Supporting Information

Iridium(III)-catalyzed photoredox cross-coupling of alkyl bromide with trialkyl amines: Access to α-alkylated aldehydes

Contents

1. Experimental Sections

1.1. General Information

The commercial reagents (phenacyl bromides, trialkyl amines and photocatalysts) were used as received from Merck, Sigma-Aldrich, TCI and Avra chemicals without any further purification. Moreover, few of alkyl bromides were synthesized by the reported procedures.[1] Acetonitrile, 1,4-dioxane and DMSO was purchased from Merck. DMF was purchased from Sigma-Aldrich. All the reactions were monitored by analytical thin layer chromatography (TLC) using Merck pre-coated aluminium sheets and visualized by a UV lamp. Flash column chromatography was performed on silica gel (100−200 mesh). The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL 500 FT-NMR spectrometer operating at 500 and 126 MHz, respectively. Chemical shifts (δ) for ^{1}H and ^{13}C {^{1}H} NMR are given in parts per million (ppm) using the residual solvent peaks as reference relative to tetramethyl silane (TMS). Coupling constant (J) values are reported in Hz. High-resolution mass spectra (HRMS, m/z) were recorded in EI or ESI mode, on Sciex X500R QTOF instrument. The Cyclic Voltammetry experiments were conducted on Autolab-PGSTAT302N operated using software NOVA 1.9. Kessil blue LED lights (40 W, 467 nm) were used for the photoredox reactions. All the reactions were carried out using oven-dried 5.0- & 15-mL sample vials of borosilicate. IUPAC names were obtained using the ChemDraw Professional 16.0 software.

1. S. Mal, S. Sarkar and M. Jana, *J. Chem. Sci.*, 2022, **134**, 118.

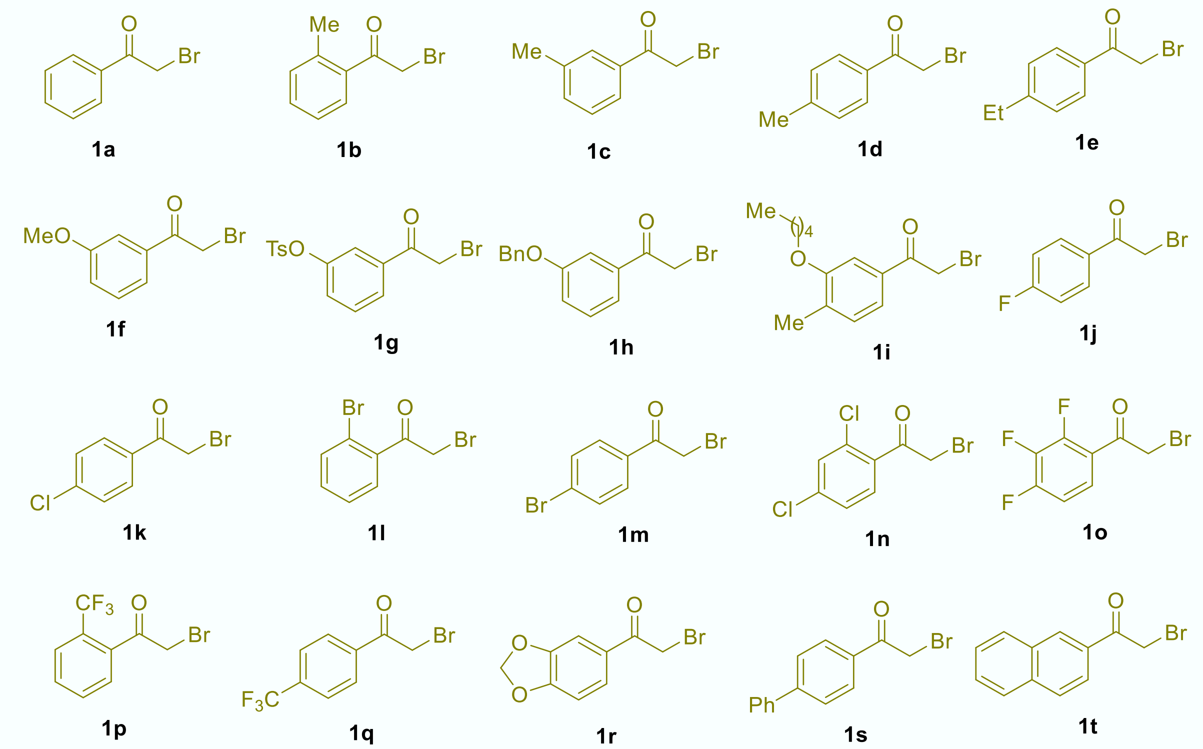
(a) Light Information and Reaction Setup

Two Kessil blue LED lights (40 W, λ_{max} = 467 nm with 50% intensity) were used as the light source for this light promoted reaction and no filter was used. A borosilicate 5.0 mL vial was used as the reaction vessel. The distance from the light source to the irradiation vessel was in between 5 to 6 cm. Regular fan was used to ventilate the area to maintain the room temperature (25–30 ^{o}C). The reaction set-up for this photochemical reaction is shown below (Figure S1).

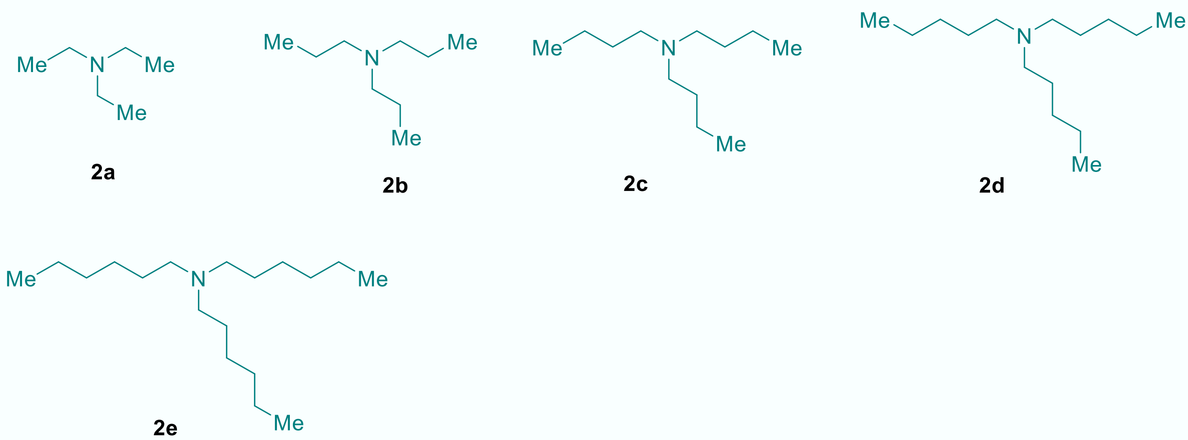
Figure S1. Photochemical reaction Set-up.

(b) List of alkyl bromides **1a**-**1t** and alkyl amines **2a**-**2e** used for the synthesis of α-functionalized aldehydes

Alkyl bromides **1a**-**1t**



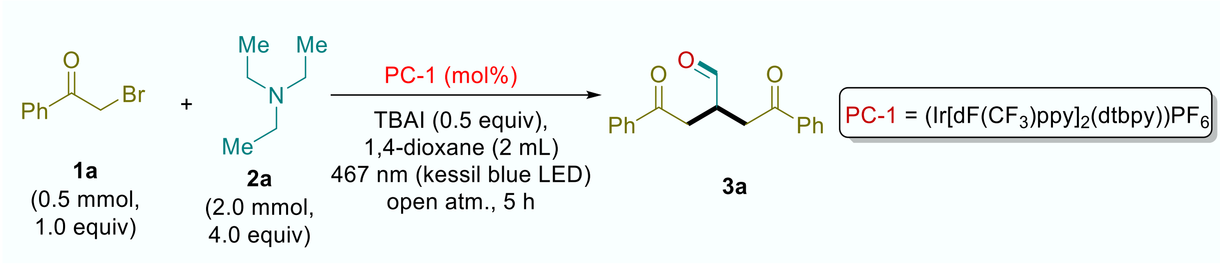
Trialkyl amines **2a**-**2e**



1.2. Optimization for the photocatalyst (PC-1) loading

The optimization of the loading of iridium photocatalyst (PC-1) is listed in table S1. Using different amount of PC-1 for the given model reaction (Table S1, entries 1-4), it was found that maximum yield was obtained when we used 2 mol% of PC-1 (Table S1, entry 1).

Table S1. Variation in loading of PC-1[a]



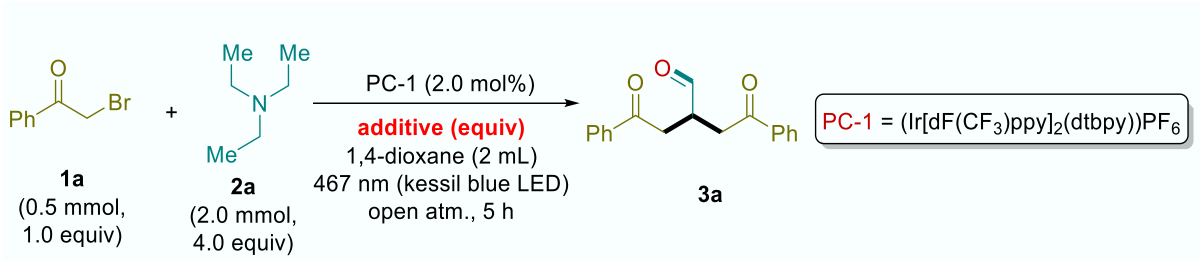
Entry	PC-1 loading in mol%	Yield (%)[b]
1.	2 mol%	76
2.	1 mol%	65
3.	1.5 mol%	67
4.	3.0 mol%	75

[a]Reaction conditions; all reactions were performed with **1a** (0.5 mmol), **2a** (2.0 mmol, 4.0 equiv.) and TBAI (0.5 equiv.) in 1,4-dioxane (2.0 mL) under open atmosphere at 30 °C for 5 h. [b]isolated yield of **3a**.

1.3. Optimization of additives

The optimization of the loading of TBAI and reaction outcomes with other additives (quaternary ammonium salts) are listed in Table S2. Using different amount of TBAI for the given model reaction, it was found that maximum yield was obtained when we use 0.5 equiv. of TBAI (Table S2, entries 1-3). Moreover, using other additives such as TBAB and TBATFB could not provide better results (Table S2, entries 4 & 5).

Table S2. Additive Variations[a]



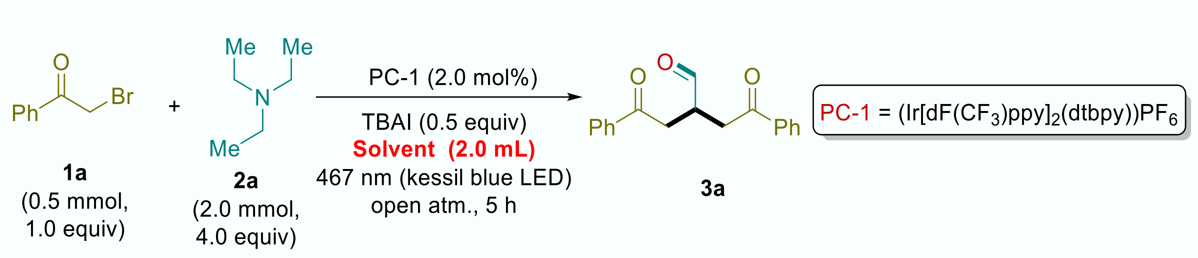
Entry	Additive (equiv)	Yield (%)[b]
1.	TBAI (0.5)	76
2.	TBAI (0.3)	65
3.	TBAI (1.0)	76
4.	TBAB (0.5)	56
5.	TBATFB (0.5)	55

[a]Reaction conditions; all reactions were performed with **1a** (0.5 mmol), **2a** (2.0 mmol, 4.0 equiv.), and PC-1 (2.0 mol%) in 1,4-dioxane (2.0 mL) under open atmosphere at 30 °C for 5 h. [b]isolated yield of **3a**; TBAI = tetra butyl ammonium iodide, TBAB = tetra butyl ammonium bromide, TBATFB = tetra butyl ammonium tetrafluoro borate.

1.4. Optimization of solvents

The given model reaction was also checked in different solvents as listed in table S3. Using 2.0 mL of 1,4-dioxane yielded desired product **3a** in maximum yield (76%, table S3, entry 1). The Photoredox reaction in ACN, DMF and DMSO could not provide better results (Table S3, entries 2-4). Moreover, using other cyclic ether such as THF also failed to provide better yield of product as compare to 1,4-dioxane (Table S3, entry 5).

Table S3. Using different non-polar and polar solvents.[a]



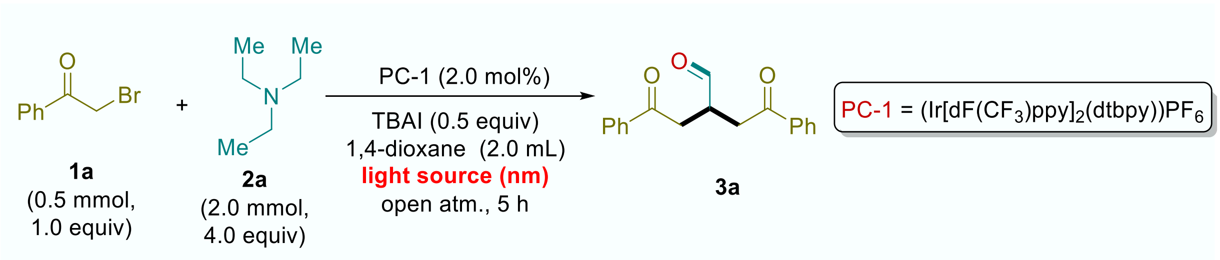
Entry	Solvent (2.0 mL)	Yield (%)[b]
1.	1,4-dioxane	76
2.	ACN	45
3.	DMF	35
4.	DMSO	trace
5.	THF	30

[a]Reaction conditions; all reactions were performed with **1a** (0.5 mmol), **2a** (2.0 mmol, 4.0 equiv.), TBAI (0.5 equiv.) and PC-1 (2.0 mol%) in solvent (2.0 mL) under open atmosphere at 30 °C for 5 h. [b]isolated yield of **3a**.

1.5. Optimization of lights

The given model reaction was also tested under different light sources as listed in table S4 (entries 1-5). The photoredox reaction in Kessil blue LED lights (2 x 40 W, 467 nm) provided better result as compared to other light sources (Table S4, entry 1).

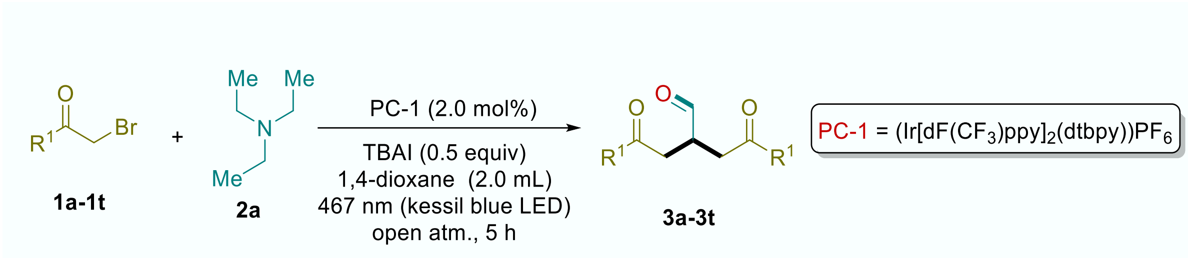
Table S4. Reaction under different light sources[a]



Entry	Light (W, nm)	Yield (%)[b]
1.	Kessil blue LED (2 x 40 W, 467 nm)	76
2.	Kessil blue LED (2 x 40 W, 390 nm)	66
3.	LUXEON blue (1 W, 480 nm)	40
4.	LUXEON green (1 W, 540 nm)	trace
5.	Bulbs (2 X 20 W, unknown)	35

[a]Reaction conditions; all reactions were performed with **1a** (0.5 mmol), **2a** (2.0 mmol, 4.0 equiv.), TBAI (0.5 equiv.) and PC-1 (2.0 mol%) in 1,4-dioxane (2.0 mL) under open atmosphere at 30 °C for 5 h. [b]isolated yield of **3a**.

1.6. General photocatalytic procedure for the synthesis of aldehydes **3a-3t**



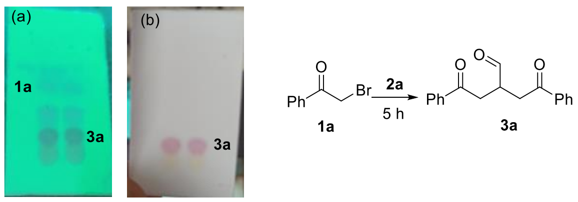
An oven-dried 5.0 mL sample vial was charged with alkyl bromide (**1**) (0.5 mmol, 1.0 equiv.), triethyl amine (**2a**) (2.0 mmol, 4.0 equiv.), TBAI (0.25 mmol, 0.5 equiv.) and PC-1 (2 mol%, 0.011 g) a magnetic stir bar in 1,4-dioxane (2 mL) and was stirred at room temperature in an open-air for 5 h under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5–6 cm. The progress of the reaction was monitored via TLC. After completion of the reaction, the solvent was removed by rotary evaporation. The reaction mixture was then mixed with water (15 mL) and extracted with ethyl acetate (2 × 20 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then purified over column chromatography by eluting with hexane: ethyl acetate mixture to afford the desired products **3a**-**3t**.

TLC observation of reaction mixture after 5 h

Developing agent (3% ethyl acetate in hexane; single run)

(a) Under UV light (λ_{max} = 254 nm; short)

(b) Without UV light **3a** appears as a red spot after 15 min.

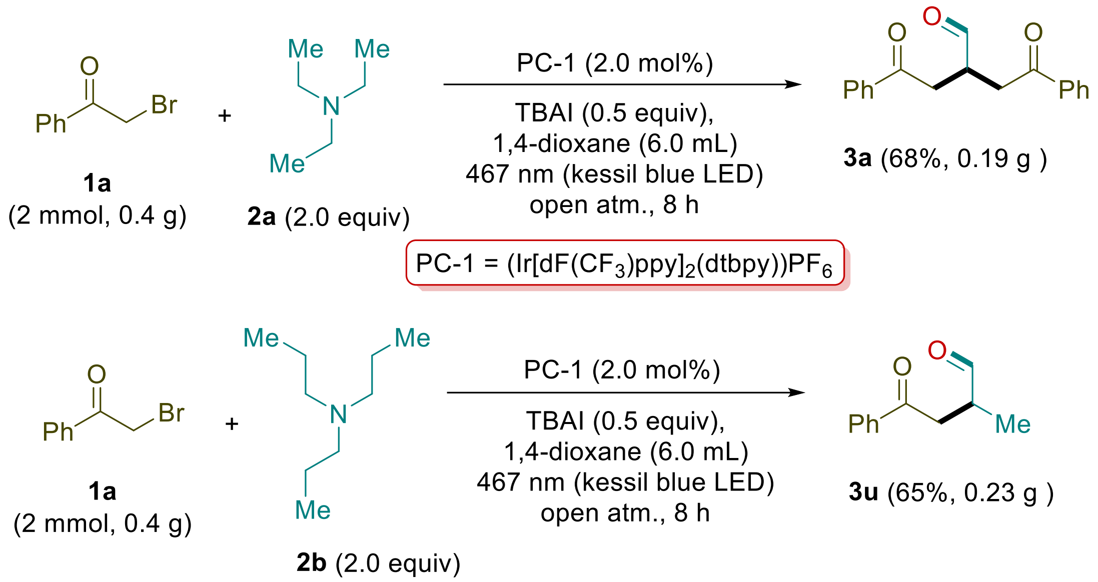


1.7. General photocatalytic procedure for the synthesis of aldehydes **3u-3ar**

Scheme S1. General reaction

An oven-dried 5.0 mL sample vial was charged with alkyl bromide (**1**) (0.5 mmol, 1.0 equiv.), trialkyl amines (**2b**-**2e**) (2.0 mmol, 4.0 equiv.), TBAI (0.25 mmol, 0.5 equiv.) and PC-1 (2 mol%, 0.011 g) a magnetic stir bar in 1,4-dioxane (2 mL) and was stirred at room temperature in an open-air for 5 h under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5–6 cm. The progress of the reaction was monitored via TLC. After completion of the reaction, the solvent was removed by rotary evaporation. The reaction mixture was then mixed with water (15 mL) and extracted with ethyl acetate (2 × 20 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then purified over column chromatography by eluting with hexane: ethyl acetate mixture to afford the desired products **3u**-**3ar**.

2. Scale up synthesis of 3a and 3u



Scheme S2. Scale-up synthesis of compounds **3a** and **3u**

2.1 General photocatalytic procedure for the 2.0 mmol scale reaction of 1a with 2a for the synthesis of 3a

An oven-dried 15.0 mL sample vial was charged with phenacyl bromide (**1a**) (2.0 mmol, 1.0 equiv.; 0.4 g), triethyl amine (**2a**) (8.0 mmol, 4.0 equiv., 0.8 g), TBAI (1.0 mmol, 0.5 equiv., 0.369 g) and PC-1 (2 mol%, 0.044 g) a magnetic stir bar in 1,4-dioxane (6 mL) and was stirred at room temperature in an open-air for 8 h under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5–6 cm. The progress of the reaction was monitored via TLC. After completion of the reaction, the solvent was removed by rotary evaporation. The reaction mixture was then mixed with water (25 mL) and extracted with ethyl acetate (2 × 30 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then purified over column chromatography by eluting with hexane: ethyl acetate mixture to afford the desired products **3a** (68%, 0.19 g).

2.2 General photocatalytic procedure for the 2.0 mmol scale reaction of 1a with 2b for the synthesis of 3u

An oven-dried 15.0 mL sample vial was charged with phenacyl bromide (**1a**) (2.0 mmol, 1.0 equiv.; 0.4 g), tripropyl amine (**2b**) (8.0 mmol, 4.0 equiv., 1.14 g), TBAI (1.0 mmol, 0.5 equiv., 0.369 g) and PC-1 (2 mol%, 0.044 g) a magnetic stir bar in 1,4-dioxane (6 mL) and was stirred at room temperature in an open-air for 8 h under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5–6 cm. The progress of the reaction was monitored via TLC. After completion of the reaction, the solvent was removed by rotary evaporation. The reaction mixture was then mixed with water (25 mL) and extracted with ethyl acetate (2 × 30 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then purified over column chromatography by eluting with hexane: ethyl acetate mixture to afford the desired products **3u** (65%, 0.23 g).

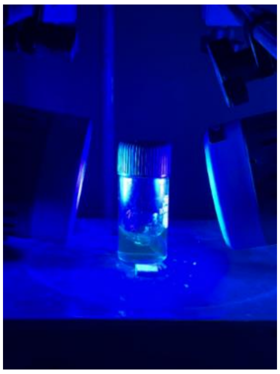
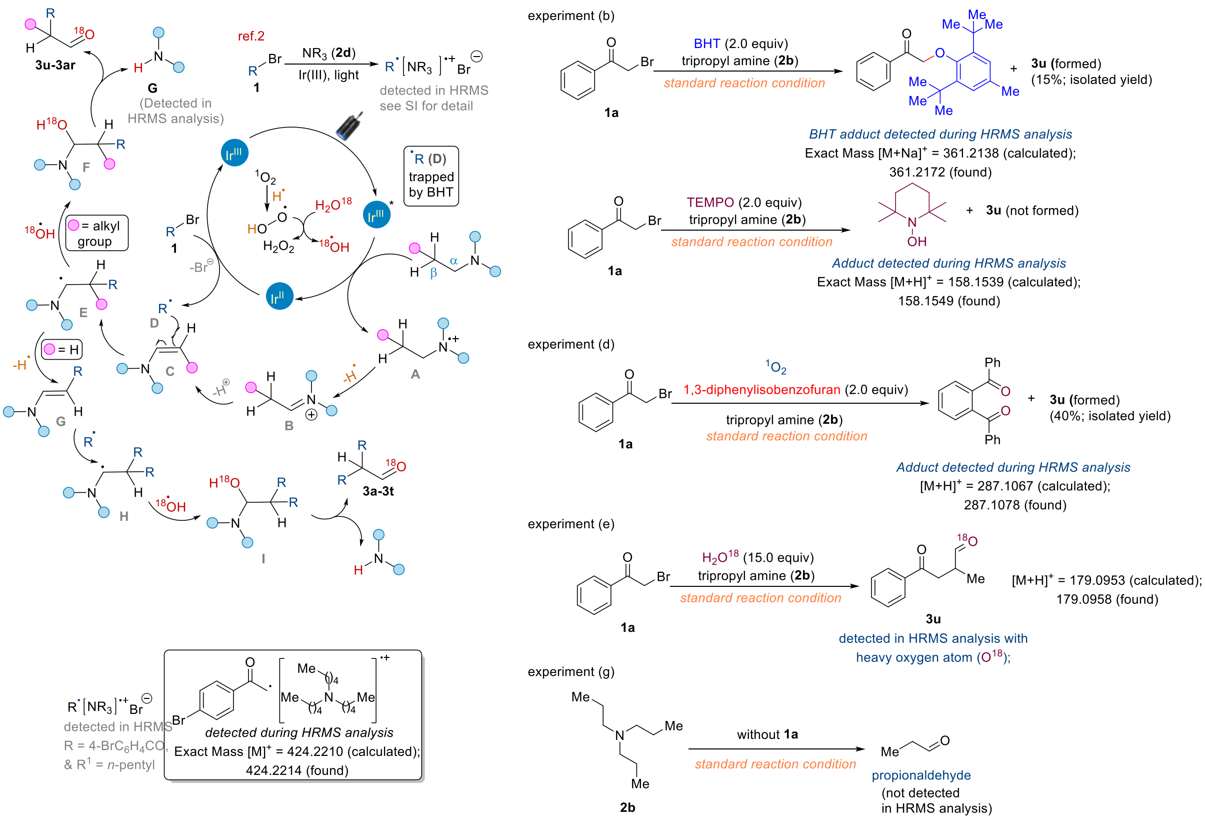


Figure S2. Scale-up photoreaction set-up.

3. Mechanistic Studies (control experiments)



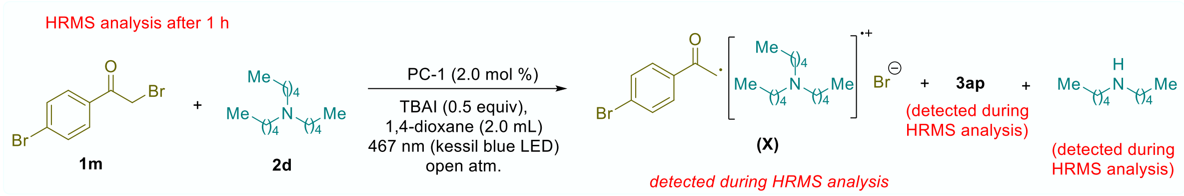
Scheme S3. Mechanistic studies

2. J. M. R. Narayanam, J. W. Tucker and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2009, **131**, 8756.

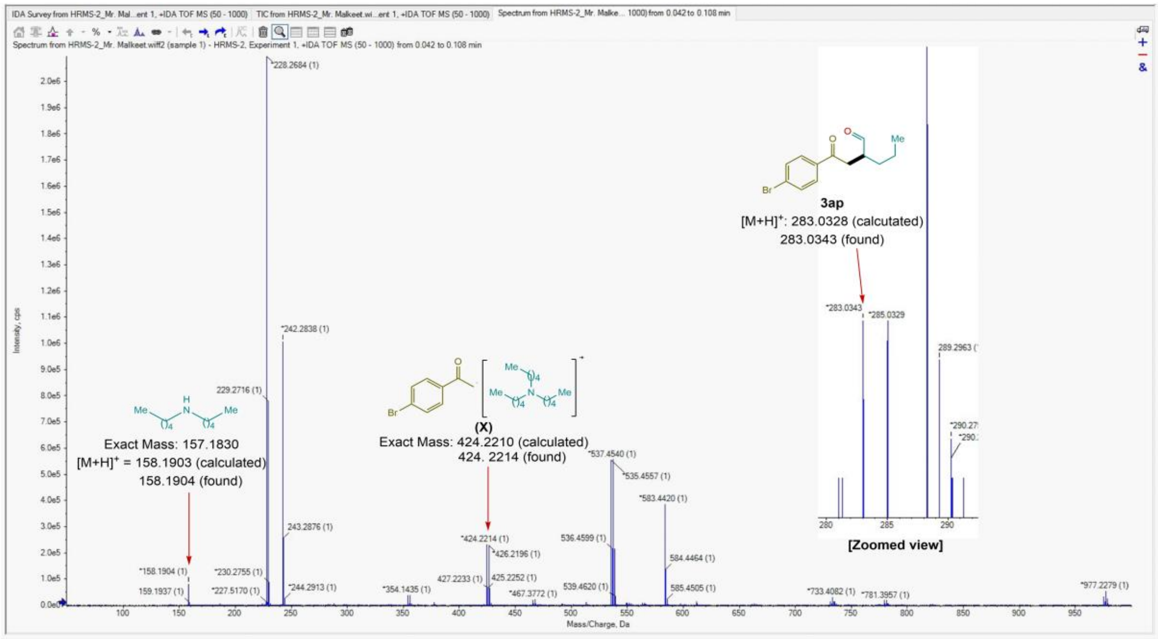
To prove the radical nature of the reaction, we carried out radical trapping experiments with BHT and TEMPO radical scavengers, separately. In **experiment (b)**, the photocatalytic cross-coupling of **1a** with **2b** in the presence of BHT under optimized conditions suppressed the yield of desired product **3u** (only 15% isolated yield) and the BHT adduct of **1a** was detected in HRMS analysis of the reaction mixture indicating the radical nature of the reaction. The model reaction in the presence of

TEMPO completely suppressed the formation of product **3u**. Although, we could not find TEMPO adduct of **1a** in HRMS analysis, but TEMPO trapped the hydrogen radical which formed during the course of the reaction, hence inhibiting the formation of hydroxy radical, responsible for the product formation. Moreover, the TEMPOH adduct was detected in HRMS analysis. Next to check the presence of singlet oxygen and superoxide, the model reaction was carried out in presence of DABCO and *p*-benzoquinone (see **experiment (c)**). The experiment supported the formation of singlet oxygen eliminated the formation of superoxide. In **experiment (d)**, to prove the role of singlet oxygen during the transformation, the model reaction was performed with singlet oxygen trapper (1,3-diphenylisobenzofuran) under standard reaction condition. After 5 h, only 40% **3u** was isolated by column chromatography and 1,2-phenylenebis(phenylmethanone) (**A**) was detected during the HRMS analysis of the crude reaction mixture. In **experiment (e)**, to prove the source of aldehyde's oxygen, we carried out a model reaction in presence of H_2O^{18}. After 5 h, the HRMS analysis of reaction mixture provided the peak of aldehyde product **3u** contain heavy oxygen atom, hence the above observation indicates that oxygen in aldehydes derived from moisture not from atmospheric oxygen. Next, we moved to check for the production of H_2O_2 in the reaction (see **experiment (f)**). In **experiment (g)**, to discard the formation of aldehyde by the oxidation of trialkyl amine under optimized photocatalytic condition, we carried out the reaction of tripropylamine **2b** without alkyl bromide **1** and subjected to the HRMS analysis after 1 h. The HRMS analysis of reaction mixture did not provide any peak close to propionaldehyde.

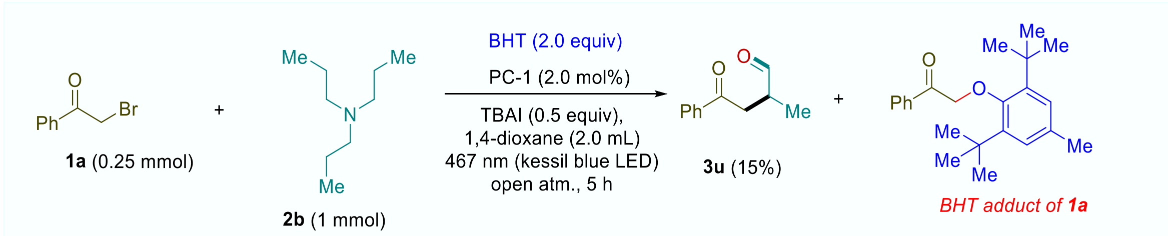
(a) HRMS analysis of reaction mixture



HRMS spectra

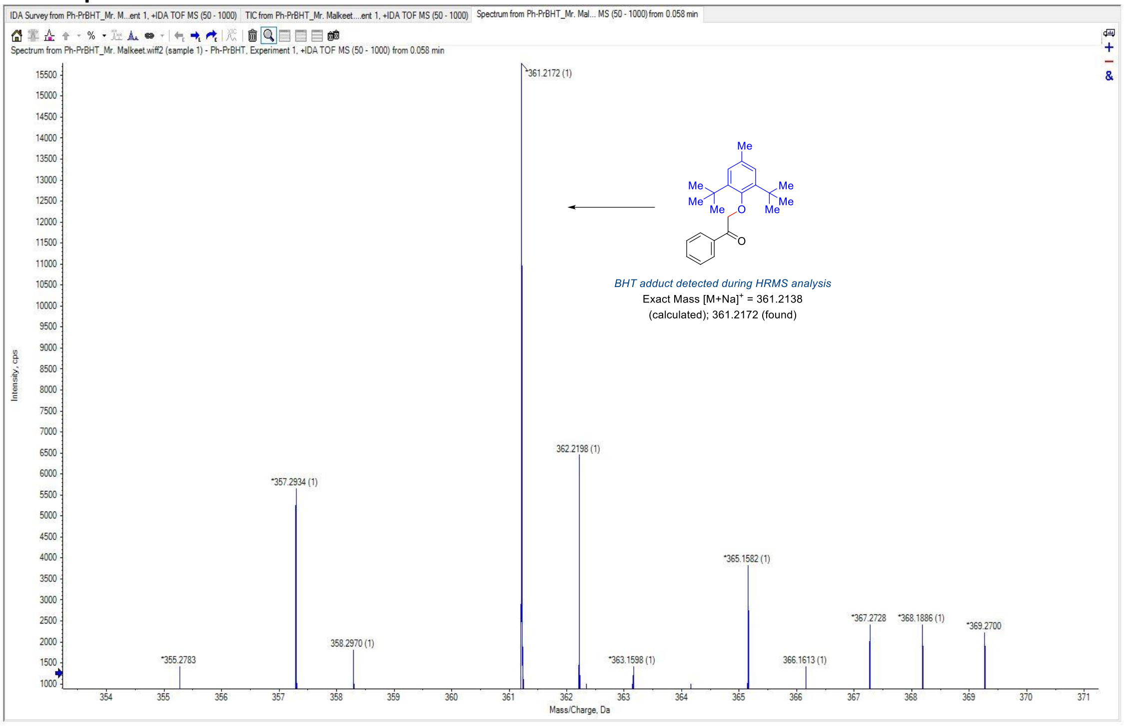


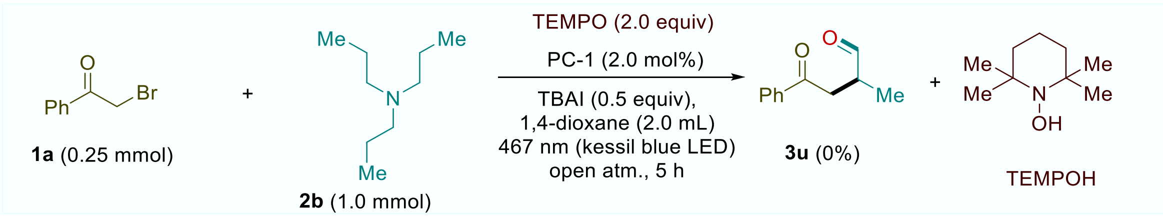
(b) Procedure for Trapping of Radicals with BHT and TEMPO



An oven-dried 5.0 mL sample vial was charged with phenacyl bromide (**1a**) (0.25 mmol, 1.0 equiv.; 0.050 g), tripropyl amine (**2b**) (1.0 mmol, 4.0 equiv., 0.143 g), TBAI (0.5 equiv., 0.046 g), BHT (0.5 mmol, 2.0 equiv., 0.110 g) and PC-1 (2 mol %, 0.006 g) a magnetic stir bar in 1,4-dioxane (2.0 mL) and was stirred at room temperature in an open-air for 5 h under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5−6 cm. After 5 h, 50 µL of the reaction mixture was taken by Hamilton microliter syringe and subjected to HRMS analysis. The HRMS analysis of reaction mixture provided the peak of BHT adduct of **1a**. This result support the radical nature of the reaction. Next, the reaction mixture was then mixed with water (10 mL) and extracted with ethyl acetate (2 × 10 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then purified over column chromatography by eluting with hexane: ethyl acetate mixture to afford the desired products **3u** in 15% yield.

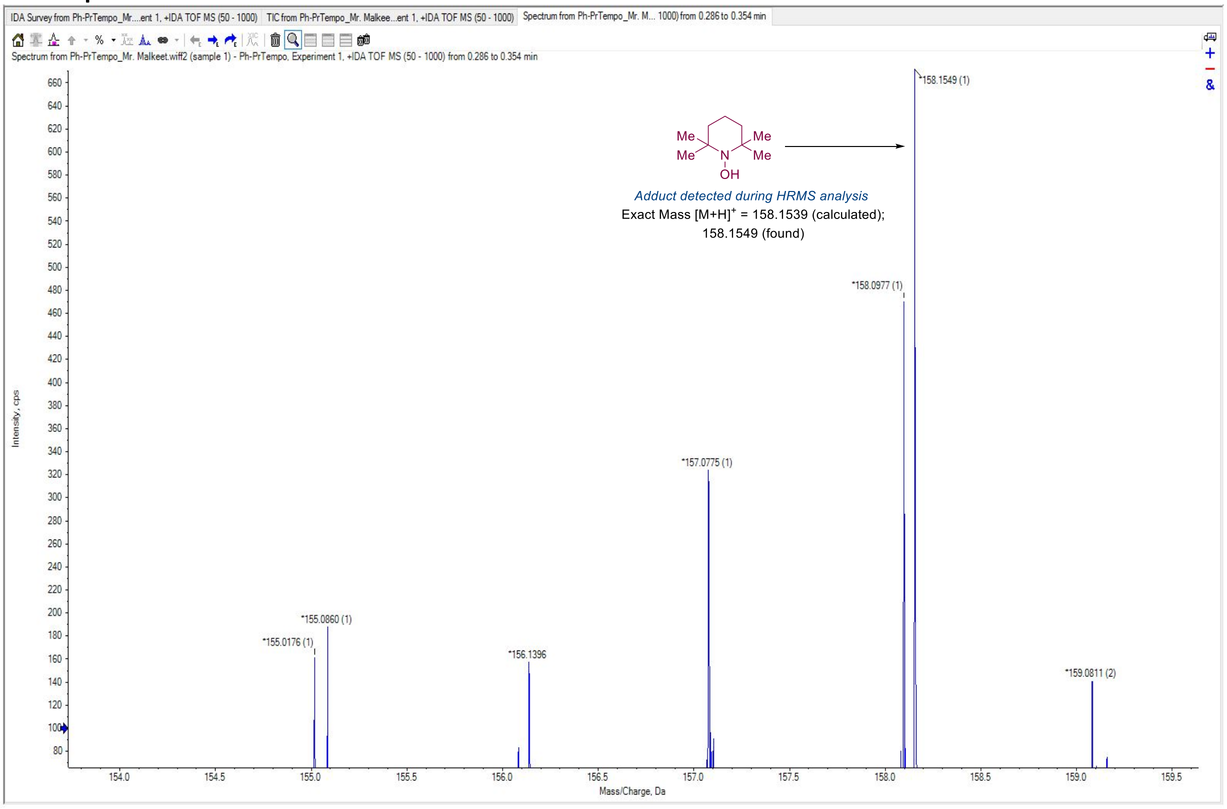
HRMS spectra



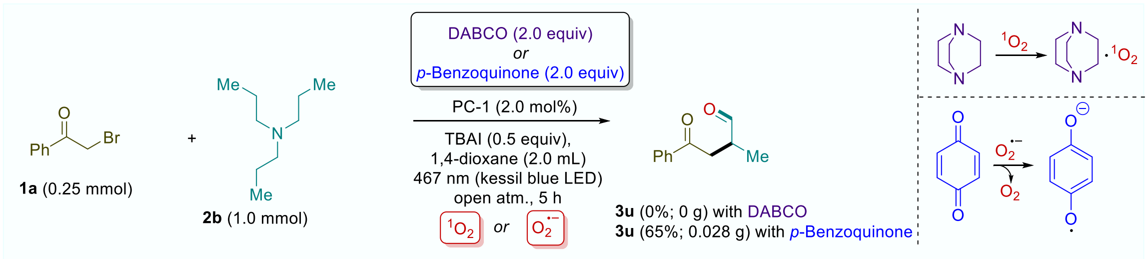


An oven-dried 5.0 mL sample vial was charged with phenacyl bromide (**1a**) (0.25 mmol, 1.0 equiv.; 0.050 g), tripropyl amine (**2b**) (1.0 mmol, 4.0 equiv., 0.143 g), TBAI (0.5 equiv., 0.046 g), TEMPO (0.5 mmol, 2.0 equiv., 0.078 g) and PC-1 (2 mol %, 0.006 g) a magnetic stir bar in 1,4-dioxane (2.0 mL) and was stirred at room temperature in an open-air for 5 h under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5−6 cm. After 5 h, 50 µL of the reaction mixture was taken by Hamilton microliter syringe and subjected to HRMS analysis. The HRMS analysis of reaction mixture provided the peak of TEMPOH. TEMPO trapped the hydrogen radical formed during the course of the reaction, hence inhibiting the formation of hydroxy radical which is responsible for the product formation (see mechanism for detail). This result further supports the radical nature of the reaction. Next, the reaction mixture was then mixed with water (10 mL) and extracted with ethyl acetate (2 × 10 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then checked by TLC under UV light, the thin layer chromatography did not show spot of desired product **3u** (not formed).

HRMS spectra



(c) Procedure for the Detection of Singlet Oxygen and Superoxide



An oven-dried 5.0 mL sample vial was charged with phenacyl bromide (**1a**) (0.25 mmol, 1.0 equiv.; 0.050 g), tripropyl amine (**2b**) (1.0 mmol, 4.0 equiv., 0.143 g), TBAI (0.5 equiv., 0.046 g), DABCO (0.5 mmol, 2 equiv.; 0.056 mg) ***or*** *p*-Benzoquinone (0.5 mmol, 2 equiv.; 0.054 mg), and PC-1 (2 mol%, 0.006 g) a magnetic stir bar in 1,4-dioxane (2.0 mL) and was stirred at room temperature in an open-air for 5 h under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5−6 cm. The reaction mixture was then mixed with water (10 mL) and extracted with ethyl acetate (2 × 15 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then purified over column chromatography by eluting with hexane: ethyl acetate mixture to afford the product **3u** as brown solid in 0 g (0% yield) for DABCO and 0.028 g (65% yield) for *p*-benzoquinone. The failure to obtain the desired product **3u** in the presence of DABCO confirms the involvement of the singlet oxygen in the reaction and for *p*-benzoquinone, the 65% yield of **3u** suggests non-involvement of superoxide in the reaction.

(d) Procedure for the Detection of Singlet Oxygen using a Fluorescence probe

For the detection of Singlet Oxygen, 9,10-Diphenylanthracene (DPA) was chosen as the fluorescence probe. DPA reacts with $^1O_2$ to form non-fluorescent DPA-endoperoxide. Two oven-dried 5.0 mL sample vials were charged with phenacyl bromide (**1a**) (0.25 mmol, 1.0 equiv.; 0.050 g), TBAI (0.5 equiv., 0.046 g), DPA (0.1 mmol, 0.033 g), and PC-1 (2 mol%, 0.006 g) a magnetic stir bar in 1,4-dioxane (2.0 mL). Tripropyl amine (**2b**) (1.0 mmol, 4.0 equiv., 0.143 g) was added in one of the vials. Both were then stirred at room temperature in an open-air atmosphere under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5−6 cm. The emission spectra of DPA were measured by exciting the reaction mixture at 375 nm. The DPA fluorescence emission exhibits a maximum around 430 nm. For the emission studies, 200 µL of the reaction mixture was taken and was made up to 3 mL (using 1,4-dioxane). Three readings from each of the vial were taken; a) Before irradiation, (b) after 1 hr of irradiation, and (c) after 2 hr of irradiation for both the vials.

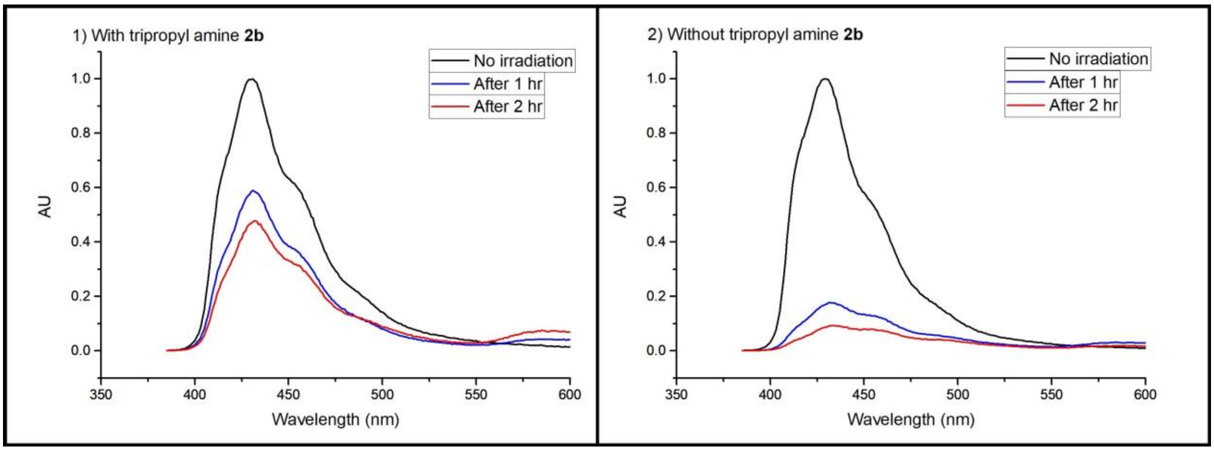
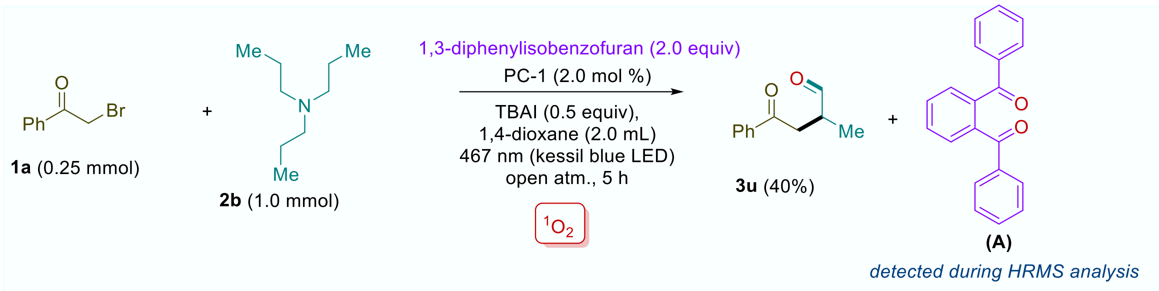


Figure S4. Fluorescence emission spectra of DPA in reaction mixtures

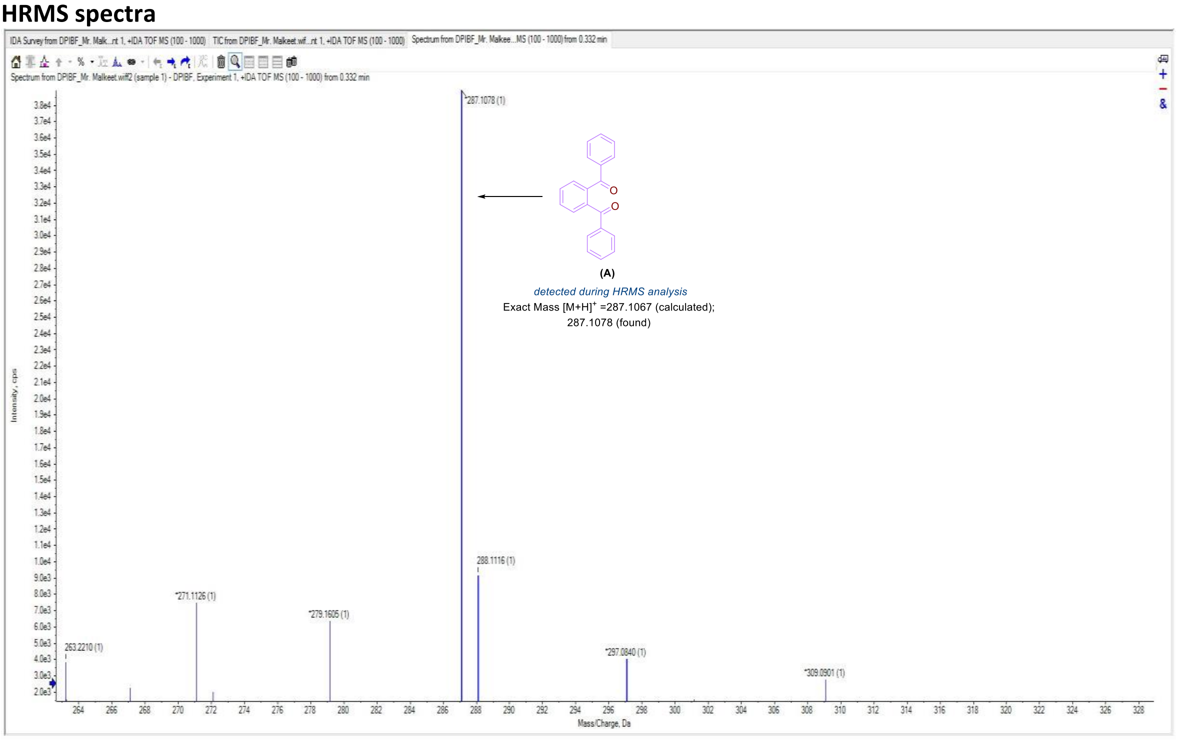
Even though the DPA fluorescence decay is observed in both the cases (confirming the presence of singlet oxygen), it can be noted that the fluorescence decay in the case of reaction mixture containing tripropyl amine was significantly less than the decay in the case of reaction mixture without tripropyl amine. This could be accounted by the quenching of singlet oxygen by the amine present in the mixture.

(e) Procedure for trapping of Singlet Oxygen ($^1O_2$)

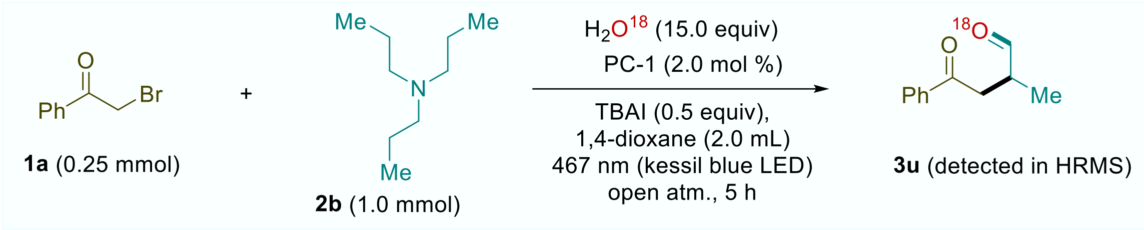


An oven-dried 5.0 mL sample vial was charged with phenacyl bromide (**1a**) (0.25 mmol, 1.0 equiv.; 0.050 g), tripropyl amine (**2b**) (1.0 mmol, 4.0 equiv., 0.143 g), TBAI (0.5 equiv., 0.046 g), 1,3-diphenylisobenzofuran (0.5 mmol, 2 equiv.; 0.135 g), and PC-1 (2 mol%, 0.006 g) a magnetic stir bar in 1,4-dioxane (2.0 mL) and was stirred at room temperature in an open-air for 5 h under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5–6 cm. After 5 h, TLC show the formation of product **3u**, but the starting material **1a** was not fully consumed even after 5 h of photochemical reaction. This observation indicated that the oxygen is required for the complete conversion of **1a** to **3a** under given optimized condition. After that, reaction mixture was mixed with water (10 mL) and extracted with ethyl acetate (2 × 15 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then purified over column chromatography by eluting with hexane: ethyl acetate mixture to afford the product **3u** as brown solid in 40% (0.017 g) yield and 1,2-phenylenebis(phenylmethanone) (**A**) was detected in HRMS analysis of the crude reaction mixture. The formation of **A** diminished the yield of desired product **3u** in given reaction time (5 h) by making unavailability of the singlet oxygen.

HRMS spectra

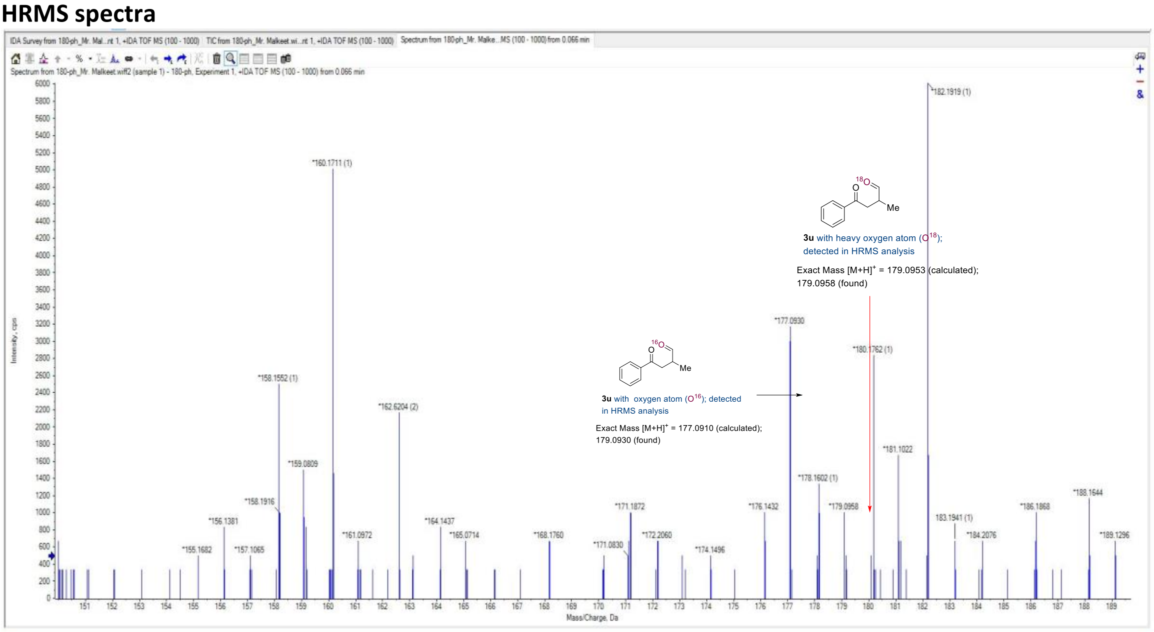


(f) H_2O^{18} labelling experiment.



An oven-dried 5.0 mL sample vial was charged with phenacyl bromide (**1a**) (0.25 mmol, 1.0 equiv.; 0.050 g), tripropyl amine (**2b**) (1.0 mmol, 4.0 equiv., 0.143 g), TBAI (0.5 equiv., 0.046 g), H_2O^{18} (15 equiv.; containing 10% O^{18} atom;) and PC-1 (2 mol%, 0.006 g) a magnetic stir bar in 1,4-dioxane (2.0 mL) and was stirred at room temperature in an open-air for 5 h under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5−6 cm. After 5 h, 0.02 mL of reaction mixture was taken from vial and subject to HRMS analysis. The HRMS analysis of reaction mixture provided the peak of aldehyde product **3u** contain heavy oxygen atom (O^{18}), hence this observation indicated that the oxygen in aldehydes derived from moisture not from atmospheric oxygen.

HRMS spectra



(g) Detection of H_2O_2

An oven-dried 5.0 mL sample vial was charged with phenacyl bromide (**1a**) (0.25 mmol, 1.0 equiv.; 0.050 g), tripropyl amine (**2b**) (1.0 mmol, 4.0 equiv., 0.143 g), TBAI (0.5 equiv., 0.046 g), and PC-1 (2 mol%, 0.006 g) a magnetic stir bar in 1,4-dioxane (2.0 mL) and was stirred at room temperature in an open-air for 5 h under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5−6 cm. In a separate test tube (5 mL), $KMnO_4$ solution was prepared by adding $KMnO_4$ (400 µM) in H_2O. A portion of the reaction mixture was added to the $KMnO_4$ solution. Instantly, the aqueous solution turned to pale yellow colour indicating the presence of H_2O_2.

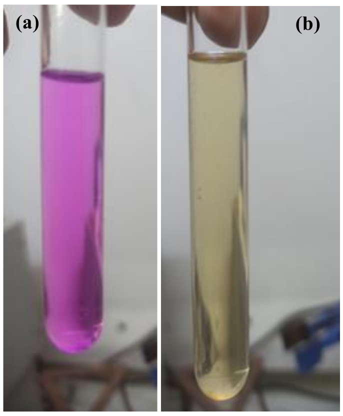
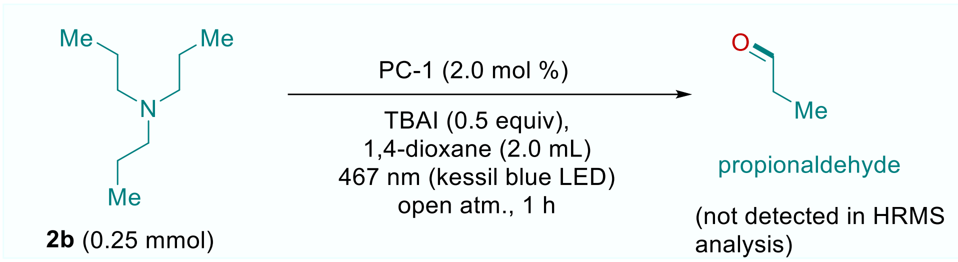


Figure S5. (a) $KMnO_4$ solution (b) KMn04 solution after addition of reaction mixture.

(h) Procedure for the detection of propionaldehyde



An oven-dried 5.0 mL sample vial was charged with tripropyl amine (**2b**; 0.25 mmol), TBAI (0.5 equiv.), and PC-1 (2 mol%) a magnetic stir bar in 1,4-dioxane (2.0 mL) and was stirred at room temperature in an open-air for 1 h under the irradiation of 2 x 40 W Kessil blue LED lights (λ_{max} = 467 nm) approximately at a distance of ~5−6 cm. After 1 h, 0.02 mL of reaction mixture was taken from vial and subject to HRMS analysis. The HRMS analysis of reaction mixture did not provide any peak close to propionaldehyde product.

(i) Cyclic voltammetry of 1a and 2a, 2d, 2e in acetonitrile.

Cyclic voltammetry (CV) was performed in an open electrochemical cell with Metrohm AutoLab PGSTAT302N potentiostat using Nova 2 software. CV analysis conditions: Working electrode: Pt Plate; counter electrode: Pt wire; reference electrode: Ag/AgCl in saturated LiCl/EtOH; scan rate, ν = 100 mV/s; T = 25 °C. A 0.10 M solution of *n*-tetra butyl ammonium tetrafluoroborate (TBATFB) in ACN was used electrolytic media. The concentration of phenacyl bromide **1a** and trialkyl amines (**2a**, **2d** and **2e**) were taken as 10 mM. Moreover, for excited Ir (III)* photocatalyst (PC-1; $E^{1/2\ *III/II}$ = + 1.21 V vs SCE) and reductant Ir (II) ($E^{1/2\ III/II}$ = - 1.37 V vs SCE).[3]

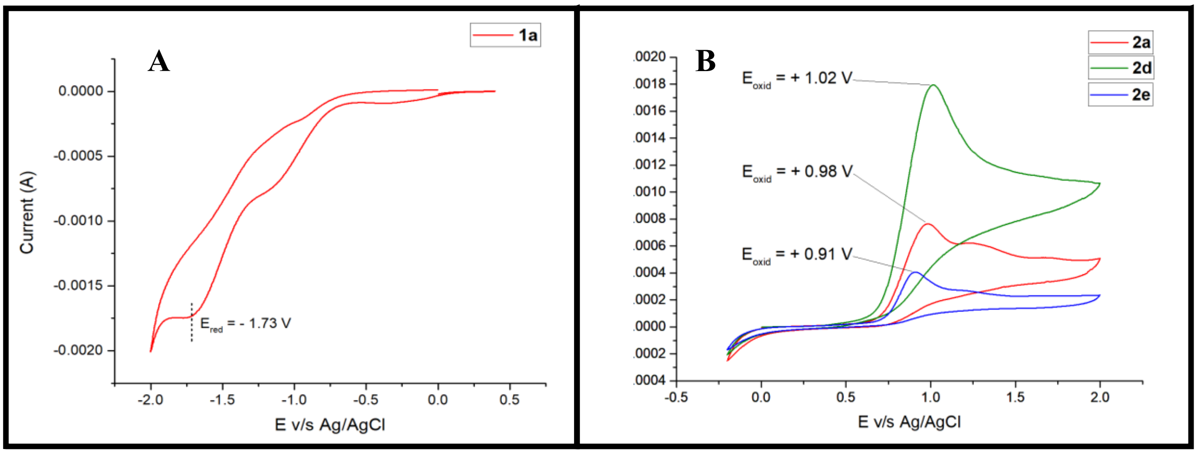
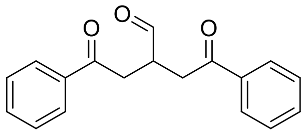


Figure S6. CV graphs: **A**. **1a** in ACN; **B**. **2a**, **2d** and **2e** in ACN.

3. C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322–5363.

4. NMR data of 3a-3ar

4-Oxo-2-(2-oxo-2-phenylethyl)-4-phenylbutanal (3a):



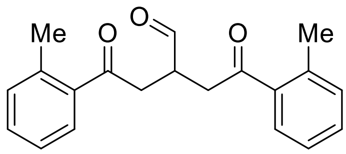
Isolated yield (54 mg, 76%); Sticky brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 4H), 7.58 (t, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 4H), 3.68 (d, *J* = 5.3 Hz, 1H), 3.64 (d, *J* = 5.6 Hz, 1H), 3.56 – 3.53 (m, 1H), 3.38 (d, *J* = 5.7 Hz, 1H), 3.35 (d, *J* = 6.4 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 202.5, 197.8, 136.4, 133.7, 128.9, 128.3, 42.2, 38.1.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{18}H_{16}O_3$ 281.1172, found 281.1179.

4-Oxo-2-(2-oxo-2-(o-tolyl)ethyl)-4-(o-tolyl)butanal (3b):



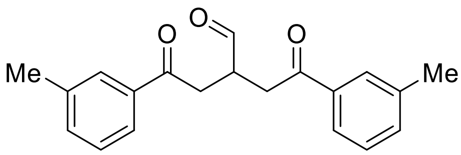
Isolated yield (56 mg, 72%); Sticky orange liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.27 (s, 1H), 7.24 (d, *J* = 7.5 Hz, 3H), 3.55 – 3.50 (m, 3H), 3.26 – 3.21 (m, 2H), 2.49 (s, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 202.6, 201.4, 138.7, 136.9, 132.3, 132.0, 128.9, 126.0, 42.9, 40.8, 21.6.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{20}H_{20}O_3$ 309.1485, found 309.1490.

4-Oxo-2-(2-oxo-2-(m-tolyl)ethyl)-4-(m-tolyl)butanal (3c):



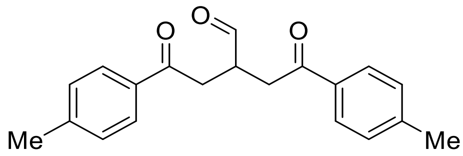
Isolated yield (54 mg, 70%); Sticky brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.76 (d, J = 9.3 Hz, 4H), 7.39 – 7.32 (m, 4H), 3.62 (dd, J = 18.4, 5.8 Hz, 2H), 3.54 – 3.50 (m, 1H), 3.33 (dd, J = 18.2, 5.8 Hz, 2H), 2.39 (s, 6H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 202.6, 198.0, 138.6, 136.4, 134.4, 128.8, 128.7, 125.5, 42.2, 38.1, 21.4.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{20}H_{20}O_3$ 309.1485, found 309.1496.

4-Oxo-2-(2-oxo-2-(p-tolyl)ethyl)-4-(p-tolyl)butanal (3d):



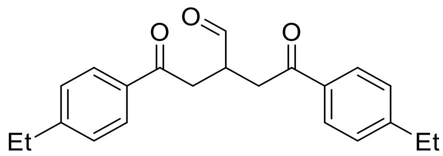
Isolated yield (62 mg, 80%); Light brown solid; mp: 96-98 °C; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.93 (s, 1H), 7.87 (d, J = 7.9 Hz, 4H), 7.26 (d, J = 7.9 Hz, 4H), 3.62 (dd, J = 18.0, 6.0 Hz, 2H), 3.53 – 3.48 (m, 1H), 3.32 (dd, J = 18.1, 5.9 Hz, 2H), 2.41 (s, 6H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 202.8, 197.5, 144.6, 134.0, 129.5, 128.4, 42.2, 38.1, 21.8.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{20}H_{20}O_3$ 309.1485, found 309.1495.

4-(4-Ethylphenyl)-2-(2-(4-ethylphenyl)-2-oxoethyl)-4-oxobutanal (3e):



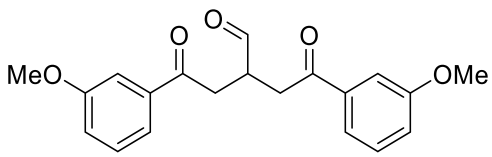
Isolated yield (67 mg, 79%); Sticky brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.93 (s, 1H), 7.89 (d, J = 8.1 Hz, 4H), 7.28 (d, J = 8.0 Hz, 4H), 3.64 – 3.60 (m, 2H), 3.53 – 3.49 (m, 1H), 3.33 (dd, J = 18.0, 6.0 Hz, 2H), 2.70 (q, J = 7.6 Hz, 4H), 1.26 – 1.23 (m, 6H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 202.8, 197.5, 150.7, 134.1, 128.5, 128.3, 42.2, 38.1, 29.1, 15.3.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{22}H_{24}O_3$ 337.1798, found 337.1808.

4-(3-Methoxyphenyl)-2-(2-(3-methoxyphenyl)-2-oxoethyl)-4-oxobutanal (3f):



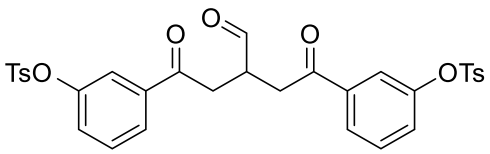
Isolated yield (66 mg, 77%); Sticky red liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.48 (s, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 6H), 3.61 (dd, *J* = 18.1, 6.0 Hz, 2H), 3.55 – 3.50 (m, 1H), 3.33 (dd, *J* = 17.8, 5.8 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 202.5, 197.7, 160.0, 137.7, 129.8, 120.9, 120.2, 112.4, 55.6, 42.3, 38.2.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{20}H_{20}O_5$ 341.1384, found 341.1391.

(3-Formylpentanedioyl)bis(3,1-phenylene) bis(4-methylbenzenesulfonate) (3g):



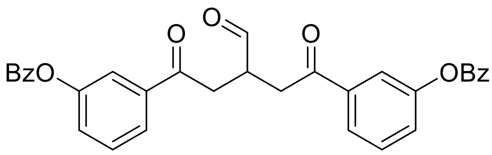
Isolated yield (126 mg, 81%); Sticky red liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 4H), 7.55 (s, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 8.4 Hz, 2H), 3.51 – 3.46 (m, 3H), 3.23 – 3.17 (m, 2H), 2.44 (s, 6H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 201.9, 196.1, 150.0, 146.0, 137.8, 132.2, 130.2, 130.1, 128.6, 127.6, 126.8, 122.2, 41.9, 38.1, 21.8.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{32}H_{28}O_9S_2$ 621.1248, found 621.1303.

4-(3-(Benzyloxy)phenyl)-2-(2-(3-(benzyloxy)phenyl)-2-oxoethyl)-4-oxobutanal (3h):



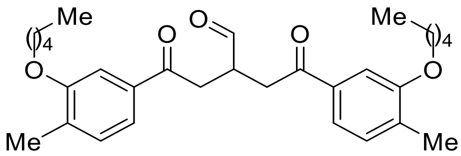
Isolated yield (85 mg, 65%); Sticky dark red liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.21 (d, *J* = 7.2 Hz, 4H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.82 (s, 2H), 7.66 (t, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 3H), 7.52 (d, *J* = 8.1 Hz, 3H), 7.46 (d, *J* = 8.0 Hz, 2H), 3.64 (dd, *J* = 18.1, 6.0 Hz, 2H), 3.58 – 3.54 (m, 1H), 3.36 (dd, *J* = 17.6, 5.6 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 202.2, 196.7, 165.1, 151.4, 137.8, 134.0, 130.4, 130.0, 129.2, 128.8, 128.8, 127.2, 125.8, 121.7, 42.1, 38.2.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{32}H_{24}O_7$ 521.1595, found 521.1616.

4-(4-Methyl-3-(pentyloxy)phenyl)-2-(2-(4-methyl-3-(pentyloxy)phenyl)-2-oxoethyl)-4-oxobutanal (3i):



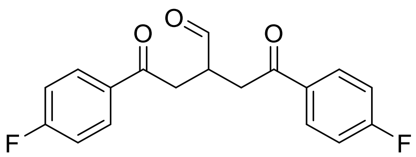
Isolated yield (84 mg, 70%); Sticky brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.53 – 7.48 (m, 2H), 7.25 – 7.21 (m, 2H), 6.82 (t, J = 7.3 Hz, 2H), 3.99 (t, J = 6.7 Hz, 4H), 3.61 – 3.54 (m, 2H), 3.51 – 3.45 (m, 1H), 3.28 (dd, J = 18.7, 5.4 Hz, 2H), 2.26 (s, 6H), 1.82 – 1.76 (m, 4H), 1.44 – 1.38 (m, 4H), 1.37 – 1.30 (m, 4H), 0.88 (t, J = 7.3 Hz, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 203.4, 199.9, 156.7, 134.6, 130.9, 130.9, 129.9, 127.1, 112.5, 68.8, 44.1, 29.0, 28.5, 22.5, 20.3, 14.1.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{30}H_{40}O_5$ 481.2949, found 481.2949.

4-(4-Fluorophenyl)-2-(2-(4-fluorophenyl)-2-oxoethyl)-4-oxobutanal (3j):



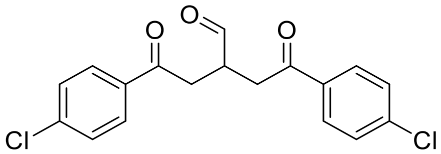
Isolated yield (65 mg, 82%); Light brown solid; mp: 89-91 ^{o}C; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.00 (dd, J = 8.7, 5.5 Hz, 4H), 7.13 (t, J = 8.6 Hz, 4H), 3.61 (dd, J = 18.1, 5.9 Hz, 2H), 3.54 – 3.50 (m, 1H), 3.32 (dd, J = 18.1, 5.9 Hz, 2H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 202.3, 196.2, 167.0, 165.3, 132.8, 132.8, 131.0, 130.9, 116.1, 115.9, 42.2, 37.9.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{18}H_{14}F_2O_3$ 317.0984, found 317.0986.

4-(4-Chlorophenyl)-2-(2-(4-chlorophenyl)-2-oxoethyl)-4-oxobutanal (3k):



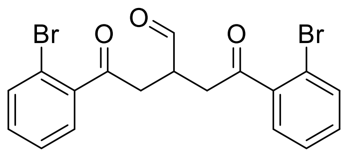
Isolated yield (66 mg, 75%); Light brown solid; mp: 89-91 ^{o}C; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.91 (d, J = 9.0 Hz, 4H), 7.45 (d, J = 9.2 Hz, 4H), 3.60 (dd, J = 18.1, 5.9 Hz, 2H), 3.55 – 3.50 (m, 1H), 3.31 (dd, J = 18.5, 5.5 Hz, 2H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 202.1, 196.6, 140.3, 134.6, 129.7, 129.2, 42.1, 38.0.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{18}H_{14}Cl_2O_3$ 349.0393, found 349.0397.

4-(2-Bromophenyl)-2-(2-(2-bromophenyl)-2-oxoethyl)-4-oxobutanal (3l):



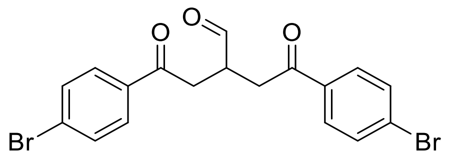
Isolated yield (83 mg, 76%); Sticky dark brown liquid; Isolation: 5% EtOAc in Hexane;

^1H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 4H), 7.59 (d, *J* = 8.6 Hz, 4H), 3.57 (dd, *J* = 18.1, 5.8 Hz, 2H), 3.53 – 3.48 (m, 1H), 3.28 (dd, *J* = 18.5, 5.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.5, 201.4, 140.8, 134.0, 132.1, 128.9, 127.7, 118.9, 43.0, 41.6.

HRMS (ESI-TOF, $[M+2+H]^+$): Calcd for $C_{18}H_{14}Br_2O_3$ 438.9362, found 438.9363.

4-(4-Bromophenyl)-2-(2-(4-bromophenyl)-2-oxoethyl)-4-oxobutanal (3m):



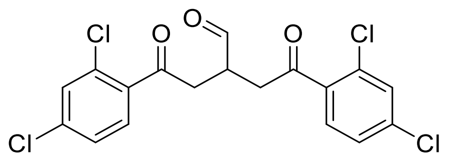
Isolated yield (81 mg, 74%); Dark brown solid; mp: 93-95 °C; Isolation: 5% EtOAc in Hexane;

^1H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 4H), 7.58 (d, *J* = 9.3 Hz, 4H), 3.57 (dd, *J* = 17.5, 5.5 Hz, 2H), 3.53 – 3.48 (m, 1H), 3.28 (dd, *J* = 17.3, 5.4 Hz, 2H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 202.0, 196.7, 135.0, 132.1, 129.7, 128.9, 42.1, 37.9.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{18}H_{14}Br_2O_3$ 436.9382, found 436.9407.

4-(2,4-Dichlorophenyl)-2-(2-(2,4-dichlorophenyl)-2-oxoethyl)-4-oxobutanal (3n):



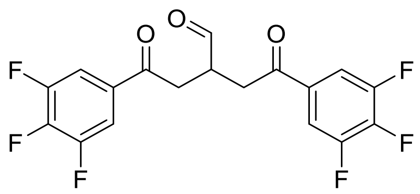
Isolated yield (84 mg, 80%); Brown solid; mp: 92-94 °C; Isolation: 5% EtOAc in Hexane;

^1H NMR (500 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.03 (s, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 3.59 – 3.51 (m, 3H), 3.29 (dd, *J* = 20.0, 5.0 Hz, 2H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 201.6, 195.5, 138.5, 135.8, 133.7, 131.0, 130.3, 127.3, 42.1, 37.8.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{18}H_{12}Cl_4O_3$ 416.9613, found 416.9637.

4-Oxo-2-(2-oxo-2-(3,4,5-trifluorophenyl)ethyl)-4-(3,4,5-trifluorophenyl)butanal (3o):



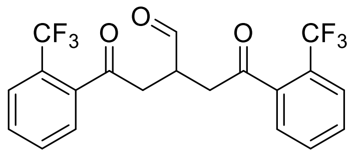
Isolated yield (63 mg, 65%); Sticky orange liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.84 (s, 1H), 7.62 (t, J = 7.3 Hz, 4H), 3.65 – 3.51 (m, 3H), 3.28 (d, J = 7.1 Hz, 1H), 3.24 (d, J = 7.3 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 201.2, 194.2, 152.6, 152.5, 150.5, 144.7, 142.7, 131.8, 113.0, 113.0, 112.9, 112.8, 42.1, 37.6.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{18}H_{10}F_6O_3$ 389.0607, found 389.0629.

4-Oxo-2-(2-oxo-2-(2-(trifluoromethyl)phenyl)ethyl)-4-(2-(trifluoromethyl)phenyl)butanal (3p):



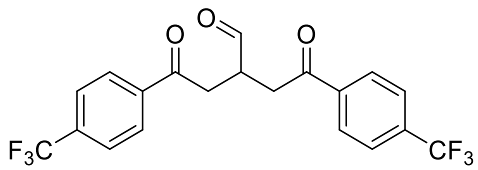
Isolated yield (77 mg, 74%); Sticky brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.86 (s, 1H), 7.73 (d, J = 7.9 Hz, 2H), 7.64 (t, J = 7.6 Hz, 2H), 7.59 (t, J = 7.9 Hz, 2H), 7.54 (d, J = 7.9 Hz, 2H), 3.53 – 3.45 (m, 3H), 3.25 (dd, J = 17.9, 4.1 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 201.9, 201.4, 139.5, 139.4, 132.2, 132.1, 130.7, 130.5, 127.6, 127.4, 127.0, 127.0, 126.9, 124.8, 122.6, 42.3, 41.7.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{20}H_{14}F_6O_3$ 417.0920, found 417.0921.

4-Oxo-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-4-(4-(trifluoromethyl)phenyl)butanal (3q):



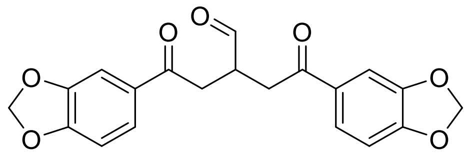
Isolated yield (74 mg, 71%); Off-white solid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.91 (s, 1H), 8.08 (d, J = 7.9 Hz, 4H), 7.74 (d, J = 8.0 Hz, 4H), 3.66 (dd, J = 18.3, 5.8 Hz, 2H), 3.62 – 3.57 (m, 1H), 3.38 (dd, J = 18.0, 5.7 Hz, 2H).

$^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$) δ 201.7, 196.8, 138.9, 135.5, 135.2, 135.0, 134.7, 128.7, 126.0, 124.7, 122.5, 42.2, 38.2.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{20}H_{14}F_6O_3$ 417.0920, found 417.0938.

4-(Benzo[d][1,3]dioxol-5-yl)-2-(2-(benzo[d][1,3]dioxol-5-yl)-2-oxoethyl)-4-oxobutanal (3r):



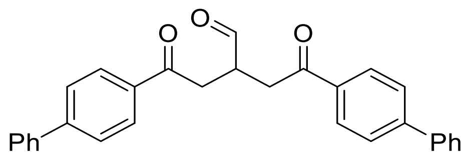
Isolated yield (74 mg, 80%); Sticky dark brown liquid; Isolation: 5% EtOAc in Hexane;

^1H NMR (500 MHz, CDCl$_3$) δ 9.90 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.04 (s, 4H), 3.54 (dd, *J* = 18.1, 5.9 Hz, 2H), 3.48 – 3.44 (m, 1H), 3.25 (dd, *J* = 18.1, 5.8 Hz, 2H).

$^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$) δ 202.6, 195.9, 152.3, 148.4, 131.3, 124.7, 108.1, 108.0, 102.1, 42.5, 37.9.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{20}H_{16}O_7$ 369.0969, found 369.0980.

4-([1,1'-Biphenyl]-4-yl)-2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-4-oxobutanal (3s):



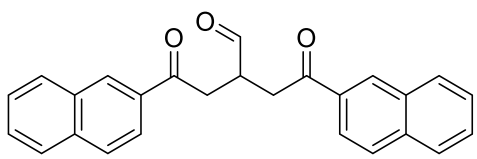
Isolated yield (74 mg, 68%); Dark brown solid; mp: 125-127 °C; Isolation: 5% EtOAc in Hexane;

^1H NMR (600 MHz, CDCl$_3$) δ 9.97 (s, 1H), 8.06 (d, *J* = 7.1 Hz, 4H), 7.70 (d, *J* = 8.0 Hz, 4H), 7.62 (d, *J* = 7.9 Hz, 4H), 7.47 (t, *J* = 7.6 Hz, 4H), 7.41 (t, *J* = 7.6 Hz, 2H), 3.70 (dd, *J* = 18.1, 5.9 Hz, 2H), 3.61 – 3.56 (m, 1H), 3.41 (dd, *J* = 18.1, 6.0 Hz, 2H).

$^{13}C\{^1H\}$ NMR (151 MHz, CDCl$_3$) δ 202.6, 197.5, 146.4, 139.9, 135.1, 129.1, 128.9, 128.5, 127.5, 127.4, 42.3, 38.1.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{30}H_{24}O_3$ 433.1798, found 433.1819.

4-(Naphthalen-2-yl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-oxobutanal (3t):



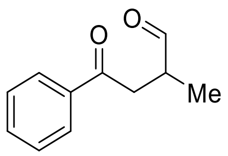
Isolated yield (67 mg, 70%); Brown solid; mp: 108-110 °C; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (600 MHz, CDCl$_3$) δ 10.02 (s, 1H), 8.51 (s, 2H), 8.04 (d, *J* = 8.6 Hz, 2H), 7.95 (d, *J* = 10.3 Hz, 2H), 7.90 – 7.86 (m, 4H), 7.60 (t, *J* = 6.4 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 3.84 (dd, *J* = 15.0, 6.2 Hz, 2H), 3.68 – 3.63 (m, 1H), 3.56 – 3.53 (m, 2H).

^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 202.7, 197.8, 135.9, 133.7, 132.6, 130.3, 129.8, 128.9, 128.8, 127.9, 127.1, 123.8, 42.4, 38.2.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{26}H_{20}O_3$ 381.1485, found 381.1483.

2-Methyl-4-oxo-4-phenylbutanal (3u):



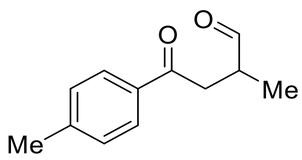
Isolated yield (68 mg, 77%); Sticky dark brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.78 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 2H), 3.47 (dd, *J* = 18.3, 6.4 Hz, 1H), 3.14 – 3.07 (m, 1H), 3.00 (dd, *J* = 17.8, 6.2 Hz, 1H), 1.23 (d, *J* = 8.0 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$) δ 203.5, 197.9, 136.6, 133.4, 128.7, 128.2, 41.7, 39.5, 13.8.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{11}H_{12}O_2$ 177.0910, found 177.0910.

2-Methyl-4-oxo-4-(p-tolyl)butanal (3v):



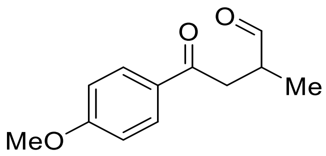
Isolated yield (74 mg, 78%); Colourless sticky liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.79 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 3.46 (dd, *J* = 17.4, 6.6 Hz, 1H), 3.14 – 3.06 (m, 1H), 2.99 (dd, *J* = 17.4, 6.6 Hz, 1H), 2.41 (s, 3H), 1.23 (d, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.7, 197.5, 144.3, 134.2, 129.5, 128.3, 41.8, 39.4, 21.8, 13.9.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{12}H_{14}O_2$ 191.1067, found 191.1067.

4-(4-Methoxyphenyl)-2-methyl-4-oxobutanal (3w):



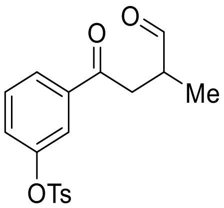
Isolated yield (83 mg, 81%); Sticky brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.77 (s, 1H), 7.94 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.1 Hz, 2H), 3.86 (s, 3H), 3.41 (dd, J = 18.4, 6.5 Hz, 1H), 3.11 – 3.04 (m, 1H), 2.96 (dd, J = 17.9, 6.0 Hz 1H), 1.21 (d, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.8, 196.4, 163.8, 130.5, 129.8, 113.9, 55.6, 41.8, 39.2, 13.8.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{12}H_{14}O_2$ 207.1016, found 207.1015.

3-(3-Methyl-4-oxobutanoyl)phenyl 4-methylbenzenesulfonate (3x):



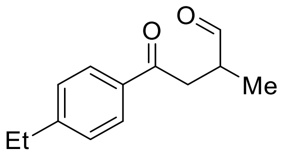
Isolated yield (133 mg, 77%); Sticky brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.72 (s, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.50 (s, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 7.9 Hz, 1H), 3.33 (dd, J = 18.6, 6.7 Hz, 1H), 3.08 – 3.01 (m, 1H), 2.85 (dd, J = 17.5, 5.4 Hz, 1H), 2.42 (s, 3H), 1.20 (d, J = 7.9 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.1, 196.3, 149.9, 145.9, 138.2, 132.1, 130.1, 130.0, 128.6, 127.2, 126.7, 122.1, 41.6, 39.4, 21.7, 13.7.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{18}H_{18}O_5S$ 347.0948, found 347.0947.

4-(4-Ethylphenyl)-2-methyl-4-oxobutanal (3y):



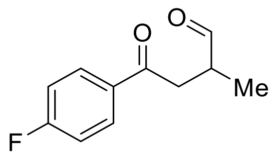
Isolated yield (70 mg, 69%); Sticky brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.79 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.46 (dd, J = 17.3, 6.7 Hz, 1H), 3.14 – 3.07 (m, 1H), 2.99 (dd, J = 17.9, 5.9 Hz, 1H), 2.71 (q, J = 7.9, 7.5 Hz, 2H), 1.26 (t, J = 7.5 Hz, 3H), 1.23 (d, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.7, 197.6, 150.5, 134.5, 128.5, 128.3, 41.8, 39.5, 29.1, 15.3, 13.9.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{13}H_{16}O_2$ 205.1223, found 205.1240.

4-(4-Fluorophenyl)-2-methyl-4-oxobutanal (3z):



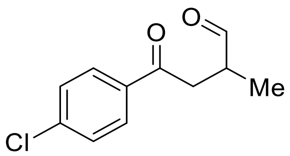
Isolated yield (69 mg, 71%); Sticky red liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.78 (s, 1H), 8.00 (dd, J = 9.1, 5.2 Hz, 2H), 7.14 (t, J = 8.7 Hz, 2H), 3.46 (dd, J = 18.6, 6.7 Hz, 1H), 3.15 – 3.08 (m, 1H), 2.96 (dd, J = 18.0, 5.9 Hz, 1H), 1.25 (d, J = 8.0 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.4, 196.3, 167.0, 165.0, 133.2, 130.9, 130.8, 116.0, 115.8, 41.8, 39.4, 13.9.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{11}H_{11}FO_2$ 195.0816, found 195.0820.

4-(4-Chlorophenyl)-2-methyl-4-oxobutanal (3aa):



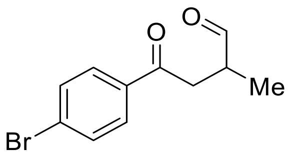
Isolated yield (79 mg, 75%); Dark green solid; mp: 94-96 °C; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.76 (s, 1H), 7.89 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 9.2 Hz, 2H), 3.44 (dd, J = 18.7, 6.7 Hz, 1H), 3.14 – 3.07 (m, 1H), 2.94 (dd, J = 17.4, 5.3 Hz, 1H), 1.23 (d, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.3, 196.7, 139.8, 135.0, 129.6, 129.0, 41.7, 39.4, 13.8.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{11}H_{11}ClO_2$ 211.0520, found 211.0518.

4-(4-Bromophenyl)-2-methyl-4-oxobutanal (3ab):



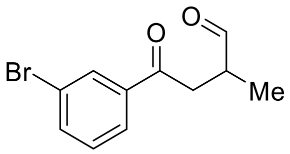
Isolated yield (94 mg, 74%); Sticky orange liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.76 (s, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 3.43 (dd, J = 18.5, 6.7 Hz, 1H), 3.13 – 3.06 (m, 1H), 2.93 (dd, J = 18.7, 5.3 Hz, 1H), 1.23 (d, J = 7.8 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.3, 196.9, 135.4, 132.0, 129.7, 128.6, 41.7, 39.3, 13.8.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{11}H_{11}BrO_2$ 255.0015, found 255.0015.

4-(3-Bromophenyl)-2-methyl-4-oxobutanal (3ac):



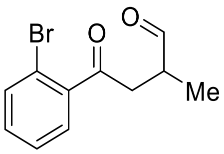
Isolated yield (103 mg, 81%); Sticky orange liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.77 (s, 1H), 8.09 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 3.45 (dd, J = 18.0, 7.3 Hz, 1H), 3.16 – 3.09 (m, 1H), 2.94 (dd, J = 17.5, 5.5 Hz, 1H), 1.25 (d, J = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 203.25, 196.60, 138.39, 136.27, 131.28, 130.38, 126.71, 123.13, 41.71, 39.46, 13.82.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{11}H_{11}BrO_2$ 255.0015, found 255.0012.

4-(2-Bromophenyl)-2-methyl-4-oxobutanal (3ad):



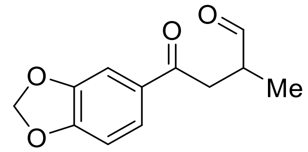
Isolated yield (97 mg, 76%); Sticky orange liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.74 (s, 1H), 7.60 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 7.0 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 8.5 Hz, 1H), 3.36 (dd, J = 17.4, 6.7 Hz, 1H), 3.14 – 3.07 (m, 1H), 2.96 (dd, J = 18.0, 6.0 Hz, 1H), 1.25 (d, J = 7.9 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.1, 141.3, 133.8, 131.9, 128.8, 127.6, 118.7, 43.4, 42.2, 13.6.

HRMS (ESI-TOF, [M+H]+): Calcd for $C_{11}H_{11}BrO_2$ 255.0015, found 255.0012.

4-(Benzo[d][1,3]dioxol-5-yl)-2-methyl-4-oxobutanal (3ae):



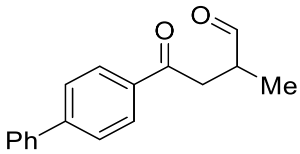
Isolated yield (94 mg, 85%); Sticky light brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.77 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.43 (s, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.04 (s, 2H), 3.40 (dd, *J* = 17.4, 6.7 Hz, 1H), 3.11 – 3.05 (m, 1H), 2.94 (dd, *J* = 17.4, 5.5 Hz, 1H), 1.22 (d, *J* = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.6, 195.9, 152.1, 148.3, 131.5, 124.5, 108.0, 107.9, 102.0, 41.8, 39.3, 13.8.

HRMS (ESI-TOF, [M+H]+): Calcd for $C_{12}H_{12}O_4$ 221.0808, found 221.0811.

4-([1,1'-Biphenyl]-4-yl)-2-methyl-4-oxobutanal (3af):



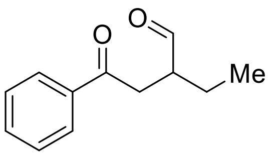
Isolated yield (101 mg, 80%); Light brown solid; mp: 89-91 °C, Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.81 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 6.9 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 3.52 (dd, *J* = 17.3, 6.7 Hz, 1H), 3.18 – 3.11 (m, 1H), 3.04 (dd, *J* = 17.3, 6.7 Hz, 1H), 1.27 (d, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.6, 197.5, 146.2, 139.9, 135.4, 129.1, 128.8, 128.4, 127.4, 127.4, 41.9, 39.6, 13.9.

HRMS (ESI-TOF, [M+H]+): Calcd for $C_{17}H_{16}O_2$ 253.1223, found 253.1224.

2-Ethyl-4-oxo-4-phenylbutanal (3ag):



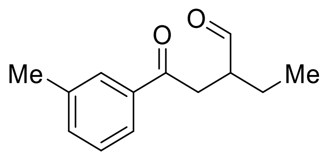
Isolated yield (69 mg, 73%); Sticky off-white liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.96 (d, J = 7.4 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 3.45 (dd, J = 18.6, 7.2 Hz, 1H), 3.01 (d, J = 17.1 Hz, 2H), 1.84 – 1.79 (m, 1H), 1.63 – 1.59 (m, 1H), 0.99 (t, J = 7.0 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 203.7, 198.1, 136.6, 133.4, 128.7, 128.1, 48.1, 37.2, 21.9, 11.5.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{12}H_{14}O_2$ 191.1067, found 191.1075.

2-ethyl-4-oxo-4-(m-tolyl)butanal (3ah):



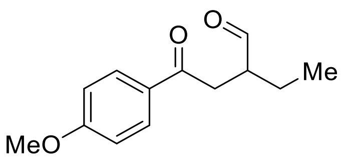
Isolated yield (81 mg, 79%); Sticky red liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.39 – 7.33 (m, 2H), 3.45 (dd, J = 17.3, 6.7 Hz, 1H), 3.08 – 2.99 (m, 2H), 2.41 (s, 3H), 1.88 – 1.80 (m, 1H), 1.67 – 1.59 (m, 1H), 1.01 (t, J = 7.4 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 203.8, 198.4, 138.6, 136.8, 134.2, 128.7, 128.7, 125.4, 48.2, 37.3, 22.0, 21.5, 11.6.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{13}H_{16}O_2$ 205.1223, found 205.1225.

2-Ethyl-4-(4-methoxyphenyl)-4-oxobutanal (3ai):



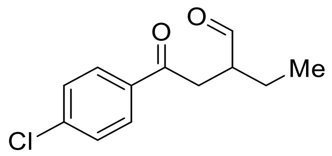
Isolated yield (79 mg, 72%); Sticky brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.95 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H), 3.43 – 3.38 (m, 1H), 3.06 – 2.96 (m, 2H), 1.87 – 1.78 (m, 1H), 1.64 – 1.57 (m, 1H), 1.00 (t, J = 7.5 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 204.0, 196.7, 163.8, 130.5, 129.8, 113.9, 55.6, 48.3, 37.0, 22.0, 11.6.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{13}H_{16}O_3$ 221.1172, found 221.1170.

4-(4-Chlorophenyl)-2-ethyl-4-oxobutanal (3aj):



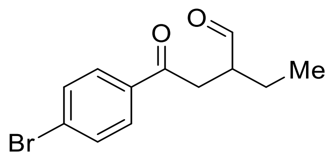
Isolated yield (91 mg, 81%); Sticky brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 3.43 (dd, *J* = 17.4, 8.0 Hz, 1H), 3.09 – 3.04 (m, 1H), 2.95 (dd, *J* = 17.9, 4.7 Hz, 1H), 1.89 – 1.80 (m, 1H), 1.68 – 1.59 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 203.5, 197.0, 139.9, 135.1, 129.6, 129.1, 48.2, 37.1, 22.0, 11.6.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{12}H_{13}ClO_2$ 225.0677, found 225.0671.

4-(4-Bromophenyl)-2-ethyl-4-oxobutanal (3ak):



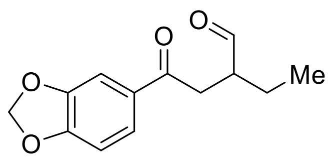
Isolated yield (110 mg, 82%); Sticky brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 3.43 (dd, *J* = 17.4, 7.9 Hz, 1H), 3.09 – 3.03 (m, 1H), 2.94 (dd, *J* = 17.9, 4.6 Hz, 1H), 1.88 – 1.80 (m, 1H), 1.67 – 1.61 (m, 1H), 1.00 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 203.5, 197.2, 135.5, 132.1, 129.7, 128.6, 48.2, 37.1, 22.0, 11.6.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{12}H_{13}BrO_2$ 269.0172, found 269.0175.

4-(Benzo[d][1,3]dioxol-5-yl)-2-ethyl-4-oxobutanal (3al):



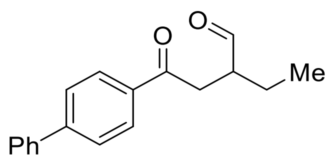
Isolated yield (87 mg, 74%); Sticky light brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.38 (s, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 2H), 3.34 (dd, *J* = 17.1, 7.7 Hz, 1H), 2.97 (q, *J* = 6.5 Hz, 1H), 2.92 (dd, *J* = 17.3, 5.3 Hz, 1H), 1.83 – 1.74 (m, 1H), 1.62 – 1.53 (m, 1H), 0.96 (t, *J* = 7.9 Hz, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 203.8, 196.1, 152.0, 148.2, 131.4, 124.4, 107.9, 107.8, 101.9, 48.2, 37.0, 21.9, 11.5.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{13}H_{14}O_4$ 235.0965, found 235.0985.

4-([1,1'-Biphenyl]-4-yl)-2-ethyl-4-oxobutanal (3am):



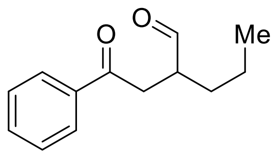
Isolated yield (106 mg, 80%); Dark grey solid; mp: 88-90 °C; Isolation: 5% EtOAc in Hexane;

^1H NMR (500 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.05 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 7.1 Hz, 2H), 7.47 (t, J = 7.4 Hz, 2H), 7.42 – 7.39 (m, 1H), 3.53 – 3.48 (m, 1H), 3.11 – 3.03 (m, 2H), 1.91 – 1.82 (m, 1H), 1.70 – 1.61 (m, 1H), 1.03 (t, J = 7.5 Hz, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 203.7, 197.7, 146.1, 139.9, 135.4, 129.1, 128.8, 128.4, 127.4, 48.2, 37.3, 22.0, 11.6.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{18}H_{18}O_2$ 267.1380, found 267.1375.

2-(2-Oxo-2-phenylethyl)pentanal (3an):



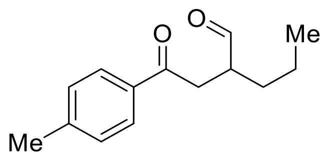
Isolated yield (77 mg, 76%); Sticky yellow liquid; Isolation: 5% EtOAc in Hexane;

^1H NMR (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.97 (d, J = 7.1 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.4 Hz, 2H), 3.47 (dd, J = 17.5, 7.9 Hz, 1H), 3.14 – 3.08 (m, 1H), 3.02 (dd, J = 17.6, 5.1 Hz, 1H), 1.82 – 1.74 (m, 1H), 1.56 – 1.49 (m, 1H), 1.46 – 1.38 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 203.8, 198.2, 136.7, 133.4, 128.8, 128.2, 46.7, 37.8, 31.1, 20.5, 14.2.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{13}H_{16}O_2$ 205.1223, found 205.1224.

2-(2-Oxo-2-(p-tolyl)ethyl)pentanal (3ao):



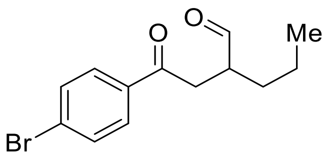
Isolated yield (77 mg, 71%)Sticky dark brown liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.82 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.25 (m, 2H), 3.44 (dd, *J* = 17.4, 7.9 Hz, 1H), 3.13 – 3.07 (m, 1H), 3.01 (dd, *J* = 17.8, 4.6 Hz, 1H), 2.41 (s, 3H), 1.81 – 1.75 (m, 1H), 1.55 – 1.48 (m, 1H), 1.46 – 1.40 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.9, 197.8, 144.3, 134.3, 129.5, 128.4, 46.7, 37.7, 31.2, 29.8, 21.8, 20.5, 14.3.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{14}H_{18}O_2$ 219.1380, found 219.1394.

2-(2-(4-Bromophenyl)-2-oxoethyl)pentanal (3ap):



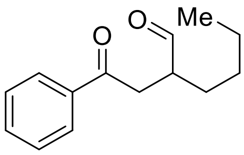
Isolated yield (115 mg, 81%); Pale yellow liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.80 (s, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 3.43 (dd, *J* = 17.4, 8.0 Hz, 1H), 3.14 – 3.09 (m, 1H), 2.94 (dd, *J* = 18.0, 4.7 Hz, 1H), 1.81 – 1.74 (m, 1H), 1.56 – 1.48 (m, 1H), 1.46 – 1.38 (m, 2H), 0.96 (t, *J* = 5.0 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.5, 197.2, 135.5, 132.1, 129.7, 128.6, 46.7, 37.6, 31.1, 20.4, 14.2.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{13}H_{15}BrO_2$ 283.0328, found 283.0343.

2-(2-Oxo-2-phenylethyl)hexanal (3aq):



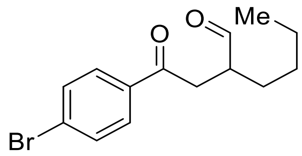
Isolated yield (85 mg, 78%); Pale yellow liquid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.81 (s, 1H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 2H), 3.47 (dd, *J* = 17.4, 8.0 Hz, 1H), 3.12 – 3.06 (m, 1H), 3.02 (dd, *J* = 17.7, 4.9 Hz, 1H), 1.83 – 1.76 (m, 1H), 1.57 – 1.50 (m, 1H), 1.39 – 1.33 (m, 4H), 0.90 (t, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.8, 198.2, 136.7, 133.4, 128.8, 128.2, 46.8, 37.8, 29.3, 28.7, 22.9, 14.0.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{14}H_{18}O_2$ 219.1380, found 219.138.

2-(2-(4-Bromophenyl)-2-oxoethyl)hexanal (3ar):



Isolated yield (123 mg, 83%); Pale yellow liquid; Isolation: 5% EtOAc in Hexane;

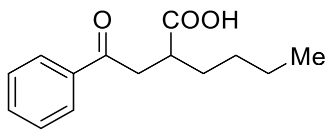
^{1}H NMR (500 MHz, CDCl$_3$) δ 9.81 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 3.43 (dd, J = 17.4, 8.0 Hz, 1H), 3.13 – 3.08 (m, 1H), 2.95 (dd, J = 17.8, 4.8 Hz, 1H), 1.83 – 1.76 (m, 1H), 1.57 – 1.52 (m, 1H), 1.38 – 1.34 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 203.5, 197.2, 135.5, 132.1, 129.8, 128.6, 46.9, 37.6, 29.4, 28.7, 22.9, 14.0.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{14}H_{17}BrO_2$ 297.0485, found 297.0495.

General procedure for carboxylic acid synthesis; An oven-dried 5.0 mL sample vial was charged with aldehydes (**3**) (0.25 mmol, 1.0 equiv.) and Oxone (0.62 mmol, 2.5 equiv.), a magnetic stir bar in DCM (2 mL) was stirred at room temperature in open-air for 12 h. The progress of the reaction was monitored via TLC. After completion of the reaction, the solvent was removed by rotary evaporation. The reaction mixture was then mixed with water (10 mL) and extracted with ethyl acetate (2 × 10 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then purified over column chromatography by eluting with hexane: ethyl acetate mixture to afford the desired carboxylic acid products **4** & **5**.

2-(2-Oxo-2-phenylethyl)hexanoic acid (4):



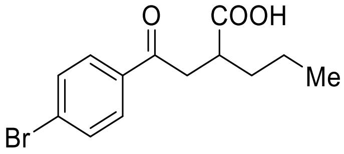
Isolated yield (44 mg, 76%); Sticky green liquid; Isolation: 10% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.97 (d, J = 7.9 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 3.45 (dd, J = 18.8, 9.5 Hz, 1H), 3.10 – 3.05 (m, 2H), 1.79 – 1.72 (m, 1H), 1.66 – 1.59 (m, 1H), 1.40 – 1.33 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 198.3, 180.8, 136.7, 133.4, 128.8, 128.2, 40.3, 40.2, 31.8, 29.4, 22.7, 14.0.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{14}H_{18}O_3$ 235.1329, found 235.1327.

2-(2-(4-Bromophenyl)-2-oxoethyl)pentanoic acid (5):



Isolated yield (52 mg, 70%); Pale yellow solid; mp: 101-103 °C; Isolation: 10% EtOAc in Hexane;

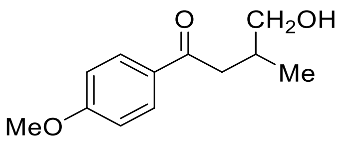
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 3.41 (dd, J = 17.9, 8.8 Hz, 1H), 3.10 – 3.05 (m, 1H), 3.00 (dd, J = 17.9, 4.7 Hz, 1H), 1.76 – 1.69 (m, 1H), 1.62 – 1.55 (m, 1H), 1.46 – 1.38 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 197.3, 181.2, 135.4, 132.1, 129.7, 128.6, 40.1, 40.0, 34.1, 20.4, 14.0.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{13}H_{15}BrO_3$ 299.0277, found 299.0294.

General procedure for alcohol synthesis; An oven-dried 5.0 mL sample vial was charged with aldehydes (**3**) (0.25 mmol, 1.0 equiv.) and a magnetic stir bar in MeOH (2 mL). To this $NaBH_4$ (2.0 equiv. for **6** and 4.0 equiv. for **7**) was added, and the reaction mixture was stirred at room temperature in open-air for 1 h. The progress of the reaction was monitored via TLC. After completion of the reaction, the solvent was removed by rotary evaporation. The reaction mixture was then mixed with water (10 mL) and extracted with ethyl acetate (2 × 10 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then purified over column chromatography by eluting with hexane: ethyl acetate mixture to afford the desired alcohol products **6** & **7**.

4-hydroxy-1-(4-methoxyphenyl)-3-methylbutan-1-one (6):



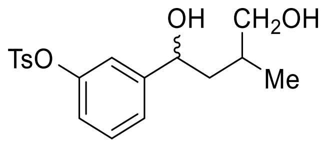
Isolated yield (40 mg, 77%); Muddy brown solid; Isolation: 5% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.96 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 8.1 Hz, 2H), 3.87 (s, 3H), 3.63 (dd, J = 10.6, 4.7 Hz, 1H), 3.50 (dd, J = 10.5, 6.9 Hz, 1H), 3.08 (dd, J = 16.1, 6.6 Hz, 1H), 2.85 (dd, J = 16.0, 6.6 Hz, 1H), 2.41 – 2.34 (m, 1H), 2.00 (s, 1H), 1.01 (d, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 199.2, 163.8, 130.7, 114.0, 68.2, 55.6, 42.6, 32.8, 17.3.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{12}H_{16}O_3$ 209.1172, found 209.1179.

3-(1,4-dihydroxy-3-methylbutyl)phenyl 4-methylbenzenesulfonate (7):



Isolated yield (63 mg, 73%); Faint pink solid; Isolation: 5% EtOAc in Hexane;

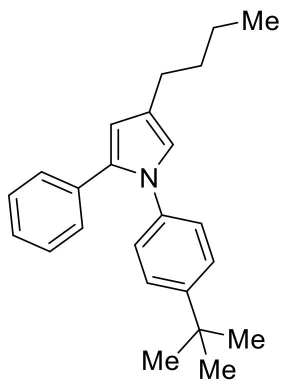
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 (d, *J* = 8.0 Hz, 4H), 7.29 (d, *J* = 8.2 Hz, 4H), 7.22 (d, *J* = 4.8 Hz, 4H), 6.96 (s, 2H), 6.84 – 6.81 (m, 2H), 4.77 (t, *J* = 5.4 Hz, 1H), 4.64 (dd, *J* = 9.5, 2.0 Hz, 1H), 3.55 (dd, *J* = 10.7, 4.0 Hz, 1H), 3.49 (dd, *J* = 10.7, 4.0 Hz, 1H), 3.43 – 3.39 (m, 1H), 3.36 – 3.32 (m, 1H), 2.43 (s, 6H), 1.90 – 1.81 (m, *J* = 6.7 Hz, 1H), 1.67 – 1.60 (m, 4H), 1.46 – 1.42 (m, 1H), 0.89 – 0.86 (m, 6H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 149.7, 147.9, 147.3, 145.5, 132.5, 129.9, 129.7, 129.6, 128.6, 124.6, 124.5, 121.2, 121.0, 120.0, 119.9, 72.8, 71.0, 68.5, 67.8, 45.4, 43.7, 34.6, 32.0, 21.8, 18.0, 17.4.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{18}H_{22}O_5S$ 351.1261, found 351.1285.

General procedure for pyrrole synthesis; An oven-dried 5.0 mL sample vial was charged with aldehydes (**3**) (0.25 mmol, 1.0 equiv.) and *p*-tert-butyl aniline (1.2 equiv.), a magnetic stir bar in MeOH (2 mL) was stirred at room temperature in open-air for 3 h. The progress of the reaction was monitored via TLC. After completion of the reaction, the solvent was removed by rotary evaporation. The reaction mixture was then mixed with water (10 mL) and extracted with ethyl acetate (2 × 10 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then purified over column chromatography by eluting with hexane to afford the desired pyrrole products **8** & **9**.

4-Butyl-1-(4-(tert-butyl)phenyl)-2-phenyl-1H-pyrrole (8):



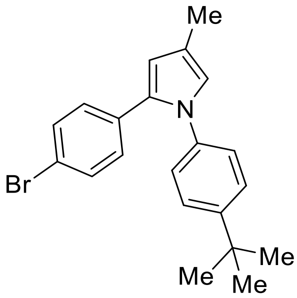
Isolated yield (56 mg, 68%); Sticky dark orange liquid; Isolation: Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.18 (m, 2H), 7.14 (d, *J* = 8.2 Hz, 3H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.72 (s, 1H), 6.31 (s, 1H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.61 (m, 2H), 1.45 (q, *J* = 7.1 Hz, 2H), 1.32 (s, 9H), 0.96 (t, *J* = 7.3 Hz, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$) δ 149.4, 138.3, 133.5, 133.4, 128.2, 128.1, 126.1, 125.9, 125.5, 125.2, 122.0, 111.2, 33.2, 31.5, 29.8, 26.7, 22.8, 14.2.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{24}H_{29}N$ 332.2373, found 332.2379.

2-(4-Bromophenyl)-1-(4-(tert-butyl)phenyl)-4-methyl-1H-pyrrole (9):



Isolated yield (55 mg, 60%); Sticky yellow liquid; Isolation: Hexane;

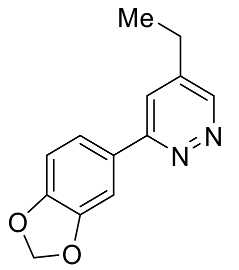
^1H NMR (500 MHz, CDCl$_3$) δ 7.33 (t, J = 7.5 Hz, 4H), 7.06 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.72 (s, 1H), 6.29 (s, 1H), 2.19 (s, 3H), 1.34 (s, 9H).

$^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$) δ 149.8, 137.9, 132.4, 132.3, 131.3, 129.6, 126.1, 125.2, 123.2, 120.1, 119.9, 112.5, 34.7, 31.5, 11.8.

HRMS (ESI-TOF, $[M+H]^+$): Calcd for $C_{21}H_{22}BrN$ 368.1008, found 368.1018.

General procedure for pyridazine synthesis; An oven-dried 5.0 mL sample vial was charged with hydrazine hydrochloride (0.5 mmol, 2.0 equiv.) and $NaHCO_3$ (1.0 mmol, 4.0 equiv.) and a magnetic stir bar in ACN (2 mL) was stirred at room temperature in an open-air for 3 h. Next, aldehydes (**3**) (0.25 mmol, 1.0 equiv.), was added to reaction mixture and the progress of the reaction was monitored via TLC. After completion of the reaction, the solvent was removed by rotary evaporation. The reaction mixture was then mixed with water (10 mL) and extracted with ethyl acetate (2 × 10 mL). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residue so obtained was then purified over column chromatography by eluting with hexane: ethyl acetate mixture to afford the desired pyridazine products **10** & **11**.

3-(Benzo[d][1,3]dioxol-5-yl)-5-ethylpyridazine (10):



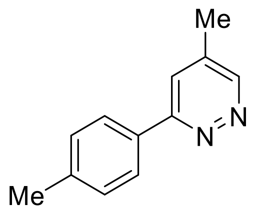
Isolated yield (43 mg, 77%); Sticky brown liquid; Isolation: 20% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.96 (s, 1H), 7.63 (s, 1H), 7.56 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 8.5 Hz, 1H), 6.03 (s, 2H), 2.72 (q, J = 7.5 Hz, 2H), 1.32 (t, J = 7.9 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 158.6, 150.7, 149.4, 148.6, 143.5, 130.9, 122.6, 121.5, 108.7, 107.6, 101.6, 26.0, 13.9.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{13}H_{12}N_2O_2$ 229.0972, found 229.0964.

5-Methyl-3-(*p*-tolyl)pyridazine (11):



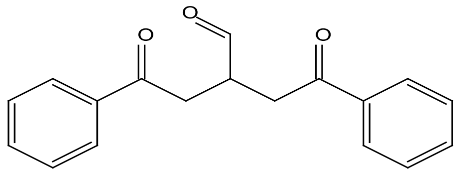
Isolated yield (33 mg, 73%); Orange solid; mp: 102-104 °C; Isolation: 20% EtOAc in Hexane;

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.00 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.64 (s, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.42 (s, 6H).

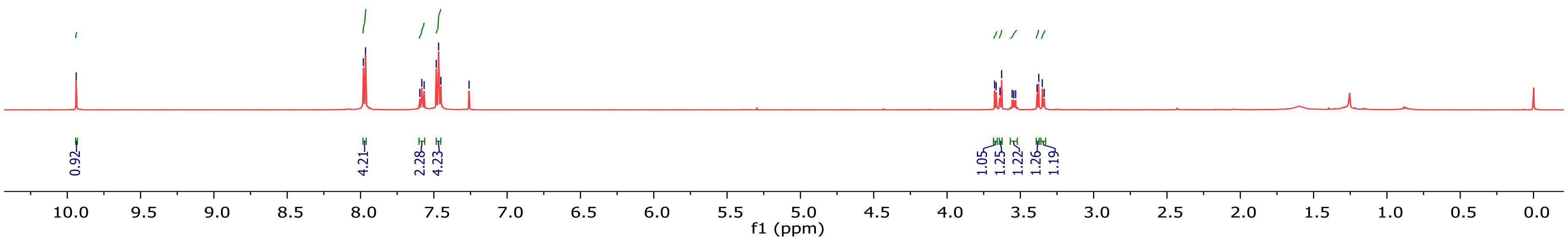
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 159.0, 151.6, 140.3, 138.0, 133.7, 129.8, 127.2, 124.3, 21.5, 18.7.

HRMS (ESI-TOF, [M+H]$^+$): Calcd for $C_{12}H_{12}N_2$ 185.1073, found 185.1070.

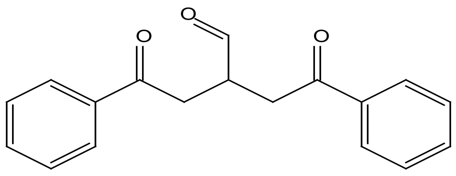
^{1}H NMR (500 MHz, $CDCl_3$) of 3a



3a



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3a



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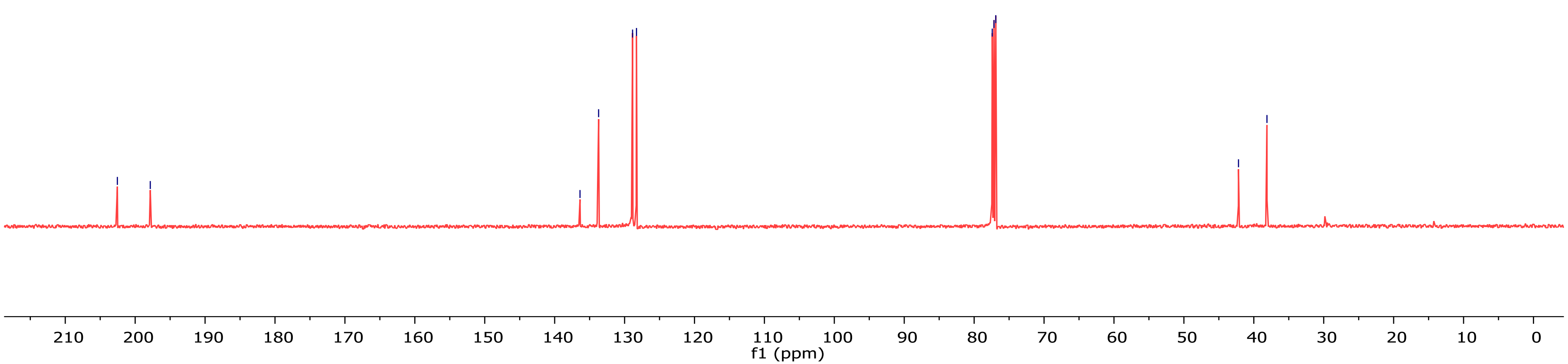
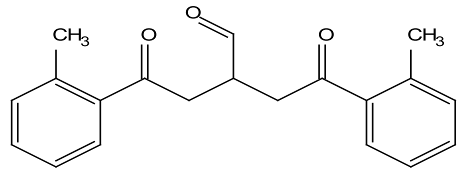


^{1}H NMR (500 MHz, $CDCl_3$) of 3b



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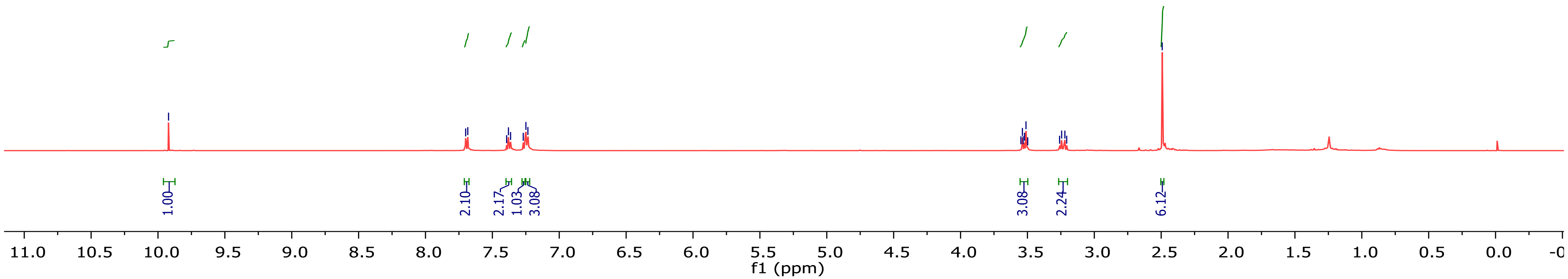
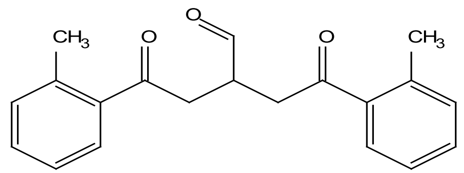


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3b



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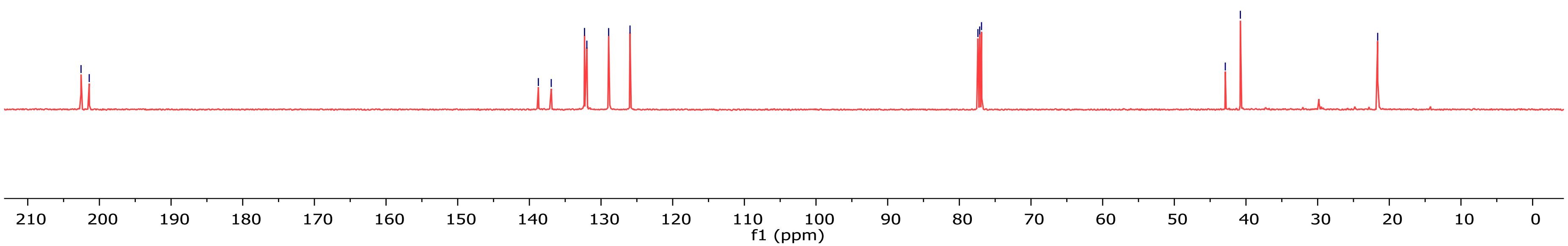
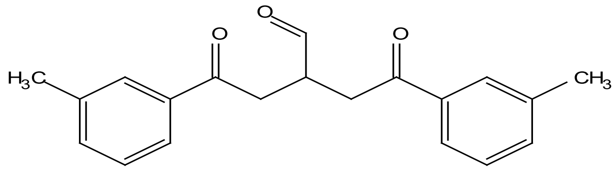
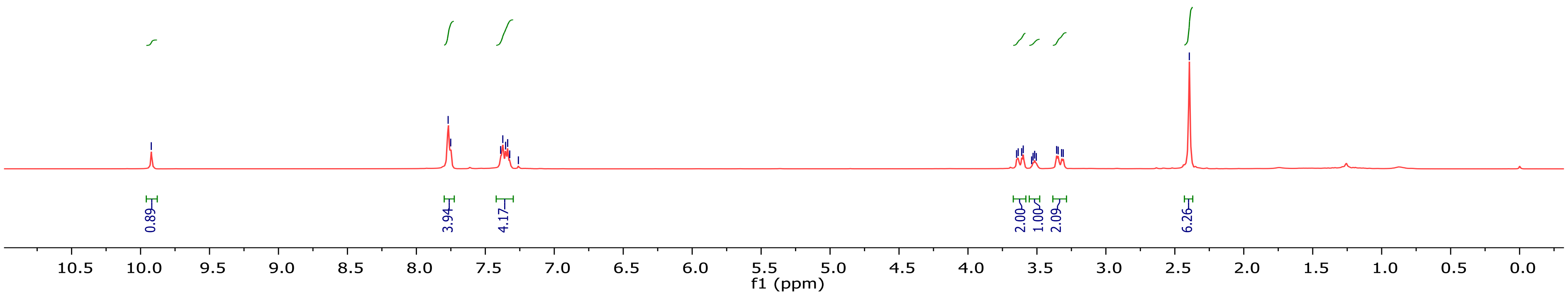


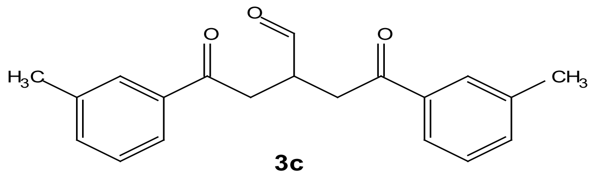
^{1}H NMR (500 MHz, $CDCl_3$) of 3c



3c



$^{13}C\{^{1}H\}$ **NMR (126 MHz, $CDCl_3$) of 3c**



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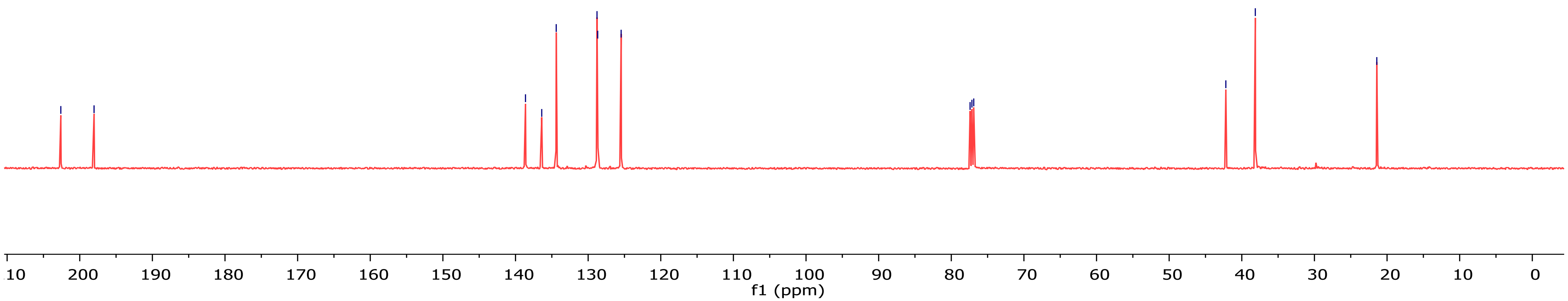
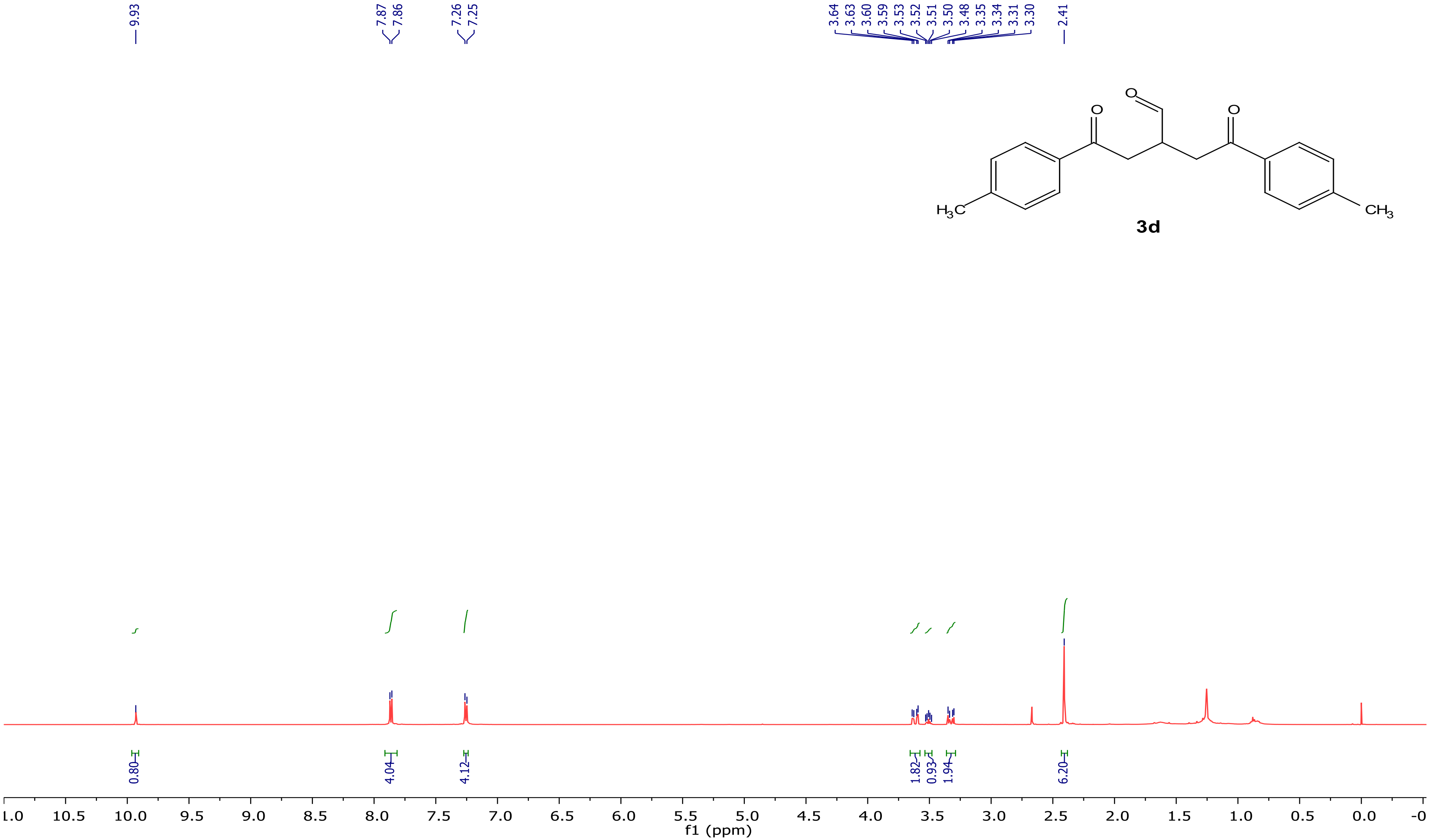
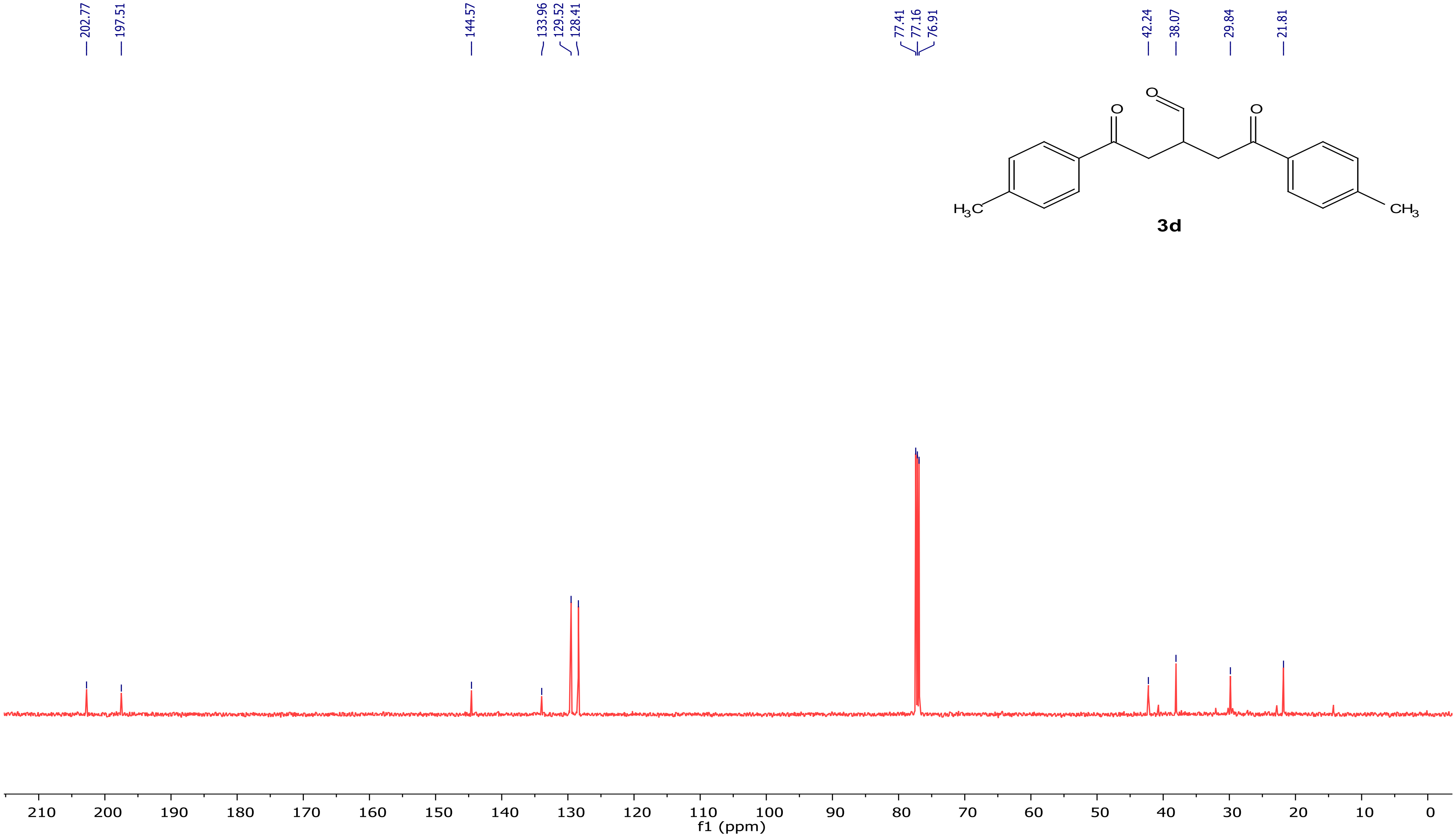


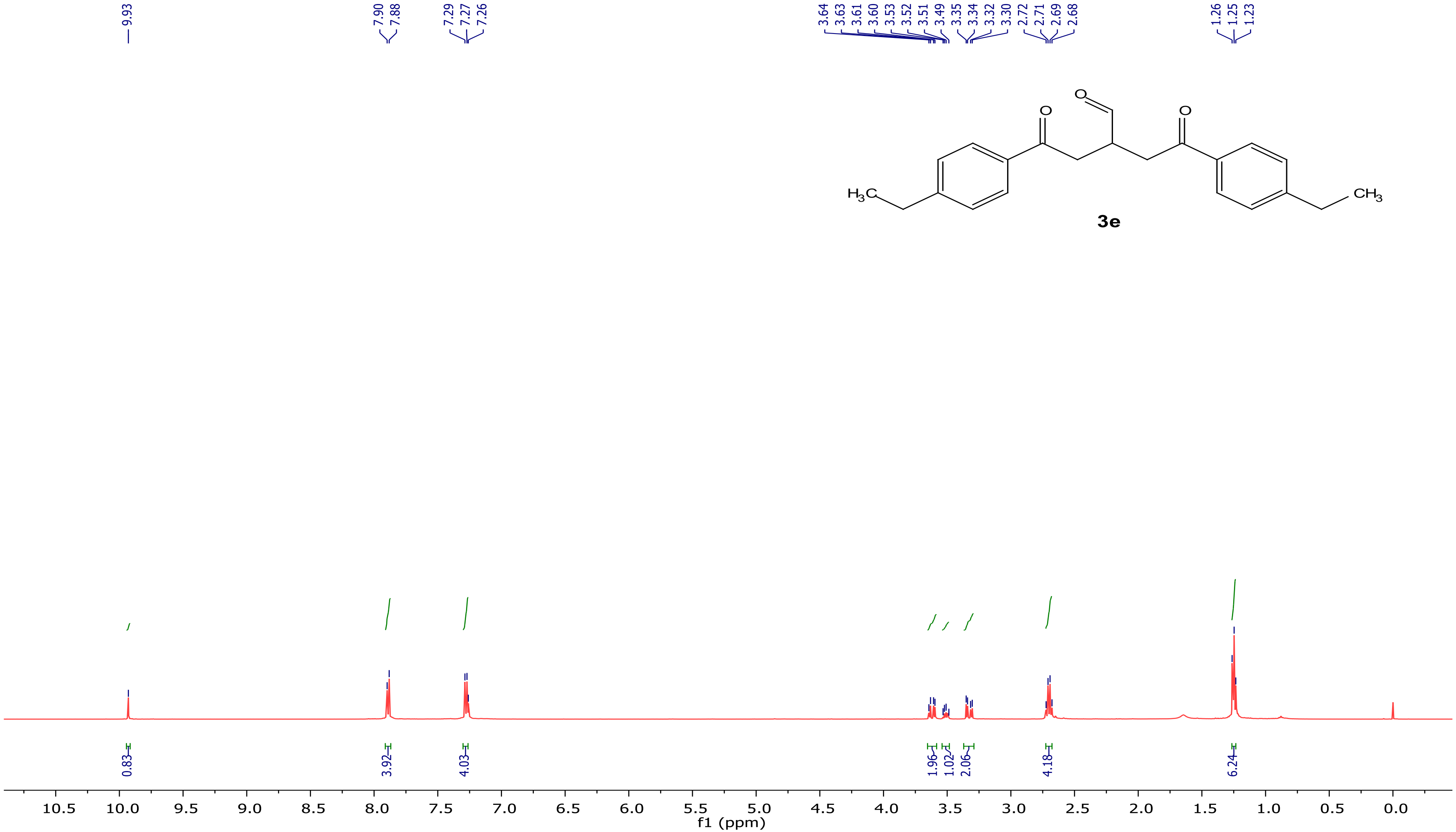
¹H NMR (500 MHz, CDCl$_3$) of 3d



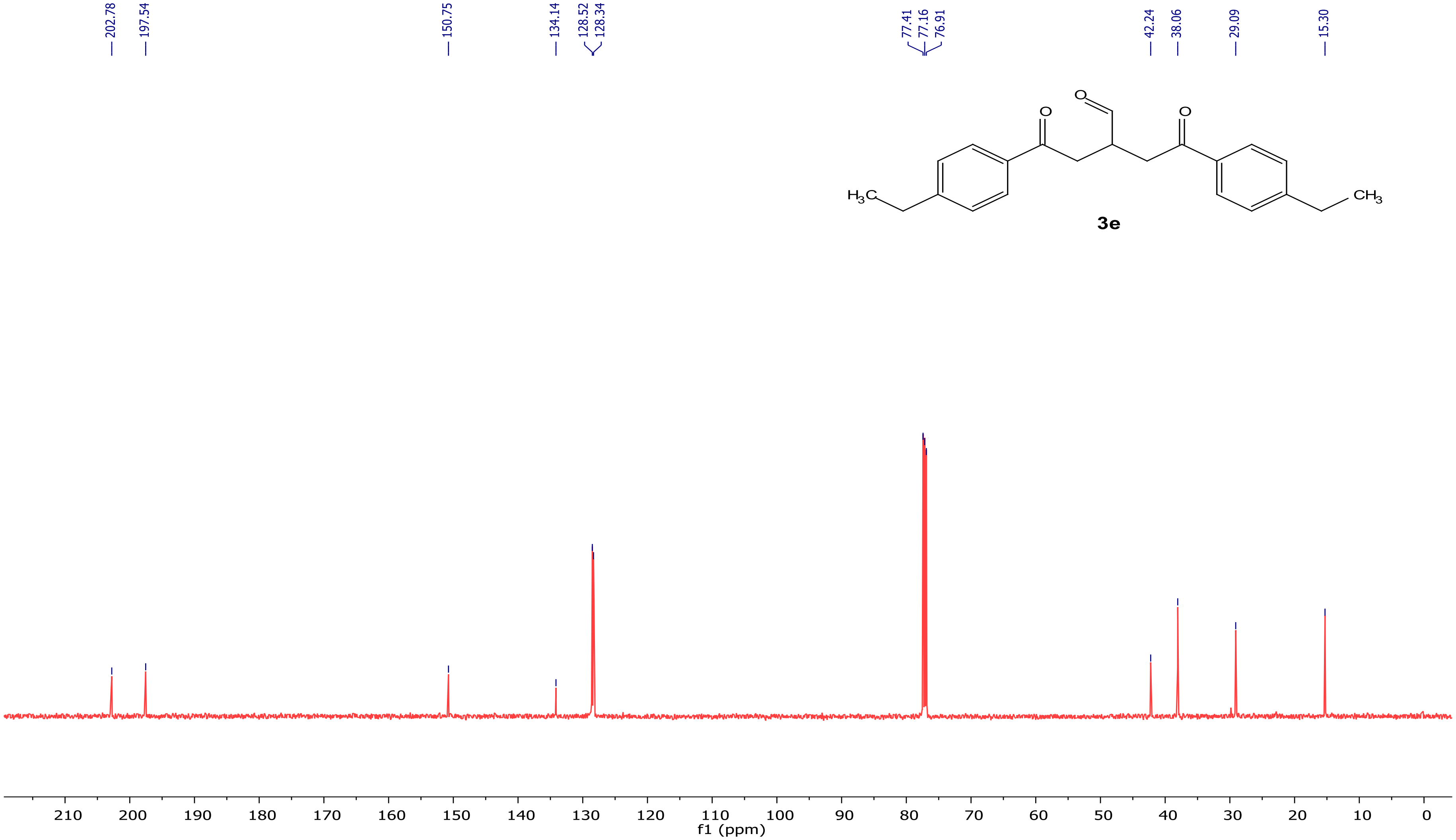
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3d



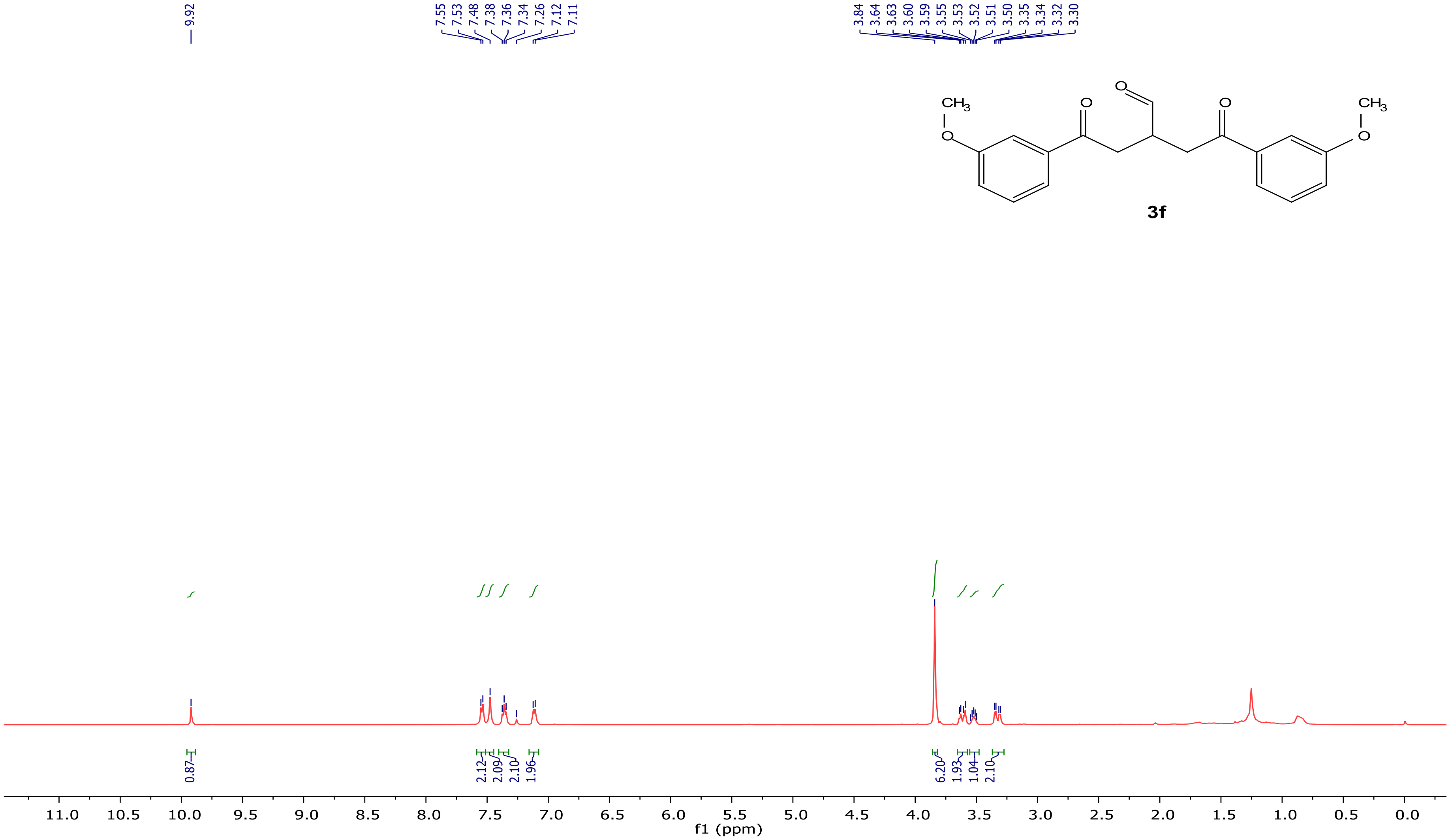
[1]H NMR (500 MHz, $CDCl_3$) of 3e



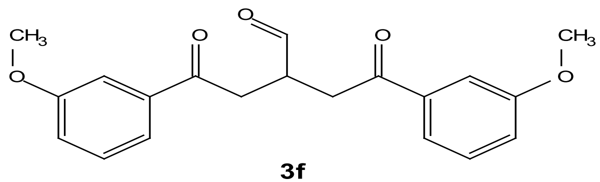
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3e



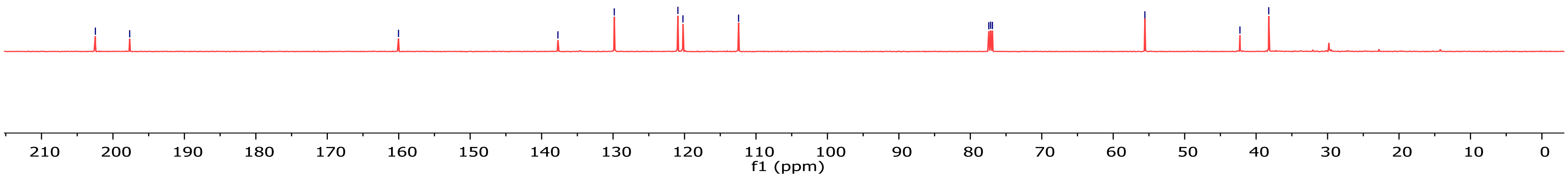
^{1}H NMR (500 MHz, $CDCl_3$) of 3f



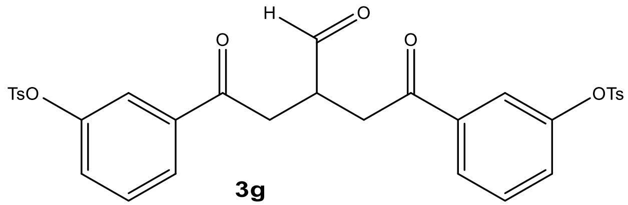
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3f



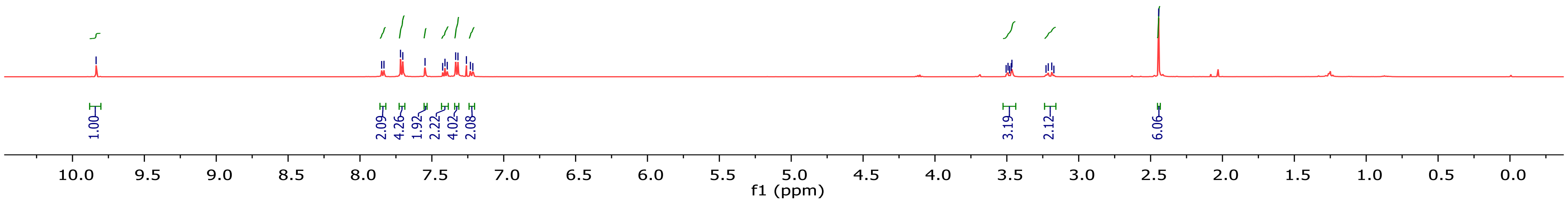
3f



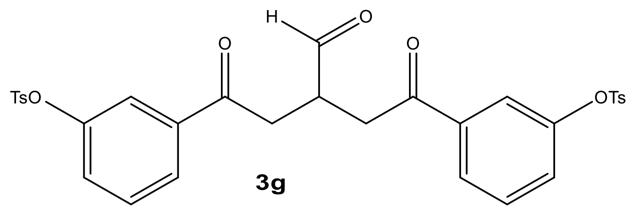
¹H NMR (500 MHz, CDCl$_3$) of 3g



3g



$^{13}C\{^{1}H\}$ NMR (126 MHz, CDCl$_3$) of 3g



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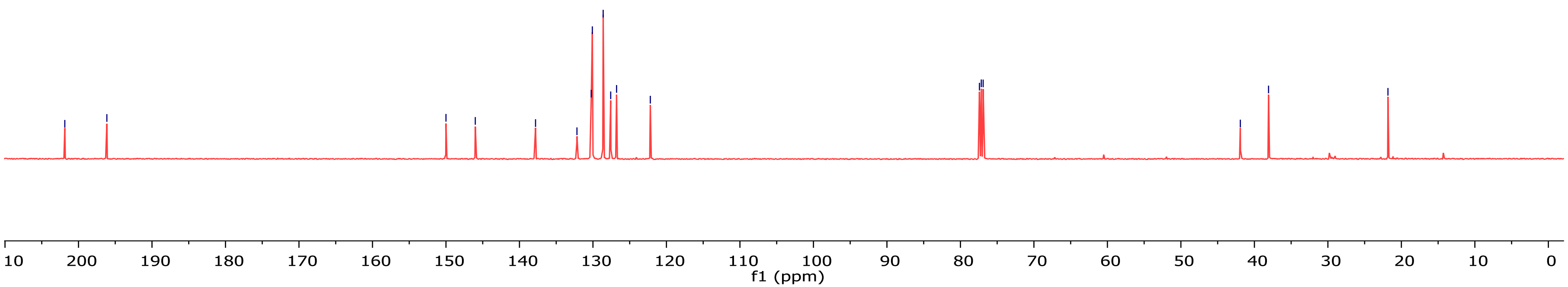
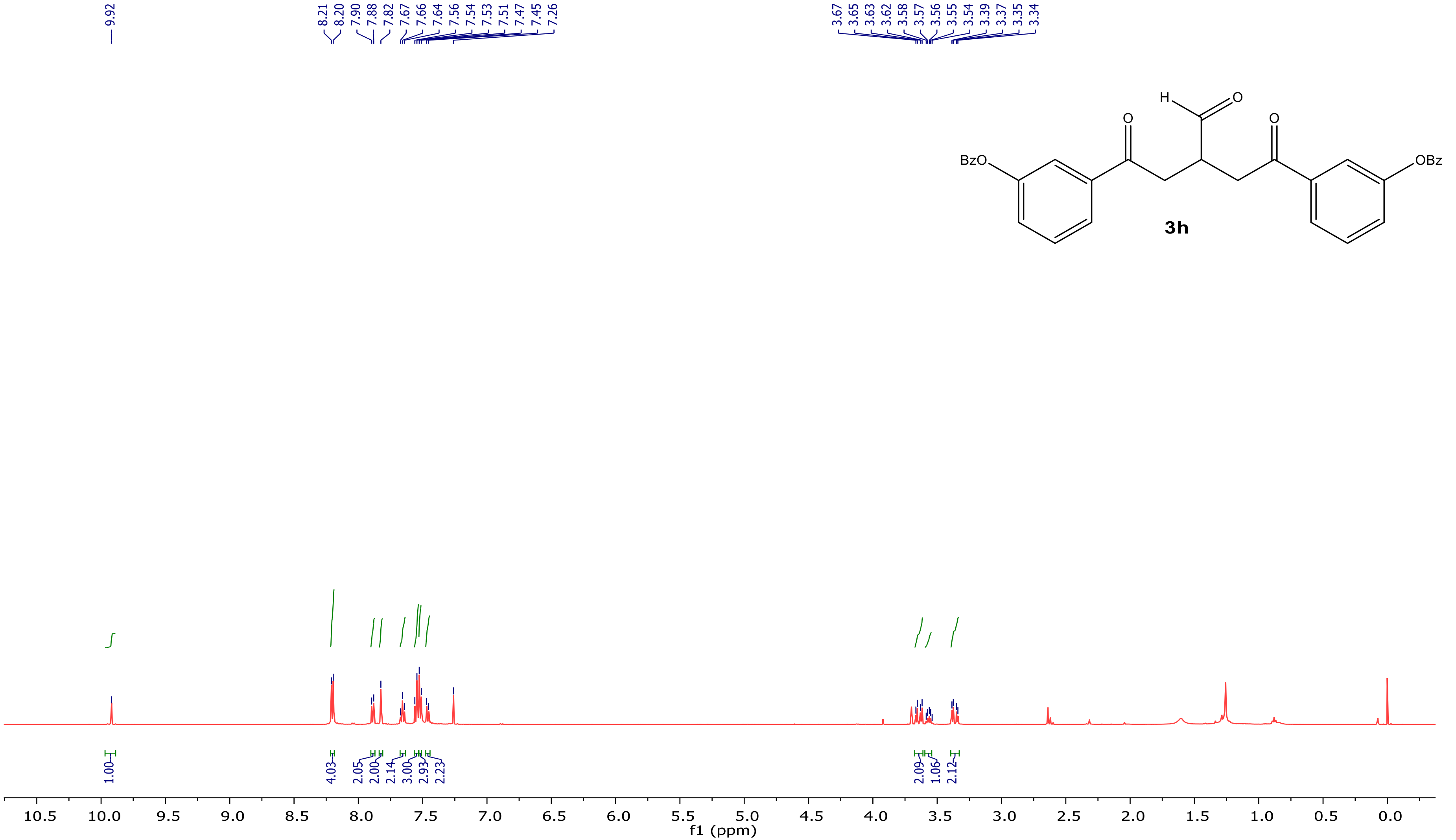
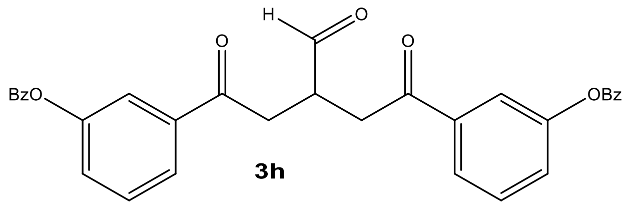


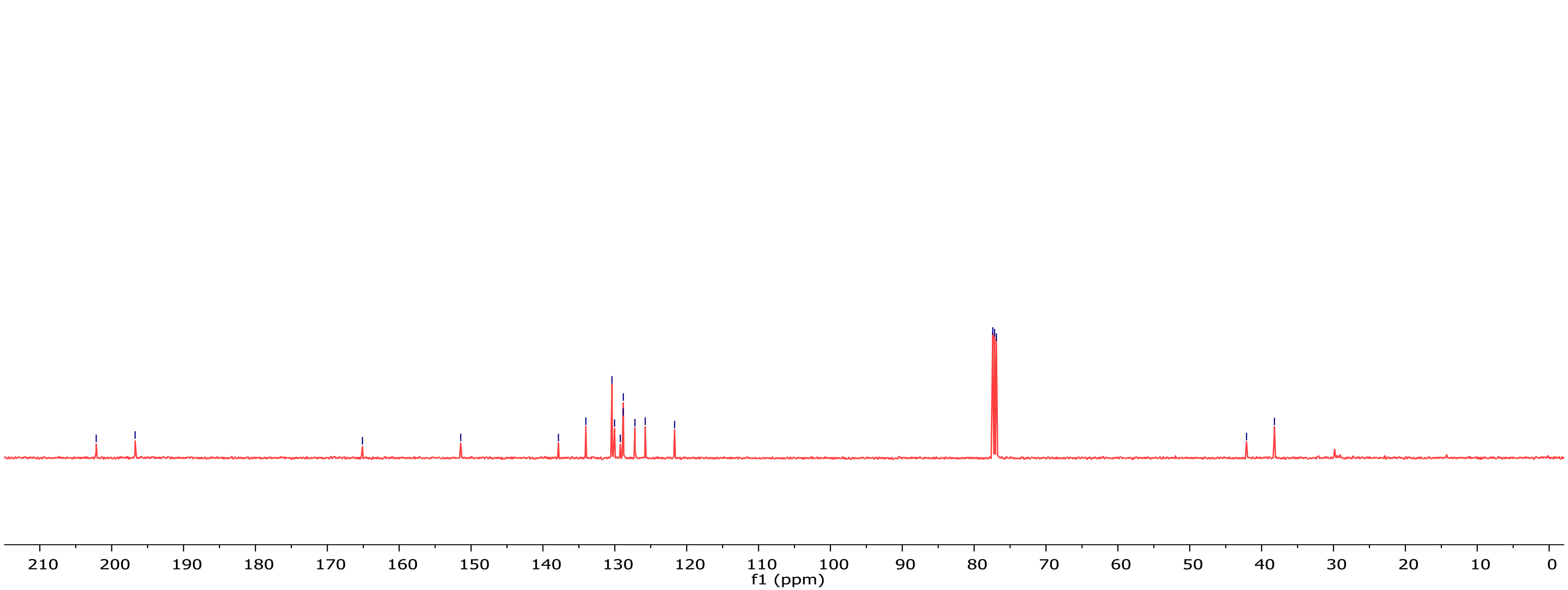
[1]H NMR (500 MHz, CDCl$_3$) of 3h



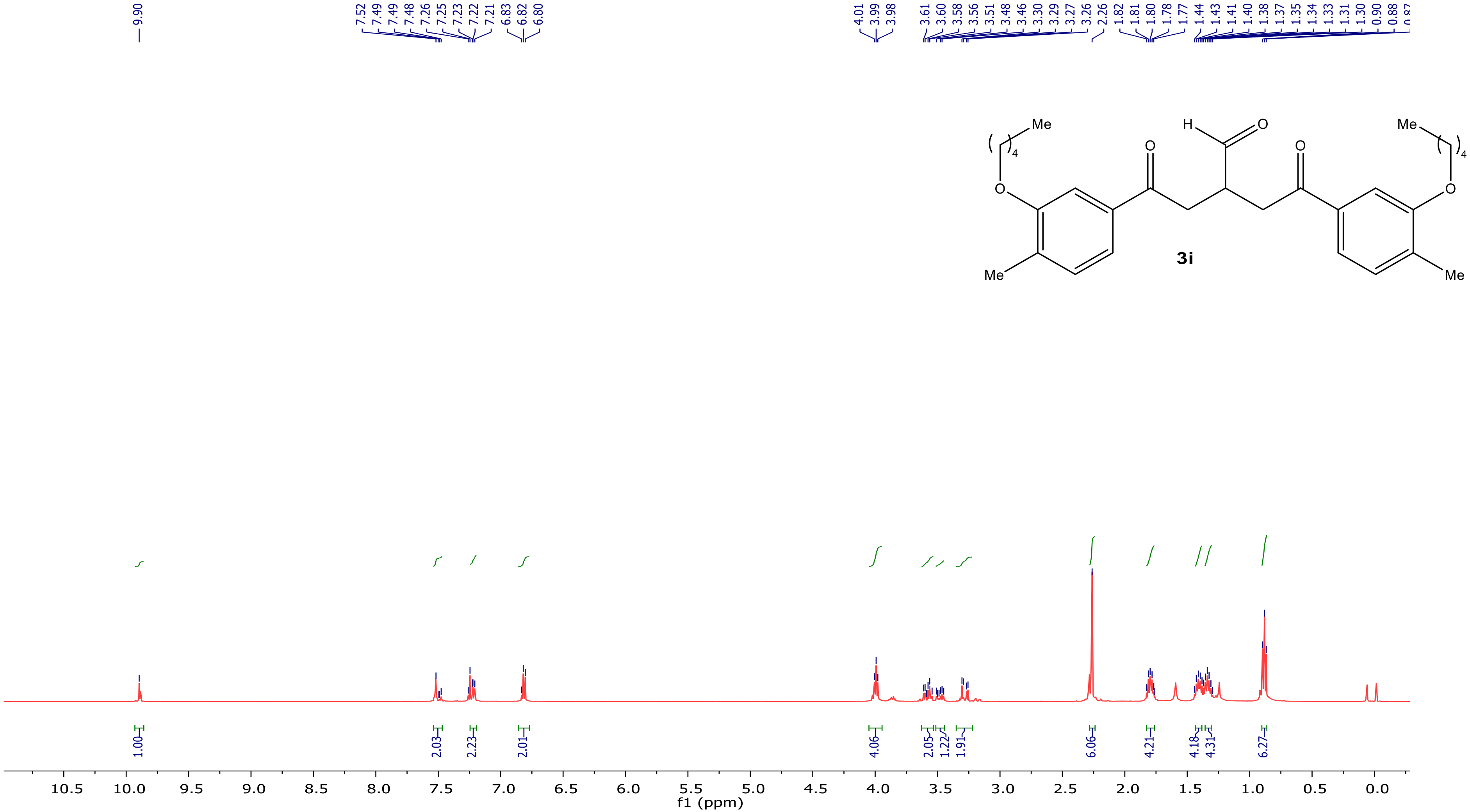
$^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$) of 3h



3h

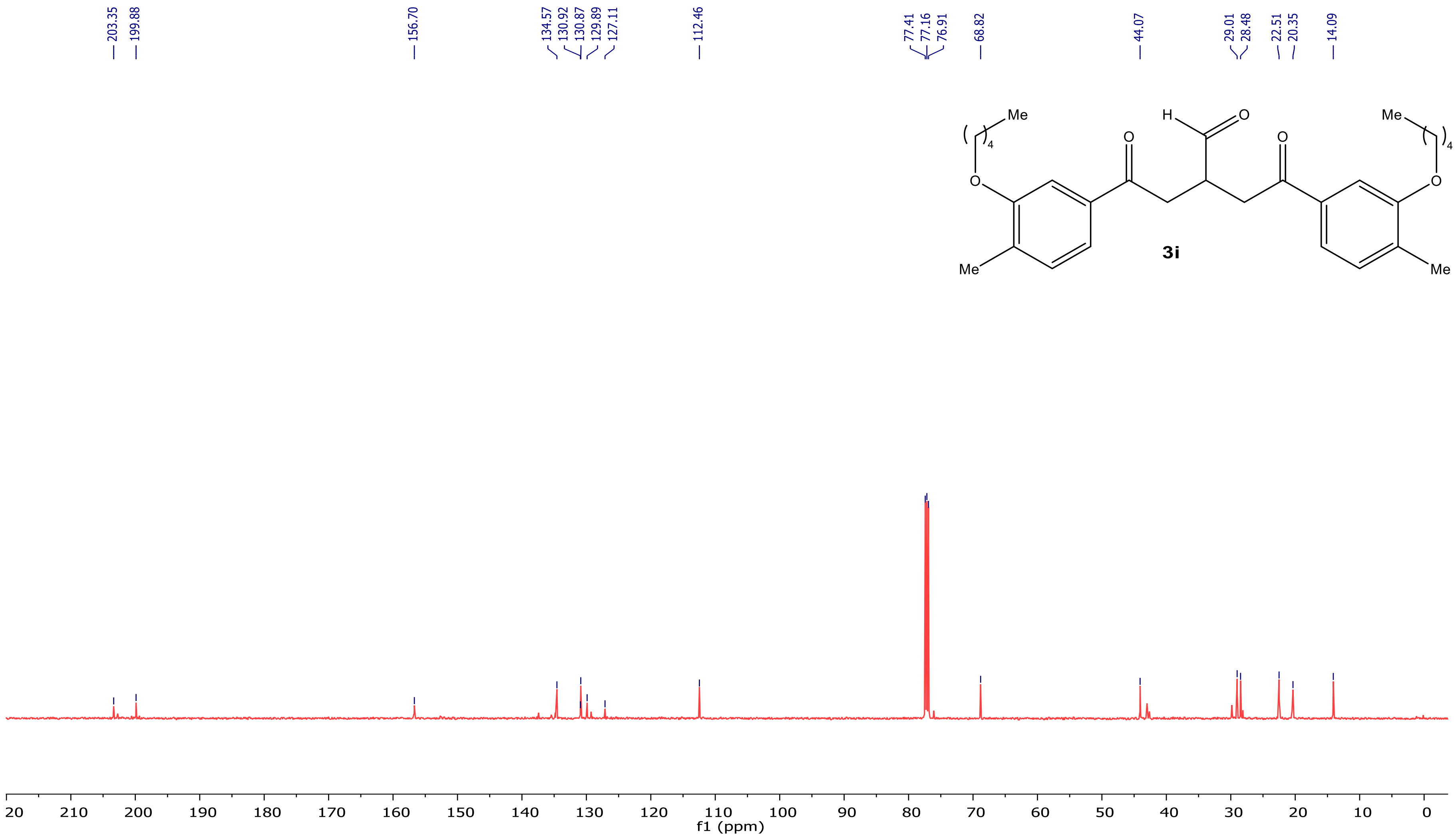


^{1}H NMR (500 MHz, CDCl$_3$) of 3i

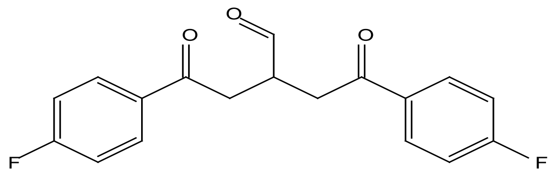


3i

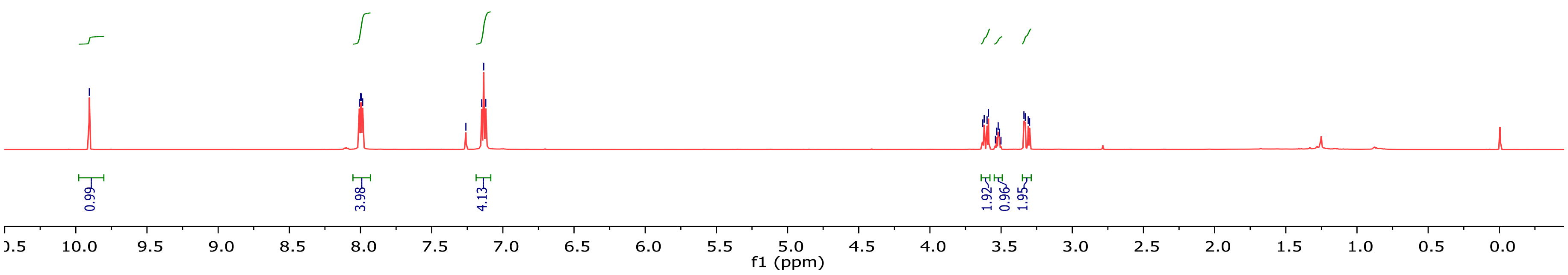
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3i



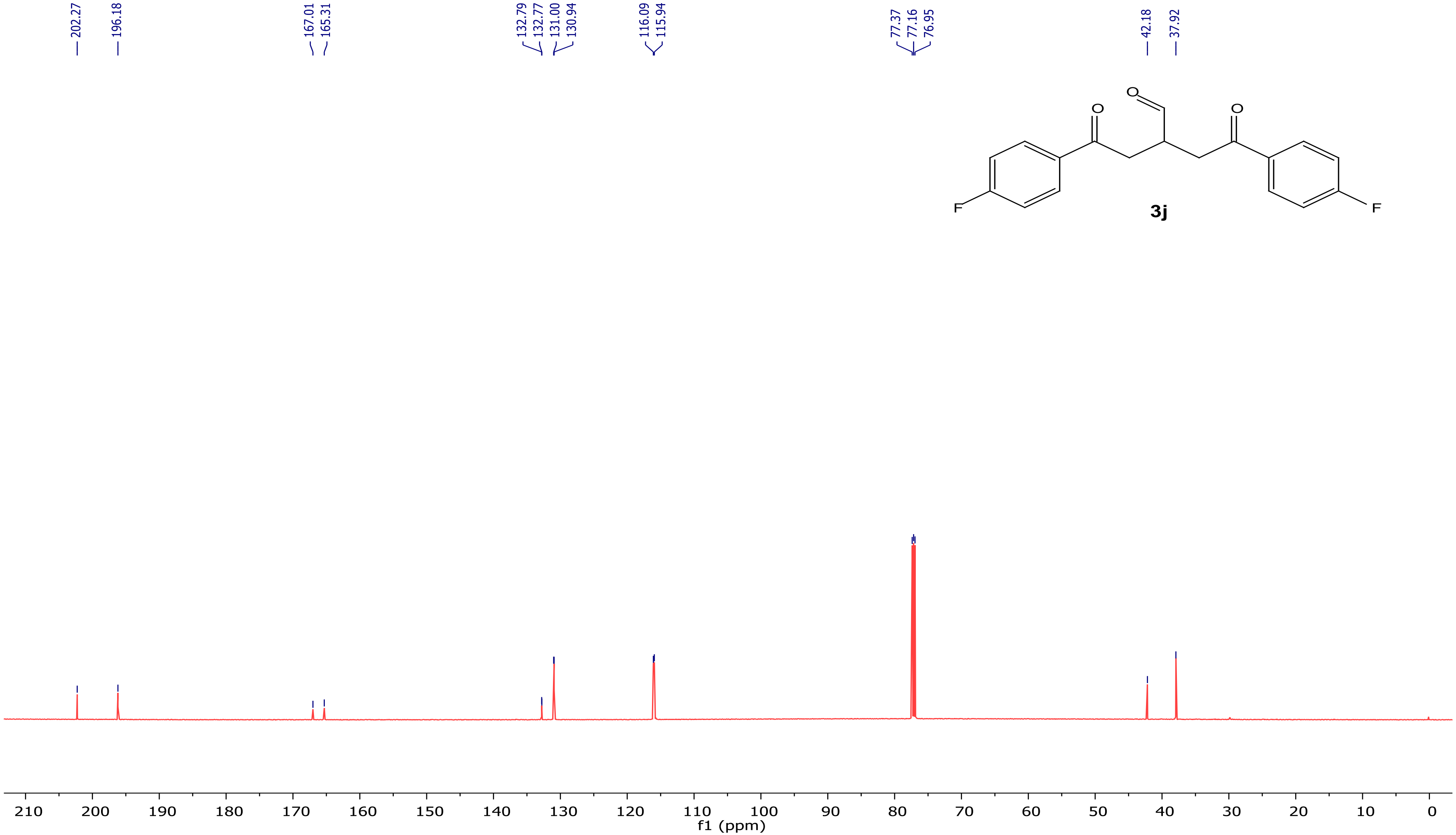
^{1}H NMR (600 MHz, $CDCl_3$) of 3j



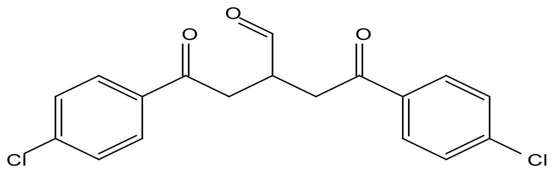
3j



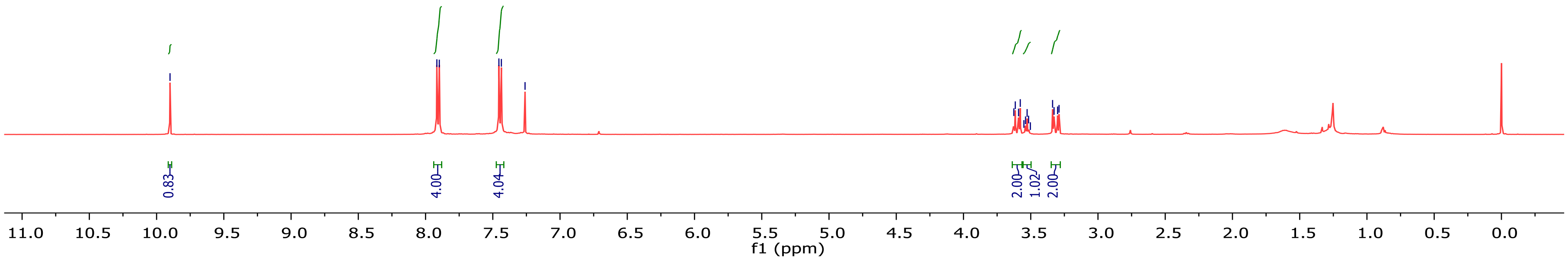
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of 3j



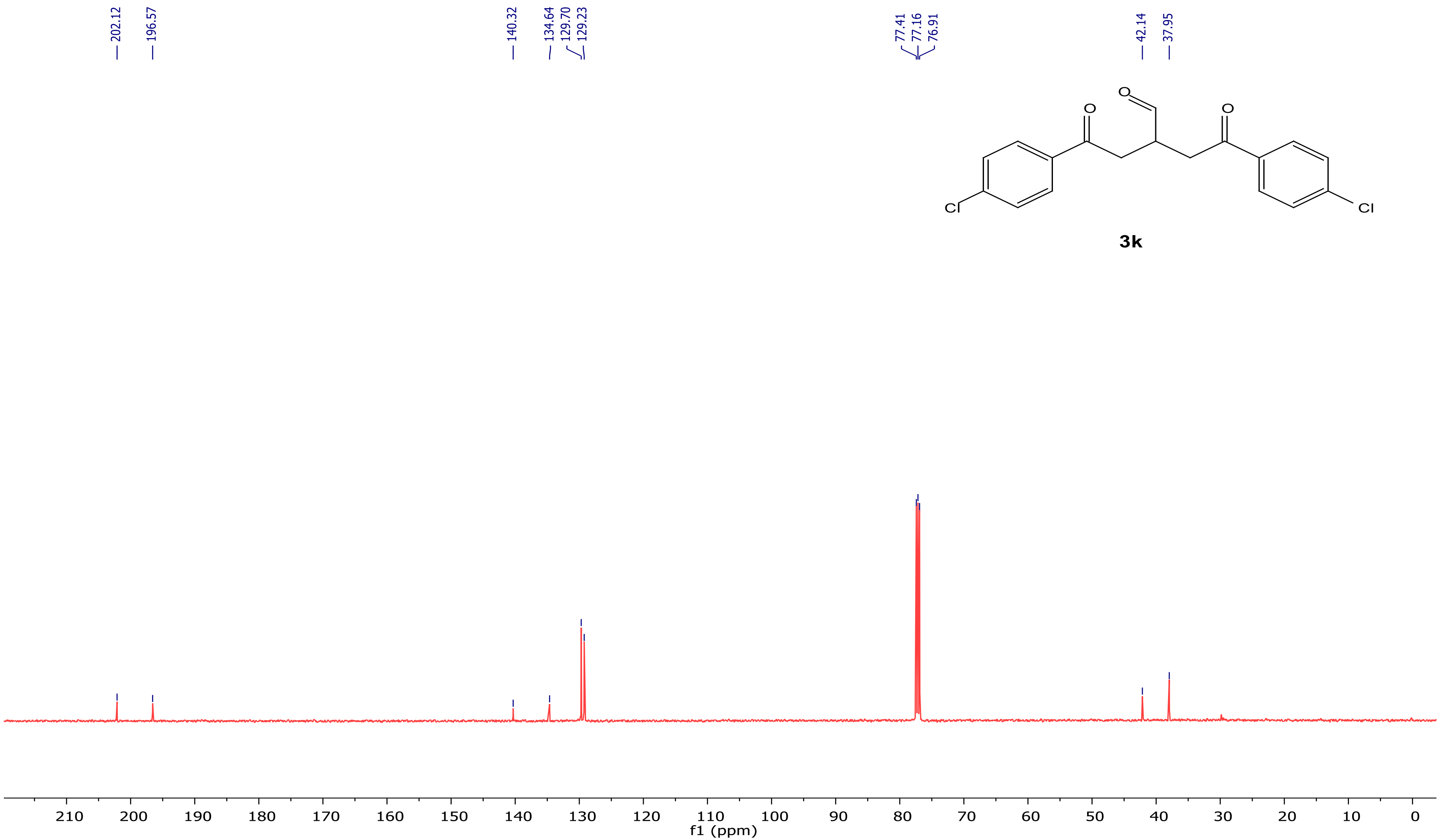
^{1}H NMR (500 MHz, $CDCl_3$) of 3k



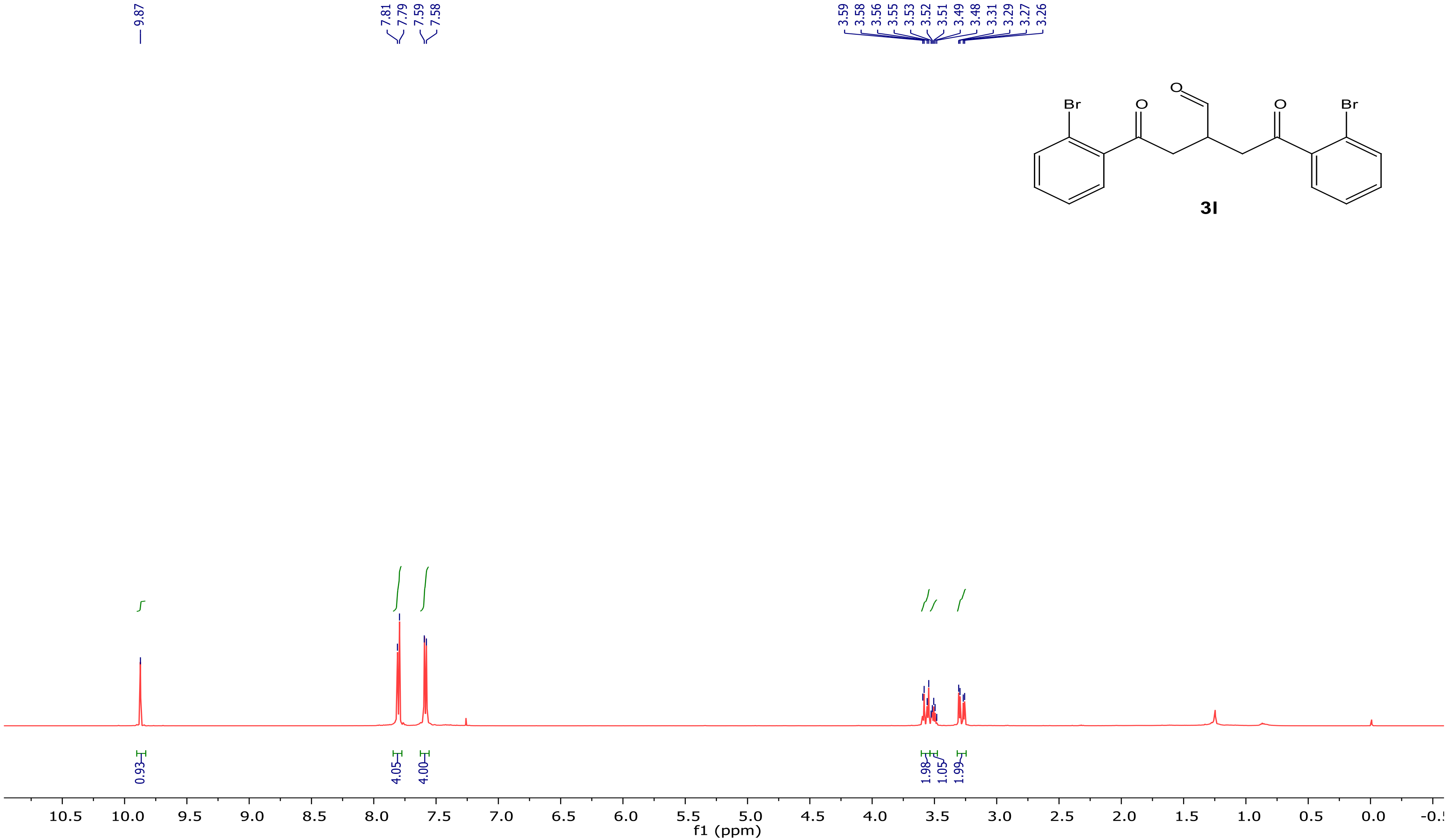
3k



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3k

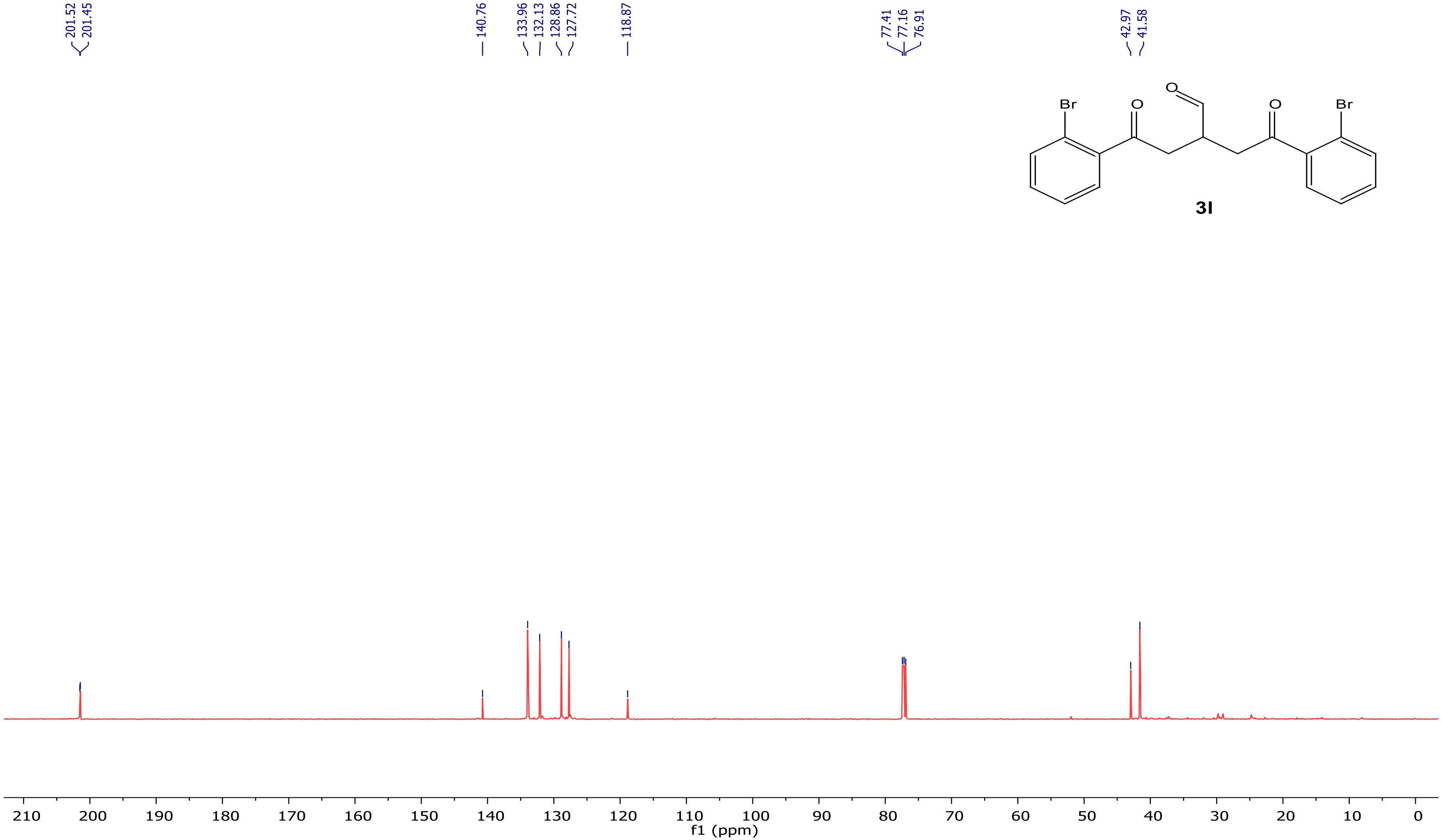


[1]H NMR (500 MHz, $CDCl_3$) of 3l

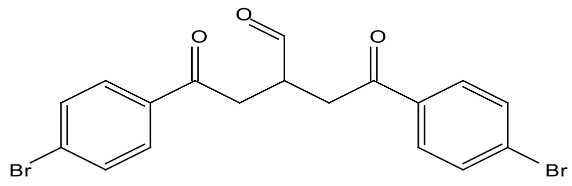


3l

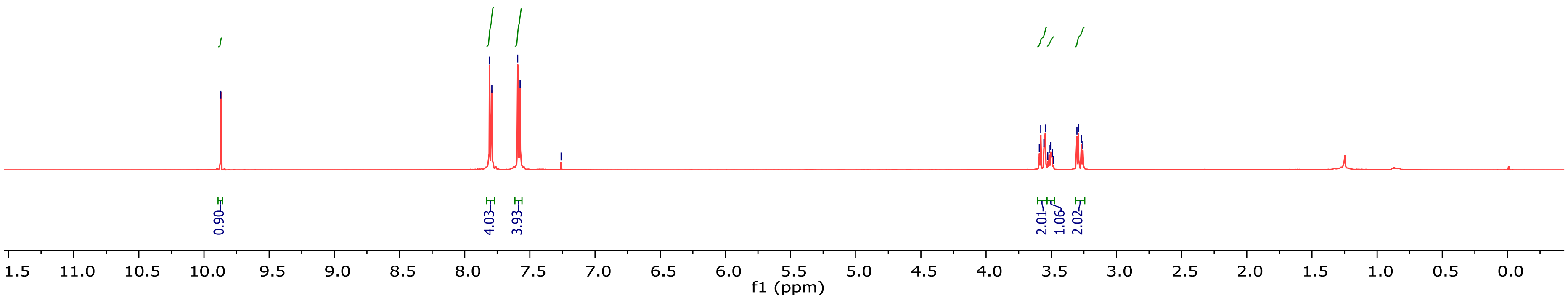
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3l



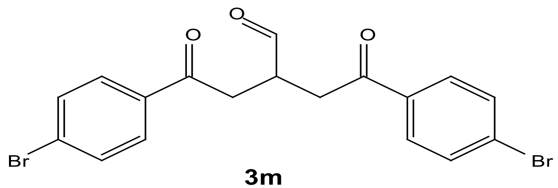
^{1}H NMR (500 MHz, CDCl$_3$) of 3m



3m



$^{13}C\{^{1}H\}$ **NMR (126 MHz, $CDCl_3$) of 3m**



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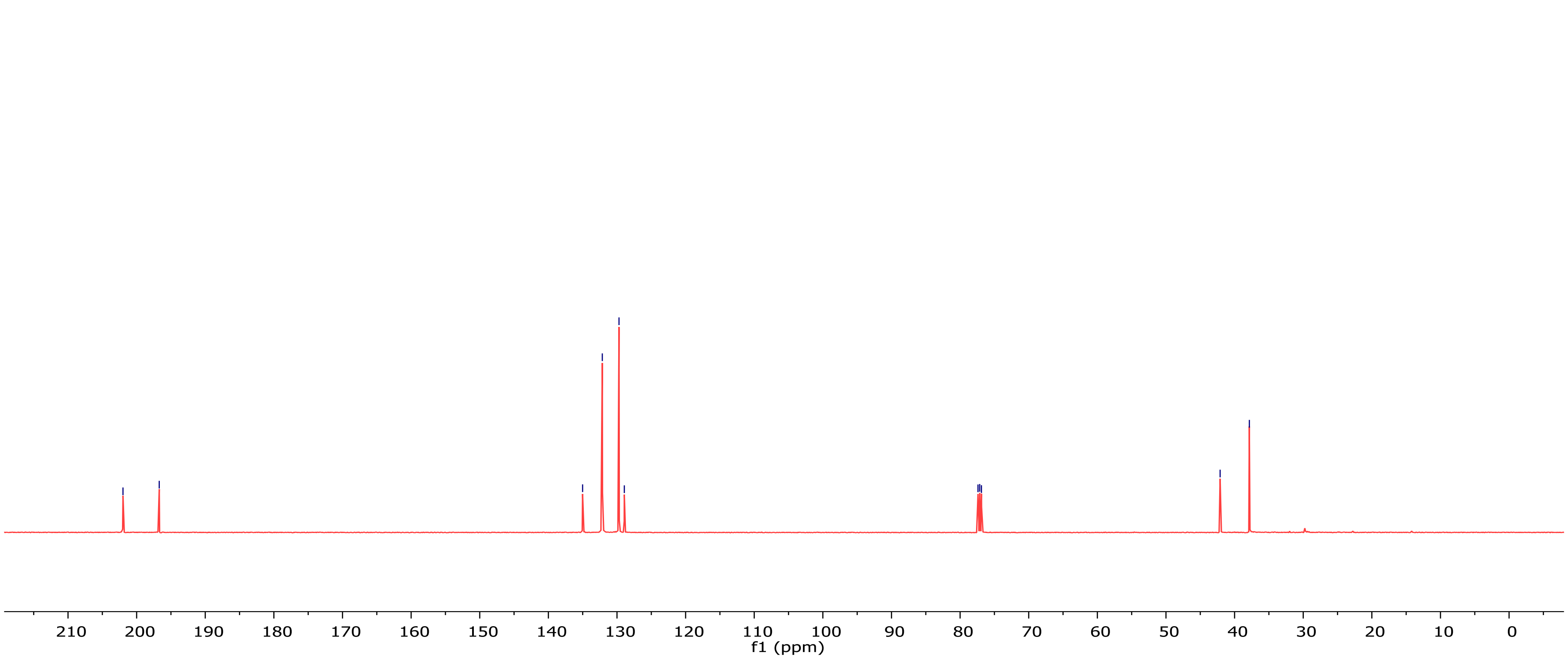
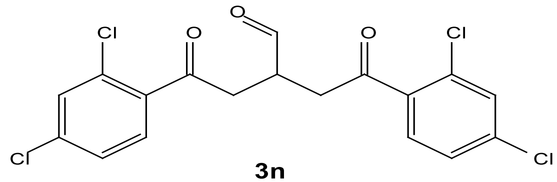


^{1}H NMR (500 MHz, $CDCl_3$) of 3n



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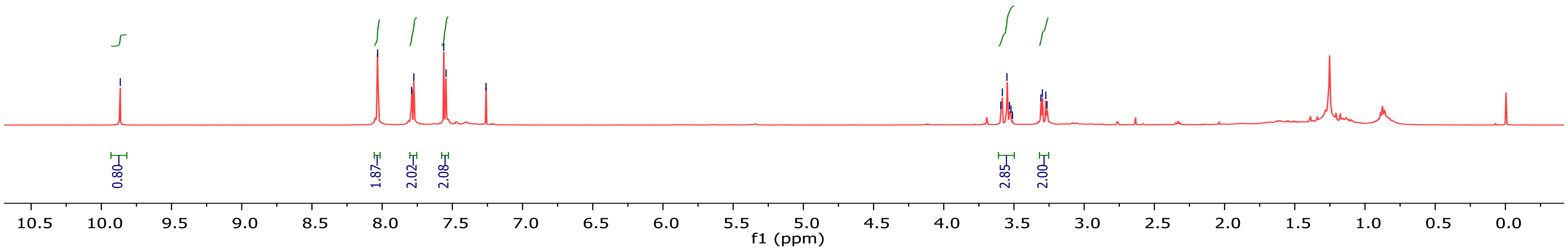
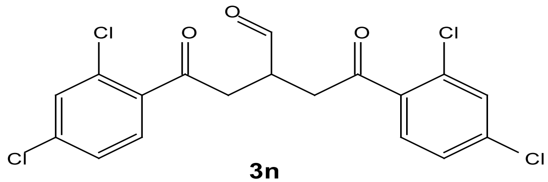


$^{13}C\{^{1}H\}$ NMR (126 MHz, CDCl$_3$) of 3n



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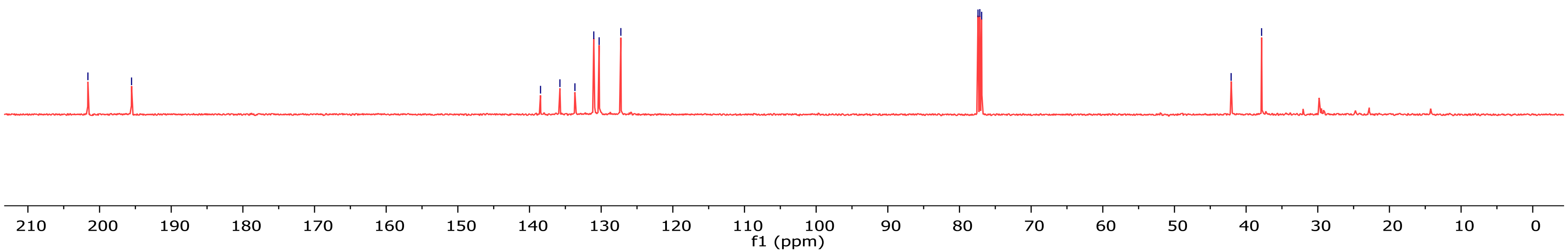
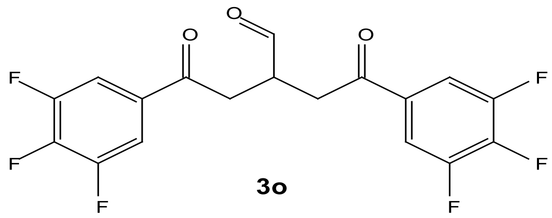
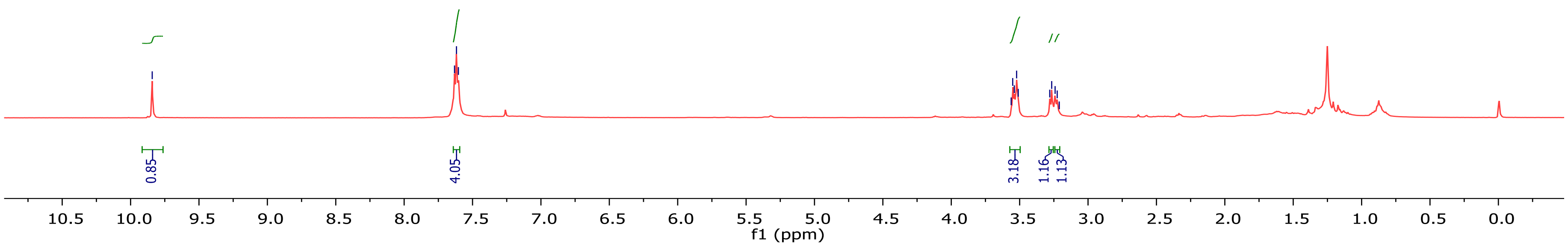


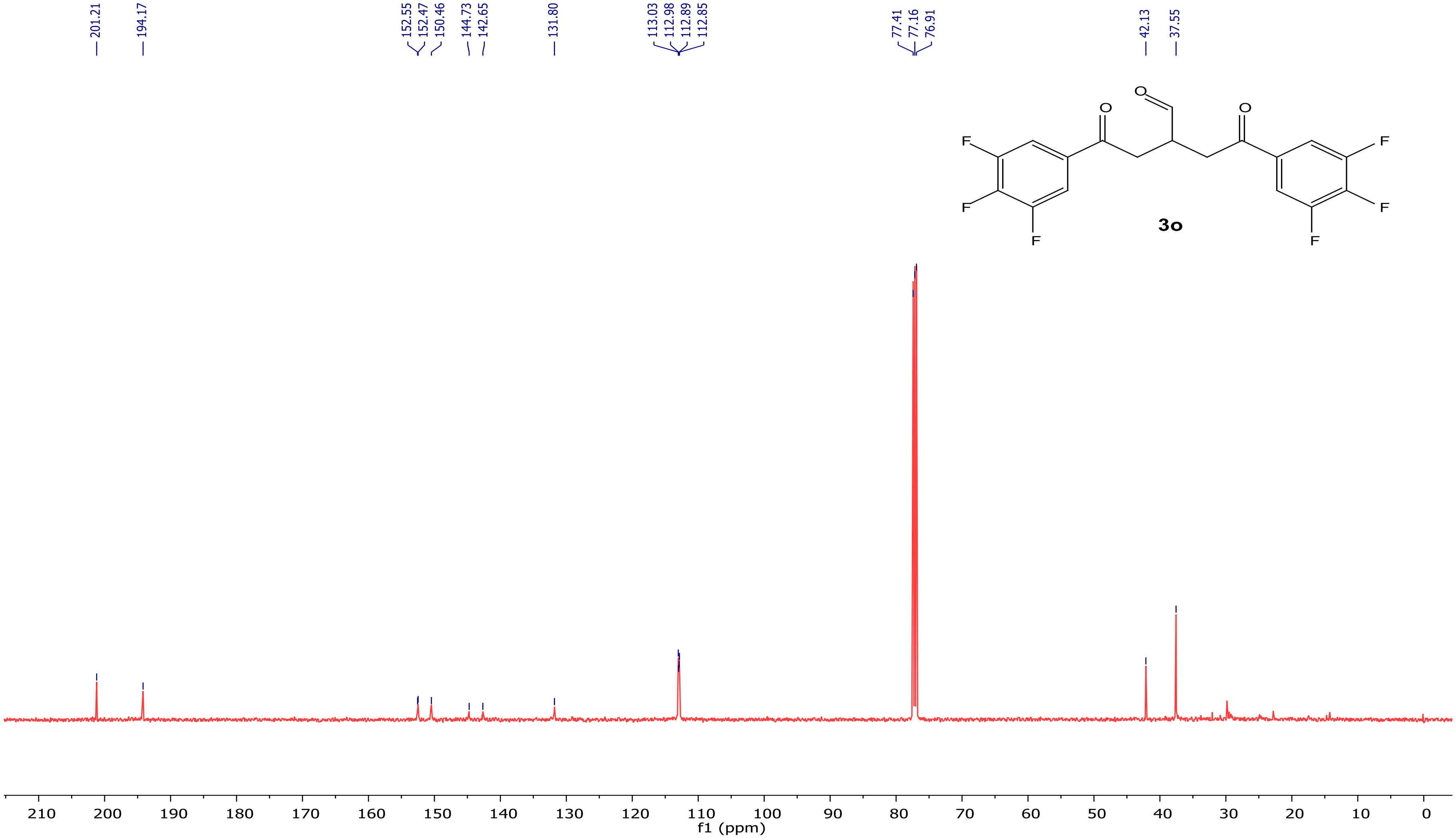
^{1}H NMR (500 MHz, $CDCl_3$) of 3o



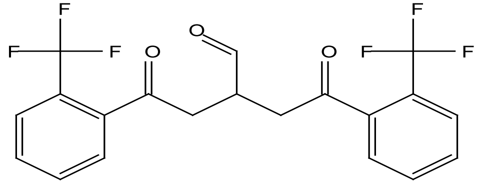
3o



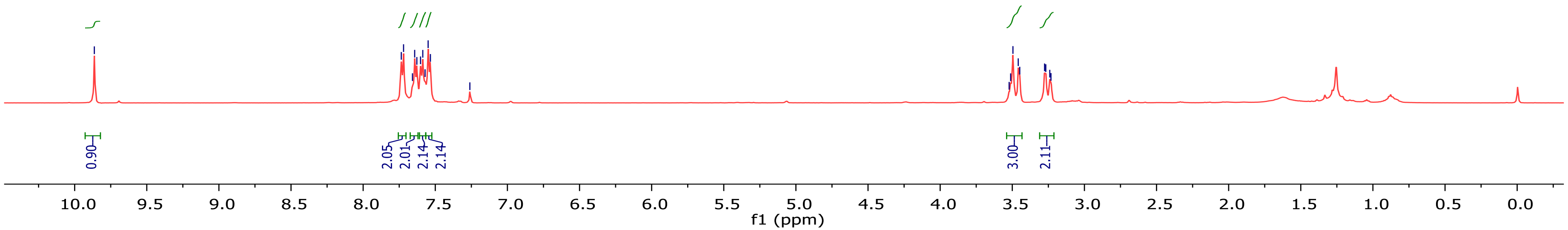
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3o



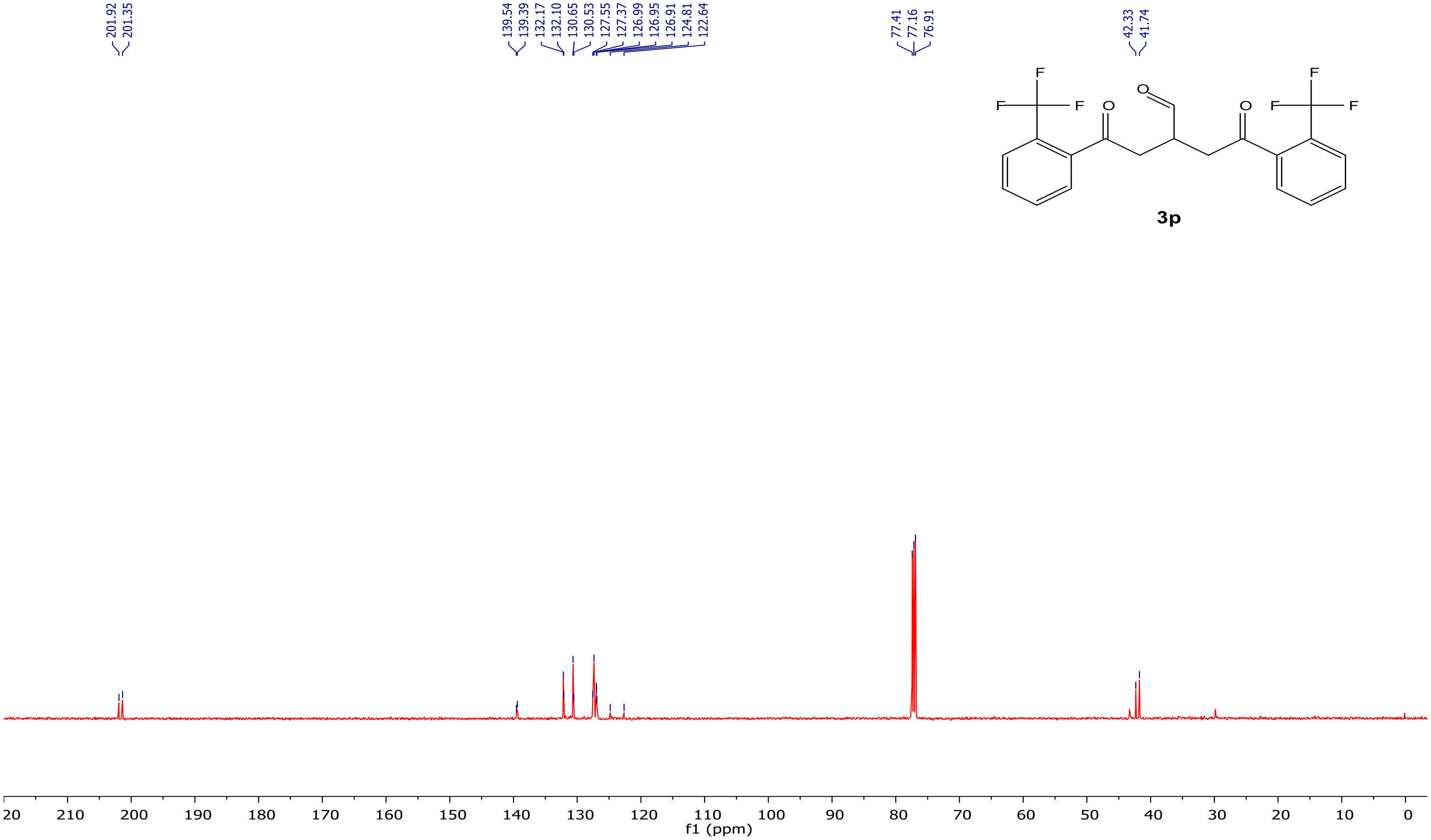
[1]H NMR (500 MHz, $CDCl_3$) of 3p



3p

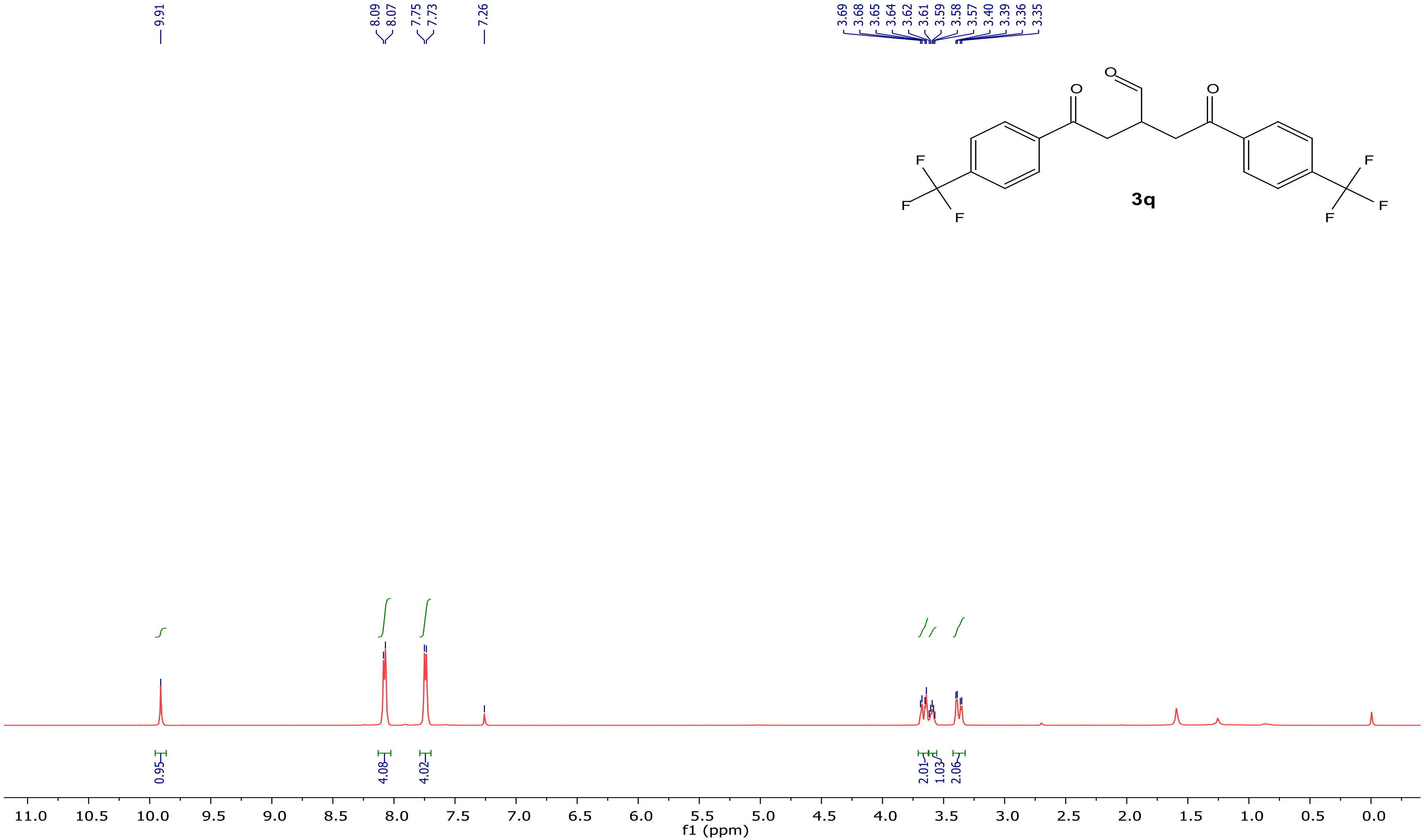


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3p

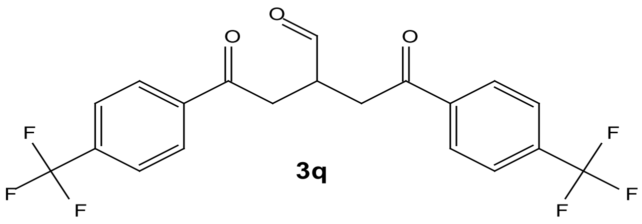


3p

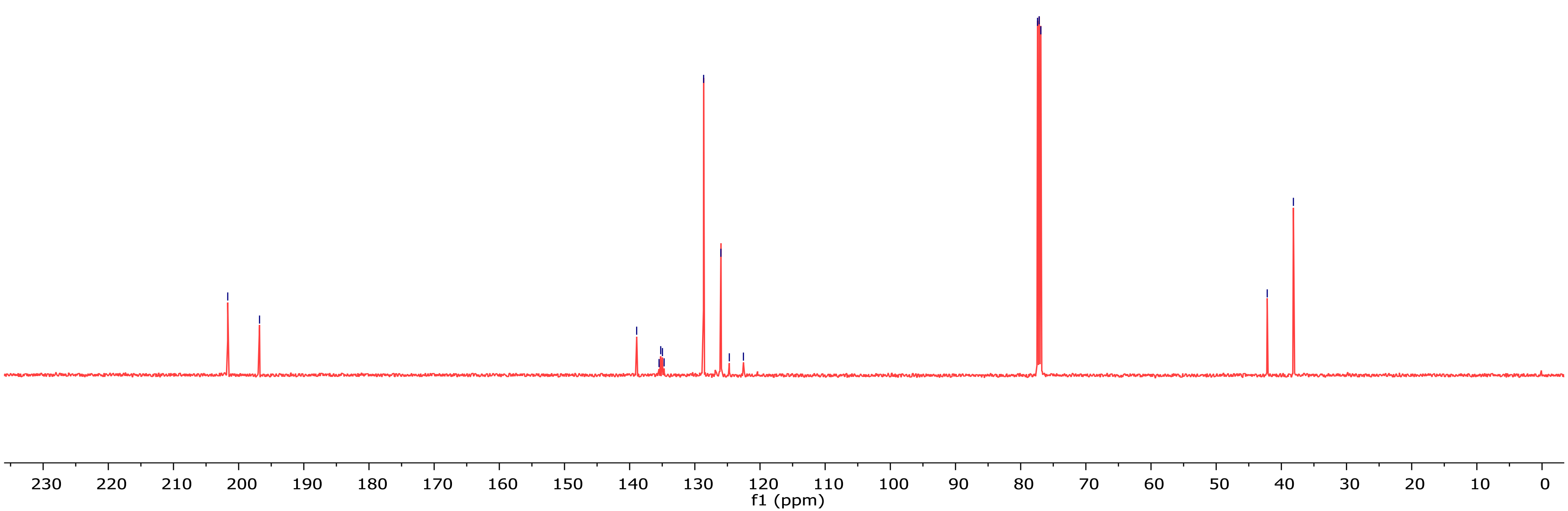
^{1}H NMR (500 MHz, $CDCl_3$) of 3q



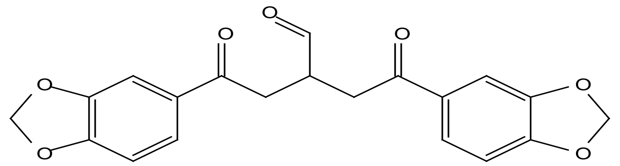
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3q



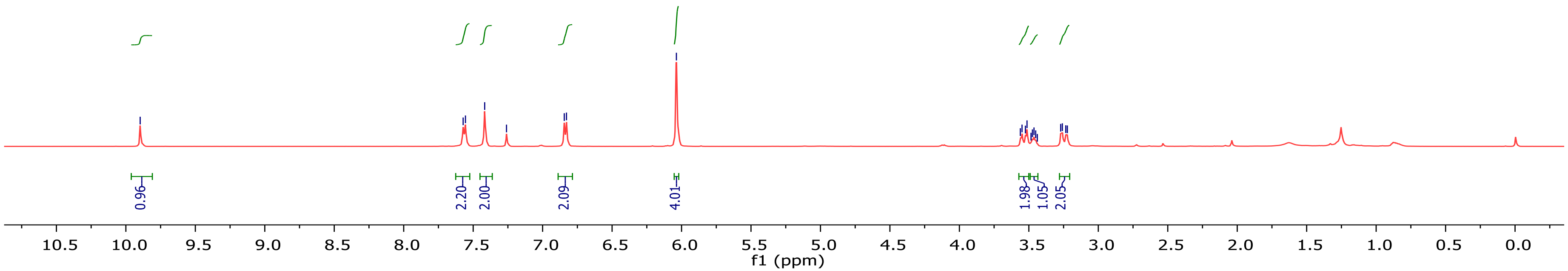
3q



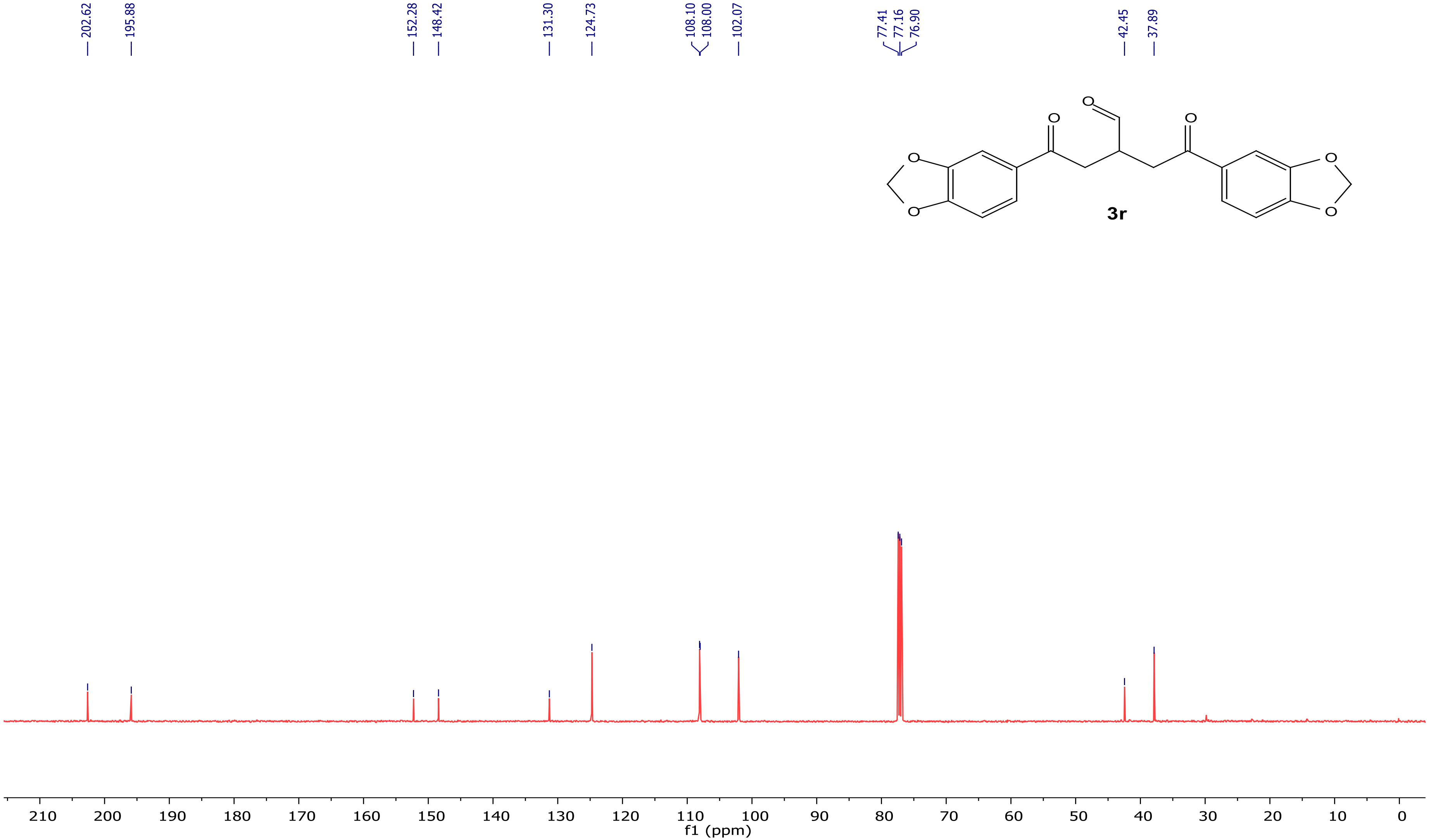
^{1}H NMR (500 MHz, $CDCl_3$) of 3r



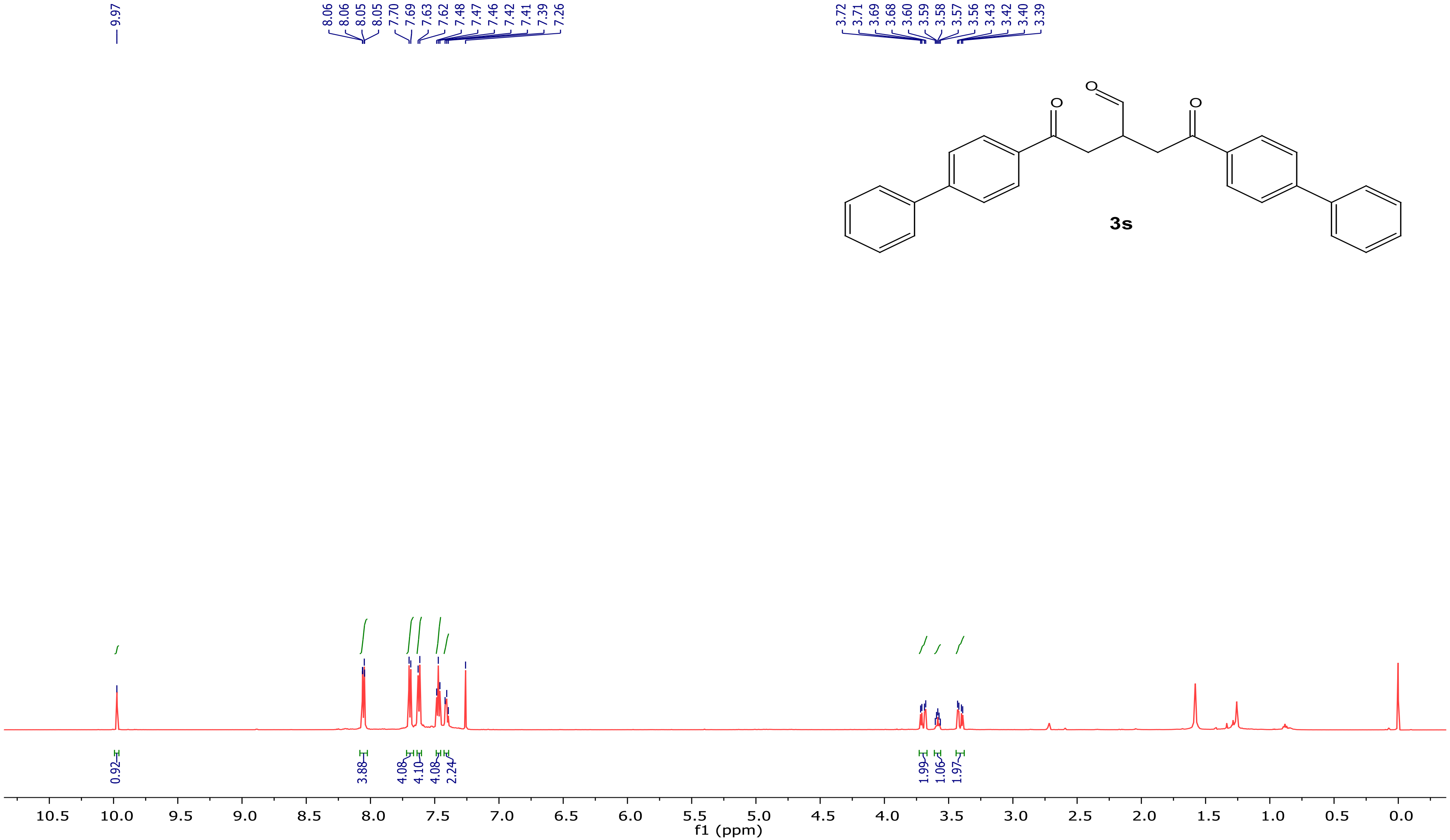
3r



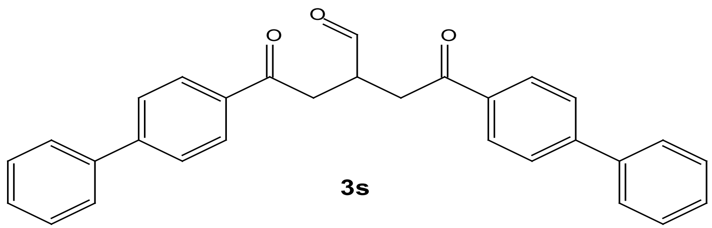
$^{13}C\{^{1}H\}$ NMR (126 MHz, CDCl$_3$) of 3r



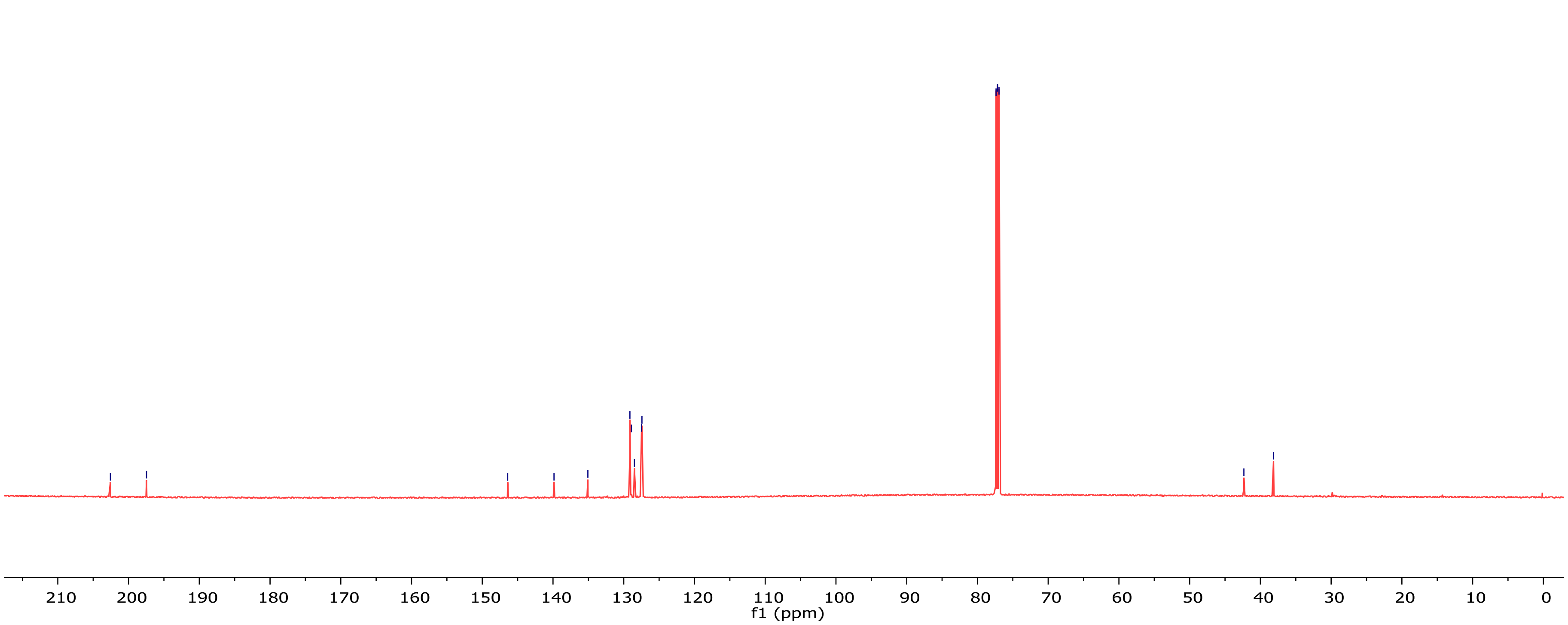
[1]H NMR (600 MHz, CDCl$_3$) of 3s



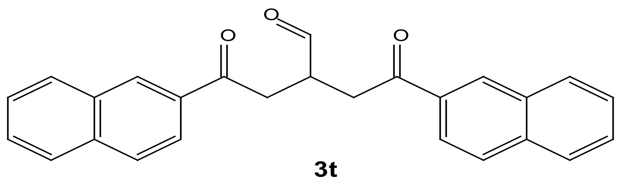
$^{13}C\{^1H\}$ **NMR (151 MHz, $CDCl_3$) of 3s**



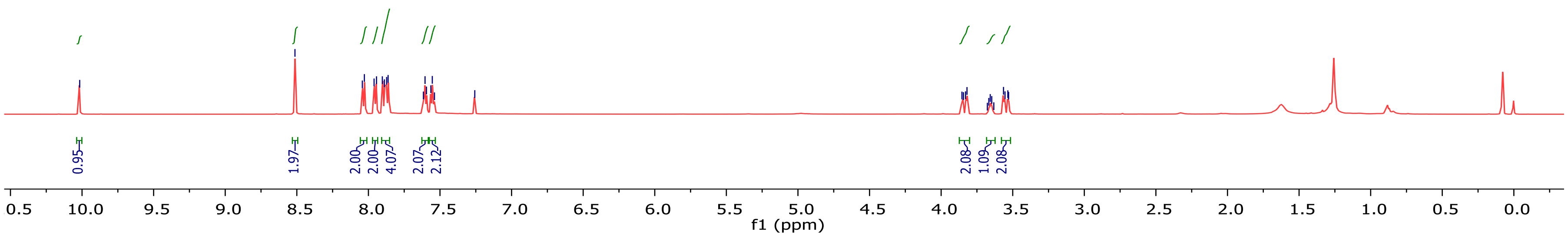
3s



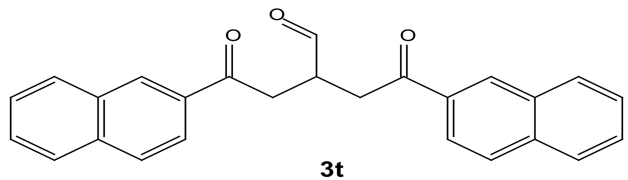
^{1}H NMR (600 MHz, CDCl$_3$) of 3t



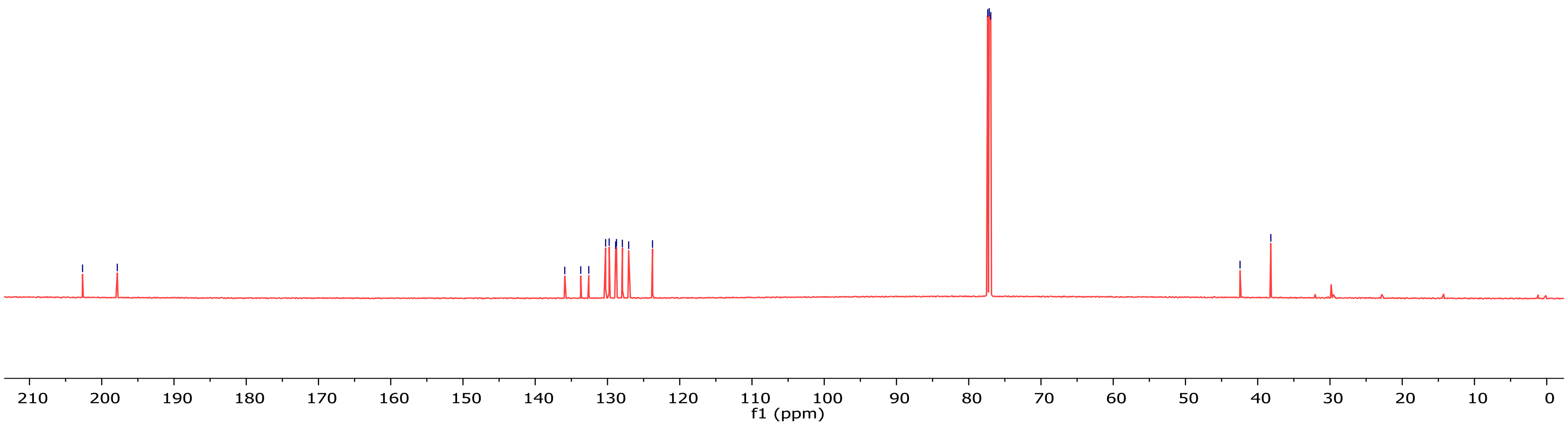
3t



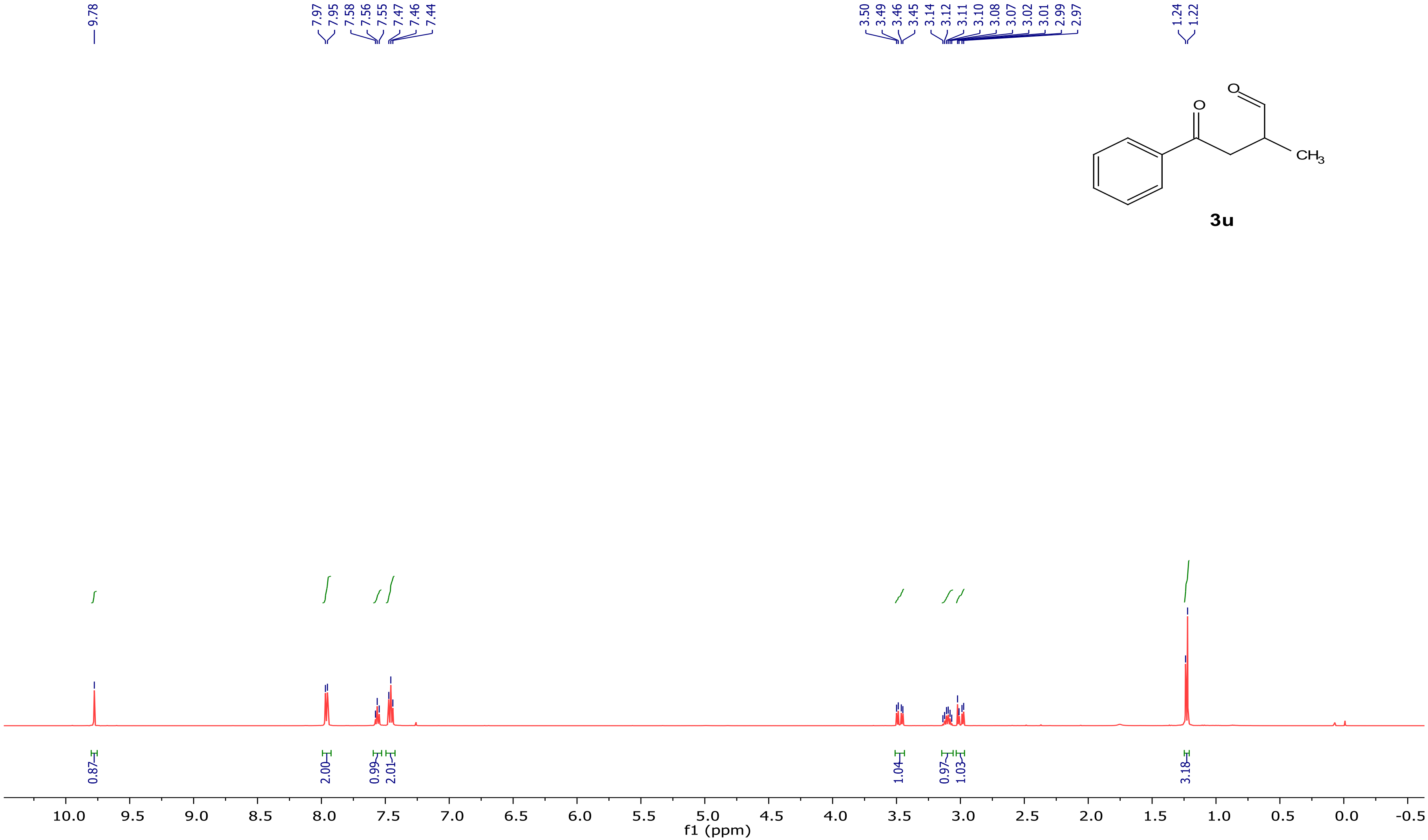
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) of 3t



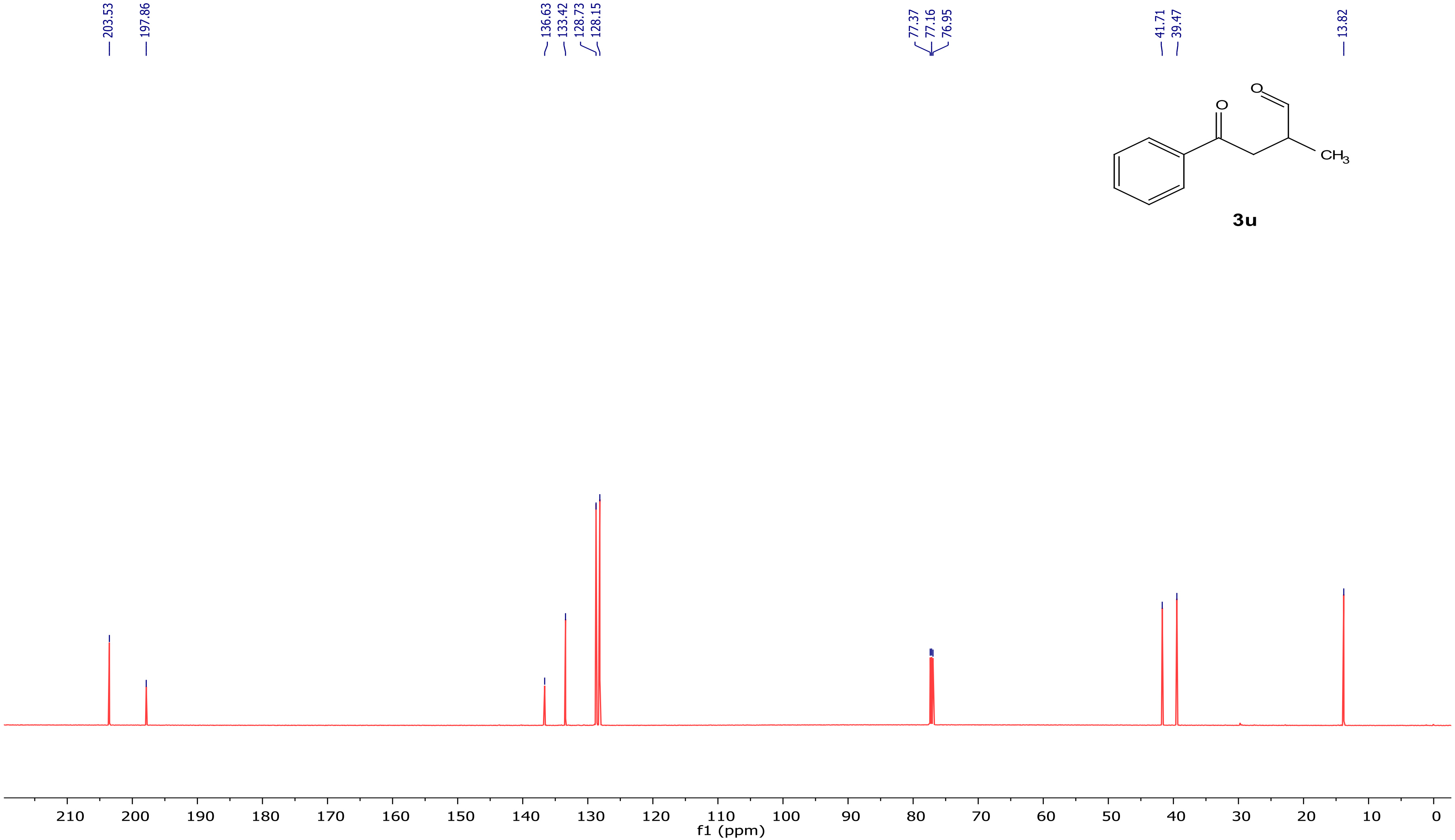
3t



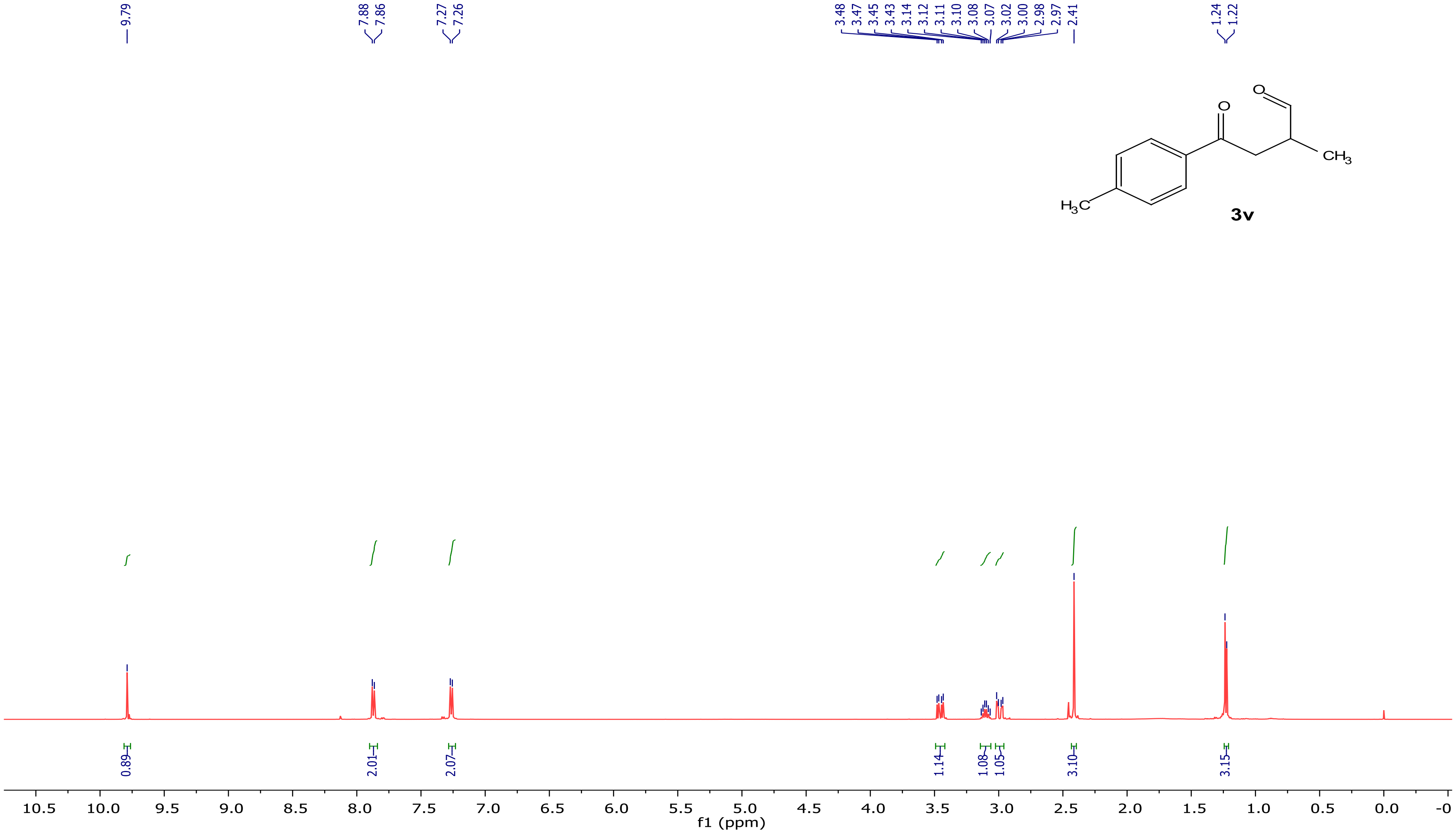
^{1}H NMR (500 MHz, $CDCl_3$) of 3u



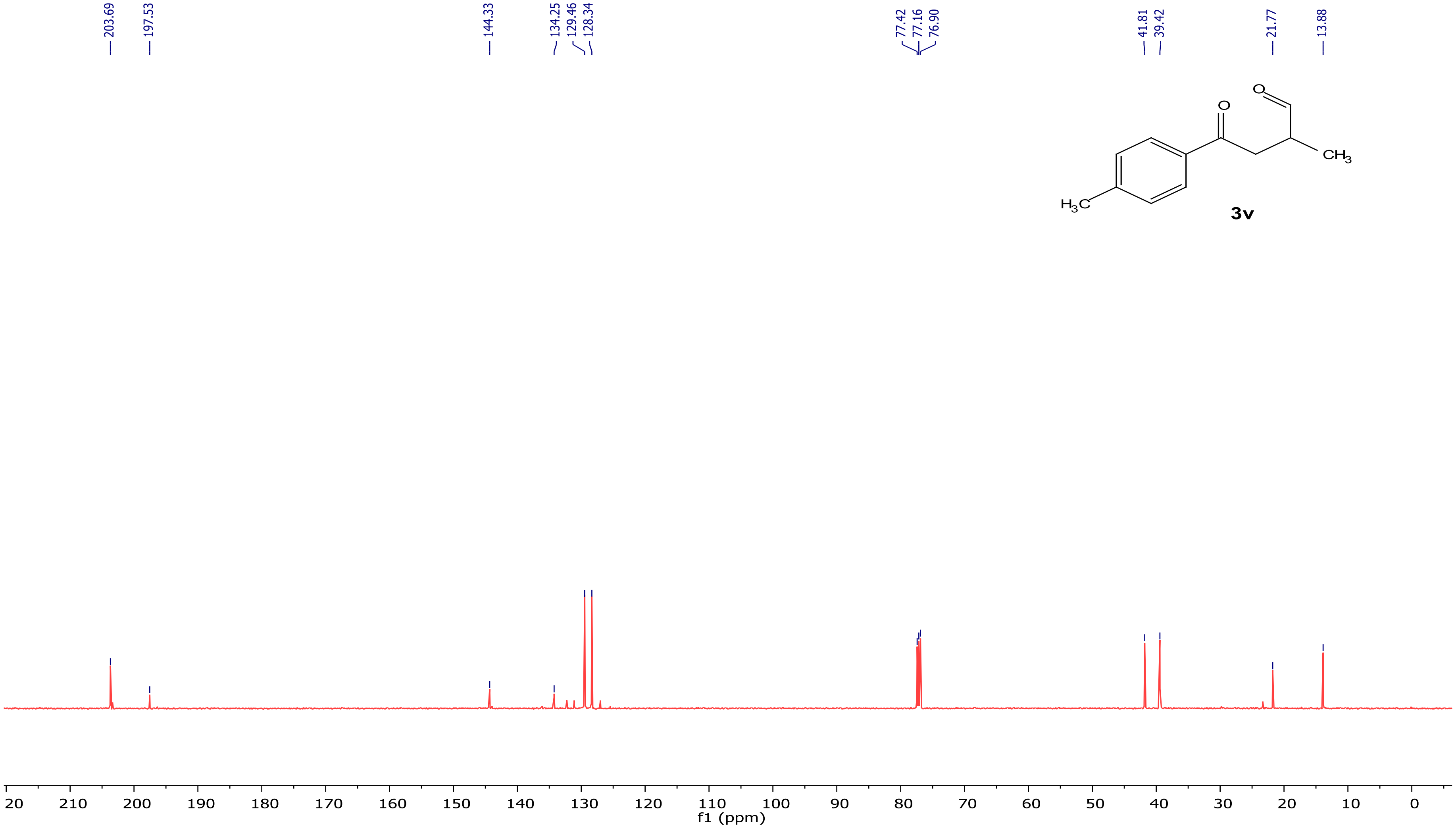
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3u



[1]H NMR (500 MHz, $CDCl_3$) of 3v



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3v



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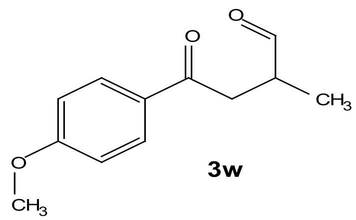
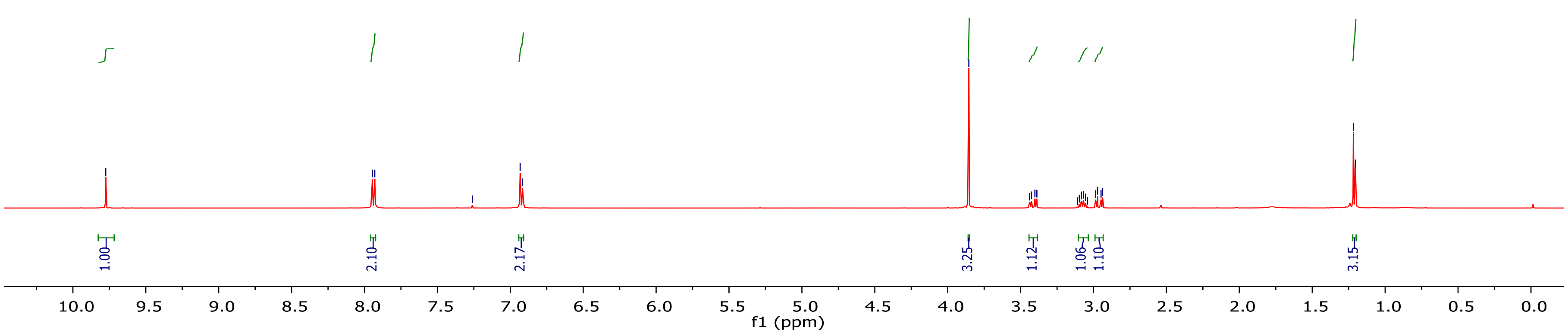
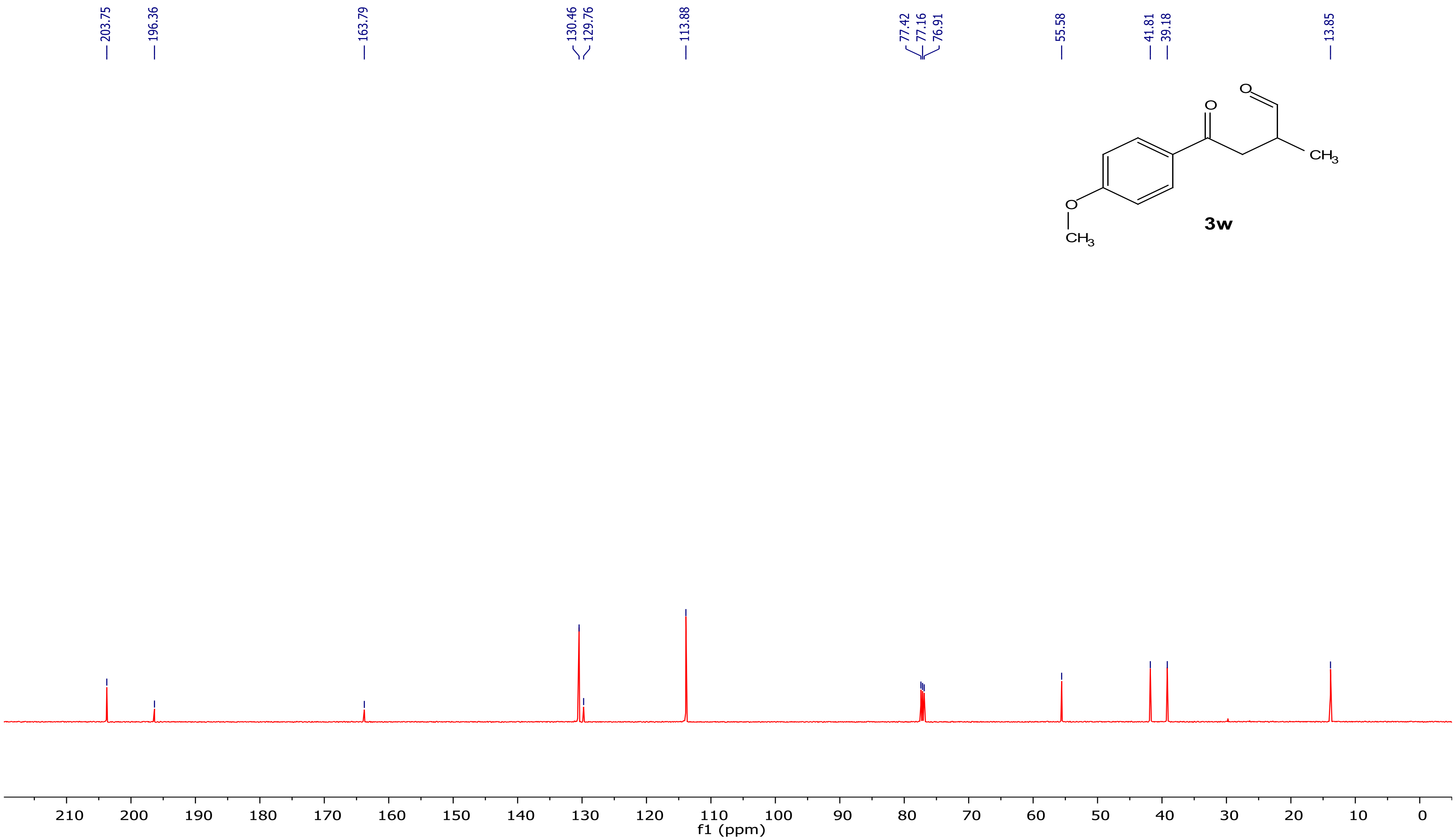
[1]H NMR (500 MHz, CDCl$_3$) of 3w



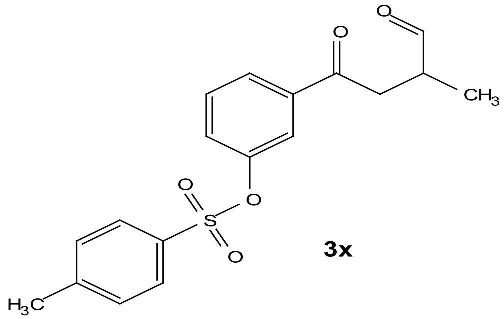
3w



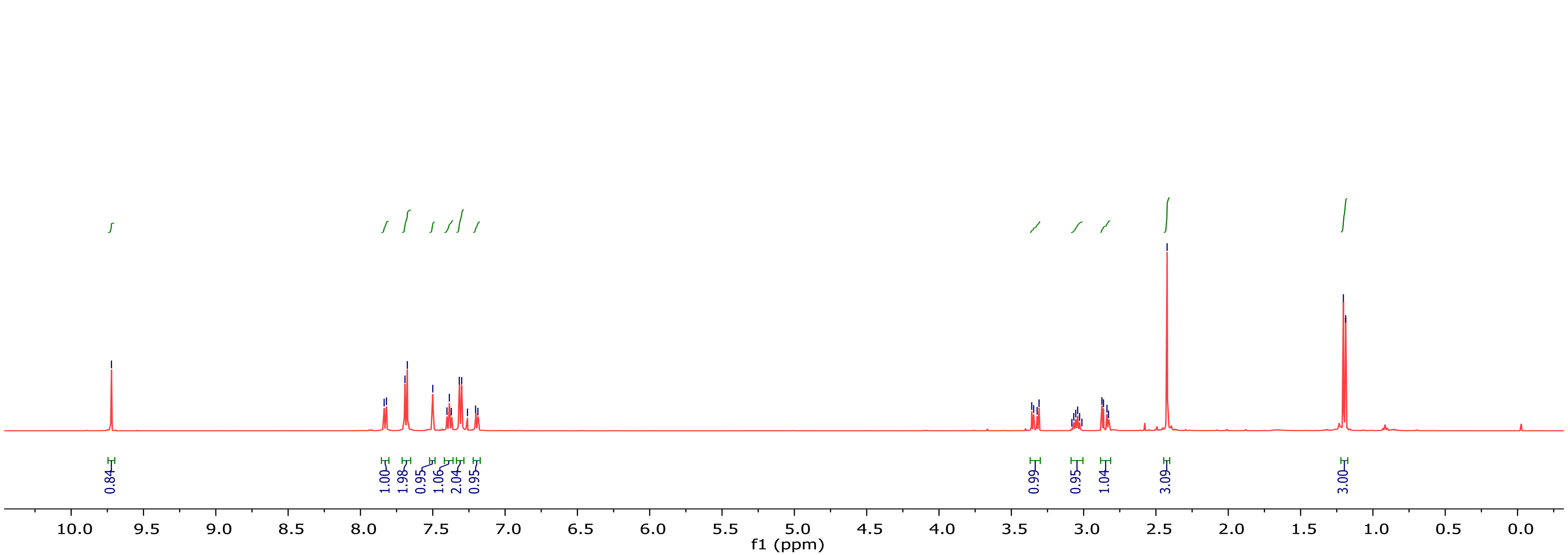
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3w



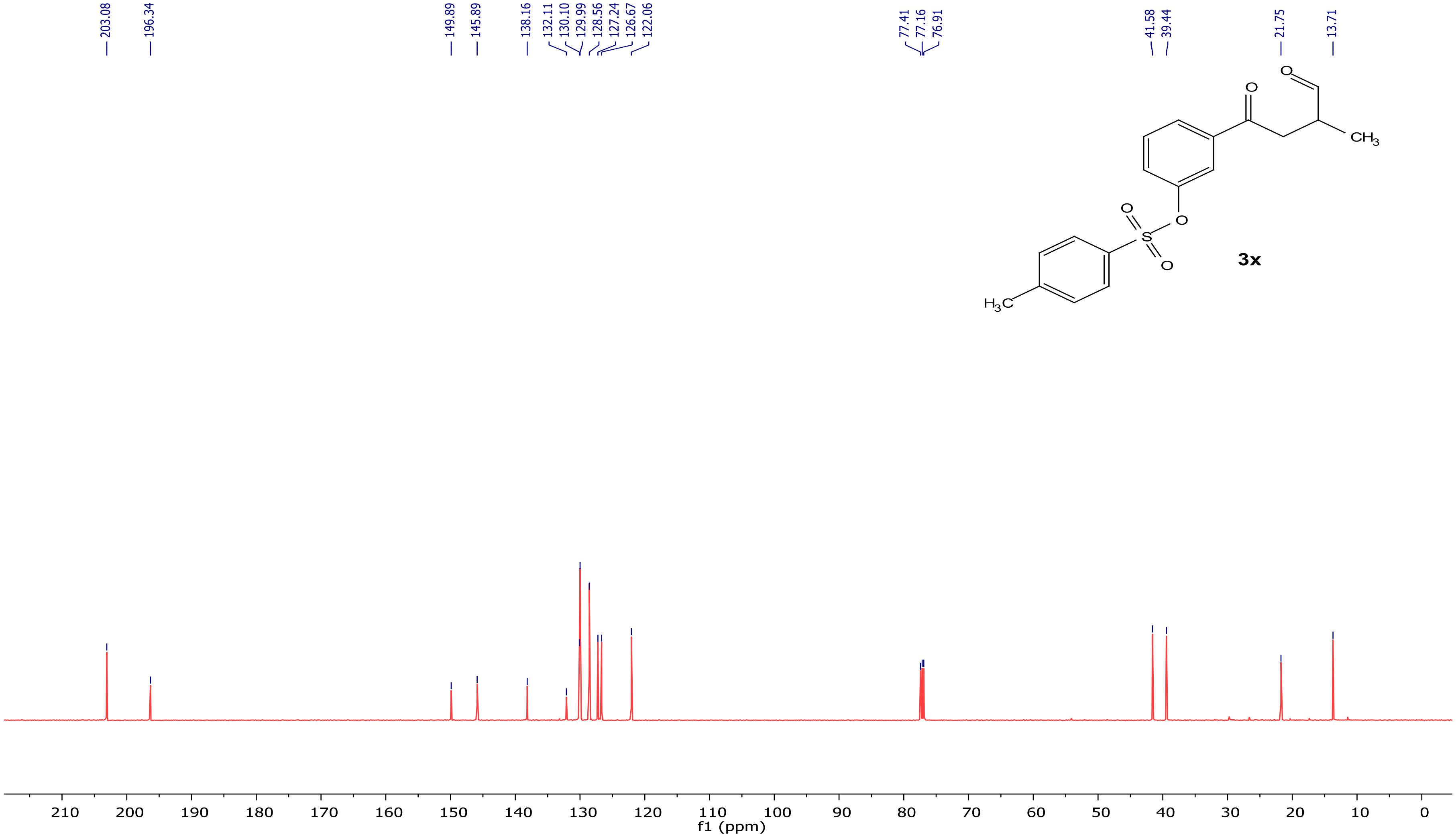
^{1}H NMR (500 MHz, $CDCl_3$) of 3x



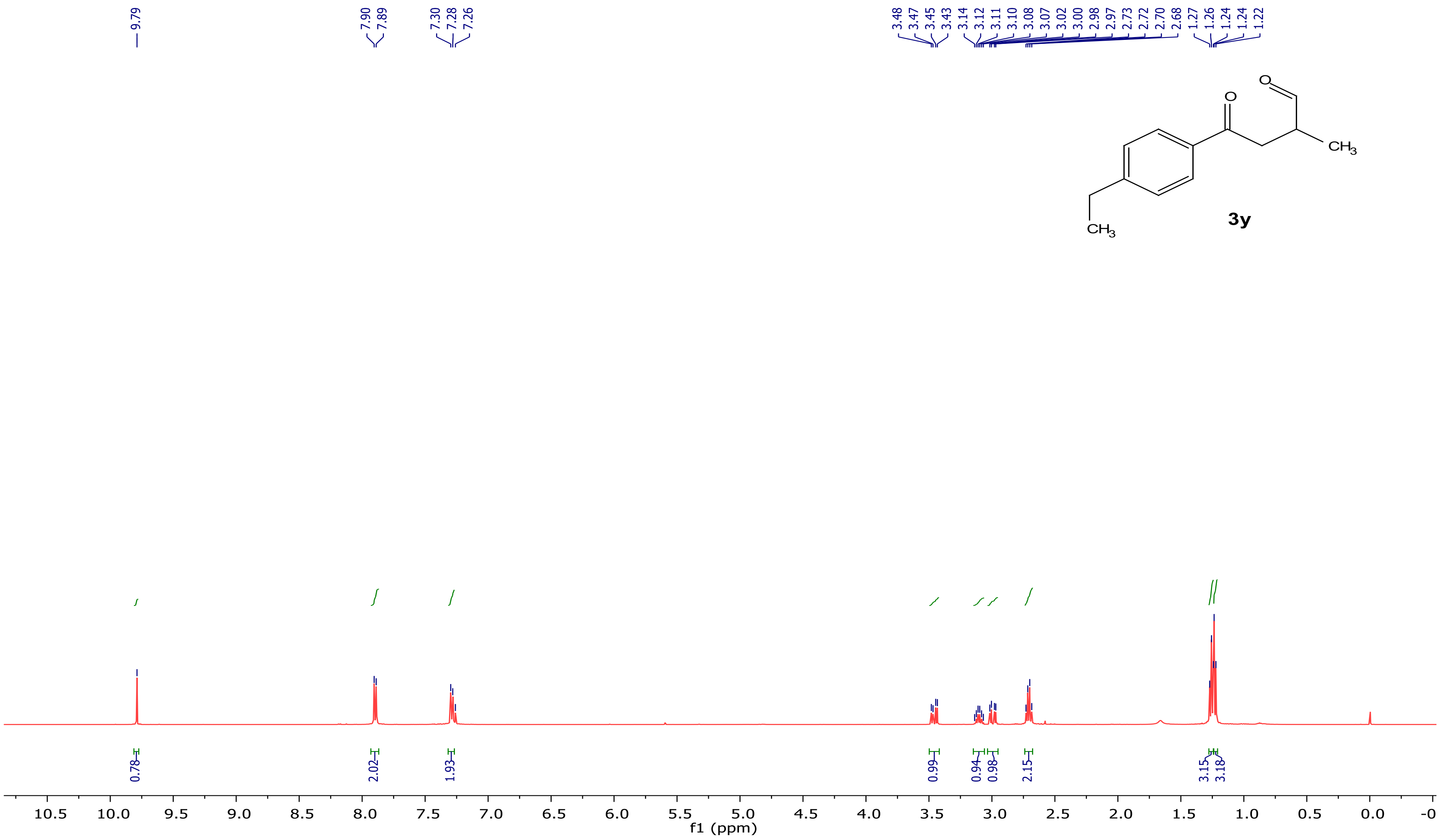
3x



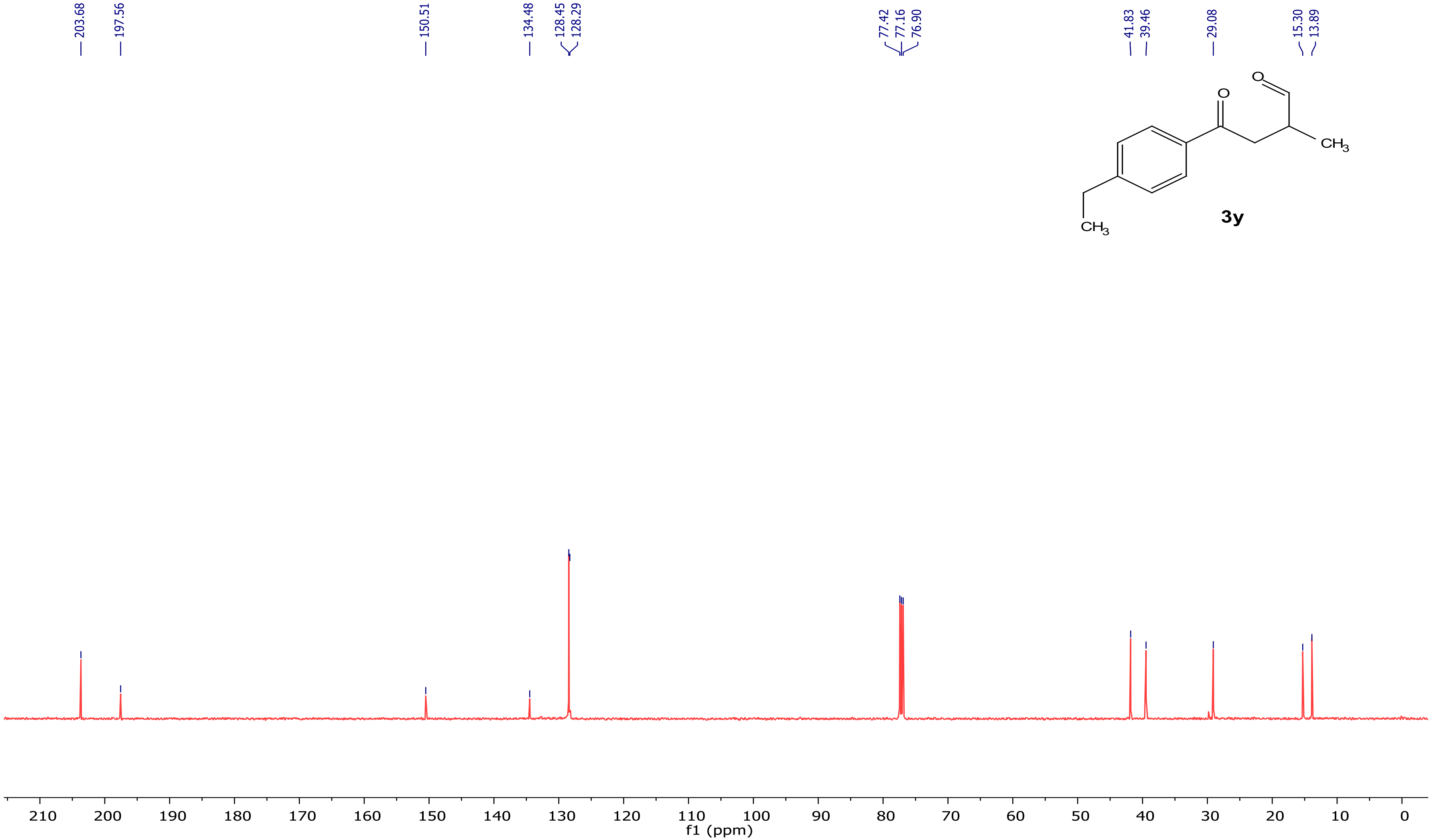
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3x



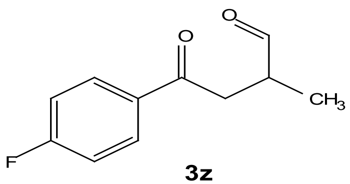
[1]H NMR (500 MHz, $CDCl_3$) of 3y



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3y



^{1}H NMR (500 MHz, $CDCl_3$) of 3z



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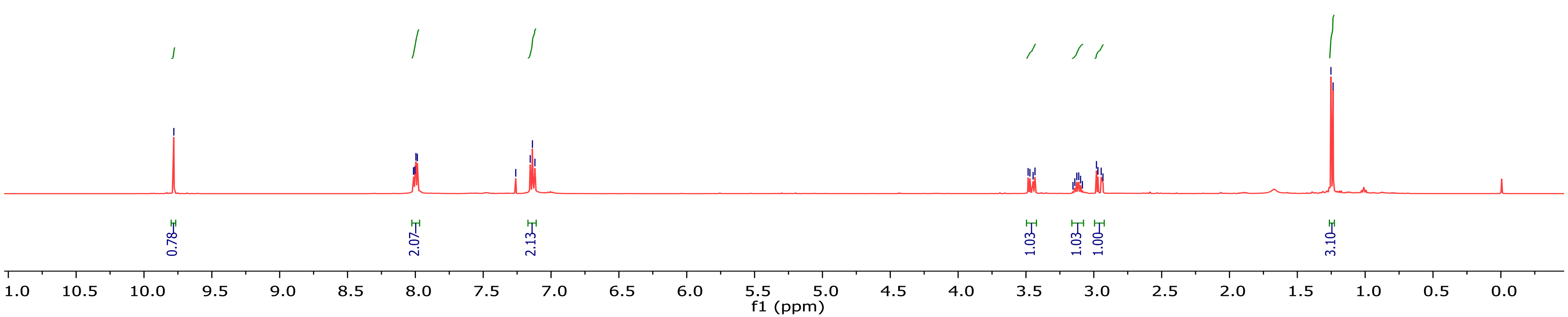
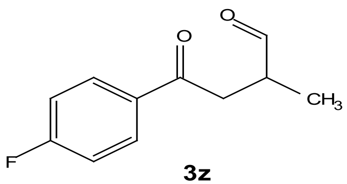


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3z



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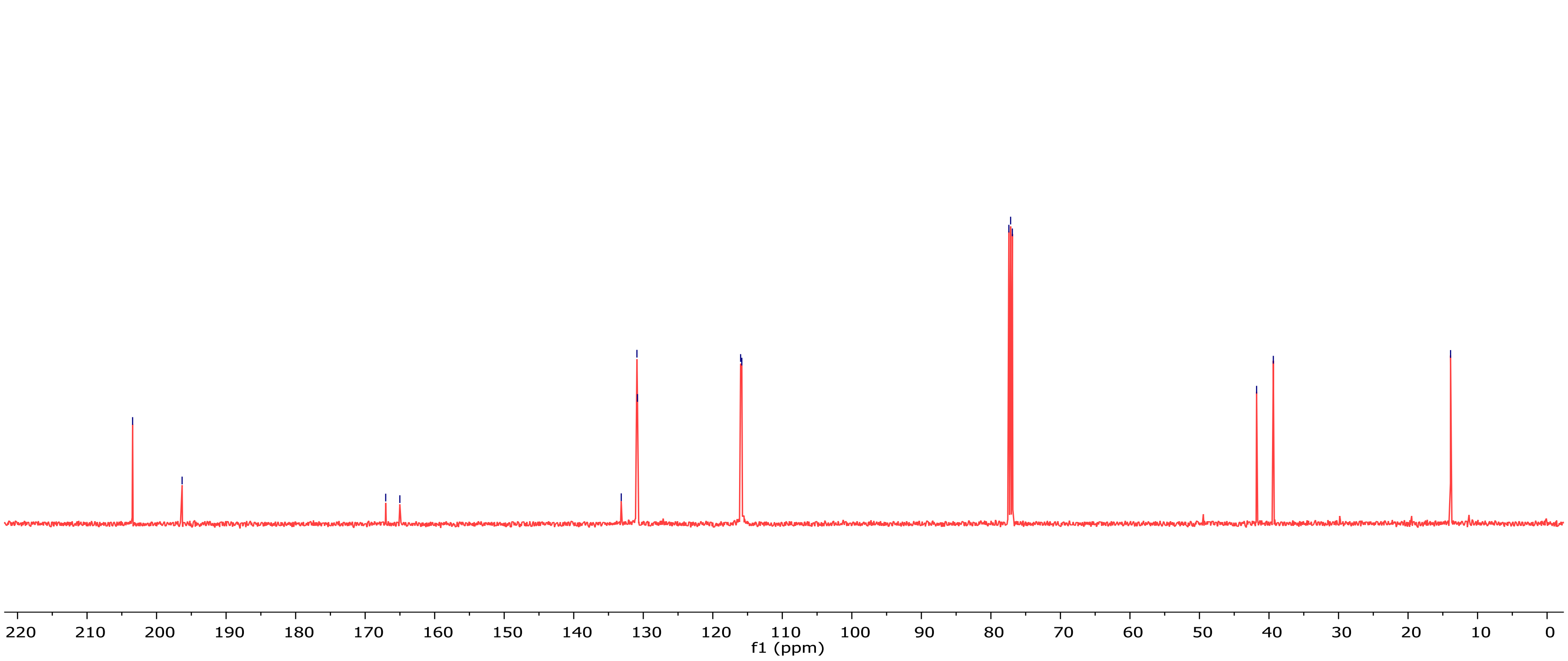
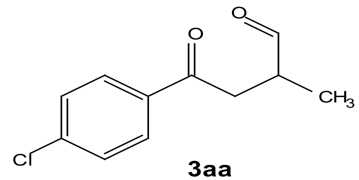
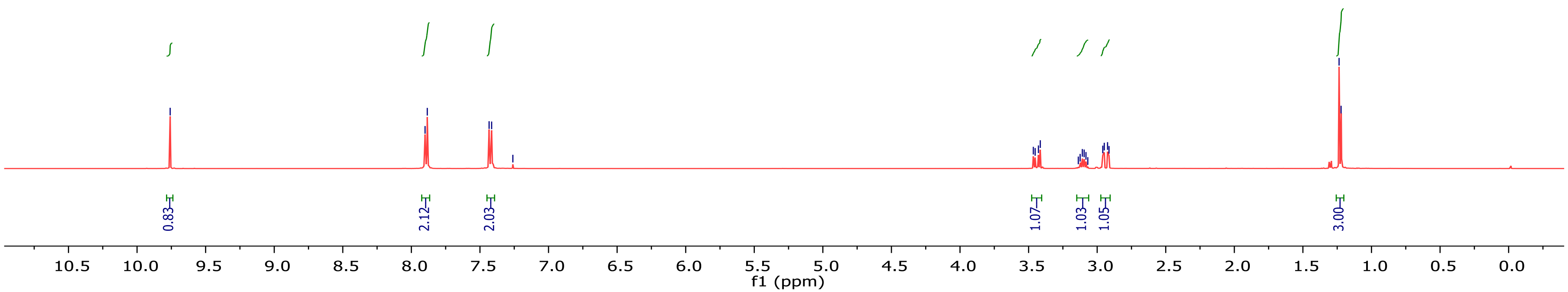


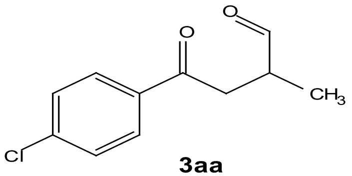
^{1}H NMR (500 MHz, $CDCl_3$) of 3aa



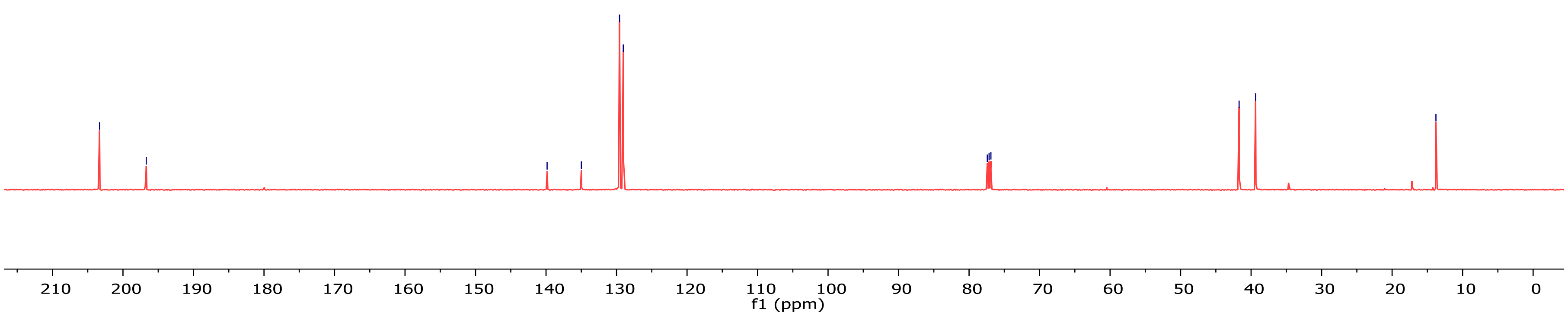
3aa



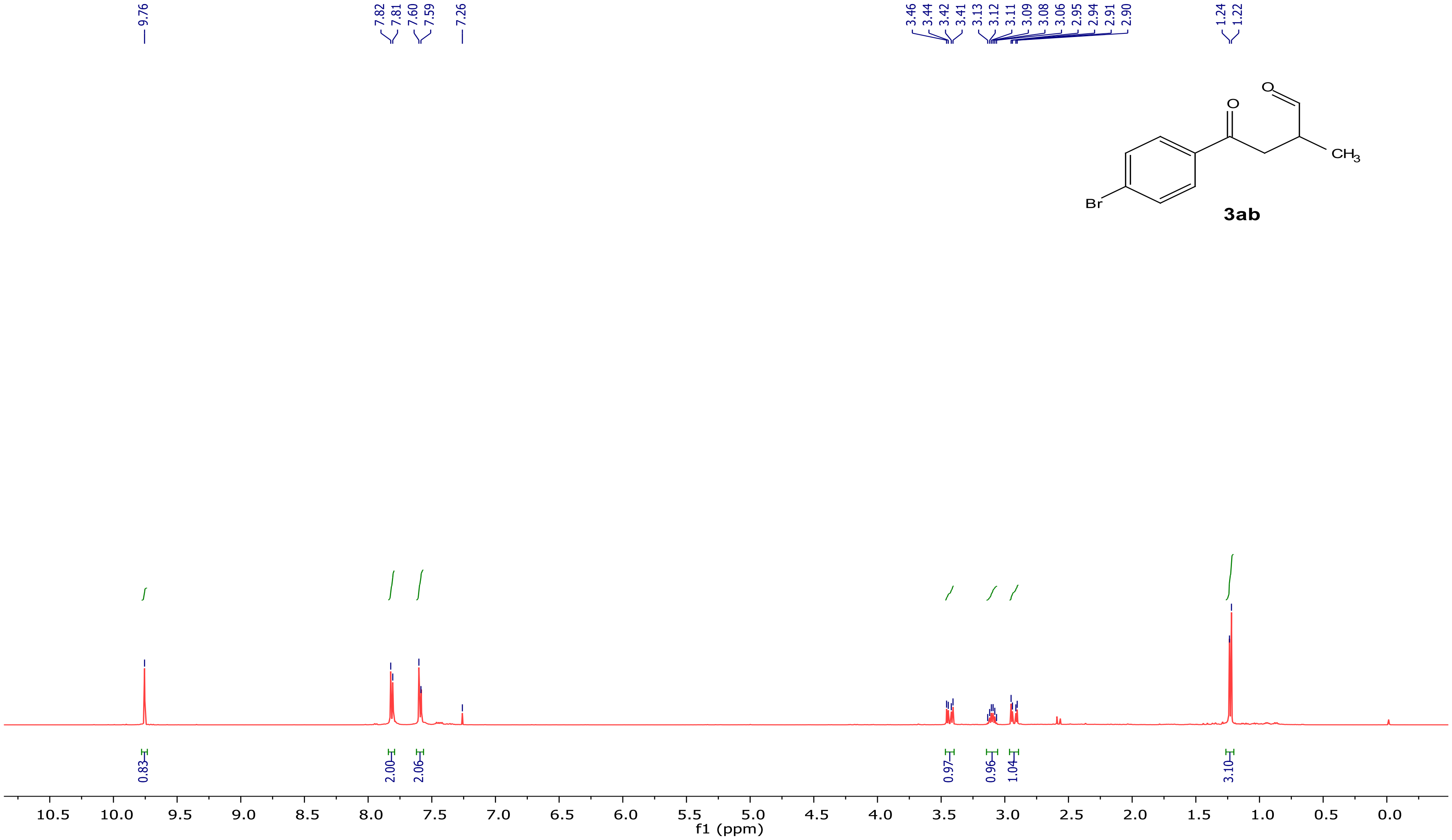
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3aa



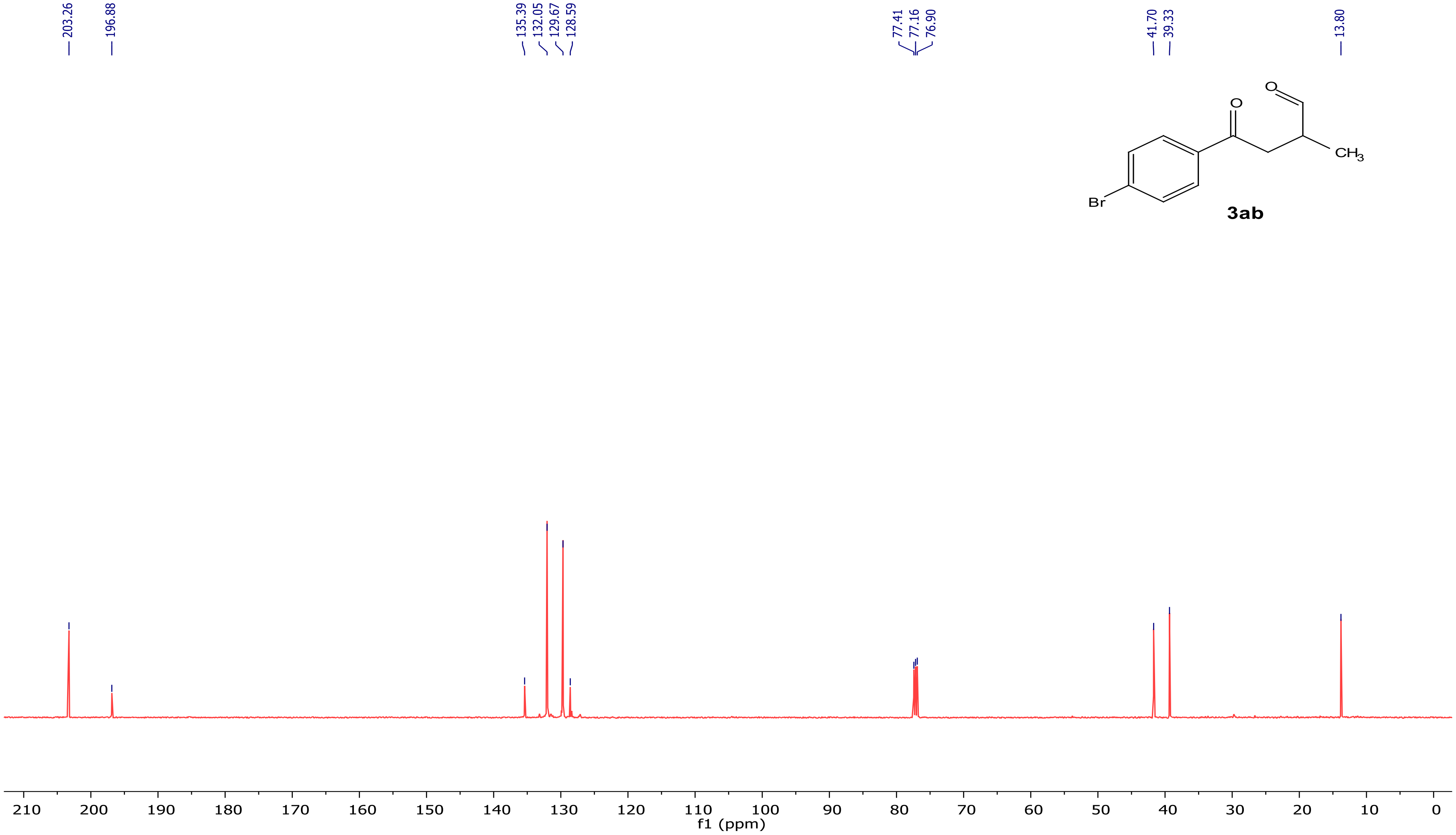
3aa



^{1}H NMR (500 MHz, $CDCl_3$) of 3ab

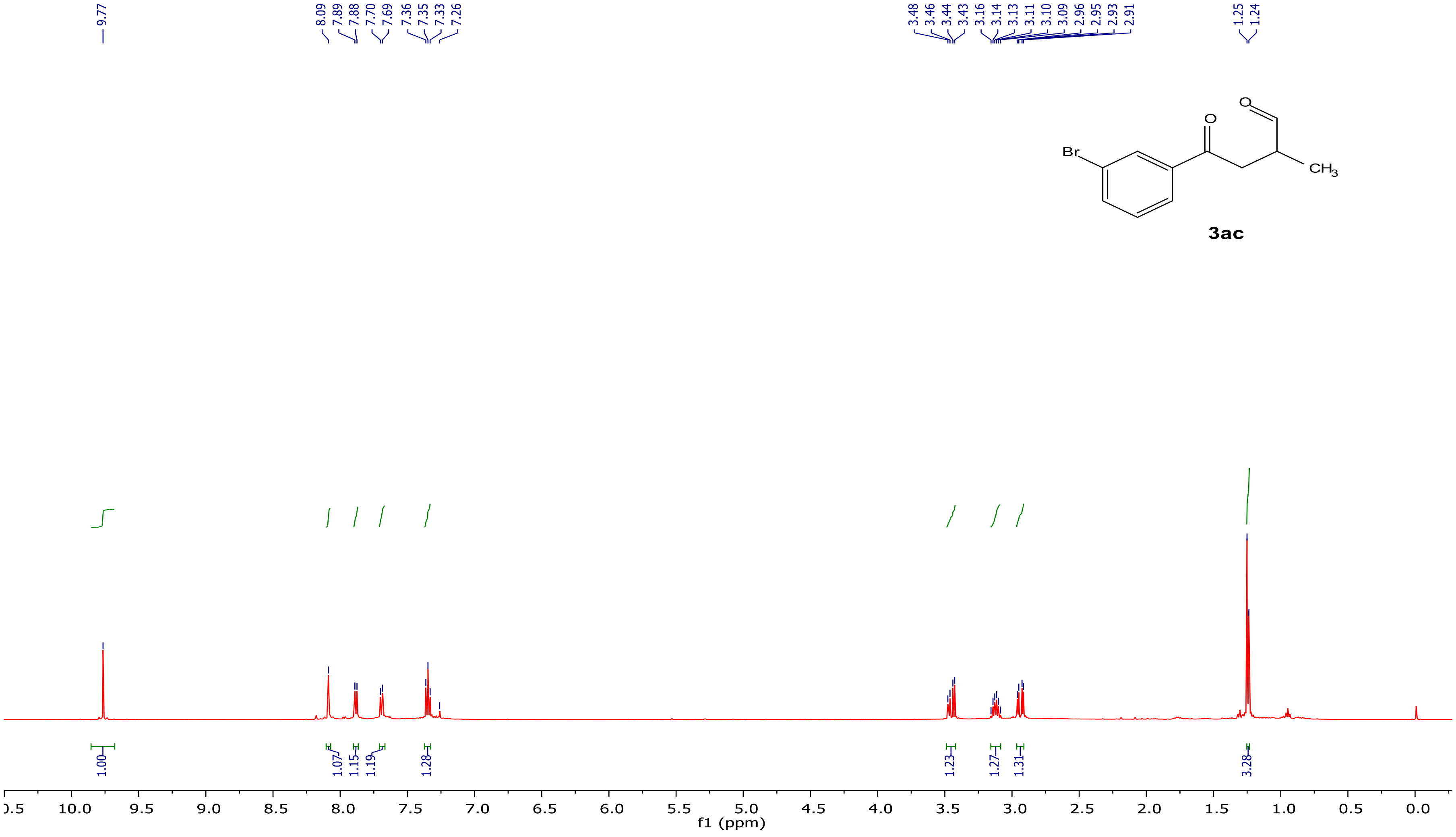


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3ab



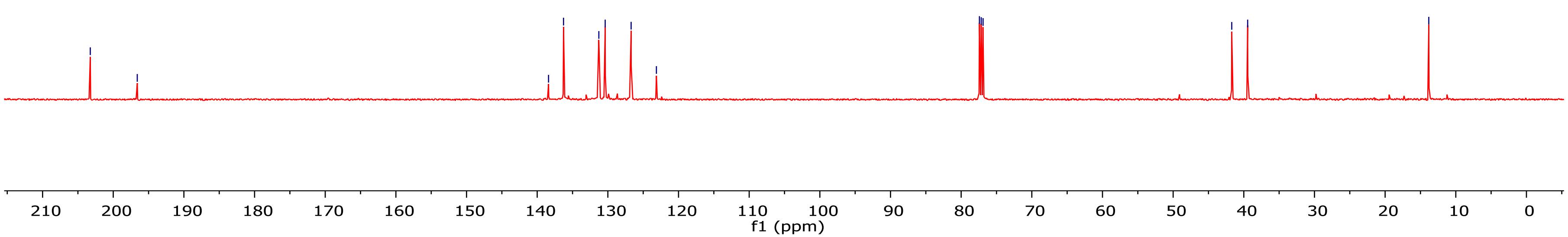
3ab

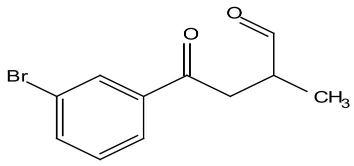
^{1}H NMR (500 MHz, $CDCl_3$) of 3ac



3ac

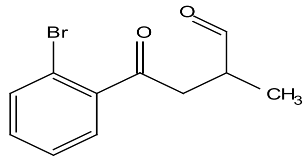
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3ac



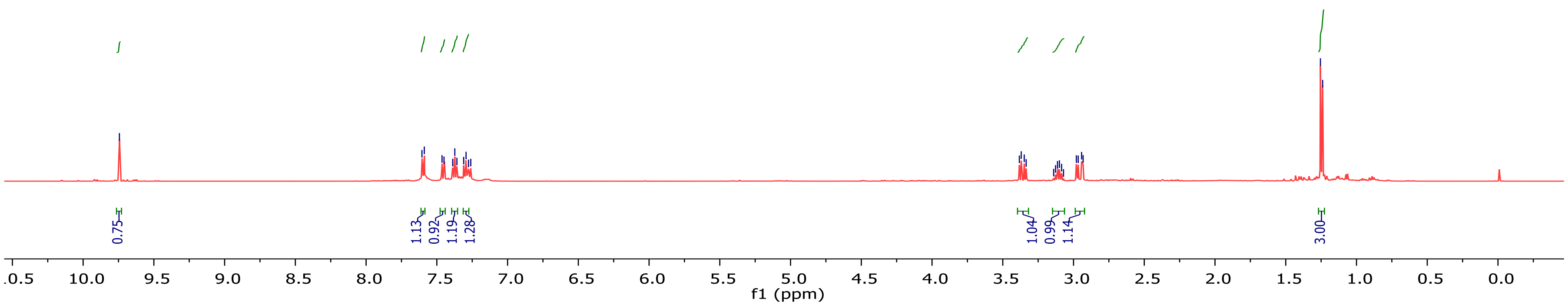


3ac

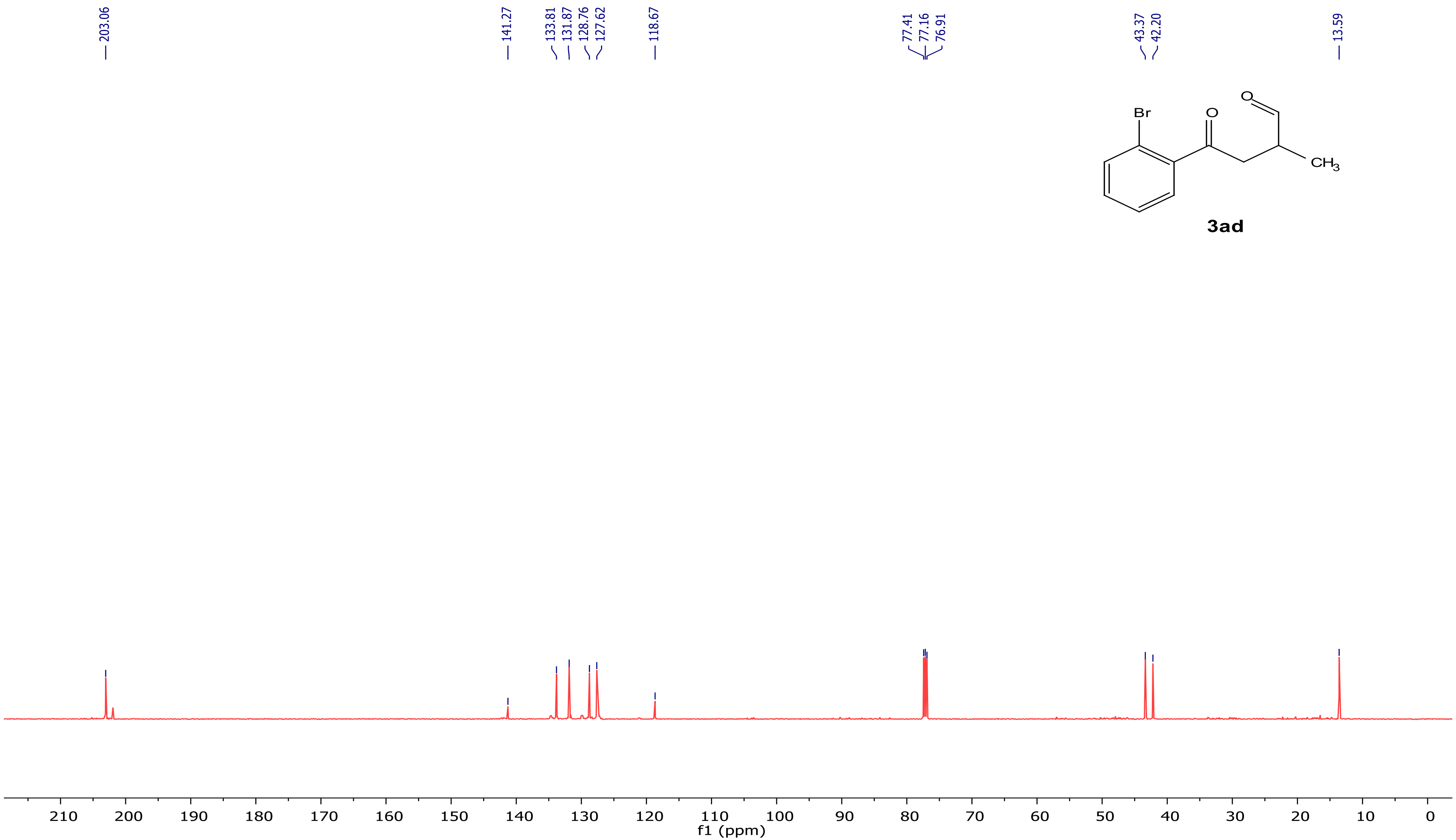
^{1}H NMR (500 MHz, CDCl$_3$) of 3ad



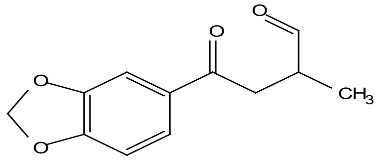
3ad



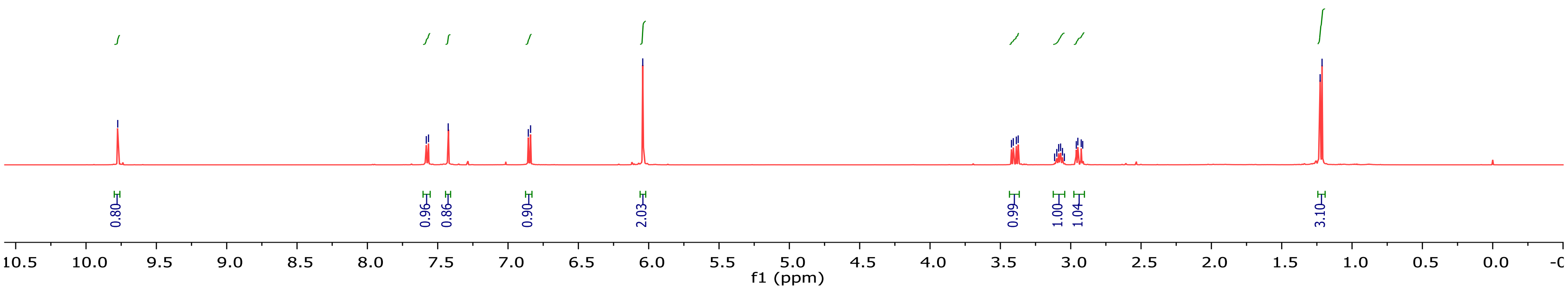
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3ad



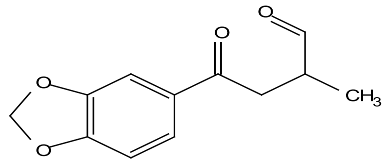
[1]H NMR (500 MHz, CDCl$_3$) of 3ae



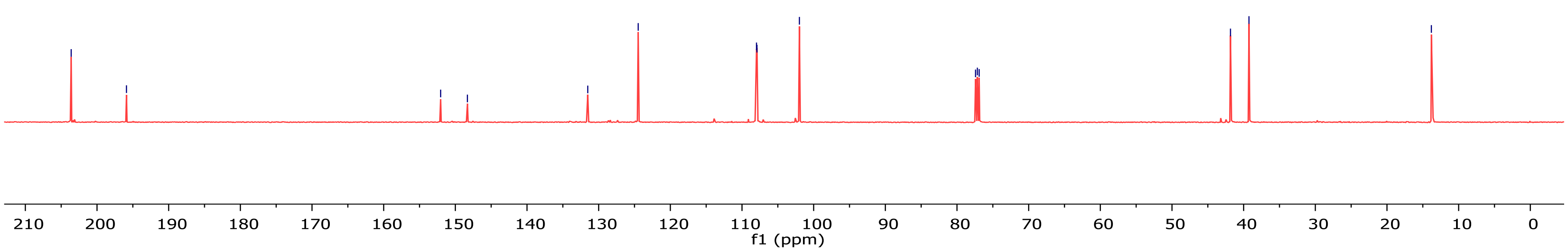
3ae



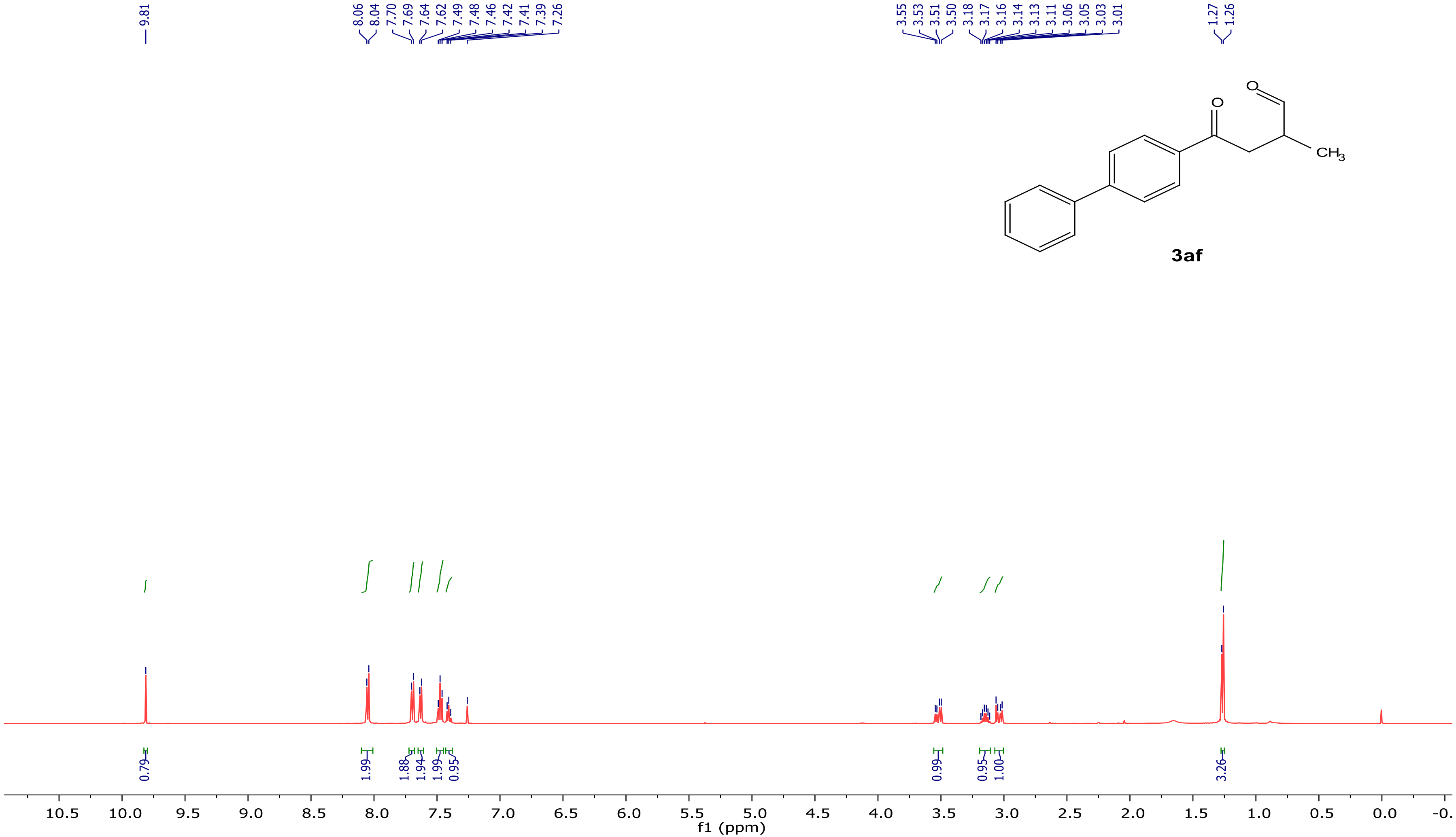
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3ae



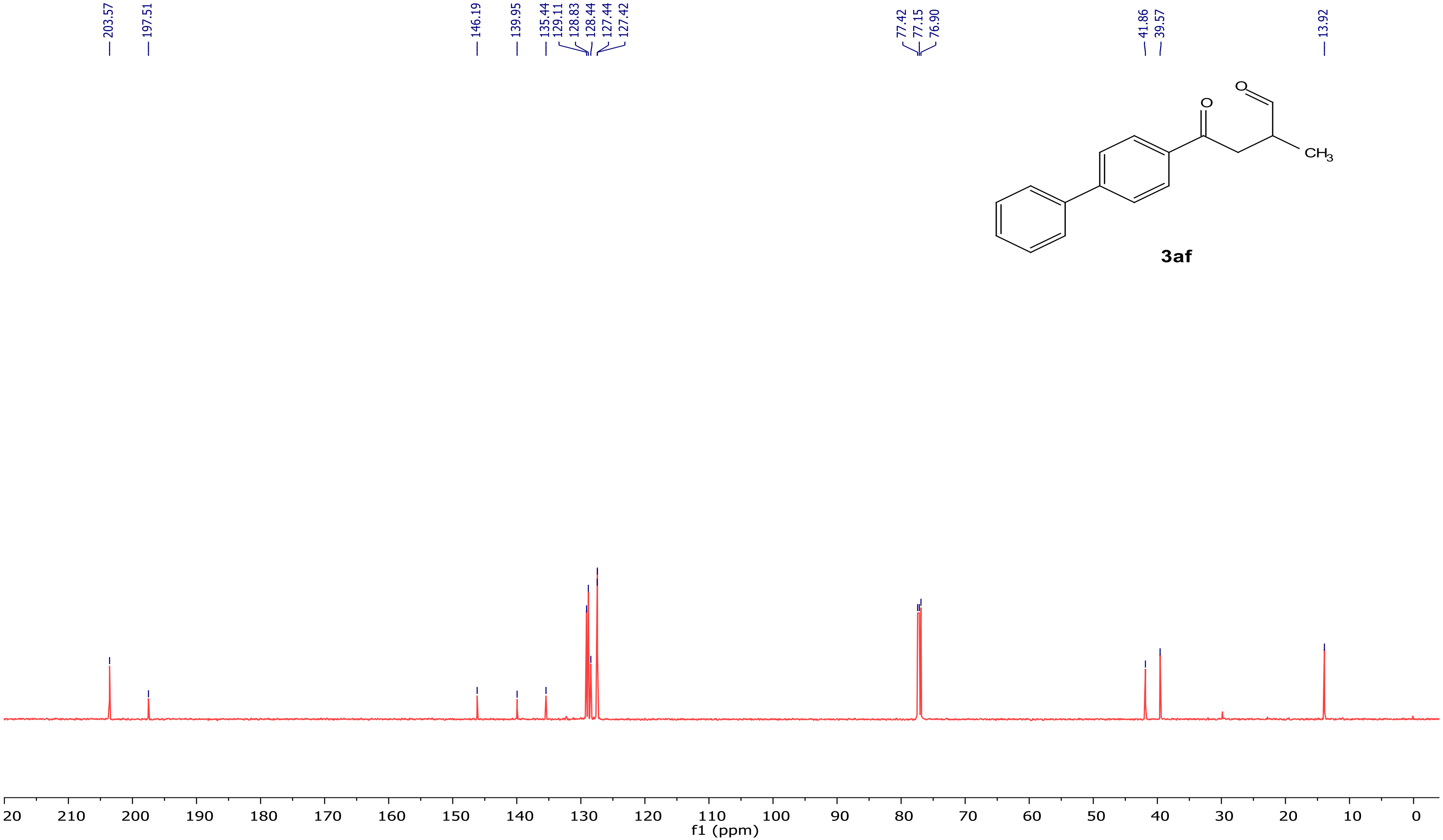
3ae



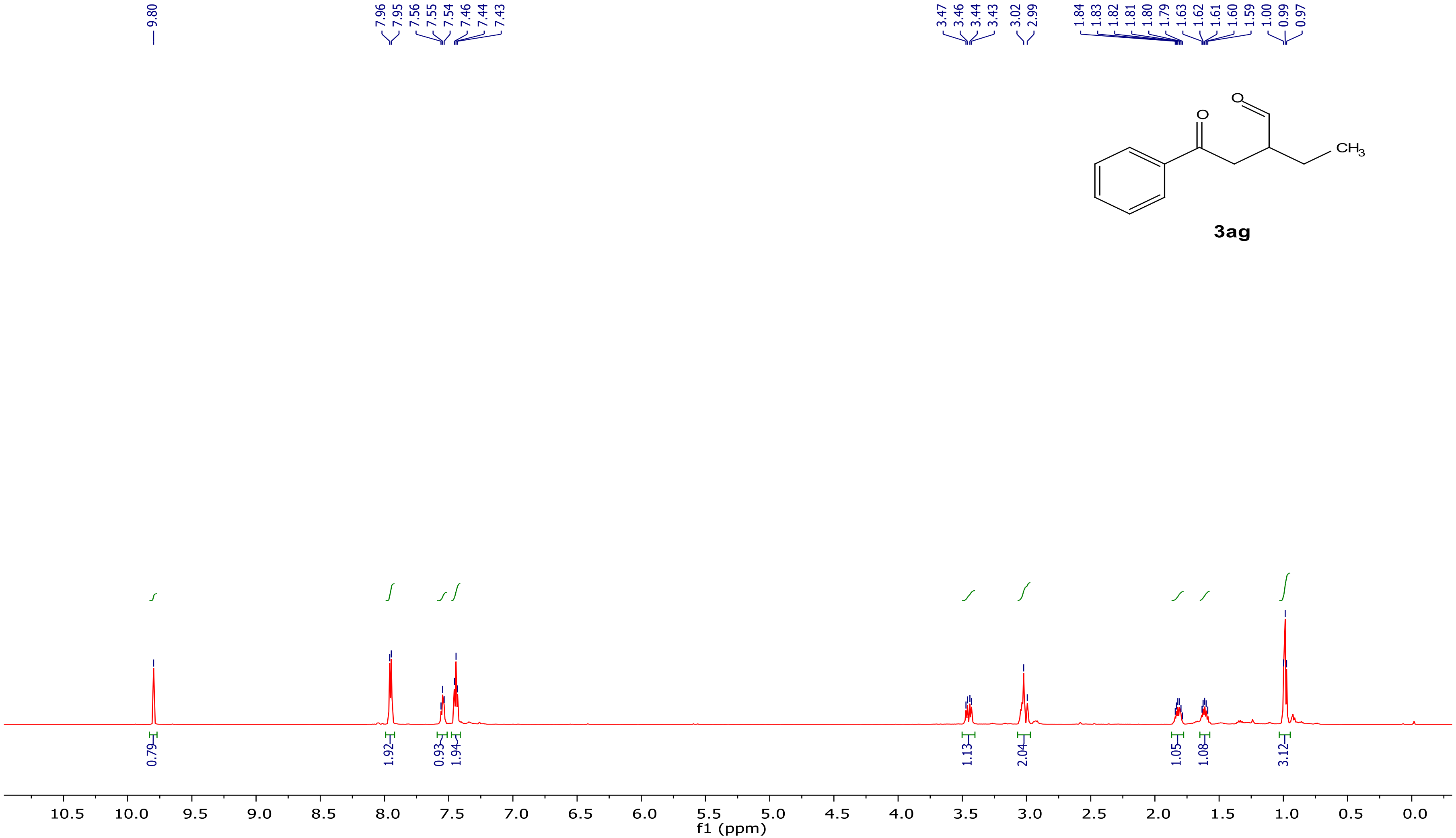
[1]H NMR (500 MHz, $CDCl_3$) of 3af



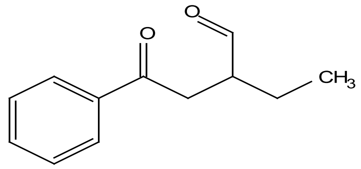
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3af



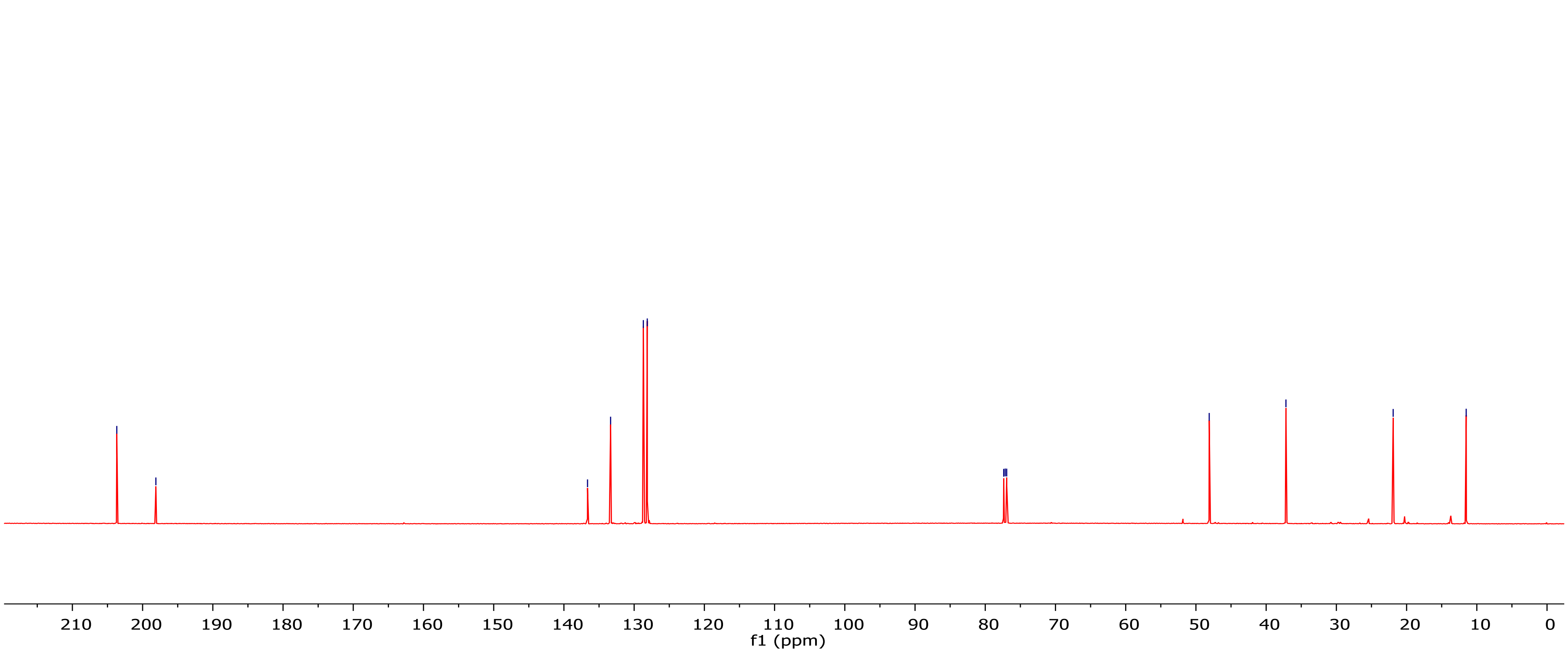
[1]H NMR (600 MHz, $CDCl_3$) of 3ag



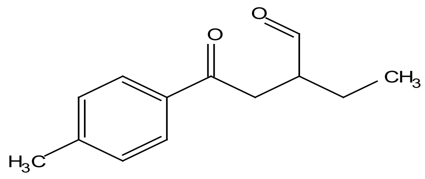
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of 3ag



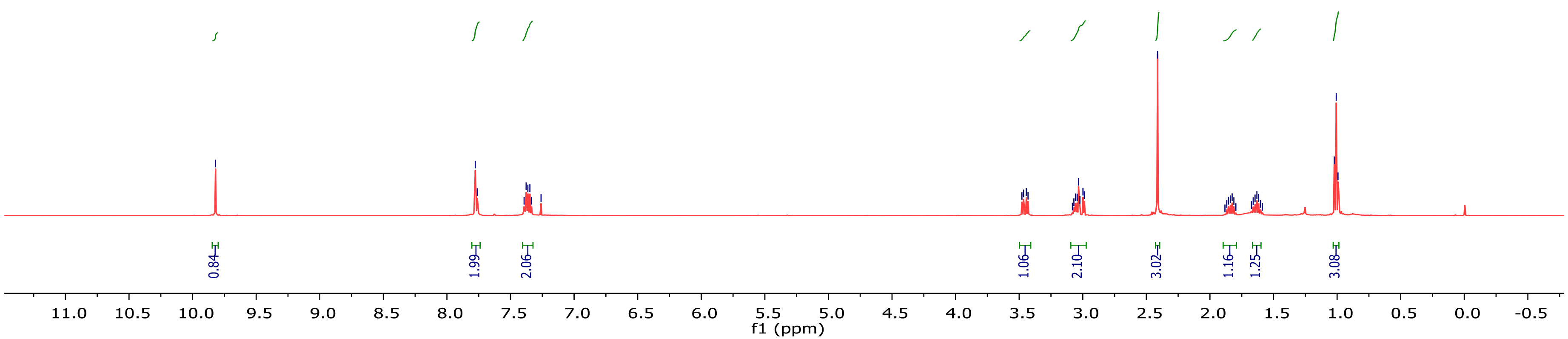
3ag



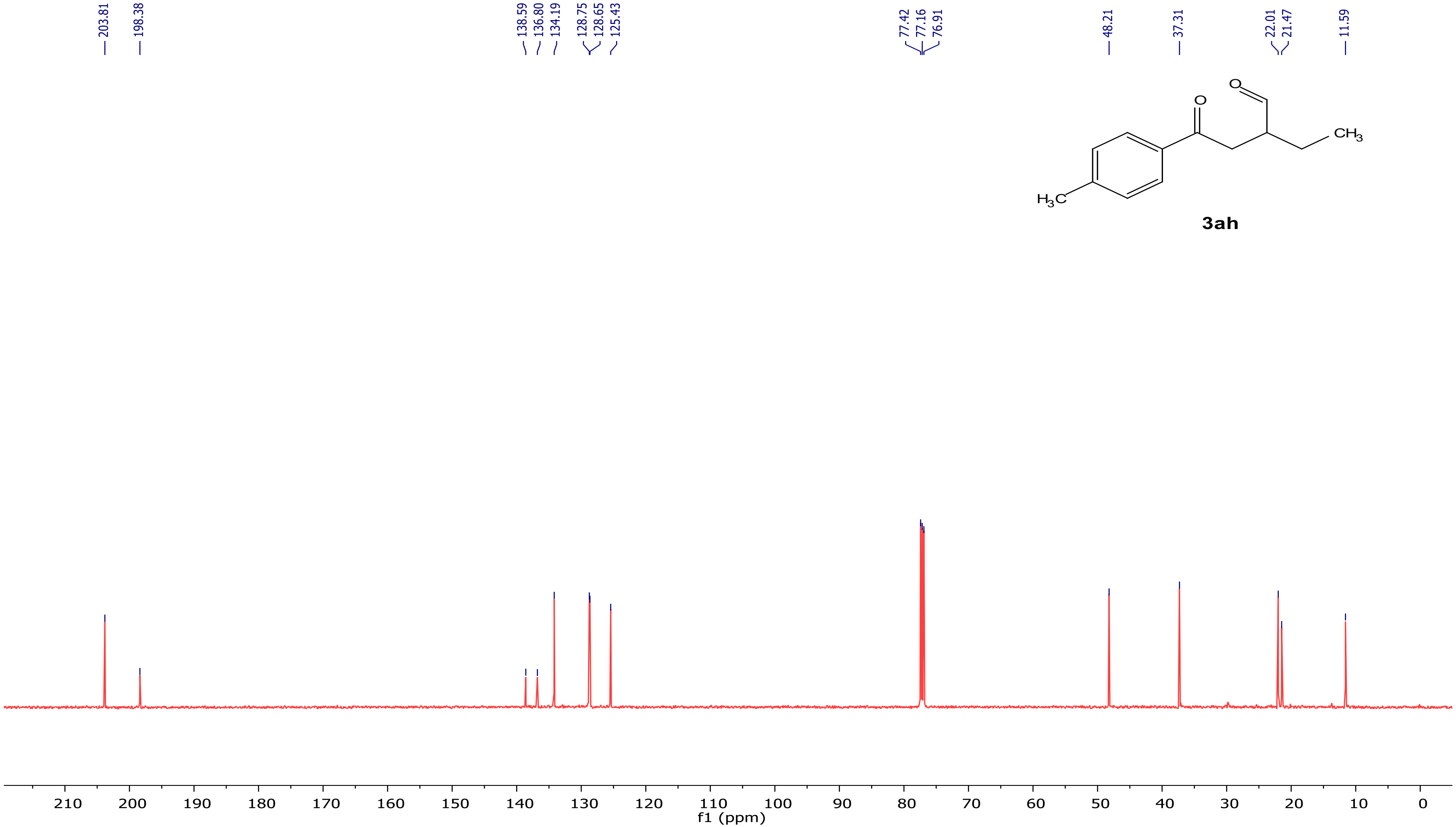
[1]H NMR (500 MHz, CDCl₃) of 3ah



3ah

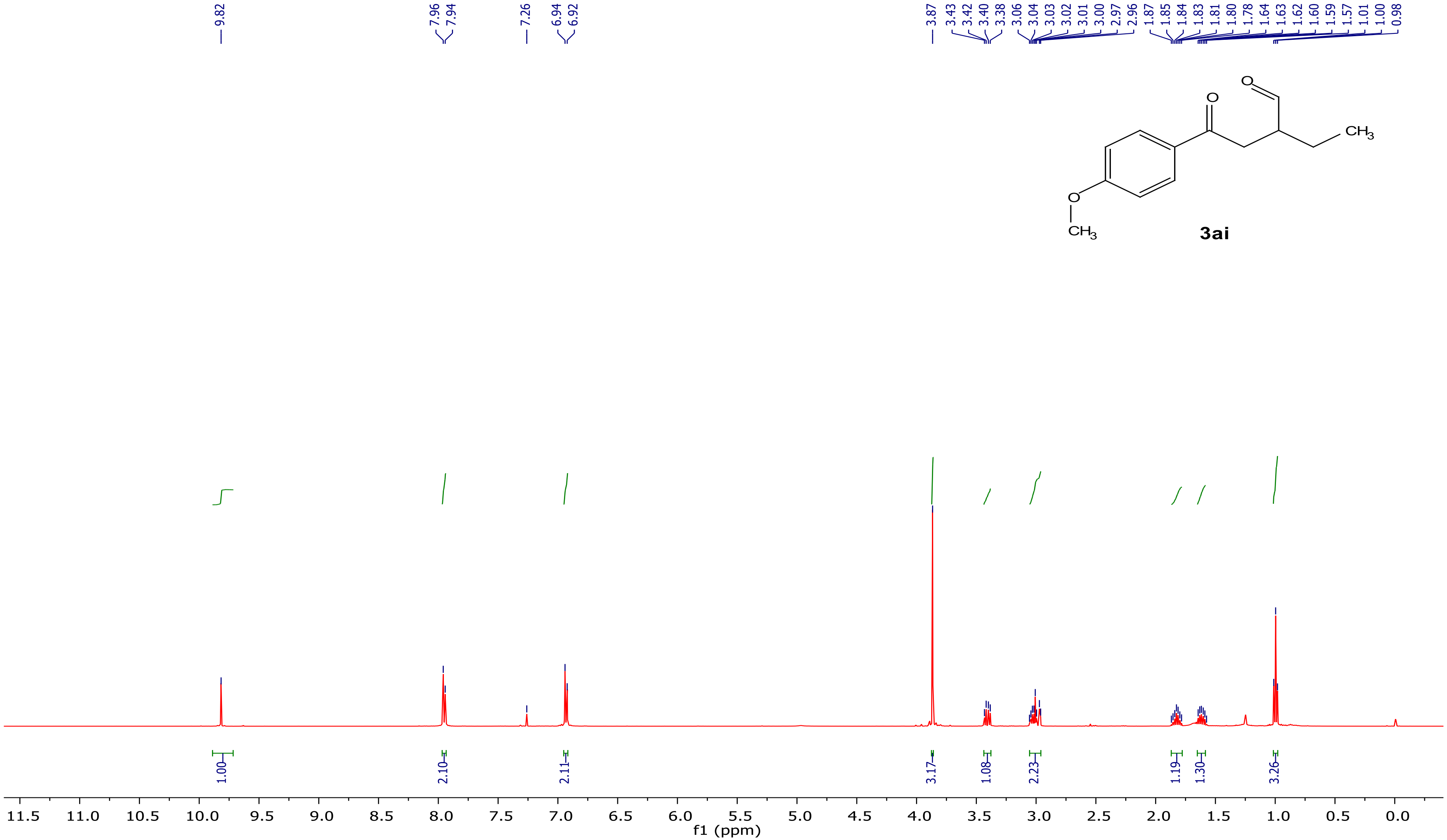


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3ah

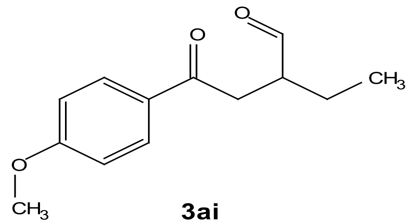


3ah

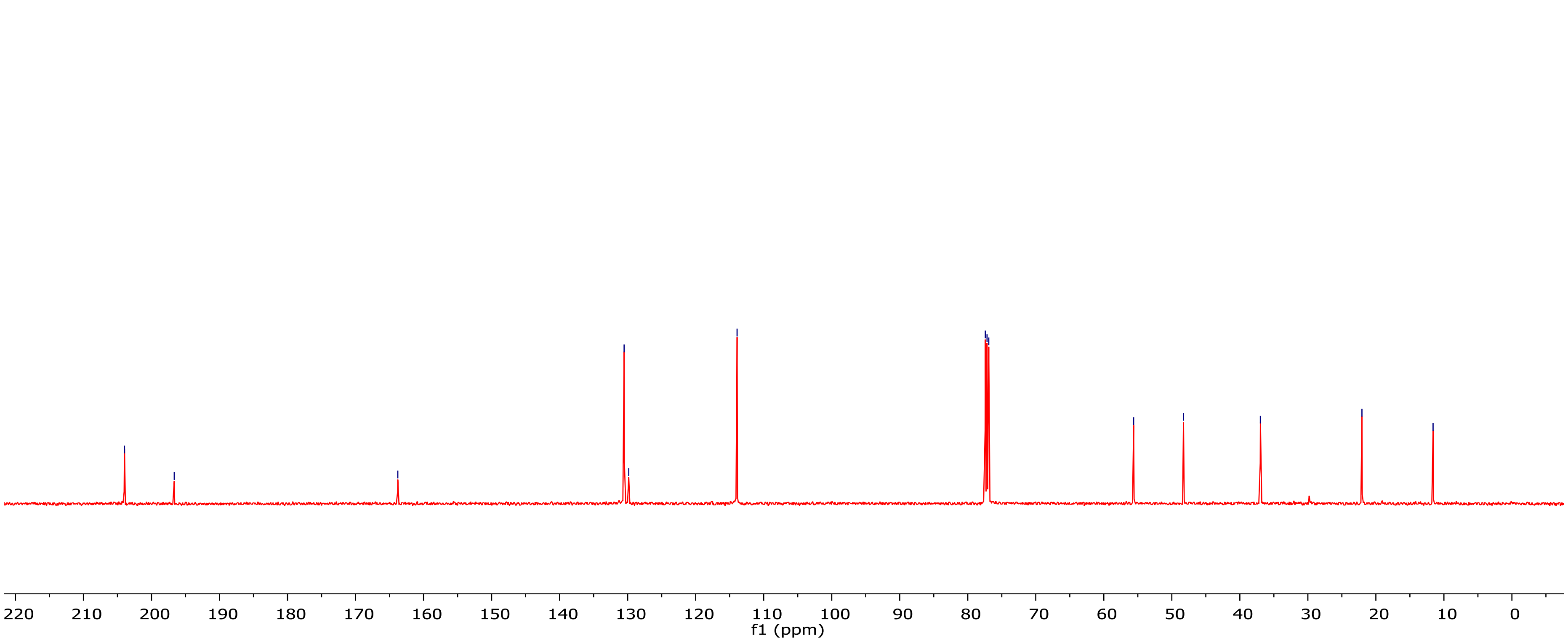
^{1}H NMR (500 MHz, $CDCl_3$) of 3ai



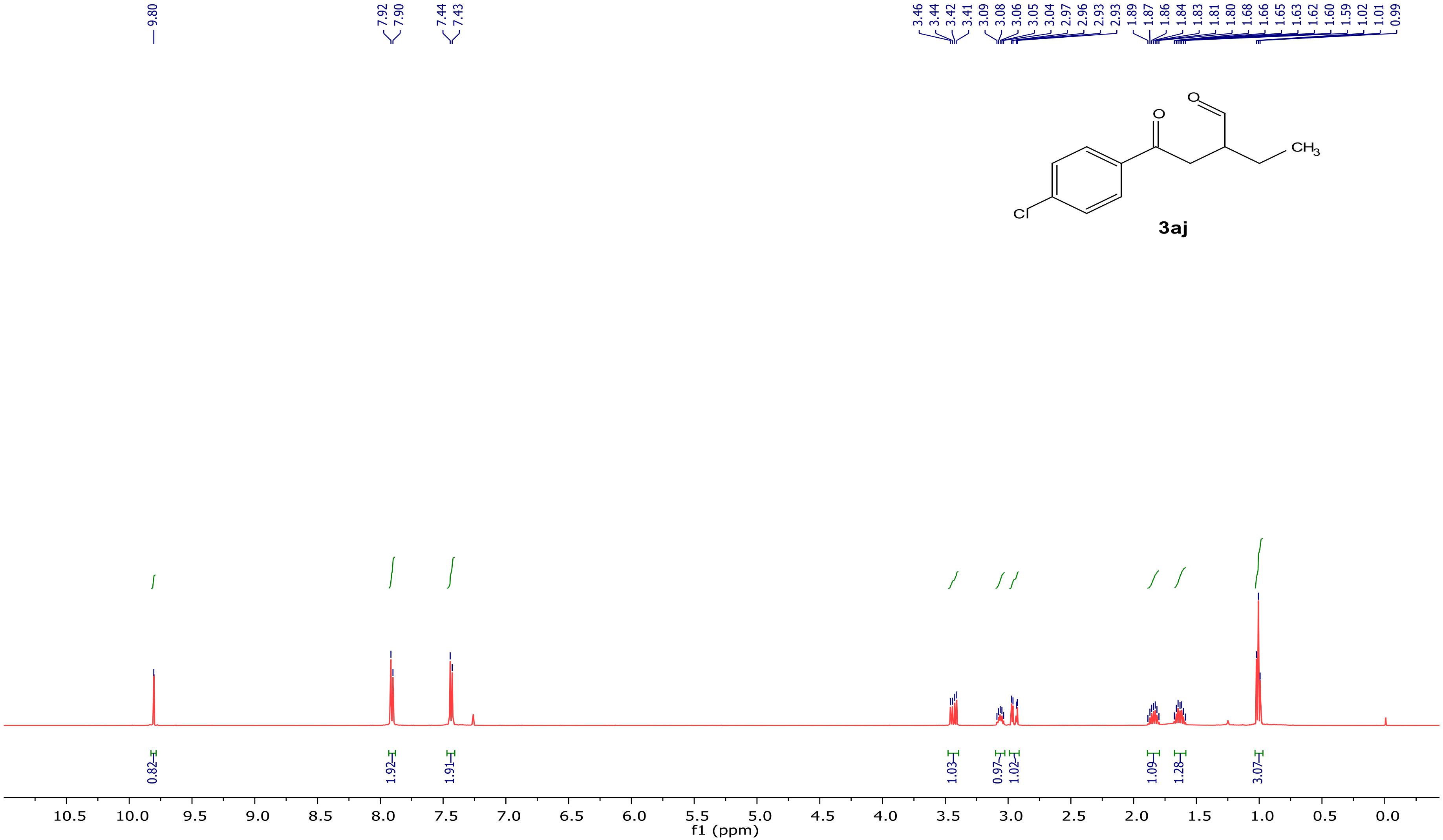
$^{13}C\{^{1}H\}$ **NMR (126 MHz, $CDCl_3$) of 3ai**



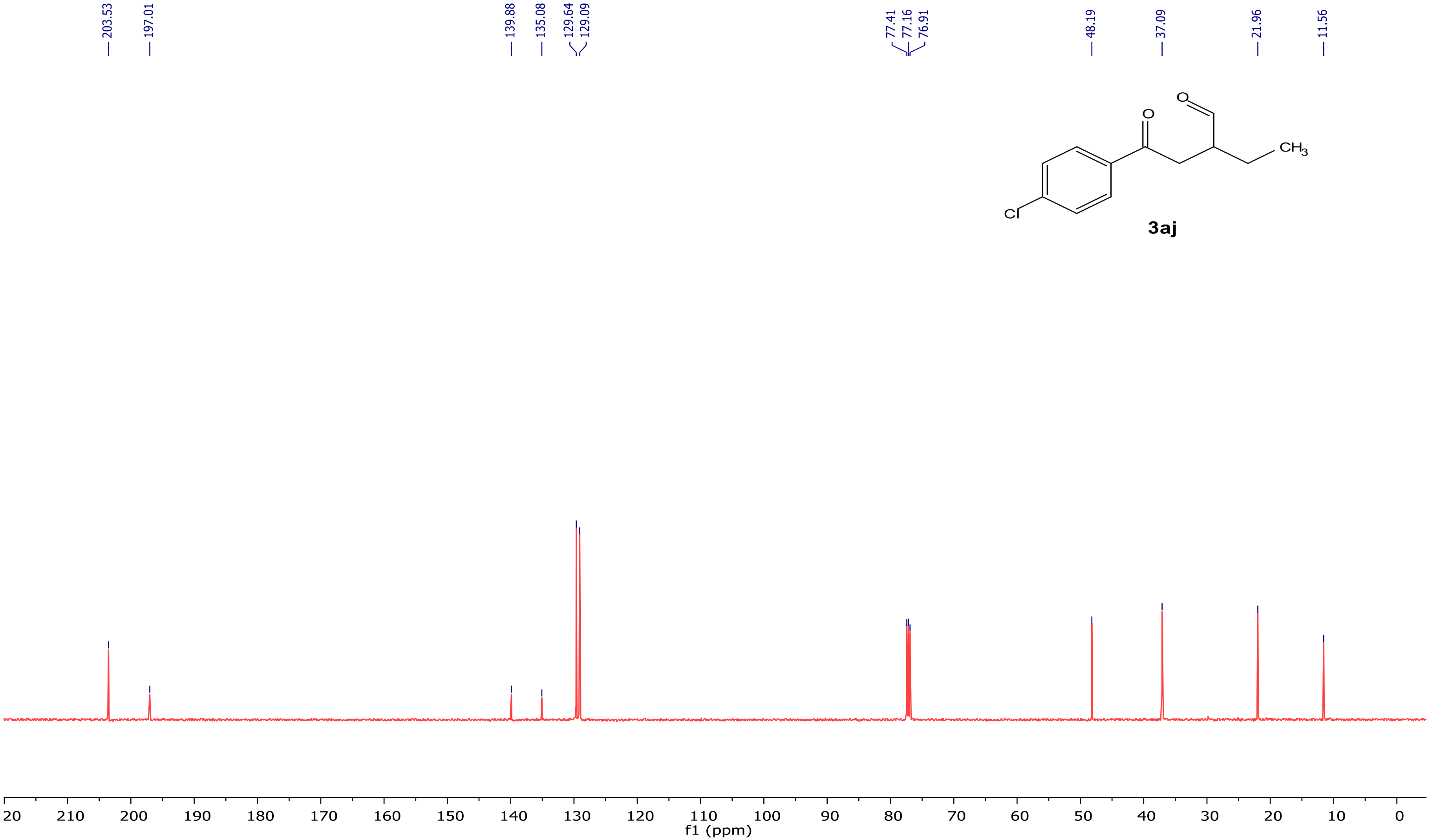
3ai



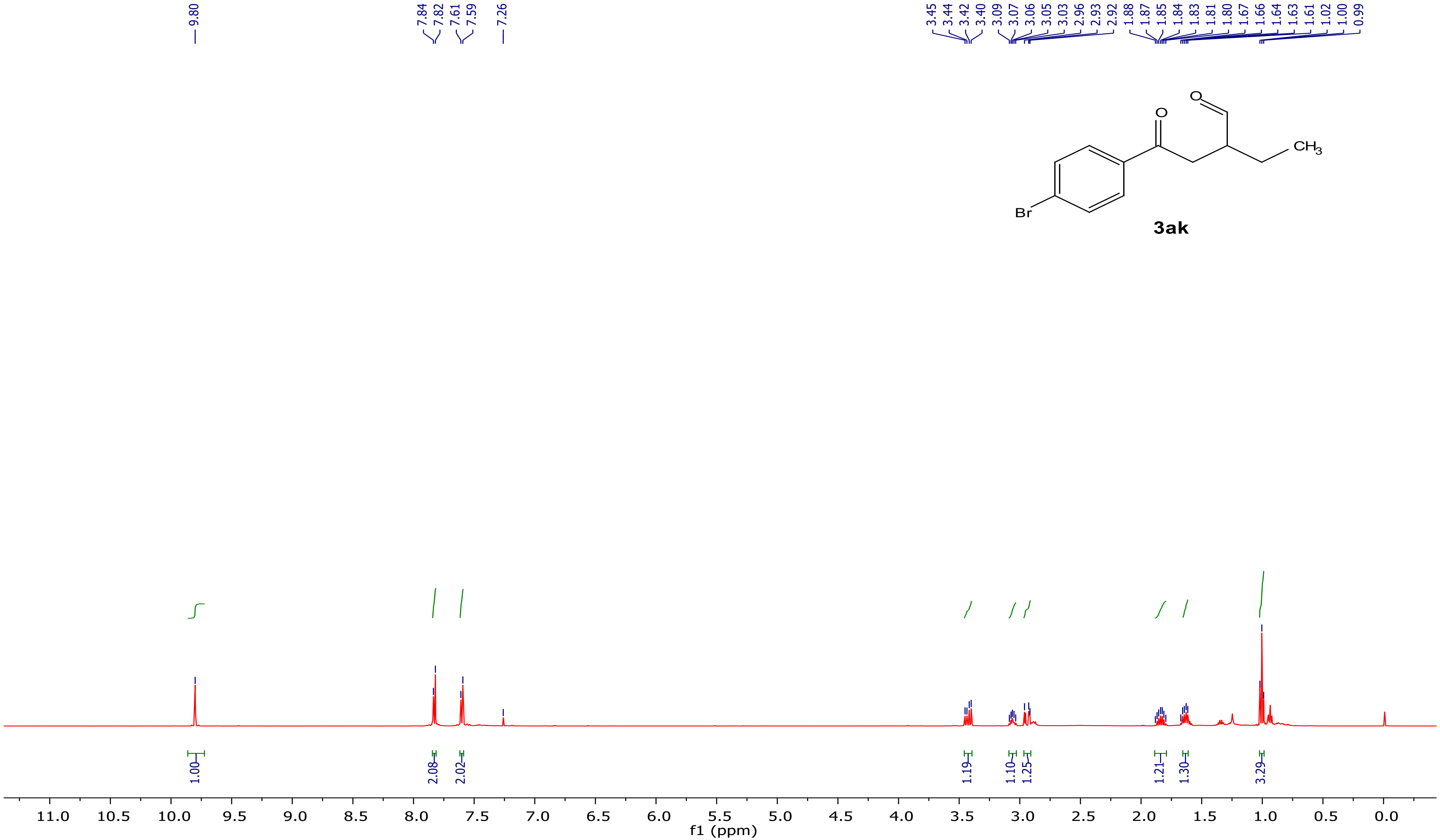
[1]H NMR (500 MHz, $CDCl_3$) of 3aj



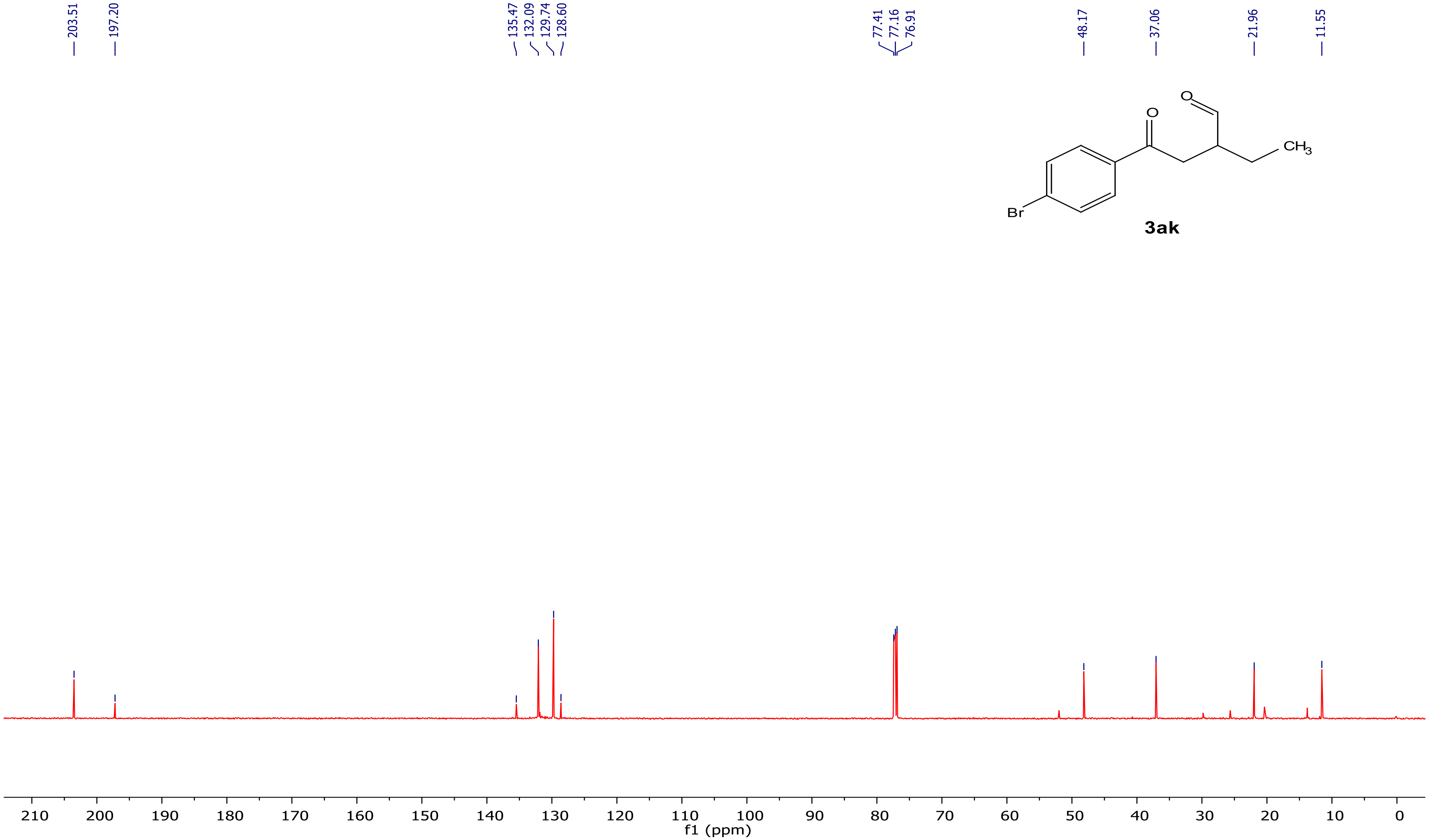
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3aj



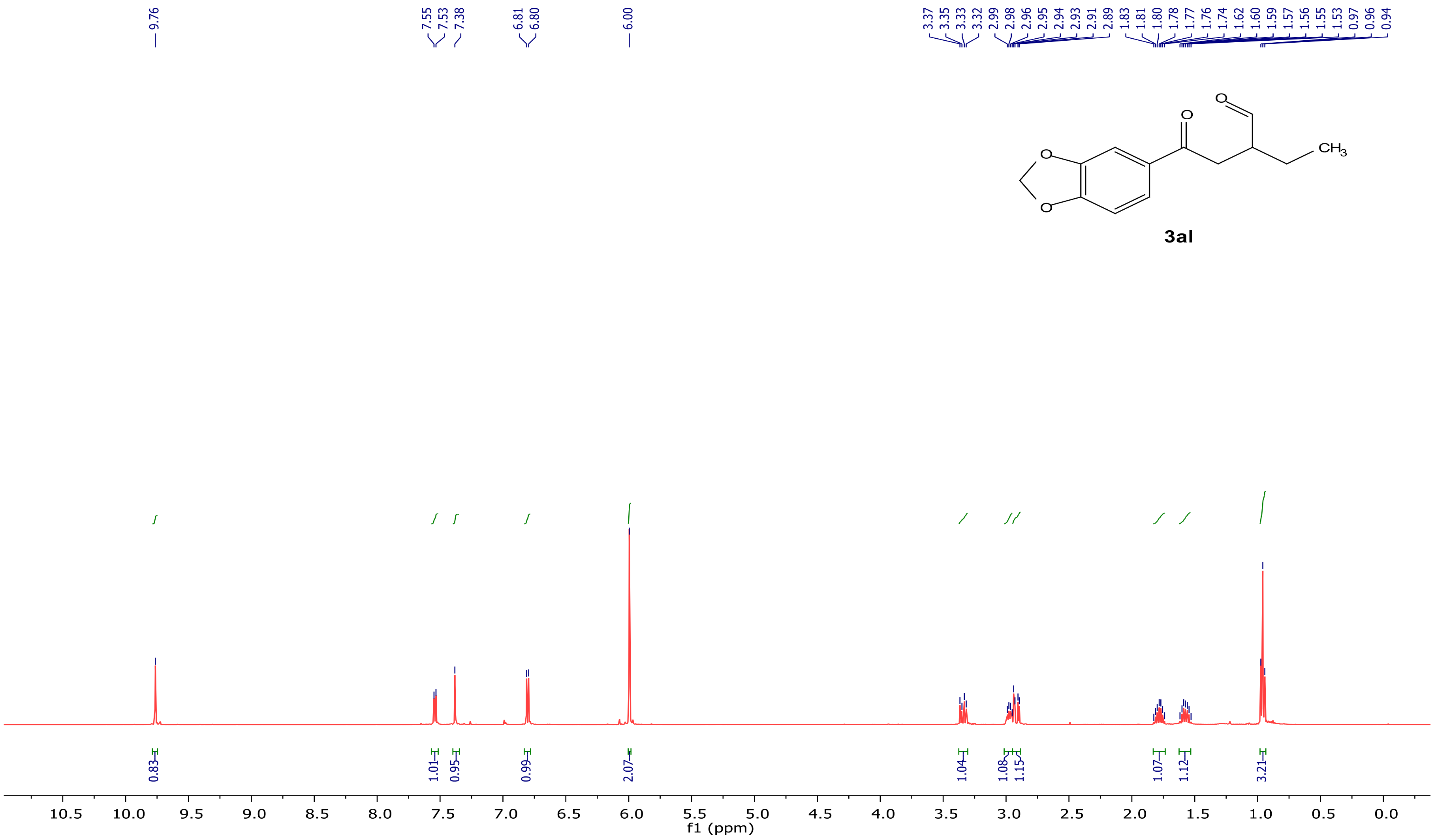
[1]H NMR (500 MHz, CDCl$_3$) of 3ak



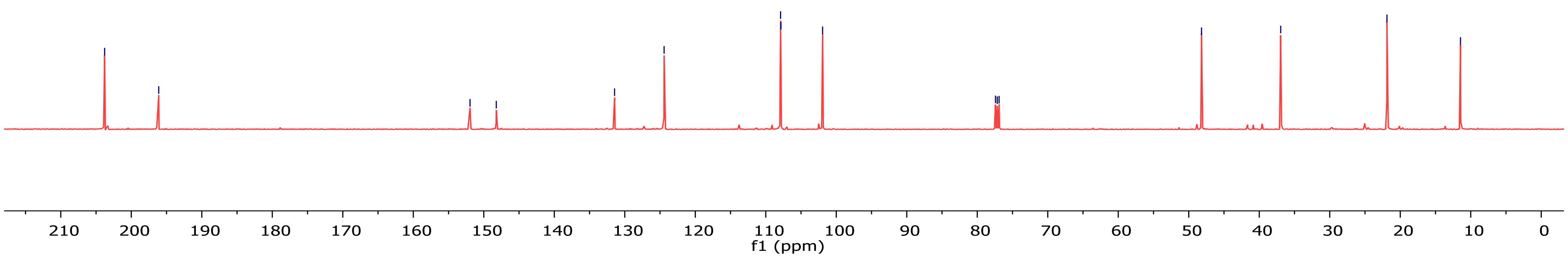
$^{13}C\{^{1}H\}$ NMR (126 MHz, CDCl$_3$) of 3ak

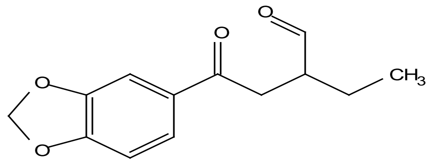


[1]H NMR (500 MHz, $CDCl_3$) of 3al



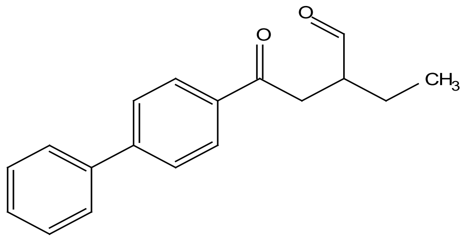
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3al



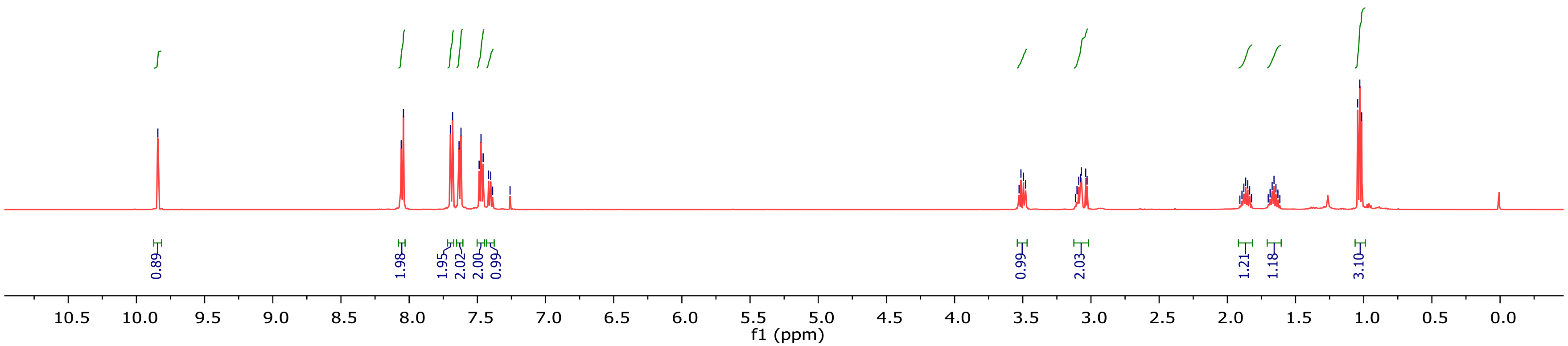


3al

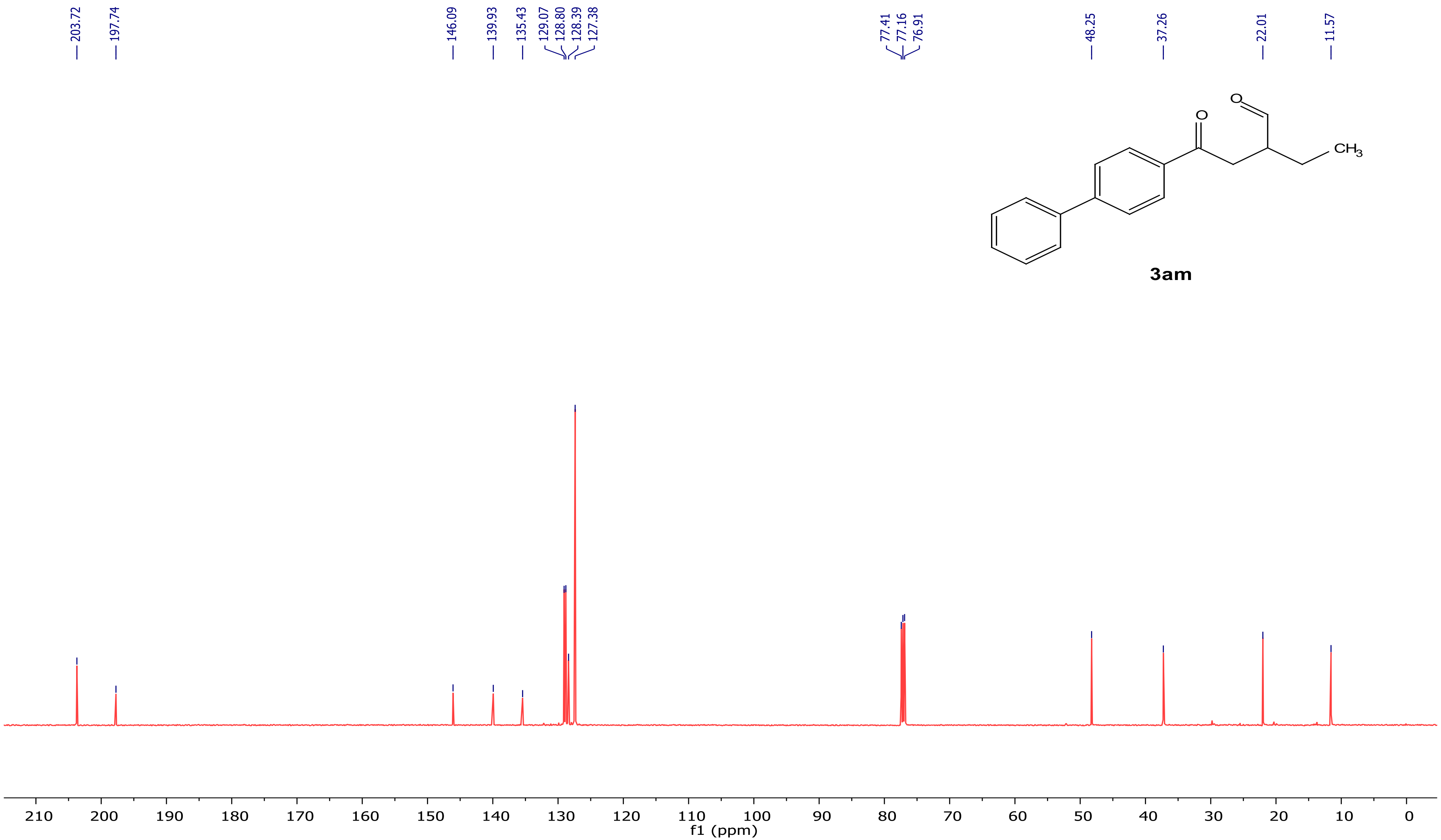
^{1}H NMR (500 MHz, $CDCl_3$) of 3am



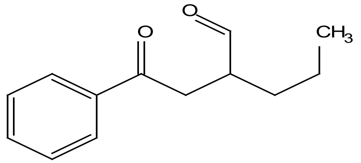
3am



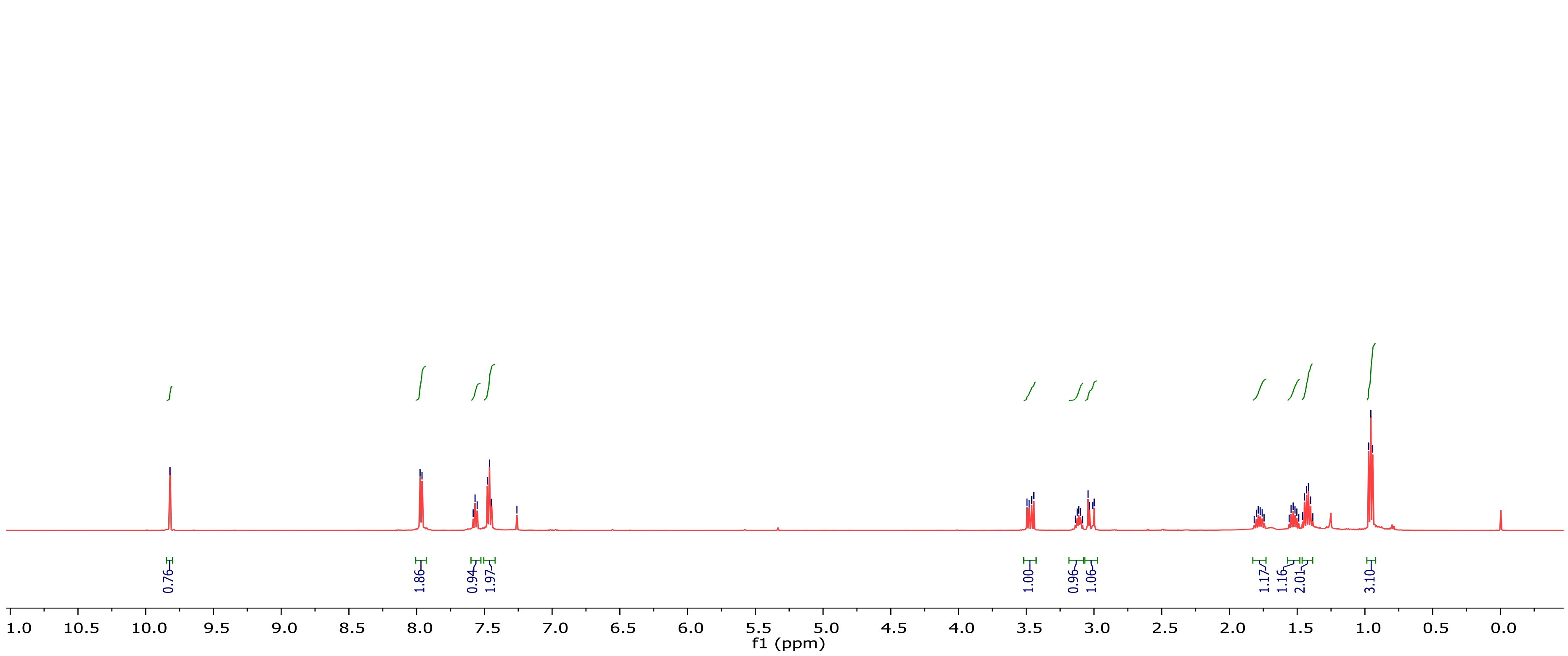
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3am



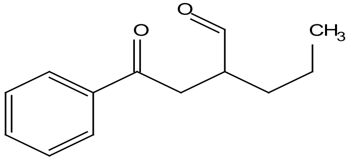
^{1}H NMR (500 MHz, $CDCl_3$) of 3an



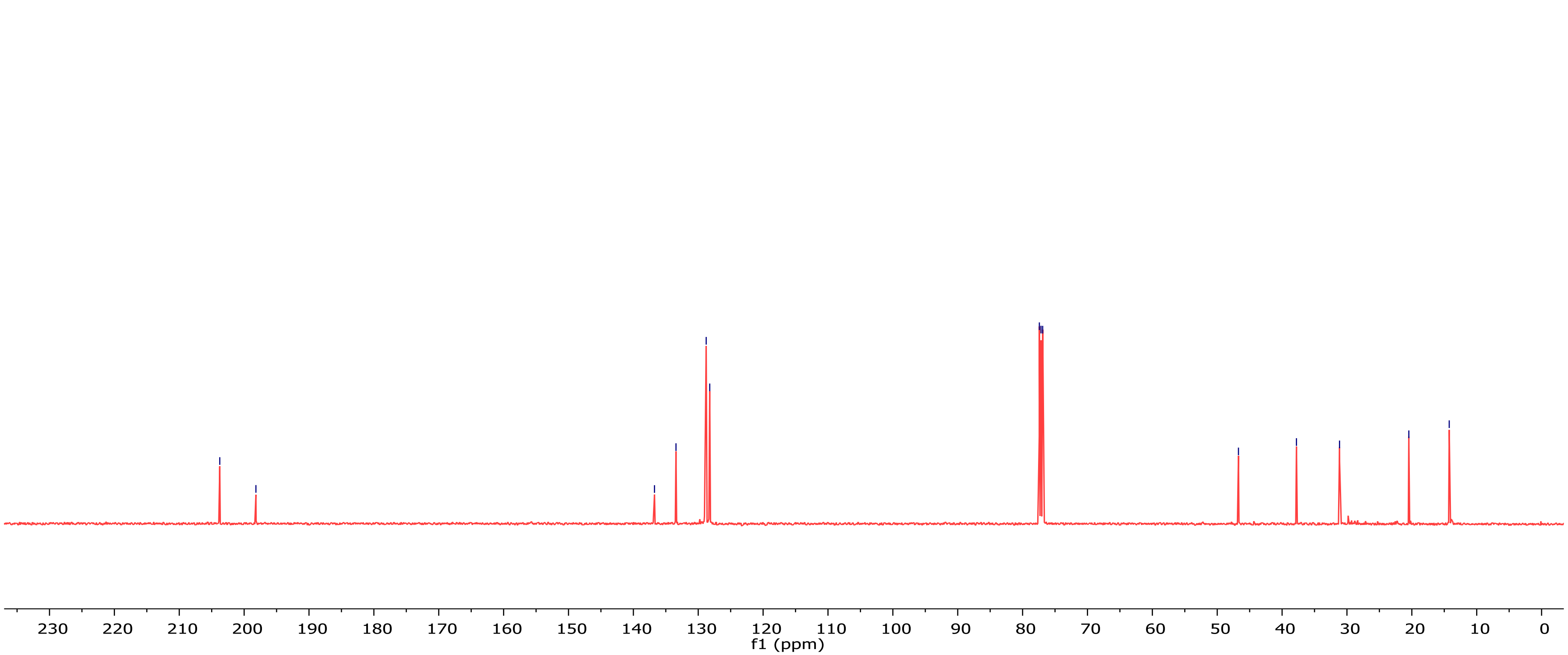
3an



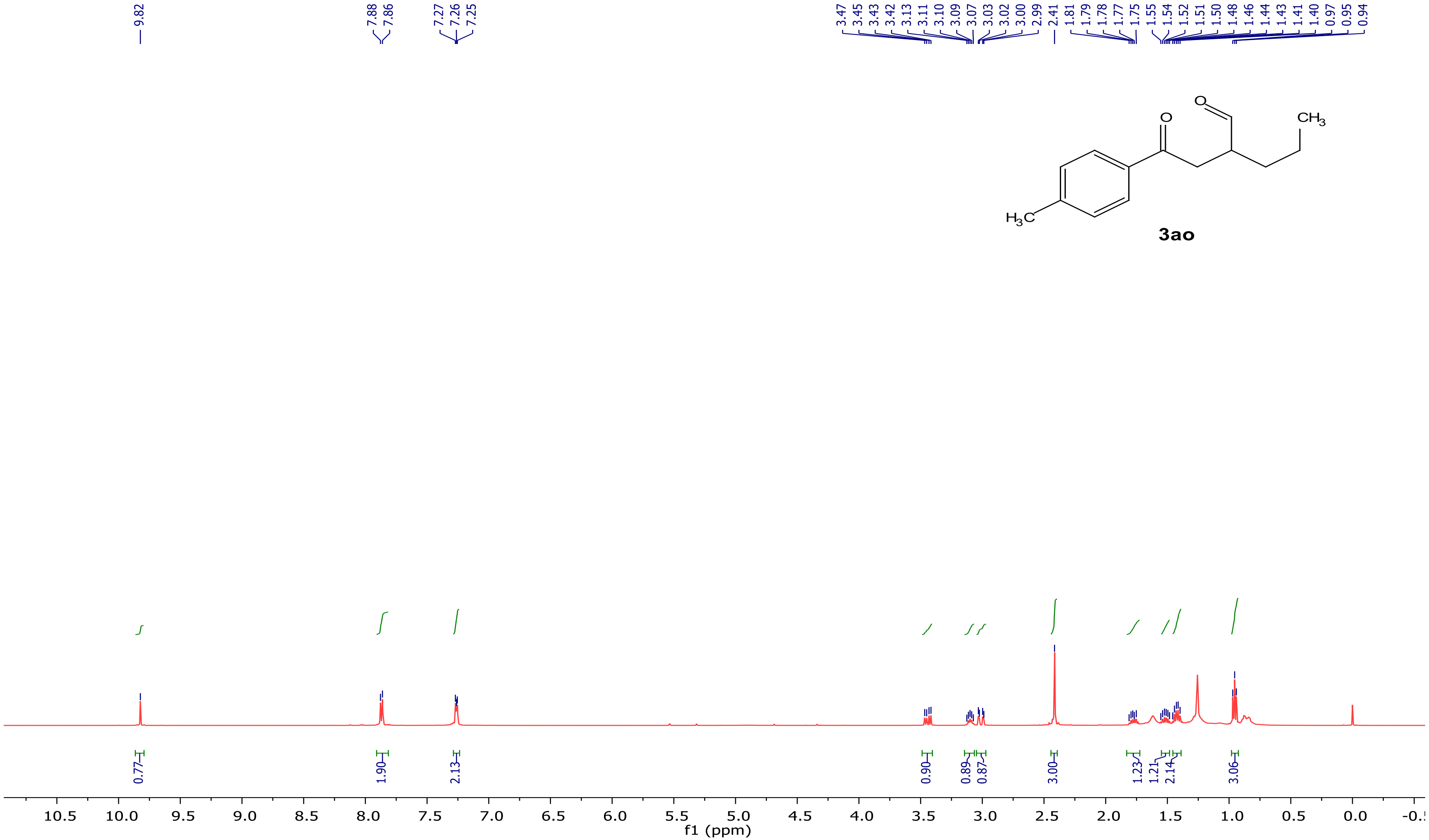
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3an



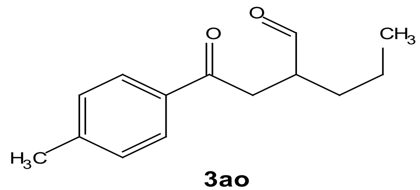
3an



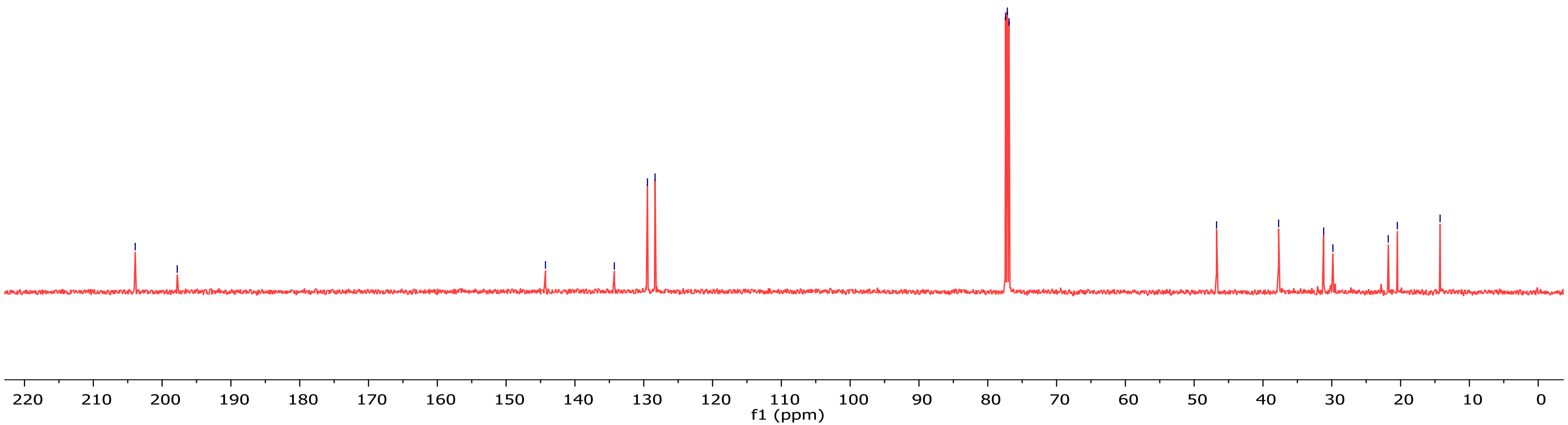
[1]H NMR (500 MHz, CDCl$_3$) of 3ao



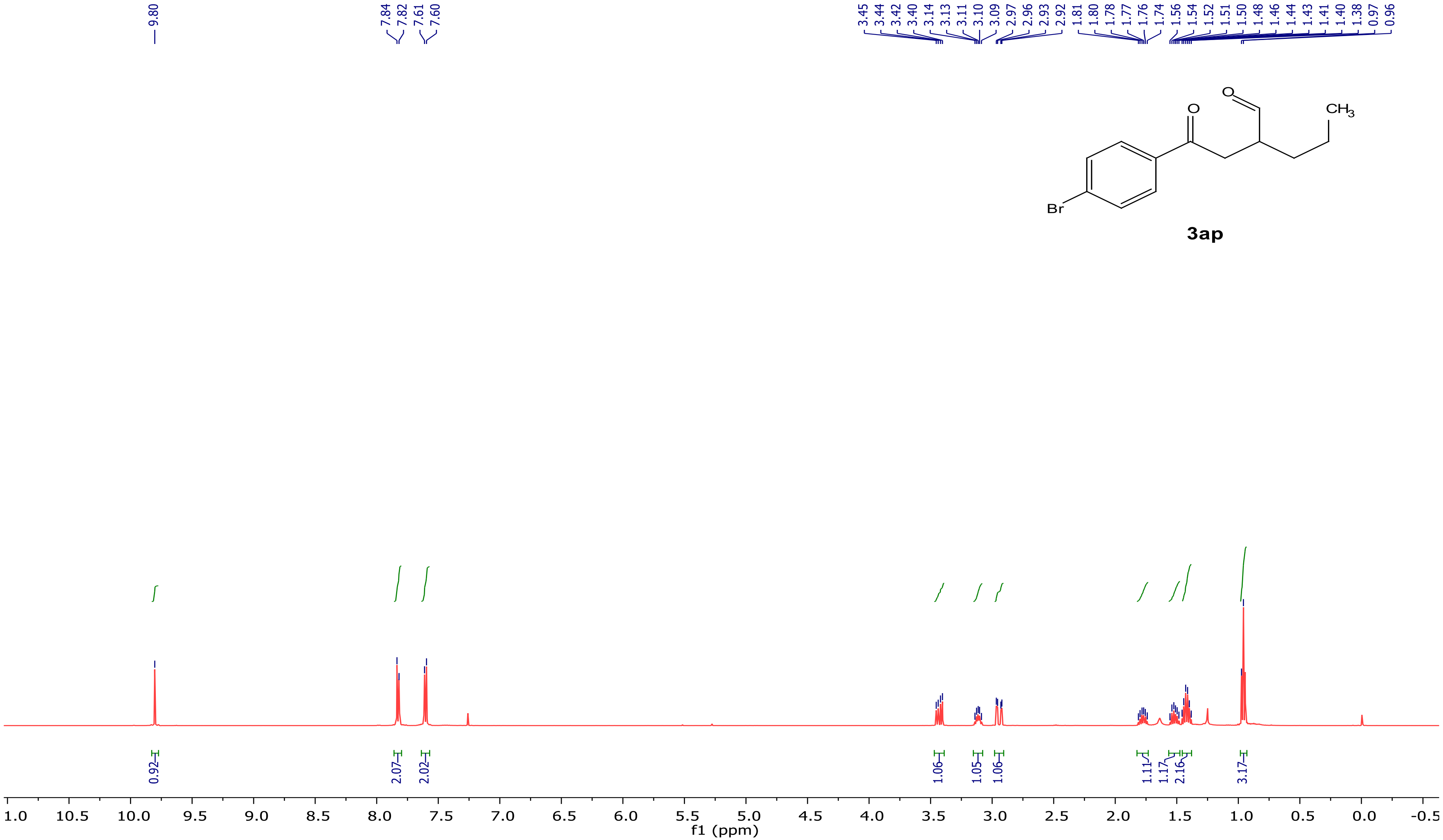
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3ao



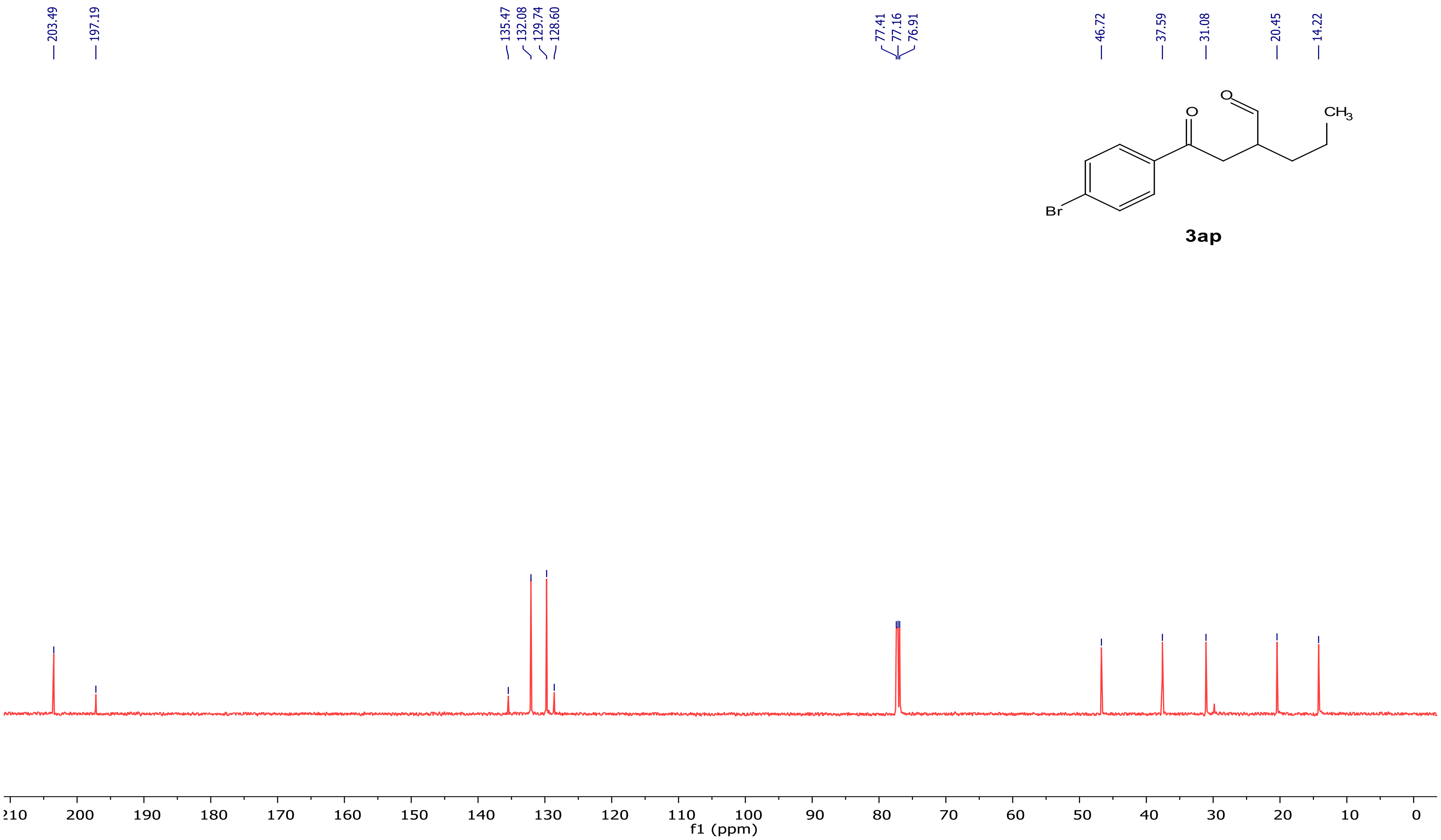
3ao



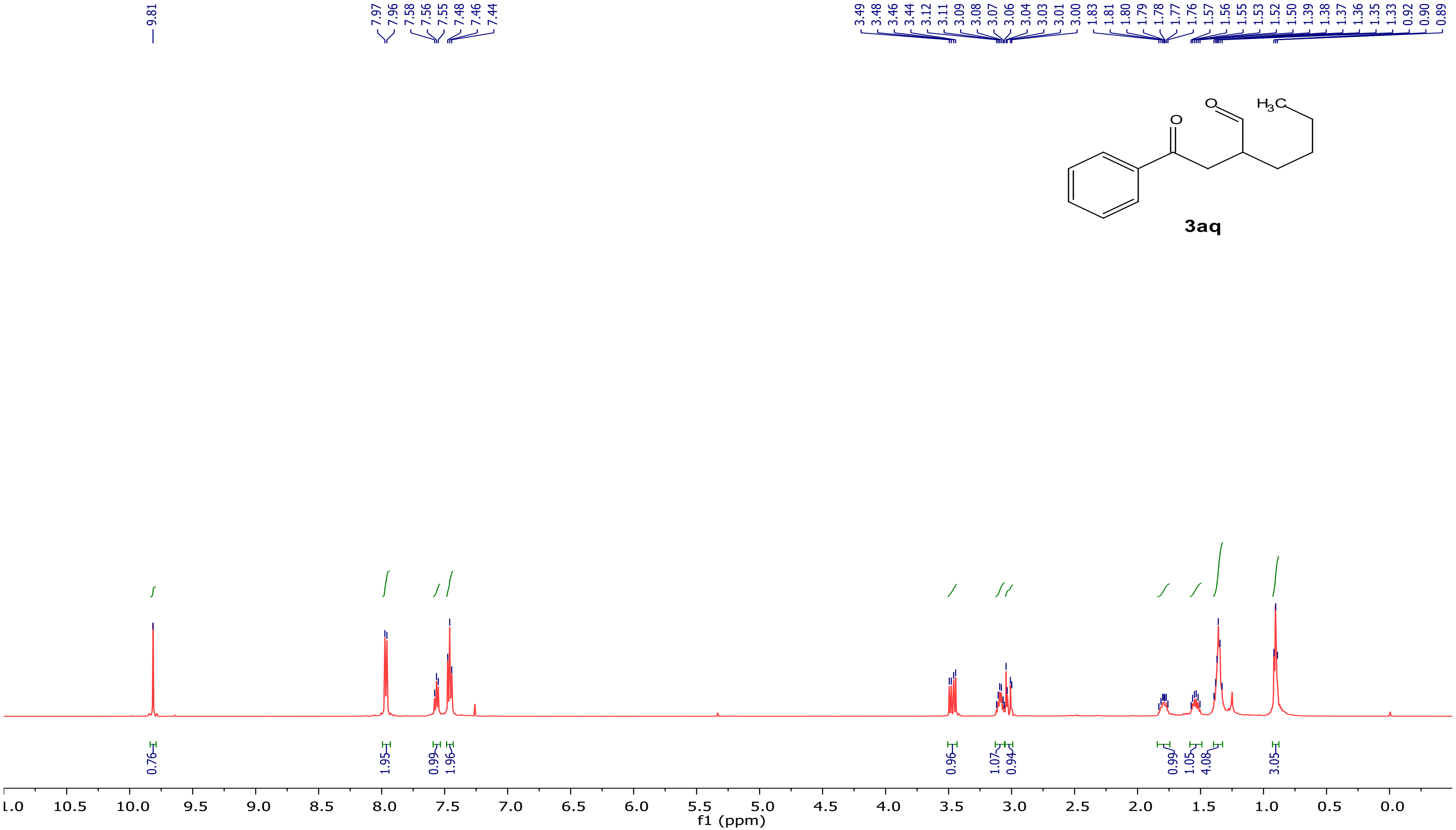
^{1}H NMR (500 MHz, $CDCl_3$) of 3ap



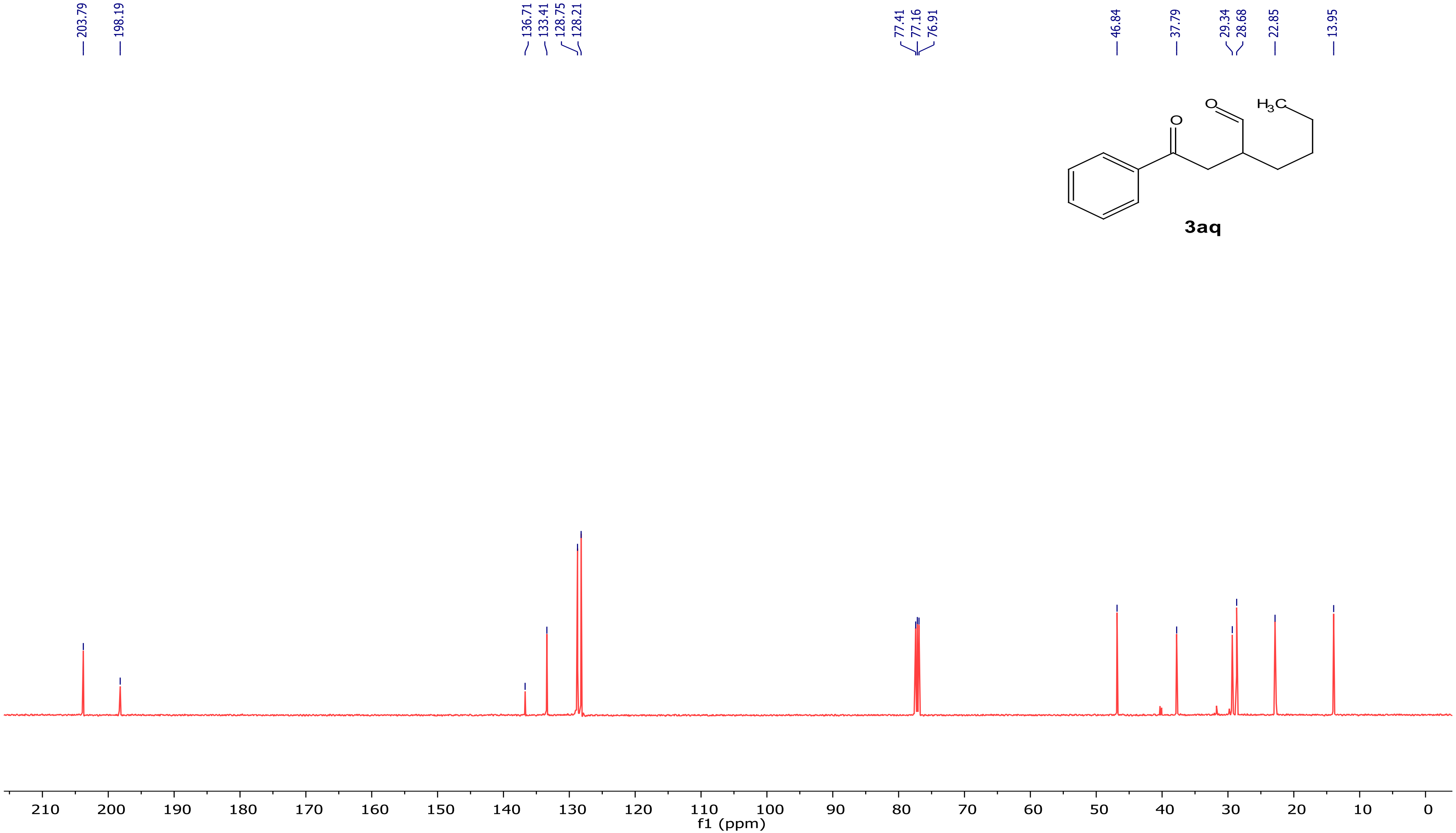
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3ap



[1]H NMR (500 MHz, $CDCl_3$) of 3aq

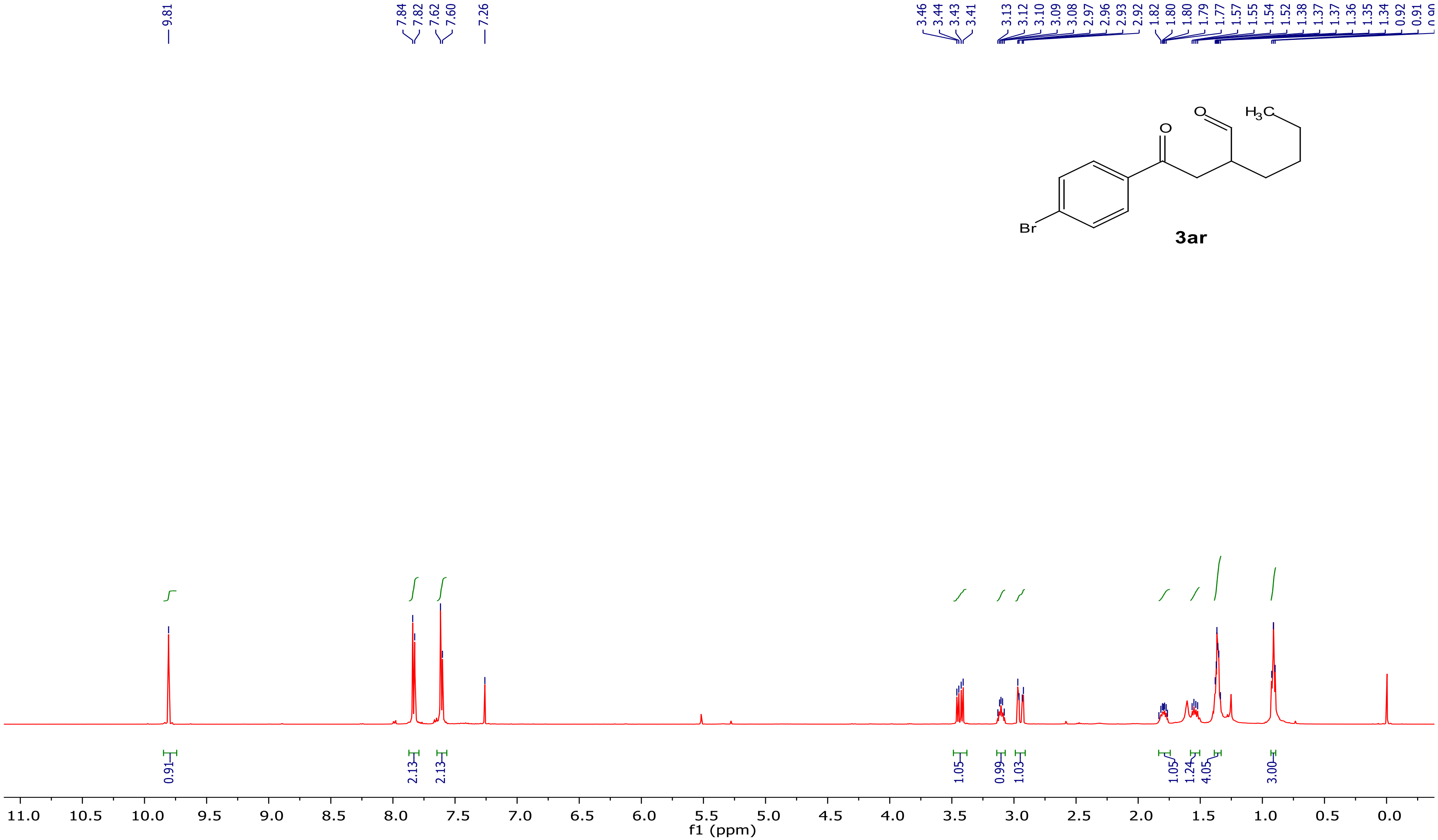


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 3aq

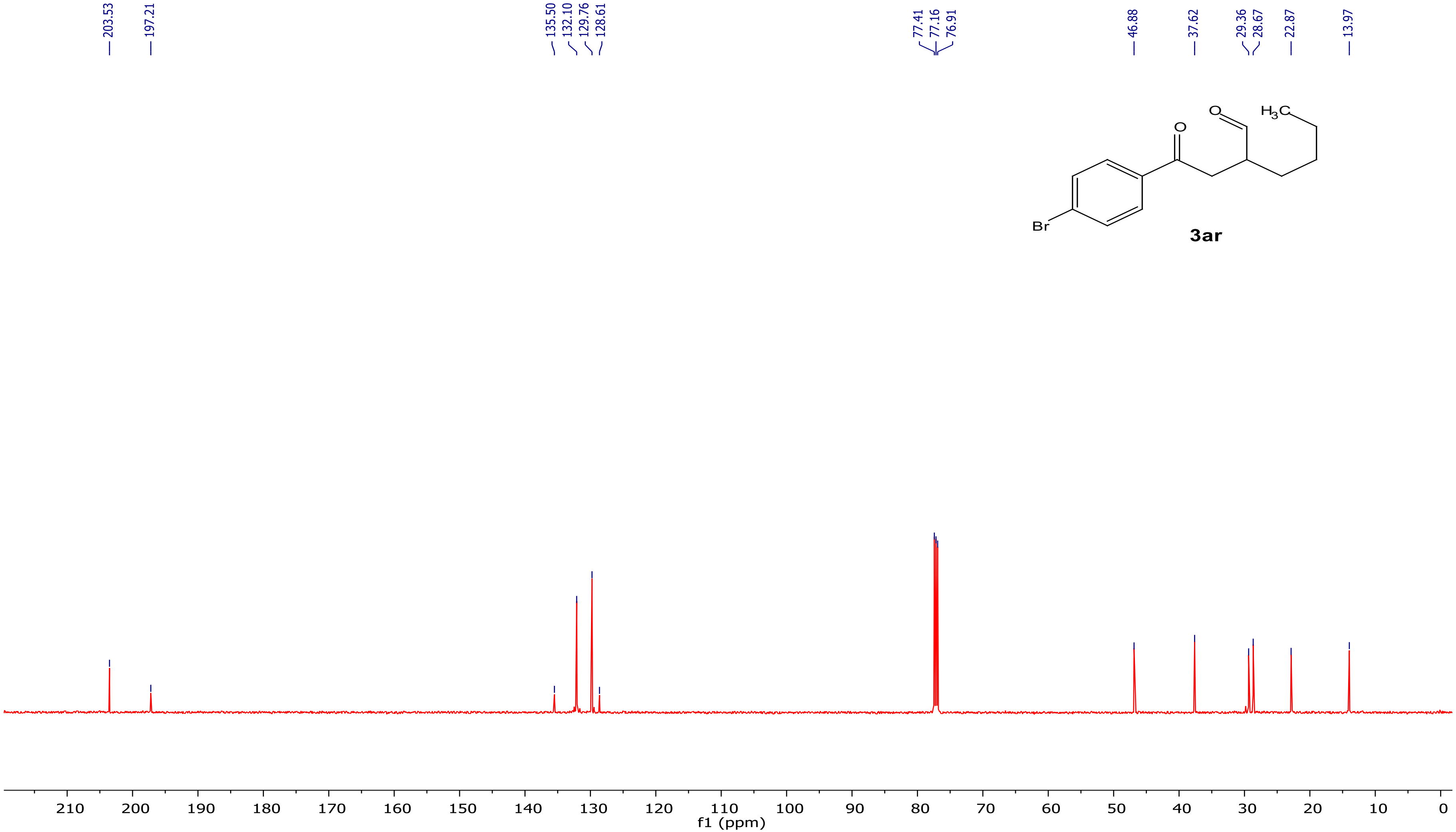


3aq

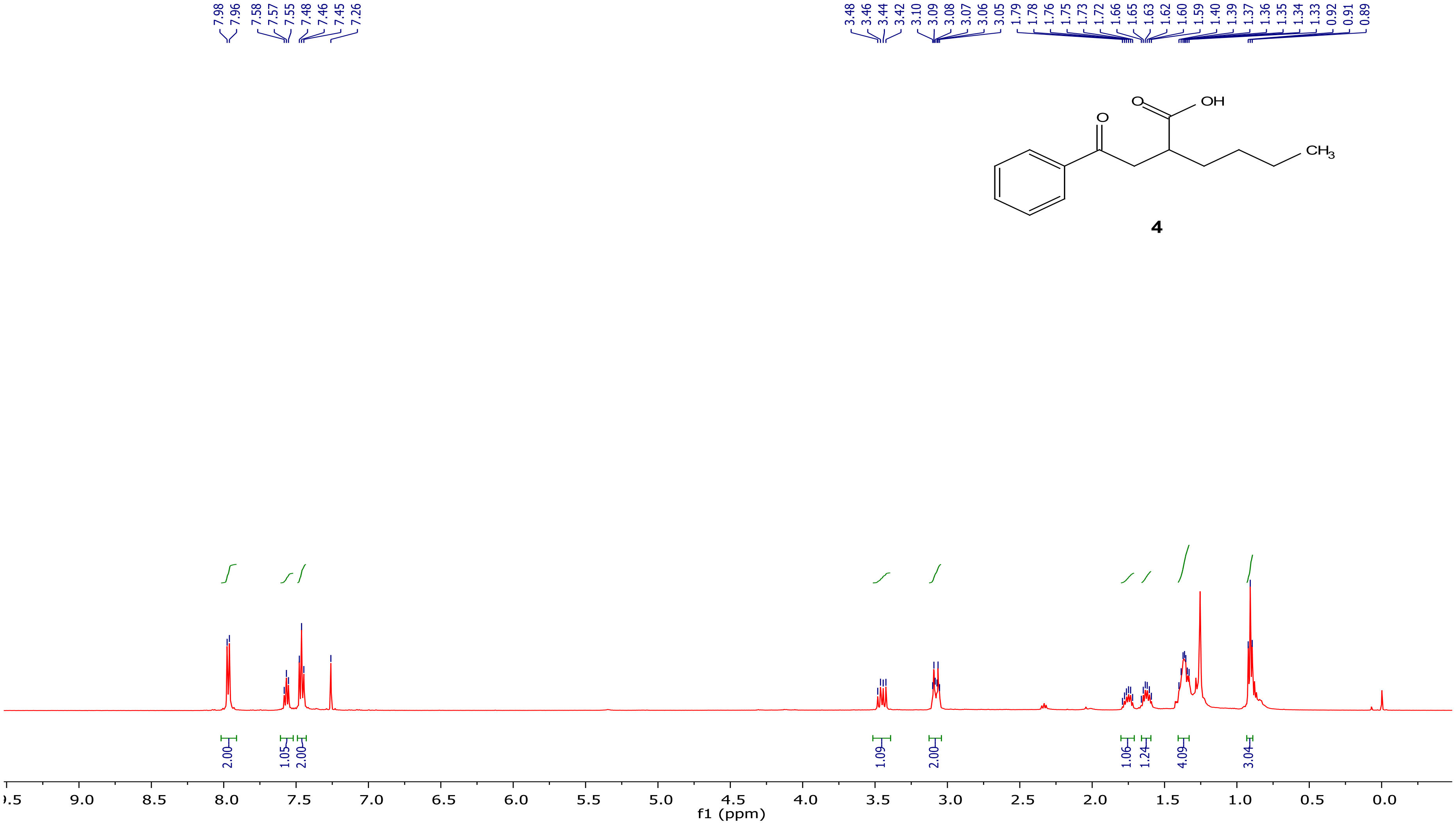
^{1}H NMR (500 MHz, $CDCl_3$) of 3ar



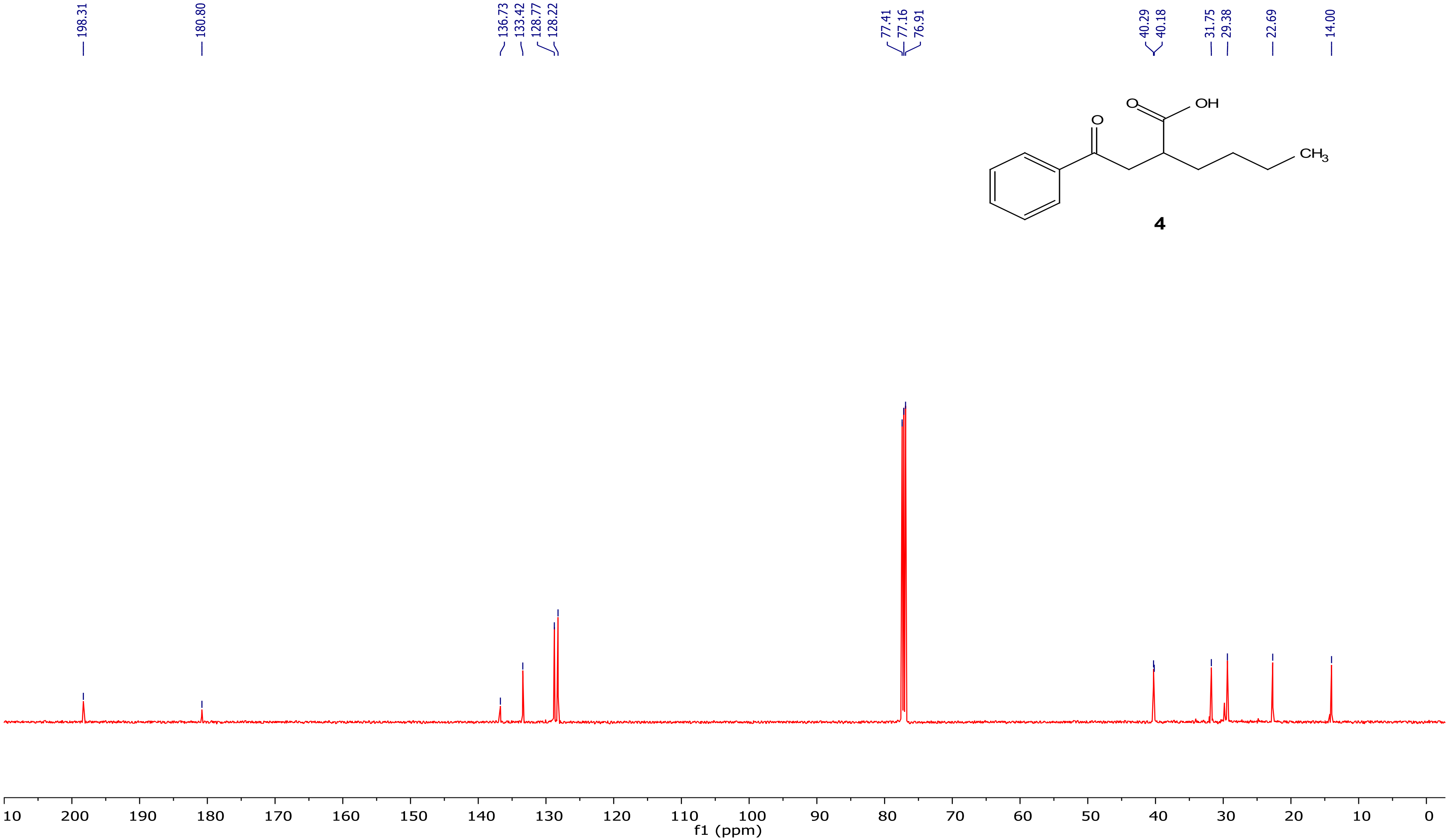
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 3ar



[1]H NMR (500 MHz, $CDCl_3$) of 4

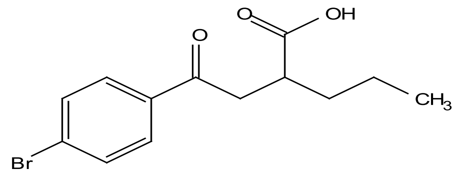


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 4



4

^{1}H NMR (500 MHz, $CDCl_3$) of 5



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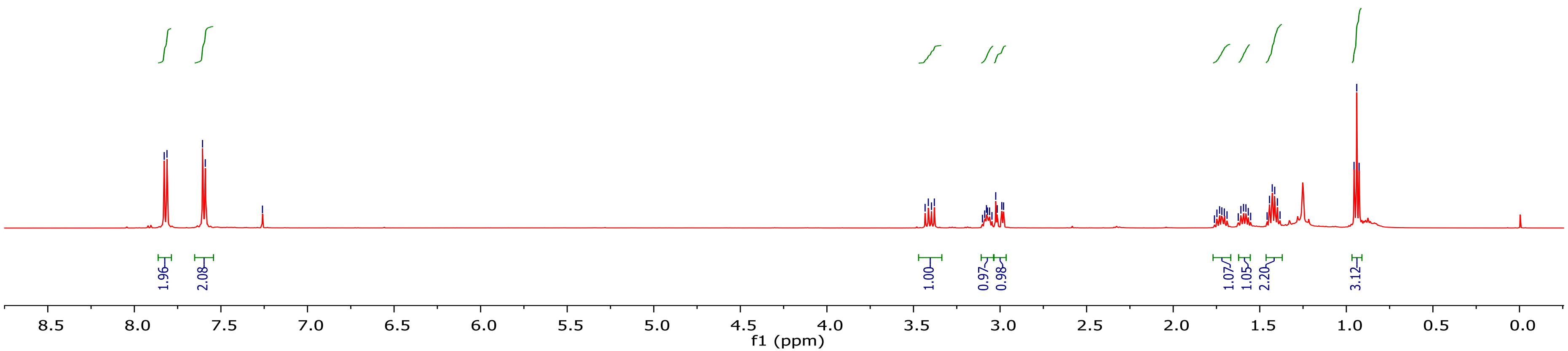
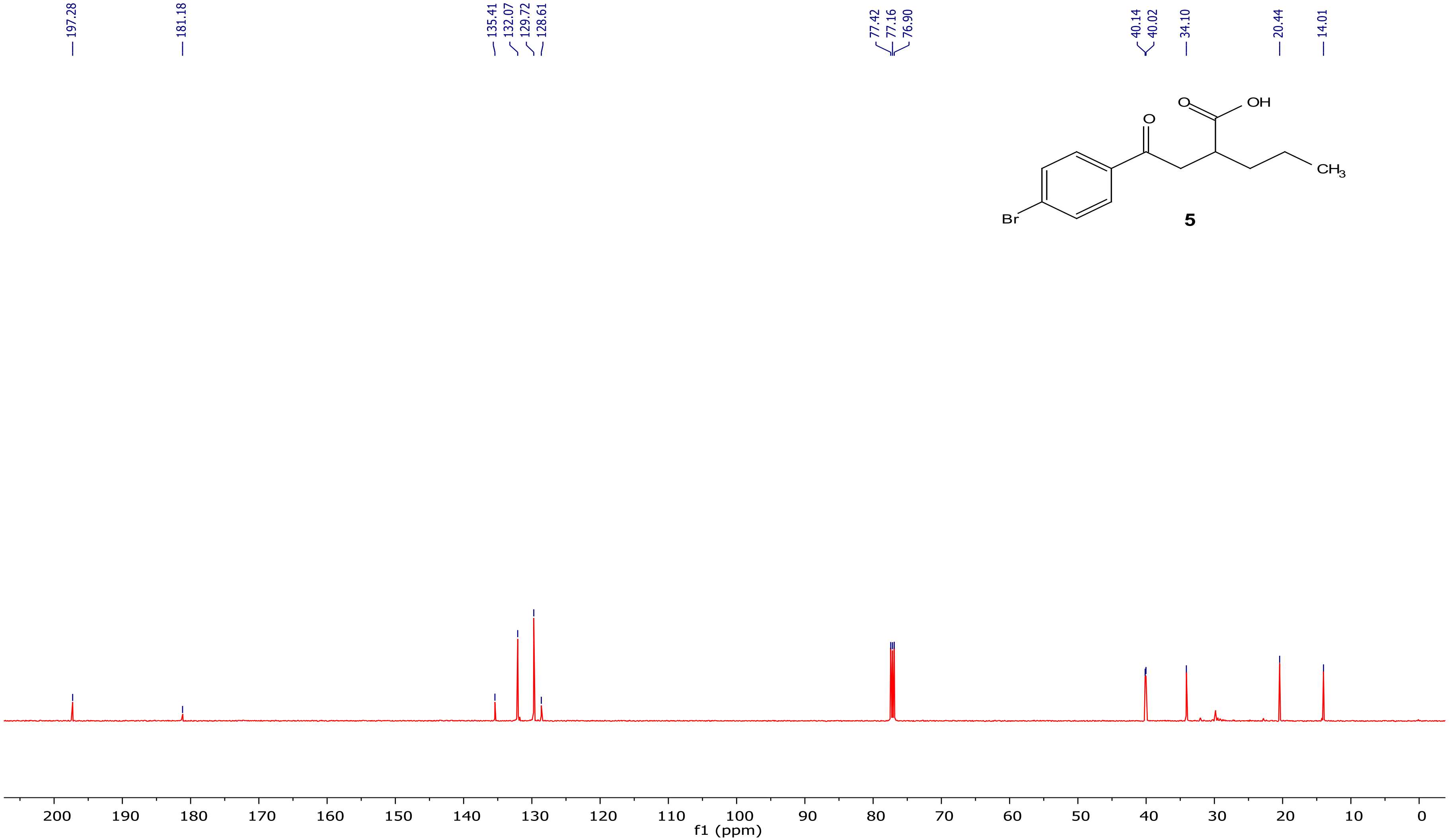
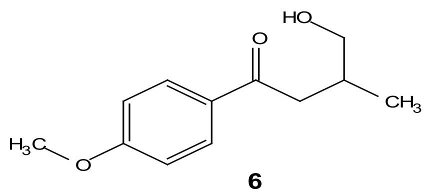


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 5



[1]H NMR (500 MHz, $CDCl_3$) of 6



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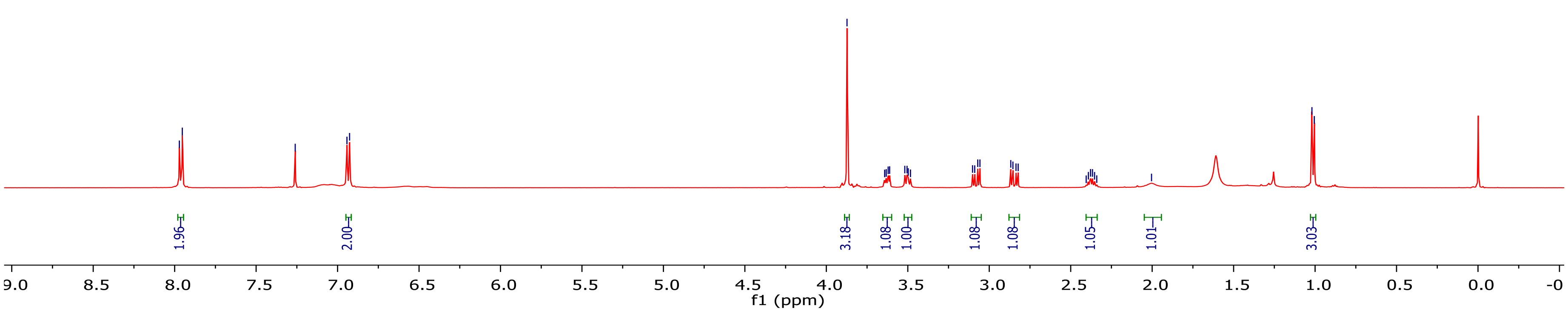
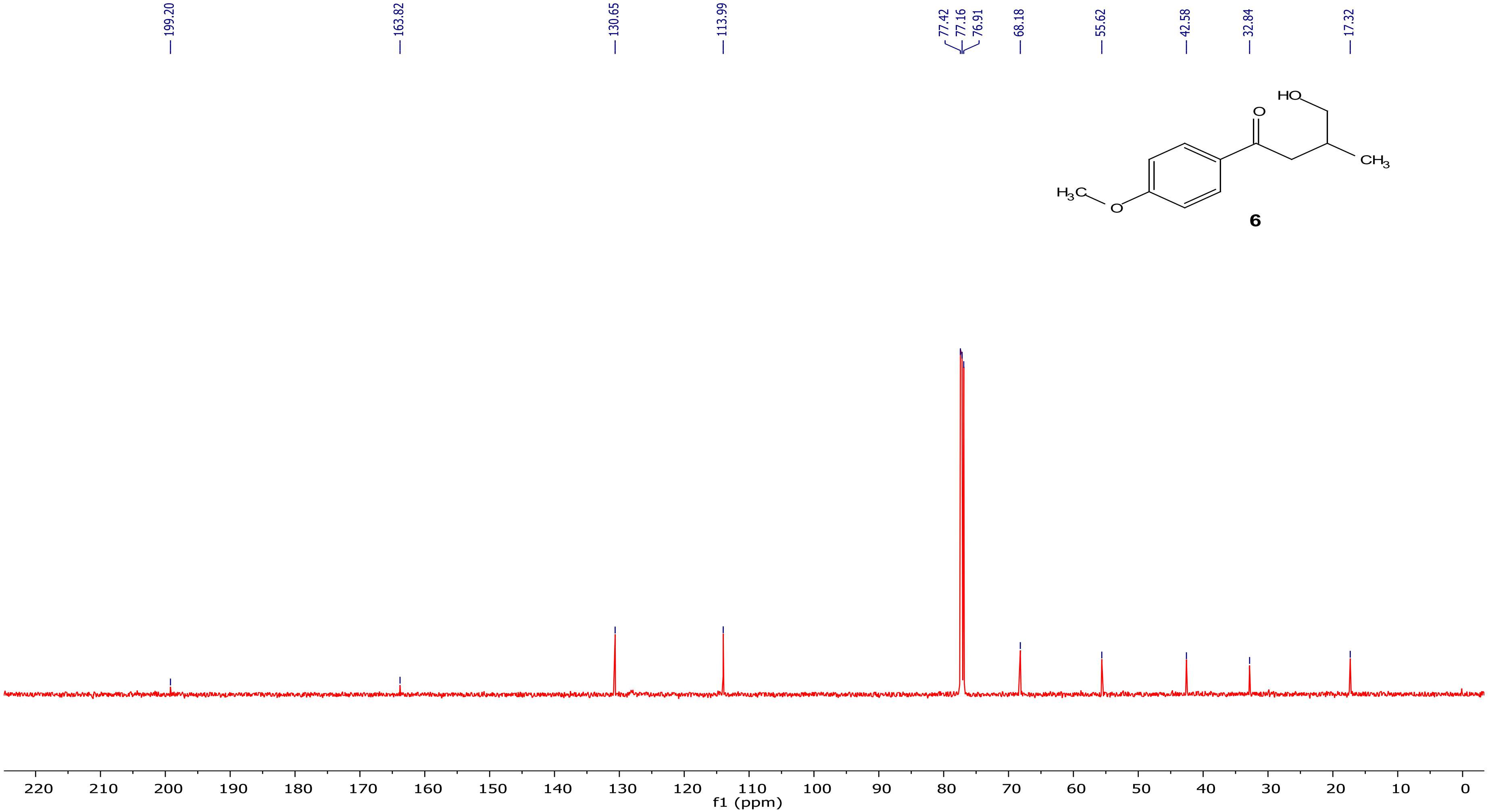
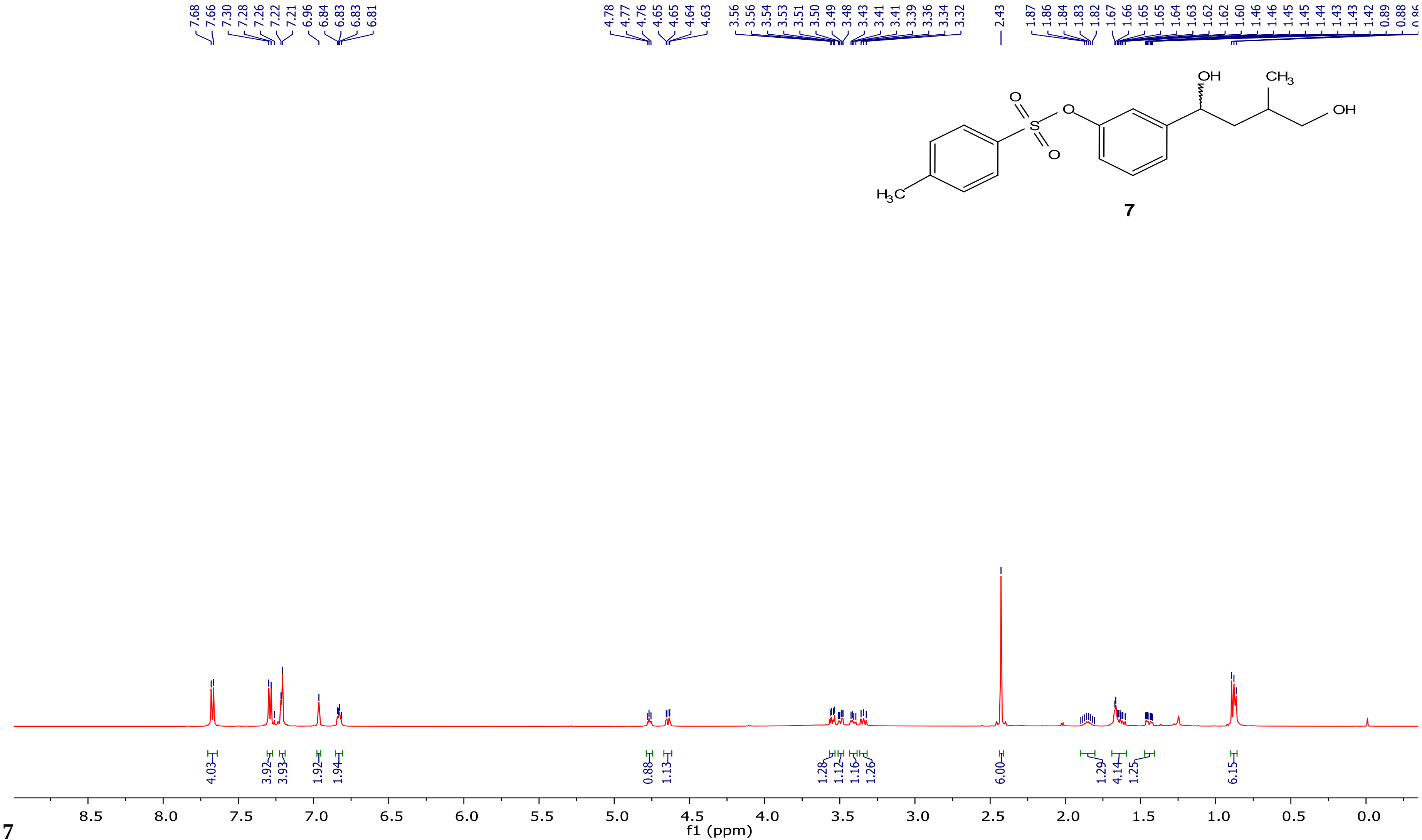


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 6

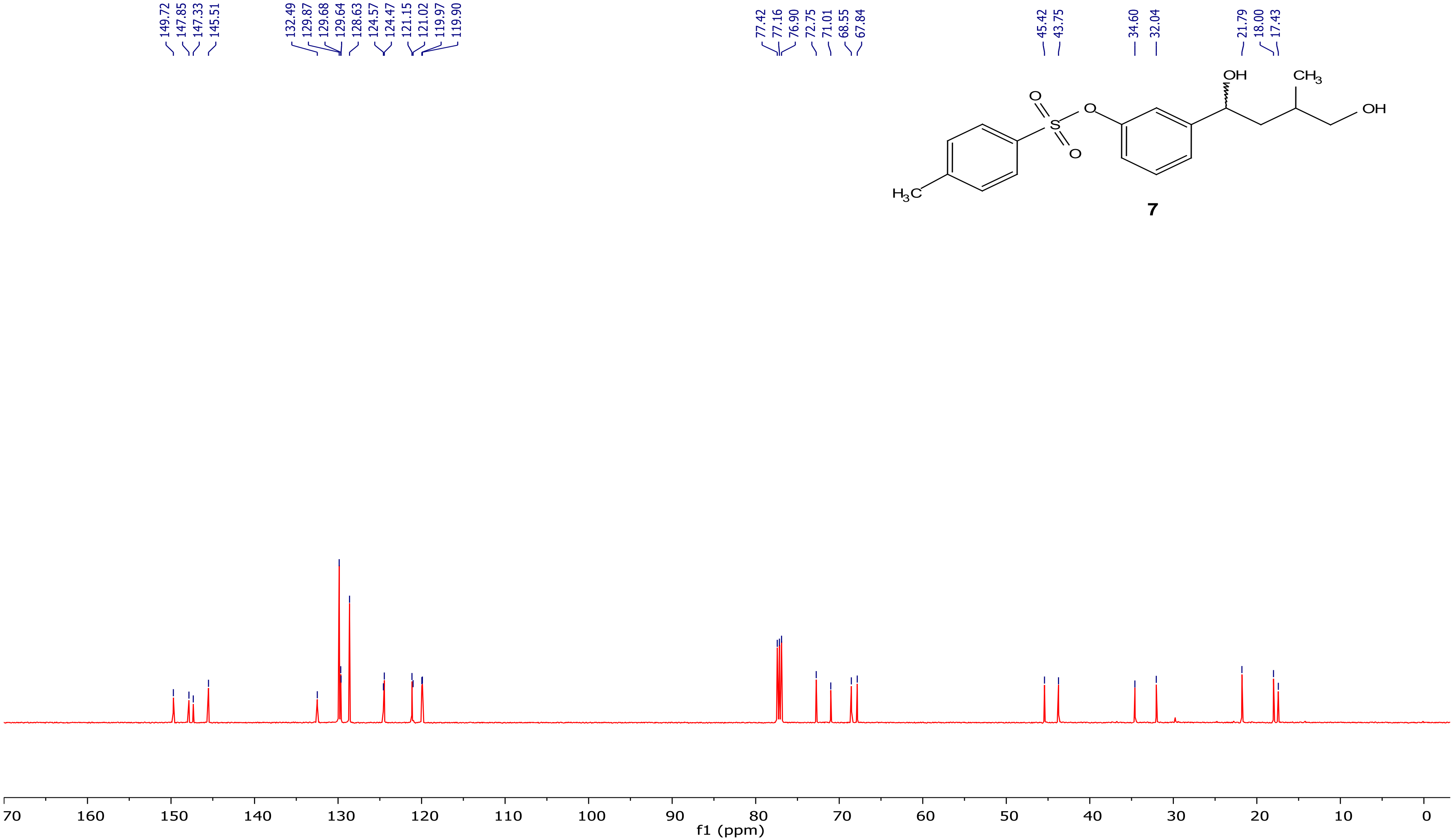


[1]H NMR (500 MHz, $CDCl_3$) of

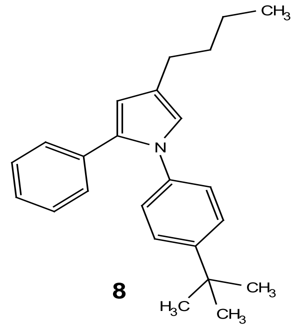


7

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 7



^{1}H NMR (500 MHz, CDCl$_3$) of 8



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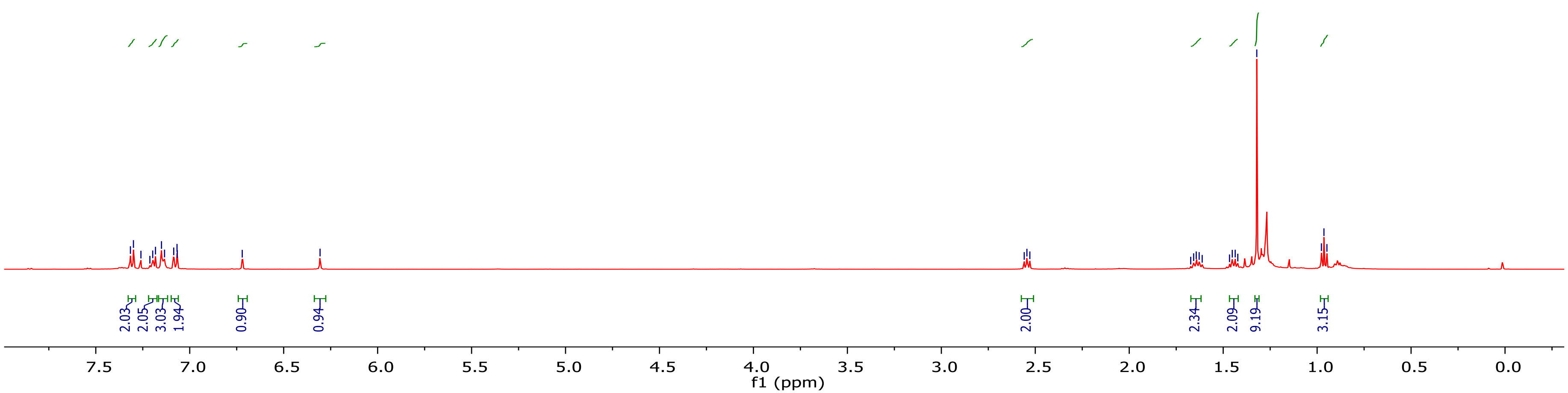
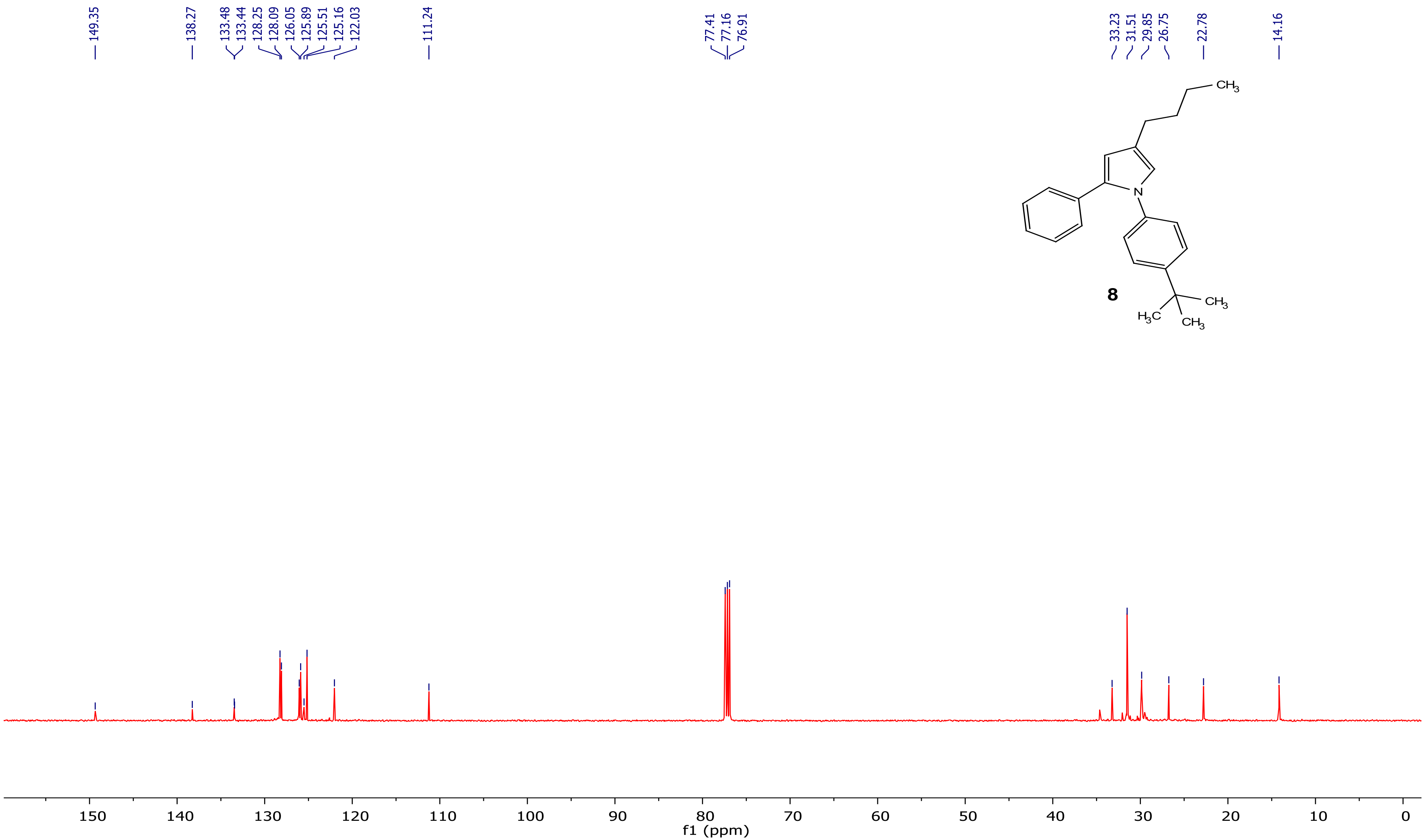
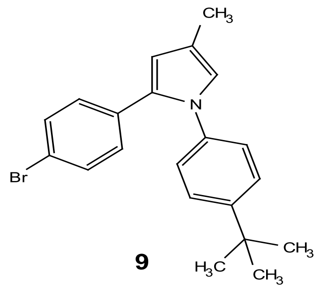


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 8



[1]H NMR (500 MHz, $CDCl_3$) of 9



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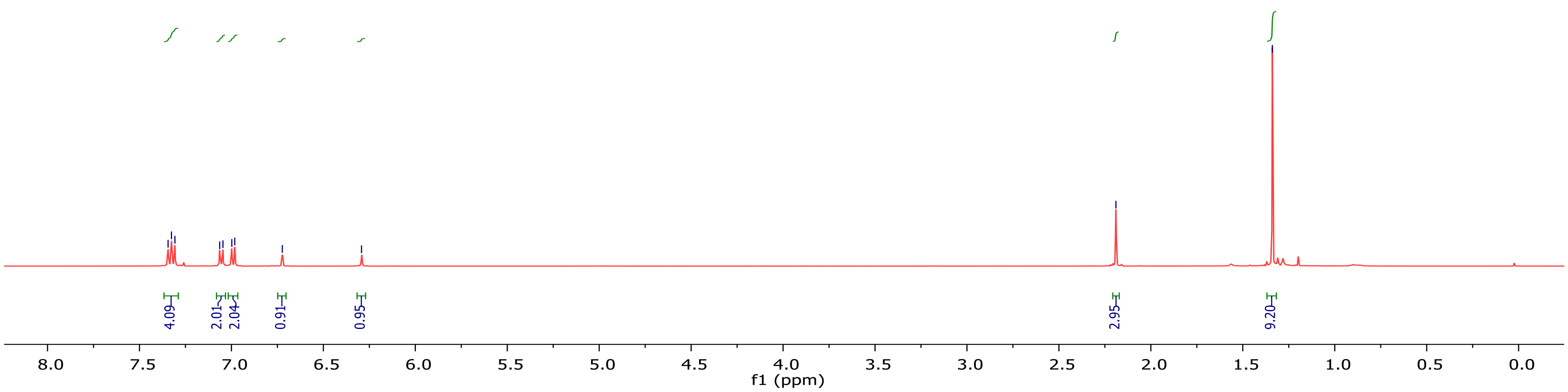
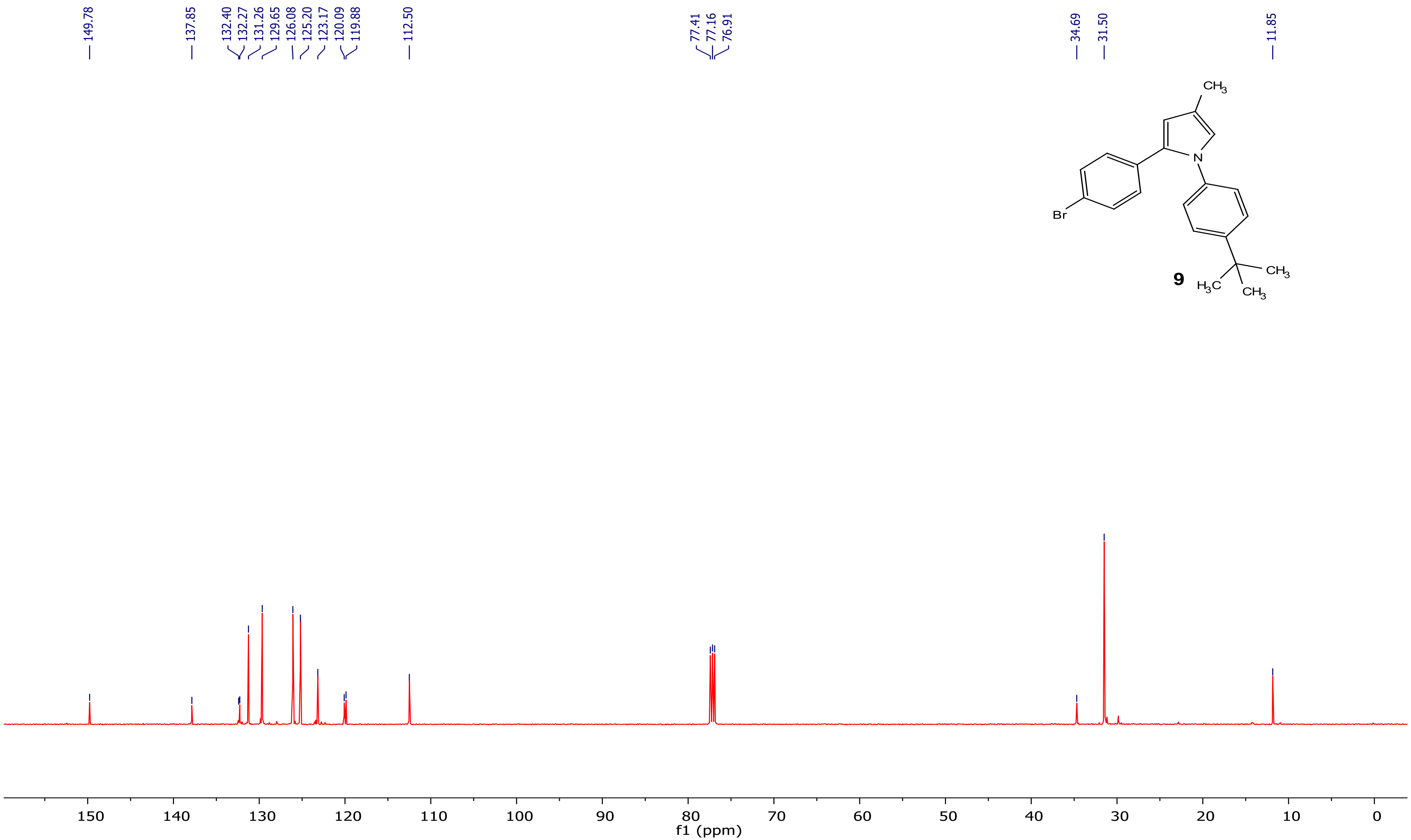
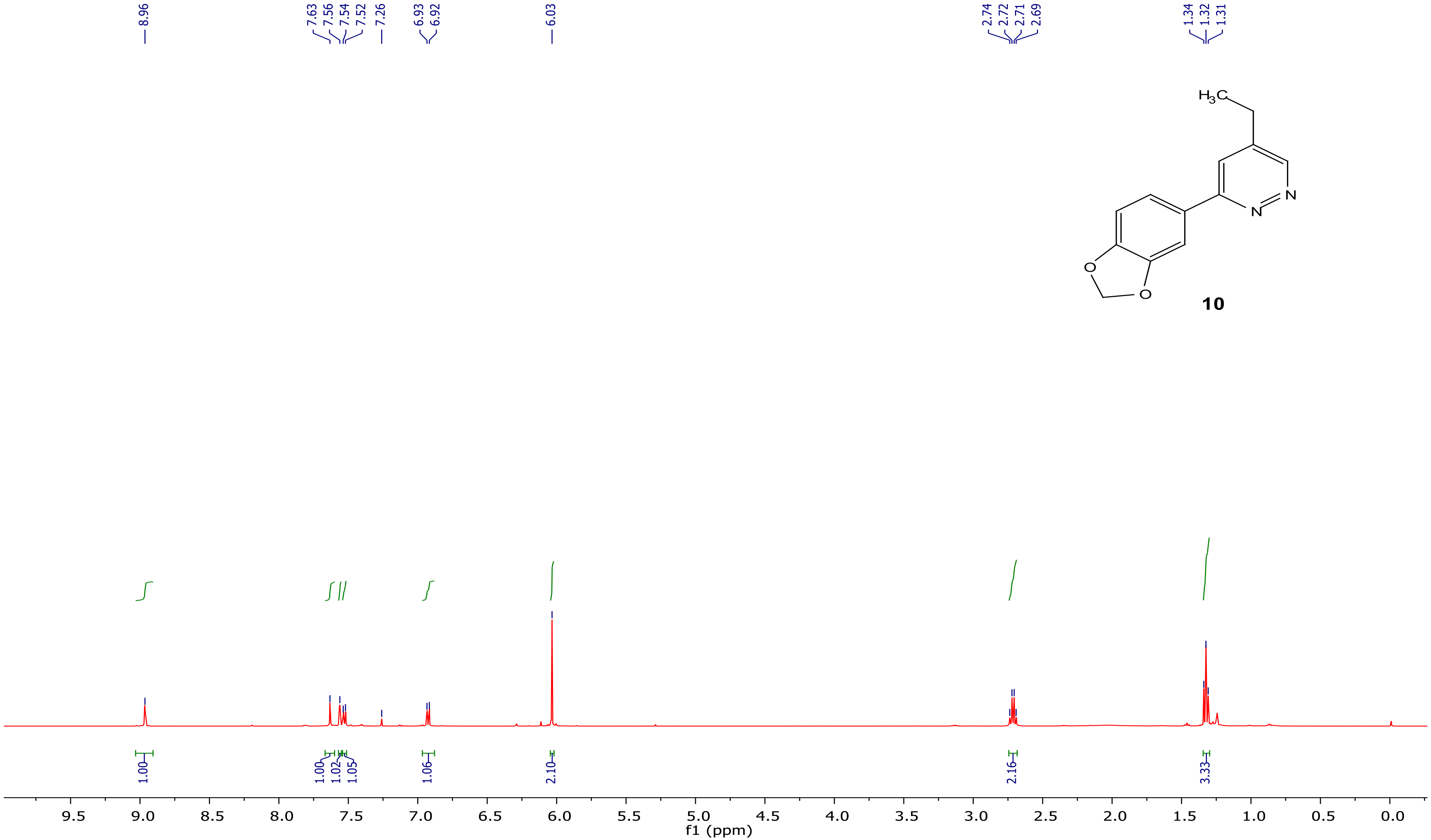


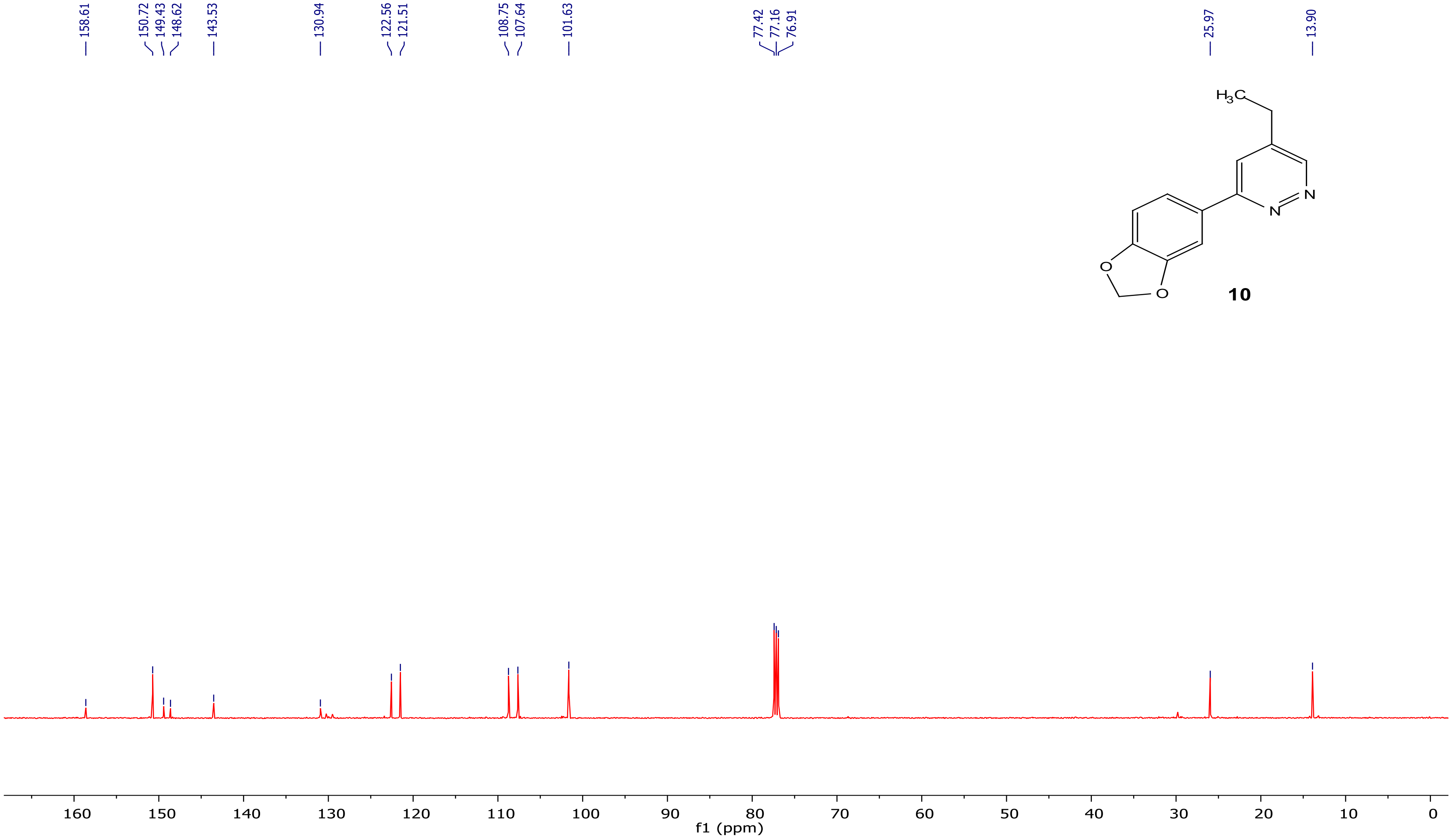
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 9



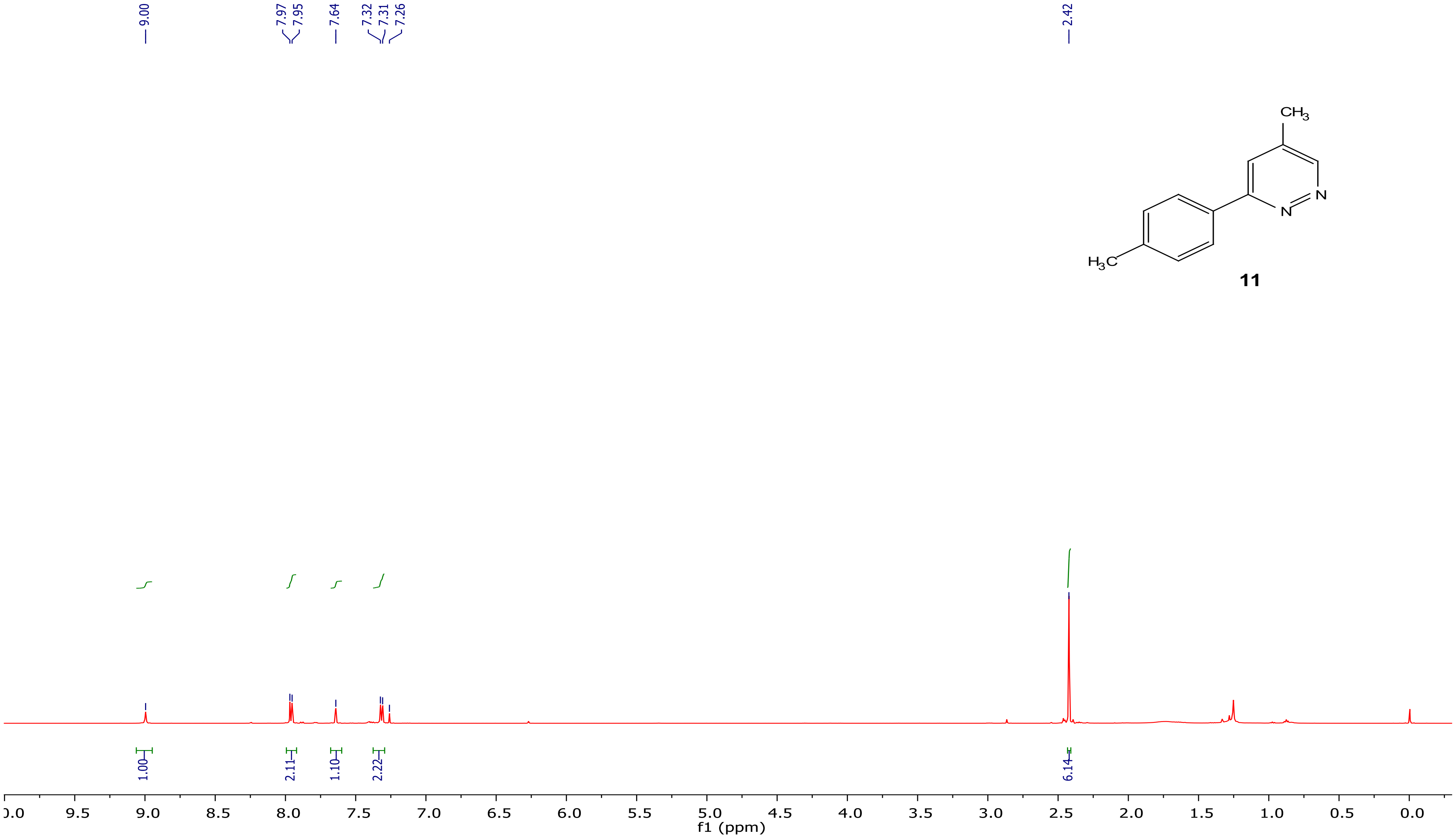
[1]H NMR (500 MHz, $CDCl_3$) of 10



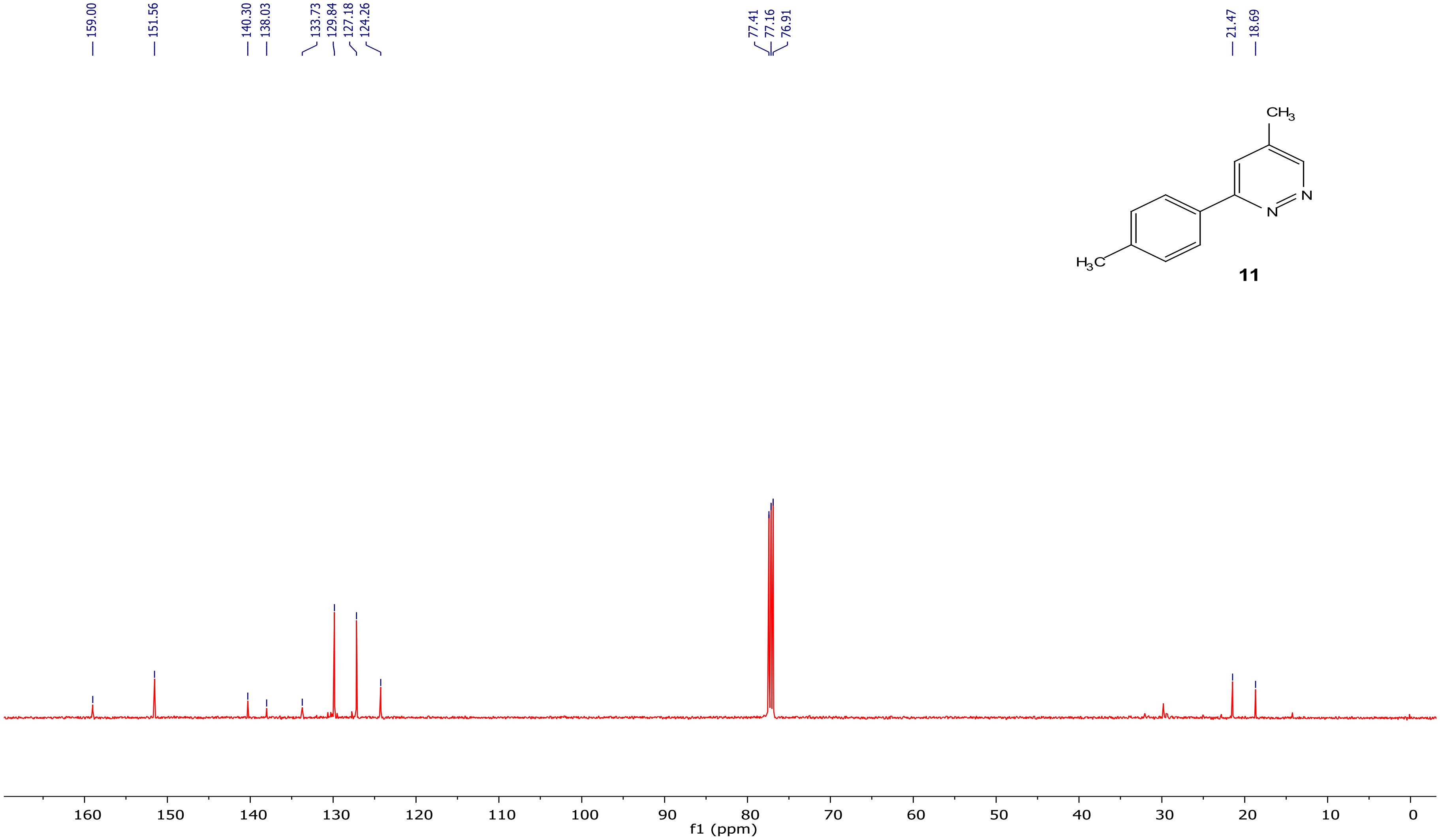
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 10



[1]H NMR (500 MHz, $CDCl_3$) of 11



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 11



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