Supporting Information

Visible Light promoted carbodifluoroalkylation of allylic alcohols via concomitant 1,2-Aryl Migration

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General Information

All reactions were carried out under Ar atmosphere unless otherwise noted. All catalysts and solvents were obtained from commercial suppliers. Dry DMF was purchased from JK. CF_3I was stored up in dry DMF. [1] Diaryl allylic alcohols were prepared according to the literature.[2] Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ^1H NMR ,^{13}C NMR spectra and ^{19}F NMR spectra were recorded on 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. High resolution mass spectra were obtained on a high–resolution mass spectrometer in the ESI mode. The 5W LEDs were directly got from the supermarket.

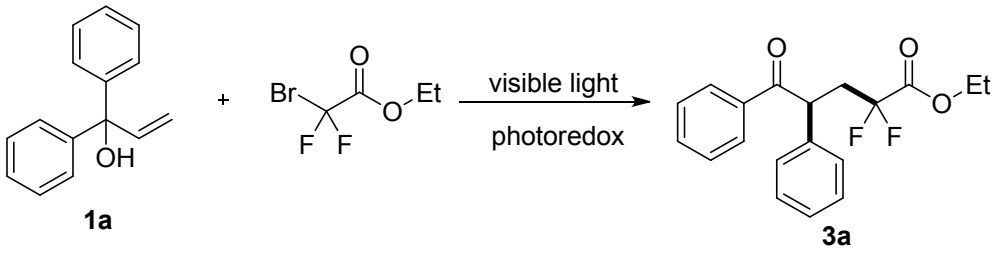
General procedure for carbodifluoroalkylation of allylic alcohols

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1a-t** (0.2 mmol), *fac*-$Ir(ppy)_3$ (0.02 equiv, 0.004mmol), 2-bromo-2,2-difluoroacetate **2** (2.5 equiv, 0.5mmol), CH_3COOK (1.5 equiv, 0.3mmol). The flask was evacuated and backfilled with Ar for 3 times. 1 ml dry DMF was added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 5w blue leds, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After the reaction was finished, the mixture was concentrated under vacuum to remove DMF., and the residue was purified by chromatography on silica gel to afford the **3a-t**.

General procedure for carboTrifluoroalkylation of allylic alcohols

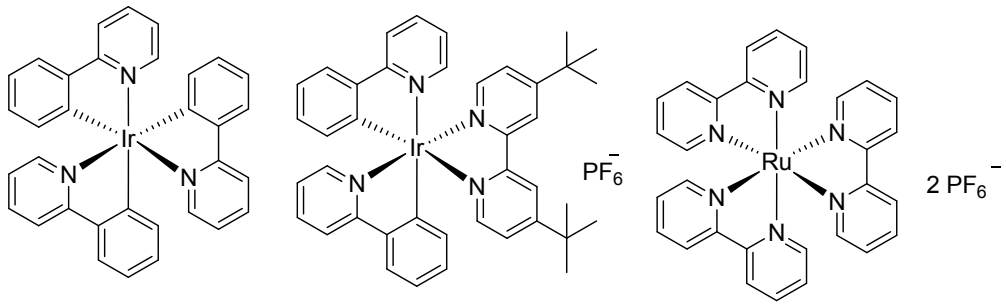
An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar and charged with allylic alcohols (0.2 mmol), $Ru(bpy)_3(PF_6)_2$ (0.02 equiv, 0.004mmol), CH_3COOK (1.5 equiv, 0.3mmol). The flask was evacuated and backfilled with Ar for 3 times. CF_3I (5 equiv, 1mmol) and 1 ml dry DMF was added in with syringe under Ar. The tube was placed at a distance (app.5 cm) from 5w blue leds, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After the reaction was finished, the mixture was concentrated under vacuum to remove DMF, and the residue was purified by chromatography on silica gel to afford the **4a-d**.

Optimization of the Reaction Conditions Of Carbodifluoroalkylation [a]



1a **3a**

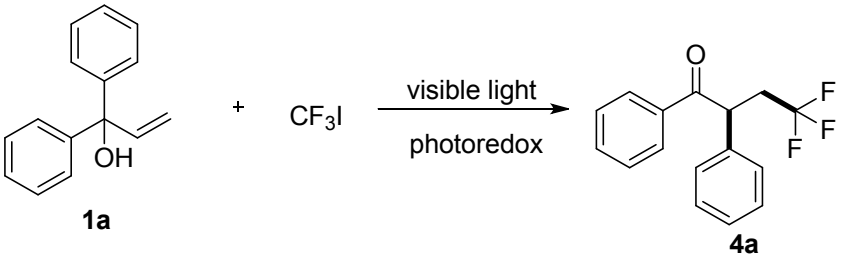
Entry	photocatalyst	Base	solvent	Yield(%)[b]
1	*fac*-Ir(ppy)$_3$	CH_3COOK	CH_3CN	69
2	*fac*-Ir(ppy)$_3$	CH_3COOK	DCM	50
3	*fac*-Ir(ppy)$_3$	CH_3COOK	DMSO	55
4	*fac*-Ir(ppy)$_3$	CH_3COOK	CH_3OH	53[c]
5	***fac-Ir(ppy)$_3$***	**CH_3COOK**	**DMF**	**83**
6	*fac-Ir(ppy)$_3$*	CH_3COOK(2 equiv)	DMF	84
7	*fac-Ir(ppy)$_3$*	CH_3COOK	DMF	73[d]
8	*fac-Ir(ppy)$_3$*	CH_3COOK	DMF	83[e]
9	Ir(ppy)$_2$(dtbpy)PF_6	CH_3COOK	DMF	69
10	Ru(bpy)$_3$(PF_6)$_2$	CH_3COOK	DMF	37
11	*fac*-Ir(ppy)$_3$	-	DMF	0
12	*fac*-Ir(ppy)$_3$	CH_3COONa	DMF	76
13	*fac*-Ir(ppy)$_3$	$NaHCO_3$	DMF	71
14	*fac*-Ir(ppy)$_3$	K_2HPO_4	DMF	56
15	*fac*-Ir(ppy)$_3$	Na_2HPO_4	DMF	38
16	*fac*-Ir(ppy)$_3$	K_2CO_3	DMF	53
17	-	CH_3COOK	DMF	0
18[f]	*fac*-Ir(ppy)$_3$	CH_3COOK	DMF	0



fac-Ir(ppy)$_3$ Ir(ppy)$_2$(dtbpy)PF_6 Ru(bpy)$_3$(PF_6)$_2$

[a] Reaction conditions: **1a** (0.2 mmol), $BrCF_2CO_2Et$ (0.5 mmol), Base (1.5equiv, 0.3 mmol), photocatalyst (2 mol%), solvent (1 mL), 5 W Blue LED light, 24 h, rt. [b] Isolated yield. [c] CF_2CO_2Me substituted product was formed [d] 0.4 mmol $BrCF_2CO_2Et$ was used. [e] 0.6 mmol $BrCF_2CO_2Et$ was used. [f] In the dark.

Brief Optimization of the Catalyst for Carbotrifluoromethylation[a]

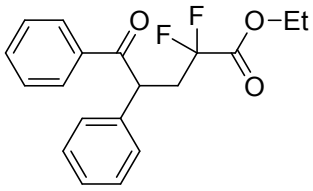


1a **4a**

Entry	photocatalyst	Yield(%)[b]
1	*fac*-Ir(ppy)$_3$	56
2	Ir(ppy)$_2$(dtbpy)PF$_6$	53
3	Ru(bpy)$_3$(PF$_6$)$_2$	64 (60)[c]
Reaction conditions: **1a** (0.2 mmol), CF_3I (1 mmol), CH_3COOK (1.5equiv, 0.3 mmol), photocatalyst (2 mol%), DMF (1 mL), 5 W Blue LED light, 24 h, rt.[b] ^{19}F NMR yield using trifluorotoluene as standard. [c] isolated yield.		

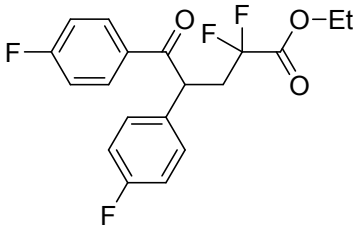
Characterization data of compounds

ethyl 2,2-difluoro-5-oxo-4,5-diphenylpentanoate **3a**



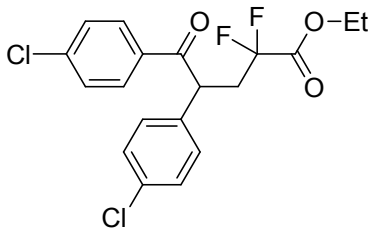
Reaction time 24h, R_f = 0.7 (EA/PE = 1:10), Yield 83%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 7.2 Hz, 2H), 7.43-7.39 (m, 1H), 7.33-7.29 (m, 2H), 7.23-7.18 (m, 4H), 7.15-7.12 (m, 1H), 4.87 (dd, J = 8.0 Hz, 4.8 Hz, 1H), 4.08 (dq, J = 7.2 Hz, 10.8 Hz, 1H), 3.97 (dq, J = 7.2 Hz, 10.8 Hz, 1H), 3.27-3.12 (m, 1H), 2.53-2.40 (m, 1H), 1.14 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 163.8 (t, J = 32.8 Hz), 137.8, 135.8, 133.3, 129.2, 128.9, 128.6, 128.3, 127.7, 115.3 (t, J = 248.1 Hz), 62.3, 46.9 (t, J = 3.8 Hz), 38.2 (t, J = 22.6 Hz), 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -105.0 (d, J = 260.6 Hz), -104.8 (d, J = 258.3 Hz) ppm. HRMS (ESI) m/z calcd for $C_{19}H_{18}F_2O_3$ $[M+H]^+$ 333.1297; found: 333.1300.

ethyl 2,2-difluoro-4,5-bis(4-fluorophenyl)-5-oxopentanoate **3b**



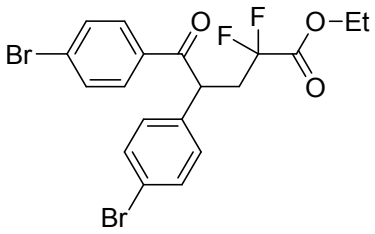
Reaction time 30h, R_f = 0.6 (EA/PE = 1:10), Yield 50%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91-7.87 (m, 2H), 7.20-7.16 (m, 2H), 7.00 (t, J = 8.4 Hz, 2H), 6.91 (t, J = 8.4 Hz, 2H), 4.83 (dd, J = 5.2 Hz, 8.0Hz, 1H), 4.15-4.01 (m, 2H), 3.14-3.08 (m, 1H), 2.50-2.36 (m, 1H), 1.18 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 165.8 (d, J = 253.7 Hz), 162.2 (d, J = 245.9 Hz), 163.7 (t, J = 31.9 Hz), 133.4 (d, J = 3.6 Hz), 132.0 (d, J = 2.5 Hz), 131.5 (d, J = 9.7 Hz), 129.8 (d, J = 8.1 Hz), 116.3 (d, J = 21.7 Hz), 115.9 (d, J = 21.9 Hz), 115.1 (t, J = 248.6 Hz), 63.0, 46.0 (t, J = 3.3 Hz), 38.2 (t, J = 22.4 Hz), 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.4 (s), -104.5 (s, Ph-F), -104.5 (s), -114.1 (s, Ph-F) ppm. HRMS (ESI) m/z calcd for $C_{19}H_{16}F_4O_3$ $[M+H]^+$ 369.1108; found: 369.1115.

ethyl 4,5-bis(4-chlorophenyl)-2,2-difluoro-5-oxopentanoate **3c**



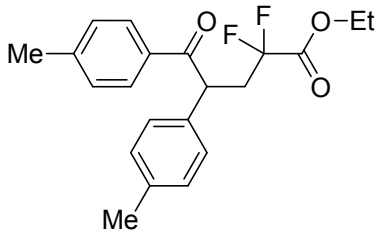
Reaction time 30h, R_f= 0.6 (EA/PE = 1:10), Yield 80%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.76 (m, 2H), 7.30-7.27 (m, 2H), 7.21-7.17 (m, 2H), 7.14-7.12 (m, 2H), 4.80 (dd, *J* = 8.0 Hz, 5.2 Hz, 1H), 4.12 (dq, *J* = 7.2 Hz, 10.8 Hz, 1H), 4.03 (dq, *J* = 7.2 Hz, 10.8 Hz, 1H), 3.22-3.08 (m, 1H), 2.48-2.35 (m, 1H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8, 163.6 (t, *J* = 33.2 Hz), 140.0, 136.0, 133.9, 133.8, 130.2, 129.5,129.4 129.1, 115.1 (t, *J* = 249.2 Hz), 63.1, 46.2 (t, *J* = 4.0 Hz), 38.0 (t, *J* = 24.0 Hz), 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.4 (s) ppm. HRMS (ESI) m/z calcd for $C_{19}H_{16}Cl_2F_2O_3$ $[M+Na]^+$ 423.0337; found: 423.0361.

ethyl 4,5-bis(4-bromophenyl)-2,2-difluoro-5-oxopentanoate **3d**



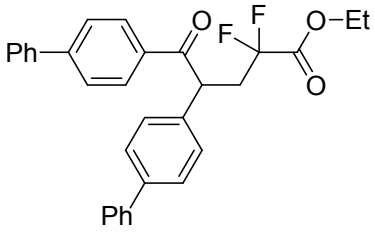
Reaction time 26h, R_f= 0.5 (EA/PE = 1:10), Yield 75%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.78 (dd, *J* = 8.0 Hz, 5.2 Hz, 1H), 4.16-3.99 (m, 2H), 3.22-3.08 (m, 1H), 2.48-2.34 (m, 1H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 163.6 (t, *J* = 32.0 Hz), 136.5, 134.2, 132.5, 132.1, 130.3, 129.9, 128.8, 122.0, 115.1 (t, *J* = 249.3 Hz), 63.1, 46.3 (t, *J* = 3.8 Hz), 37.9 (t, *J* = 23.0 Hz), 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.4 (s) ppm. HRMS (ESI) m/z calcd for $C_{19}H_{16}Br_2F_2O_3$ $[M+Na]^+$ 510.9326; found: 510.9326.

ethyl 2,2-difluoro-5-oxo-4,5-di-p-tolylpentanoate **3e**



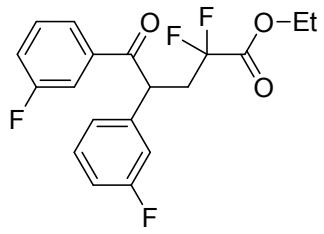
Reaction time 26h, R_f = 0.8 (EA/PE = 1:10), Yield 65%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.0 Hz, 2H), 7.10-7.08 (m, 4H), 6.99 (d, J = 8.0 Hz, 2H), 4.81 (dd, J = 8.0 Hz, 5.2 Hz, 1H), 4.07 (dq, J = 7.2 Hz, 10.8 Hz, 1H), 3.95 (dq, J = 7.2 Hz, 10.8 Hz, 1H), 3.23-3.09 (m, 1H), 2.49-2.36 (m, 1H), 2.25 (s, 3H), 2.17 (s, 3H), 1.13 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 163.8 (t, J = 32.7 Hz), 144.0, 137.3, 135.0, 133.3, 129.9, 129.3,129.0, 128.1, 115.4 (t, J = 248.7 Hz), 62.9, 46.4 (t, J = 4.0 Hz), 38.2 (t, J = 22.2 Hz), 21.6, 21.0, 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.0 (d, J = 257.9 Hz), -104.7 (d, J = 259.1 Hz) ppm. HRMS (ESI) m/z calcd for $C_{21}H_{22}F_2O_3$ $[M+H]^+$ 361.1610; found: 361.1618.

ethyl 4,5-di([1,1'-biphenyl]-4-yl)-2,2-difluoro-5-oxopentanoate **3f**



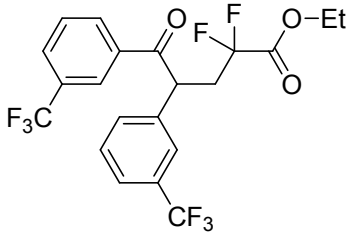
Reaction time 40h, R_f = 0.7 (EA/PE = 1:10), Yield 57%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.56-7.54 (m, 2H), 7.53-7.49 (m, 4H), 7.44-7.28 (m, 8H), 5.04 (dd, J = 8.0 Hz, 4.8 Hz, 1H), 4.17 (dq, J = 7.2 Hz, 10.8 Hz, 1H), 4.07 (dq, J = 7.2 Hz, 10.8 Hz, 1H), 3.40-3.26 (m, 1H), 2.67-2.54 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 163.8 (t, J = 32.6 Hz), 146.0, 140.7, 140.3, 139.7, 136.8, 134.5, 129.5, 129.0, 128.8, 128.7, 128.3, 128.0, 127.5, 127.4, 127.3, 127.0, 115.4 (t, J = 249.1 Hz), 63.0, 46.6 (t, J = 4.3 Hz), 38.3 (t, J = 22.2 Hz), 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.80 (d, J = 259.1 Hz), -104.61 (d, J = 258.4 Hz) ppm. HRMS (ESI) m/z calcd for $C_{31}H_{26}F_2O_3$ $[M+Na]^+$ 507.1742; found: 507.1747.

ethyl 2,2-difluoro-4,5-bis(3-fluorophenyl)-5-oxopentanoate **3g**



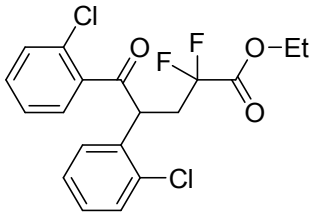
Reaction time 28h, R_f = 0.5 (EA/PE = 1:10), Yield 55%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.0 Hz, 1H), 7.53 (dt, *J* = 2.0 Hz, 9.2 Hz, 1H), 7.34-7.29 (m, 1H), 7.23-7.01 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.93-6.83 (m, 2H), 4.83 (dd, *J* = 8.0 Hz, 4.8 Hz, 1H), 4.16-4.01 (m, 2H), 3.21-3.11 (m, 1H), 2.50-2.37 (m, 1H), 1.18 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 164.2 (d, *J* = 28.1 Hz), 163.6 (t, *J* = 32.5 Hz), 161.7 (d, *J* = 29.5 Hz), 139.7 (d, *J* = 7.2 Hz), 137.7 (d, *J* = 6.2 Hz), 130.9 (d, *J* = 7.9 Hz), 130.4 (d, *J* = 7.9 Hz), 124.5 (d, *J* = 2.7 Hz), 124.0 (d, *J* = 2.9 Hz), 120.5 (d, *J* = 20.3 Hz), 115.6 (d, *J* = 22.2 Hz), 115.2 (d, *J* = 17.0 Hz), 114.9 (d, *J* = 15.8 Hz), 115.0 (t, *J* = 249.7 Hz), 63.1, 46.3 (t, *J* = 3.8 Hz), 37.9 (t, *J* = 23.0 Hz), 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.5 (s), -111.2 (s), -111.3 (s) ppm. HRMS (ESI) m/z calcd for $C_{19}H_{16}F_4O_3$ $[M+H]^+$ 369.1108; found: 369.1115.

ethyl 2,2-difluoro-4,5-bis(3-fluorophenyl)-5-oxopentanoate **3h**



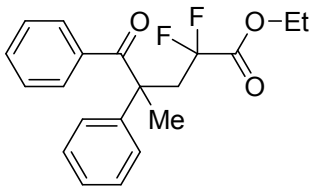
Reaction time 28h, R_f = 0.5 (EA/PE = 1:10), Yield 74%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.49-7.34 (m, 5H), 4.96 (dd, *J* = 8.0 Hz, 5.2 Hz, 1H), 4.15-4.01 (m, 2H), 3.26-3.16 (m, 1H), 2.54-2.41 (m, 1H), 1.18 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 163.5 (t, *J* = 33.1 Hz), 138.2, 136.0, 131.8 (q, *J* = 32.1 Hz), 131.8, 131.6, 131.5 (q, *J* = 32.8 Hz), 130.0(2C), 129.5(2C), 125.6 (q, *J* = 4.0 Hz), 124.9 (q, *J* = 4.0 Hz), 123.7 (q, *J* = 270.7 Hz), 123.5 (q, *J* = 270.5 Hz), 114.9 (t, *J* = 249.5 Hz), 63.2, 46.7 (t, *J* = 3.6 Hz), 38.0 (t, *J* = 23.5 Hz), 13.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.8, -63.1, -104.1 (d, *J* = 260.6 Hz), -104.8 (d, *J* = 261.7 Hz) ppm. HRMS (ESI) m/z calcd for $C_{21}H_{16}F_8O_3$ $[M+Na]^+$ 491.0864; found: 491.0860.

ethyl 4,5-bis(2-chlorophenyl)-2,2-difluoro-5-oxopentanoate **3i**



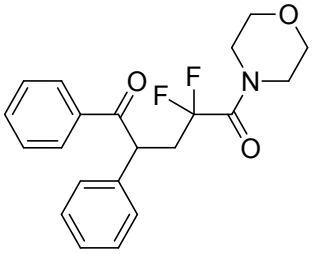
Reaction time 26h, R_f = 0.8 (EA/PE = 1:10), Yield 81%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.28 (m, 1H), 7.30-7.28 (m, 4H), 7.15-7.10 (m, 2H), 7.10-7.06 (m, 1H), 5.31 (t, J = 6.4 Hz, 1H), 4.17-4.07 (m, 2H), 3.28-3.15 (m, 1H), 2.52-2.39 (m, 1H), 1.22 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 163.7 (t, J = 32.9 Hz), 137.7, 134.2, 134.1, 131.9, 131.4, 130.5, 130.1, 129.7, 129.3, 129.1, 127.4, 126.6, 115.1 (t, J = 248.9 Hz), 63.1, 46.8, 36.0 (t, J = 23.1 Hz), 13.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.2 (s) ppm. HRMS (ESI) m/z calcd for $C_{19}H_{16}Cl_2F_2O_3$ $[M+Na]^+$ 423.0337; found: 423.0360.

ethyl 2,2-difluoro-4-methyl-5-oxo-4,5-diphenylpentanoate **3j**



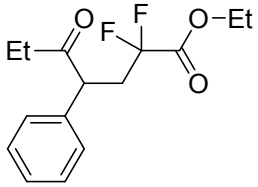
Reaction time 28h, Rf = 0.8 (EA/PE = 1:10), Yield 77%, colourless oil. ^{1}H NMR (400 MHz, CDCl3): δ = 7.40-7.29 (m, 8H), 7.20 (d, J = 8.0 Hz, 2H), 4.11-3.91 (m, 2H), 3.02-2.81 (m, 2H), 1.84 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.0, 163.9 (t, J = 32.7 Hz), 140.9, 136.2, 131.7, 129.3, 129.1, 128.0, 127.8, 126.8, 115.9 (t, J = 248.2 Hz), 62.7, 52.4 (d, J = 3.6 Hz), 44.2 (t, J = 20.9 Hz), 22.2 (t, J = 1.9 Hz), 13.8 ppm; ^{19}F NMR (376 MHz, CDCl3): δ -96.8 (d, J = 265.1 Hz), -99.9 (d, J = 262.8 Hz) ppm. HRMS (ESI) m/z calcd for $C_{20}H_{20}F_2O_3$ $[M+H]^+$ 347.1453; found: 347.1472.

2,2-difluoro-1-morpholino-4,5-diphenylpentane-1,5-dione **3k**



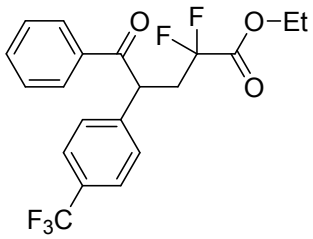
Reaction time 30h, R_f = 0.5 (EA/PE = 1:10), Yield 72%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90-7.88 (m, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 8.0 Hz, 2H), 7.26-7.18 (m, 4H), 7.15-7.11 (m, 1H), 4.96 (dd, J = 3.6 Hz, 8.4 Hz, 1H), 3.65-3.50 (m, 8H), 3.41-3.33 (m, 1H), 2.52-2.39 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 161.8 (t, J = 28.5 Hz), 138.5, 136.1, 133.1, 129.2, 128.8, 128.6, 128.1, 127.5, 118.4 (t, J = 252.9 Hz), 66.7, 46.7 (t, J = 4.4 Hz), 46.5 (t, J = 5.2 Hz), 43.3, 38.5 (t, J = 22.3 Hz), ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.5 (d, J = 275.2 Hz), -98.5 (d, J = 275.6 Hz) ppm. HRMS (ESI) m/z calcd for $C_{21}H_{21}F_2NO_3$ $[M+H]^+$ 374.1562; found: 374.1570.

ethyl 2,2-difluoro-5-oxo-4-phenylheptanoate **3l**

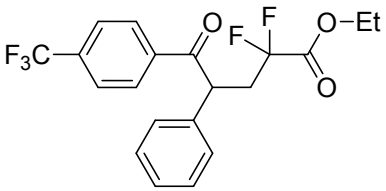


Reaction time 24h, R_f = 0.6 (EA/PE = 1:10), Yield 33%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.26 (m, 3H), 7.21-7.20 (d, J = 8.0 Hz, 2H), 4.20-4.07 (m, 2H), 4.01 (dd, J = 6.8 Hz, 7.6 Hz, 1H), 3.18-3.05 (m, 1H), 2.41 (q, J = 7.2 Hz, 2H), 2.38-2.26 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.3, 163.8 (t, J = 32.4 Hz), 137.6, 129.1, 128.3, 127.8, 115.3 (t, J = 249.6 Hz), 62.9, 51.5 (d, J = 3.5 Hz), 36.9 (t, J = 23.1 Hz), 34.7, 13.8, 7.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.2 (d, J = 257.6 Hz), -105.3 (d, J = 258.3 Hz) ppm. HRMS (ESI) m/z calcd for $C_{15}H_{18}F_2O_3$ $[M+Na]^+$ 307.1116; found: 307.1128.

ethyl 2,2-difluoro-5-oxo-5-phenyl-4-(4-(trifluoromethyl)phenyl)pentanoate **3m**
ethyl 2,2-difluoro-5-oxo-4-phenyl-5-(4-(trifluoromethyl)phenyl)pentanoate **3m'**



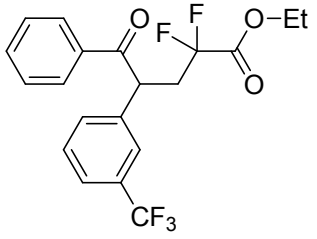
3m



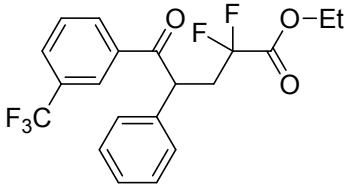
3m'

Reaction time 26h, R_f = 0.8 (EA/PE = 1:10), Yield 70%, colourless oil. **3m**:**3m'** = 50:1. **3m**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 6.4Hz, 1H), 7.37-7.31 (m, 4H), 4.97 (dd, J = 5.2 Hz, 7.6 Hz, 1H), 4.11 (dq, J = 7.2 Hz, 10.8 Hz, 1H), 4.01 (dq, J = 6.8 Hz, 10.4 Hz, 1H), 3.27-3.13 (m, 1H), 2.52-2.39 (m, 1H), 1.15 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 163.6 (t, J = 32.7 Hz), 141.8, 135.5, 133.6, 130.0 (q, J = 32.7 Hz), 128.8, 128.7, 126.2 (q, J = 3.8 Hz), 123.9 (q, J = 270.4 Hz), 115.1 (t, J = 249.9 Hz), 63.1, 46.5 (t, J = 3.5 Hz), 38.0 (t, J = 22.3 Hz), 13.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.8, -104.4 (s) ppm. HRMS (ESI) m/z calcd for $C_{20}H_{17}F_5O_3$ $[M+Na]^+$ 423.0990; found: 423.0993.

ethyl 2,2-difluoro-5-oxo-5-phenyl-4-(3-(trifluoromethyl)phenyl)pentanoate **3n**
ethyl 2,2-difluoro-5-oxo-4-phenyl-5-(3-(trifluoromethyl)phenyl)pentanoate **3n'**



3n

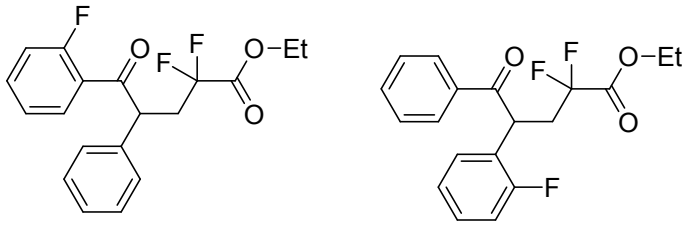


3n'

Reaction time 24h, R_f = 0.5 (EA/PE = 1:10), Yield 63%, colourless oil. **3n** : **3n'** = 3.6：1. **3n** and **3n' :** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 0.21H), 8.11 (d, J = 7.6 Hz, 0.22H), 7.95 (d, J = 7.2 Hz, 1.51H), 7.73 (d, J = 8.0 Hz, 0.28H), 7.58-7.26 (m, 7.19H), 5.06 (dd, J = 5.2 Hz, 7.6 Hz, 0.73H), 4.94 (dd, J = 4.8 Hz, 8.0 Hz, 0.20H), 4.21-4.08 (m, 2H), 3.37-3.22 (m, 1H), 2.61-2.48 (m, 1H), 1.26-1.22 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 198.0, 163.6 (t, J = 32.0 Hz), 138.8, 137.1, 136.3, 135.5, 133.6, 131.9, 131.7, 131.4, 129.8, 129.6 (q, J = 4.0 Hz), 129.5, 129.3, 128.8 (d, J = 1.9 Hz), 128.2, 128.0, 125.6 (q, J = 3.4 Hz), 123.8 (q, J = 270.8 Hz), 125.1, 125.0 (q, J = 3.9 Hz), 124.7 (q, J = 3.5 Hz), 122.4, 115.0 (t, J = 250.2 Hz), 63.1, 63.0, 47.2

(t, J = 4.2 Hz), 46.4 (t, J = 3.7 Hz), 38.2 (t, J = 23.9 Hz), 38.0 (t, J = 23.0 Hz), 13.8, 13.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7, -63.0, 104.0 (d, J = 259.8 Hz), -104.4， 104.8 (d, J = 259.8 Hz) ppm. HRMS (ESI) m/z calcd for $C_{20}H_{17}F_5O_3$ $[M+H]^+$ 401.1171; found: 401.1174.

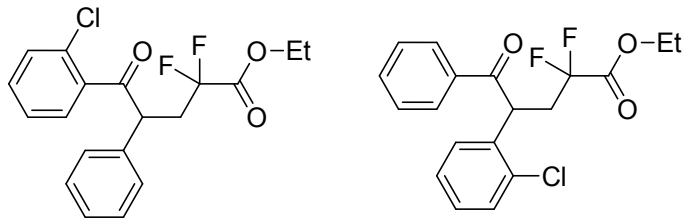
ethyl 2,2-difluoro-5-(2-fluorophenyl)-5-oxo-4-phenylpentanoate **3o**
ethyl 2,2-difluoro-4-(2-fluorophenyl)-5-oxo-5-phenylpentanoate **3o'**



3o **3o'**

Reaction time 24h, R_f = 0.7 (EA/PE = 1:10), Yield 79%, colourless oil. **3o** : **3o'** = 2.5：1. **3o** and **3o':** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 6.8 Hz, 0.55H), 7.75 (dt, J = 2.0 Hz, 7.6 Hz, 0.69H), 7.49 (t, J = 7.2 Hz, 0.31H), 7.44-7.37 (m, 1.28H), 7.25-7.00 (m, 6.21H), 5.31 (dd, J = 5.2 Hz, 7.6 Hz, 0.28H), 4.91 (dd, J = 5.2 Hz, 8.0 Hz, 0.70H), 4.24-4.04 (m, 2H), 3.35-3.19 (m, 1H), 2.59-2.45 (m, 1H), 1.24 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 196.1 (d, J = 4.1Hz), 163.8 (t, J = 32.3 Hz), 163.7 (t, J = 31.8 Hz), 161.1 (d, J = 253.7 Hz), 159.7 (d, J = 244.9 Hz), 136.8, 135.4, 134.6 (d, J = 9.2 Hz), 134.5, 131.2 (d, J = 3.4 Hz), 129.5 (d, J = 9.9 Hz), 129.5 (d, J = 3.9 Hz), 129.0, 128.7, 128.6, 127.8, 125.0(d, J = 11.6 Hz), 124.8 (d, J = 3.4 Hz), 124.5 (d, J = 4.1 Hz), 116.7 (d, J = 22.9 Hz), 116.0 (d, J = 23.0 Hz), 115.3 (t, J = 249.2 Hz), 115.2 (t, J = 249.3 Hz), 63.0, 62.9, 50.7 (m), 38.5 (m), 37.8 (t, J = 23.9 Hz), 37.2 (t, J = 22.5 Hz), 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.7 (d, J = 260.2 Hz), 104.0, 104.8 (d, J = 259.8 Hz), -109.4, -117.5 ppm. HRMS (ESI) m/z calcd for $C_{19}H_{17}F_3O_3$ $[M+H]^+$ 351.1203; found: 351.1214.

ethyl 5-(2-chlorophenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate **3p**
ethyl 4-(2-chlorophenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate **3p'**

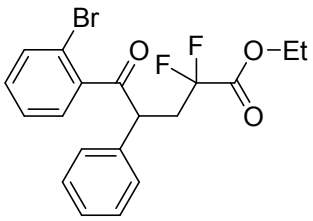


3p **3p'**

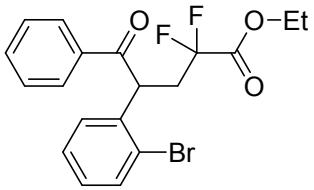
Reaction time 24h, R_f = 0.7 (EA/PE = 1:10), Yield 60%, colourless oil. **3p : 3p'** = 7.7:1. **3p** and **3p'** :^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96-7.95 (m, 0.18H), 7.50 (t, J = 7.2 Hz, 0.15H), 7.39 (t, J = 7.6 Hz, 0.47H), 7.33-7.16 (m, 8.19H), 5.48 (dd, J = 4.4 Hz,

8.4 Hz, 0.11H), 4.80 (t, *J* = 6.4 Hz, 0.85H), 4.27-4.05 (m, 2H), 3.29-3.21 (m, 1H), 2.69-2.55 (m, 0.85H), 2.46-2.33 (m, 0.13H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 197.1, 163.8 (t, *J* = 32.5 Hz), 138.2, 135.9, 135.7, 135.6, 133.5, 133.3, 131.6, 131.0, 130.4, 130.3, 129.1, 129.0, 129.0, 128.9, 128.8, 128.7, 128.0, 127.6, 126.6, 115.3 (t, *J* = 248.9 Hz), 63.0, 62.9, 51.1 (t, *J* = 3.4 Hz), 45.8 (t, *J* = 4.0 Hz), 36.7 (t, *J* = 23.6 Hz), 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.2 (d, *J* = 259.1 Hz), -103.4 (d, *J* = 257.9 Hz), -105.0 (d, *J* = 260.2 Hz), -105.2 (d, *J* = 259.8 Hz) ppm. HRMS (ESI) m/z calcd for $C_{19}H_{17}ClF_2O_3$ $[M+H]^+$ 367.0907; found: 367.0927.

ethyl 5-(2-bromophenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate **3q**
ethyl 4-(2-bromophenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate **3q'**



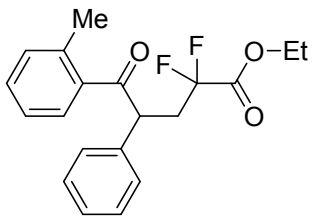
3q



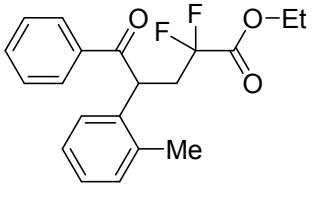
3q'

Reaction time 30h, R_f = 0.5 (EA/PE = 1:10), Yield 60%, colourless oil. **3q**: **3q'**= 6.2:1. **3q** and **3q':** ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.97-7.95 (m, 0.30H), 7.54-7.52 (m, 0.17H), 7.44-7.42 (m, 0.94H), 7.34-7.32 (m, 0.42H), 7.20-7.07 (m, 7.05H), 7.03-6.99 (m, 0.19H), 5.39 (dd, *J* = 3.6 Hz, 9.2 Hz, 0.13H), 4.69 (t, *J* = 6.8 Hz, 0.80H), 4.21-3.97 (m, 2H), 3.24-3.12 (m, 1H), 2.62-2.55 (m, 0.86H), 2.35-2.22 (m, 0.17H), 1.20-1.44 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.2, 197.1, 163.7 (t, *J* = 31.4 Hz), 140.3, 137.3, 135.6, 133.8, 133.6, 133.5, 131.6, 129.3, 129.0, 128.9, 128.8, 128.7, 128.3, 128.0, 127.1, 124.1, 119.2, 115.4 (t, *J* = 248.7 Hz), 63.0, 62.9, 51.1 (t, *J* = 4.6 Hz), 45.8 (t, *J* = 4.0 Hz), 37.4 (t, *J* = 24.5 Hz), 36.6 (t, *J* = 23.6 Hz), 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.2 (d, *J* = 260.6 Hz), -103.3 (d, *J* = 259.4 Hz), -105.1 (d, *J* = 259.4 Hz), -105.2 (d, *J* = 259.4 Hz) ppm. HRMS (ESI) m/z calcd for $C_{19}H_{17}BrF_2O_3$ $[M+H]^+$ 411.0402; found: 411.0403.

ethyl 2,2-difluoro-5-oxo-4-phenyl-5-(o-tolyl)pentanoate **3r**
ethyl 2,2-difluoro-5-oxo-5-phenyl-4-(o-tolyl)pentanoate **3r'**



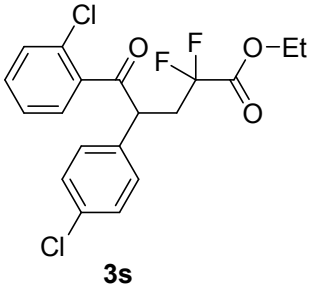
3r



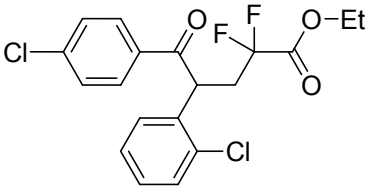
3r'

Reaction time 24h, R_f = 0.8 (EA/PE = 1:10), Yield 61%, colourless oil. **3r** : **3r'**=10:1. **3r**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.4 Hz, 1H), 7.30-7.26 (m, 3H), 7.21-7.18 (m, 4H), 7.12 (d, J = 7.6 Hz, 1H), 4.78 (dd, J = 4.8 Hz, 8.4 Hz, 1H), 4.20-4.08 (m, 2H), 3.39-3.25 (m, 1H), 2.58-2.45 (m, 1H), 2.24 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8, 163.9 (t, J = 32.4 Hz), 138.4, 137.6, 137.0, 131.6, 131.2, 129.0, 128.4, 128.0, 127.7, 125.5, 115.4 (t, J = 249.1 Hz), 63.0, 49.8 (t, J = 3.5 Hz), 37.4 (t, J = 23.9 Hz), 20.6, 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.1 (d, J = 258.3 Hz), -104.9 (d, J = 258.7 Hz) ppm. HRMS (ESI) m/z calcd for $C_{20}H_{20}F_2O_3$ $[M+H]^+$ 347.1453; found: 347.1472.

ethyl 5-(2-chlorophenyl)-4-(4-chlorophenyl)-2,2-difluoro-5-oxopentanoate **3s**
ethyl 4-(2-chlorophenyl)-5-(4-chlorophenyl)-2,2-difluoro-5-oxopentanoate **3s'**



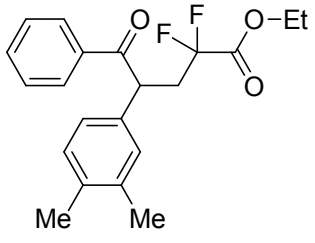
3s



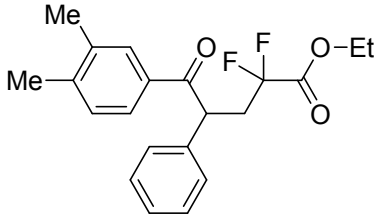
3s'

Reaction time 24h, R_f = 0.7 (EA/PE = 1:10), Yield 77%, colourless oil. **3s**: **3s'**=19:1. **3s**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.21 (m, 2H), 7.19-7.11 (m, 4H), 7.05-7.03 (m, 2H), 4.73 (t, J = 6.4 Hz, 1H), 4.13-4.03 (m, 2H), 3.21-3.08 (m, 1H), 2.57-2.43 (m, 1H), 1.20 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 163.7 (t, J = 33.0 Hz), 138.0, 134.5, 134.0, 131.9, 131.0, 130.6, 130.1, 129.2, 129.1, 126.7, 115.2 (t, J = 249.0 Hz), 63.1, 50.4 (t, J = 3.5 Hz), 36.7 (t, J = 23.3 Hz), 13.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.7 (d, J = 260.2 Hz), -104.7 (d, J = 260.9 Hz) ppm. HRMS (ESI) m/z calcd for $C_{19}H_{16}Cl_2F_2O_3$ [M+Na]+ 423.0337; found: 423.0372.

ethyl 4-(3,4-dimethylphenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate **3t**
ethyl 5-(3,4-dimethylphenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate **3t'**



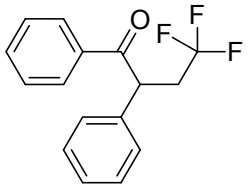
3t



3t'

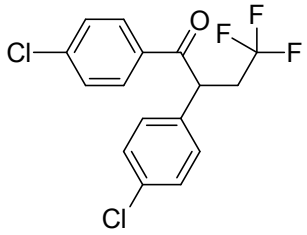
Reaction time 30h, R_f= 0.8 (EA/PE = 1:10), Yield 76%, colourless oil. **3t**: **3t'**=2:1. **3t** and **3t'**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.86 (m, 0.81H), 7.65-7.62 (m, 1.29H), 7.38-7.36 (m, 0.42H), 7.31-7.27 (m, 0.76H), 7.22-7.16 (m, 2.52H), 7.12-7.08 (m, 0.68H), 7.03 (d, *J* = 8.0 Hz, 0.67H), 6.93-6.37 (m, 1.06H), 4.85 (dd, *J* = 5.2 Hz, 8.0 Hz, 0.63H), 4.80 (dd, *J* = 4.8 Hz, 8.0 Hz, 0.32H), 4.10-3.93 (m, 2H), 3.24-3.10 (m, 1H), 2.51-2.38 (m, 1H), 2.16 (s, 2H), 2.15 (s, 2H), 2.10 (s, 1H), 2.08 (s, 1H), 1.15-1.10 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 197.1, 163.83 (t, *J* = 31.7 Hz), 163.81 (t, *J* = 32.3 Hz), 162.5, 142.9, 138.2, 137.5, 137.0, 136.1, 136.0, 135.2, 133.7, 133.1, 130.4, 130.0, 129.8, 129.2, 129.1, 128.9, 128.6, 128.2, 127.6, 126.6, 125.7, 115.39 (t, *J* = 248.9 Hz), 115.37 (t, *J* = 247.7 Hz), 62.9, 46.7 (t, *J* = 3.9 Hz), 46.5 (t, *J* = 3.6 Hz), 38.3 (t, *J* = 22.8 Hz), 38.2 (t, *J* = 22.6 Hz), 36.4, 31.4, 20.0, 19.8, 19.3, 13.8, 13.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.8 (d, *J* = 258.7 Hz), -103.9 (d, *J* = 258.3 Hz), -104.7 (d, *J* = 265.8 Hz), -104.8 (d, *J* = 265.5 Hz) ppm. HRMS (ESI) m/z calcd for $C_{19}H_{16}Cl_2F_2O_3$ [M+Na]+ 423.0337; found: 423.0372.

4,4,4-trifluoro-1,2-diphenylbutan-1-one **4a**[2]



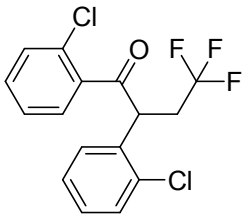
Reaction time 30h, R_f= 0.5 (EA/PE = 1:20), Yield 60%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 4.4 Hz, 4H), 7.17-7.15 (m, 1H), 4.83 (dd, *J* = 7.6 Hz, 5.2 Hz, 1H), 3.30-3.16 (m, 1H), 2.53-2.40 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 137.4, 135.7, 133.4, 129.4, 128.8, 128.7, 128.0, 127.9, 126.4 (q, *J* = 275.8 Hz), 47.2 (q, *J* = 2.7 Hz), 37.3 (q, *J* = 27.9 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.6 ppm.

1,2-bis(4-chlorophenyl)-4,4,4-trifluorobutan-1-one **4b**[2]



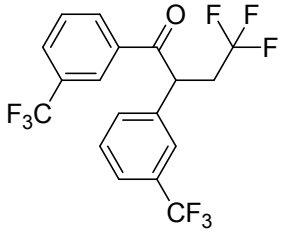
Reaction time 24h, R_f= 0.9 (EA/PE = 1:10), Yield 80%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 4.81 (t, J = 6.8 Hz, 1H), 3.30-3.17 (m, 1H), 2.59-2.46 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 140.2, 135.5, 134.1, 133.7, 130.2, 129.7, 129.4, 129.1, 126.2 (q, J = 275.1 Hz), 46.6 (q, J = 3.4 Hz), 37.2 (q, J = 27.6 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.4 ppm.

1,2-bis(2-chlorophenyl)-4,4,4-trifluorobutan-1-one **4c**[2]



Reaction time 24h, R_f= 0.7 (EA/PE = 1:10), Yield 90%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.25 (m, 5H), 7.24-7.14 (m, 3H), 5.40 (t, J = 6.4 Hz, 1H), 3.38-3.25 (m, 1H), 2.63-2.49 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 137.7, 134.2, 133.8, 132.0, 131.3, 130.6, 130.2, 129.4, 129.3, 129.0, 127.5, 126.6, 126.2 (q, J = 275.5 Hz), 47.1, 35.4 (q, J = 28.7 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -64.6 ppm.

4,4,4-trifluoro-1,2-bis(3-(trifluoromethyl)phenyl)butan-1-one **4d**[2]



Reaction time 24h, R_f= 0.6 (EA/PE = 1:10), Yield 81%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 1H), 8.10 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.60-7.47 (m, 5H), 4.97 (t, J = 6.4 Hz, 1H), 3.38-3.25 (m, 1H), 2.67-2.54 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 137.6, 135.8, 132.0 (q, J = 31.6 Hz), 131.8, 131.6 (q, J = 32.5 Hz), 131.4, 130.16 (q, J = 3.4 Hz), 130.12, 129.6, 126.0 (q, J = 275.5 Hz), 125.6 (q, J = 4.0 Hz), 125.2 (q, J = 3.9 Hz), 124.8 (q, J = 3.9 Hz), 123.6 (q, J = 270.7 Hz), 123.4 (q, J = 273.7 Hz), 47.1, 37.3 (q, J = 28.6 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.9, -63.1, -64.5 ppm.

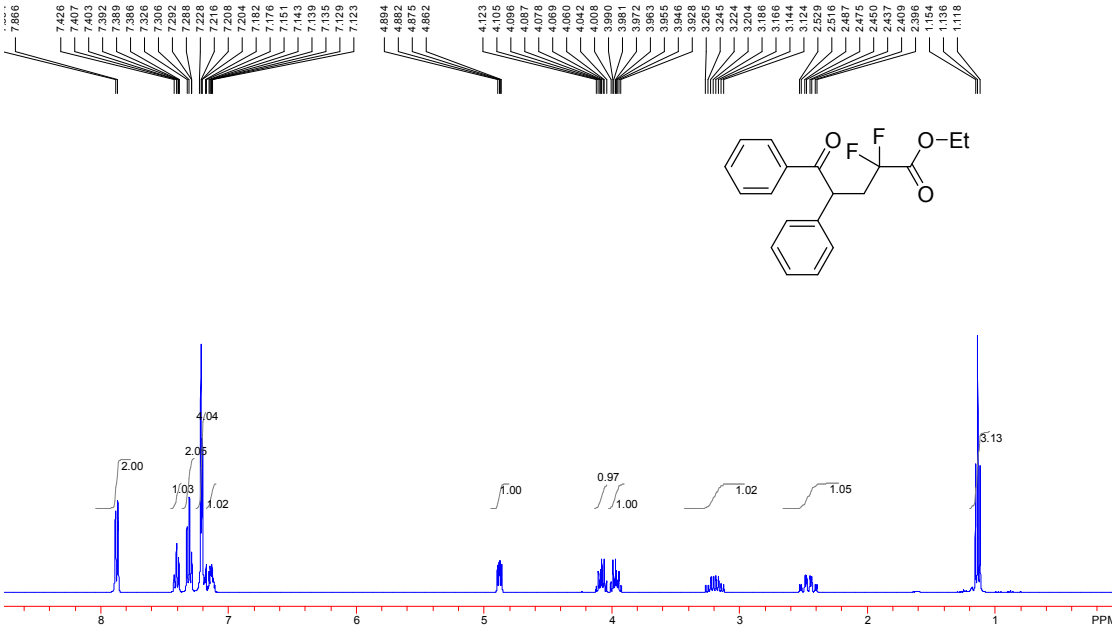
References:

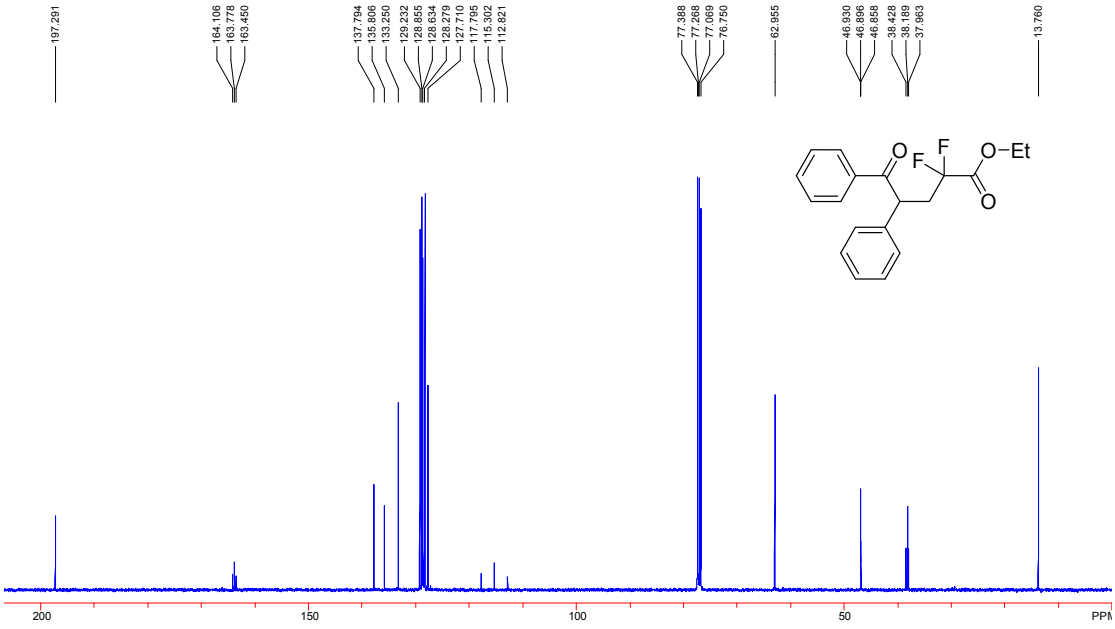
[1] Ye, Y.; Sanford, M. S., *J. Am. Chem. Soc.* **2012**, *123*, 9034-9037.

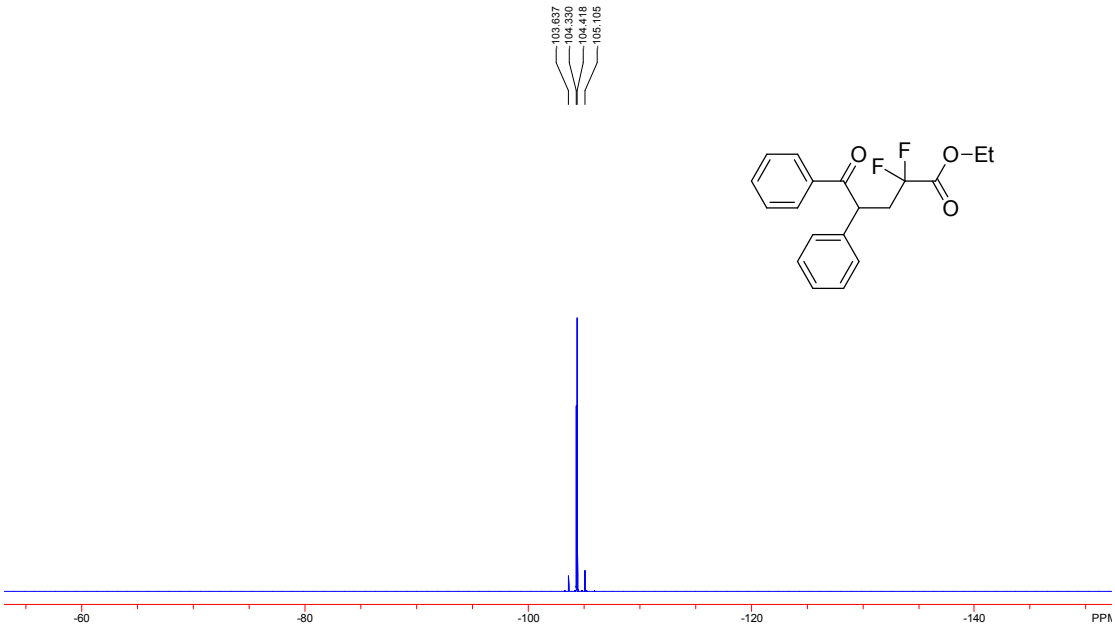
[2] Liu, X.; Xiong, F,; Huang, X,; Xu, L.; Li, P.; Wu, X. *Angew. Chem. Int. Ed.* **2013,** *52*, 6962 –6966

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

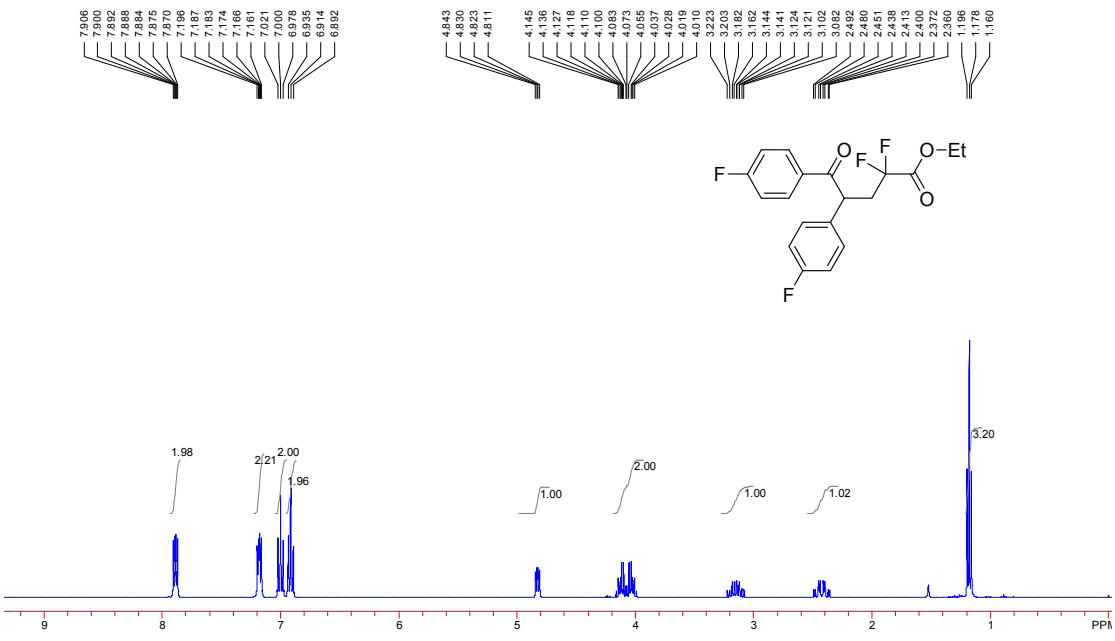
ethyl 2,2-difluoro-5-oxo-4,5-diphenylpentanoate **3a**

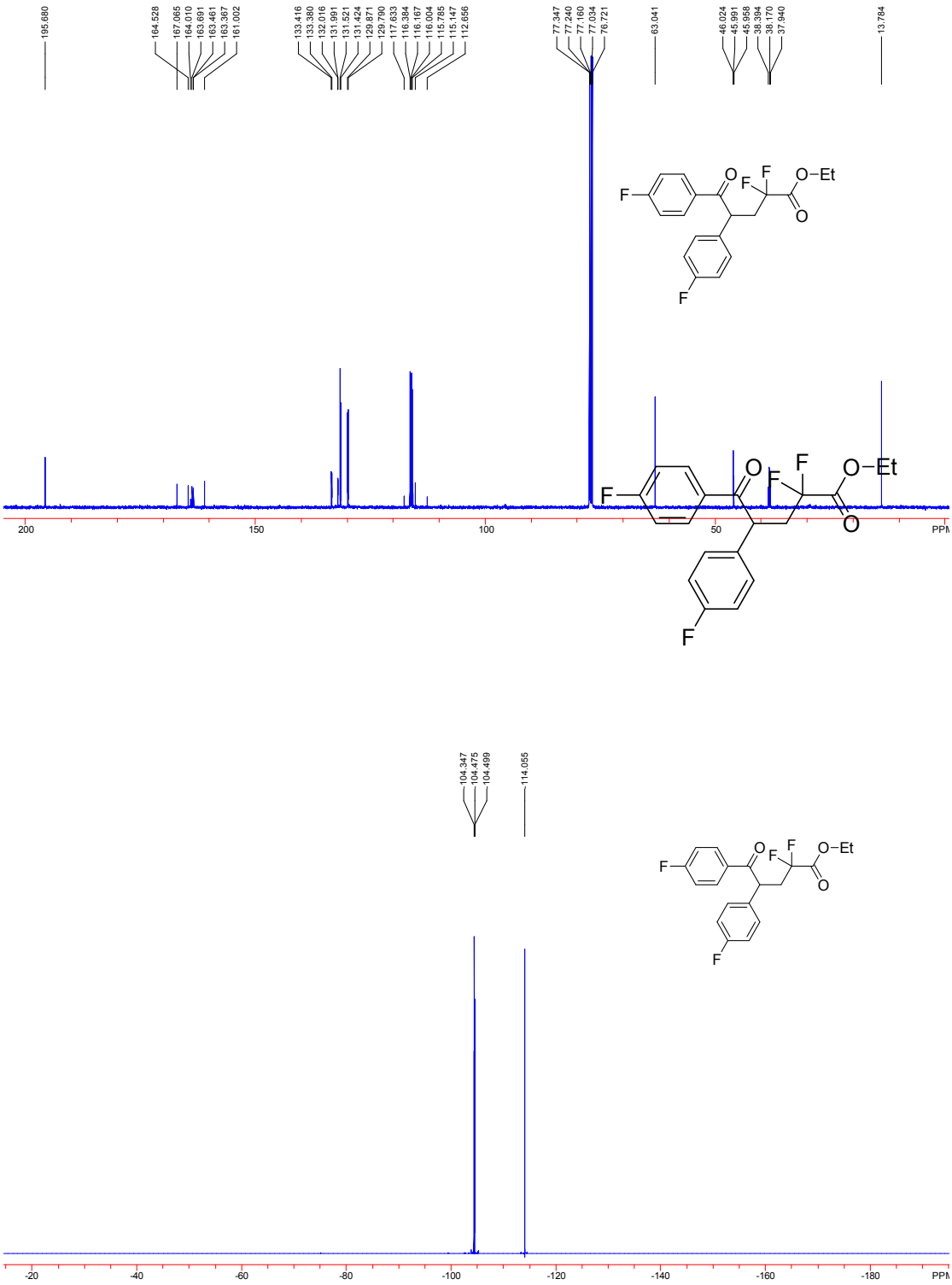




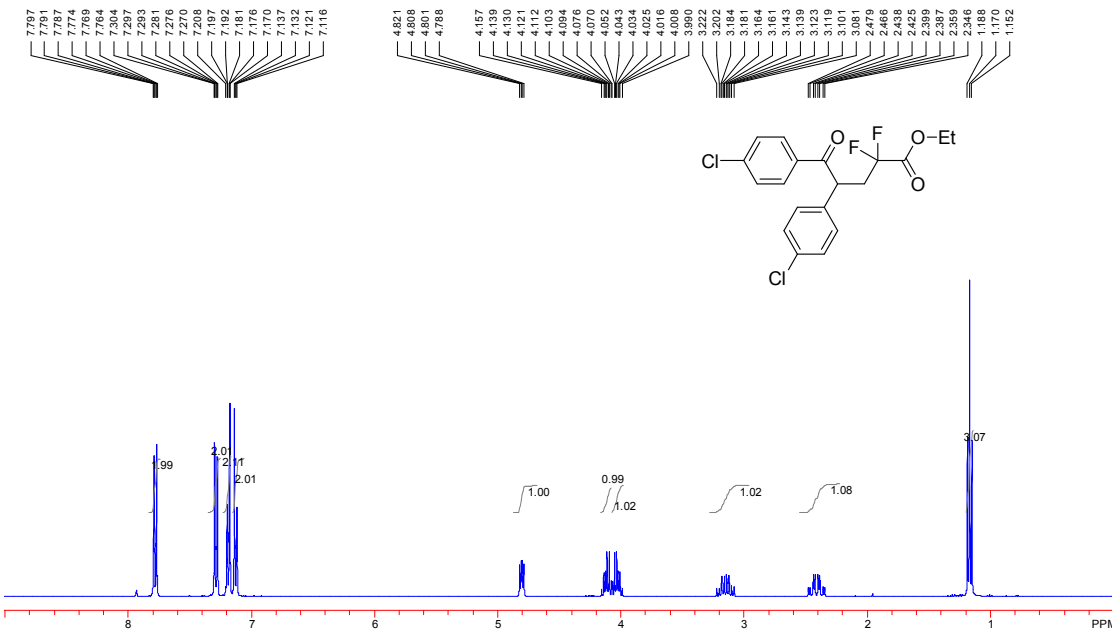


ethyl 2,2-difluoro-4,5-bis(4-fluorophenyl)-5-oxopentanoate **3b**





ethyl 4,5-bis(4-chlorophenyl)-2,2-difluoro-5-oxopentanoate **3c**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7.270
7.208
7.197
7.192
7.181
7.176
7.170
7.137
7.132
7.121
7.116
4.821
4.808
4.801
4.788
4.157
4.139
4.130
4.121
4.112
4.103
4.094
4.076
4.070
4.052
4.043
4.034
4.025
4.016
4.008
3.990
3.222
3.202
3.184
3.181
3.164
3.161
3.143
3.139
3.123
3.119
3.101
3.081
2.479
2.466
2.438
2.425
2.399
2.387
2.359
2.346
1.188
1.170
1.152
Cl
O
F
F
O−Et
O
Cl
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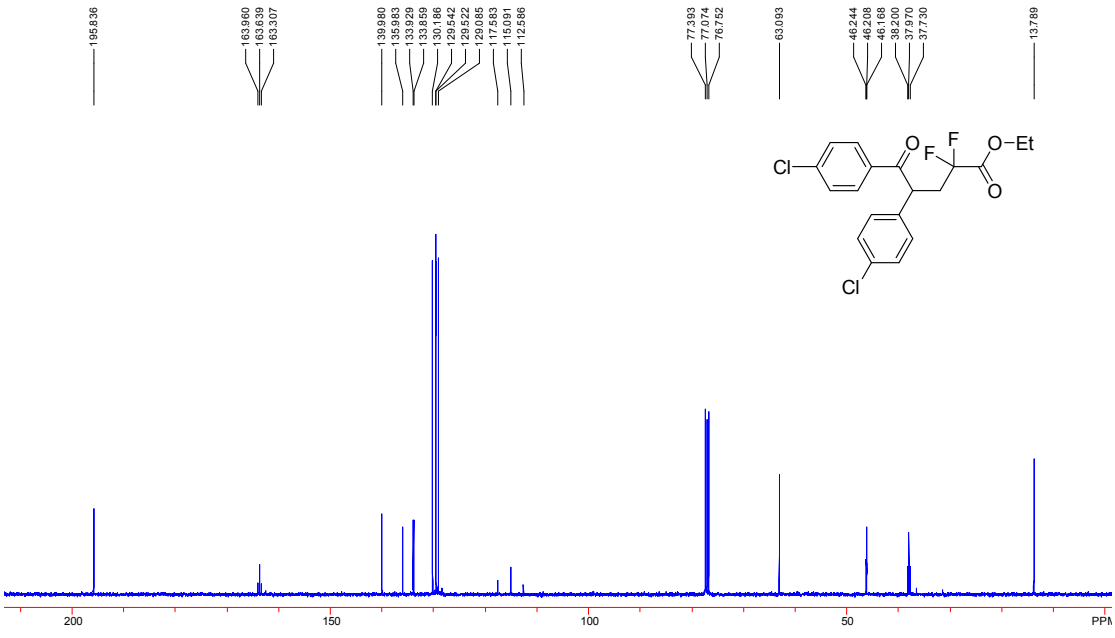
2.01
2.01
2.01
1.00
0.99
1.02
1.02
1.08
3.07
8
7
6
5
4
3
2
1
PPM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163.639
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112.586
77.393
77.074
76.752
63.093
46.244
46.208
46.168
38.200
37.970
37.730
13.789
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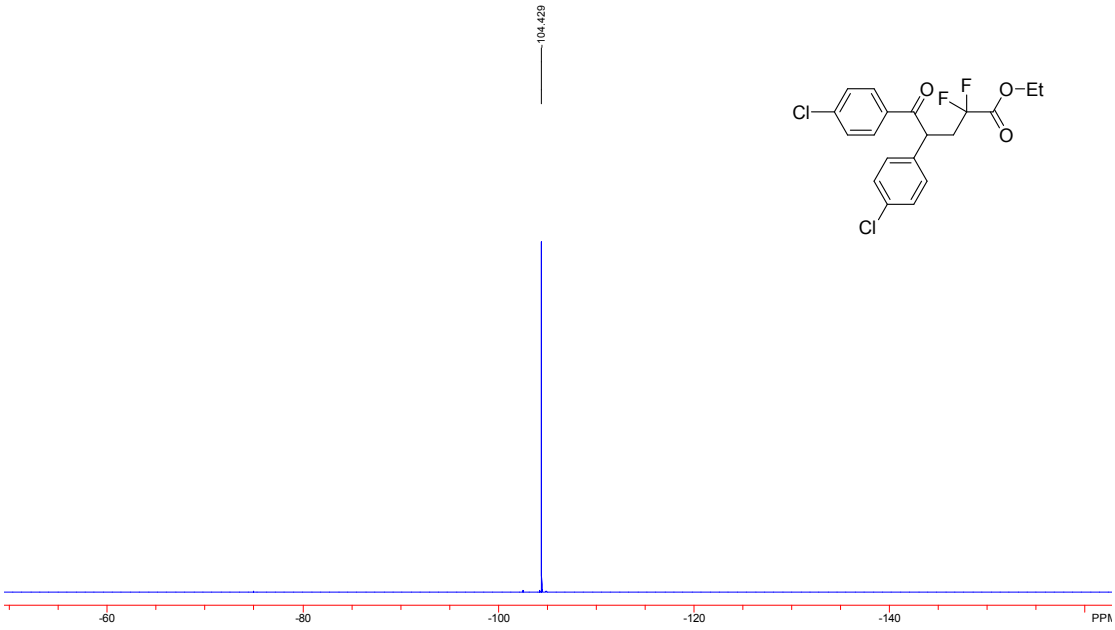
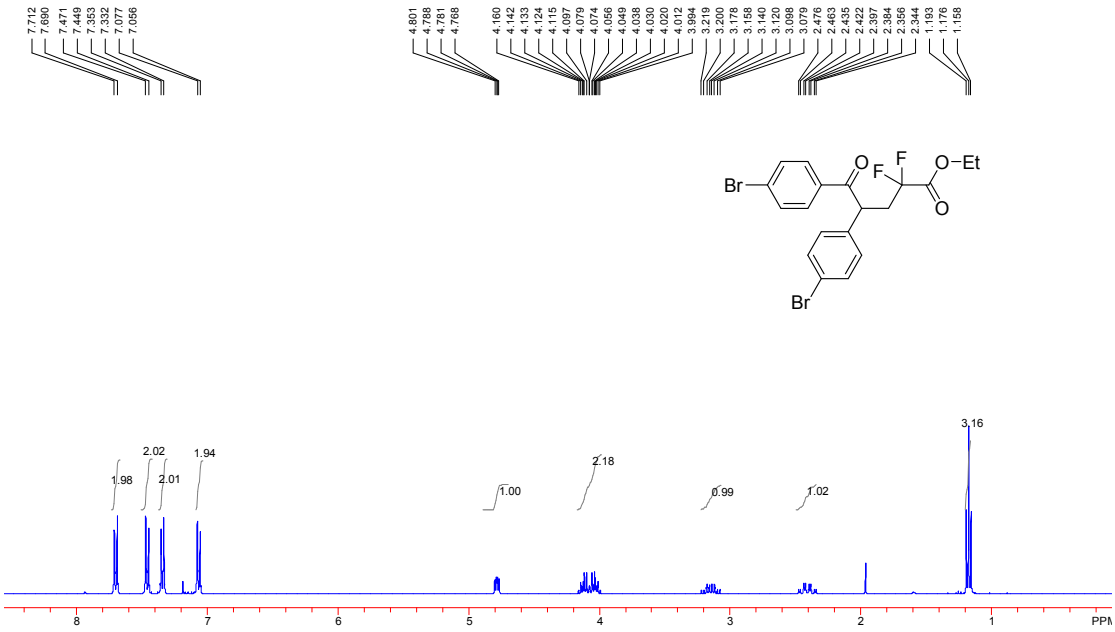
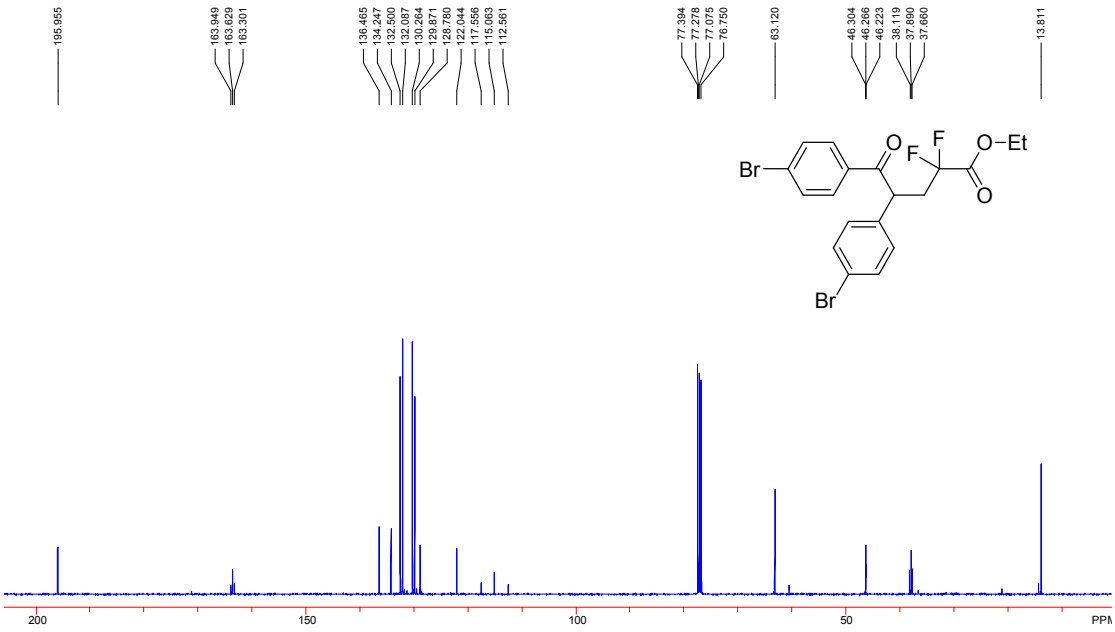
F
F
O−Et
O
Cl
200
150
100
50
PPM



ethyl 4,5-bis(4-bromophenyl)-2,2-difluoro-5-oxopentanoate **3d**

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132.500
132.087
130.264
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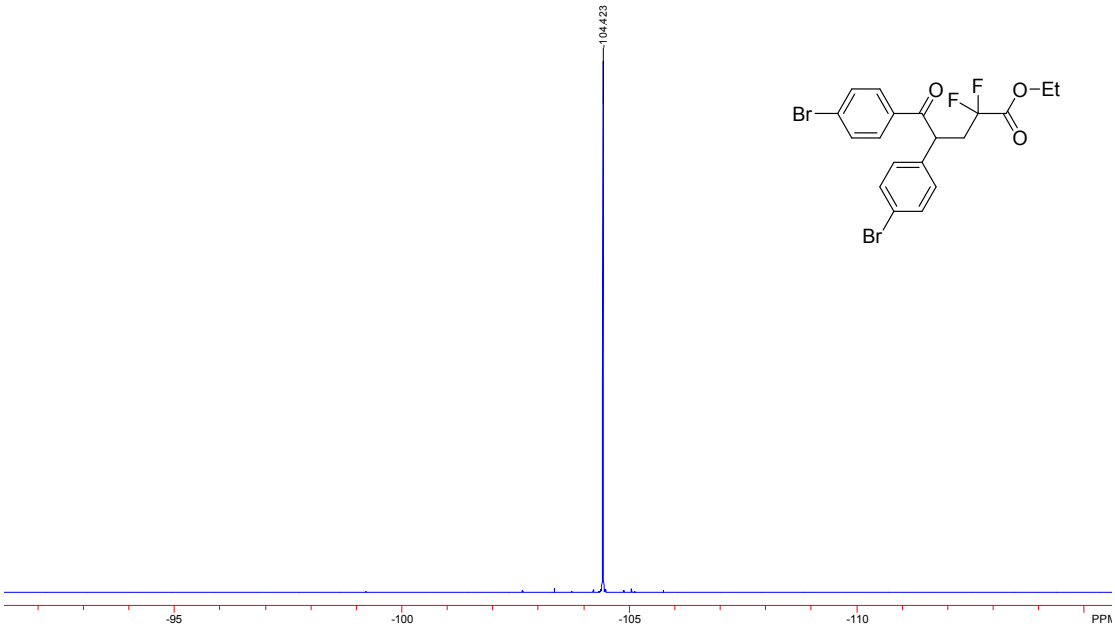
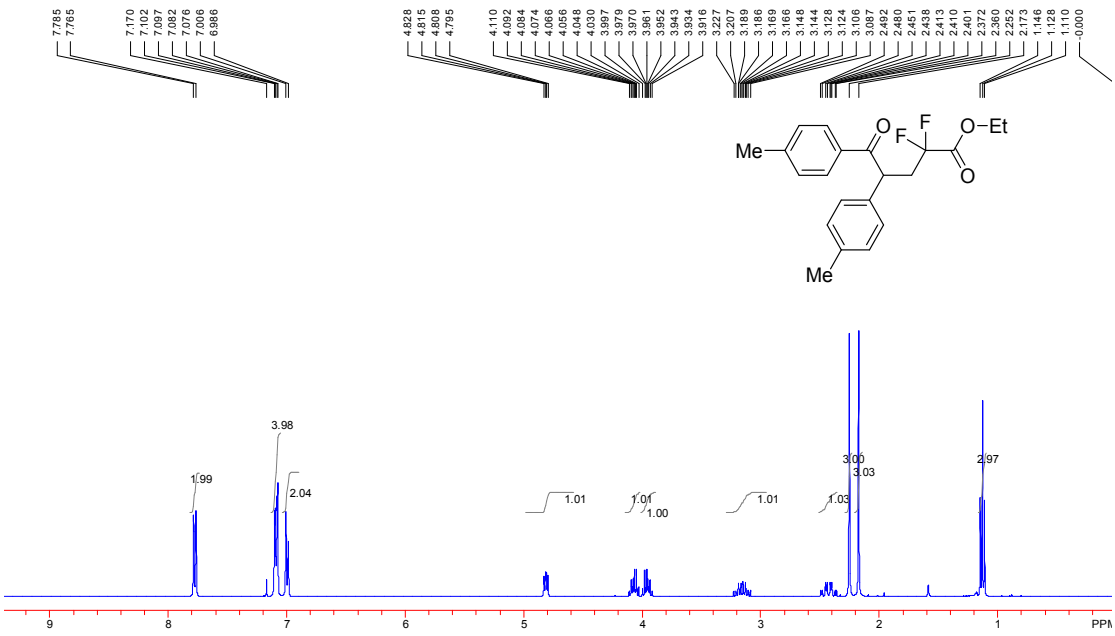
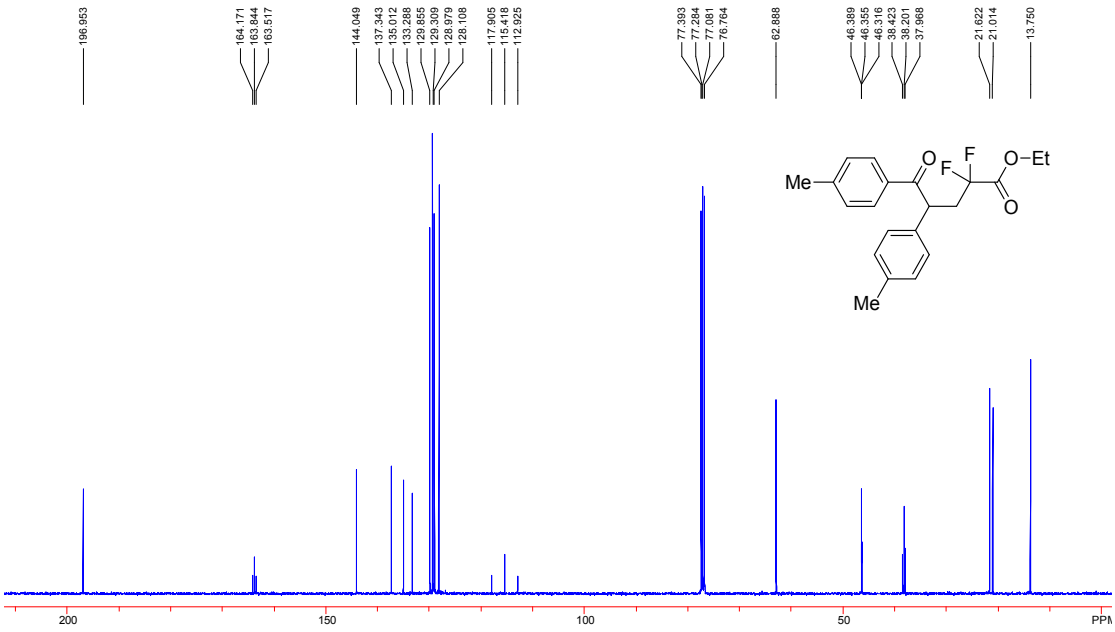
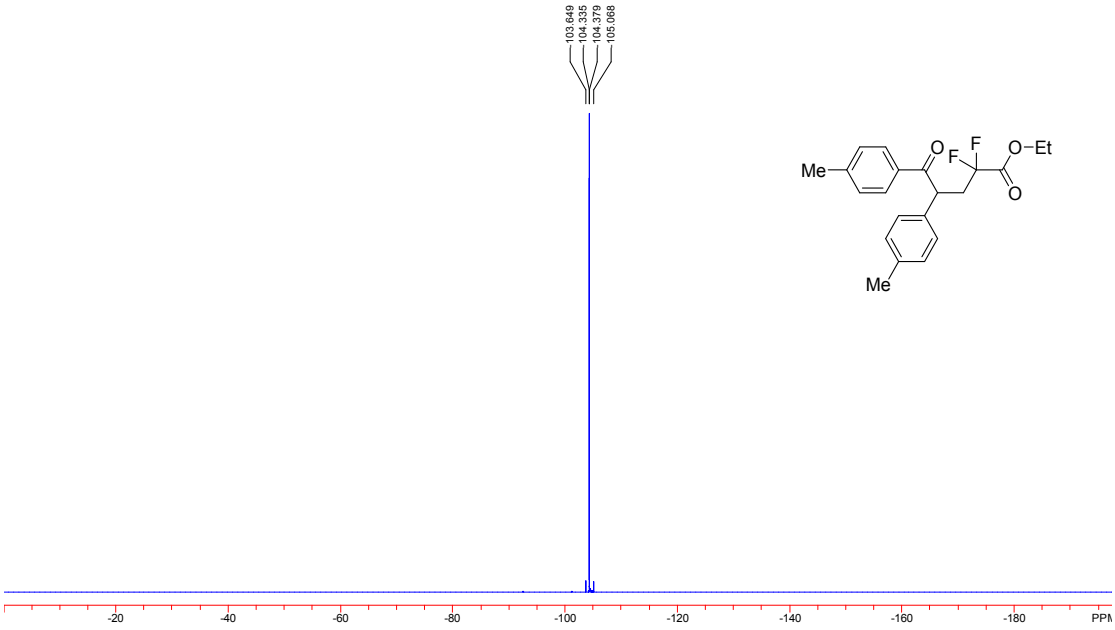
122.044
117.556
115.063
112.561
77.394
77.278
77.075
76.750
63.120
46.304
46.266
46.223
38.119
37.890
37.660
13.811
Br
O
F
O–Et
O
Br
200
150
100
50
PPM


-104.423
Br
O
F
F
O–Et
O
Br
-95
-100
-105
-110
PPM

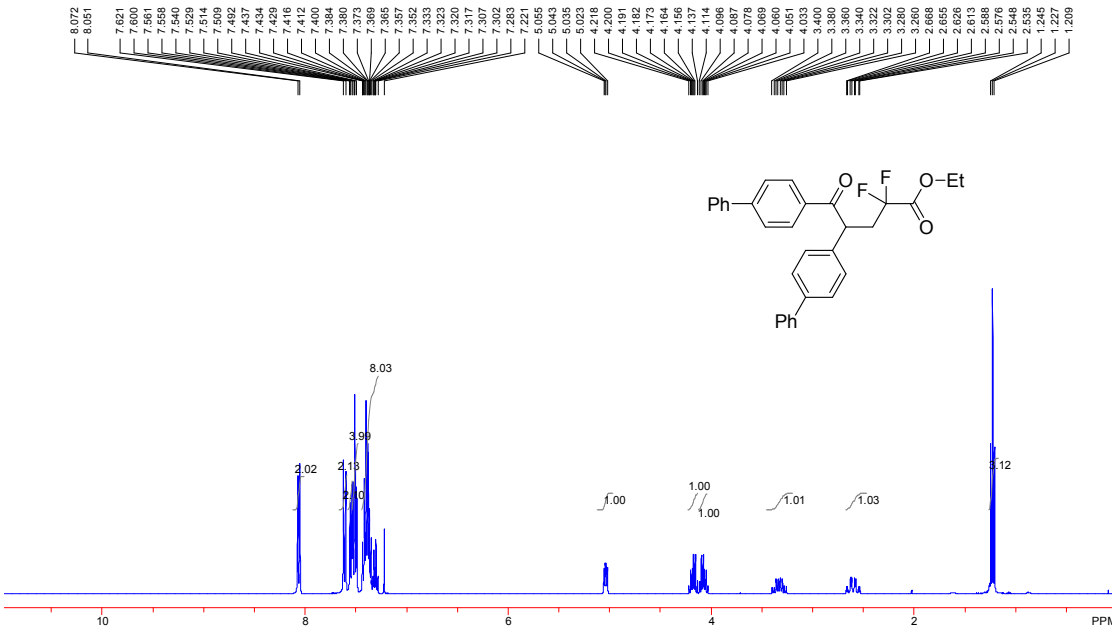
ethyl 2,2-difluoro-5-oxo-4,5-di-p-tolylpentanoate **3e**

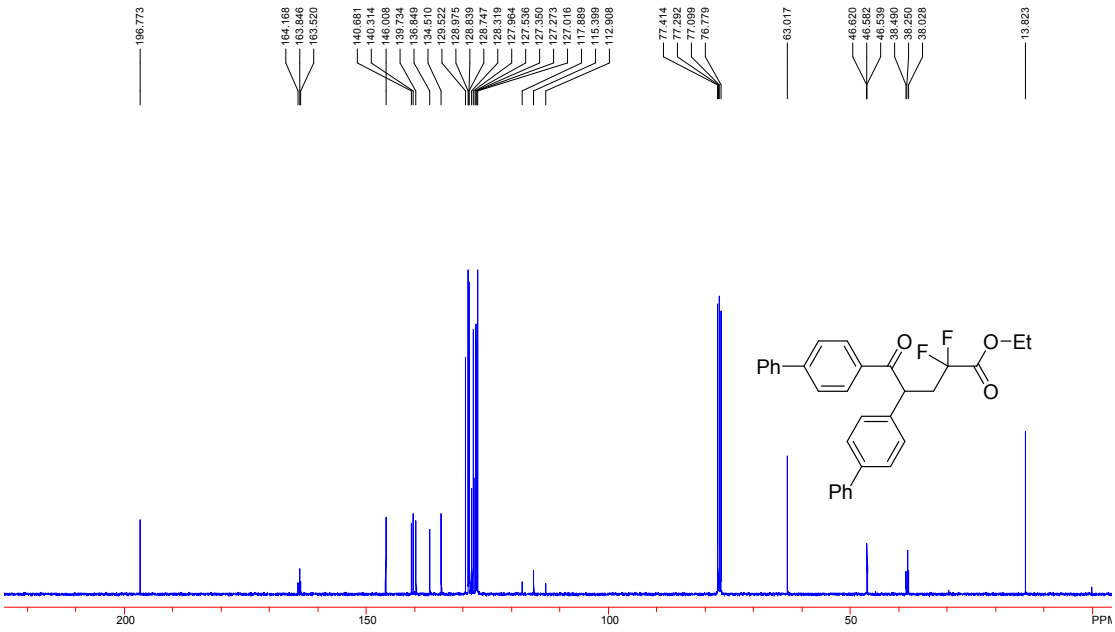






ethyl 4,5-di([1,1'-biphenyl]-4-yl)-2,2-difluoro-5-oxopentanoate **3f**

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128.747
128.319
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127.536
127.350
127.273
127.016
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115.399
112.908
77.414
77.292
77.099
76.779
63.017
46.620
46.582
46.539
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38.250
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O−Et
O
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Ph
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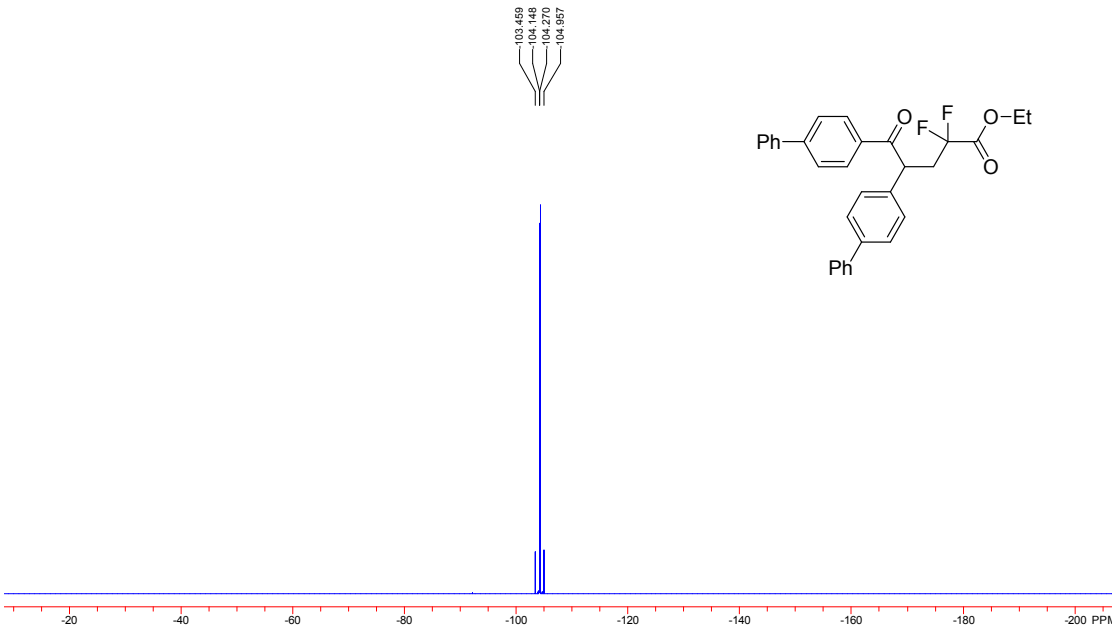
150
100
50
PPM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F
O−Et
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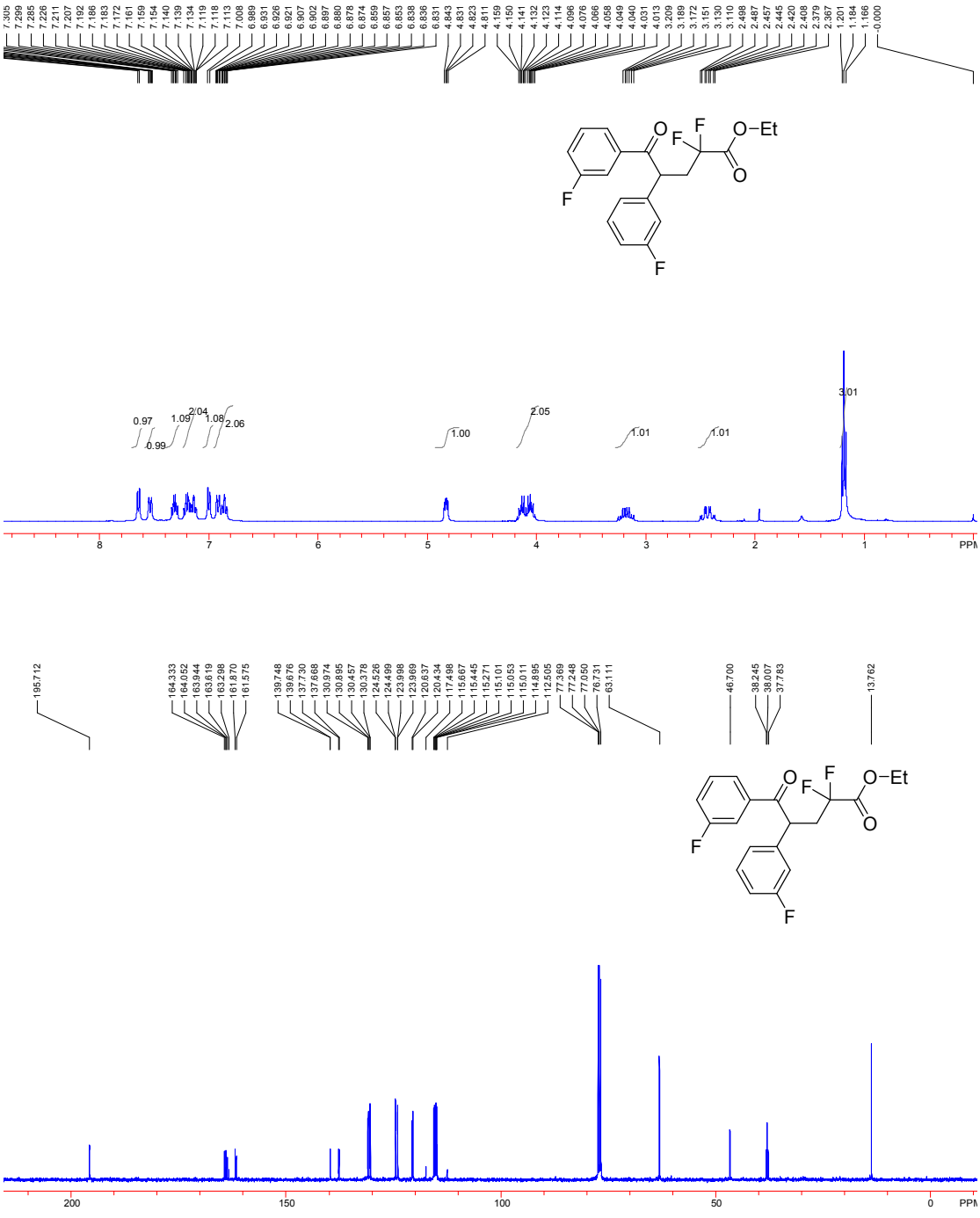
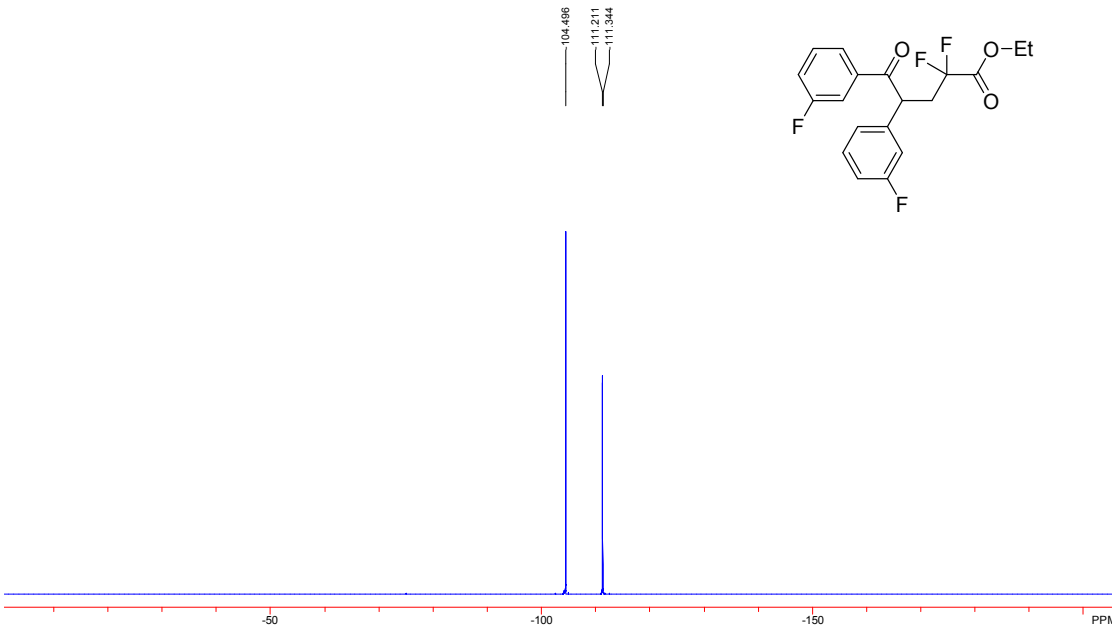
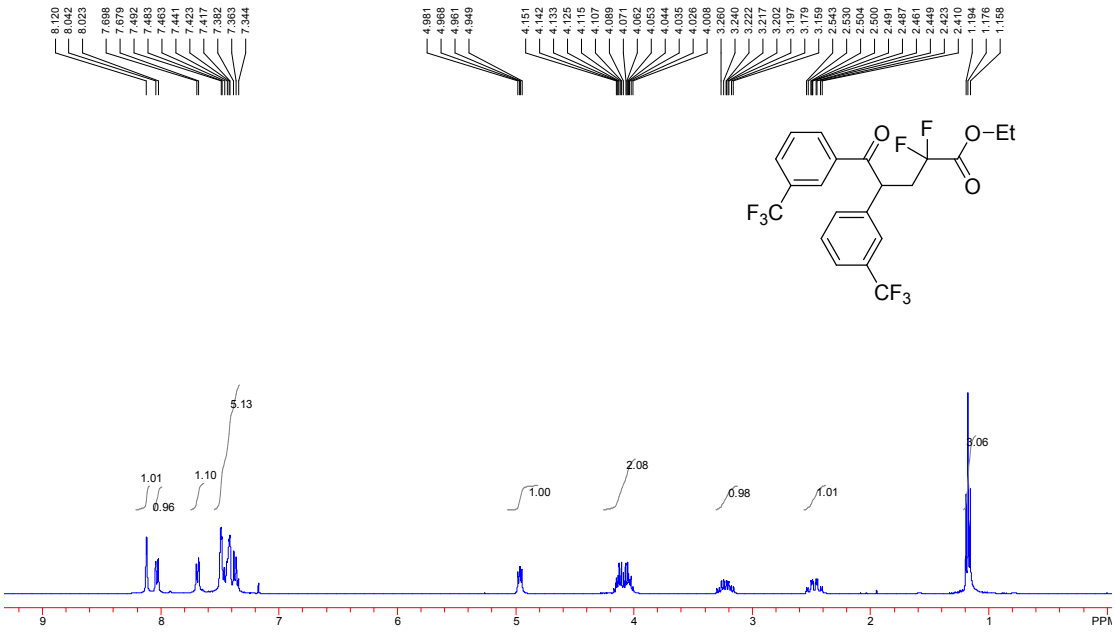
Ph
Ph
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200 PPM

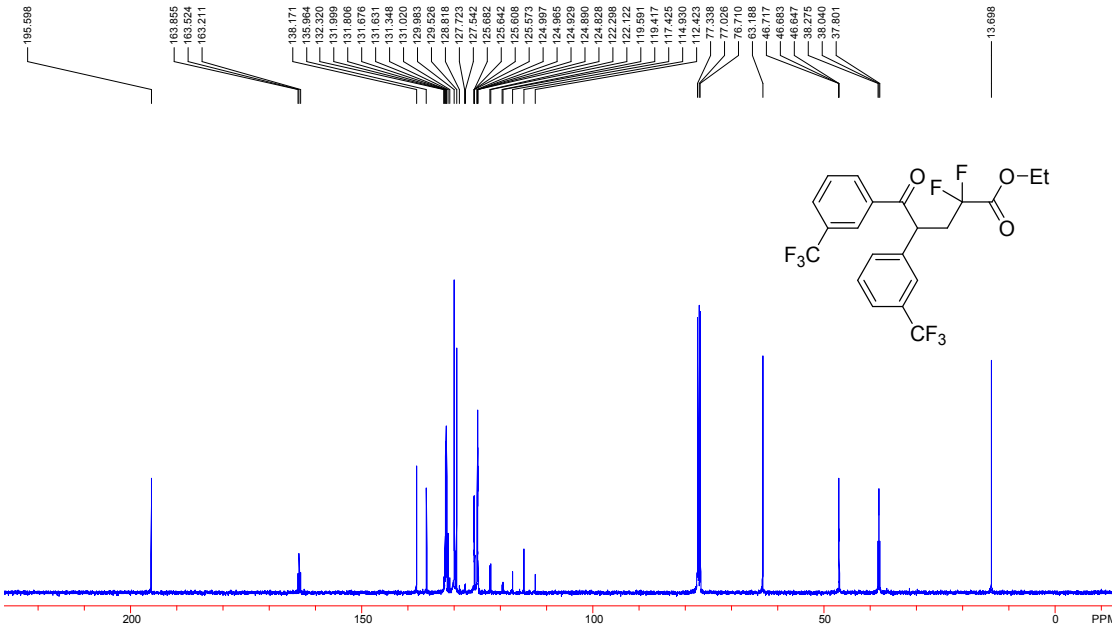
ethyl 2,2-difluoro-4,5-bis(3-fluorophenyl)-5-oxopentanoate **3g**





ethyl 2,2-difluoro-4,5-bis(3-fluorophenyl)-5-oxopentanoate **3h**

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119.417
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77.026
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F
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100
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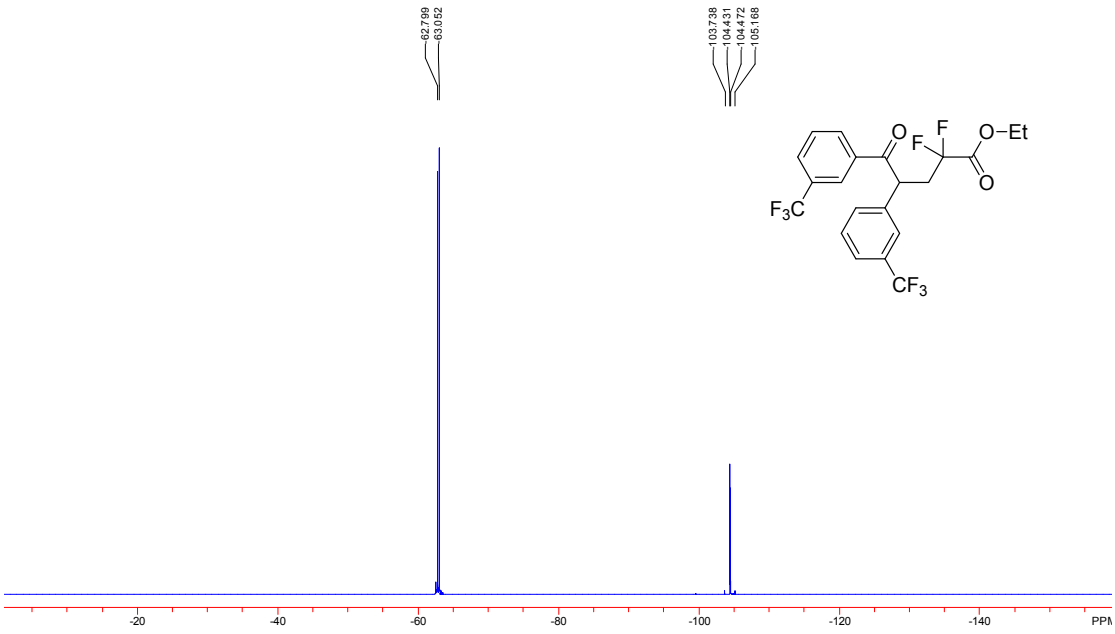
PPM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CF3
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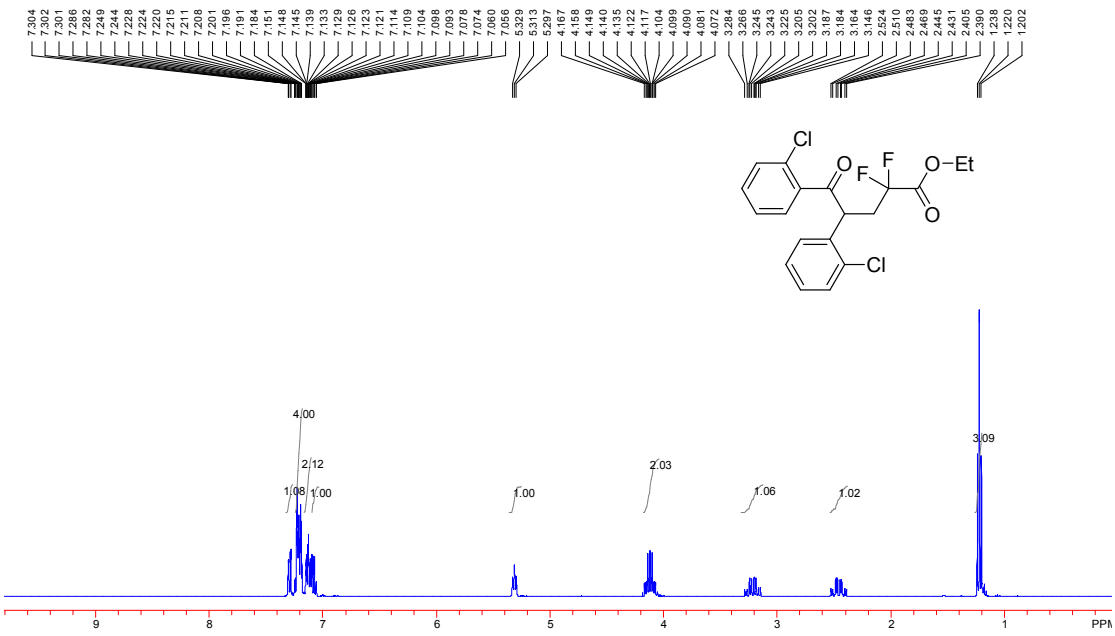
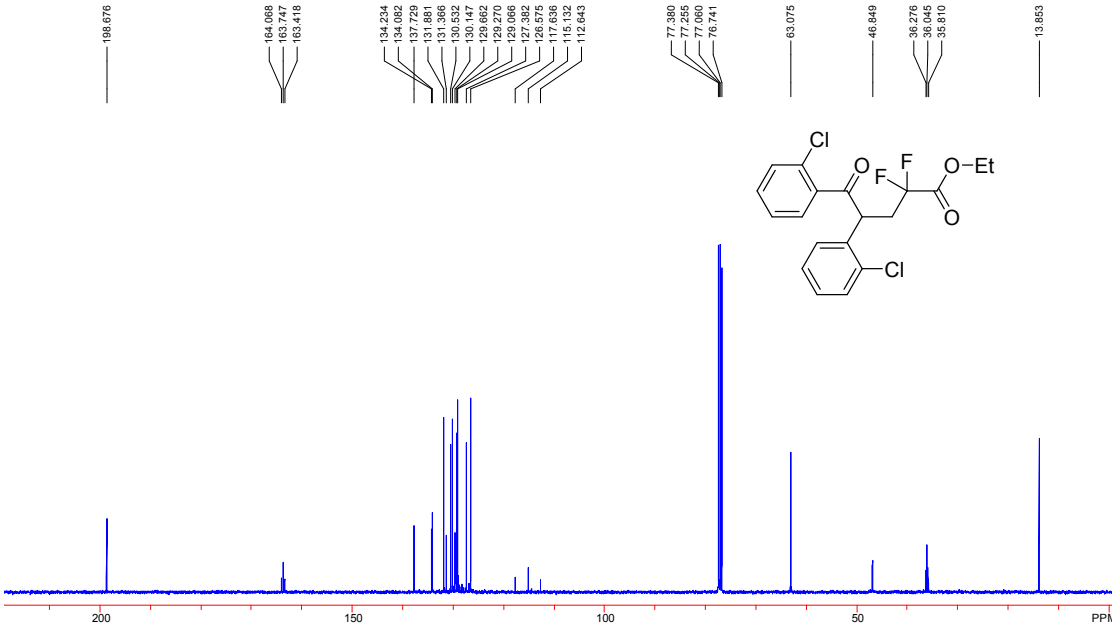
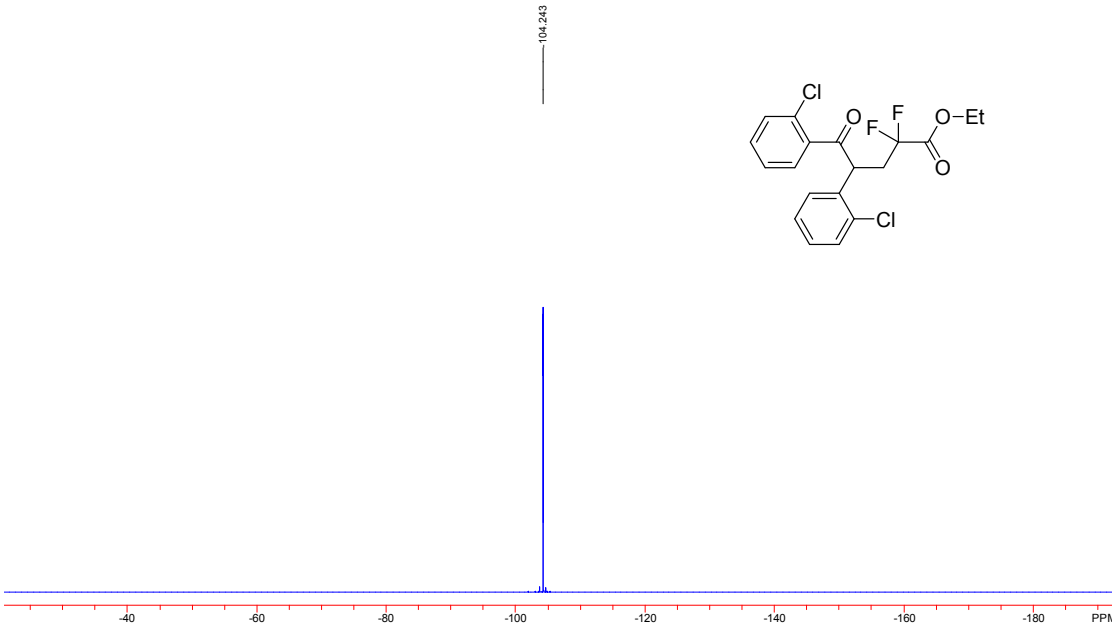
-100
-120
-140
PPM

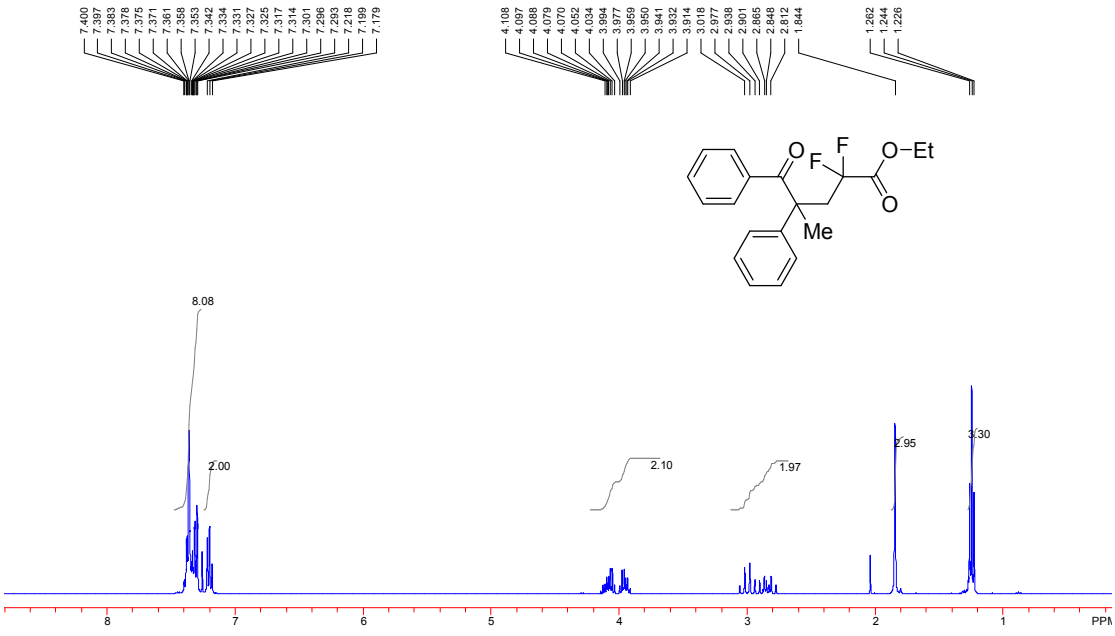
ethyl 4,5-bis(2-chlorophenyl)-2,2-difluoro-5-oxopentanoate **3i**

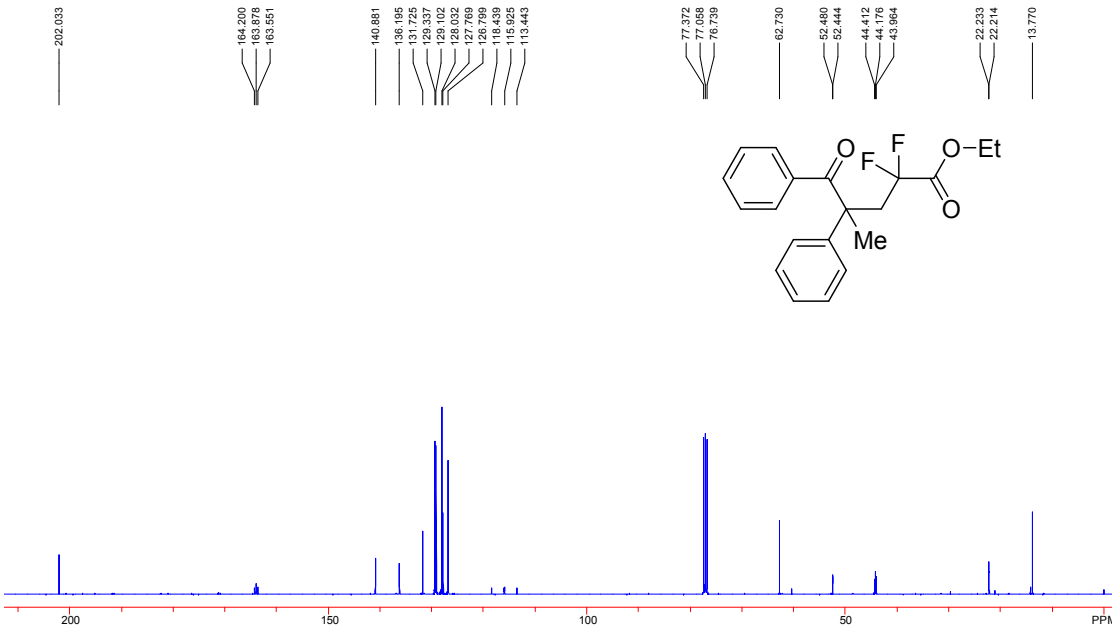






ethyl 2,2-difluoro-4-methyl-5-oxo-4,5-diphenylpentanoate **3j**

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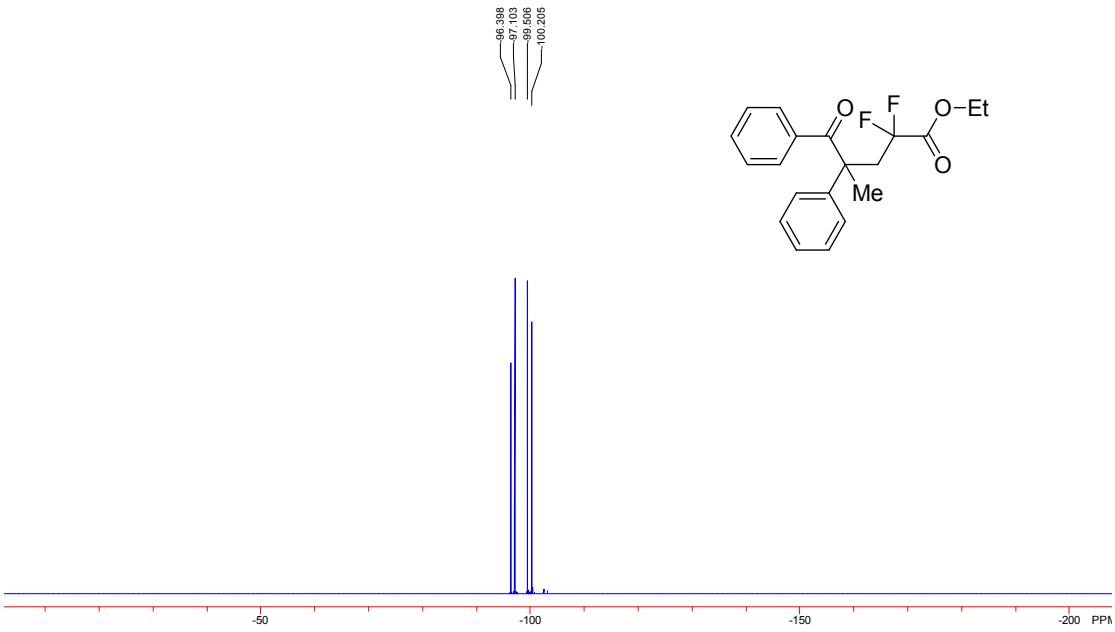
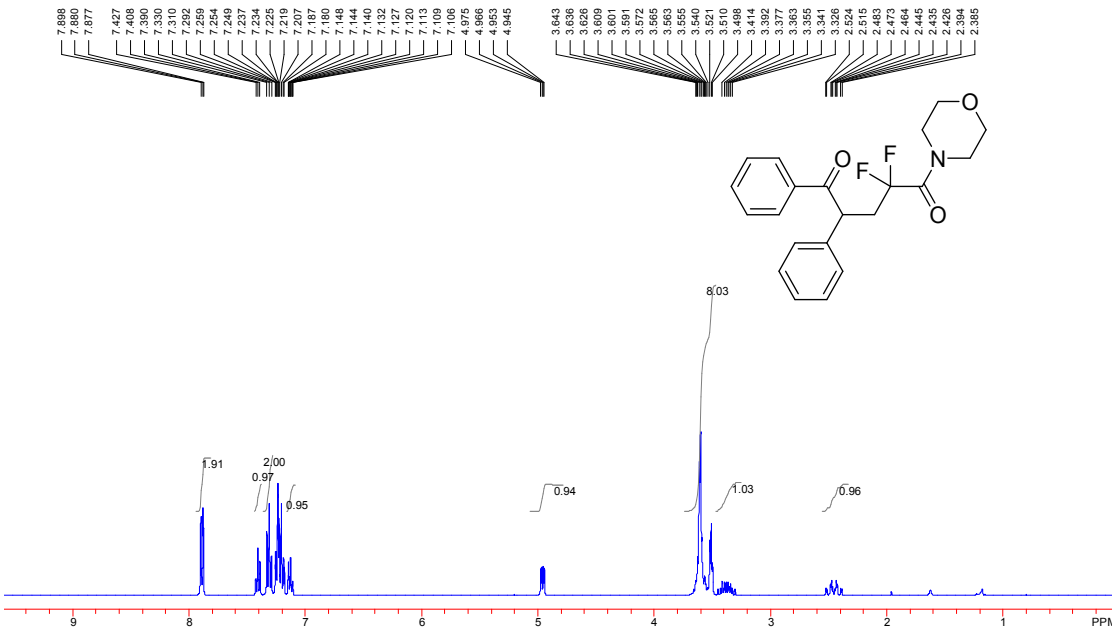
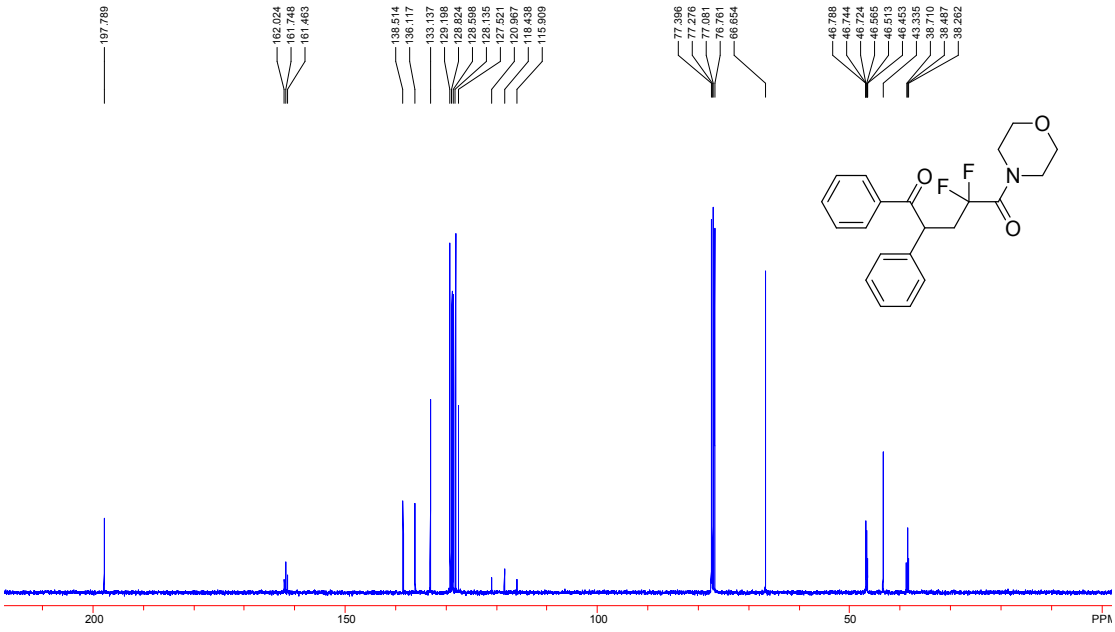
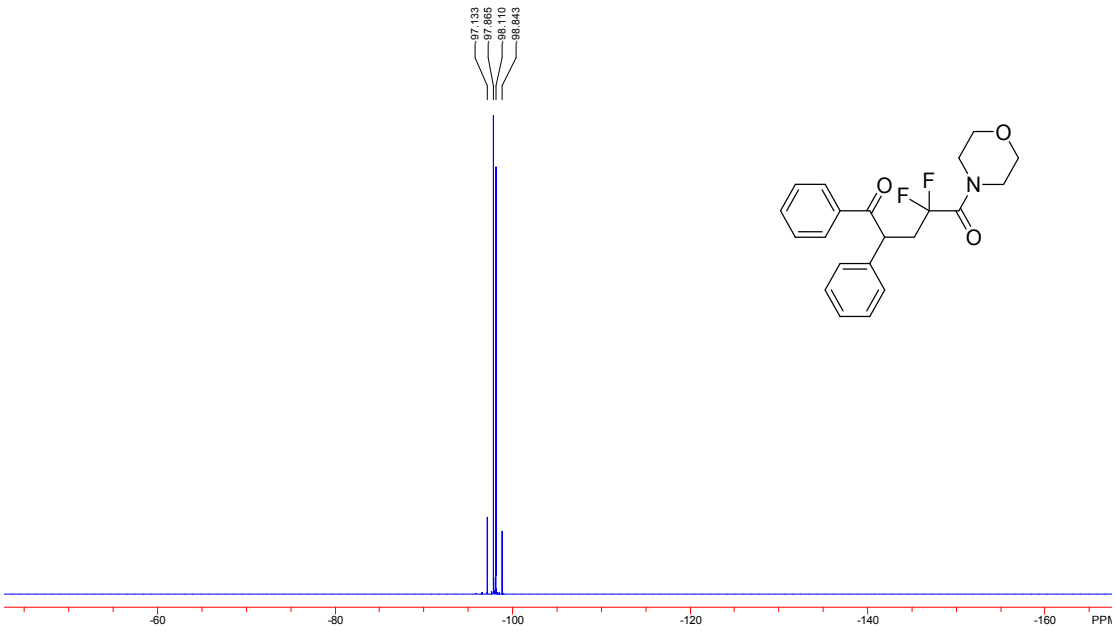
131.725
129.337
129.102
128.032
127.769
126.799
118.439
115.925
113.443
77.372
77.058
76.739
62.730
52.480
52.444
44.412
44.176
43.964
22.233
22.214
13.770
O
F
O−Et
O
Me
200
150
100
50
PPM


96.398
97.103
99.506
100.205
O
F
O−Et
O
Me
-50
-100
-150
-200
PPM

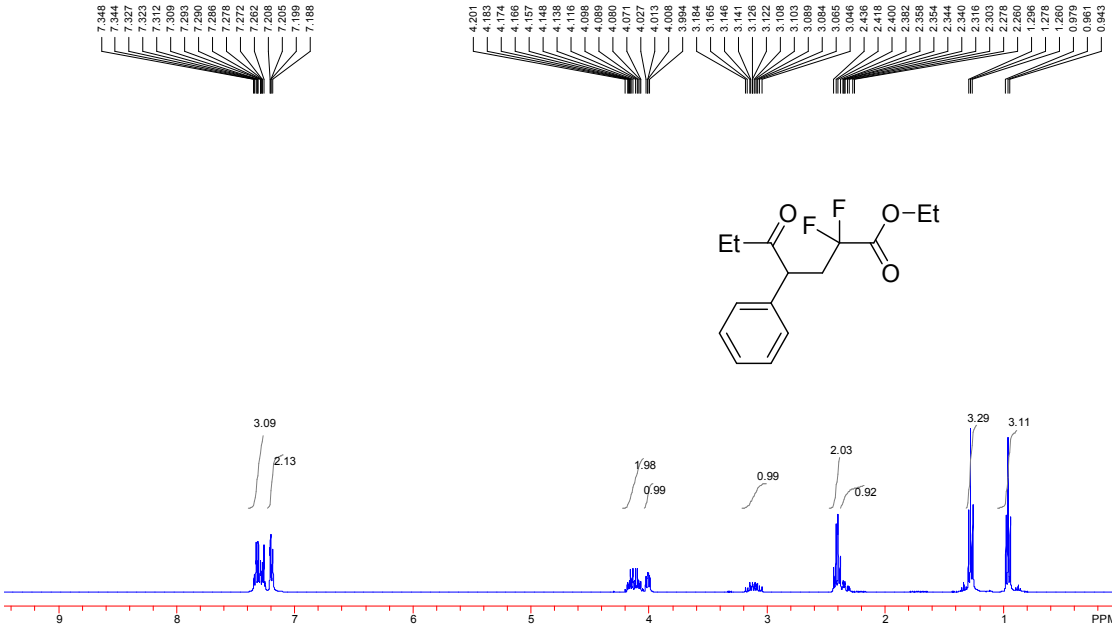
2,2-difluoro-1-morpholino-4,5-diphenylpentane-1,5-dione **3k**

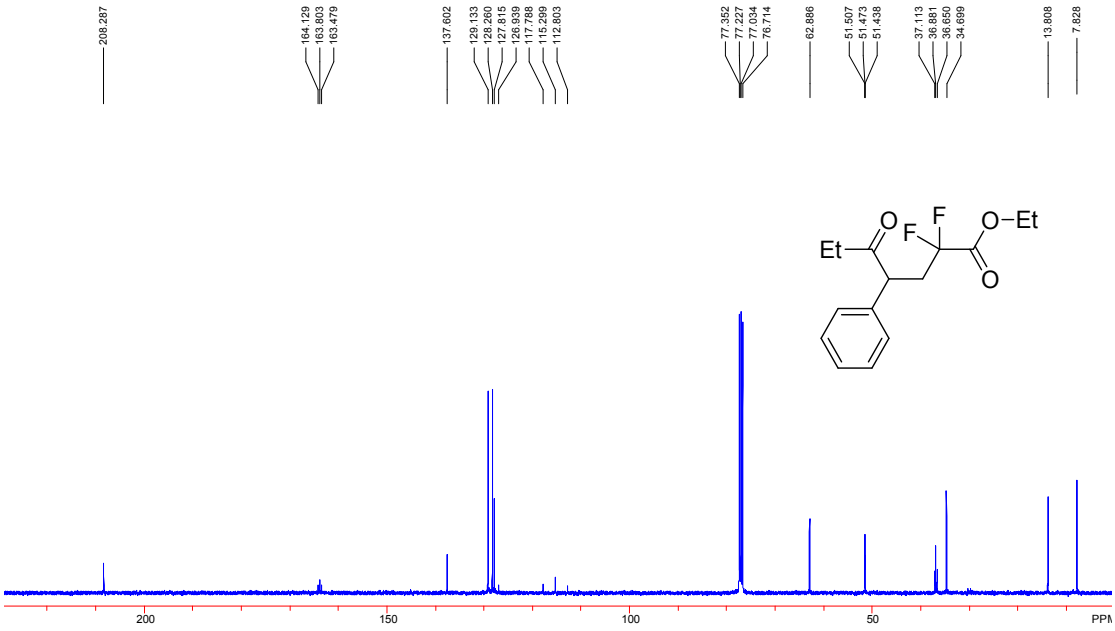


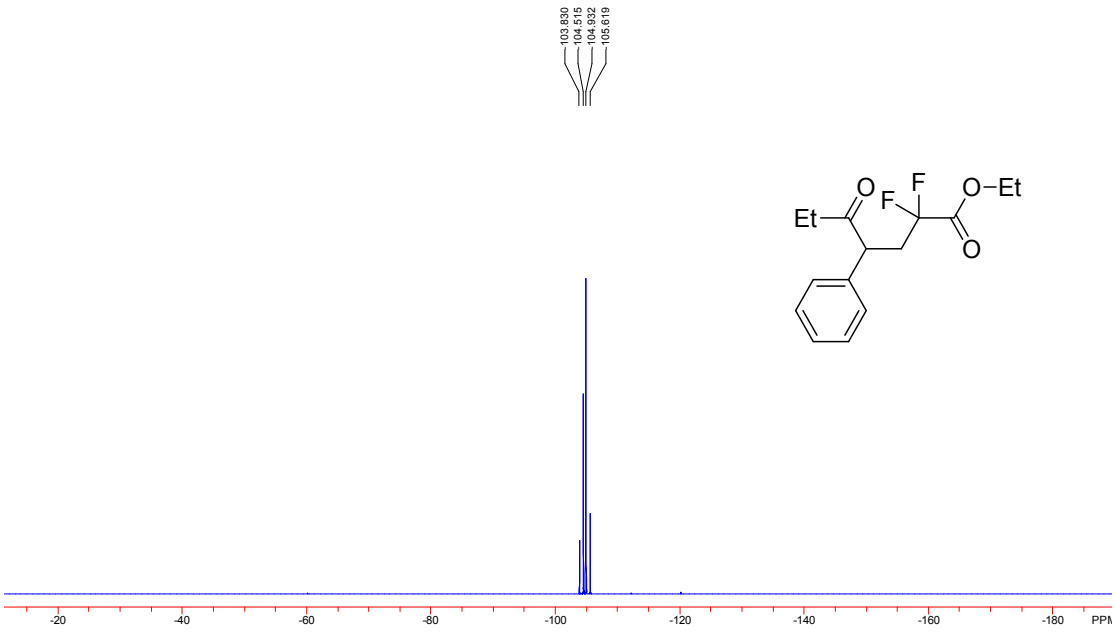




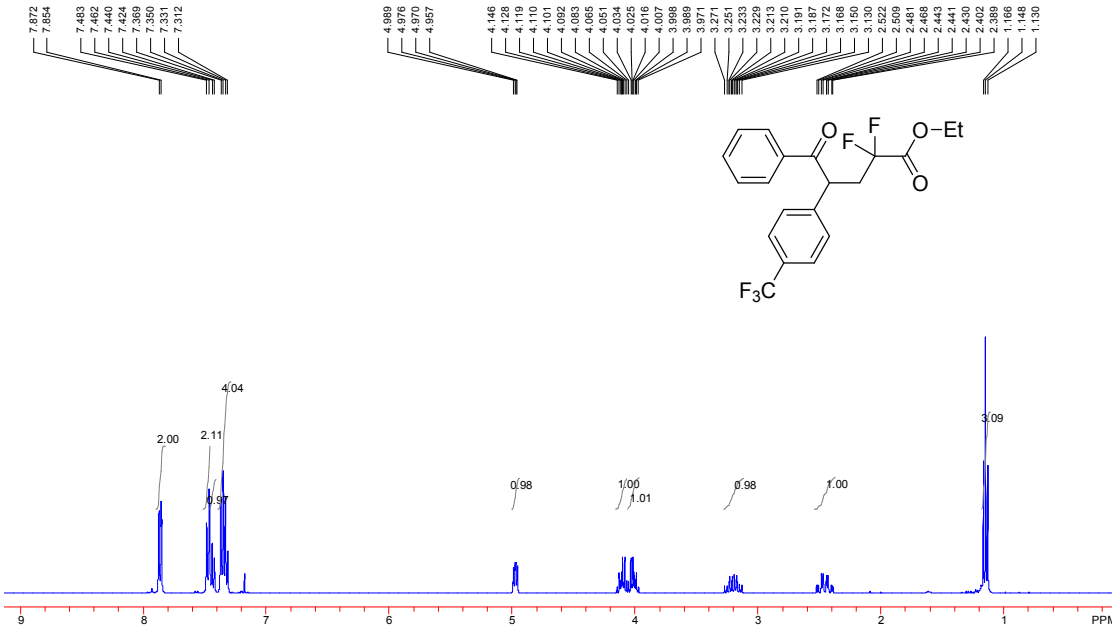
ethyl 2,2-difluoro-5-oxo-4-phenylheptanoate **3l**

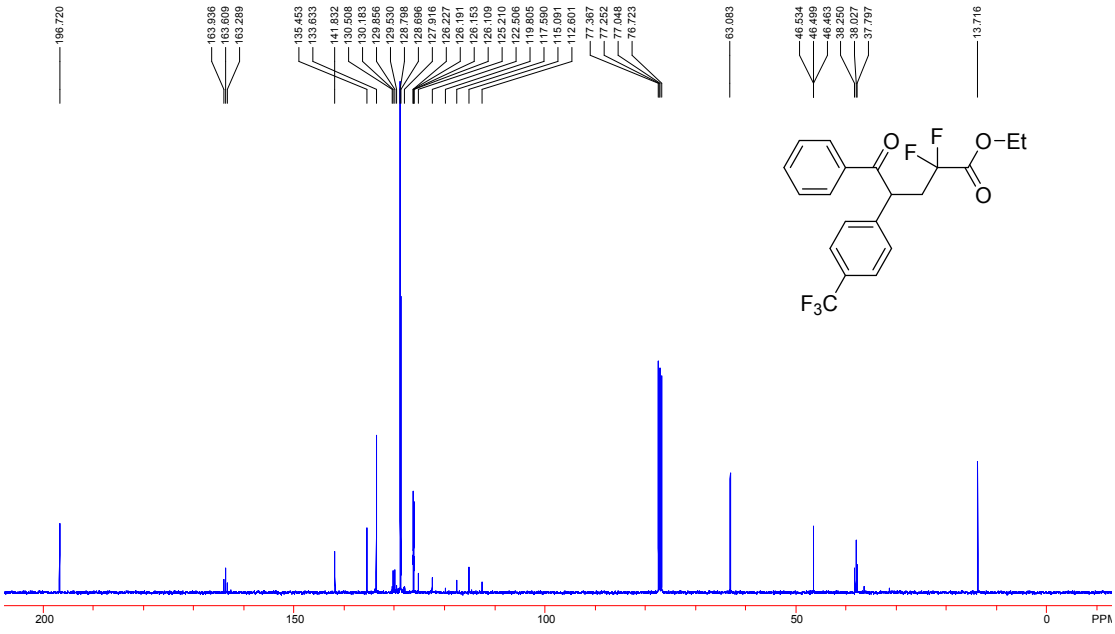


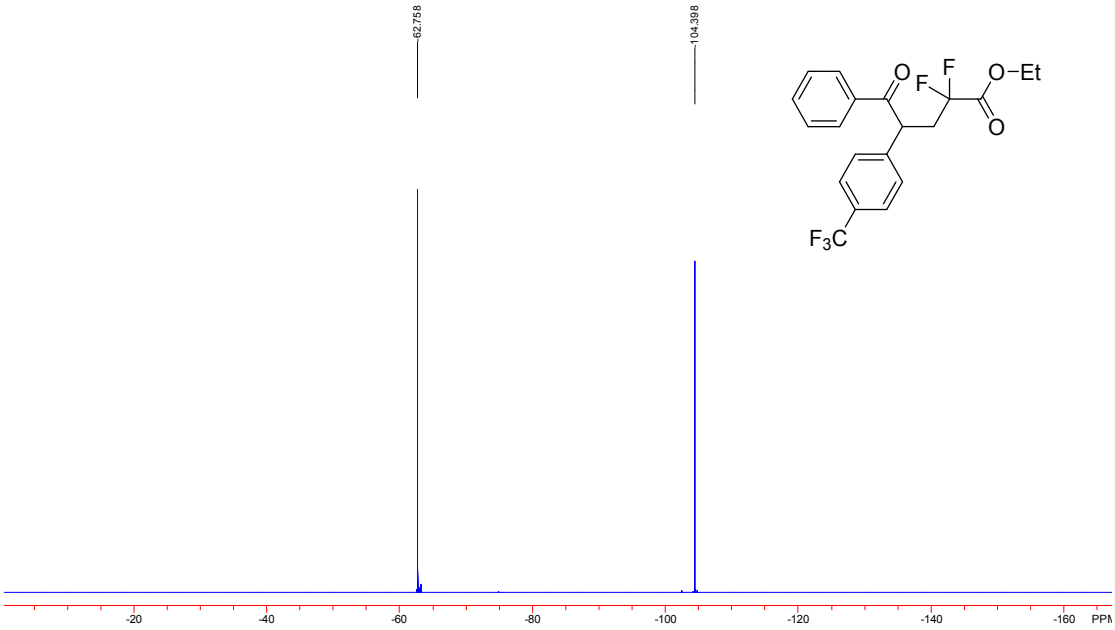

208.287
164.129
163.803
163.479
137.602
129.133
128.260
127.815
126.939
117.788
115.299
112.803
77.352
77.227
77.034
76.714
62.886
51.507
51.473
51.438
37.113
36.881
36.650
34.699
13.808
7.828
O
F
O−Et
Et
O
200
150
100
50
PPM


103.830
104.515
104.932
105.619
O
F
F
O−Et
Et
O
-20
-40
-60
-80
-100
-120
-140
-160
-180
PPM

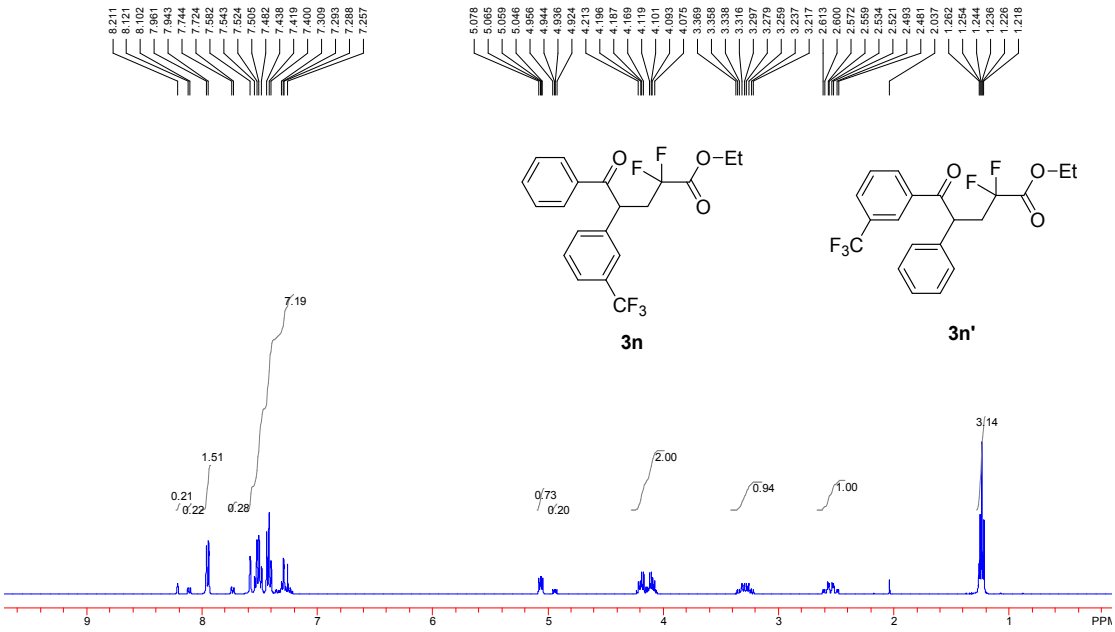
ethyl 2,2-difluoro-5-oxo-5-phenyl-4-(4-(trifluoromethyl)phenyl)pentanoate **3m**

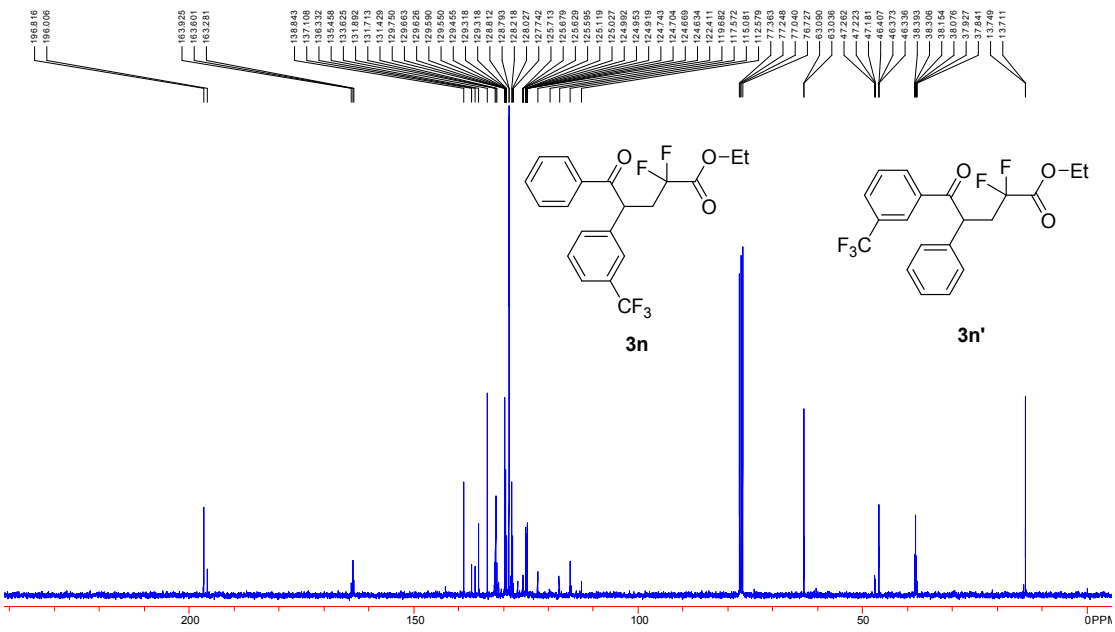


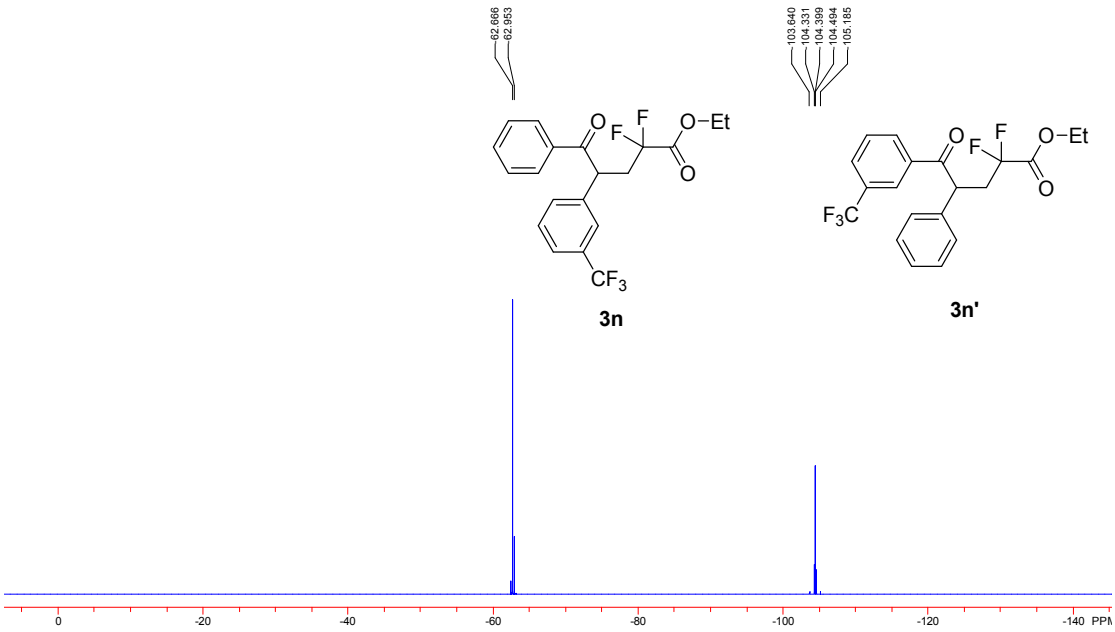




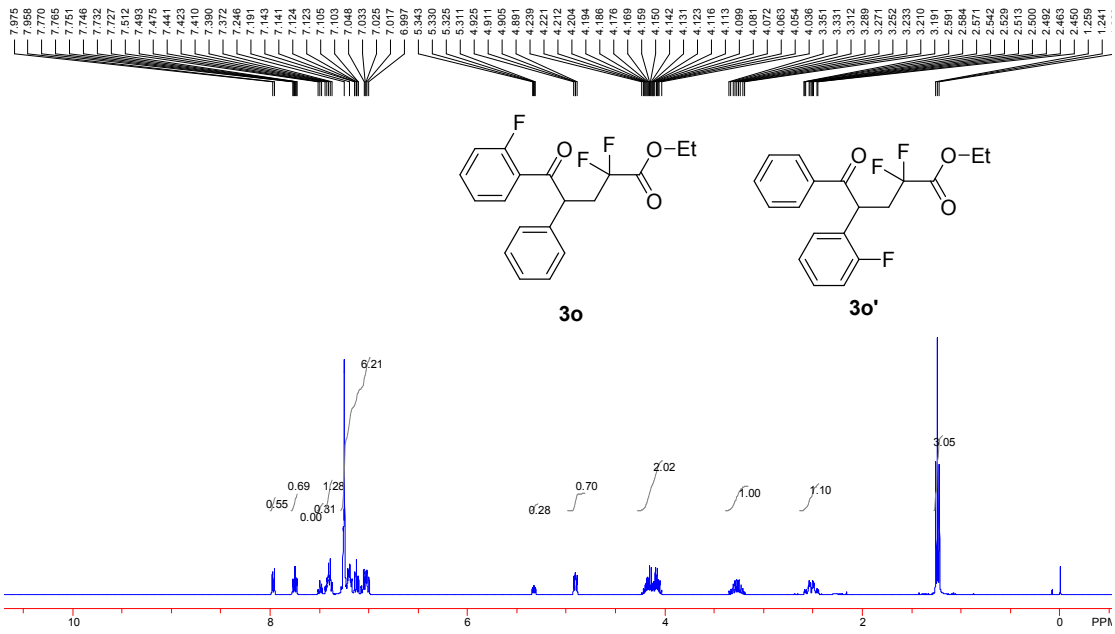
ethyl 2,2-difluoro-5-oxo-5-phenyl-4-(3-(trifluoromethyl)phenyl)pentanoate **3n**
ethyl 2,2-difluoro-5-oxo-4-phenyl-5-(3-(trifluoromethyl)phenyl)pentanoate **3n'**

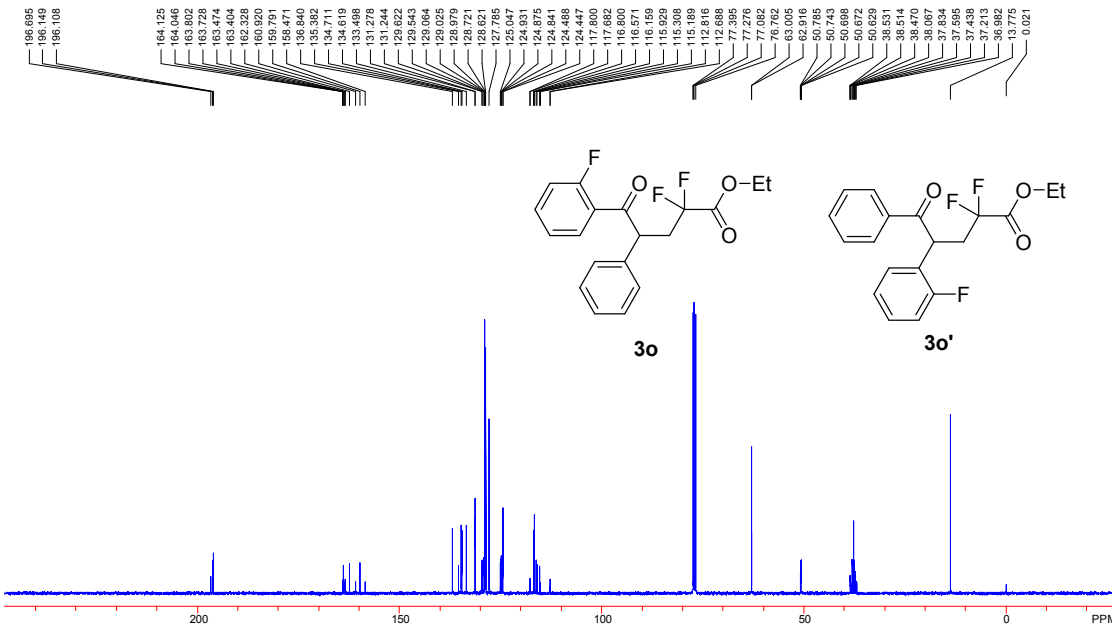


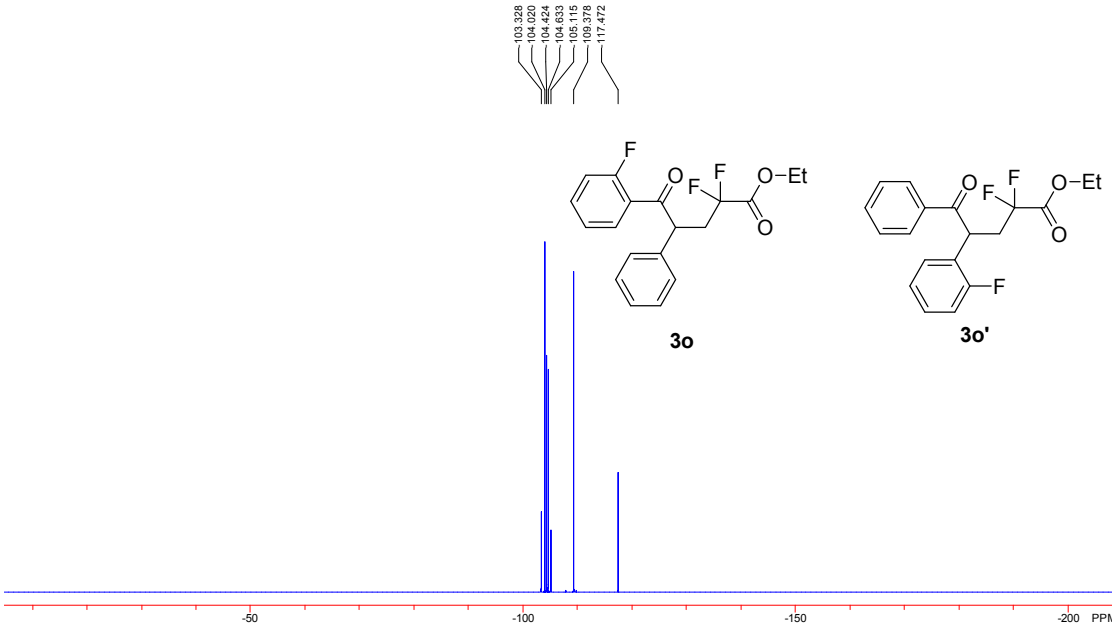

196.816
196.006
163.925
163.601
163.281
138.843
137.108
136.332
135.488
133.625
131.892
131.713
131.439
129.750
129.663
129.626
129.590
129.550
129.495
129.316
129.216
128.812
128.793
128.218
128.027
127.742
125.713
125.679
125.638
125.595
125.119
125.027
124.992
124.919
124.743
124.704
124.669
124.634
122.411
119.682
117.572
115.081
115.079
77.365
77.248
77.040
76.727
63.090
63.036
47.262
47.223
47.161
46.407
46.373
46.336
38.393
38.306
38.154
38.076
37.927
37.841
13.749
13.711
O
F
F
O−Et
O
CF3
3n
F3C
3n'
200
150
100
50
0PPM


62.666
62.953
103.640
104.331
104.399
104.494
105.185
O
F
F
O−Et
O
CF3
3n
F3C
3n'
0
-20
-40
-60
-80
-100
-120
-140 PPM

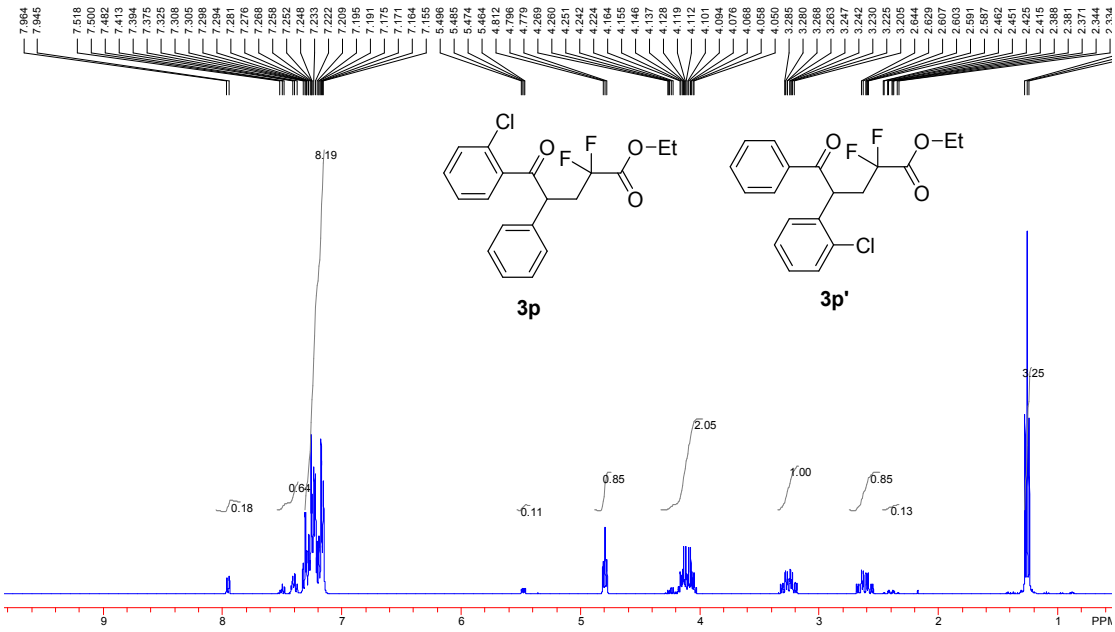
ethyl 2,2-difluoro-5-(2-fluorophenyl)-5-oxo-4-phenylpentanoate **3o**
ethyl 2,2-difluoro-4-(2-fluorophenyl)-5-oxo-5-phenylpentanoate **3o'**

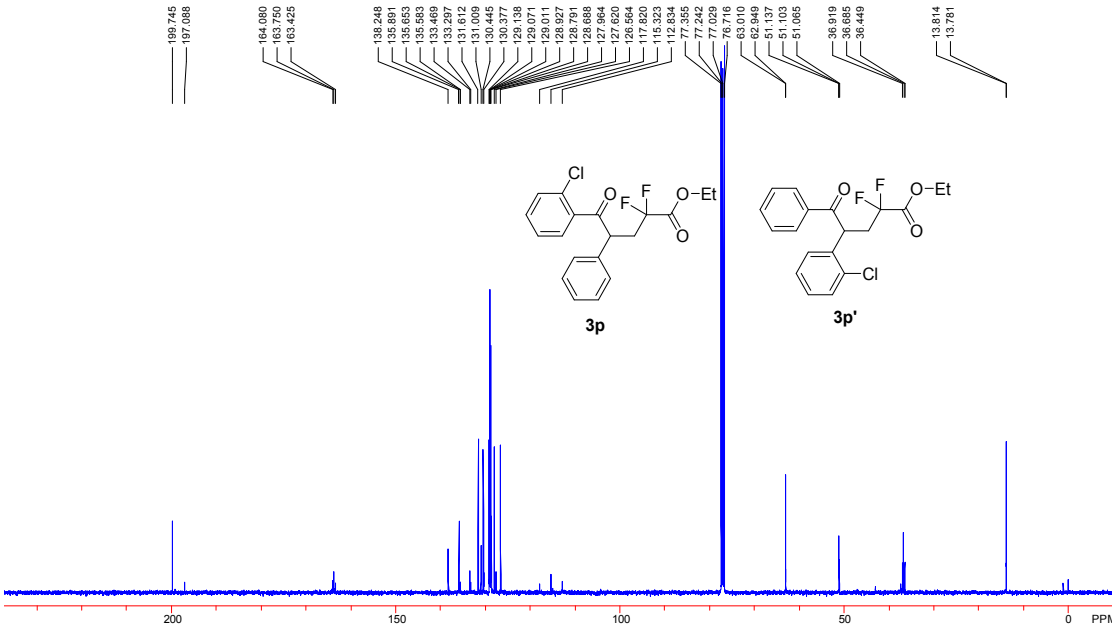


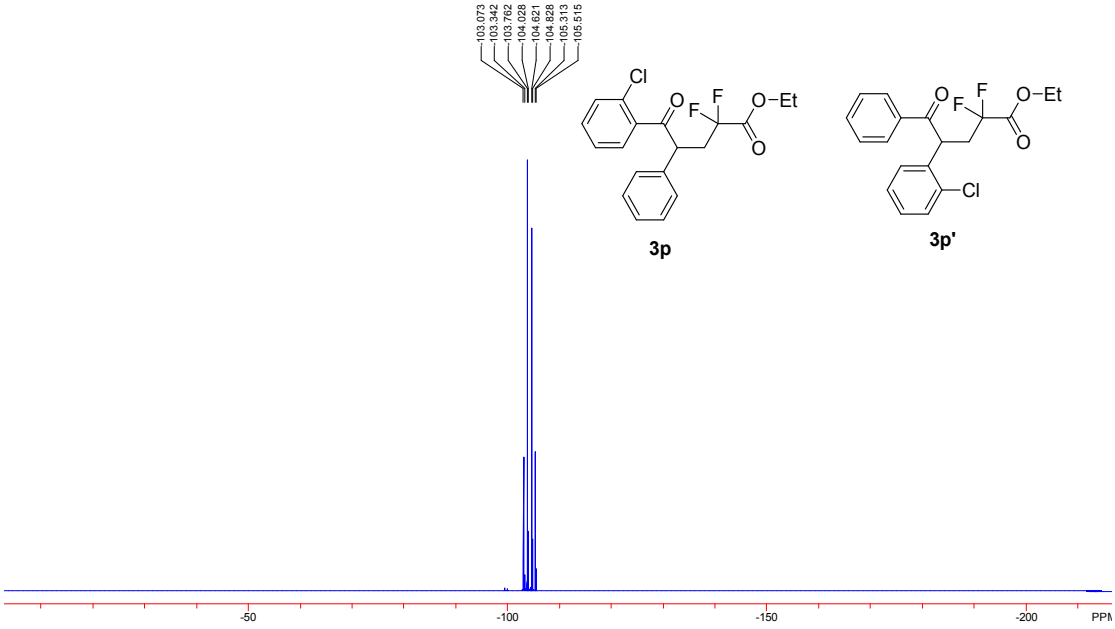




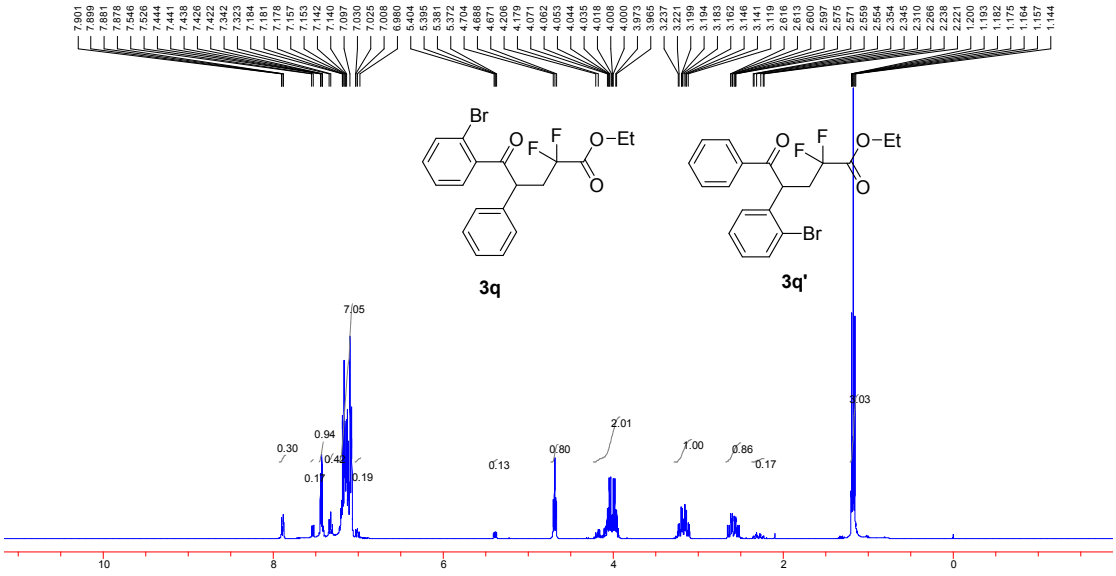
ethyl 5-(2-chlorophenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate **3p**
ethyl 4-(2-chlorophenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate **3p'**

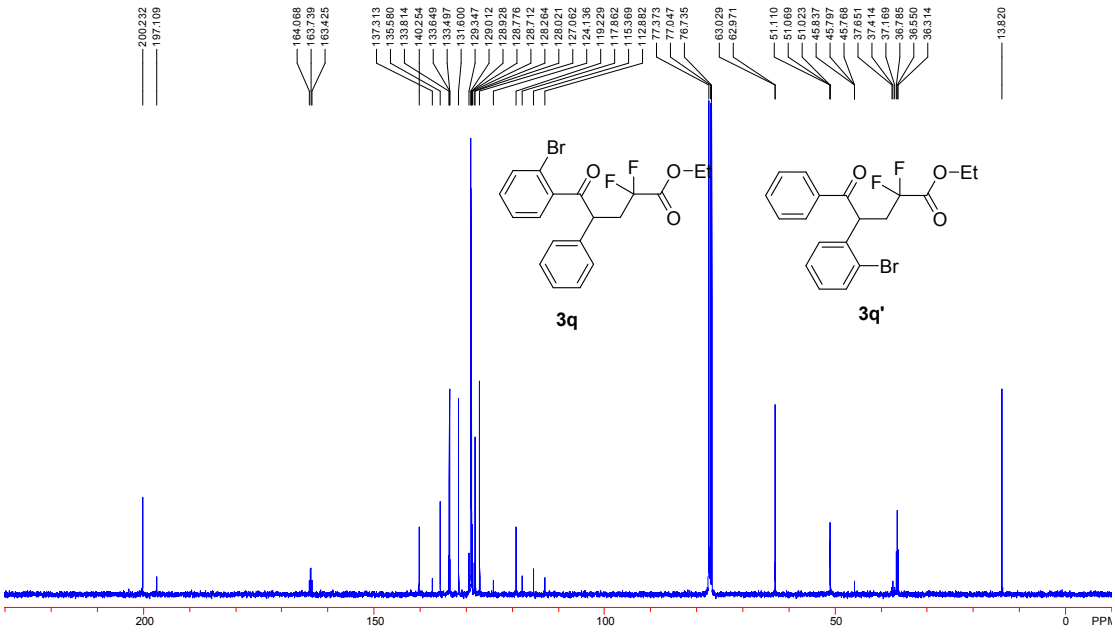


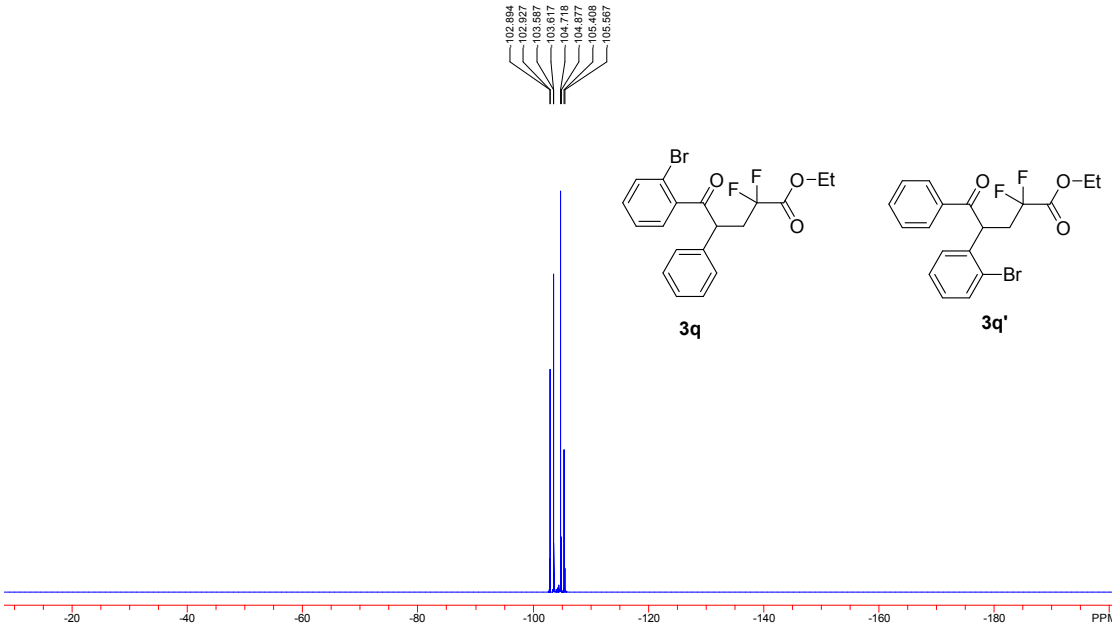

199.745
197.088
164.080
163.750
163.425
138.248
135.891
135.653
135.583
133.469
133.297
131.612
131.009
130.445
130.377
129.138
129.071
129.011
128.927
128.791
128.688
127.964
127.620
126.564
117.820
115.323
112.834
77.355
77.242
77.029
76.716
63.010
62.949
51.137
51.103
51.065
36.919
36.685
36.449
13.814
13.781
Cl
O
F
F
O−Et
O
3p
O
F
F
O−Et
O
Cl
3p'
200
150
100
50
0
PPM


103.073
103.342
103.762
104.028
104.621
104.828
105.313
105.515
Cl
O
F
F
O−Et
O
3p
O
F
F
O−Et
O
Cl
3p'
-50
-100
-150
-200
PPM

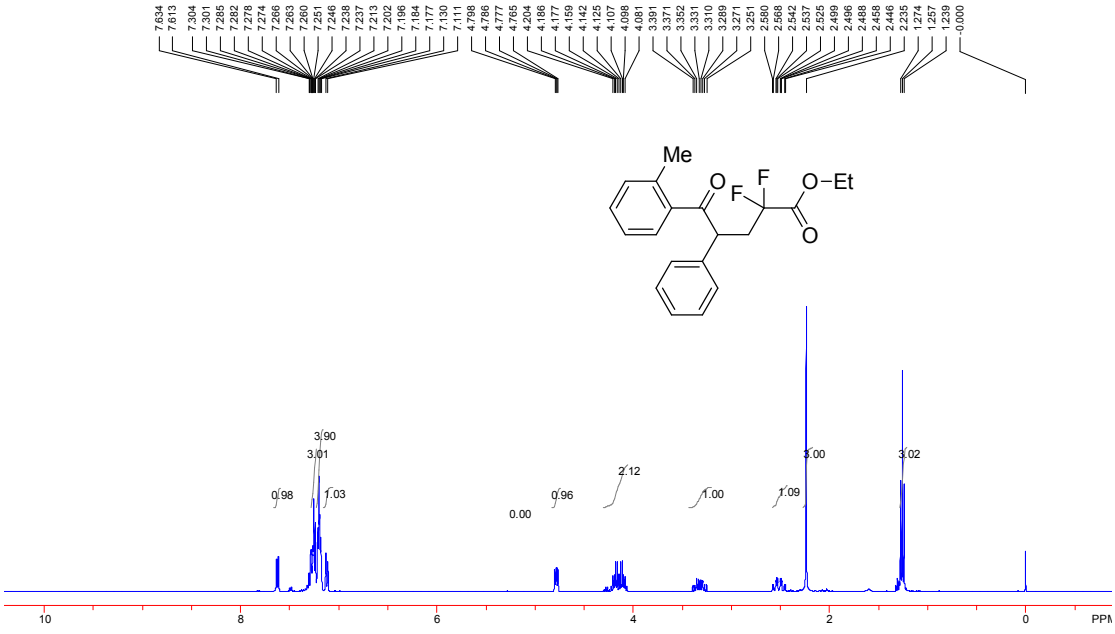
ethyl 5-(2-bromophenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate **3q**
ethyl 4-(2-bromophenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate **3q'**

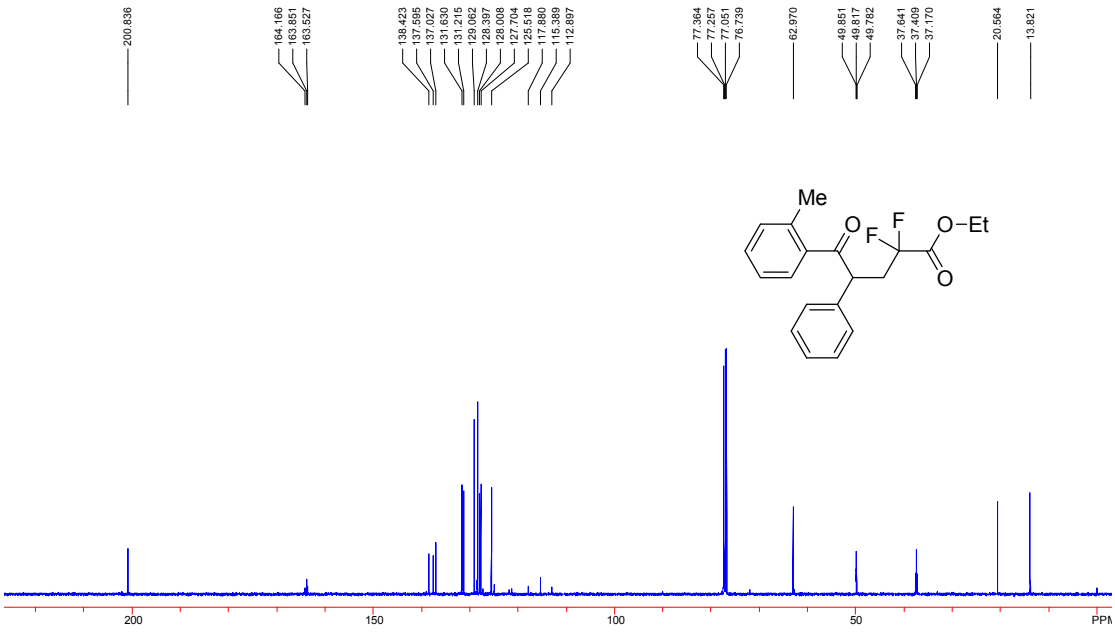


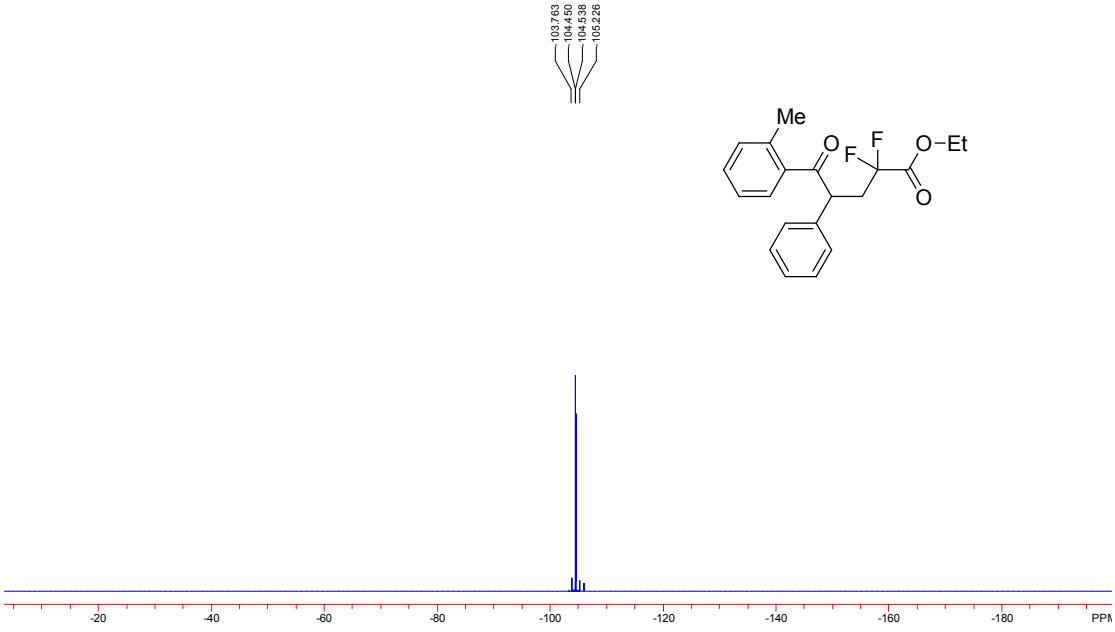




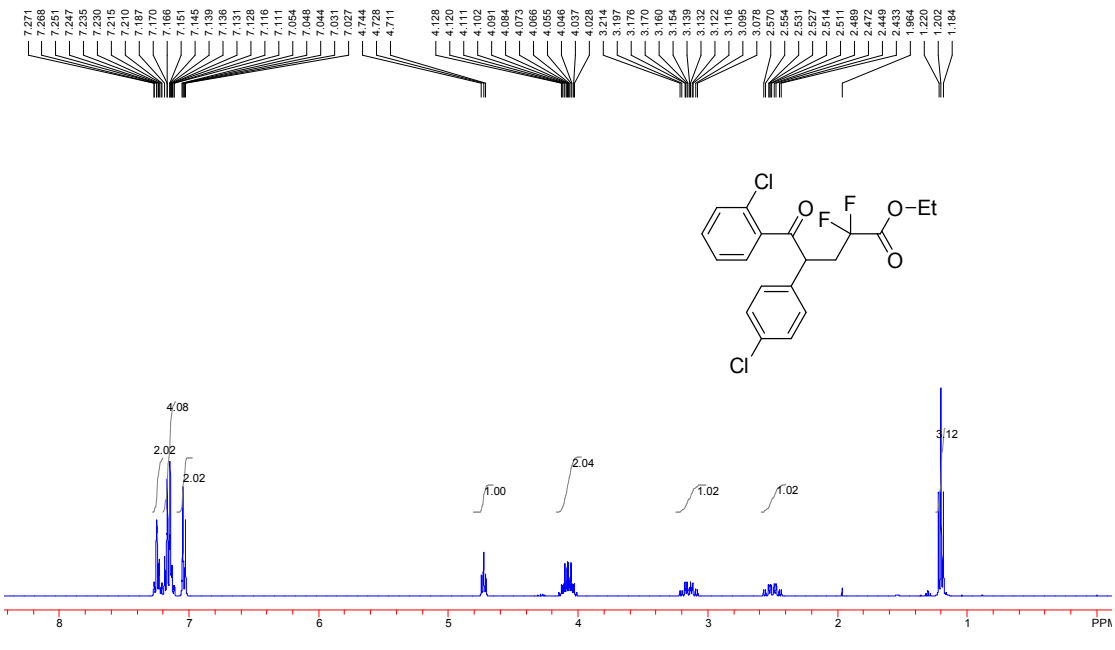
ethyl 2,2-difluoro-5-oxo-4-phenyl-5-(o-tolyl)pentanoate **3r**

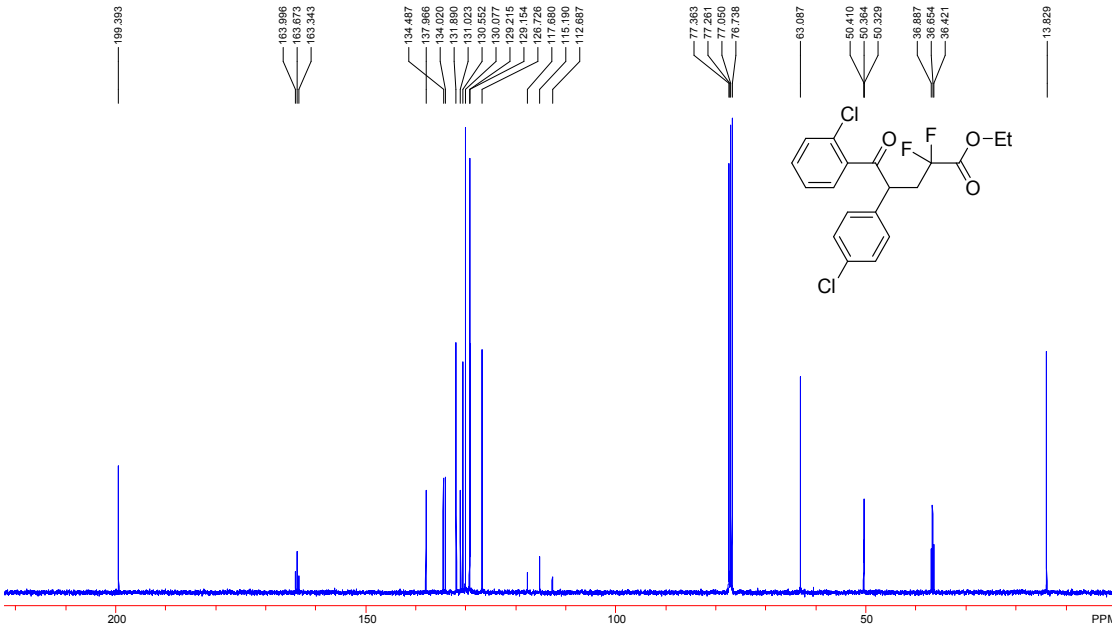


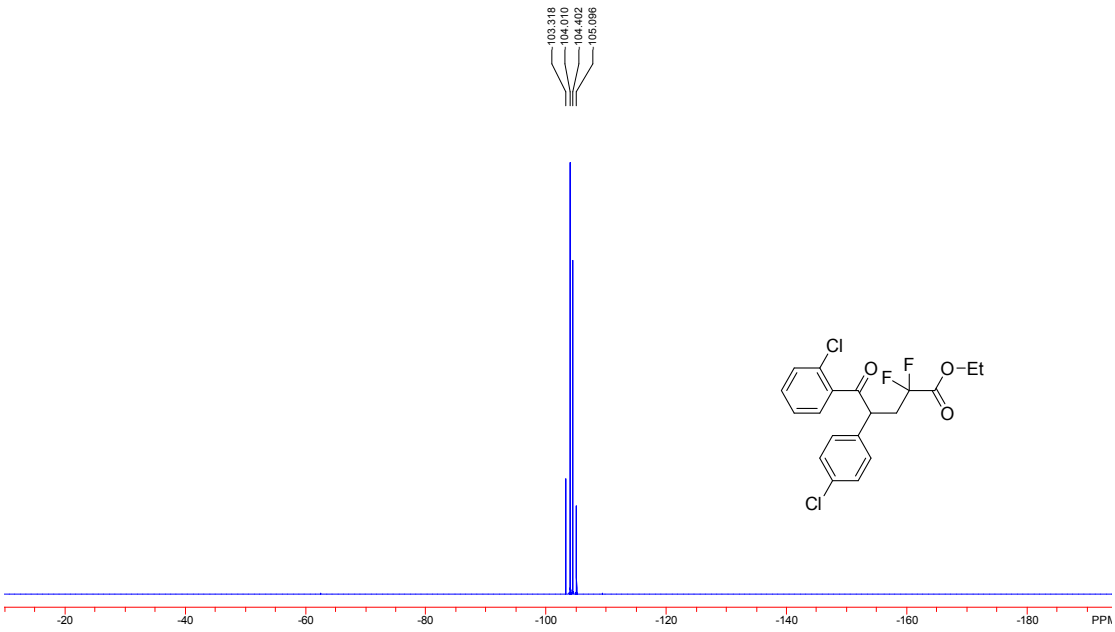

200.836
164.166
163.851
163.527
138.423
137.595
137.027
131.630
131.215
129.062
128.397
128.008
127.704
125.518
117.880
115.389
112.897
77.364
77.257
77.051
76.739
62.970
49.851
49.817
49.782
37.641
37.409
37.170
20.564
13.821
Me
O
F
F
O−Et
O
200
150
100
50
PPM


103.763
104.450
104.538
105.226
Me
O
F
F
O−Et
O
-20
-40
-60
-80
-100
-120
-140
-160
-180
PPM

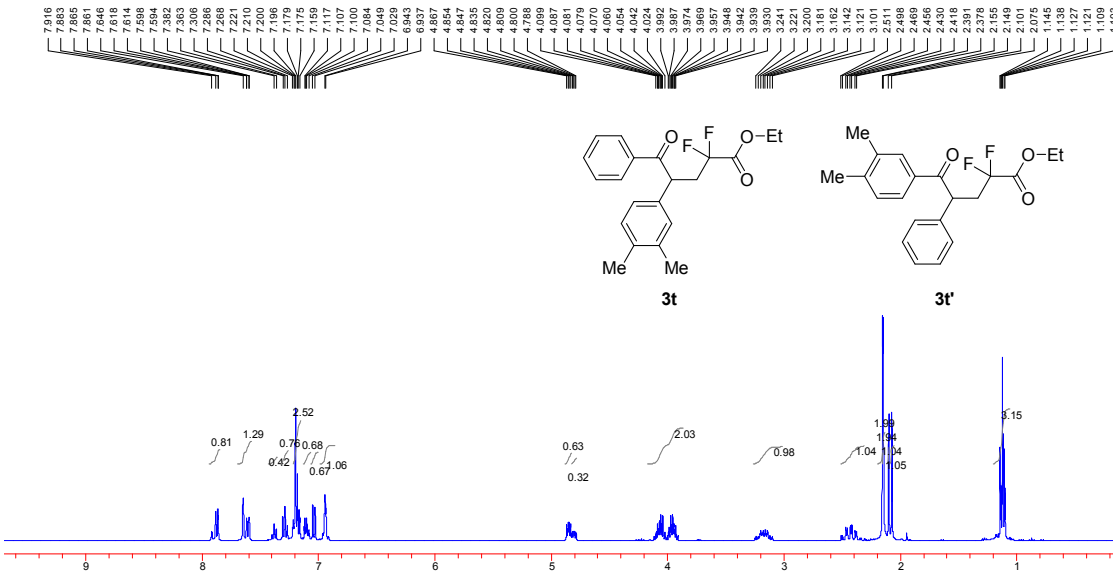
ethyl 5-(2-chlorophenyl)-4-(4-chlorophenyl)-2,2-difluoro-5-oxopentanoate **3s**

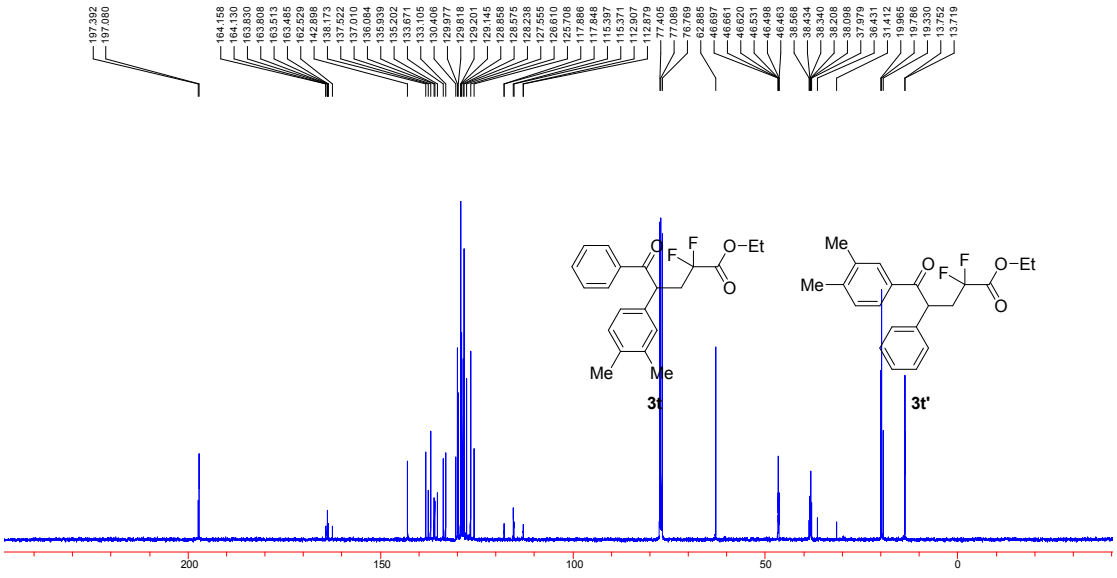


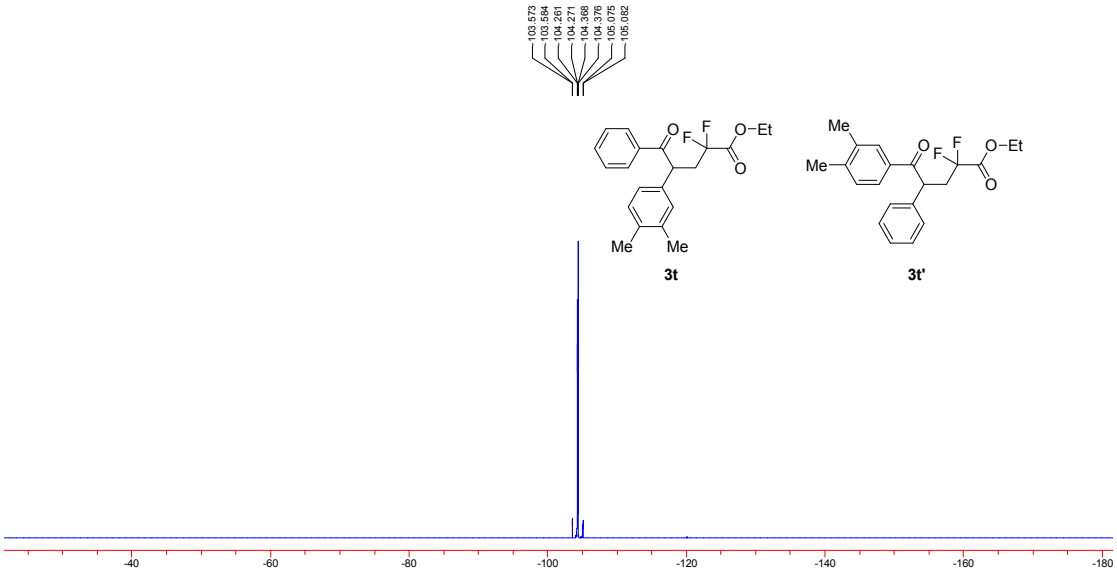




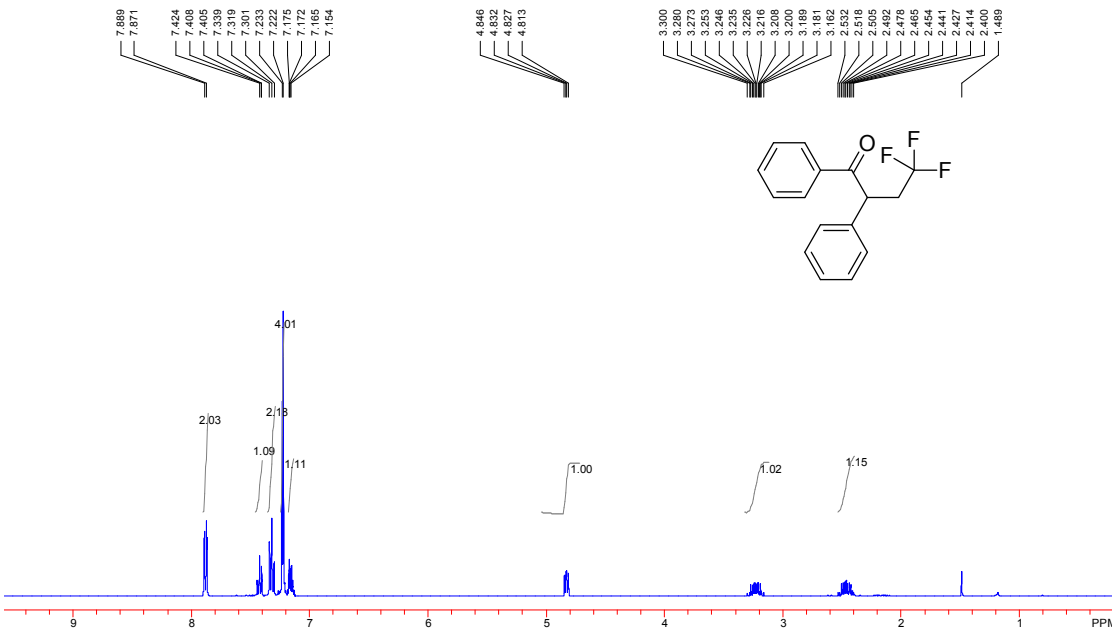
ethyl 4-(3,4-dimethylphenyl)-2,2-difluoro-5-oxo-5-phenylpentanoate **3t**
ethyl 5-(3,4-dimethylphenyl)-2,2-difluoro-5-oxo-4-phenylpentanoate **3t'**

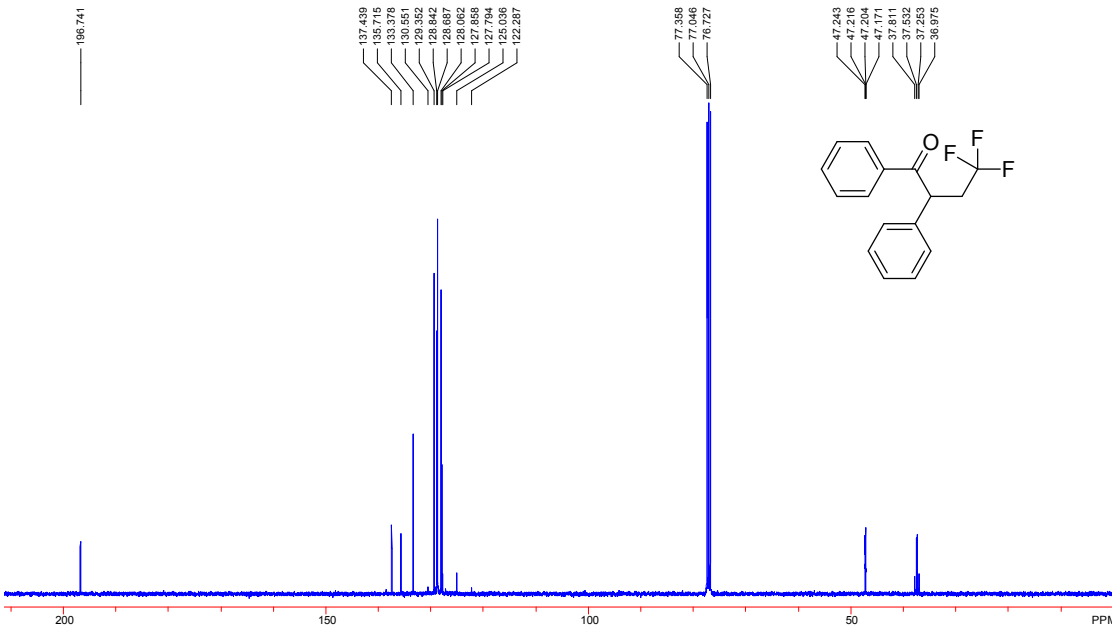


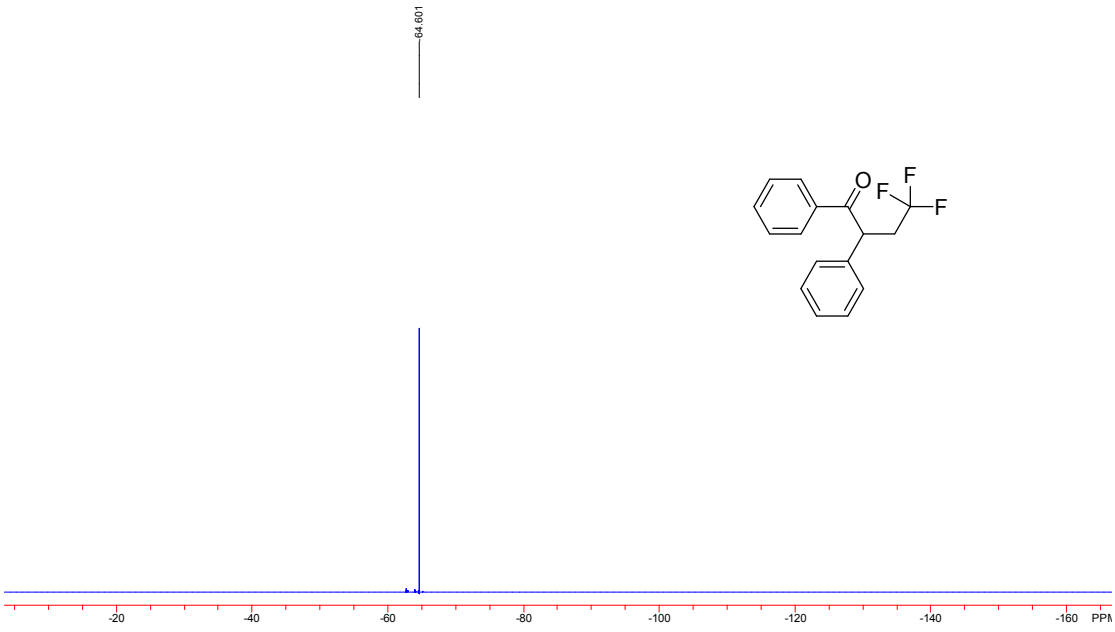

197.392
197.080
164.158
164.130
163.830
163.808
163.513
163.485
162.529
142.898
138.173
137.522
137.010
136.084
135.639
135.272
133.671
133.105
130.406
129.977
129.818
129.201
129.145
128.858
128.575
128.238
127.555
126.610
125.708
117.886
117.848
115.397
115.371
112.907
112.879
77.465
77.048
76.769
62.885
46.697
46.661
46.620
46.531
46.498
46.463
38.568
38.434
38.340
38.208
38.098
37.979
36.431
31.412
19.965
19.786
19.330
13.752
13.719
O
F
F
O−Et
O
Me
Me
3t
Me
Me
O
F
F
O−Et
O
3t'
200
150
100
50
0


103.573
103.584
104.261
104.271
104.368
104.376
105.075
105.082
O
F
F
O−Et
O
Me
Me
3t
Me
Me
O
F
F
O−Et
O
3t'
-40
-60
-80
-100
-120
-140
-160
-180

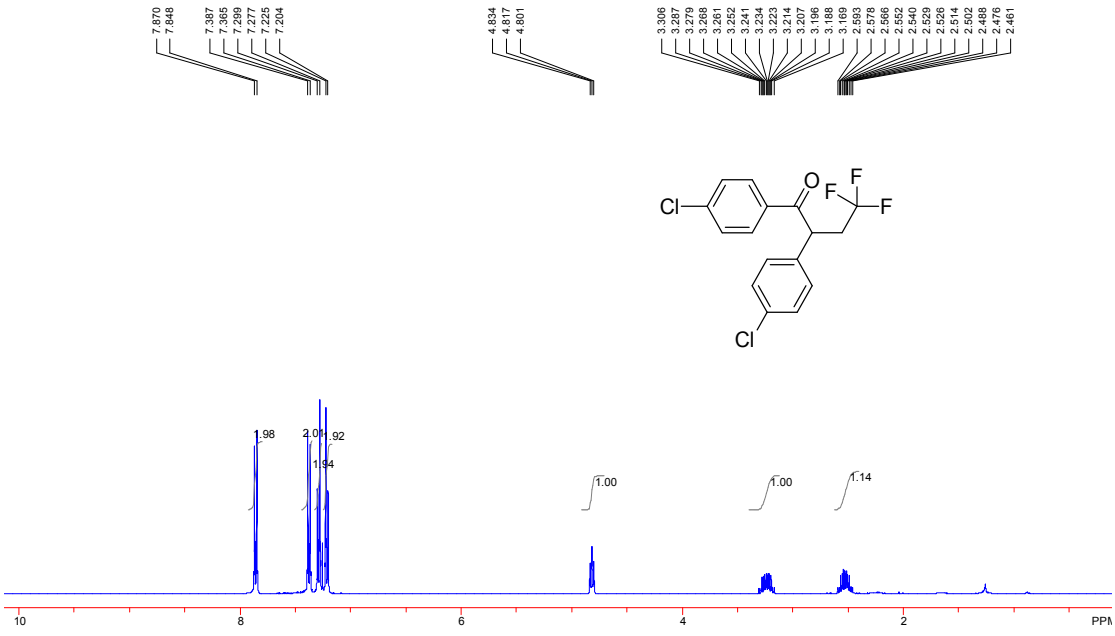
4,4,4-trifluoro-1,2-diphenylbutan-1-one **4a**

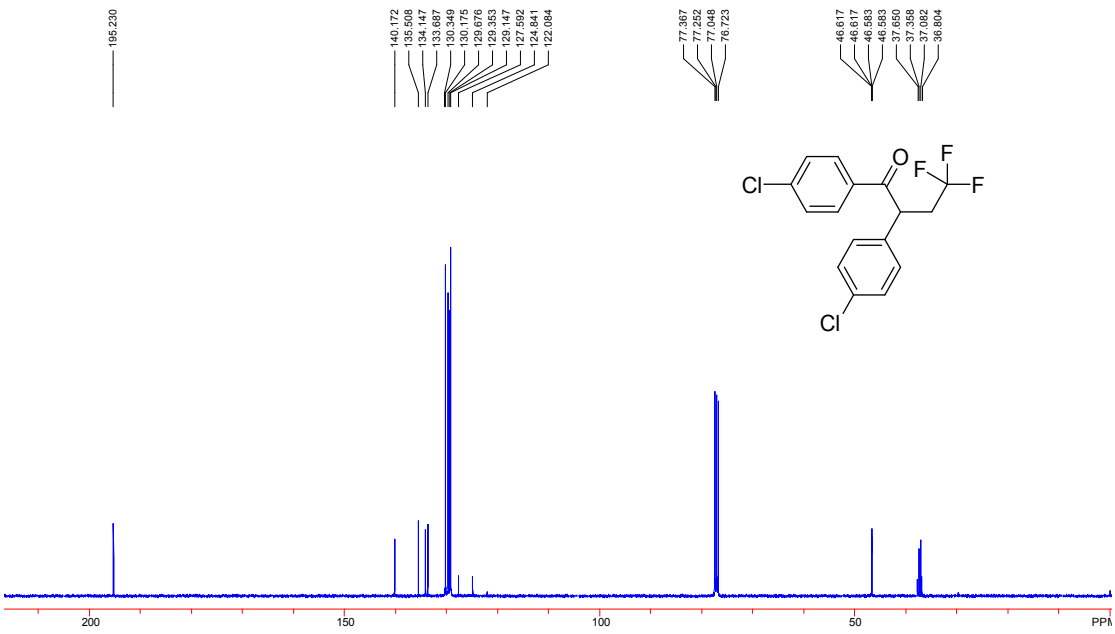


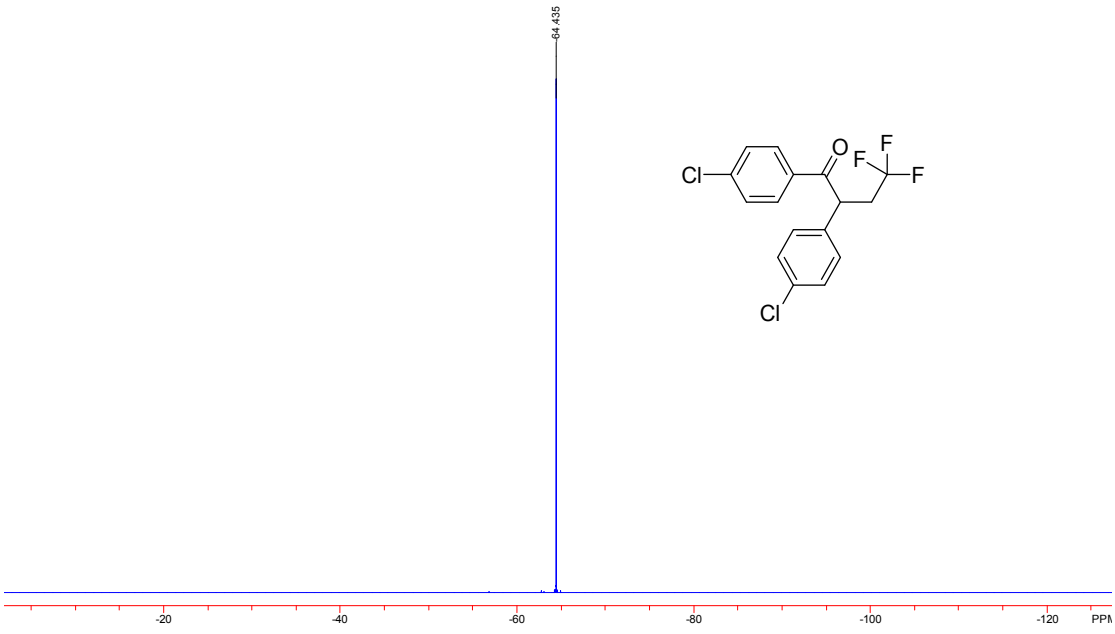




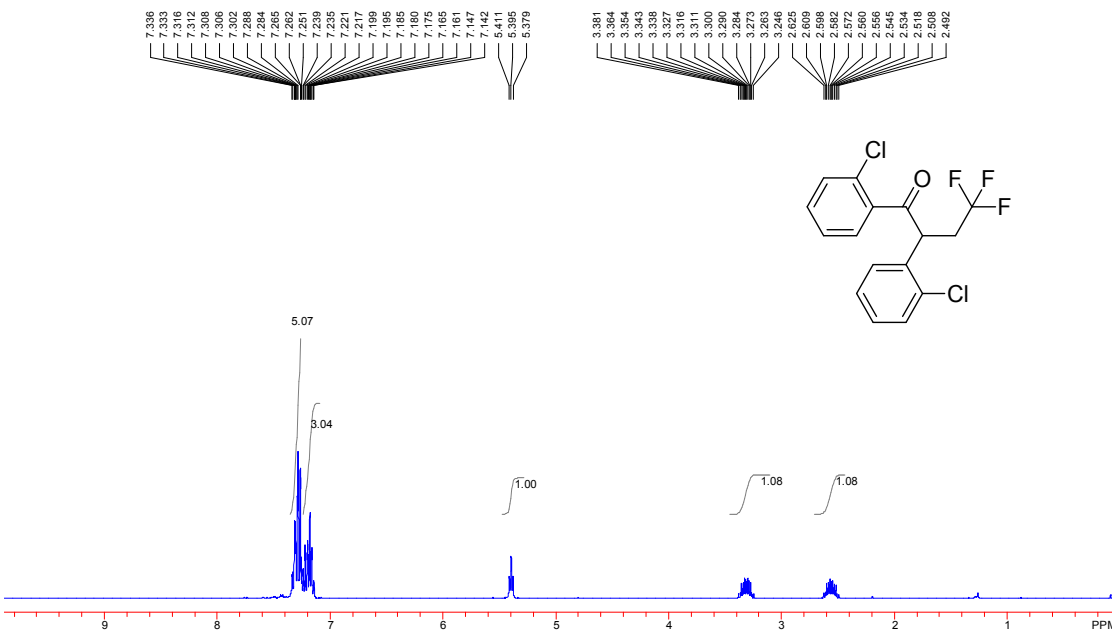
1,2-bis(4-chlorophenyl)-4,4,4-trifluorobutan-1-one **4b**

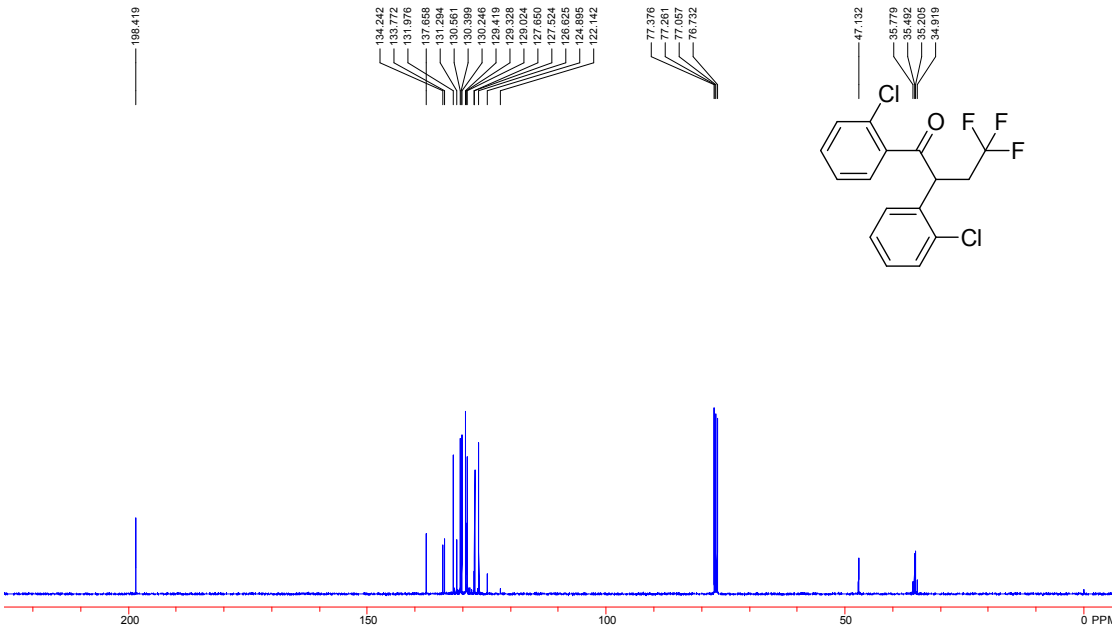


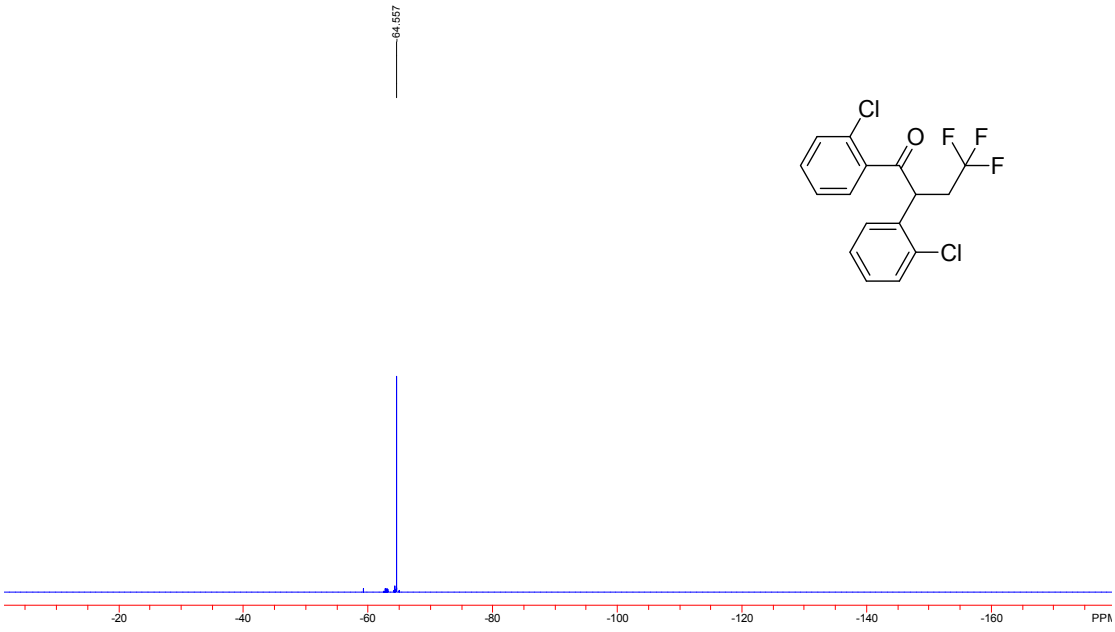

195.230
140.172
135.508
134.147
133.687
130.349
130.175
129.676
129.353
129.147
127.592
124.841
122.084
77.367
77.252
77.048
76.723
46.617
46.617
46.583
46.583
37.650
37.358
37.082
36.804
Cl
O
F
F
F
Cl
200
150
100
50
PPM


-64.435
Cl
O
F
F
F
Cl
-20
-40
-60
-80
-100
-120
PPM

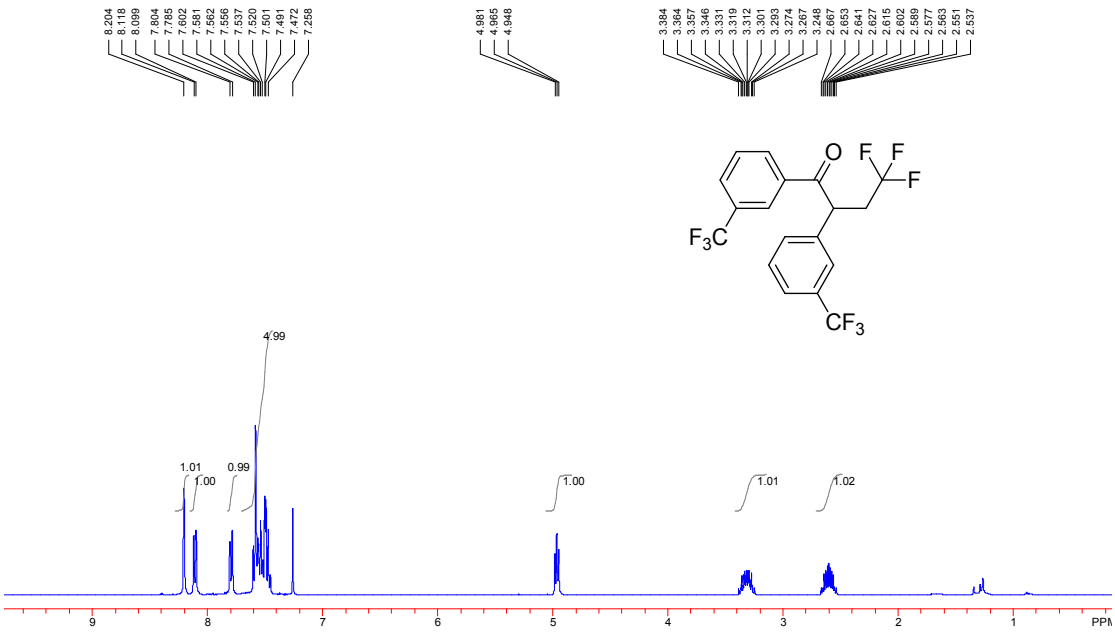
1,2-bis(2-chlorophenyl)-4,4,4-trifluorobutan-1-one **4c**

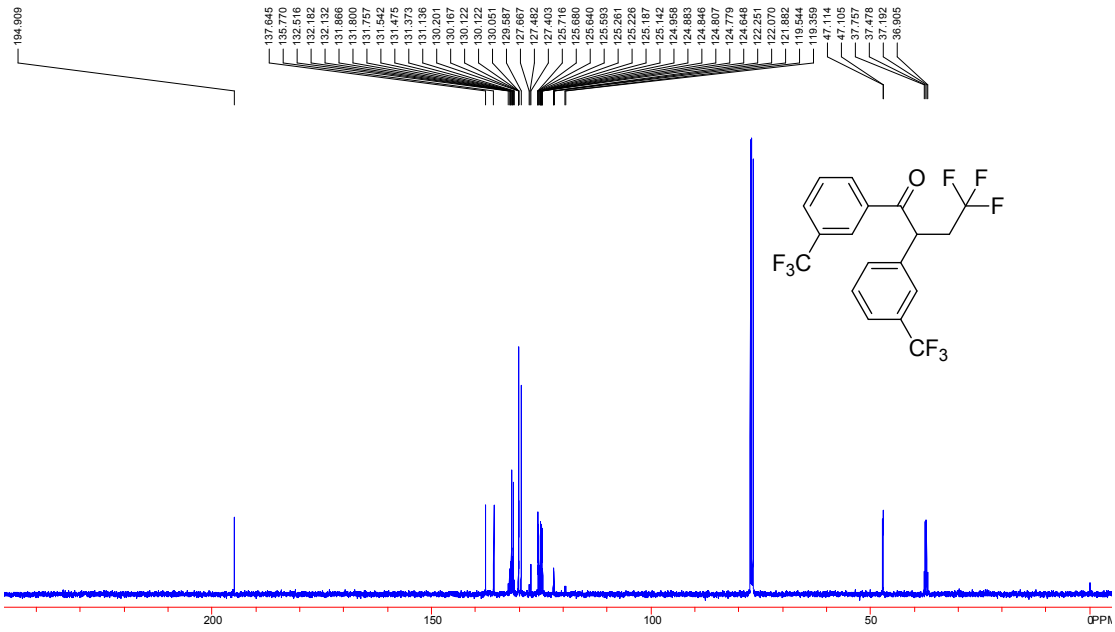






4,4,4-trifluoro-1,2-bis(3-(trifluoromethyl)phenyl)butan-1-one **4d**

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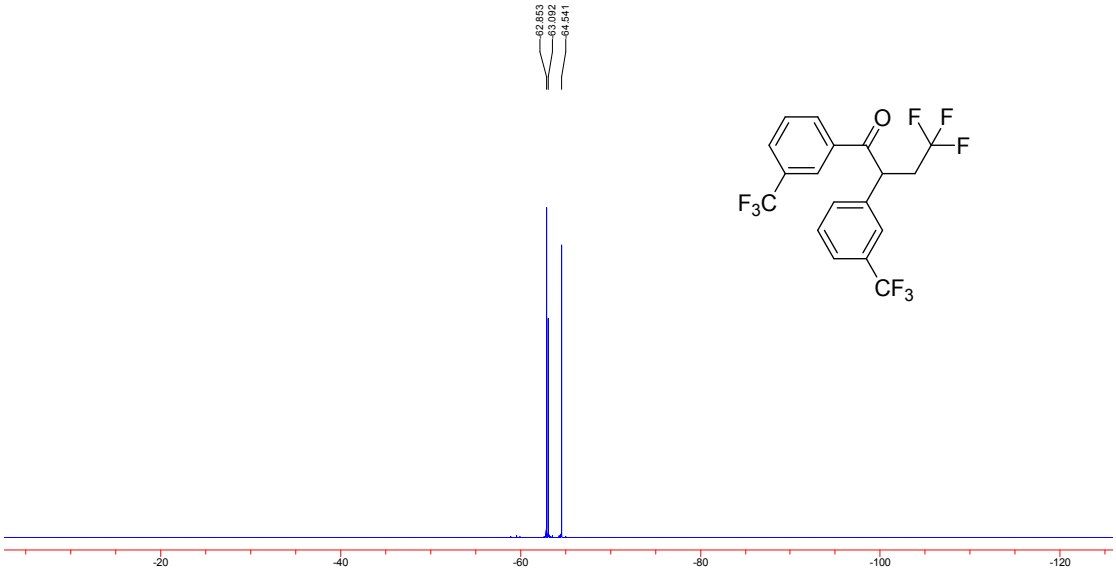
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