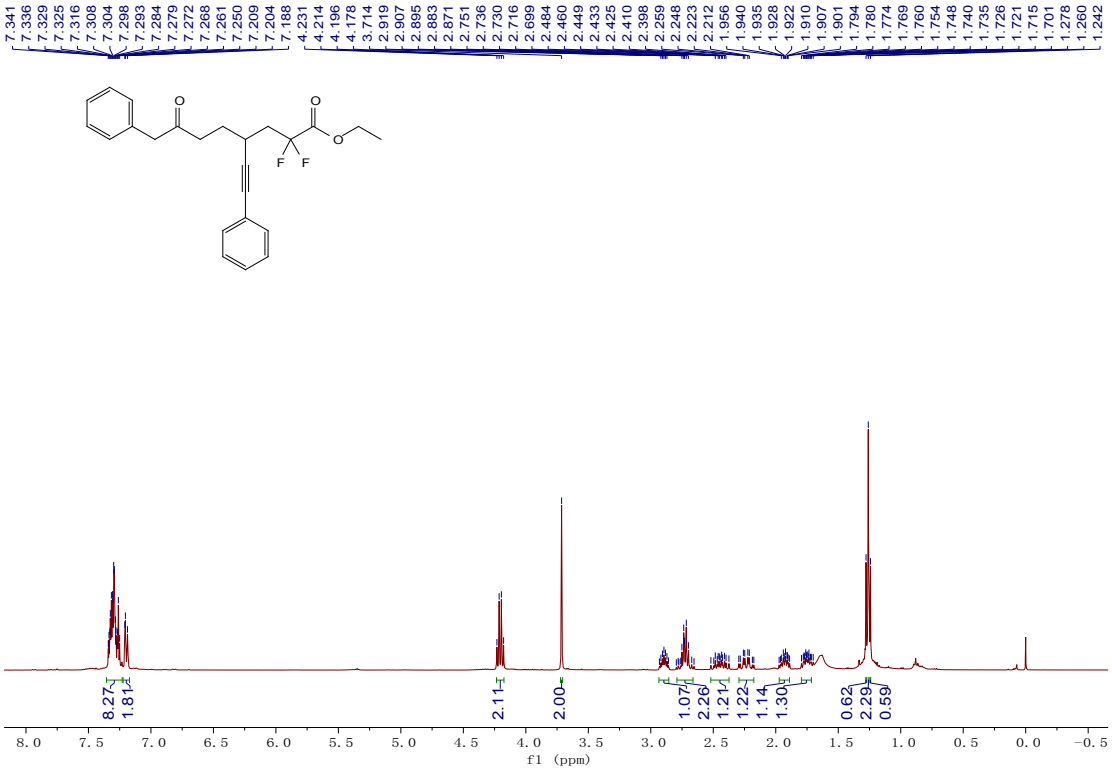
ethyl 2,2-difluoro-7-oxo-4-(phenylethynyl)-7-(thiophen-2-yl)heptanoate (**3h**)

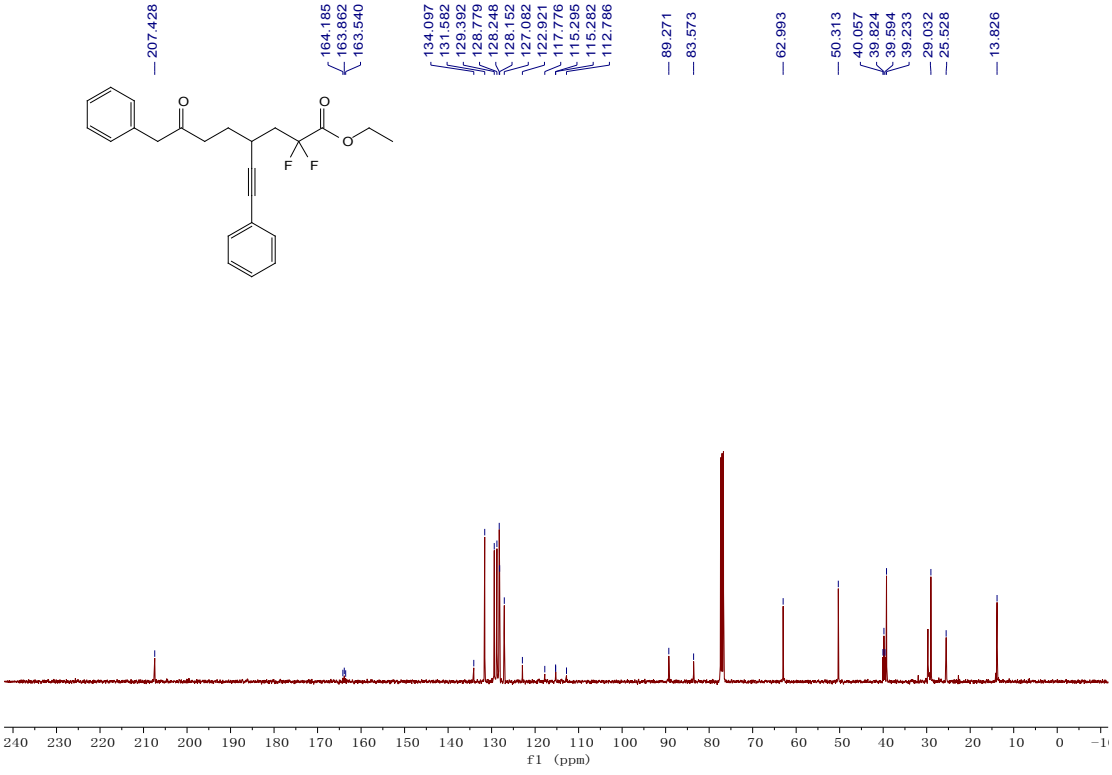


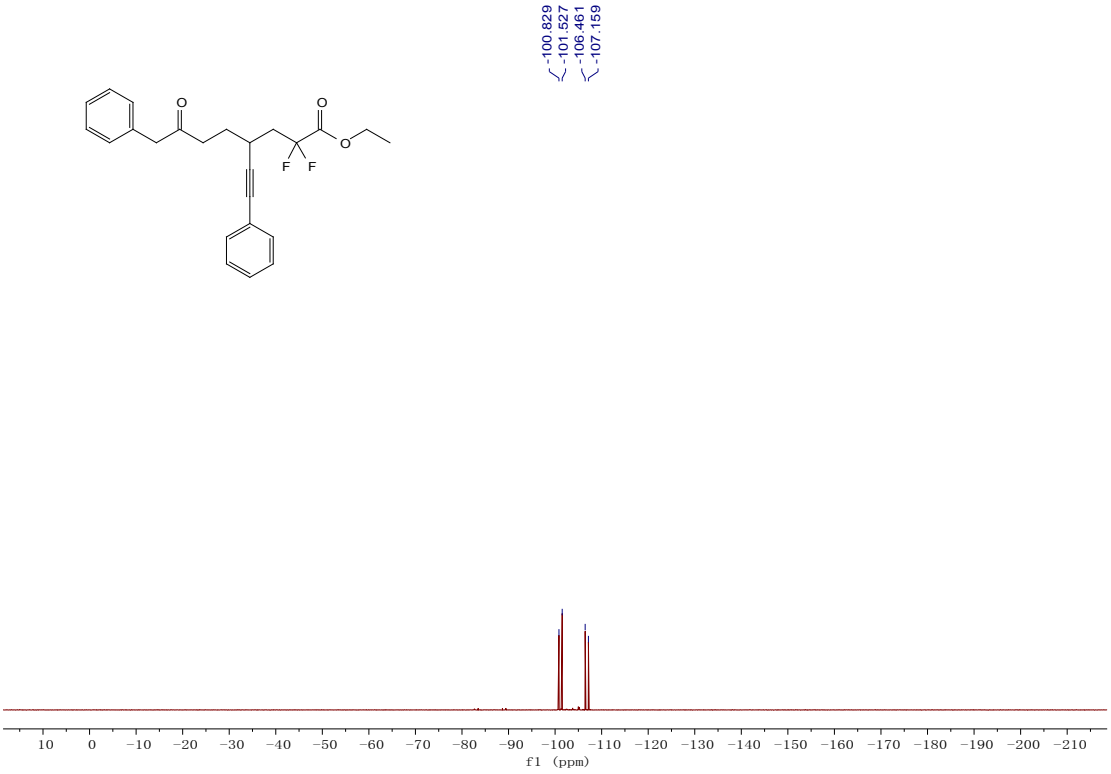

192.174
164.205
163.883
163.560
144.090
133.701
131.970
131.587
128.273
128.175
128.147
122.935
117.818
115.327
112.830
89.353
83.771
63.034
40.136
39.906
39.675
36.679
29.836
25.809
13.844
O
O
O
S
F
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-100.784
-101.482
-106.362
-107.060
O
O
O
S
F
F
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

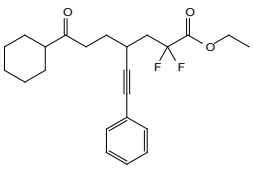
ethyl 2,2-difluoro-7-oxo-8-phenyl-4-(phenylethynyl)octanoate (**3i**)

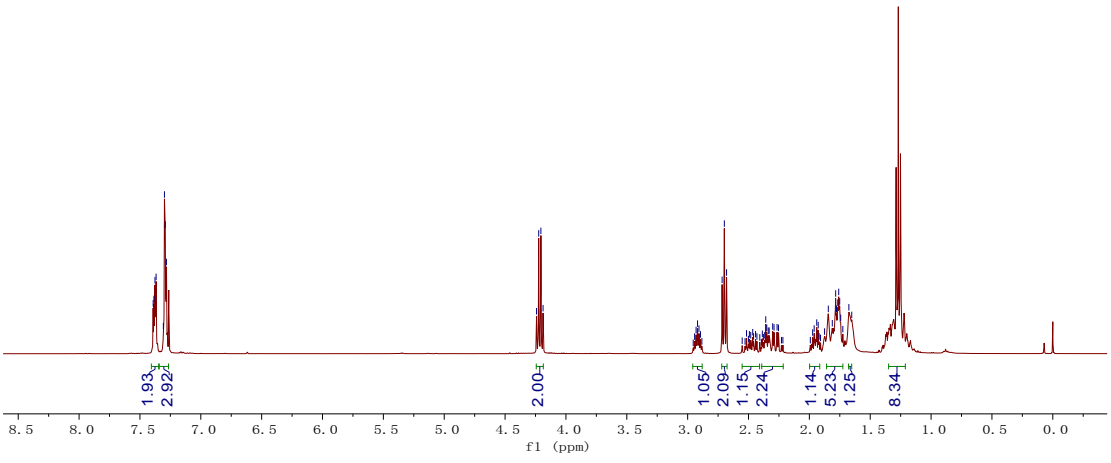


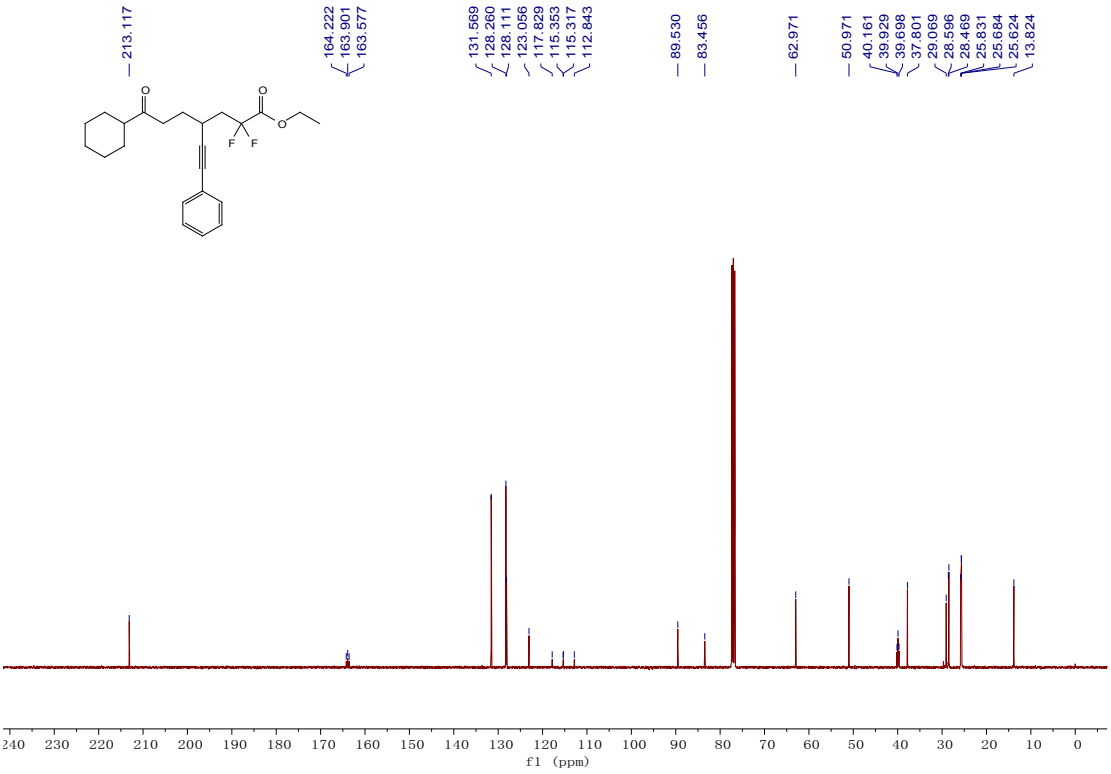


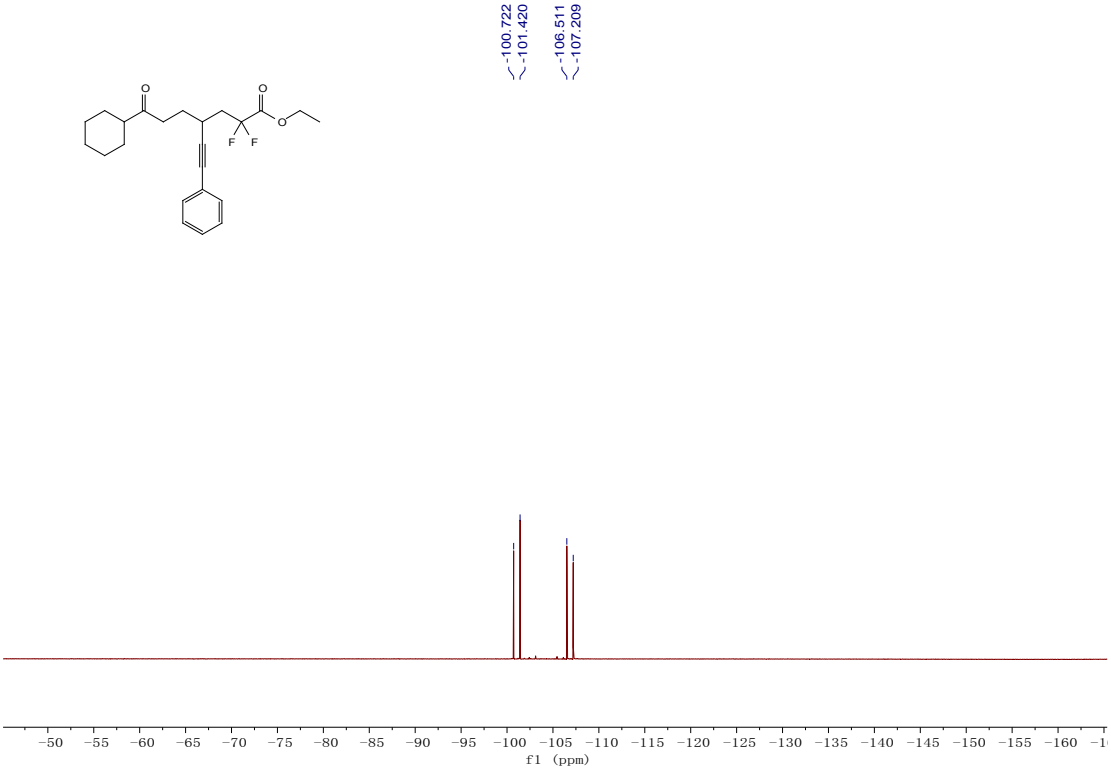


ethyl 7-cyclohexyl-2,2-difluoro-7-oxo-4-(phenylethynyl)heptanoate (**3j**)

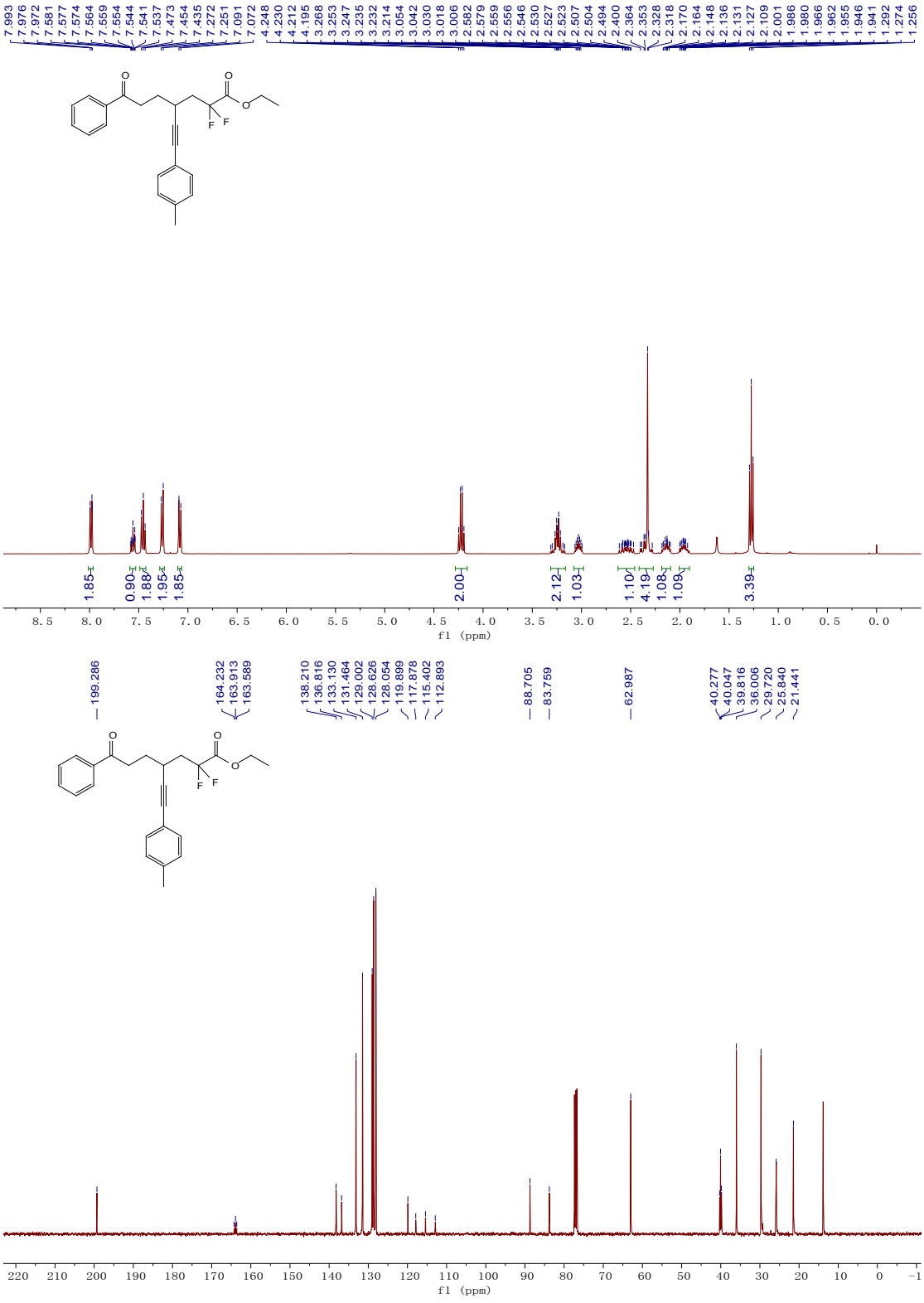


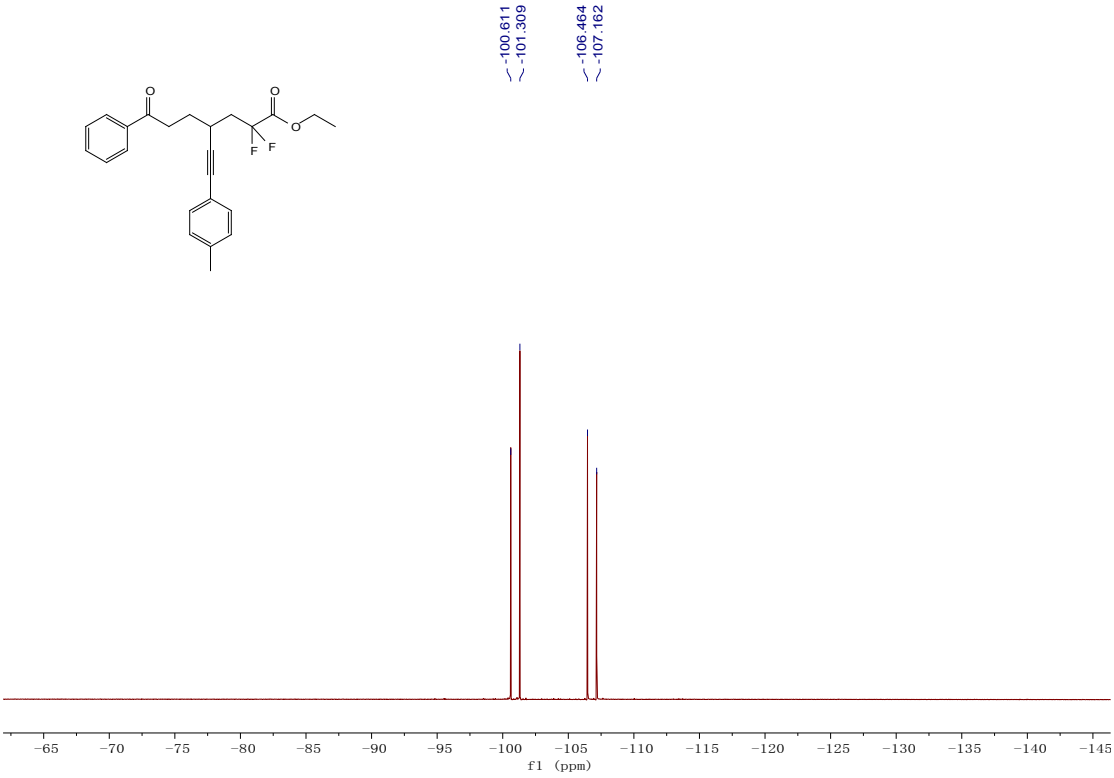



213.117
164.222
163.901
163.577
131.569
128.260
128.111
123.056
117.829
115.353
115.317
112.843
89.530
83.456
62.971
50.971
40.161
39.929
39.698
37.801
29.069
28.596
28.469
25.831
25.684
25.624
13.824
O
O
O
F
F
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

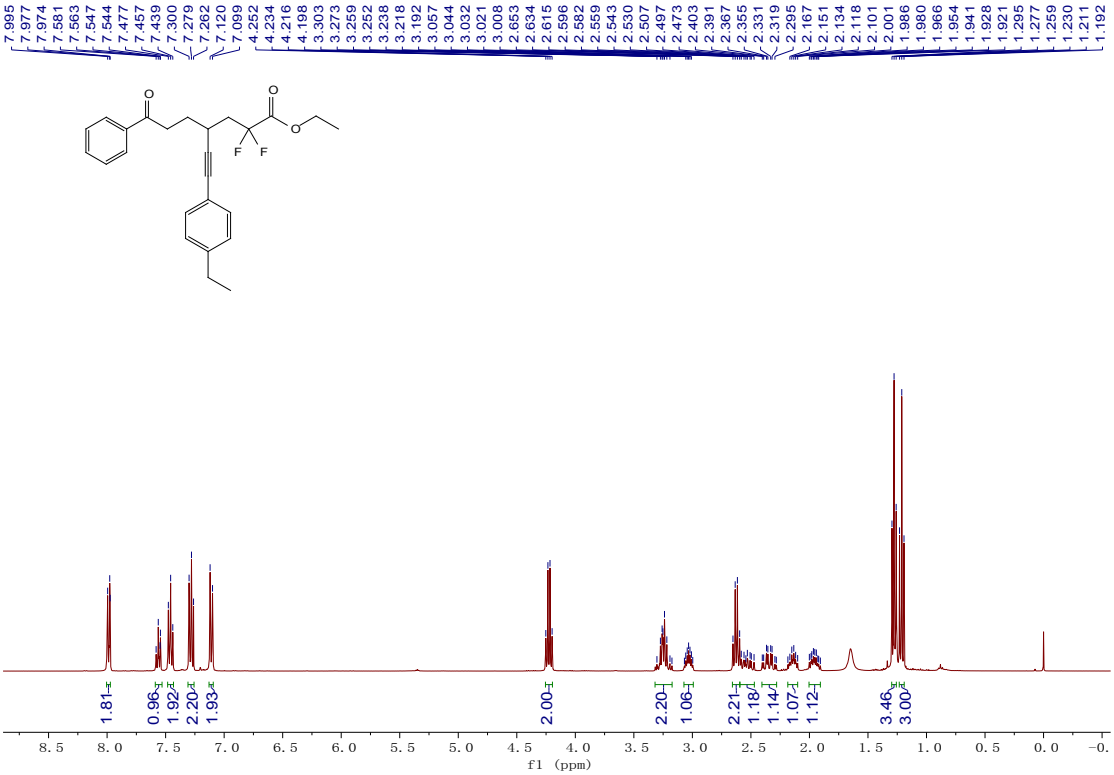

-100.722
-101.420
-106.511
-107.209
O
O
O
F
F
−50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160
f1 (ppm)

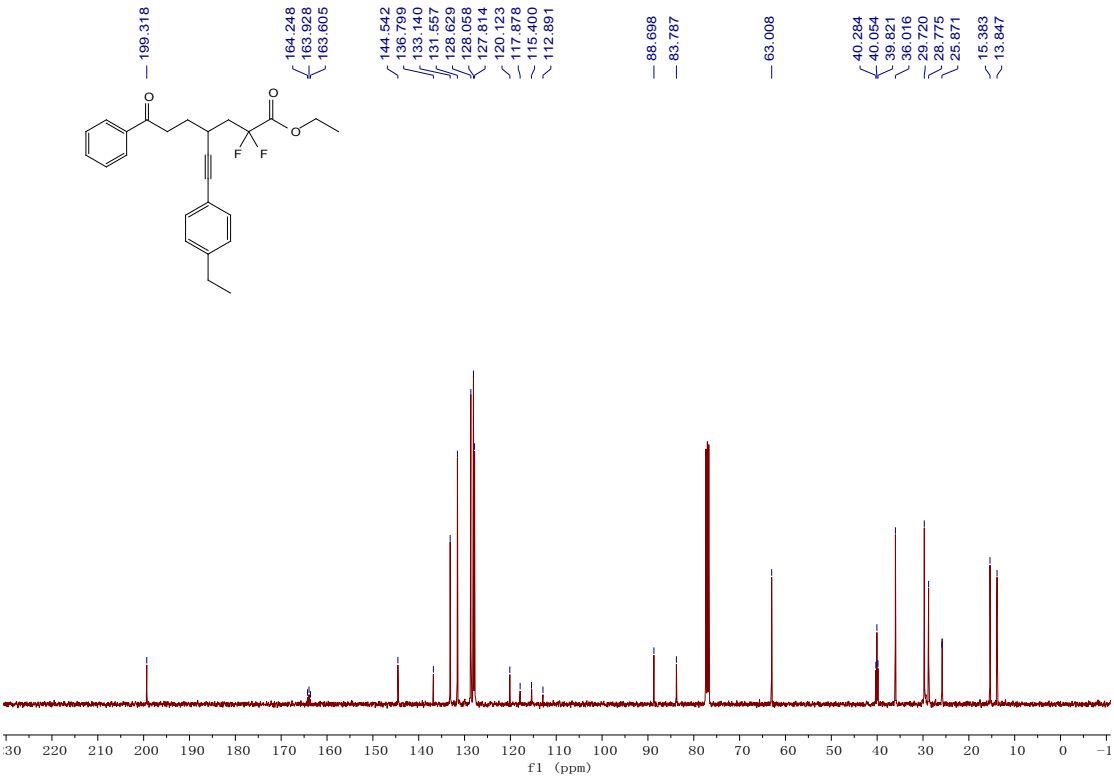
ethyl 2,2-difluoro-7-oxo-7-phenyl-4-(p-tolylethynyl)heptanoate (**3k**)

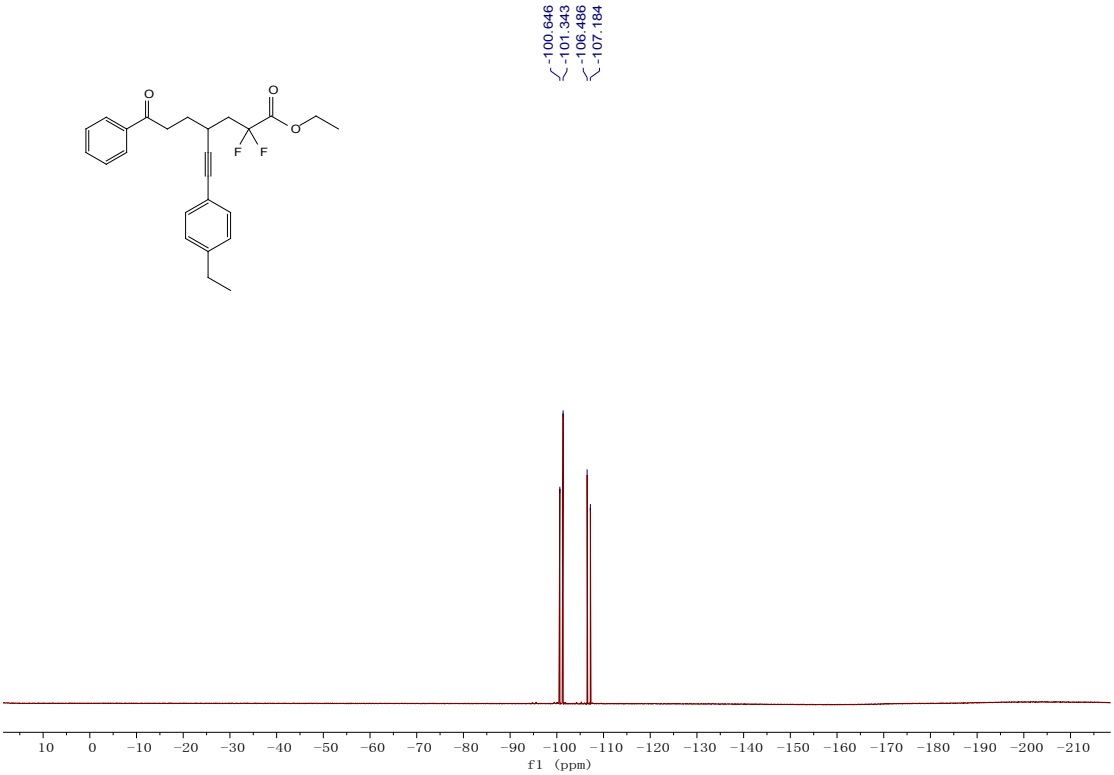




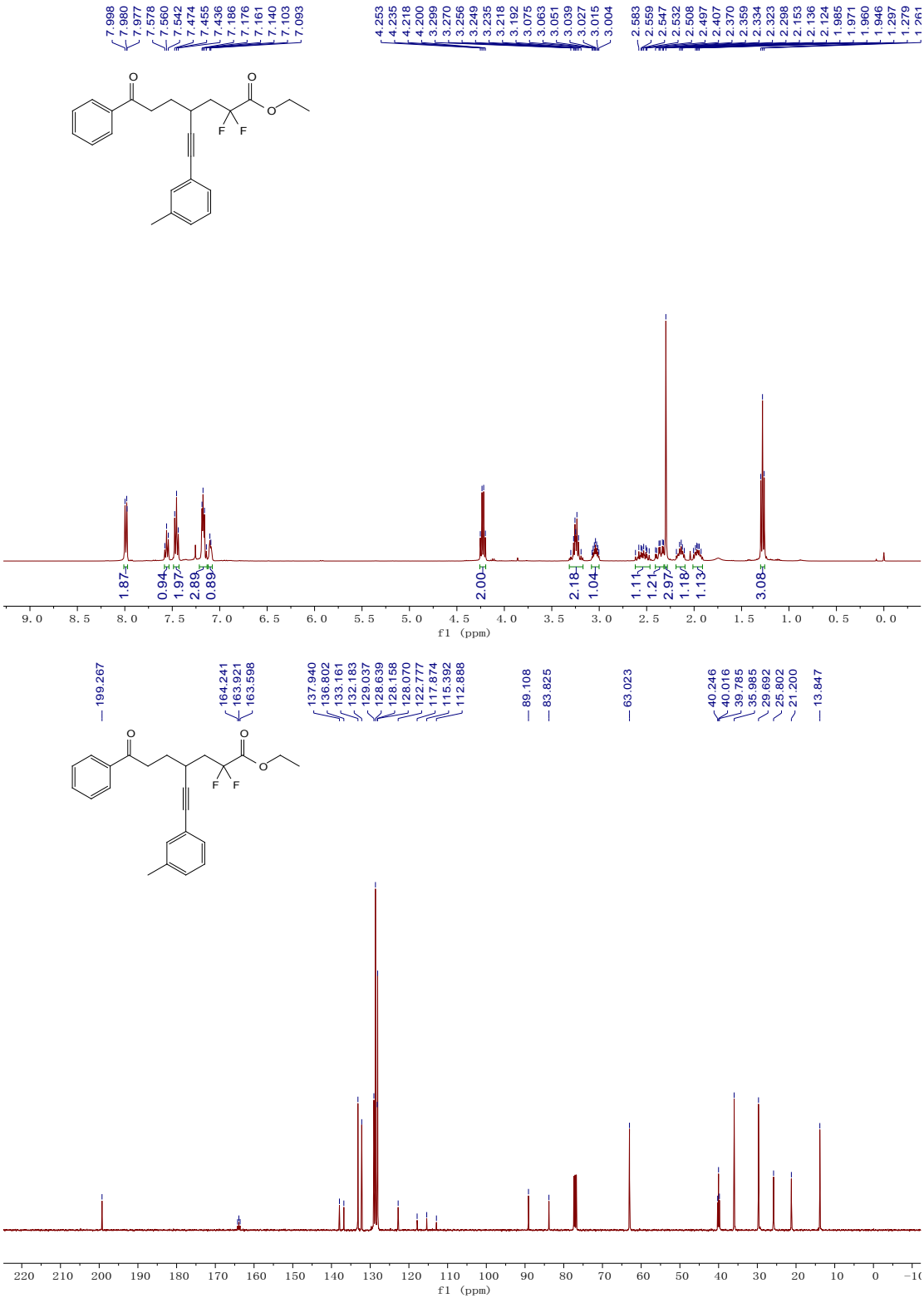
ethyl 4-((4-ethylphenyl)ethynyl)-2,2-difluoro-7-oxo-7-phenylheptanoate (**3l**)

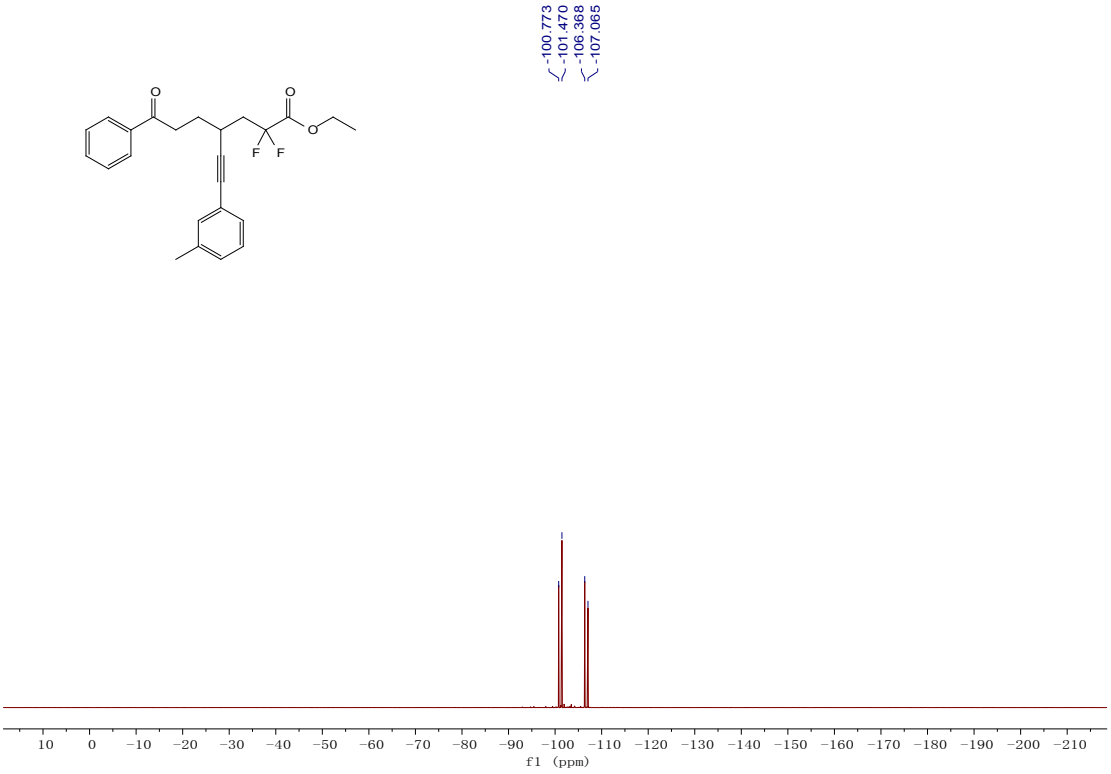



199.318
164.248
163.928
163.605
144.542
136.799
133.140
131.557
128.629
128.058
127.814
120.123
117.878
115.400
112.891
88.698
83.787
63.008
40.284
40.054
39.821
36.016
29.720
28.775
25.871
15.383
13.847
O
O
O
F
F
f1 (ppm)

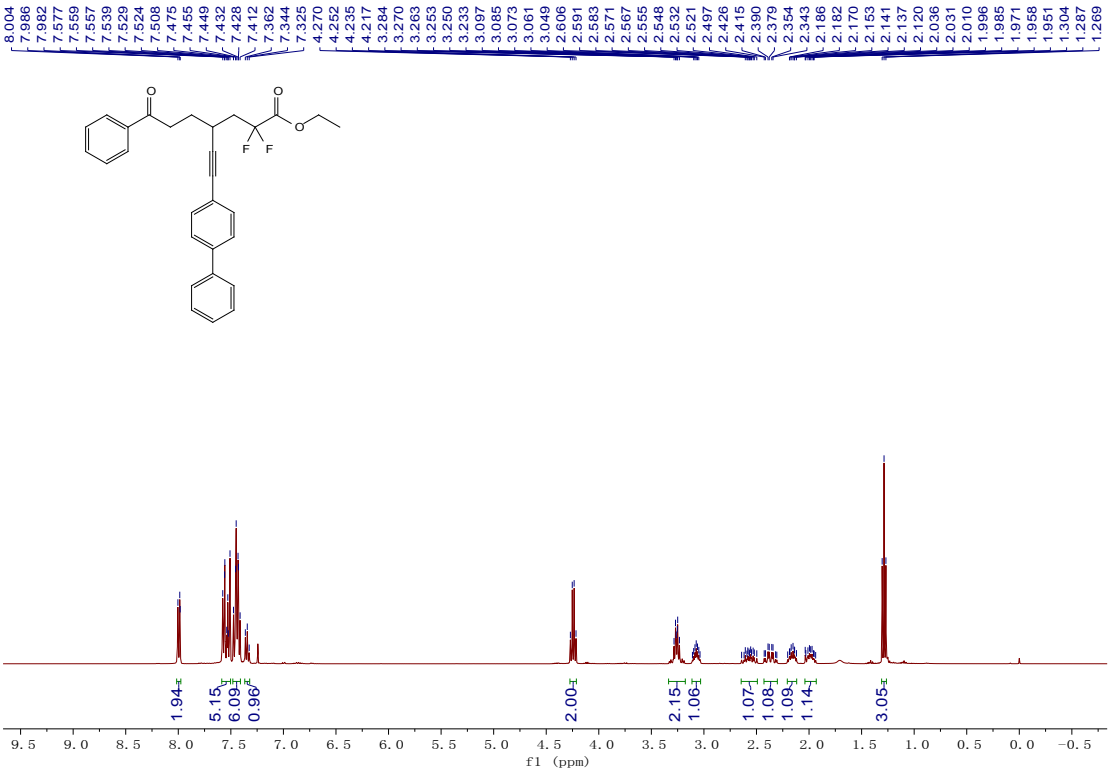

-100.646
-101.343
-106.486
-107.184
O
O
O
F
F
f1 (ppm)

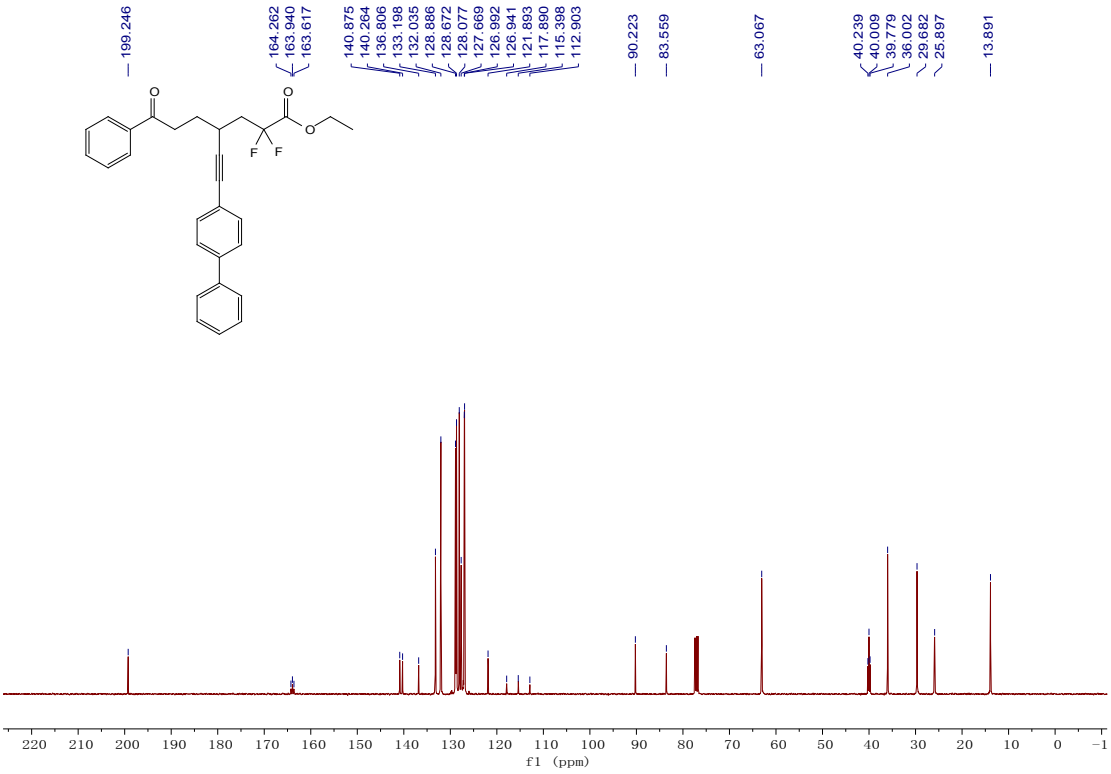
ethyl 2,2-difluoro-7-oxo-7-phenyl-4-(m-tolylethynyl)heptanoate (**3m**)

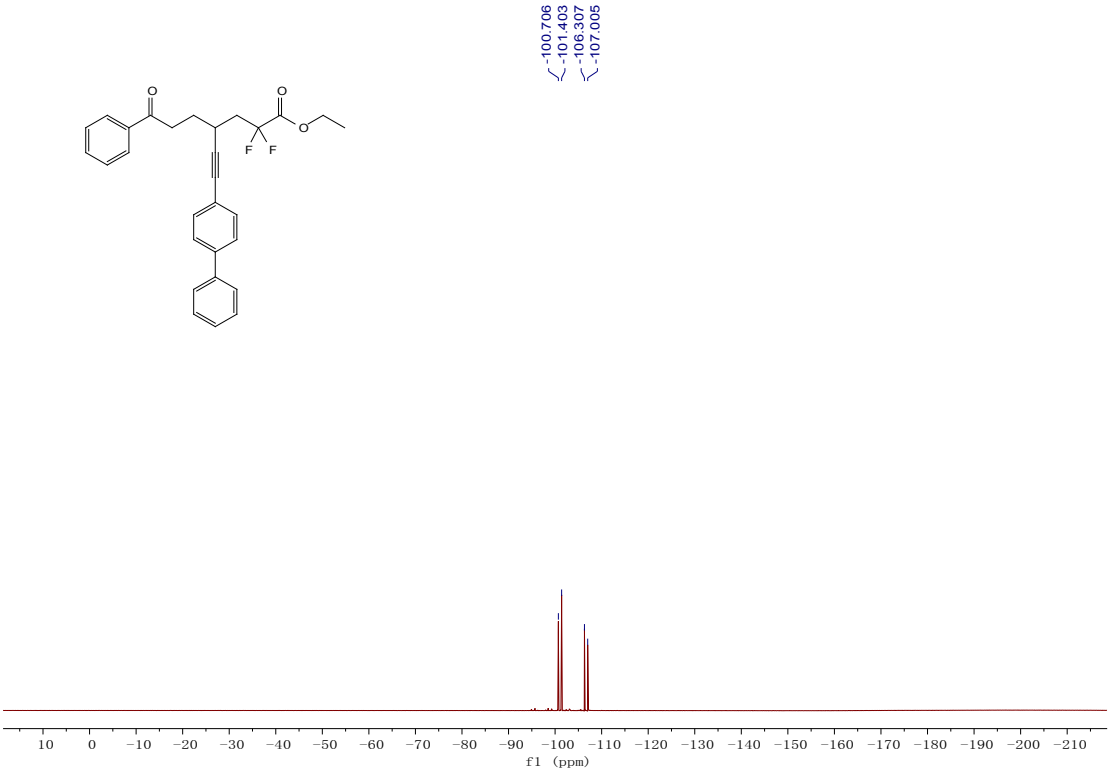




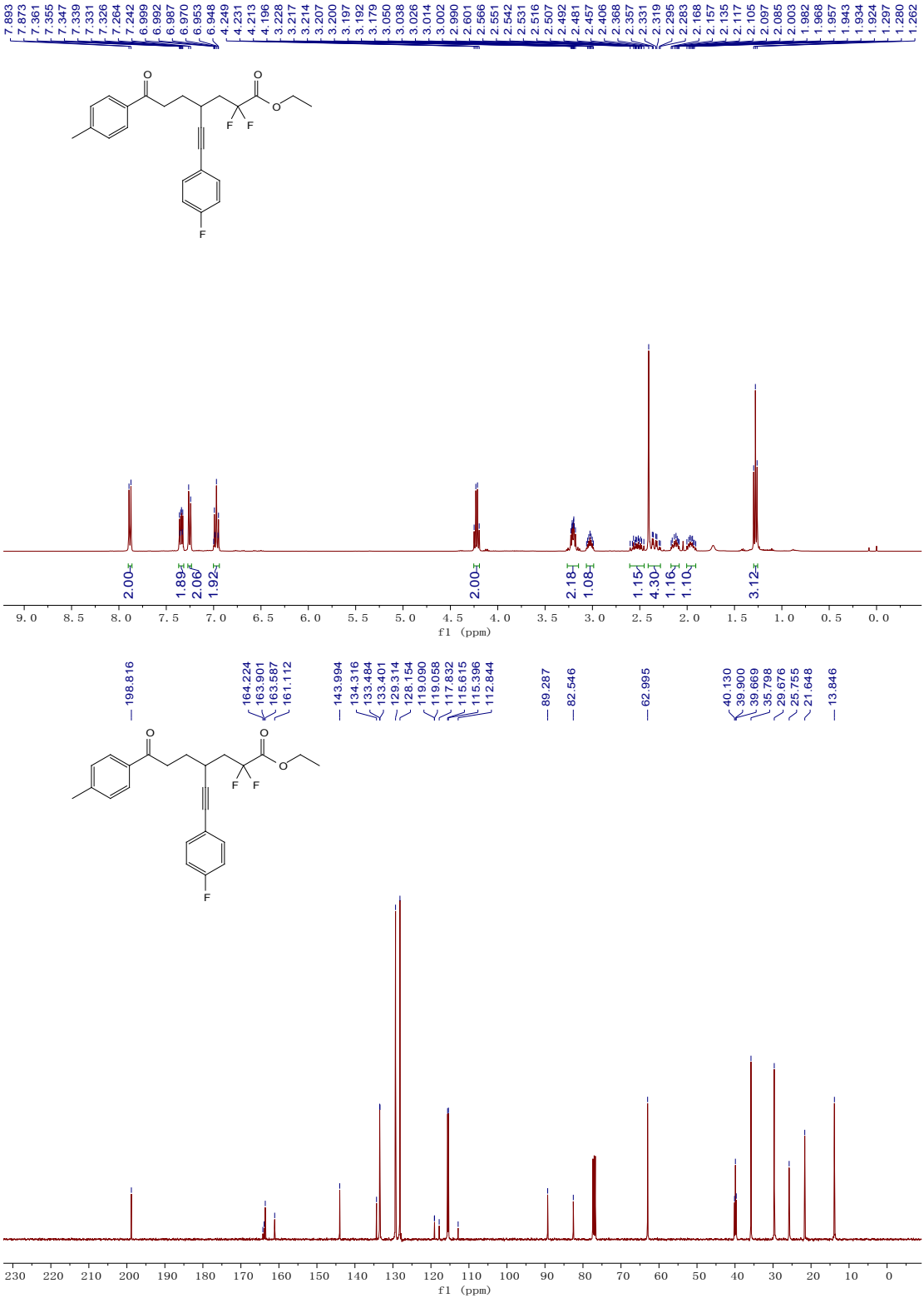
ethyl 4-([1,1'-biphenyl]-4-ylethynyl)-2,2-difluoro-7-oxo-7-phenylheptanoate (**3n**)

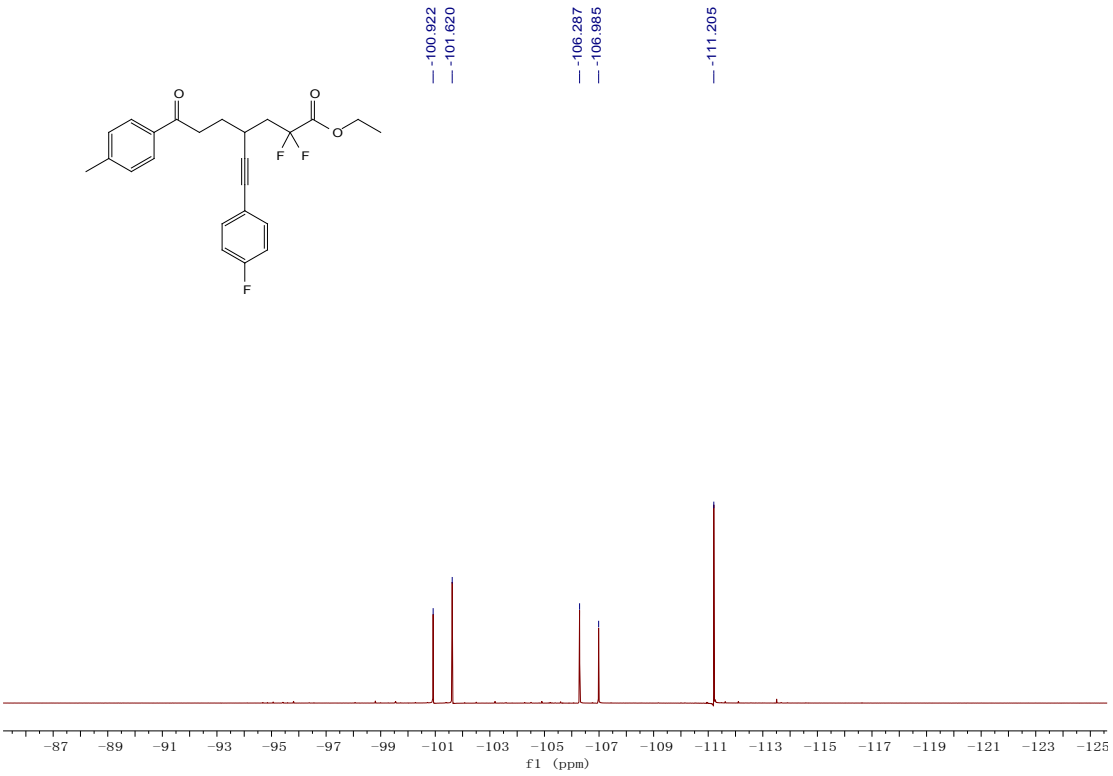



199.246
164.262
163.940
163.617
140.875
140.264
136.806
133.198
132.035
128.886
128.672
128.077
127.669
126.992
126.941
121.893
117.890
115.398
112.903
90.223
83.559
63.067
40.239
40.009
39.779
36.002
29.682
25.897
13.891
O
O
O
F
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

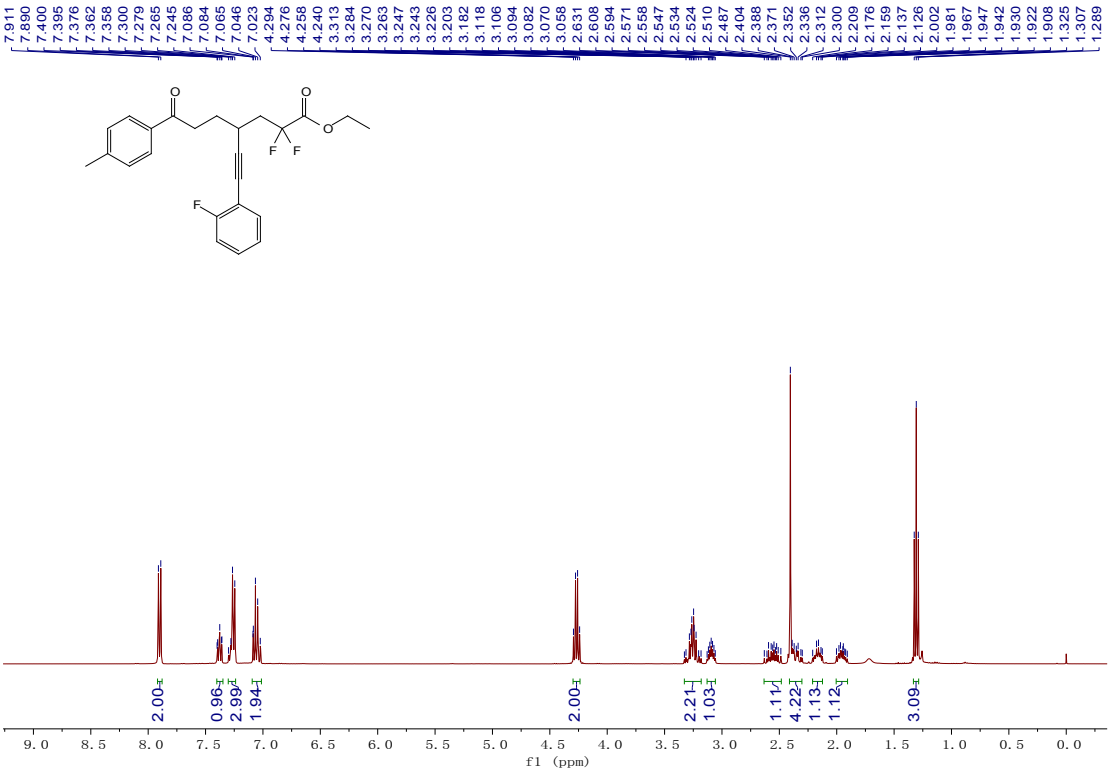

-100.706
-101.403
-106.307
-107.005
O
O
O
F
F
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

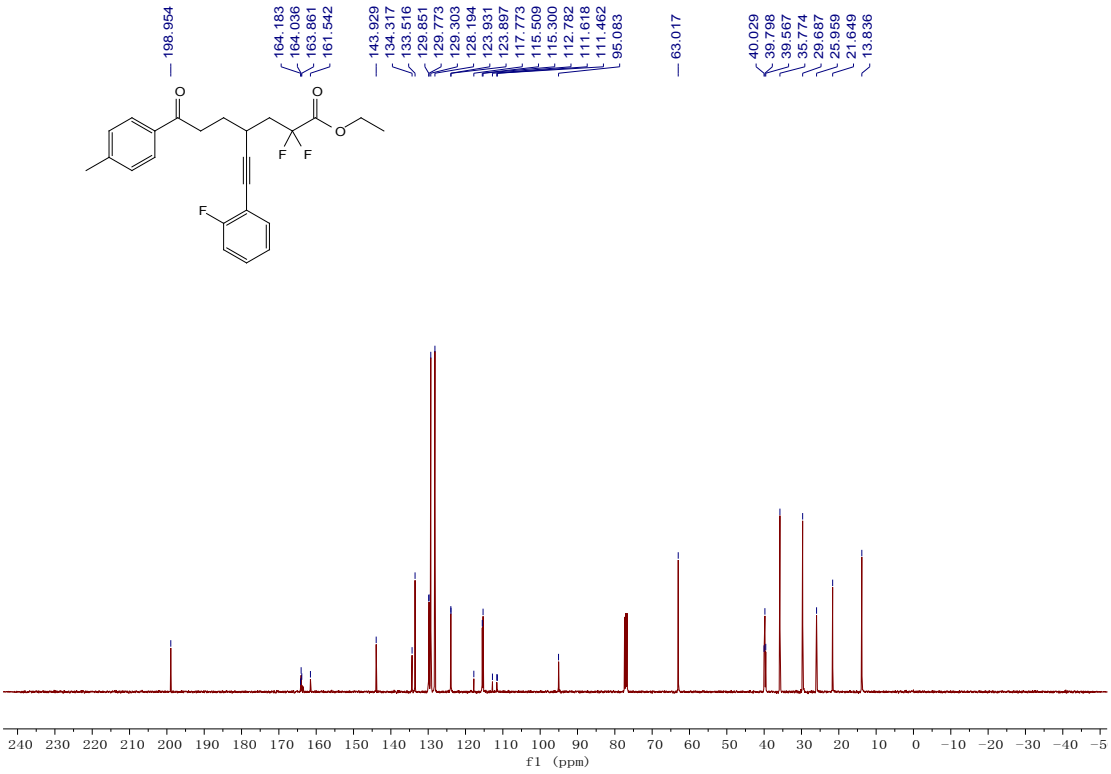
ethyl 2,2-difluoro-4-((4-fluorophenyl)ethynyl)-7-oxo-7-(p-tolyl)heptanoate (**3o**)

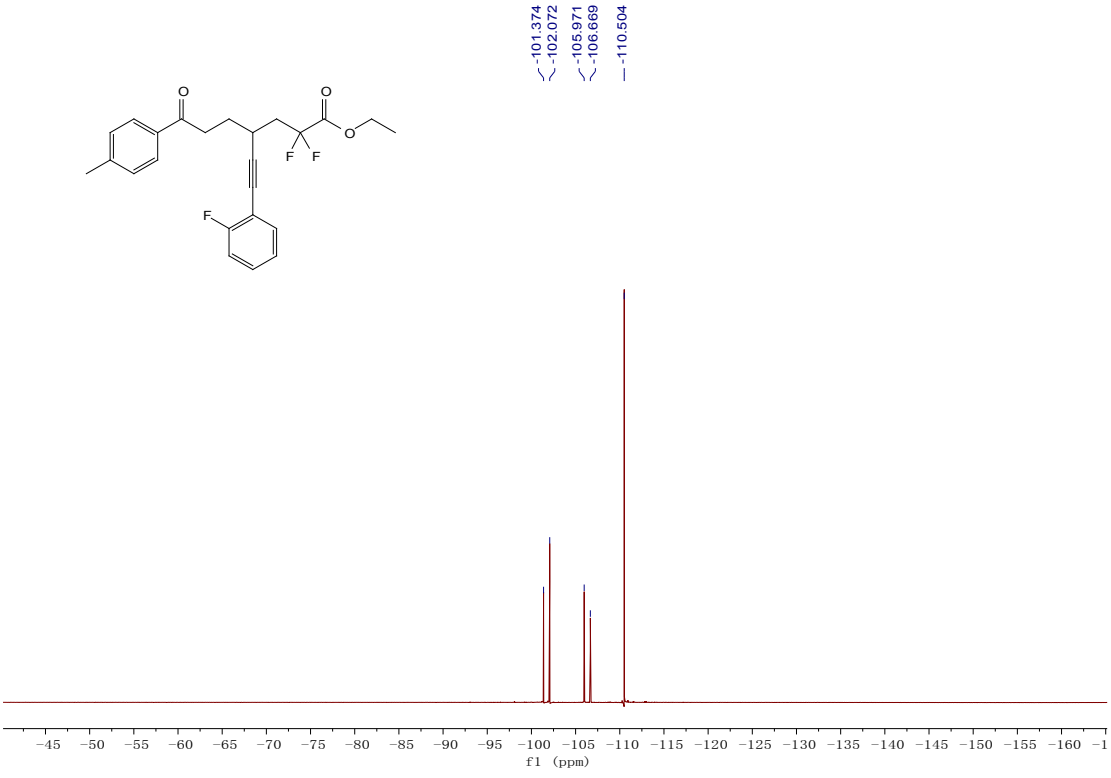




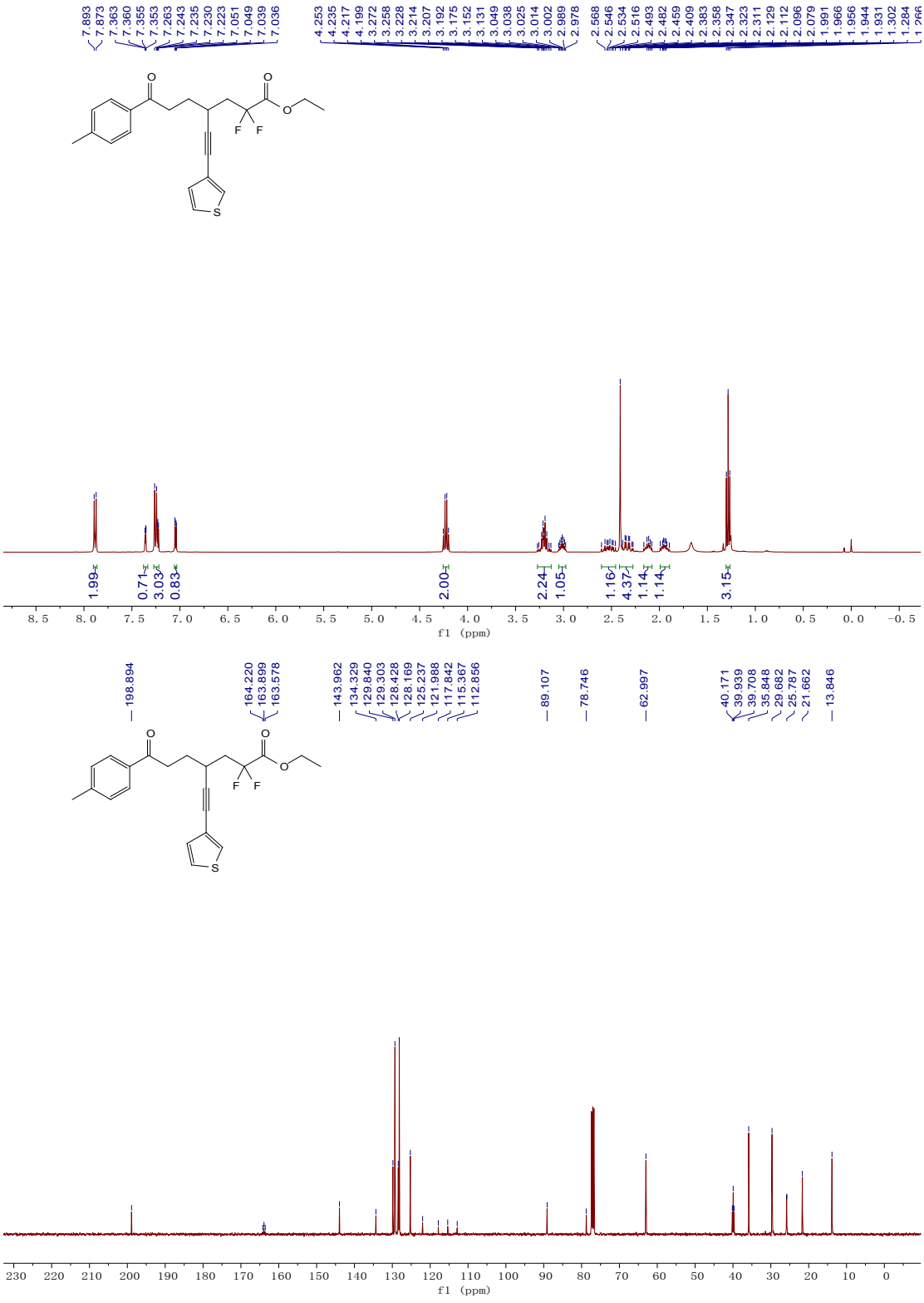
ethyl 2,2-difluoro-4-((2-fluorophenyl)ethynyl)-7-oxo-7-(p-tolyl)heptanoate (**3p**)

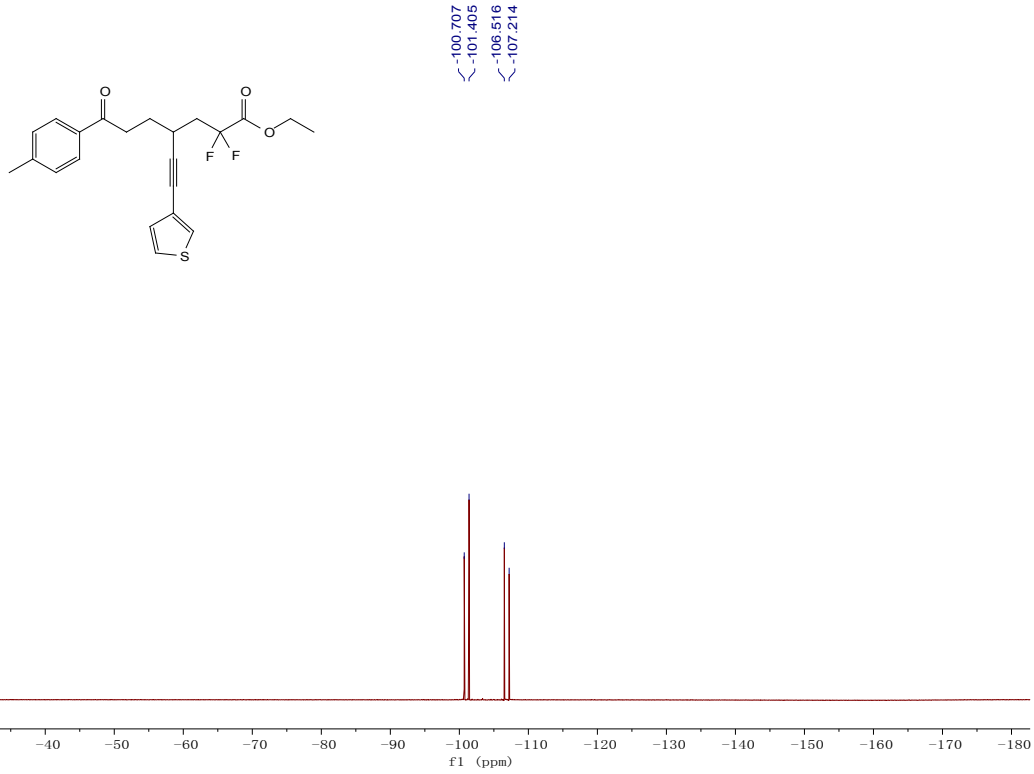



198.954
164.183
164.036
163.861
161.542
143.929
134.317
133.516
129.851
129.773
129.303
128.194
123.931
123.897
117.773
115.509
115.300
112.782
111.618
111.462
95.083
63.017
40.029
39.798
39.567
35.774
29.687
25.959
21.649
13.836
O
O
O
F
F
F
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −5
f1 (ppm)

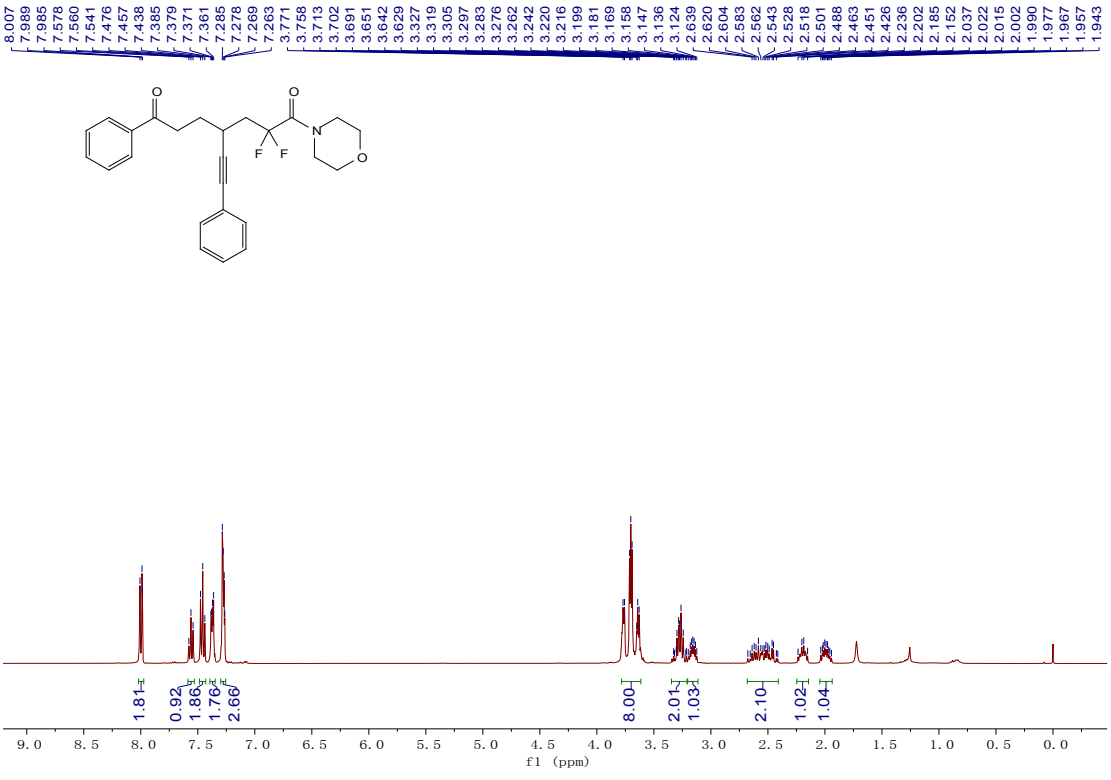

-101.374
-102.072
-105.971
-106.669
-110.504
O
O
O
F
F
F
−45 −50 −55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160 −1
f1 (ppm)

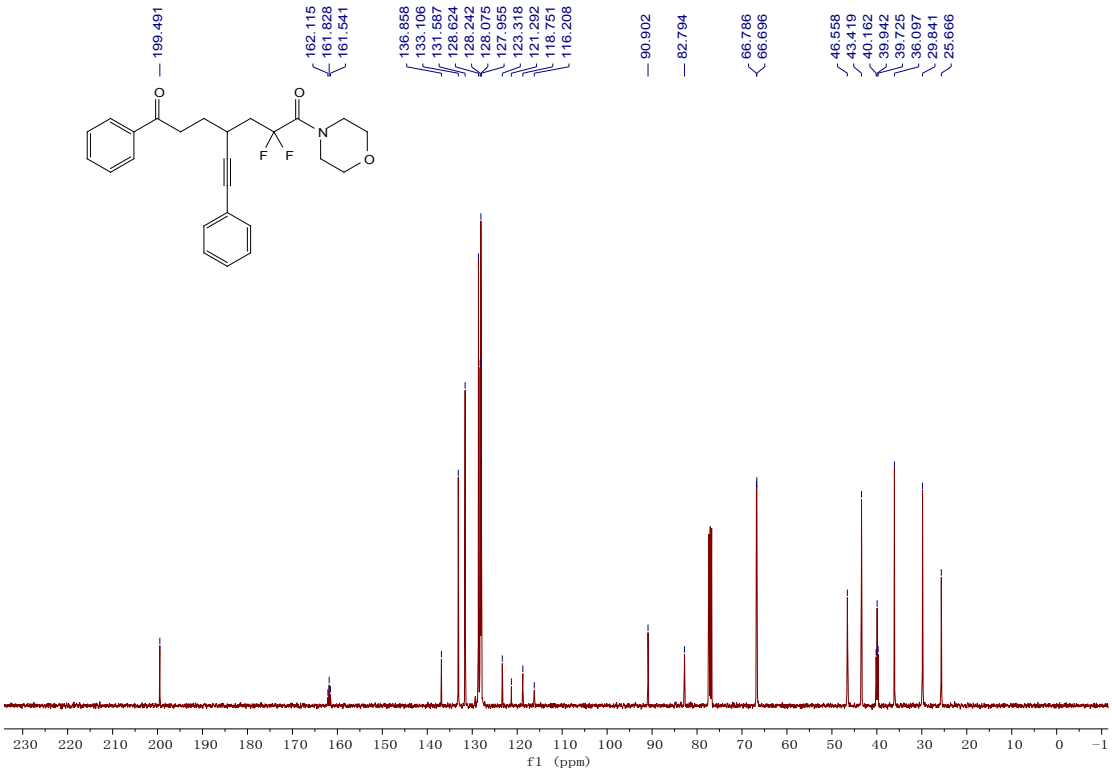
ethyl 2,2-difluoro-7-oxo-4-(thiophen-3-ylethynyl)-7-(p-tolyl)heptanoate (**3q**)

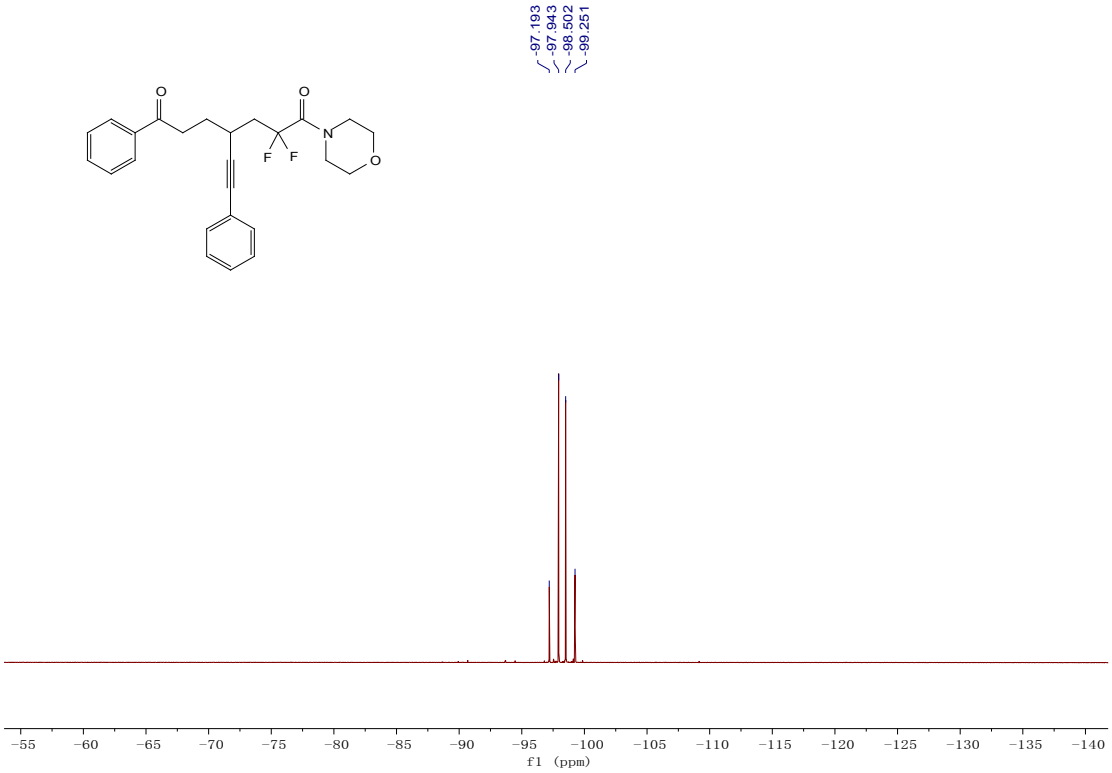




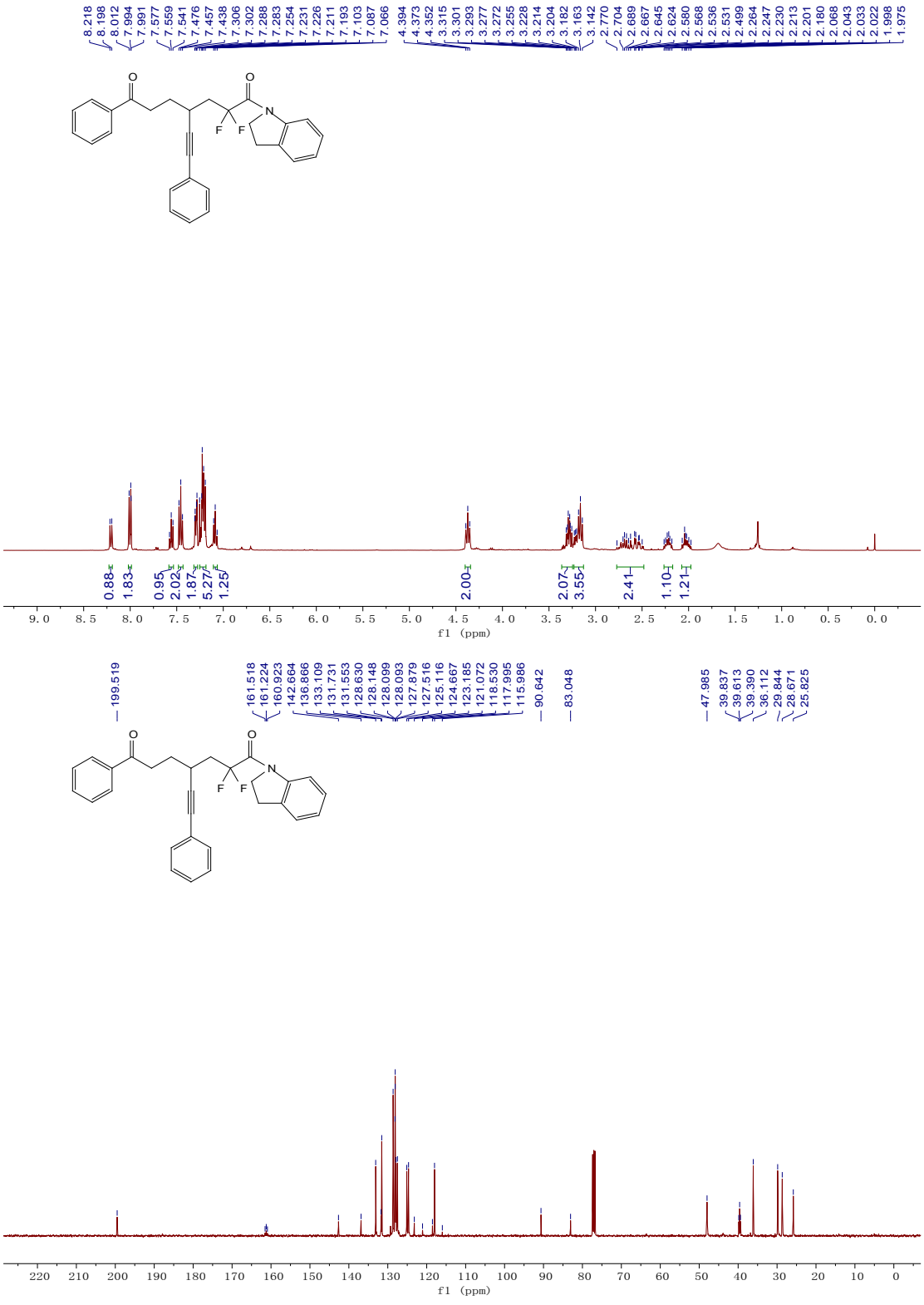
2,2-difluoro-1-morpholino-7-phenyl-4-(phenylethynyl)heptane-1,7-dione (**3s**)

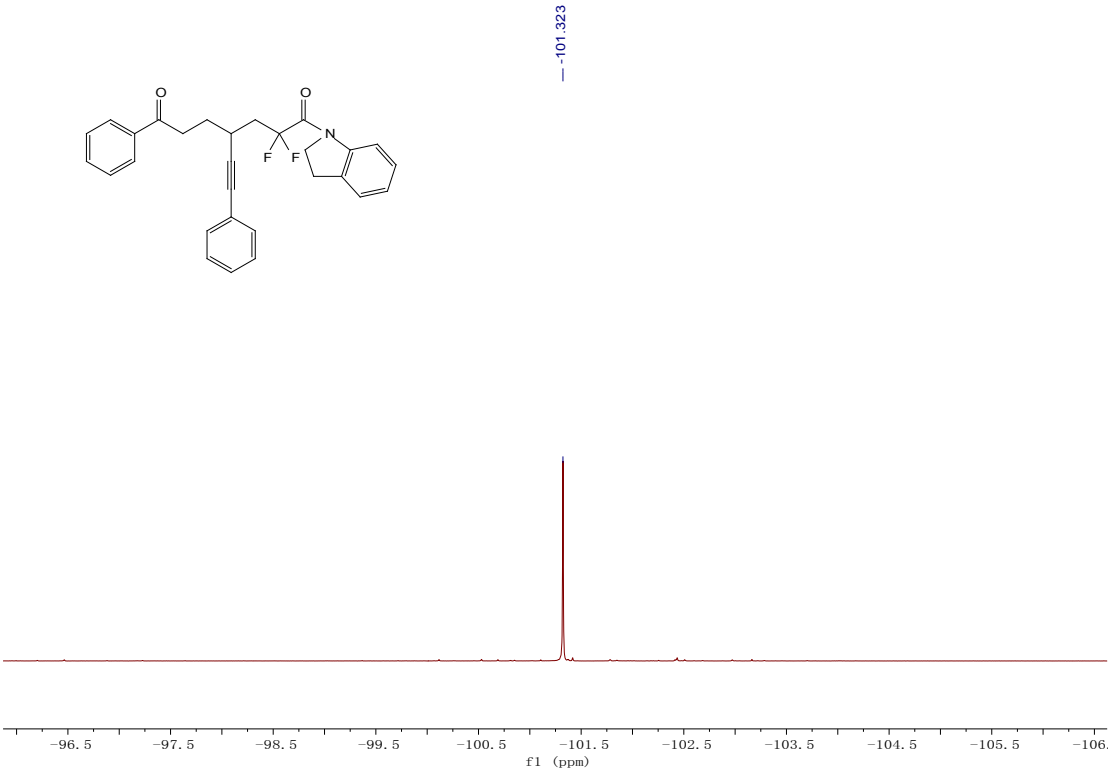



199.491
162.115
161.828
161.541
136.858
133.106
131.587
128.624
128.242
128.075
127.955
123.318
121.292
118.751
116.208
90.902
82.794
66.786
66.696
46.558
43.419
40.162
39.942
39.725
36.097
29.841
25.666
O
O
N
O
F
F
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

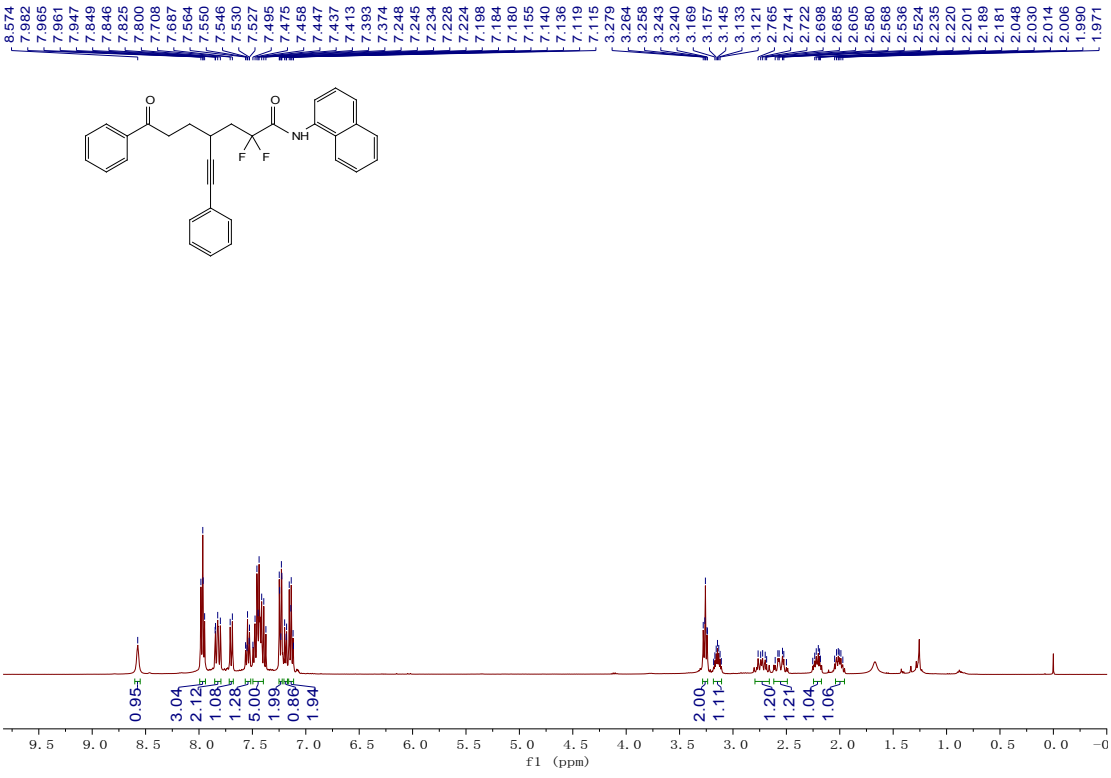

-97.193
-97.943
-98.502
-99.251
O
O
N
O
F
F
−55 −60 −65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140
f1 (ppm)

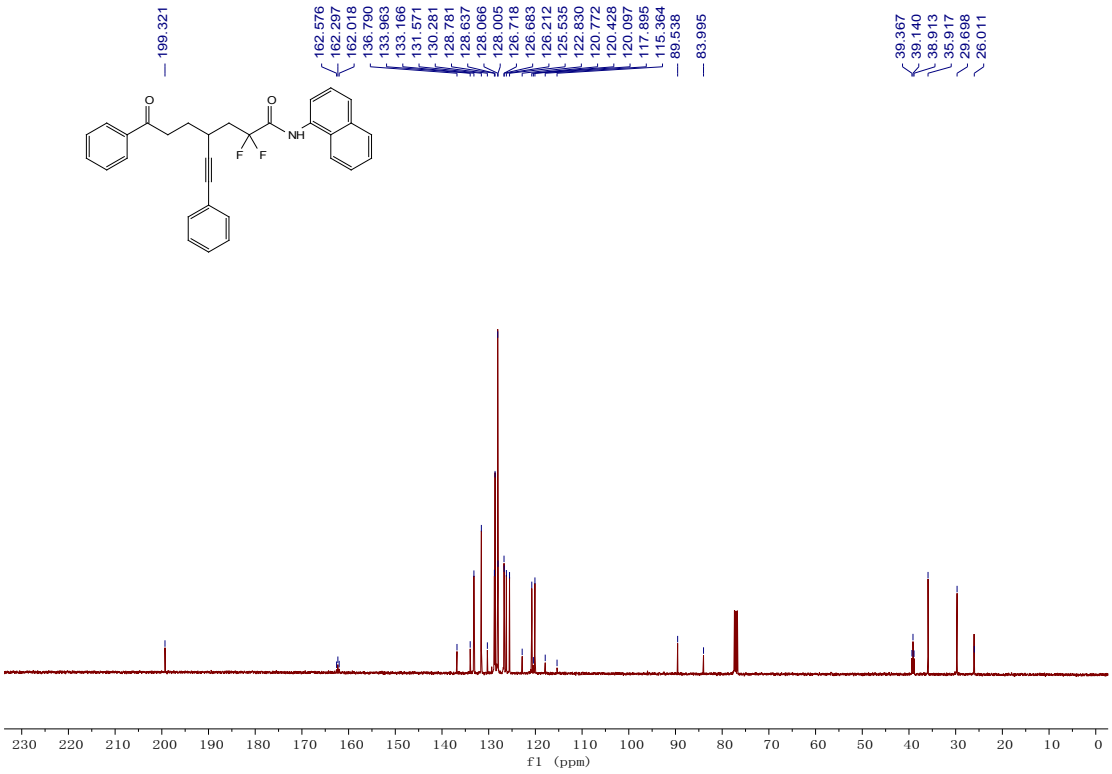
2,2-difluoro-1-(indolin-1-yl)-7-phenyl-4-(phenylethynyl)heptane-1,7-dione (**3t**)

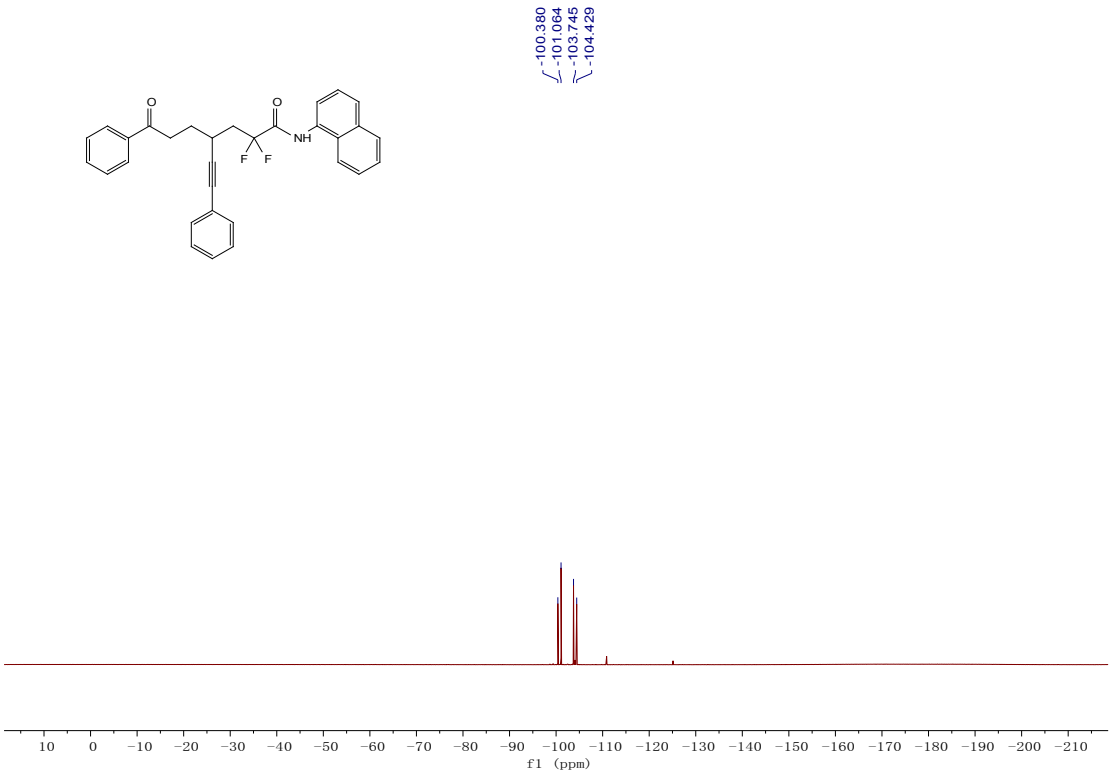




2,2-difluoro-N-(naphthalen-1-yl)-7-oxo-7-phenyl-4-(phenylethynyl)heptanamide (**3u**)




199.321
162.576
162.297
162.018
136.790
133.963
133.166
131.571
130.281
128.781
128.637
128.066
128.005
126.718
126.683
126.212
125.535
122.830
120.772
120.428
120.097
117.895
115.364
89.538
83.995
39.367
39.140
38.913
35.917
29.698
26.011
O
O
NH
F
F
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-100.380
-101.064
-103.745
-104.429
O
O
NH
F
F
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)