Photoredox Catalyzed Reductive Trifluoromethylation of imines via radical umpolung strategy

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Supporting Information

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1. General Information:

All the reactions were performed in flame-dried glassware under an argon atmosphere unless otherwise stated. Liquids and solutions were transferred with syringes. The solvents used were dried and purified by following standard procedures. Technical grade solvents for extraction or chromatography (ethyl acetate, and petroleum ether) were distilled before use. $CDCl_3$ was stored over 4Å molecular sieves. Chemicals used in this project were purchased from Sigma-Aldrich, TCI, Alfa-Aesar and Sisco Research Laboratories (SRL) and used without further purification. All the liquid chemicals were distilled freshly prior to use. Blue LEDs purchased from APSTRONICS. Analytical thin-layer chromatography (TLC) was performed on using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by UV radiation, and basic aqueous potassium permangante ($KMnO_4$) stain as developing agents.

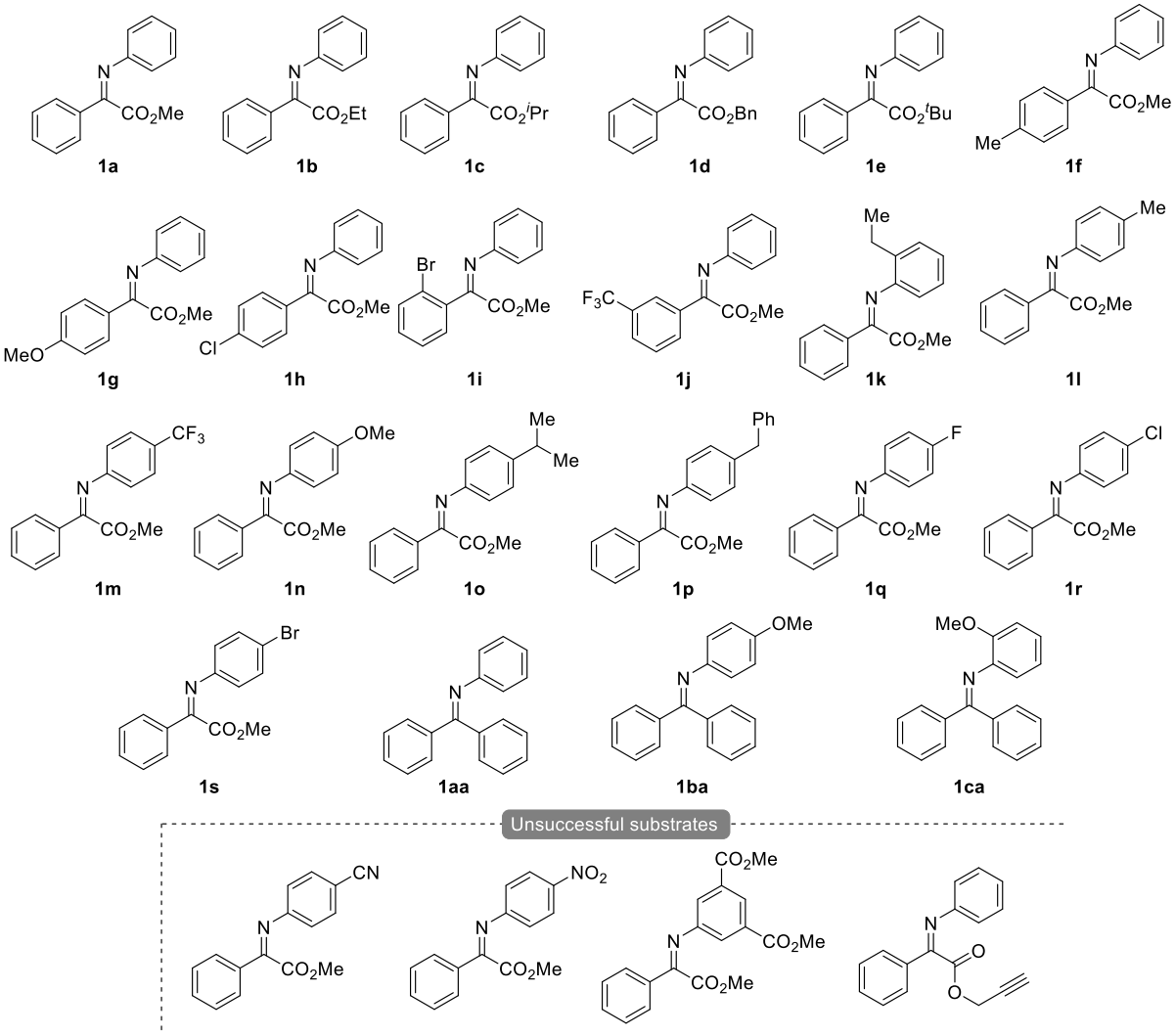
Column chromatography was performed on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) from Merck using the indicated solvents. Organic solutions were concentrated under reduced pressure on Heidolph rotary evaporator. NMR spectra were acquired on a JEOL JNM ECS-400, instrument running at 400 MHz for ^{1}H, 101 MHz ^{13}C and 376 MHz for ^{19}F. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for **^{1}H NMR**, $CDCl_3$, 77.16 ppm for **^{13}C NMR**). Fluorobenzene was used as an internal standard to calculate NMR yields. Data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, ddd = doublet of doublet of doublet, td = triplet of doublet, m = multiplet), coupling constants (Hz), and integration. All fluorescence data were recorded using Perkin Elmer LS55 fluorescence spectrophotometer instrument.

Figure S1: *Photochemical reaction set up.*

2. List of starting substrates prepared:

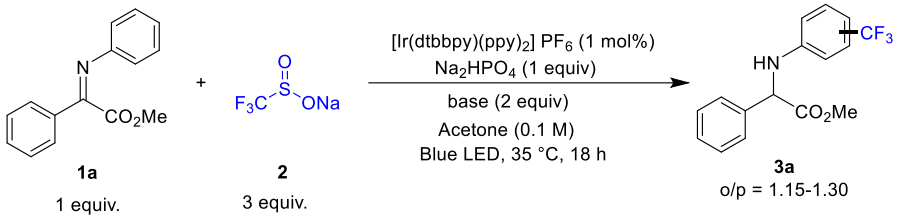
The lists of substrates prepared according to **GP-1** are given below.

List of Successful imines synthesis



3.1 Optimization Table:

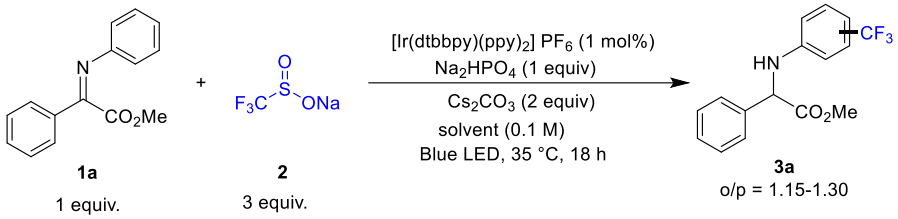
Table S1: *Evaluation of bases*



Entry	base	Yield (%)[a]
1	K_2CO_3	36
2	Na_2CO_3	20
3	K_3PO_4	15
4	$MgSO_4$	n.r.
5	**Cs_2CO_3**	**78 (71)[b]**
6	Li_2CO_3	n.r.
7	NEt_3	n.r.
8	DIPEA	Trace
9	DABCO	35
10	Quinuclidine	44
11	Na_3PO_4	Trace

[a]Reaction scale 0.1 mmol, yields reported are the NMR yield using Fluorobenzene as internal standard. [b]Yields reported are the isolated yield.

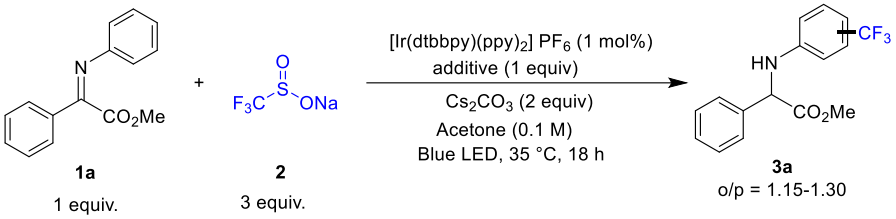
Table S2: *Evaluation of solvents*



Entry	solvent	Yield (%)[a]
1	ACN	15
2	DCM	45
3	Benzene	10
4	HFIP	n.r.
5	EtOH	25
6	DMF	50
7	DMSO	74
8	DMA	72
9	**Acetone**	**78 (71)[b]**
10	THF	Trace
11	EtOAc	20
12	1,4-Dioxane	7
13	$CHCl_3$	40
14	DMPU	42

[a]Reaction scale 0.1 mmol, yields reported are the NMR yield using Fluorobenzene as internal standard. [b]Yields reported are the isolated yield.

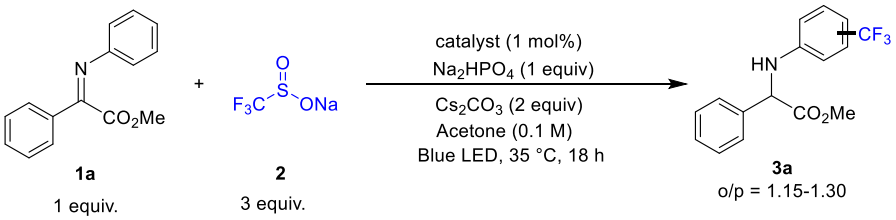
Table S3: *Evaluation of additives*



Entry	Additive	Yield (%)[a]
1	KH_2PO_4	28
2	K_2HPO_4	32
3	**Na_2HPO_4**	**78 (71)[b]**
4	NaH_2PO_4	48
5	$(NH_4)_3PO_4$	Trace

[a]Reaction scale 0.1 mmol, yields reported are the NMR yield using Fluorobenzene as internal standard. [b]Yields reported are the isolated yield.

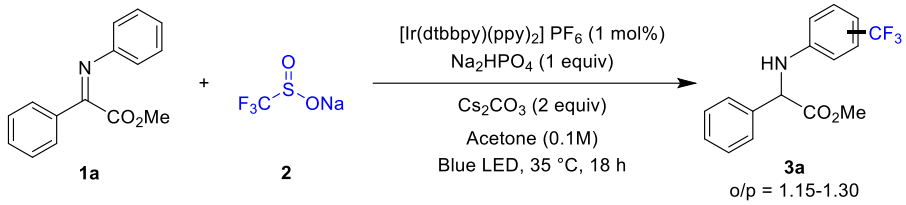
Table S4: *Evaluation of catalyst*



Entry	catalyst	Yield (%)[a]
1	*fac*-Ir(ppy) $_3$	74
2	4-CzIPN	57
3	Eosin Y	n.r.
4	*Acr-Mes* BF_4	30
5	$Ru(bpy)_3(PF_6)_2$	trace
6	**$[Ir(dtbbpy)(ppy)_2]PF_6$**	**78 (71)[b]**
7	$Ir[(dFCF_3ppy)_2dtbbpy]PF_6$	70

[a]Reaction scale 0.1 mmol, yields reported are the NMR yield using Fluorobenzene as internal standard. [b]Yields reported are the isolated yield.

Table S5: *Evaluation of equivalency*



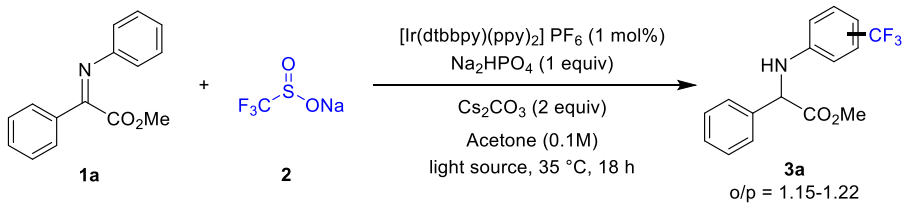
1a **2** **3a**

o/p = 1.15-1.30

Entry	1d	2	Yield (%)[a]
1	1	1	35%
2	1	2	52%
3	**1**	**3**	**78%**
4	2	4	75%
5	3	1	30%

[a]Reaction scale 0.1 mmol, yields reported are the NMR yield using Fluorobenzene as internal standard. [b]Yields reported are the isolated yield.

Table S6: *Evaluation of light source*



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

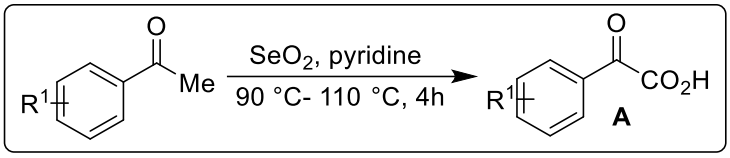
o/p = 1.15-1.22

Entry	Light source	Yield (%)[a]	*o/p* ration
1	455 nm	78	1.22
2	427 nm	54	1.15
3	390 nm	Trace	-
4	370 nm	-	-

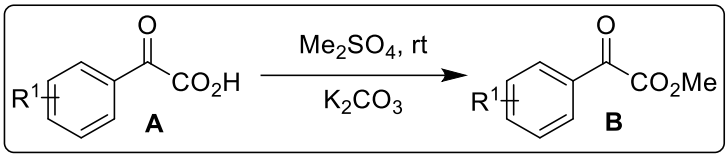
[a]Reaction scale 0.1 mmol, yields reported are the NMR yield using Fluorobenzene as internal standard. [b]Yields reported are the isolated yield.

4. General Procedures:

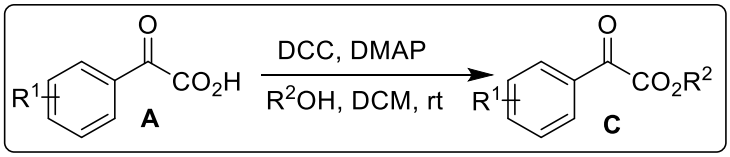
4.1 General Procedure 1: Preparation of imines with C-aryl variation (**GP-1**).



According to previous literature, [1] A round-bottomed flask was charged with Selenium Dioxide (1.5 equiv), aryl ketone derivative (1 equiv), and 20 ml pyridine was added to it. The reaction mixture was then stirred at 110°C for 1 h in an oil bath, and then the temperature was reduced to 90°C for 4 h. The desired product was isolated by column chromatography on silica gel using EtOAc-PE (5%) to give the substituted 2-Oxo-2- phenylacetic acid (**A**) in 65−90%yield.

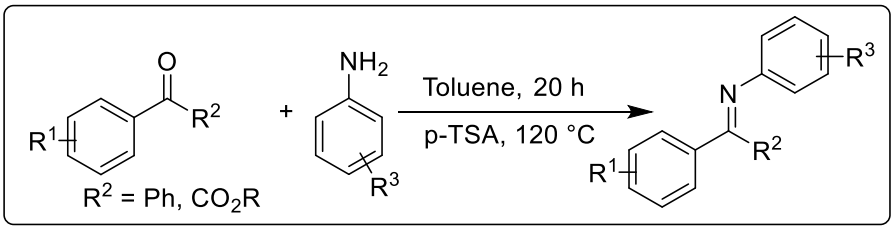


According to previous literature, [2] Dimethyl sulfate (DMS) is in the presence of K_2CO_3, with DMSO being taken as solvent. A 100 ml round bottom flask was charged with the phenylacetic acid (1 equiv), and combined with potassium carbonate (1.45 equiv) in 0.5 M of DMSO. Dimethyl sulfate (1.20 equiv) was added drop-wise. After 20 min of stirring at room temperature, the reaction mixture was then transferred to a separatory funnel, mixed with ether, and the organic layer was washed three times with a dilute potassium carbonate solution and once with brine. The organic layer was dried with anhydrous magnesium sulfate, filtered, and dried by rotary evaporation to yield the desired product **B** (40-90% yield).



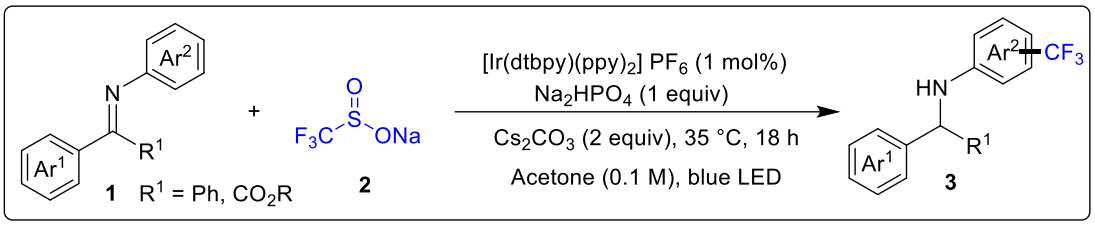
According to previous literature, [3] To a solution of 2-oxo-2-phenylacetic acid (1.0 equiv) in anhydrous DCM (0.3 M) under ice bath and N2 atmosphere, DMAP (0.1 equiv), DCC (1.0 equiv) and anhydrous EtOH (2.0 equiv) were added in turn. The mixture was then allowed to ambient temperature automatically and stirred until the full conversion of the starting material

by TLC monitoring. The mixture was filtered through celite, with DCM as eluant. The mother liquid and the DCM eluate were combined, and washed by 5% CuSO4 aqueous solution, water and brine, then dried over Na_2SO_4. The solvent was concentrated in vacuo and purified by column chromatography to afford the corresponding α-keto ester.



For obtaining product imines according to the previous literature,[4] a round bottom flask charged with a solution of aniline derivative (1.05 equiv) in benzene (5 mL per mmol of aniline derivative) Tosic acid monohydrate (5 mol %) was added. The keto-ester (1 equiv) produced in the previous step was then poured into this solution. The solution was then heated at reflux with azeotropic removal of water under N_2 (Dean-Stark conditions) for 20 h. The mixture was then cooled, passed through SiO_2 with EtOAc/Hexanes, and concentrated. The resulting crude solid product was recrystallized from hexanes to afford the corresponding α-iminoester in the form of a bright yellow crystalline solid.

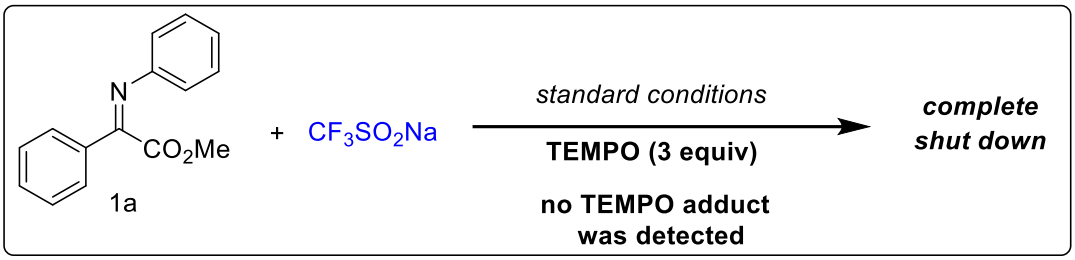
4.2 General Procedure 2: Photoredox catalyzed reductive trifluoromethylation of imines Reaction (GP-2).



Inside the glove box, an oven-dried glass vial was charged with a magnetic stir bar, Ir-photocatalyst (0.002 mmol, 1 mol%), 1 (0.2 mmol, 1.0 equiv), 2 (0.6 mmol, 3.0 equiv), Na2HPO4 (0.2 mmol, 1.0 equiv), Cs2CO3 (0.4 mmol, 2.0 equiv). After that, the reaction mixture was dissolved in 0.1 M of freshly distilled Acetone, followed by the vial being sealed with a teflon cap and wrapped with parafilm. The reaction mixture was then stirred under the irradiation of blue LEDs for about 18 h at 35 °C. Then, the reaction mixture was filtered through celite using a G-4 sintered funnel. After that, the crude mixture was concentrated and purified by flash column chromatography to afford the corresponding coupling product.

5. Mechanistic study and proposal

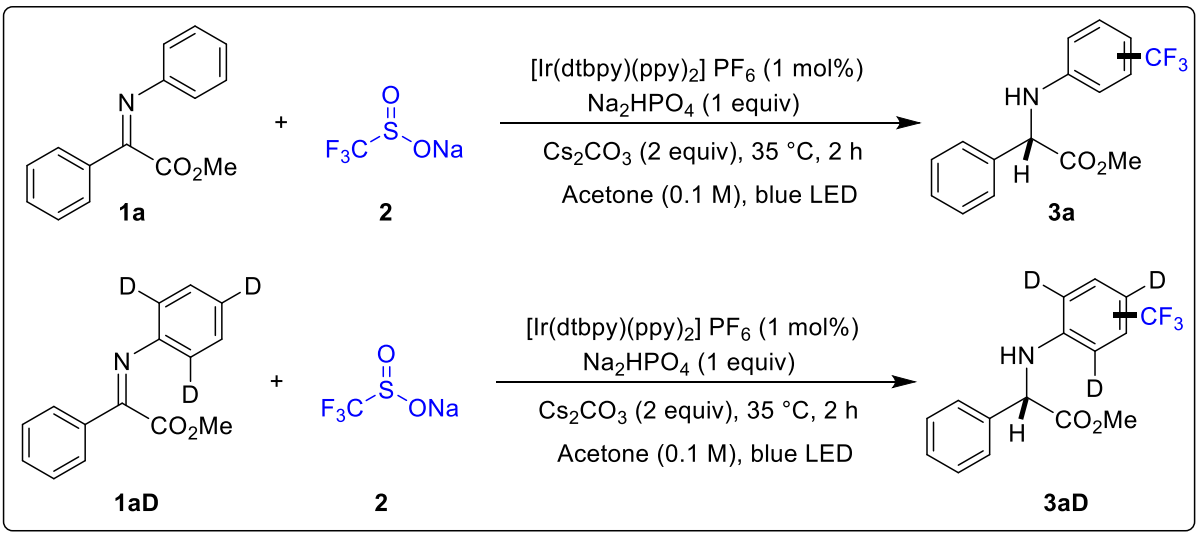
5.1 Using TEMPO as a radical scavenger



Inside the glove box, an oven-dried 5 mL glass vial was charged with **1a** (48.0 mg, 0.2 mmol, 1.0 equiv), **2** (94.0 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.5 mg, 0.2 mmol, 1 equiv), **TEMPO** (63.0 mg, 0.4 mmol, 2.0 equiv) and $[Ir(dtbbpy)(ppy)_2]PF_6$ (1.8 mg, 0.002 mmol, 1 mol%) under argon atmosphere in glove box. The reaction mixture was dissolved in 0.1 M dry Acetone and the vial was sealed with a Teflon cap and wrapped with parafilm in glove box. The resulting mixture was stirred under the irradiation of Blue LEDs for 18 h at 35 °C. The corresponding coupling product **3a** was not observed based on ^1H and ^{19}F NMR analysis.

5.2 Kinetic isotope exchange (KIE) study

Following GP–2, five sets of reactions were performed independently with non–deuterated and deuterated analogs of 1a for 3 h, 6 h, 9 h, 12 h, and 15 h. The NMR yields were calculated at a particular time and repeated three times to minimize the error. Then, the graph of %yield vs. Reaction time was plotted for both analogs and from the slopes of the graphs, the K_H/K_D was calculated.



Procedure: According to GP–2, Inside the glove box an oven-dried 5 mL glass vial was charged with **1a** (48.0 mg, 0.2 mmol, 1.0 equiv), **2** (94.0 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.5 mg, 0.2 mmol, 1 equiv) and $[Ir(dtbbpy)(ppy)_2]PF_6$ (1.8 mg, 0.002 mmol, 1 mol%) under argon atmosphere in glove box. The reaction mixture was dissolved in 0.1 M dry Acetone, and five sets of reactions were performed separately for 3 h, 6 h, 9 h, 12 h, and 15 h. After the mentioned time, the progress of the reaction was checked using TLC, and correspondingly, NMR yield was determined using Fluorobenzene as standard.

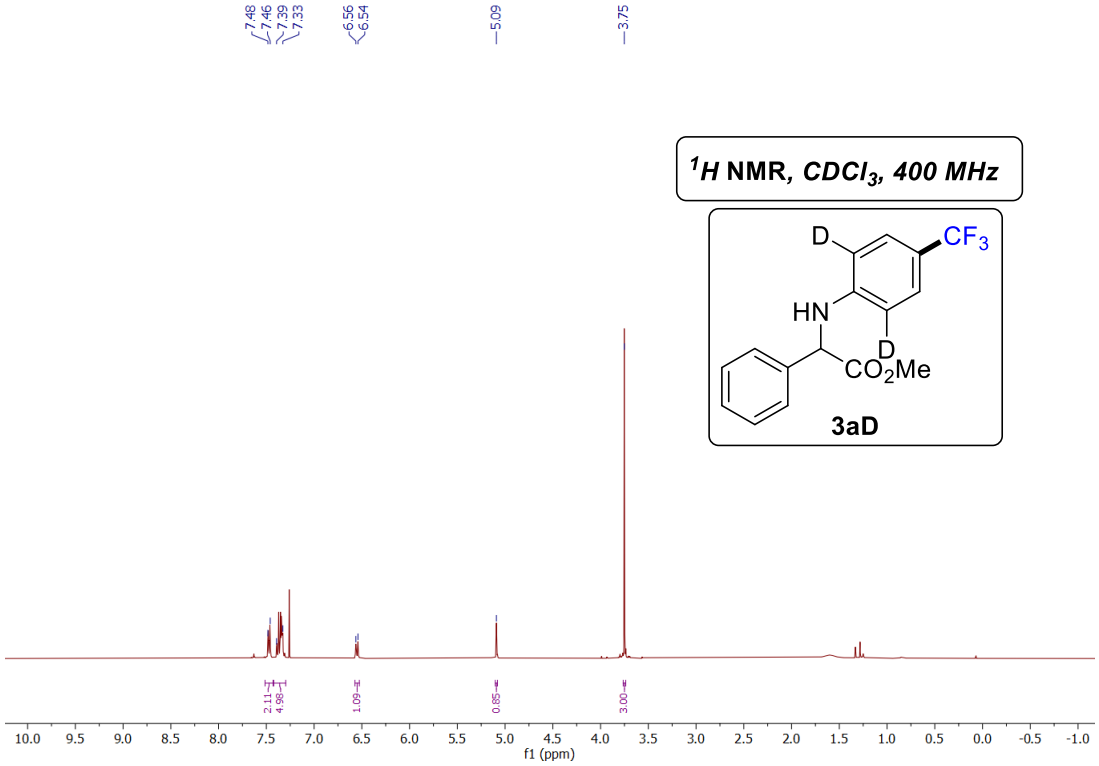
The same procedure was followed for the deuterated analogs using **1aD** (48.5 mg, 0.2 mmol, 1.0 equiv), **2** (94.0 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.5 mg, 0.2 mmol, 1 equiv) and $[Ir(dtbbpy)(ppy)_2]PF_6$ (1.8 mg, 0.002 mmol, 1 mol%) under argon atmosphere in glove box.

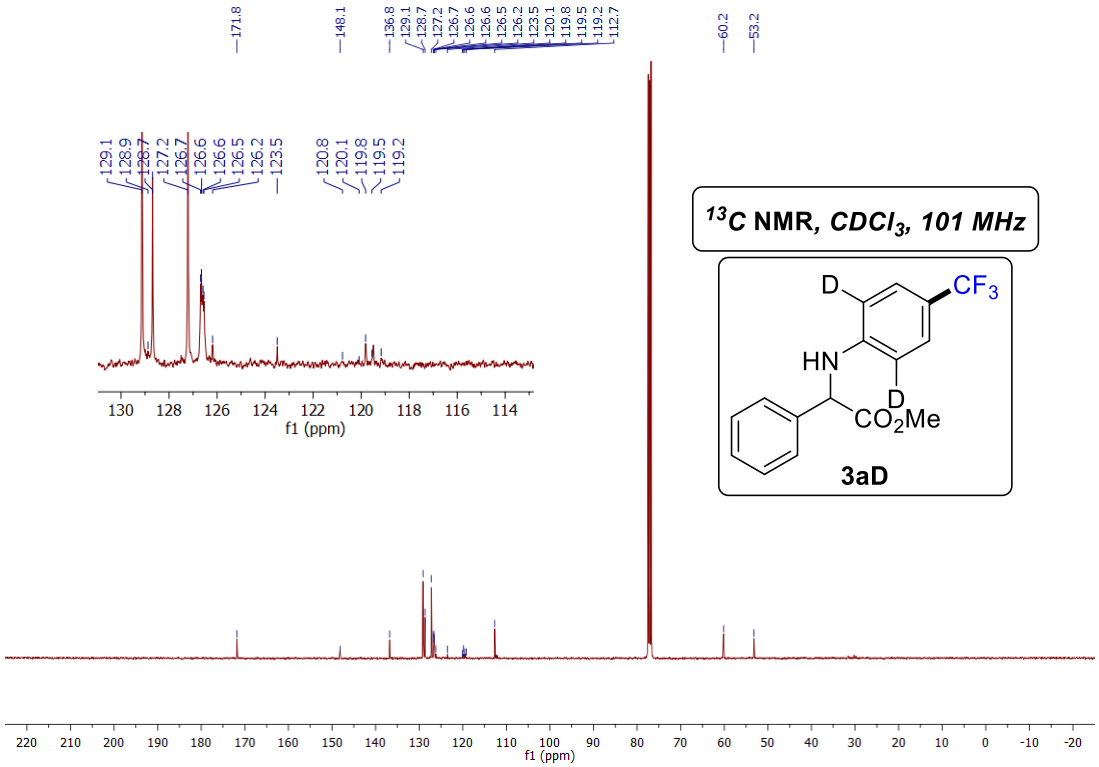
Linear fitting of the experimental points has been done by keeping intercept = 0. Ratio of the slopes of the straight lines for **3a** and **3aD** indicates the value of k_H/k_D which is 1.14 in this case.

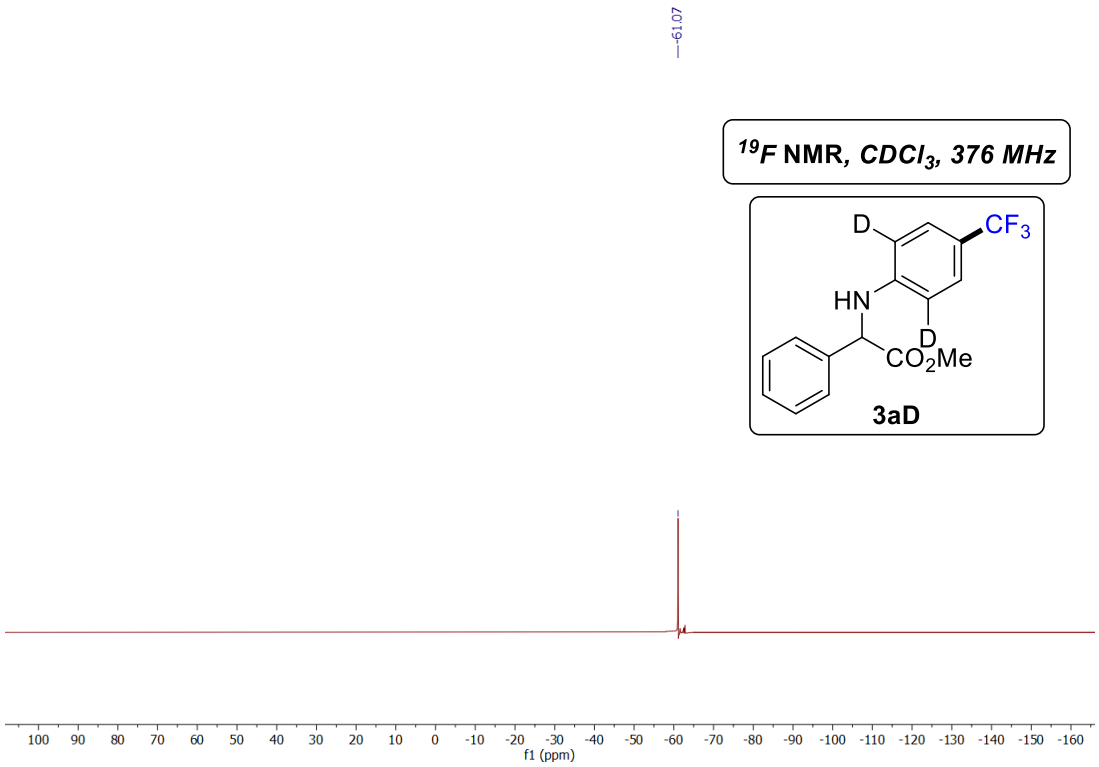
For compound 3aD: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.39–7.33 (m, 5H), 6.55 (d, J = 8.7 Hz, 1H), 5.09 (s, 1H), 3.75 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.07. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 148.1, 136.8, 129.1, 128.7, 127.2, 126.6 (q, J = 4.7 Hz), 124.9 (q, J = 272.7 Hz), 119.7 (q, J = 30.3 Hz), 112.7, 60.2, 53.2

For compound 3aD': ^{1}H NMR (400 MHz, $CDCl_3$)) δ 7.50–7.45 (m, 3H), 7.39–7.33 (m, 3H), 7.22–7.18 (m, 1H), 6.71 (t, J = 7.5 Hz, 1H), 6.41 (d, J = 8.4 Hz, 1H), 5.84 (s, 1H), 5.14 (d, J = 1.8 Hz, 1H), 3.75 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.38. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.6, 143.1, 136.9, 132.9, 129.1, 128.6, 127.2, 126.8 (q, J = 4.7 Hz),125.2 (q, J = 272.7 Hz), 116.8, 114.3 (q, J = 30.3 Hz), 112.8, 60.1, 53.2

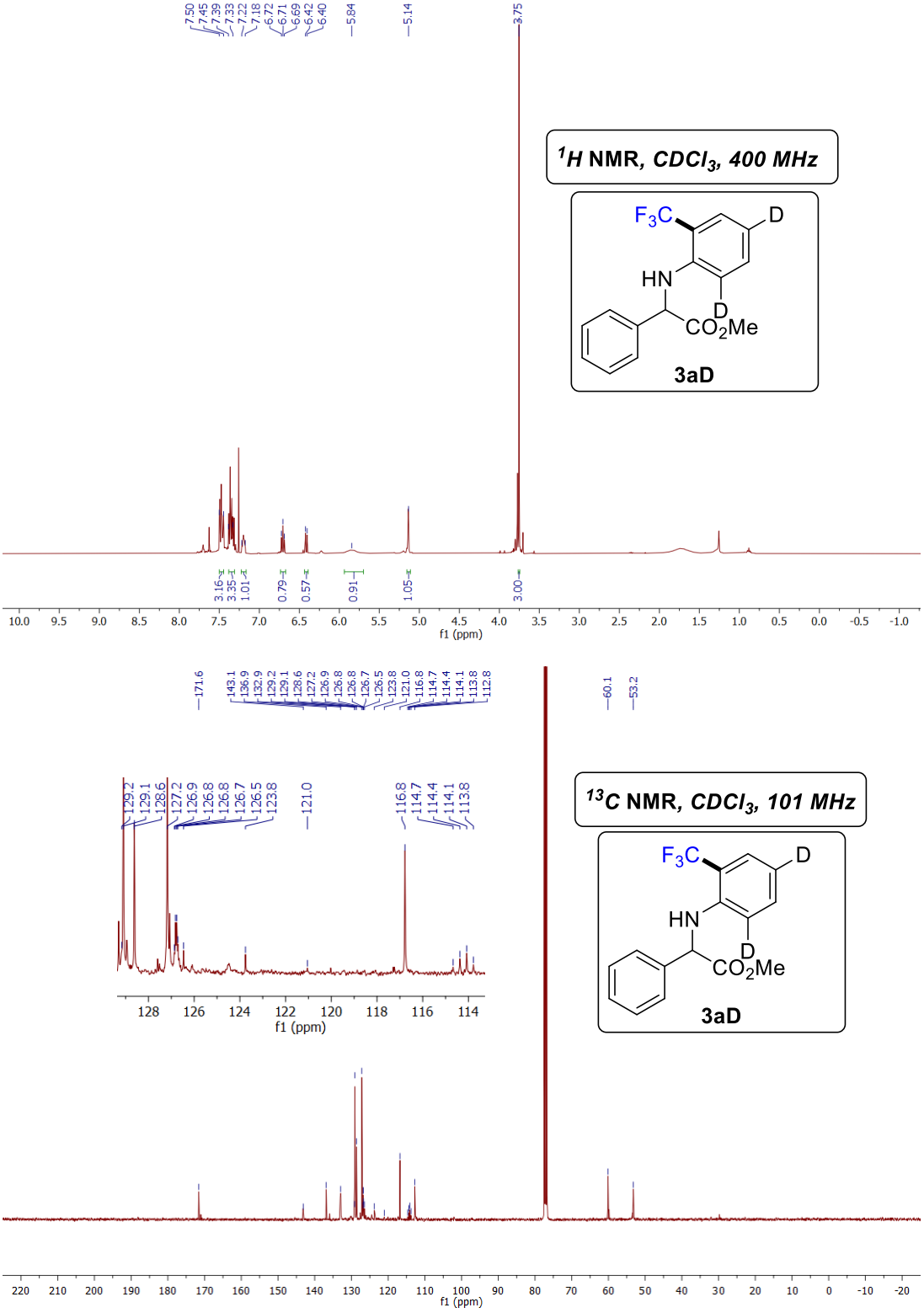
methyl 2-phenyl-2-((4-(trifluoromethyl)phenyl-2,6-d2)amino)acetate (3a$_D$)

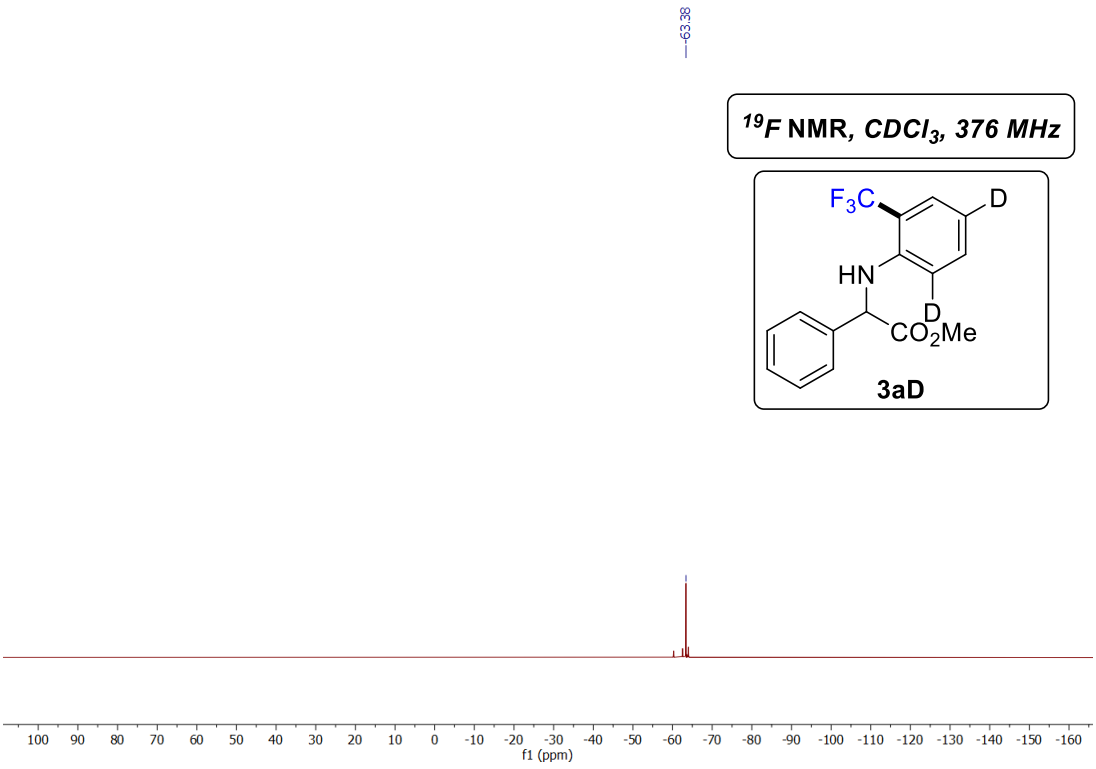





-61.07
^{19}F NMR, $CDCl_3$, 376 MHz
D
CF_3
HN
D
CO_2Me
3aD
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

methyl 2-phenyl-2-((2-(trifluoromethyl)phenyl-4,6-d2)amino)acetate (3aD')





Calculated K_H/K_D = 1.14

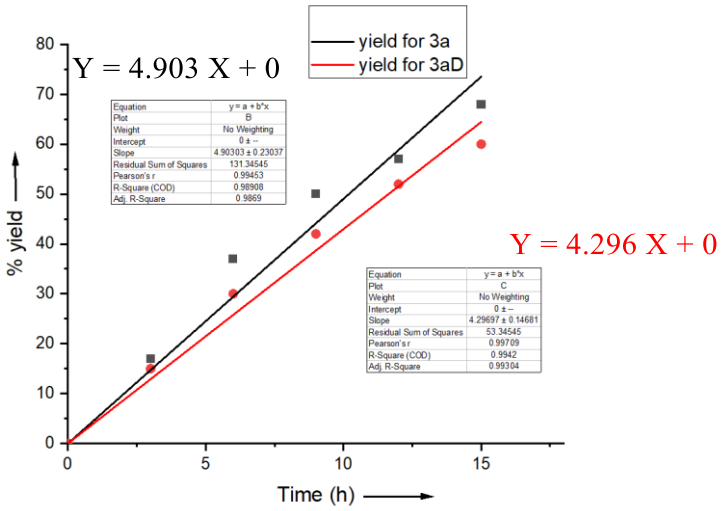
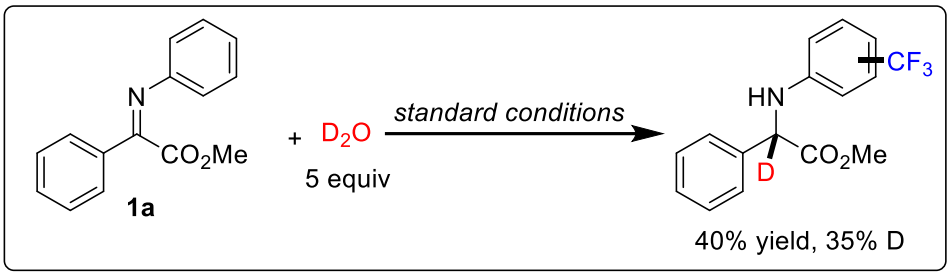
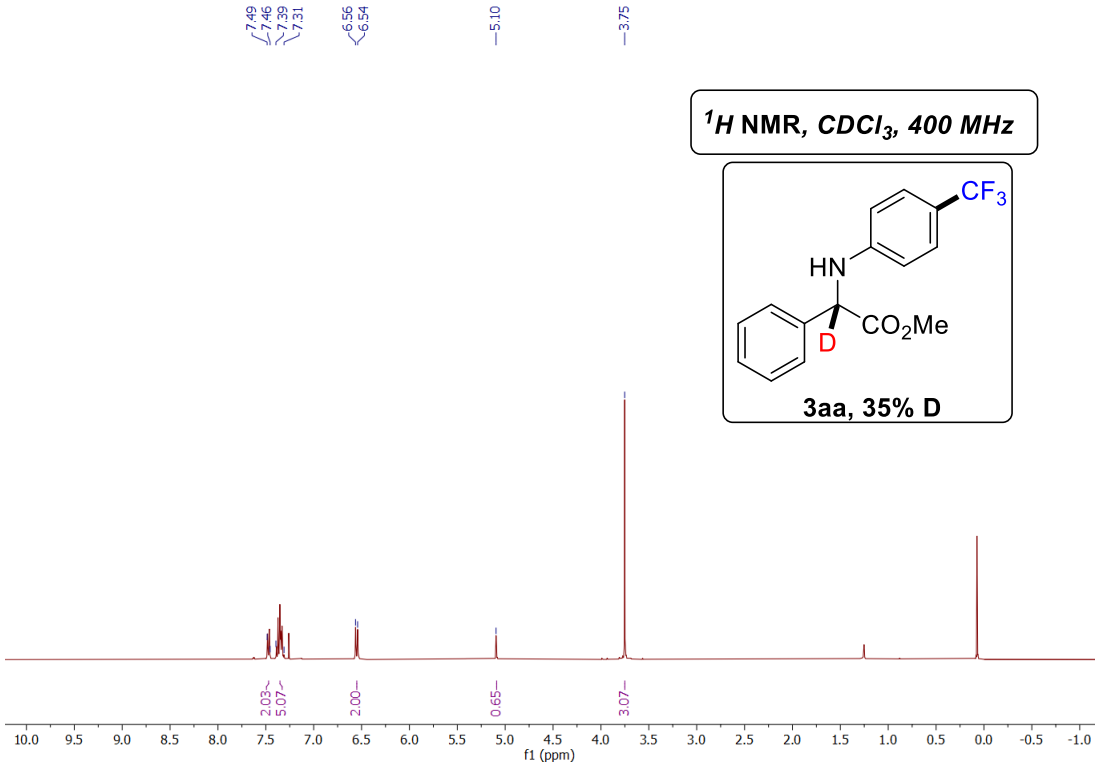


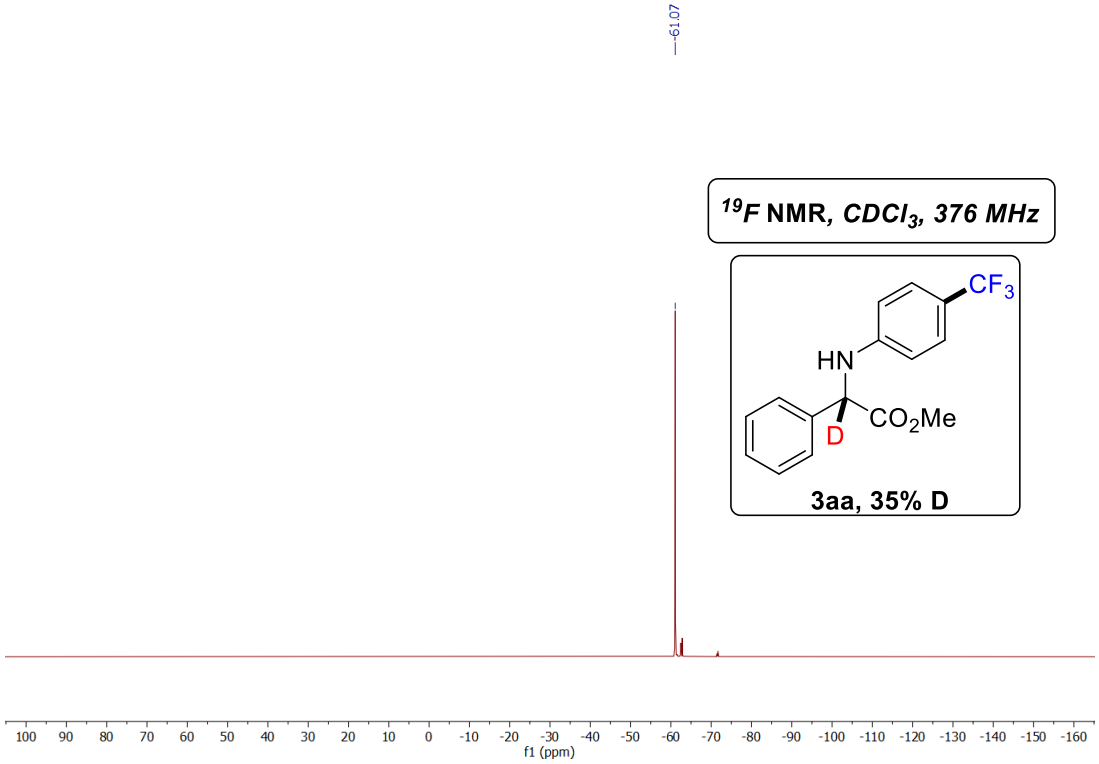
Figure S2 Yield vs time plot for determining K_H/K_D

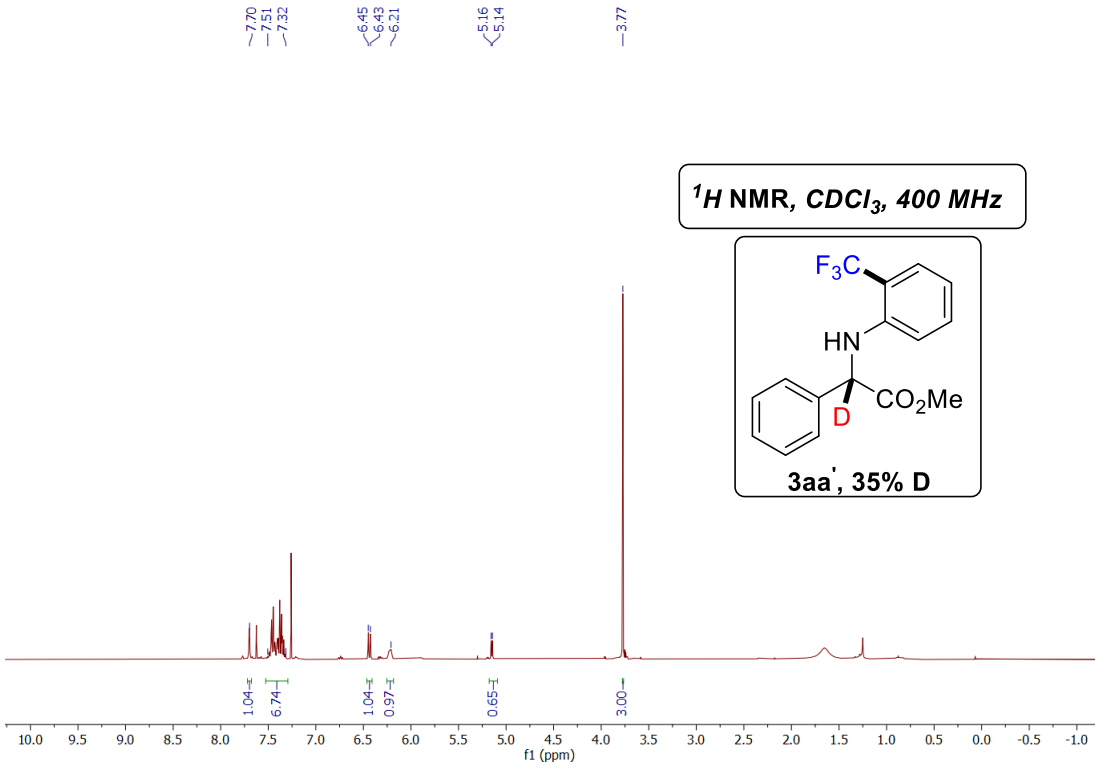
5.3 Deuterium-incorporation Experiment

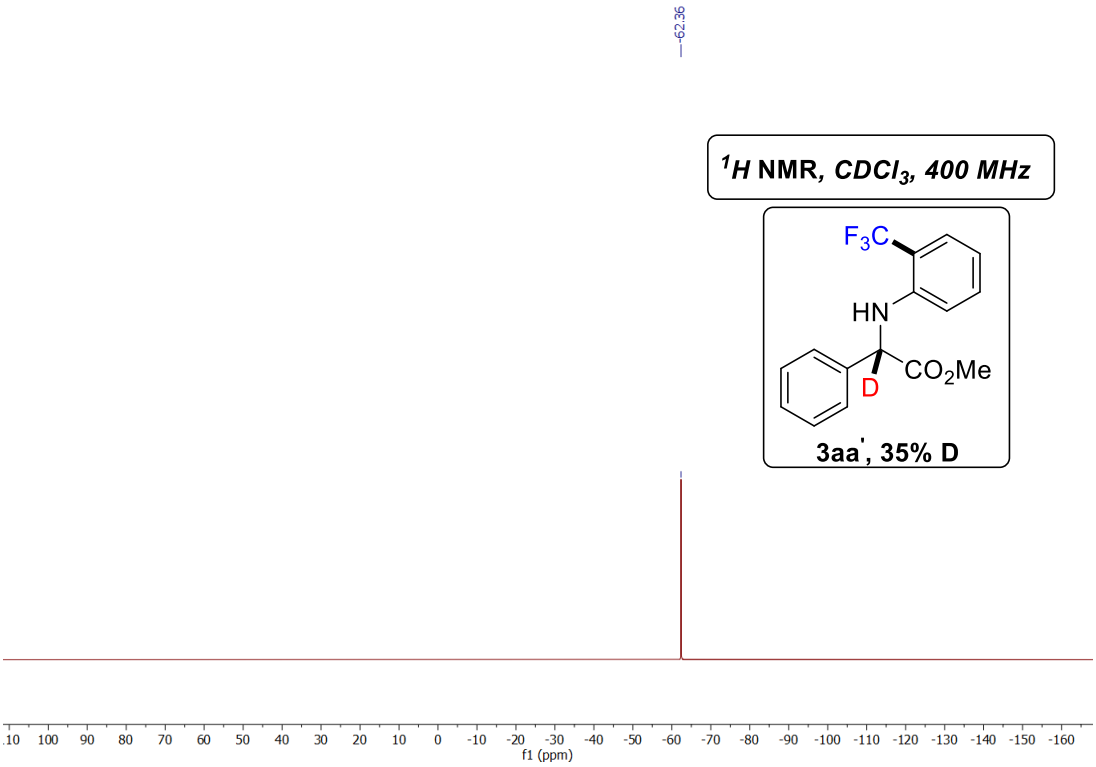


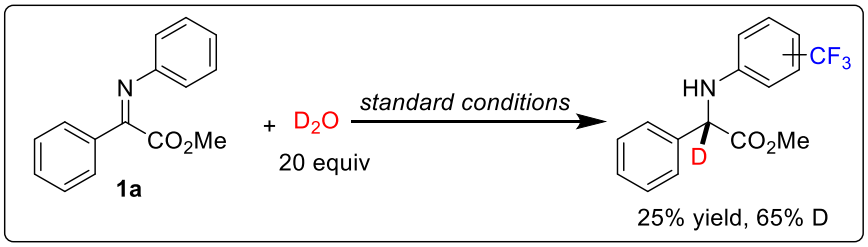
Inside the glove box, an oven-dried 5 mL glass vial was charged with **1a** (48.0 mg, 0.2 mmol, 1.0 equiv), **2** (94.0 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.5 mg, 0.2 mmol, 1 equiv), **D_2O** (18.0 µL, 1.0 mmol, 5.0 equiv) and $[Ir(dtbbpy)(ppy)_2]PF_6$ (1.8 mg, 0.002 mmol, 1 mol%) under argon atmosphere in glove box. The reaction mixture was dissolved in 0.1 M dry Acetone, and the vial was sealed with a Teflon cap and wrapped with parafilm in a glove box. The resulting mixture was stirred under the irradiation of Blue LEDs for 18 h at 35 °C. After that, the crude mixture was concentrated and purified by column chromatography to give the pure desired product having 35% D incorporation at the quaternary carbon center.



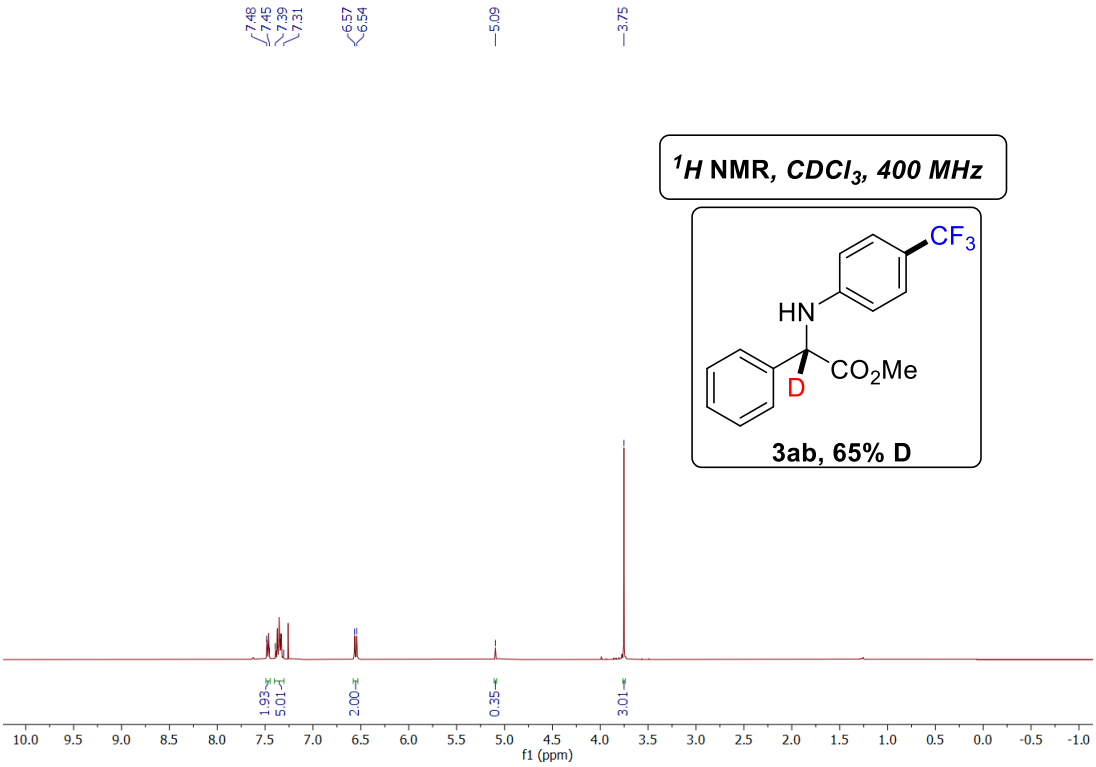

-61.07
19F NMR, CDCl3, 376 MHz
CF3
HN
CO2Me
D
3aa, 35% D
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

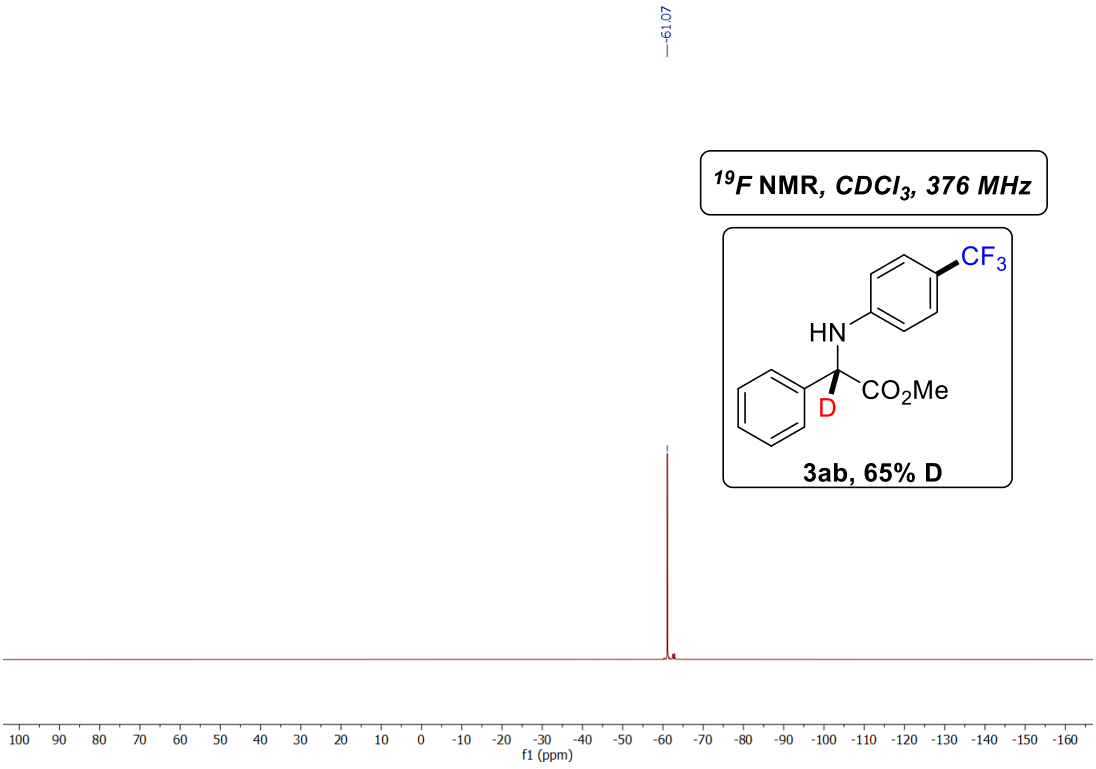

7.70
7.51
7.32
6.45
6.43
6.21
5.16
5.14
3.77
1H NMR, CDCl3, 400 MHz
F3C
HN
CO2Me
D
3aa', 35% D
1.04
6.74
1.04
0.97
0.65
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

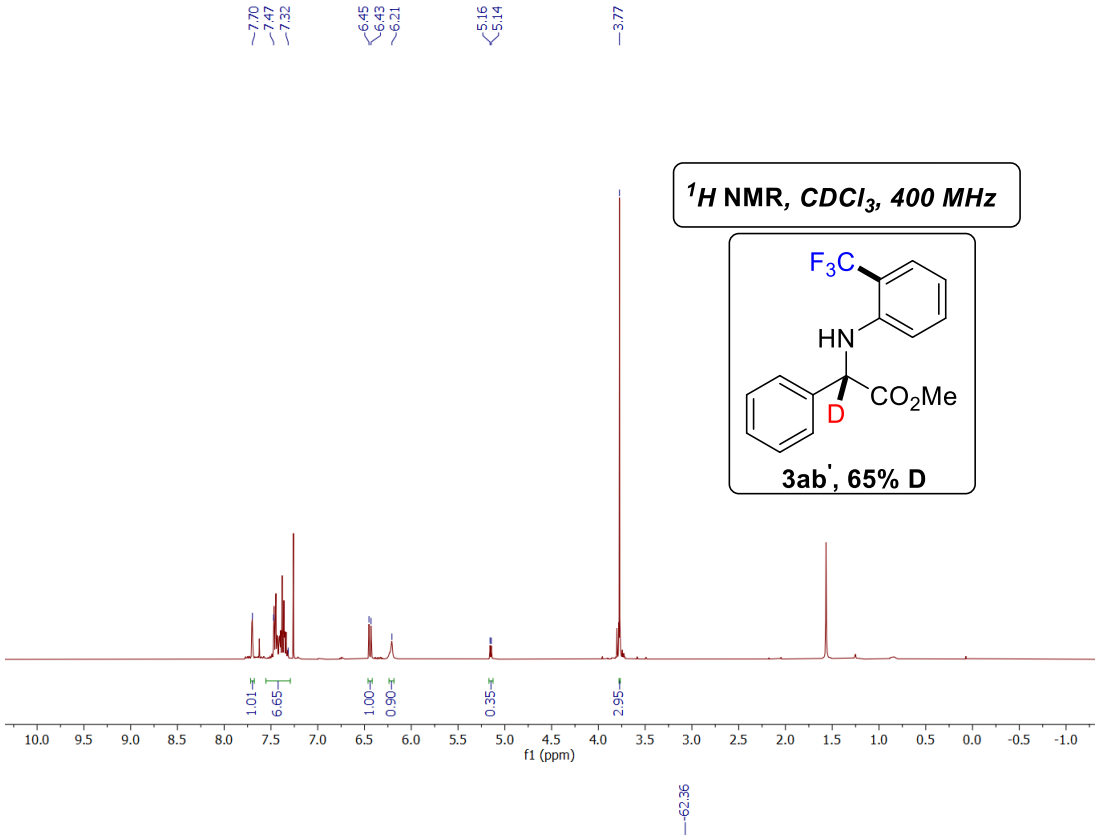


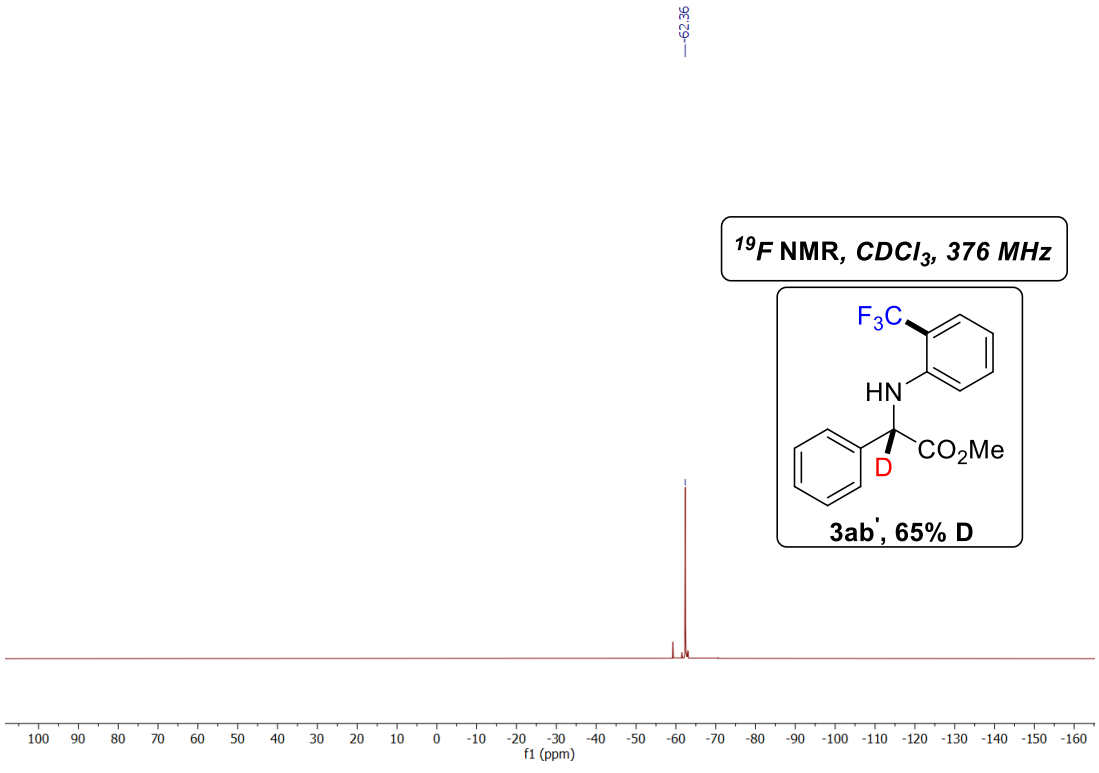


Inside the glove box, an oven-dried 5 mL glass vial was charged with **1a** (48.0 mg, 0.2 mmol, 1.0 equiv), **2** (94.0 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.5 mg, 0.2 mmol, 1 equiv), **D_2O** (72.0 µL, 4.0 mmol, 20.0 equiv) and $[Ir(dtbbpy)(ppy)_2]PF_6$ (1.8 mg, 0.002 mmol, 1 mol%) under argon atmosphere in glove box. The reaction mixture was dissolved in 0.1 M dry Acetone, and the vial was sealed with a Teflon cap and wrapped with parafilm in a glove box. The resulting mixture was stirred under the irradiation of Blue LEDs for 18 h at 35 ^oC. After that, the crude mixture was concentrated and purified by column chromatography to give the pure desired product having 65% D incorporation at the quaternary carbon center.


7.48
7.45
7.39
7.31
6.57
6.54
5.09
3.75
^1H NMR, $CDCl_3$, 400 MHz
CF_3
HN
CO_2Me
D
3ab, 65% D
1.93
5.01
2.00
0.35
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


61.07
^{19}F NMR, $CDCl_3$, 376 MHz
CF_3
HN
CO_2Me
D
3ab, 65% D
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)


7.70
7.47
7.32
6.45
6.43
6.21
5.16
5.14
3.77
1H NMR, CDCl3, 400 MHz
F3C
HN
CO2Me
D
3ab', 65% D
1.01
6.65
1.00
0.90
0.35
2.95
f1 (ppm)


-62.36
19F NMR, CDCl3, 376 MHz
F3C
HN
CO2Me
D
3ab', 65% D
f1 (ppm)

5.4 Fluorescence quenching experiments (Stern-Volmer study)

Emission intensities were recorded using a Perkin Elmer LS55 fluorescence spectrophotometer. In a typical experiment, a 0.01 mM solution of {[Ir(dtbbpy)(ppy)$_2$]PF$_6$ } (PC) in acetone was added to the appropriate amount of quencher in a PTEF capped 1.0 cm quartz cuvette. After degassing by bubbling a stream of nitrogen for 10 minutes, the emission of the sample was collected. All solutions were excited at λ = 456 nm (absorption maximum of the photocatalyst) and the emission intensity was collected at 546 nm (emission maximum).[S5]

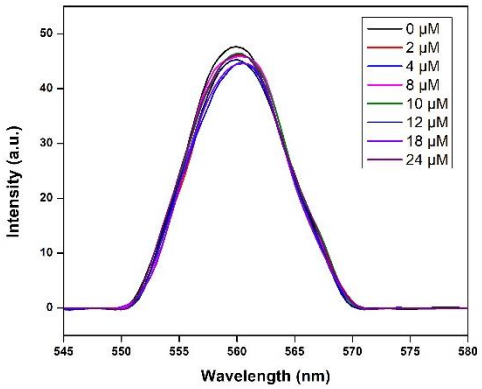


Fig S3 Quenching of PC by Na_2HPO_4

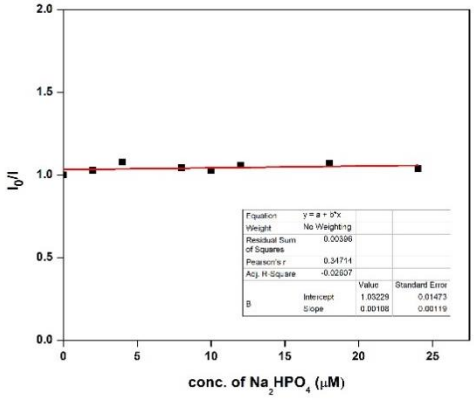


Fig S4 Stern-Volmer plot of Na_2HPO_4

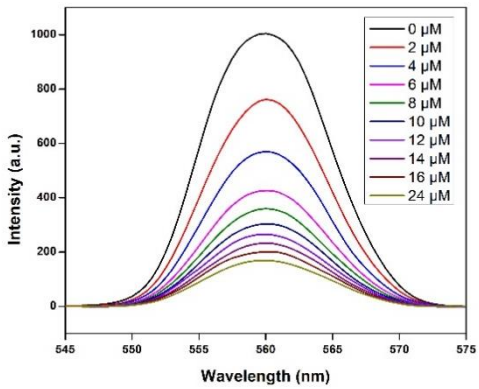


Fig S5 Quenching of PC by CF_3SO_2Na (2)

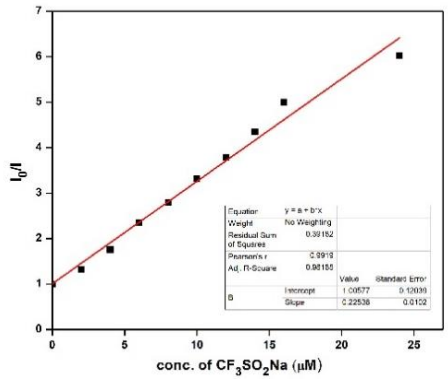
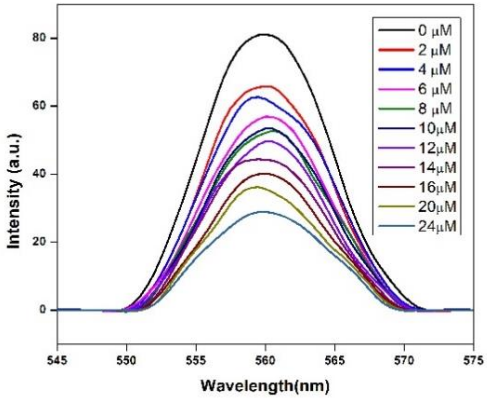


Fig S6 Stern-Volmer plot of CF_3SO_2Na



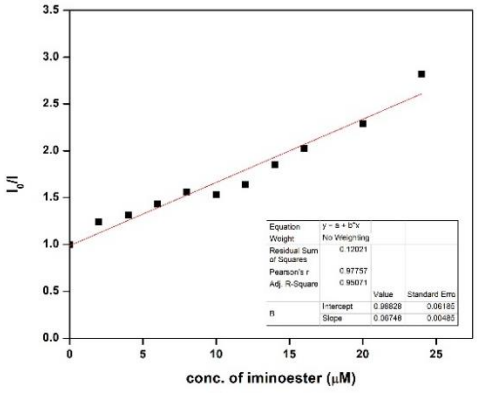


Fig S7 Quenching of PC by Iminoester

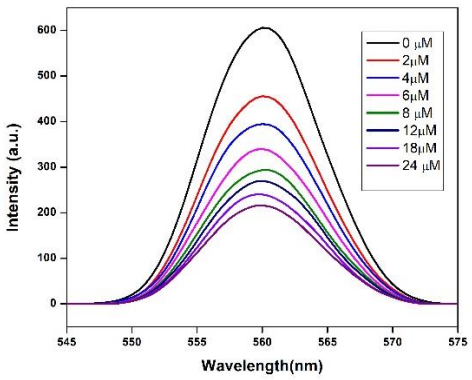


Fig S8 Stern-Volmer plot of Iminoester

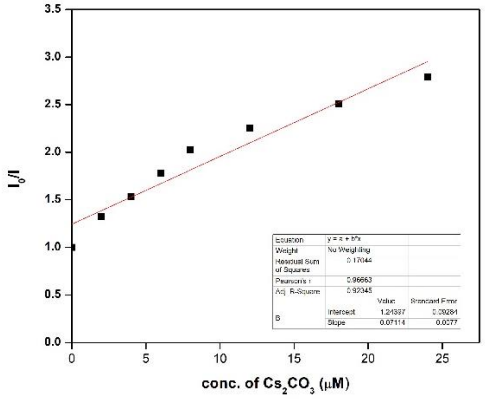


Fig S9 Quenching of PC by Cs_2CO_3

Fig 10 Stern-Volmer plot of Cs_2CO_3

5.5. Determination of quantum yield

i) Determination of light intensity of Blue LEDs:

The determination of photon flux was done by using standard ferrioxalate actinometry.[5] A 0.15 M solution of ferrioxalate was prepared by the addition of 737 mg of potassium ferrioxalate hydrate in 10 mL of 0.05 M H_2SO_4. After that a buffered solution of phenanthroline was prepared by mixing 25 mg of phenanthroline and 5.63 g of sodium acetate in 25 mL of 0.5 M H_2SO_4. Both of these solutions were kept in the dark. Next for the determination of the photon flux, 1.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 60.0 seconds at λ = 456 nm placing 4 cm away from hepatochem blue LED lamp. After irradiation, 0.175 mL of the phenanthroline solution was added to the cuvette. The solution was then kept for 1 h to permit the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was determined at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was determined. The conversion was calculated using eq.1,

$$mol \text{ of } Fe^{2+} = \frac{V.\ \Delta A}{\varepsilon.l} \quad \text{.....(1)}$$

Where V stands for the total volume (0.001175 L) of the solution after the addition of the phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (which is 11,100 L mol^{-1} cm^{-1}).

$$mol \text{ of } Fe^{2+} = \frac{0.001175\ L.(0.712-0.184)}{1cm.11100\ L.cm^{-1}.mol^{-1}} = 8.3243 \times 10^{-8}\ \text{mol.}$$

The photon flux can be calculated using eq 2.,

$$\text{Photon Flux} = \frac{mol\ Fe^{2+}}{\Phi.t.f} \quad \text{..... (2)}$$

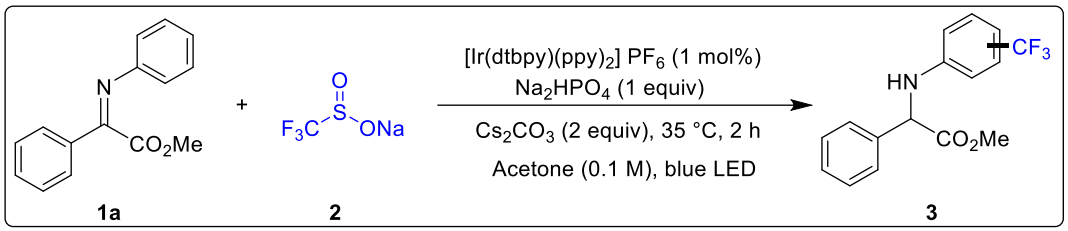
Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at λ = 456 nm), t is the time (60 s), and f is the fraction of light absorbed at λ = 456 nm, f = $1.000–10^{-A}$.

Calculated f = $1.000–10^{-A}$ = $1.000\text{-}10^{-0.712}$ = 0.806.

$$\text{Photon Flux} = \frac{8.3243 \times 10^{-8}\ mol}{1.01 \times 60s \times 0.806}$$

$$= 1.7044 \times 10^{-9}\ \text{Einstein}\ s^{-1}$$

ii) Quantum Yield Calculation



In an oven-dried glass vial charged with a magnetic stir bar, Ir-based photocatalyst (0.001 mmol, 1 mol%), methyl-2-phenyl-2-(phenylimino) acetate (1a) (0.1 mmol, 1.0 equiv), CF_3SO_2Na (0.3 mmol, 3.0 equiv), Na_2HPO_4 (0.1 mmol, 1.0 equiv), Cs_2CO_3 (0.2 mmol, 2.0 equiv) were added. After that, the reaction mixture was dissolved in 0.1 M of freshly distilled Acetone followed by the vial being sealed with a teflon cap and wrapped with parafilm in the glove box. The reaction mixture was then stirred under the irradiation of blue LEDs for **2 h** at 35 °C. Then the reaction mixture was filtered through celite using a G-4 sintered funnel. After that, the crude mixture was concentrated under reduced pressure. It was then purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluents to generate the pure product, **3a**. The product revealed **10%** isolated yield (1.0×10^{-5} mol).

The quantum yield was calculated as follows:

$$\Phi = \frac{mol\ product}{flux.\ t.\ f}$$

where, flux is the photon flux determined by ferrioxalate actinometry (1.5648×10^{-9} Einstein/s), t is the time (7200 s), and f (> 0.999) is the fraction of light absorbed by $[Ir(ppy)_2(dtbpy)]PF_6$ at 510 nm under the reaction condition mentioned above.

$$\Phi = \frac{1.0 \times 10^{-5}}{1.7044 \times 10^{-9} \times 7200 \times 1}$$

$$= 0.81$$

5.6. Mechanistic Evidence for the dimer formation:-

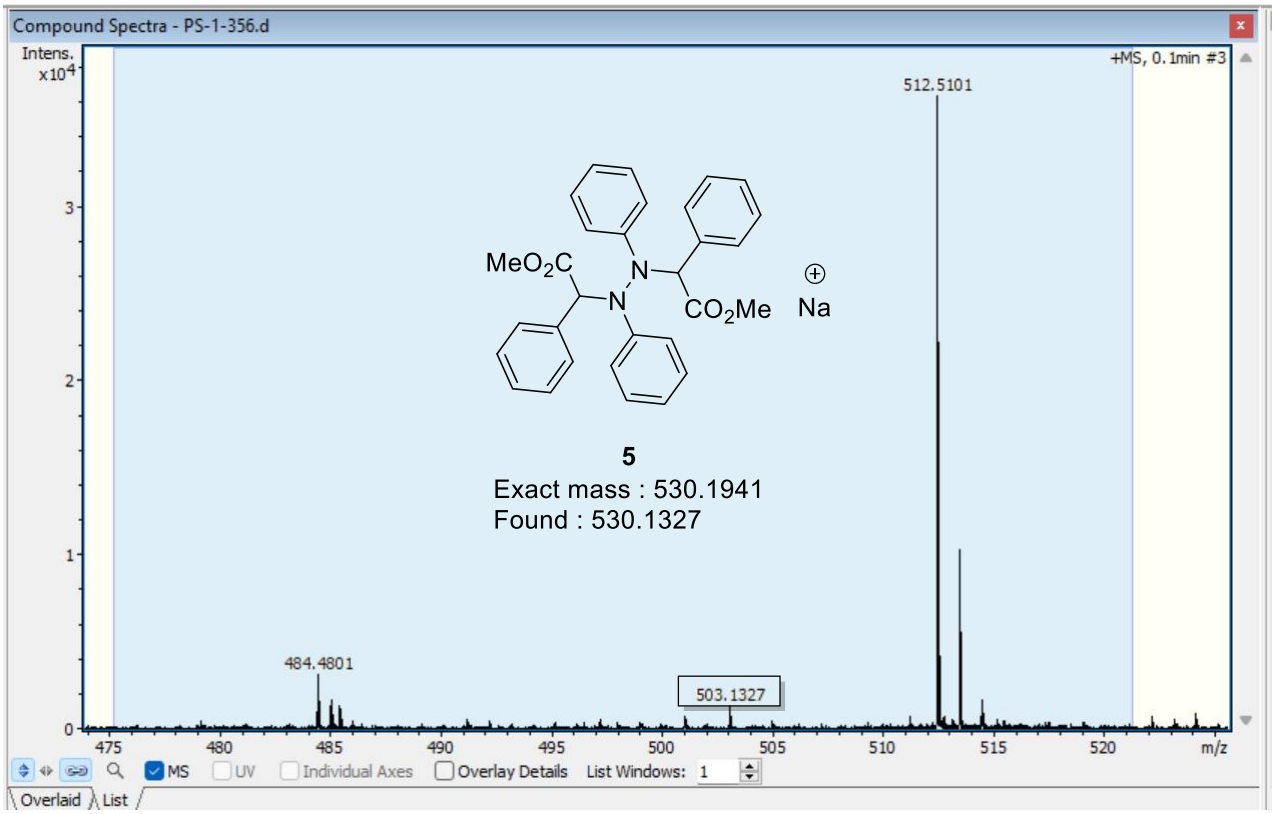
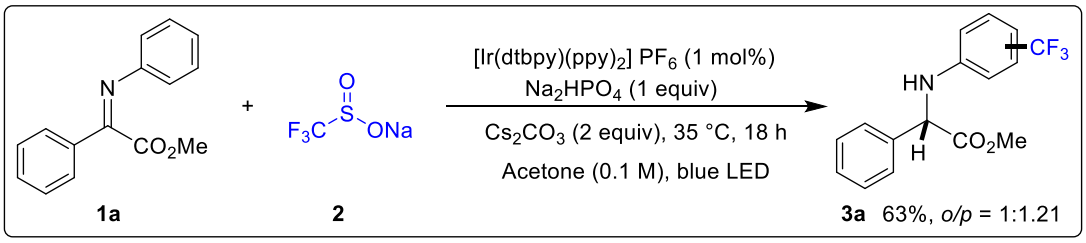


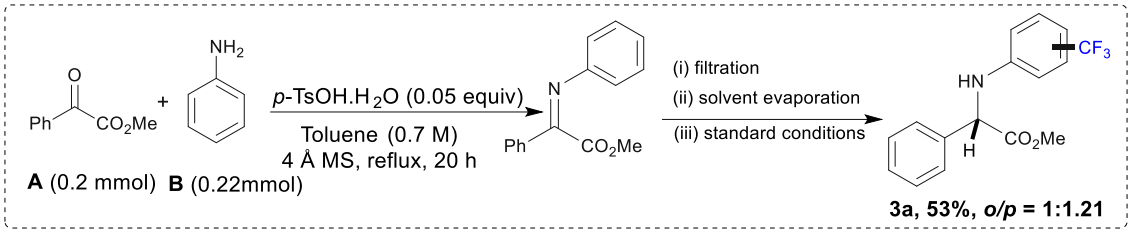
Fig 11 Mass spectrometry data of 5

6.0 1 mmol scale Synthesis:



Inside the glove box, an oven-dried glass vial was charged with a magnetic stir bar, Ir-photocatalyst (0.01 mmol, 1 mol%); α-iminoester **1a** (1.0 mmol, 1.0 equiv), Langlois reagent, **2** (3.0 mmol, 3.0 equiv), Na_2HPO_4 (1.0 mmol, 1.0 equiv), Cs_2CO_3 (2.0 mmol, 2.0 equiv). After that, the reaction mixture was dissolved in 0.1 M of freshly distilled Acetone, followed by the vial being sealed with a Teflon cap and wrapped with parafilm in the glove box. The reaction mixture was then stirred under the irradiation of blue LEDs for about 18 h at 35 °C. Then, the reaction mixture was filtered through celite using a G-4 sintered funnel. After that, the crude mixture was concentrated and purified by flash column chromatography to afford the corresponding coupling product yield of 63% (194.5 mg).

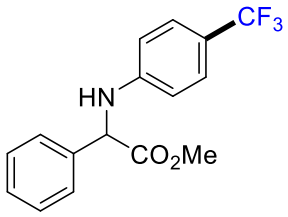
7.0 One pot sequential synthesis:



An oven-dried glass vial was charged with a magnetic stir bar, compound A (0.2 mmol, 1.0 equiv), compound B (0.22 mmol, 1.1 equiv), and *p*-TsOH·H2O (0.01 mmol, 0.05 equiv).and 4 Å molecular sieves in Toluene (0.7 M) was added to the vial, and the reaction mixture was refluxed for 20 hours. The mixture was then filtered through Celite using a G-4 sintered funnel, and the solvent was evaporated. The resulting crude material was then subjected to a high vacuum. After this, the material was taken into a glove box and subjected to our standard reaction conditions for approximately 18 hours. The reaction mixture was subsequently filtered through Celite using a G-4 sintered funnel. The crude mixture was then concentrated and purified by flash column chromatography to afford the corresponding coupling product with a yield of 53% (33.0 mg).

Experimental Details for the Substrate Scope

8.1. methyl 2-phenyl-2-((4-(trifluoromethyl)phenyl)amino) acetate (3a)



3a

$C_{16}H_{14}NO_2F_3$

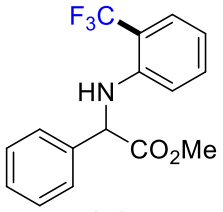
M. W. 309.2882 g/mol

Following General Procedure **GP-2** for the title compound **3a** and by using **1a** (47.8 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane / EtOAc = 39:1).to afford **3a** as colourless oil (24.0 mg, 39%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{16}H_{15}F_3NO_2]^+$: 310.1049; Found: 310.1049.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7 Hz, 2H), 7.40–7.34 (m, 5H), 6.57 (d, *J* = 8.3 Hz, 2H), 5.38 (s, 1H), 5.11 (s, 1H), 3.76 (d, *J* = 1.6 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.04. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 148.2, 136.8, 129.1, 128.7, 127.2, 126.7 (q, *J* = 4.7 Hz), 124.9 (q, *J* = 272.7 Hz), 119.6 (q, *J* = 30.3 Hz), 112.7, 60.1, 53.1.

8.2. methyl 2-phenyl-2-((2-(trifluoromethyl)phenyl)amino) acetate (3a')



3a'

$C_{16}H_{14}NO_2F_3$

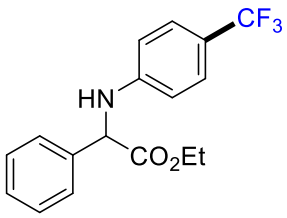
M. W. 309.2882 g/mol

Following General Procedure **GP-2** for the title compound **3a'**, by using **1a** (47.8 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 49:1).to afford **3a'** as a colorless oil (20.0 mg, 32%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{16}H_{15}F_3NO_2]^+$: 310.1049; Found: 310.1049.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.46 (m, 3H), 7.46–7.40 (m, 3H), 7.21 (t, *J* = 8.5 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 8.3 Hz, 1H), 5.87 (s, 1H), 5.16 (d, *J* = 4.3 Hz, 1H), 3.76 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.36. ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 143.2, 136.9, 133.0, 129.1, 128.6, 127.2, 126.8 (q, *J* = 4.7 Hz) 125.2 (q, *J* = 272.7 Hz), 116.8, 114.2 (q, *J* = 30.3 Hz), 112.8, 60.1, 53.1.

8.3. ethyl 2-phenyl-2-((4-(trifluoromethyl)phenyl)amino) acetate (3b)



3b

$C_{17}H_{16}NO_2F_3$

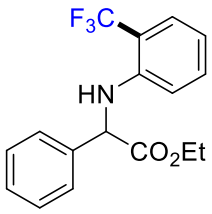
M. W. 323.3152 g/mol

Following General Procedure **GP-2** for the title compound **3b**, by using **1b** (50.5 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 39:1).to afford **3b** as a colorless oil (26.5 mg, 41%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{17}NO_2F_3]^+$ 324.1206; Found: 324.1206.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.47 (m, 2H), 7.39–7.30 (m, 5H), 6.56 (d, *J* = 8.4 Hz, 2H), 5.36 (s, 1H), 5.08 (s, 1H), 4.26 (dq, *J* = 10.9, 7.1 Hz, 1H), 4.15 (dq, *J* = 10.9, 7.1 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.07. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.3, 148.3, 136.9, 129.0, 128.6, 127.2, 126.7 (q, *J* = 10.1 Hz), 125.9 (q, *J* = 272.7 Hz), 119.6 (q, *J* = 30.3 Hz), 112.7, 62.2, 60.2, 14.1.

8.4. ethyl 2-phenyl-2-((2-(trifluoromethyl)phenyl)amino) acetate (3b')



3b'

$C_{17}H_{16}NO_2F_3$

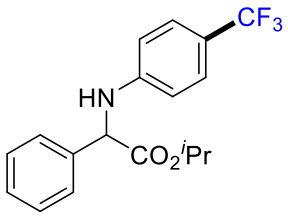
M. W. 323.3152 g/mol

Following General Procedure **GP3** for the title compound **3b'**, by using **1b** (50.7 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 49:1).to afford **3b'** as colourless oil (21.5 mg, 33%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{17}NO_2F_3]^+$: 324.1206; Found: 324.1206.

^{1}H NMR (400 MHz, $CDCl_3$ δ 7.51–7.46 (m, 3H), 7.39–7.30 (m, 3H), 7.20 (t, *J* = 7.9 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 8.3 Hz, 1H), 5.86 (s, 1H), 5.13 (d, *J* = 5.0 Hz, 1H), 4.25 (dq, *J* = 11.1, 7.4 Hz, 1H), 4.16 (dq, *J* = 10.6, 7.0 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H).**^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.36. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.0, 143.3, 137.0, 133.0, 129.0, 128.5, 127.1, 126.8 (q, *J* = 4.7 Hz), 125.2 (q, *J* = 272.2 Hz), 116.7,114.2 (q, *J* = 30.3 Hz), 112.8, 62.2, 60.2, 14.0.

8.5. isopropyl 2-phenyl-2-((4-(trifluoromethyl)phenyl)amino) acetate (3c)



3c

$C_{18}H_{18}NO_2F_3$

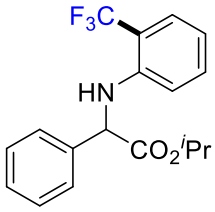
M. W. 337.3422 g/mol

Following General Procedure **GP-2** for the title compound **3c**, by using **1c** (53.5 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 39:1).to afford **3c** as a colorless oil (25.5 mg, 38%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{18}H_{19}NO_2F_3]^+$:338.1362; Found:. 338.1371.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.38–7.29 (m, 5H), 6.56 (d, *J* = 8.8 Hz, 2H), 5.35 (s, 1H), 5.09–5.00 (m, 2H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H).**^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.04.**^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.8, 148.4, 137.0, 129.0, 128.5, 127.1, 126.7 (q, *J* = 4.7 Hz), 124.9 (q, *J* = 272.7 Hz), 119.6 (q, *J* = 30.3 Hz), 112.7, 70.0, 60.3, 21.8, 21.4.

8.6. isopropyl 2-phenyl-2-((2-(trifluoromethyl)phenyl)amino) acetate (3c')



3c'

$C_{18}H_{18}NO_2F_3$

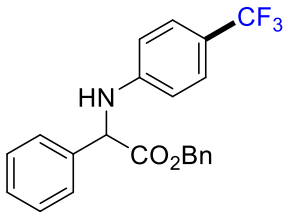
M. W. 337.3422 g/mol

Following General Procedure **GP-2** for the title compound **3c'**, by using **1c** (53.5 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 49:1).to afford **3c'** as a colorless oil (21.5 mg, 32%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{18}H_{19}NO_2F_3]^+$:338.1362; Found:. 338.1365.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.50 (m, 3H), 7.41–7.31 (m, 3H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 8.1 Hz, 1H), 5.94 (s, 1H), 5.15 (s, 1H), 5.09 (m, 1H), 1.32 (d, *J* = 6.0 Hz, 3H), 1.12 (d, *J* = 6.4 Hz, 3H).**^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.42. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.4, 143.3, 137.0, 133.0, 128.9, 128.4, 127.0, 126.7 (q, *J* = 4.7 Hz), 125.2 (q, *J* = 272.7 Hz), 116.6, 114.1 (q, *J* = 30.3 Hz) 112.8, 70.0, 60.3, 21.7, 21.3.

8.7. benzyl 2-phenyl-2-((4-(trifluoromethyl)phenyl)amino) acetate (3d)



3d

$C_{22}H_{18}NO_2F_3$

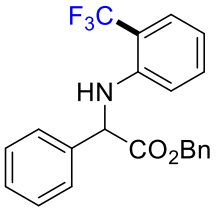
M. W. 385.3862 g/mol

Following General Procedure **GP-2** for the title compound **3d**, by using **1d** (63.0 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 39:1).to afford **3d** as a colourless oil (25.5 mg, 33%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{22}H_{19}NO_2F_3]^+$: 386.1362; Found:. 386.1375.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.45 (m, 3H), 7.38–7.28 (m, 6H), 7.22–7.16 (m, 3H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 5.85 (s, 1H), 5.24 – 5.11 (m, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.19. **^{13}C NMR (101 MHz, $CDCl_3$** δ 171.2, 148.3, 136.7, 135.1, 129.1, 128.7, 128.6, 128.5, 128.0, 127.2, 126.7 (q, *J* = 4.7 Hz), 124.9 (q, *J* = 272.7 Hz), 119.6 (q, *J* = 30.3 Hz) 112.7, 67.7, 60.3.

8.8. benzyl 2-phenyl-2-((2-(trifluoromethyl)phenyl)amino) acetate (3d')



3d'

$C_{22}H_{18}NO_2F_3$

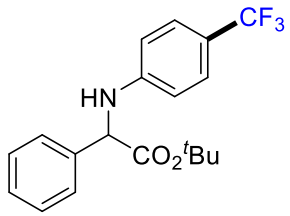
M. W. 385.3862 g/mol

Following General Procedure **GP3** for the title compound **3d'**, by using **1d** (68.7 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 49:1).to afford **3d'** as a colorless oil (22.5 mg, 29%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{22}H_{19}NO_2F_3]^+$: 386.1362; Found:.386.1362.

^{1}H NMR (400 MHz, $CDCl_3$ δ 7.50–7.45 (m, 3H), 7.38–7.28 (m, 6H), 7.28–7.20 (m, 3H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 5.85 (s, 1H), 5.23–5.12 (m, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.36. **^{13}C NMR (101 MHz, $CDCl_3$)**. δ 170.9, 143.2, 136.8, 135.1, 133.0, 129.1, 128.6, 128.5, 127.9, 127.2, 126.8 (q, *J* = 4.7 Hz), 125.2 (q, *J* = 272.2 Hz), 116.8, 114.3 (q, *J* = 30.3 Hz), 112.8, 67.7, 60.3.

8.9. tert-butyl 2-phenyl-2-((4-(trifluoromethyl)phenyl)amino) acetate (3e)



3e

$C_{19}H_{20}NO_2F_3$

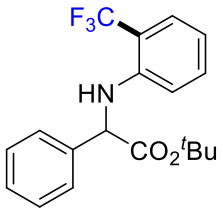
M. W. 351.3692 g/mol

Following General Procedure **GP-2** for the title compound **3e**, by using **1e** (56.3 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 39:1).to afford **3e** as colorless oil (23.0 mg, 33%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{19}H_{20}NNaO_2F_3]^+$: 374.1339; Found:.374.1339.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.30 (m, 5H), 5.11 (s, 2H), 2.31–2.27 (m, 2H), 1.78–1.73 (m, 2H), 1.70–1.65 (m, 2H), 1.61–1.59 (m, 3H), 1.19–1.09 (m, 3H), 1.03–0.93 (m, 3H), 0.80 (s, 6H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.18. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.4, 148.5, 137.4, 128.9, 128.3, 127.0, 126.6 (q, *J* = 4.7 Hz), 125.0 (q, *J* = 272.7 Hz), 119.4 (q, *J* = 30.3 Hz), 112.6, 82.9, 60.7, 27.8.

8.10. tert-butyl 2-phenyl-2-((2-(trifluoromethyl)phenyl)amino) acetate (3e')



3e'

$C_{19}H_{20}NO_2F_3$

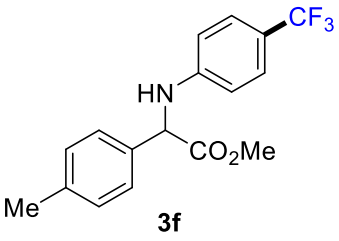
M. W. 351.3692 g/mol

Following General Procedure **GP-2** for the title compound **3e'**, by using **1e** (56.0 mg, 0.2 mmol, 1.0 equiv), **2** (93.60 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 49:1).to afford **3e'** as colourless oil (19.0 mg, 27%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{19}H_{20}NNaO_2F_3]^+$: 374.1339; Found:.374.1339.

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.29 (m, 5H), 6.54 (d, *J* = 8.6 Hz, 2H), 4.97 (s, 1H), 1.39 (s, 9H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.39. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.0, 143.4, 137.5, 133.0, 128.8, 128.3, 127.0, 126.7 (q, *J* = 4.7 Hz), 125.2 (q, *J* = 272.2 Hz), 116.4, 114.1 (q, *J* = 30.3 Hz) 112.8, 83.0, 60.7, 27.8.

8.11. methyl 2-(*p*-tolyl)-2-((4-(trifluoromethyl)phenyl)amino) acetate (3f)



3f

$C_{17}H_{16}NO_3F_3$

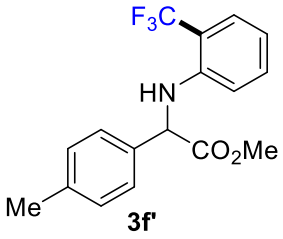
M. W. 323.3152 g/mol

Following General Procedure **GP2** for the title compound **3f**, by using **1f** (50.5 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 39:1).to afford **3f** as colourless oil (26.0 mg, 40%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{17}NO_3F_3]^+$: 324.1206; Found:. 324.1221.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.8 Hz, 4H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 5.37 (s, 1H), 5.09 (s, 1H), 3.75 (s, 3H), 2.36 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.01. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.0, 148.4, 138.5, 133.8, 129.8, 127.1, 126.7 (q, *J* = 4.7 Hz), 124.9 (q, *J* = 272.2 Hz), 119.6 (q, *J* = 30.3 Hz)112.6, 112.3, 59.9, 53.1, 21.2.

8.12. methyl 2-(*p*-tolyl)-2-((2-(trifluoromethyl)phenyl)amino) acetate (3f')



3f'

$C_{17}H_{16}NO_2F_3$

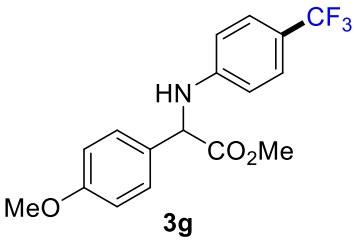
M. W. 323.3152 g/mol

Following General Procedure **GP3** for the title compound **3f'**, by using **1f** (50.7 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 49:1).to afford **3f'** as colourless oil (21.0 mg, 32%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{17}NO_3F_3]^+$: 324.1206; Found:. 324.1210.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 9.6 Hz, 1H), 7.37 (d, *J* = 6.4 Hz, 2H), 7.22–7.16 (m, 3H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 8.2 Hz, 1H), 5.80 (s, 1H), 5.10 (d, *J* = 5.0 Hz, 1H), 3.75 (s, 3H), 2.33 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.36. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 143.3, 138.4, 133.9, 133.0, 129.8, 127.1, 126.8 (q, *J* = 4.7 Hz), 125.2 (q, *J* = 272.7 Hz), 114.3 (q, *J* = 30.3 Hz) 116.7, 112.7, 59.9, 53.1, 21.2.

8.13. methyl 2-(4-methoxyphenyl)-2-((4-(trifluoromethyl)phenyl)amino) acetate (3g)



3g

$C_{17}H_{16}NO_3F_3$

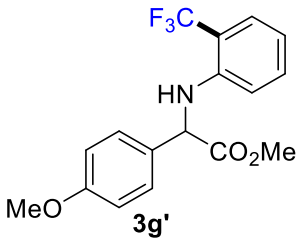
M. W. 339.3142 g/mol

Following General Procedure **GP-2** for the title compound **3g**, by using **1g** (54.0 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 39:1).to afford **3g** as colourless oil (33.0 mg, 48%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{17}NO_3F_3]^+$: 340.1155; Found:. 340.1155.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 8.7 Hz, 2H), 5.04 (s, 1H), 3.79 (s, 3H), 3.75 (s, 3H).**^{19}F NMR** (376 MHz, CDCl3) δ -61.19. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.1, 159.8, 148.3, 128.6, 128.4, 126.7 (q, *J* = 4.7 Hz), 124.9 (q, *J* = 272.7 Hz), 119.6 (q, *J* = 30.3 Hz)114.5, 114.3, 113.5, 112.7, 112.2, 59.5, 55.4, 53.1.

8.14. methyl 2-(4-methoxyphenyl)-2-((2-(trifluoromethyl)phenyl)amino) acetate (3g')



3g'

$C_{17}H_{16}NO_3F_3$

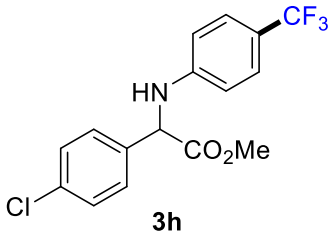
M. W. 339.3142 g/mol

Following General Procedure **GP3** for the title compound **3g'**, by using **1g** (54.0 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 49:1).to afford **3g'** as colourless oil (26.0 mg, 38%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{17}NO_3F_3]^+$: 340.1155; Found:. 340.1155.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 8.2 Hz, 1H), 5.78 (s, 1H), 5.08 (d, *J* = 4.1 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H). **^{19}F NMR** (376 MHz, CDCl3) δ -62.36. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 159.8, 143.3, 133.0, 128.3, 126.8 (q, *J* = 4.7 Hz), 125.2 (q, *J* = 272.7 Hz), 116.7, 114.2 (q, *J* = 30.3 Hz) 114.5, 112.8, 59.5, 55.3, 53.1.

8.15. methyl 2-(4-chlorophenyl)-2-((4-(trifluoromethyl)phenyl)amino) acetate (3h)



3h

$C_{16}H_{13}NO_2F_3Cl$

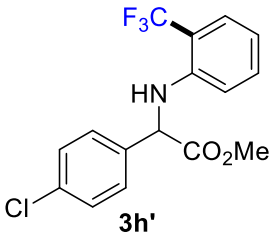
M. W. 343.7302 g/mol

Following General Procedure **GP-2** for the title compound **3h**, by using **1h** (54.7 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 39:1).to afford **3h** as colourless oil (25.5 mg, 37%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{16}H_{14}NO_2F_3Cl]^+$: 344.0660; Found:. 344.0665.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.35–7.32 (m, 4H), 6.52 (d, *J* = 8.7 Hz, 2H), 5.37 (s, 1H), 5.06 (s, 1H), 3.75 (s, 3H).**^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.13. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.3, 147.9, 135.3, 134.5, 129.3, 128.5, 126.7 (q, *J* = 4.7 Hz), 124.8 (q, *J* = 272.7 Hz), 119.9 (q, *J* = 30.3 Hz), 112.7, 59.5, 53.3.

8.16. methyl 2-(4-chlorophenyl)-2-((2-(trifluoromethyl)phenyl)amino) acetate (3h')



3h'

$C_{16}H_{13}NO_2F_3Cl$

M. W. 343.7302 g/mol

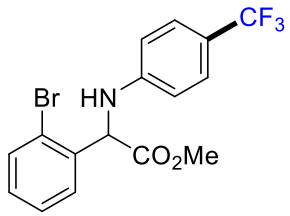
Following General Procedure **GP-2** for the title compound **3h'**, by using **1h** (54.7 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 49:1).to afford **3h'** as colourless oil (21.5 mg, 31%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{16}H_{14}NO_2F_3Cl]^+$: 344.0660; Found:. 344.0670.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.22–7.18 (m, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 8.2 Hz, 1H), 5.85 (s, 1H), 5.11 (d, *J* = 4.1 Hz, 1H), 3.76 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.36.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 141.8, 136.5, 132.9, 129.3, 128.9, 127.2, 126.9 (q, *J* = 4.7 Hz), 124.4 (q, *J* = 272.7 Hz), 115.5 (q, *J* = 30.3 Hz), 121.8, 114.3, 60.18, 53.39.

8.17. methyl 2-(2-bromophenyl)-2-((4-(trifluoromethyl)phenyl)amino) acetate (3i)



3i

$C_{16}H_{13}NO_2F_3Br$

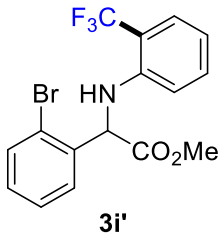
M. W. 387.0082 g/mol

Following General Procedure **GP-2** for the title compound **3i**, by using **1i** (63.5 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 39:1).to afford **3i** as colourless oil (24.0 mg, 31%).

HRMS (ESI): m/z $[M-H]^+$ Calculated for $[C_{16}H_{14}NO_2F_3Br]^+$: 388.0155; Found:.388.0154.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 1H), 7.42 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.18 (td, *J* = 7.7, 1.8 Hz, 1H), 6.57 (d, *J* = 8.6 Hz, 2H), 5.63 (s, 1H), 5.48 (s, 1H), 3.76 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.13. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.4, 148.0, 136.5, 133.5, 130.1, 128.3, 128.2, 126.8 (q, *J* = 4.7 Hz), 124.9 (q, *J* = 272.7 Hz) 124.6, 119.9 (q, *J* = 30.3 Hz) 112.7, 58.9, 53.3.

8.18. methyl 2-(2-bromophenyl)-2-((2-(trifluoromethyl)phenyl)amino) acetate (3i')



3i'

$C_{16}H_{13}NO_2F_3Br$

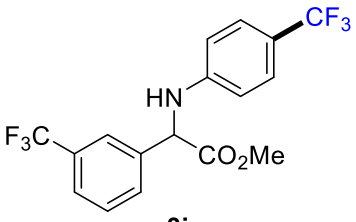
M. W. 387.0082 g/mol

Following General Procedure **GP-2** for the title compound **3i'**, by using **1i** (63.6 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 49:1).to afford **3i'** as colourless oil (24.0 mg, 31%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{16}H_{14}NO_2F_3Br]^+$: 388.0155; Found:.388.0154.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.43 (ddd, *J* = 7.8, 4.4, 1.7 Hz, 2H), 7.28–7.21 (m, 2H), 7.16 (td, *J* = 7.6, 1.8 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.39 (d, *J* = 8.3 Hz, 1H), 5.98 (s, 1H), 5.66 (d, *J* = 2.8 Hz, 1H), 3.75 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.36. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.1, 142.8, 136.6, 133.4, 133.2, 130.0, 128.4, 128.1, 126.8 (q, *J* = 4.7 Hz), 125.1 (q, *J* = 272.7 Hz), 124.6, 117.0, 114.4 (q, *J* = 30.3 Hz) 112.8, 58.7, 53.3.

8.19. methyl 2-(3-(trifluoromethyl)phenyl)-2-((4-(trifluoromethyl)phenyl)amino)acetate (3j)



3j

$C_{17}H_{13}NO_2F_6$

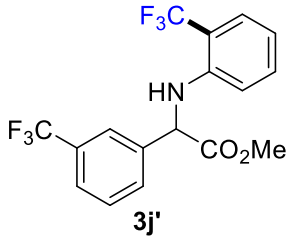
M. W. 377.2864 g/mol

Following General Procedure **GP-2** for the title compound **3j**, by using **1j** (61.5 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 39:1).to afford **3j** as colourless oil (25.0 mg, 33%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{14}NO_2F_6]^+$: 378.0923; Found:. 378.1001.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 8.7 Hz, 2H), 5.44 (s, 1H), 5.15 (d, *J* = 4.6 Hz, 1H), 3.78 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.04, -62.45. **^{13}C NMR (101 MHz, $CDCl_3$)** 171.1, 147.9, 138.1, 130.5, 131.5 (q, *J* = 30.3 Hz) 129.7, 126.8 (q, *J* = 10.1 Hz), 125.7 (q, *J* = 4.7 Hz), 124.8 (q, *J* = 272.7 Hz), 124.1 (q, *J* = 4.7 Hz), 123.9 (q, *J* = 272.7 Hz), 120.2 (q, *J* = 30.3 Hz), 112.8, 59.8, 53.4.

8.20. methyl 2-(3-(trifluoromethyl)phenyl)-2-((2-(trifluoromethyl)phenyl)amino) acetate (3j')



3j'

$C_{17}H_{13}NO_2F_6$

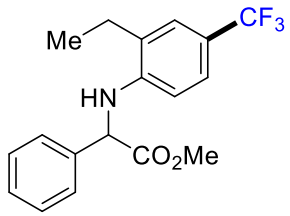
M. W. 377.2864 g/mol

Following General Procedure **GP-2** for the title compound **3j'**, by using **1j** (61.5 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 40:1).to afford **3j'** as colourless oil (22.0 mg, 29%).

HRMS (ESI): m/z $[M-H]^+$ Calculated for $[C_{17}H_{14}NO_2F_6]^+$: 378.0923; Found:. 378.0933.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.34 (d, *J* = 8.2 Hz, 1H), 5.90 (s, 1H), 5.19 (d, *J* = 5.0 Hz, 1H), 3.78 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.33, -62.52. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.79, 142.76, 138.14, 133.11, 131.5 (q, *J* = 30.3 Hz), 130.26, 129.67, 127.0 (q, *J* = 4.7 Hz), 125.6 (q, *J* = 4.7 Hz),125.0 (q, *J* = 272.7 Hz), 124.2 (q, *J* = 4.7 Hz), 124.0 (q, *J* = 272.7 Hz), 117.28, 114.6, 112.71, 59.80, 53.49.

8.21. methyl 2-((2-ethyl-4-(trifluoromethyl)phenyl)amino)-2-phenyl acetate (3k)



3k

$C_{18}H_{18}NO_2F_3$

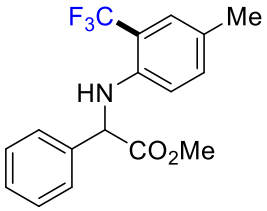
M. W. 337.3422 g/mol

Following General Procedure **GP-2** for the title compound **3k**, by using **1k** (53.5 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 39:1).to afford **3k** as colourless oil (40.5 mg, 60%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{18}H_{18}NNaO_2F_3]^+$: 360.1182; Found:. 360.3296.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.39–7.32 (m, 3H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.20 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.31 (d, *J* = 8.3 Hz, 1H), 5.37 (s, 1H), 5.13 (s, 1H), 3.76 (s, 3H), 2.67 (q, *J* = 7.5 Hz, 2H), 1.36 (t, *J* = 7.5 Hz, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.13. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.1, 145.8, 137.0, 129.1, 128.6, 127.8, 127.2, 125.1 (q, *J* = 272.7 Hz), 124.9 (q, *J* = 4.7 Hz), 124.4 (q, *J* = 4.7 Hz), 119.4 (30.3 Hz), 110.0, 60.2, 53.2, 23.9, 12.5.

8.22. methyl 2-((4-methyl-2-(trifluoromethyl) phenyl) amino)-2-phenylacetate (3l)



3l

$C_{18}H_{18}NO_2F_3$

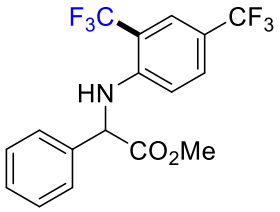
M. W. 323.3152 g/mol

Following General Procedure **GP-2** for the title compound **3l**, by using **1l** (50.7 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 40:1).to afford **3l** as colourless oil (31.0 mg, 48%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{18}H_{19}NO_2F_3]^+$: 324.1206; Found:. 324.1214.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.48 (m, 2H), 7.39–7.30 (m, 3H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.01 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.34 (d, *J* = 8.5 Hz, 1H), 5.69 (s, 1H), 5.14 (s, 1H), 3.75 (s, 3H), 2.21 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.21. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.7, 140.9, 137.1, 133.5, 129.0, 128.5, 127.2, 127.1 (q, *J* = 4.7 Hz), 126.1, 125.2 (q, *J* = 272.7 Hz), 114.2 (q, *J* = 30.3 Hz)113.0, 60.2, 53.1, 20.2.

8.23. methyl 2-((2,4-bis(trifluoromethyl)phenyl)amino)-2-phenylacetate (3m)



3m

$C_{17}H_{13}NO_2F_6$

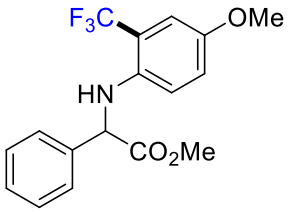
M. W. 377.0850 g/mol

Following General Procedure **GP-2** for the title compound **3m**, by using **1m** (61.5 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 40:1).to afford **3m** as colourless oil (34.0 mg, 45%).

MS-MS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{14}NO_2F_6]^+$: 378.29; Found:. 378.29.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.47–7.32 (m, 6H), 6.44 (d, *J* = 8.7 Hz, 1H), 6.22 (s, 1H), 5.15 (d, *J* = 5.5 Hz, 1H), 3.77 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.65, -63.15. **^{13}C NMR (101 MHz, $CDCl_3$** δ 171.0, 145.5, 135.9, 130.1, 129.3, 128.9, 127.1, 124.5 (q, *J* = 4.7 Hz), 124.4 (q, *J* = 272.7 Hz), 124.2 (q, *J* = 272.2 Hz), 118.8 (q, *J* = 30.3 Hz), 114.0 (q, *J* = 30.3 Hz), 112.6, 59.9, 53.4.

8.24. methyl 2-((4-methoxy-2-(trifluoromethyl)phenyl)amino)-2-phenylacetate (3n)



3n

$C_{17}H_{16}NO_3F_3$

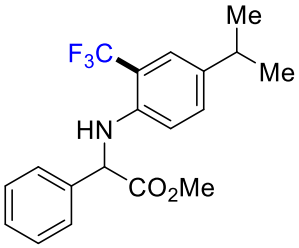
M. W. 339.3142 g/mol

Following General Procedure **GP-2** for the title compound **3n**, by using **1n** (54.0 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 40:1).to afford **3n** as colourless oil (27.0 mg, 40%).

MS-MS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{17}NO_3F_3]^+$: 340.32; Found:. 340.39.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 6.4 Hz, 2H), 7.38–7.29 (m, 3H), 7.04 (d, *J* = 2.7 Hz, 1H), 6.81 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.39 (d, *J* = 9.2 Hz, 1H), 5.52 (s, 1H), 5.10 (s, 1H), 3.74 (s, 3H), 3.71 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.24. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 151.0, 137.5, 137.2, 129.0, 128.5, 127.2, 124.6 (q, *J* = 272.6 Hz), 123.4 (q, *J* = 4.7 Hz), 115.1 (q, *J* = 30.3 Hz), 119.0, 114.4, 60.7, 55.9, 53.1.

8.25. methyl 2-((4-isopropyl-2-(trifluoromethyl) phenyl) amino)-2-phenylacetate (3o)



3o

$C_{19}H_{20}NO_2F_3$

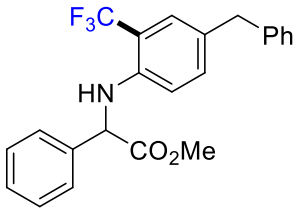
M. W. 351.3692 g/mol

Following General Procedure **GP-2** for the title compound **3o**, by using **1o** (56.3 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 3:7).to afford **3o** as a colourless oil (38.0 mg, 54%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{19}H_{20}NNaO_2F_3]^+$: 374.1338; Found: 374.1357.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 6.4, 3.7 Hz, 2H), 7.40–7.30 (m, 4H), 7.09 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.40 (d, *J* = 8.2 Hz, 1H), 5.73 (s, 1H), 5.14 (s, 1H), 3.75 (s, 3H), 2.80 (hept, *J* = 6.9 Hz, 1H), 1.19 (d, *J* = 1.4 Hz, 3H), 1.17 (d, *J* = 1.4 Hz, 3H).).**^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.02. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.7, 141.3, 137.3, 137.2, 131.0, 129.0, 128.5, 127.2, 125.3 (q, *J* = 272.7 Hz), 124.6 (q, *J* = 4.7 Hz), 114.1 (q, *J* = 30.3 Hz) 112.9, 60.3, 53.0, 33.0, 24.0.

8.26. methyl 2-((4-benzyl-2-(trifluoromethyl) phenyl) amino)-2-phenylacetate (3p)



3p

$C_{23}H_{20}NO_2F_3$

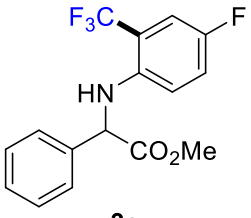
M. W. 399.4132 g/mol

Following General Procedure **GP-2** for the title compound **3p**, by using **1p** (65.9 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 40:1).to afford **3p** as colourless oil (38.0 mg, 48%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{23}H_{21}NO_2F_3]^+$: 400.4205; Found:. 400.4217.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.44 (m, 2H), 7.37–7.23 (m, 6H), 7.19–7.13 (m, 1H), 7.11 (dd, *J* = 7.3, 1.7 Hz, 2H), 6.99 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.34 (d, *J* = 8.5 Hz, 1H), 5.73 (s, 1H), 5.09 (s, 1H), 3.83 (s, 2H), 3.73 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.15. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.6, 141.5, 141.0, 137.0, 133.4, 129.5, 129.1, 128.8, 128.6, 127.2, 127.0 (q, *J* = 4.7 Hz), 126.2, 125.1 (q, *J* = 272.7 Hz), 114.2 (q, *J* = 30.3 Hz), 113.0, 60.2, 53.1, 40.7.

8.27. methyl 2-((4-fluoro-2-(trifluoromethyl) phenyl) amino)-2-phenylacetate (3q)



3q

$C_{16}H_{13}NO_2F_4$

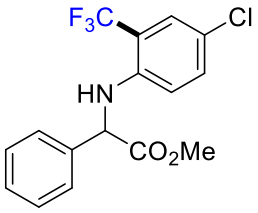
M. W. 327.2786 g/mol

Following General Procedure **GP-2** for the title compound **3q**, by using **1q** (51.5 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 40:1).to afford **3q** as colourless oil (38.5 mg, 59%).

MS-MS (ESI): m/z $[M+H]^+$ Calculated for $[C_{16}H_{14}NO_2F_4]^+$: 328.09; Found: 328.16.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H), 7.39–7.31 (m, 3H), 7.20 (dd, *J* = 8.8, 3.1 Hz, 1H), 6.93 (td, *J* = 8.3, 3.0 Hz, 1H), 6.35 (dd, *J* = 9.0, 4.3 Hz, 1H), 5.73 (s, 1H), 5.09 (s, 1H), 3.75 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.79, -127.38. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.5, 155.5, 154.4 (d, *J* = 238.3 Hz), 153.2, 139.6, 136.7, 129.2, 128.7, 127.2, 124.2 (q, *J* = 272.7 Hz), 119.8 (d, *J* = 22.2 Hz), 114.9 (qd, *J* = 7.1 Hz, *J* = 30.3 Hz), 114.1 (d, *J* = 8.08 Hz), 113.7 (m), 60.5, 53.2.

8.28. methyl 2-((4-chloro-2-(trifluoromethyl) phenyl) amino)-2-phenylacetate (3r)



3r

$C_{16}H_{13}NO_2F_3Cl$

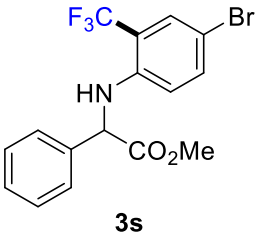
M. W. 343.7302 g/mol

Following General Procedure **GP-2** for the title compound **3r**, by using **1r** (54.7 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 39:1).to afford **3r** as colourless oil (46.0 mg, 67%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{16}NO_2F_3Cl]^+$: 344.7377; Found:. 344.7385.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.43 (m, 3H), 7.38–7.32 (m, 3H), 7.14 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.33 (d, *J* = 8.7 Hz, 1H), 5.87 (s, 1H), 5.09 (d, *J* = 5.0 Hz, 1H), 3.75 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.91. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.3, 141.7, 136.4, 132.8, 129.2, 128.8, 127.1, 126.8 (q, *J* = 4.7 Hz), 124.3 (q, *J* = 272.7 Hz), 121.7, 115.4 (q, *J* = 30.3 Hz) 114.2, 60.1, 53.3.

8.29. methyl 2-((4-bromo-2-(trifluoromethyl) phenyl) amino)-2-phenylacetate (3s)



3s

$C_{16}H_{13}NO_2F_3Br$

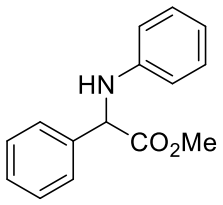
M. W. 387.1842 g/mol

Following General Procedure **GP-2** for the title compound **3s**, by using **1s** (63.6 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 7:3).to afford **3s** as colourless oil (48.0 mg, 62%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{17}H_{16}NO_2F_3Br]^+$: 388.0155; Found: 388.0155.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 3H), 7.39–7.32 (m, 3H), 7.14 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.33 (d, *J* = 9.2 Hz, 1H), 5.87 (d, *J* = 5.0 Hz, 1H), 5.09 (d, *J* = 5.5 Hz, 1H), 3.75 (s, 3H).**^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.82. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.3, 141.7, 136.4, 132.8, 129.2, 128.8, 127.1, 126.8 (q, *J* = 4.7 Hz), 124.2 (q, *J* = 272.7 Hz), 121.7, 115.4 (30.3 Hz), 114.2, 60.1, 53.3.

8.30. methyl 2-phenyl-2-(phenylamino)acetate (4)



4

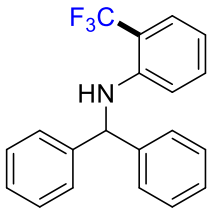
$C_{15}H_{15}NO_2$

M. W. 241.2900 g/mol

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{15}H_{16}NO_2]^+$: 242.1176; Found: 242.1170.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2H), 7.39–7.29 (m, 3H), 7.15–7.11 (m, 2H), 6.71 (td, *J* = 7.4, 1.3 Hz, 1H), 6.57 (d, *J* = 8.1 Hz, 2H), 5.09 (d, *J* = 5.8 Hz, 1H), 4.97 (d, *J* = 5.9 Hz, 1H), 3.74 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.4, 146.0, 137.6, 129.3, 129.0, 128.4, 127.3, 118.2, 113.4, 60.8, 52.9.

8.31. N-benzhydryl-2-(trifluoromethyl)aniline (3aa)



3aa

$C_{20}H_{16}F_3N$

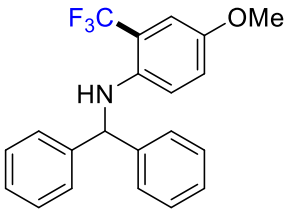
M. W. 327.3502 g/mol

Following General Procedure **GP-2** for the title compound **3aa**, by using **1aa** (51.50 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 99:1).to afford **3aa** as colourless oil (19.50 mg, 30%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{20}H_{17}NF_3]^+$: 328.1308; Found:.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 4.1 Hz, 6H), 7.29 (dt, *J* = 9.2, 4.4 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 8.2 Hz, 1H), 5.62 (d, *J* = 4.6 Hz, 1H), 4.95 (s, 1H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.36. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.5, 142.1, 133.1, 129.1, 127.8, 127.4, 126.6 (q, J = 4.7 Hz), 125.4 (q, J = 272.7 Hz), 116.5,113.6 (q, 30.3 Hz), 113.4, 62.4.

8.32. N-benzhydryl-4-methoxy-2-(trifluoromethyl)aniline (3ba)



3ba

$C_{21}H_{18}F_3NO$

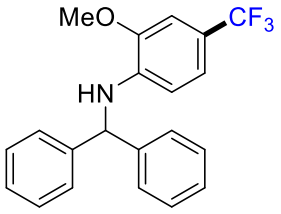
M. W. 357.3762 g/mol

Following General Procedure **GP-2** for the title compound **3ba**, by using **1ba** (57.50 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 99:1).to afford **3ba** as colourless oil (21.50 mg, 30%).

HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{21}H_{19}NOF_3]^+$: 358.1413; Found:.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.24 (m, 8H), 7.28–7.24 (m, 2H), 7.04 (d, *J* = 3.2 Hz, 1H), 6.82 (dd, *J* = 9.2, 3.2 Hz, 1H), 6.52 (d, *J* = 9.2 Hz, 1H), 5.54 (d, *J* = 4.1 Hz, 1H), 4.65 (s, 1H), 3.72 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.33. **^{13}C NMR (101 MHz, $CDCl_3$)**. δ 150.9, 142.5, 138.8, 129.0, 127.7, 127.4,125.0 (q, *J* = 272.7 Hz), 119.1, 115.1, 114.8 (q, 30.3 Hz), 112.3(q, *J* = 4.7 Hz) 62.9, 56.0.

8.33. N-benzhydryl-2-methoxy-4-(trifluoromethyl)aniline (3ca)



3ca

$C_{21}H_{18}F_3NO$

M. W. 357.3762 g/mol

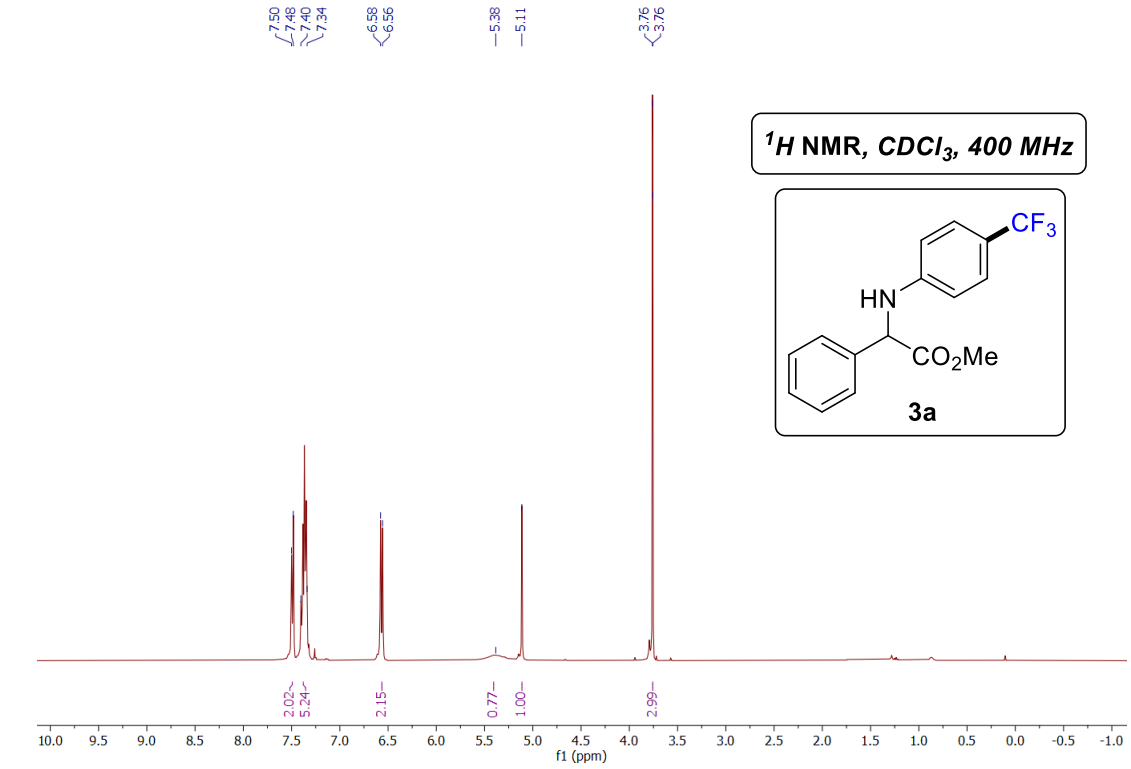
Following General Procedure **GP-2** for the title compound **3ca**, by using **1ca** (57.50 mg, 0.2 mmol, 1.0 equiv), **2** (93.6 mg, 0.6 mmol, 3.0 equiv), Cs_2CO_3 (130.0 mg, 0.4 mmol, 2.0 equiv), Na_2HPO_4 (28.4 mg, 0.2 mmol, 1.0 equiv) and $[Ir(ppy)_2(dtbpy)]PF_6$ (2.0 mg, 0.002 mmol, 1 mol%), in Acetone for 18 h at 35 °C. Purification was carried out by column chromatography on silica gel or PTLC (Hexane/EtOAc = 99:1).to afford **3ca** as colourless oil (25.00 mg, 30%).

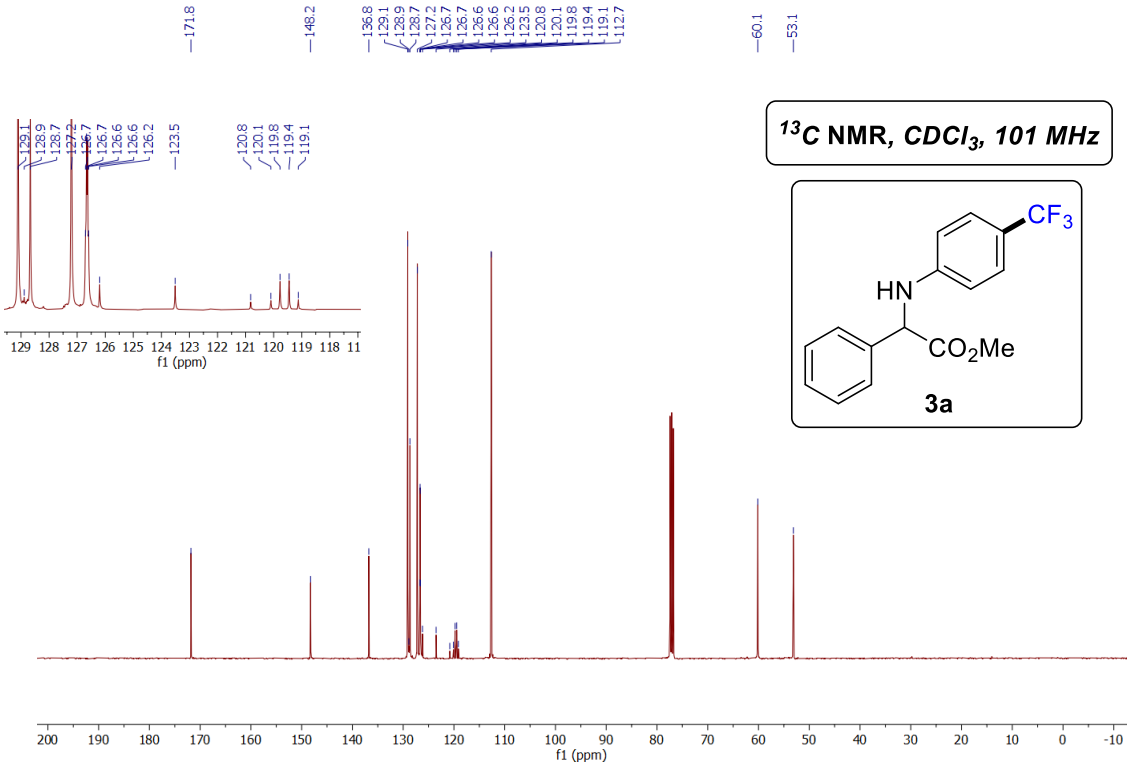
HRMS (ESI): m/z $[M+H]^+$ Calculated for $[C_{21}H_{19}NOF_3]^+$: 358.1413; Found:.

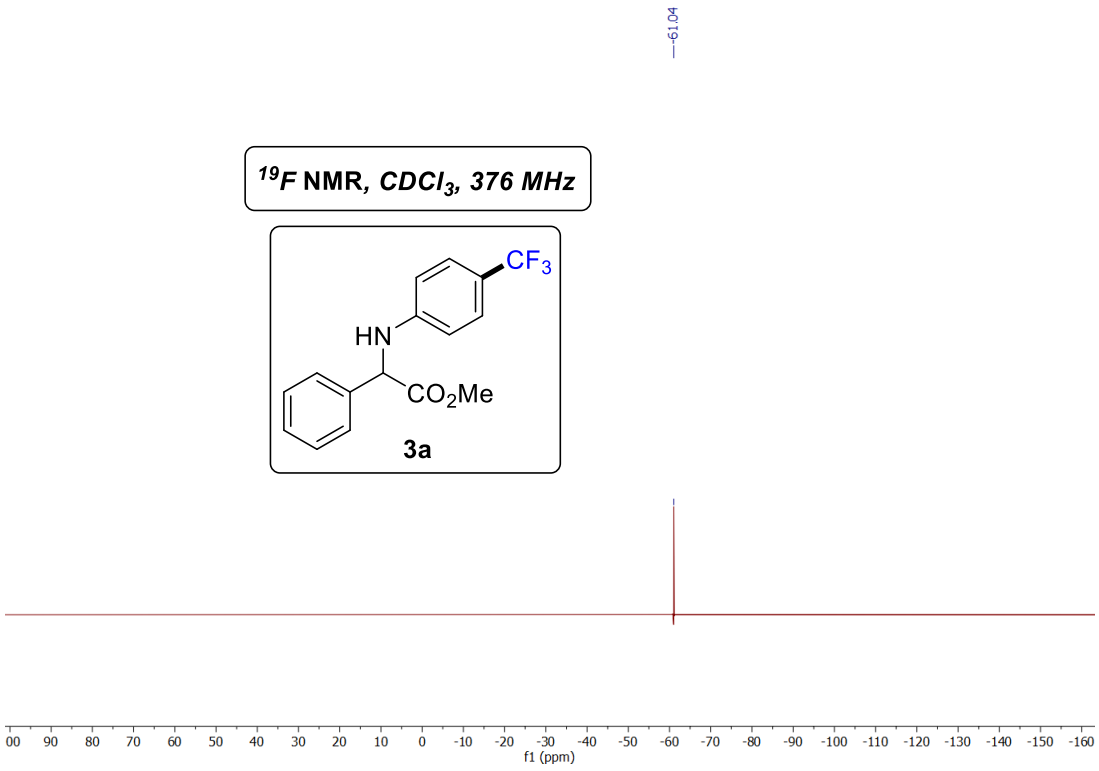
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.1 Hz, 8H), 7.31–7.27 (m, 2H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 2.3 Hz, 1H), 6.38 (d, *J* = 8.2 Hz, 1H), 5.55 (d, *J* = 4.6 Hz, 1H), 5.12 (d, *J* = 4.6 Hz, 1H), 3.89 (s, 3H).**^{19}F NMR (376 MHz, $CDCl_3$)** δ -60.70. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.3, 142.3, 139.9, 129.0,127.8(q, *J* = 272.7 Hz), 127.7, 127.5, 118.9 (q, *J* = 4.7 Hz), 118.3 (q, 30.3 Hz), 109.9, 105.9 (q, *J* = 4.7 Hz) 62.5, 55.7.

8. Experimental Details for the Substrate Scope

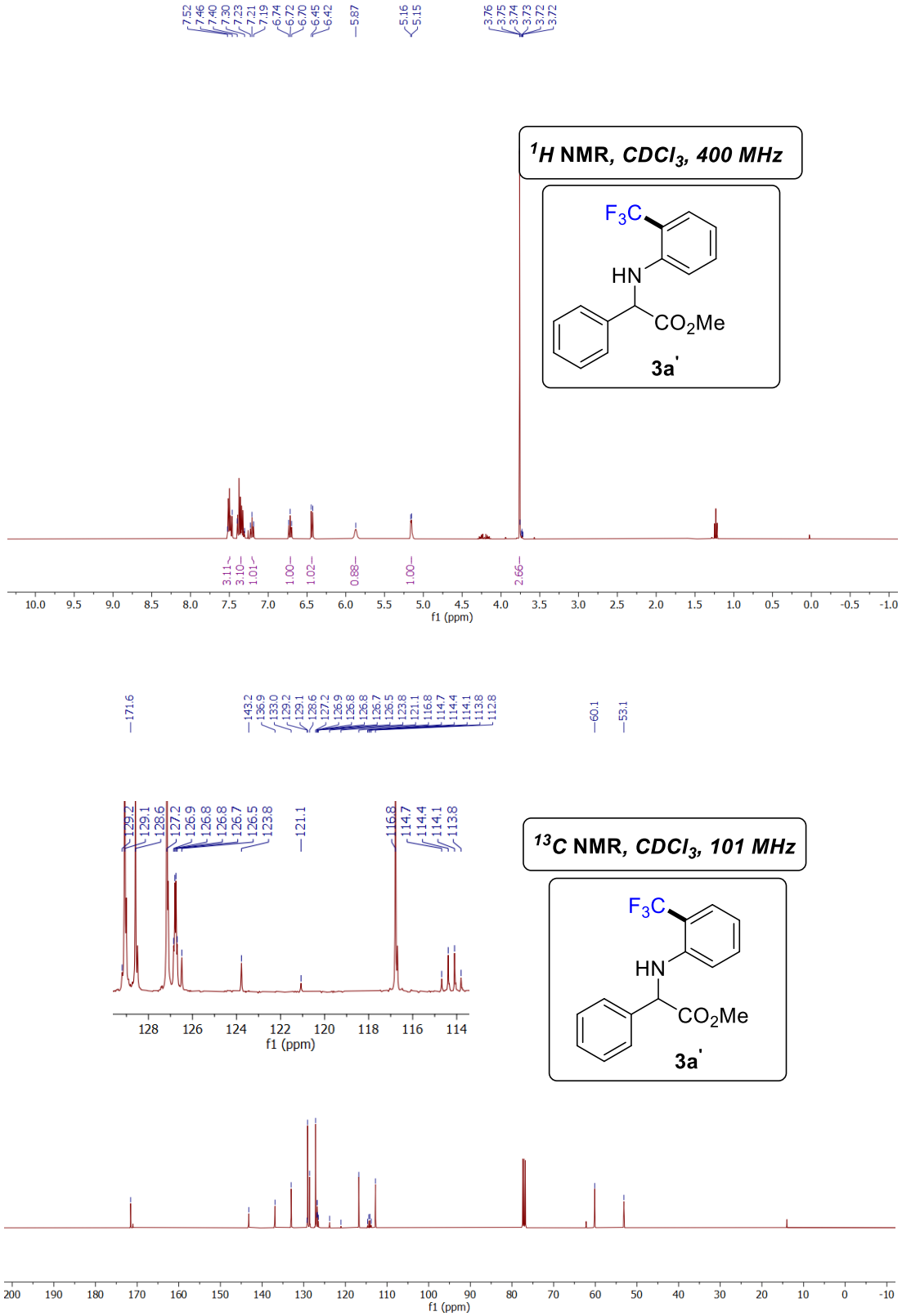
8.1. Methyl 2-phenyl-2-((4-(trifluoromethyl)phenyl)amino) acetate (3a)

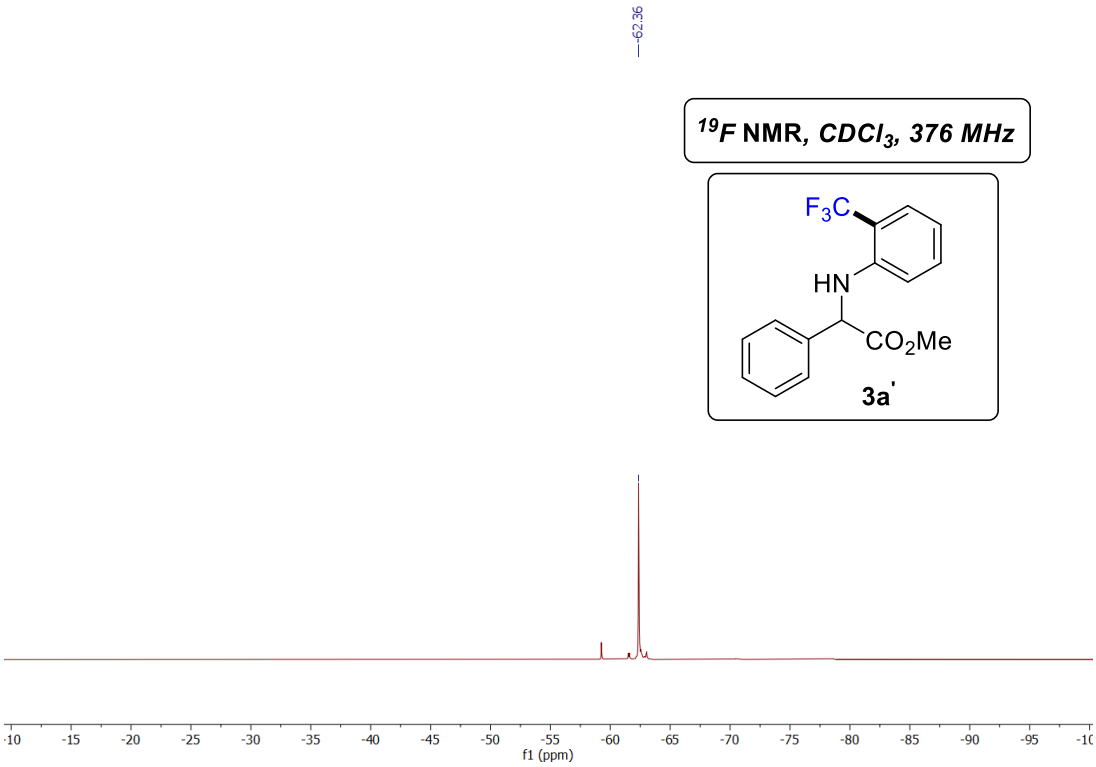




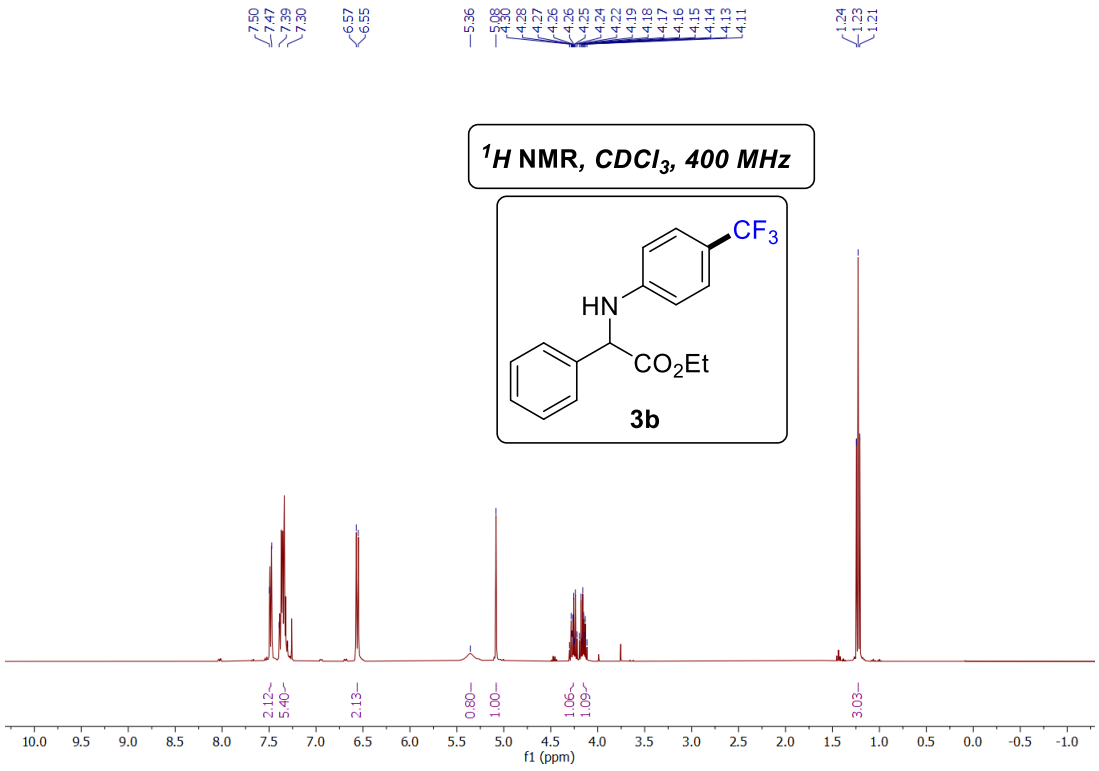

-61.04
19F NMR, CDCl3, 376 MHz
CF3
HN
CO2Me
3a
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

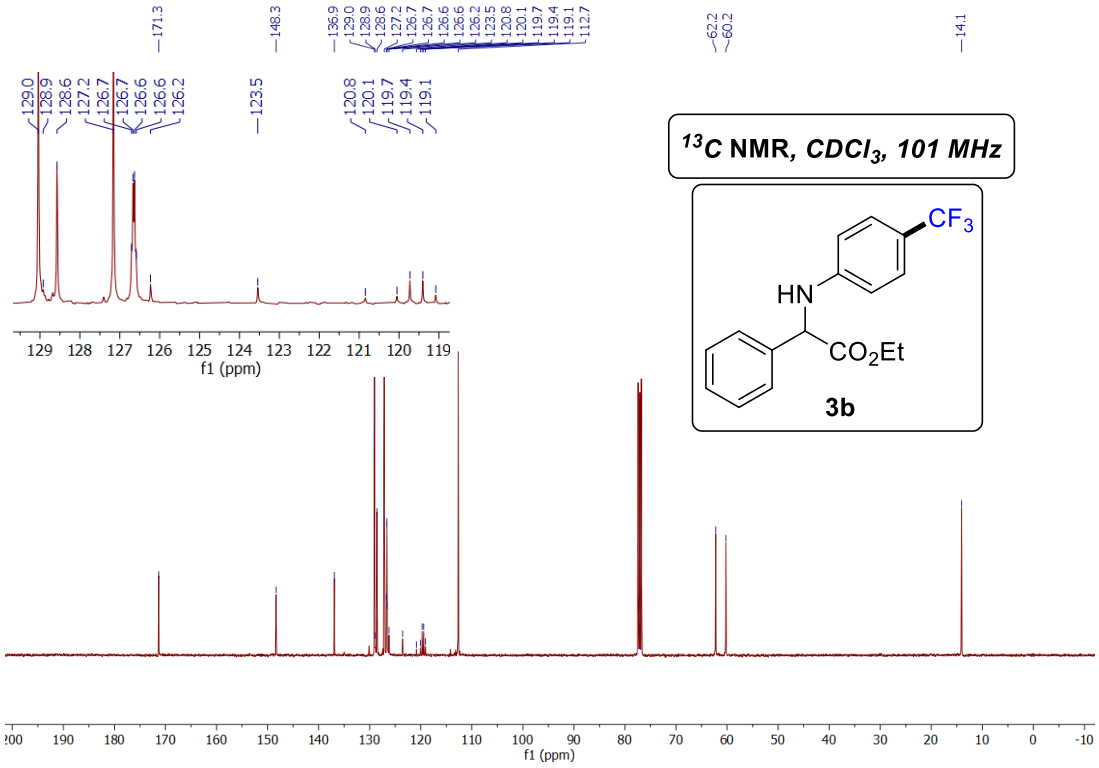
8.2 Methyl 2-phenyl-2-((2-(trifluoromethyl)phenyl)amino) acetate (3a′)

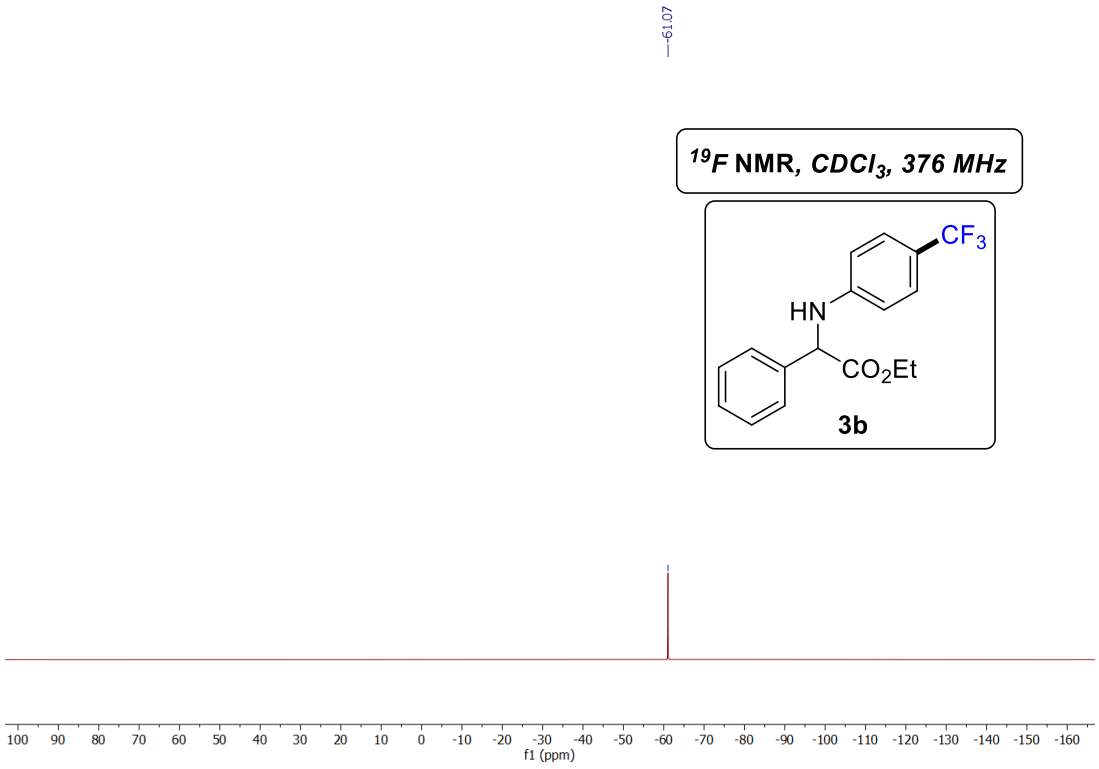



-62.36
19F NMR, CDCl3, 376 MHz
F3C
HN
CO2Me
3a'
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)

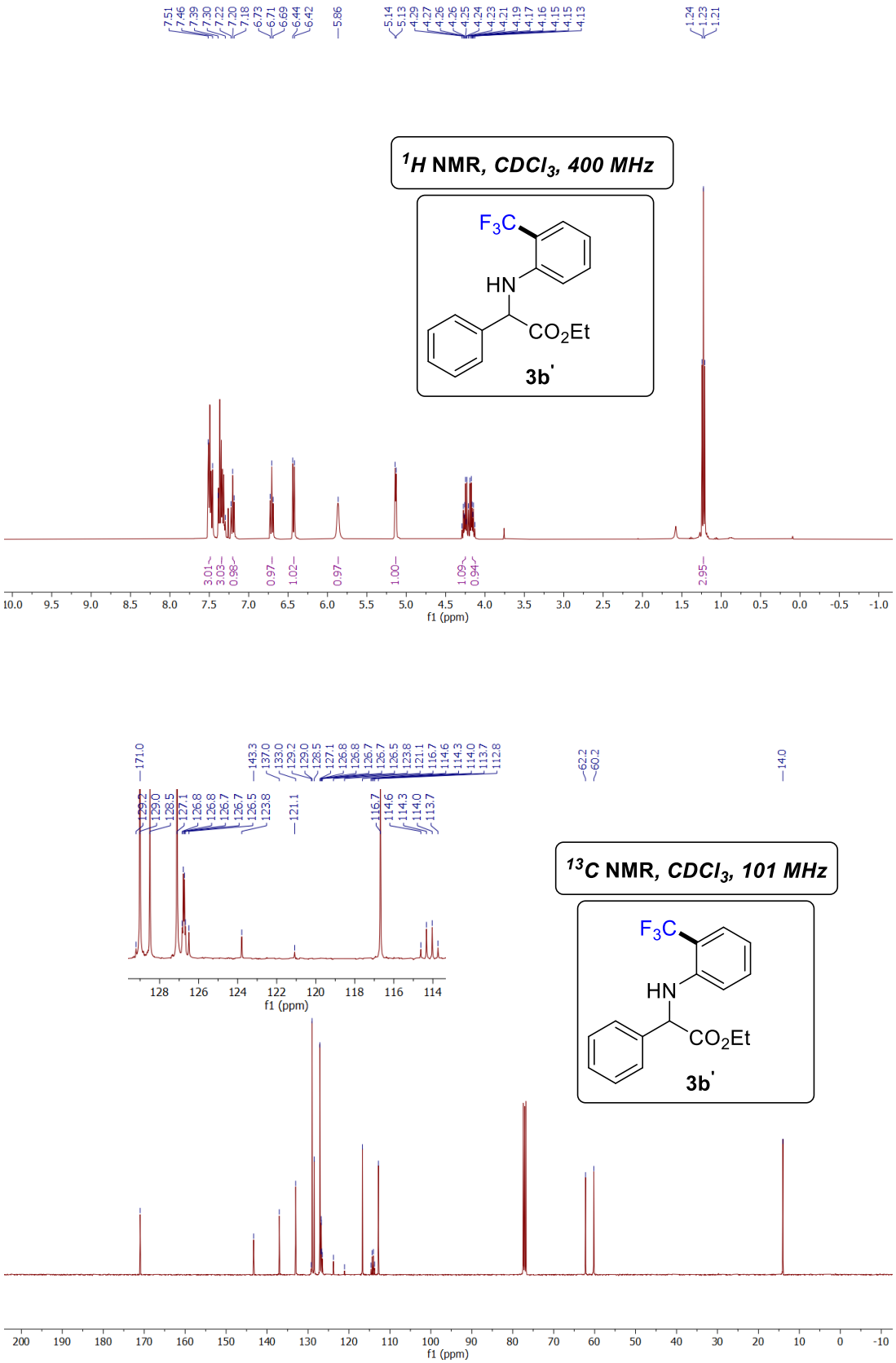
8.3 Ethyl 2-phenyl-2-((4-(trifluoromethyl)phenyl)amino) acetate (3b)

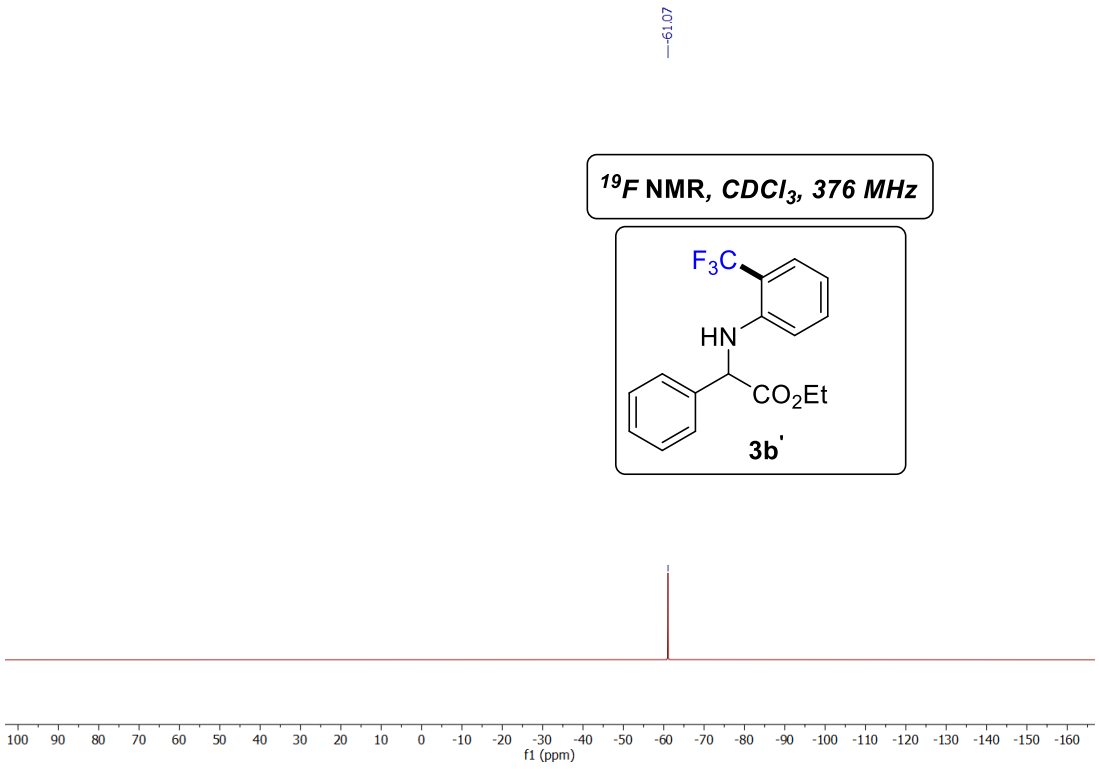




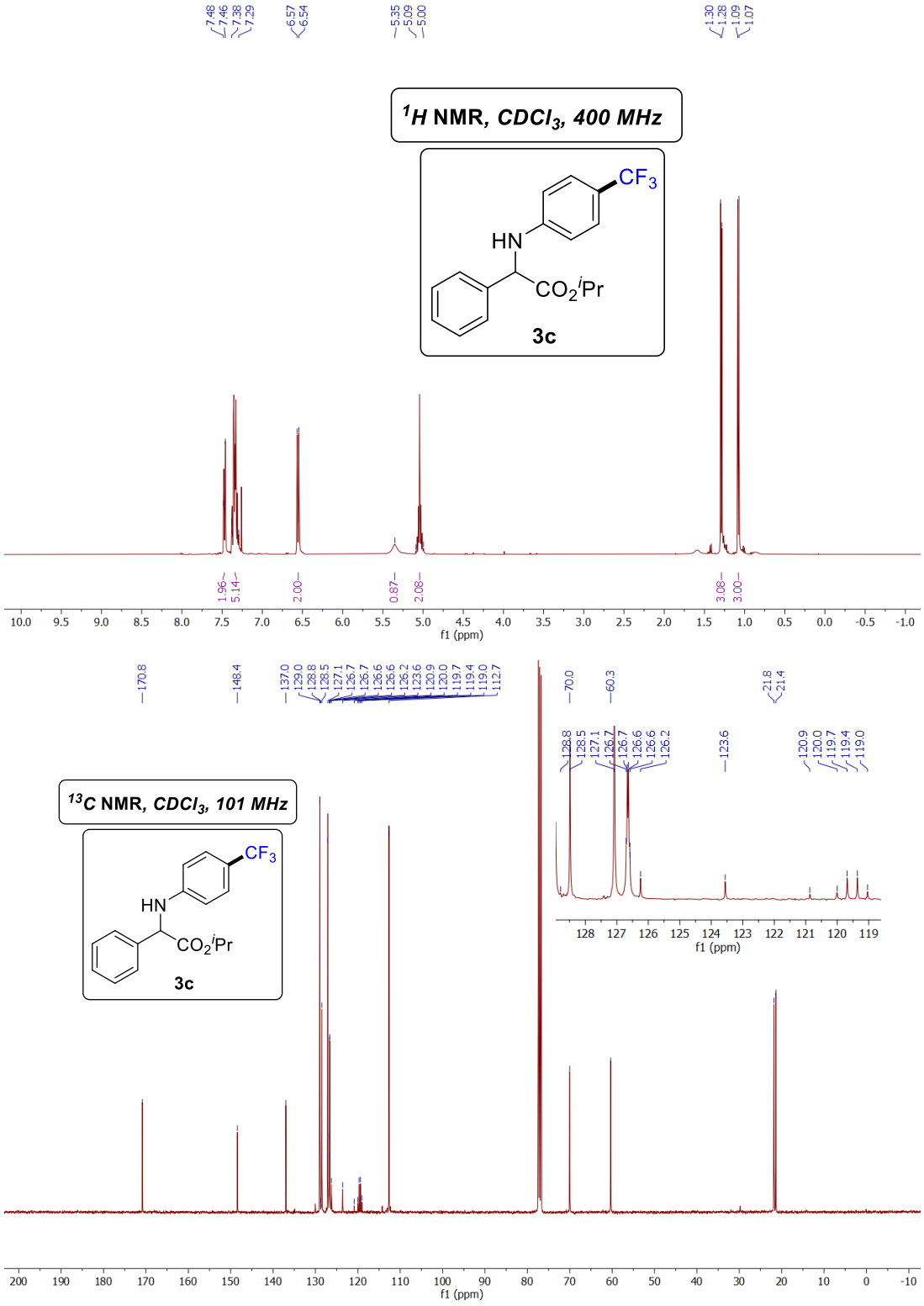

-61.07
19F NMR, CDCl3, 376 MHz
CF3
HN
CO2Et
3b
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

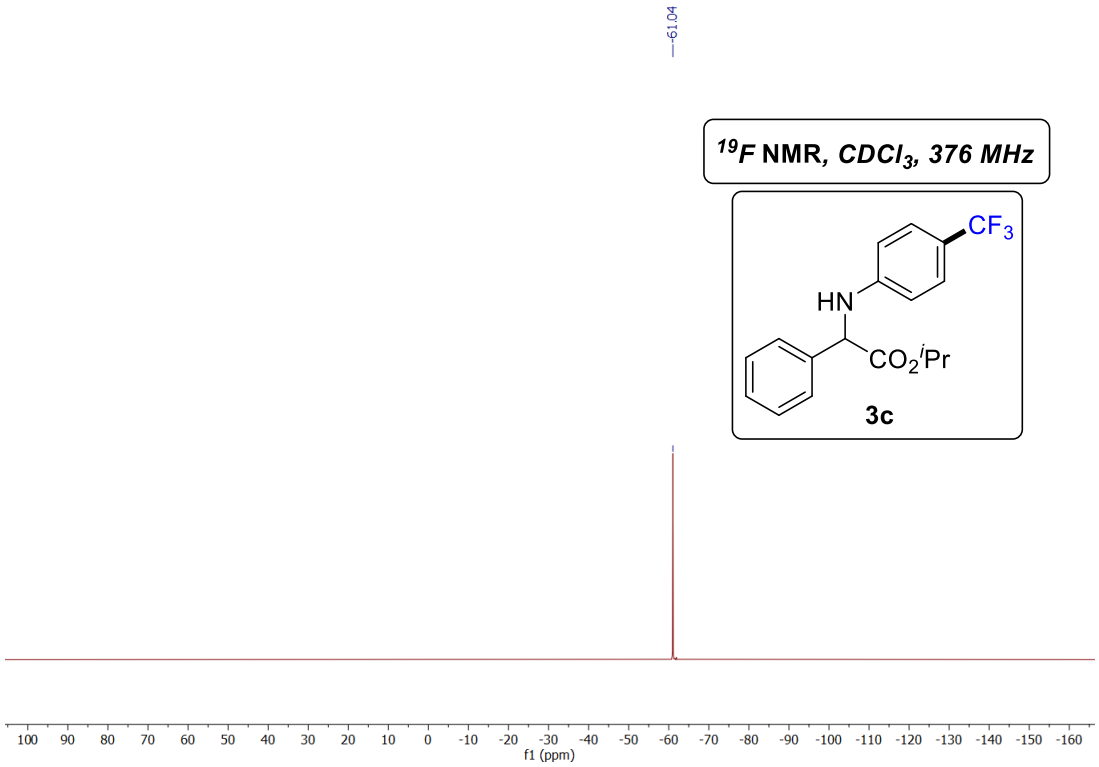
8.4 Ethyl 2-phenyl-2-((2-(trifluoromethyl)phenyl)amino) acetate (3b′)



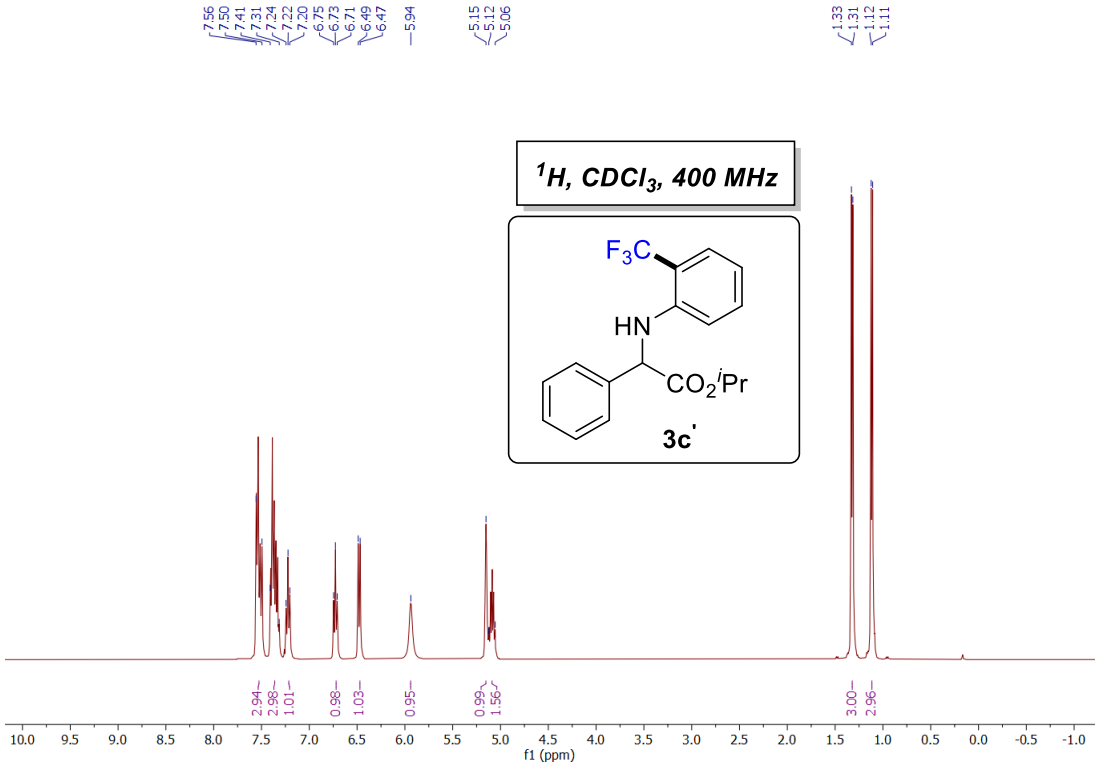

-61.07
19F NMR, CDCl3, 376 MHz
F3C
HN
CO2Et
3b'
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

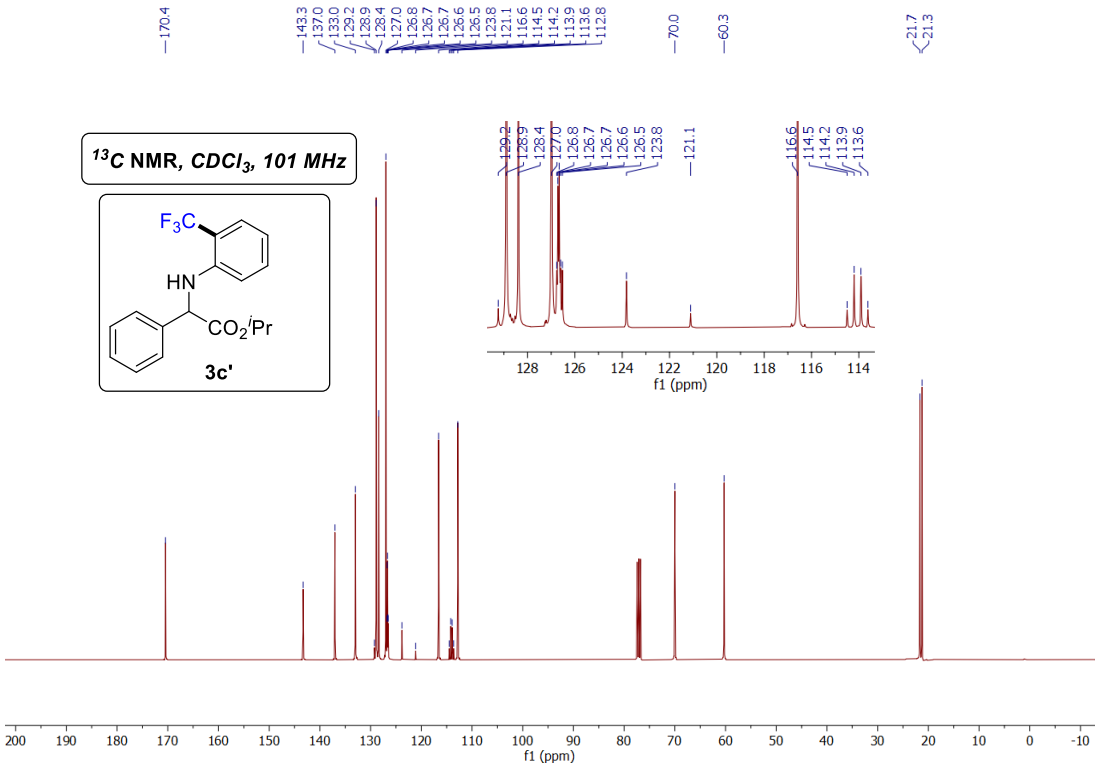
8.5 Isopropyl 2-phenyl-2-((4-(trifluoromethyl)phenyl)amino) acetate (3c)

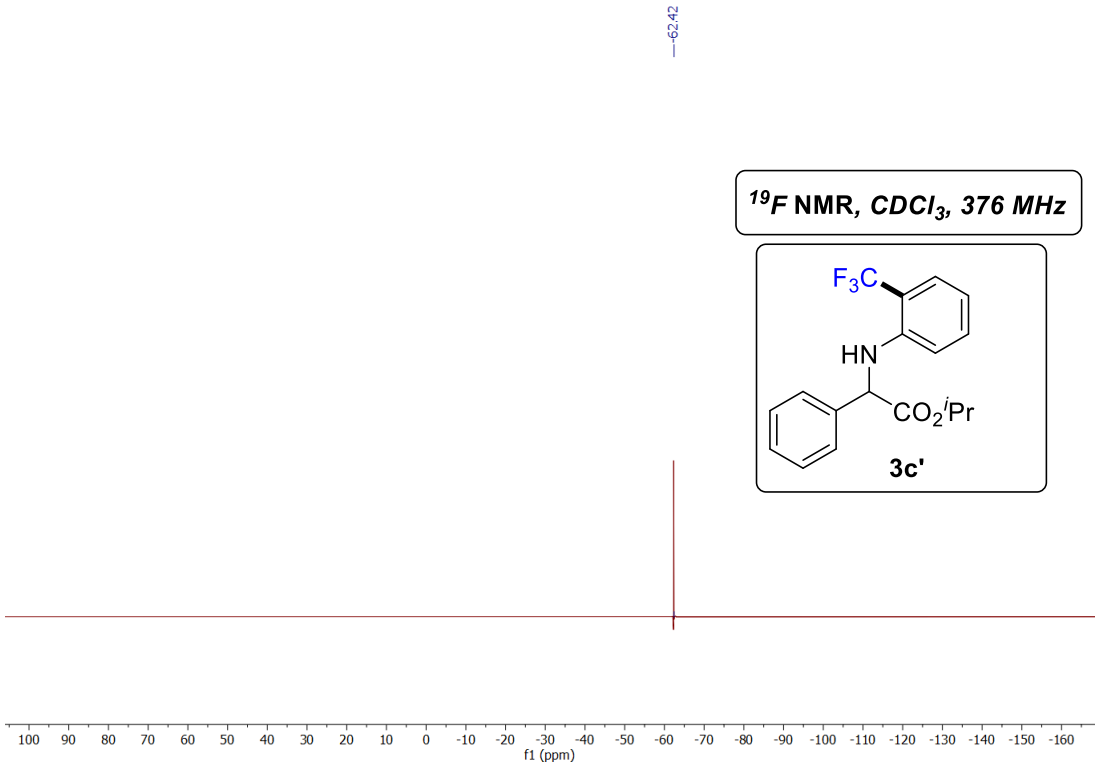



-61.04
19F NMR, CDCl3, 376 MHz
CF3
HN
CO2iPr
3c
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

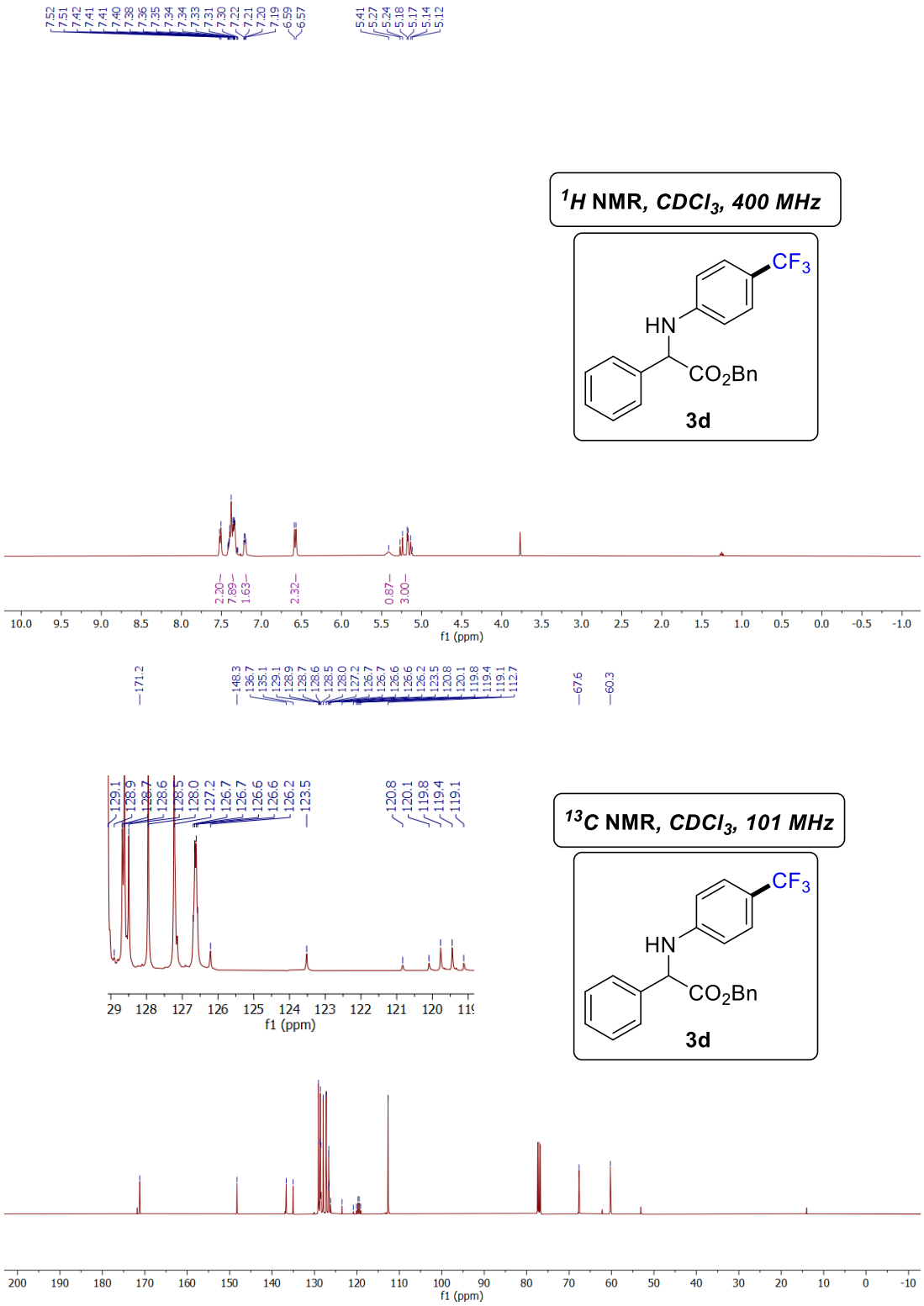
8.6 Isopropyl 2-phenyl-2-((2-(trifluoromethyl)phenyl)amino) acetate (3c′)

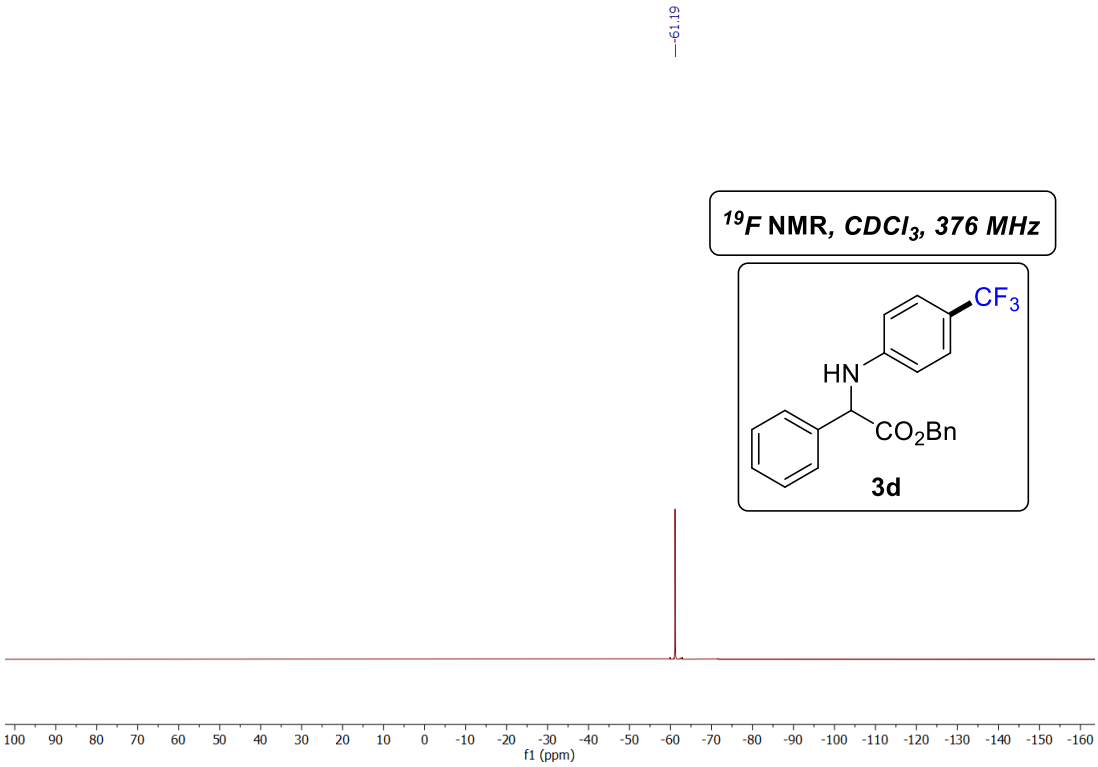




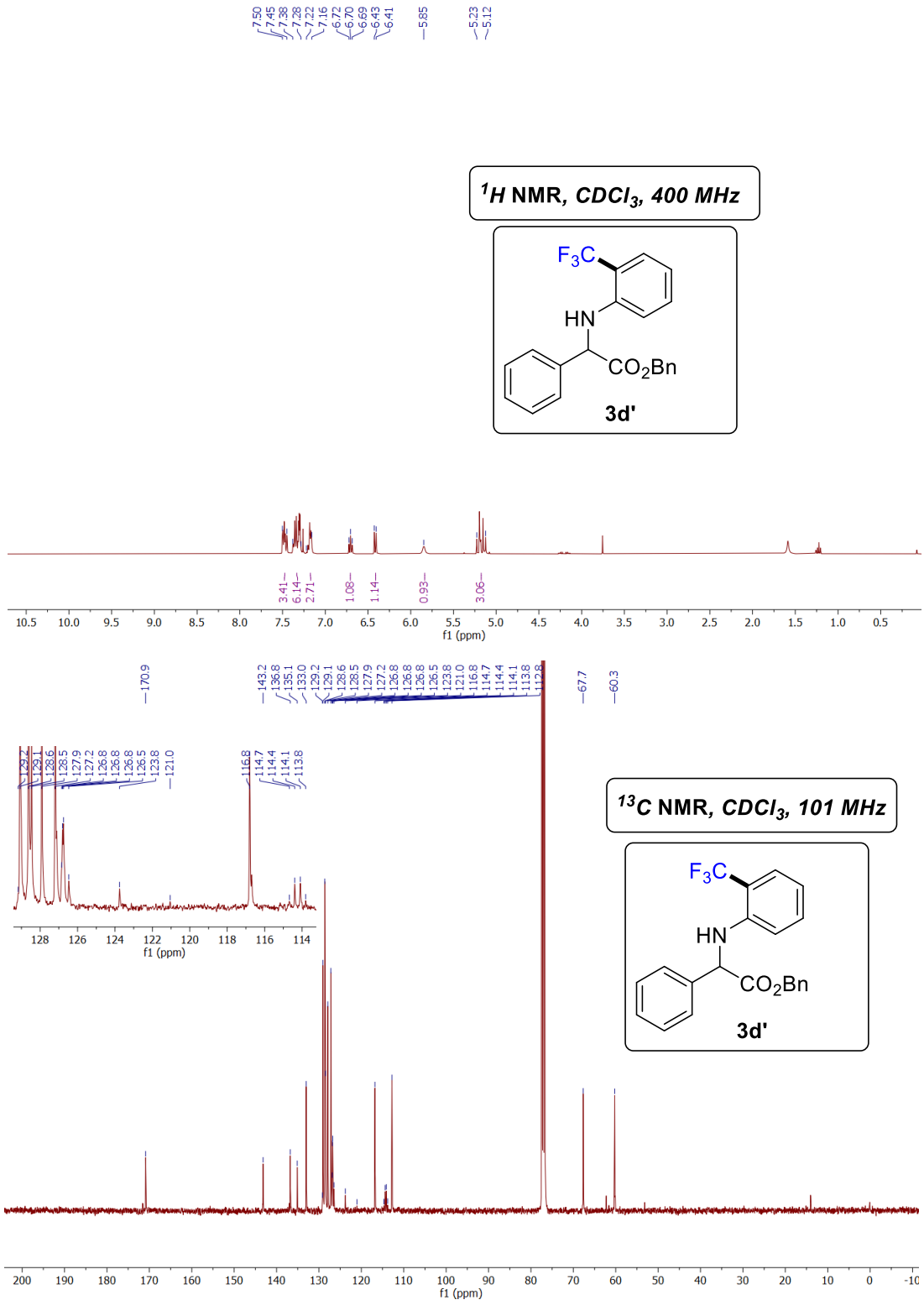

-62.42
^{19}F NMR, $CDCl_3$, 376 MHz
F_3C
HN
$CO_2{}^iPr$
3c'
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

8.7 Benzyl 2-phenyl-2-((4-(trifluoromethyl)phenyl)amino) acetate (3d)

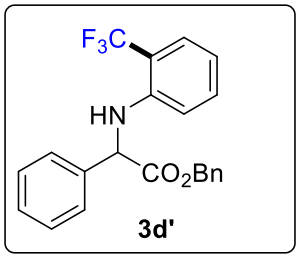



-61.19
^{19}F NMR, $CDCl_3$, 376 MHz
CF_3
HN
CO_2Bn
3d
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

8.8 Benzyl 2-phenyl-2-((2-(trifluoromethyl)phenyl)amino) acetate (3d′)

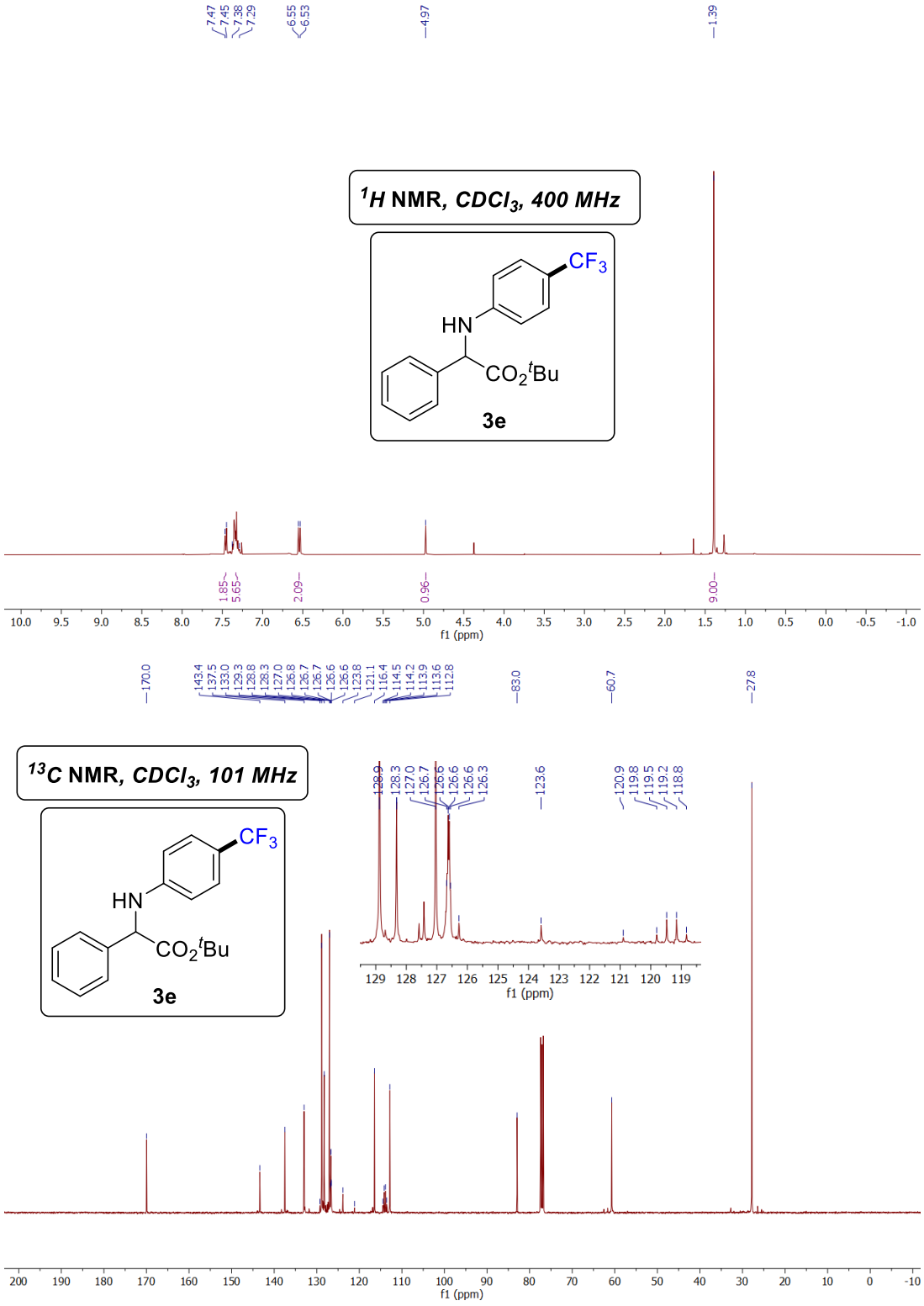


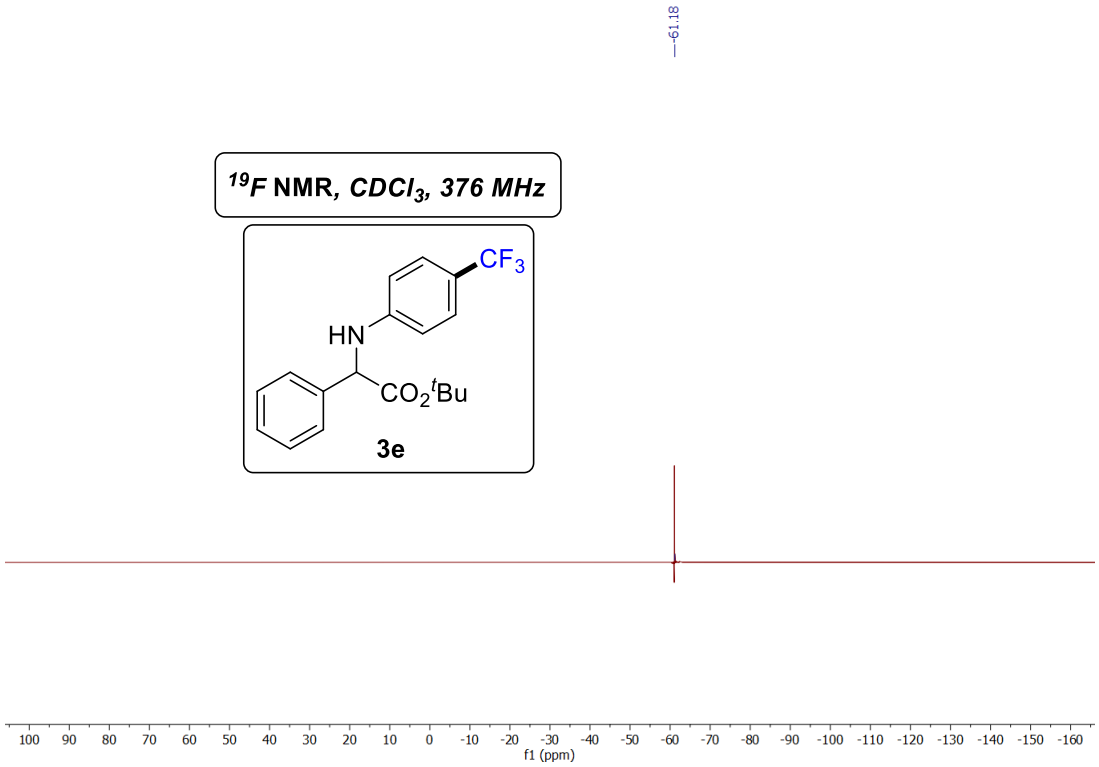
^{19}F NMR, $CDCl_3$, 376 MHz



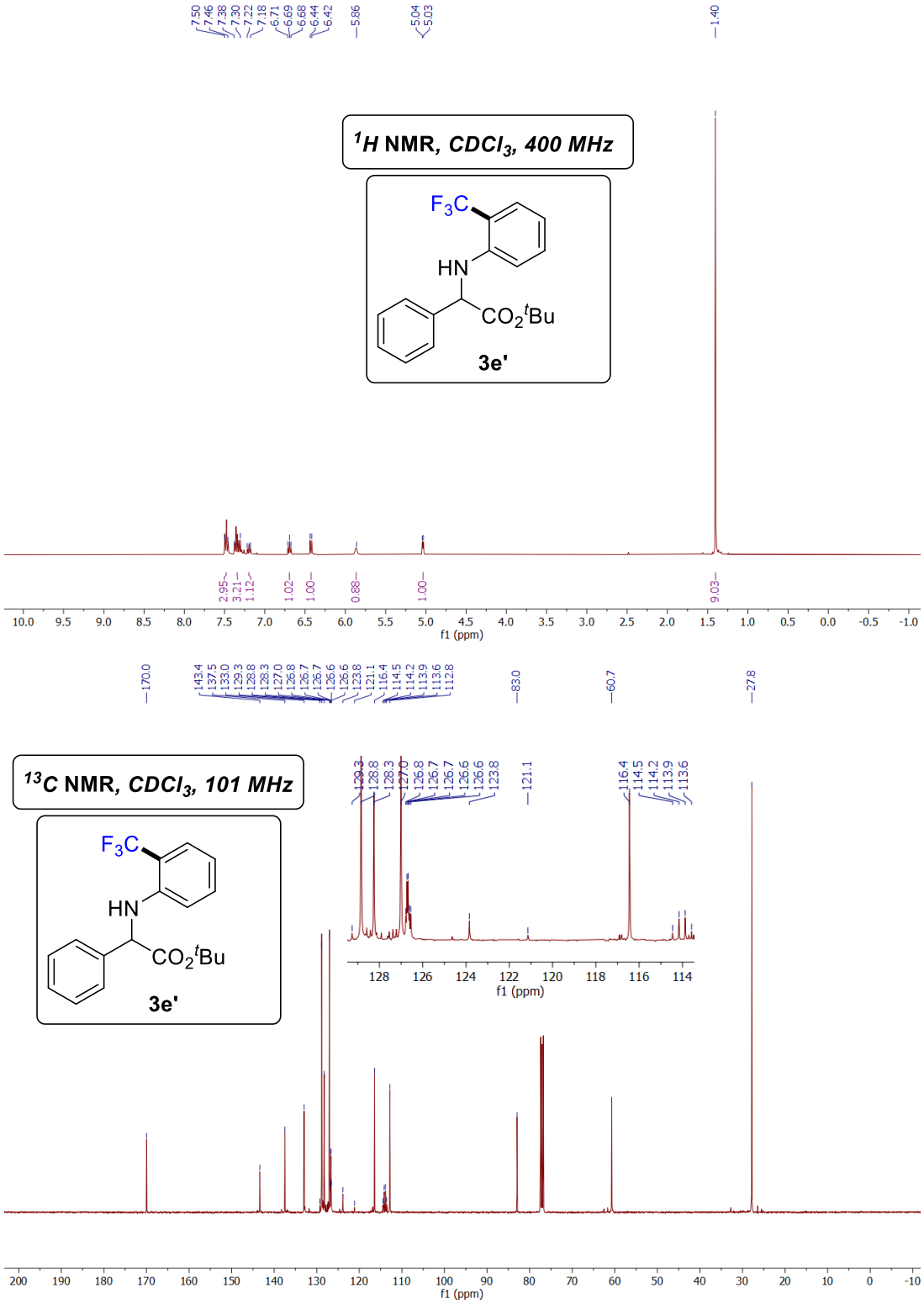
3d'

8.9 Tert-butyl 2-phenyl-2-((4-(trifluoromethyl)phenyl)amino) acetate (3e)

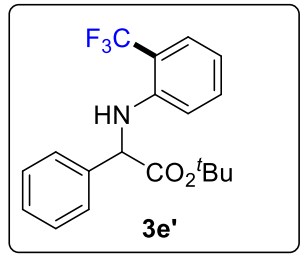



-61.18
19F NMR, CDCl3, 376 MHz
CF3
HN
CO2tBu
3e
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

8.10 Tert-butyl 2-phenyl-2-((2-(trifluoromethyl)phenyl)amino) acetate (3e′)

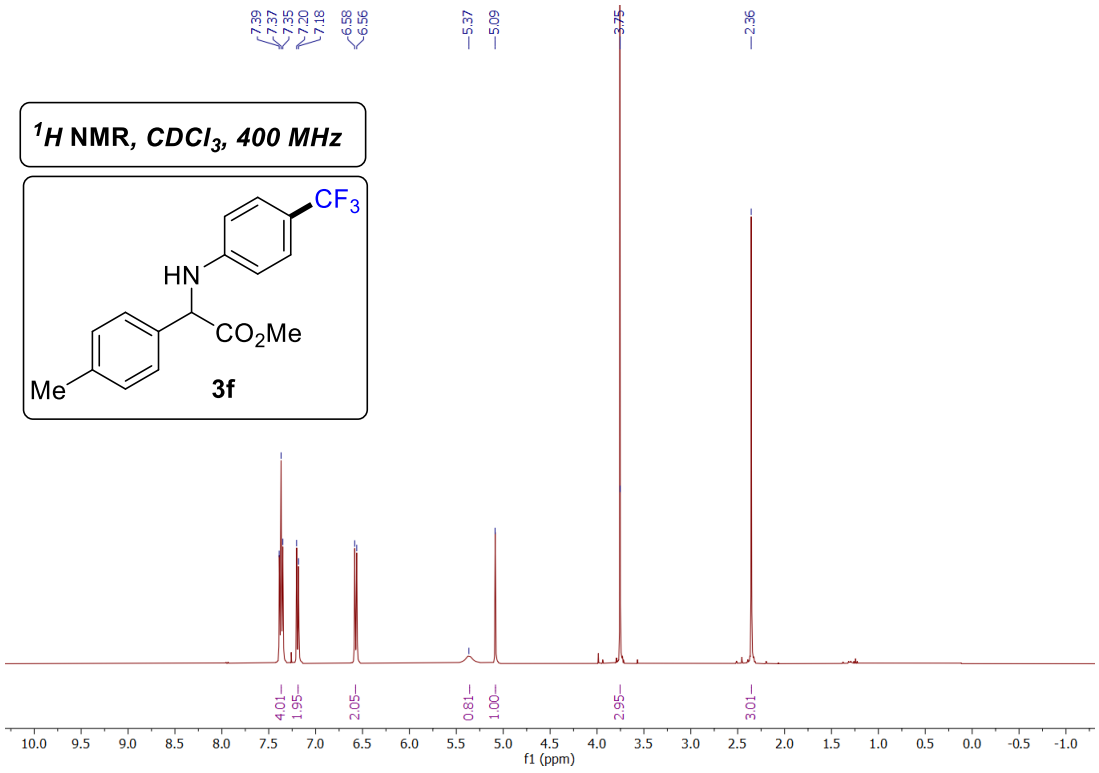


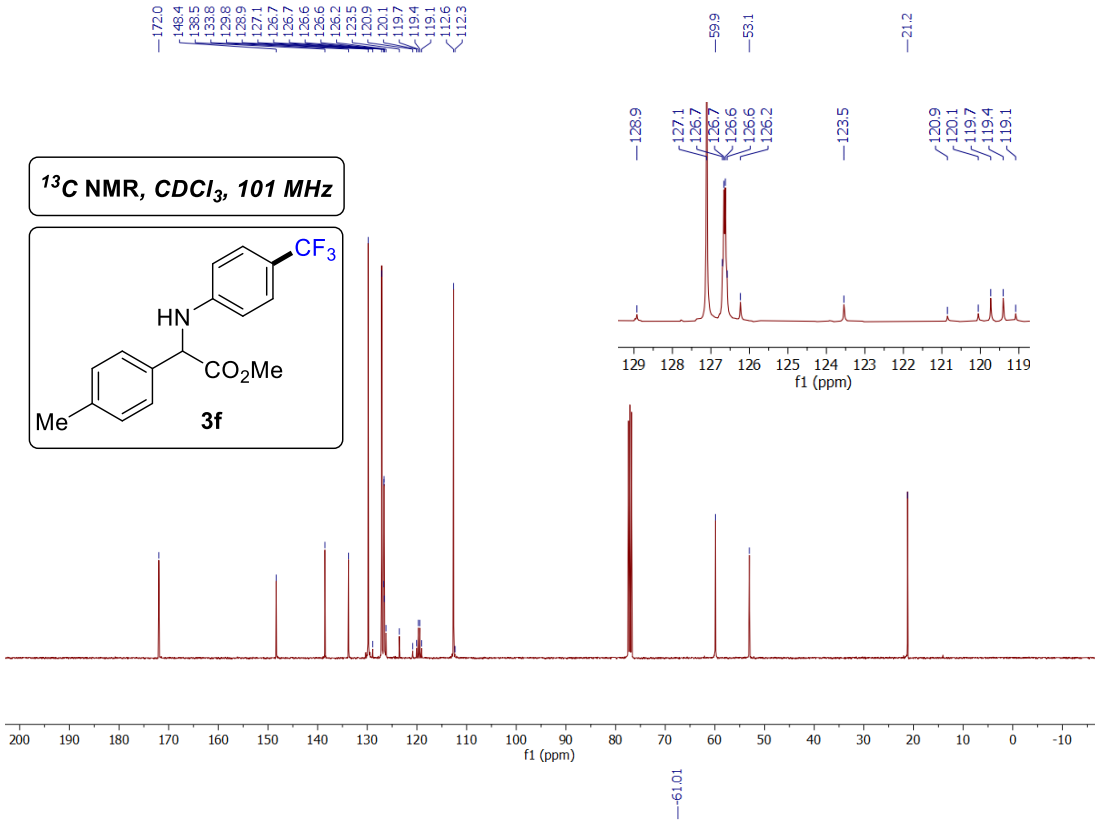
^{19}F NMR, $CDCl_3$, 376 MHz

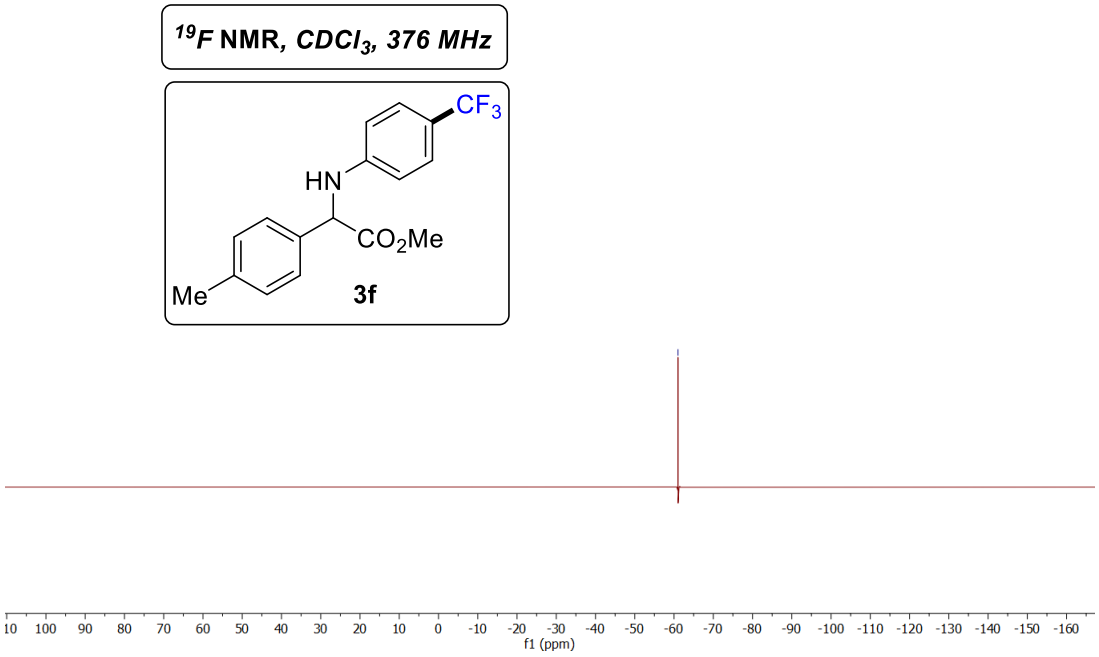


3e'

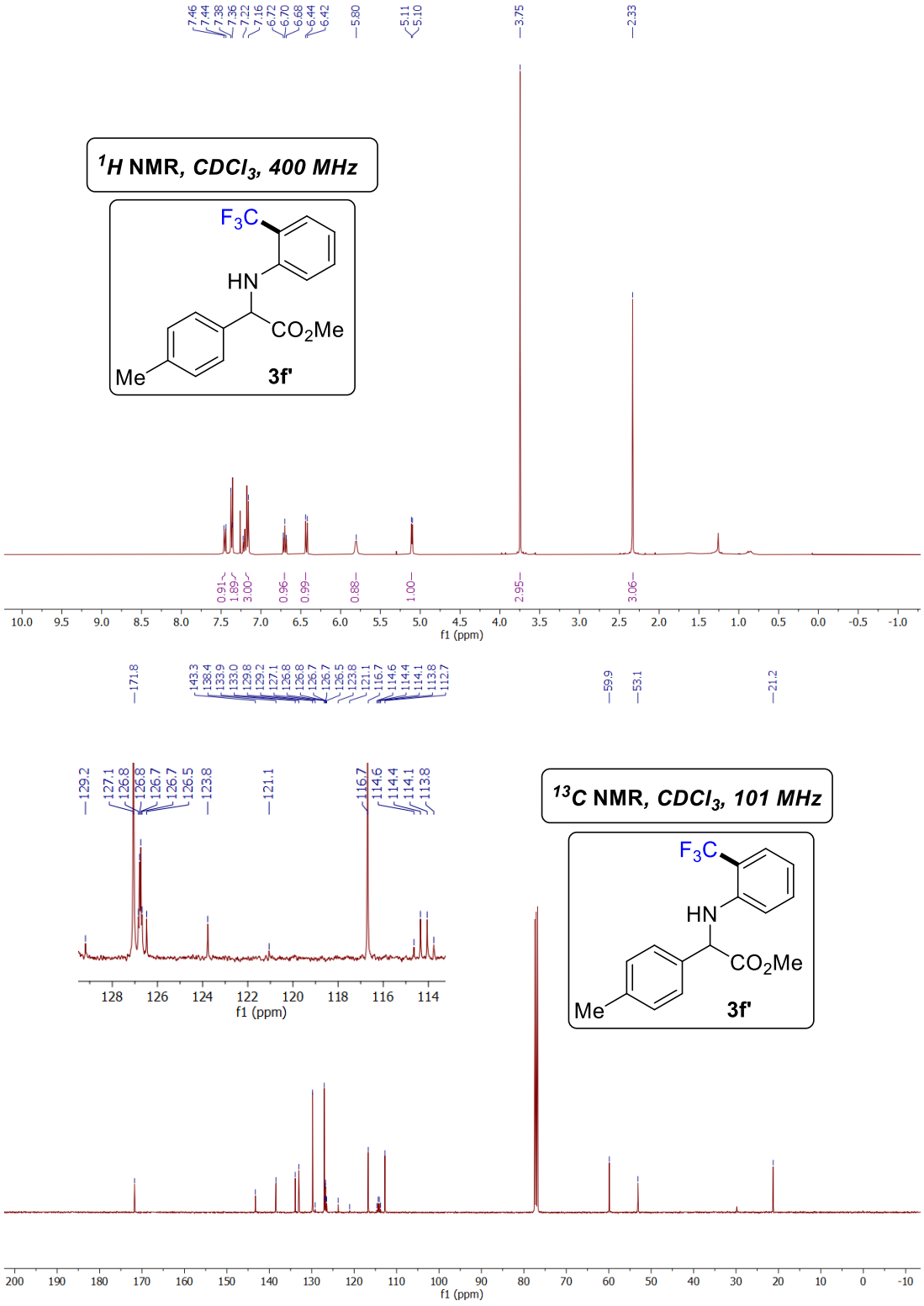
8.11 Methyl 2-(p-tolyl)-2-((4-(trifluoromethyl)phenyl)amino) acetate (3f)

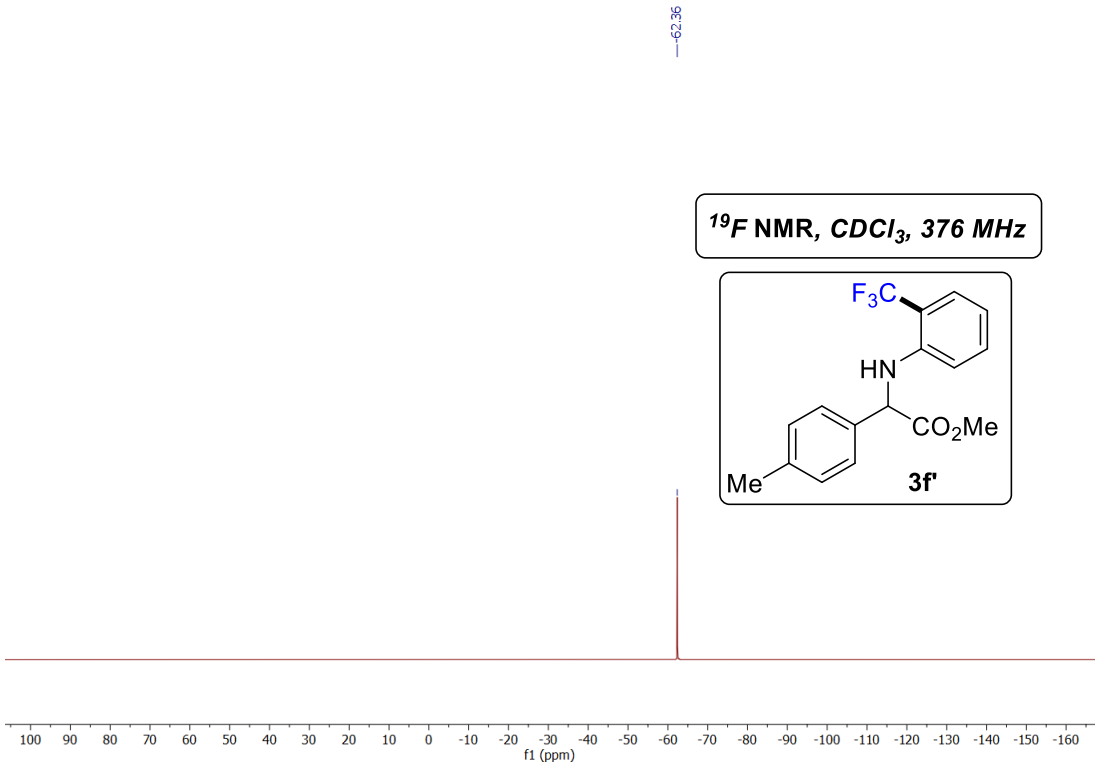



172.0
148.4
138.5
133.8
129.8
128.9
127.1
126.7
126.7
126.6
126.6
126.2
123.5
120.9
120.1
119.7
119.4
119.1
112.6
112.3
59.9
53.1
21.2
128.9
127.1
126.7
126.7
126.6
126.6
126.2
123.5
120.9
120.1
119.7
119.4
119.1
129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)
13C NMR, CDCl3, 101 MHz
CF3
HN
CO2Me
Me
3f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

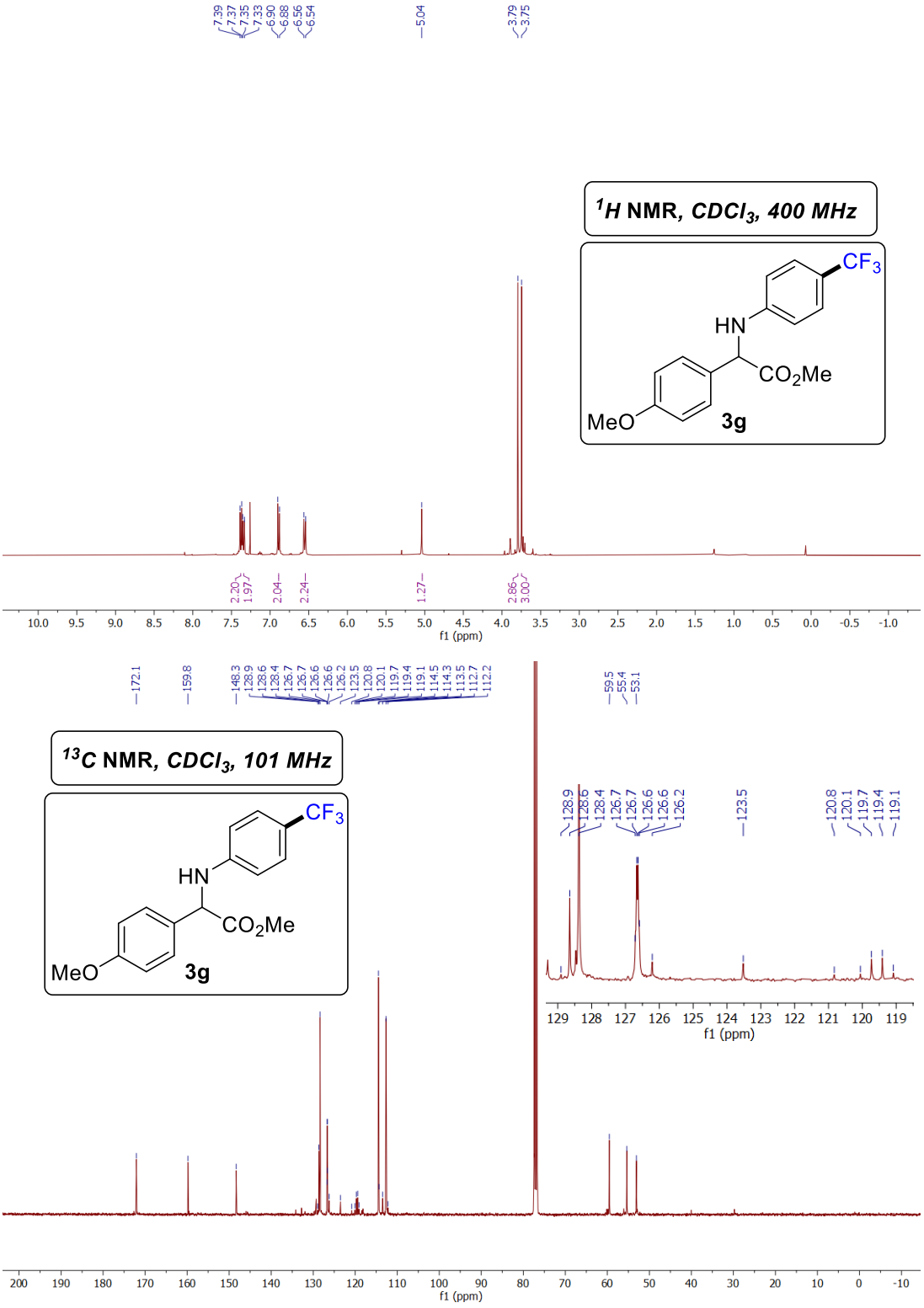

-61.01
19F NMR, CDCl3, 376 MHz
CF3
HN
CO2Me
Me
3f
10 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

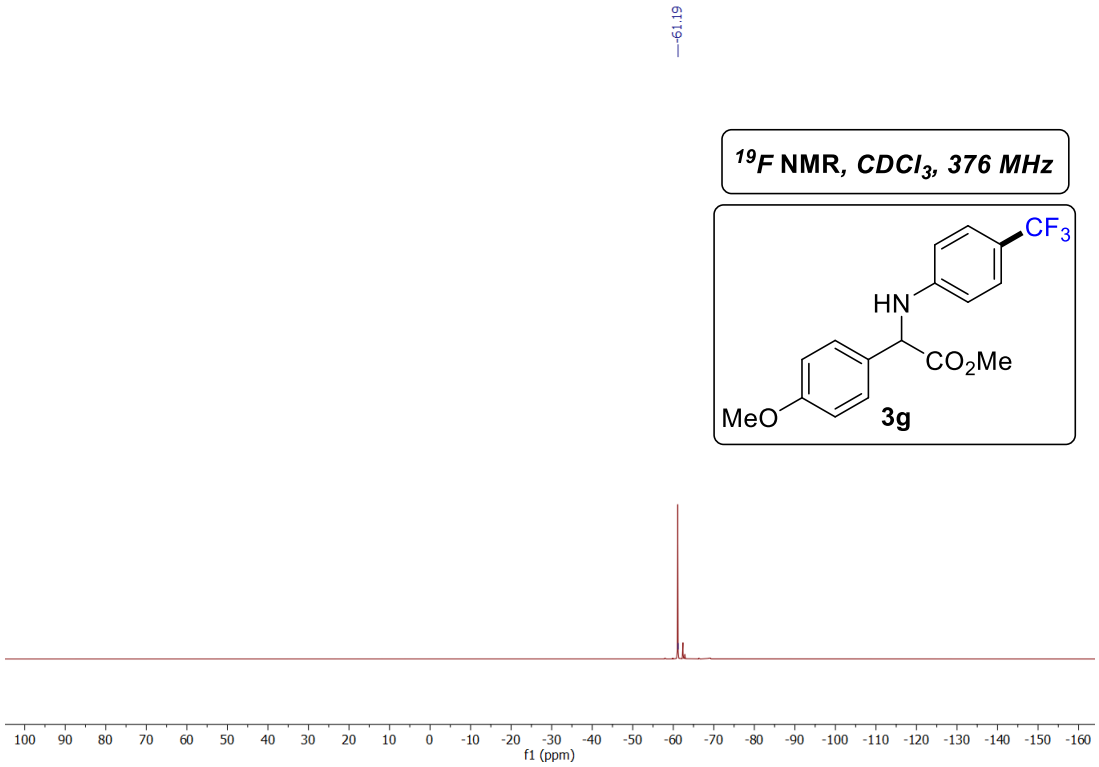
8.12 Methyl 2-(*p*-tolyl)-2-((2-(trifluoromethyl)phenyl)amino) acetate (3f′)



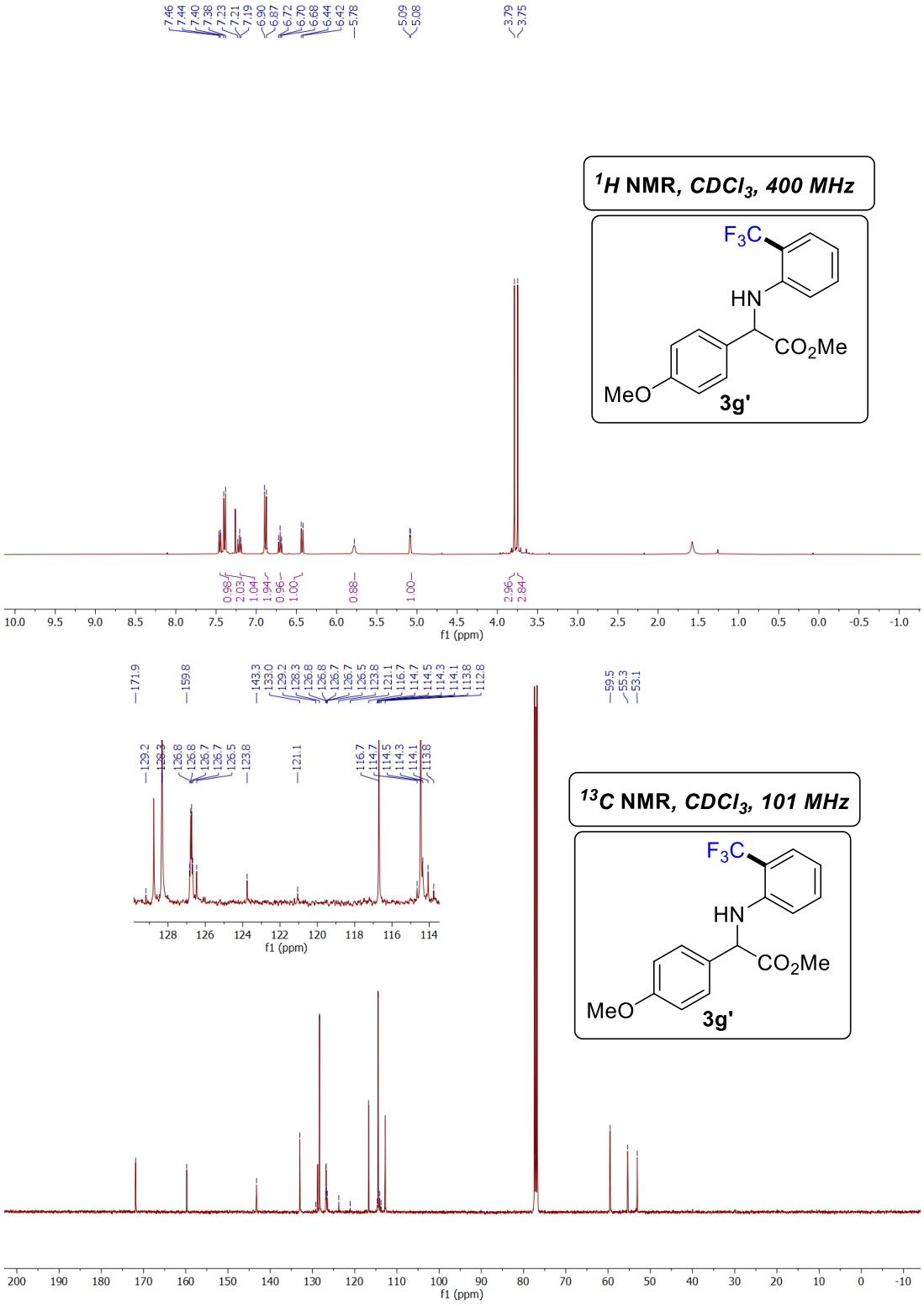

-62.36
19F NMR, CDCl3, 376 MHz
F3C
HN
CO2Me
Me
3f'
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

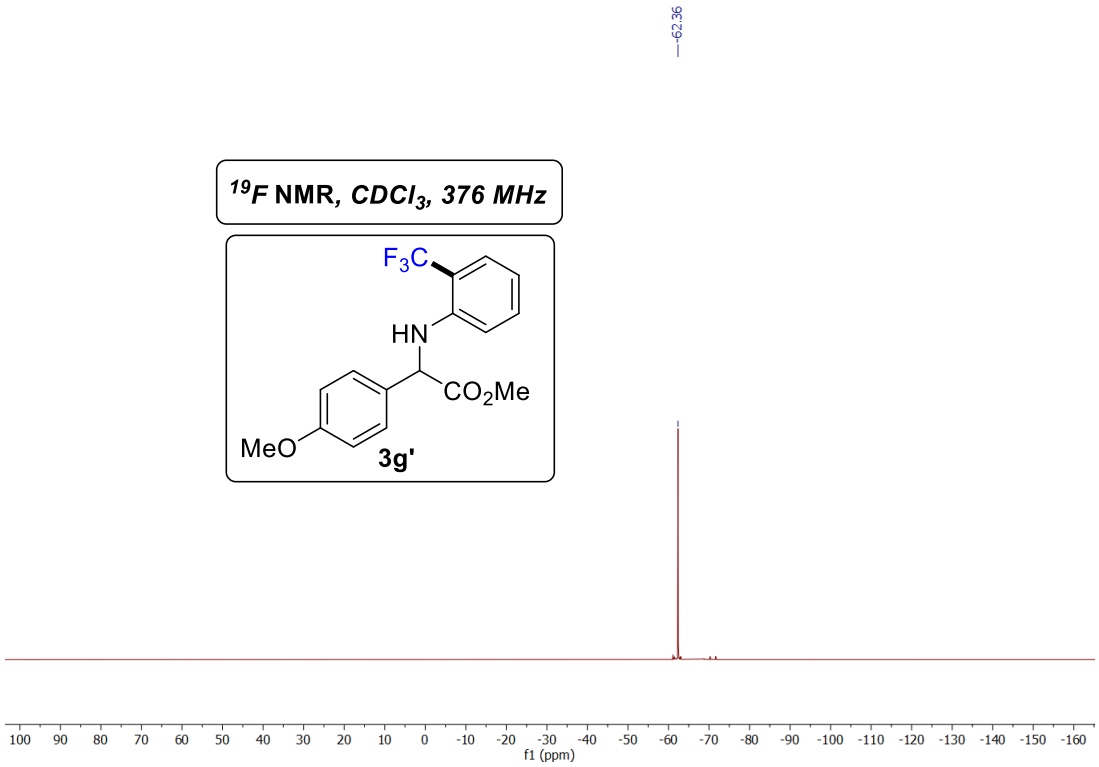
8.13 Methyl 2-(4-methoxyphenyl)-2-((4-(trifluoromethyl)phenyl)amino) acetate (3g)



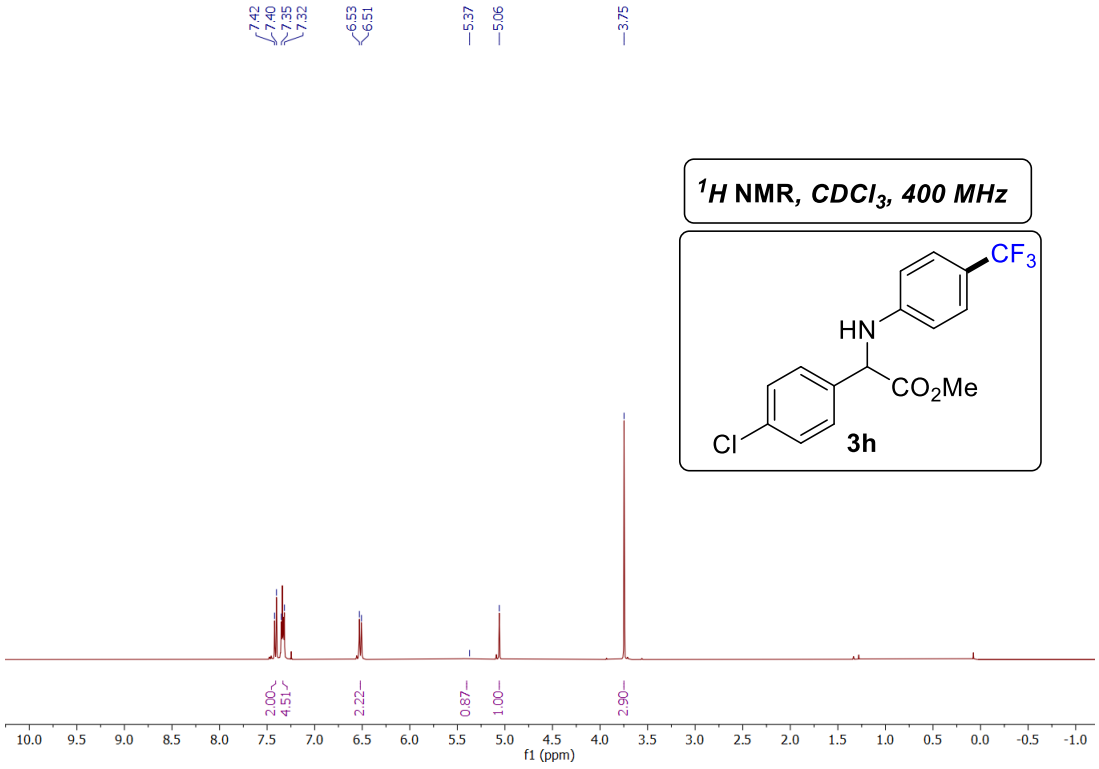

-61.19
^{19}F NMR, $CDCl_3$, 376 MHz
CF_3
HN
CO_2Me
MeO
3g
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

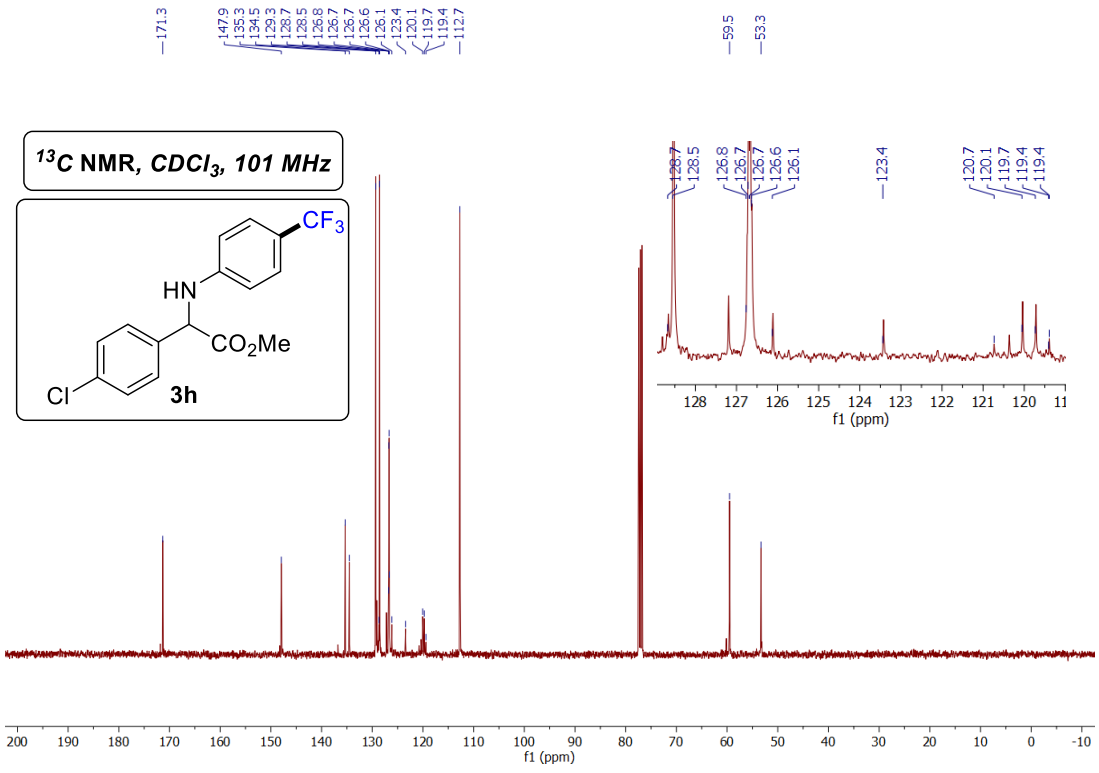
8.14 Methyl 2-(4-methoxyphenyl)-2-((2-(trifluoromethyl)phenyl)amino) acetate (3g′)

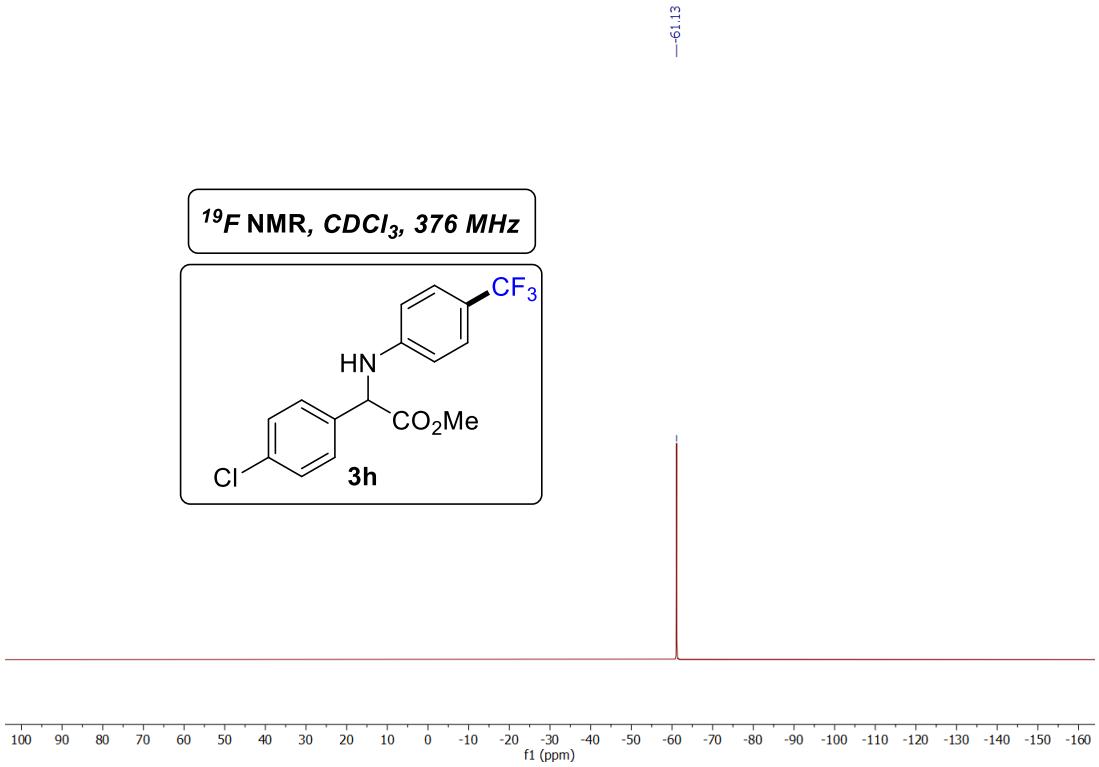



-62.36
19F NMR, CDCl3, 376 MHz
F3C
HN
CO2Me
MeO
3g'
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

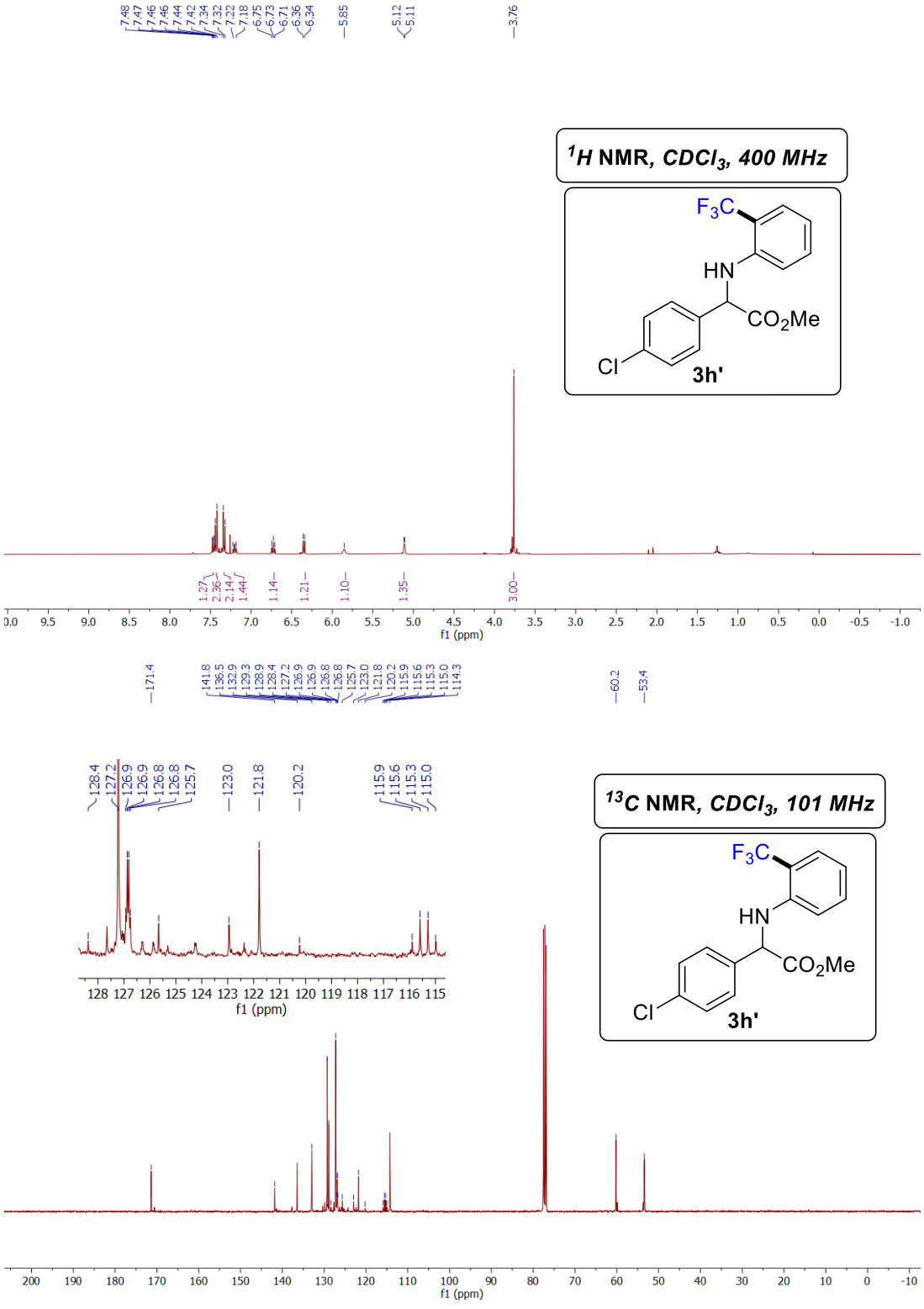
8.15 Methyl 2-(4-chlorophenyl)-2-((4-(trifluoromethyl)phenyl)amino) acetate (3h)



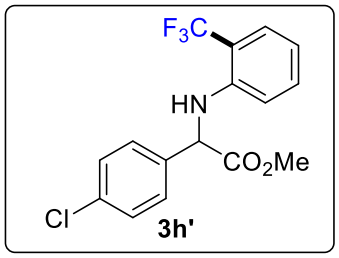



-61.13
^{19}F NMR, $CDCl_3$, 376 MHz
CF_3
HN
CO_2Me
Cl
3h
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

8.16 Methyl 2-(4-chlorophenyl)-2-((2-(trifluoromethyl)phenyl)amino) acetate (3h′)

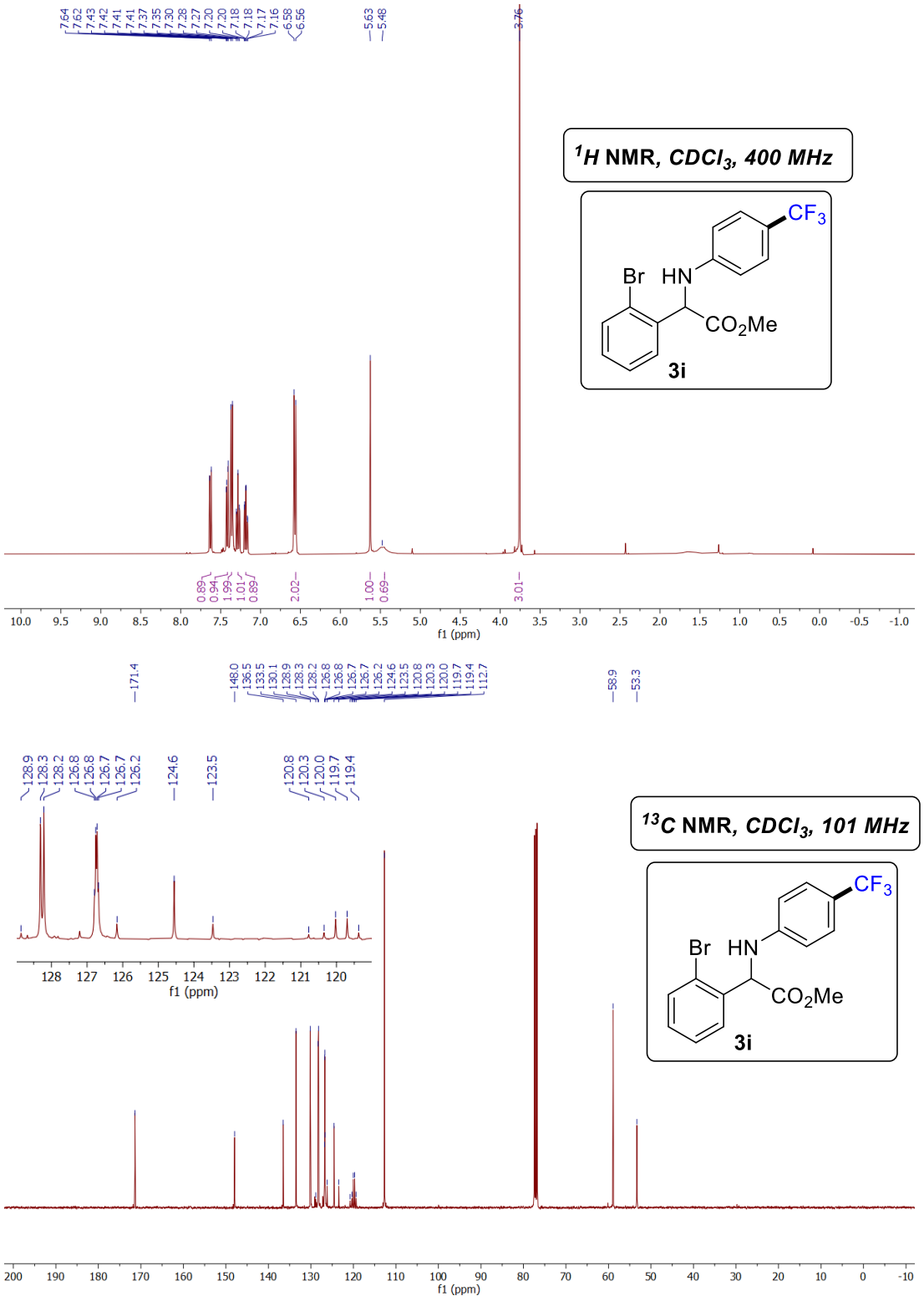


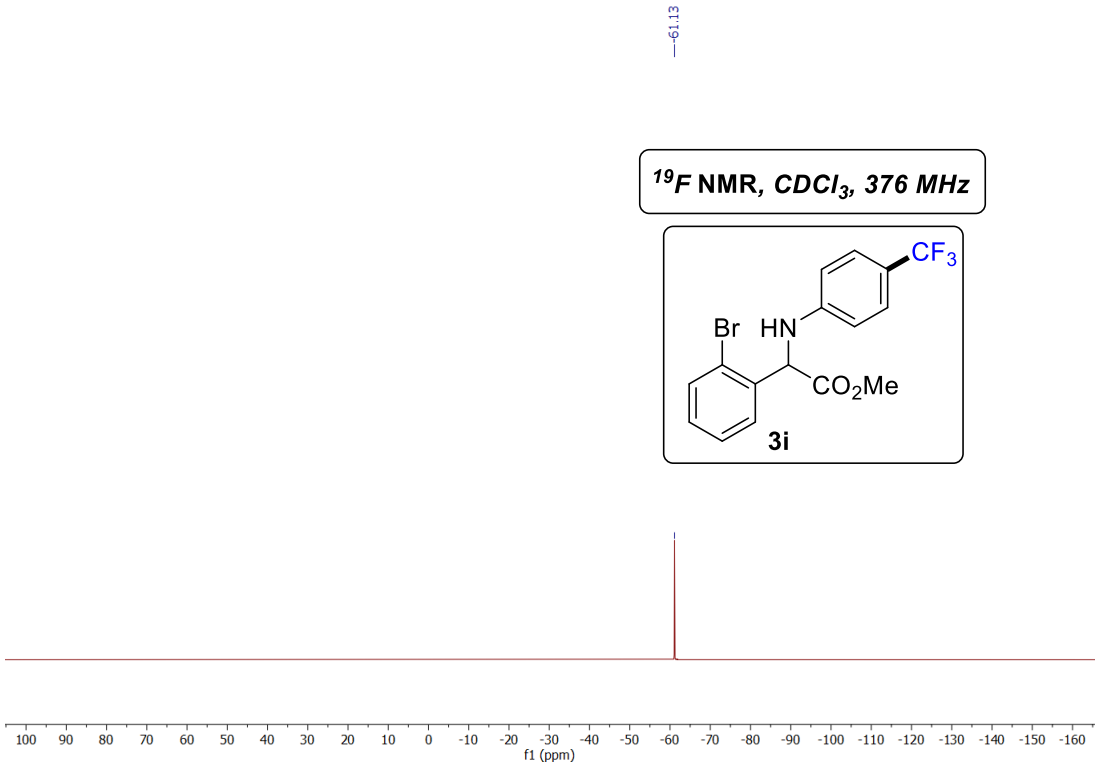
^{19}F NMR, $CDCl_3$, 376 MHz



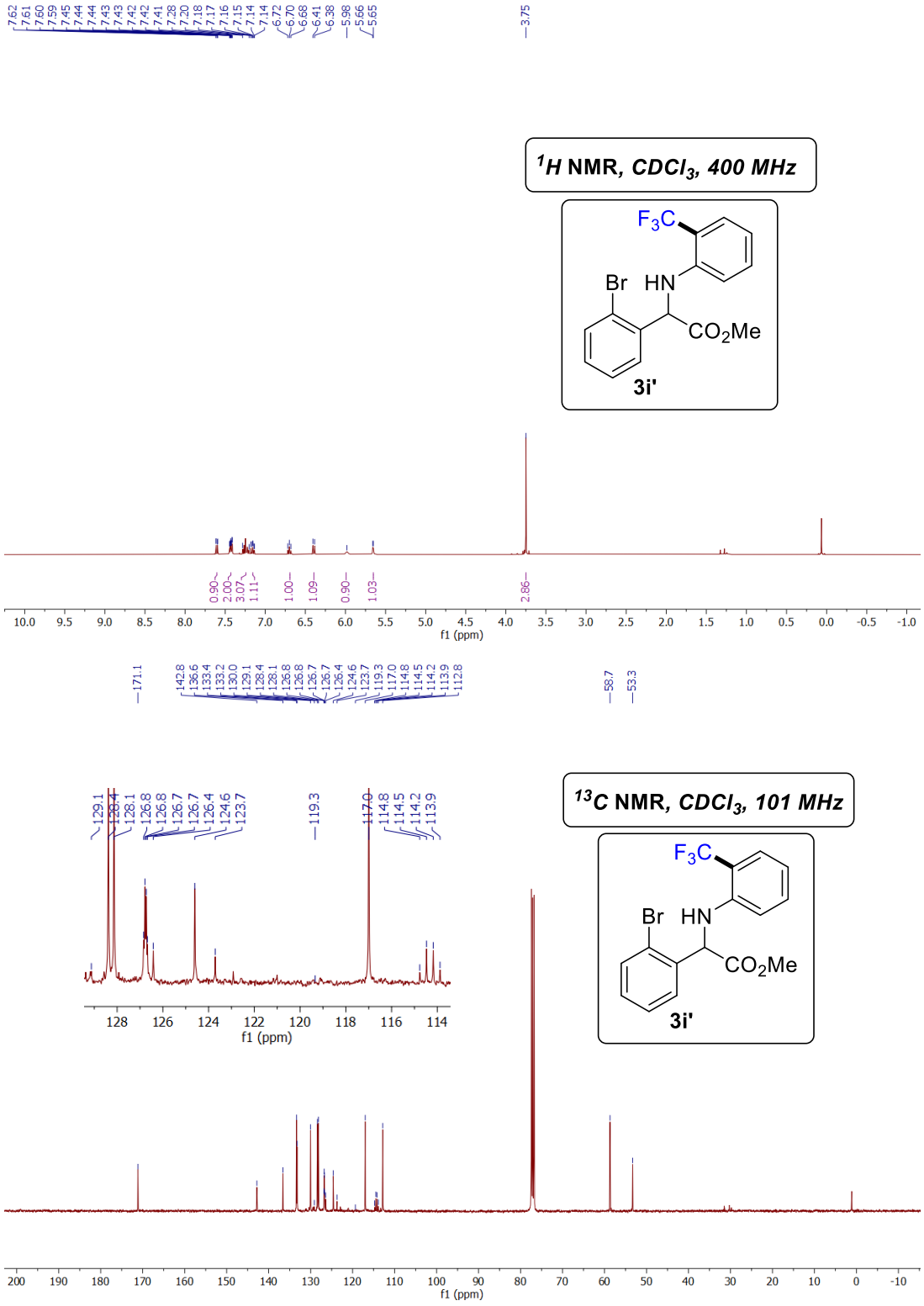
3h'

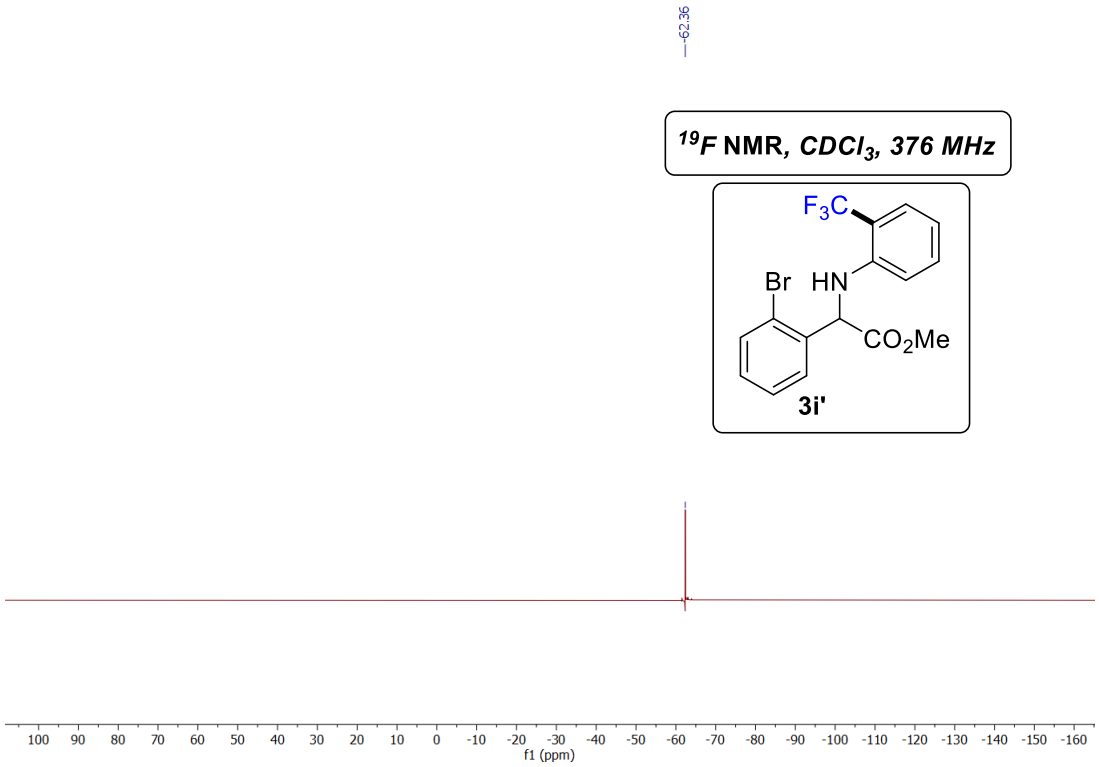
8.17 Methyl 2-(2-bromophenyl)-2-((4-(trifluoromethyl)phenyl)amino) acetate (3i)



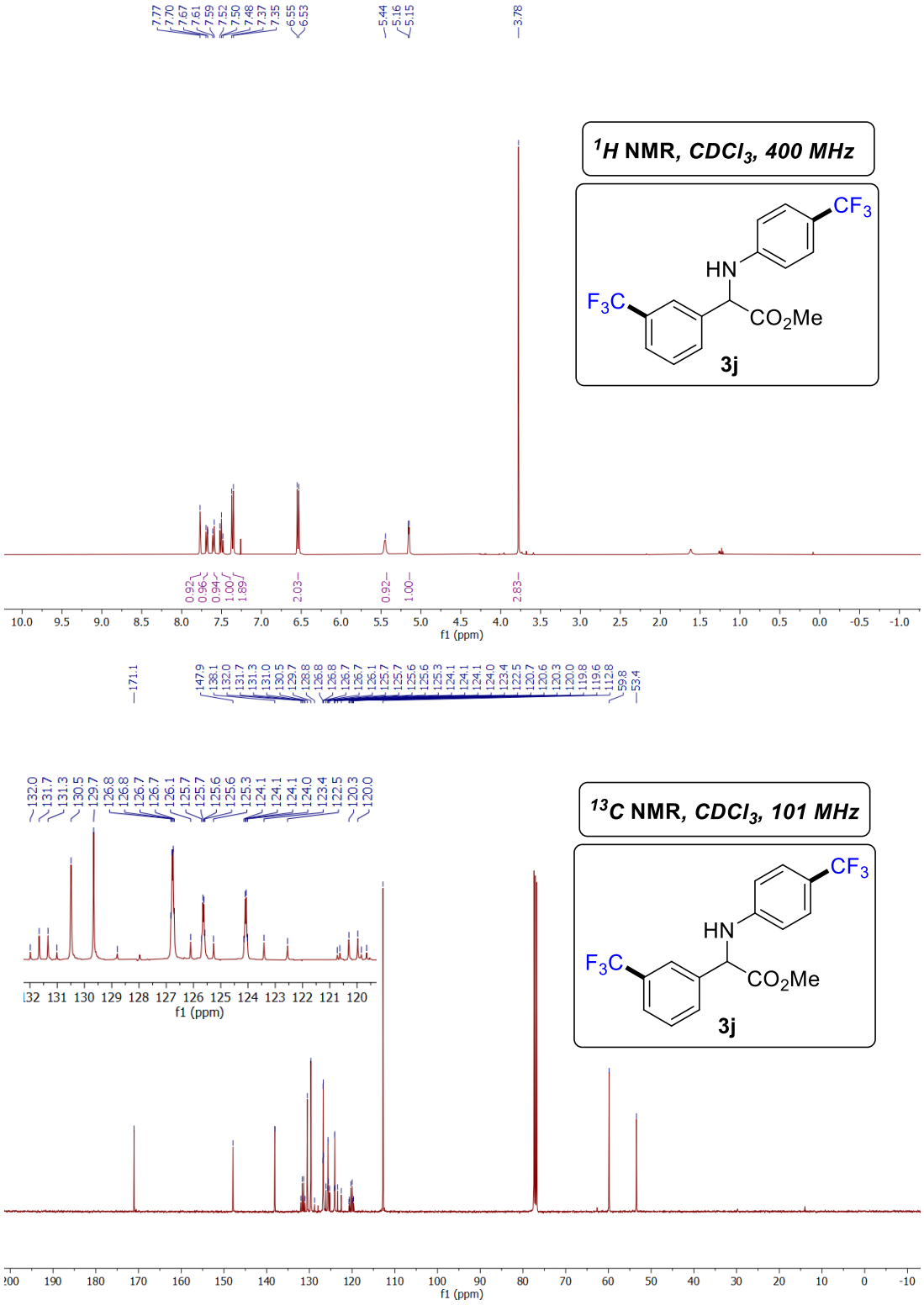

-61.13
^{19}F NMR, $CDCl_3$, 376 MHz
CF_3
Br HN
CO_2Me
3i
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

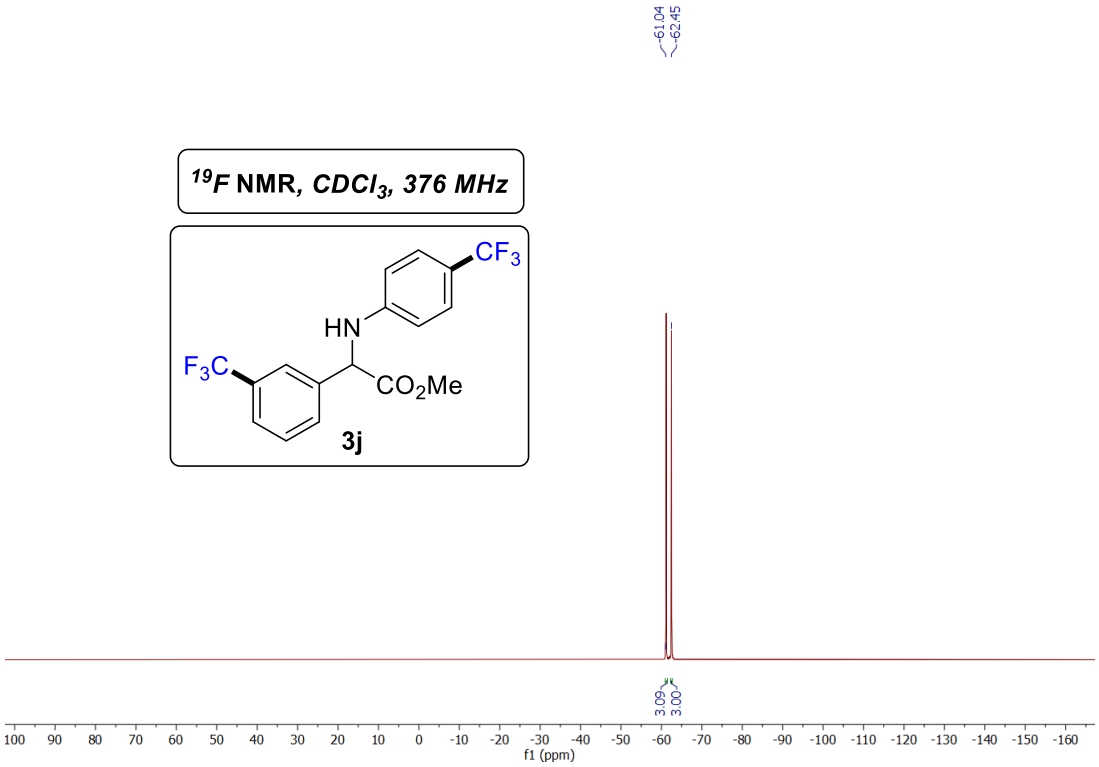
8.18 Methyl 2-(2-bromophenyl)-2-((2-(trifluoromethyl)phenyl)amino) acetate (3i')



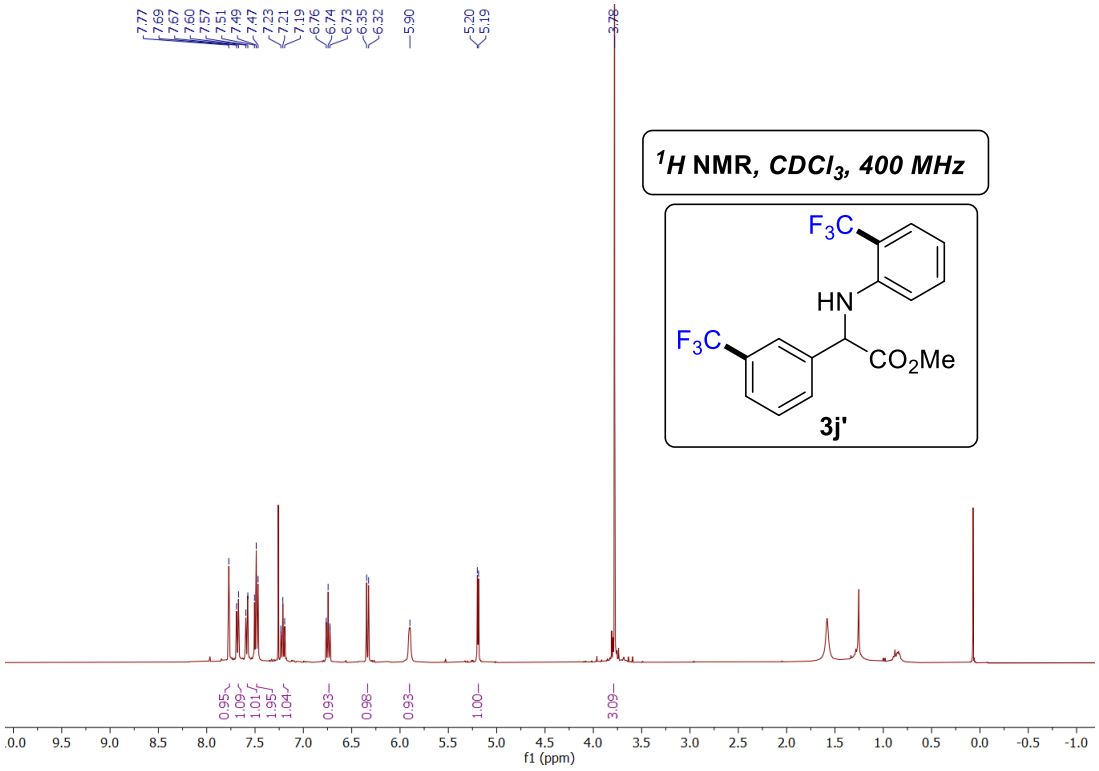

-62.36
19F NMR, CDCl3, 376 MHz
F3C
Br
HN
CO2Me
3i'
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

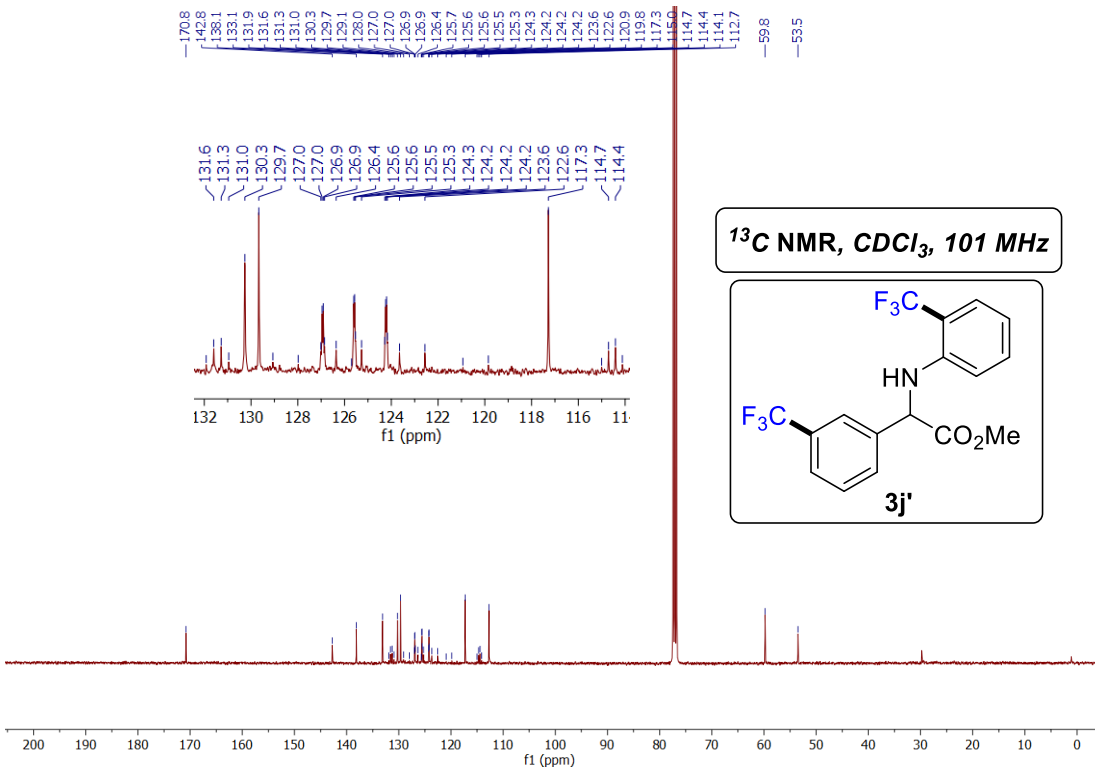
8.19 Methyl 2-(3-(trifluoromethyl)phenyl)-2-((4-(trifluoromethyl)phenyl)amino) acetate(3j)

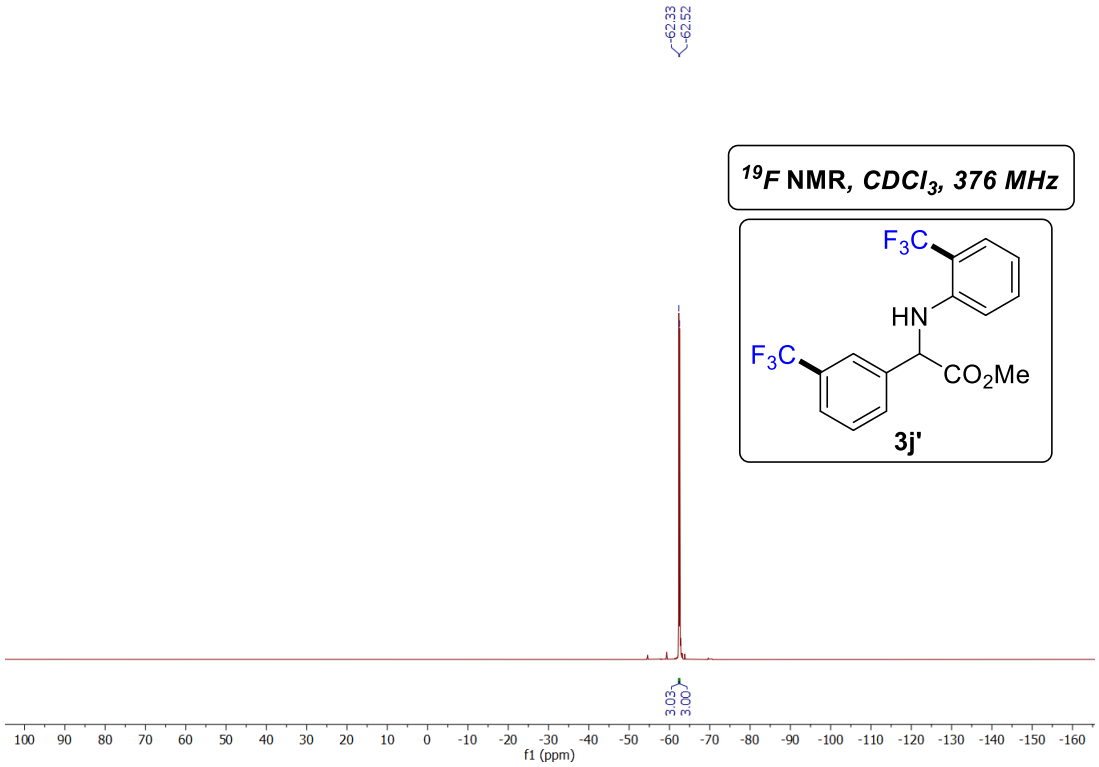



-61.04
-62.45
^{19}F NMR, $CDCl_3$, 376 MHz
CF_3
HN
F_3C
CO_2Me
3j
3.09
3.00
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

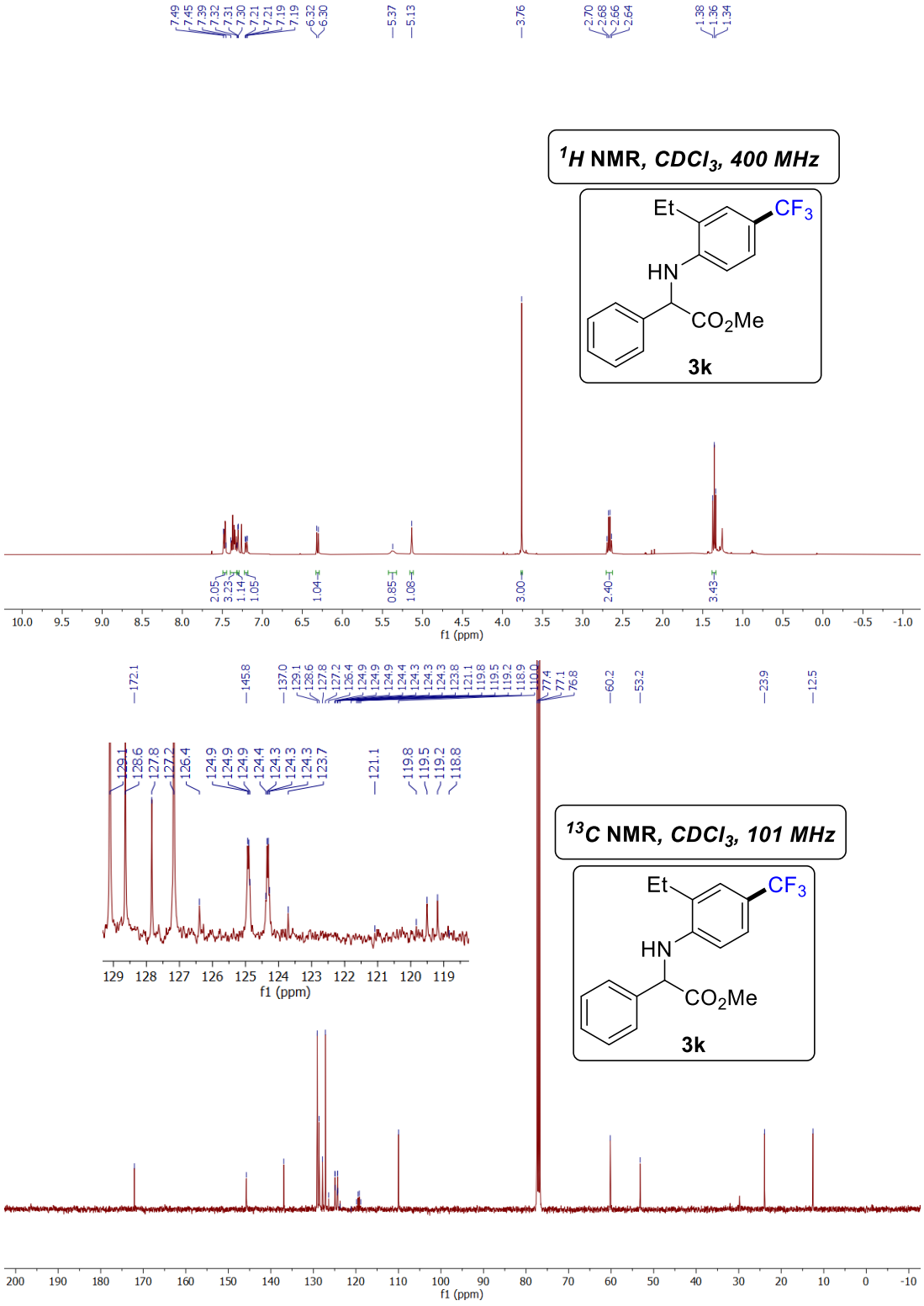
8.20 Methyl 2-(3-(trifluoromethyl)phenyl)-2-((2-(trifluoromethyl)phenyl)amino) acetate(3j′)

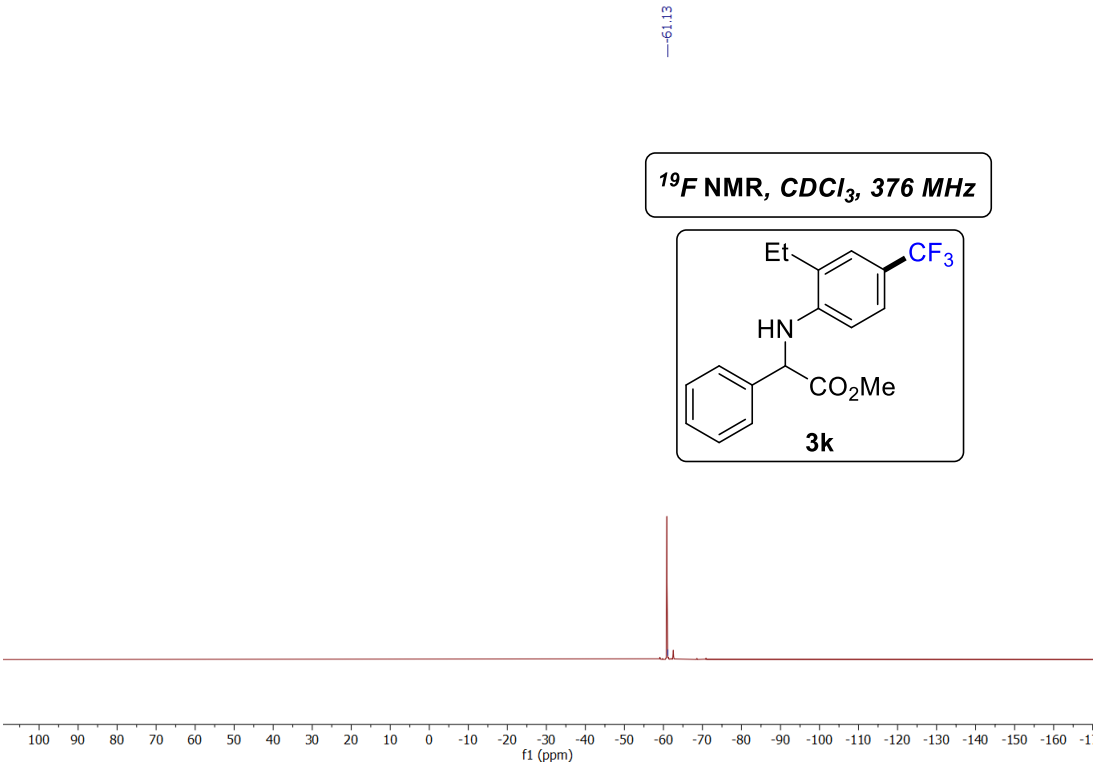




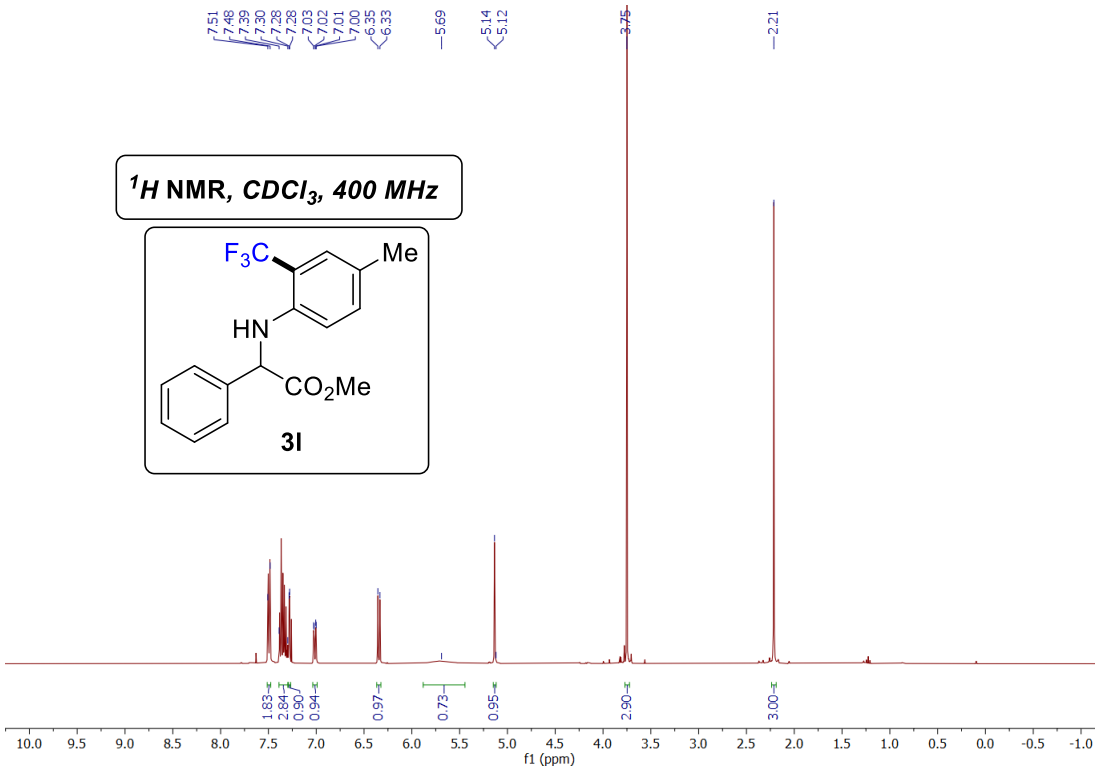

-62.33
-62.52
^{19}F NMR, $CDCl_3$, 376 MHz
F_3C
HN
F_3C
CO_2Me
3j'
3.03
3.00
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

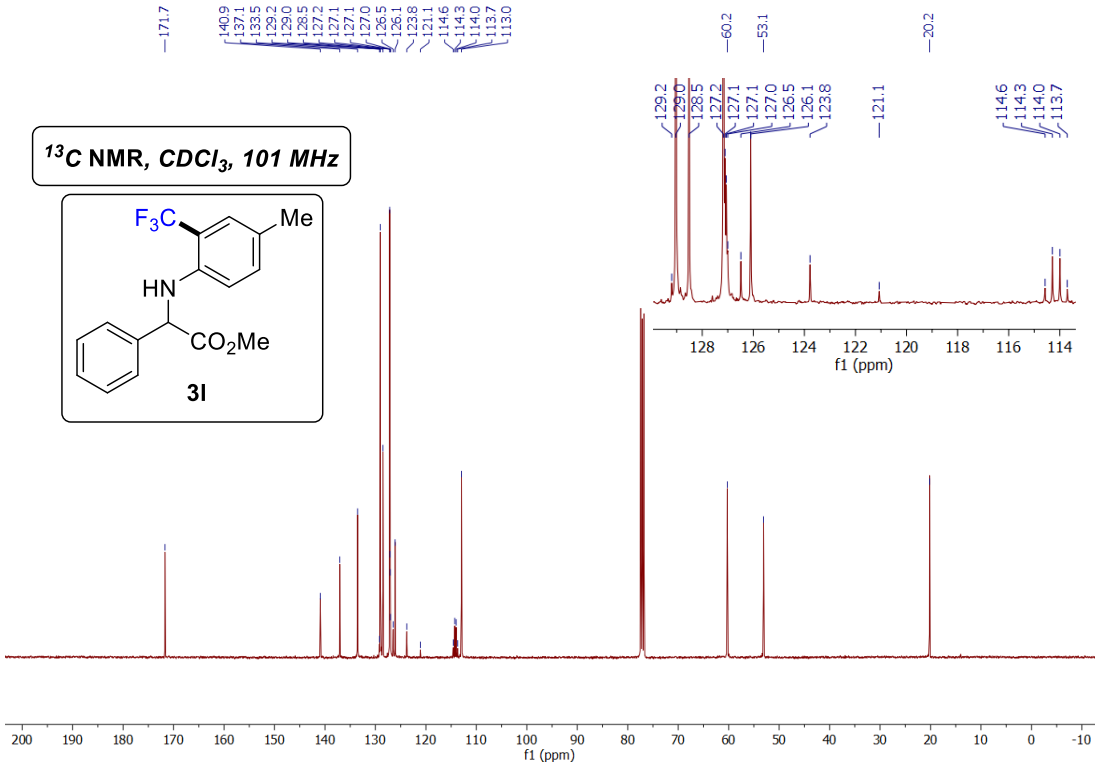
8.21 Methyl 2-((2-ethyl-4-(trifluoromethyl)phenyl)amino)-2-phenyl acetate (3k)

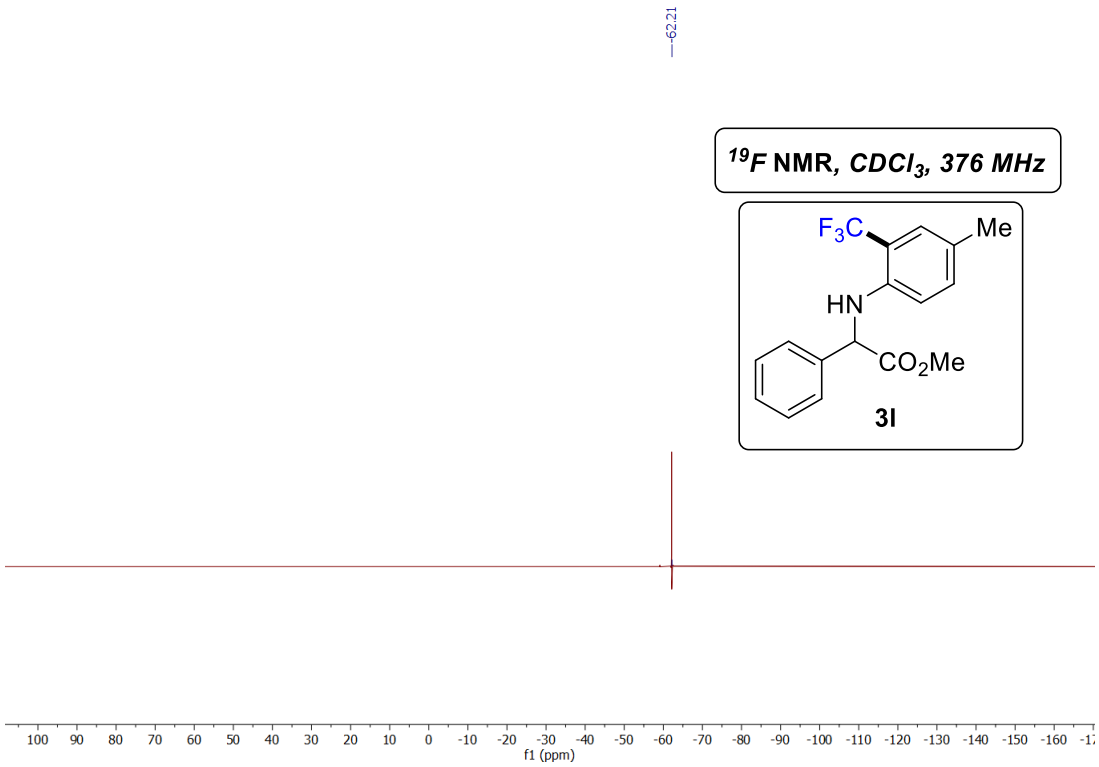



-61.13
19F NMR, CDCl3, 376 MHz
Et
CF3
HN
CO2Me
3k
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

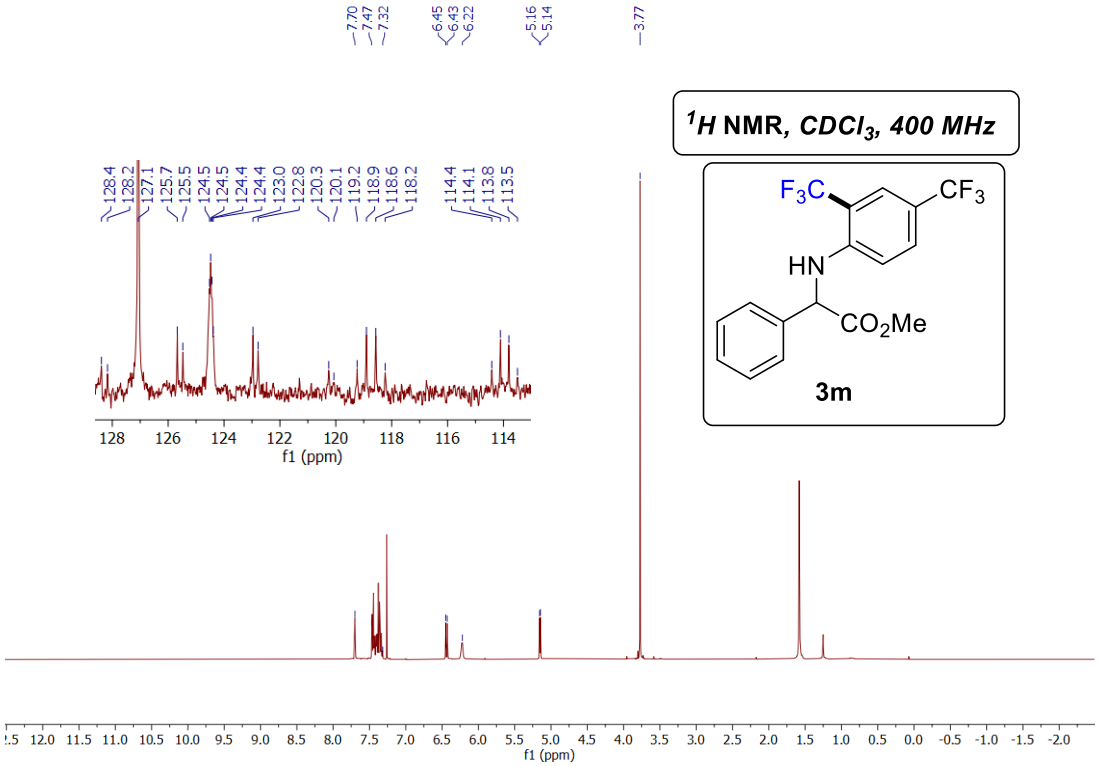
8.22 Methyl 2-((4-methyl-2-(trifluoromethyl) phenyl) amino)-2-phenylacetate (3l)

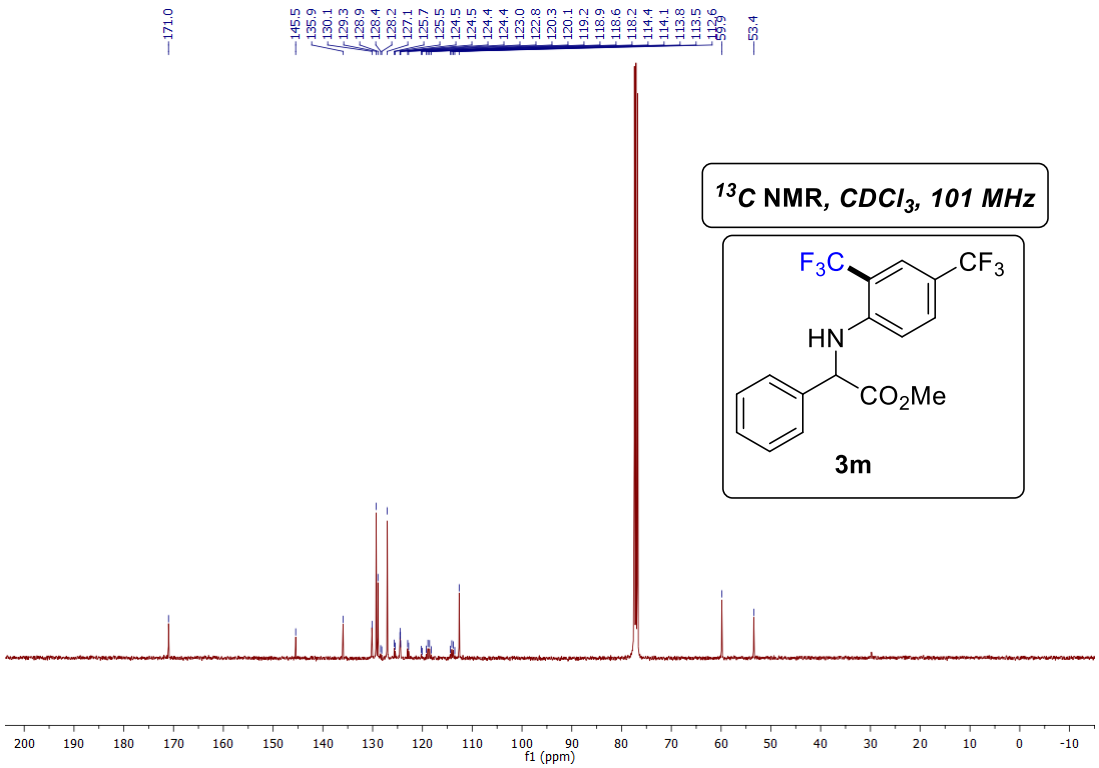


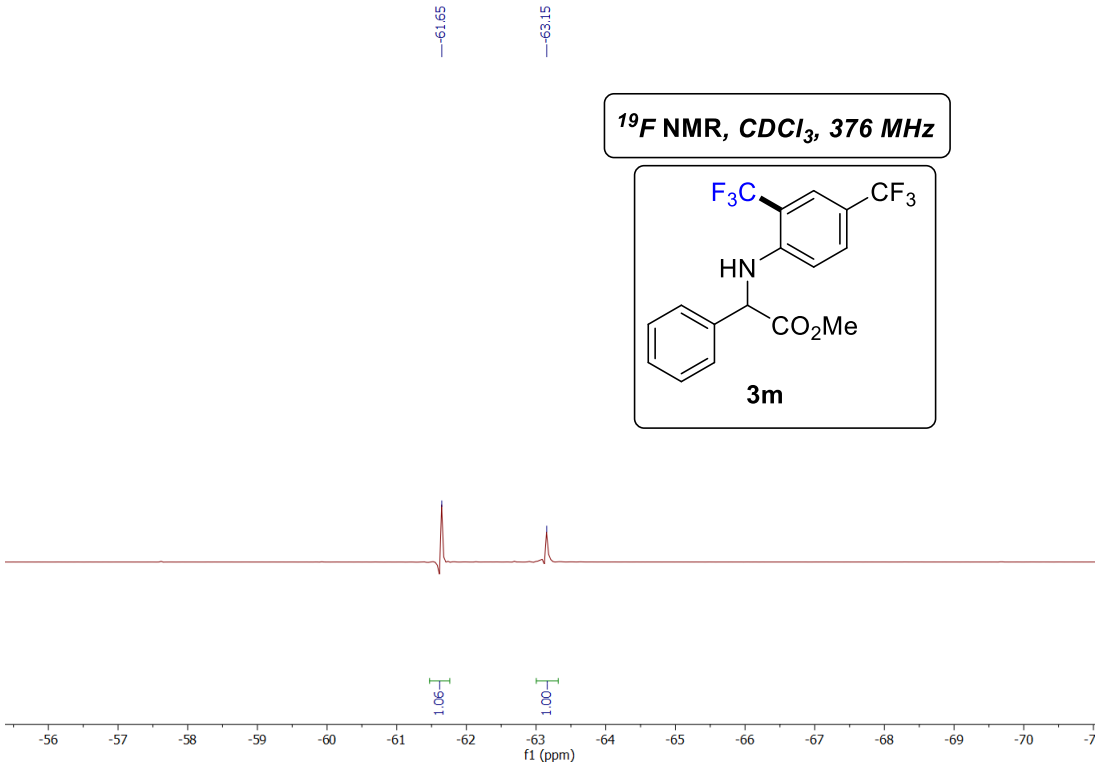



-62.21
^{19}F NMR, $CDCl_3$, 376 MHz
F_3C
Me
HN
CO_2Me
3l
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

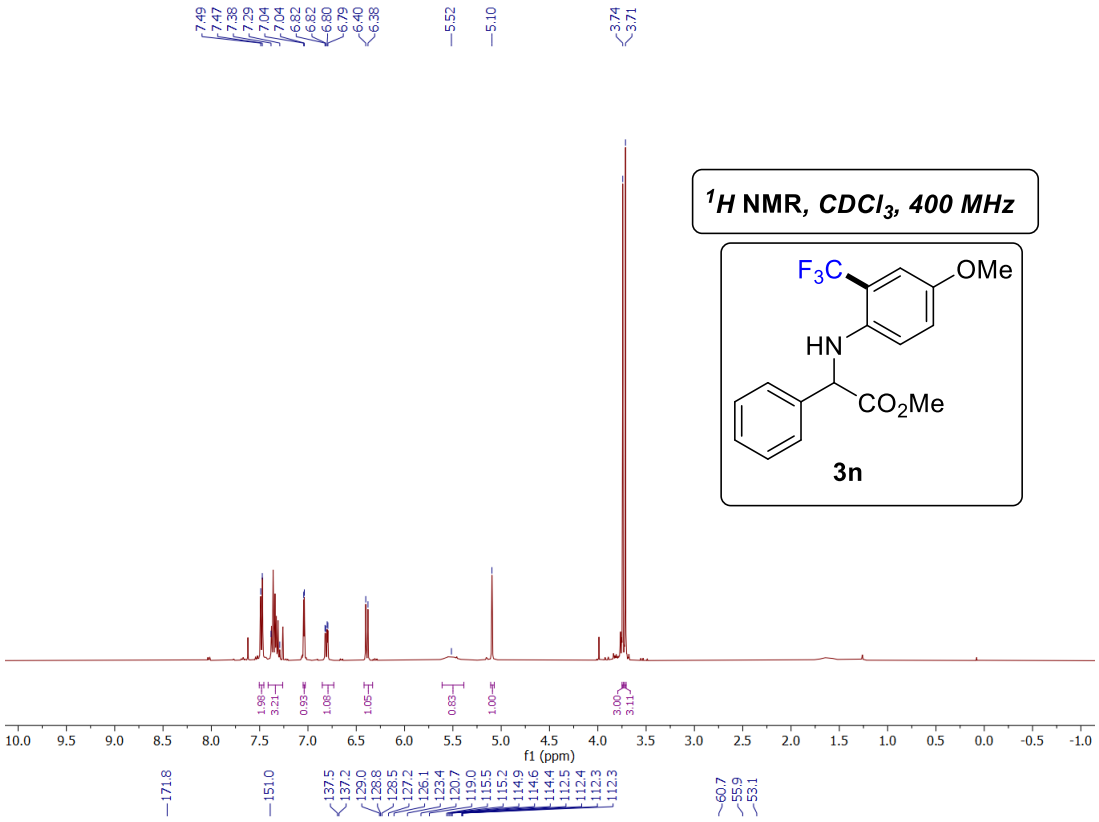
8.23 methyl 2-((2,4-bis(trifluoromethyl)phenyl)amino)-2-phenylacetate (3m)

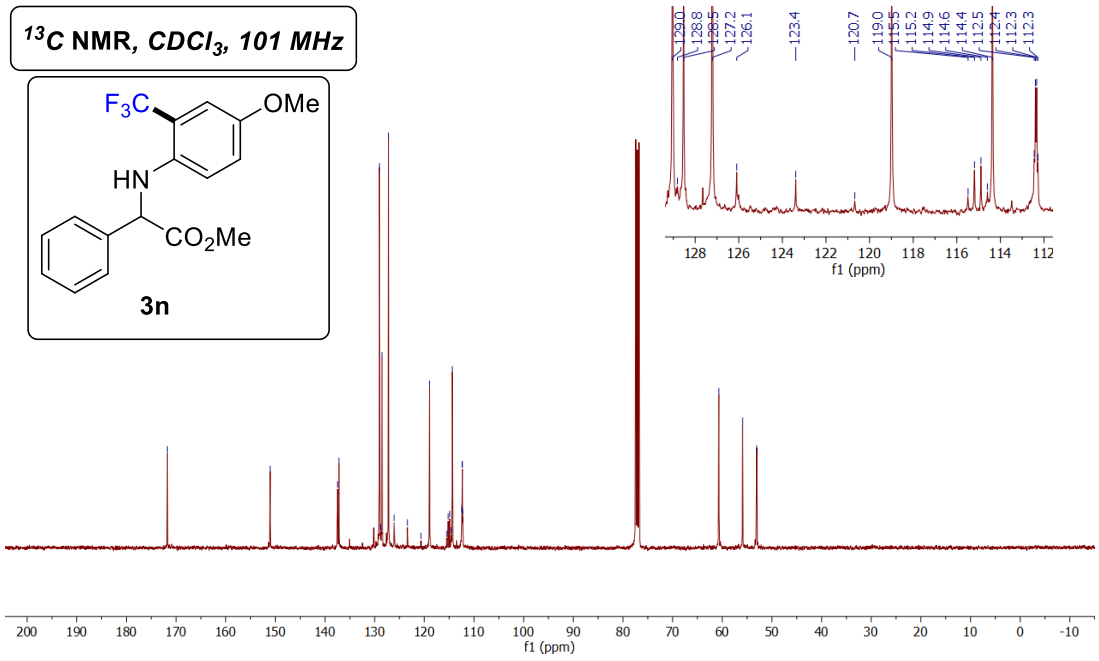


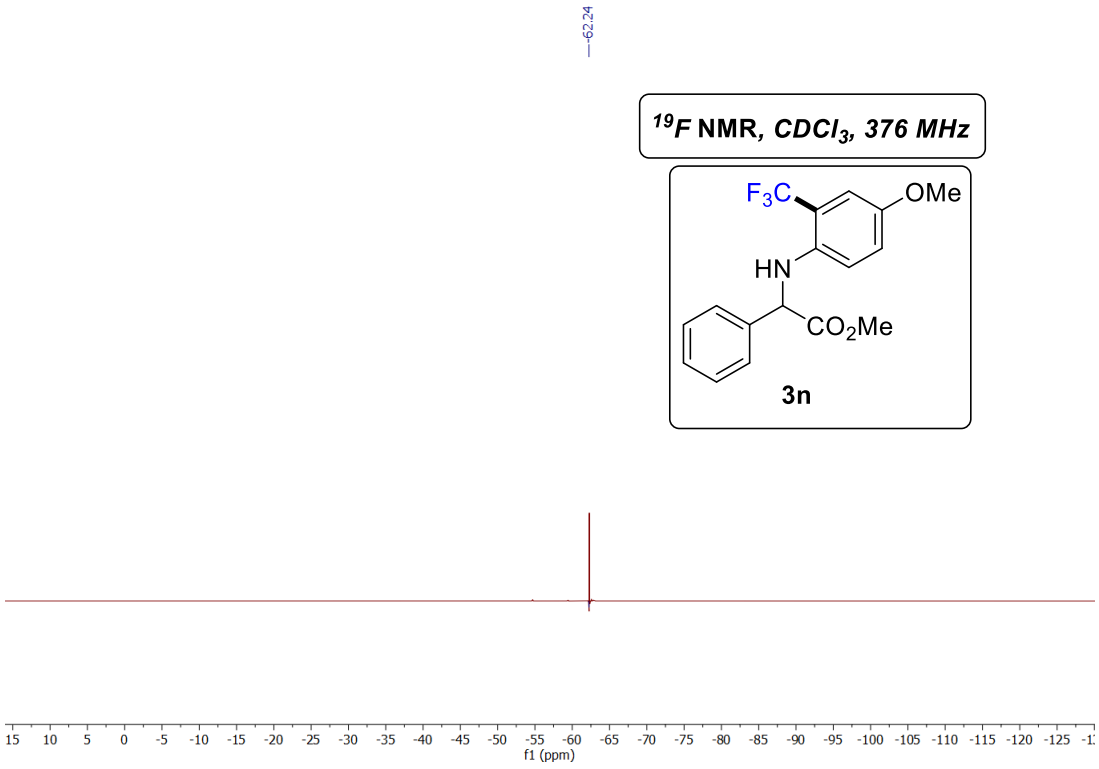



-61.65
-63.15
19F NMR, CDCl3, 376 MHz
F3C
CF3
HN
CO2Me
3m
1.06
1.00
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-7
f1 (ppm)

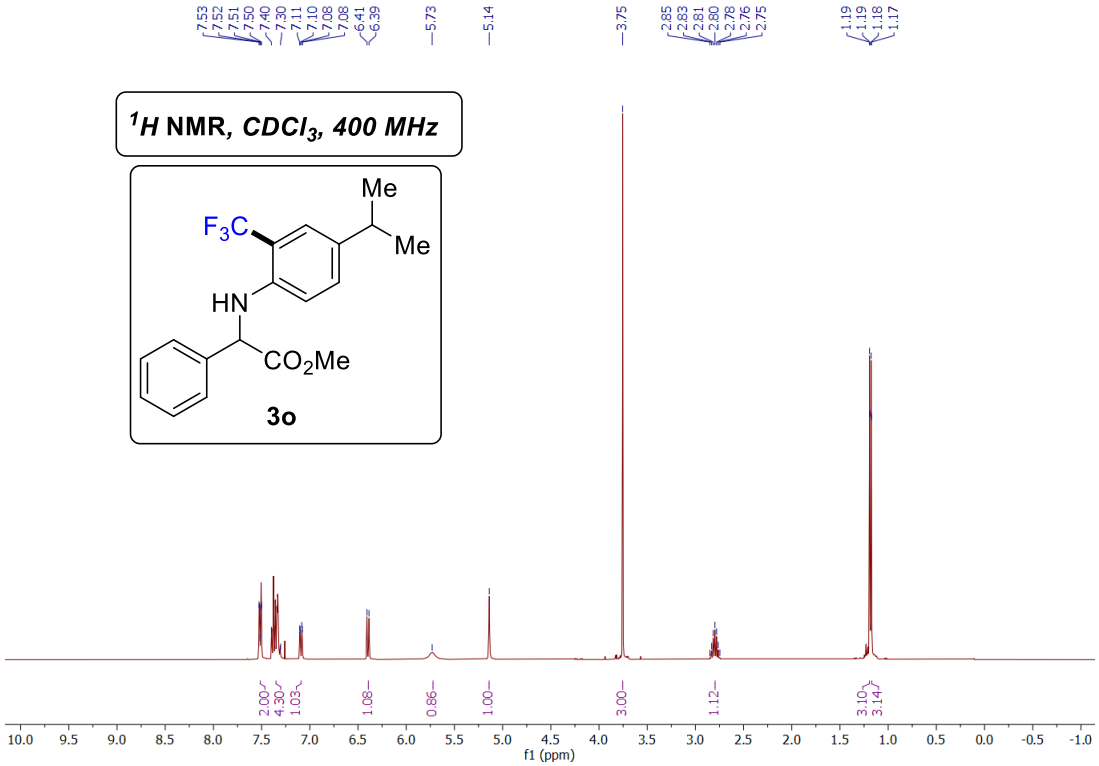
8.24 methyl 2-((4-methoxy-2-(trifluoromethyl)phenyl)amino)-2-phenylacetate (3n)

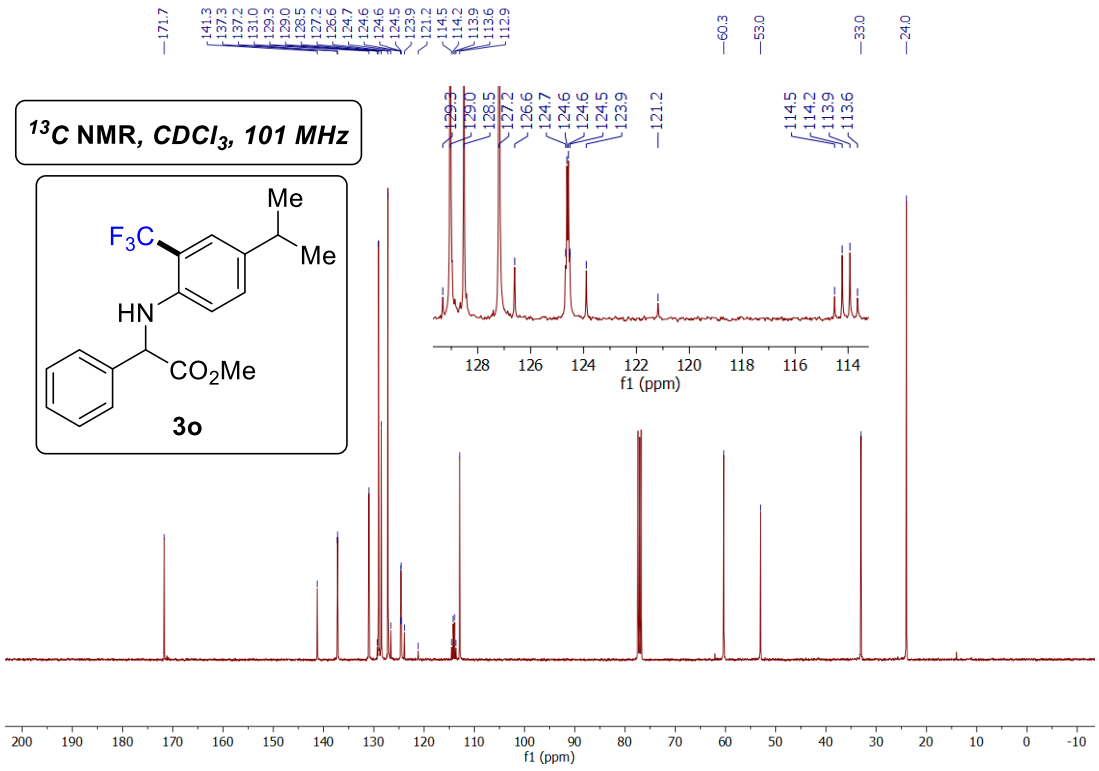


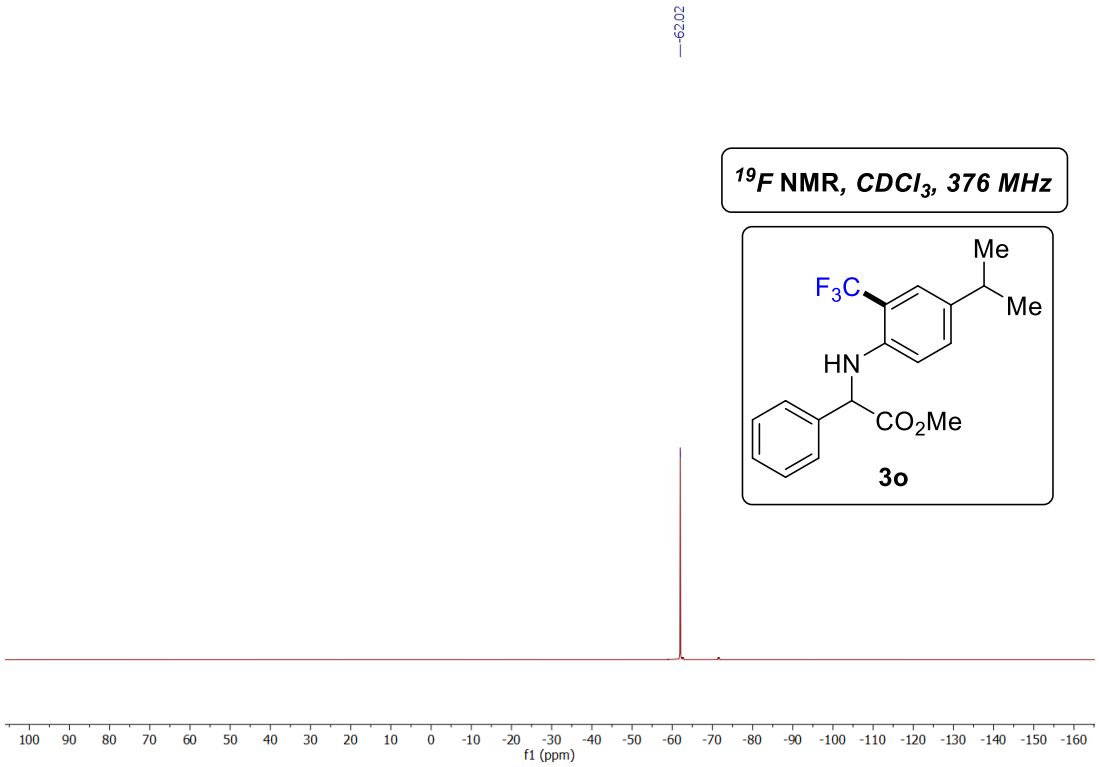



-62.24
19F NMR, CDCl3, 376 MHz
F3C
OMe
HN
CO2Me
3n
15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125
f1 (ppm)

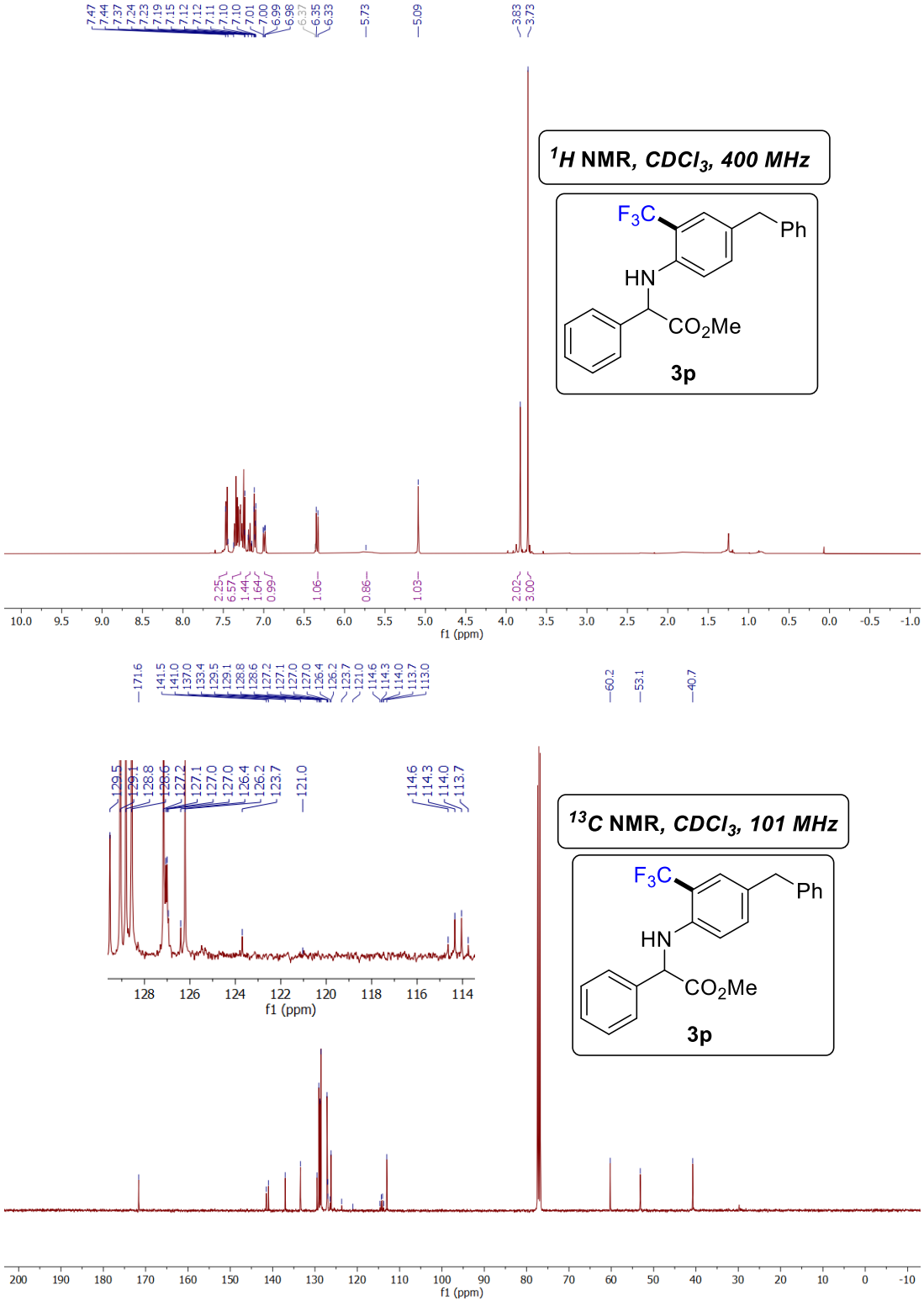
8.25 Methyl 2-((4-isopropyl-2-(trifluoromethyl) phenyl) amino)-2-phenylacetate (3o)

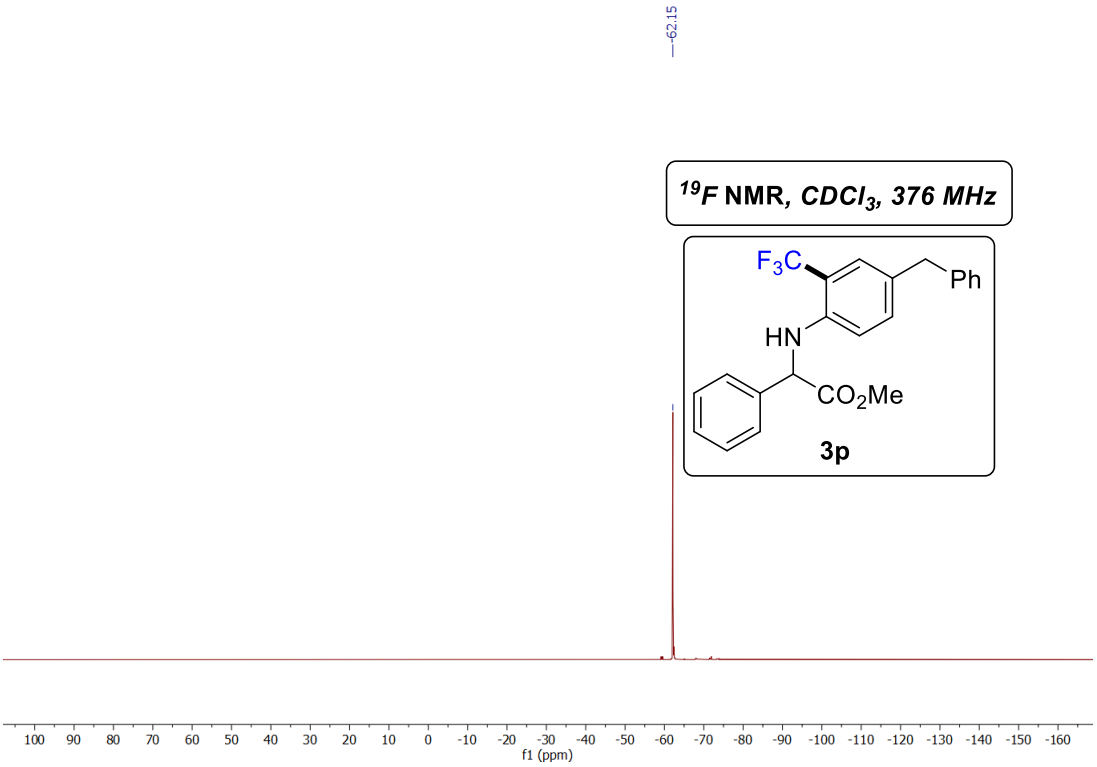




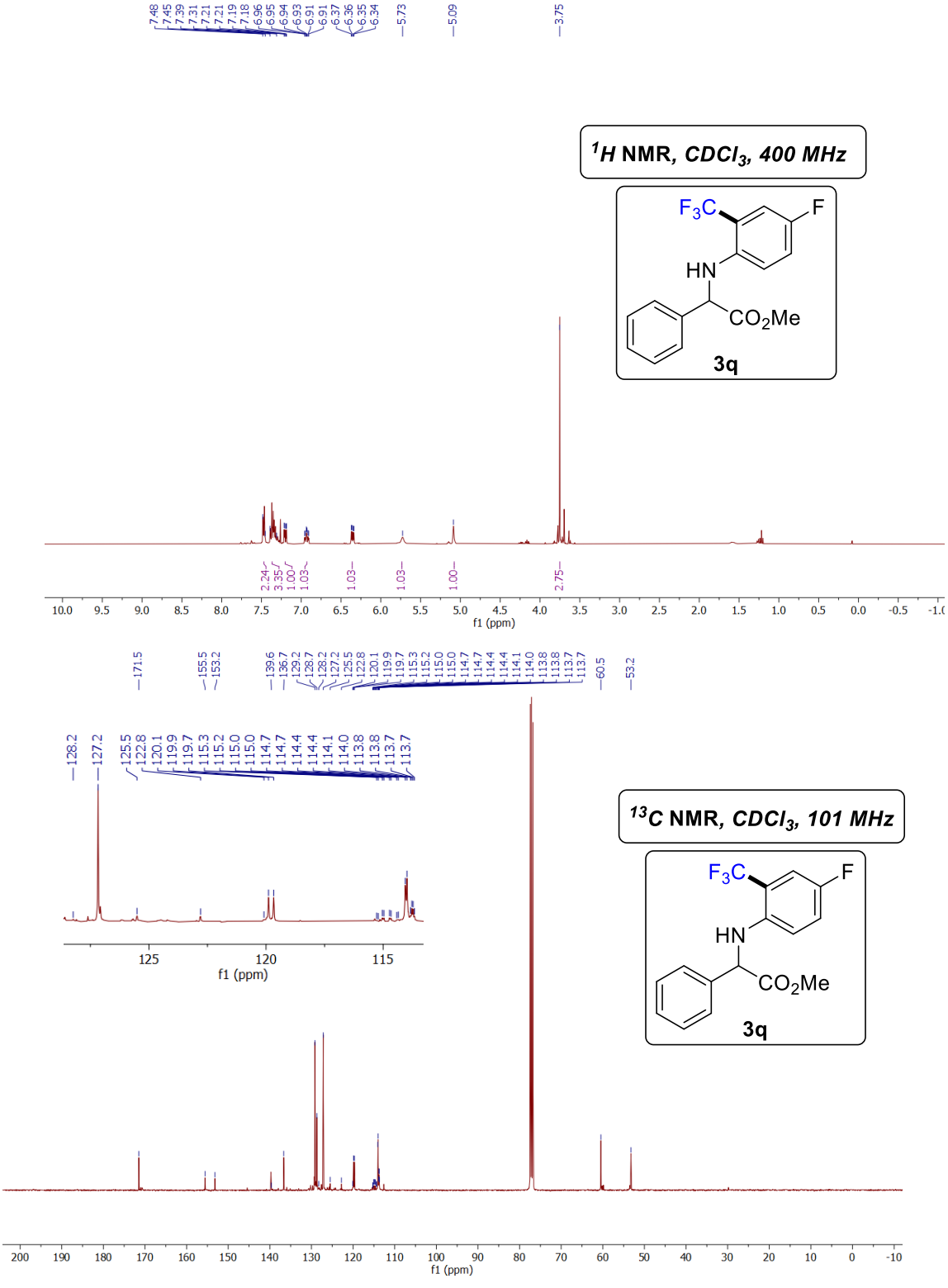

-62.02
^{19}F NMR, $CDCl_3$, 376 MHz
Me
F_3C
Me
HN
CO_2Me
3o
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

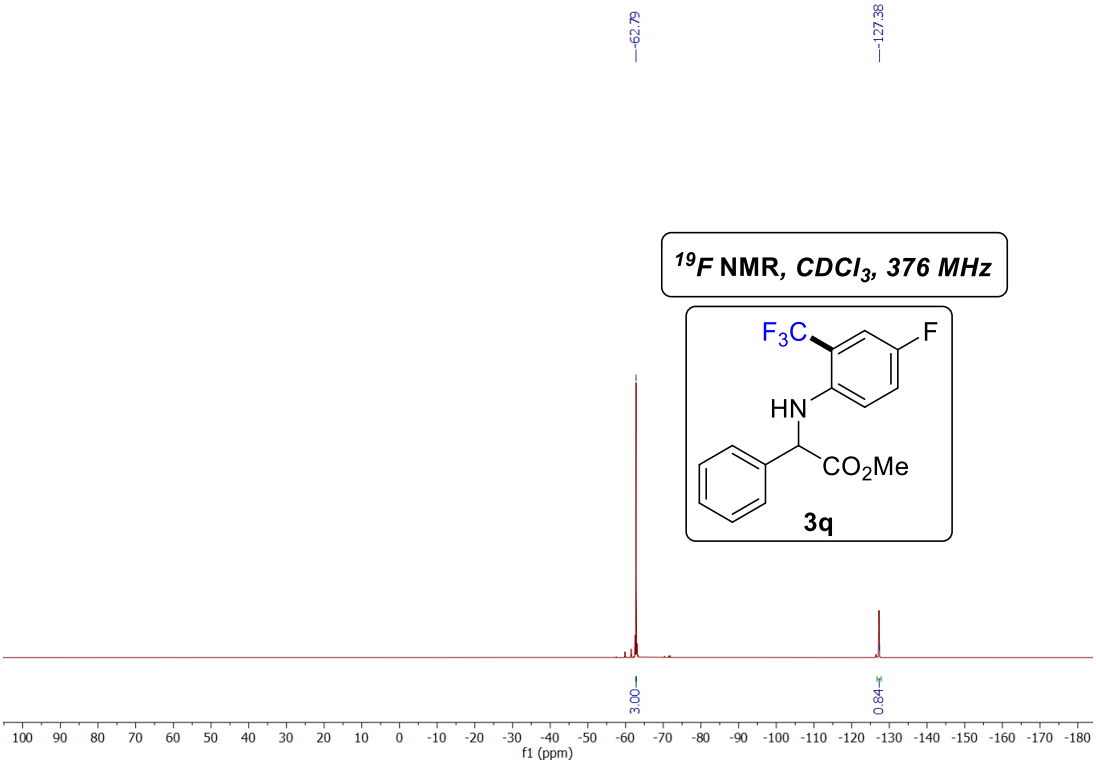
8.26 Methyl 2-((4-benzyl-2-(trifluoromethyl)phenyl)amino)-2-phenylacetate (3p)



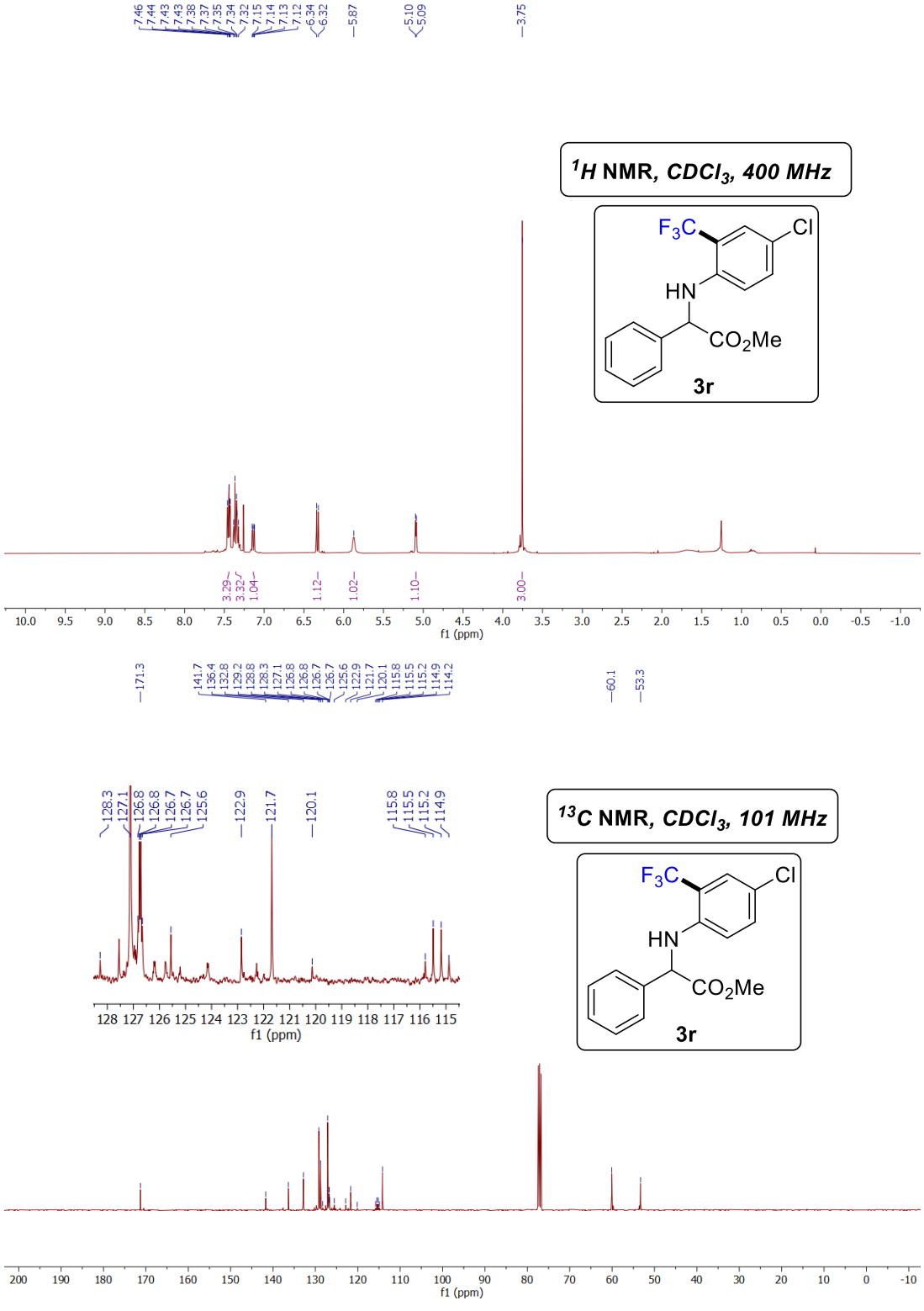

-62.15
19F NMR, CDCl3, 376 MHz
F3C
Ph
HN
CO2Me
3p
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

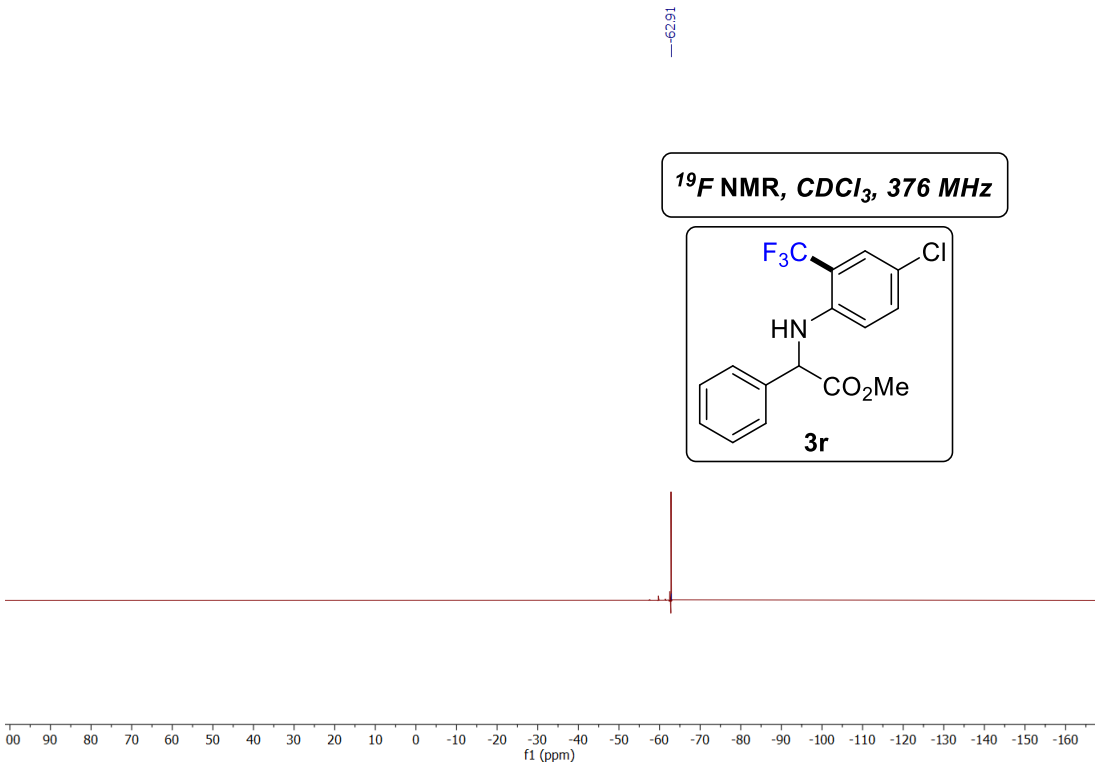
8.27 Methyl 2-((4-fluoro-2-(trifluoromethyl) phenyl) amino)-2-phenylacetate (3q)



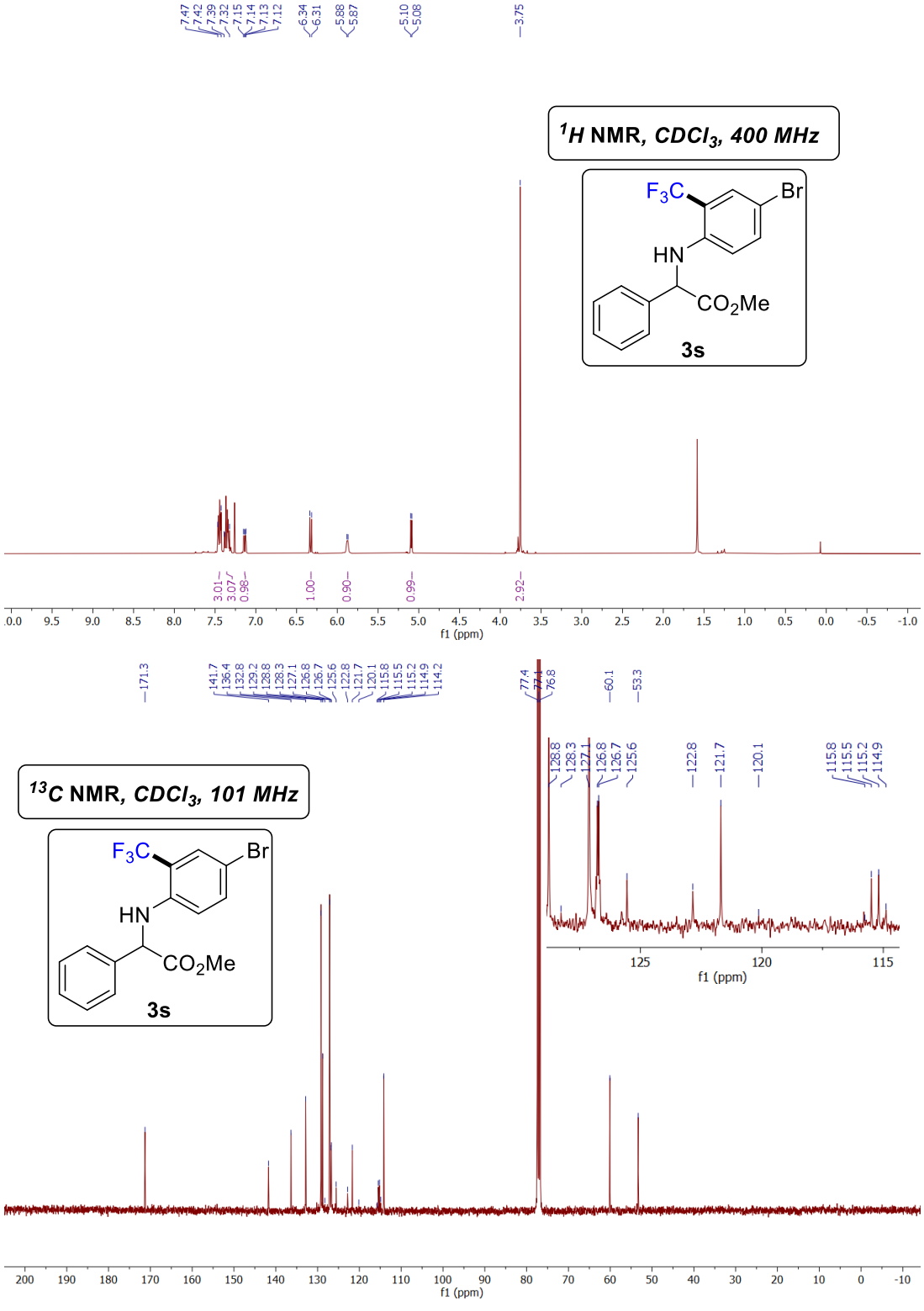

-62.79
-127.38
19F NMR, CDCl3, 376 MHz
F3C
F
HN
CO2Me
3q
3.00
0.84
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)

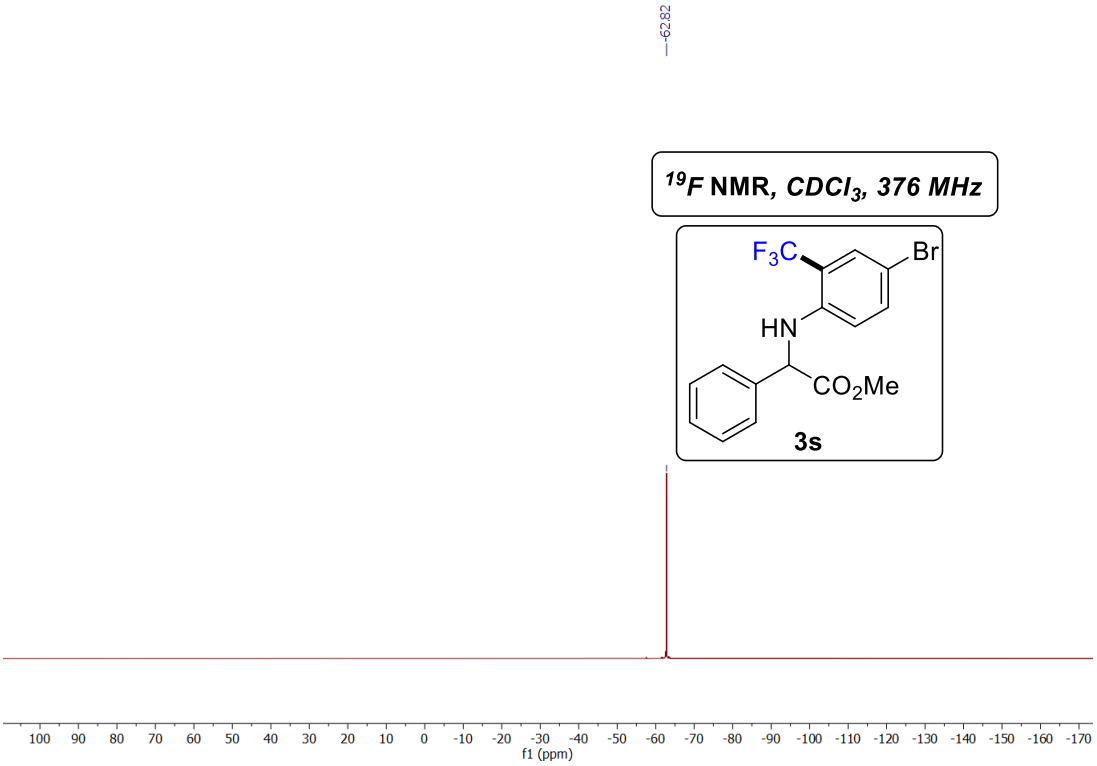
8.28 Methyl 2-((4-chloro-2-(trifluoromethyl) phenyl) amino)-2-phenylacetate (3r)



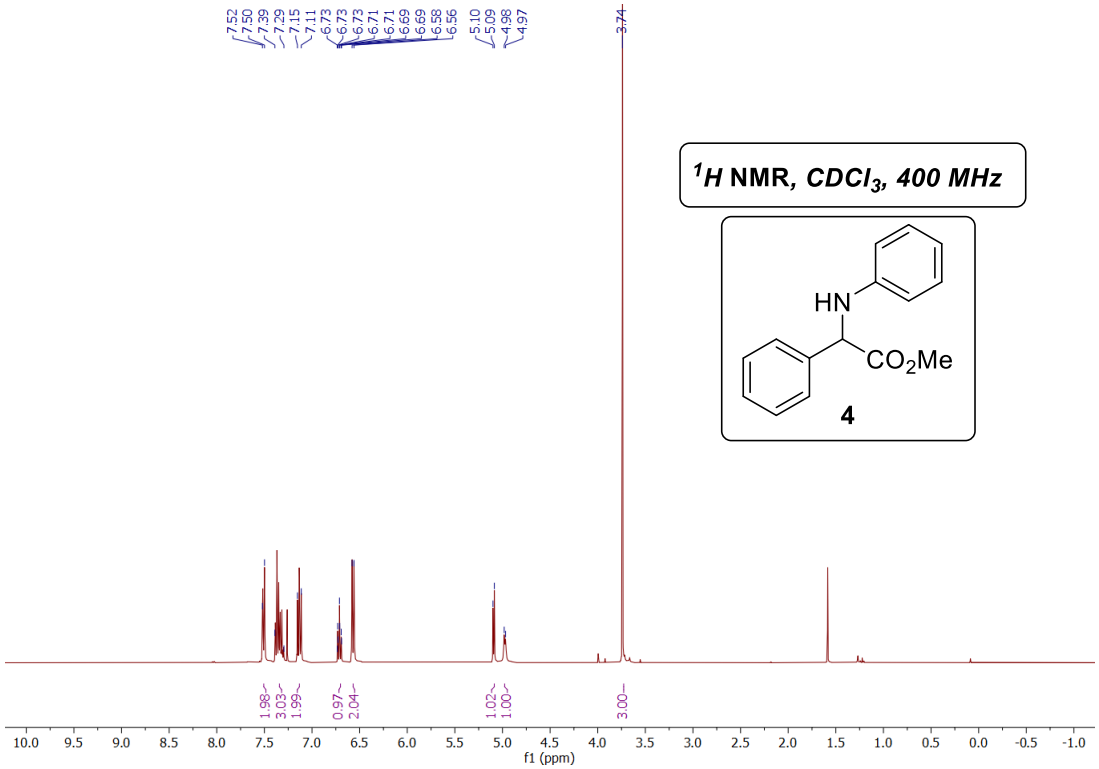

-62.91
19F NMR, CDCl3, 376 MHz
F3C
Cl
HN
CO2Me
3r
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

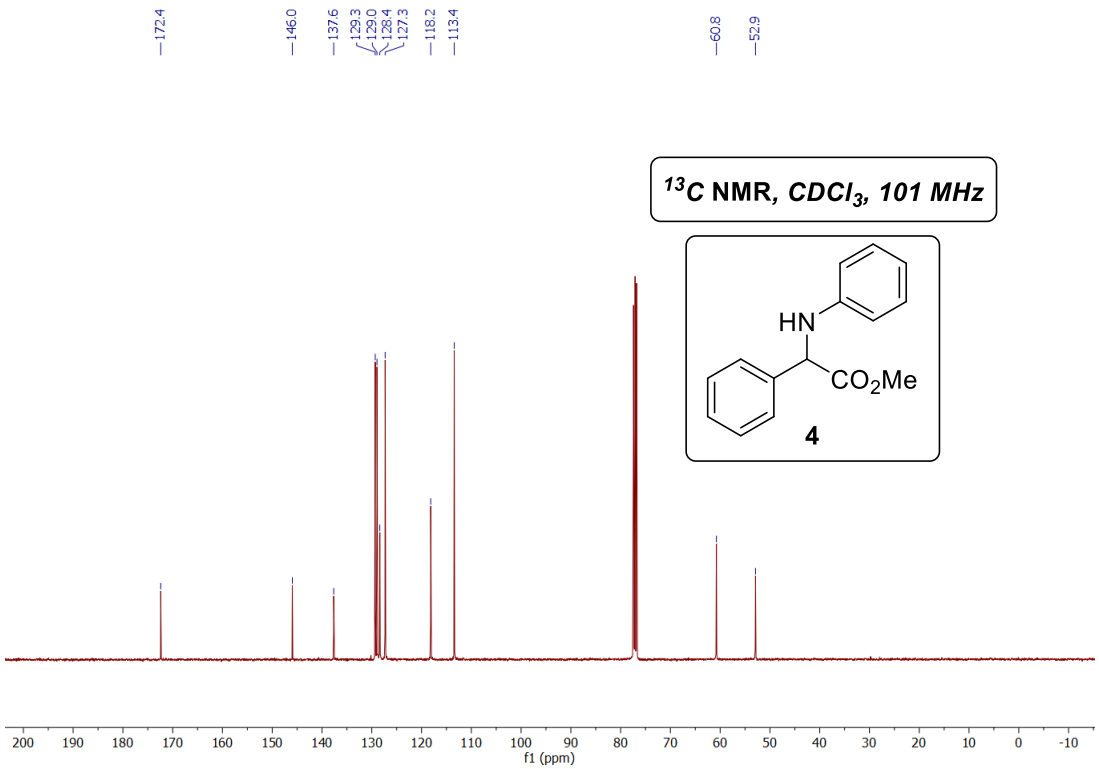
8.29 Methyl 2-((4-bromo-2-(trifluoromethyl) phenyl) amino)-2-phenylacetate (3s)



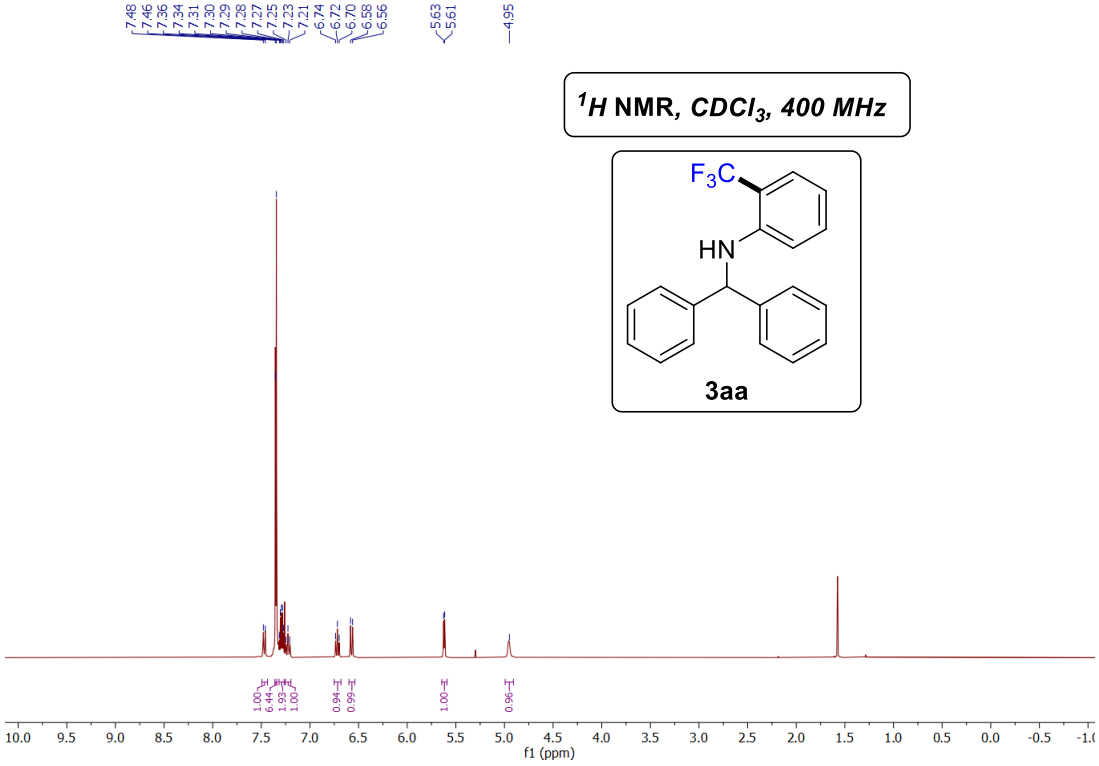

-62.82
19F NMR, CDCl3, 376 MHz
F3C
Br
HN
CO2Me
3s
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

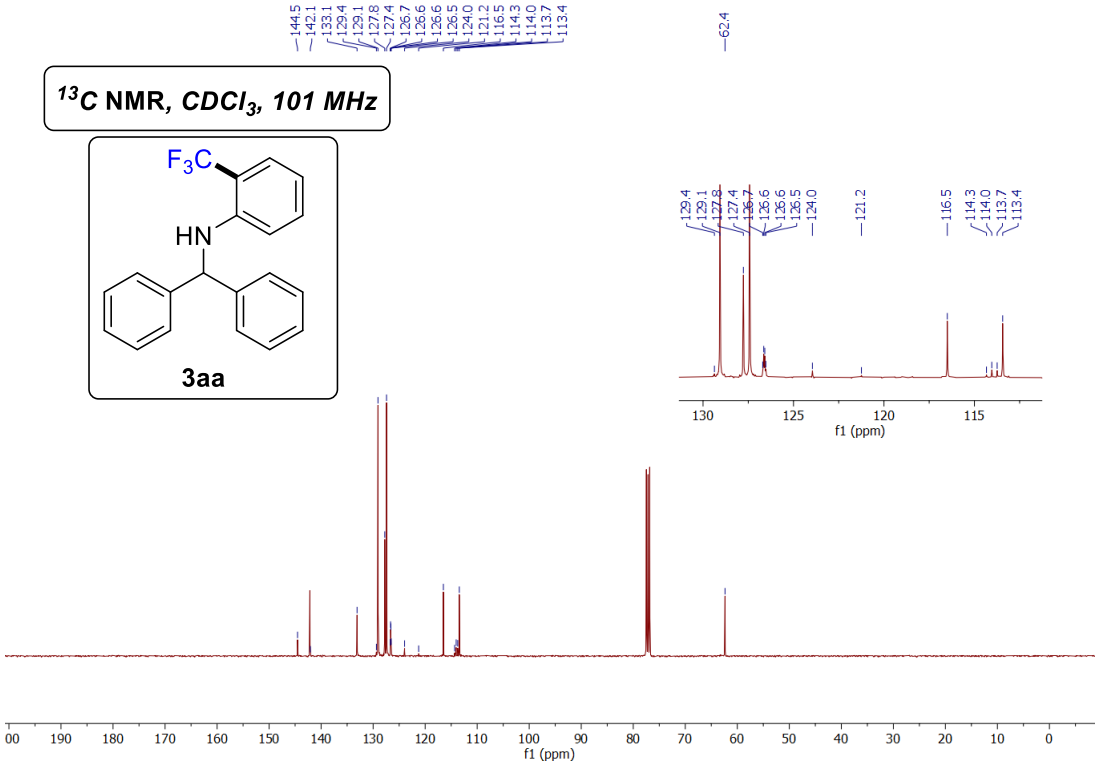
8.30 methyl 2-phenyl-2-(phenylamino)acetate (4)

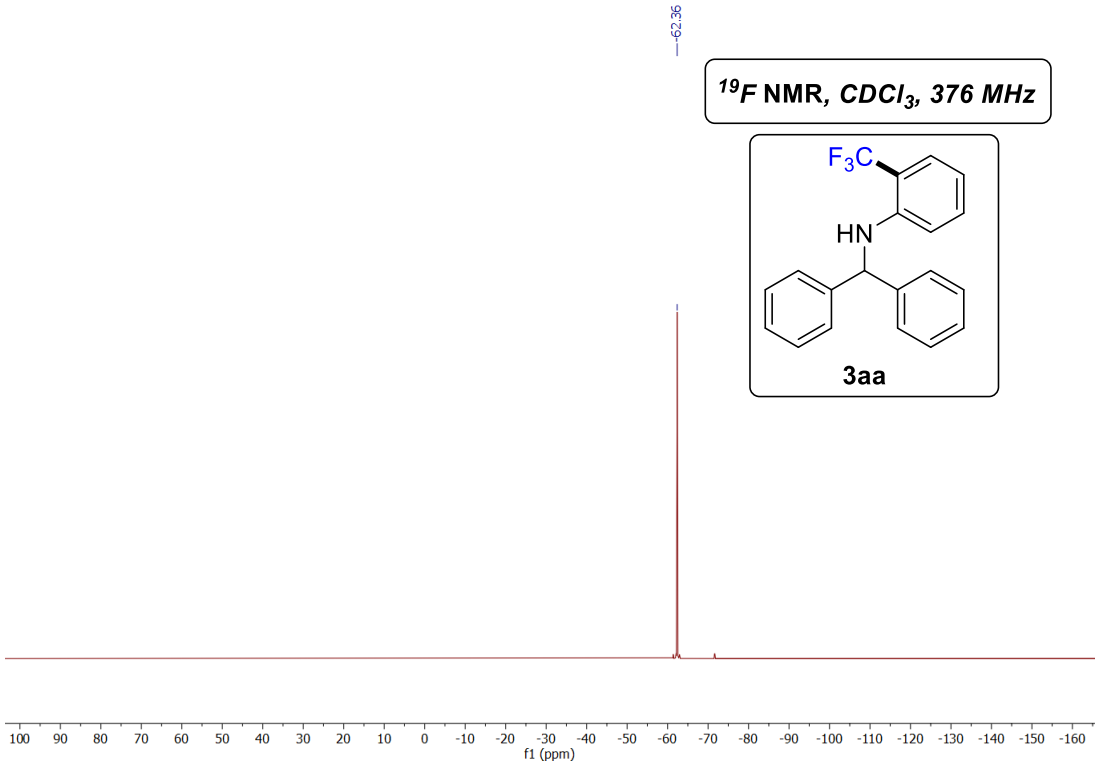




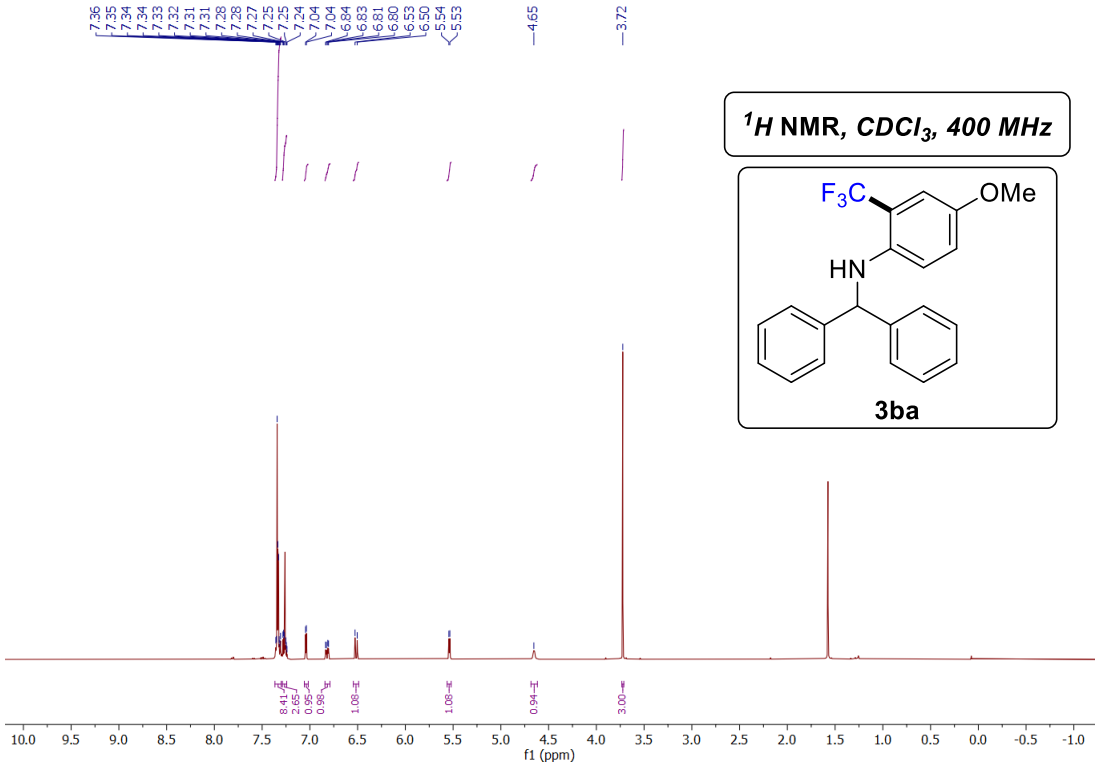
8.31 N-benzhydryl-2-(trifluoromethyl)aniline (3aa)

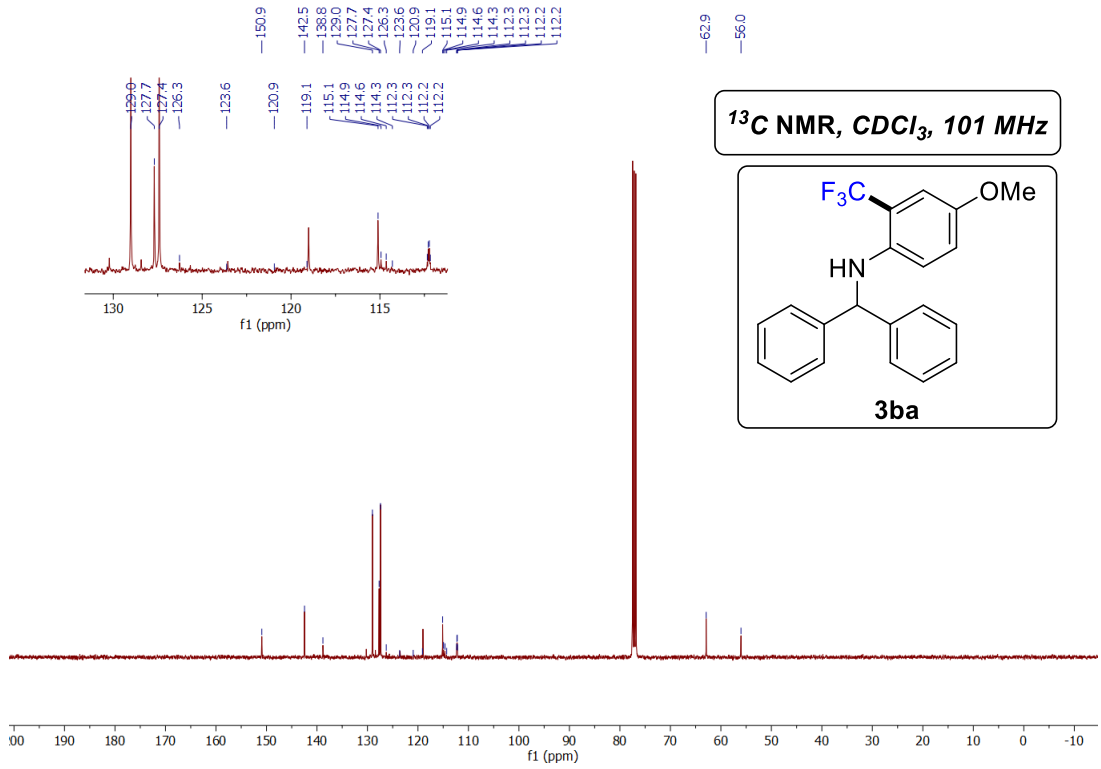


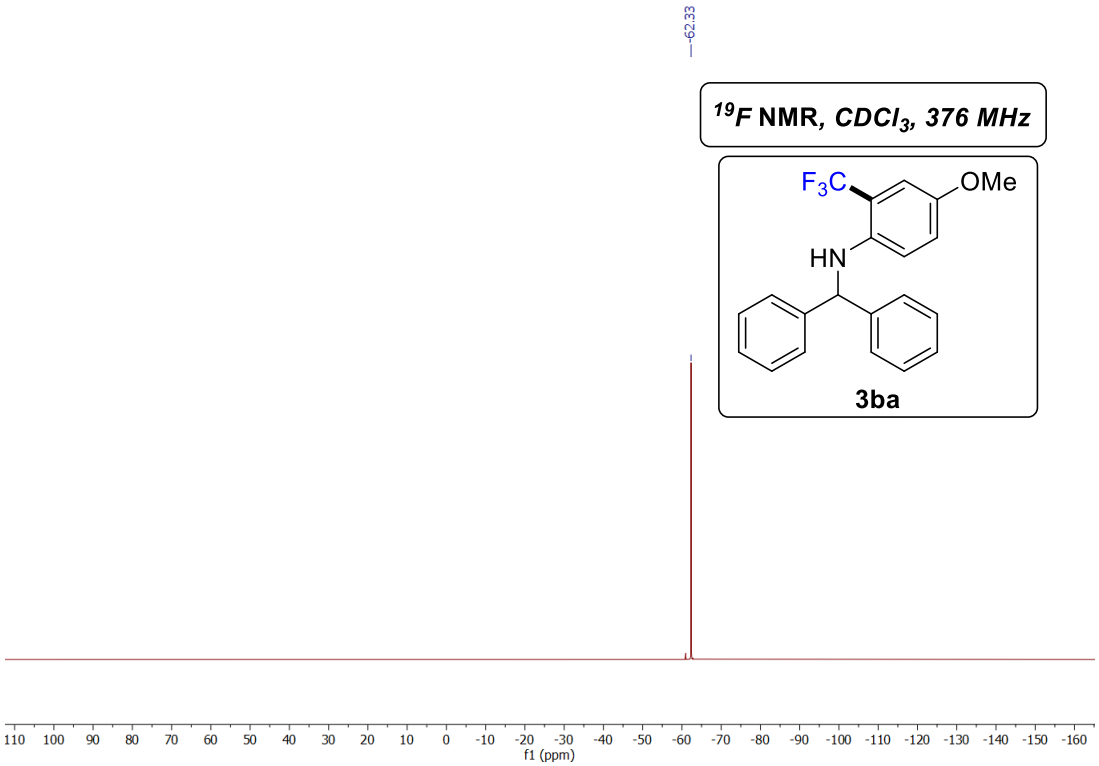



-62.36
^{19}F NMR, $CDCl_3$, 376 MHz
F_3C
HN
3aa
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

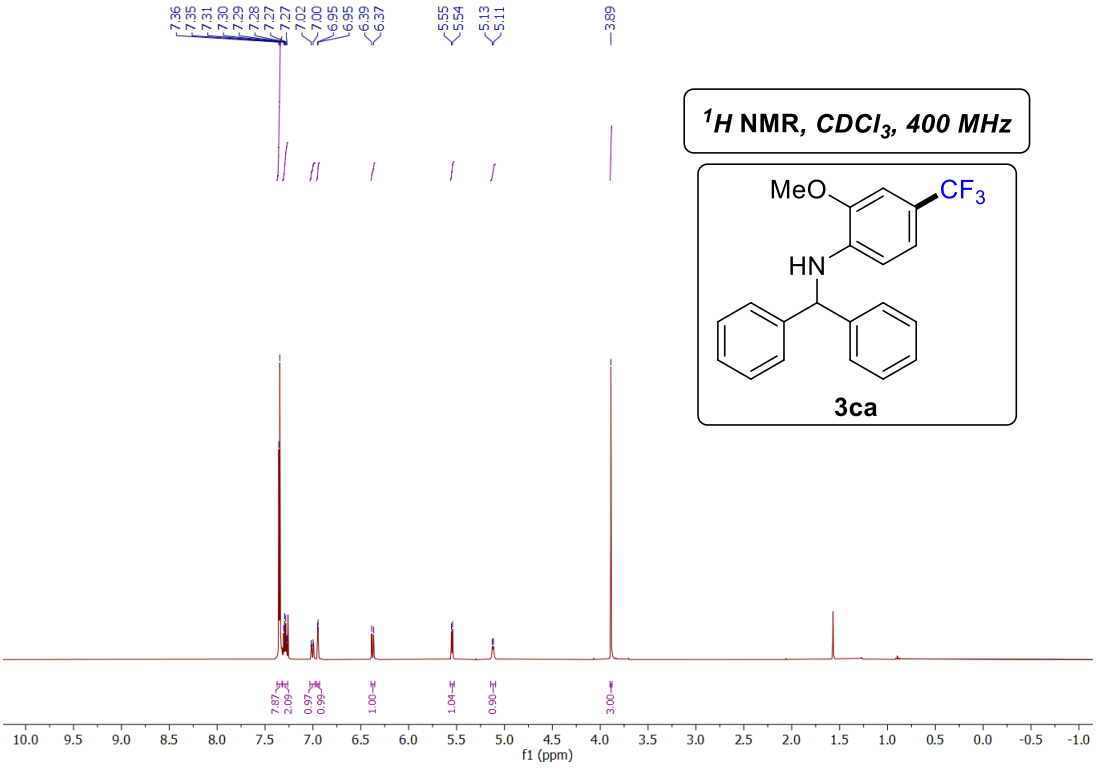
8.32 N-benzhydryl-4-methoxy-2-(trifluoromethyl)aniline (3ba)

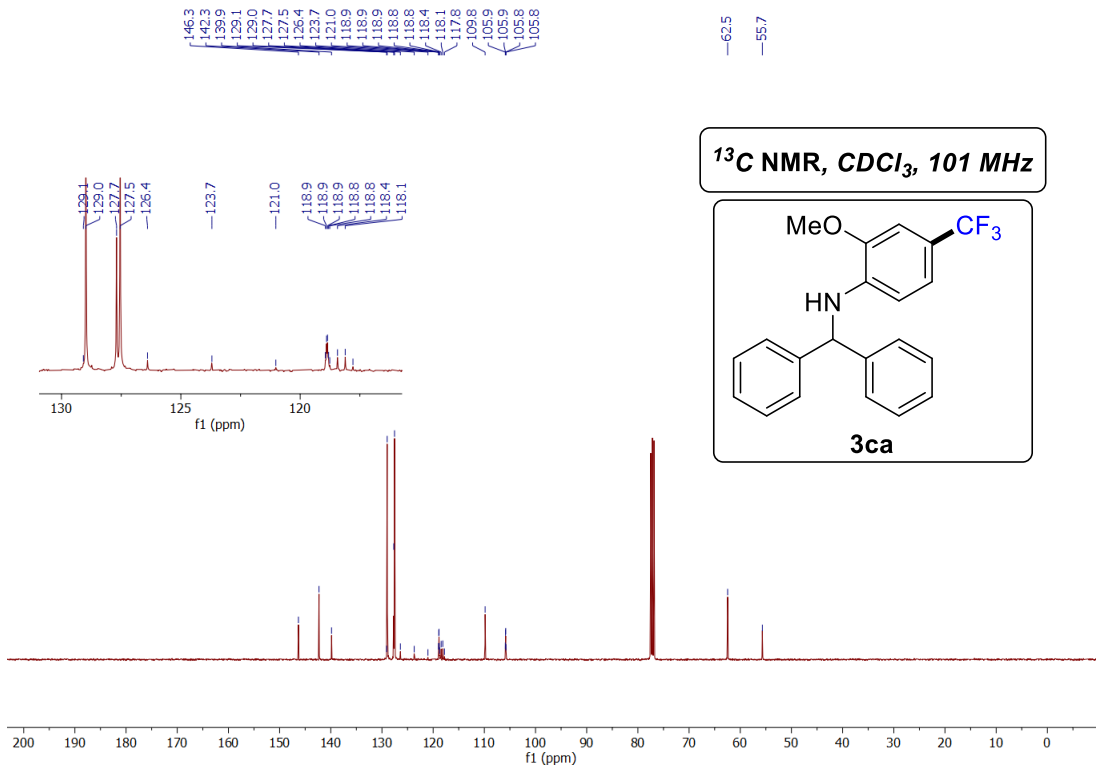


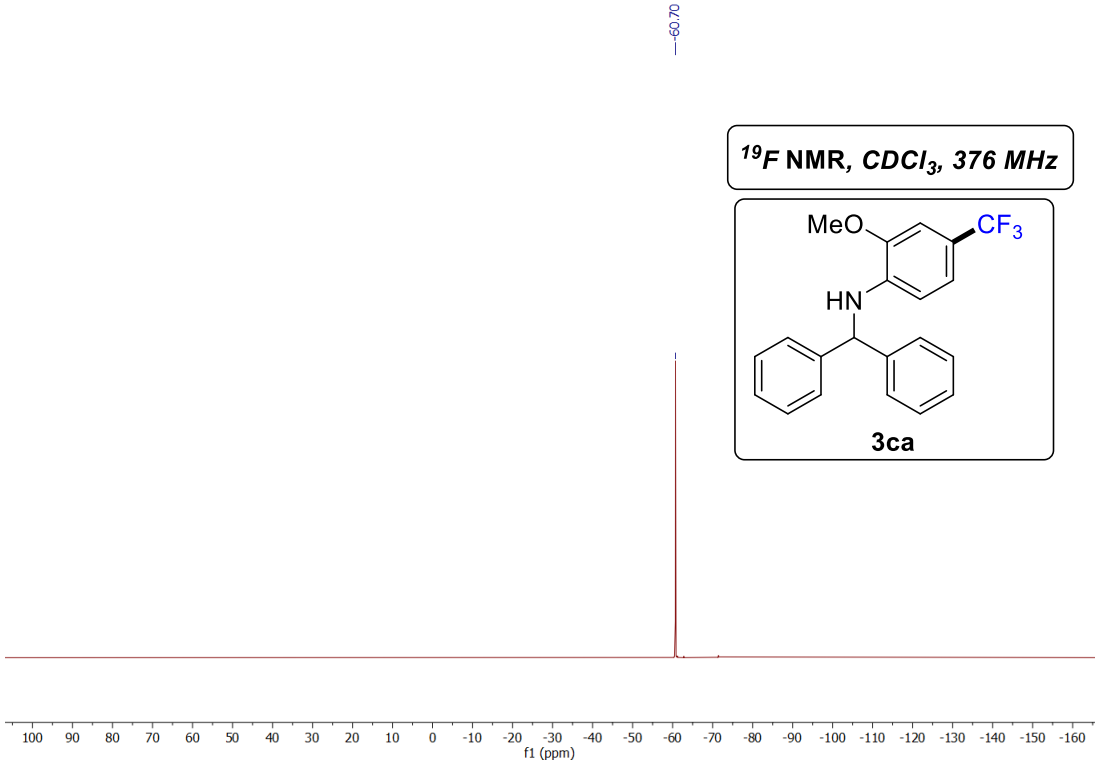



-62.33
19F NMR, CDCl3, 376 MHz
F3C
OMe
HN
3ba
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

8.33 N-benzhydryl-2-methoxy-4-(trifluoromethyl)aniline (3ca)






-60.70
^{19}F NMR, $CDCl_3$, 376 MHz
MeO
CF_3
HN
3ca
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

9.0 References:

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