

## Supporting Information

### Carbene-Catalyzed Alkylation of Carboxylic Esters via Direct Photoexcitation of Acyl Azolium Intermediates

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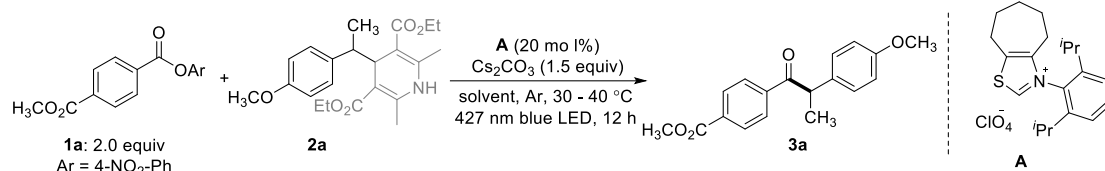
## 1. General information

All reactions and manipulations involving air-sensitive compounds were carried out using standard Schlenk techniques. Anhydrous toluene, hexane, Et<sub>2</sub>O and THF were distilled from sodium benzophenone ketyl. Anhydrous CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> were distilled from CaH<sub>2</sub> under an atmosphere of nitrogen. Anhydrous DCE were purchased from Sigma-Aldrich Co., Inc. All reactions were monitored by TLC. TLC analysis was performed by illumination with a UV lamp (254 nm). All flash chromatography was packed with silica-gel as the stationary phase. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance (300 or 500 MHz) or Bruker BBFO (400 MHz) instrument, and chemical shifts were reported in ppm downfield from internal TMS with the solvent resonance as the internal standard (CDCl<sub>3</sub>, δ = 7.26 ppm). <sup>13</sup>C NMR spectra were recorded on a Bruker BBFO (101 MHz) or Bruker Avance (125 MHz) instrument, and chemical shifts were reported in ppm downfield from TMS with the solvent resonance as the internal standard (CDCl<sub>3</sub>, δ = 77.0 ppm). <sup>19</sup>F NMR spectra were recorded on a Bruker Avance 300 (282 MHz) or Bruker BBFO (376 MHz) instrument. High resolution mass spectra (HRMS) (EI<sup>+</sup>) were recorded on an a Finnigan MAT 95 XP mass spectrometer. UV/vis absorption spectra were recorded on a SHIMADZU UV-3600 UV/Vis spectrometer. Fluorescence spectroscopy was recorded on a SHIMADZU RF-5301pc spectrometer. Cyclic voltammetry studies were carried out on a Thermo Fisher SP50 electrochemical workstation. Melting points are uncorrected and were recorded on an MPA 100 OptiMelt Automated Melting Point System. Flash column chromatography was performed using Merck silica gel 60 with distilled solvents. Commercially available reagents were purchased from Energy Chemical, J & K Scientific, Adamas-beta and Sigma-Aldrich Co., Inc.

Carboxylic acid esters<sup>[1]</sup> and 4-alkyl-1,4-dihydropyridines<sup>[2]</sup> were prepared according to the literature procedure. The conversion of Hantzsch ester (2) and the yield of Hantzsch ester-derived pyridine (by-product) were calculated based on crude <sup>1</sup>H NMR of the reaction mixture.

## 2. Condition optimizations

### 2.1 Screening of solvent<sup>[a]</sup>



entry	solvent	yield/ %
1	DCE	70 (68) <sup>[b]</sup>
2	MeCN	22
3	THF	20
4	DMSO	0
5	PhCl	0

[a] Reaction conditions: **2** (0.1-0.2 mmol), **1** (2.0 equiv), **A** (20 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in solvent (1.5 mL), blue LED (Kessil PR160 series,  $\lambda_{\text{max}}$  = 427 nm), Ar atmosphere, 30-40 °C, 12 h. [b] Isolated yield.

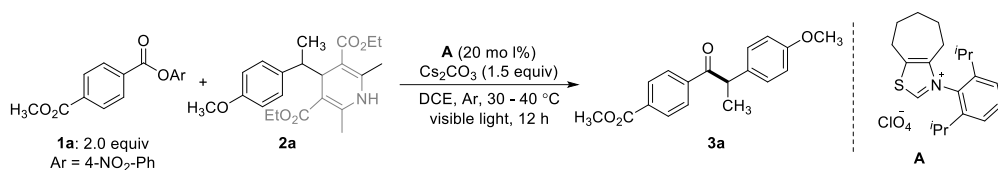
### 2.2 Screening of base<sup>[a]</sup>



entry	base	solvent	yield/ %
1	Cs <sub>2</sub> CO <sub>3</sub>	DCE	70 (68) <sup>[b]</sup>
2	K <sub>2</sub> CO <sub>3</sub>	DCE	trace
3	Li <sub>2</sub> CO <sub>3</sub>	DCE	0
4	Na <sub>2</sub> CO <sub>3</sub>	DCE	0
5	K <sub>2</sub> CO <sub>3</sub>	Acetone	16
6	K <sub>2</sub> CO <sub>3</sub>	MeCN	30
7	Li <sub>2</sub> CO <sub>3</sub>	MeCN	2
8	Na <sub>2</sub> CO <sub>3</sub>	MeCN	2
9	DBU	DCE	0
10	DMAP	DCE	0
11	DIPEA	DCE	0
12	DABCO	DCE	0

[a] Reaction conditions: **2** (0.1-0.2 mmol), **1** (2.0 equiv), **A** (20 mol%) and base (1.5 equiv) in solvent (1.5 mL), blue LED (Kessil PR160 series,  $\lambda_{\text{max}}$  = 427 nm), Ar atmosphere, 30 - 40 °C 12 h; [b] Isolated yield.

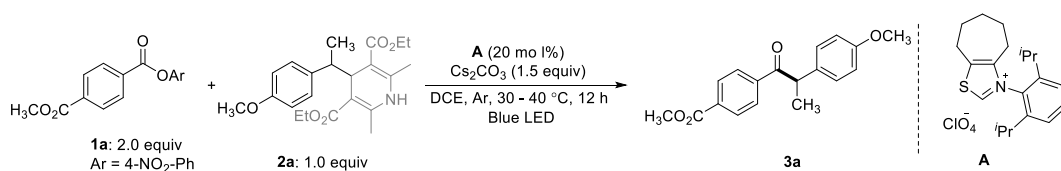
## 2.3 Influence of light wavelength<sup>[a]</sup>



entry	wavelength & intensity	yield
1	427 nm	70 (68%) <sup>[b]</sup>
2	440 nm	66%
3	456 nm	69%
4	467 nm	66%

[a] Reaction conditions: **2** (0.1 mmol), **1** (2.0 equiv), **A** (20 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in DCE (1.5 mL), blue LED (Kessil PR160 series,  $\lambda_{\text{max}}$  = 427, 440, 456, 467 nm), Ar atmosphere, 30 - 40 °C, 12 h; [b] isolated yield

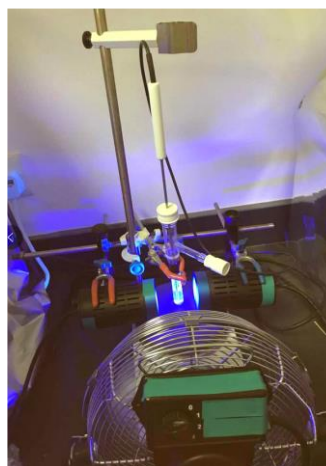
## 3. General procedure for catalytic synthesis of **3** and **6**



**General procedure:** To a 10 mL Schlenk tube equipped with a stir bar was added methyl (4-nitrophenyl) terephthalate **1a** (120.4 mg, 0.40 mmol), **2a** (77.5 mg, 0.20 mmol), **A** (16.4 mg, 0.04 mmol), and dry Cs<sub>2</sub>CO<sub>3</sub> powder (97.6 mg, 0.30 mmol). The Schlenk tube was sealed and placed under argon before 2 mL of dry DCE was added. The reaction was stirred and irradiated with two blue LED Kessil lamp ( $\lambda_{\text{max}}$  = 427 nm, intensity = 75%, 3 cm away from the Schlenk tube, with cooling fan to keep the reaction temperature at 30 - 40 °C. Reaction set-up see Figure S1) for 12 hours. Then the reaction mixture was diluted with ethyl acetate. The resulting mixture was extracted three times with ethyl acetate. The combined extracts were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude material was purified by column chromatography (silica gel, EtOAc/hexanes), to give product **3a** in 68% isolated yield as a white solid.



reaction setup



temperature measurement

**Figure S1:** Picture of reaction set-up and temperature measurement

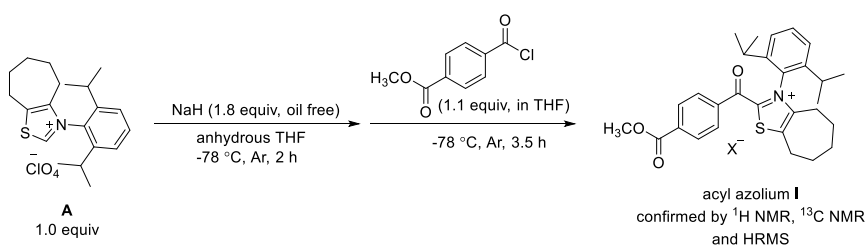
We measured the temperature many times during this project by using the same experimental setup (Figure S1). One of the results was presented in Table S1.

Time	0 min	5 min	1 h	2 h	4 h	12 h
Temperature/ °C	23	30	31	34	34	35

**Table S1:** Reaction temperature

## 4. Mechanistic studies

### 4.1 Synthesis and characterization of acyl azolium intermediate (I)

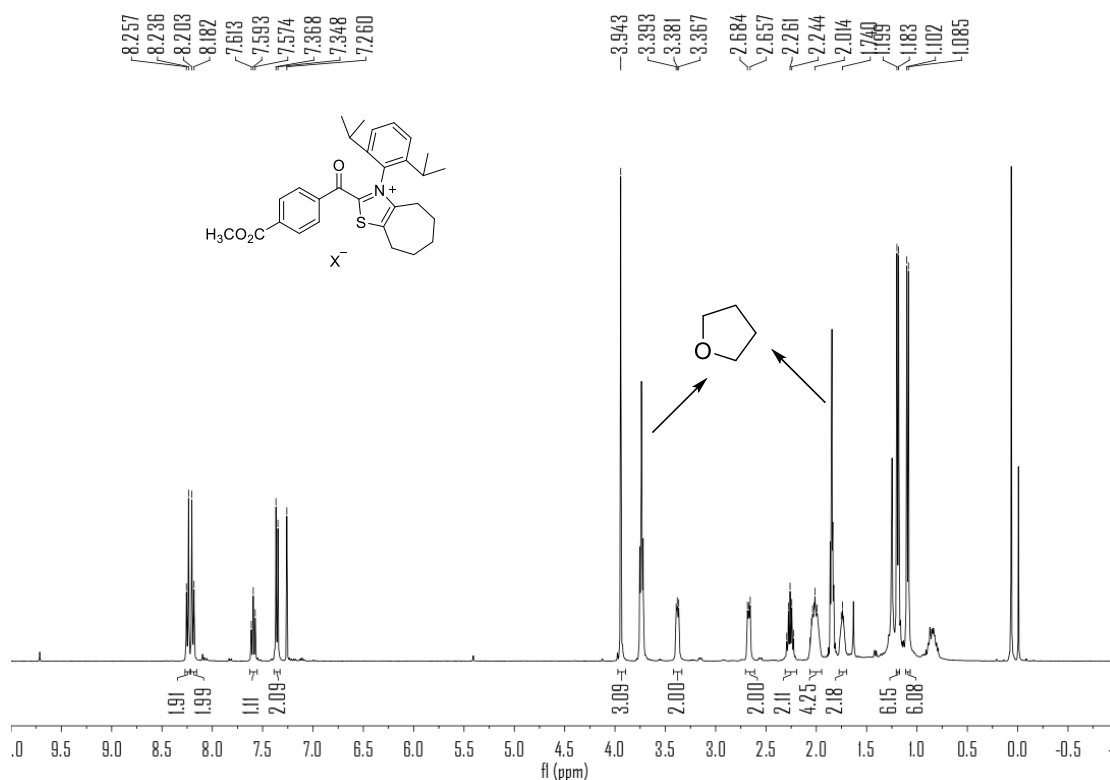


**General procedure:** In gloves box, to a dried 25 mL Schlenk tube equipped with a stir bar was added oil free NaH (4.3 mg, 0.18 mmol) and NHC precatalyst **A** (41.4 mg, 0.1 mmol). The Schlenk tube was sealed and took out from the gloves box and cooled to -78 °C by acetone/dry ice bath, freshly distilled THF (2.5 mL) was added. The mixture was stirred at -78 °C for 2 hours followed by addition of a THF solution of methyl 4-(chlorocarbonyl)benzoate (22.0 mg,

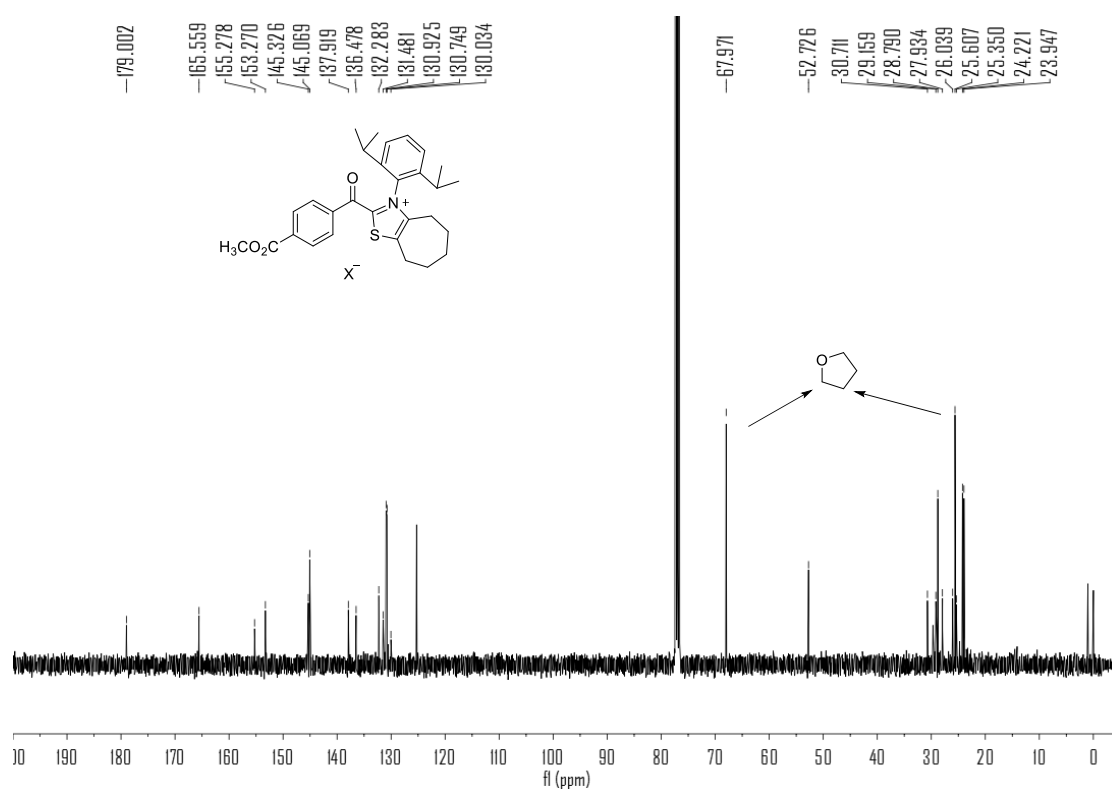
0.11 mmol, dissolved in 0.8 mL THF). The reaction mixture was stirred for additional 3.5 hours. Then the mixture was warm to room temperature followed by filtered in gloves box to give a light yellow solution. The solvent was removed, affording the desired acyl azolium intermediate (**I**). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.27-8.22 (2H, m), 8.21-8.16 (2H, m), 7.59 (1H, t, *J* = 7.8 Hz), 7.39-7.33 (2H, m), 3.94 (3H, s), 3.42-3.33 (2H, m), 2.70-2.61 (2H, m), 2.26 (2H, quint, *J* = 6.8 Hz), 2.08-1.95 (4H, m), 1.78-1.70 (2H, m), 1.91 (6H, d, *J* = 6.7 Hz), 1.09 (6H, d, *J* = 6.7 Hz). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 179.0, 165.6, 155.3, 153.3, 145.3, 145.1, 137.9, 136.5, 132.3, 131.5, 130.9, 130.7, 125.3, 52.7, 30.7, 29.2, 28.8, 27.9, 26.0, 25.4, 24.2, 23.9. **HRMS (ESI)**: Found: *m/z* 476.2267. Calcd for C<sub>29</sub>H<sub>34</sub>NO<sub>3</sub>S (M)<sup>+</sup> 476.2254.

*Note: The acyl azolium intermediate (I) was characterized and used directly without purification due to its sensitivity to moisture.*

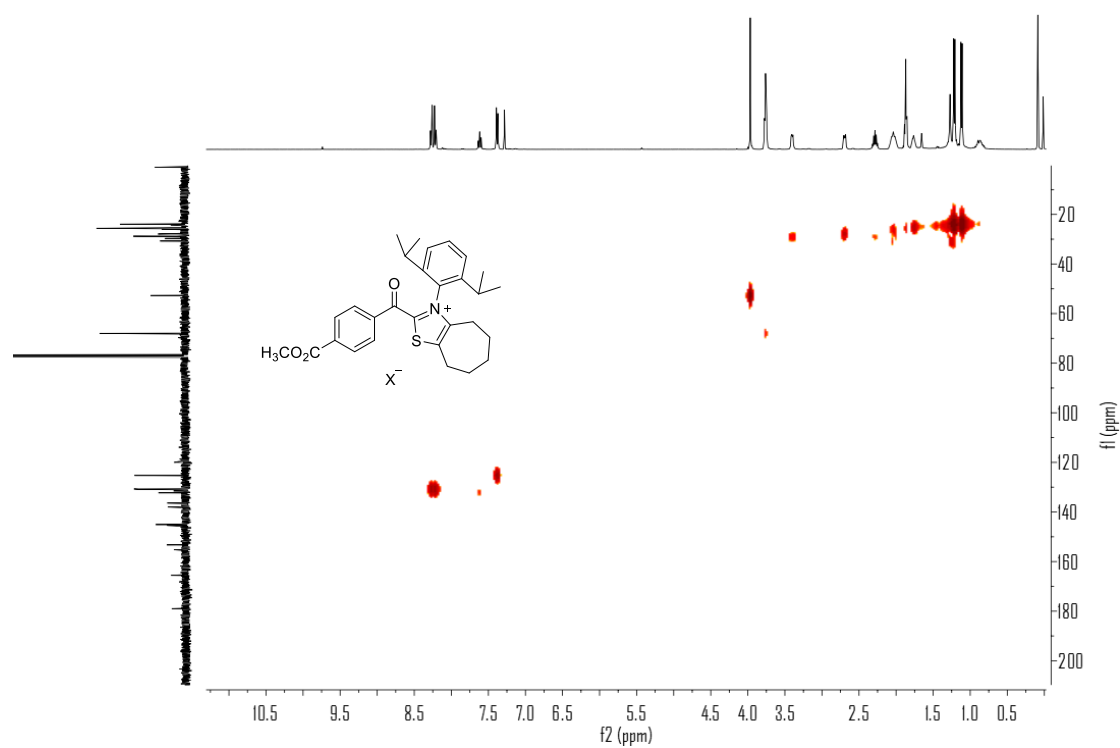
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) spectrum of acyl azolium intermediate **I**



**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of acyl azolium intermediate **I****



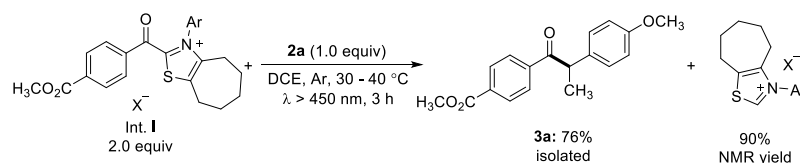
**HMQC spectrum of acyl azolium intermediate **I****





## 4.2 Direction alkylation of acyl azolium intermediate

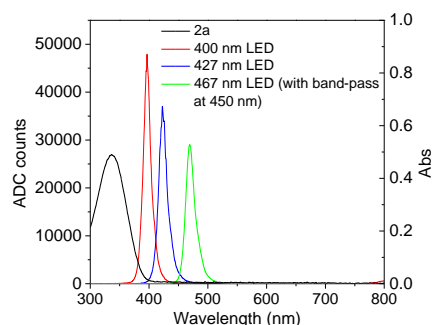
Direct irradiation of a solution of pre-formed acyl azolium (**I**) and Hantzsch ester (**2a**) in DCE under light of  $\lambda > 450$  nm without the presence of  $\text{Cs}_2\text{CO}_3$  resulted in 76% yield of desired product and 90% yield of carbene precursor. This result suggests that formation of EDA complex involving carbonate anion is not necessary for the reaction to proceed.



Experimental protocol: To a 10 mL Schlenk tube equipped with a stir bar and Hantzsch ester **2a** (19.4 mg, 0.005 mmol) was added freshly prepared solution of acyl azolium intermediate **I** (0.1 mmol in DCE). The Schlenk tube was sealed and took out of gloves box. The reaction was stirred and irradiated with two blue LED Kessil lamp ( $\lambda_{\text{max}} = 467$  nm, with band-pass at 450 nm. Cooling fan was used to keep the reaction temperature at 30 - 40 °C) for 2 hours. Then the reaction mixture was filtered through a pad of Celite and washed with ethyl acetate. The filtrate was dried under vacuuo. The yield of pre-catalyst was measured as 90% by using 1,1,2,2-tetrachlororthane as internal standard. The desired product **3a** was isolated in 76% yield.

## 4.3 Exclusion of the direct photoexcitation of Hantzsch ester 2a

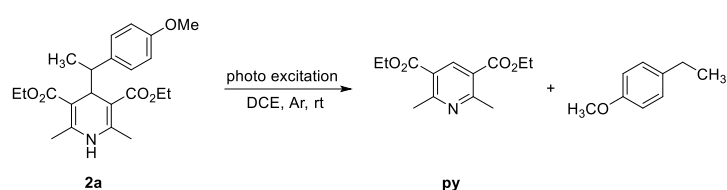
### 4.3.1 UV-Vis absorption spectrum and emission spectra of LEDs



**Figure S2:** Emission spectra of LEDs and the absorption spectrum of **2a**

### 4.3.2 Destructive test experiments of Hantzsch ester (2a)

Direct illumination of a solution of Hantzsch ester **2a** in DCE by 400 nm LED resulted in complete decomposition of **2a** after 1.5 h, with the corresponding pyridine was detected in 82% NMR yield (Table S2, entry 1). While 427 nm LED led to 26% yield of pyridine formation, with 68% of **2a** were recovered (Table S2, entry 2). The 467 nm LEDs (with band-pass at 450 nm) which smoothly promote our reaction were also tested. Hantzsch ester (**2a**) was recovered in 96% yield after 24 hours of irradiation under 467 nm LEDs (Table S2, entry 3).

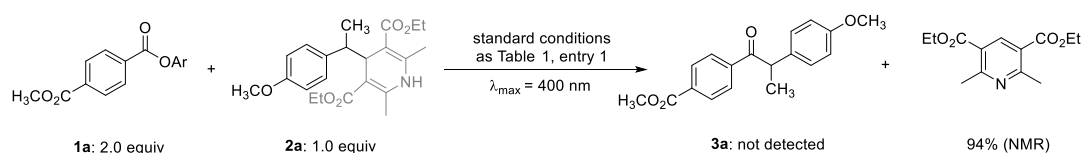


**Table S2:** destructive test experiments of Hantzsch eater **2a**<sup>a</sup>

Entry	LEDs	1.5 h		24 h	
		yield of py	recovery of <b>2a</b>	yield of py	recovery of <b>2a</b>
1	$\lambda_{\max} = 400$ nm	82%	0	--	--
2	$\lambda_{\max} = 427$ nm	26%	68%	--	--
3	$\lambda_{\max} = 467$ nm <sup>b</sup>	--	--	4%	96%

<sup>a</sup>The results are consistent with reported literature (Angew. Chem. Int. Ed., 2017, 56, 15039). <sup>b</sup>Band-pass at 450 nm was used.

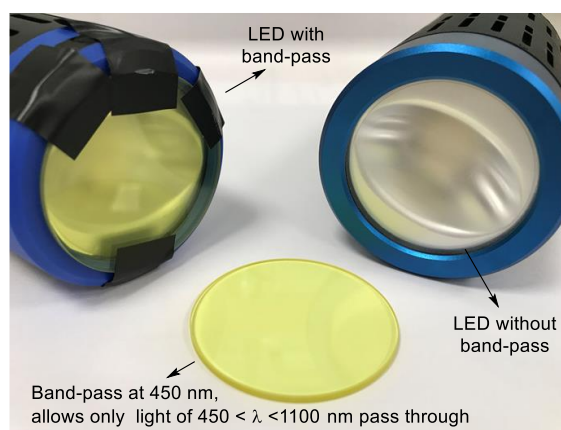
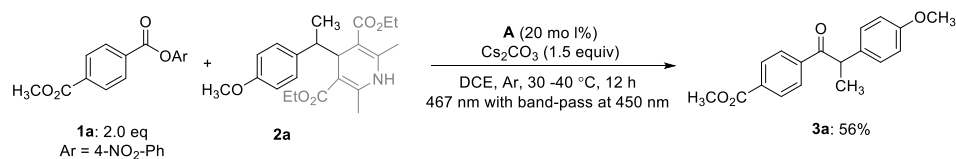
### 4.3.3 Reaction under irradiation of light of short wavelength ( $\lambda_{\max} = 400$ nm)



According to the general procedure, **1a** (60.2 mg, 0.20 mmol), **2a** (38.7 mg, 0.10 mmol) **A** (8.2 mg, 0.02 mmol), dry Cs<sub>2</sub>CO<sub>3</sub> powder (48.8 mg, 0.15 mmol), and DCE (1.5 ml) were used. After stirred for 12 h under irradiation of two blue LED (Kessil PR160 series,  $\lambda_{\max} = 400$  nm, intensity = 75%, 3 cm away from the Schlenk tube, with

cooling fan to keep the reaction temperature at 30-40 °C), the reaction mixture was diluted with ethyl acetate. The resulting mixture was extracted three times with ethyl acetate. The combined extracts were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude material was analyzed by <sup>1</sup>H NMR with 1,1,2,2-tetrachloroethane as internal standard.

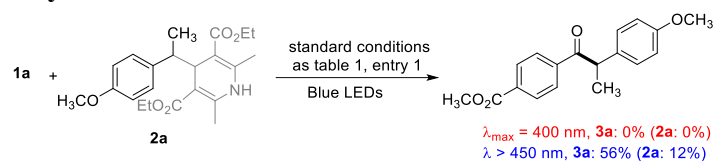
#### 4.3.4 Reaction under irradiation of light of long wavelength ( $\lambda > 450$ nm)



**Figure S3:** Blue LED and band-pass

According to the general procedure, **1a** (60.2 mg, 0.20 mmol), **2a** (38.7 mg, 0.10 mmol) **A** (8.2 mg, 0.02 mmol), dry Cs<sub>2</sub>CO<sub>3</sub> powder (48.8 mg, 0.15 mmol), and DCE (1.5 ml) were used. After stirred for 12 h under irradiation of two blue LED (Kessil PR160 series,  $\lambda_{\text{max}}$  = 467 nm, intensity = 100%, 3 cm away from the Schlenk tube, with cooling fan to keep the reaction temperature at 30 - 40 °C) with band-pass at 450 nm,<sup>[4]</sup> the reaction mixture was diluted with ethyl acetate. The resulting mixture was extracted three times with ethyl acetate. The combined extracts were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude material was analyzed by <sup>1</sup>H NMR with 1,1,2,2-tetrachloroethane as internal standard.

### 4.3.5 Results analysis:

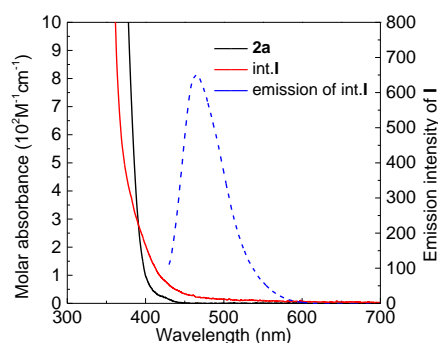


**Figure S4:** Reactions under light of different wavelength

Hantzsch ester (**2a**) is known to have little absorptions at the visible light region ( $\lambda > 420$  nm).<sup>[3]</sup> This was further confirmed by the emission spectra of LEDs and the absorption spectrum of **2a** (Figure S2). However, the reaction works well under the irradiation of long wavelength visible lights ( $\lambda > 450$  nm) where Hantzsch ester has no absorption (Figure S4). In contrast, when the reaction was carried out under irradiation of LED of  $\lambda_{\text{max}} = 400$  nm (instead of 427 nm in our standard conditions), whose emission region overlaps lightly with the strong absorption region of **2a** (Figure S2, black line and red line), no radical coupling product (**3a**) was observed and **2a** decomposed completely to form the corresponding pyridine and alkane (Figure S4). These results suggest that direct excitation of the Hantzsch ester is not responsible for the radical coupling reactions observed in our study.

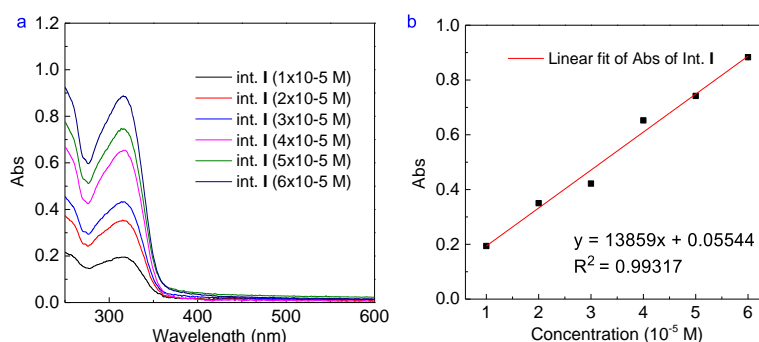
### 4.4 UV-Vis absorption experiment of acyl azolium (I) and Hantzsch ester (2a)

The UV-Vis absorption spectrum of acyl azolium **I** ( $10^{-3}$  M in DCE, red line) was measured on a SHIMADZU UV-3600 UV/Vis spectrometer. The absorption spectrum revealed a significant absorption of visible light, and the tail wavelength of acyl azolium (**I**) reached over 520 nm (Figure S5, red line). In contrast, **2a** ( $10^{-3}$  M in DCE, black line) has little absorptions at the visible light region ( $\lambda > 420$  nm). In addition, the corresponding emission spectrum of acyl azolium **I** upon excitation at 400 nm was also recorded (Figure S5, blue dashed line).



**Figure S5:** Absorption spectrum of **2a** & acyl azolium (**I**); and emission of acyl azolium (**I**).

The absorption spectra of pre-formed **I** were measured at different concentrations in DCE (obtained by opportunely diluting the original solution with anhydrous DCE). The absorbances (maximum absorbance at 319 nm) showed a typical Lambert-Beer linear correlation with the concentrations.



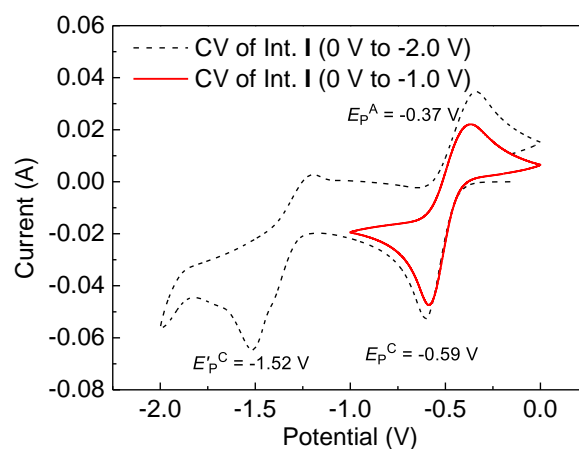
**Figure S6:** a. Absorption spectra of the pre-formed acyl azolium intermediate (**I**) at different concentrations in anhydrous DCE. The wavelength of maximum absorbance is 319 nm; b. Lambert-Beer linear correlation between absorbance and concentration at 319 nm for acyl azolium **I**.

#### 4.5 Cyclic Voltammetry Studies

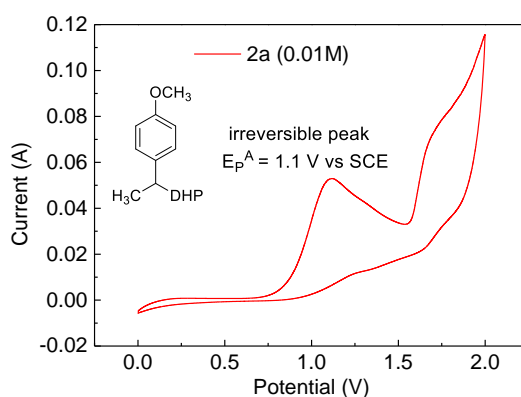
The cyclic voltammograms of pre-formed **I** solution in MeCN features two successive reductive peak at  $E_{\text{red}} = -0.59$  V and  $-1.52$  V vs SCE, which we attributed to the two successive single electron reduction of acyl azolium **I** respectively<sup>5</sup>. The reversible peak at  $E_{1/2} = (E_{\text{P}}^{\text{C}} + E_{\text{P}}^{\text{A}})/2 = -0.48$  V vs SCE belongs to the [**I**/ **III**] couple.  $E_{\text{P}}^{\text{C}}$  is the cathodic peak potential,  $E_{\text{P}}^{\text{A}}$  is the anodic peak potential, while  $E_{1/2}$  value

describes the electrochemical properties of the ground state acyl azolium intermediate

**I.**



**Figure S7:** Cyclic voltammograms of the pre-formed acyl azolium intermediate **I** (0.001M) in [0.1 M] TBAPF<sub>6</sub> in CH<sub>3</sub>CN. Sweep rate: 100 mV/s. Pt electrode working electrode, calomel electrode reference electrode, Pt wire auxiliary electrode.



**Figure S8:** Cyclic voltammograms of **2a** (0.001M) in [0.1 M] TBAPF<sub>6</sub> in CH<sub>3</sub>CN. Sweep rate: 100 mV/s. Pt electrode working electrode, calomel electrode reference electrode, Pt wire auxiliary electrode. Cyclic voltammogram of **2a** solutions feature irreversible peak at  $E_{ox} = E_p^A = +1.1$  V vs SCE.  $E_p^A$  is the anodic peak potential, while  $E_{ox}$  value describes the electrochemical properties of **2a**.

#### 4.6 Evaluation of the Excited State Potential of the acyl azolium intermediate **I**

Based on the data collected from the UV-vis absorption spectra (Figure S5) and cyclic voltammetry studies (Figure S8), the excited state potential of acyl azolium intermediate **I** was estimated from the following equation (Equation S1)<sup>6</sup>:

$$E(I^*/III) = E(I/III) + E_{0-0}(I^*/I) \quad \text{Equation S1}$$

$E(I/III)$  was measured as -0.48 V by cyclic voltammetry studies (Figure S8). The excited state energy of acyl azolium intermediate **I** ( $E_{0-0}(I^*/I)$ ) was estimated spectroscopically from the position of the tail wavelength of absorption spectrum of **I** (Figure S5). The tail wavelength of absorption spectrum of azolium intermediate **I** was estimated at 520 nm, which translates into an  $E_{0-0}(I^*/I)$  of 2.38 eV.

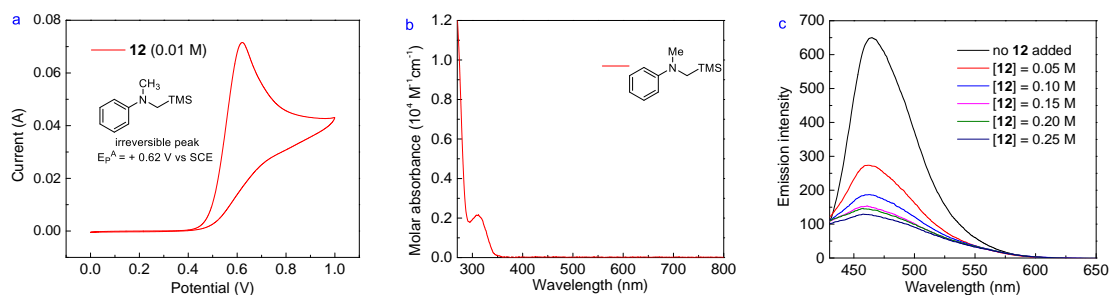
$$E(I^*/III) = -0.48 \text{ V} + 2.38 \text{ V} = +1.9 \text{ V (vs SCE)} \quad \text{Equation S2}$$

The estimated redox potential (Equation S2) of excited state of acyl azolium **I** is higher than Hantzsch ester (**2a**,  $E_{\text{ox}} = +1.1 \text{ V vs SCE}$ ), indicating that thermodynamically SET oxidation of **2a** by **I** (at its excited state) is feasible

#### 4.7 Stern-Volmer quenching experiments

To provide additional evidence that supports the direct photoexcitation of acyl azolium **I**, we conducted Stern-Volmer quenching experiments. It was reported that the decomposition of Hantzsch ester is likely to form a strongly emitting compound<sup>2c</sup>, which would frustrate the attempt to perform Stern-Volmer quenching experiments. Therefore, N-methyl-N-((trimethylsilyl)methyl)aniline (**12**) ( $E_{\text{P}}^{\text{A}} = +0.62$  V vs SCE, Figure S9a) which cannot react with ground state of acyl azolium **I** ( $E_{1/2} = -0.48$  V vs SCE, Figure S7) was chosen as a quenching reagent. It was found that N-methyl-N-((trimethylsilyl)methyl)aniline (**12**) could effectively quench the emission of **I** (Figure S9c), suggesting the oxidative property of excited state of acyl azolium **I**.

Experimental protocol: The emission spectra of freshly prepared solution of **I** ( $1 \times 10^{-3}$  M in DCE) was recorded. Then, N-methyl-N-((trimethylsilyl)methyl)aniline (**12**) (5  $\mu\text{L}$ ) was added to the solution, and another emission spectra was recorded. The addition of **12** and the recordation were repeated 4 consecutive times.

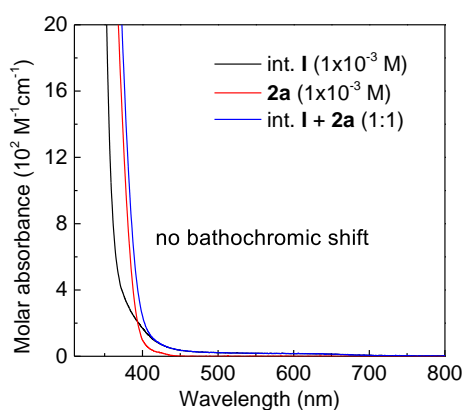


**Figure S9:** a. Cyclic voltammograms of N-methyl-N-((trimethylsilyl)methyl)aniline (**12**, 0.001M) in [0.1 M] TBAPF<sub>6</sub> in CH<sub>3</sub>CN. Cyclic voltammogram of **12** solutions feature irreversible peak at  $E_{\text{ox}} = E_{\text{P}}^{\text{A}} = +0.62$  V vs SCE; b. Absorption spectrum of **12**; c. Quenching of the pre-formed acyl azolium **I** emission ( $10^{-3}$  M in DCE) in the presence of N-methyl-N-((trimethylsilyl)methyl)aniline **12**.



#### 4.8 Exclude the formation of EDA complex between acyl azolium (I) and Hantzsch ester 2a

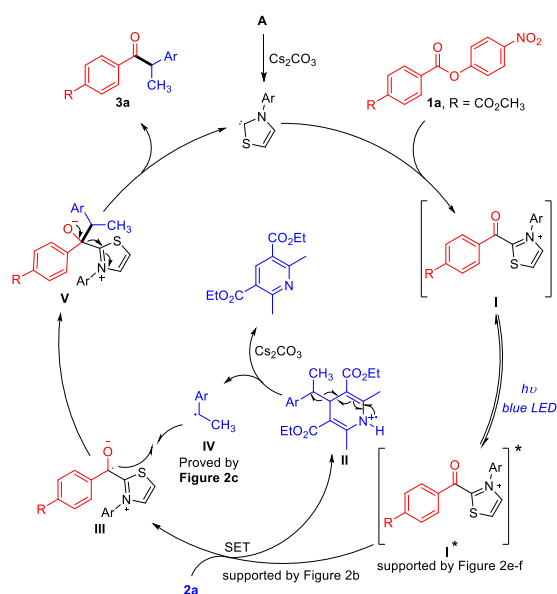
There was no bathochromic shift when mixing acyl azolium intermediate **I** and Hantzsch ester **2a**, which excludes the possibility of the formation of the EDA complex between Hantzsch ester and acyl azolium intermediate **I**.



**Figure S10:** UV-Vis absorption spectra between acyl azolium **I** and Hantzsch ester **2a**

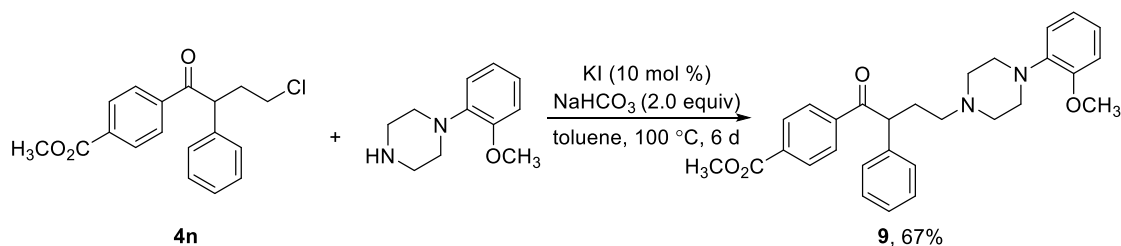
#### 4.9 Conclusion

Based on all the results of the mechanistic studies, a reasonable mechanisms were proposed and outlined below:



**Figure S11:** Proposed mechanism

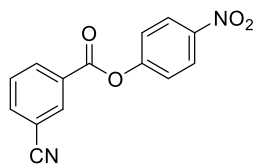
## 5. Synesthetic transformation of 4n



A solution of **4n** (32.1 mg, 0.10 mmol), 1-(2-methoxyphenyl)piperazine (38.5 mg, 0.20 mmol), KI (3.4 mg, 0.02 mmol) and NaHCO<sub>3</sub> (16.8 mg, 0.2 mmol) in toluene (1 mL) was stirred at 100 °C under nitrogen atmosphere for 6 days. When the reaction finished, the volatiles were removed and the resulting crude material was purified by flash column chromatography to give product **9** in 67% yield as white solid (31.5 mg). mp 120-121 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09-7.99 (4H, m), 7.34-7.25 (4H, m), 7.23-7.16 (1H, m), 6.98 (1H, td, *J* = 7.8, 1.7 Hz), 6.93-6.81 (3H, m), 4.73 (1H, dd, *J* = 7.7, 6.3 Hz), 3.91 (3H, s), 3.83 (3H, s), 2.95 (4H, brs), 2.70-2.48 (5H, m), 2.45-2.35 (2H, m), 2.03-1.91 (1H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.9, 166.2, 152.2, 141.3, 140.6, 139.1, 133.3, 129.6, 128.9, 128.5, 128.3, 127.1, 122.8, 120.9, 118.1, 111.2, 56.2, 55.3, 53.2, 52.3, 51.8, 50.5, 31.4; HRMS (ESI): Found: *m/z* 473.2443. Calcd for C<sub>29</sub>H<sub>33</sub>N<sub>2</sub>O<sub>4</sub> (M+H)<sup>+</sup> 473.2440. IR (KBr, cm<sup>-1</sup>): 1726, 1666, 1377, 1278, 1109, 740, 702.

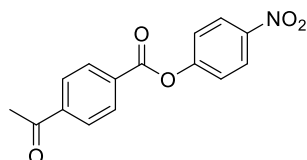
## 6. Characterizations of substrates and products

### 4-nitrophenyl 3-cyanobenzoate (1f)



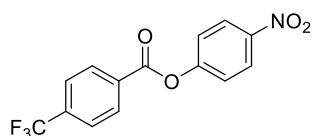
Yellow solid, mp 156-158 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.52-8.49 (1H, m), 8.44 (1H, dt,  $J = 8.0, 1.4$  Hz), 8.39-8.33 (2H, m), 7.97 (1H, dt,  $J = 7.8, 1.3$  Hz), 7.71 (1H, t,  $J = 7.9$  Hz), 7.47 – 7.42 (2H, m);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 155.0, 145.8, 137.1, 134.2, 133.9, 129.9, 129.9, 125.4, 122.5, 117.5, 113.6; **HRMS (ESI)**: Found:  $m/z$  269.0565. Calcd for  $\text{C}_{14}\text{H}_9\text{N}_2\text{O}_4$  ( $\text{M}+\text{H}$ ) $^+$  269.0562. **IR (KBr,  $\text{cm}^{-1}$ )**: 2220, 1743, 1558, 1517, 1375, 744.

### 4-nitrophenyl 4-acetylbenzoate (1g)



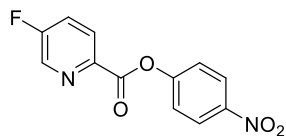
Yellow solid, mp 148-150 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38-8.32 (2H, m), 8.32-8.25 (2H, m), 8.14-8.06 (2H, m), 7.48-7.40 (2H, m), 2.69 (3H, s);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  197.3, 163.4, 155.4, 145.6, 141.2, 132.2, 130.6, 128.5, 125.3, 122.5, 26.9; **HRMS (ESI)**: Found:  $m/z$  286.0709. Calcd for  $\text{C}_{15}\text{H}_{12}\text{NO}_5$  ( $\text{M}+\text{H}$ ) $^+$  286.0715. **IR (KBr,  $\text{cm}^{-1}$ )**: 1741, 1687, 1558, 1267, 1080, 883.

### 4-nitrophenyl 4-(trifluoromethyl)benzoate (1h)



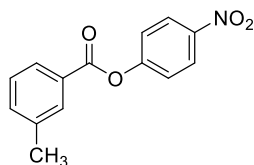
White solid, mp 93-95 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39-8.29 (4H, m), 7.86-7.77 (2H, m), 7.47-7.40 (2H, m);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 165.3, 145.7, 135.6 (q,  $J = 32.7$  Hz), 131.8, 130.7, 125.8 (q,  $J = 3.7$  Hz), 125.4, 123.4 (q,  $J = 271.3$ ), 122.5;  $^{19}\text{F}$  NMR (376MHz,  $\text{CDCl}_3$ )  $\delta$  -63.3 (s); **HRMS (ESI)**: Found:  $m/z$  312.0486. Calcd for  $\text{C}_{14}\text{H}_9\text{NO}_4\text{F}_3$  ( $\text{M}+\text{H}$ ) $^+$  312.0484. **IR (KBr,  $\text{cm}^{-1}$ )**: 1747, 1519, 1263, 1132, 764.

#### 4-nitrophenyl 5-fluoropicolinate (1k)



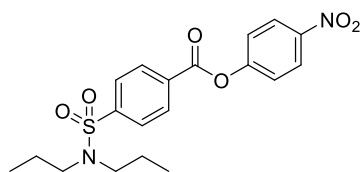
White solid, mp 149-150 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.69 (1H, d,  $J = 2.8$  Hz), 8.37-8.30 (3H, m), 7.64 (1H, ddd,  $J = 8.6, 7.7, 2.8$  Hz), 7.48-7.42 (2H, m);  $^{13}\text{C NMR}$  (125MHz,  $\text{CDCl}_3$ )  $\delta$  161.9, 161.7 (d,  $J = 264.5$  Hz), 155.4, 145.7, 142.7 (d,  $J = 4.0$  Hz), 139.2 (d,  $J = 25.0$  Hz), 128.1 (d,  $J = 6.0$  Hz), 125.4, 123.9 (d,  $J = 18.7$  Hz), 122.6; **HRMS (ESI)**: Found:  $m/z$  263.0470. Calcd for  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4\text{F}$  ( $\text{M}+\text{H}$ ) $^+$  263.0468. **IR (KBr,  $\text{cm}^{-1}$ )**: 1745, 1583, 1350, 1265, 1083, 864, 736.

#### 4-nitrophenyl 3-methylbenzoate (1m)



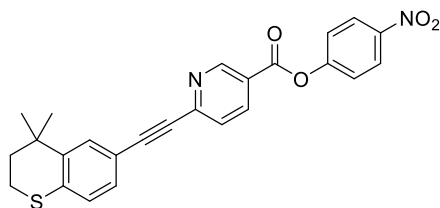
White solid, mp 95-96 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36-8.29 (2H, m), 8.04-7.98 (2H, m), 7.49 (1H, d,  $J = 7.7$  Hz), 7.47-7.38 (3H, m), 2.46 (3H, s);  $^{13}\text{C NMR}$  (100MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 155.8, 145.4, 138.7, 135.0, 130.8, 128.7, 128.5, 127.5, 125.3, 122.6, 21.3; **HRMS (ESI)**: Found:  $m/z$  258.0763. Calcd for  $\text{C}_{14}\text{H}_{12}\text{NO}_4$  ( $\text{M}+\text{H}$ ) $^+$  258.0766. **IR (KBr,  $\text{cm}^{-1}$ )**: 1728, 1521, 1209, 1083, 904, 744.

#### 4-nitrophenyl 4-(N,N-dipropylsulfamoyl)benzoate (1p)



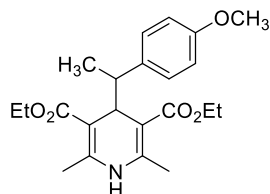
White solid;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 – 8.29 (4H, m), 7.97 (2H, m), 7.47-7.41 (2H, m), 3.17-3.11 (4H, m), 1.57 (4H, m), 0.89 (6H, t,  $J = 7.4$  Hz);  $^{13}\text{C NMR}$  (125MHz,  $\text{CDCl}_3$ )  $\delta$  163.0, 155.2, 145.6, 131.8, 131.0, 127.3, 125.4, 122.5, 109.9, 49.9, 21.9, 11.2; **HRMS (ESI)**: Found:  $m/z$  407.1272. Calcd for  $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_6\text{S}$  ( $\text{M}+\text{H}$ ) $^+$  407.1277. **IR (KBr,  $\text{cm}^{-1}$ )**: 1745, 1593, 1525, 1348, 1205, 777, 597.

**4-nitrophenyl 6-((4,4-dimethylthiochroman-6-yl)ethynyl)nicotinate (1q)**



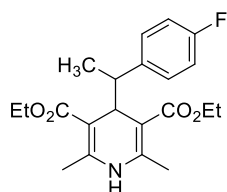
Yellow solid, mp 181-183 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.37-9.33 (1H, m), 8.42 (1H, dd, *J* = 8.2, 2.2 Hz), 8.38-8.32 (2H, m), 7.71-7.60 (2H, m), 7.48-7.42 (2H, m), 7.31-7.27 (1H, m), 7.10 (1H, d, *J* = 8.2 Hz), 3.10-3.02 (2H, m), 2.00-1.93 (2H, m), 1.35 (6H, s); **<sup>13</sup>C NMR** (100MHz, CDCl<sub>3</sub>) δ 162.7, 155.1, 151.7, 148.5, 145.7, 142.3, 137.7, 135.6, 130.6, 129.5, 126.7, 126.6, 125.4, 122.7, 122.5, 116.5, 94.6, 87.9, 37.0, 33.0, 29.9, 23.3; **HRMS (ESI)**: Found: *m/z* 445.1224. Calcd for C<sub>25</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub>S (M+H)<sup>+</sup> 445.1222. **IR (KBr, cm<sup>-1</sup>)**: 2194, 1732, 1587, 1377, 1274, 1201, 1074, 765.

**diethyl 4-(1-(4-methoxyphenyl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2a)**



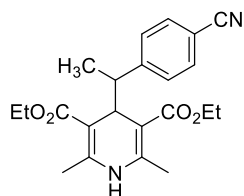
Yellow solid, mp 103-105 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.03-6.96 (2H, m), 6.77-6.70 (2H, m), 5.27 (s, 1H), 4.23 (1H, d, *J* = 4.9 Hz), 4.11-4.01 (3H, m), 3.99-3.89 (1H, m), 3.76 (3H, s), 2.75-2.65 (1H, m), 2.18 (6H, s), 1.28 (3H, t, *J* = 7.2 Hz), 1.21 (3H, t, *J* = 7.1 Hz), 1.13 (3H, d, *J* = 7.3 Hz); **<sup>13</sup>C NMR** (100MHz, CDCl<sub>3</sub>) δ 168.4, 168.3, 158.0, 145.0, 144.7, 136.2, 129.3, 112.5, 101.2, 100.9, 59.6, 59.5, 55.2, 45.1, 40.1, 19.2, 19.1, 15.8, 14.3, 14.3; **HRMS (ESI)**: Found: *m/z* 388.2121. Calcd for C<sub>22</sub>H<sub>30</sub>NO<sub>5</sub> (M+H)<sup>+</sup> 388.2124. **IR (KBr, cm<sup>-1</sup>)**: 3334, 1651, 1369, 1300, 1209, 1093, 744.

**diethyl 4-(1-(4-fluorophenyl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2f)**



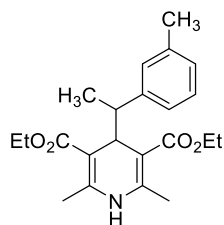
Yellow solid, mp 138-140 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.08-6.98 (2H, m), 6.93-6.81 (2H, m), 5.32 (1H, brs), 4.24 (1H, d,  $J = 4.9$  Hz), 4.14-4.00 (3H, m), 4.00 – 3.88 (1H, m), 2.80-2.67 (1H, m), 2.18 (6H, s), 1.28 (3H, t,  $J = 7.1$  Hz), 1.21 (3H, t,  $J = 7.1$  Hz), 1.14 (3H, d,  $J = 7.2$  Hz);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 168.2, 161.5 (d,  $J = 243.3$  Hz), 145.1, 144.9, 139.7 (d,  $J = 3.2$  Hz), 129.7 (d,  $J = 7.6$  Hz), 113.7 (d,  $J = 20.8$  Hz), 101.0, 100.7, 59.6, 59.6, 45.2, 40.1, 19.2, 19.1, 15.8, 14.3, 14.3; HRMS (ESI): Found:  $m/z$  376.1923. Calcd for  $\text{C}_{21}\text{H}_{27}\text{NO}_4\text{F}$  ( $\text{M}+\text{H}$ ) $^+$  376.1924. IR (KBr,  $\text{cm}^{-1}$ ): 3332, 1666, 1645, 1377, 1261, 1118, 744.

**diethyl 4-(1-(4-cyanophenyl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2h)**



Yellow solid, mp 137-139 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.45 (2H, m), 7.22-7.19 (2H, m), 5.36 (1H, brs), 4.30 (1H, d,  $J = 4.9$  Hz), 4.15-3.99 (3H, m), 3.93-3.85 (1H, m), 2.87-2.79 (1H, m), 2.20 (6H, s), 1.30-1.26 (3H, m), 1.21-1.14 (6H, m);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ )  $\delta$  168.0, 167.9, 150.2, 145.6, 145.4, 130.8, 129.2, 119.3, 109.4, 100.3, 100.3, 59.7, 59.7, 46.2, 40.0, 19.2, 19.1, 15.09 (s), 14.3, 14.2; HRMS (ESI): Found:  $m/z$  383.1970. Calcd for  $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_4$  ( $\text{M}+\text{H}$ ) $^+$  383.1971. IR (KBr,  $\text{cm}^{-1}$ ): 3350, 2222, 1678, 1377, 1269, 1114, 734.

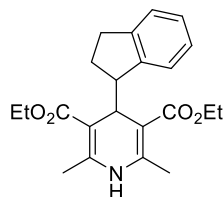
**diethyl 2,6-dimethyl-4-(1-(m-tolyl)ethyl)-1,4-dihydropyridine-3,5-dicarboxylate (2i)**



Yellow solid, mp 94-96 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.07 (1H, t,  $J = 7.5$  Hz), 6.97-6.84 (3H, m), 5.28 (1H, brs), 4.26 (1H, d,  $J = 5.0$  Hz), 4.12-3.98 (3H, m), 3.87 (1H, m), 2.75-2.66 (1H, m), 2.29 (3H, s), 2.19 (6H, d,  $J = 1.2$  Hz), 1.28 (3H, t,  $J = 7.1$

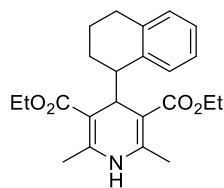
Hz), 1.17 (6H, m);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 168.3, 145.1, 144.7, 144.0, 136.5, 129.4, 127.0, 126.5, 125.6, 101.1, 101.0, 59.5, 59.5, 45.9, 40.1, 21.4, 19.3, 19.1, 15.4, 14.3, 14.2; **HRMS (ESI)**: Found:  $m/z$  372.2173. Calcd for  $\text{C}_{22}\text{H}_{30}\text{NO}_4$  ( $\text{M}+\text{H}$ ) $^+$  372.2175. **IR (KBr,  $\text{cm}^{-1}$ )**: 3332, 1392, 1220, 906, 783, 686.

**diethyl 4-(2,3-dihydro-1H-inden-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2n)**



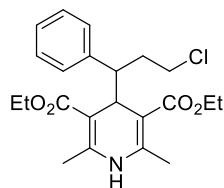
Yellow solid, mp 140-142 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18-6.99 (4H, m), 5.78 (1H, s), 4.26 (1H, d,  $J = 5.8$  Hz), 3.95 (4H, m), 3.06-2.91 (2H, m), 2.77-2.66 (1H, m), 2.33 (3H, s), 2.27 (3H, s), 2.05-1.86 (2H, m), 1.22 (3H, t,  $J = 6.8$  Hz), 1.10 (3H, t,  $J = 6.7$  Hz);  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ )  $\delta$  168.5, 168.0, 145.4, 145.0, 144.8, 144.5, 126.3, 125.5, 125.2, 124.0, 102.3, 102.0, 59.6, 59.5, 51.5, 36.8, 31.5, 28.4, 19.4, 19.2, 14.2, 14.1; **HRMS (ESI)**: Found:  $m/z$  370.2015. Calcd for  $\text{C}_{22}\text{H}_{28}\text{NO}_4$  ( $\text{M}+\text{H}$ ) $^+$  370.2018. **IR (KBr,  $\text{cm}^{-1}$ )**: 3294, 1693, 1643, 1213, 1099, 744.

**diethyl 2,6-dimethyl-4-(1,2,3,4-tetrahydronaphthalen-1-yl)-1,4-dihydropyridine-3,5-dicarboxylate (2o)**



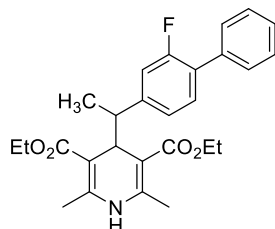
Yellow solid, mp 149-151 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.05-6.96 (4H, m), 5.73 (1H, brs), 4.41 (1H, d,  $J = 7.1$  Hz), 4.03-3.95 (1H, m), 3.91-3.79 (2H, m), 3.78-3.70 (1H, m), 2.84-2.76 (1H, m), 2.72-2.64 (1H, m), 2.63-2.57 (1H, m), 2.39 (3H, s), 2.30 (3H, s), 2.13-2.05 (1H, m), 1.79 (1H, m), 1.70-1.55 (2H, m), 1.18 (3H, t,  $J = 7.1$  Hz), 1.09 (3H, t,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  168.7, 167.6, 145.3, 143.8, 138.0, 130.7, 128.3, 125.5, 124.4, 103.0, 102.4, 59.6, 59.4, 43.6, 37.9, 29.7, 29.4, 23.9, 19.6, 19.2, 14.13, 14.06; **HRMS (ESI)**: Found:  $m/z$  384.2173. Calcd for  $\text{C}_{23}\text{H}_{30}\text{NO}_4$  ( $\text{M}+\text{H}$ ) $^+$  384.2175. **IR (KBr,  $\text{cm}^{-1}$ )**: 3319, 1651, 1377, 1211, 1099, 744.

**diethyl 4-(3-chloro-1-phenylpropyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2p)**



Yellow solid, mp 99-101 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20-7.14 (3H, m), 7.04-6.99 (2H, m), 5.16 (1H, s), 4.32 (1H, d,  $J = 4.5$  Hz), 4.16-4.04 (4H, m), 3.43 (1H, ddd,  $J = 10.7, 7.5, 5.5$  Hz), 3.29 (1H, dt,  $J = 10.7, 7.7$  Hz), 2.79-2.72 (1H, m), 2.15 (3H, s), 2.14-2.06 (5H, m), 1.29 (3H, t,  $J = 7.1$  Hz), 1.28 (3H, t,  $J = 7.1$  Hz);  $^{13}\text{C NMR}$  (125MHz,  $\text{CDCl}_3$ )  $\delta$  168.2, 167.8, 145.8, 145.6, 140.5, 129.1, 127.2, 126.2, 100.6, 99.9, 59.7, 59.6, 49.6, 43.7, 38.5, 33.4, 19.2, 19.0, 14.3, 14.28; **HRMS (ESI)**: Found:  $m/z$  406.1783. Calcd for  $\text{C}_{22}\text{H}_{29}\text{NO}_4\text{Cl}$  ( $\text{M}+\text{H}$ ) $^+$  406.1785. **IR (KBr,  $\text{cm}^{-1}$ )**: 3334, 1643, 1377, 1301, 1211, 1099, 744.

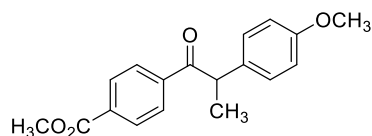
**Diethyl 4-(1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2q)**



Yellow solid, mp 152-153 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55-7.50 (2H, m), 7.45-7.40 (2H, m), 7.36-7.32 (1H, m), 7.30-7.25 (1H, m), 6.96 (1H, s), 6.95-6.92 (1H, m), 5.47 (1H, s), 4.31 (1H, d,  $J = 5.0$  Hz), 4.09 (2H, q,  $J = 7.5$  Hz), 4.06-4.00 (1H, m), 3.93-3.85 (1H, m), 2.84-2.76 (1H, m), 2.254 (3H, s), 2.251 (3H, m), 1.29 (3H, t,  $J = 7.0$  Hz), 1.22-1.15 (6H, m);  $^{13}\text{C NMR}$  (125MHz,  $\text{CDCl}_3$ )  $\delta$  168.2, 168.1, 159.1 (d,  $J = 245.3$ ), 146.4 (d,  $J = 7.3$  Hz), 145.3, 145.0, 136.0, 129.2 (d,  $J = 3.8$  Hz), 128.9 (d,  $J = 2.9$  Hz), 128.4, 127.3, 126.2 (d,  $J = 13.4$  Hz), 124.5 (d,  $J = 3.0$  Hz), 115.8 (d,  $J = 22.5$  Hz), 101.1, 100.8, 59.67, 59.65, 45.8, 40.2, 19.4, 19.2, 15.1, 14.3, 14.2;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -119.77 (m); **HRMS (ESI)**: Found:  $m/z$  452.2236. Calcd for  $\text{C}_{27}\text{H}_{31}\text{NO}_4\text{F}$  ( $\text{M}+\text{H}$ ) $^+$  452.2237. **IR (KBr,  $\text{cm}^{-1}$ )**: 3319, 1687, 1639, 1373, 1209, 767, 744.

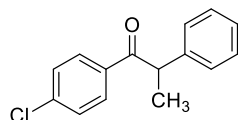


### methyl 4-(2-(4-methoxyphenyl)propanoyl)benzoate (3a)



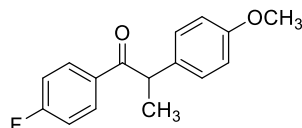
According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2a** (77.5 mg, 0.20 mmol) were used. The product was isolated in 68% yield as white solid (40.6 mg). mp 87-89 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.51 (3H, d, *J* = 6.8 Hz), 3.75 (3H, s), 3.91 (3H, s), 4.62 (1H, q, *J* = 6.8 Hz), 6.82 (2H, d, *J* = 8.4 Hz), 7.16 (2H, d, *J* = 8.8 Hz), 7.96 (2H, d, *J* = 8.4 Hz), 8.03 (2H, d, *J* = 8.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.0, 166.2, 158.6, 139.9, 133.4, 132.8, 129.6, 128.8, 128.6, 114.5, 55.2, 52.3, 47.5, 19.3; HRMS (ESI): Found: *m/z* 299.1277. Calcd for C<sub>18</sub>H<sub>19</sub>O<sub>4</sub> (M+H)<sup>+</sup> 299.1283. IR (KBr, cm<sup>-1</sup>): 1726, 1687, 1375, 1280, 1109, 835.

### 1-(4-chlorophenyl)-2-phenylpropan-1-one (3b)



According to the general procedure, **1b** (111.2 mg, 0.40 mmol) and **2d** (71.4 mg, 0.20 mmol) were used. The product was isolated in 60% yield as colorless liquid (29.4 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.91-7.85 (2H, m), 7.38-7.33 (2H, m), 7.32-7.28 (2H, m), 7.27-7.24 (2H, m), 7.23-7.19 (1H, m), 4.62 (1H, q, *J* = 6.7 Hz), 1.53 (3H, d, *J* = 6.7 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 199.0, 141.2, 139.2, 134.7, 130.2, 129.1, 128.8, 127.7, 127.0, 48.1, 19.4; HRMS (ESI): Found: *m/z* 245.0726. Calcd for C<sub>15</sub>H<sub>14</sub>OCl (M+H)<sup>+</sup> 245.0733. IR (KBr, cm<sup>-1</sup>): 2929, 1678, 1589, 1219, 1093, 756, 700.

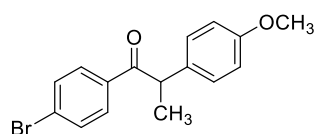
### 1-(4-fluorophenyl)-2-(4-methoxyphenyl)propan-1-one (3c)



According to the general procedure, **1c** (52.2 mg, 0.20 mmol) and **2a** (38.7 mg, 0.10 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 94% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 55% yield as colorless liquid (14.1 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99-7.94 (2H,

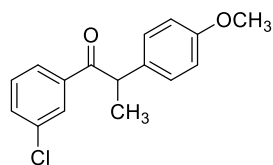
m), 7.21-7.14 (2H, m), 7.07-7.01 (2H, m), 6.85-6.80 (2H, m), 4.58 (1H, q,  $J = 6.8$  Hz), 3.76 (3H, s), 1.49 (3H, d,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.9, 165.4 (d,  $J = 254.5$  Hz), 158.6, 133.4, 132.9 (d,  $J = 3.0$  Hz), 131.4 (d,  $J = 9.2$  Hz), 128.7, 115.5 (d,  $J = 21.8$  Hz), 114.5, 55.2, 47.1, 19.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.76 (m); **HRMS (ESI)**: Found:  $m/z$  259.1128. Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{F}$  ( $\text{M}+\text{H}$ ) $^+$  259.1134. **IR (KBr,  $\text{cm}^{-1}$ )**: 2974, 2931, 1680, 1597, 1510, 1155, 831.

### 1-(4-bromophenyl)-2-(4-methoxyphenyl)propan-1-one (3d)



According to the general procedure, **1d** (64.4 mg, 0.20 mmol) and **2a** (38.7 mg, 0.10 mmol) was used. The conversion of Hantzsch ester was more than 99%, and 86% yield of the pyridine (by-product) was detected. The corresponding was isolated in 54% yield as colorless liquid (17.2 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83-7.75 (2H, m), 7.53-7.47 (2H, m), 7.19-7.12 (2H, m), 6.86-6.79 (2H, m), 4.56 (1H, q,  $J = 6.8$  Hz), 3.76 (3H, s), 1.49 (3H, d,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.4, 158.7, 135.3, 133.2, 131.8, 130.3, 128.7, 127.8, 114.5, 55.2, 47.2, 19.4; **HRMS (ESI)**: Found:  $m/z$  319.0326. Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Br}$  ( $\text{M}+\text{H}$ ) $^+$  319.0334. **IR (KBr,  $\text{cm}^{-1}$ )**: 1687, 1510, 1257, 1172, 1010, 746.

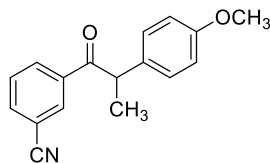
### 1-(3-chlorophenyl)-2-(4-methoxyphenyl)propan-1-one (3e)



According to the general procedure, **1e** (55.5 mg, 0.20 mmol) and **2a** (38.7 mg, 0.10 mmol) were used. The corresponding product was isolated in 66% yield as colorless liquid (18.2 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93-7.89 (1H, m), 7.81-7.77 (1H, m), 7.45-7.41 (1H, m), 7.33-7.28 (1H, m), 7.19-7.14 (2H, m), 6.86-6.81 (2H, m), 4.57 (1H, q,  $J = 6.8$  Hz), 3.76 (3H, s), 1.50 (3H, d,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  199.2, 158.6, 138.1, 134.8, 132.9, 132.6, 129.8, 128.8, 128.7, 126.8, 114.5, 55.2, 47.2, 19.4; **HRMS (ESI)**: Found:  $m/z$  275.0830. Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Cl}$  ( $\text{M}+\text{H}$ ) $^+$  275.0839.

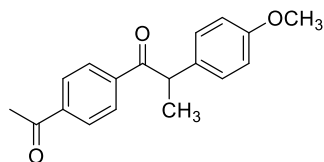
**IR (KBr, cm<sup>-1</sup>):** 2931, 2910, 1678, 1510, 1246, 1178, 763.

**3-(2-(4-methoxyphenyl)propanoyl)benzonitrile (3f)**



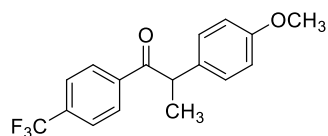
According to the general procedure, **1f** (53.6 mg, 0.20 mmol) and **2a** (38.7 mg, 0.10 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 96% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 51% yield as white solid (13.5 mg). mp 68-70 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.19 (1H, s), 8.13 (1H, d, *J* = 8.1 Hz), 7.73 (1H, d, *J* = 7.8 Hz), 7.50 (1H, t, *J* = 7.8 Hz), 7.15 (2H, d, *J* = 8.5 Hz), 6.84 (2H, d, *J* = 8.5 Hz), 4.55 (1H, q, *J* = 6.7 Hz), 3.76 (3H, s), 1.51 (3H, d, *J* = 6.8 Hz); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 198.3, 158.8, 137.3, 135.5, 132.7, 132.41, 132.36, 129.5, 128.7, 118.0, 114.7, 113.0, 55.2, 47.5, 19.3; **HRMS (ESI):** Found: *m/z* 266.1175. Calcd for C<sub>17</sub>H<sub>16</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 266.1181. **IR (KBr, cm<sup>-1</sup>):** 2233, 1728, 1693, 1510, 1375, 773, 738.

**1-(4-acetylphenyl)-2-(4-methoxyphenyl)propan-1-one (3g)**



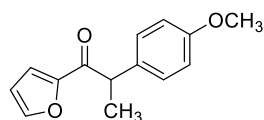
According to the general procedure, **1g** (57.1 mg, 0.20 mmol) and **2a** (38.7 mg, 0.10 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 96% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 56% yield as white solid (15.8 mg). mp 76-78 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.03-7.96 (2H, m), 7.95-7.90 (2H, m), 7.21-7.13 (2H, m), 6.86-6.77 (2H, m), 4.61 (1H, q, *J* = 6.8 Hz), 3.74 (3H, s), 2.58 (3H, s), 1.51 (3H, d, *J* = 6.8 Hz); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 199.9, 197.4, 158.6, 139.8, 139.7, 132.8, 128.9, 128.8, 128.3, 114.5, 55.2, 47.6, 26.8, 19.3; **HRMS (ESI):** Found: *m/z* 283.1329. Calcd for C<sub>18</sub>H<sub>19</sub>O<sub>3</sub> (M+H)<sup>+</sup> 283.1334. **IR (KBr, cm<sup>-1</sup>):** 1681, 1666, 1510, 1377, 1263, 829, 744.

### 2-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)propan-1-one (3h)



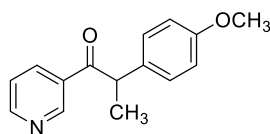
According to the general procedure, **1h** (124.5 mg, 0.40 mmol) and **2a** (77.5 mg, 0.20 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 89% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 51% yield as colorless liquid (31.7 mg). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.02 (2H, m), 7.63 (2H, m), 7.17 (2H, m), 6.83 (2H, m), 4.60 (1H, q, *J* = 6.8 Hz), 3.75 (3H, s), 1.52 (3H, d, *J* = 6.8 Hz); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 199.4, 158.7, 139.2, 133.9 (q, *J* = 33.1 Hz), 132.7, 129.0, 128.8, 125.5 (q, *J* = 3.7 Hz), 124.6 (q, *J* = 273.6 Hz), 114.6, 55.2, 47.6, 19.3; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -63.2 (s); **HRMS (ESI)**: Found: *m/z* 309.1098. Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>F<sub>3</sub> (M+H)<sup>+</sup> 309.1102. **IR (KBr, cm<sup>-1</sup>)**: 2933, 1687, 1510, 1323, 1130, 833, 779.

### 1-(furan-2-yl)-2-(4-methoxyphenyl)propan-1-one (3i)



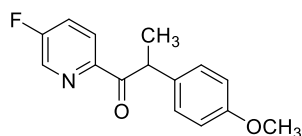
According to the general procedure, **1i** (46.6 mg, 0.20 mmol) and **2a** (38.7 mg, 0.10 mmol) were used. The corresponding product was isolated in 62% yield (14.2 mg). The product was contaminated with inseparable side product-1-(2-chloroethoxy)-4-nitrobenzene<sup>[7]</sup> which formed via the nucleophilic attack the solvent by 4-nitrophenol (3oa:by product = 1:0.26). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.55-7.49 (1H, m), 7.27-7.21 (2H, m), 7.13 (1H, d, *J* = 3.6 Hz), 6.87-6.80 (2H, m), 6.45 (1H, dd, *J* = 3.6, 1.7 Hz), 4.44 (1H, q, *J* = 7.0 Hz), 3.76 (3H, s), 1.49 (3H, d, *J* = 7.0 Hz); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 189.7, 158.6, 152.2, 146.2, 132.8, 128.9, 117.7, 114.2, 112.1, 55.2, 47.0, 18.3; **HRMS (ESI)**: Found: *m/z* 231.1026. Calcd for C<sub>14</sub>H<sub>15</sub>O<sub>3</sub> (M+H)<sup>+</sup> 231.1021. **IR (KBr, cm<sup>-1</sup>)**: 2931, 1666, 1463, 1249, 1031, 763.

### 2-(4-methoxyphenyl)-1-(pyridin-3-yl)propan-1-one (3j)



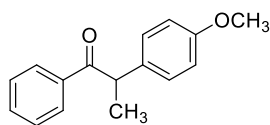
According to the general procedure, **1j** (48.8 mg, 0.20 mmol) and **2a** (38.7 mg, 0.10 mmol) were used. The corresponding product was isolated in 60% yield as brown liquid (14.5mg). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.13 (1H, d, *J* = 1.7 Hz), 8.66 (1H, dd, *J* = 4.8, 1.7 Hz), 8.18 (1H, dt, *J* = 8.0, 2.0 Hz), 7.32 (1H, ddd, *J* = 8.0, 4.8, 0.5 Hz), 7.20-7.13 (2H, m), 6.86-6.79 (2H, m), 4.57 (1H, q, *J* = 6.8 Hz), 3.75 (3H, s), 1.51 (3H, d, *J* = 6.8 Hz); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 199.2, 158.7, 152.9, 150.2, 136.1, 132.5, 131.7, 128.8, 123.5, 114.6, 55.2, 47.7, 19.1; **HRMS (ESI)**: Found: *m/z* 242.1179. Calcd for C<sub>15</sub>H<sub>16</sub>NO<sub>2</sub> (M+H)<sup>+</sup> 242.1181. **IR (KBr, cm<sup>-1</sup>)**: 2931, 1681, 1510, 1249, 1031, 704.

### 1-(5-fluoropyridin-2-yl)-2-(4-methoxyphenyl)propan-1-one (3k)



According to the general procedure, **1k** (52.4mg, 0.20 mmol) and **2a** (38.7 mg, 0.10 mmol) were used. The corresponding product was isolated in 87% yield as colorless liquid (22.6 mg). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.49-8.45 (1H, m), 8.10-8.03 (1H, m), 7.48-7.40 (1H, m), 7.34-7.23 (2H, m), 6.85-6.74 (2H, m), 5.35 (1H, q, *J* = 7.0 Hz), 3.74 (3H, s), 1.52 (3H, d, *J* = 7.1 Hz); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 200.2, 161.2 (d, *J* = 263.3 Hz), 158.4, 149.5 (d, *J* = 3.5 Hz), 137.1 (d, *J* = 24.4 Hz), 132.7, 129.4, 124.7 (d, *J* = 5.6 Hz), 123.4 (d, *J* = 18.5 Hz), 113.9, 55.1, 44.1, 18.1; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -120.3 (m); **HRMS (ESI)**: Found: *m/z* 260.1090. Calcd for C<sub>17</sub>H<sub>17</sub>O<sub>3</sub> (M+H)<sup>+</sup> 260.1087. **IR (KBr, cm<sup>-1</sup>)**: 2972, 1693, 1246, 1178, 1035, 794.

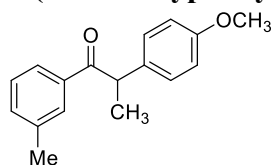
### 2-(4-methoxyphenyl)-1-phenylpropan-1-one (3l)



According to the general procedure, **1l** (48.6 mg, 0.20 mmol), **2a** (38.7 mg, 0.10 mmol)

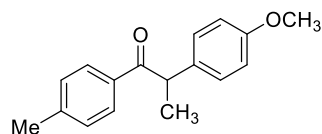
and Cs<sub>2</sub>CO<sub>3</sub> (195.0 mg, 0.6 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 92% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 36% yield as colorless liquid (8.7 mg). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.99-7.90 (2H, m), 7.47 (1H, t, *J* = 7.3 Hz), 7.38 (2H, t, *J* = 7.6 Hz), 7.23-7.15 (2H, m), 6.83 (2H, m), 4.64 (1H, q, *J* = 6.8 Hz), 3.75 (3H, s), 1.51 (3H, d, *J* = 6.8 Hz); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 200.5, 158.5, 136.5, 133.5, 132.7, 128.76, 128.73, 128.4, 114.4, 55.2, 47.0, 19.5; **HRMS (ESI)**: Found: *m/z* 241.1227. Calcd for C<sub>16</sub>H<sub>17</sub>O<sub>2</sub> (M+H)<sup>+</sup> 241.1229. **IR (KBr, cm<sup>-1</sup>)**: 1737, 1377, 1263, 1058, 889, 744.

**2-(4-methoxyphenyl)-1-(m-tolyl)propan-1-one (3m)**



According to the general procedure, **1l** (51.5 mg, 0.20 mmol), **2a** (38.7 mg, 0.10 mmol), blue LED ( $\lambda_{\text{max}}$  = 440 nm) were used. The conversion of Hantzsch ester was more than 99%, and 94% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 41% yield as colorless liquid (10.4 mg). **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.77 (1H, s), 7.73 (1H, d, *J* = 7.3 Hz), 7.32-7.23 (2H, m), 7.22-7.16 (2H, m), 6.85-6.80 (2H, m), 4.64 (1H, q, *J* = 6.8 Hz), 3.75 (3H, s), 2.36 (3H, s), 1.50 (3H, d, *J* = 6.9 Hz); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 200.8, 158.4, 138.2, 136.6, 133.55, 133.48, 129.2, 128.8, 128.3, 126.0, 114.3, 55.2, 46.9, 21.4, 19.5; **HRMS (ESI)**: Found: *m/z* 255.1389. Calcd for C<sub>17</sub>H<sub>19</sub>O<sub>2</sub> (M+H)<sup>+</sup> 255.1385. **IR (KBr, cm<sup>-1</sup>)**: 2929, 1674, 1510, 1247, 1033, 761.

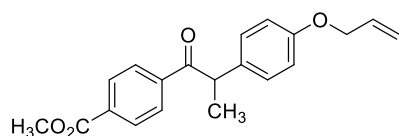
**2-(4-methoxyphenyl)-1-(p-tolyl)propan-1-one (3n)**



According to the general procedure, **1m** (51.5 mg, 0.20 mmol), **2a** (38.7 mg, 0.10 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 90% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 31% yield as colorless liquid (7.9 mg). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.89-7.81 (2H, m),

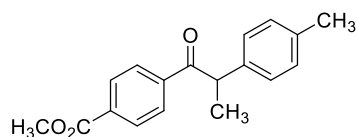
7.23-7.14 (4H, m), 6.85-6.78 (2H, m), 4.62 (1H, q,  $J = 6.8$  Hz), 3.75 (3H, s), 2.35 (3H, s), 1.49 (3H, d,  $J = 6.9$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.2, 158.4, 143.4, 134.0, 133.7, 129.1, 128.9, 128.7, 114.3, 55.2, 46.8, 21.5, 19.5; **HRMS (ESI)**: Found:  $m/z$  255.1386. Calcd for  $\text{C}_{17}\text{H}_{19}\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$  255.1385. **IR (KBr,  $\text{cm}^{-1}$ )**: 2970, 2929, 1674, 1606, 1510, 1246, 769.

**methyl 4-(2-(4-(allyloxy)phenyl)propanoyl)benzoate (4a)**



According to the general procedure, **1a** (60.2 mg, 0.20 mmol) and **2c** (41.4 mg, 0.10 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 96% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 56% yield as brown oil (18.0 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05-8.00 (2H, m), 7.99-7.93 (2H, m), 7.19-7.12 (2H, m), 6.87-6.80 (2H, m), 6.08-5.94 (1H, m), 5.37 (1H, ddt,  $J = 17.0, 10.1, 5.3$  Hz), 5.26 (1H, m), 4.61 (1H, q,  $J = 7.2$  Hz), 4.47 (2H, m), 3.91 (3H, s), 1.51 (3H, d,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.0, 166.2, 157.7, 139.9, 133.4, 133.2, 133.0, 129.7, 128.8, 128.6, 117.7, 115.3, 68.8, 52.4, 47.5, 19.3; **HRMS (ESI)**: Found:  $m/z$  325.1431. Calcd for  $\text{C}_{20}\text{H}_{21}\text{O}_4$  ( $\text{M}+\text{H}$ ) $^+$  325.1440. **IR (KBr,  $\text{cm}^{-1}$ )**: 1716, 1681, 1278, 1107, 952, 833, 752.

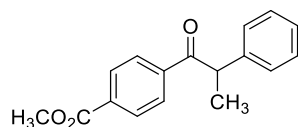
**methyl 4-(2-(p-tolyl)propanoyl)benzoate (4b)**



According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2d** (74.3 mg, 0.20 mmol) were used. The corresponding product was isolated in 67% yield as yellow solid (37.8 mg). mp 87-88  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.4$  Hz, 2H), 7.97 (d,  $J = 8.5$  Hz, 2H), 7.14 (d,  $J = 8.1$  Hz, 2H), 7.09 (d,  $J = 8.0$  Hz, 2H), 4.63 (q,  $J = 6.8$  Hz, 1H), 3.90 (s, 3H), 2.28 (s, 3H), 1.52 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.9, 166.2, 139.9, 137.9, 136.7, 133.4, 129.8, 129.6, 128.6, 127.6, 52.3, 48.0, 20.9, 19.3; **HRMS (ESI)**: Found:  $m/z$  283.1326. Calcd for  $\text{C}_{18}\text{H}_{19}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$

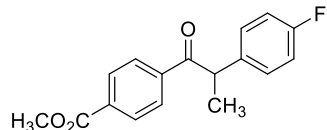
283.1334. **IR (KBr, cm<sup>-1</sup>):** 1710, 1687, 1377, 1286, 1118, 746.

**methyl 4-(2-phenylpropanoyl)benzoate (4c)**



According to the general procedure, **1a** (60.2 mg, 0.20 mmol) and **2e** (35.7 mg, 0.10 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 99% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 54% yield as white solid (14.5 mg). mp 90-91 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.05-8.00 (2H, m), 7.99-7.94 (2H, m), 7.32-7.23 (4H, m), 7.23-7.17 (1H, m), 4.66 (1H, q, *J* = 6.8 Hz), 3.90 (3H, s), 1.54 (3H, d, *J* = 6.8 Hz); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 199.8, 166.2, 140.9, 139.8, 133.5, 129.7, 129.1, 128.6, 127.8, 127.1, 52.4, 48.5, 19.3; **HRMS (ESI):** Found: *m/z* 269.1176. Calcd for C<sub>17</sub>H<sub>17</sub>O<sub>3</sub> (M+H)<sup>+</sup> 269.1178. **IR (KBr, cm<sup>-1</sup>):** 1720, 1680, 1404, 1107, 948, 759.

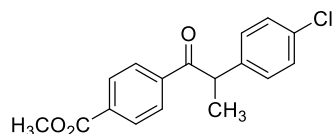
**methyl 4-(2-(4-fluorophenyl)propanoyl)benzoate (4d)**



According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2f** (75.1 mg, 0.20 mmol) were used. The corresponding product was isolated in 68% yield as white solid (39.2 mg). mp 88-90 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.07-8.01 (2H, m), 7.99-7.93 (2H, m), 7.25-7.19 (2H, m), 7.02-6.94 (2H, m), 4.66 (1H, q, *J* = 7.0 Hz), 3.91 (3H, s), 1.52 (3H, d, *J* = 6.9 Hz); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 199.7, 166.1, 161.9 (d, *J* = 244.4 Hz), 139.6, 136.5 (d, *J* = 3.3 Hz), 133.6, 129.7, 129.3 (d, *J* = 8.0 Hz), 128.6, 116.0 (d, *J* = 21.3 Hz), 52.4, 42.5, 19.4; **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -115.39 (m); **HRMS (ESI):** Found: *m/z* 287.1077. Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>3</sub>F (M+H)<sup>+</sup> 287.1083. **IR (KBr, cm<sup>-1</sup>):** 1716, 1668, 1377, 1290, 1111, 840, 746.

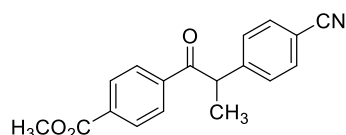
**methyl 4-(2-(4-chlorophenyl)propanoyl)benzoate (4e)**





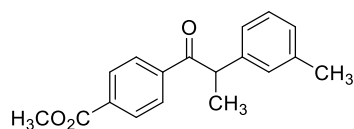
According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2g** (78.2 mg, 0.20 mmol) were used. The corresponding product was isolated in 44% yield as white solid (24.0 mg). mp 80-81 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (2H, d,  $J = 8.3$  Hz), 7.95 (2H, d,  $J = 8.4$  Hz), 7.30-7.24 (2H, m), 7.19 (2H, d,  $J = 8.4$  Hz), 4.65 (1H, q,  $J = 6.8$  Hz), 3.91 (3H, s), 1.52 (3H, d,  $J = 6.8$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.5, 166.1, 139.5, 139.29, 133.7, 133.0, 129.8, 129.2, 129.1, 128.6, 52.4, 47.6, 19.2; **HRMS (ESI)**: Found:  $m/z$  303.0779. Calcd for  $\text{C}_{17}\text{H}_{16}\text{O}_3\text{Cl}$  ( $\text{M}+\text{H}$ ) $^+$  303.0788. **IR (KBr,  $\text{cm}^{-1}$ )**: 1720, 1680, 1278, 1107, 823, 759.

**methyl 4-(2-(4-cyanophenyl)propanoyl)benzoate (4f)**



According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2h** (76.5 mg, 0.20 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 92% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 35% yield as white solid (20.5 mg). mp 117-118 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (2H, d,  $J = 8.6$  Hz), 7.94 (2H, d,  $J = 8.6$  Hz), 7.60 (2H, d,  $J = 8.4$  Hz), 7.39 (2H, d,  $J = 8.3$  Hz), 4.75 (1H, q,  $J = 6.9$  Hz), 3.92 (1H, s), 1.56 (3H, d,  $J = 6.9$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.8, 166.0, 146.1, 139.2, 134.0, 132.8, 129.9, 128.6, 128.5, 118.5, 111.2, 52.5, 48.1, 19.2; **HRMS (ESI)**: Found:  $m/z$  294.1124. Calcd for  $\text{C}_{18}\text{H}_{16}\text{NO}_3$  ( $\text{M}+\text{H}$ ) $^+$  294.1130. **IR (KBr,  $\text{cm}^{-1}$ )**: 2200, 1681, 1585, 1377, 1024, 765, 698.

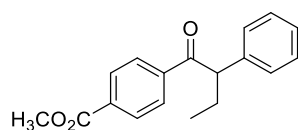
**methyl 4-(2-(m-tolyl)propanoyl)benzoate (4g)**



According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2i** (74.3 mg, 0.20 mmol) were used. The corresponding product was isolated in 65% yield as yellow solid

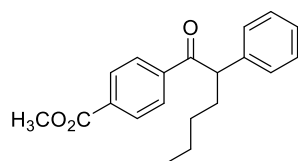
(36.7 mg). mp 63-65 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 8.00 (2H, m), 8.00-7.95 (2H, m), 7.21-7.15 (1H, m), 7.08-7.03 (2H, m), 7.01 (1H, d,  $J = 7.5$  Hz), 4.62 (1H, q,  $J = 6.8$  Hz), 3.91 (3H, s), 2.30 (3H, s), 1.52 (3H, d,  $J = 6.8$  Hz);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  199.9, 166.2, 140.8, 139.8, 138.8, 133.4, 129.7, 129.0, 128.6, 128.3, 127.9, 124.8, 52.4, 48.4, 21.4, 19.3; **HRMS (ESI)**: Found:  $m/z$  283.1329. Calcd for  $\text{C}_{18}\text{H}_{19}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  283.1334. **IR (KBr,  $\text{cm}^{-1}$ )**: 1737, 1732, 1435, 1278, 1109, 742, 704.

**methyl 4-(2-phenylbutanoyl)benzoate (4h)**



According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2j** (74.3 mg, 0.20 mmol) were used. The corresponding product was isolated in 60% yield as yellow solid (33.8 mg). mp 69-70 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06-8.01 (2H, m), 8.00-7.95 (2H, m), 7.33-7.24 (4H, m), 7.24-7.16 (1H, m), 4.42 (1H, t,  $J = 7.2$  Hz), 3.90 (3H, s), 2.27-2.14 (1H, m), 1.93-1.80 (1H, m), 0.91 (3H, t,  $J = 7.4$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.6, 166.2, 140.4, 139.1, 133.5, 129.7, 128.9, 128.5, 128.3, 127.1, 56.0, 52.3, 26.9, 12.2; **HRMS (ESI)**: Found:  $m/z$  283.1330. Calcd for  $\text{C}_{18}\text{H}_{19}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  283.1334. **IR (KBr,  $\text{cm}^{-1}$ )**: 1732, 1678, 1377, 1274, 1111, 756, 700.

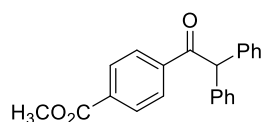
**methyl 4-(2-phenylhexanoyl)benzoate (4i)**



According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2k** (79.9 mg, 0.20 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 91% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 49% yield as yellow solid (30.6 mg). mp 56-57 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 – 8.01 (2H, m), 7.98 (2H, m), 7.32-7.25 (4H, m), 7.24-7.17 (m, 1H), 4.51 (t,  $J = 7.2$  Hz, 1H), 3.91 (s, 3H), 2.18 (dddd,  $J = 11.9, 10.3, 7.1, 5.1$  Hz, 1H), 1.89-1.77 (m, 1H), 1.41-1.16 (m, 5H), 0.87 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.7, 166.2, 140.4, 139.3, 133.5, 129.7, 128.9, 128.5, 128.2, 127.1, 54.2, 52.3, 33.6, 29.8, 22.7, 13.9;

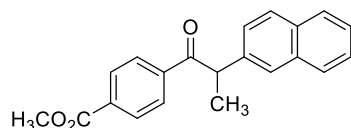
**HRMS (ESI):** Found:  $m/z$  311.1642. Calcd for  $C_{20}H_{23}O_3$  (M+H)<sup>+</sup> 311.1647. **IR (KBr,  $cm^{-1}$ ):** 1724, 1674, 1280, 1109, 704.

#### methyl 4-(2,2-diphenylacetyl)benzoate (4j)



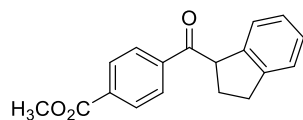
According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2l** (84.3 mg, 0.20 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 78% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 24% yield as yellow solid (16.1 mg). mp 105-107 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08-8.00 (4H, m), 7.36-7.29 (4H, m), 7.29-7.22 (6H, m), 6.01 (1H, s), 3.91 (3H, s); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 197.8, 166.1, 140.2, 138.6, 133.8, 129.8, 129.1, 128.8 (two peaks overlapped), 127.3, 59.9, 52.4; HRMS (ESI): Found: *m/z* 331.1335. Calcd for C<sub>22</sub>H<sub>19</sub>O<sub>3</sub> (M+H)<sup>+</sup> 331.1334. IR (KBr, cm<sup>-1</sup>): 1728, 1674, 1276, 1111, 1008, 744.

#### methyl 4-(2-(naphthalen-2-yl)propanoyl)benzoate (4k)



According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2b** (81.4 mg, 0.20 mmol) were used. The corresponding product was isolated in 63% yield as white solid (36.8 mg). mp 126-128 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03-7.98 (4H, m), 7.82-7.74 (3H, m), 7.72-7.67 (1H, m), 7.48-7.37 (3H, m), 4.83 (1H, q, *J* = 6.8 Hz), 3.89 (3H, s), 1.63 (3H, d, *J* = 6.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.8, 166.1, 139.8, 138.4, 133.7, 133.5, 132.4, 129.7, 129.0, 128.6, 127.7, 127.6, 126.5, 126.3, 125.9, 125.8, 52.3, 48.6, 19.3; HRMS (ESI): Found: *m/z* 319.1328. Calcd for C<sub>21</sub>H<sub>19</sub>O<sub>3</sub> (M+H)<sup>+</sup> 319.1334. IR (KBr, cm<sup>-1</sup>): 1724, 1674, 1558, 1280, 1111, 821, 742.

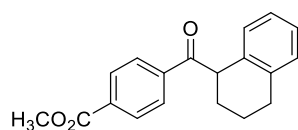
#### methyl 4-(2,3-dihydro-1H-indene-1-carbonyl)benzoate (4l)



According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2m** (73.9 mg, 0.20 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 89% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 55% yield as grey solid (31.0 mg). mp 73-75 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20-

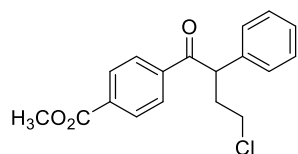
8.15 (2H, m), 8.11-8.06 (2H, m), 7.29 (1H, d,  $J = 7.6$  Hz), 7.20 (1H, t,  $J = 7.4$  Hz), 7.10 (1H, t,  $J = 7.4$  Hz), 7.03 (1H, d,  $J = 7.6$  Hz), 5.04 (1H, t,  $J = 7.6$  Hz), 3.97 (s, 3H), 3.22-3.10 (1H, m), 3.08-2.96 (1H, m), 2.57-2.38 (2H, m);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.9, 166.2, 144.6, 140.9, 140.3, 133.9, 129.9, 128.8, 127.5, 126.4, 125.0, 124.9, 52.9, 52.4, 31.9, 29.4; **HRMS (ESI)**: Found:  $m/z$  281.1177. Calcd for  $\text{C}_{18}\text{H}_{17}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  281.1178. **IR (KBr,  $\text{cm}^{-1}$ )**: 1728, 1681, 1377, 1278, 1107, 756.

**methyl 4-(1,2,3,4-tetrahydronaphthalene-1-carbonyl)benzoate (4m)**



According to the general procedure, **1a** (120.4 mg, 0.40 mmol) and **2n** (76.6 mg, 0.20 mmol) were used. The intensity of the blue LED was set at 25%. The corresponding product was isolated in 73% yield as white solid (42.9 mg). mp 94-95 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (2H, d,  $J = 8.4$  Hz), 8.03 (2H, d,  $J = 8.2$  Hz), 7.22-7.14 (2H, m), 7.12-7.05 (1H, m), 6.90 (1H, d,  $J = 7.7$  Hz), 4.81 (1H, t,  $J = 6.4$  Hz), 3.96 (3H, s), 2.97-2.76 (2H, m), 2.24-2.13 (1H, m), 2.11-2.00 (1H, m), 1.98-1.87 (1H, m), 1.86-1.72 (1H, m);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.1, 166.2, 134.0, 137.6, 134.13 (s), 133.7, 129.9, 129.5, 129.3, 128.6, 126.8, 125.9, 52.4, 47.9, 29.2, 27.4, 20.6; **HRMS (ESI)**: Found:  $m/z$  295.1337. Calcd for  $\text{C}_{19}\text{H}_{19}\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  295.1334. **IR (KBr,  $\text{cm}^{-1}$ )**: 1681, 1375, 1286, 1195, 1120, 987, 758.

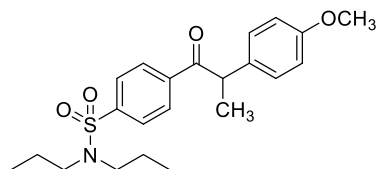
**methyl 4-(4-chloro-2-phenylbutanoyl)benzoate (4n)**



According to the general procedure, **1a** (30.1 mg, 0.10 mmol) and **2o** (20.3 mg, 0.05 mmol) were used. The conversion of Hantzsch ester was 76%, and 75% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 40% yield as yellow solid (6.4 mg). mp 65-67 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-7.91 (4H, m), 7.32-7.14 (5H, m), 4.88 (1H, d,  $J = 6.6, 7.8$  Hz), 3.87 (3H, s), 3.62-3.51 (1H, m), 3.45-3.34 (1H, m), 2.65-2.48 (1H, m), 2.35-2.19 (1H, m);  $^{13}\text{C}$  NMR (125 MHz,

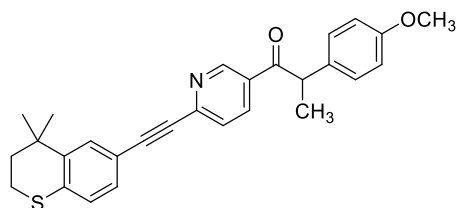
CDCl<sub>3</sub>)  $\delta$  198.5, 166.1, 139.6, 137.6, 133.7, 129.7, 129.3, 128.7, 128.3, 127.6, 52.4, 50.6, 42.9, 35.8; **HRMS (ESI)**: Found:  $m/z$  317.0949. Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>Cl (M+H)<sup>+</sup> 317.0944. **IR (KBr, cm<sup>-1</sup>)**: 1712, 1681, 1375, 1290, 1111, 775, 702.

**4-(2-(4-methoxyphenyl)propanoyl)-N,N-dipropylbenzenesulfonamide (5)**



According to the general procedure, **1p** (81.3 mg, 0.20 mmol) and **2a** (38.7 mg, 0.10 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 88% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 51% yield as colorless oil (22.8 mg). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (2H, d,  $J$  = 8.3 Hz), 7.79 (2H, d,  $J$  = 8.3 Hz), 7.16 (2H, d,  $J$  = 8.5 Hz), 6.83 (2H, d,  $J$  = 8.5 Hz), 4.58 (1H, q,  $J$  = 6.7 Hz), 3.76 (3H, s), 3.05 (4H, t,  $J$  = 7.50 Hz), 1.57-1.43 (4H, m), 0.84 (6H, t,  $J$  = 7.4 Hz); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.5, 158.7, 143.7, 139.4, 132.6, 129.2, 128.8, 127.1, 114.6, 55.2, 50.0, 47.7, 22.0, 19.3, 11.1; **HRMS (ESI)**: Found:  $m/z$  404.1893. Calcd for C<sub>22</sub>H<sub>30</sub>NO<sub>4</sub>S (M+H)<sup>+</sup> 404.1896. **IR (KBr, cm<sup>-1</sup>)**: 2933, 2875, 1687, 1558, 1512, 1157, 833.

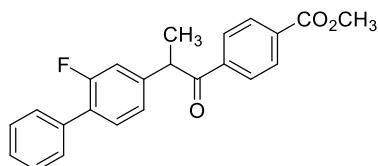
**1-(6-((4,4-dimethylthiochroman-6-yl)ethynyl)pyridin-3-yl)-2-(4-methoxyphenyl)propan-1-one (6)**



According to the general procedure, **1q** (44.5 mg, 0.10 mmol) and **2a** (19.4 mg, 0.05 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 92% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 41% yield as yellow solid (9.1 mg). mp 101-103 °C; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.11 (1H, d,  $J$  = 1.5 Hz), 8.15 (1H, dd,  $J$  = 8.2, 2.2 Hz), 7.59 (1H, d,  $J$  = 1.6 Hz), 7.49 (1H, d,  $J$  = 8.2 Hz), 7.22 (1H, dd,  $J$  = 8.2, 1.7 Hz), 7.19-7.14 (2H, m), 7.06 (1H, d,  $J$  = 8.2 Hz), 6.87-6.80 (2H, m), 4.56 (1H, q,  $J$  = 6.8 Hz), 3.75 (3H, s), 3.08-3.00 (2H, m),

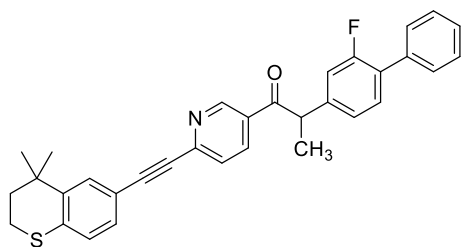
1.98-1.90 (2H, m), 1.52 (3H, d,  $J = 6.8$  Hz), 1.32 (6H, s);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.5, 158.8, 150.5, 146.7, 142.2, 136.2, 135.1, 132.5, 130.5, 129.8, 129.4, 128.8, 126.6, 126.4, 116.8, 114.7, 93.3, 88.0, 55.2, 47.8, 37.0, 33.0, 29.9, 23.2, 19.0, 1.0; HRMS (ESI): Found:  $m/z$  442.1845. Calcd for  $\text{C}_{28}\text{H}_{28}\text{NO}_2\text{S}$  ( $\text{M}+\text{H}$ ) $^+$  442.1841. IR (KBr,  $\text{cm}^{-1}$ ): 2208, 1672, 1583, 1510, 1377, 1184, 1031, 744.

**methyl 4-(2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoyl)benzoate (7)**



According to the general procedure, **1a** (60.2 mg, 0.20 mmol) and **2p** (45.2 mg, 0.10 mmol) were used. The conversion of Hantzsch ester was more than 99%, and 84% yield of the pyridine (by-product) was detected. The corresponding product was isolated in 51% yield as white solid (18.4 mg). mp: 101-103 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (2H, d,  $J = 8.4$  Hz), 8.01 (2H, d,  $J = 8.3$  Hz), 7.53-7.46 (2H, m), 7.45-7.30 (4H, m), 7.15-7.02 (2H, m), 4.72 (1H, q,  $J = 6.8$  Hz), 3.92 (3H, s), 1.58 (3H, d,  $J = 6.8$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.3, 166.1, 159.9 (d,  $J = 247.6$  Hz), 142.1 (d,  $J = 7.5$  Hz), 139.6, 135.2, 133.8, 131.3 (d,  $J = 4.0$  Hz), 129.8, 128.9 (d,  $J = 2.9$  Hz), 128.6, 128.4, 127.9 (d,  $J = 13.4$  Hz), 127.7, 123.7 (d,  $J = 3.4$  Hz), 115.4 (d,  $J = 23.5$  Hz), 52.4, 47.4, 19.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.8 (t); HRMS (ESI): Found:  $m/z$  363.1396. Calcd for  $\text{C}_{23}\text{H}_{20}\text{O}_3\text{F}$  ( $\text{M}+\text{H}$ ) $^+$  363.1396. IR (KBr,  $\text{cm}^{-1}$ ): 1716, 1681, 1377, 1284, 1111, 960, 748.

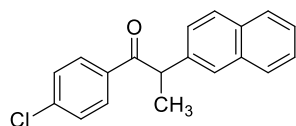
**1-(6-((4,4-dimethylthiochroman-6-yl)ethynyl)pyridin-3-yl)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propan-1-one (8)**



According to the general procedure, **1q** (44.5 mg, 0.10 mmol) and **2p** (22.6 mg, 0.05 mmol) were used. The corresponding product was isolated in 40% yield as yellow oil

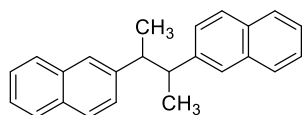
(10.1 mg). mp 153-155 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.15 (1H, d,  $J = 1.6$  Hz), 8.21 (1H, dd,  $J = 8.2, 2.3$  Hz), 7.59 (1H, d,  $J = 1.6$  Hz), 7.54 (1H, d,  $J = 8.2$  Hz), 7.51-7.47 (2H, m), 7.45-7.32 (4H, m), 7.23 (1H, dd,  $J = 8.2, 1.7$  Hz), 7.12 (1H, dd,  $J = 7.9, 1.7$  Hz), 7.10-7.05 (2H, m), 4.66 (1H, q,  $J = 6.8$  Hz), 3.09-3.00 (2H, m), 1.98-1.91 (2H, m), 1.59 (3H, d,  $J = 6.9$  Hz), 1.32 (6H, s);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.7, 160.0 (d,  $J = 248.0$  Hz), 150.5, 147.1, 142.2, 141.8 (d,  $J = 7.5$  Hz), 136.2, 135.20, 135.18, 131.5 (d,  $J = 4.0$  Hz), 130.5, 129.5, 128.9 (d,  $J = 2.8$  Hz), 128.4, 128.1 (d,  $J = 13.5$  Hz), 127.7, 126.6, 123.8 (d,  $J = 3.3$  Hz), 116.7, 115.4 (d,  $J = 23.5$  Hz), 93.7, 87.9, 47.9, 37.0, 33.0, 29.9, 23.2, 19.0;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.5 (t); **HRMS (ESI)**: Found:  $m/z$  506.1962. Calcd for  $\text{C}_{33}\text{H}_{29}\text{NOFS}$  ( $\text{M}+\text{H}$ ) $^+$  506.1954. **IR (KBr,  $\text{cm}^{-1}$ )**: 2960, 2918, 2200, 1681, 1581, 1112, 767.

#### 1-(4-chlorophenyl)-2-(naphthalen-2-yl)propan-1-one (10)



According to the general procedure, **1d** (111.2 mg, 0.40 mmol) and **2i** (81.4 mg, 0.20 mmol) were used. The corresponding product was isolated in 36% yield as colorless oil (21.9 mg).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94-7.89 (2H, m), 7.82-7.74 (3H, m), 7.69 (1H, s), 7.49-7.41 (2H, m), 7.39 (1H, dd,  $J = 8.5, 1.7$  Hz), 7.35-7.29 (2H, m), 4.78 (1H, q,  $J = 6.8$  Hz), 1.61 (3H, d,  $J = 6.8$  Hz);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.0, 139.2, 138.7, 134.8, 133.7, 132.4, 130.2, 129.0, 128.8, 127.7, 127.7, 126.4, 126.3, 125.9, 125.7, 48.24, 19.4; **HRMS (ESI)**: Found:  $m/z$  295.0892. Calcd for  $\text{C}_{19}\text{H}_{16}\text{OCl}$  ( $\text{M}+\text{H}$ ) $^+$  295.0890. **IR (KBr,  $\text{cm}^{-1}$ )**: 2929, 1681, 1591, 1091, 958, 746.

#### 2,2'-(butane-2,3-diyl)dinaphthalene (11)



According to the general procedure, **1d** (111.2 mg, 0.40 mmol) and **2i** (81.4 mg, 0.20 mmol) were used. The corresponding product was isolated in 4% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75-7.67 (4H, m), 7.64 (d,  $J = 8.5$  Hz, 2H), 7.50 (s, 2H), 7.41-7.33 (m, 4H), 7.25-7.22 (2H, m), 3.31-3.22 (2H, m), 1.39 (d,  $J = 6.5$  Hz, 6H);  $^{13}\text{C NMR}$  (100



MHz, CDCl<sub>3</sub>)  $\delta$  143.3, 133.3, 132.0, 127.6, 127.5, 127.3, 126.7, 126.1, 125.6, 125.0, 46.2, 18.0; **HRMS (ESI)**: Found:  $m/z$  311.1814. Calcd for C<sub>24</sub>H<sub>23</sub> (M+H)<sup>+</sup> 311.1800. **IR (KBr, cm<sup>-1</sup>)**: 2924, 1683, 1653, 1506, 1456.

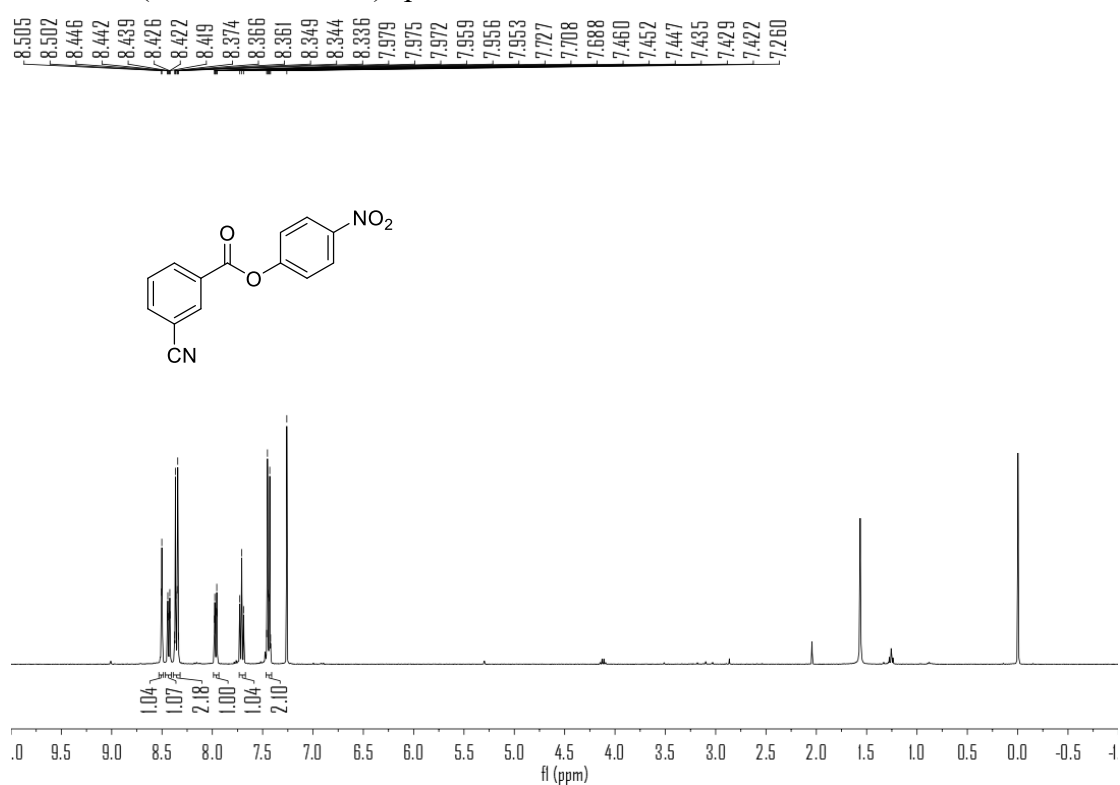
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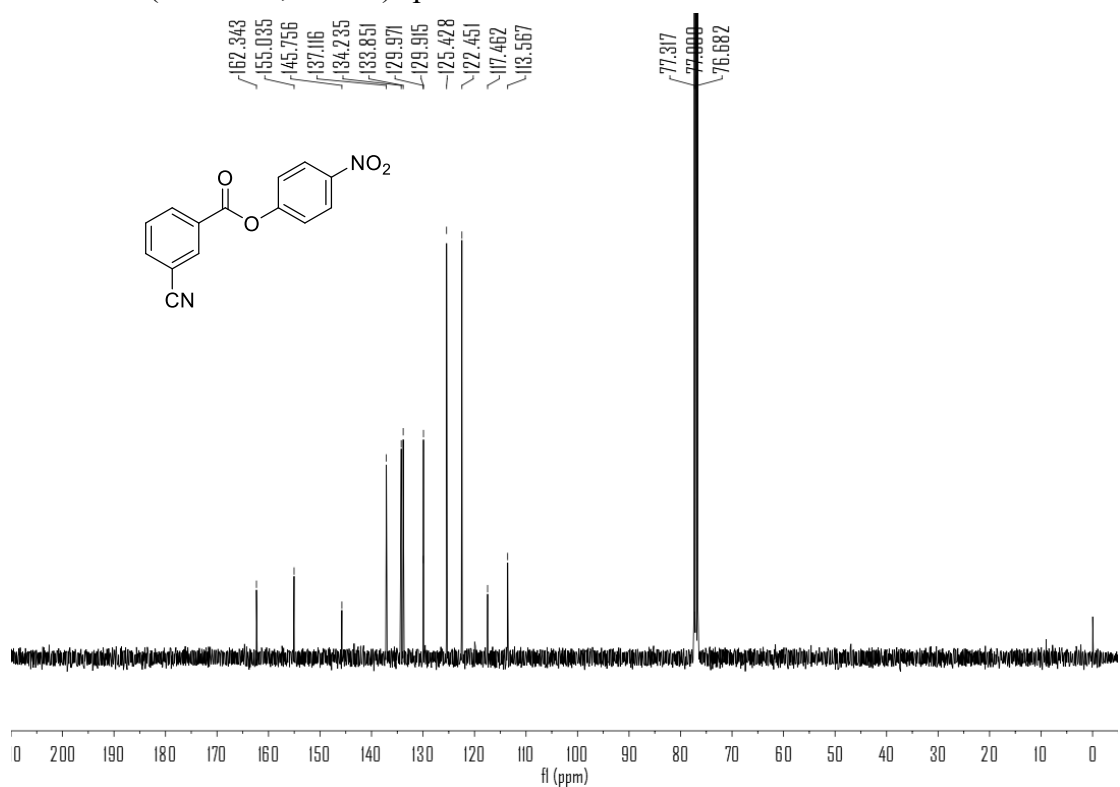
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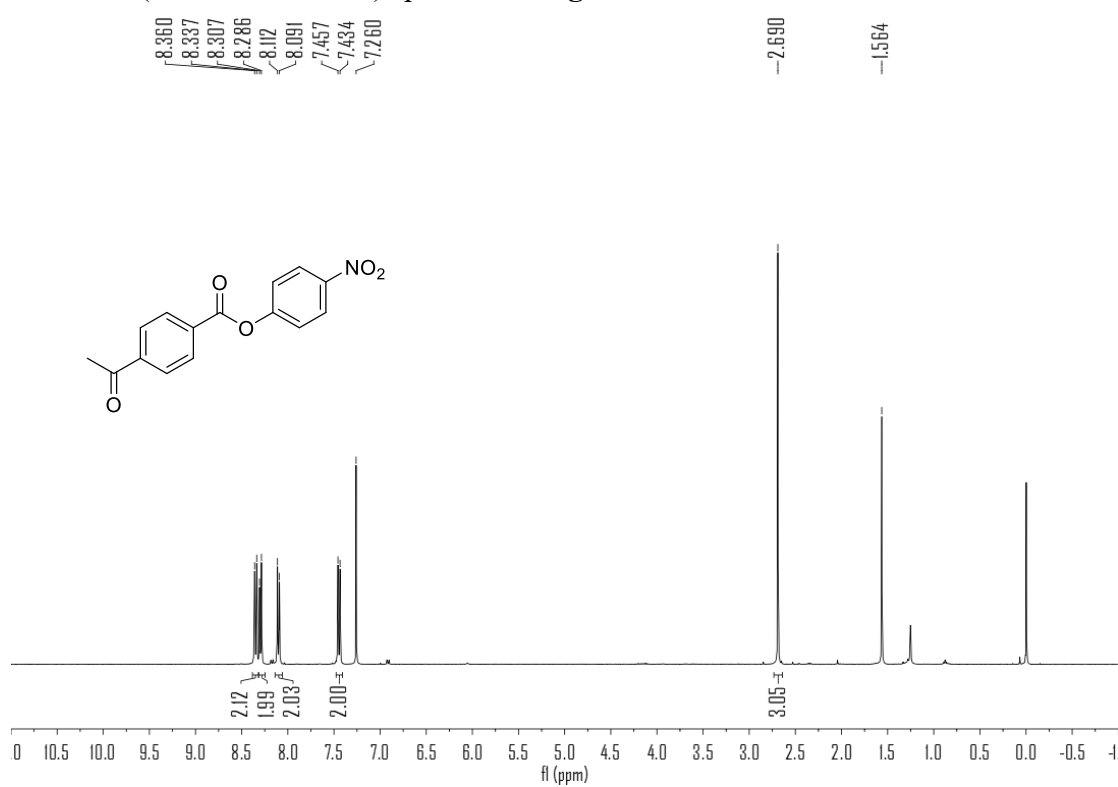
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **1f****



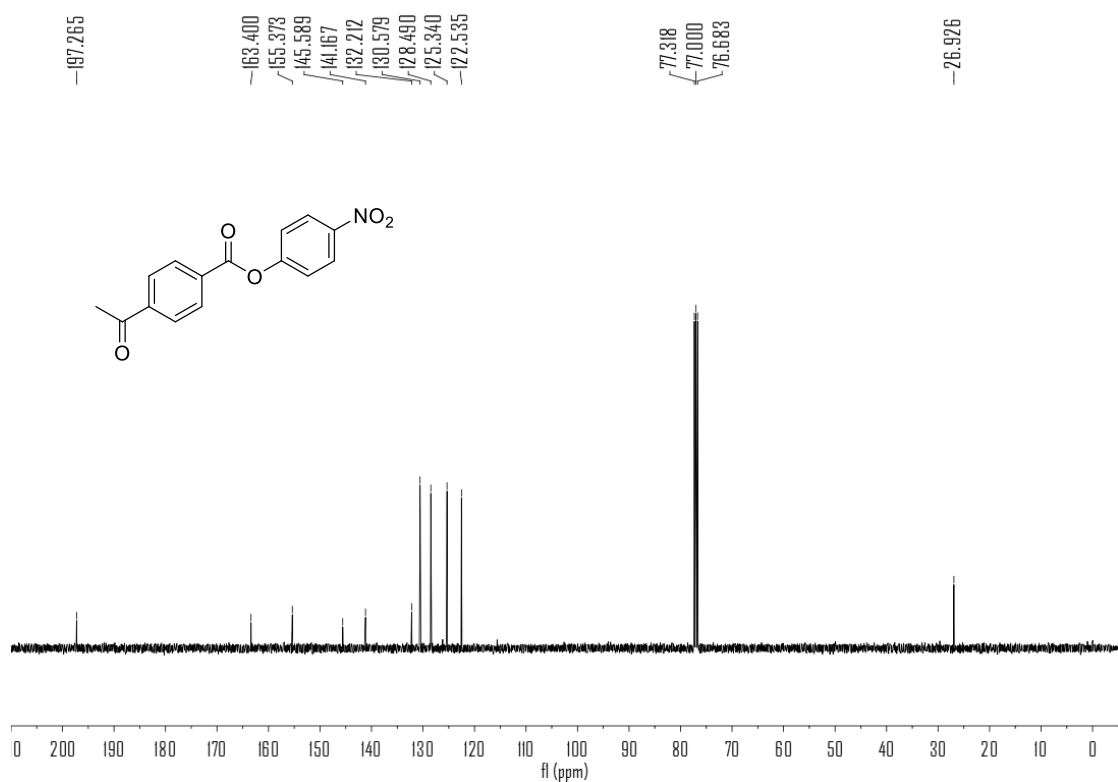
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **1f****



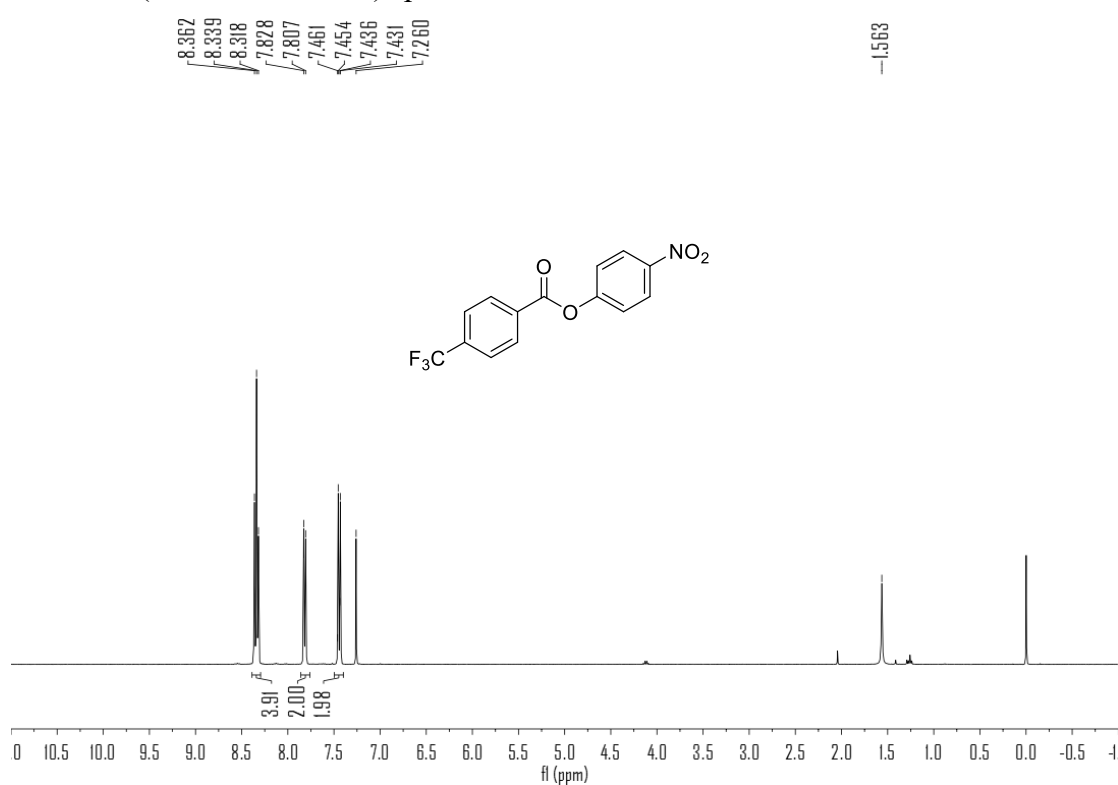
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **1g****



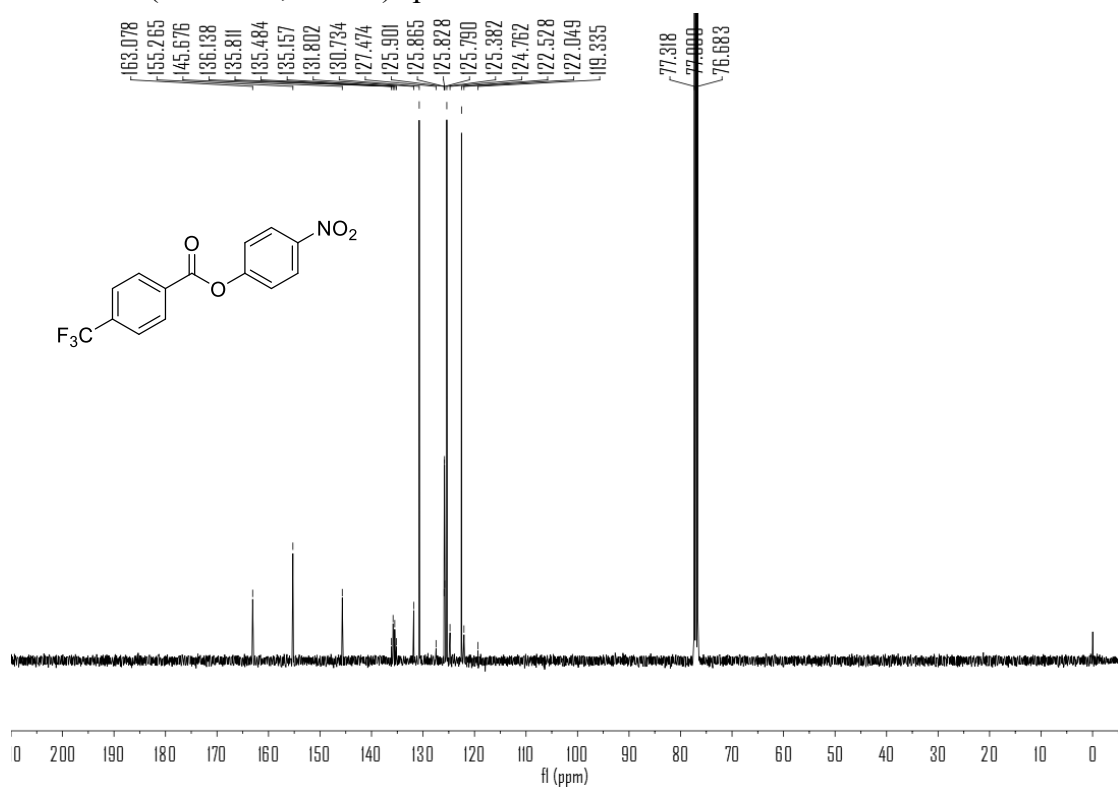
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **1g****



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **1h****



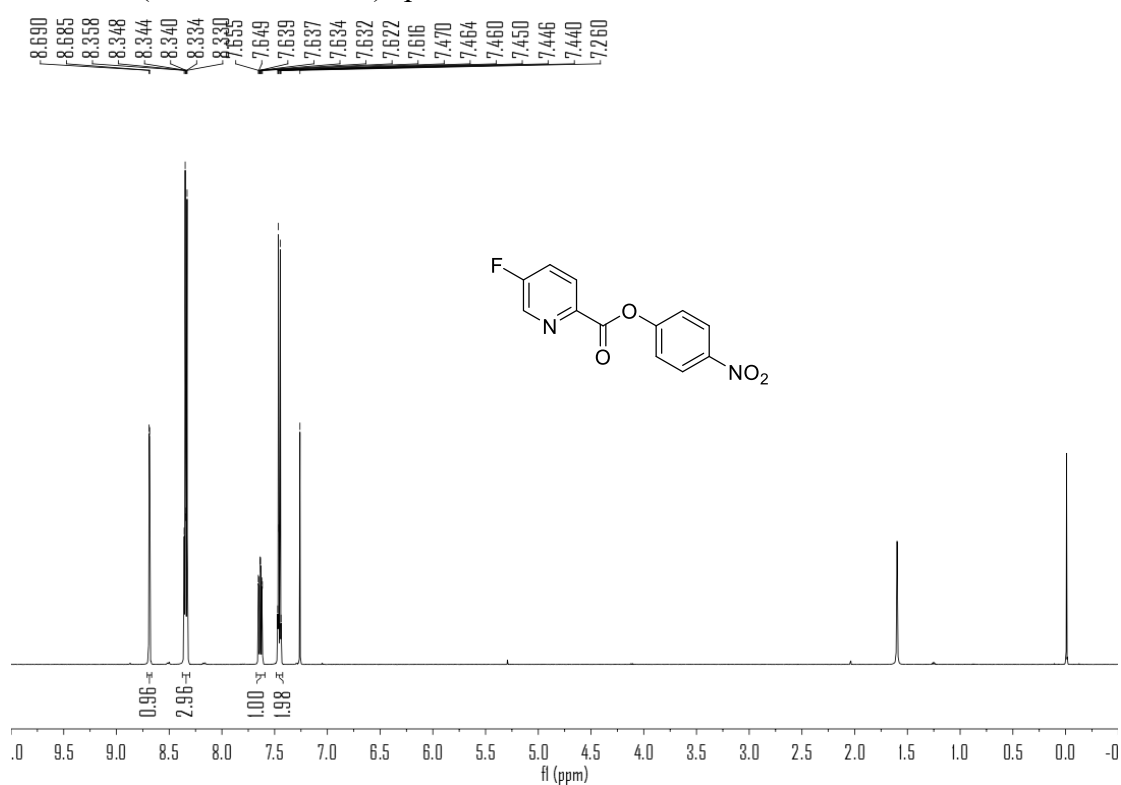
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **1h****



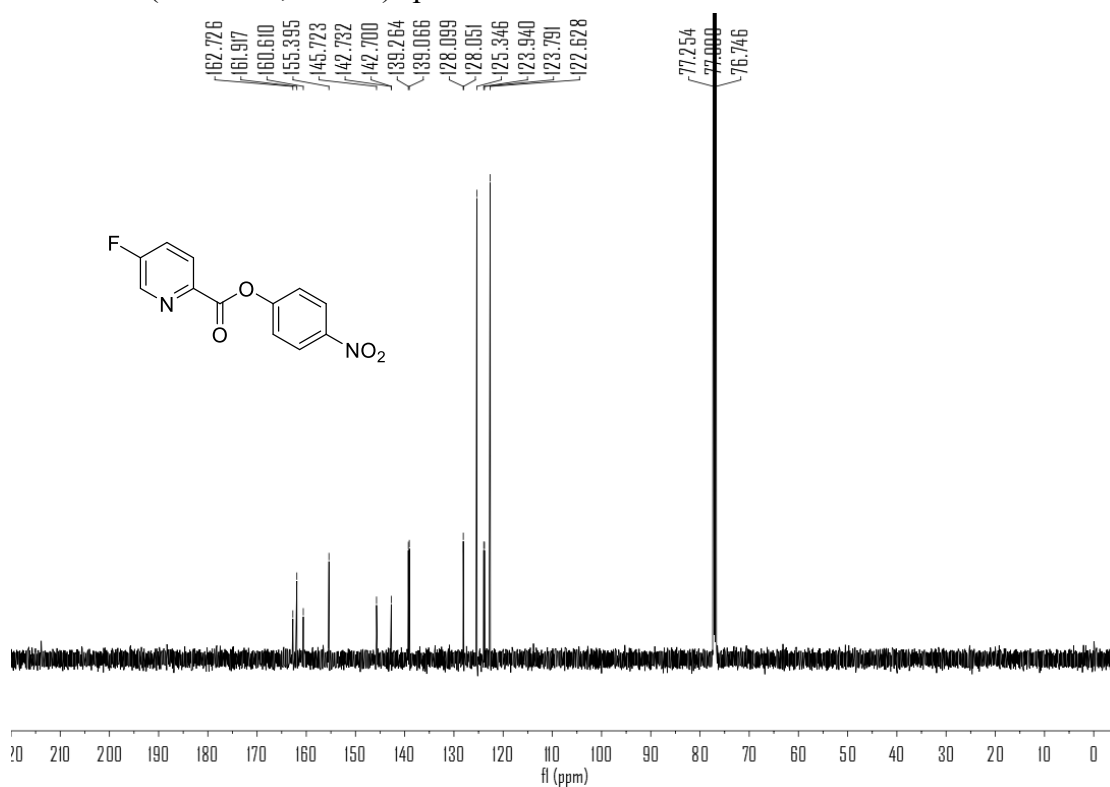
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectrum of **1h****



**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **1k****

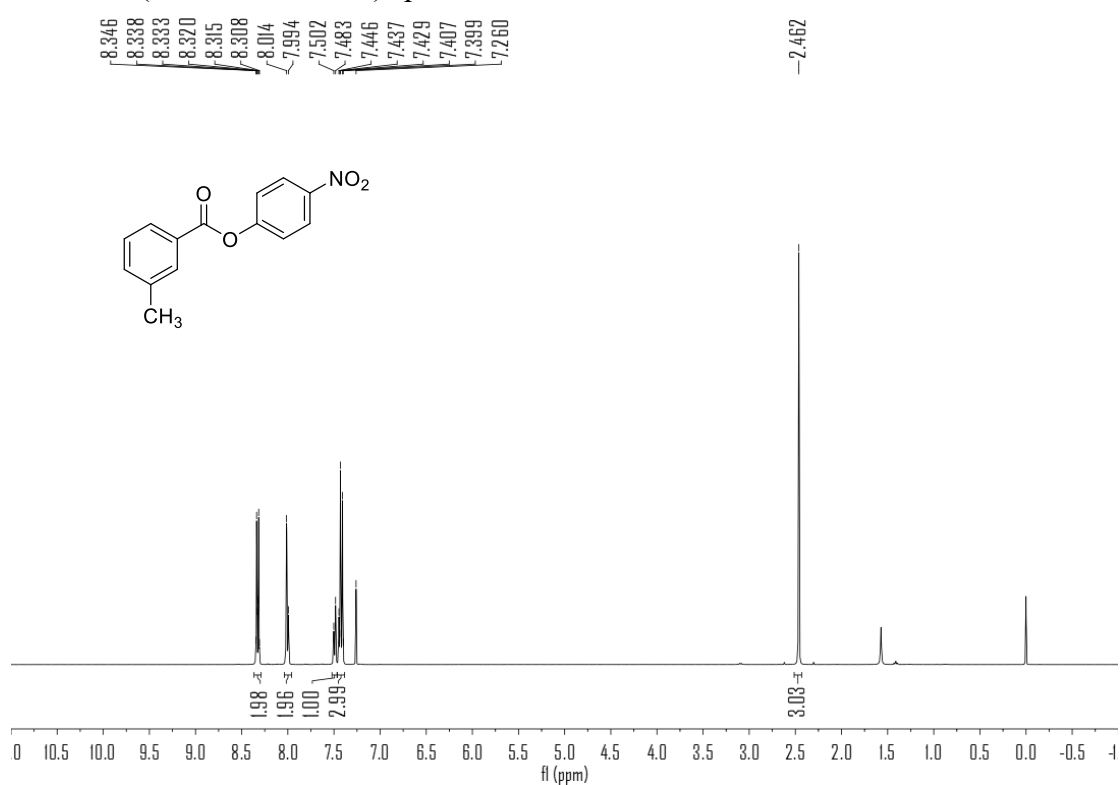


**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **1k****

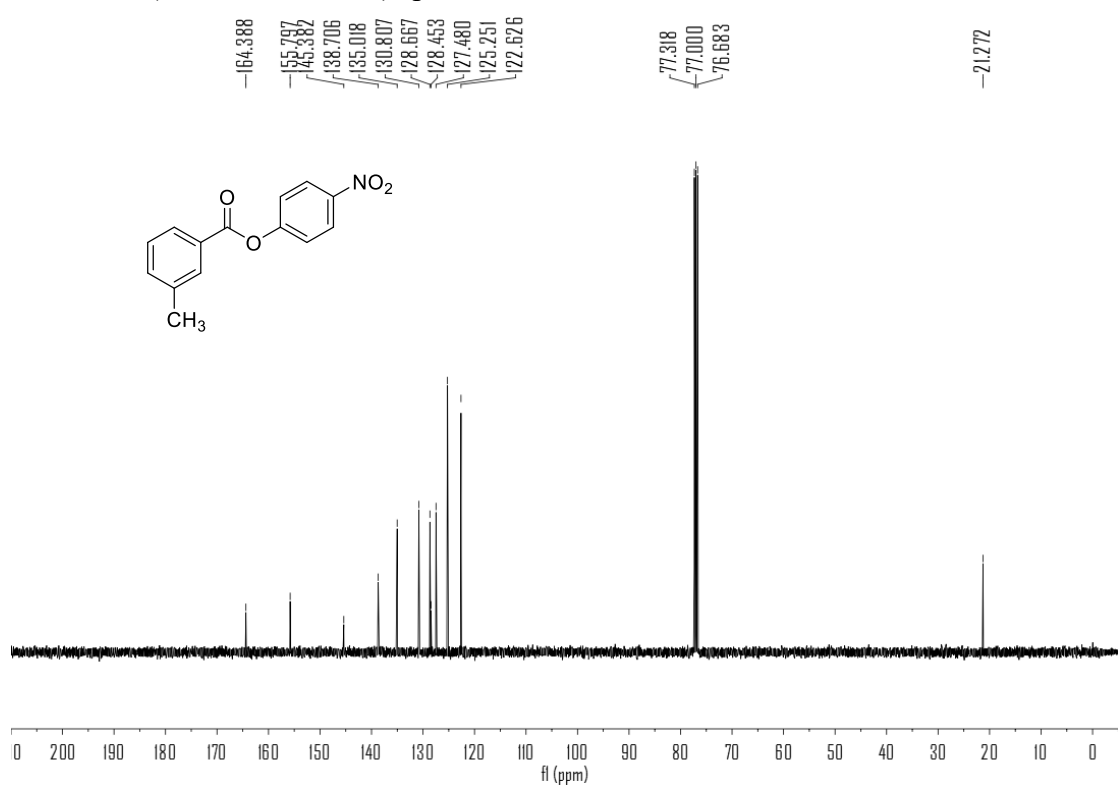




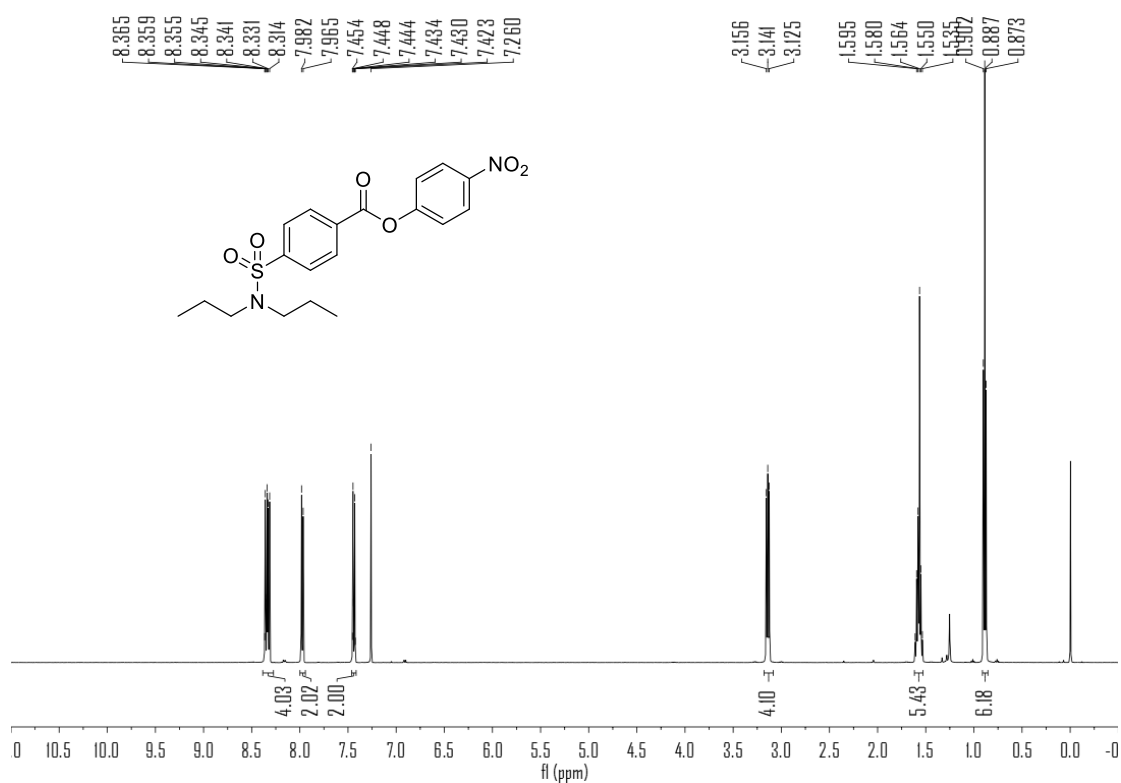
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **1m****



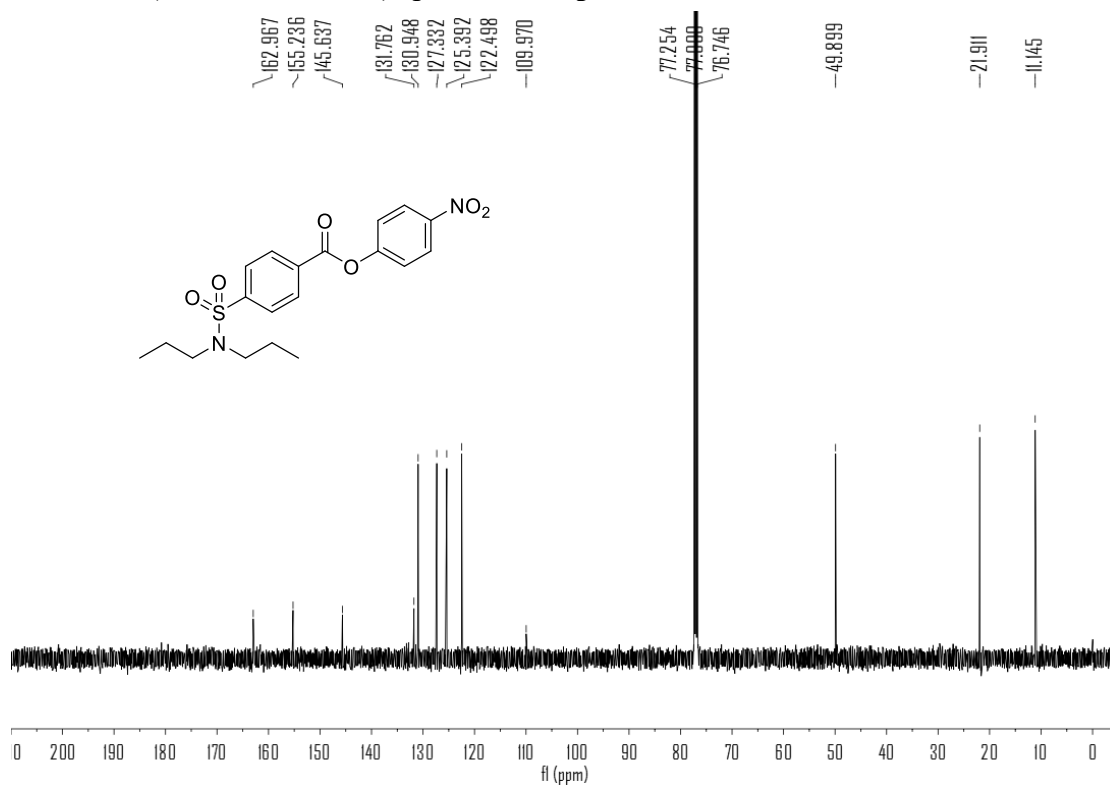
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **1m****



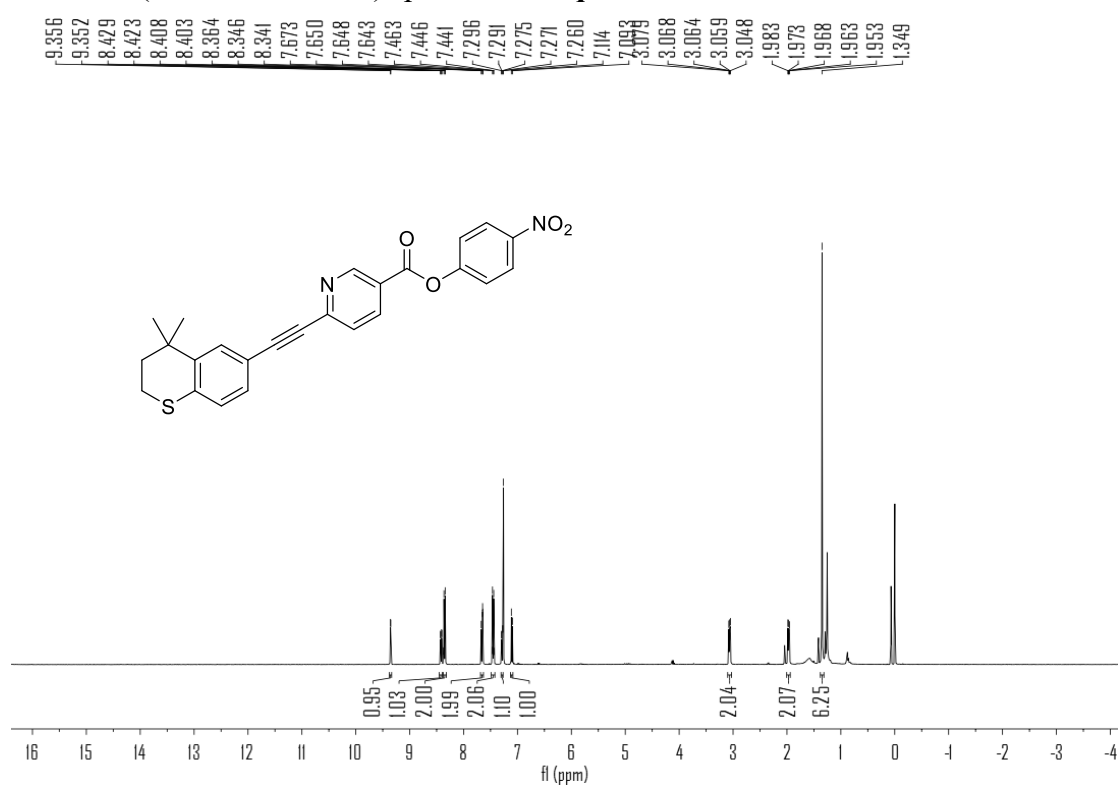
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **1p****



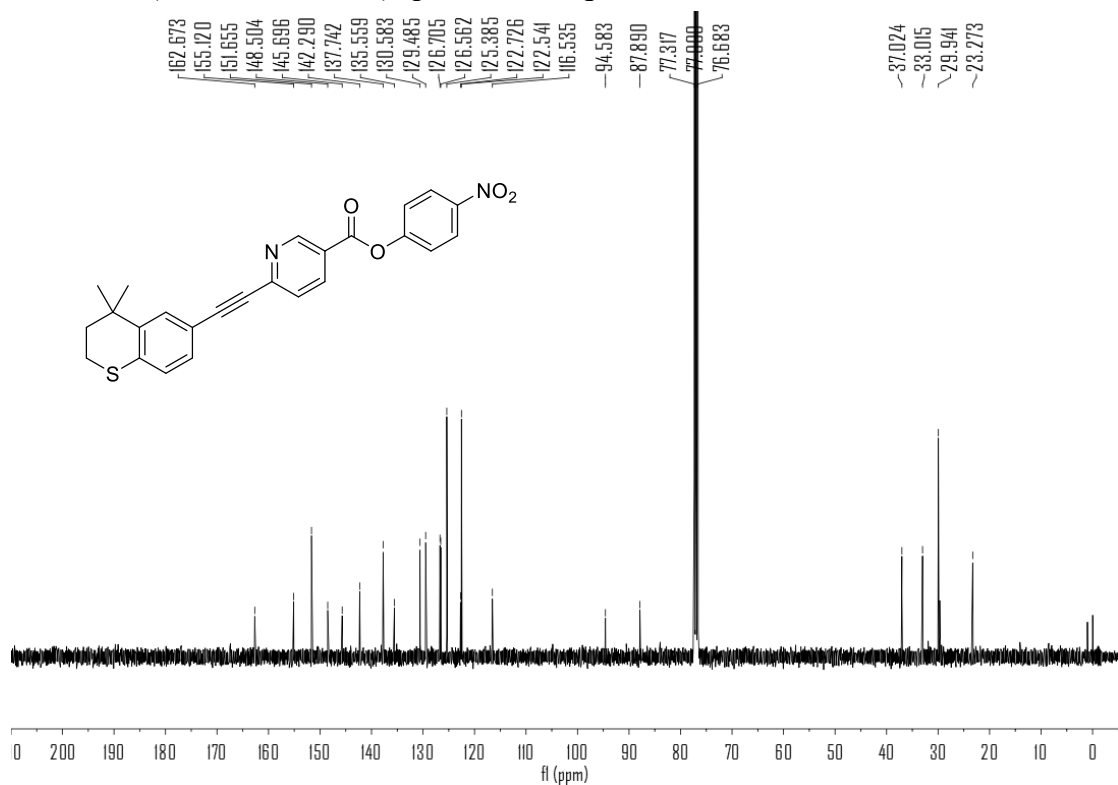
**$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum of **1p****



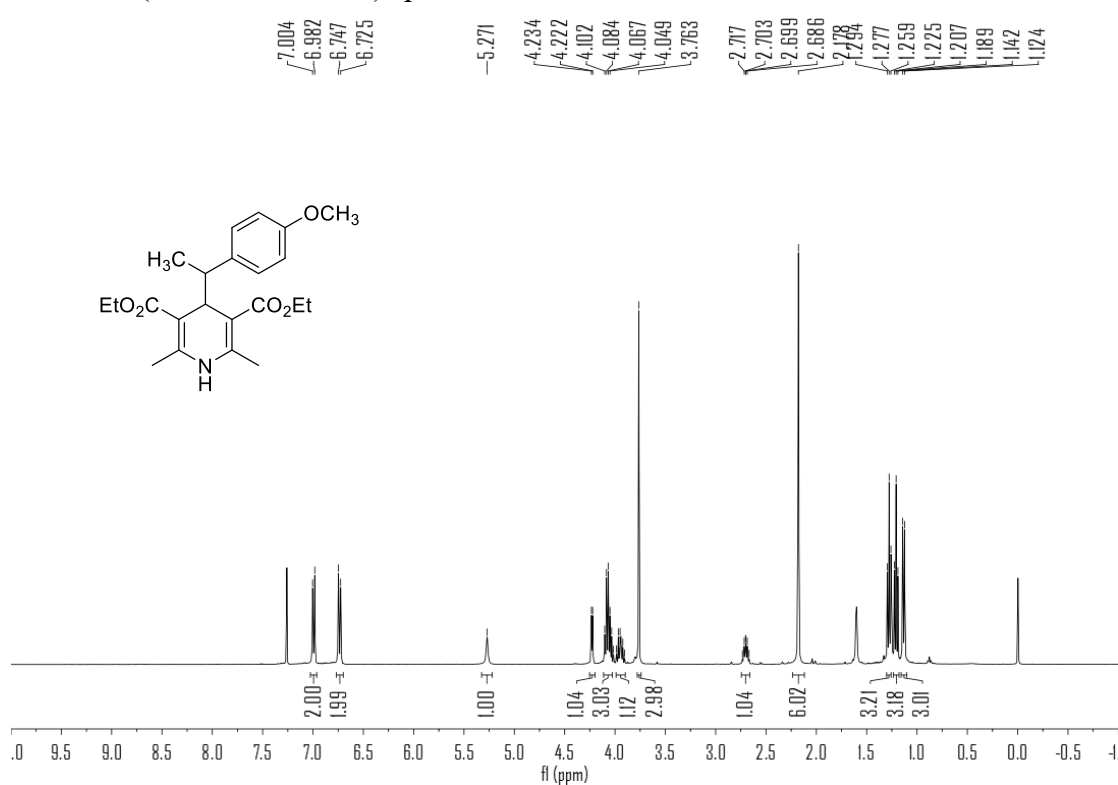
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **1q****



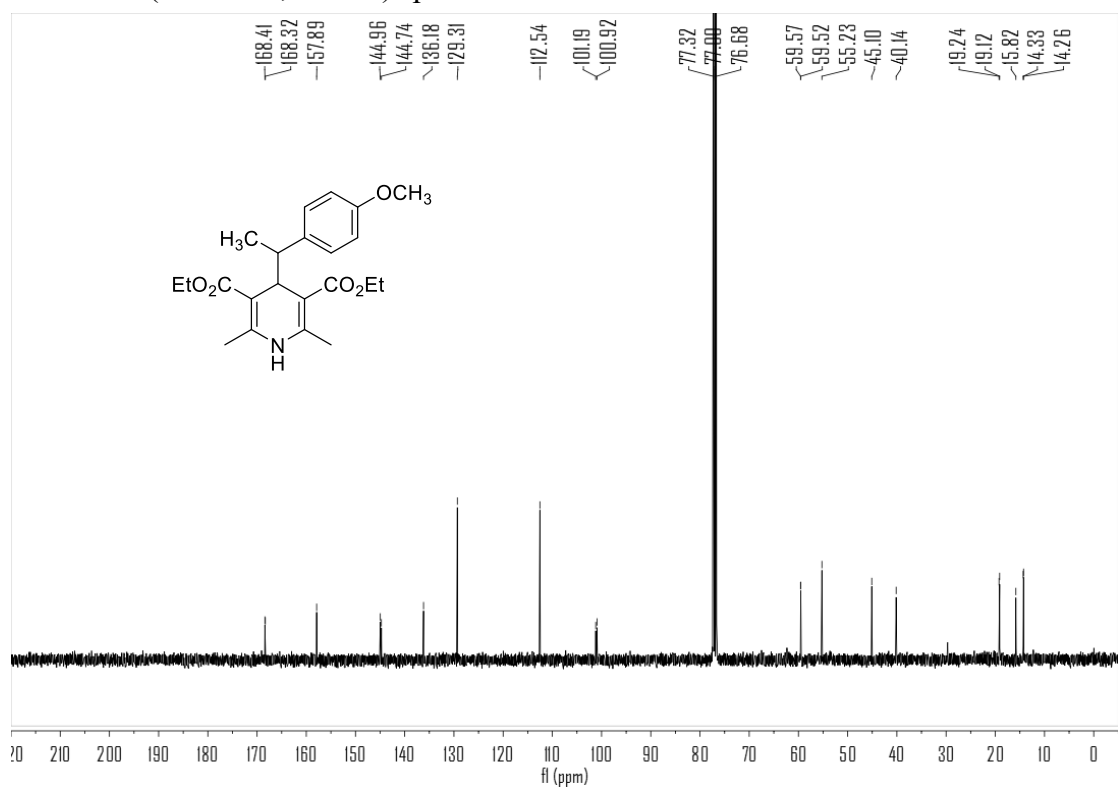
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **1q****



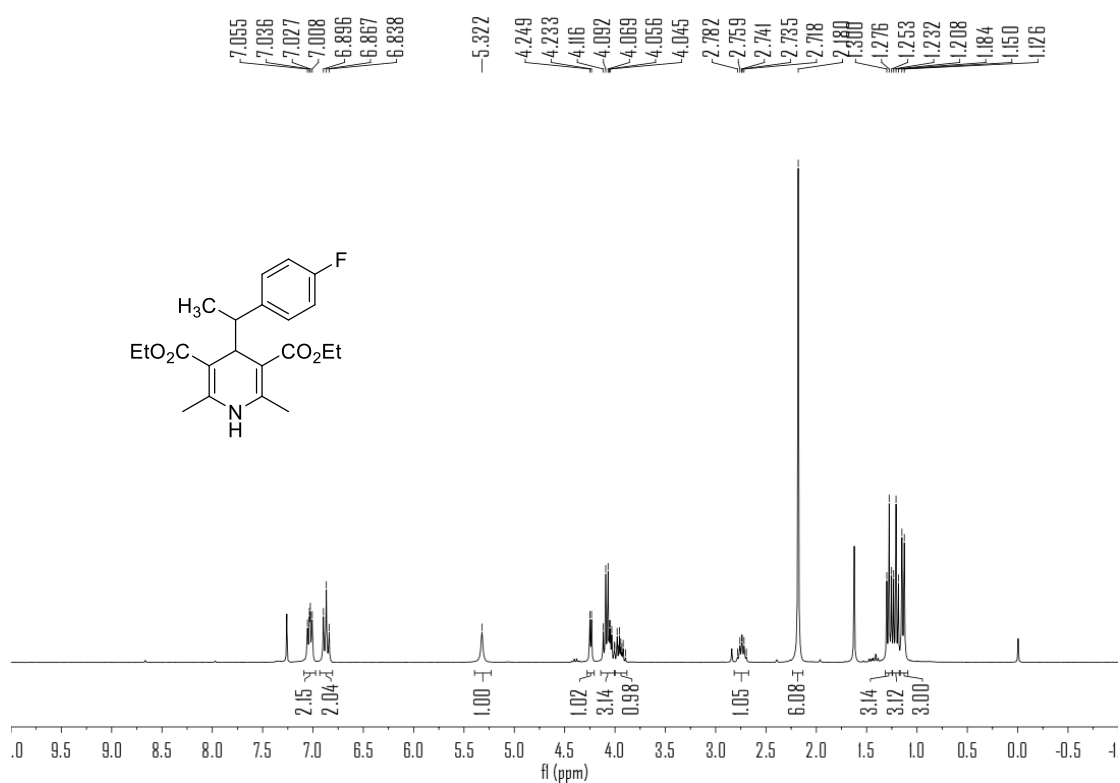
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 2a**



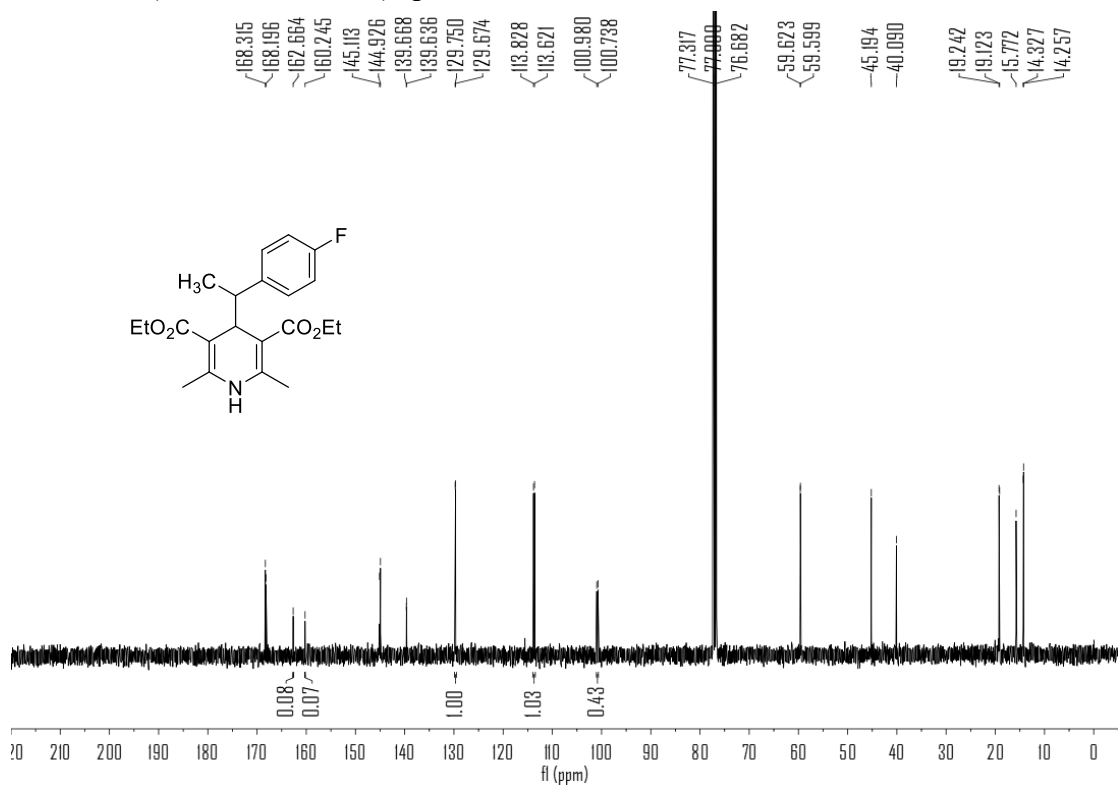
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 2a**



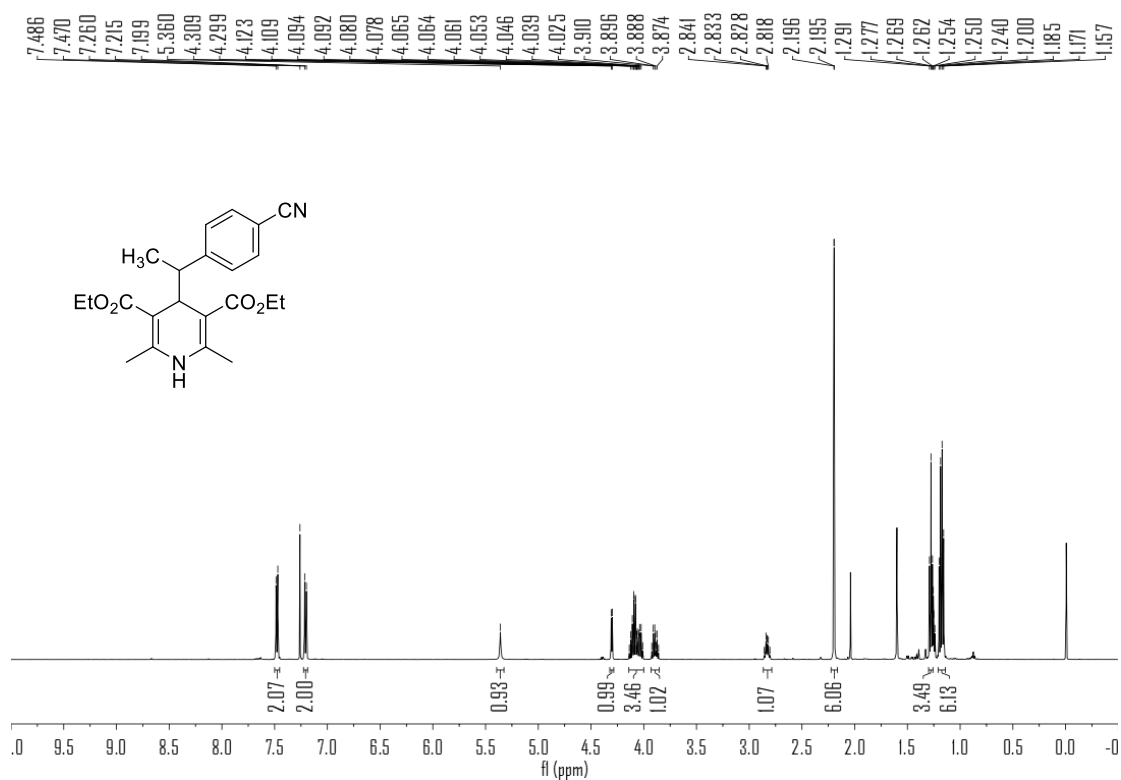
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 2f**



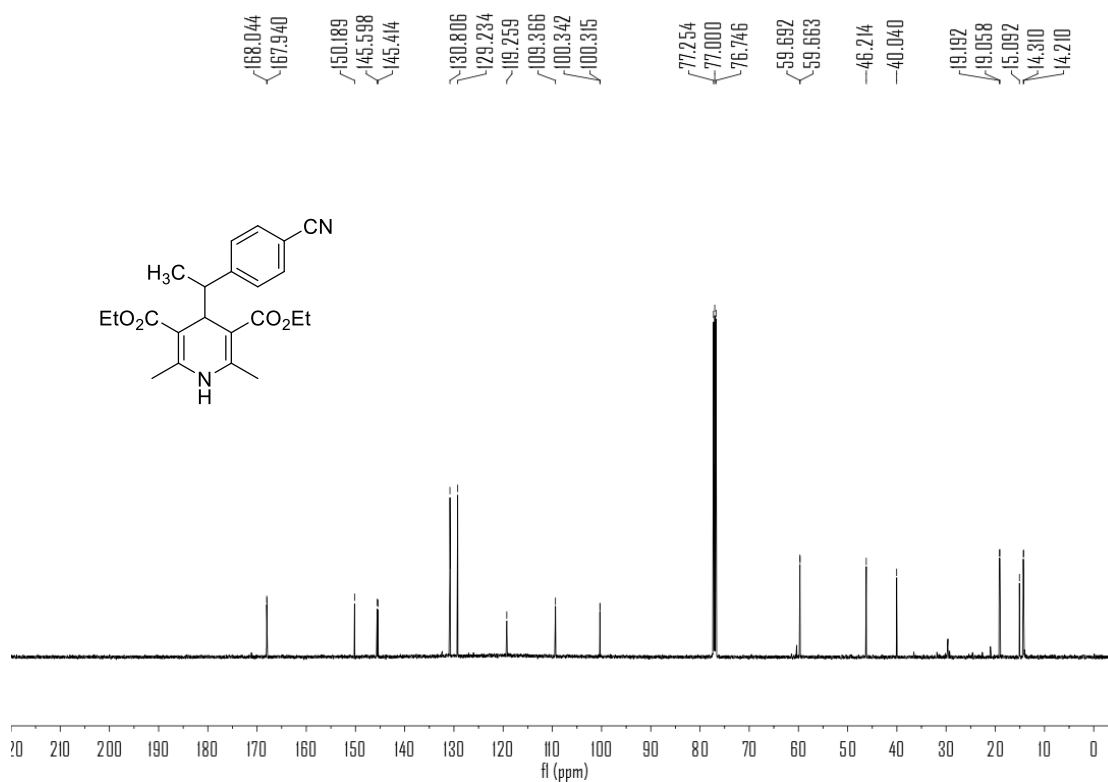
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 2f**



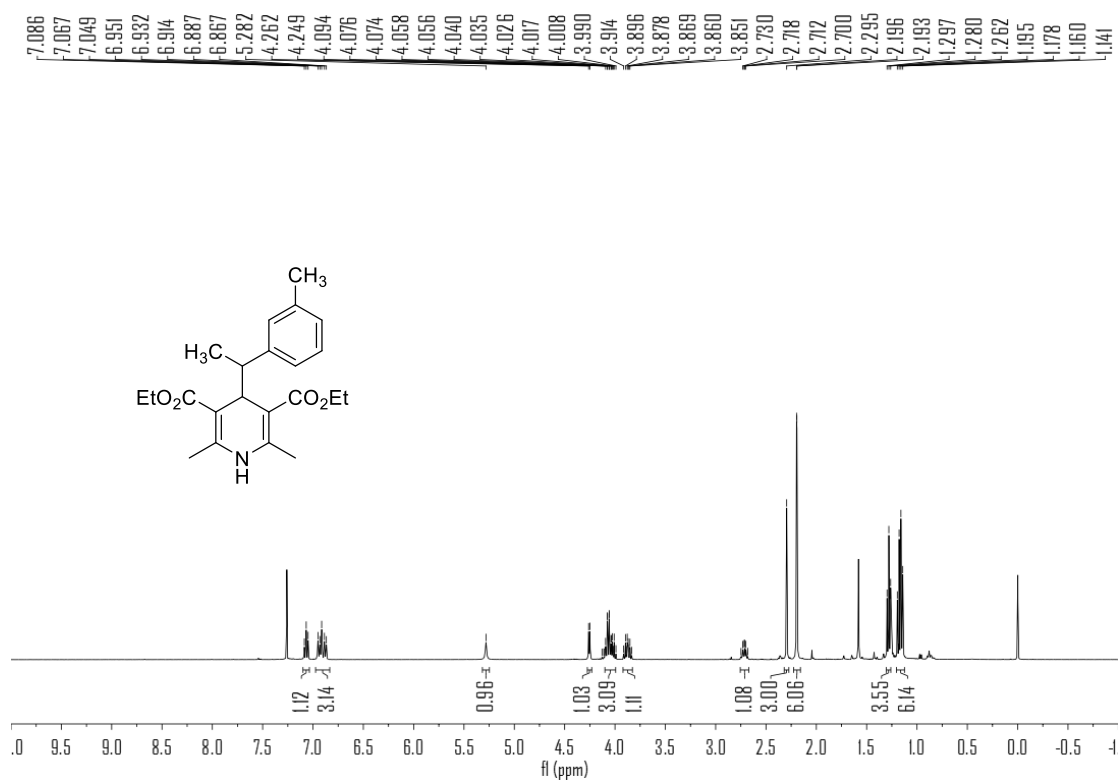
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 2h**



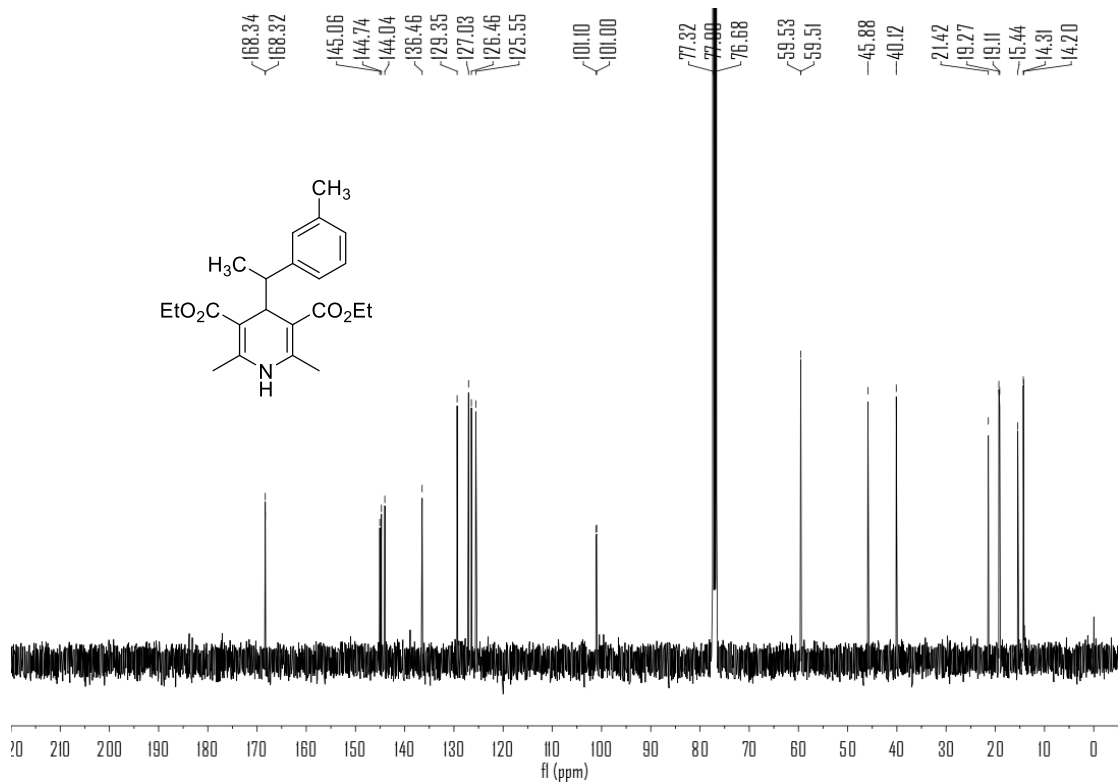
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 2h**



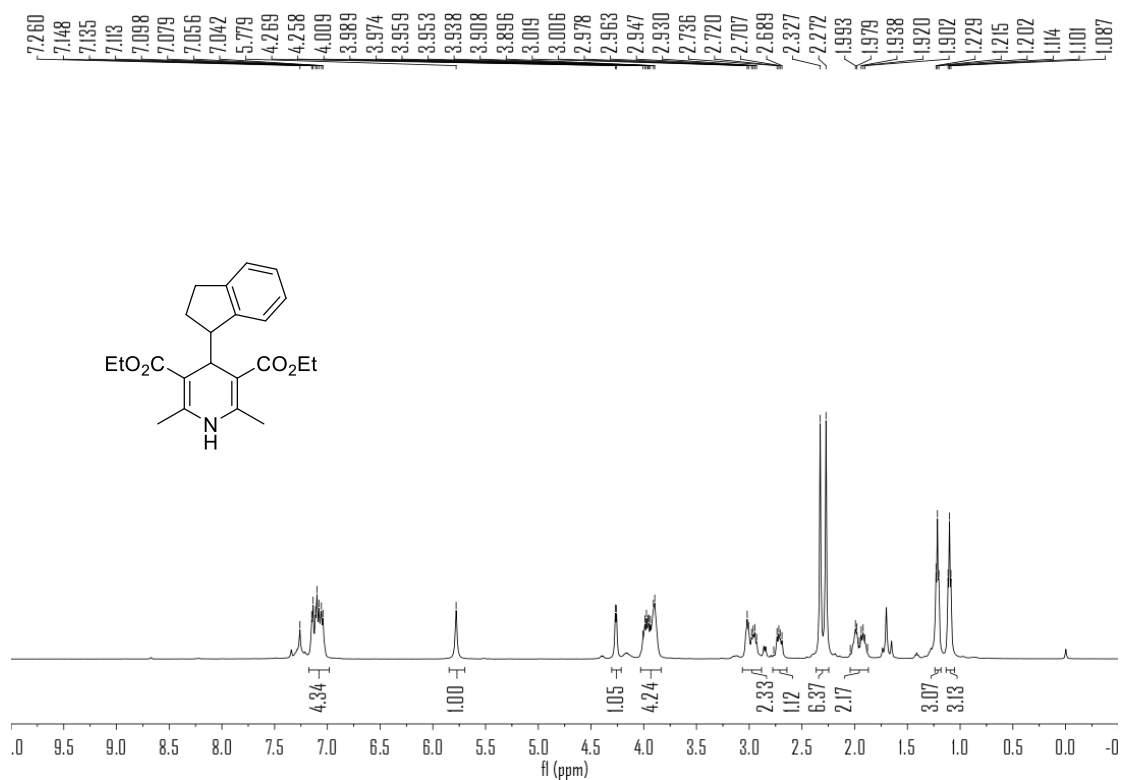
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 2i**



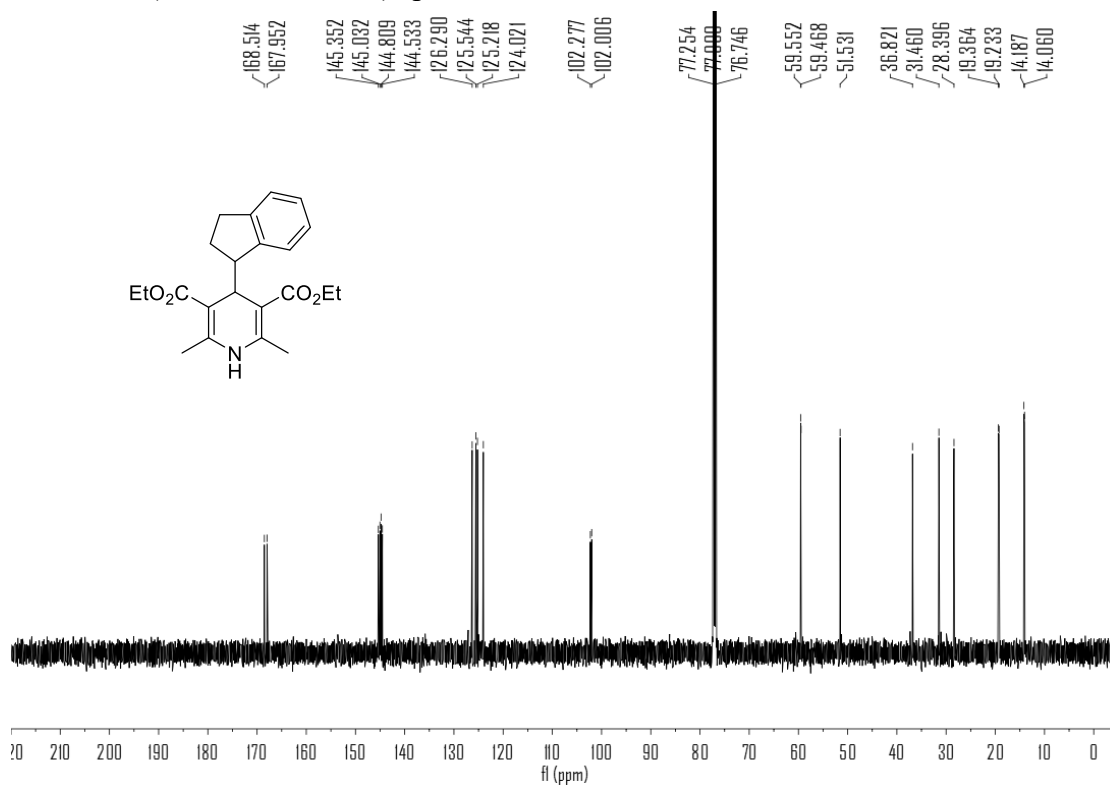
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 2i**



**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 2n**

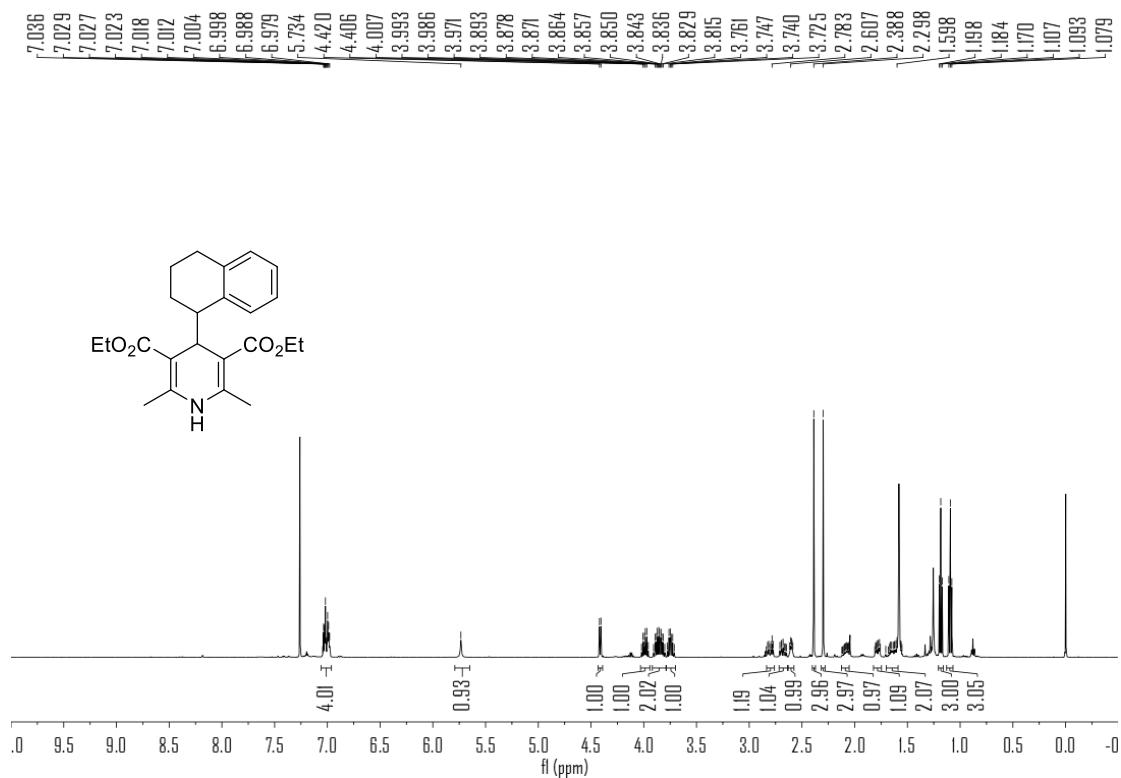


**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 2n**

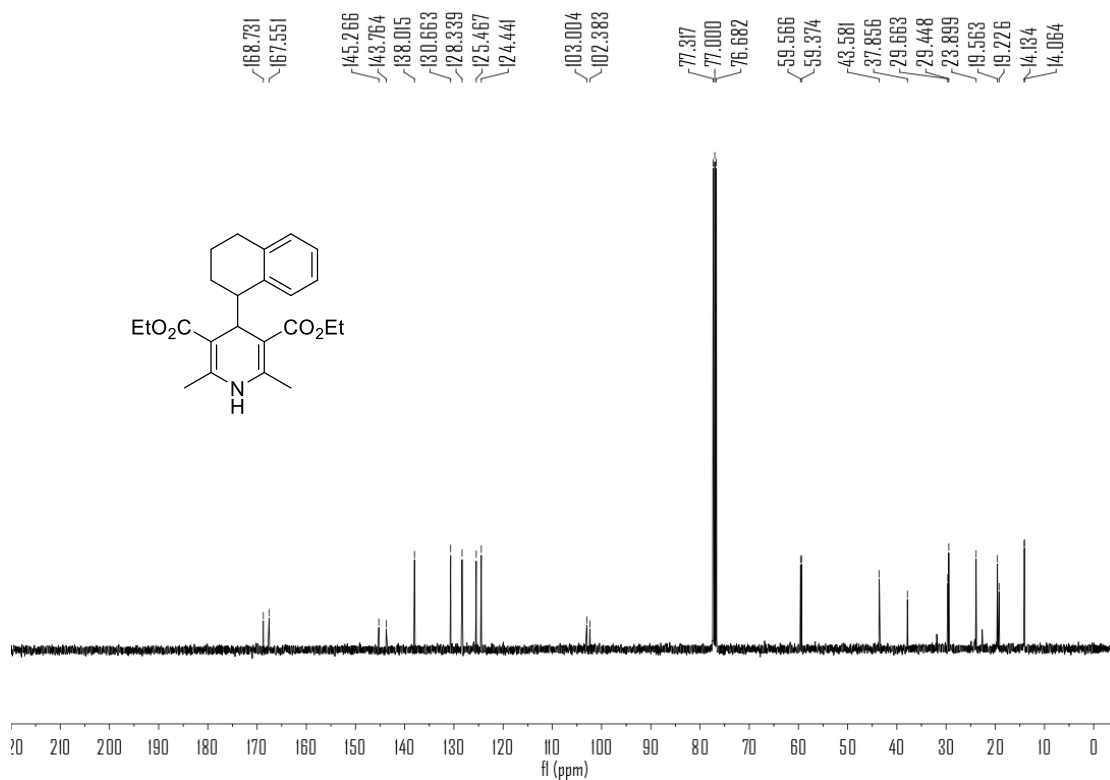




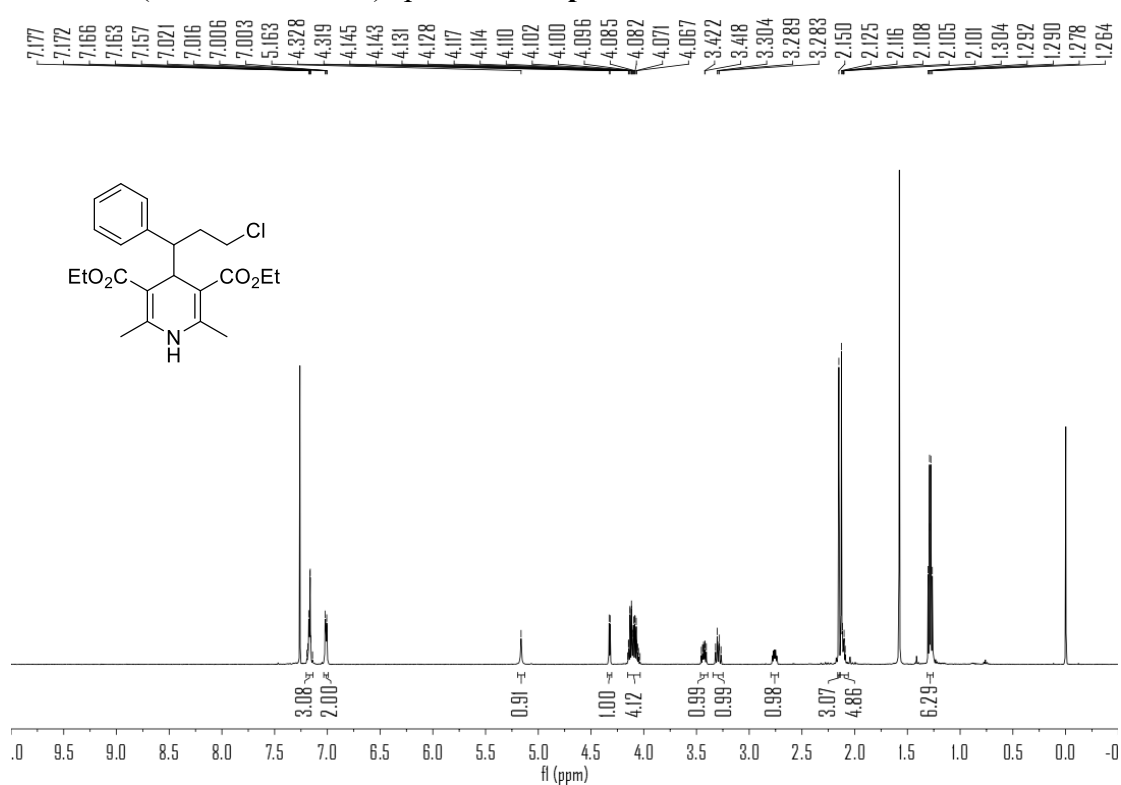
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 2o**



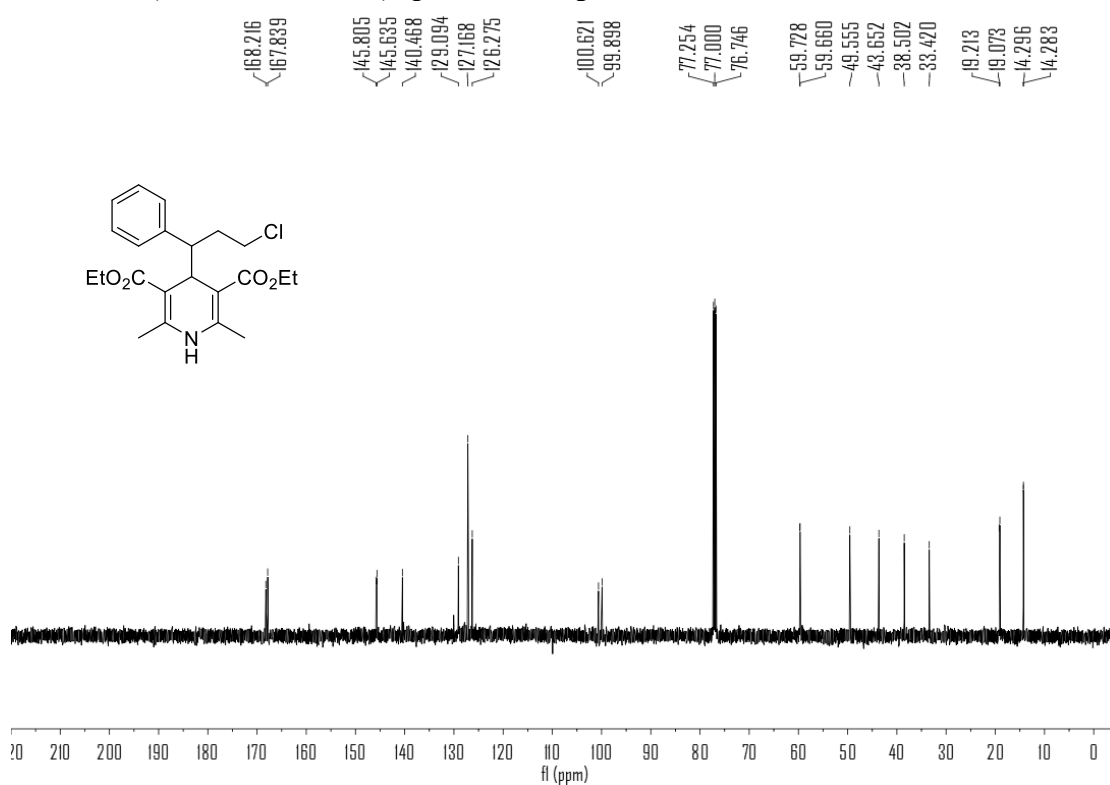
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 2o**



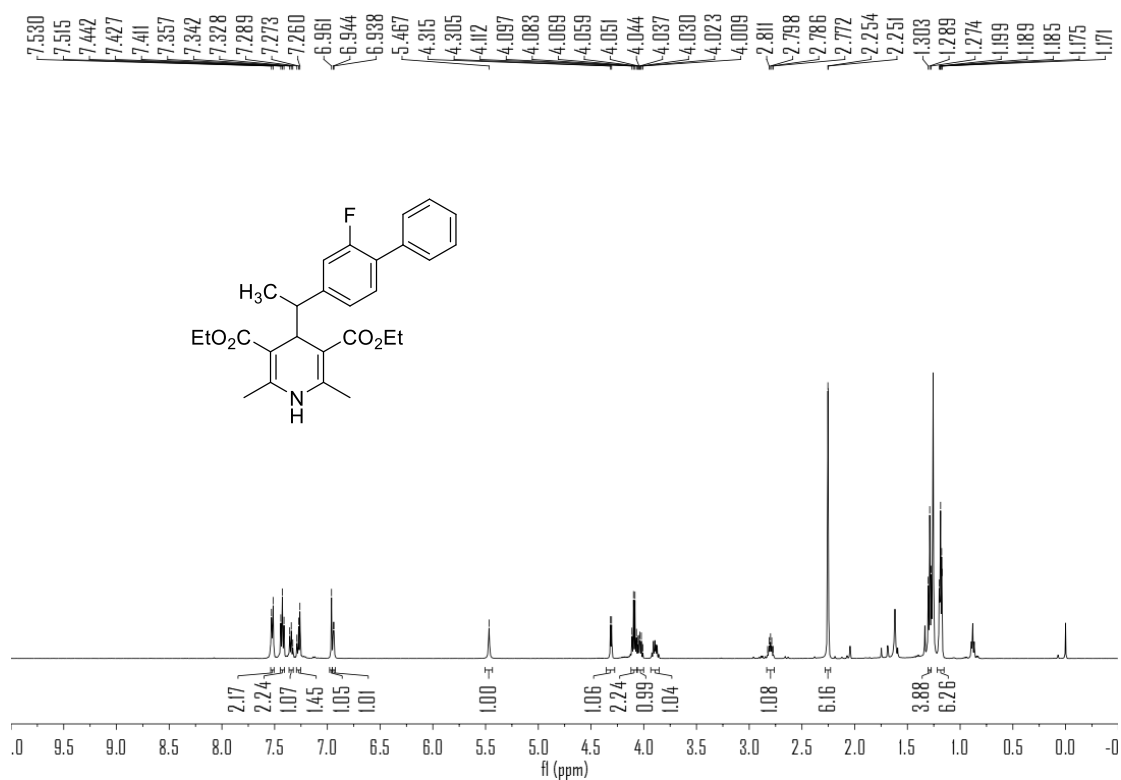
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 2p**



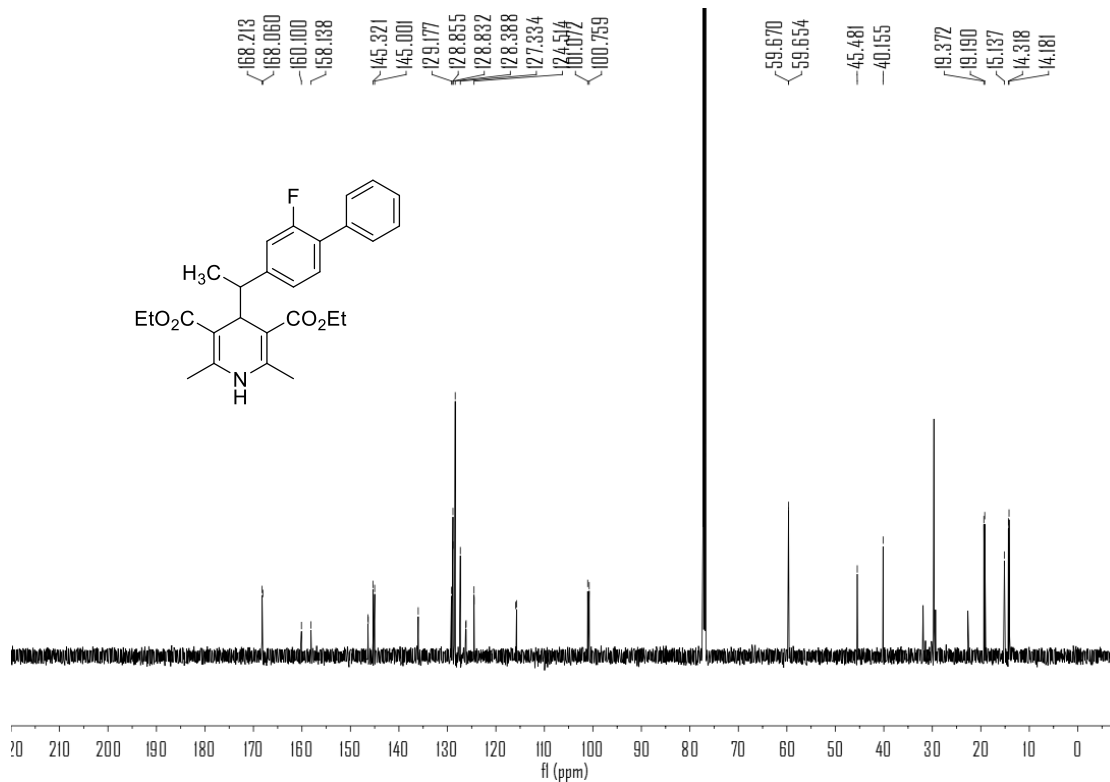
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 2p**



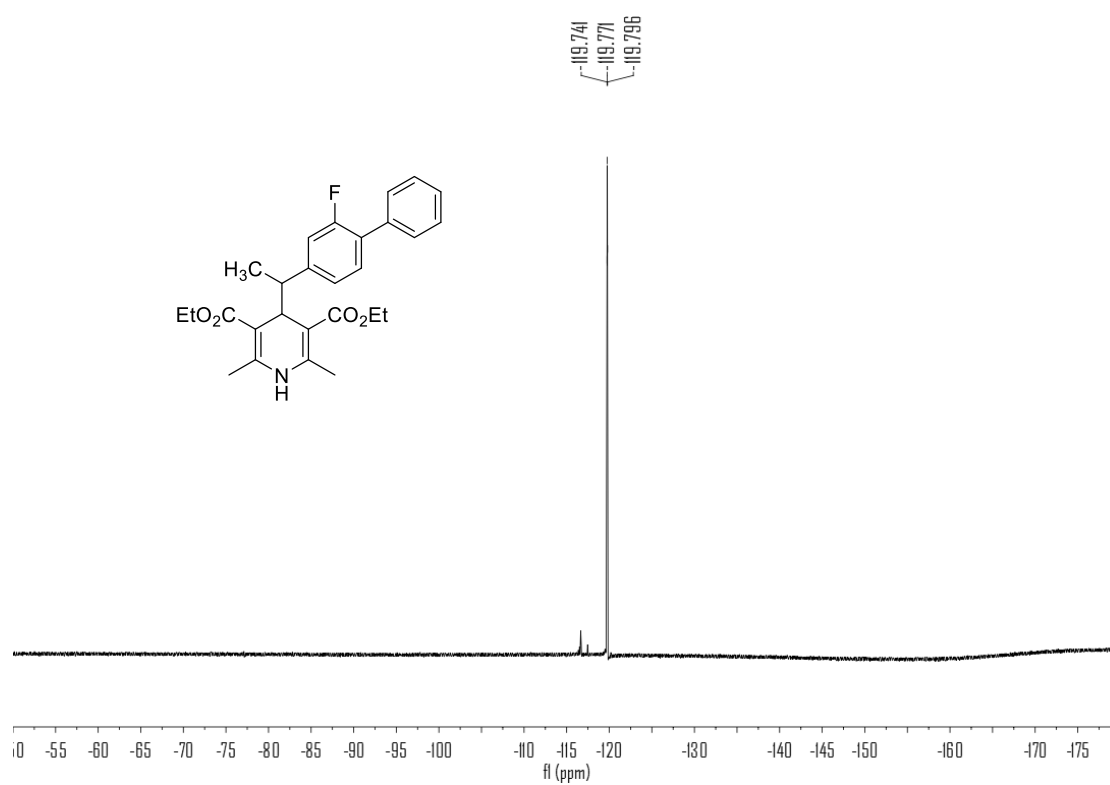
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 2q**



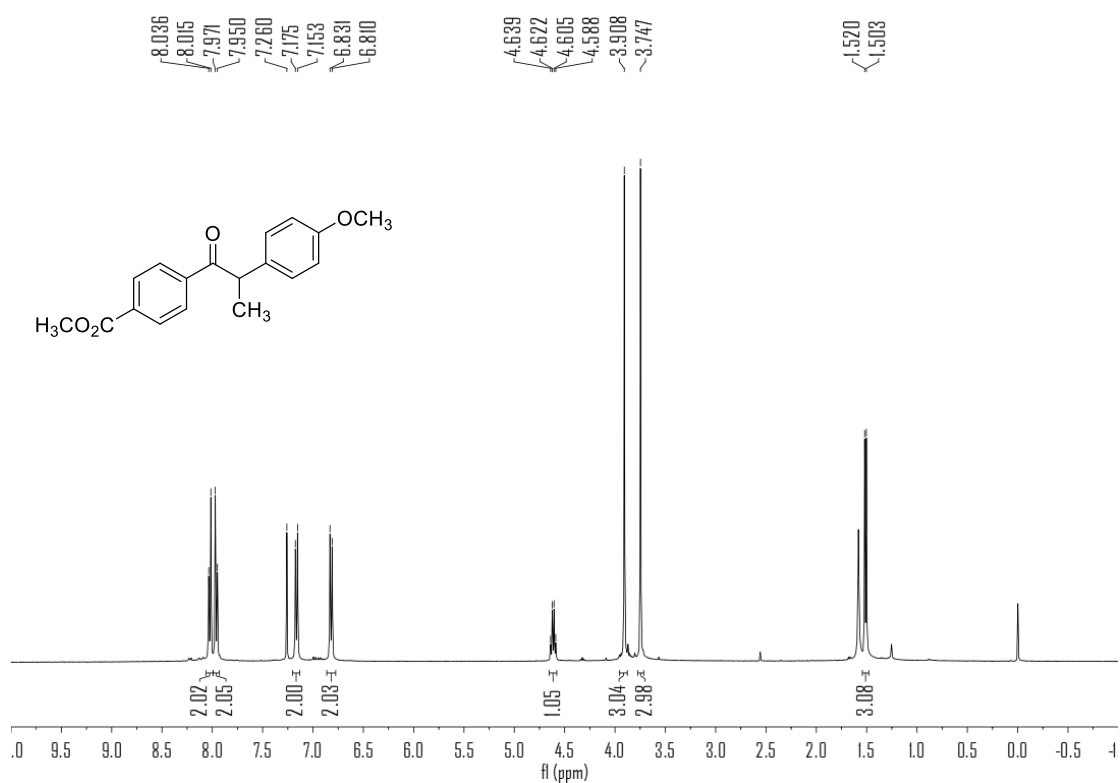
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 2q**



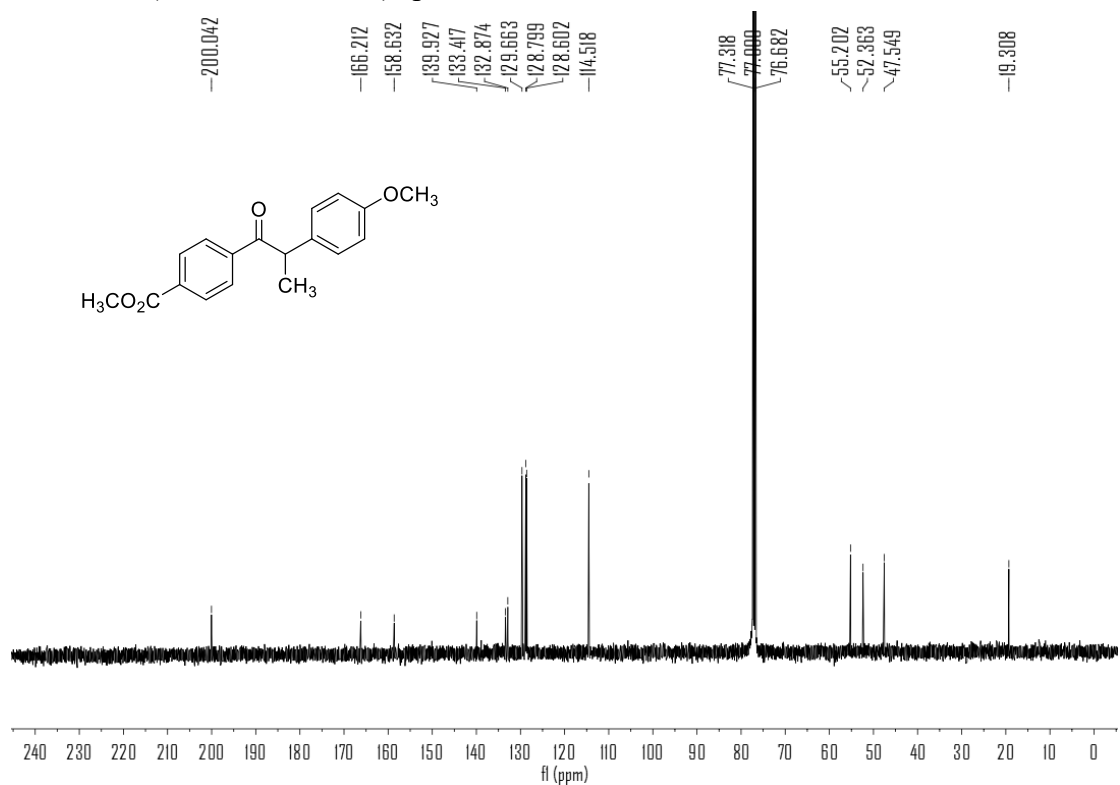
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectrum of **2q****



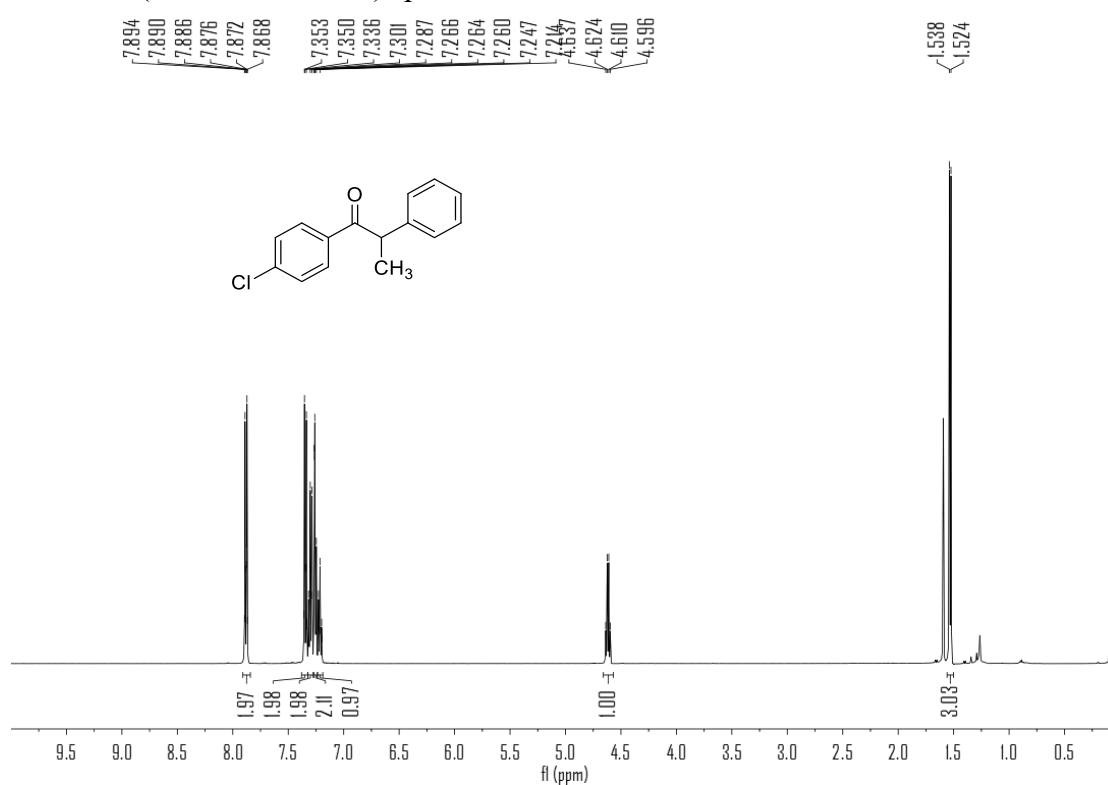
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3a****



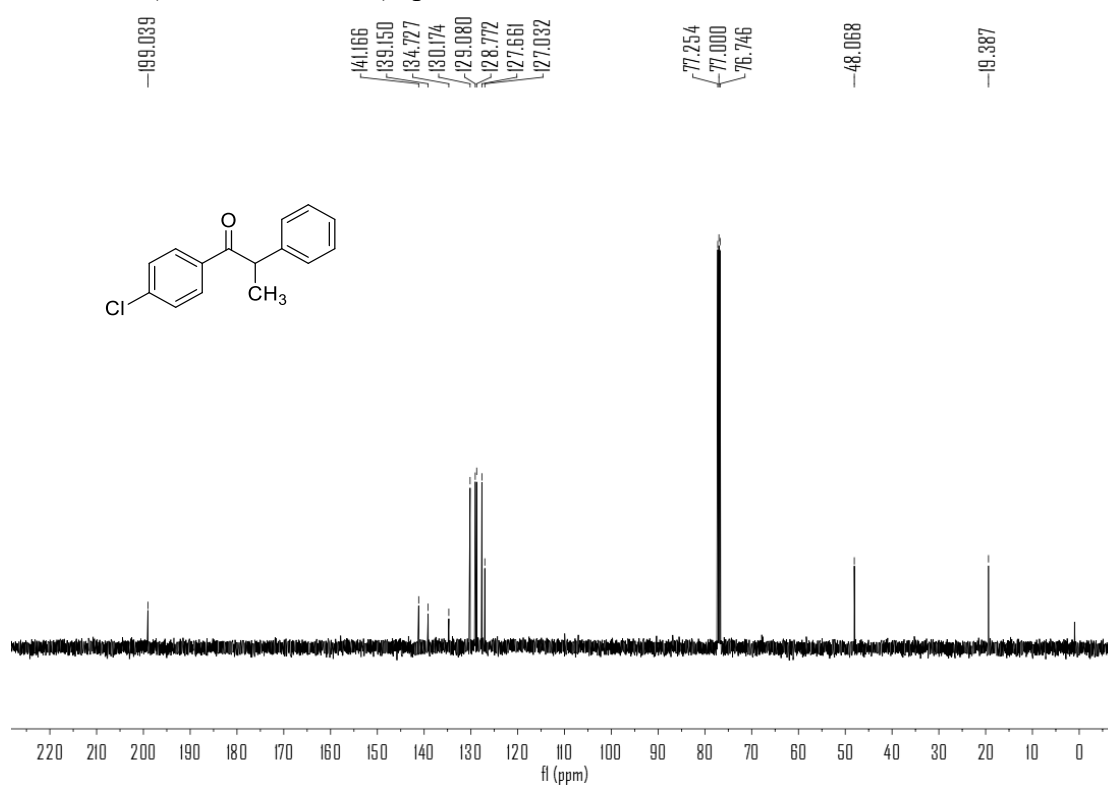
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3a****



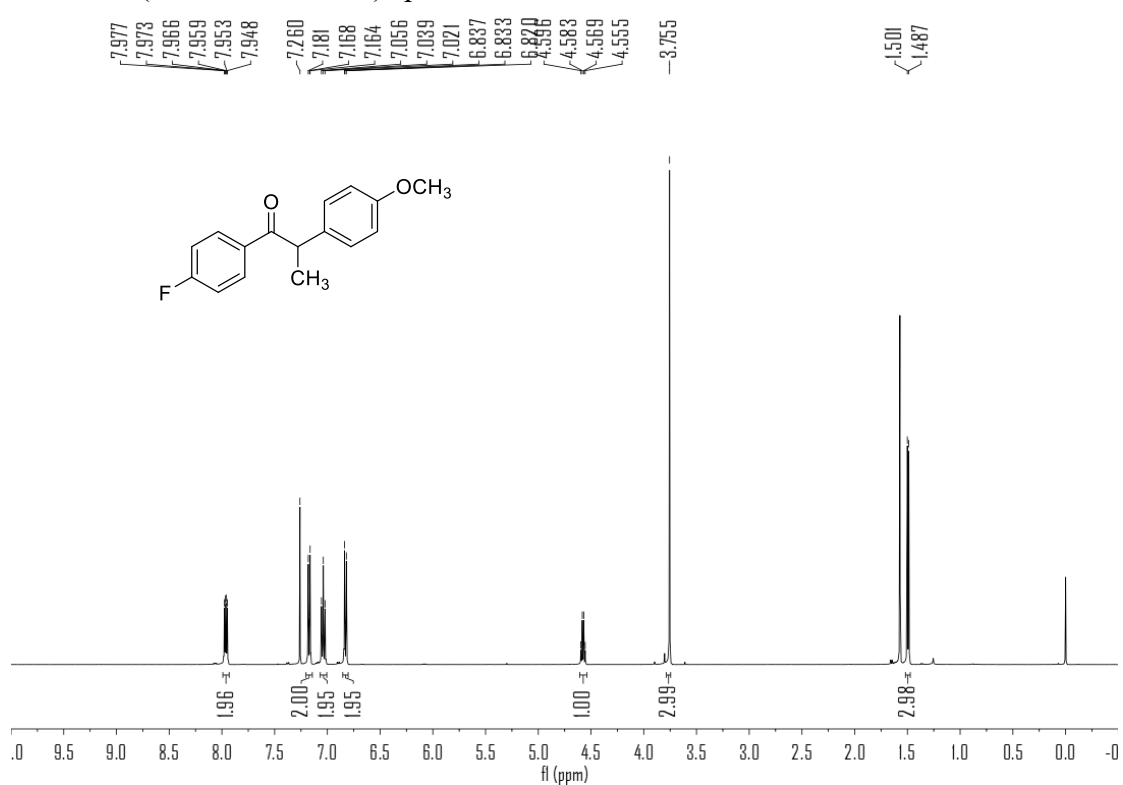
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **3b****



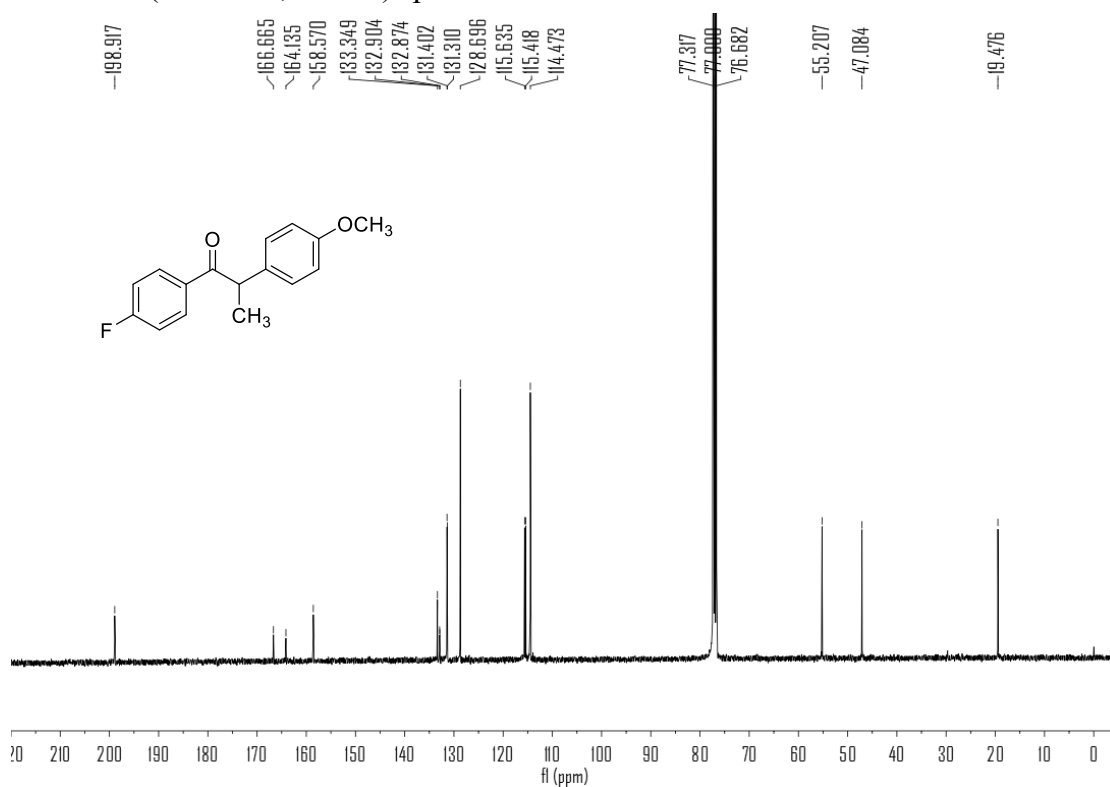
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **3b****



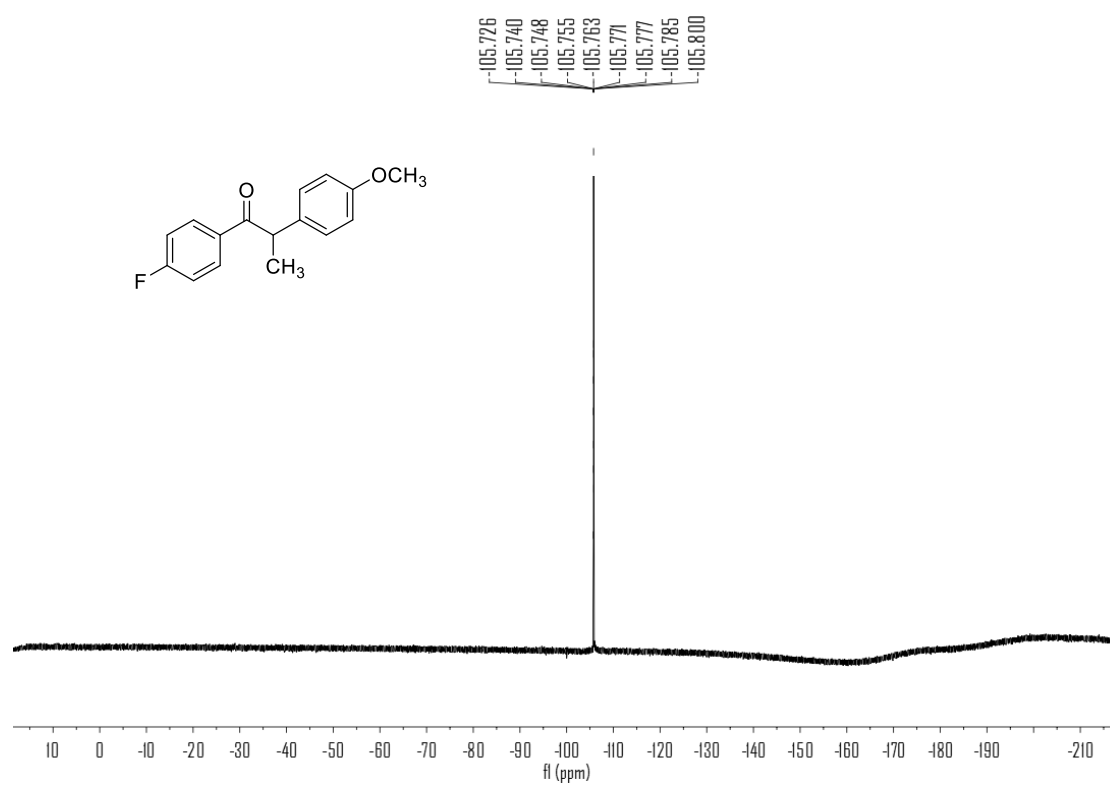
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 3c**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 3c**

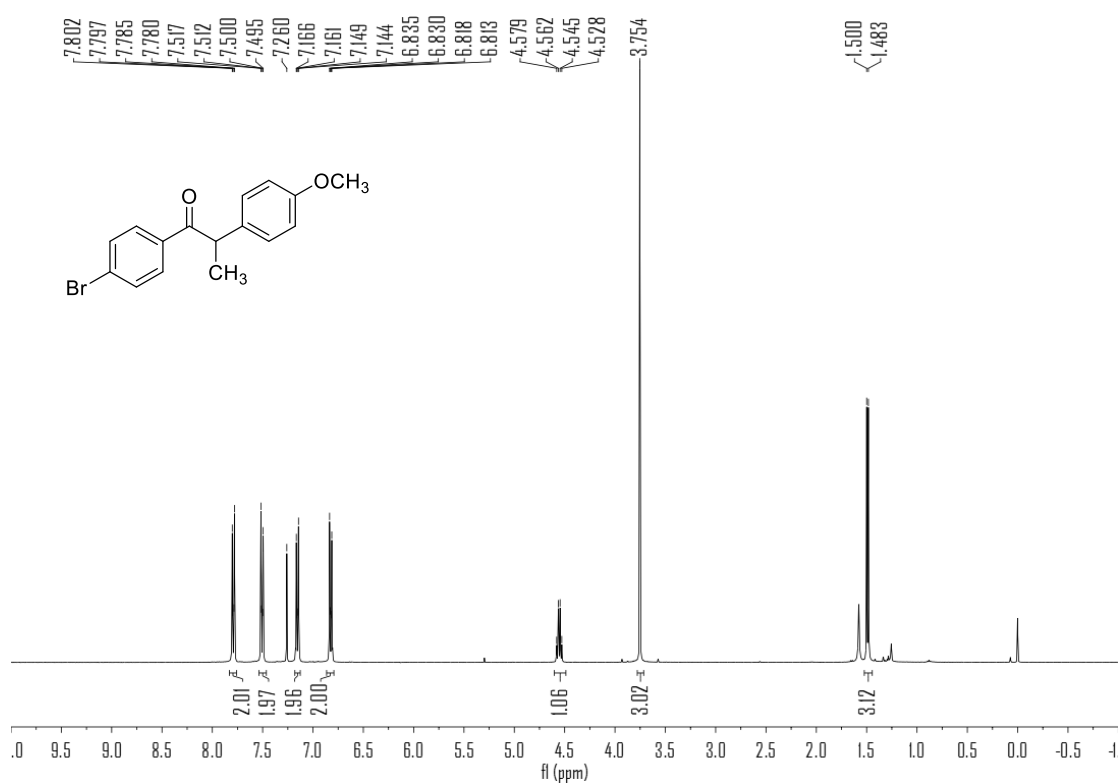


**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectrum of **3c****

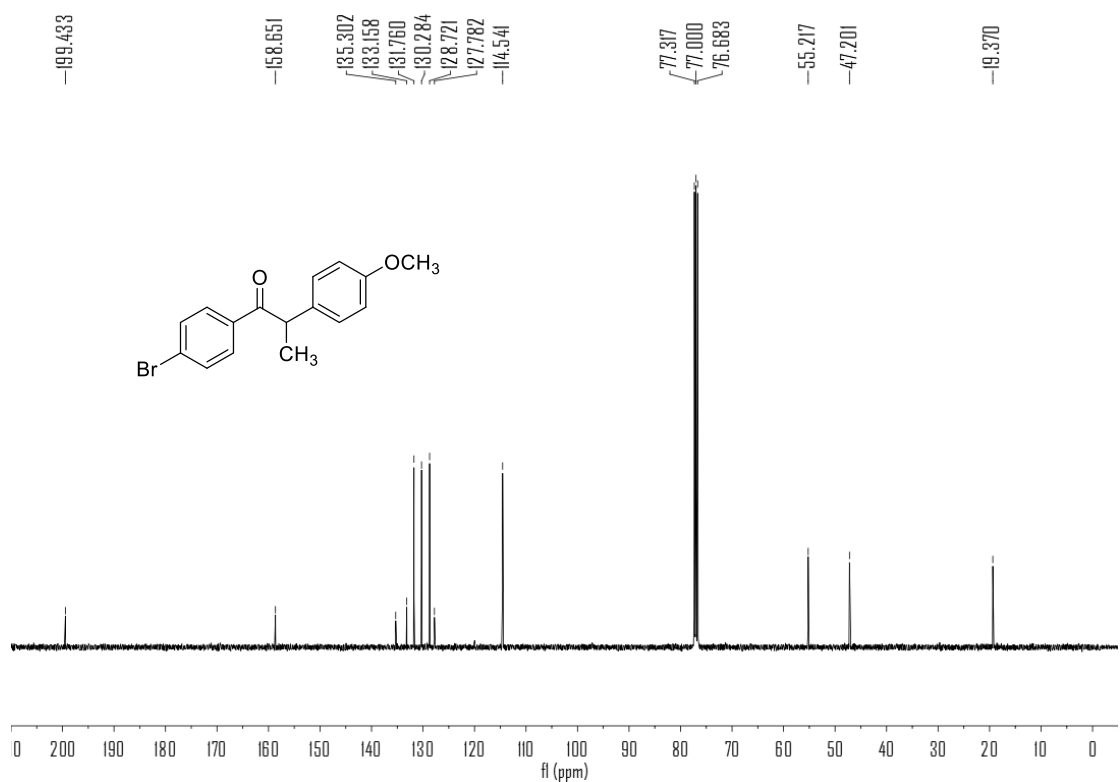




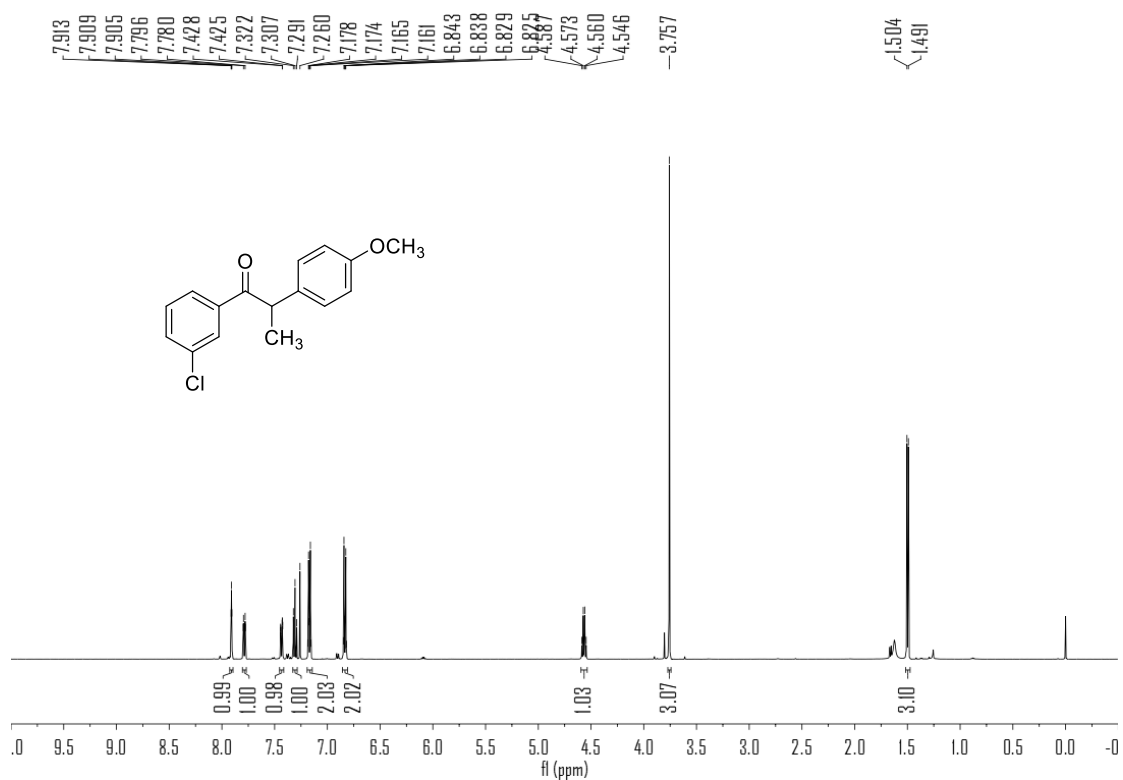
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 3d**



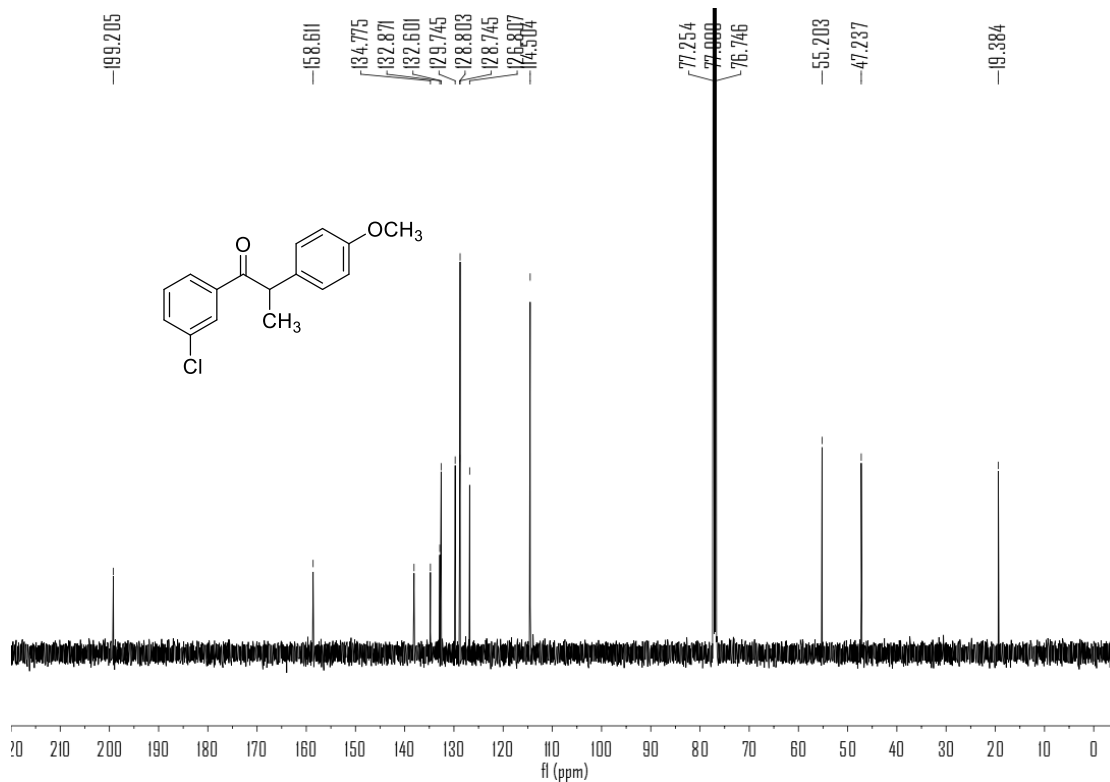
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 3d**



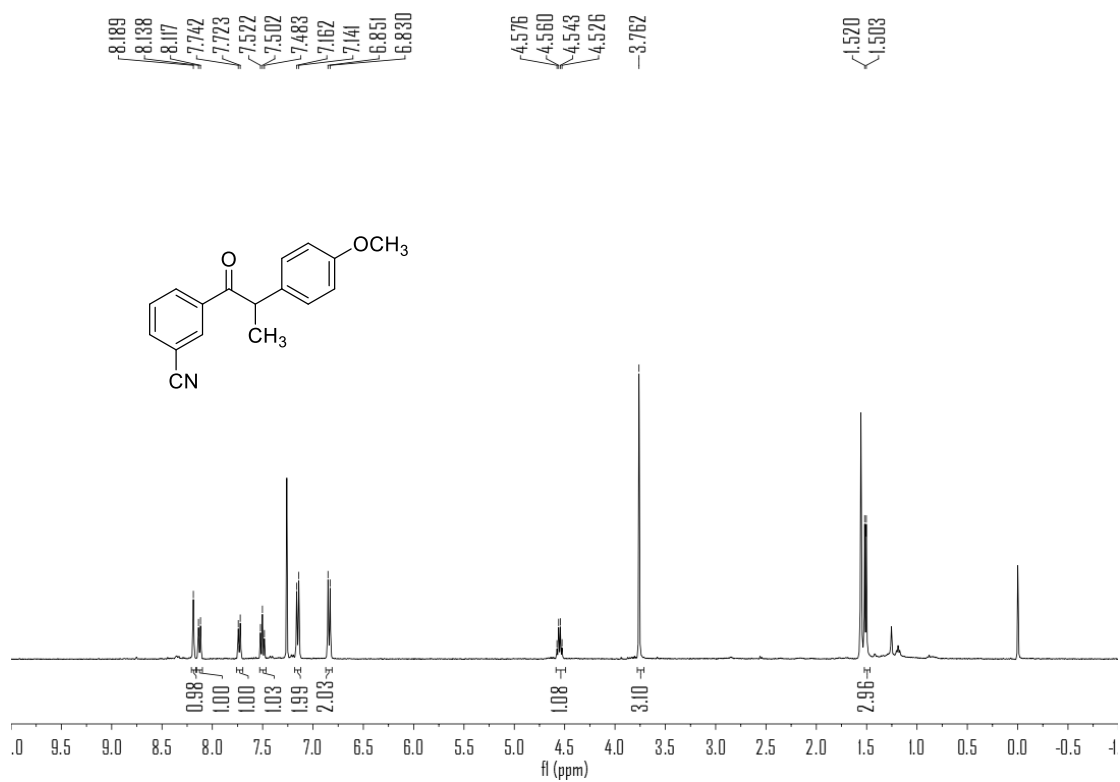
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **3e****



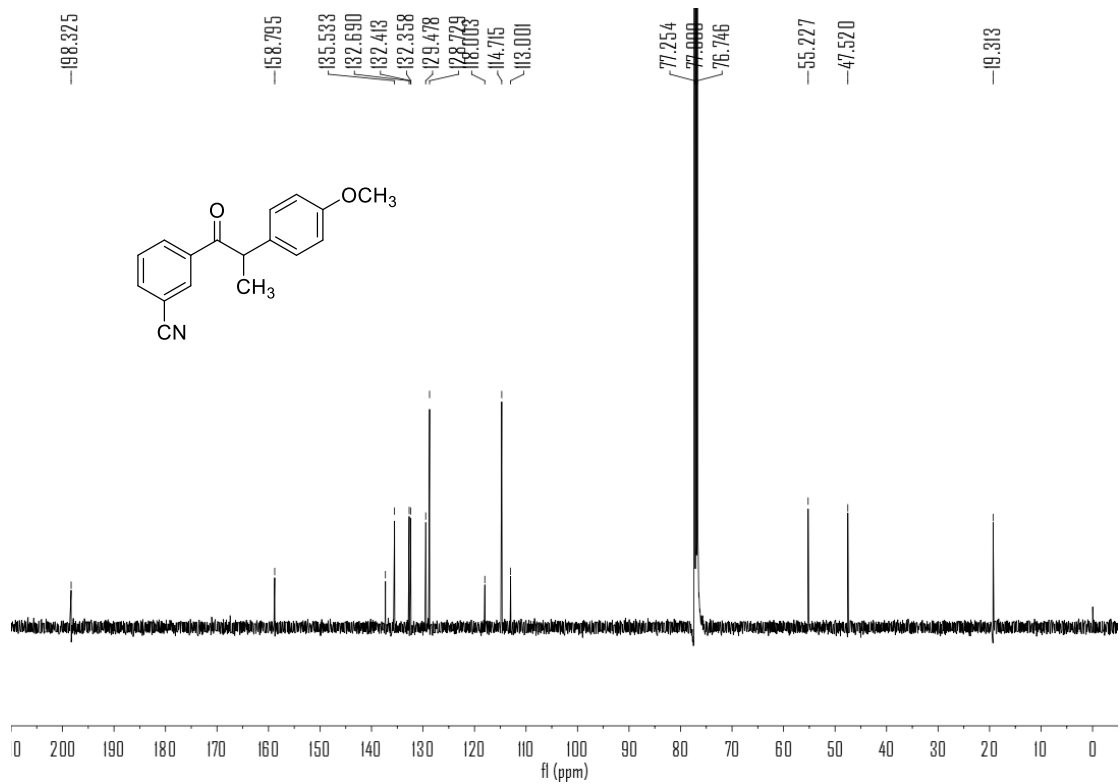
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **3e****



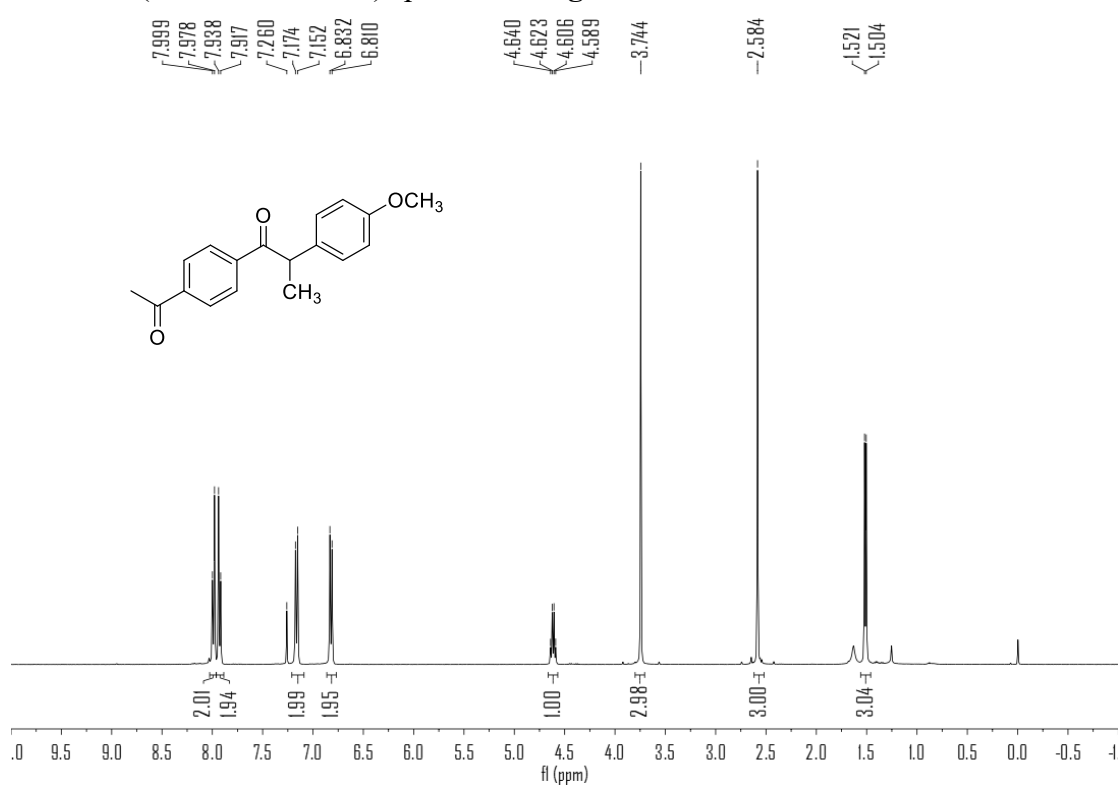
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3f****



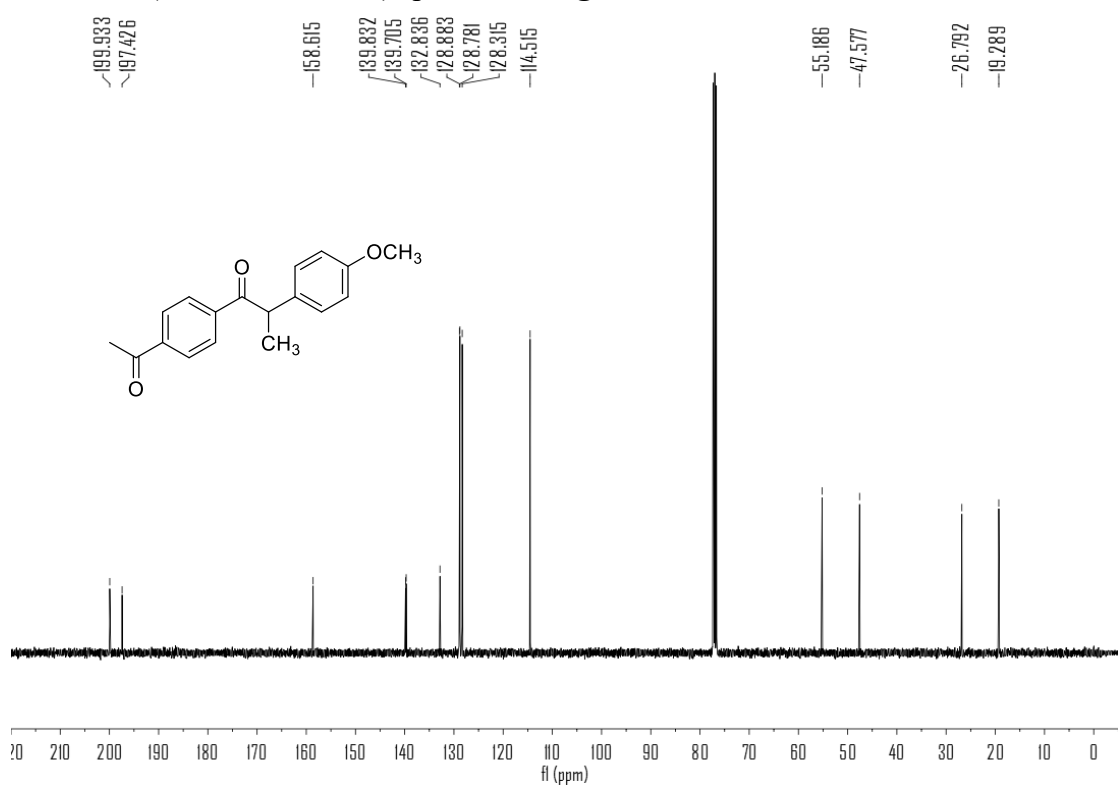
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **3f****



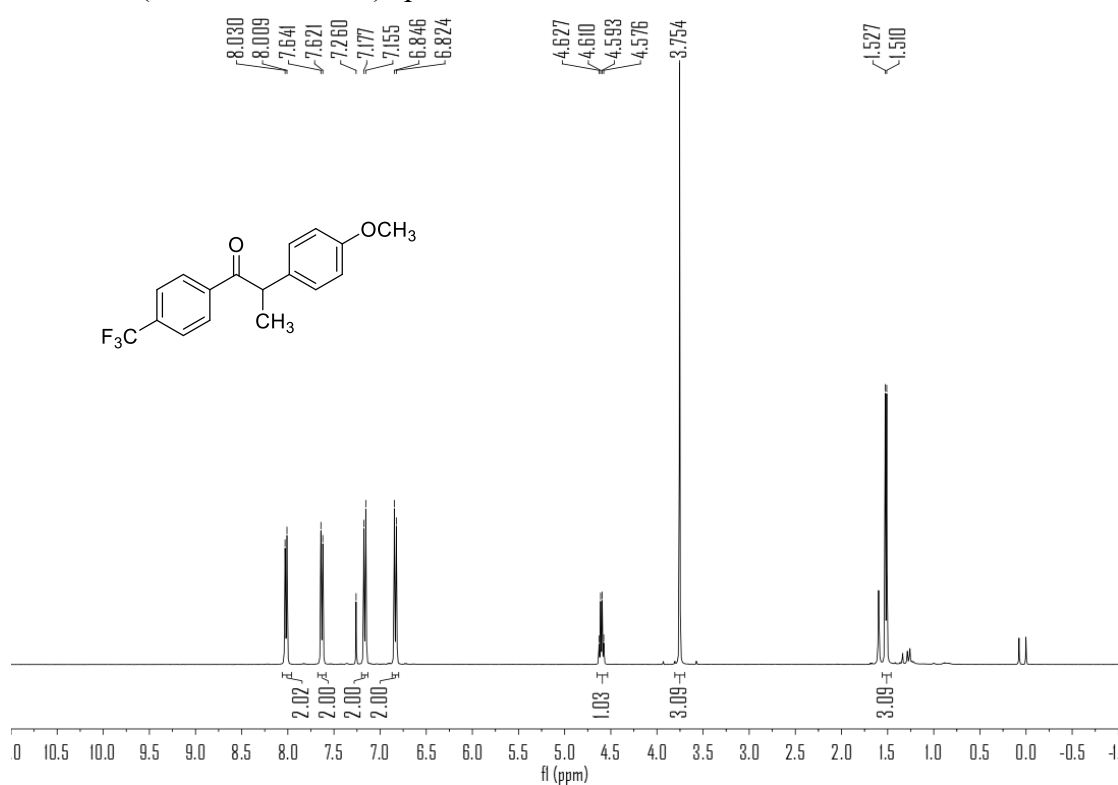
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3g****



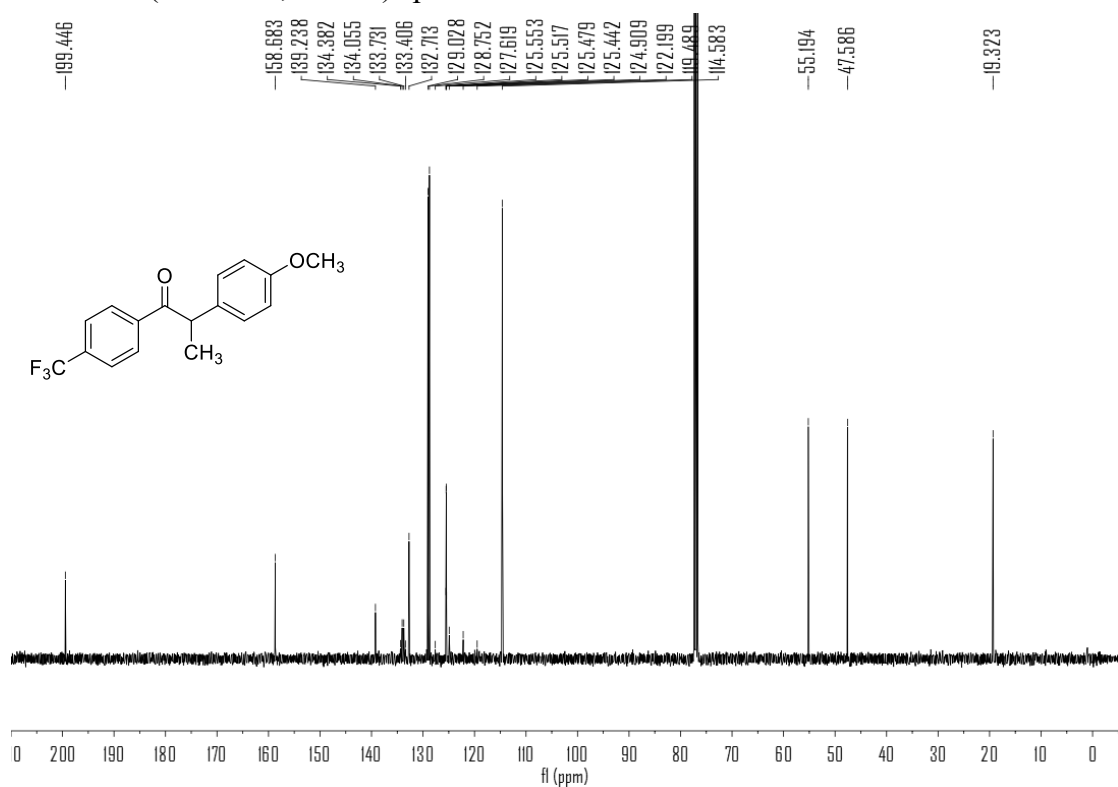
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3g****



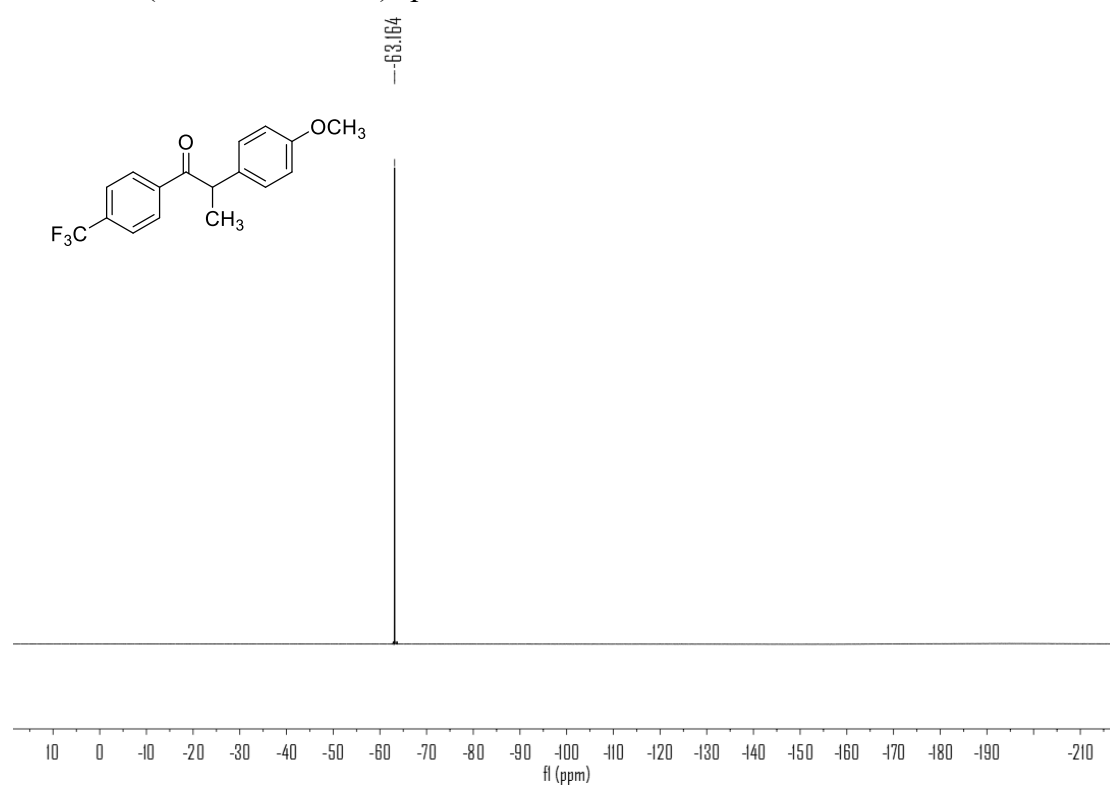
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3h****



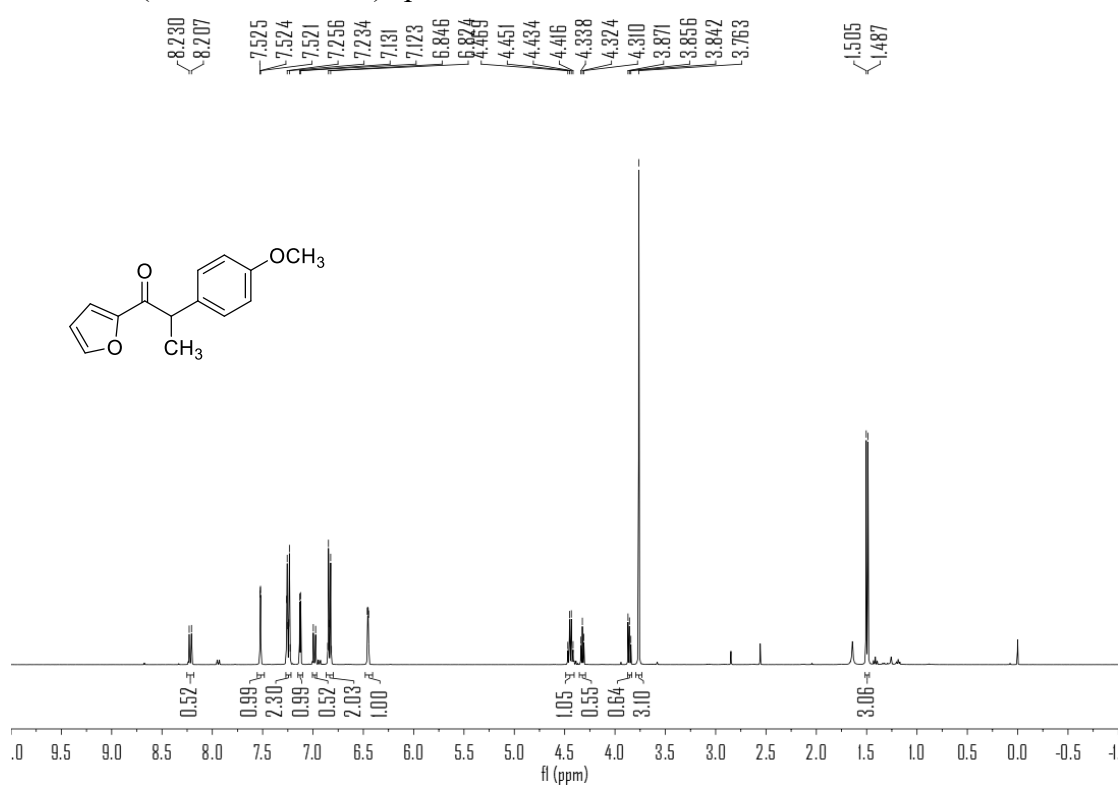
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3h****



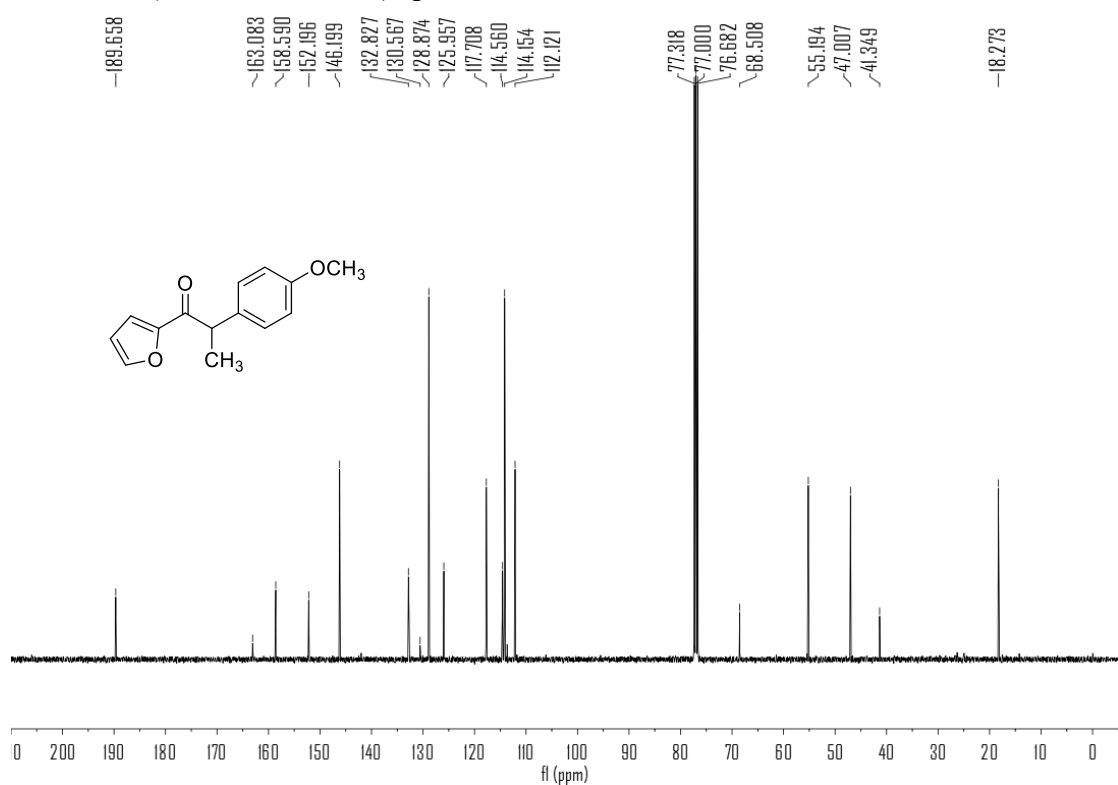
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) spectrum of **3h**



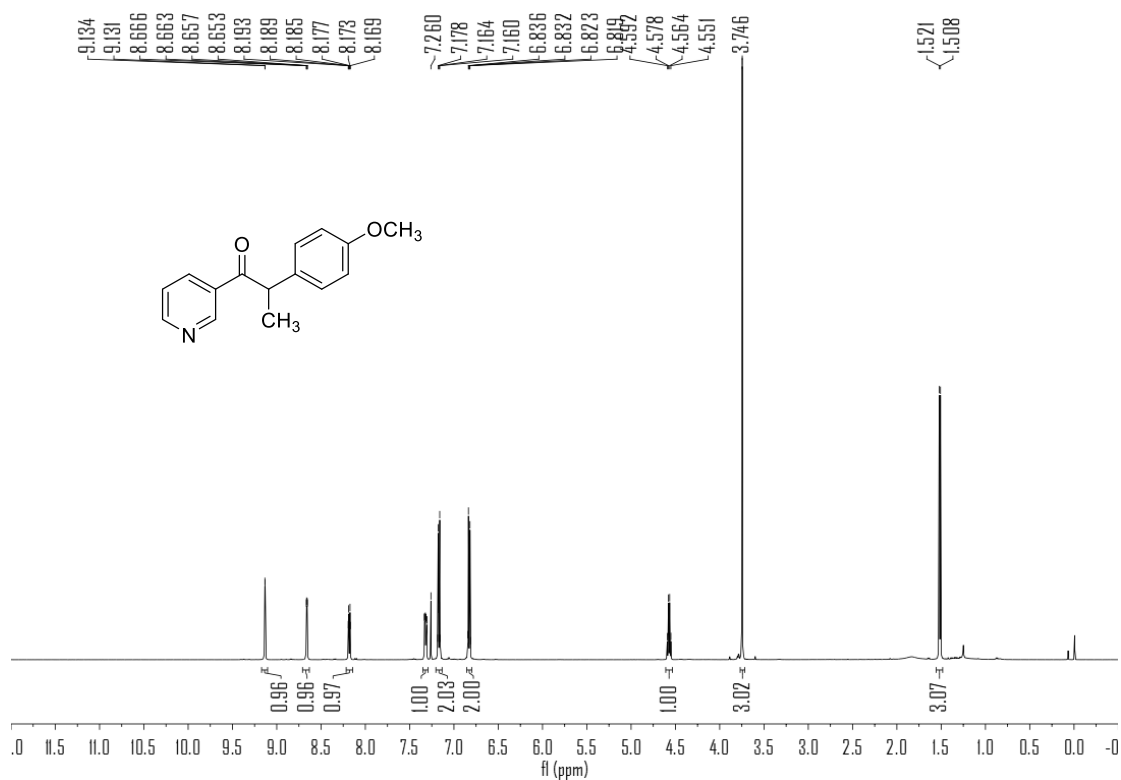
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3i****



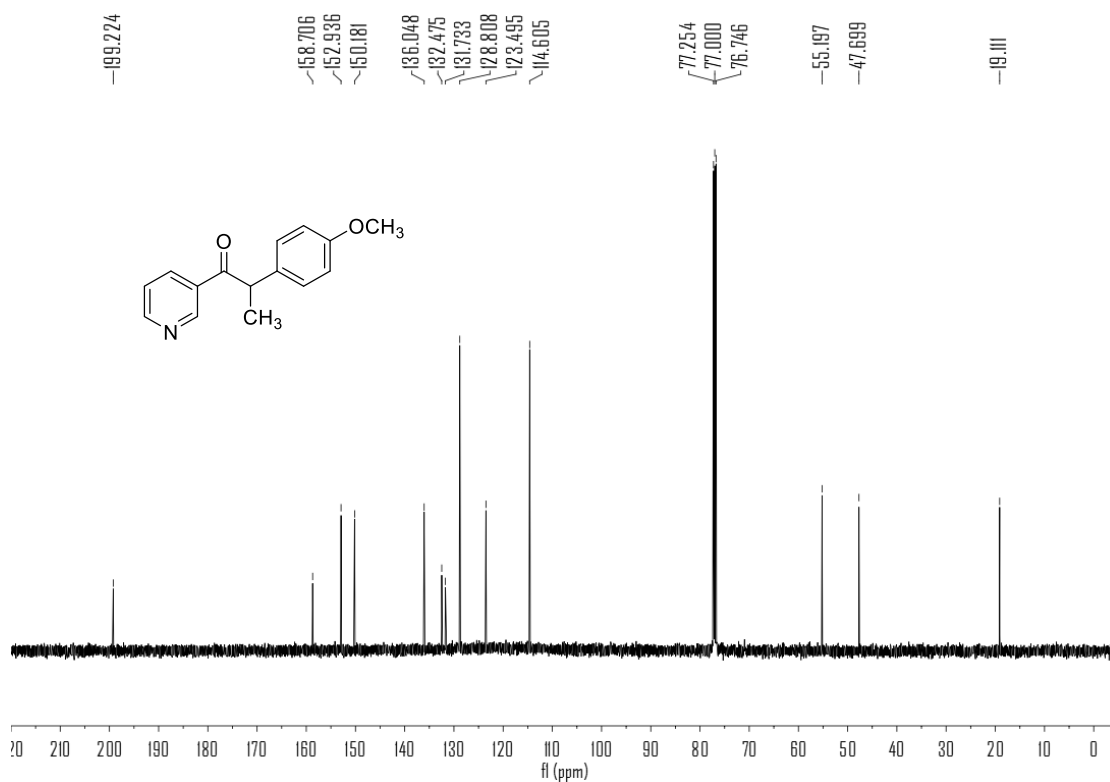
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3i****



**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **3j****

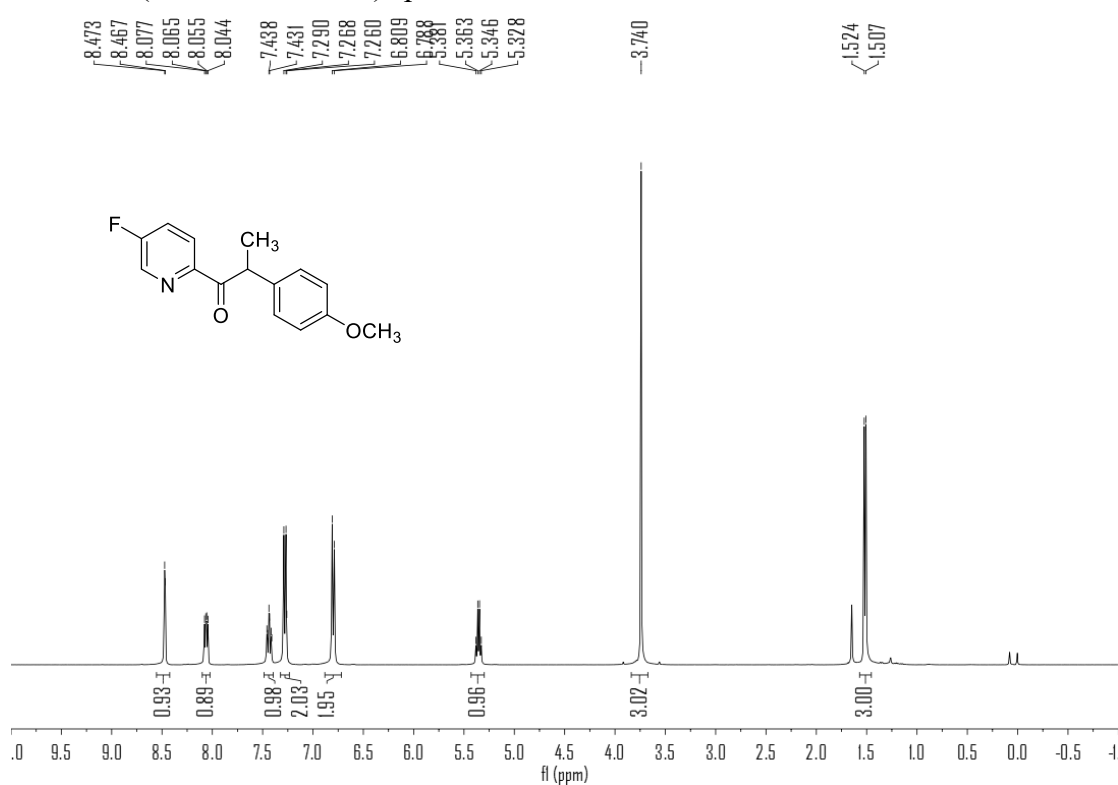


**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **3j****

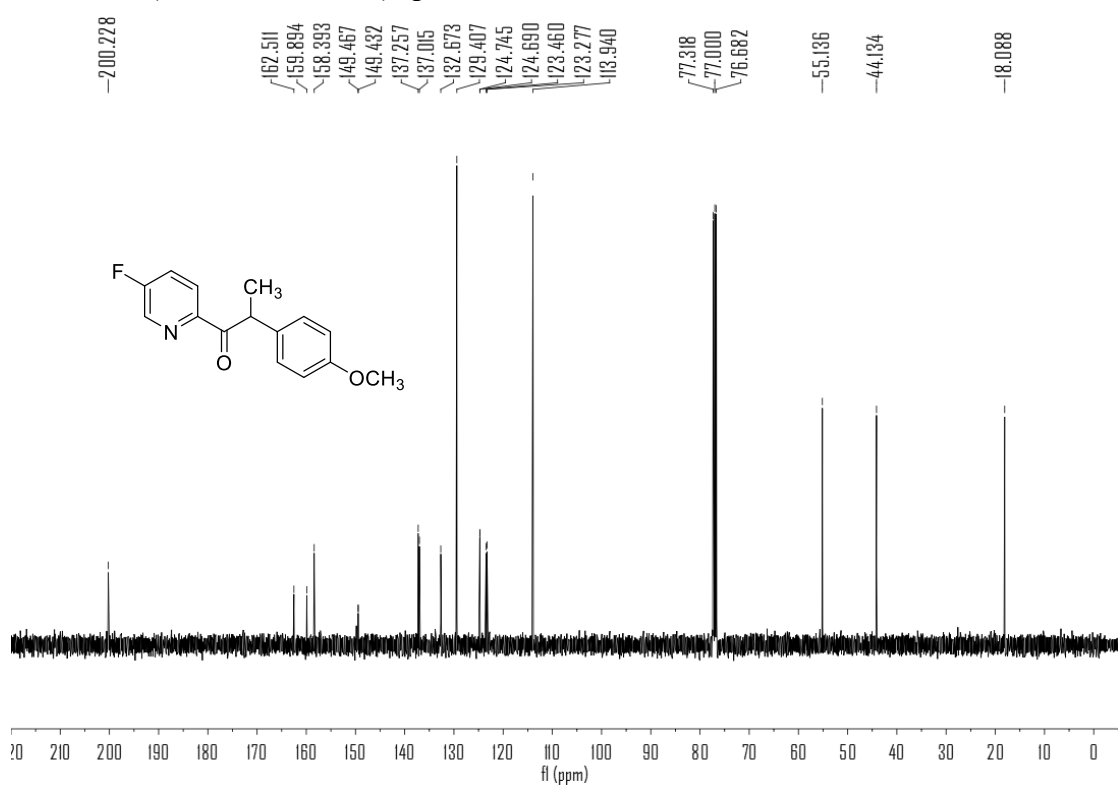




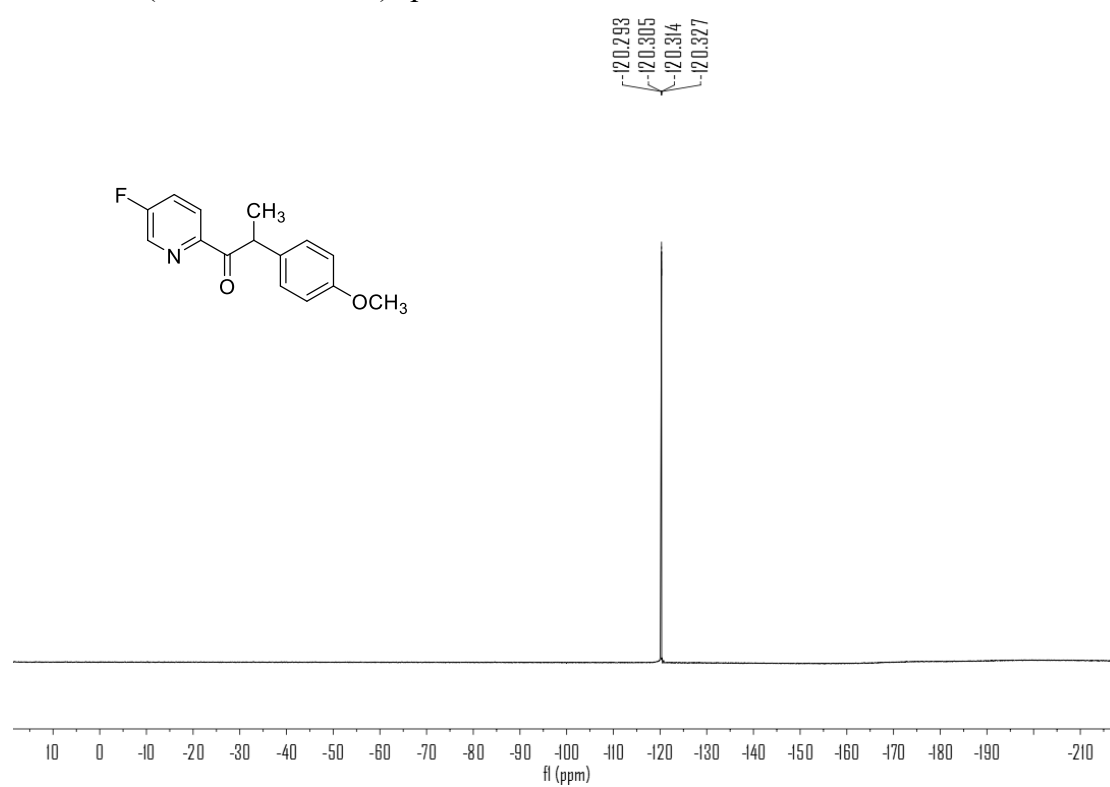
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3k****



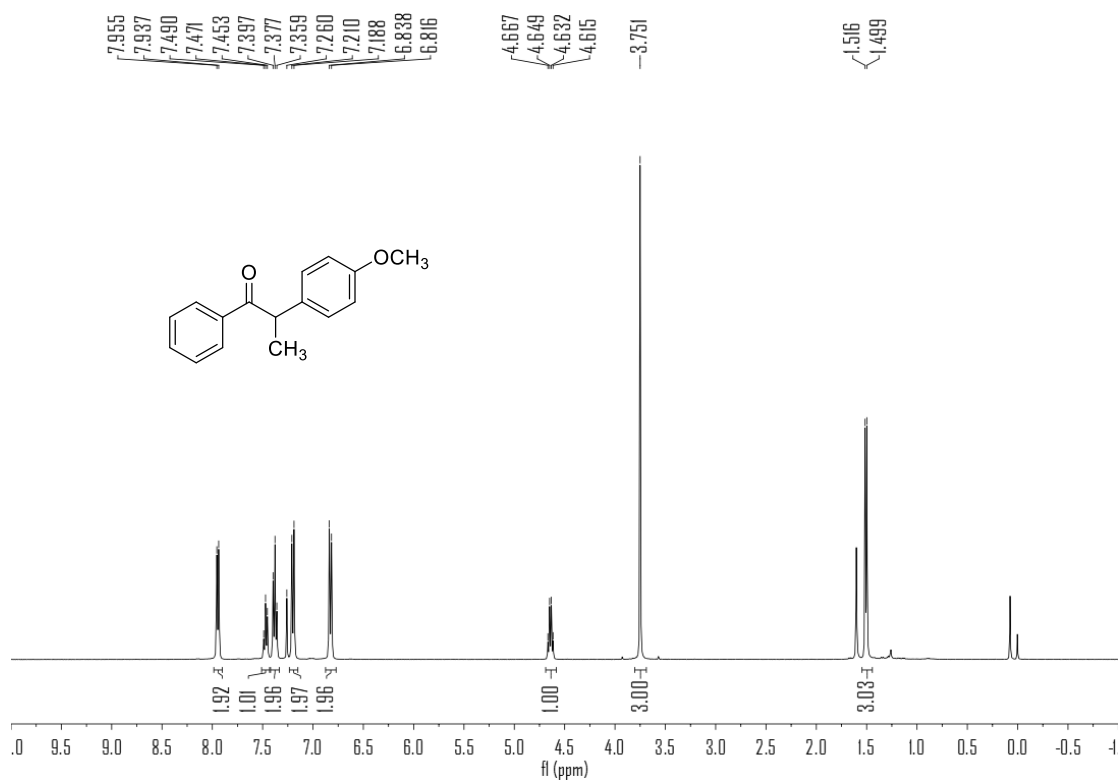
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3k****



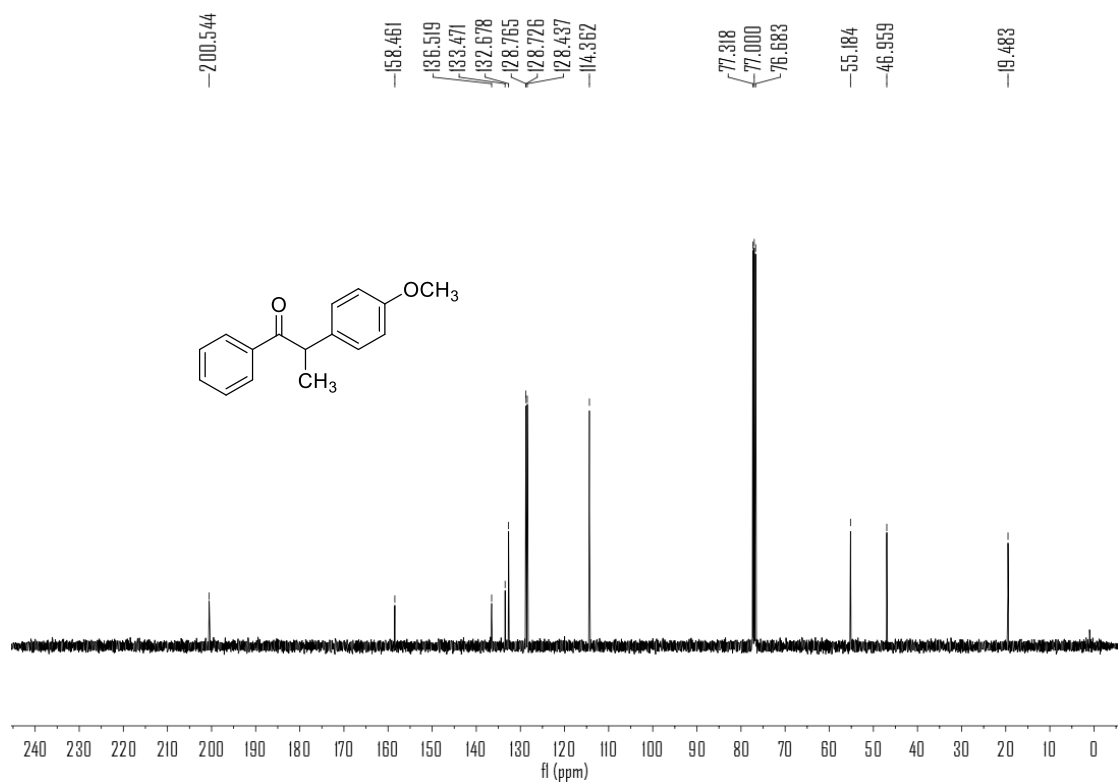
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectrum of **3k****



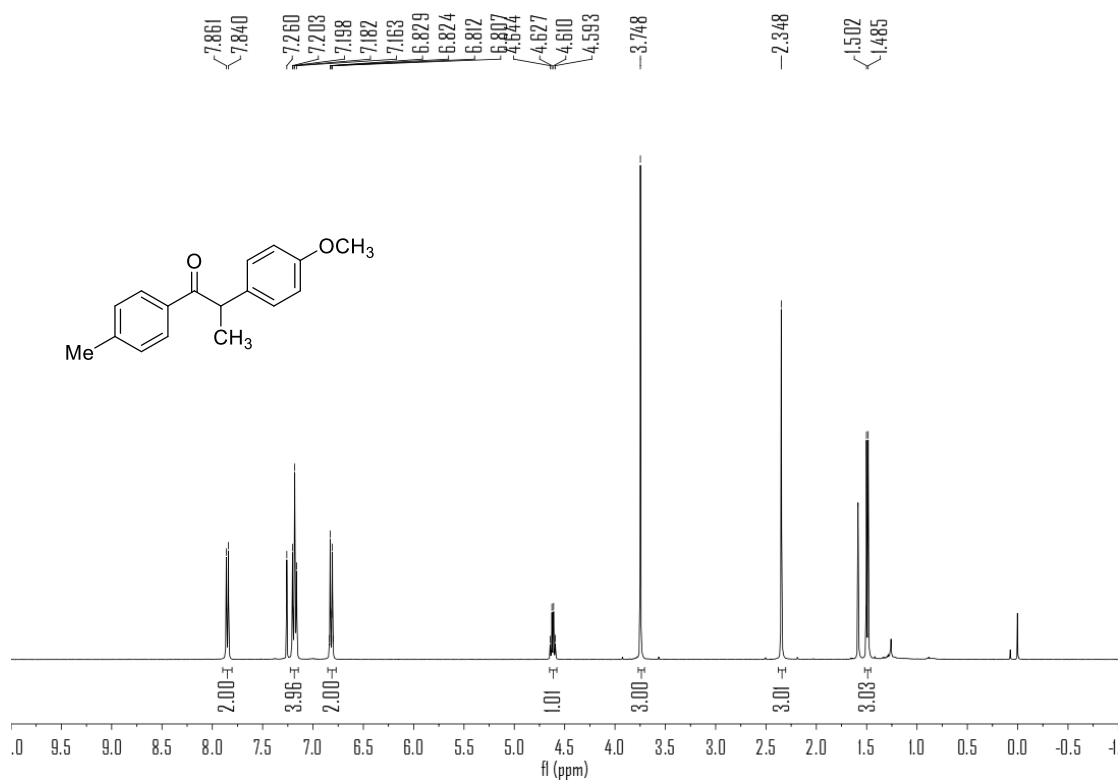
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **31****



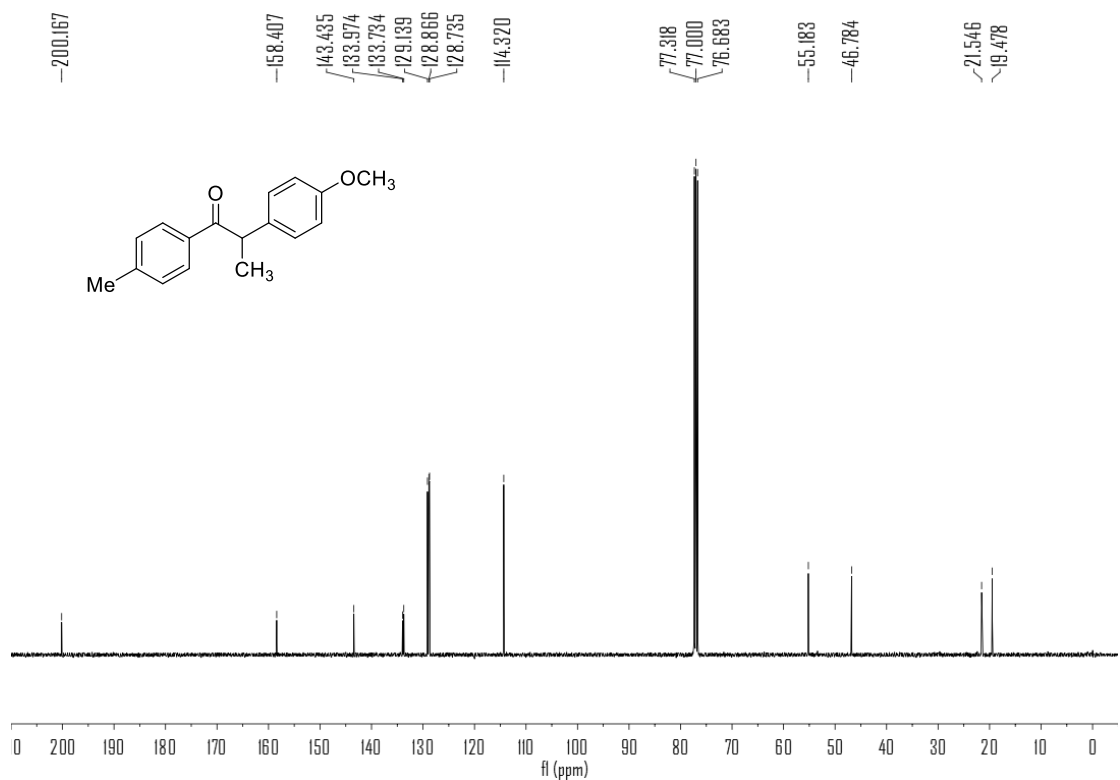
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **31****



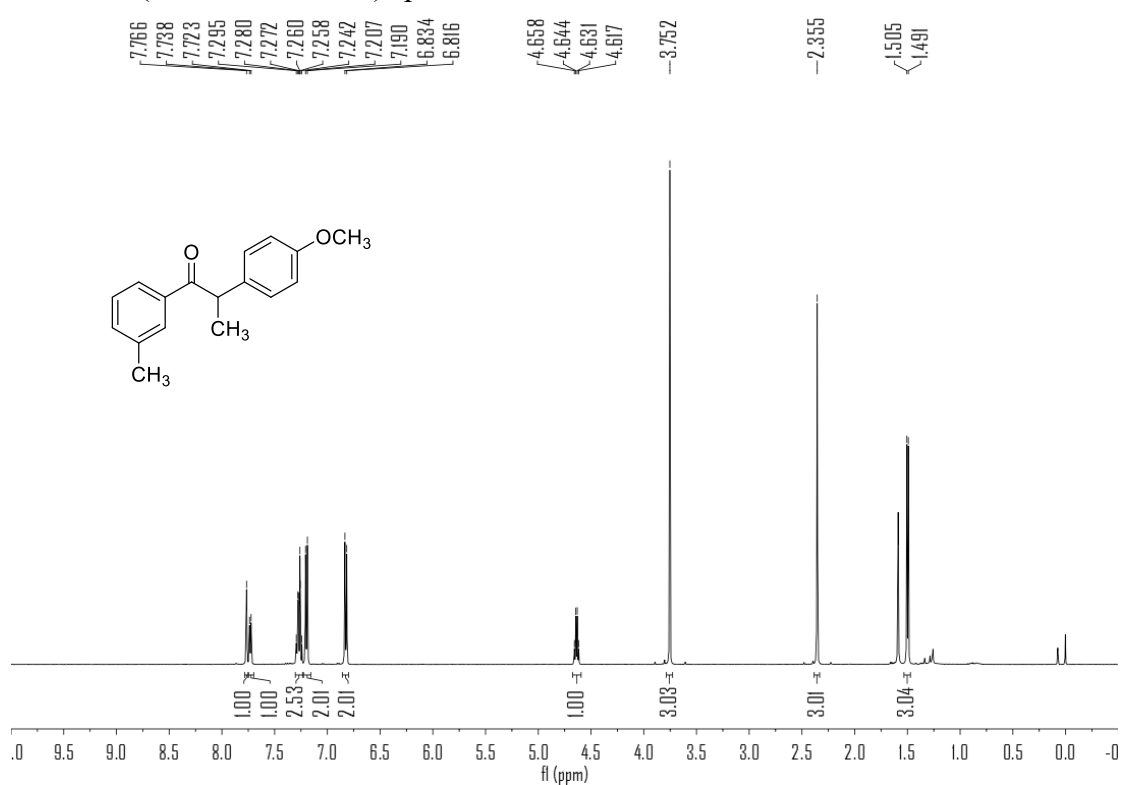
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3m****



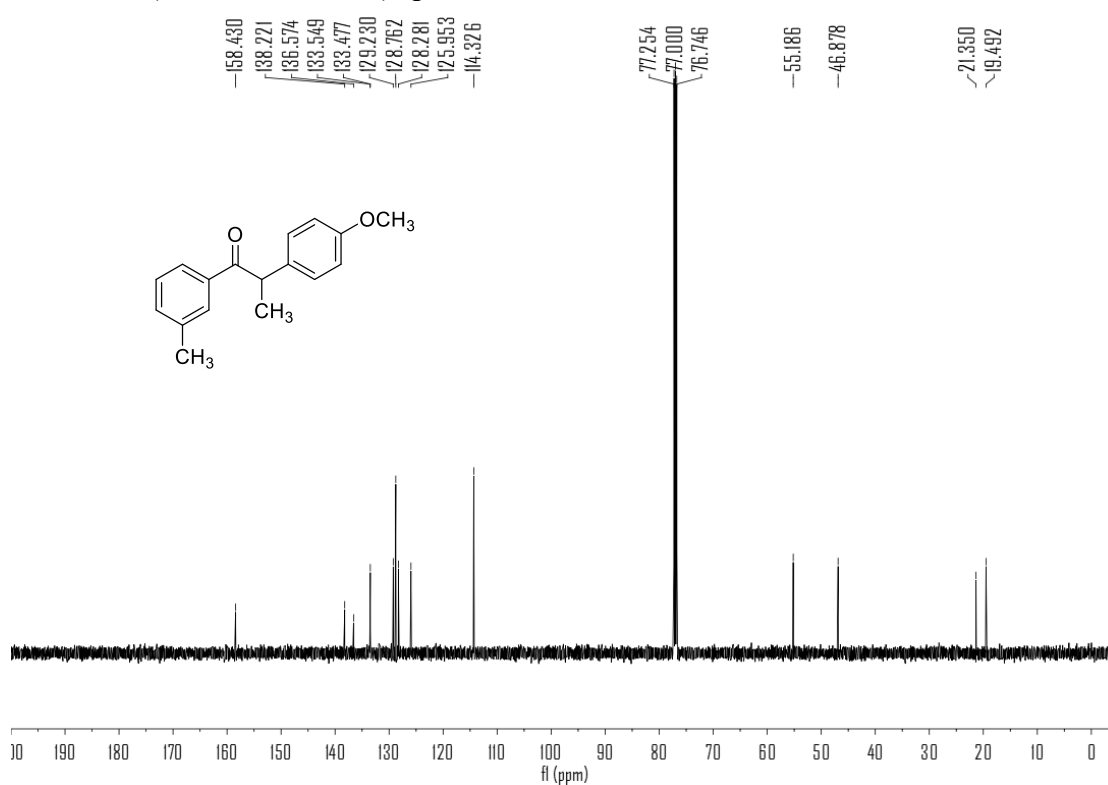
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3m****



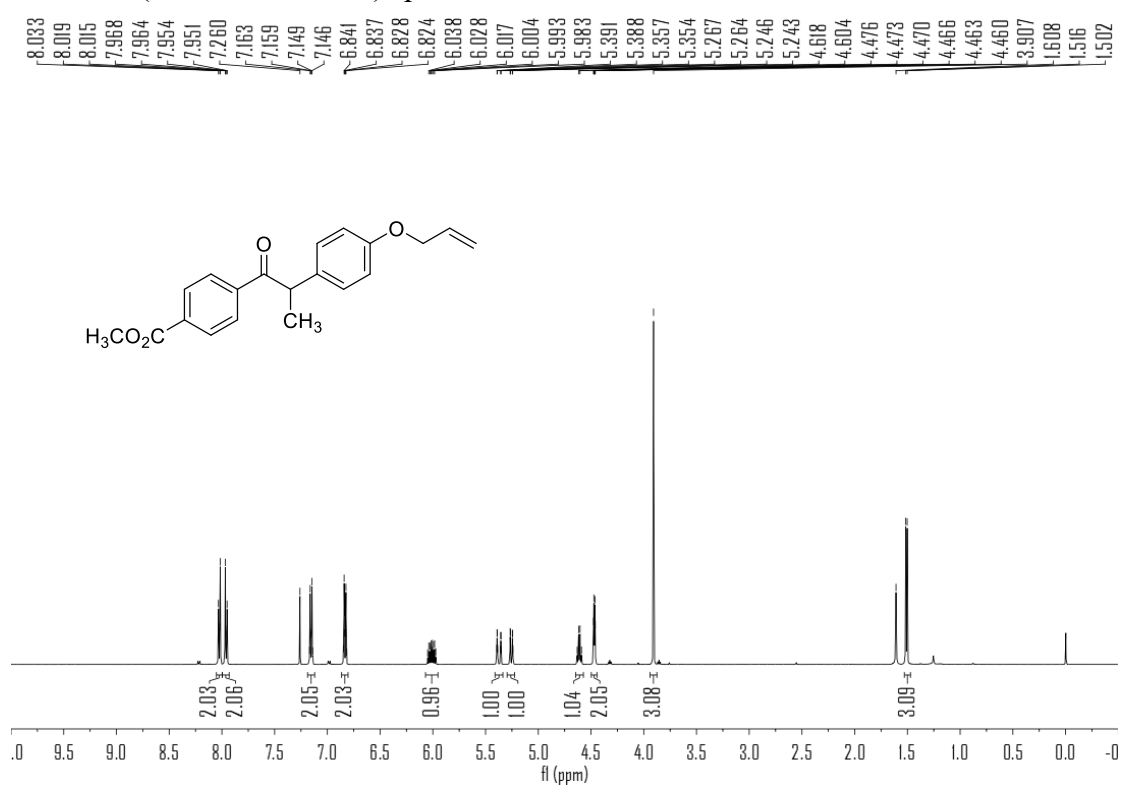
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **3n****



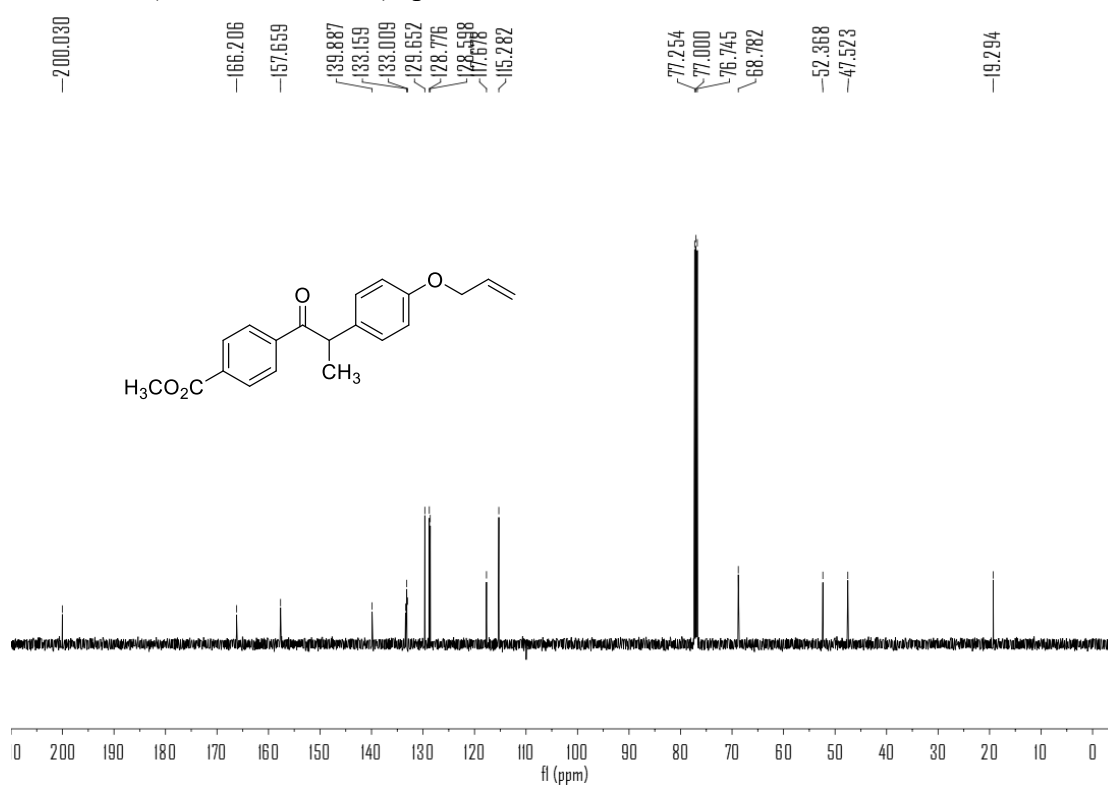
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **3n****



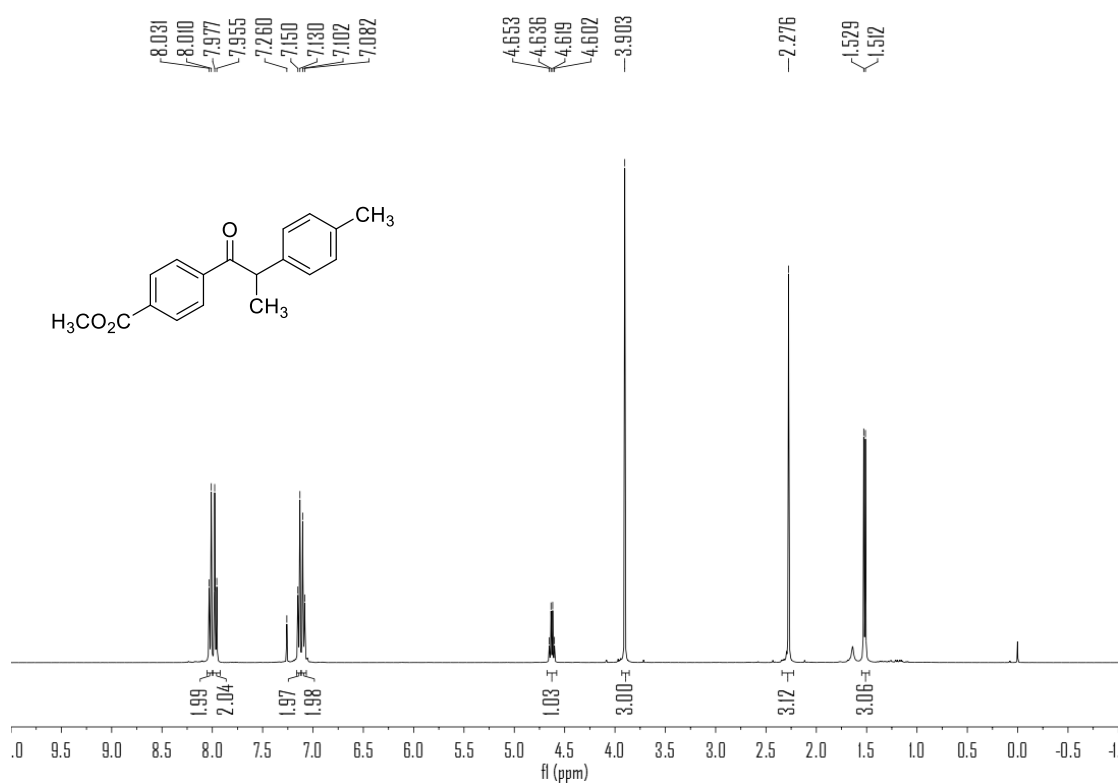
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4a**



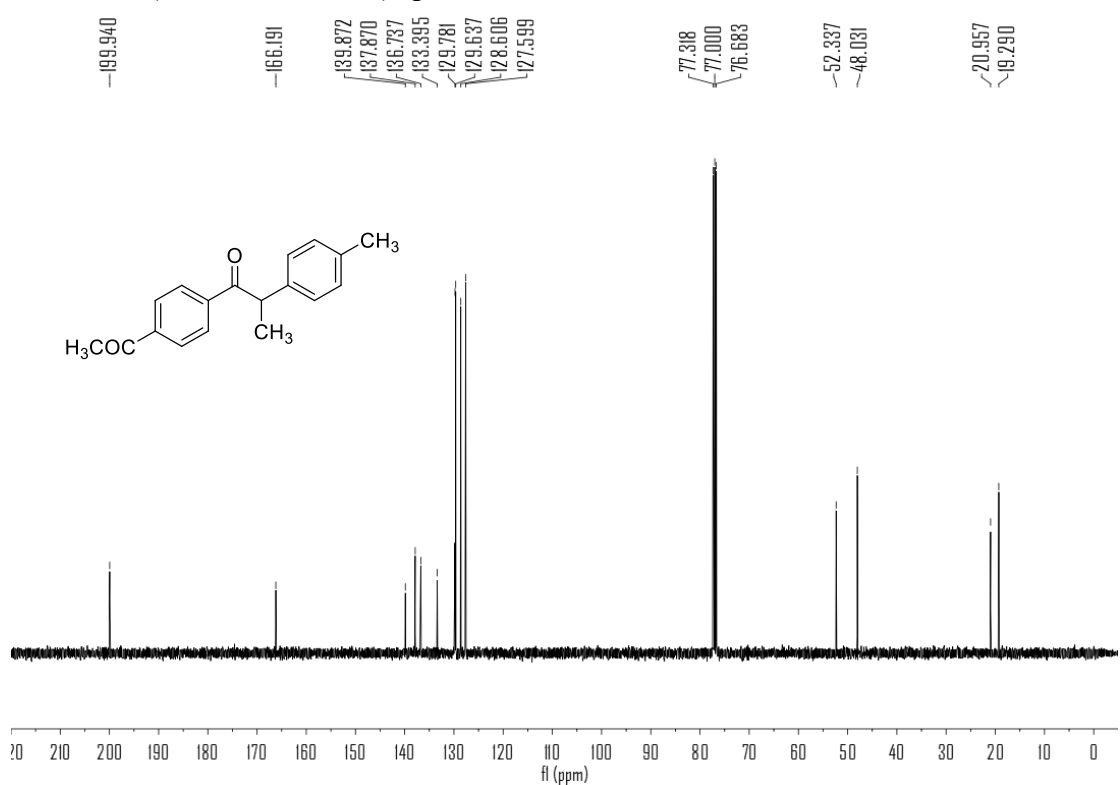
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4a**



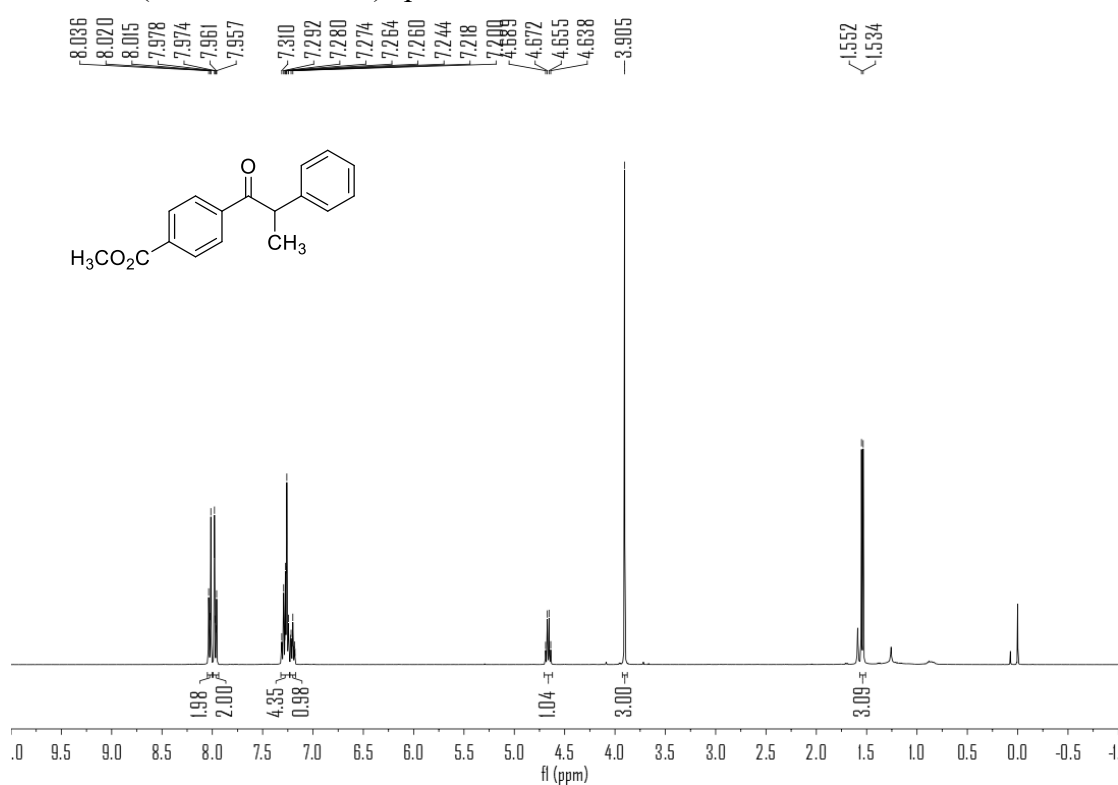
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4b**



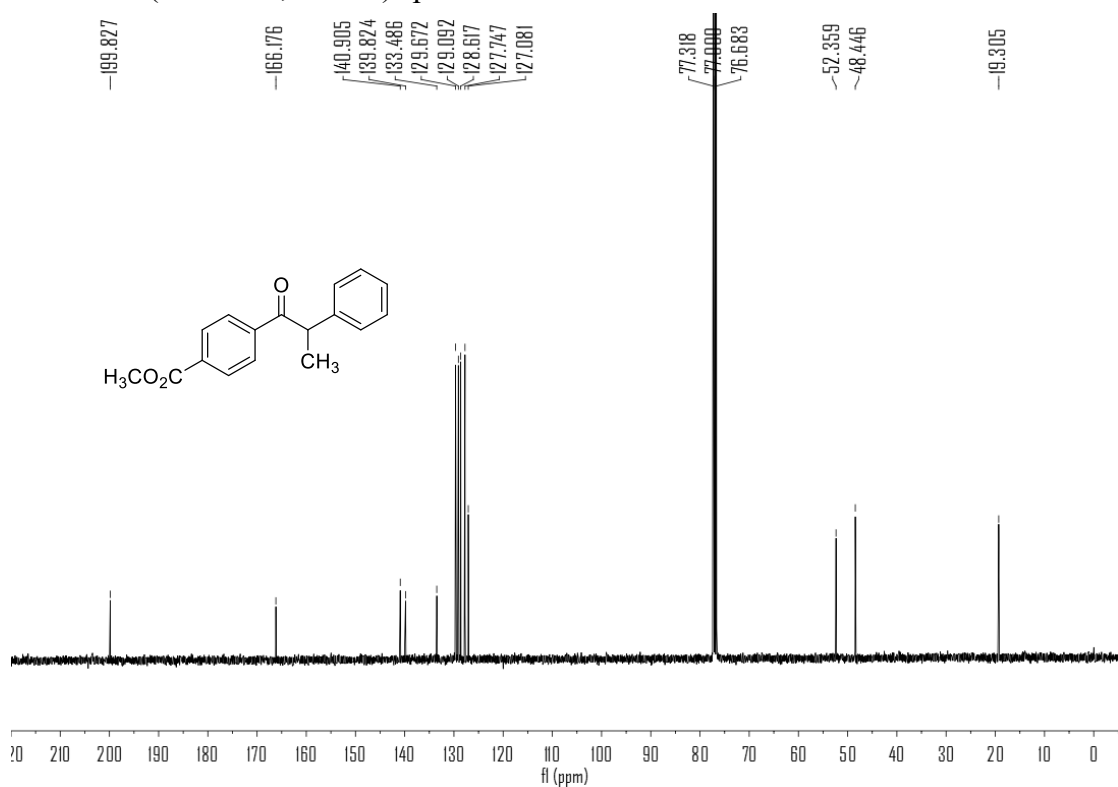
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4b**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4c**

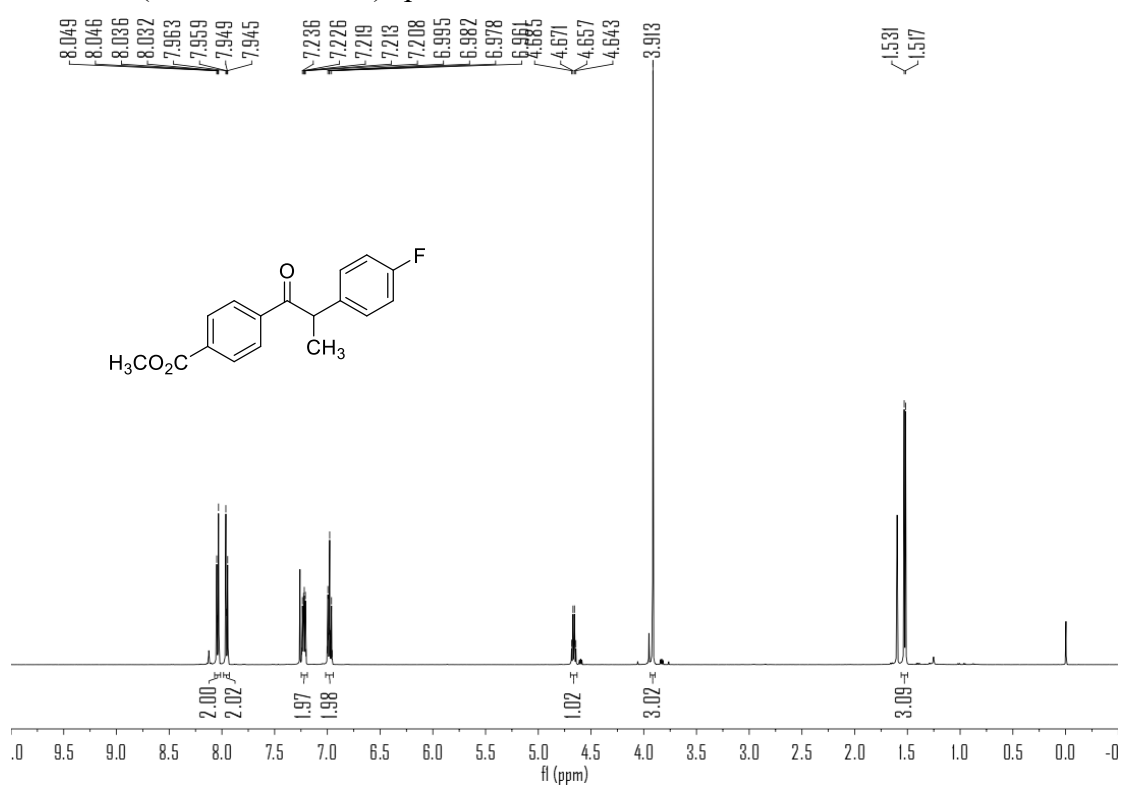


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4c**

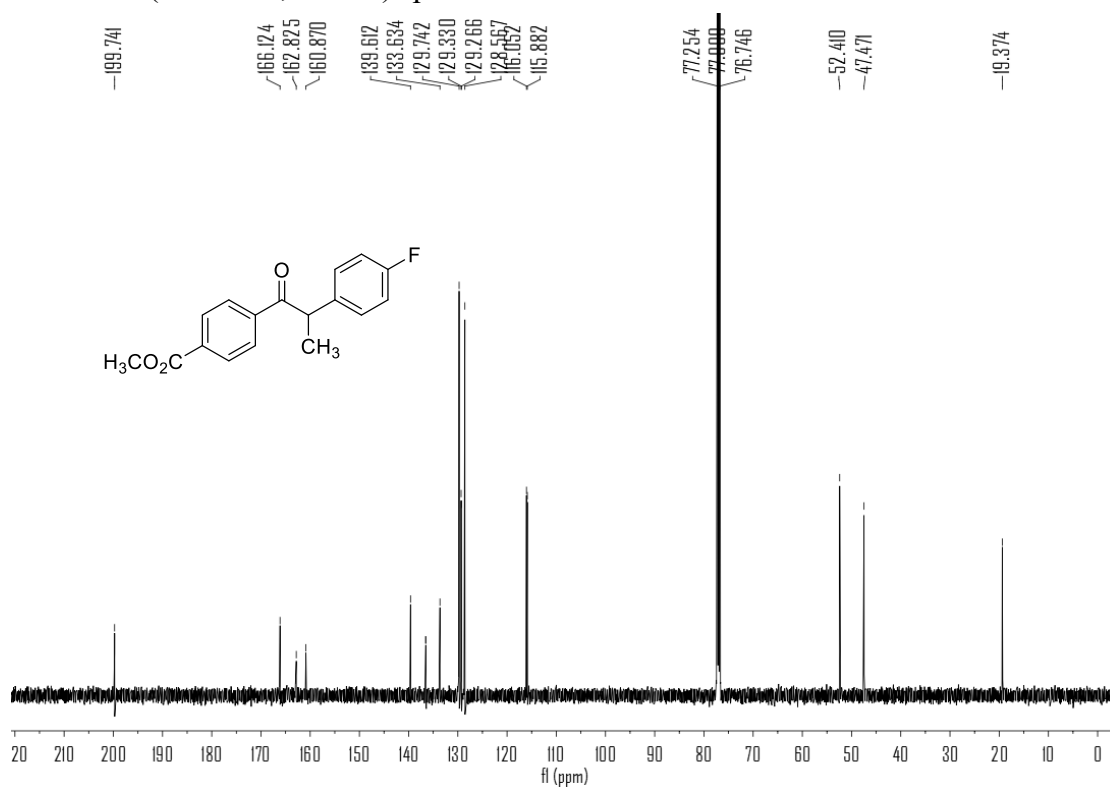




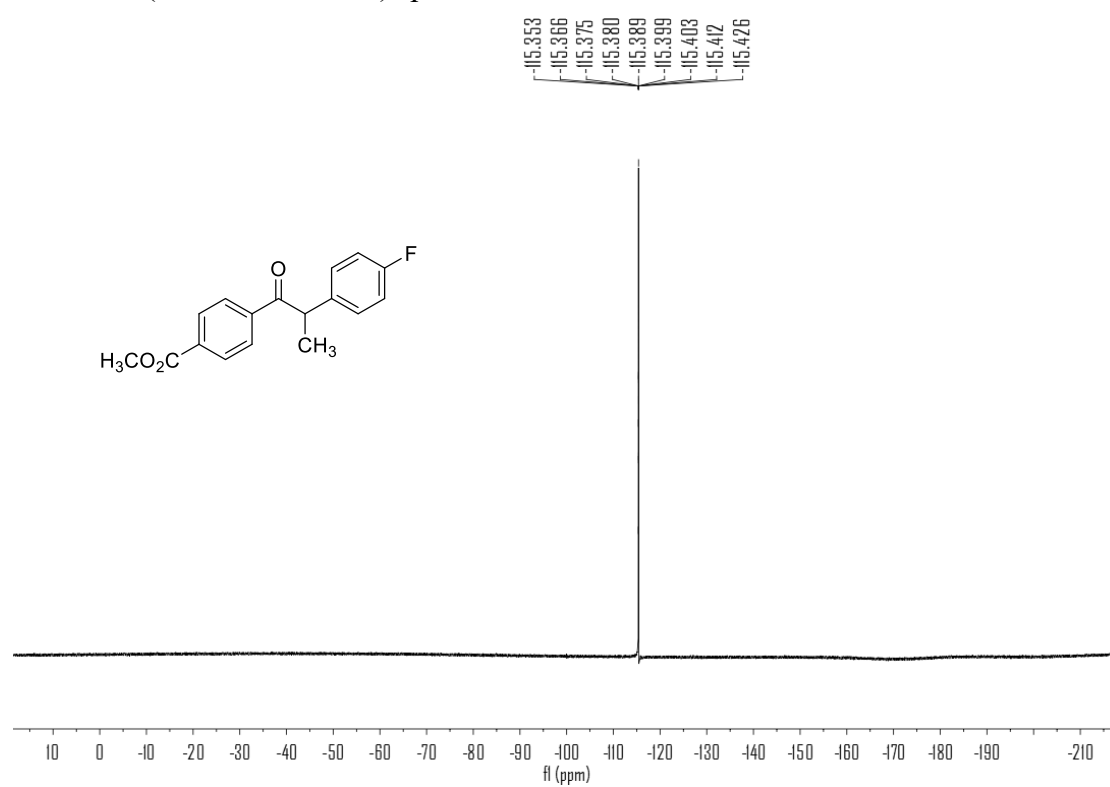
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 4d**



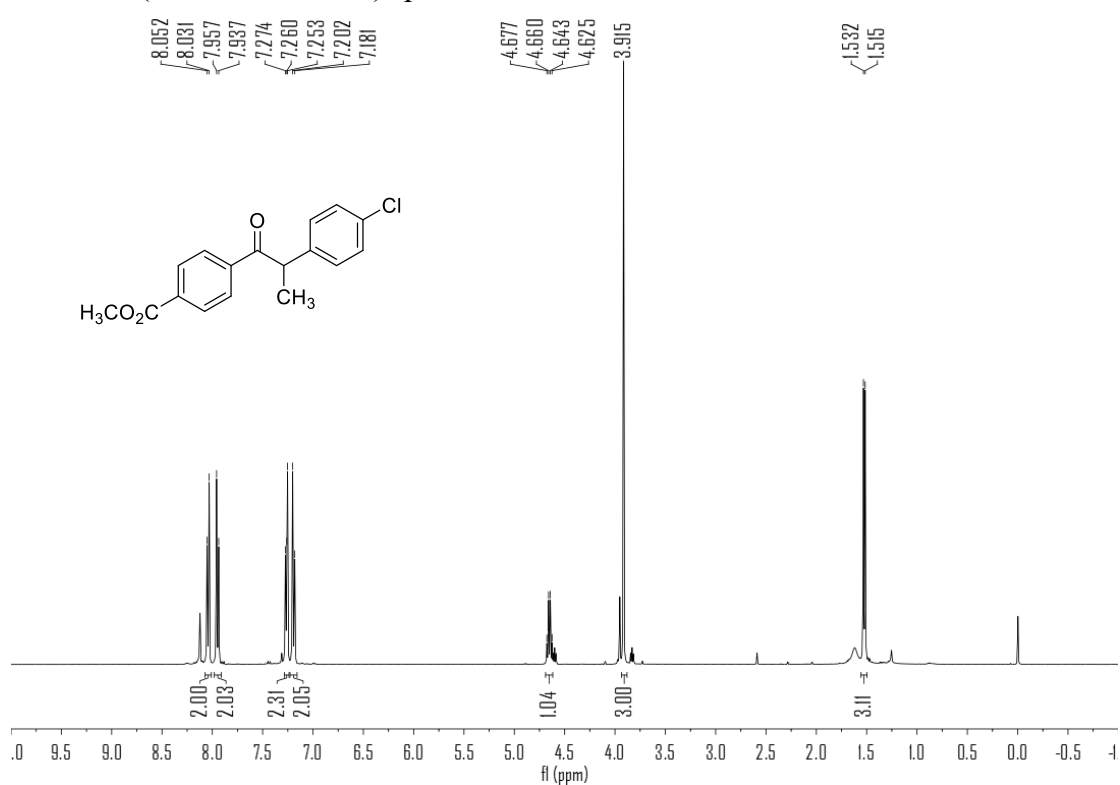
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 4d**



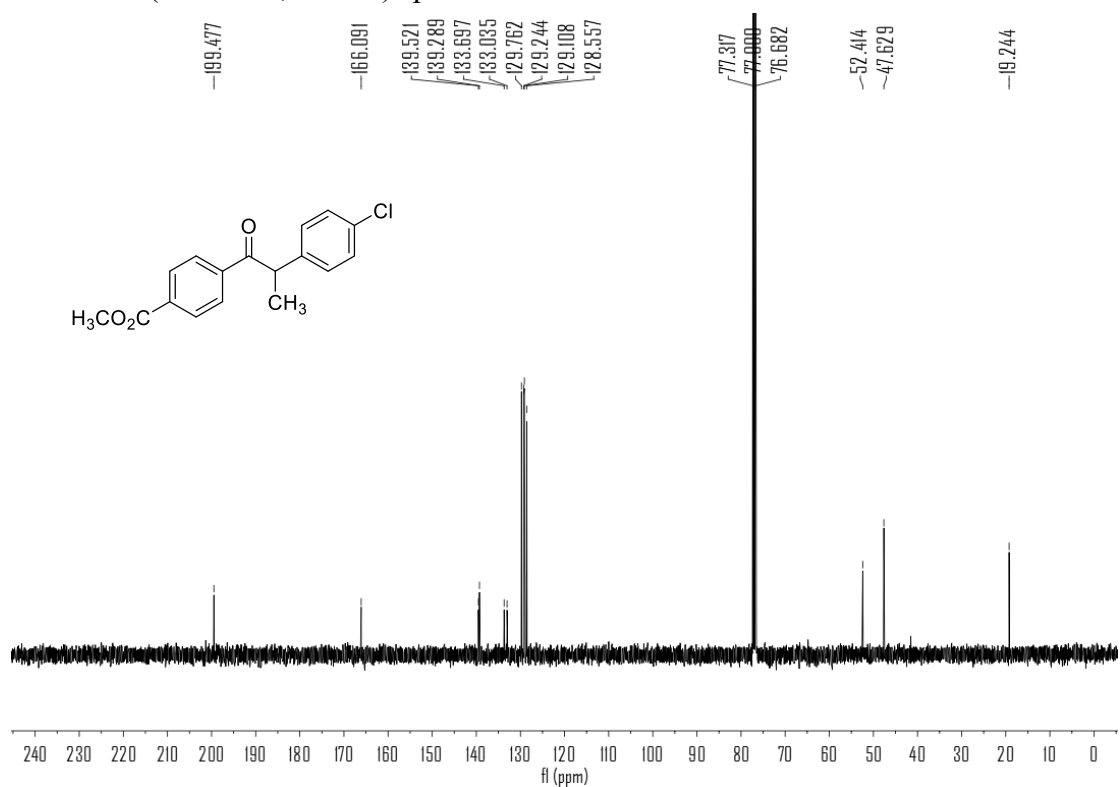
**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectrum of **4d****



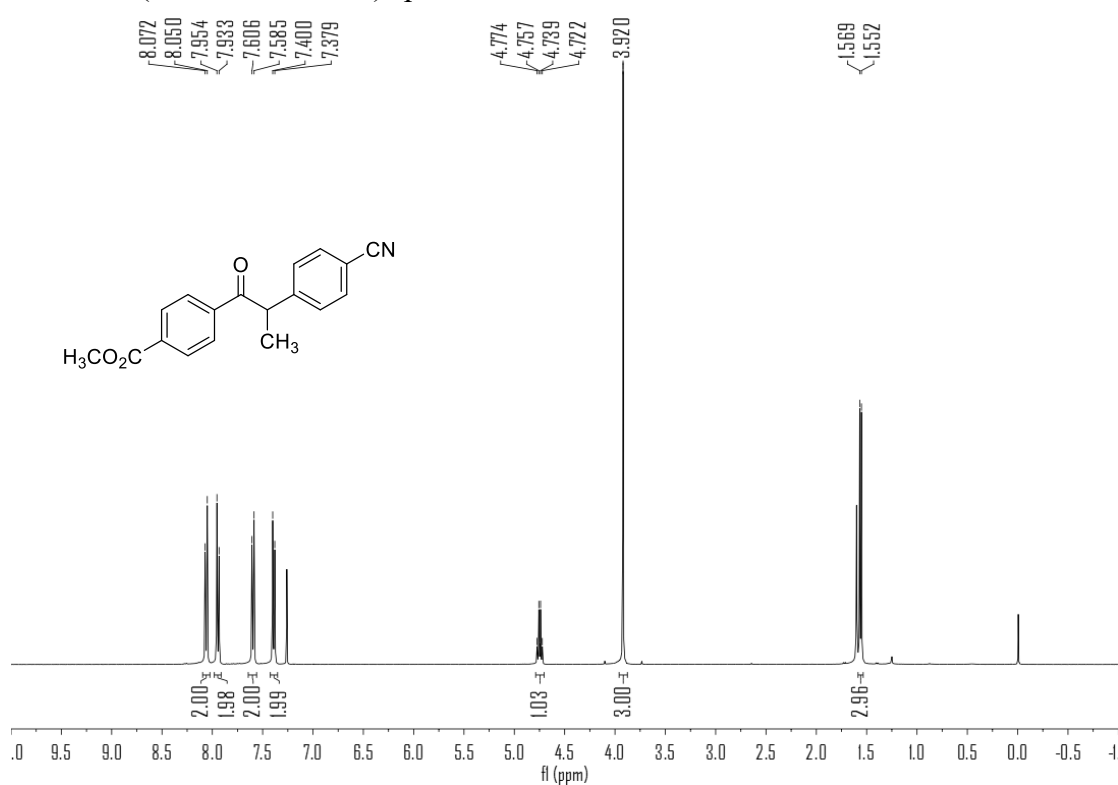
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4e**



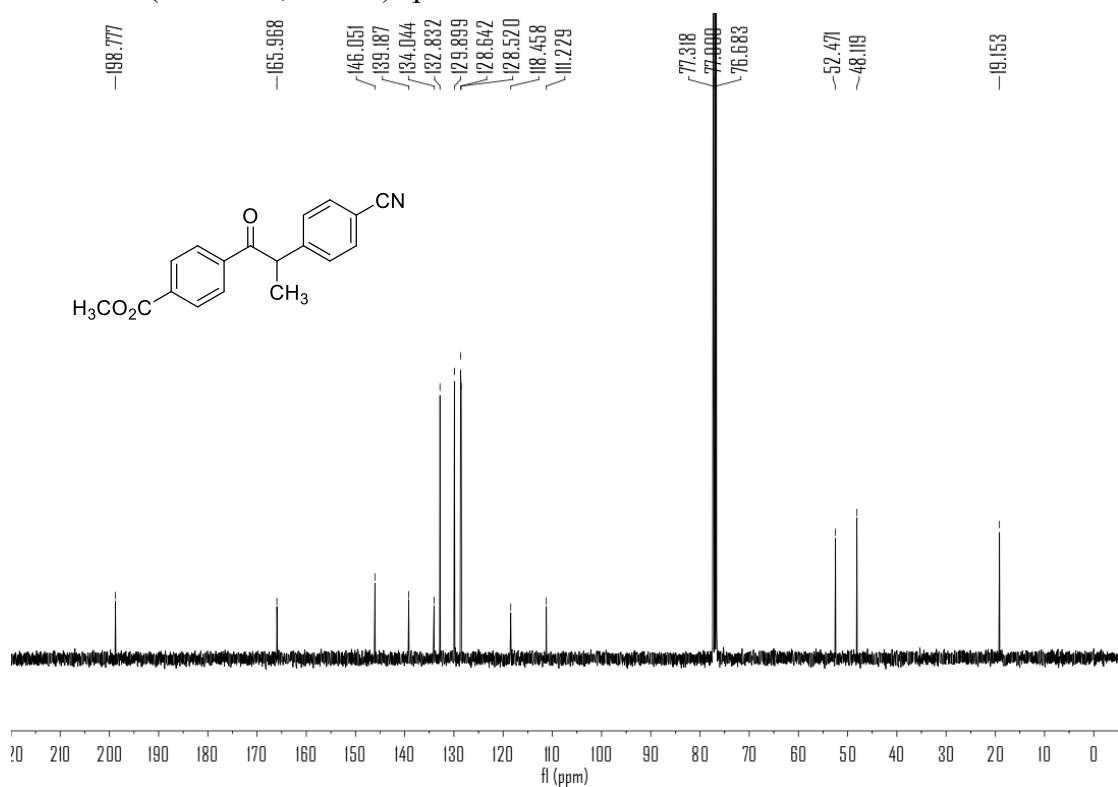
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4e**



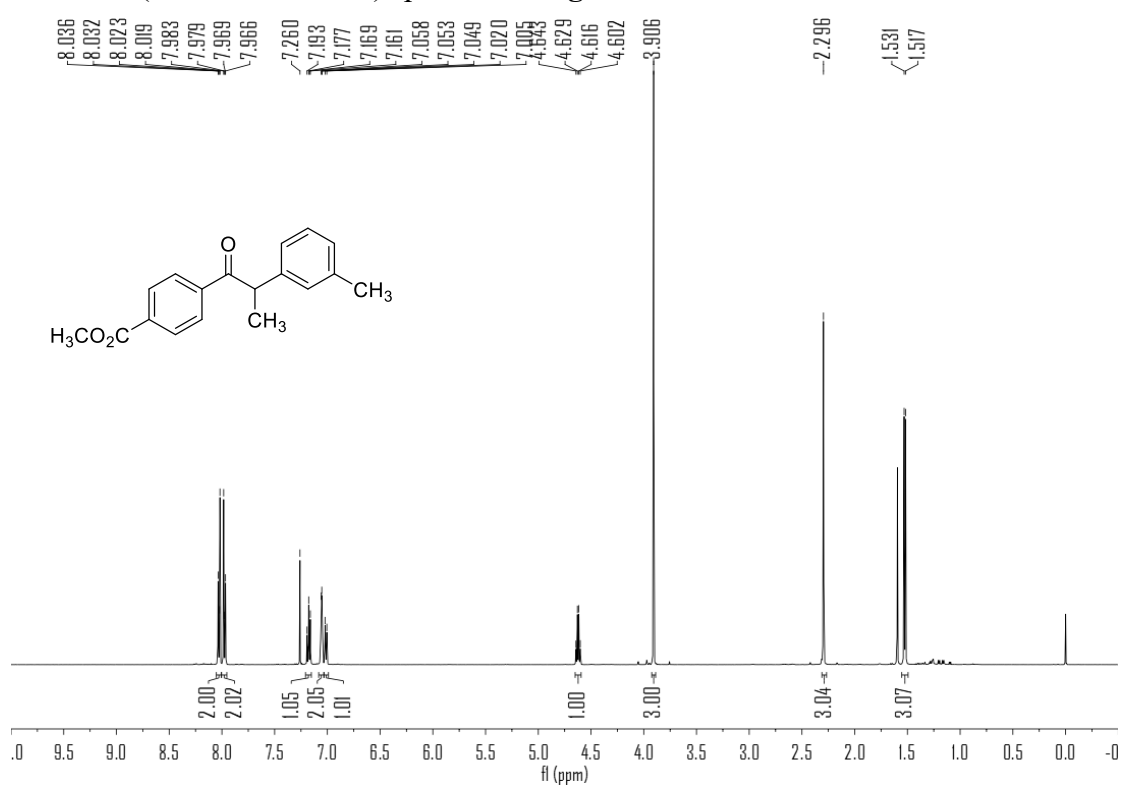
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4f**



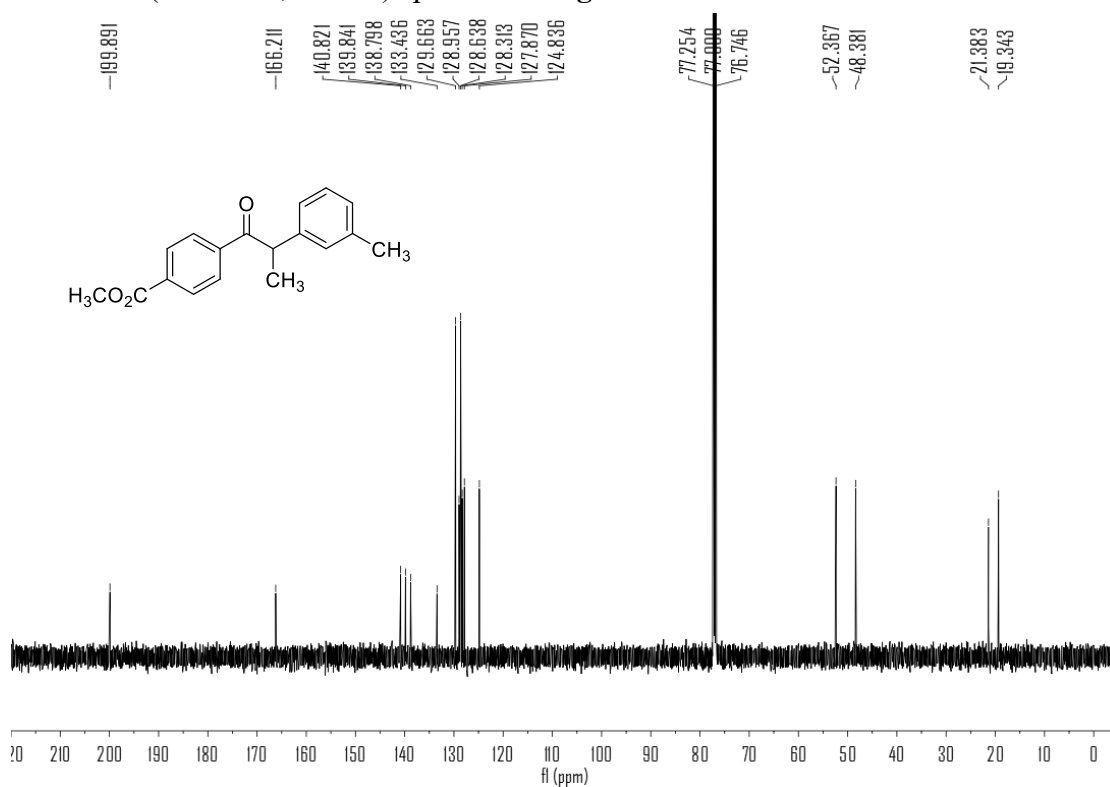
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4f**



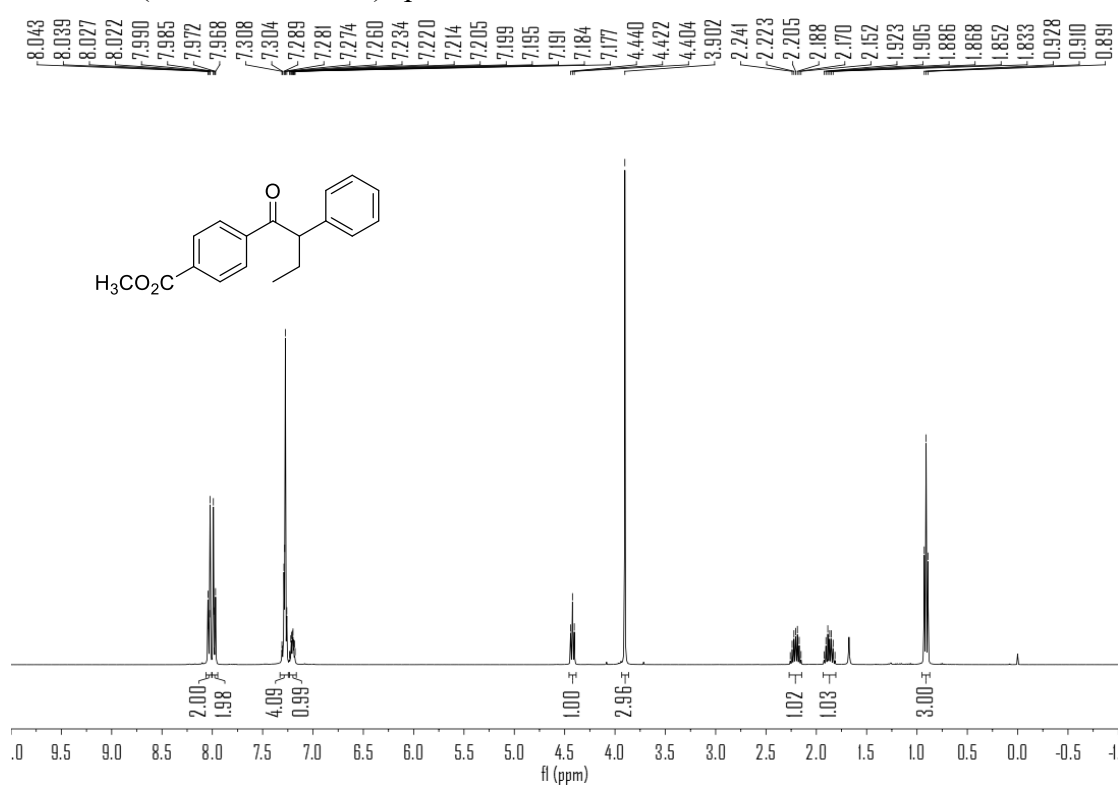
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of 4g**



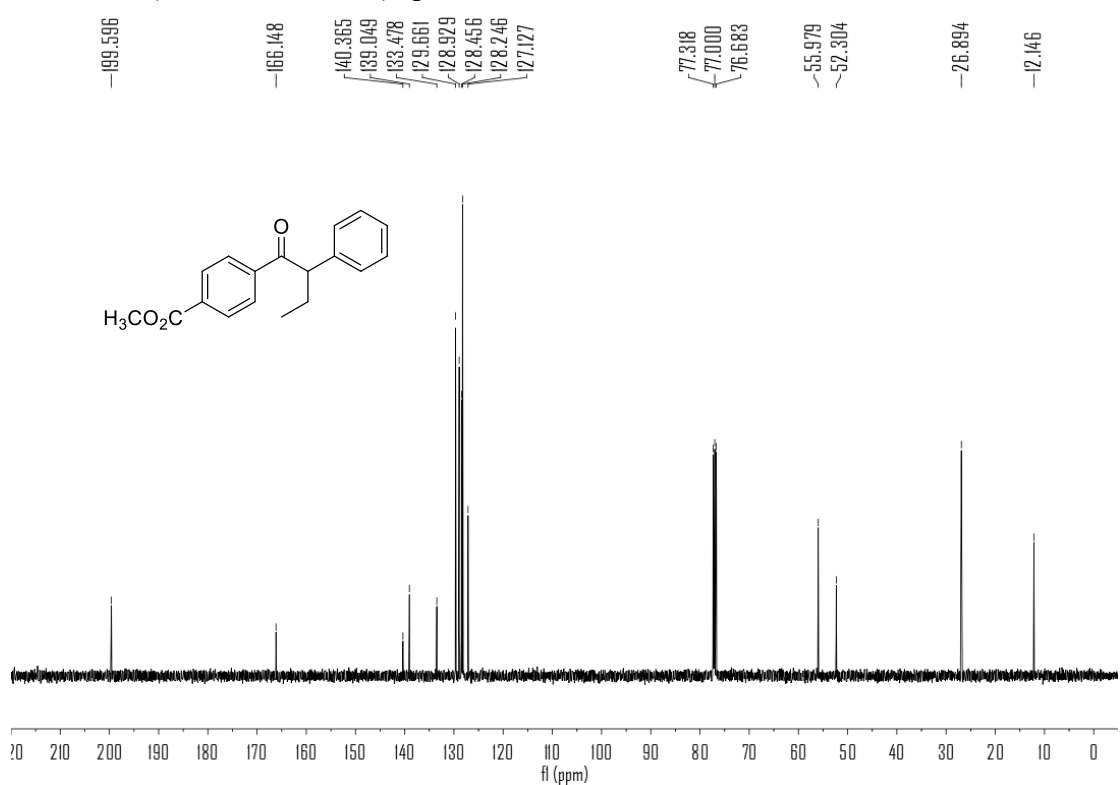
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 4g**



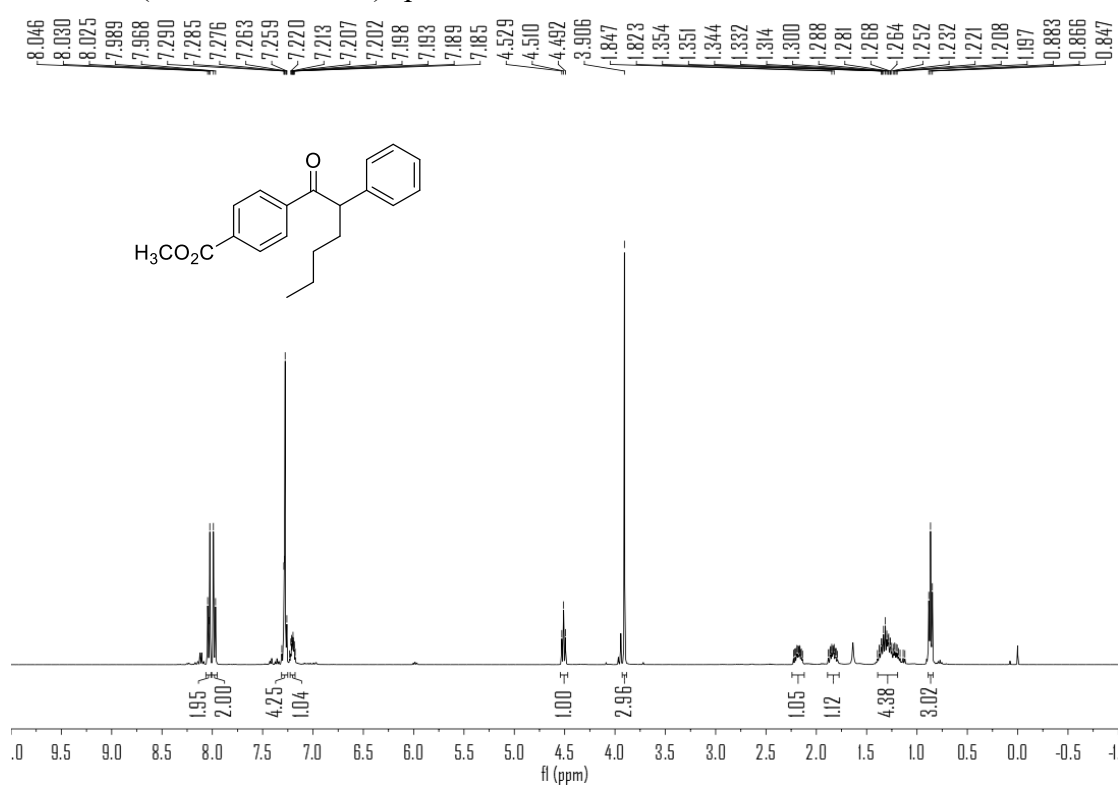
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4h**



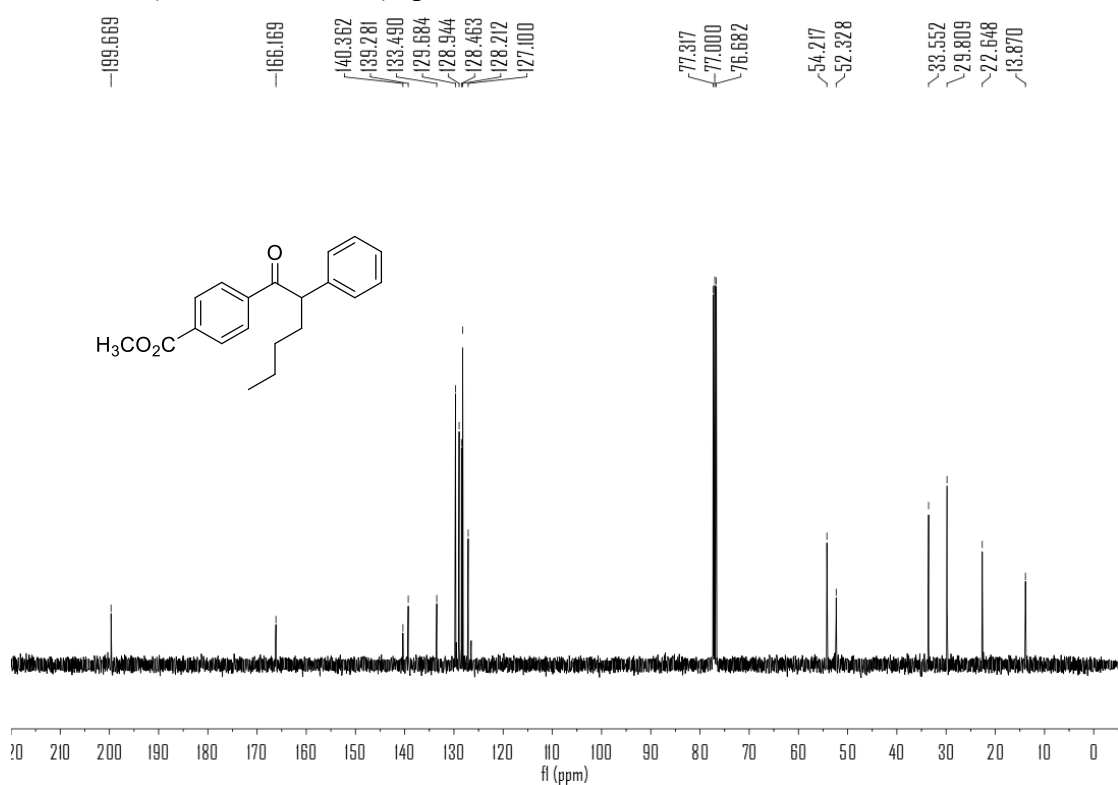
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4h**



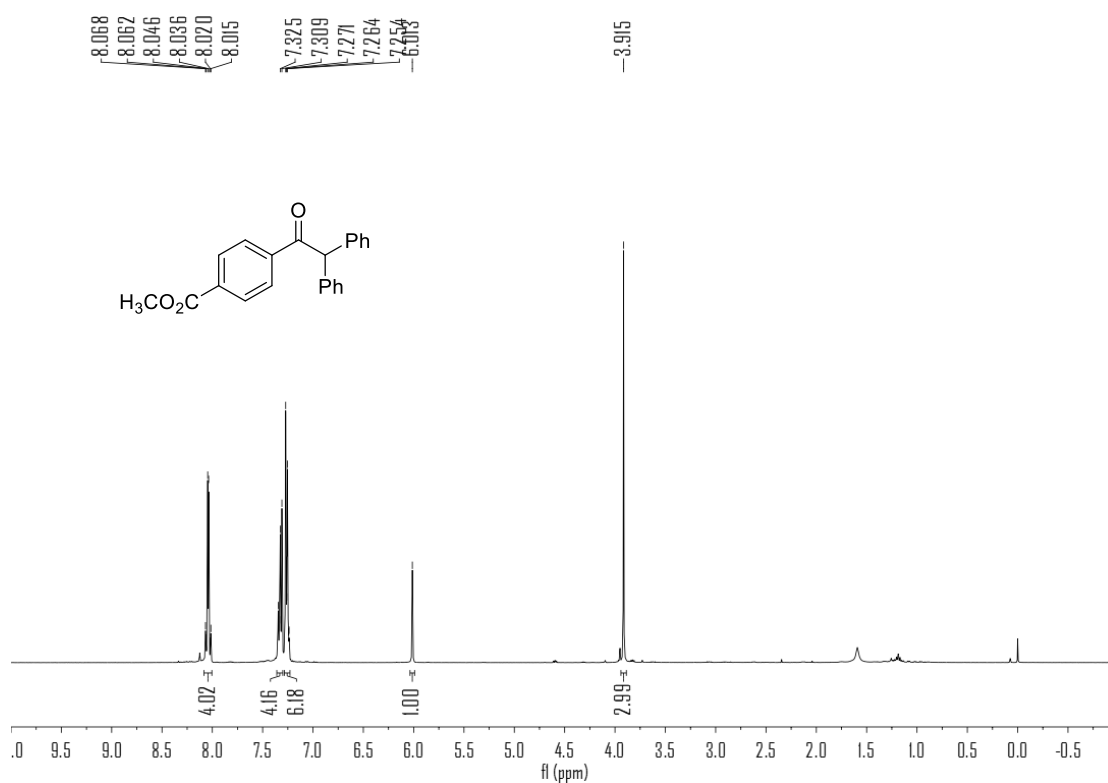
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4i**



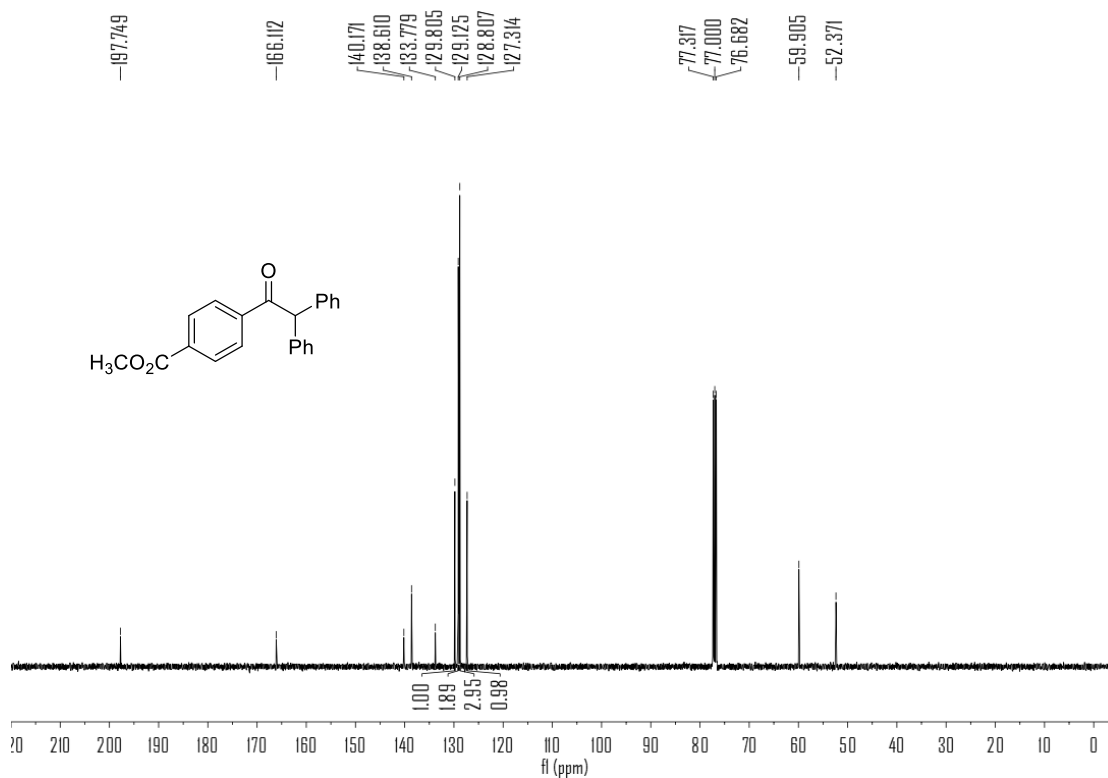
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4i**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **4j****

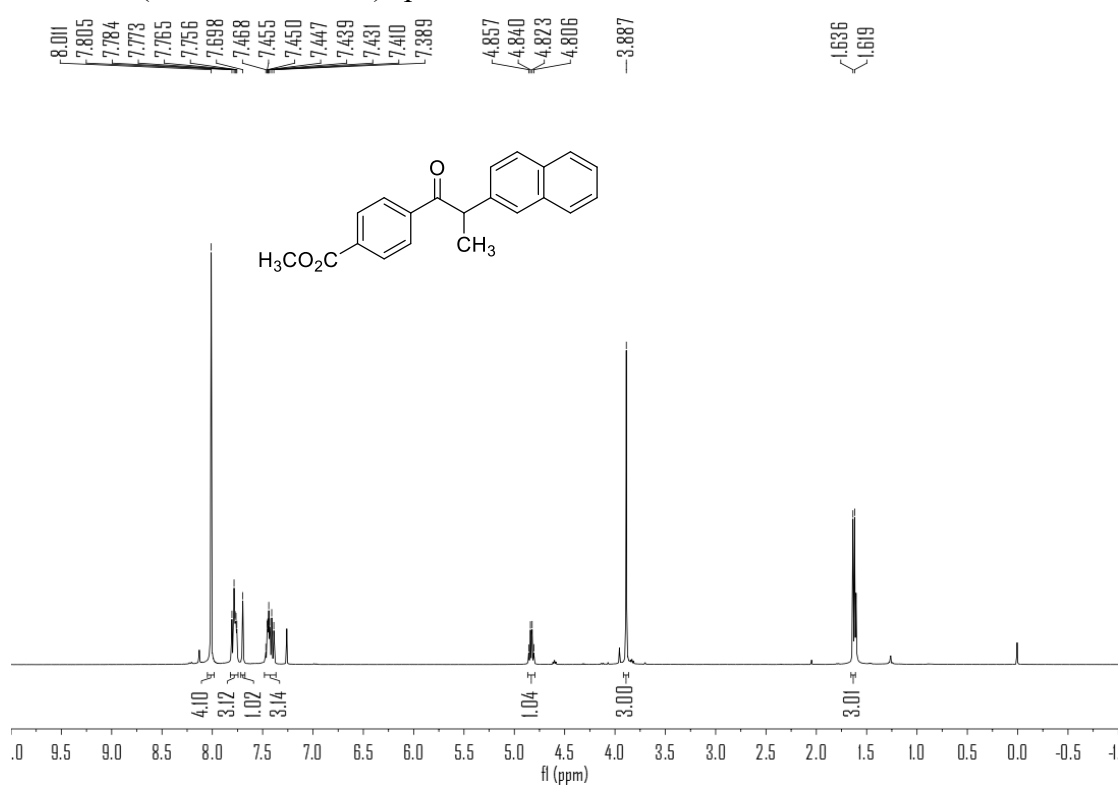


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **4j****

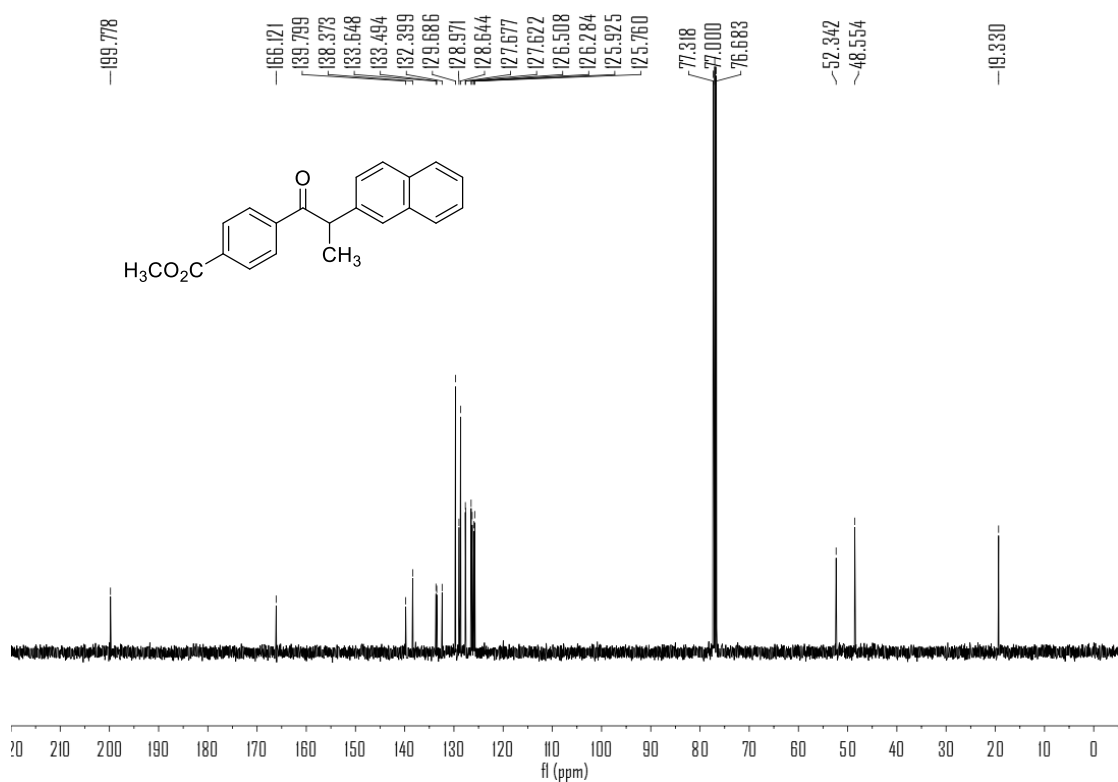




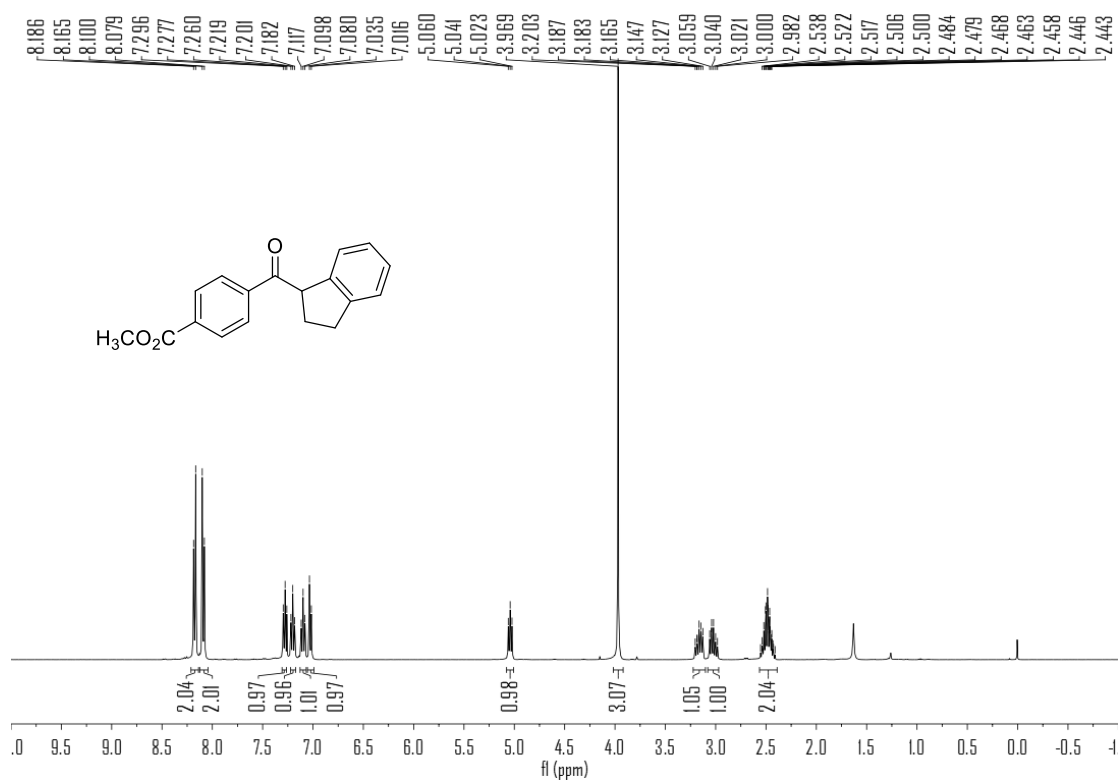
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4k**



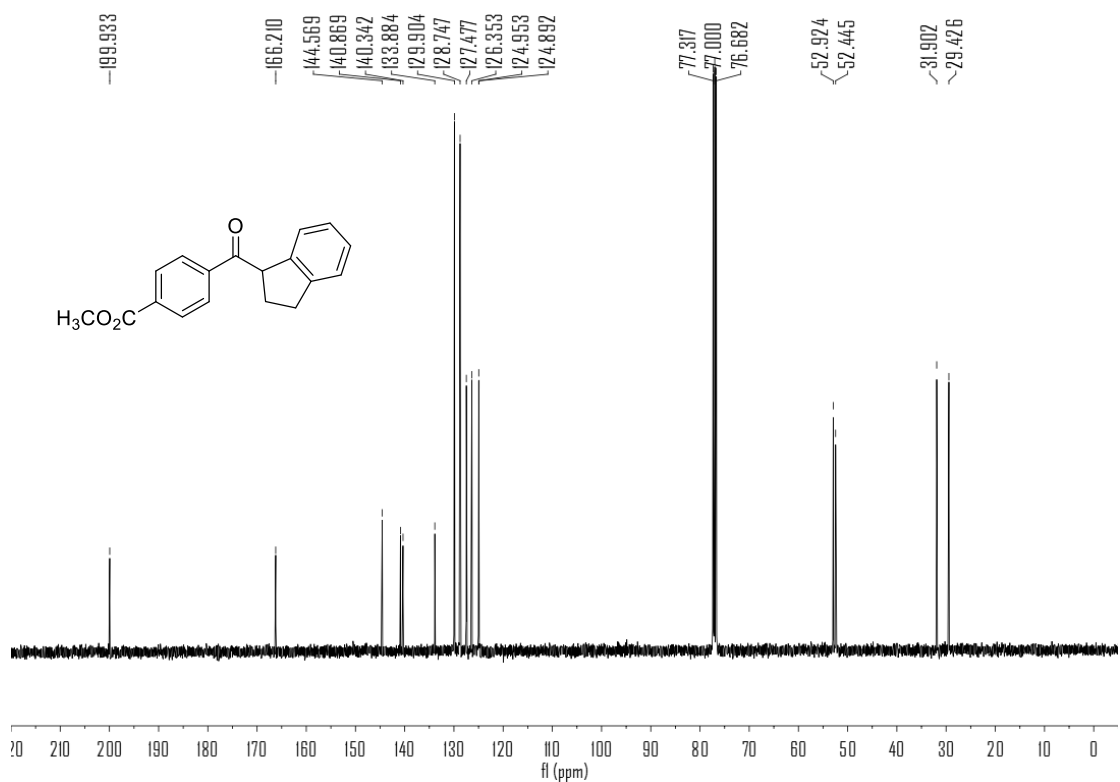
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4k**



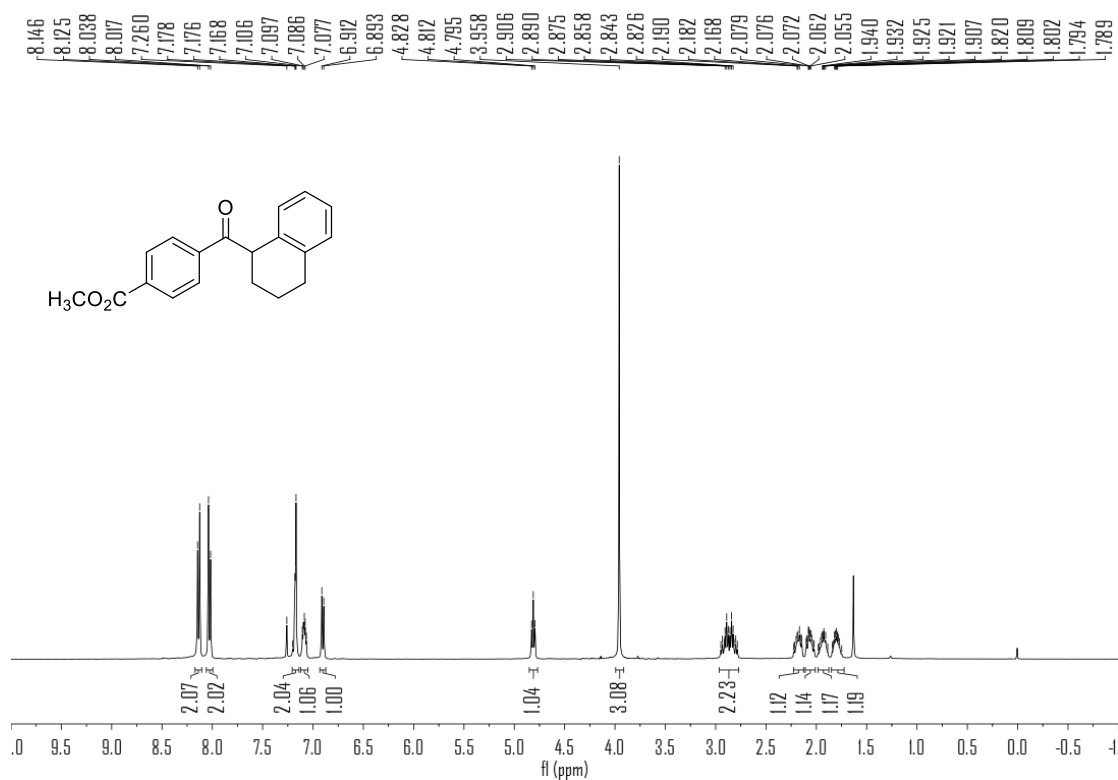
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4l**



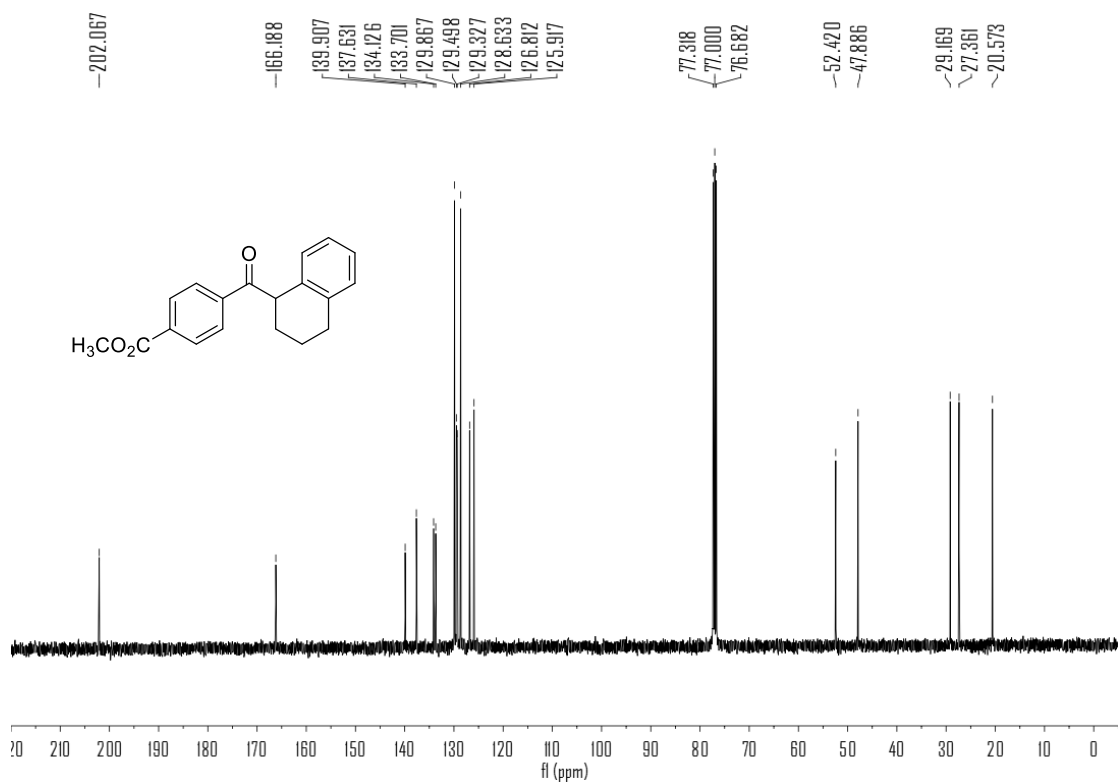
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4l**



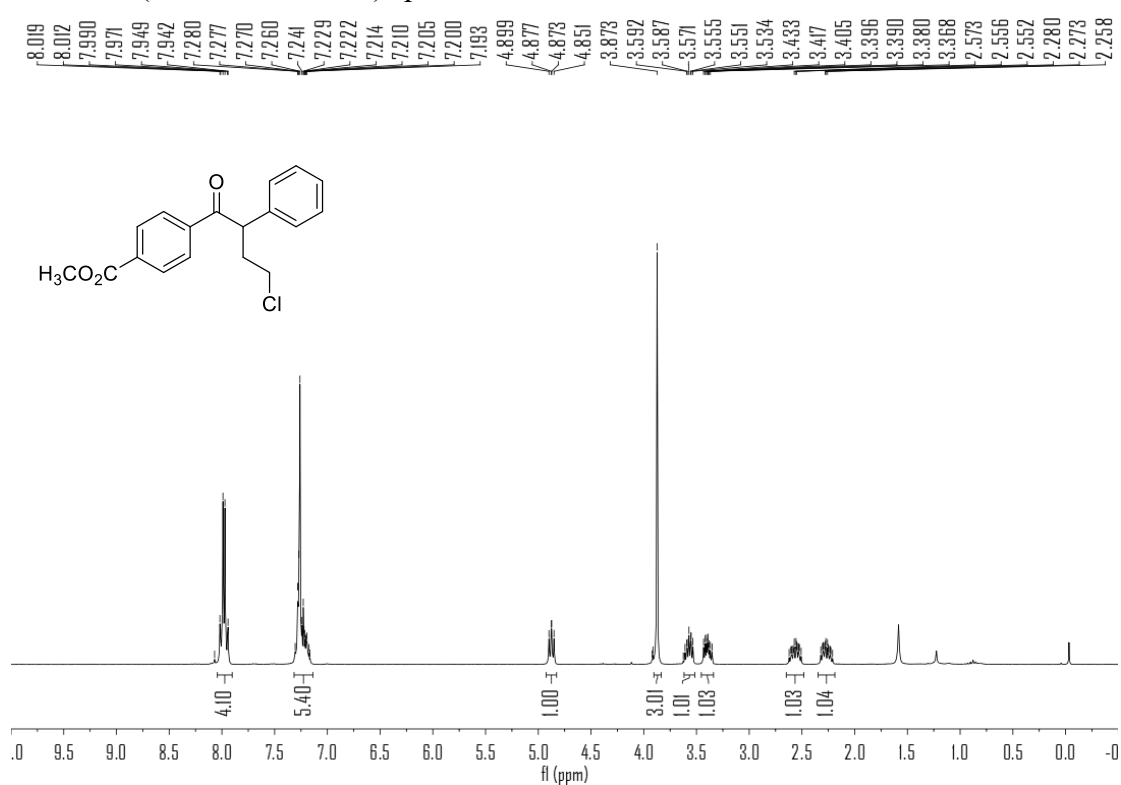
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 4m**



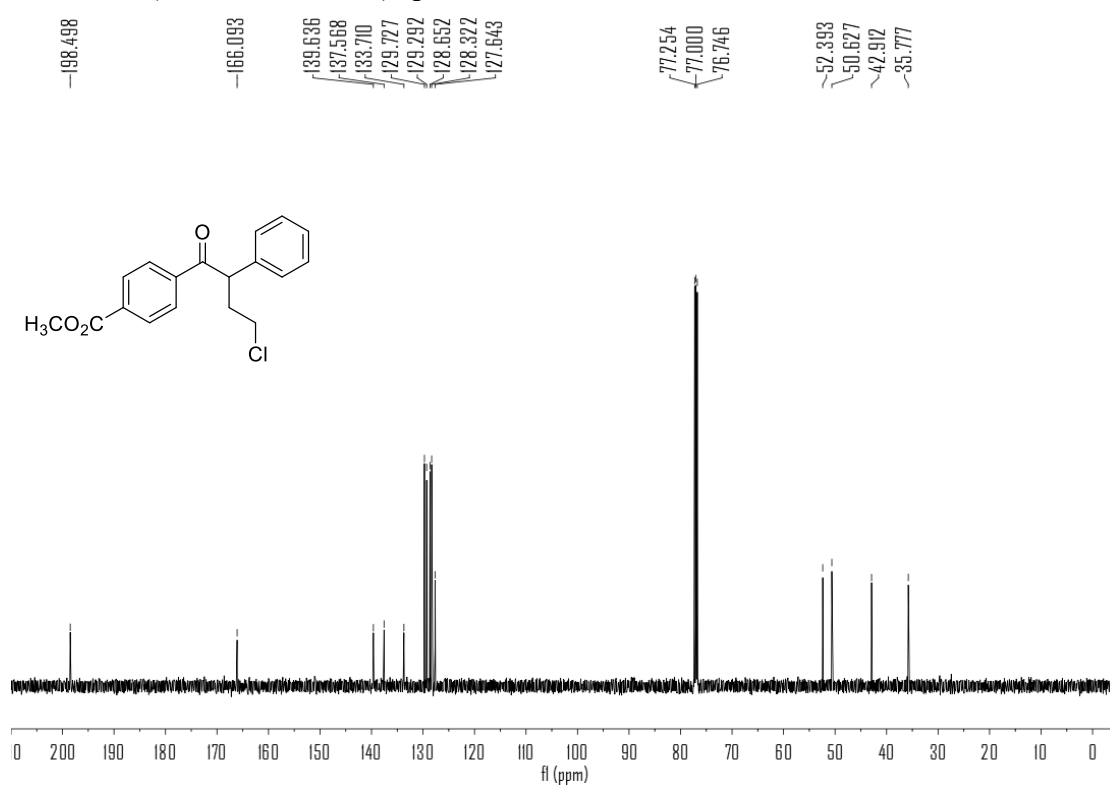
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 4m**



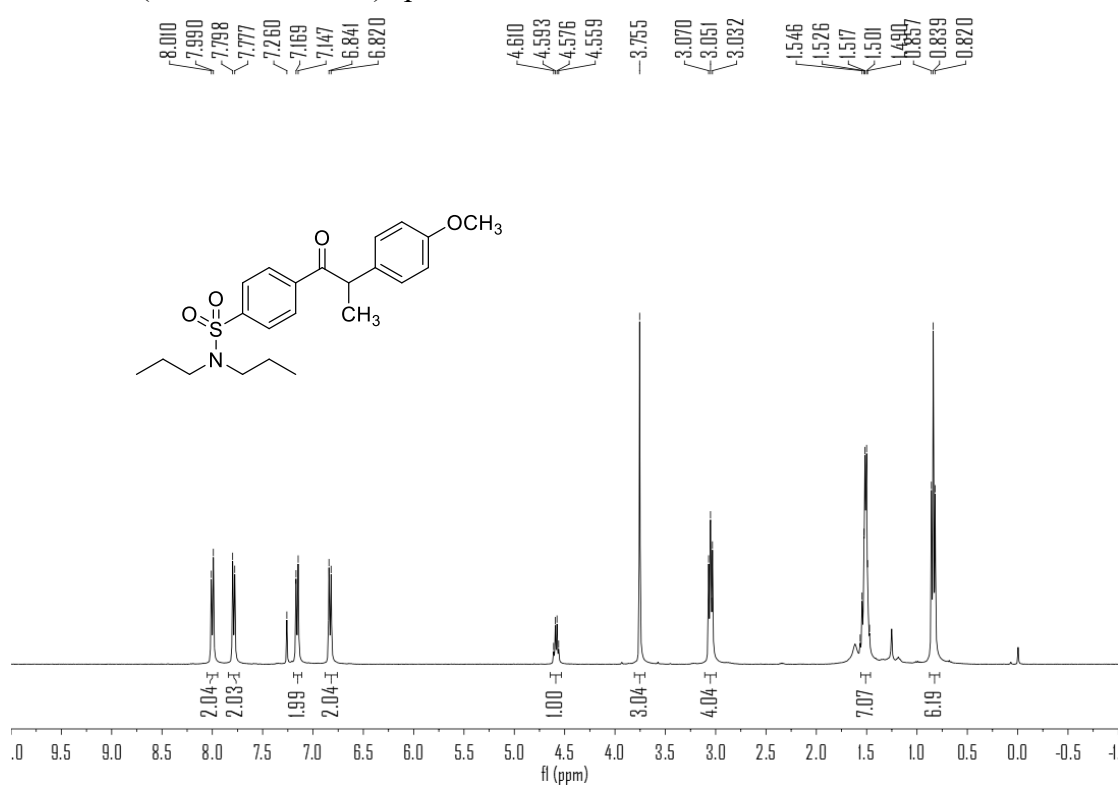
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of 4n**



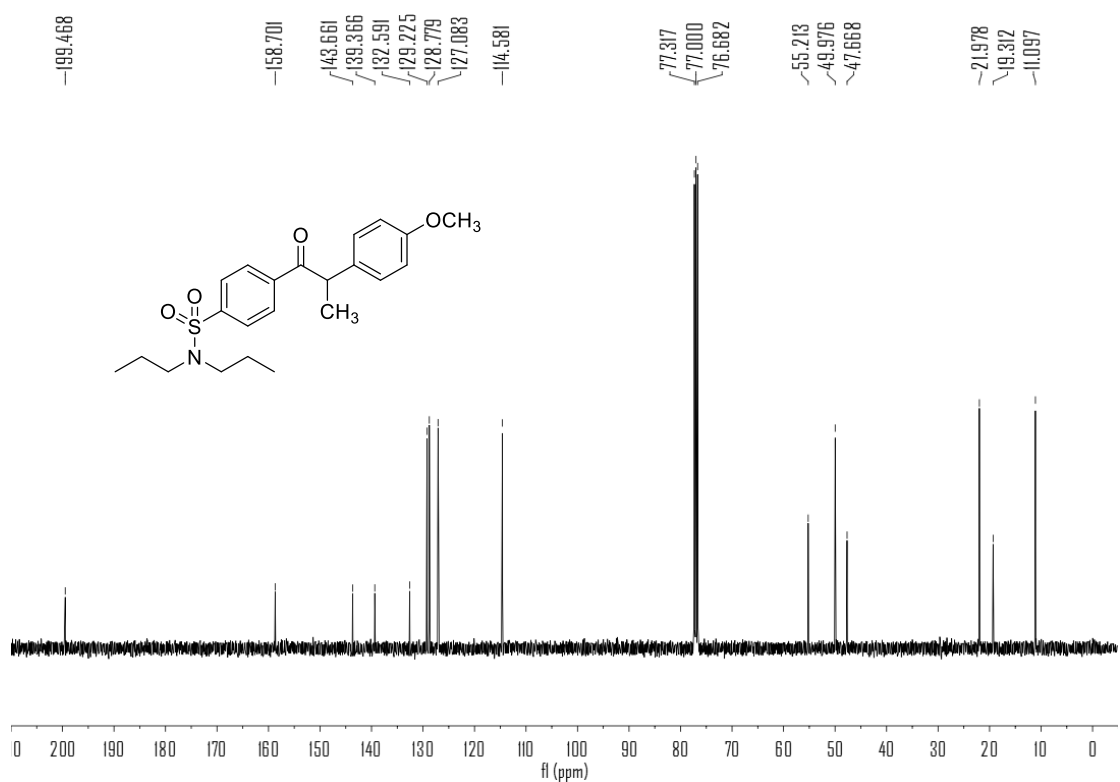
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of 4n**



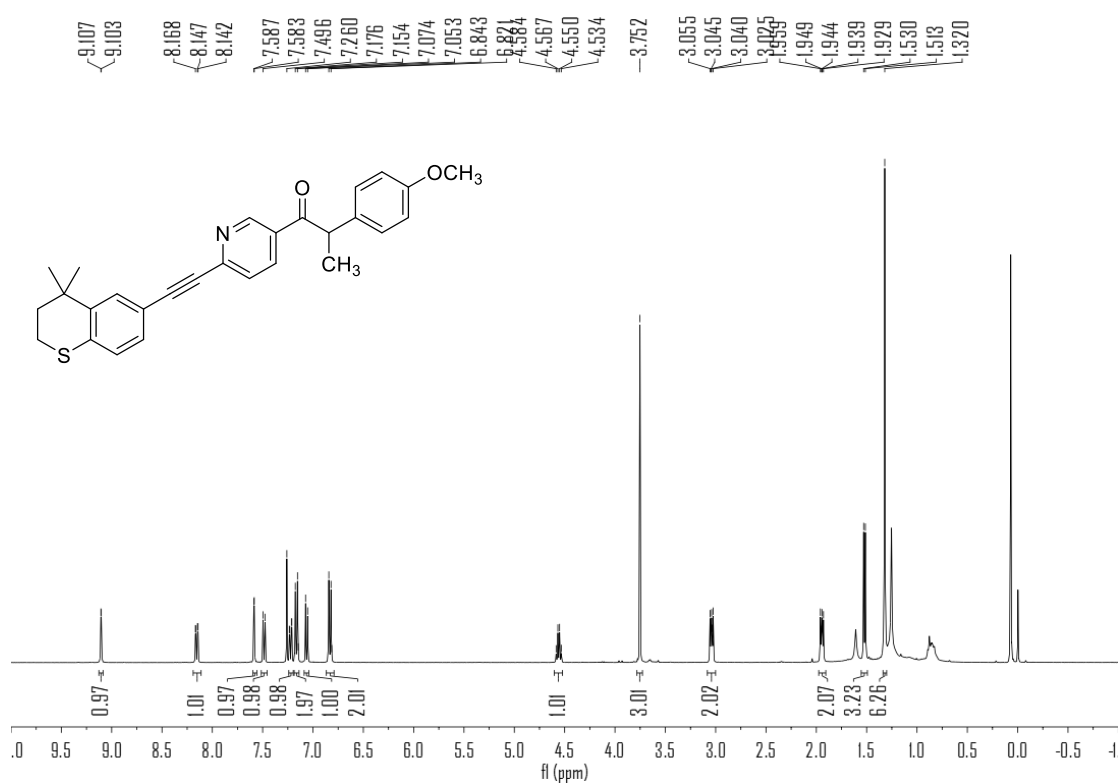
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **5****



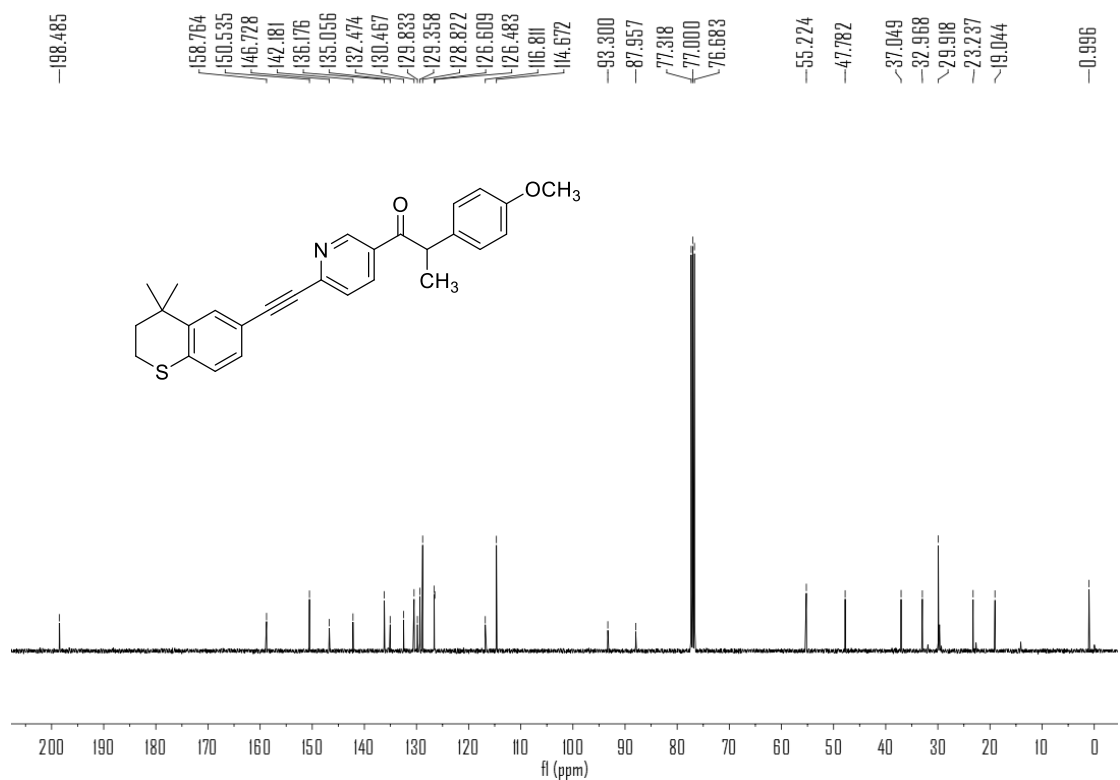
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **5****



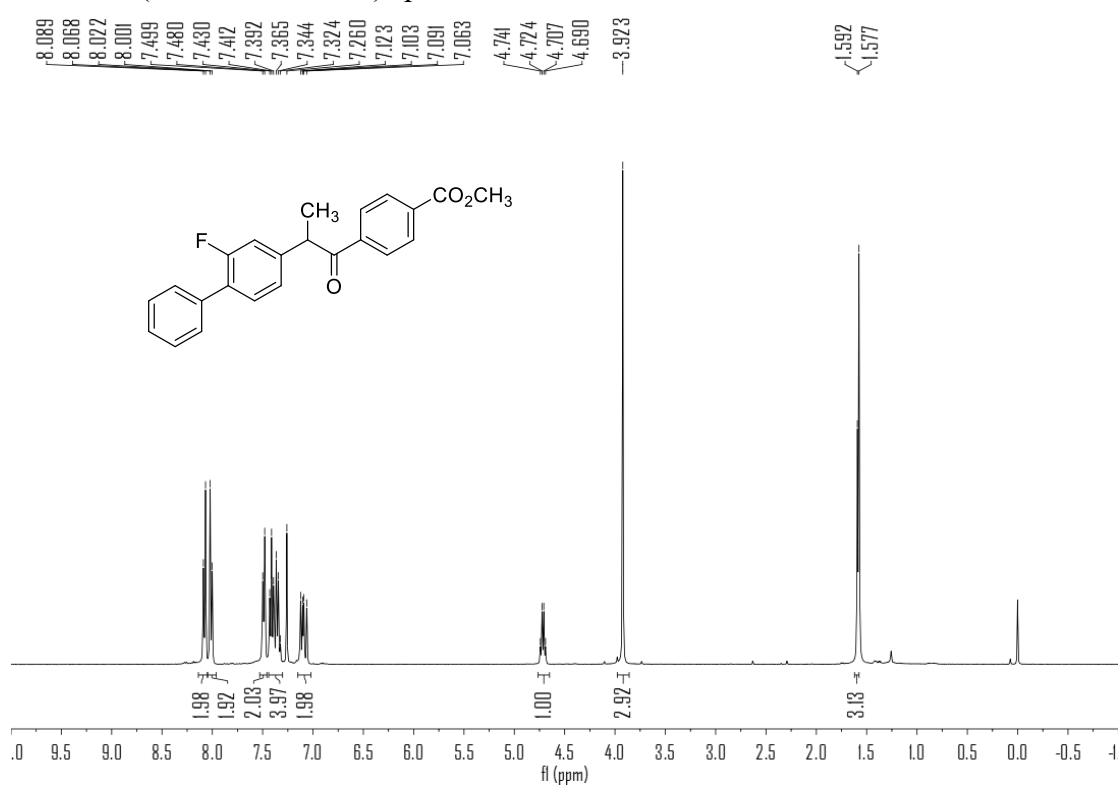
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 6**



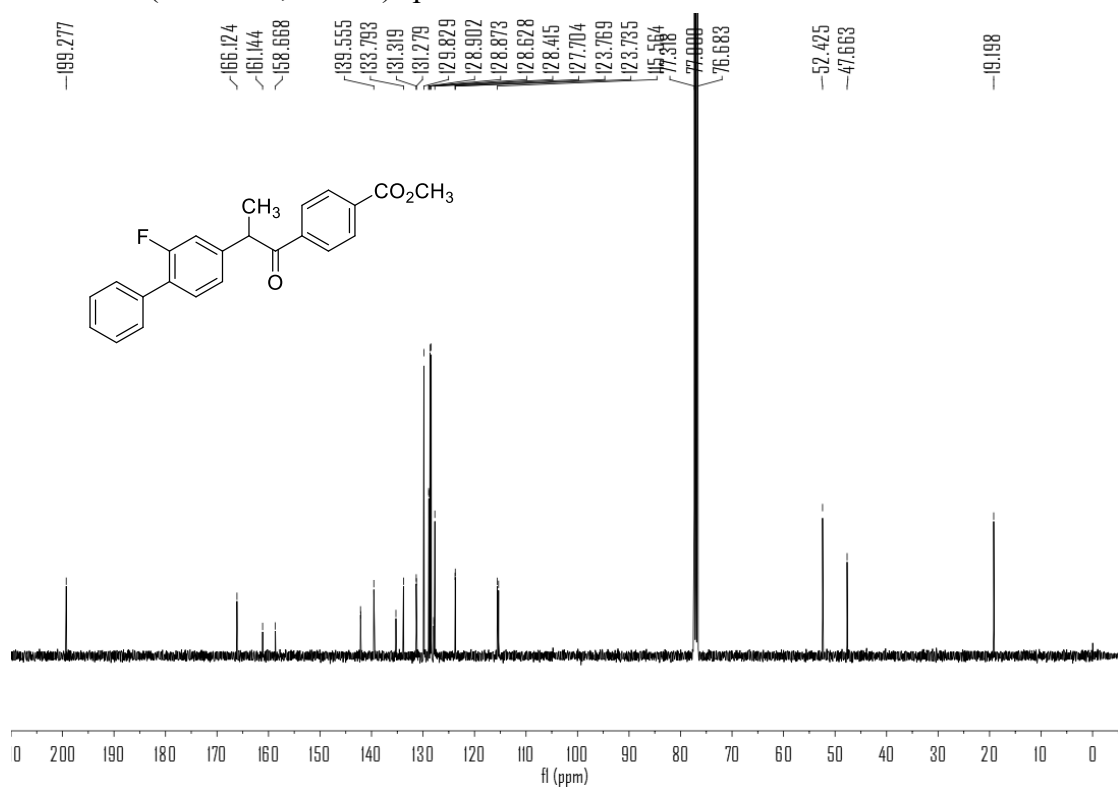
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 6**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 7**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 7**

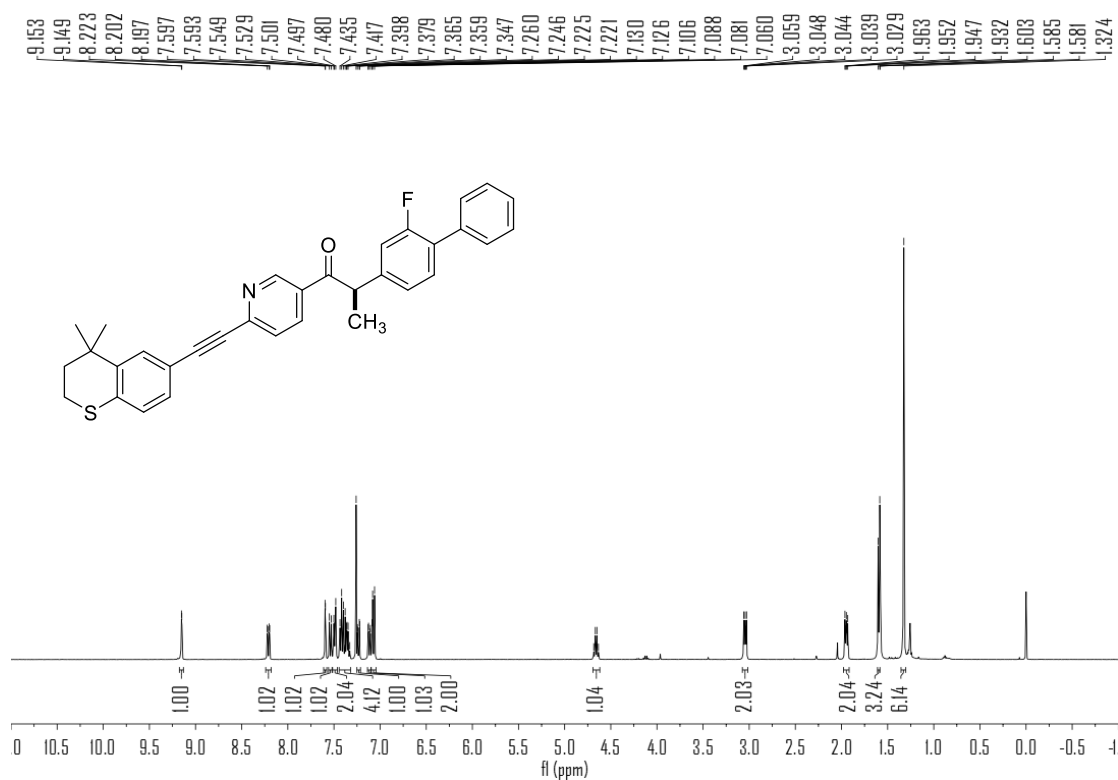


**$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectrum of 7**

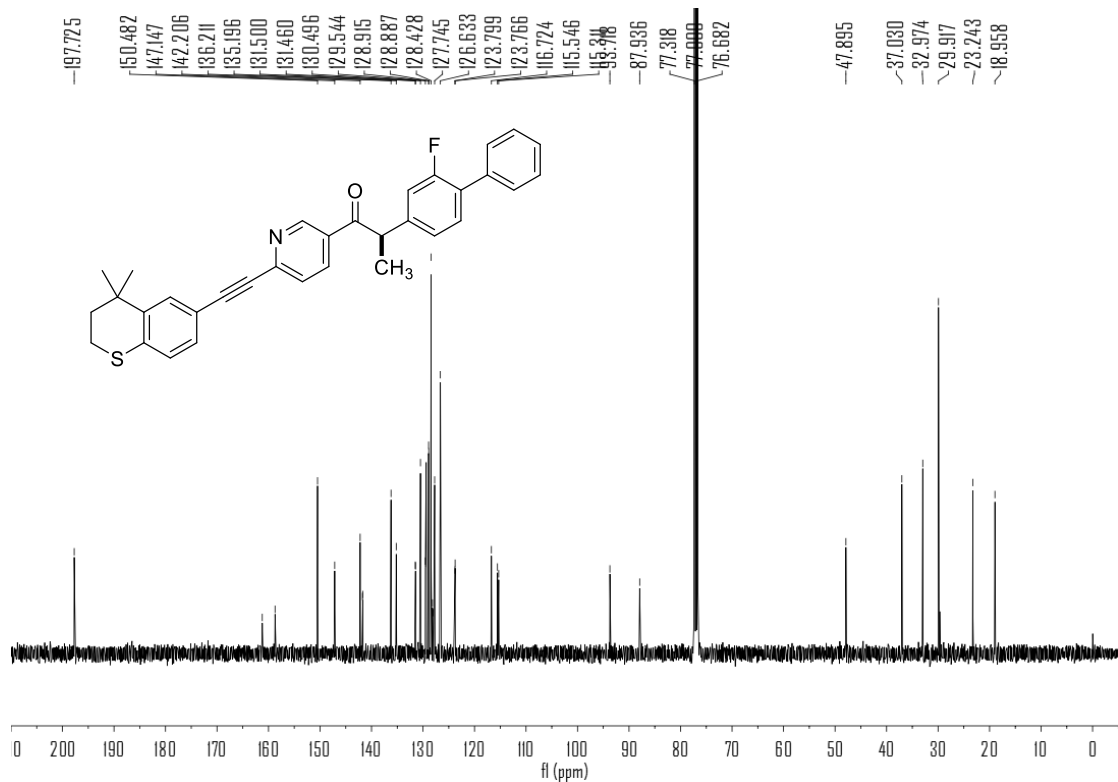




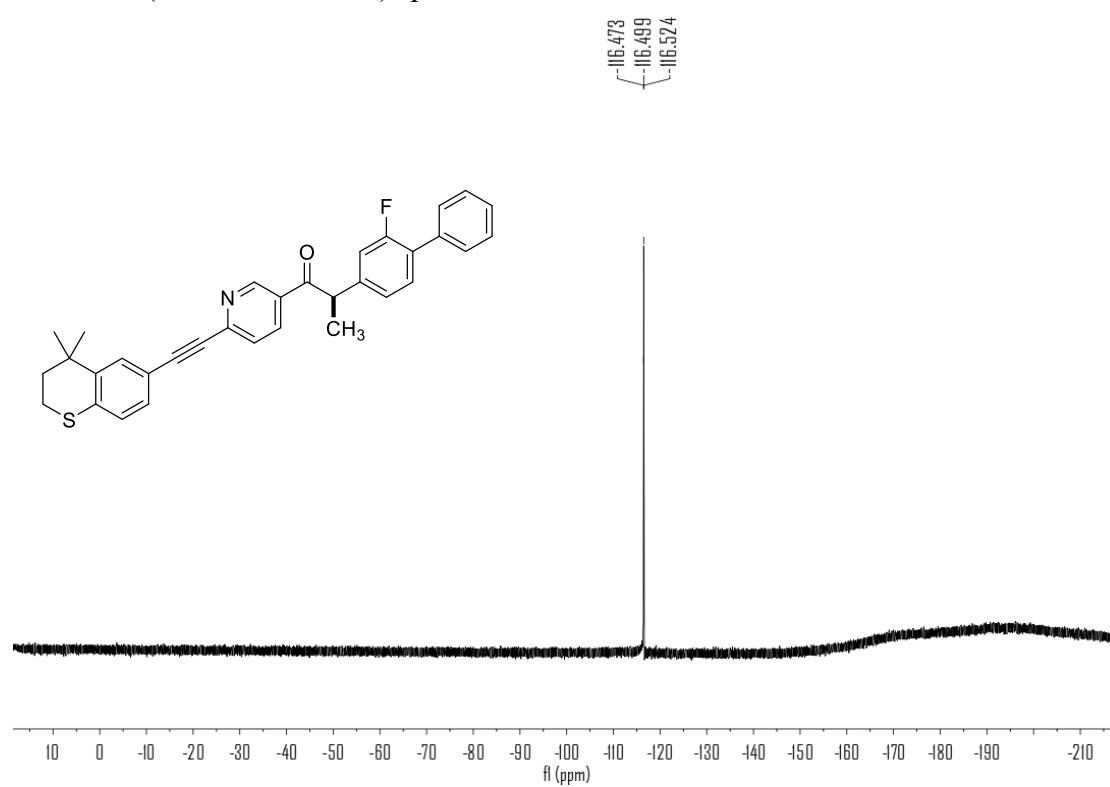
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **8****



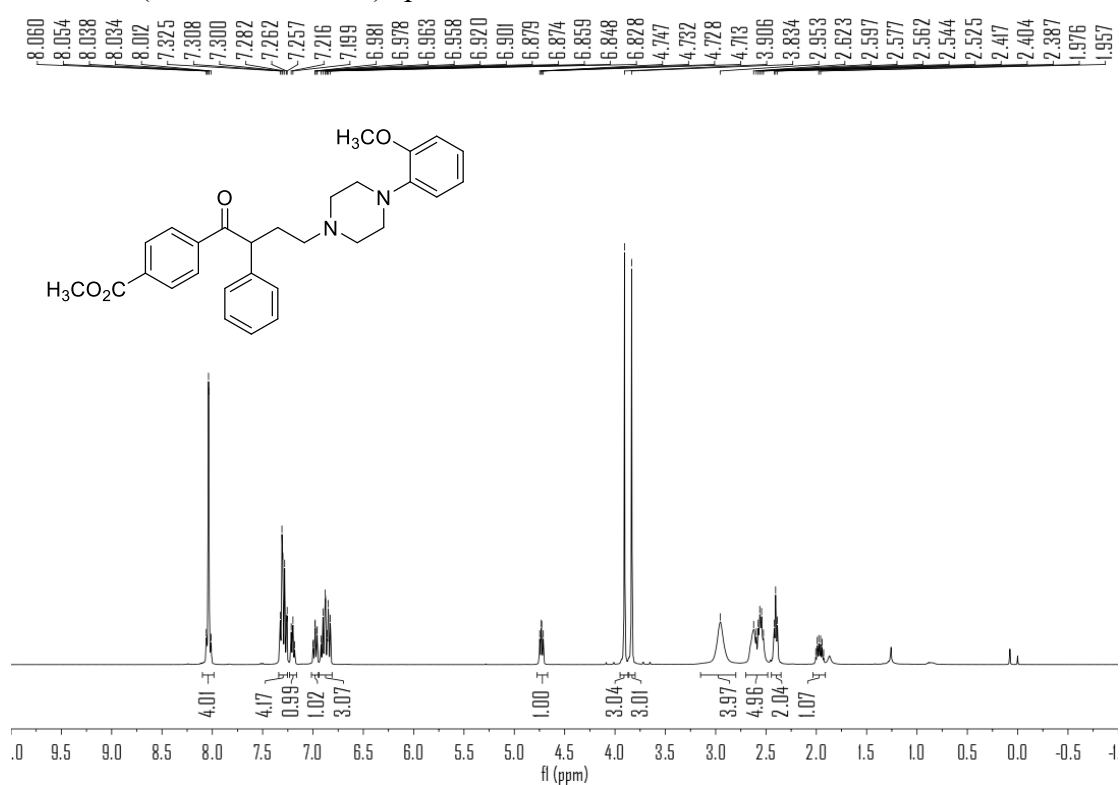
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **8****



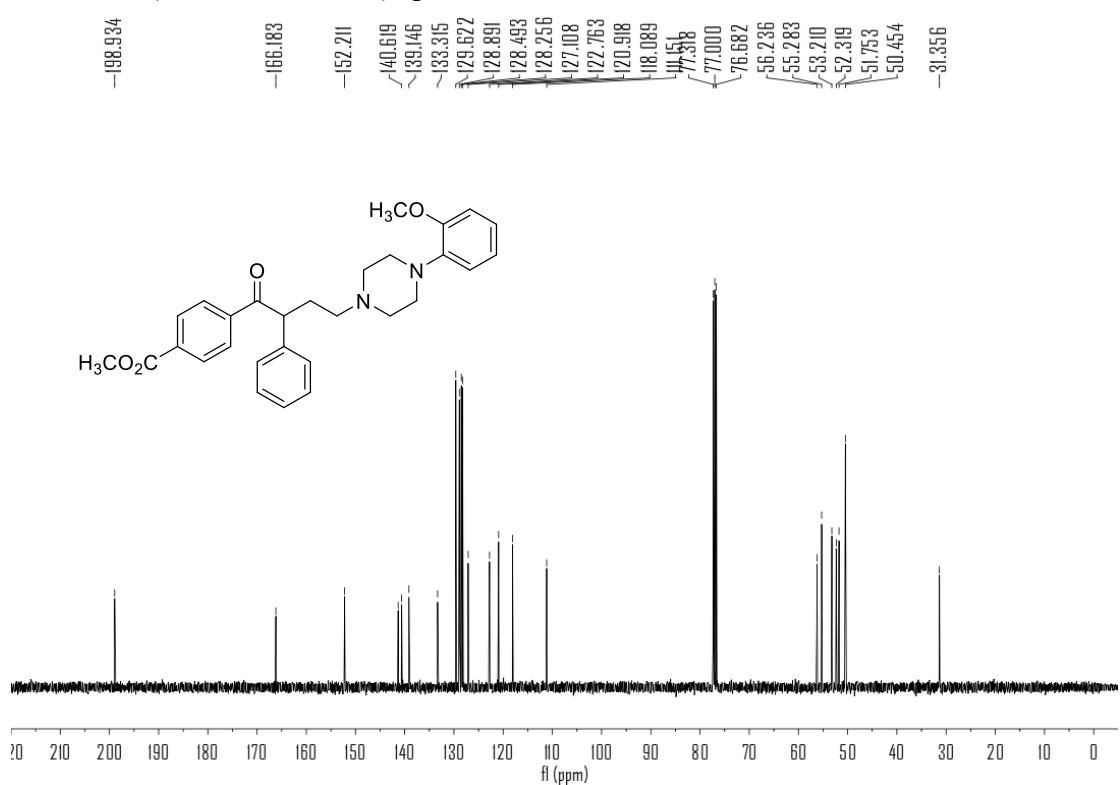
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectrum of **8****



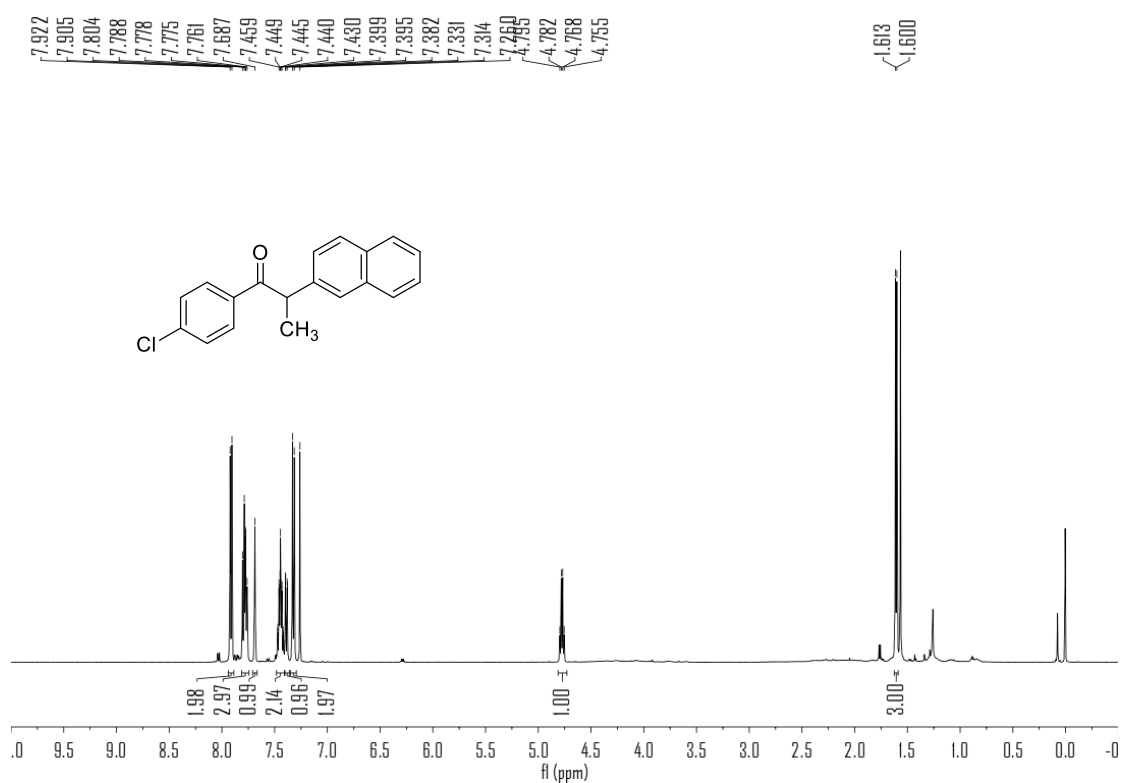
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **9****



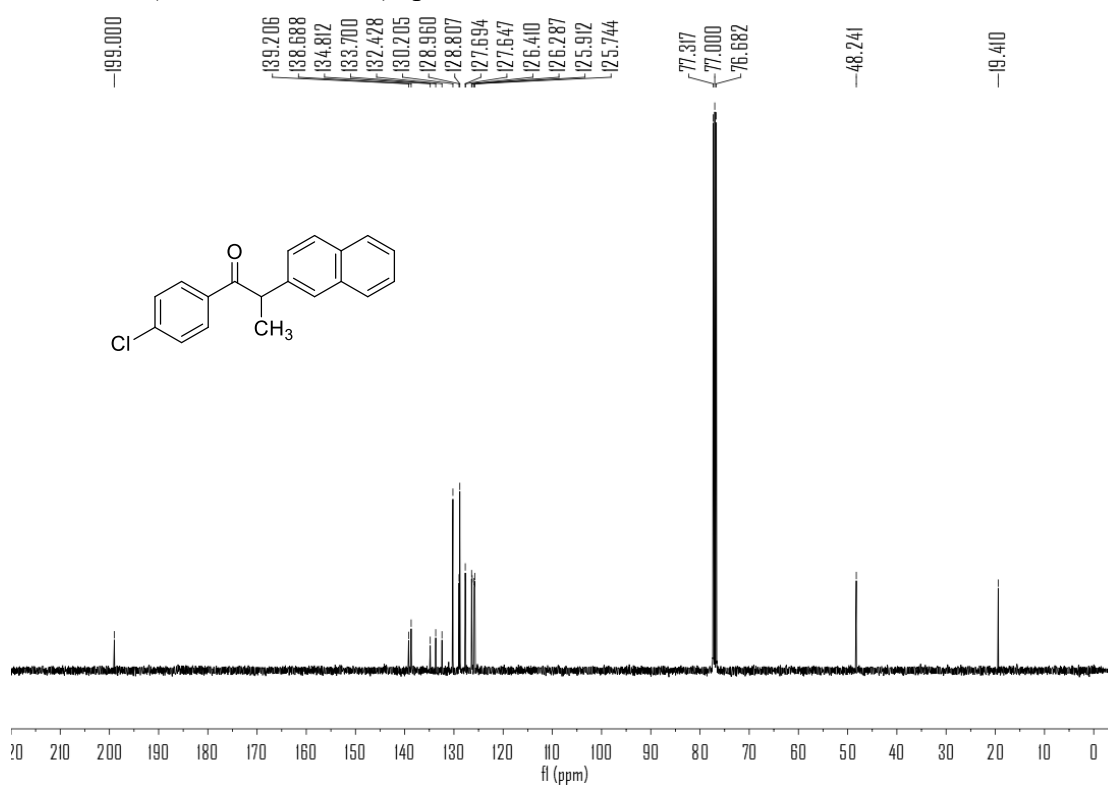
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **9****



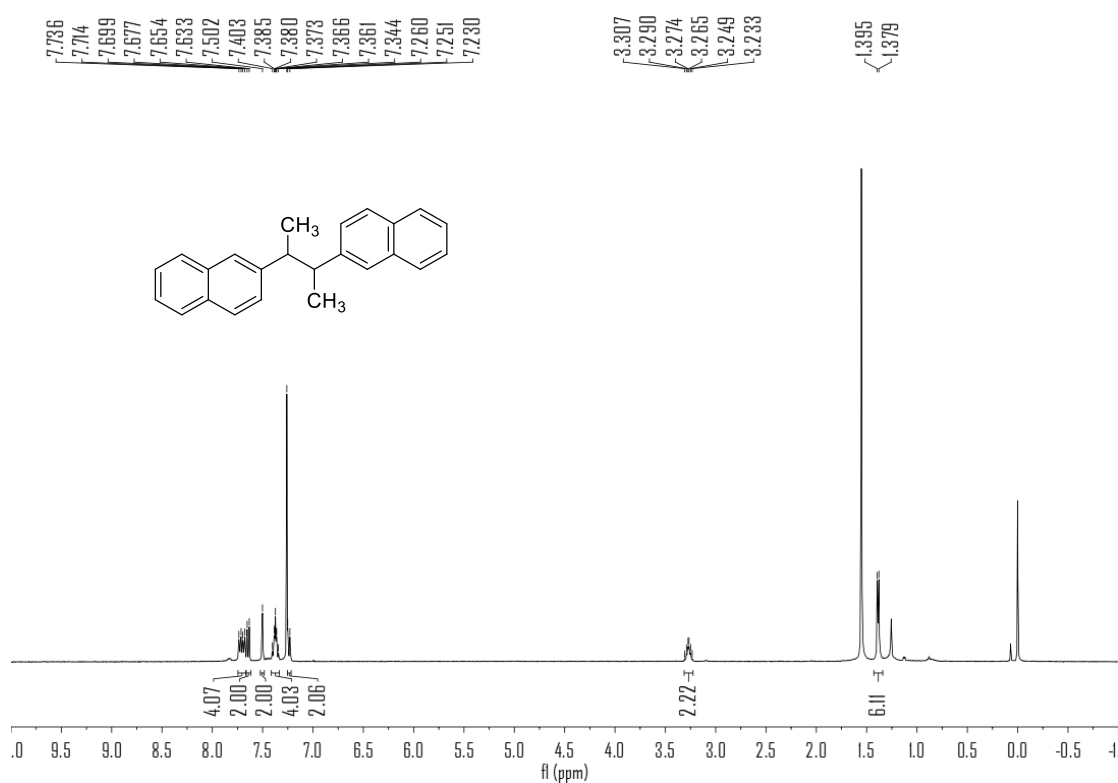
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **10****



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **10****



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **11****



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **11****

