Supplementary Information for

Photoredox-Catalyzed Generation of α-Carbonyl Carbocations: General Access to α-Tertiary Amino Acid Derivatives

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I. General Information

General procedures:

Solvents and reagents were bought from Sigma-Aldrich, J&K, Alfa-Aesar, Energy and TCI chemicals, and used directly without further purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel 60 F-254 plates or GC-MS. TLC plates were normally visualized by UV irradiation (254 nm or 365 nm), stained with basic $KMnO_4$. Flash chromatography was performed using silica gel 60 (200-300 mesh). Olefins were either commercially available or synthesized according to the reported general procedures.[1-3] Trifluoromethyl-thianthrenium salts (**2c** and **2d**) and benzoimidazolium salt (**2g**) were synthesized according to the reported general procedures.[4, 5]

Instrumentation:

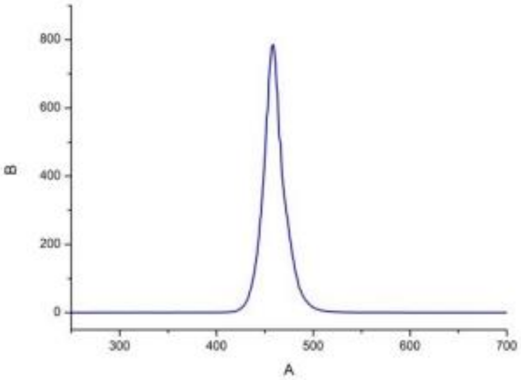
Proton nuclear magnetic resonance (^1H NMR) spectra, fluorine nuclear magnetic resonance (^{19}F NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker Ascend 600 MHz. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to the NMR solvent residual peak ($CDCl_3$: δ 7.26). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$: δ 77.16). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants in Hertz (Hz), and integration. High resolution mass spectra (HRMS) were recorded on a Thermo Fisher Scientific Exactive Plus by Electrospray Ionisation (ESI) or Atmospheric Pressure Photo-Ionization (APCI). GC-MS measurements were performed on a SHIMADZU GCMS-QP2010 SE.

Abbreviations:

LED–light emitting diode; TLC–thin layer chromatography; PE–Petroleum Ethers; THF–tetrahydrofuran; DMF–N, N-dimethylformamide; DMSO–dimethyl sulfoxide

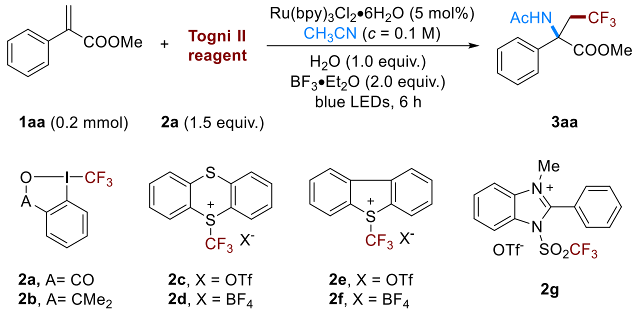
Photoreaction Setup:

All manipulations for the photocatalyzed radical α-carbonyl carbocation relay reactions were set up in a 10 mL test tube Tubes (unless otherwise noted) under an inert N_2 atmosphere. The reactions were conducted in photo-reactors (Model:H106062, GEAO CHEMICAL, purchased from http://www.geaochem.com/), which comprise a fan for cooling (approximately room temperature) and six 1W blue LED beads for each place. The average power output of the photo-reactor was recorded at 30 mW/cm^2. The emission spectra of the blue LEDs were recorded on an Ocean Optics HR4000CG-UVNIR spectrometer. One place/hole with three 1W blue LED beads (λ_{max} = 460 nm) on both sides, and the distance between the Schlenk tube and LED beads is ca. 2 cm. The spectra was normalised to 1.0 at the maximum (450 nm).



II. Optimization of Reaction Conditions

Table S1. Reaction Condition Optimization.[a]



Entry	P.C.	**2**	additive (equiv.)	equiv. of H_2O	Yield of **3aa**
1	$Ru(bpy)_3Cl_2•6H_2O$	**2a**	$BF_3•Et_2O$ (1.0)	1.0	34%
2	$Ru(bpy)_3Cl_2•6H_2O$	**2a**	$BF_3•Et_2O$ (1.5)	1.0	58%
2	$Ru(bpy)_3Cl_2•6H_2O$	**2a**	$BF_3•Et_2O$ (2.0)	1.0	93% (90%)[b]
3	$Ru(bpy)_3Cl_2•6H_2O$	**2a**	$BF_3•Et_2O$ (4.0)	1.0	63%
4	$Ru(bpy)_3Cl_2•6H_2O$	**2a**	-	1.0	trace
5	$Ru(bpy)_3Cl_2•6H_2O$	**2a**	$BF_3•Et_2O$ (2.0)	-	trace
6	$Ru(bpy)_3Cl_2•6H_2O$	**2a**	$BF_3•Et_2O$ (2.0)	0.5	64%
7	$Ru(bpy)_3Cl_2•6H_2O$	**2a**	$BF_3•Et_2O$ (2.0)	1.5	78%
8	$Ru(bpy)_3Cl_2•6H_2O$	**2a**	$BF_3•Et_2O$ (2.0)	2.0	60%
9	$Ru(bpy)_3Cl_2•6H_2O$	**2a**	TFA (2.0)	1.0	35%
10	$Ru(bpy)_3Cl_2•6H_2O$	**2a**	KF (2.0)	1.0	trace
11	$Ir[dF(CF_3ppy)_2(dtbpy)]PF_6$	**2a**	$BF_3•Et_2O$ (2.0)	1.0	64%
12	*fac*-$Ir(ppy)_3$	**2a**	$BF_3•Et_2O$ (2.0)	1.0	37%
13	$Ru(bpy)_3(PF_6)_2$	**2a**	$BF_3•Et_2O$ (2.0)	1.0	75%
14	4CzIPN	**2a**	$BF_3•Et_2O$ (2.0)	1.0	77%

15	Rodamine 6G	**2a**	BF_3•Et_2O (2.0)	1.0	trace.
16	Eosin Y	**2a**	BF_3•Et_2O (2.0)	1.0	trace.
17	$Ru(bpy)_3Cl_2$•$6H_2O$	**2b**	BF_3•Et_2O (2.0)	1.0	63%
18	$Ru(bpy)_3Cl_2$•$6H_2O$	**2c**	BF_3•Et_2O (2.0)	1.0	69%
19	$Ru(bpy)_3Cl_2$•$6H_2O$	**2d**	BF_3•Et_2O (2.0)	1.0	81%
20	$Ru(bpy)_3Cl_2$•$6H_2O$	**2e**	BF_3•Et_2O (2.0)	1.0	76%
21	$Ru(bpy)_3Cl_2$•$6H_2O$	**2f**	BF_3•Et_2O (2.0)	1.0	88%
22	$Ru(bpy)_3Cl_2$•$6H_2O$	**2g**	BF_3•Et_2O (2.0)	1.0	44%
23	w/o PC	**2a**	BF_3•Et_2O (2.0)	1.0	N.P.
24	In darkness	**2a**	BF_3•Et_2O (2.0)	1.0	N.P.

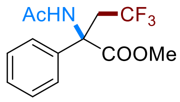
[a] Reaction conditions: methyl 2-phenylacrylate (**1aa**, 0.2 mmol), **2** (0.3 mmol, 1.5 equiv.), PC (5 mol%), N_2, blue LEDs (λ_{max} = 460 nm), rt, 6 h. [b] Yield Determined by gas chromatography (GC) using dodecane as an internal standard. [c] In parenthesis is isolated yield.

III. General Procedures for the Access to α-Tertiary Amino Acid Derivatives

General Procedure for the Synthesis of 3.

The $Ru(bpy)_3Cl_2•6H_2O$ (0.01 mmol, 5 mol%) and Togni II reagent (**2a**, 0.3 mmol, 1.5 equiv.) were weighed into an oven-dried quartz tube. After the tube was evacuated and backfilled with N_2 three times, anhydrous CH_3CN (2 mL), α,β-unsaturated carbonyl compounds **1** (0.2 mmol, 1 equiv.), H_2O (0.2 mmol, 1.0 equiv.) and $BF_3•Et_2O$ (0.4 mmol, 2.0 equiv.) were added through a syringe. The reaction mixture was allowed to stir at room temperature under irradiation with blue LEDs for 6 h. Upon the completion of reaction, the resulted mixture was quenched with saturated $NaHCO_3$ (aq., 2 mL), extracted with EA (2 mL × 3), dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford the crude product, which was then purified via silica gel flash column chromatography or preparative thin layer chromatography to afford the desired pure product. Photo-induced reactions were conducted in photo-reactors, which comprise a fan for cooling (approximately room temperature) and six 1W blue LED beads for each place (6 W). The average power output of the photo-reactor was ca. 30 mW/cm^2. The emission spectra of the blue LEDs were recorded on an Ocean Optics HR4000CG-UVNIR spectrometer. The spectra was normalised to 1.0 at the maximum (460 nm).

IV. Experimental Characterization Data for Products



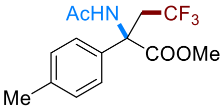
Methyl-2-acetamido-4,4,4-trifluoro-2-phenylbutanoate (3aa):

Pure **3aa** was prepared from **1aa** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (42 mg, 90% yield), the characterization data are in accordance with the literature[1].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 4H), 7.33 – 7.28 (m, 1H), 7.13 (s, 1H), 4.0 – 3.9 (m, 1H), 3.71 (s, 3H), 3.48 – 3.37 (m, 1H), 2.04 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.83;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 169.4, 138.1, 129.0, 128.5, 125.9 (q, *J* =277.8 Hz), 125.3, 61.1, 53.9, 36.1 (q, *J* = 27.2 Hz), 23.8.



Methyl-2-acetamido-4,4,4-trifluoro-2-(*p*-tolyl)butanoate (3ab):

Pure **3ab** was prepared from **1ab** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (51 mg, 84% yield), m.p. 130–131 °C.

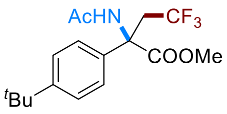
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.11 (s, 1H), 3.97 – 3.88 (m, 1H), 3.71 (s, 3H), 3.45 – 3.35 (m, 1H), 2.32 (s, 3H), 2.03 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.82;

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 170.5, 138.4, 134.8, 129.7, 125.9 (q, *J* = 277.8 Hz), 125.1, 61.0, 53.9, 36.2 (q, *J* = 27.1 Hz), 23.9, 21.1;

IR ν_{max} (neat)/cm^{-1}: 3363, 3352, 3025, 2959, 1745, 1659, 1527, 1440, 1365, 1320, 1266, 1132, 735, 610;

HRMS (ESI): *m/z* calcd. for $C_{14}H_{17}F_3NO_3$ $[M+H]^+$ 304.1155; found 304.1158.



Methyl-2-acetamido-2-(4-(*tert*-butyl)phenyl)-4,4,4-trifluorobutanoate (3ac):

Pure **3ac** was prepared from **1ac** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) white solid (48 mg, 70% yield), m.p. 113–115 °C.

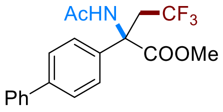
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.09 (s, 1H), 4.0 – 3.89 (m, 1H), 3.71 (s, 3H), 3.47 – 3.36 (m, 1H), 2.04 (s, 3H), 1.29 (s, 9H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.84;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 169.4, 151.3, 134.9, 125.94, 125.92 (q, *J* = 277.8 Hz), 125.0, 61.0, 53.9, 36.2 (q, *J* = 27.1 Hz), 34.6, 31.3, 23.9;

IR ν_{max} (neat)/cm^{-1}: 3264, 2963, 1741, 1658, 1518, 1435, 1302, 1132, 1049, 871, 632, 563;

HRMS (ESI): *m/z* calcd. for $C_{17}H_{23}F_3NO_3$ $[M+H]^+$ 346.1625; found 346.1627.



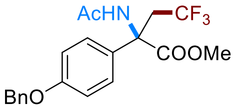
Methyl-2-([1,1'-biphenyl]-4-yl)-2-acetamido-4,4,4-trifluorobutanoate (3ad):

Pure **3ad** was prepared from **1ad** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (57 mg, 78% yield), the characterization data are in accordance with the literature[1].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 4H), 7.43 (t, *J* = 7.9 Hz, 5H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.18 (s, 1H), 4.06 – 3.95 (m, 1H), 3.75 (s, 3H), 3.51 – 3.41 (m, 1H), 2.07 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.82;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 169.5, 141.4, 140.3, 137.1, 128.9, 127.72, 127.70, 127.2, 125.9 (q, *J* = 277.8 Hz), 125.7, 61.0, 54.0, 36.2 (q, *J* = 27.2 Hz), 23.9.



Methyl-2-acetamido-2-(4-(benzyloxy)phenyl)-4,4,4-trifluorobutanoate (3ae):

Pure **3ae** was prepared from **1ae** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (53 mg, 67% yield), m.p. 124–126 °C.

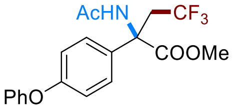
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 4H), 7.26 – 7.17 (m, 3H), 7.02 (s, 1H), 6.88 (d, J = 8.9 Hz, 2H), 4.96 (s, 2H), 3.92 – 3.80 (m, 1H), 3.64 (s, 3H), 3.36 – 3.26 (m, 1H), 1.97 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.87;

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 169.5, 158.8, 136.8, 130.3, 128.8, 128.2, 127.7, 126.6, 125.8 (q, J = 277.9 Hz), 115.2, 70.2, 60.8, 53.9, 36.2 (d, J = 27.2 Hz), 23.9;

IR ν_{max} (neat)/cm^{-1}: 3233, 3038, 2954, 2924, 1735, 1637, 1511, 1434, 1248, 1132, 1010, 755, 702, 629;

HRMS (ESI): m/z calcd. for $C_{20}H_{21}F_3NO_4$ $[M+H]^+$ 396.1417; found 396.1420.



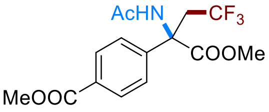
Methyl-2-acetamido-4,4,4-trifluoro-2-(4-phenoxyphenyl)butanoate (3af):

Pure **3af**[1] was prepared from **1af** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (68 mg, 89% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (t, J = 7.9 Hz, 2H), 7.30 (d, J = 8.9 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 7.10 (s, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.99 – 3.89 (m, 1H), 3.73 (s, 3H), 3.44 – 3.33 (m, 1H), 2.05 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.98;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 169.4, 157.7, 156.4, 132.4, 130.0, 126.8, 125.8 (q, J = 279.4 Hz), 124.1, 119.8, 118.4, 60.8, 54.0, 36.2 (q, J = 27.0 Hz), 23.9.



Methyl-4-(2-acetamido-4,4,4-trifluoro-1-methoxy-1-oxobutan-2-yl)benzoate (3ag):

Pure **3ag** was prepared from **1ag** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (60 mg, 86% yield), m.p. 113–115 °C.

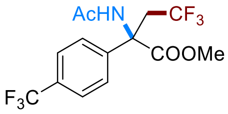
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.16 (s, 1H), 3.99 – 3.92 (m, 1H), 3.90 (s, 3H), 3.71 (s, 3H), 3.48 – 3.37 (m, 1H), 2.04 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.91;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 169.4, 166.5, 143.1, 130.32, 130.26, 125.6 (q, *J* = 277.8 Hz), 125.4, 61.1, 54.1, 52.3, 36.1 (q, *J* = 27.3 Hz), 23.7;

IR ν_{max} (neat)/cm^{-1}: 3263, 3022, 2960, 1742, 1722, 1658, 1527, 1435, 1411, 1288, 1134, 1017, 964, 741, 632;

HRMS (ESI): *m/z* calcd. for $C_{15}H_{17}F_3NO_5$ $[M+H]^+$ 348.1053; found 348.1050.



Methyl-2-acetamido-4,4,4-trifluoro-2-(4-(trifluoromethyl)phenyl)butanoate (3ah):

Pure **3ah** was prepared from **1ah** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (66 mg, 92% yield), m.p. 122–124 °C.

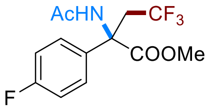
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.16 (s, 1H), 4.03 – 3.91 (m, 1H), 3.73 (s, 3H), 3.47 – 3.36 (m, 1H), 2.06 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.97, -62.80;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 169.5, 142.2, 130.7 (q, *J* = 32.8 Hz), 126.1 (q, *J* = 3.8 Hz), 125.8, 125.6 (q, *J* = 277.8 Hz), 123.9 (q, *J* = 271.8 Hz) 61.0, 54.3, 36.1 (q, *J* = 27.4 Hz), 23.8;

IR ν_{max} (neat)/cm^{-1}: 3308, 3039, 1751, 1666, 1533, 1333, 1295, 1272, 1172, 1133, 1072, 1017, 848, 717, 633;

HRMS (ESI): *m/z* calcd. for $C_{14}H_{14}F_6NO_3$ $[M+H]^+$ 358.0872; found 358.0872.



Methyl-2-acetamido-4,4,4-trifluoro-2-(4-fluorophenyl)butanoate (3ai):

Pure **3ai** was prepared from **1ai** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (50 mg, 82% yield), m.p. 122–124 °C.

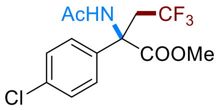
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.11 (s, 1H), 7.04 (t, *J* = 8.6 Hz, 2H), 3.97 – 3.88 (m, 1H), 3.72 (s, 3H), 3.42 – 3.33 (m, 1H), 2.04 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.96, -113.67;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 169.5, 162.6 (d, *J* = 248.5 Hz), 134.0 (d, *J* = 4.0 Hz), 127.2 (d, *J* = 7.9 Hz), 125.7 (q, *J* = 279.4 Hz), 116.0 (d, *J* = 21.8 Hz), 60.7, 54.0, 36.2 (q, *J* = 27.5 Hz), 23.8;

IR ν_{max} (neat)/cm^{-1}: 3247, 3055, 1740, 1644, 1551, 1512, 1442, 1373, 1310, 1257, 1209, 1140, 1103, 1047, 1017, 957, 833, 633;

HRMS (ESI): *m/z* calcd. for $C_{13}H_{14}F_4NO_3$ $[M+H]^+$ 308.0904; found 308.0900.



Methyl)-2-acetamido-2-(4-chlorophenyl)-4,4,4-trifluorobutanoate (3aj):

Pure **3aj** was prepared from **1aj** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (54 mg, 83% yield), m.p. 127–129 °C.

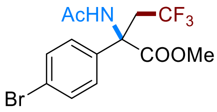
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 4H), 7.12 (s, 1H), 3.96 – 3.87 (m, 1H), 3.72 (s, 3H), 3.41 – 3.33 (m, 1H), 2.04 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.95;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 169.5, 136.8, 134.6, 129.2, 126.8, 125.7 (q, *J* = 277.9 Hz), 60.8, 54.1, 36.1 (q, *J* = 27.4 Hz), 23.8;

IR ν_{max} (neat)/cm^{-1}: 3300, 3045, 1750, 1666, 1534, 1495, 1376, 1266, 1133, 1095, 970, 763, 732, 634;

HRMS (ESI): *m/z* calcd. for $C_{13}H_{14}ClF_3NO_3$ $[M+H]^+$ 324.0609; found 324.0606.



Methyl-2-acetamido-2-(4-bromophenyl)-4,4,4-trifluorobutanoate (3ak):

Pure **3ak** was prepared from **1ak** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (59 mg, 80% yield), m.p. 136–137 °C.

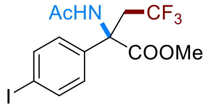
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.11 (s, 1H), 3.97 – 3.86 (m, 1H), 3.72 (s, 3H), 3.43 – 3.30 (m, 1H), 2.04 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.96;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 169.4, 137.4, 132.2, 127.1, 125.7 (q, *J* = 277.8 Hz), 122.8, 60.8, 54.1, 36.0 (q, *J* = 27.0 Hz), 23.8;

IR ν_{max} (neat)/cm^{-1}: 3301,3044, 2962, 1750, 1670, 1530, 1489, 1436, 1377, 1267, 1203, 1133, 1048, 1010, 970, 834, 725, 632;

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{14}BrF_3NO_3$ $[M+H]^+$ 368.0104; found 368.0105.



Methyl-2-acetamido-4,4,4-trifluoro-2-(4-iodophenyl)butanoate (3al):

Pure **3al** was prepared from **1al** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (74 mg, 89% yield), m.p. 152–153 °C.

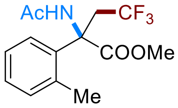
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.7 Hz, 2H), 7.13 – 7.07 (m, 3H), 3.96 – 3.84 (m, 1H), 3.72 (s, 3H), 3.40 – 3.29 (m, 1H), 2.03 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.93;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 169.4, 138.1, 138.1, 127.2, 125.6 (q, *J* = 277.8 Hz), 94.5, 60.9, 54.1, 35.9 (q, *J* = 27.4 Hz), 23.8;

IR ν_{max} (neat)/cm^{-1}: 3300, 3040, 1750, 1662, 1534, 1488, 1440, 1373, 1269, 1202, 1133, 1048, 1005, 969, 838, 756, 633;

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{14}IF_3NO_3$ $[M+H]^+$ 415.9965; found 415.9968.



Methyl-2-acetamido-4,4,4-trifluoro-2-(*o*-tolyl)butanoate (3am):

Pure **3am** was prepared from **1am** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (50 mg, 83% yield), m.p. 79–81 °C.

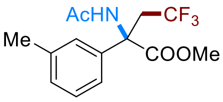
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.06 (s, 1H), 4.20 – 4.09 (m,1H), 3.74 (s, 3H), 3.30 – 3.20 (m, 1H), 2.27 (s, 3H), 1.99 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.57;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 168.8, 136.1, 135.4, 133.0, 128.5, 126.7, 126.4, 125.8 (q, *J* = 279.4 Hz), 60.8, 54.0, 37.3 (q, *J* = 27.1 Hz), 23.5, 20.8;

IR ν_{max} (neat)/cm^{-1}: 3363, 3252, 3025, 2959, 1745, 1659, 1527, 1440, 1365, 1320, 1266, 1151, 1132, 1049, 987, 735, 610;

HRMS (ESI): *m*/*z* calcd. for $C_{14}H_{17}F_3NO_3$ $[M+H]^+$ 304.1155; found 304.1158.



Methyl-2-acetamido-4,4,4-trifluoro-2-(*m*-tolyl)butanoate (3an):

Pure **3an** was prepared from **1an** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (53 mg, 87% yield), m.p. 128–130 °C.

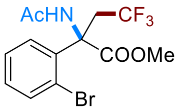
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 1H), 7.16 (d, *J* = 6.9 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 3.99 – 3.88 (m, 1H), 3.71 (s, 3H), 3.46 – 3.36 (m, 1H), 2.35 (s, 3H), 2.04 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.81;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 169.4, 138.7, 138.1, 129.4, 128.8, 125.91 (q, *J* = 277.8 Hz), 125.89, 122.3, 61.0, 53.9, 36.1 (q, *J* = 27.2 Hz), 23.9, 21.8;

IR ν_{max} (neat)/cm^{-1}: 3280, 3043, 1735, 1652, 1534, 1489, 1372, 1303, 1258, 1175, 1136, 1048, 1027, 848, 762, 693, 516;

HRMS (ESI): *m*/*z* calcd. for $C_{14}H_{17}F_3NO_3$ $[M+H]^+$ 304.1155; found 304.1156.



Methyl-2-acetamido-2-(2-bromophenyl)-4,4,4-trifluorobutanoate (3ao):

Pure **3ao** was prepared from **1ao** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (55 mg, 75% yield), m.p. 147–148 °C.

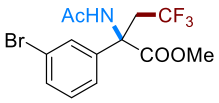
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.23 (s, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 4.26 – 4.15 (m, 1H), 3.78 (s, 3H), 3.16 – 3.06 (m, 1H), 1.98 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.58;

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.6, 169.0, 137.3, 135.3, 129.9, 129.1, 127.4, 125.4 (q, *J* = 277.8 Hz), 121.3, 61.3, 54.2, 37.3 (q, *J* = 27.7 Hz), 23.6;

IR ν_{max} (neat)/cm^{-1}: 3386, 3016, 2962, 1750, 1673, 1504, 1435, 1364, 1312, 1232, 1136, 1111, 1044, 748, 602;

HRMS (ESI): *m/z* calcd. for $C_{13}H_{14}BrF_3NO_3$ $[M+H]^+$ 368.0104; found 368.0109.



Methyl-2-acetamido-2-(3-bromophenyl)-4,4,4-trifluorobutanoate (3ap):

Pure **3ap** was prepared from **1ap** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (59 mg, 80% yield), m.p. 86–89 °C.

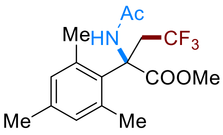
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.9 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.12 (s, 1H), 3.97 – 3.86 (m, 1H), 3.73 (s, 3H), 3.41 – 3.31 (m, 1H), 2.05 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.93;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 169.4, 140.5, 131.7, 130.5, 128.6, 125.7 (q, *J* = 277.8 Hz), 124.0, 123.2, 60.8, 54.2, 36.0 (q, *J* = 27.4 Hz), 23.8;

IR ν_{max} (neat)/cm^{-1}: 3247, 3055, 2955, 1735, 1650, 1573, 1550, 1440, 1373, 1311, 1259, 1207, 1141, 756, 686, 655, 632, 516;

HRMS (ESI): *m/z* calcd. for $C_{13}H_{14}BrF_3NO_3$ $[M+H]^+$ 368.0104; found 368.0108.



Methyl-2-acetamido-4,4,4-trifluoro-2-mesitylbutanoate (3aq):

Pure **3aq** was prepared from **1aq** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (50 mg, 76% yield), m.p. 156–158 °C.

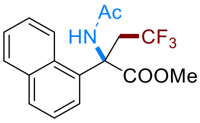
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (s, 1H), 6.82 (s, 2H), 4.16 – 4.26 (m, 1H), 3.77 (s, 3H), 3.33 – 3.21 (m, 1H), 2.45 (s, 6H), 2.21 (s, 3H), 2.00 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.27;

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 168.8, 137.3, 136.9, 133.3, 132.7, 125.6 (q, *J* = 279.0 Hz), 63.3, 54.0, 39.8 (q, *J* = 26.4 Hz), 24.5, 23.6, 20.5;

IR ν_{max} (neat)/cm^{-1}: 3386, 2976, 1737, 1680, 1500, 1465, 1317, 1265, 1172, 1140, 1103, 1048, 972, 873, 656, 617, 571;

HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{21}F_3NO_3$ $[M+H]^+$ 332.1468; found 332.1461.



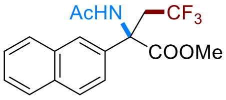
Methyl-2-acetamido-4,4,4-trifluoro-2-(naphthalen-1-yl)butanoate (3ar):

Pure **3ar** was prepared from **1ar** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (42 mg, 79% yield), the characterization data are in accordance with the literature[1].

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 1H), 7.90 – 7.78 (m, 2H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.54 – 7.40 (m, 3H), 7.29 (s, 1H), 4.26 – 4.37(m, 1H), 3.66 (s, 3H), 3.41 – 3.39 (m, 1H), 1.92 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.21;

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.8, 169.1, 134.8, 133.4, 130.1, 130.0, 129.8, 126.6, 125.9 (q, *J* = 277.8 Hz), 125.6, 125.3, 124.9, 123.4, 61.0, 54.1, 37.8 (q, *J* = 26.9 Hz), 23.6.



Methyl-2-acetamido-4,4,4-trifluoro-2-(naphthalen-2-yl)butanoate (3as):

Pure **3as** was prepared from **1as** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (56 mg, 82% yield), m.p. 184–185 °C.

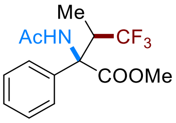
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 4H), 7.53 – 7.47 (m, 2H), 7.44 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.21 (s, 1H), 4.15 – 4.05 (m, 1H), 3.70 (s, 3H), 3.60 – 3.50 (m, 1H), 2.07 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.77;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 169.4, 135.5, 133.2, 133.1, 129.0, 128.5, 127.7, 126.9, 126.7, 125.9 (q, *J* = 277.8 Hz), 124.9, 122.6, 61.2, 54.0, 36.2 (d, *J* = 27.3 Hz), 23.9;

IR ν_{max} (neat)/cm^{-1}: 3327, 2960, 1749, 1665, 1522, 1435, 1372, 1318, 1262, 1190, 1134, 1047, 969, 755, 740, 648, 478;

HRMS (ESI): *m/z* calcd. for $C_{17}H_{17}F_3NO_3$ $[M+H]^+$ 340.1155; found 340.1158.



Methyl-2-acetamido-4,4,4-trifluoro-3-methyl-2-phenylbutanoate (3at):

Pure **3at** was prepared from **1at** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (48 mg, 79% yield, dr = 1.4:1), m.p. 127–128 °C.

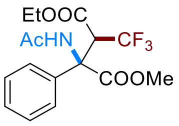
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 6.89 (s, 0.6H), 6.84 (s, 0.4H), 4.43 – 4.28 (m, 0.6H), 3.89 – 3.81 (m, 0.4H), 3.79 (s, 2H), 3.69 (s, 1H), 2.11 (s, 1H), 1.95 (s, 2H), 1.37 (d, *J* = 7.2 Hz, 1.8H), 1.35 (d, *J* = 7.2 Hz, 1.2H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -65.89, -66.76;

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.3, 171.9, 169.5, 169.3, 137.6, 135.1, 128.6, 128.4, 128.3, 128.2, 127.6 (q, *J* = 282.1 Hz), 127.5 (q, *J* = 282.2 Hz), 127.0, 126.8, 65.9, 65.6, 53.9, 53.3, 44.0 (q, *J* = 24.0 Hz), 40.9 (q, *J* = 24.0 Hz), 24.2, 24.1, 11.9, 11.2;

IR ν_{max} (neat)/cm^{-1}: 3292, 3062, 2954, 1736, 1658, 1538, 1297, 1257, 1185, 1041, 940, 725, 701, 663, 493;

HRMS (ESI): *m/z* calcd. for $C_{14}H_{17}F_3NO_3$ $[M+H]^+$ 304.1155; found 304.1155.



4-Ethyl 1-methyl-2-acetamido-2-phenyl-3-(trifluoromethyl)succinate (3au):

Pure **3au** was prepared from **1au** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (57 mg, 79% yield, dr = 1.5:1), m.p. 163–165 °C.

isomer 1:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.30 (m, 3H), 6.98 (s, 1H), 4.54 (q, *J* = 8.2 Hz, 1H), 4.05 – 3.91 (m, 2H), 3.73 (s, 3H), 2.12 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.54;

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7, 165.5, 135.8, 128.7, 128.5, 126.6, 123.4 (d, *J* = 282.3 Hz), 64.2, 62.3, 58.9 (q, *J* = 26.2 Hz), 53.5, 23.6, 13.6;

IR ν_{max} (neat)/cm^{-1}: 3401, 2993, 1743, 1725, 1697, 1513, 1372, 1288, 1254, 1203, 1172, 1103, 1018, 763, 709, 609, 516;

HRMS (ESI): *m/z* calcd. for $C_{16}H_{19}F_3NO_5$ $[M+H]^+$ 362.1210; found 362.1215.

isomer 2:

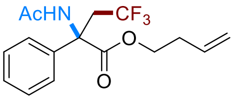
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.04 (s, 1H), 4.42 (q, *J* = 8.2 Hz, 1H), 4.32 – 4.18 (m, 2H), 3.72 (s, 3H), 2.11 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -60.71;

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 170.0, 165.6, 134.5, 128.7, 128.3, 127.1, 123.5 (q, *J* = 282.3 Hz), 64.6, 62.7, 55.1 (q, *J* = 25.6 Hz), 53.5, 23.4, 14.0;

IR ν_{max} (neat)/cm^{-1}: 3403, 2994, 1743, 1725, 1697, 1511, 1372, 1289, 1253, 1201, 1170, 1101, 1018, 761, 708, 607, 516;

HRMS (ESI): *m/z* calcd. for $C_{16}H_{19}F_3NO_5$ $[M+H]^+$ 362.1210; found 362.1213.



But-3-en-1-yl-2-acetamido-4,4,4-trifluoro-2-phenylbutanoate (3av):

Pure **3av** was prepared from **1av** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as colorless oil (41 mg, 62% yield), m.p. 104–106 °C.

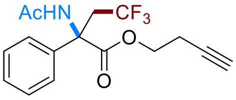
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 7.10 (s, 1H), 5.60 – 5.51 (m, 1H), 4.99 – 4.91 (m, 2H), 4.20 – 4.10 (m, 2H), 3.98 – 3.87 (m, 1H), 3.48 – 3.37 (m, 1H), 2.30 – 2.22 (m, 2H), 2.05 (s, 3H);

^{19}F NMR (565 MHz, CDCl$_3$) δ -61.65;

^{13}C NMR (151 MHz, CDCl$_3$) δ 171.2, 169.4, 138.2, 133.1, 128.9, 128.4, 125.9 (q, J = 277.8 Hz), 125.3, 117.8, 66.0, 61.2, 36.2 (q, J = 27.2 Hz), 32.6, 23.9;

IR ν_{max} (neat)/cm^{-1}: 3237, 3055, 1732, 1643, 1558, 1449, 1378, 1311, 1259, 1235, 1133, 1103, 1053, 918, 733, 717, 694, 634, 516;

HRMS (ESI): m/z calcd. for $C_{16}H_{19}F_3NO_3$ $[M+H]^+$ 330.1312; found 330.1317.



But-3-yn-1-yl-2-acetamido-4,4,4-trifluoro-2-phenylbutanoate (3aw):

Pure **3aw** was prepared from **1aw** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as colorless oil (39 mg, 60% yield), m.p. 58–60 °C.

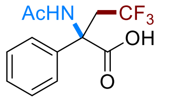
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.41 – 7.33 (m, 4H), 7.30 (t, J = 7.1 Hz, 1H), 7.07 (s, 1H), 4.27 – 4.20 (m, 1H), 4.18 – 4.12 (m, 1H), 3.98 – 3.87 (m, 1H), 3.53 – 3.38 (m, 1H), 2.42 (t, J = 6.9 Hz, 2H), 2.06 (s, 3H), 1.91 (t, J = 2.7 Hz, 1H);

^{19}F NMR (565 MHz, CDCl$_3$) δ -61.56;

^{13}C NMR (151 MHz, CDCl$_3$) δ 171.0, 169.4, 137.9, 129.0, 128.5, 125.9 (q, J = 277.8 Hz), 125.3, 79.0, 70.4, 64.4, 61.3, 36.3 (q, J = 27.3 Hz), 23.8, 18.6;

IR ν_{max} (neat)/cm^{-1}: 3301, 3039, 2970, 1740, 1647, 1528, 1497, 1448, 1368, 1317, 1262, 1198, 1140, 1043, 840, 725, 634, 516;

HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{17}F_3NO_3$ $[M+H]^+$ 328.1155; found 328.1154.



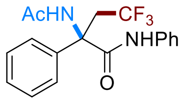
2-Acetamido-4,4,4-trifluoro-2-phenylbutanoic acid (3ax):

Pure **3ax** was prepared from **1ax** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 1:1) as white solid (40 mg, 71% yield), the characterization data are in accordance with the literature[1].

^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 13.33 (s, 1H), 8.44 (s, 1H), 7.62 – 7.47 (m, 2H), 7.42 – 7.19 (m, 3H), 3.60 (qd, *J* = 12.0, 7.2 Hz, 2H), 1.96 (s, 3H);

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -59.54;

^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 171.8, 169.8, 138.8, 128.3, 127.7, 126.3 (q, *J* = 278.0 Hz), 125.6, 60.8 (q, *J* = 2.5 Hz), 35.7 (q, *J* = 25.8 Hz), 22.8.



2-Acetamido-4,4,4-trifluoro-*N*,2-diphenylbutanamide (3ay):

Pure **3ay** was prepared from **1ay** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (46 mg, 65% yield), m.p. 177–179 °C.

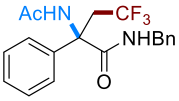
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.62 (s, 1H), 7.46 (s, 1H), 7.43 – 7.38 (m, 2H), 7.38 – 7.32 (m, 3H), 7.29 – 7.23 (m, 4H), 7.11 (t, *J* = 6.9 Hz, 1H), 3.95 – 3.84 (m, 1H), 3.30 – 3.19 (m, 1H), 1.96 (s, 3H);

^{19}F NMR (565 MHz, CDCl$_3$) δ -60.69;

^{13}C NMR (151 MHz, CDCl$_3$) δ 170.1, 168.8, 138.9, 136.9, 129.4, 129.2, 128.9, 125.3, 125.8 (q, *J* = 277.8 Hz), 120.7, 61.8, 36.9 (q, *J* = 26.9 Hz), 23.9;

IR ν_{max} (neat)/cm^{-1}: 3352, 3062, 1689, 1651, 1496, 1443, 1326, 1264, 1126, 1039, 755, 709, 671, 534;

HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{18}F_3N_2O_2$ $[M+H]^+$ 351.1315; found 351.1320.



2-Acetamido-*N*-benzyl-4,4,4-trifluoro-2-phenylbutanamide (3az):

Pure **3az** was prepared from **1az** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (64 mg, 88% yield), m.p. 125–126 °C.

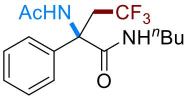
^{1}H NMR (600 MHz, Acetone-d_6) δ 7.92 (s, 1H), 7.65 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.15 – 7.06 (m, 3H), 6.92 – 6.87 (m, 2H), 4.31 – 4.19 (m, 2H), 3.84 – 3.73 (m, 1H), 3.73 – 3.62 (m, 1H), 1.98 (s, 3H);

^{19}F NMR (565 MHz, Acetone-d_6) δ -60.80;

^{13}C NMR (151 MHz, Acetone-d_6) δ 170.5, 169.5, 140.0, 139.0, 128.4, 128.1, 127.7, 126.9, 126.7, 126.1 (q, *J* = 277.8 Hz), 125.3, 61.4, 43.0, 35.4 (q, *J* = 26.2 Hz), 22.7;

IR ν_{max} (neat)/cm^{-1}: 3357, 3237, 3062, 1656, 1499, 1445, 1373, 1317, 1257, 1203, 1126, 1035, 702, 610, 508;

HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{20}F_3N_2O_2$ [M+H]$^+$ 365.1471; found 365.1475.



3-Acetamido-*N*-butyl-5,5,5-trifluoro-2-oxo-3-phenylpentanamide (3ba):

Pure **3ba** was prepared from **1ba** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (55 mg, 84% yield), m.p. 143–144 °C.

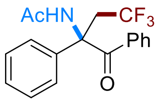
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.59 (s, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 3H), 5.53 (t, *J* = 5.6 Hz, 1H), 4.02 – 3.85 (m, 1H), 3.20 – 3.05 (m, 2H), 3.07 – 2.99 (m, 1H), 1.96 (s, 3H), 1.36 – 1.24 (m, 2H), 1.15 – 1.04 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H);

^{19}F NMR (565 MHz, CDCl$_3$) δ -61.12;

^{13}C NMR (151 MHz, CDCl$_3$) δ 170.6, 169.5, 140.3, 129.2, 128.5, 125.8 (q, *J* = 277.7 Hz), 125.0, 60.7, 40.2, 36.5 (q, *J* = 27.2 Hz), 31.0, 23.9, 19.8, 13.7;

IR ν_{max} (neat)/cm^{-1}: 3336, 3065, 2962, 2934, 2875, 1654, 1500, 1448, 1373, 1318, 1260, 1172, 1126, 1040, 840, 708, 632, 608, 547;

HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{22}F_3N_2O_2$ $[M+H]^+$ 331.1628; found 331.1630.



***N*-(4,4,4-Trifluoro-1-oxo-1,2-diphenylbutan-2-yl)acetamide (3bb):**

Pure **3bb** was prepared from **1bb** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (43 mg, 65% yield), m.p. 169–171 °C.

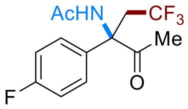
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.46 – 7.34 (m, 8H), 7.24 (d, *J* = 8.5 Hz, 2H), 4.17 (s, 1H), 3.40 – 3.29 (m, 1H), 1.97 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -60.09;

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.6, 169.3, 137.4, 134.6, 132.7, 129.5, 129.4, 128.9, 128.5, 126.9, 126.1, 125.1 (q, *J* = 277.8 Hz), 64.9, 37.2 (q, *J* = 27.2 Hz), 23.8;

IR ν_{max} (neat)/cm^{-1}: 3301, 3020, 1683, 1650, 1521, 1496, 1450, 1373, 1264, 1210, 1126, 763, 701, 623, 517;

HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{17}F_3NO_2$ $[M+H]^+$ 336.1206; found 336.1207.



***N*-(1,1,1-Trifluoro-3-(4-fluorophenyl)-4-oxopentan-3-yl)acetamide (3bc):**

Pure **3bc** was prepared from **1bc** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (47 mg, 80% yield), m.p. 155–157 °C.

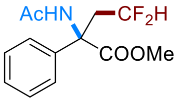
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 3H), 7.08 (t, *J* = 8.6 Hz, 2H), 4.04 – 3.93 (m, 1H), 3.29 – 3.18 (m, 1H), 2.02 (s, 3H), 1.98 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -60.69, -112.87;

^{13}C NMR (151 MHz, $CDCl_3$) δ 201.9, 169.7, 162.7 (d, *J* = 249.6 Hz), 133.0, 127.5 (d, *J* = 7.9 Hz), 125.8 (q, *J* = 277.8 Hz), 116.5 (d, *J* = 22.1 Hz), 65.5, 35.3 (q, *J* = 27.2 Hz), 23.7, 23.1;

IR ν_{max} (neat)/cm^{-1}: 3334, 2962, 1705, 1673, 1510, 1372, 1258, 1242, 1218, 1187, 1127, 1104, 1033, 831, 810, 602, 563, 478;

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{14}F_4NO_2$ $[M+H]^+$ 292.0955; found 292.0959.



***N*-(1,1-Difluoro-4-oxo-3-phenylpentan-3-yl)acetamide (3bd):**

Pure **3bd** was prepared from **1bd** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (44 mg, 82% yield), m.p. 108–109 °C.

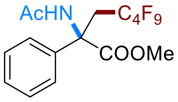
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 7.33 – 7.29 (m, 1H), 7.16 (s, 1H), 6.02 – 5.76 (m, 1H), 3.70 (s, 3H), 3.65 – 3.51 (m, 1H), 3.18 – 3.07 (m, 1H), 2.06 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -117.12 (q, *J* = 116.6 Hz);

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.5, 169.4, 138.7, 129.0, 128.5, 125.4, 116.0 (t, *J* = 239.2 Hz), 61.9 (d, *J* = 8.4 Hz), 53.8, 37.3 (dd, *J* = 23.4, 20.3 Hz), 23.9;

IR ν_{max} (neat)/cm^{-1}: 3241, 3047, 1740, 1640, 1545, 1449, 1304, 1233, 1120, 1033, 994, 721, 694, 517, 501;

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{14}F_4NO_2$ $[M+H]^+$ 272.1093; found 272.1096.



***N*-(8,8,8,8,8,8,8,8,8-Nonafluoro-2-oxo-3-phenyl-8l12-octa-5,7-diyn-3-yl)acetamide (3be):**

Pure **3be** was prepared from **1be** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (70 mg, 80% yield), m.p. 105–106 °C.

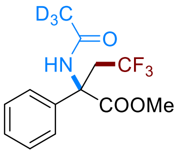
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 7.17 (s, 1H), 3.98 – 3.86 (m, 1H), 3.71 (s, 3H), 3.52 – 3.41 (m, 1H), 2.05 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -81.03 (t, *J* = 10.0 Hz), -111.61 (d, *J* = 275.1 Hz), -115.15 (d, *J* = 273.1 Hz), -124.61 – -124.89 (m), -125.03 – -126.95 (m);

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 169.5, 138.3, 129.0, 128.5, 125.2, 60.9, 53.9, 32.6, 32.3 (t, *J* = 18.1 Hz), 23.9;

IR ν_{max} (neat)/cm^{-1}: 3241, 3047, 1738, 1643, 1546, 1435, 1357, 1309, 1220, 1134, 878, 694, 664, 616, 516;

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{14}F_4NO_2$ [M+H]$^+$ 440.0903; found 440.0903.



***N*-(1,1,1-Trifluoro-4-oxo-3-phenylpentan-3-yl)acetamide-2,2,2-*d*$_3$ (3bf):**

Pure **3bf** was prepared from **1bf** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (50 mg, 86% yield), m.p. 152–154 °C.

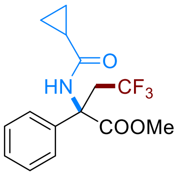
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 7.33 – 7.28 (m, 1H), 7.14 (s, 1H), 4.00 – 3.89 (m, 1H), 3.70 (s, 3H), 3.48 – 3.37 (m, 1H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.82;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 169.5, 138.1, 129.0, 128.5, 125.8 (q, *J* = 277.8 Hz), 125.2, 61.1, 53.9, 36.2 (q, *J* = 27.2 Hz);

IR ν_{max} (neat)/cm^{-1}: 3239, 3044, 2954, 1736, 1641, 1543, 1447, 1373, 1326, 1135, 1038, 956, 719, 694, 655, 625, 491;

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{14}F_4NO_2$ [M+H]$^+$ 293.1187; found 293.1189.



***N*-(1,1,1-Trifluoro-4-oxo-3-phenylpentan-3-yl)cyclopropanecarboxamide (3bg):**

Pure **3bg** was prepared from **1bg** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (52 mg, 83% yield), m.p. 109–110 °C.

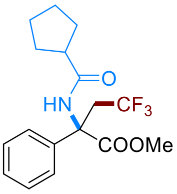
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 3.98 – 3.88 (m, 1H), 3.71 (s, 3H), 3.48 – 3.38 (m, 1H), 1.59 – 1.50 (m, 1H), 0.97 – 0.82 (m, 2H), 0.79 – 0.68 (m, 2H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.70;

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.6, 171.9, 138.4, 129.0, 128.4, 125.9 (q, J = 277.8 Hz), 125.2, 61.2, 53.9, 36.4 (q, J = 27.1 Hz), 15.1, 7.3, 7.0;

IR ν_{max} (neat)/cm^{-1}: 3322, 3020, 2959, 1756, 1649, 1524, 1435, 1358, 1311, 1265, 1127, 1038, 978, 832, 726, 701, 610, 571;

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{14}F_4NO_2$ $[M+H]^+$ 316.1155; found 316.1152.



N-(1,1,1-Trifluoro-4-oxo-3-phenylpentan-3-yl)cyclopentanecarboxamide (3bh):

Pure **3bh** was prepared from **1bh** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (49 mg, 72% yield), m.p. 118–120 °C.

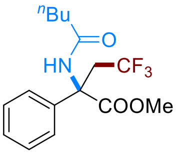
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, J = 4.3 Hz, 4H), 7.32 – 7.28 (m, 1H), 7.14 (s, 1H), 4.04 – 3.91 (m, 1H), 3.70 (s, 3H), 3.48 – 3.38 (m, 1H), 2.70 – 2.62 (m, 1H), 1.91 – 1.83 (m, 2H), 1.81 – 1.74 (m, 1H), 1.73 – 1.64 (m, 3H), 1.62 – 1.51 (m, 2H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.51;

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 172.0, 138.4, 129.0, 128.4, 125.8 (q, J = 277.8 Hz), 125.1, 60.9, 53.9, 46.1, 36.4 (q, J = 27.1 Hz), 30.1, 25.9 (d, J = 4.2 Hz);

IR ν_{max} (neat)/cm^{-1}: 3292, 2959, 1758, 1642, 1524, 1449, 1524, 1449, 1365, 1232, 1138, 1033, 977, 694, 647;

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{14}F_4NO_2$ $[M+H]^+$ 344.1468; found 344.1467.



N-(1,1,1-Trifluoro-4-oxo-3-phenylpentan-3-yl)pentanamide (3bi):

Pure **3bi** was prepared from **1bi** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as colorless oil (44 mg, 67% yield).

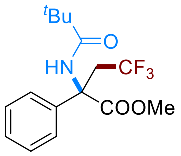
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 4.3 Hz, 4H), 7.34 – 7.27 (m, 1H), 7.10 (s, 1H), 4.02 – 3.91 (m, 1H), 3.71 (s, 3H), 3.48 – 3.37 (m, 1H), 2.26 (t, *J* = 7.7 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.39 – 1.26 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.61;

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 171.9, 138.3, 129.0, 128.5, 125.9 (q, *J* = 279.3 Hz), 125.2, 61.0, 53.9, 36.7, 36.3 (q, *J* = 27.3 Hz), 27.4, 22.4, 13.9;

IR ν_{max} (neat)/cm^{-1}: 3245, 3043, 2969, 1738, 1640, 1538, 1449, 1372, 1256, 1142, 1110, 1038, 724, 694, 640, 523;

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{14}F_4NO_2$ $[M+H]^+$ 332.1468; found 332.1463.



_N_-(1,1,1-Trifluoro-4-oxo-3-phenylpentan-3-yl)pivalamide (3bj):

Pure **3bj** was prepared from **1bj** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (51 mg, 78% yield), m.p. 74–76 °C.

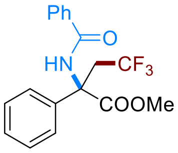
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.4 Hz, 1H), 7.37 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 4.02 – 3.91 (m, 1H), 3.71 (s, 3H), 3.49 – 3.38 (m, 1H), 1.22 (s, 9H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.51;

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 172.2, 138.5, 129.0, 128.5, 125.9 (q, *J* = 279.3 Hz), 125.0, 60.7, 53.9, 39.2, 36.2 (q, *J* = 26.8 Hz), 27.4;

IR ν_{max} (neat)/cm^{-1}: 3440, 2964, 1735, 1673, 1495, 1435, 1368, 1315, 1249, 1211, 1164, 1139, 1035, 963, 871, 732, 701, 671, 586, 563;

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{14}F_4NO_2$ $[M+H]^+$ 332.1468; found 332.1471.



N-(1,1,1-Trifluoro-4-oxo-3-phenylpentan-3-yl)benzamide (3bk):

Pure **3bk** was prepared from **1bk** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as colorless oil (45 mg, 64% yield).

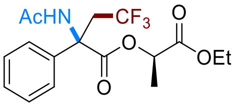
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.87 (d, *J* = 43.0 Hz, 3H), 7.61 – 7.28 (m, 8H), 4.22 – 4.04 (m, 1H), 3.76 (s, 3H), 3.63 – 3.47 (m, 1H);

^{19}F NMR (565 MHz, CDCl$_3$) δ -61.74;

^{13}C NMR (151 MHz, CDCl$_3$) δ 172.0, 166.4, 138.1, 134.3, 132.1, 129.1, 128.9, 128.6, 127.2, 126.0 (q, *J* = 277.8 Hz), 125.3, 61.4, 54.1, 36.4 (q, *J* = 27.3 Hz);

IR ν_{max} (neat)/cm^{-1}: 3425, 3031, 1735, 1674, 1514, 1480, 1441, 1365, 1319, 1265, 1241, 1104, 948, 863, 709, 609, 570;

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{14}F_4NO_2$ $[M+H]^+$ 352.1155; found 352.1156.



(*R*)-1-Ethoxy-1-oxopropan-2-yl-2-acetamido-4,4,4-trifluoro-2-phenylbutanoate (3bl):

Pure **3bl** was prepared from **1bl** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as colorless oil (67 mg, 90% yield, dr = 1.5:1).

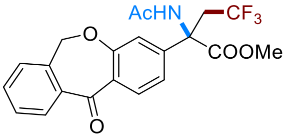
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40 (t, *J* = 8.5 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 7.12 (s, 0.4H), 7.07 (s, 0.6H), 5.12 (q, *J* = 7.0 Hz, 0.4H), 5.07 (q, *J* = 7.0 Hz, 0.6H), 4.13 (q, *J* = 7.2 Hz, 1.2H), 4.02 – 3.91 (m, 1.2H), 3.90 – 3.78 (m, 0.8H), 3.60 – 3.42 (m, 0.8H), 2.02 (s, 3H), 1.45 (d, *J* = 7.0 Hz, 1.2H), 1.27 (d, *J* = 7.0 Hz, 1.8H), 1.19 (t, *J* = 7.1 Hz, 1.8H) , 1.03 (t, *J* = 7.1 Hz, 1.2H);

^{19}F NMR (565 MHz, CDCl$_3$) δ -61.08, -61.55;

^{13}C NMR (151 MHz, CDCl$_3$) δ 170.3, 170.2, 169.6, 169.52, 169.48, 169.3, 137.6, 137.4, 128.9, 128.8, 128.53, 128.50, 125.83 (q, *J* = 279.4 Hz), 125.75 (q, *J* = 277.8 Hz), 125.5, 125.3, 70.79, 70.75, 61.7, 61.5, 61.3, 61.2, 36.4 (q, J = 27.2 Hz), 36.2 (q, J = 27.2 Hz), 23.7, 23.6, 16.64, 16.62, 13.93, 13.89;

IR ν_{max} (neat)/cm^{-1}: 3241, 2987, 1740, 1643, 1541, 1449, 1378, 1265, 1199, 1127, 856, 724, 694, 633, 516;

HRMS (ESI): *m/z* calcd. for $C_{17}H_{21}F_3NO_5$ $[M+H]^+$ 376.1366; found 376.1368.



Methyl-2-acetamido-4,4,4-trifluoro-2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-3-yl)butanoate (3bm):

Pure **3bm** was prepared from **1bm** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (77 mg, 91% yield), m.p. 117–118 °C.

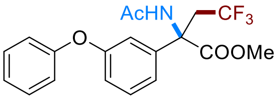
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, J = 2.7 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.56 (t, J = 8.2 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.35 (d, J = 7.4 Hz, 1H), 7.17 (s, 1H), 7.04 (d, J = 8.8 Hz, 1H), 5.18 (s, 2H), 4.0 – 3.9 (m, 1H), 3.72 (s, 3H), 3.53 – 3.43 (m, 1H), 2.07 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.92;

^{13}C NMR (151 MHz, $CDCl_3$) δ 190.7, 171.5, 169.6, 161.2, 140.5, 135.4, 133.1, 132.1, 132.0, 129.7, 129.5, 129.0, 128.0, 125.8 (q, J = 277.8 Hz), 125.2, 121.7, 73.6, 60.7, 54.1, 36.3 (q, J = 27.2 Hz), 23.9;

IR ν_{max} (neat)/cm^{-1}: 3423, 2979, 2932, 1716, 1590, 1441, 1396, 1294, 1223, 1111, 1043, 771, 717, 563;

HRMS (ESI): *m/z* calcd. for $C_{21}H_{19}F_3NO_5$ $[M+H]^+$ 422.1210; found 422.1211.



Methyl-2-acetamido-4,4,4-trifluoro-2-(3-phenoxyphenyl)butanoate (3bn):

Pure **3bn** was prepared from **1bn** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (53 mg, 70% yield), m.p. 138–140 °C.

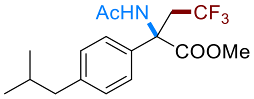
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.97 (s, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.83 (dd, *J* = 8.1, 2.3 Hz, 1H), 3.96 – 3.86 (m, 1H), 3.73 (s, 3H), 3.43 – 3.33 (m, 1H), 2.02 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.89;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 169.4, 157.8, 156.8, 140.2, 130.2, 130.0, 123.7, 125.8 (q, *J* = 277.9 Hz), 120.0, 119.1, 118.4, 116.1, 61.0, 54.0, 36.2 (q, *J* = 27.3 Hz), 23.8;

IR ν_{max} (neat)/cm^{-1}: 3231, 3047, 1736, 1643, 1589, 1490, 1373, 1311, 1255, 1133, 751, 687, 516;

HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{19}F_3NO_4$ [M+H]$^+$ 382.1261; found 382.1262.



Methyl-2-acetamido-4,4,4-trifluoro-2-(4-isobutylphenyl)butanoate (3bo):

Pure **3bo** was prepared from **1bo** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (60 mg, 87% yield), m.p. 81–82 °C.

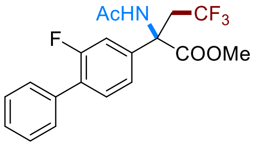
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 3H), 3.95 – 3.88 (m, 1H), 3.70 (s, 3H), 3.46 – 3.36 (m, 1H), 2.43 (d, *J* = 7.3 Hz, 2H), 2.02 (s, 3H), 1.88 – 1.79 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 6H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.78;

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 169.5, 142.1, 135.2, 129.6, 125.9 (q, *J* = 273.3 Hz), 125.0, 61.0, 53.8, 45.0, 36.2 (q, *J* = 27.1 Hz), 30.1, 23.8, 22.51, 22.48;

IR ν_{max} (neat)/cm^{-1}: 3292, 2954, 2924, 1750, 1736, 1658, 1525, 1440, 1367, 1255, 1133, 1103, 1040, 979, 763, 631, 609, 509;

HRMS (ESI): *m*/*z* calcd. for $C_{17}H_{23}F_3NO_3$ [M+H]$^+$ 346.1625; found 346.1627.



Methyl-2-acetamido-4,4,4-trifluoro-2-(2-fluoro-[1,1'-biphenyl]-4-yl)butanoate (3bp): Pure **3bp** was prepared from **1bp** with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as white solid (64 mg, 84% yield), the characterization data are in accordance with the literature[1].

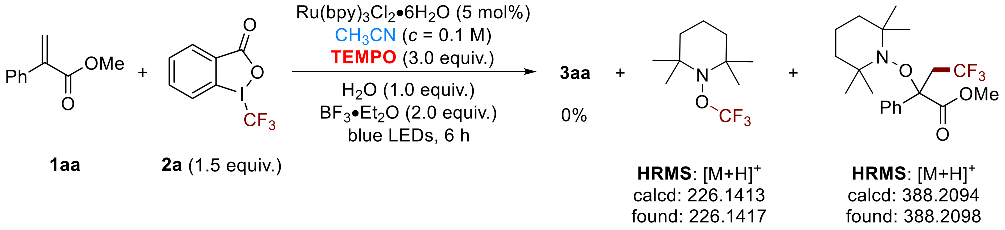
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.14 (m, 3H), 4.03 – 3.93 (m, 1H), 3.76 (s, 3H), 347 – 3.37 (m, 1H), 2.08 (s, 3H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.92, -116.36;

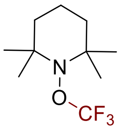
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 169.6, 159.9 (d, *J* = 248.7 Hz), 139.5 (d, *J* = 7.5 Hz), 135.0, 131.2 (d, *J* = 4.2 Hz), 129.2 (d, *J* = 14.0 Hz), 129.1 (d, *J* = 3.1 Hz), 128.6, 128.1, 125.7 (q, *J* = 277.8 Hz), 121.2 (d, *J* = 3.3 Hz), 113.6 (d, *J* = 25.3 Hz), 60.8, 54.2, 36.2 (q, *J* = 27.3 Hz), 23.8.

V. Mechanistic Studies.

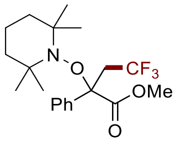
a. TEMPO trapping experiment:



The TEMPO trapping experiment was carried out according to the general procedure A on 0.2 mmol scale using **1aa** as the substrate with 3.0 equivalents of TEMPO. After 6 hours, the reaction mixture was passed through a short silica gel for HRMS analysis. Product **3aa** was not observed. TEMPO traped product was detected by HRMS.

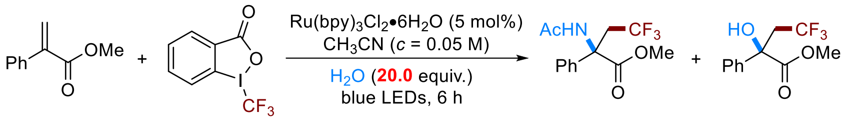


2,2,6,6-Tetramethyl-1-(trifluoromethoxy)piperidine: **HRMS**: $[M+H]^+$ calcd: 226.1413, found: 226.1417.



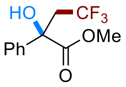
Methyl 4,4,4-trifluoro-2-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanoate: **HRMS**: $[M+H]^+$ calcd: 388.2094, found: 388.2098.

b. H_2O trapped experiment:



1aa **2a** (1.5 equiv.) **3aa**, trace **6**, 31%

The $Ru(bpy)_3Cl_2{\bullet}6H_2O$ (0.01 mmol, 5 mol%) and Togni II reagent (**2a**, 0.3 mmol, 1.5 equiv.) were weighed into an oven-dried quartz tube. After the tube was evacuated and backfilled with N_2 three times, anhydrous CH_3CN (2 mL), α,β-unsaturated carbonyl compounds **1aa** (0.2 mmol, 1 equiv.) and H_2O (4 mmol, 20.0 equiv.) were added through a syringe. The reaction mixture was allowed to stir at room temperature under irradiation with blue LEDs for 6 h. Purification by column chromatography gave the α-hydroxylation product as colorless oil (15 mg, 31% yield), the characterization data are in accordance with the literature[1].



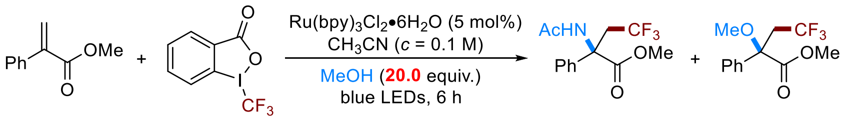
Methyl-4,4,4-trifluoro-2-hydroxy-2-phenylbutanoate (6)[1]:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 4.00 (s, 1H), 3.84 (s, 3H), 3.29 – 3.19 (m, 1H), 2.84 – 2.74 (m, 1H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.00;

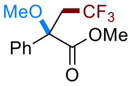
^{13}C NMR (151 MHz, $CDCl_3$) δ 173.9, 140.3, 128.8, 128.7, 125.3 (q, *J* = 279.3 Hz), 125.2, 74.9, 54.0, 43.1 (q, *J* = 27.3 Hz).

c. MeOH trapped experiment:



1aa **2a** (1.5 equiv.) **3aa**, trace **7**, 26%

The $Ru(bpy)_3Cl_2{\bullet}6H_2O$ (0.01 mmol, 5 mol%) and Togni II reagent (**2a**, 0.3 mmol, 1.5 equiv.) were weighed into an oven-dried quartz tube. After the tube was evacuated and backfilled with N_2 three times, anhydrous CH_3CN (2 mL), α,β-unsaturated carbonyl compounds **1aa** (0.2 mmol, 1 equiv.) and MeOH (4 mmol, 20.0 equiv.) were added through a syringe. The reaction mixture was allowed to stir at room temperature under irradiation with blue LEDs for 6 h. Purification by column chromatography gave the α-alkoxylation product as colorlesss oil (14 mg, 26% yield), the characterization data are in accordance with the literature[1].



Methyl 4,4,4-trifluoro-2-methoxy-2-phenylbutanoate (7)[1]:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.39 – 7.29 (m, 3H), 3.71 (s, 3H), 3.35 – 3.24 (m, 1H), 3.23 (s, 3H), 3.12 – 2.98 (m, 1H);

^{19}F NMR (471 MHz, $CDCl_3$) δ -61.07;

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 137.4, 128.7, 125.9, 125.3 (q, *J* = 278.5 Hz), 80.9, 52.9, 52.4, 37.8 (q, *J* = 27.6 Hz).

VI. References

[1] H. Jia, T. Ritter, *Angew. Chem. Int. Ed.* **2022**, *61*, e202208978.

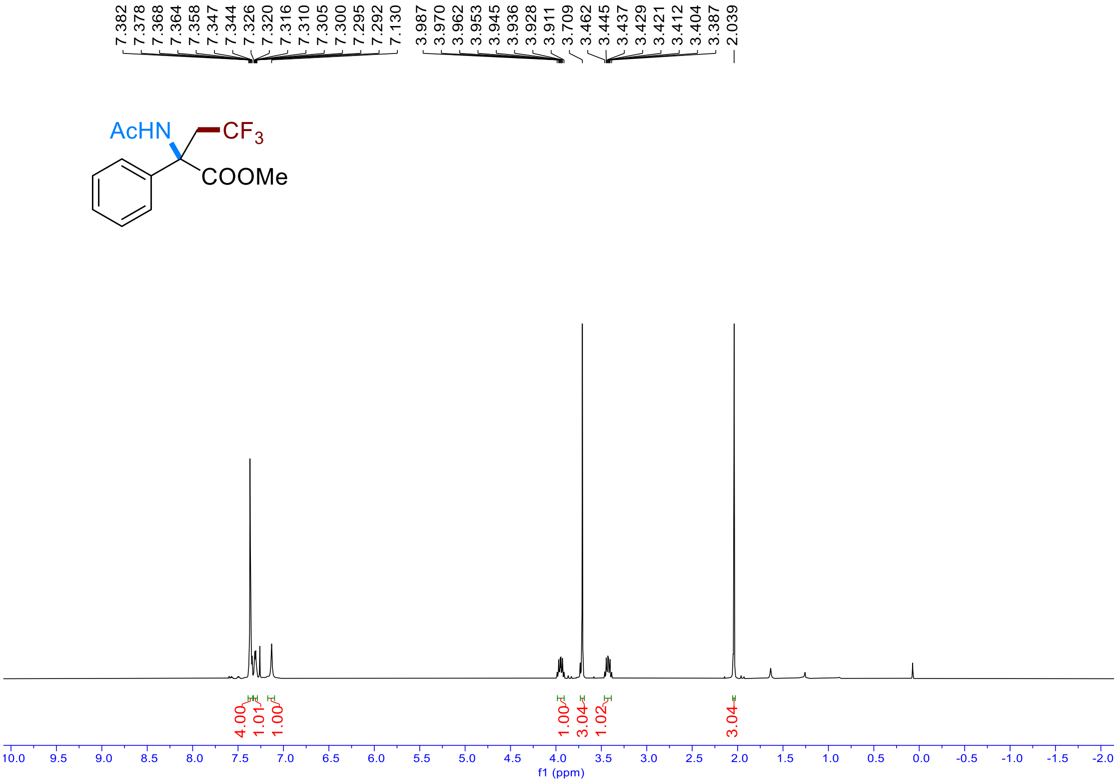
[2] Y. Xiong, X. Zhang, H.-M. Guo, X. Wu, *Org. Front. Chem.* **2022,** *9*, 3532–3539.

[3] B. Li, D. Xing, X. Li, S. Chang, H. Jiang, L. Huang, *Org. Lett.* **2023**, *25*, 6633–6637.

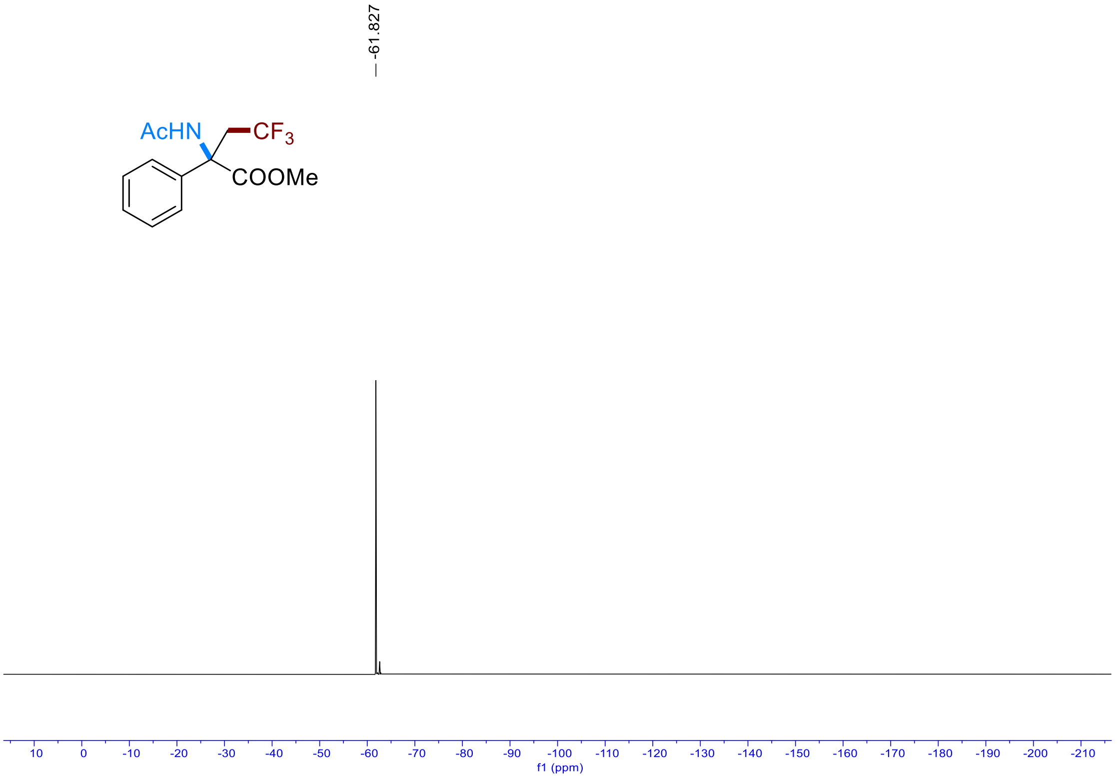
[4] H. Jia, A. P. Häring, F. Berger, L. Zhang, T. Ritter, *J. Am. Chem. Soc.* **2021**, *143*, 7623–7628.

[5] W. Zhang, Z. Zou, W. Zhao, S. Lu, Z. Wu, M. Huang, X. Wang, Y. Wang, Y. Liang, Y. Zhu, Y. Zheng, Y. Pan, *Nat. Commun.* **2020**, *11*, 2572.

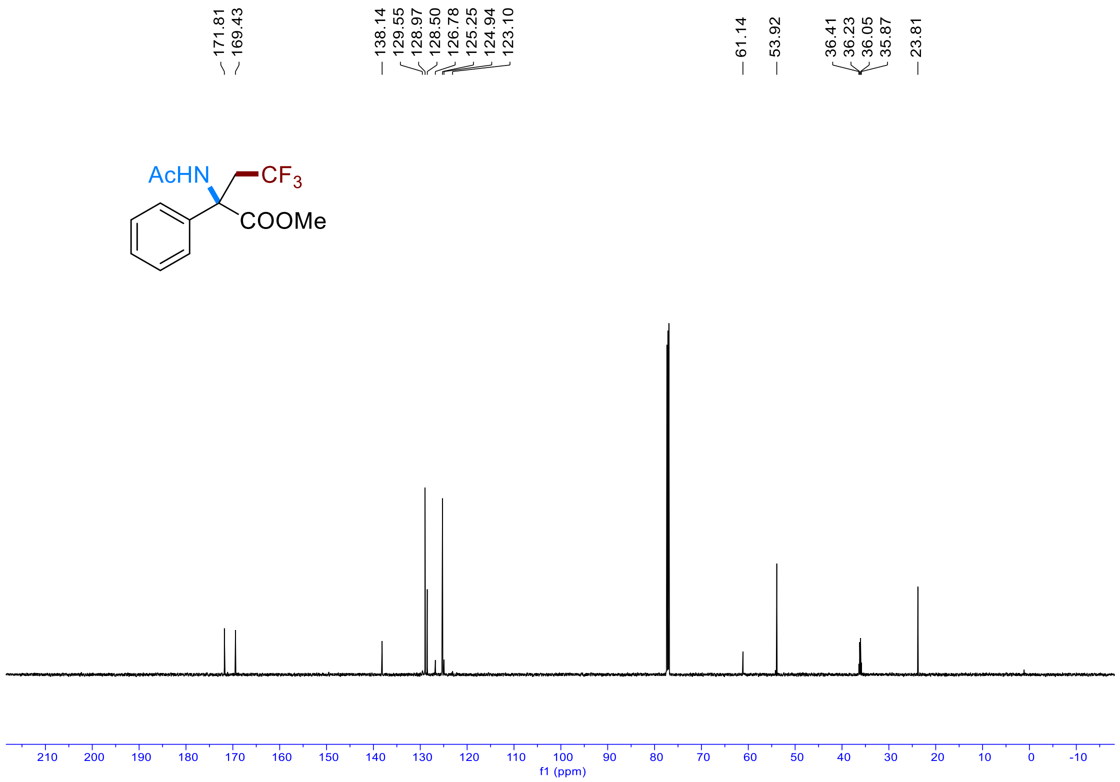
VII. NMR Spectra



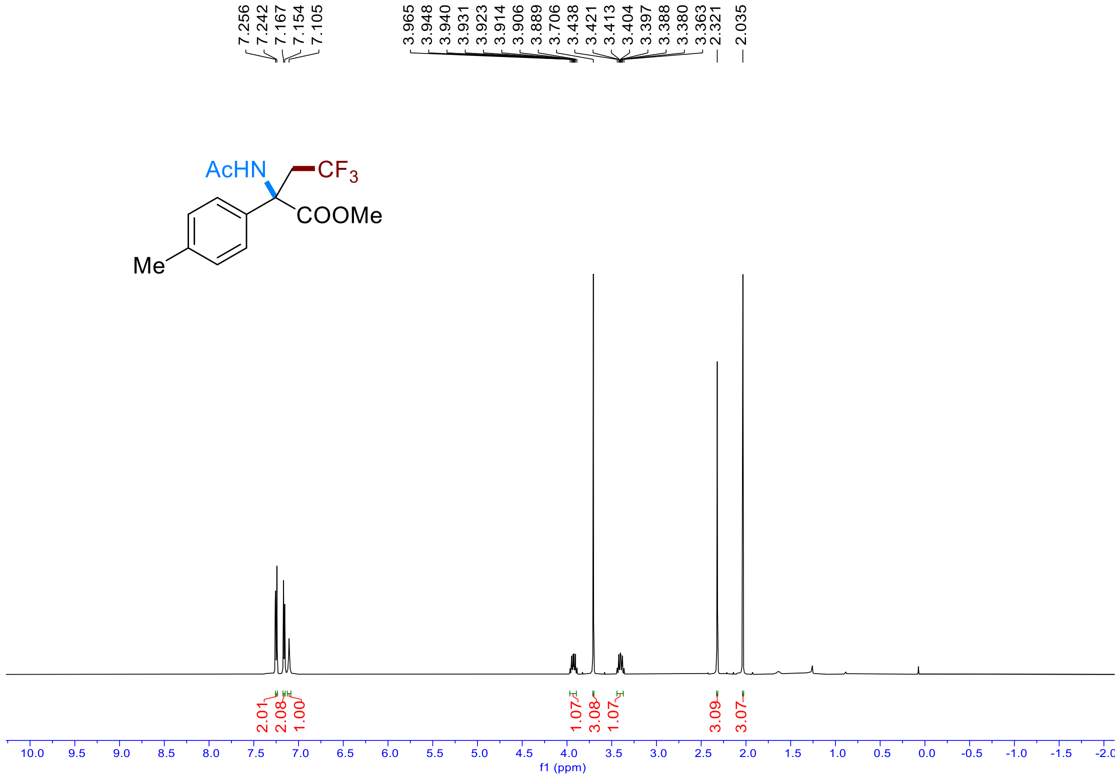
^{1}**H NMR** (600 MHz, CDCl$_3$) – (**3aa**)



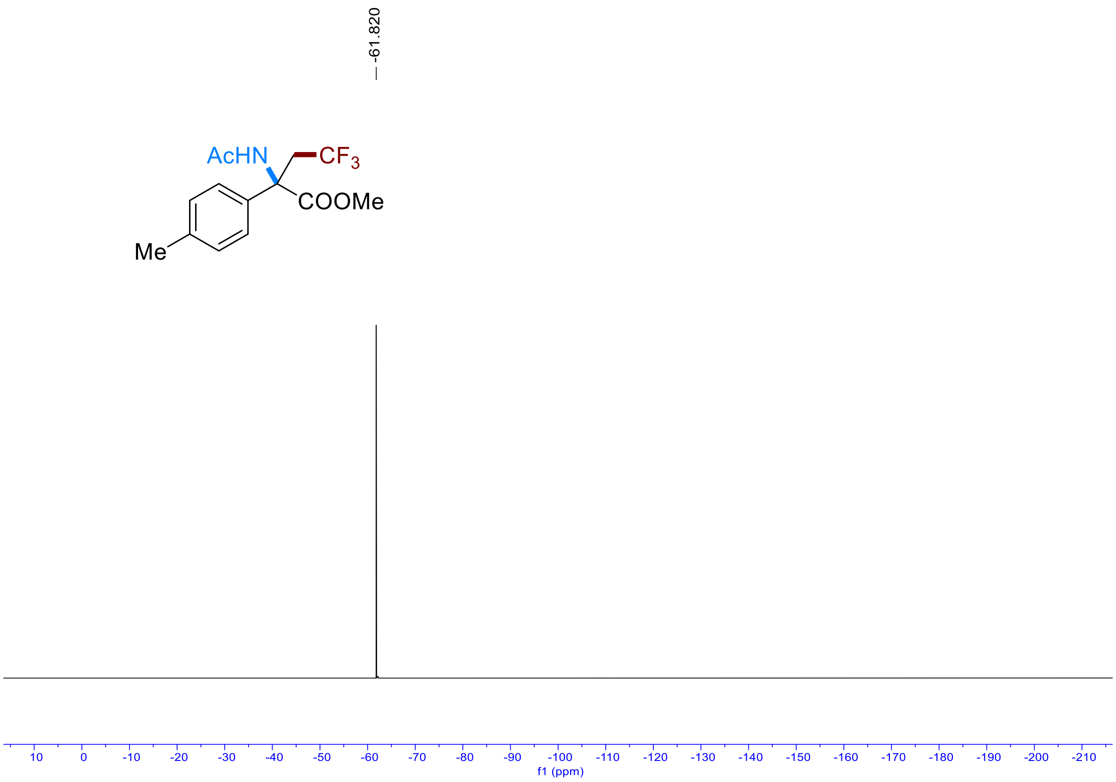
^{19}**F NMR** (565 MHz, CDCl$_3$) – (**3aa**)



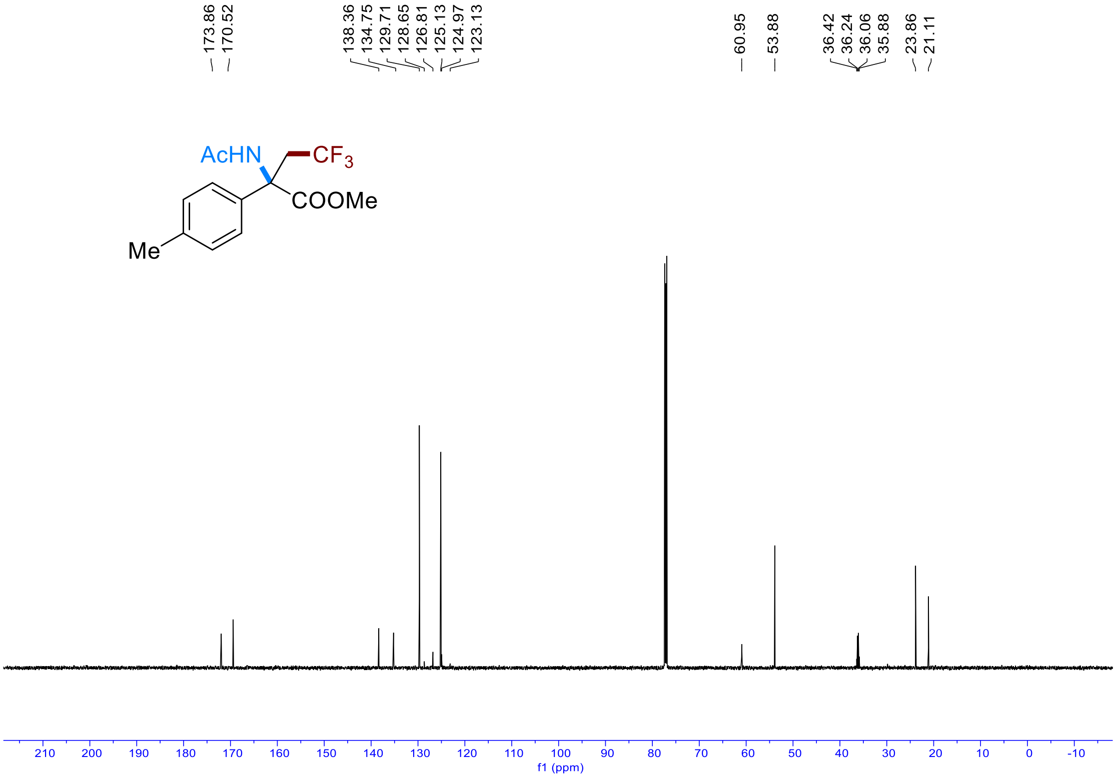
^{13}**C NMR** (151 MHz, $CDCl_3$) – (**3aa**)



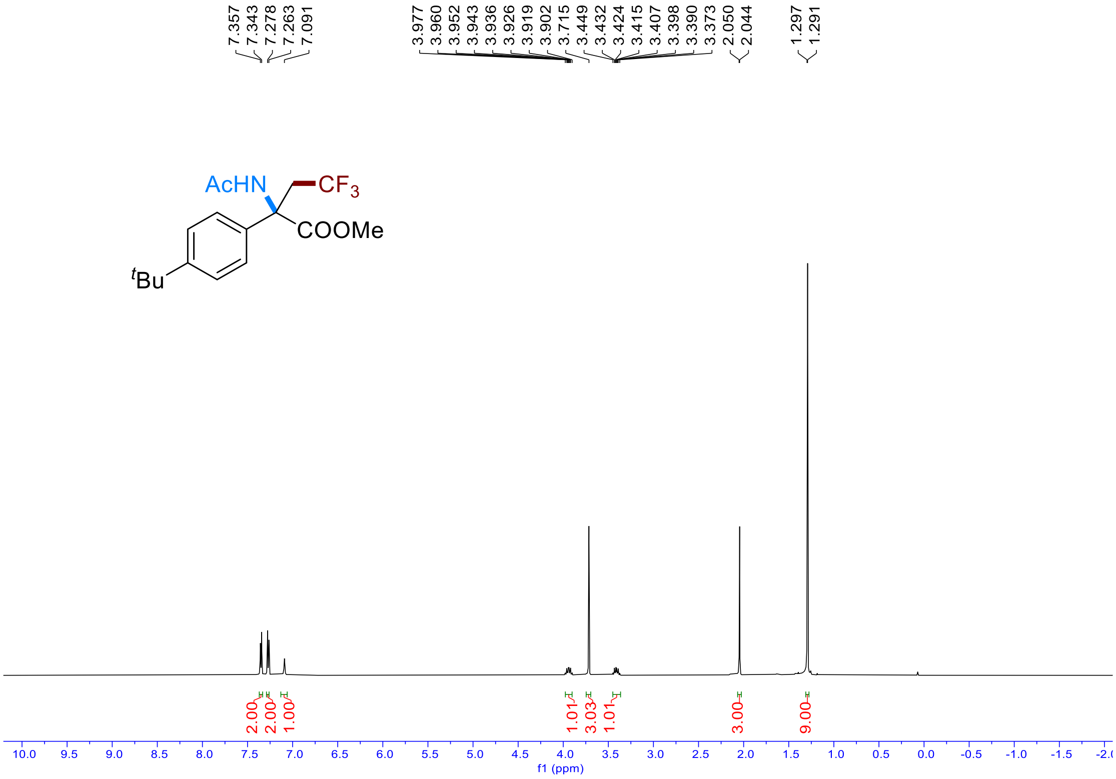
^{1}**H NMR** (600 MHz, $CDCl_3$) – (**3ab**)



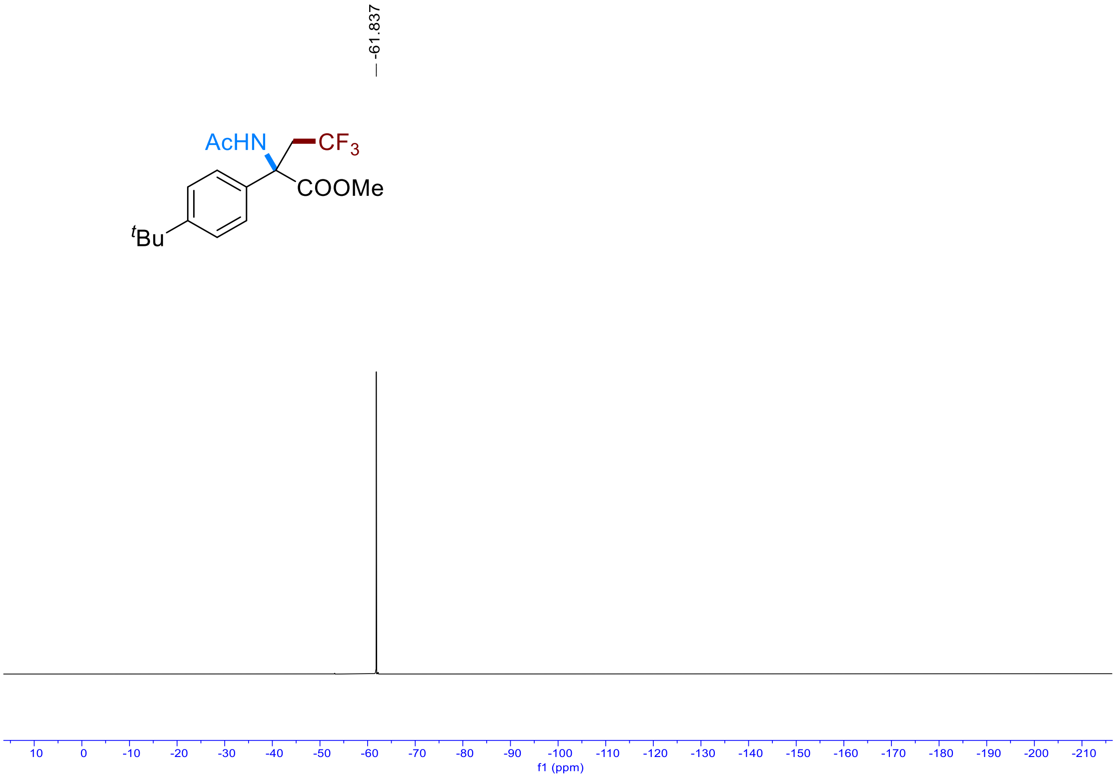
^{19}**F NMR** (565 MHz, CDCl$_3$) – (**3ab**)



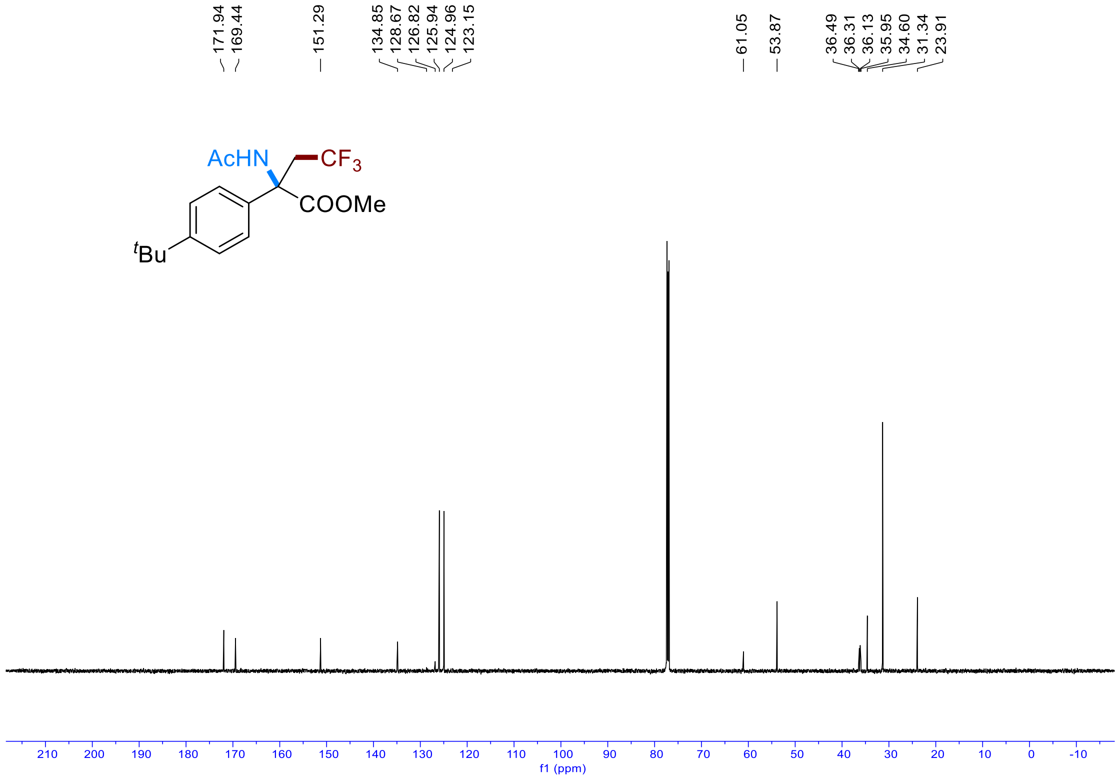
^{13}**C NMR** (151 MHz, CDCl$_3$) – (**3ab**)



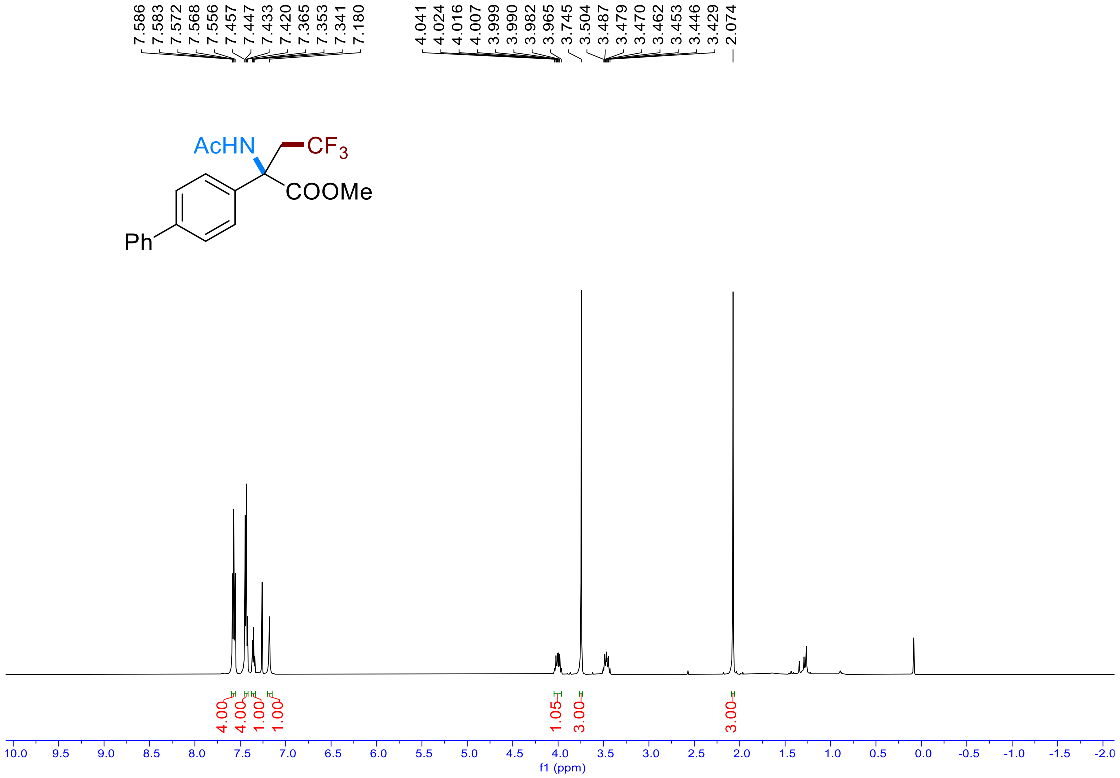
^{1}H NMR (600 MHz, CDCl$_3$) – (**3ac**)



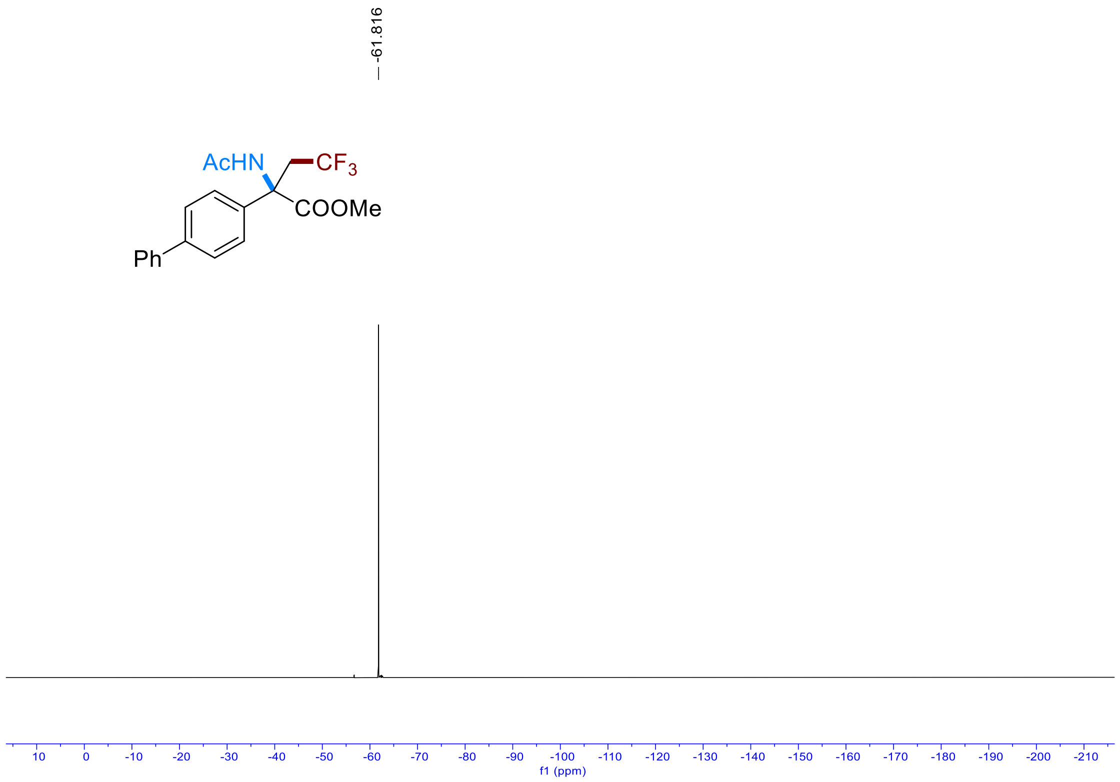
^{19}F NMR (565 MHz, CDCl$_3$) – (**3ac**)



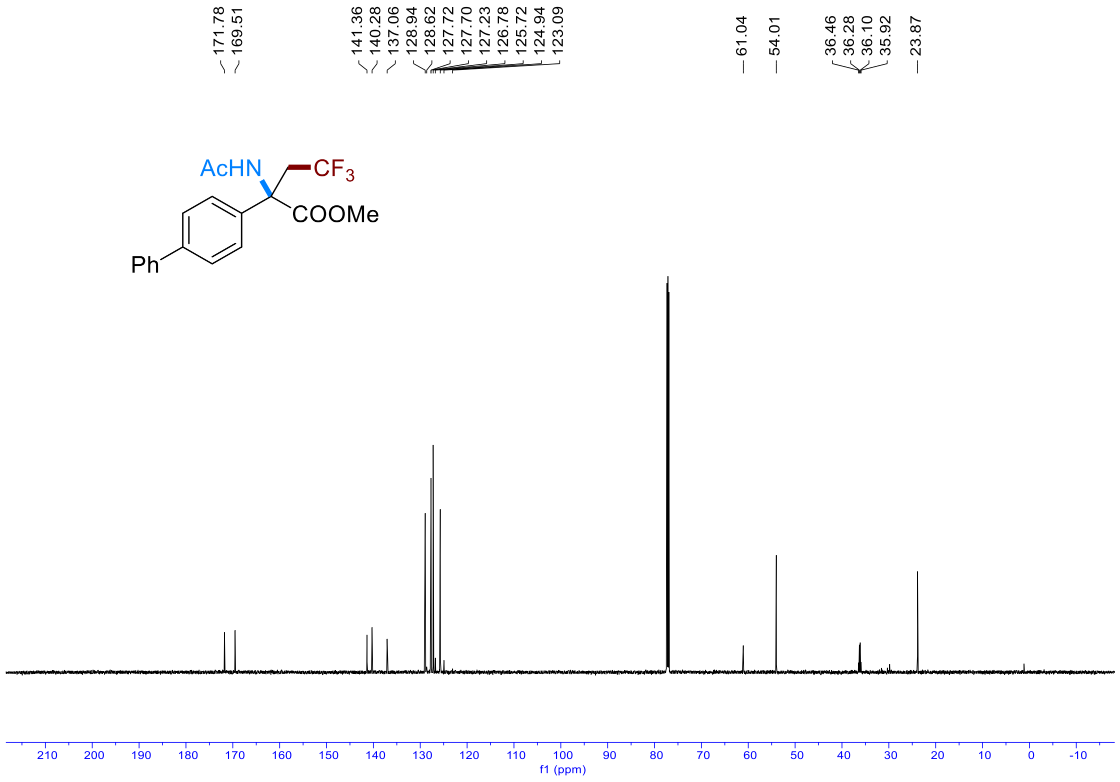
^{13}C NMR (151 MHz, CDCl$_3$) – (**3ac**)



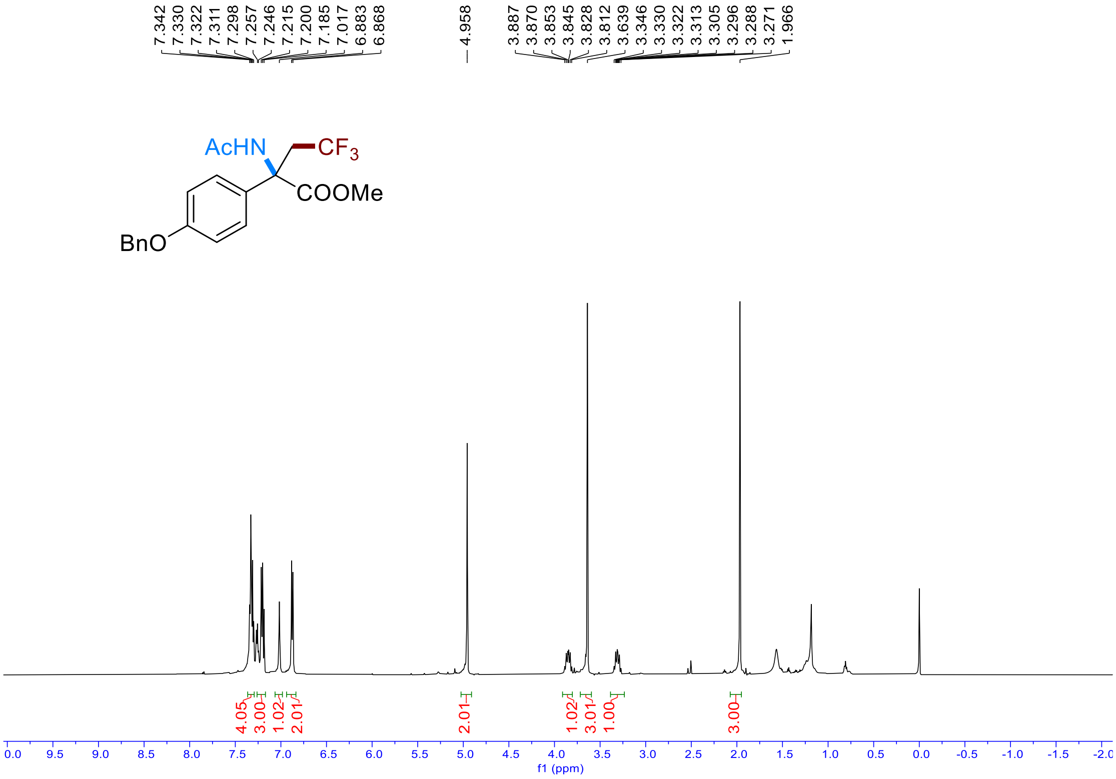
^{1}H NMR (600 MHz, CDCl$_3$) – (**3ad**)



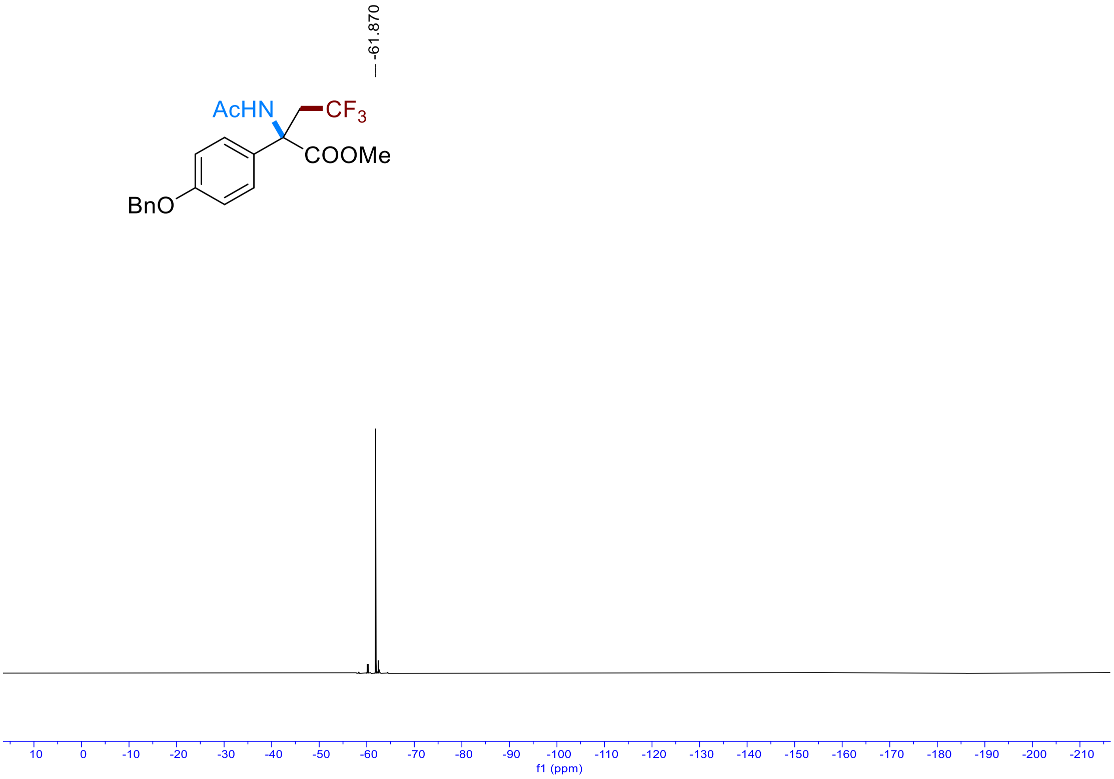
^{19}**F NMR** (565 MHz, CDCl$_3$) – (**3ad**)



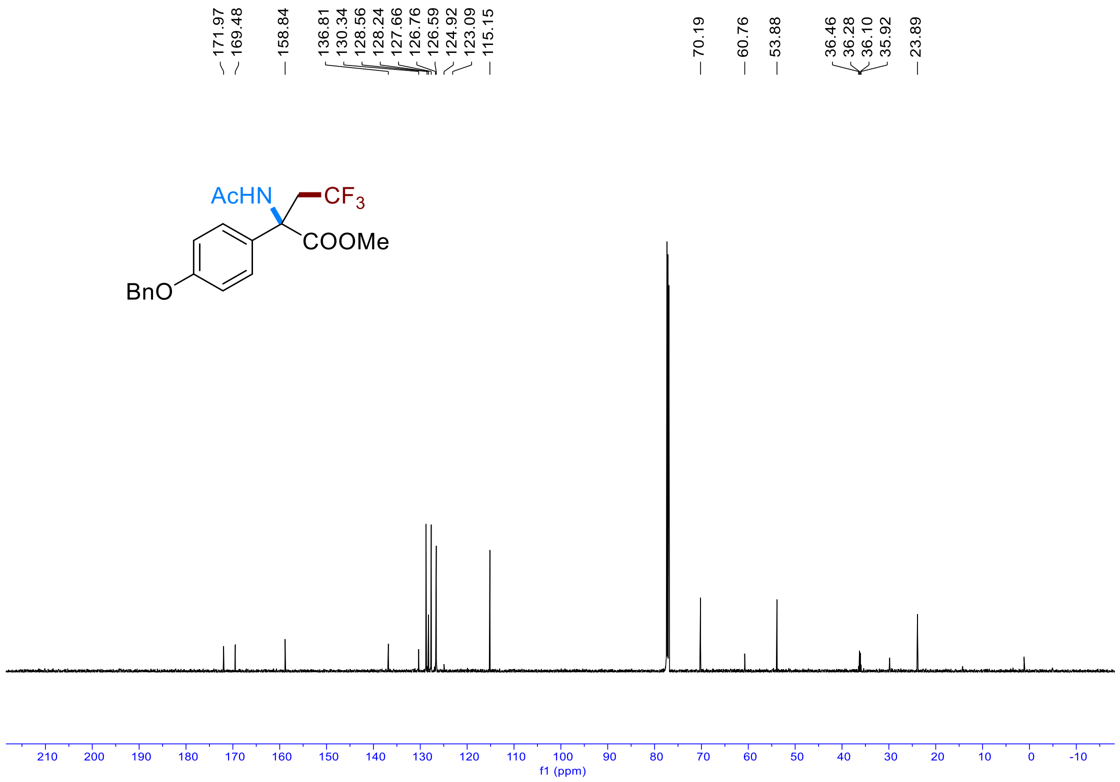
^{13}**C NMR** (151 MHz, CDCl$_3$) – (**3ad**)



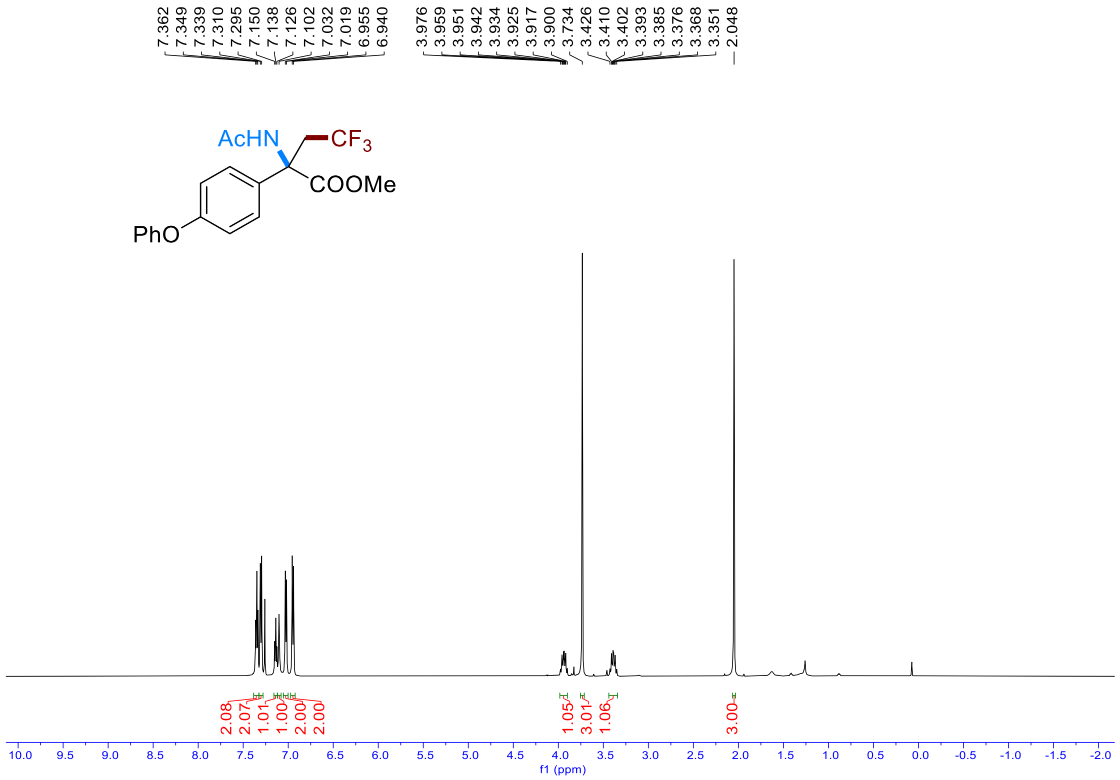
^{1}**H NMR** (600 MHz, CDCl$_3$) – (**3ae**)



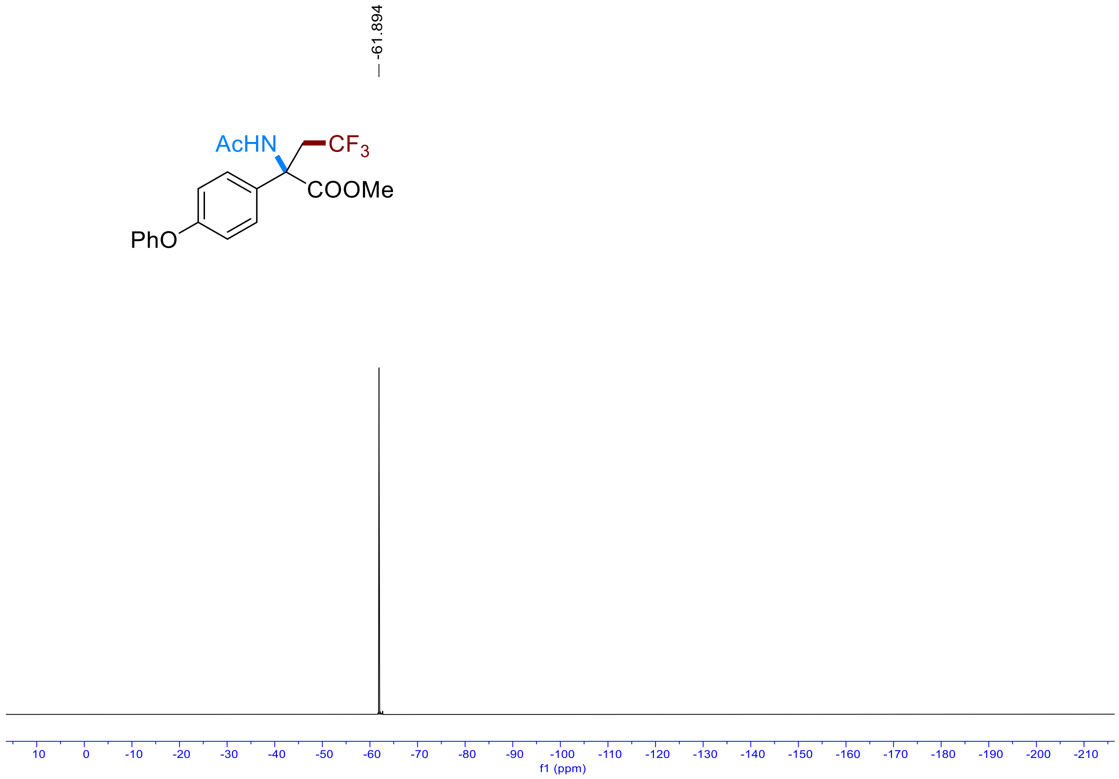
^{19}**F NMR** (565 MHz, CDCl$_3$) – (**3ae**)



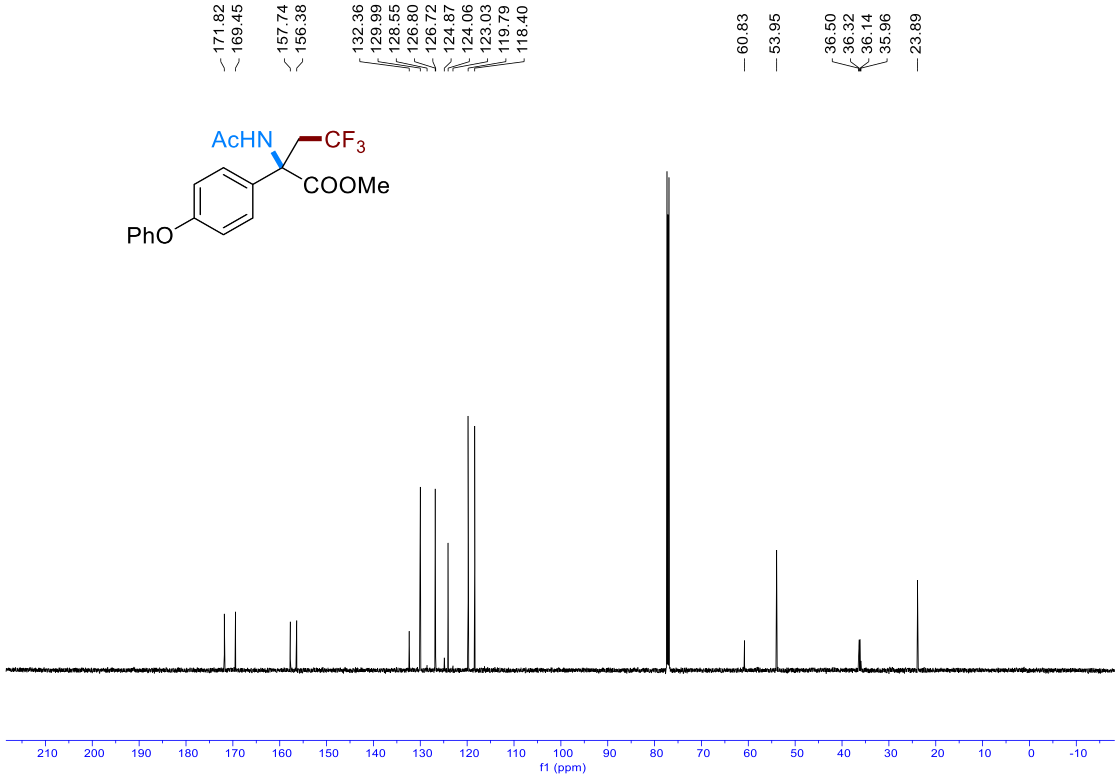
^{13}C NMR (151 MHz, CDCl$_3$) – (**3ae**)



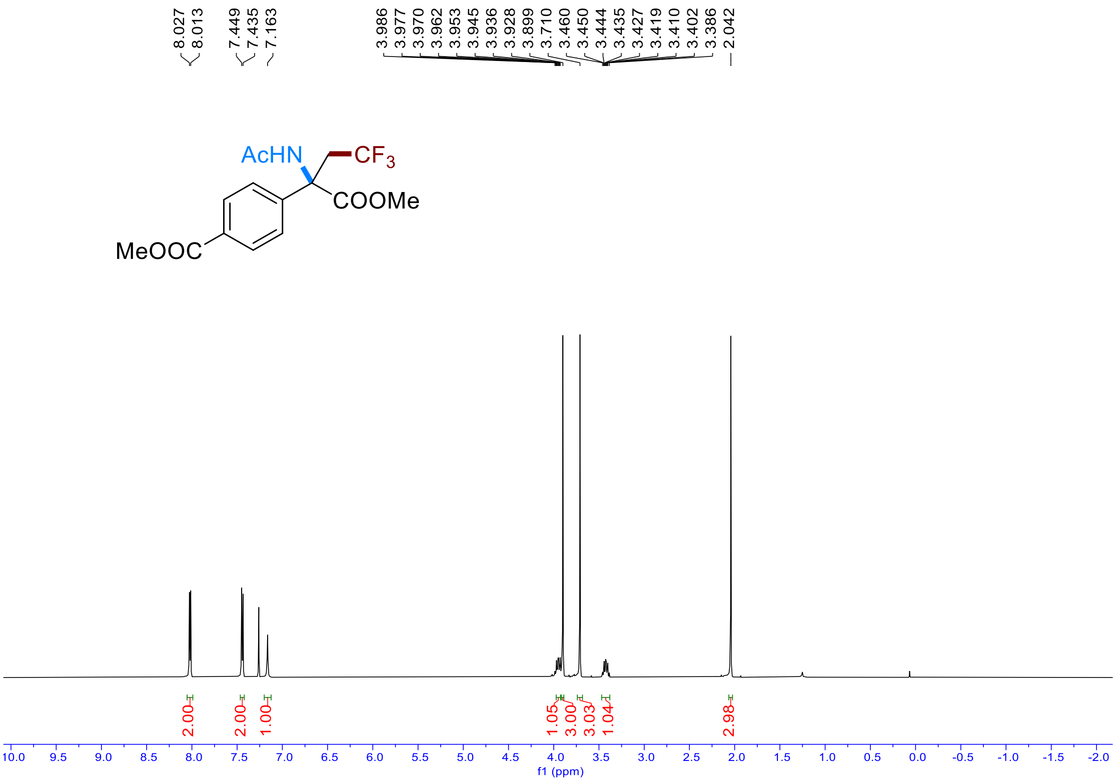
^{1}H NMR (600 MHz, CDCl$_3$) – (**3af**)



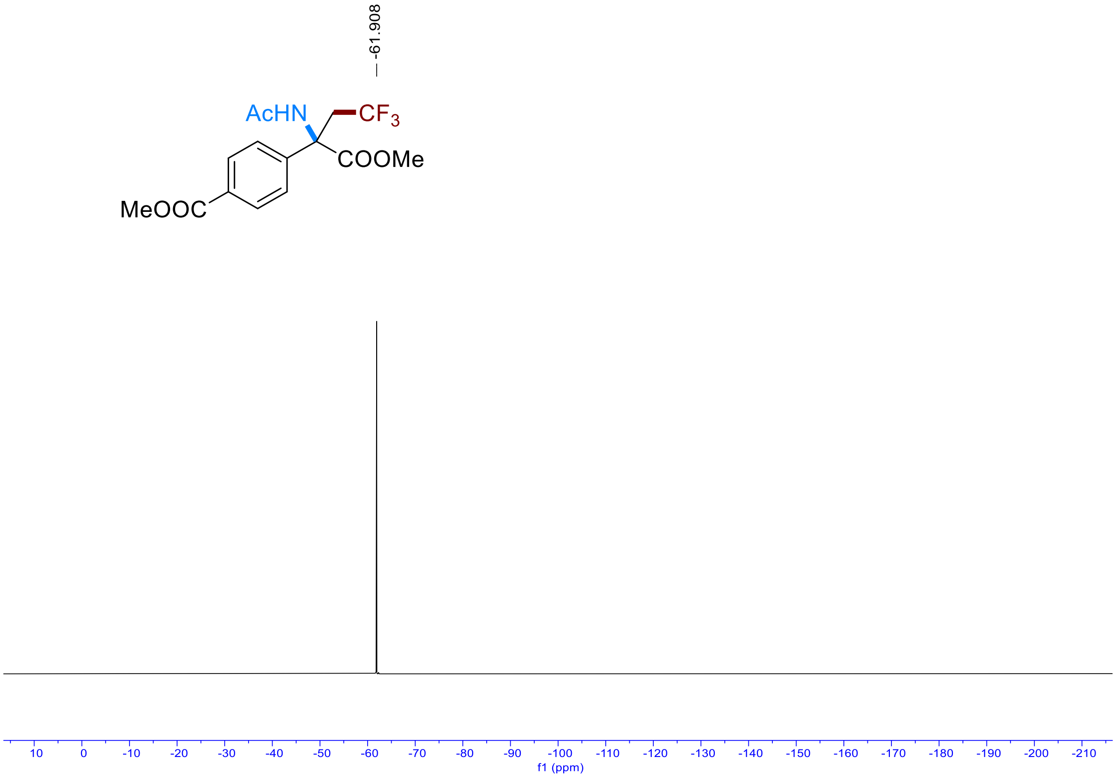
^{19}F NMR (565 MHz, CDCl$_3$) – (**3af**)



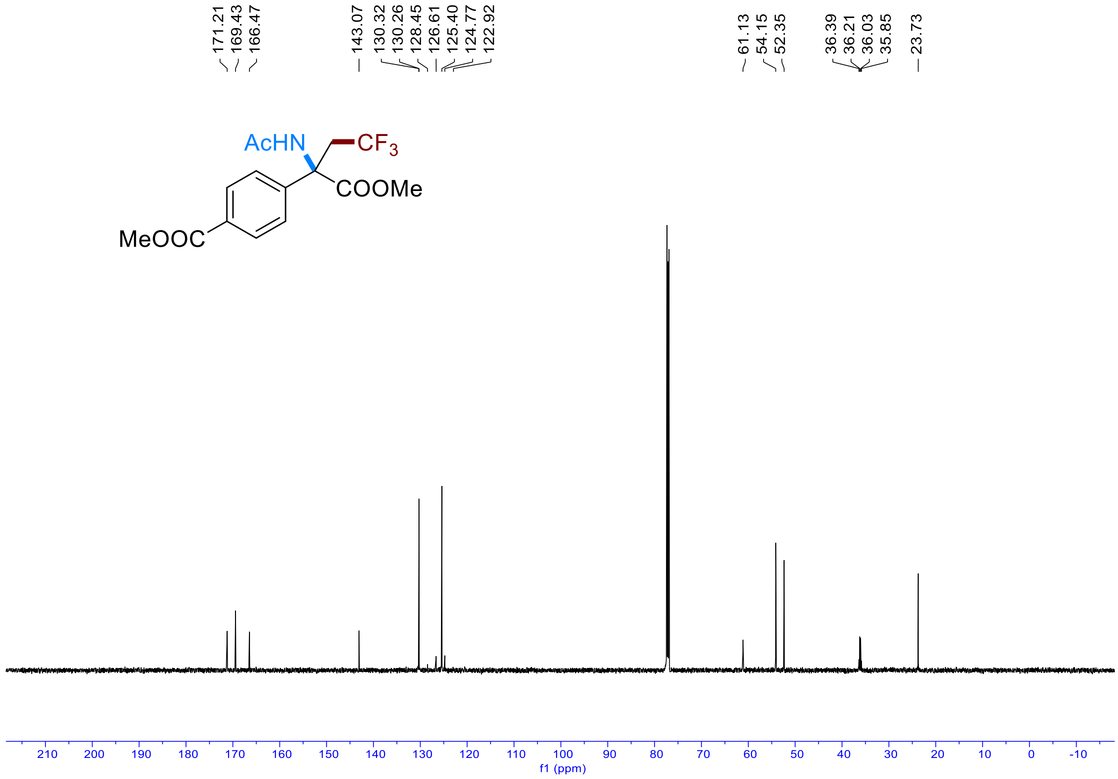
^{13}C NMR (151 MHz, CDCl$_3$) – (**3af**)



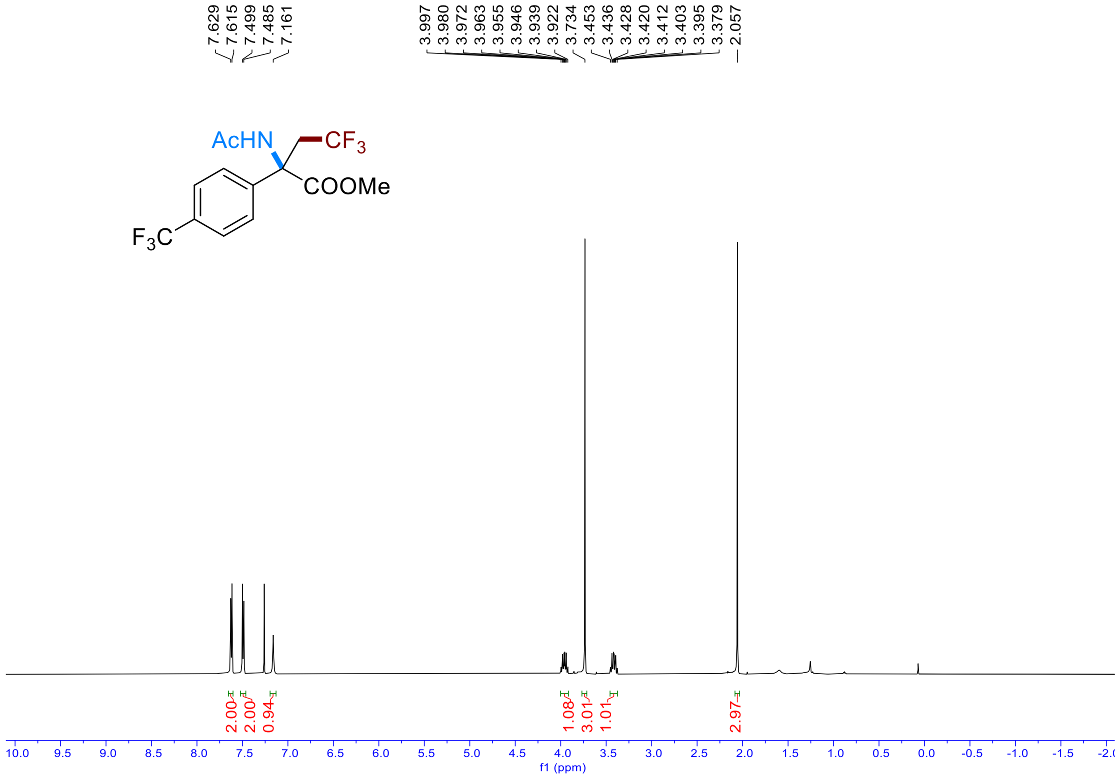
^{1}H NMR (600 MHz, CDCl$_3$) – (**3ag**)



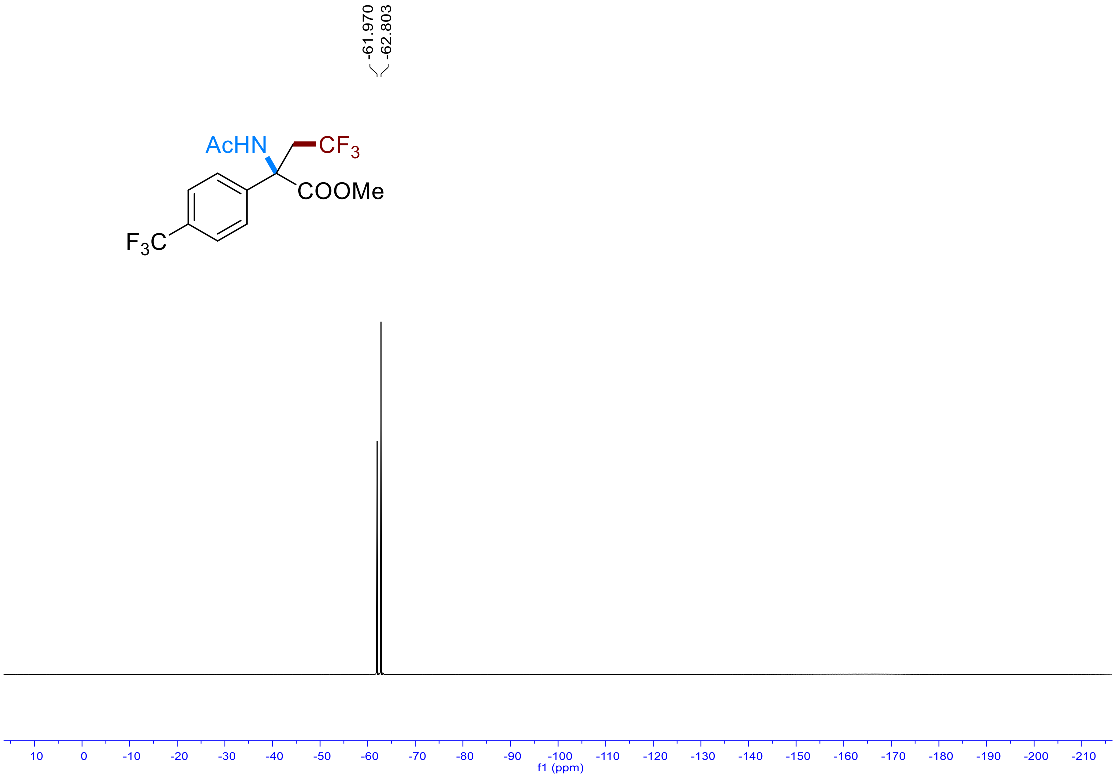
^{19}F NMR (565 MHz, CDCl$_3$) – (**3ag**)



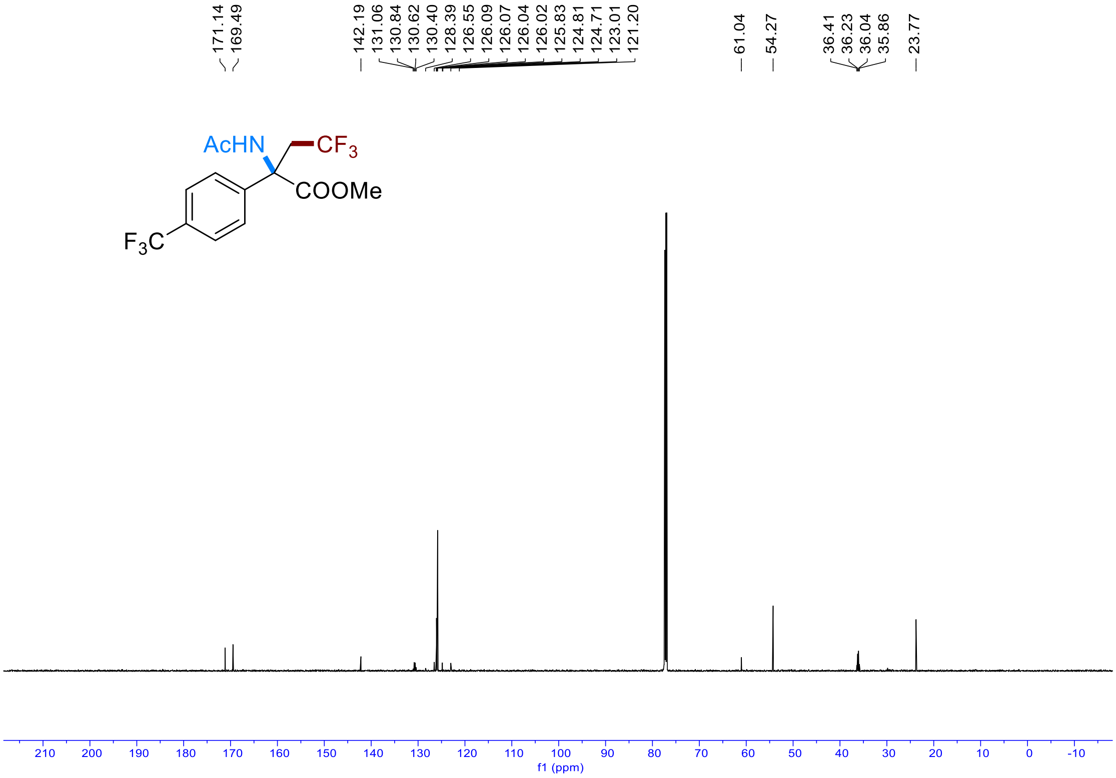
^{13}C NMR (151 MHz, $CDCl_3$) – (**3ag**)



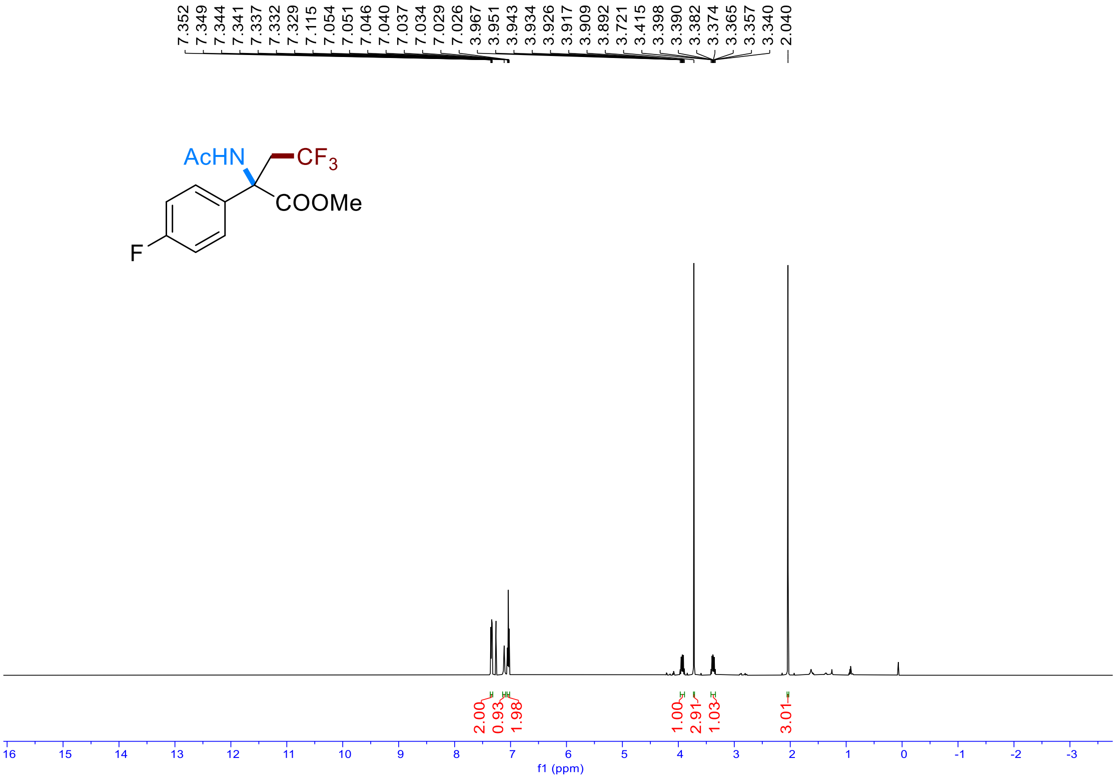
^{1}H NMR (600 MHz, $CDCl_3$) – (**3ah**)



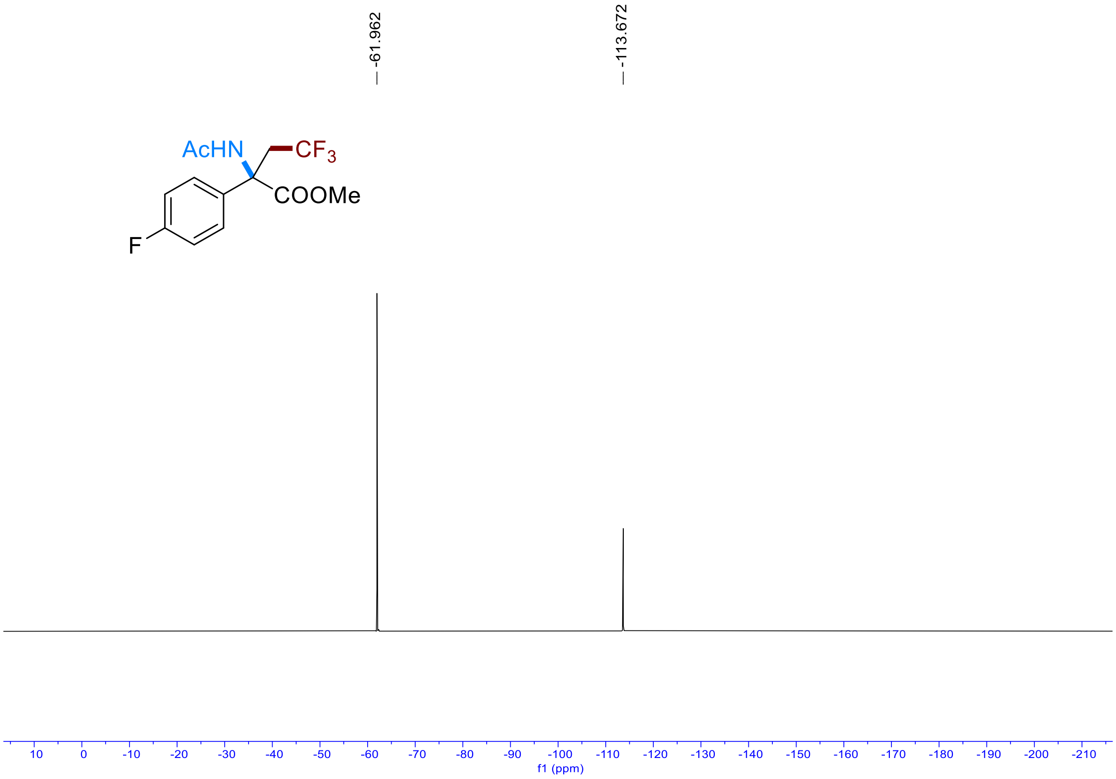
^{19}F NMR (565 MHz, CDCl$_3$) – (**3ah**)



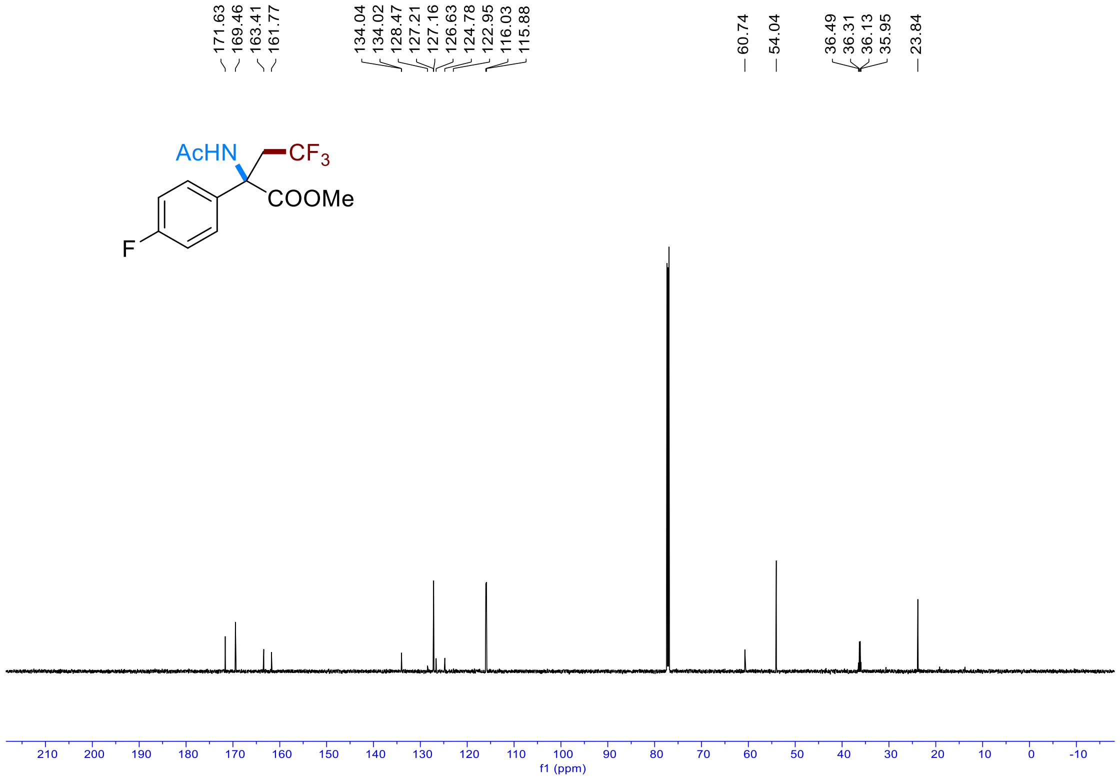
^{13}C NMR (151 MHz, CDCl$_3$) – (**3ah**)



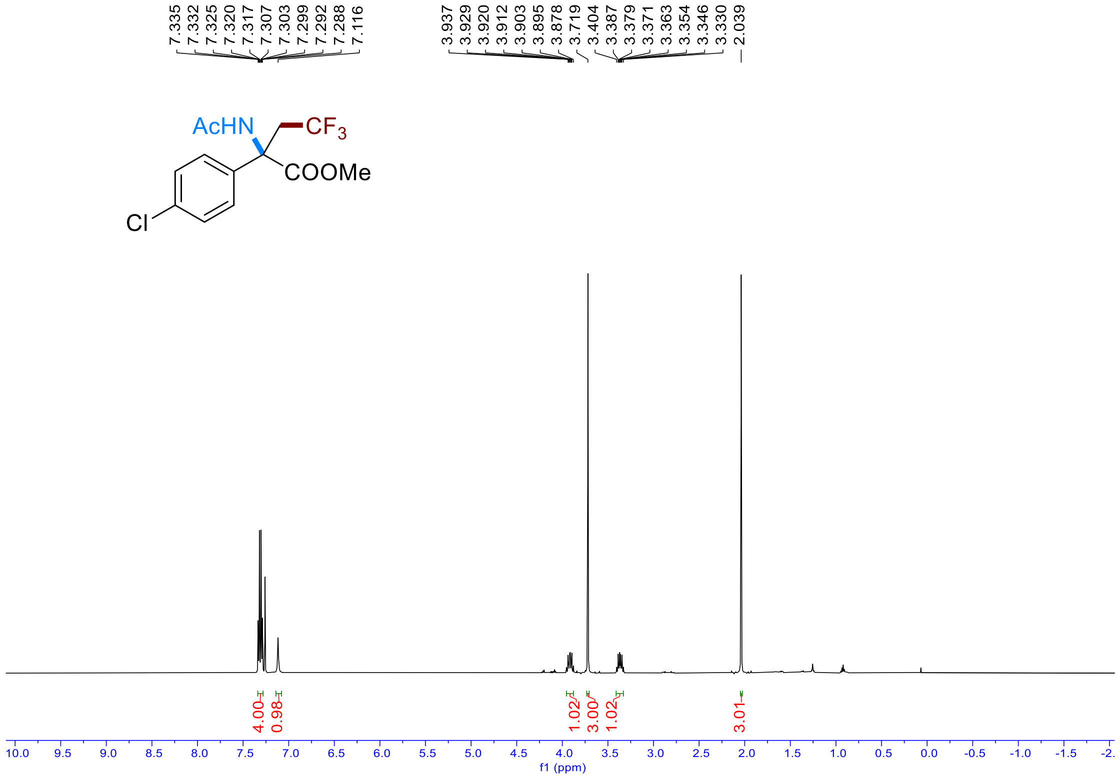
^{1}H NMR (600 MHz, CDCl$_3$) – (**3ai**)



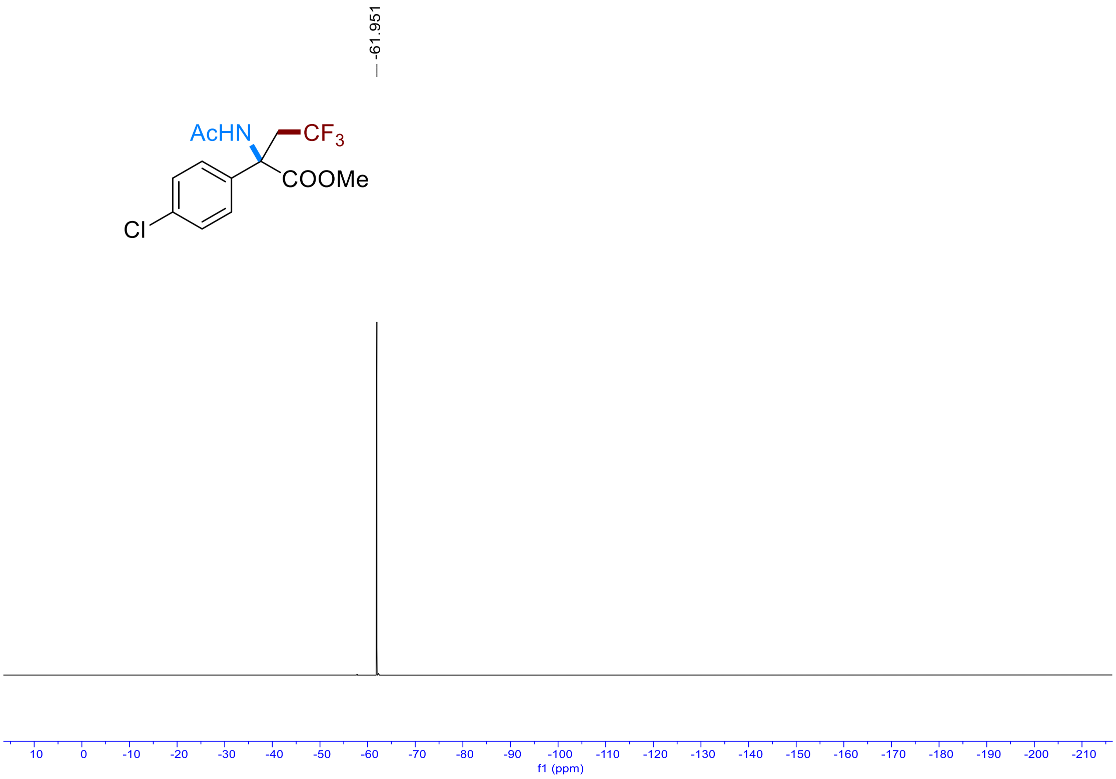
^{19}F NMR (565 MHz, CDCl$_3$) – (**3ai**)



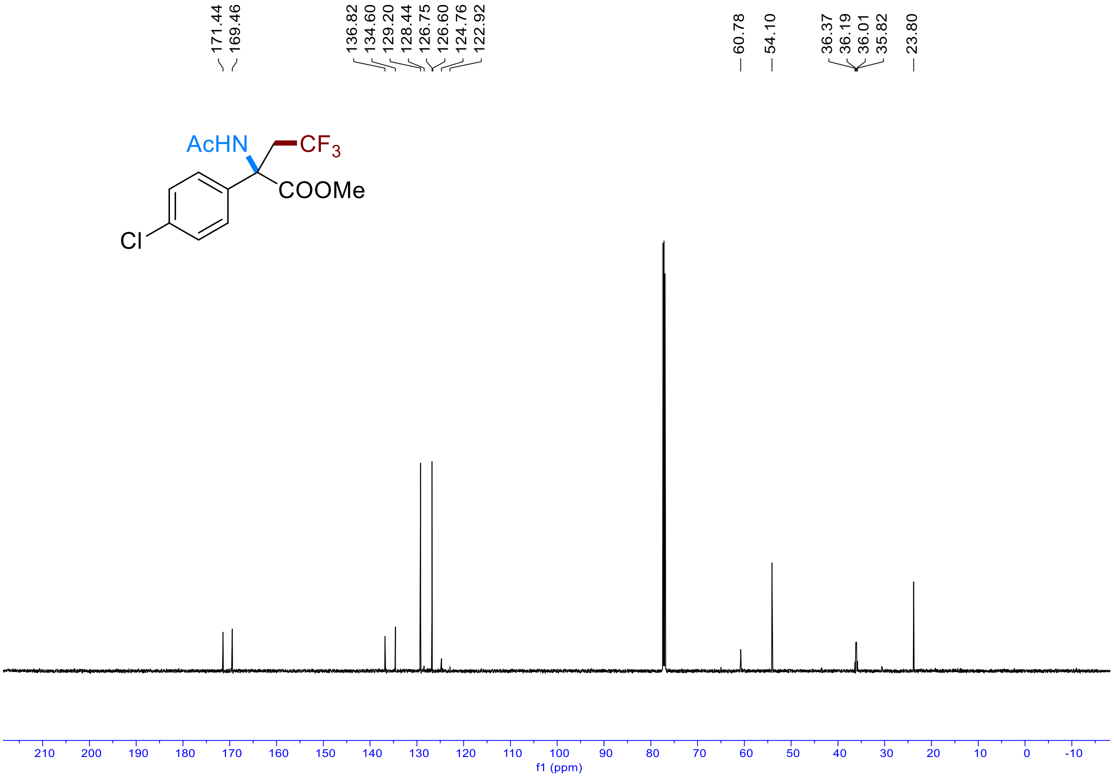
^{13}C NMR (151 MHz, CDCl$_3$) – (**3ai**)



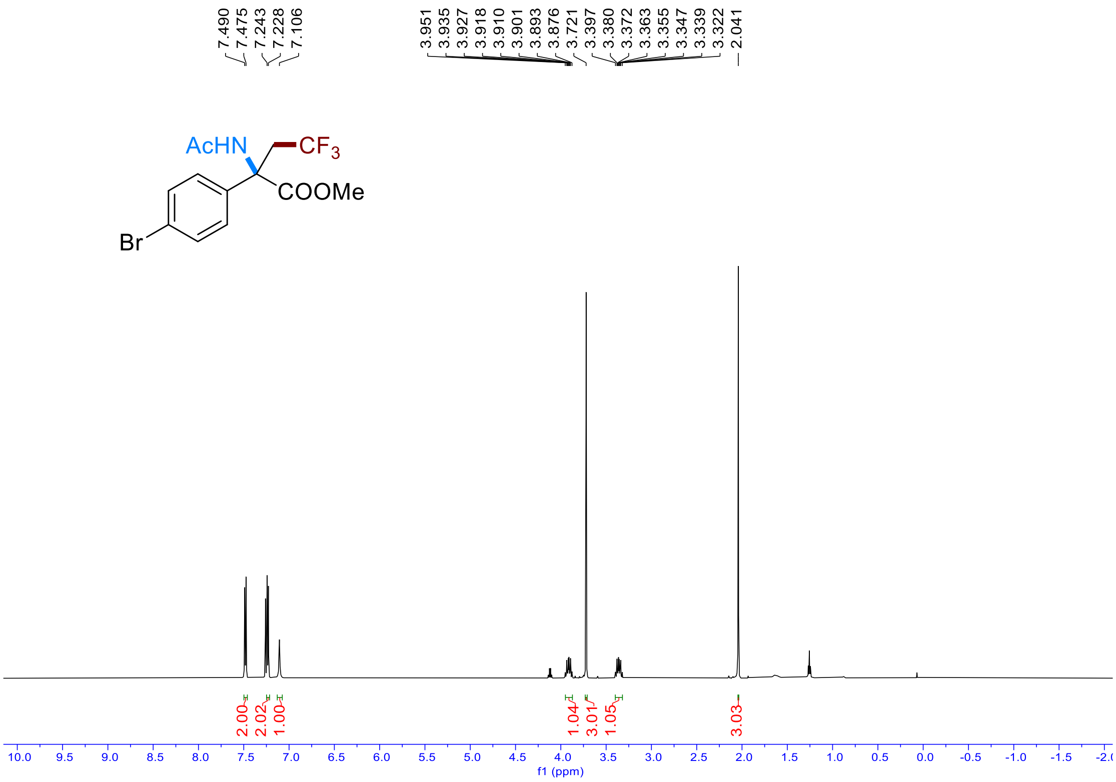
^{1}H NMR (600 MHz, CDCl$_3$) – (**3aj**)



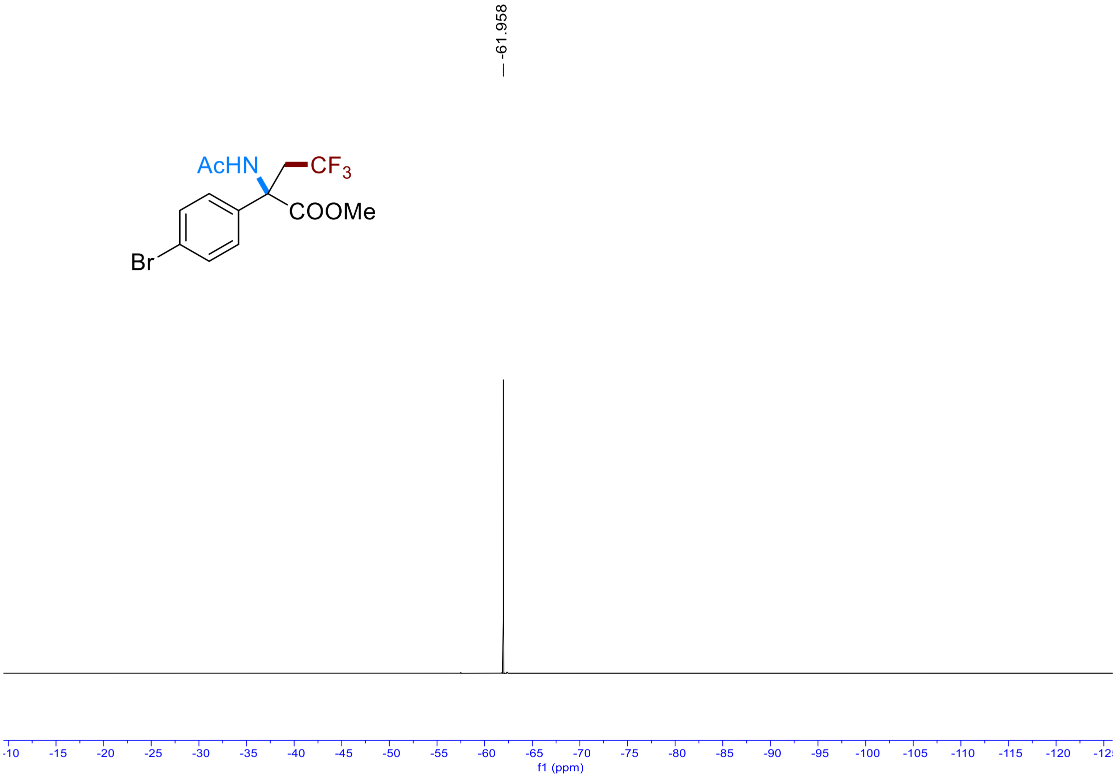
^{19}F NMR (565 MHz, CDCl$_3$) – (**3aj**)



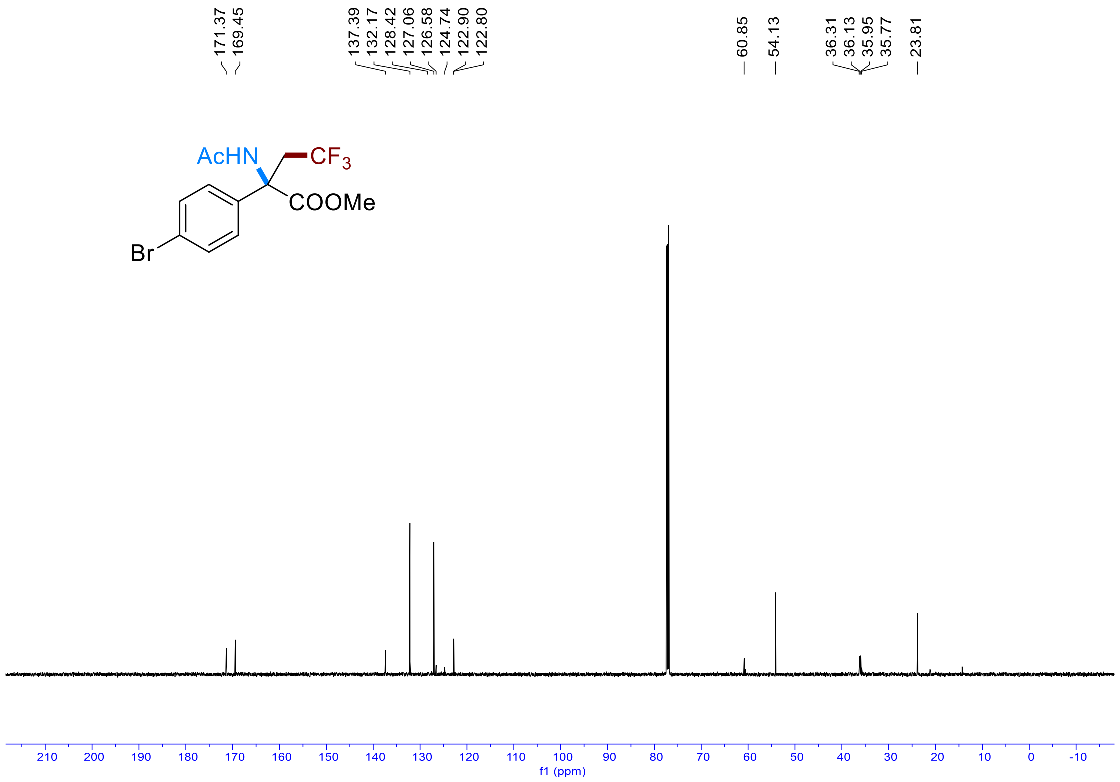
^{13}C NMR (151 MHz, CDCl$_3$) – (**3aj**)



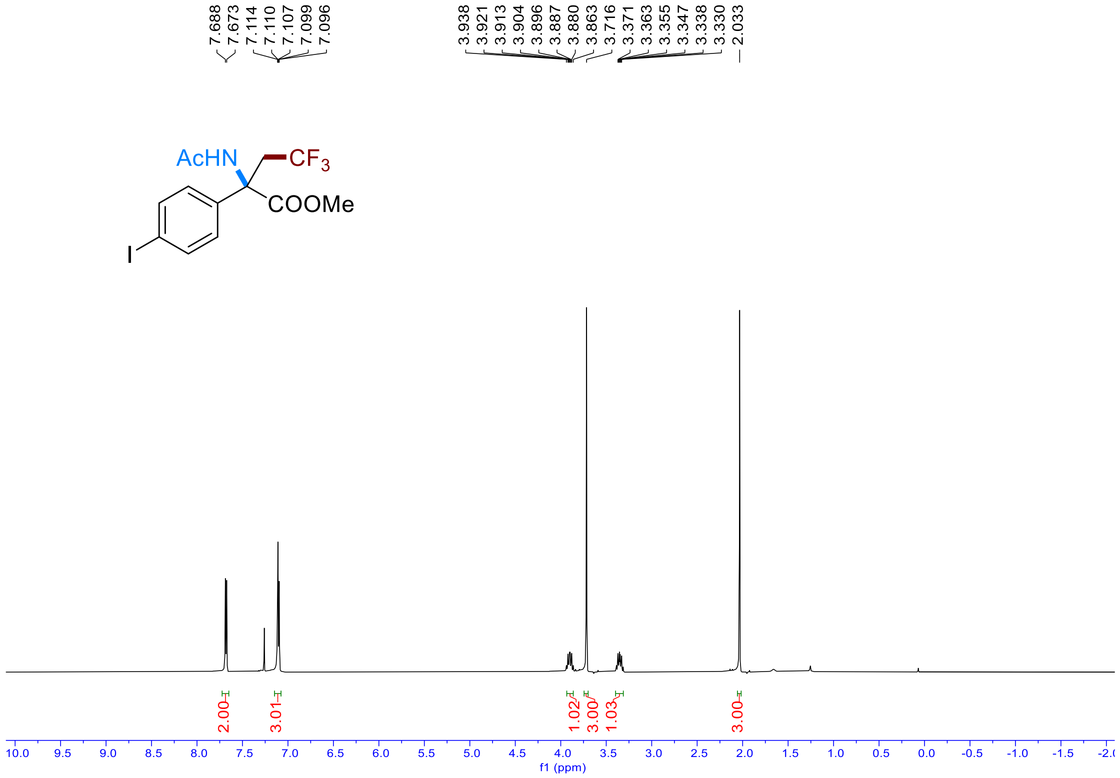
^{1}**H NMR** (600 MHz, $CDCl_3$) – (**3ak**)



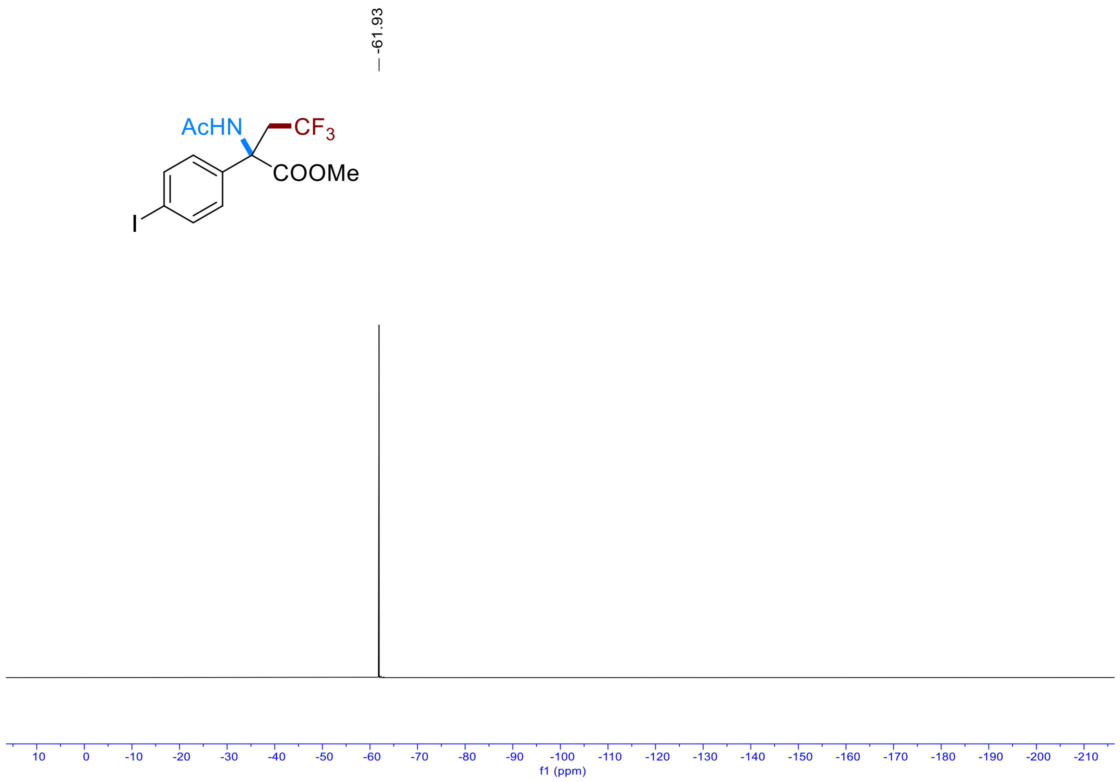
^{19}**F NMR** (565 MHz, $CDCl_3$) – (**3ak**)



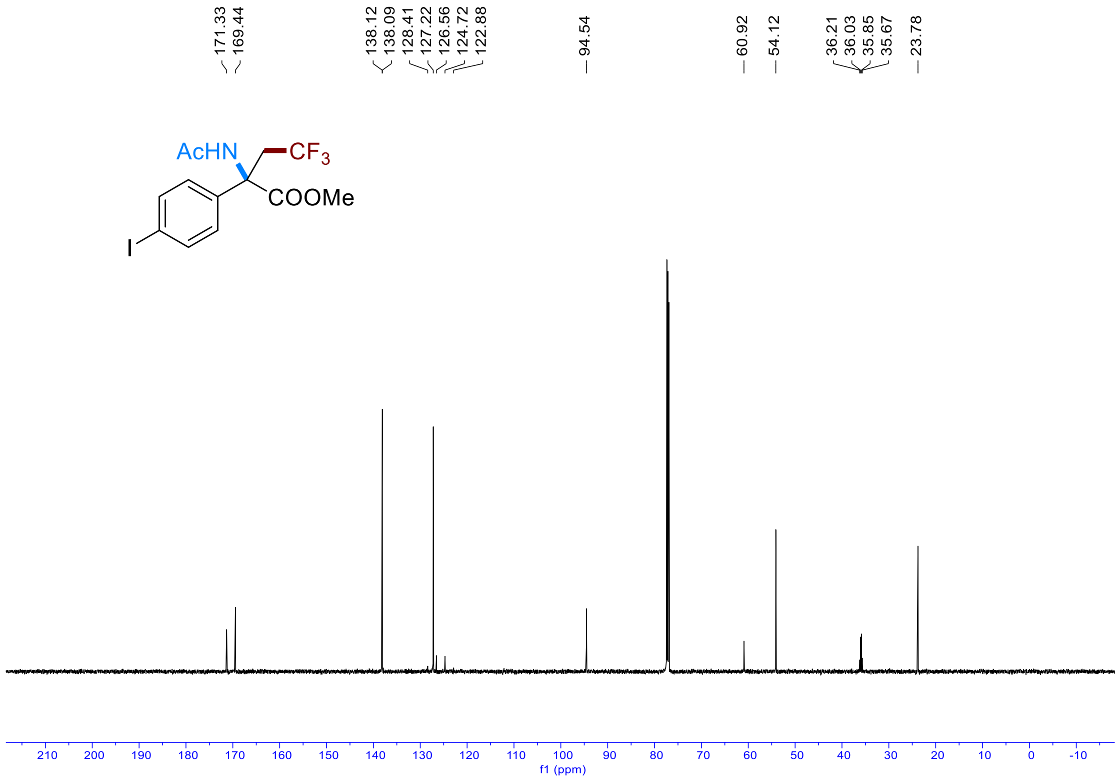
^{13}C NMR (151 MHz, CDCl$_3$) – (**3ak**)



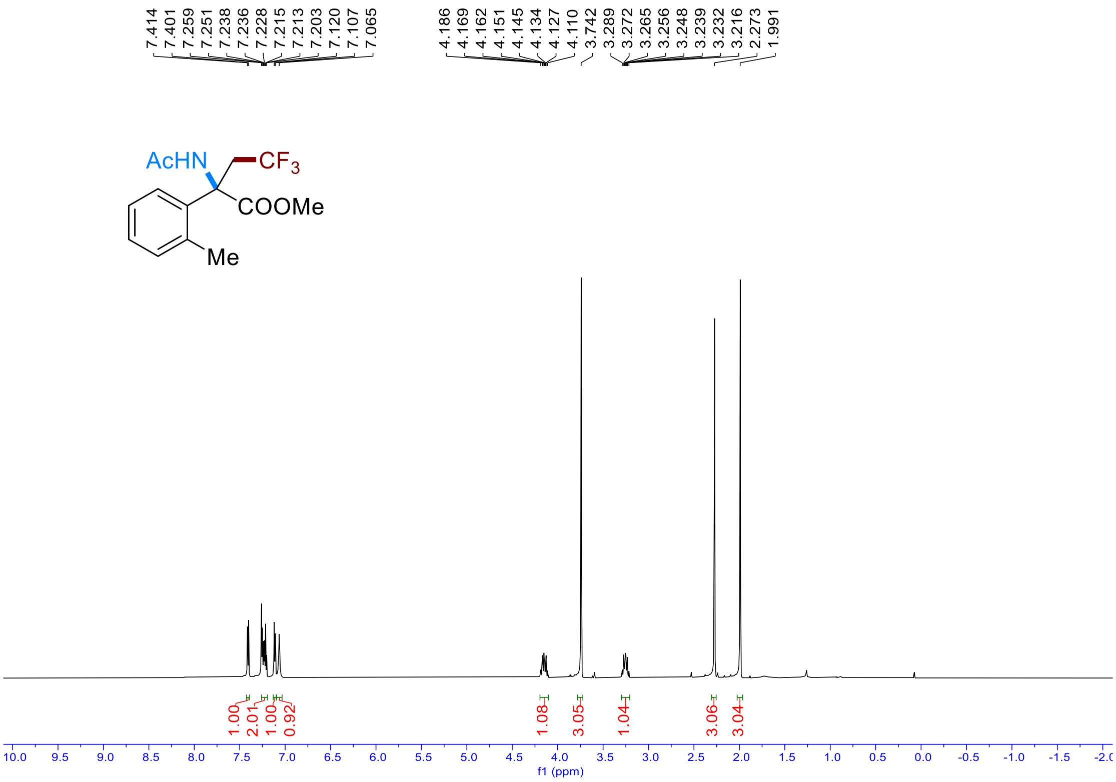
^{1}H NMR (600 MHz, CDCl$_3$) – (**3al**)



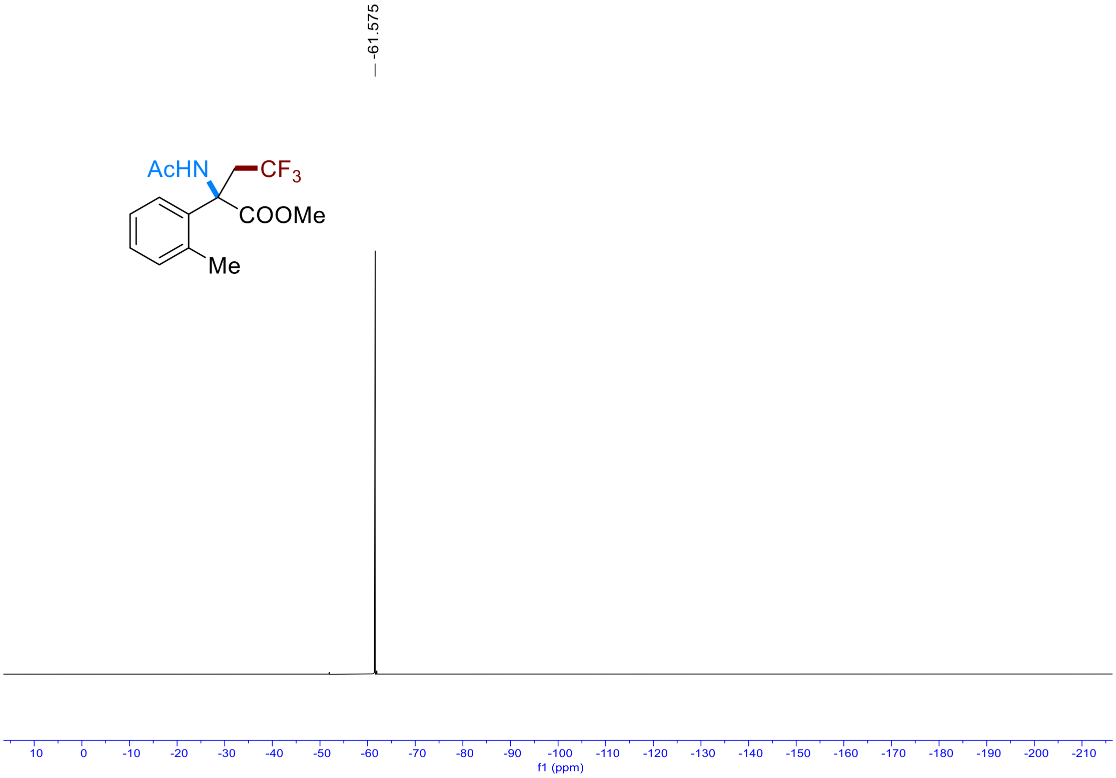
^{19}**F NMR** (565 MHz, CDCl$_3$) – (**3al**)



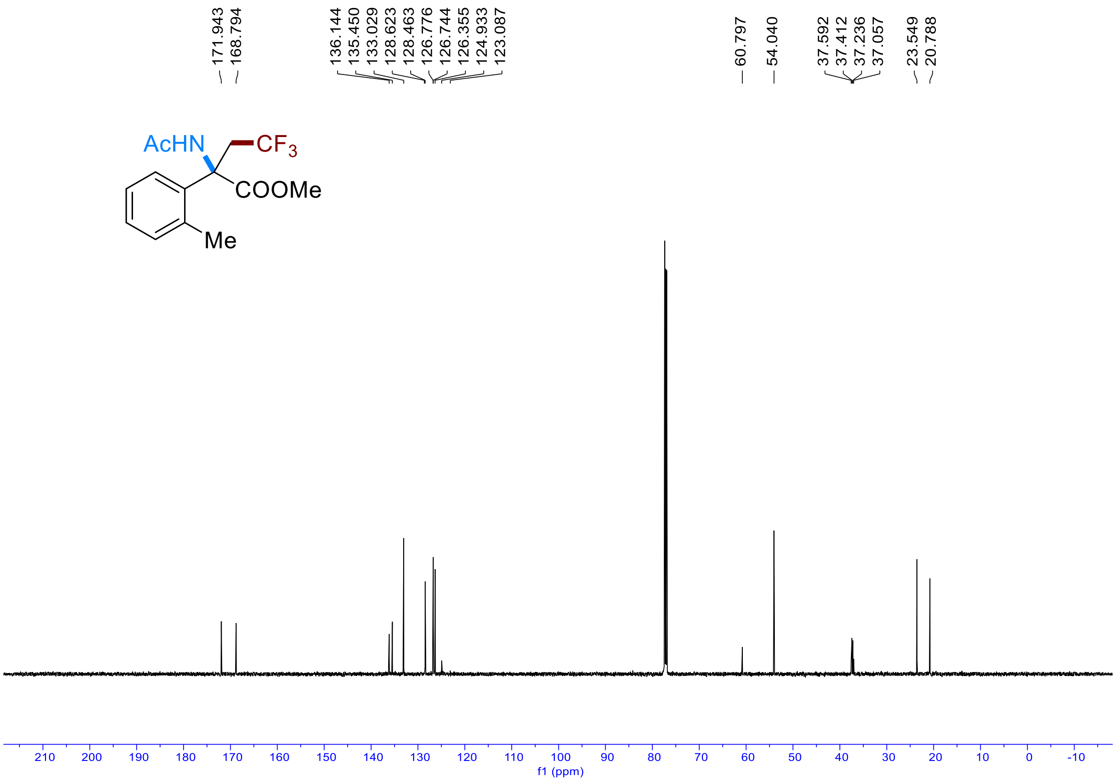
^{13}**C NMR** (151 MHz, CDCl$_3$) – (**3al**)



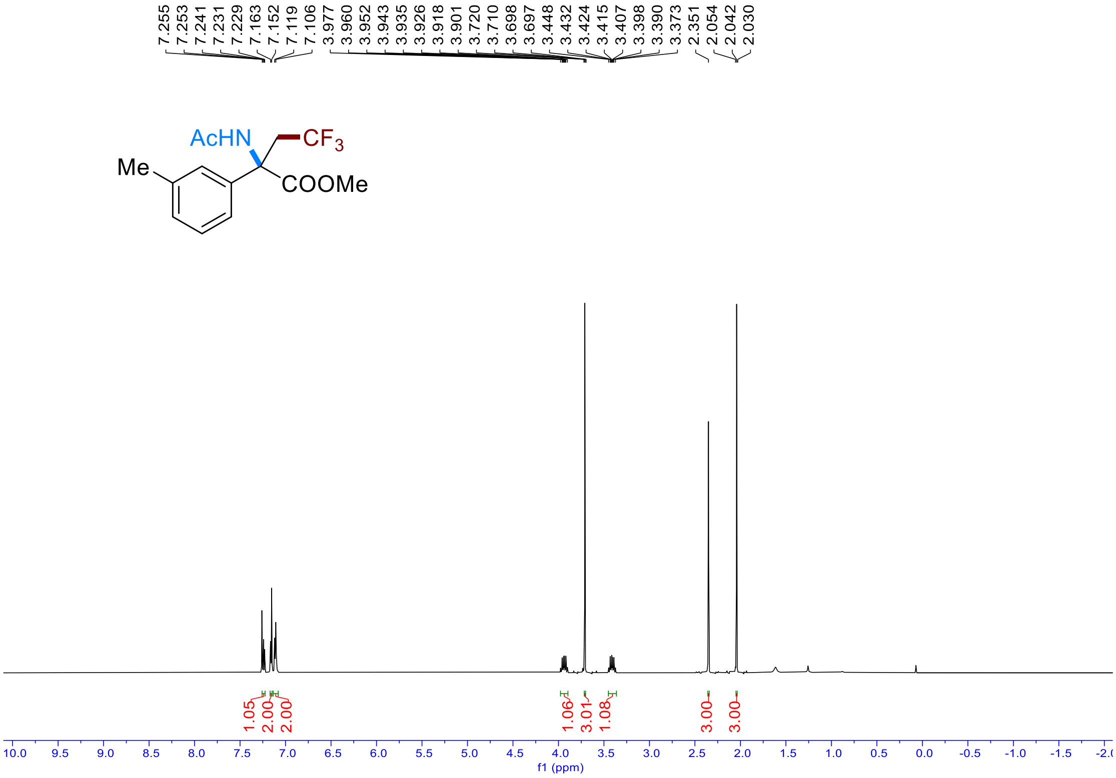
^{1}H NMR (600 MHz, CDCl$_3$) – (**3am**)



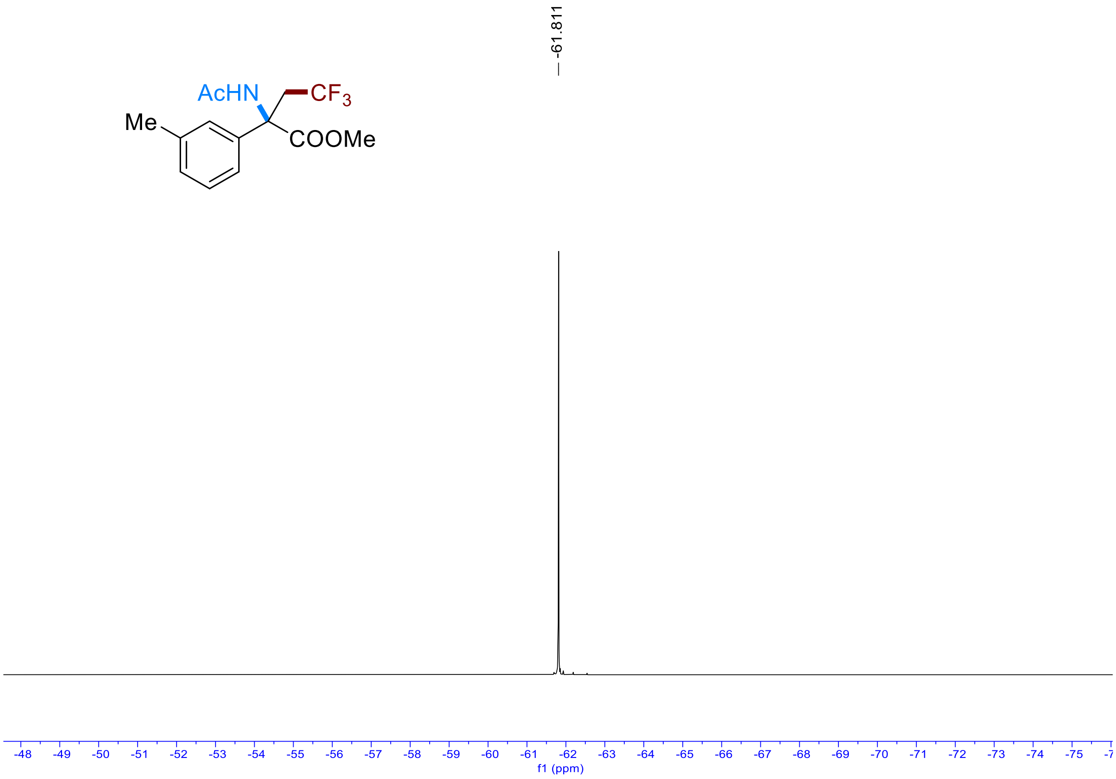
^{19}F NMR (565 MHz, CDCl$_3$) – (**3am**)



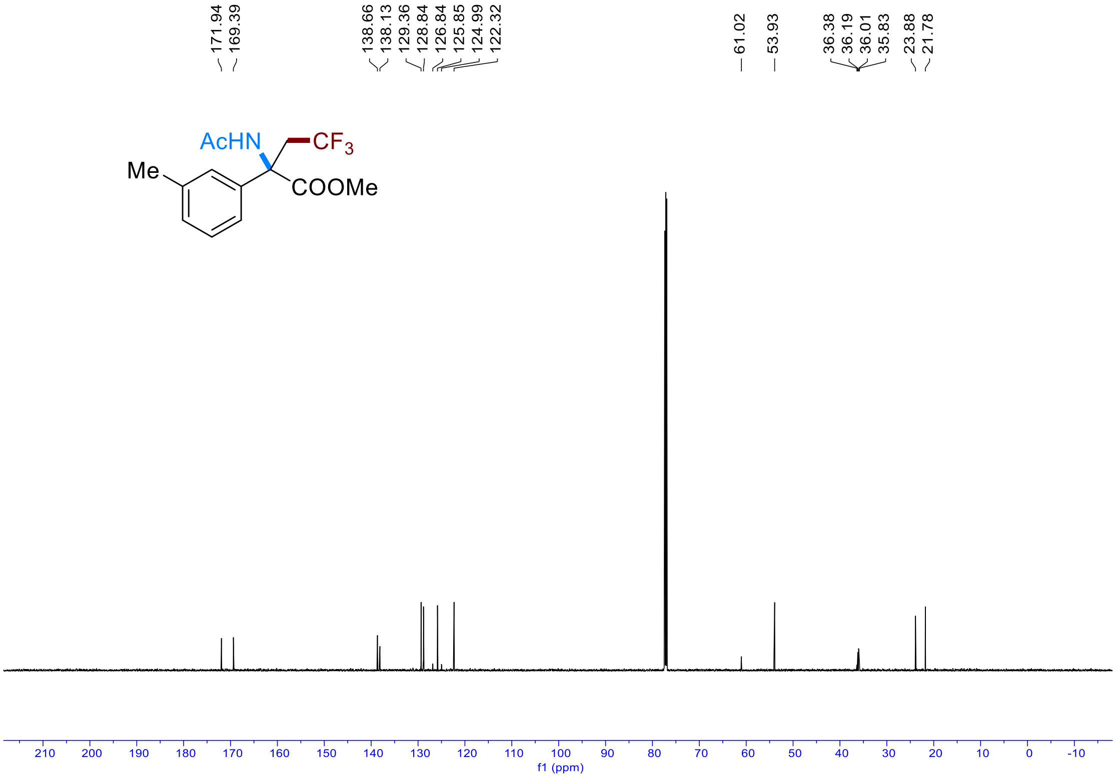
^{13}**C NMR** (151 MHz, CDCl$_3$) – (**3am**)



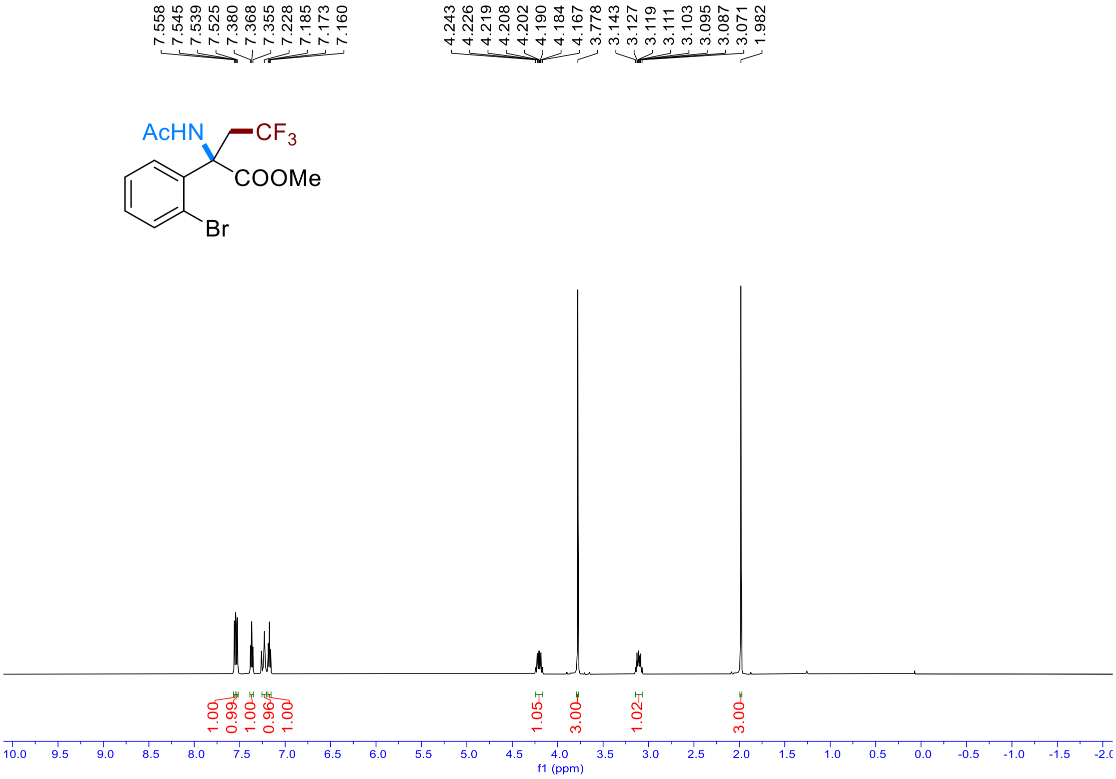
^{1}**H NMR** (600 MHz, CDCl$_3$) – (**3an**)



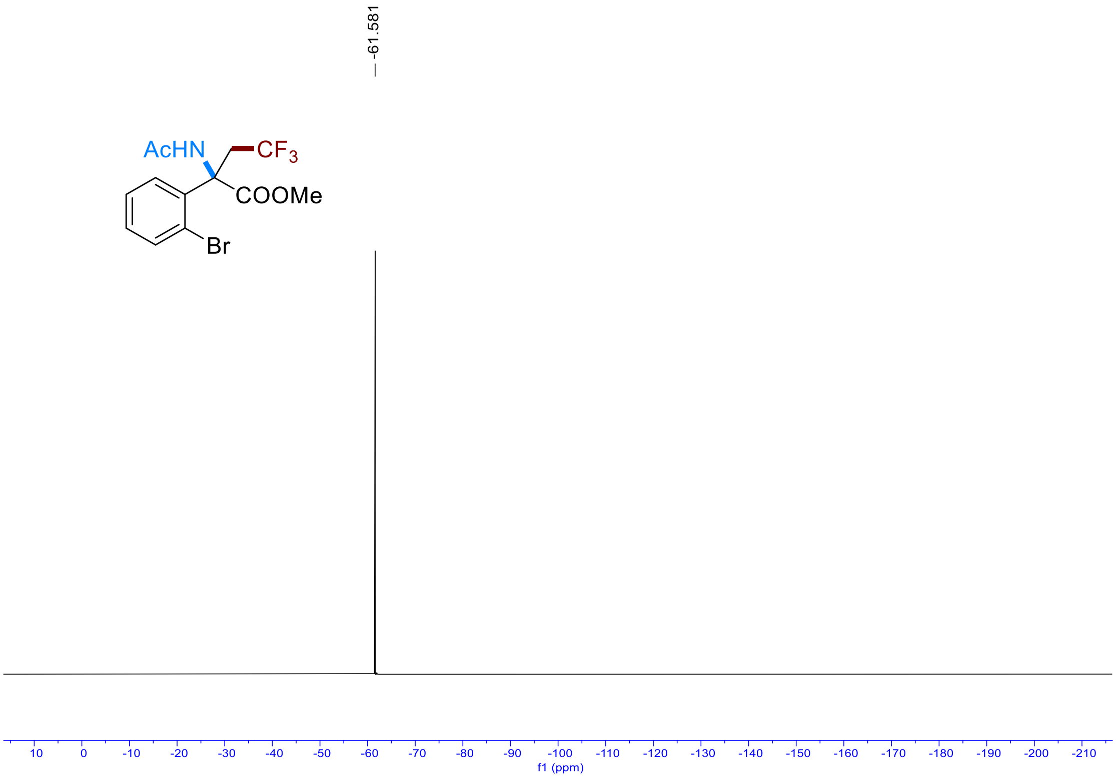
^{19}F NMR (565 MHz, $CDCl_3$) – (**3an**)



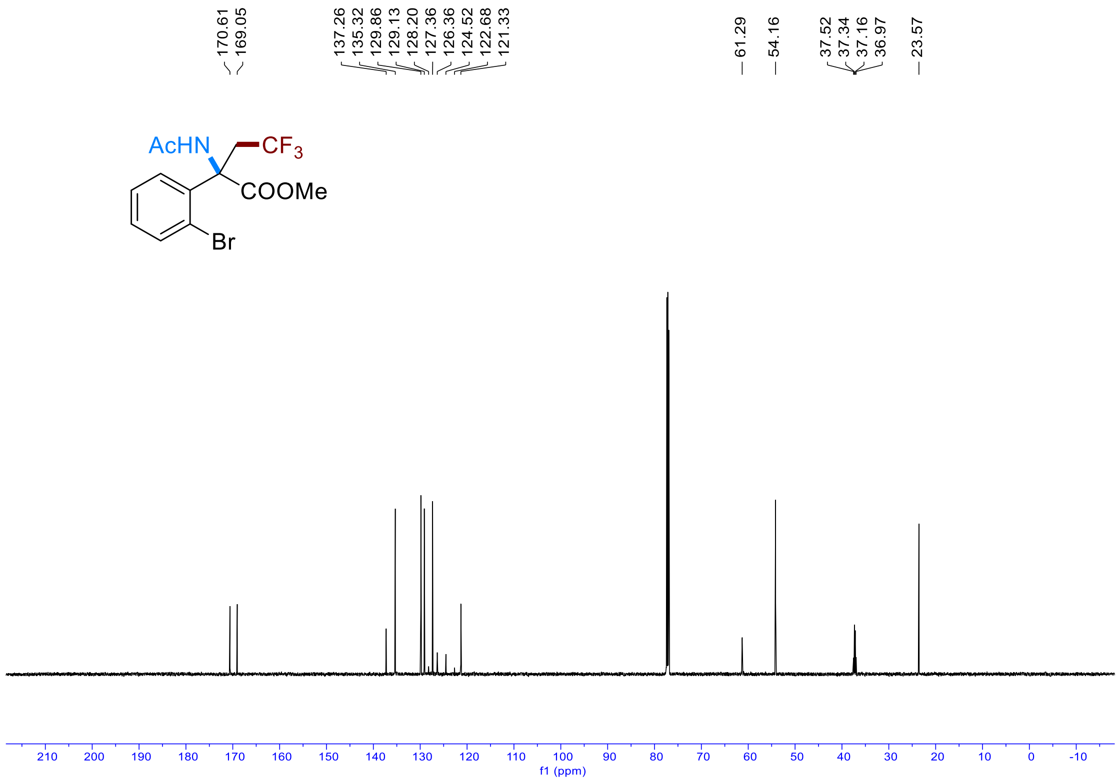
^{13}C NMR (151 MHz, $CDCl_3$) – (**3an**)



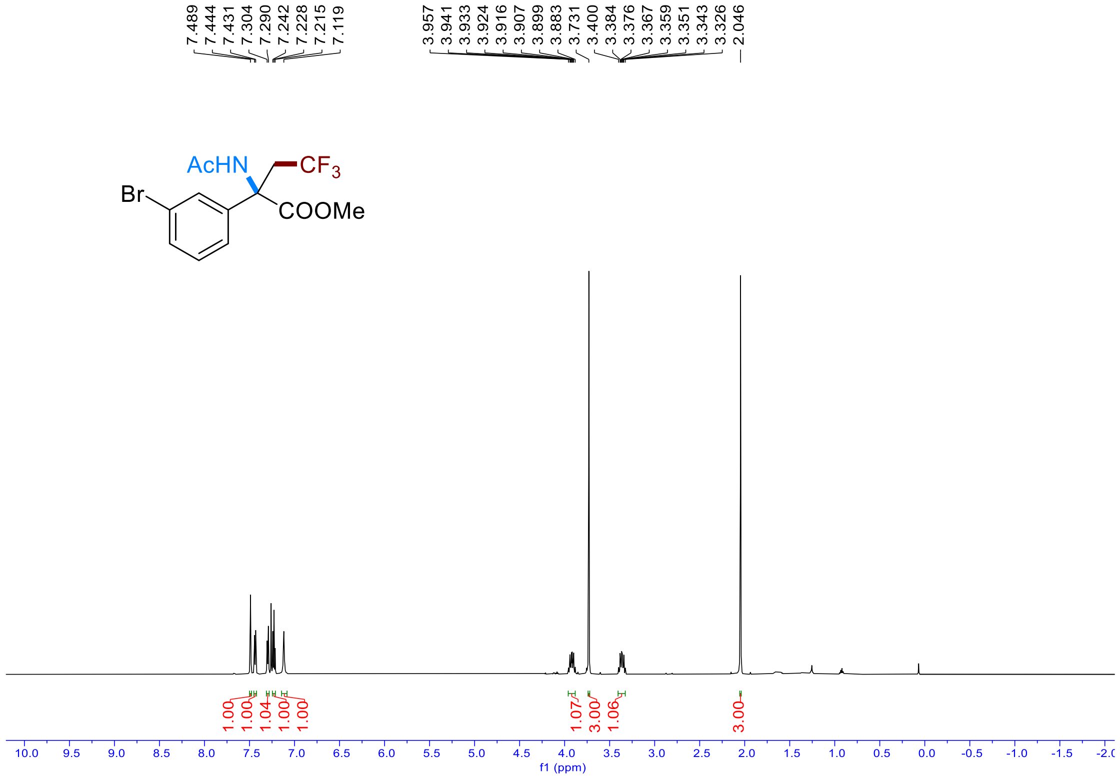
^{1}H NMR (600 MHz, CDCl$_3$) – (**3ao**)



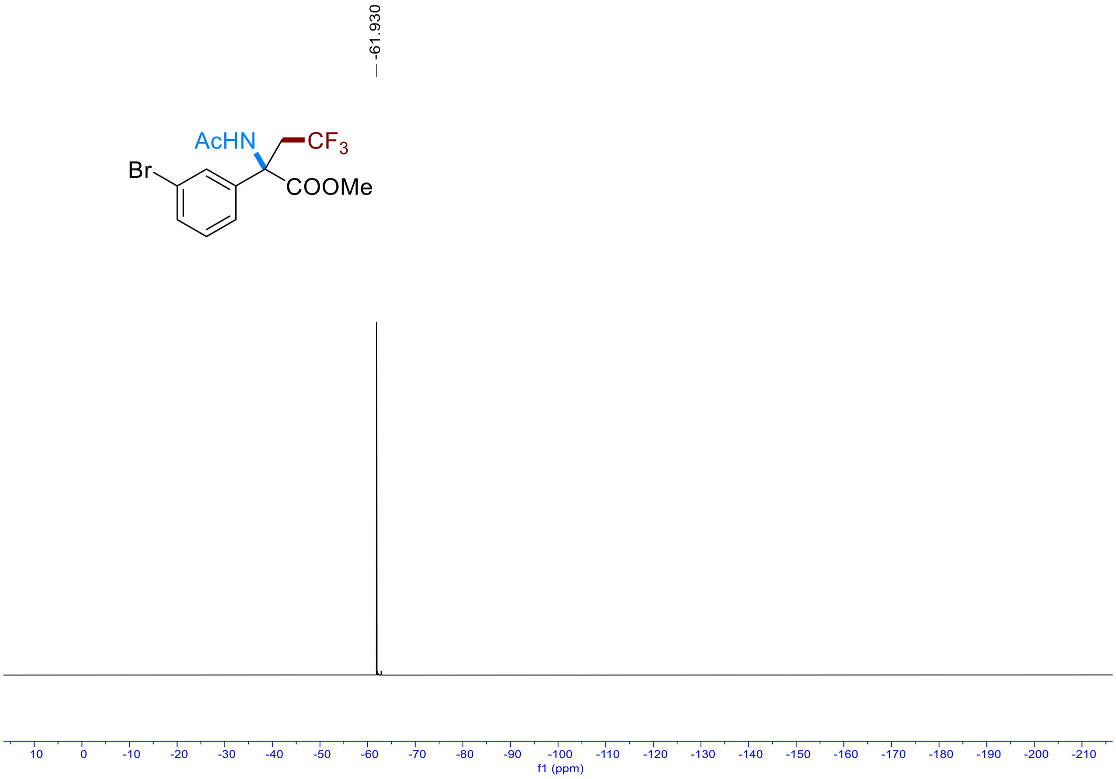
^{19}F NMR (565 MHz, CDCl$_3$) – (**3ao**)



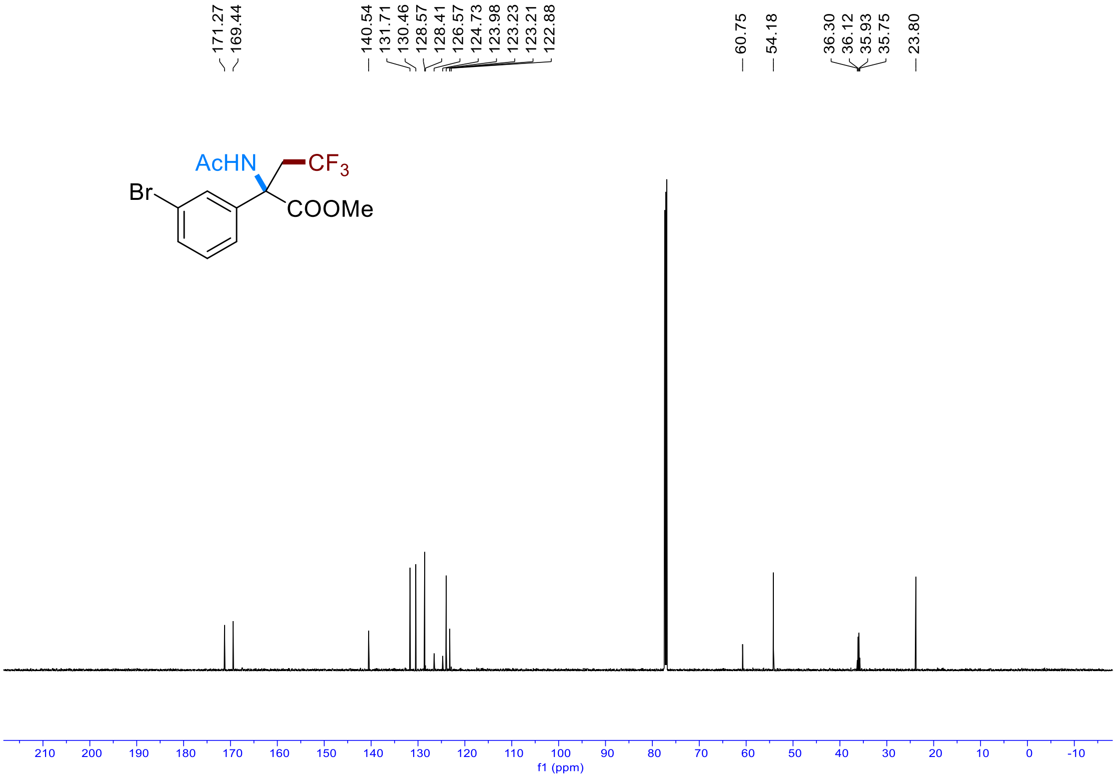
^{13}C NMR (151 MHz, CDCl$_3$) – (**3ao**)



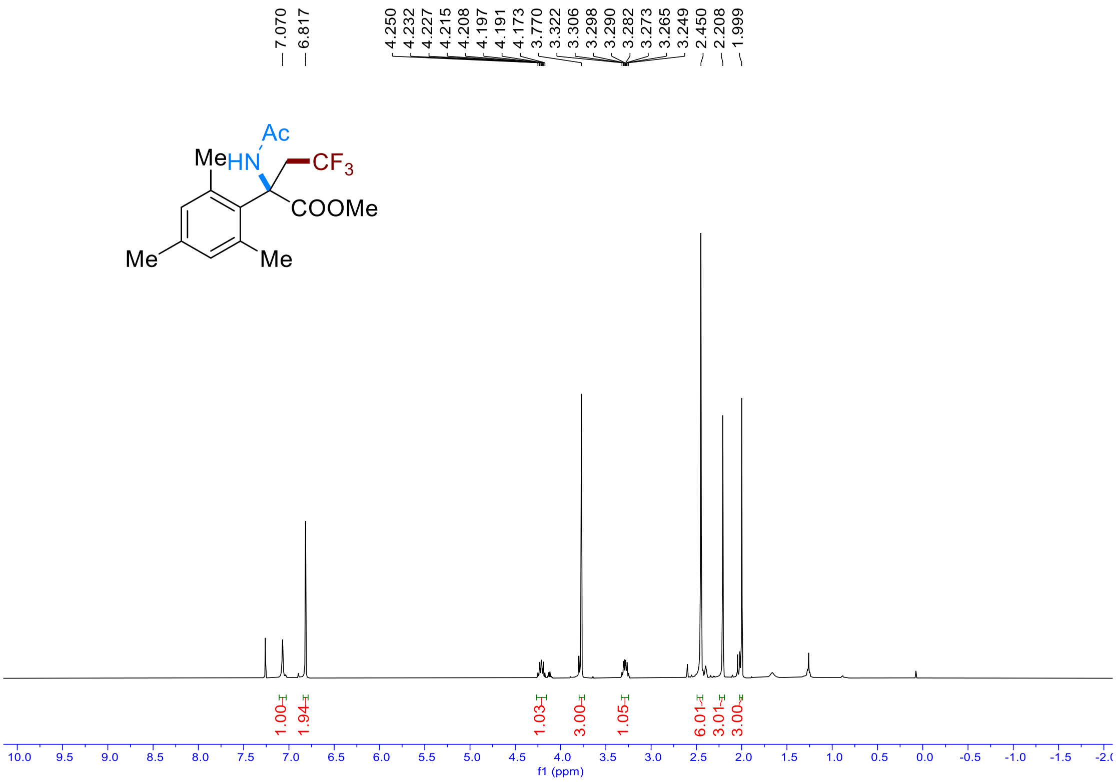
^{1}H NMR (600 MHz, CDCl$_3$) – (**3ap**)



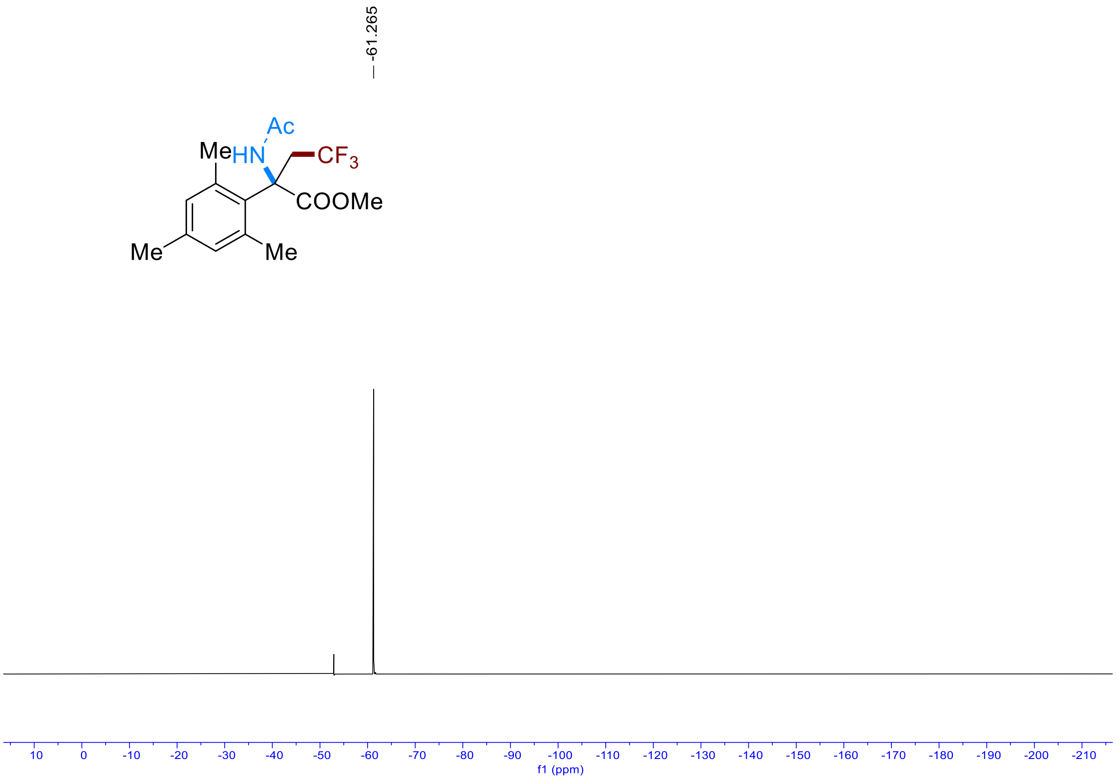
^{19}F NMR (565 MHz, CDCl$_3$) – (**3ap**)



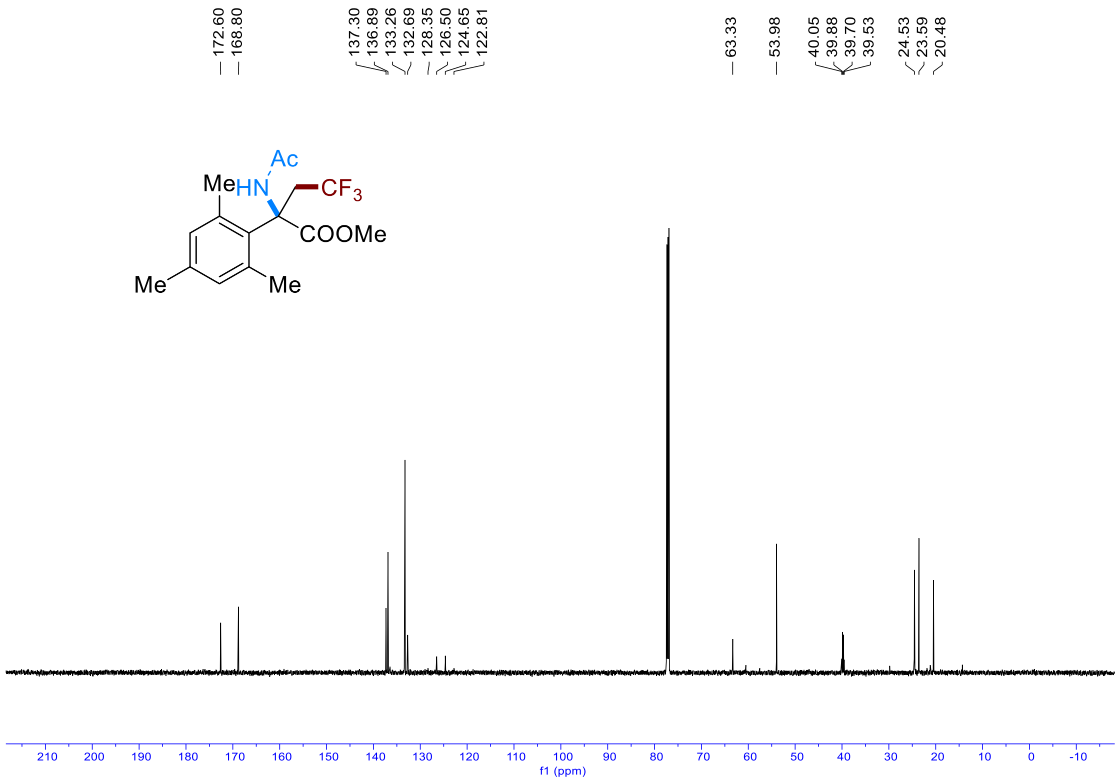
^{13}C NMR (151 MHz, CDCl$_3$) – (**3ap**)



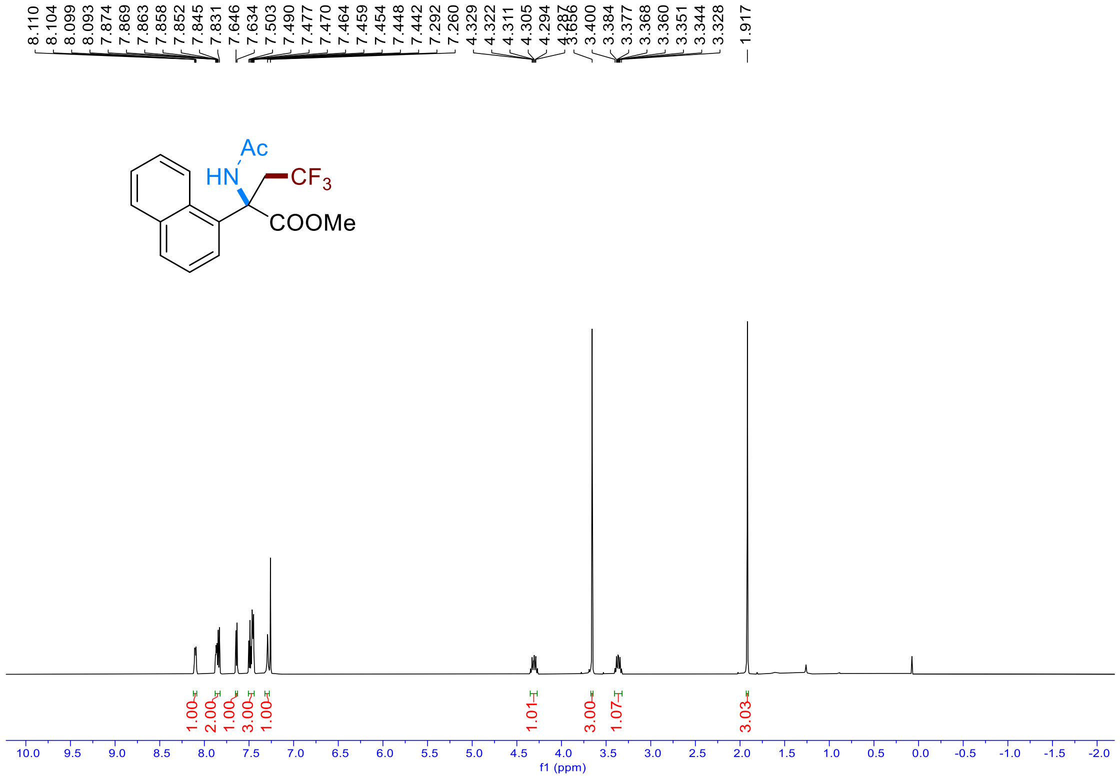
^{1}H NMR (600 MHz, CDCl3) – (**3aq**)



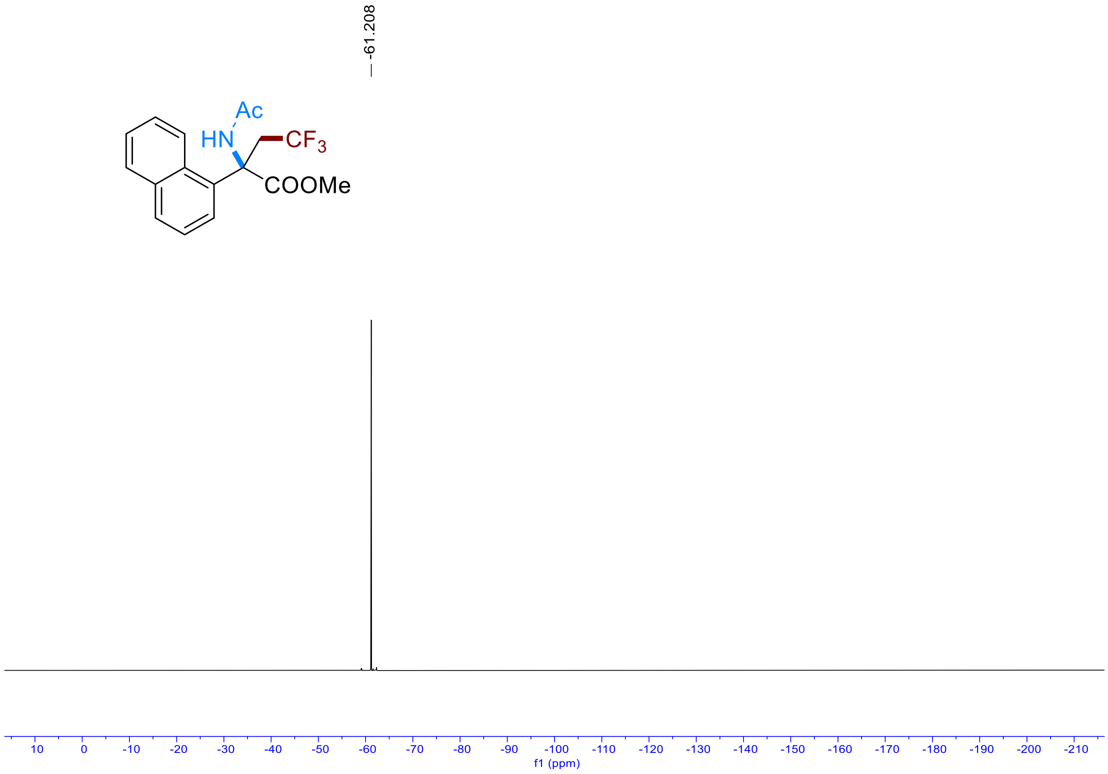
^{19}F NMR (565 MHz, $CDCl_3$) – (**3aq**)



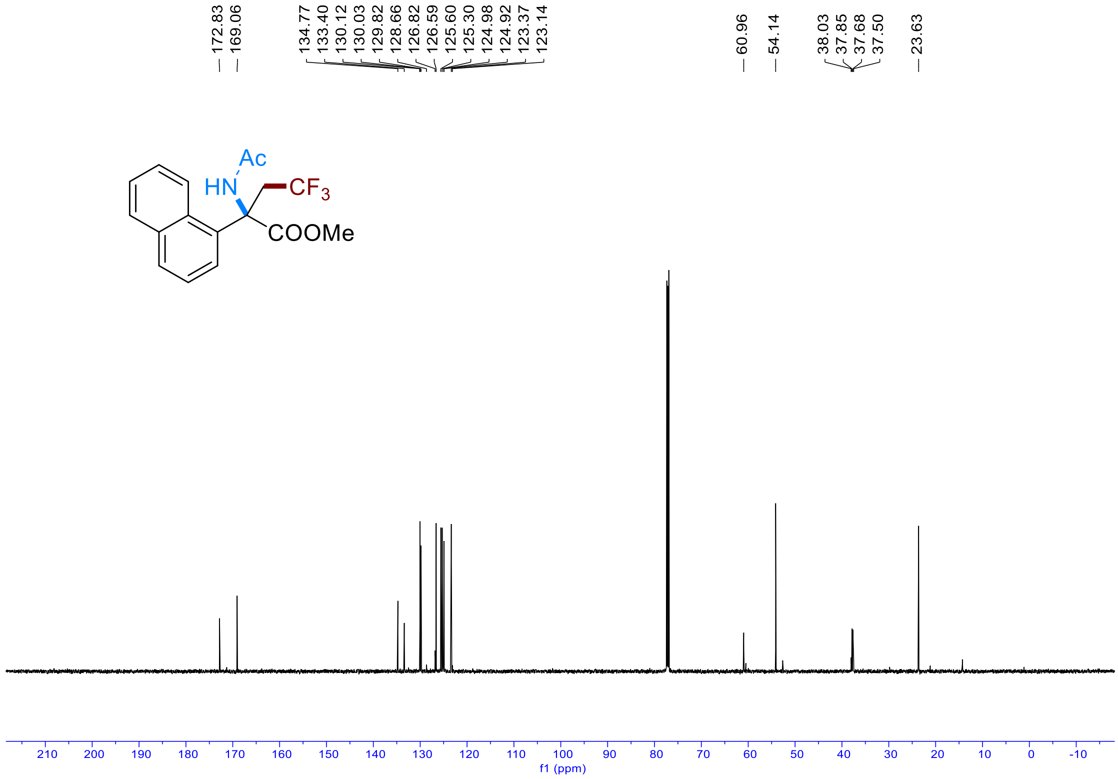
^{13}C NMR (151 MHz, CDCl$_3$) – (**3aq**)



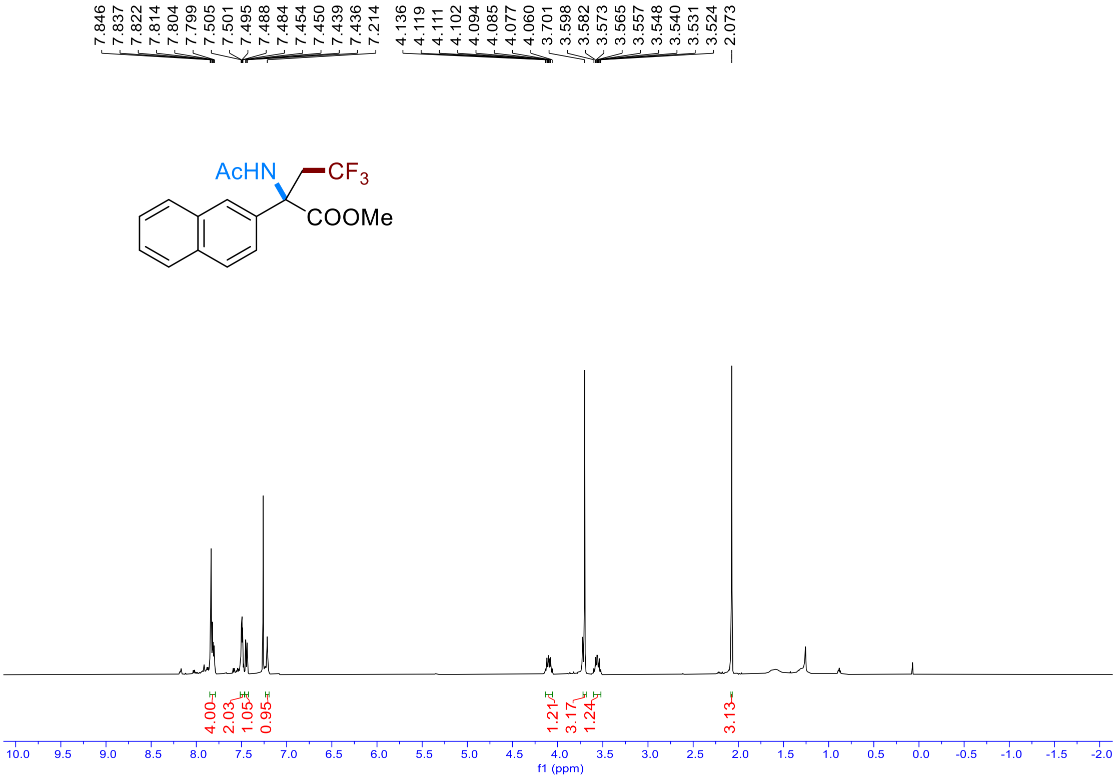
^{1}H NMR (600 MHz, CDCl$_3$) – (**3ar**)



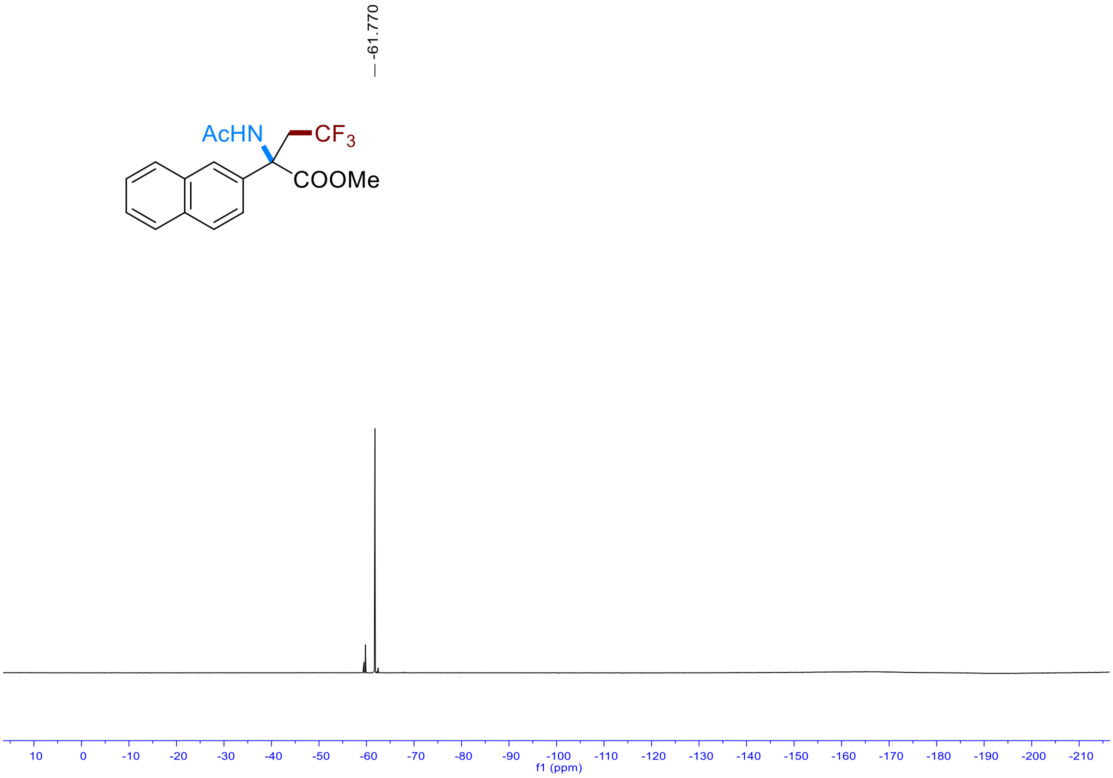
^{19}F NMR (565 MHz, CDCl$_3$) – (**3ar**)



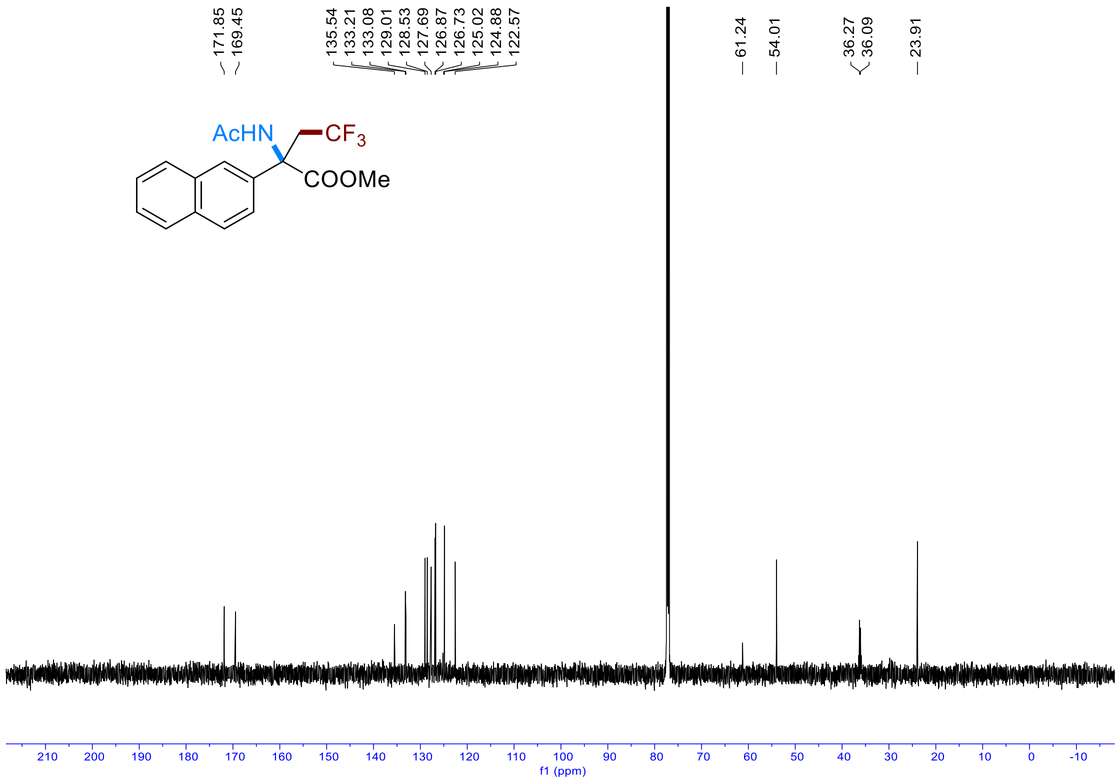
Supplementary Figure 54: ^{13}C NMR (151 MHz, CDCl$_3$) – (**3ar**)



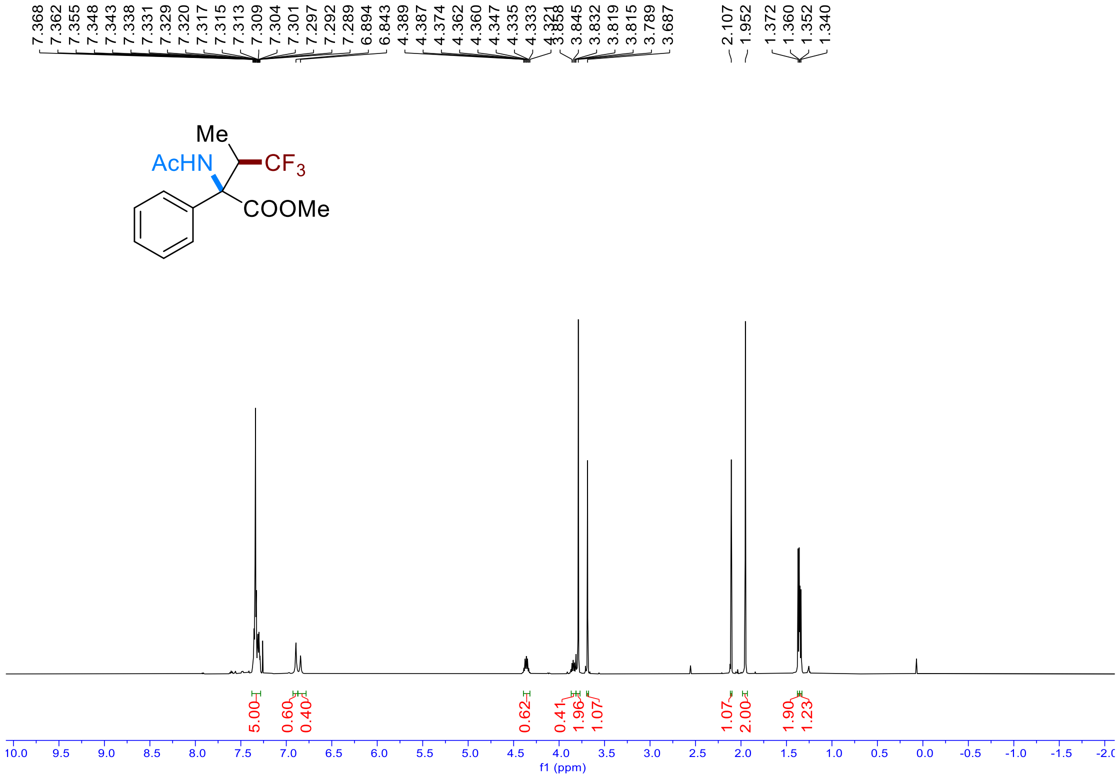
^{1}H NMR (600 MHz, $CDCl_3$) – (**3as**)



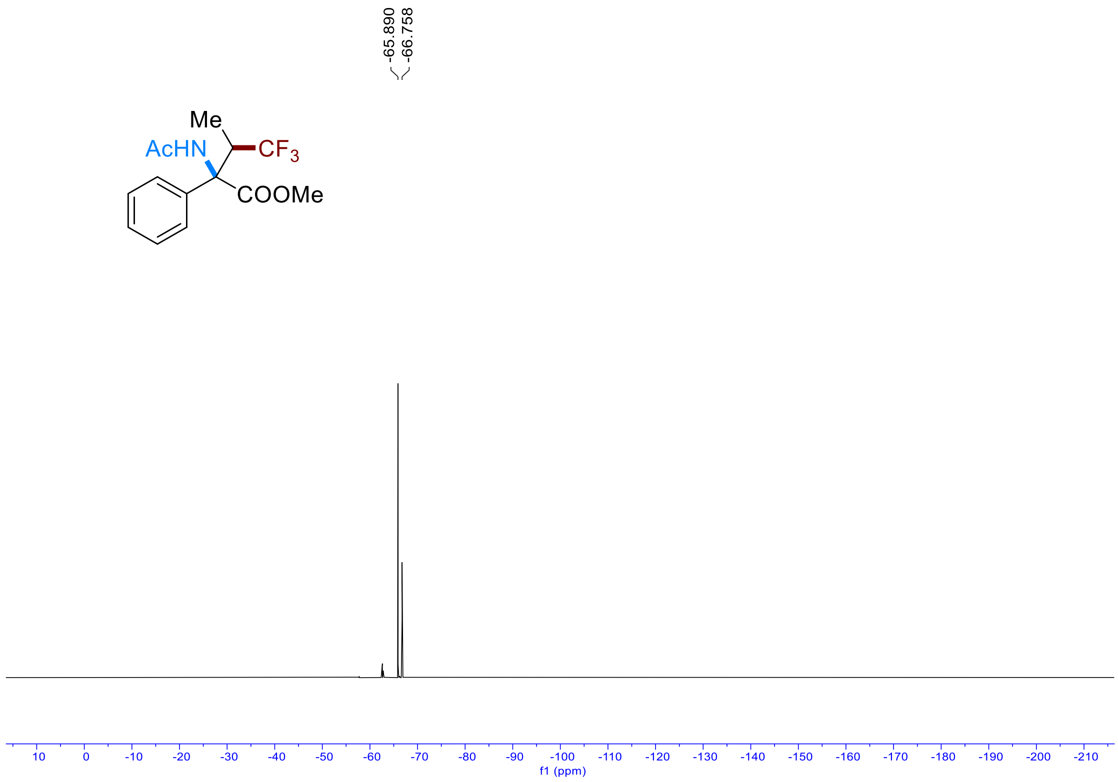
^{19}F NMR (565 MHz, $CDCl_3$) – (**3as**)



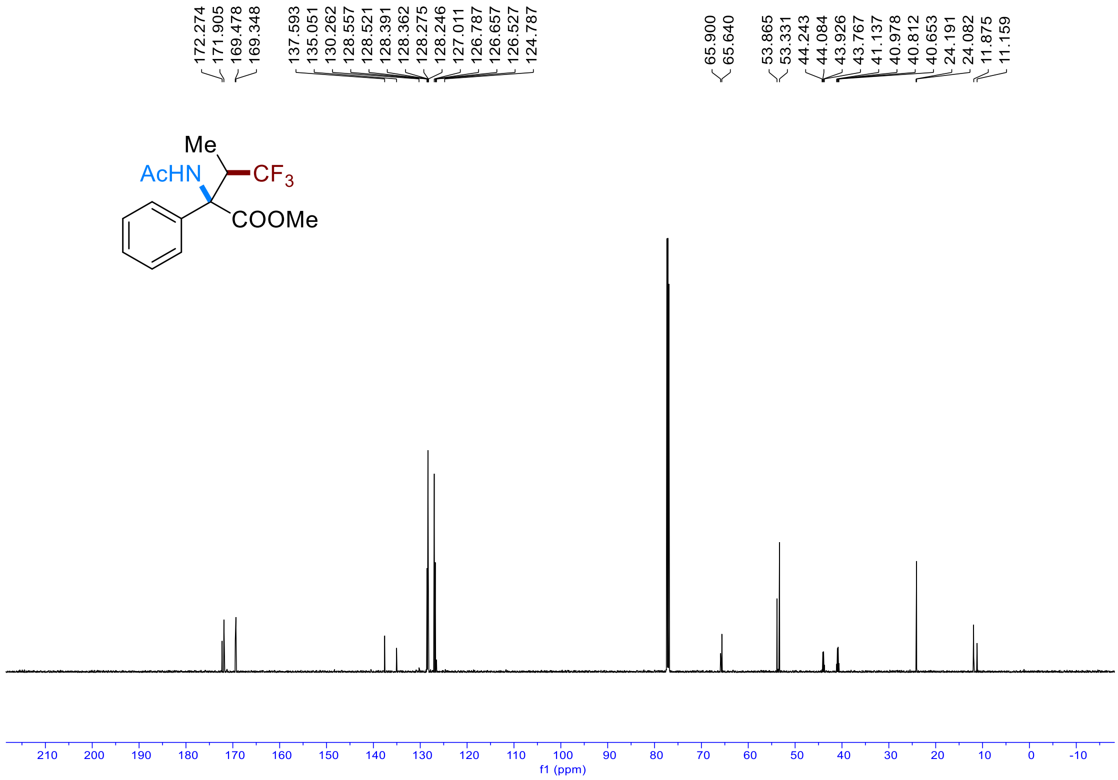
^{13}C NMR (151 MHz, CDCl$_3$) – (**3as**)



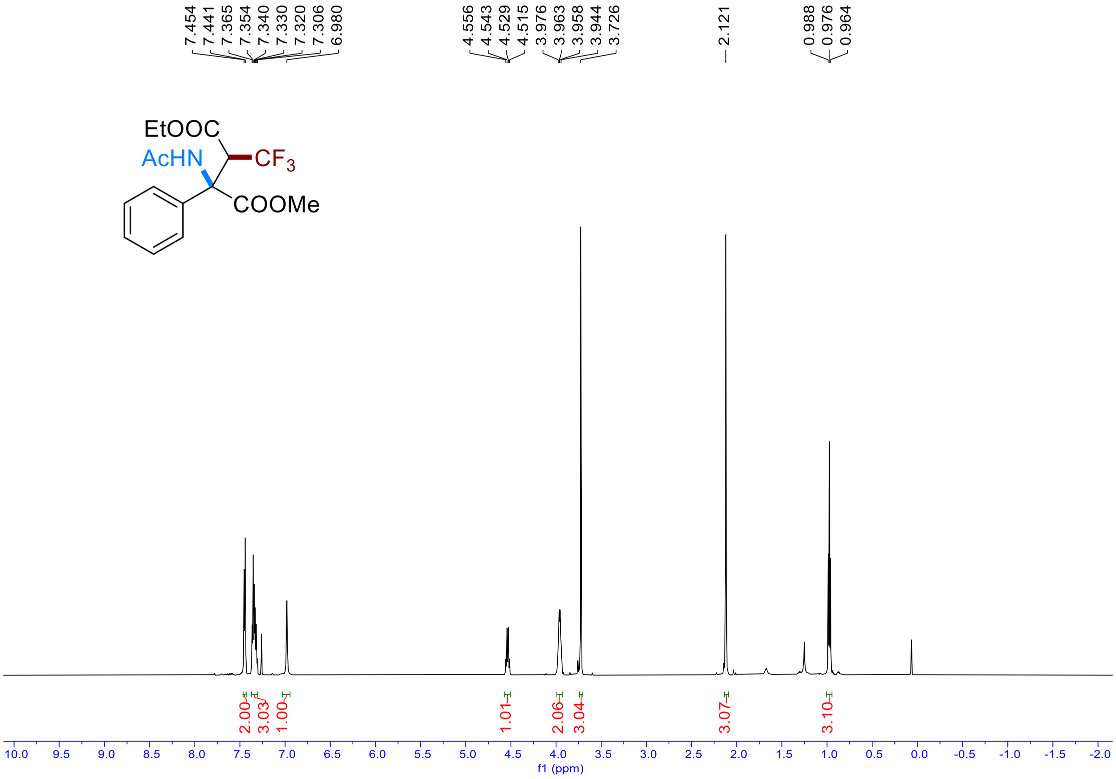
^{1}H NMR (600 MHz, CDCl$_3$) – (**3at**)



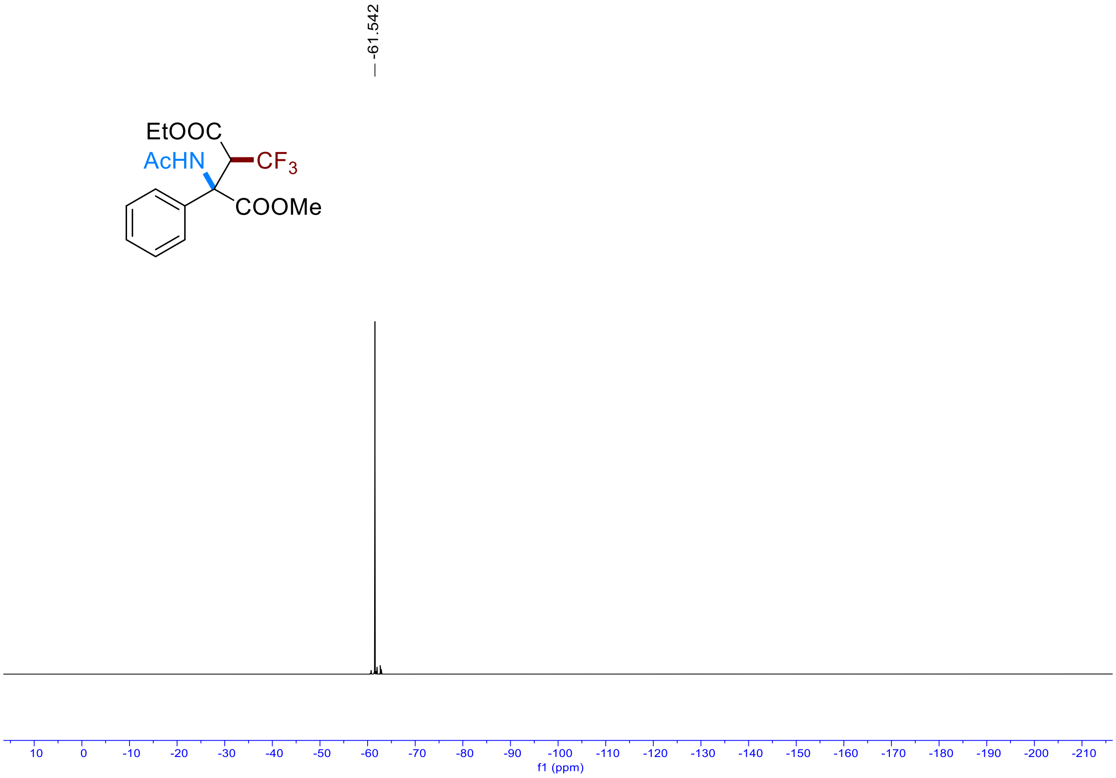
^{19}F NMR (565 MHz, $CDCl_3$) – (**3at**)



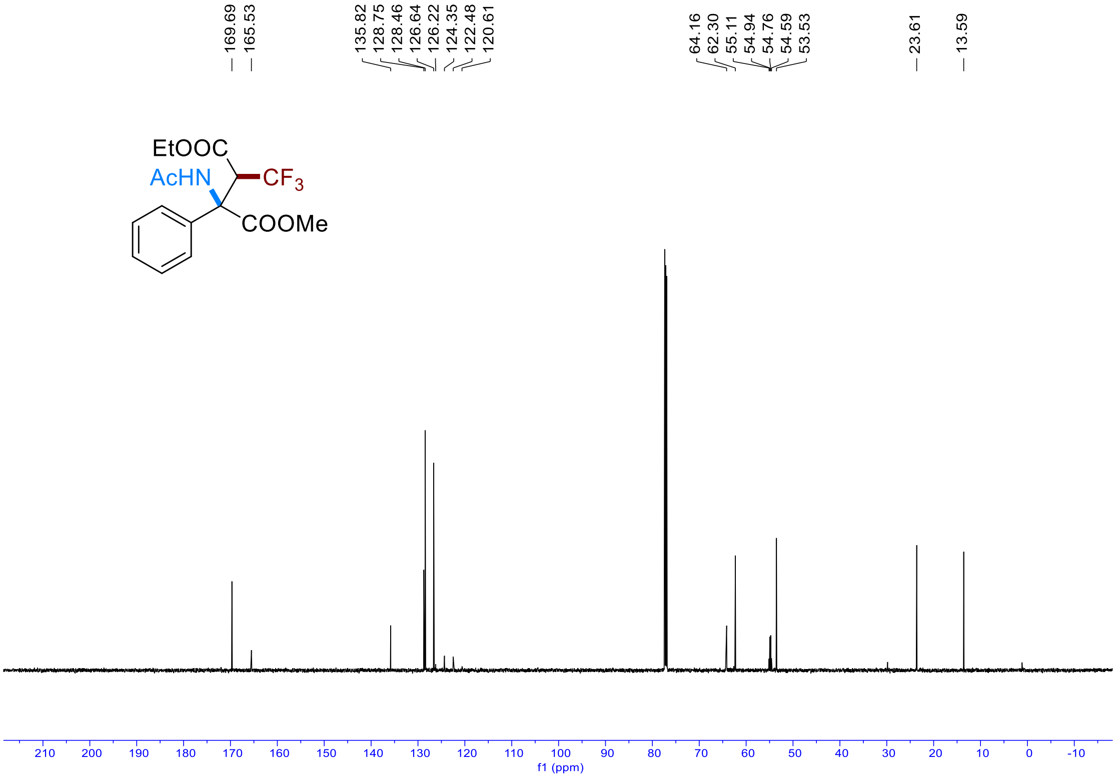
^{13}C NMR (151 MHz, $CDCl_3$) – (**3at**)



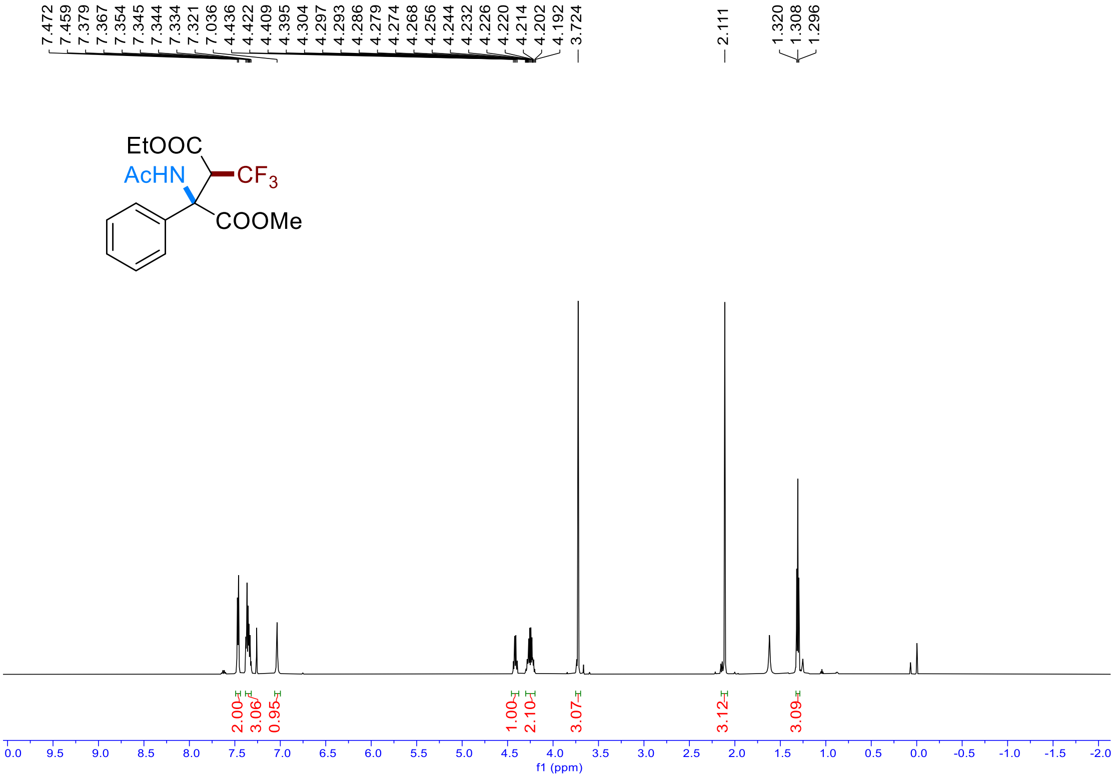
^{1}H NMR (600 MHz, $CDCl_3$) – (**3au**, isomer 1)



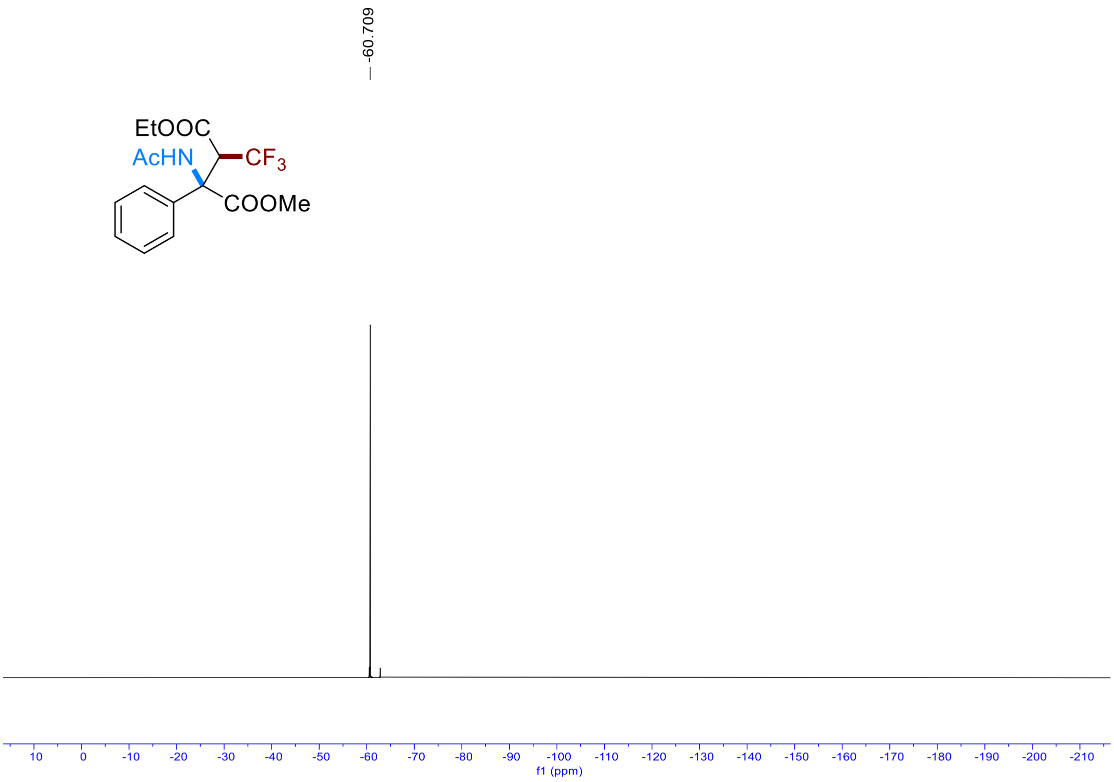
^{19}F NMR (565 MHz, $CDCl_3$) – (**3au**, isomer 1)



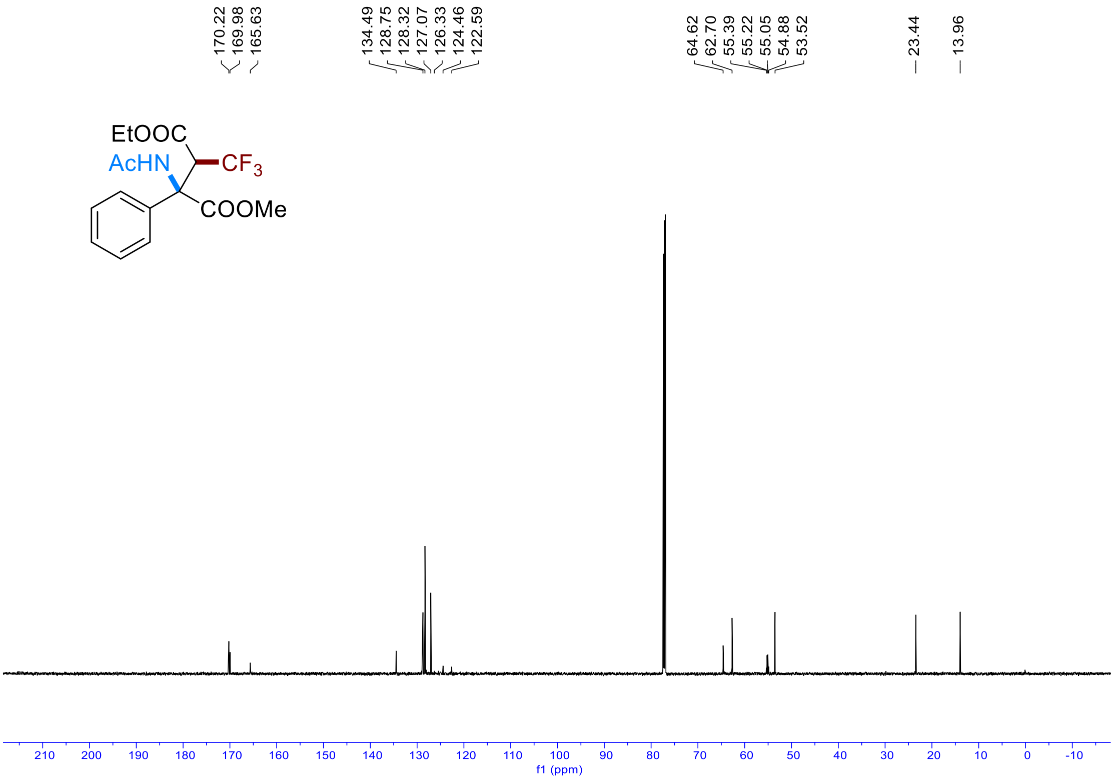
^{13}**C NMR** (151 MHz, CDCl$_3$) – (**3au**, isomer 1)



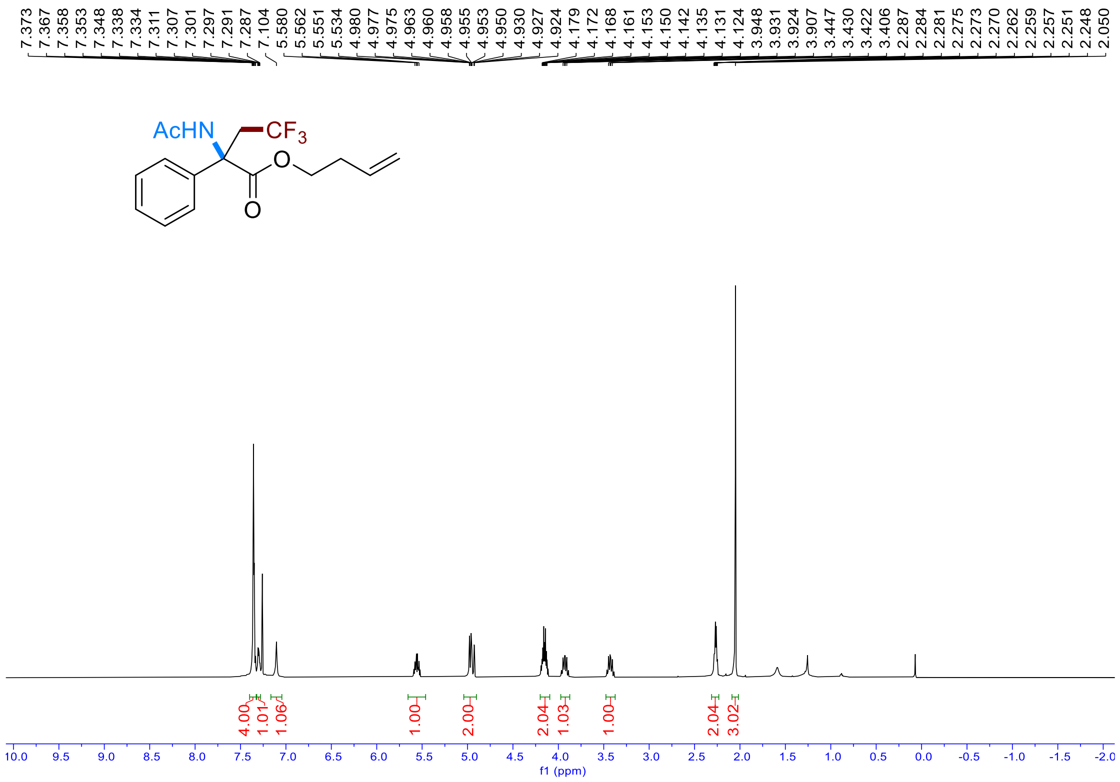
^{1}**H NMR** (600 MHz, CDCl$_3$) – (**3au**, isomer 2)



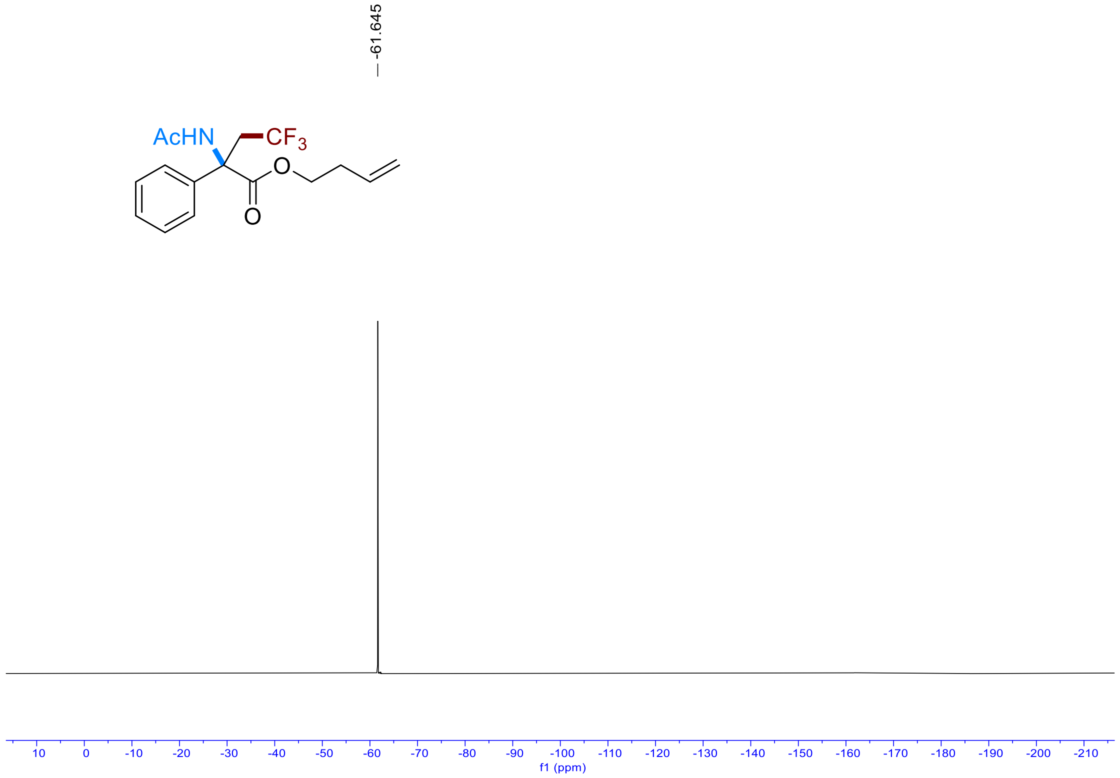
^{19}F NMR (565 MHz, $CDCl_3$) – (**3au**, isomer 2)



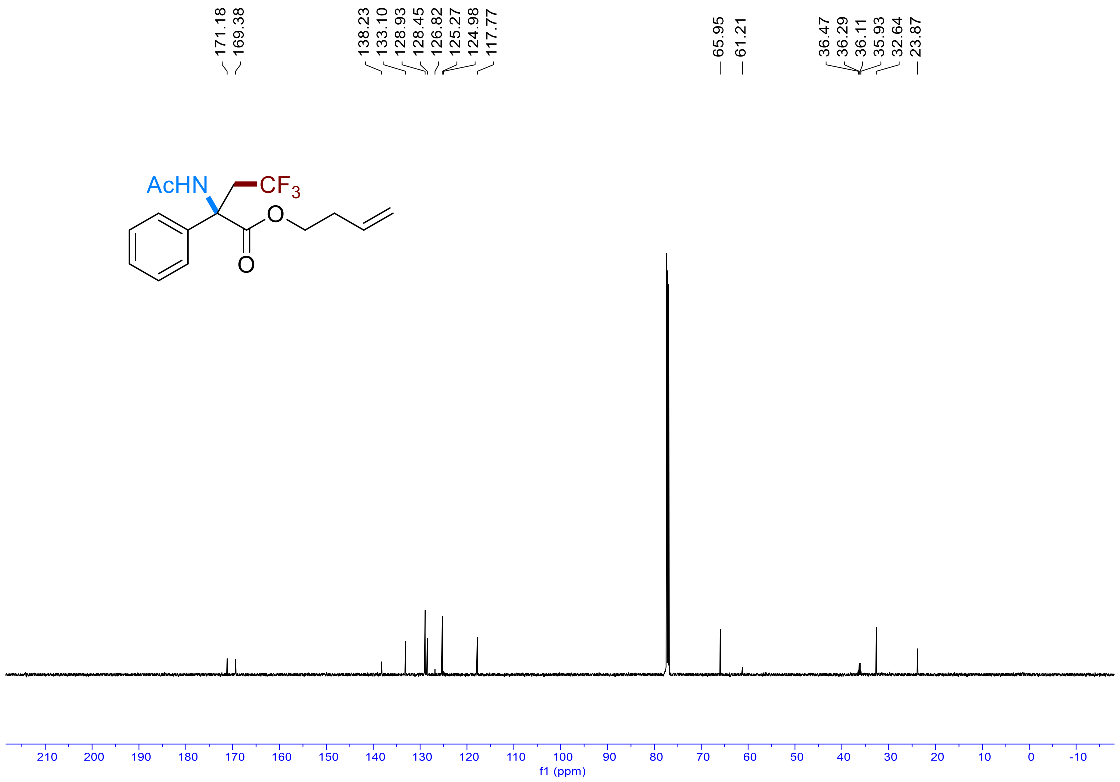
^{13}C NMR (151 MHz, $CDCl_3$) – (**3au**, isomer 2)



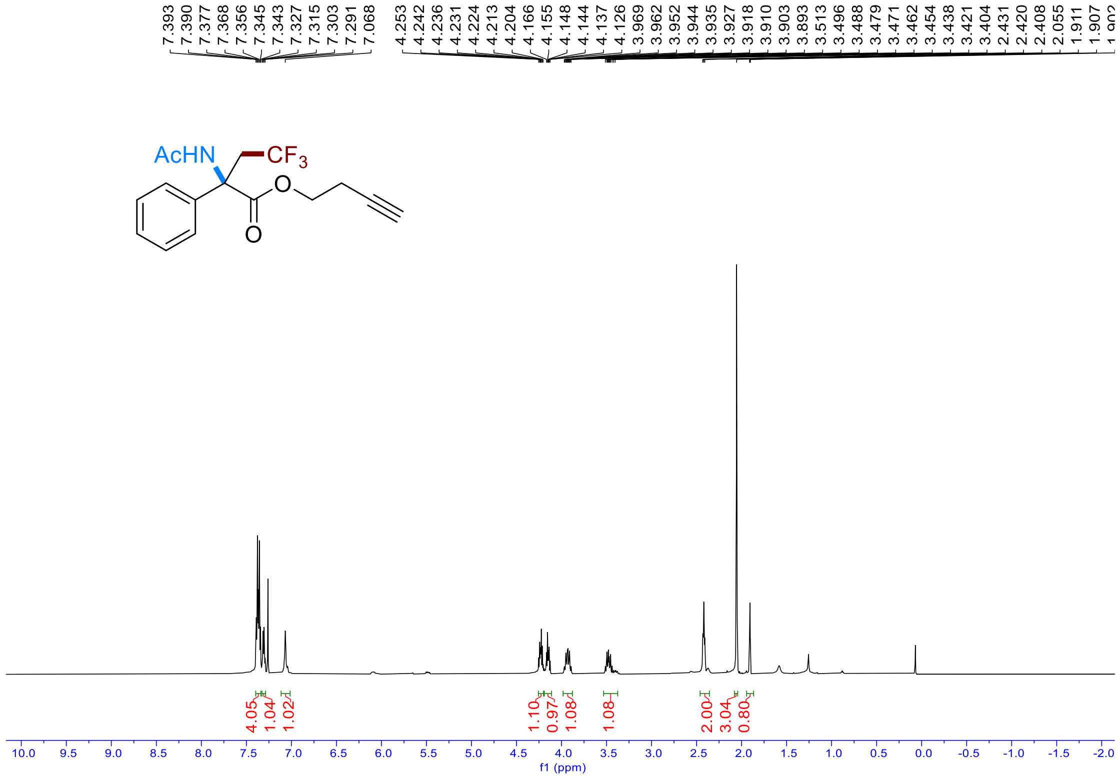
^{1}H NMR (600 MHz, CDCl$_3$) – (**3av**)



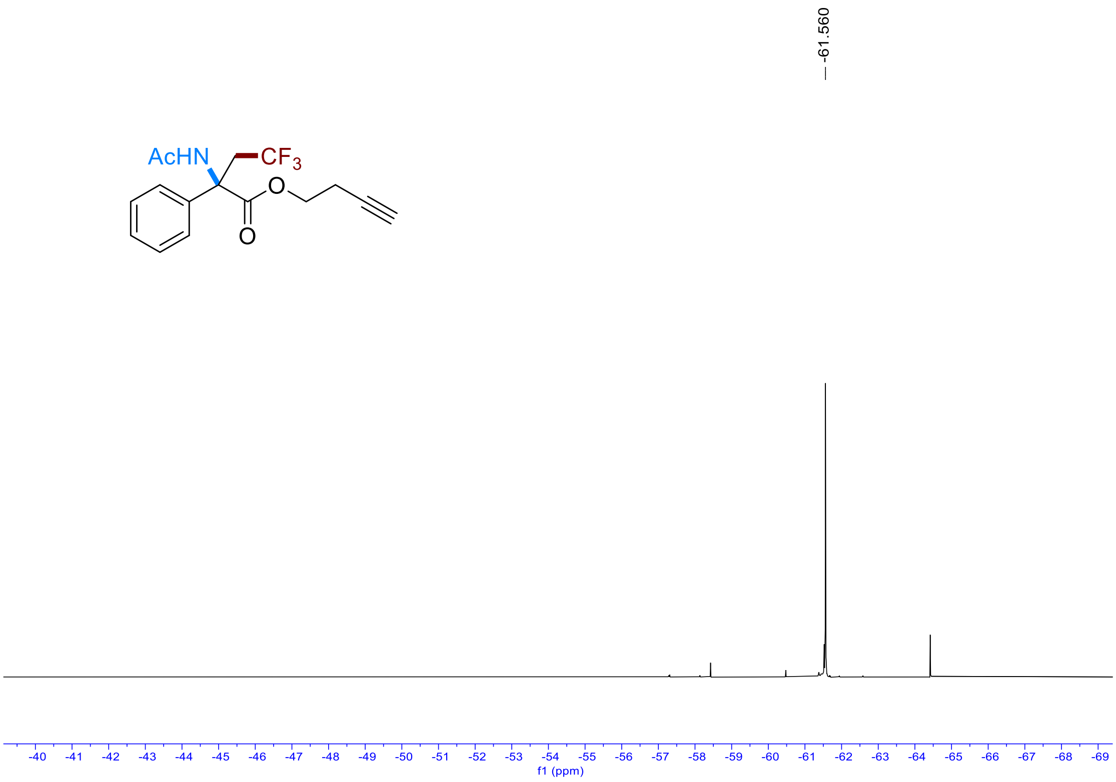
^{19}F NMR (565 MHz, CDCl$_3$) – (**3av**)



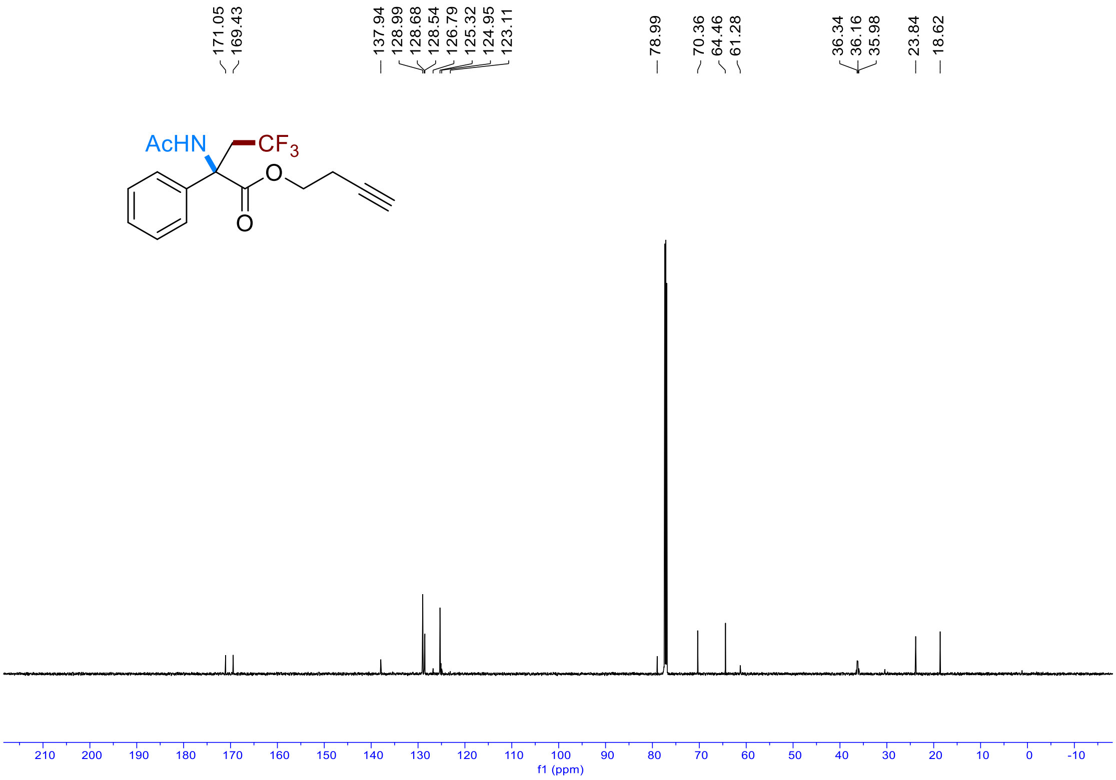
^{13}C NMR (151 MHz, CDCl$_3$) – (**3av**)



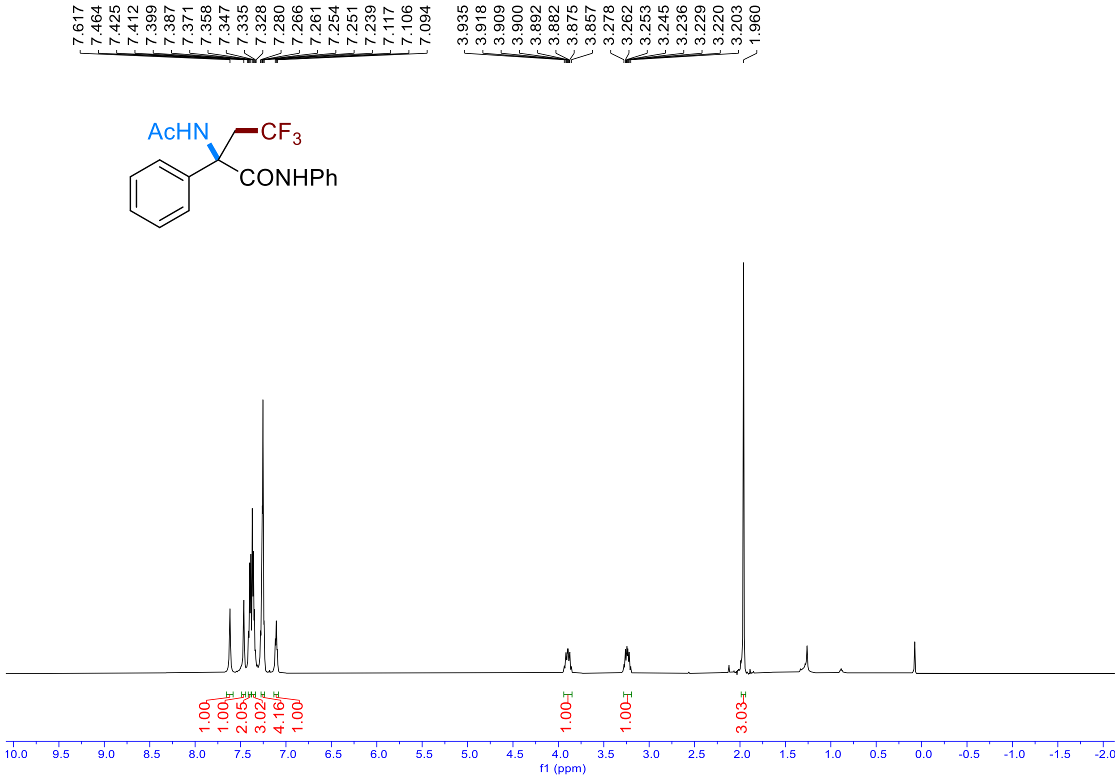
^{1}H NMR (600 MHz, CDCl$_3$) – (**3aw**)



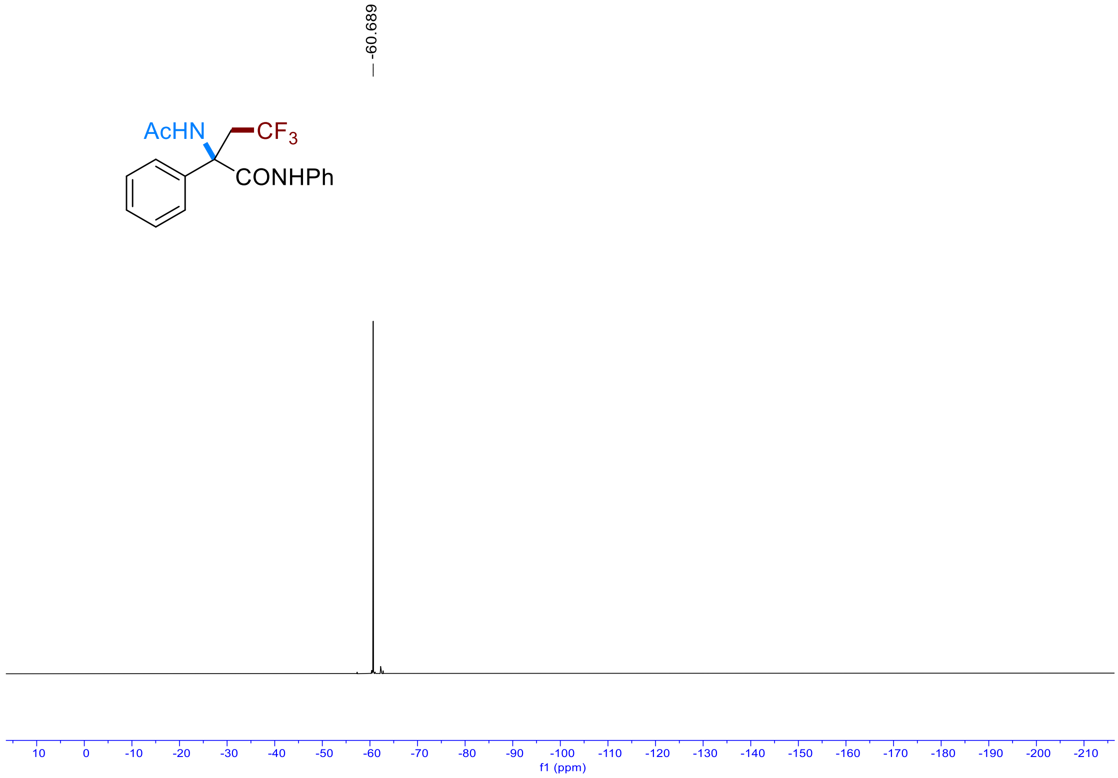
^{19}F NMR (565 MHz, CDCl$_3$) – (**3aw**)



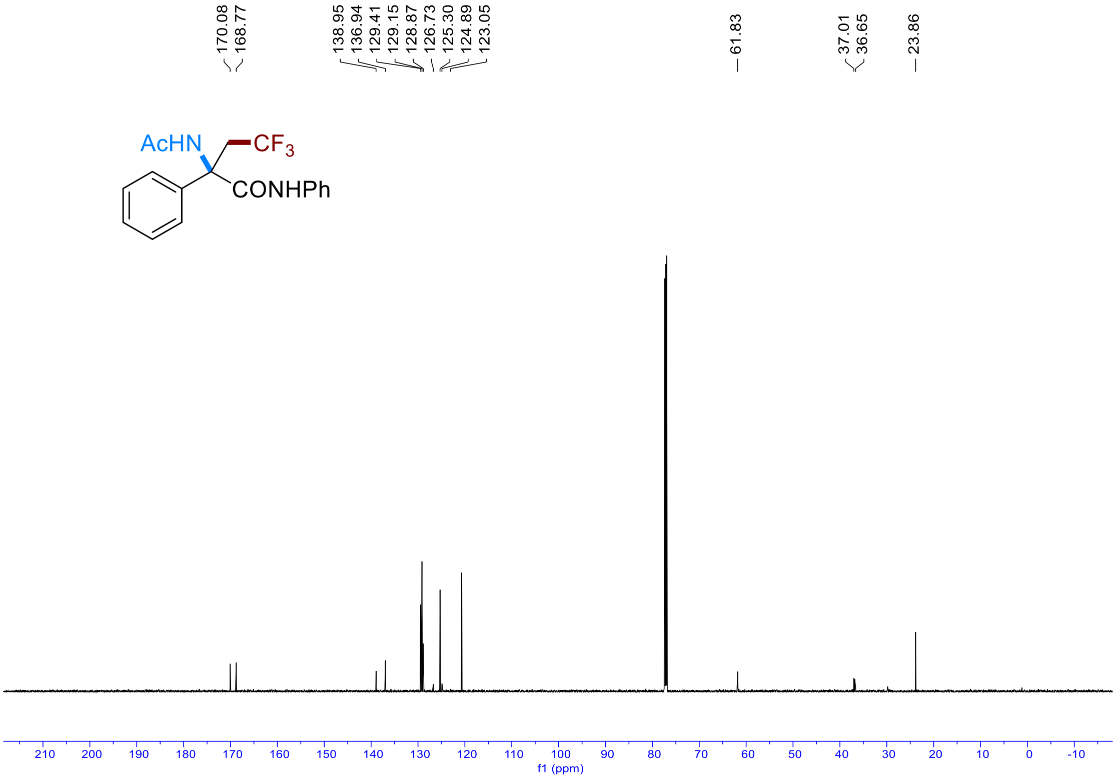
^{13}C NMR (151 MHz, CDCl$_3$) – (**3aw**)



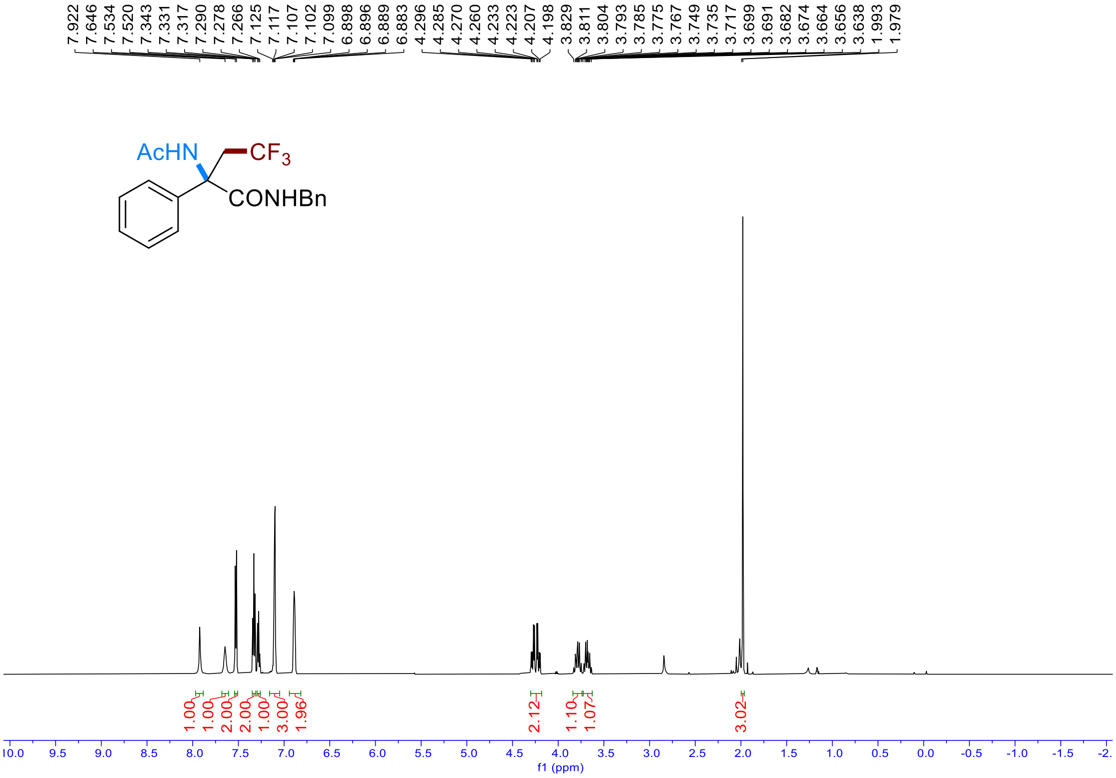
^{1}H NMR (600 MHz, CDCl$_3$) – (**3ay**)



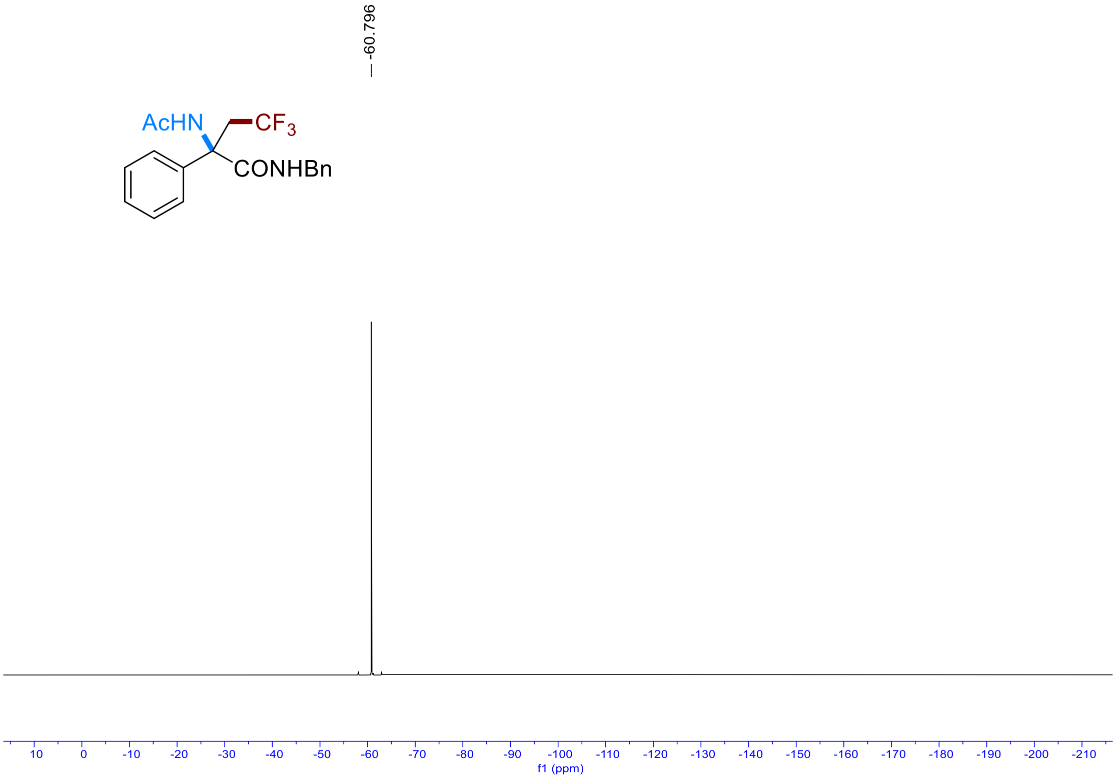
^{19}F NMR (565 MHz, CDCl$_3$) – (**3ay**)



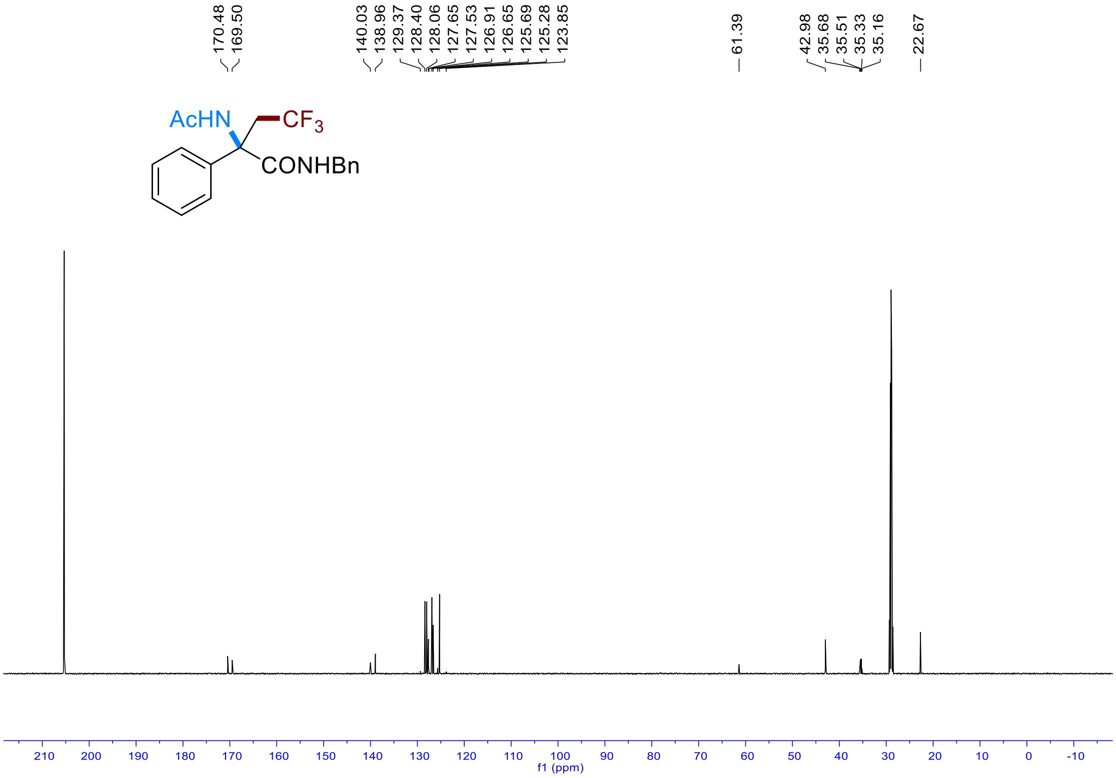
^{13}C NMR (151 MHz, CDCl$_3$) – (**3ay**)



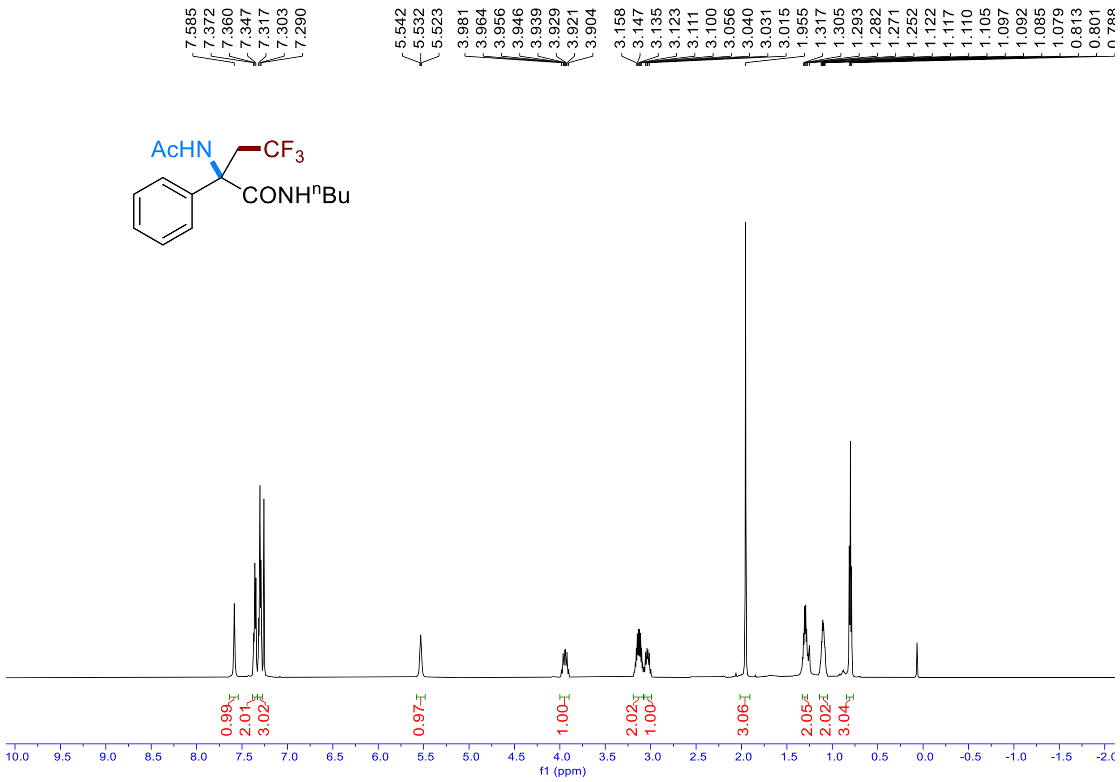
^{1}H NMR (600 MHz, Acetone-d_6) – (**3az**)



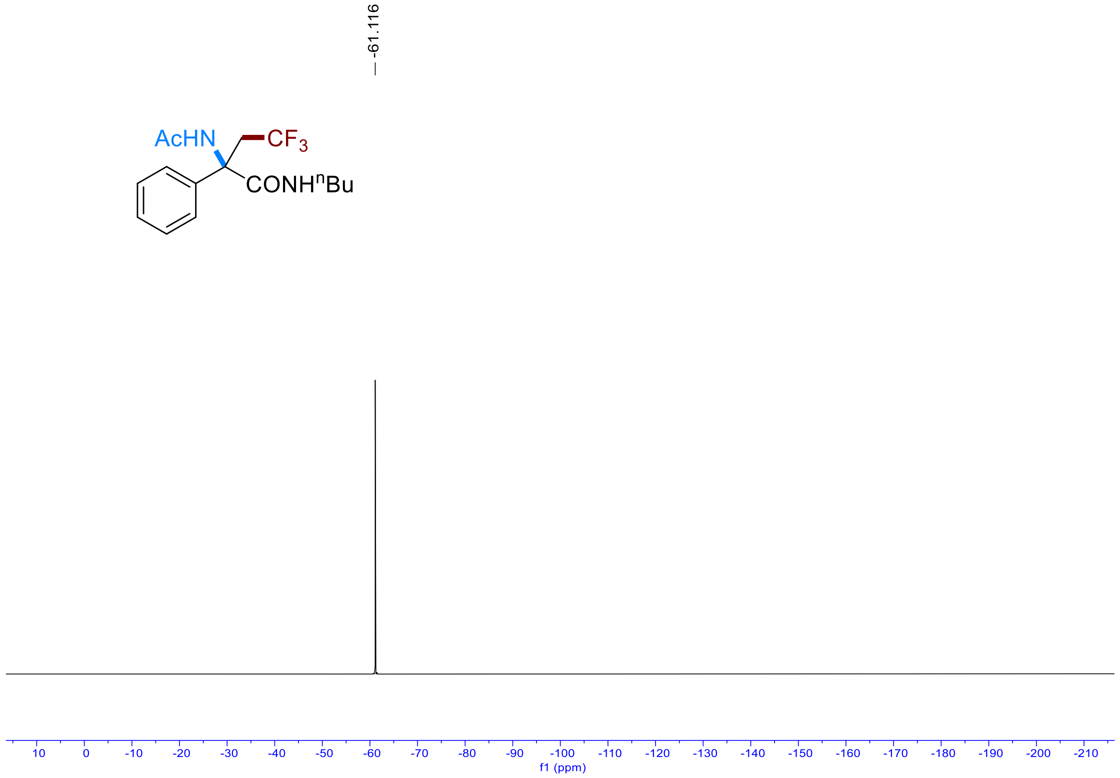
^{19}**F NMR** (565 MHz, Acetone-*d*$_6$) – (**3az**)



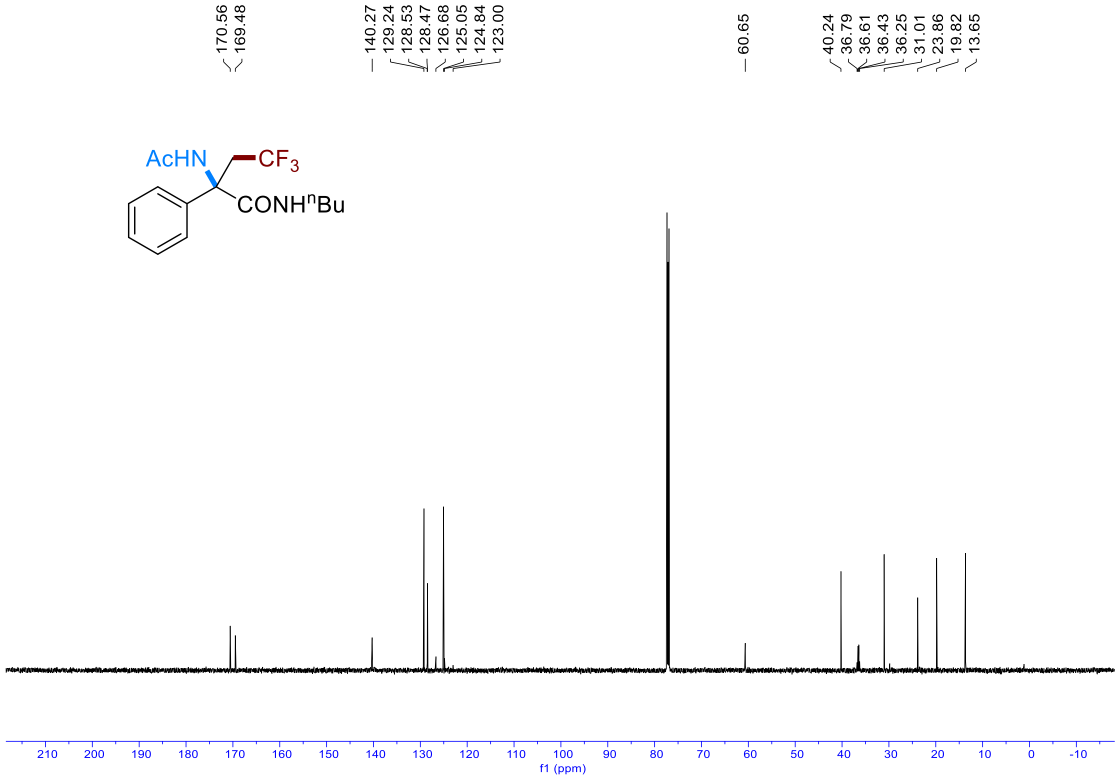
^{13}**C NMR** (151 MHz, Acetone-*d*$_6$) – (**3az**)



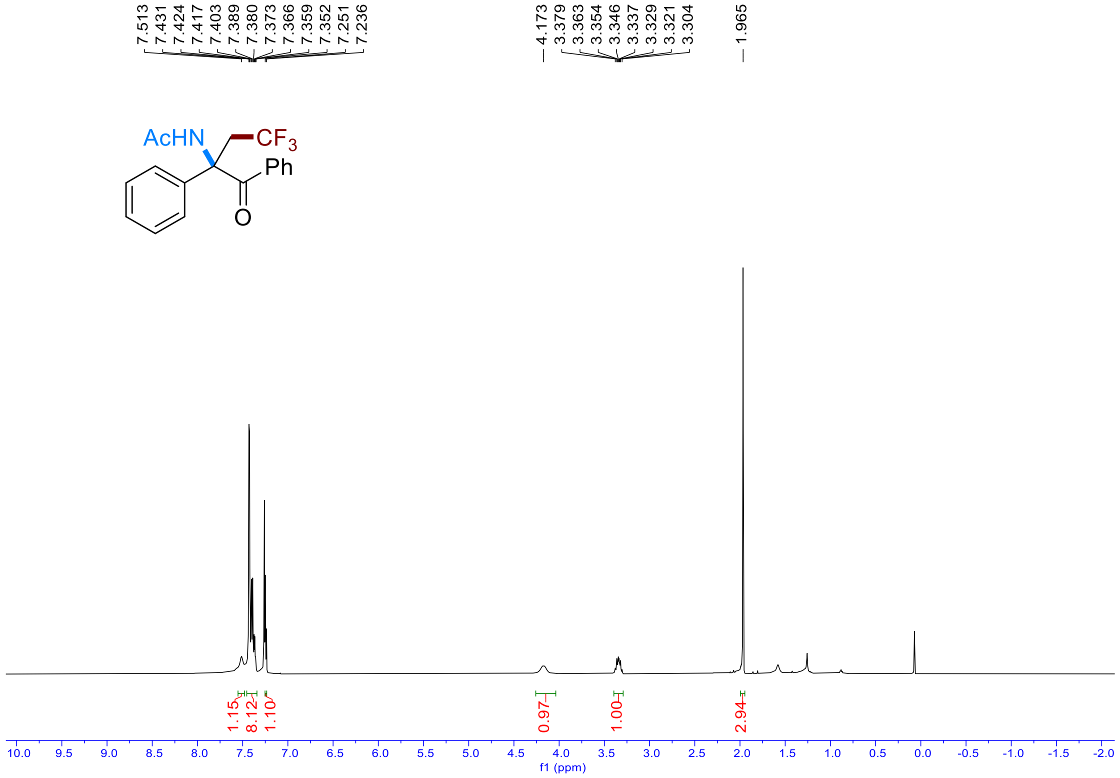
^{1}**H NMR** (600 MHz, CDCl$_3$) – (**3ba**)



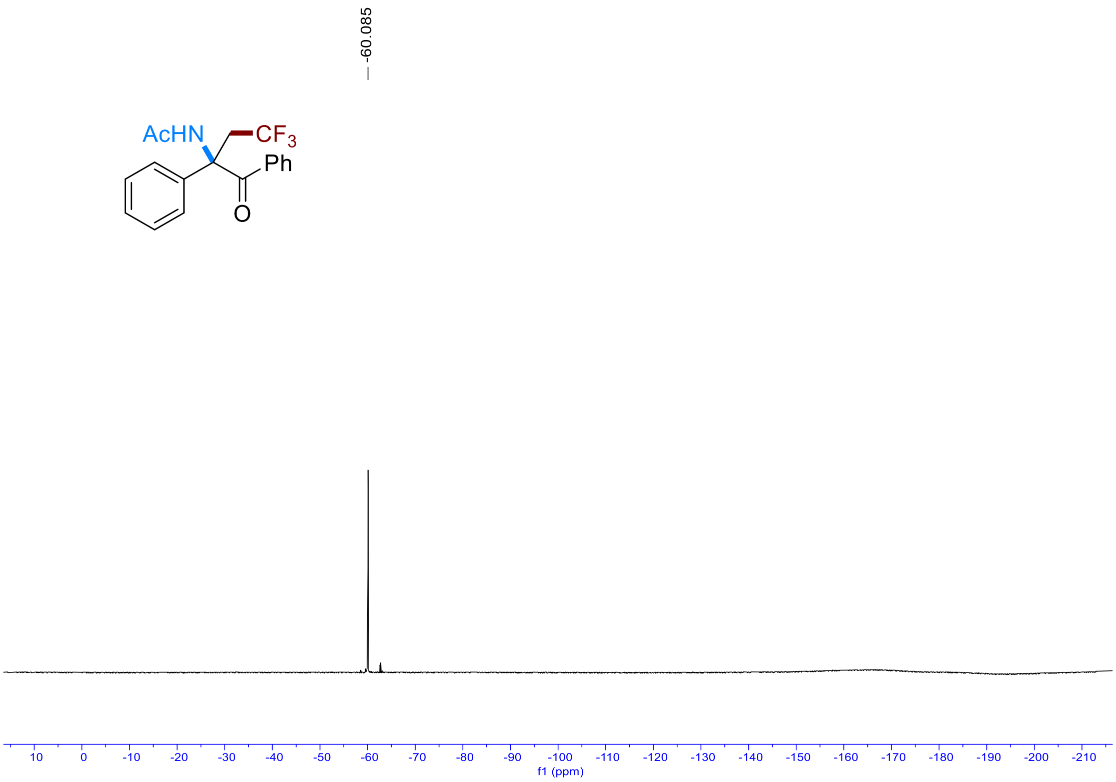
^{19}**F NMR** (565 MHz, CDCl$_3$) – (**3ba**)



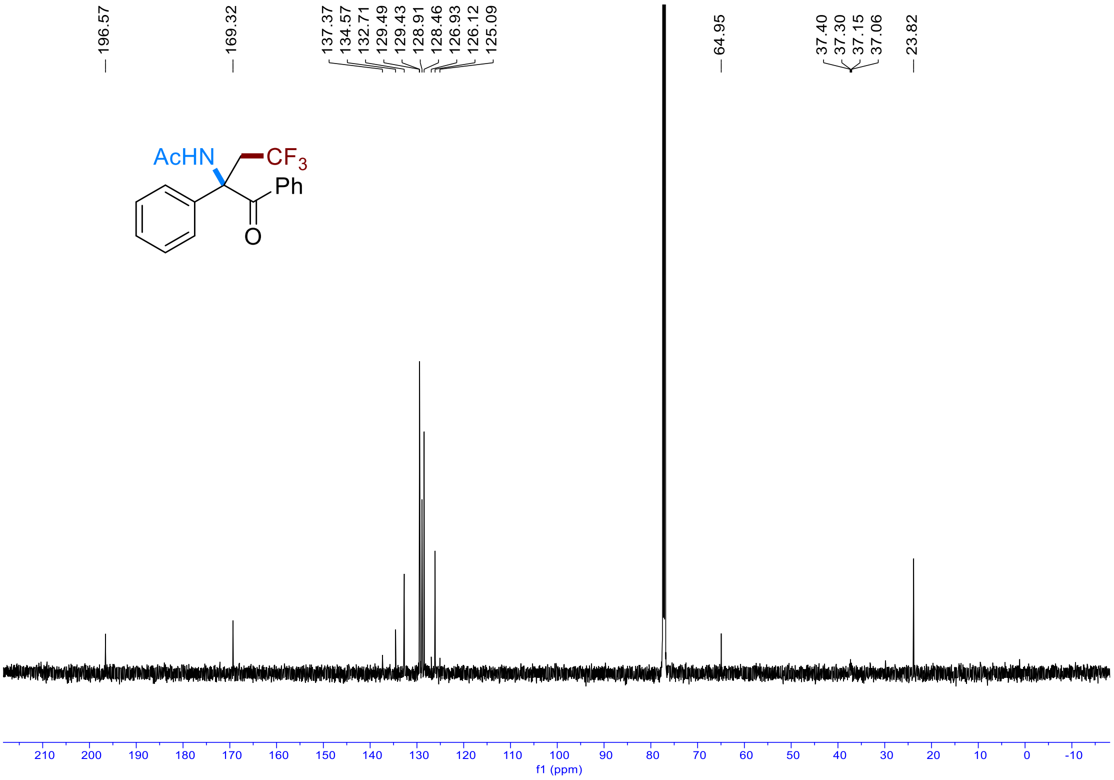
^{13}C NMR (151 MHz, CDCl$_3$) – (**3ba**)



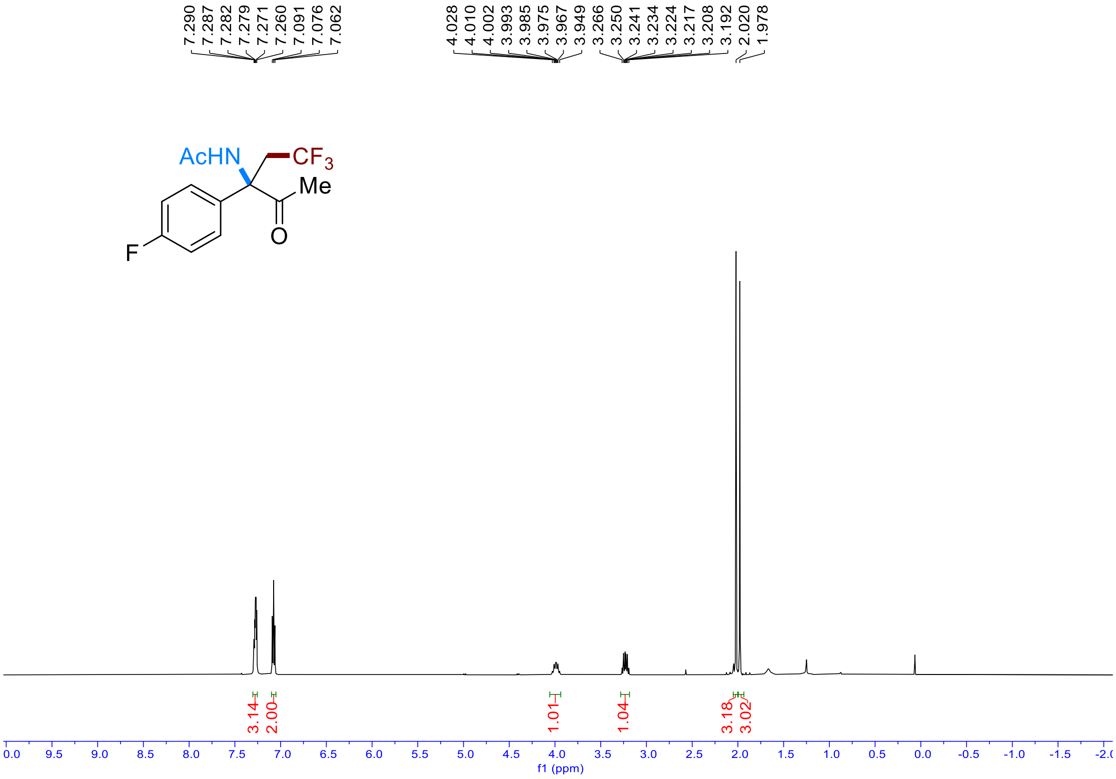
^{1}H NMR (600 MHz, CDCl$_3$) – (**3bb**)



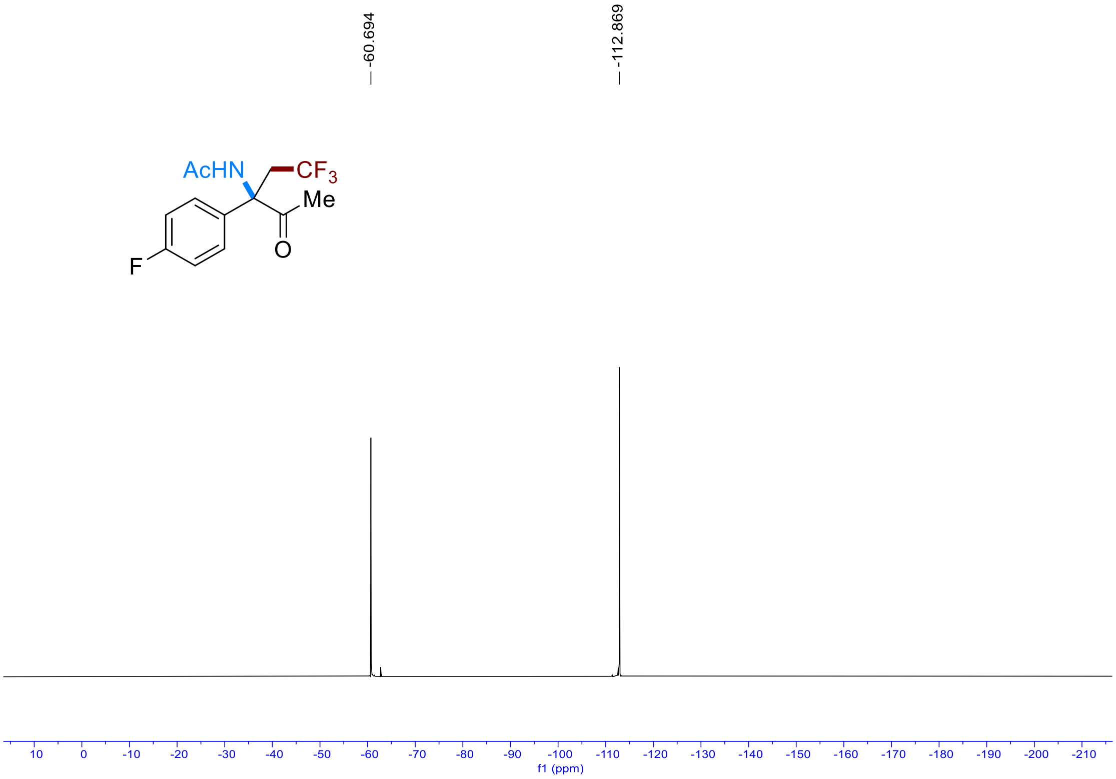
^{19}**F NMR** (565 MHz, CDCl$_3$) – (**3bb**)



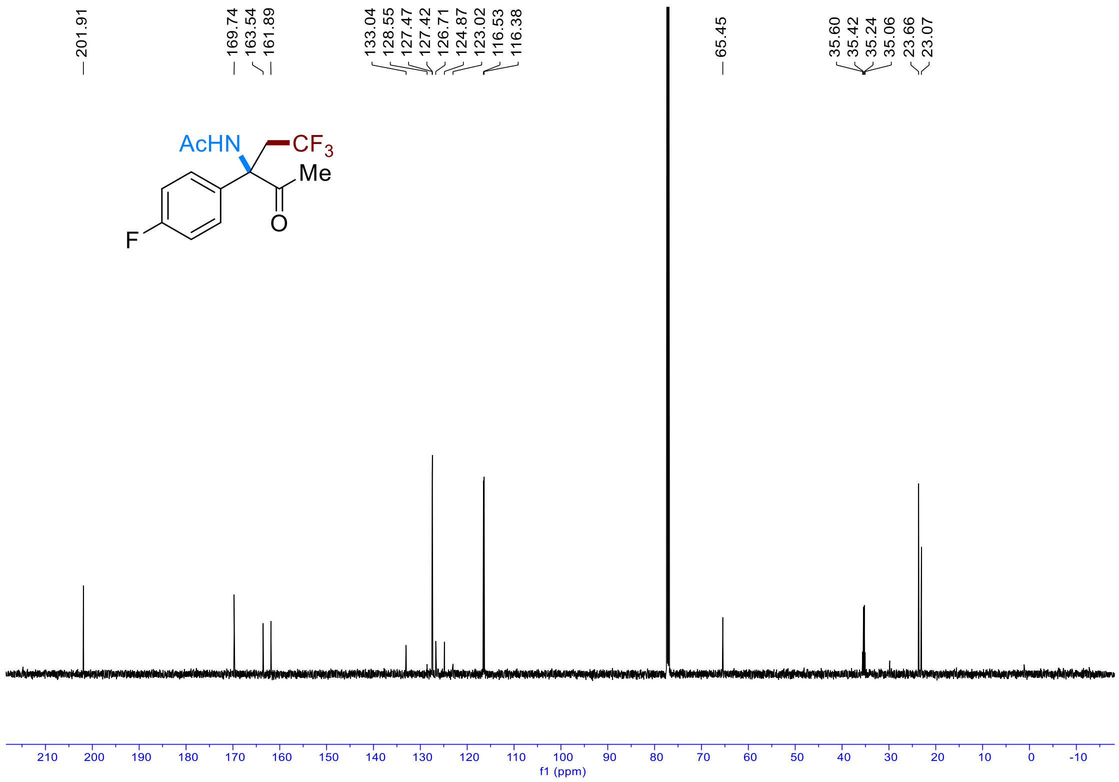
^{13}**C NMR** (151 MHz, CDCl$_3$) – (**3bb**)



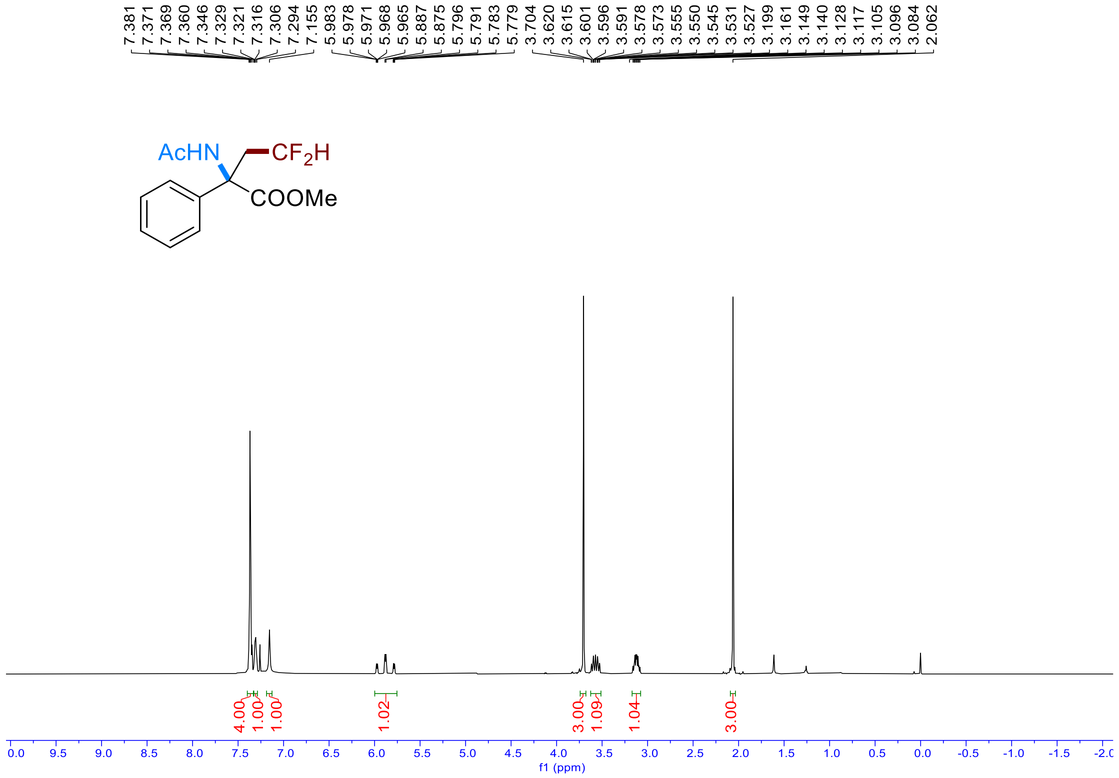
^{1}**H NMR** (600 MHz, CDCl$_3$) – (**3bc**)



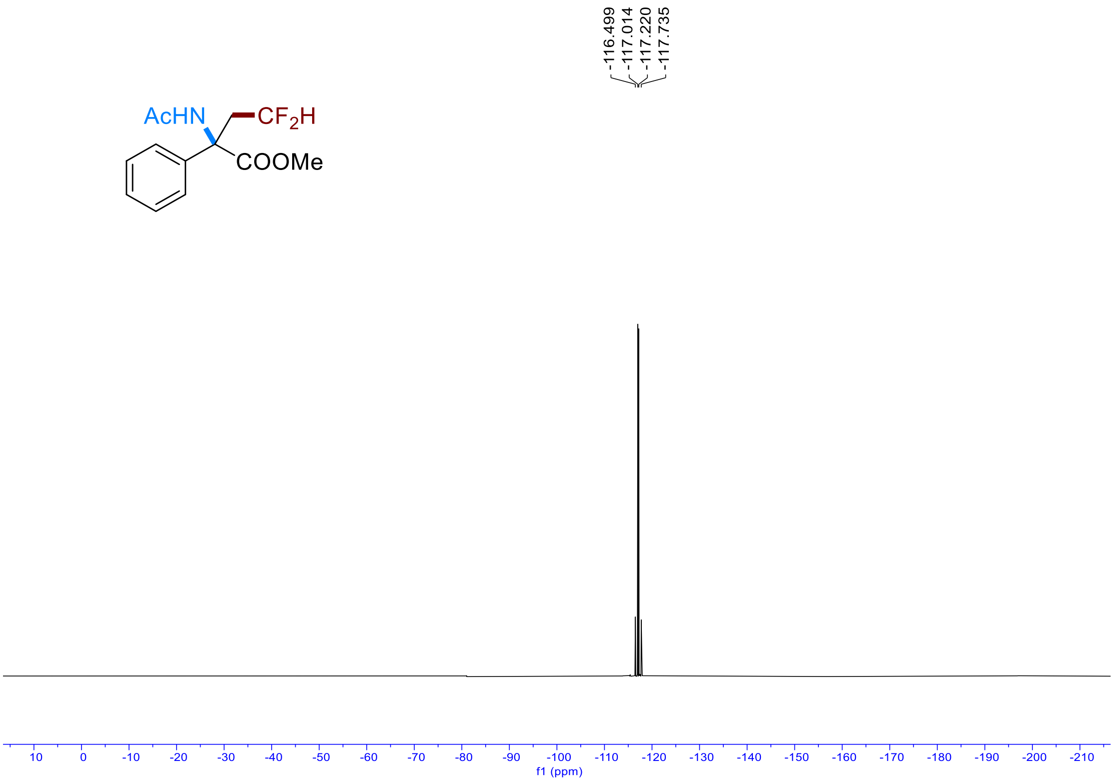
^{19}**F NMR** (565 MHz, CDCl$_3$) – (**3bc**)



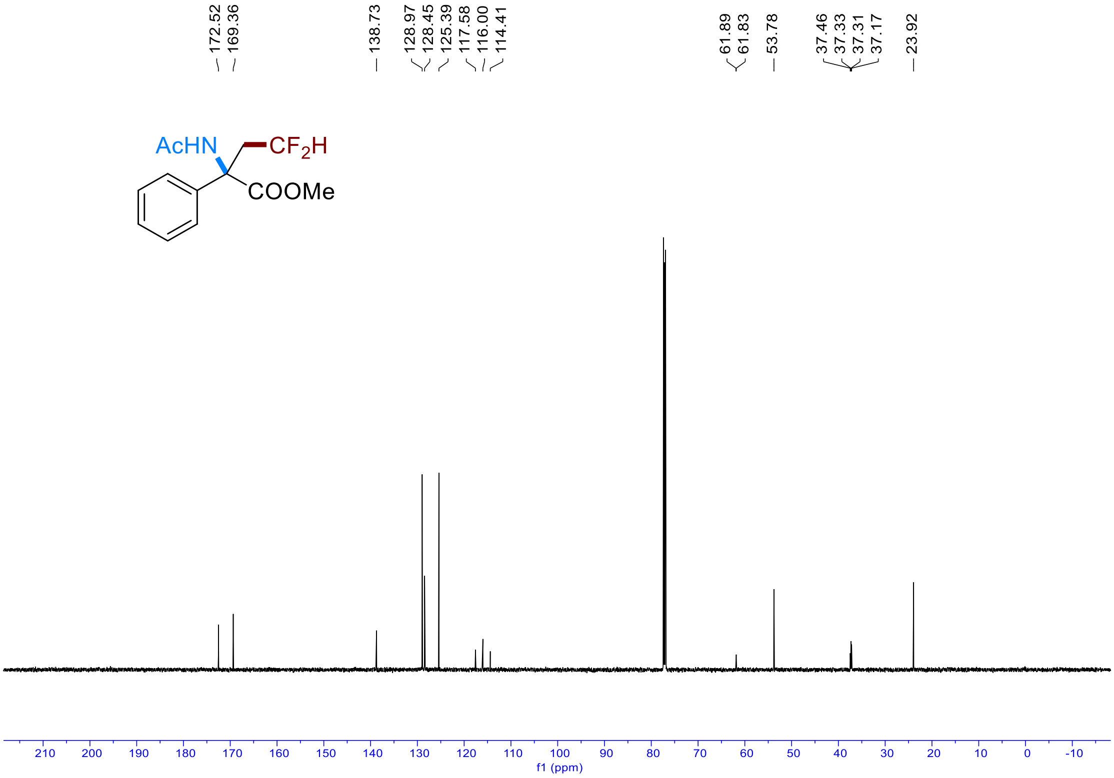
^{13}**C NMR** (151 MHz, CDCl$_3$) – (**3bc**)



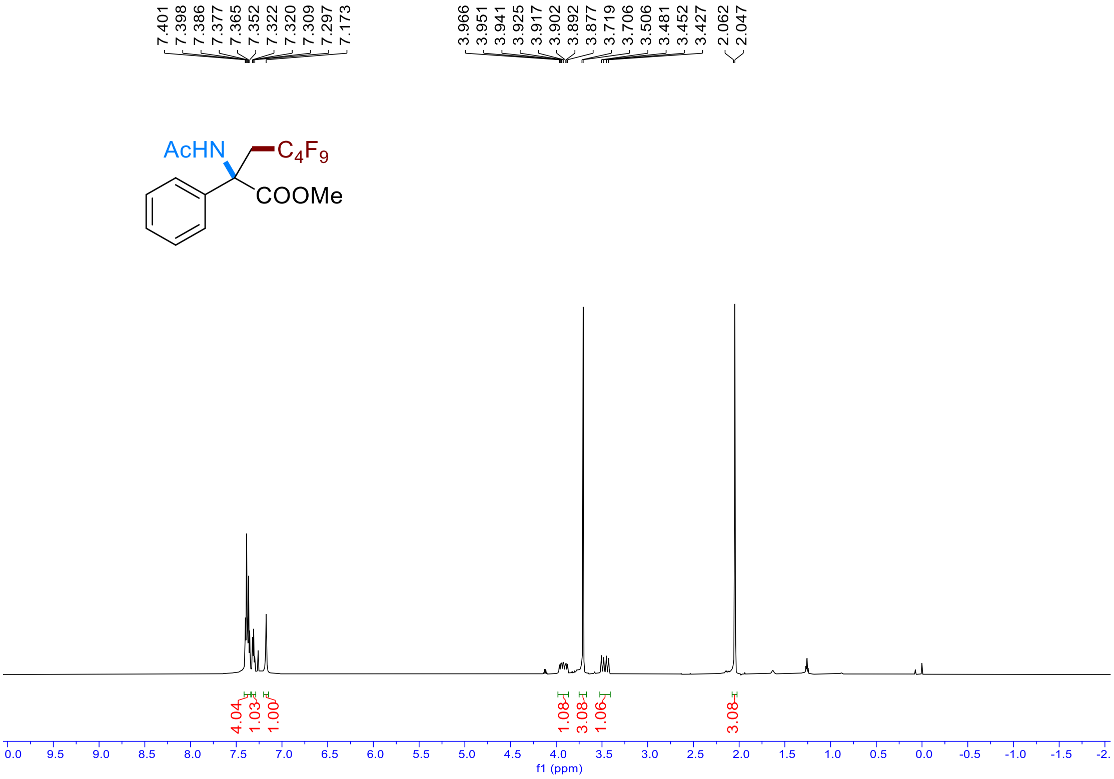
^{1}**H NMR** (600 MHz, CDCl$_3$) – (**3bd**)



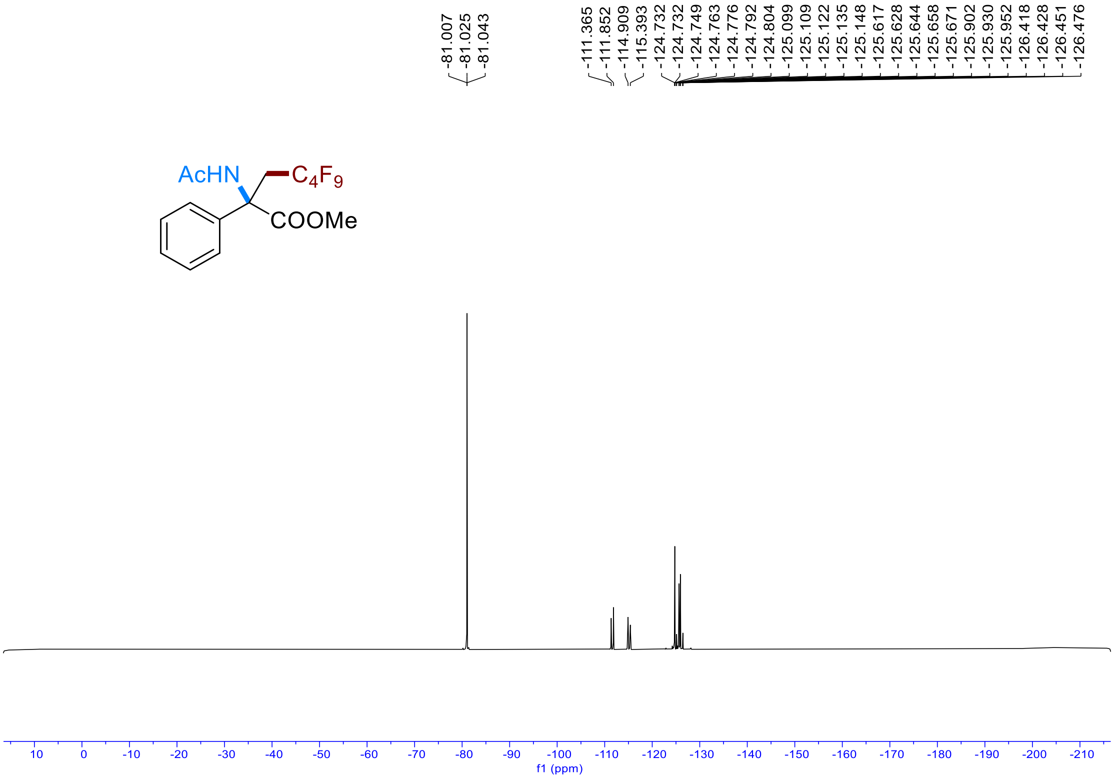
^{19}F NMR (565 MHz, CDCl$_3$) – (**3bd**)



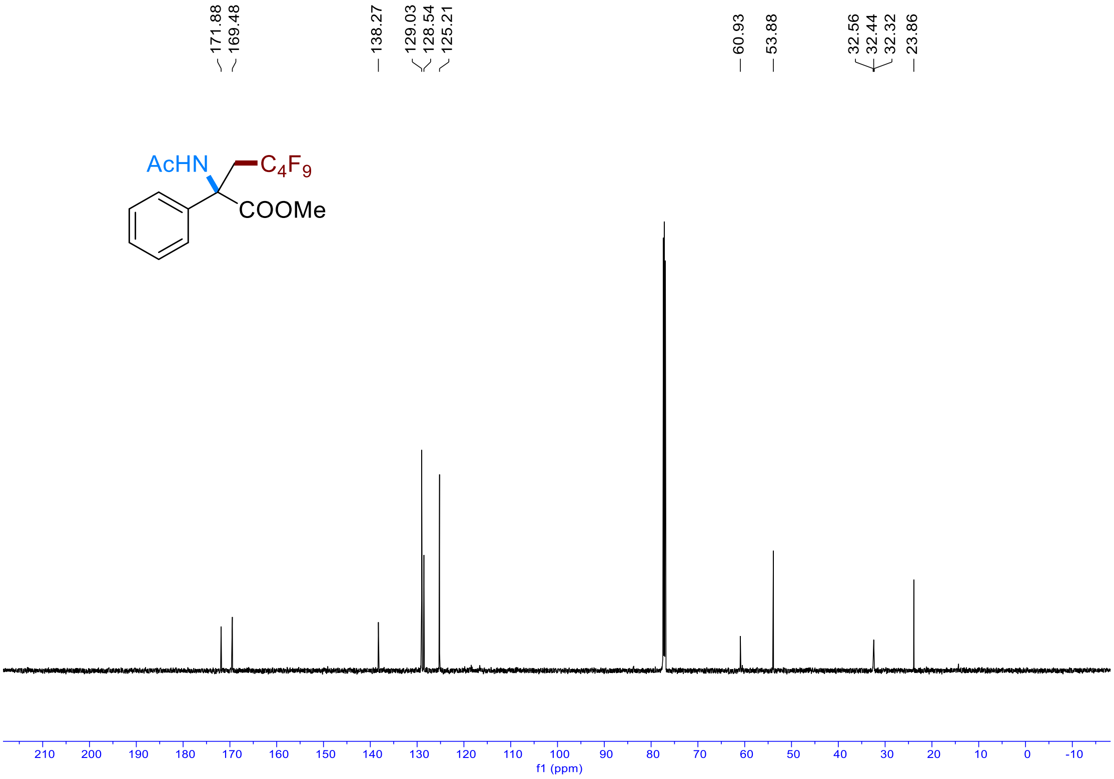
^{13}C NMR (151 MHz, CDCl$_3$) – (**3bd**)



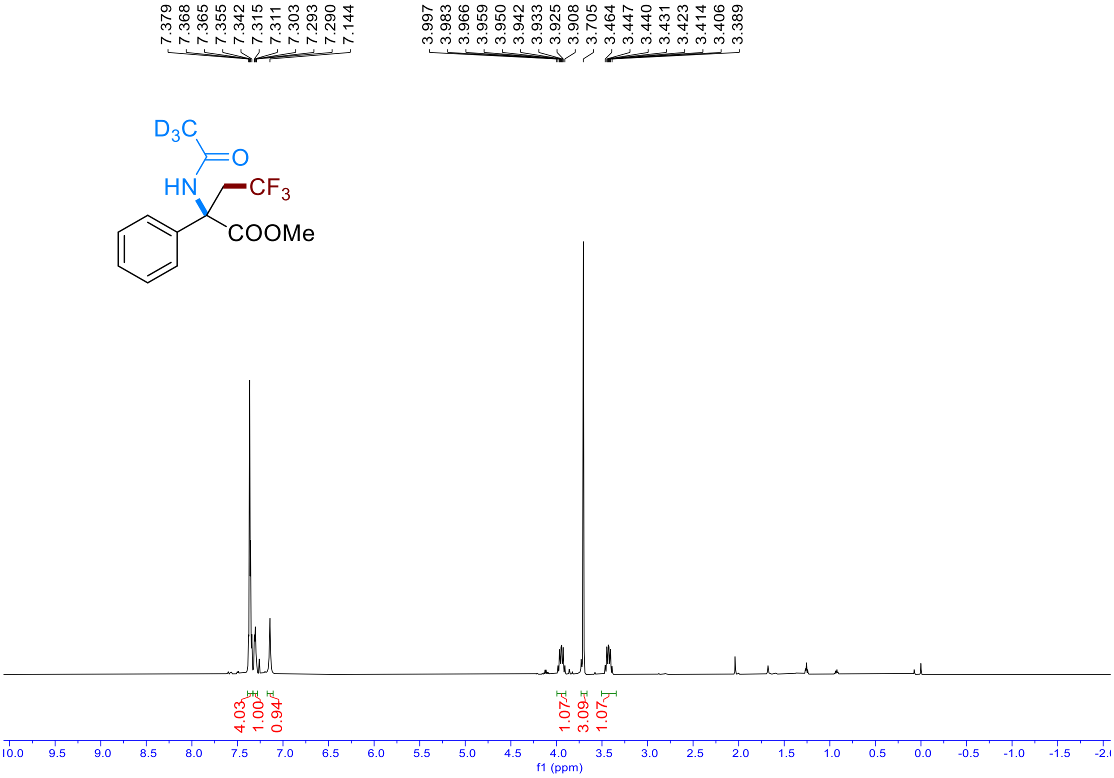
^{1}H NMR (600 MHz, CDCl$_3$) – (**3be**)



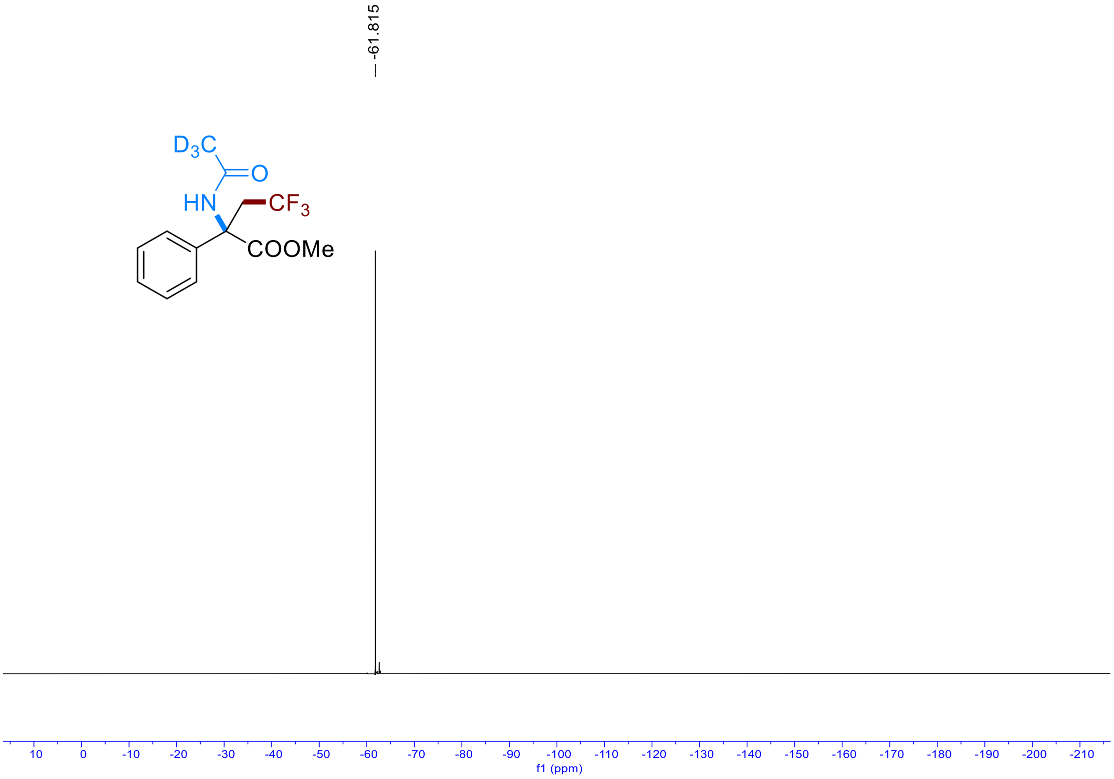
^{19}F NMR (565 MHz, CDCl$_3$) – (**3be**)



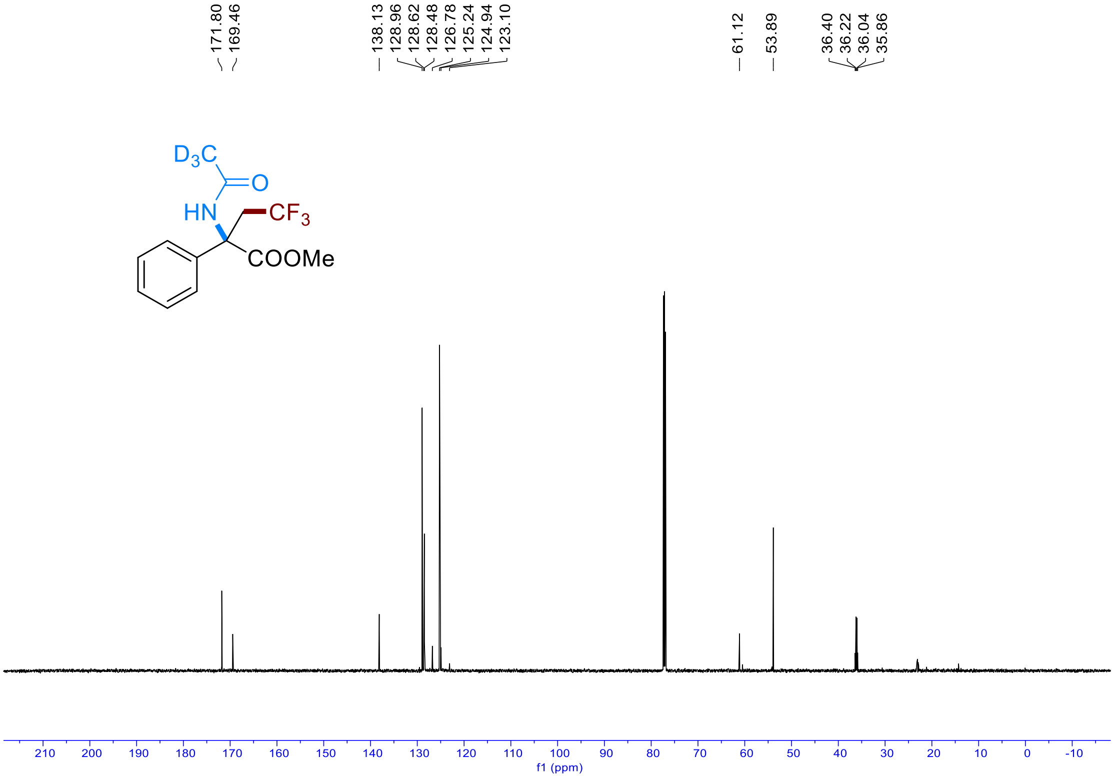
^{13}C NMR (151 MHz, CDCl$_3$) – (**3be**)



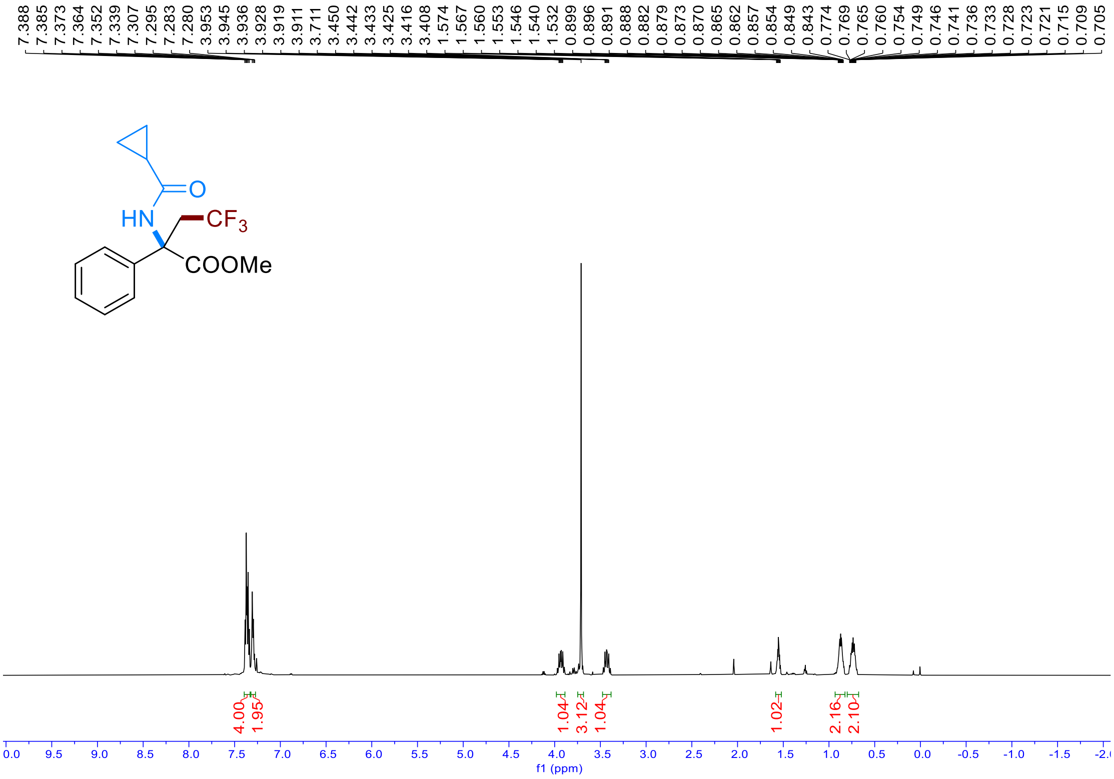
^{1}H NMR (600 MHz, CDCl$_3$) – (**3bf**)



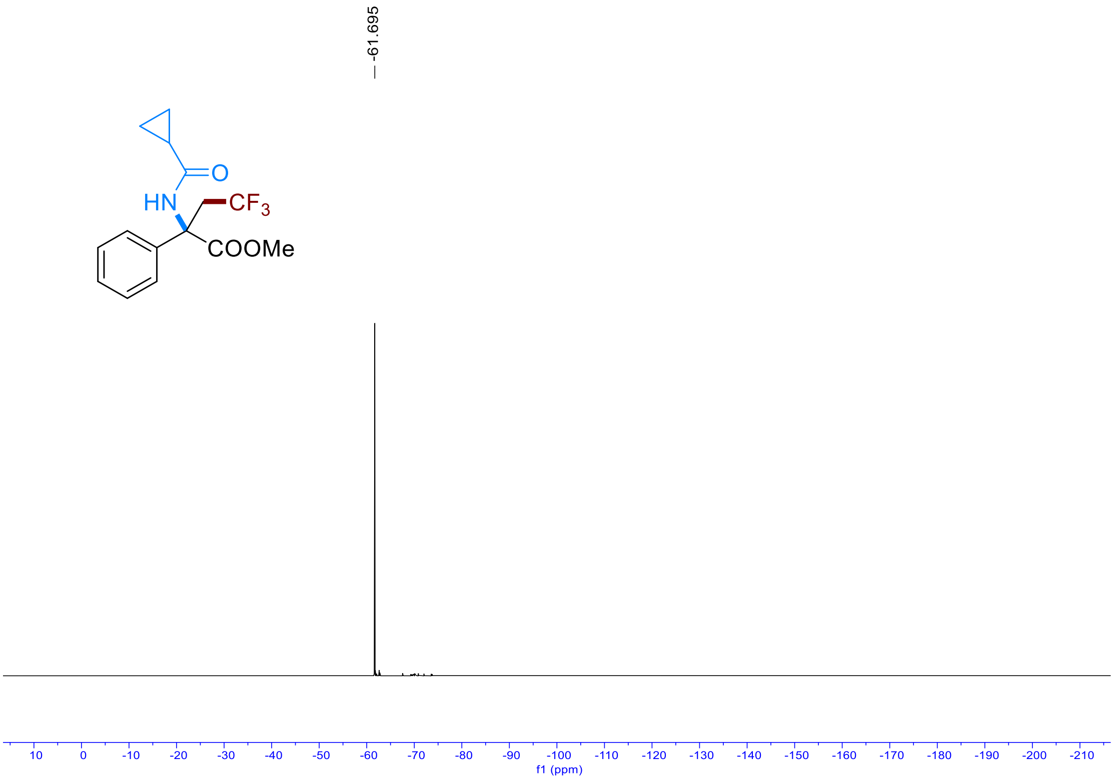
^{19}**F NMR** (565 MHz, CDCl$_3$) – (**3bf**)



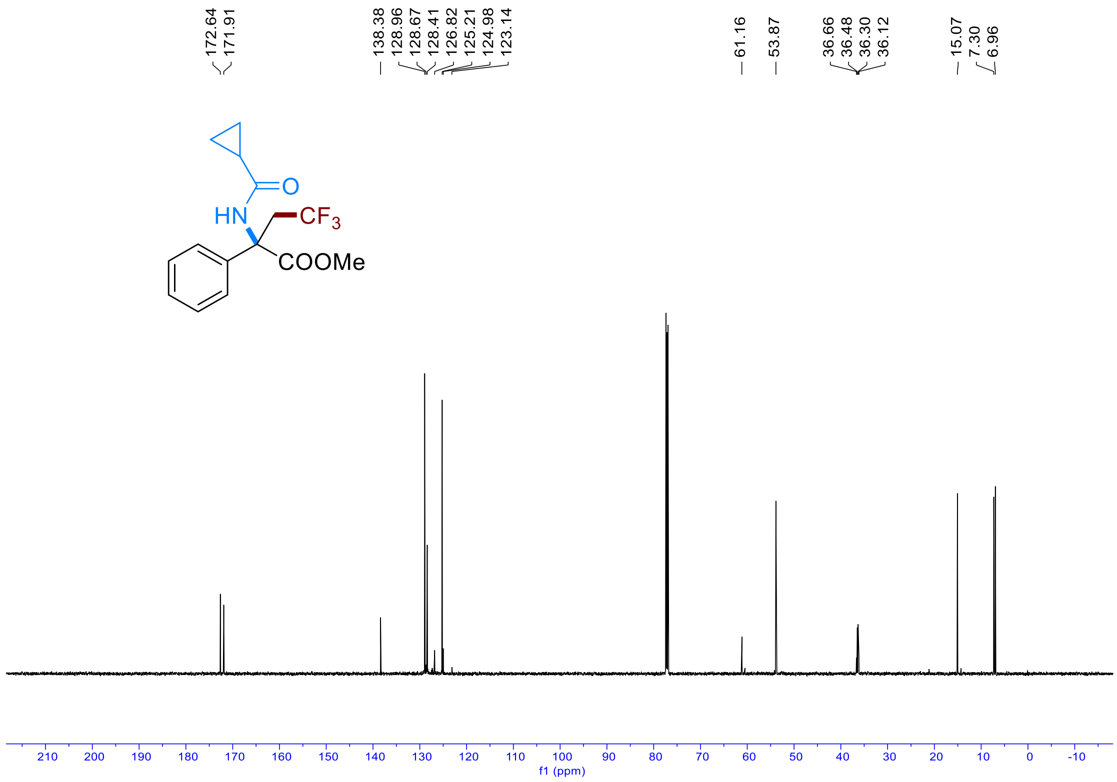
^{13}**C NMR** (151 MHz, CDCl$_3$) – (**3bf**)



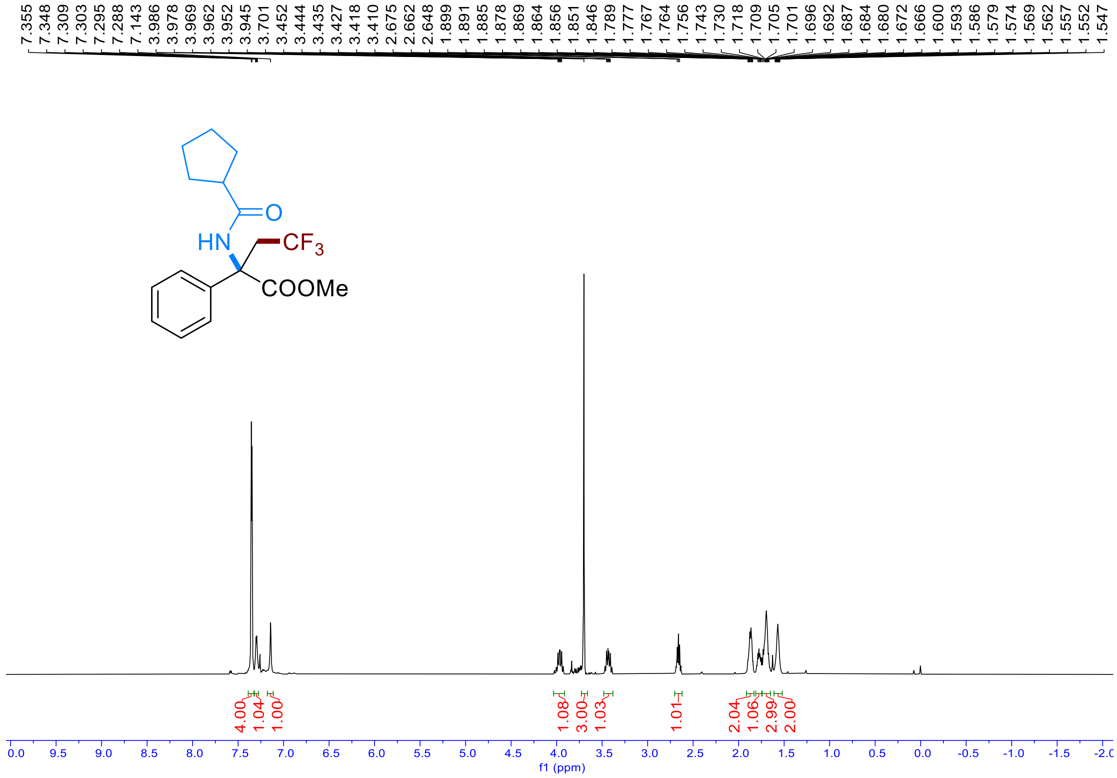
^{1}H NMR (600 MHz, $CDCl_3$) – (**3bg**)



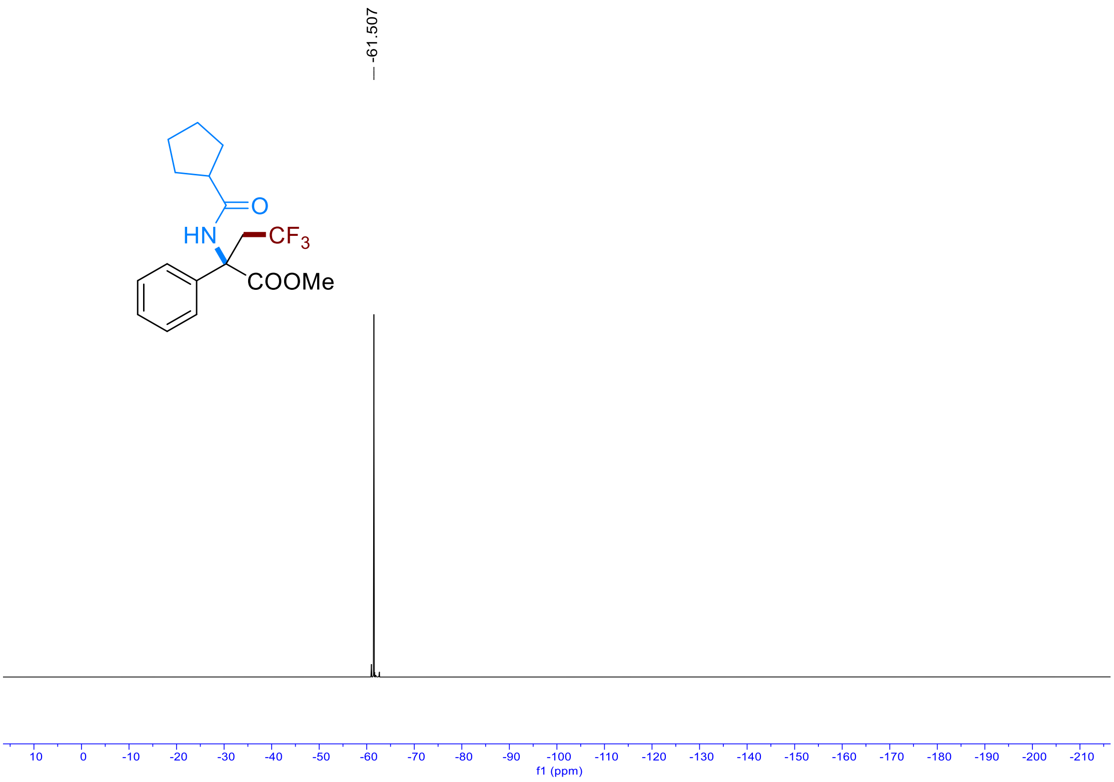
^{19}F NMR (565 MHz, $CDCl_3$) – (**3bg**)



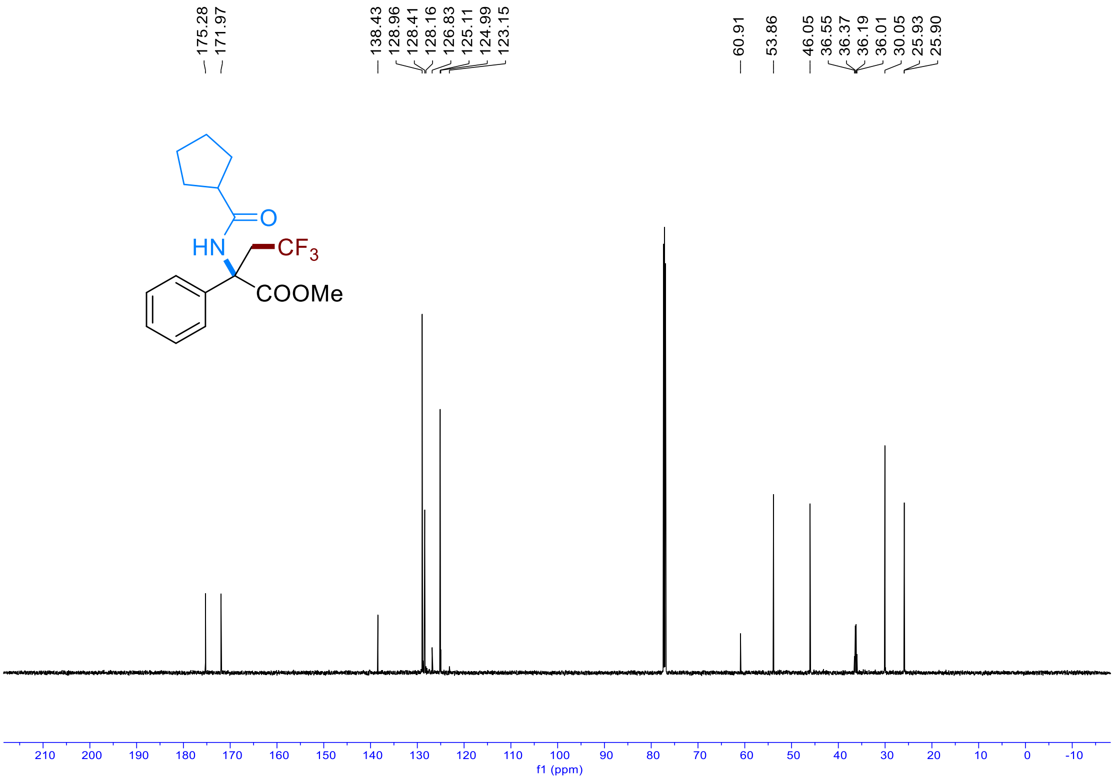
^{13}C NMR (151 MHz, CDCl$_3$) – (**3bg**)



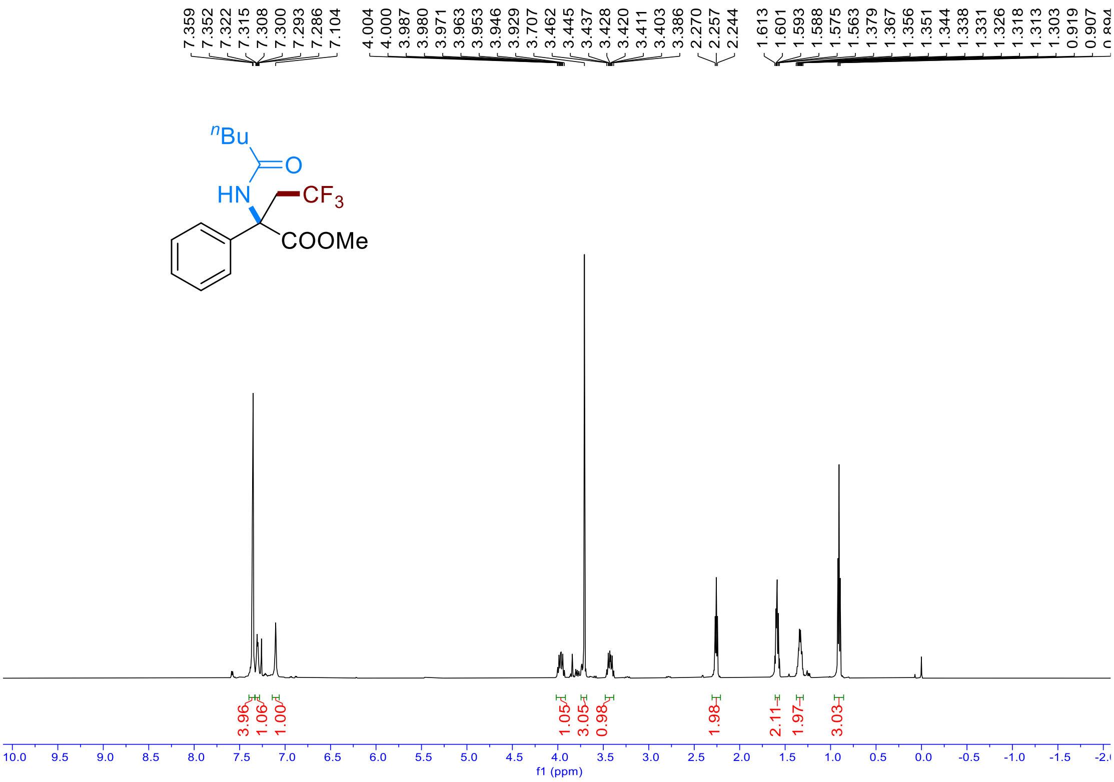
^{1}H NMR (600 MHz, CDCl$_3$) – (**3bh**)



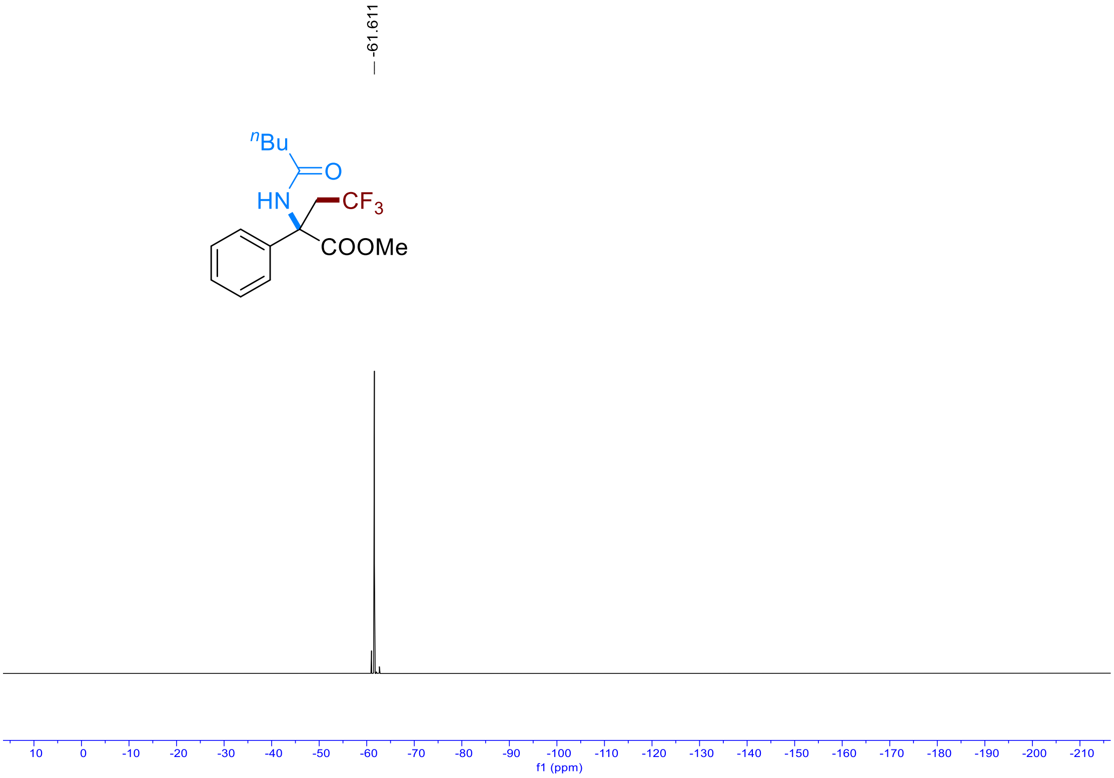
^{19}F NMR (565 MHz, CDCl$_3$) – (**3bh**)



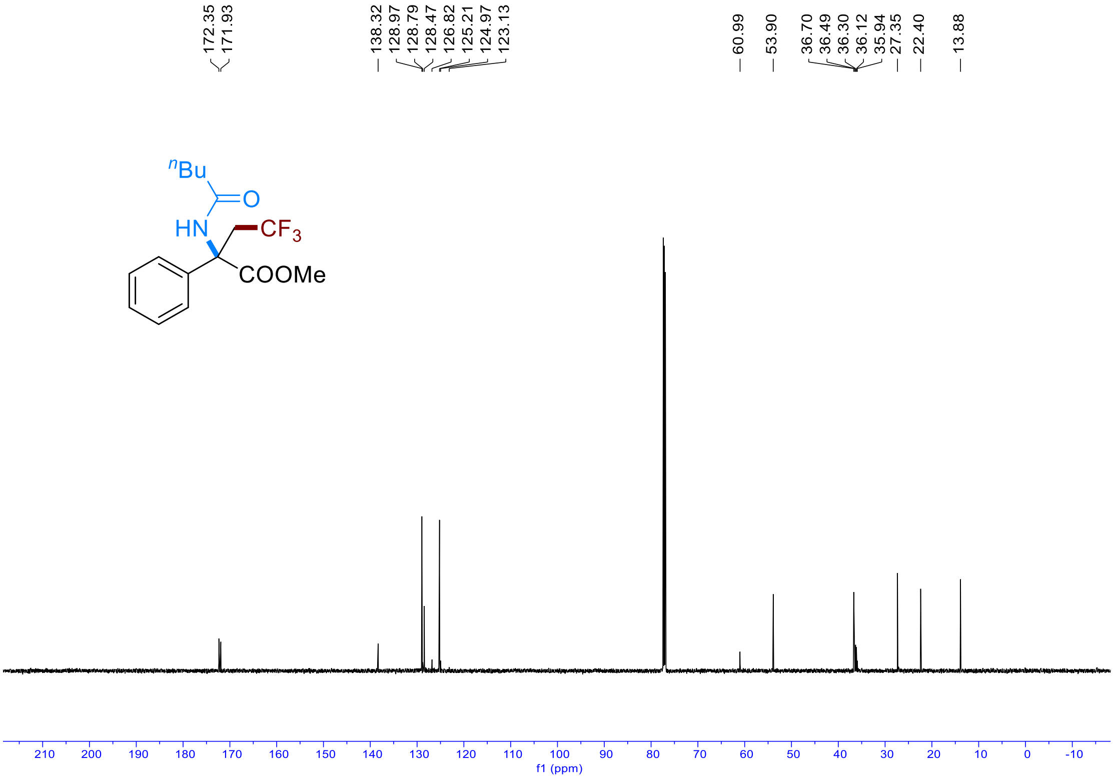
^{13}C NMR (151 MHz, CDCl$_3$) – (**3bh**)



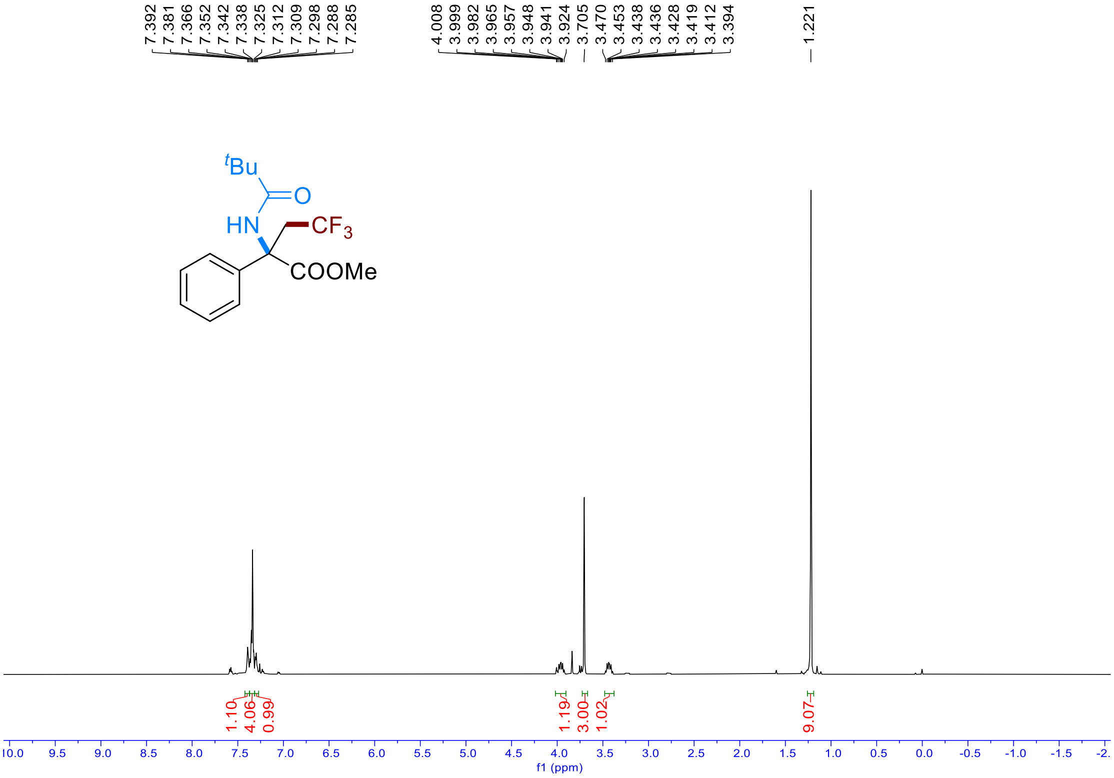
^{1}H NMR (600 MHz, CDCl$_3$) – (**3bi**)



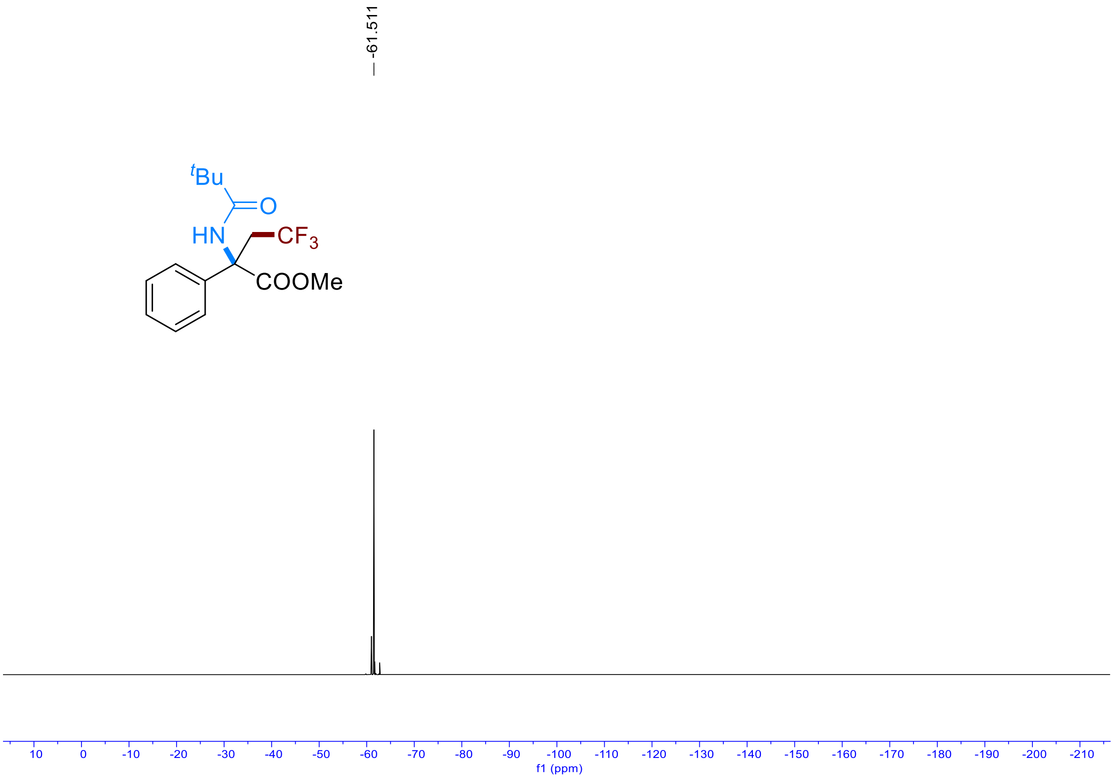
^{19}F NMR (565 MHz, CDCl$_3$) – (**3bi**)



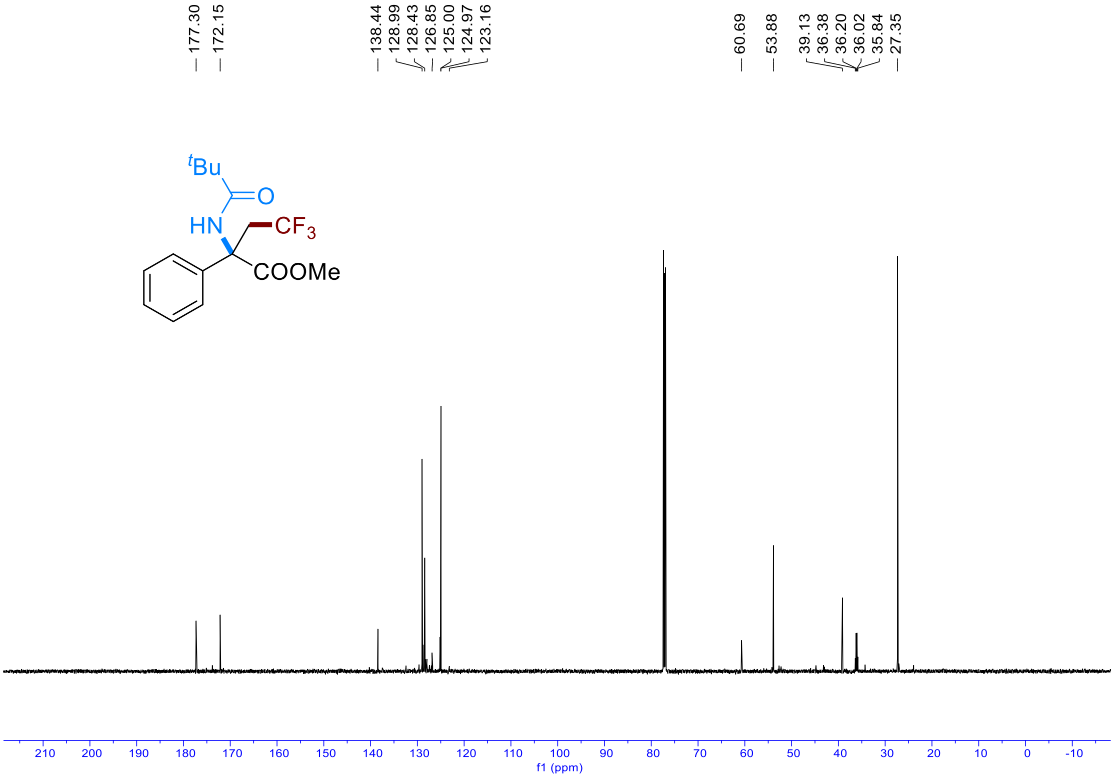
^{13}C NMR (151 MHz, CDCl$_3$) – (**3bi**)



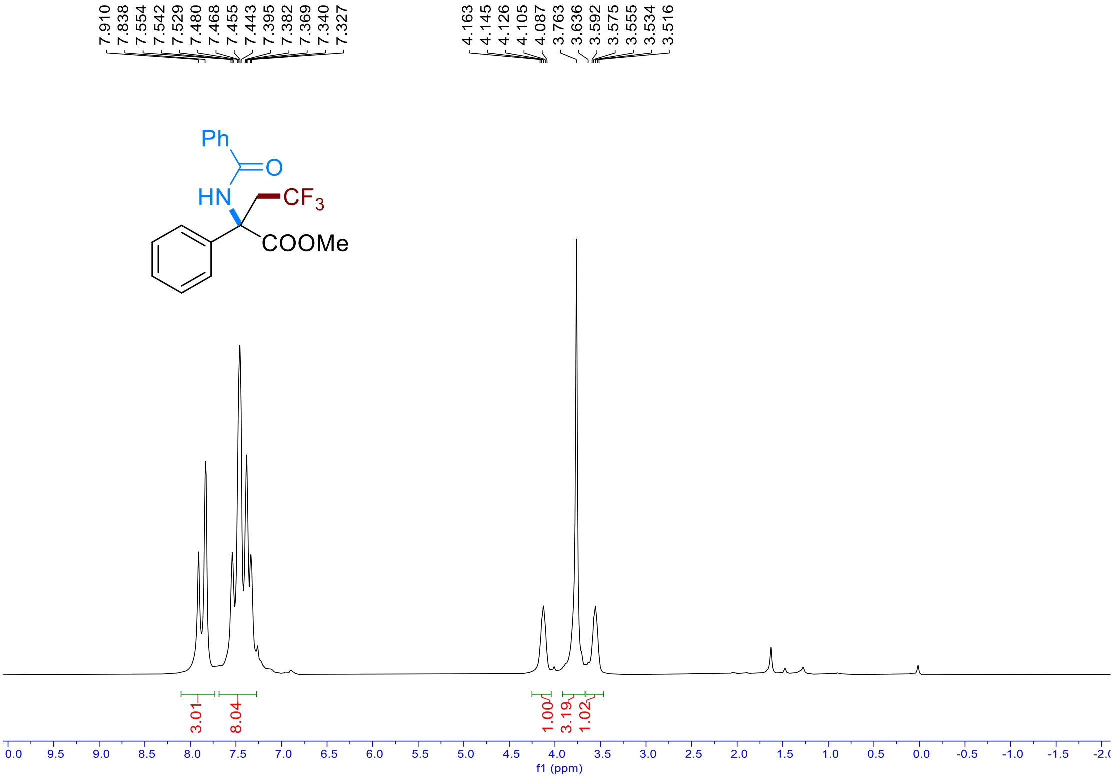
^{1}H NMR (600 MHz, CDCl$_3$) – (**3bj**)



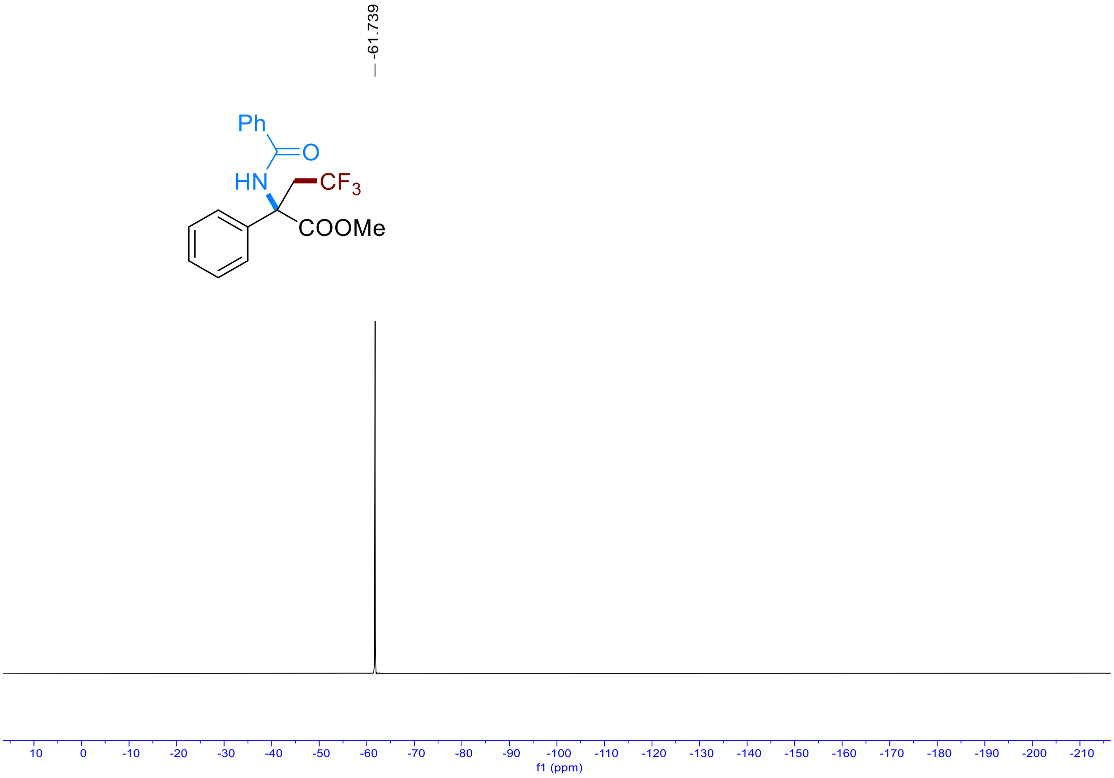
^{19}**F NMR** (565 MHz, CDCl$_3$) – (**3bj**)



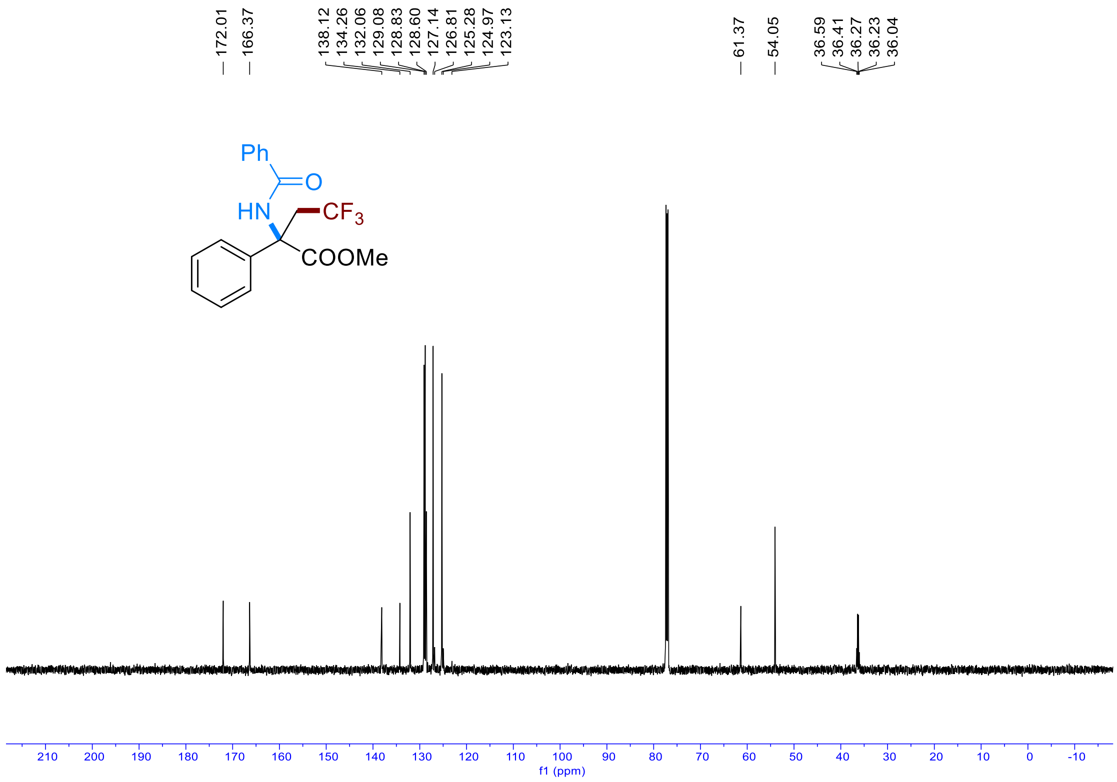
^{13}**C NMR** (151 MHz, CDCl$_3$) – (**3bj**)



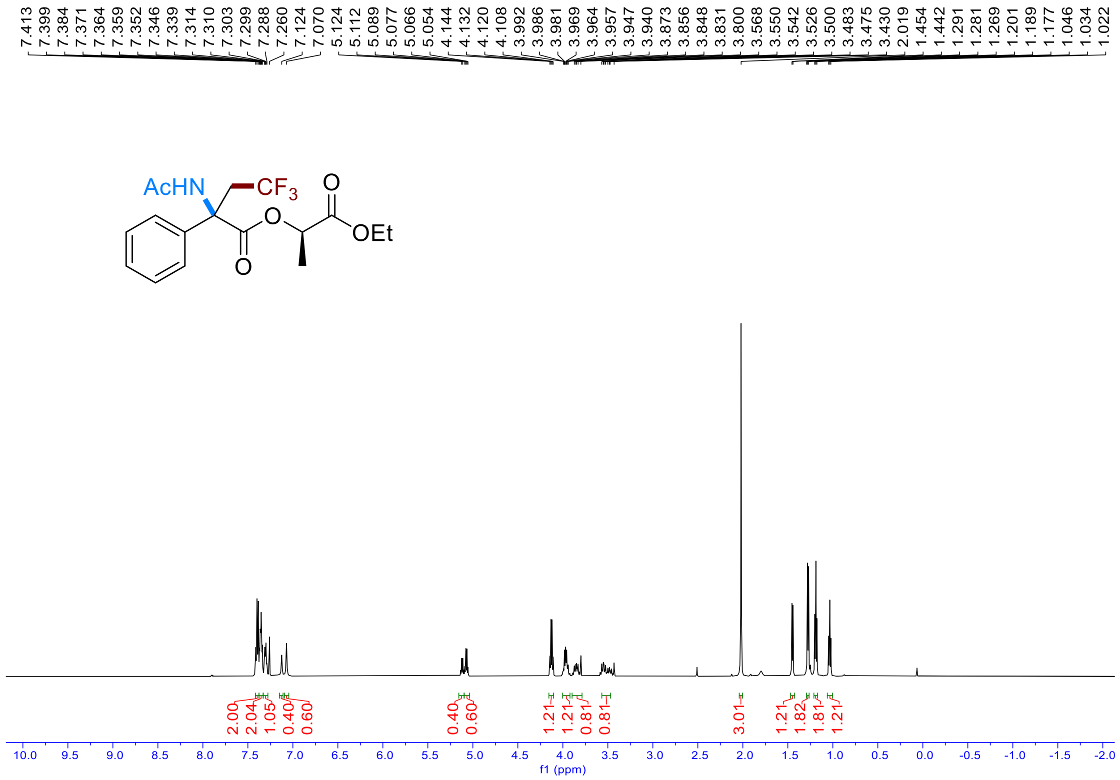
^{1}**H NMR** (600 MHz, CDCl$_3$) – (**3bk**)



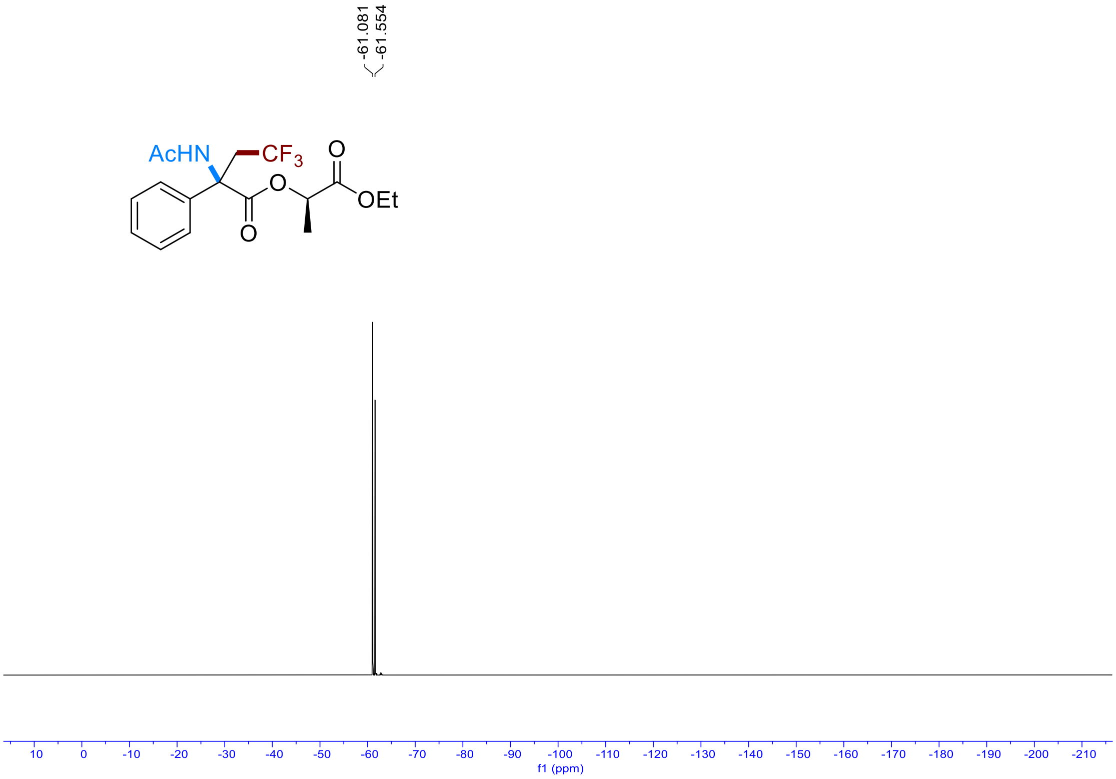
^{19}**F NMR** (565 MHz, CDCl$_3$) – (**3bk**)



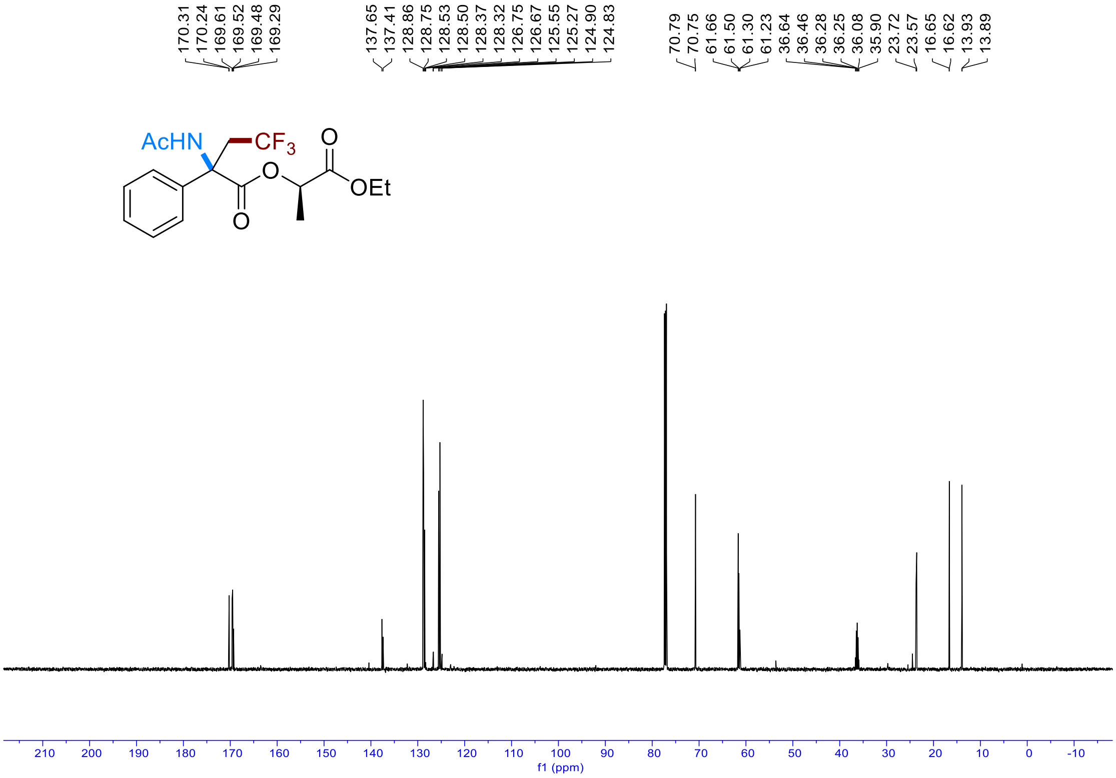
^{13}C NMR (151 MHz, CDCl$_3$) – (**3bk**)



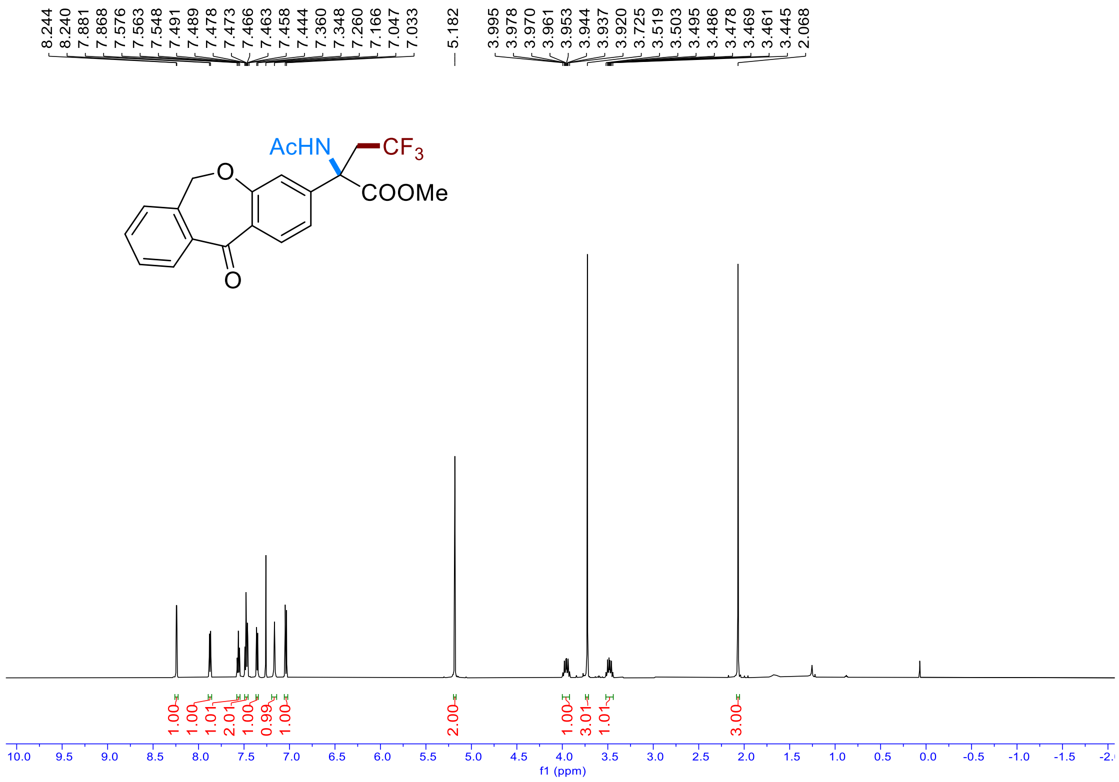
^{1}H NMR (600 MHz, CDCl$_3$) – (**3bl**)



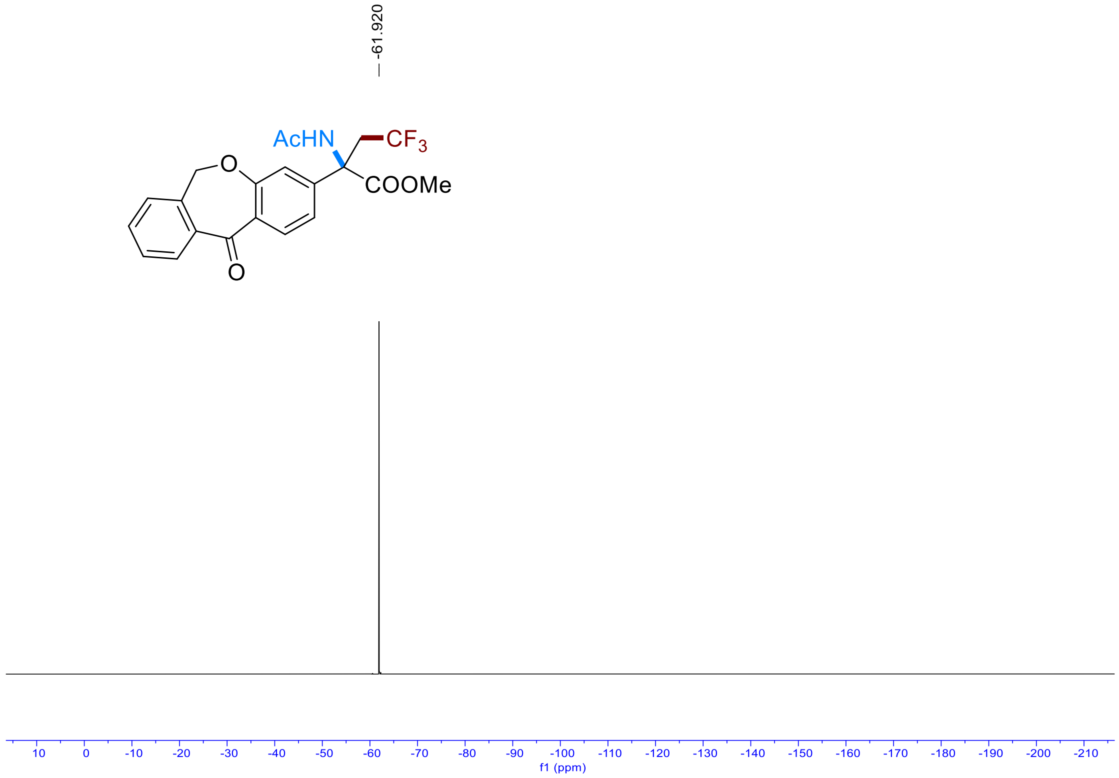
^{19}F NMR (565 MHz, CDCl$_3$) – (**3bl**)



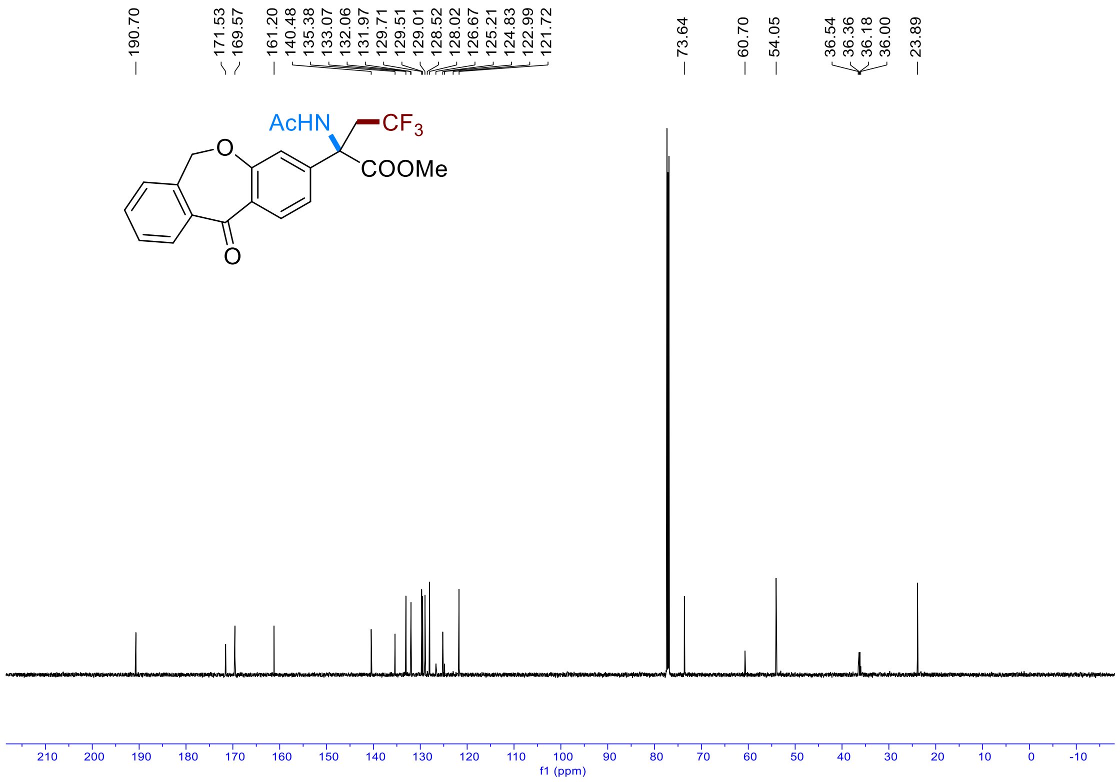
^{13}C NMR (151 MHz, CDCl$_3$) – (**3bl**)



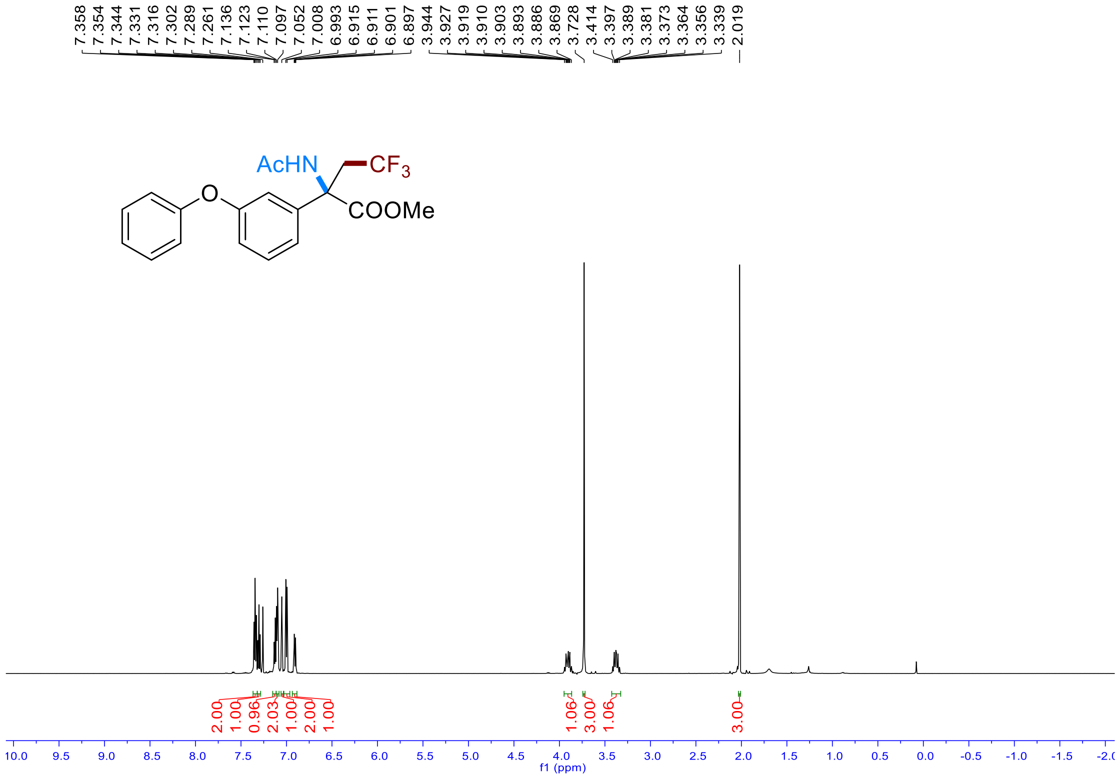
^{1}H NMR (600 MHz, CDCl$_3$) – (**3bm**)



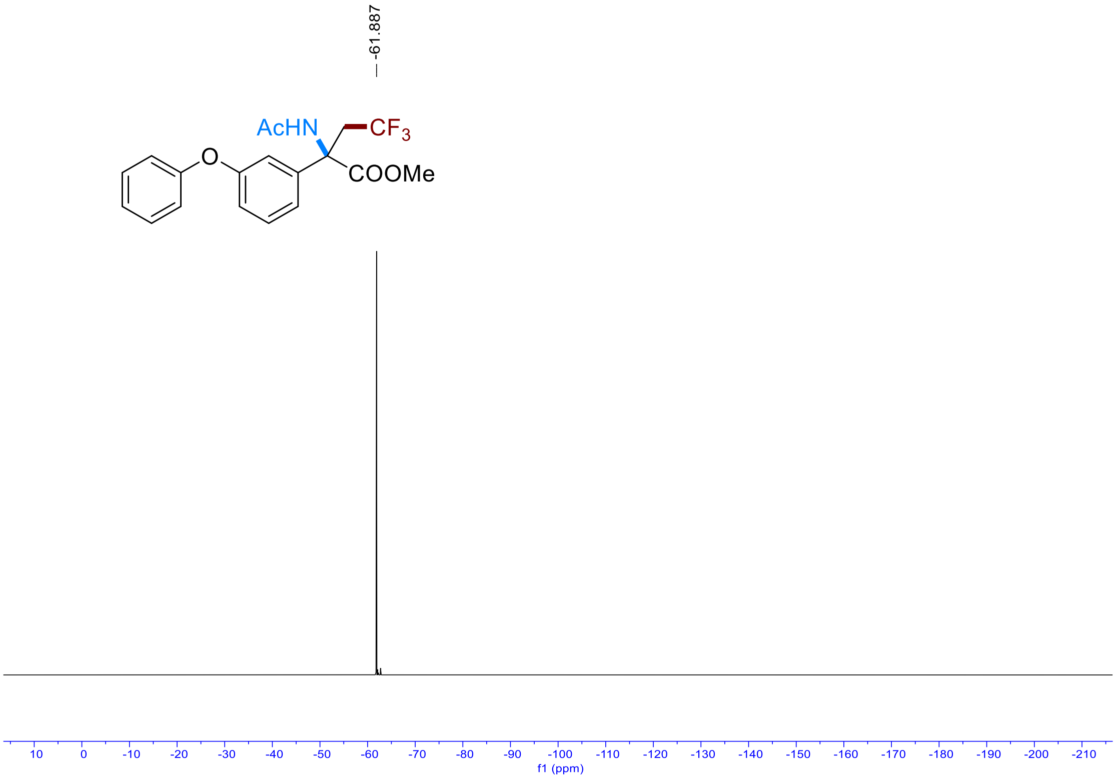
^{19}F NMR (565 MHz, CDCl$_3$) – (**3bm**)



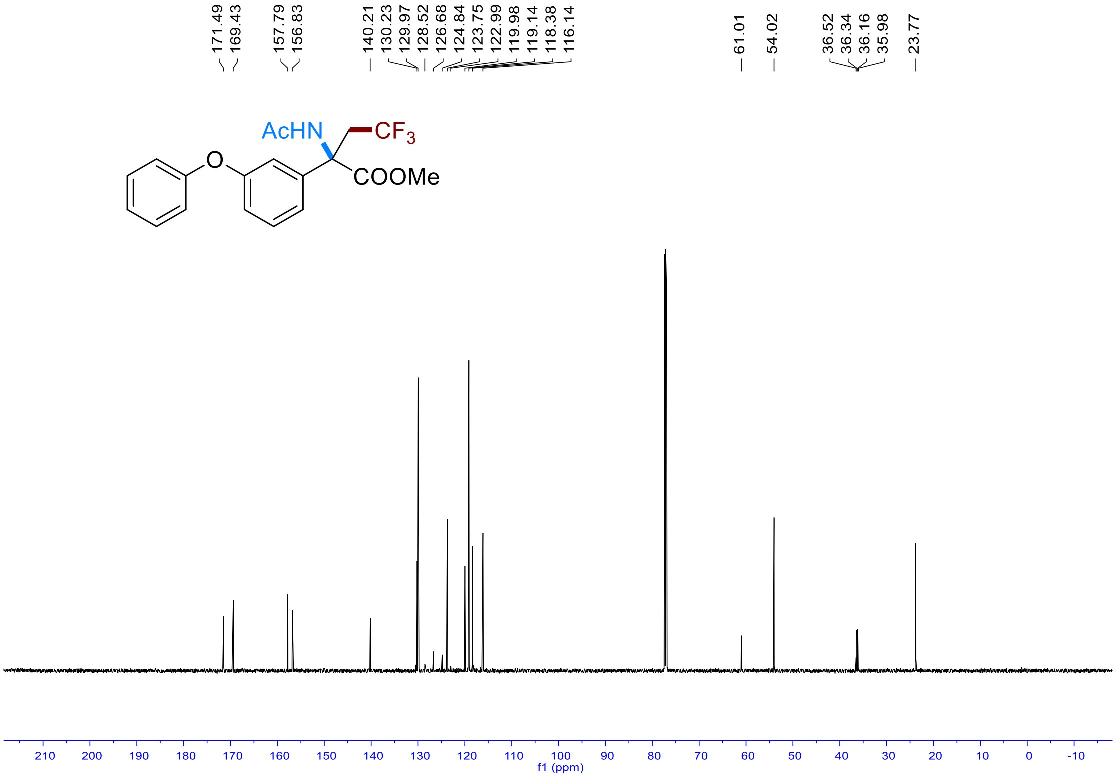
^{13}C NMR (151 MHz, CDCl$_3$) – (**3bm**)



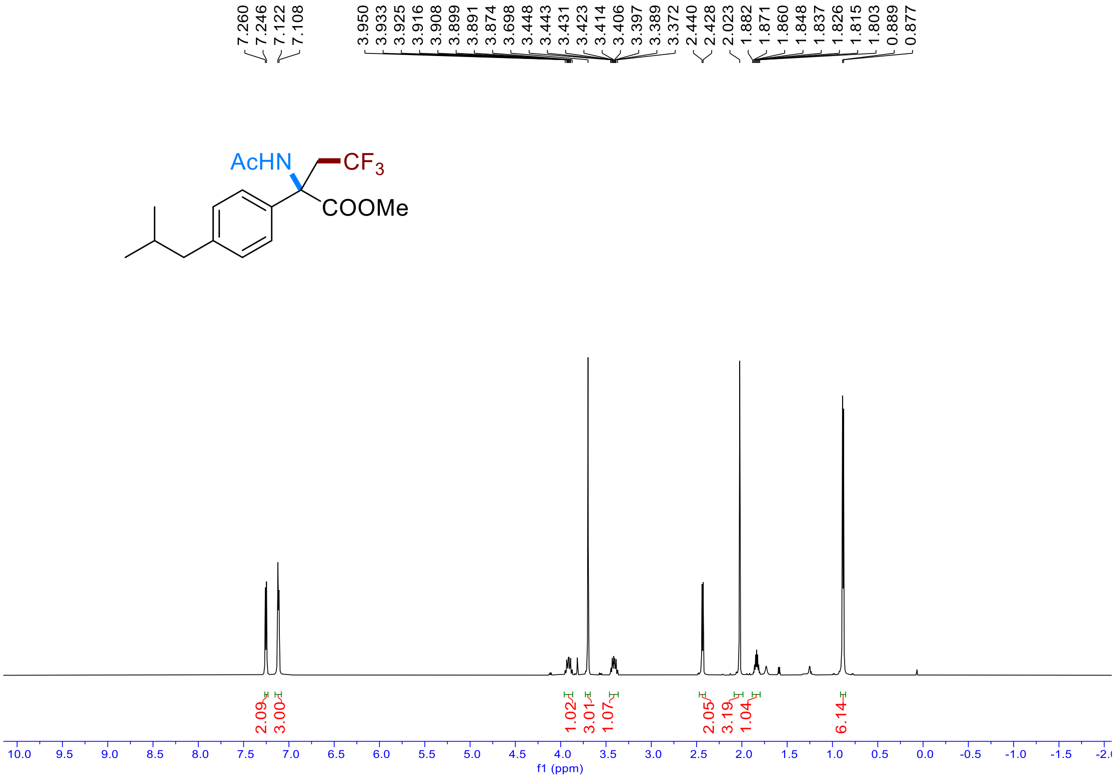
^{1}H NMR (600 MHz, CDCl$_3$) – (**3bn**)



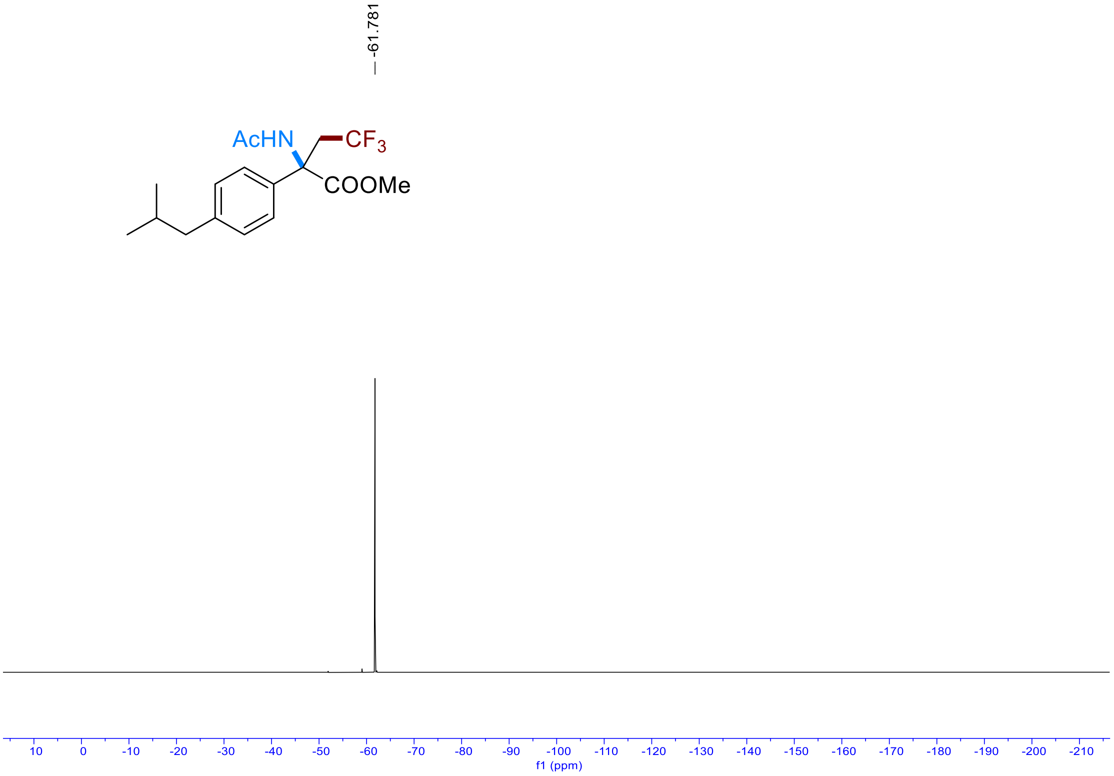
^{19}F NMR (565 MHz, CDCl$_3$) – (**3bn**)



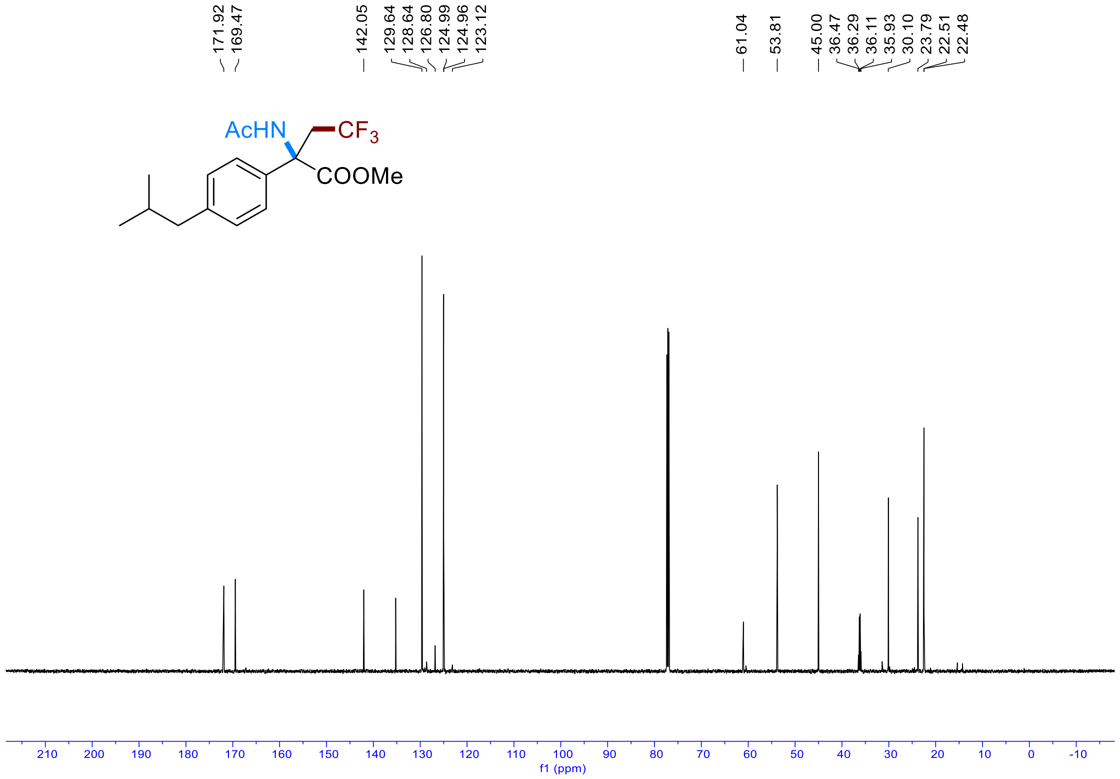
^{13}C NMR (151 MHz, CDCl$_3$) – (**3bn**)



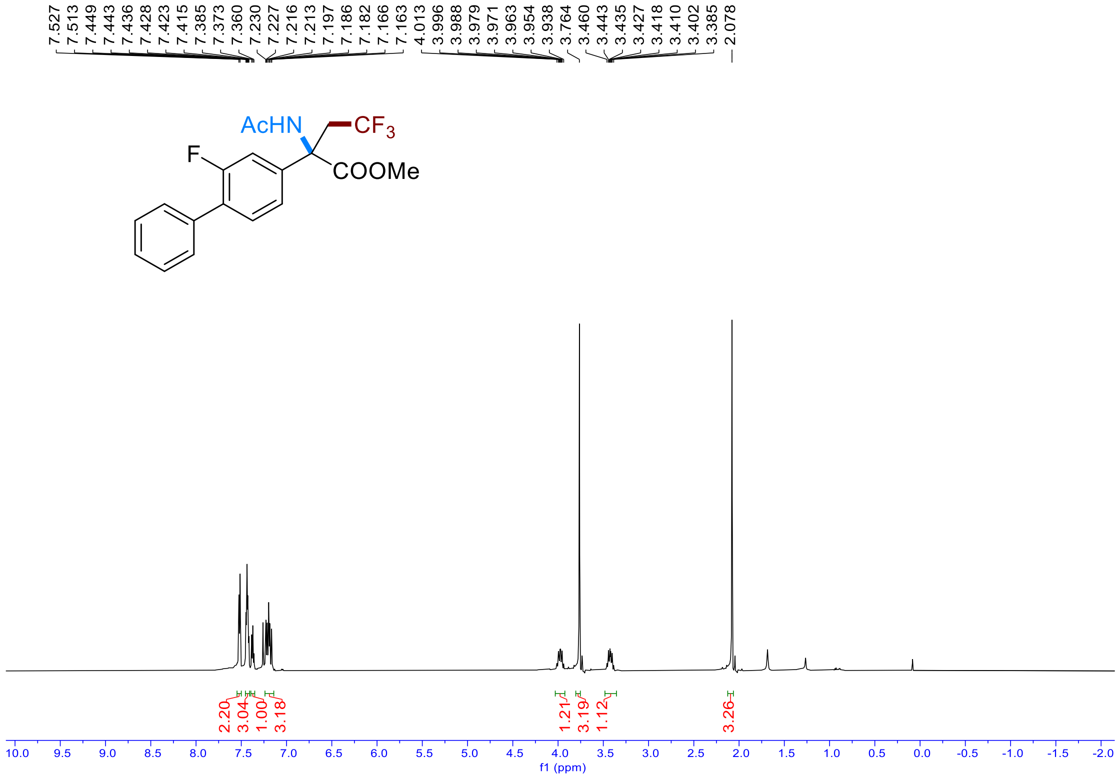
^{1}**H NMR** (600 MHz, $CDCl_3$) – (**3bo**)



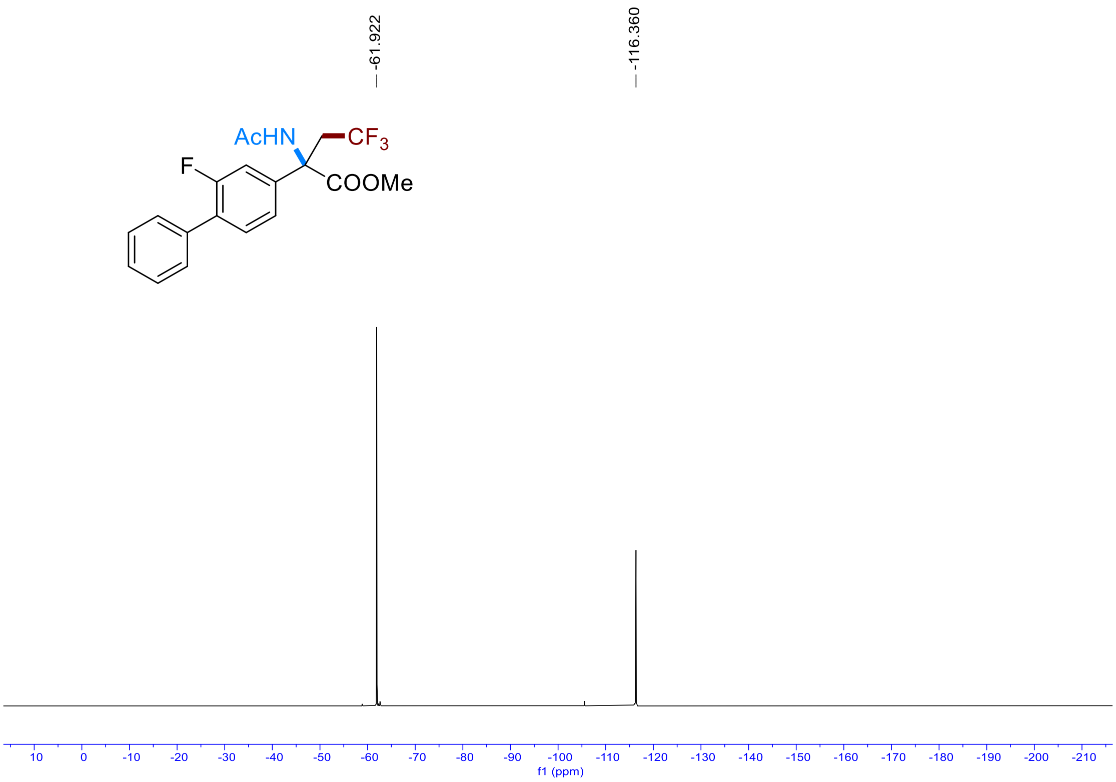
^{19}**F NMR** (565 MHz, $CDCl_3$) – (**3bo**)



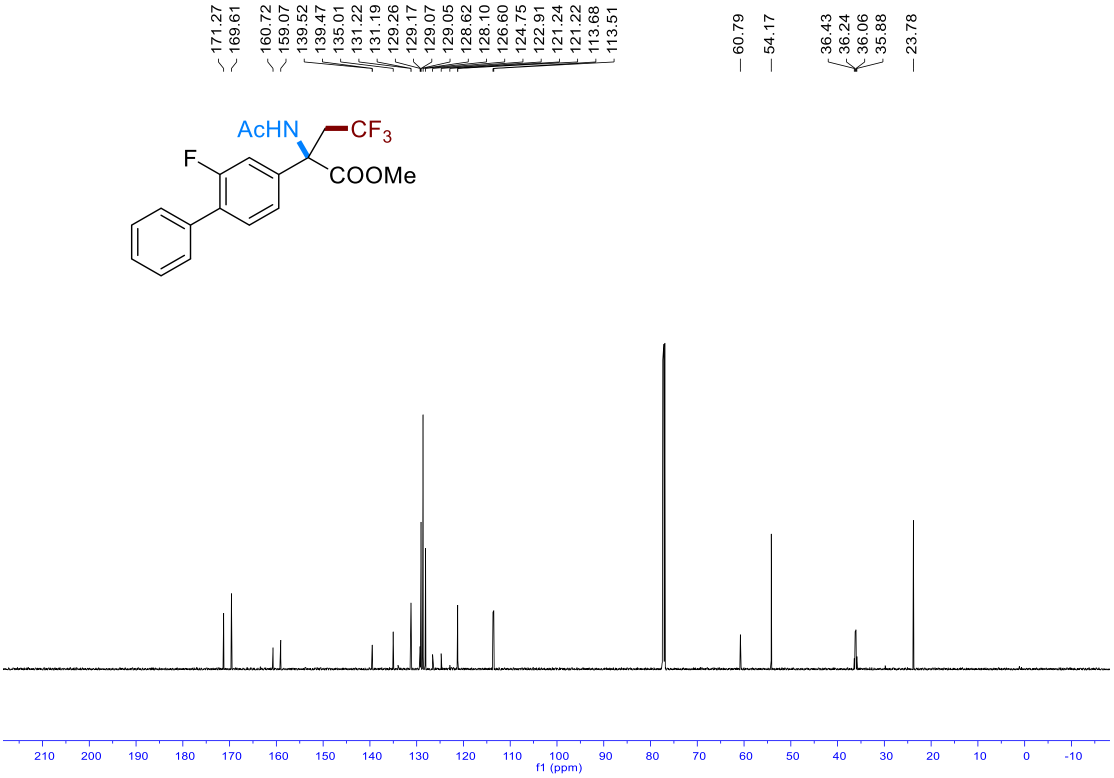
^{13}**C NMR** (151 MHz, CDCl$_3$) – (**3bo**)



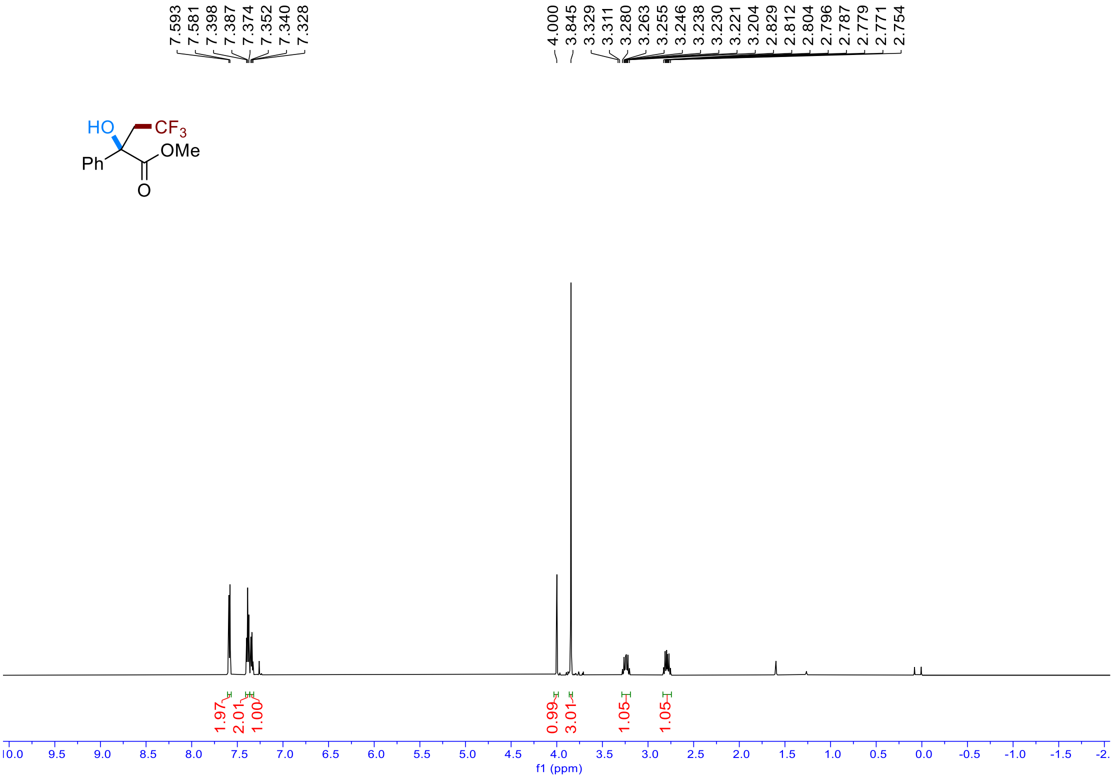
^{1}**H NMR** (600 MHz, CDCl$_3$) – (**3bp**)



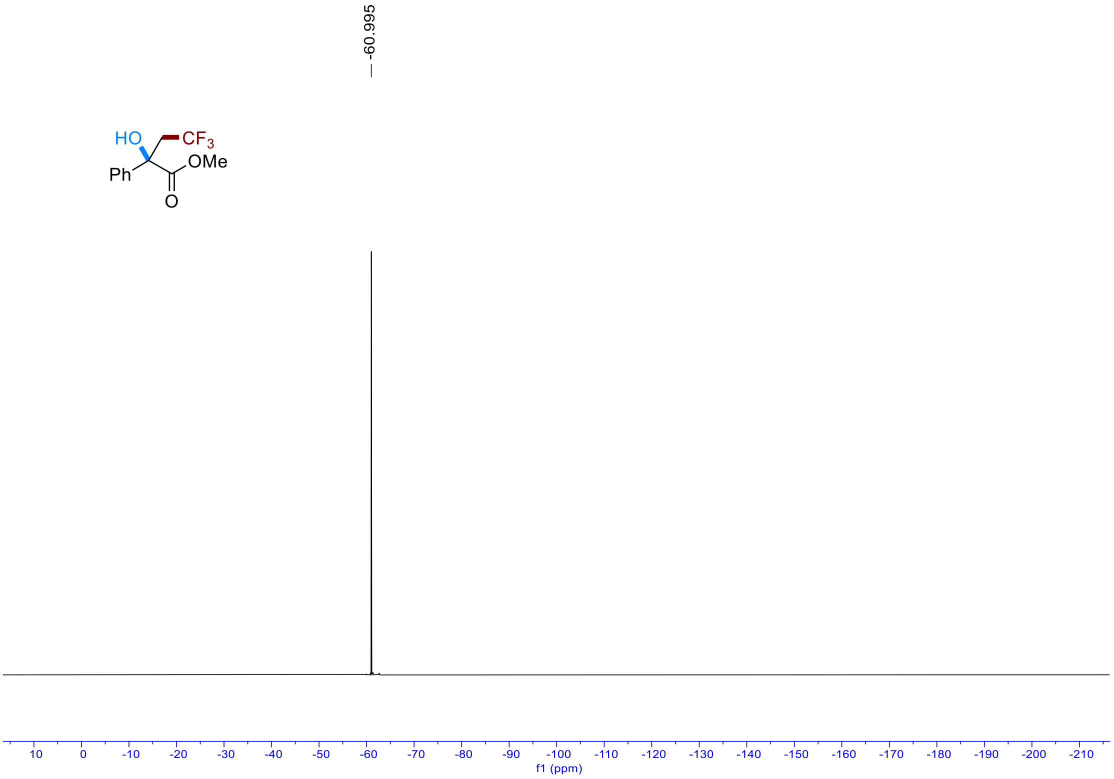
^{19}F NMR (565 MHz, CDCl$_3$) – (**3bp**)



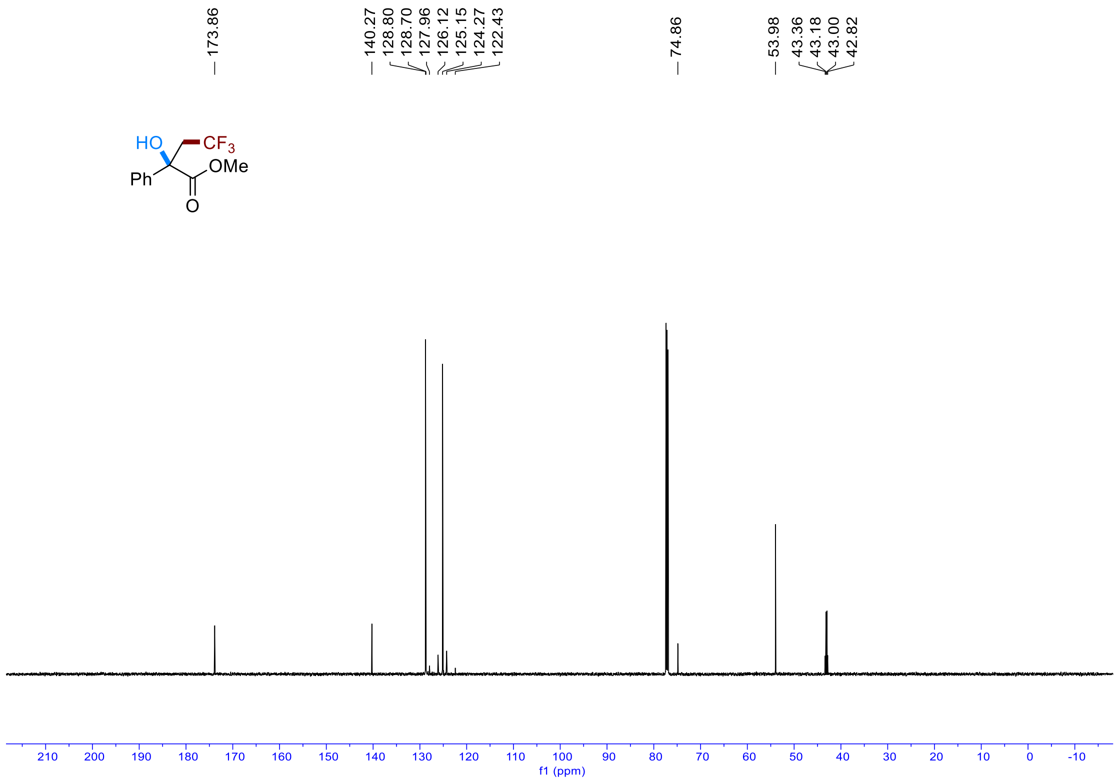
^{13}C NMR (151 MHz, CDCl$_3$) – (**3bp**)



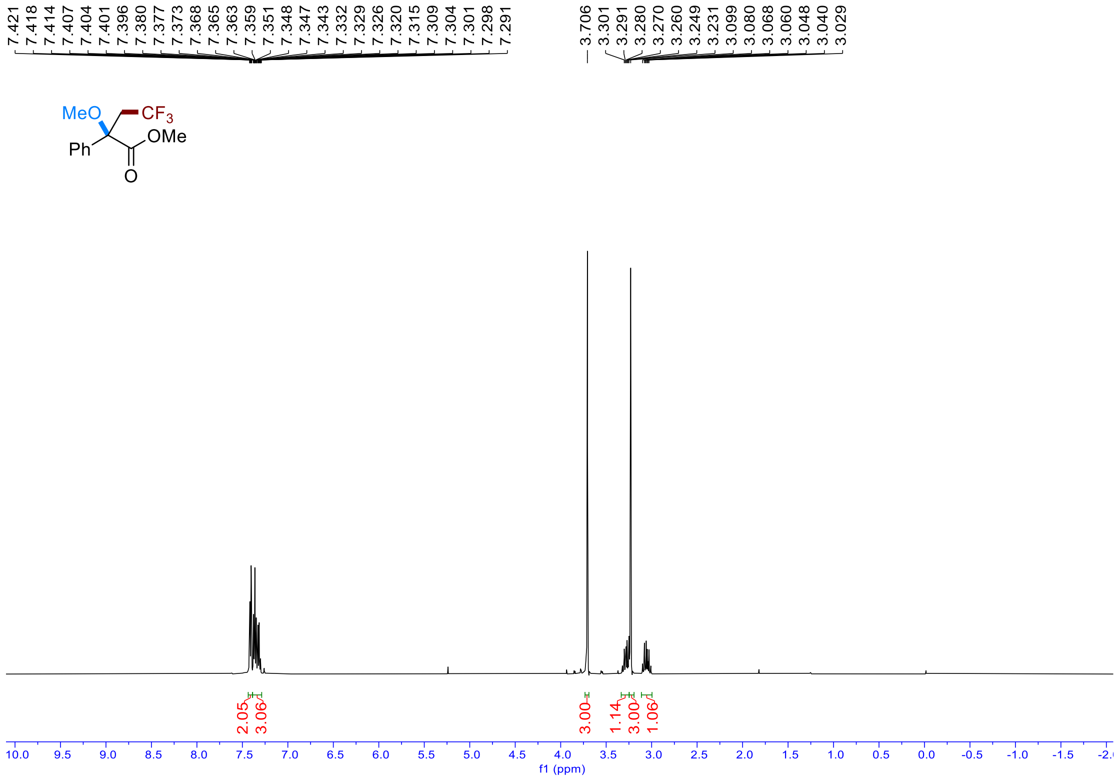
^{1}H NMR (600 MHz, CDCl$_3$) – (**6**)



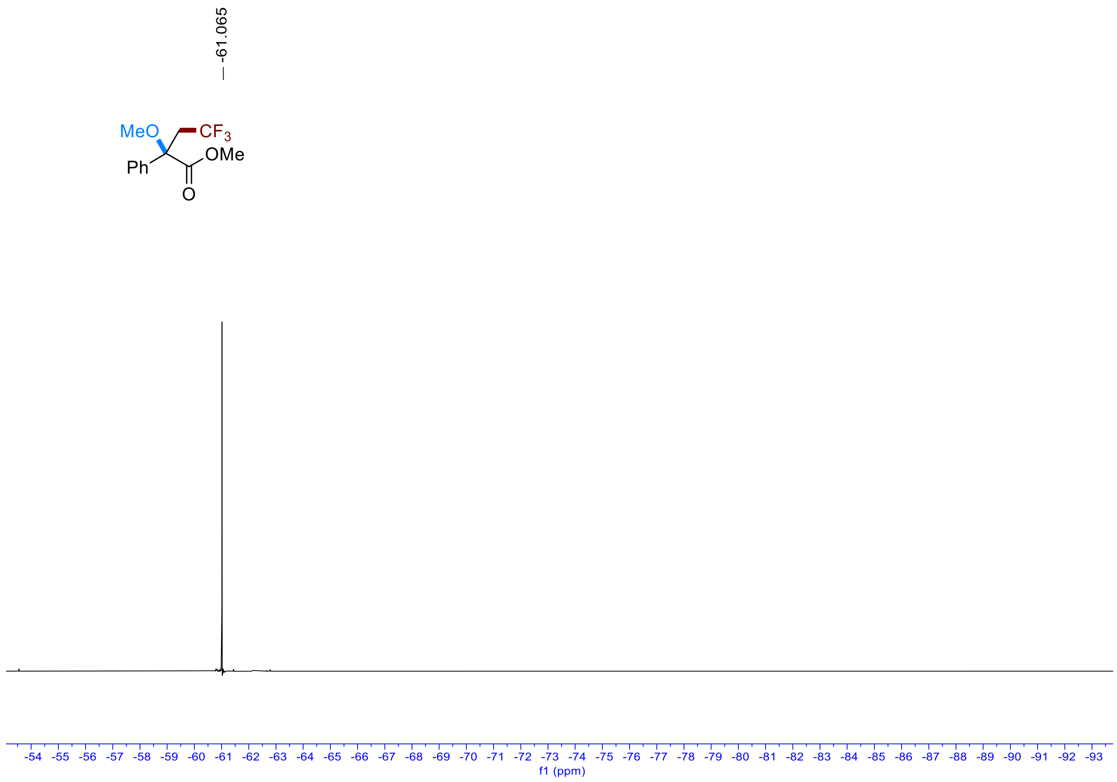
^{19}F NMR (565 MHz, CDCl$_3$) – (**6**)



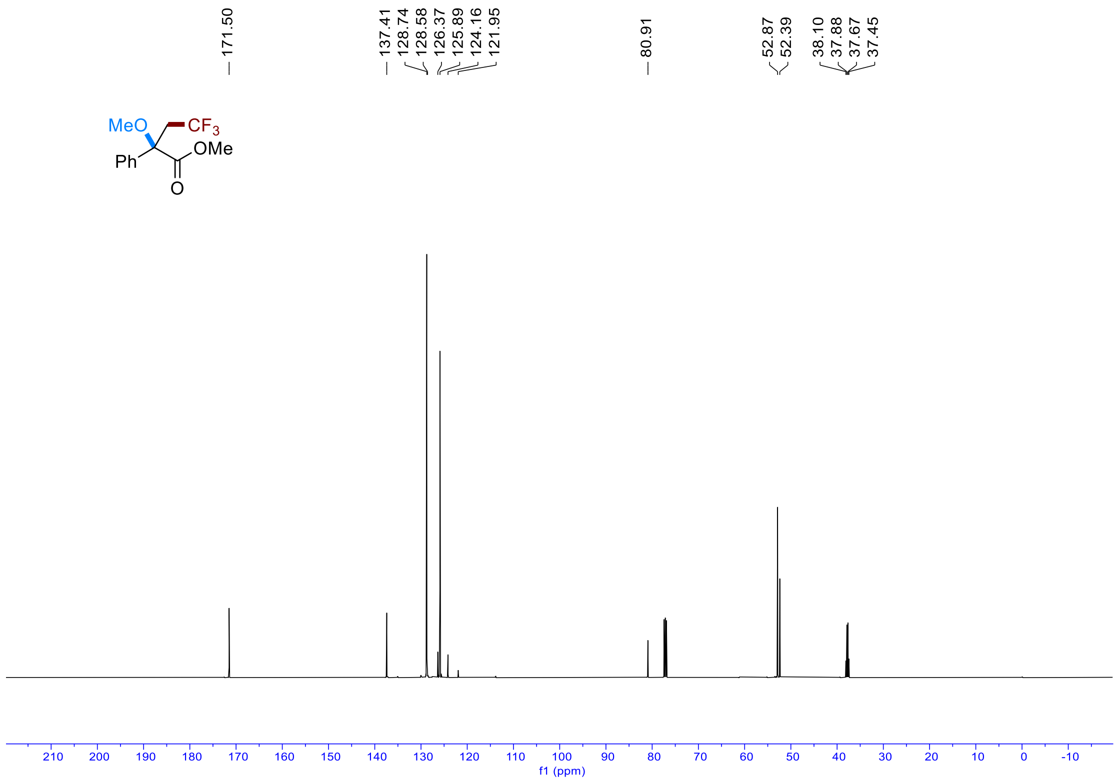
^{13}C NMR (151 MHz, CDCl$_3$) – (**6**)



^{1}H NMR (500 MHz, CDCl$_3$) – (**7**)



^{19}F NMR (471 MHz, CDCl$_3$) – (**7**)



^{13}C NMR (126 MHz, CDCl$_3$) – (**7**)