Supporting Information

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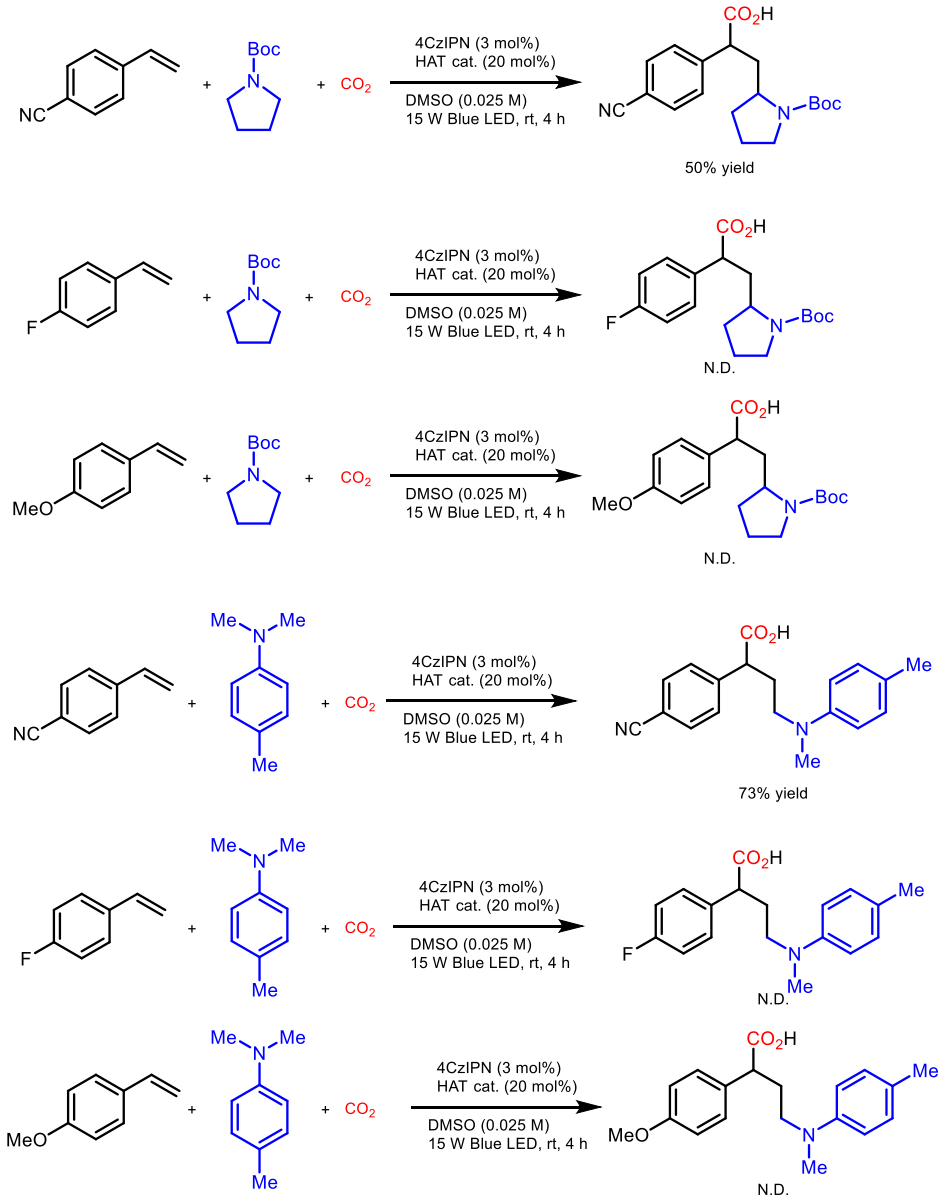
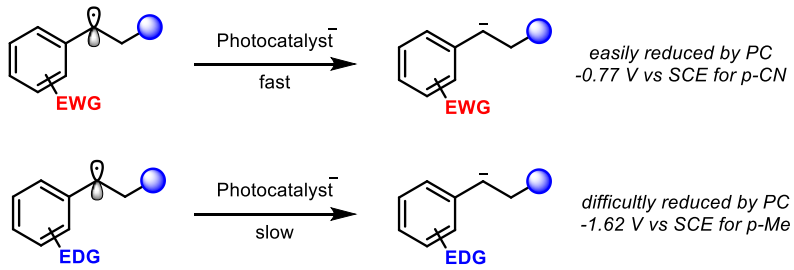
Table of Contents

1. Challenging substrates and 4CzBnBN synthesis

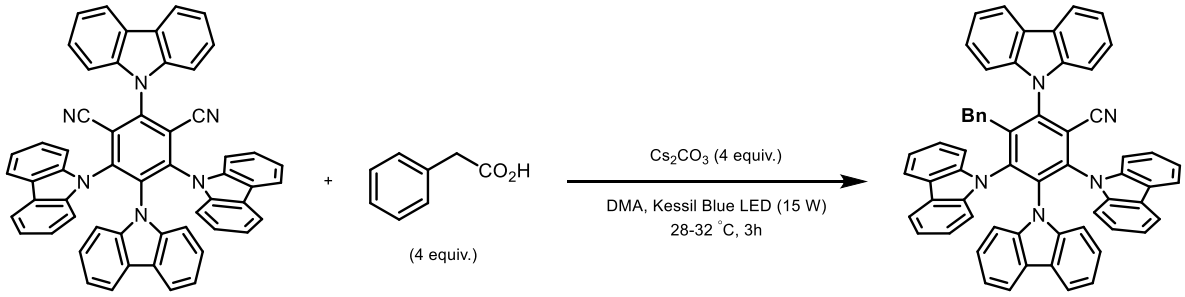
Scheme S1. The reactivity of challenging substrates under known conditions.



Scheme S2. Benzyl radical quenching process



Synthetic procedure for 4CzBnBN[1]

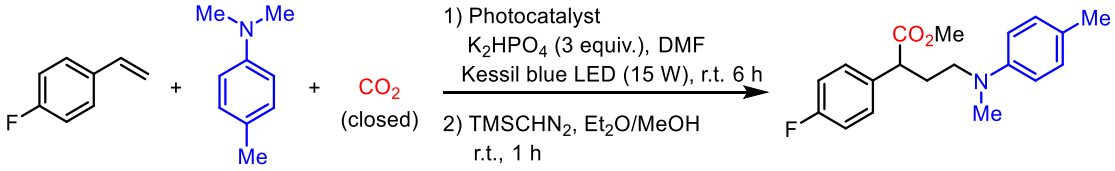


4CzIPN 4CzBnBN

A 10 mL Schlenk tube was charged with 4CzIPN (94.8 mg, 0.12 mmol), Cs_2CO_3 (156.4 mg, 0.48 mmol), and 2-phenylacetic acid (65.4 mg, 0.48 mmol) in the glovebox. The Schlenk tube was taken out of the glovebox. DMA (8 mL) was added under Ar balloon. Then, the reaction was irradiated with Kessil LED light (A80, Tuna Blue, 15 W; the distance between the schlenk tube and the LED was about 6-8 cm) for 6 h at room temperature (28-32 °C). The reaction was cooled by fan. After completion of the reaction, the mixture was quenched with H_2O (20 mL) and brine (60 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic phase was dried using $MgSO_4$, filtered, and evaporated of ethyl acetate. The crude material was obtained by recrystallization from Hexane/EA (4:1).

2. Detailed optimization process and reaction setup

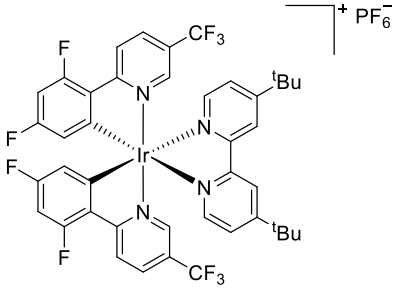
Table S1. *Screening of photocatalysts* [a]



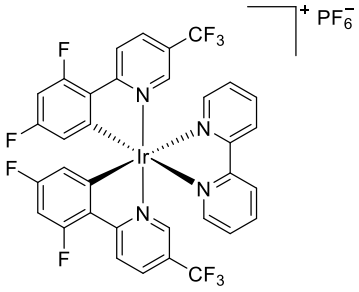
1a **2a** **3aa**

entry	photocatalyst (x mol%)	yield[b]
1	$[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ (1 mol%)	<1%
2	$[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ (1 mol%)	<1%
3	$[Ir(ppy)_2(dtbpy)]PF_6$ (1 mol%)	10%
4	$Ir(ppy)_3$ (1 mol%)	<1%
5	4CzIPN (3 mol%)	<1%
6	$Ir(ppy)_3$ (1 mol%) + $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ (1 mol%)	20%
7	**4CzBnBN (5 mol%)**	**64%**
8	4CzBnBN (3 mol%)	56%

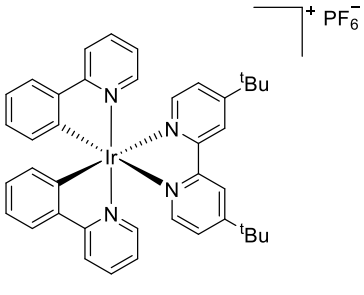
[a] Conditions: 1) 0.2 mmol **1a**, 0.6 mmol **2a**, 0.6 mmol K_2HPO_4, 1-5 mol% photocatalyst, DMF (2 mL), CO_2 (closed), Kessil blue LED (15 W), 6 h, 2) $TMSCHN_2$ 2 M in Et_2O (0.2 mL), Et_2O (8 mL), MeOH (2 mL), 1 h. [b] Isolated yield.



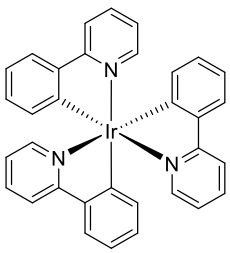
$[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$



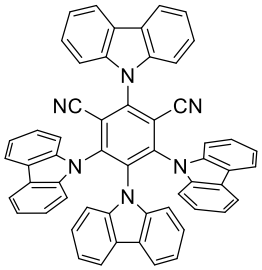
$[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$



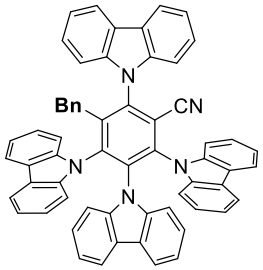
$[Ir(ppy)_2(dtbpy)]PF_6$



$Ir(ppy)_3$

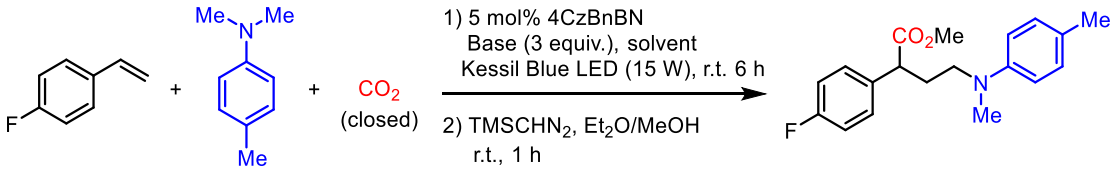


4CzIPN



4CzBnBN

Table S2. *Screening of base and solvent*[a]

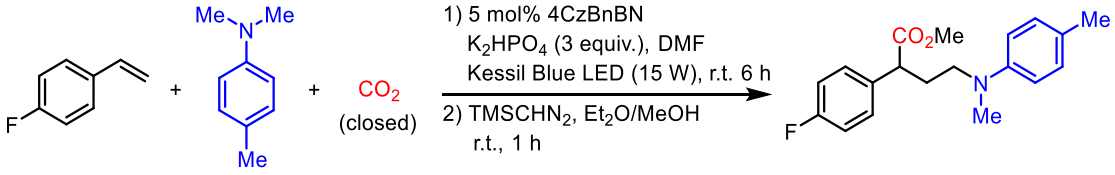


1a **2a** **3aa**

entry	base	solvent	yield[b]
1	CsOAc	DMF	50%
2	KOAc	DMF	51%
3	NaOAc	DMF	50%
4	$KOCOCF_3$	DMF	23%
5	$KHCO_3$	DMF	51%
6	**K_2HPO_4**	**DMF**	**64%**
7	K_2CO_3	DMF	35%
8	KOH	DMF	37%
9	K_2HPO_4	DMA	60%
10	K_2HPO_4	NMP	61%
11	K_2HPO_4	DMSO	36%

[a] Conditions: 1) 0.2 mmol **1a**, 0.6 mmol **2a**, 0.6 mmol base, 5 mol% 4CzBnBN, solvent (2 mL), CO_2 (closed), Kessil blue LED (15 W), 15 h, 2) $TMSCHN_2$ 2 M in Et_2O (0.2 mL), Et_2O (8 mL), MeOH (2 mL), 1 h. [b] Isolated yield.

Table S3. ***Screening of different stoichiometry***[a]



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

Entry	1a : 2a ratio	Yield[b]
1	1:1	21%
2	1:3	64%
3	1:5	61%
4	3:1	9%

[a] Conditions: 1) **1a**, **2a**, 0.2-0.6 mmol K_2HPO_4, 5 mol% 4CzBnBN, DMF (2 mL), CO_2 (closed), Kessil blue LED (15 W), 15 h, 2) $TMSCHN_2$ 2M in Et_2O (0.2 mL), Et_2O (8 mL), MeOH (2 mL), 1 h. [b] Isolated yield. [b] Isolated yield.

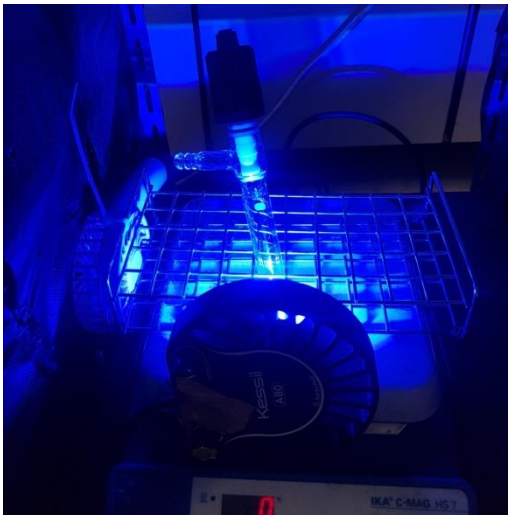


Figure S1. Photochemical reaction set-up

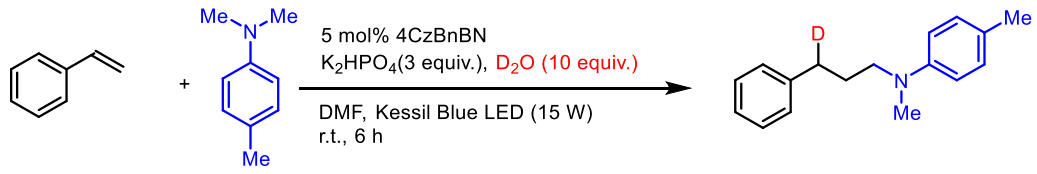
3. Mechanism experiments

Radical inhibition experiment and Isotope-labelling study

Scheme S3. (a)TEMPO was used as additive for the carbocarboxylation (b) D_2O was used as electrophile instead of CO_2

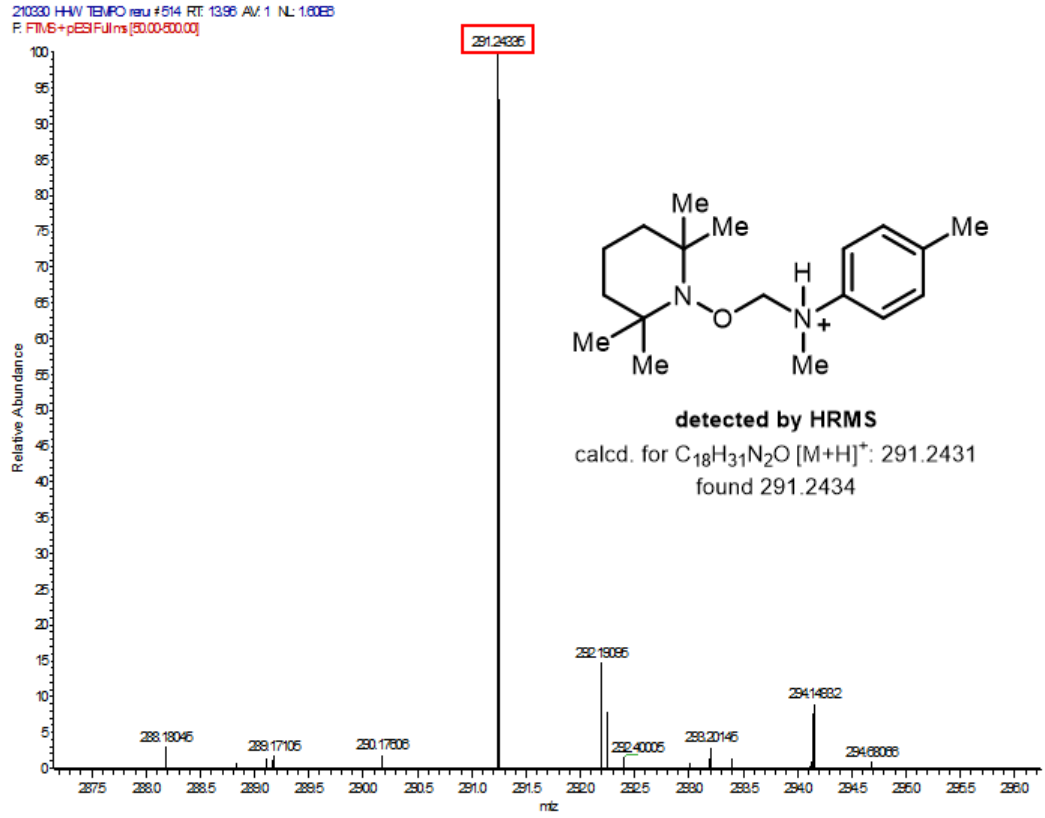
(a) Radical trapping study

(b) Isotope labelling study with D_2O



Radical trapping study

A 10 mL Schleck tube was charged with 4CzBnBN (8.5 mg), K_2HPO_4 (104.5 mg) and TEMPO (0.6 mmol, 93.8 mg) which was evacuated and refilled with carbon dioxide (CO_2) for 3 times following the usual Schlenk technique. DMF (2 mL), **1f** (0.2 mmol) and **2a** (0.6 mmol) was added under a flow of CO_2 and the Schlenk tube was closed. Then, the reaction was conducted in the schlenk tube irradiated with Kessil LED light (A80, Tuna Blue, 15 W; the distance between the schlenk tube and the LED was about 6-8 cm) for 6 h at room temperature (28-32 °C). The reaction was cooled by fan. After completion of the reaction, the mixture was quenched with 1 M HCl (2 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic phase was dried using $MgSO_4$, filtered, and evaporated of ethyl acetate. When using TEMPO (3 equiv.) as radical inhibitor, the desired product was not detected by TLC. The formation of **3fa** was inhibited and TEMPO-trapping products were detected by HRMS.



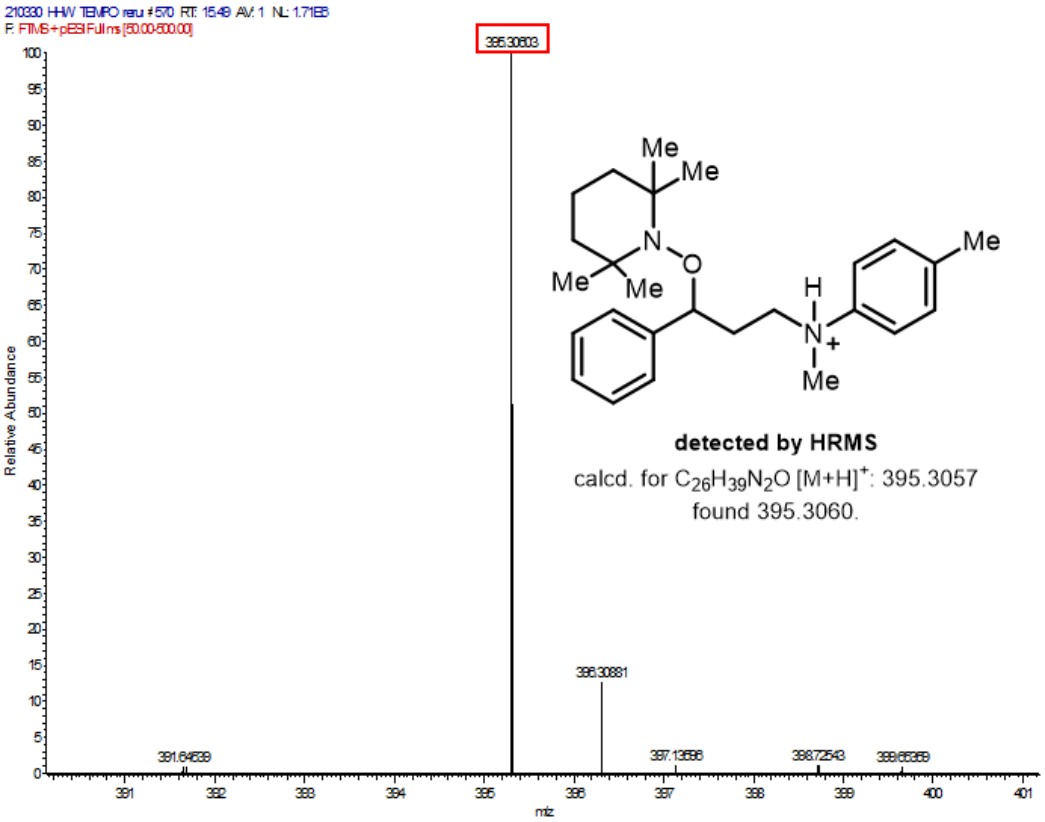


Figure S2. TEMPO-trapping products detected by HRMS

Isotope labelling study with D_2O

A 10 mL Schleck tube was charged with 4CzBnBN (8.5 mg) and K_2HPO_4 (104.5 mg) which was evacuated and refilled with argon for 3 times following the usual Schlenk technique. DMF (2 mL), **1f** (0.2 mmol) and **2a** (0.6 mmol) was added under a flow of Ar and the Schlenk tube was closed. Then, the reaction was conducted in the schlenk tube irradiated with Kessil LED light (A80, Tuna Blue, 15 W; the distance between the schlenk tube and the LED was about 6-8 cm) for 6 h at room temperature (28-32 °C). The reaction was cooled by fan. After completion of the reaction, the mixture was quenched with 1 M HCl (2 mL) and extracted with ethyl acetate (5 mL x 3).). The combined organic phase was dried using $MgSO_4$, filtered, and evaporated of ethyl acetate. The crude material was separated by silica gel column chromatography (5-10% ethyl acetate/*n*-hexane) and afforded 99%-deuterated product **4** as colorless oil in 65% yield (31 mg).

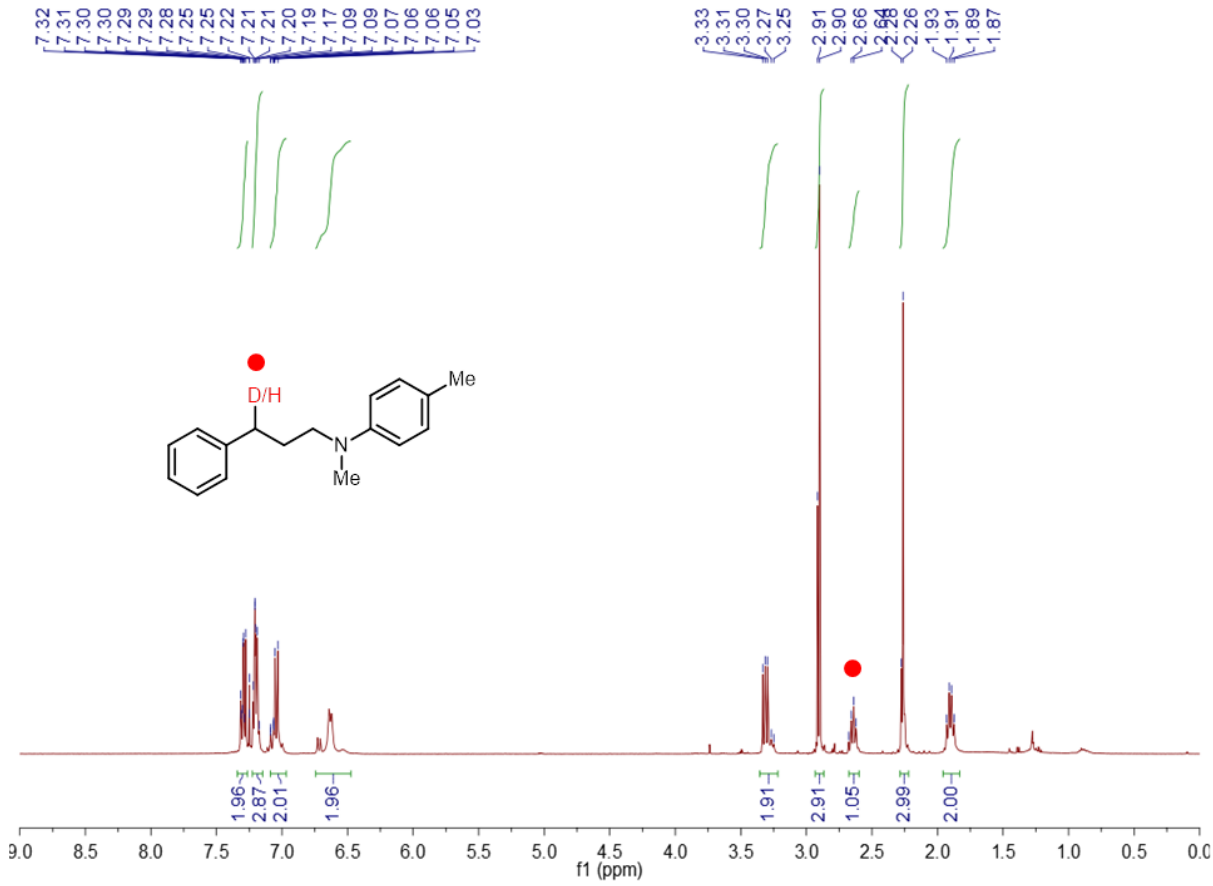


Figure S3. Isotope labelling study with **1f** and D_2O

Luminescence quenching experiments

Emission quenching of 4CzBnBN with styrene

Stock solutions of 4CzBnBN (150 µM) and styrene (15 mM) were prepared in DMF. Samples containing 4CzBnBN (15 µM) in absence and presence of styrene (0.15, 0.30, 0.45, 0.60, 0.75, 0.90, 1.05, 1.20, 1.35, 1.50 mM) were prepared. Then the fluorescence spectra were

recorded by the fluorescence spectrophotometer under excitation at 289 nm.

Emission quenching of 4CzBnBN with *N*,*N*,4-trimethylaniline

Stock solutions of 4CzBnBN (150 µM) and *N*,*N*,4-trimethylaniline (15 mM) were prepared in DMF. Samples containing 4CzBnBN (15 µM) in absence and presence of *N*,*N*,4-trimethylaniline (0.15, 0.30, 0.45, 0.60, 0.75, 0.90, 1.05, 1.20, 1.35, 1.50 mM) were prepared. Then the fluorescence spectra were recorded by the fluorescence spectrophotometer under excitation at 289 nm.

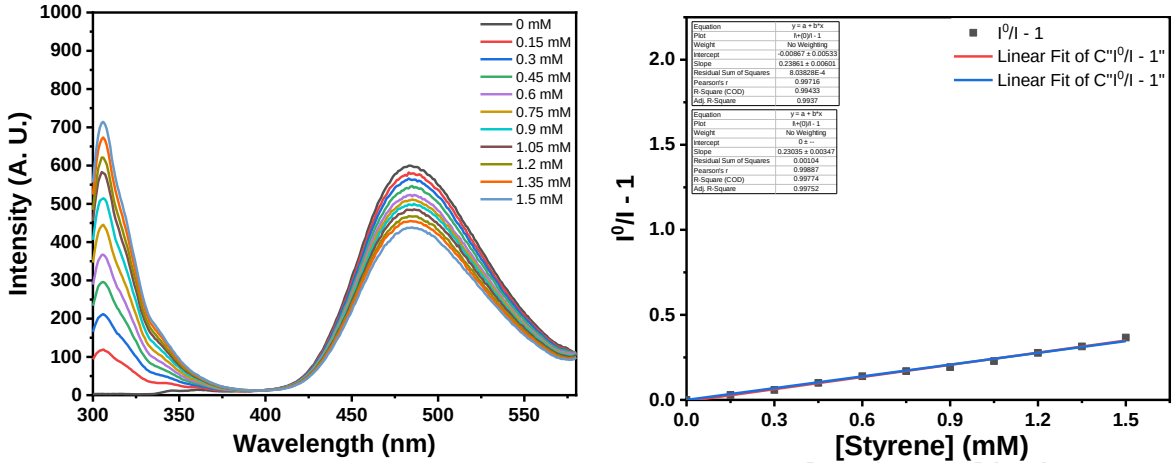


Figure S4. Left: Emission quenching of 4CzBnBN (15 µM in dry DMF) upon titration with styrene (1f). Right: Corresponding Stern-Volmer plot with a Stern-Volmer constant K_{sv} = 23.0 μM^{-1}.

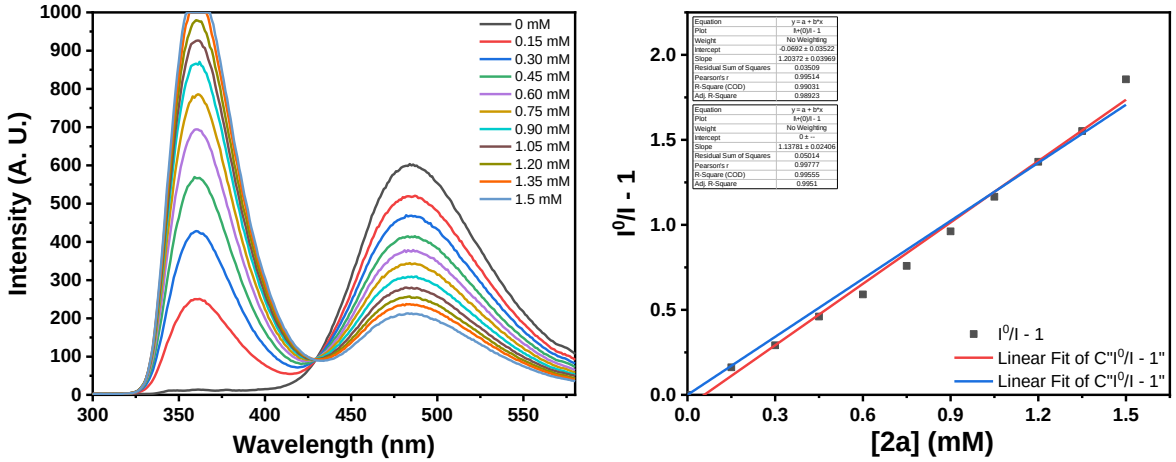


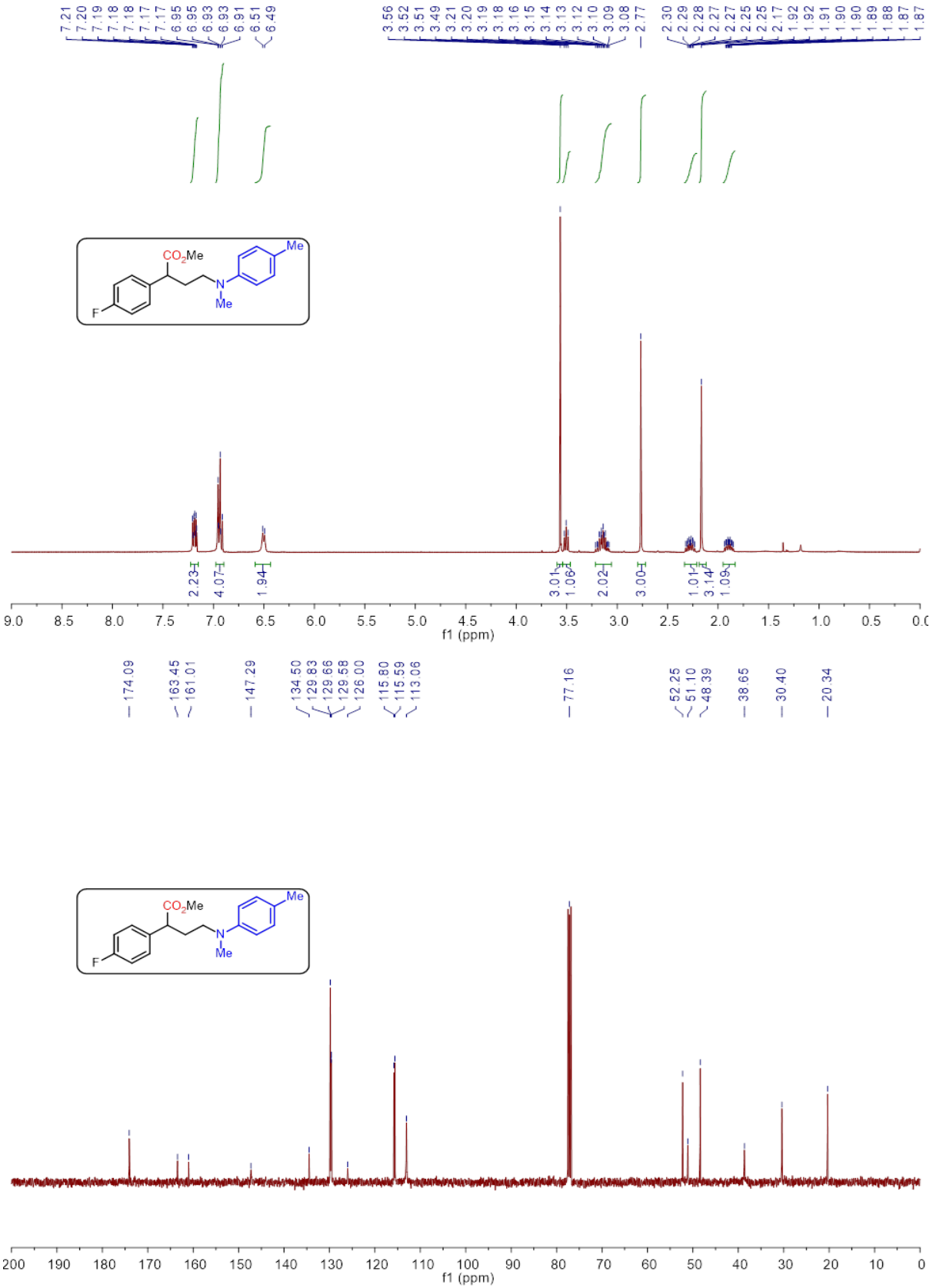
Figure S5. Left: Emission quenching of 4CzBnBN (15 µM in dry DMF) upon titration with 4-*N*,*N*-trimethylaniline (2a). Right: Corresponding Stern-Volmer plot with a Stern-Volmer constant K_{sv} = 113.8 μM^{-1}.

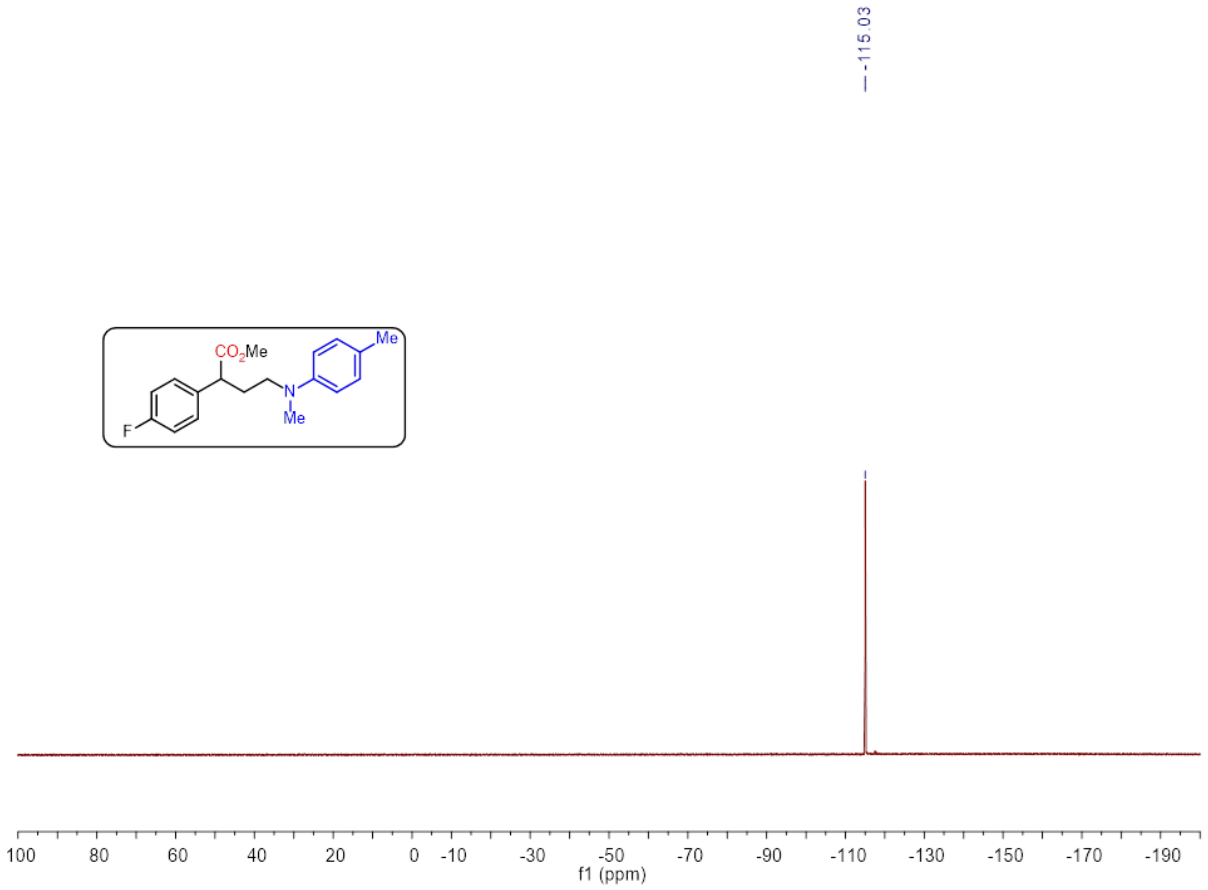
4. Reference

(1) K. Donabauer, M. Maity, A. L. Berger, G. S. Huff, S. Crespi, and B. König, *Chem. Sci.,* **2019**, *10*, 5162-5166.

5. ^{1}H, ^{13}C, and ^{19}F NMR spectra

Methyl 2-(4-fluorophenyl)-4-(methyl(p-tolyl)amino)butanoate (3aa)

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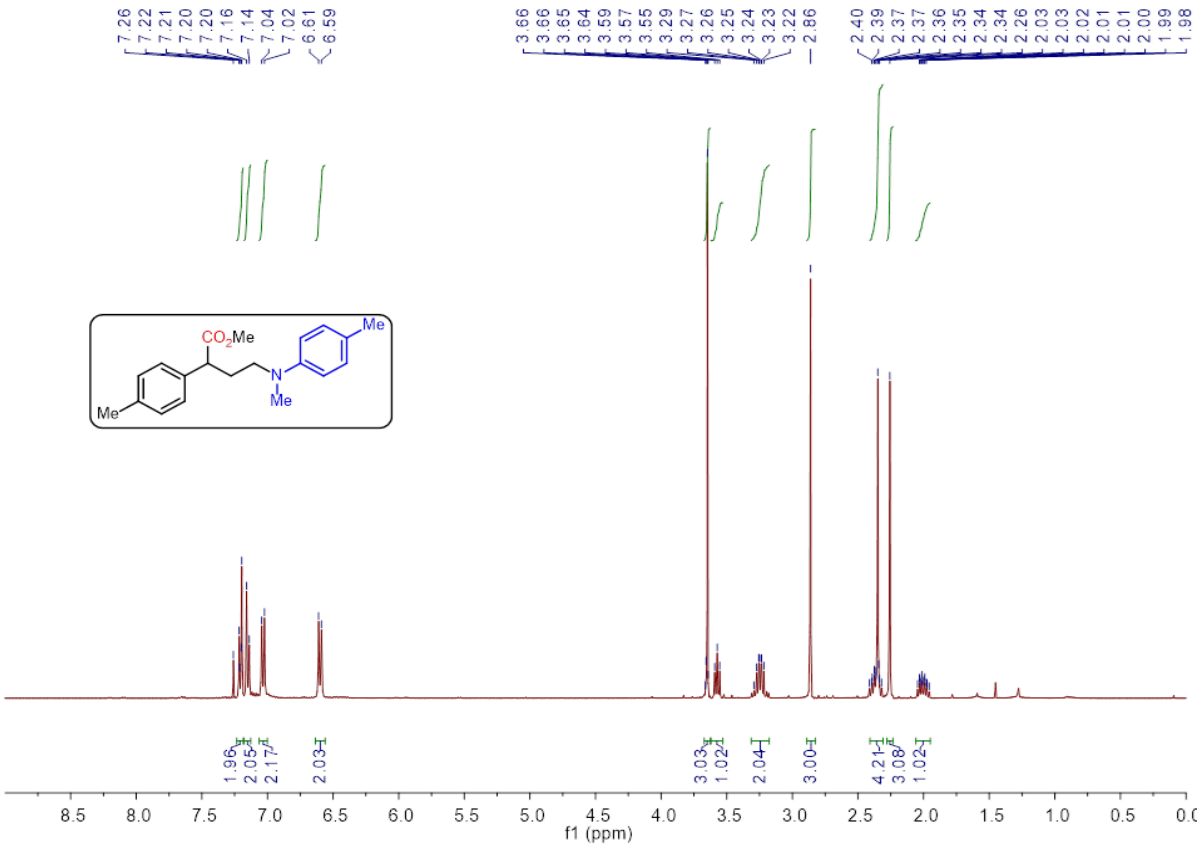
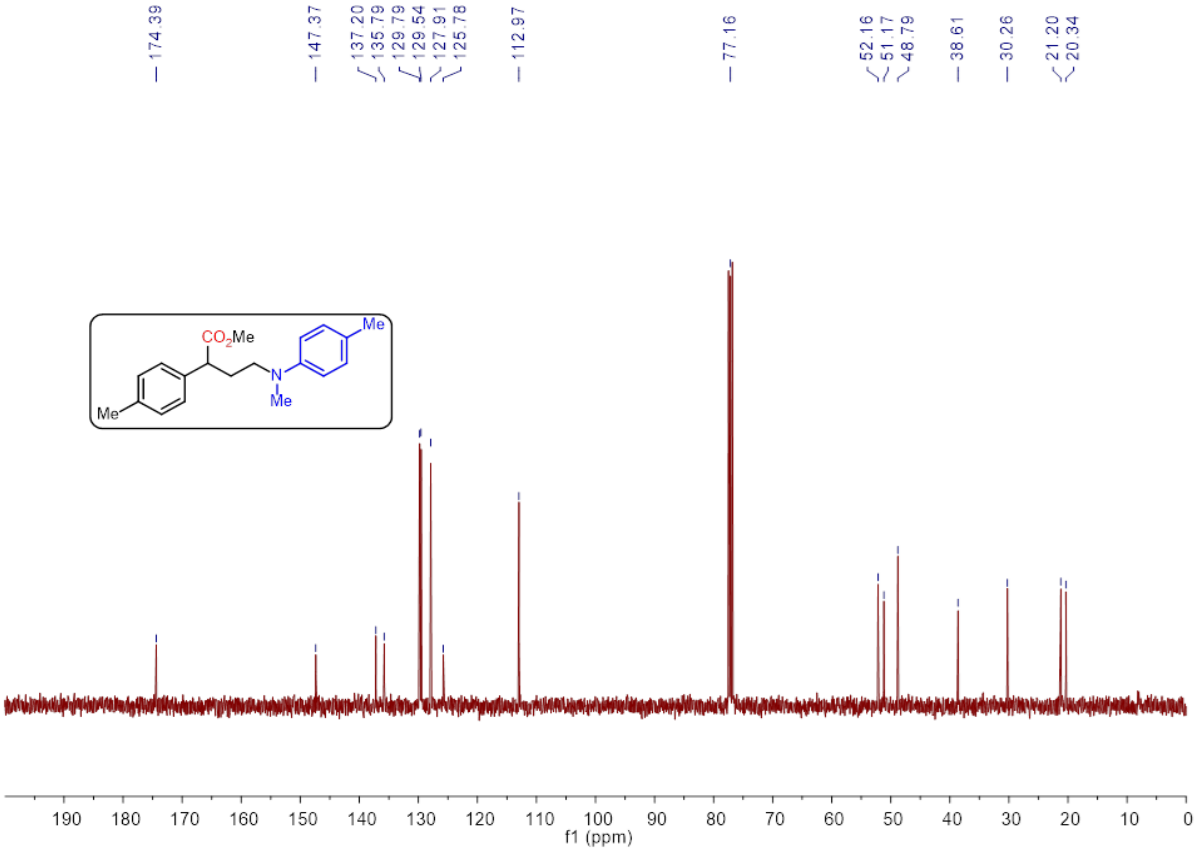
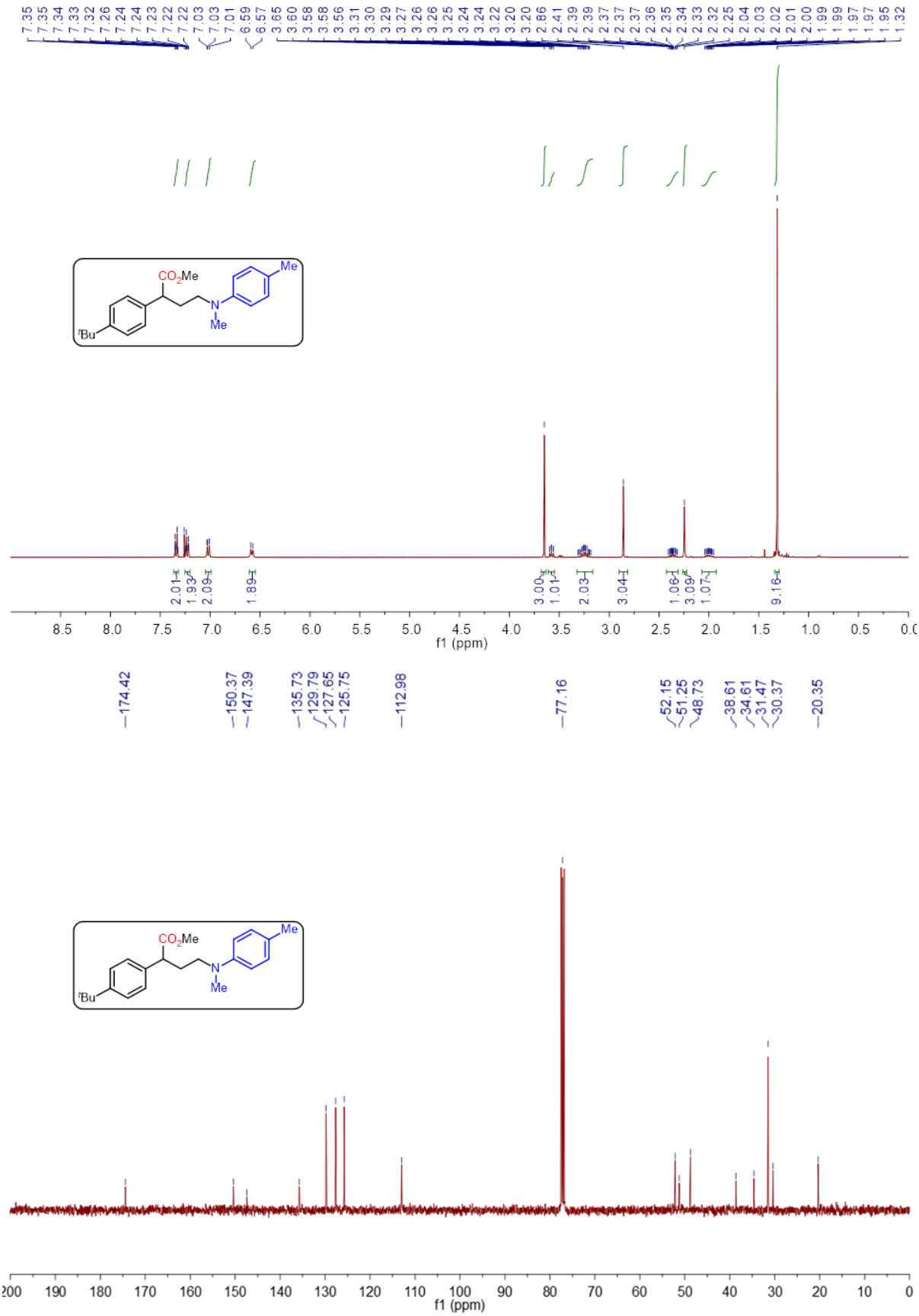
CO2Me
Me
N
Me
F
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

Methyl 4-(methyl(p-tolyl)amino)-2-(p-tolyl)butanoate (3ba)

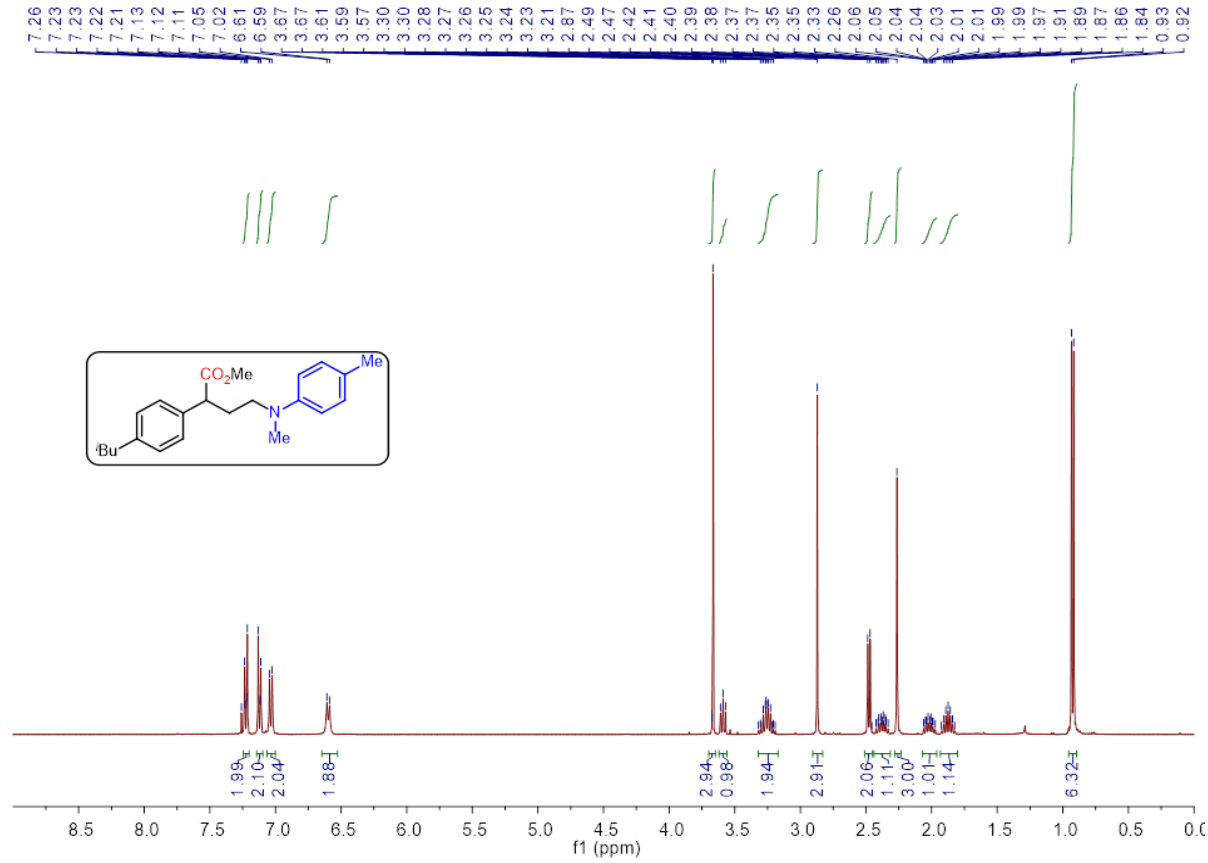


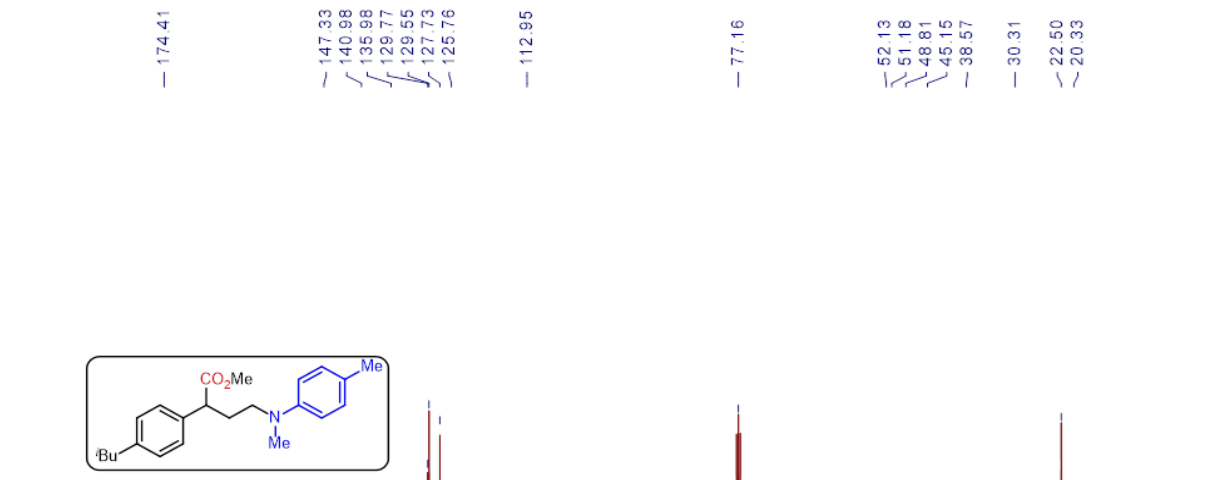


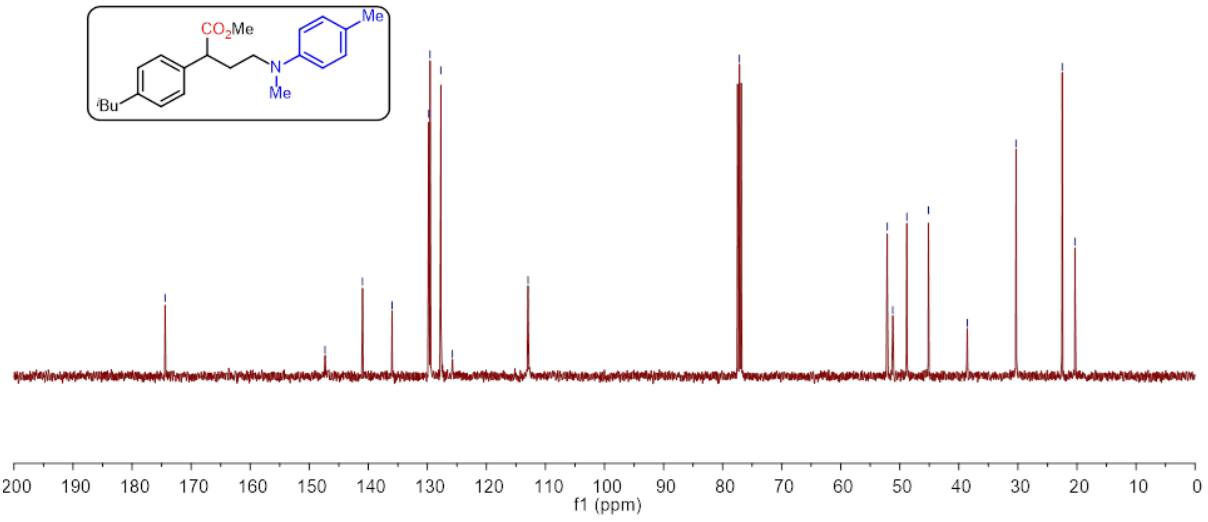
Methyl 2-(4-(tert-butyl)phenyl)-4-(methyl(p-tolyl)amino)butanoate (3ca)



Methyl 2-(4-isobutylphenyl)-4-(methyl(p-tolyl)amino)butanoate (3da)







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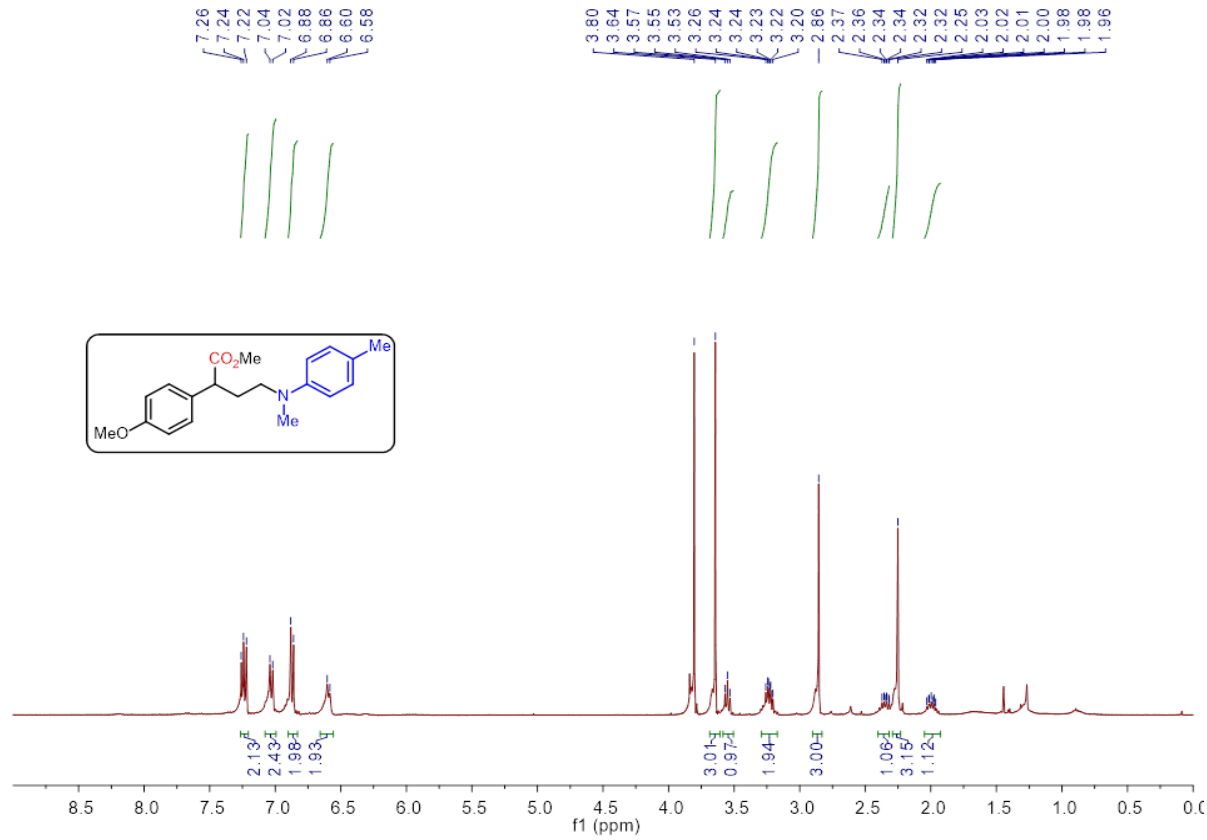
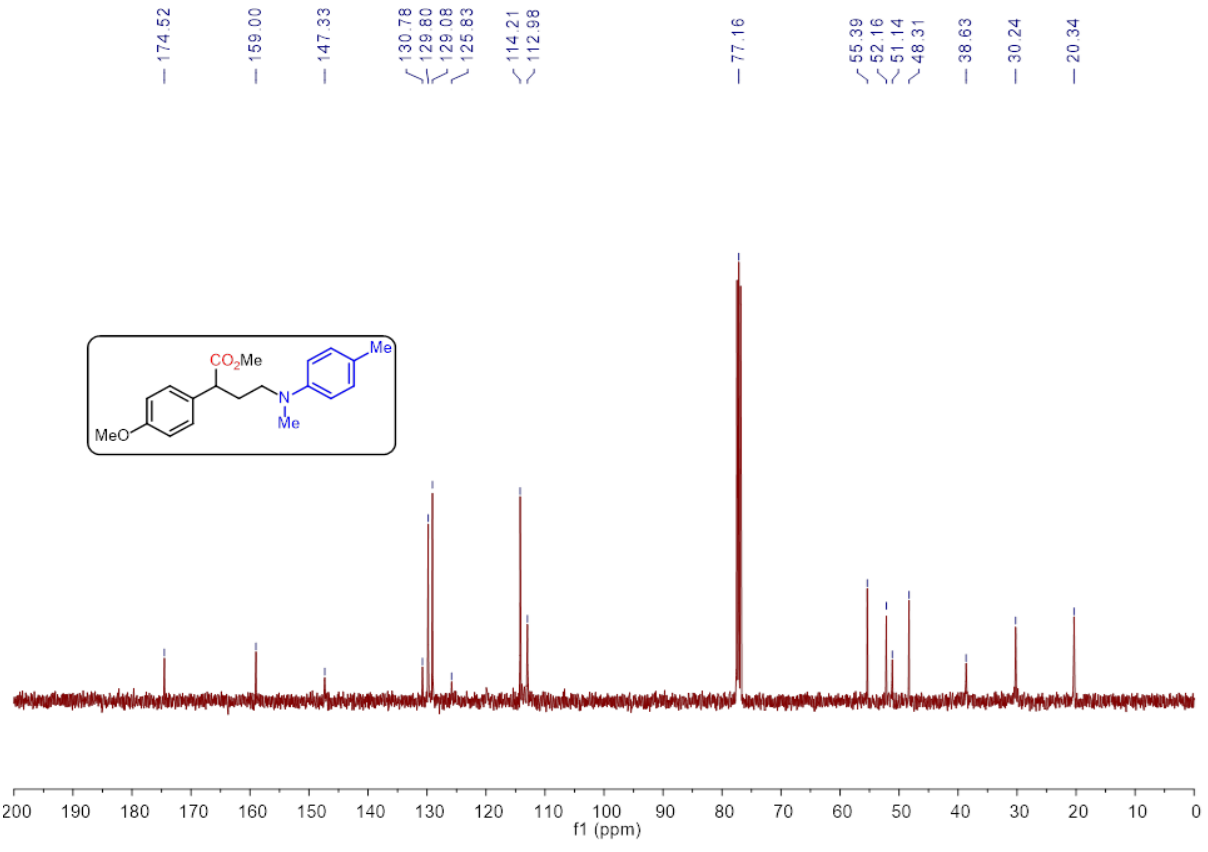
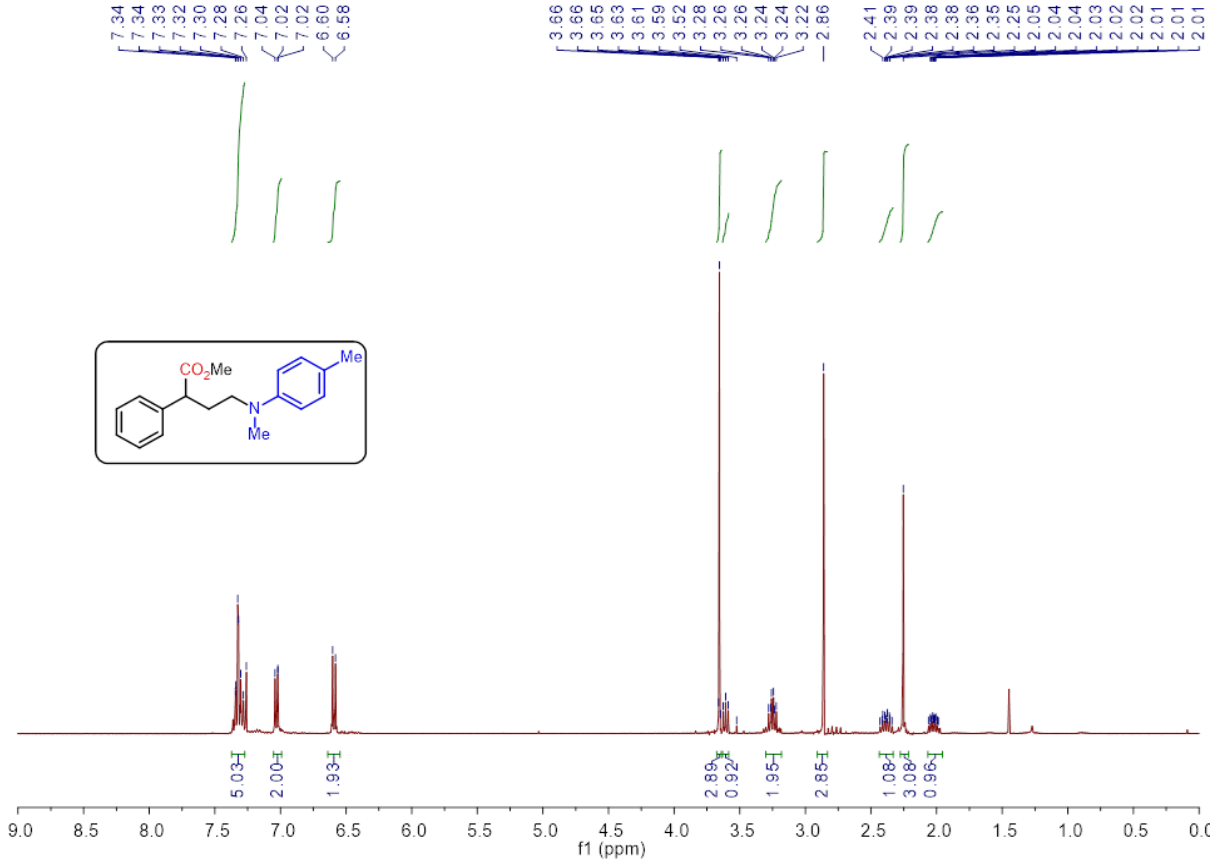
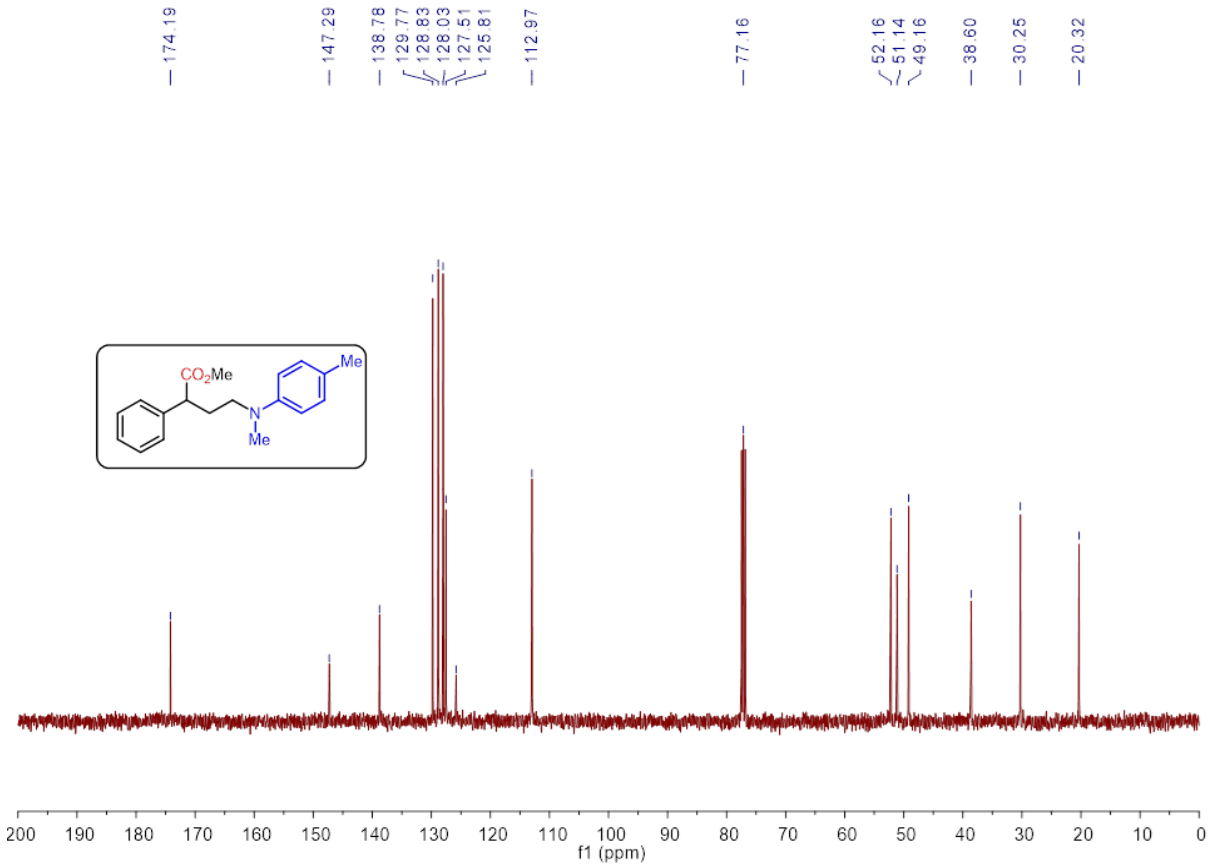


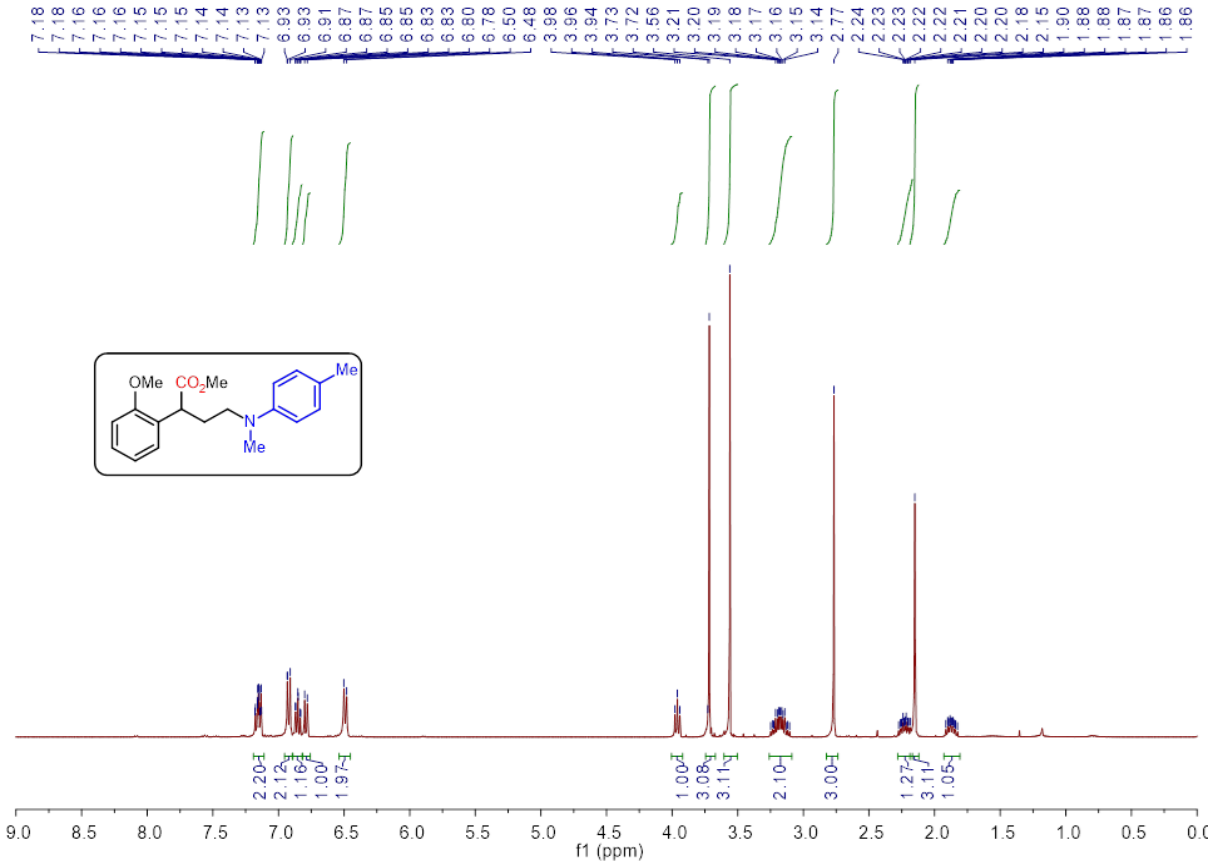


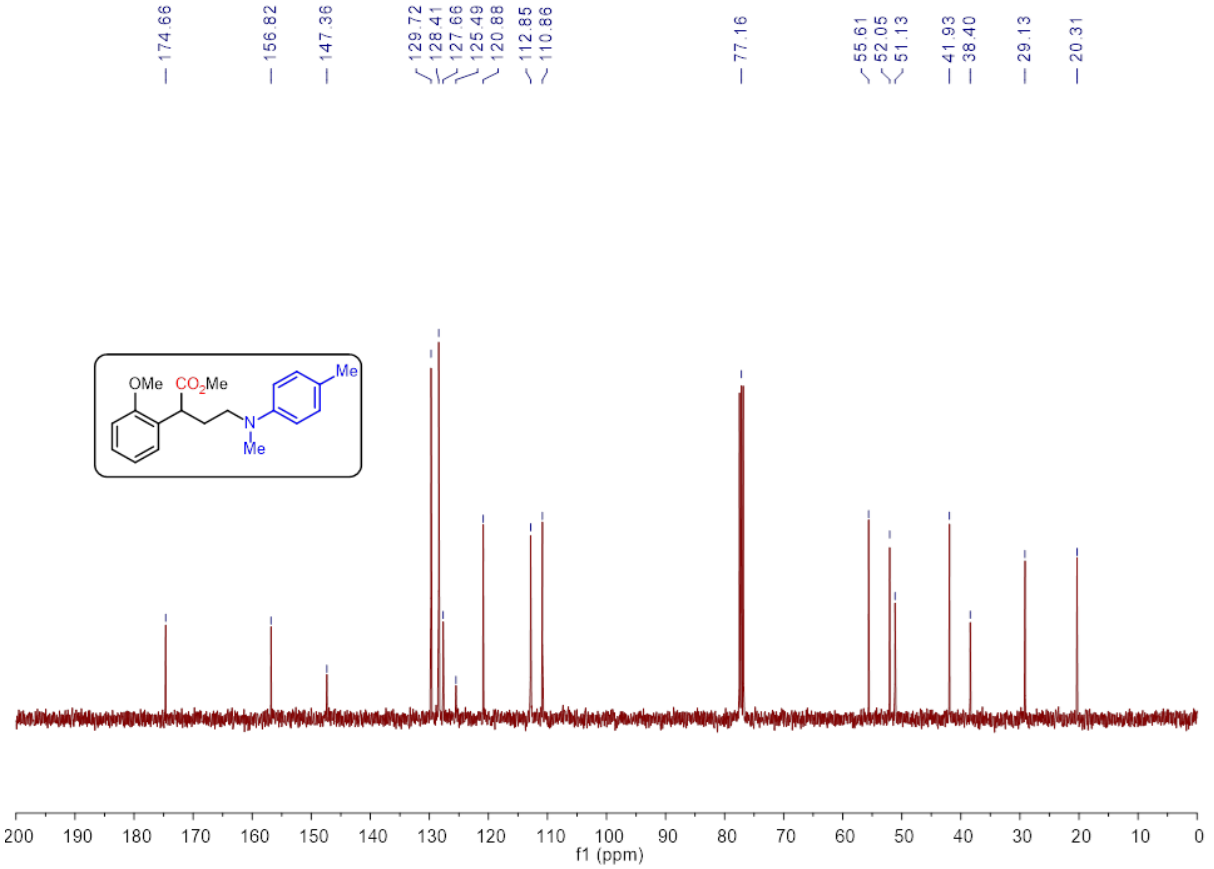
Methyl 4-(methyl(p-tolyl)amino)-2-phenylbutanoate (3fa)





Methyl 2-(2-methoxyphenyl)-4-(methyl(p-tolyl)amino)butanoate (3ga)





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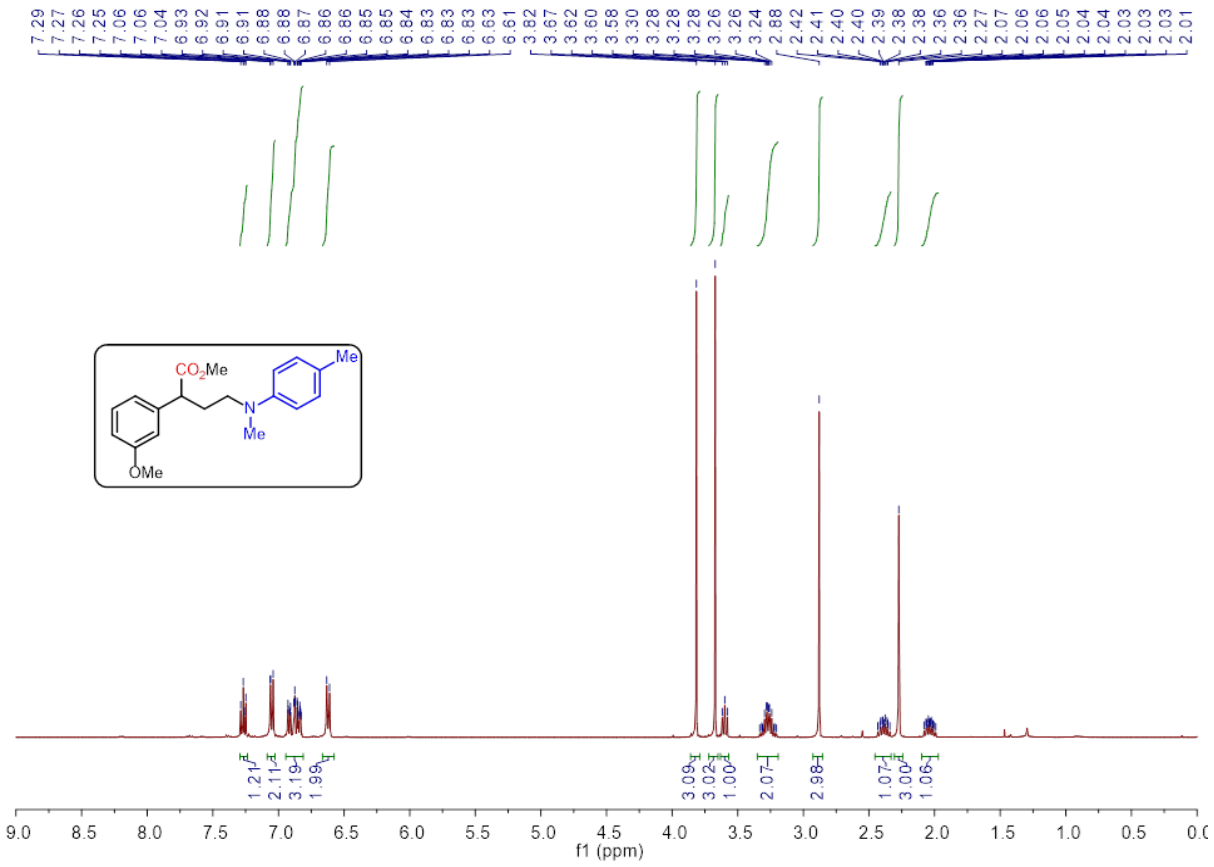

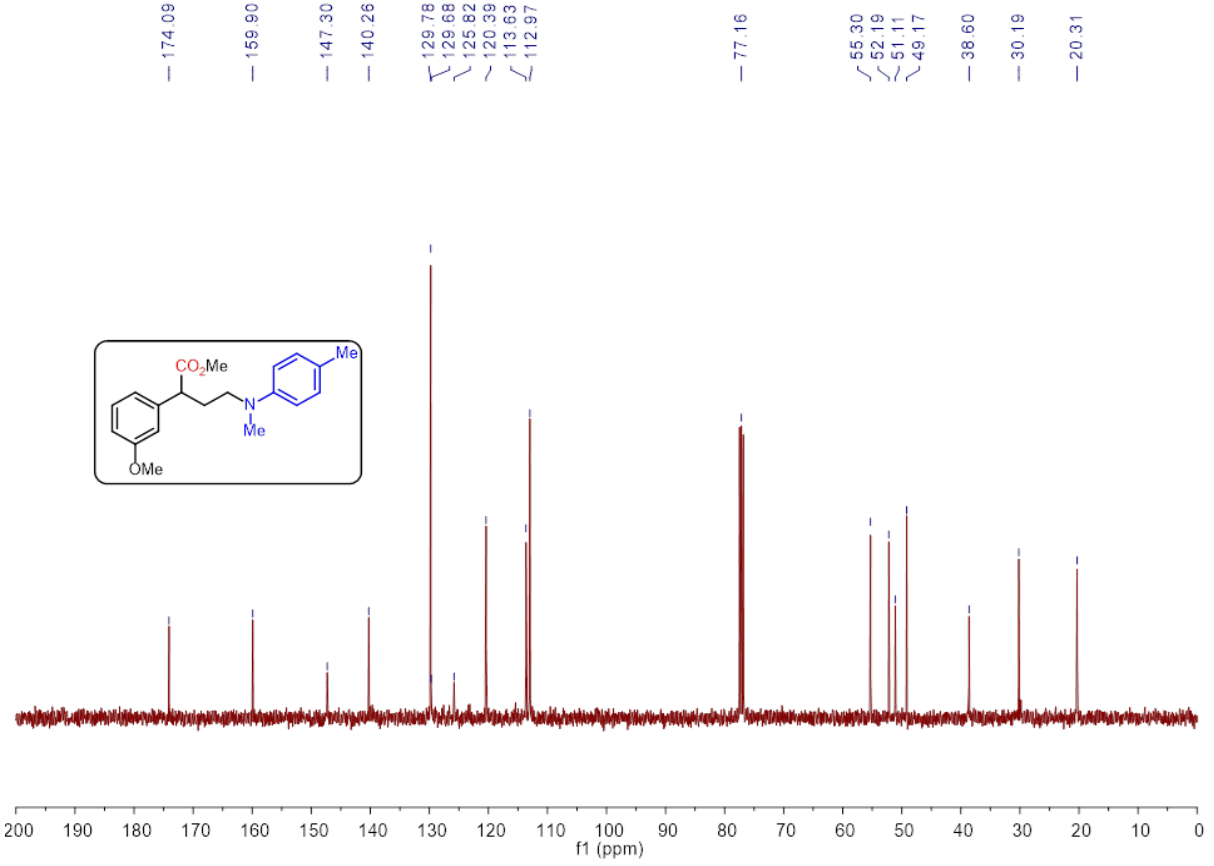

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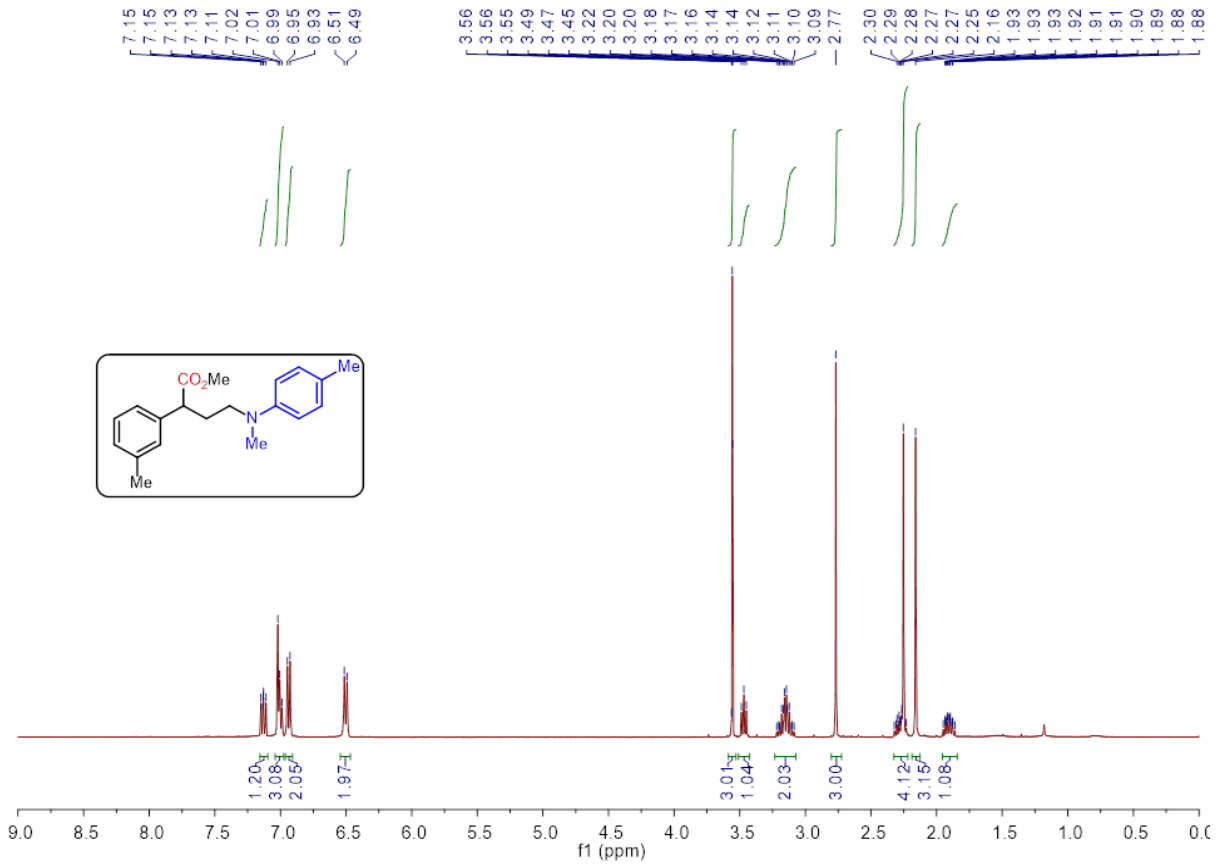
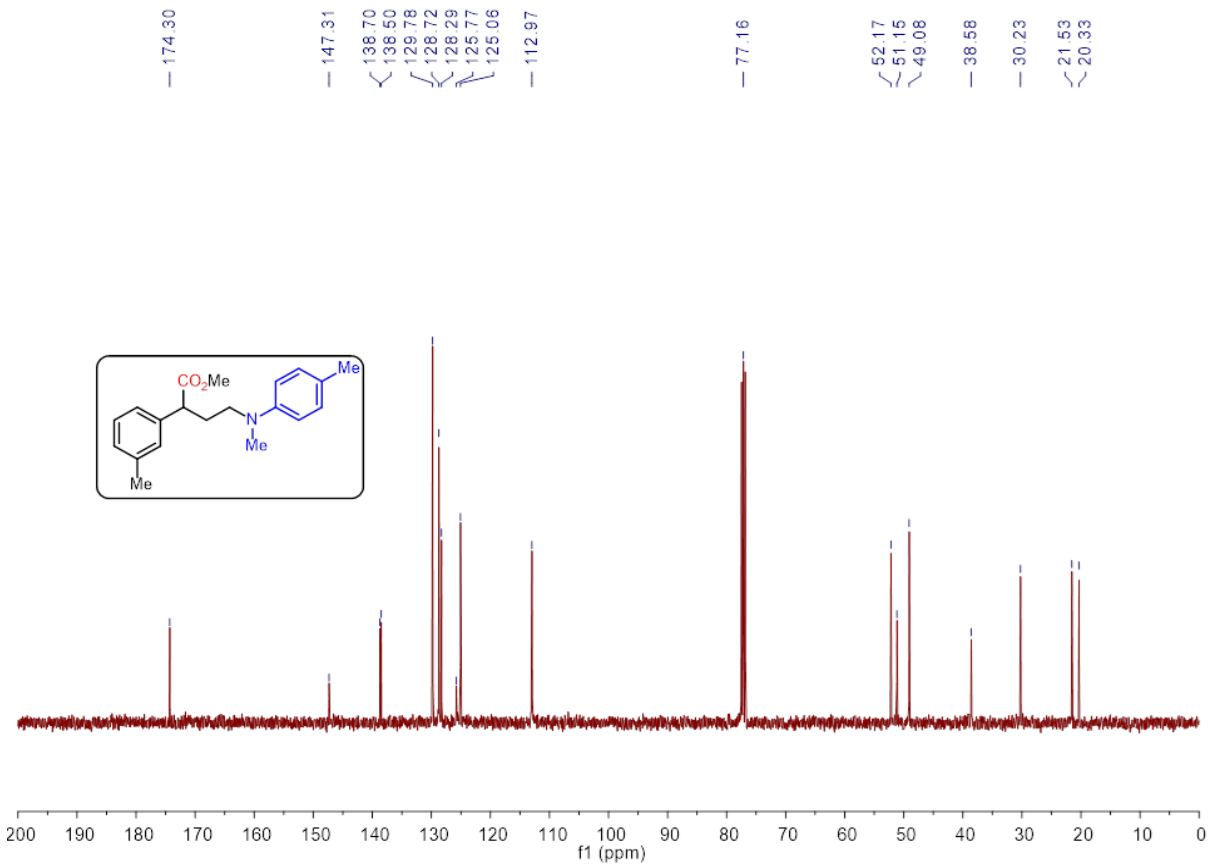
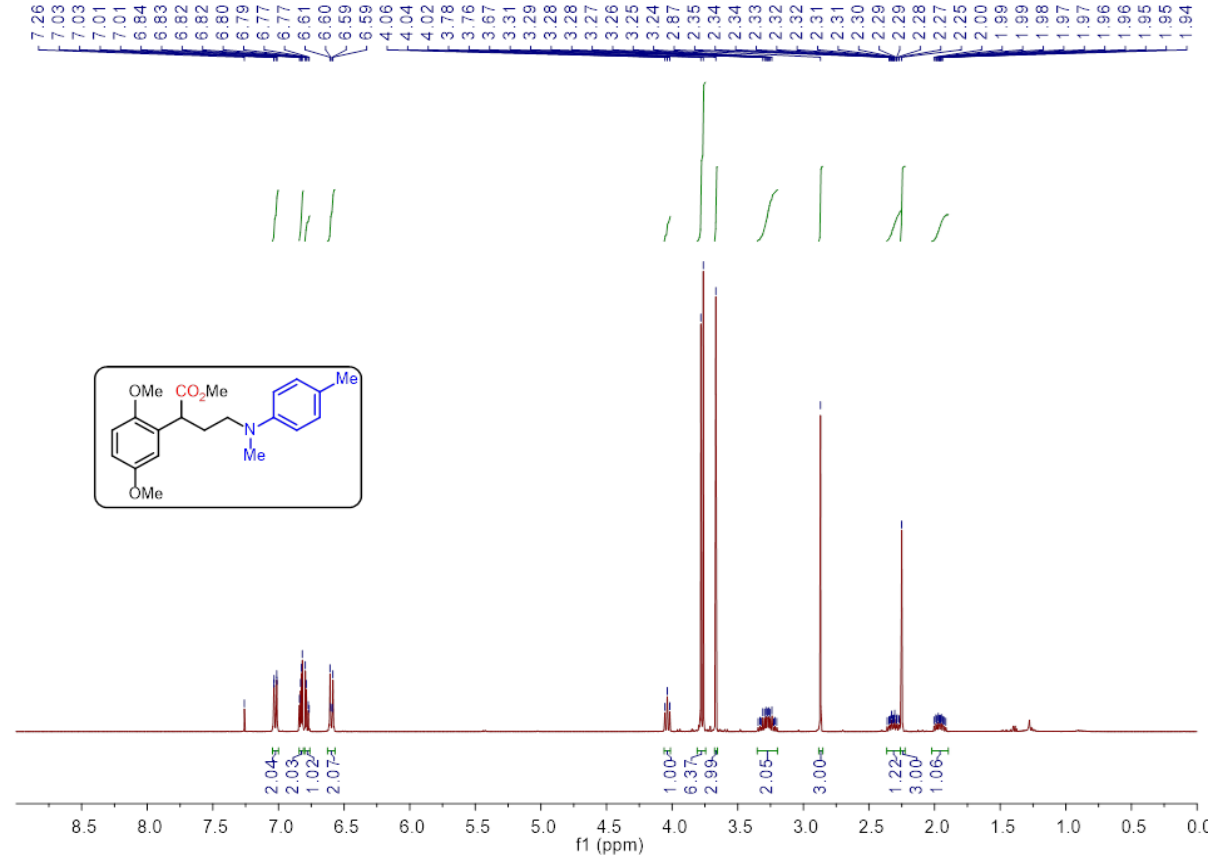
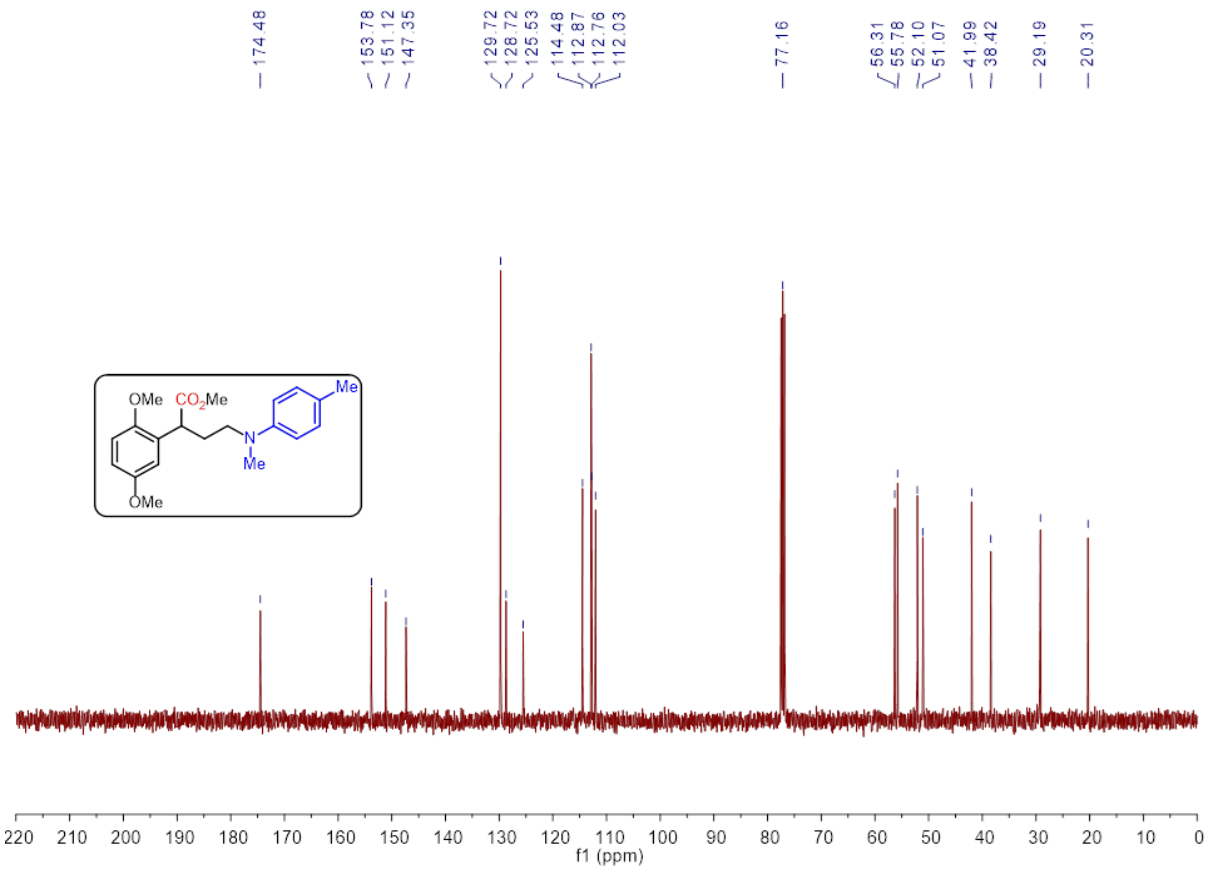


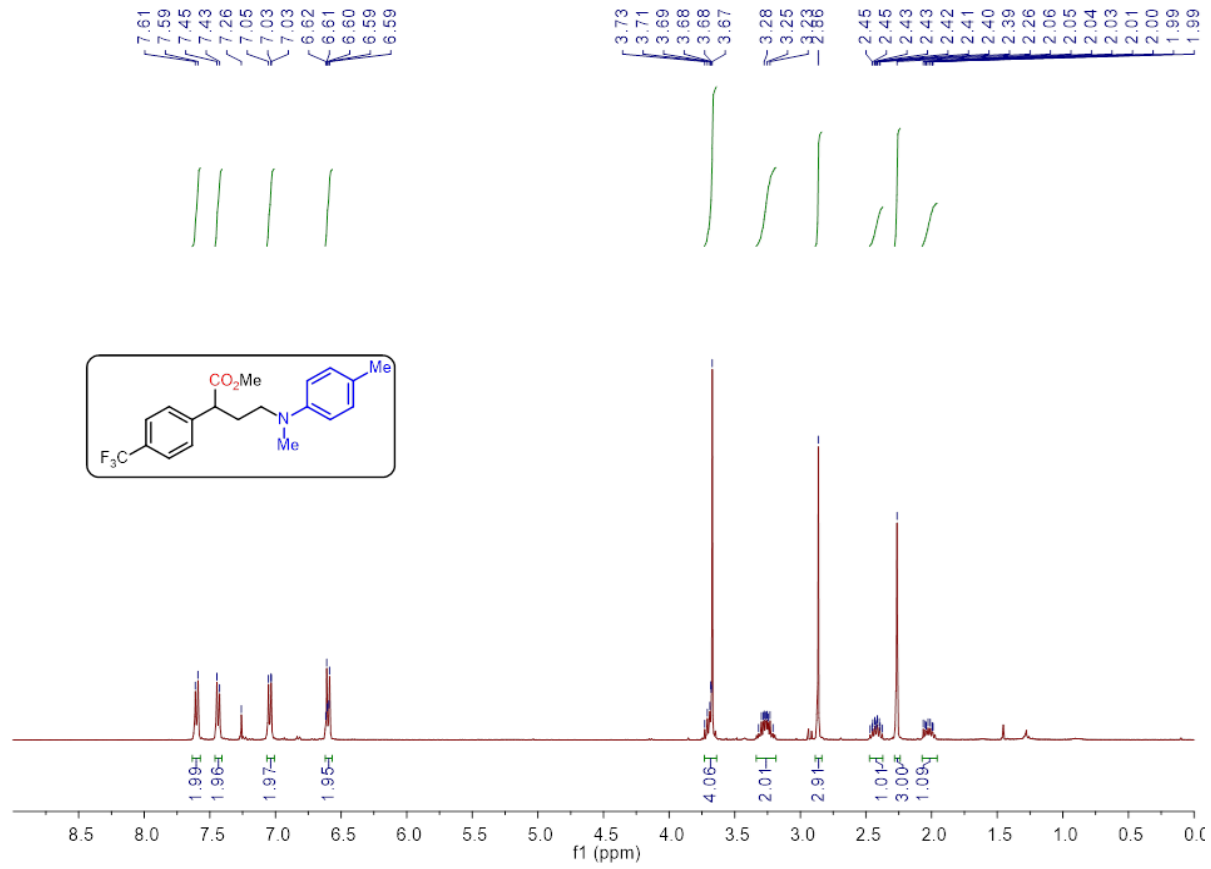


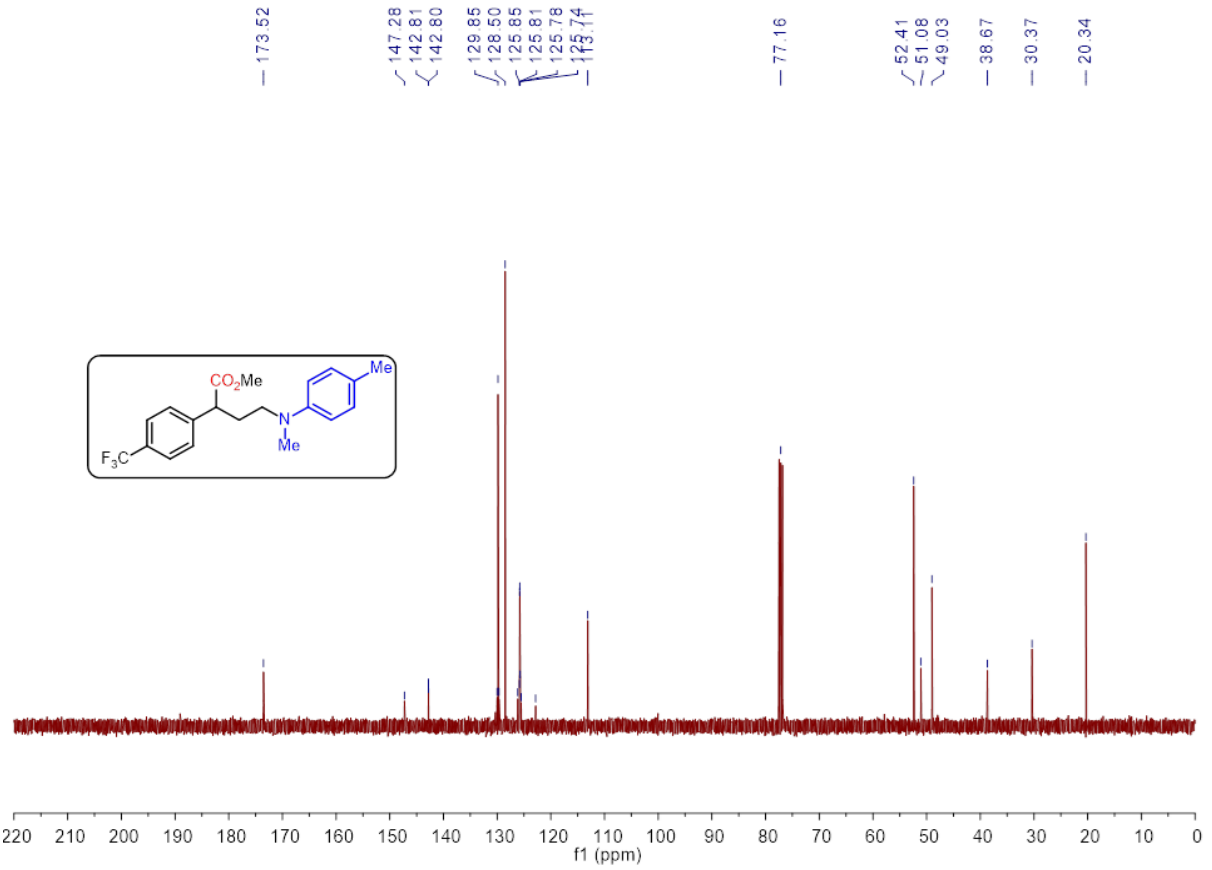
Methyl 2-(2,5-dimethoxyphenyl)-4-(methyl(p-tolyl)amino)butanoate (3ja)

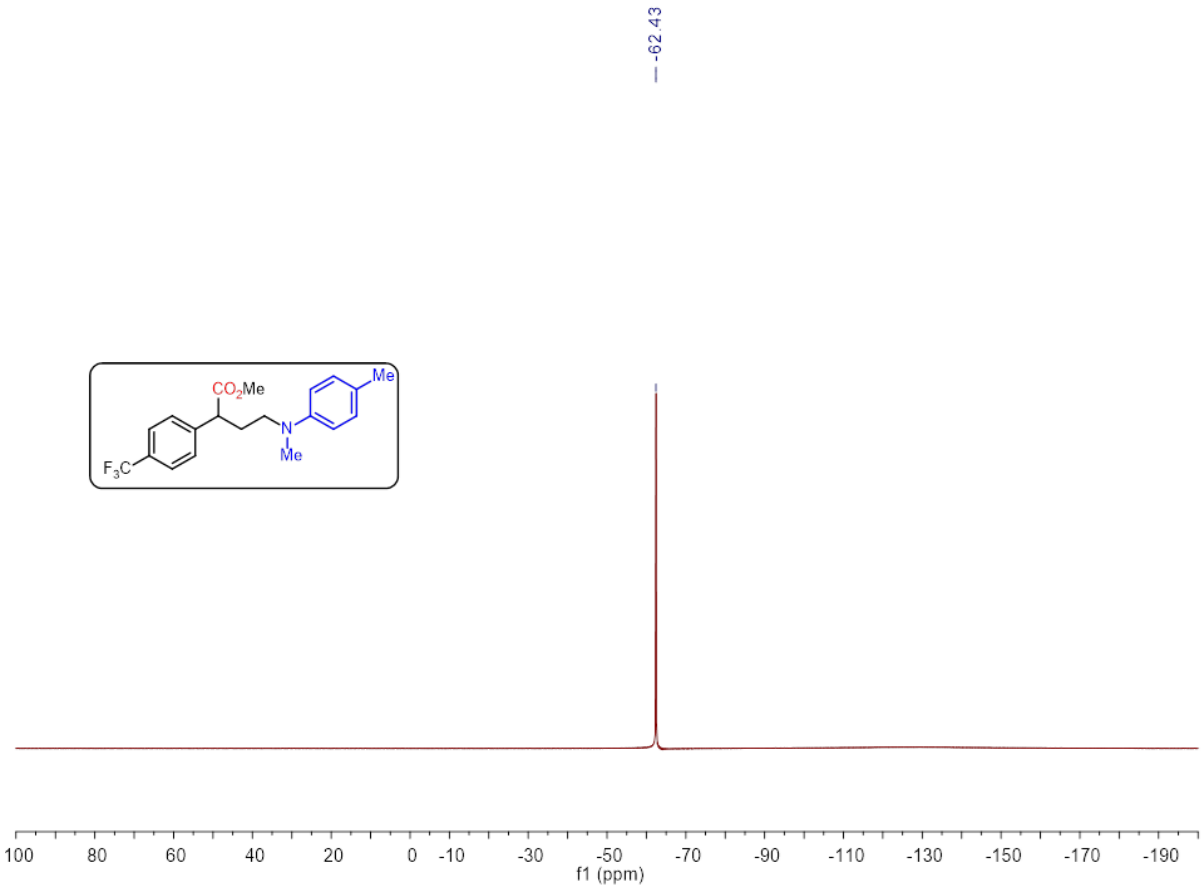




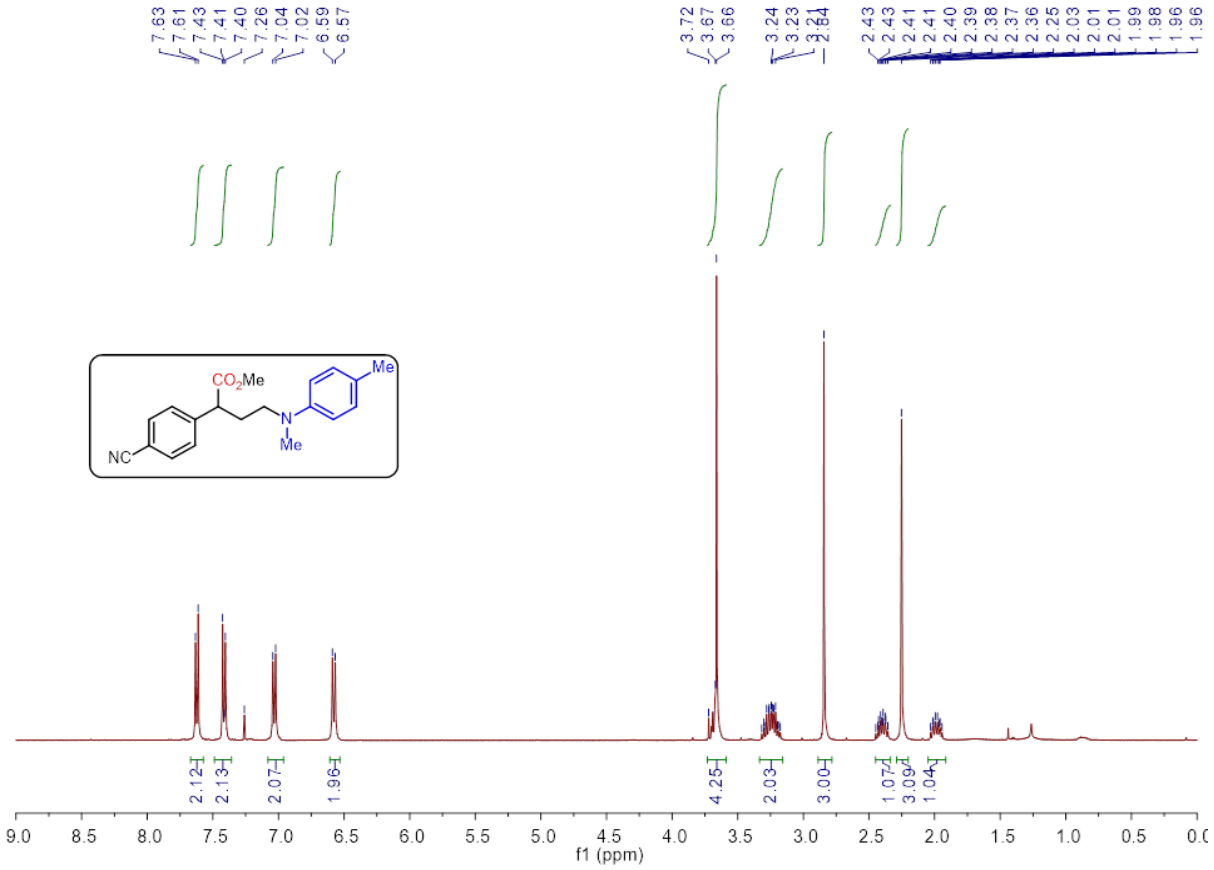
Methyl 4-(methyl(p-tolyl)amino)-2-(4-(trifluoromethyl)phenyl)butanoate (3ka)

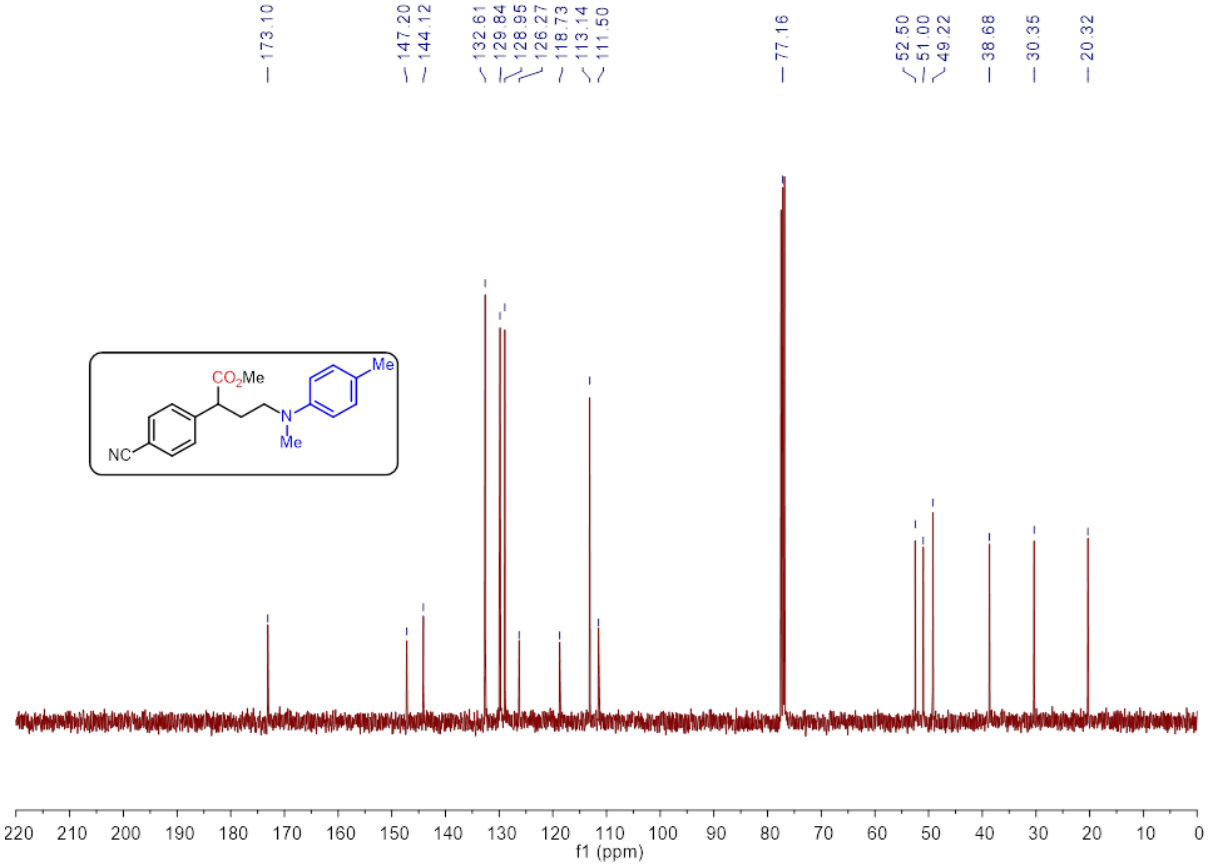




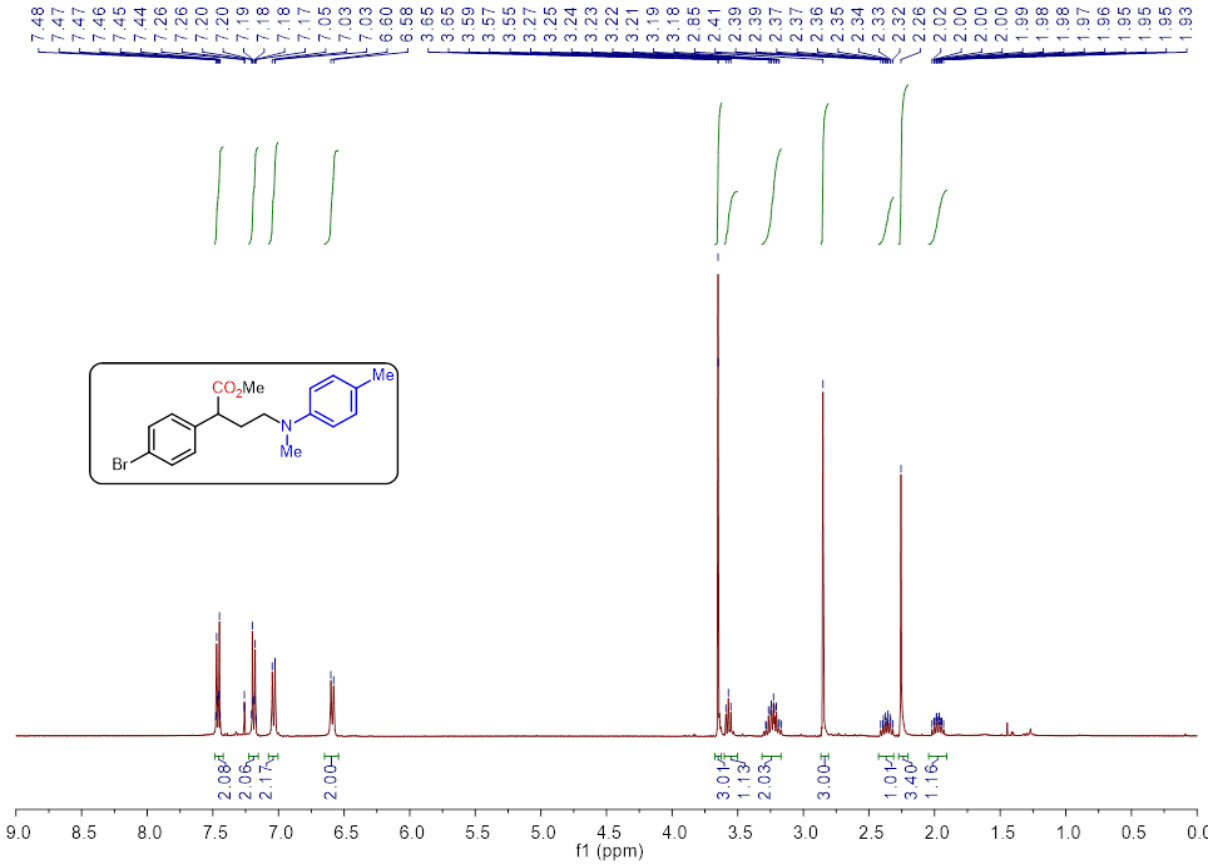

-62.43
CO2Me
Me
N
Me
F3C
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

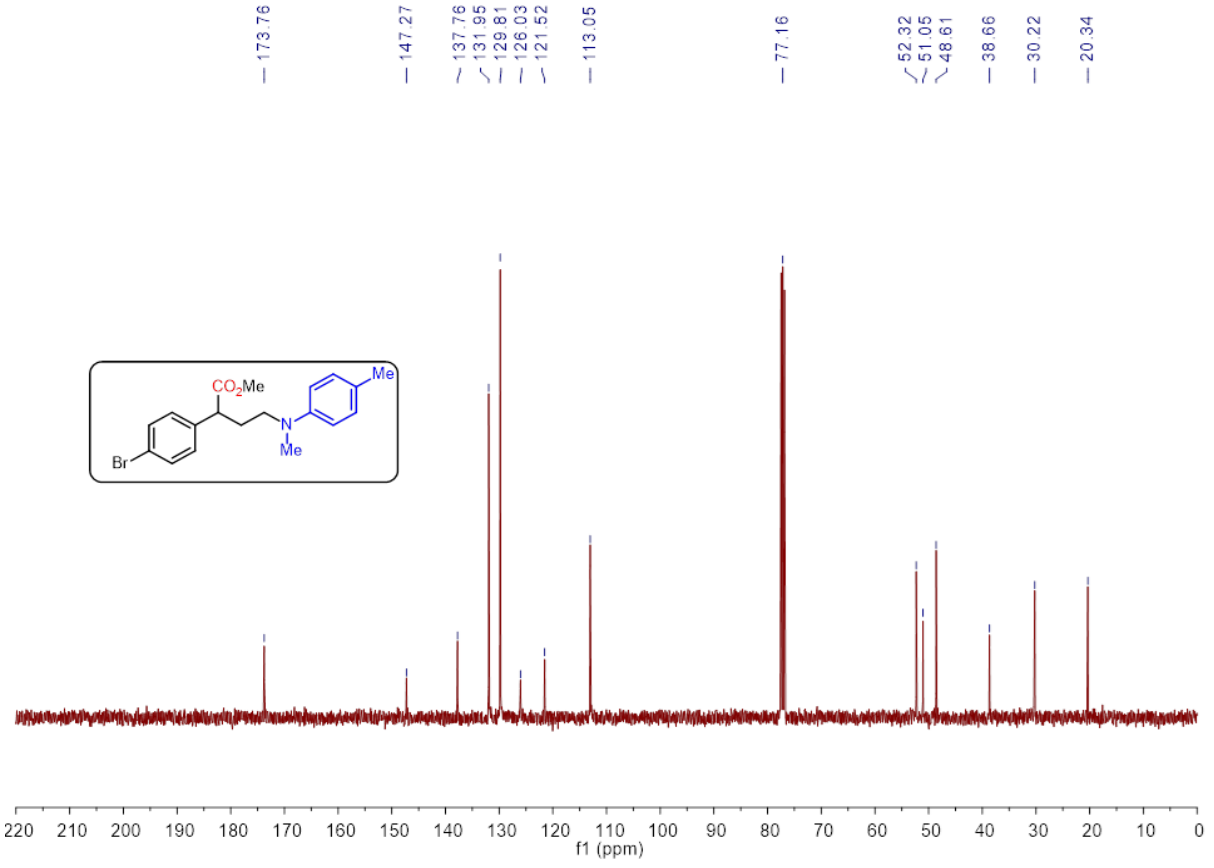
Methyl 2-(4-cyanophenyl)-4-(methyl(p-tolyl)amino)butanoate (3la)



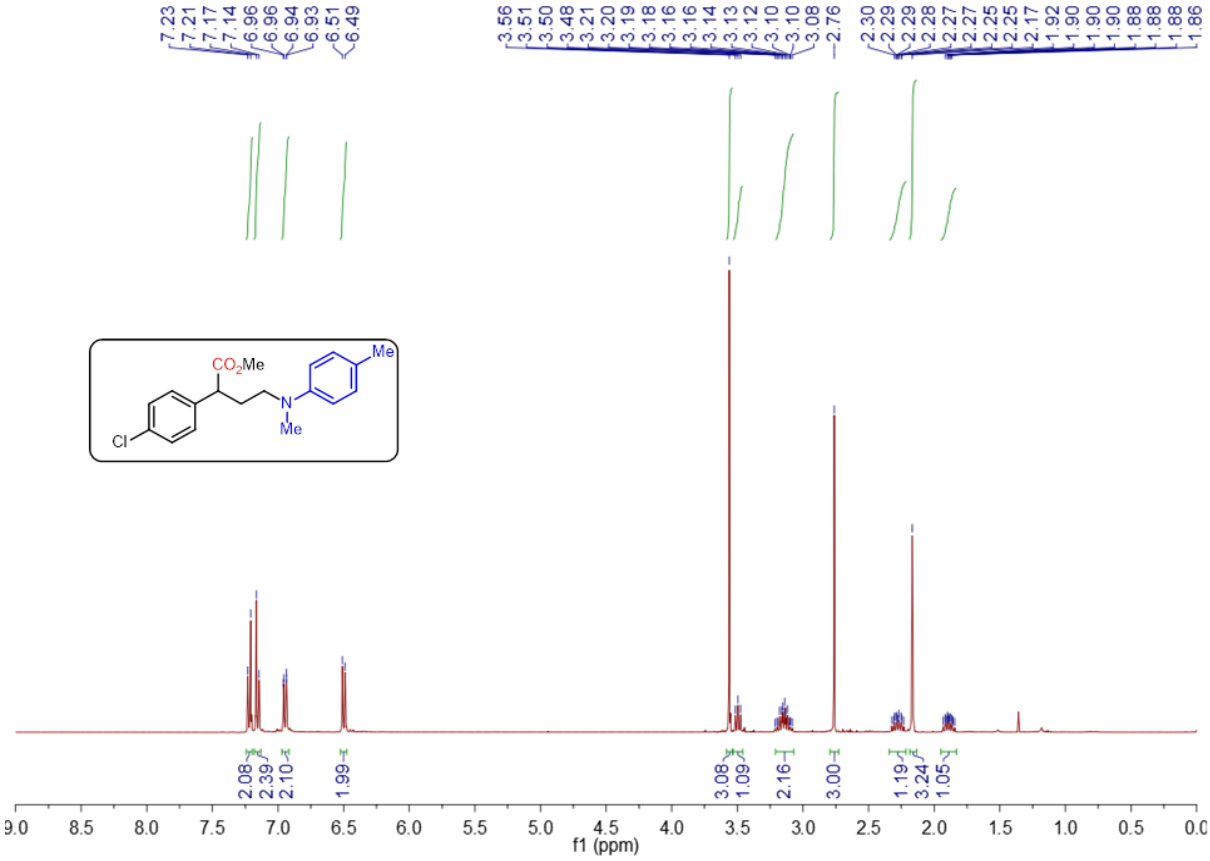


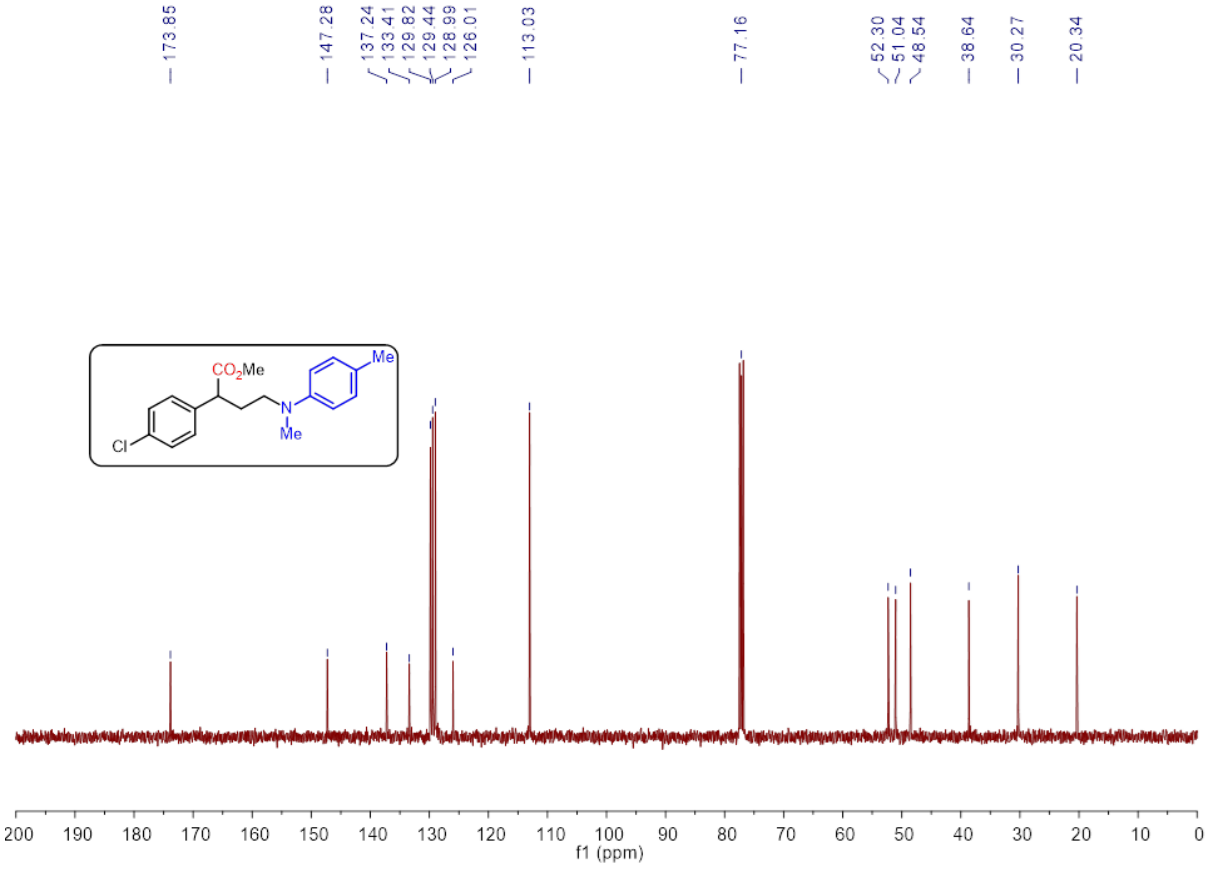
Methyl 2-(4-bromophenyl)-4-(methyl(p-tolyl)amino)butanoate (3ma)



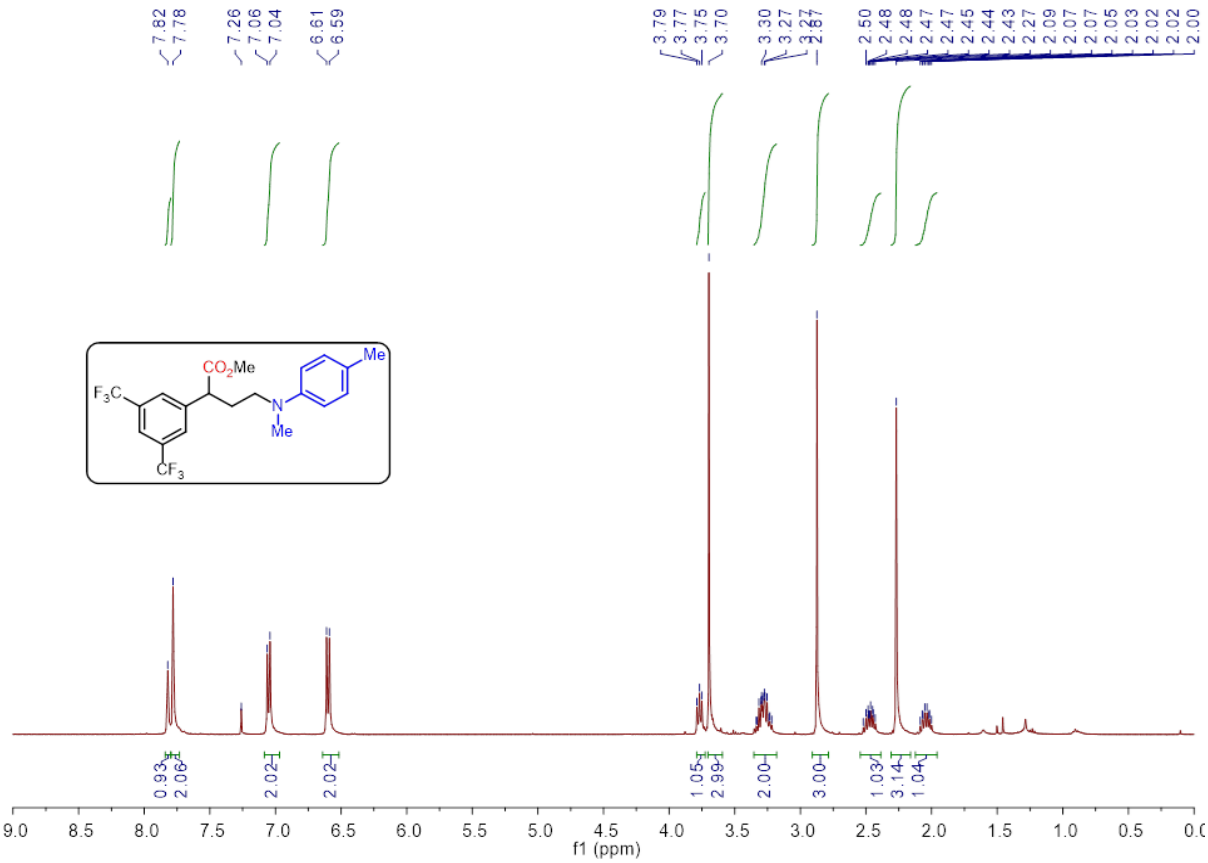


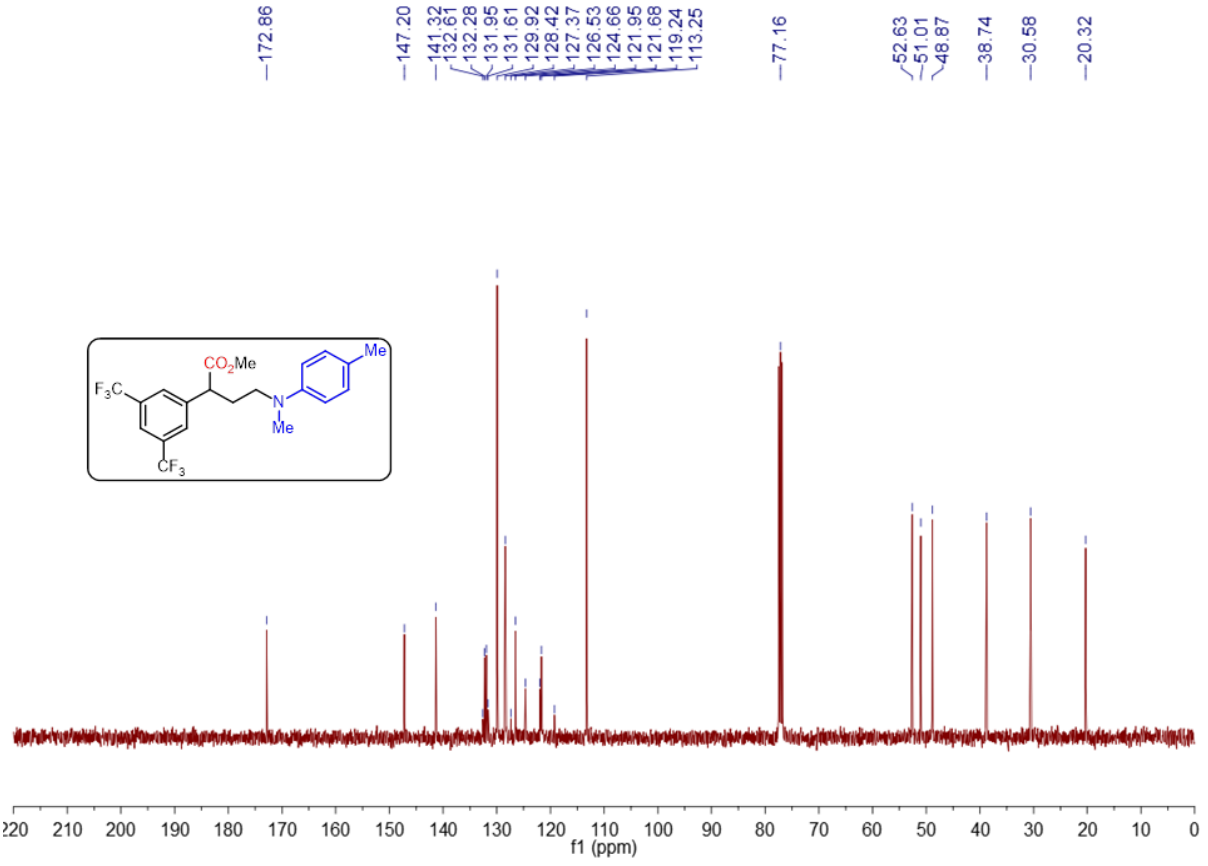
Methyl 2-(4-chlorophenyl)-4-(methyl(p-tolyl)amino)butanoate (3na)

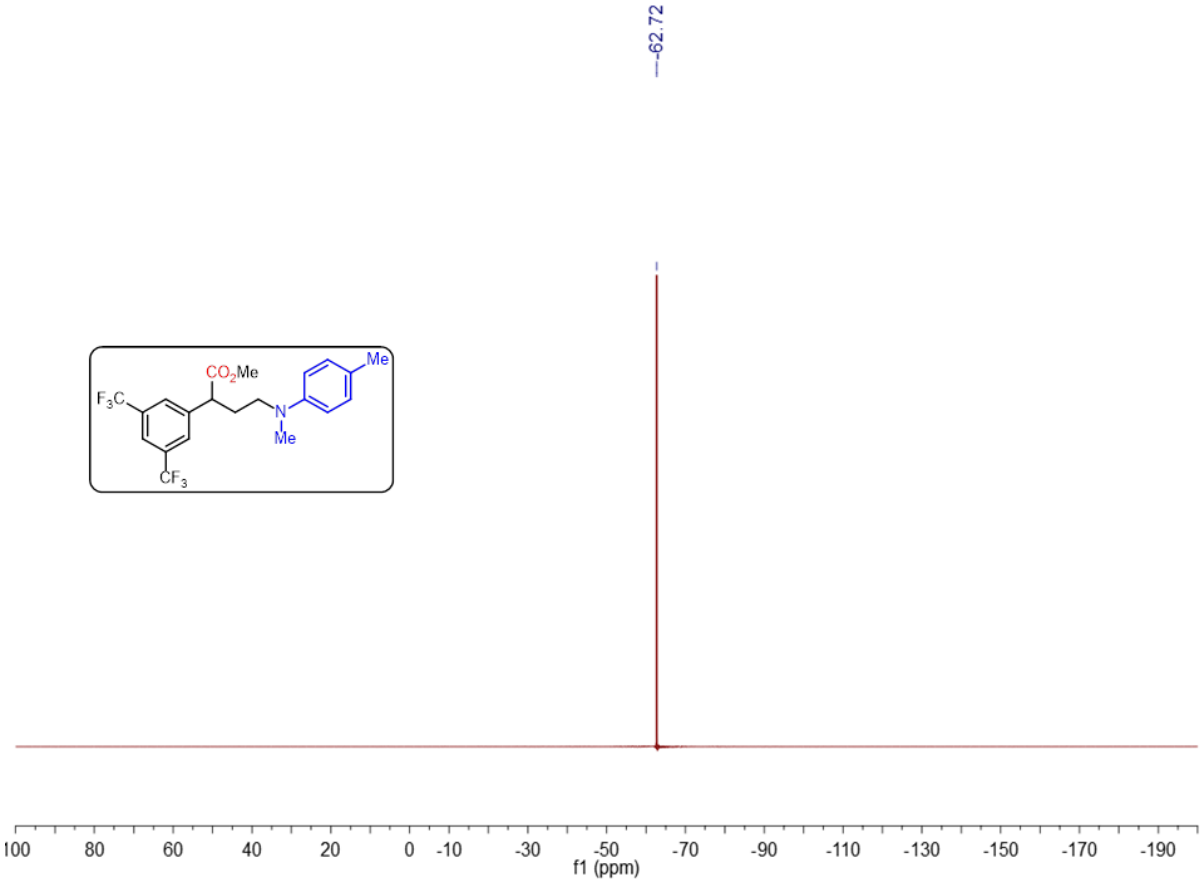




Methyl 2-(3,5-bis(trifluoromethyl)phenyl)-4-(methyl(p-tolyl)amino)butanoate (3oa)



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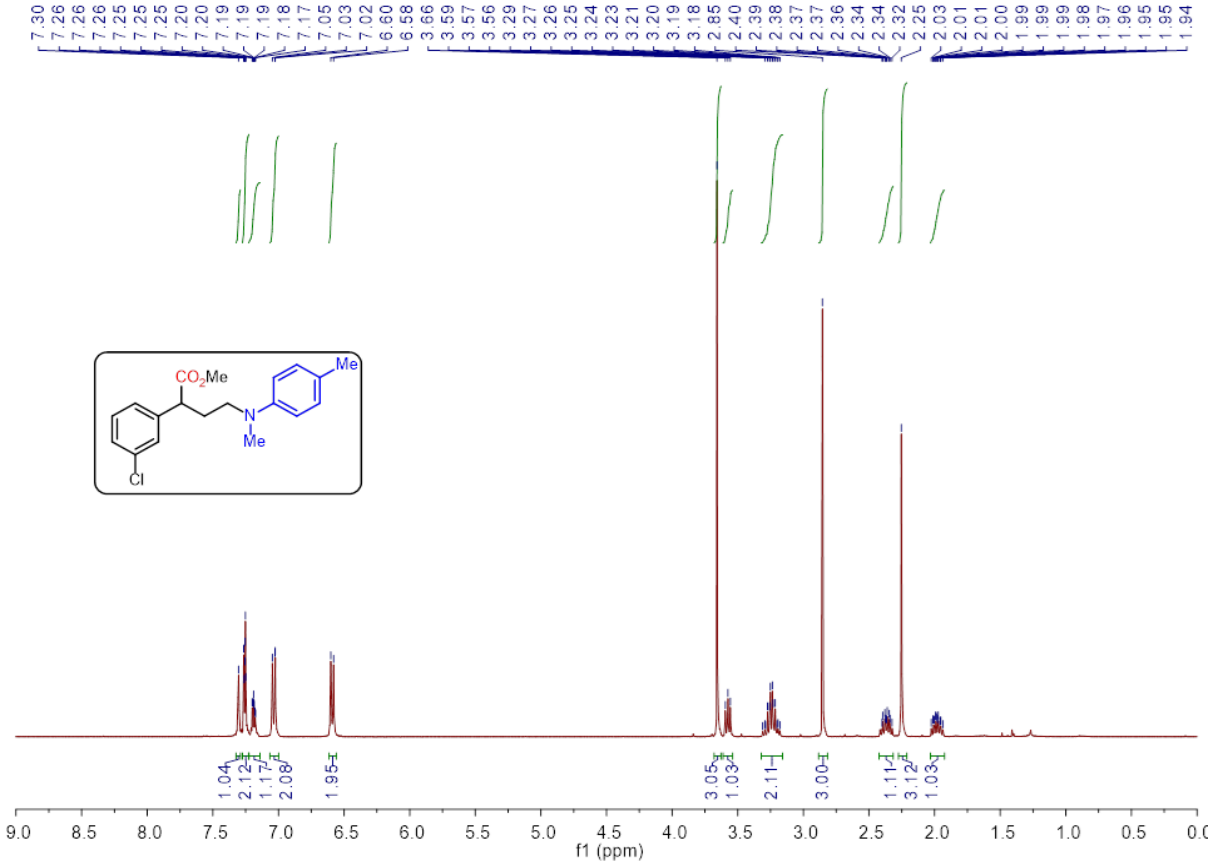
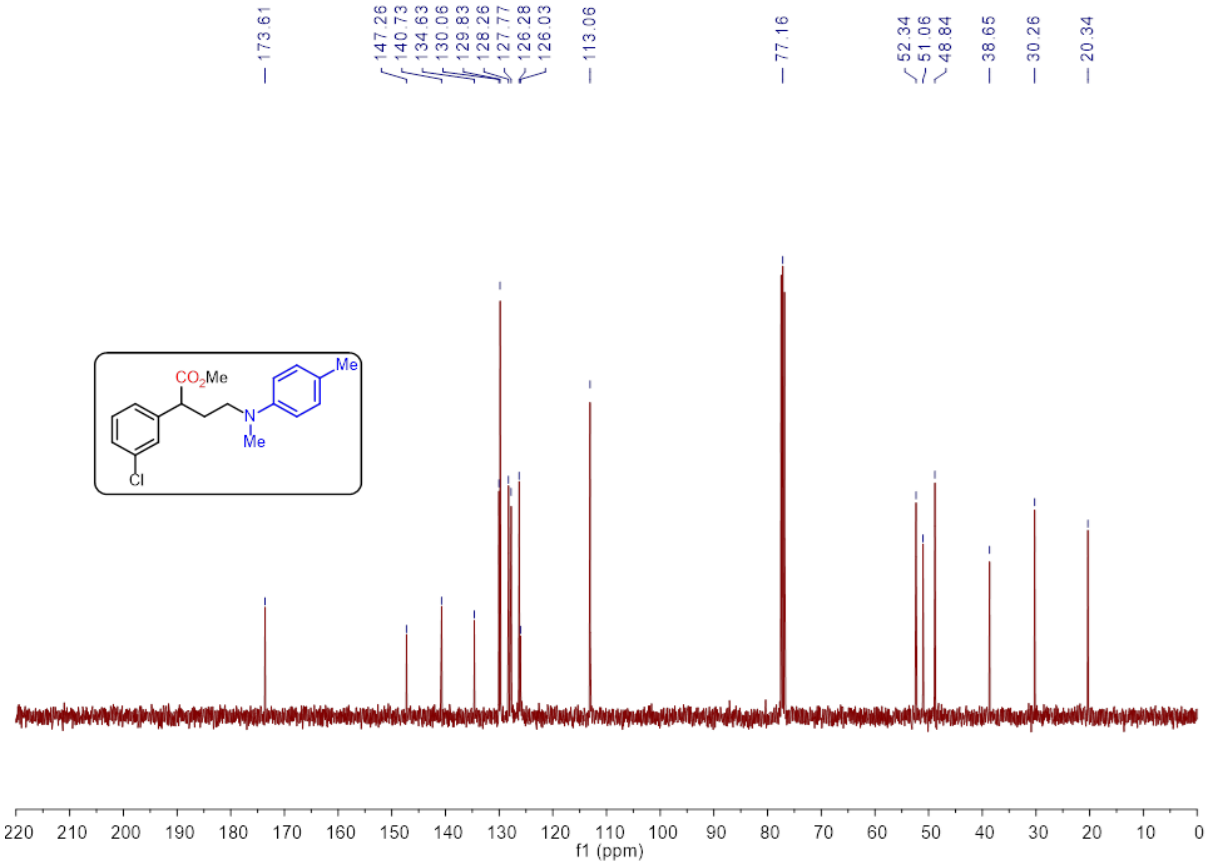
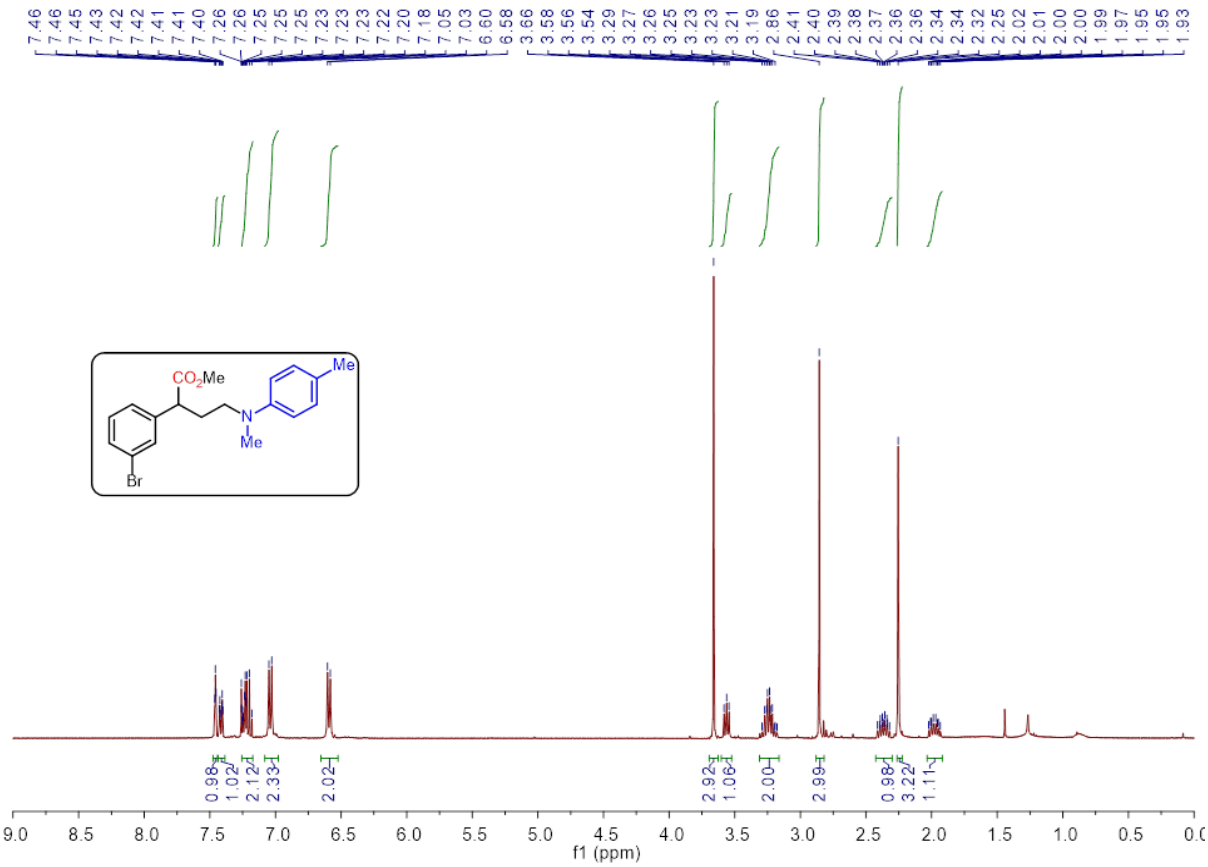
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

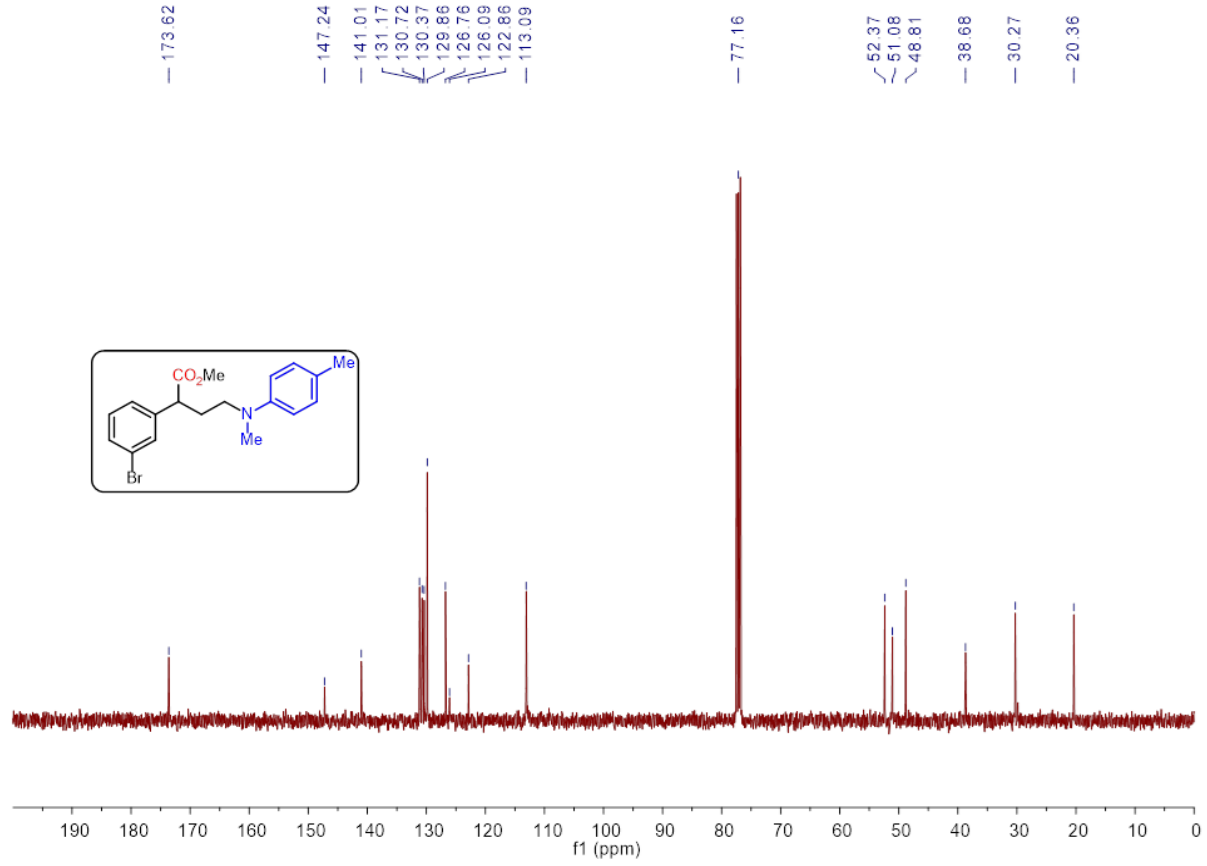
Methyl 2-(3-chlorophenyl)-4-(methyl(p-tolyl)amino)butanoate (3pa)



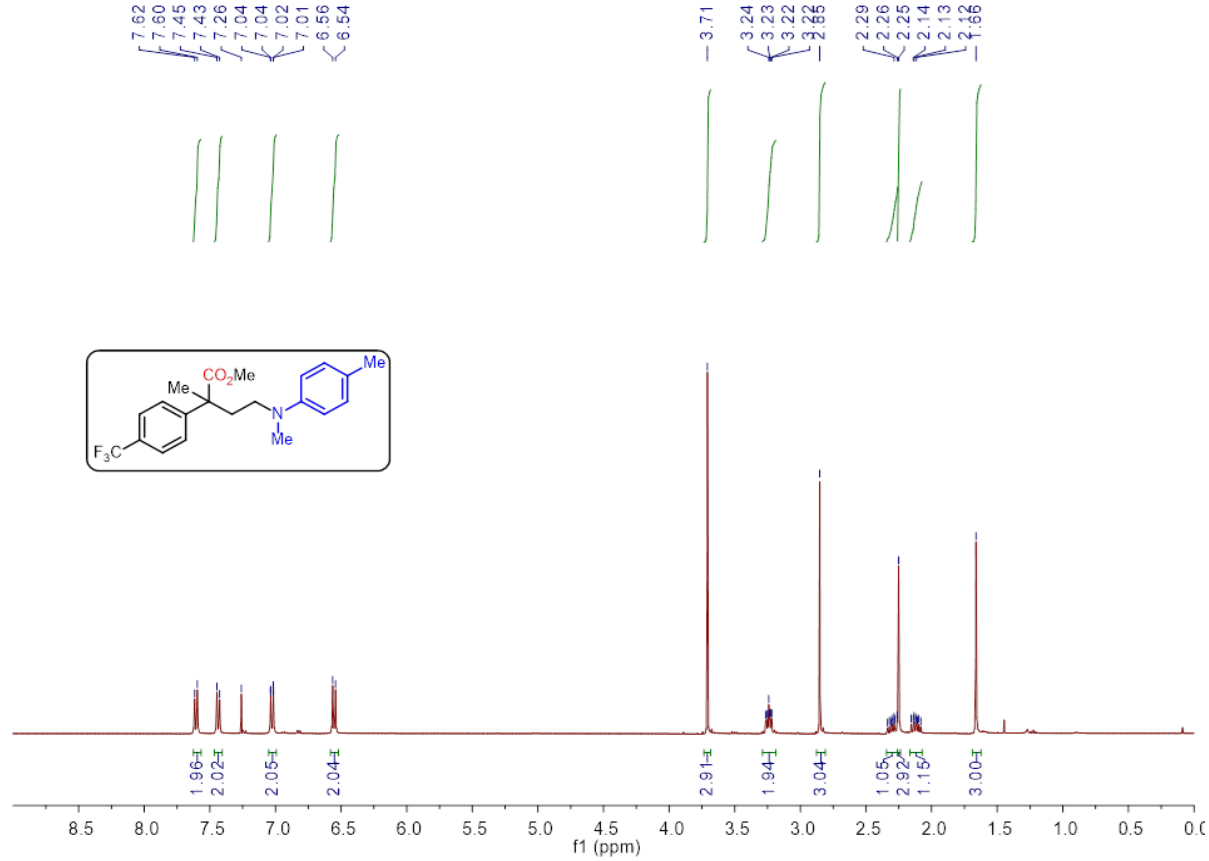


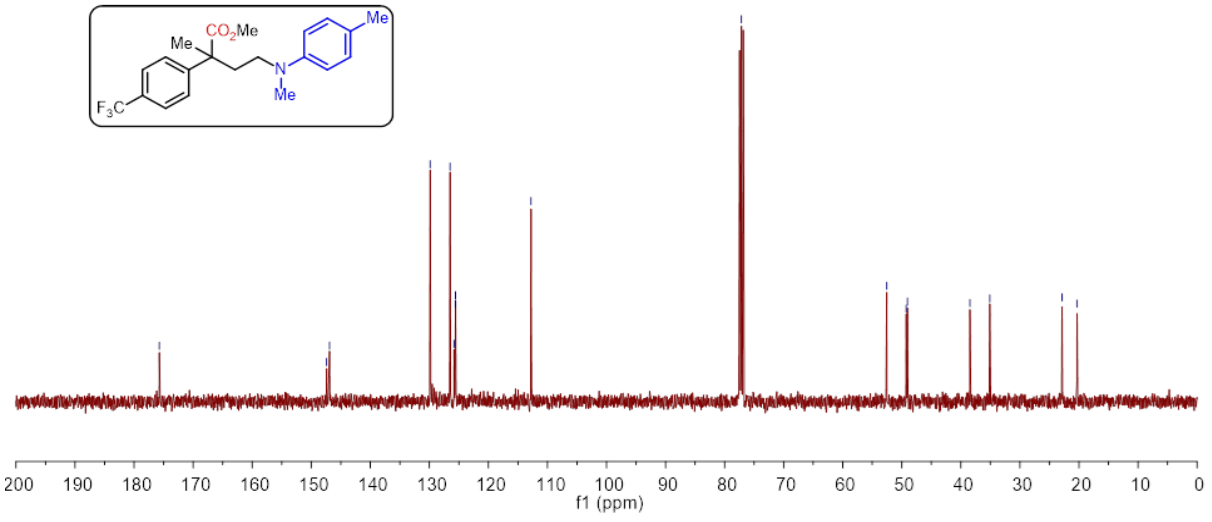
Methyl 2-(3-bromophenyl)-4-(methyl(p-tolyl)amino)butanoate (3qa)

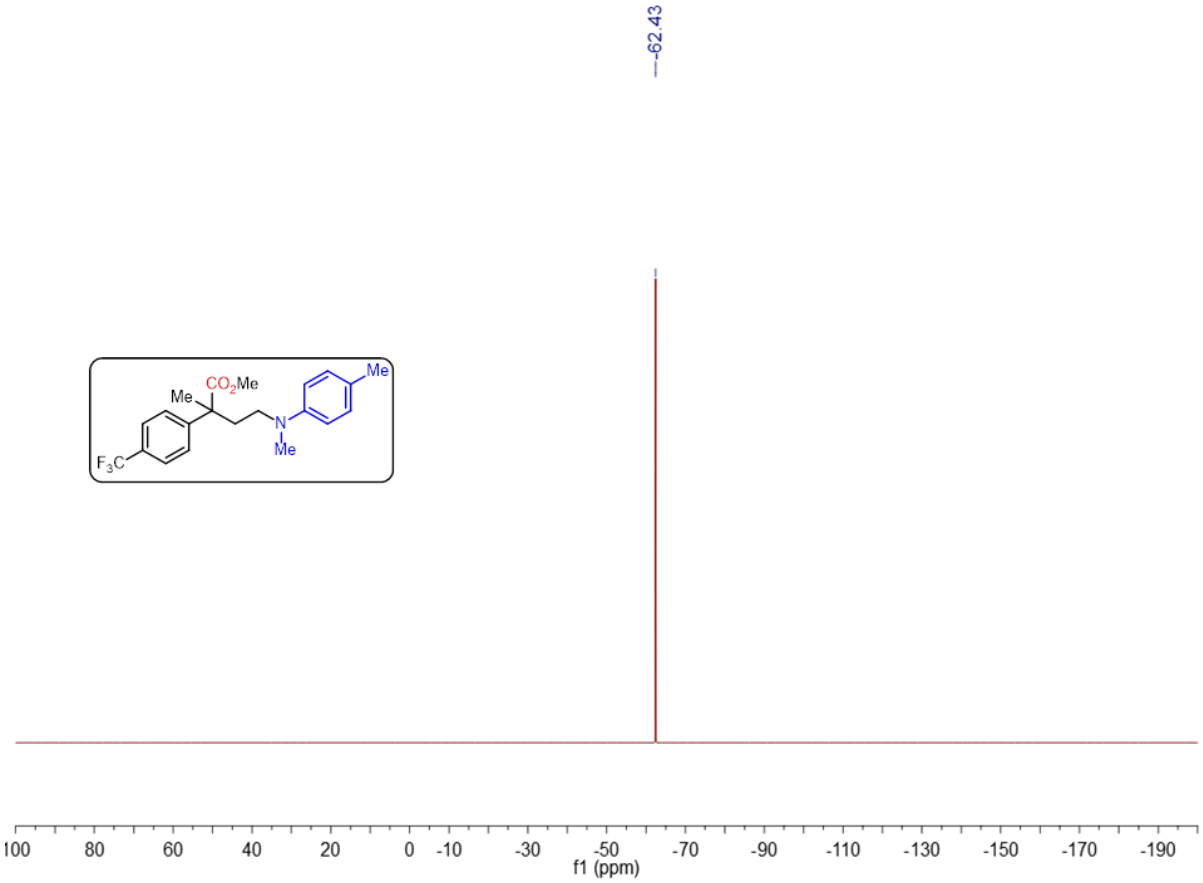




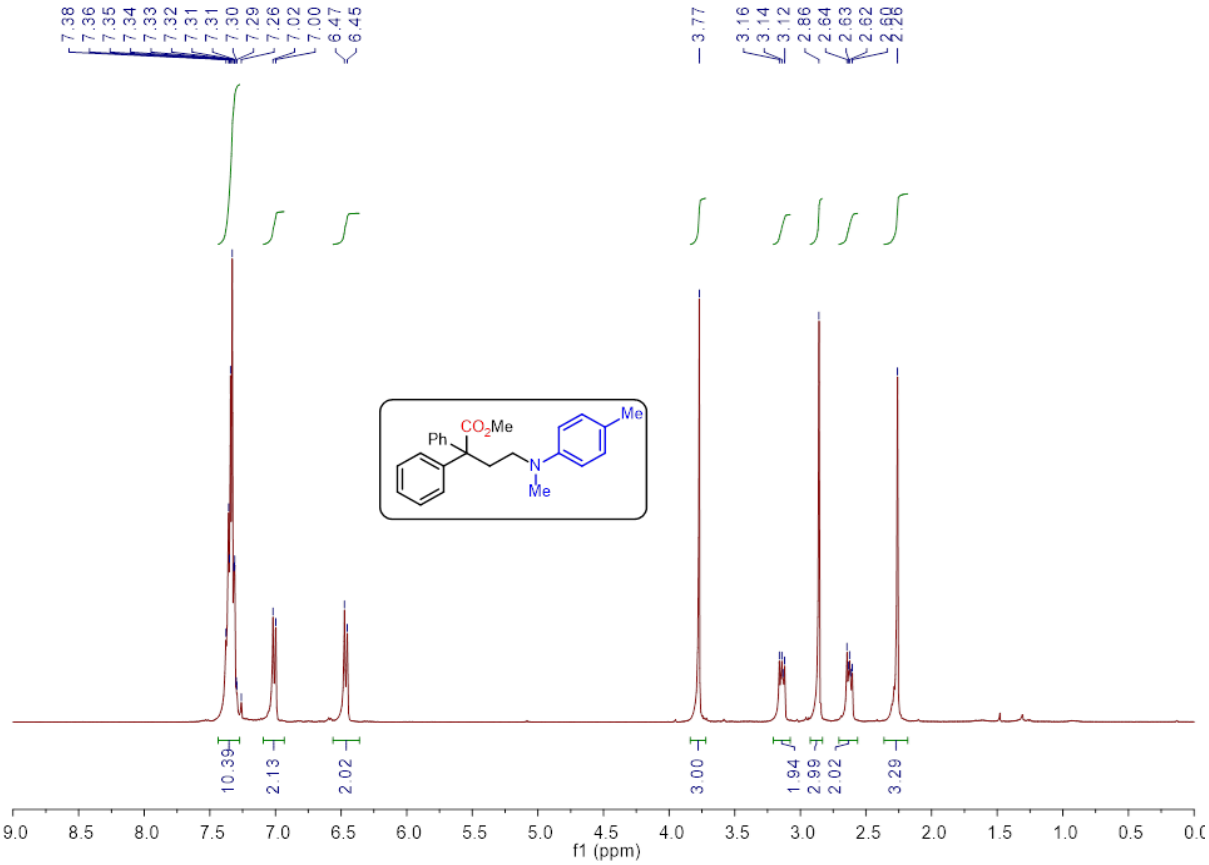
Methyl 2-methyl-4-(methyl(p-tolyl)amino)-2-(4-(trifluoromethyl)phenyl)butanoate (3ra)

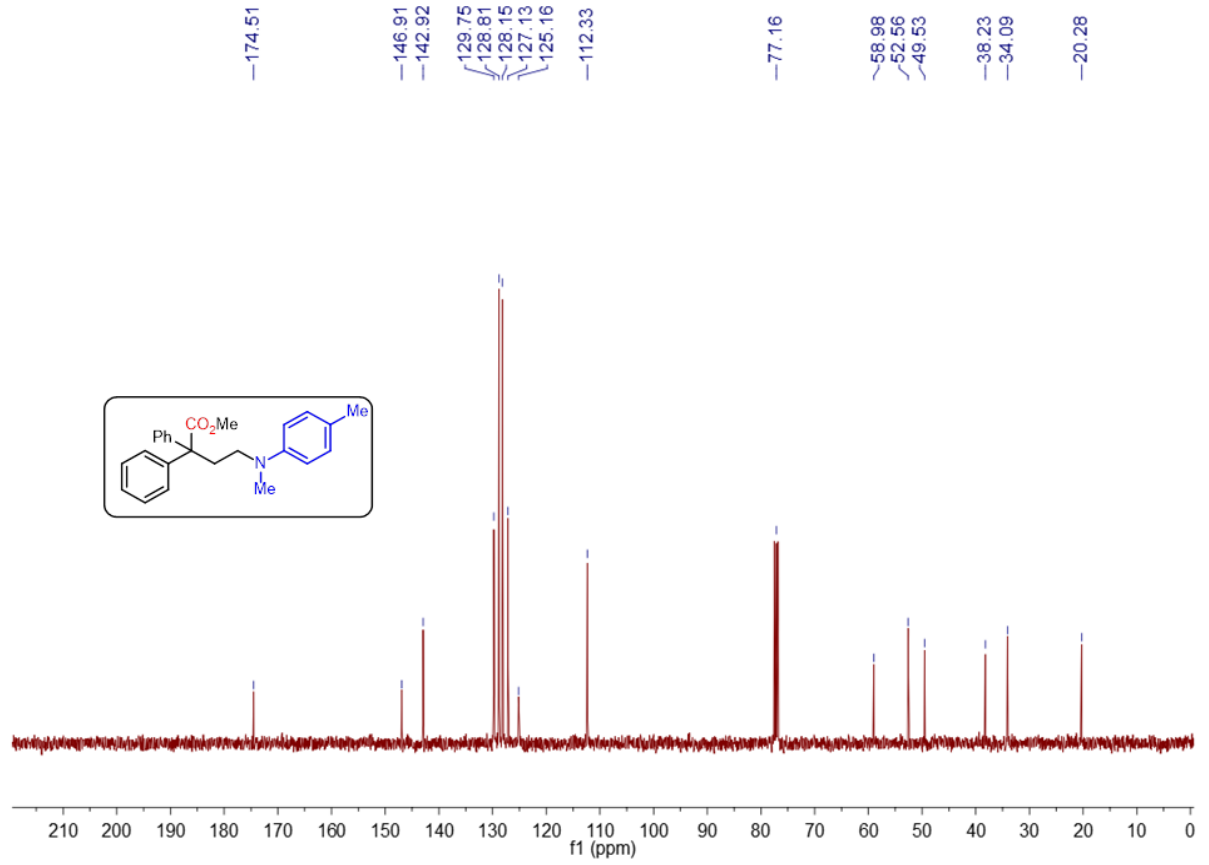




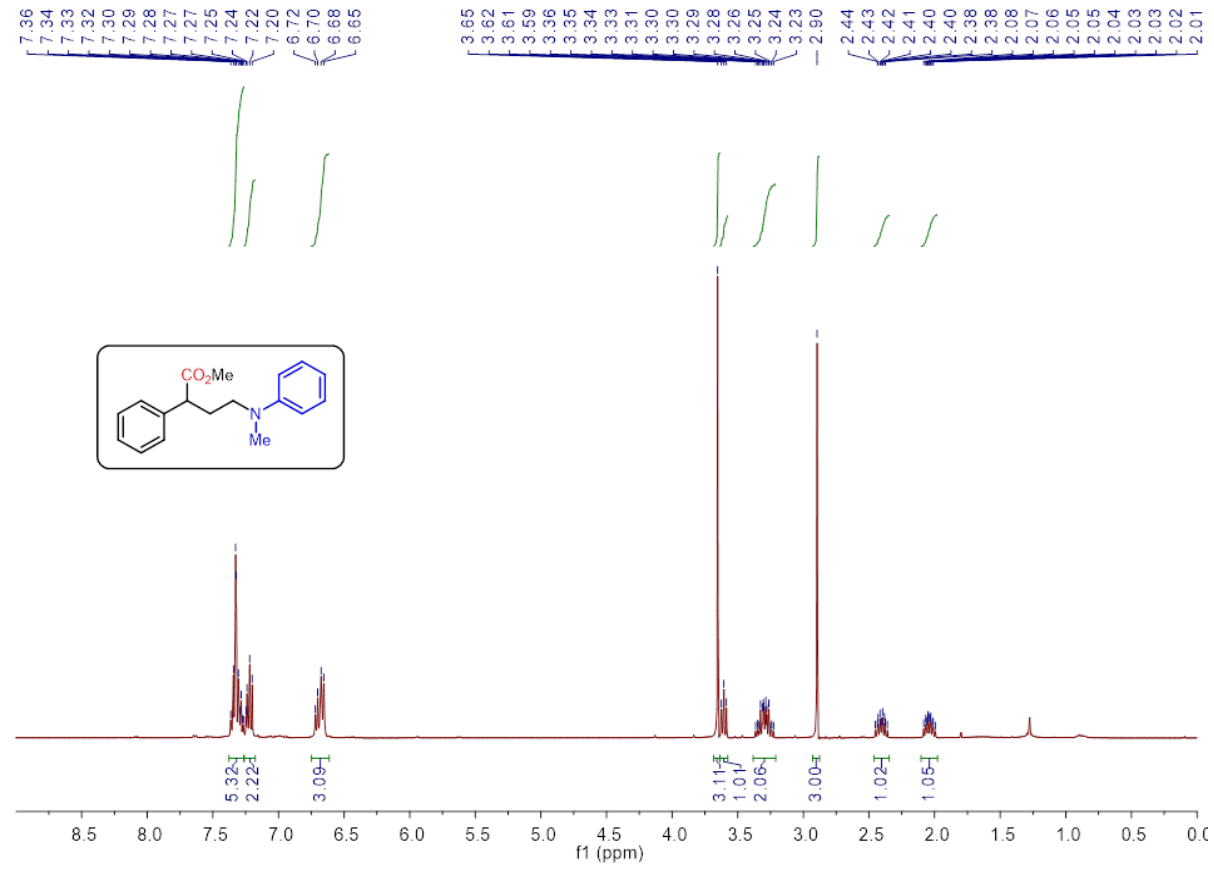

-62.43
CO2Me
Me
Me
N
Me
F3C
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

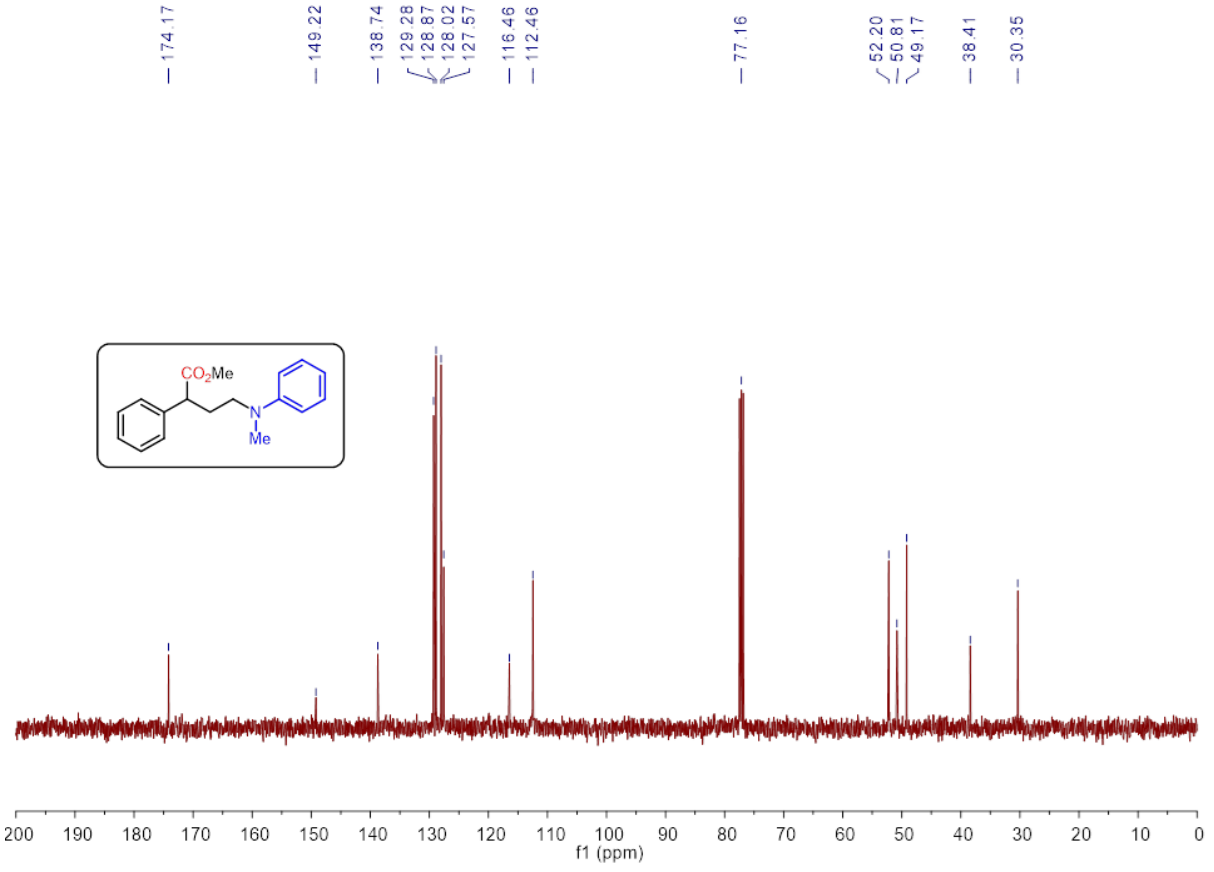
Methyl 4-(methyl(p-tolyl)amino)-2,2-diphenylbutanoate (3sa)



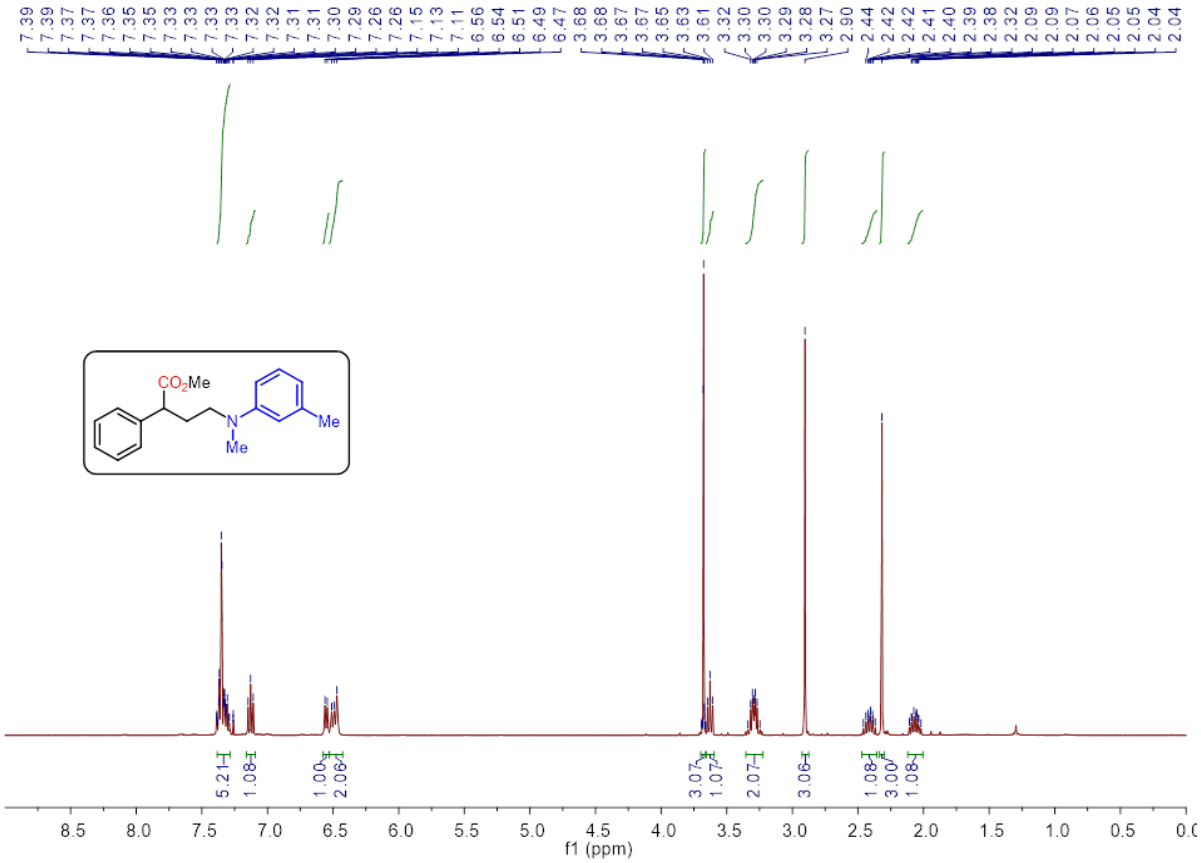


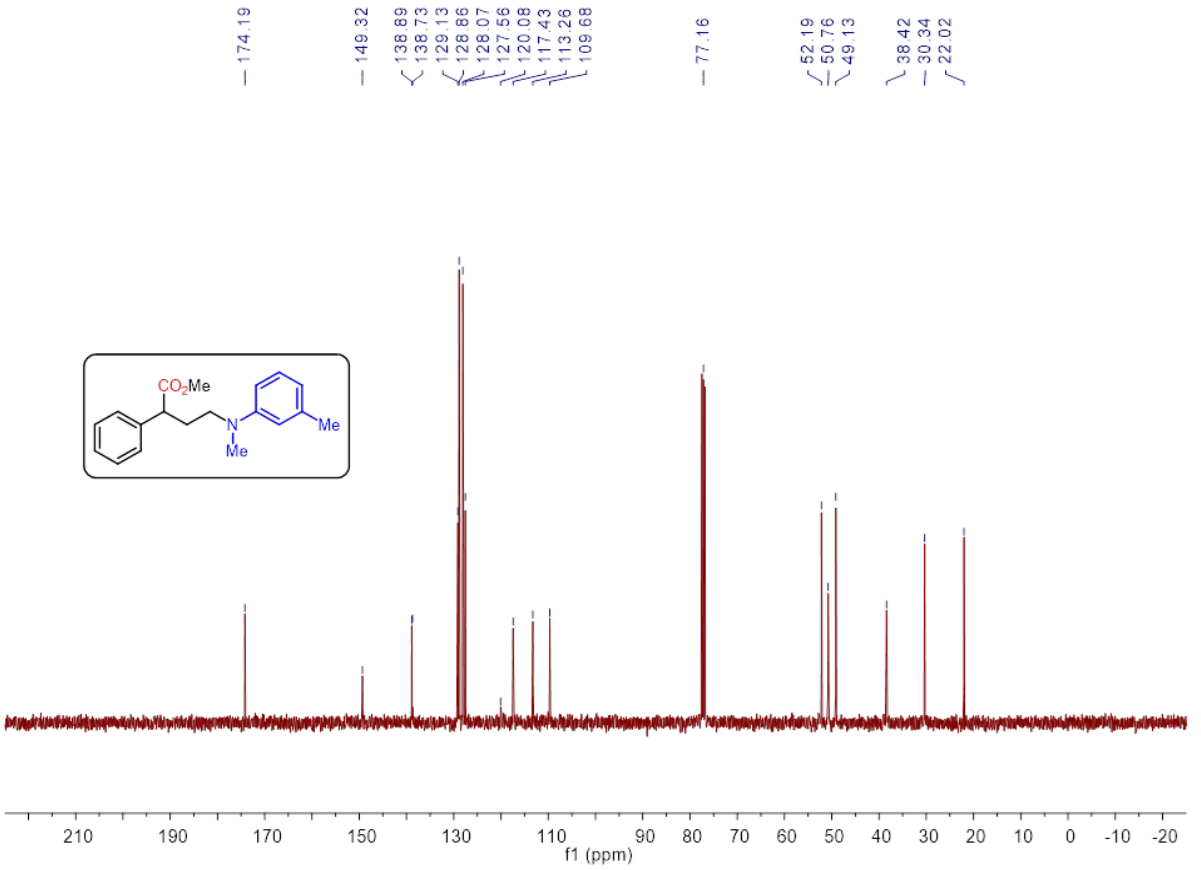
Methyl 4-(methyl(phenyl)amino)-2-phenylbutanoate (3fb)



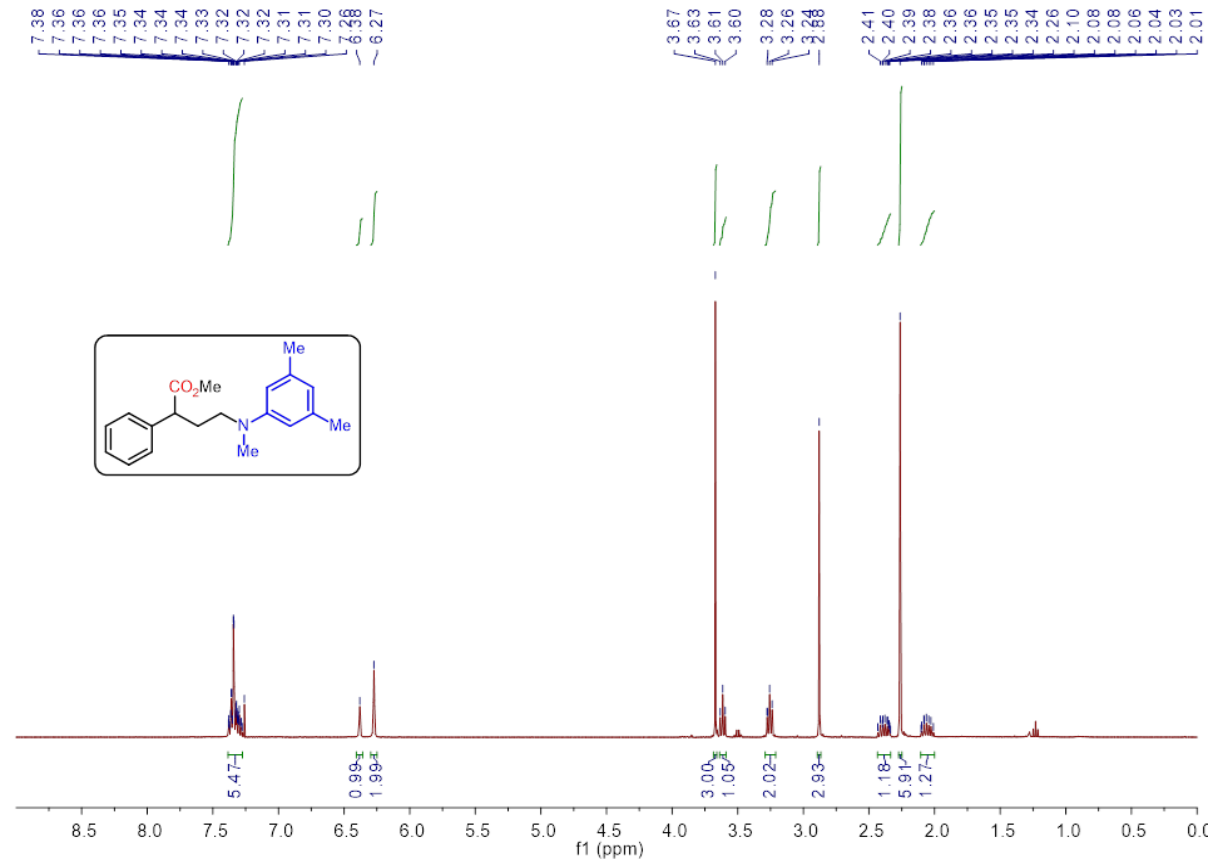


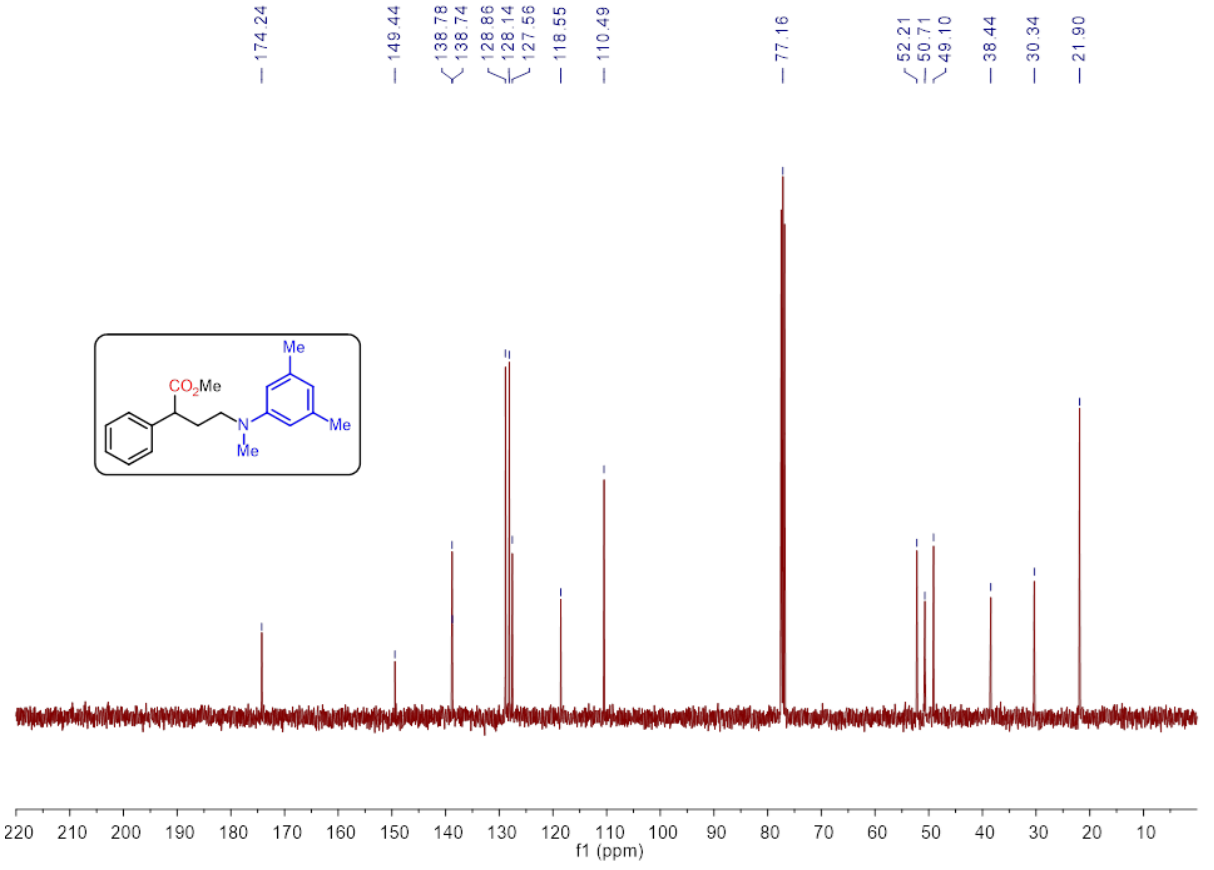
Methyl 4-(methyl(m-tolyl)amino)-2-phenylbutanoate (3fc)



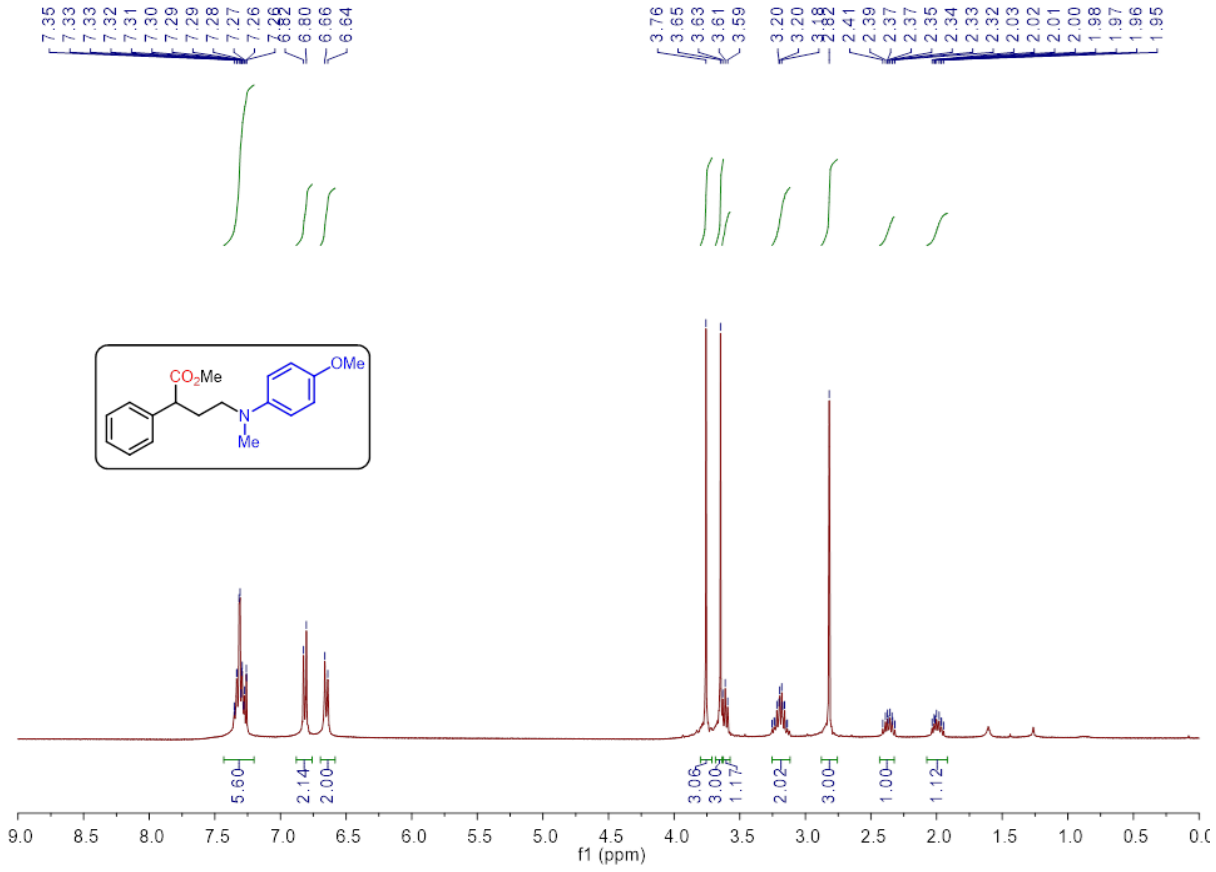


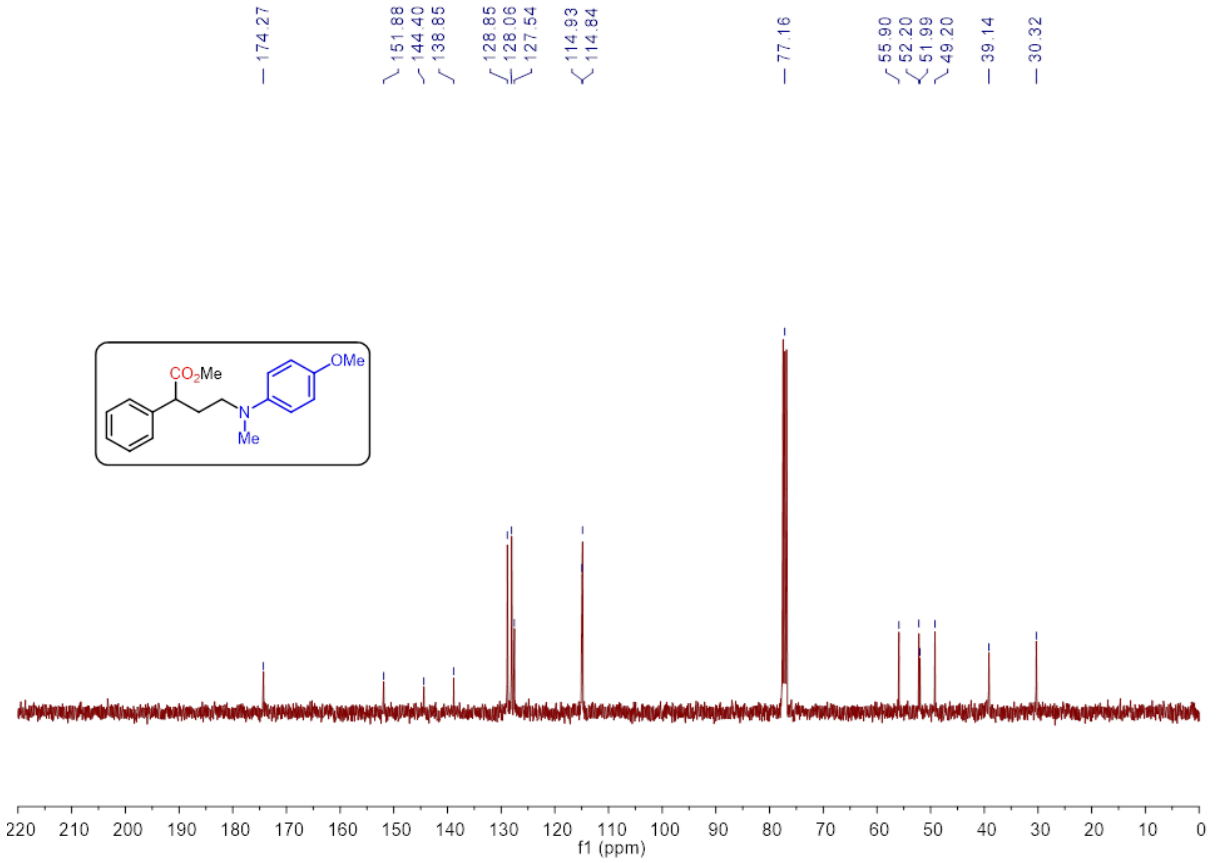
Methyl 4-((3,5-dimethylphenyl)(methyl)amino)-2-phenylbutanoate (3fd)



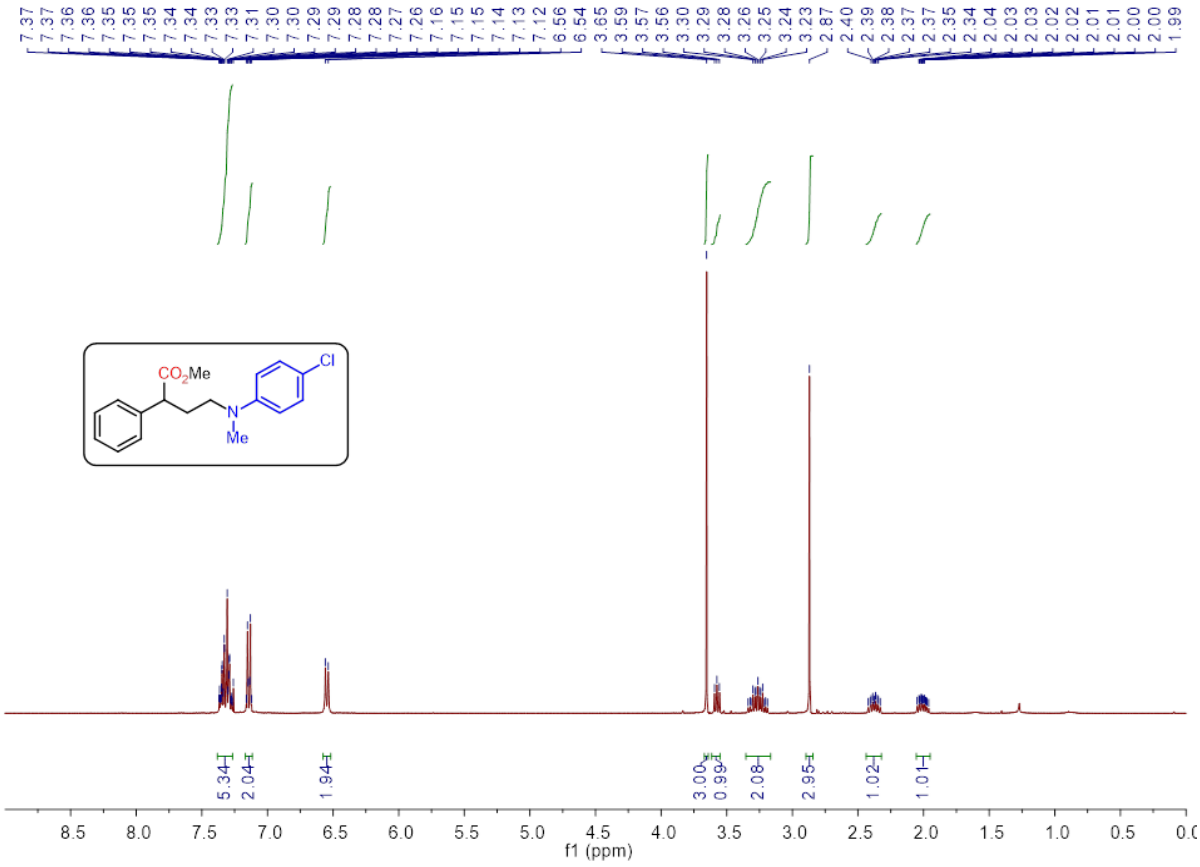


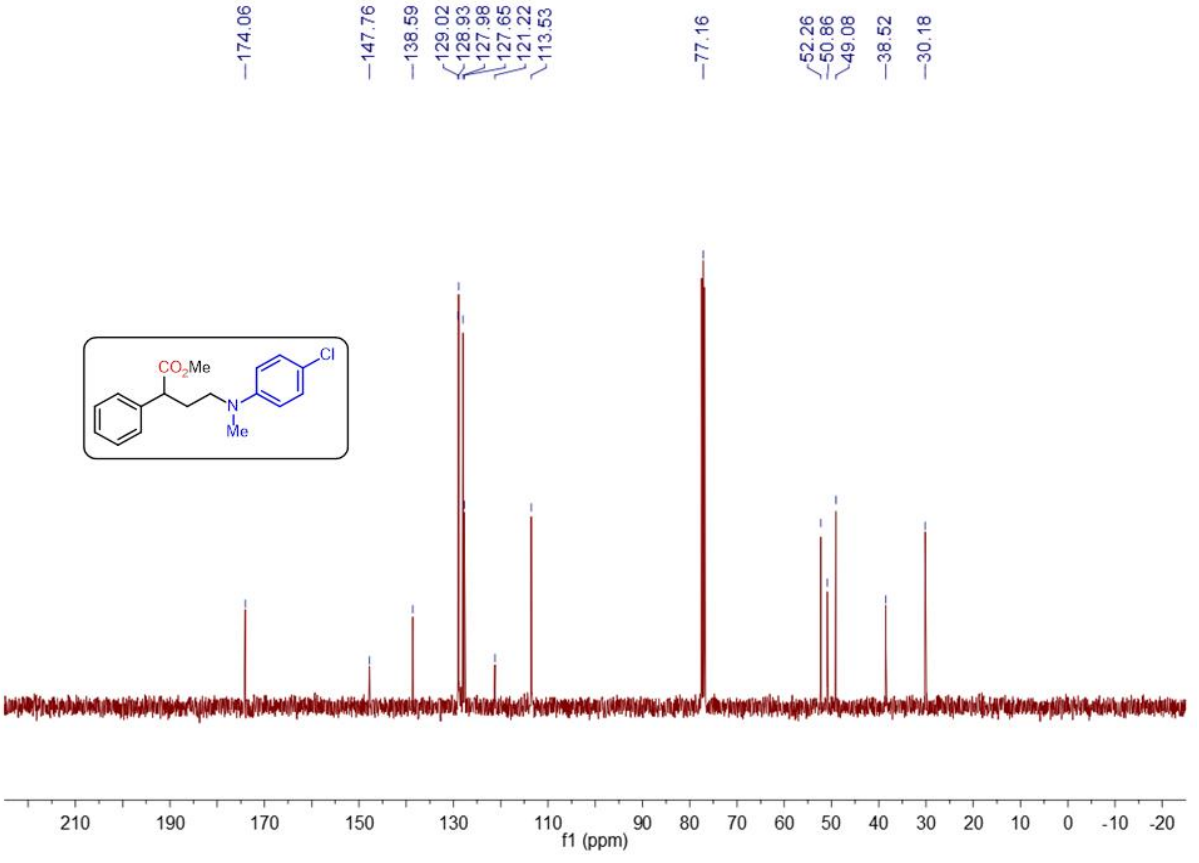
Methyl 4-((4-methoxyphenyl)(methyl)amino)-2-phenylbutanoate (3fe)



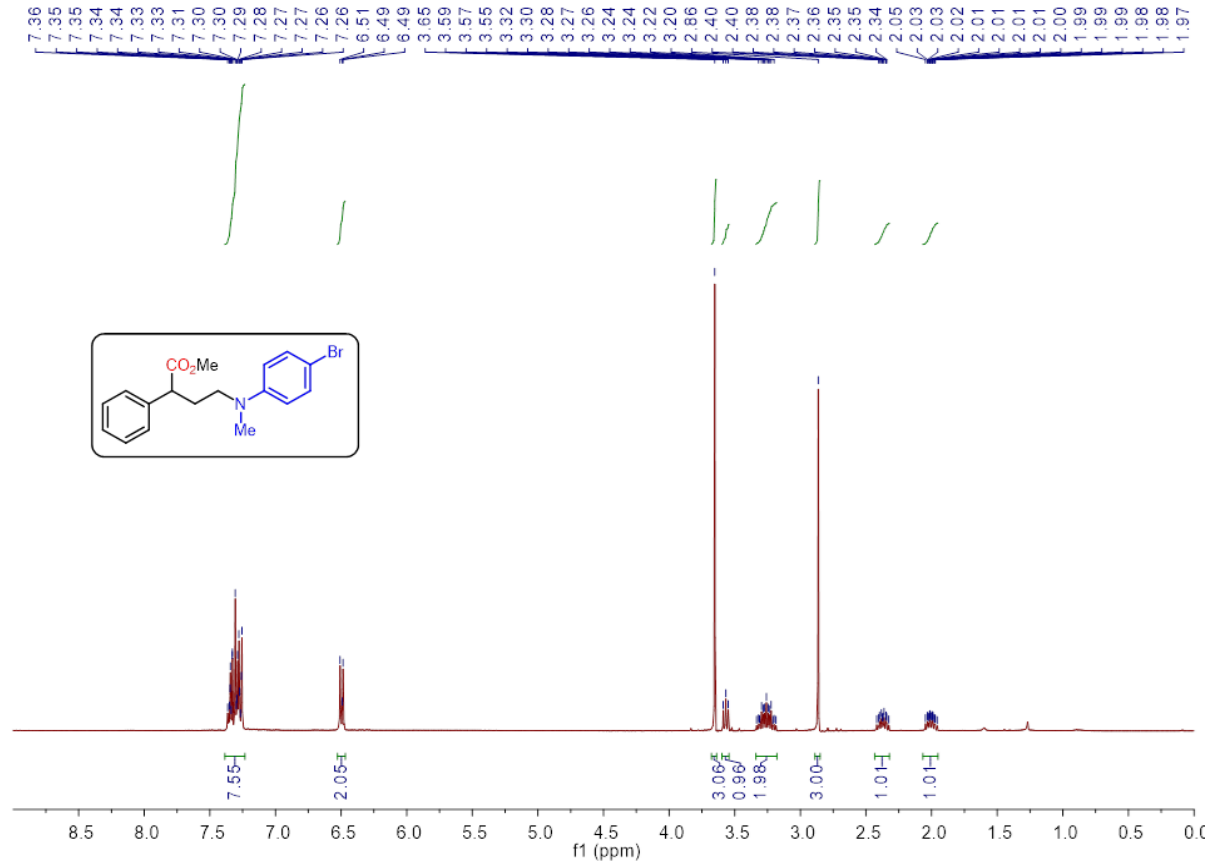


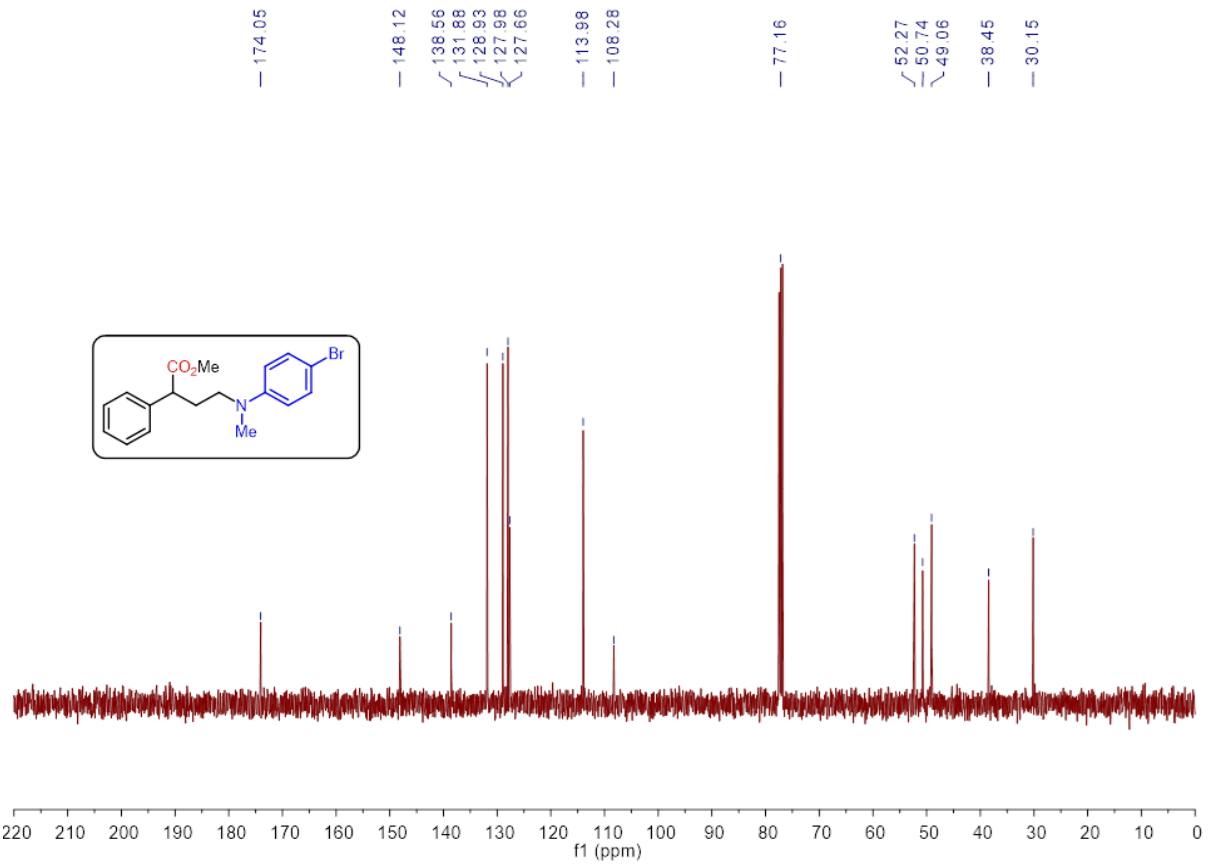
Methyl 4-((4-chlorophenyl)(methyl)amino)-2-phenylbutanoate (3ff)



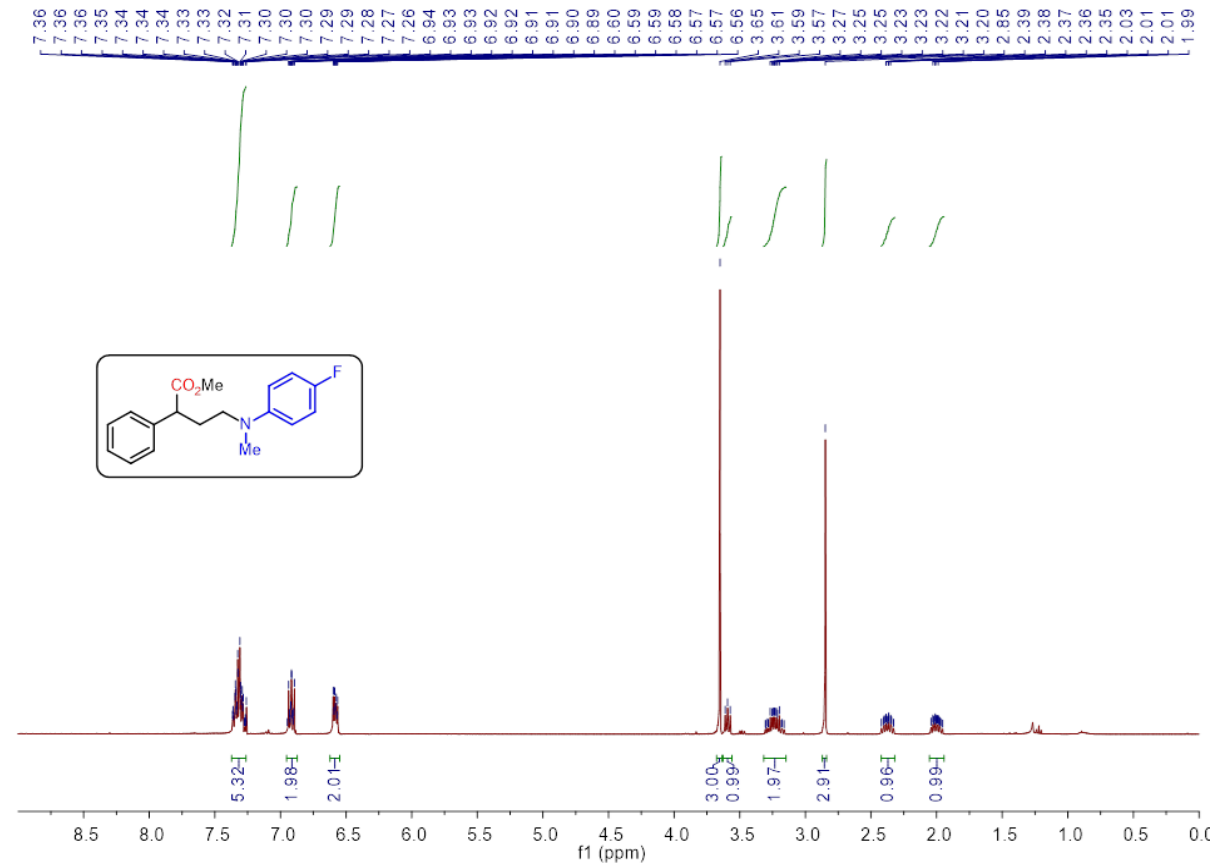


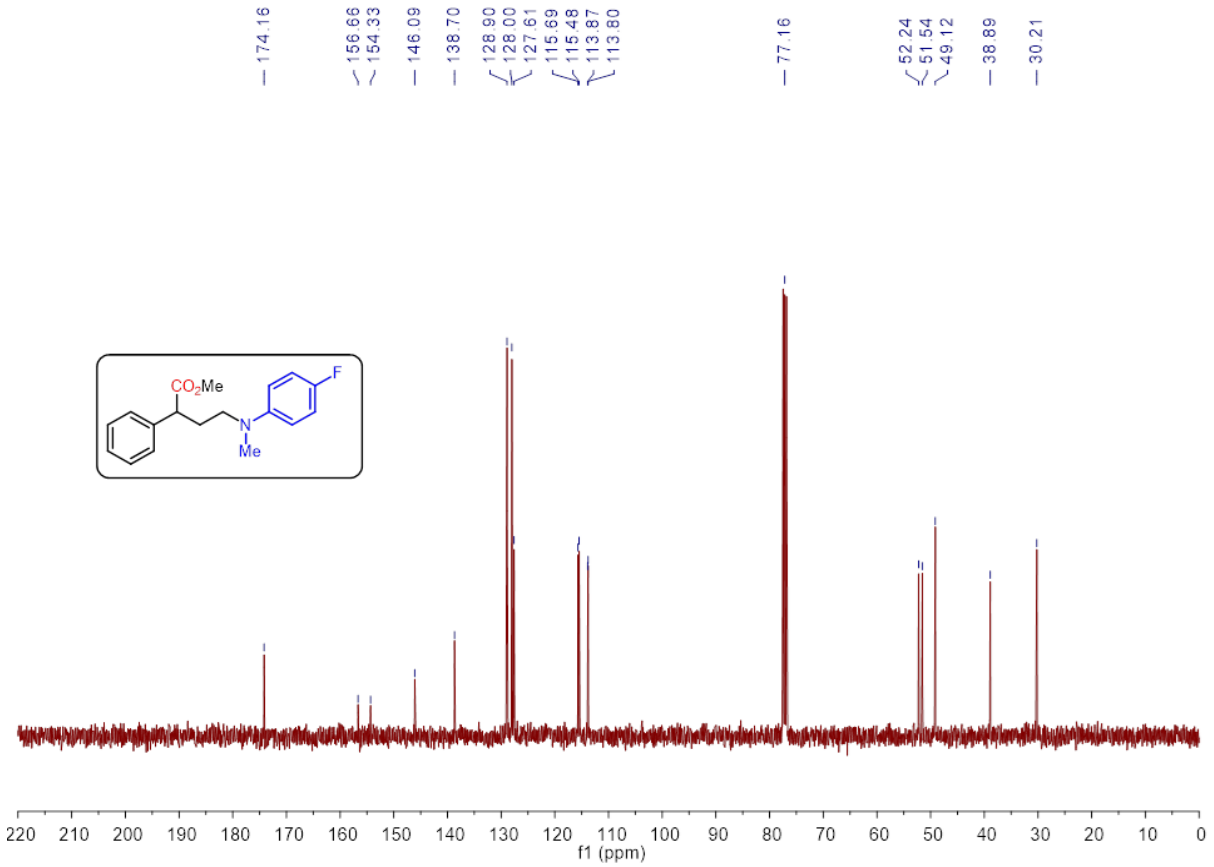
Methyl 4-((4-bromophenyl)(methyl)amino)-2-phenylbutanoate (3fg)

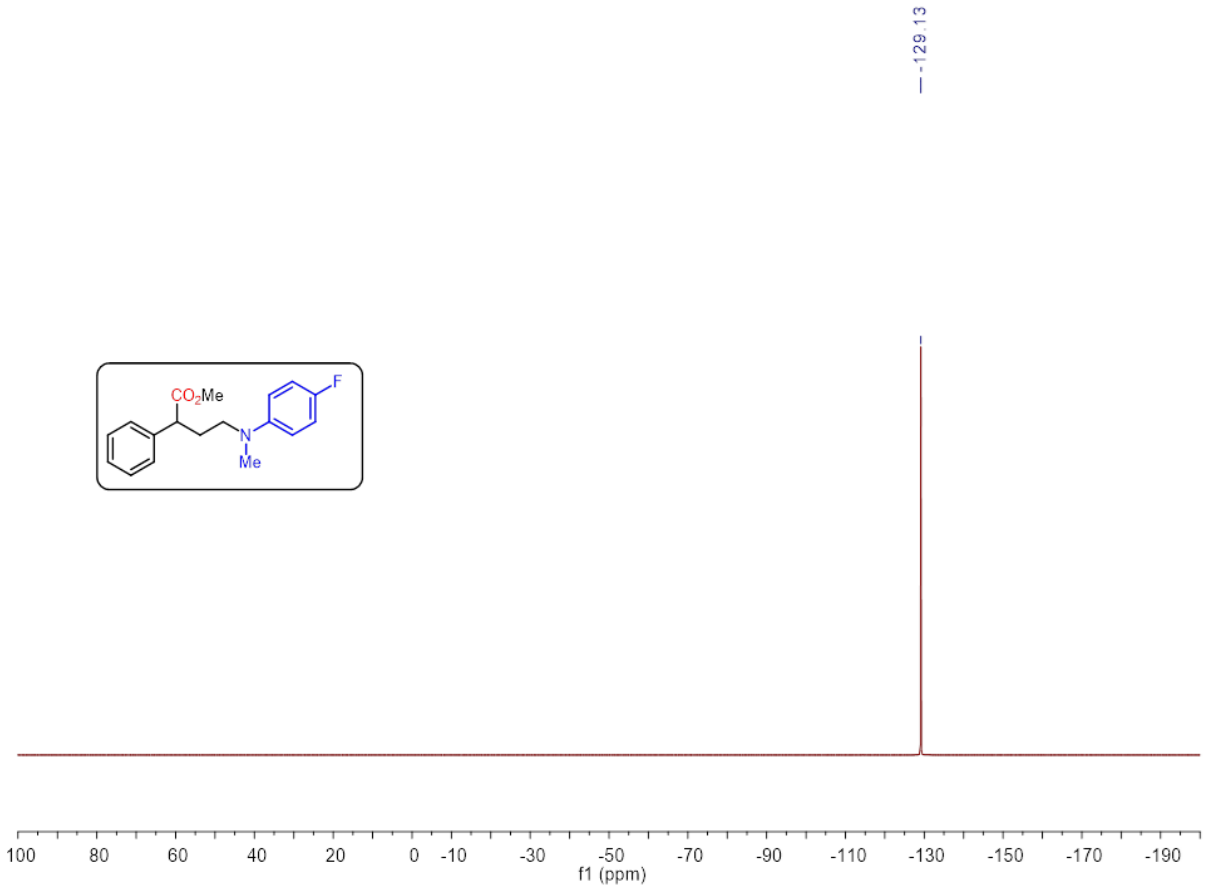




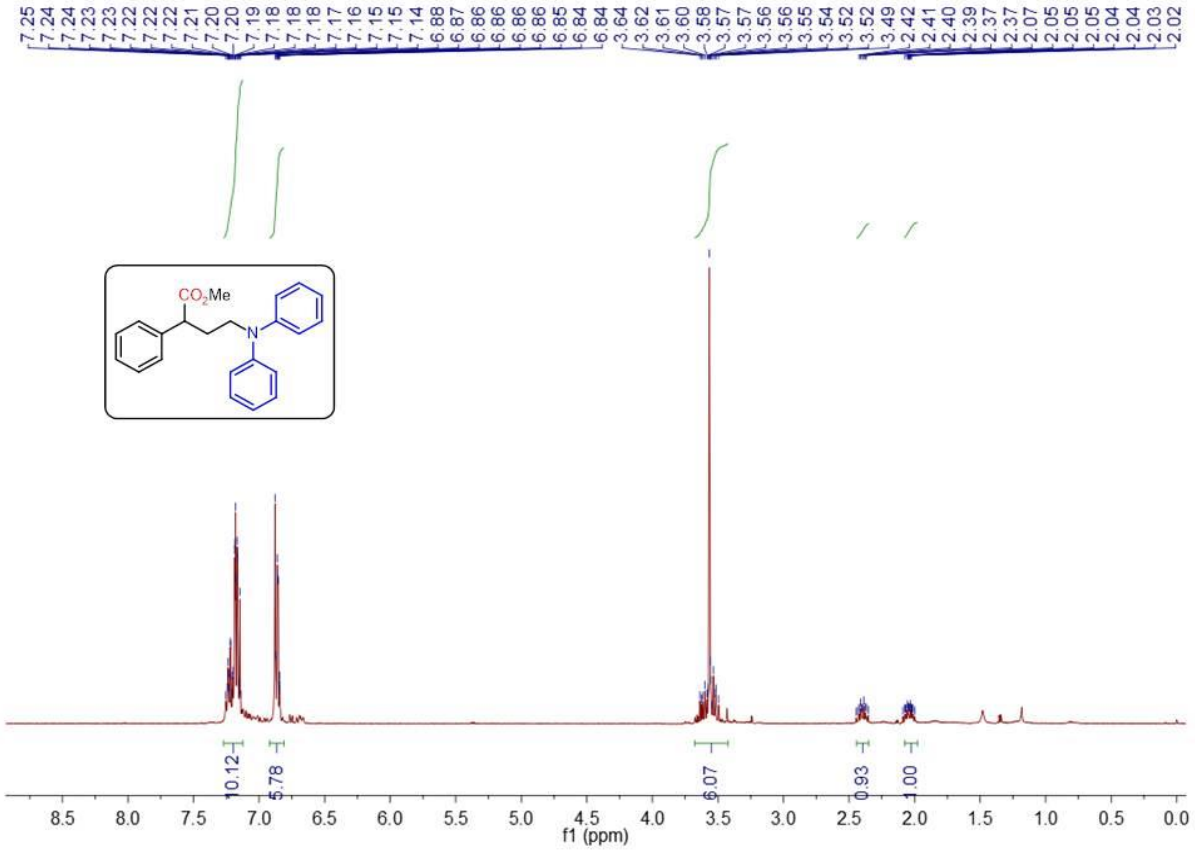
Methyl 4-((4-fluorophenyl)(methyl)amino)-2-phenylbutanoate (3fh)

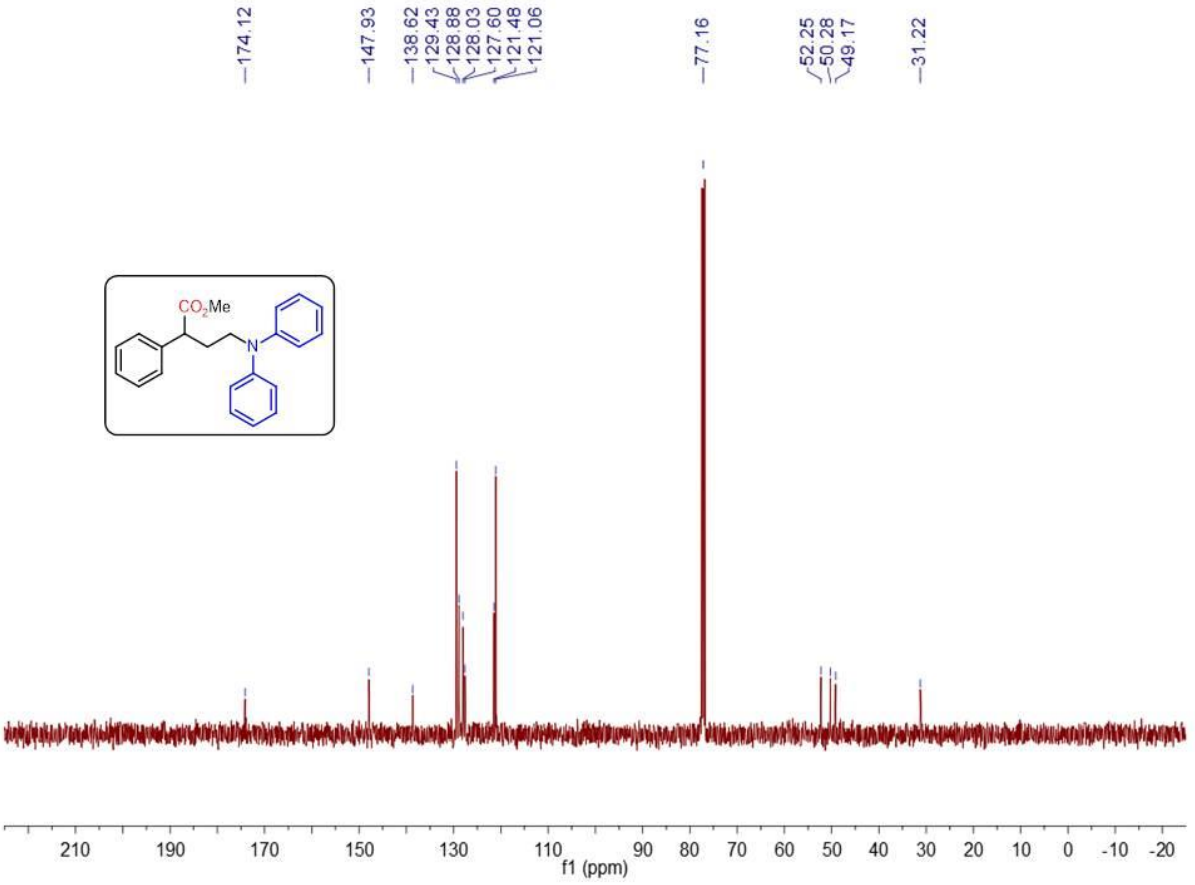




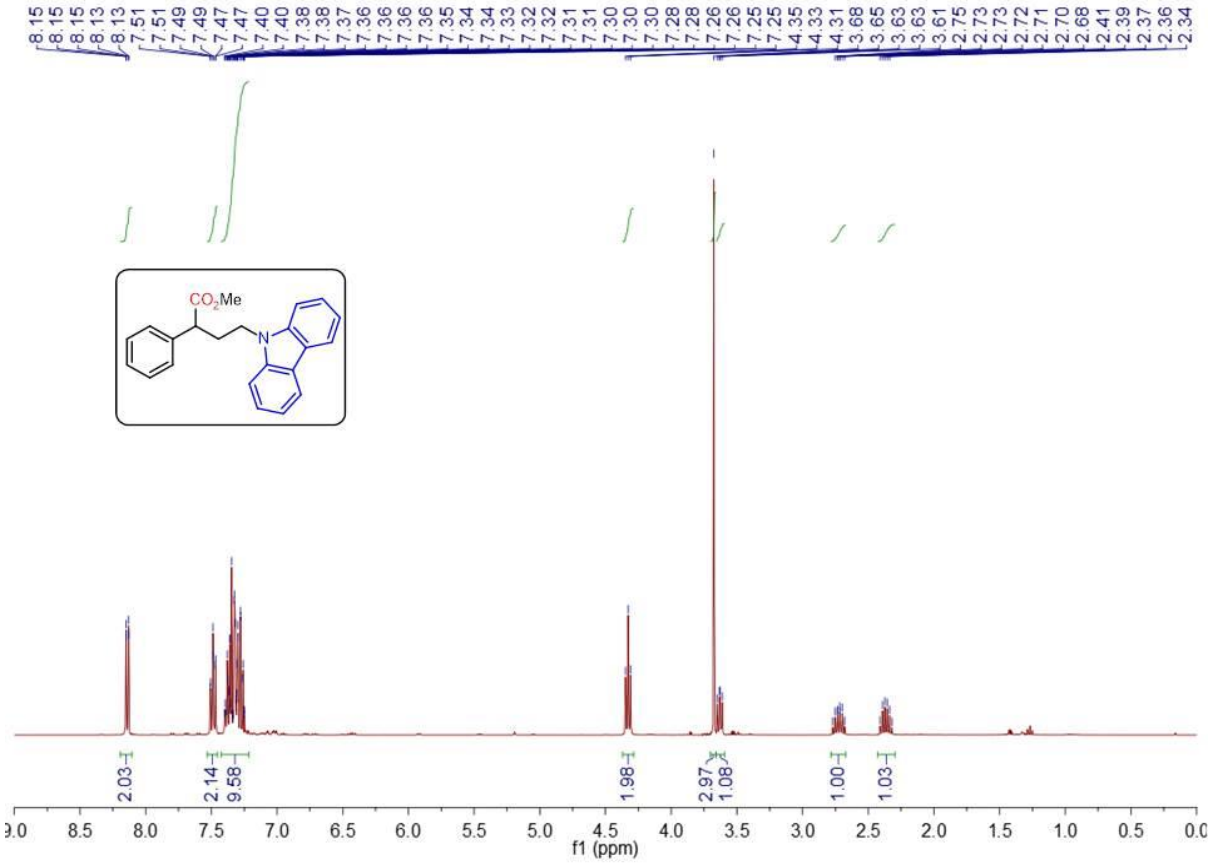

-129.13
CO2Me
N
Me
F
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

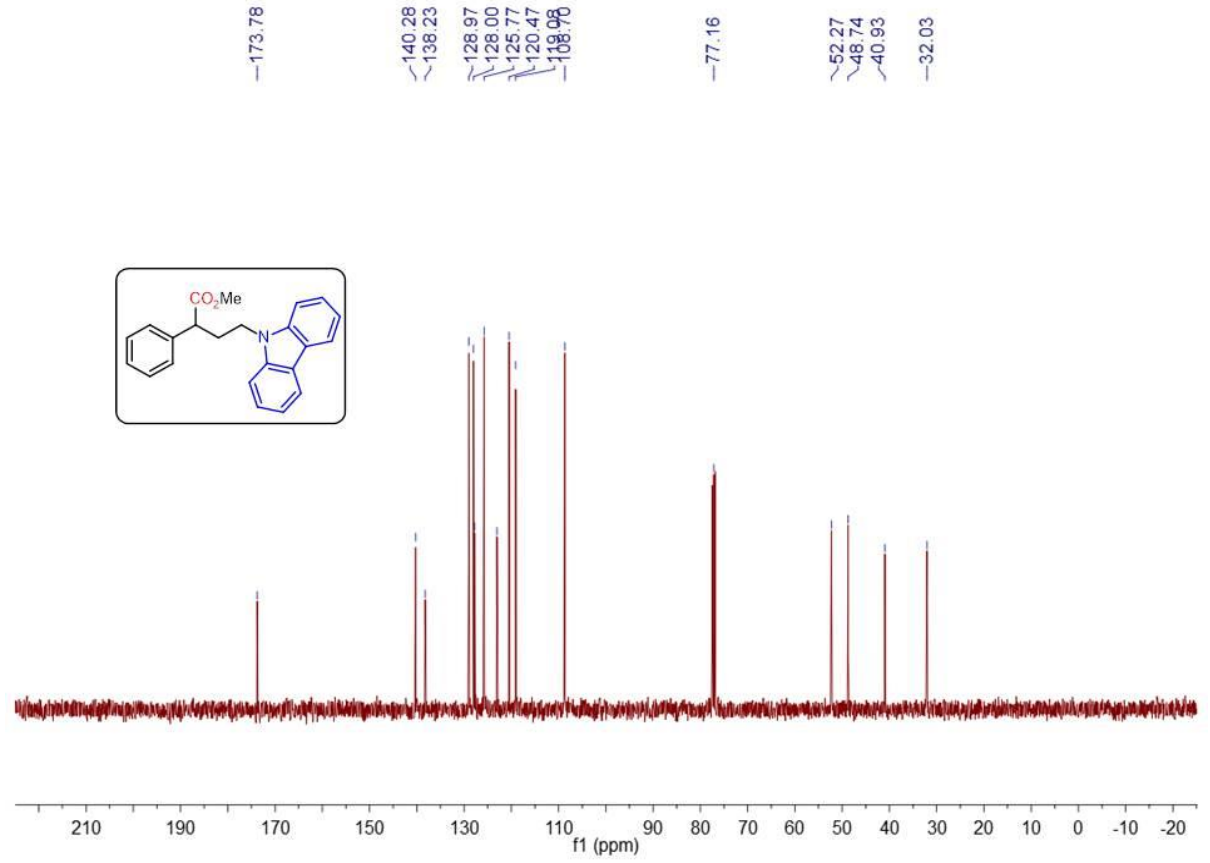
Methyl 4-(diphenylamino)-2-phenylbutanoate (3fi)



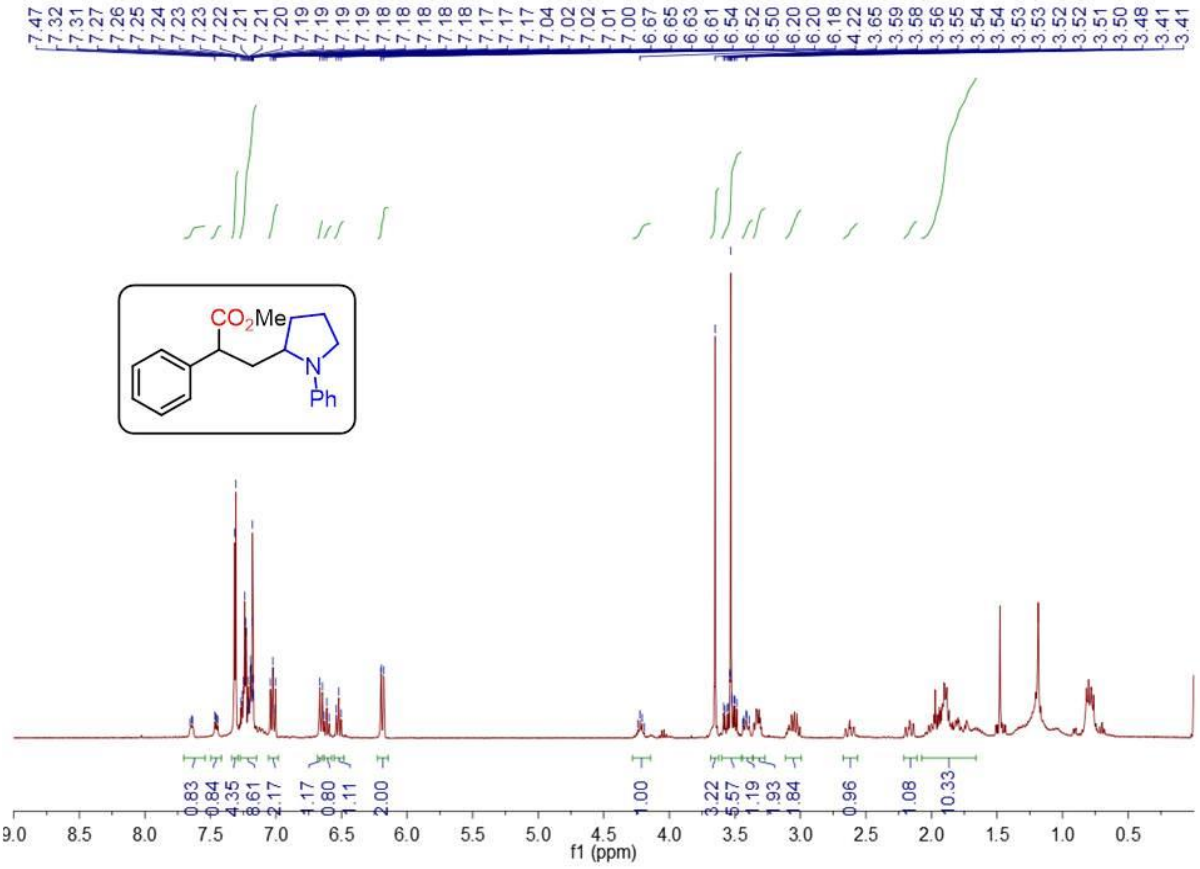


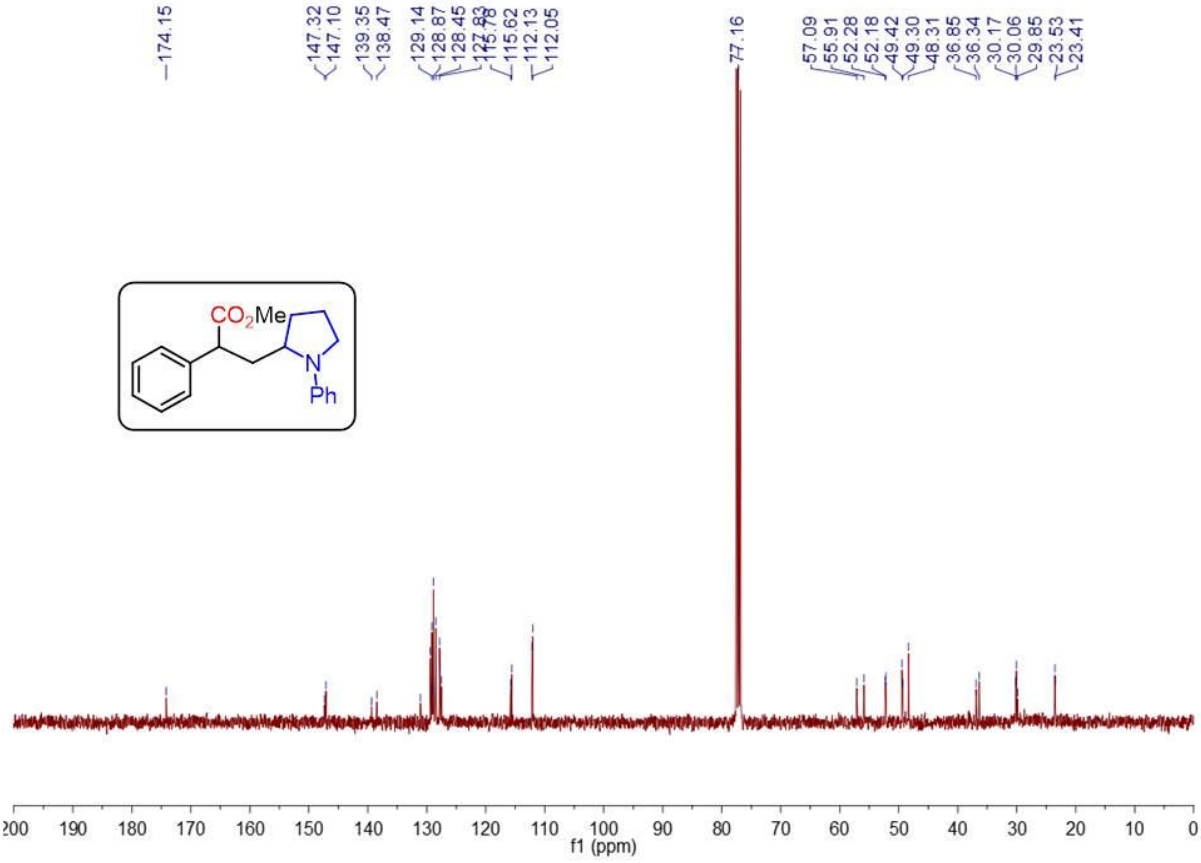
Methyl 4-(9H-carbazol-9-yl)-2-phenylbutanoate (3fj)



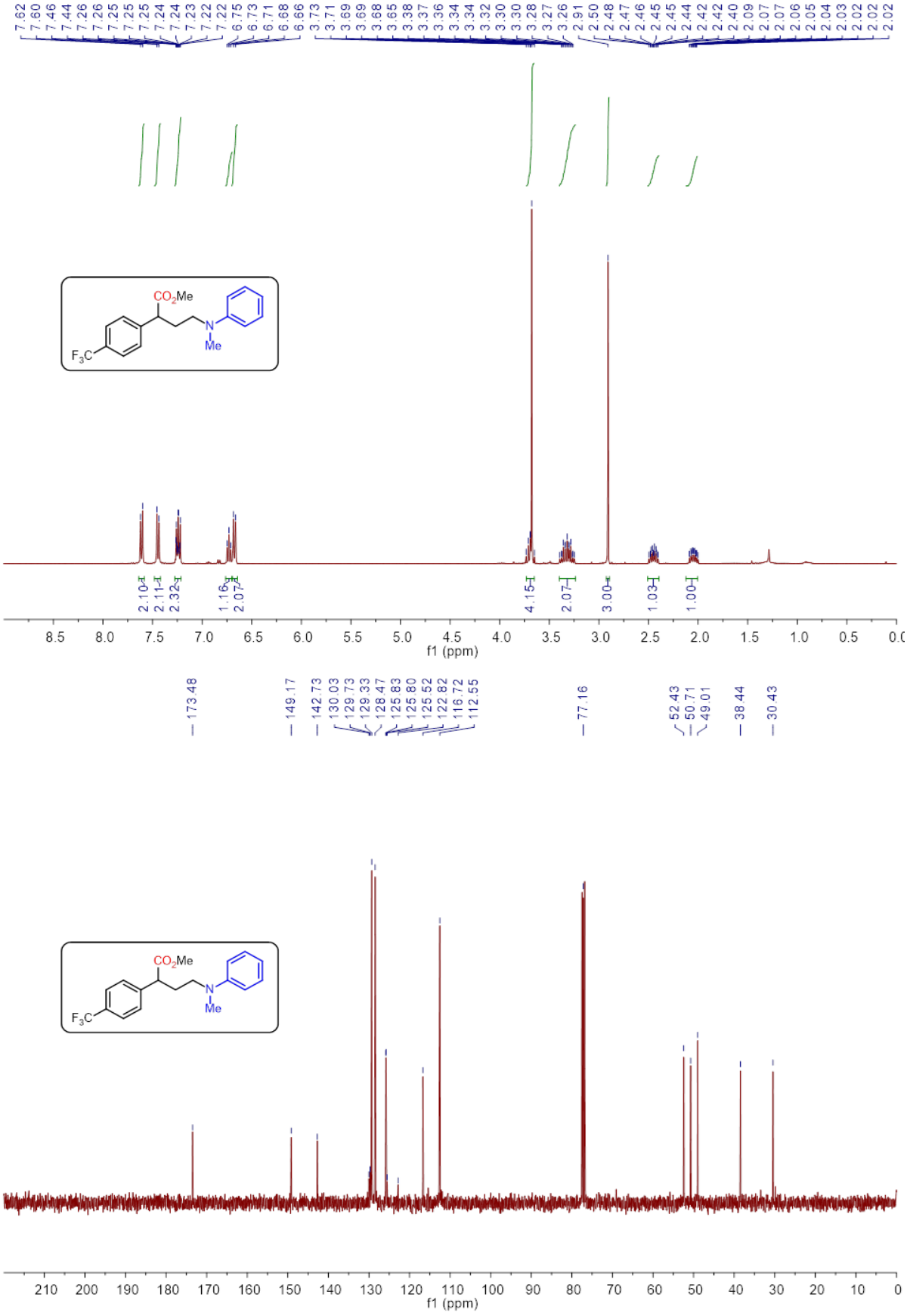


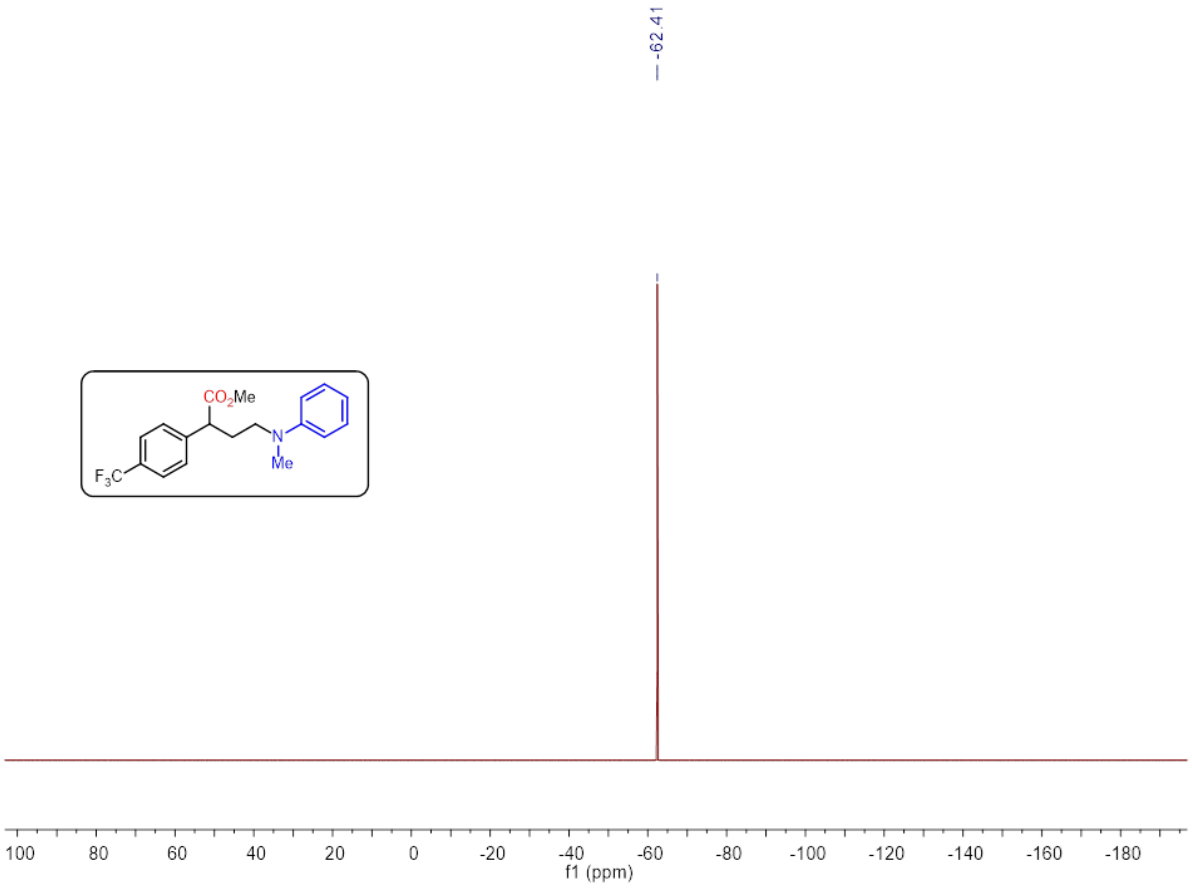
Methyl 2-phenyl-3-(1-phenylpyrrolidin-2-yl)propanoate (3fk)



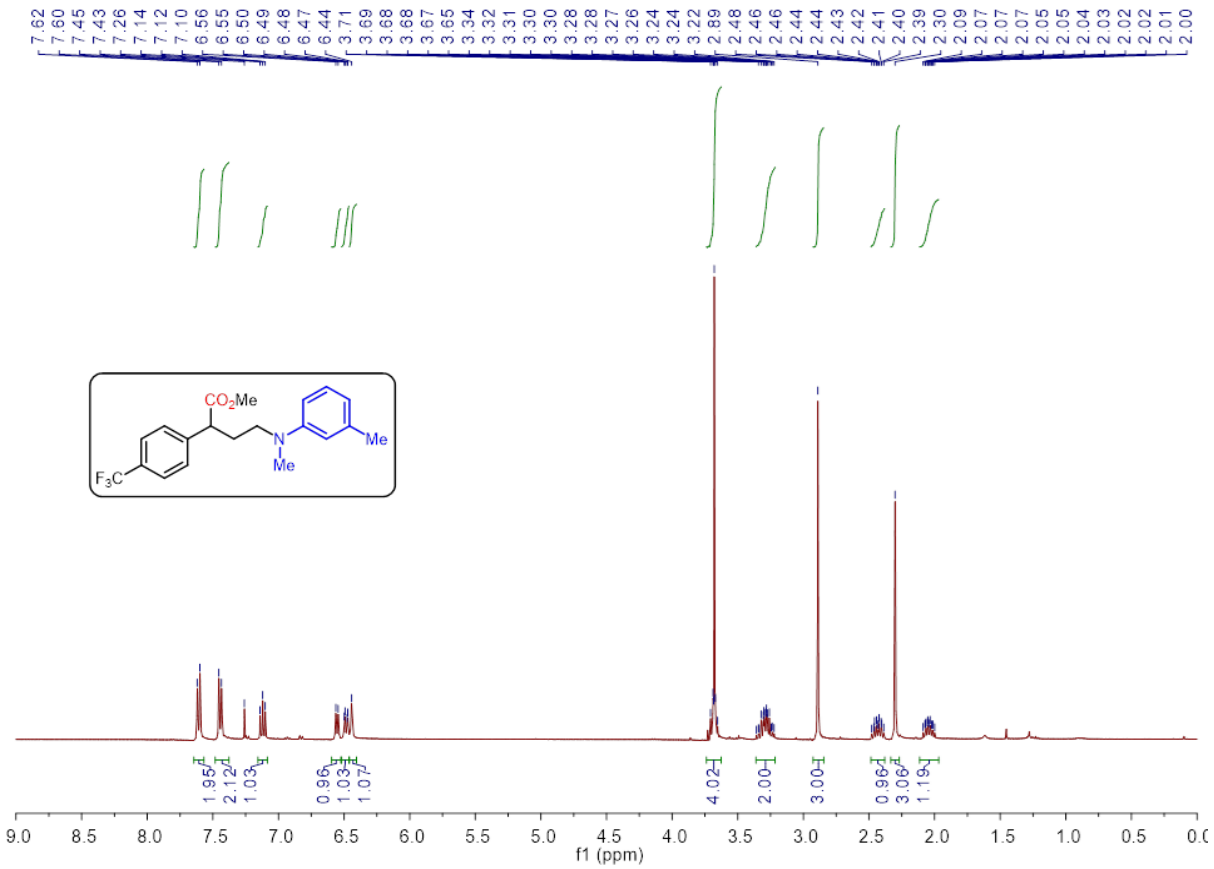


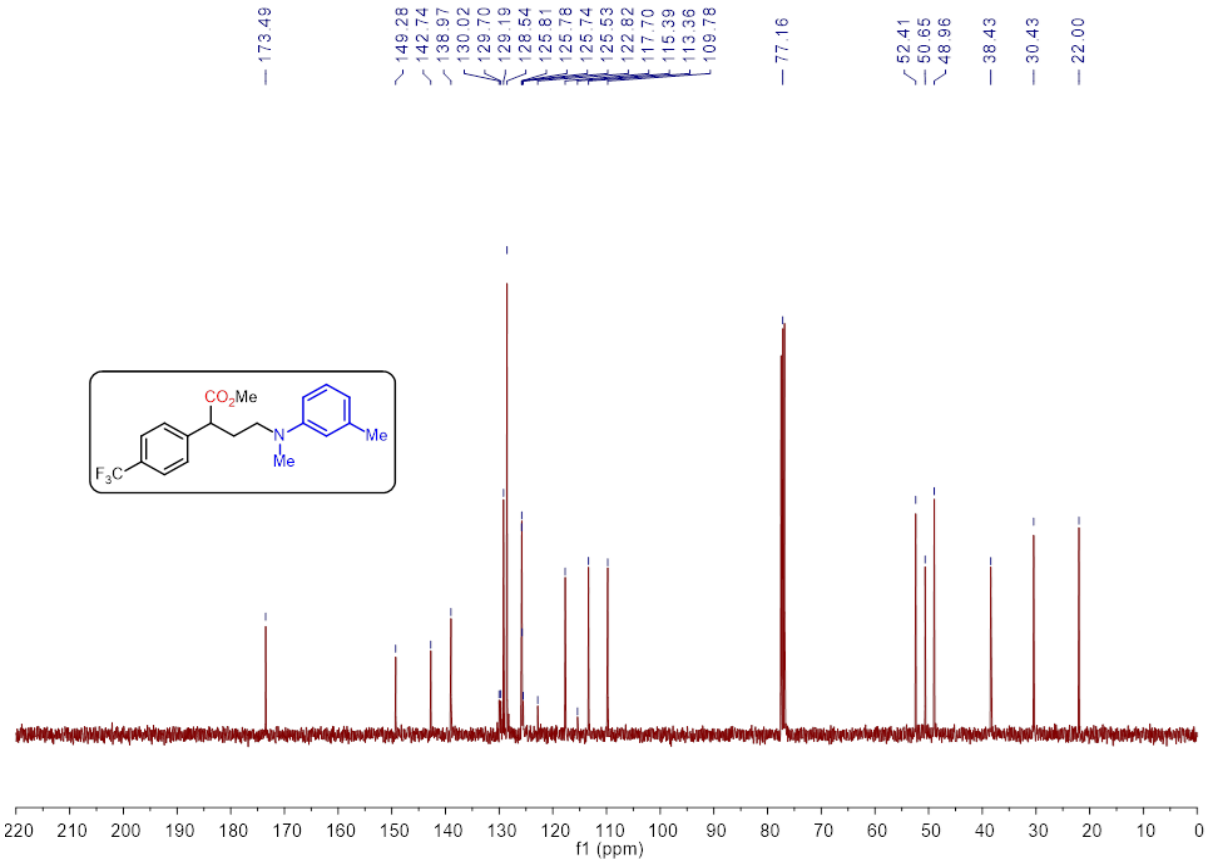
Methyl 4-(methyl(phenyl)amino)-2-(4-(trifluoromethyl)phenyl)butanoate (3kb)

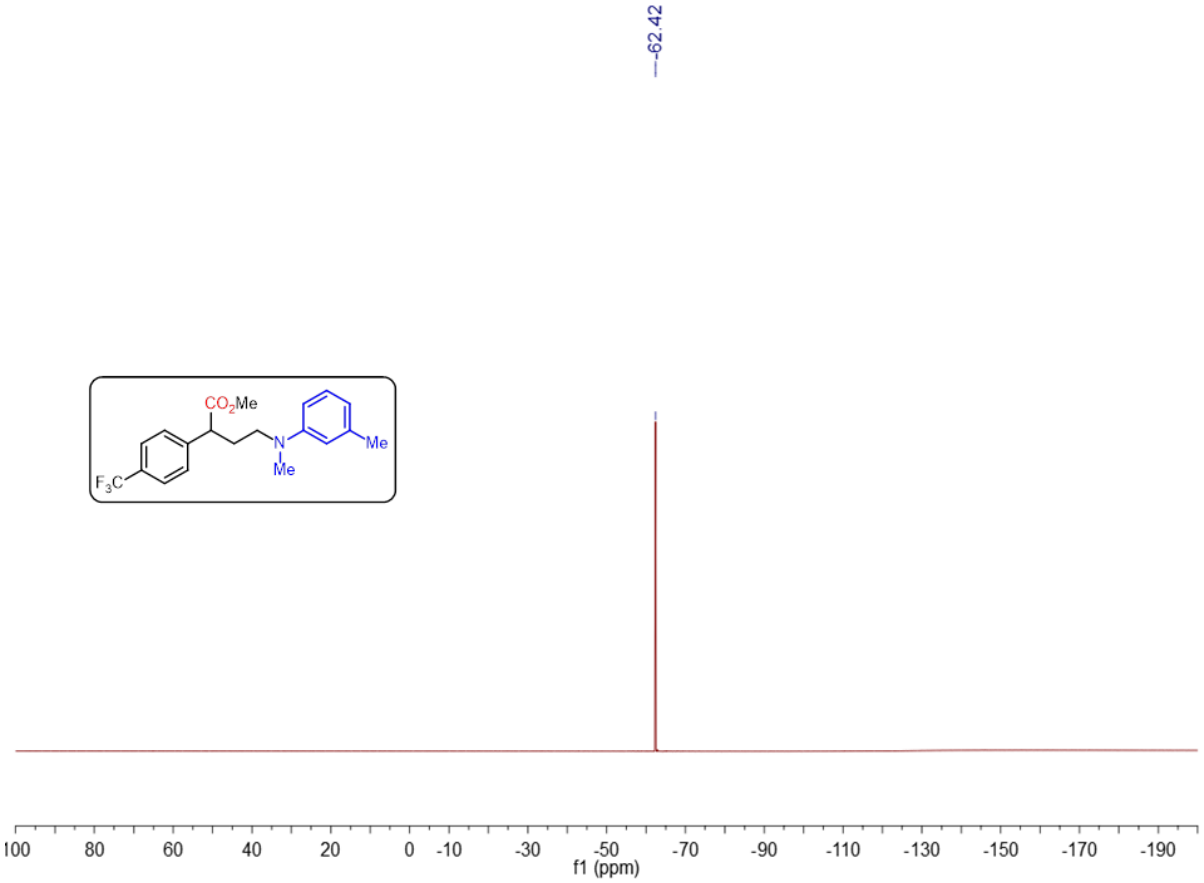



-62.41
CO2Me
N
Me
F3C
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

Methyl 4-(methyl(m-tolyl)amino)-2-(4-(trifluoromethyl)phenyl)butanoate (3kc)






-62.42
CO2Me
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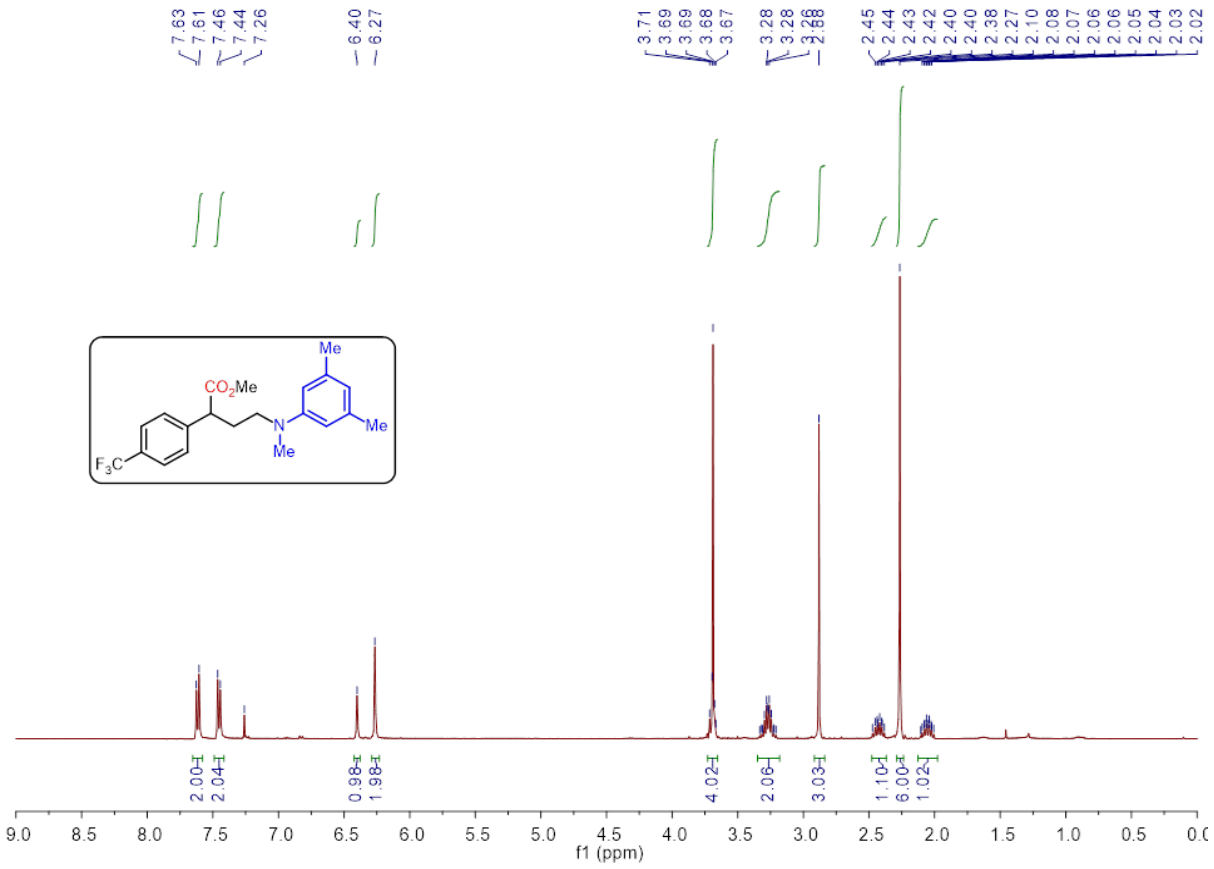
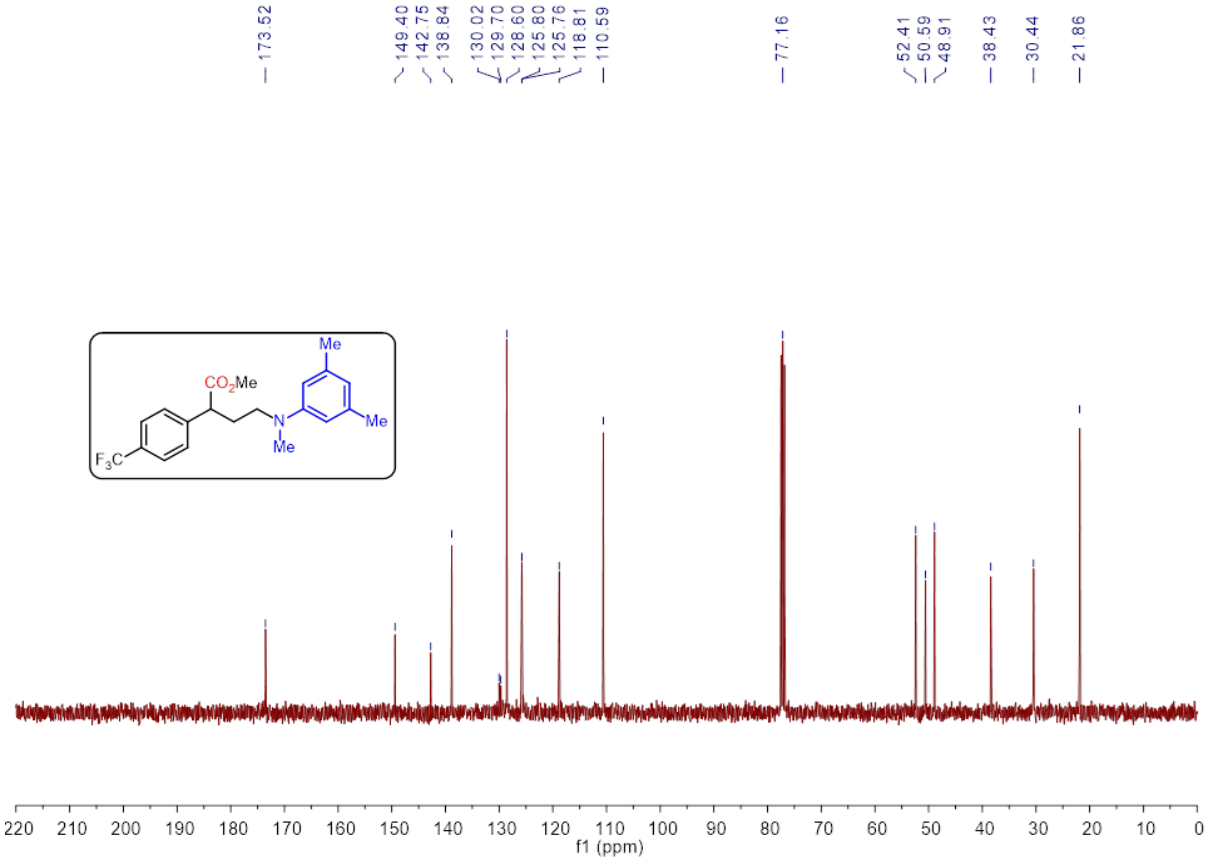
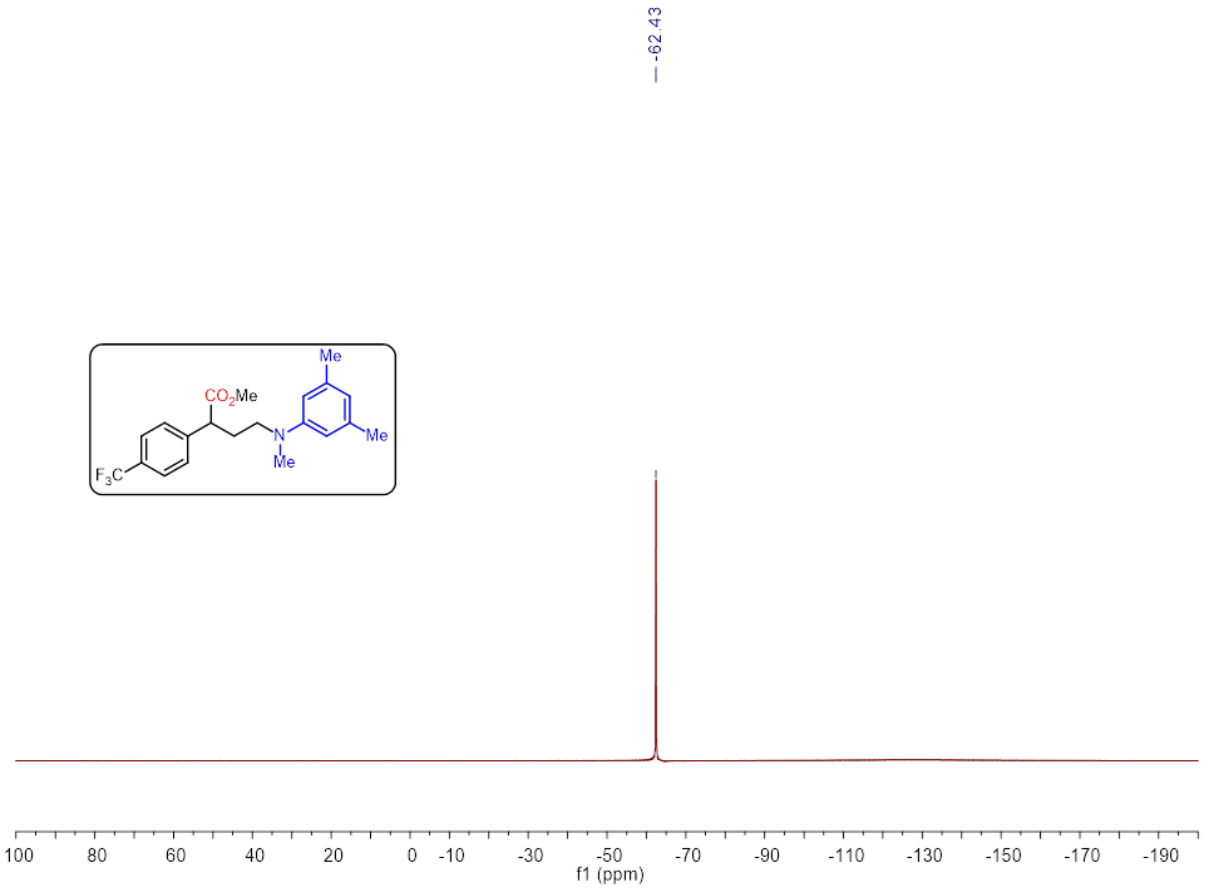
Me
Me
F3C
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

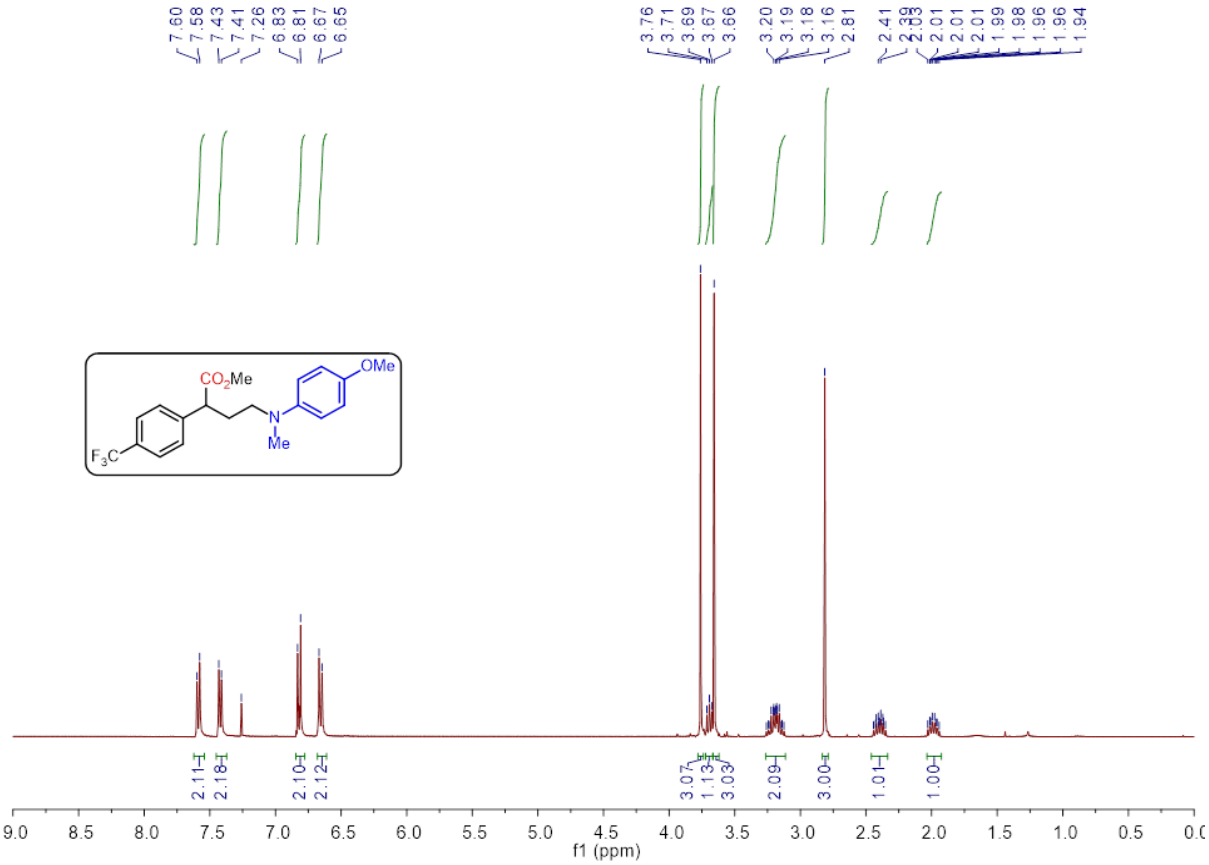
Methyl 4-((3,5-dimethylphenyl)(methyl)amino)-2-(4-(trifluoromethyl)phenyl)butanoate (3kd)

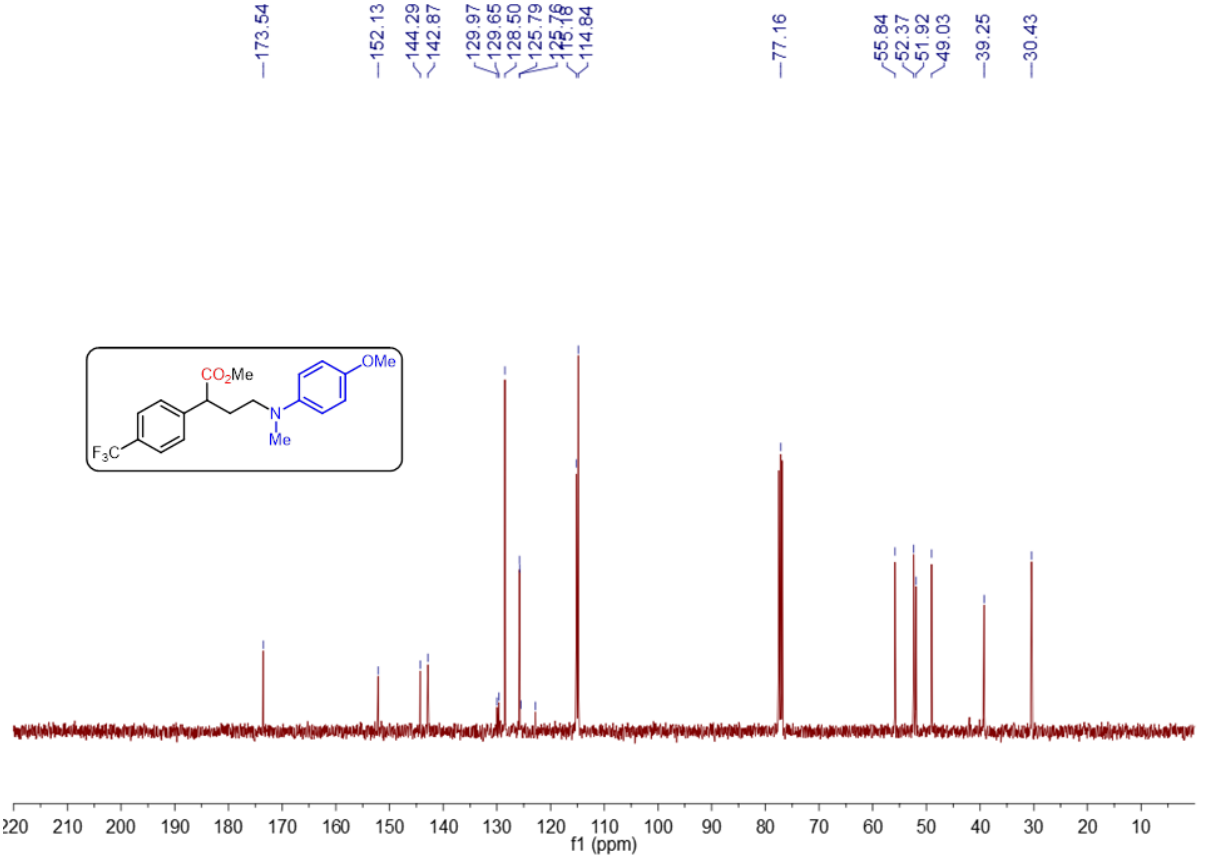


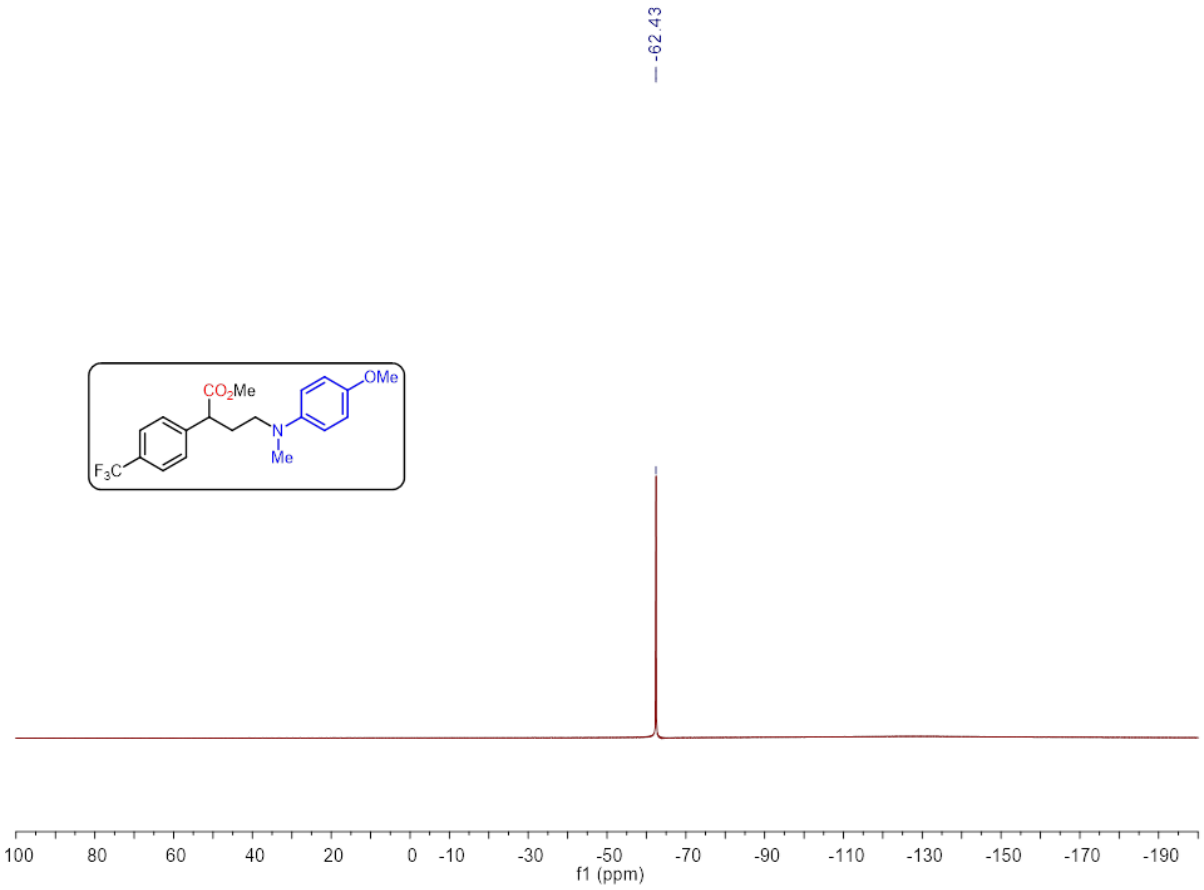



-62.43
Me
CO2Me
N
Me
Me
F3C
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

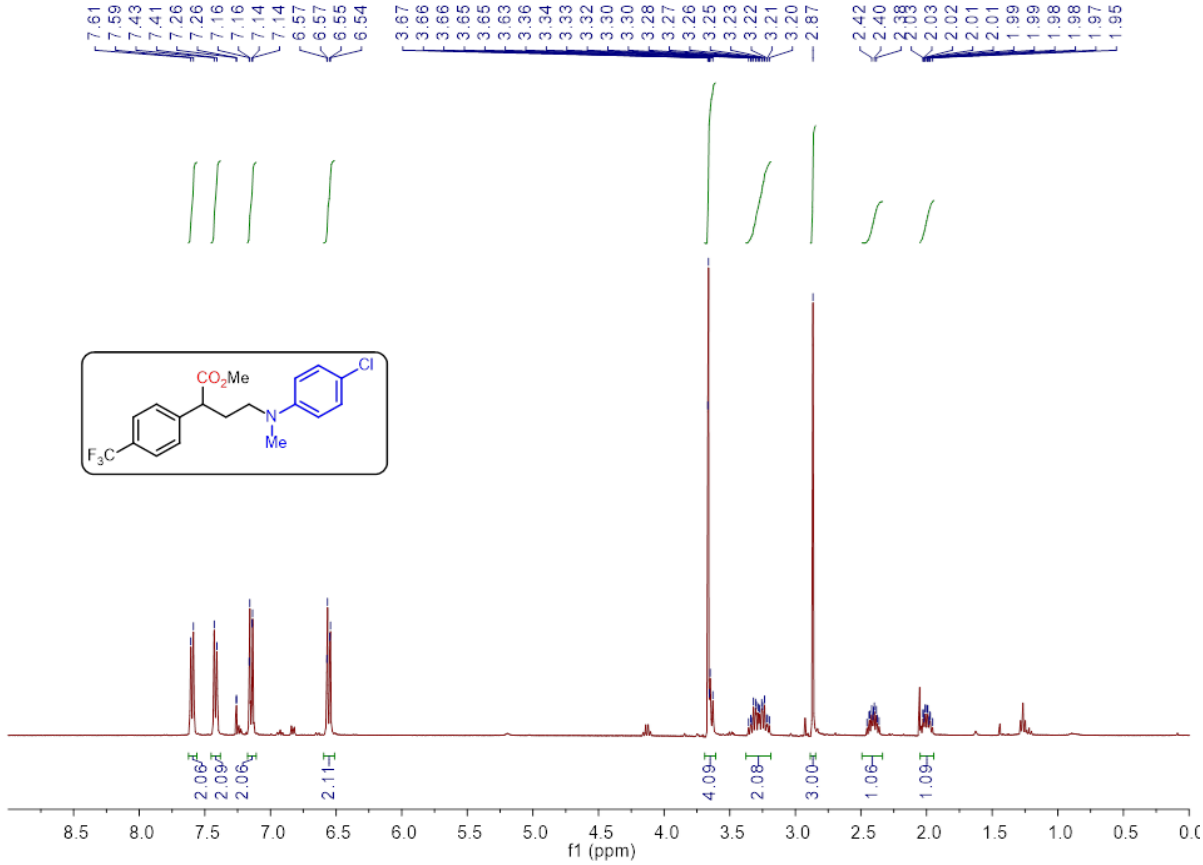
Methyl 4-((4-methoxyphenyl)(methyl)amino)-2-(4-(trifluoromethyl)phenyl)butanoate (3ke)

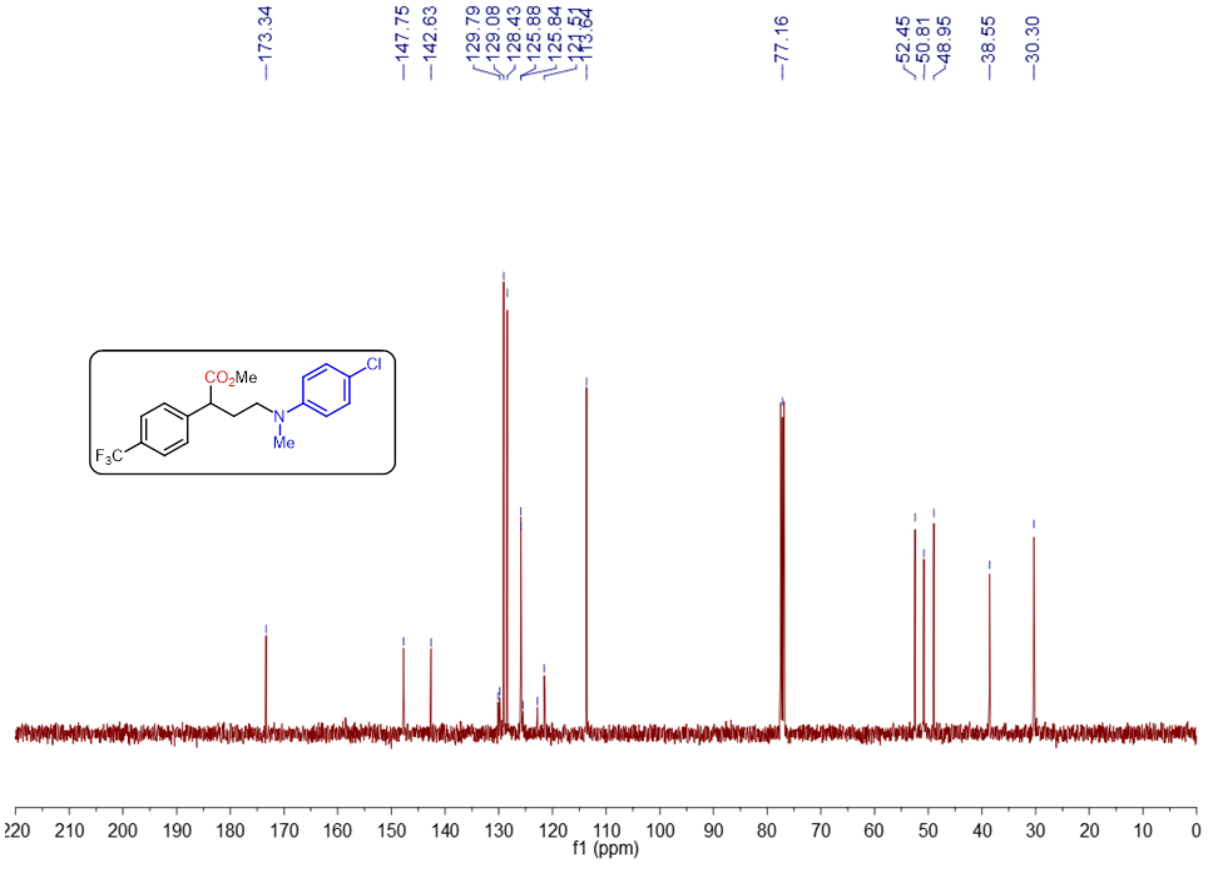


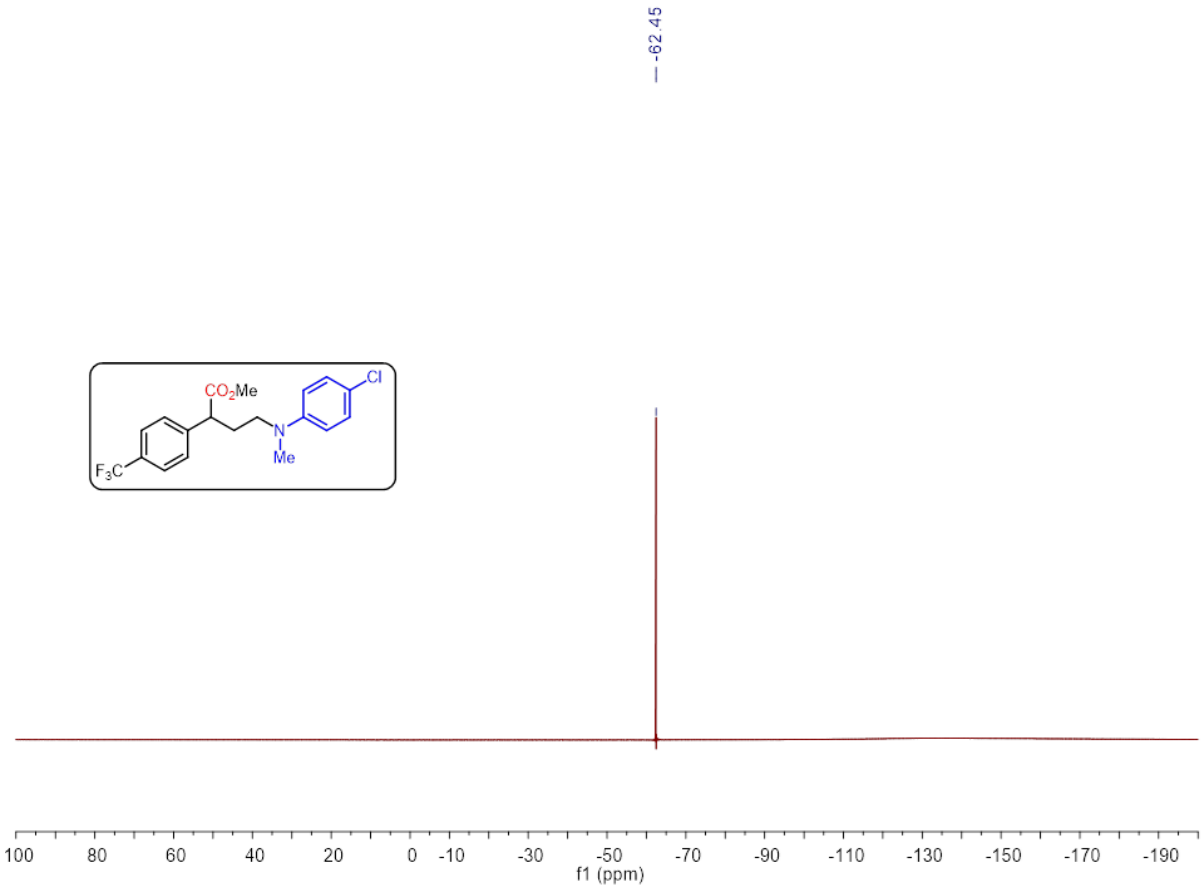



-62.43
CO2Me
OMe
N
Me
F3C
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

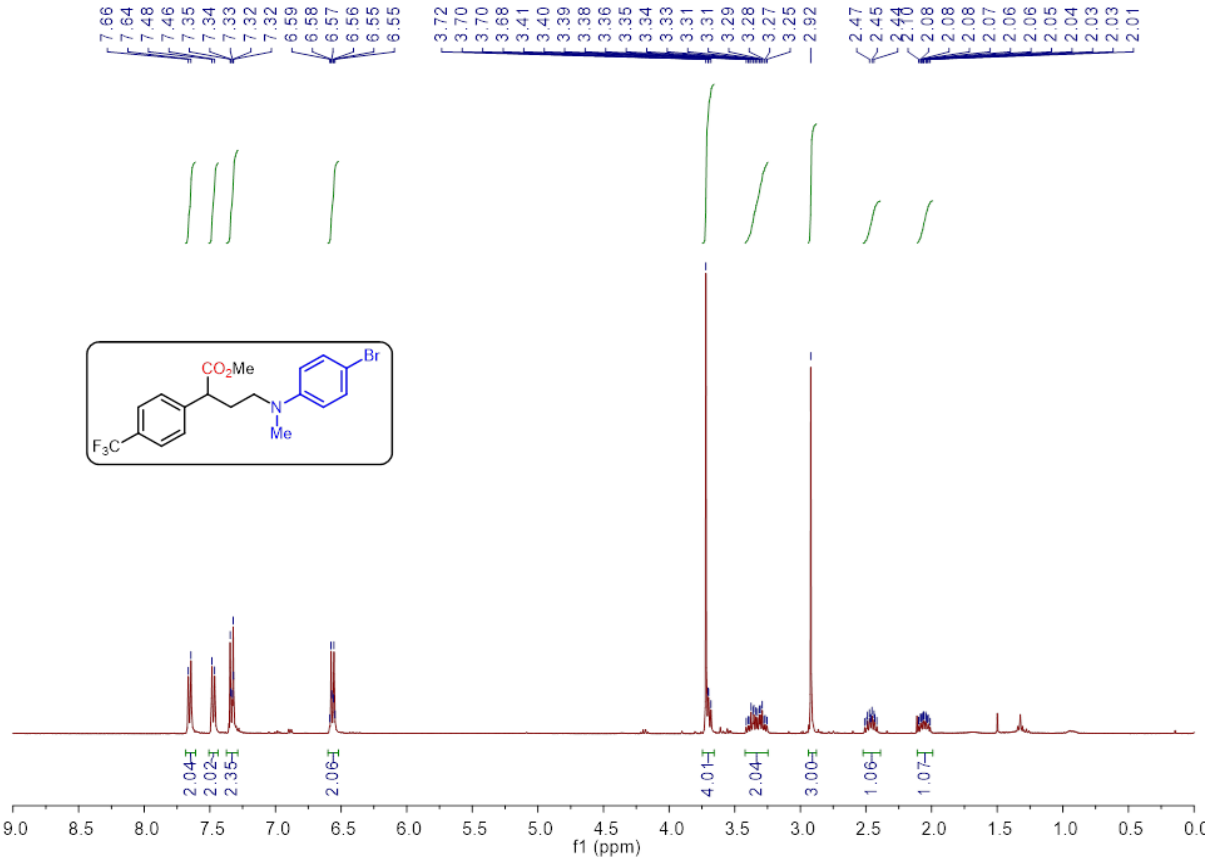
Methyl 4-((4-chlorophenyl)(methyl)amino)-2-(4-(trifluoromethyl)phenyl)butanoate (3kf)

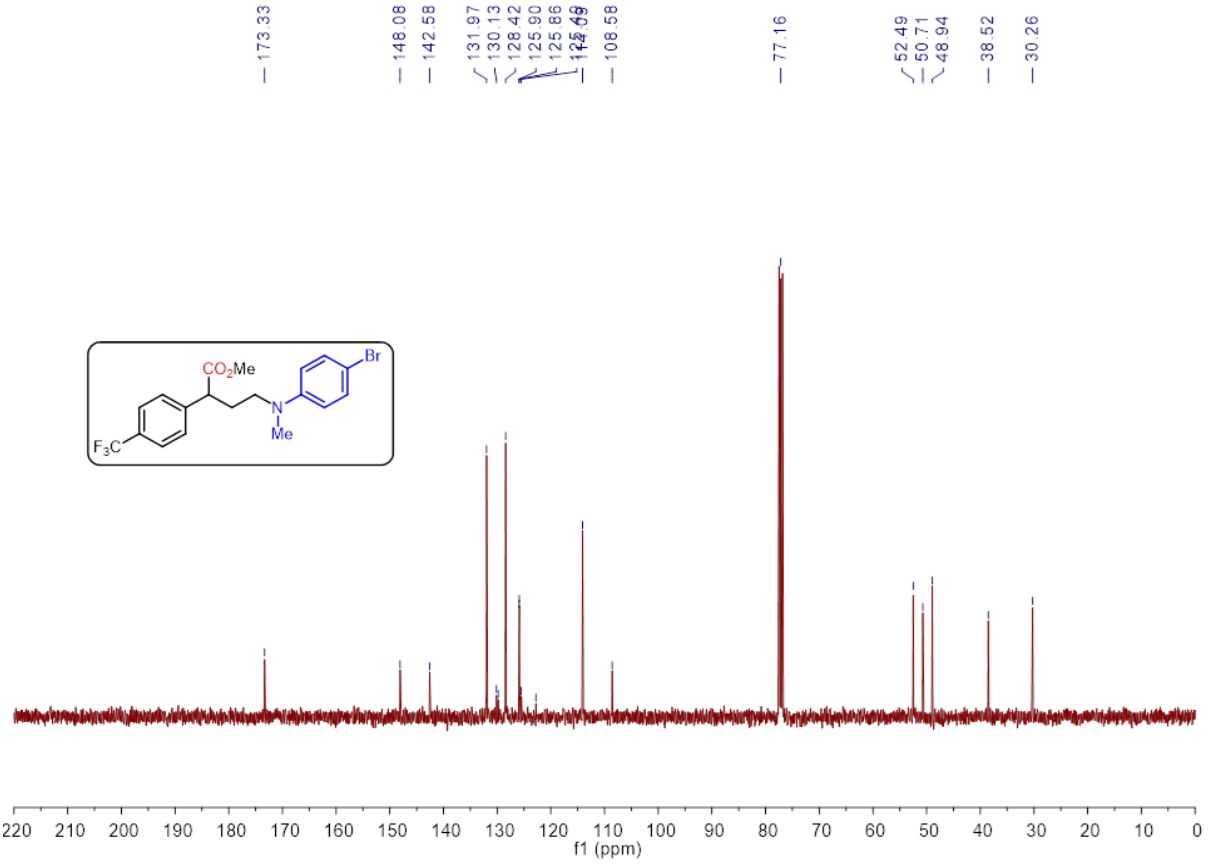


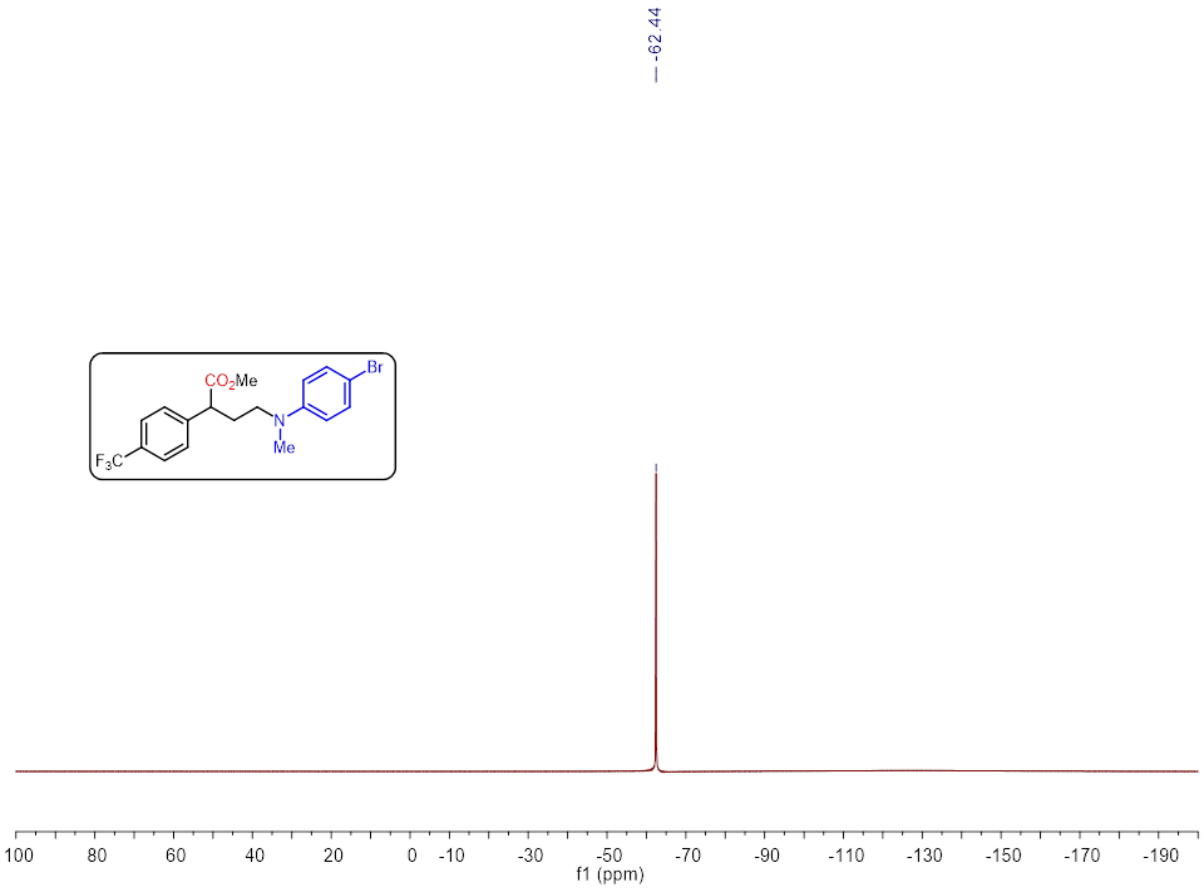



-62.45
CO2Me
Cl
N
Me
F3C
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

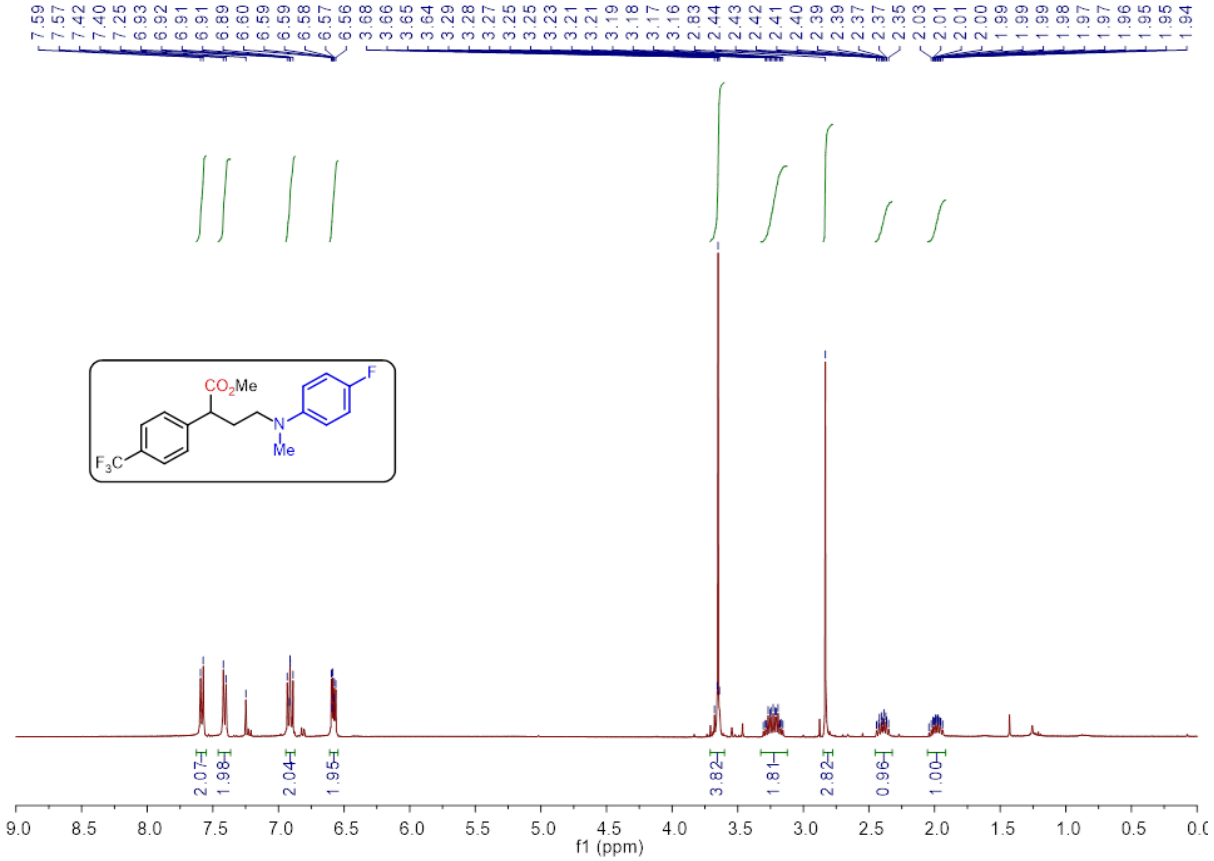
Methyl 4-((4-bromophenyl)(methyl)amino)-2-(4-(trifluoromethyl)phenyl)butanoate (3kg)

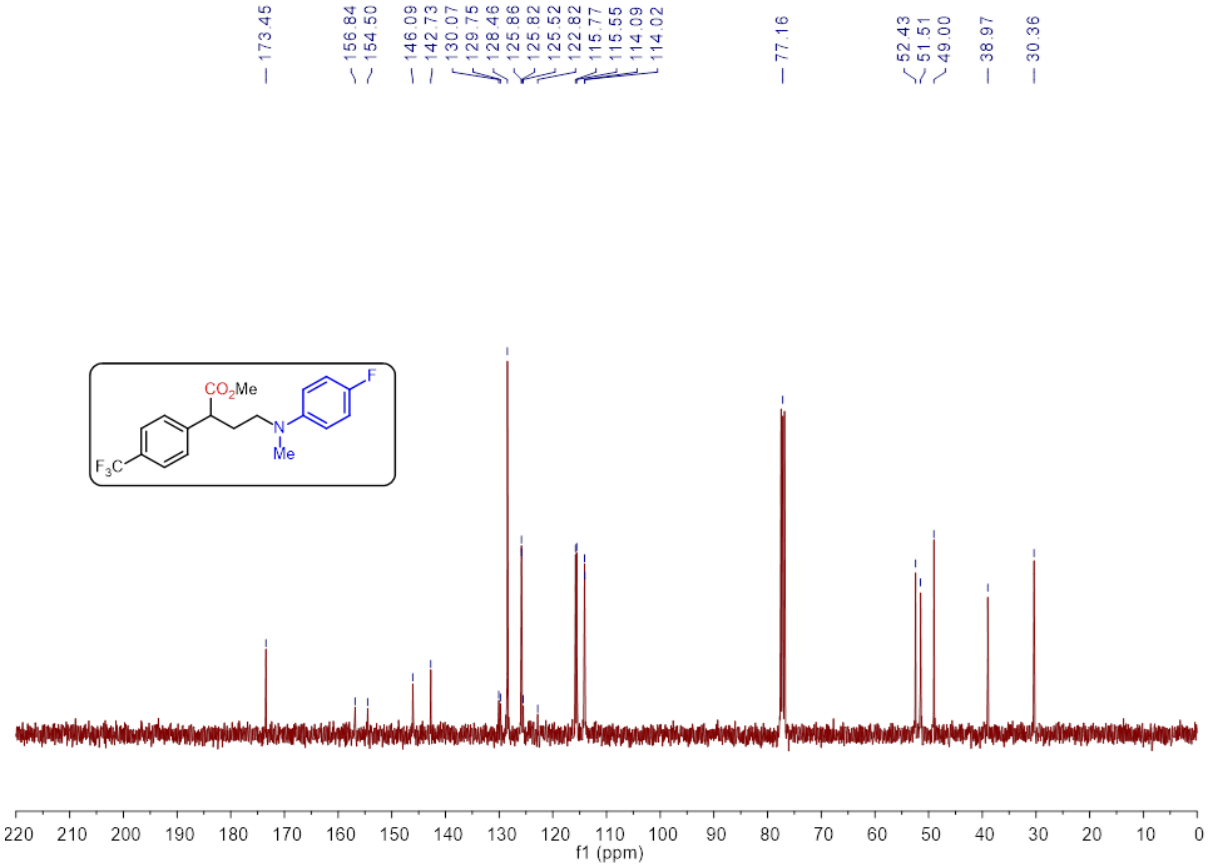


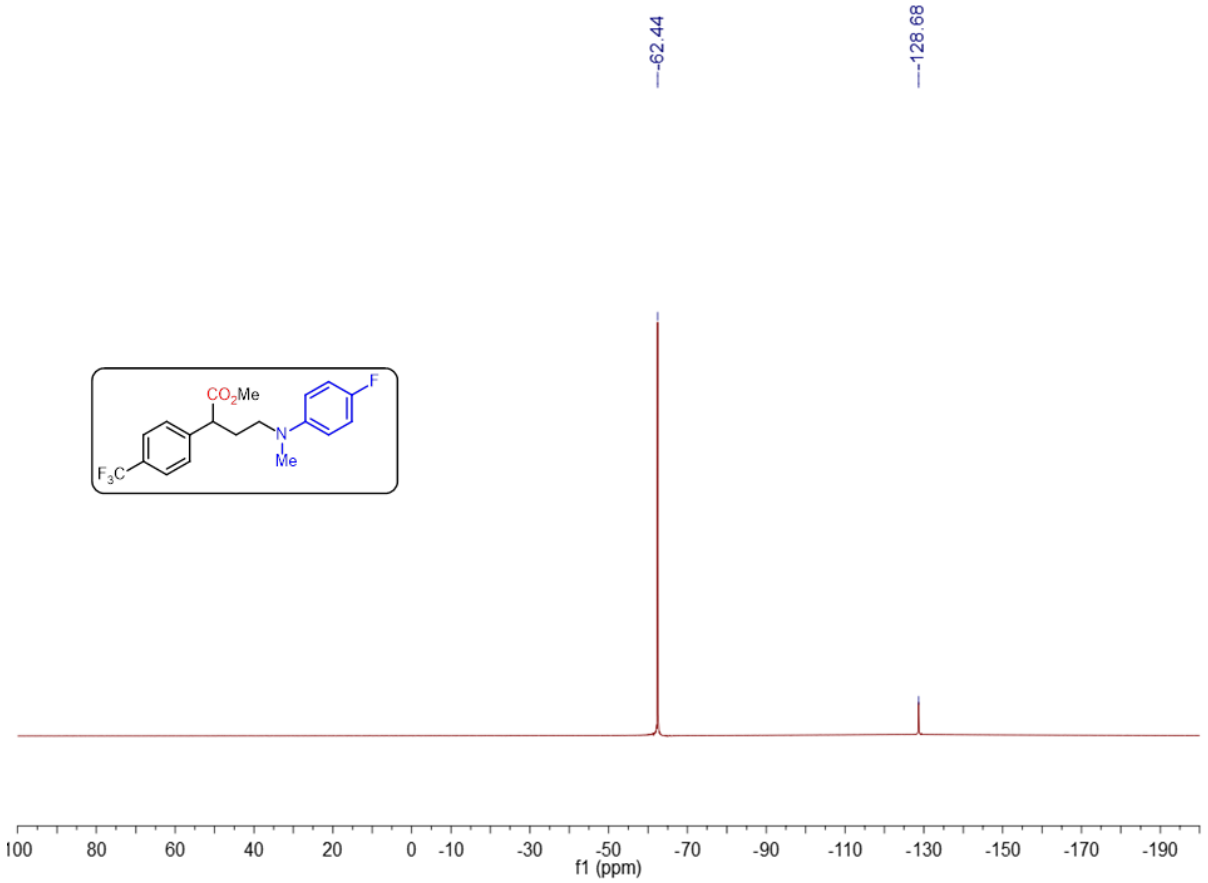



-62.44
CO2Me
Br
N
Me
F3C
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

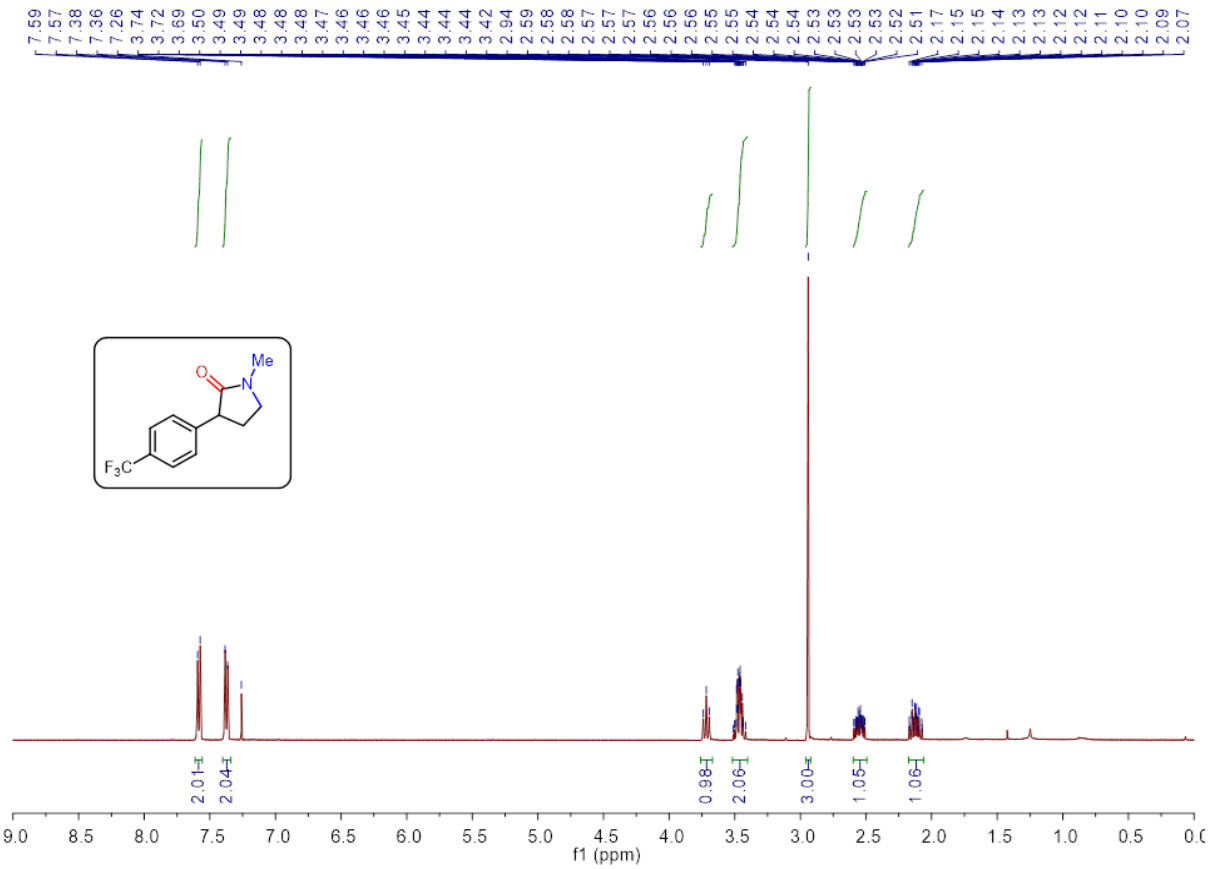
Methyl 4-((4-fluorophenyl)(methyl)amino)-2-(4-(trifluoromethyl)phenyl)butanoate (3kh)

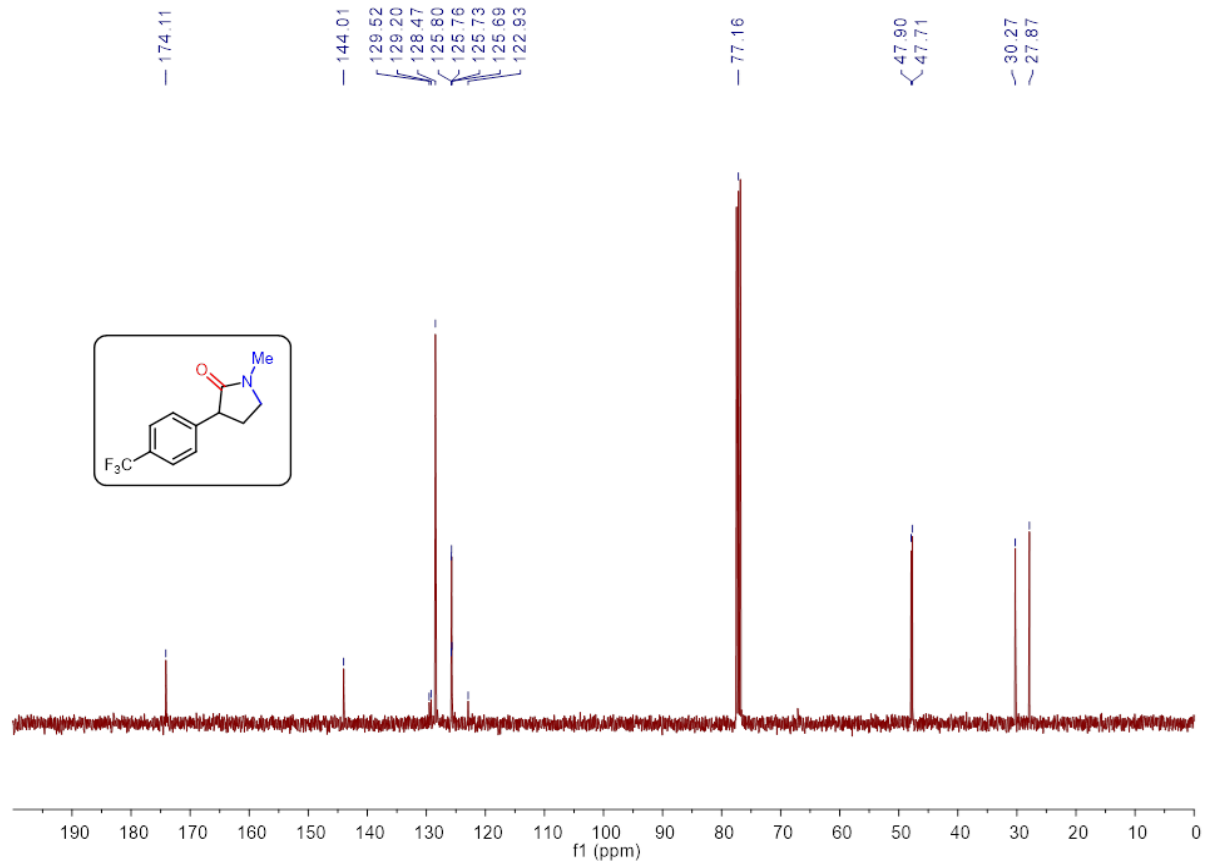


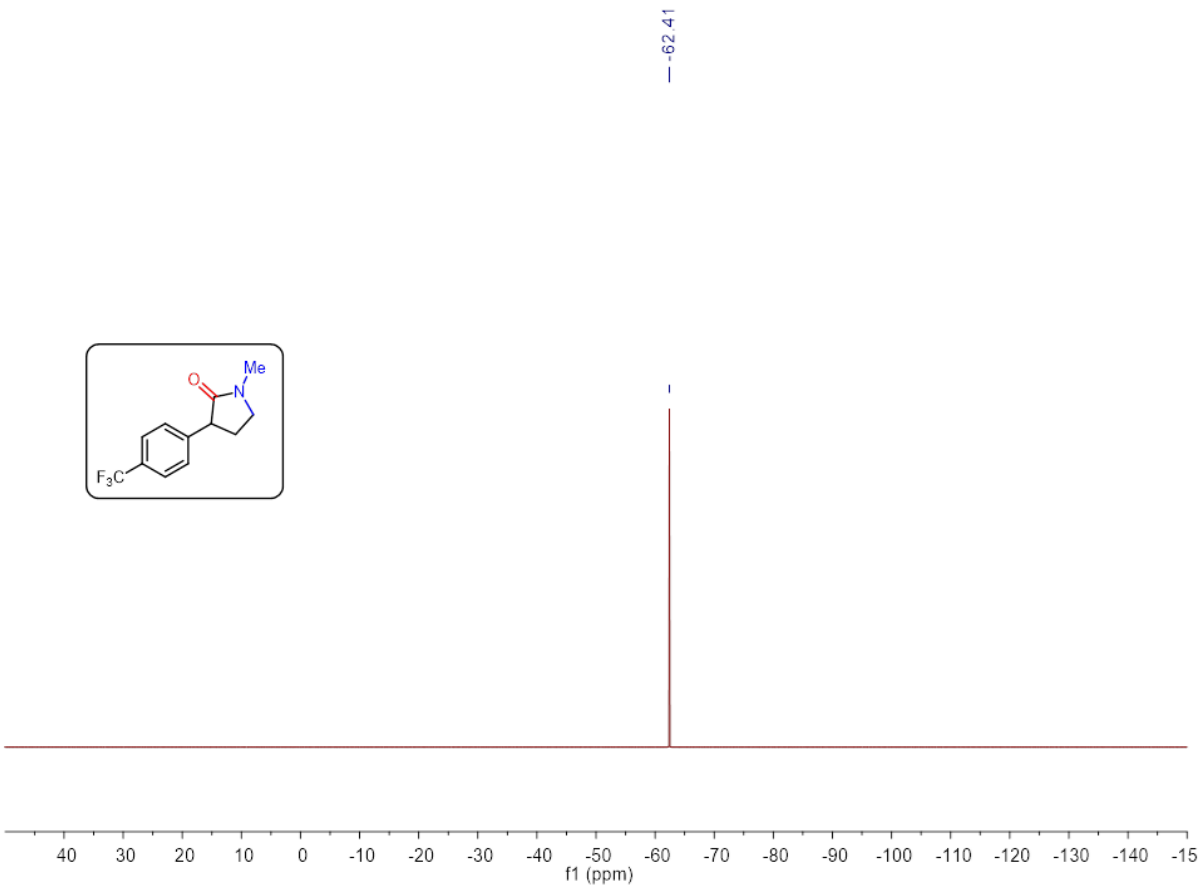



-62.44
-128.68
CO2Me
F
N
Me
F3C
100
80
60
40
20
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
f1 (ppm)

1-methyl-3-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (5)






-62.41
Me
O
N
F3C
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-15
f1 (ppm)