

Supporting Information

Eosin-Y/Cu(OAc)₂ Catalyzed Aerobic Oxidative Coupling Reaction of Glycine Esters in the Dark

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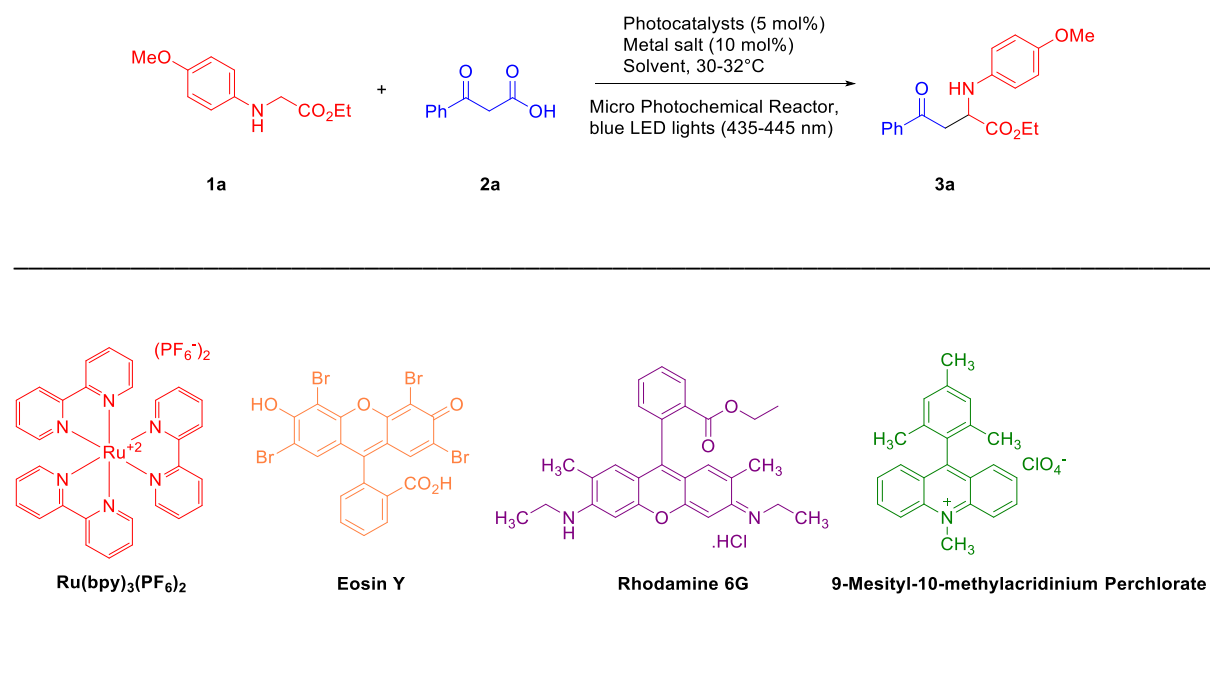
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1. General experimental

Solvent removal was performed with a rotary evaporator that was connected to a dry ice condenser. TLC was carried out using Merck TLC plate. Column chromatography was performed on silica gel (230-400 mesh). The ^1H and ^{13}C NMR spectroscopic data were recorded with 600 MHz (^1H NMR: 600 MHz, ^{13}C NMR: 150 MHz), 600 MHz (^1H NMR: 600 MHz, ^{13}C NMR: 150 MHz) Jeol spectrometer, 300 MHz (^1H NMR), and 800 MHz (^{13}C NMR: 200 MHz) Bruker spectrometer. The ^1H and ^{13}C chemical shifts are given in ppm (δ scale) and are measured relative to CHCl_3 (7.27 ppm) and CDCl_3 (77.0 ppm), respectively. High resolution mass spectra were recorded under ESI-Q-TOF conditions. Melting points (mp) were measured in a Büchi B-540 apparatus and uncorrected. ATR was recorded in Bruker tensor II. All the solvents were distilled out prior to use. Solvent were dried according to literature procedure. 1,2-dichloroethane was distilled over CaH_2 and stored over 4Å molecular sieves. Eosin Y (dye content~99%) was purchased from Sigma-Aldrich and used as received. Rhodamine 6G was purchased from sigma and used as received. $\text{Ru}(\text{bpy})_3\text{PF}_6$, Mes-Acr $^+\text{ClO}_4^-$ and Eosin Y disodium salt were purchased from TCI chemicals and used as received. $\text{Cu}(\text{OAc})_2$ was purchased from Merck and used as received. The electrochemical measurements were performed at room temperature ($T = 298\text{ K}$) using a CHI 760D electrochemical workstation in a conventional three-electrode cell. All electrodes are procured from CH Instruments, Inc. Pt ($\Phi = 2\text{ mm}$), Pt wire gauze and $\text{Ag}/\text{AgCl}/3\text{M KCl}$ ($E_{\text{Ag}/\text{AgCl}}^0 = +0.210\text{ V}$ vs. standard hydrogen electrode, SHE). XPS data was collected from X-ray photo-spectrometer and UPS model K-alpha (Make- M/s Thermo Fisher Scientific Instruments UK). Photochemical reactions were carried out in Aldrich® Micro Photochemical Reactor, blue LED lights (435-445nm). Ground-state absorption spectra were recorded with the help of UV-Visible Spectrophotometer (model# V-650) from JASCO.

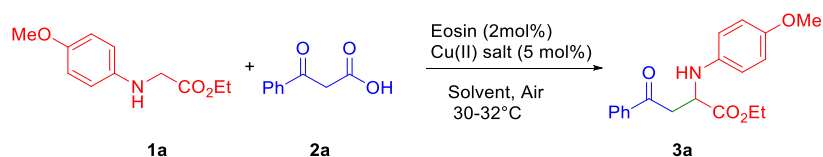
2. Table S1. Optimization study under blue light irradiation^a



Entry	Catalyst (mol%)	Metal Salt (mol%)	Time (h)	Solvent	Oxidant	3a^b
1 ^c	Ru(bpy) ₃ PF ₆ (5)	Cu(OAc) ₂ (10)	5+2	CH ₃ CN	O ₂ (balloon)	62
2	Eosin Y (5)	Cu(OAc) ₂ (10)	4+2	CH ₃ CN	O ₂ (balloon)	70
3 ^c	Rhodamine 6G (5)	Cu(OAc) ₂ (10)	24+2	CH ₃ CN	O ₂ (balloon)	48
4	Mes-Acr ⁺ ClO ₄ ⁻ (5)	Cu(OAc) ₂ (10)	8	DCE	Air	NR ^d
5	eosin-Y (5)	Cu(OAc) ₂ (10)	4+2	CH ₃ CN	Air	71
6	eosin-Y (5)	Cu(OAc) ₂ (10)	4+2	DCE	Air	78
7	eosin-Y (5)	Cu(OAc) ₂ (10)	4+2	Toluene	Air	69
8	eosin-Y (5)	CuSO ₄ ·5H ₂ O (10)	4+2	DCE	Air	58
9	eosin-Y (5)	FeSO ₄ ·7H ₂ O (10)	4+2	DCE	Air	50
10	eosin-Y (2)	Cu(OAc)₂ (5)	4+2	DCE	Air	77
11	-----	Cu(OAc) ₂ (5)	8	DCE	Air	NR
12	eosin-Y (2)	Cu(OAc) ₂ (5)	8+2	DCE	Argon	trace

^aTwo 4-mL clear glass vials (Supelco®) equipped with a PTFE septum and magnetic stirring bar, each one was charged with glycinate ester **1a** (0.2 mmol, ~42 mg) and photocatalyst (2-5 mol%). In each vial, dry solvent (1.0 mL) was added via syringe followed by addition of Cu(OAc)₂ (5-10 mol%). Then the reaction mixture was irradiated in Aldrich® Micro Photochemical Reactor, blue LED lights (435-445 nm) at a distance of 2 cm under air atmosphere at room temperature (30-32°C). Once the glycinate ester **1a** was consumed (monitored by TLC), the irradiation was stopped. Then, β-ketoacid **2a** (0.6 mmol) was added in one shot. The reaction mixture was further stirred for 2h without irradiation. After completion of the reaction (monitored by TLC), the reaction mixture (combined both the vials) was directly loaded to column and purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to afford product **3a**. ^b Isolated yield after column chromatography. ^c Incomplete reaction (first step). ^dNo imine formation, only starting material.

Table S2. Optimization study in the dark^a



Entry	Eosin Y (mol%)	Cu(II) Salt (mol%)	Solvent	Time (h)	3a ^b
1	eosin-Y (2)	Cu(OAc) ₂ (5)	DCE	8+2	78
2	eosin-Y (2)	Cu(OAc) ₂ (5)	CH ₃ CN	8+2	73
3	eosin-Y (2)	Cu(OAc) ₂ (5)	Toluene	8+2	75
4	eosin-Y (2)	Cu(OAc) ₂ (5)	C ₆ H ₅ CF ₃	8+2	72
5	eosin-Y (2)	CuSO ₄ ·5H ₂ O (5)	DCE	8+2	70
6	eosin-Y (2)	CuCl ₂ (5)	DCE	8+2	74
7 ^c	eosin-Y (2)	Cu(OAc) ₂ (5)	DCE	8+2	68

8 ^d	eosin-Y (4)	Cu(OAc) ₂ (10)	DCE	8+2	77
9 ^{e,f}	eosin-Y (2)	-	DCE	8+2	24
10 ^g	-	Cu(OAc) ₂ (5)	DCE	8+2	NR
12 ^h	eosin-Y (2)	Cu(OAc) ₂ (5)	DCE	8	NA ^h

^aUnless otherwise stated, reactions were carried out with 0.4 mmol of **1a**, eosin-Y (2 mol%), Cu(II) salt (5 mol%), solvent (2 mL) under dark in air for 8h at 30-32 °C, then **2a** (0.6 mmol) was added and stirred for another 2h. ^bIsolated yield of the product after column chromatography. ^c20 mol% of Et₃N was added after the addition of β-ketoacid **2a**. ^dthe reaction was carried out using 4 mol% eosin Y. ^ethe reaction was carried out using freshly dried DCE. ^ffirst step of the reaction remained incomplete and the yield of the first step is not reproducible. ^gthe reaction was conducted in absence of eosin Y, no imine formation was observed. ^h A 4-mL clear glass vials equipped with a PTFE septum and magnetic stirring bar was charged with glycinate ester **1a** (0.4 mmol, ~84 mg), Eosin Y (2 mol%) and Cu(OAc)₂ (5 mol%). The vial was wrapped in aluminium foil and degassed for 50 min by bubbling argon stream. Then under argon atmosphere, dry degassed DCE (1.0 mL) was added via syringe and the reaction mixture was stirred for 8h. small amount of imine formation was observed. (both the reaction mixture and DCE were degassed for 50 min by bubbling argon stream).

[#]It should be noted the above reaction is super-sensitive to oxygen (air). Therefore, for oxygen free reactions, all the weighing of reagents and drying of DCE were carried out under argon atmosphere.

3. Experimental setup

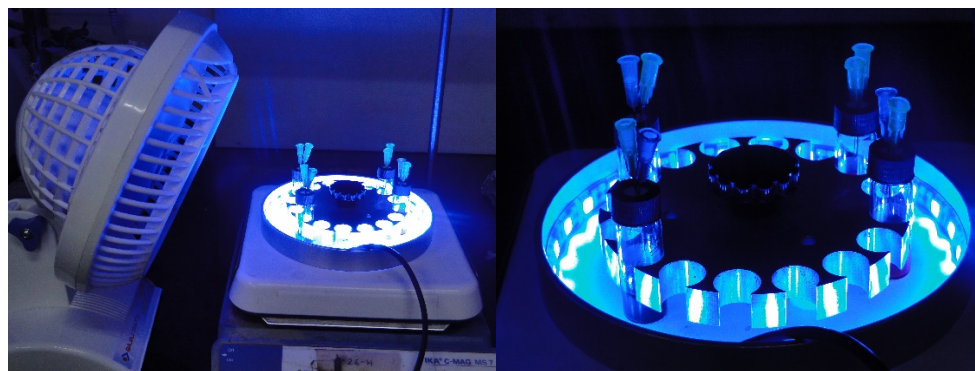


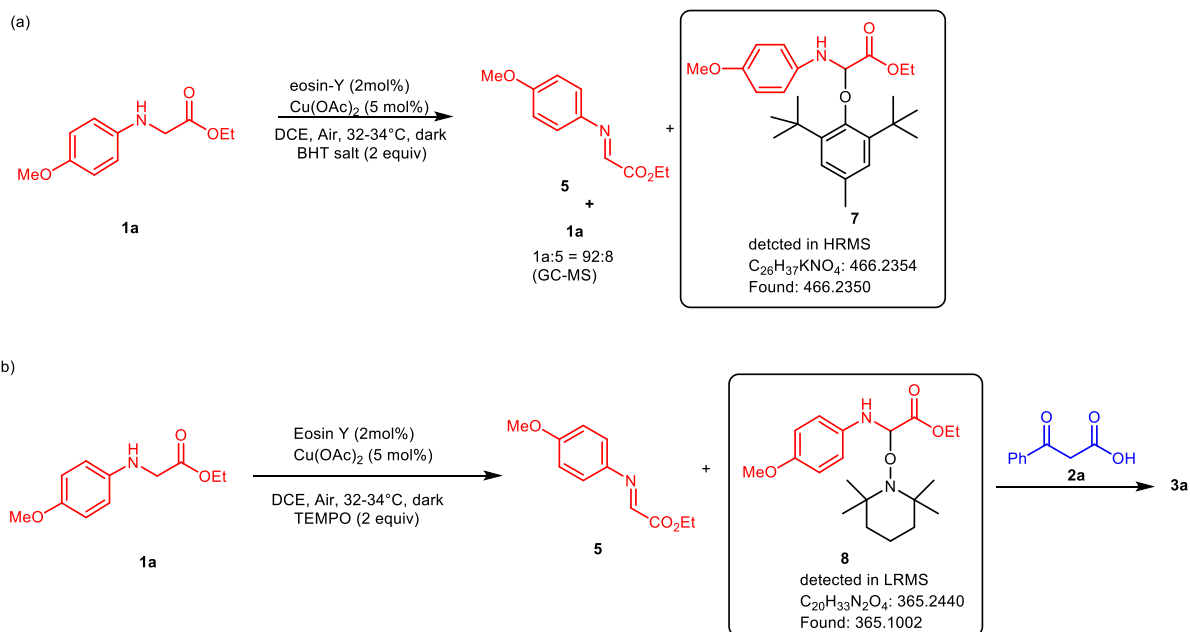
Figure S1: left: Reaction set-up used for the photochemical reaction. Right: Photoreactor (Aldrich® Micro Photochemical Reactor, blue LED lights, 435-445 nm) used in this study.

4. Mechanistic study

eosin-Y/Cu(OAc)₂ complex catalysed reaction

When the radical scavenger 2,6-di-tert-butyl-4-methylphenol (BHT) was added into the solution of **1a** under standard reaction conditions (**Scheme S1a**), very small amount of imine intermediate **5** was observed (**1a/5** = 92:8) and the BHT trapped product **7** was detected in HRMS (**Figure S2**). However, when the reaction of **1a** was carried out in presence of radical scavenger TEMPO (2.0 equiv), desired imine intermediate **5** was formed as the major product and at the same time TEMPO addition adduct **8** was identified in mass-spectrometry (**Figure S3**). Addition of β -ketoacid **2a** to this solution and stirring for 2h, the desired product **3a** was isolated with 71% yield (**Scheme S1b**). Probably, TEMPO is involved in the catalytic cycle^{1,2} which facilitated the imine **5** formation.

These facts indicate that a radical process may be involved in this first step of this method.



Scheme S1: Mechanistic experiments

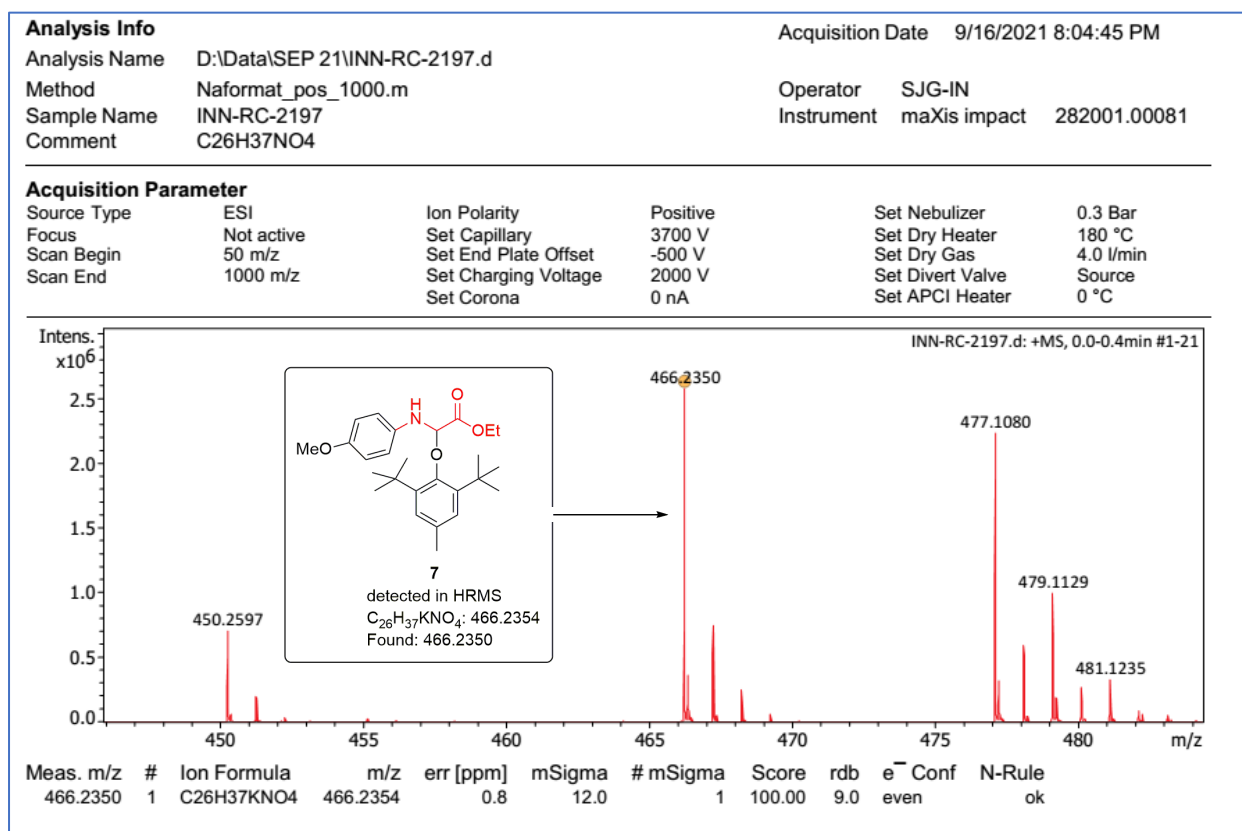


Figure S2: HRMS analysis of the reaction mixture (1a, BHT salt under standard reaction conditions)

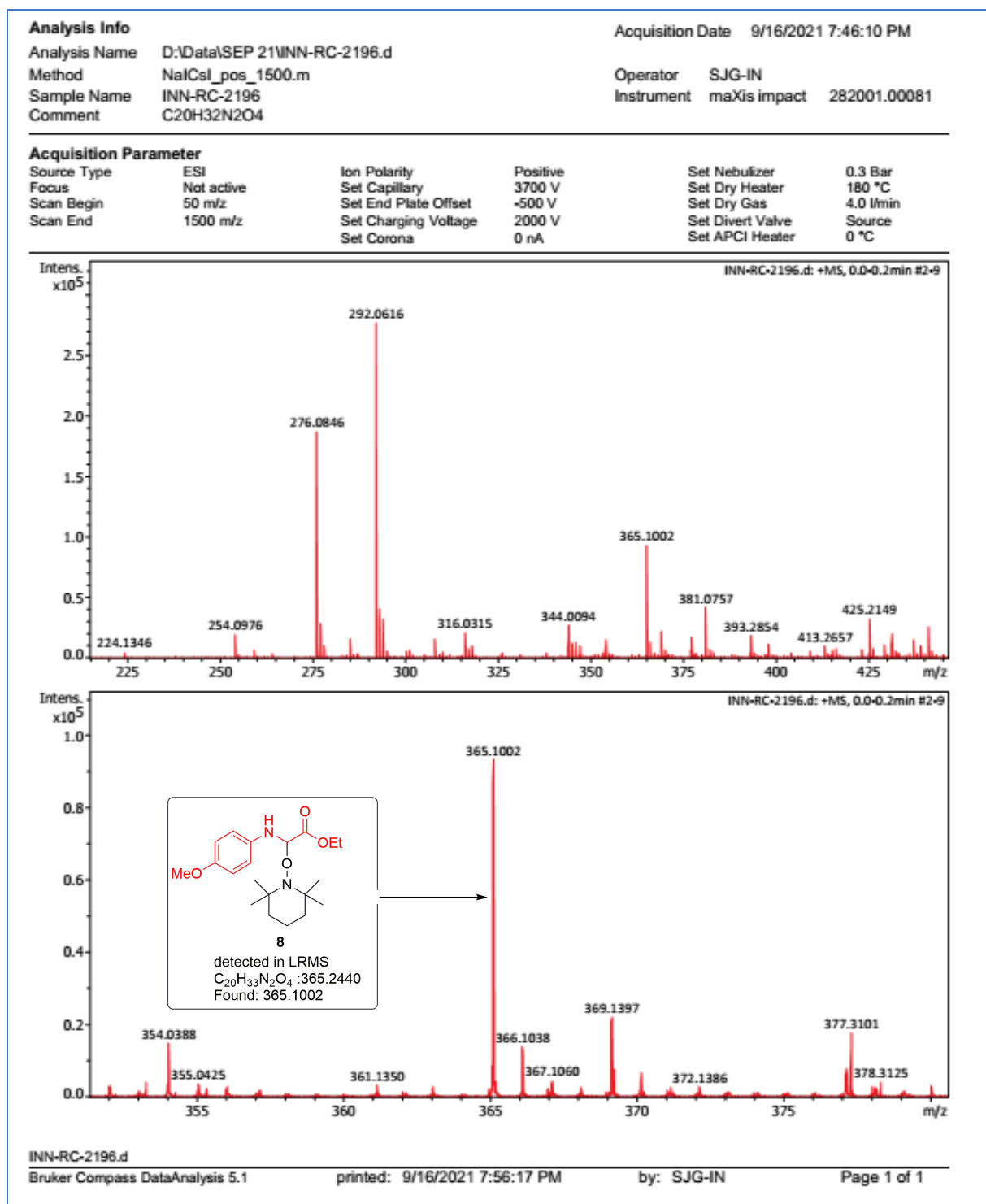


Figure S3: LRMS analysis of the reaction mixture (**1a**, TEMPO under standard reaction conditions)

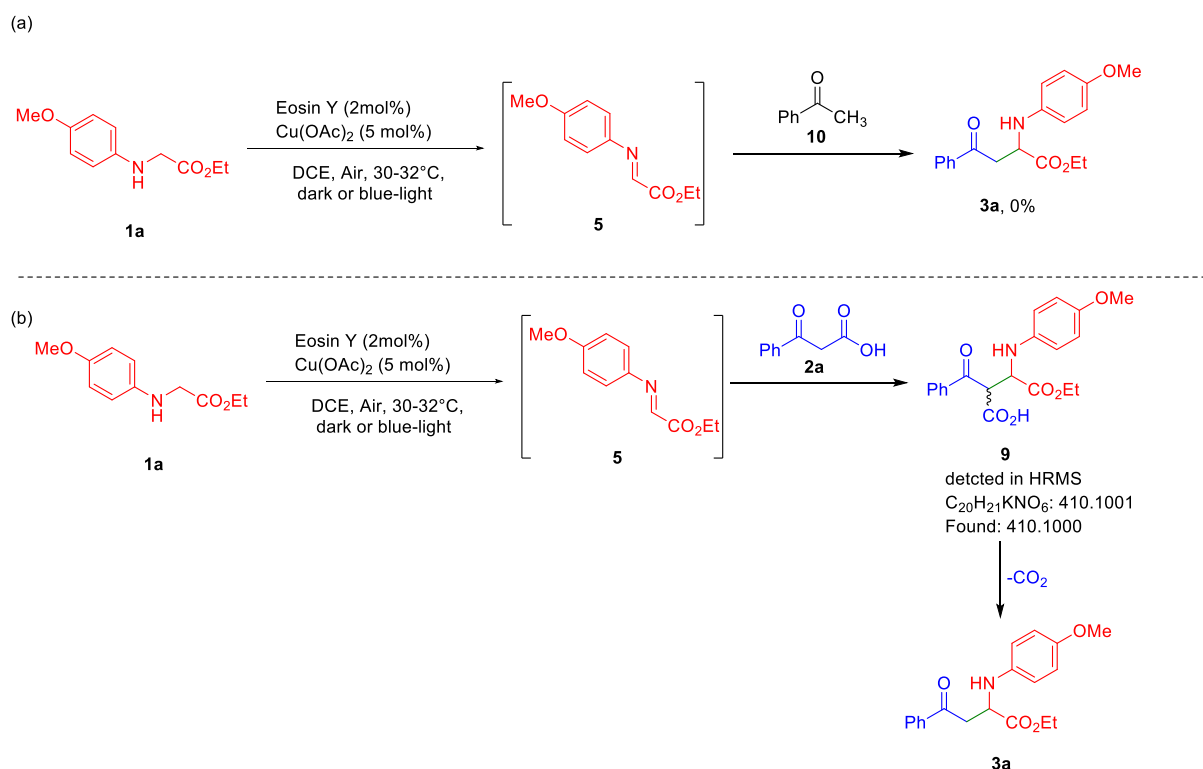
Next, effort was given to probe the decarboxylation step since there is feasibility of two reaction pathway-(i) nucleophilic addition of β -ketoacid to imine **5** followed by decarboxylation or (ii)

decarboxylation of β -ketoacid to form ketone enolate equivalent and subsequent addition to the imine **5**.

Stirring the solution of **1a** in presence of eosin-Y (2 mol%) and $\text{Cu}(\text{OAc})_2$ in DCE under air in dark or irradiation of light for 8 h followed by addition of 1.5 equivalent of acetophenone **10**, the product **3a** was not observed (**Scheme S2a**).

In situ electrospray ionization mass spectroscopy analysis of the reaction mixture (**1a**, **2a** in presence of eosin-Y 2 mol% and $\text{Cu}(\text{OAc})_2$ in DCE) under standard reaction conditions (**Scheme S2b**), the peak at m/z 410.1001 was observed which correspond to the adduct **9**+K (**Figure S4**).

These experimental finding suggested that the reaction operates by nucleophilic addition of β -ketoacid **2a** to imine **5** and subsequent decarboxylation step.



Scheme S2: Mechanistic experiments.

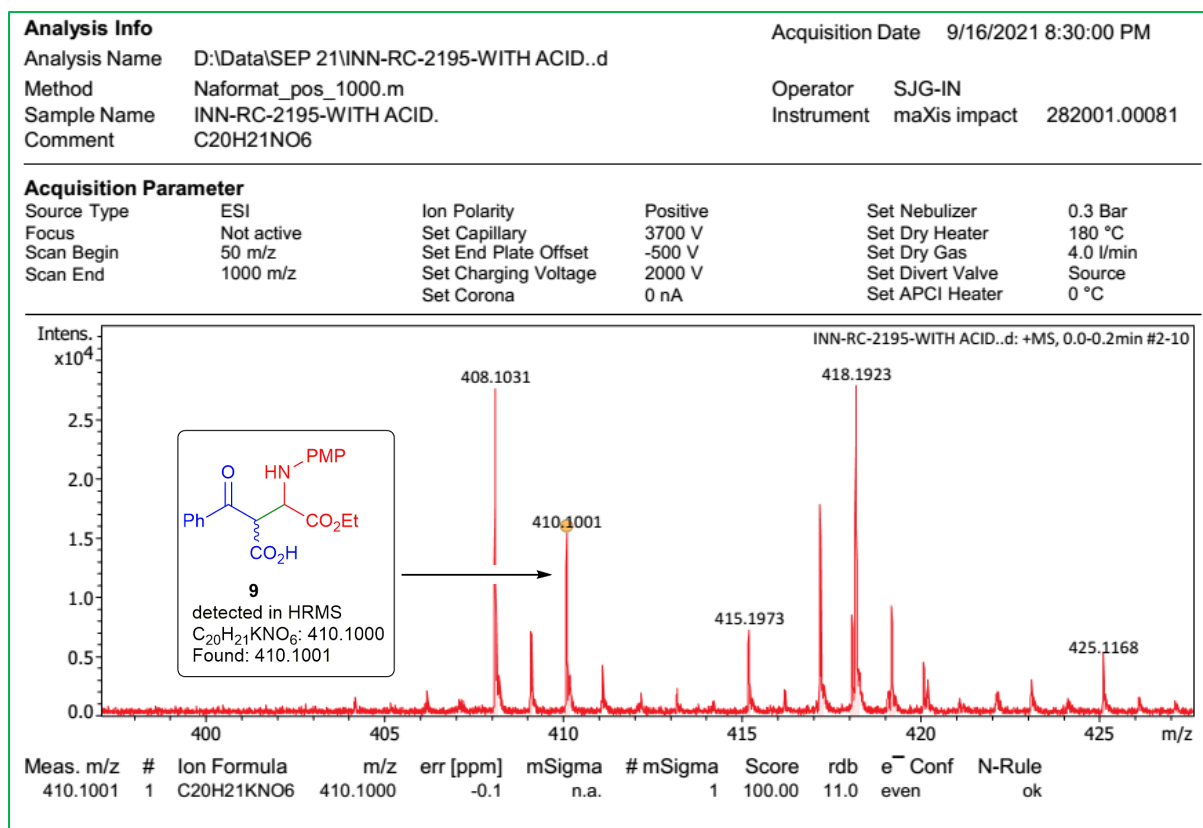


Figure S4: HRMS analysis of the reaction mixture (**1a**, **2a** under optimized conditions)

Detection of H₂O₂ in the reaction mixture:³

To an oven dried 25mL round bottom flask (wrapped in aluminium foil) with a magnetic stirring bar were added glycinate ester **1** (0.8 mmol, 1 equiv) and eosin Y (10.2 mg, 0.008 mmol, 2 mol%). Then 4mL of dry DCE was added via syringe followed by addition of Cu(OAc)₂ (7.32 mg, 5 mol%). The reaction mixture was stirred (for 8h) under air at room temperature (25-27 °C). After completion of the reaction, the reaction mixture was poured into a separatory funnel and dichloromethane (60 ml) was added. This organic phase was extracted with distilled water (4×20 mL). The combined aqueous solution was passed through activated charcoal followed by celite. To this aqueous solution, 2 M H₂SO₄ (6 ml) and aqueous solution of KI (0.8 mmol in 5 mL H₂O) were added and stirred well. Then, 3mL of freshly prepared starch solution was added and stirred vigorously. Within 2-3 min, the aqueous solution turned to deep blue color.

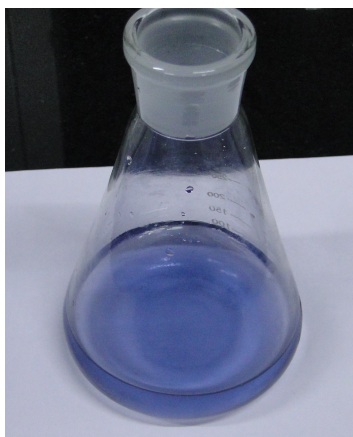
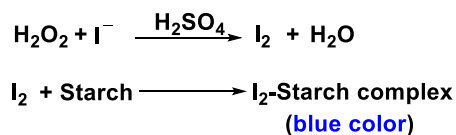


Figure S5: Detection of H_2O_2 via KI-Starch experiment

5. UV-Vis absorption spectra

The titration of eosin Y with $\text{Cu}(\text{OAc})_2$ was carried out. It was observed that with progressive addition of $\text{Cu}(\text{OAc})_2$, the λ_{max} of eosin Y increases (**Figure S6**). This may be due to chelation of $\text{Cu}(\text{II})$ with eosin-Y.⁴

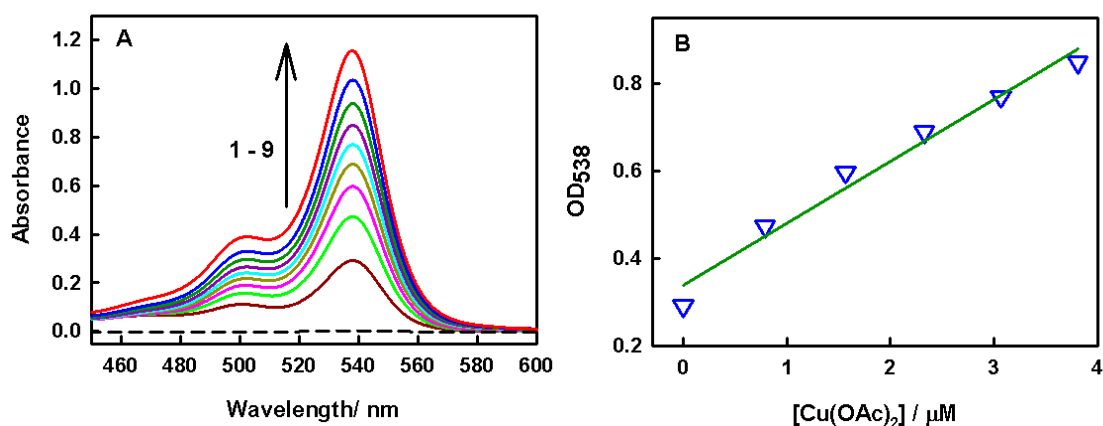


Figure S6: (A) Ground-state absorption spectra of 40 μM eosin-Y in acetonitrile (degassed) with increasing concentrations of $\text{Cu}(\text{OAc})_2$ (1) 0 μM (2) 0.79 μM (3) 1.57 μM (4) 2.3 μM (5) 3.1 μM (6) 3.8 μM (7) 5.2 μM (8) 6.6 μM (9) 10.4 μM . The dashed black line represents the absorption spectrum of 10.4 μM $\text{Cu}(\text{OAc})_2$ in acetonitrile. (B) Variation in the absorbance of

Eosin-Y at 538 nm with increasing concentrations of $\text{Cu}(\text{OAc})_2$. The solid green line represents the linear fit to the data points. $\text{OD}_{538} = 0.14 [\text{Cu}(\text{OAc})_2] / \mu\text{M} + 0.34$, $R^2 = 0.968$.

On the other hand, the interaction of glycine ester **1a** with ground state of eosin-Y was also observed (**Figure S7**) but it is less significant compared to the interaction of $\text{Cu}(\text{OAc})_2$ with eosin-Y.

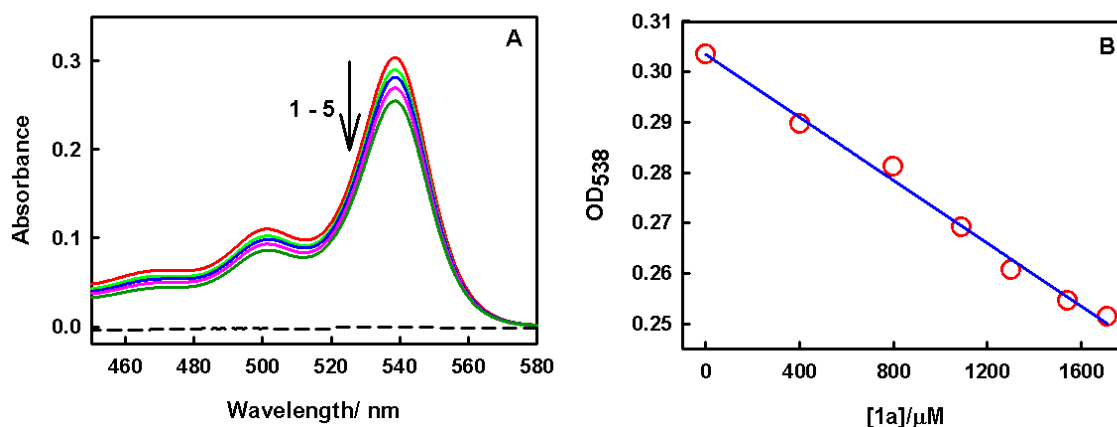


Figure S7: (A) Ground-state absorption spectra of 40 μM eosin-Y in acetonitrile (degassed) with increasing concentrations of **1a** (1) 0 μM (2) 400 μM (3) 800 μM (4) 1090 μM (5) 1540 μM . The dashed black line represents the absorption spectrum of 1540 μM **1a** in acetonitrile. (B) Variation in the absorbance of eosin-Y at 538 nm with increasing concentrations of **1a**. The solid blue line represents the linear fit to the data points. $\text{OD}_{538} = -3.12 \times 10^{-5} [1a] / \mu\text{M} + 0.303$, $R^2 = 0.991$.

Moreover, we found that with progressive addition of glycine ester **1a** into eosin-Y solution (40 μM in CH_3CN), the λ_{max} of eosin-Y decreases slightly. When $\text{Cu}(\text{OAc})_2$ solution (80 μM solution in CH_3CN) was added to the mixture of glycine ester **1a** and eosin-Y, the λ_{max} of eosin-Y increases to a significant amount (**Figure S8**). These experimental observations disclose that the chelation of eosin-Y with $\text{Cu}(\text{OAc})_2$ was stronger than that of with the glycine ester **1a**.

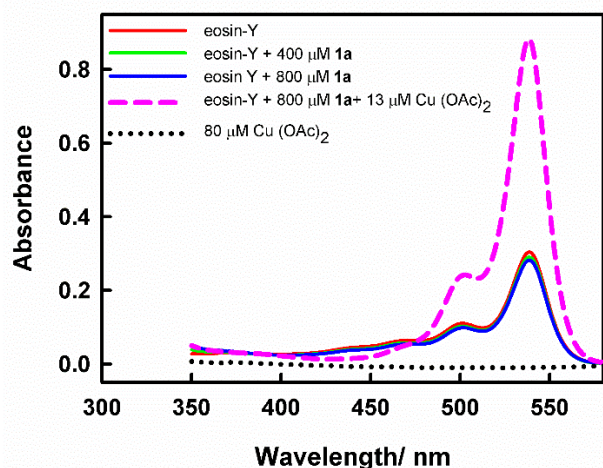


Figure S8: The UV-vis absorption spectra of eosin-Y, eosin-Y+ glycine ester **1a** and eosin-Y+ glycine ester **1a** + Cu(OAc)₂

6. Cyclic Voltammograms

The electrochemical measurements are performed at room temperature ($T = 298$ K) using a CHI 760D electrochemical workstation in a conventional three-electrode cell. All electrodes are procured from CH Instruments, Inc. Pt ($\Phi = 2$ mm), Pt wire gauze and Ag/AgCl/3M KCl ($E_{Ag/AgCl}^0 = +0.210$ V vs. standard hydrogen electrode, SHE) electrodes are used as the working, counter and the reference electrode, respectively. Unless specified, all the potentials quoted are with respect to Ag/AgCl. High purity argon gas is purged through the working solutions for 10 minutes to expel dissolved oxygen from solution prior to electrochemical experiments. The Pt working electrode which was cleaned electrochemically by repetitive CV scan (-0.5 to 1.5 V) in 1 M H_2SO_4 at a scan rate of 100 $mV\ s^{-1}$ (20–30 cycles).

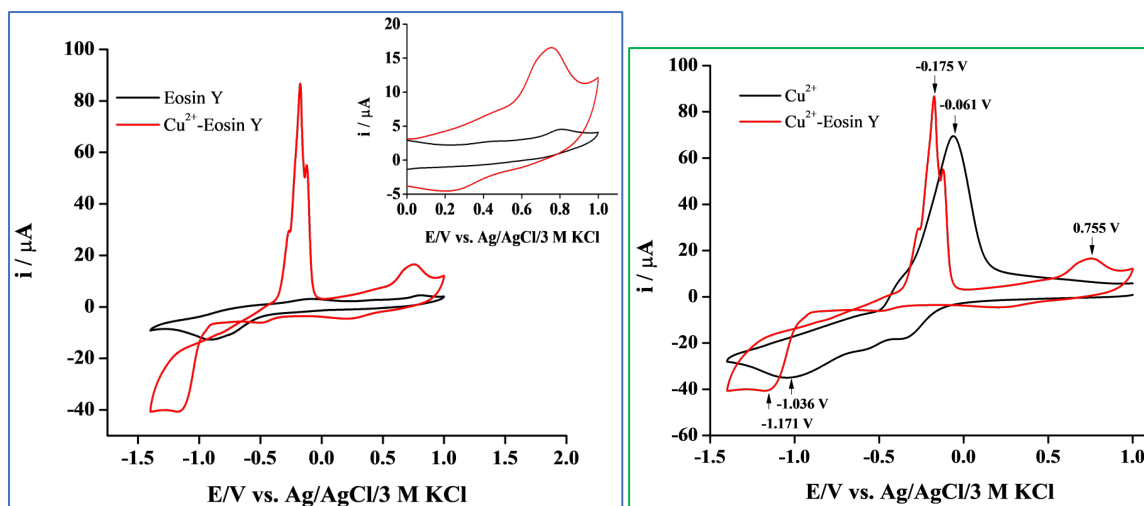


Figure S9. Left. Cyclic Voltammograms of Eosin Y (black line) 2×10^{-3} mol/L. The mixture of 2×10^{-3} mol/L eosin Y and 5×10^{-3} mol/L $\text{Cu}(\text{OAc})_2$ (red line) in 0.1 M tetrabutyl ammonium hexafluorophosphate in acetonitrile using Pt electrode at a scan rate of 100 mV s^{-1} . Right: Cyclic Voltammograms of 5×10^{-3} mol/L $\text{Cu}(\text{OAc})_2$ (black line). The mixture of 2×10^{-3} mol/L eosin Y and 5×10^{-3} mol/L $\text{Cu}(\text{OAc})_2$ (red line) in 0.1 M tetrabutyl ammonium hexafluorophosphate in acetonitrile using Pt electrode at a scan rate of 100 mV s^{-1}

The Eosin Y shows an oxidation peak at 0.812 V. On the other hand, the same amount of eosin-Y/ $\text{Cu}(\text{OAc})_2$ mixture shows almost at the same peak (0.755V) with much higher peak current density (**Figure S9**, Left, insert shows the zoomed portion,). No such peak was observed in the CV of $\text{Cu}(\text{OAc})_2$ (**Figure S9**, right). Therefore, the enhancement in the peak current density may be due to chelation of eosin-Y with $\text{Cu}(\text{OAc})_2$.

7. XPS study of the eosin-Y/ $\text{Cu}(\text{OAc})_2$ mixture

Preparation of eosin-Y/ $\text{Cu}(\text{OAc})_2$ mixture: In a 100 mL oven dried round bottom flask equipped with a magnetic stirring bar and rubber septum, eosin-Y (64.7 mg, 0.1 mmol) and $\text{Cu}(\text{OAc})_2$ (20 mg, 0.1 mmol) were taken. The flask was degassed and then dry DCE (25 ml) was added to the reaction flask under argon balloon. The solution was then stirred at room temperature for 1h at room temperature (24-25 °C). Next, 5 mL CH_3CN was added and the reaction mixture was stirred for another 30 minutes.

After that, solvent was removed in rotary evaporator. The residue was dried in vacuum and was used for XPS analysis.

X-ray photoelectron spectroscopic (XPS) analysis was carried out to elucidating the oxidation state of copper in the eosin-Y/Cu(OAc)₂ mixture (**Figure S10**). XPS detected the peak at 932.71 eV and 952.38 (**Figure S10**) which are characteristic binding energy values of Cu(I) 2p_{3/2} and Cu 2p_{1/2} and well-agreement with the reported values.⁴ Moreover, the reported binding energy of copper (2p_{3/2}) is 935.0 eV.^{5a} In the eosin-Y/Cu(OAc)₂ mixture, XPS detected the peak of Cu(II) 2p_{3/2} at 934.68. The shift of the peak of Cu(II) 2p_{3/2} from 935 eV to 934.68 is probably due to chelation of Cu(II) with eosin-Y.^{5b-c} The above experimental facts imply that there could be simultaneous formation of eosin-Y radical cation and Cu(I) from eosin-Y/Cu(OAc)₂ complex through inner-sphere electron transfer.

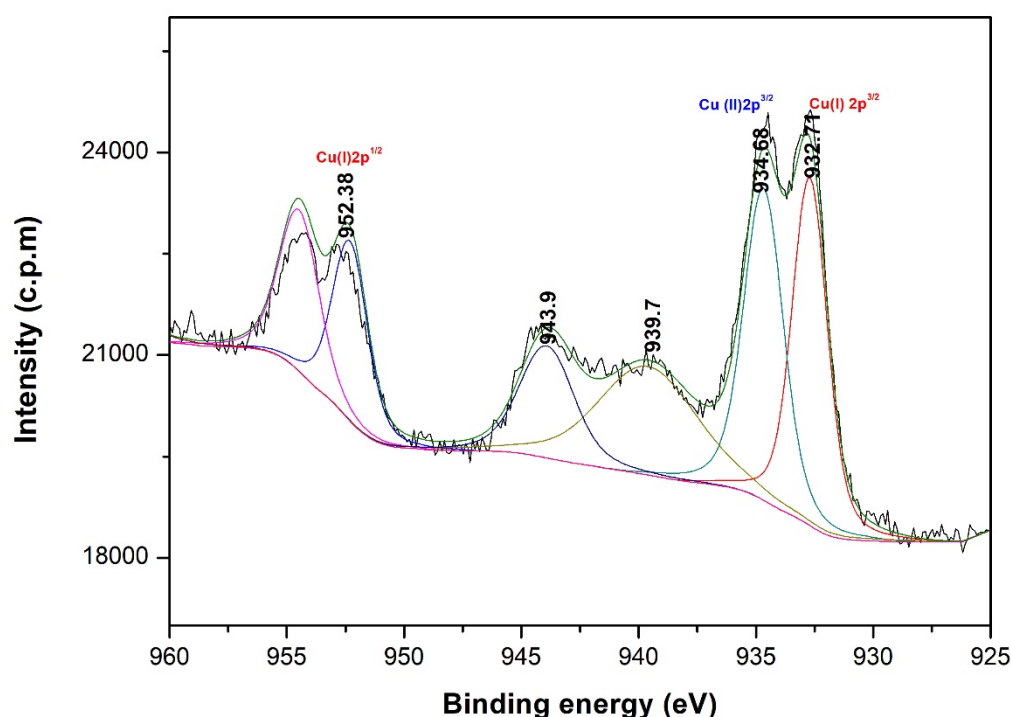
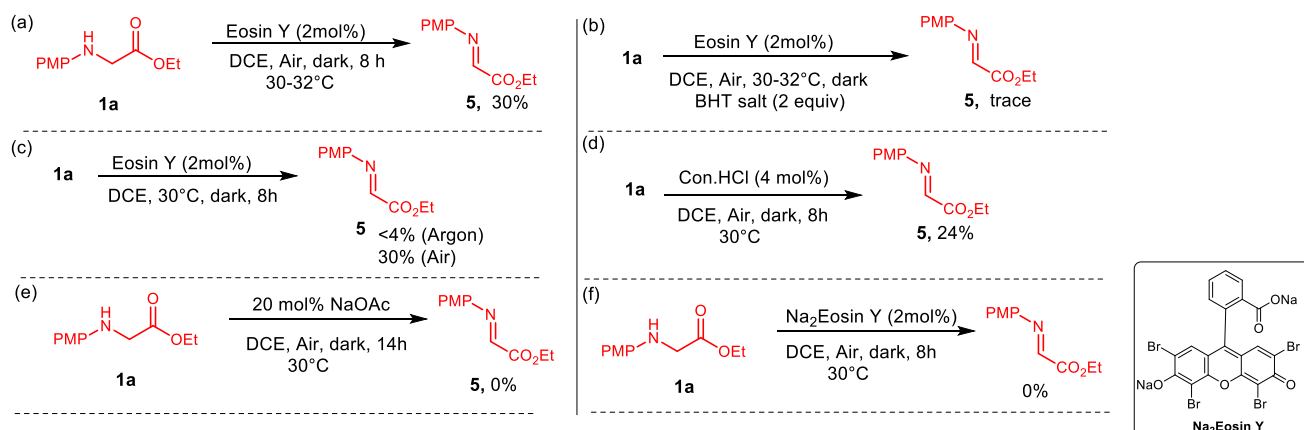


Figure S10. The XPS spectra of eosin-Y/Cu(OAc)₂ mixture

8. Mechanistic study of eosin-Y catalysed reaction

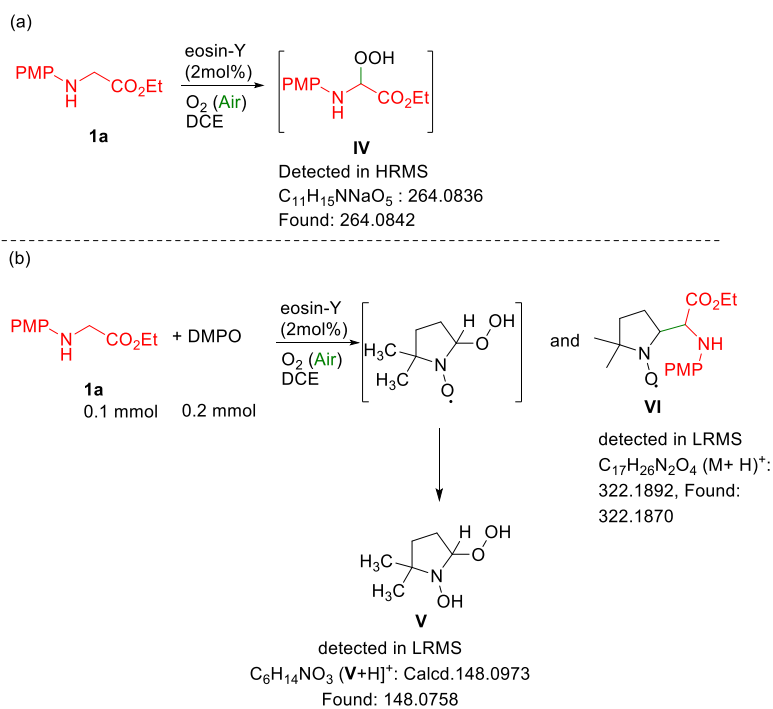
Eosin-Y solely catalyses reaction of **1a** with **2a** and desired product **3a** was isolated in irreproducible yield when the reaction was carried out in freshly distilled (dry) DCE solvent. (The yield of eosin-Y catalysed reaction was not reproduceable. Several times the reaction was carried out under similar reaction conditions, same batch of **1a** but failed to reproduced the yield.) To understand, how eosin-Y catalyses this reaction, a number of mechanistic experiments were carried out. Under reaction conditions (**1a**, 2 mol% eosin-Y, freshly dried DCE solvent, in air), imine **5** was isolated in irreproducible yield (~30% yield) (**Scheme S5a**). This fact demonstrates that imine **5** is the productive intermediate for eosin-Y catalysed reaction too. On the other hand, the reaction yielded a trace amount (in TLC) of imine **5** (**Scheme S5b**) in presence of radical scavenger 2,6-di-tert-butyl-4-methylphenol (BHT). This observation suggesting that this reaction may undergo a radical pathway. Reaction of **1a** with **2a** in presence of 2 mol% eosin-Y in DCE under argon atmosphere, resulted in <4% yield of imine **5** (**Scheme S5c**). This finding confirmed air is essential for good yield of the reaction.

Next, **1a** was stirred in freshly dry DCE in air for 8h, a trace of the imine **5** was observed in TLC. Next, the reaction was carried out in presence of 4 mol% of Con. HCl using freshly dried DCE in air for 8h, 24% of the imine **5** was isolated (**Scheme S5d**). This result implies for an acid catalysed reaction.⁶ To further confirm this hypothesis, the same reaction was conducted using 20 mol% of NaOAc, the imine **5** was not detected (in TLC) even after 14 h (**Scheme S5e**). When **1a** and Na₂EosinY were dissolved in freshly dried DCE and stirred under air for 8h, no trace of imine **5** (**Scheme S4f**) formation was observed (in TLC). As there are no acidic protons in Na₂EosinY. The results of the control experiments (**Scheme S4d-f**) support in favour of an acid catalysed reaction.



Scheme S5: Control experiments

Moreover, when an aliquot of the reaction mixture (**1a**, 2 mol% eosin-Y, freshly dried DCE solvent, in air at room temperature) was subjected to high-resolution mass spectrometry, the hydroperoxide intermediate **IV** (Scheme S6a) was detected (Figure S11). In addition to that when the same reaction was carried out in presence of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a radical scavenger, the peaks at m/z value 148.0758 and 322.1870 were detected in mass spectrometry (Figure S12) which are probably the decomposition adduct of DMPO-O₂⁻ and DMPO-**1a** adduct respectively (Scheme S6b).



Scheme S6: Mechanistic experiments

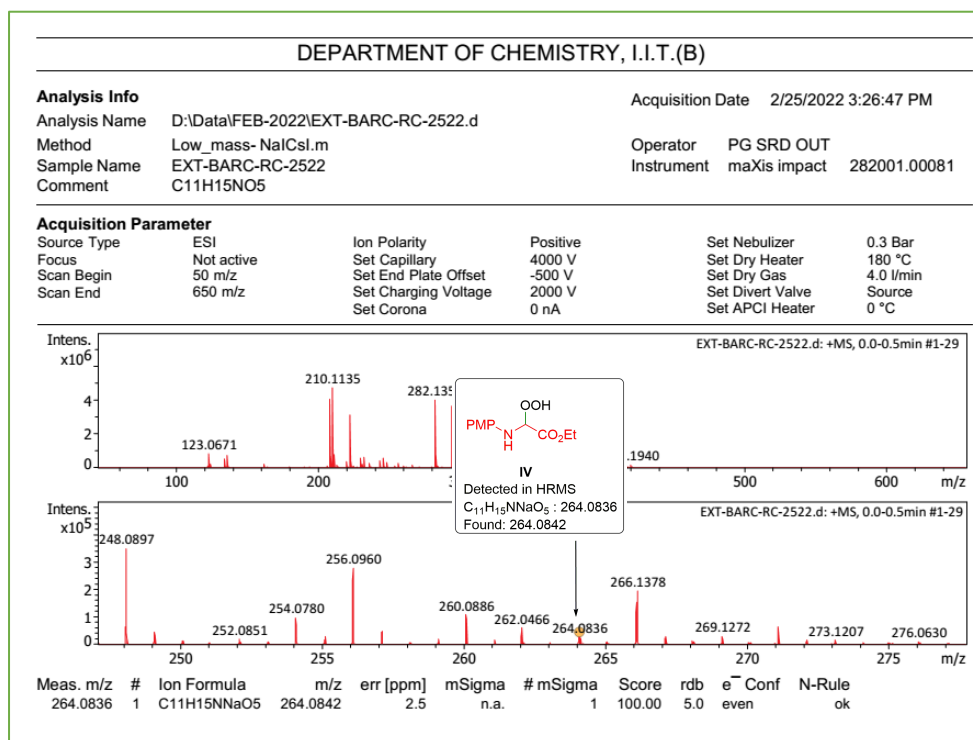


Figure S11. Detection of intermediate IV in HRMS

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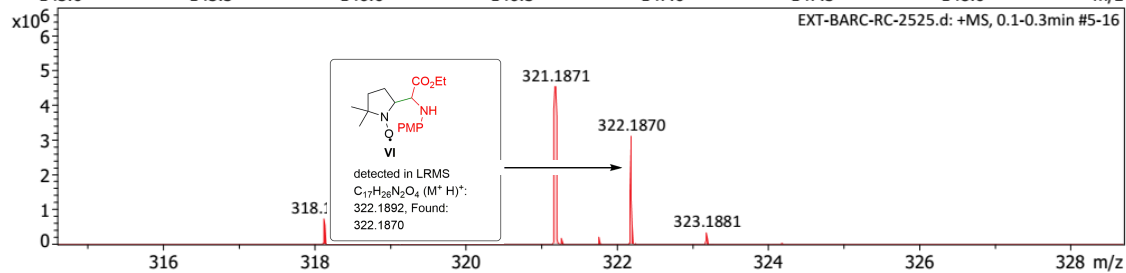
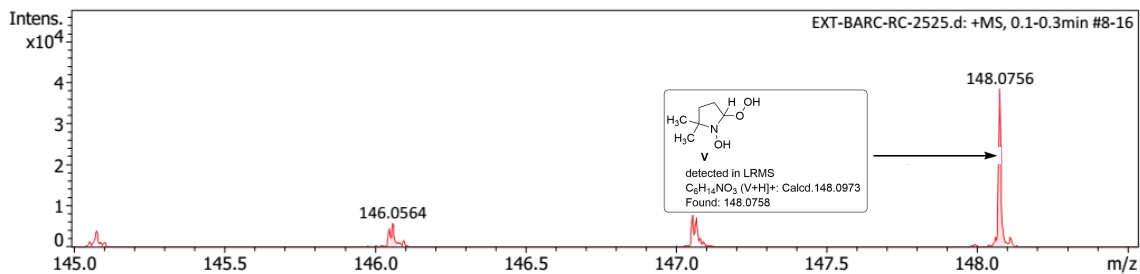
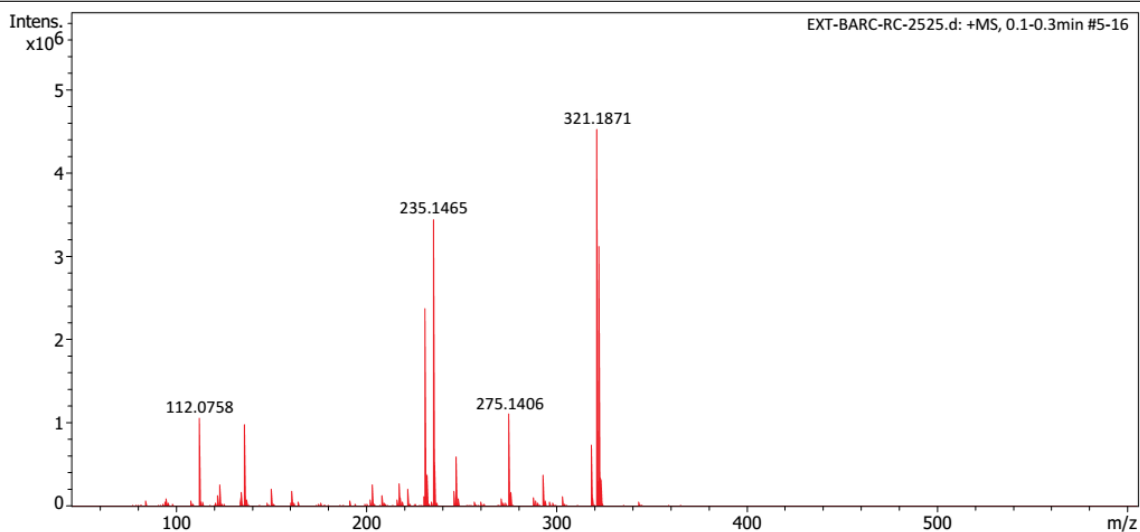
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 Sample Name EXT-BARC-RC-2525
 Comment C6H12NO3

Acquisition Date 2/25/2022 4:13:47 PM
 Operator PG SRD OUT
 Instrument maXis impact 282001.00081

Acquisition Parameter

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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	600 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



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Figure S12. Detection of intermediate V and VI in LRMS

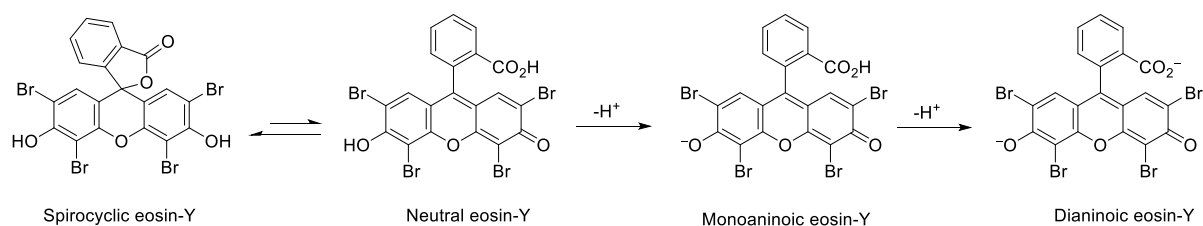
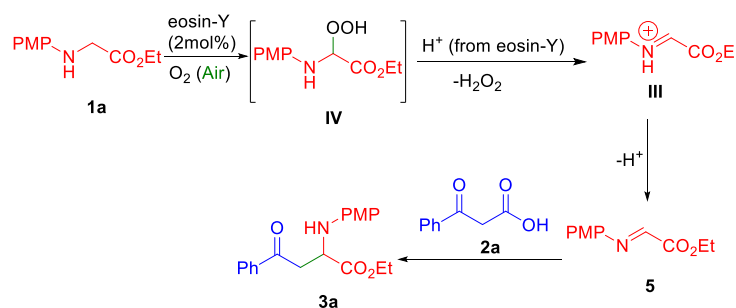


Figure S13: Different form of eosin-Y

Based on the above preliminary experimental findings, literature reports⁶ and considering marked acid properties of eosin-Y due to its unique structural scaffold (**Figure S13**), a possible mechanistic pathway was proposed as described in **Scheme S7**. Auto-oxidation of glycine ester **1a** in presence of oxygen (air) lead to hydroperoxide intermediate **IV** which accepts a proton from eosin Y and undergoes a S_N1 type reaction to form the intermediate **III**. Subsequently, release of proton from **III** leads to iminium intermediate **5**. Then, addition reaction of β -ketoacid **2a** to **5** followed by decarboxylation finally produce product **3a**. (Other mechanistic pathways cannot be ruled out at this stage.)



Scheme S7: Plausible reaction mechanism

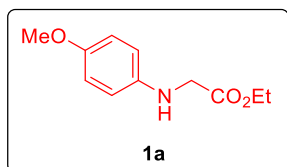
9. The Preparation of Substrates

*General procedure for the synthesis of glycine derivatives*⁷

In a 50 mL oven dried round bottom flask equipped with a magnetic stirring bar, *p*-methoxyaniline (20 mmole, 1 equiv), ethyl bromoacetate (20 mmole, 1 equiv) and anhydrous sodium acetate (20 mmol, 2 equiv) were taken and then 20 ml ethanol was added. The reaction

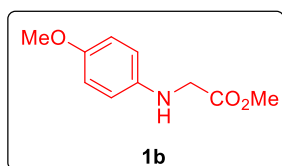
mixture was stirred in oil bath (90 °C) for 24h under N₂ atmosphere. After cooling, the solvent was evaporated and residue was subjected to column chromatography (230-400 mesh silica gel). The resulting product **1a** was crystalized and gave the product **1a** as off-white solid.

Following the general procedure, other glycine derivatives **1b-1d** were prepared.



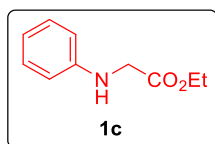
Ethyl (4-methoxyphenyl)glycinate **1a**²

¹H NMR (600MHz, CDCl₃): δ 6.79 (d, *J* = 8.5 Hz, 2 H), 6.59 (d, *J* = 8.3 Hz, 2 H), 4.23 (q, *J* = 7.0Hz, 2 H), 3.86 (2 H), 3.74 (s, 3 H), 1.29 (t, *J* = 7.0 Hz, 3 H); ¹³C{¹H} NMR (201.2 MHz, CDCl₃): δ 171.4, 152.6, 141.2, 114.9 (2 C), 114.4 (2 C), 61.2, 55.7, 46.8, 14.1. Spectral data is close agreement with literature.²



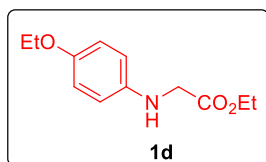
Methyl (4-methoxyphenyl)glycinate **1b**²

¹H NMR (600MHz, CDCl₃): δ 6.79 (d, *J* = 9.0 Hz, 2 H), 6.59 (d, *J* = 7.9 Hz, 2 H), 3.88 (s, 2 H), 3.77 (s, 3 H), 3.74 (s, 3 H); ¹³C{¹H} NMR (201.2 MHz, CDCl₃): δ 171.9, 152.7, 141.2, 114.9 (2 C), 114.4 (2 C), 55.7, 52.2, 46.7. Spectral data is close agreement with literature.²



Ethyl phenylglycinate **1c**

¹H NMR (600MHz, CDCl₃): δ 7.20 (t, *J* = 7.5 Hz, 2 H), 6.76 (t, *J* = 7.1 Hz, 1 H), 6.62 (t, *J* = 7.8 Hz, 2 H), 4.25 (q, *J* = 7.0 Hz, 2 H), 3.90 (2 H), 1.30 (t, *J* = 7.0 Hz, 3 H); ¹³C{¹H} NMR (201.2 MHz, CDCl₃): δ 171.1, 147.2, 129.3 (2 C), 118.1, 113.0 (2 C), 61.3, 45.8, 14.2.

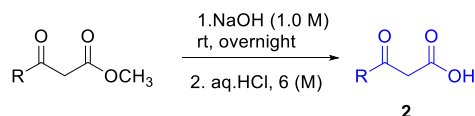


Ethyl (4-ethoxyphenyl)glycinate **1d**²

¹H NMR (600MHz, CDCl₃): δ 6.78 (d, *J* = 8.5 Hz, 2 H), 6.57 (d, *J* = 8.4 Hz, 2 H), 4.24-4.21 (m, 2 H), 3.97-3.94 (m, 2 H), 3.85 (s, 2 H), 1.38-1.35 (m, 3 H), 1.29-1.27 (m, 3 H). ¹³C{¹H} NMR (201.2 MHz, CDCl₃): δ 171.4, 151.9, 141.2, 115.7 (2 C), 114.4 (2 C), 64.0, 61.2, 46.8, 14.9, 14.2. Spectral data is close agreement with literature.²

General Procedure for Preparation of β-ketoacids

The β-ketoacids were prepared following the literature procedure.⁸



In a 50 mL round bottom flask, β-ketoester¹⁰ (10 mmol, 1. equiv) was taken. Aqueous NaOH (1 M, 12 mL) was added slowly and then the reaction mixture was stirred overnight at room temperature. The reaction mixture was extracted with Et₂O (2× 10 mL). The aqueous phase was then cooled to 0 °C and acidified to pH 1-2 with aq.HCl (6 M), precipitate was formed. EtOAc was added to the resulting suspension. The organic layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure (bath set to 25 °C). The resulting solid was washed with petroleum ether (2-3 times), dried in vacuum and used without further purification.

(It should be noted that instead of DCM, EtOAc was used as extracting solvent in the present study)

10. General procedure for the synthesis of product 3a-3p and 4a-4j in the dark

To an oven dried 5mL round bottom flask (wrapped in aluminium foil) with a magnetic stirring bar were added glycinate ester **1** (0.4 mmol, 1 equiv) and eosin Y (5.2 mg, 0.008 mmol, 2 mol%). Then 2 mL of dry DCE was added via syringe followed by addition of Cu(OAc)₂ (3.66 mg, 0.02 mmol, 5 mol%). Two small needles were inserted through the rubber septum to maintain the oxygen (air) level inside the flask. The reaction mixture was stirred (for 8h) under air atmosphere at room temperature (30-32°C). Once the glycinate ester **1** was consumed (monitored by TLC-run the plate three times, 10% EtOAc/ petroleum ether), then β-ketoacid (0.6 mmol or 0.8 mmol) or indole (0.44 mmol or 0.48 mmol) or naphthol (0.44 mmol) or pyrrole (0.44 mmol) was added in one shot (in case of liquid, the nucleophile was *dissolved in 0.5 mL of dry DEC and then added slowly to the reaction mixture*). The reaction mixture was further stirred for 2-4h (for β-ketoacid) or 4-5h (indole derivatives, naphthol and pyrrole) . After completion of the reaction, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to afford product **3** or **4**.

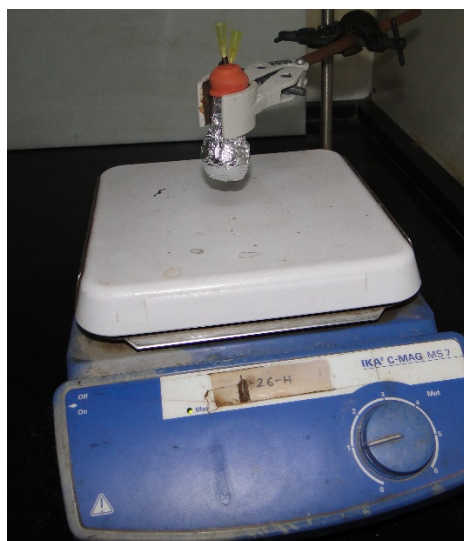
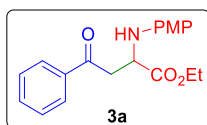


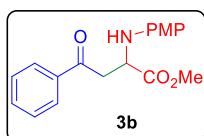
Figure S14. Reaction set-up for the dark reaction

11. Characterization data



Ethyl 2-((4-methoxyphenyl)amino)-4-oxo-4-phenylbutanoate (3a)

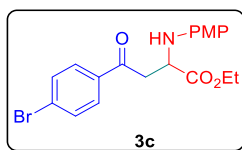
Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as slightly yellow liquid which solidified in refrigerator. Yield =103 mg (78%); Mp: 65.5-66.5°C; **¹H NMR (600MHz, CDCl₃):** δ 7.93 (d, *J* = 7.8 Hz, 2 H), 7.57 (t, *J* = 7.8 Hz, 1 H), 7.46 (t, *J* = 7.8 Hz, 2 H), 6.77 (d, *J* = 8.4 Hz, 2 H), 6.68 (d, *J* = 9.0 Hz, 2 H), 4.53 (t, *J* = 5.4 Hz, 1 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 3.73 (s, 3 H), 3.52 (d, *J* = 5.4 Hz, 2 H), 1.20 (t, *J* = 6.9 Hz, 3 H); **¹³C{¹H} NMR (201.2 MHz, CDCl₃):** δ 197.4, 173.2, 153.0, 140.6, 136.5, 133.5, 128.7 (2 C), 128.1 (2 C), 115.7 (2 C), 114.9 (2 C), 61.5, 55.7, 54.5, 41.1, 14.1; **HRMS (ESI)** calcd for C₁₉H₂₂NO₄ [M + H]⁺: 328.1543, found: 328.1555. Spectral data is close agreement with literature.⁹



Methyl 2-((4-methoxyphenyl)amino)-4-oxo-4-phenylbutanoate (3b)

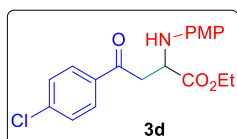
Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated slightly yellow liquid which solidified in refrigerator. Yield = 95 mg (~75%); **¹H NMR (600MHz, CDCl₃):** δ 7.93 (d, *J* = 7.6 Hz, 2 H), 7.57 (t, *J* = 7.2 Hz, 1 H), 7.46 (t, *J* = 7.7 Hz, 2 H), 6.77 (d, *J* = 8.5 Hz, 2 H), 6.67 (d, *J* = 8.6 Hz, 2 H), 4.55 (t, *J* = 5.1 Hz, 1 H), 3.73 (s, 3 H), 3.72 (s, 3 H), 3.53 (d, *J* = 5.4 Hz, 2 H); **¹³C{¹H} NMR (201.2 MHz, CDCl₃):** δ 197.4, 173.7, 153.0, 140.5, 136.4, 133.6, 128.7

(2 C), 128.2 (2 C), 115.7 (2 C), 114.9 (2 C), 55.7, 54.3, 52.5, 41.1. Spectral data is close agreement with literature.¹⁰



Ethyl 4-(4-bromophenyl)-2-((4-methoxyphenyl)amino)-4-oxobutanoate (3c)

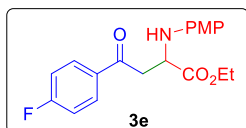
Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as slightly yellow solid. Yield =125 mg (77%); Mp:67-68 °C; **¹H NMR (600MHz, CDCl₃):** δ 7.79 (d, J = 7.9 Hz, 2 H), 7.59 (d, J = 8.2 Hz, 2 H), 6.76 (d, J = 8.4 Hz, 2 H), 6.68 (d, J = 8.4 Hz, 2 H), 4.52 (t, J = 5.3Hz, 1 H), 4.17 (q, J = 7.1 Hz, 2 H), 3.73 (s, 3 H), 3.47 (d, J = 5.3 Hz, 2 H), 1.20 (t, J = 7.0 Hz, 3 H), **¹³C{¹H} NMR (201.2 MHz, CDCl₃):** δ 196.4, 173.0, 153.1, 140.3, 135.2, 132.0 (2 C), 129.6 (2 C), 128.7, 115.9 (2 C), 114.8 (2 C), 61.5, 55.6, 54.5, 41.0, 14.1; **ATR:** 3339, 2980, 1711, 1680, 1509, 1235, 1208, 1172, 817 cm⁻¹; **HRMS (ESI)** calcd for C₁₉H₂₁BrNO₄ [M + H]⁺: 406.0648, found: 406.0647.



Ethyl 4-(4-chlorophenyl)-2-((4-methoxyphenyl)amino)-4-oxobutanoate (3d)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as slightly yellow liquid which solidified in refrigerator. Yield = 112 mg (>77%); Mp:76.5-77.5 °C; **¹H NMR (600MHz, CDCl₃):** δ 7.86 (d, J = 8.2 Hz, 2 H), 7.43 (d, J = 8.1 Hz, 2 H), 6.77 (d, J = 8.6 Hz, 2 H), 6.67 (d, J = 8.6 Hz, 2 H), 4.52 (t, J = 5.2 Hz, 1 H), 4.17 (q, J = 7.1 Hz, 2 H), 3.73 (s, 3 H), 3.48 (d,

$J = 5.3$ Hz, 2 H), 1.20 (t, $J = 7.1$ Hz, 3 H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (201.2 MHz, CDCl_3):** δ 196.2, 173.1, 153.1, 140.5, 140.0, 134.8, 129.6 (2 C), 129.0 (2 C), 115.8 (2 C), 114.9 (2 C), 61.5, 55.7, 55.5, 41.0, 14.1; **ATR:** 3339, 2977, 1708, 1685, 1510, 1236, 1208, 1175, 822 cm^{-1} ; **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{21}\text{ClNO}_4$ $[\text{M} + \text{H}]^+$: 362.1153, found: 362.1154.



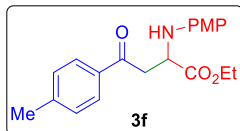
Ethyl 4-(4-fluorophenyl)-2-((4-methoxyphenyl)amino)-4-oxobutanoate (3e)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow solid. Yield = 102 mg (74%); Mp:75.0 -75.5 °C; **^1H NMR (600MHz, CDCl_3):** δ 7.97-7.94 (m, 2 H), 7.12 (t, $J = 8.3$ Hz, 2 H), 6.76 (d, $J = 8.6$ Hz, 2 H), 6.67 (d, $J = 8.6$ Hz, 2 H), 4.51 (t, $J = 5.3$ Hz, 1 H), 4.17 (q, $J = 7.1$ Hz, 2 H), 3.73 (s, 3 H), 3.49 (d, $J = 5.4$ Hz, 2 H), 1.20 (t, $J = 7.1$ Hz, 3 H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (201.2 MHz, CDCl_3):** δ 195.8, 173.1, 165.97 (d, $J_{\text{C-F}} = 253.9$ Hz), 153.0, 140.5, 133.0, 130.8 (d, $J_{\text{C-F}} = 8.7$ Hz), 115.9, 115.8 (4 C), 114.9 (2 C), 61.5, 55.7, 54.5, 41.0, 14.1; **ATR:** 3328, 2983, 1729, 1673, 1593, 1509, 1236, 1237, 1178, 821 cm^{-1} ; **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{21}\text{FNO}_4$ $[\text{M} + \text{H}]^+$: 346.1449, found: 346.1441.

Synthesis of 3e in 1 mmol scale:

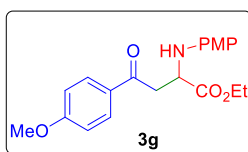
To an oven dried 25mL round bottom flask (wrapped in aluminium foil) with a magnetic stirring bar were added glycinate ester **1a** (209 mg, 1 mmol) and eosin Y (13 mg, 0.02 mmol, 2 mol%). Then 5 mL of dry DCE was added via syringe followed by addition of $\text{Cu}(\text{OAc})_2$ (9.0 mg, 0.05 mmol, 5 mol%). The reaction mixture was stirred (for 10h) under air atmosphere at room temperature (32-34 °C). Once the glycinate ester **1a** was consumed (monitored by TLC), then β -ketoacid **1e** (273 mg, 1.5 mmol) was added in one portion. The reaction mixture was further stirred for 2h. After completion of the reaction, the reaction mixture was

concentrated to one-third of the total volume. The crude residue was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to afford product **3e** as light-yellow solid (252 mg, 73%).



Ethyl 4-((4-methoxyphenyl)amino)-4-oxo-4-(p-tolyl)butanoate (3f)

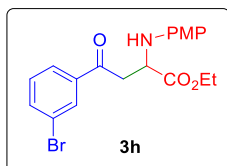
Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow solid. Yield = 103 mg (75%); Mp: 81-82°C; **¹H NMR (600MHz, CDCl₃):** δ 7.83 (d, J = 7.9 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H), 6.76 (d, J = 8.6 Hz, 2 H), 6.68 (d, J = 8.6 Hz, 2 H), 4.51 (t, J = 5.5 Hz, 1 H), 4.16 (q, J = 7.2 Hz, 2 H), 3.73 (s, 3 H), 3.50 (d, J = 5.3 Hz, 2 H), 2.40 (s, 3 H), 1.19 (t, J = 7.1 Hz, 3 H); **¹³C{¹H} NMR (201.2 MHz, CDCl₃):** δ 197.4, 173.0, 144.2, 136.5, 133.5, 129.8 (2 C), 128.7 (2 C), 128.1 (2 C), 127.9, 114.1 (2 C), 61.5, 53.6, 41.0 (2 C), 20.4, 14.1; **ATR :** 3347, 2987, 2832, 1728, 1699, 1512, 1275, 1235, 1174, 1029, 813 cm⁻¹; **HRMS (ESI)** calcd for C₂₀H₂₄NO₄ [M + H]⁺: 342.1699, found: 342.1700.



Ethyl 4-(4-methoxyphenyl)-2-((4-methoxyphenyl)amino)-4-oxobutanoate (3g)

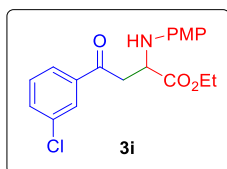
Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as colourless solid. Yield = 109 mg (76%); Mp:73-74°C (petroleum ether/EtOAc); **¹H NMR (600MHz, CDCl₃):** δ 7.92-7.89 (m, 2 H), 6.93-6.91 (m, 2 H), 6.77-6.74 (m, 2 H), 6.68-6.67 (m, 2 H), 4.50 (t, J = 5.5 Hz, 1 H), 4.16 (q, J = 7.1 Hz, 2 H), 3.85 (s, 3 H), 3.72 (s, 3 H), 3.46 (d, J = 5.6 Hz, 2 H), 1.18 (t, J = 7.1 Hz,

3 H); **¹³C{¹H}** NMR (201.2 MHz, CDCl₃): δ 195.8, 173.3, 163.8, 153.0, 140.7, 130.5 (2 C), 129.6, 115.7 (2 C), 114.8 (2 C), 113.8 (2 C), 61.4, 55.7, 55.5, 54.6, 40.7, 14.1; **ATR**: 3337, 2958, 1728, 1665, 1512, 1253, 1169, 1030, 820 cm⁻¹; **HRMS (ESI)** calcd for C₂₀H₂₄NO₅ [M + H]⁺: 358.1648, found: 358.1647.



Ethyl 4-(3-bromophenyl)-2-((4-methoxyphenyl)amino)-4-oxobutanoate (3h)

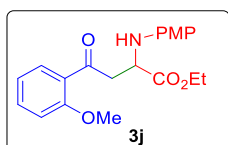
Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as light brown solid. Yield = 114 mg (70%); Mp:93-94°C; **¹H NMR (600MHz, CDCl₃)**: δ 8.04 (t, *J* = 1.7 Hz, 1 H), 7.84 (ddd, *J* = 7.8, 1.7, 1.0 Hz, 1 H), 7.68 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1 H), 7.33 (t, *J* = 7.8 Hz, 1 H), 6.78-6.75 (m, 2 H), 6.71-6.68 (m, 2 H), 4.52 (t, *J* = 5.5 Hz, 1 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 3.73 (s, 3 H), 3.49 (d, *J* = 5.5 Hz, 2 H), 1.20 (t, *J* = 7.3 Hz, 3 H); **¹³C{¹H}** NMR (201.2 MHz, CDCl₃): δ 196.1, 172.9, 153.1, 140.3, 138.2, 136.3, 131.2, 130.3, 126.6, 123.0, 115.8 (2 C), 114.9 (2 C), 61.5, 55.7, 54.5, 40.1, 14.1; **HRMS (ESI)** calcd for C₁₉H₂₁⁷⁹BrNO₄ [M + H]⁺: 406.0648, found: 406.0648, C₁₉H₂₁⁸¹BrNO₄ [M + H]⁺: found: 406.0634.



Ethyl 4-(3-chlorophenyl)-2-((4-methoxyphenyl)amino)-4-oxobutanoate (3i)

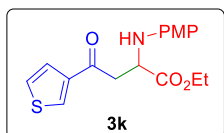
Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow solid. Yield = 119 mg (82%); Mp:74.5-75.5°C; **¹H NMR (600MHz, CDCl₃)**: δ 7.90 (s, 1 H), 7.80 (d, *J* = 7.7 Hz, 1

H), 7.54 (d, $J = 7.8$ Hz, 1 H), 7.40 (t, $J = 7.7$ Hz, 1 H), 6.77 (d, $J = 8.5$ Hz, 2 H), 6.68 (d, $J = 8.5$ Hz, 2 H), 4.52 (t, $J = 5.0$ Hz, 1 H), 4.17 (q, $J = 7.0$ Hz, 2 H), 3.73 (s, 3 H), 3.49 (d, $J = 5.2$ Hz, 2 H), 1.20 (t, $J = 7.3$ Hz, 3 H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (201.2 MHz, CDCl_3):** δ 196.2, 173.0, 153.2, 140.4, 138.0, 135.1, 133.4, 130.0, 128.3, 126.2, 115.9 (2 C), 114.9 (2 C), 61.6, 55.7, 55.5, 41.2, 14.1; **ATR :** 3370, 3017, 2907, 1730, 1688, 1512, 1212, 1036, 748 cm^{-1} ; **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{21}\text{ClNO}_4$ $[\text{M} + \text{H}]^+$: 362.1153, found: 362.1157.



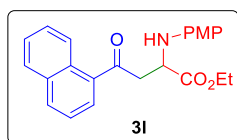
Ethyl 4-(2-methoxyphenyl)-2-((4-methoxyphenyl)amino)-4-oxobutanoate (3j)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as light-yellow liquid. Yield = 113mg (79%); **^1H NMR (600MHz, CDCl_3):** δ 7.73 (d, $J = 7.8$, 1 H), 7.47 (t, $J = 7.6$ Hz, 1 H), 6.99 (t, $J = 7.5$ Hz, 1 H), 6.96 (d, $J = 8.3$, 1.0 Hz, 1 H), 6.76 (d, $J = 8.7$ Hz, 2 H), 6.65 (d, $J = 8.6$ Hz, 2 H), 4.47 (t, $J = 5.8$ Hz, 1 H), 4.16 (q, $J = 7.0$ Hz, 2 H), 3.89 (s, 3 H), 3.73 (s, 3 H), 3.54 (dd, $J = 17.4$, 5.3 Hz, 1 H), 3.50 (dd, $J = 17.2$, 5.7 Hz, 1 H), 1.20 (t, $J = 7.3$ Hz, 3 H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (201.2 MHz, CDCl_3):** δ 198.9, 173.5, 158.8, 152.8, 140.8, 134.1, 130.6, 127.3, 120.7, 115.6 (2 C), 114.8 (2 C), 111.5, 61.2, 55.6, 55.4, 54.7, 46.4, 14.1; **ATR :** 3370, 2987, 2940, 1731, 1668, 1596, 1511, 1236, 1022, 821, 758 cm^{-1} ; **HRMS (ESI)** calcd for $\text{C}_{20}\text{H}_{24}\text{NO}_5$ $[\text{M} + \text{H}]^+$: 358.1648, found: 358.1649.



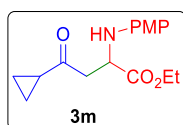
Ethyl 2-((4-methoxyphenyl)amino)-4-oxo-4-(thiophen-3-yl)butanoate (3k)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow solid. Yield = 100 mg (75%); Mp: 51-52°C; $^1\text{H NMR}$ (600MHz, CDCl_3): δ 8.03 (dd, $J = 2.9, 1.4$ Hz, 1 H), 7.52 (dd, $J = 5.1, 1.3$ Hz, 1 H), 7.30 (dd, $J = 5.0, 2.9$ Hz, 1 H), 6.77-6.74 (m, 2 H), 6.68-6.66 (m, 2 H), 4.50 (t, $J = 5.5$ Hz, 1 H), 4.16 (q, $J = 7.1$ Hz, 2 H), 3.72 (s, 3 H), 3.41 (d, $J = 5.7$ Hz, 2 H), 1.19 (t, $J = 7.1$ Hz, 3 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (201.2 MHz, CDCl_3): δ 191.5, 173.1, 153.0, 141.9, 140.6, 132.6, 126.8, 126.6, 115.7 (2 C), 114.9 (2 C), 61.5, 55.7, 54.5, 42.2, 14.1; ATR: 3349, 2985, 2833, 1738, 1663, 1508, 1168, 1038, 823, 793 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_4\text{S} [\text{M} + \text{H}]^+$: 334.1107, found: 334.1108.



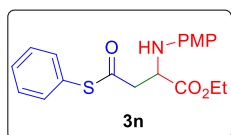
Ethyl 2-((4-methoxyphenyl)amino)-4-(naphthalen-1-yl)-4-oxobutanoate (3l)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow liquid. Yield = 118mg (78%); $^1\text{H NMR}$ (600MHz, CDCl_3): δ 8.60 (dd, $J = 8.8, 0.9$ Hz, 1 H), 7.98 (d, $J = 8.8$ Hz, 1 H), 7.85 (td, $J = 7.9, 1.00$ Hz, 2 H), 7.57 (ddd, $J = 8.3, 6.8, 1.4$ Hz, 1 H), 7.52 (ddd, $J = 8.1, 6.8, 1.3$ Hz, 1 H), 7.49-7.46 (m, 1 H), 6.79-6.76 (m, 2 H), 6.72-6.70 (m, 2 H), 4.59 (t, $J = 5.6$ Hz, 1 H), 4.19 (q, $J = 7.1$ Hz, 2 H), 3.73 (s, 3 H), 3.60 (d, $J = 5.6$ Hz, 2 H), 1.20 (t, $J = 7.1$ Hz, 3 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (201.2 MHz, CDCl_3): δ 201.3, 173.3, 153.1, 140.6, 135.2, 133.9, 133.1, 130.1, 128.4, 128.1, 127.9, 126.5, 125.7, 124.3, 115.8 (2 C), 114.8 (2 C), 61.5, 55.6, 55.0, 44.4, 14.1; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_4 [\text{M} + \text{H}]^+$: 378.1699, found: 378.1700.



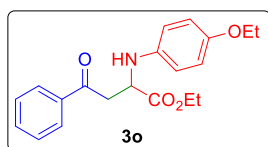
Ethyl 4-cyclopropyl-2-((4-methoxyphenyl)amino)-4-oxobutanoate (3m)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether). The above titled compound was isolated as yellow liquid. Yield = 90 mg (77%); **¹H NMR (600MHz, CDCl₃)**: δ 6.76 (d, *J* = 8.5Hz, 2 H), 6.64 (d, *J* = 8.5Hz, 2 H), 4.35 (t, *J* = 5.6Hz, 1 H), 4.20-4.12 (m, 2 H), 3.73 (s, 3 H), 3.13 (d, *J* = 5.5 Hz, 2 H), 1.94-1.90 (m, 1 H), 1.22 (t, *J* = 7.1 Hz, 3 H), 1.08-1.03 (m, 2 H), 0.91-0.87 (m, 2 H); **¹³C{¹H} NMR (201.2 MHz, CDCl₃)**: δ 207.8, 173.0, 152.9, 140.6, 115.7 (2 C), 114.8 (2 C), 61.3, 55.6, 54.2, 45.4, 20.9, 14.0, 11.1, 11.0; **ATR**: 3402, 2982, 2833, 1726, 1606, 1510, 1234, 1033, 820, 742 cm⁻¹; **HRMS (ESI)** calcd for C₁₆H₂₂NO₄ [M + H]⁺: 292.1543, found: 292.1548.



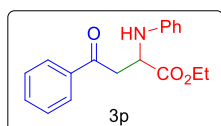
Ethyl 2-((4-methoxyphenyl)amino)-4-oxo-4-(phenylthio)butanoate (3n)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether). The above titled compound was isolated as yellow liquid. Yield = 61mg (43%); **¹H NMR (600MHz, CDCl₃)**: δ 7.41-7.40 (m, 5 H), 6.77 (d, *J* = 8.6 Hz, 2 H), 6.65 (d, *J* = 8.7 Hz, 2 H), 4.42 (t, *J* = 5.9 Hz, 1 H), 4.24-4.16 (m, 2 H), 3.74 (s, 3 H), 3.15 (d, *J* = 5.7 Hz, 2 H), 1.26 (t, *J* = 6.9 Hz, 3H); **¹³C{¹H} NMR (201.2 MHz, CDCl₃)**: δ 194.7, 172.2, 153.2, 140.1, 134.4 (2 C), 129.6, 129.3 (2 C), 127.1, 115.8 (2 C), 114.9 (2 C), 61.7, 55.7, 55.2, 45.7, 14.1; **ATR**: 3368, 2981, 2832, 1733, 1700, 1511, 1236, 1180, 1033, 854, 820 cm⁻¹; **HRMS (ESI)** calcd for C₁₉H₂₂NO₄S [M + H]⁺: 360.1264, found: 360.1267.



Ethyl 2-((4-ethoxyphenyl)amino)-4-oxo-4-phenylbutanoate (3o)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow solid. Yield = 110 mg (>80%); Mp: 89-90°C; ¹H NMR (600MHz, CDCl₃): δ 7.93 (d, *J* = 7.9 Hz, 2 H), 7.57 (t, *J* = 7.3 Hz, 1 H), 7.46 (t, *J* = 7.3 Hz, 2 H), 6.76 (d, *J* = 8.6 Hz, 2 H), 6.68 (d, *J* = 8.6 Hz, 2 H), 4.53 (t, *J* = 5.4Hz, 1 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 3.94 (q, *J* = 7.0 Hz, 2 H), 3.52 (d, *J* = 5.2 Hz, 2 H), 1.36 (t, *J* = 7.0 Hz, 3 H), 1.19 (t, *J* = 7.0 Hz, 3 H); ¹³C{¹H} NMR (201.2 MHz, CDCl₃): δ 197.4, 173.2, 152.3, 140.5, 136.5, 133.5, 128.7 (2 C), 128.1 (2 C), 115.7 (2 C), 115.6 (2 C), 64.0, 61.4, 54.5, 41.1, 14.9, 14.1; ATR : 3363, 2975, 2862, 1733, 1675, 1518, 1189, 826 cm⁻¹; HRMS (ESI) calcd for C₂₀H₂₄NO₄ [M + H]⁺: 342.1699, found: 342.1701.

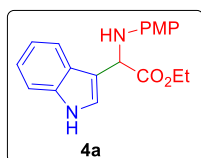


Ethyl-4-oxo-4-phenyl-2-(phenylamino)butanoate (3p)

To a oven dried 5mL round bottom flask (wrapped in aluminium foil) with a magnetic stirring bar were added glycinate ester **1c** (0.4 mmol, 1 equiv) and eosin Y (5.2 mg, 0.008 mmol, 2 mol%). Then 2 mL of dry DCE was added via syringe followed by addition of Cu(OAc)₂ (3.66 mg, 0.02 mmol, 5 mol%). Then 200 μL of TBHP(70% in H₂O) was added. The reaction mixture was stirred (for 16h) at room temperature (32-34 °C). Once the glycinate ester **1c** was consumed (monitored by TLC), then β-ketoacid **2a** (0.6 mmol, 96 mg) was added in one shot. The reaction mixture was further stirred for 2h. After completion of the reaction, the reaction mixture was purified by column chromatography on silica gel (10% EtOAc/ petroleum ether –15% EtOAc/ petroleum ether) to afford product **3p** as yellow oil. Yield = 70 mg (59%); ¹H NMR (600MHz, CDCl₃): δ 7.93 (d, *J* = 7.9 Hz, 2 H), 7.57 (t, *J* = 7.3 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 6.75 (t, *J* = 7.3 Hz, 1 H), 6.69 (d, *J* = 7.9 Hz, 2 H), 4.62 (t, *J* = 5.2 Hz, 1 H), 4.19 (q, *J* = 6.8 Hz, 2 H), 3.58 (dd, *J* = 17.3, 5.1 Hz, 2 H), 1.20 (t, *J* = 6.8 Hz, 3 H); ¹³C{¹H}

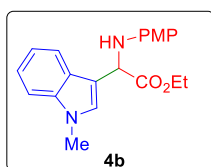
NMR (201.2 MHz, CDCl₃): δ 197.3, 172.8, 146.4, 136.4, 133.5, 129.3 (2 C), 128.6 (2 C), 128.1 (2 C), 118.5, 113.7 (2 C), 61.5, 53.0, 40.8, 14.1; **ATR :** 3380, 2981, 1730, 1681, 1502, 1180, 748 cm⁻¹; **HRMS (ESI)** calcd for C₁₈H₂₀NO₃ [M + H]⁺: 298.1437, found: 298.1437.

(In all the above compounds **3a-3p**, NH protons could not be detected)



Ethyl 2-(1H-indol-3-yl)-2-((4-methoxyphenyl)amino)acetate (4a)

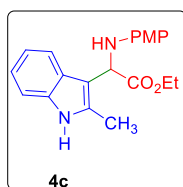
Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow liquid. Yield = 117 mg (90%). **¹H NMR (600MHz, CDCl₃):** δ 8.27 (brs, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.18-7.16 (m, 2 H), 6.77 (d, *J* = 8.5 Hz, 2 H), 6.63 (d, *J* = 8.6 Hz, 2 H), 5.34 (s, 1 H), 4.25 (dq, *J* = 15.4, 7.4 Hz, 1 H), 4.13 (dq, *J* = 15.0, 7.2 Hz, 1 H), 3.73 (s, 3 H), 1.21 (t, *J* = 7.1 Hz, 3H); **¹³C{¹H} NMR (201.2 MHz, CDCl₃):** δ 172.8, 152.5, 140.7, 136.4, 125.7, 123.0, 122.4, 119.9, 119.5, 114.84 (2 C), 114.81 (2 C), 112.6, 111.4, 61.5, 55.7, 55.2, 14.1; **ATR :** 3400, 2981, 2833, 1725, 1510, 1234, 1180, 1130, 933, 820, 742 cm⁻¹; **HRMS (ESI)** calcd for C₁₉H₂₀N₂NaO₃ [M + Na]⁺: 347.1366, found: 347.1366. Spectral data is close agreement with literature.¹¹



Ethyl 2-((4-methoxyphenyl)amino)-2-(1-methyl-1H-indol-3-yl)-acetate (4b)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow liquid. Yield = 116 mg

(86%). **¹H NMR (600MHz, CDCl₃):** δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.32-7.30 (m, 1 H), 7.25 (s, 1 H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.11 (s, 1 H), 6.74 (d, *J* = 8.5 Hz, 2 H), 6.62 (d, *J* = 8.5 Hz, 2 H), 5.30 (s, 1 H), 4.25 (dq, *J* = 15.0, 7.3 Hz, 2 H), 4.13 (dq, *J* = 15.2, 7.3 Hz, 1 H), 3.74 (s, 3 H), 3.72 (s, 3 H), 1.22 (t, *J* = 7.1 Hz, 3H); **¹³C{¹H} NMR (201.2 MHz, CDCl₃):** δ 172.8, 152.4, 140.8, 137.2, 127.5, 126.3, 122.0, 119.6, 119.5, 114.8 (2 C), 114.7 (2 C), 111.1, 109.4, 61.4, 55.7, 55.1, 32.8, 14.1; **ATR:** 3397, 2935, 2832, 1729, 1511, 1235, 1024, 820, 742 cm⁻¹. **HRMS (ESI)** calcd for C₂₀H₂₂N₂NaO₃ [M + Na]⁺: 361.1522, found: 361.1515. Spectral data is close agreement with literature.¹¹



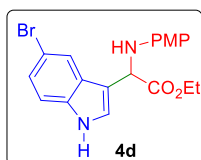
Ethyl 2-((4-methoxyphenyl)amino)-2-(2-methyl-1H-indol-3-yl)-acetate (4c)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow liquid. Yield = 124.5 mg (92%). **¹H NMR (600MHz, CDCl₃):** δ 8.03 (brs, 1H), 7.80 (dd, *J* = 6.2, 1.8 Hz, 1H), 7.21 (dd, *J* = 6.5, 2.8 Hz, 1H), 7.14-7.10 (m, 2 H), 6.75 (d, *J* = 8.6 Hz, 2 H), 6.60 (d, *J* = 8.6 Hz, 2 H), 5.25 (s, 1 H), 4.27-4.21 (m, 1 H), 4.11-4.05 (m, 1 H), 3.72 (s, 3 H), 2.42 (s, 3 H), 1.18 (t, *J* = 7.0 Hz, 3 H); **¹³C{¹H} NMR (201.2 MHz, CDCl₃):** δ 172.6, 152.3, 140.9, 135.1, 133.3, 126.7, 121.3, 119.8, 118.7, 114.8 (2 C), 114.6 (2 C), 110.4, 107.5, 61.3, 55.7, 54.9, 14.1, 12.0; **ATR:** 3394, 2983, 1725, 1510, 1297, 1234, 1175, 822 cm⁻¹; **HRMS (ESI)** calcd for C₂₀H₂₂N₂NaO₃ [M + Na]⁺: 361.1522, found: 361.1520. Spectral data is close agreement with literature.¹¹

Synthesis of 4c in 1 mmol scale:

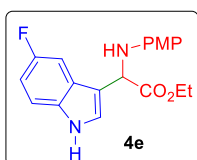
To a oven dried 25mL round bottom flask (wrapped in aluminium foil) with a magnetic stirring bar were added glycinate ester **1a** (209 mg, 1 mmol) and eosin Y (13 mg, 0.02 mmol, 2 mol%).

Then 5 mL of dry DCE was added via syringe followed by addition of $\text{Cu}(\text{OAc})_2$ (9.0 mg, 0.05 mmol, 5 mol%). The reaction mixture was stirred (for 10h) under air atmosphere at room temperature (30-32 °C). Once the glycinate ester **1a** was consumed (monitored by TLC), then 2-methyl-Indole (144 mg, 1.1 mmol) was added in one portion. The reaction mixture was further stirred for 4h. After completion of the reaction, the reaction mixture was concentrated to one-third of the total volume. The crude residue was purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to afford product **3e** as light-yellow liquid (306 mg, 90%).



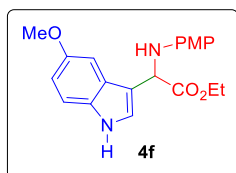
Ethyl 2-(5-bromo-1H-indol-3-yl)-2-((4-methoxyphenyl)amino)acetate (4d)

Purified by column chromatography on silica gel (15% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow liquid. Yield = 115 mg (71%). **^1H NMR (600MHz, CDCl_3):** δ 8.35 (s, 1H), 7.97 (s, 1 H), 7.28 (d, $J = 8.5$ Hz, 1H), 7.18-7.16 (m, 2 H), 6.75 (d, $J = 8.5$ Hz, 2 H), 6.60 (d, $J = 8.5$ Hz, 2 H), 5.26 (s, 1 H), 4.28-4.22 (m, 1 H), 4.17-4.11 (m, 1 H), 3.72 (s, 3 H), 1.23 (t, $J = 7.2$ Hz, 3 H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (201.2 MHz, CDCl_3):** δ 172.6, 152.7, 140.6, 135.2, 127.5, 125.4, 124.3, 122.2, 115.0 (2 C), 114.9 (2 C), 113.3, 112.9, 112.5, 61.8, 55.8, 55.1, 14.1; **HRMS (ESI)** calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3\text{Br}$ [$\text{M} + \text{H}$] $^+$: 403.0640, found: 403.0652. Spectral data is close agreement with literature.¹²



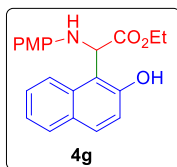
Ethyl 2-(5-fluoro-1H-indol-3-yl)-2-((4-methoxyphenyl)amino)acetate (4e)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow liquid. Yield = 102 mg (74%). **¹H NMR (600MHz, CDCl₃):** δ 8.27(bris, 1H), 7.48 (d, *J* = 9.6 Hz, 1H), 7.24-7.22 (m, 2 H), 6.96 (td, *J* = 8.9, 1.6 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 2 H), 6.61 (d, *J* = 8.6 Hz, 2H), 5.26 (s, 1 H), 4.26 (dq, *J* = 11.3, 7.3 Hz, 1H), 4.15 (dq, *J* = 10.7, 7.3 Hz, 1H), 3.72 (s, 3 H), 1.22 (t, *J* = 7.0 Hz, 3H); **¹³C{¹H} NMR (201.2 MHz, CDCl₃):** δ 172.6, 157.9 (d, *J*_{C-F} = 236.2 Hz), 152.6, 140.6, 132.9, 126.1 (d, *J*_{C-F} = 9.4 Hz), 124.7, 114.9 (2 C), 114.8 (2 C), 112.9, 112.0 (d, *J*_{C-F} = 8.4 Hz), 110.8 (d, *J*_{C-F} = 26.4 Hz), 104.5 (d, *J*_{C-F} = 26.1 Hz), 61.6, 55.7, 55.1, 14.1; **HRMS (ESI)** calcd for C₁₉H₂₀N₂O₃F [M + H]⁺: 343.1452, found: 343.1443.



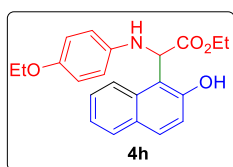
Ethyl 2-(5-methoxy-1H-indol-3-yl)-2-((4-methoxyphenyl)amin)acetate (4f)

Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow liquid. Yield = 111 mg (78%). **¹H NMR (600MHz, CDCl₃):** δ 8.21(bris, 1H), 7.26 (s, 1 H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 1.9 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 2 H), 6.63 (d, *J* = 8.9 Hz, 2 H), 5.29 (s, 1 H), 4.26 (dq, *J* = 11.2, 7.3 Hz, 1H), 4.15 (dq, *J* = 10.6, 6.7 Hz, 1H), 3.86 (s, 3 H), 3.73 (s, 3 H), 1.23 (t, *J* = 6.7 Hz, 3H); **¹³C{¹H} NMR (201.2 MHz, CDCl₃):** δ 172.8, 154.2, 152.5, 140.8, 131.5, 126.1, 123.7, 114.81(2 C), 114.79 (2 C), 112.7, 112.13, 112.09, 101, 61.4, 55.8, 55.6, 55.2, 14.1; **HRMS (ESI)** calcd for C₂₀H₂₃N₂O₄ [M + H]⁺: 355.1652, found: 355.1646. Spectral data is close agreement with literature.¹²



Ethyl 2-(2-hydroxynaphthalen-1-yl)-2-((4-methoxyphenyl)amino)acetate (4g)

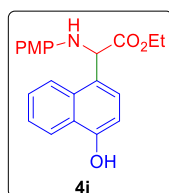
Purified by column chromatography on silica gel (20% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as red liquid. Yield = 119 mg (84.0 %). **¹H NMR (600MHz, CDCl₃):** δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 6.67 (s, 4 H), 5.80 (s, 1 H), 4.26-4.21(m, 1 H), 4.12-4.05 (m, 1 H), 3.67 (s, 3 H), 1.08 (t, *J* = 7.0 Hz, 3H), (OH and NH protons could not be detected); **¹³C{¹H} NMR (201.2 MHz, CDCl₃):** δ 171.1, 156.1, 154.6, 138.7, 132.4, 130.5, 129.1, 128.9, 126.8, 122.9, 121.8, 119.7, 117.7 (2 C), 114.7 (2 C), 111.3, 62.3, 57.9, 55.4, 13.8; **ATR :** 3326, 2983, 2834, 1726, 1510, 1212, 1163, 1121, 933, 822, 745 cm⁻¹; **HRMS (ESI)** calcd for C₂₁H₂₂NO₄ [M + H]⁺: 352.1543, found: 352.1545. Spectral data is close agreement with literature.¹³



Ethyl 2-((4-ethoxyphenyl)amino)2-(2-hydroxynaphthalen-1-yl)- acetate (4h)

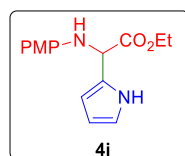
Purified by column chromatography on silica gel (15% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as white solid. Yield = 114 mg (78%); Mp: 149-151°C; Mp: 148-149°C^{lit11}; **¹H NMR (600MHz, CDCl₃):** δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.3Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.66 (s, 4 H), 5.80 (s, 1 H), 4.26-4.21 (m, 1 H), 4.11-4.05 (m, 1 H), 3.87 (q, *J* = 7.0 Hz, 2 H), 1.32 (t, *J* = 7.0 Hz, 3 H), 1.08 (t, *J* = 7.0 Hz, 3 H); (OH

and NH protons could not be detected); **$^{13}\text{C}\{^1\text{H}\}$ NMR (201.2 MHz, CDCl_3):** δ 171.1, 156.1, 154.0, 138.6, 132.4, 130.5, 129.1, 128.9, 126.8, 122.9, 121.9, 119.8, 117.7 (2 C), 115.4 (2 C), 111.2, 63.7, 62.4, 58.0, 14.8, 13.8; **ATR :** 3327, 2981, 2902, 1726, 1510, 1212, 1163, 1117, 821, 745 cm^{-1} ; **HRMS (ESI)** calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_4$ $[\text{M} + \text{H}]^+$: 366.1699, found: 366.1699. Spectral data is close agreement with literature.¹³



Ethyl 2-(4-hydroxynaphthalen-1-yl)-2-((4-methoxyphenyl)amino)acetate (4i)

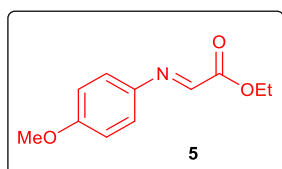
Purified by column chromatography on silica gel (10% EtOAc/ petroleum ether –15% EtOAc/ petroleum ether). The above titled compound was isolated as red liquid. Yield = 120 mg (85.0 %). **^1H NMR (600MHz, CDCl_3):** δ 8.27 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 7.8$ Hz, 1H), 7.51-7.45 (m, 2H), 7.42 (d, $J = 8.3$ Hz, 1H), 7.36 (d, $J = 8.5$ Hz, 1H), 6.79-6.78 (m, 2 H), 6.75-6.74 (m, 2 H), 5.08 (s, 1 H), 4.31-4.26 (m, 1 H), 4.20-4.14 (m, 1 H), 3.71 (s, 3 H), 1.21 (t, $J = 7.0$ Hz, 3H), (OH and NH protons could not be detected); **$^{13}\text{C}\{^1\text{H}\}$ NMR (201.2 MHz, CDCl_3):** δ 171.2, 154.7, 153.0, 138.8, 134.2, 127.2, 126.8, 126.6, 125.4, 125.1, 122.4, 119.4, 117.9 (2 C), 114.7 (2 C), 113.2, 63.4, 62.4, 55.5, 13.9; **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_4$ $[\text{M} + \text{H}]^+$: 352.1543, found: 352.1543. Spectral data is close agreement with literature.¹³



Ethyl 2-((4-methoxyphenyl)amino)-2-(1H-pyrro)acetate (4j)

Purified by column chromatography on silica gel (15% EtOAc/ petroleum ether –25% EtOAc/ petroleum ether). The above titled compound was isolated as yellow liquid which turns to black

with time. Yield = 75 mg (68%); $^1\text{H NMR}$ (600MHz, CDCl_3): δ 8.6 (brs, 1H), 6.75 (d, $J = 8.6$ Hz, 2 H), 6.72 (s, 1 H), 6.60 (d, $J = 8.6$ Hz, 2 H), 6.24 (brs, 1 H), 6.19-6.17 (m, 1 H), 5.07 (s, 1H), 4.28-4.23 (m, 1 H), 4.22-4.17(m, 1H), 3.73 (s, 3 H), 1.27 (t, $J = 7.3$ Hz, 3 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (201.2 MHz, CDCl_3): δ 171.5, 153.0, 140.5, 126.9, 117.9, 115.2 (2 C), 114.8 (2 C), 108.9, 106.9, 61.9, 56.6, 55.7, 14.1. Spectral data is close agreement with literature.¹³



Ethyl-(E)-2-((4-methoxyphenyl)imino)acetate (5)¹⁴

$^1\text{H NMR}$ (300MHz, CDCl_3): δ 7.94 (s, 1 H), 7.36 (d, $J = 9.0$ Hz, 2 H), 6.94 (d, $J = 9.0$ Hz, 2 H), 4.42 (q, $J = 7.1$ Hz, 2 H), 3.84 (s, 3 H), 1.41 (t, $J = 7.1$ Hz, 3 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (201.2 MHz, CDCl_3): δ 163.6, 160.5, 148.0, 141.4, 123.6, 114.5, 61.9, 55.5, 14.2. LRMS: $[\text{M}+\text{Na}]^+$: 230.05.

12. References

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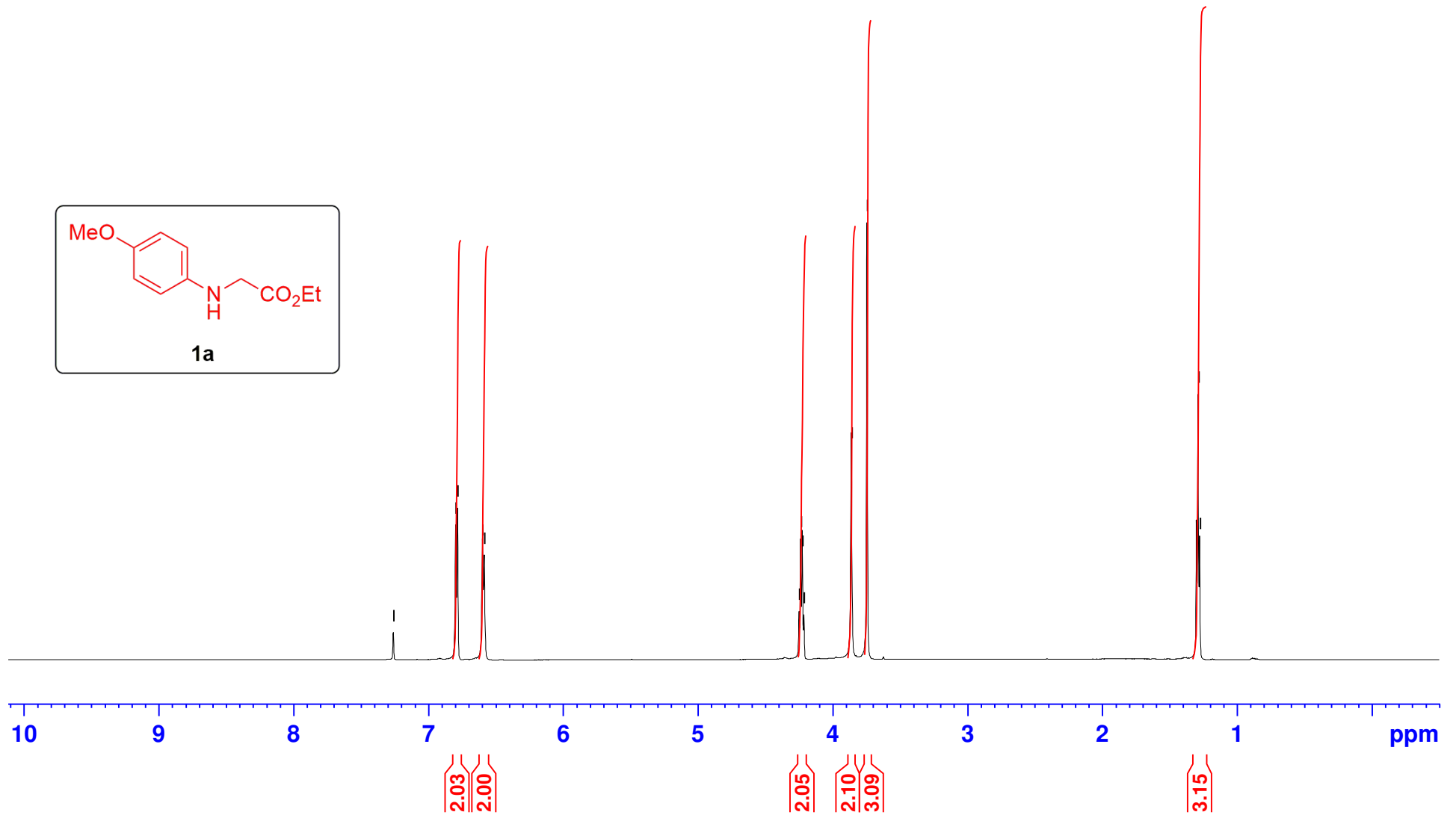
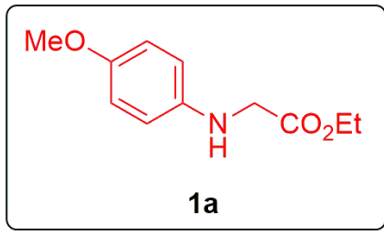
¹H NMR, 600 MHz, CDCl₃

CDCl₃

7.258
6.796
6.782
6.596
6.583

4.246
4.235
4.223
4.211
3.859
3.742

1.298
1.286
1.274



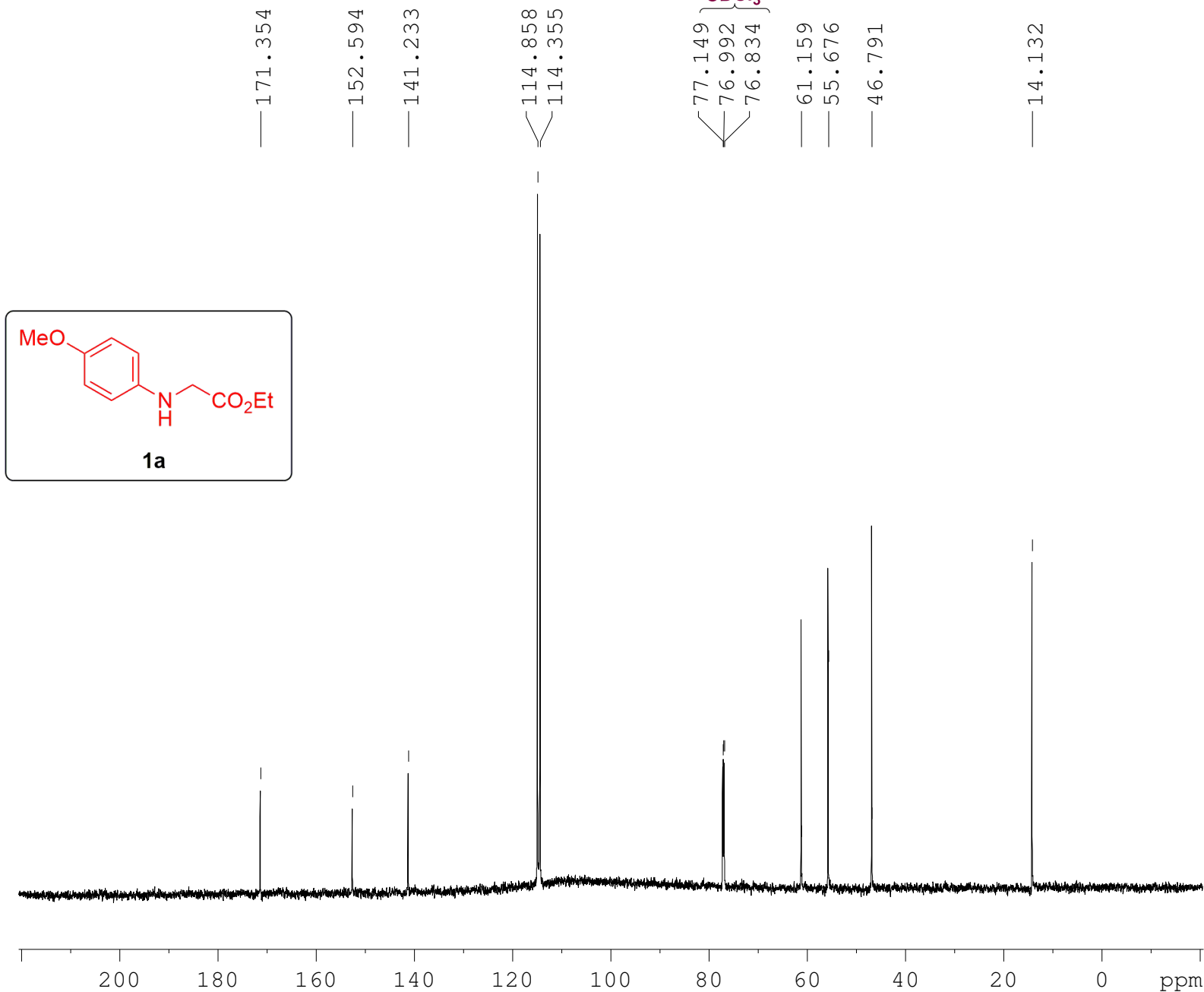
¹³C NMR, 201.2 MHz, CDCl₃



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PROCNO 1

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FIDRES 5.925743 Hz
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DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SF01 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SF02 800.0332001 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 60.00 usec
PLW2 13.0000000 W
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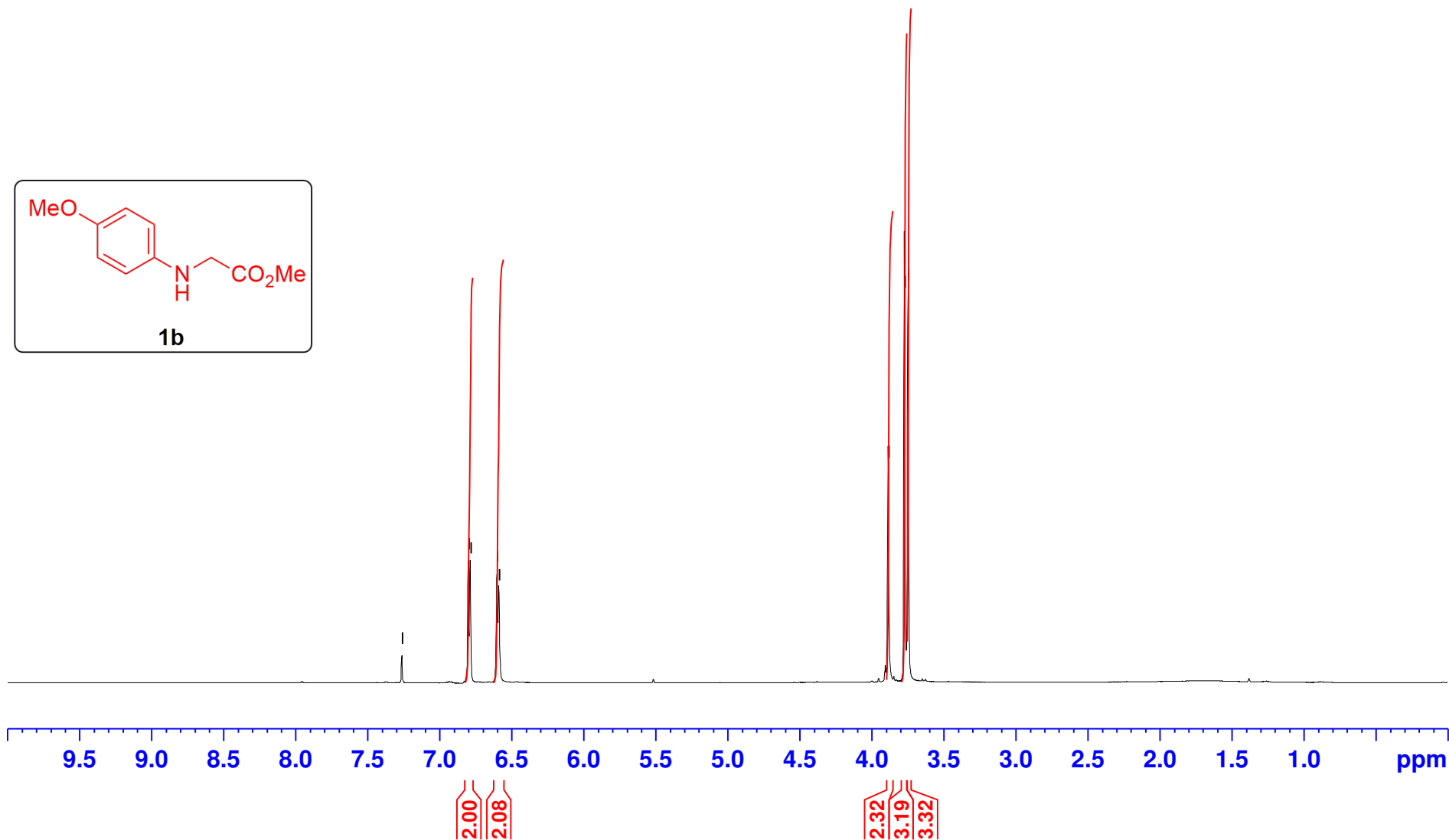
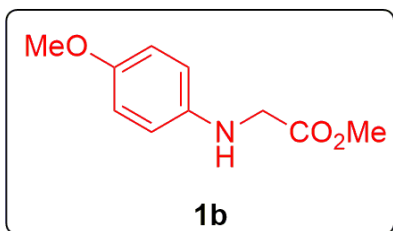


¹H NMR, 600 MHz, CDCl₃

CDCl₃

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6.784
6.599
6.586

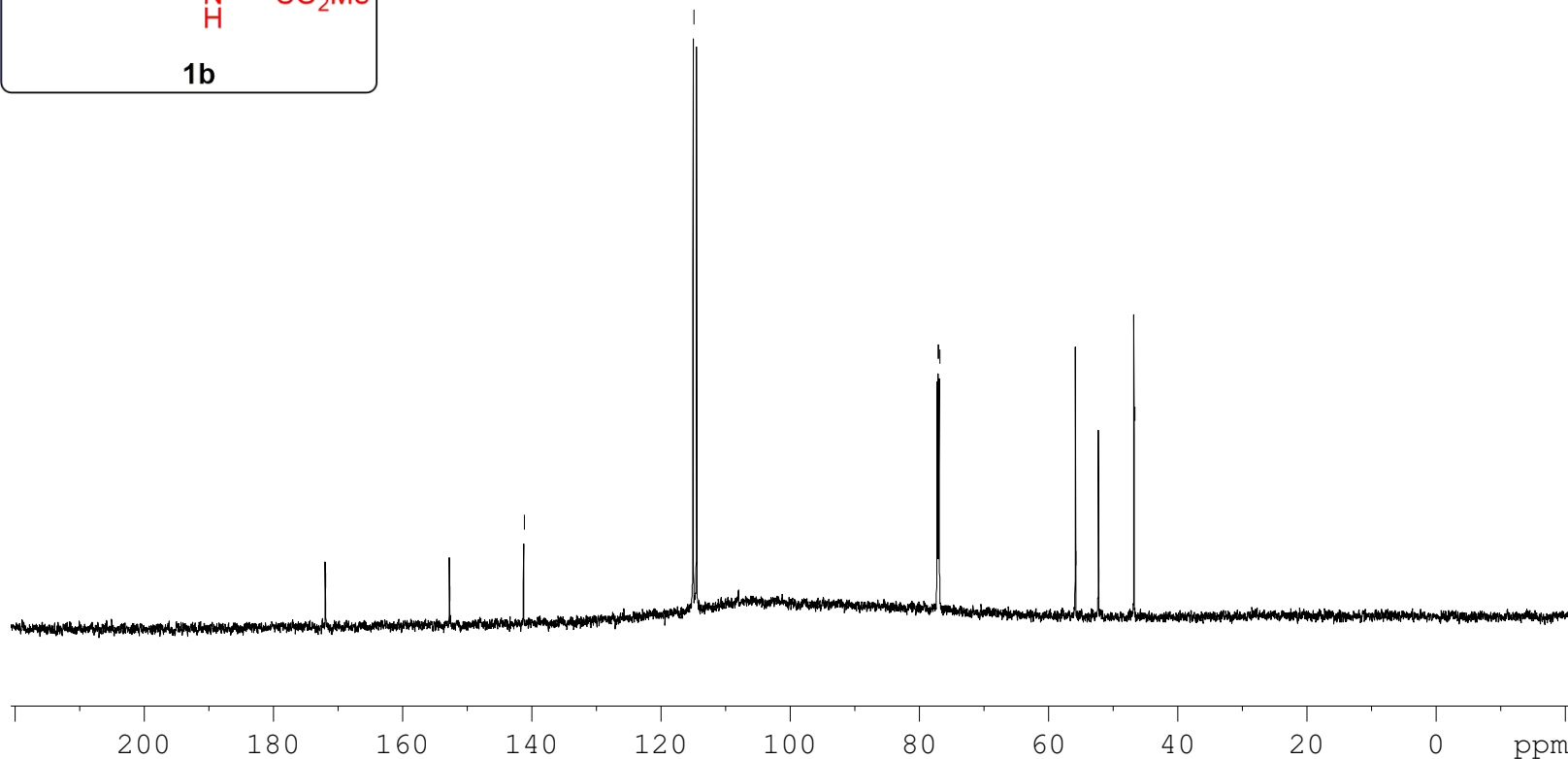
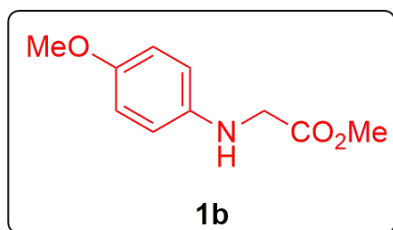
3.882
3.769
3.744



¹³C NMR, 201.2 MHz, CDCl₃



— 171.883
— 152.685
— 141.174
114.918
114.389
CDCl₃
77.155
76.996
76.839
55.724
52.162
46.651



Current Data Parameters
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PROCNO 1
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D11 0.03000000 sec
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NUC1 13C
P1 9.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
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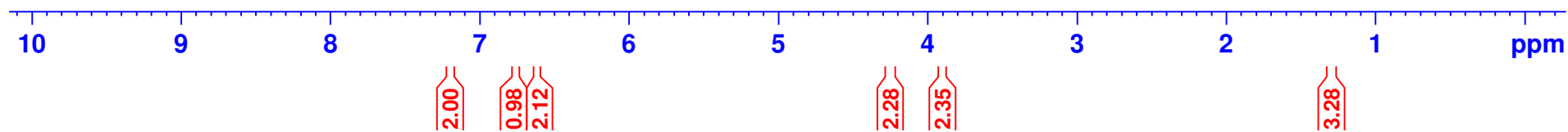
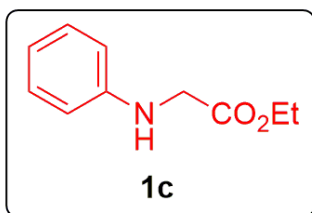
^1H NMR, 600 MHz, CDCl_3

CDCl_3

7.259
7.211
7.199
7.186
6.770
6.758
6.746
6.626
6.613

4.268
4.256
4.244
4.232
3.904

1.313
1.301
1.290



¹³C NMR, 201.2 MHz, CDCl₃

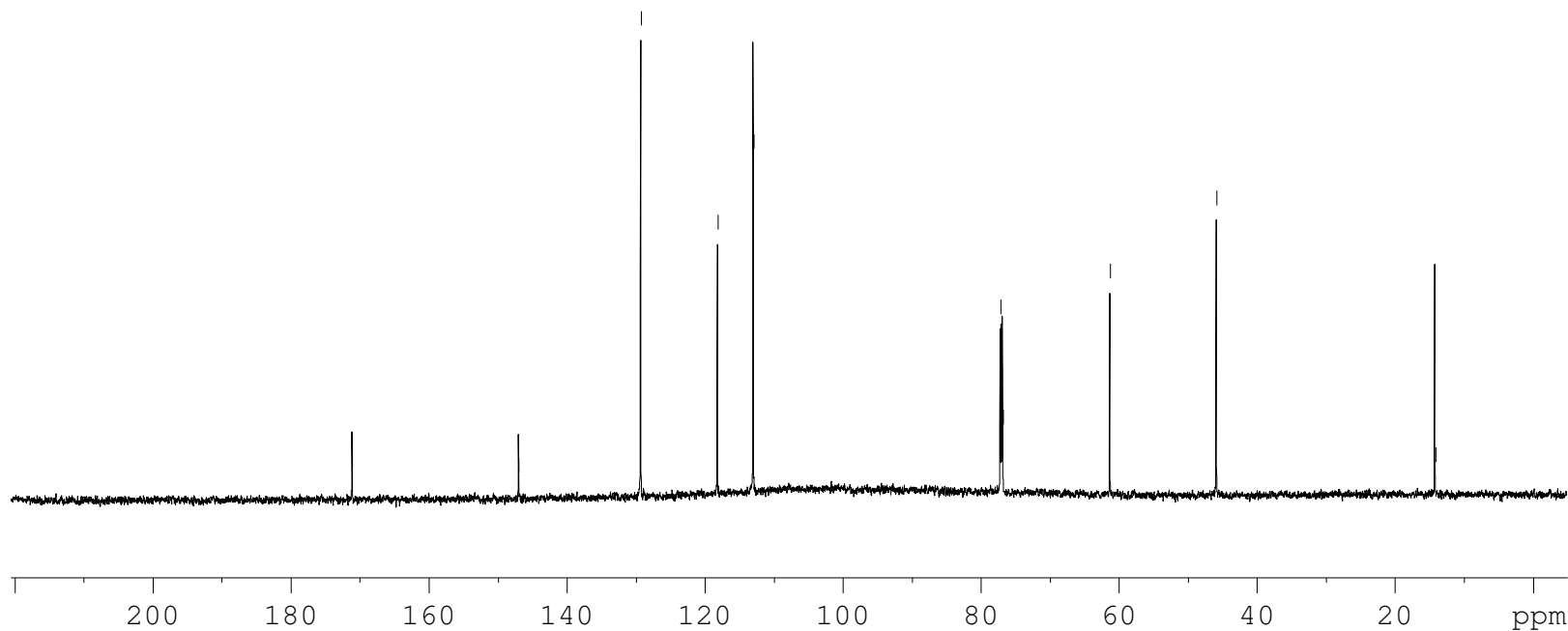
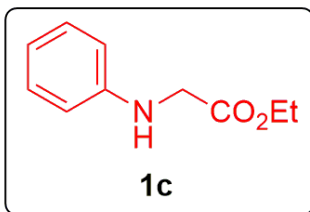


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RG 71.8
DW 10.300 usec
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TE 298.1 K
D1 3.0000000 sec
D11 0.0300000 sec
TDO 1
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P1 9.00 usec
PLW1 312.79998779 W
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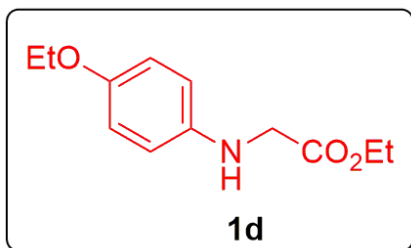
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— 171.097
— 146.988
— 129.267
— 118.145
— 112.961
— 77.147 } CDCl₃
— 76.990 }
— 76.832 }
— 61.269
— 45.819
— 14.147



CDCl_3

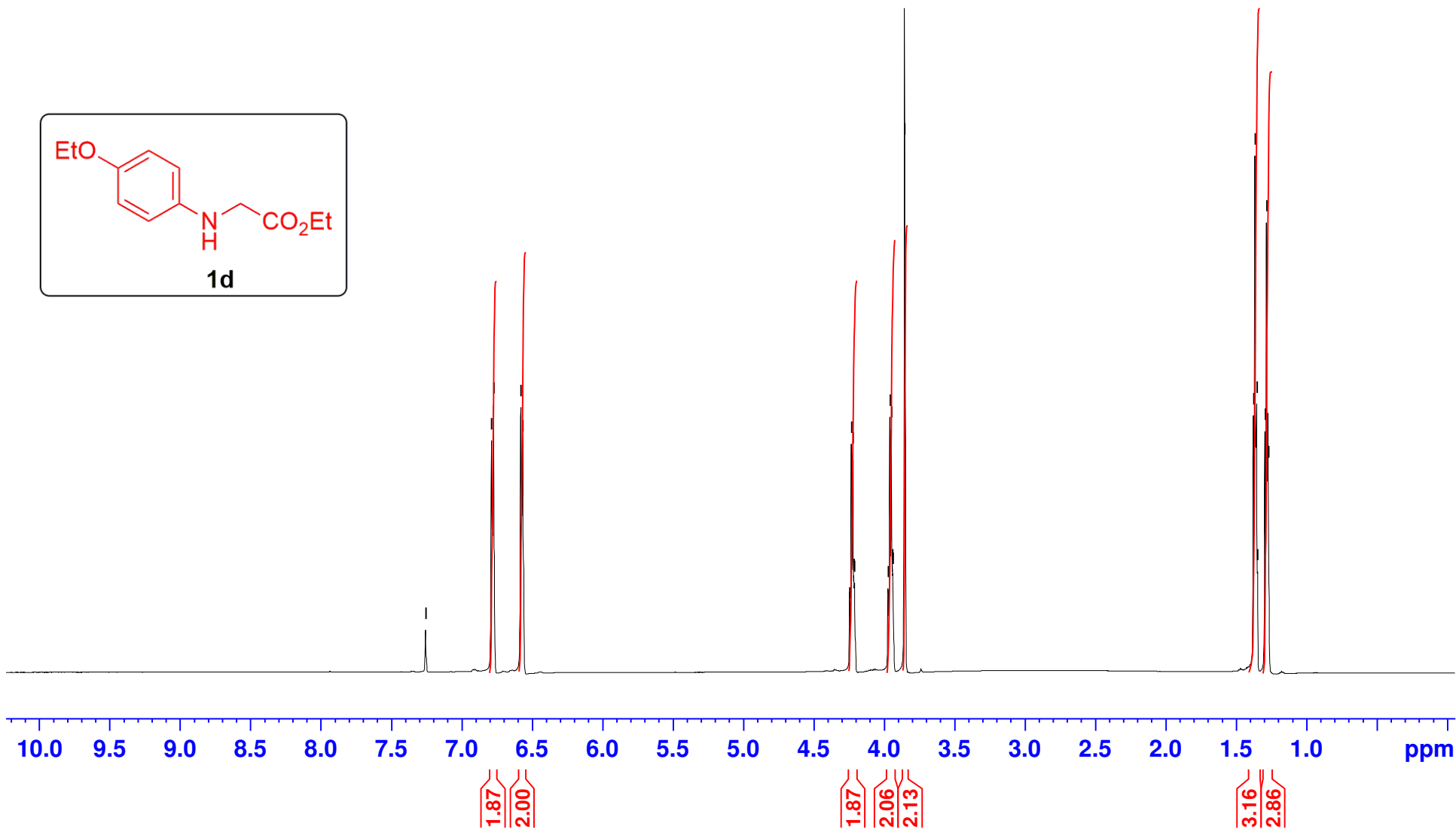
$^1\text{H NMR}$, 600 MHz, CDCl_3



— 7.257
6.788
6.774
6.580
6.566

4.244
4.232
4.220
4.213
4.210
3.970
3.959
3.947
3.940
3.937
3.854

1.376
1.365
1.353
1.347
1.294
1.283
1.275
1.271



¹³C NMR, 201.2 MHz, CDCl₃

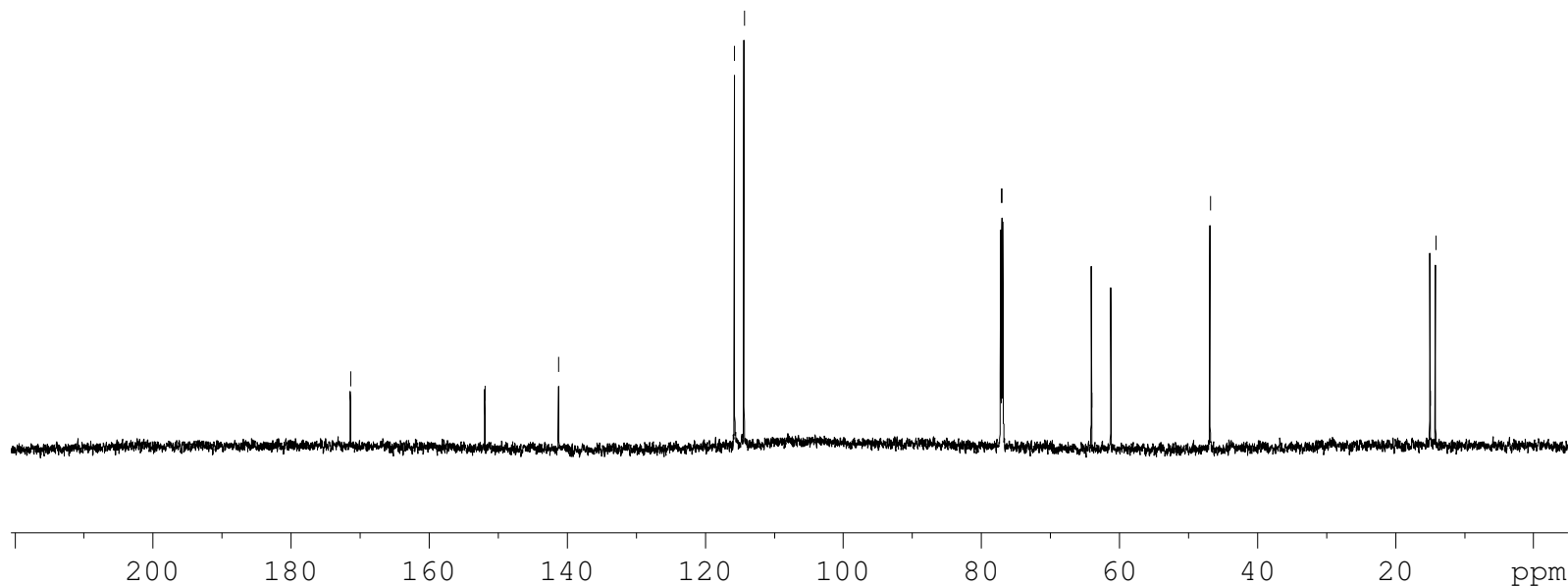
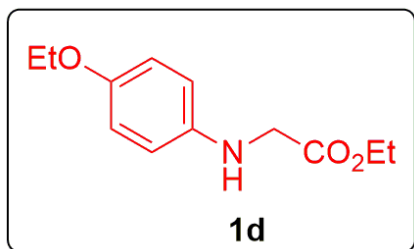


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PROCNO 1

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DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 9.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
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PLW12 0.29249999 W

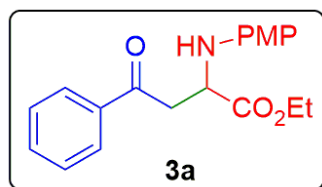
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— 171.383
— 151.901
— 141.219
— 115.733
— 114.360
— 77.154
— 76.995
— 76.837
— 64.015
— 61.187
— 46.832
— 14.957
— 14.165



¹H NMR, 600 MHz, CDCl₃

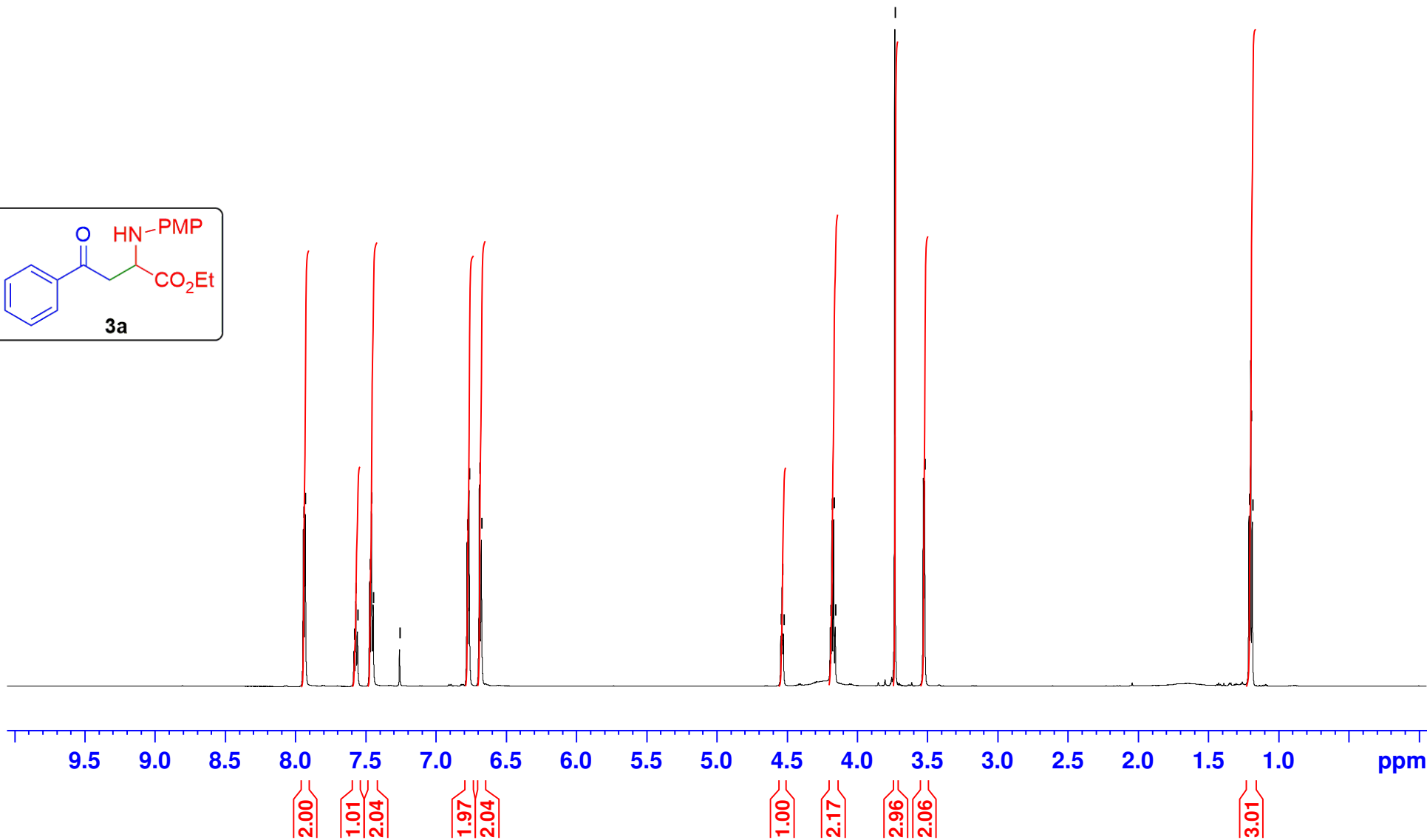
CDCl₃



7.942
7.929
7.581
7.569
7.557
7.470
7.458
7.445
7.257
6.776
6.762
6.689
6.674

4.542
4.533
4.524
4.189
4.178
4.166
4.154
3.730
3.527
3.518

1.207
1.196
1.184



¹³C NMR, 201.2 MHz, CDCl₃



Current Data Parameters
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TE 298.0 K
D1 3.0000000 sec
D11 0.03000000 sec
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SFO1 201.1878208 MHz
NUC1 13C
P1 15.00 usec
PLW1 141.03999329 W
SFO2 800.0332001 MHz
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CPDPRG[2] waltz16
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PLW12 0.16679481 W

F2 - Processing parameters
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LB 5.00 Hz
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— 197.396

— 173.206

— 153.017

— 140.599

— 136.520

— 133.499

— 128.694

— 128.141

— 115.748

— 114.866

CDCl₃

77.207

77.047

76.888

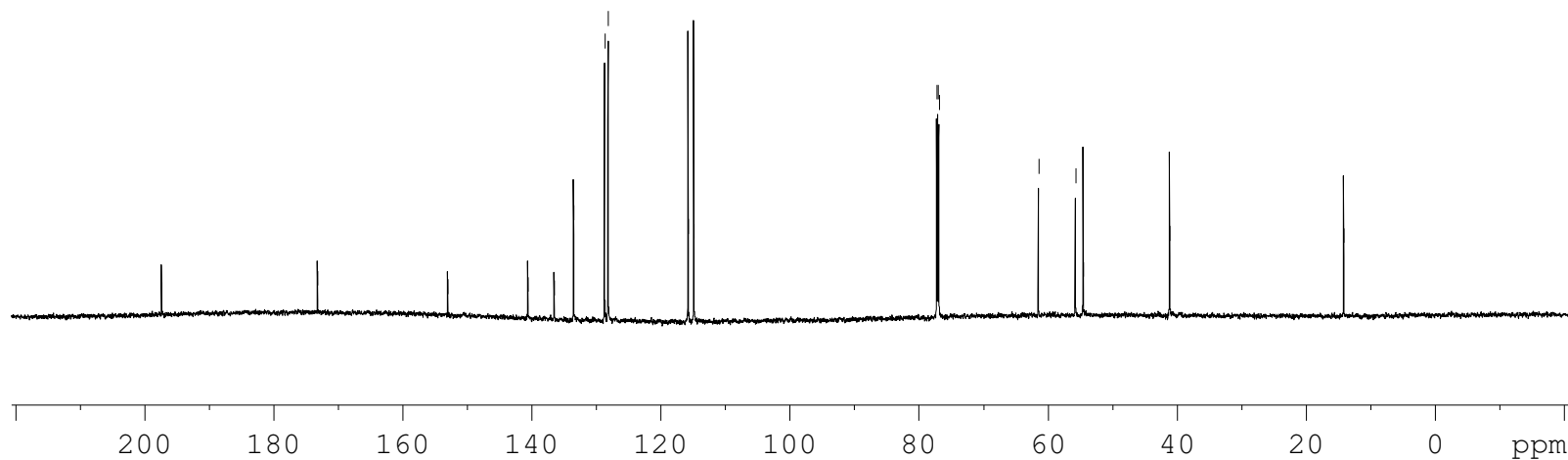
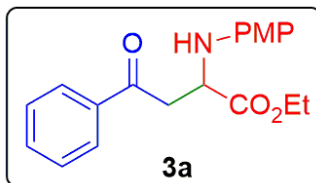
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55.701

54.509

— 41.099

— 14.099



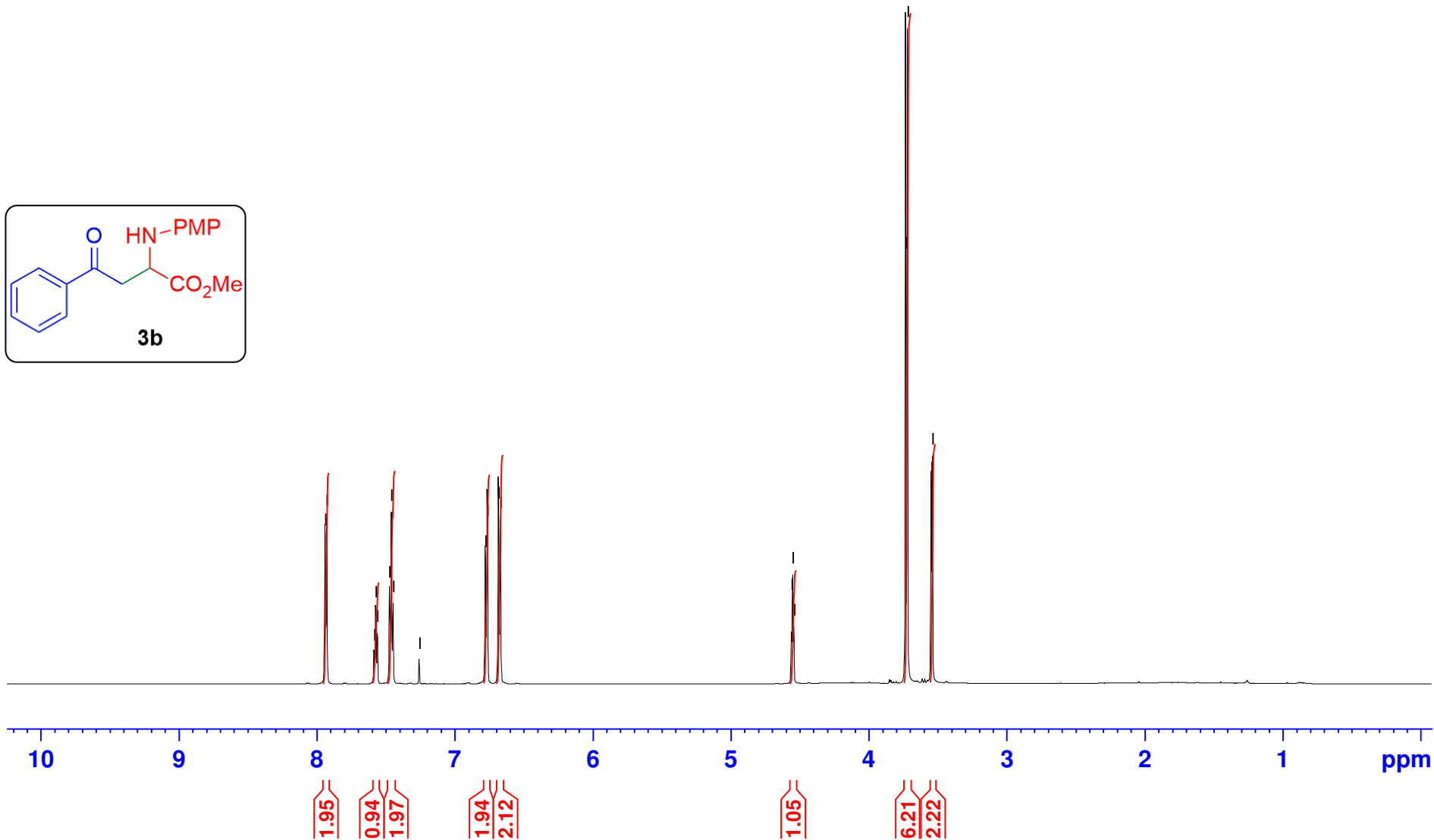
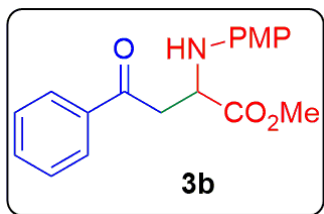
¹H NMR, 600 MHz, CDCl₃

CDCl₃

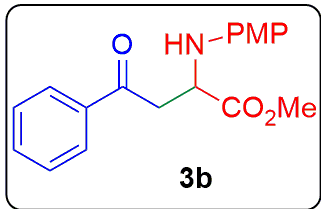
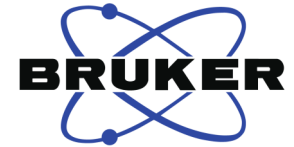
7.938
7.925
7.583
7.571
7.559
7.471
7.458
7.445
7.256
6.777
6.763
6.681
6.667

4.557
4.549
4.540

3.729
3.716
3.544
3.536



¹³C NMR, 201.2 MHz, CDCl₃



— 197.392

— 173.752

— 153.037

< 140.527

< 136.407

— 133.557

< 128.709

< 128.148

< 115.678

< 114.901

CDCl₃
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< 77.083
< 76.925

< 55.688

< 54.303

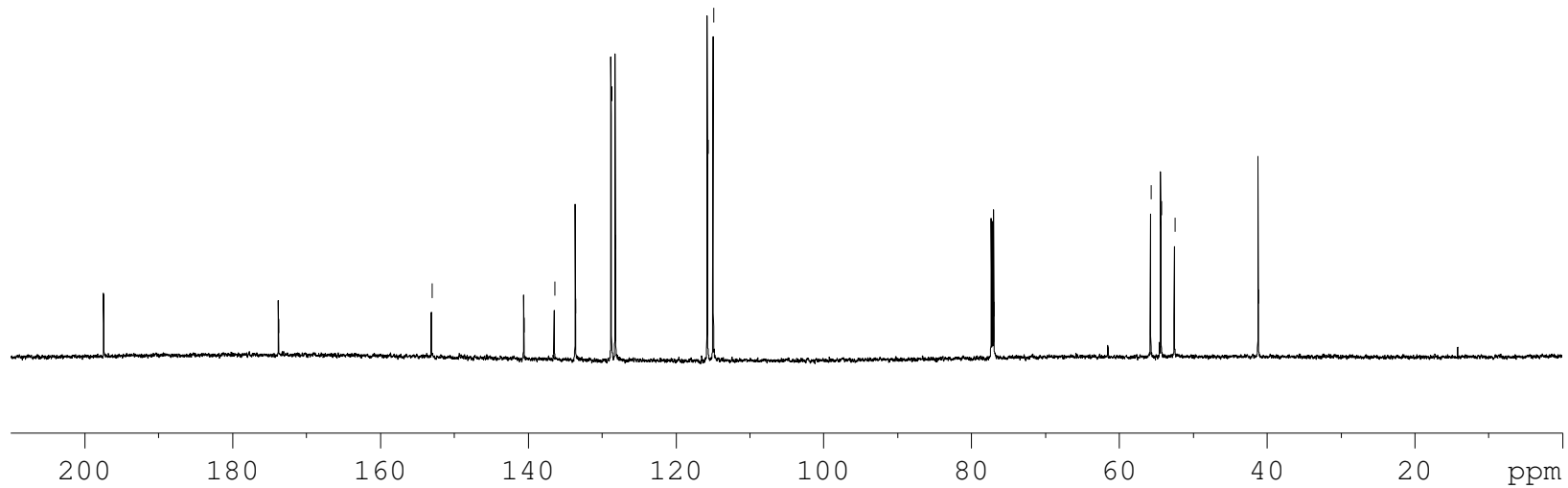
< 52.460

— 41.137

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INSTRUM spect
PROBHD 244909_0011 (C
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 332
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 18.00 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.03000000 sec
TDO 1
SF01 201.1878208 MHz
NUC1 13C
P1 15.00 usec
PLW1 141.03999329 W
SF02 800.0332001 MHz
NUC2 1H
PCPD2 waltz16
PCPD2 60.00 usec
PLW2 10.18999958 W
PLW12 0.16679481 W

F2 - Processing parameters
SI 16384
SF 201.1677040 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40



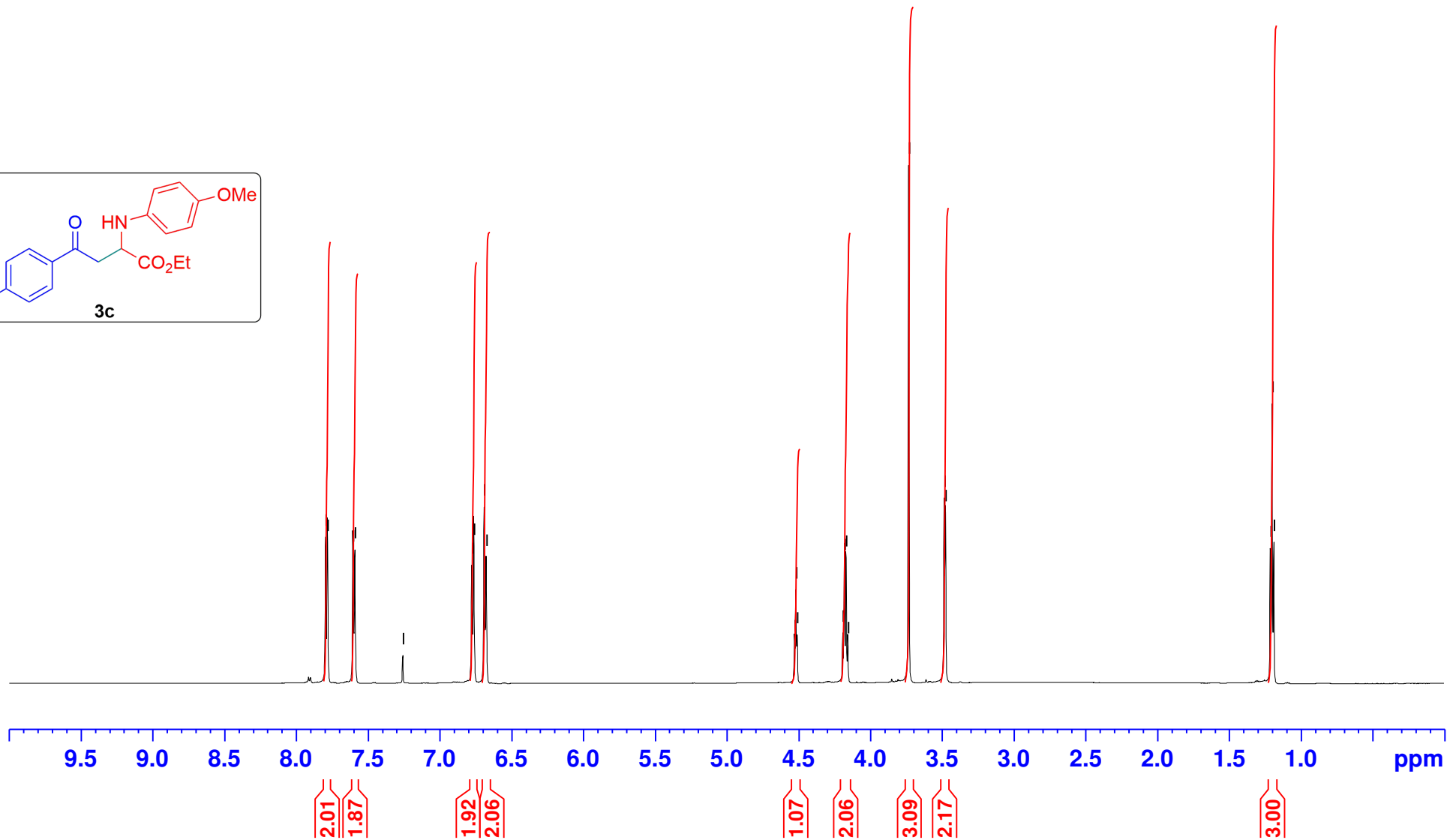
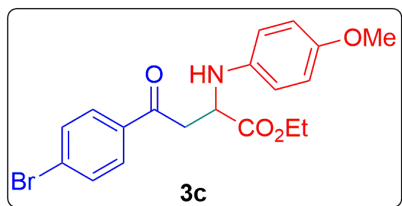
¹H NMR, 600 MHz, CDCl₃

CDCl₃

7.793
7.780
7.603
7.589
7.256
6.775
6.761
6.688
6.674

4.526
4.517
4.508
4.190
4.178
4.166
4.155
3.730
3.483
3.474

1.210
1.198
1.186



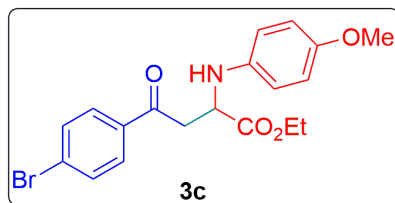
¹³C NMR, 201.2 MHz, CDCl₃



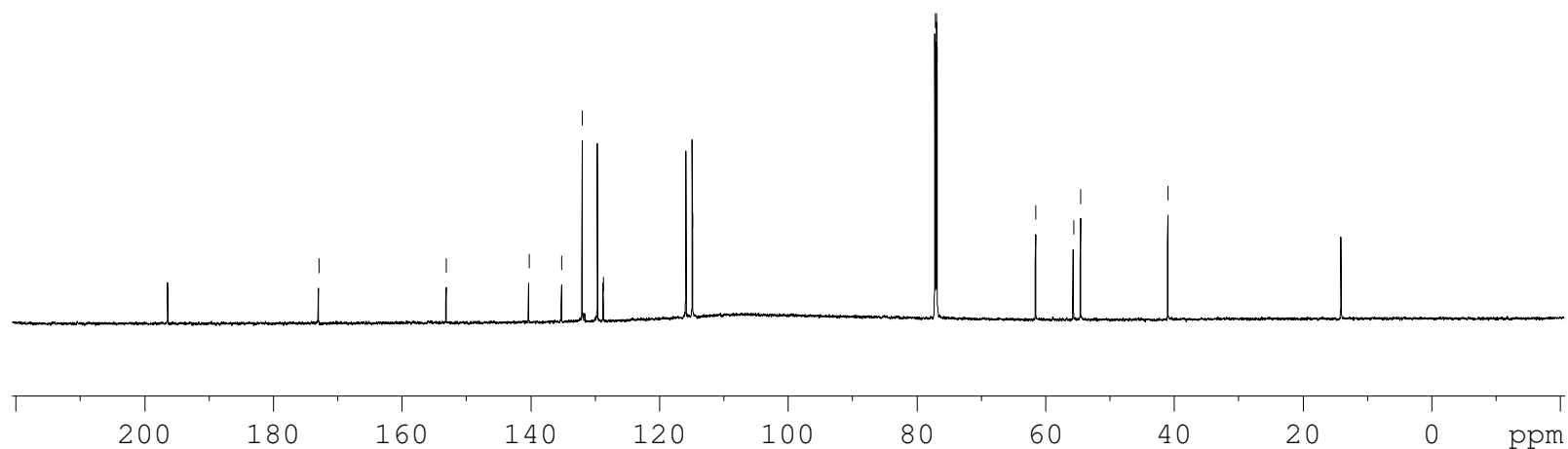
Current Data Parameters
NAME barc-RC-2106-13C-2July21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210702
Time_ 14.33 h
INSTRUM spect
PROBHD Z555801_0012 (
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 613
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.3 K
D1 3.0000000 sec
D11 0.03000000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W

F2 - Processing parameters
SI 16384
SF 201.1677138 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40



—196.385
—172.962
—153.129
140.289
135.187
131.979
129.594
128.713
115.846
114.838
CDCl₃
77.148
76.990
76.832
61.505
55.649
54.522
40.960
—14.057



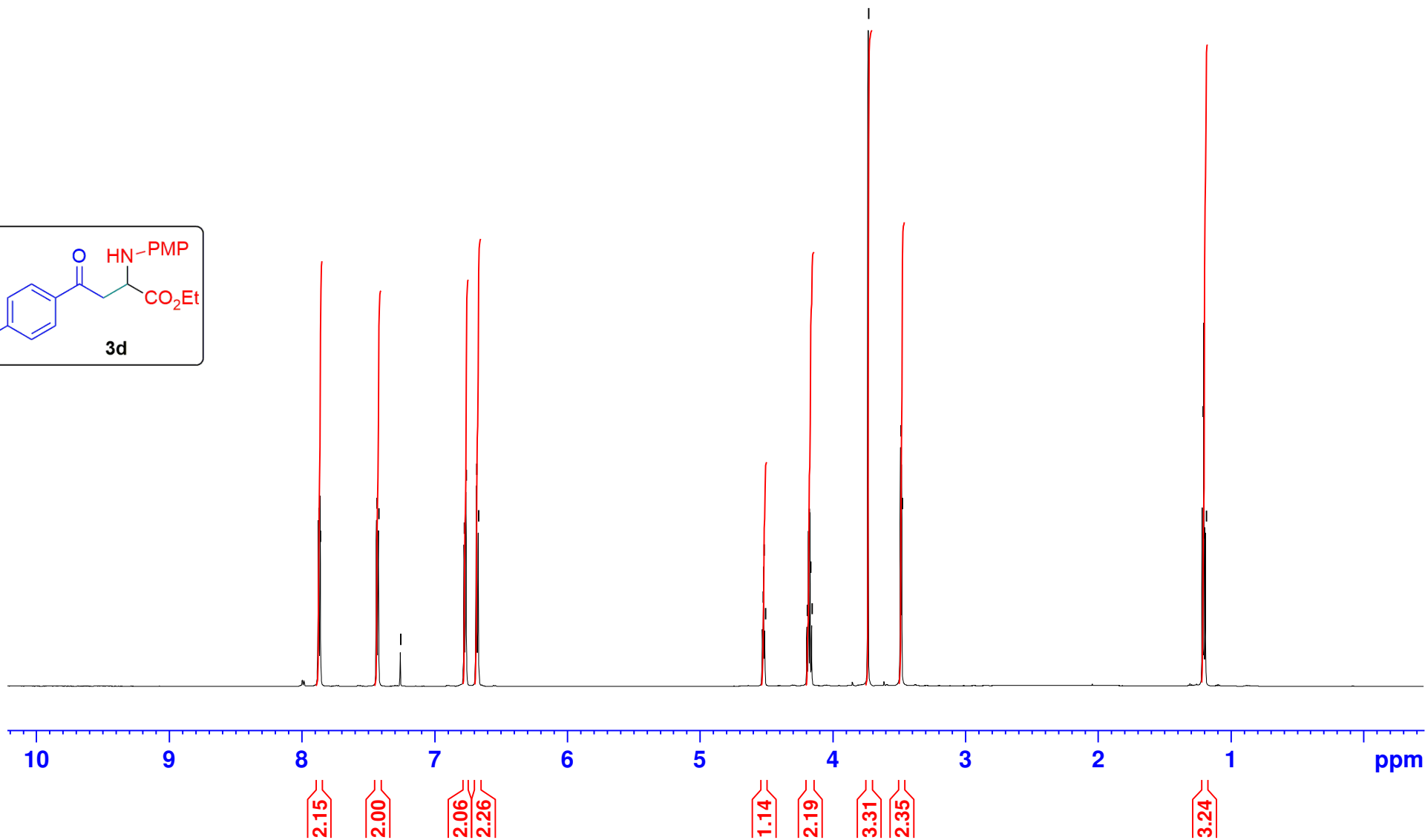
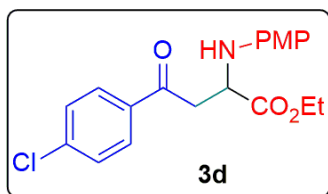
¹H NMR, 600 MHz, CDCl₃

CDCl₃

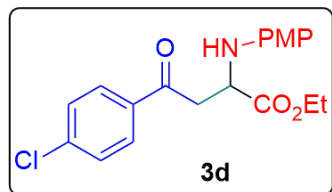
7.873
7.860
7.435
7.421
7.256
6.775
6.761
6.683
6.669

4.526
4.517
4.508
4.190
4.179
4.167
4.155
3.730
3.486
3.477

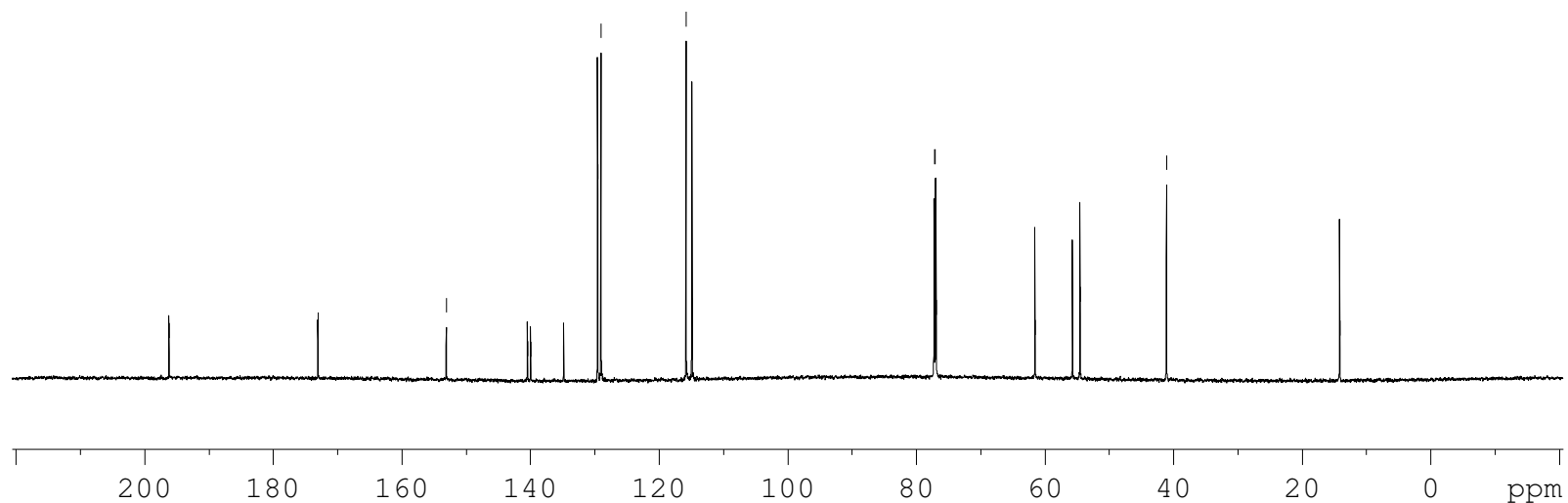
1.211
1.198
1.187



¹³C NMR, 201.2 MHz, CDCl₃



— 196.230
— 173.058
— 153.090
140.475
139.991
134.842
129.552
129.022
115.780
114.877
CDCl₃
77.218
77.059
76.899
61.521
55.688
54.501
— 41.051
— 14.110



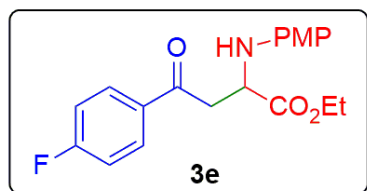
Current Data Parameters
NAME barc-RC-2000-13C-24Jan21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210224
Time 11.52 h
INSTRUM spect
PROBHD 244909_0011 (C
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 100
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 18.00 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SF01 201.1878208 MHz
NUC1 13C
P1 15.00 usec
PLW1 141.03999329 W
SF02 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 10.18999958 W
PLW12 0.16679481 W

F2 - Processing parameters
SI 16384
SF 201.1677040 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

¹H NMR, 600 MHz, CDCl₃

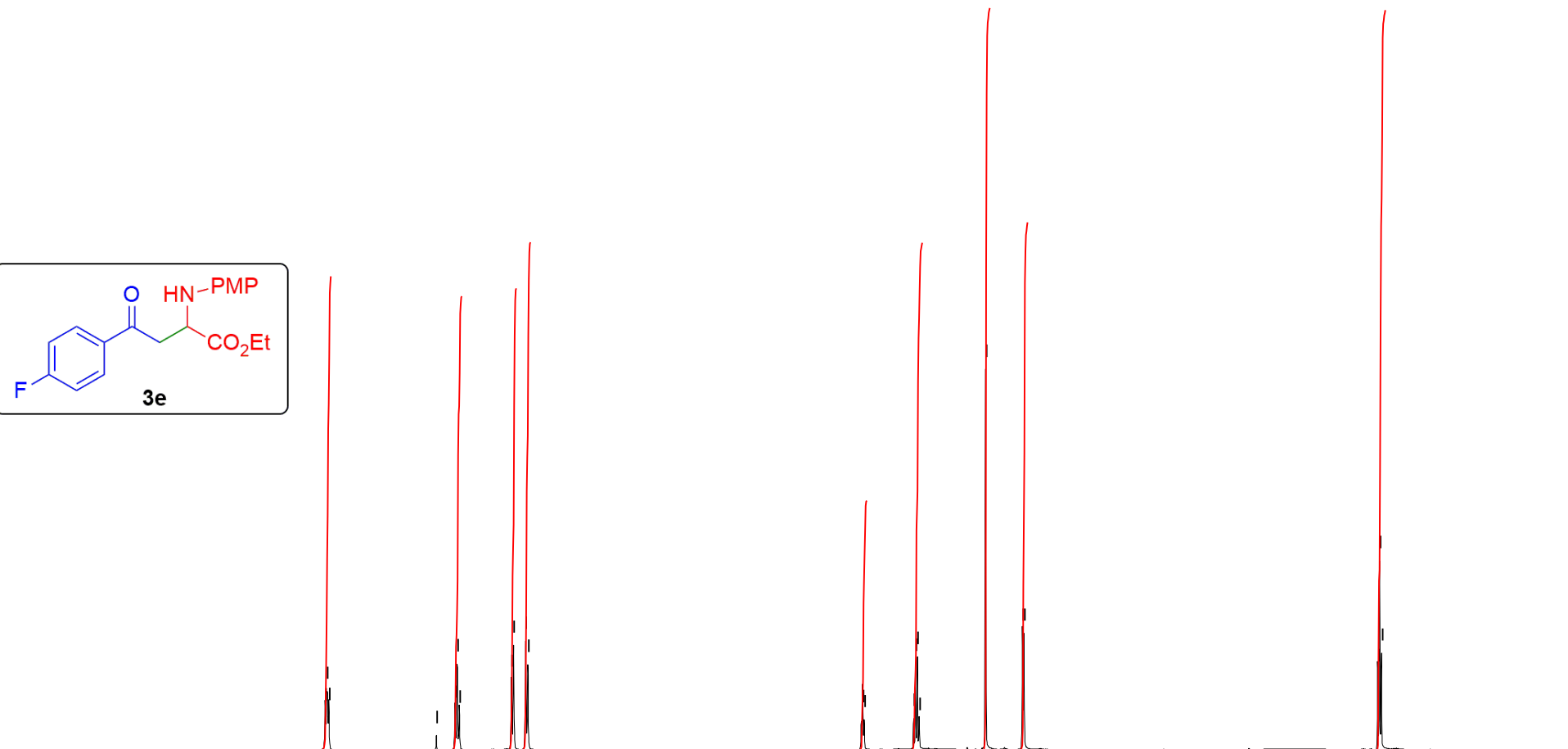
CDCl₃



7.970
7.957
7.947
7.256
7.137
7.123
7.109
6.774
6.760
6.683
6.668

4.526
4.518
4.509
4.191
4.179
4.167
4.155
3.729
3.491
3.482

1.210
1.198
1.186



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 ppm

2.00

1.92

1.95

2.14

1.06

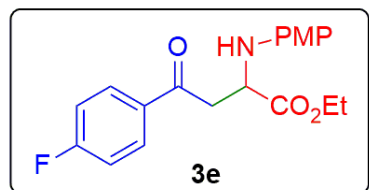
2.14

3.12

2.22

3.12

¹³C NMR, 201.2 MHz, CDCl₃



— 195.814

— 173.109
— 166.597
— 165.327

— 153.075

— 140.507
— 132.985
— 130.844
— 130.801

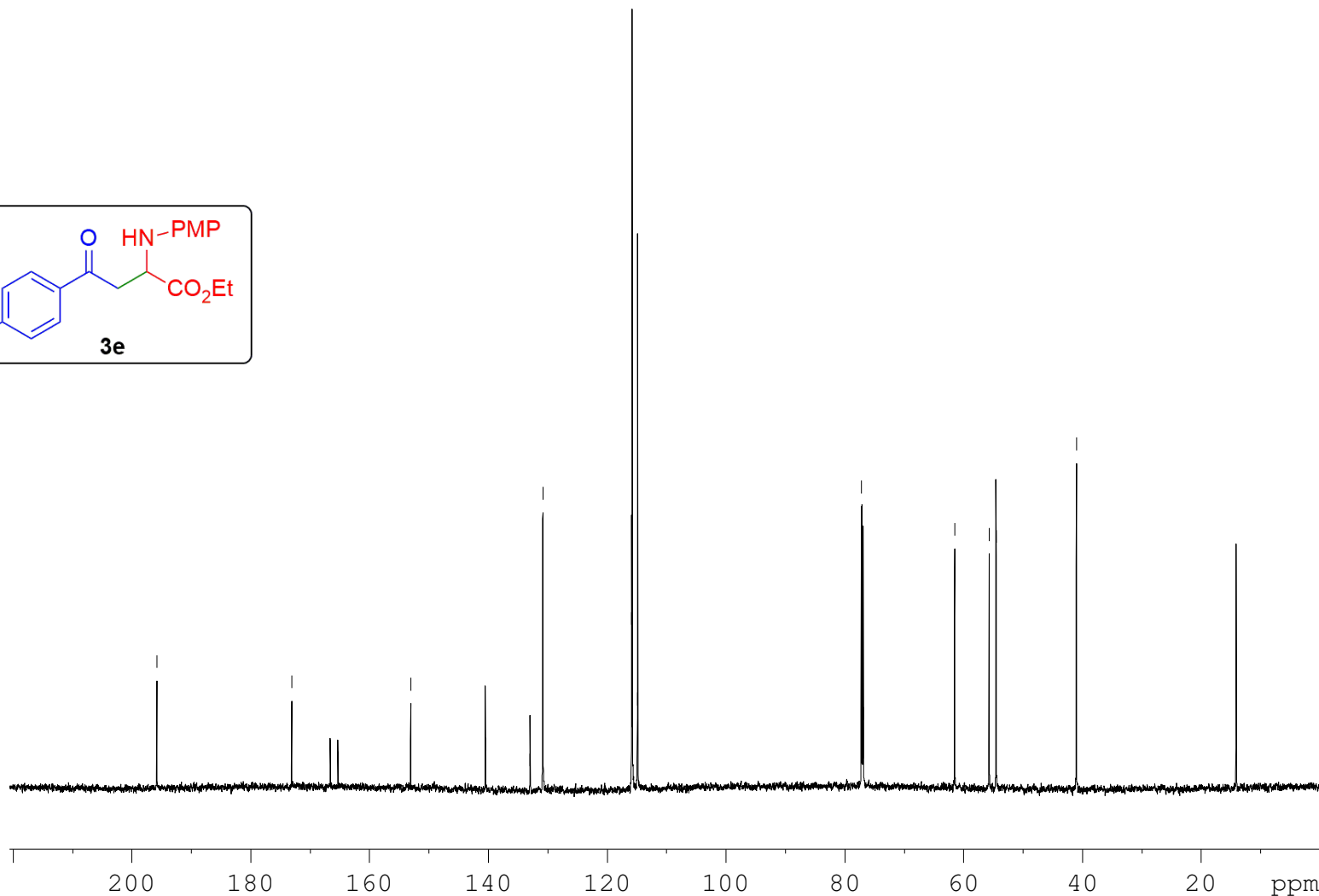
— 115.883
— 115.771
— 114.870

CDCl₃
— 77.208
— 77.049
— 76.891

— 61.495
— 55.688
— 54.523

— 40.993

— 14.101



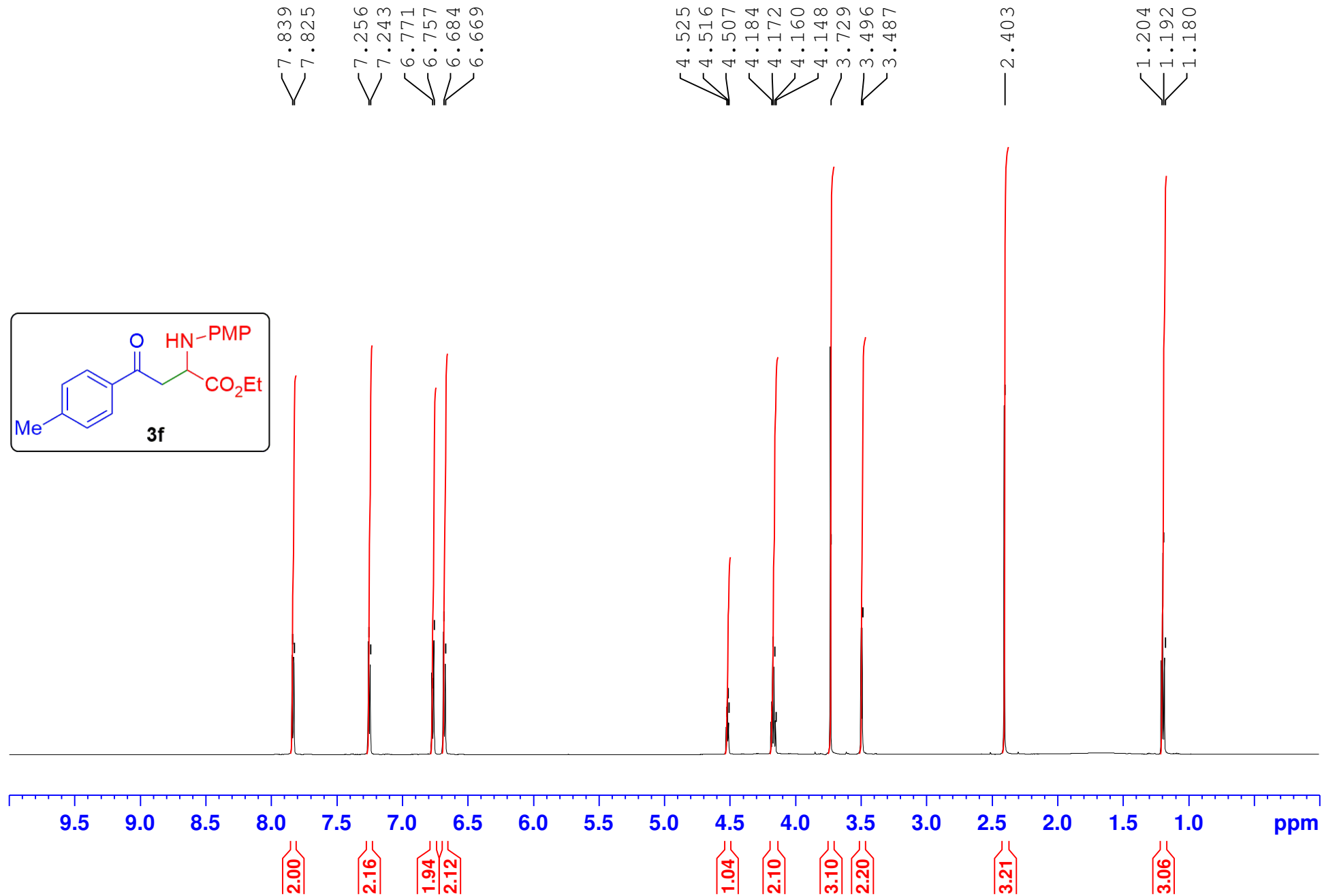
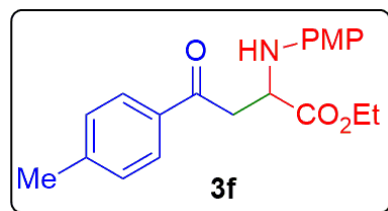
Current Data Parameters
NAME barc-RC-2018-13C-24Jan21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210224
Time 12.34 h
INSTRUM spect
PROBHD Z44909_0011 (C
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 217
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 18.00 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 15.00 usec
PLW1 141.03999329 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 10.18999958 W
PLW12 0.16679481 W

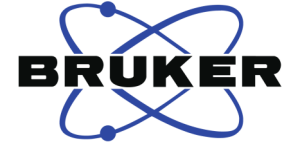
F2 - Processing parameters
SI 16384
SF 201.1677040 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

¹H NMR, 600 MHz, CDCl₃

CDCl₃



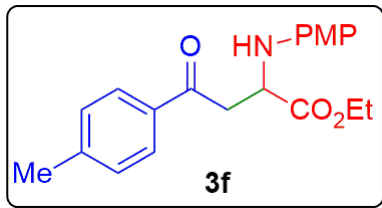
¹³C NMR, 201.2 MHz, CDCl₃



```
Current Data Parameters
NAME      barc-RC-2005-13C-24Jan21
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_     20210224
Time      15.19 h
INSTRUM   spect
PROBHD    Z44909_0011 (C
PULPROG   zgpg
TD         16384
SOLVENT   CDCl3
NS         159
DS         4
SWH        48543.688 Hz
FIDRES     5.925743 Hz
AQ         0.1687532 sec
RG         71.8
DM         10.300 usec
DE         18.00 usec
TE         298.0 K
D1         3.0000000 sec
D11        0.03000000 sec
TDO        1
SFO1       201.1878208 MHz
NUC1        13C
P1         15.00 usec
PLW1       141.83999329 W
SFO2       800.0322001 MHz
NUC2        1H
CPDPRG2    waltz16
PCPD2      60.00 usec
PLW2       10.18999958 W
PLW12      0.16679481 W

F2 - Processing parameters
SI         16384
SF         201.1677040 MHz
WDW        EM
SSB        0
LB         0
GB         0
PC         1.40
```



—197.395

—173.047

144.182
136.516
133.495
129.848
128.689
128.148
127.895
—114.085

CDCl₃
77.232
77.073
76.913

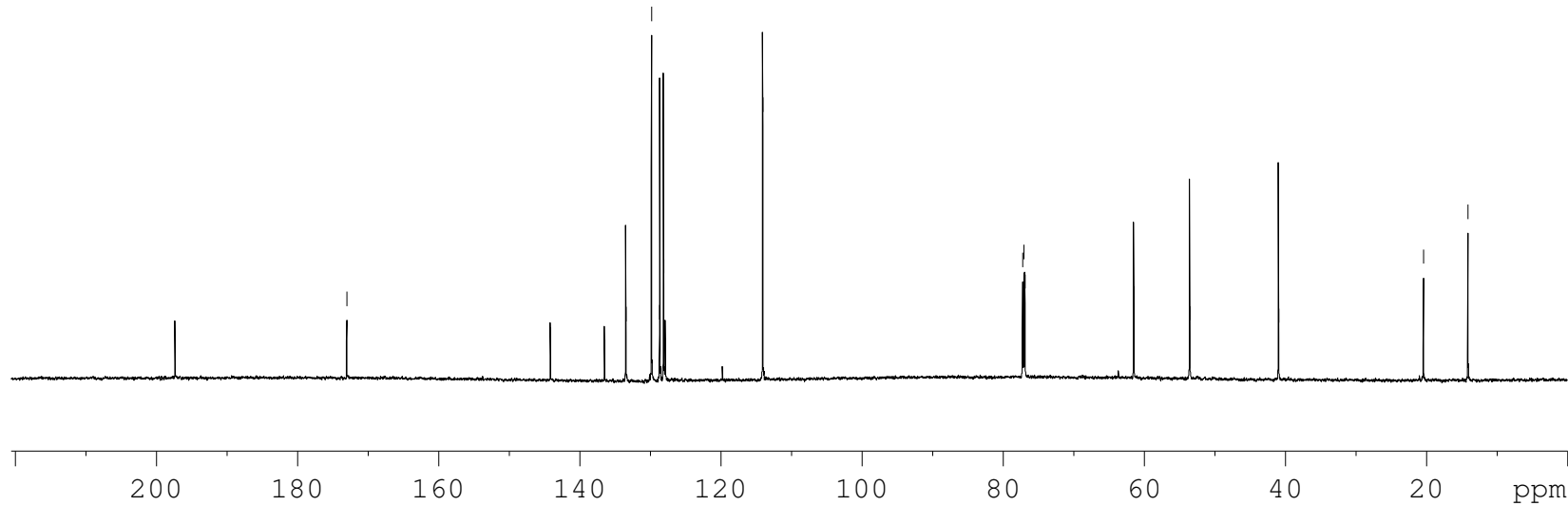
—61.480

—53.567

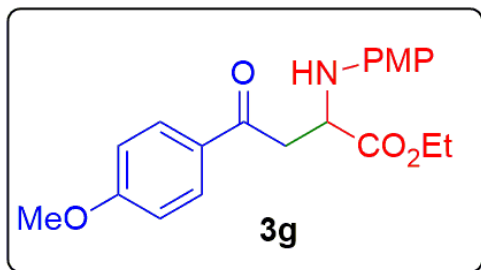
—40.976

—20.424

—14.105



¹H NMR, 600 MHz, CDCl₃

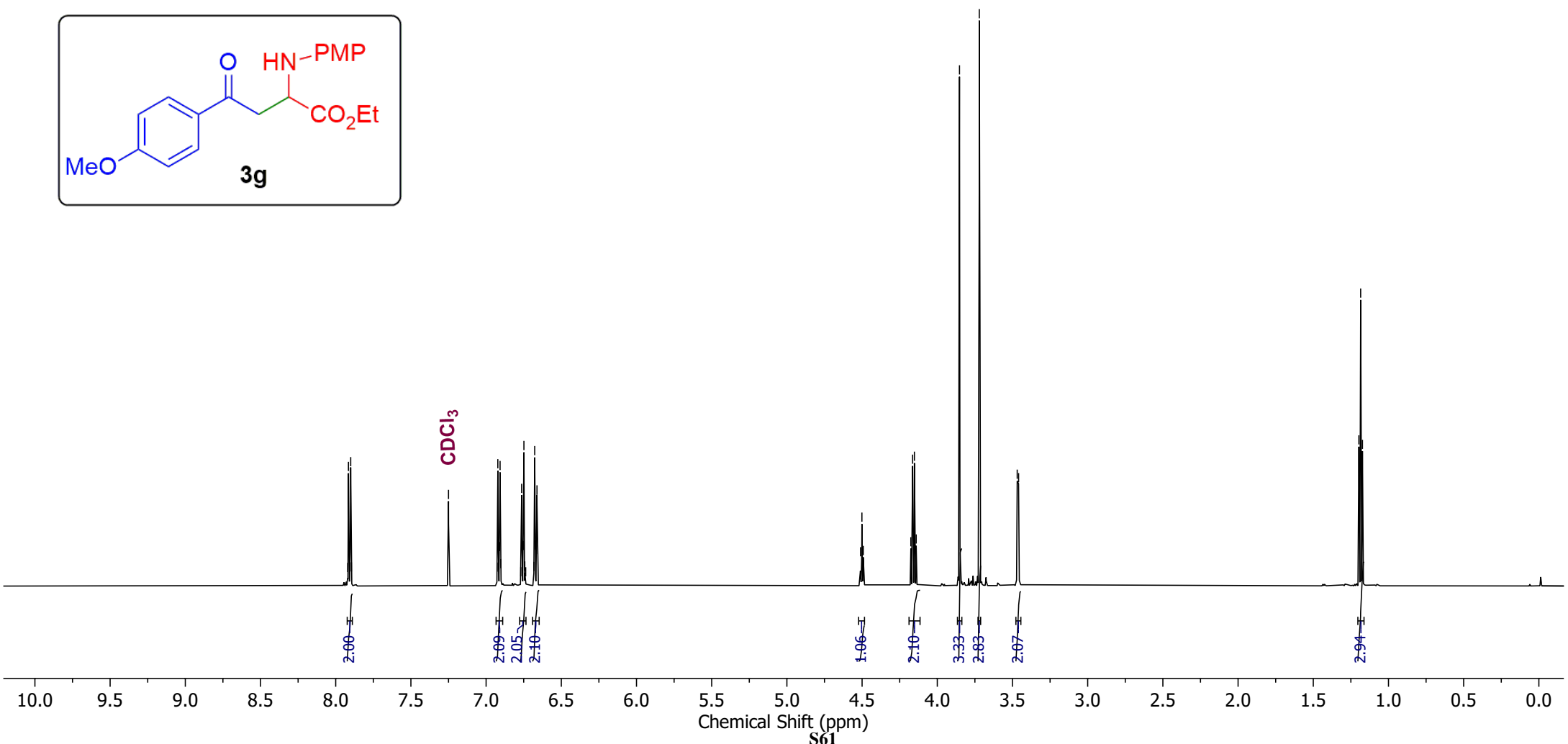


7.9202
7.9153
7.9117
7.9038
7.9002
7.8956

7.2500
6.9269
6.9220
6.9186
6.9105
6.9071
6.9023
6.7695
6.7637
6.7597
6.7526
6.7485
6.7427
6.7368
6.6827
6.6768
6.6728
6.6656
6.6617

4.5103
4.5012
4.4922
4.1758
4.1639
4.1521
4.1402
3.8523
3.7208
3.4687
3.4594

1.1967
1.1849
1.1730



¹³C NMR, 201.2 MHz, CDCl₃

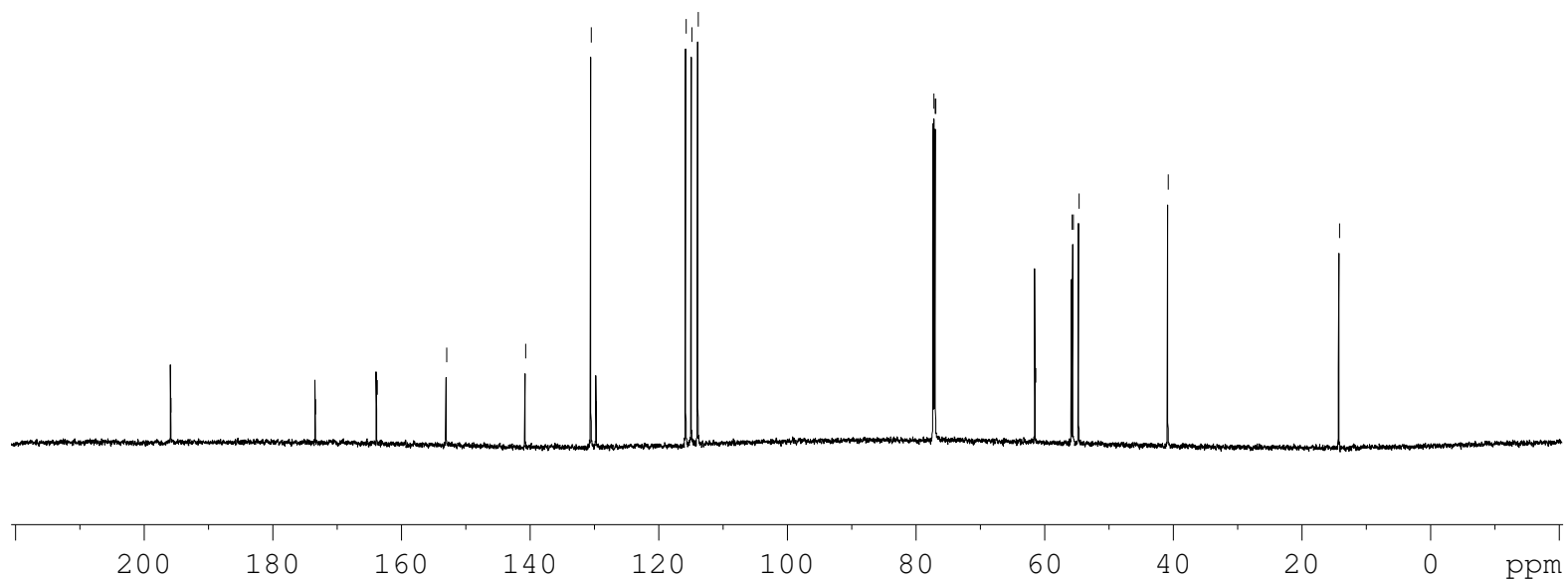
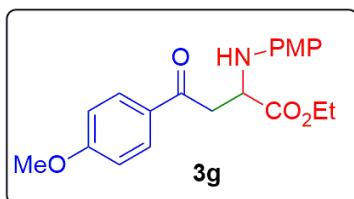


Current Data Parameters
NAME barc-RC-2007-13C-24Jan21
EXPNO 1
PROCNO 1

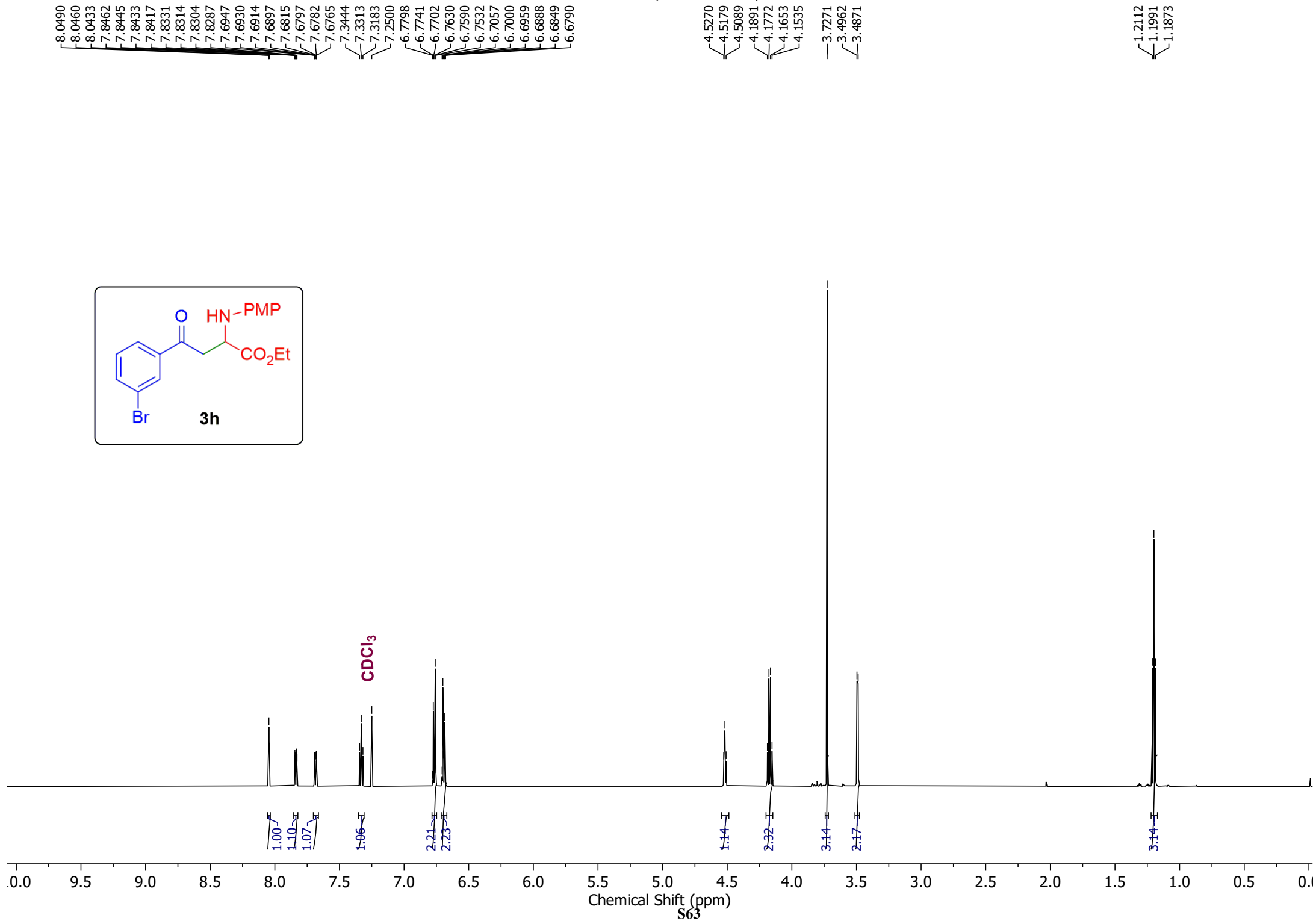
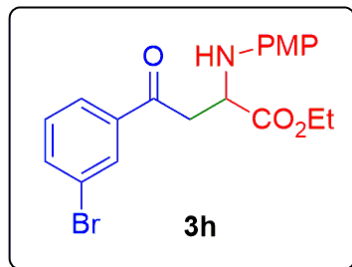
F2 - Acquisition Parameters
Date_ 20210224
Time 13.06 h
INSTRUM spect
PROBHD z44909_0011 (C
PULPROG zgdc
TD 16384
SOLVENT cdcl3
NS 160
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 18.00 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 15.00 usec
PLW1 141.03999329 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 10.18999958 W
PLW12 0.16679481 W

F2 - Processing parameters
SI 16384
SF 201.1677040 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

— 195.819
— 173.333
— 163.797
— 152.957
— 140.684
— 130.468
— 129.644
— 115.711
— 114.843
— 113.825
— 77.207 } CDCl₃
— 77.047 }
— 76.889 }
— 61.385
— 55.699
— 55.510
— 54.589
— 40.713
— 14.109



¹H NMR, 600 MHz, CDCl₃



¹³C NMR, 201.2 MHz, CDCl₃



Current Data Parameters
NAME barc-RC-2059-13C-23Sep21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20210923
Time 12.43 h
INSTRUM spect
PROBHD Z555801_0012 (
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 427
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W

F2 - Processing parameters
SI 16384
SF 201.1677102 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

— 196.093

— 172.931

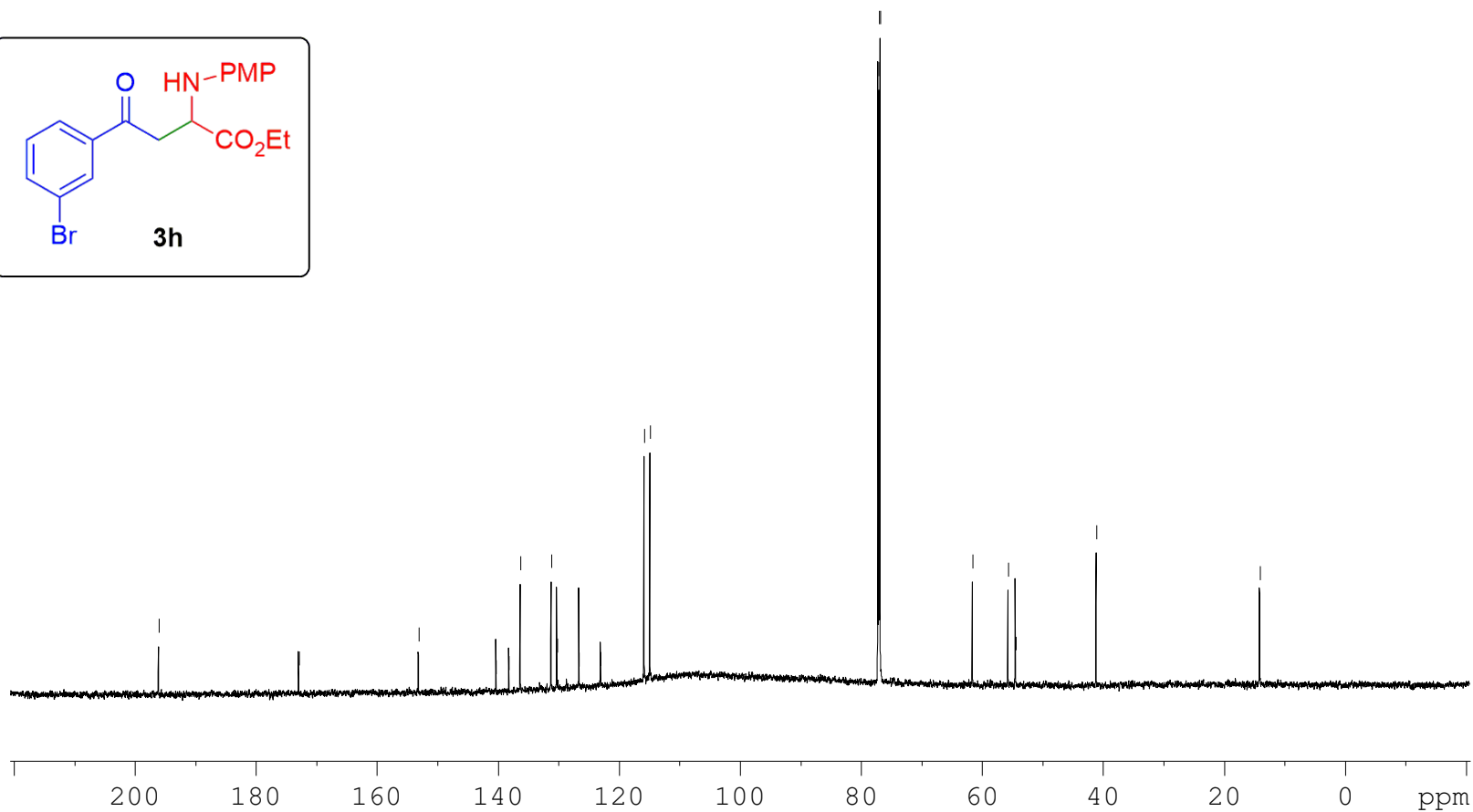
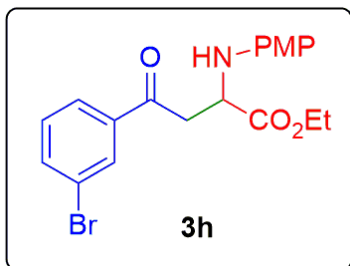
153.125
140.332
138.192
136.298
131.199
130.256
126.618
123.026
115.826
114.866

CDCl₃
77.151
76.993
76.835

61.549
55.671
54.472

— 41.108

— 14.075



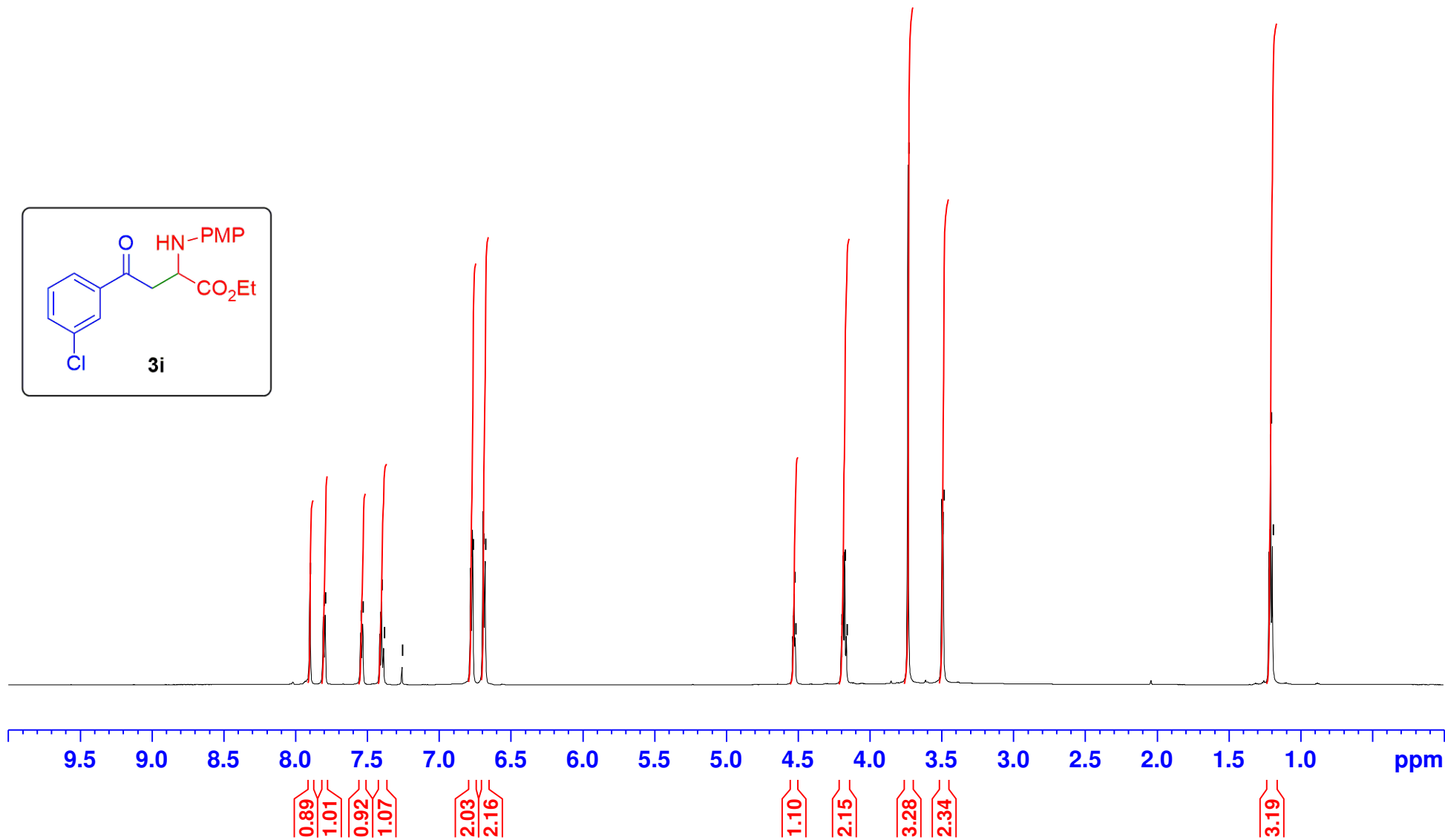
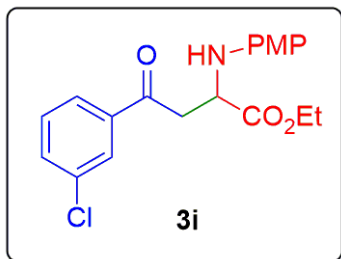
CDCl₃

¹H NMR, 600 MHz, CDCl₃

7.896
7.803
7.790
7.542
7.529
7.409
7.396
7.383
7.255
6.777
6.763
6.690
6.676

4.532
4.524
4.515
4.194
4.182
4.171
4.159
3.730
3.494
3.485

1.215
1.204
1.192



¹³C NMR, 201.2 MHz, CDCl₃



Current Data Parameters
NAME barc-RC-2026-13C-24Jan21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210224
Time 12.18 h
INSTRUM spect
PROBHD Z44909_0011 (C)
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 108
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 18.00 usec
TE 298.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TDO 1
SFO1 201.1878208 MHz
NUC1 13C
P1 15.00 usec
PLW1 141.03999329 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 60.00 usec
PLW2 10.18999958 W
PLW12 0.16679481 W

F2 - Processing parameters
SI 16384
SF 201.1677040 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

— 196.225

— 173.011

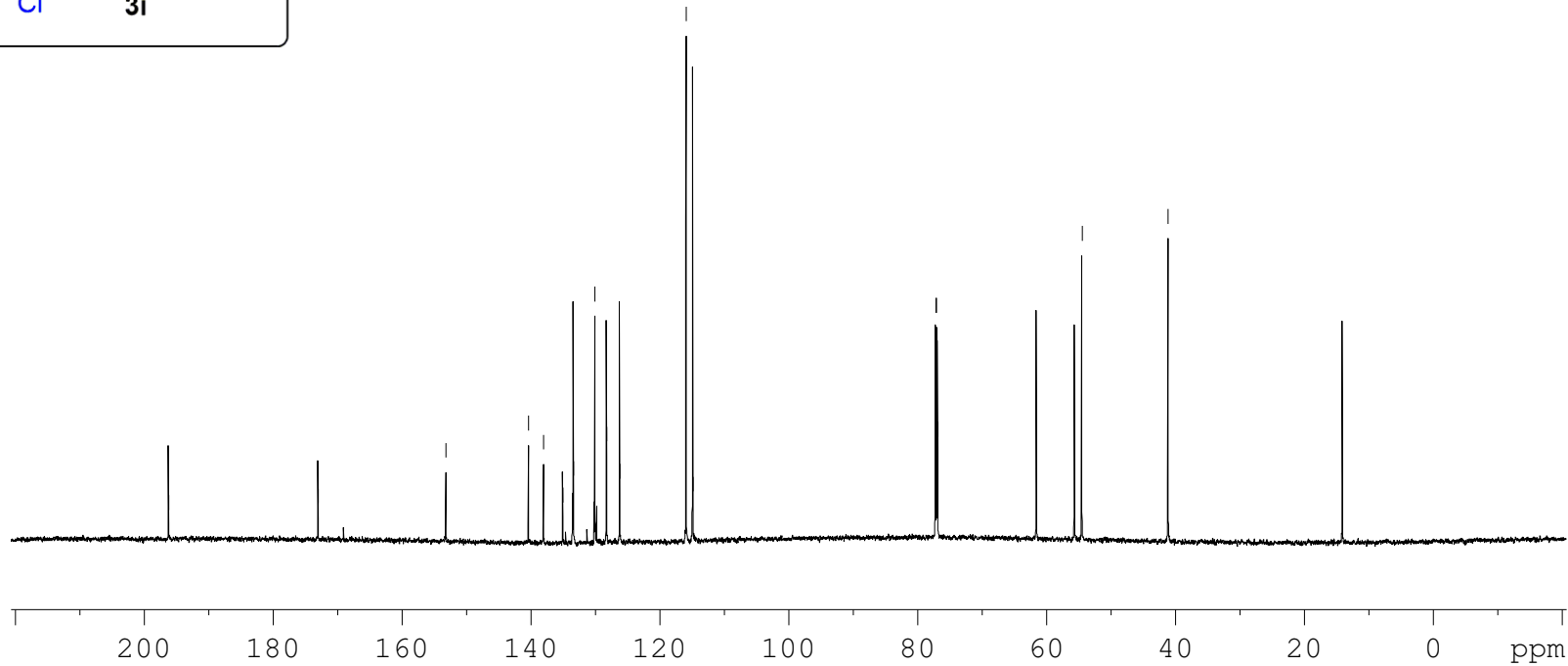
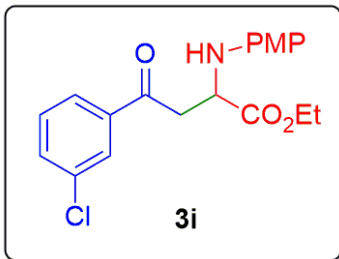
153.170
140.365
138.016
135.051
133.410
130.042
128.263
126.224
115.915
114.894

CDCl₃
77.224
77.065
76.907

61.582
55.690
54.528

— 41.153

— 14.107



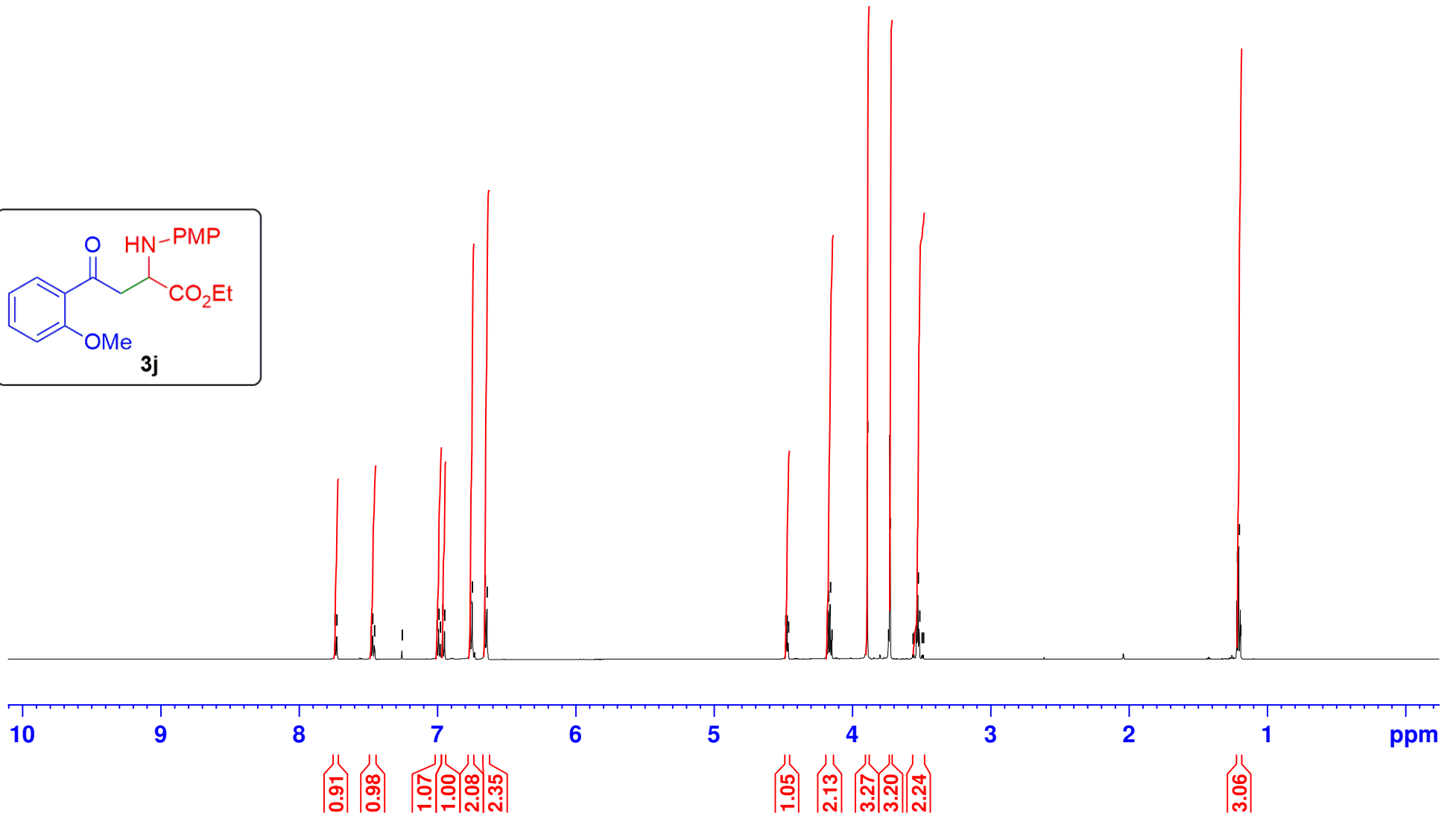
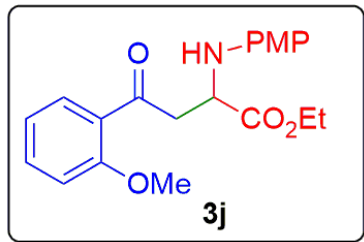
¹H NMR, 600 MHz, CDCl₃

CDCl₃

7.740
7.727
7.480
7.467
7.455
7.256
7.003
6.991
6.978
6.961
6.948
6.762
6.747
6.655
6.641

4.481
4.472
4.462
4.182
4.170
4.159
4.147
3.890
3.725
3.561
3.552
3.532
3.523
3.514
3.495
3.485

1.215
1.203
1.191



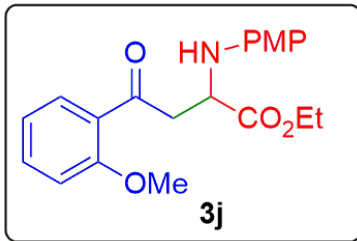
¹³C NMR, 201.2 MHz, CDCl₃



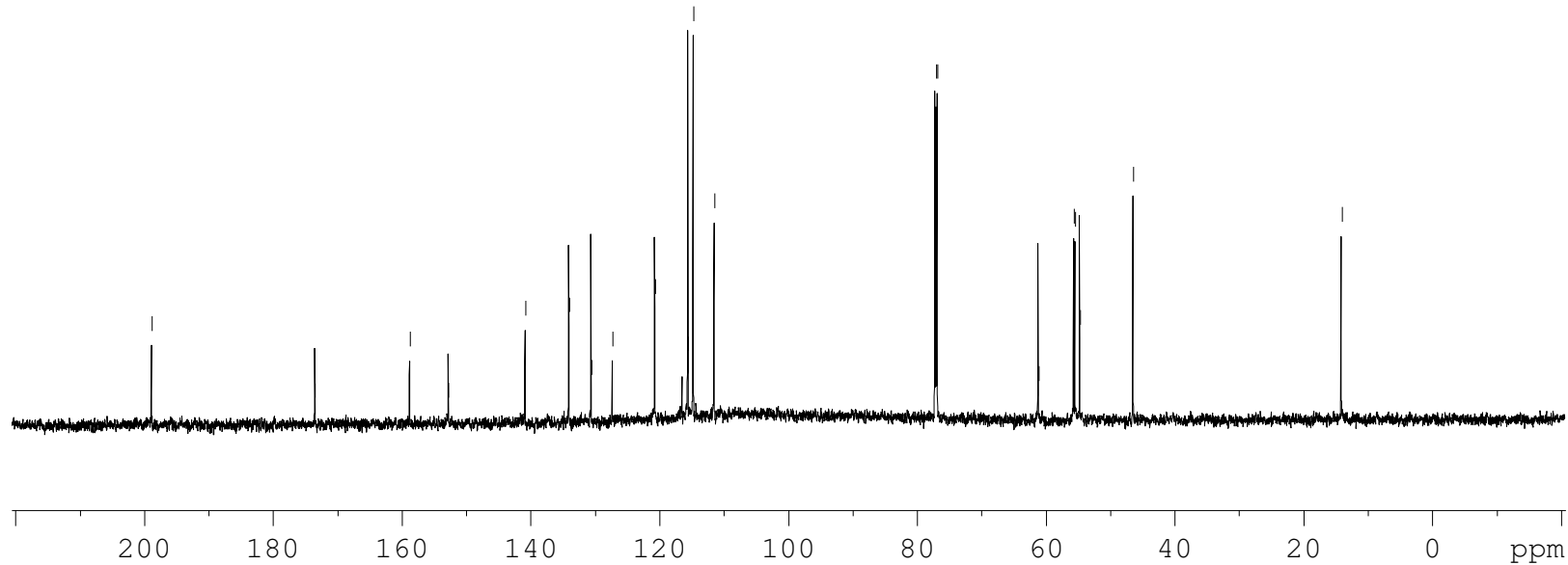
Current Data Parameters
NAME barc-RC-2119-13C-2July21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210702
Time 15.32 h
INSTRUM spect
PROBHD z555801_0012 (z)
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 58
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TDD 1
SF01 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SF02 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W

F2 - Processing parameters
SI 16384
SF 201.1677188 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40



—198.876
—173.493
—158.792
—152.775
—140.835
—134.045
—130.600
—127.279
—120.700
—115.557
—114.729
—111.481
—77.151
—76.993
—76.835
—61.158
—55.632
—55.428
—54.693
—46.409
—14.057

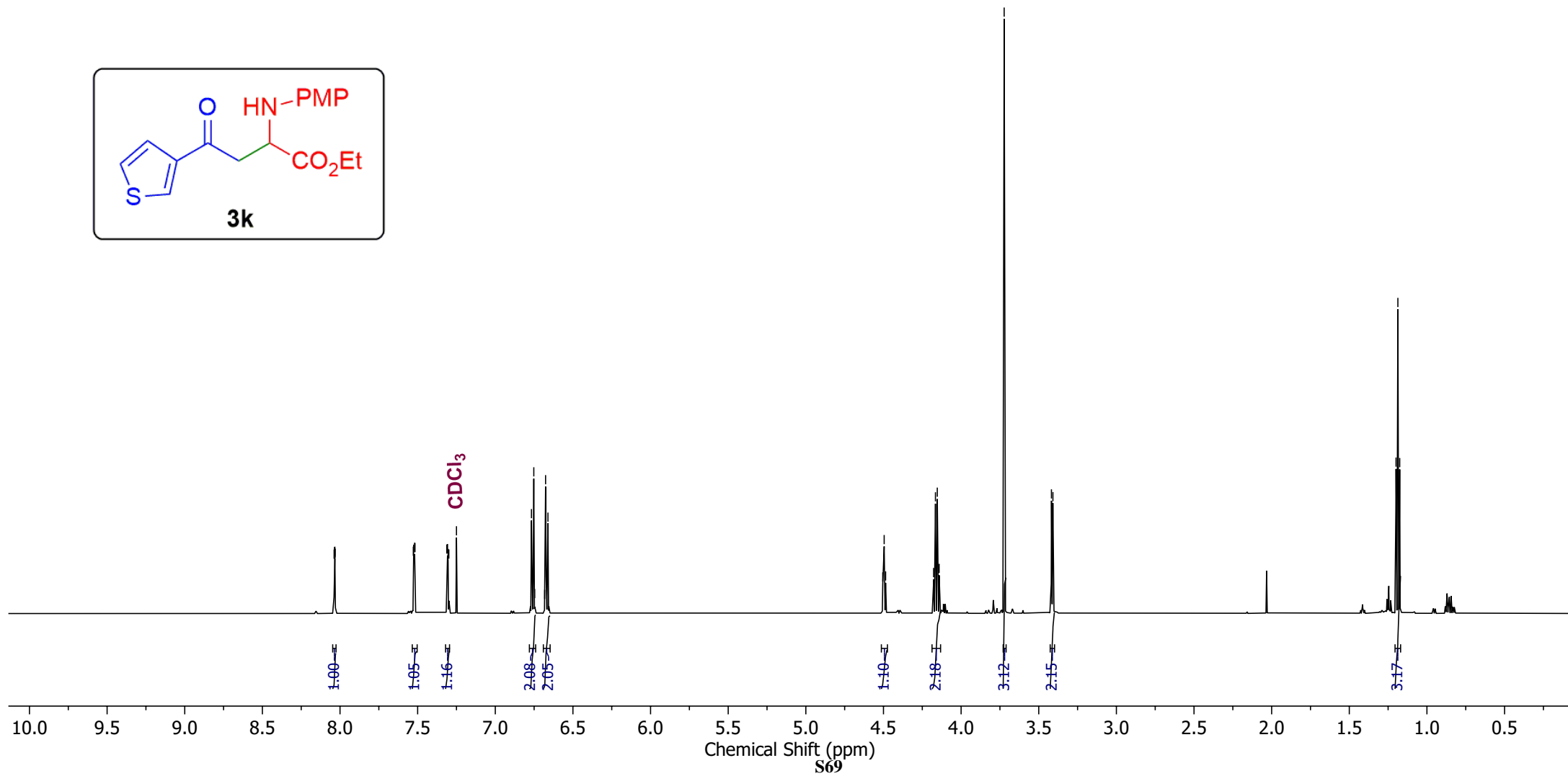
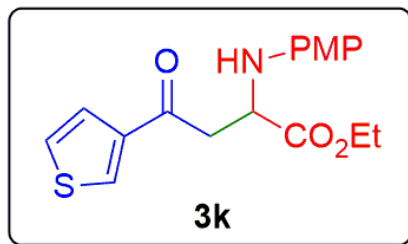


¹H NMR, 600 MHz, CDCl₃

8.0380
8.0357
8.0331
8.0309
7.5279
7.5258
7.5195
7.5172
7.3124
7.3076
7.3040
7.2992
7.2500
6.7671
6.7631
6.7559
6.7520
6.7461
6.6820
6.6761
6.6722
6.6649
6.6610

4.5046
4.4955
4.4862
4.1772
4.1653
4.1535
4.1416
— 3.7227
3.4183
3.4088

1.1990
1.1871
1.1752



¹³C NMR, 201.2 MHz, CDCl₃



```
Current Data Parameters
NAME      bare-NC-2103-13C-2July21
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20210702
Time     13.37 h
INSTRUM  spect
PROBHD   z515801_001z (
PULPROG  zgpg
TD        65536
SOLVENT  CDCl3
NS        50
DS        4
SWH       48841.488 Hz
FIDRES    0.3225743 Hz
AQ        0.1487552 sec
RG         71.8
DW        10.300 usec
DE         6.00 usec
TE        298.0 K
D1        3.0000000 sec
D11       0.0300000 sec
TD0       1
SFO1     201.1878208 MHz
NUC1      13C
P1        8.00 usec
PL1      312.79998779 W
SFO2     800.0330001 MHz
NUC2      1H
CPDPRG2  waltz16
PCPD2    60.00 usec
PLM2     13.0000000 W
PLM12    0.29249999 W

F2 - Processing parameters
SI        16384
SF        201.1677040 MHz
WDW       EM
SSB       0
LB        5.00 Hz
GB        0
PC        1.40
```

— 191.530

— 173.147

— 153.025

< 141.888

< 140.551

— 132.580

< 126.825

< 126.635

< 115.734

< 114.871

CDCl₃
< 77.238
< 77.079
< 76.921

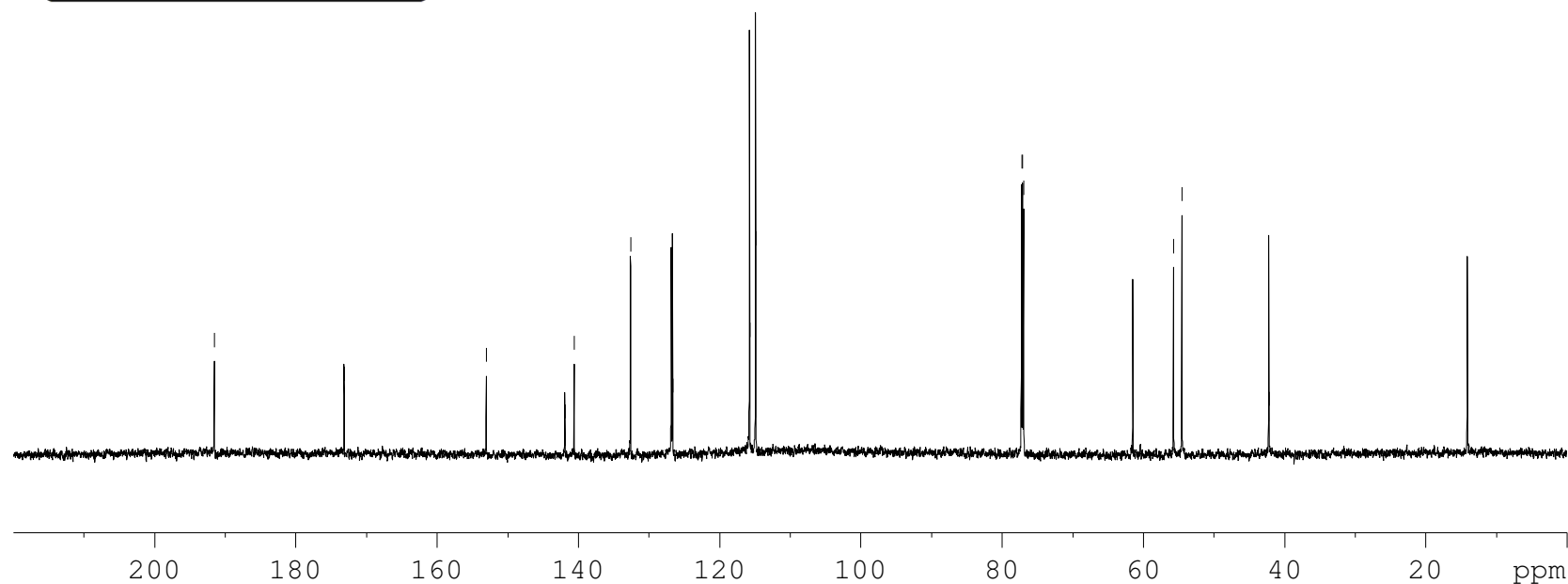
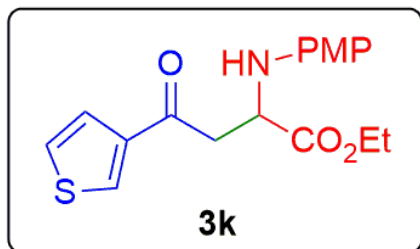
— 61.469

< 55.691

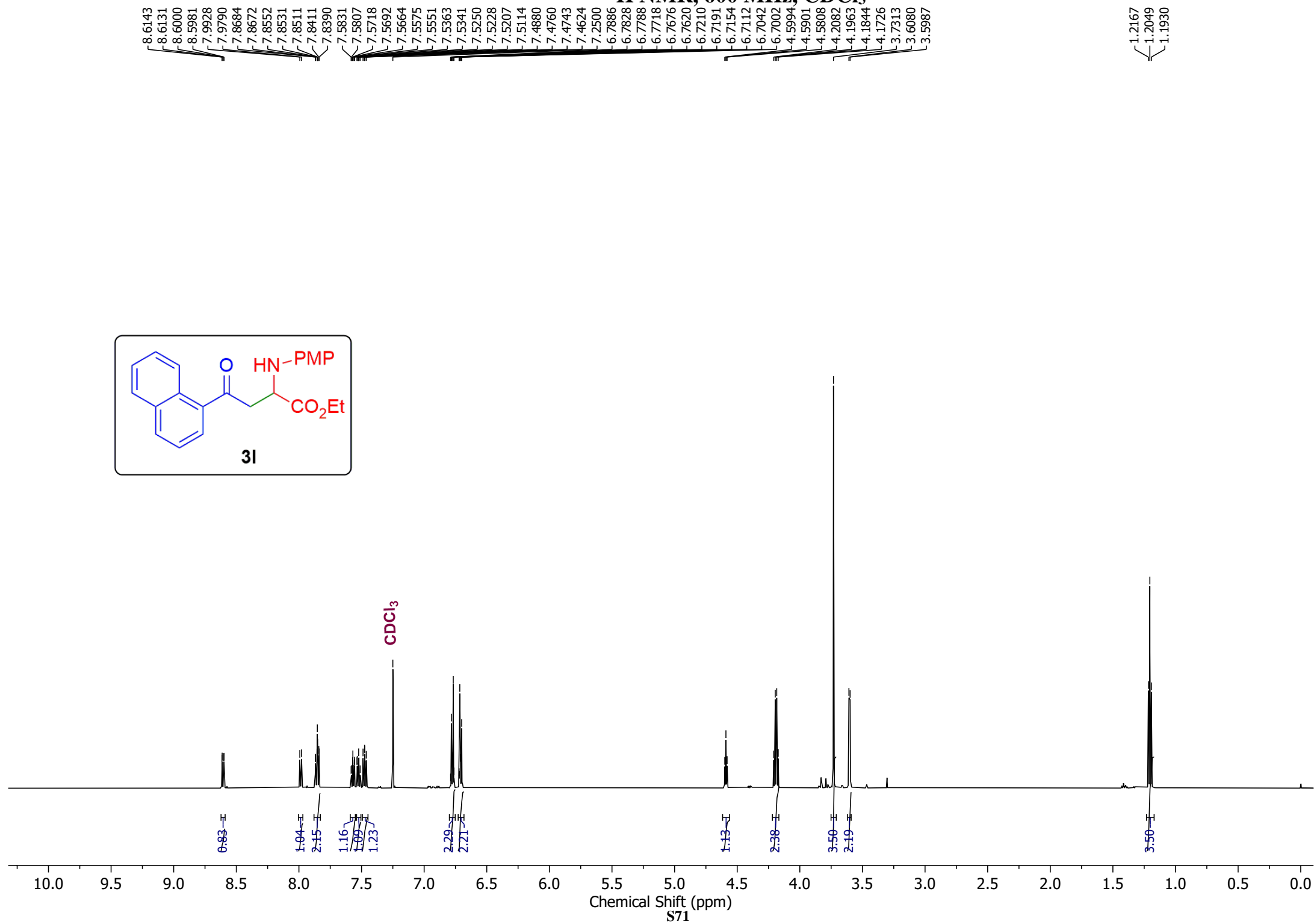
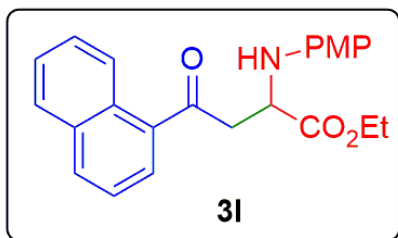
< 54.513

— 42.218

— 14.088



¹H NMR, 600 MHz, CDCl₃



¹³C NMR, 201.2 MHz, CDCl₃



Current Data Parameters
NAME barc-RC-2120-13C-2July21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210702
Time 16.06 h
INSTRUM spect
PROBHD Z555801_0012 ()
PULPROG zgpg
TD 16384
SOLVENT CDCl3
NS 97
DS 4
SWH 48543.698 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.03000000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
F1 8.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W

F2 - Processing parameters
SI 16384
SF 201.1677171 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

— 201.274

— 173.159

153.024

140.558

135.219

133.878

133.062

130.029

128.366

128.038

127.895

126.528

125.718

124.257

115.820

114.829

CDCl₃

77.152

76.994

76.834

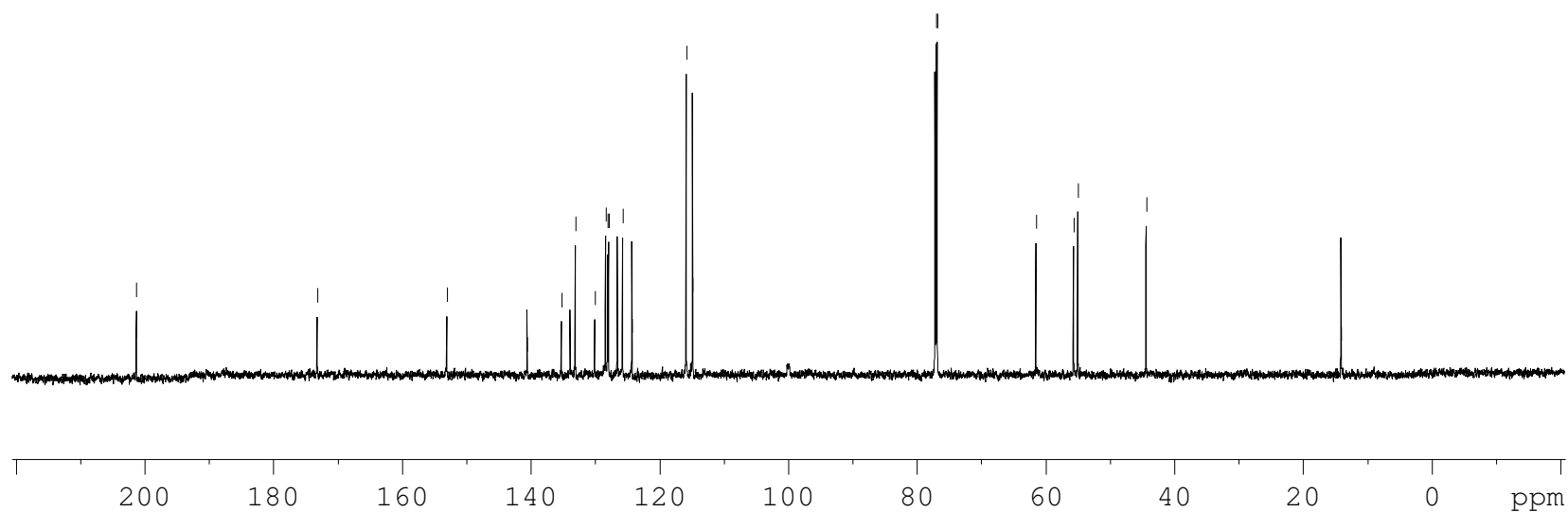
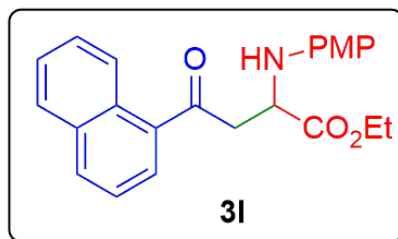
61.470

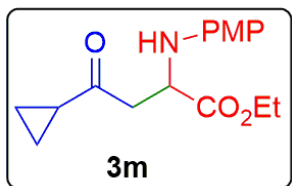
55.641

54.977

44.362

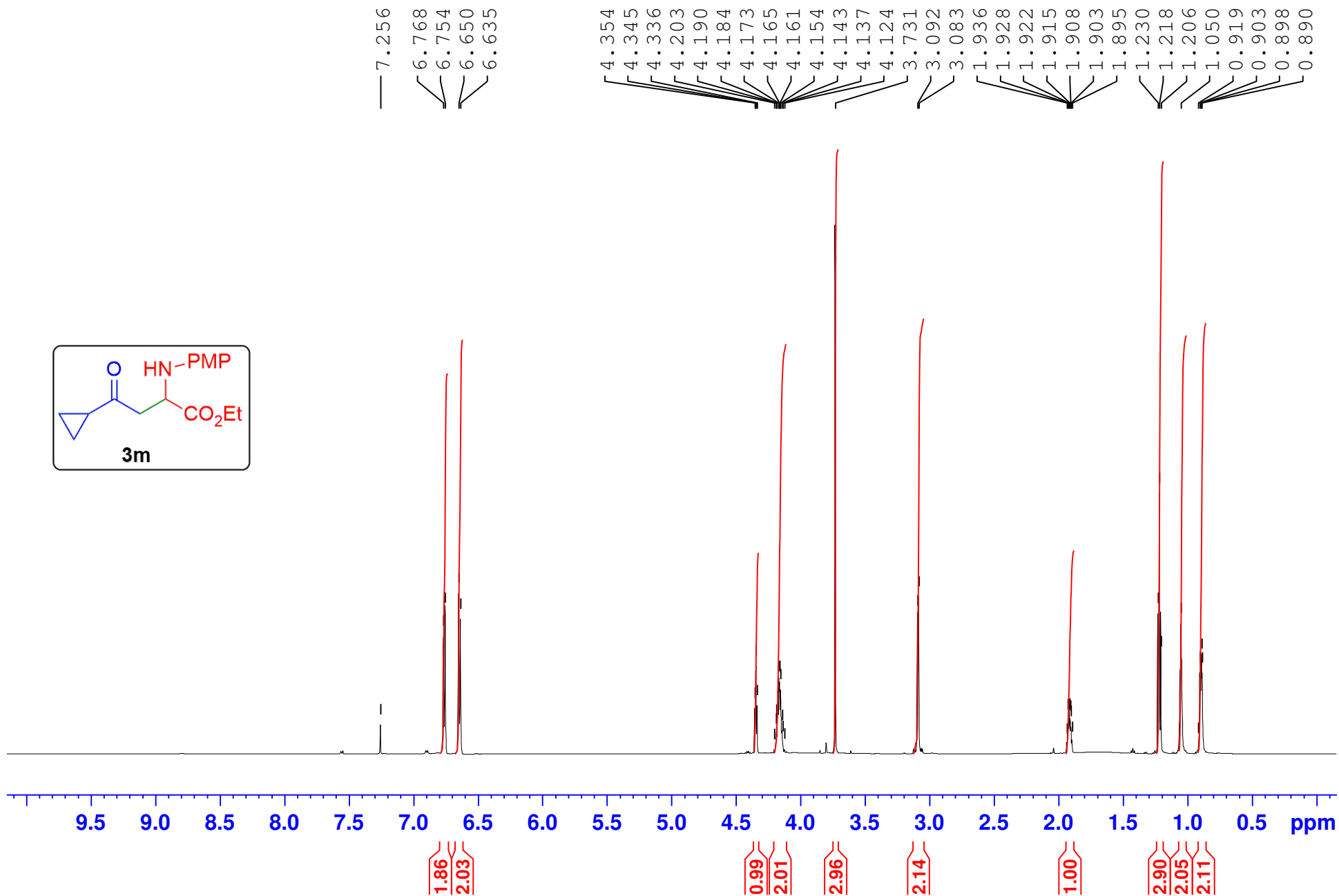
— 14.080



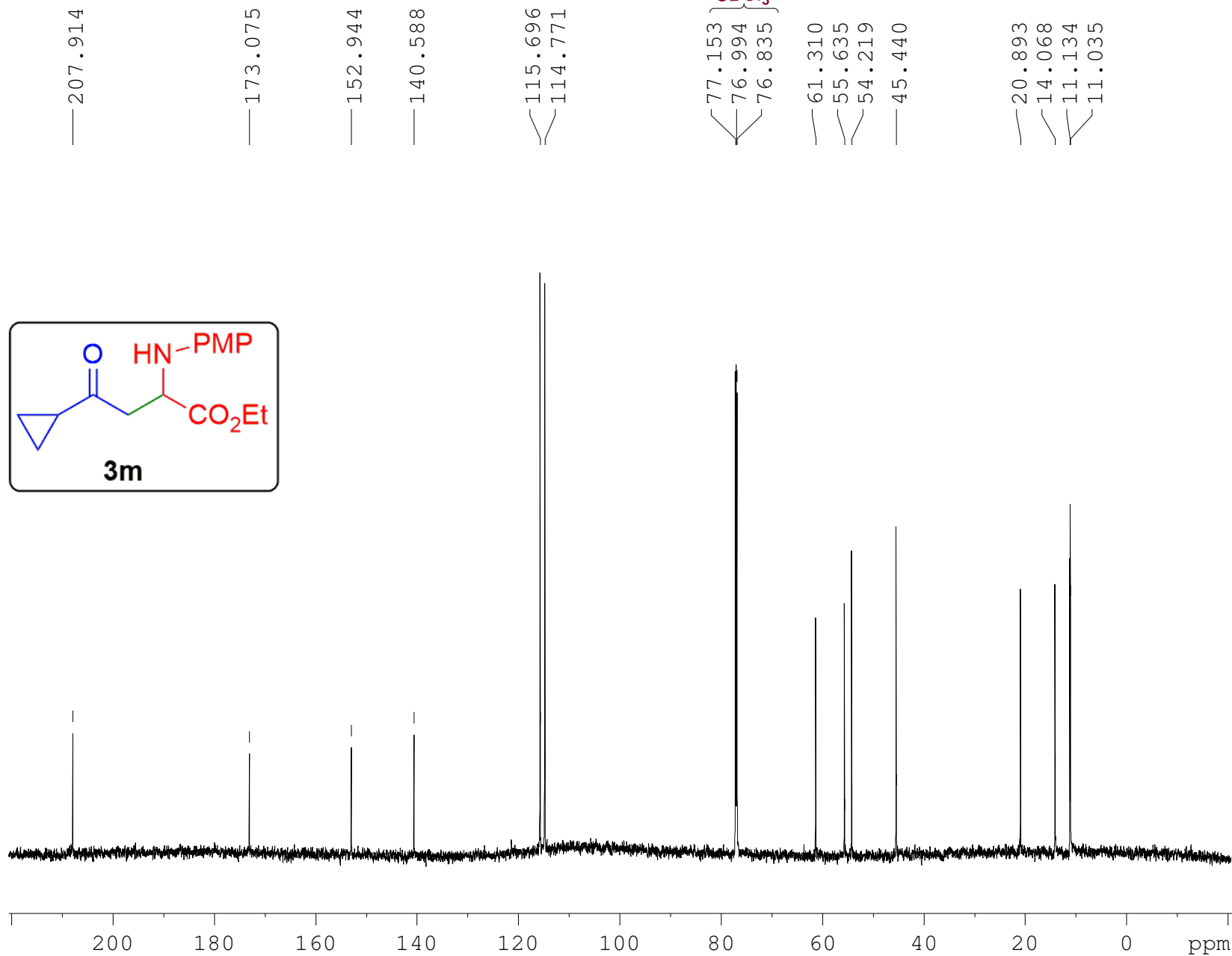


CDCl₃

¹H NMR, 600 MHz, CDCl₃



¹³C NMR, 201.2 MHz, CDCl₃



Current Data Parameters
NAME barc-RC-2121-13C-2July21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210702
Time 16.14 h
INSTRUM spect
PROBHD Z555801_0012 (4
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 112
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SFO2 800.032001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 13.0000000 W
PLW12 0.29249999 W

F2 - Processing parameters
SI 16384
SF 201.1677150 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

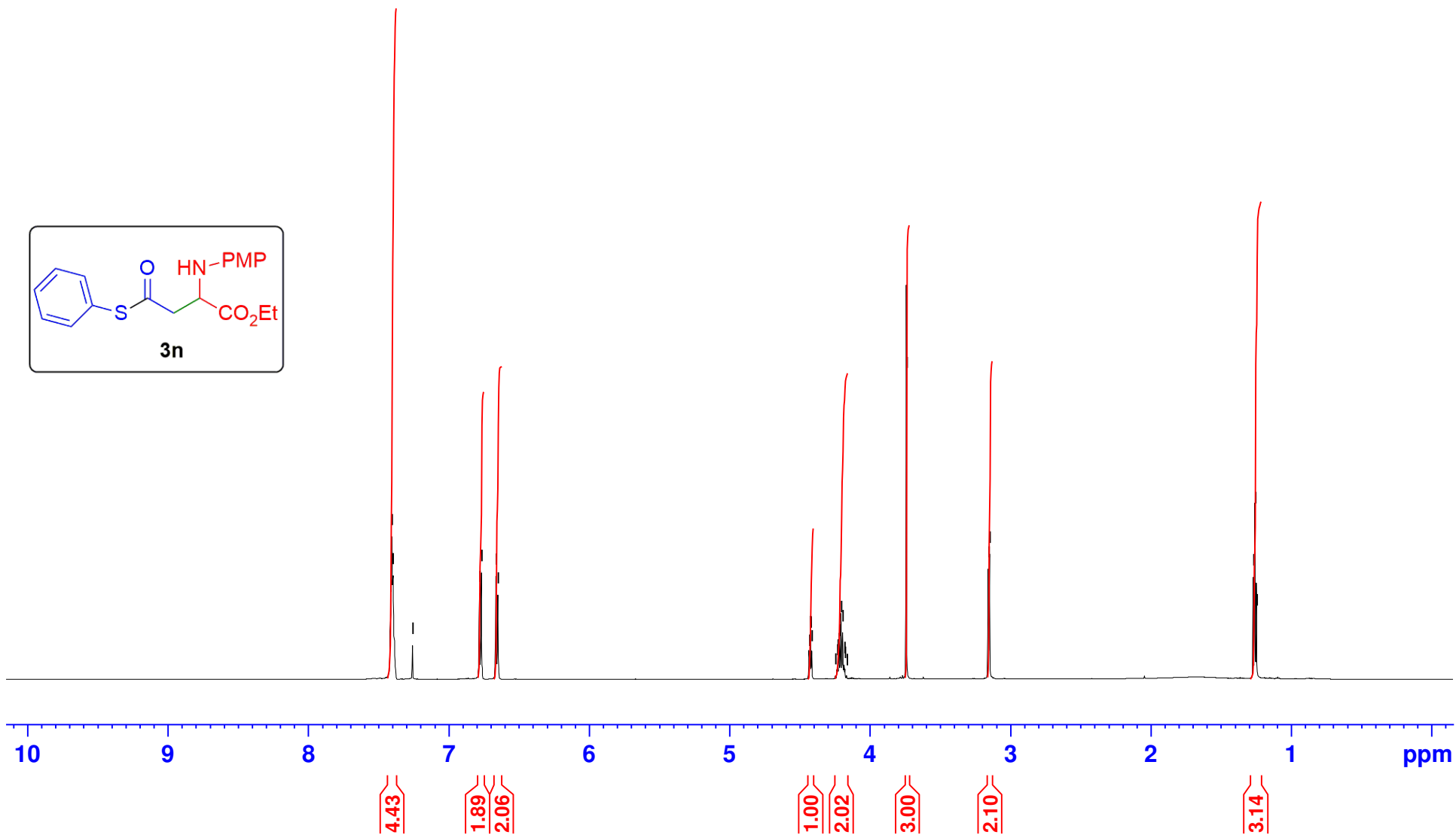
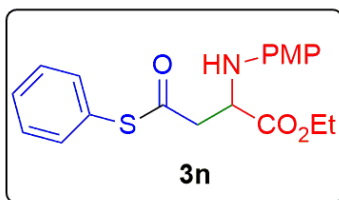
¹H NMR, 600 MHz, CDCl₃

CDCl₃

7.403
7.395
7.256
6.780
6.765
6.662
6.648

4.432
4.422
4.412
4.244
4.232
4.226
4.215
4.204
4.193
4.182
4.176
4.163
3.738
3.155
3.145

1.267
1.255
1.244



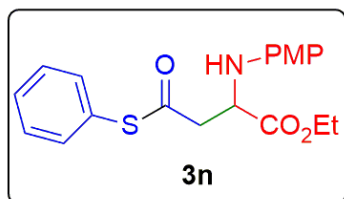
¹³C NMR, 201.2 MHz, CDCl₃



Current Data Parameters
NAME barc-RC-2107-13C-2July21
EXPRO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210702
Time 15.05 h
INSTRUM spect
PROBHD z55801_0012 (zgc
PULPROG zgdc
TD 16384
SOLVENT cdcl3
NS 524
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
EW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SFO2 800.9332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W

F2 - Processing parameters
SI 16384
SF 201.1677109 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40



— 194.740

— 172.215

— 153.163

— 140.121

— 134.421

— 129.625

— 129.257

— 127.106

— 115.820

— 114.856

CDCl₃

77.160

77.001

76.843

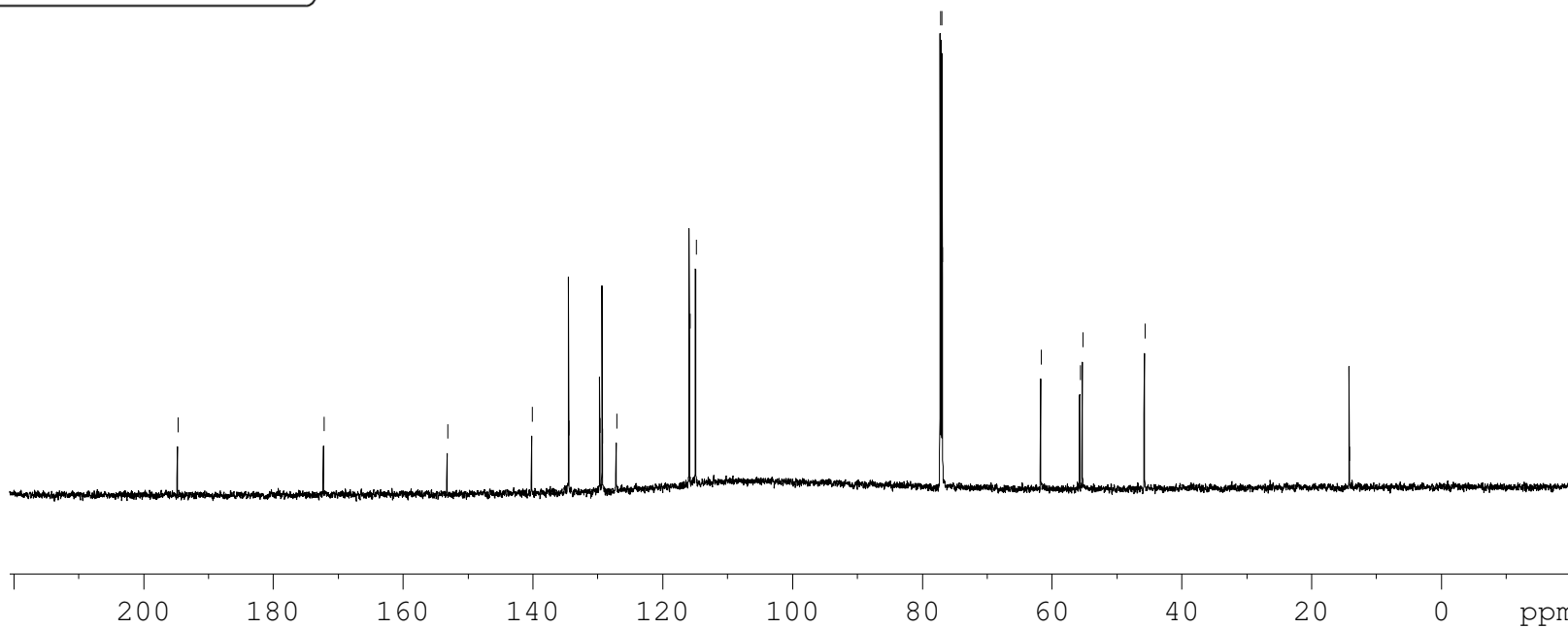
61.680

55.662

55.249

45.684

— 14.133



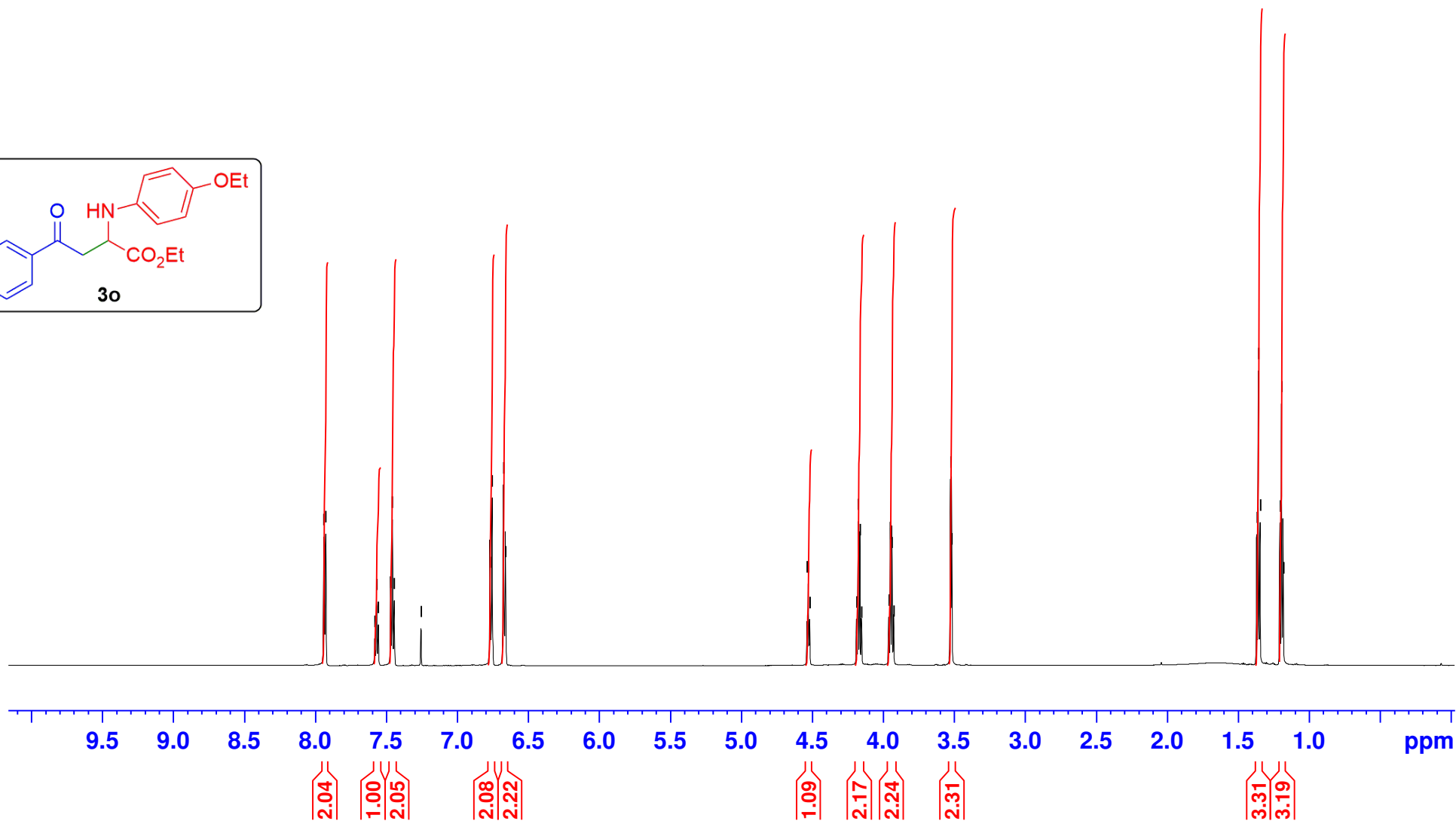
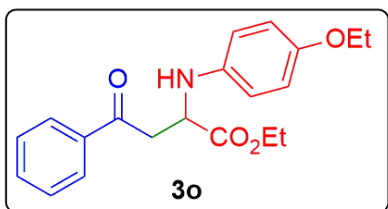
¹H NMR, 600 MHz, CDCl₃

CDCl₃

7.940
7.927
7.581
7.569
7.557
7.470
7.457
7.445
7.256
6.769
6.755
6.675
6.661

4.536
4.527
4.518
4.188
4.176
4.164
4.152
3.961
3.949
3.937
3.926
3.525
3.517

1.368
1.357
1.345
1.205
1.193
1.181



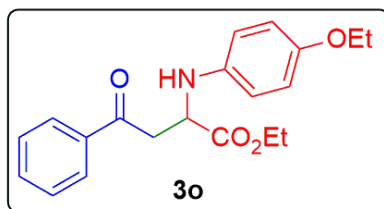
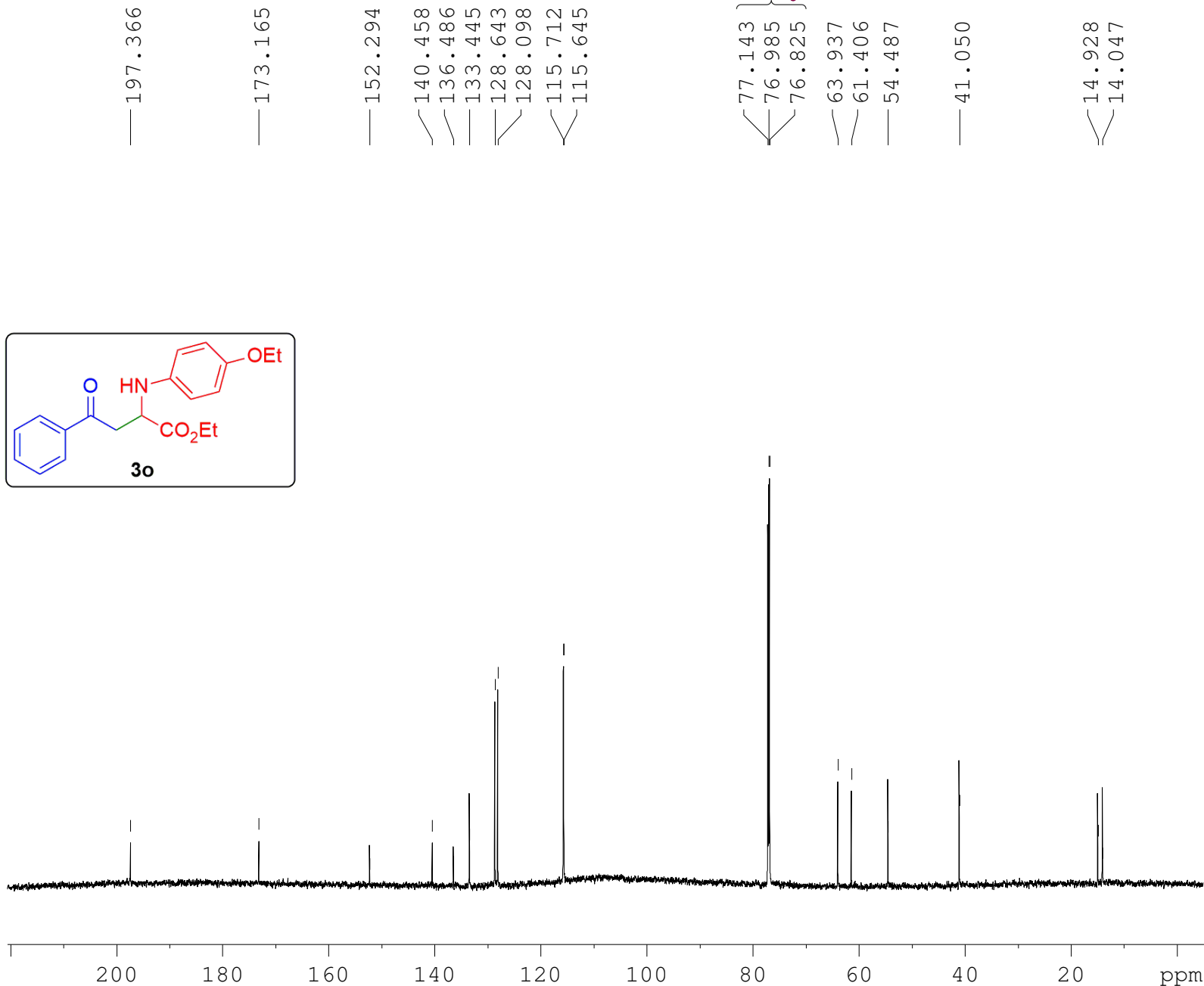
¹³C NMR, 201.2 MHz, CDCl₃



Current Data Parameters
NAME barc-RC-2111-13C-2July21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210702
Time 12.53 h
INSTRUM spect
PROBHD Z555801_0012 ()
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 304
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W

F2 - Processing parameters
SI 16384
SF 201.1677127 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40



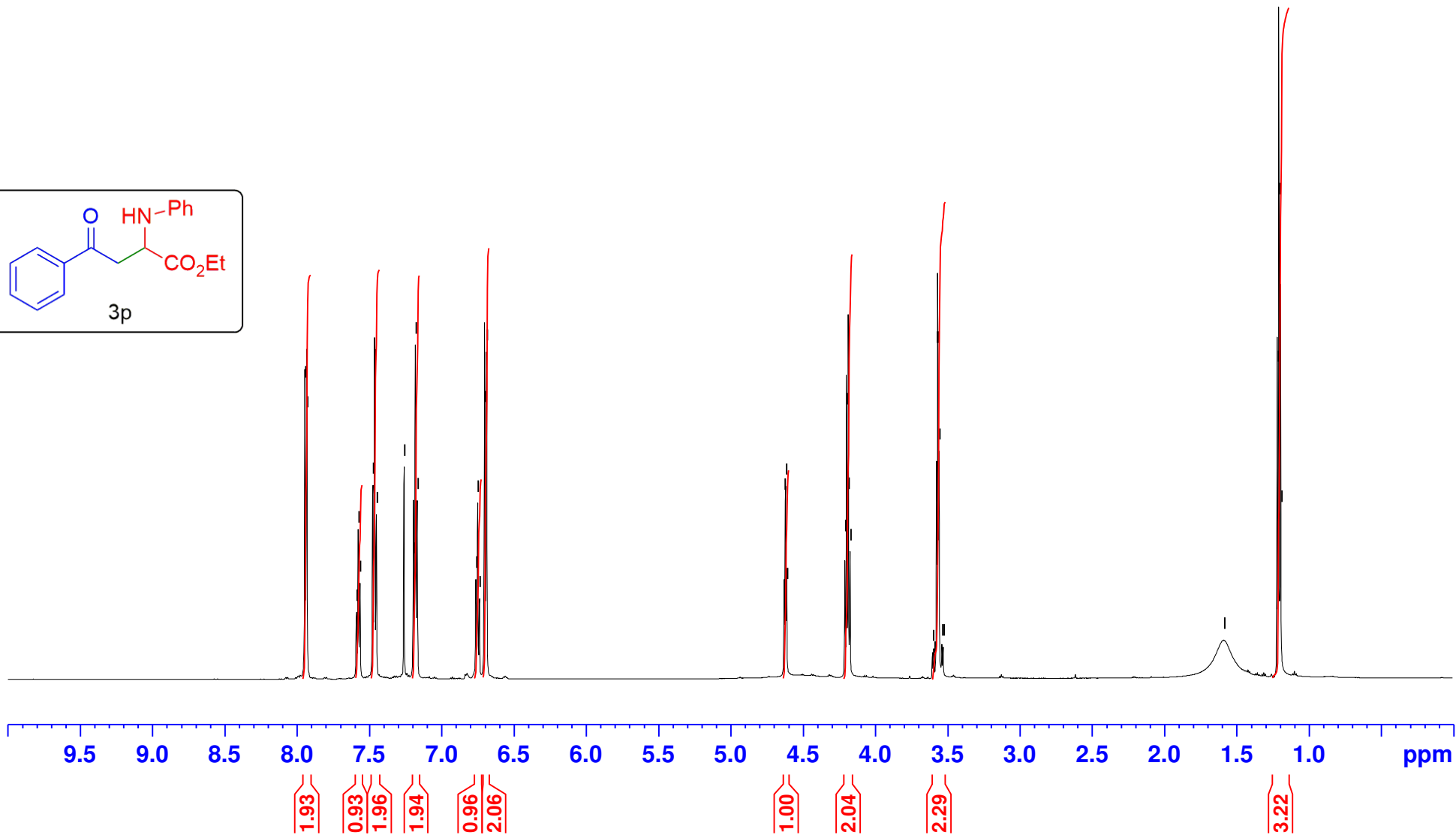
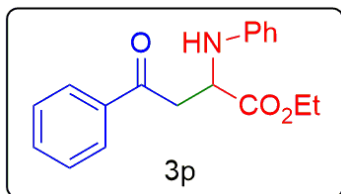
¹H NMR, 600 MHz, CDCl₃

CDCl₃

7.942
7.929
7.585
7.573
7.561
7.473
7.460
7.447
7.256
7.190
7.178
7.165
6.759
6.747
6.735
6.698
6.685

4.625
4.616
4.608
4.205
4.194
4.182
4.170
3.598
3.590
3.570
3.562
3.554
3.534
3.525

1.584
1.213
1.202
1.190

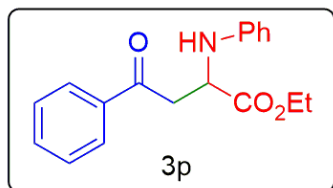


¹³C NMR, 201.2 MHz, CDCl₃



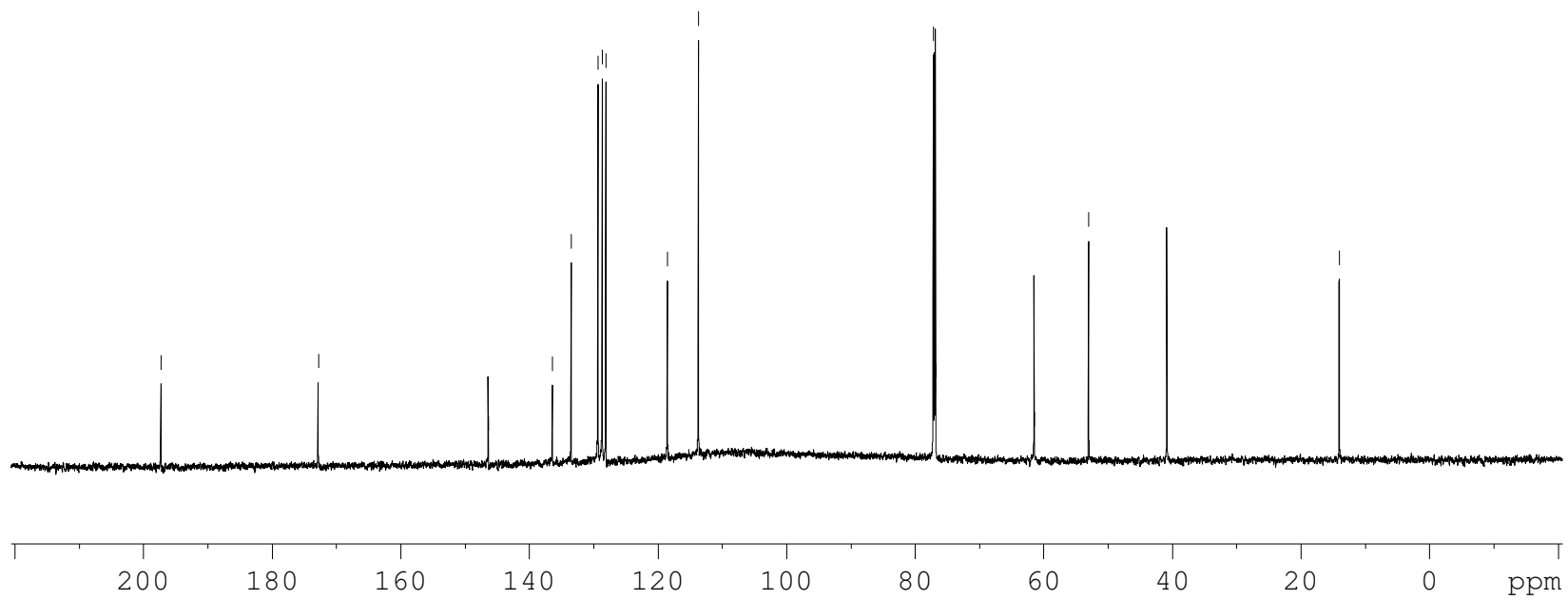
Current Data Parameters
NAME barc-RC-2124-13C-2July21
EXPNO 1
PROCNO 1

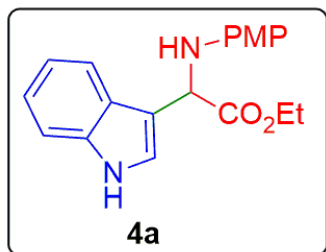
F2 - Acquisition Parameters
Date_ 20210702
Time 15.26 h
INSTRUM spect
PROBHD 2555801_0012 ()
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 339
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SF01 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SF02 800.0322001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W
F2 - Processing parameters
SI 16384
SF 201.1671710 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40



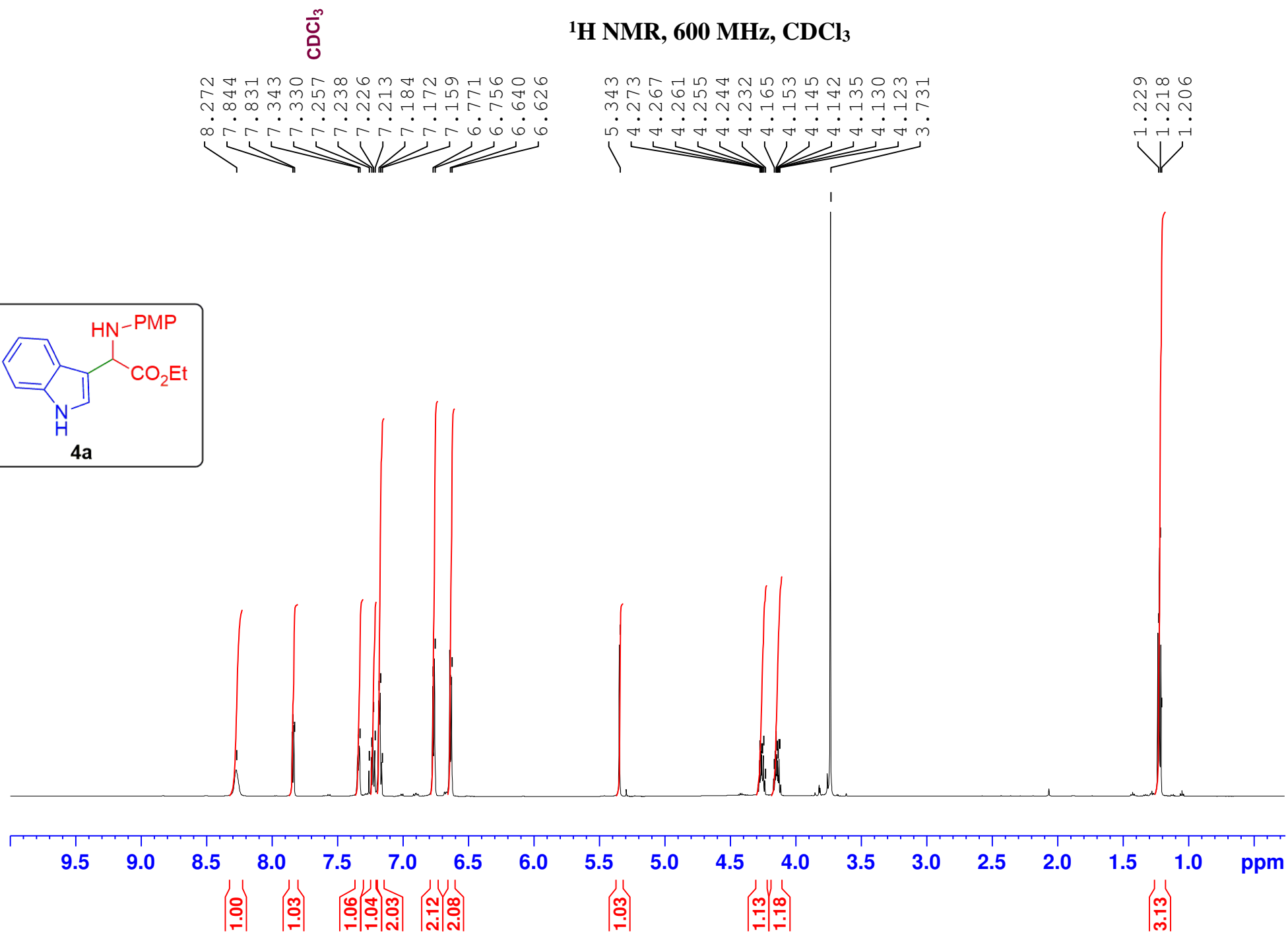
— 197.286
— 172.820
— 146.394
— 136.408
— 133.480
— 129.309
— 128.647
— 128.086
— 118.508
— 113.686
— 77.148
— 76.990
— 76.832
— 61.500
— 53.002
— 40.834
— 14.025

CDCl₃

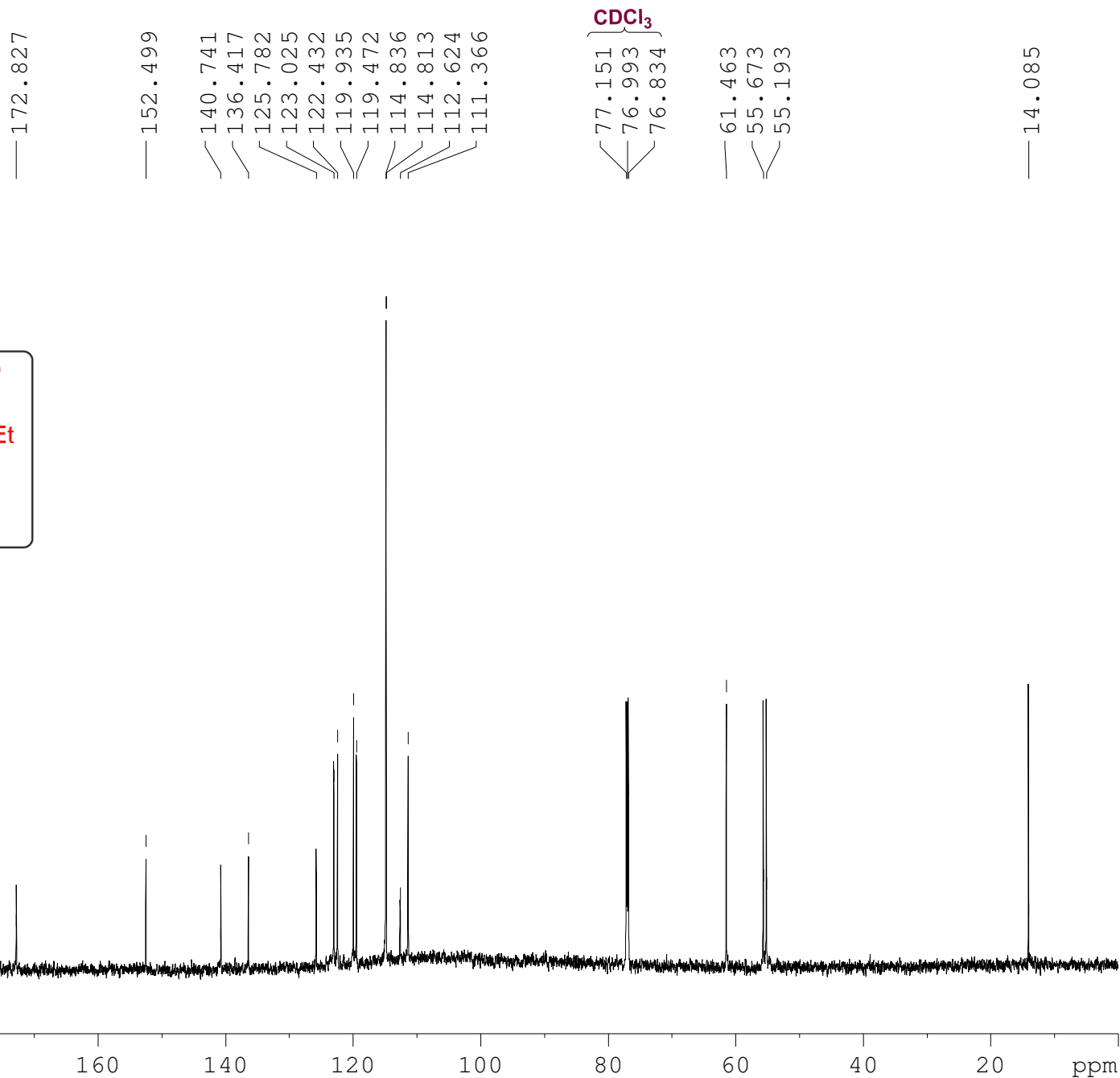
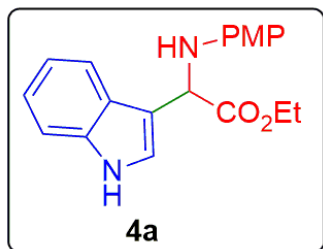




$^1\text{H NMR}$, 600 MHz, CDCl_3



¹³C NMR, 201.2 MHz, CDCl₃



Current Data Parameters
NAME barc-RC2179-13C-25Aug21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210825
Time 14.55 h
INSTRUM spect
PROBHD Z555801_0012 (
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 108
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 60.00 usec
PLW2 13.0000000 W
PLW12 0.29249999 W

F2 - Processing parameters
SI 16384
SF 201.1677189 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

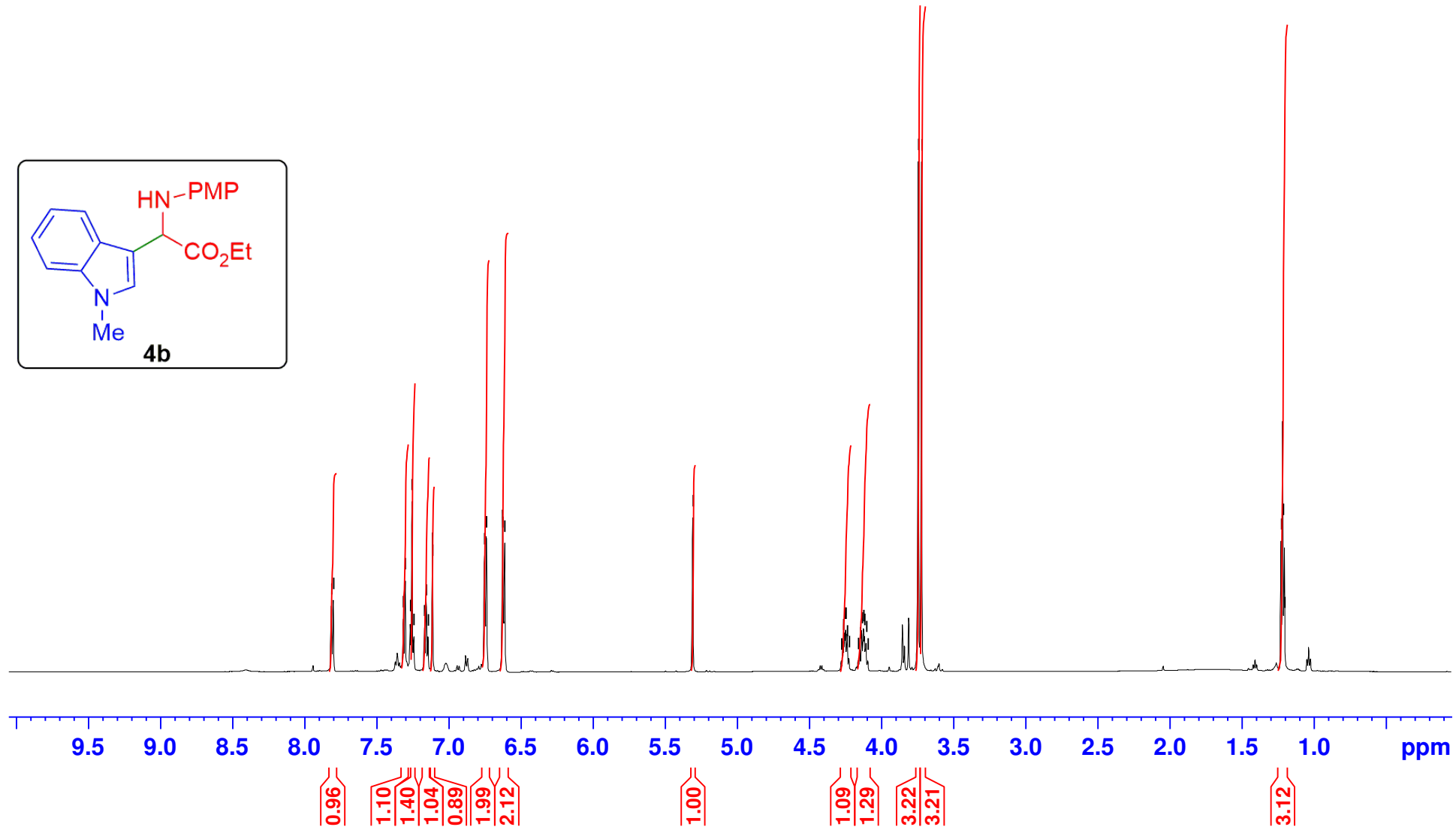
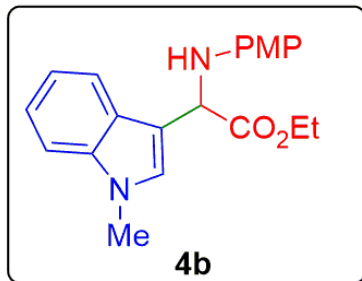
¹H NMR, 600 MHz, CDCl₃

CDCl₃

7.815
7.802
7.316
7.302
7.268
7.255
7.243
7.169
7.157
7.144
7.113
6.753
6.739
6.627
6.613

5.308
4.278
4.266
4.253
4.248
4.236
4.225
4.161
4.148
4.135
4.123
4.117
4.106
4.094
3.743
3.721

1.227
1.215
1.204



¹³C NMR, 201.2 MHz, CDCl₃

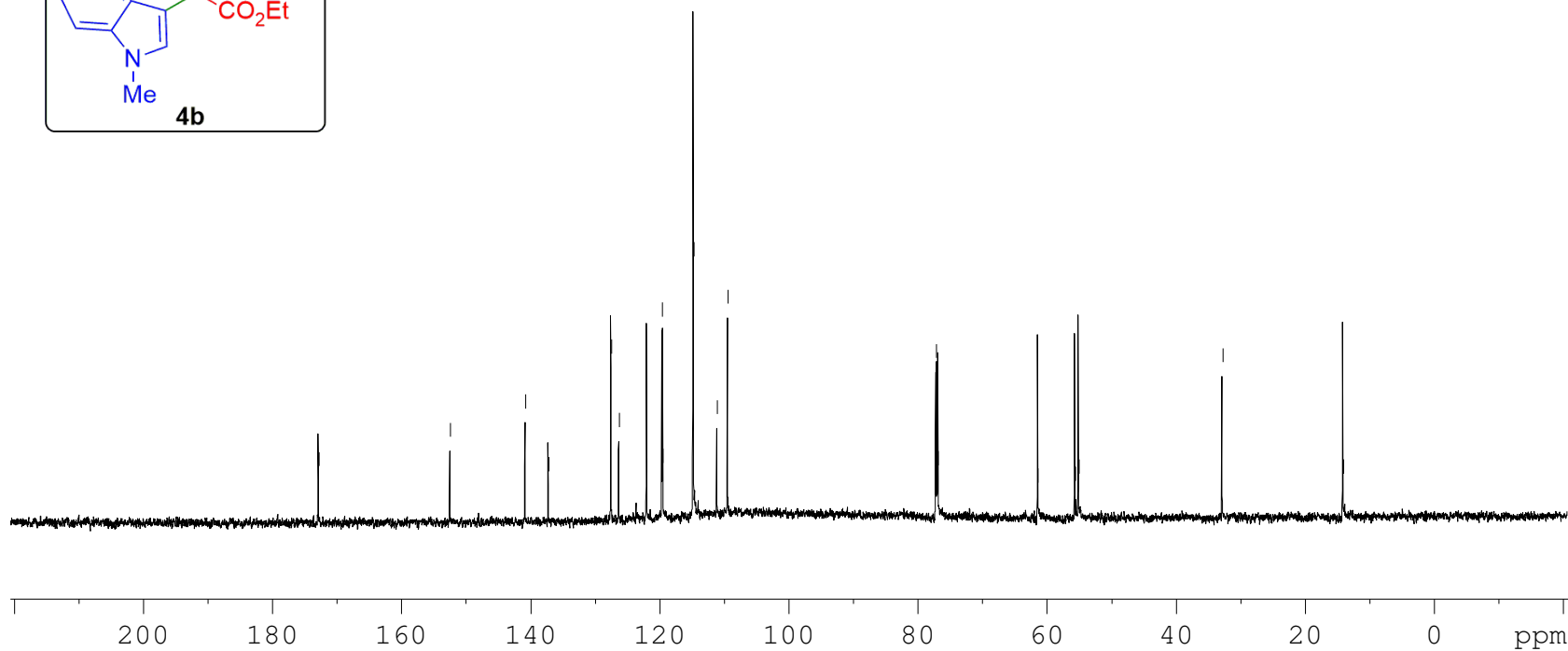
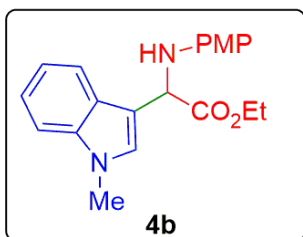


Current Data Parameters
NAME barc-RC-2183-13C-23Sep21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210923
Time 13.51 h
INSTRUM spect
PROBHD Z555801_0012 (
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 120
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.03000000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.7998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPDZ 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W

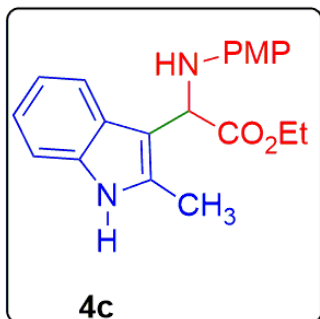
F2 - Processing parameters
SI 16384
SF 201.1677200 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
FC 1.40

— 172.835
— 152.443
— 140.812
— 137.223
— 127.497
— 126.282
— 121.979
— 119.598
— 119.481
— 114.773
— 114.734
— 111.079
— 109.425
} CDCl₃
77.152
76.993
76.834
61.392
55.650
55.088
— 32.796
— 14.099

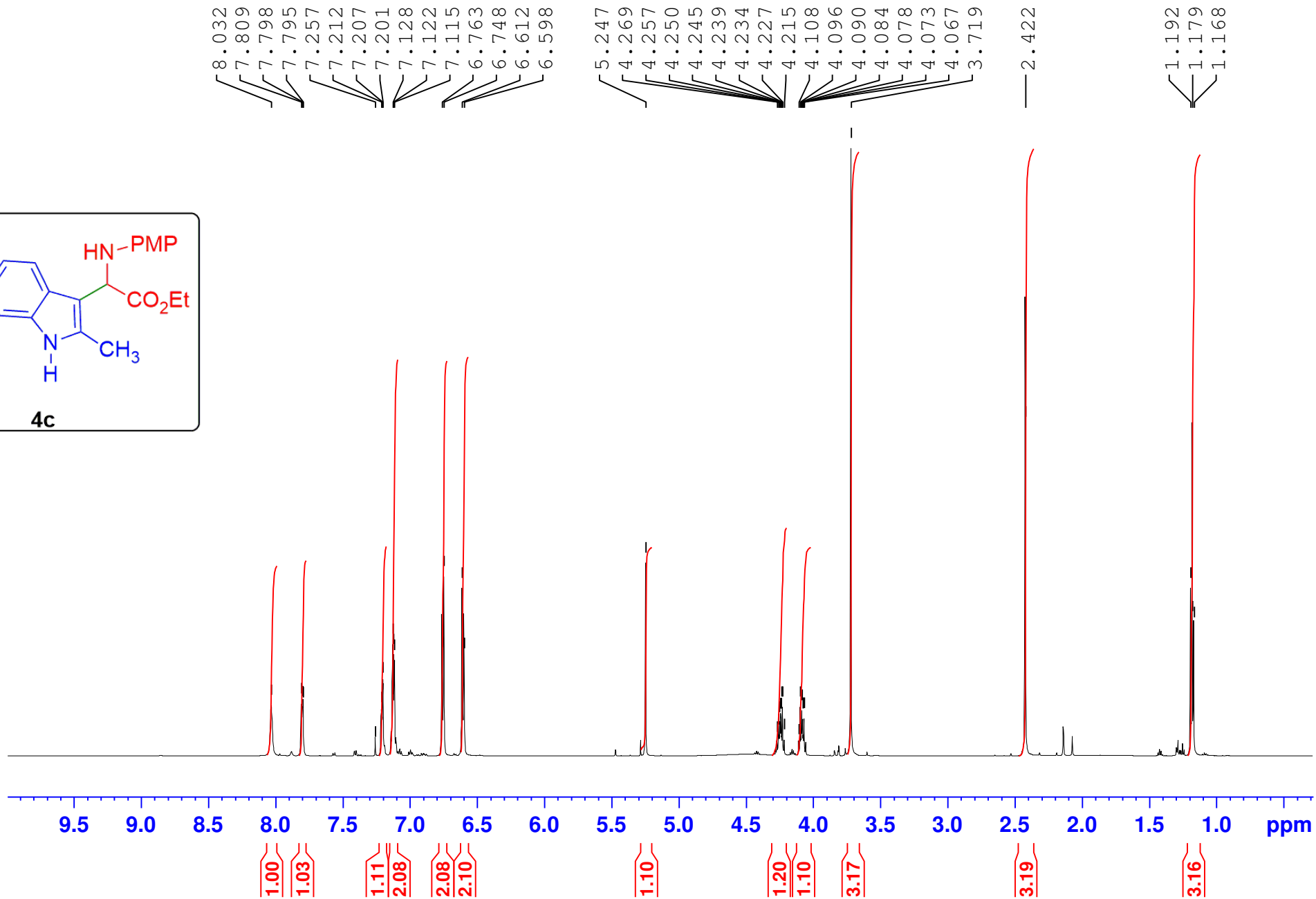


¹H NMR, 600 MHz, CDCl₃

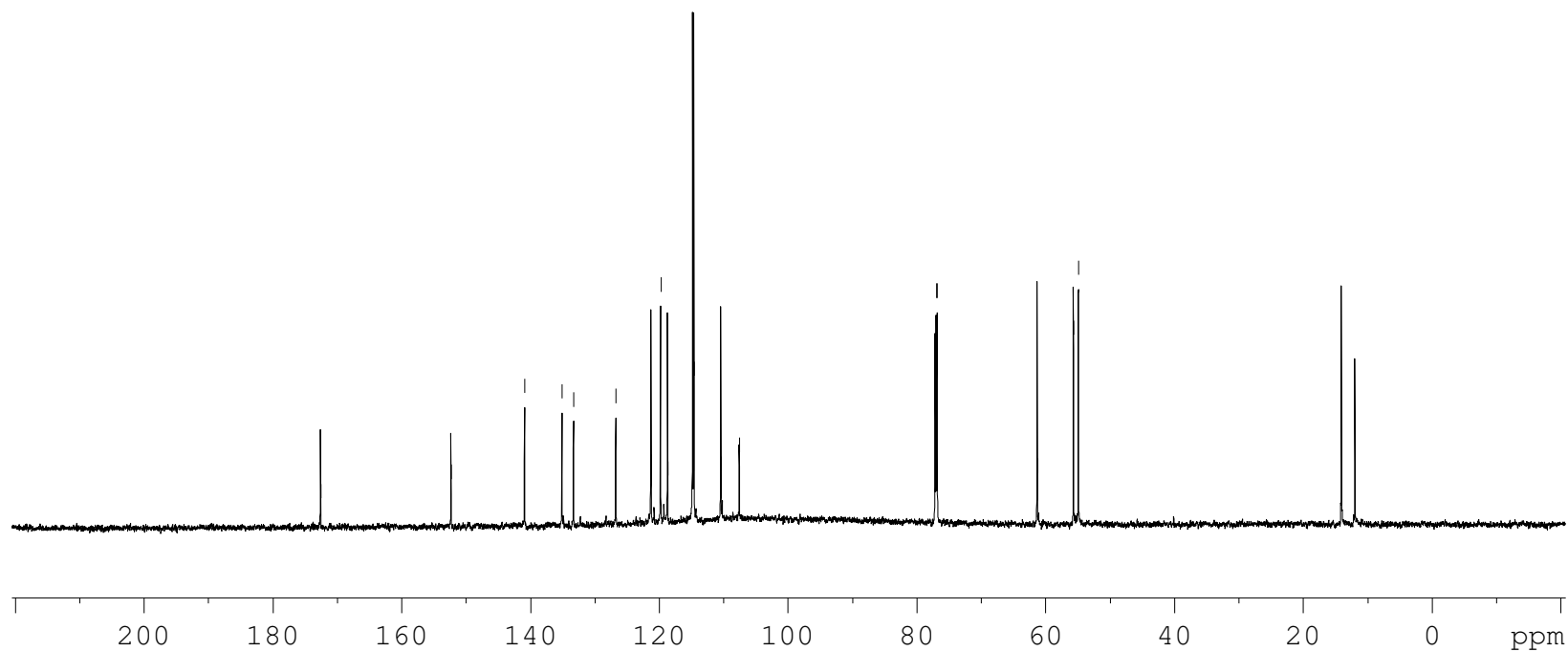
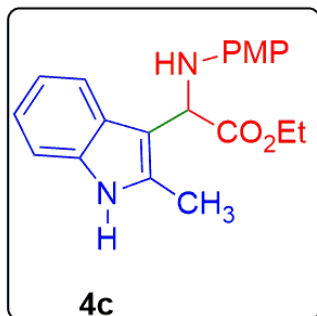
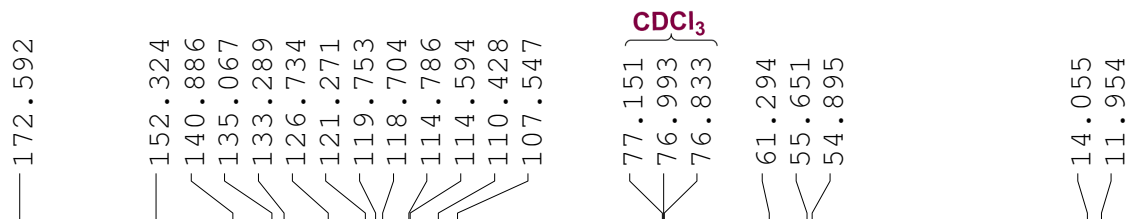
CDCl₃



4c



¹³C NMR, 201.2 MHz, CDCl₃



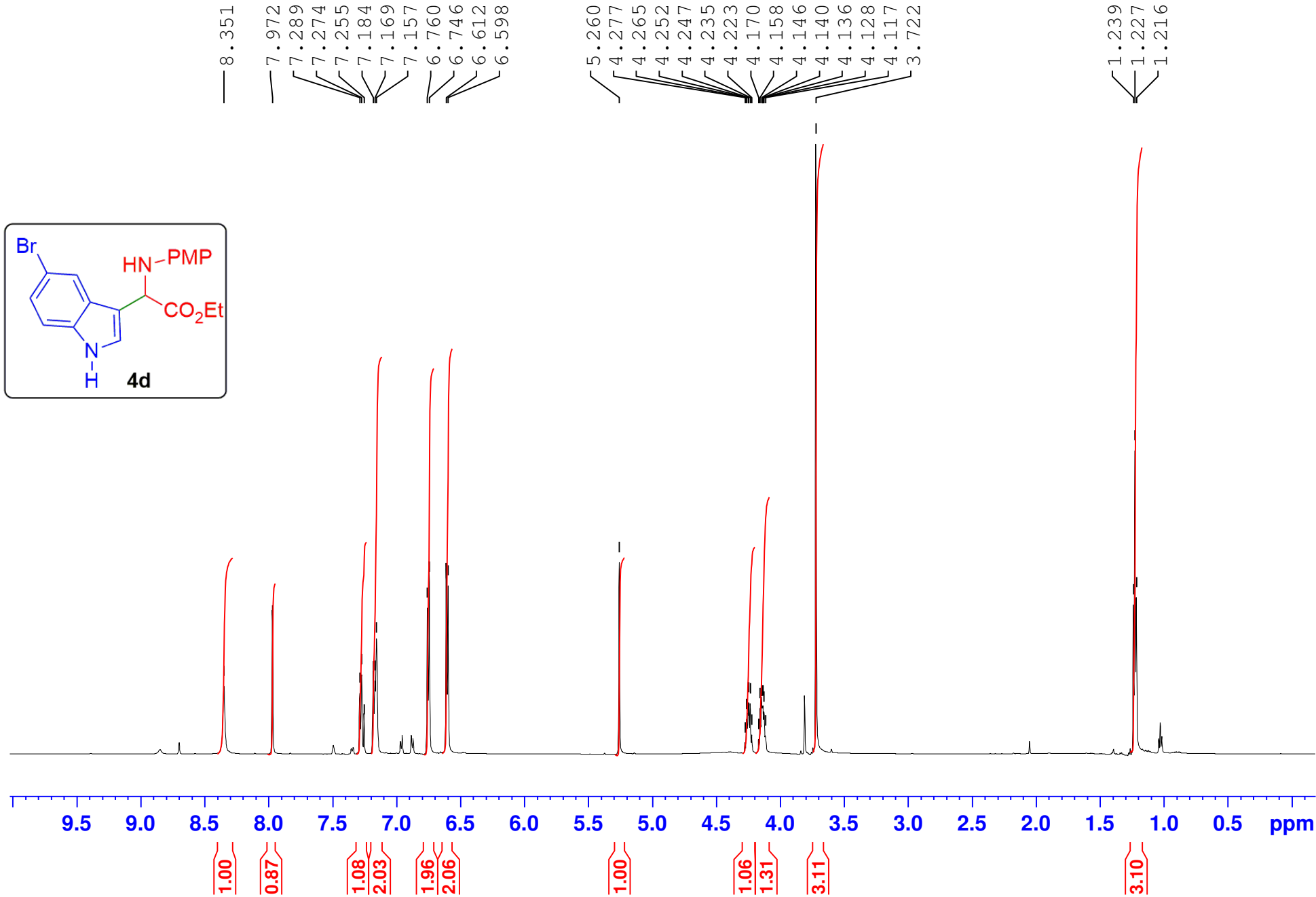
Current Data Parameters
NAME barc-RC2163-13C-25Aug21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210825
Time 14.08 h
INSTRUM spect
PROBHD 2555801_0012 ()
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 133
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.1 K
D1 3.0000000 sec
D11 0.03000000 sec
TDO 1
SFO1 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W

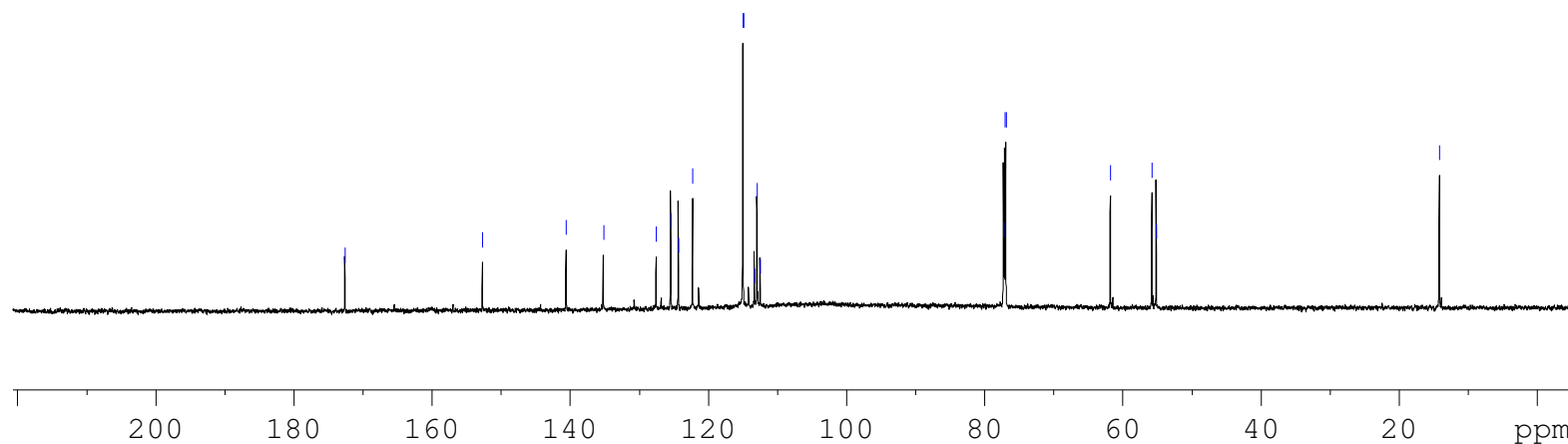
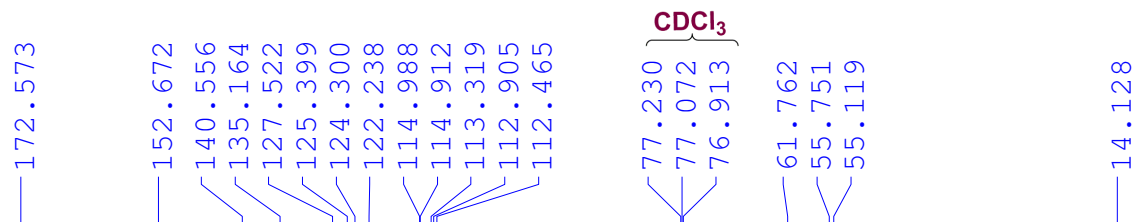
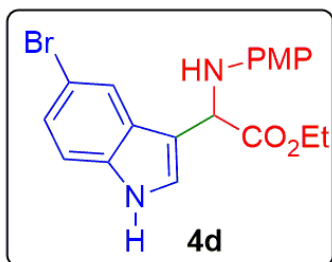
F2 - Processing parameters
SI 16384
SF 201.1677260 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

¹H NMR, 600 MHz, CDCl₃

CDCl₃



¹³C NMR, 201.2 MHz, CDCl₃



Current Data Parameters
NAME barc-RC-2505-13C-Feb22
EXPNO 3
PROCNO 1

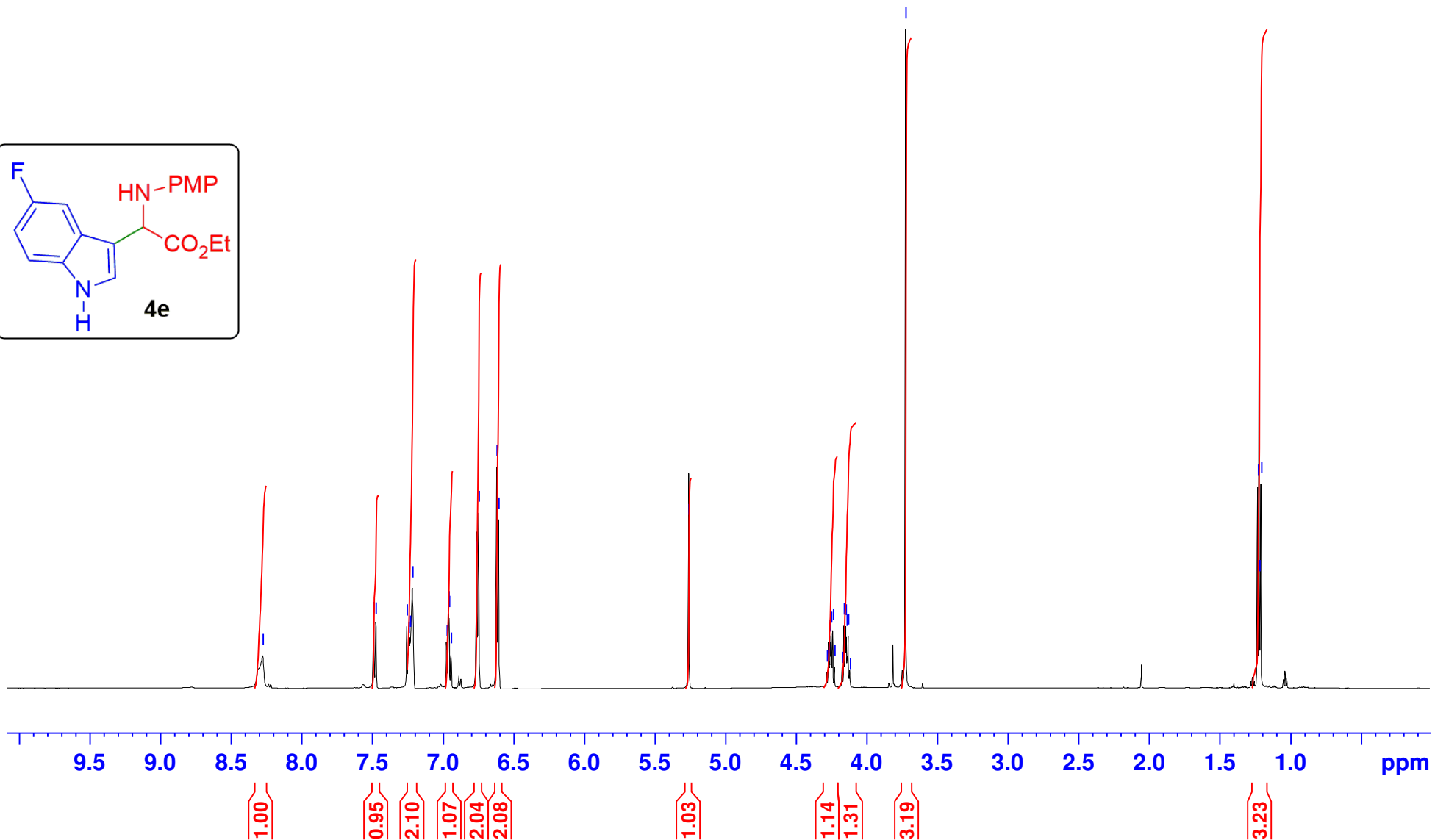
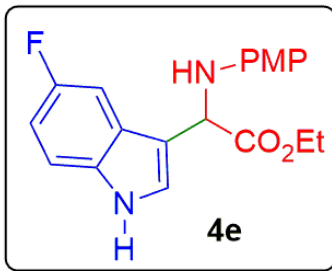
F2 - Acquisition Parameters
Date_ 20220209
Time 12.59 h
INSTRUM spect
PROBHD Z555801_0012 (
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 180
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TDO 1
SFO1 201.1878208 MHz
NUC1 13C
P1 9.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 13.0000000 W
PLW12 0.29249999 W

F2 - Processing parameters
SI 16384
SF 201.1677040 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

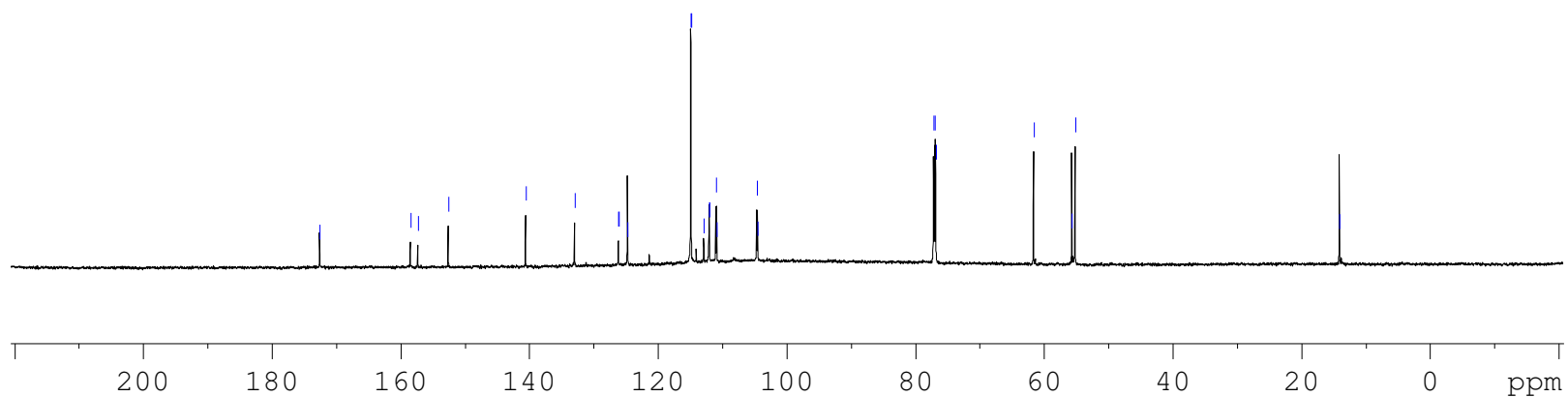
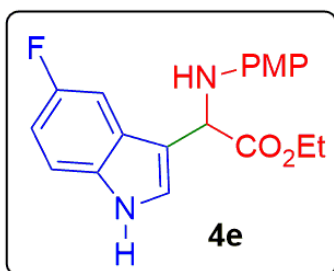
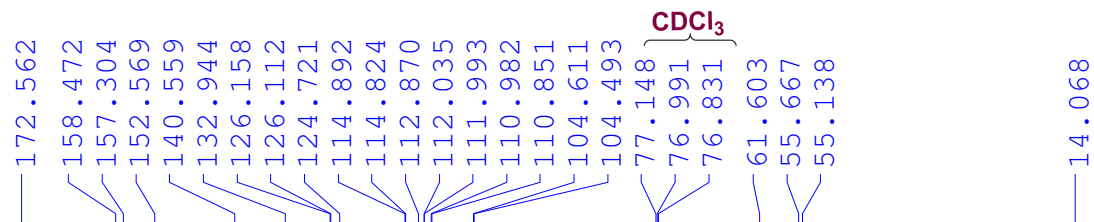
¹H NMR, 600 MHz, CDCl₃

CDCl₃

8.276
7.490
7.474
7.255
7.240
7.233
7.216
6.973
6.970
6.958
6.956
6.942
6.760
6.746
6.619
6.605
5.258
4.280
4.267
4.261
4.255
4.249
4.238
4.226
4.171
4.159
4.147
4.141
4.135
4.130
4.118
3.722
1.230
1.218
1.206



¹³C NMR, 201.2 MHz, CDCl₃



Current Data Parameters
NAME barc-RC-2506-13C-Feb22
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220209
Time 13.31 h
INSTRUM spect
PROBHD z555801_0012 ()
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 474
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.1 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 9.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 13.0000000 W
PLW12 0.29249999 W

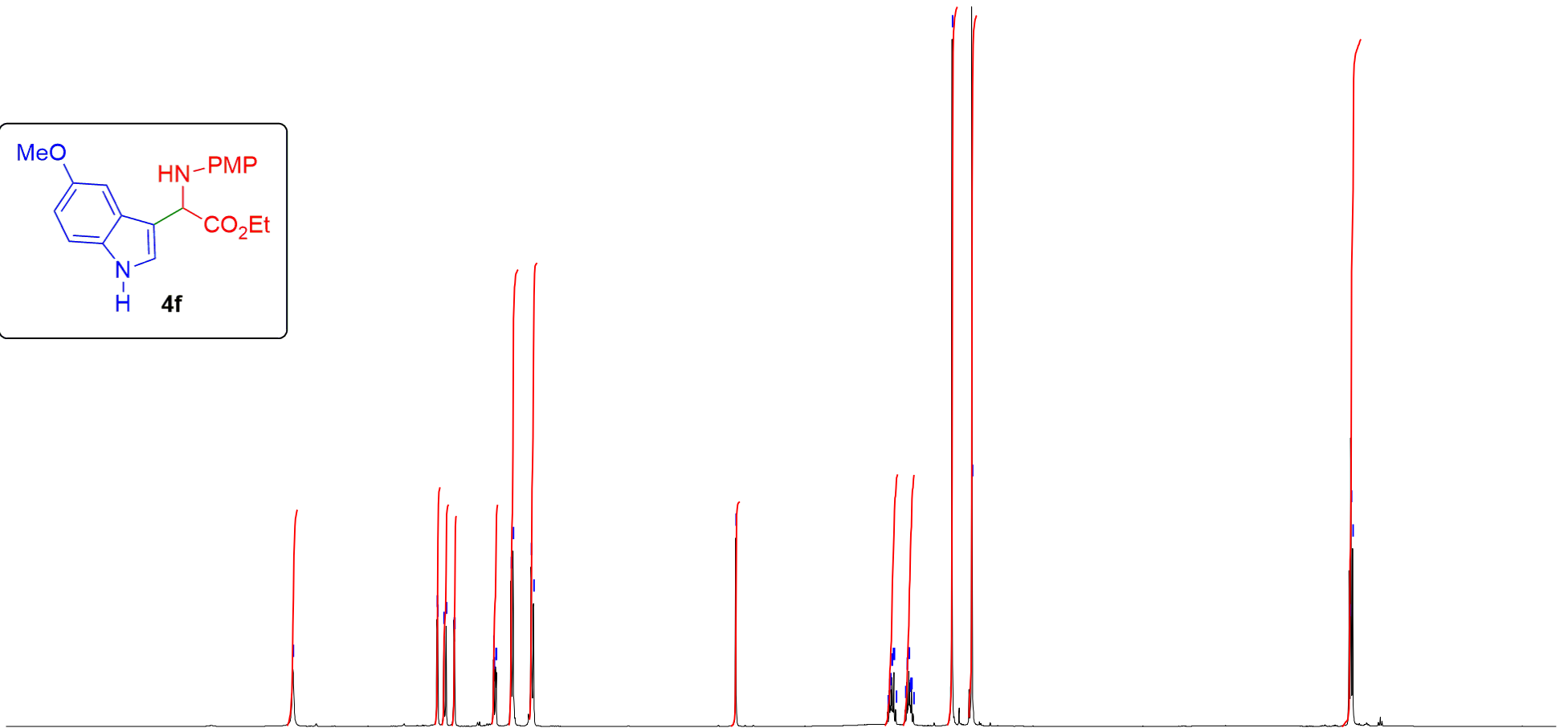
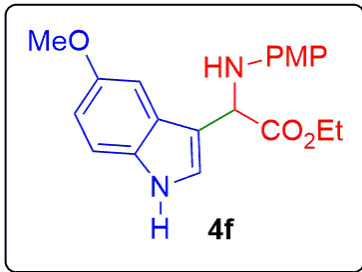
F2 - Processing parameters
SI 16384
SF 201.1677173 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

¹H NMR, 600 MHz, CDCl₃

CDCl₃

8.212
7.260
7.257
7.216
7.201
7.148
7.145
6.888
6.884
6.873
6.870
6.773
6.759
6.639
6.624
5.288
4.286
4.274
4.267
4.263
4.256
4.251
4.244
4.232
4.170
4.158
4.152
4.146
4.140
4.134
4.128
4.117
3.861
3.729

1.238
1.227
1.215



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 ppm

1.00
1.11
1.02
0.98
1.03
2.11
2.14

1.04

1.17
1.16
3.32
3.28

3.17

¹³C NMR, 201.2 MHz, CDCl₃

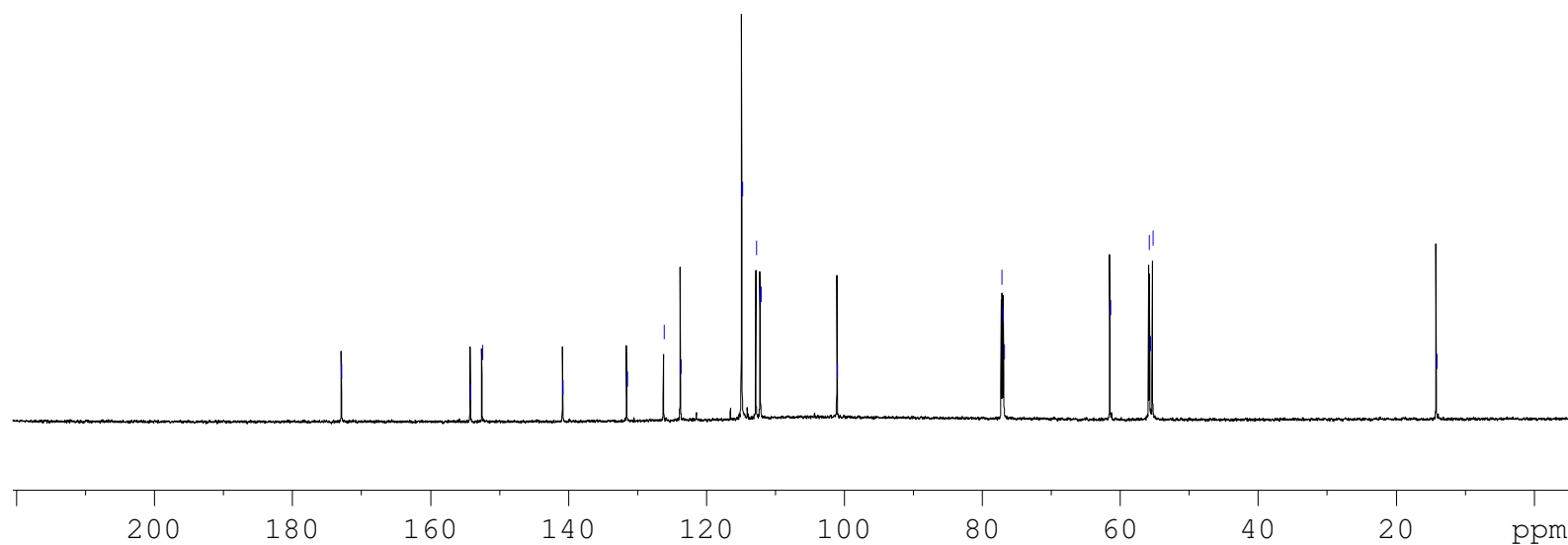
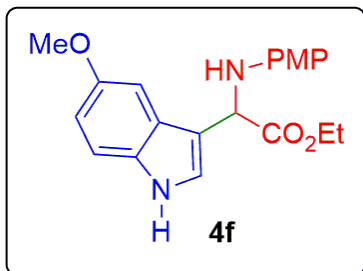


Current Data Parameters
NAME barc-RC-2507-13C-Feb22
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220209
Time 12.45 h
INSTRUM spect
PROBHD 2555801_0012 (
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 232
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SF01 201.1878208 MHz
NUC1 13C
P1 9.00 usec
PLW1 312.79998779 W
SF02 800.0332001 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W

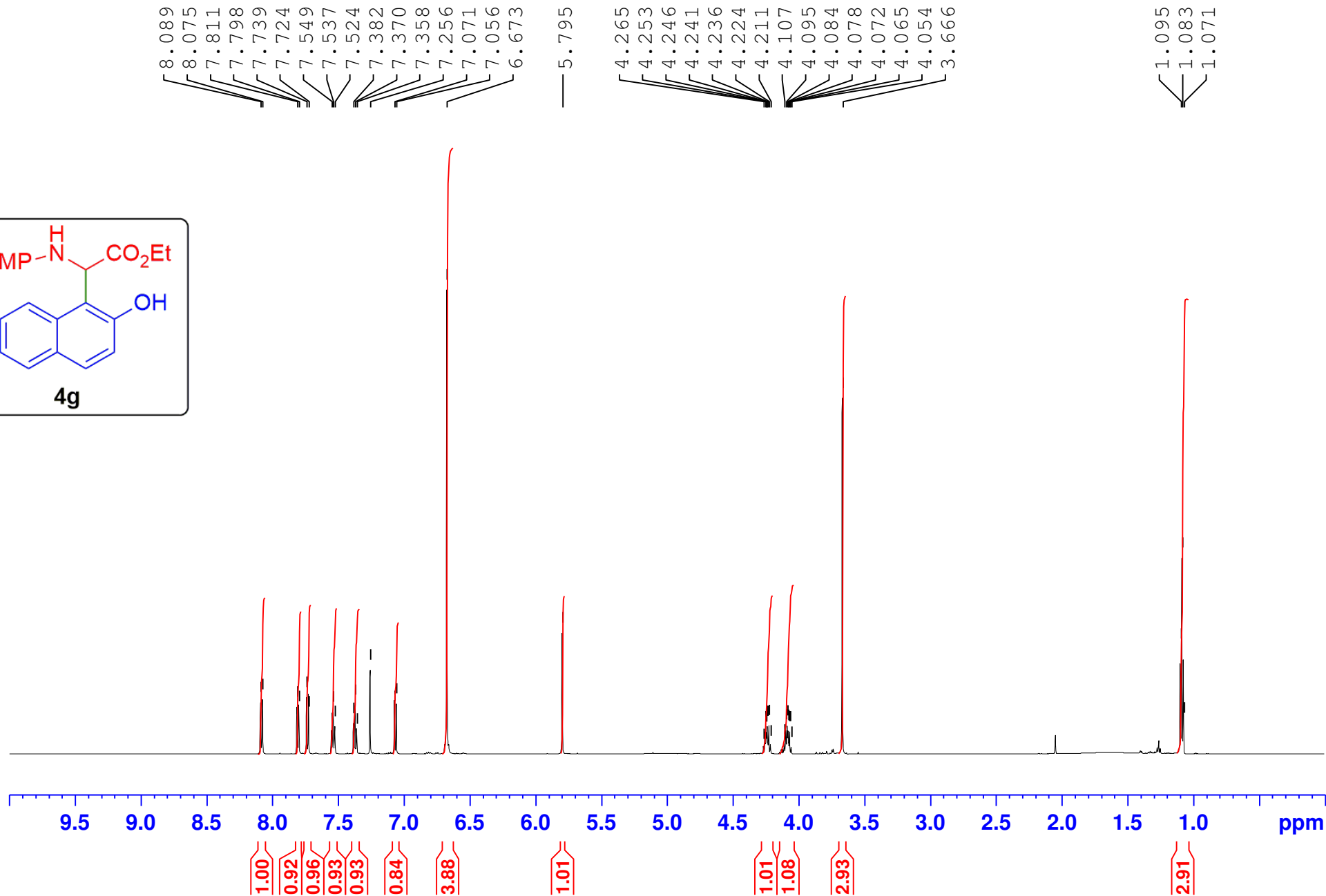
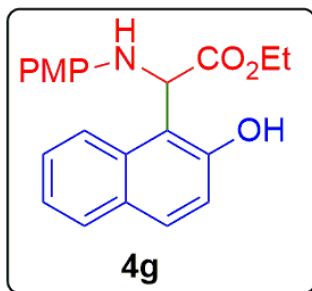
F2 - Processing parameters
SI 16384
SF 201.1677298 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

172.848
154.166
152.473
140.771
131.486
126.134
123.697
114.810
114.788
112.734
112.128
112.092
100.972
CDCl₃
77.151
76.991
76.832
61.408
55.778
55.627
55.216
14.089



¹H NMR, 600 MHz, CDCl₃

CDCl₃



¹³C NMR, 201.2 MHz, CDCl₃

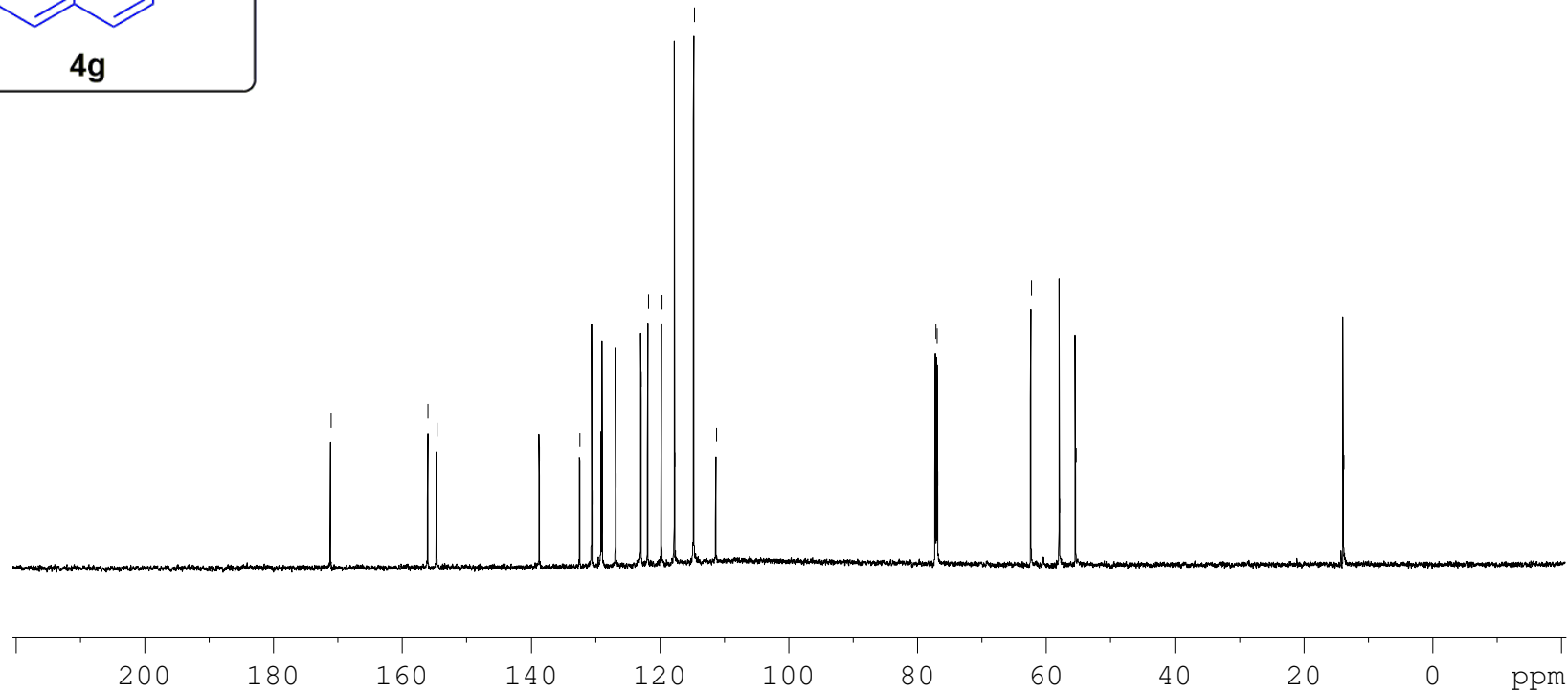
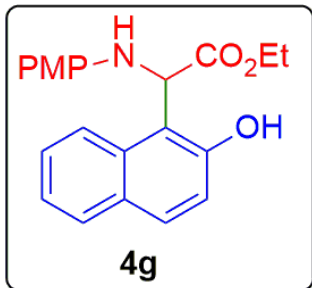


Current Data Parameters
NAME barc-RC-2127-13C-2July21
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210702
Time 13.57 h
INSTRUM spect
PROBHD Z555801_0012 ()
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 111
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.03000000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W

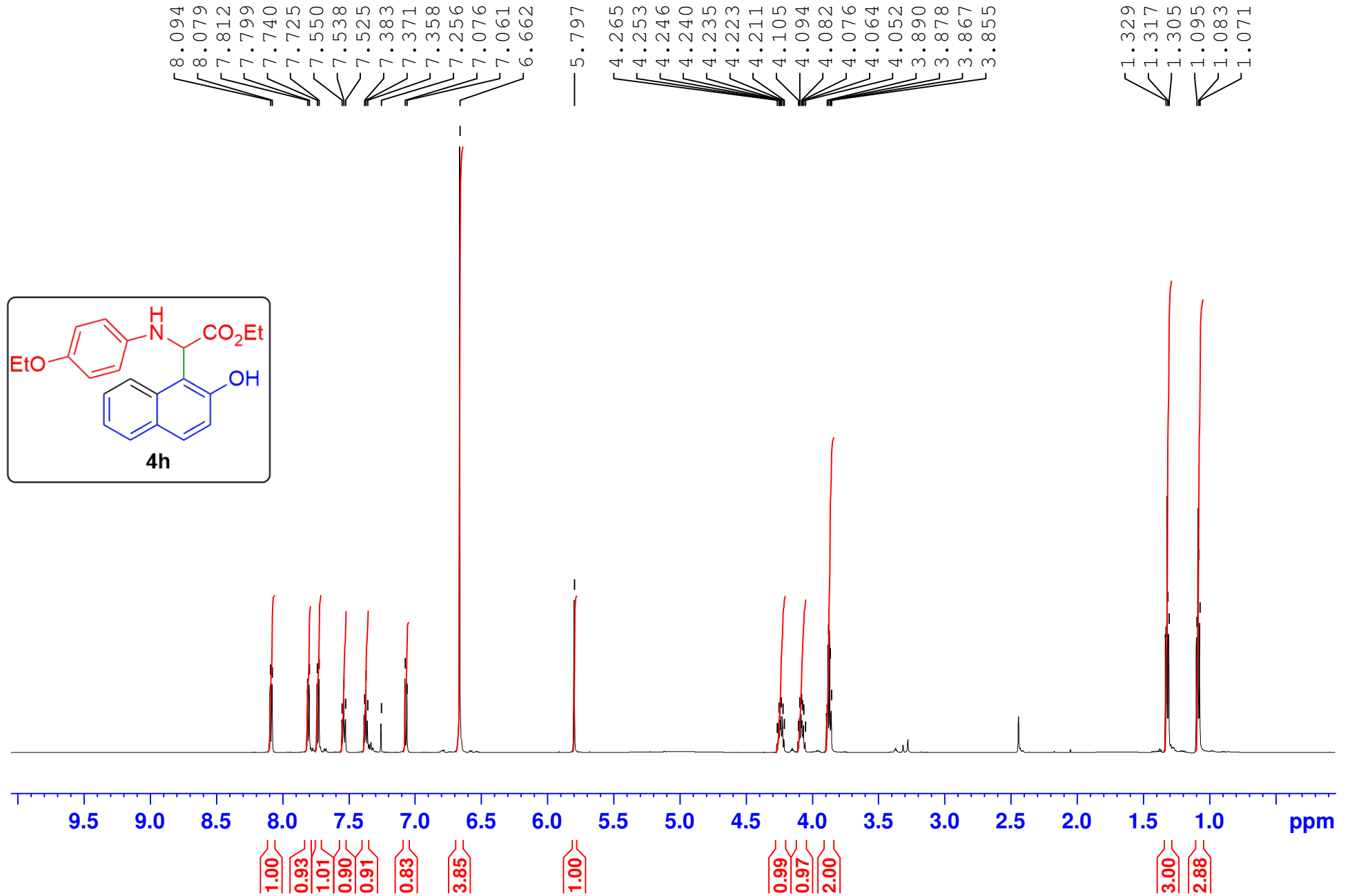
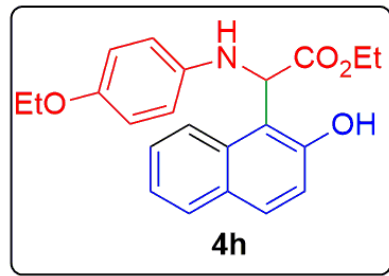
F2 - Processing parameters
SI 16384
SF 201.1677250 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

171.113
156.003
154.635
138.696
132.402
130.526
129.095
128.924
126.807
122.892
121.831
119.715
117.676
114.695
111.252
CDCl₃
77.162
77.002
76.842
62.333
57.914
55.401
13.810

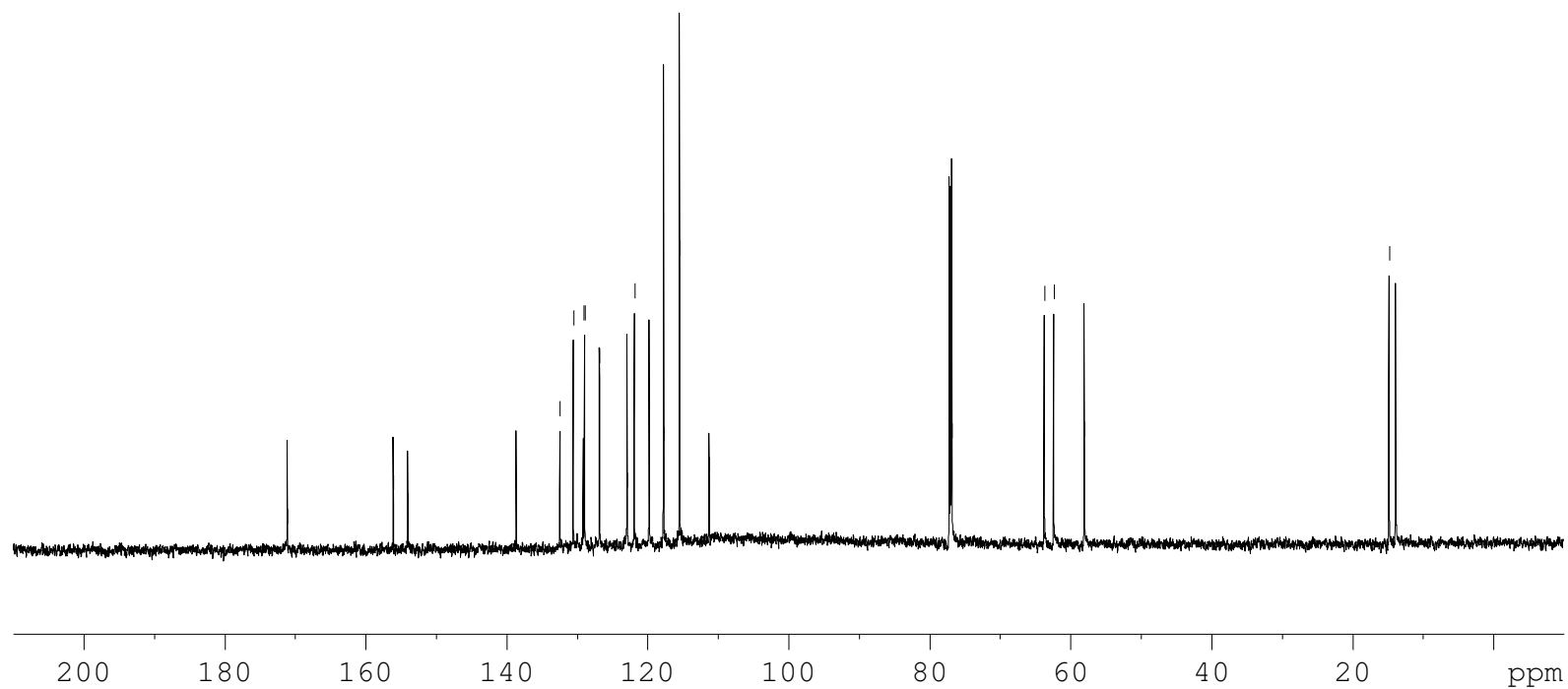
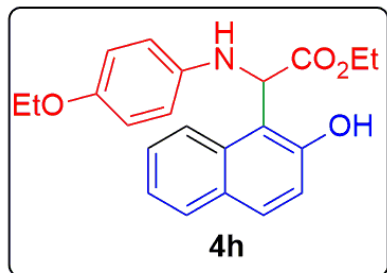
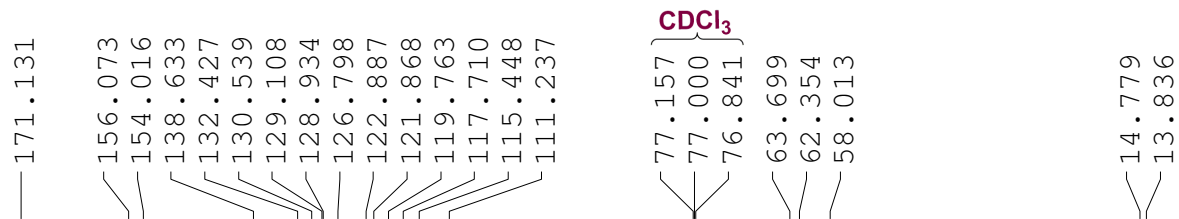


¹H NMR, 600 MHz, CDCl₃

CDCl₃



¹³C NMR, 201.2 MHz, CDCl₃



Current Data Parameters
NAME barc-RC-2130-13C-2July21
EXPNO 1
PROCNO 1

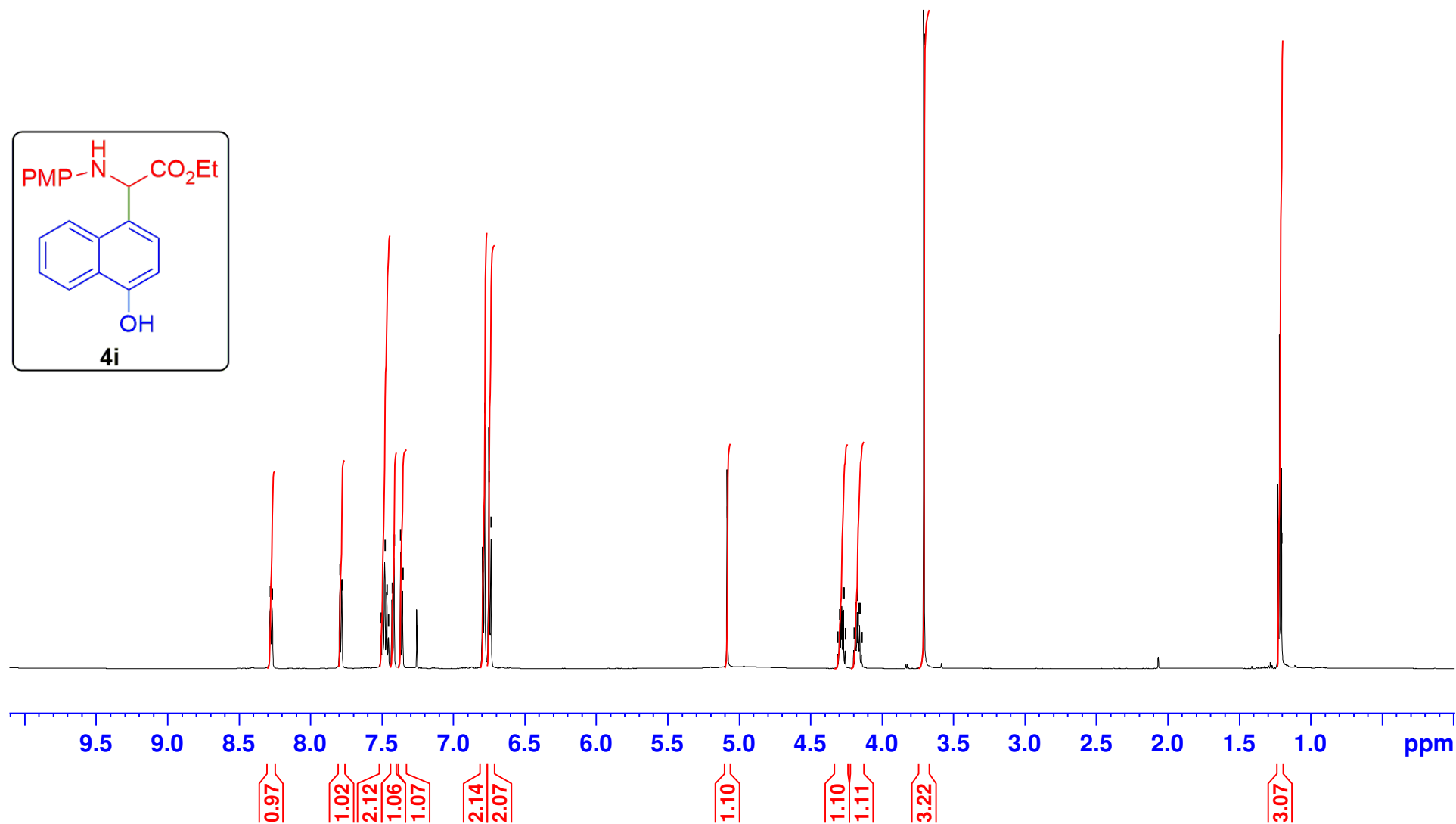
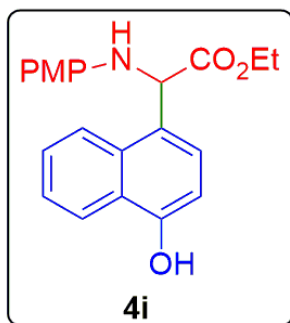
F2 - Acquisition Parameters
Date_ 20210702
Time 13.01 h
INSTRUM spect
PROBHD Z555801_0012 (
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 72
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.03000000 sec
TD0 1
SF01 201.1878208 MHz
NUC1 13C
P1 8.00 usec
PLW1 312.79998779 W
SF02 800.0332001 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 60.00 usec
PLW2 13.00000000 W
PLW12 0.29249999 W

F2 - Processing parameters
SI 16384
SF 201.1677179 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

¹H NMR, 600 MHz, CDCl₃

CDCl₃

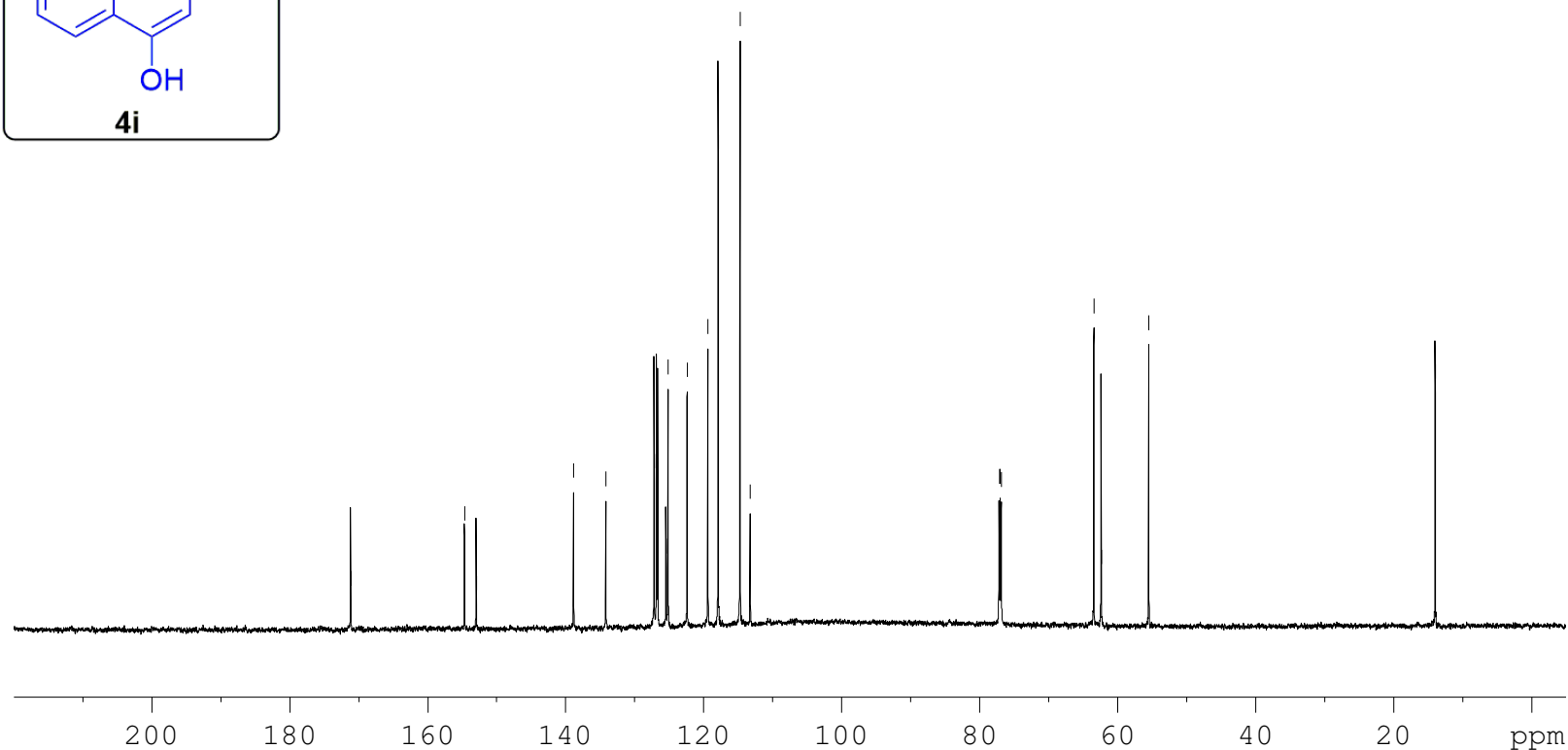
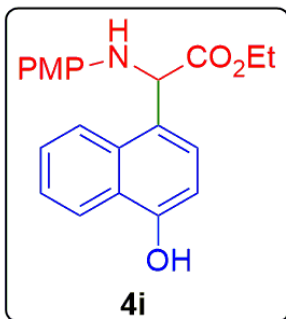
8.281
8.268
7.793
7.780
7.506
7.495
7.480
7.465
7.454
7.429
7.415
7.369
7.355
7.255
6.794
6.780
6.751
6.736
5.083
4.309
4.298
4.292
4.286
4.280
4.274
4.267
4.256
4.196
4.184
4.173
4.167
4.161
4.155
4.143
3.705
1.226
1.214
1.202



¹³C NMR, 201.2 MHz, CDCl₃



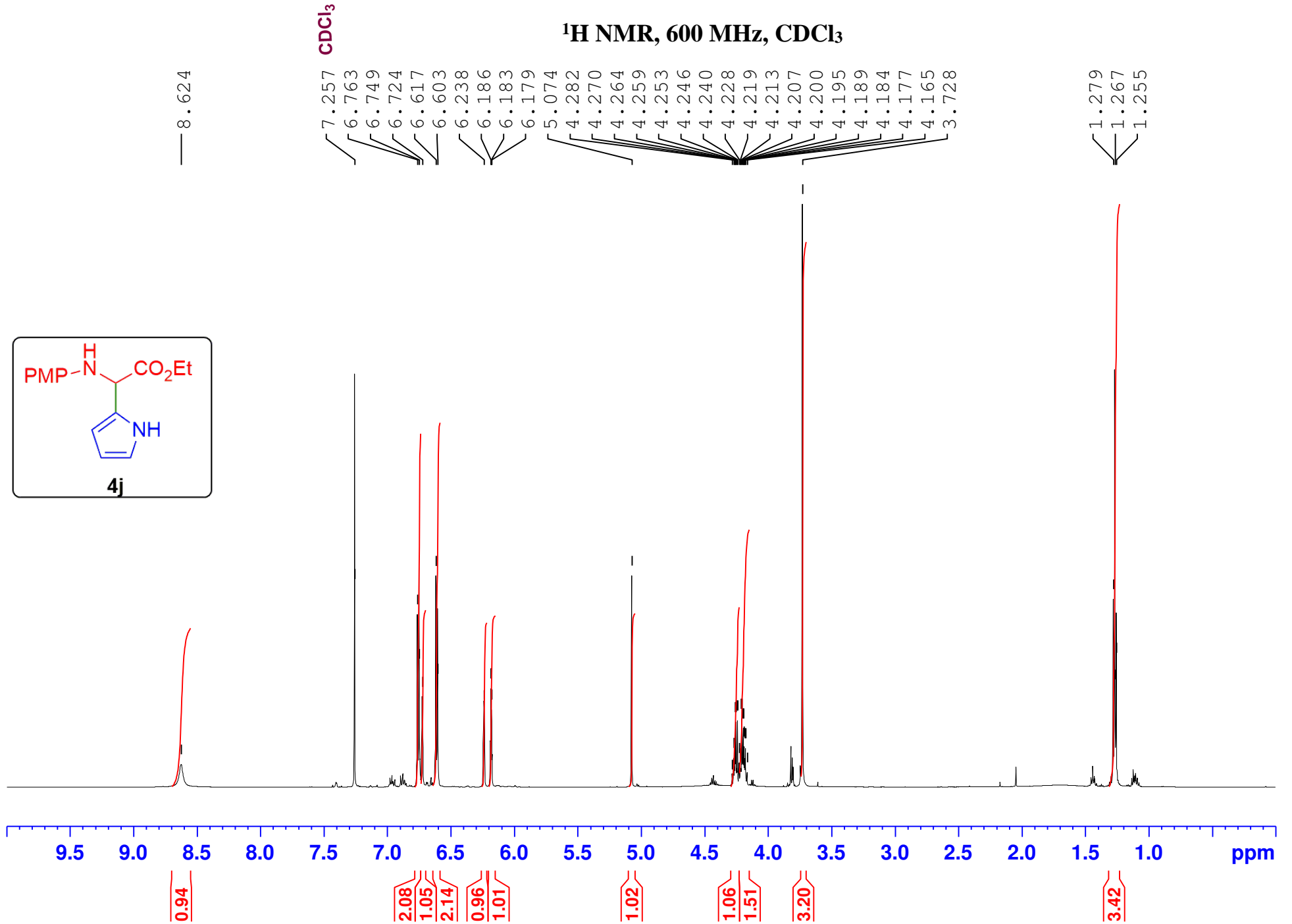
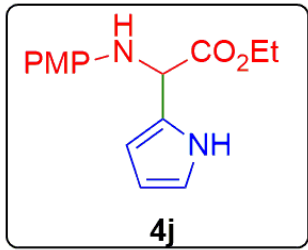
—171.168
154.653
152.959
138.825
134.156
127.162
126.790
126.633
125.441
125.134
122.366
119.356
117.863
114.698
113.225
77.156 } CDCl₃
76.997 }
76.838 }
63.422
62.364
—55.450
—13.925



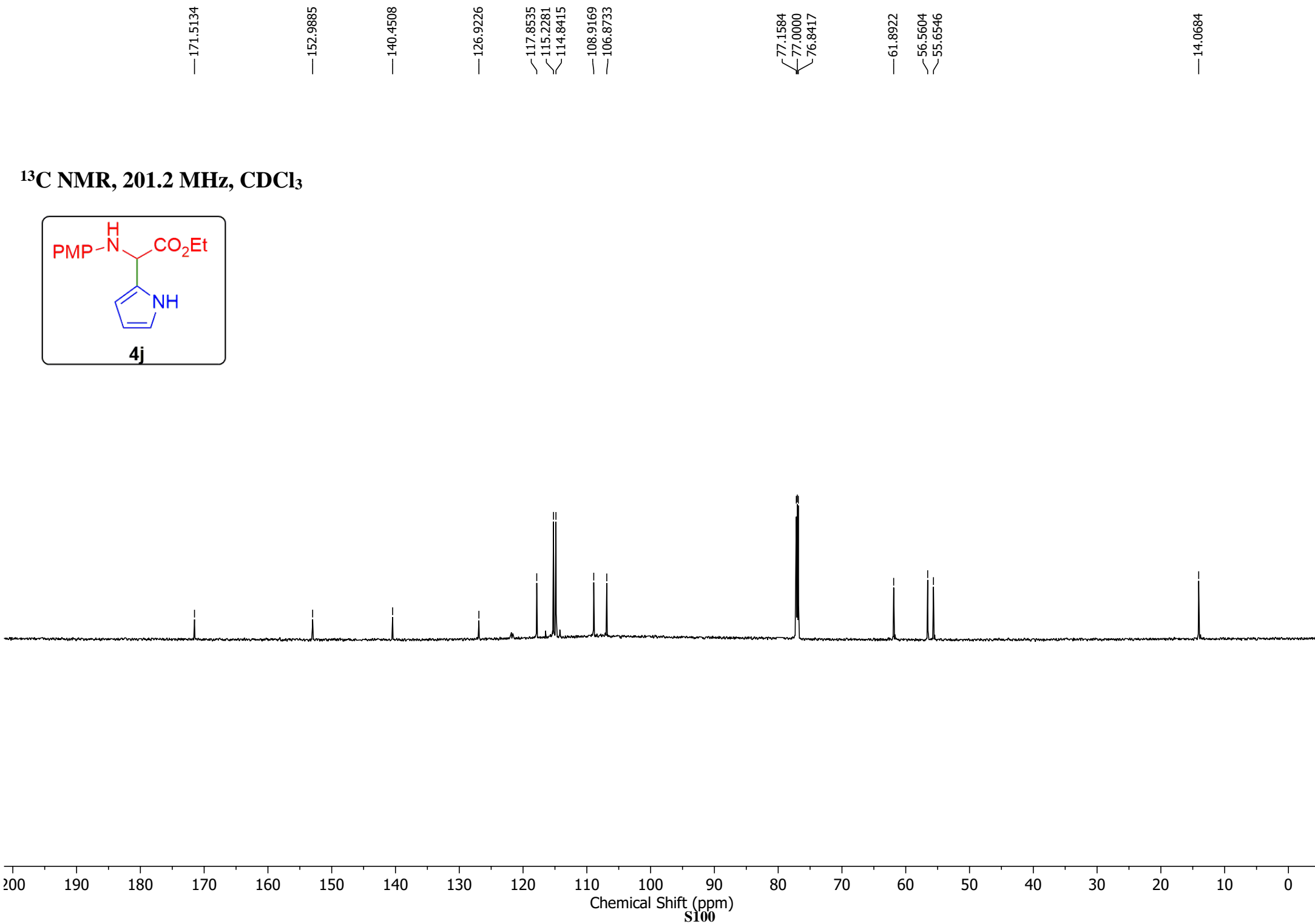
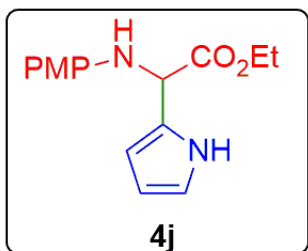
Current Data Parameters
NAME barc-RC-2504-13C-Feb22
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220209
Time 14.09 h
INSTRUM spect
PROBHD Z555801_0012 ()
PULPROG zgdc
TD 16384
SOLVENT CDCl3
NS 151
DS 4
SWH 48543.688 Hz
FIDRES 5.925743 Hz
AQ 0.1687552 sec
RG 71.8
DW 10.300 usec
DE 6.50 usec
TE 298.0 K
D1 3.0000000 sec
D11 0.0300000 sec
TD0 1
SFO1 201.1878208 MHz
NUC1 13C
P1 9.00 usec
PLW1 312.79998779 W
SFO2 800.0332001 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 60.00 usec
PLW2 13.0000000 W
PLW12 0.29249999 W

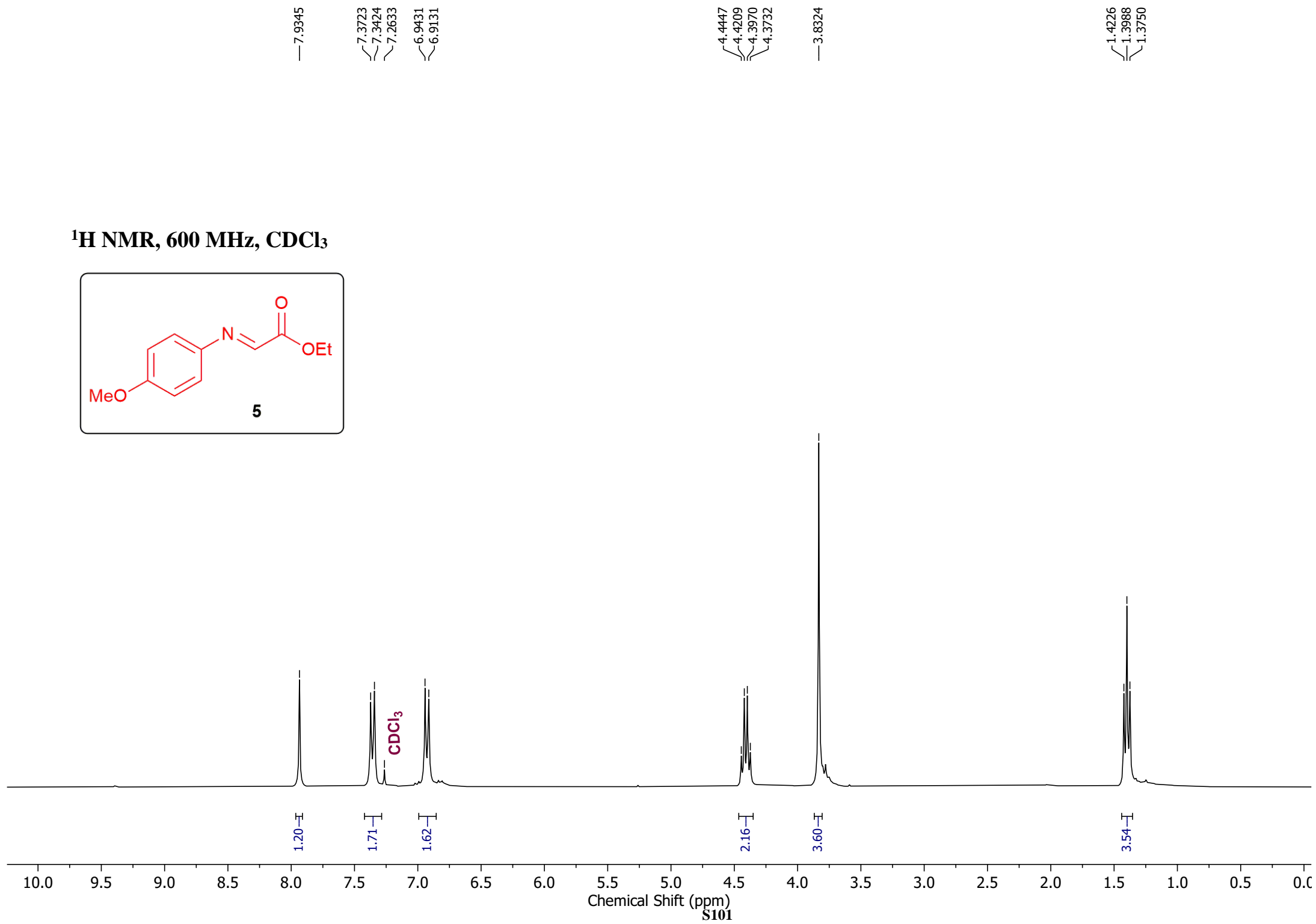
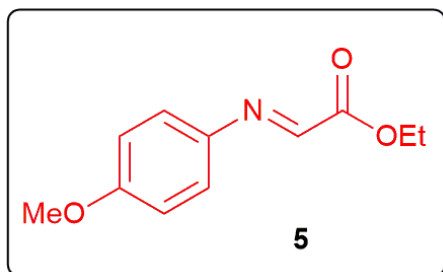
F2 - Processing parameters
SI 16384
SF 201.1677259 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40



¹³C NMR, 201.2 MHz, CDCl₃



¹H NMR, 600 MHz, CDCl₃



¹³C NMR, 75 MHz, CDCl₃

