

## **Supporting Information**

### **Phosphorous-doped graphitic material as solid acid catalyst for microwave-assisted synthesis of $\beta$ -ketoenamines and Baeyer-Villiger oxidation**

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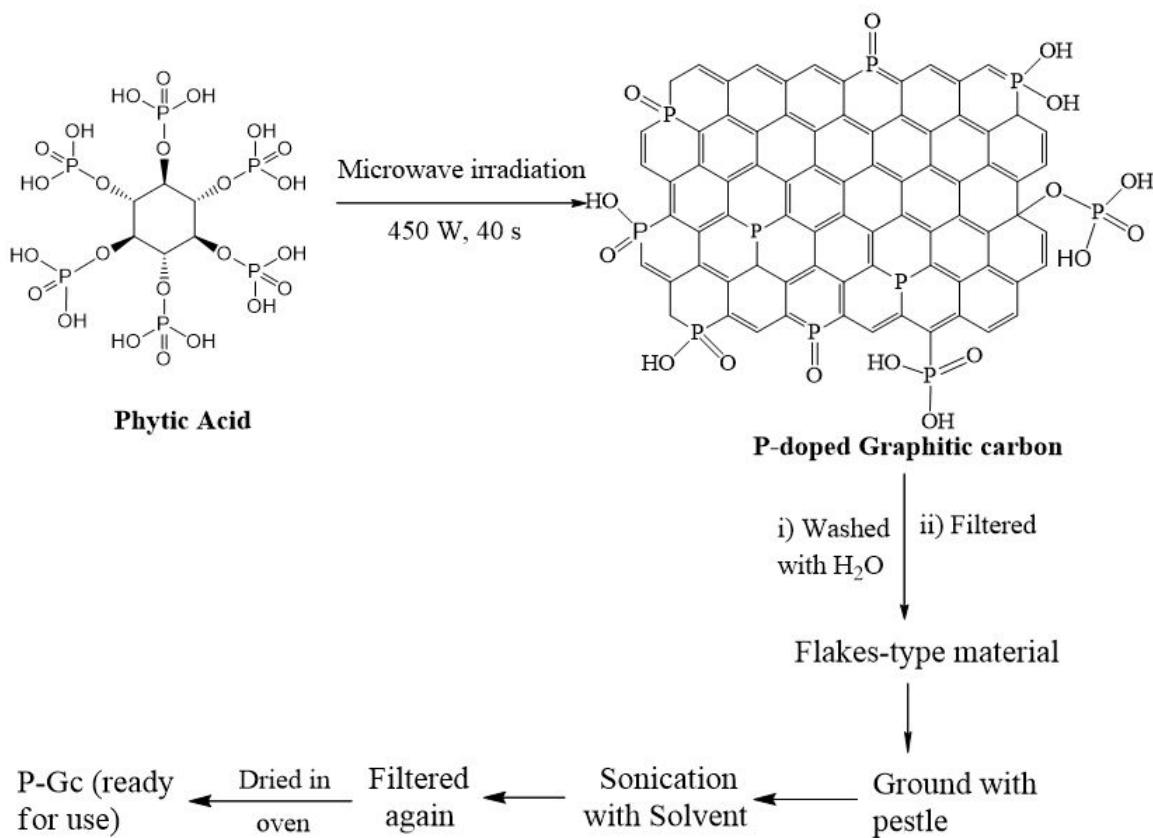
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## Synthesis of Catalyst



**Scheme SI1: Synthesis of P-doped Graphite from Phytic Acid**

## FTIR

FTIR was performed in ATR mode with 2 mg of the sample

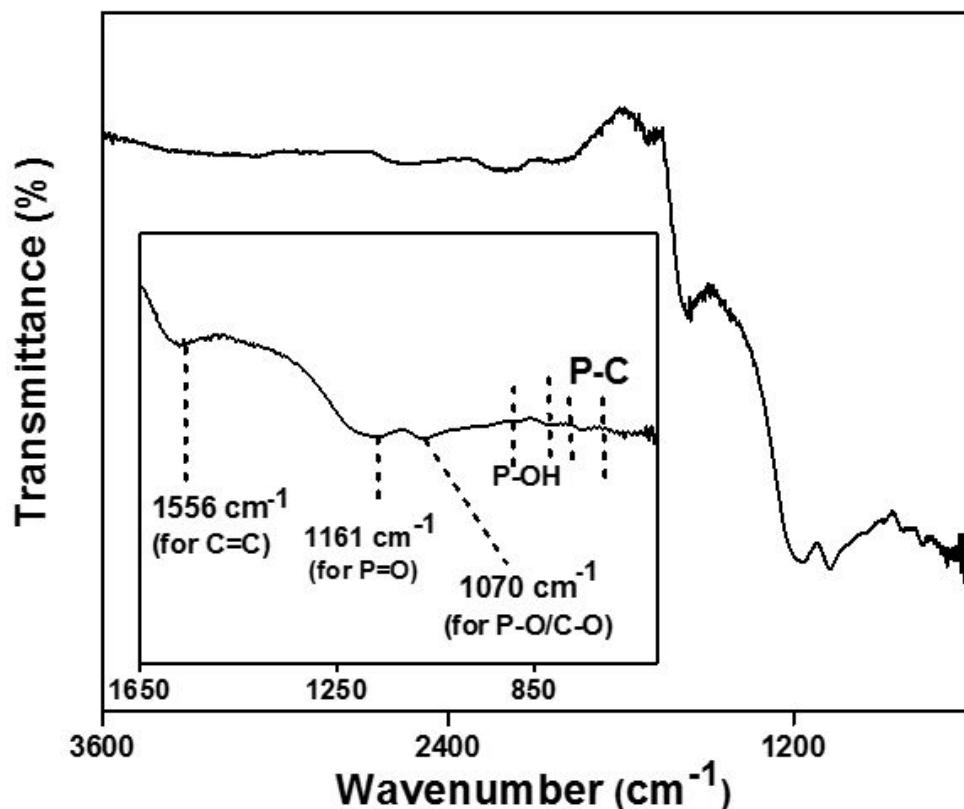


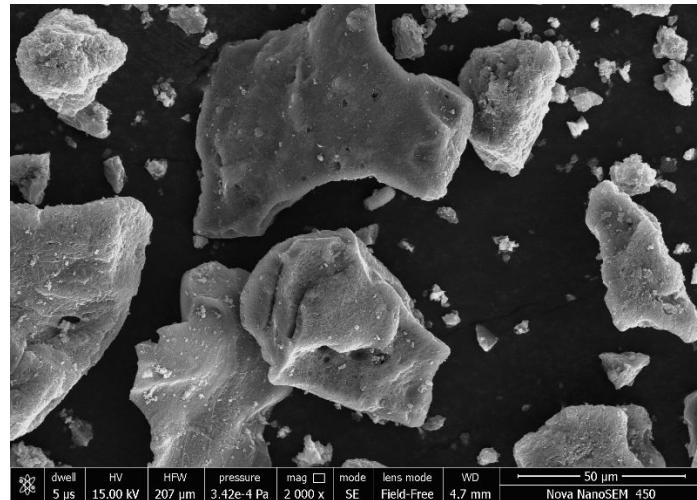
Figure SI1: FTIR Spectrum of P-Gc (Inset: Zoomed Region)

## SEM

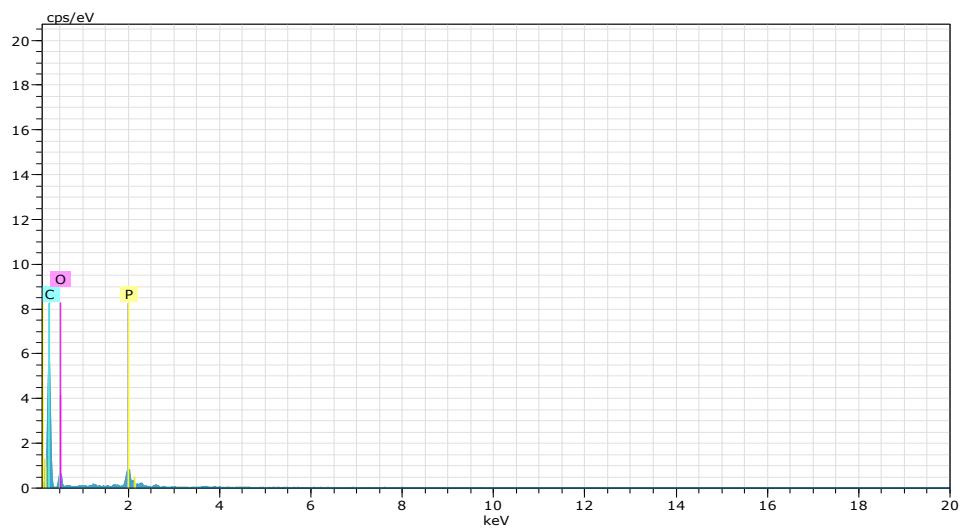
### Sample preparation for SEM

Pinch of P-Gc was taken in a sample holder (made of stainless steel and alumina alloy) with conducting coating of Gold and double sided carbon tape.

EDS analysis (Figure SI3) was done with SEM. Relative atomic percentages of the elements are given in Table SI1



**Figure SI2: SEM Images of 50  $\mu\text{m}$  magnification.**



**Figure SI3: Energy dispersive X-ray Spectrum of P-Gc**

**Table SI1: Relative percentages of Elements present in P-Gc by EDS Analysis**

El	A.N.	Series	Unn. C. (Wt. %)	Norm. C (Wt. %)	Atom. C (At. %)	Err. (1 Sigma) (Wt. %)
C	6	K-Series	75.47	75.47	81.63	11.16
O	18	K-Series	20.60	20.60	16.73	4.84
P	15	K-Series	3.93	3.93	1.65	0.22

Unn. C. (Wt. %) : Unnormalised concentration in weight percent of element

Norm C (Wt. %) : Normalised concentration in weight percent of element

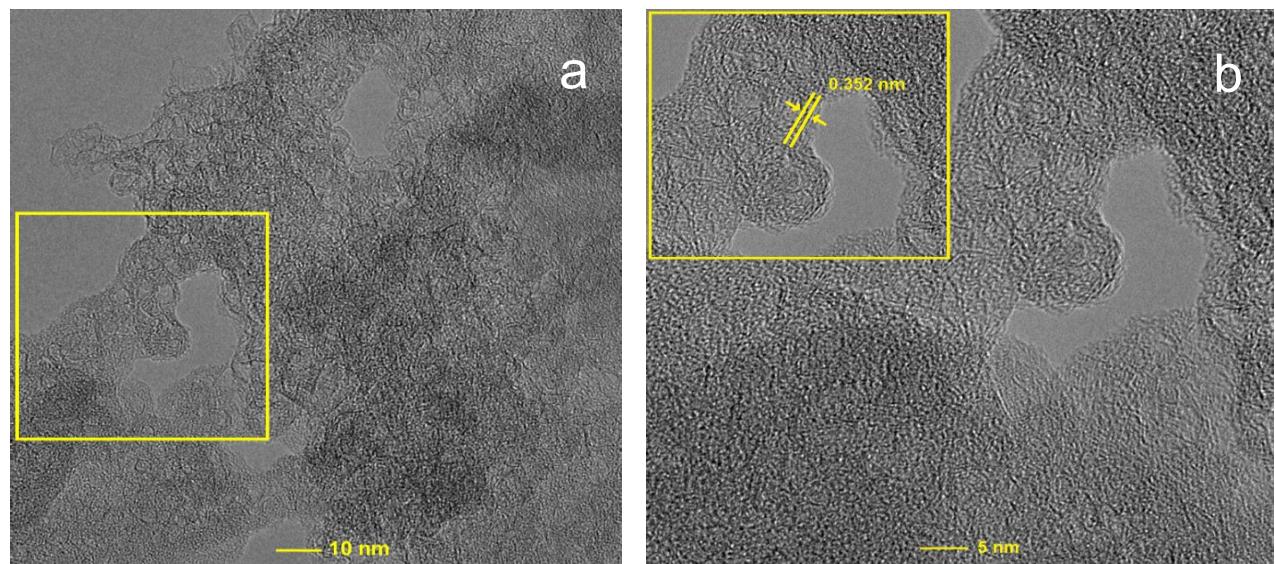
Atom C (At. %) : Atomic weight percent

Err. (1 Sigma) (Wt. %) : The error in the weight percent concentration at the 1 sigma level

## TEM

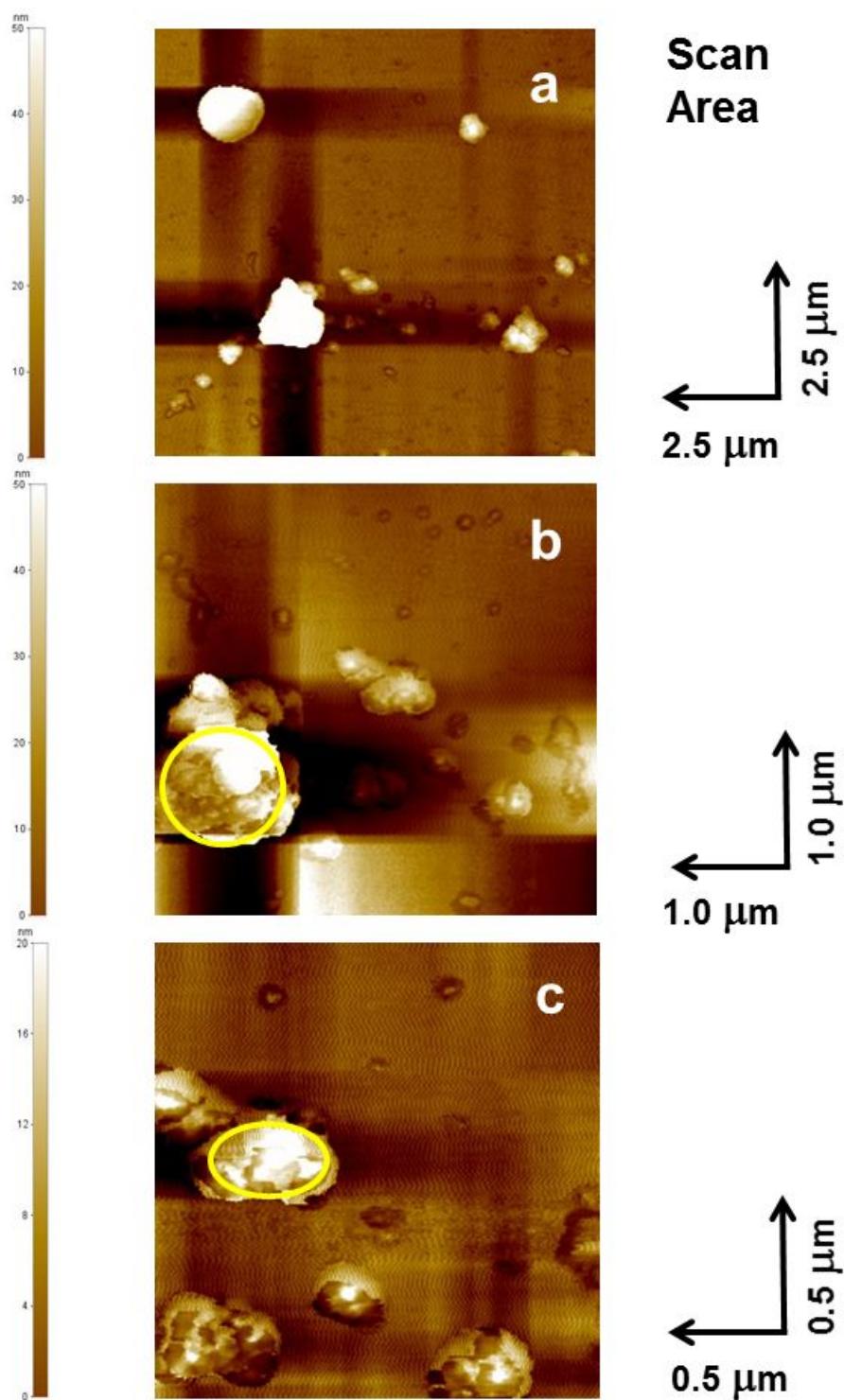
### Sample Preparation for TEM

1 mg of P-Gc was sonicated in 20 to 25 mL Methanol using probe sonicator for two hours. Then it was dropped on a copper grid and dried in oven overnight. Now, the sample is ready for analysis.



**Figure SI4:** TEM Images of (a) 10 nm, (b) 5 nm magnification

AFM



**Figure SI5: AFM Images**

**Table SI2: Roughness measurement from AFM topography images (marked areas)**

Figure	Scan Area ( $\mu\text{m} \times \mu\text{m}$ )	Max Roughness (nm)	Avg Roughness (nm)
SI5b	1.0 x 1.0	24.156	20.476
SI5c	0.5 x 0.5	7.705	6.122

## BET Surface Area and Porosimetry Analysis

Specific Surface Area was calculated using BET Theory. Volume of the sorbed gas (Nitrogen) was plotted against Relative Pressure to get type-V curve (Figure SI6a, SI7a) in multilayer adsorption-desorption which corresponds to mesoporous material. From the linear graph (Figure SI6a and SI7a, inset), the total and specific surface areas were determined as follows:

$$W_m = \frac{1}{\text{Slope} + \text{Intercept}}$$

Where,  $W_m$  = Weight of the adsorbate as monolayer

$$\text{Total Surface Area, } S_{\text{total}} = \frac{W_m \cdot N_A \cdot A_{\text{CS}}}{M}$$

$N_A$  = Avogadro Number,

$A_{\text{CS}}$  = Cross sectional area of the adsorbate,

$M$  = MW of Adsorbate

$$\text{Specific Surface Area, } S = \frac{S_{\text{total}}}{W}$$

$W$  = Weight of the adsorbent taken

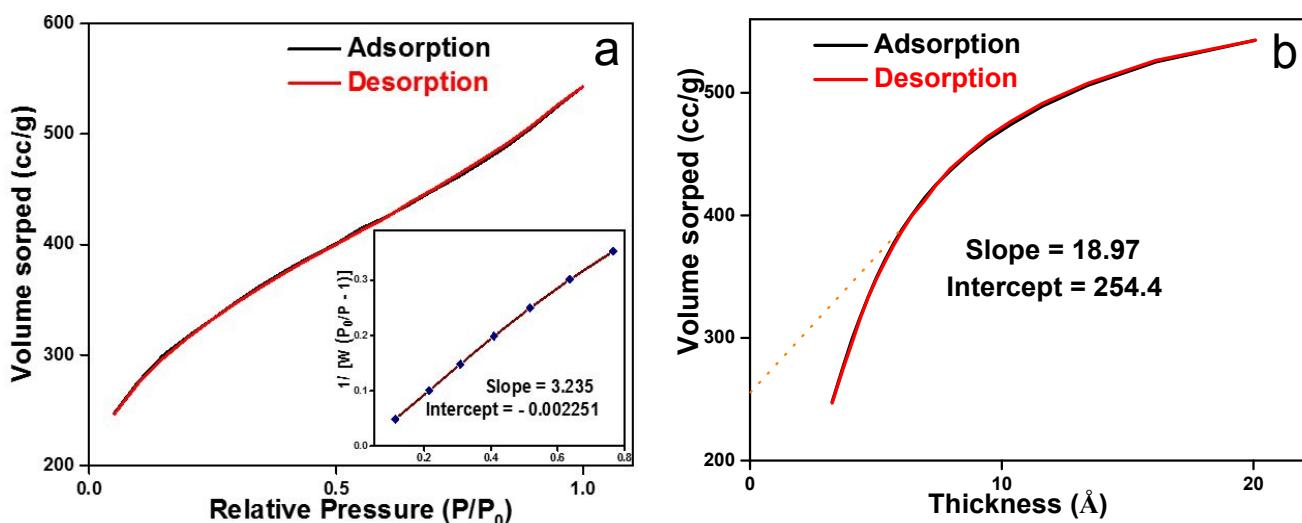
Thickness of the adsorbed layer of Nitrogen was calculated according to de Boer's equation:

$$\text{Thickness of adsorbent (in } \text{\AA}) = 0.88(P/P_0)^2 + 6.45(P/P_0) + 2.98$$

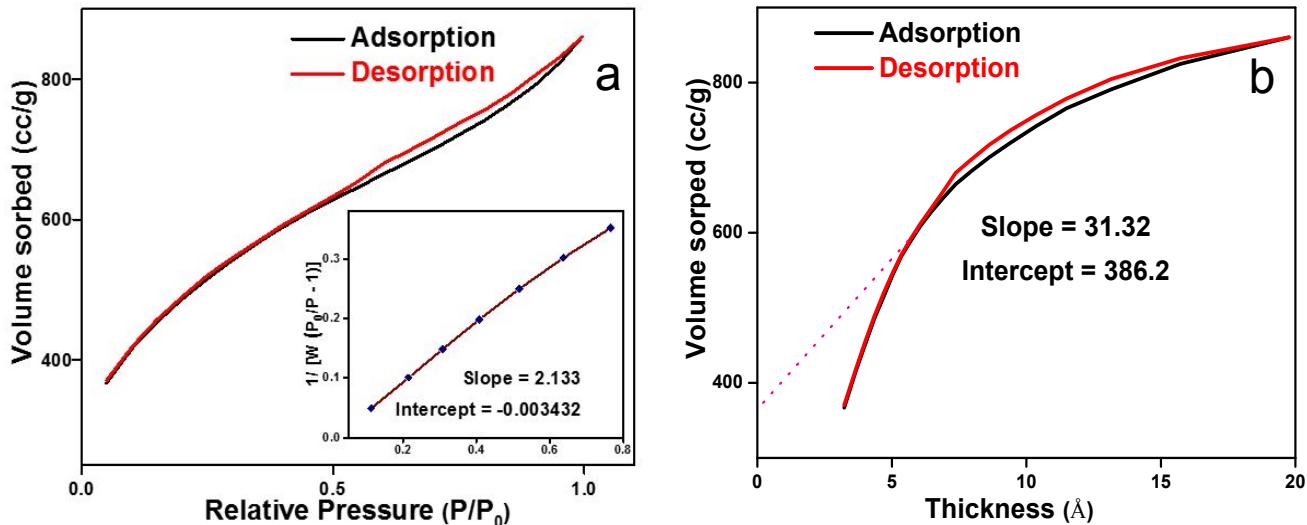
Volume of adsorbed and desorbed gas was plotted against thickness (Figure SI4b, SI5b) and micropore area and micropore volume were calculated according to de Boer's formula,

$$\text{Micropore area} = \text{slope} \times 15.47$$

$$\text{Micropore volume} = \text{intercept} \times 0.001547$$



**Figure SI6:** (a) Multilayer adsorption of liquid Nitrogen by P-doped Graphite (Flakes Material) at 77K, inset: linear graph for surface area measurement and (b) Porosimetry Analysis of P-doped Graphite through t-plot



**Figure SI7:** (a) Multilayer adsorption of liquid Nitrogen by P-doped Graphite (Sonicated Material) at 77K, inset: linear graph for surface area measurement and (b) Porosimetry Analysis of P-doped Graphite through t-plot

Detailed result from porosimetry study is given in Table SI3. According to IUPAC convention, it's a mesoporous material as the average pore diameter falls between 2 to 50 nm

**Table SI3: Porosimetry Analysis of P-Gc with Adsorption-Desorption**

Material	Sp. Surface Area	Micropore Area	Micropore Vol.	Avg. Pore Dia.
Flakes (before sonication)	1077 m <sup>2</sup> /g	782.9 m <sup>2</sup> /g	0.3945 cc/g	3.126 nm
Powdered (after sonication)	1635 m <sup>2</sup> /g	1150 m <sup>2</sup> /g	0.5988 cc/g	3.263 nm

**Table SI4: Specific Surface Area from BET Analysis from Previous Reports**

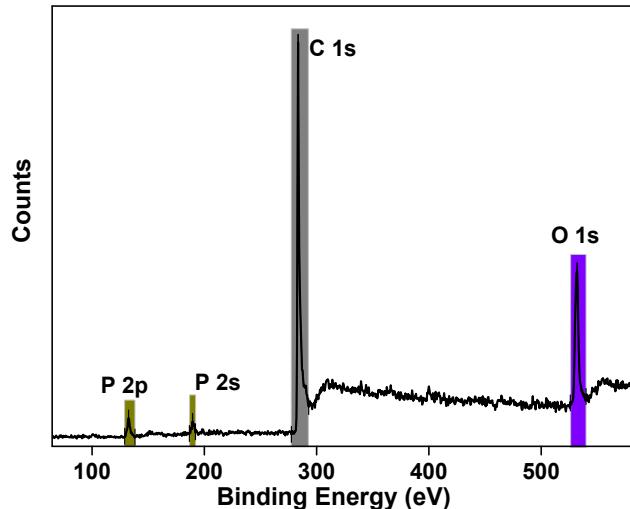
Material	S (m <sup>2</sup> g <sup>-1</sup> )	Reference
B-doped Graphene Oxide	18.42	Chem Nano Mat. 2017, 3, 794 – 797
FeN & N-doped Graphene	116	Adv. Funct. Mater. 2014, 24, 2930–2937
B & N co-doped Graphene	305	RSC Adv., 2013, 3, 22597-22604
S-doped Graphene	440	ACS Nano, 2012, 6, 1, 205-211
Borane-reduced Graphene oxide	466	ACS Nano, 2013, 7, 1, 19–26
N, P dual doped graphene	457.9	Nano-Micro Lett., 2019, 11, 30
P-doped Carbon Nanosheets	549.844	Adv. Sci. 2017, 4, 1600243
P-doped Graphitic Carbon (Synthesized from phytic acid)	1260	ACS Nano 2016, 10, 2305–2315

## XPS

The intensities of C, O and P atoms in survey spectrum of P-Gc (Figure SI8) were used alongwith their relative sensitivity factor to calculate the atomic percentage using the following equation.<sup>1</sup>

$$\text{Concentraion of atom } x = \frac{n_x}{\sum_i n_i} = \frac{I_x/S_x}{\sum_i I_i/S_i} \dots \text{Eqn (1)}$$

Where n is the number of atom, I is the area/intensity of photoemission peak and S is sensitivitiy factor for respective atom.



**Figure SI8: XPS survey spectrum of P-Gc**

**Table SI5: Atomic Percentage of Different Elements from XPS Survey**

Serial No	Atom	Atom %
1	C	83.30
2	O	13.51
3	P	3.18

## Ref:

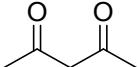
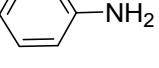
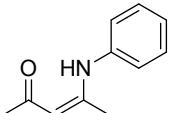
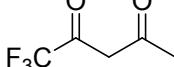
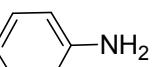
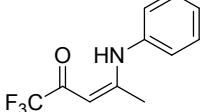
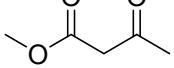
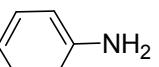
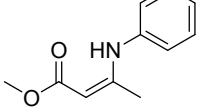
1. Wagner, C.D., Davis, L.E., Zeller, M.V., Taylor, J.A., Raymond, R.H. and Gale, L.H., 1981. Empirical atomic sensitivity factors for quantitative analysis by electron spectroscopy for chemical analysis. *Surface and interface analysis*, 3(5), 211 - 225

## Effect of Surface Area of P-Gc on Product Yield

Table SI3 shows ultrasound treatment enhances the surface area of P-Gc from 1077 m<sup>2</sup>/g to 1635 m<sup>2</sup>/g. P-Gc synthesized in our work is different from the previous report (Patel M.A. *et al*, ACS Nano 2016, 10, 2305–2315) mainly due to this characteristics (Table SI4). So, the effect of surface area was checked on the following reactions (Table SI6) including three β-ketoenamine synthesis and two Baeyer Villiger Oxidation.

The reactions were performed following the reaction condition (Table 3 &Table 5 in manuscript)

**Table SI6: Comparison of product yield in reactions performed with P-Gc Flakes and P-Gc Sonicated**

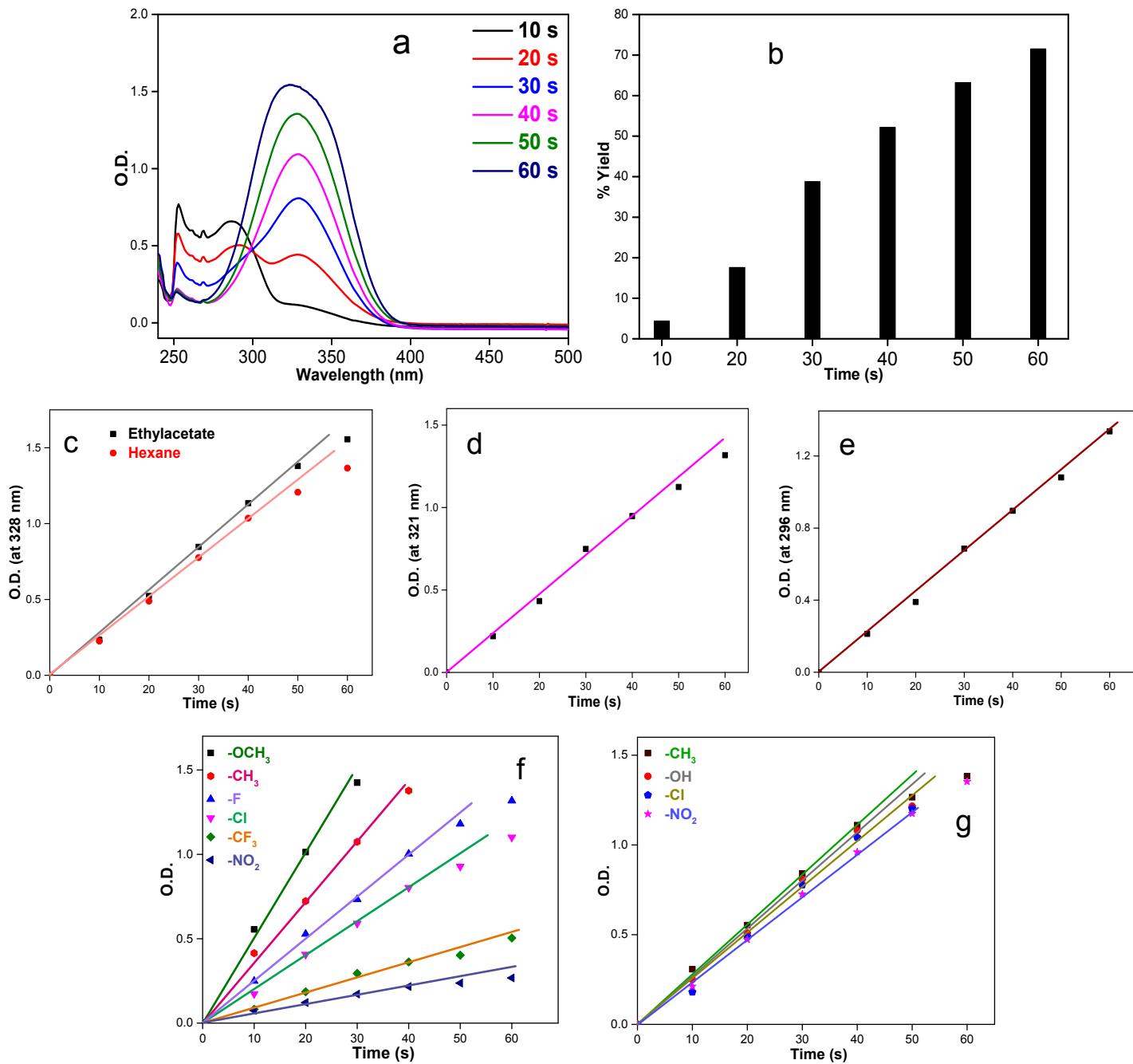
Reactants	Product	Yield (%)	
		P-Gc Flakes (1077 m <sup>2</sup> /g)	P-Gc Sonicated (1635 m <sup>2</sup> /g)
 + 		81 <sup>a</sup> , 74 <sup>b</sup>	94 <sup>a</sup> , 91 <sup>b</sup>
 + 		86 <sup>a</sup> , 83 <sup>b</sup>	97 <sup>a</sup> , 92 <sup>b</sup>
 + 		84 <sup>a</sup> , 80 <sup>b</sup>	93 <sup>a</sup> , 87 <sup>b</sup>
 + 50% H <sub>2</sub> O <sub>2</sub>		75 <sup>a</sup> , 69 <sup>b</sup>	82 <sup>a</sup> , 81 <sup>b</sup>
 + 50% H <sub>2</sub> O <sub>2</sub>		75 <sup>a</sup> , 70 <sup>b</sup>	84 <sup>a</sup> , 78 <sup>b</sup>

<sup>a</sup>yield from MW assisted synthesis, <sup>b</sup>yield from OB reaction

## Reaction Kinetics

### $\beta$ -ketoenamine synthesis

We got three separate peaks for two reactants and one product in UV-vis spectrum for each batches of reaction mixture in  $\beta$ -ketoenamine synthesis. Initial concentration of both of the reactants were 0.2 Molar. All the aliquots were diluted to mMolar range after catalyst separation. For each reaction, rate was measured taking the increasing O.D. value of the product (Figure SI9a) which is directly proportional to its concentration, according to Beer-Lambert's Law. Rates of all the reactions performed are given in Table SI7.



**Figure SI9:** (a) UV-vis spectrum of the MW assisted reaction between 1 1 1-trifluoropentane-2 4-dione and Aniline; (b) % Yield per time of the same reaction; Rate determination of MW assisted  $\beta$ -ketoenamine synthesis reactions of (c) 1 1 1-trifluoropentane-2 4-dione and Aniline

(d) Acetylacetone and Aniline (e) Methylacetoacetate and Aniline (f) 1 1 1-trifluoropentane-2 4-dione and different *para* substituted Anilines and (g) different *meta* substituted Anilines<sup>a</sup>.

<sup>a</sup>(b) in Ethylacetate and Hexane ; (a) and (c) to (f) in Ethylacetate only

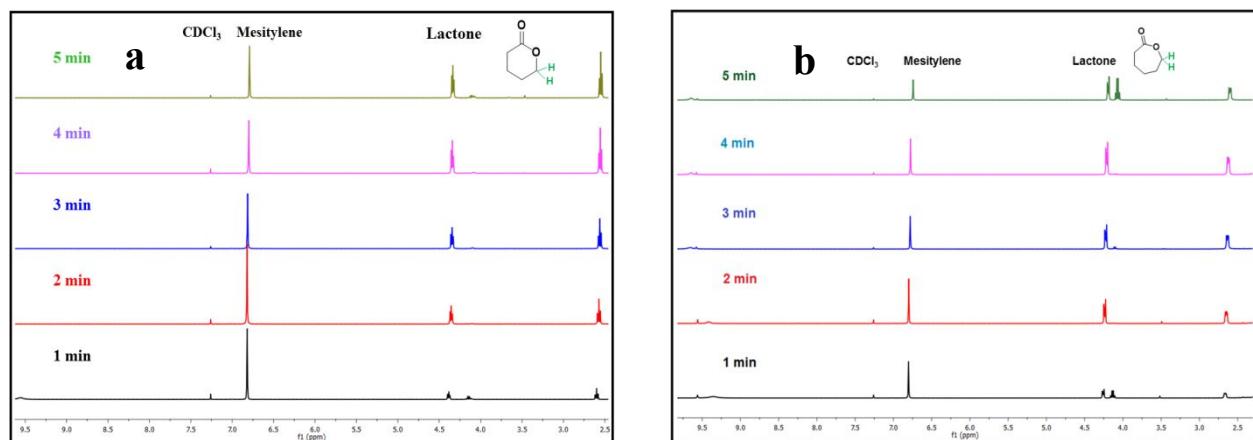
**Table SI7: Rates of different  $\beta$ -ketoenamine synthesis reactions in Microwave irradiation (both the reactants are in 0.2 Molar initial concentration)**

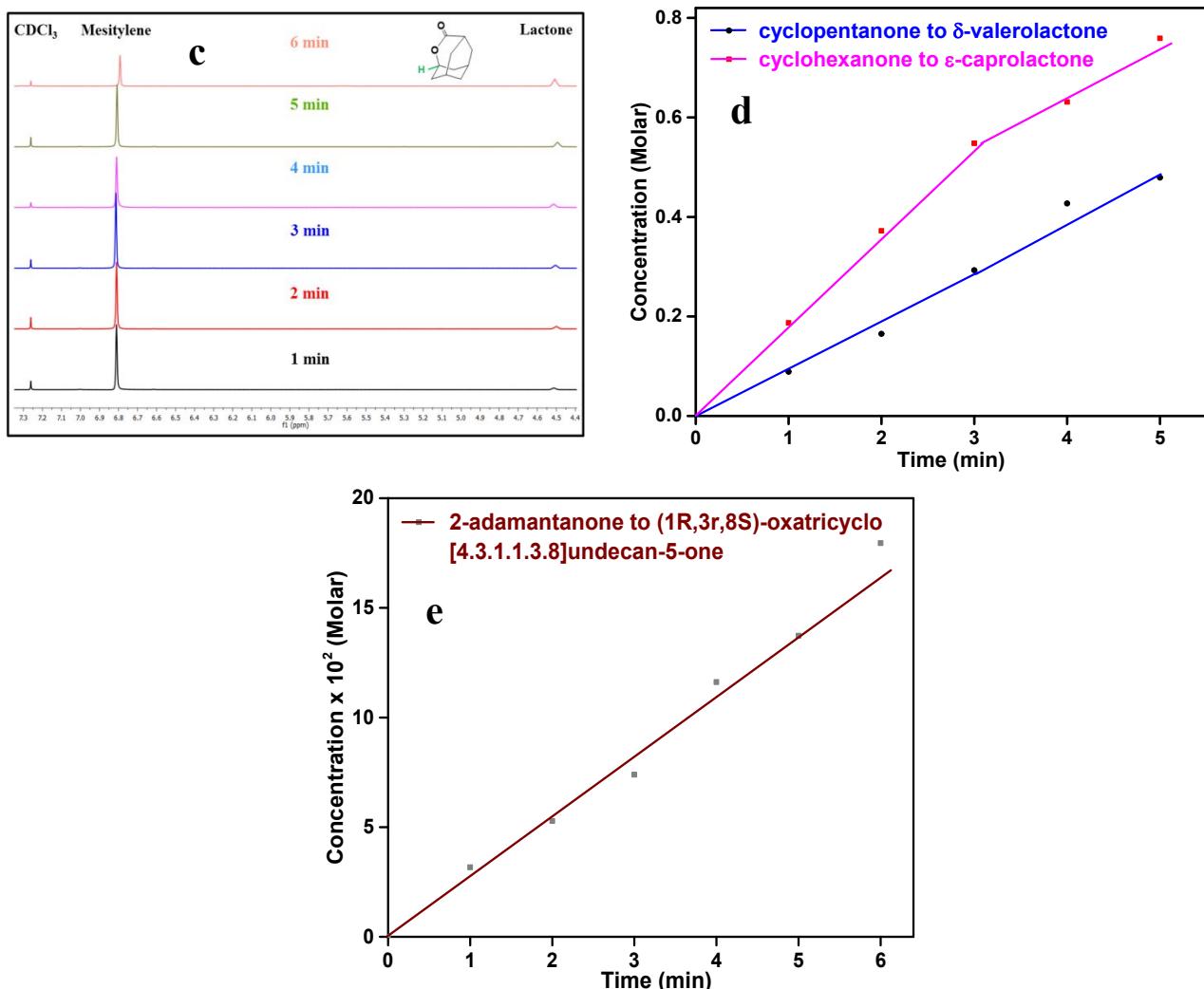
Reactions	Solvent	Rate/mole lit <sup>-1</sup> s <sup>-1</sup>
1,1,1-trifluoro-2,4-pentanedione + Aniline	Ethylacetate	27.74
1,1,1-trifluoro-2,4-pentanedione + 4 Anisidine	Ethylacetate	48.98
1,1,1-trifluoro-2,4-pentanedione + 4 Toluidine	Ethylacetate	35.30
1,1,1-trifluoro-2,4-pentanedione + 4 Fluoroaniline	Ethylacetate	24.85
1,1,1-trifluoro-2,4-pentanedione + 4 Chloroaniline	Ethylacetate	19.80
1,1,1-trifluoro-2,4-pentanedione + 4 (trifluoromethyl)aniline	Ethylacetate	9.02
1,1,1-trifluoro-2,4-pentanedione + 4 Nitroaniline	Ethylacetate	5.96
1,1,1-trifluoro-2,4-pentanedione + 3 Toluidine	Ethylacetate	26.74
1,1,1-trifluoro-2,4-pentanedione + 3 Aminophenol	Ethylacetate	20.635
1,1,1-trifluoro-2,4-pentanedione + 3 Chloroaniline	Ethylacetate	25.54
1,1,1-trifluoro-2,4-pentanedione + 3 Nitroaniline	Ethylacetate	24.81
1,1,1-trifluoro-2,4-pentanedione + Aniline	Hexane	25.58
Acetylacetone + Aniline	Ethylacetate	23.74
Methylaetoacetate + Aniline	Ethylacetate	22.21

### Baeyer Villiger Oxidation

For  $\delta$ -valerolactone (or, Tetrahydro-2H-pyran-2-one) and  $\epsilon$ -caprolactone (or, Oxepan-2-one), the peak of interest corresponds to 2H (triplet, full 1H-NMR spectrum in Figure SI49a and SI50a, respectively). For (1R,3r,8S)-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecan-5-one, it corresponds to 1H (multiplet, full 1H-NMR spectrum in Figure SI52a).

8 known standard solutions of the each of the products, from 0.1 Molar to 0.8 Molar, were run to draw the calibration curves.





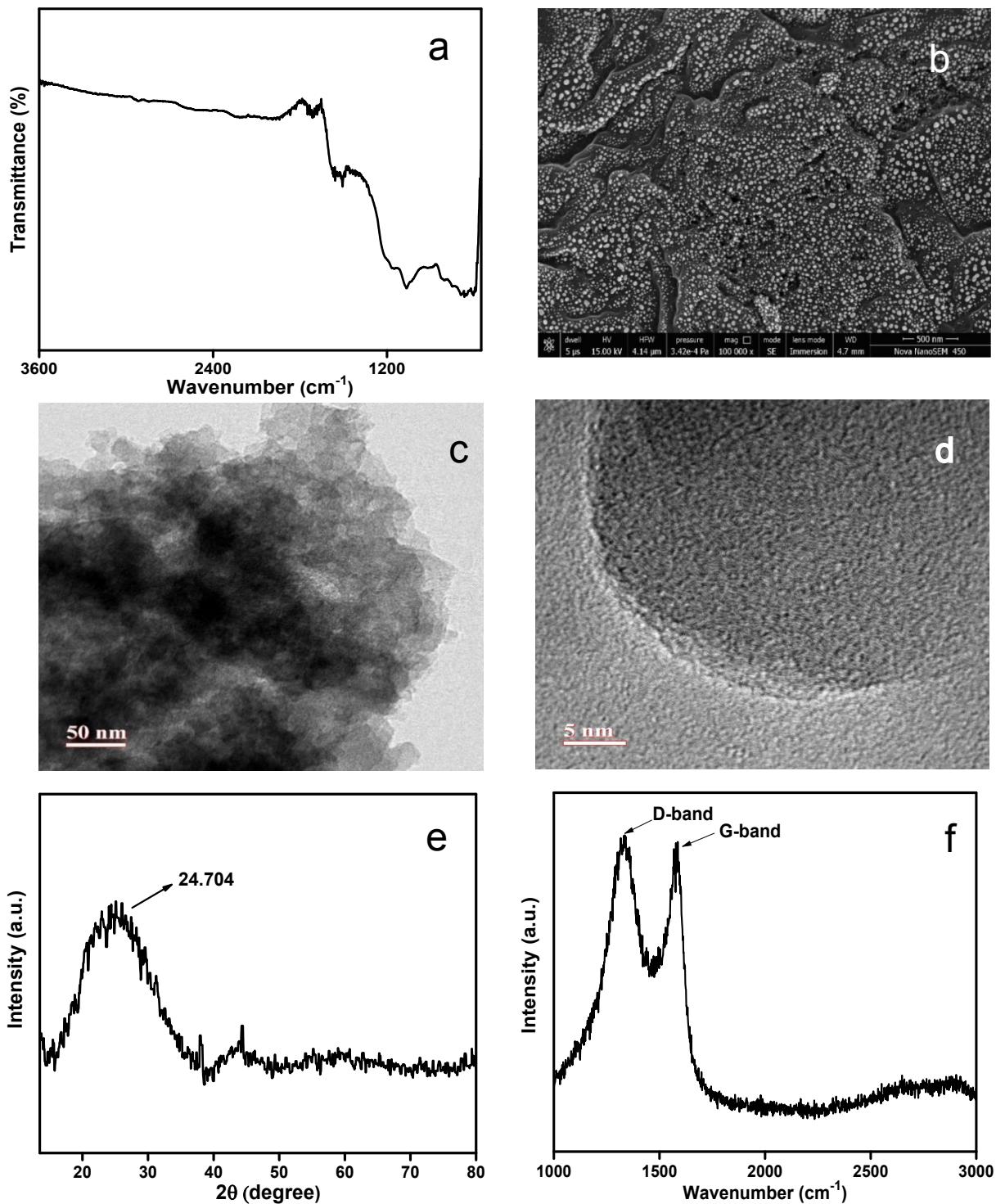
**Figure SI10:** 1H-NMR Spectrum of Reaction kinetics of conversion of (a) cyclopentanone to  $\delta$ -valerolactone; (b) cyclohexanone to  $\epsilon$ -caprolactone; (c) 2-Adamantanone to (1R,3r,8S)-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecan-5-one; (d) Rate determination of the first two reactions; (e) Rate determination of BV Oxidation of 2-adamantanone

**Table SI8:** Rates of different BV Oxidation reaction for lactone production from cyclic ketones (0.5 Molar) and 50% H<sub>2</sub>O<sub>2</sub> in Microwave irradiation

Reactant	Product	Rate/mole lit <sup>-1</sup> s <sup>-1</sup>
Cyclopentanone + H <sub>2</sub> O <sub>2</sub>	$\delta$ -valerolactone	$1.68 \times 10^{-3}$
Cyclohexanone + H <sub>2</sub> O <sub>2</sub>	$\epsilon$ -caprolactone	$3.06 \times 10^{-3}$
2-Adamantanone + H <sub>2</sub> O <sub>2</sub>	(1R,3r,8S)-4-oxatricyclo[4.3.1.1 <sup>3,8</sup> ]undecan-5-one	$4.56 \times 10^{-4}$

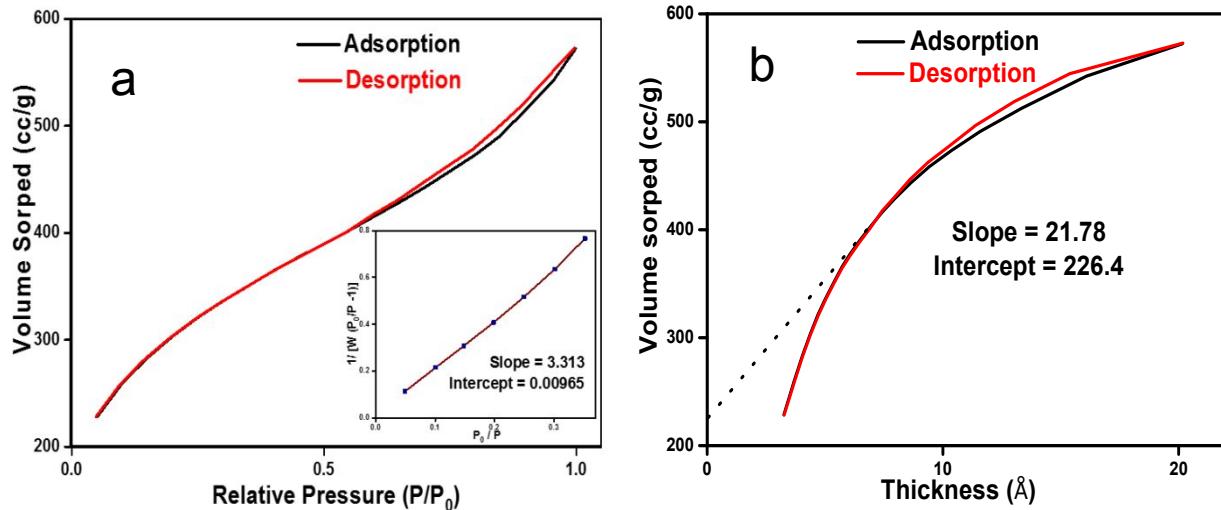
## Characterization of recovered catalyst after five cycles

The recovered catalyst after each cycles was washed with solvents like water, acetone, methanol to drive away the remaining reaction mixtures and dried in oven at 60°C for 24 hours. Cleaning of the catalyst was done without sonication as the effect of ultrasound can preferably change its surface area and pore size further. After five cycles, the material was examined through FTIR (Figure SI11a), SEM (Figure SI11b) and TEM (Figure SI11c), BET analysis (Figure SI12) and XPS (Figure SI13). The major change was observed in BET and XPS analysis.



**Figure SI11: (a) FTIR spectrum, (b) SEM Image (500 nm resolution), (c) TEM Image (50 nm resolution), (d) TEM Image (5 nm resolution), (e) Powder XRD pattern, (f) Raman spectrum of recovered P-Gc**

#### B.E.T. Analysis of Recovered P-Gc

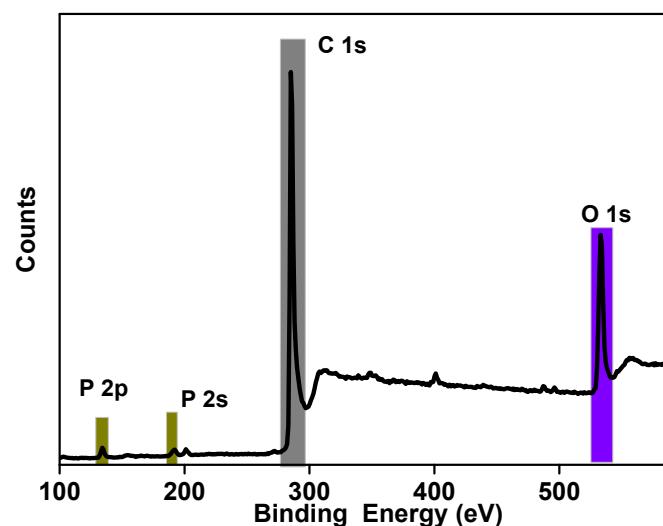


**Figure SI12: (a) Multilayer adsorption of liquid Nitrogen by recovered P-Gc at 77K, inset: linear graph for surface area measurement and (b) Porosimetry Analysis of recovered P-doped Graphite through t-plot**

**Table SI9: Comparison of Surface areas and porosimetry values of P-Gc before and after five cycles**

Parameters	Sp. surface area	Micropore area	Micropore volume	Avg. Pore Diam.
P-Gc	1635 m <sup>2</sup> /g	1150 m <sup>2</sup> /g	0.5988 cc/g	3.263 nm
Recovered P-Gc	1048 m <sup>2</sup> /g	710.4 m <sup>2</sup> /g	0.3511 cc/g	3.387 nm

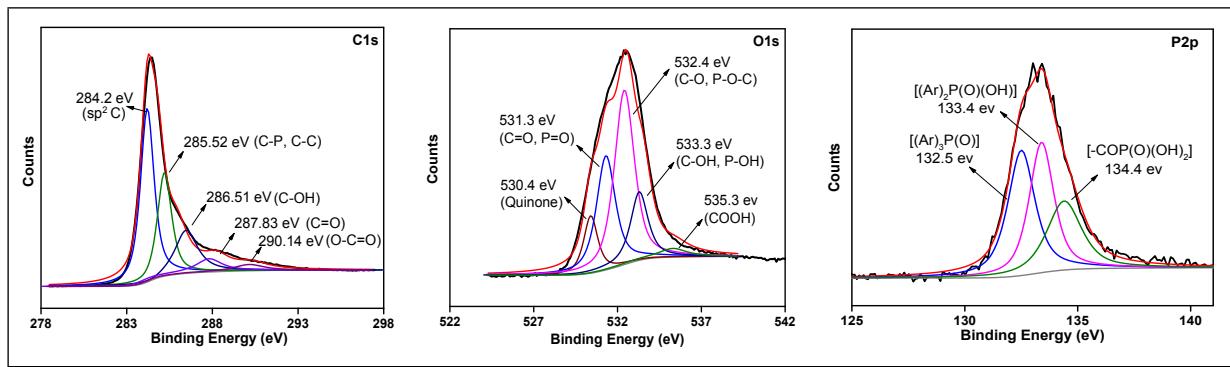
#### XPS of Recovered P-Gc



**Figure SI13: XPS Survey Spectrum of Recovered P-Gc**

**Table SI10: Atomic percentages of different elements present in recovered P-Gc from XPS**

Serial No	Atom	Atom %
1	C	81.71
2	O	16.73
3	P	1.55



**Figure SI14: Deconvoluted XPS peaks for C1s, O1s and P2p in Recovered P-Gc**

**Table SI11: Relative percentages of functional groups of C, O, and P obtained from XPS of Recovered P-Gc after five cycles**

Gr.	Area	Contribution	Gr.	Area	Contribution	Gr.	Area	Contribution
C=C	98655	42.7%	Quinone	9830	9.3%	(Ar) <sub>3</sub> P(=O)	2391	35.7%
C-P, C-C	67938	29.4%	C=O, P=O	27212	25.9%	(Ar) <sub>2</sub> P(O)(OH)	2469	36.9%
C-OH	45243	19.5%	C-O, P-O-C	48154	45.9%	-COP(O)(OH) <sub>2</sub>	1830	27.4%
C=O	12855	5.5%	C-OH, P-OH	18728	17.8%			
COOH	6298	2.7%	COOH	1055	1.0%			

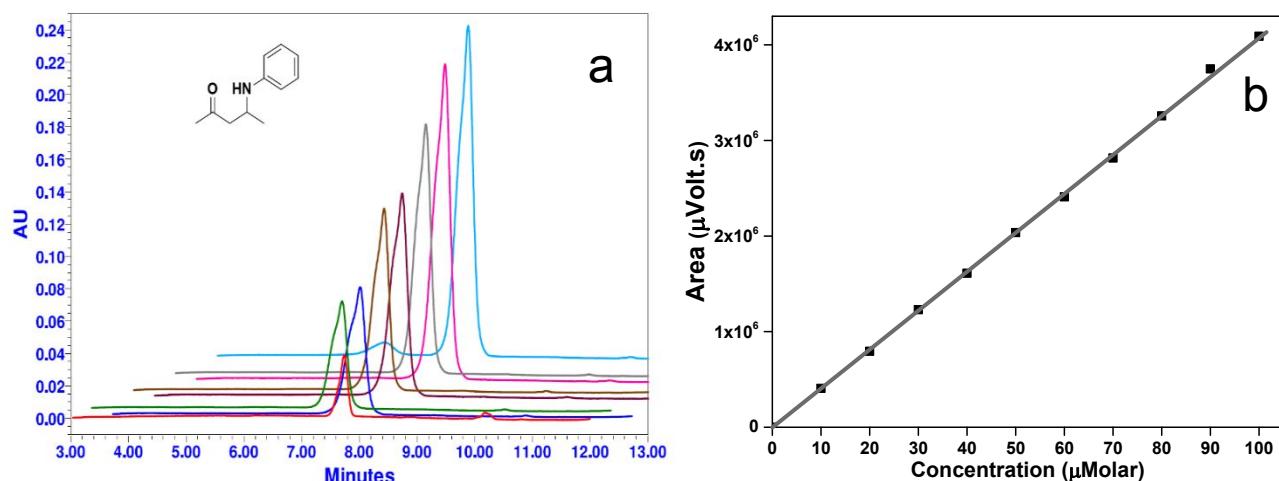
## Yield percentage of $\beta$ -ketoenamine measurement in HPLC

Total 10 known concentrations of  $\beta$ -ketoenamine were taken in Acetonitrile and run in HPLC in the following method (Table SI12) to draw a calibration curve (Figure SI15b) with the corresponding peak areas. Then the reaction mixture was run in the same method with proper dilution. From the peak area of the product, yield percentage was calculated (Figure SI16)

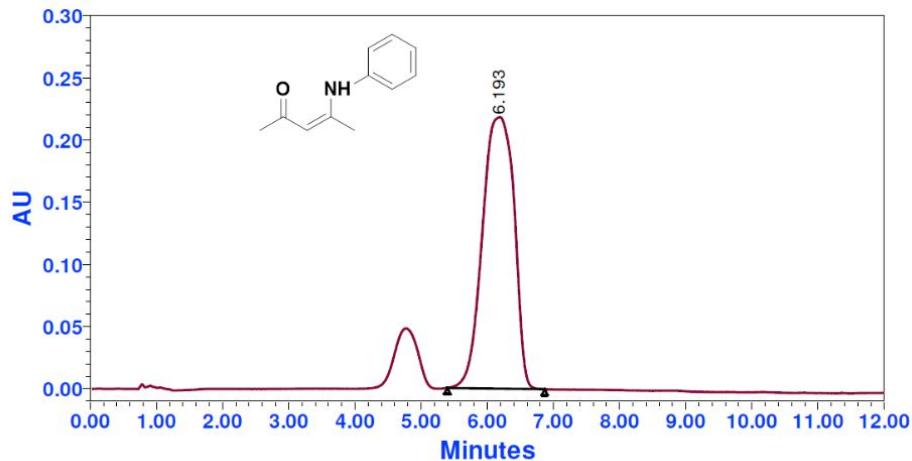
**Table SI12: HPLC method for measuring yield for  $\beta$ -ketoenamine**

Pump mode: Gradient ; solvent flow: 0.5 mL/min ; sample taken 20  $\mu$ L

Time (min.)	0.1% HCOOH in H <sub>2</sub> O (%)	CH <sub>3</sub> CN (%)
0	70	30
2	50	50
5	50	50
7	15	85
9	0	100
10	0	100
11	70	30
12	70	30

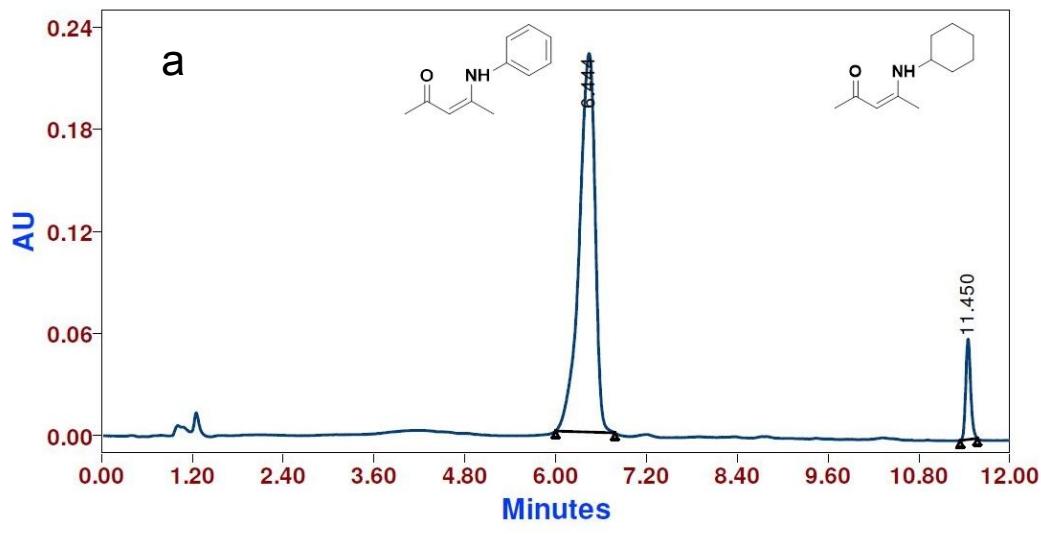


**Figure SI15: (a) Overlaid HPLC data for 4-(phenylamino)pentan-2-one and (b) Calibration curve with the peak areas of different concentrations**

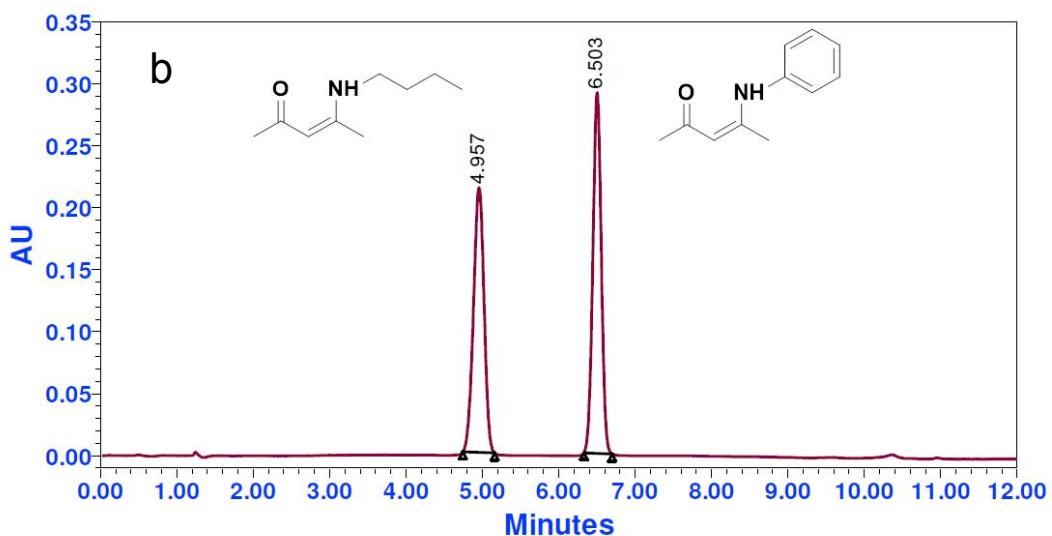


**Figure SI16: Yield measurement of synthesized  $\beta$ -ketoenamine [4-(phenylamino)pentan-2-one, in oil bath] from HPLC**

To observe the selectivity of P-Gc between aromatic and aliphatic amines, (i.e. aniline vs cyclohexylamine and aniline vs n-butylamine) only the oil-bath reaction of the amines with acetylacetone was monitored in HPLC, not the microwave one. This is to make sure that no external factor like dipole moment is playing for the selectivity (Figure SI17).



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 Ch1 309nm@1.2nm	6.444	3246456	92.43	222512
2	2998 Ch1 309nm@1.2nm	11.450	265758	7.57	59029



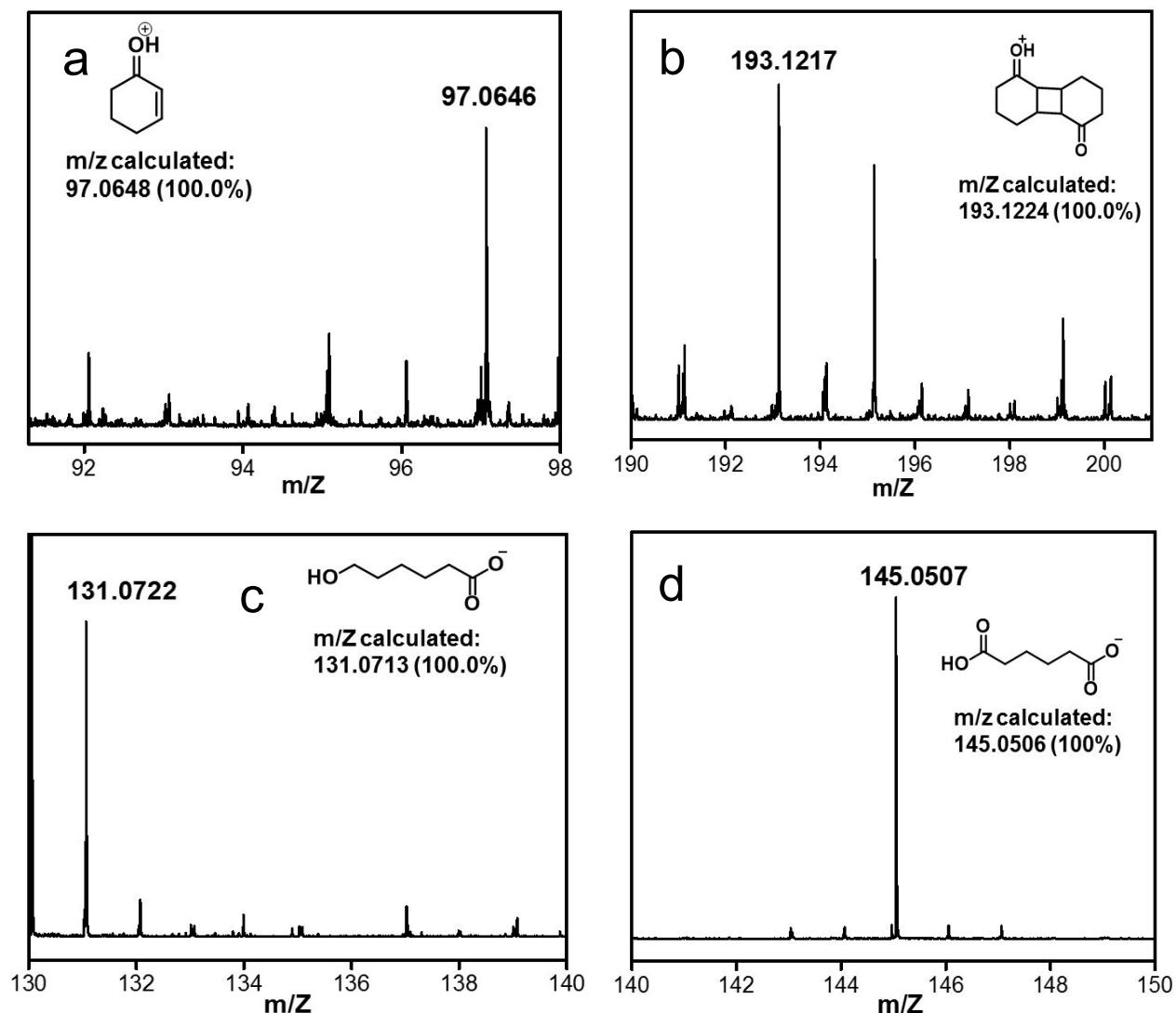
Processed Channel: 2998 Ch1  
309nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	2998 Ch1 309nm@1.2nm	4.957	2057354	47.90	213892
2	2998 Ch1 309nm@1.2nm	6.503	2237391	52.10	291346

**Figure SI17: Selectivity for  $\beta$ -ketoenamine synthesis. Yield measurement of two products from HPLC (a) 4-(phenylamino)pentan-2-one and 4-(cyclohexylamino)pentan-2-one (b) 4-(butylamino)pentan-2-one and 4-(cyclohexylamino)pentan-2-one**

## Identifying Intermediates of BV Oxidation from HRMS data

The crude reaction mixture from cyclohexanone to oxepan-2-one (or  $\epsilon$ -caprolactone), after proper dilution in acetonitrile, was run in HRMS in both positive and negative mode. Several side products (Figure SI16 a, b, c, d) and spiro-bisperoxide compound (Figure 7) as intermediate were found in trace quantity. Aliquots from the same reaction were taken in several time intervals and run in HRMS to get peaks for same m/Z values, certainly of various abundances. These intermediates are observed from both MW and OB reactions



**Figure SI18 (a) to (d):** HRMS data of trace amount of intermediates from reaction mixture of cyclohexanone and hydrogen peroxide to oxepan-2-one

## Comparison of Catalytic activity of P-Gc over other carbocatalysts in $\beta$ -ketoenamine synthesis and Baeyer Villiger oxidation with $H_2O_2$

Both of the reactions had been reported with metal-based catalysts for most of the time while very few were MFCs. We have excluded the metal-based ones to compare the greenness of our work. It is also mention-worthy that, ours is the first report of both of the reactions occurring in microwave oven, hence following cleaner and time-saving synthetic scheme.

**Table SI13: Comparison for  $\beta$ -ketoenamine synthesis**

Cat	Synthesis of Cat	Reaction Condition for $\beta$ -ketoenamine synthesis	Max. Yield (%)	Ref
GO- $SnO_2^*$	More than 17:30 hrs, max Temp 180°C (in autoclave). Required: GO, $SnCl_4$ , $H_2O$	Solvent free: 60°C, 40 min, 10 wt% cat  In MeOH: 60°C, 75 min. 10 wt% cat	Solvent free: 98  Solvent: 96	15
IQGO	Purchased	Solvent-free, 60°C, 3h. 10 mg cat	99	16a
P-Gc	MW irradiation (450 W) of 50% Phytic acid for 40s + Sonication for 15 min	MW: 450W, 60°C, 3 min, EtOAc & solvent free, 8mg cat  OB: 60°C, 60 min, EtOAc & solvent free, 10 mg cat	MW: 98 (solvent), 78 (solvent-free)  OB: 94 (solvent), 70 (solvent-free)	This work

In case of Baeyer-Villiger oxidation with  $H_2O_2$  as oxidant, excluding metal-based catalysts, several hazardous and costly organic compounds had been used as catalyst, co-catalyst, additive or even as solvent. But no report has been found so far showing any carbon material and  $H_2O_2$  together. We've reported it for the first time. As the cyclic ketones have imparted maximum yield in all of the previous reports, we have also mentioned the reaction condition and yield of cyclic ketones only for comparison purpose.

**Table SI14: Comparison for Baeyer-Villiger oxidation with  $H_2O_2$**

Cat	Synthesis of Cat	Reaction Condition for BV Oxidation	Max. Yield (%)	Ref
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Octanoic Acid	Purchased (hazardous)	Solvent: Ionic liquid [1-(3-hydroxy propyl)-3methylimidazolium Nitrate]. Additive: 25mg Novozym 435. 50°C, 5h, 1 mmole cat, 50% H <sub>2</sub> O <sub>2</sub>	99	16b
2,3,4,5,6 –penta Fluorobenzoic acid	Purchased (hazardous)	Solvent: DCM, H <sub>2</sub> O. Additive: Diisopropyl carbodiimide, N-methylimidazole. r.t., 3h, 1 mol% cat, 3 eqv H <sub>2</sub> O <sub>2</sub>	96	28b
Sn[N(SO <sub>2</sub> C <sub>8</sub> F <sub>17</sub> ) <sub>2</sub> ] <sup>4-</sup> *	15hr, 50°C for synthesis. 8hr, 80°C for drying <sup>2</sup>	Solvent: 1,4-dioxane. Additive: CF <sub>3</sub> C <sub>6</sub> H <sub>11</sub> . 25°C, 2h, 1 mol% cat, 35% H <sub>2</sub> O <sub>2</sub>	96	28c
p-Toluene sulphonic Acid	Purchased (hazardous)	Solvent: 1,1,1,3,3,3-hexafluoro-2-propanol, 55°C, 50% H <sub>2</sub> O <sub>2</sub>	71	33
P-Gc	As mentioned earlier	MW: 700 W, 6 min, 80°C, MeCN Solvent, 15 mg P-Gc, 50% H <sub>2</sub> O <sub>2</sub>  OB: 1hr, 80°C, MeCN solvent, 20mg P-Gc, 50% H <sub>2</sub> O <sub>2</sub>	84  81	This work

\*Entry 1 in Table SI13 and Entry 3 in Table SI14 is not completely metal-free. Still these two are enlisted here to compare with the present work, for being comparatively greener catalyst.

### Ref:

2. Hao, X.; Yamazaki, O.; Yoshida, A.; Nishikido J. Tin(IV) bis(perfluoroalkanesulfonyl) amide complex as a highly selective Lewis acid catalyst for Baeyer–Villiger oxidation using hydrogen peroxide in a fluorous recyclable phase. *Tet. Lett.*, 2003, **44**, 27, 4977–4980.

(Solvent for synthesis: 1,2-DCE and MeCN, Solvent for work up: perfluorodecane)

Characterizations for all the synthesized compounds:

**(Z)-4-(phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.47 (s, 1H, N-H), δ = 7.35 - 7.31 (t, 2H, aromatic H), δ = 7.19 – 7.16 (t, 1H, aromatic H), δ = 7.11 – 7.08 (t, 2H, aromatic H), δ = 5.18 (s, 1H, C-H), δ = 2.09 (s, 3H, -CH<sub>3</sub>), δ = 1.98 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 196.09, 160.25, 138.71, 129.09, 125.55, 124.70, 97.63, 29.16, 19.83. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>14</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 176.1070, found 176.1078

**(Z)-4-((4-fluorophenyl)amino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.34 (s, 1H, N-H), δ = 7.09 – 7.01 (m, 4H, aromatic H), δ = 5.19 (s, 1H, C-H), δ = 2.09 (s, 3H, -CH<sub>3</sub>), δ = 1.92 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 196.38, 160.51, 134.72, 126.91, 126.83, 116.04, 115.81, 97.50, 29.16, 19.66. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>13</sub>FNO<sup>+</sup> [M + H<sup>+</sup>] = 194.0976, found 194.0986

**(Z)-4-((4-methylphenyl)amino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.39 (s, 1H, N-H), δ = 7.13 – 7.11 (d, J=8, 2H, aromatic H), δ = 6.98 – 6.96 (d, J=8, 2H, aromatic H), δ = 5.15 (s, 1H, C-H), δ = 2.32 (s, 3H, -CH<sub>3</sub> in aromatic), δ = 2.07 (s, 3H, -CH<sub>3</sub>), δ = 1.94 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 195.91, 160.68, 136.07, 135.49, 129.65, 124.88, 97.19, 29.12, 20.91, 19.76. HRMS (ESI) Exact mass calculated for C<sub>12</sub>H<sub>16</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 190.1226, found 190.1236

**(Z)-4-((4-methoxylphenyl)amino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.28 (s, 1H, N-H), δ = 7.04 – 7.02 (d, J=8, 2H, aromatic H), δ = 6.87 – 6.85 (d, J=8, 2H, aromatic H), δ = 5.15 (s, 1H, C-H), δ = 3.80 (s, 3H, -OCH<sub>3</sub> in aromatic), δ = 2.08 (s, 3H, -CH<sub>3</sub>), δ = 1.90 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 194.81, 160.20, 156.77, 130.57, 125.68, 113.28, 95.83, 54.46, 28.04, 18.60. HRMS (ESI) Exact mass calculated for C<sub>12</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 206.1176, found 206.1187

**(Z)-4-((4-(1,1,1 trifluoromethyl)phenyl)amino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.61 (s, 1H, N-H), δ = 7.60 – 7.58 (d, J=8, 2H, aromatic H), δ = 7.20 – 7.18 (d, J=8, 2H, aromatic H), δ = 5.26 (s, 1H, C-H), δ = 2.12 (s, 3H, -CH<sub>3</sub>), δ = 2.08 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 197.13, 158.66, 142.21, 126.40, 126.36, 123.60, 99.29, 29.40, 20.12. HRMS (ESI) Exact mass calculated for C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 244.0944, found 244.0963

**(Z)-4-((4-hydroxyphenyl)amino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.23 (s, 1H, N-H), δ = 8.21 – 8.19 (d, J=8, 2H, aromatic H), δ = 7.19 – 7.17 (d, J=8, 2H, aromatic H), δ = 5.16 (s, 1H, C-H), δ = 2.11 (s, 3H, -CH<sub>3</sub>), δ = 1.91 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 195.77, 163.07, 155.39, 130.28, 126.88, 116.17, 96.82, 29.80, 28.76, 19.80. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 192.1019, found 192.1033

**(Z)-4-((4-nitroamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.78 (s, 1H, N-H), δ = 6.90 – 6.84 (m, 4H, aromatic H), δ = 5.33 (s, 1H, C-H), δ = 2.19 (s, 3H, -CH<sub>3</sub>), δ = 2.14 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 196.72, 159.41, 140.10, 134.63, 130.28, 125.41, 122.58, 98.50, 29.28, 19.90. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> [M + H<sup>+</sup>] = 221.0921, found 221.0936

**(Z)-4-(butylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.83 (s, 1H, N-H), δ = 4.90 (s, 1H, C-H), δ = 3.21 – 3.16 (m, 2H, -CH<sub>2</sub> nearest to NH), δ = 1.95 (s, 3H, -CH<sub>3</sub>), δ = 1.87 (s, 3H, -CH<sub>3</sub>), δ = 1.56 – 1.49 (m, 2H, -CH<sub>2</sub>), δ = 1.39 – 1.34 (m, 2H, -CH<sub>2</sub>), δ = 0.91 – 0.87 (m, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 194.54, 163.19, 94.96, 42.69, 32.09, 28.67, 19.97, 18.77, 13.69. HRMS (ESI) Exact mass calculated for C<sub>9</sub>H<sub>18</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 156.1383, found 156.1394

**(Z)-4-(cyclohexylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.95 (s, 1H, N-H), δ = 4.87 (s, 1H, C-H), δ = 3.35 – 3.31 (m, 2H, -CH nearest to NH), δ = 1.94 (s, 3H, -CH<sub>3</sub>), δ = 1.90 (s, 3H, -CH<sub>3</sub>), δ = 1.84 – 1.79 (m, 2H, cyclohexyl ring), δ = 1.74 – 1.72 (t, 2H, cyclohexyl ring), δ = 1.55 – 1.52 (t, 2H, cyclohexyl ring), δ = 1.35 – 1.25 (m, 5H, cyclohexyl ring) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 194.27, 161.83, 94.87, 51.46, 33.76, 28.65, 25.28, 24.37, 18.56. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>20</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 182.1539, found 182.1545

#### (Z)-methyl 3-(phenylamino)but-2-enoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.35 (s, 1H, N-H), δ = 7.34 - 7.31 (t, 2H, aromatic H), δ = 7.18 – 7.16 (t, 1H, aromatic H), δ = 7.14 – 7.08 (t, 2H, aromatic H), δ = 4.70 (s, 1H, C-H), δ = 3.69 (s, 3H, -OCH<sub>3</sub>), δ = 2.00 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 170.71, 159.10, 139.31, 129.05, 125.02, 124.51, 85.61, 50.24, 20.29. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 192.1019, found 192.1015

#### (Z)-methyl 3-((4-fluorophenyl)amino)but-2-enoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.21 (s, 1H, N-H), δ = 7.08 - 6.99 (m, 4H, aromatic H), δ = 4.70 (s, 1H, C-H), δ = 3.68 (s, 3H, -OCH<sub>3</sub>), δ = 1.91 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 169.76, 160.66, 158.28, 134.30 – 130.27 (d, J=12), 125.85 – 125.77 (d, J=32), 114.95 – 114.72 (d, J=92), 84.52, 49.25, 19.05. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>13</sub>FNO<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 210.0925, found 210.0943

#### (Z)-methyl 3-((4-methylphenyl)amino)but-2-enoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.26 (s, 1H, N-H), δ = 7.13 - 7.11 (d, J=8, 2H, aromatic H), δ = 6.99 – 6.97 (d, J=8, 1H, aromatic H), δ = 4.67 (s, 1H, C-H), δ = 3.68 (s, 3H, -OCH<sub>3</sub>), δ = 2.33 (s, 3H, -CH<sub>3</sub> in aromatic), δ = 1.95 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 170.78, 159.63, 136.59, 134.99, 129.63, 124.80, 84.86, 50.24, 20.89, 20.25. HRMS (ESI) Exact mass calculated for C<sub>12</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 206.1176, found 206.1198

#### (Z)-methyl 3-((4-methoxyphenyl)amino)but-2-enoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.12 (s, 1H, N-H), δ = 7.04 - 7.01 (d, J=12, 2H, aromatic H), δ = 6.87 – 6.84 (d, J=12, 1H, aromatic H), δ = 4.65 (s, 1H, C-H), δ = 3.80 (s, 3H, -OCH<sub>3</sub> in aromatic), δ = 3.67 (s, 3H, -OCH<sub>3</sub>), δ = 1.88 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 170.83, 160.22, 157.51, 132.05, 126.89, 114.21, 84.27, 55.46, 50.22, 20.13. HRMS (ESI) Exact mass calculated for C<sub>12</sub>H<sub>16</sub>NO<sub>3</sub><sup>+</sup> [M + H<sup>+</sup>] = 222.1125, found 222.1131

#### (Z)-methyl 3-((4-(1,1,1 trifluoromethyl)phenyl)amino)but-2-enoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.58 (s, 1H, N-H), δ = 7.57 - 7.55 (d, J=8, 2H, aromatic H), δ = 7.16 – 7.14 (d, J=8, 1H, aromatic H), δ = 4.79 (s, 1H, C-H), δ = 3.69 (s, 3H, -OCH<sub>3</sub>), δ = 2.10 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 169.56, 156.46, 141.65, 125.34, 124.57, 121.78, 87.21, 49.50, 28.68, 19.53. HRMS (ESI) Exact mass calculated for C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 260.0893, found 260.0899

#### (Z)-methyl 3-((4-hydroxyphenyl)amino)but-2-enoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.01 (s, 1H, N-H), δ = 6.92 – 6.89 (d, J=12, 2H, aromatic H), δ = 6.81 – 6.79 (d, J=8, 1H, aromatic H), δ = 4.65 (s, 1H, C-H), δ = 3.68 (s, 3H, -OCH<sub>3</sub>), δ = 1.87 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 171.15, 160.71, 154.08, 131.68, 127.16, 115.87, 84.09, 50.40, 20.12. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>14</sub>NO<sub>3</sub><sup>+</sup> [M + H<sup>+</sup>] = 208.0968, found 208.0980

#### (Z)-methyl 3-((4-nitrophenyl)amino)but-2-enoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.88 (s, 1H, N-H), δ = 8.20 – 8.18 (d, J=8, 2H, aromatic H), δ = 8.14 – 8.12 (d, J=8, 1H, aromatic H), δ = 4.89 (s, 1H, C-H), δ = 3.71 (s, 3H, -OCH<sub>3</sub>), δ = 2.22 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 170.38, 155.93, 145.75, 125.34, 120.76, 91.09, 50.78, 21.02. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>13</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> [M + H<sup>+</sup>] = 237.0870, found 237.0881

#### (Z)-methyl 3-((3-chlorophenyl)amino)but-2-enoate

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 10.42 (s, 1H, N-H), δ = 7.30 – 7.28 (d, J=8, 1H, aromatic H), δ = 7.17 – 7.13 (m, 2H, aromatic H), δ = 7.01 - 6.99 (d, J=8, 1H, aromatic H), δ = 4.77 (s, 1H, C-H), δ = 3.72 (s, 3H, -OCH<sub>3</sub>), δ = 2.06 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 170.62, 158.19, 140.64, 134.62, 130.05, 124.82, 124.07, 122.16, 87.00, 50.41, 20.36. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>13</sub>ClNO<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 226.0629, found 226.0643

**(Z)-methyl 3-(cyclohexylamino)but-2-enoate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.63 (s, 1H, N-H), δ = 4.39 (s, 1H, C-H), δ = 3.61 (s, 3H, -OCH<sub>3</sub>), δ = 3.33 – 3.29 (m, 2H, -CH nearest to NH), δ = 1.93 (s, 3H, -CH<sub>3</sub>), δ = 1.87 – 1.85 (d, 2H, J=8, cyclohexyl ring), δ = 1.77 – 1.74 (m, 2H, cyclohexyl ring), δ = 1.62 – 1.57 (t, 2H, cyclohexyl ring), δ = 1.34 – 1.25 (m, 5H, cyclohexyl ring) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 170.94, 160.97, 81.22, 51.43, 49.85, 34.26, 25.39, 24.66, 19.24. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>20</sub>NO<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 198.1489, found 198.1498

**(Z)-1,1,1-trifluoro-4-(phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.59 (s, 1H, N-H), δ = 7.44 - 7.32 (m, 3H, aromatic H), δ = 7.18 – 7.16 (d, J=8, 2H, aromatic H), δ = 5.54 (s, 1H, C-H), δ = 2.11 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 175.50, 166.82, 136.07, 128.50, 126.44, 124.26, 89.89, 19.23. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>11</sub>F<sub>3</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 230.0787, found 230.0829

**(Z)-1,1,1-trifluoro-4-((4-fluoro)phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.47 (s, 1H, N-H), δ = 7.17 - 7.09 (m, 4H, aromatic H), δ = 5.55 (s, 1H, C-H), δ = 2.07 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 176.69, 168.12, 162.84, 160.37, 133.01, 127.44, 116.61, 90.91 – 90.90 (d, J =4), 20.17. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>10</sub>F<sub>4</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 248.0693, found 248.0714

**(Z)-1,1,1-trifluoro-4-((4-methyl)phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.55 (s, 1H, N-H), δ = 7.22 - 7.20 (d, J=8, 2H, aromatic H), δ = 7.05 - 7.03 (d, J=8, 2H, aromatic H), δ = 5.52 (s, 1H, C-H), δ = 2.37 (s, 3H, -CH<sub>3</sub> in aromatic), δ = 2.08 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 176.13, 168.18, 137.52, 134.38, 130.04, 125.06, 119.01, 116.15, 90.64 – 90.62 (d, J =8), 20.93, 20.13. HRMS (ESI) Exact mass calculated for C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 244.0944, found 244.0962

**(Z)-1,1,1-trifluoro-4-((4-methoxy)phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.46 (s, 1H, N-H), δ = 7.10 - 7.08 (d, J=8, 2H, aromatic H), δ = 6.93 - 6.91 (d, J=8, 2H, aromatic H), δ = 5.51 (s, 1H, C-H), δ = 3.83 (s, 3H, -OCH<sub>3</sub> in aromatic), δ = 2.05 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 176.43, 168.54, 158.84, 129.76, 126.72, 119.02, 114.54, 90.46 – 90.45 (d, J = 4), 55.53, 20.15. HRMS (ESI) Exact mass calculated for C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 260.0893, found 260.0913

**(Z)-1,1,1-trifluoro-4-(((1,1,1-trifluoro)methyl)phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.64 (s, 1H, N-H), δ = 7.69 - 7.68 (d, J=4, 2H, aromatic H), δ = 7.30 - 7.28 (d, J=8, 2H, aromatic H), δ = 5.61 (s, 1H, C-H), δ = 2.18 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 177.98, 165.88, 145.64, 142.98, 125.23, 124.41, 93.20, 29.71, 20.78. HRMS (ESI) Exact mass calculated for C<sub>12</sub>H<sub>10</sub>F<sub>6</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 298.0661, found 298.0676

**(Z)-1,1,1-trifluoro-4-((4-hydroxy)phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.46 (s, 1H, N-H), δ = 7.78 (s, 1H, O-H), δ = 6.96 - 6.94 (d, J=8, 2H, aromatic H), δ = 6.90 - 6.88 (d, J=8, 2H, aromatic H), δ = 5.56 (s, 1H, C-H), δ = 2.07 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 175.76, 170.00, 156.04, 128.80, 126.68, 119.17, 116.36, 90.82 – 90.80 (d, J=8), 29.71, 20.78. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>11</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 246.0736, found 246.0759

**(Z)-1,1,1-trifluoro-4-((4-nitro)phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.69 (s, 1H, N-H), δ = 8.31 - 8.29 (d, J=8, 2H, aromatic H), δ = 7.34 – 7.31 (d, J=12, 2H, aromatic H), δ = 5.66 (s, 1H, C-H), δ = 2.27 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C

NMR (400 MHz, CDCl<sub>3</sub>): δ = 178.33, 165.90, 145.66, 142.99, 126.36, 125.24, 124.42, 113.39, 93.20, 20.77. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> [M + H<sup>+</sup>] = 275.0638, found 275.0671

**(Z)-1,1,1-trifluoro-4-((3-chloro)phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.51 (s, 1H, N-H), δ = 7.35 - 7.27 (m, 2H, aromatic H), δ = 7.15 (s, 1H, aromatic H), δ = 7.06 - 7.04 (d, J=8, 2H, aromatic H), δ = 5.55 (s, 1H, C-H), δ = 2.11 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 176.91, 167.70, 138.27, 135.15, 130.61, 127.60, 125.39, 123.48, 91.50, 20.33. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>10</sub>ClF<sub>3</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 264.0398, found 264.0415

**(Z)-1,1,1-trifluoro-4-((3-nitro)phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.63 (s, 1H, N-H), δ = 8.19 - 8.17 (dd, J=8, 1H, aromatic H), δ = 8.08 - 8.07 (d, J=4, 1H, aromatic H), δ = 7.65 - 7.61 (t, 1H, aromatic H), δ = 7.53 - 7.51 (d, J=8, 2H, aromatic H), δ = 5.64 (s, 1H, C-H), δ = 2.20 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 177.04, 165.74, 147.79, 137.38, 129.80, 129.54, 120.85, 118.86, 114.70, 91.29, 19.41. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> [M + H<sup>+</sup>] = 275.0638, found 275.0653

**(Z)-1,1,1-trifluoro-4-((3-methyl)phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.56 (s, 1H, N-H), δ = 7.31 - 7.28 (t, 1H, aromatic H), δ = 7.14 - 7.12 (d, J=8, 1H, aromatic H), δ = 6.98 - 6.96 (d, J=8, 2H, aromatic H), δ = 5.53 (s, 1H, C-H), δ = 2.38 (s, 3H, -CH<sub>3</sub> in aromatic), δ = 2.11 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 175.24, 166.94, 138.63, 135.89, 128.22, 127.21, 124.82, 121.23, 89.74 - 89.73 (d, J=4), 20.28, 19.26. HRMS (ESI) Exact mass calculated for C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 244.0944, found 244.0971

**(Z)-1,1,1-trifluoro-4-((3-hydroxy)phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.58 (s, 1H, N-H), δ = 7.24 - 7.20 (t, 1H, aromatic H), δ = 6.86 - 6.84 (dd, J=8, 1H, aromatic H), δ = 6.70 - 6.64 (m, 2H, aromatic H), δ = 5.57 (s, 1H, C-H), δ = 2.14 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 175.54, 169.86, 157.58, 137.36, 130.46, 119.14, 116.67, 115.32, 112.15, 91.27 - 91.26 (d, J=4), 20.32. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>11</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 246.0736, found 246.0748

**(Z)-1,1,1-trifluoro-4-((4-chloro)phenylamino)pent-3-en-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 12.51 (s, 1H, N-H), δ = 7.39 - 7.37 (t, 2H, aromatic H), δ = 7.11 - 7.09 (t, 2H, aromatic H), δ = 5.55 (s, 1H, C-H), δ = 2.10 (s, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 176.74, 167.67, 135.57, 133.20, 129.68, 126.50, 91.27 - 91.25 (d, J=8), 20.20. HRMS (ESI) Exact mass calculated for C<sub>11</sub>H<sub>10</sub>ClF<sub>3</sub>NO<sup>+</sup> [M + H<sup>+</sup>] = 264.0398, found 264.0410

**Tetrahydro-2H-pyran-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 4.29 - 4.27 (t, 2H), δ = 2.50 - 2.47 (t, 2H), δ = 1.87 - 1.77 (m, 4H) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 171.39, 69.37, 29.70, 22.15, 18.91. HRMS (ESI) Exact mass calculated for C<sub>5</sub>H<sub>9</sub>O<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 101.0597, found 101.0607

**Oxepan-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 4.18 - 4.16 (t, 2H), δ = 2.59 - 2.56 (t, 2H), δ = 1.81 - 1.77 (m, 2H), δ = 1.73 - 1.66 (m, 4H) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 176.23, 69.27, 34.49, 29.24, 28.85, 22.90. HRMS (ESI) Exact mass calculated for C<sub>6</sub>H<sub>11</sub>O<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 115.0754, found 115.0764

**5-(tert-butyl)oxepan-2-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 4.35 - 4.30 (m, 1H), δ = 4.16 - 4.11 (m, 1H), δ = 2.72 - 2.66 (m, 1H), δ = 2.59 - 2.52 (m, 1H), δ = 2.08 - 2.00 (m, 2H), δ = 1.55 - 1.46 (m, 1H), δ = 1.35 - 1.30 (m, 2H), δ = 0.88 (s, 9H) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 176.35, 68.65, 50.75, 33.46, 33.00, 30.33, 27.45, 23.77. HRMS (ESI) Exact mass calculated for C<sub>10</sub>H<sub>19</sub>O<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 171.1380, found 171.1392

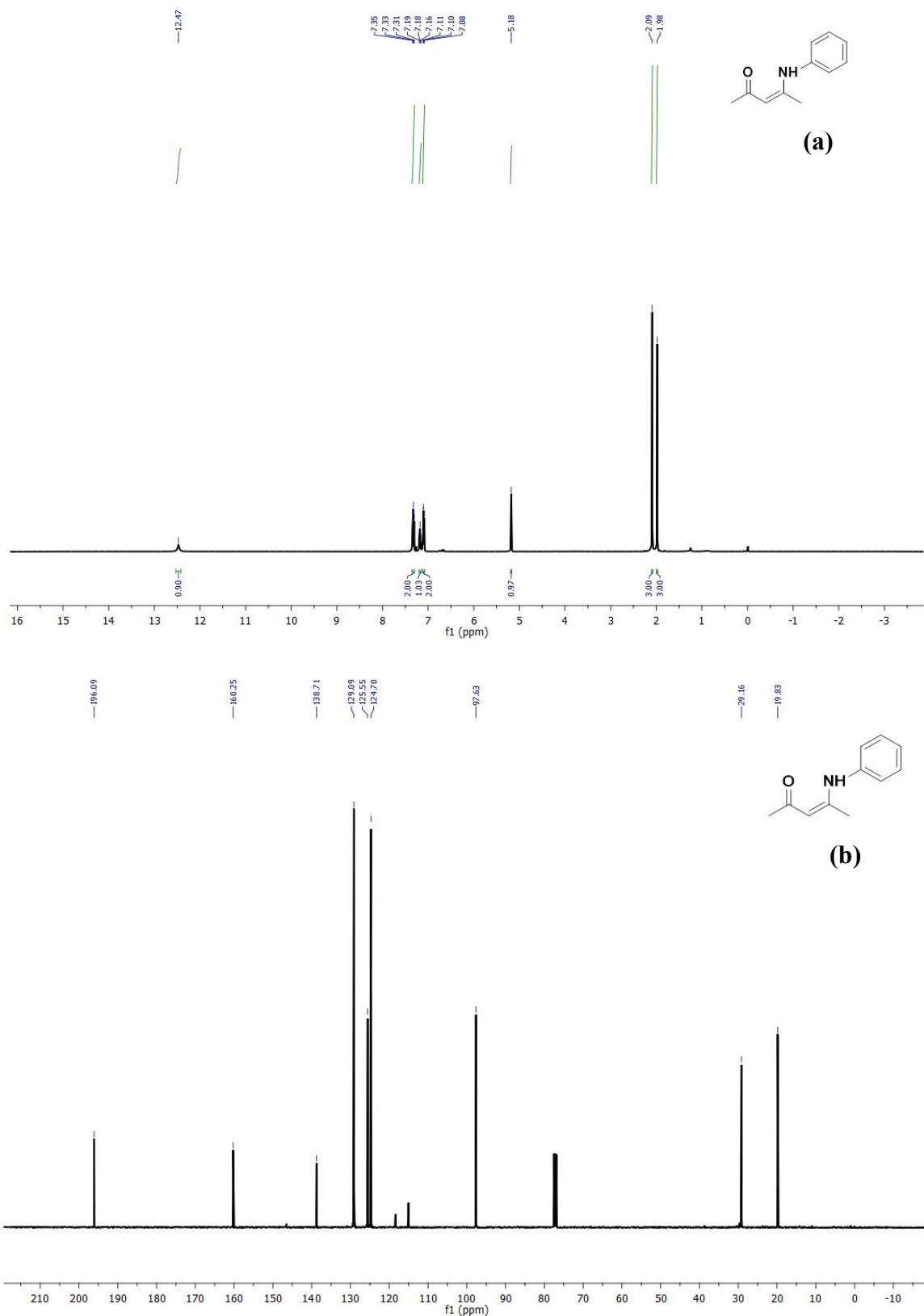
**(1R,3r,8S)-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecan-5-one**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 4.49 – 4.45 (m, 1H), δ = 3.07 – 3.04 (m, 1H), δ = 2.09 (t, 2H), δ = 2.04 – 1.98 (m, 4H), δ = 1.95 – 1.90 (t, 2H), δ = 1.84 – 1.78 (m, 2H), δ = 1.72 – 1.71 (t, 2H) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 179.08, 73.22, 41.22, 35.74, 33.77, 30.93, 25.82. HRMS (ESI) Exact mass calculated for C<sub>10</sub>H<sub>15</sub>O<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 167.1067, found 167.1082

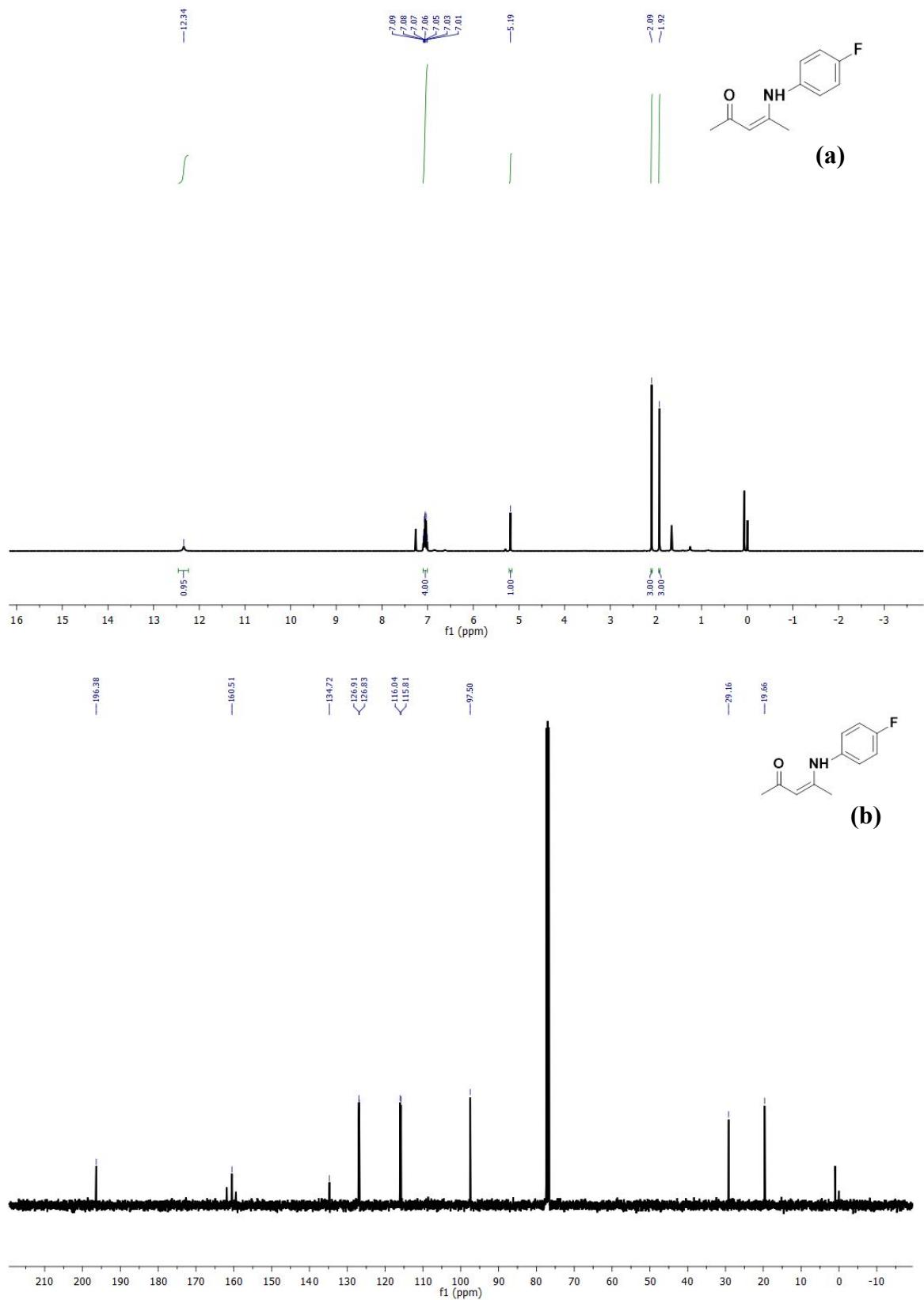
**Phenyl Acetate**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.45 – 7.41 (m, 2H, aromatic H, *ortho* to acetate group), δ = 7.30 – 7.27 (m, 1H, aromatic, *para* to acetate group), δ = 7.15 – 7.12 (m, 2H, aromatic H, *meta* to acetate group), δ = 2.35 (m, 3H, -CH<sub>3</sub>) ; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ = 169.48, 150.71, 129.42, 125.82, 121.57, 21.13, HRMS (ESI) Exact mass calculated for C<sub>8</sub>H<sub>9</sub>O<sub>2</sub><sup>+</sup> [M + H<sup>+</sup>] = 137.0597, found 137.0603

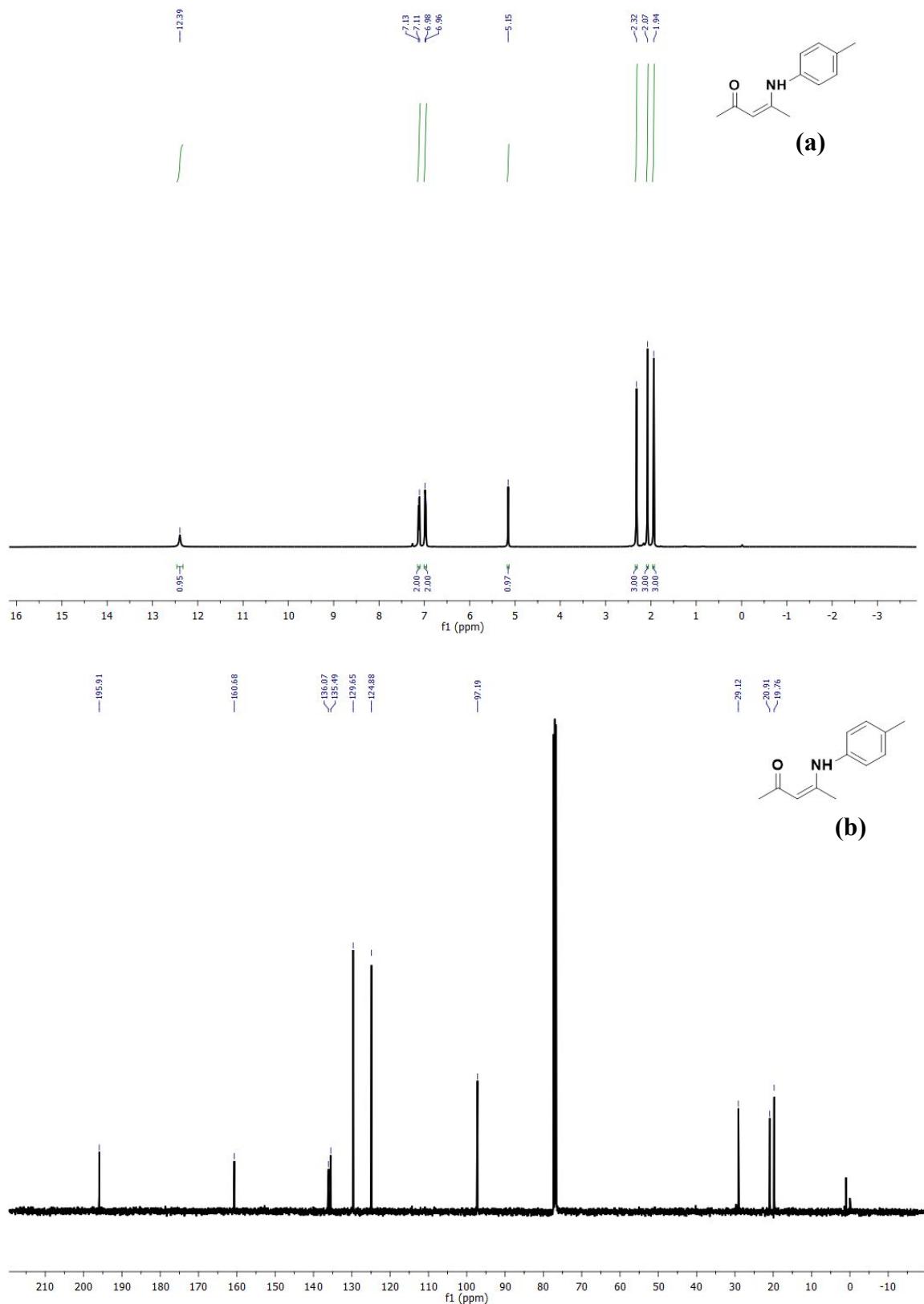
## NMR Spectrum



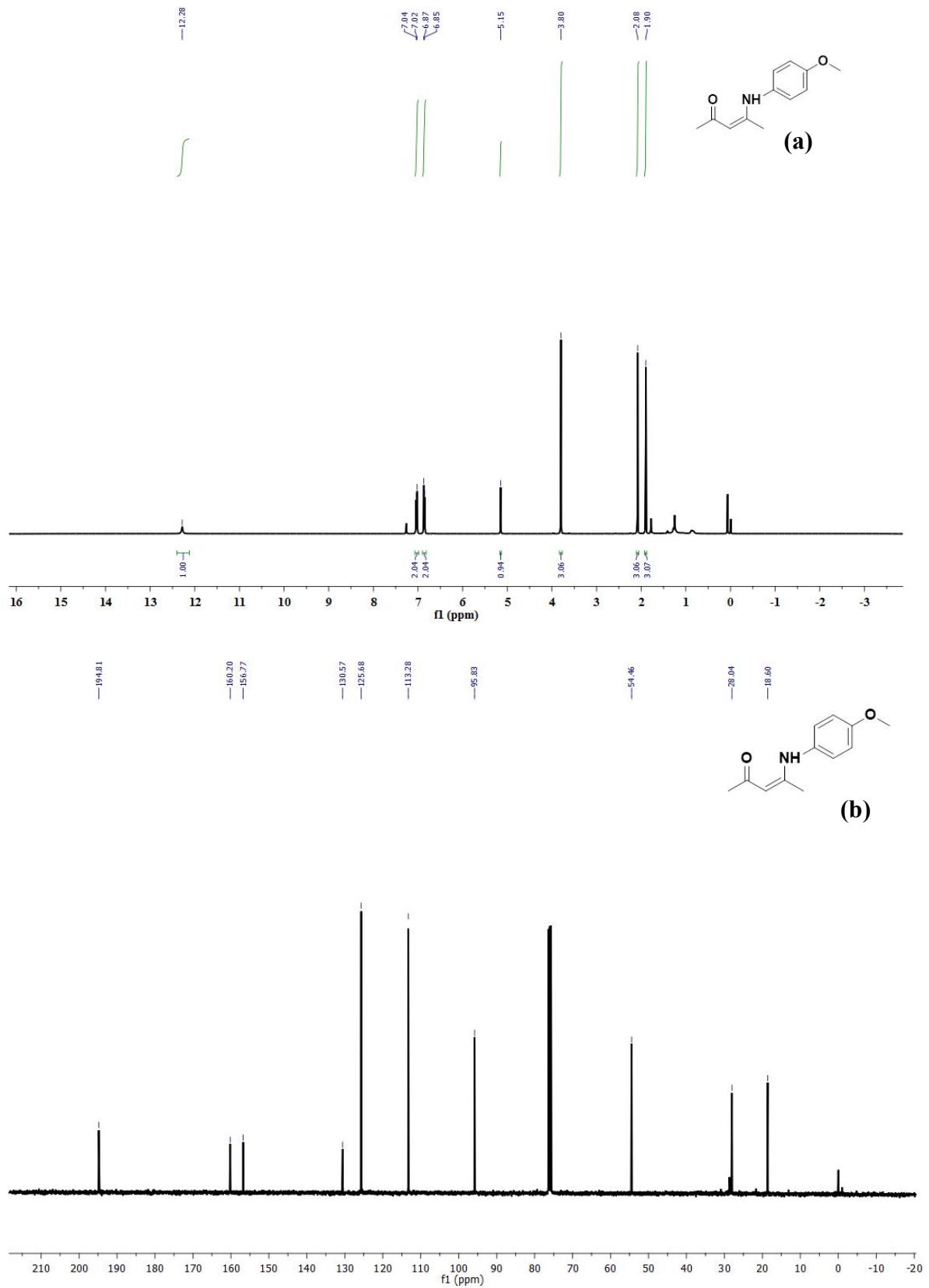
**Figure SI19 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-4-(phenylamino)pent-3-en-2-one**



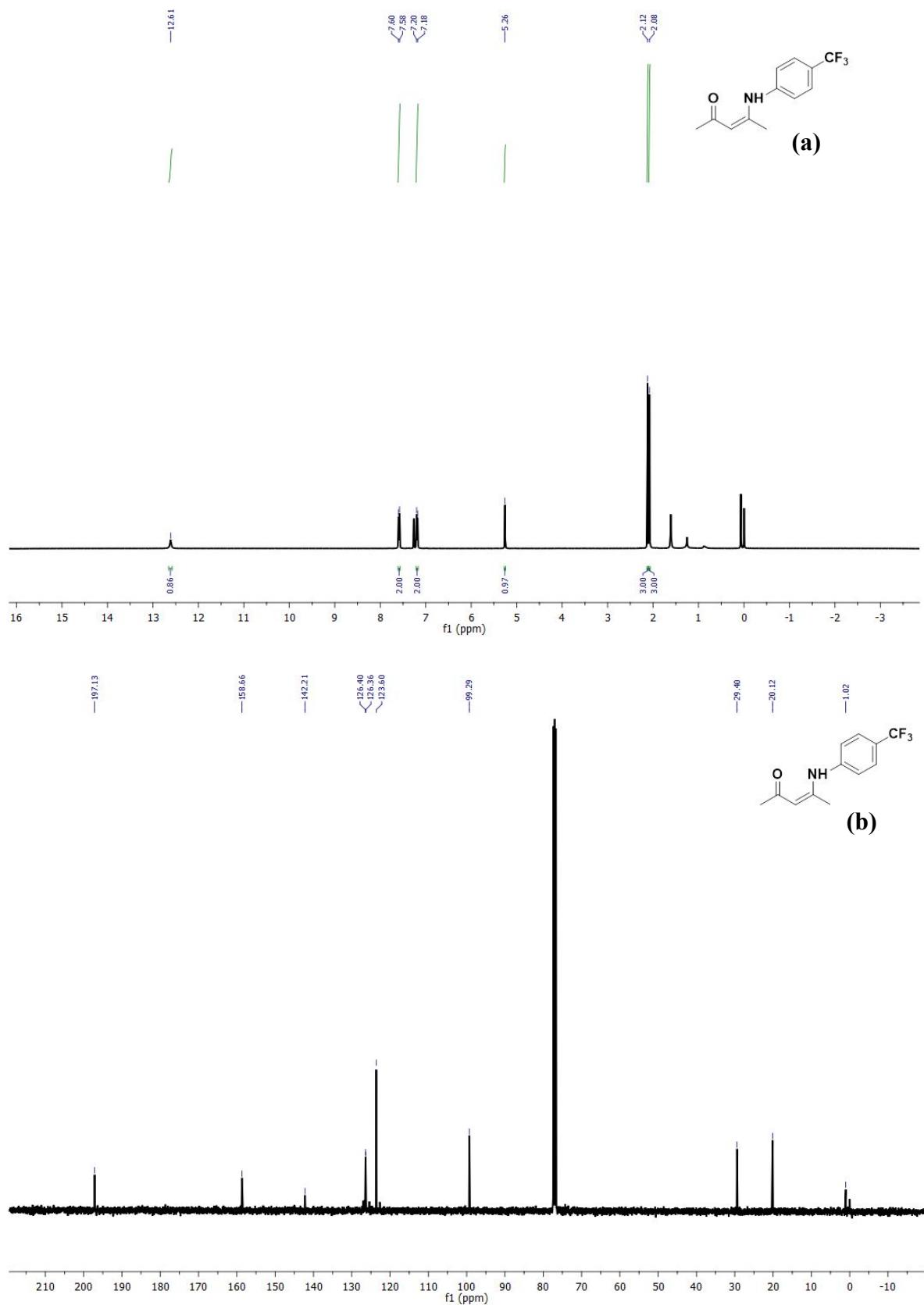
**Figure SI20 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-4-((4-fluorophenyl)amino)pent-3-en-2-one**



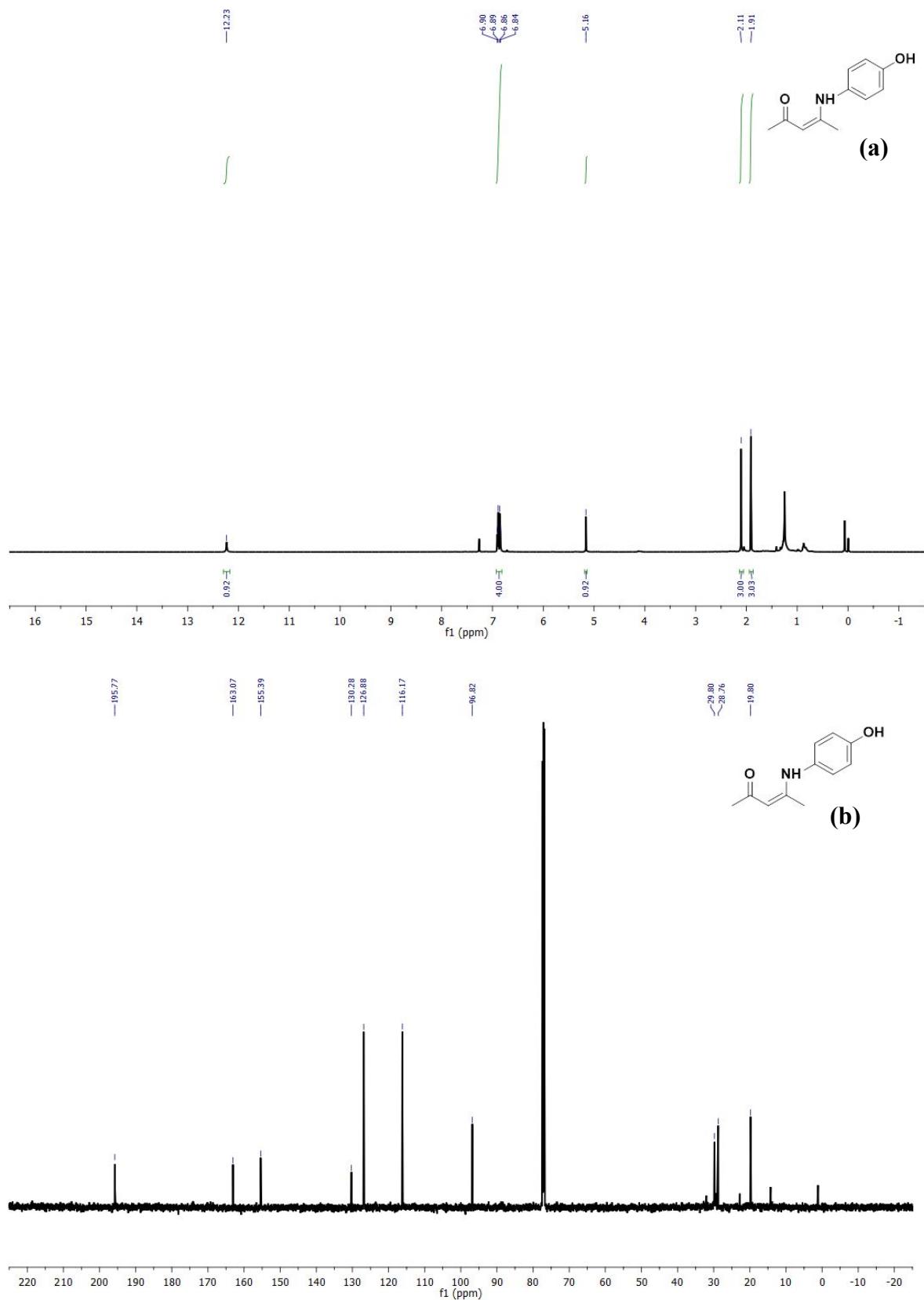
**Figure SI21 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-4-((4-methylphenyl)amino)pent-3-en-2-one**



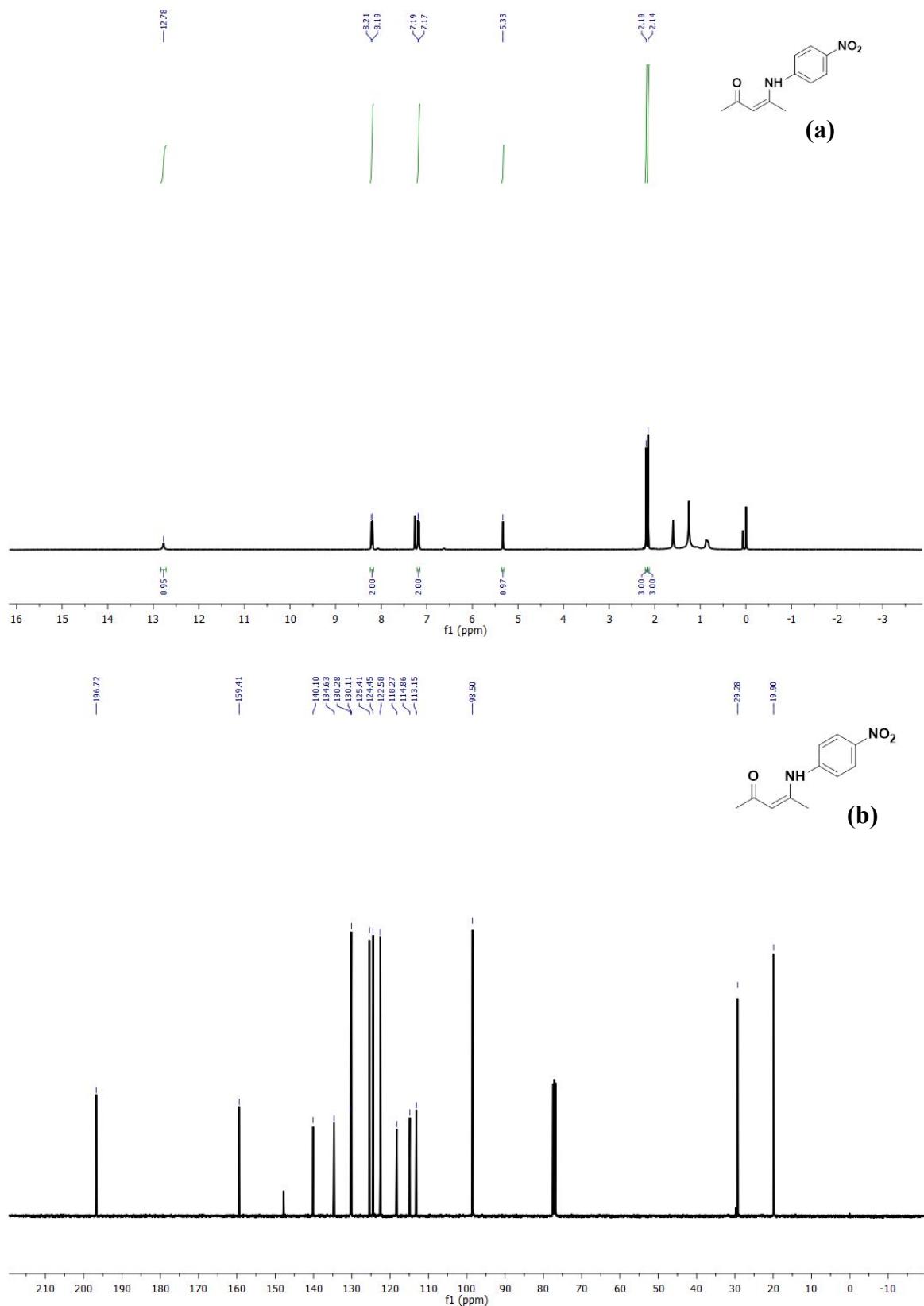
**Figure SI22 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-4-((4-methoxyphenyl)amino)pent-3-en-2-one**



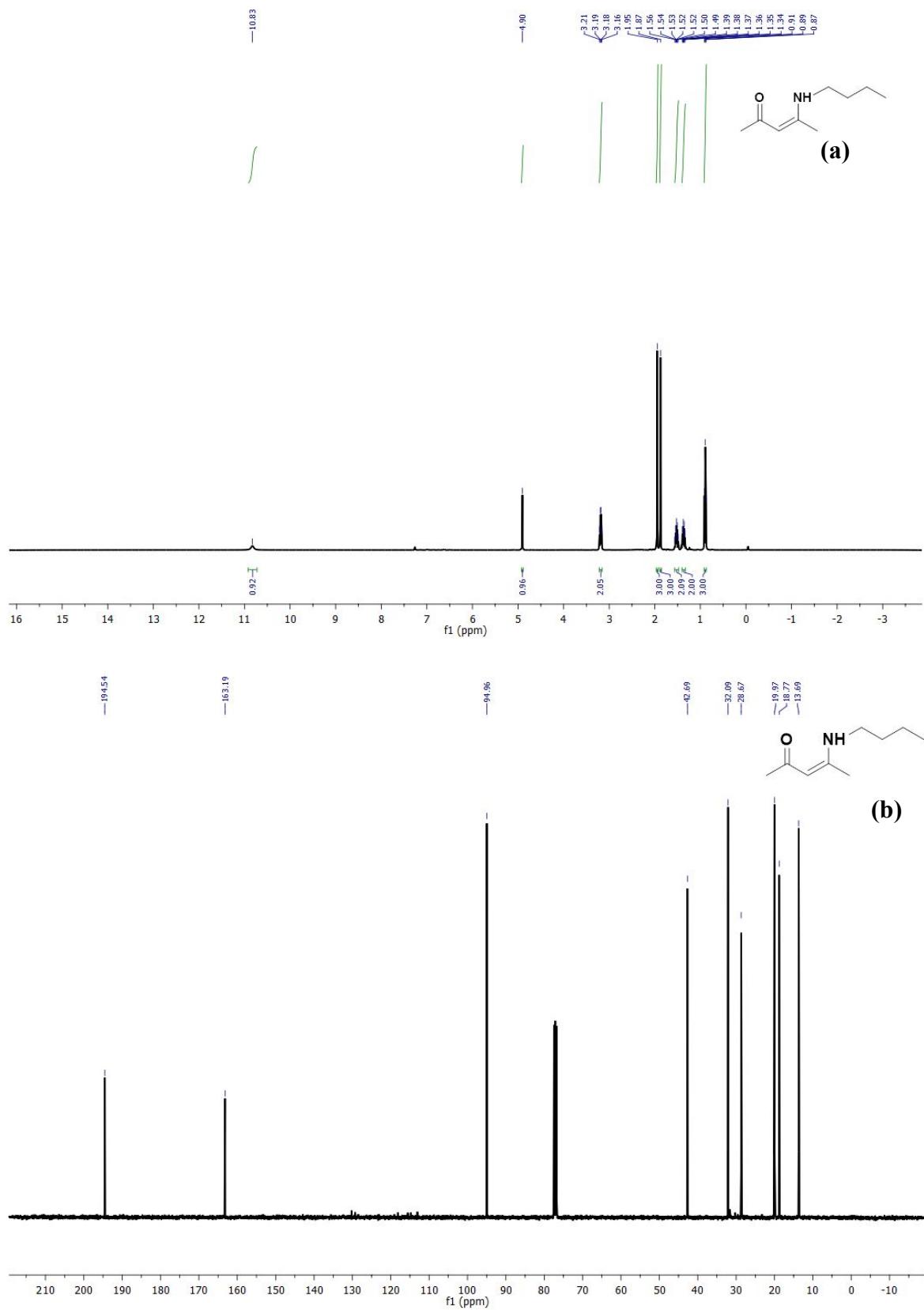
**Figure SI23 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-4-((4-(1,1,1-trifluoromethyl)phenyl)amino)pent-3-en-2-one**



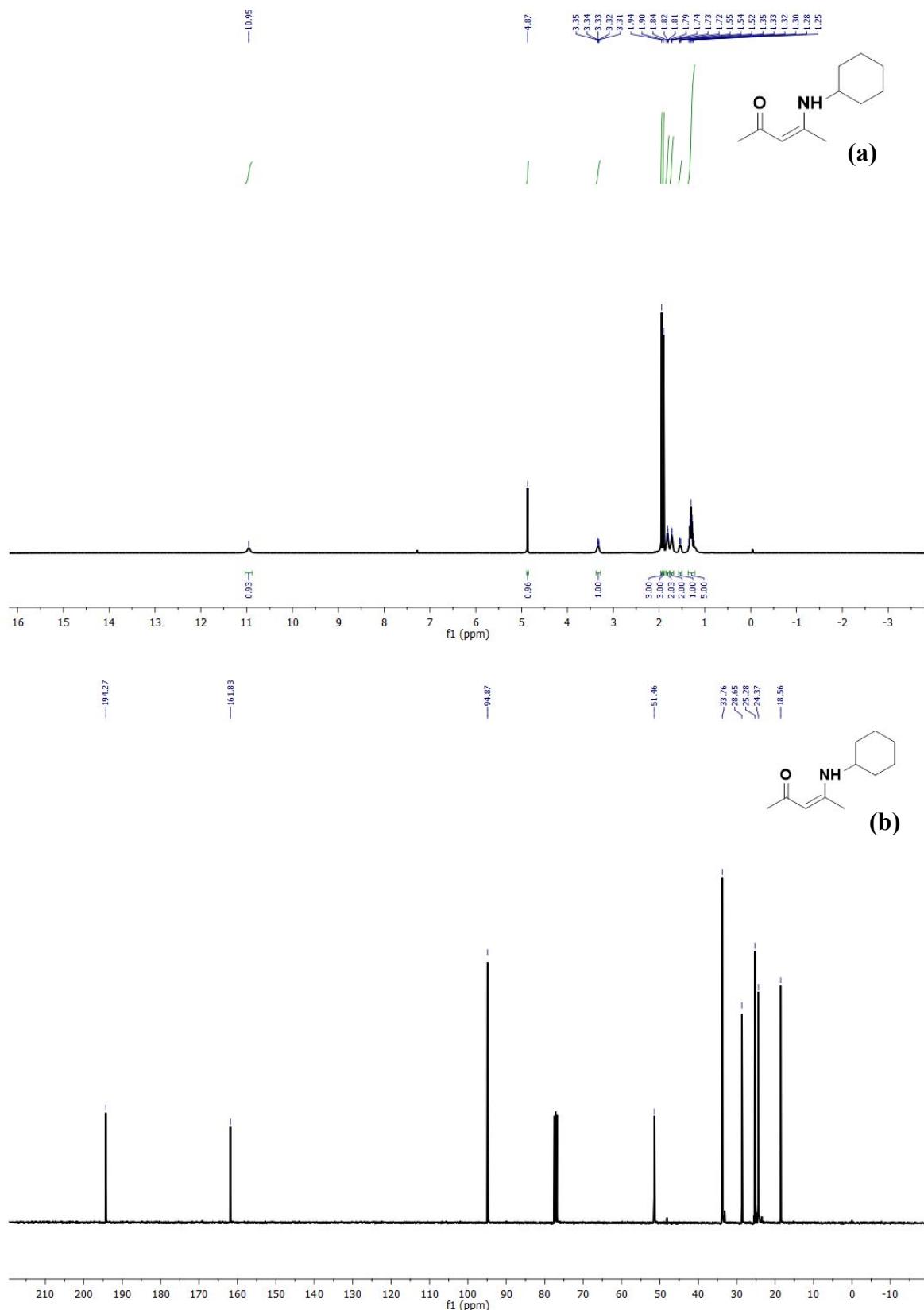
**Figure SI24 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-4-((4-hydroxyphenyl)amino)pent-3-en-2-one**



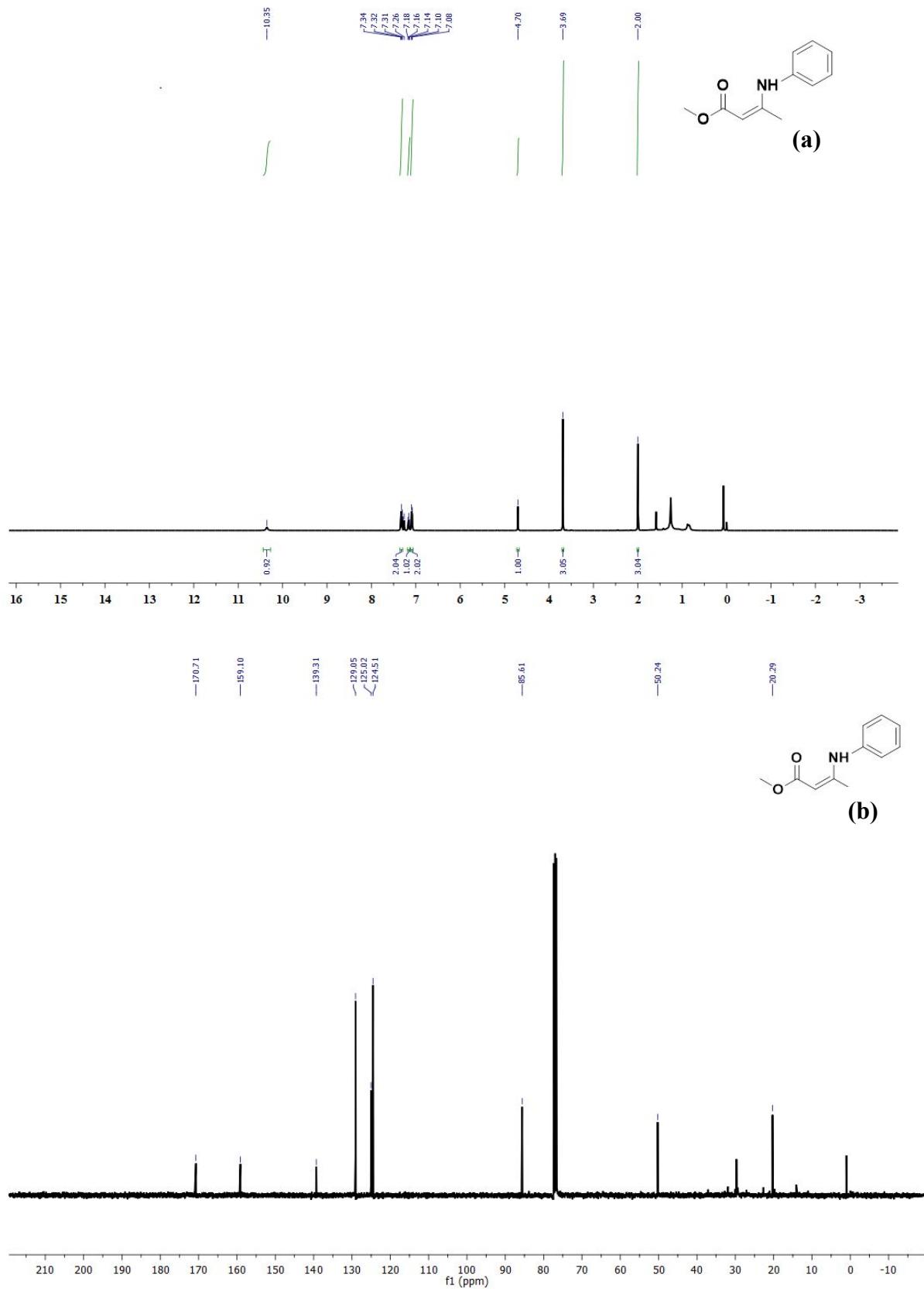
**Figure SI25 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-4-((4-nitrophenyl)amino)pent-3-en-2-one**



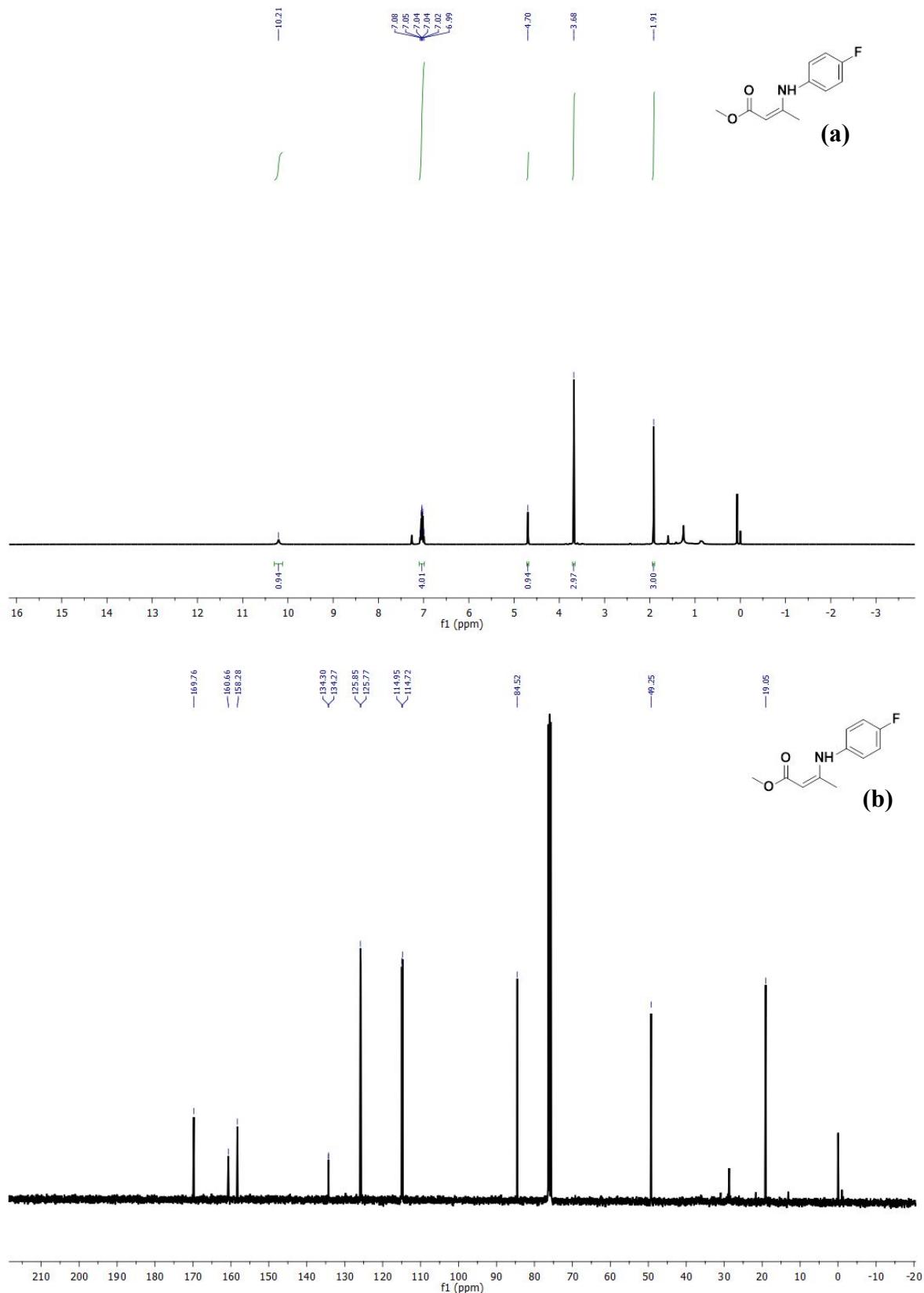
**Figure SI26 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-4-(butylamino)pent-3-en-2-one**



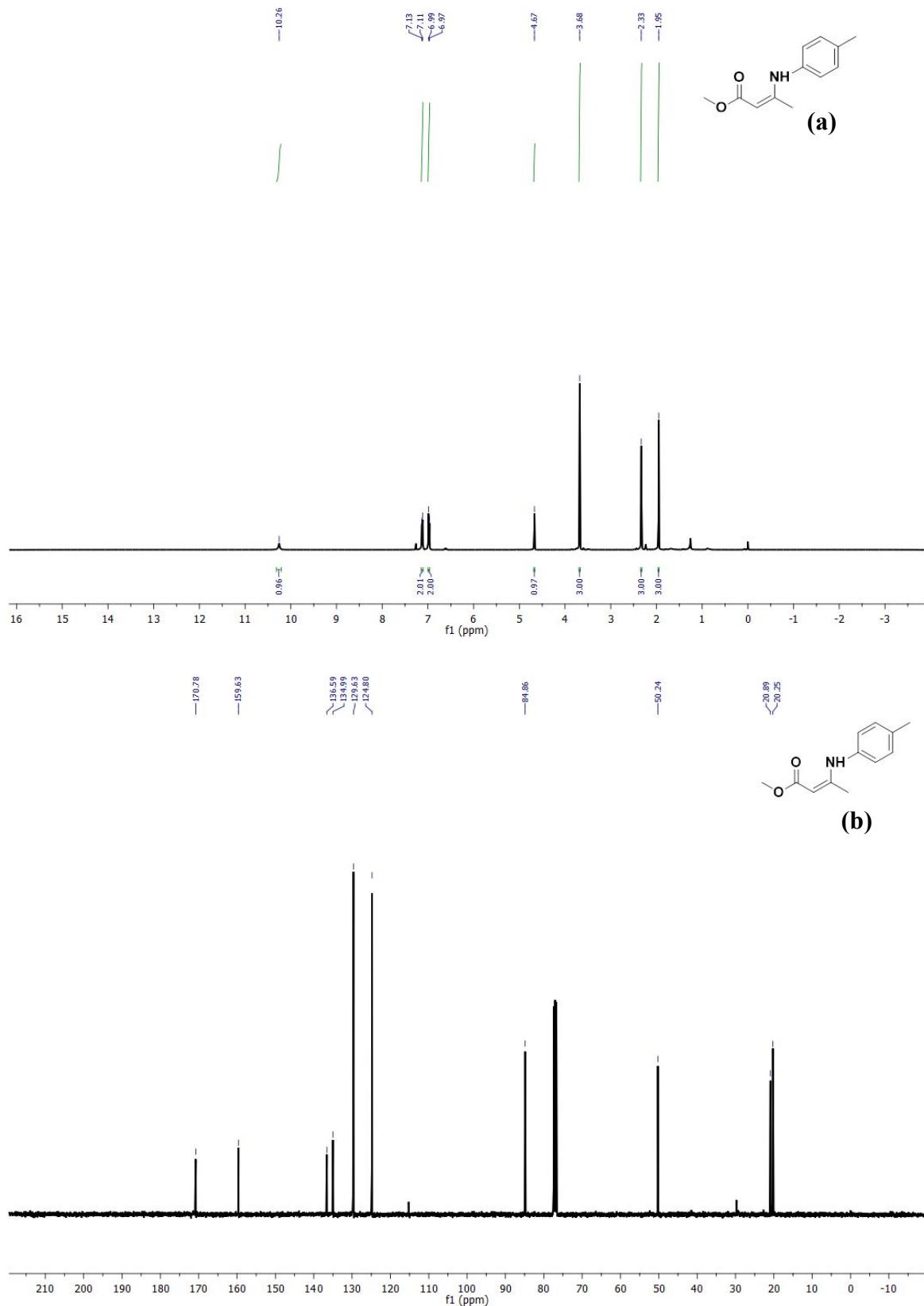
**Figure SI27 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-4-(cyclohexylamino)pent-3-en-2-one**



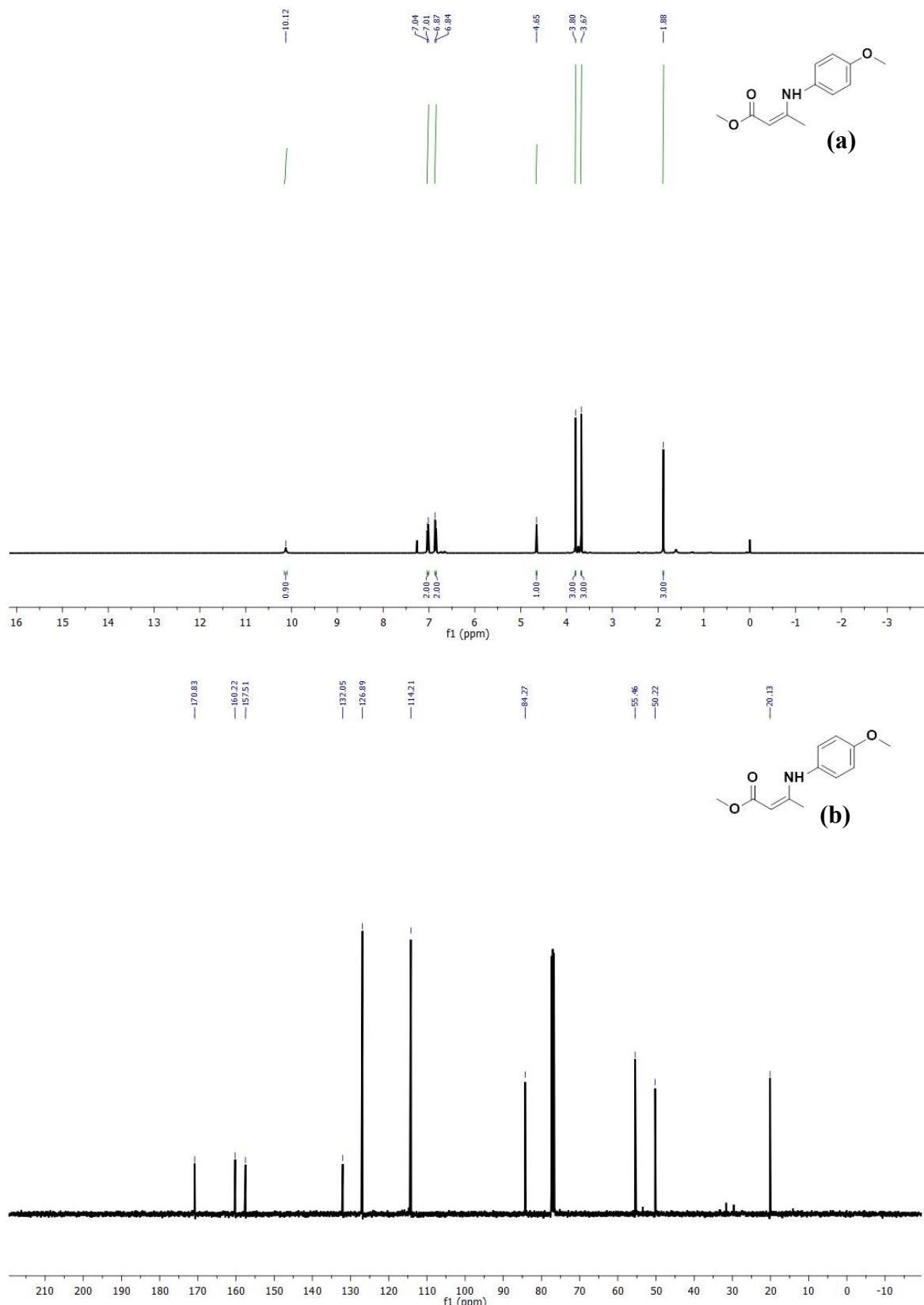
**Figure SI28 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-methyl 3-(phenylamino)but-2-enoate**



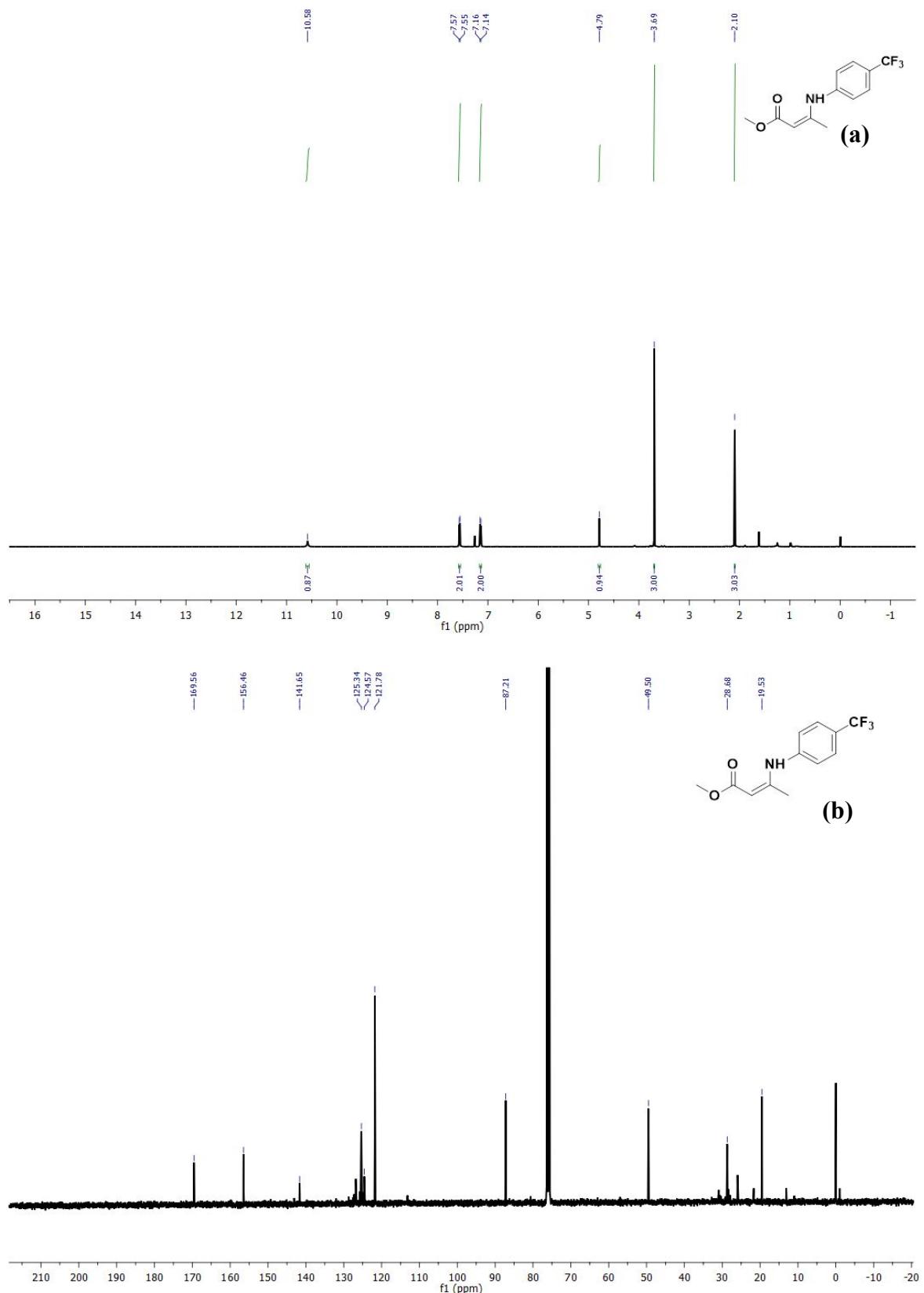
**Figure SI29 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-methyl 3-((4-fluorophenyl)amino)but-2-enoate**



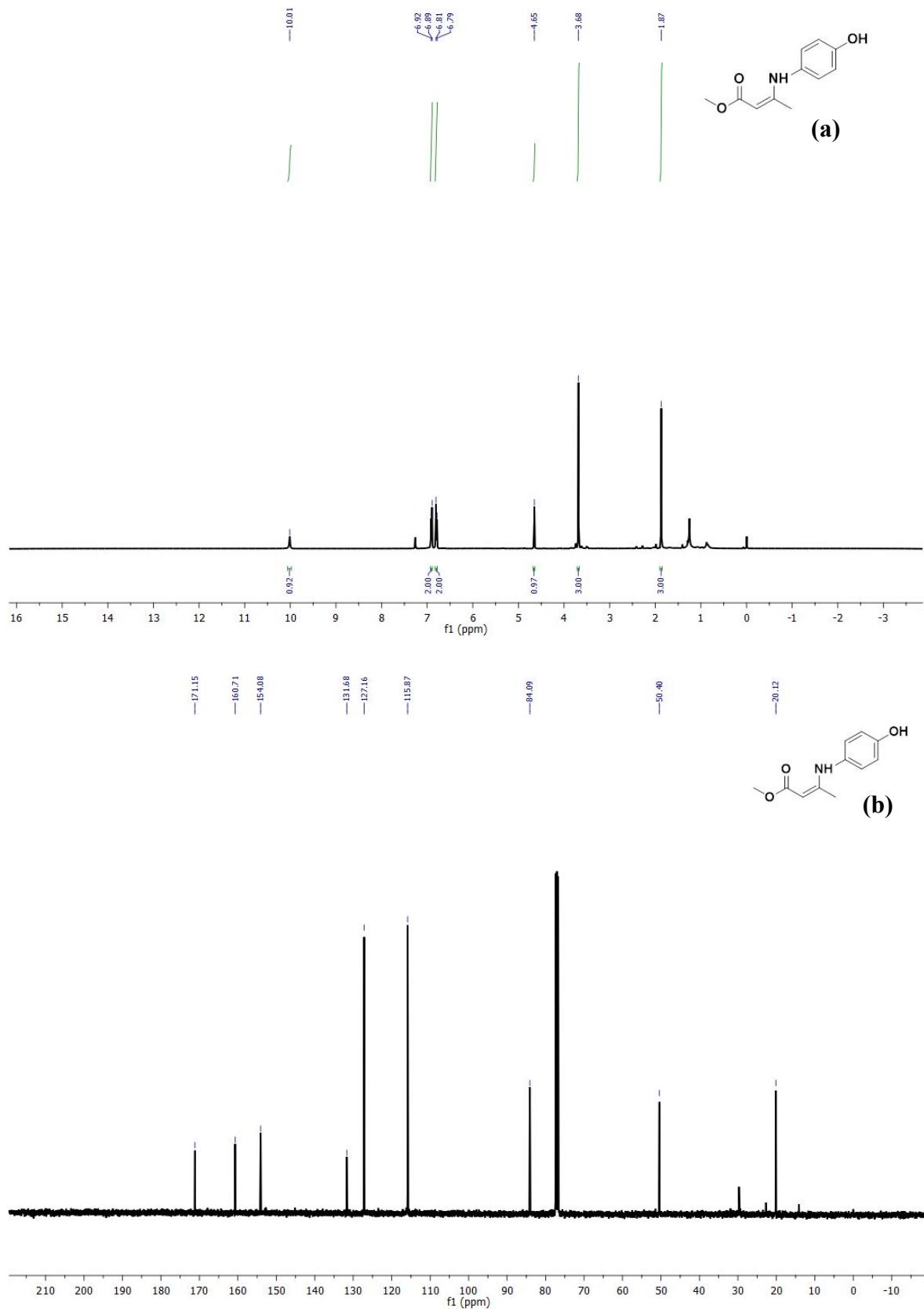
**Figure SI30 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-methyl 3-((4-methylphenyl)amino)but-2-enoate**



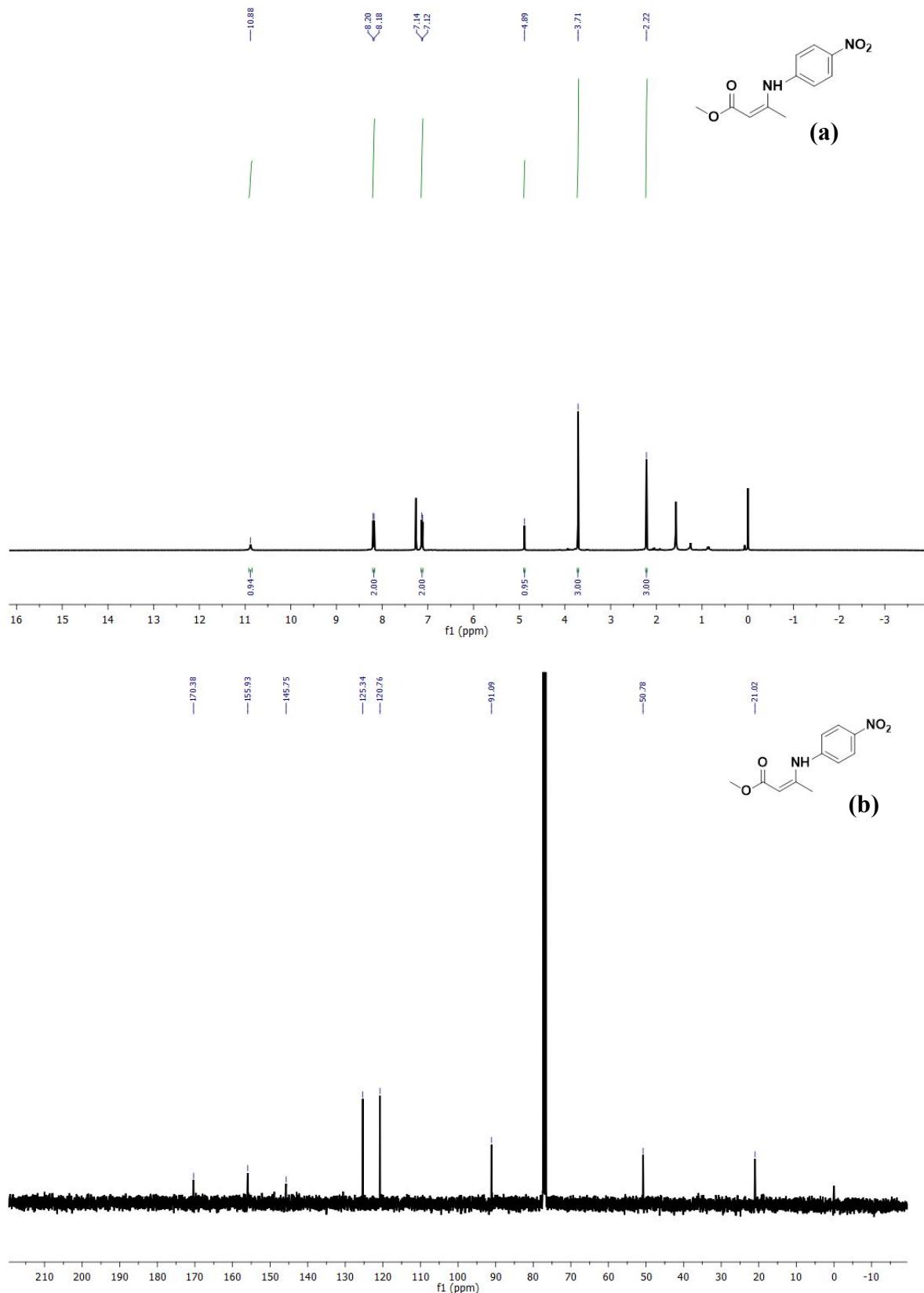
**Figure SI31 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-methyl 3-((4-methoxyphenyl)amino)but-2-enoate**



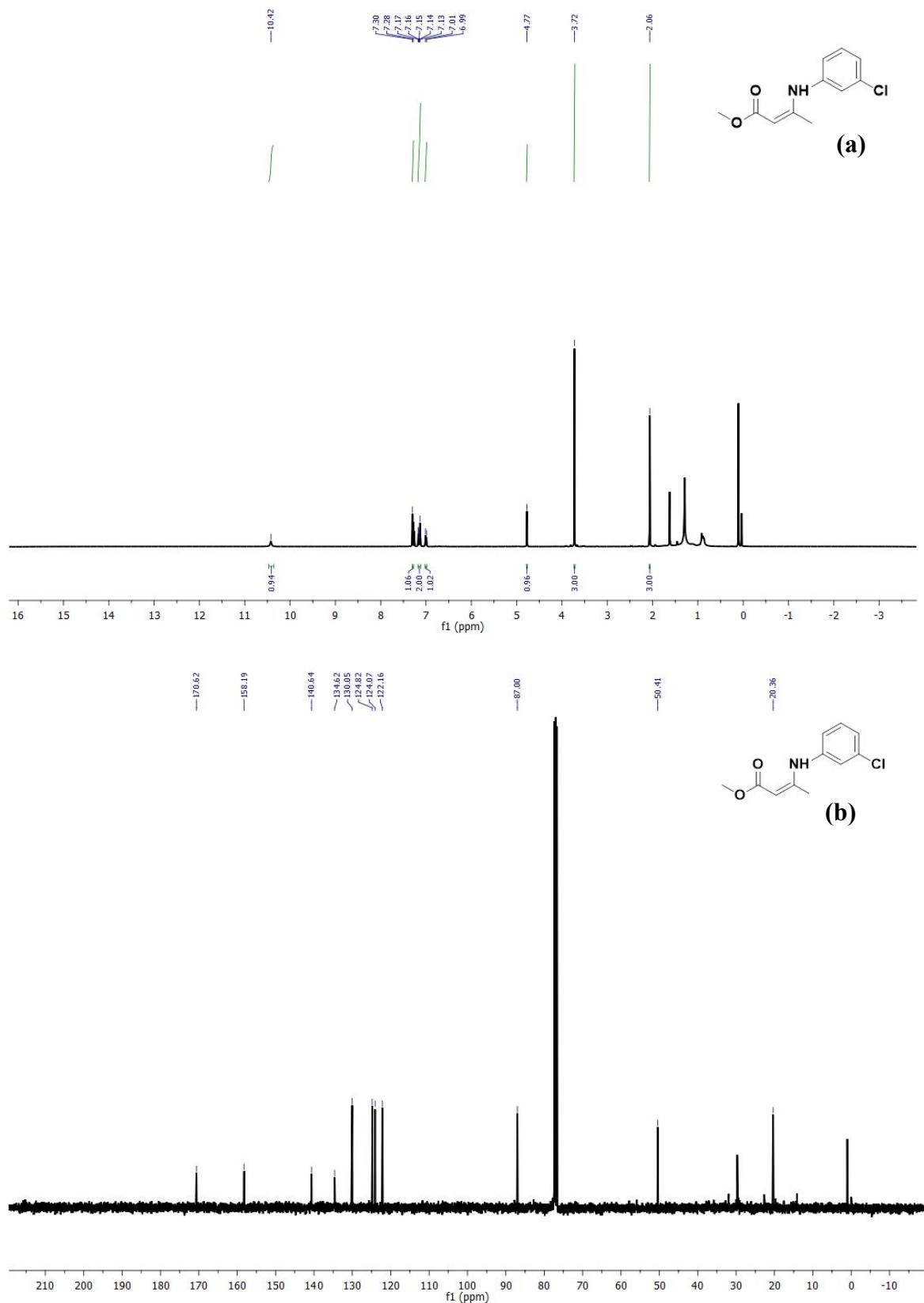
**Figure SI32 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-methyl 3-((4-(1,1,1-trifluoro)methylphenyl)amino)but-2-enoate**



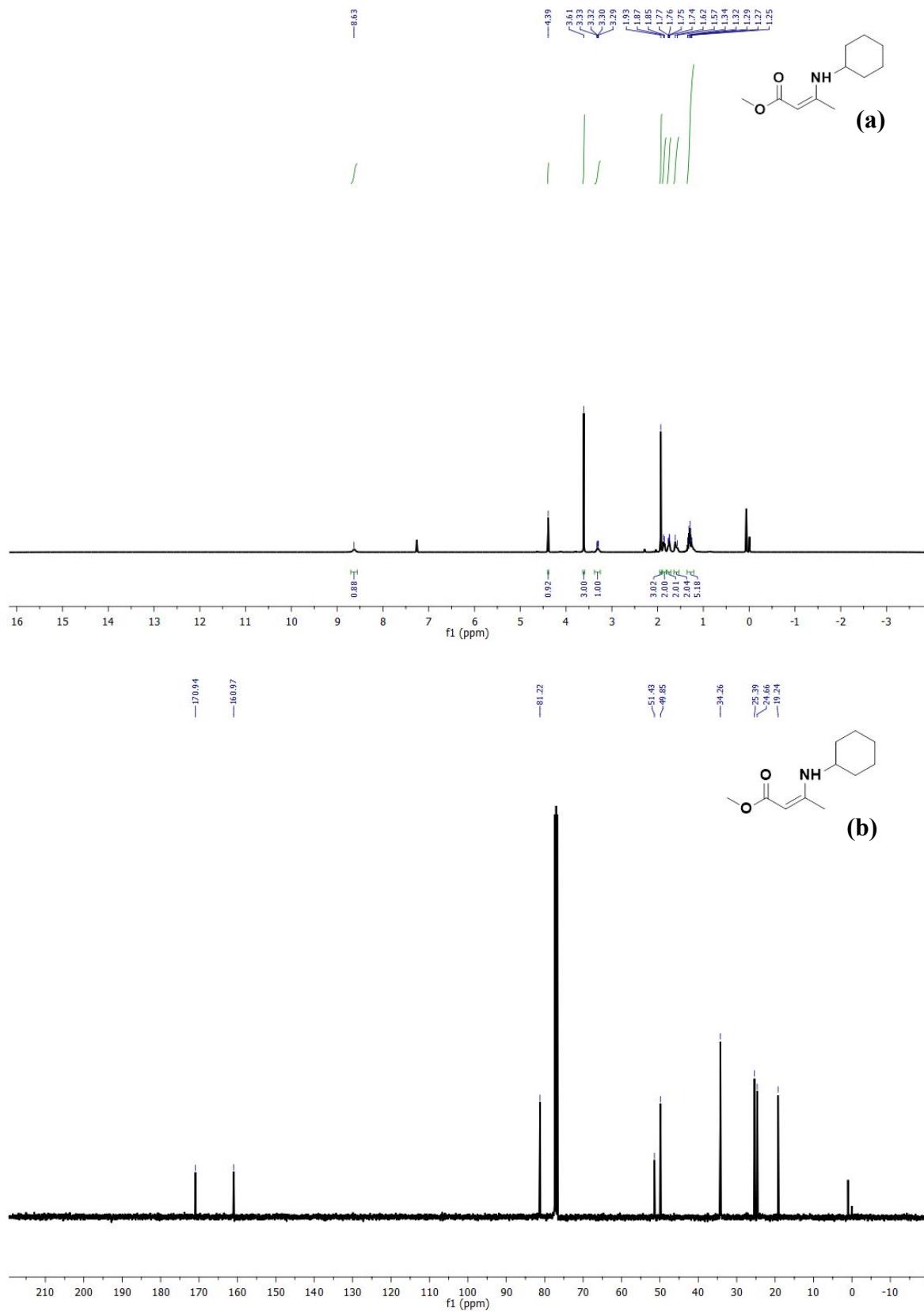
**Figure SI33 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-methyl 3-((4-hydroxyamino)but-2-enoate**



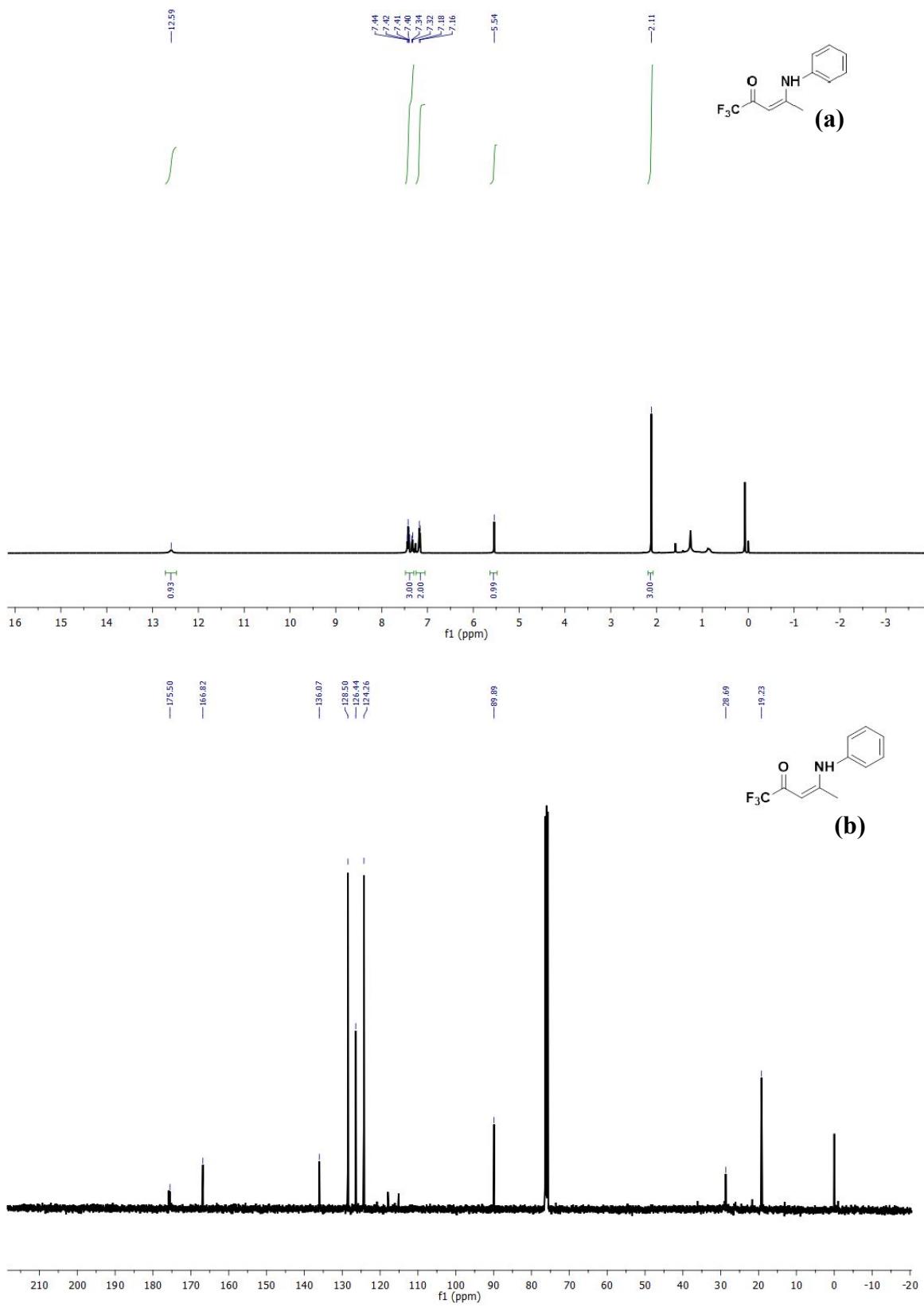
**Figure SI34 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-methyl 3-((4-nitrophenyl)amino)but-2-enoate**



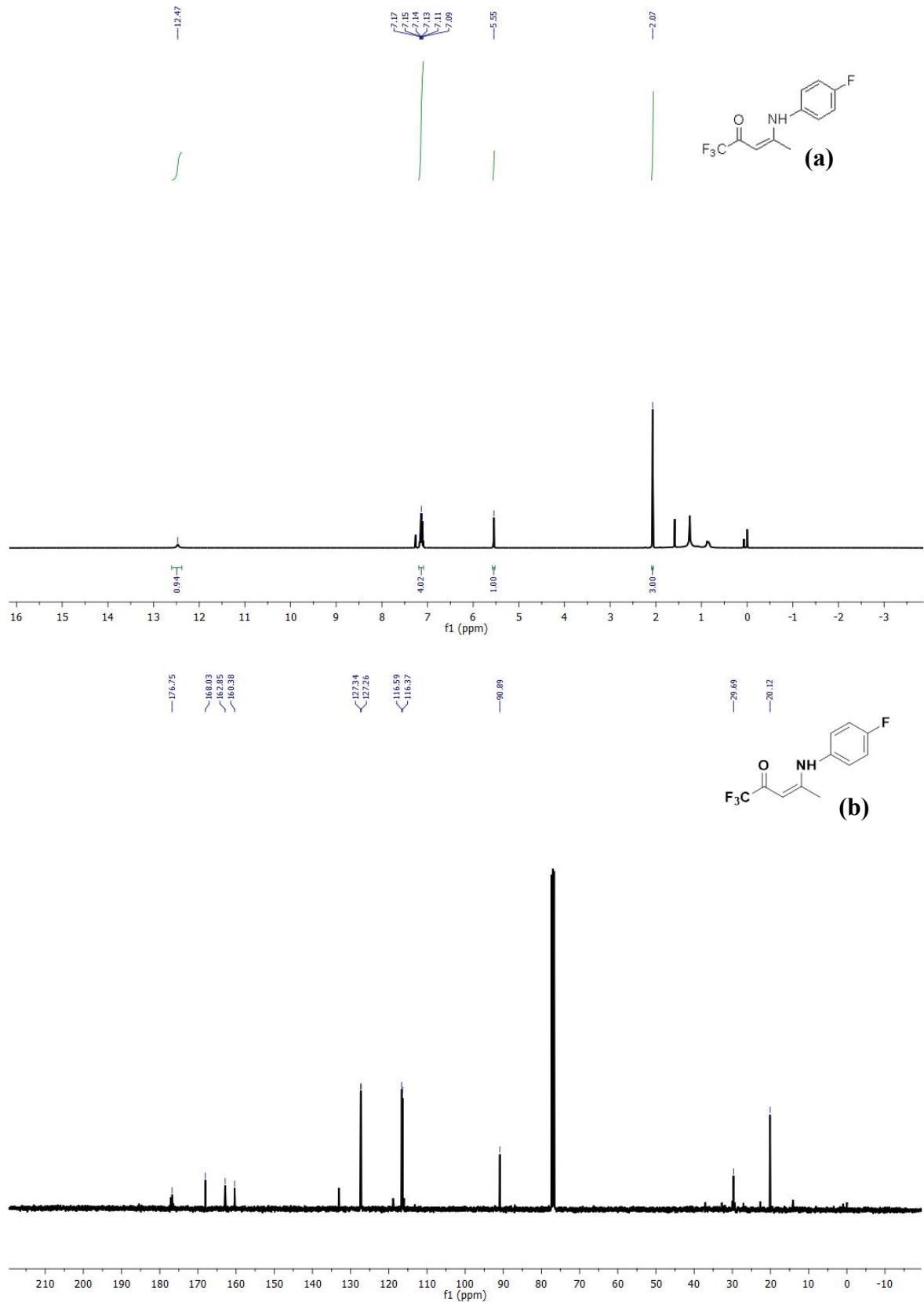
**Figure SI35 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-methyl 3-((3-chlorophenyl)amino)but-2-enoate**



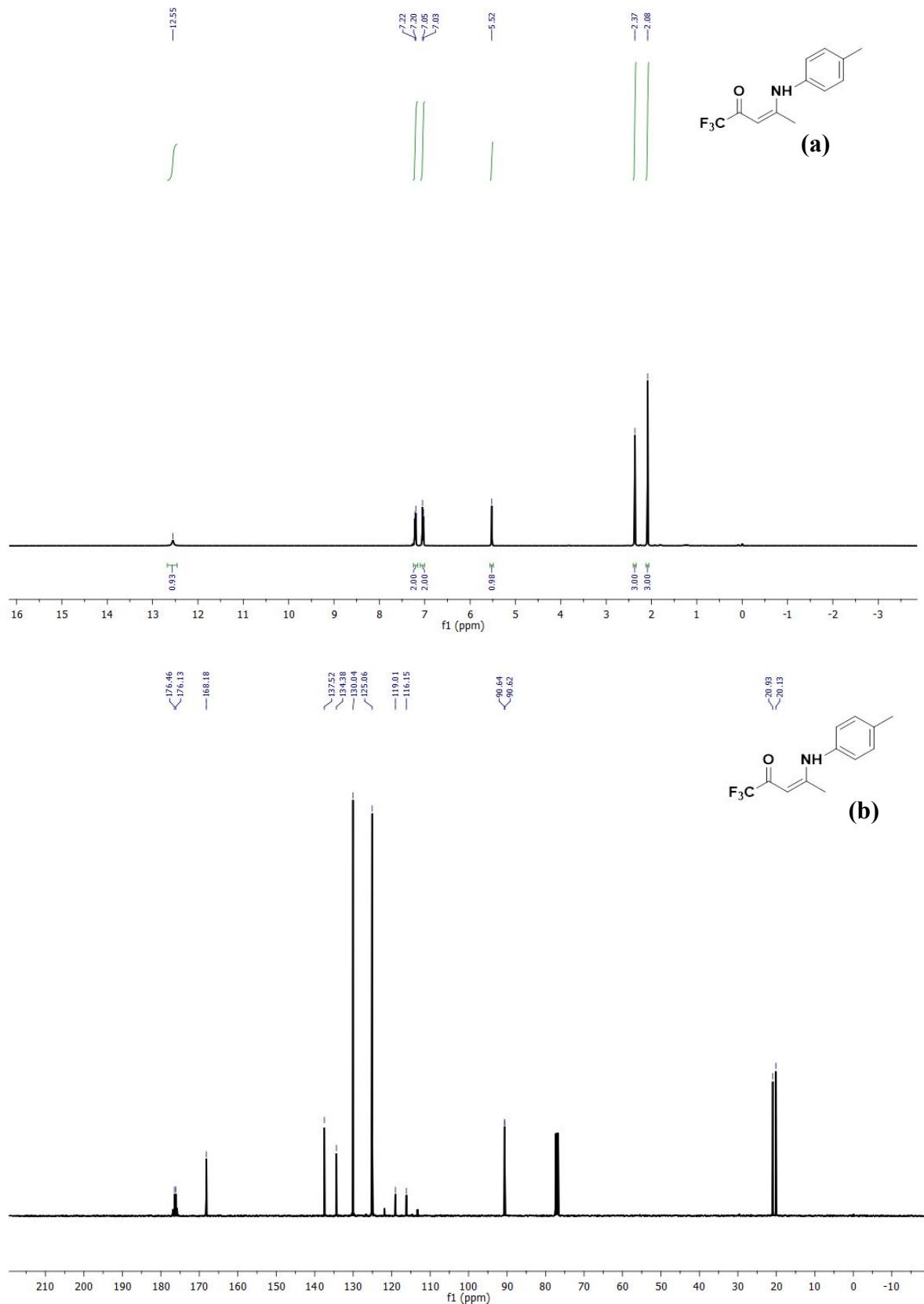
**Figure SI36 (a): 1H-NMR and (b) 13C NMR spectra of (Z)-methyl 3-(cyclohexylamino)but-2-enoate**



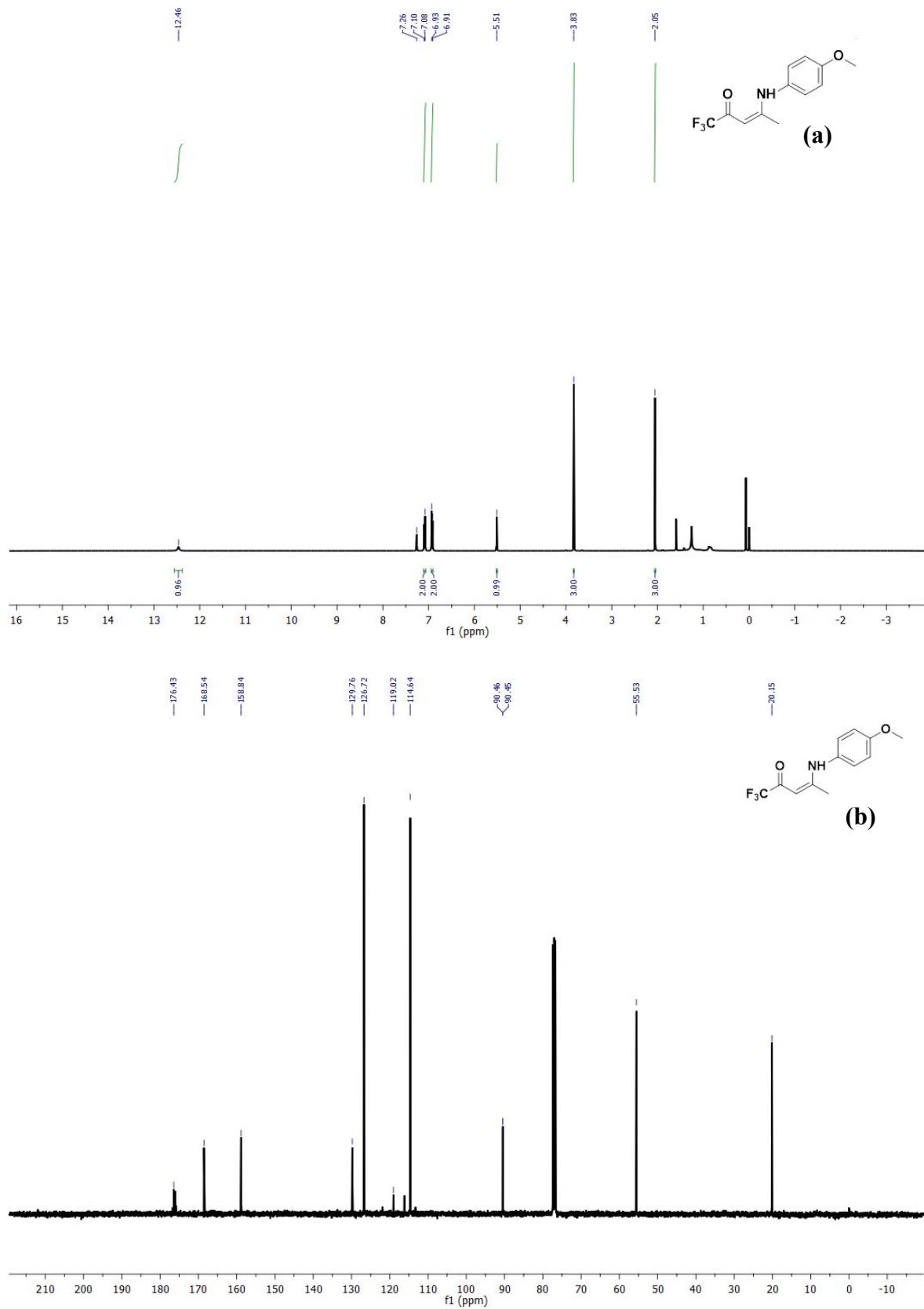
**Figure SI37 (a):**  $^1\text{H}$ -NMR and **(b)**  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-(phenylamino)pent-3-en-2-one



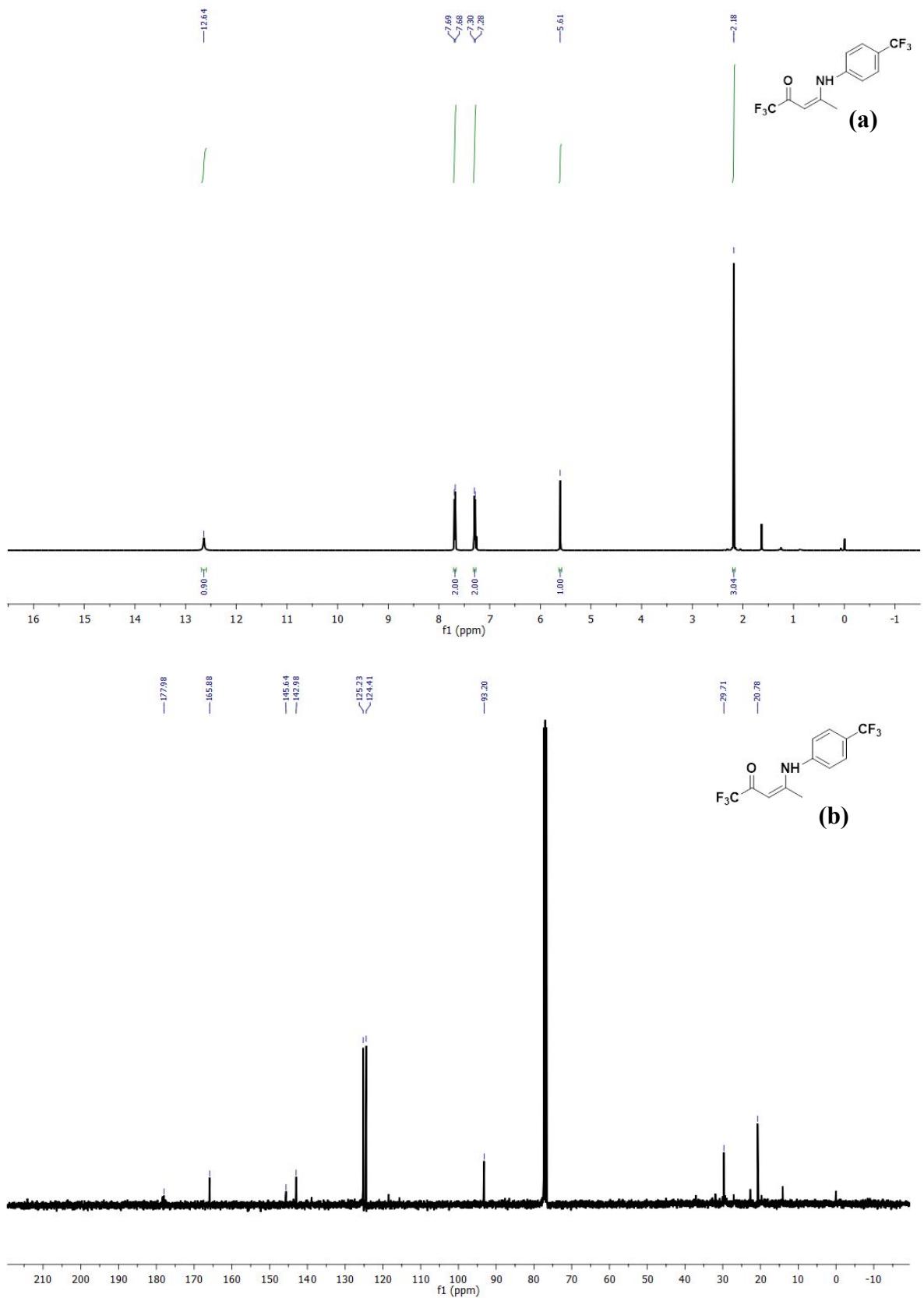
**Figure SI38 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-((4-fluoro)phenylamino)pent-3-en-2-one**



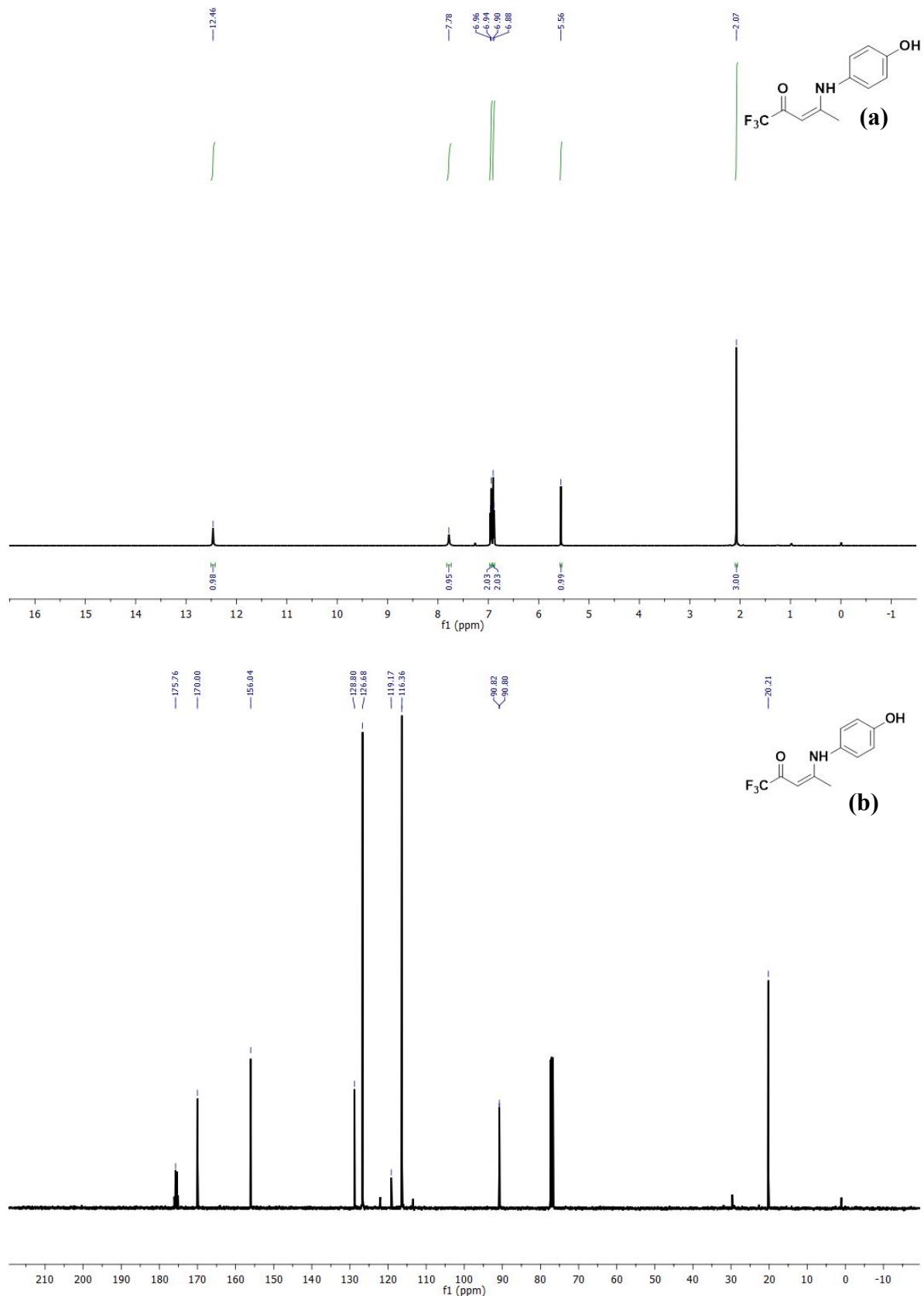
**Figure SI39 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of Fig (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-((4-methyl)phenylamino)pent-3-en-2-one**



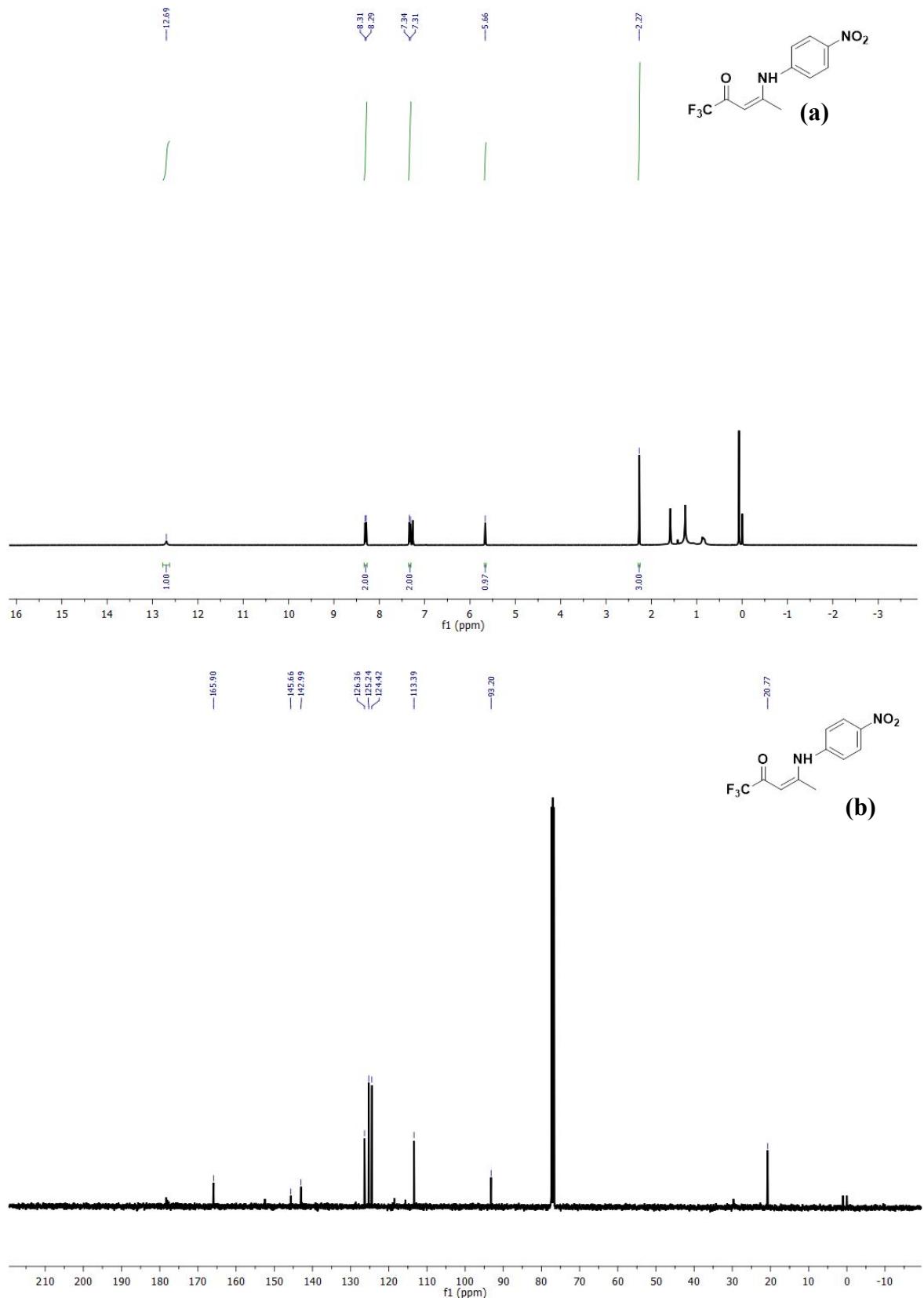
**Figure SI40 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-((4-methoxy)phenylamino)pent-3-en-2-one**



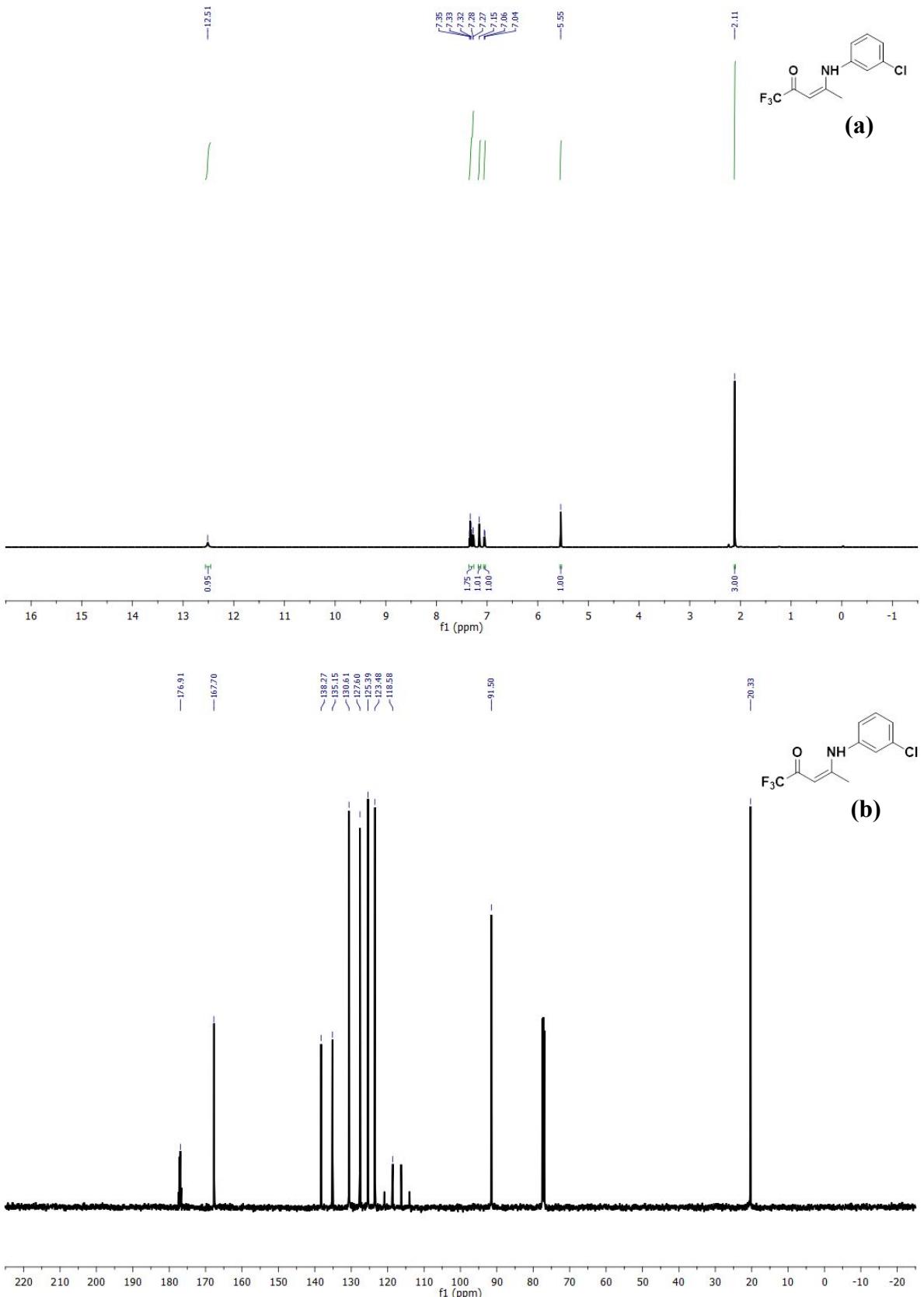
**Figure SI41 (a):**  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-((4-(1,1,1-trifluoro)methyl)phenylamino)pent-3-en-2-one



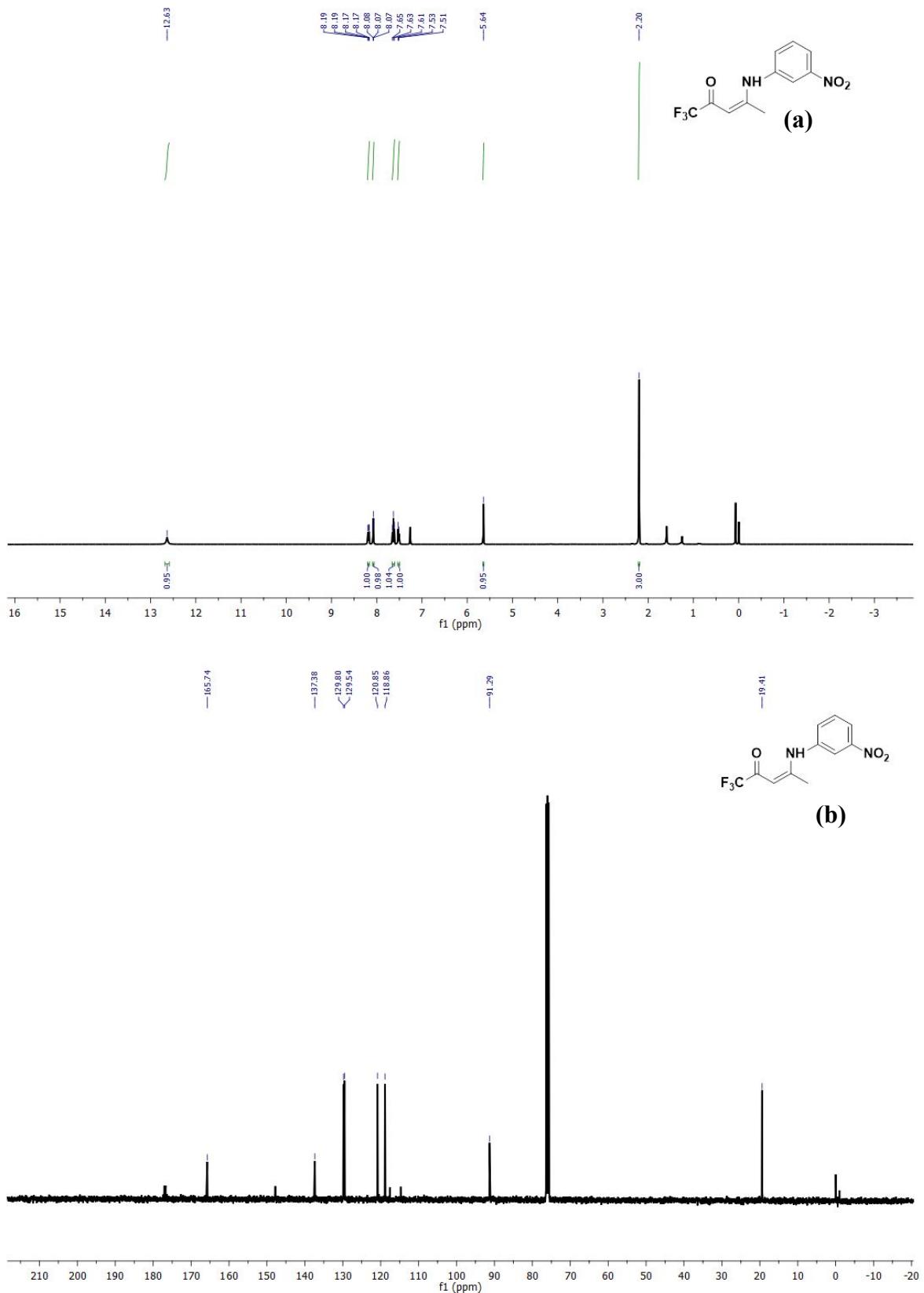
**Figure SI42 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-((4-hydroxy)phenylamino)pent-3-en-2-one**



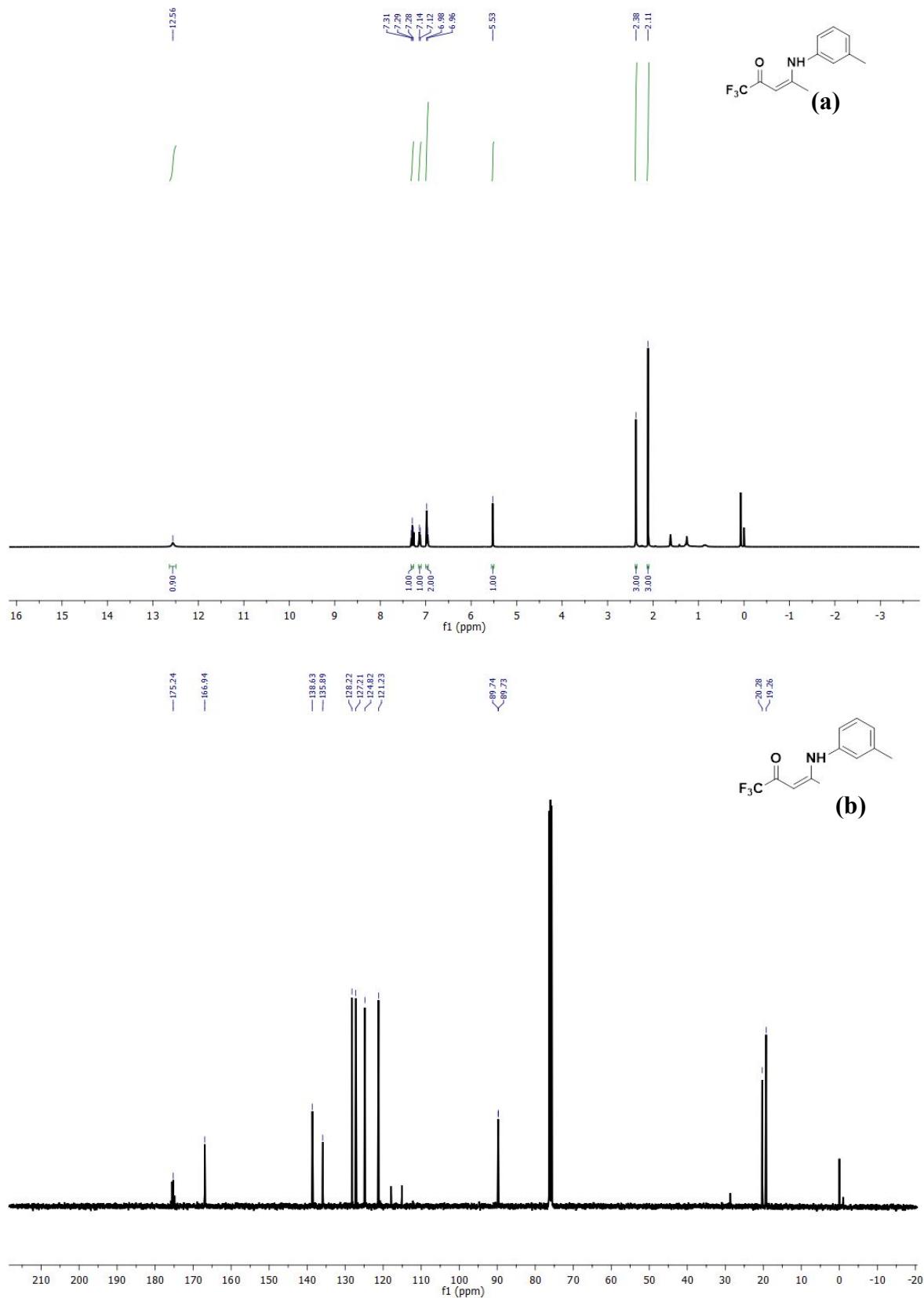
**Figure SI43 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-((4-nitro)phenylamino)pent-3-en-2-one**



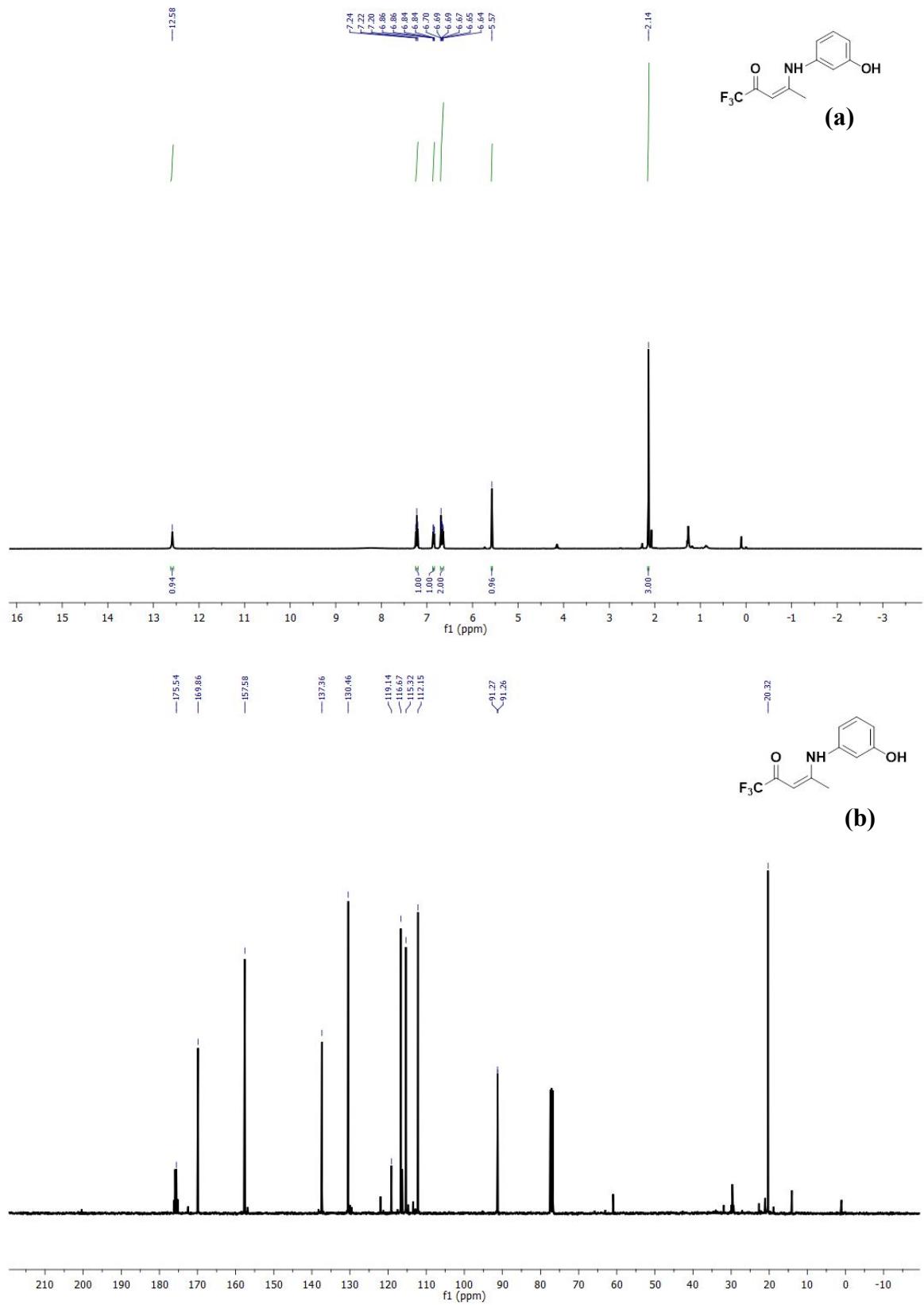
**Figure SI44 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-((3-chlorophenylamino)pent-3-en-2-one**



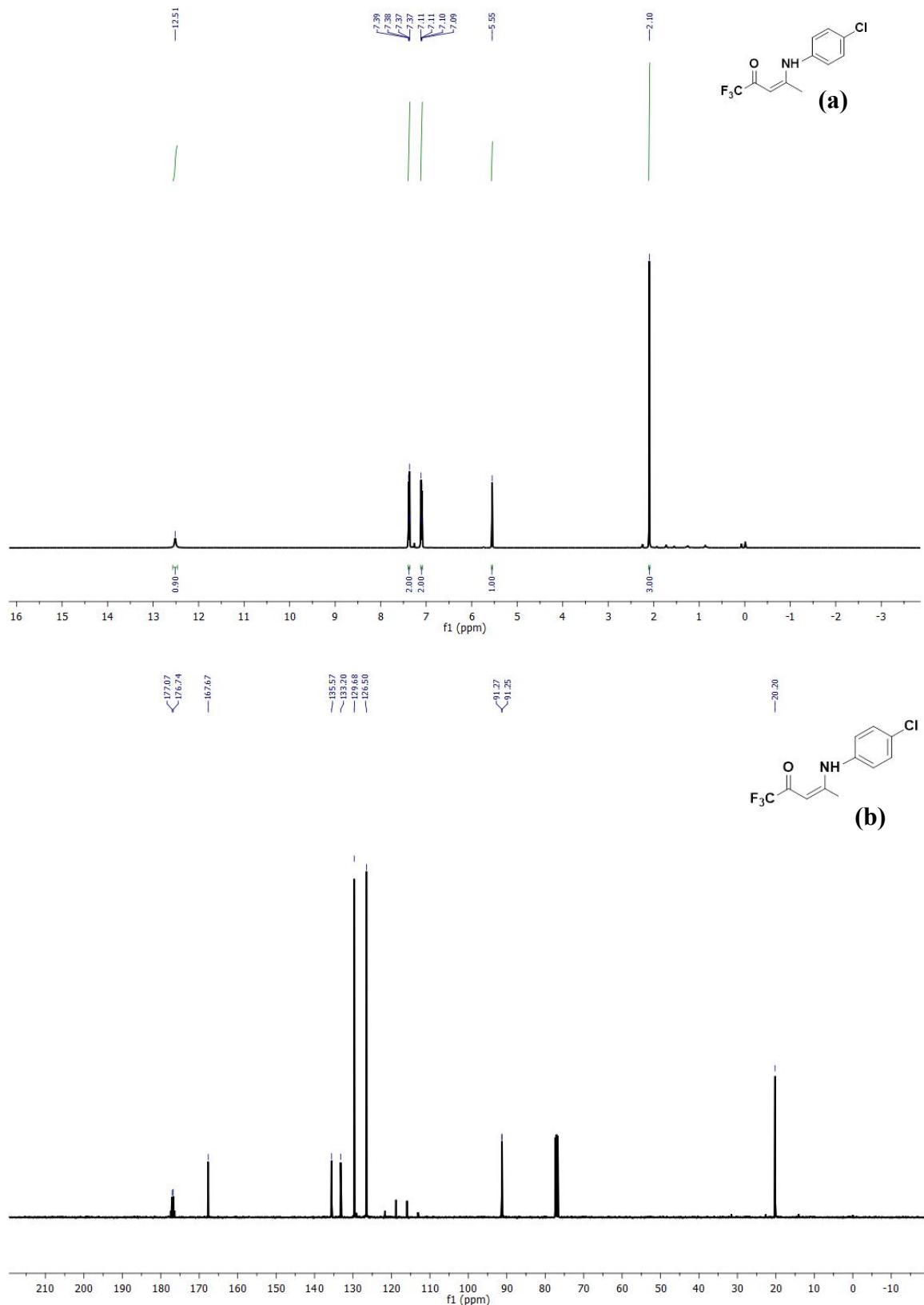
**Figure SI45 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-((3-nitro)phenylamino)pent-3-en-2-one**



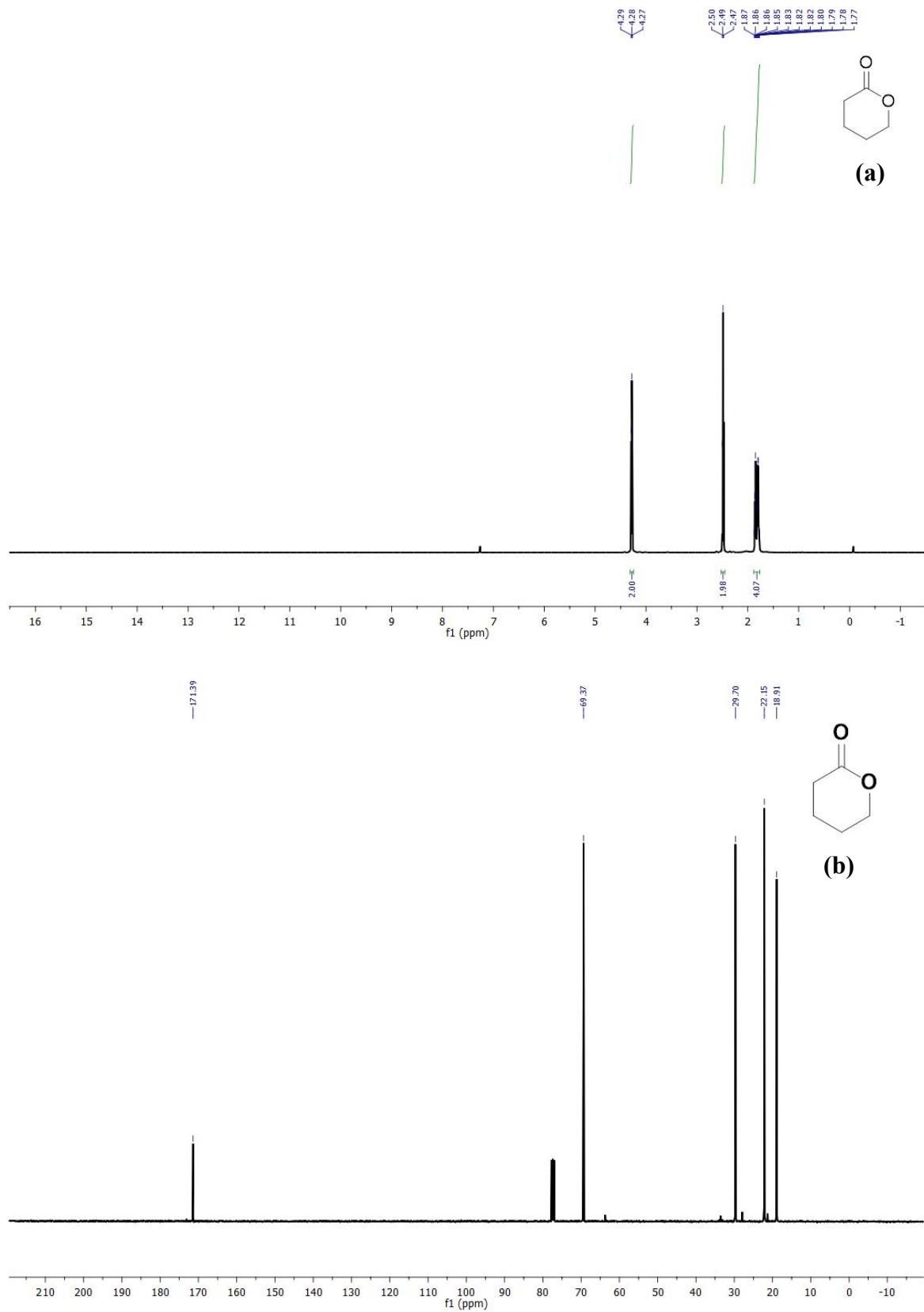
**Figure SI46 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-((3-methyl)phenylamino)pent-3-en-2-one**



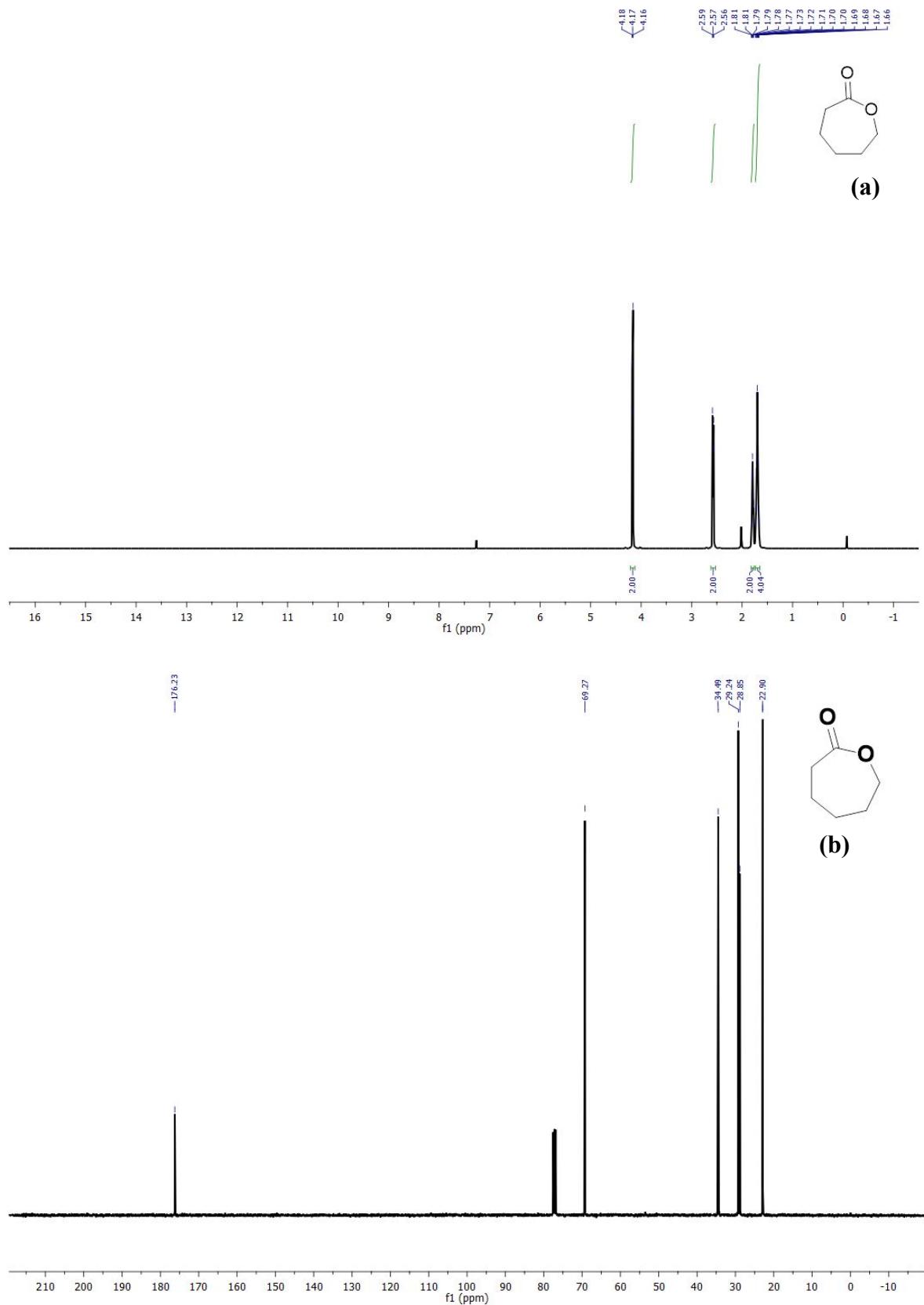
**Figure SI47 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-((3-hydroxy)phenylamino)pent-3-en-2-one**



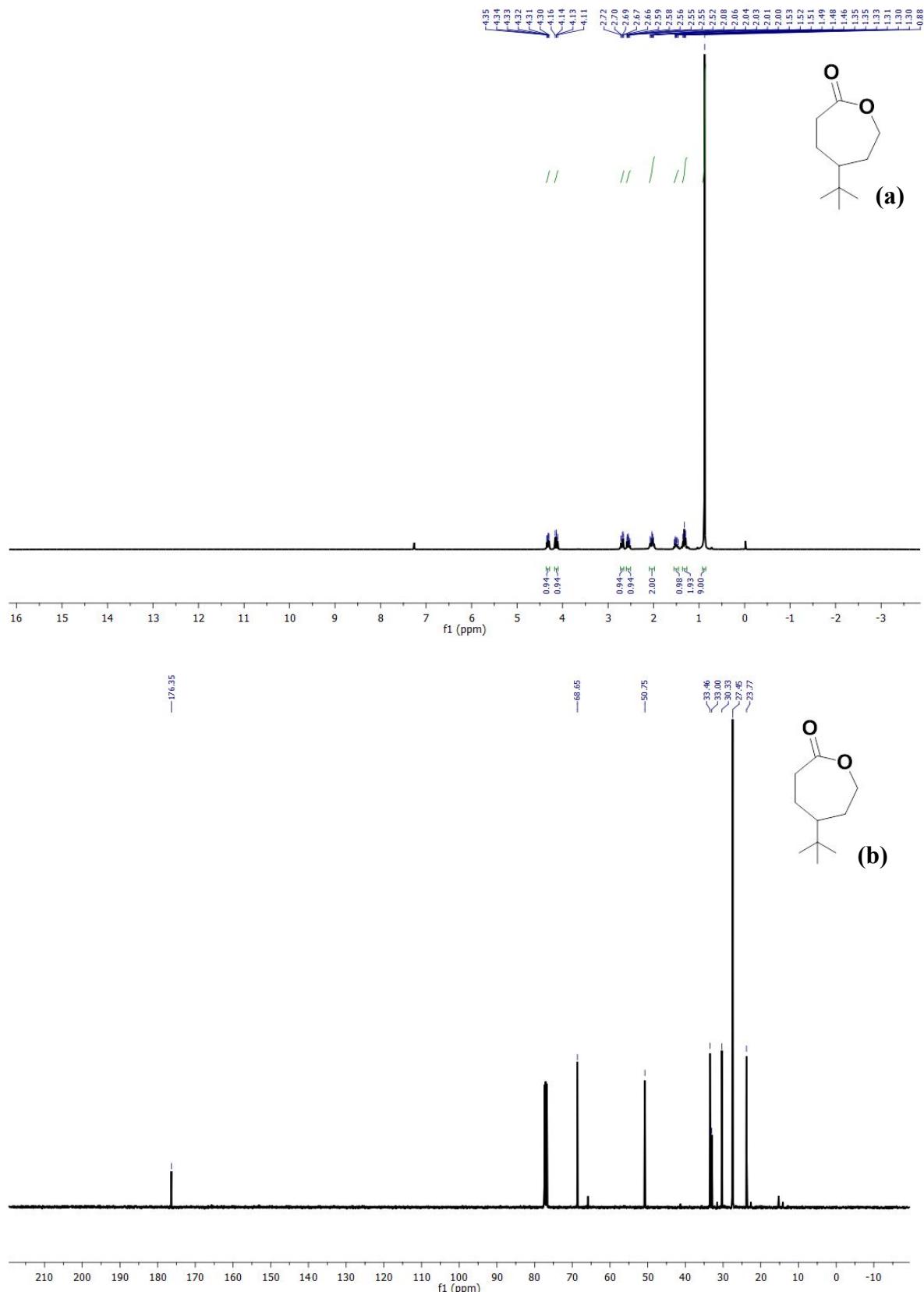
**Figure SI48 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (Z)-1,1,1-trifluoro-4-((4-chlorophenyl)amino)pent-3-en-2-one**



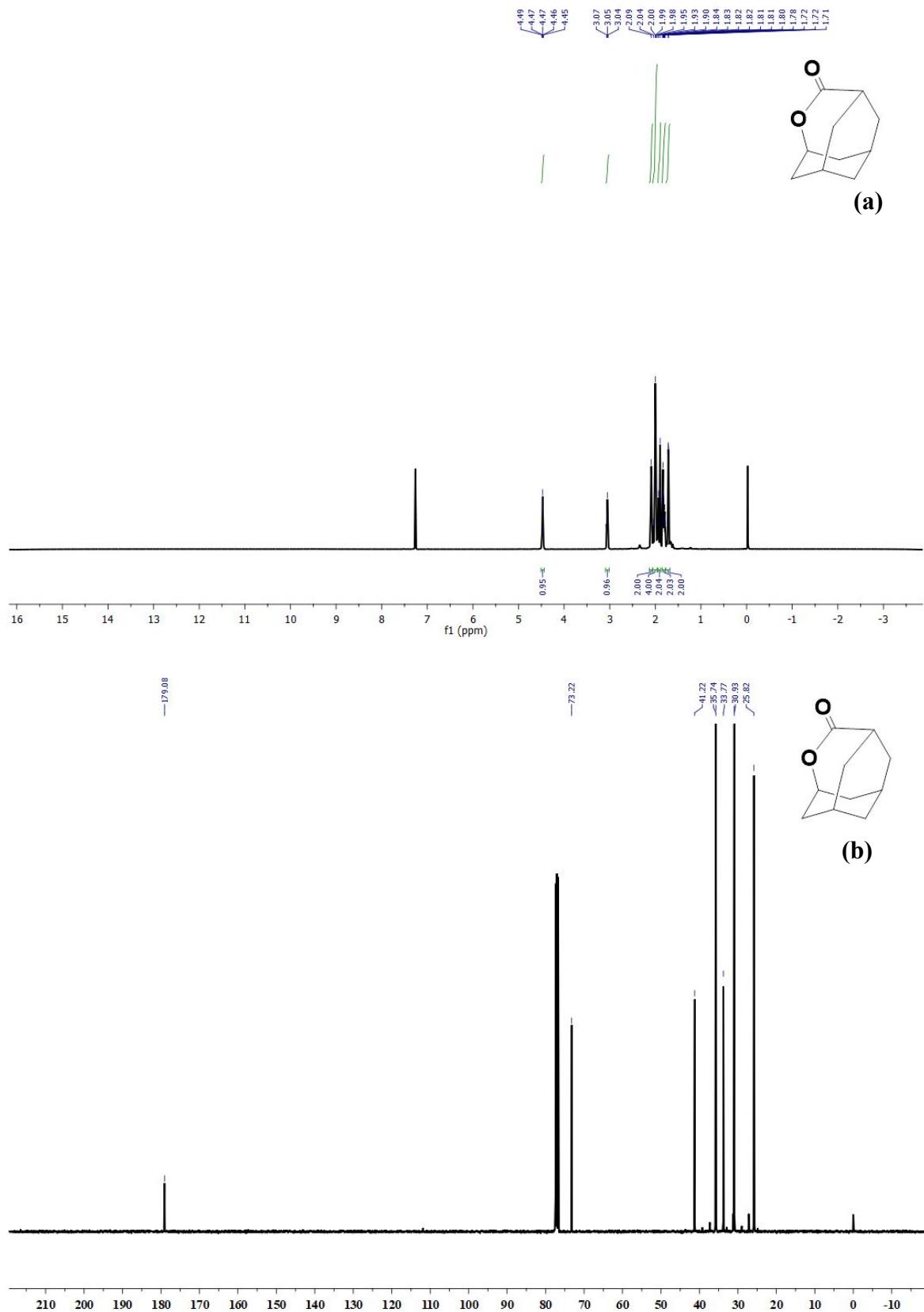
**Figure SI49 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of Tetrahydro-2H-pyran-2-one**



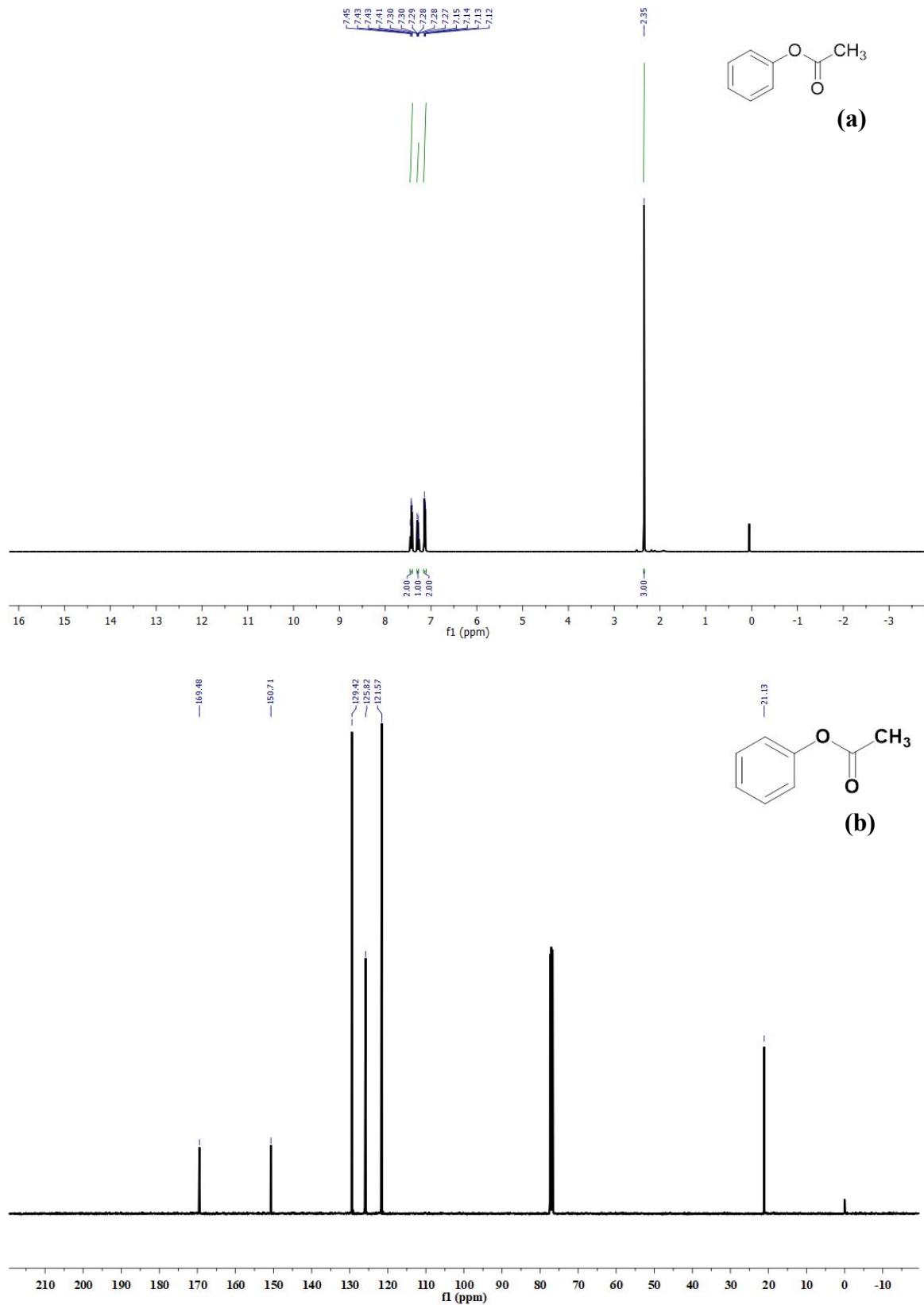
**Figure SI50 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of Oxepan-2-one**



**Figure SI51 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of 5-(tert-butyl)-Oxepan-2-one**



**Figure SI52 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of (1R,3r,8S)-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecan-5-one**



**Figure SI53 (a):  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$  NMR spectra of Phenyl Acetate**