Photoredox-catalyzed Cross-coupling of Enamides for the Assembly of β-Difluoroimine Synthons

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Supporting Information

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General Information

Unless otherwise stated, all commercial reagents were used as received. Reactions were conducted in dry glassware using anhydrous solvents (pass through activated alumina columns). Reaction temperatures were controlled using IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt). Thin-layer chromatography (TLC) was conducted on plates (GF254) supplied by Yantai Chemicals (China) and visualized using a combination of UV, anisaldehyde, iodine, and potassium permanganate staining. Silica gel (300-400 mesh) supplied by Tsingdao Haiyang Chemicals (China) was used for flash column chromatography. ^{1}H, ^{13}C NMR spectra were recorded on Bruker spectrometers (400 MHz). Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.00) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra were obtained from the Tsinghua University Mass Spectrometry Facility.

(A) Typical Experimental Procedure

(a) Materials:

(1) Substrates (Enamides) were prepared according to the known procedures.[1]

(2) Synthesis of difluoro amides:

Synthetic procedure: we followed similar procedures as those reported in refenerce.[2]

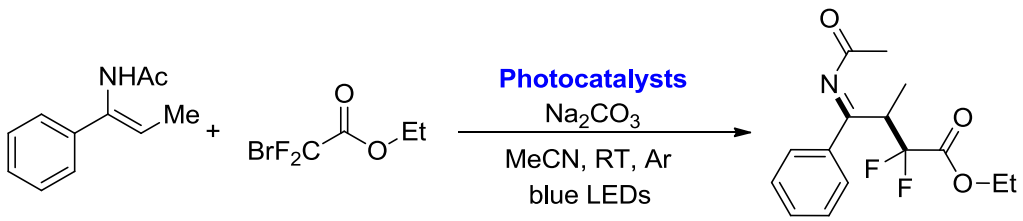
(b) General Experimental Procedures

Typical experimental procedure for visible-light photoredox-catalyzed difluoroalkylation of enamides:

To a Schlenk tube were added enamides **1** (0.20 mmol), **2** (0.3 mmol), *fac*-Ir(ppy)$_3$ (0.02 equiv, 0.004 mmol), KOAc (2.0 equiv, 0.4 mmol), 4Å molecular sieve (80 mg) and Et_2O (1.5 mL). Then the tube was charged with argon, and was stirred at room temperature for the indicated time (12-48 h) until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was filtered through Celite, washed with ethyl acetate. The combined organic mixture was concentrated under reduced pressure and purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product.

(c) Optimization of the reaction conditions.

Table S1. Evaluation of different photocatalysts [a]



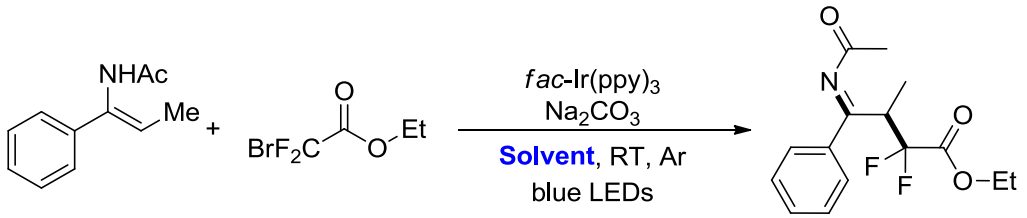
1a **2a** **3a**

entry	Cat. (mol %)	Base (equiv)	Solvent	Yield (%) [b]
1	***fac*-Ir(ppy)$_3$**	**Na_2CO_3**	**MeCN**	**65**
2	Ir(ppy)$_2$(dtbbpy)PF_6	Na_2CO_3	MeCN	34
3	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	Na_2CO_3	MeCN	10
4	Ir[dF(CF_3)ppy]$_2$(bpy)PF_6	Na_2CO_3	MeCN	28

5	$Ru(bpy)_3(PF_6)_2$	Na_2CO_3	MeCN	6
6	EosinY	Na_2CO_3	MeCN	trace

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), Cat. (2 mol %), Base (2.0 equiv), Solvent (1.5 mL), 36 W blue LEDs, at room temperature under argon atmosphere for 12 h. [b] Yield of isolated product. N.R. = No Reaction.

Table S2. Evaluation of different solvents [a]

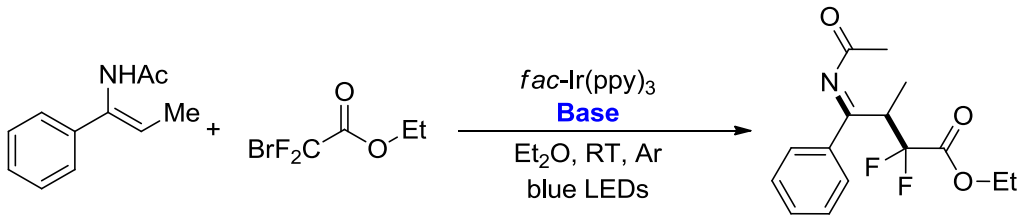


1a **2a** **3a**

entry	Cat. (mol %)	Base (equiv)	**Solvent**	Yield (%) [b]
1	*fac*-Ir(ppy)$_3$	Na_2CO_3	MeCN	65
2	*fac*-Ir(ppy)$_3$	Na_2CO_3	DMF	72
3	*fac*-Ir(ppy)$_3$	Na_2CO_3	DCM	trace
4	*fac*-Ir(ppy)$_3$	Na_2CO_3	1,4-dioxane	18
5	*fac*-Ir(ppy)$_3$	Na_2CO_3	$CHCl_3$	trace
6	*fac*-Ir(ppy)$_3$	Na_2CO_3	THF	46
7	*fac*-Ir(ppy)$_3$	Na_2CO_3	toluene	trace
8	***fac*-Ir(ppy)$_3$**	**Na_2CO_3**	**Et_2O**	**83**
9	*fac*-Ir(ppy)$_3$	Na_2CO_3	*i*Pr_2O	5
10	*fac*-Ir(ppy)$_3$	Na_2CO_3	DME	62
11	*fac*-Ir(ppy)$_3$	Na_2CO_3	MTBE	40
12	*fac*-Ir(ppy)$_3$	Na_2CO_3	anisole	trace

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), Cat. (2 mol %), Base (2.0 equiv), Solvent (1.5 mL), 36 W blue LEDs, at room temperature under argon atmosphere for 12 h. [b] Yield of isolated product.

Table S3. Evaluation of different bases [a]

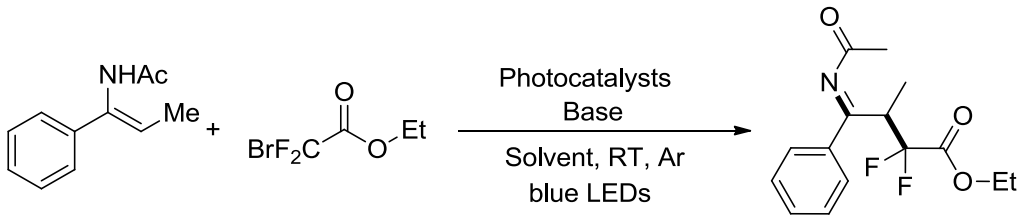


1a **2a** **3a**

entry	Cat. (mol %)	**Base (equiv)**	Solvent	Yield (%) [b]
1	*fac*-Ir(ppy)$_3$	Na_2CO_3	Et_2O	83
2	*fac*-Ir(ppy)$_3$	Na_2HPO_4	Et_2O	20
3	*fac*-Ir(ppy)$_3$	K_2HPO_4	Et_2O	63
4	*fac*-Ir(ppy)$_3$	NaOAc	Et_2O	65
5	***fac*-Ir(ppy)$_3$**	**KOAc**	**Et_2O**	**88 (91) [c]**
6	***fac*-Ir(ppy)$_3$**	**KOAc**	**Et_2O**	**89 [c,d]**
7	*fac*-Ir(ppy)$_3$	CsOAc	Et_2O	79
8	*fac*-Ir(ppy)$_3$	K_2CO_3	Et_2O	66
9	*fac*-Ir(ppy)$_3$	Cs_2CO_3	Et_2O	67
10	*fac*-Ir(ppy)$_3$	$NaHCO_3$	Et_2O	60
11	*fac*-Ir(ppy)$_3$	$KHCO_3$	Et_2O	15
12	*fac*-Ir(ppy)$_3$	$PhCO_2Na$	Et_2O	53
13	*fac*-Ir(ppy)$_3$	HCO_2Na	Et_2O	45
14	*fac*-Ir(ppy)$_3$	NaOMe	Et_2O	50
15	*fac*-Ir(ppy)$_3$	2,6-lutidine	Et_2O	78
16	*fac*-Ir(ppy)$_3$	Et_3N	Et_2O	38
17	*fac*-Ir(ppy)$_3$	DIEA	Et_2O	15
18	*fac*-Ir(ppy)$_3$	DBU	Et_2O	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Cat. (2 mol%), Base (2.0 equiv), Solvent (1.5 mL), 36W blue LEDs, at room temperature under argon atmosphere for 12 h. [b] Yield of isolated product. [c] 80 mg 4ÅMS was added. [d] (*E*)-*N*-(1-phenylprop-1-en-1-yl)acetamide **1a'** as substrate.

Table S4. Control experiments [a]

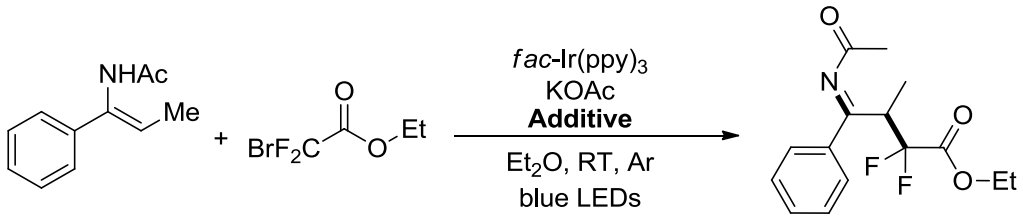


1a **2a** **3a**

entry	Cat. (mol %)	Base (equiv)	Solvent	Yield (%) [b]
1	---	Na_2CO_3	MeCN	N.R.
2	*fac*-Ir(ppy)$_3$	---	MeCN	trace
3 [c]	*fac*-Ir(ppy)$_3$	KOAc	Et_2O	N.R.
4 [d]	*fac*-Ir(ppy)$_3$	KOAc	Et_2O	47
5 [e]	*fac*-Ir(ppy)$_3$	KOAc	Et_2O	76
6 [f]	*fac*-Ir(ppy)$_3$	KOAc	Et_2O	58

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), Cat. (2 mol %), Base (2.0 equiv), Solvent (1.5 mL), 36 W blue LEDs, at room temperature under argon atmosphere for 12 h. [b] Yield of isolated product. [c] no light . [d] 25 W white LEDs. [e] Cat. (1 mol %) was used. [f] under Air. N.R. = No Reaction.

Table S5. Radical inhibition experiments.



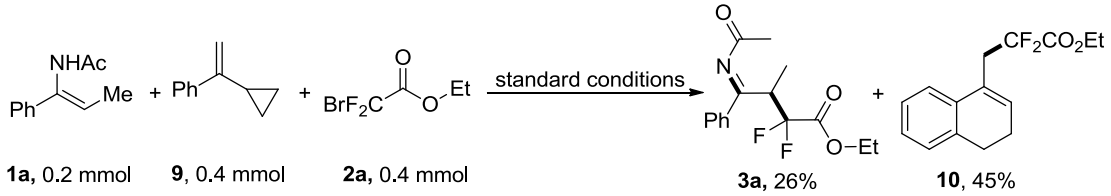
1a **2a** **3a**

Entry	Additive (equiv)	Yield [%] [a]
1	---	91
2	TEMPO (0.2)	65
3	TEMPO (1.0)	10
4	TEMPO (2.0)	trace

[a] reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), *fac*-Ir(ppy)$_3$ (2 mol %), KOAc (2.0 equiv), Et_2O (1.5 mL), 80 mg 4 Å MS, 36W blue LEDs, at room temperature under argon atmosphere for 12 h, Yield of isolated product.

To gain the mechanistic insight into the current reaction, addition of radical inhibitor 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) significantly inhibited this transformation, indicating that a single-electron-transfer radical process is operating.

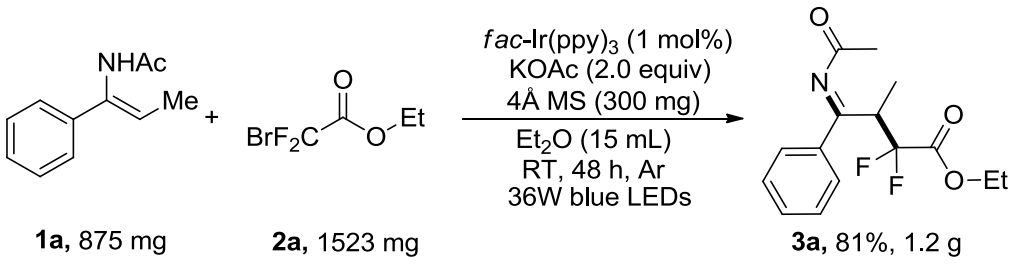
Fig. S1. Radical clock experiment.



To identify whether a fluoroalkyl radical pathway is involved in the reaction, α-cyclopropylstyrene **9** was added in the reaction of **1a** with **2a** under the standard reaction conditions (Fig. S1). A ring-expanded product **10** was obtained in 45% yield, suggesting that a single electron transfer (SET) pathway via a difluoroalkyl radical is involved in the reaction process.

Procedure: To a 25 mL of Schlenck tube were added **1a** (0.2 mmol, 1.0 equiv), (1-cyclopropylvinyl)benzene **9** (0.4 mmol, 2.0 equiv), **2a** (0.2 mmol, 2.0 equiv), *fac*-Ir(ppy)$_3$ (2 mol %), KOAc (0.2 mmol, 2.0 equiv) , 4Å MS (80 mg), 36 W blue LEDs, at room temperature under argon atmosphere for 12 h. Yield of isolated product (**3a**: 26%, based on **1a**; **10** [3]: 45%, based on (1-cyclopropylvinyl)benzene **9**).

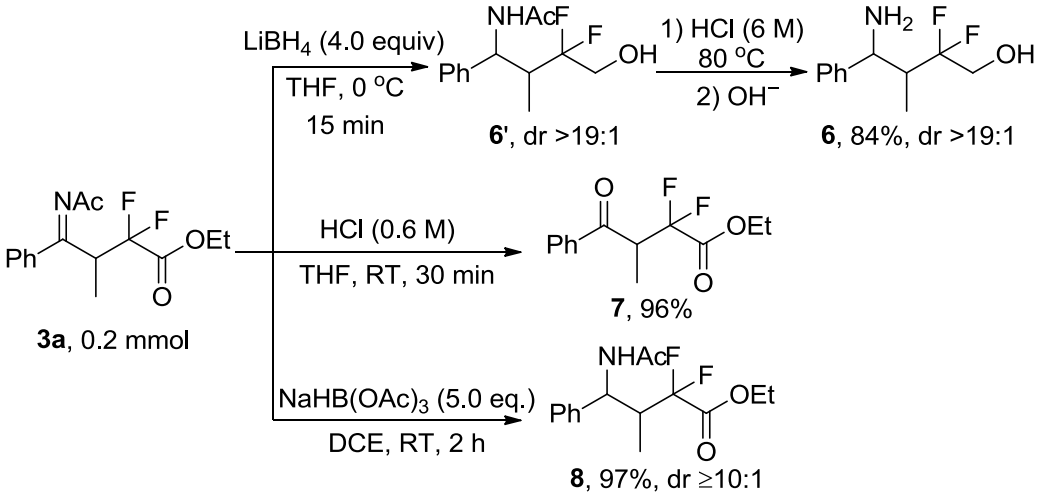
(d) Gram-scale synthesis of 3a



To a Schlenk tube were added enamide **1a** (5.0 mmol), **2a** (7.5 mmol), *fac*-Ir(ppy)$_3$ (0.02 equiv, 0.1 mmol), KOAc (2.0 equiv, 10.0 mmol), 4Å molecular sieve (2.0 g) and Et_2O (37.5 mL). Then the tube was charged with argon, and was stirred at room temperature for the indicated time (48 h) until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the mixture was filtered through Celite, washed with ethyl acetate. The combined organic mixture was concentrated under reduced pressure and purified by silica gel column

chromatography (petroleum ether/ethyl acetate = 20:1) to afford **3a** in 81% yield.

(e) Further transformation of 3a.



Procedure:

1) To a dried flask were added the difluoroalkylated product **3a** (59.4 mg, 0.20 mmol) and anhydrous THF (2 mL), and then $LiBH_4$ (4.0 equiv) was added slowly at 0 °C. When the reaction was finished (about 0.25 hour), ethyl acetate was added to quench the reaction. After filtration, the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 1/1) to afford **6'** (dr >19:1) as colorless oil.

To a sealed tube were added **6'** and 6 M HCl (2.0 mL). Then the tube was stirred at 80 °C overnight. After the reaction was finished, the mixture was carefully basified to pH = 13 with aqueous NaOH (3 M) and extracted with ethyl ether (2 × 5 mL) and DCM (1 × 5 mL). The combined organic extracts were concentrated under reduced pressure and purified by silica gel column chromatography to afford the desired product **6** (36 mg, 84%, dr >19:1) as colorless oil.

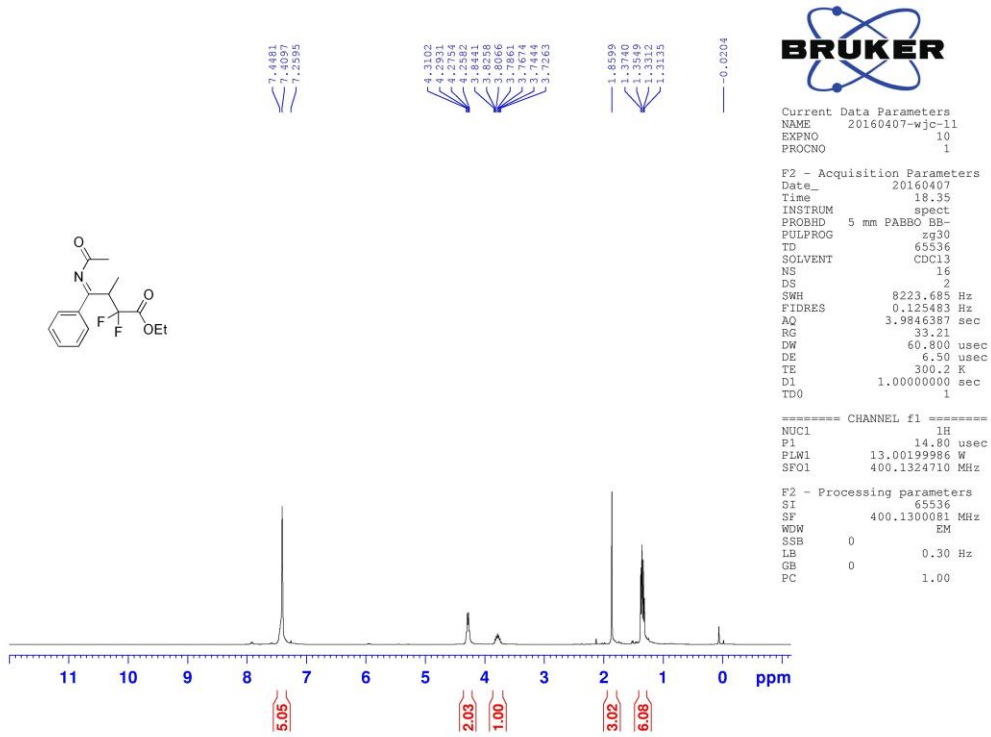
2) **3a** (59.4 mg, 0.20 mmol) was added to a 1/1 mixture of 0.6 M HCl/THF. The resulting solution was stirred at room temperature and monitored by TLC. The reaction mixture was extracted with DCM and washed with aq. $NaHCO_3$. Then organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (silica gel, petroleum ether /ethyl acetate = 20/1) to afford **7** (49 mg, 96%) as colorless oil.

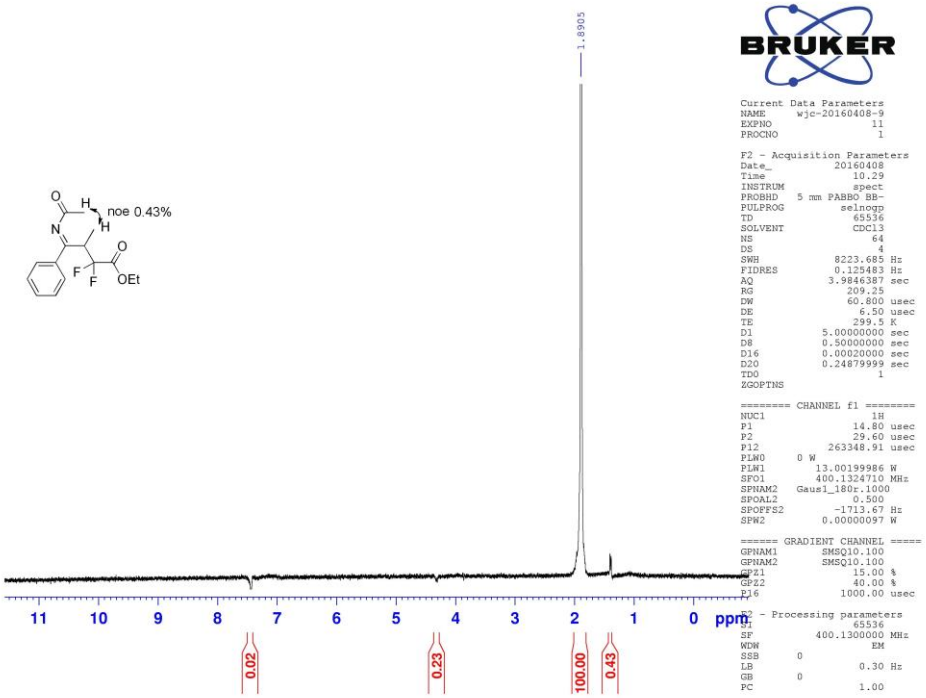
3) To a dried flask were added the difluoroalkylated product **3a** (59.4 mg, 0.20 mmol) and anhydrous DCE (2 mL), and then $NaHB(OAc)_3$ (5.0 equiv) was added. The reaction was finished after 1 hour. After filtration, the filtrate was concentrated in vacuo. The residue was purified by flash

chromatography (silica gel, petroleum ether/ethyl acetate 1/1) to afford **8** (dr ≥10:1, 58 mg, 97%) as colorless oil.

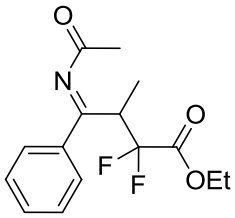
(f) Determination of the geometry of the CN double bond

NOESY experiment

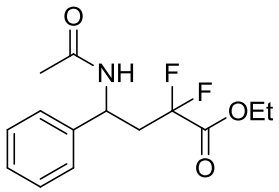




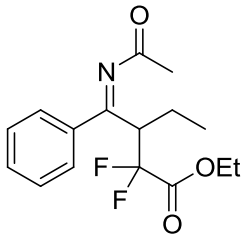
(B) Analytical data



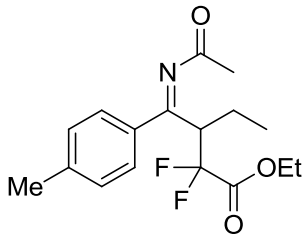
(*E*)-Ethyl 4-(acetylimino)-2,2-difluoro-3-methyl-4-phenylbutanoate (3a): 12 h, 54 mg, 91% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.41 (m, 5H), 4.28 (dd, J = 14.0, 6.9 Hz, 2H), 3.79 (dt, J = 16.6, 8.4 Hz, 1H), 1.86 (s, 3H), 1.37-1.31 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.5, 165.2 (d, J = 6.3 Hz, 1C), 163.4 (t, J = 31.8 Hz, 1C), 135.8, 130.8, 128.8, 127.1, 115.2 (dd, J = 260.0, 248.8 Hz, 1C), 62.9, 46.3 (t, J = 23.3 Hz, 1C), 24.7, 13.8, 11.5 (d, J = 4.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.3 (dd, *J* = 267.0, 11.3 Hz, 1F), -112.7 (dd, *J* = 265.1, 16.9 Hz, 1F); HRMS (ESI) for $C_{15}H_{18}F_2NO_3$ ($[M+H]^+$): calcd 298.1249, found 298.1255.



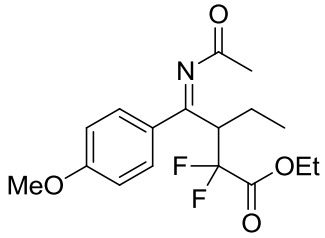
Ethyl 4-acetamido-2,2-difluoro-4-phenylbutanoate (3b): 24 h, then $NaHB(OAc)_3$ (5.0 equiv) in DCE for 2 h, 46 mg, 80% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.28 (m, 5H), 6.59 (d, J = 3.9 Hz, 1H), 5.33-5.27 (m, 1H), 4.18-4.13 (m, 2H), 2.75-2.50 (m, 2H), 1.92 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.3, 163.6 (t, J = 32 Hz, 1C), 140.6, 128.7, 127.8, 126.4, 114.9 (t, J = 250.1 Hz, 1C), 63.0, 48.0 (t, J = 4.7 Hz, 1C), 40.2 (t, J = 22.7 Hz, 1C), 23.0, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -102.3 - -104.3 (m, 2F); HRMS (ESI) for $C_{14}H_{18}F_2NO_3$ ($[M+H]^+$): calcd 286.1249, found 286.1255.



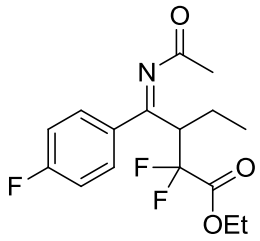
(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluoropentanoate (3c): 16 h, 49.8 mg, 80% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.39 (m, 5H), 4.33-4.20 (m, 2H), 3.64-3.54 (m, 1H), 2.01-1.87 (m, 5H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.7, 164.3, 163.4 (t, *J* = 32.1 Hz, 1C), 137.2, 130.9, 128.8, 127.2, 115.6 (dd, *J* = 258.7, 251.9 Hz, 1C), 63.0, 53.1 (t, *J* = 22.3 Hz, 1C), 24.6, 21.1 (t, *J* = 3.4 Hz, 1C), 13.8, 12.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.24 (dd, *J* = 263.3, 12.4 Hz, 1F), -108.37 (dd, *J* = 263.4, 13.7 Hz, 1F); HRMS (ESI) for $C_{16}H_{20}F_2NO_3$ ($[M+H]^+$): calcd 312.1406, found 312.1410.



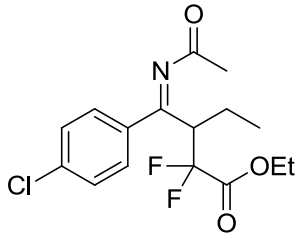
(*E*)-Ethyl 3-((acetylimino)(p-tolyl)methyl)-2,2-difluoropentanoate (3d): 16 h, 59.8 mg, 92% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.32-4.20 (m, 2H), 3.63-3.53 (m, 1H), 2.36 (s, 3H), 2.00-1.87 (m, 5H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.7, 164.1 (dd, *J* = 5.4, 3.0 Hz, 1C), 163.3 (t, *J* = 32.1 Hz, 1C), 141.6, 134.4, 129.5, 127.3, 115.6 (dd, *J* = 258.7, 251.5 Hz, 1C), 62.9, 52.9 (t, *J* = 22.2 Hz, 1C), 24.6, 21.3, 21.2 (t, *J* = 3.4, 1C), 13.8, 11.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.1 (dd, *J* = 263.0, 12.4 Hz, 1F), -108.5 (dd, *J* = 263.0, 13.8 Hz, 1F); HRMS (ESI) for $C_{17}H_{22}F_2NO_3$ ($[M+H]^+$): calcd 326.1562, found 326.1566.



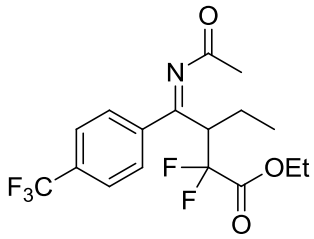
(*E*)-Ethyl 3-((acetylimino)(4-methoxyphenyl)methyl)-2,2-difluoropentanoate (3e): 16 h, 58.7 mg, 86% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.32-4.19 (m, 2H), 3.81 (s, 3H), 3.63-3.53 (m, 1H), 2.00-1.88 (m, 5H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.7, 163.4 (t, *J* = 32.1 Hz, 1C), 161.7, 129.6, 129.3, 115.6 (dd, *J* = 258.6, 251.7 Hz, 1C), 114.2, 62.9, 55.3, 52.7 (t, *J* = 22.4 Hz, 1C), 24.5, 21.4 (t, *J* = 3.4 Hz, 1C), 13.8, 11.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.1 (dd, *J* = 262.6, 12.4 Hz, 1F), -108.3 (dd, *J* = 262.6, 13.6 Hz, 1F); HRMS (ESI) for $C_{17}H_{22}F_2NO_4$ ($[M+H]^+$): calcd 342.1511, found 342.1515.



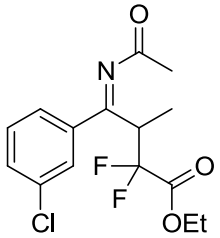
(*E*)-Ethyl 3-((acetylimino)(4-fluorophenyl)methyl)-2,2-difluoropentanoate (3f): 12 h, 61.2 mg, 93% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.09 (t, *J* = 8.5 Hz, 2H), 4.34-4.22 (m, 2H), 3.58-3.48 (m, 1H), 1.97-1.88 (m, 5H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.4, 165.2, 163.1 (dd, *J* = 63.1, 30.8 Hz, 1C), 133.4 (d, *J* = 3.4 Hz, 1C), 129.6 (d, *J* = 8.7 Hz, 1C), 116.1, 115.9, 115.5 (dd, *J* = 258.7, 252.4 Hz, 1C), 63.0, 53.2 (t, *J* = 22.3 Hz, 1C), 24.6, 21.1 (t, *J* = 3.3 Hz, 1C), 13.8, 11.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.44 (dd, *J* = 263.8, 12.7 Hz, 1F), -107.86 (dd, *J* = 263.8, 13.2 Hz, 1F), -107.91; HRMS (ESI) for $C_{16}H_{19}F_3NO_3$ ($[M+H]^+$): calcd 330.1312, found 330.1310.



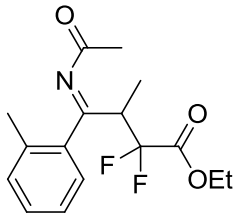
(*E*)-Ethyl 3-((acetylimino)(4-chlorophenyl)methyl)-2,2-difluoropentanoate (3g): 12 h, 59.4 mg, 86% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43-7.37 (m, 4H), 4.35-4.23 (m, 2H), 3.57-3.47 (m, 1H), 1.99-1.86 (m, 5H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.4, 163.3 (t, *J* = 32.0 Hz, 1C), 163.0 (dd, *J* = 4.9, 3.2 Hz, 1C), 137.2, 135.5, 129.1, 128.6, 115.5 (dd, *J* = 258.9, 252.5 Hz, 1C), 63.1, 53.2 (t, *J* = 22.3 Hz, 1C), 24.6, 21.1 (t, *J* = 3.4 Hz, 1C), 13.8, 11.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.5 (dd, *J* = 264.0, 12.8 Hz, 1F), -107.8 (dd, *J* = 264.0, 13.2 Hz, 1F); HRMS (ESI) for $C_{16}H_{19}ClF_2NO_3$ ($[M+H]^+$): calcd 346.1016, found 346.1018.



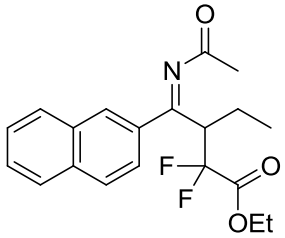
(*E*)-Ethyl 3-((acetylimino)(4-(trifluoromethyl)phenyl)methyl)-2,2-difluoropentanoate (3h): 18 h, 59.9 mg, 79% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 4.37-4.24 (m, 2H), 3.59-3.49 (m, 1H), 2.00-1.86 (m, 5H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.2, 163.2 (t, *J* = 31.8 Hz， 1C), 140.4, 132.5 (q, *J* = 32.9 Hz), 127.6 (2C), 125.8 (q, *J* = 3.7 Hz, 1C), 119.4 (t, *J* = 202.7 Hz, 1C), 115.5 (dd, *J* = 258.7, 253.1 Hz, 1C), 63.2, 53.5 (t, *J* = 22.3 Hz, 1C), 24.7, 20.8, 13.8, 11.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -63.2, -103.78 (dd, *J* = 264.6, 13.2 Hz, 1F), -107.31 (dd, *J* = 264.5, 13.2 Hz, 1F); HRMS (ESI) for $C_{17}H_{19}F_5NO_3$ ($[M+H]^+$): calcd 380.1280, found 380.1286.



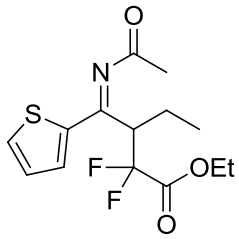
(*E*)-Ethyl 4-(acetylimino)-4-(3-chlorophenyl)-2,2-difluoro-3-methylbutanoate (3i): 18 h, 53 mg, 80% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.27 (m, 4H), 4.33-4.25 (m, 2H), 3.77-3.66 (m, 1H), 1.90 (s, 3H), 1.35 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.1, 163.8 (d, *J* = 6.4 Hz, 1C), 163.3 (t, *J* = 31.8 Hz, 1C), 137.4, 135.0, 130.9, 130.2, 126.9, 125.4, 115.1 (dd, *J* = 260.2, 249.6 Hz, 1C), 63.0, 46.4 (t, *J* = 23.3 Hz, 1C), 24.8, 13.9, 11.4 (t, *J* = 4.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.5 (dd, *J* = 267.7, 10.7 Hz, 1F), -112.3 (dd, *J* = 267.7, 15.5 Hz, 1F); HRMS (ESI) for $C_{15}H_{17}ClF_2NO_3$ ($[M+H]^+$): calcd 332.0860, found 332.0866.



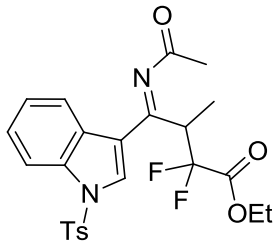
(*E*)-Ethyl 4-(acetylimino)-2,2-difluoro-3-methyl-4-(o-tolyl)butanoate (3j): 32 h, 47.3 mg, 76% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 4.38-4.26 (m, 2H), 3.65-3.53 (m, 1H), 2.33 (s, 3H), 1.85 (s, 3H), 1.37 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.9, 167.6 (d, *J* = 7.0 Hz, 1C), 163.5 (t, *J* = 31.8 Hz, 1C), 135.6, 134.1, 130.8, 129.6, 126.3, 125.5, 115.1 (dd, *J* = 259.8, 247.9 Hz, 1C), 62.9, 47.3 (t, *J* = 23.1 Hz, 1C), 24.8, 19.8, 13.9, 10.4 (t, *J* = 4.1 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.5 (dd, *J* = 268.8, 9.1 Hz, 1F), -114.2 (dd, *J* = 268.9, 15.9 Hz, 1F); HRMS (ESI) for $C_{16}H_{20}F_2NO_3$ ($[M+H]^+$): calcd 312.1406, found 312.1410.



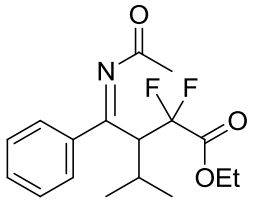
(*E*)-Ethyl 3-((acetylimino)(naphthalen-2-yl)methyl)-2,2-difluoropentanoate (3k): 24 h, 49.1 mg, 68% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (s, 1H), 7.91-7.85 (m, 3H), 7.60-7.54 (m, 3H), 4.35-4.23 (m, 2H), 3.80-3.70 (m, 1H), 2.08-1.94 (m, 2H), 1.90 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.6, 164.3, 163.4 (t, *J* = 32.1 Hz, 1C), 134.6, 134.0, 132.5, 128.9 (2C), 128.0, 127.9, 127.7, 127.1, 123.6, 115.7 (dd, *J* = 258.9, 251.8 Hz, 1C), 63.0, 53.2 (t, *J* = 22.4 Hz, 1C), 24.7, 21.3 (t, *J* = 3.4 Hz, 1C), 13.9, 12.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.0 (dd, *J* = 263.6, 12.4 Hz, 1F), -108.2 (dd, *J* = 263.6, 13.7 Hz, 1F); HRMS (ESI) for $C_{20}H_{22}F_2NO_3$ ($[M+H]^+$): calcd 362.1562, found 362.1568.



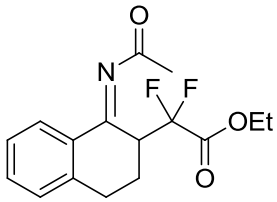
(*E*)-Ethyl 3-((acetylimino)(thiophen-2-yl)methyl)-2,2-difluoropentanoate (3l): 32 h, 32.4 mg, 51% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 5.0 Hz, 1H), 7.53 (d, *J* = 3.7 Hz, 1H), 7.12 (t, *J* = 4.4 Hz, 1H), 4.33-4.21 (m, 2H), 3.67-3.57 (m, 1H), 2.14 (s, 3H), 2.07-1.92 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.3, 163.2 (t, *J* = 32.3 Hz, 1C), 153.4, 138.9, 131.8 (2C), 128.4, 115.3 (t, *J* = 254.3 Hz, 1C), 63.1, 53.3 (t, *J* = 22.7 Hz, 1C), 24.2, 21.6, 13.8, 11.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.8 (dd, *J* = 261.1, 13.0 Hz, 1F), -107.3 (dd, *J* = 261.0, 10.9 Hz, 1F); HRMS (ESI) for $C_{14}H_{18}F_2NO_3S$ ($[M+H]^+$): calcd 318.0970, found 318.0968.



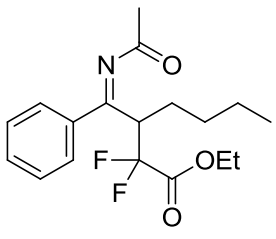
(*E*)-Ethyl 4-(acetylimino)-2,2-difluoro-3-methyl-4-(1-tosyl-1H-indol-3-yl)butanoate (3m): 28 h, 56.8 mg, 58% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, *J* = 8.3 Hz, 1H), 7.92 (s, 1H), 7.85-7.78 (m, 3H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 4.26 (q, *J* = 6.9 Hz, 2H), 3.93-3.81 (m, 1H), 2.35 (s, 3H), 1.94 (s, 3H), 1.41 (d, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.4, 163.3 (t, *J* = 31.9 Hz, 1C), 158.0 (d, *J* = 6.3 Hz, 1C), 145.7, 134.4, 130.3, 130.1, 129.0, 127.3, 127.1, 127.0, 125.8, 124.4, 122.2, 115.1 (t, *J* = 253.4 Hz, 1C), 113.7, 63.1, 46.3 (t, *J* = 23.4 Hz, 1C), 24.6, 21.6, 13.8, 11.93 (t, *J* = 4.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -105.1 (dd, *J* = 265.7, 12.7 Hz, 1F), -110.7 (dd, *J* = 265.4, 13.1 Hz, 1F); HRMS (ESI) for $C_{24}H_{25}F_2N_2O_5S$ ($[M+H]^+$): calcd 491.1447, found 491.1451.



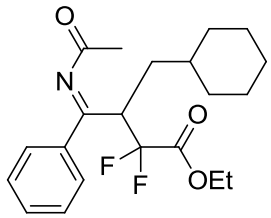
(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluoro-4-methylpentanoate (3n): 24 h, 47.5 mg, 73% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 7.4 Hz, 2H), 7.46-7.40 (m, 3H), 4.36-4.26 (m, 2H), 3.62-3.54 (m, 1H), 2.47-2.39 (m, 1H), 1.86 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.5, 164.7, 163.8 (t, J = 31.9 Hz, 1C), 137.9, 131.0, 128.9, 127.4, 115.2 (dd, J = 260.0, 248.8 Hz, 1C), 63.0, 56.7 (t, J = 21.3 Hz, 1C), 28.9, 24.6, 21.6, 21.0, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -100.2 (dd, *J* = 270.3, 13.2 Hz, 1F), -106.8 (dd, *J* = 270.3, 14.7 Hz, 1F); HRMS (ESI) for $C_{17}H_{22}F_2NO_3$ ($[M+H]^+$): calcd 326.1562, found 326.1566.



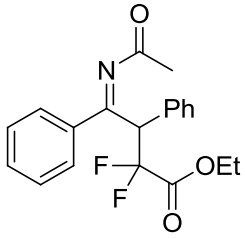
(*E*)-Ethyl 2-(1-(acetylimino)-1,2,3,4-tetrahydronaphthalen-2-yl)-2,2-difluoroacetate (3o): 16 h, 46.4 mg, 75% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.23 (dd, *J* = 14.9, 7.7 Hz, 2H), 4.34-4.27 (m, 2H), 3.81-3.70 (m, 1H), 3.15-3.08 (m, 1H), 2.92-2.85 (m, 1H), 2.38-2.31(m, 1H), 2.22 (s, 3H), 2.20-2.11 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.6, 163.1 (t, *J* = 31.5 Hz, 1C), 156.5 (d, *J* = 6.0 Hz, 1C), 141.6, 132.3, 130.4, 129.3, 127.4, 126.7, 115.5 (t, *J* = 252.5 Hz, 1C), 63.0, 44.4 (t, *J* = 22.5 Hz, 1C), 26.5, 24.9, 22.1 (d, *J* = 4.0 Hz, 1C), 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -107.3 (dd, *J* = 263.2, 15.0 Hz, 1F), -109.5 (dd, *J* = 263.2, 11.3 Hz, 1F); HRMS (ESI) for $C_{16}H_{18}F_2NO_3$ ($[M+H]^+$): calcd 310.1249, found 310.1255.



(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluoroheptanoate (3p): 18 h, 61 mg, 90% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.38 (m, 5H), 4.31-4.21 (m, 2H), 3.69-3.59 (m, 1H), 1.94-1.81 (m, 5H), 1.35-1.25 (m, 7H), 0.81 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.6, 164.4 (t, *J* = 4.1 Hz, 1C), 163.3 (t, *J* = 32.2 Hz, 1C), 137.2, 130.9, 128.8, 127.1, 115.55 (dd, *J* = 258.5, 252.2 Hz, 1C), 63.0, 51.5 (t, *J* = 22.4 Hz, 1C), 29.3, 27.4, 24.6, 22.4, 13.8, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.5 (dd, *J* = 262.6, 12.6 Hz, 1F), -108.1 (dd, *J* = 262.6, 13.4 Hz, 1F); HRMS (ESI) for $C_{18}H_{24}F_2NO_3$ ($[M+H]^+$): calcd 340.1719, found 340.1721.

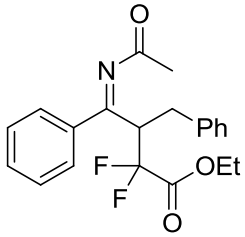


(*E*)-Ethyl 4-(acetylimino)-3-(cyclohexylmethyl)-2,2-difluoro-4-phenylbutanoate (3q): 32 h, 69 mg, 91% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.38 (m, 5H), 4.33-4.20 (m, 2H), 3.82-3.72 (m, 1H), 1.88-1.81 (m, 4H), 1.70-1.58 (m, 6H), 1.34-1.27 (m, 4H), 1.15-0.96 (m, 3H), 0.89-0.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.6, 164.5, 163.3 (t, *J* = 32.3 Hz, 1C), 137.2, 130.8, 128.8, 127.2, 115.7 (dd, *J* = 258.0, 252.9 Hz, 1C), 62.9, 48.8 (t, *J* = 22.3 Hz, 1C), 35.1, 34.9, 33.7, 32.4, 26.2, 26.0, 25.8, 24.6, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.9 (dd, *J* = 262.2, 13.3 Hz, 1F), -107.6 (dd, *J* = 262.2, 12.9 Hz, 1F); HRMS (ESI) for $C_{21}H_{28}F_2NO_3$ ($[M+H]^+$): calcd 380.2032, found 380.2036.

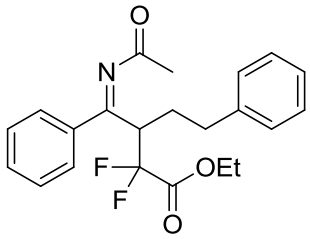


(*E*)-Ethyl 4-(acetylimino)-2,2-difluoro-3,4-diphenylbutanoate (3r): 48 h, 40.2 mg, 56% yield;

Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43-7.28 (m, 10H), 4.97 (dd, *J* = 19.5, 10.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.93 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.2, 163.9 (t, *J* = 31.3 Hz, 1C), 163.2 (d, *J* = 8.0 Hz), 135.7, 130.7, 130.7, 130.1, 128.8, 128.7 (2C), 127.1, 113.6 (t, *J* = 253.5 Hz, 1C), 63.1, 56.7 (dd, *J* = 25.3, 20.0 Hz, 1C), 24.8, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -101.0 (dd, *J* = 273.5, 10.3 Hz, 1F), -112.7 (dd, *J* = 273.5, 19.5 Hz, 1F); HRMS (ESI) for $C_{20}H_{20}F_2NO_3$ ($[M+H]^+$): calcd 360.1406, found 360.1410.

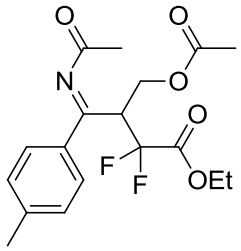


(*E*)-Ethyl 4-(acetylimino)-3-benzyl-2,2-difluoro-4-phenylbutanoate (3s): 18 h, 60.4 mg, 81% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34-7.15 (m, 8H), 7.06 (d, *J* = 7.6 Hz, 2H), 4.32-4.17 (m, 2H), 4.03-3.93 (m, 1H), 3.30-3.22 (m, 2H), 1.80 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.7, 163.4, 163.0 (t, *J* = 31.9 Hz, 1C), 137.4, 137.2, 130.5, 129.2, 128.5, 128.5, 126.8, 115.1 (t, *J* = 255.0 Hz, 1C), 63.1, 54.0 (t, *J* = 22.1 Hz, 1C), 33.6 (t, *J* = 3.8 Hz, 1C), 24.7, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.8 (dd, *J* = 260.5, 12.7 Hz, 1F), -107.0 (dd, *J* = 260.5, 12.1 Hz, 1F); HRMS (ESI) for $C_{21}H_{22}F_2NO_3$ ($[M+H]^+$): calcd 374.1562, found 374.1566.

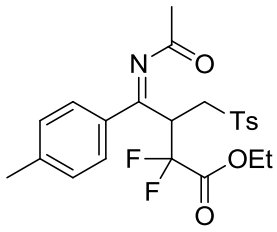


(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluoro-5-phenylpentanoate (3t): 18 h, 64.2 mg, 83% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-7.39 (m, 5H), 7.25-7.16 (m, 3H), 7.02 (d, *J* = 7.2 Hz, 2H), 4.32-4.19 (m, 2H), 3.73-3.63 (m, 1H), 2.81-2.74 (m, 1H), 2.65-2.57 (m, 1H),

2.34-2.18 (m, 2H), 1.91 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.6, 164.0, 163.2 (t, *J* = 32.1 Hz, 1C), 140.2, 136.9, 131.0, 128.8, 128.4, 128.3, 127.3, 126.2, 115.6 (dd, *J* = 258.8, 252.2 Hz, 1C), 63.0, 50.5 (t, *J* = 22.5 Hz, 1C), 33.0, 29.1, 24.7, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.1 (dd, *J* = 262.8, 12.3 Hz, 1F), -107.9 (dd, *J* = 262.8, 13.6 Hz, 1F); HRMS (ESI) for $C_{22}H_{24}F_2NO_3$ ($[M+H]^+$): calcd 388.1719, found 388.1721.

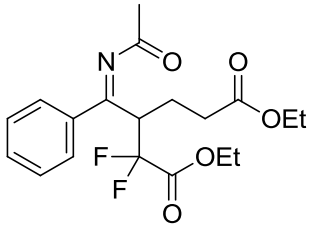


(*E*)-Ethyl 3-(acetoxymethyl)-4-(acetylimino)-2,2-difluoro-4-(p-tolyl)butanoate (3u): 24 h, 51 mg, 68% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 4.60-4.51 (m, 2H), 4.34-4.25 (m, 2H), 4.16-4.06 (m, 1H), 2.37 (s, 3H), 1.92 (s, 3H), 1.90 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.3, 170.2, 162.7 (t, *J* = 31.4 Hz, 1C), 161.7, 141.9, 133.5, 129.6, 127.3, 114.4 (t, *J* = 254.8 Hz, 1C), 63.3, 61.3 (d, *J* = 4.5 Hz, 1C), 50.5 (t, *J* = 22.6 Hz, 1C), 24.6, 21.4, 20.5, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.2 (dd, *J* = 267.8, 12.2 Hz, 1F), -108.0 (dd, *J* = 267.8, 12.6 Hz, 1F); HRMS (ESI) for $C_{18}H_{22}F_2NO_5$ ($[M+H]^+$): calcd 370.1461, found 370.1465.

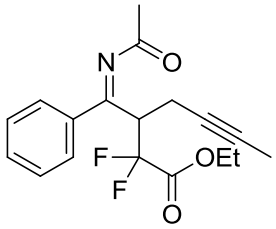


(*E*)-ethyl 4-(acetylimino)-2,2-difluoro-4-(p-tolyl)-3-(tosylmethyl)butanoate (3v): 24 h, 62.2 mg, 69% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 4.34 (dd, *J* = 21.8, 10.8 Hz, 1H), 4.23-3.99 (m,

3H), 3.55 (d, *J* = 13.9 Hz, 1H), 2.45 (s, 3H), 2.38 (s, 3H), 1.89 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.1, 161.9 (t, *J* = 31.4 Hz, 1C), 160.6, 145.3, 142.0, 136.1, 133.5, 130.1, 129.5, 127.8, 114.0 (t, *J* = 259.4 Hz, 1C), 63.6, 53.6, 46.5 (t, *J* = 23.6 Hz, 1C), 24.1, 21.6, 21.4, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.6 (dd, *J* = 252.7, 10.5 Hz, 1F), -106.2 (dd, *J* = 252.7, 11.8 Hz, 1F); HRMS (ESI) for $C_{23}H_{26}F_2NO_5S$ ($[M+Na]^+$): calcd 466.1494, found 466.1500.

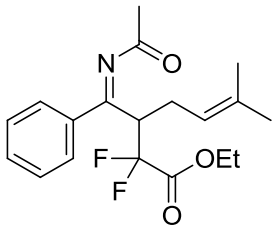


(*E*)-Diethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluorohexanedioate (3w): 36 h, 58.2 mg, 76% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.39 (m, 5H), 4.31-4.17 (m, 2H), 4.10-4.04 (m, 2H), 3.93-3.84 (m, 1H), 2.51-2.44 (m, 1H), 2.39-2.31 (m, 1H), 2.23-2.18 (m, 2H), 1.88 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.5, 172.3, 163.7 (d, *J* = 5.5 Hz, 1C), 163.0 (t, *J* = 32.0 Hz, 1C), 136.6, 131.1, 128.9, 127.3, 115.40 (dd, *J* = 259.5, 252.0 Hz, 1C), 63.1, 60.5, 50.0 (t, *J* = 22.4 Hz, 1C), 31.1, 24.6, 22.7, 14.0, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -102.64 (dd, *J* = 263.8, 11.9 Hz, 1F), -108.60 (dd, *J* = 263.8, 13.9 Hz, 1F); HRMS (ESI) for $C_{19}H_{24}F_2NO_5$ ($[M+H]^+$): calcd 384.1617, found 384.1621.

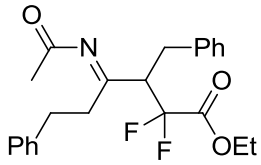


(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluorohept-5-ynoate (3x): 24 h, 59 mg, 88% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.43 (m, 5H), 4.32-4.18 (m, 2H), 3.93-3.83 (m, 1H), 2.88-2.82 (m, 1H), 2.70 (d, *J* = 16.4 Hz, 1H), 1.89 (s, 3H), 1.65 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ: 183.6, 163.2, 162.7 (t, *J* = 31.8 Hz, 1C), 137.2, 130.8, 128.6, 127.3, 114.6 (t, *J* = 255.0 Hz, 1C), 78.4, 74.7, 63.1, 51.4 (t, *J* = 22.5 Hz, 1C), 24.5, 17.9, 13.7, 3.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.79 (dd, *J* = 262.4, 11.7 Hz, 1F), -108.87 (dd, *J* = 262.4, 12.9 Hz, 1F); HRMS (ESI) for $C_{18}H_{20}F_2NO_3$ ($[M+H]^+$): calcd 336.1406, found 336.1410.

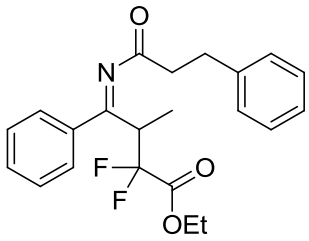


(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluoro-6-methylhept-5-enoate (3y): 36 h, 39 mg, 56% yield; Corlorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.39 (m, 5H), 5.00 (t, *J* = 7.3 Hz, 1H), 4.35-4.21 (m, 2H), 3.74-3.64 (m, 1H), 2.71-2.63 (m, 1H), 2.58-2.51 (m, 1H), 1.86 (s, 3H), 1.58 (s, 6H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.7, 164.3, 163.3 (t, *J* = 32.0 Hz, 1C), 137.4, 135.2, 130.7, 128.7, 127.1, 119.4, 115.4 (t, *J* = 254.0 Hz, 1C), 63.0, 52.0 (t, *J* = 22.0 Hz, 1C), 26.5, 25.6, 24.7, 17.8, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.40 (dd, *J* = 263.2, 12.9 Hz, 1F), -108.15 (dd, *J* = 263.2, 13.1 Hz, 1F); HRMS (ESI) for $C_{19}H_{24}F_2NO_3$ ($[M+H]^+$): calcd 352.1719, found 352.1721.

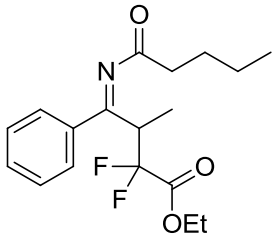


(*E*)-Ethyl 4-(acetylimino)-3-benzyl-2,2-difluoro-6-phenylhexanoate (3z): 32 h, 52.1 mg, 65% yield; Corlorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.15 (m, 8H), 6.98 (d, *J* = 7.3 Hz, 2H), 4.36-4.23 (m, 2H), 3.55-3.45 (m, 1H), 3.15-3.04 (m, 2H), 2.50-2.45 (m, 3H), 2.39-2.30 (m, 1H), 1.92 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.3, 166.0, 162.9 (t, *J* = 32.0 Hz, 1C), 140.0, 137.2, 129.2, 128.8, 128.5, 128.1, 1271, 126.3, 115.1 (t, *J* = 256.5 Hz, 1C), 63.3, 53.2 (t, *J* = 21.8 Hz, 1C), 39.3, 33.2 (t, *J* = 4.1 Hz, 1C), 31.3, 24.7, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -105.2 (dd, *J* =

260.9, 11.1 Hz, 1F), -107.0 (dd, *J* = 260.9, 14.8 Hz, 1F); HRMS (ESI) for $C_{23}H_{26}F_2NO_3$ ($[M+H]^+$): calcd 402.1875, found 402.1877.

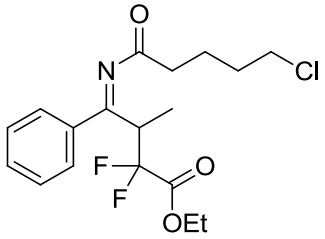


(*E*)-Ethyl 2,2-difluoro-3-methyl-4-phenyl-4-((3-phenylpropanoyl)imino)butanoate (4a): 32 h, 61.2 mg, 79% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.31 (m, 5H), 7.22-7.13 (m, 3H), 7.03 (d, *J* = 7.3 Hz, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.87-3.75 (m, 1H), 2.82-2.69 (m, 2H), 2.51-2.43 (m, 1H), 2.36-2.28 (m, 1H), 1.38 (d, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.1, 165.8 (d, *J* = 6.1 Hz, 1C), 163.4 (t, *J* = 32.0 Hz, 1C), 140.4, 135.9, 130.9, 128.8, 128.4, 128.2, 127.2, 126.0, 115.2 (dd, *J* = 259.8, 248.9 Hz, 1C), 62.9, 46.4 (t, *J* = 23.3 Hz, 1C), 39.1, 29.9, 13.9, 11.7 (t, *J* = 4.1 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.4 (dd, *J* = 267.2, 10.5 Hz, 1F), -112.5 (dd, *J* = 267.2, 15.5 Hz, 1F); HRMS (ESI) for $C_{22}H_{24}F_2NO_3$ ($[M+H]^+$): calcd 388.1719, found 388.1721.

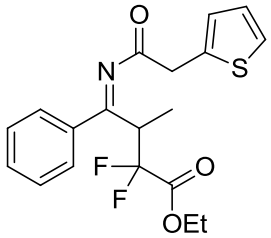


(*E*)-Ethyl 2,2-difluoro-3-methyl-4-(pentanoylimino)-4-phenylbutanoate (4b): 24 h, 61 mg, 90% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43-7.31 (m, 5H), 4.27 (q, *J* = 7.0 Hz, 2H), 3.82-3.74 (m, 1H), 2.15-2.08 (m, 1H), 2.01-1.94 (m, 1H), 1.39-1.31 (m, 7H), 1.14-1.08 (m, 2H), 0.74 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.2, 165.1 (d, *J* = 6.4 Hz, 1C), 163.4 (t, *J* = 31.9 Hz, 1C), 136.1, 130.7, 128.7, 127.2, 115.2 (dd, *J* = 259.9, 248.7 Hz, 1C), 62.8, 46.4 (t, *J* = 23,2 Hz, 1C), 37.2, 25.9, 21.9, 13.8, 13.5, 11.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.3 (dd, *J* = 267.4, 10.5 Hz, 1F),

-112.8 (dd, *J* = 267.4, 15.7 Hz, 1F); HRMS (ESI) for $C_{18}H_{24}F_2NO_3$ ($[M+H]^+$): calcd 340.1719, found 340.1721.

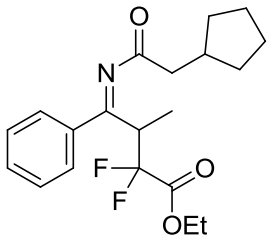


(*E*)-Ethyl 4-((5-chloropentanoyl)imino)-2,2-difluoro-3-methyl-4-phenylbutanoate (4c): 24 h, 58.2 mg, 78% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.39 (m, 5H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.85-3.73 (m, 1H), 3.34 (t, *J* = 5.4 Hz, 1.75H), 3.21 (t, *J* = 6.4 Hz, 0.25H), 2.19-2.13 (m, 1H), 2.02-1.96 (m, 1H), 1.62-1.51 (m, 4H), 1.37-1.32 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.5, 165.7 (d, *J* = 6.6 Hz, 1C), 163.4 (t, *J* = 32.0 Hz, 1C), 135.9, 130.9, 128.8, 127.2, 115.2 (dd, *J* = 259.8, 248.9 Hz, 1C), 62.9, 46.4 (dd, *J* = 24.5, 22.3 Hz, 1C), 44.3, 36.3, 31.4, 21.1, 13.9, 11.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.4 (dd, *J* = 267.5, 10.5 Hz, 1F), -112.7 (dd, *J* = 267.5, 15.6 Hz, 1F); HRMS (ESI) for $C_{18}H_{23}ClF_2NO_3$ ($[M+H]^+$): calcd 374.1329, found 374.1327.

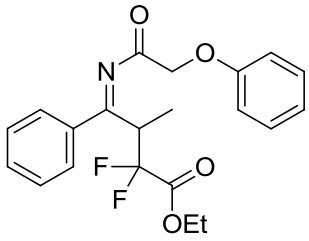


(*E*)-Ethyl 2,2-difluoro-3-methyl-4-phenyl-4-((2-(thiophen-2-yl)acetyl)imino)butanoate (4d): 32 h, 38.7 mg, 51% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (t, *J* = 6.9 Hz, 1H), 7.38-7.33 (m, 4H), 7.11 (d, *J* = 5.1 Hz, 1H), 6.85 (t, *J* = 4.2 Hz, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.86-3.71 (m, 1H), 3.74 (d, *J* = 16.9 Hz, 1H), 3.57 (d, *J* = 17.0 Hz, 1H), 1.37-1.32 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 181.9, 166.5 (d, *J* = 8.0 Hz, 1C), 163.4 (t, *J* = 31.9 Hz, 1C), 136.0, 134.0, 131.0, 128.8, 127.3, 127.2, 126.8, 125.2, 115.2 (dd, *J* = 259.4, 250.1 Hz, 1C), 63.0, 46.3 (t, *J* = 23.4 Hz,

1C), 38.4, 13.9, 11.8 (t, *J* = 4.1 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.4 (dd, *J* = 266.3, 10.8 Hz, 1F), -111.9 (dd, *J* = 266.3, 15.0 Hz, 1F); HRMS (ESI) for $C_{19}H_{20}F_2NO_3S$ ($[M+H]^+$): calcd 380.1126, found 380.1130.

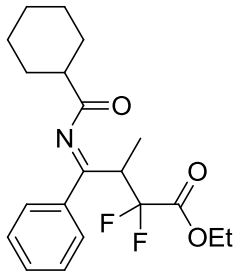


(*E*)-Ethyl 4-((2-cyclopentylacetyl)imino)-2,2-difluoro-3-methyl-4-phenylbutanoate (4e): 24 h, 56.9 mg, 78% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.37 (m, 5H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.85-3.73 (m, 1H), 2.28-2.10 (m, 1H), 2.02-1.94 (m, 1H), 1.56-1.32 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.4, 165.2 (d, *J* = 6.8 Hz, 1C), 163.5 (t, *J* = 31.9 Hz, 1C), 136.1, 130.8, 128.7, 127.2, 115.2 (dd, *J* = 259.9, 248.5 Hz, 1C), 62.9, 46.3 (dd, *J* = 24.6, 22.2 Hz, 1C), 39.2, 36.7, 32.2, 32.1, 30.0, 24.93 (d, *J* = 2.5 Hz, 1C), 13.9, 11.6 (t, *J* = 4.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.3 (dd, *J* = 267.4, 10.5 Hz, 1F), -112.9 (dd, *J* = 267.4, 15.8 Hz, 1F); HRMS (ESI) for $C_{20}H_{26}F_2NO_3$ ($[M+H]^+$): calcd 366.1875, found 366.1877.

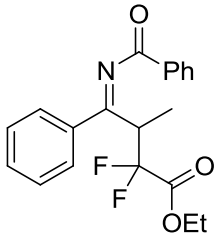


(*E*)-Ethyl 2,2-difluoro-3-methyl-4-((2-phenoxyacetyl)imino)-4-phenylbutanoate (4f): 32 h, 55.3 mg, 71% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-7.39 (m, 5H), 7.18 (t, *J* = 7.8 Hz, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.48 (d, *J* = 16.3 Hz, 1H), 4.34 (d, *J* = 16.3 Hz, 1H), 4.26 (dd, *J* = 14.1, 7.0 Hz, 2H), 3.91-3.83 (m, 1H), 1.38-1.31(m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 181.0, 168.9 (d, *J* = 6.5 Hz, 1C), 163.3 (t, *J* = 32.0 Hz, 1C), 157.5, 136.1, 131.2, 129.4, 128.9, 127.3,

121.5, 115.1 (dd, *J* = 258.5, 248.4 Hz, 1C), 114.4, 67.6, 63.0, 46.5 (t, *J* = 23.3 Hz, 1C), 13.8, 11.62 (d, *J* = 4.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.6 (dd, *J* = 266.6, 10.6 Hz, 1F), -112.2 (dd, *J* = 266.7, 15.4 Hz, 1F); HRMS (ESI) for $C_{21}H_{22}F_2NO_4$ ($[M+H]^+$): calcd 390.1511, found 390.1515.

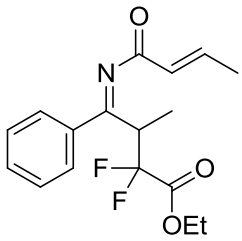


(*E*)-Ethyl 4-((cyclohexanecarbonyl)imino)-2,2-difluoro-3-methyl-4-phenylbutanoate (4g): 24 h, 65 mg, 89% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42-7.36 (m, 5H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.87-3.75 (m, 1H), 2.01-1.95 (m, 1H), 1.67-1.48 (m, 5H), 1.37-1.31 (m, 6H), 1.24-1.04 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 188.8, 164.8 (d, *J* = 6.2 Hz, 1C), 163.4 (t, *J* = 32.0 Hz, 1C), 136.6, 130.6, 128.6, 127.3, 115.2 (dd, *J* = 259.2, 248.7 Hz, 1C), 62.8, 46.7, 46.3 (t, *J* = 23.2 Hz, 1C), 28.7, 28.4, 25.6, 25.4 (2C), 13.8, 11.65 (t, *J* = 4.1 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ:-104.3 (dd, *J* = 268.0, 10.5 Hz, 1F), -112.8 (dd, *J* = 268.0, 15.5 Hz, 1F); HRMS (ESI) for $C_{20}H_{26}F_2NO_3$ ($[M+H]^+$): calcd 366.1875, found 366.1877.

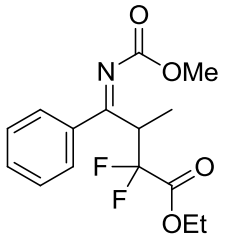


(*E*)-Ethyl 4-(benzoylimino)-2,2-difluoro-3-methyl-4-phenylbutanoate (4h): 32 h, 50.3 mg, 70% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.36-7.26 (m, 5H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.05-3.93 (m, 1H), 1.49 (d, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.1, 168.7 (d, *J* = 5.7 Hz, 1C), 163.5 (t, *J* = 31.7 Hz, 1C), 135.7, 133.1, 132.7, 130.7, 129.1, 128.7, 128.5, 127.0, 115.3 (dd, *J* = 259.0,

249.1 Hz, 1C), 62.9, 46.7 (t, *J* = 23.4 Hz, 1C), 13.8, 11.8 (t, *J* = 4.1 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -105.0 (dd, *J* = 266.6, 10.3 Hz, 1F), -113.1 (dd, *J* = 266.6, 15.9 Hz, 1F); HRMS (ESI) for $C_{20}H_{20}F_2NO_3$ ($[M+H]^+$): calcd 360.1406, found 360.1410.

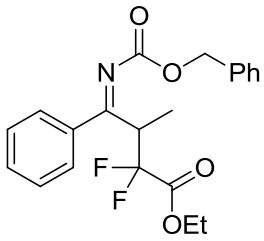


(*E*)-Ethyl 4-((E)-but-2-enoylimino)-2,2-difluoro-3-methyl-4-phenylbutanoate (4i): 24 h, 32.3 mg, 50% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.37 (m, 5H), 6.74-6.65(m, 1H), 5.77 (d, *J* = 15.7 Hz, 1H), 4.29-4.23 (m, 2H), 3.92-3.80 (m, 1H), 1.81 (d, *J* = 6.8 Hz, 3H), 1.40 (d, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.0, 167.6 (d, *J* = 6.5 Hz, 1C), 163.6 (t, *J* = 31.8 Hz, 1C), 145.3, 135.9, 130.7, 128.7, 127.1, 126.5, 115.3 (t, *J* = 252.6 Hz, 1C), 62.9, 46.7 (t, *J* = 23.4 Hz, 1C), 18.3, 13.8, 11.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.8 (dd, *J* = 266.5, 10.4 Hz, 1F), -113.02 (dd, *J* = 266.5, 15.7 Hz, 1F); HRMS (ESI) for $C_{17}H_{20}F_2NO_3$ ($[M+H]^+$): calcd 324.1406, found 324.1410.

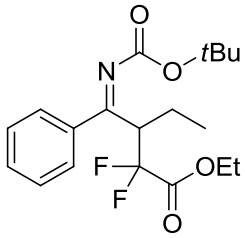


(*E*)-Ethyl 2,2-difluoro-4-((methoxycarbonyl)imino)-3-methyl-4-phenylbutanoate (4j): 24 h, 53.8 mg, 86% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.37 (m, 5H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.87-3.75 (m, 1H), 3.59 (s, 3H), 1.38-1.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.7 (d, *J* = 7.5 Hz, 1C), 163.3 (d, *J* = 32.7 Hz, 1C), 161.6, 135.9, 130.8, 128.7, 126.4, 115.0 (dd, *J* = 260.1, 248.1 Hz, 1C), 62.9, 53.1, 46.9 (dd, *J* = 24.9, 22.1 Hz, 1C), 13.7, 11.2 (d, *J* = 3.5 Hz); ^{19}F NMR (376 MHz,

$CDCl_3$) δ: -104.2 (dd, *J* = 267.3, 10.2 Hz, 1F), -113.5 (dd, *J* = 267.3, 16.4 Hz, 1F); HRMS (ESI) for $C_{15}H_{18}F_2NO_4$ ($[M+H]^+$): calcd 314.1198, found 314.1204.

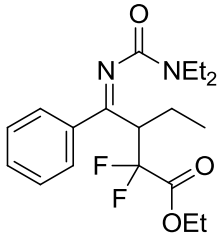


(*E*)-Ethyl 4-(((benzyloxy)carbonyl)imino)-2,2-difluoro-3-methyl-4-phenylbutanoate (4k): 24 h, 63 mg, 81% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (t, *J* = 6.7 Hz, 1H), 7.33-7.24 (m, 7H), 7.09 (d, *J* = 6.3 Hz, 2H), 5.05-4.96 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.87-3.74 (m, 1H), 1.37 (d, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.9 (d, *J* = 7.9 Hz, 1C), 163.26 (t, *J* = 31.8 Hz, 1C), 160.9, 135.8, 135.1, 130.7, 128.6, 128.4, 128.4, 128.2, 126.5, 115.0 (dd, *J* = 260.1, 248.0 Hz, 1C), 68.0, 62.9, 46.9 (dd, *J* = 24.9, 22.1 Hz, 1C), 13.7, 11.1 (d, *J* = 3.4 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.0 (dd, *J* = 267.1, 10.1 Hz, 1F), -113.4 (dd, *J* = 267.1, 16.6 Hz, 1F); HRMS (ESI) for $C_{21}H_{22}F_2NO_4$ ($[M+H]^+$): calcd 390.1511, found 390.1515.

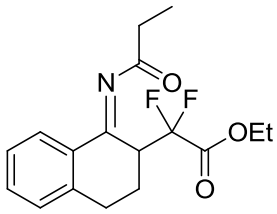


(*E*)-Ethyl 3-(((tert-butoxycarbonyl)imino)(phenyl)methyl)-2,2-difluoropentanoate (4l): 24 h, 65.7 mg, 89% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.37 (m, 5H), 4.33-4.19 (m, 2H), 3.61-3.50 (m, 1H), 1.99-1.86 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.24 (s, 9H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.6, 163.3 (t, *J* = 31.8 Hz, 1C), 160.1, 137.3, 130.3, 128.4, 126.7, 115.5 (dd, *J* = 259.6, 250.5 Hz, 1C), 82.0, 62.9 53.7 (t, *J* = 22.2 Hz, 1C), 27.7, 20.3 (t, *J* = 3.2 Hz, 1C), 13.8, 12.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -102.5 (dd, *J* = 263.7, 9.0 Hz, 1F), -109.9 (d, *J* = 262.9 Hz,

1F); HRMS (ESI) for $C_{19}H_{26}F_2NO_4$ ($[M+H]^+$): calcd 370.1824, found 370.1826.

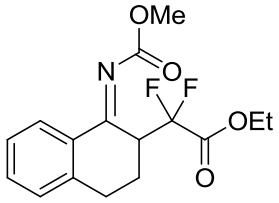


(*E*)-Ethyl 3-(((diethylcarbamoyl)imino)(phenyl)methyl)-2,2-difluoropentanoate (4m): 24 h, 54.5 mg, 74% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.36 (m, 5H), 4.27-4.13 (m, 2H), 3.68-3.58 (m, 1H), 3.36-3.10 (m, 4H), 2.07-1.98 (m, 1H), 1.94-1.86 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.03-0.97 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.1, 163.4 (t, *J* = 32.2 Hz, 1C), 161.6, 137.5, 130.2, 128.4, 126.7, 115.7 (t, *J* = 252.9 Hz, 1C), 62.8, 53.6 (t, *J* = 22.0 Hz, 1C), 41.6, 39.9, 20.9, 13.7, 13.4, 12.7, 12.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -104.9 (dd, *J* = 263.0, 11.4 Hz, 1F), -108.49 (d, *J* = 266.0 Hz, 1F); HRMS (ESI) for $C_{19}H_{27}F_2N_2O_3$ ($[M+H]^+$): calcd 369.1990, found 369.1996.

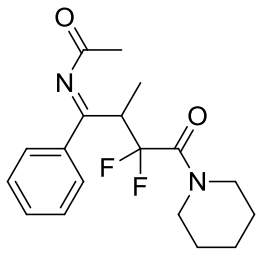


(*E*)-Ethyl 2,2-difluoro-2-(1-(propionylimino)-1,2,3,4-tetrahydronaphthalen-2-yl)acetate (4n): 18 h, 45.9 mg, 71% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.24 (dd, *J* = 14.1, 5.9 Hz, 2H), 4.36-4.25 (m, 2H), 3.79-3.68 (m, 1H), 3.15-3.07 (m, 1H), 2.95-2.87 (m, 1H), 2.47 (q, *J* = 7.4 Hz, 2H), 2.37 (dt, *J* = 12.5, 5.1 Hz, 1H), 2.17 (qd, *J* = 8.0, 5.2 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 186.9, 163.1 (t, *J* = 31.9 Hz, 1C), 156.7 (d, *J* = 6.2 Hz, 1C), 141.6, 132.2, 130.3, 129.3, 127.4, 126.7, 115.5 (t, *J* = 251.7 Hz, 1C), 63.0, 45.1 (t, *J* = 23.2 Hz, 1C), 30.9, 26.8, 22.1, 13.8, 8.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -107.25 (dd, *J* = 263.6, 12.8 Hz, 1F), -111.28 (dd, *J* = 263.8, 13.8 Hz, 1F); HRMS (ESI) for

$C_{17}H_{20}F_2NO_3$ ([M+H]$^+$): calcd 324.1406, found 324.1410.

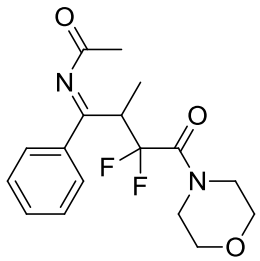


(*E*)-Ethyl 2,2-difluoro-2-(1-((methoxycarbonyl)imino)-1,2,3,4-tetrahydronaphthalen-2-yl)acetate (4o): 24 h, 42.3 mg, 65% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.24 (dd, *J* = 18.7, 7.5 Hz, 2H), 4.37-4.26 (m, 2H), 3.88-3.78 (m, 4H), 3.19-3.11 (m, 1H), 2.93-2.86 (m, 1H), 2.35 (dq, *J* = 9.9, 5.3 Hz, 1H), 2.23 (td, *J* = 12.2, 6.0 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3, 163.1 (t, *J* = 31.9 Hz, 1C), 162.4, 141.7, 132.6, 130.8, 129.1, 126.9, 126.7, 115.2 (t, *J* = 255.3 Hz, 1C), 63.1, 53.3, 44.5, 26.2, 22.2, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -107.11 (d, *J* = 256.6 Hz, 2F); HRMS (ESI) for $C_{16}H_{18}F_2NO_4$ ([M+H]$^+$): calcd 326.1198, found 326.1204.

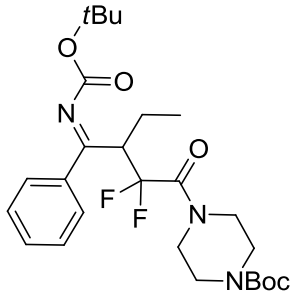


(*E*)-*N*-(3,3-Difluoro-2-methyl-4-oxo-1-phenyl-4-(piperidin-1-yl)butylidene)acetamide (5a): 24 h, 54.4 mg, 81% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 7.2, 2H), 7.42-7.35 (m, 3H), 3.88-3.76 (m, 1H), 3.71 (d, *J* = 4.9 Hz, 2H), 3.61-3.48 (m, 2H), 1.77 (s, 3H), 1.60-1.55 (m, 6H), 1.33 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.2, 166.9 (d, J = 9.3 Hz, 1C), 161.4 (t, J = 28.2 Hz, 1C), 136.9, 130.5, 128.6, 127.7, 119.1 (dd, J = 269.4, 253.3 Hz, 1C), 46.9 (dd, J = 9.6, 4.2 Hz, 1C), 45.8 (dd, J = 24.7, 20.2 Hz, 1C), 44.6, 26.5, 25.7, 24.4, 24.2, 11.5 (t, J = 4.5 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -99.4 (dd, *J* = 284.4, 9.8 Hz, 1F), -106.3 (dd, *J* = 284.4, 20.1 Hz, 1F); HRMS

(ESI) for $C_{18}H_{23}F_2N_2O_2$ ([M+H]$^+$): calcd 337.1722, found 337.1726.



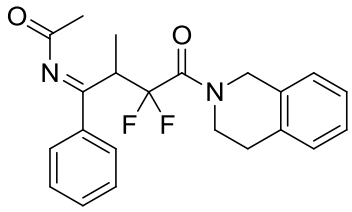
(*E*)-*N*-(3,3-Difluoro-2-methyl-4-morpholino-4-oxo-1-phenylbutylidene)acetamide (5b): 24 h, 56.8 mg, 84% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 7.2 Hz, 2H), 7.44-7.36 (m, 3H), 3.88-3.64 (m, 8H), 3.55 (dd, *J* = 15.7, 6.2 Hz, 1H), 1.77 (s, 3H), 1.34 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.1, 166.7 (d, *J* = 9.3 Hz, 1C), 161.7 (t, *J* = 28.6 Hz, 1C), 136.7, 130.6, 128.6, 127.6, 118.9 (dd, *J* = 268.8, 252.7 Hz, 1C), 66.8, 66.6, 46.5 (dd, *J* = 9.3, 3.9 Hz, 1C), 45.7 (dd, *J* = 24.5, 20.0 Hz, 1C), 43.5, 24.3, 11.4 (t, *J* = 4.5 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -99.06 (dd, *J* = 285.7, 10.0 Hz, 1F), -106.54 (dd, *J* = 285.7, 20.1 Hz, 1F); HRMS (ESI) for $C_{17}H_{21}F_2N_2O_3$ ([M+H]$^+$): calcd 339.1515, found 339.1517.



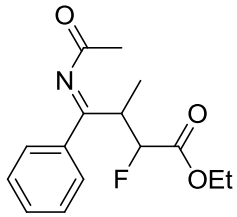
(*E*)-*tert*-Butyl

4-(3-(((tert-butoxycarbonyl)imino)(phenyl)methyl)-2,2-difluoropentanoyl)piperazine-1-carboxylate (5c): 24 h, 72.3 mg, 71% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.47 (m, 2H), 7.39-7.36 (m, 3H), 3.81-3.40 (m, 9H), 1.97-1.88 (m, 2H), 1.45 (s, 9H), 1.25 (s, 9H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.7, 161.9 (t, J = 28.6 Hz, 1C), 160.6, 154.4, 138.3, 130.0, 128.2, 126.9, 119.2 (t, J = 259.5 Hz, 1C), 81.9, 80.3, 53.1 (t, J = 21.1 Hz, 1C), 45.8, 44.6, 43.4, 28.3,

28.0, 27.7, 20.9 (d, J = 3.8 Hz, 1C), 12.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -99.7 (d, *J* = 279.9 Hz, 1F), -101.3 (d, *J* = 285.3 Hz, 1F); HRMS (ESI) for $C_{26}H_{38}F_2N_3O_5$ ($[M+H]^+$): calcd 510.2774, found 510.2776.

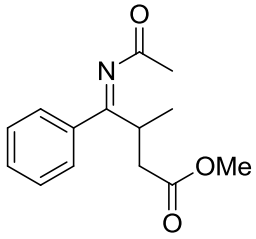


(*E*)-*N*-(4-(3,4-Dihydroisoquinolin-2(1H)-yl)-3,3-difluoro-2-methyl-4-oxo-1-phenylbutylidene)aceta mide (5d): 24 h, 53.8 mg, 70% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58-7.55 (m, 2H), 7.43-7.37 (m, 3H), 7.23 -7.10 (m, 4H), 4.96 (q, *J* = 16.6 Hz, 0.72H), 4.74 (q, *J* = 17.0 Hz, 1.25H), 4.13-4.07 (m, 0.68H), 4.00-3.86 (m, 2H), 3.72-3.66 (m, 0.38H), 3.06-2.83 (m, 2H), 1.75 (s, 1.26H), 1.67 (s, 1.90H), 1.37 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.2 (2), 166.8 (d, J = 9.5 Hz), 162.3 (dd, J = 33.7, 23.1 Hz), 136.7, 134.2, 134.0, 132.6, 132.1, 130.6, 128.6 (3), 127.7, 127.6, 127.1, 126.9, 126.6 (2), 126.4, 126.1, 119.0 (dd, J = 269.2, 252.4 Hz), 47.0 (dd, J = 11.1, 4.5 Hz), 46.1 (dd, J = 20.3, 5.3 Hz), 45.8, 45.6 (d, J = 5.8 Hz), 43.5 (dd, J = 19.5, 4.0 Hz), 41.9, 29.4, 28.0, 24.2, 24.1, 11.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -99.34 (dd, *J* = 93.3, 9.9 Hz), -100.10 (dd, *J* = 93.4, 9.9 Hz), -107.02 (dd, *J* = 114.5, 19.9 Hz), -107.77 (dd, *J* = 114.6, 19.9 Hz); HRMS (ESI) for $C_{22}H_{23}F_2N_2O_2$ ($[M+H]^+$): calcd 385.1722, found 385.1726.

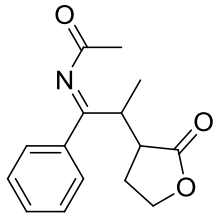


(*E*)-Ethyl 4-(acetylimino)-2-fluoro-3-methyl-4-phenylbutanoate (5e, d.r. = 1:1**):** 28 h, 45.2 mg, 81% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49-7.40 (m, 10H), 5.14 (dd, *J* = 18.8, 6.1 Hz,

1H), 5.03 (dd, *J* = 18.5, 6.1 Hz, 1H), 4.27-4.18 (m, 4H), 3.54-3.45 (m, 2H), 1.90 (s, 3H), 1.89 (s, 3H), 1.31-1.21 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.5, 184.3, 168.4 (dd, *J* = 37.7, 23.4 Hz), 167.5 (d, *J* = 4.0 Hz), 166.7 (d, *J* = 3.7 Hz), 136.3, 135.8, 130.7, 130.6, 128.8, 128.7, 127.1, 127.0, 90.8 (d, *J* = 38.1 Hz), 89.0 (d, *J* = 38.5 Hz), 61.8, 61.7, 44.2 (d, *J* = 21.4 Hz), 43.7 (d, *J* = 21.7 Hz), 24.9, 24.8, 14.0 (2), 13.42 (d, *J* = 5.5 Hz), 12.6 (d, *J* = 5.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -190.45 (dd, *J* = 47.5, 16.1 Hz), -199.70 (dd, *J* = 47.8, 20.2 Hz); HRMS (ESI) for $C_{15}H_{19}FNO_3$ ($[M+H]^+$): calcd 280.1343, found 280.1345.

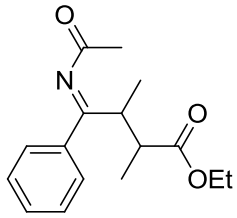


(*E*)-Methyl 4-(acetylimino)-3-methyl-4-phenylbutanoate (5f): 12 h, 35.6 mg, 72% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.36 (m, 5H), 3.64 (s, 3H), 3.40-3.37 (m, 1H), 2.86 (dd, *J* = 16.2, 8.4 Hz, 1H), 2.40 (dd, *J* = 16.7, 2.9 Hz, 1H), 1.79 (s, 3H), 1.12 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.8, 172.8, 170.8, 136.9, 130.3, 128.6, 127.2, 51.4, 37.9, 37.9, 24.6, 18.1; HRMS (ESI) for $C_{14}H_{18}NO_3$ ($[M+H]^+$): calcd 248.1281, found 248.1285.

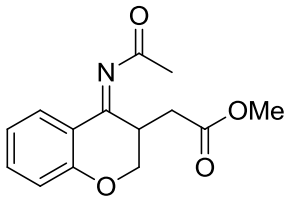


(*E*)-*N*-(2-(2-Oxotetrahydrofuran-3-yl)-1-phenylpropylidene)acetamide (5g, d.r. = 1.6:1**):** 16 h, 44 mg, 85% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.36 (m, 8H), 4.44-4.34 (m, 1.6H), 4.27-4.18 (m, 1.6H), 3.52-3.45 (m, 1H), 3.39-3.33 (m, 0.6H), 3.16-3.09 (m, 0.6H), 2.87-2.81 (m, 1H), 2.61-2.51 (m, 1H), 2.39-2.27 (m, 1.6H), 1.86 (s, 1.8H), 1.79 (s, 3H), 1.24 (d, *J* = 7.3Hz, 1H), 1.13 (d, *J*

= 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.1, 184.6, 178.5, 178.1, 169.9, 169.0, 136.4, 136.3, 130.6 (2), 128.8, 127.2, 127.1, 66.7, 42.4, 42.0, 41.2, 40.3, 24.9, 24.7 (2), 24.3, 16.3, 14. 7; HRMS (ESI) for $C_{15}H_{18}NO_3$ ([M+H]$^+$): calcd 260.1281, found 260.1285.



(*E*)-Ethyl 4-(acetylimino)-2,3-dimethyl-4-phenylbutanoate (5h, dr = 2.2:1**):** 24 h, 36.9 mg, 67% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.39 (m, 7.25H), 4.14-4.09 (m, 2.9H), 3.24-3.12 (m, 1.45H), 2.85-2.79 (m, 1.45H), 1.93 (s, 1.35H), 1.78 (s, 3H), 1.26-1.18 (m, 10H), 1.10 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 184.9, 184.4, 176.3, 175.0, 171.8, 169.7, 137.4, 137.1, 130.5, 130.4, 128.7, 128.6, 127.4, 127.1, 60.4, 44.5, 43.9, 43.1, 42.3, 25.0, 24.6, 16.7, 15.7, 15.1, 14.6, 14.2, 14.2; HRMS (ESI) for $C_{16}H_{22}NO_3$ ([M+H]$^+$): calcd 276.1594, found 276.1596.



(*E*)-Methyl 2-(4-(acetylimino)chroman-3-yl)acetate (5i): 12 h, 32.4 mg, 62% yield; Corlorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.02-6.92 (m, 2H), 4.44 (dd, *J* = 11.7, 3.0 Hz, 1H), 4.30 (dd, *J* = 11.6, 2.5 Hz, 1H), 3.70 (s, 3H), 3.21-3.17 (m, 1H), 2.73 (d, *J* = 7.4 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 185.5, 171.3, 158.9 (2C), 134.4, 127.3, 121.7, 117.8, 68.3, 52.0, 36.8, 32.6, 25.5; HRMS (ESI) for $C_{14}H_{16}NO_4$ ([M+H]$^+$): calcd 262.1074, found 262.1078.

(C) References

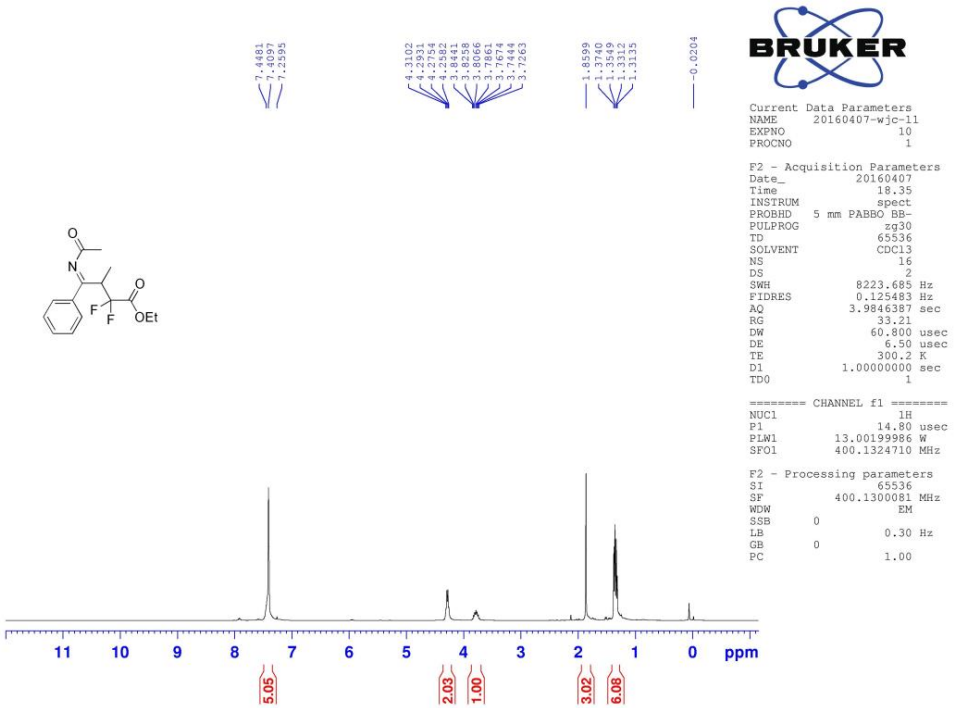
[1] (*a*) M. J. Burk, G. Casy, N. B. Johnson, *J. Org. Chem*. 1998, **63**, 6084; (*b*) M. Berg, R. M. Haak, A. J. Minnaard, A. H. M. Vries, J. G. Vries, B. L. Feringa, *Adv. Synth. Catal.* 2002, **344**, 1003; (*c*) H. Kiyohara, R. Matsubara, S. Kobayashi, *Org. Lett.* 2006, **8**, 5333; (*d*) M. Terada, K. Soga, N. Momiyama, *Angew. Chem. Int. Ed*. 2008, **47**, 4122; (*e*) Z.-H. Guan, Z.-Y. Zhang, Z.-H. Ren, Y.-Y. Wang, X. Zhang, *J. Org. Chem.* 2011, **76**, 339; (*f*) T. Sun, G. Hou, M. Ma, X. Zhang, *Adv. Synth. Catal.* 2011, **353**, 253; (*g*) J. T. Reeves, Z. Tan, Z. S. Han, G. Li, Y. Zhang, Y. Xu, D. C. Reeves, N. C. Gonnella, S. Ma, H. Lee, B. Z. Lu, C. H. Senanayake, *Angew. Chem. Int. Ed*. 2012, **51**, 1400.

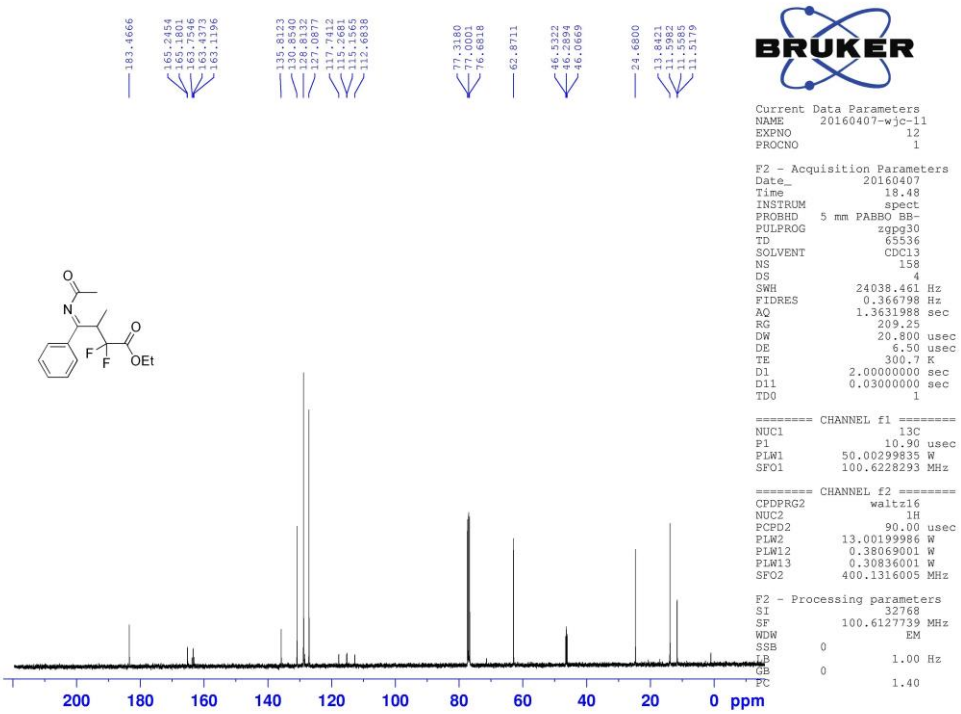
[2] (*a*) H. Morimoto, R. Fujiwara, Y. Shimuzu, K. Morisaki, T. Ohshima, *Org. Lett.* 2014, **16**, 2018; (*b*) L. Wang, X. Wei, W. Jia, J. Zhong, Li. Wu, Q. Liu, *Org. Lett.* 2014, **16**, 5842.

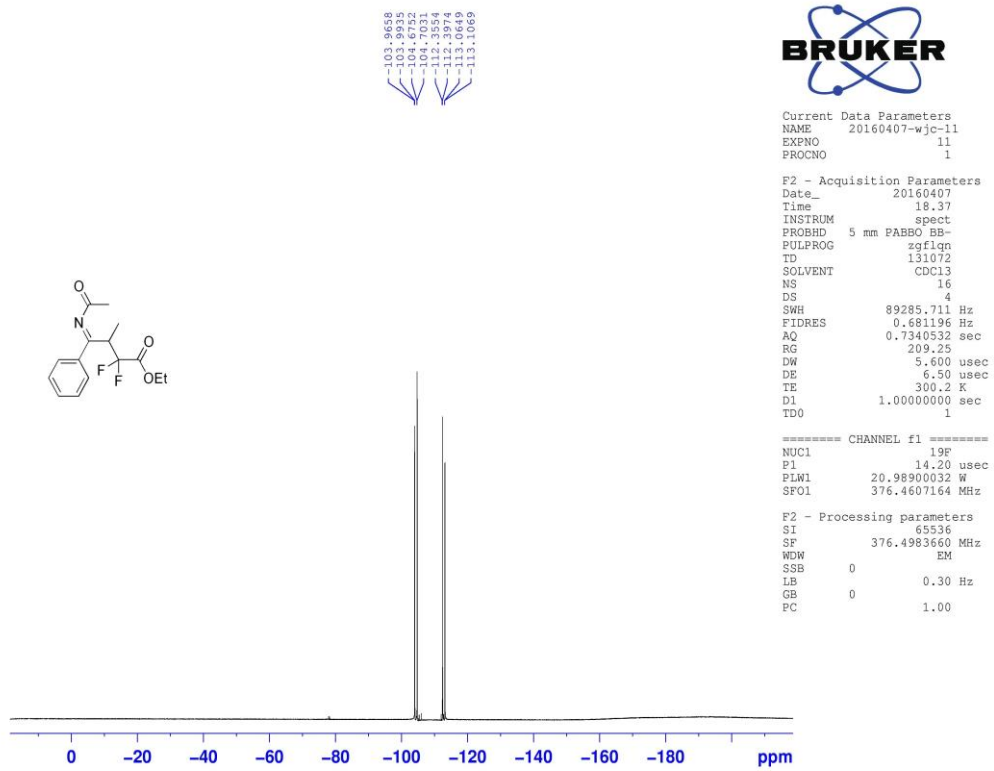
[3] F. Zhang, Q.-Q. Min, X. Zhang, *Synthesis* 2015, **19**, 2912.

(D) Spectra

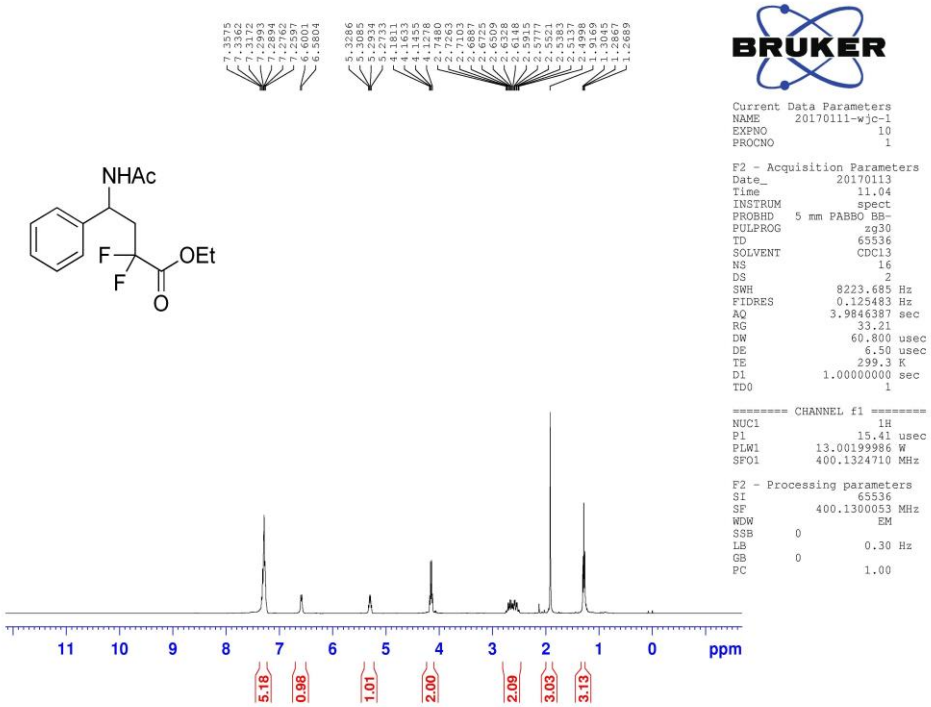
(*E*)-Ethyl 4-(acetylimino)-2,2-difluoro-3-methyl-4-phenylbutanoate (3a)

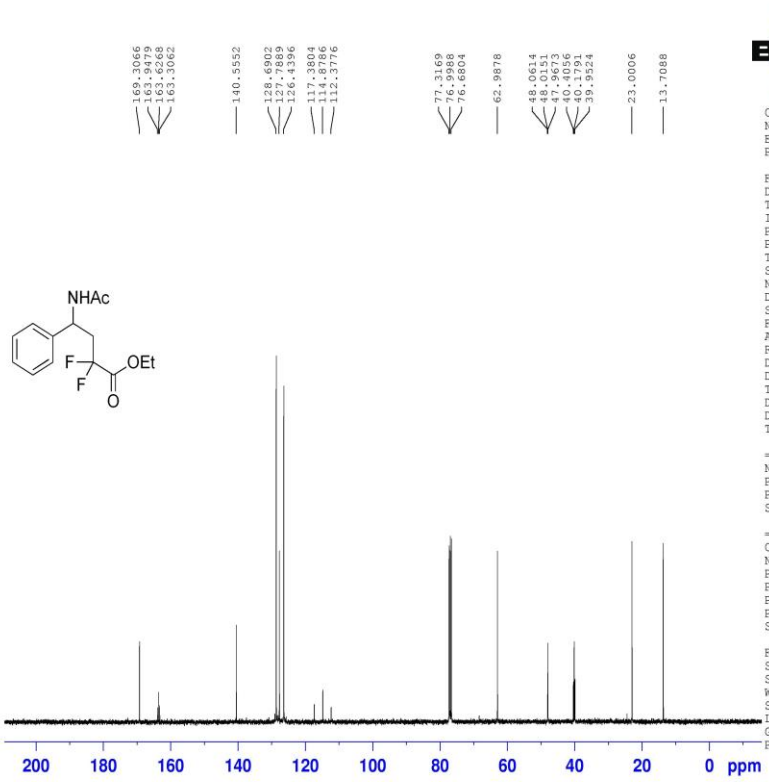






Ethyl 4-acetamido-2,2-difluoro-4-phenylbutanoate (3b)



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DE                6.50 usec
TE                299.3 K
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D11           0.03000000 sec
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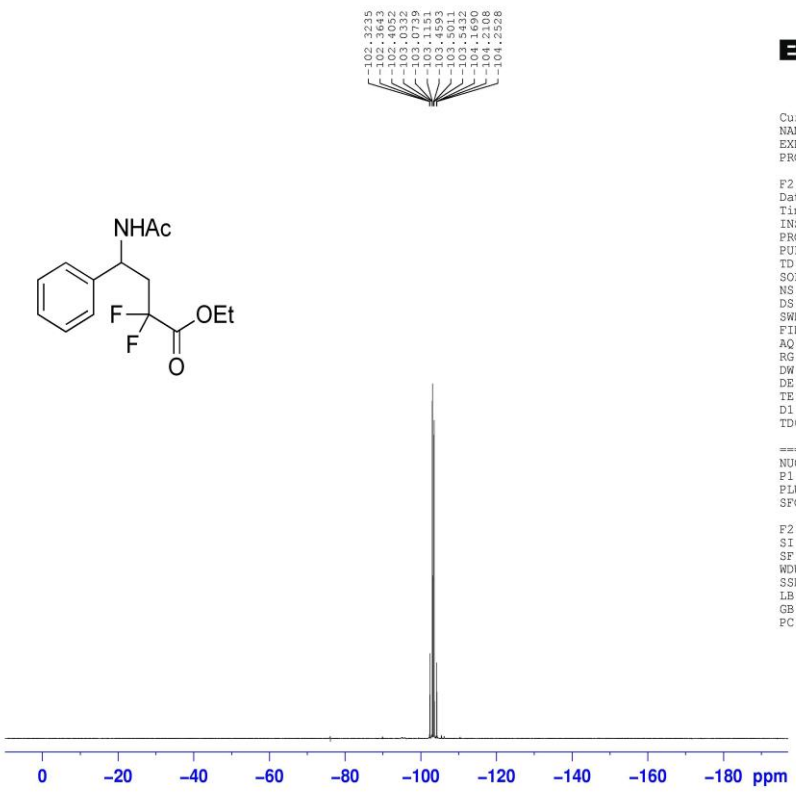


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TE                299.3 K
D1            1.00000000 sec
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F2 - Processing parameters
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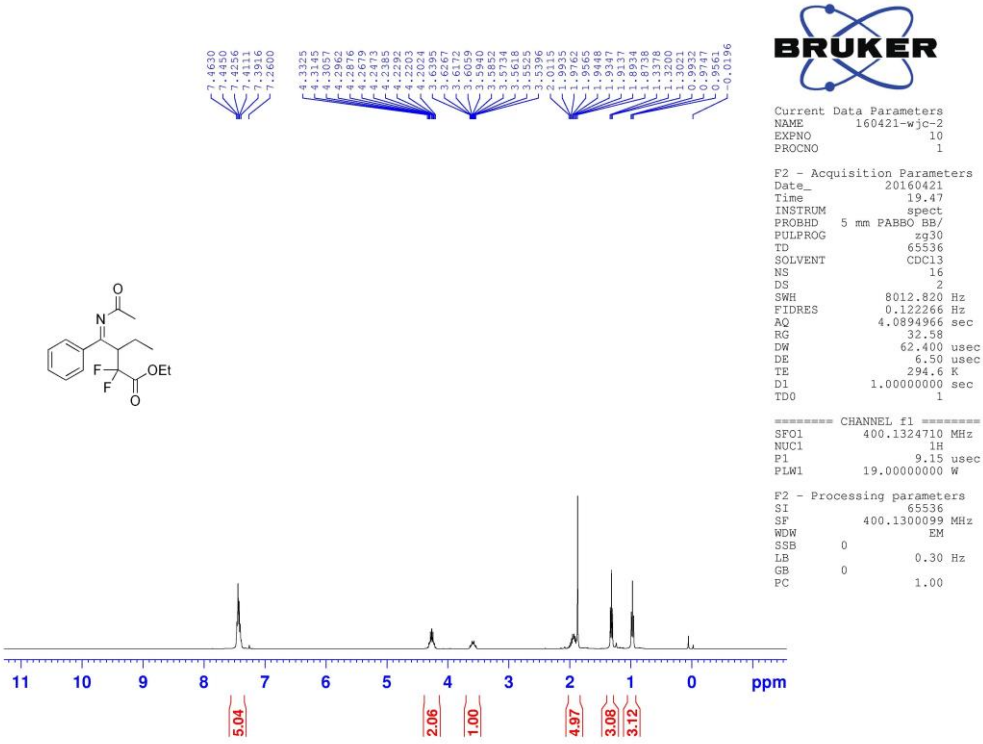
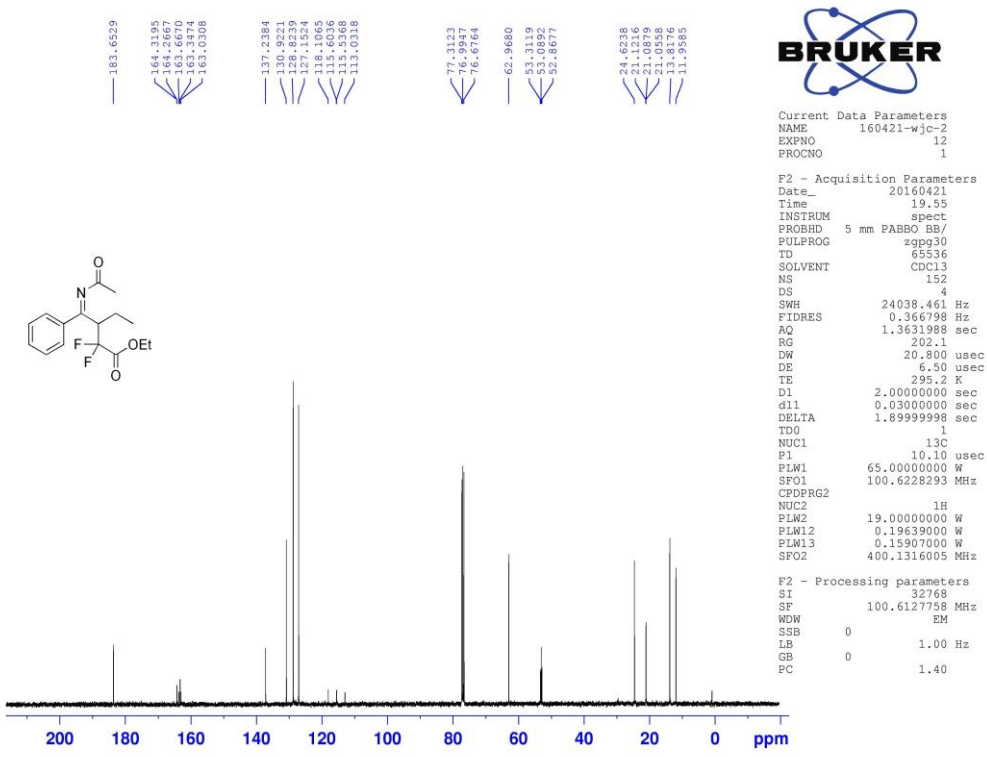
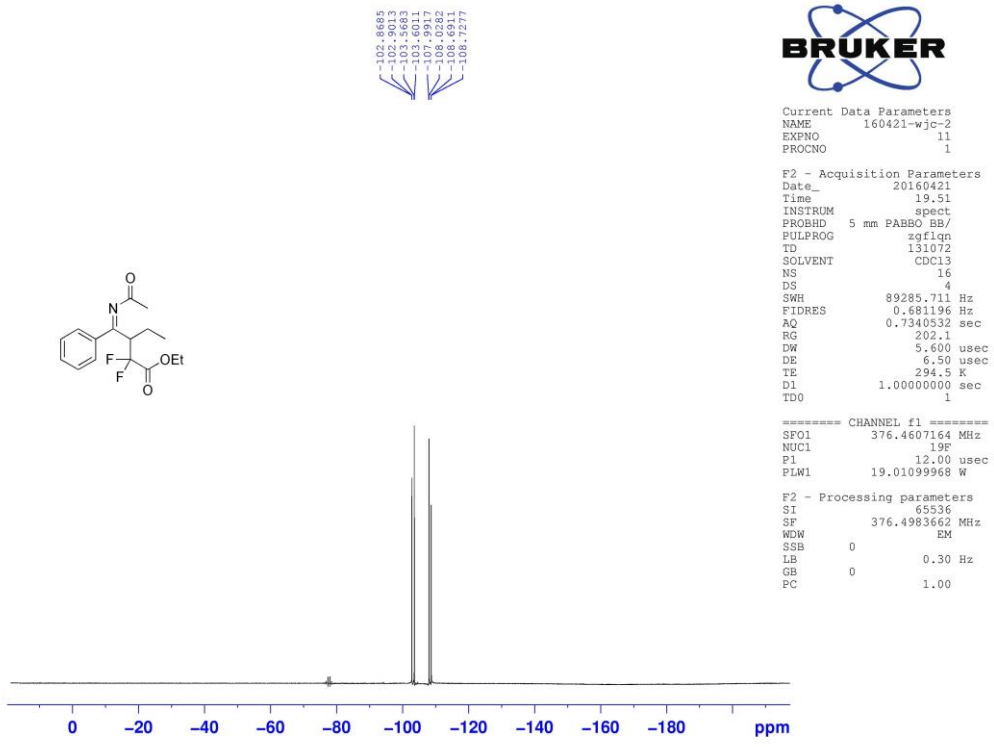
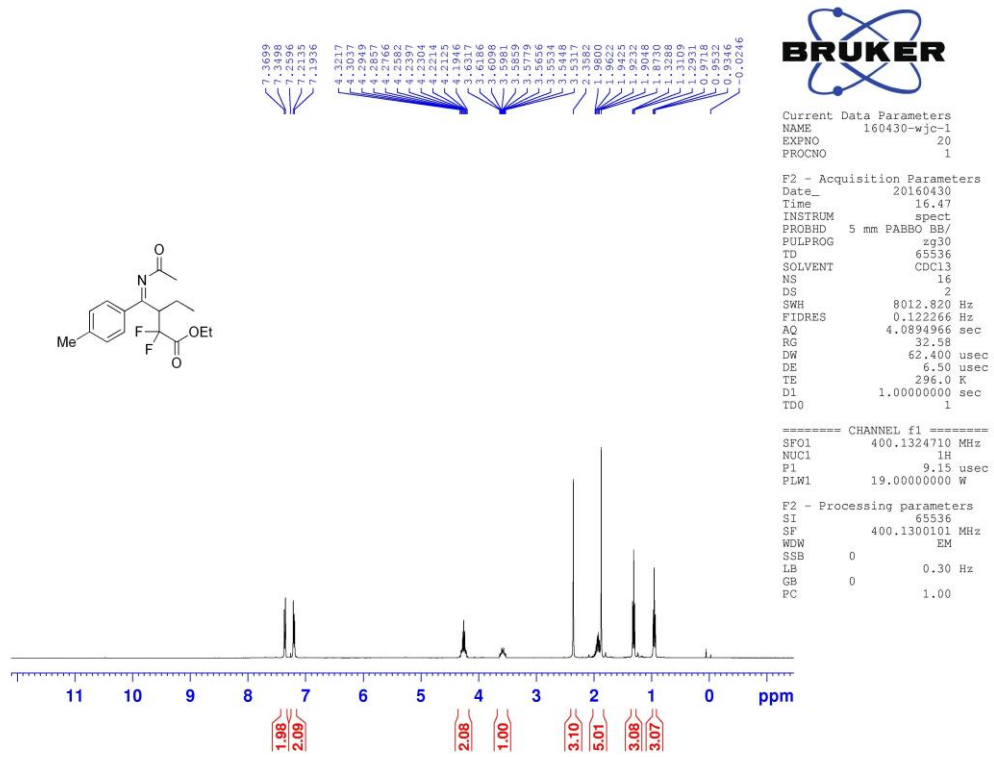
(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluoropentanoate (3c)

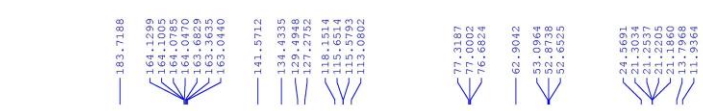


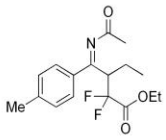


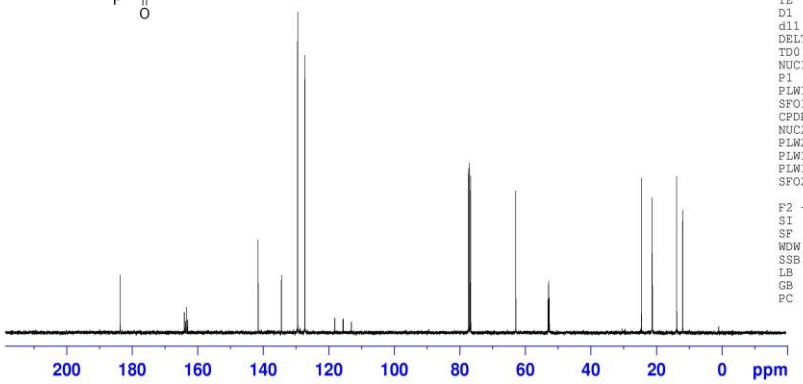


(*E*)-Ethyl 3-((acetylimino)(p-tolyl)methyl)-2,2-difluoropentanoate (3d)









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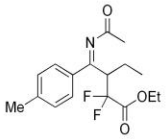

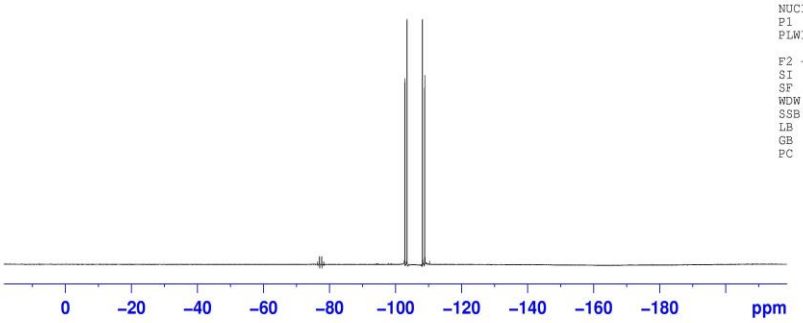

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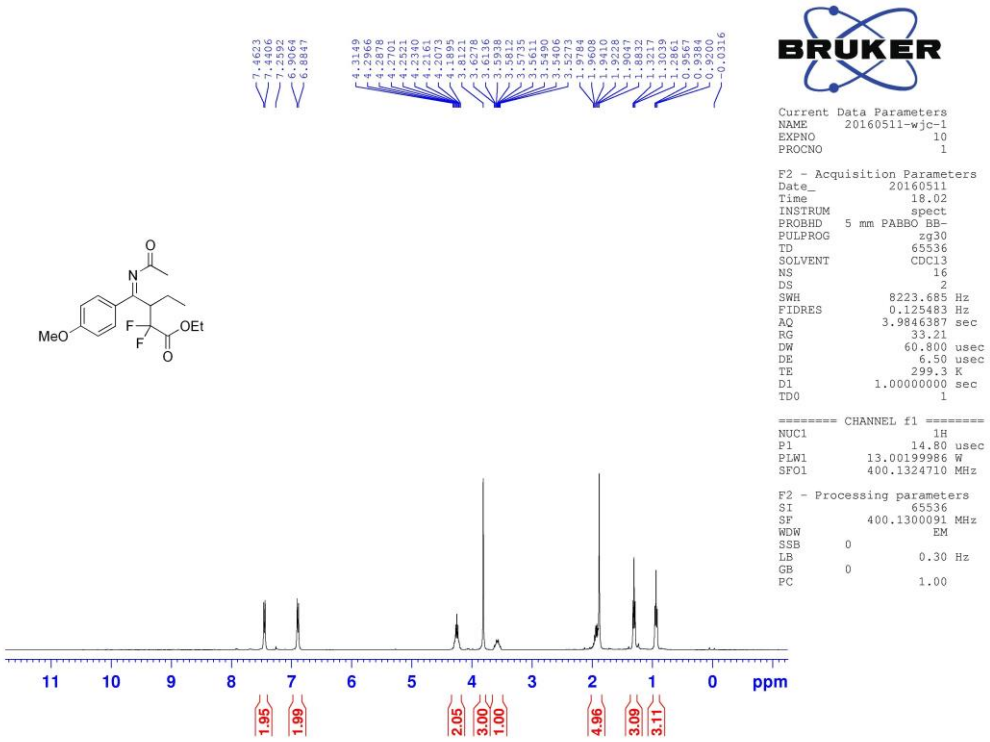
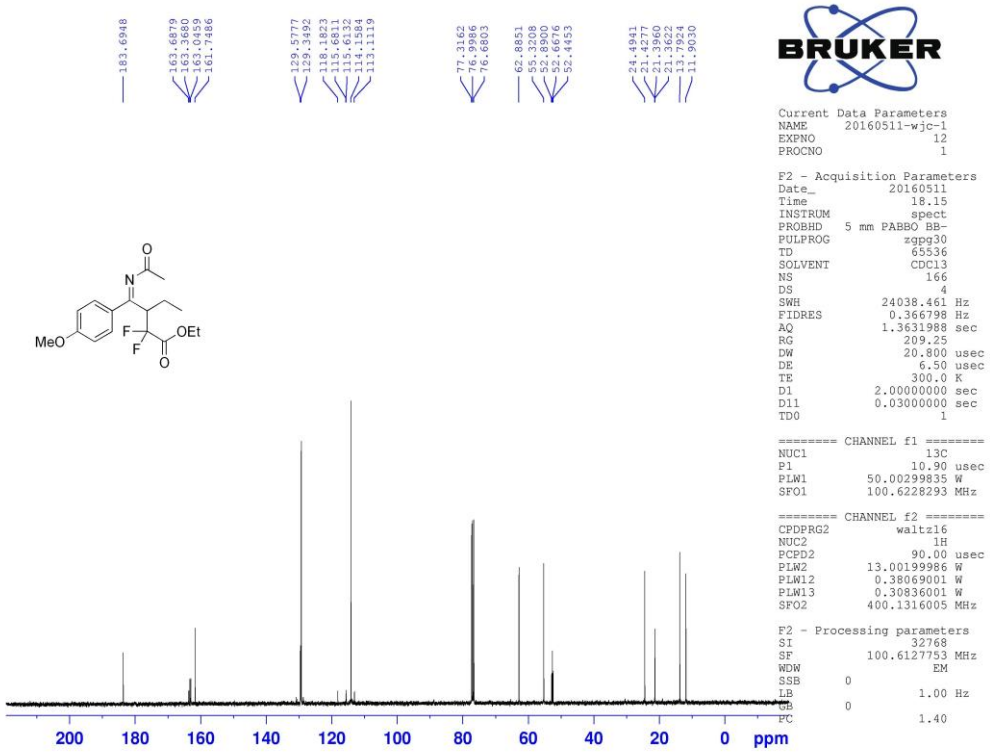
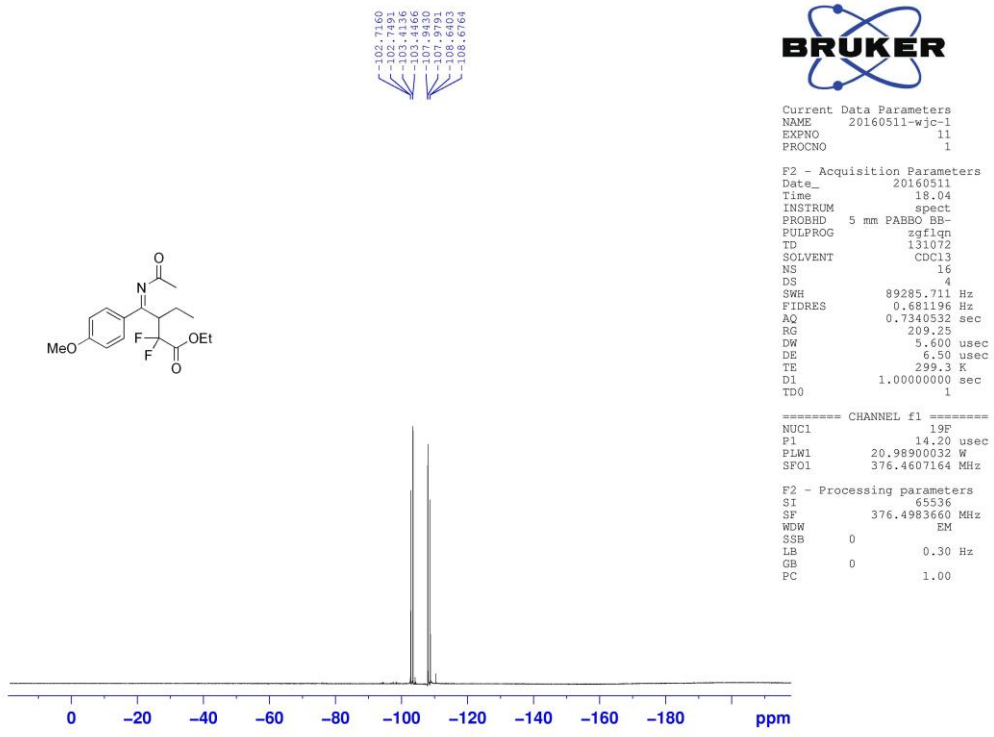
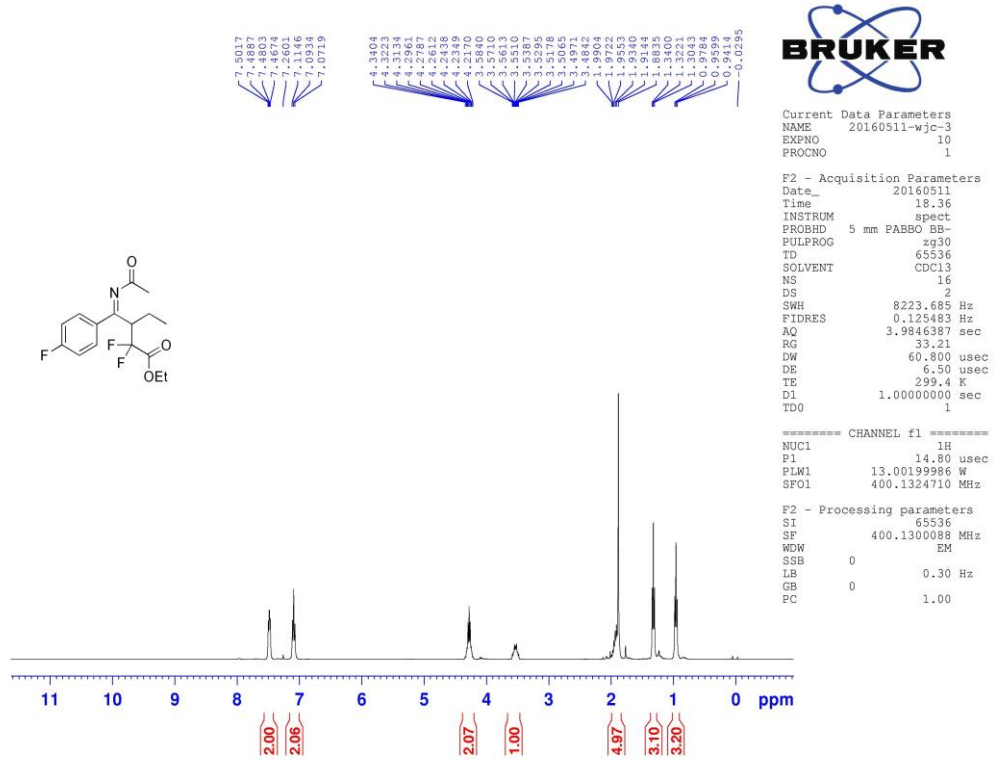
(*E*)-Ethyl 3-((acetylimino)(4-methoxyphenyl)methyl)-2,2-difluoropentanoate (3e)

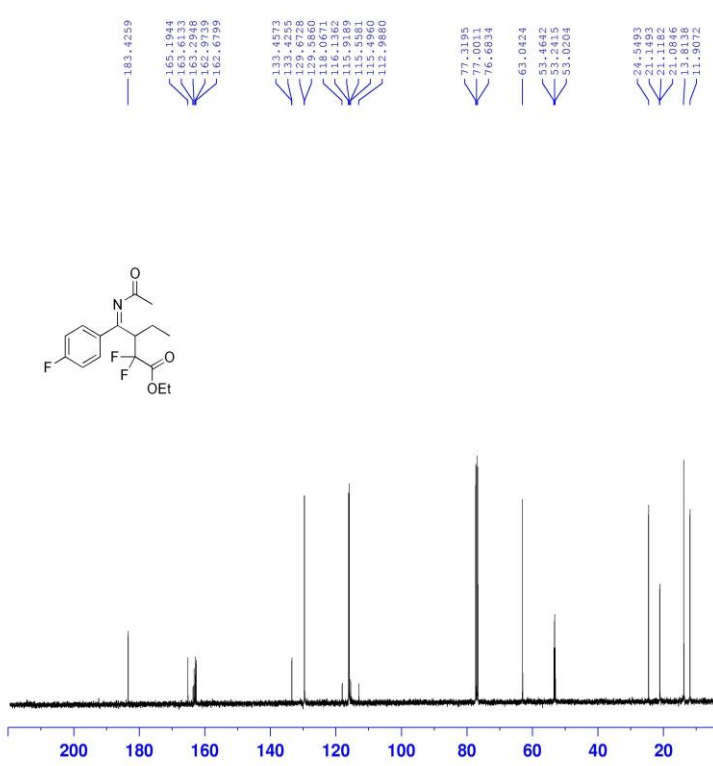






(*E*)-Ethyl 3-((acetylimino)(4-fluorophenyl)methyl)-2,2-difluoropentanoate (3f)



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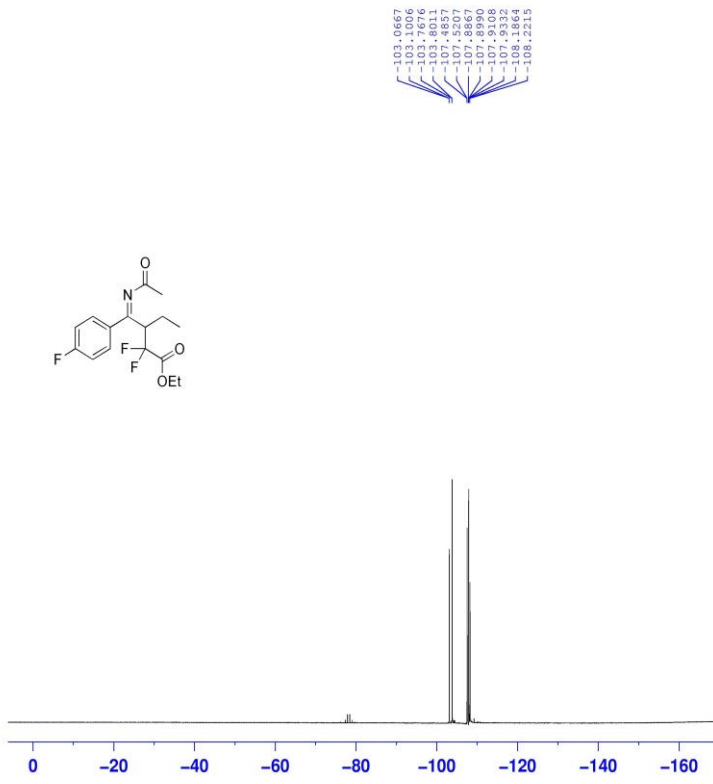
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                209.25
DW                20.800 usec
DE                 6.50 usec
TE                300.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.90 usec
PLW1         50.00299835 W
SFO1        100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PLW2         13.00199986 W
PLW12         0.38069001 W
PLW13         0.30836001 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127731 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



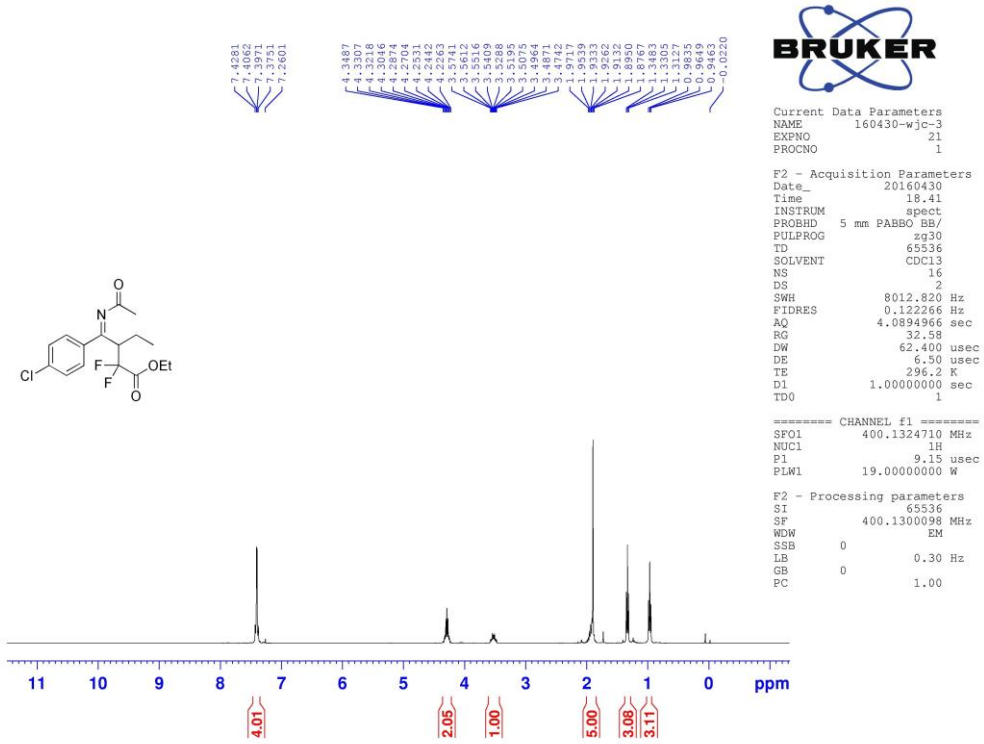

```
Current Data Parameters
NAME      20160511-wjc-3
EXPNO                 11
PROCNO                 1

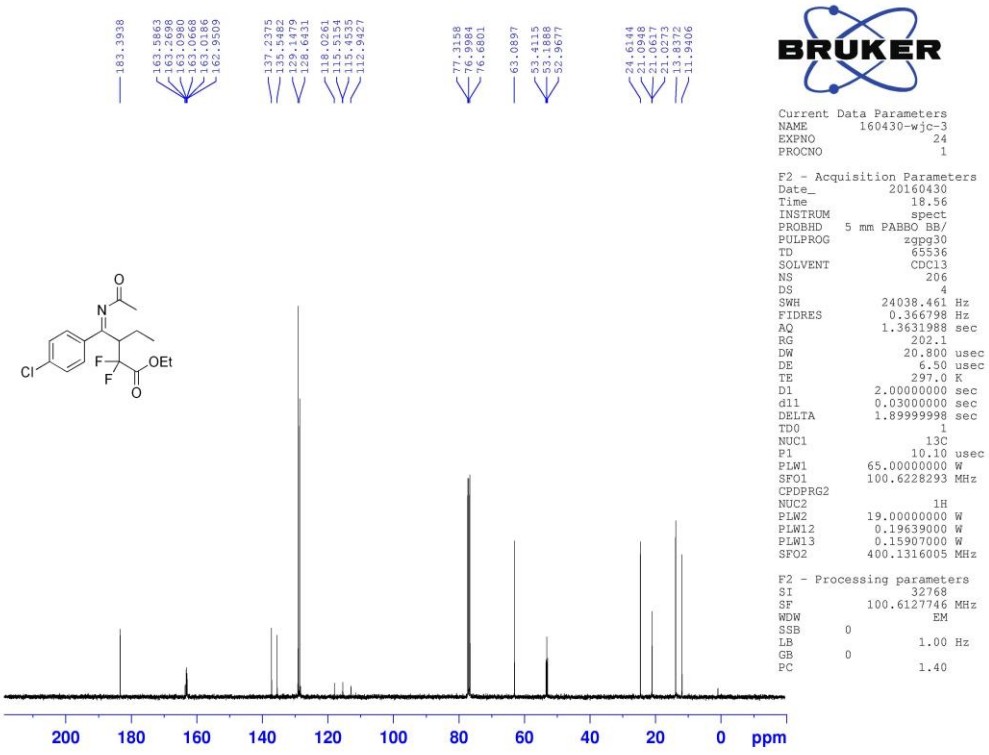
F2 - Acquisition Parameters
Date_           20160511
Time              18.38
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgflqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ             0.7340532 sec
RG                209.25
DW                 5.600 usec
DE                 6.50 usec
TE                299.4 K
D1            1.00000000 sec
TD0                   1

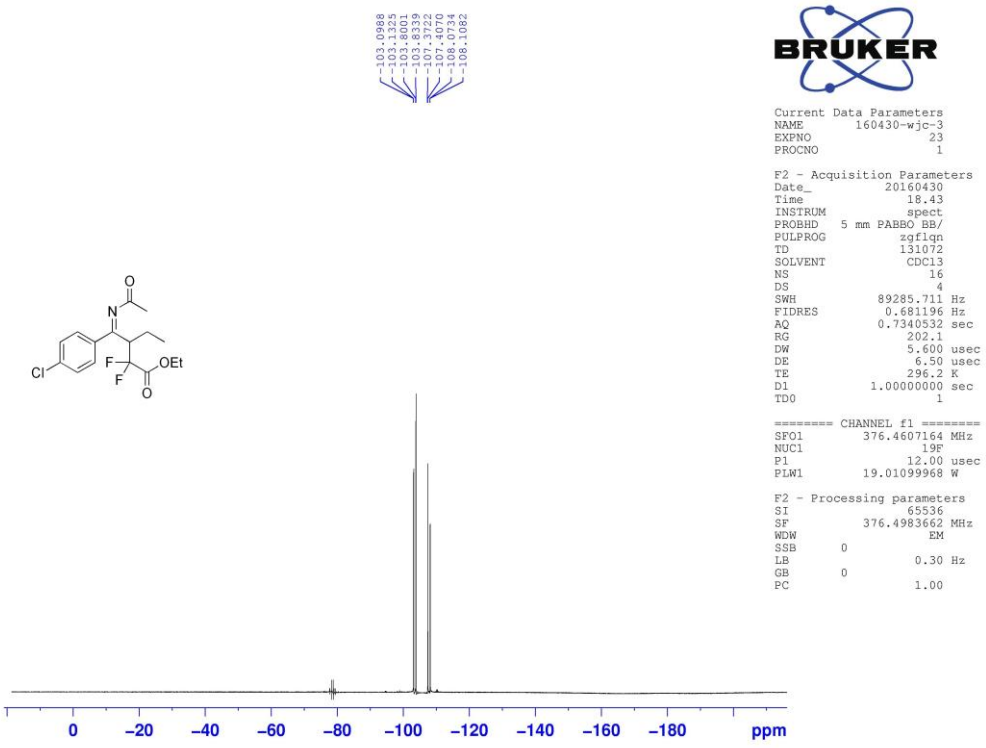
======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PLW1         20.98900032 W
SFO1        376.4607164 MHz

F2 - Processing parameters
SI                65536
SF          376.4983660 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

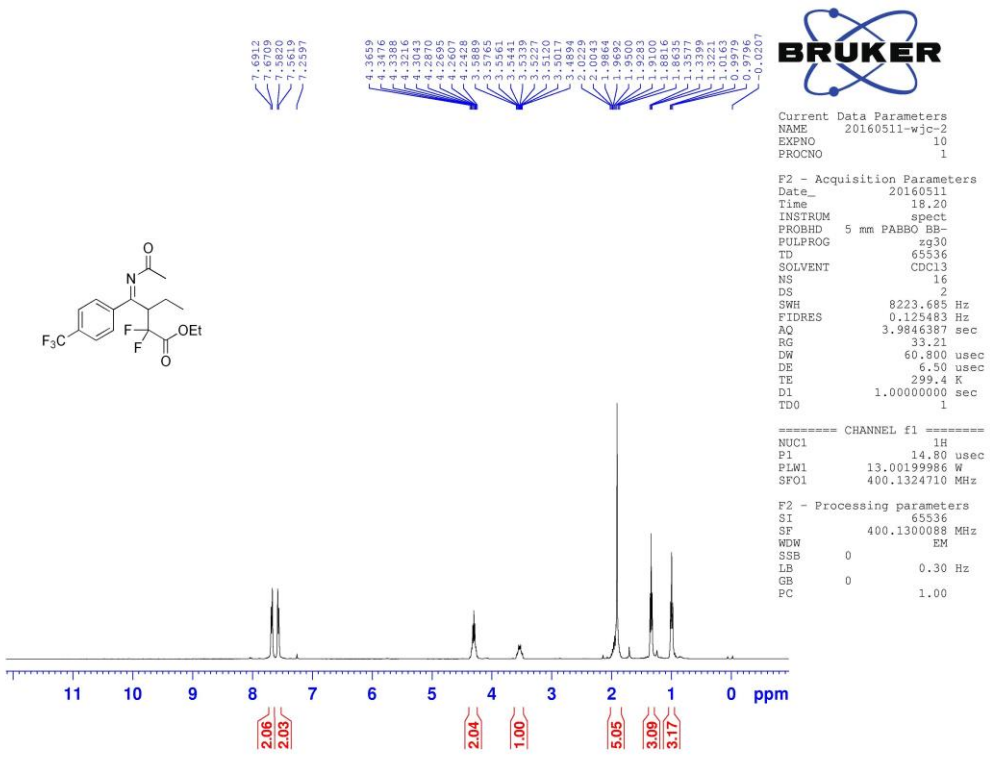
(*E*)-Ethyl 3-((acetylimino)(4-chlorophenyl)methyl)-2,2-difluoropentanoate (3g)

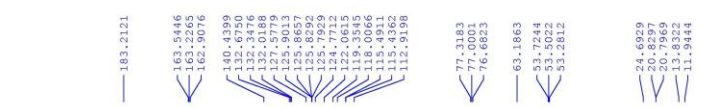


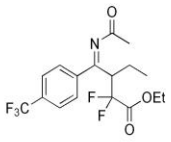


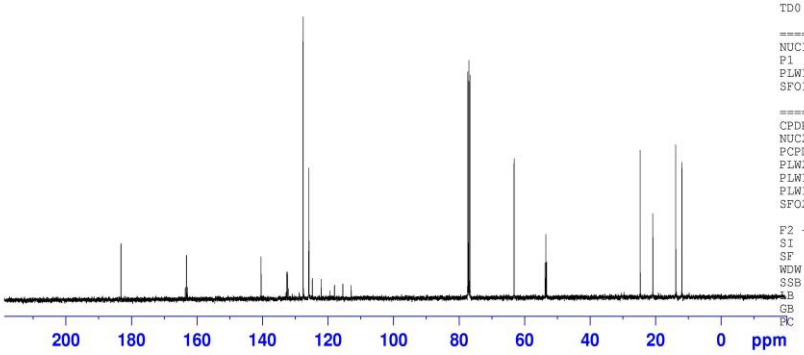


(*E*)-Ethyl 3-((acetylimino)(4-(trifluoromethyl)phenyl)methyl)-2,2-difluoropentanoate (3h)









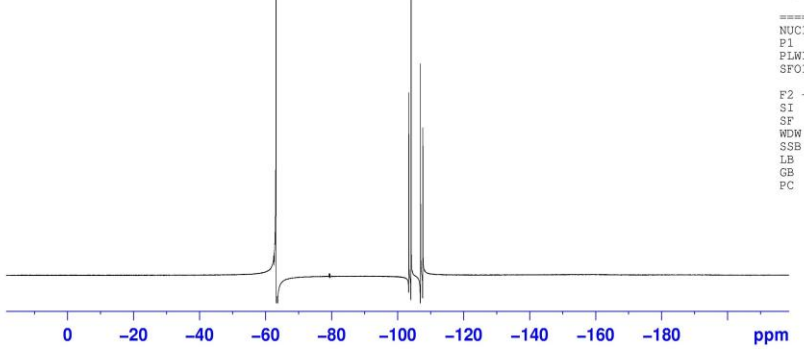

```
Current Data Parameters
NAME      20160511-wjc-2
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160511
Time               18.32
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  166
DS                    4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG               209.25
DW               20.800 usec
DE                6.50 usec
TE               300.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.90 usec
PLW1        50.00299835 W
SFO1       100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PLW2        13.00199986 W
PLW12        0.38069001 W
PLW13        0.30836001 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF         100.6127710 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



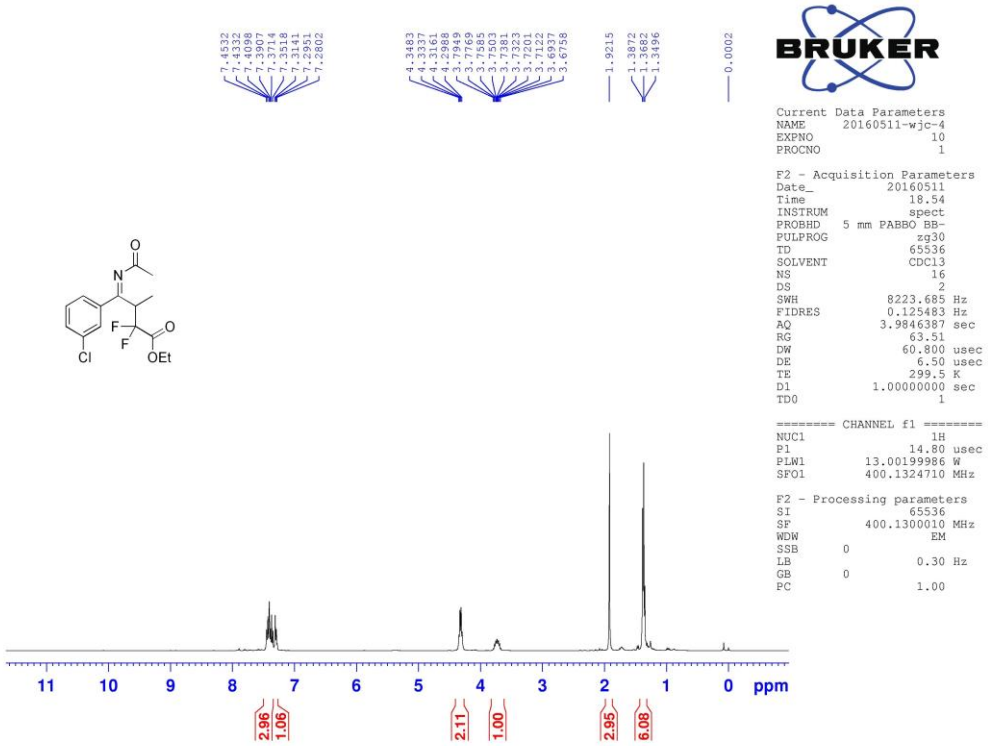

```
Current Data Parameters
NAME      20160511-wjc-2
EXPNO                 11
PROCNO                 1

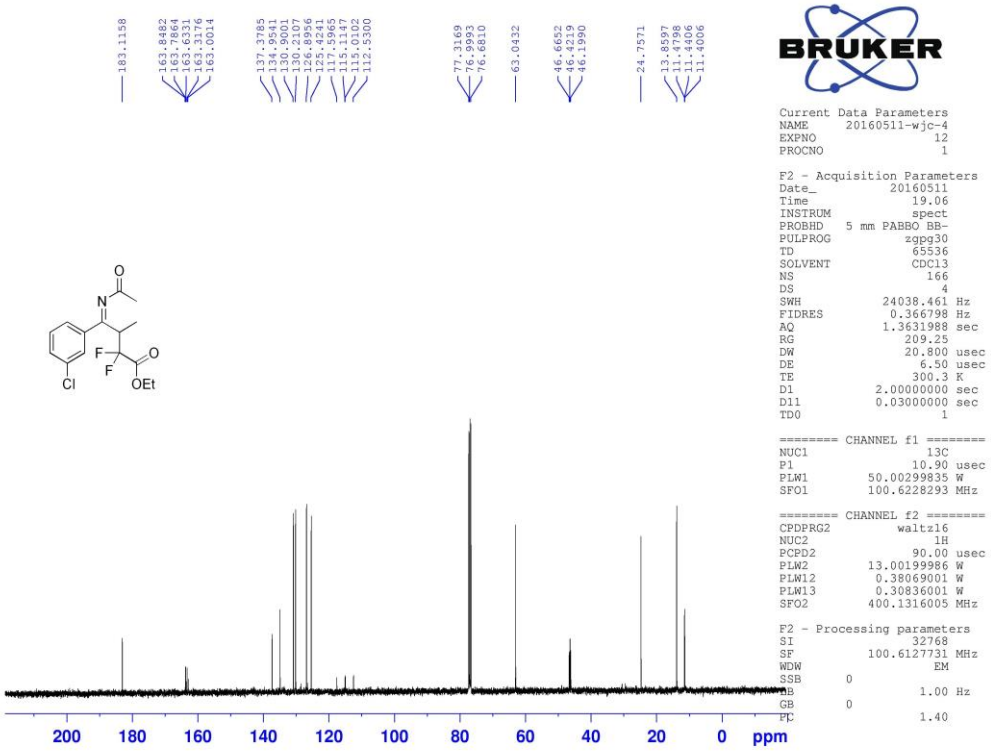
F2 - Acquisition Parameters
Date_           20160511
Time               18.21
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgflqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES        0.681196 Hz
AQ            0.7340532 sec
RG               209.25
DW                5.600 usec
DE                6.50 usec
TE               299.3 K
D1           1.00000000 sec
TD0                   1

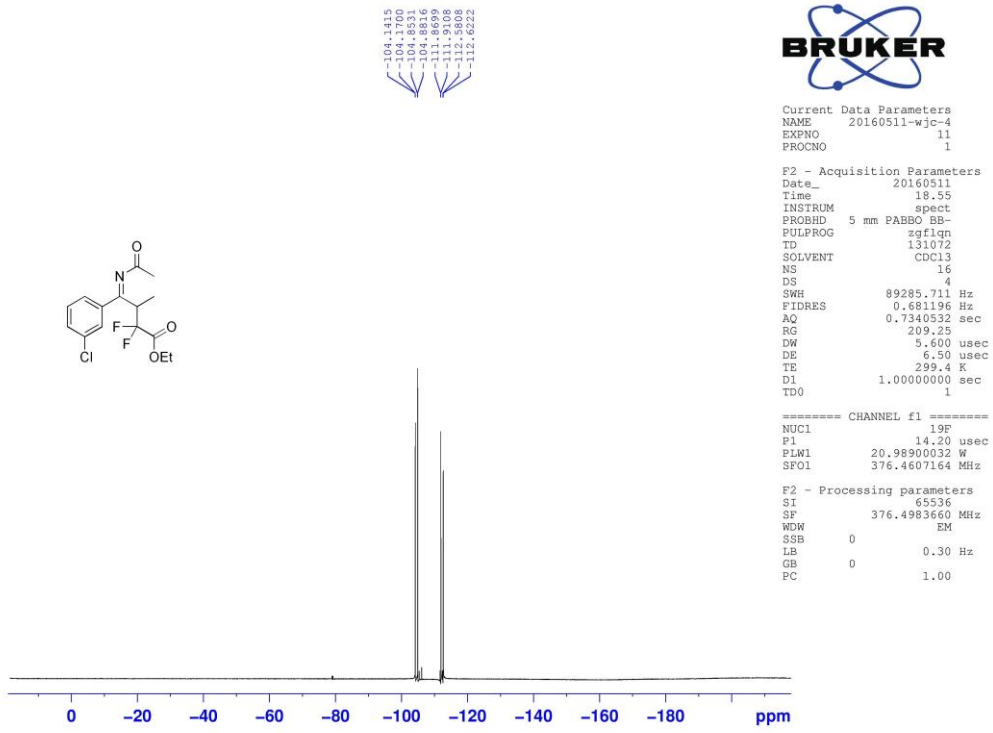
======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PLW1        20.98900032 W
SFO1       376.4607164 MHz

F2 - Processing parameters
SI                65536
SF         376.4983660 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

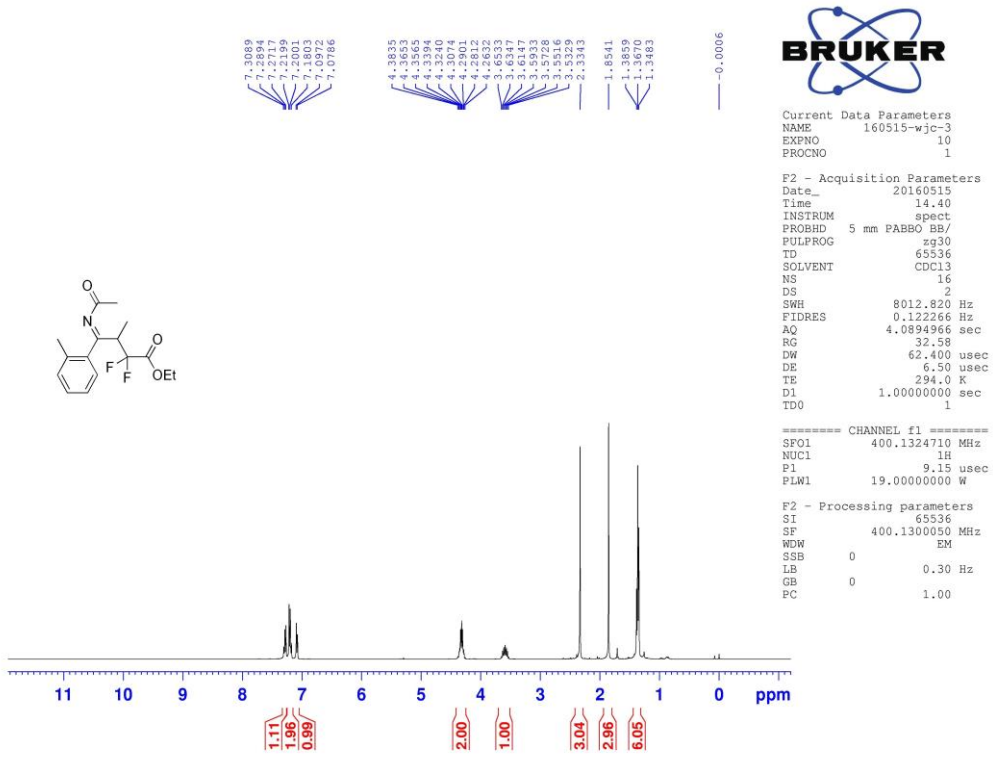
(*E*)-Ethyl 4-(acetylimino)-4-(3-chlorophenyl)-2,2-difluoro-3-methylbutanoate (3i)

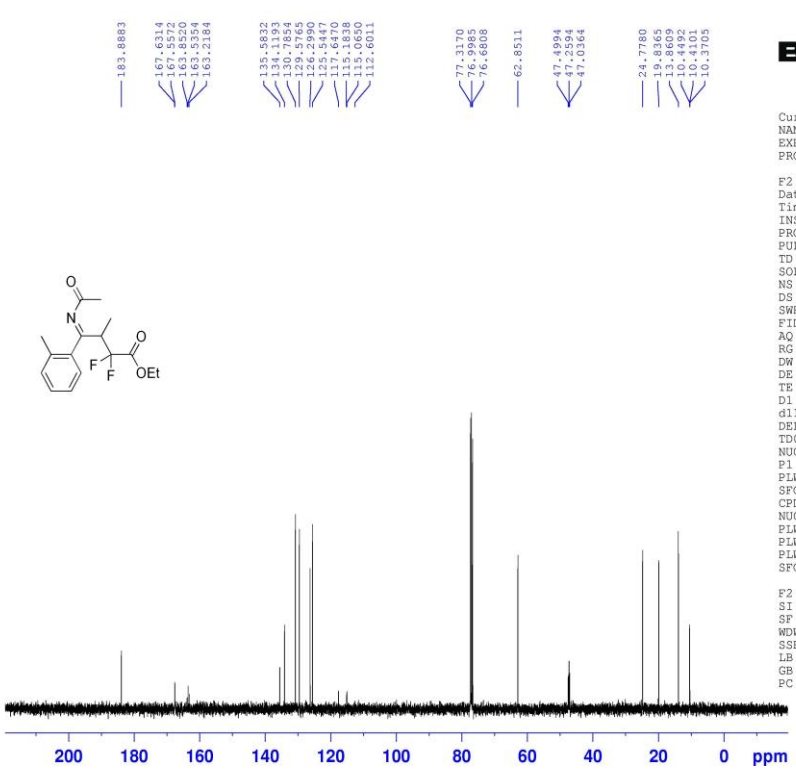






(*E*)-Ethyl 4-(acetylimino)-2,2-difluoro-3-methyl-4-(o-tolyl)butanoate (3j)



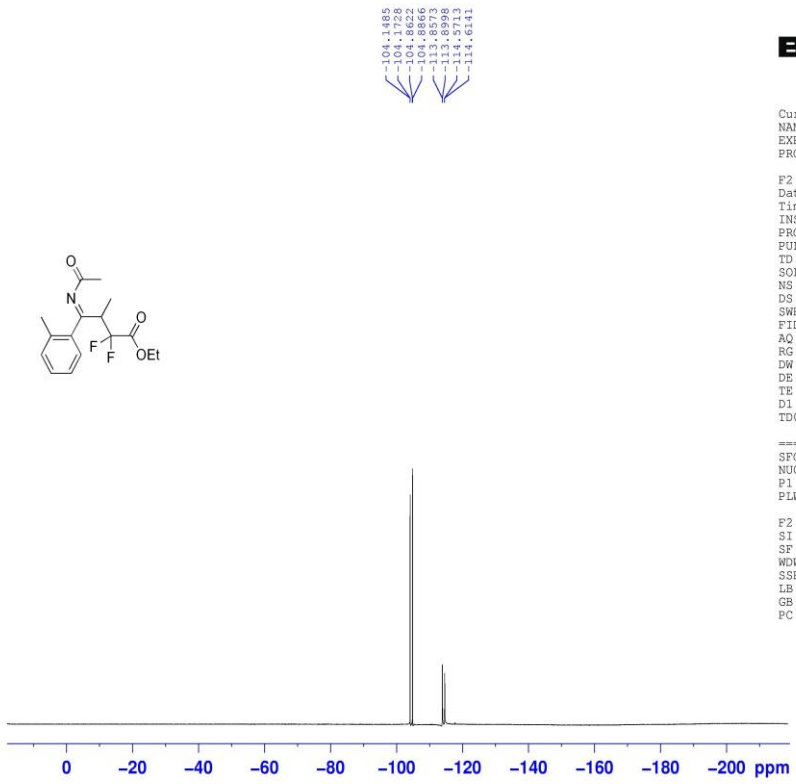


BRUKER

```
Current Data Parameters
NAME        160515-wjc-3
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160515
Time               14.47
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  161
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                202.1
DW               20.800 usec
DE                6.50 usec
TE                294.6 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1
NUC1                 13C
P1                10.10 usec
PLW1         65.00000000 W
SFO1        100.6228293 MHz
CPDPRG2
NUC2                  1H
PLW2         19.00000000 W
PLW12         0.19639000 W
PLW13         0.15907000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6127755 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



BRUKER

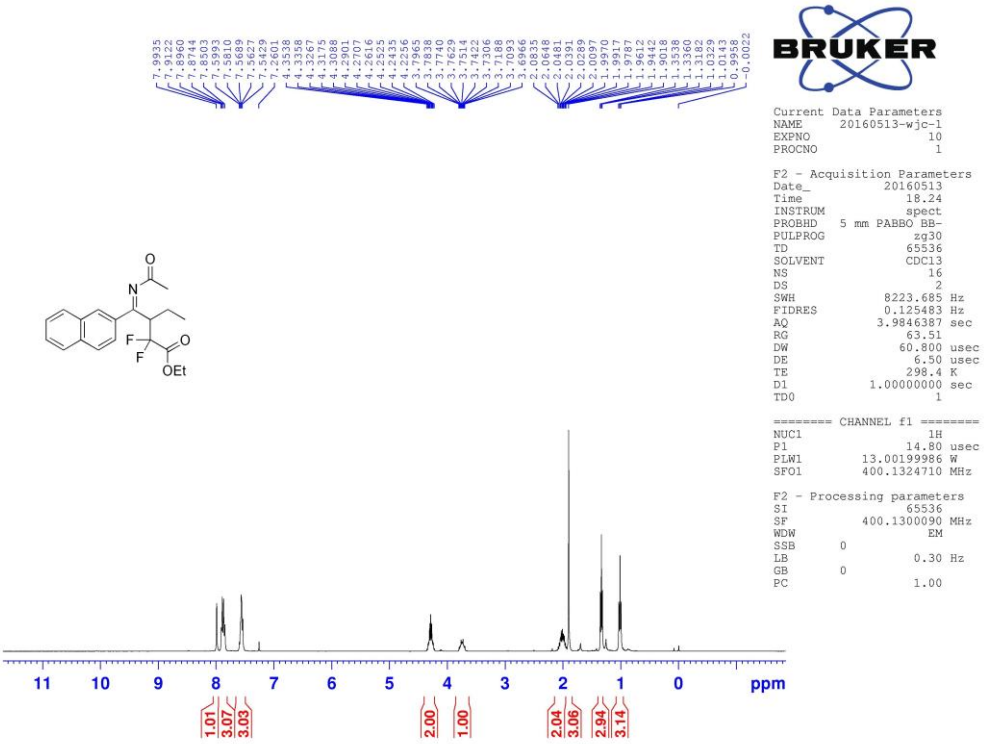
```
Current Data Parameters
NAME        160515-wjc-3
EXPNO                 11
PROCNO                 1

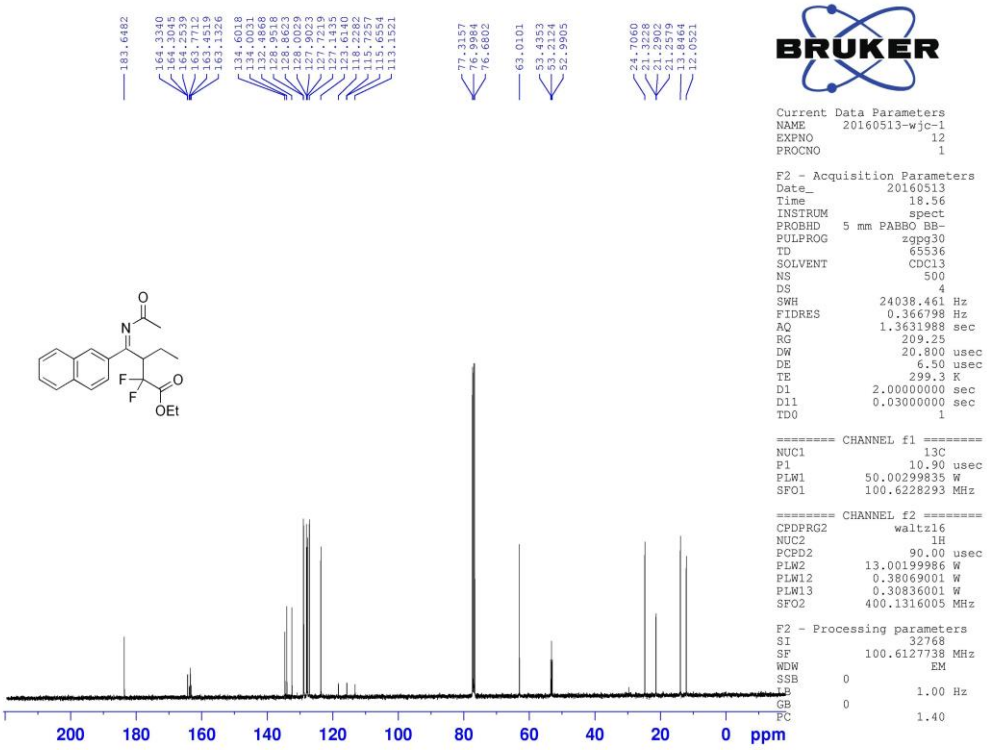
F2 - Acquisition Parameters
Date_           20160515
Time               14.44
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ             0.7340532 sec
RG                202.1
DW               5.600 usec
DE                6.50 usec
TE                294.0 K
D1            1.00000000 sec
TD0                   1

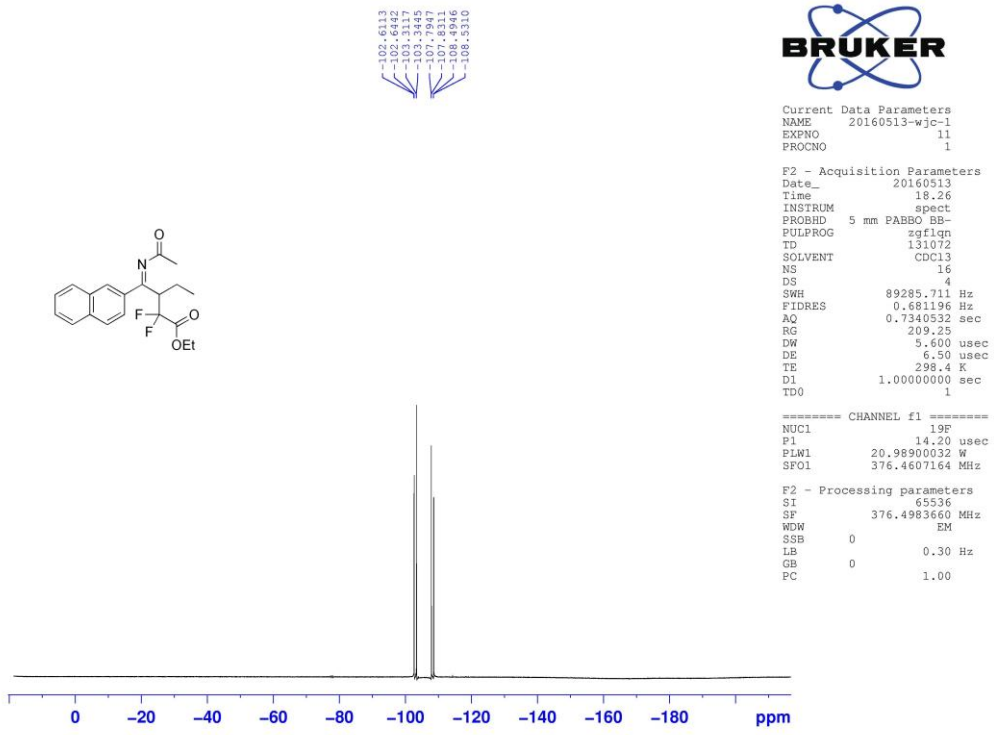
======== CHANNEL f1 ========
SFO1        376.4607164 MHz
NUC1                 19F
P1                12.00 usec
PLW1         19.01099968 W

F2 - Processing parameters
SI                65536
SF           376.4983662 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

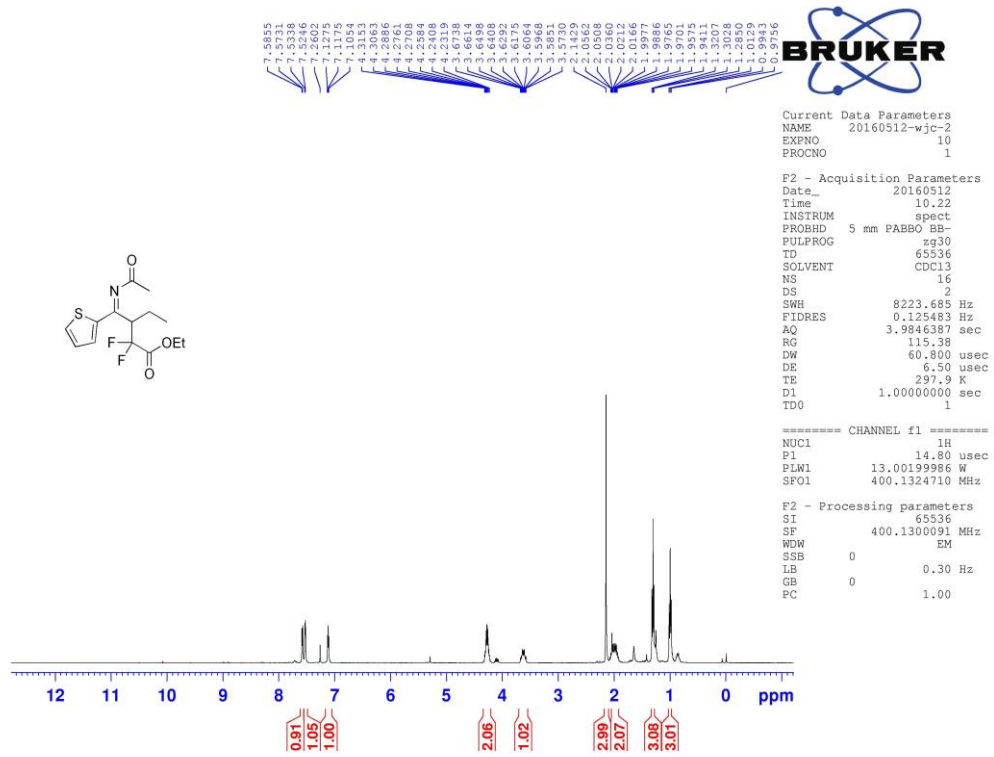
(*E*)-Ethyl 3-((acetylimino)(naphthalen-2-yl)methyl)-2,2-difluoropentanoate (3k)

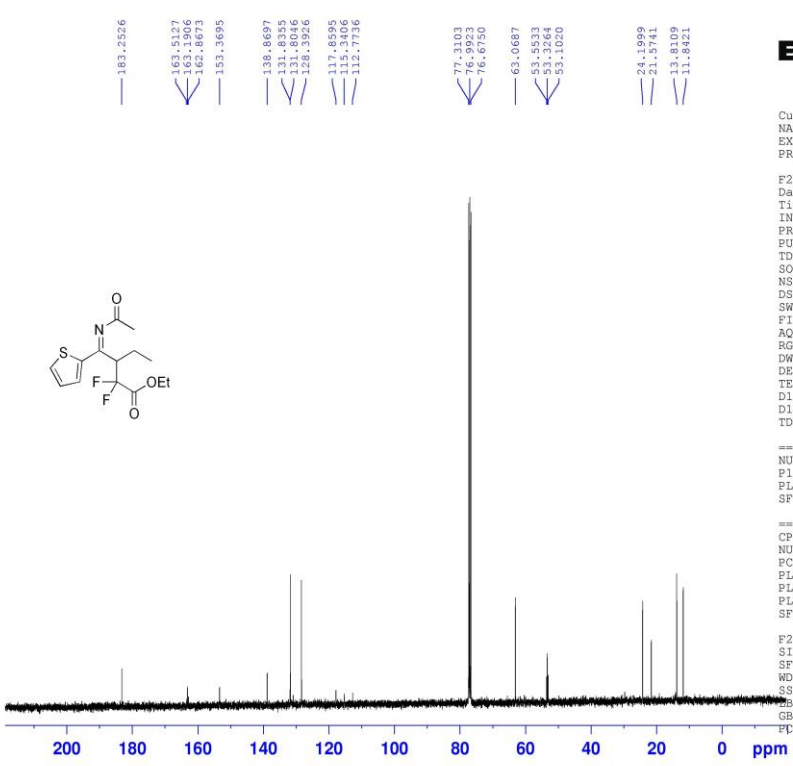






(*E*)-Ethyl 3-((acetylimino)(thiophen-2-yl)methyl)-2,2-difluoropentanoate (3l)





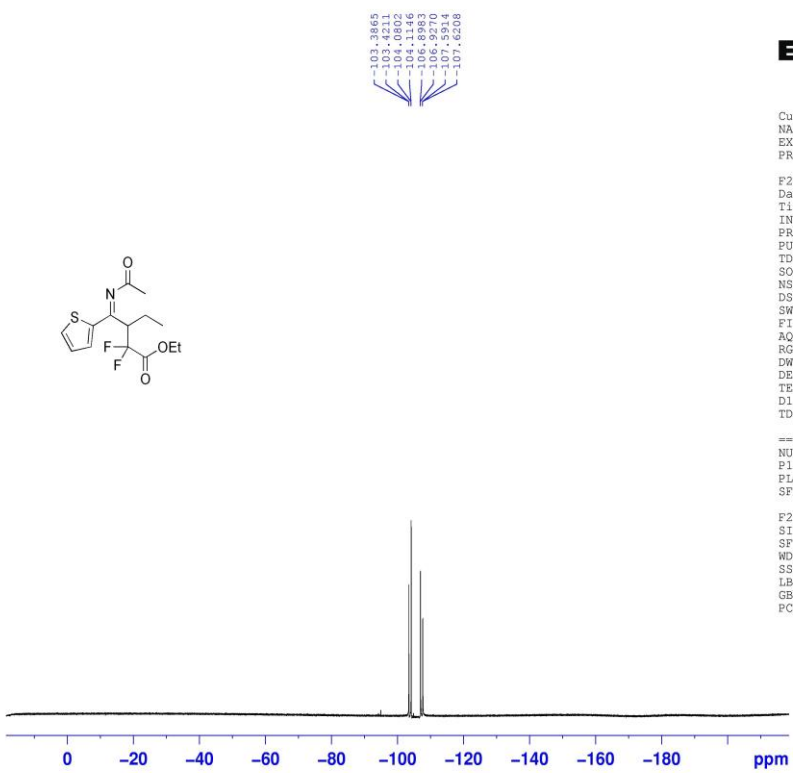
Current Data Parameters
NAME 20160512-wjc-2
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160512
Time 10.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 209.25
DW 20.800 usec
DE 6.50 usec
TE 298.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.90 usec
PLW1 50.00299835 W
SFO1 100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 13.00199986 W
PLW12 0.38069001 W
PLW13 0.30836001 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127719 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



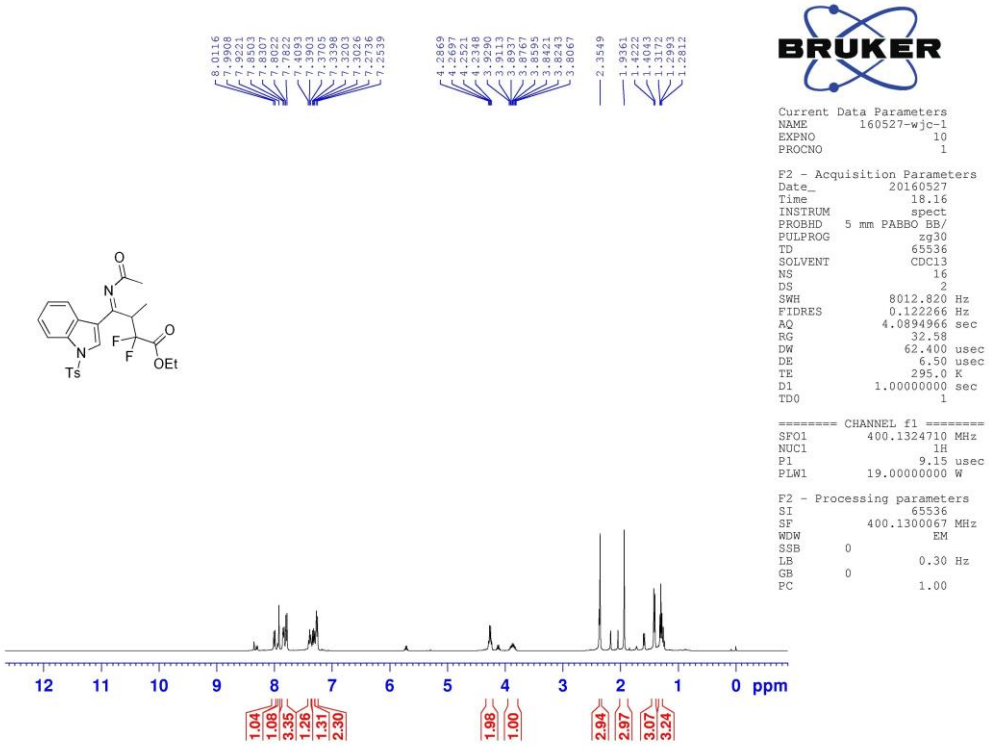
Current Data Parameters
NAME 20160512-wjc-2
EXPNO 11
PROCNO 1

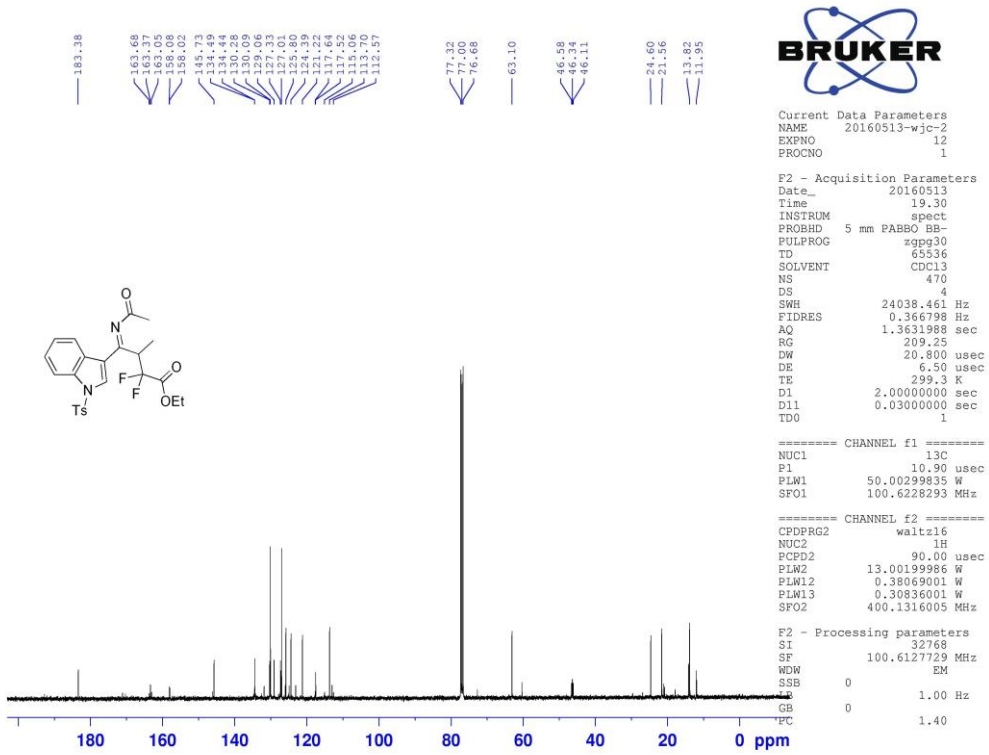
F2 - Acquisition Parameters
Date_ 20160512
Time 10.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 209.25
DW 5.600 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1

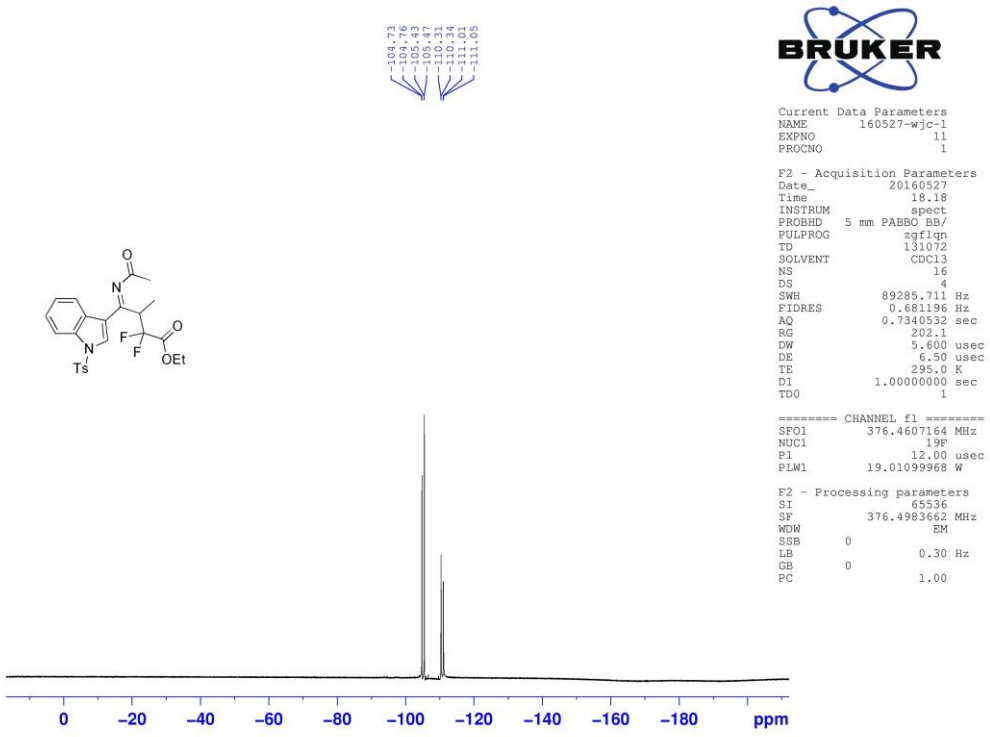
======== CHANNEL f1 ========
NUC1 19F
P1 14.20 usec
PLW1 20.98900032 W
SFO1 376.4607164 MHz

F2 - Processing parameters
SI 65536
SF 376.4983660 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

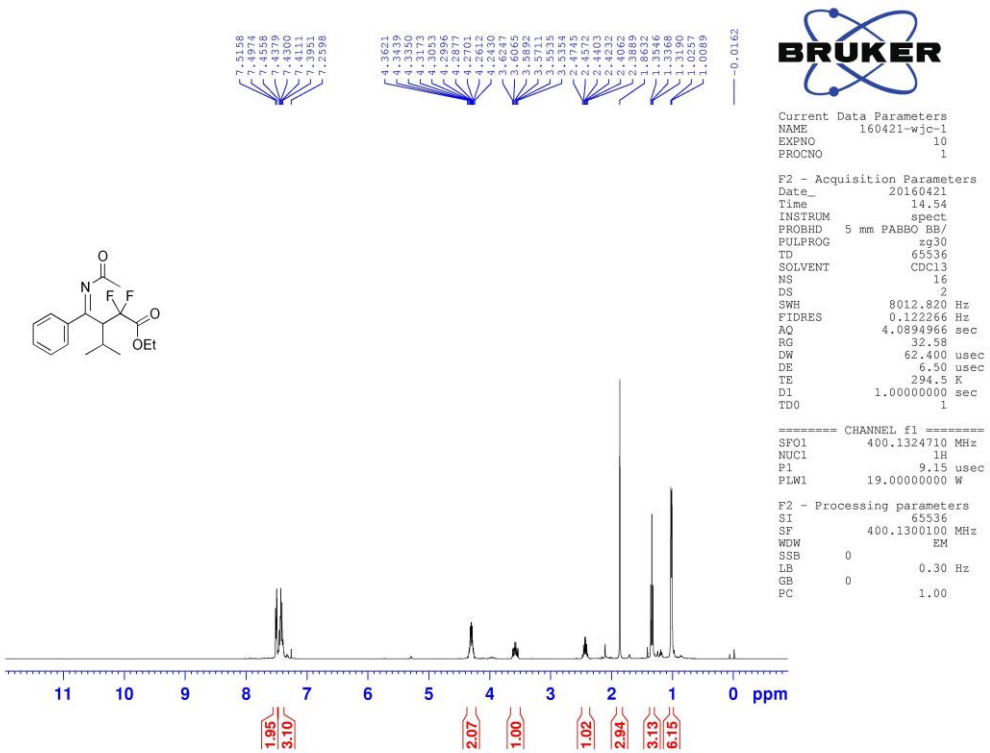
(*E*)-Ethyl 4-(acetylimino)-2,2-difluoro-3-methyl-4-(1-tosyl-1H-indol-3-yl)butanoate (3m)

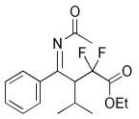


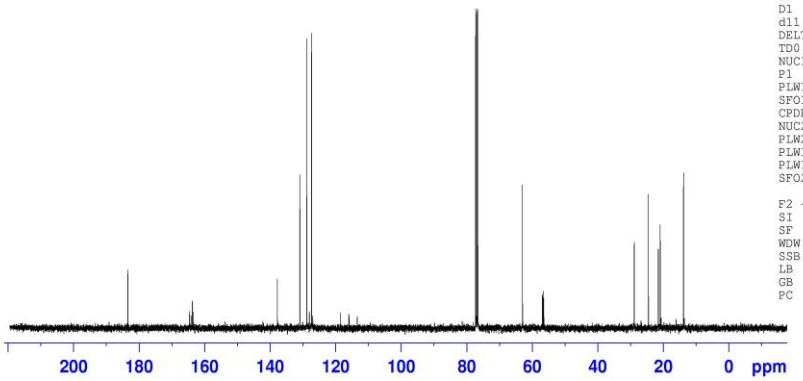




(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluoro-4-methylpentanoate (3n)



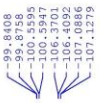




```
Current Data Parameters
NAME        160421-wjc-1
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160421
Time               15.00
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  161
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                202.1
DW                20.800 usec
DE                 6.50 usec
TE                295.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                   1
NUC1                 13C
P1                10.10 usec
PLW1          65.00000000 W
SFO1         100.6228293 MHz
CPDPRG2
NUC2                  1H
PLW2          19.00000000 W
PLW12          0.19639000 W
PLW13          0.15907000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127751 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

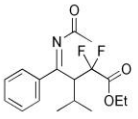


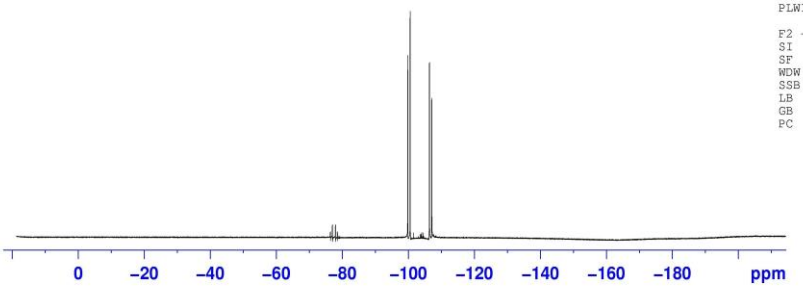
```
Current Data Parameters
NAME        160425-wjc-1
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160425
Time               18.07
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ             0.7340532 sec
RG                202.1
DW                5.600 usec
DE                 6.50 usec
TE                295.2 K
D1             1.00000000 sec
TD0                   1

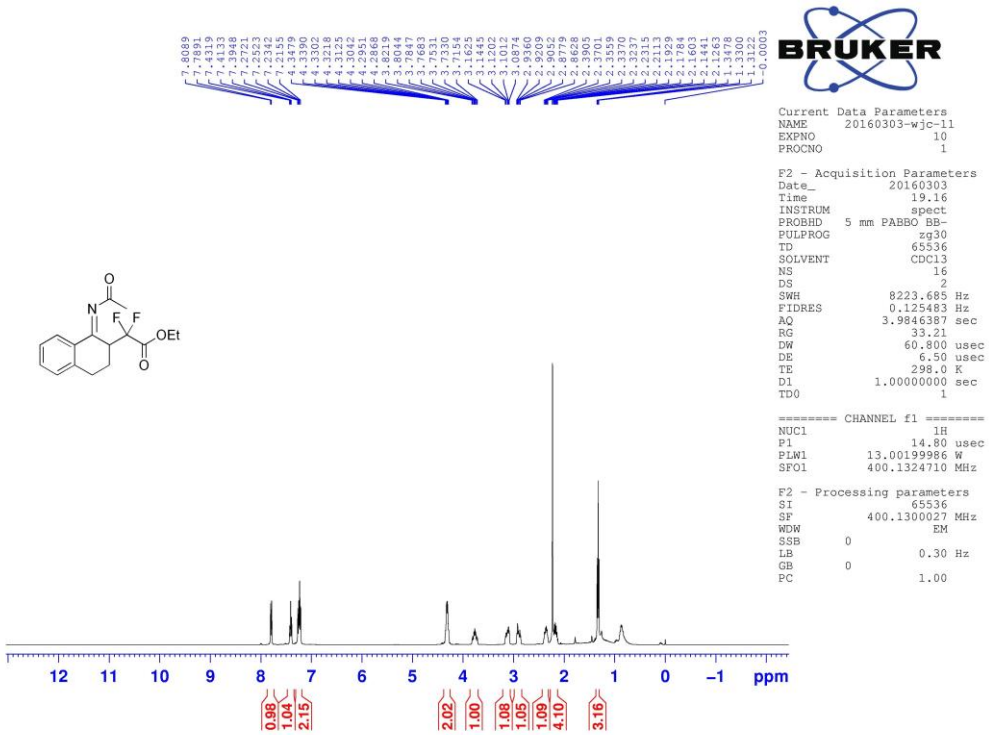
======== CHANNEL f1 ========
SFO1         376.4607164 MHz
NUC1                  19F
P1                12.00 usec
PLW1          19.01099968 W

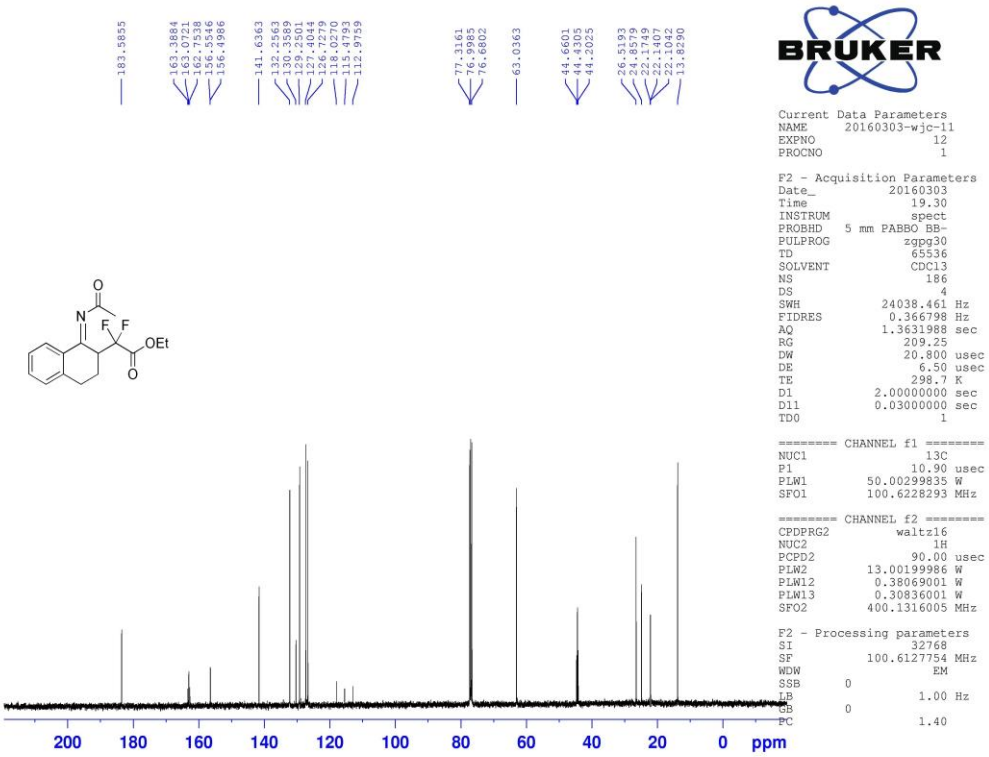
F2 - Processing parameters
SI                 65536
SF           376.4983662 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

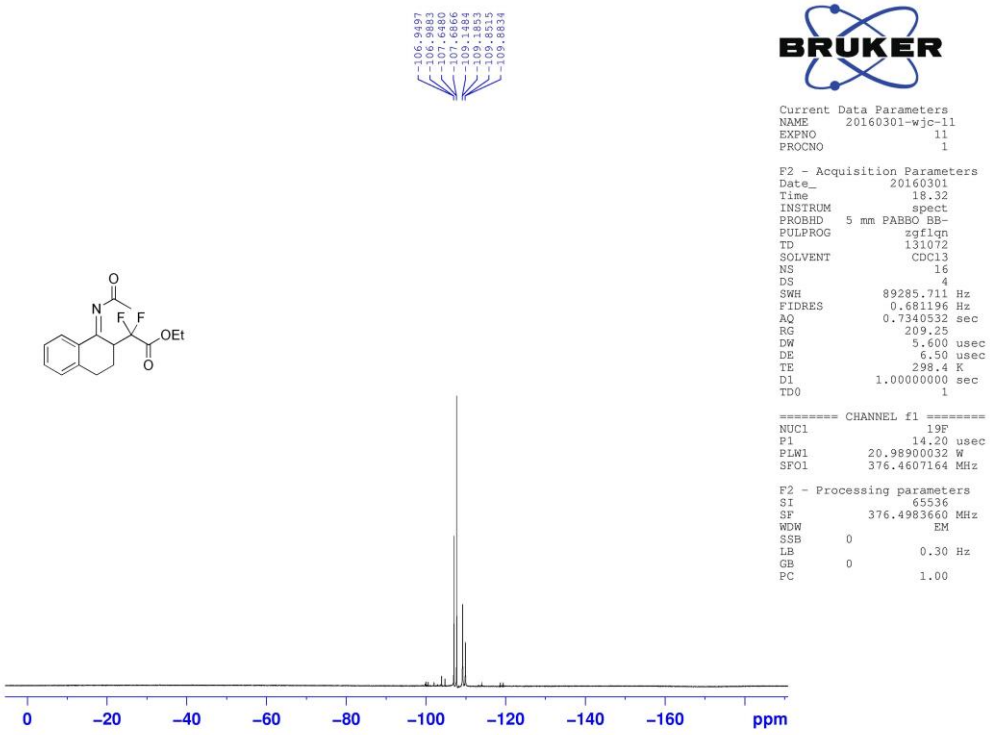




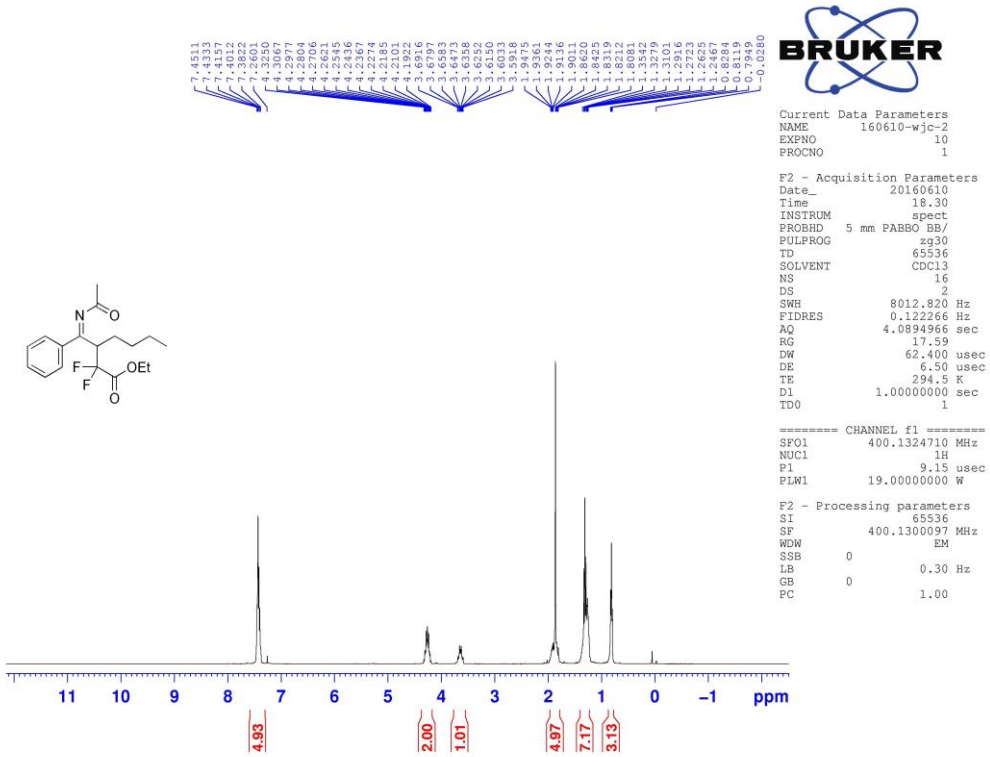
(*E*)-Ethyl 2-(1-(acetylimino)-1,2,3,4-tetrahydronaphthalen-2-yl)-2,2-difluoroacetate (3o)

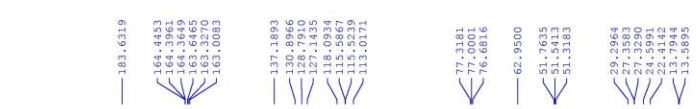


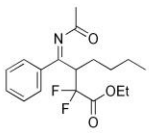




(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluoroheptanoate (3p)



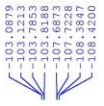




```
Current Data Parameters
NAME        160610-wjc-2
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160610
Time               18.47
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                202.1
DW                20.800 usec
DE                 6.50 usec
TE                295.1 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                   1
NUC1                13C
P1                10.10 usec
PLW1          65.00000000 W
SFO1         100.6228293 MHz
CPDPRG2
NUC2                1H
PLW2          19.00000000 W
PLW12          0.19639000 W
PLW13          0.15907000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF            100.6127767 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

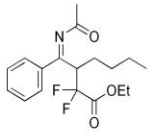


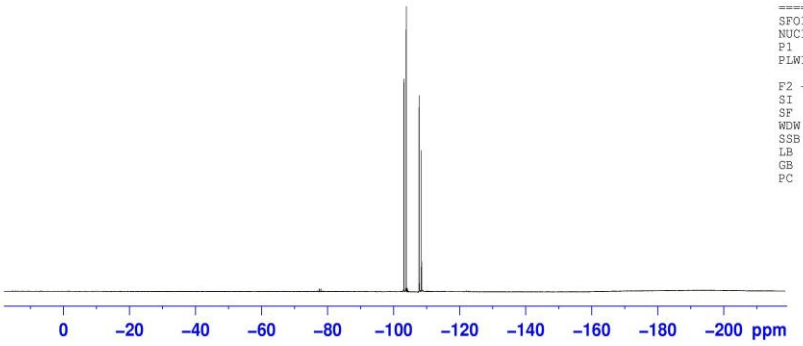
```
Current Data Parameters
NAME        160610-wjc-2
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160610
Time               18.31
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD                131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ             0.7340532 sec
RG                202.1
DW                5.600 usec
DE                 6.50 usec
TE                294.5 K
D1             1.00000000 sec
TD0                   1

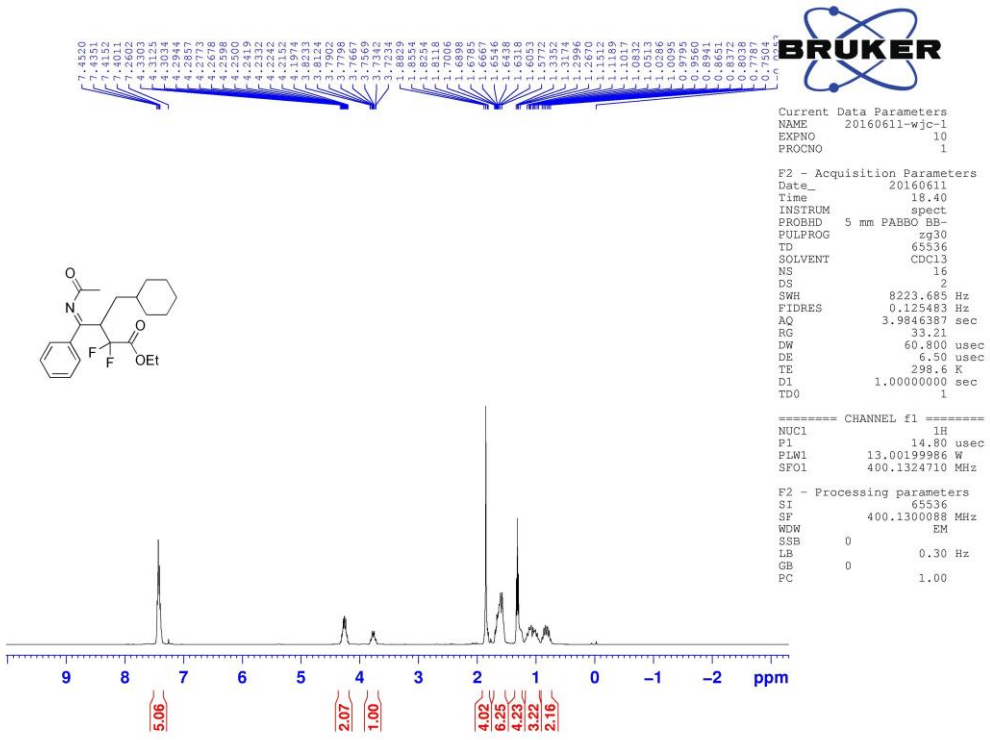
======== CHANNEL f1 ========
SFO1         376.4607164 MHz
NUC1                19F
P1                12.00 usec
PLW1          19.01099968 W

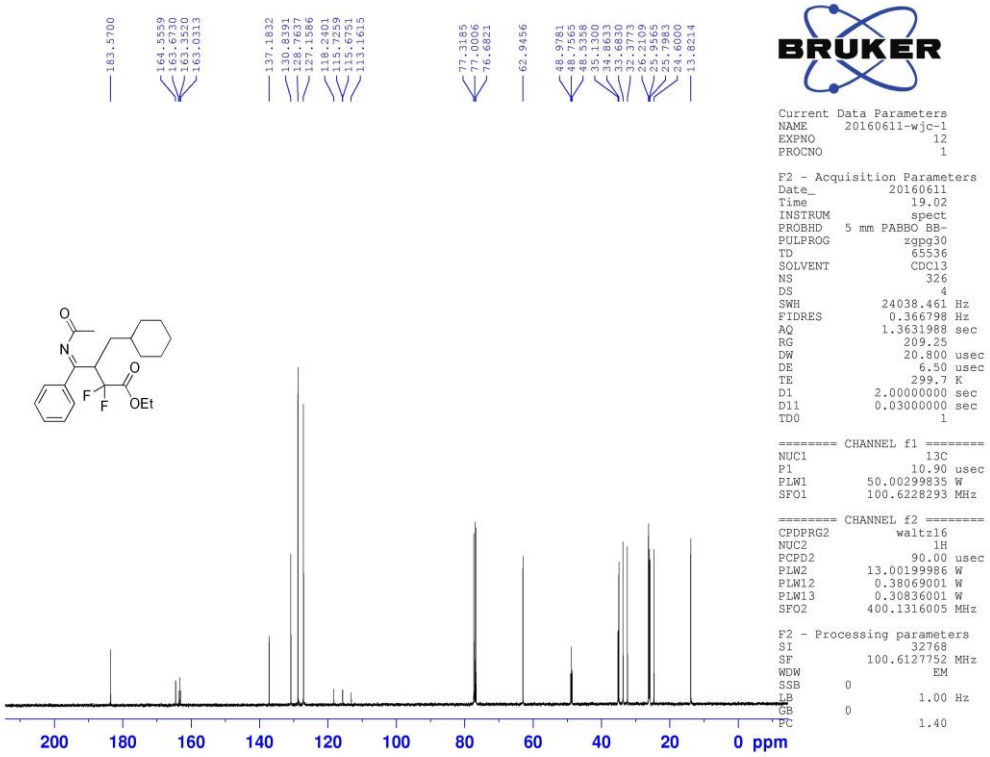
F2 - Processing parameters
SI                 65536
SF            376.4983662 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

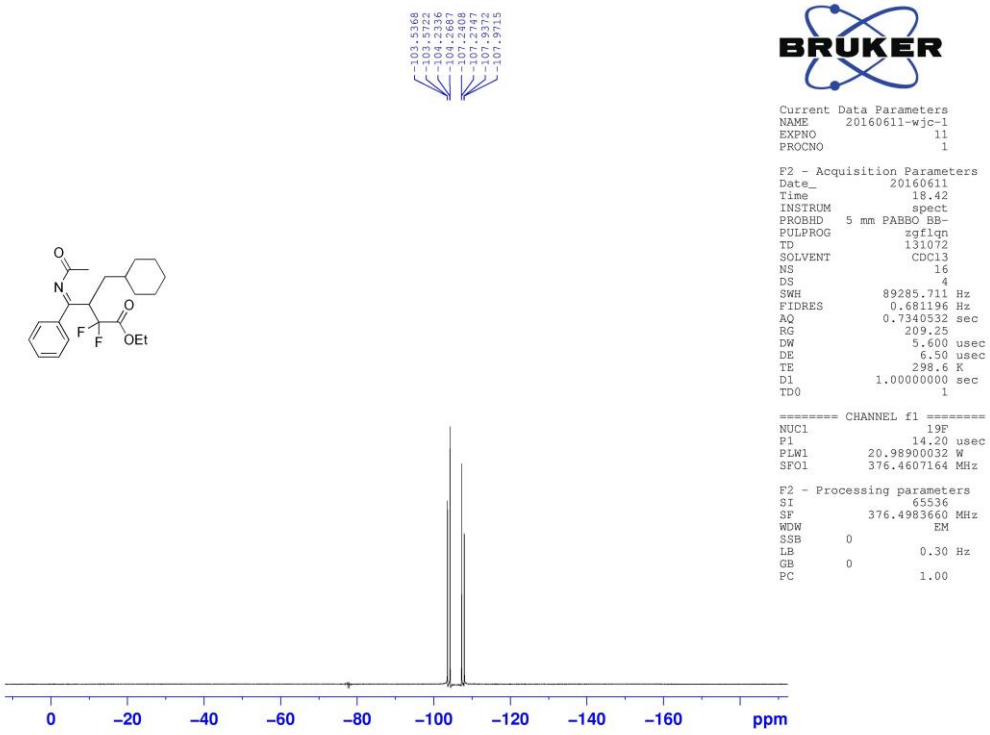




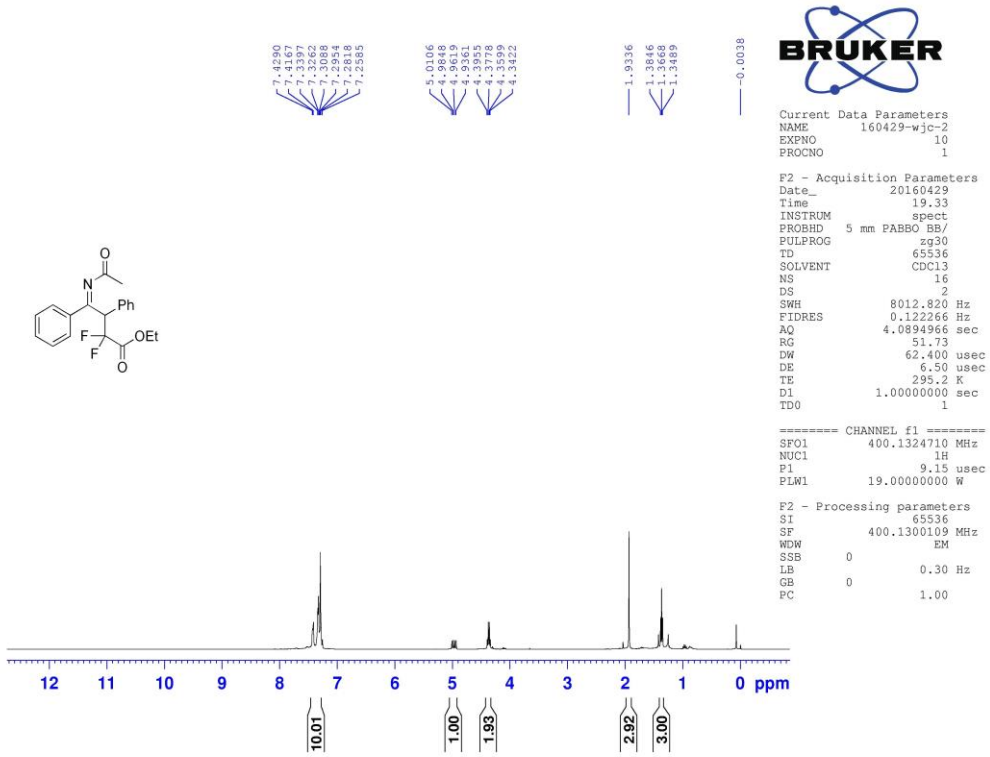
(*E*)-Ethyl 4-(acetylimino)-3-(cyclohexylmethyl)-2,2-difluoro-4-phenylbutanoate (3q)

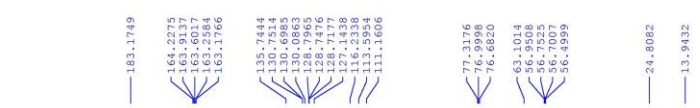


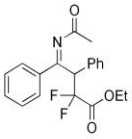


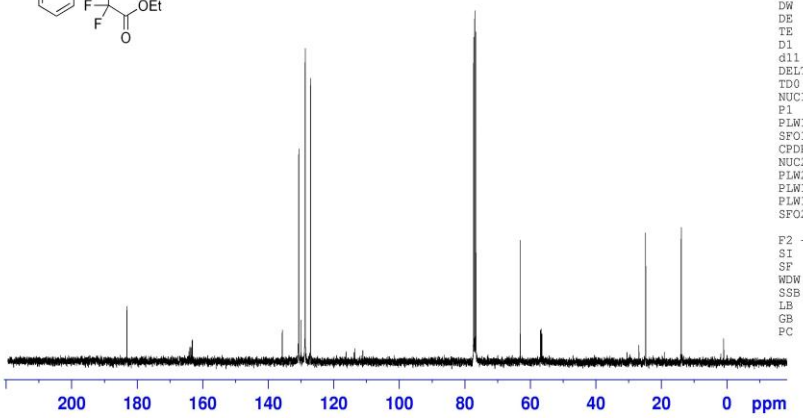


(*E*)-Ethyl 4-(acetylimino)-2,2-difluoro-3,4-diphenylbutanoate (3r)







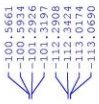


BRUKER

```
Current Data Parameters
NAME        160429-wjc-2
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160429
Time               19.47
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD              65536
SOLVENT           CDCl3
NS                  180
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                202.1
DW               20.800 usec
DE                6.50 usec
TE                295.9 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1
NUC1                 13C
P1                10.10 usec
PLW1         65.00000000 W
SFO1        100.6228293 MHz
CPDPRG2
NUC2                 1H
PLW2         19.00000000 W
PLW12         0.19639000 W
PLW13         0.15907000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6127739 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



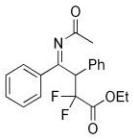
BRUKER

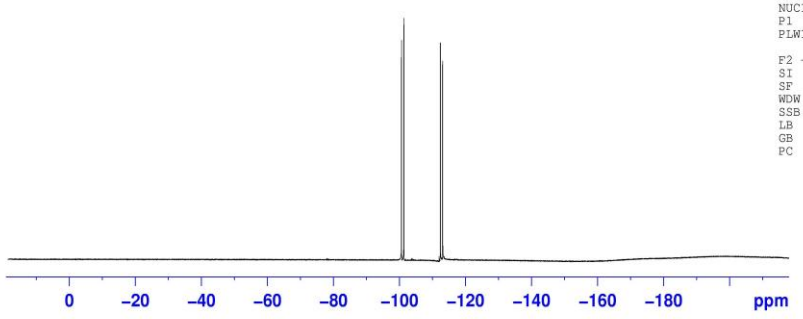
```
Current Data Parameters
NAME        160429-wjc-2
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160429
Time               19.35
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD              131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ             0.7340532 sec
RG                202.1
DW                5.600 usec
DE                6.50 usec
TE                295.2 K
D1            1.00000000 sec
TD0                   1

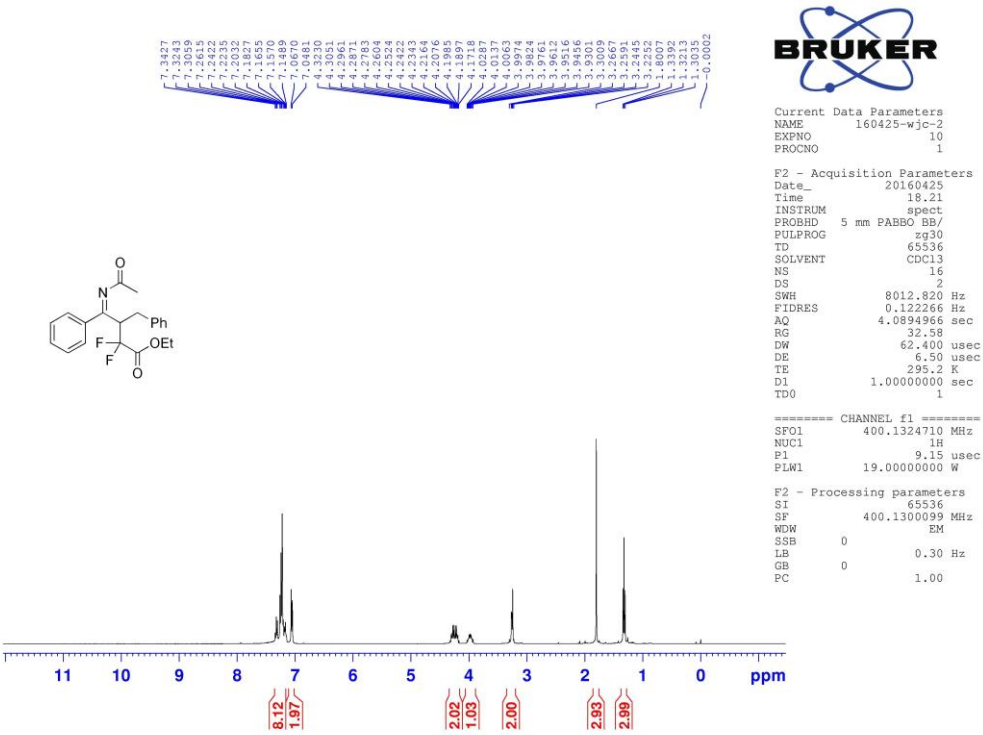
======== CHANNEL f1 ========
SFO1        376.4607164 MHz
NUC1                 19F
P1                12.00 usec
PLW1         19.01099968 W

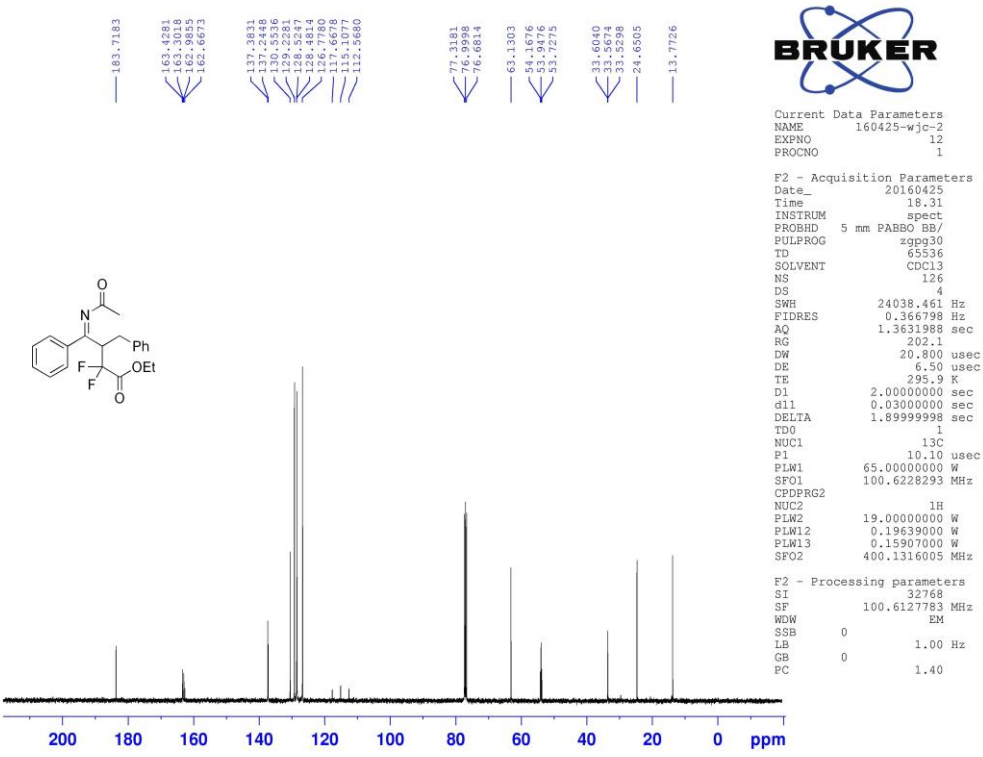
F2 - Processing parameters
SI                65536
SF           376.4983662 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

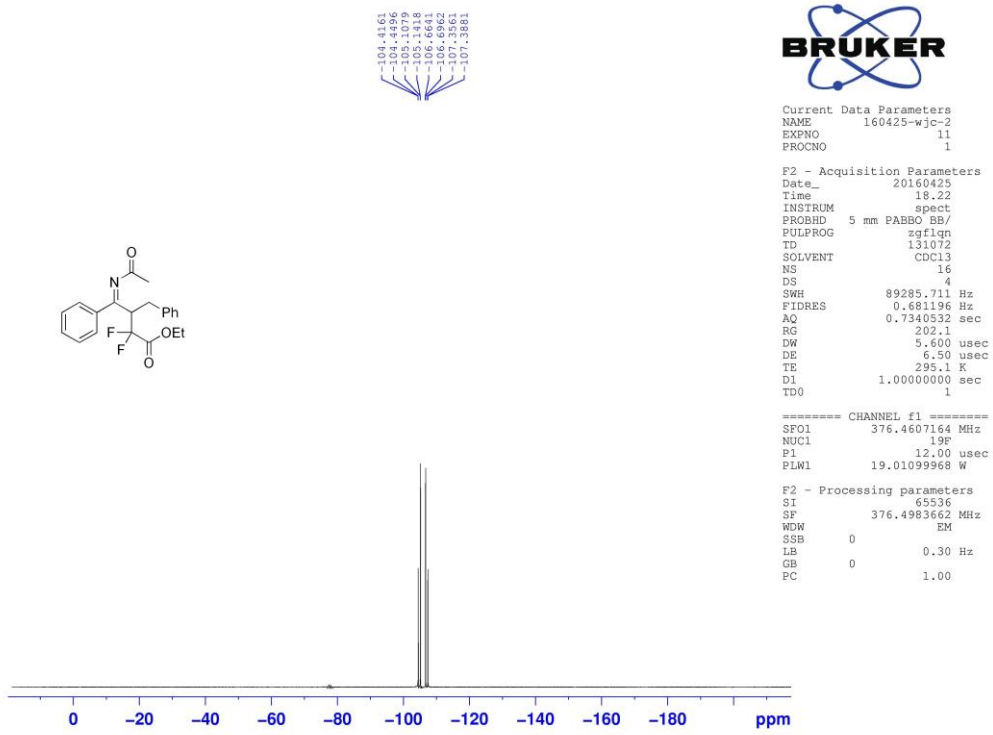




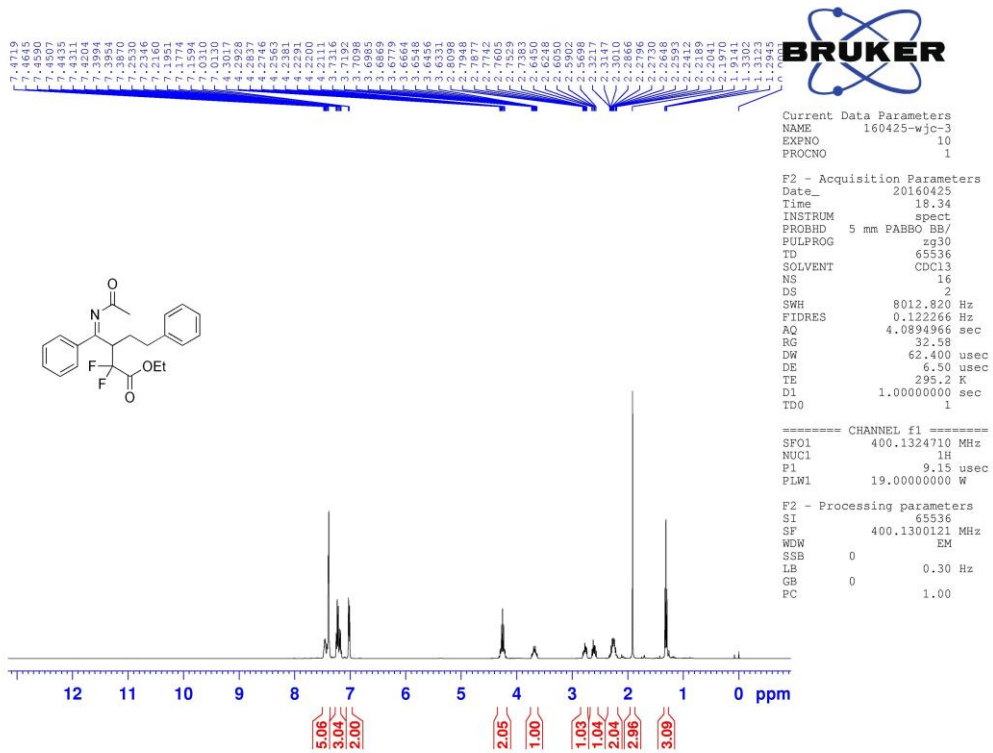
(*E*)-Ethyl 4-(acetylimino)-3-benzyl-2,2-difluoro-4-phenylbutanoate (3s)

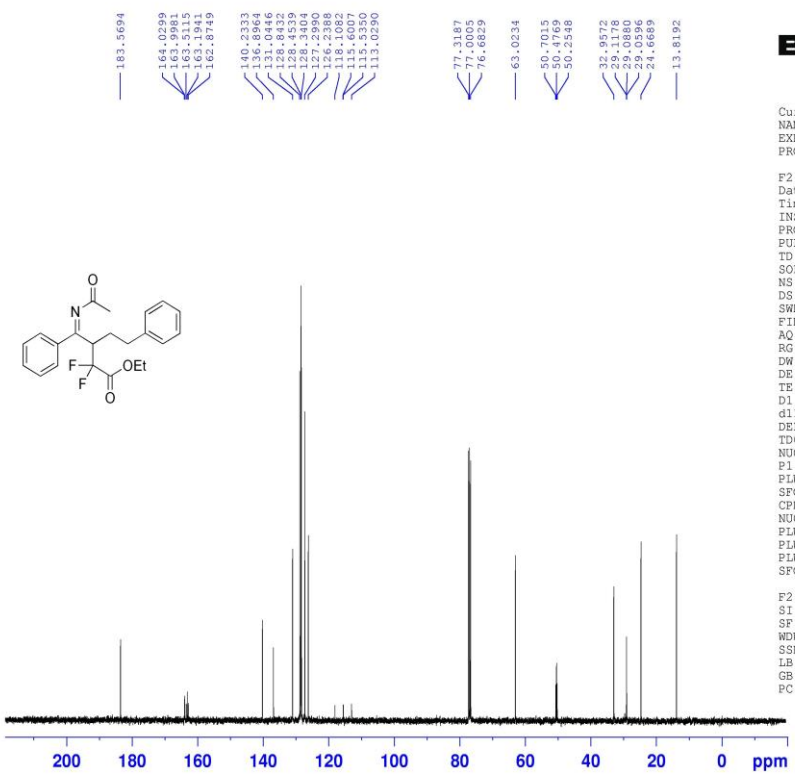






(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluoro-5-phenylpentanoate (3t)

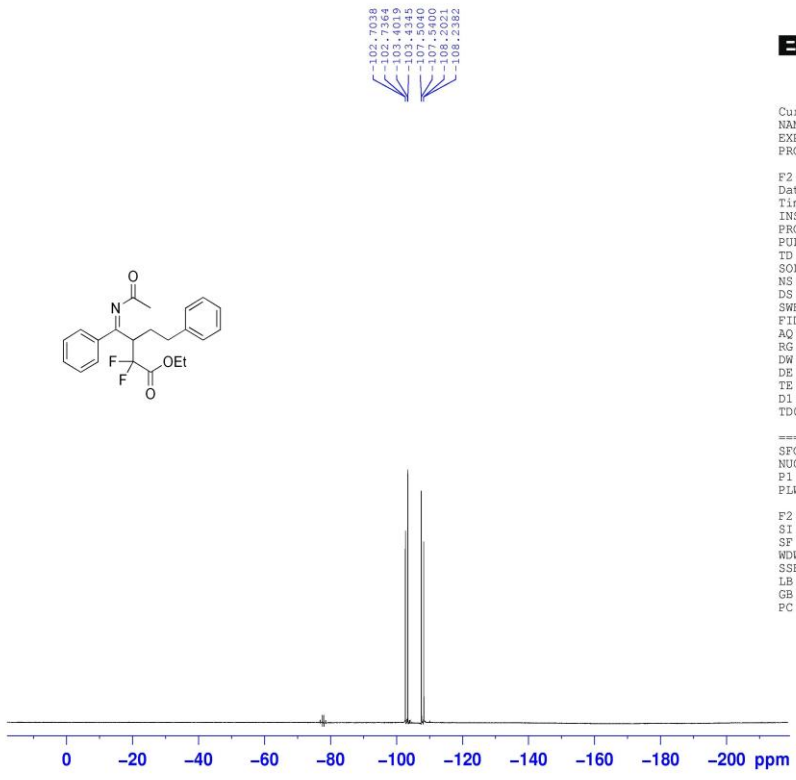




Current Data Parameters
NAME 160425-wjc-3
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160425
Time 18.45
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 126
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 202.1
DW 20.800 usec
DE 6.50 usec
TE 295.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
NUC1 13C
P1 10.10 usec
PLW1 65.00000000 W
SFO1 100.6228293 MHz
CPDPRG2
NUC2 1H
PLW2 19.00000000 W
PLW12 0.19639000 W
PLW13 0.15907000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127769 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



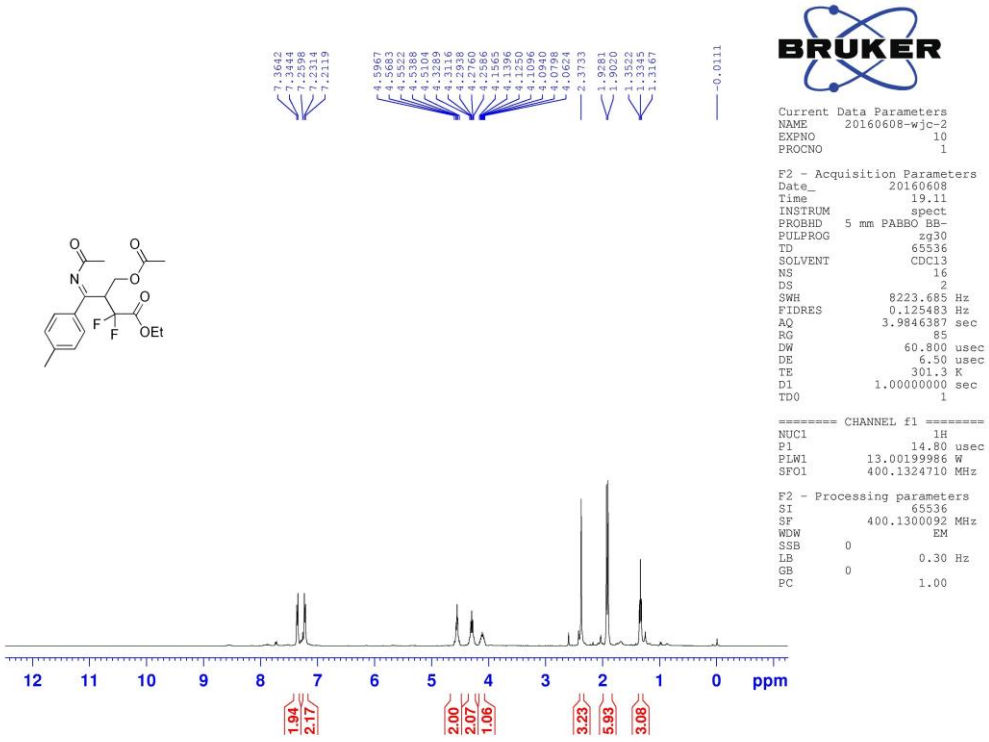
Current Data Parameters
NAME 160425-wjc-3
EXPNO 11
PROCNO 1

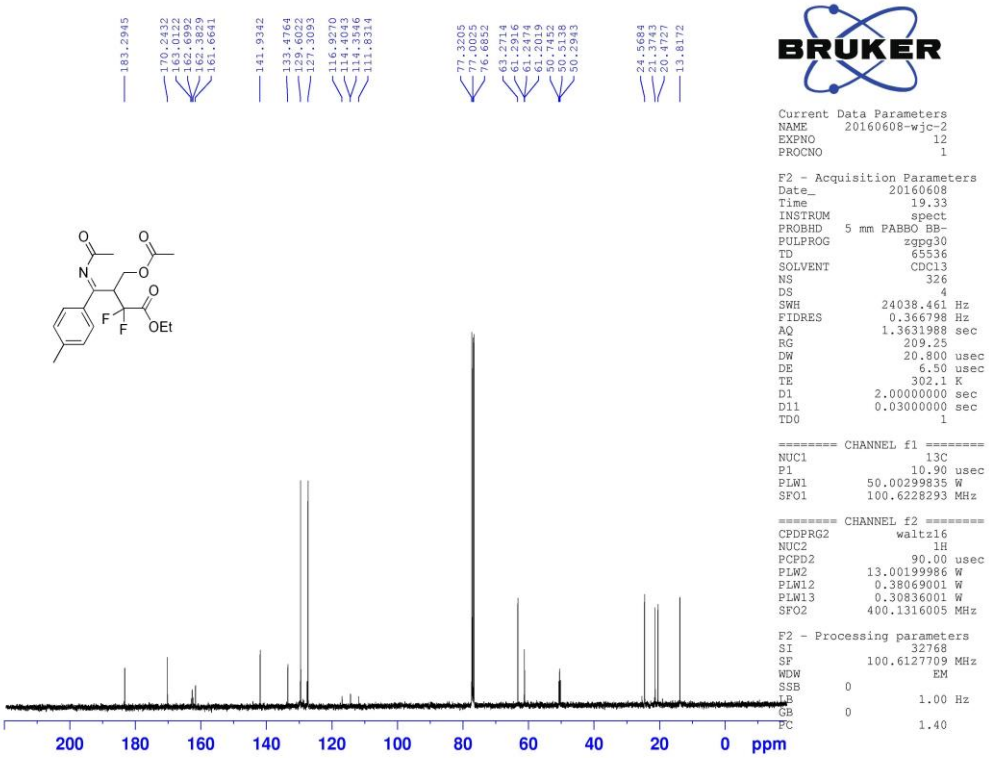
F2 - Acquisition Parameters
Date_ 20160425
Time 18.36
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 202.1
DW 5.600 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1

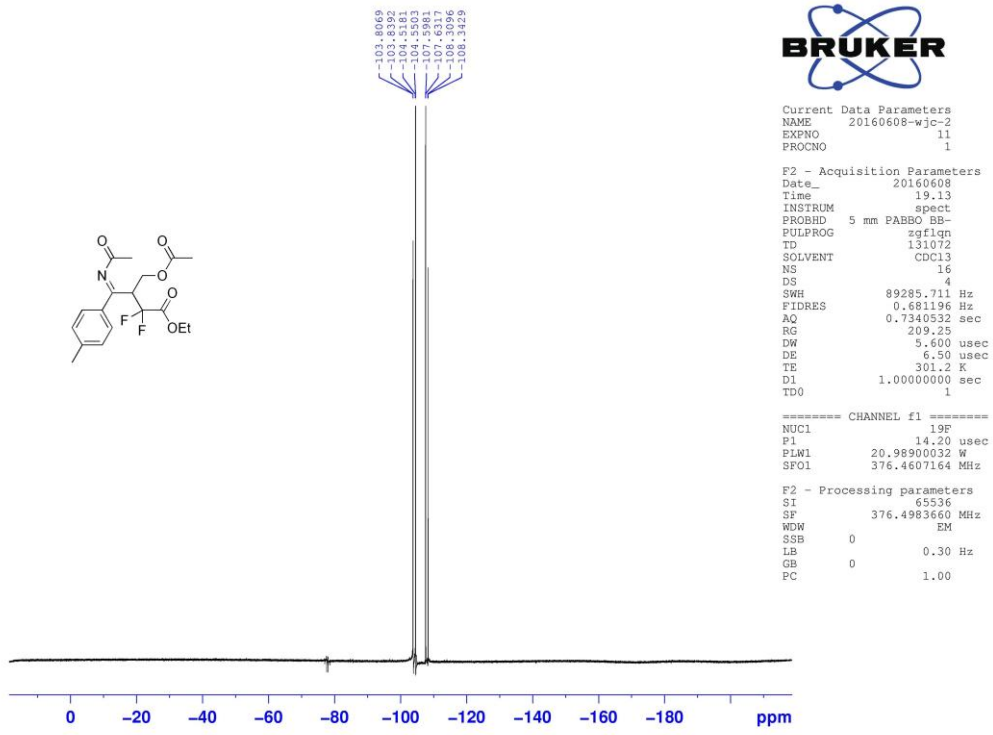
======== CHANNEL f1 ========
SFO1 376.4607164 MHz
NUC1 19F
P1 12.00 usec
PLW1 19.01099968 W

F2 - Processing parameters
SI 65536
SF 376.4983662 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

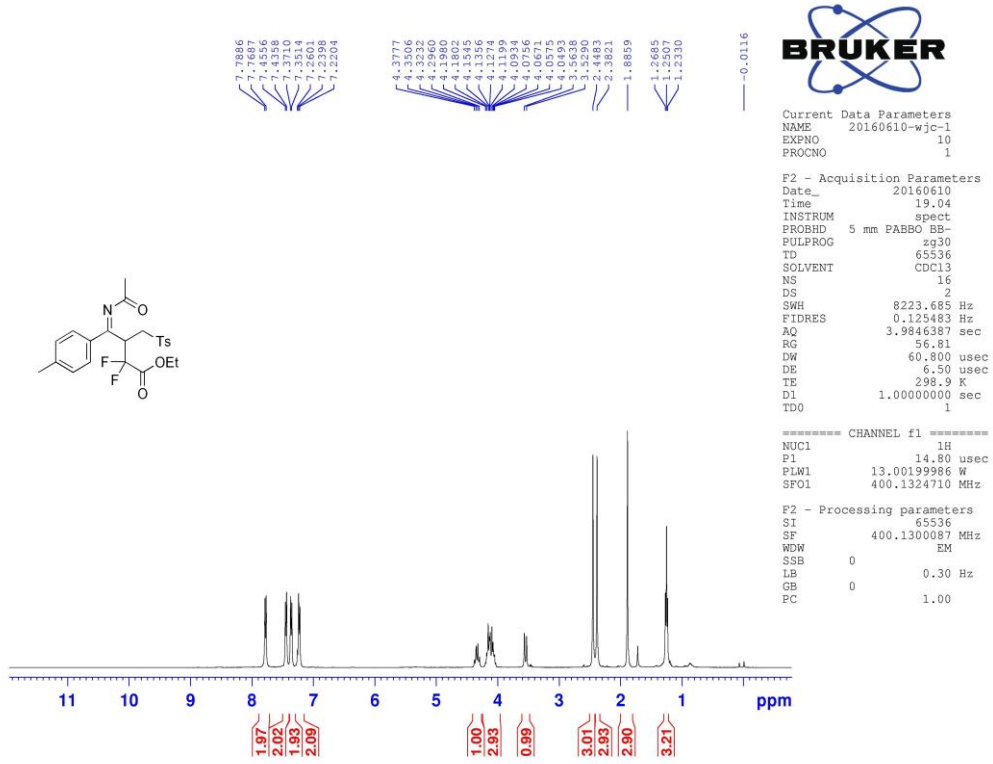
(*E*)-Ethyl 3-(acetoxymethyl)-4-(acetylimino)-2,2-difluoro-4-(p-tolyl)butanoate (3u)

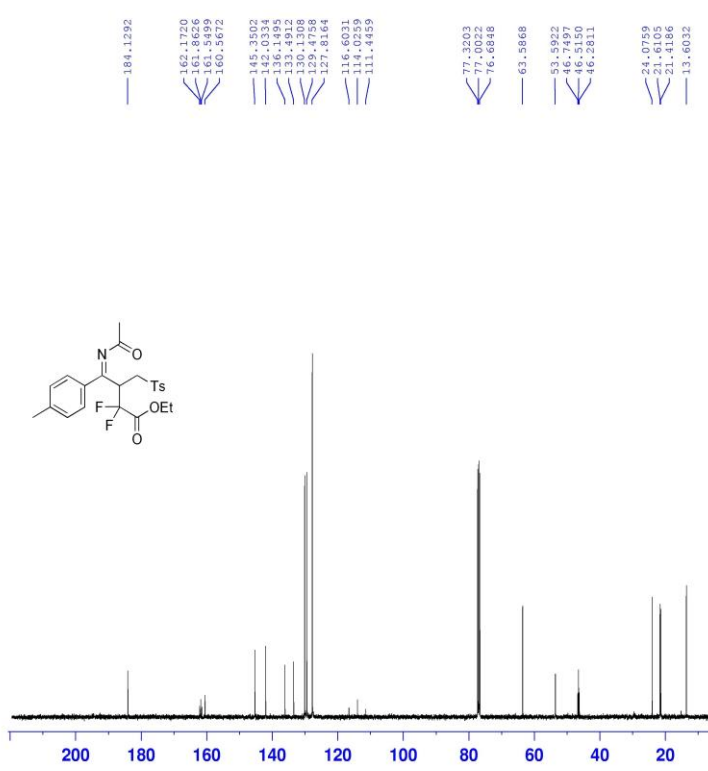






(*E*)-ethyl 4-(acetylimino)-2,2-difluoro-4-(p-tolyl)-3-(tosylmethyl)butanoate (3v)





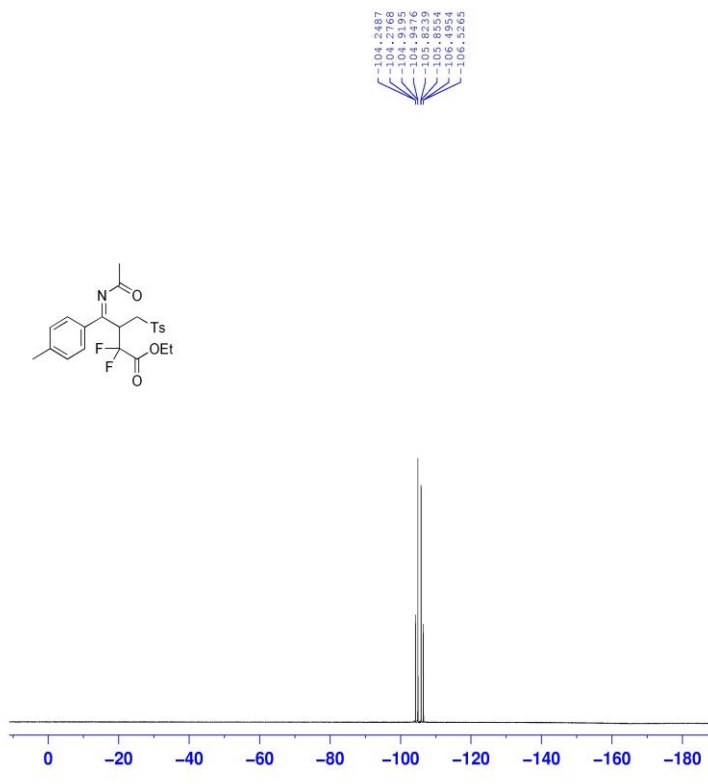
Current Data Parameters
NAME 20160610-wjc-1
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160610
Time 19.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 332
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 209.25
DW 20.800 usec
DE 6.50 usec
TE 299.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.90 usec
PLW1 50.00299835 W
SFO1 100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 13.00199986 W
PLW12 0.38069001 W
PLW13 0.30836001 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127738 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



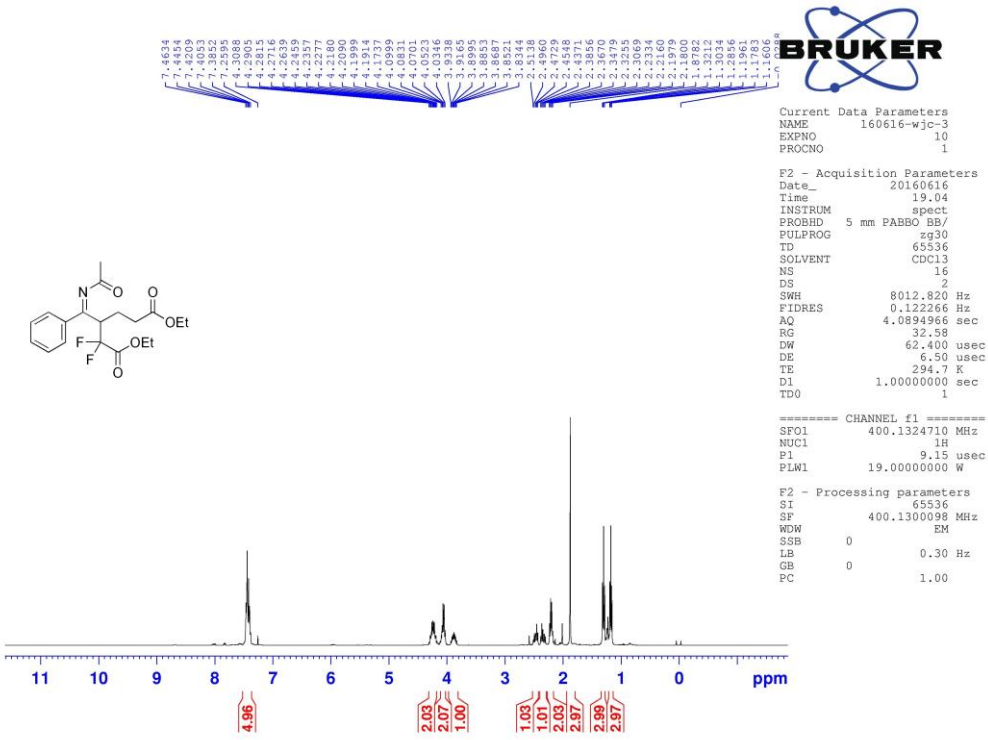
Current Data Parameters
NAME 20160610-wjc-1
EXPNO 11
PROCNO 1

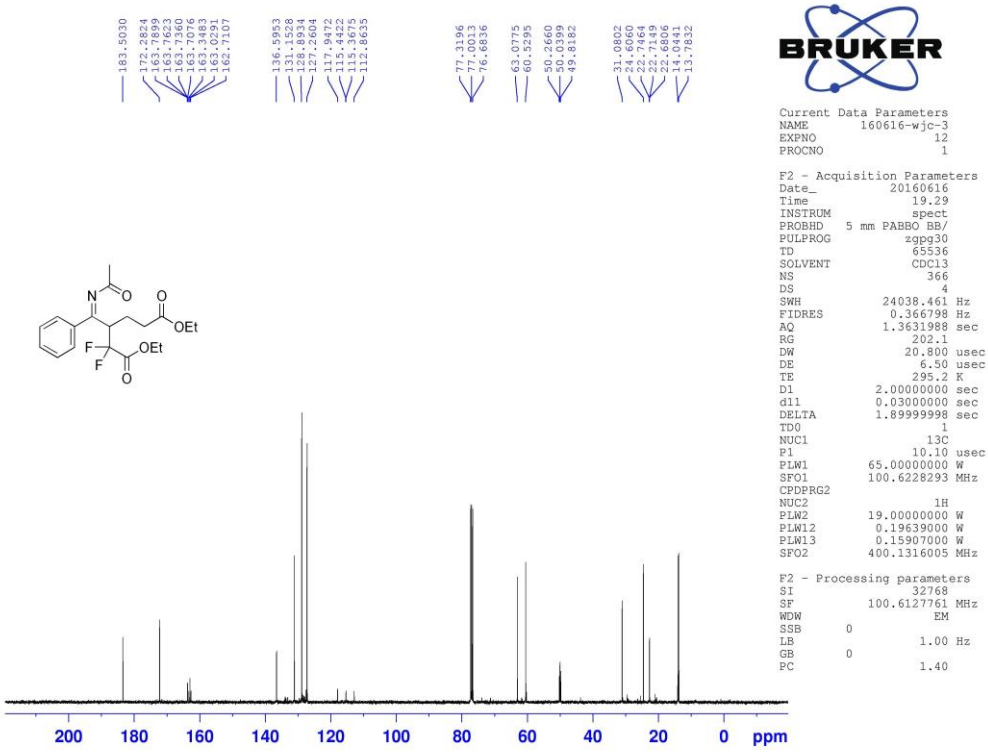
F2 - Acquisition Parameters
Date_ 20160610
Time 19.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 209.25
DW 5.600 usec
DE 6.50 usec
TE 298.8 K
D1 1.00000000 sec
TD0 1

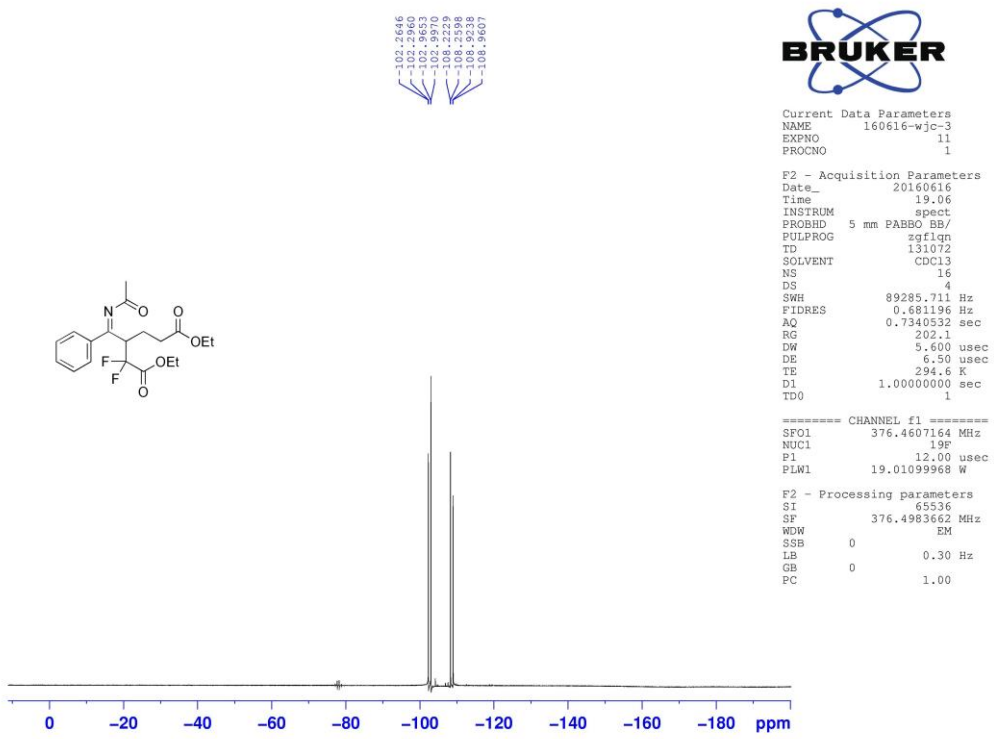
======== CHANNEL f1 ========
NUC1 19F
P1 14.20 usec
PLW1 20.98900032 W
SFO1 376.4607164 MHz

F2 - Processing parameters
SI 65536
SF 376.4983660 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

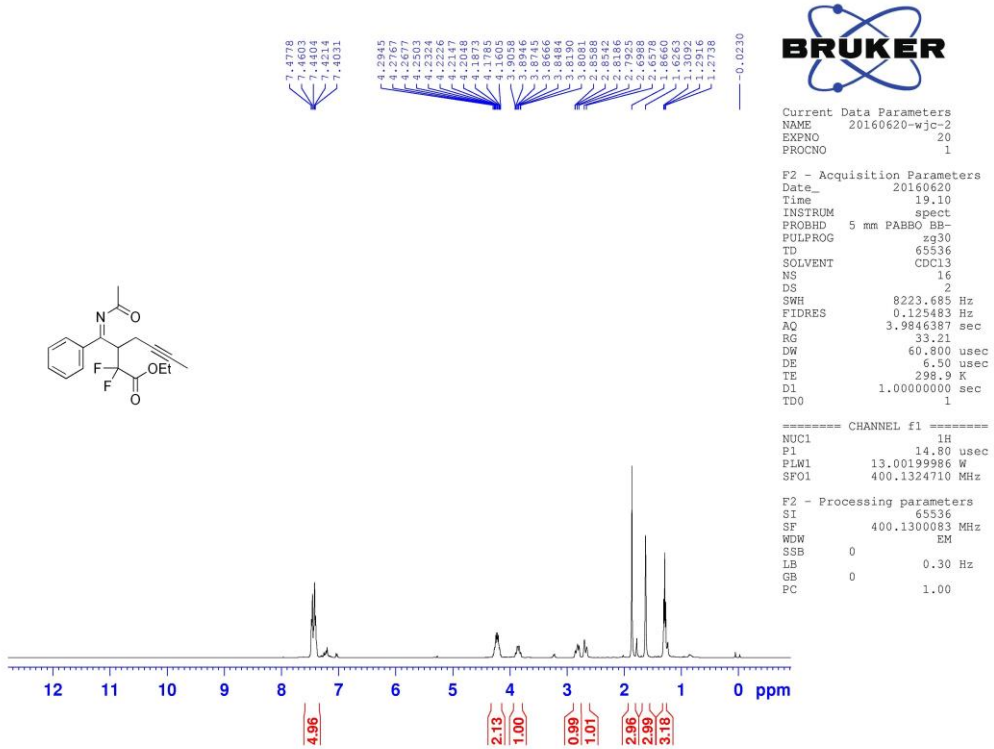
(*E*)-Diethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluorohexanedioate (3w)

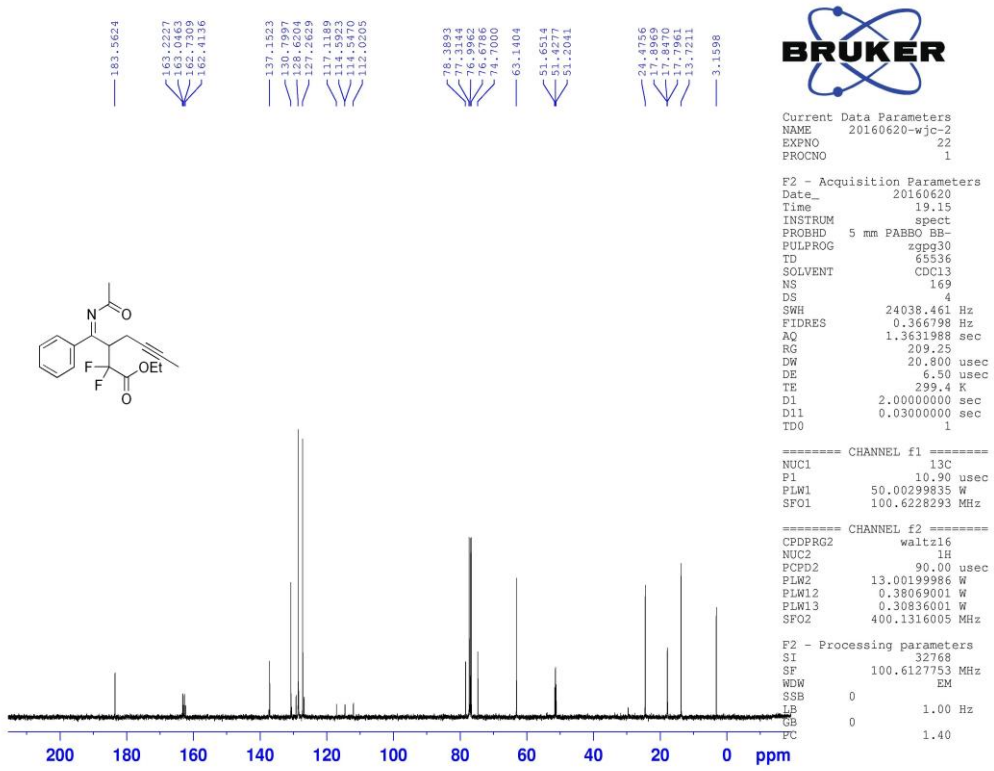






(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluorohept-5-ynoate (3x)





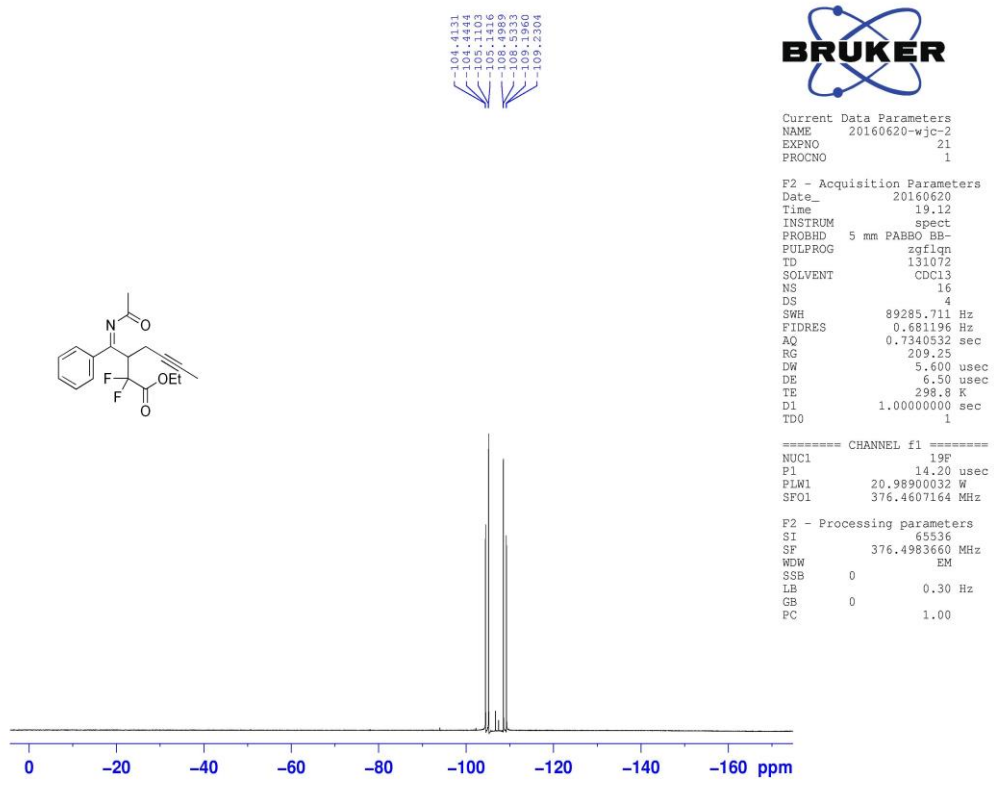
Current Data Parameters
NAME 20160620-wjc-2
EXPNO 22
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160620
Time 19.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 169
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 209.25
DW 20.800 usec
DE 6.50 usec
TE 299.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.90 usec
PLW1 50.00299835 W
SFO1 100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 13.00199986 W
PLW12 0.38069001 W
PLW13 0.30836001 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127753 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



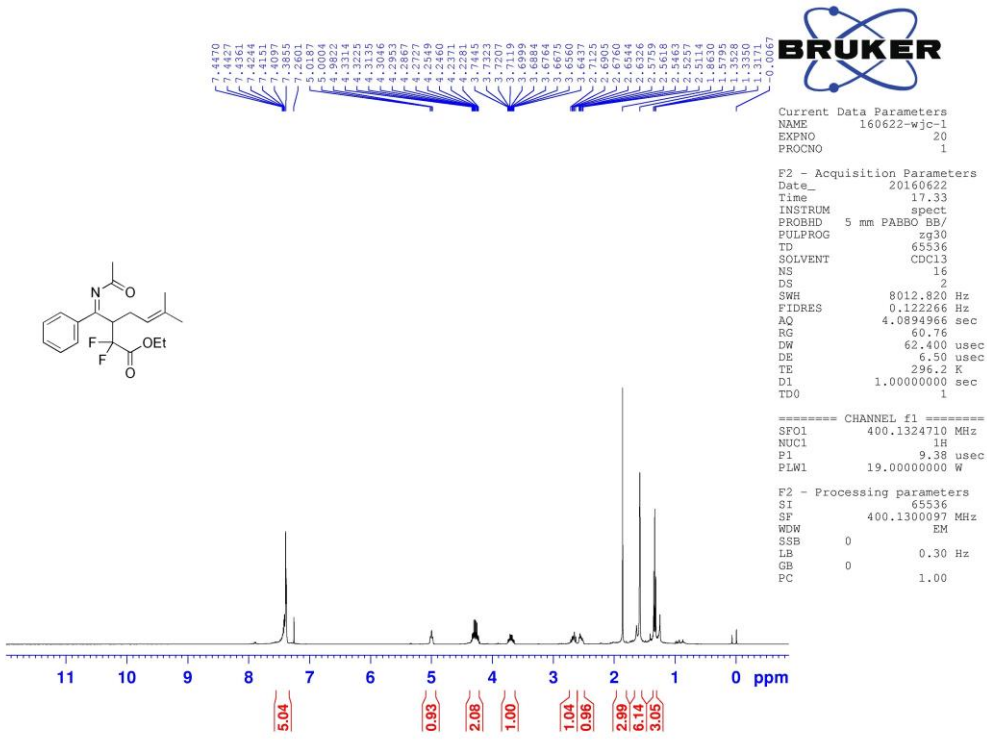
Current Data Parameters
NAME 20160620-wjc-2
EXPNO 21
PROCNO 1

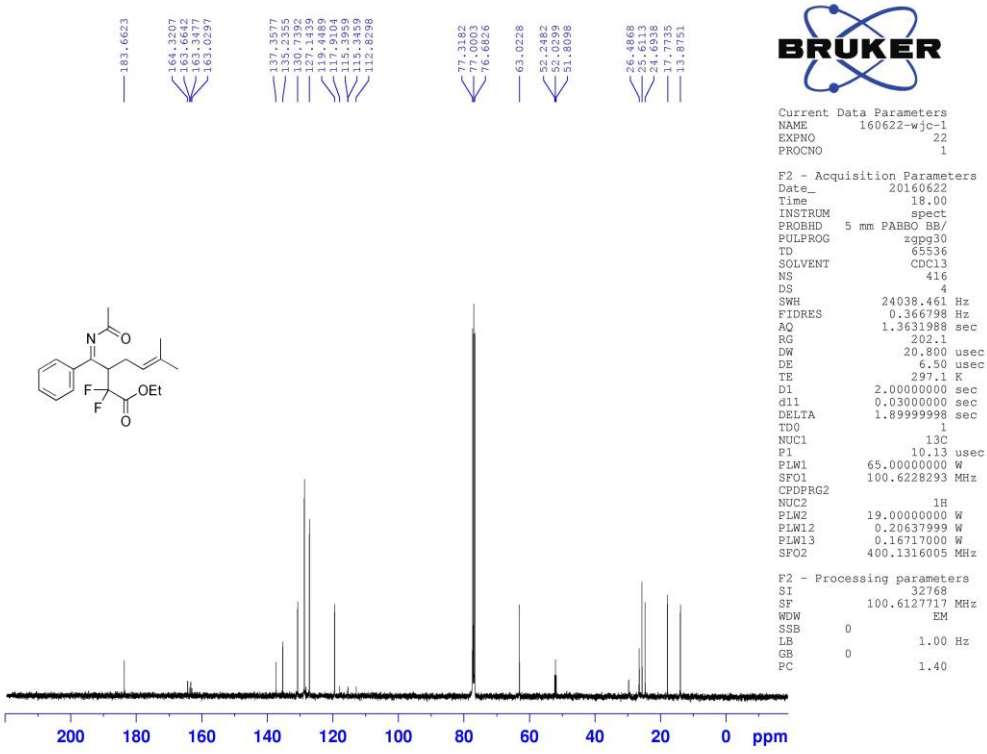
F2 - Acquisition Parameters
Date_ 20160620
Time 19.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 209.25
DW 5.600 usec
DE 6.50 usec
TE 298.8 K
D1 1.00000000 sec
TD0 1

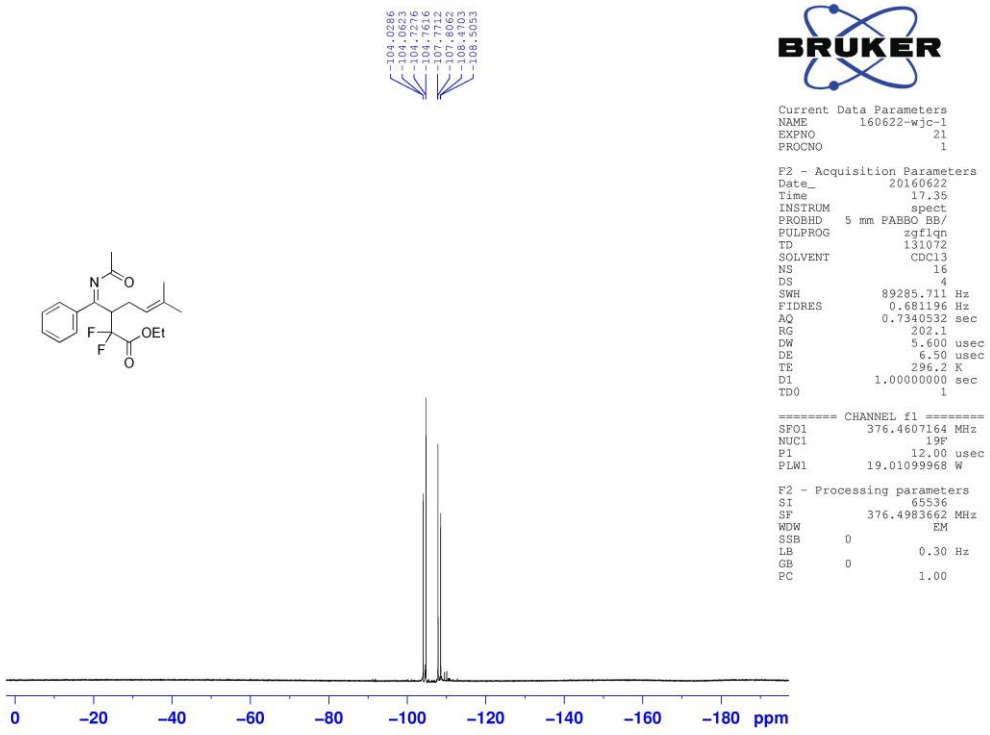
======== CHANNEL f1 ========
NUC1 19F
P1 14.20 usec
PLW1 20.98900032 W
SFO1 376.4607164 MHz

F2 - Processing parameters
SI 65536
SF 376.4983660 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

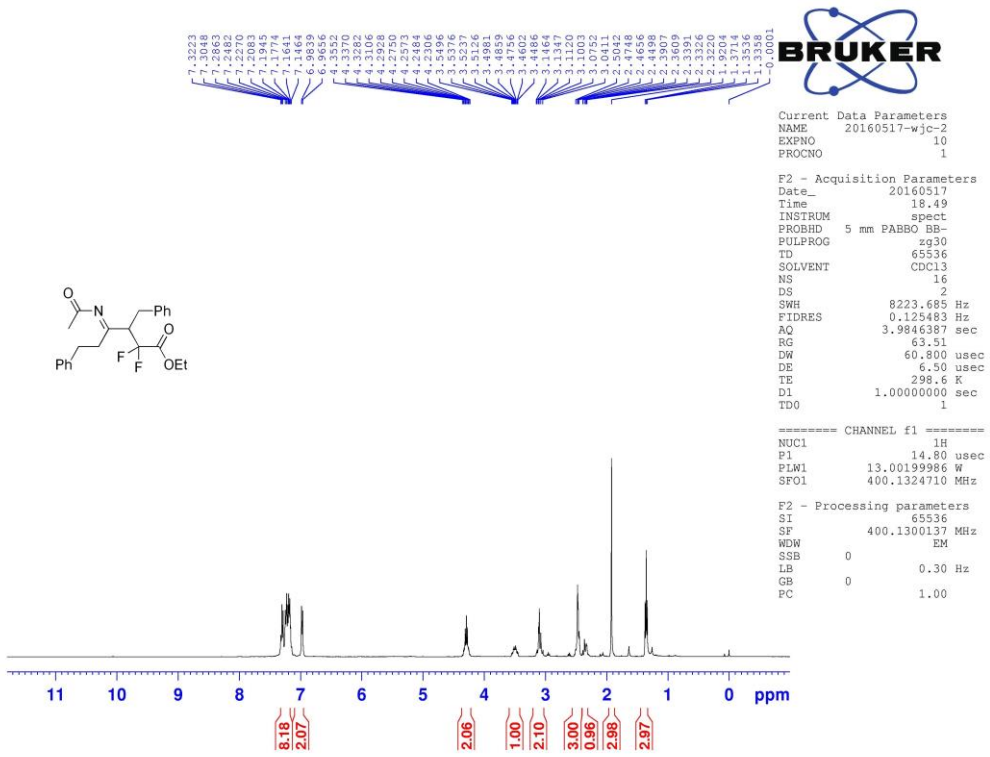
(*E*)-Ethyl 3-((acetylimino)(phenyl)methyl)-2,2-difluoro-6-methylhept-5-enoate (3y)

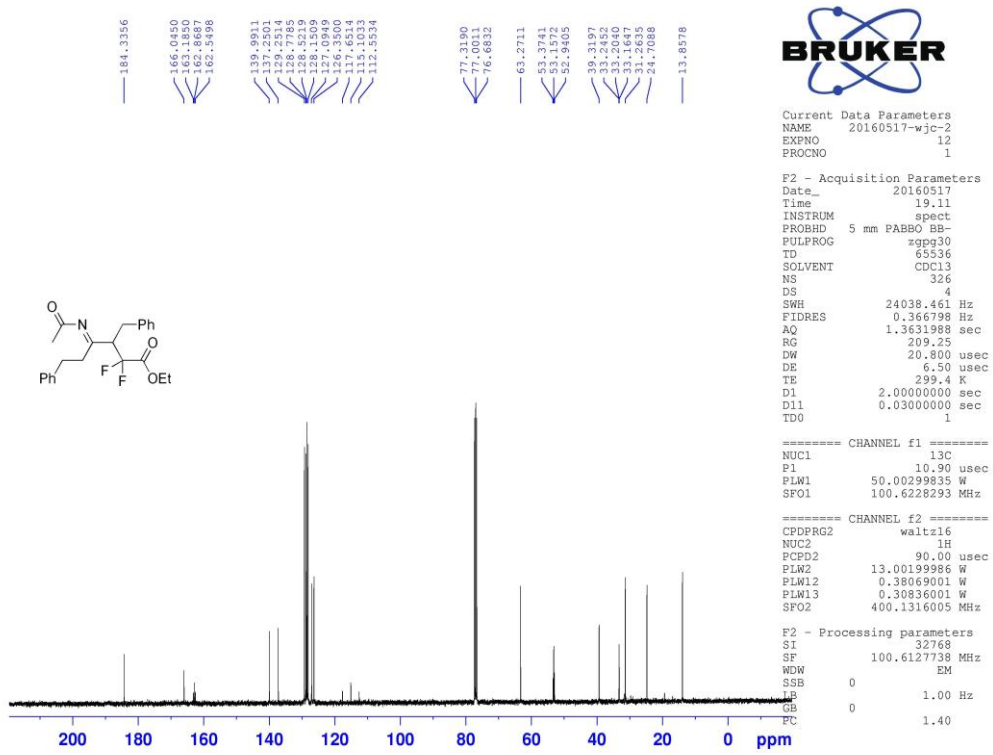






(*E*)-Ethyl 4-(acetylimino)-3-benzyl-2,2-difluoro-6-phenylhexanoate (3z)





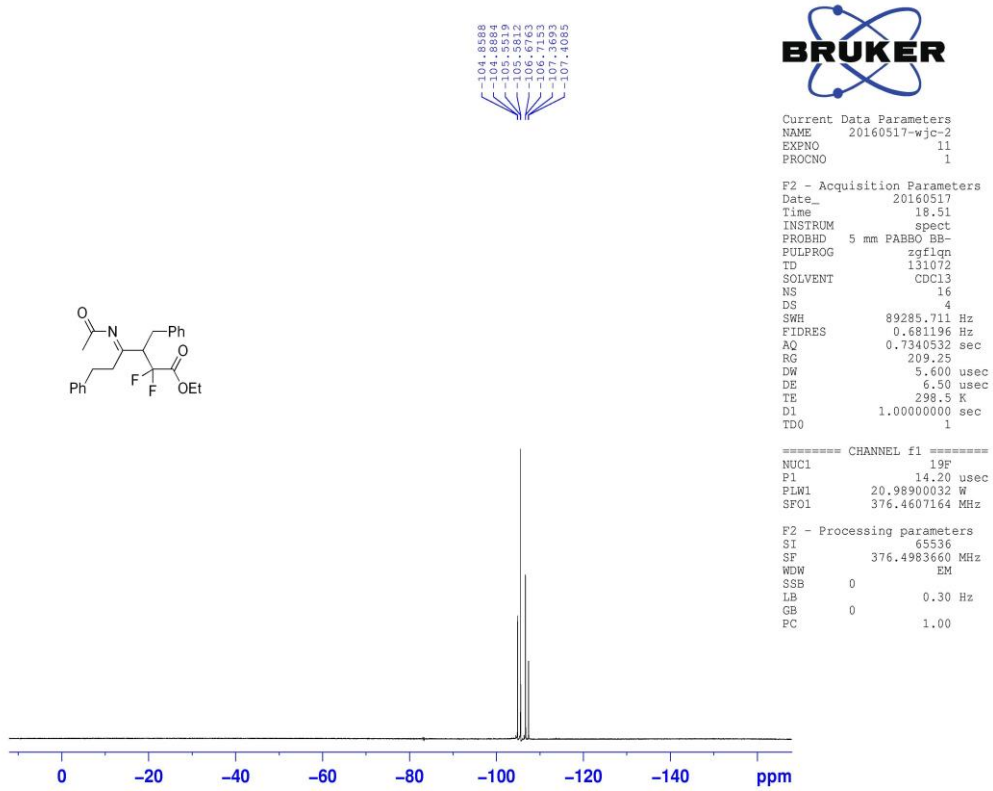

```
Current Data Parameters
NAME      20160517-wjc-2
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160517
Time               19.11
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  326
DS                    4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                209.25
DW                20.800 usec
DE                 6.50 usec
TE                299.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.90 usec
PLW1         50.00299835 W
SFO1        100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PLW2         13.00199986 W
PLW12         0.38069001 W
PLW13         0.30836001 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127738 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



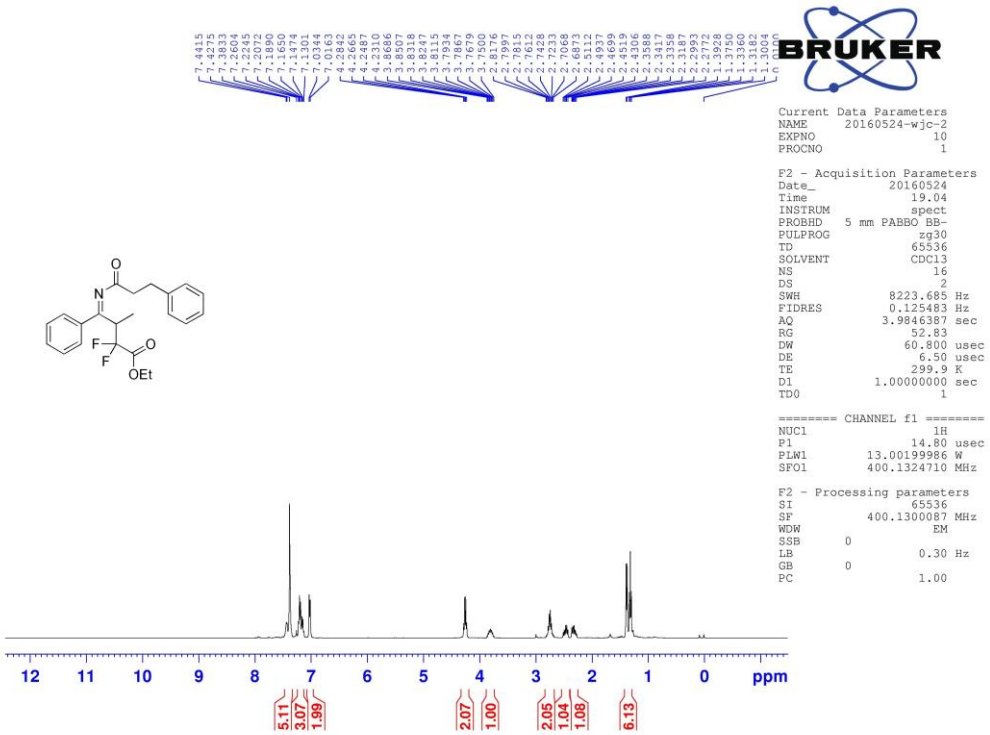

```
Current Data Parameters
NAME      20160517-wjc-2
EXPNO                 11
PROCNO                 1

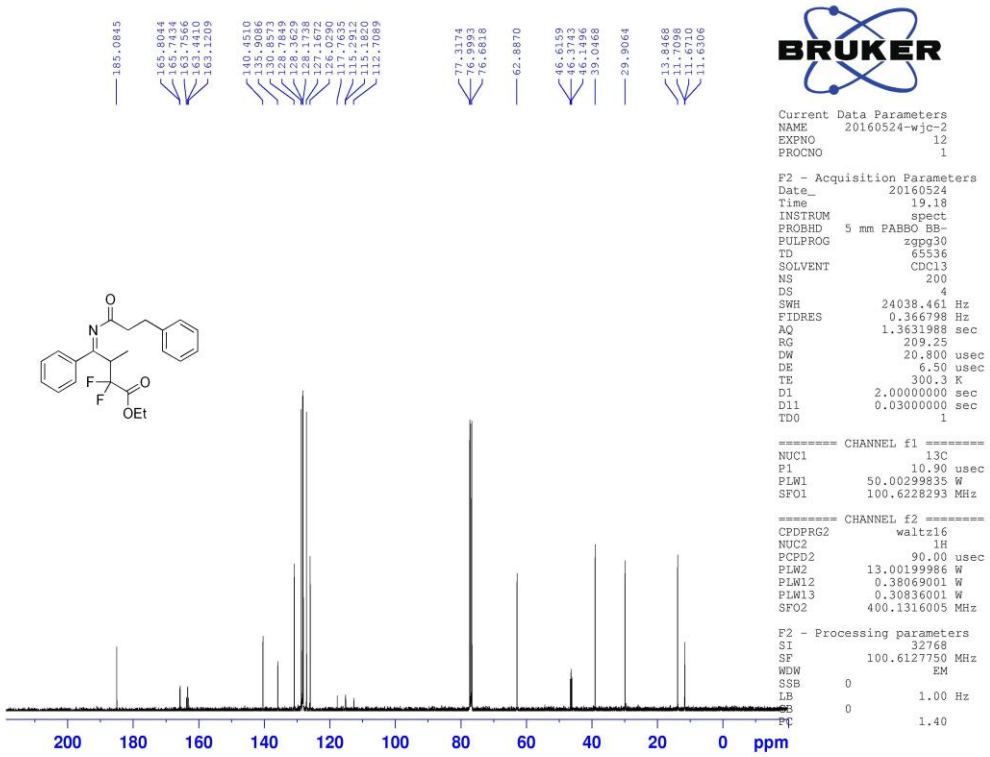
F2 - Acquisition Parameters
Date_           20160517
Time               18.51
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgflqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES        0.681196 Hz
AQ            0.7340532 sec
RG                209.25
DW                 5.600 usec
DE                 6.50 usec
TE                298.5 K
D1           1.00000000 sec
TD0                   1

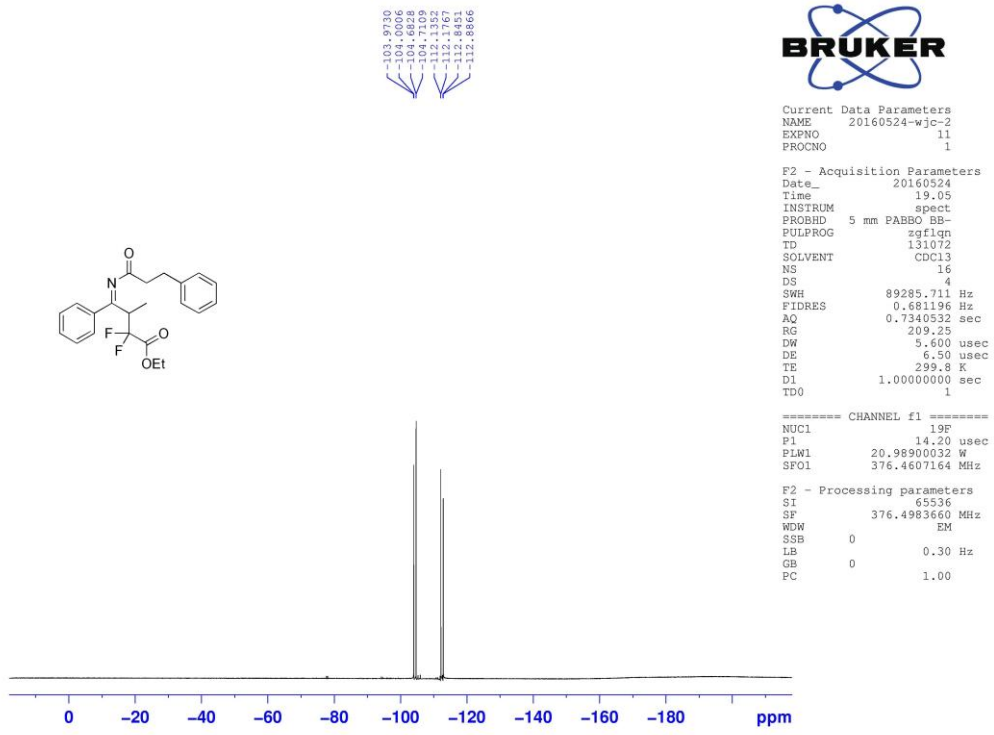
======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PLW1         20.98900032 W
SFO1        376.4607164 MHz

F2 - Processing parameters
SI                 65536
SF          376.4983660 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

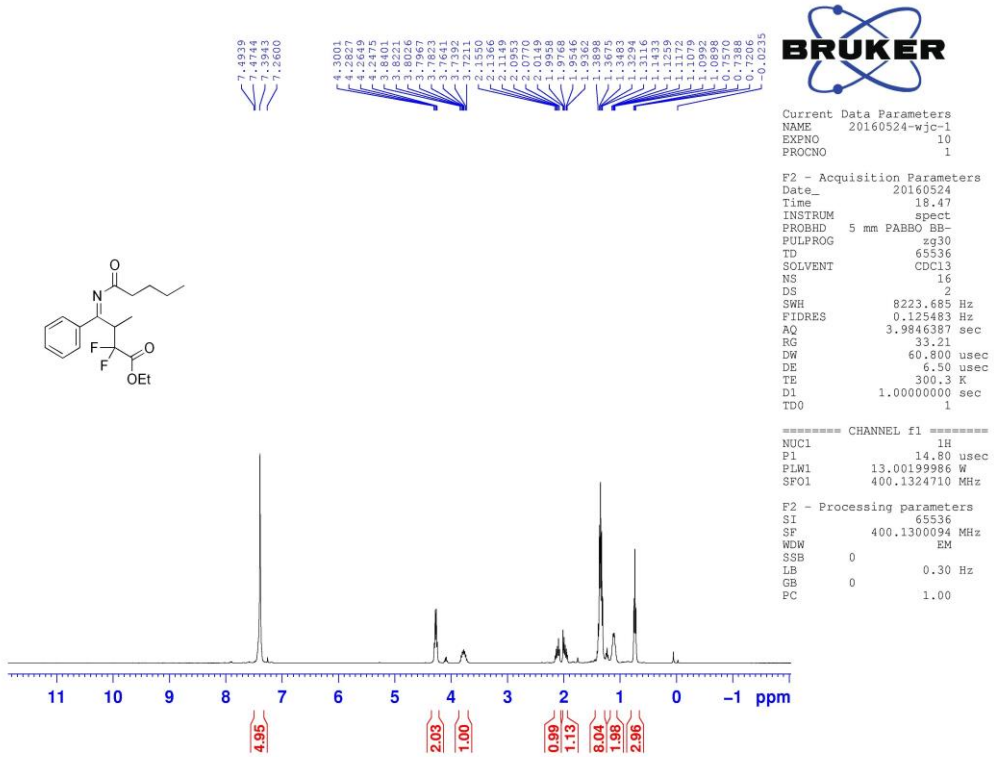
(*E*)-Ethyl 2,2-difluoro-3-methyl-4-phenyl-4-((3-phenylpropanoyl)imino)butanoate (4a)

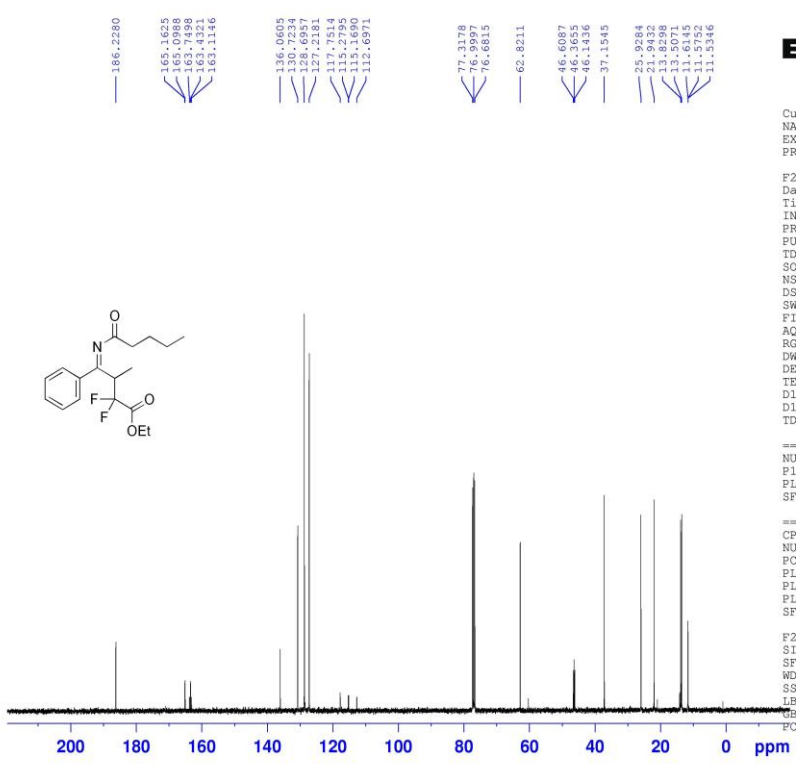






(*E*)-Ethyl 2,2-difluoro-3-methyl-4-(pentanoylimino)-4-phenylbutanoate (4b)





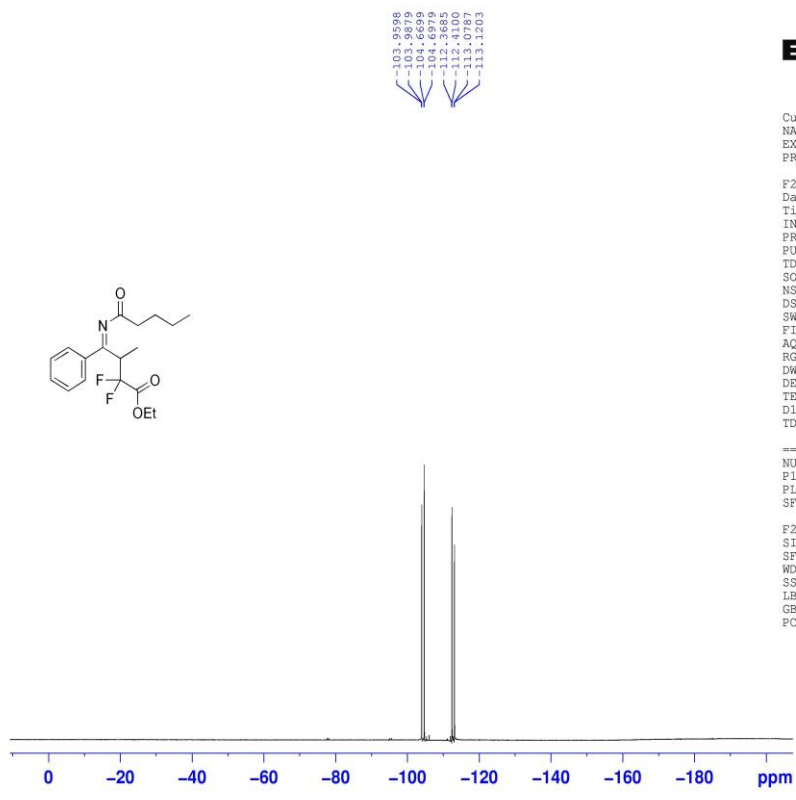

```
Current Data Parameters
NAME      20160524-wjc-1
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160524
Time               18.59
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  158
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                209.25
DW                20.800 usec
DE                 6.50 usec
TE                300.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.90 usec
PLW1         50.00299835 W
SFO1        100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PLW2         13.00199986 W
PLW12         0.38069001 W
PLW13         0.30836001 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127738 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



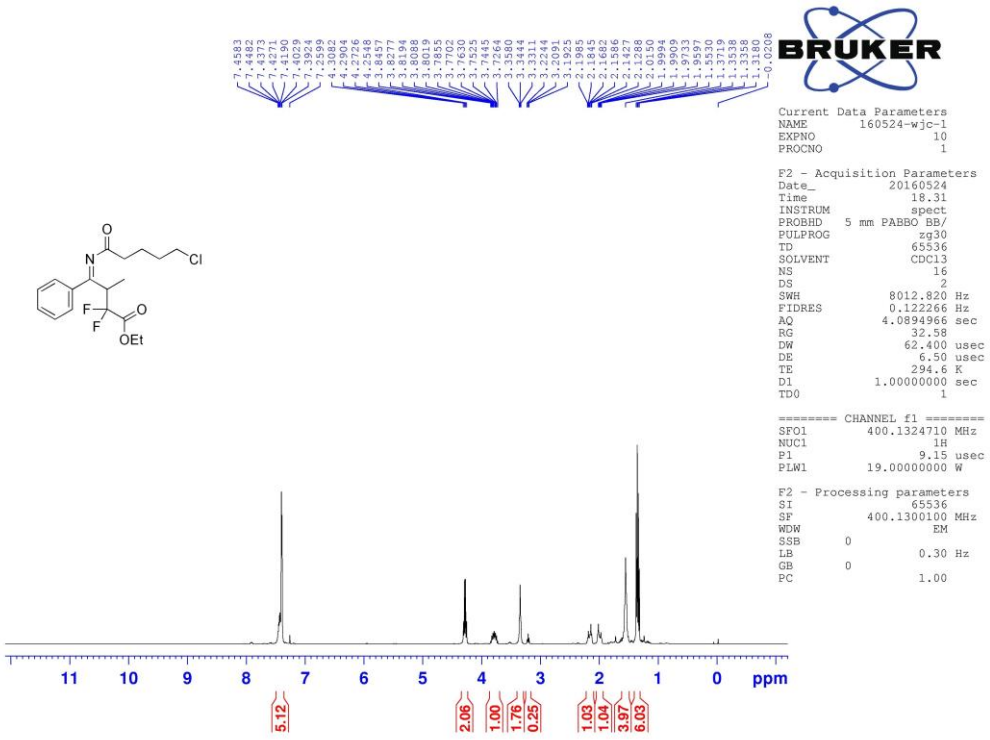

```
Current Data Parameters
NAME      20160524-wjc-1
EXPNO                 11
PROCNO                 1

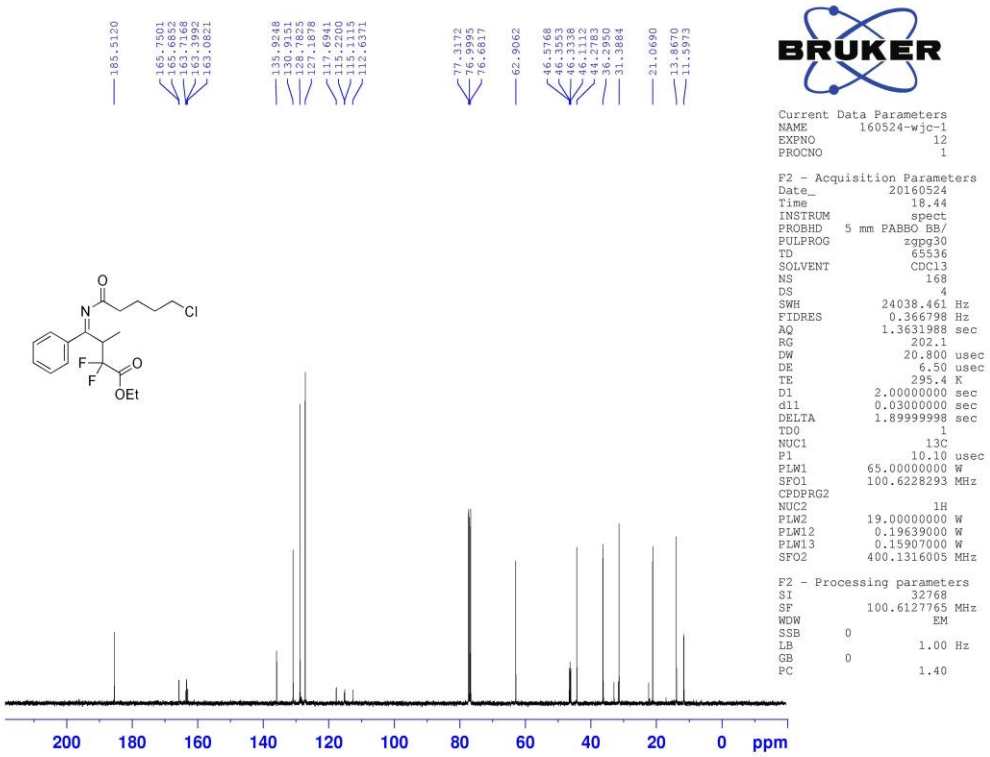
F2 - Acquisition Parameters
Date_           20160524
Time               18.49
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgflqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ             0.7340532 sec
RG                209.25
DW                 5.600 usec
DE                 6.50 usec
TE                300.2 K
D1            1.00000000 sec
TD0                   1

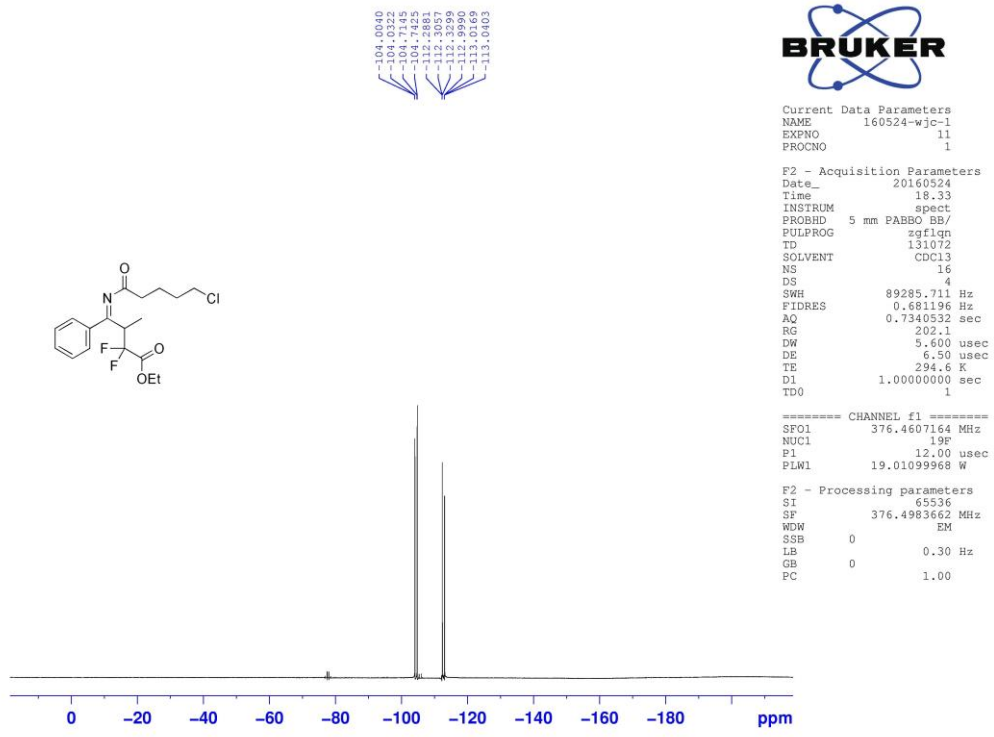
======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PLW1         20.98900032 W
SFO1        376.4607164 MHz

F2 - Processing parameters
SI                 65536
SF          376.4983660 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

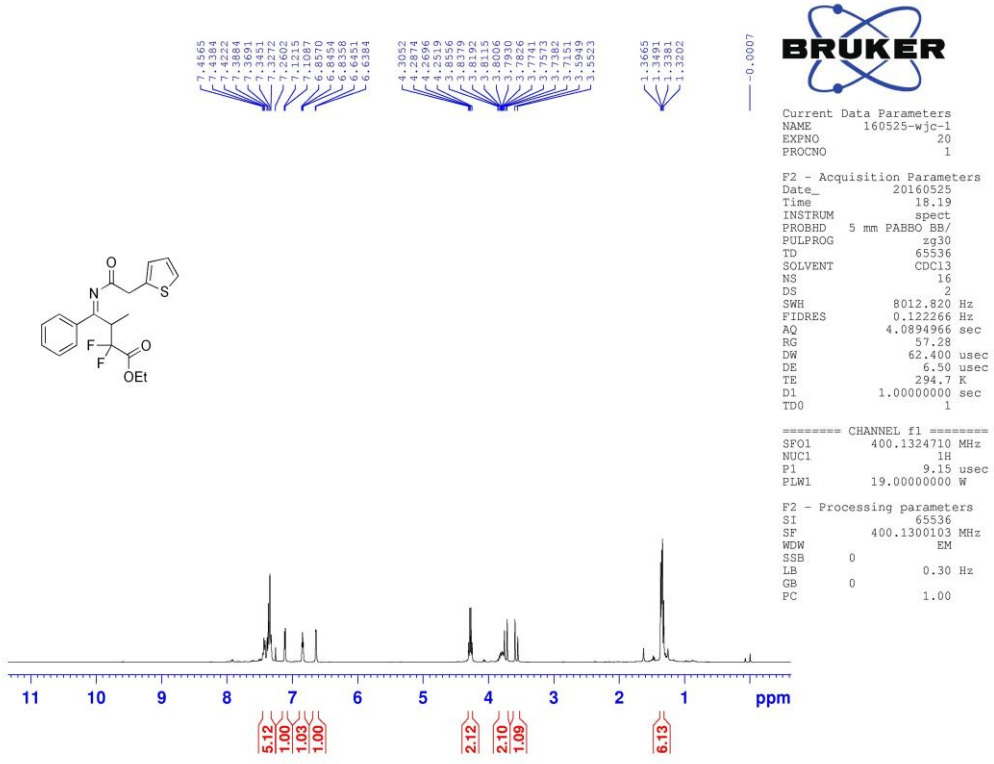
(*E*)-Ethyl 4-((5-chloropentanoyl)imino)-2,2-difluoro-3-methyl-4-phenylbutanoate (4c)

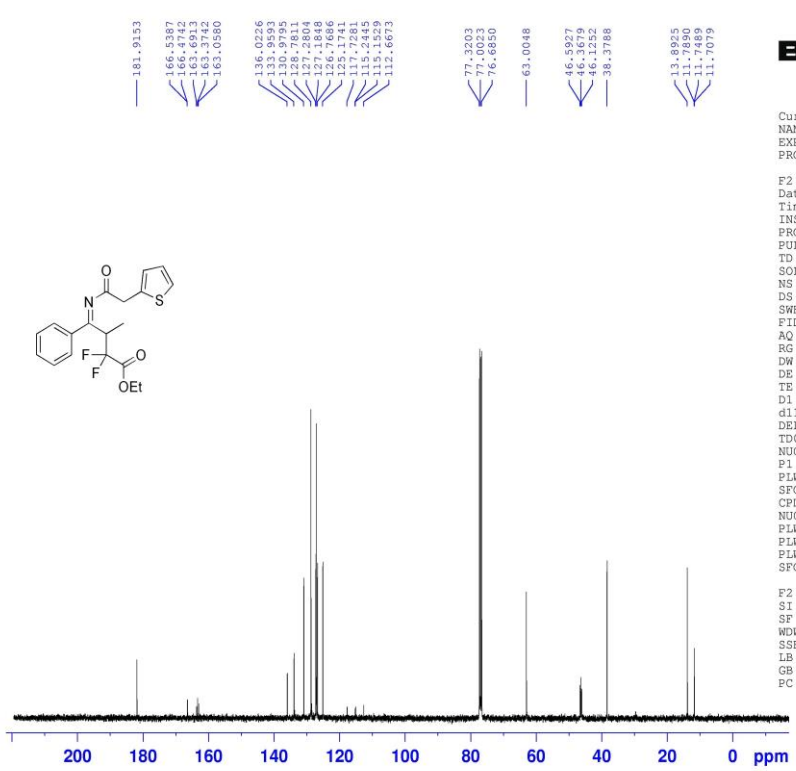






(*E*)-Ethyl 2,2-difluoro-3-methyl-4-phenyl-4-((2-(thiophen-2-yl)acetyl)imino)butanoate (4d)

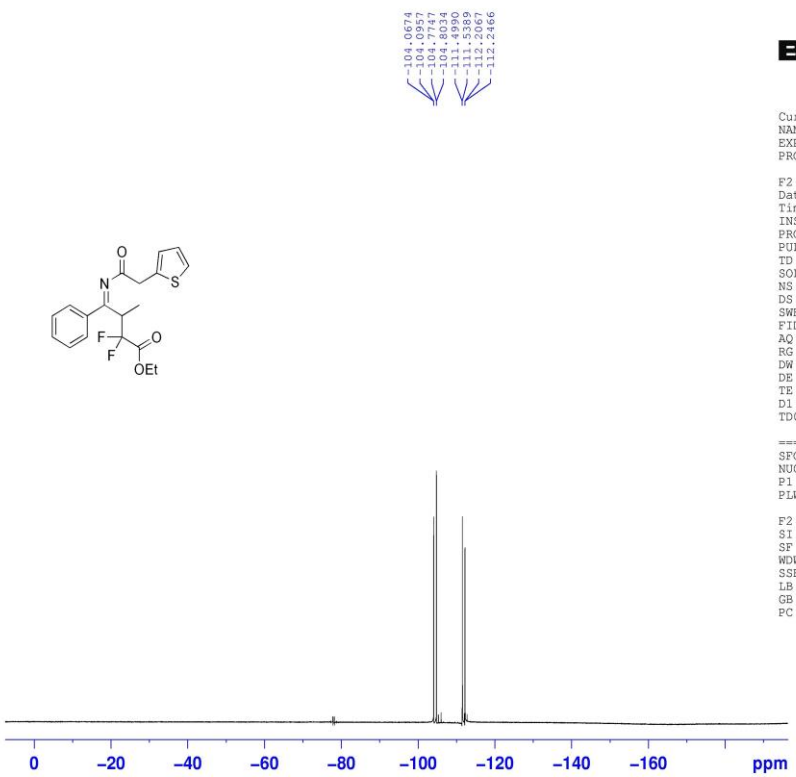




Current Data Parameters
NAME 160525-wjc-1
EXPNO 23
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160525
Time 18.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 416
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 202.1
DW 20.800 usec
DE 6.50 usec
TE 295.6 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
NUC1 13C
P1 10.10 usec
PLW1 65.00000000 W
SFO1 100.6228293 MHz
CPDPRG2
NUC2 1H
PLW2 19.00000000 W
PLW12 0.19639000 W
PLW13 0.15907000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127739 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



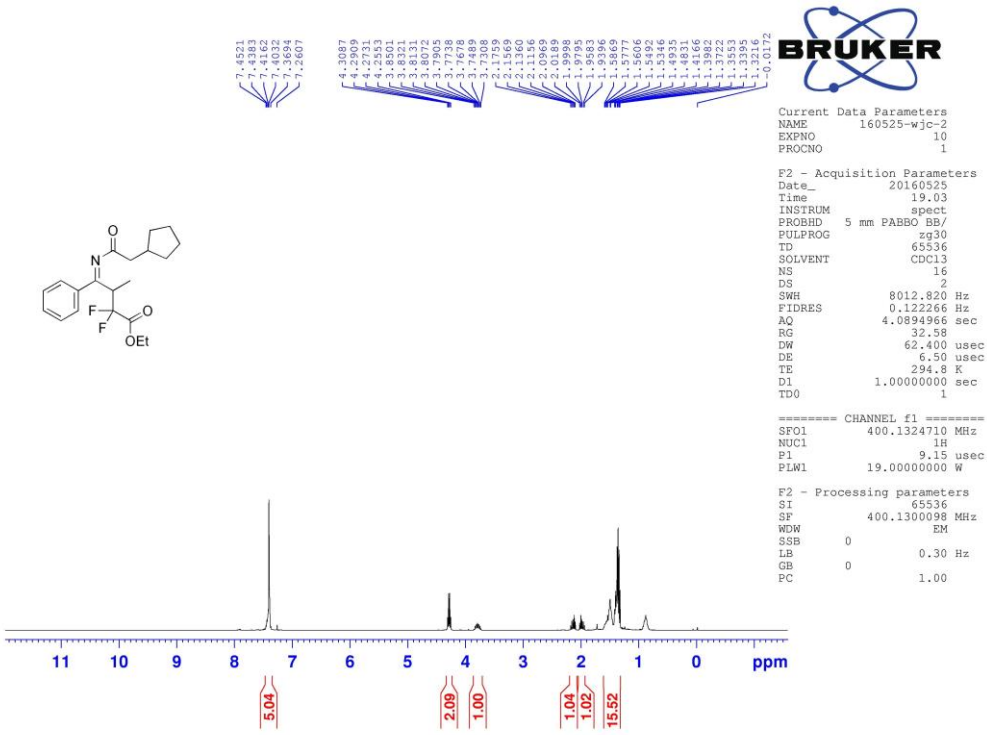
Current Data Parameters
NAME 160525-wjc-1
EXPNO 21
PROCNO 1

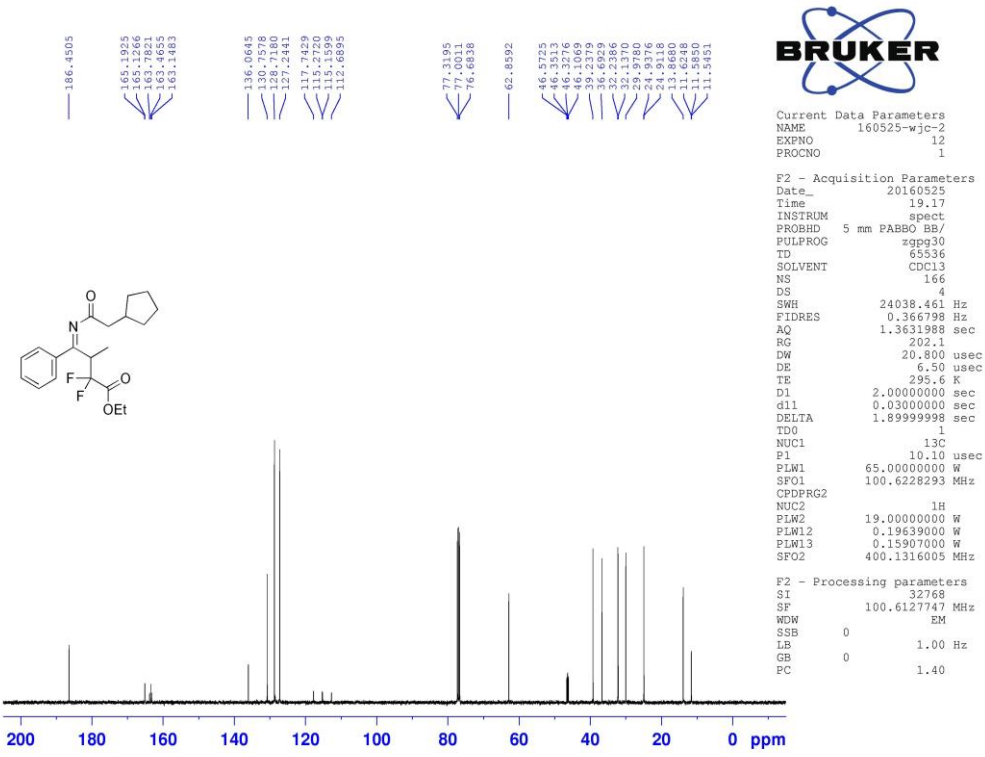
F2 - Acquisition Parameters
Date_ 20160525
Time 18.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 202.1
DW 5.600 usec
DE 6.50 usec
TE 294.7 K
D1 1.00000000 sec
TD0 1

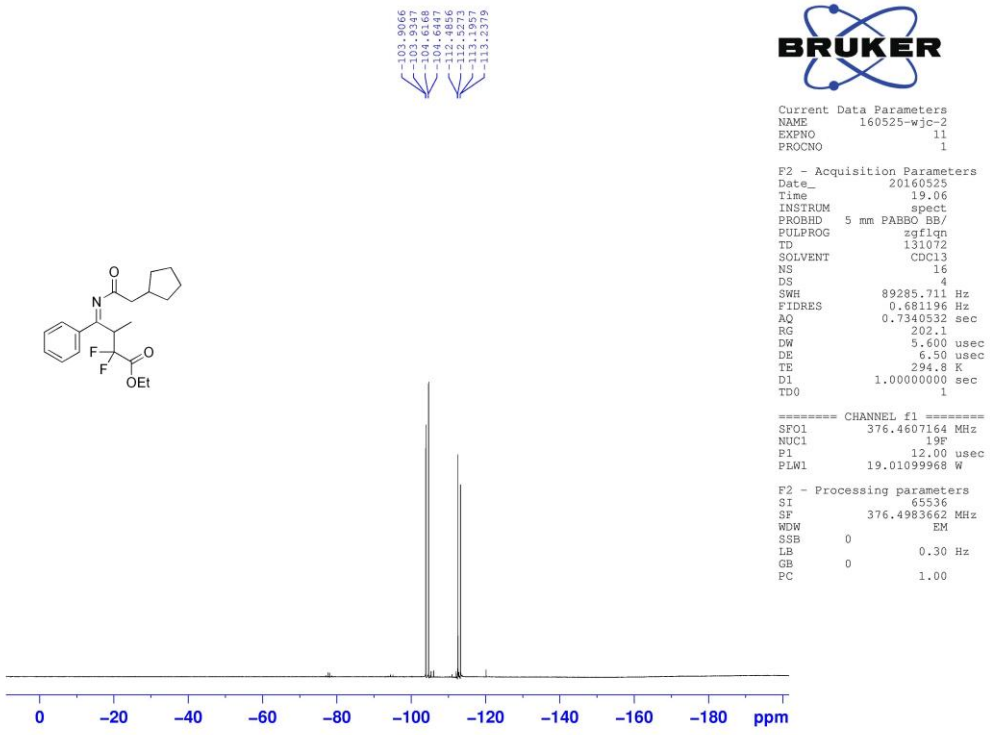
======== CHANNEL f1 ========
SFO1 376.4607164 MHz
NUC1 19F
P1 12.00 usec
PLW1 19.01099968 W

F2 - Processing parameters
SI 65536
SF 376.4983662 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

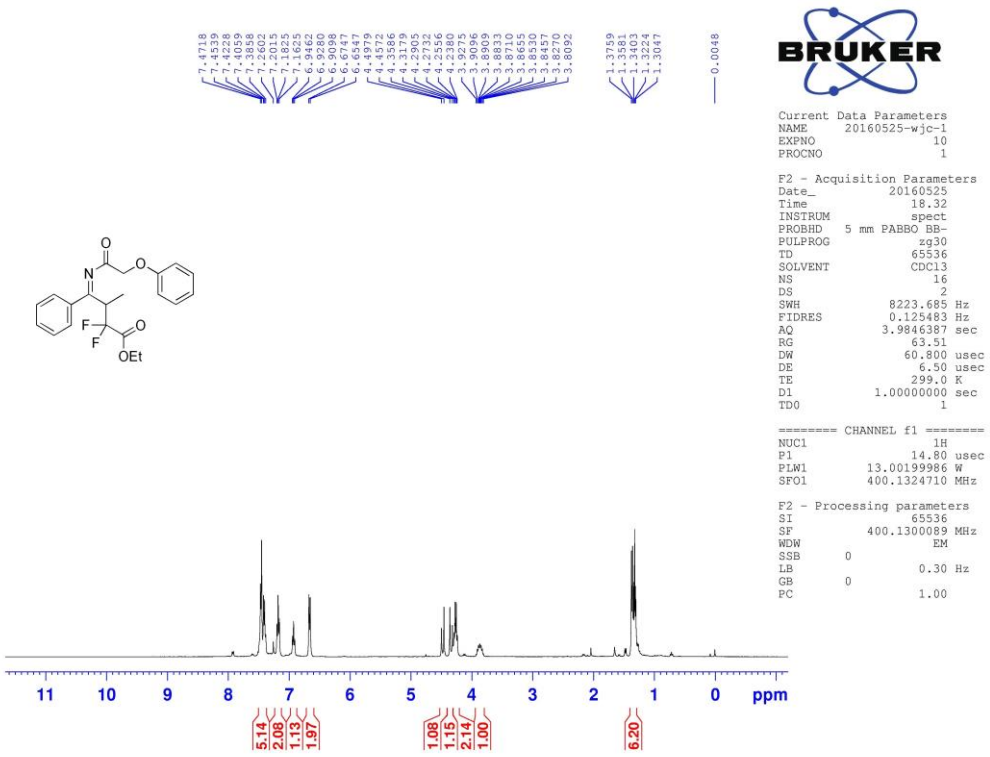
(*E*)-Ethyl 4-((2-cyclopentylacetyl)imino)-2,2-difluoro-3-methyl-4-phenylbutanoate (4e)

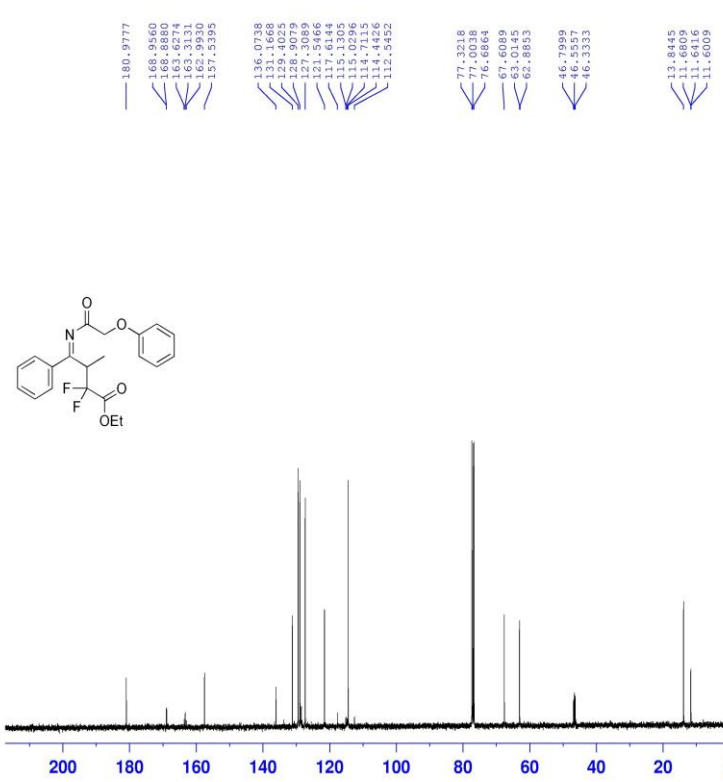






(*E*)-Ethyl 2,2-difluoro-3-methyl-4-((2-phenoxyacetyl)imino)-4-phenylbutanoate (4f)





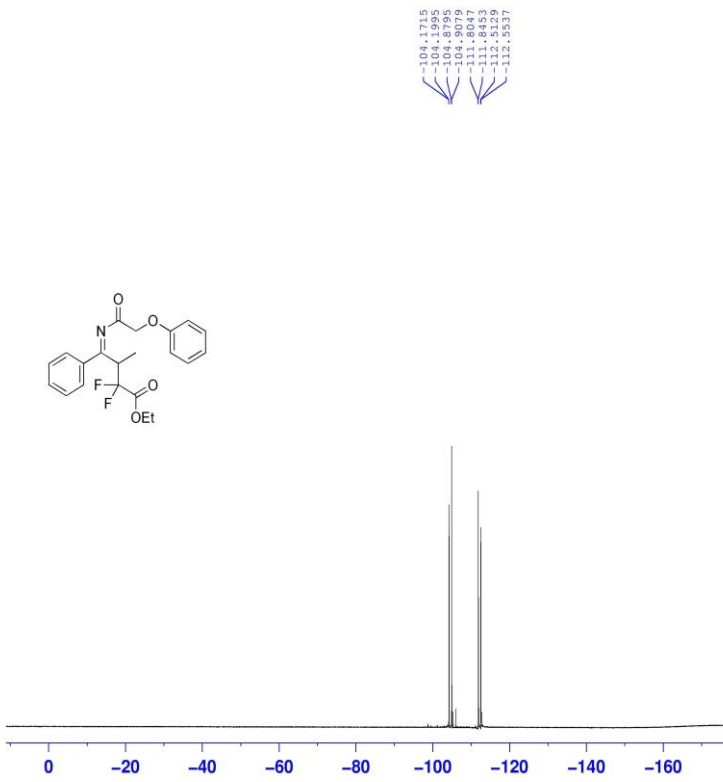
Current Data Parameters
NAME 20160525-wjc-1
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160525
Time 18.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 176
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 209.25
DW 20.800 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.90 usec
PLW1 50.00299835 W
SFO1 100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 13.00199986 W
PLW12 0.38069001 W
PLW13 0.30836001 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127745 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



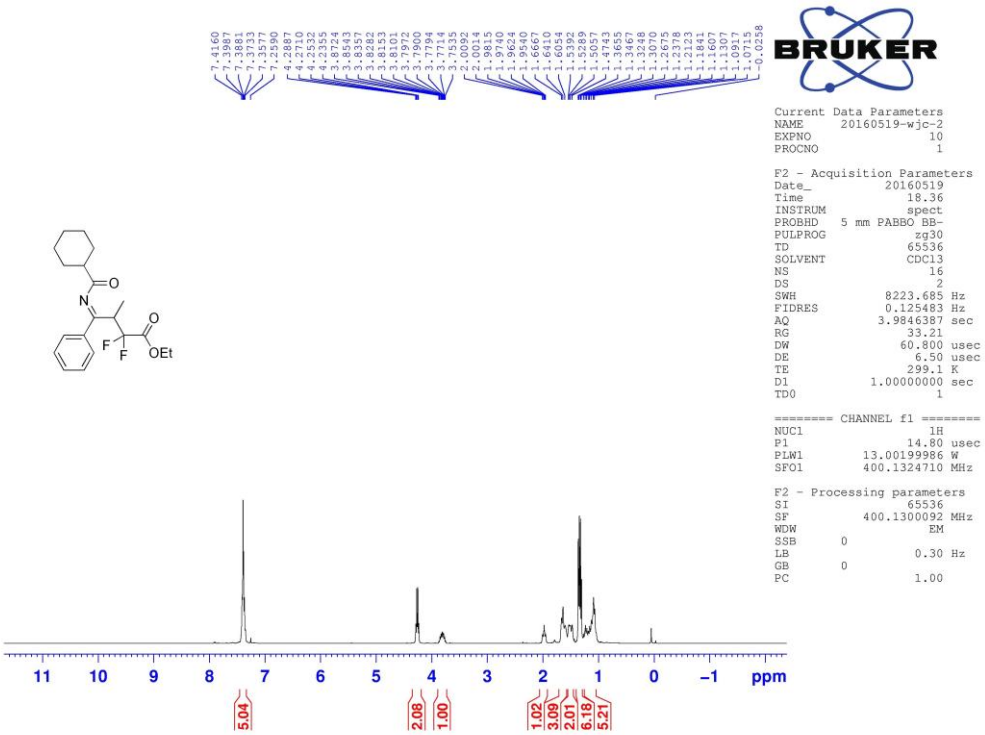
Current Data Parameters
NAME 20160525-wjc-1
EXPNO 11
PROCNO 1

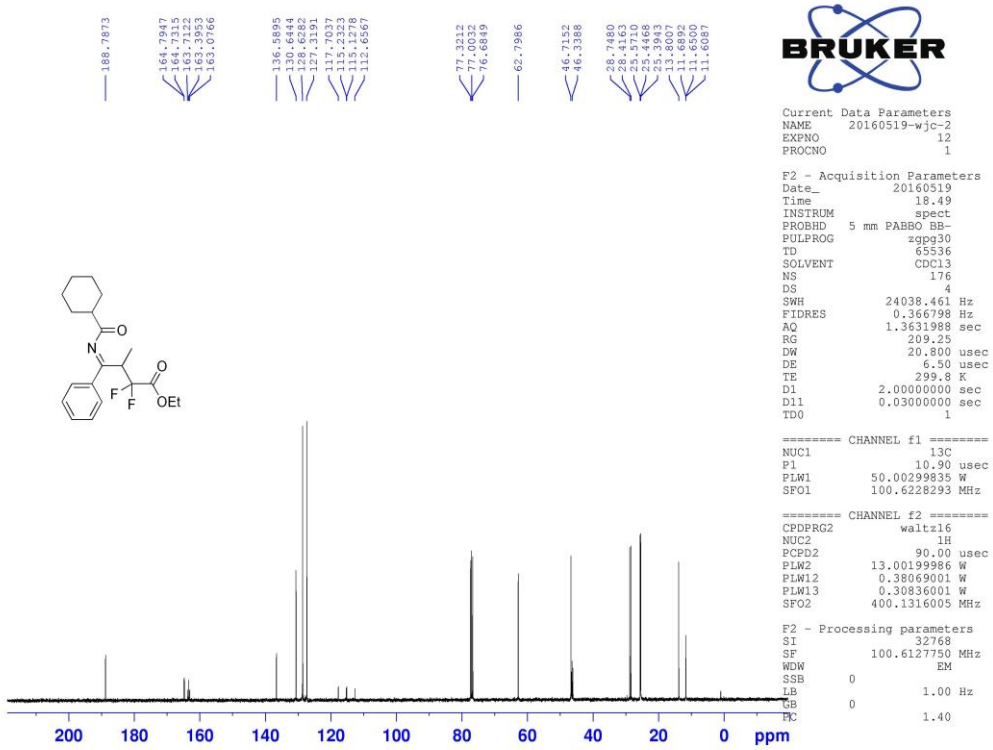
F2 - Acquisition Parameters
Date_ 20160525
Time 18.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 209.25
DW 5.600 usec
DE 6.50 usec
TE 299.0 K
D1 1.00000000 sec
TD0 1

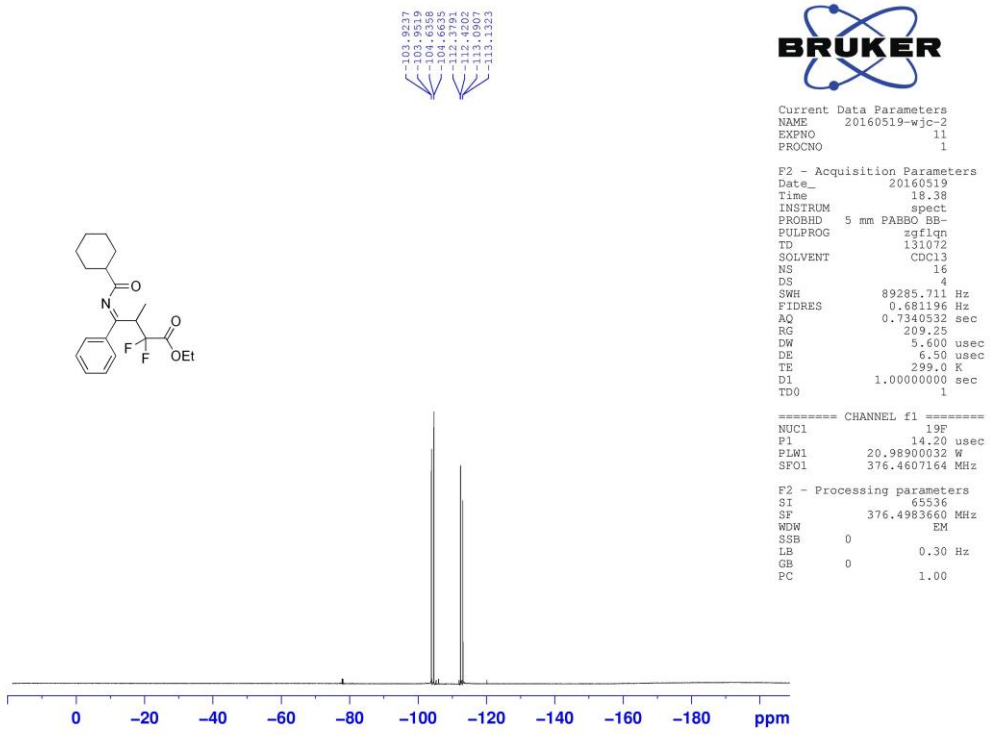
======== CHANNEL f1 ========
NUC1 19F
P1 14.20 usec
PLW1 20.98900032 W
SFO1 376.4607164 MHz

F2 - Processing parameters
SI 65536
SF 376.4983660 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

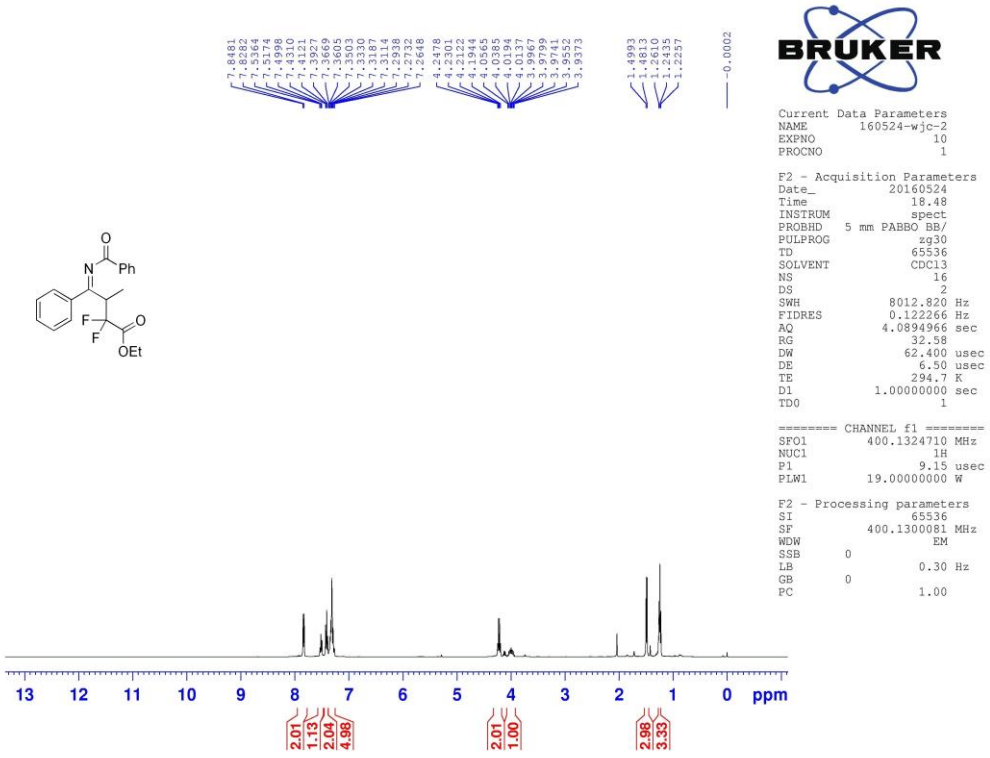
(*E*)-Ethyl 4-((cyclohexanecarbonyl)imino)-2,2-difluoro-3-methyl-4-phenylbutanoate

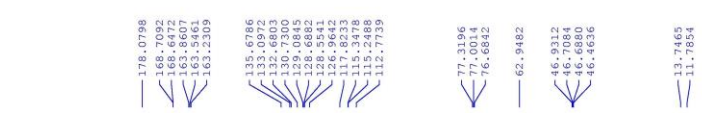


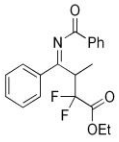


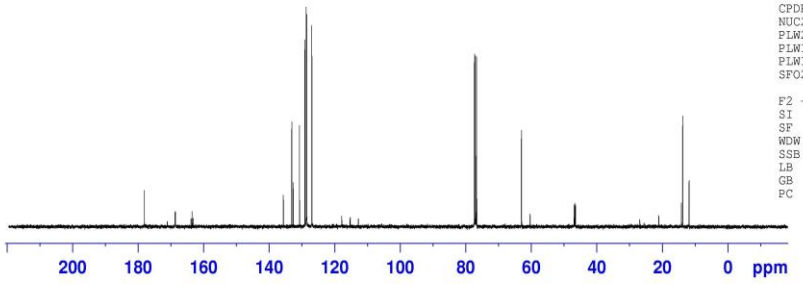


(*E*)-Ethyl 4-(benzoylimino)-2,2-difluoro-3-methyl-4-phenylbutanoate (4h)





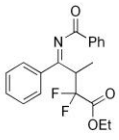


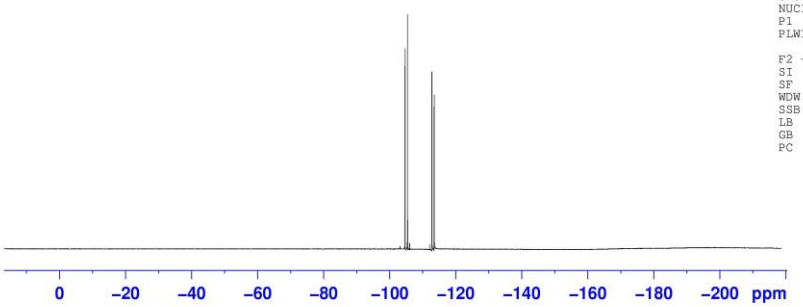


Current Data Parameters
NAME 160524-wjc-2
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160524
Time 19.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 190
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 202.1
DW 20.800 usec
DE 6.50 usec
TE 295.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
NUC1 13C
P1 10.10 usec
PLW1 65.00000000 W
SFO1 100.6228293 MHz
CPDPRG2
NUC2 1H
PLW2 19.00000000 W
PLW12 0.19639000 W
PLW13 0.15907000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127755 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40





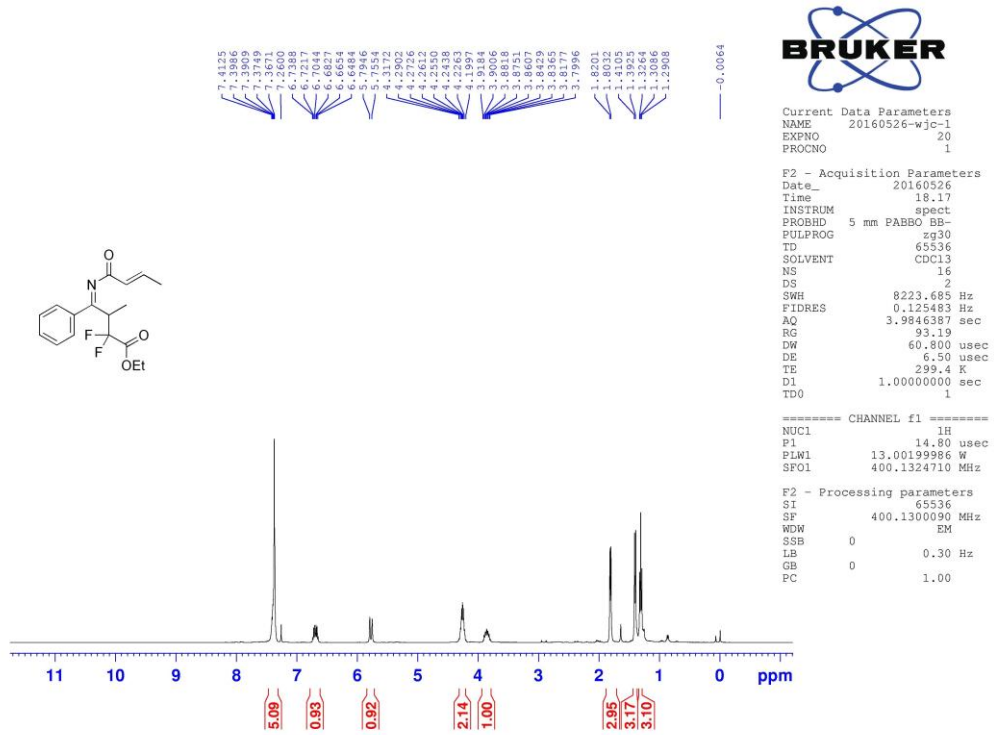
Current Data Parameters
NAME 160524-wjc-2
EXPNO 11
PROCNO 1

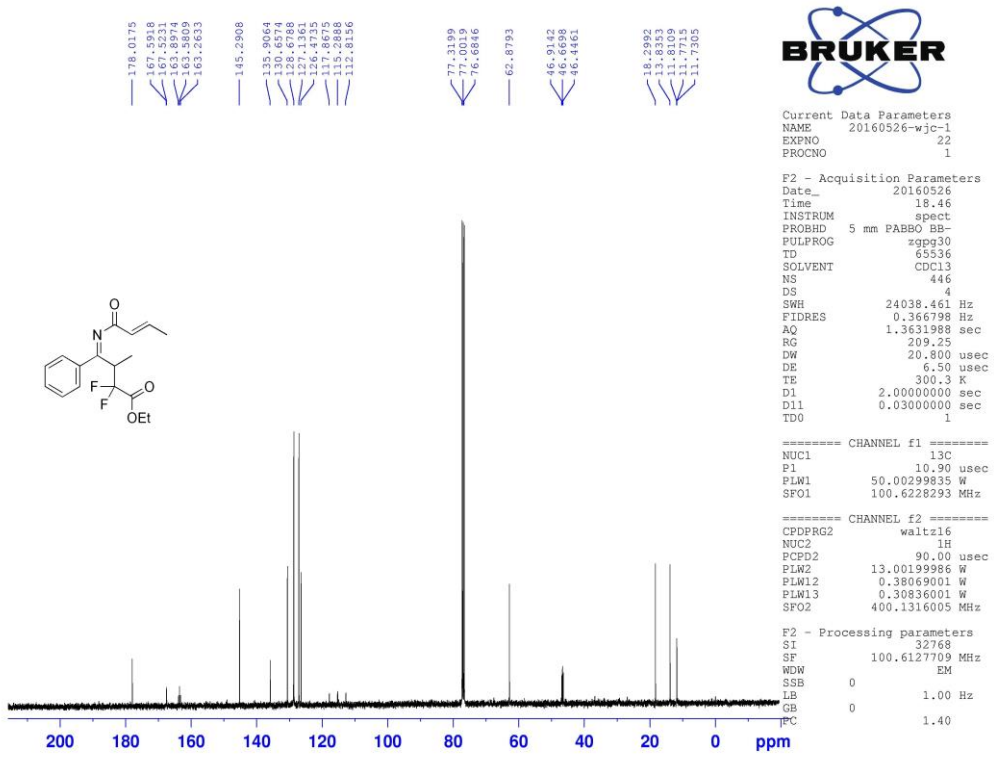
F2 - Acquisition Parameters
Date_ 20160524
Time 18.49
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 202.1
DW 5.600 usec
DE 6.50 usec
TE 294.7 K
D1 1.00000000 sec
TD0 1

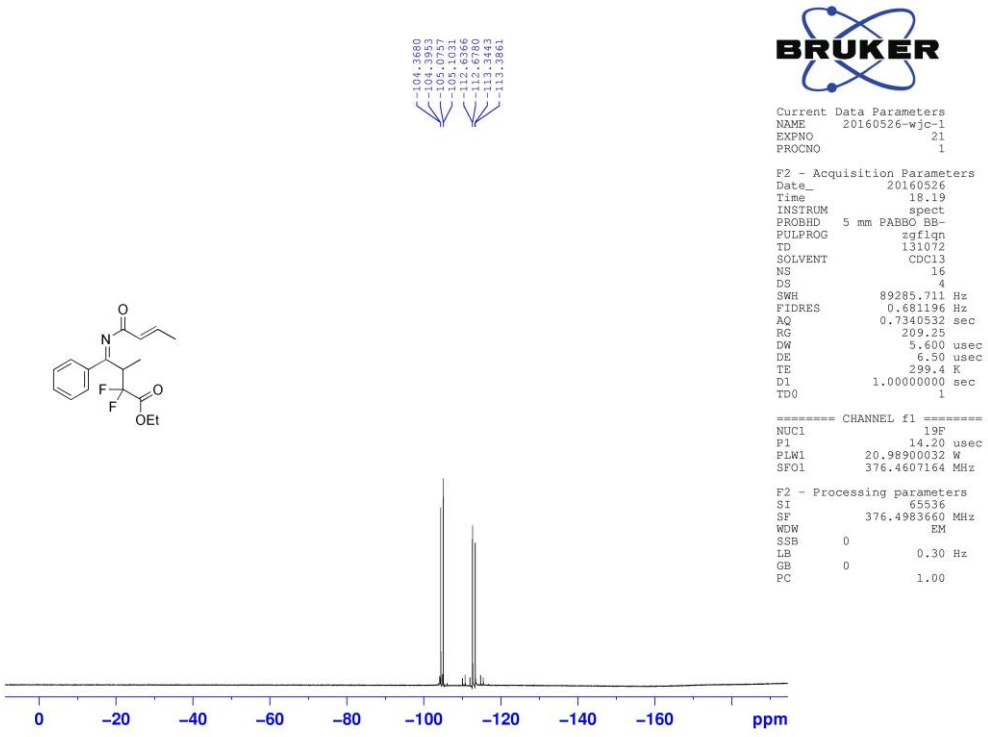
======== CHANNEL f1 ========
SFO1 376.4607164 MHz
NUC1 19F
P1 12.00 usec
PLW1 19.01099968 W

F2 - Processing parameters
SI 65536
SF 376.4983662 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

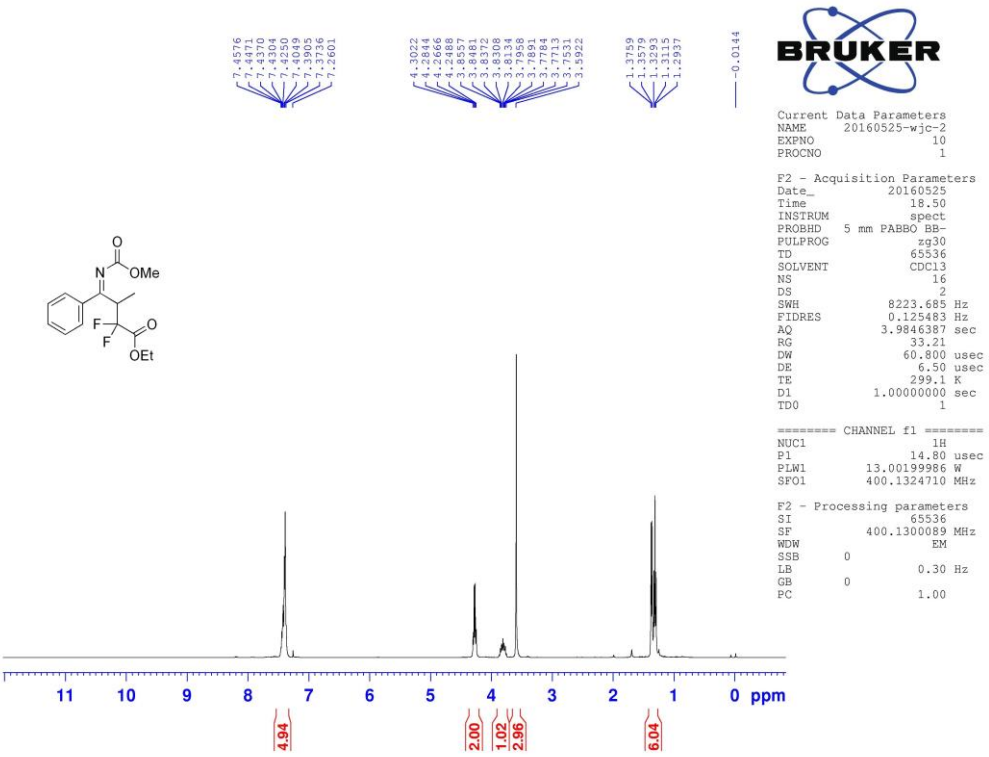
(*E*)-Ethyl 4-((E)-but-2-enoylimino)-2,2-difluoro-3-methyl-4-phenylbutanoate (4i)

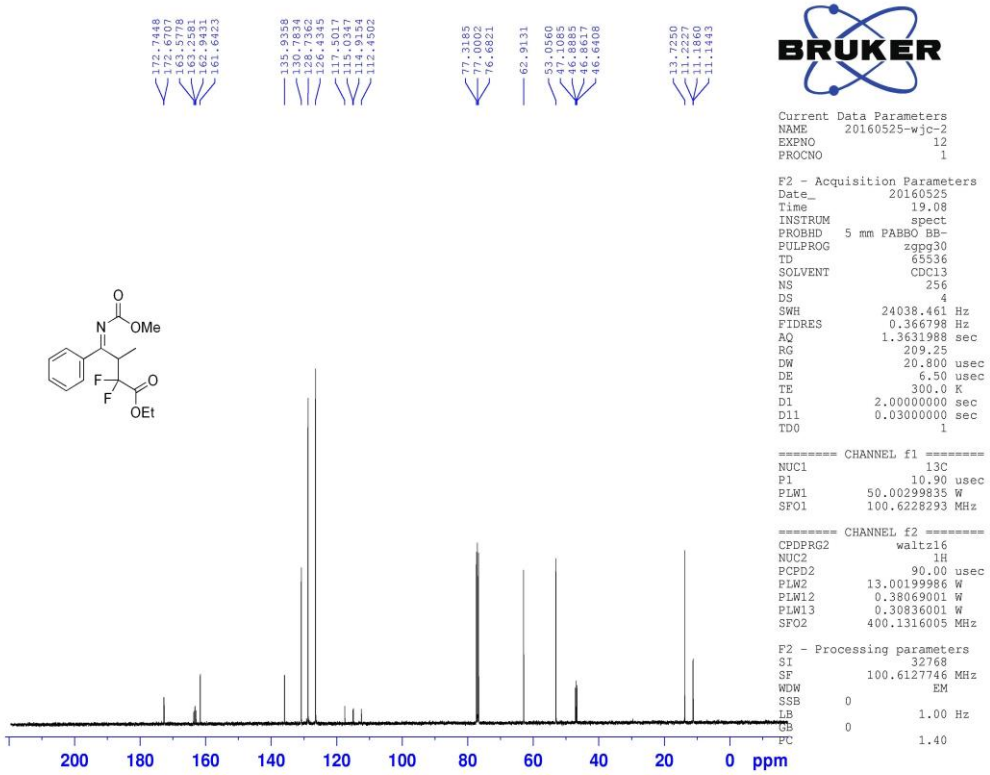






(*E*)-Ethyl 2,2-difluoro-4-((methoxycarbonyl)imino)-3-methyl-4-phenylbutanoate (4j)





BRUKER

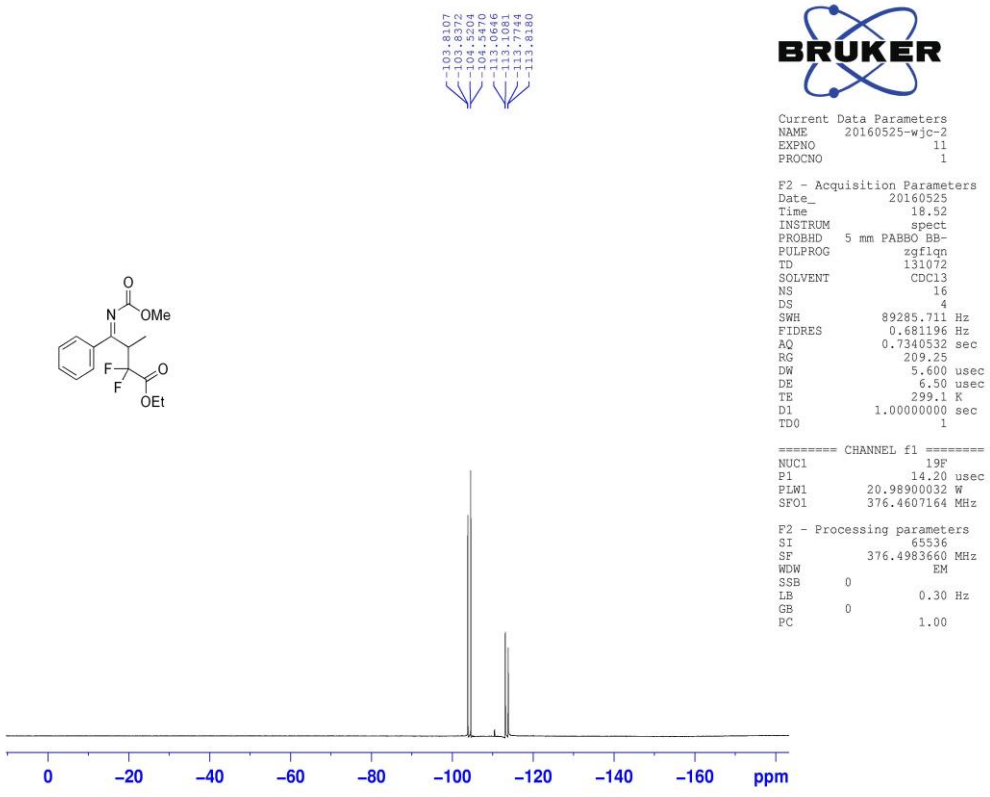
```
Current Data Parameters
NAME      20160525-wjc-2
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160525
Time               19.08
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD              65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                209.25
DW               20.800 usec
DE                6.50 usec
TE               300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.90 usec
PLW1         50.00299835 W
SFO1        100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PLW2         13.00199986 W
PLW12         0.38069001 W
PLW13         0.30836001 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127746 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



BRUKER

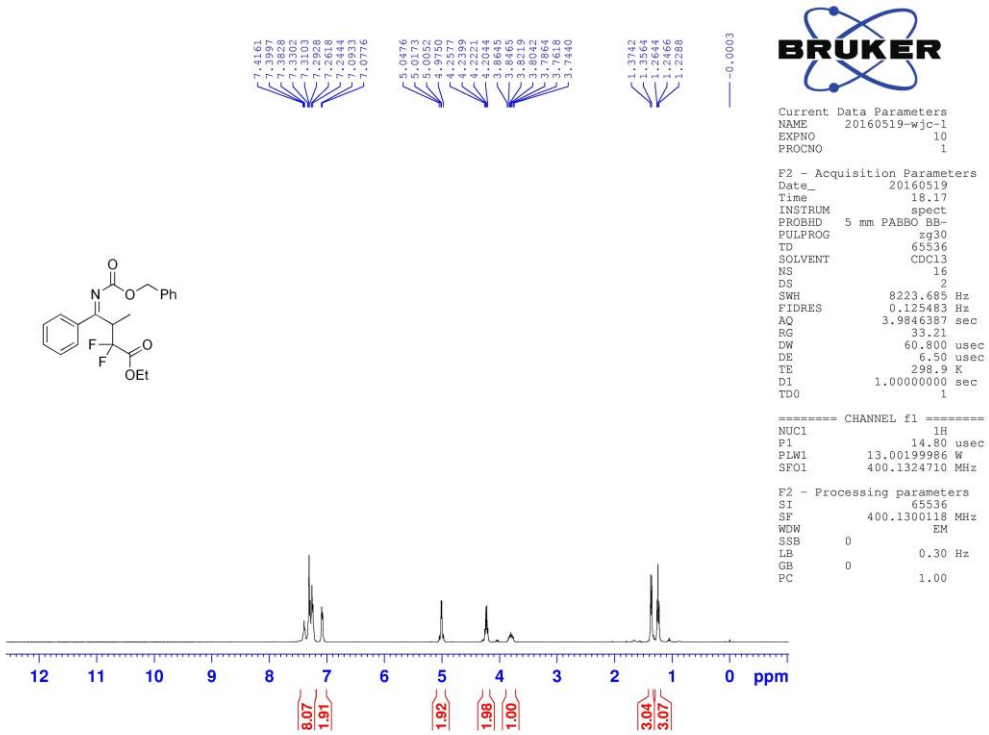
```
Current Data Parameters
NAME      20160525-wjc-2
EXPNO                 11
PROCNO                 1

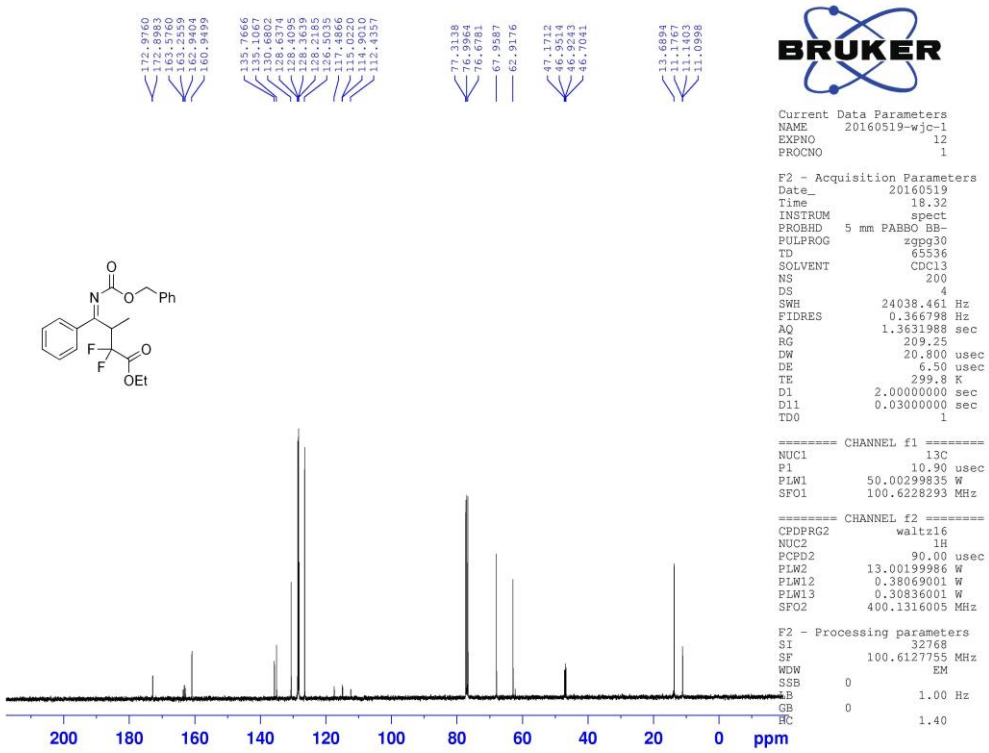
F2 - Acquisition Parameters
Date_           20160525
Time               18.52
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgflqn
TD              131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES        0.681196 Hz
AQ            0.7340532 sec
RG                209.25
DW                5.600 usec
DE                6.50 usec
TE               299.1 K
D1            1.00000000 sec
TD0                   1

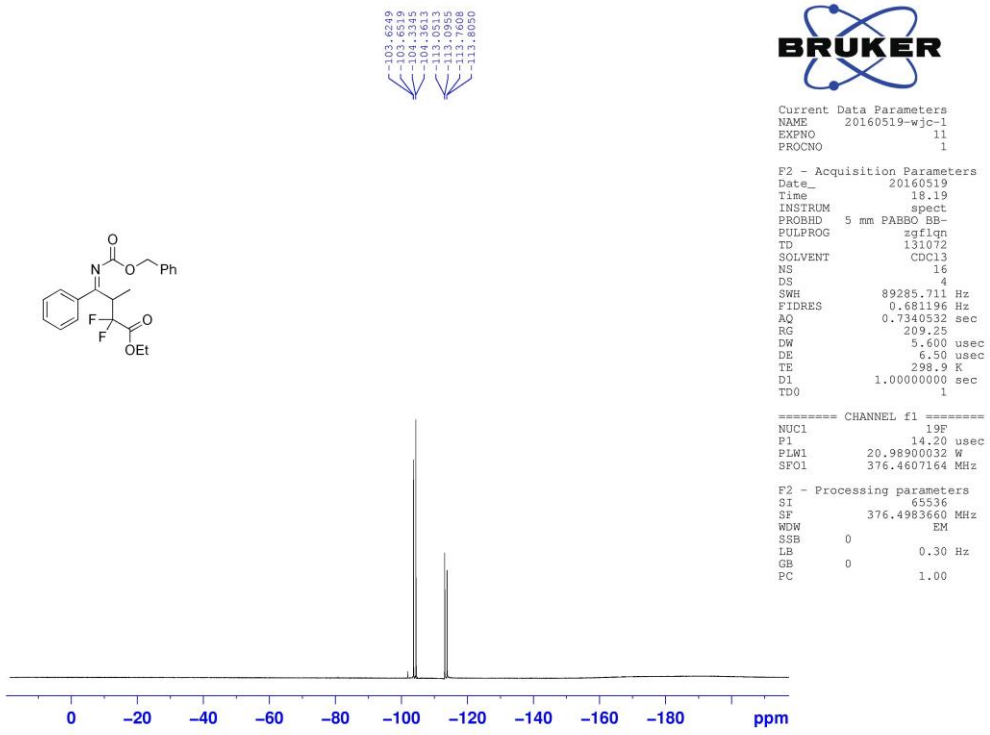
======== CHANNEL f1 ========
NUC1                 19F
P1                 14.20 usec
PLW1         20.98900032 W
SFO1        376.4607164 MHz

F2 - Processing parameters
SI                 65536
SF          376.4983660 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

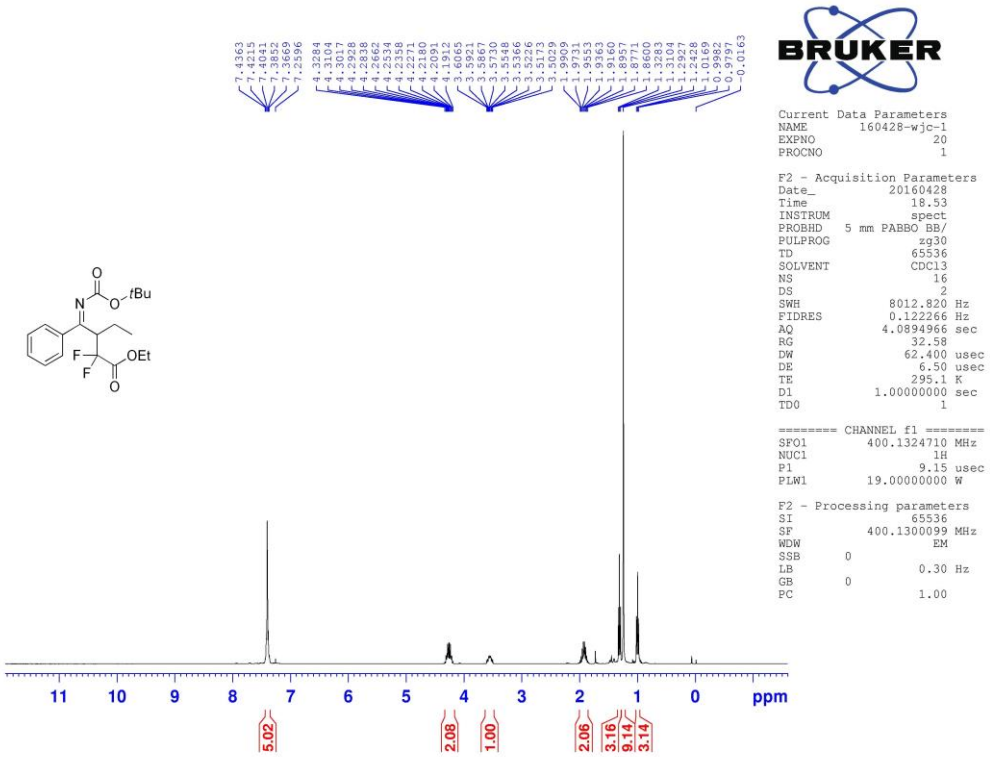
(*E*)-Ethyl 4-(((benzyloxy)carbonyl)imino)-2,2-difluoro-3-methyl-4-phenylbutanoate (4k)

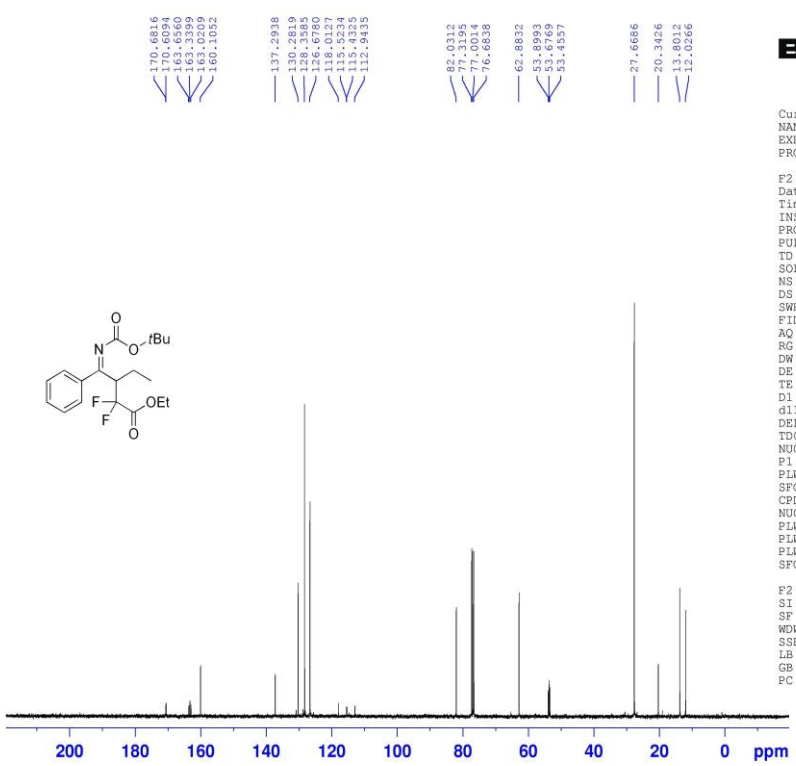






(*E*)-Ethyl 3-(((tert-butoxycarbonyl)imino)(phenyl)methyl)-2,2-difluoropentanoate (4l)

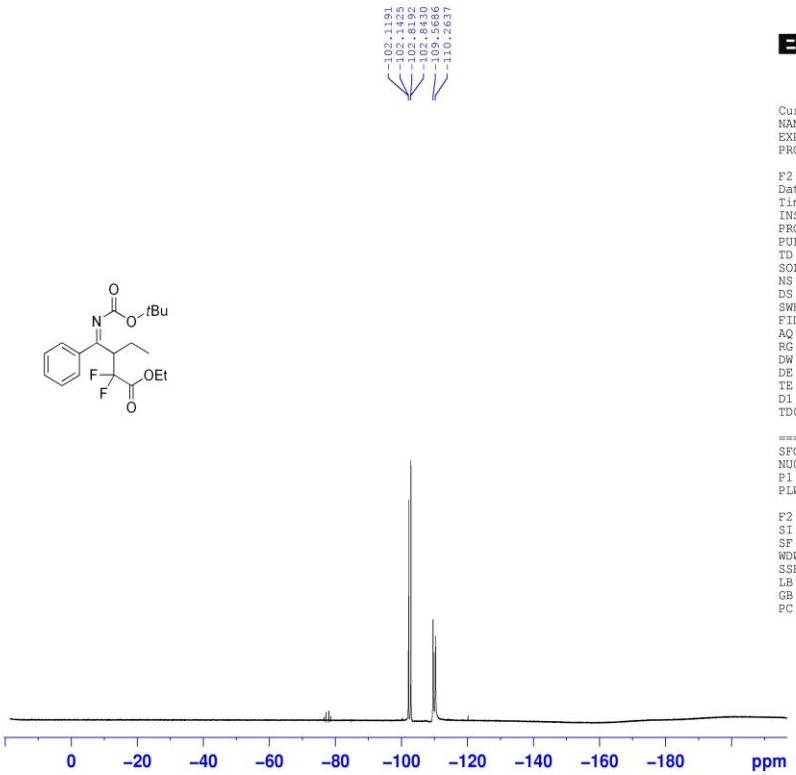




Current Data Parameters
NAME 160428-wjc-1
EXPNO 22
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160428
Time 19.06
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 170
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 202.1
DW 20.800 usec
DE 6.50 usec
TE 295.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
NUC1 13C
P1 10.10 usec
PLW1 65.00000000 W
SFO1 100.6228293 MHz
CPDPRG2
NUC2 1H
PLW2 19.00000000 W
PLW12 0.19639000 W
PLW13 0.15907000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127747 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



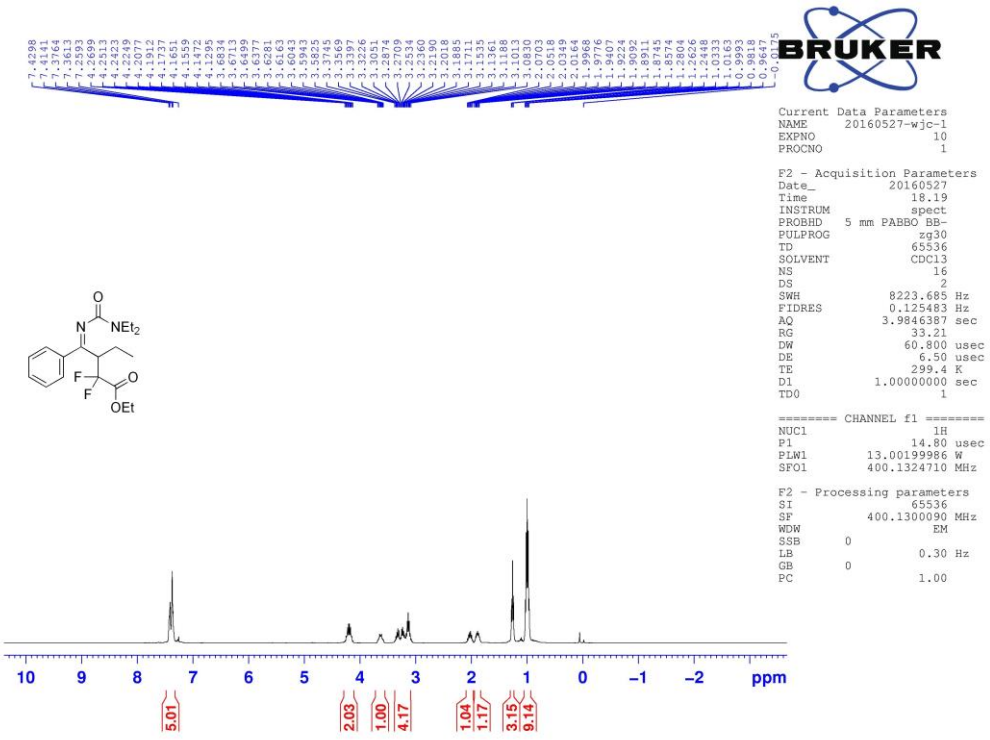
Current Data Parameters
NAME 160428-wjc-1
EXPNO 21
PROCNO 1

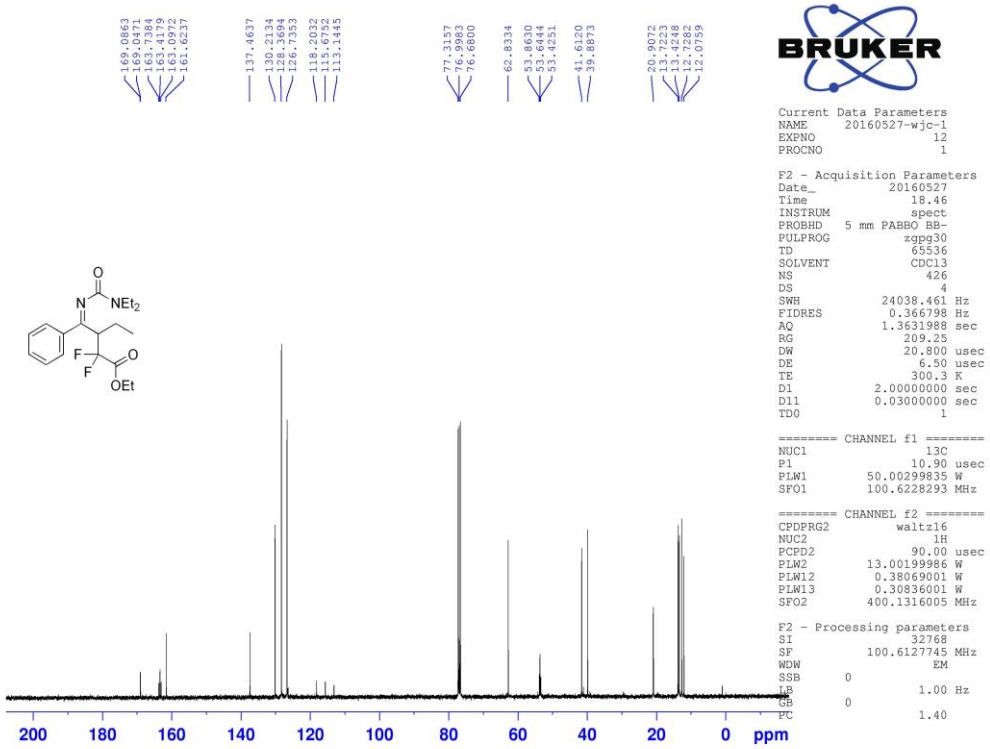
F2 - Acquisition Parameters
Date_ 20160428
Time 18.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 202.1
DW 5.600 usec
DE 6.50 usec
TE 295.1 K
D1 1.00000000 sec
TD0 1

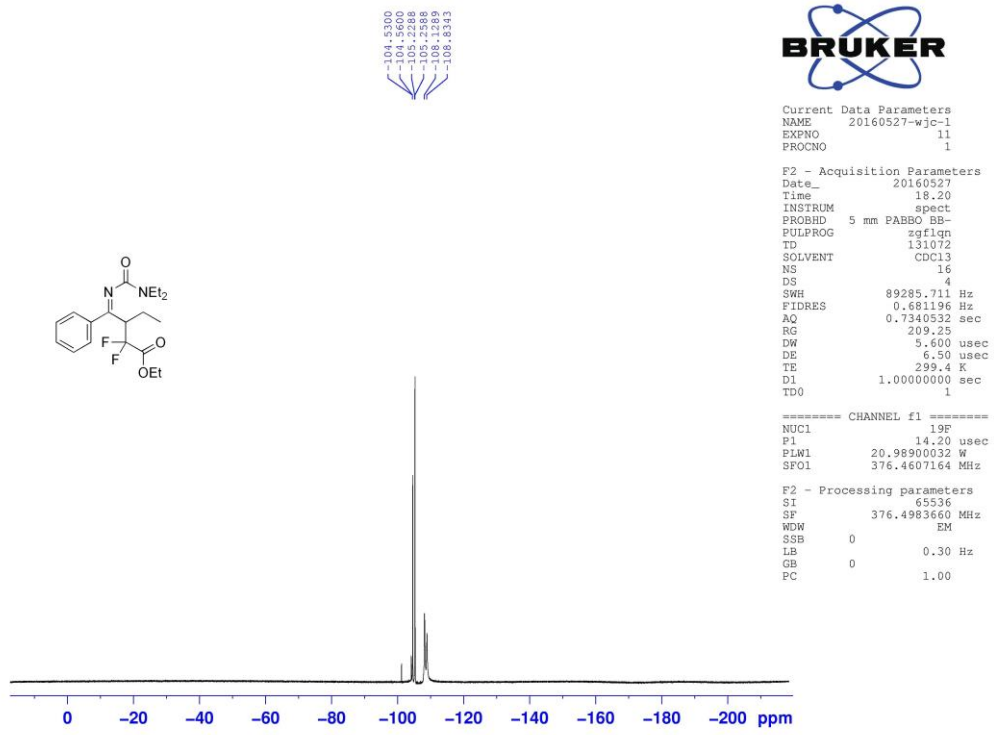
======== CHANNEL f1 ========
SFO1 376.4607164 MHz
NUC1 19F
P1 12.00 usec
PLW1 19.01099968 W

F2 - Processing parameters
SI 65536
SF 376.4983662 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

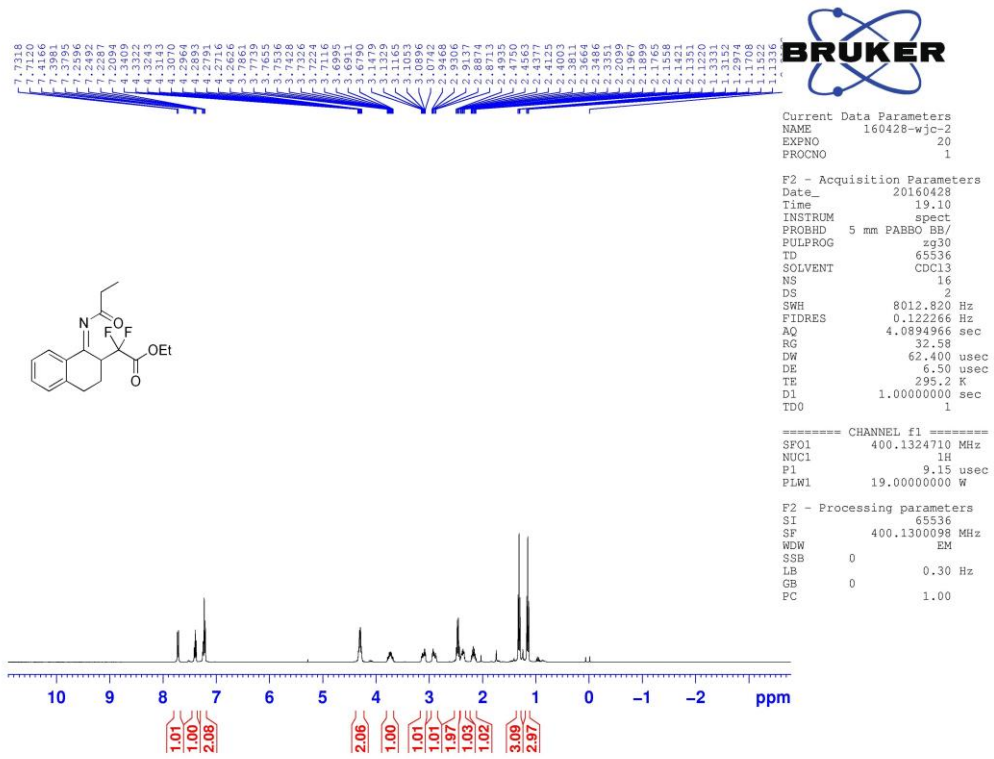
(*E*)-Ethyl 3-(((diethylcarbamoyl)imino)(phenyl)methyl)-2,2-difluoropentanoate (4m)

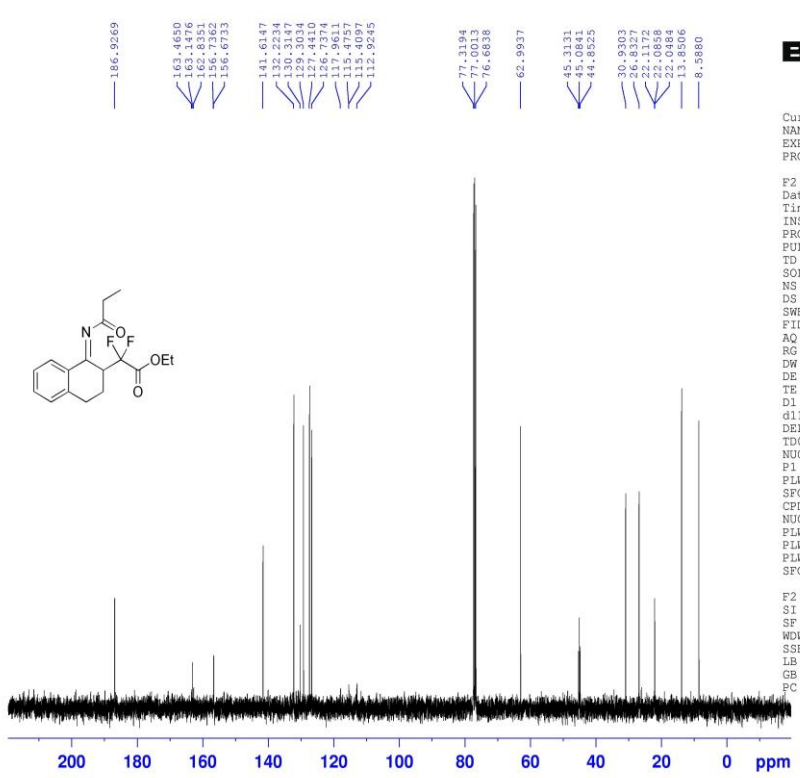






(*E*)-Ethyl 2,2-difluoro-2-(1-(propionylimino)-1,2,3,4-tetrahydronaphthalen-2-yl)acetate (4n)

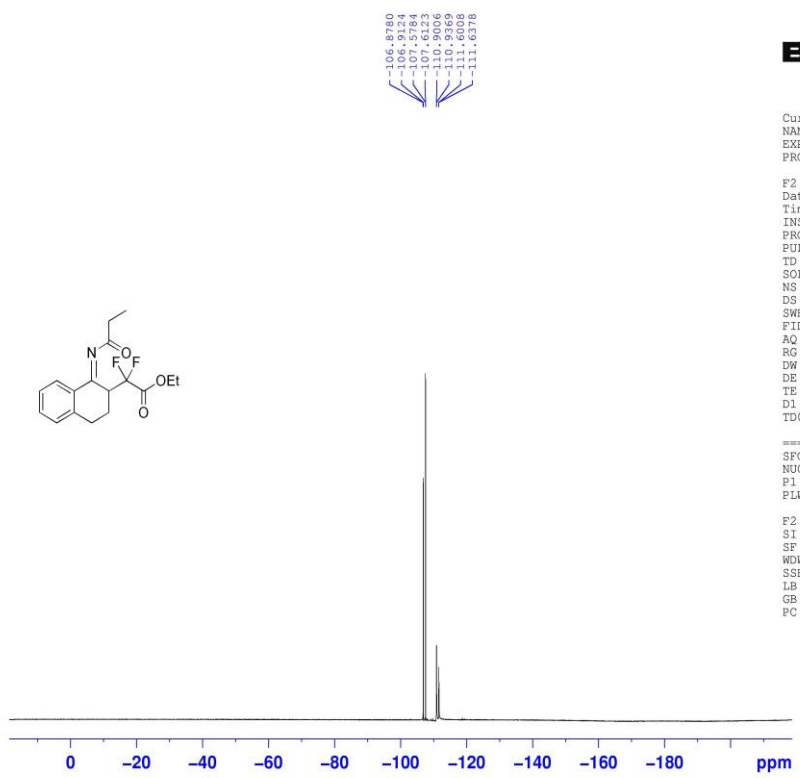




```
Current Data Parameters
NAME        160428-wjc-2
EXPNO                 22
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160428
Time               19.14
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                202.1
DW                20.800 usec
DE                 6.50 usec
TE                295.7 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                   1
NUC1                13C
P1                10.10 usec
PLW1          65.00000000 W
SFO1         100.6228293 MHz
CPDPRG2
NUC2                1H
PLW2          19.00000000 W
PLW12          0.19639000 W
PLW13          0.15907000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127753 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



```
Current Data Parameters
NAME        160428-wjc-2
EXPNO                 21
PROCNO                 1

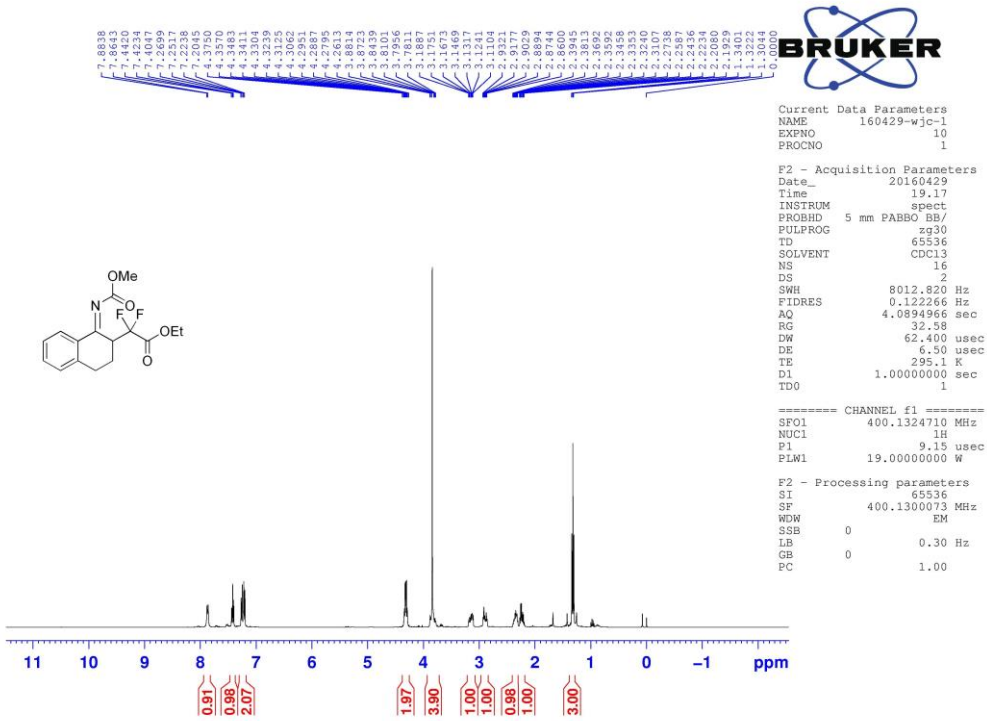
F2 - Acquisition Parameters
Date_           20160428
Time               19.12
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ             0.7340532 sec
RG                202.1
DW                 5.600 usec
DE                 6.50 usec
TE                295.2 K
D1             1.00000000 sec
TD0                   1

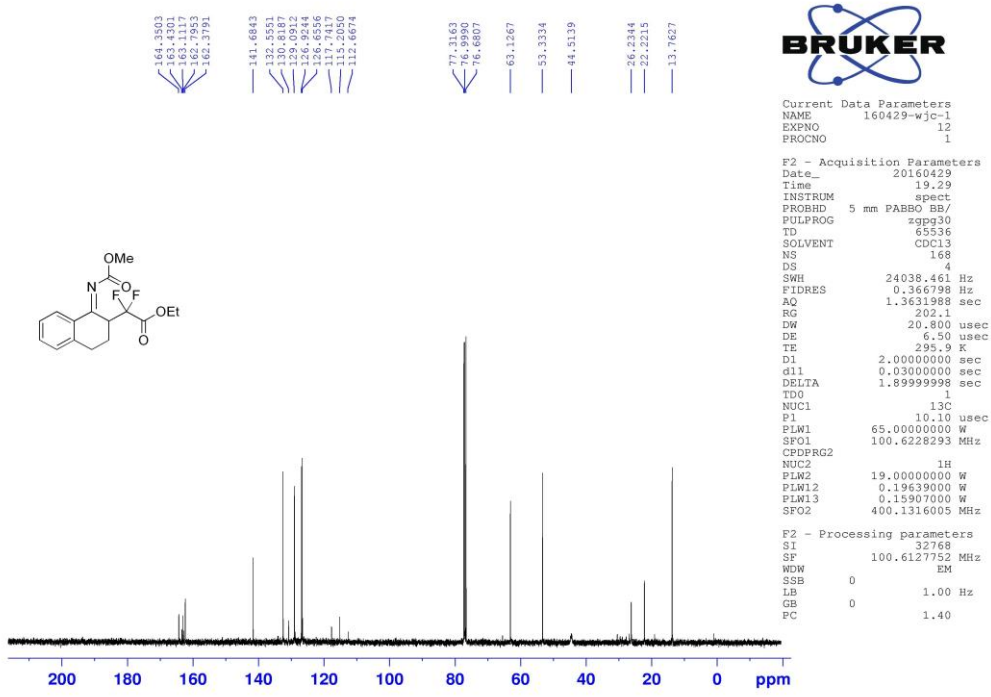
======== CHANNEL f1 ========
SFO1         376.4607164 MHz
NUC1                19F
P1                12.00 usec
PLW1          19.01099968 W

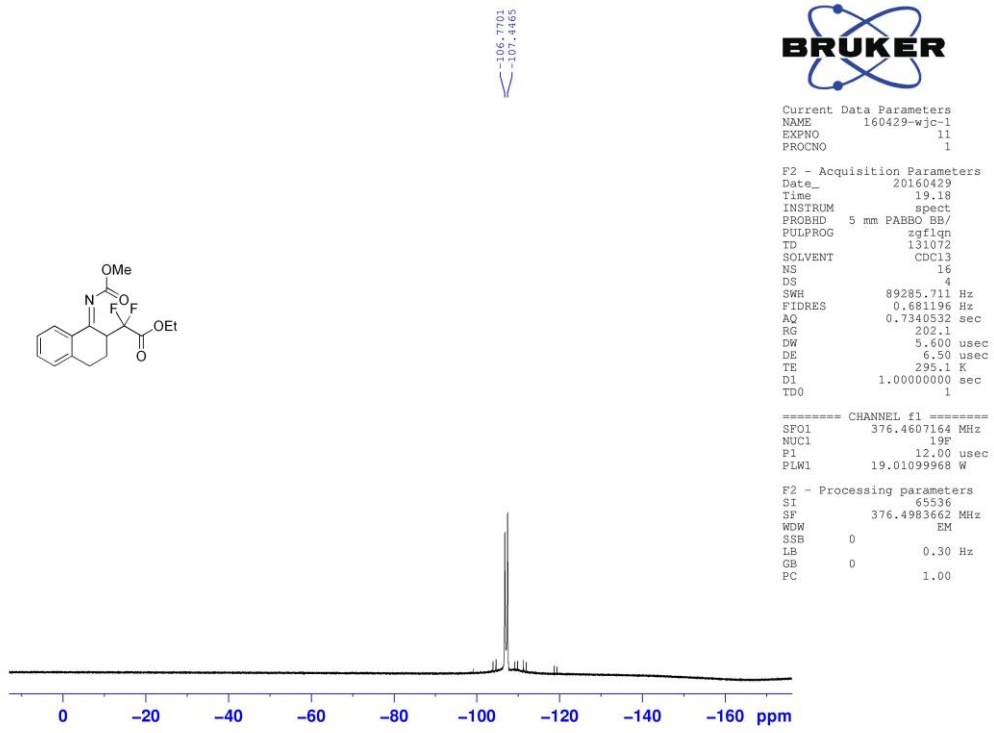
F2 - Processing parameters
SI                 65536
SF           376.4983662 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

(*E*)-Ethyl 2,2-difluoro-2-(1-((methoxycarbonyl)imino)-1,2,3,4-tetrahydronaphthalen-2-yl)acetate

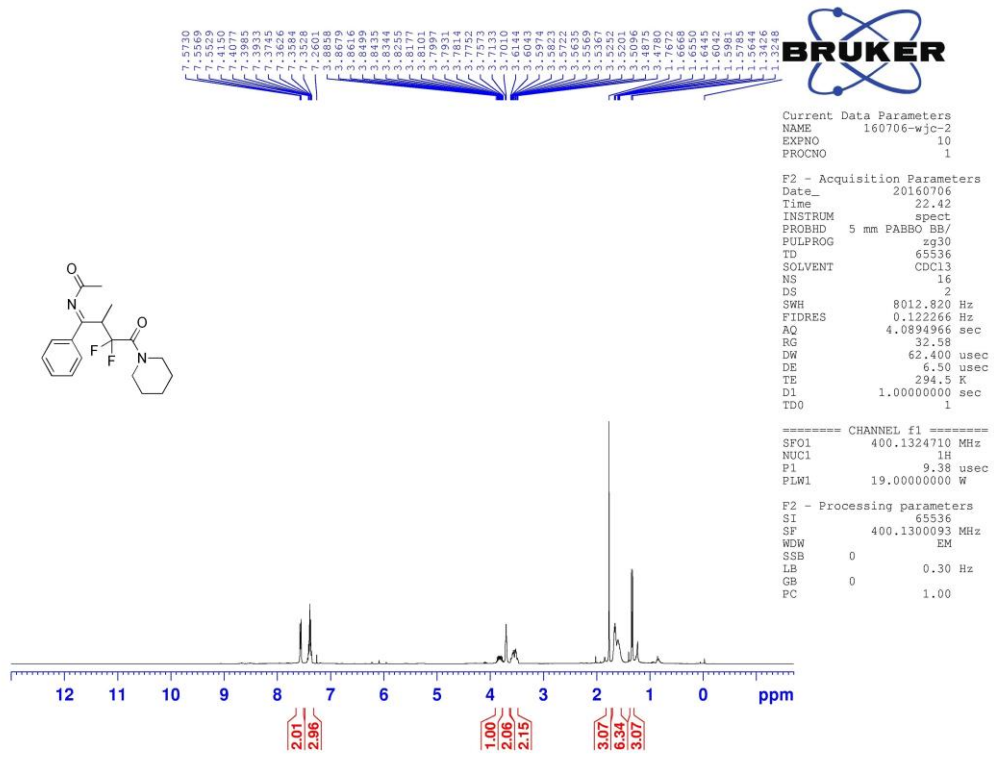
(4o)

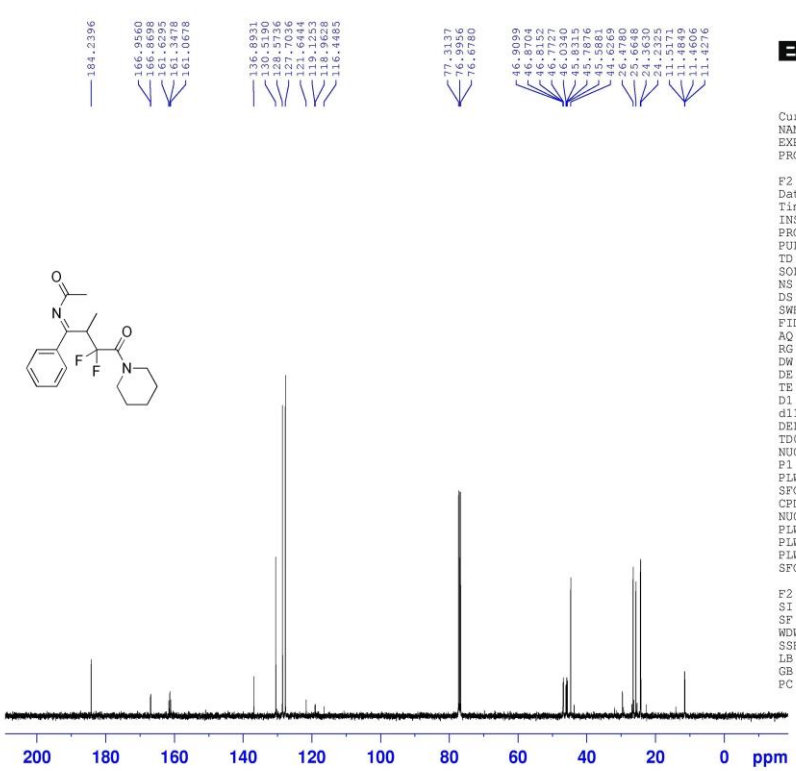






(*E*)-*N*-(3,3-Difluoro-2-methyl-4-oxo-1-phenyl-4-(piperidin-1-yl)butylidene)acetamide (5a)

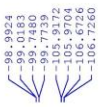


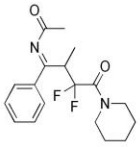


```
Current Data Parameters
NAME        160706-wjc-2
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160706
Time               22.47
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  167
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                202.1
DW               20.800 usec
DE                6.50 usec
TE                295.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1
NUC1                13C
P1                10.13 usec
PLW1         65.00000000 W
SFO1        100.6228293 MHz
CPDPRG2
NUC2                1H
PLW2         19.00000000 W
PLW12         0.20637999 W
PLW13         0.16717000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127768 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



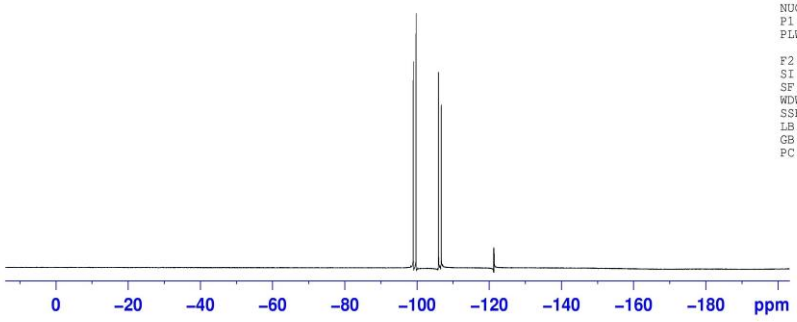


```
Current Data Parameters
NAME        160706-wjc-2
EXPNO                 13
PROCNO                 1

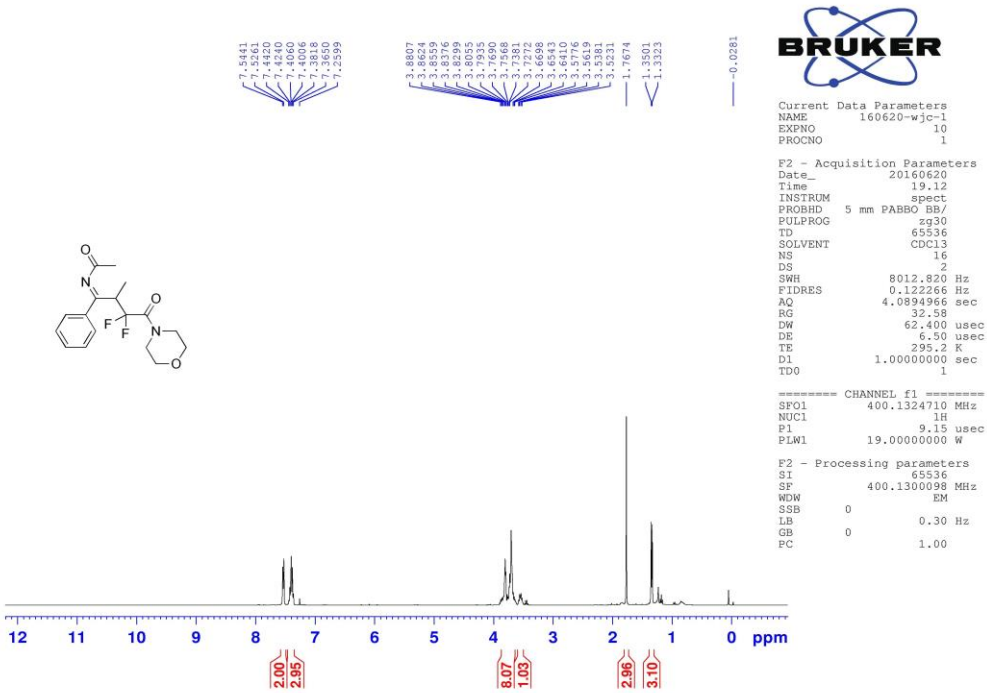
F2 - Acquisition Parameters
Date_           20160706
Time               22.56
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ             0.7340532 sec
RG                202.1
DW               5.600 usec
DE                6.50 usec
TE                294.7 K
D1            1.00000000 sec
TD0                   1

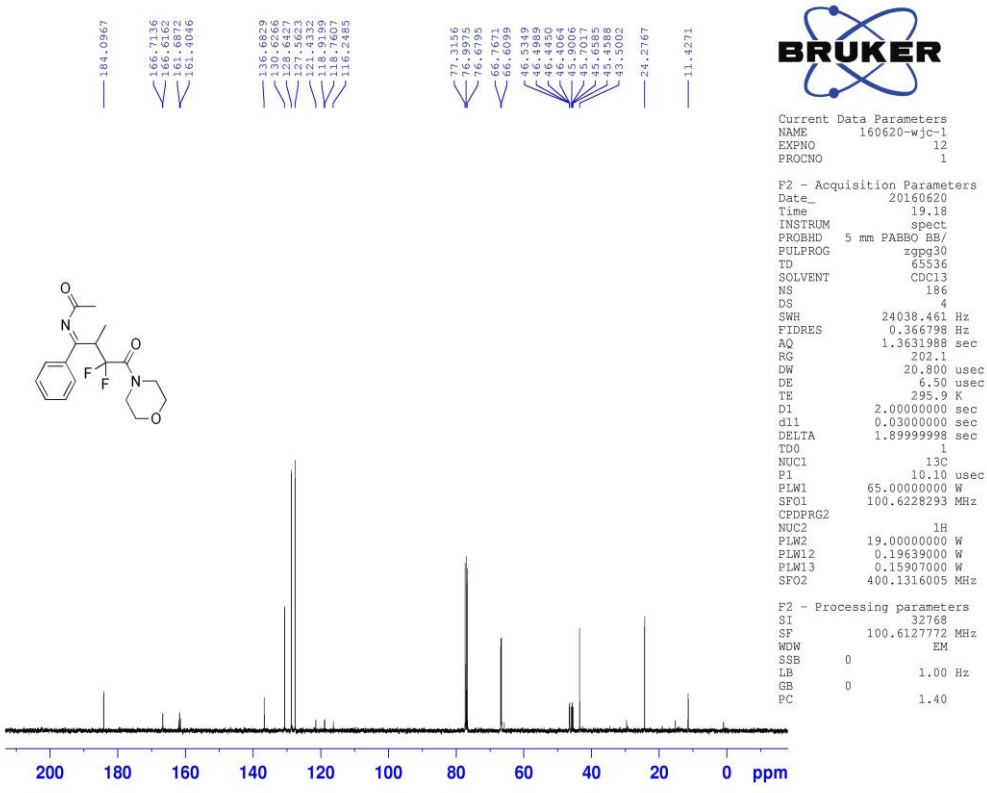
======== CHANNEL f1 ========
SFO1        376.4607164 MHz
NUC1                19F
P1                12.00 usec
PLW1         19.01099968 W

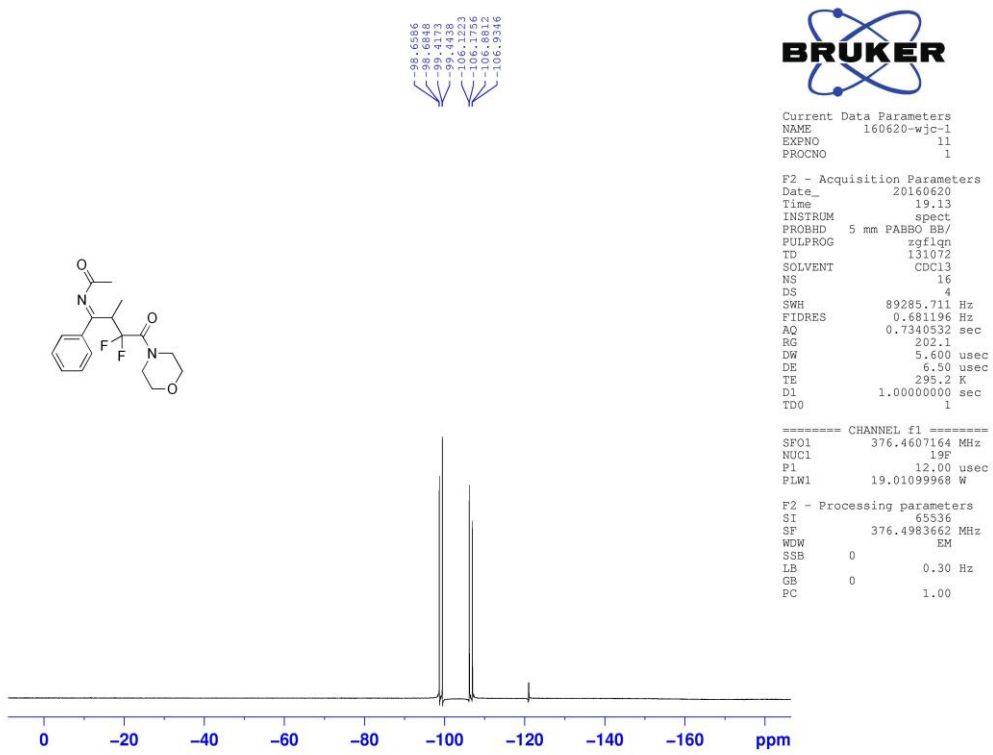
F2 - Processing parameters
SI                 65536
SF          376.4983662 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



(*E*)-*N*-(3,3-Difluoro-2-methyl-4-morpholino-4-oxo-1-phenylbutylidene)acetamide (5b)

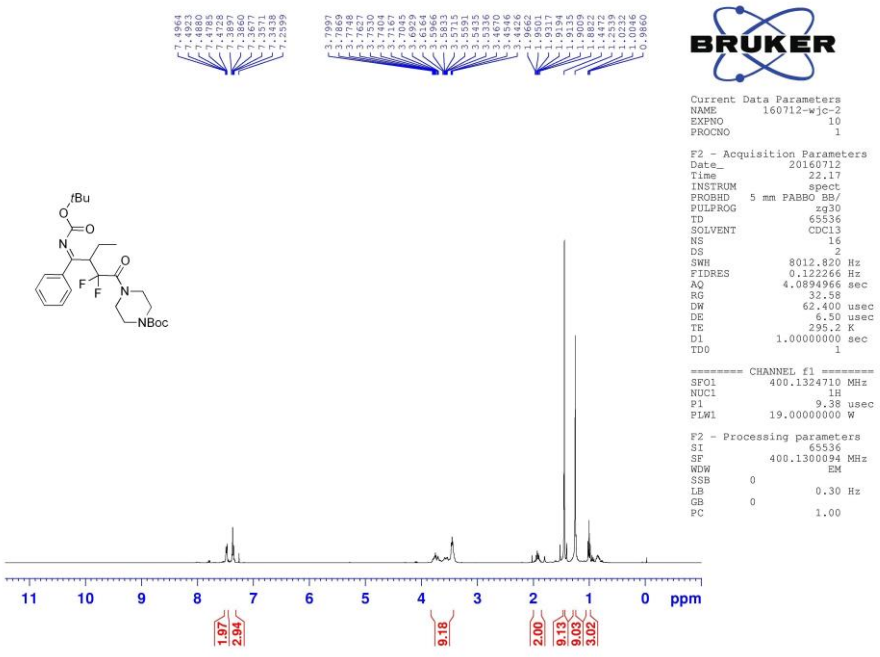


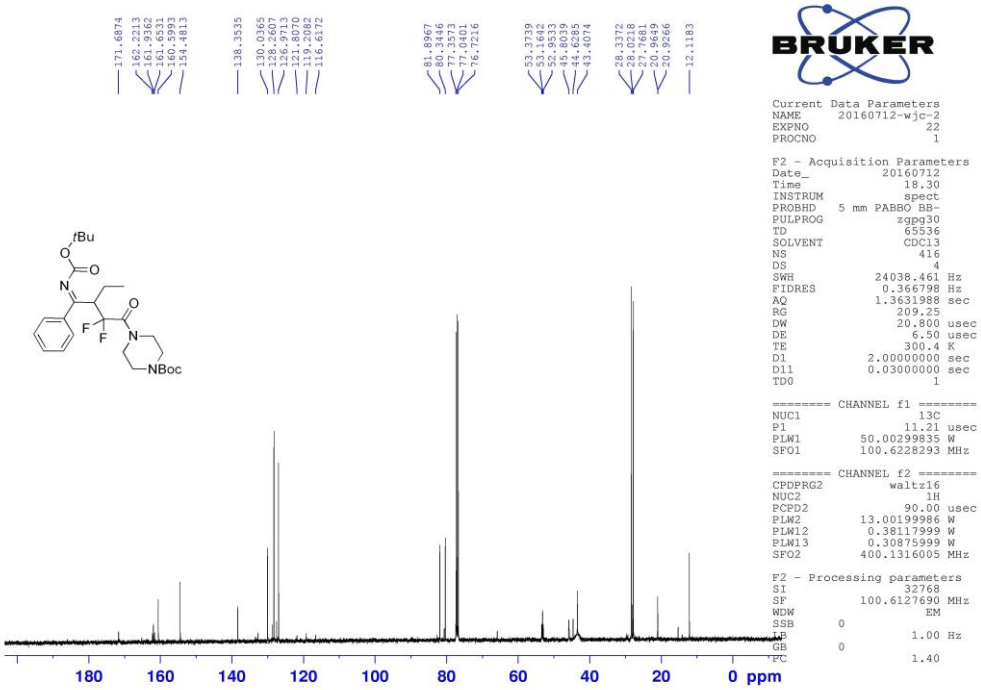


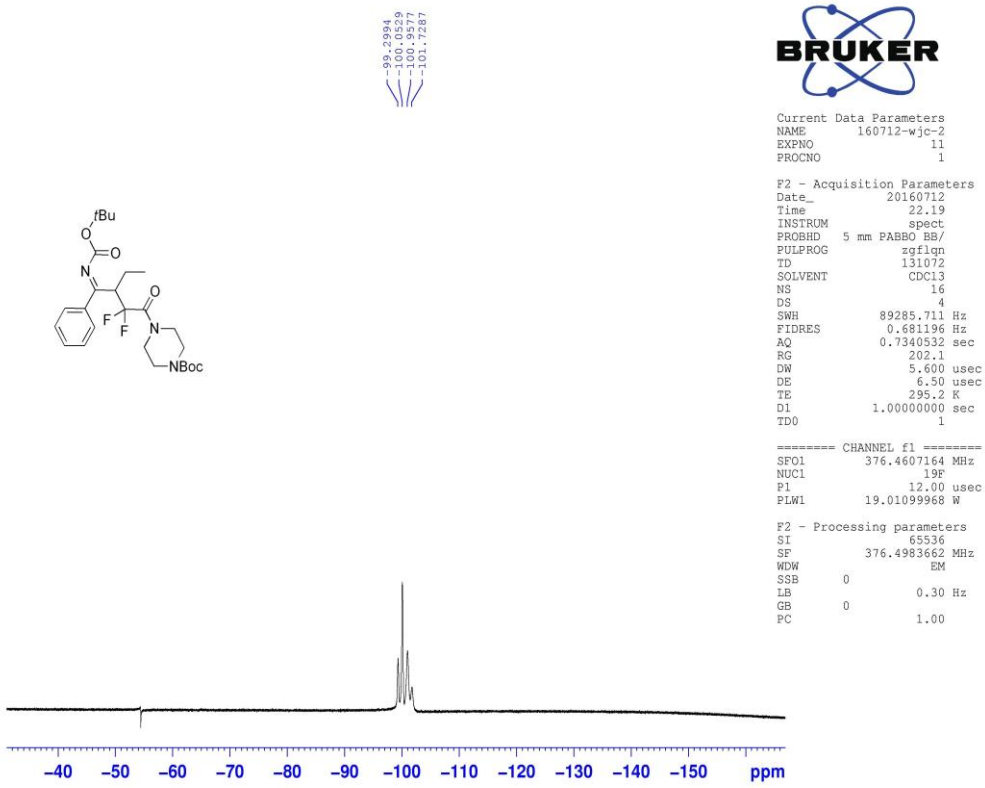


(*E*)-*tert*-Butyl

4-(3-(((tert-butoxycarbonyl)imino)(phenyl)methyl)-2,2-difluoropentanoyl)piperazine-1-carboxylate (5c)

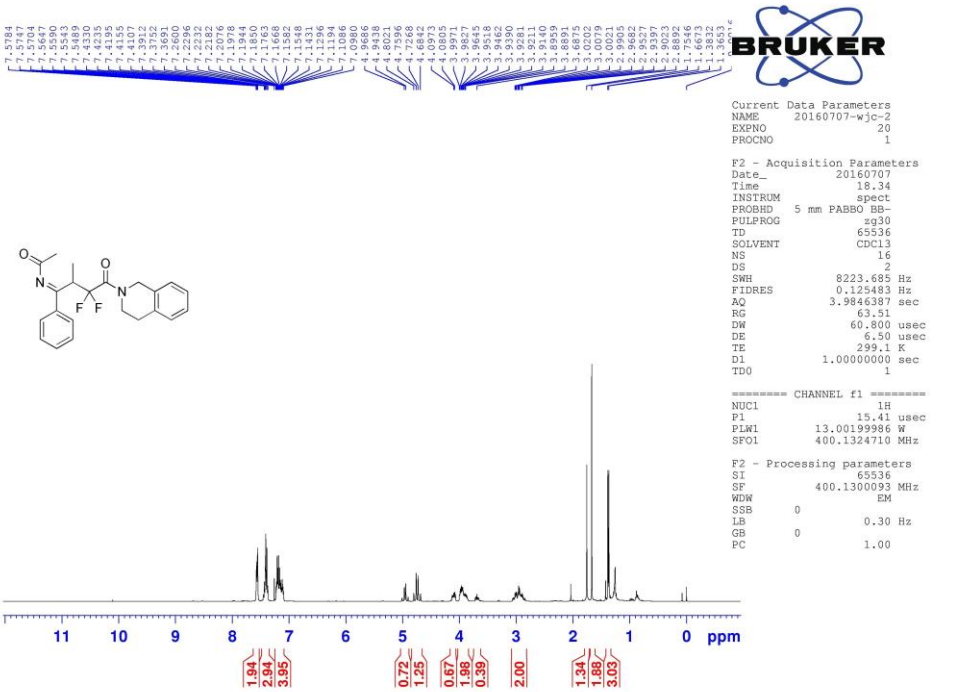


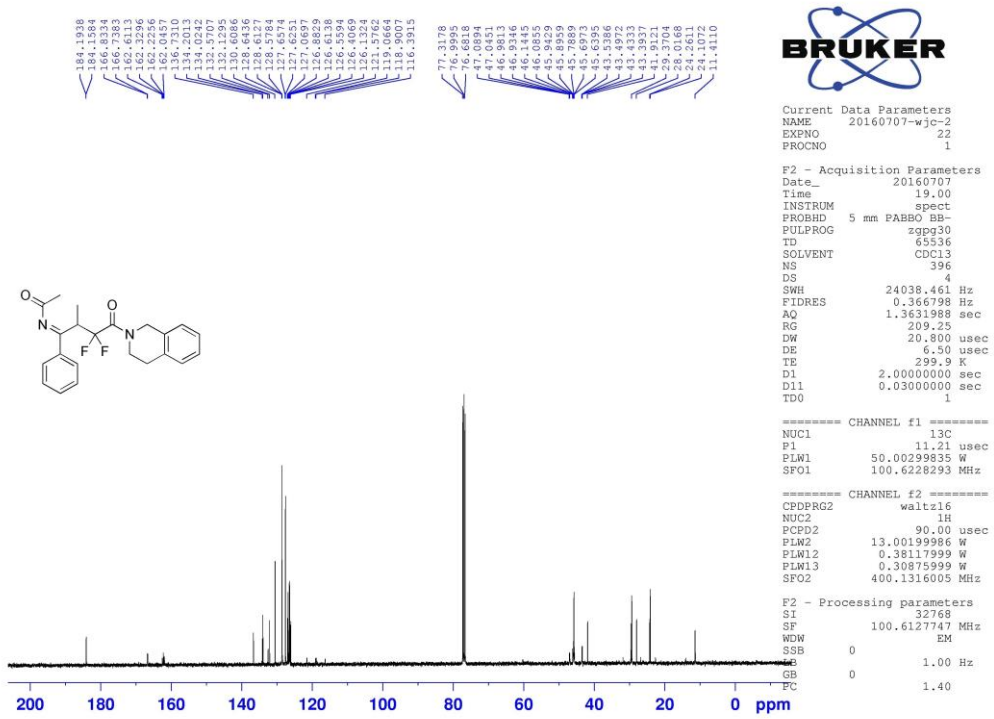

171.6874
162.2213
161.9362
161.6531
160.5993
154.4813
138.3535
130.0365
128.2607
126.9713
121.8070
119.0082
116.6172
81.8967
80.3446
77.3573
77.0401
76.7216
53.3739
53.1642
52.9533
45.8039
44.6285
43.4074
28.3372
28.0218
25.7681
20.9649
20.9266
12.1183
tBu
O
O
N
O
F
F
N
NBoc
180
160
140
120
100
80
60
40
20
0 ppm
BRUKER
Current Data Parameters
NAME 20160712-wjc-2
EXPNO 22
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160712
Time 18.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 416
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 209.25
DW 20.800 usec
DE 6.50 usec
TE 300.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 11.21 usec
PLW1 50.00299835 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 13.00199986 W
PLW12 0.38117999 W
PLW13 0.30875999 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

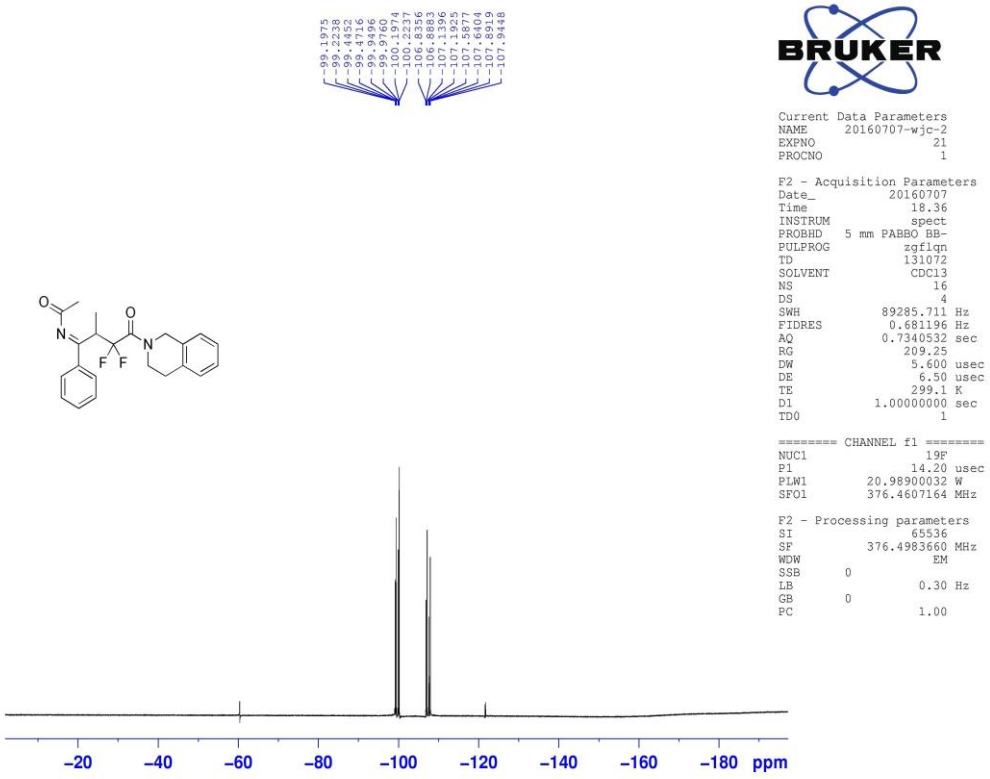

-99.2994
-100.0529
-100.9577
-101.7287
tBu
O
O
N
O
F
F
N
NBoc
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
ppm
BRUKER
Current Data Parameters
NAME 160712-wjc-2
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160712
Time 22.19
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 202.1
DW 5.600 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 376.4607164 MHz
NUC1 19F
P1 12.00 usec
PLW1 19.01099968 W
F2 - Processing parameters
SI 65536
SF 376.4983662 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

(*E*)-*N*-(4-(3,4-Dihydroisoquinolin-2(1H)-yl)-3,3-difluoro-2-methyl-4-oxo-1-phenylbutylidene)acet

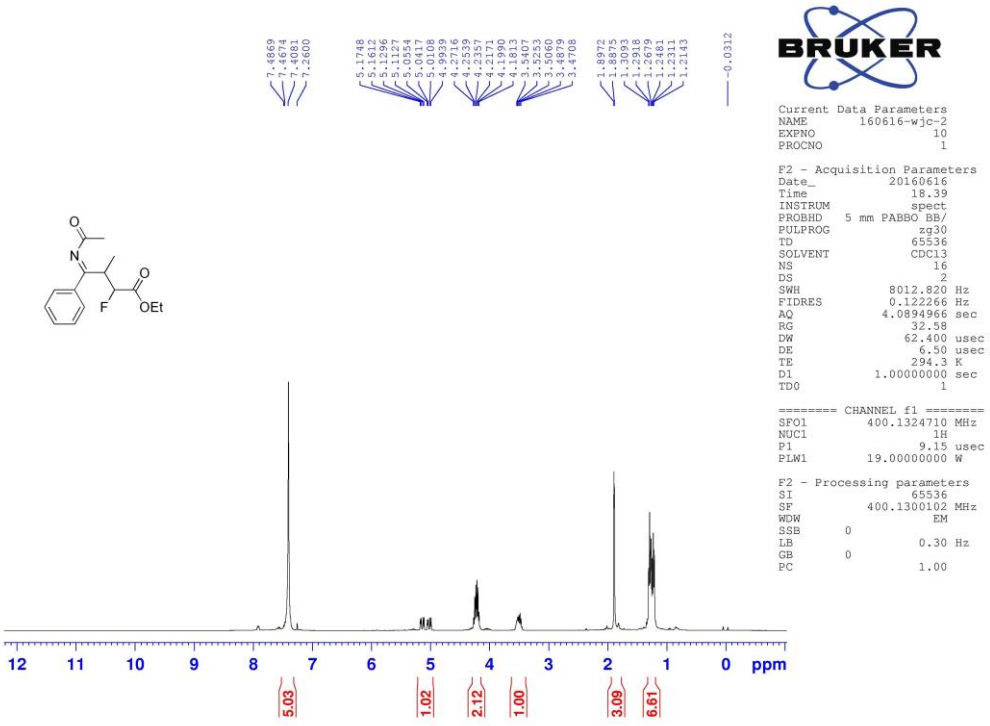
amide (5d)

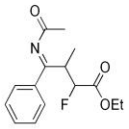


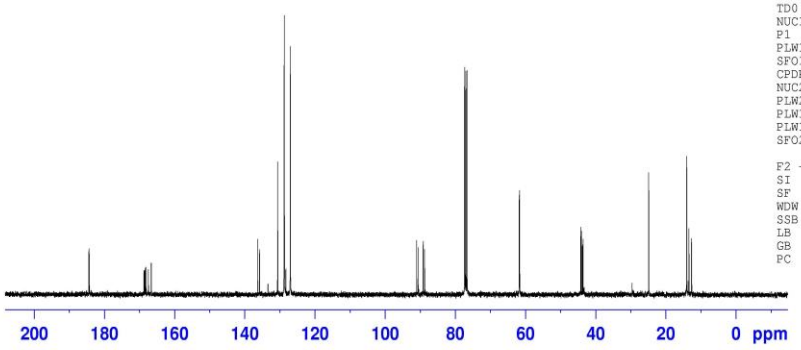




(*E*)-Ethyl 4-(acetylimino)-2-fluoro-3-methyl-4-phenylbutanoate (5e, dr = 1:1**)**



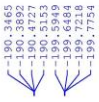


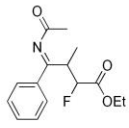


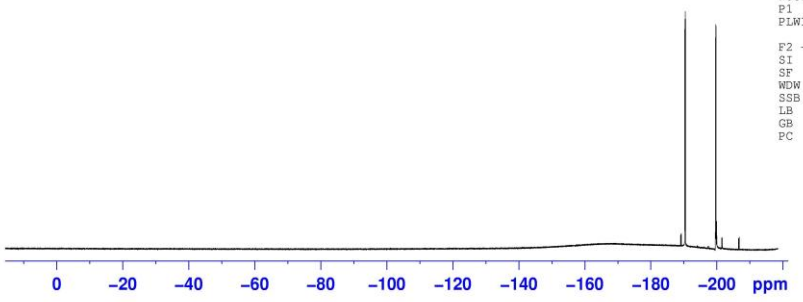

```
Current Data Parameters
NAME        160616-wjc-2
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160616
Time               19.00
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 326
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                202.1
DW               20.800 usec
DE                6.50 usec
TE               295.4 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                  1
NUC1               13C
P1               10.10 usec
PLW1         65.00000000 W
SFO1        100.6228293 MHz
CPDPRG2
NUC2                1H
PLW2         19.00000000 W
PLW12         0.19639000 W
PLW13         0.15907000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127777 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```







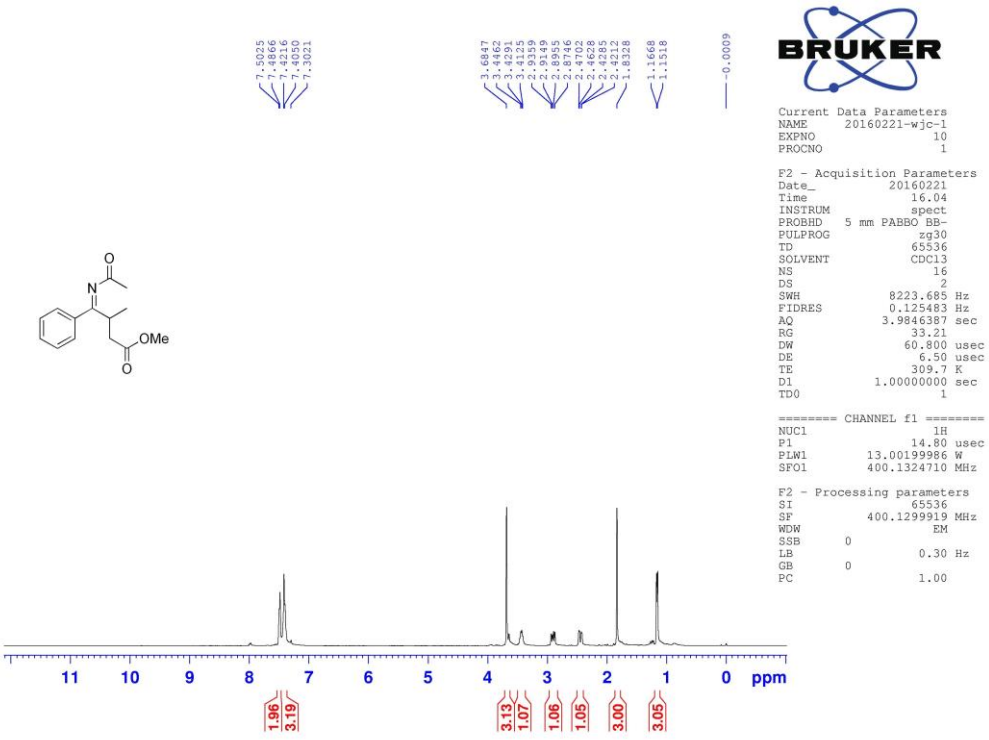

```
Current Data Parameters
NAME        160616-wjc-2
EXPNO                 11
PROCNO                 1

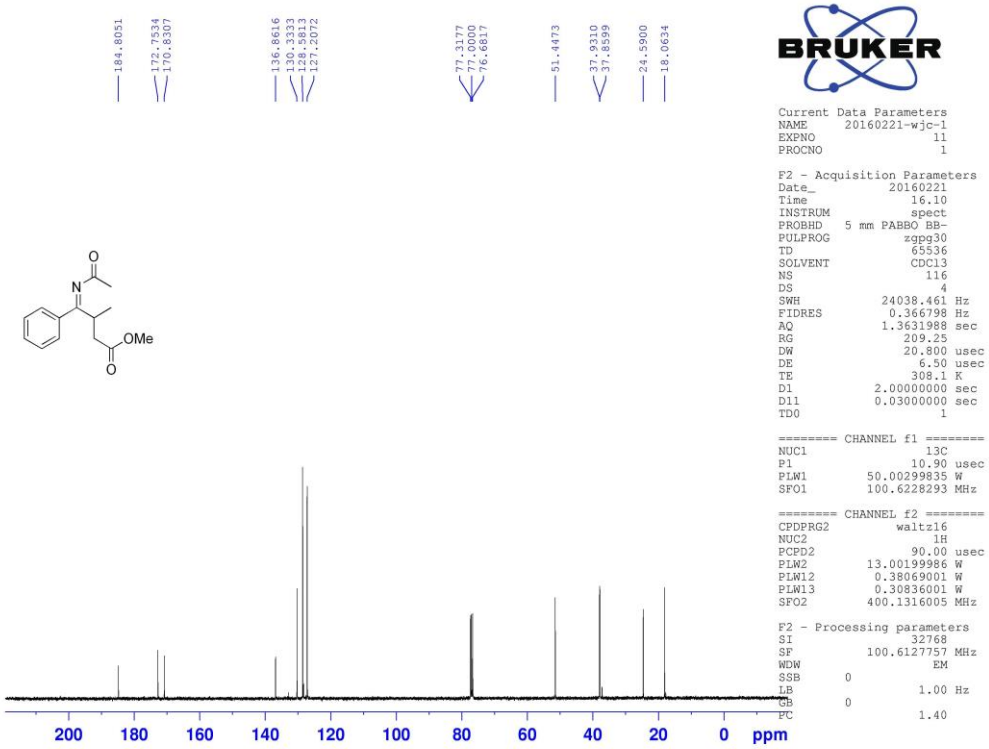
F2 - Acquisition Parameters
Date_           20160616
Time               18.41
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG         zgflqn
TD              131072
SOLVENT          CDCl3
NS                  16
DS                   4
SWH          89285.711 Hz
FIDRES        0.681196 Hz
AQ            0.7340532 sec
RG                202.1
DW                5.600 usec
DE                6.50 usec
TE               294.4 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        376.4607164 MHz
NUC1               19F
P1               12.00 usec
PLW1         19.01099968 W

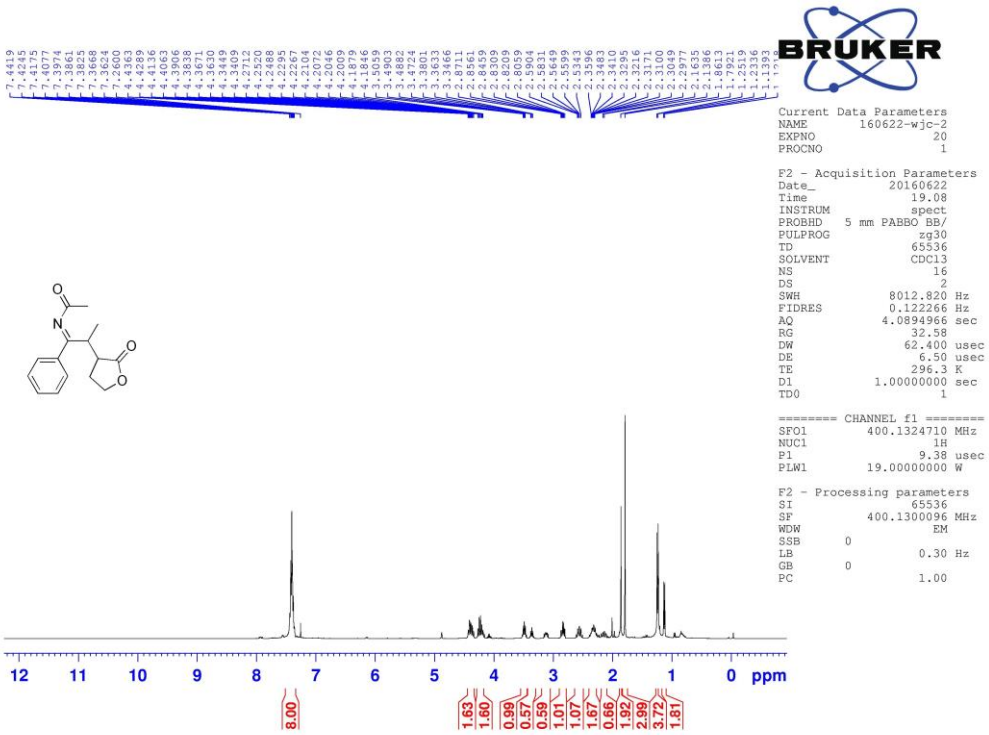
F2 - Processing parameters
SI                 65536
SF          376.4983662 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

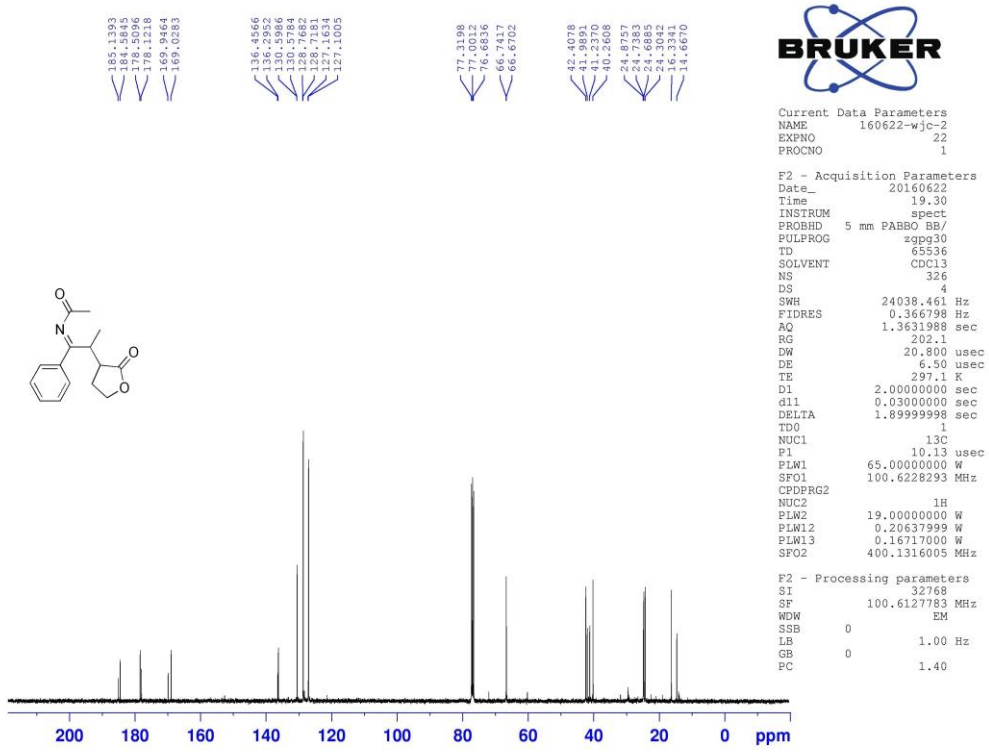
(*E*)-Methyl 4-(acetylimino)-3-methyl-4-phenylbutanoate (5f)



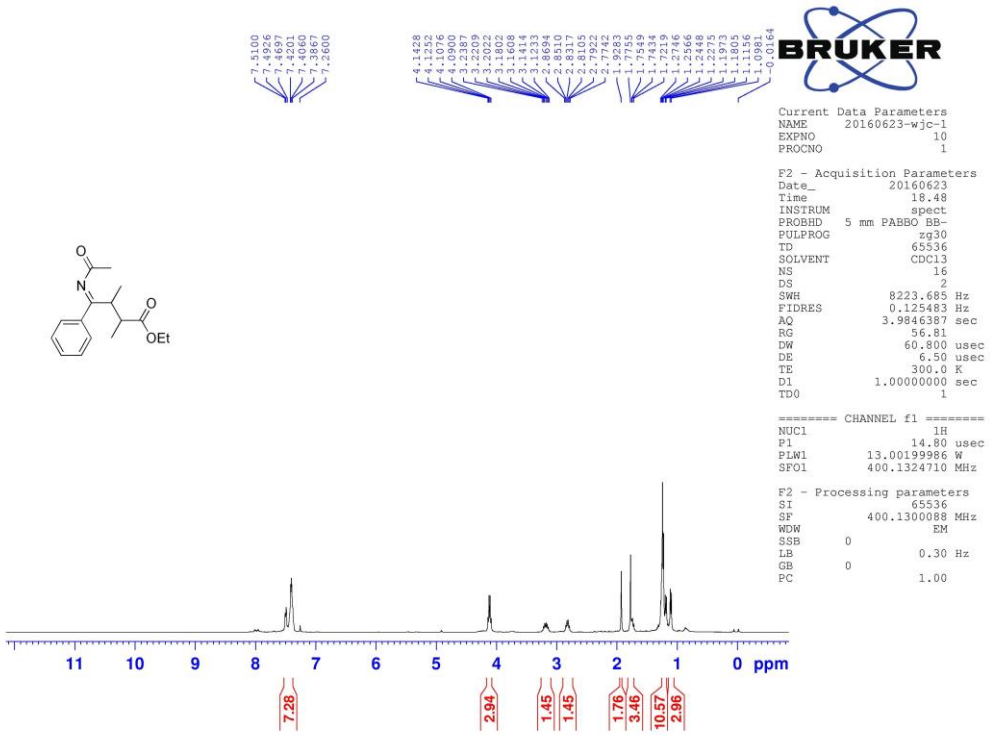


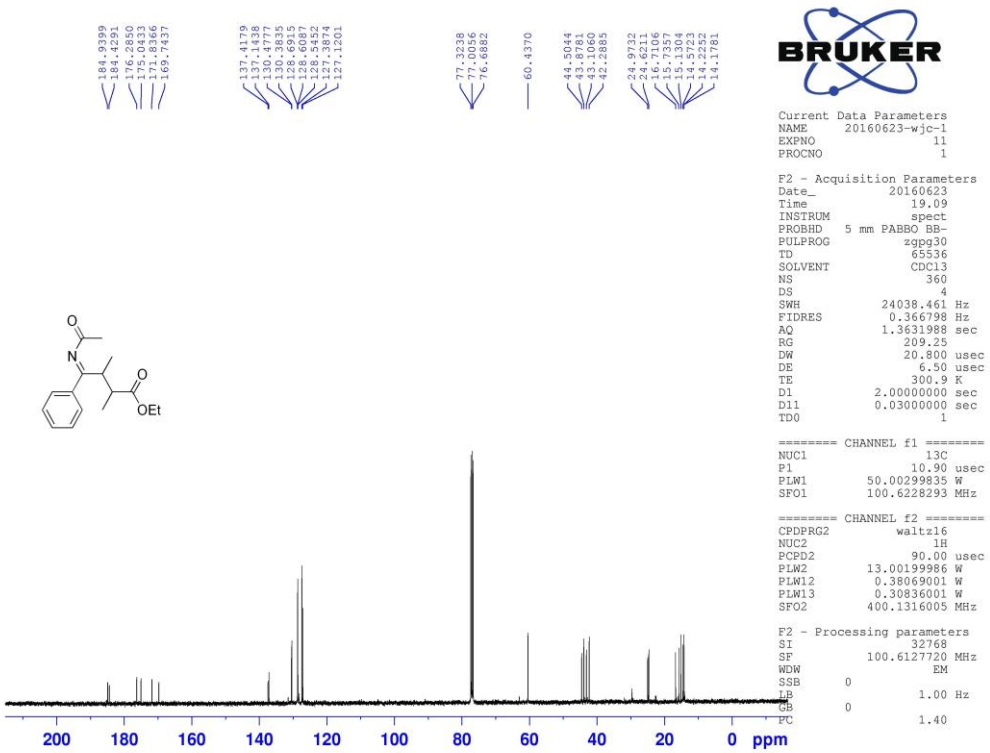
(*E*)-*N*-(2-(2-Oxotetrahydrofuran-3-yl)-1-phenylpropylidene)acetamide (5g, d.r. = 1.6:1**)**



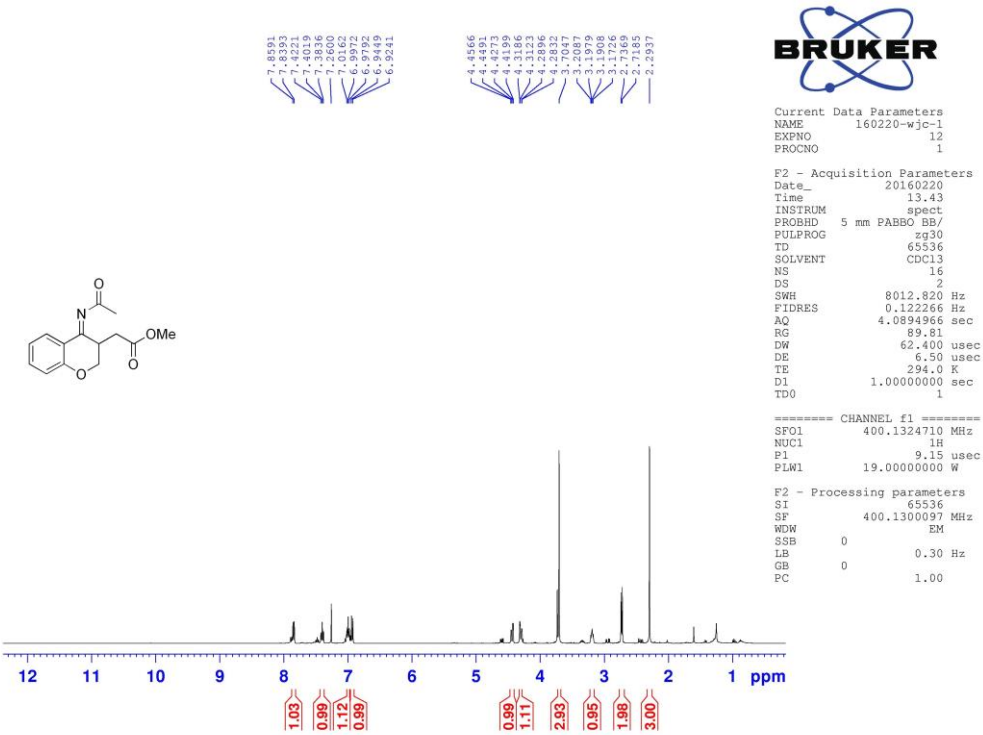


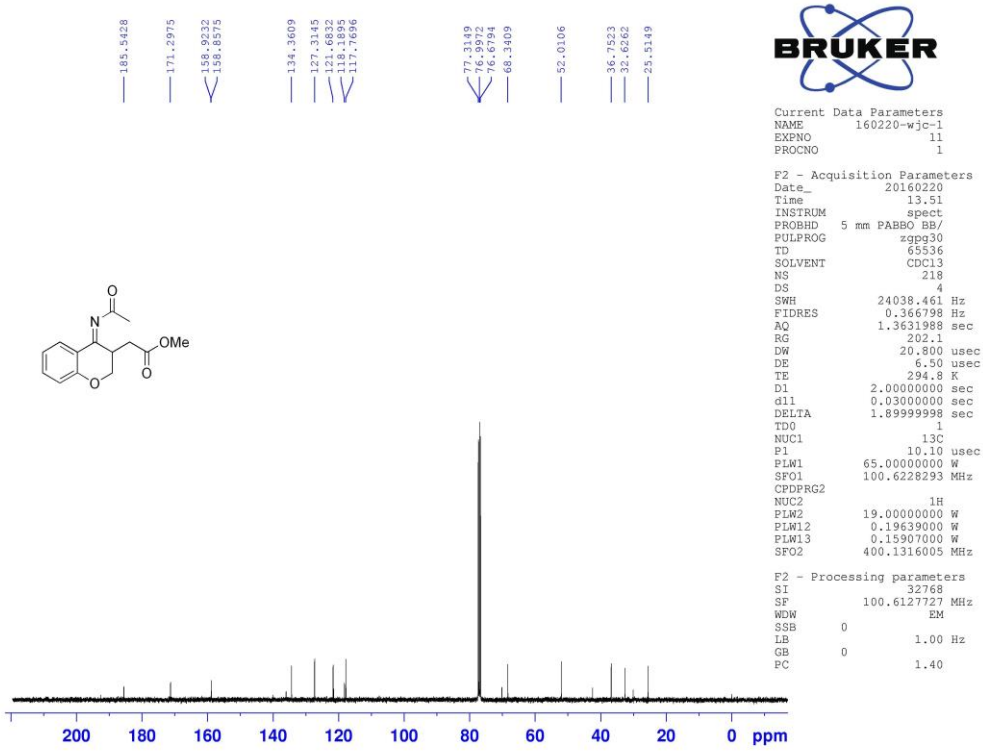
(*E*)-Ethyl 4-(acetylimino)-2,3-dimethyl-4-phenylbutanoate (5h, d.r. = 2.2:1**)**



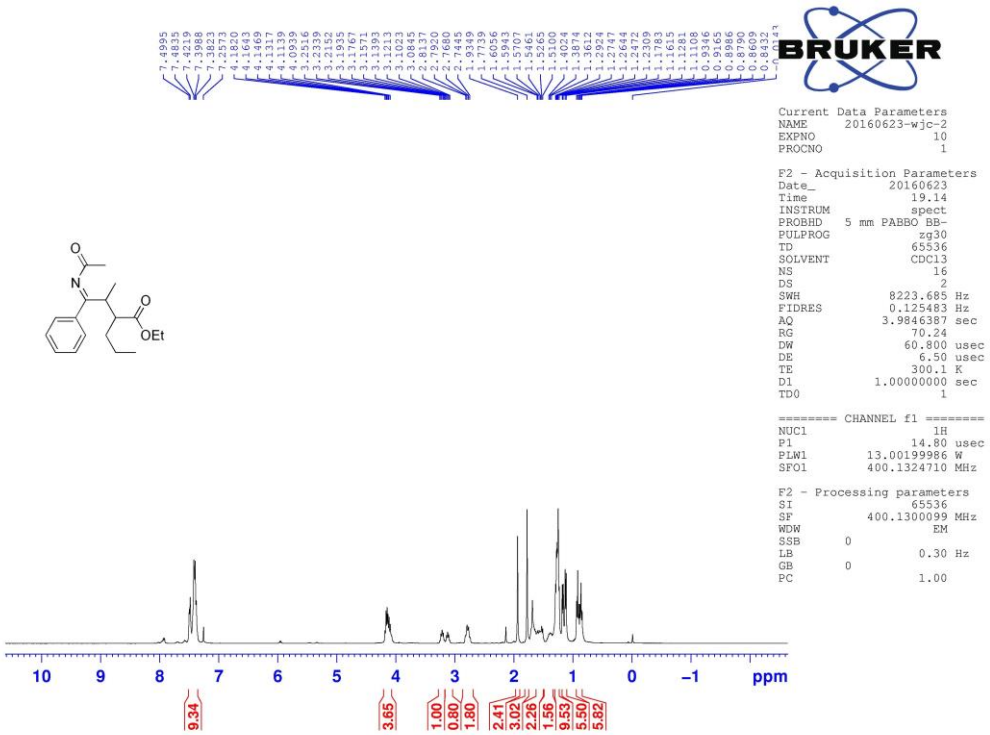


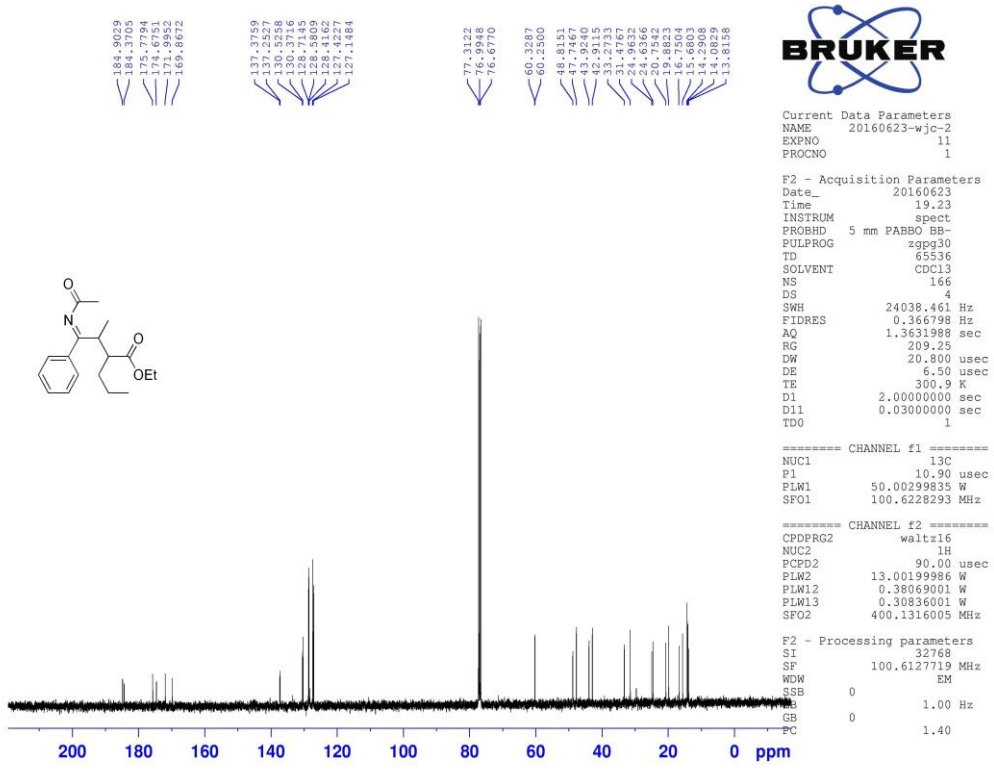
(*E*)-Methyl 2-(4-(acetylimino)chroman-3-yl)acetate (5i)



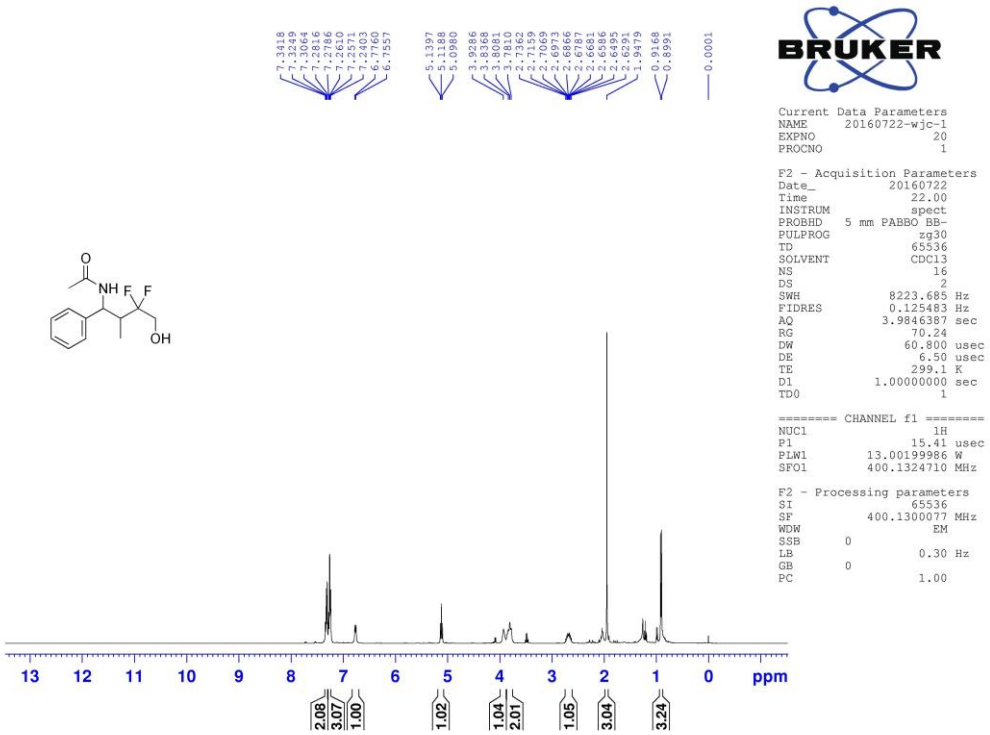


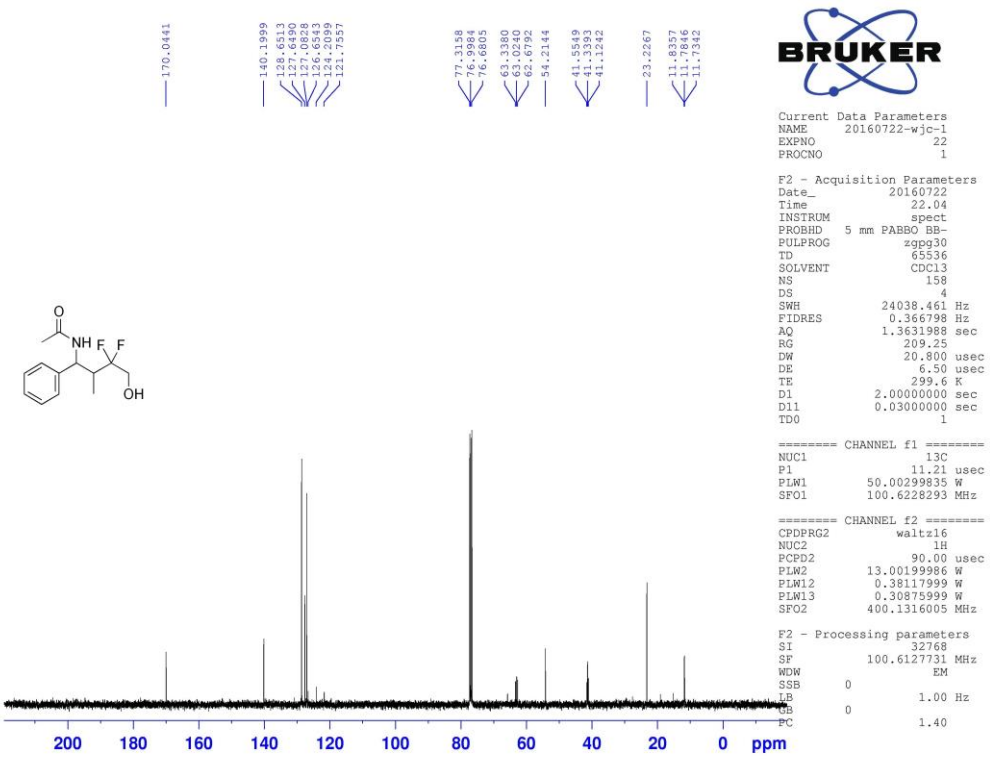
(*E*)-Ethyl 2-(1-(acetylimino)-1-phenylpropan-2-yl)pentanoate (5j, d.r. = 1.3:1**)**

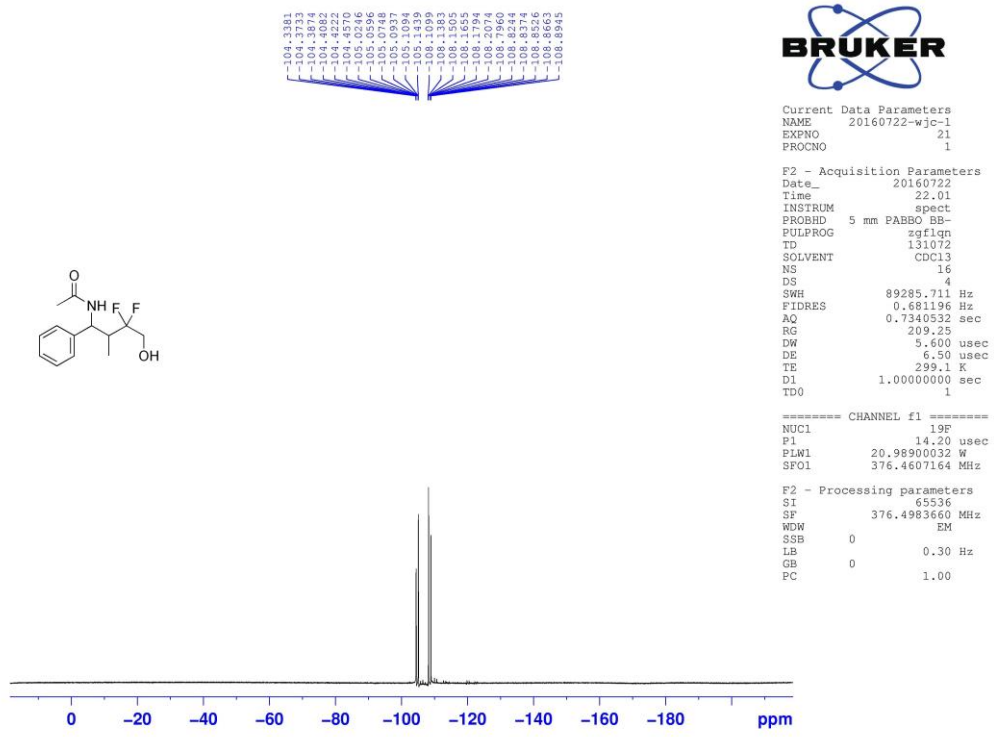




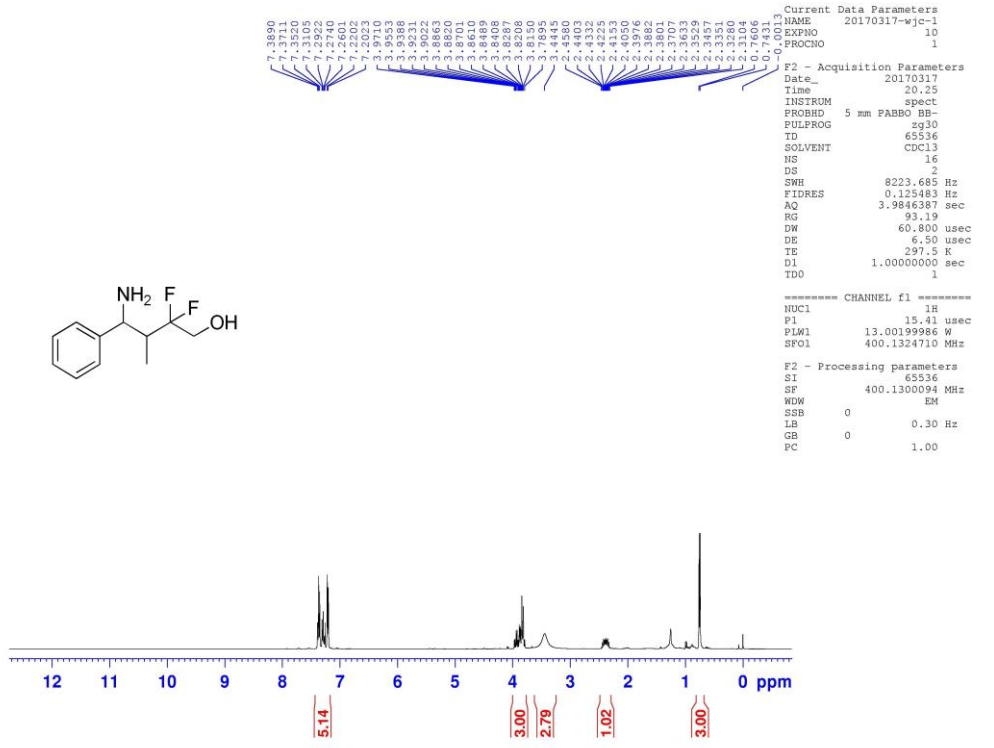
***N*-(3,3-Difluoro-4-hydroxy-2-methyl-1-phenylbutyl)acetamide (6'**, d.r.>19:1**)**

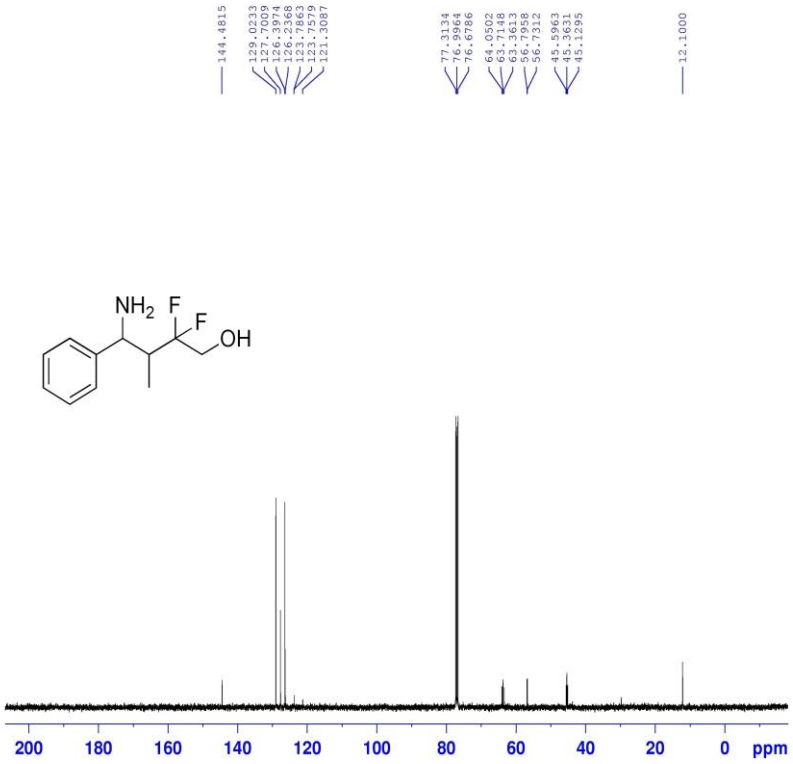






4-Amino-2,2-difluoro-3-methyl-4-phenylbutan-1-ol (6, dr >19:1**)**





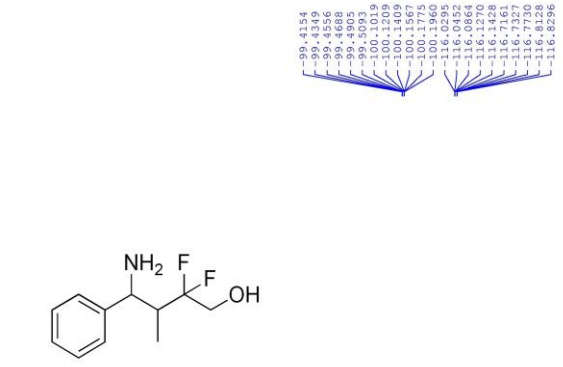

```
Current Data Parameters
NAME      20170317-wjc-1
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170317
Time               20.33
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  178
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                209.25
DW                20.800 usec
DE                 6.50 usec
TE                298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 11.21 usec
PLW1         50.00299835 W
SFO1        100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PLW2         13.00199986 W
PLW12         0.38117999 W
PLW13         0.30875999 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127725 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



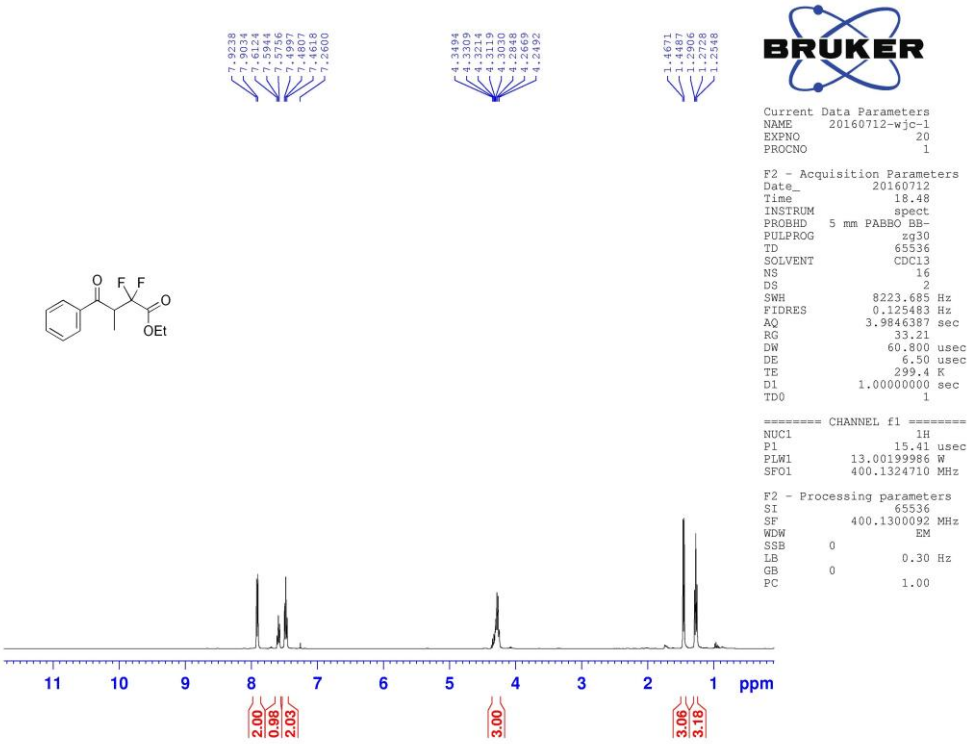

```
Current Data Parameters
NAME      20170317-wjc-1
EXPNO                 11
PROCNO                 1

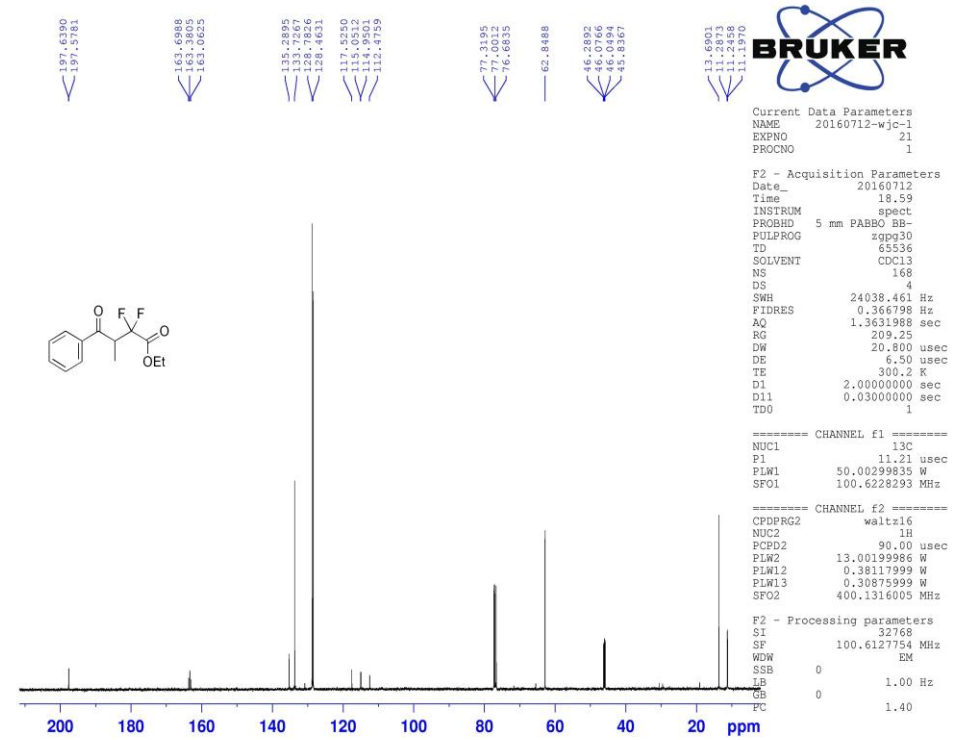
F2 - Acquisition Parameters
Date_           20170317
Time               20.27
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgflqn
TD                131072
SOLVENT           CDCl3
NS                    16
DS                     4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ             0.7340532 sec
RG                209.25
DW                 5.600 usec
DE                 6.50 usec
TE                297.5 K
D1             1.00000000 sec
TD0                    1

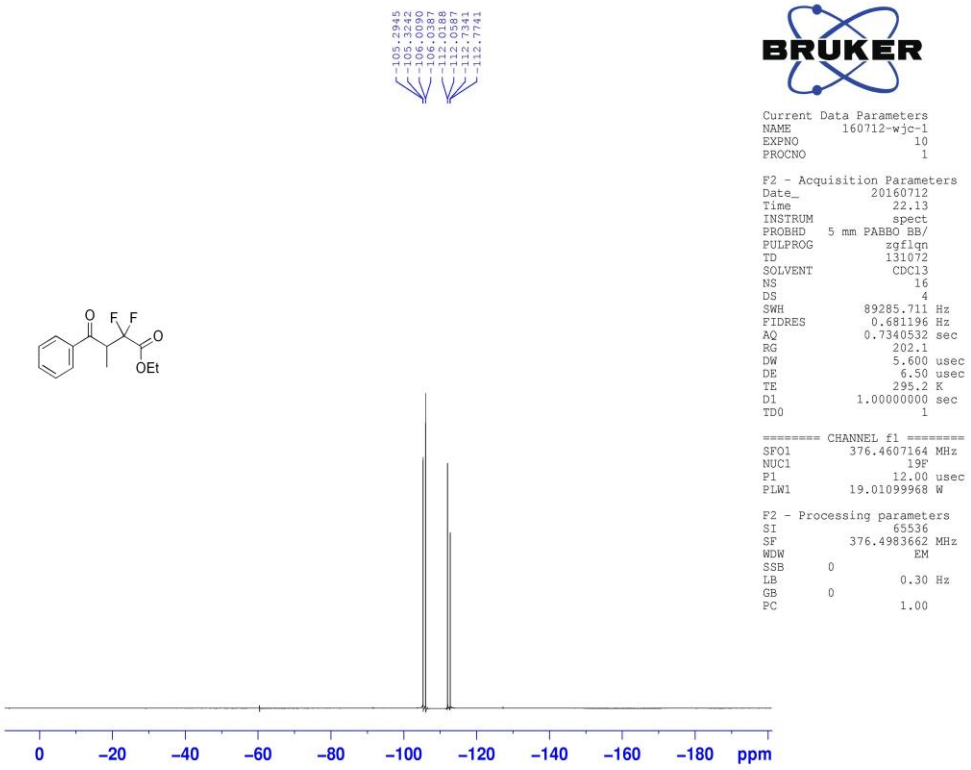
======== CHANNEL f1 ========
NUC1                  19F
P1                 14.20 usec
PLW1         20.98900032 W
SFO1        376.4607164 MHz

F2 - Processing parameters
SI                 65536
SF          376.4983660 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

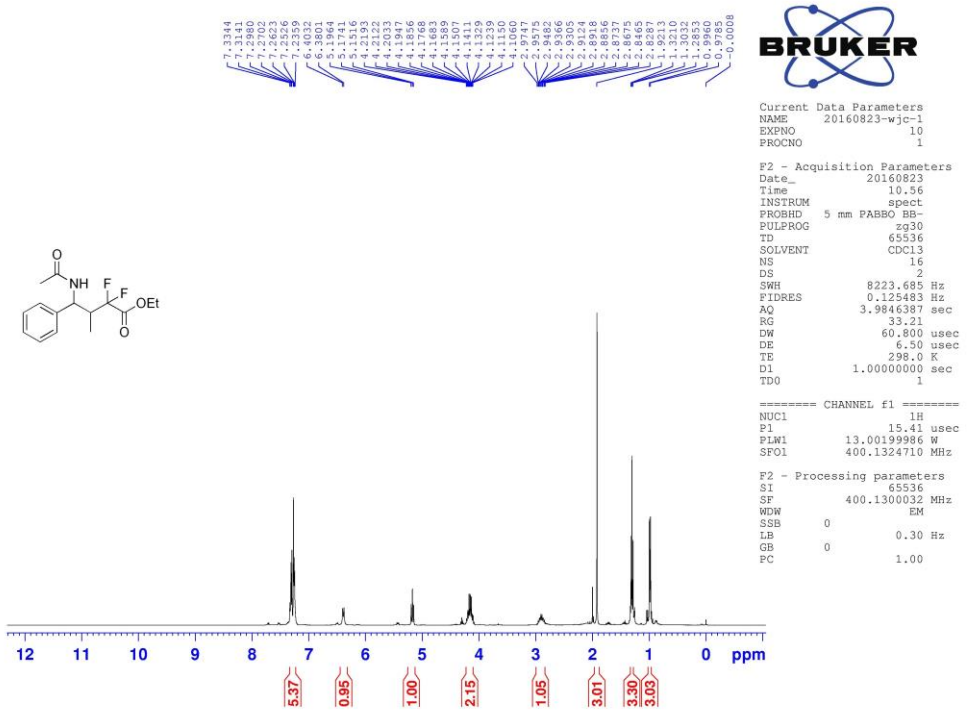
Ethyl 2,2-difluoro-3-methyl-4-oxo-4-phenylbutanoate (7)

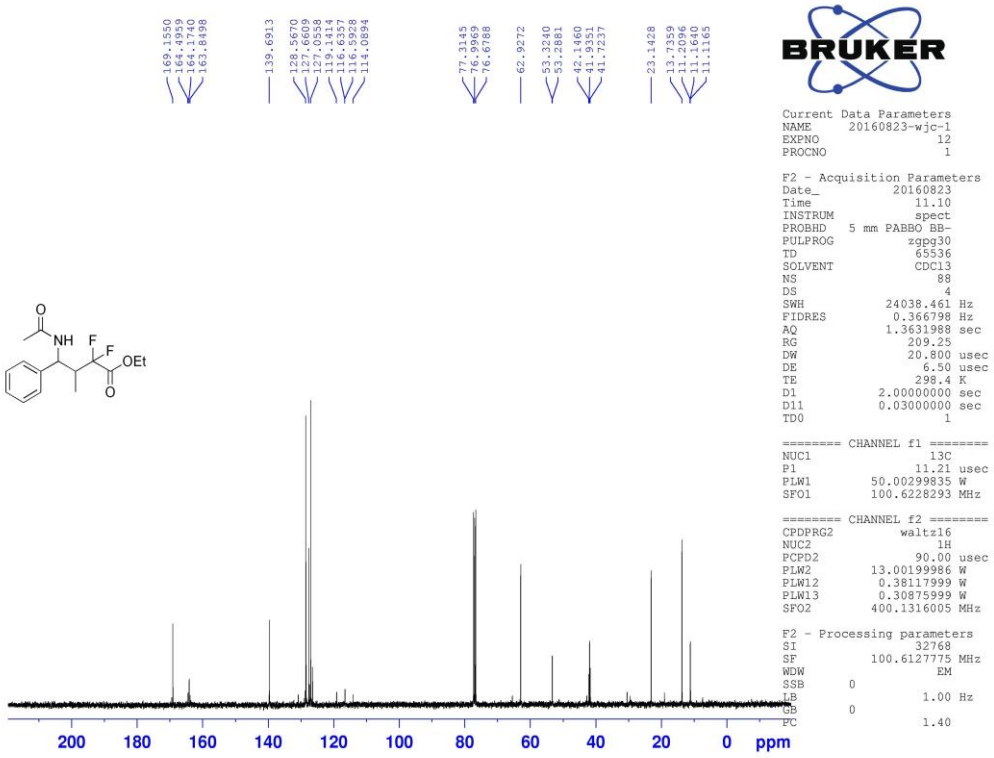






Ethyl 4-acetamido-2,2-difluoro-3-methyl-4-phenylbutanoate (8, dr ≥10:1**)**





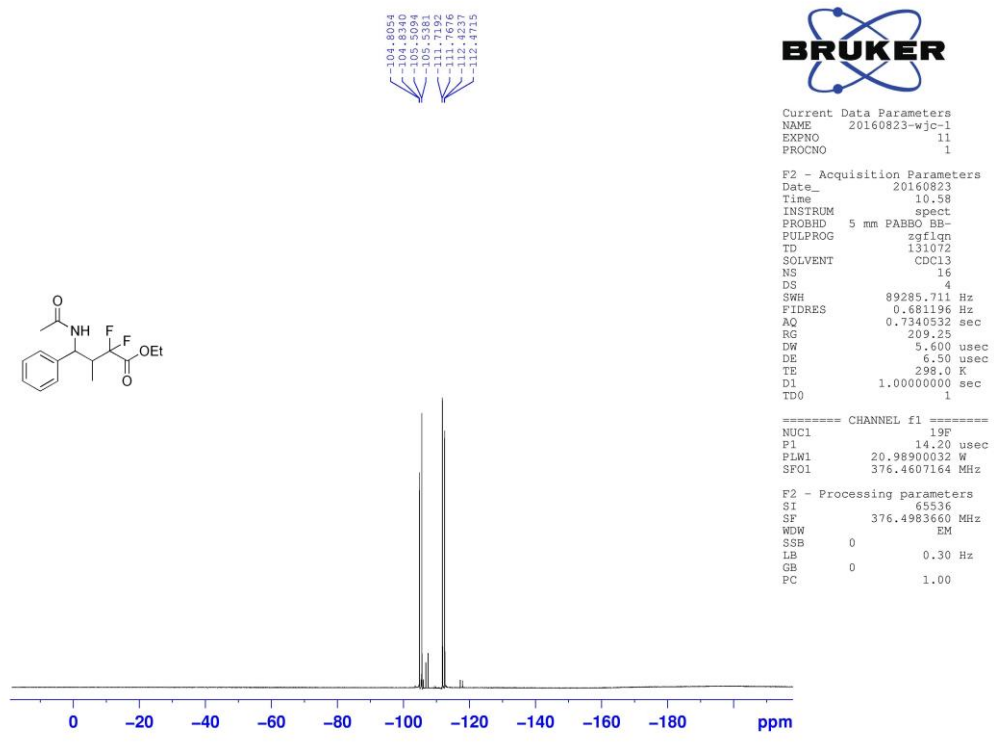

```
Current Data Parameters
NAME      20160823-wjc-1
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160823
Time               11.10
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   88
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                209.25
DW                20.800 usec
DE                 6.50 usec
TE                298.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.21 usec
PLW1          50.00299835 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              90.00 usec
PLW2          13.00199986 W
PLW12          0.38117999 W
PLW13          0.30875999 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6127775 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```




```
Current Data Parameters
NAME      20160823-wjc-1
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160823
Time               10.58
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgflqn
TD               131072
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ             0.7340532 sec
RG                209.25
DW                 5.600 usec
DE                 6.50 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  19F
P1                  14.20 usec
PLW1          20.98900032 W
SFO1         376.4607164 MHz

F2 - Processing parameters
SI                65536
SF           376.4983660 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```