

# Supporting Information

## Electrochemically Promoted N-Heterocyclic Carbene Polymer-Catalyzed Cycloaddition of Aldehyde with Isocyanide Acetate

Chu-Hong Ou, Ying-Ming Pan, Hai-Tao Tang\*

State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, People's Republic of China.

Email: [httang@gxnu.edu.cn](mailto:httang@gxnu.edu.cn)

### Table of Contents

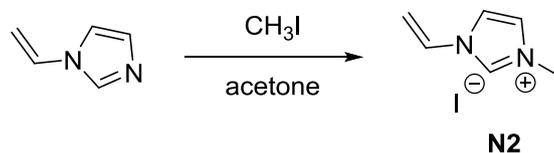
1. General Information.....	2
2. Experiment procedures .....	3
3. General Characterization of the <b>N4</b> .....	13
4. Characterization Data.....	15
5. NMR Spectra .....	24

## 1. General Information

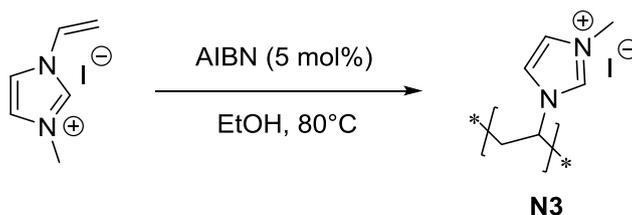
Without special instructions, all reagents and solvents were commercially available and were not further purified. Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 °C petroleum ether and analytical grade ethyl acetate (without further purification). <sup>1</sup>H NMR spectra were recorded on Bruker 400 or 600 MHz spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal solvent signal (7.26 ppm in CDCl<sub>3</sub>). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet. The coupling constants, J, are reported in Hertz (Hz). <sup>13</sup>C NMR spectra were obtained at Bruker 100 or 150 MHz and referenced to the internal solvent signals (central peak is 77.000 ppm in CDCl<sub>3</sub>). CDCl<sub>3</sub> was used as the NMR solvent. The HRMS spectrum was measured by micromass QTOF2 Quadrupole/Time of Flight Tandem mass spectrometer with electron spray ionization. Cyclic voltammogram and differential pulse voltammetry (DPV) measurement were recorded on a CHI660E potentiostat. FT-IR spectra of the samples were recorded by Perkin Elmer. Nitrogen sorption isotherms were obtained with Micromeritics ASAP 2460 3.01 M+C accelerated surface area and porosimetry analyzers at certain temperatures. The samples were degassed for 6 h at 393 K before the measurements were obtained. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. Field emission scanning electron microscopy (SEM) observations were performed on a TESCAN MIRA LMS microscope operated at an accelerating voltage of 15.0 kV. The thermal gravity analysis (TGA) measurement was conducted on Simultaneous. Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (Rigaku TG/DTA8122), during which the sample was heated at the rate of 10 K min<sup>-1</sup> from room temperature up to 1073 K under a nitrogen atmosphere.

## 2. Experiment procedures

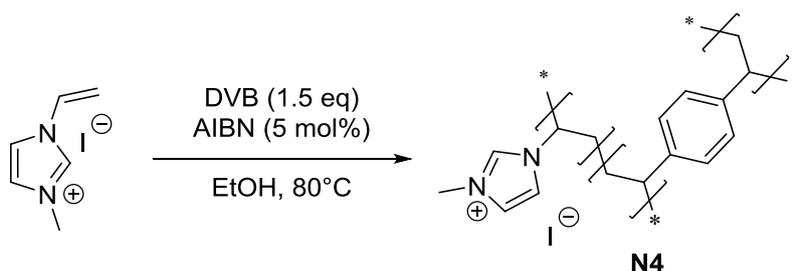
### 2.1 Synthesis of NHC Precatalysts



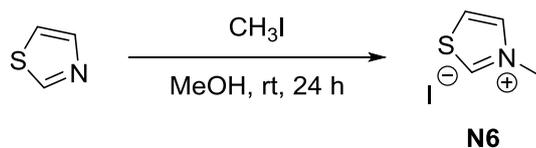
To a solution of 1-vinylimidazole (7.2 mL, 80 mmol) in acetone (20 mL) was added iodomethane (6 mL, 96 mmol, 1.2 equiv) drop wisely under room temperature. Stir the reaction mixture at room temperature for 12 h. Remove the acetone and unreacted iodomethane under reduced pressure. Recrystallize from acetonitrile/ethyl acetate. (14.14 g, 90%).  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.46 (s, 1H), 8.19 (t,  $J = 1.9$  Hz, 1H), 7.86 (t,  $J = 1.9$  Hz, 1H), 7.31 (dd,  $J = 15.6, 8.7$  Hz, 1H), 5.95 (dd,  $J = 15.7, 2.4$  Hz, 1H), 5.41 (dd,  $J = 8.7, 2.4$  Hz, 1H), 3.89 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{DMSO-}d_6$ )  $\delta$  135.80, 128.75, 124.37, 118.83, 108.57, 36.21.



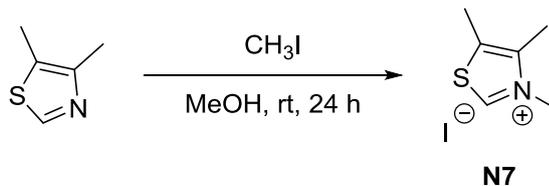
Obtained **N2** was polymerized with 2,2'-azobis(2-methylpropionitrile) (AIBN) as a radical polymerization initiator in ethanol at 70 °C for 5 h. The **N3** was obtained by removing ethanol from the solution and drying under vacuum at 60 °C for 24 h. **N3** was obtained as white powder at room temperature.



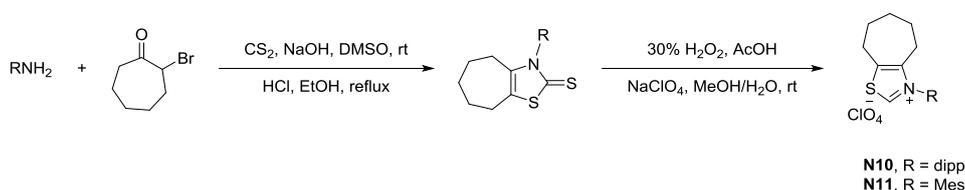
DVB (1.5 eq.) and **N2** (5 mmol) were added to a solution containing 0.05 eq of AIBN and DMSO (1.5 M). After stirring at room temperature for 0.5 h, the mixture was heated at 100 °C for 24 h. When the reaction was completed, the solution was filtered and washed with acetonitrile, deionized water, ethyl alcohol, ethyl acetate, and ether successively. Then the white solid **N4** was obtained. The nitrogen content of polymer **N4** was 4.52% by elemental analysis. Accordingly, the content of imidazolium in the polymer was calculated to be 1.614 mmol/g.



To a solution of thiazole (0.7 mL, 10 mmol) in methanol (10 mL) was added excess of iodomethane (5 mL). The mixture was stirred at room temperature for 24 h and the resulting white solid was collected by filtration, washed with EtOAc and dried to give the desired product **N5** as a white solid (1.41 g, 62%). Analytical data are in accordance with those previously reported for this compound.<sup>1</sup>



To a solution of 4,5-dimethylthiazole (1.07 g, 9.45 mmol) in methanol (10 mL) was added excess of iodomethane (5 mL). The mixture was stirred at room temperature for 48 h and the resulting white solid was collected by filtration, washed with EtOAc and dried to give the desired product **N6** as a white solid (2.05 g, 85%). Analytical data are in accordance with those previously reported for this compound.<sup>2</sup>

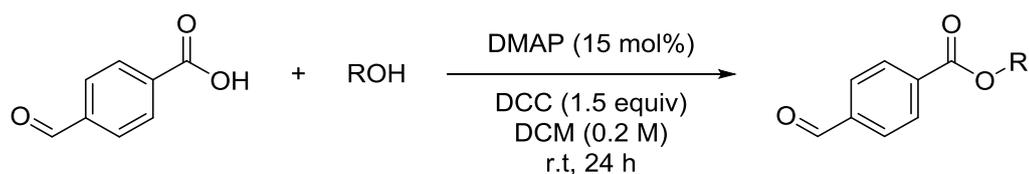


A solution of amine (25 mmol) in DMSO (10 mL) were treated with 20 N aq. NaOH solution (2 mL, 26 mmol, 1 equiv). To the solution was added CS<sub>2</sub> (1.56 mL, 26 mmol, 1 equiv) drop wisely at 0 °C. The resulting solution was allowed to room temperature and stirred at room temperature for 1 h. Then, 2-bromocycloheptanone (4.96 g, 26 mmol, 1 equiv) was added to the reaction mixture at 0 °C, and the mixture was stirred at room temperature at 12 h. H<sub>2</sub>O (20 mL) was added to reaction mixture at 0 °C, and the mixture was stirred at the same temperature for 30 min. The resulting supernatant solution was decanted three times. The resulting slurry was suspended in EtOH (20 mL), and concd. HCl (20 mL) was added to the mixture. After being heated at reflux for 1 h, the mixture was evaporated. The residue was dissolved in H<sub>2</sub>O (10 mL) and mixture was extracted three times with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. Then, the drying agent was removed by filtration and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel eluting from PE/EtOAc (20:1–10:1) to provide a yellow solid.

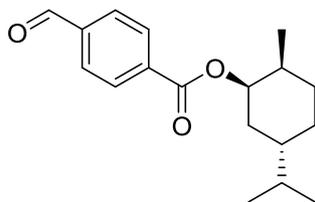
To a solution of the solid obtained above (1.51 mg, 5 mmol) in acetic acid (20 mL) was added 30% aq. H<sub>2</sub>O<sub>2</sub> solution (465 μL, 20 mmol) drop wisely under water bath cooling. The mixture was stirred at the same temperature for 1 h. Then, volatiles were removed under reduced pressure. The residue was dissolved in MeOH (3 mL). To the solution was added a solution of

NaClO<sub>4</sub> (2.45 g, 20 mmol) in MeOH/H<sub>2</sub>O (2:1, 10 mL) at 0 °C. The resulting solution was allowed to room temperature and stirred for 30 min. Then, H<sub>2</sub>O (10 mL) was added to the mixture. The mixture was extracted three times with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. Then, the drying agent was removed by filtration and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (100:0–95:5, CH<sub>2</sub>Cl<sub>2</sub>/MeOH) to provide product. Analytical data are in accordance with those previously reported for this compound.<sup>3</sup>

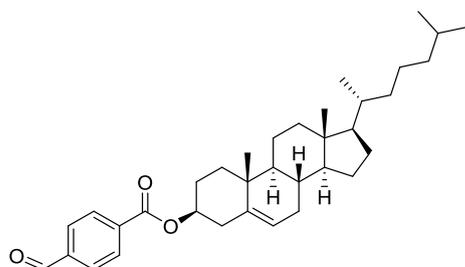
## 2.2 Synthesis of aldehydes 1q-1s.



To a stirred solution of 4-formylbenzoic acid (10.00 mmol, 1.00 equiv), alcohol (10.00 mmol, 1.00 equiv) and DMAP (4-dimethylaminepyridine) (1.5 mmol, 15 mol%) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) were added a solution of DCC (15 mmol, 1.5 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The reaction mixture was stirred at room temperature until the acid was consumed as monitored by TLC. Then diluted with diethyl ether (30 mL). The mixture was filtered through Celite<sup>®</sup>. The filtrate was successively washed with aqueous HCl (1N, 50 mL), saturated aqueous NaHCO<sub>3</sub> (50 mL) and brine (50 mL). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo to give the crude product. The residue was purified by flash column chromatography on silica gel.

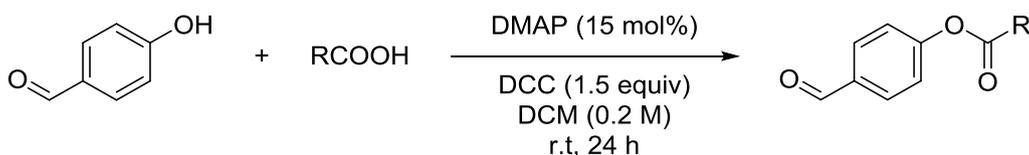


Following the general procedure, purified by flash column chromatography on silica gel (PE:EA=10:1), **1q** was obtained as a colorless oil. Analytical data are in accordance with those previously reported for this compound.<sup>4</sup>

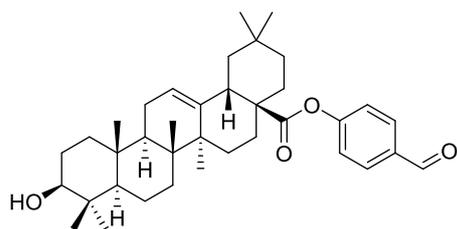


Following the general procedure, washed with ethanol, **1o** was obtained as a white solid (4.05g, 78% yield). Analytical data are in accordance with those previously reported for this compound.<sup>5</sup> <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 10.10 (s, 1H), 8.19 (d, *J* = 8.3 Hz, 2H), 7.94 (d,

$J = 8.3$  Hz, 2H), 5.43 (d,  $J = 4.3$  Hz, 1H), 4.91 – 4.86 (m, 1H), 2.49 – 2.47 (m, 2H), 2.03 – 1.94 (m, 4H), 1.84 – 1.74 (m, 2H), 1.58 – 1.42 (m, 7H), 1.38 – 1.33 (m, 3H), 1.22 – 1.09 (m, 7H), 1.07 (s, 3H), 1.02 – 0.97 (m, 3H), 0.92 (d,  $J = 6.5$  Hz, 3H), 0.87 (d,  $J = 2.8$  Hz, 3H), 0.86 (d,  $J = 2.8$  Hz, 3H), 0.69 (s, 3H).  $^{13}\text{C NMR}$  (151 MHz, Chloroform-*d*)  $\delta$  191.92, 165.12, 139.53, 139.14, 135.97, 130.30, 129.62, 123.20, 75.52, 56.81, 56.25, 50.15, 42.45, 39.85, 39.65, 38.27, 37.12, 36.78, 36.31, 35.94, 32.07, 32.00, 28.37, 28.16, 27.96, 24.43, 23.96, 22.97, 22.71, 21.19, 19.51, 18.86, 12.00.

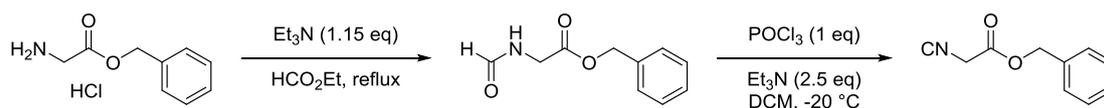


To a stirred solution of 4-hydroxybenzaldehyde (10.00 mmol, 1.00 equiv), acid (10.00 mmol, 1.00 equiv) and DMAP (4-dimethylaminepyridine) (1.5 mmol, 15 mol%) in  $\text{CH}_2\text{Cl}_2$  (30 ml) were added a solution of DCC (15 mmol, 1.5 equiv) in  $\text{CH}_2\text{Cl}_2$  (20 ml). The reaction mixture was stirred at room temperature until the acid was consumed as monitored by TLC. Then diluted with diethyl ether (30 mL). The mixture was filtered through Celite<sup>®</sup>. The filtrate was successively washed with aqueous HCl (1N, 50 mL), saturated aqueous  $\text{NaHCO}_3$  (50 mL) and brine (50 mL). The organic phase was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated in vacuo to give the crude product. The residue was purified by flash column chromatography on silica gel.



Following the general procedure, purified by flash column chromatography on silica gel (PE:EA=20:1-5:1), **1q** was obtained as a white solid (3.65 g, 65% yield). Analytical data are in accordance with those previously reported for this compound.<sup>5</sup>  $^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  9.98 (s, 1H), 7.90 (d,  $J = 8.5$  Hz, 2H), 7.20 (d,  $J = 8.5$  Hz, 2H), 5.36 (t,  $J = 3.7$  Hz, 1H), 3.22 (dd,  $J = 11.3, 4.6$  Hz, 1H), 2.96 (dd,  $J = 13.9, 4.6$  Hz, 1H), 2.13 – 2.08 (m, 1H), 1.95 – 1.91 (m, 2H), 1.80 – 1.75 (m, 3H), 1.61 – 1.54 (m, 6H), 1.50 (d,  $J = 4.2$  Hz, 1H), 1.45 – 1.37 (m, 3H), 1.35 – 1.27 (m, 4H), 1.19 (s, 3H), 0.99 (s, 3H), 0.97 (s, 3H), 0.94 (s, 3H), 0.91 (s, 3H), 0.91 – 0.85 (m, 2H), 0.83 (s, 3H), 0.78 (s, 3H), 0.76 – 0.72 (m, 1H).  $^{13}\text{C NMR}$  (151 MHz, Chloroform-*d*)  $\delta$  191.17, 175.78, 156.15, 143.21, 133.90, 131.31, 123.20, 122.54, 79.11, 55.33, 47.70, 47.50, 45.86, 41.96, 41.57, 39.62, 38.89, 38.59, 37.16, 37.11, 33.94, 33.18, 32.93, 32.47, 30.86, 28.24, 27.92, 27.31, 25.97, 23.73, 23.58, 23.19, 18.44, 17.53, 15.72, 15.49.

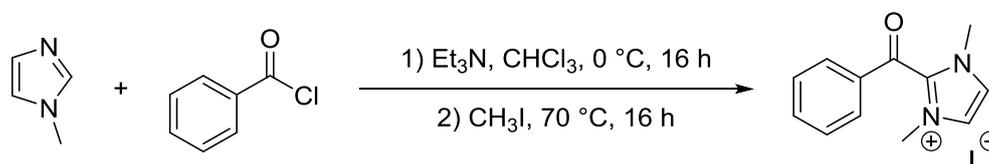
### 2.3 Synthesis of isocyanide acetates **1d**.



To a stirred solution of benzyl glycinate hydrochloride (20.00 mmol, 1.00 equiv) in ethyl formate (20 ml) were added Et<sub>3</sub>N (23 mmol, 1.15 equiv). After being heated at reflux for 24 h, the mixture was evaporated. Remove the ethyl formate under reduced pressure. The crude residue was purified by flash column chromatography on silica gel eluting from PE/EA (1:1) to provide a yellow liquid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 7.73 – 7.60 (m, 5H), 5.49 (s, 2H), 4.40 (d, *J* = 5.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 169.40, 161.64, 135.01, 128.57, 128.49, 128.27, 67.17, 39.85.

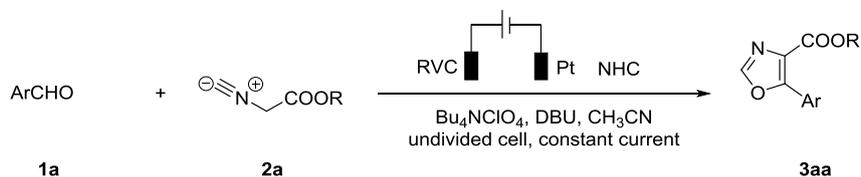
Dissolve the yellow liquid obtained above in DCM (1.2 M) and Et<sub>3</sub>N (2.5 eq) was added. POCl<sub>3</sub> (1.0 eq) was added dropwise over 5 minutes to a stirred solution at -20 °C. After stirring at -20 °C for 1.5 hours, the reaction was quenched with NaHCO<sub>3</sub> aqueous solution. The biphasic reaction mixture was stirred at room temperature for 10 minutes, water (20 mL) was then added and the phases were separated. The aqueous layer was extracted twice with DCM (20 × 3 mL), then the combined organic phases were washed with brine, dried over K<sub>2</sub>CO<sub>3</sub> and filtered. Evaporation of solvents afforded a brown oil, which was purified by flash column chromatography (PE:EA=3:1) to provide brown oil of benzyl 2-isocyanoacetate (3.06 g, 87%). <sup>1</sup>H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.30 (m, 5H), 5.24 (s, 2H), 4.24 (s, 2H). <sup>13</sup>C NMR (151 MHz, Chloroform-*d*) δ 163.92, 161.23, 134.41, 128.95, 128.80, 128.68, 68.36, 43.65 – 43.50 (m).

## 2.4 Synthesis of acylazolium 4.

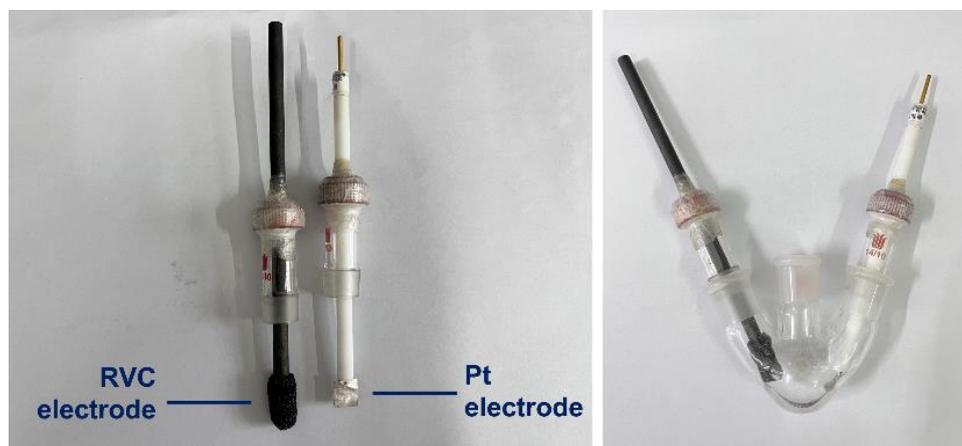


Charge a 100 mL round bottom flask equipped with a stir bar with 1-methylimidazole (0.82 g, 10 mmol). Placed the reaction mixture under a positive pressure of nitrogen. Add chloroform (15 mL) to the reaction mixture with stirring follow with addition of Et<sub>3</sub>N (2.02 g, 2 equiv) at 0 °C. Add benzoyl chloride (1.55 g, 1.1 equiv) dropwise to the reaction mixture at 0 °C, and the reaction mixture was stirred for 12 h at room temperature. After the indicated time, the reaction mixture was diluted with water (100 mL), extracted with chloroform (15 mL × 2) and concentrated to obtain pale yellow oil. Then the oil was dissolved in 3 mL of dioxane. CH<sub>3</sub>I (7.1 g, 5 equiv) was added, and the reaction mixture was heated at 70 °C for 16 h. The precipitated solid was filtered and washed with dioxane (3 mL), followed by hexanes (25 mL), to give the acylazolium **4** as pale yellow solid. Analytical data are in accordance with those previously reported for this compound.<sup>6</sup> <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ 8.03 (s, 2H), 7.96 – 7.94 (m, 2H), 7.87 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.70 – 7.67 (m, 2H), 3.80 (s, 6H). <sup>13</sup>C NMR (151 MHz, DMSO-*d*<sub>6</sub>) δ 180.46, 138.38, 136.04, 134.69, 130.32, 129.55, 125.46, 37.38.

## 2.5 General procedures for the Electrolysis.



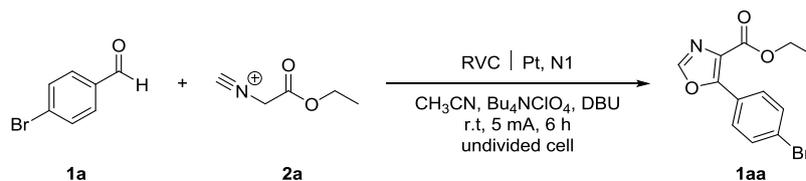
A 10 ml three-necked round bottom flask was charged with aldehyde compound (0.3 mmol, 1 equiv), isocyanide acetate (0.36 mmol, 1.2 equiv),  $\text{Bu}_4\text{NClO}_4$  (0.15 mmol 0.5 equiv), and NHC (0.06 mmol, 20 mol%). The flask was equipped with a RVC (100 PPI, 1 cm  $\times$  1 cm  $\times$  1.2 cm) anode and a platinum plate (1 cm x 1 cm x 0.1 cm) cathode.  $\text{CH}_3\text{CN}$  (5 mL) and base (0.3 mmol, 1 equiv) were added. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA for 6 h. After completed, the reaction was quenched with 55% HI (1 equiv). The mixture was filtered to recover the solid NHC catalyst, washed successively with  $\text{CH}_3\text{CN}$ , deionized water, EtOH, EtOAc, and ether, and dried under vacuum. The filtrate was extracted with EtOAc (3 $\times$ 15 mL). The organic layers were combined, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel to afford the desired products.



**Figure S1.** Undivided cell for current controlled electrolysis

## 2.6 Optimization of the Reaction Conditions.

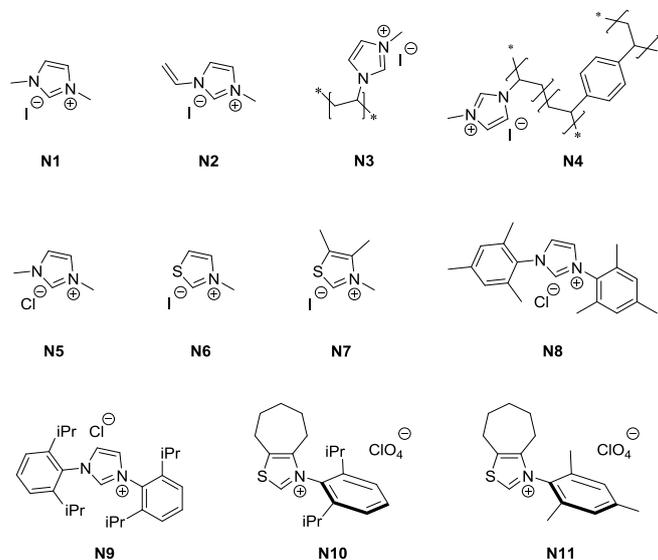
**Table S1.** Optimization of the reaction conditions for the synthesis of **3aa**<sup>a</sup>



entry	Variation from standard conditions	yield (%) <sup>b</sup>
1	none	51
2	<b>N2</b> instead of <b>N1</b>	57
3	<b>N3</b> instead of <b>N1</b>	55 <sup>c</sup>
4	<b>N3</b> instead of <b>N1</b>	58 <sup>d</sup>
7	<b>N4</b> instead of <b>N1</b>	88 <sup>c</sup>
8	<b>N4</b> instead of <b>N1</b>	75 <sup>d</sup>
9	<b>N4</b> instead of <b>N1</b>	85 <sup>e</sup>
10	<b>N5</b> instead of <b>N1</b>	0
11	<b>N6</b> instead of <b>N1</b>	10
12	<b>N7</b> instead of <b>N1</b>	30
13	<b>N8</b> instead of <b>N1</b>	41
14	<b>N9</b> instead of <b>N1</b>	15
15	<b>N10</b> instead of <b>N1</b>	trace
16	<b>N11</b> instead of <b>N1</b>	5
17	DCE instead of CH <sub>3</sub> CN	19
18	DMF instead of CH <sub>3</sub> CN	30
19	DMSO instead of CH <sub>3</sub> CN	12
20	THF instead of CH <sub>3</sub> CN	0
21	DCM instead of CH <sub>3</sub> CN	39
22	NMP instead of CH <sub>3</sub> CN	10
23	Bu <sub>4</sub> NBr instead of Bu <sub>4</sub> NClO <sub>4</sub>	41
24	Bu <sub>4</sub> NI instead of Bu <sub>4</sub> NClO <sub>4</sub>	45
25	Bu <sub>4</sub> NOTs instead of Bu <sub>4</sub> NClO <sub>4</sub>	47
26	Bu <sub>4</sub> NBF <sub>4</sub> instead of Bu <sub>4</sub> NClO <sub>4</sub>	44
27	Bu <sub>4</sub> NPF <sub>6</sub> instead of Bu <sub>4</sub> NClO <sub>4</sub>	48
28	Et <sub>3</sub> N instead of DBU	0
29	KHCO <sub>3</sub> instead of DBU	13
30	Cs <sub>2</sub> CO <sub>3</sub> instead of DBU	41
31	DABCO instead of DBU	20
32	TBD instead of DBU	47
33	Pt plate as anode, Pt plate as cathode	44
34	RVC plate as anode, RVC plate as cathode	49
35	Graphite as anode, Ni plate as cathode	18
36	<b>1a</b> : <b>2a</b> = 2:1	25
37	<b>1a</b> : <b>2a</b> = 1:2	35

<sup>a</sup> Reaction conditions: Reticulated vitreous carbon (RVC) anode (100 PPI, 1 cm × 1 cm × 1.2 cm), Pt plate cathode (1 cm × 1 cm), undivided cell, 4-bromobenzaldehyde **1a** (0.3 mmol, 1.0 equiv), ethyl isocyanoacetate **2a** (0.36 mmol, 1.2 equiv), NHC catalyst (20 mol%), electrolyte (0.5 equiv)

and base (1.0 equiv) in CH<sub>3</sub>CN (0.05 M) at room temperature, 5 mA for 6 h; <sup>b</sup>Isolated yields. <sup>c</sup>NHC (30 mg). <sup>d</sup>NHC (25 mg). <sup>e</sup>NHC (35 mg).



## 2.5 General procedures for gram-scale reaction.

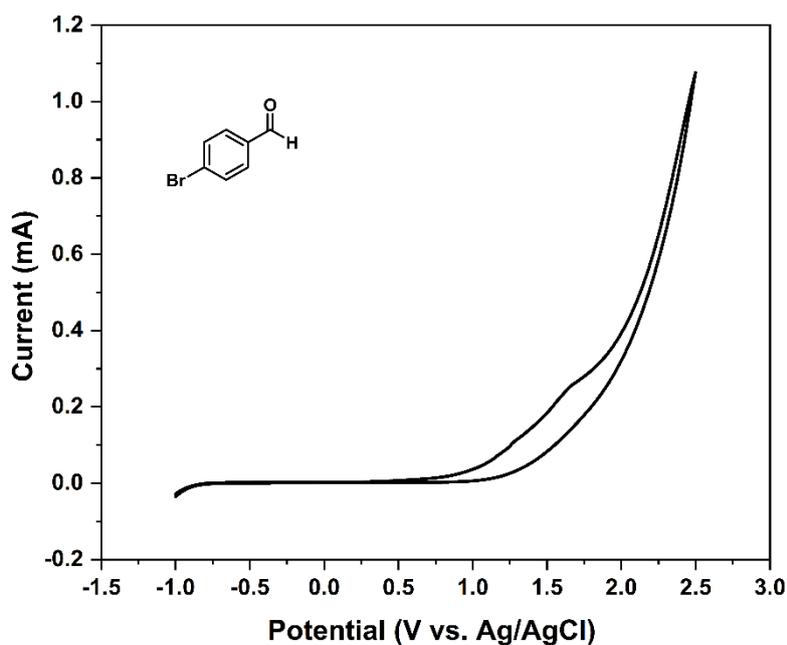
A single-chamber electrolytic cell was charged with 4-bromobenzaldehyde (12 mmol, 2.22 g), Bu<sub>4</sub>NClO<sub>4</sub> (6 mmol 2.05 g), and NHC (0.44 g, 20 %wt of aldehyde). The flask was equipped with a RVC (100 PPI, 3 cm × 3 cm × 1.5 cm) anode and a platinum plate (3 cm x 3 cm x 0.1 cm) cathode. CH<sub>3</sub>CN (0.06 M) and base (0.3 mmol, 1 equiv) were added. Slowly add ethyl isocyanoacetate (15 mmol 1.69 g) when the reaction mixture was stirred and electrolyzed at a constant current of 50 mA at room temperature. After 24 h, the mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was dissolved with EtOAc, washed with water and extracted with EtOAc (3×50 mL). The organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel to afford **1aa**.



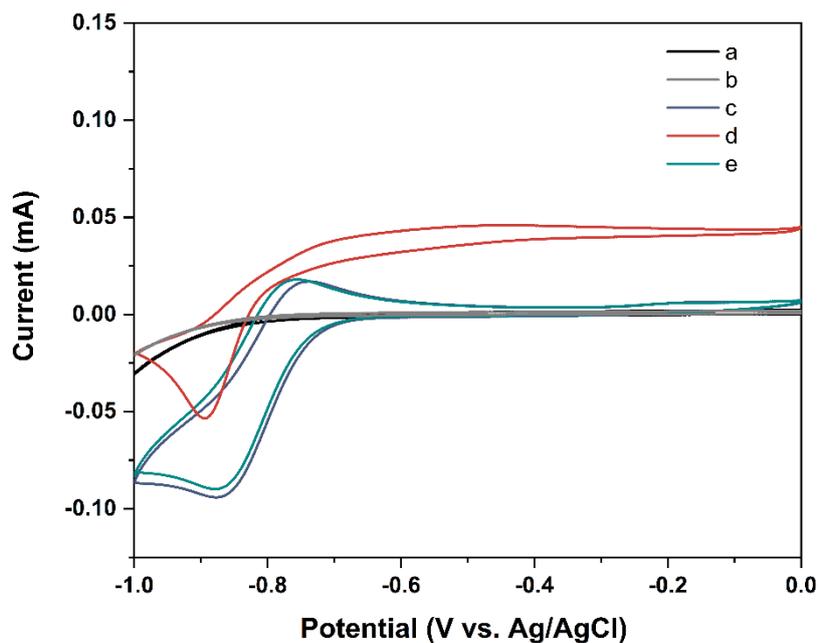
**Figure S2.** Gram-scale reaction

## 2.6 Procedure for cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

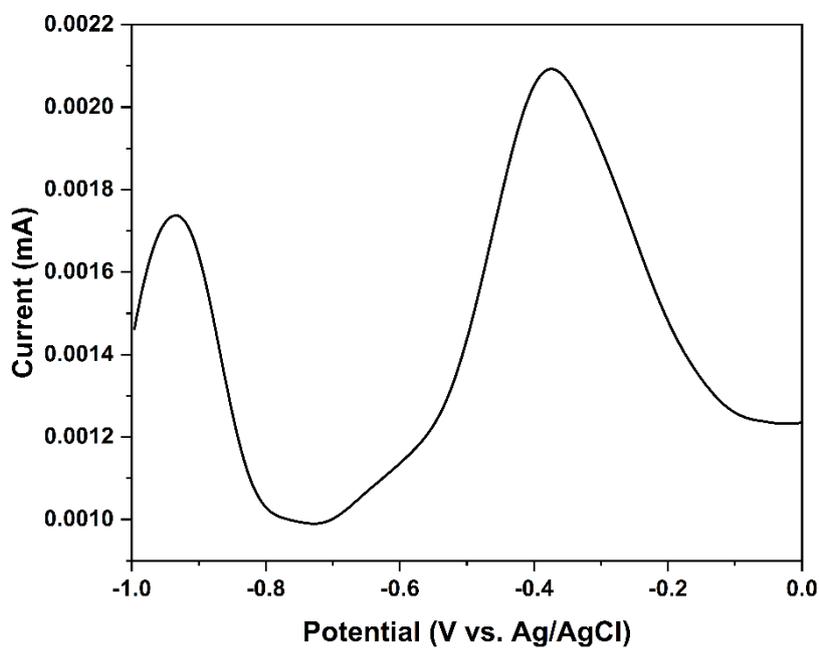
Cyclic voltammograms and differential pulse voltammetry are depicted in Figure S2. They were performed in a three electrodes cell at room temperature after bubbling with nitrogen for 15 minutes. The electrodes cell was charged with  $\text{CH}_3\text{CN}$  (5 mL) and  $\text{Bu}_4\text{NClO}_4$  (0.2 M) and equipped with a steady glassy carbon disk electrode, platinum wire counter electrode and Ag/AgCl reference electrode (submerged in saturated aqueous KCl solution and separated from reaction by a salt bridge). For CV of aldehyde, the aldehyde (0.02 M) was added to the mixture. Alternatively, for CV and DPV of the Breslow intermediate, aldehyde (0.02 M) NHC precatalyst (0.01 M) and DBU (0.02 M) were added to the mixture. The cyclic voltammograms for the aldehyde was taken from -1.0 V to +2.5 V vs. Ag/AgCl and the cyclic voltammograms for the Breslow intermediates was taken from -1.0 V to -0.2 V vs. Ag/AgCl with a sweep rate of 0.10 V/s. The differential pulse voltammetry for the Breslow intermediate is based on its CV condition.



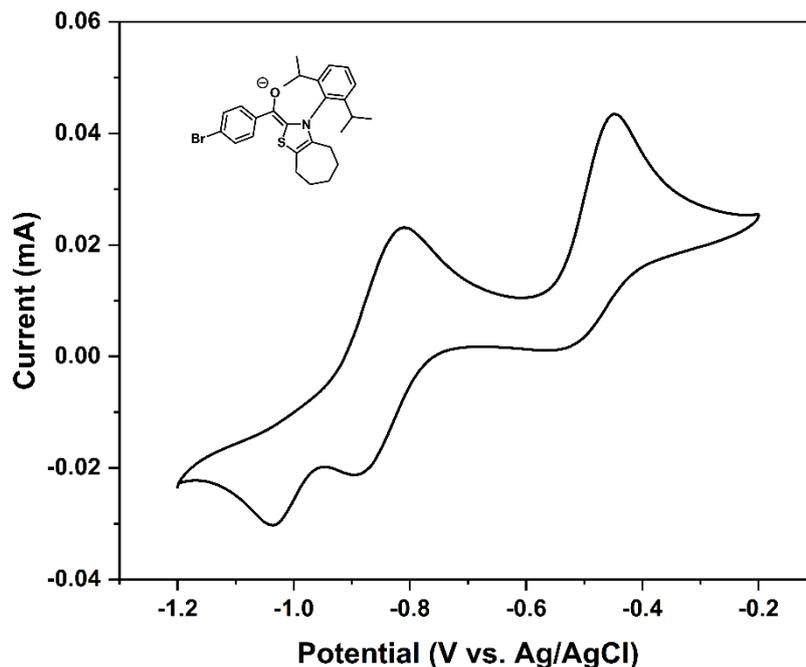
**Figure S3.** CV of 4-bromobenzaldehyde



**Figure S4** Cyclic voltammograms in an electrolyte solution of  $\text{Bu}_4\text{NClO}_4$  (0.2 M) in  $\text{CH}_3\text{CN}$  using a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl as counter and reference electrode at 0.10 mV/s scan rate: (a) DBU (0.02 M); (b) 4-bromobenzaldehyde (0.02 M) + DBU (0.02 M); (c) **N1** (0.01 M) + DBU (0.02 M); (d) 4-bromobenzaldehyde (0.02 M) + **N1** (0.01 M) + DBU (0.02 M); (e) **N5** (0.01 M) + DBU (0.02 M).



**Figure S5** DPV of Breslow intermediate derived with **N1** and aldehyde 4-bromobenzaldehyde.

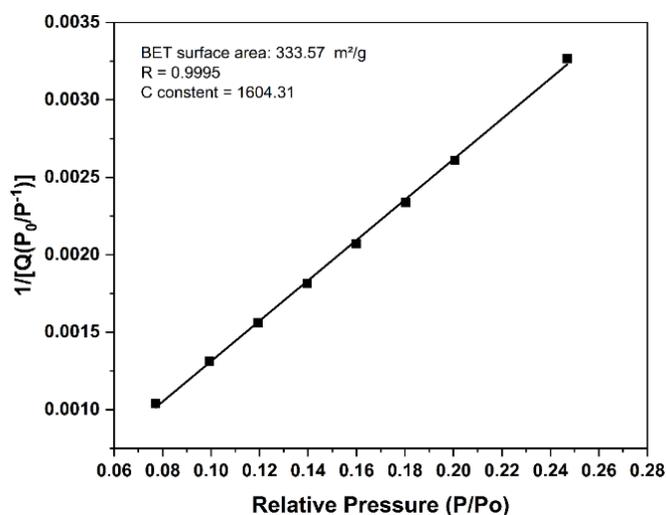


**Figure S6** CV of Breslow intermediate derived with **N10** and aldehyde 4-bromobenzaldehyde.

When **N1** NHC catalyst was added, no obvious oxidation current peak was observed in CV. The overpotential for the oxidation of the Breslow intermediate at the electrode may be high. Or the electron-transfer step is faster than the preceding chemical step, resulting the concentration of Breslow intermediate in solution is low, and no obvious oxidation current peak due to its formation will be hard to be observed in CV. Two oxidation peaks were observed ( $-0.93$  and  $-0.38$  V) in differential pulse voltammetry (DPV).

### 3. General Characterization of the **N4**.

#### 3.1 BET of **N4**.



**Figure S6** BET plot of **N4**

### 3.2 SEM image and FT-IR spectra of N4 recycle.

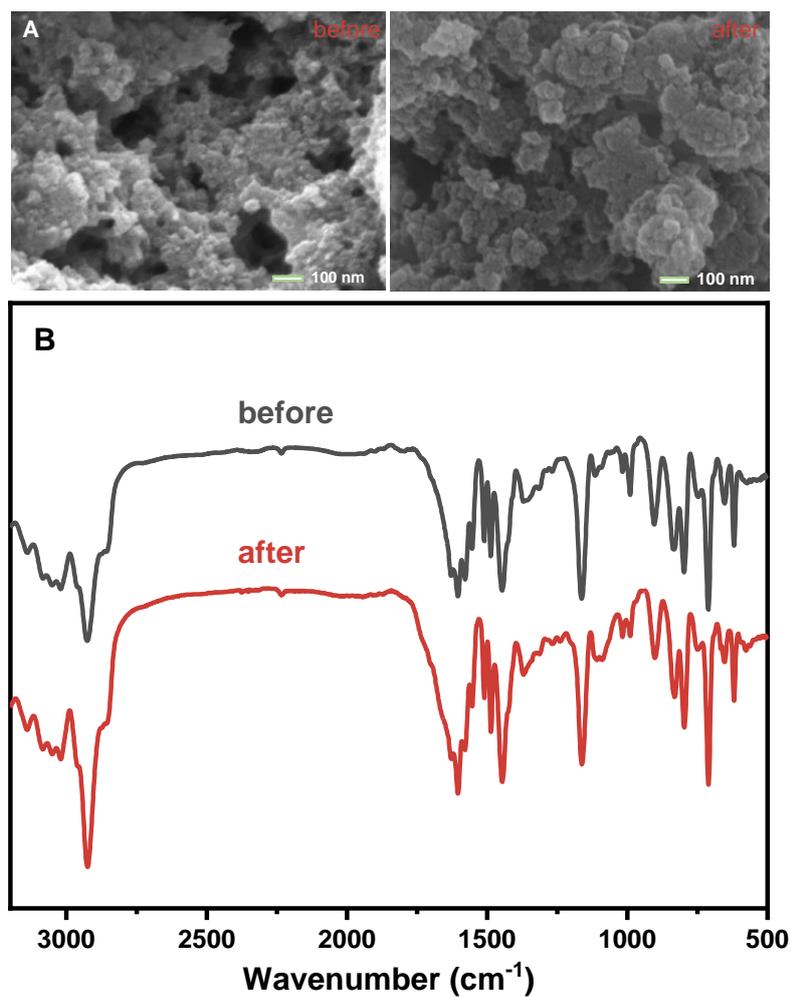
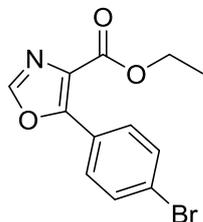


Figure S7 A: SEM image of N4 that refers to N4 reused for 5 times, scale bar 100 nm; B: FT-IR spectra of N4 and N4-after recorded as KBr pellets.

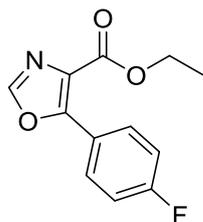
## 4. Characterization Data

### Ethyl 5-(4-bromophenyl)oxazole-4-carboxylate (3aa).



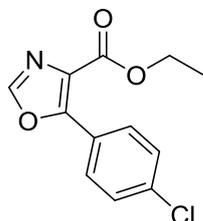
White solid (78.17 mg, 88%). Petroleum ether/ethyl acetate = 50/1–10/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.99 – 7.96 (m, 2H), 7.91 (s, 1H), 7.62 – 7.58 (m, 2H), 4.41 (q,  $J = 7.1$  Hz, 2H), 1.40 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  161.97, 154.60, 149.19, 131.84, 130.02, 127.12, 125.68, 125.16, 61.71, 14.35. **HRMS** (m/z) [ESI]: calculated for  $[\text{C}_{12}\text{H}_{10}\text{BrNO}_3+\text{H}]^+$ : 295.9917, found: 295.9925.

### Ethyl 5-(4-fluorophenyl)oxazole-4-carboxylate (3ba).



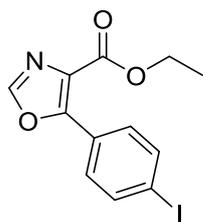
White solid (55.75 mg, 79%). Petroleum ether/ethyl acetate = 50/1–10/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.12 – 8.07 (m, 2H), 7.89 (s, 1H), 7.17 – 7.11 (m, 2H), 4.40 (q,  $J = 7.1$  Hz, 2H), 1.39 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  165.17, 162.67, 162.04, 154.79, 148.98, 130.88, 130.79, 123.00, 115.84, 115.63, 61.60, 14.32. **HRMS** (m/z) [ESI]: calculated for  $[\text{C}_{12}\text{H}_{10}\text{FNO}_3+\text{H}]^+$ : 236.0723, found: 236.0727.

### Ethyl 5-(4-chlorophenyl)oxazole-4-carboxylate (3ca).



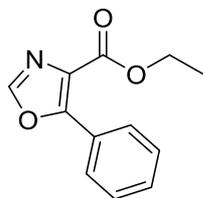
White solid (63.42 mg, 84%). Petroleum ether/ethyl acetate = 50/1–10/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.03 (d,  $J = 8.7$  Hz, 2H), 7.90 (s, 1H), 7.42 (d,  $J = 8.7$  Hz, 2H), 4.39 (q,  $J = 7.1$  Hz, 2H), 1.39 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  161.93, 154.50, 149.14, 136.66, 129.81, 128.82, 126.97, 125.18, 61.65, 14.30. **HRMS** (m/z) [ESI]: calculated for  $[\text{C}_{12}\text{H}_{10}\text{ClNO}_3+\text{H}]^+$ : 252.0427, found: 252.0435.

### Ethyl 5-(4-iodophenyl)-4-oxazolecarboxylate (3da).



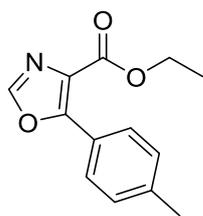
White solid (78.17 mg, 89%). Petroleum ether/ethyl acetate = 50/1–10/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.90 (s, 1H), 7.85 – 7.76 (m, 4H), 4.40 (q,  $J = 7.1$  Hz, 2H), 1.39 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  161.90, 154.64, 149.21, 137.76, 129.95, 127.18, 126.19, 97.29, 61.67, 14.32. **HRMS** (m/z) [ESI]: calculated for  $[\text{C}_{12}\text{H}_{10}\text{INO}_3+\text{H}]^+$ :343.9778, found: 343.9793.

### Ethyl 5-phenyloxazole-4-carboxylate (3ea).



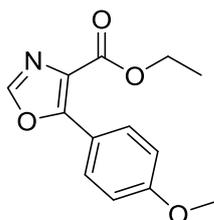
Colorless oil (54.74 mg, 84%). Petroleum ether/ethyl acetate = 50/1–10/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.07 – 8.05 (m, 2H), 7.90 (s, 1H), 7.49 – 7.44 (m, 3H), 4.41 (q,  $J = 7.1$  Hz, 2H), 1.40 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  162.05, 155.64, 149.11, 130.59, 128.59, 128.53, 126.80, 126.72, 61.54, 14.34. **HRMS** (m/z) [ESI]: calculated for  $[\text{C}_{12}\text{H}_{11}\text{NO}_3+\text{H}]^+$ : 218.0812, found: 218.0818.

### Ethyl 5-(*p*-tolyl)oxazole-4-carboxylate (3fa).



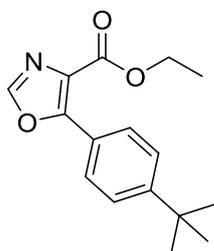
White solid (58.96 mg, 85%). Petroleum ether/ethyl acetate = 50/1–10/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  7.96 (d,  $J = 8.3$  Hz, 2H), 7.88 (s, 1H), 7.28 (d,  $J = 8.0$  Hz, 2H), 4.41 (q,  $J = 7.1$  Hz, 2H), 2.41 (s, 3H), 1.40 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  162.16, 155.97, 148.84, 141.03, 129.27, 128.52, 126.18, 124.01, 61.48, 21.65, 14.39. **HRMS** (m/z) [ESI]: calculated for  $[\text{C}_{13}\text{H}_{13}\text{NO}_3+\text{H}]^+$ :232.0968, found: 232.0979.

### Ethyl 5-(4-methoxyphenyl)oxazole-4-carboxylate (3ga).



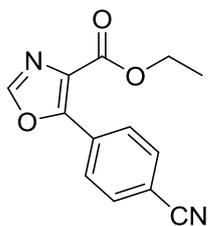
White solid (60.82 mg, 82%). Petroleum ether/ethyl acetate = 50/1–10/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.08 – 8.05 (m, 2H), 7.86 (s, 1H), 7.01 – 6.97 (m, 2H), 4.41 (q,  $J = 7.1$  Hz, 2H), 3.86 (s, 3H), 1.41 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  162.32, 161.40, 155.95, 148.54, 130.31, 125.44, 119.36, 114.00, 61.46, 55.52, 14.42. **HRMS** ( $m/z$ ) [ESI]: calculated for  $[\text{C}_{13}\text{H}_{13}\text{NO}_4+\text{Na}]^+$ :270.0737, found: 270.0750.

**Ethyl 5-(4-(tert-butyl)phenyl)oxazole-4-carboxylate (3ha).**



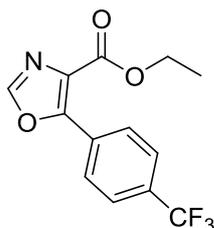
Colorless oil (68.87 mg, 84%). Petroleum ether/ethyl acetate = 50/1–10/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.00 (d,  $J = 8.6$  Hz, 2H), 7.88 (s, 1H), 7.49 (d,  $J = 8.6$  Hz, 1H), 4.41 (q,  $J = 7.1$  Hz, 2H), 1.41 (t,  $J = 7.1$  Hz, 3H), 1.34 (s, 9H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  162.16, 155.95, 154.03, 148.90, 128.36, 126.25, 125.53, 123.96, 61.47, 35.02, 31.22, 14.38. **HRMS** ( $m/z$ ) [ESI]: calculated for  $[\text{C}_{16}\text{H}_{19}\text{NO}_3+\text{Na}]^+$ :296.1257, found: 296.1270.

**Ethyl 5-(4-cyanophenyl)oxazole-4-carboxylate (3ia).**



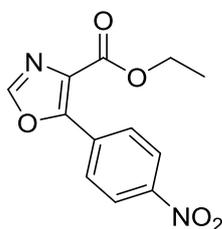
White solid (57.4 mg, 79%). Petroleum ether/ethyl acetate = 10/1–6.5/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.26 (d,  $J = 8.2$  Hz, 2H), 7.98 (d,  $J = 1.0$  Hz, 1H), 7.76 (d,  $J = 8.2$  Hz, 2H), 4.43 (q,  $J = 7.6, 7.1$  Hz, 2H), 1.46 – 1.38 (m, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  161.74, 153.28, 149.92, 132.33, 130.81, 128.96, 128.74, 118.35, 113.87, 62.04, 14.32. **HRMS** ( $m/z$ ) [ESI]: calculated for  $[\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3+\text{H}]^+$ :243.0764, found: 243.0768.

**Ethyl 5-(4-(trifluoromethyl)phenyl)oxazole-4-carboxylate (3ja).**



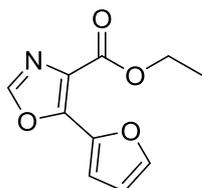
White solid (47.34 mg, 83%). Petroleum ether/ethyl acetate = 20/1–8/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.23 (d,  $J$  = 8.1 Hz, 2H), 7.96 (s, 1H), 7.73 (d,  $J$  = 8.3 Hz, 2H), 4.43 (q,  $J$  = 7.1 Hz, 2H), 1.42 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  161.83, 153.96, 149.69, 132.63, 132.31, 131.98, 131.66, 130.11, 128.90, 128.13, 125.61, 125.57, 125.53, 125.50, 122.49, 61.88, 14.34. **HRMS** (m/z) [ESI]: calculated for  $[\text{C}_{13}\text{H}_{10}\text{F}_3\text{NO}_3+\text{H}]^+$ :286.0686, found: 286.0693.

#### Ethyl 5-(4-nitrophenyl)oxazole-4-carboxylate (3ka).



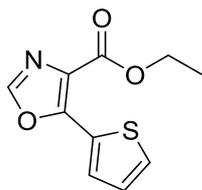
Light yellow solid (52.70 mg, 67%). Petroleum ether/ethyl acetate = 20/1–8/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.36 – 8.31 (m, 4H), 8.01 (s, 1H), 4.45 (q,  $J$  = 7.2 Hz, 2H), 1.43 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$   $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.71, 152.96, 150.12, 148.57, 132.54, 129.42, 129.14, 123.82, 62.12, 14.34. **HRMS** (m/z) [ESI]: calculated for  $[\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_5+\text{H}]^+$ :263.0662, found: 263.0673.

#### Ethyl 5-(furan-2-yl)oxazole-4-carboxylate (3la).



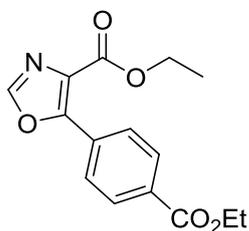
White solid (43.51 mg, 70%). Petroleum ether/ethyl acetate = 50/1–10/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.85 (s, 1H), 7.65 (dd,  $J$  = 3.6, 0.8 Hz, 1H), 7.60 (dd,  $J$  = 1.8, 0.8 Hz, 1H), 6.58 (dd,  $J$  = 3.6, 1.8 Hz, 1H), 4.43 (q,  $J$  = 7.1 Hz, 2H), 1.43 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  161.52, 148.63, 147.37, 144.81, 142.04, 125.19, 115.82, 112.47, 61.53, 14.44. **HRMS** (m/z) [ESI]: calculated for  $[\text{C}_{10}\text{H}_9\text{NO}_4+\text{Na}]^+$ :230.0424, found: 230.0423.

#### Ethyl 5-(thiophen-2-yl)oxazole-4-carboxylate (3ma).



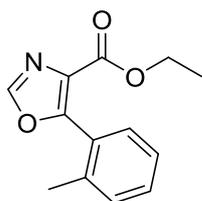
Colorless oil (42.19 mg, 63%). Petroleum ether/ethyl acetate = 50/1–10/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.08 (dd,  $J = 3.9, 1.2$  Hz, 1H), 7.81 (s, 1H), 7.53 (dd,  $J = 5.0, 1.2$  Hz, 1H), 7.15 (dd,  $J = 5.1, 3.8$  Hz, 1H), 4.45 (q,  $J = 7.2$  Hz, 2H), 1.44 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  162.02, 151.55, 148.22, 130.60, 129.98, 128.23, 127.89, 124.72, 61.57, 14.46. **HRMS** ( $m/z$ ) [ESI]: calculated for  $[\text{C}_{10}\text{H}_9\text{NO}_3\text{S}+\text{H}]^+$ :224.0376, found: 224.0381.

### Ethyl 5-(4-(ethoxycarbonyl)phenyl)oxazole-4-carboxylate (3na)



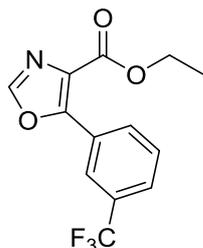
White solid (64.22 mg, 74%). Petroleum ether/ethyl acetate = 50/1–10/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.17 – 8.11 (m, 4H), 7.95 (s, 1H), 4.41 (dq,  $J = 10.2, 7.1$  Hz, 4H), 1.40 (td,  $J = 7.1, 1.8$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  165.98, 161.84, 154.36, 149.62, 131.98, 130.68, 129.68, 128.42, 128.00, 61.79, 61.41, 14.41, 14.34. **HRMS** ( $m/z$ ) [ESI]: calculated for  $[\text{C}_{15}\text{H}_{15}\text{NO}_5+\text{H}]^+$ :290.1023, found: 290.1033.

### Ethyl 5-(*o*-tolyl)oxazole-4-carboxylate (3oa)



Colorless oil (52.03 mg, 75%). Petroleum ether/ethyl acetate = 10/1–7/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.95 (s, 1H), 7.46 – 7.43 (m, 1H), 7.39 (td,  $J = 7.5, 1.5$  Hz, 1H), 7.31 – 7.27 (m, 2H), 4.30 (d,  $J = 7.1$  Hz, 2H), 2.27 (s, 3H), 1.27 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  161.52, 156.29, 149.94, 138.10, 131.01, 130.64, 130.49, 128.44, 126.72, 125.54, 61.27, 20.14, 14.20. **HRMS** ( $m/z$ ) [ESI]: calculated for  $[\text{C}_{13}\text{H}_{13}\text{NO}_3+\text{H}]^+$ :232.0968, found: 232.0966.

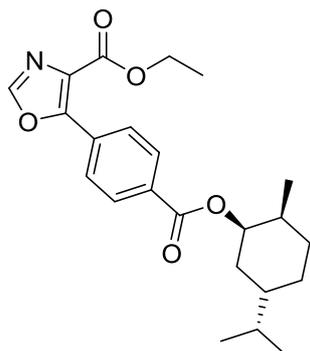
### Ethyl 5-(2-(trifluoromethyl)phenyl)oxazole-4-carboxylate (3pa)



Colorless oil (46.77 mg, 82%). Petroleum ether/ethyl acetate = 10/1–7/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.36 (s, 1H), 8.29 (d,  $J = 8.0$  Hz, 1H), 7.95 (s, 1H), 7.69 (d,  $J = 7.9$  Hz, 1H), 7.59 (t,  $J = 7.9$  Hz, 1H), 4.41 (q,  $J = 6.8$  Hz, 2H), 1.39 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  161.73, 153.81, 149.57, 131.70, 131.27, 130.95, 129.14, 127.74, 127.57, 127.02 (q,  $J = 3.7$  Hz), 125.44 (q,  $J = 3.9$  Hz), 61.82, 14.22. **HRMS** ( $m/z$ ) [ESI]: calculated for  $[\text{C}_{13}\text{H}_{10}\text{F}_3\text{NO}_3+\text{H}]^+$ :286.0686, found: 286.0681.

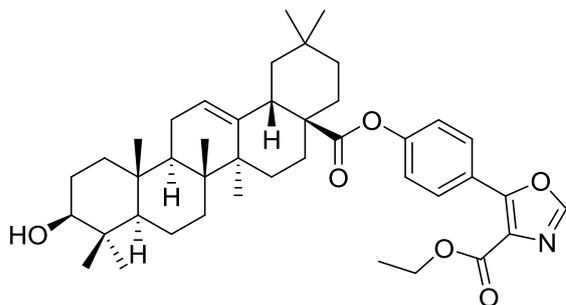
### Ethyl

#### 5-(4-(((1S,2R,5S)-5-isopropyl-2-methylcyclohexyl)oxy)carbonyl)phenyl)oxazole-4-carboxylate (3qa).



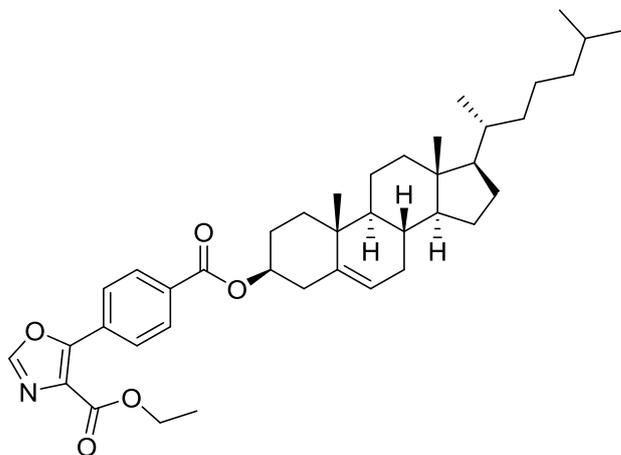
Colorless oil (85.09 mg, 71%). Petroleum ether/ethyl acetate = 20/1–9/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.17 – 8.12 (m, 4H), 7.96 (s, 1H), 4.94 (td,  $J = 10.9, 4.4$  Hz, 1H), 4.43 (q,  $J = 7.1$  Hz, 2H), 2.16 – 2.10 (m, 1H), 1.95 – 1.91 (m, 1H), 1.75 – 1.67 (m, 3H), 1.60 – 1.52 (m, 2H), 1.41 (t,  $J = 7.1$  Hz, 3H), 1.19 – 1.07 (m, 2H), 0.94 – 0.91 (m, 6H), 0.79 (d,  $J = 6.9$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  165.48, 161.86, 154.48, 149.62, 132.38, 130.59, 129.71, 128.45, 127.98, 75.42, 61.80, 47.38, 41.04, 34.40, 31.57, 26.66, 23.75, 22.16, 20.88, 16.65, 14.36. **HRMS** ( $m/z$ ) [ESI]: calculated for  $[\text{C}_{23}\text{H}_{29}\text{NO}_5+\text{H}]^+$ :400.2118, found: 400.2131.

#### Ethyl 5-(4-(((4aS,6aS,6bR,8aR,10S,12aR,12bR,14bS)-10-hydroxy-2,2,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydricene-4a-carbonyl)oxy)phenyl)oxazole-4-carboxylate (3ra)



White solid (139.08 mg, 69%). Petroleum ether/ethyl acetate = 10/1–5/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.13 – 8.09 (m, 2H), 7.89 (s, 1H), 7.16 – 7.12 (m, 2H), 5.35 (t,  $J = 3.6$  Hz, 1H), 4.41 (q,  $J = 7.1$  Hz, 2H), 3.23 – 3.19 (m, 1H), 2.97 (dd,  $J = 13.8, 4.6$  Hz, 1H), 2.13 – 2.06 (m, 1H), 1.96 – 1.70 (m, 8H), 1.67 – 1.44 (m, 9H), 1.40 (t,  $J = 7.1$  Hz, 3H), 1.35 – 1.24 (m, 4H), 1.18 (s, 3H), 0.99 (s, 3H), 0.97 (s, 3H), 0.93 (s, 3H), 0.91 (s, 3H), 0.84 (s, 3H), 0.78 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  175.97, 162.05, 155.02, 152.86, 149.02, 143.30, 129.87, 126.63, 124.09, 123.09, 121.86, 79.08, 61.59, 55.33, 47.71, 47.37, 45.89, 41.94, 41.56, 39.62, 38.86, 38.58, 37.14, 33.94, 33.18, 32.93, 32.48, 30.84, 28.22, 27.90, 27.29, 25.96, 23.72, 23.56, 23.16, 18.43, 17.55, 15.71, 15.46, 14.37. **HRMS** ( $m/z$ ) [ESI]: calculated for  $[\text{C}_{42}\text{H}_{57}\text{NO}_6 + \text{Na}]^+$ : 694.4078, found: 694.4074.

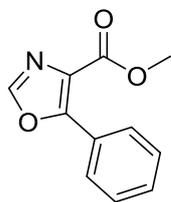
**Ethyl 5-(4-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)carbonyl)phenyl)oxazole-4-carboxylate (1sa)**



White solid (83.14 mg, 44%). Petroleum ether/ethyl acetate = 10/1–8/1 (v/v) as eluent for column chromatography.  $^1\text{H NMR}$  (600 MHz, Chloroform-*d*)  $\delta$  8.17 – 8.13 (m, 4H), 7.96 (s, 1H), 5.44 – 5.42 (m, 1H), 4.91 – 4.86 (m, 1H), 4.43 (q,  $J = 7.1$  Hz, 2H), 2.48 (d,  $J = 7.6$  Hz, 2H), 2.05 – 1.91 (m, 6H), 1.61 – 1.51 (m, 10H), 1.42 (t,  $J = 7.1$  Hz, 4H), 1.25 (s, 9H), 1.08 (s, 3H), 0.92 (d,  $J = 6.5$  Hz, 3H), 0.87 (d,  $J = 2.8$  Hz, 3H), 0.86 (d,  $J = 2.8$  Hz, 3H), 0.69 (s, 3H).  $^{13}\text{C NMR}$  (151 MHz, Chloroform-*d*)  $\delta$  165.41, 161.88, 154.47, 149.62, 139.67, 132.37, 130.63, 129.73, 128.44, 128.01, 123.08, 75.15, 61.83, 56.83, 56.26, 50.16, 42.46, 39.86, 39.65, 38.32, 37.15, 36.79, 36.32, 35.94, 32.08, 32.01, 28.38, 28.16, 28.00, 27.35, 25.68, 24.44, 23.97, 22.98, 22.71,

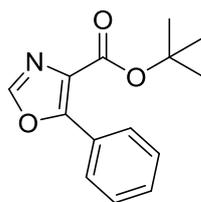
21.19, 19.53, 18.86, 14.39, 12.01. **HRMS** (m/z) [ESI]: calculated for  $[C_{40}H_{55}NO_5+NH_4]^+$ :647.4418, found: 647.4477.

**Methyl 5-phenyloxazole-4-carboxylate. (3eb)**



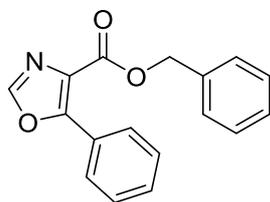
Light yellow oil (52.42 mg, 86%). Petroleum ether/ethyl acetate = 8/1 (v/v) as eluent for column chromatography. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.09 – 8.06 (m, 2H), 7.91 (s, 1H), 7.49 – 7.46 (m, 3H), 3.94 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  162.48, 155.81, 149.09, 130.68, 128.59, 128.52, 126.69, 126.43, 52.44. **HRMS** (m/z) [ESI]: calculated for  $[C_{11}H_9NO_3+H]^+$ :204.0655, found: 204.0647.

**Tert-butyl 5-phenyloxazole-4-carboxylate (3ec)**



Colorless oil (53.71 mg, 73%). Petroleum ether/ethyl acetate = 8/1 (v/v) as eluent for column chromatography. **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.99 – 7.97 (m, 2H), 7.89 (s, 1H), 7.48 – 7.44 (m, 3H), 1.59 (s, 9H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  161.24, 154.94, 149.12, 130.36, 128.77, 128.45, 128.03, 127.21, 82.53, 28.32. **HRMS** (m/z) [ESI]: calculated for  $[C_{14}H_{15}NO_3+Na]^+$ :268.0944, found: 268.0939.

**Benzyl 5-phenyloxazole-4-carboxylate (3ed)**



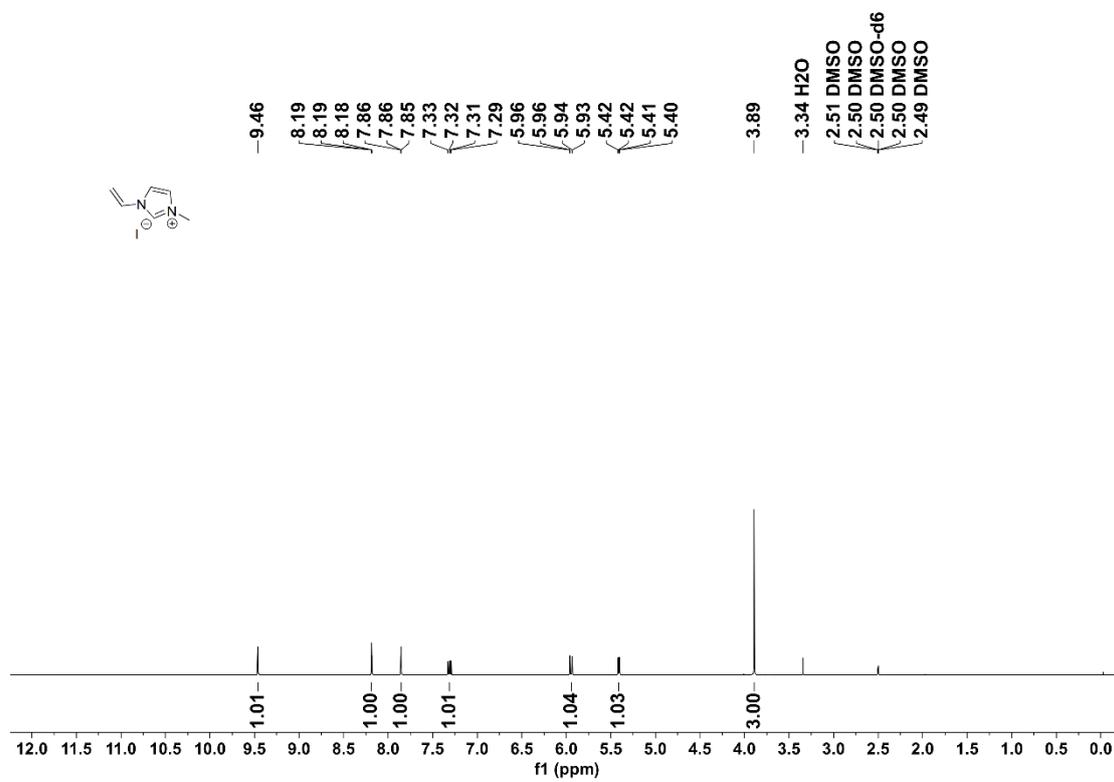
White solid (76.24 mg, 91%). Petroleum ether/ethyl acetate = 8/1 (v/v) as eluent for column chromatography. **<sup>1</sup>H NMR** (600 MHz, Chloroform-*d*)  $\delta$  8.03 – 8.01 (m, 2H), 7.91 (s, 1H), 7.45 – 7.42 (m, 5H), 7.36 – 7.31 (m, 3H), 5.40 (s, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>)  $\delta$  161.82, 155.87, 149.18, 135.53, 130.61, 128.66, 128.63, 128.52, 128.45, 128.39, 126.69, 126.50, 77.37, 76.95, 67.07. **HRMS** (m/z) [ESI]: calculated for  $[C_{17}H_{13}NO_3+H]^+$ :280.0968, found: 280.0964.

## Reference

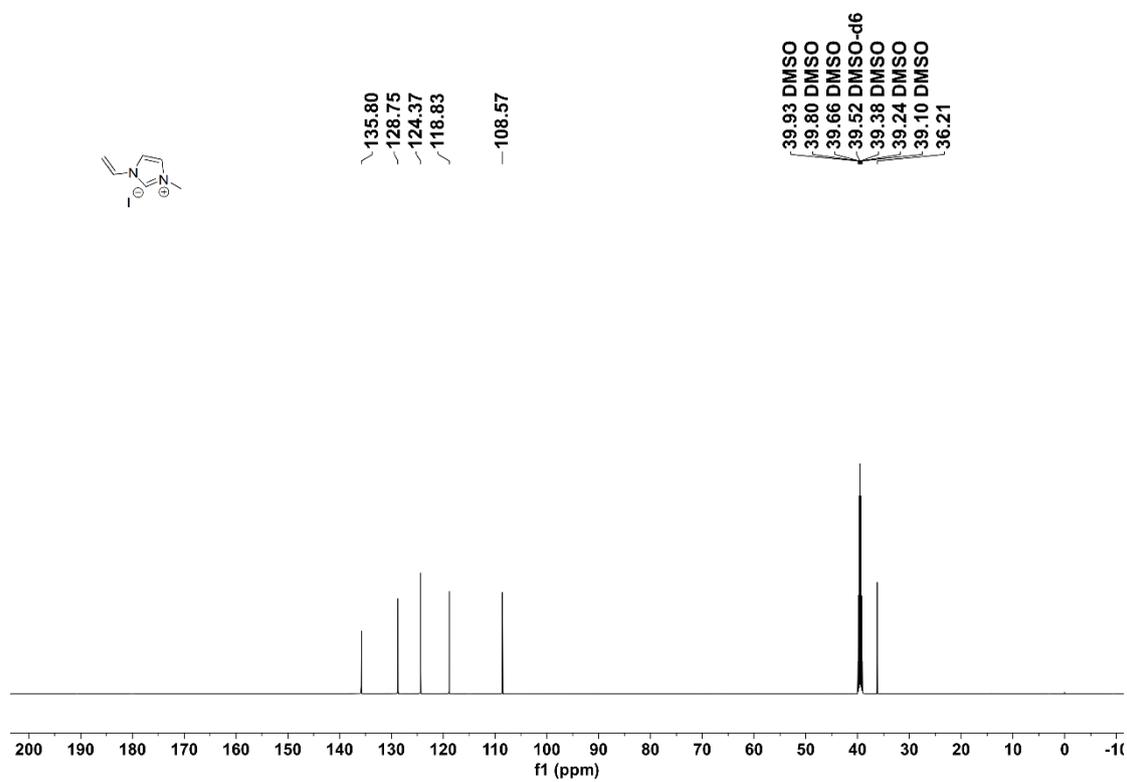
- [1] Kena Diba, A.; Noll, C.; Richter, M.; Gieseler, M. T.; Kalesse, M. Intramolecular stereoselective protonation of aldehyde-derived enolates. *Angew Chem Int Ed* **2010**, *49*, 8367-8369.
- [2] Draskovits, M.; Kalas, H.; Stanetty, C.; Mihovilovic, M. D. Intercepted dehomologation of aldoses by N-heterocyclic carbene catalysis - a novel transformation in carbohydrate chemistry. *Chem Commun* **2019**, *55*, 12144-12147.
- [3] Piel, I.; Pawelczyk, M. D.; Hirano, K.; Fröhlich, R.; Glorius, F. A Family of Thiazolium Salt Derived N-Heterocyclic Carbenes (NHCs) for Organocatalysis: Synthesis, Investigation and Application in Cross-Benzoin Condensation. *Eur. J. Org. Chem.* **2011**, *2011*, 5475-5484.
- [4] Liu, R. H.; Shen, Z. Y.; Wang, C.; Loh, T. P.; Hu, X. H. Selective Dehydrogenative Acylation of Enamides with Aldehydes Leading to Valuable beta-Ketoenamides. *Org Lett* **2020**, *22*, 944-949.
- [5] Liu, M.-S.; Shu, W. Catalytic, Metal-Free Amide Synthesis from Aldehydes and Imines Enabled by a Dual-Catalyzed Umpolung Strategy under Redox-Neutral Conditions. *ACS Catalysis* **2020**, *10*, 12960-12966.
- [6] Karthik, S.; Muthuvel, K.; Gandhi, T. Base-Promoted Amidation and Esterification of Imidazolium Salts via Acyl C-C bond Cleavage: Access to Aromatic Amides and Esters. *J Org Chem* **2019**, *84*, 738-751.

## 5. NMR Spectra

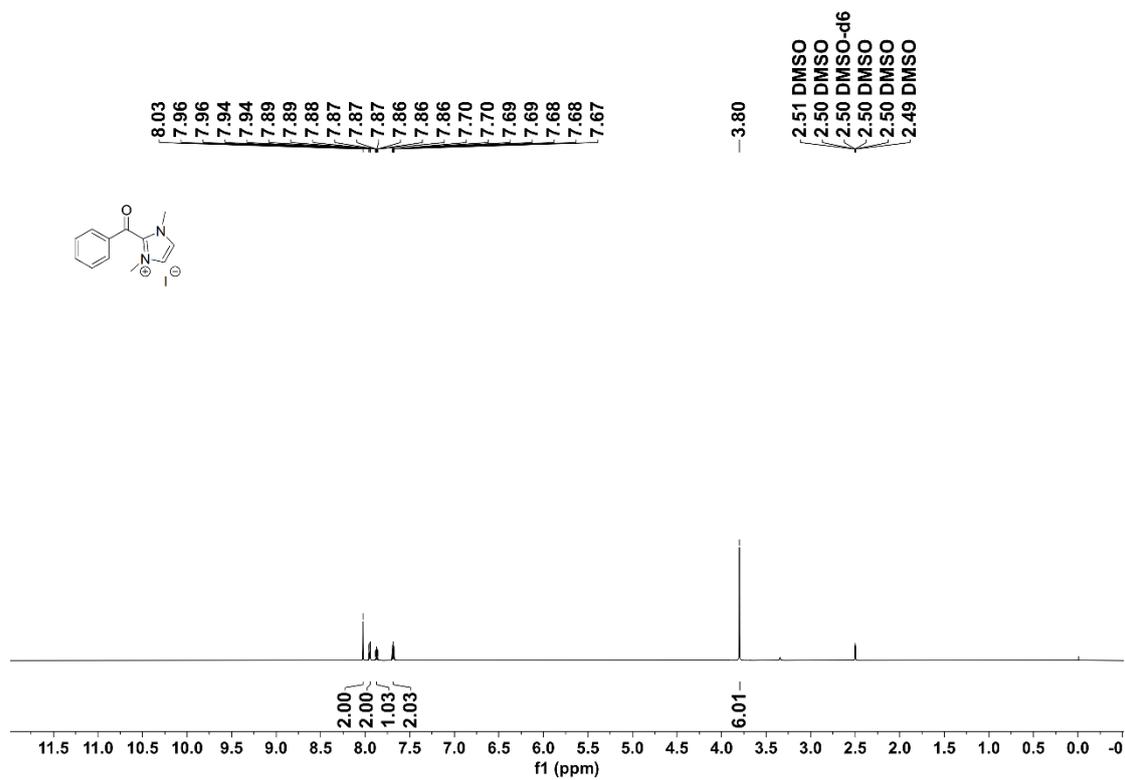
$^1\text{H}$  NMR spectrum of **N2**



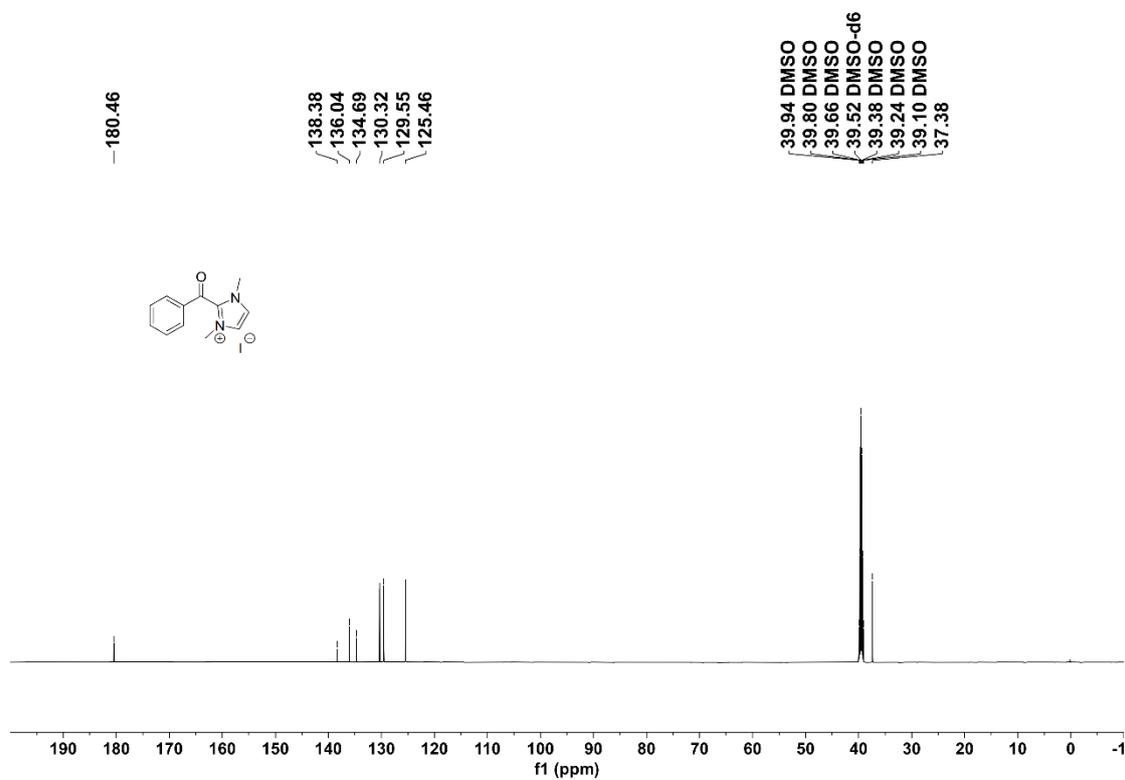
$^{13}\text{C}$  NMR spectrum of **N2**



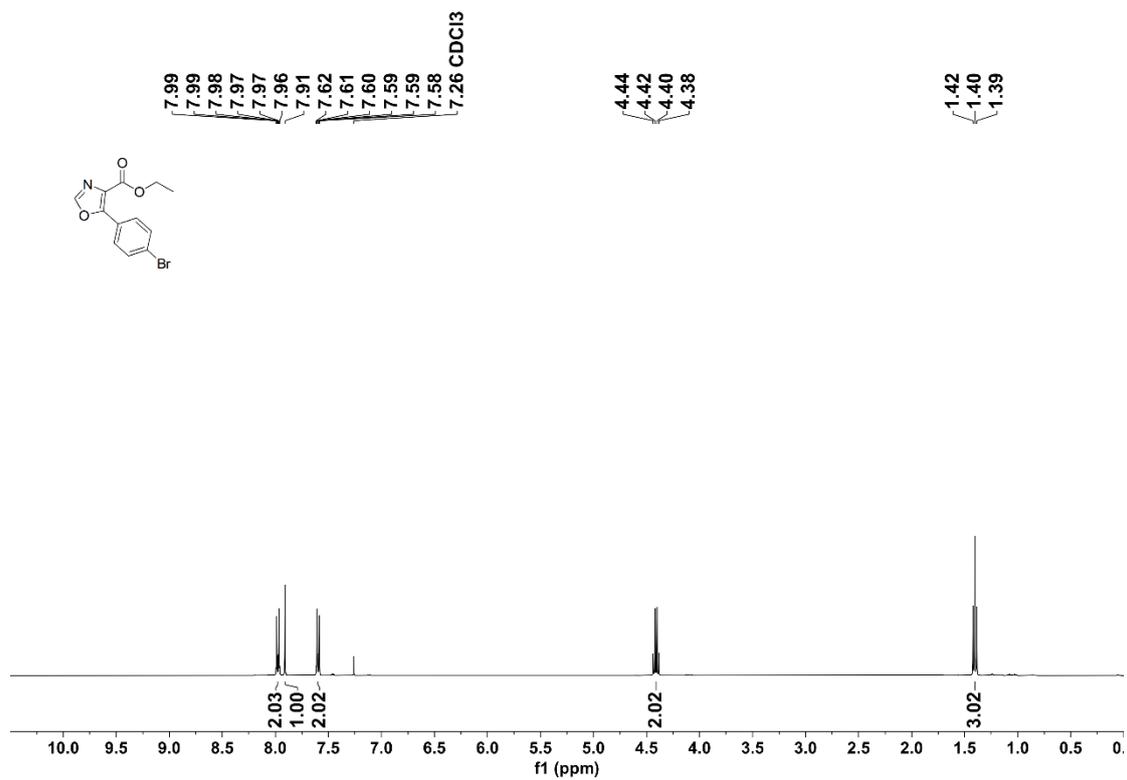
<sup>1</sup>H NMR spectrum of **4**



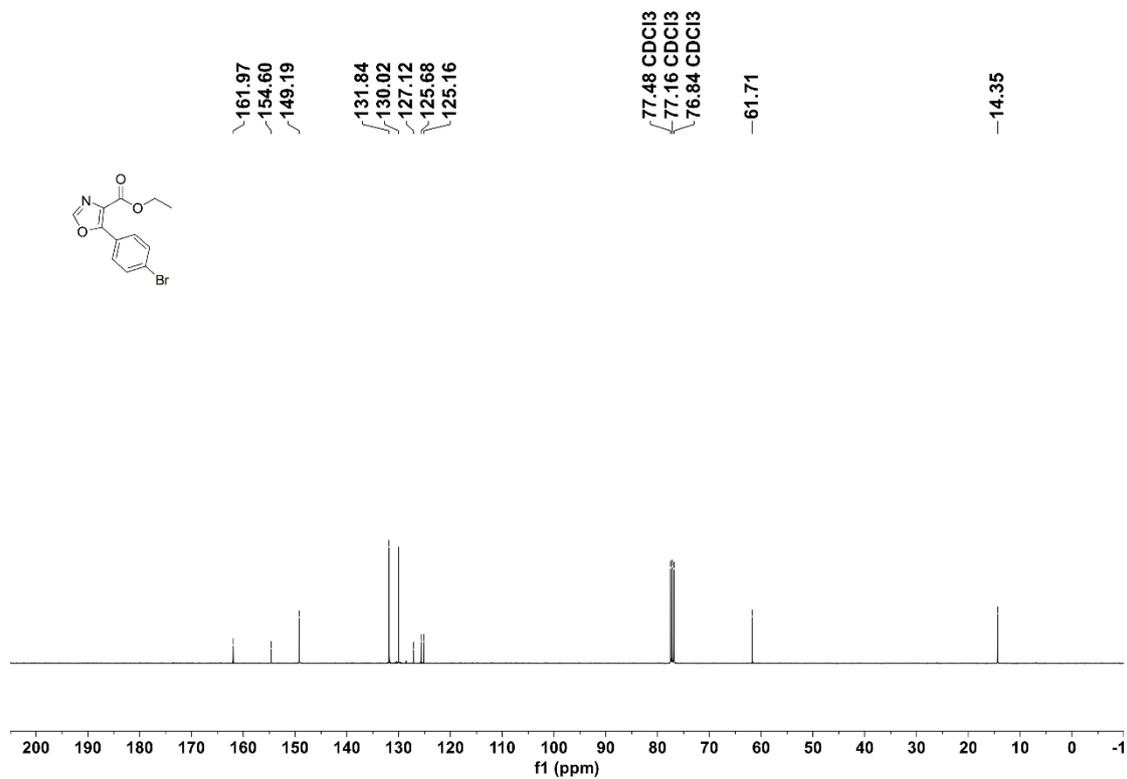
<sup>13</sup>C NMR spectrum of **4**



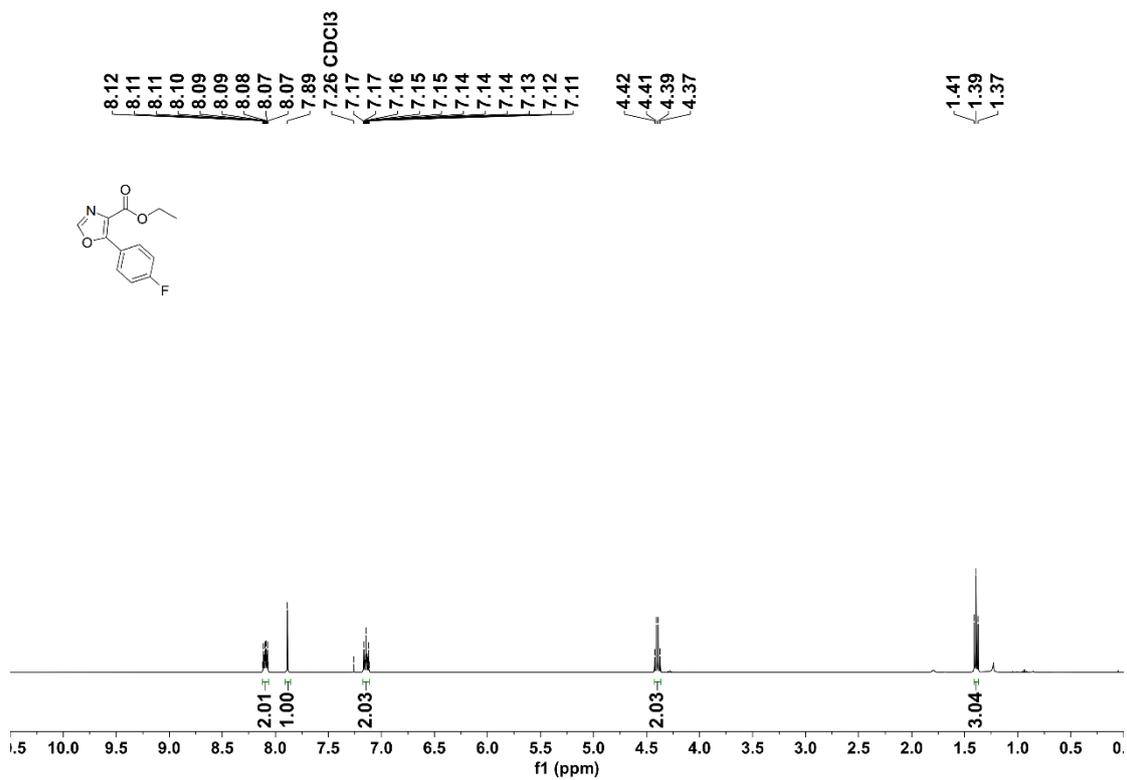
<sup>1</sup>H NMR spectrum of **3aa**



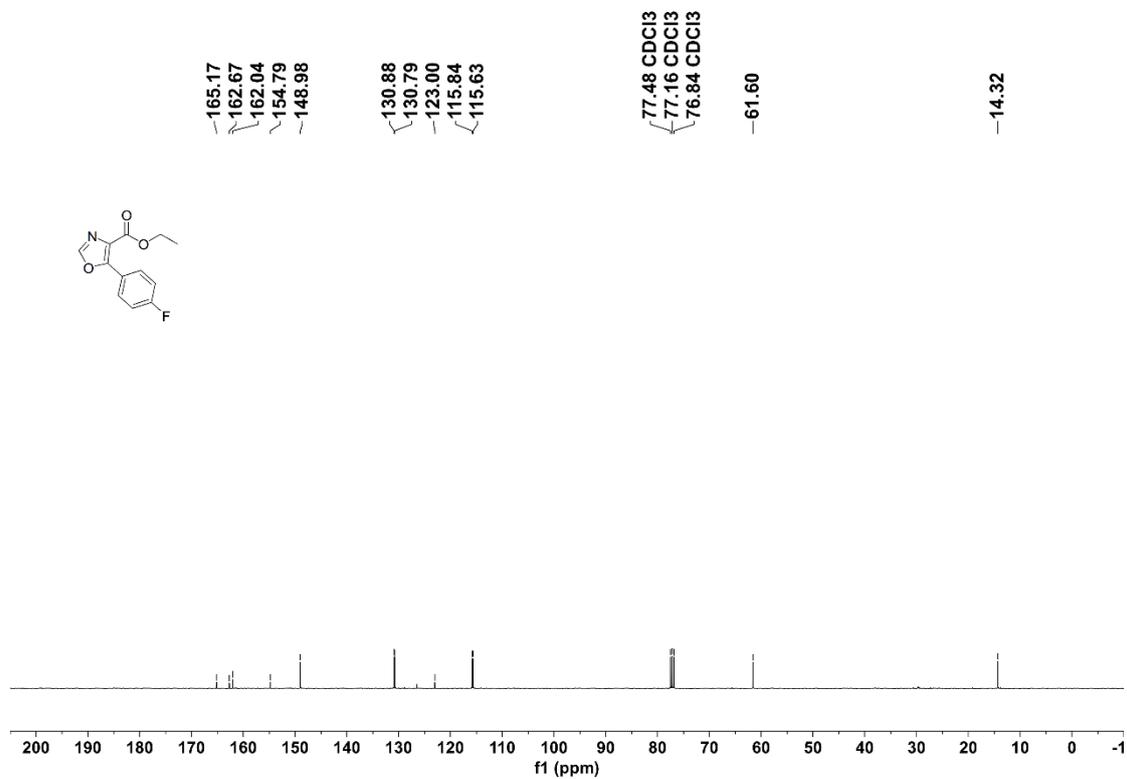
<sup>13</sup>C NMR spectrum of **3aa**



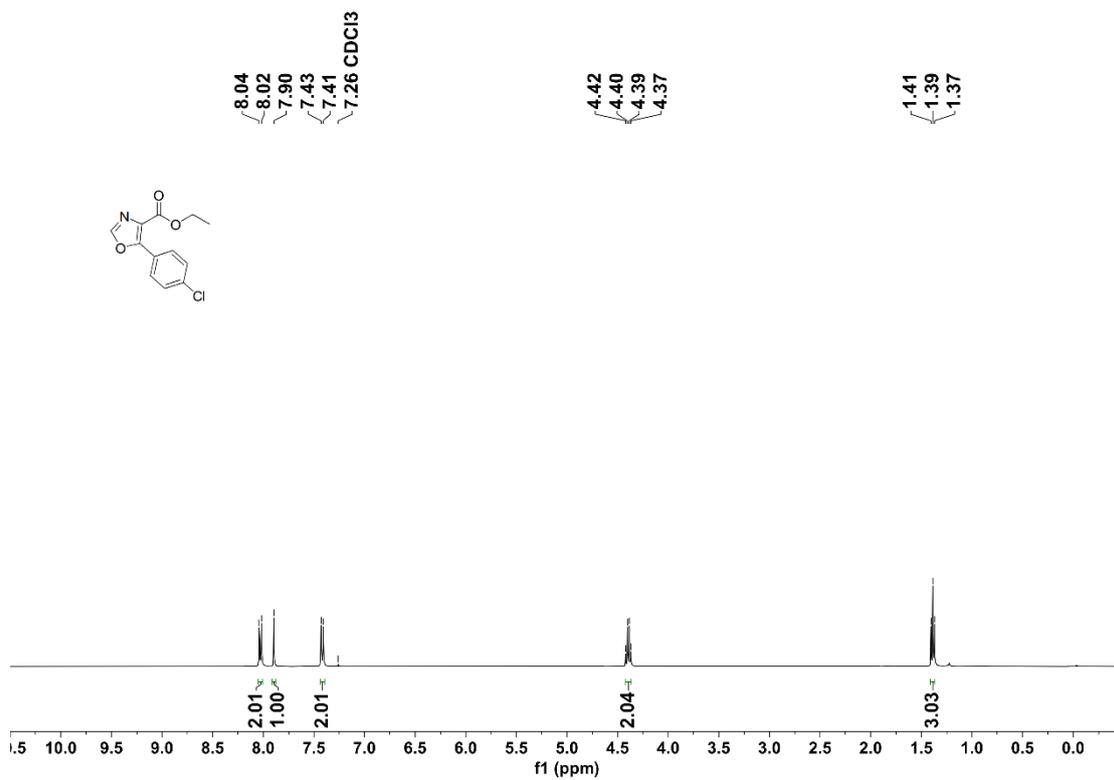
<sup>1</sup>H NMR spectrum of **3ba**



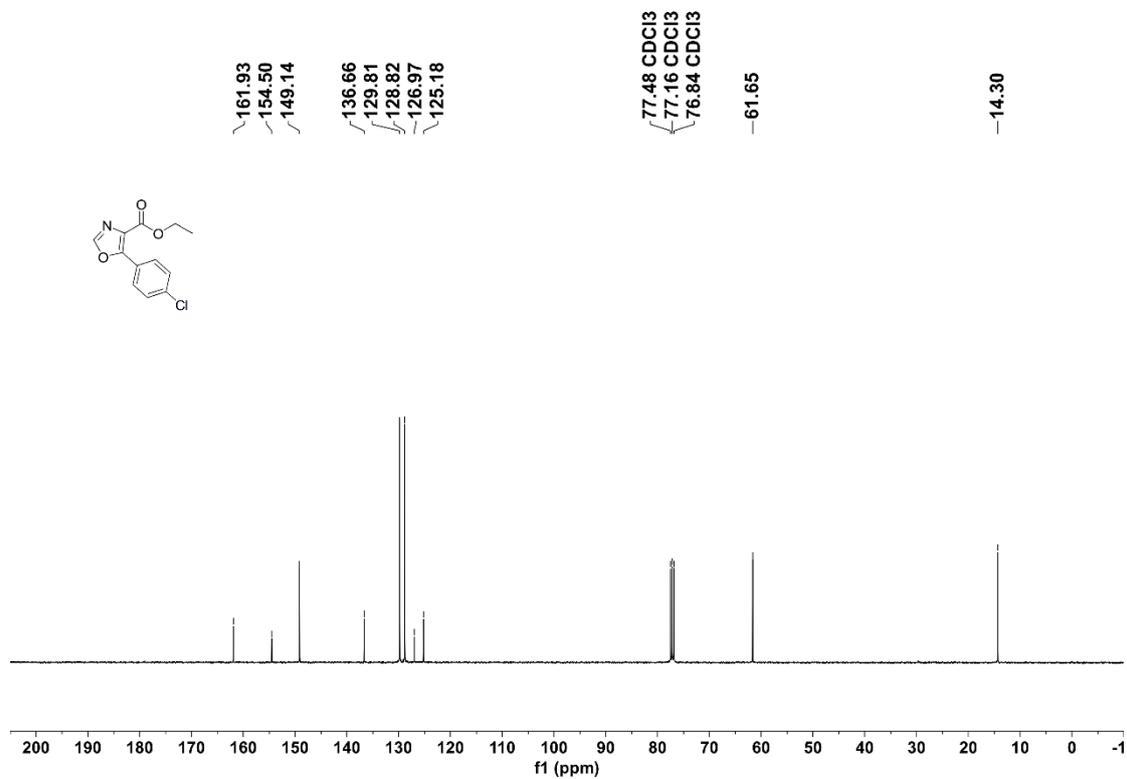
<sup>13</sup>C NMR spectrum of **3ba**



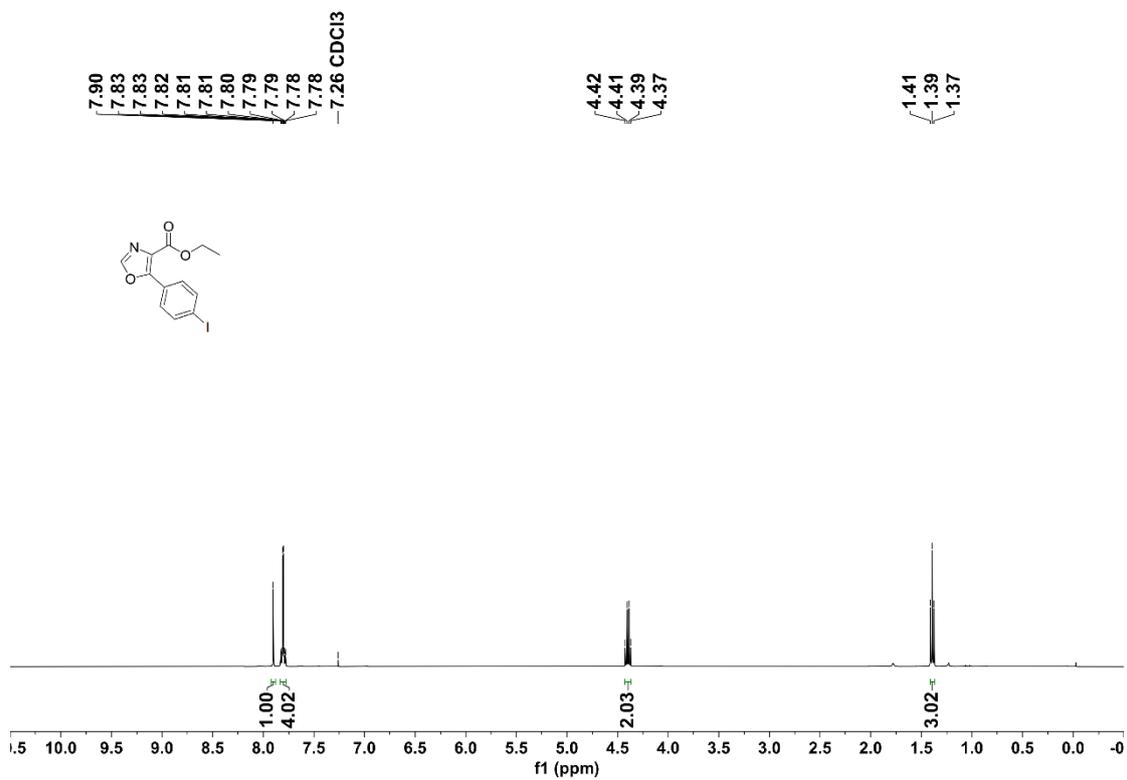
<sup>1</sup>H NMR spectrum of **3ca**



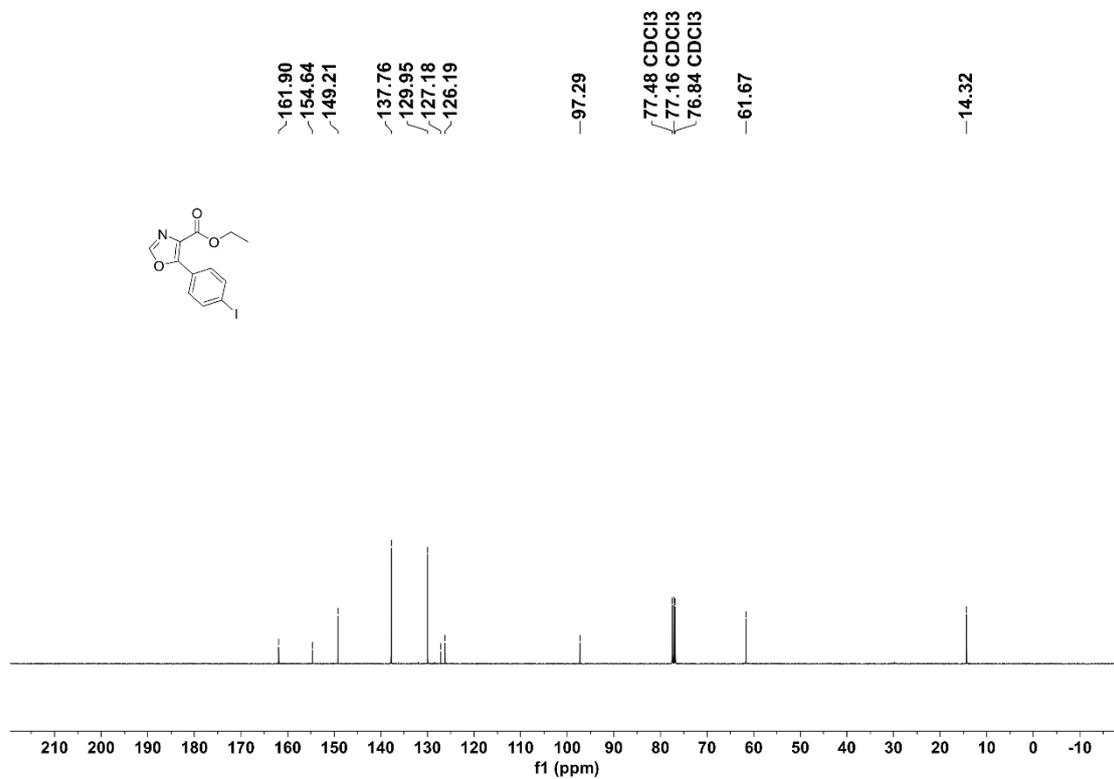
<sup>13</sup>C NMR spectrum of **3ca**



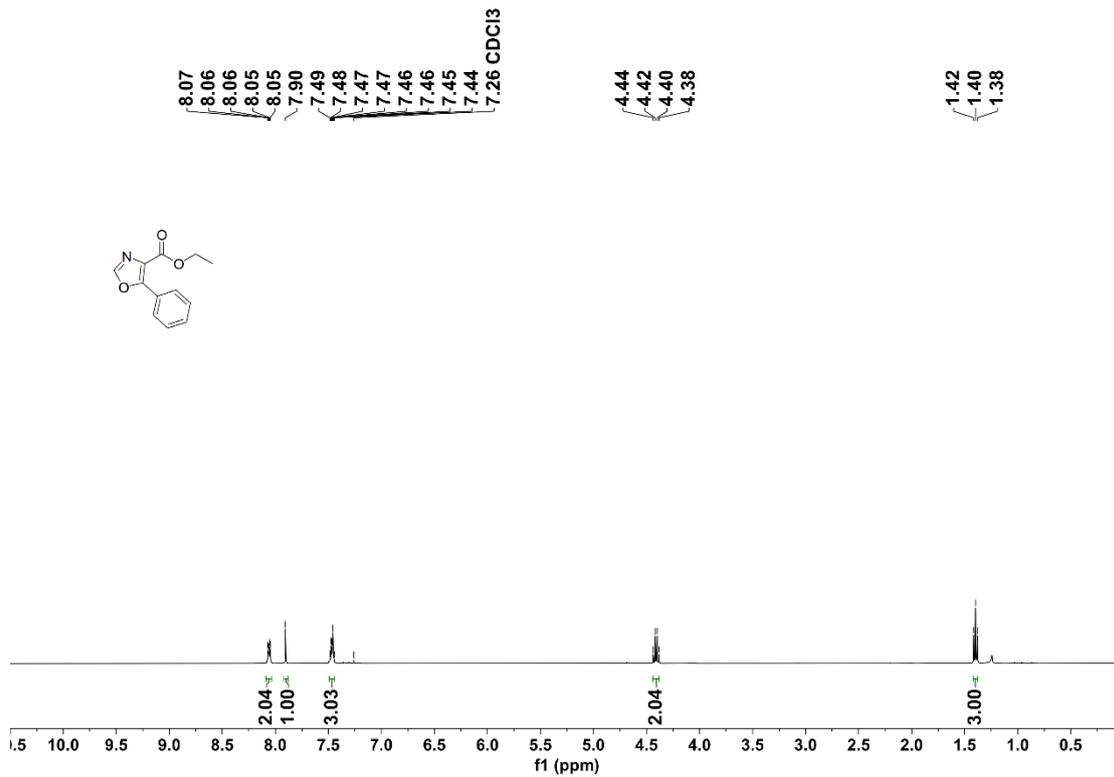
<sup>1</sup>H NMR spectrum of **3da**



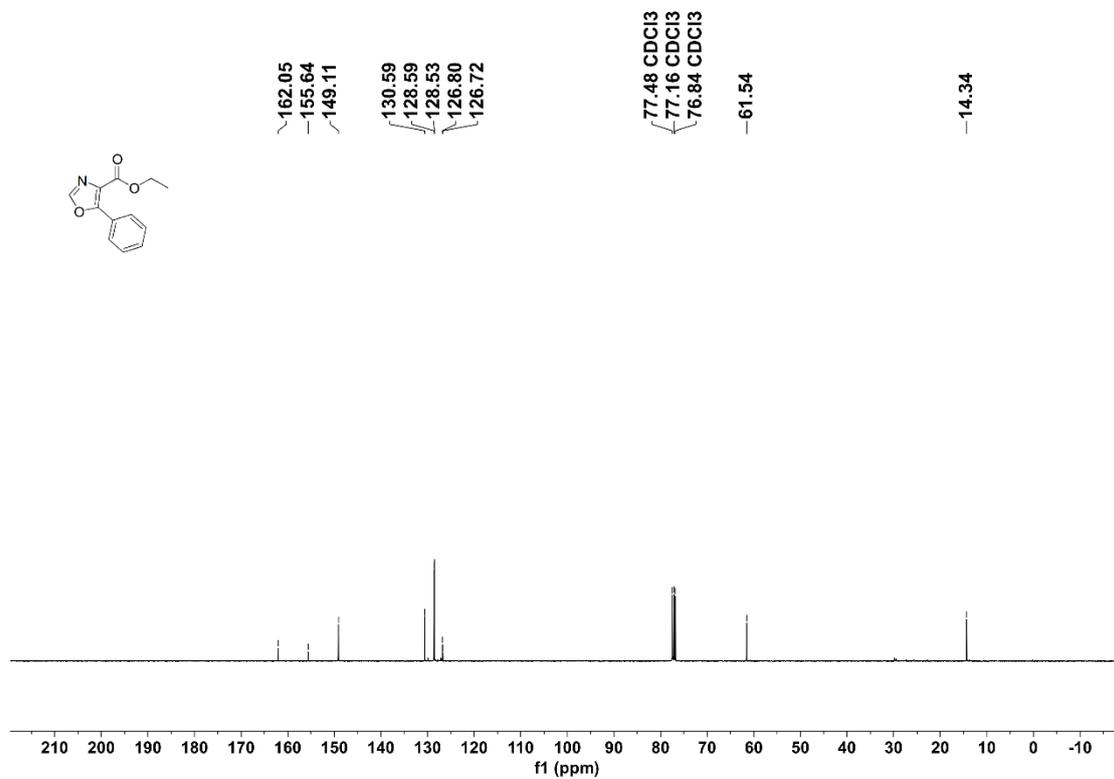
<sup>13</sup>C NMR spectrum of **3da**



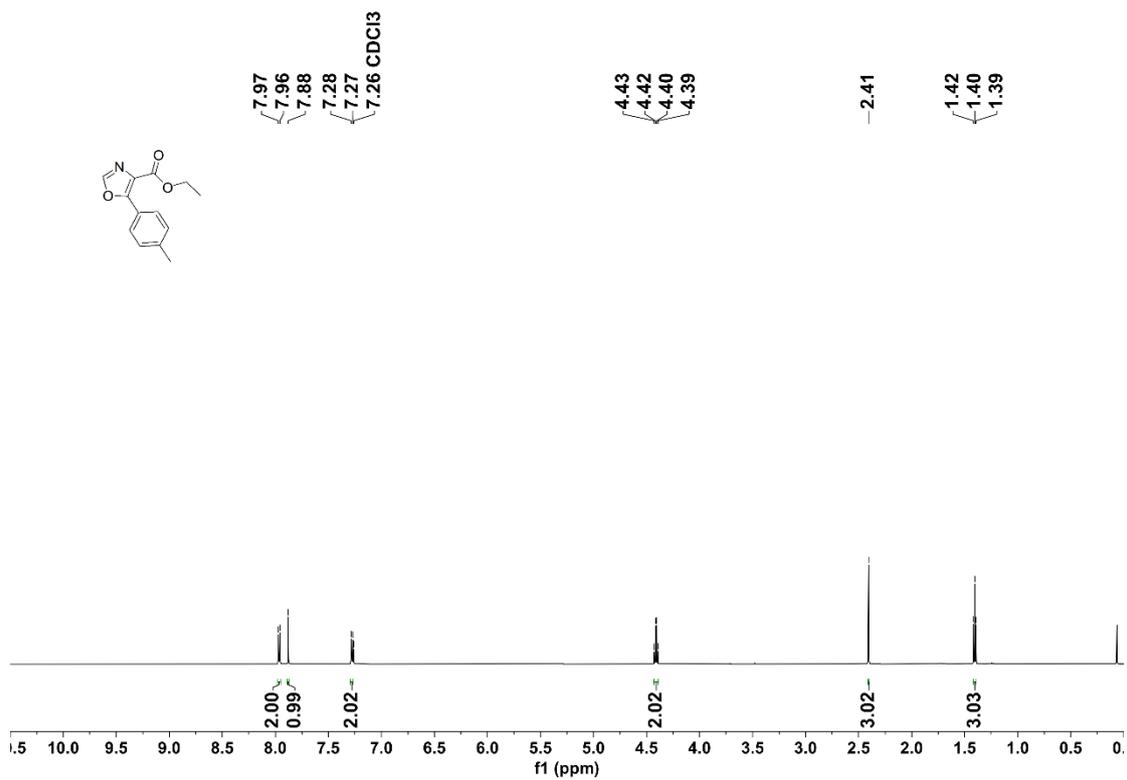
<sup>1</sup>H NMR spectrum of **3ea**



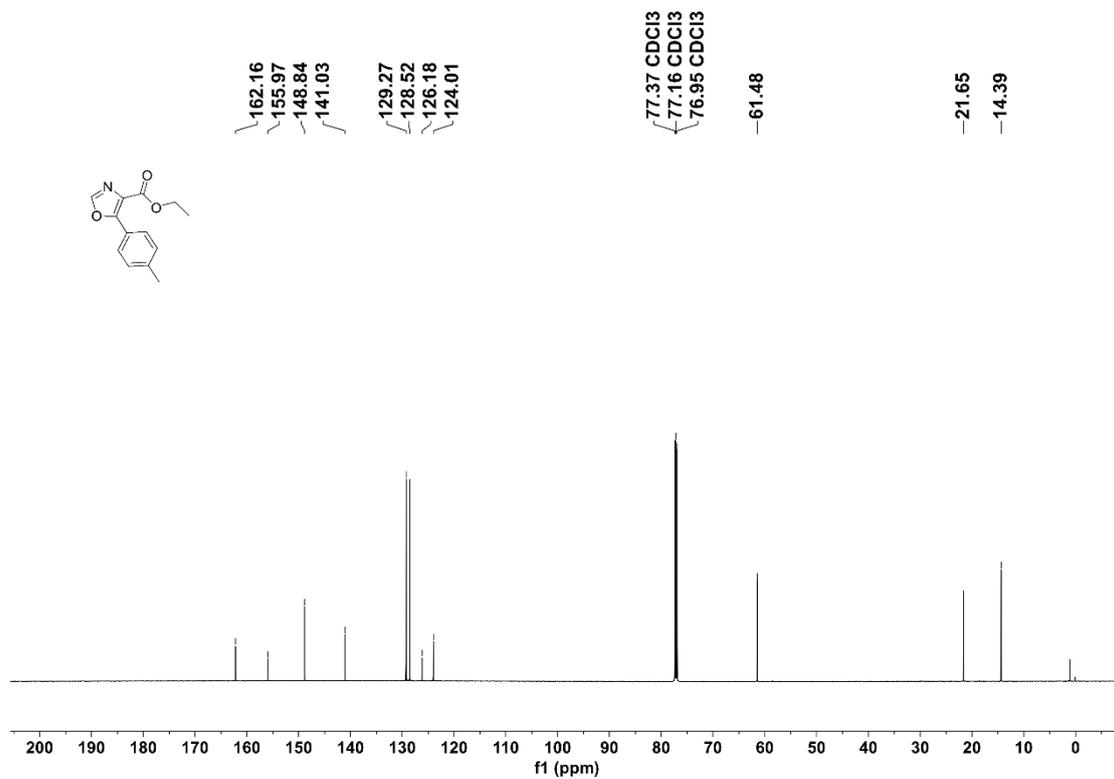
<sup>13</sup>C NMR spectrum of **3ea**



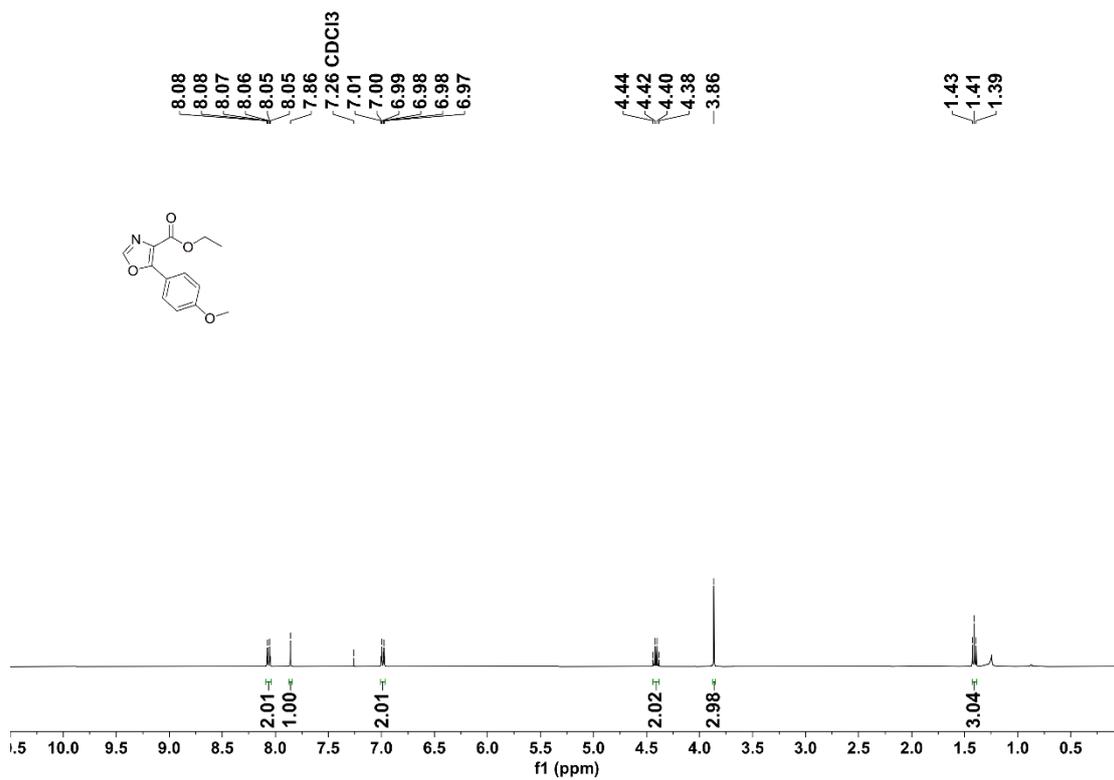
<sup>1</sup>H NMR spectrum of **3fa**



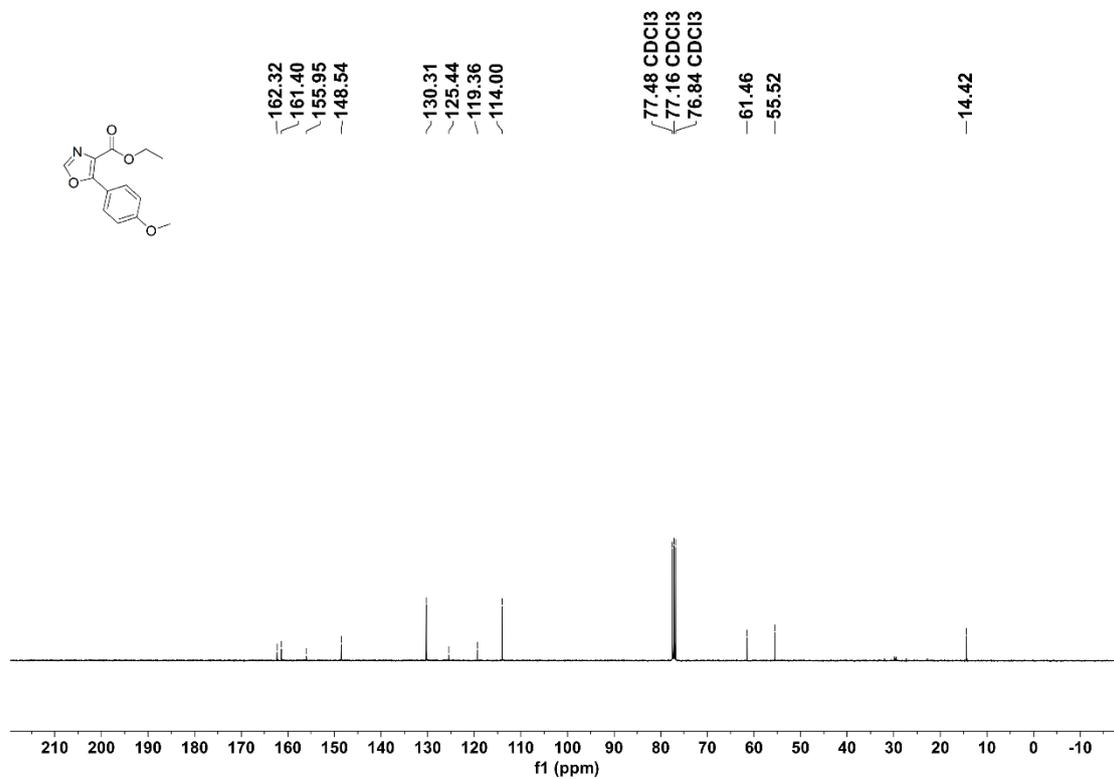
<sup>13</sup>C NMR spectrum of **3fa**



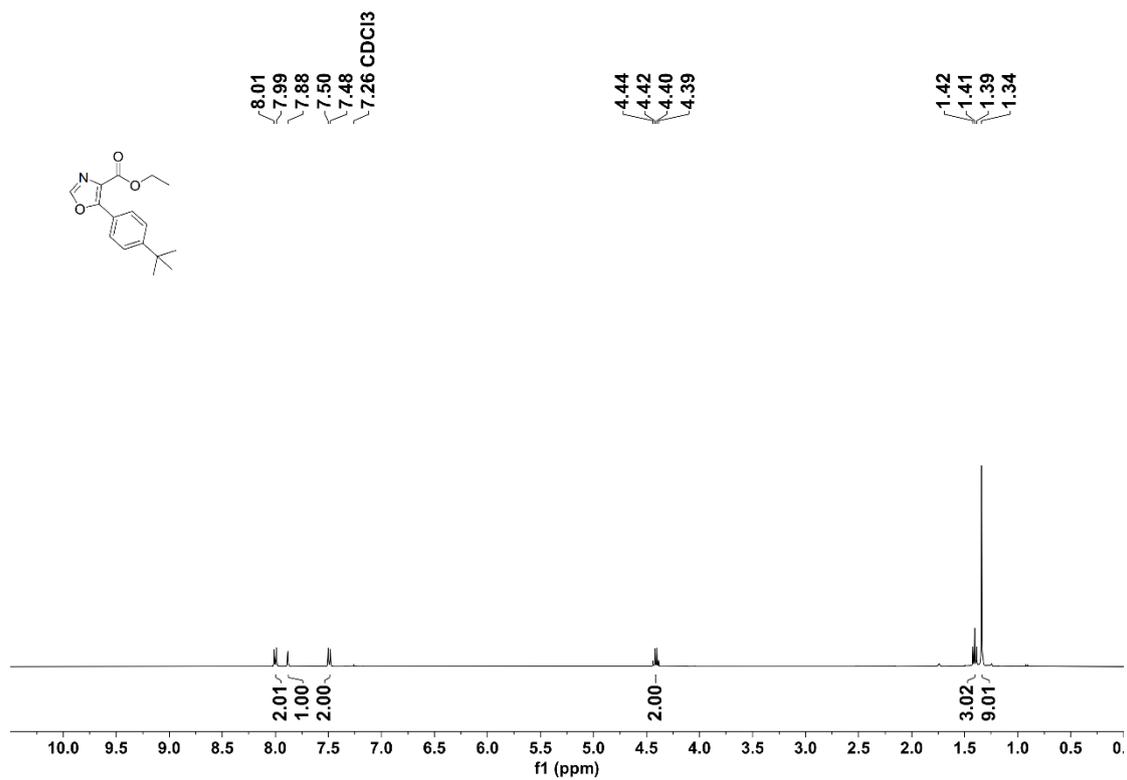
<sup>1</sup>H NMR spectrum of **3ga**



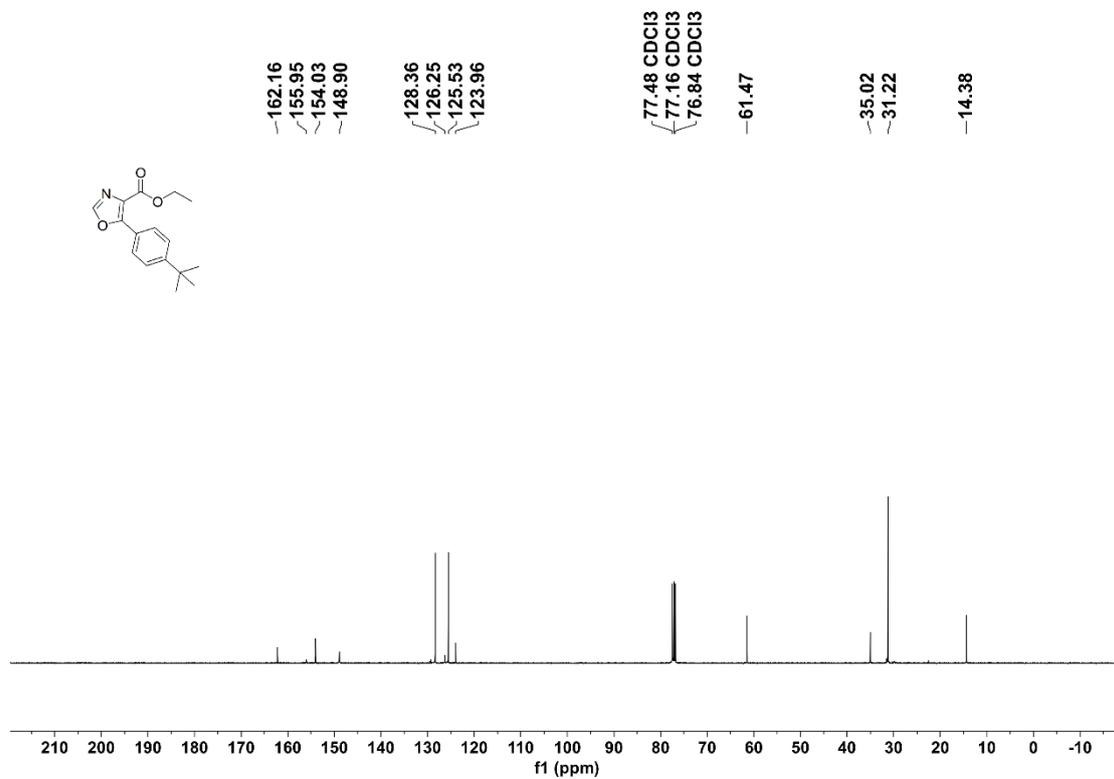
<sup>13</sup>C NMR spectrum of **3ga**



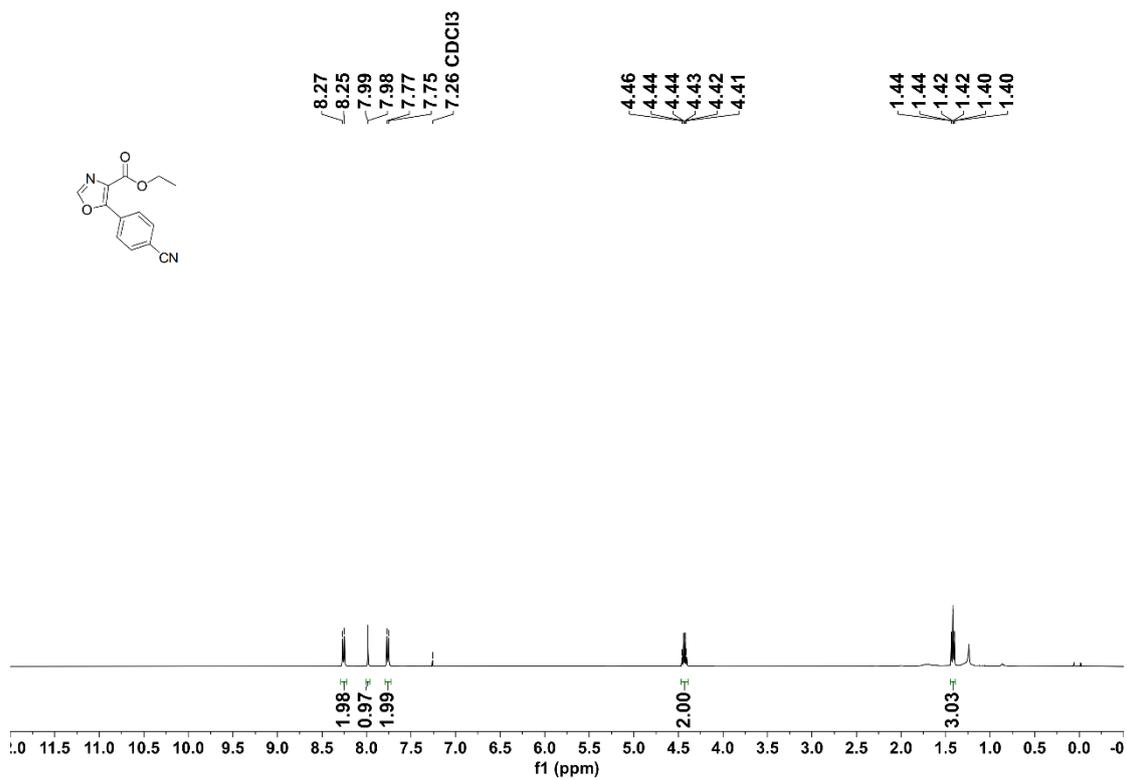
<sup>1</sup>H NMR spectrum of **3ha**



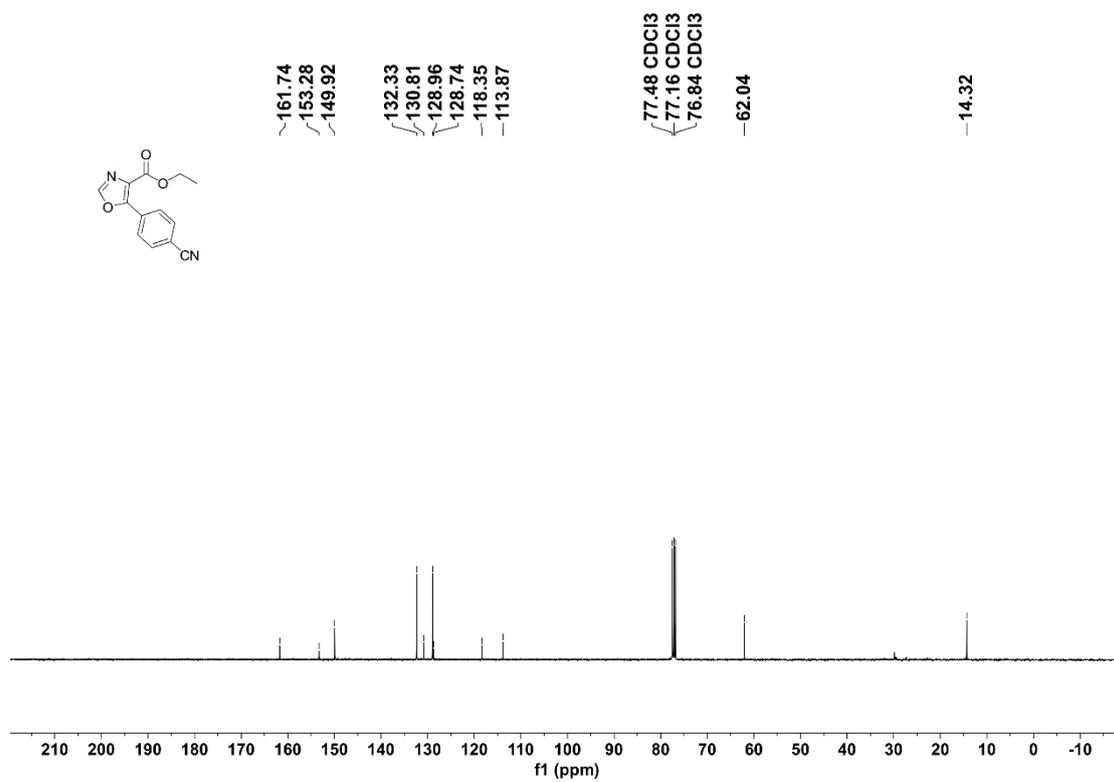
<sup>13</sup>C NMR spectrum of **3ha**



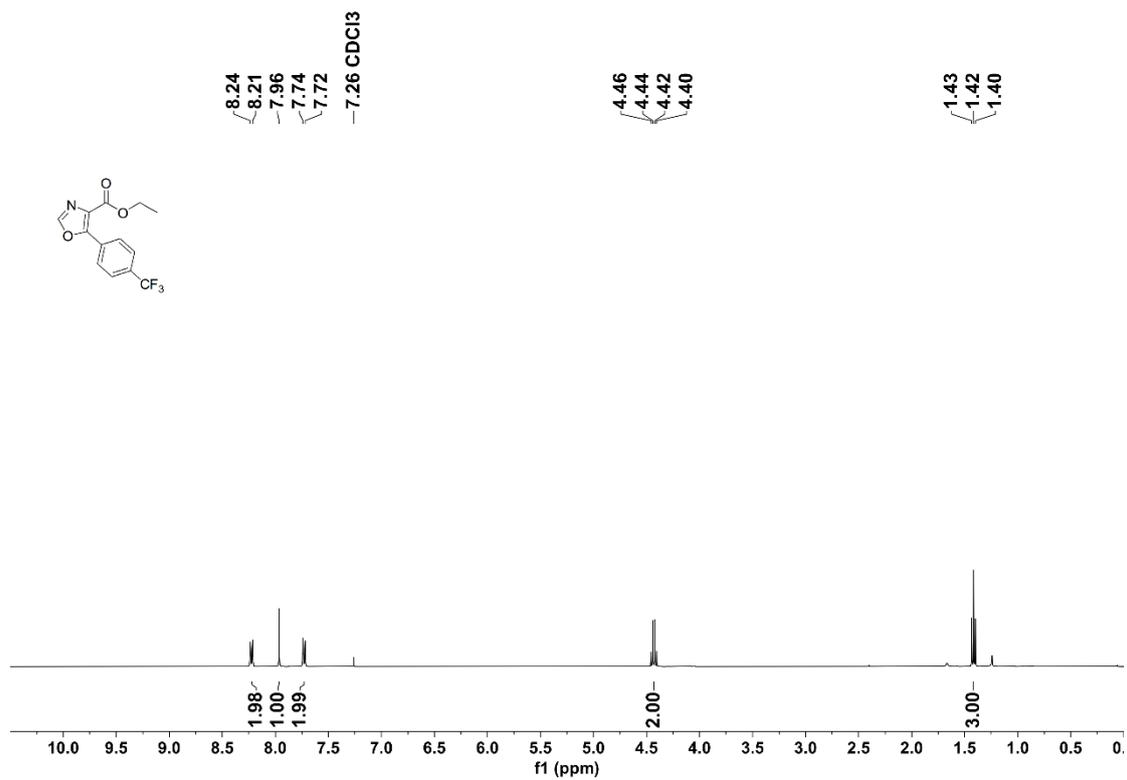
<sup>1</sup>H NMR spectrum of **3ia**



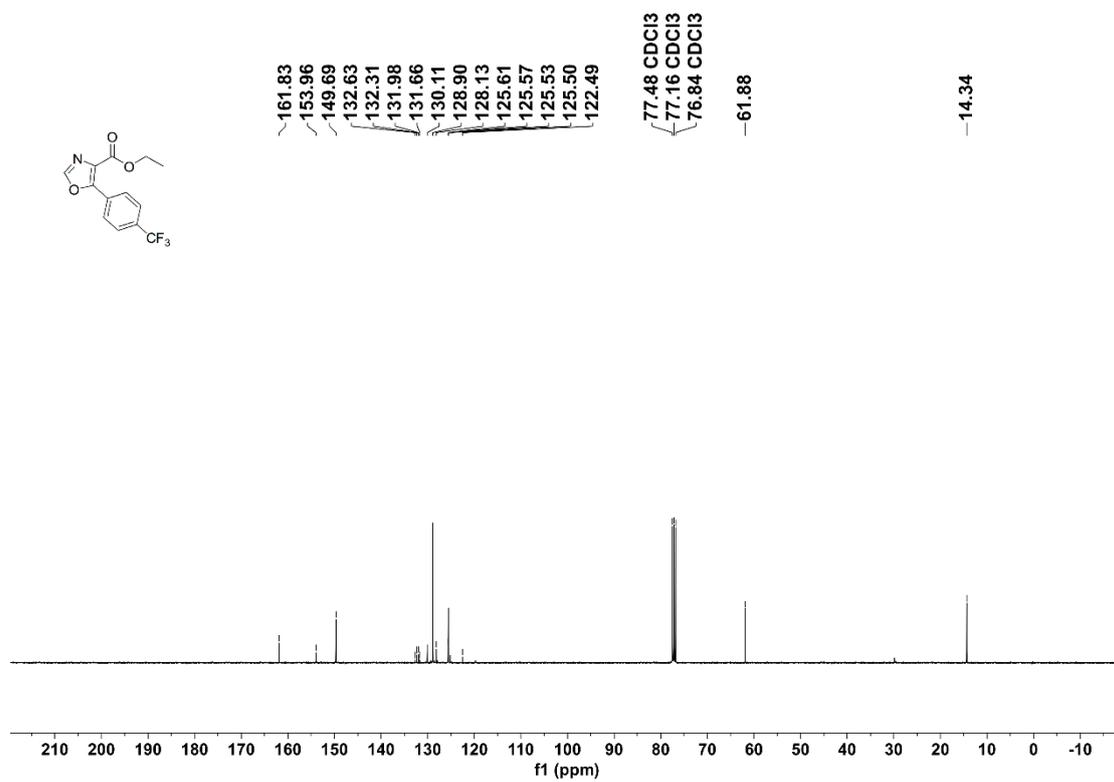
<sup>13</sup>C NMR spectrum of **3ia**



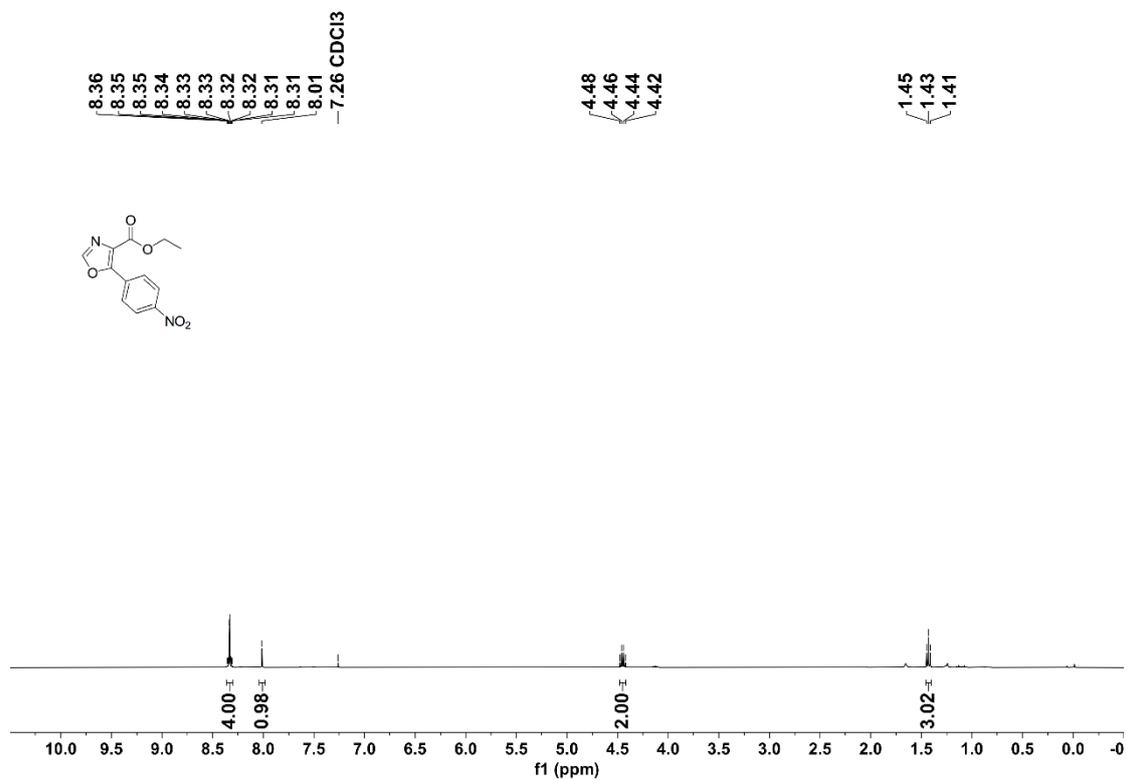
<sup>1</sup>H NMR spectrum of **3ja**



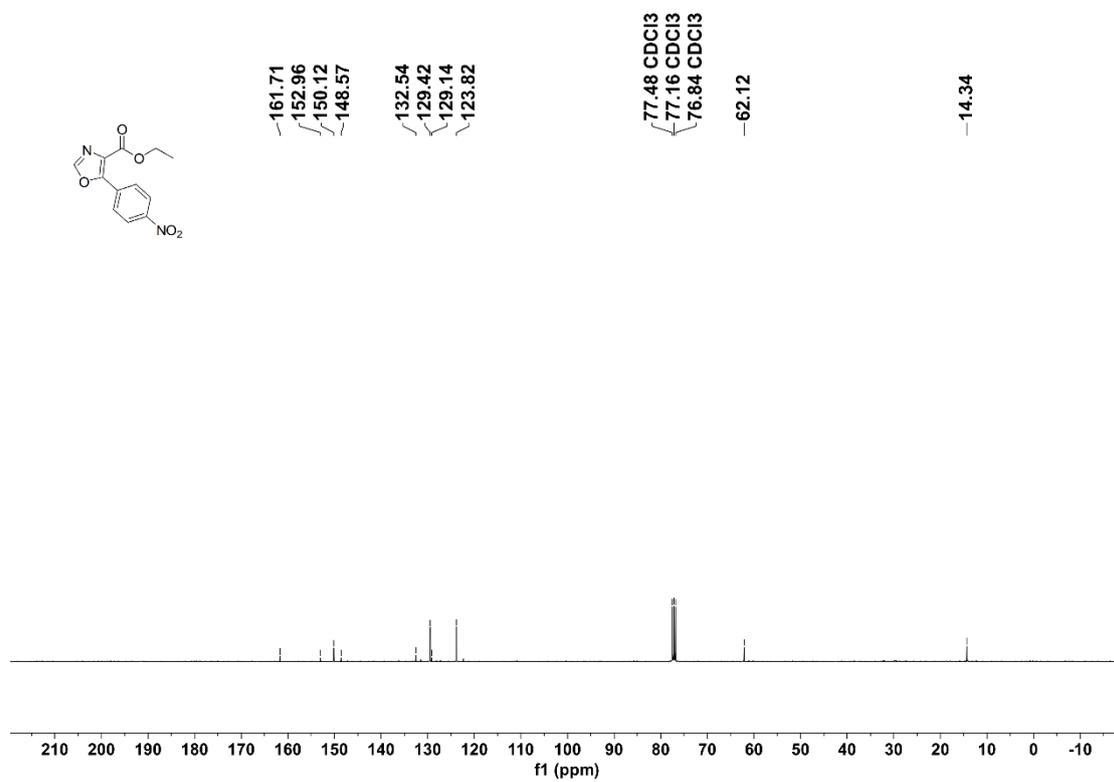
<sup>13</sup>C NMR spectrum of **3ja**



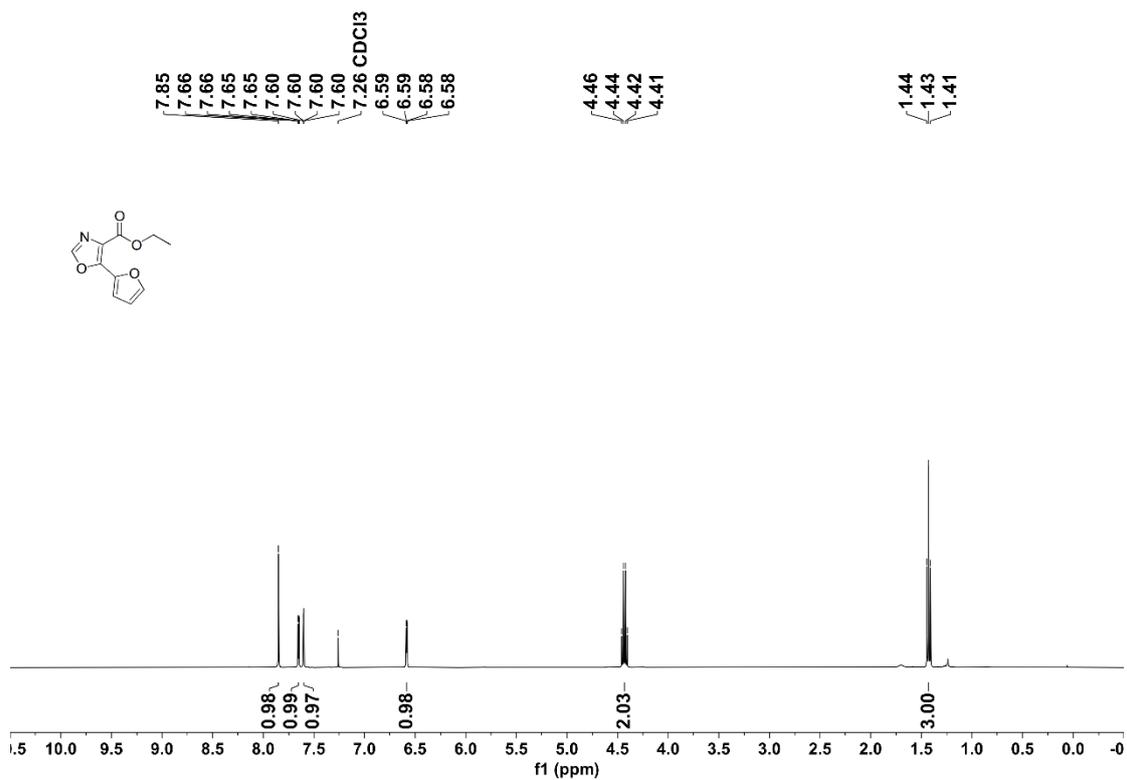
<sup>1</sup>H NMR spectrum of **3ka**



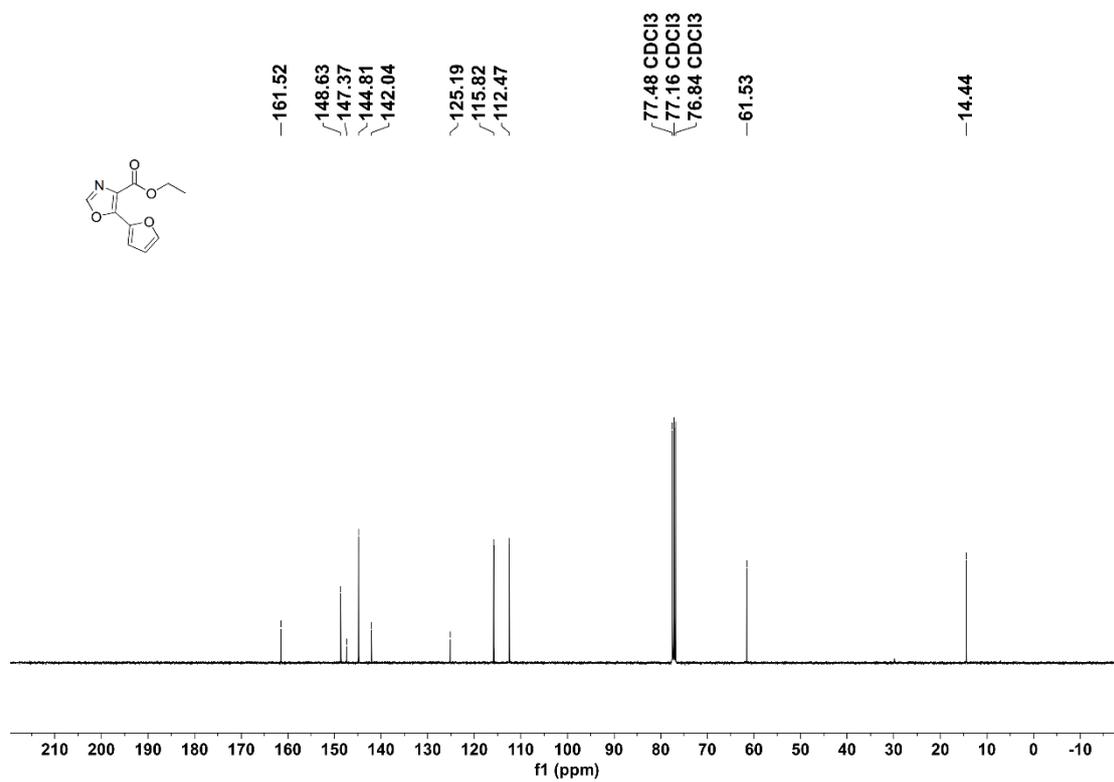
<sup>13</sup>C NMR spectrum of **3ka**



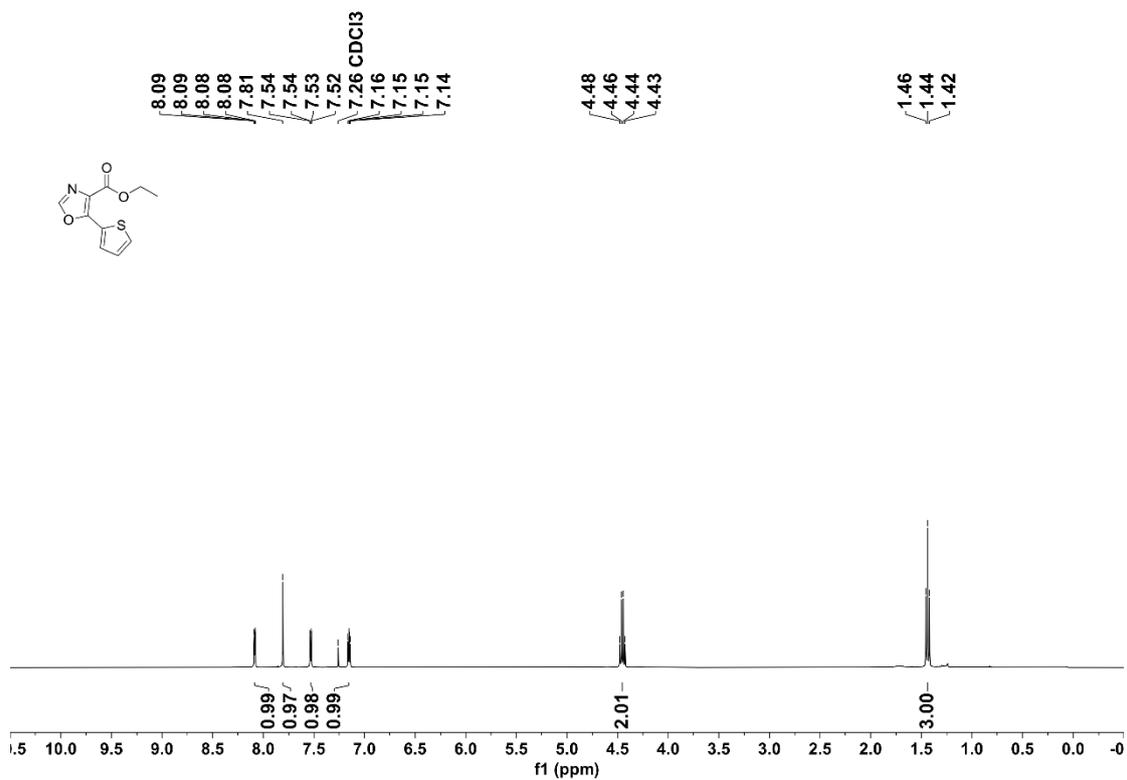
<sup>1</sup>H NMR spectrum of **3la**



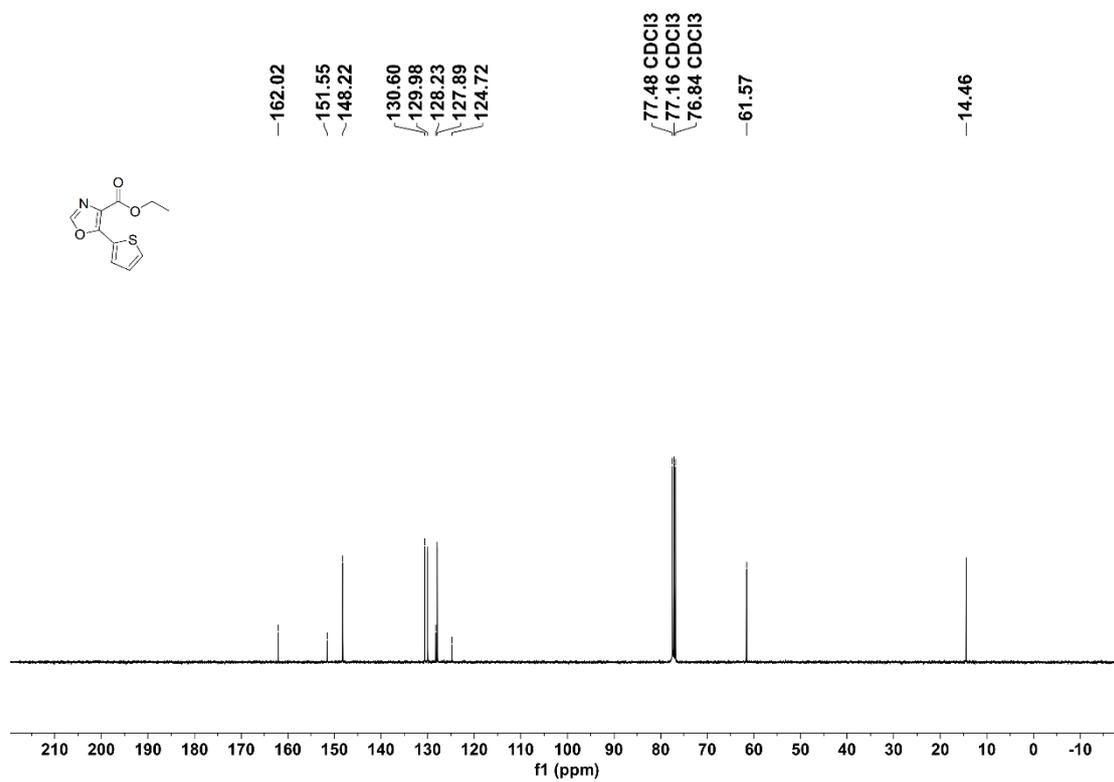
<sup>13</sup>C NMR spectrum of **3la**



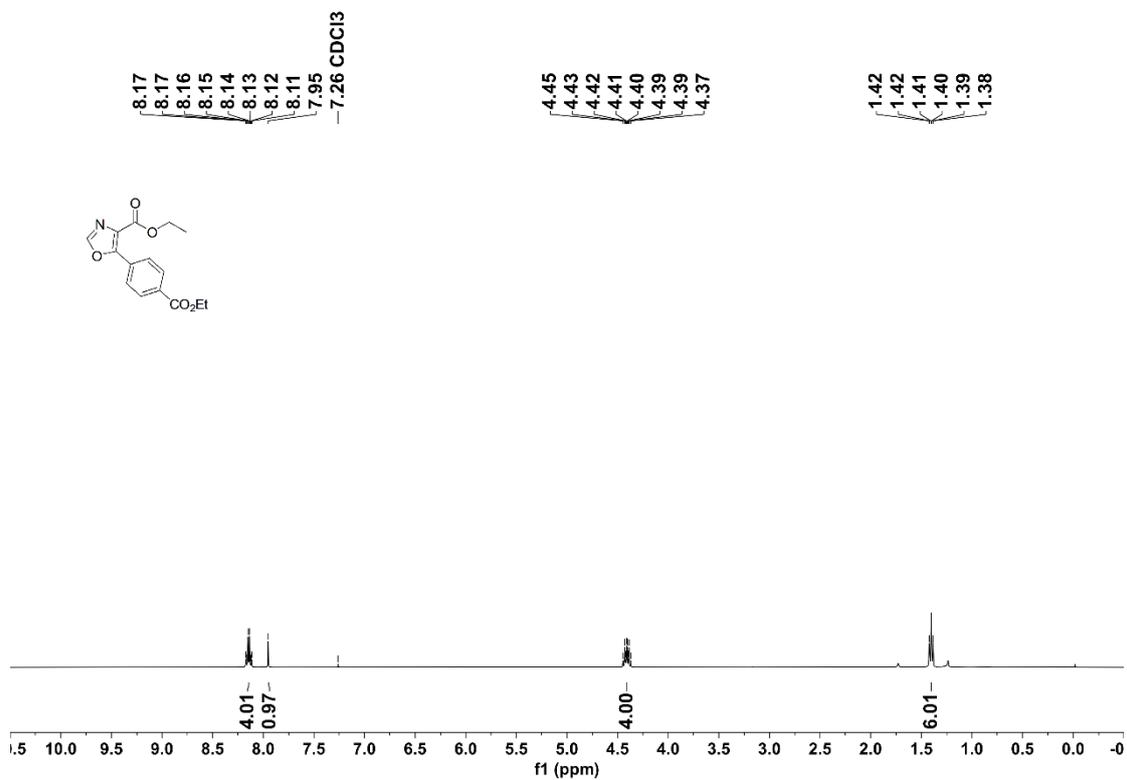
<sup>1</sup>H NMR spectrum of **3ma**



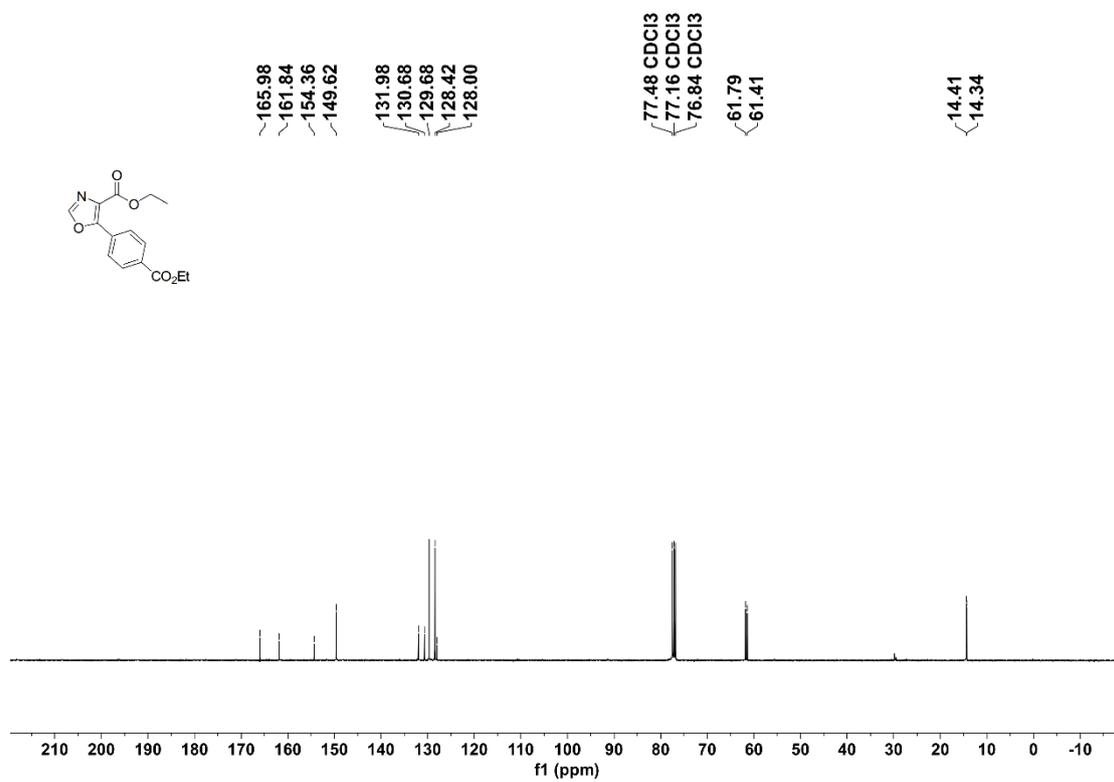
<sup>13</sup>C NMR spectrum of **3ma**



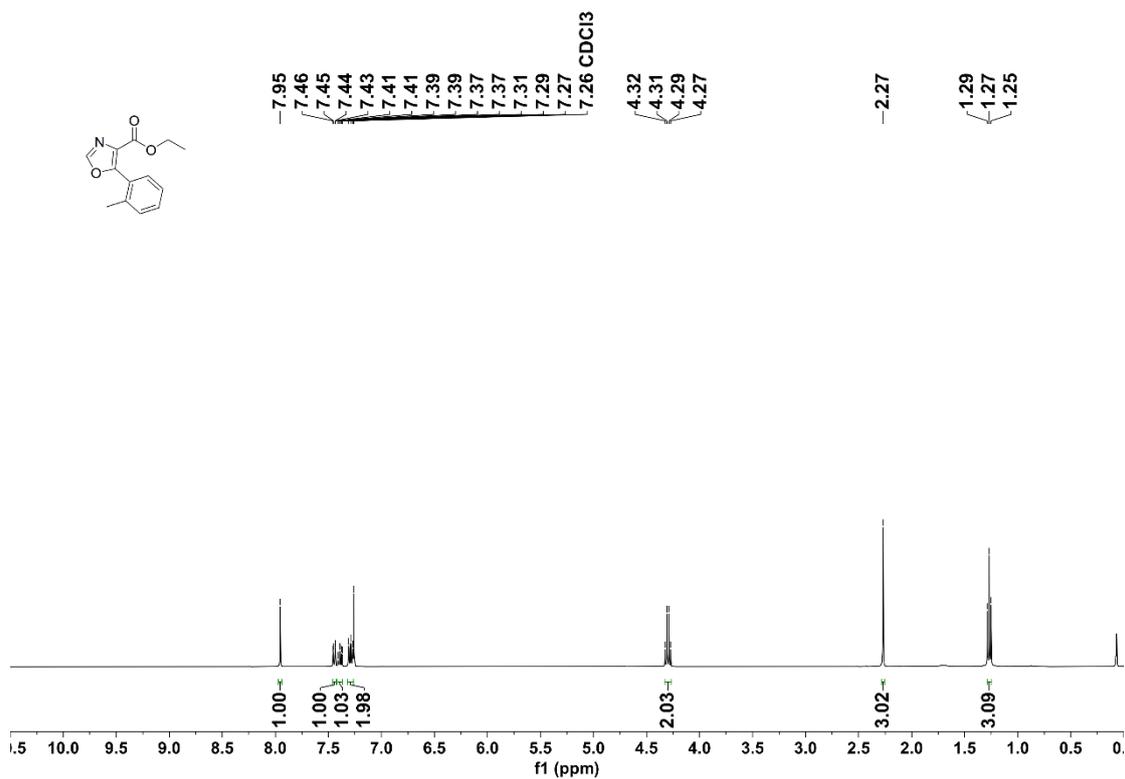
<sup>1</sup>H NMR spectrum of **3na**



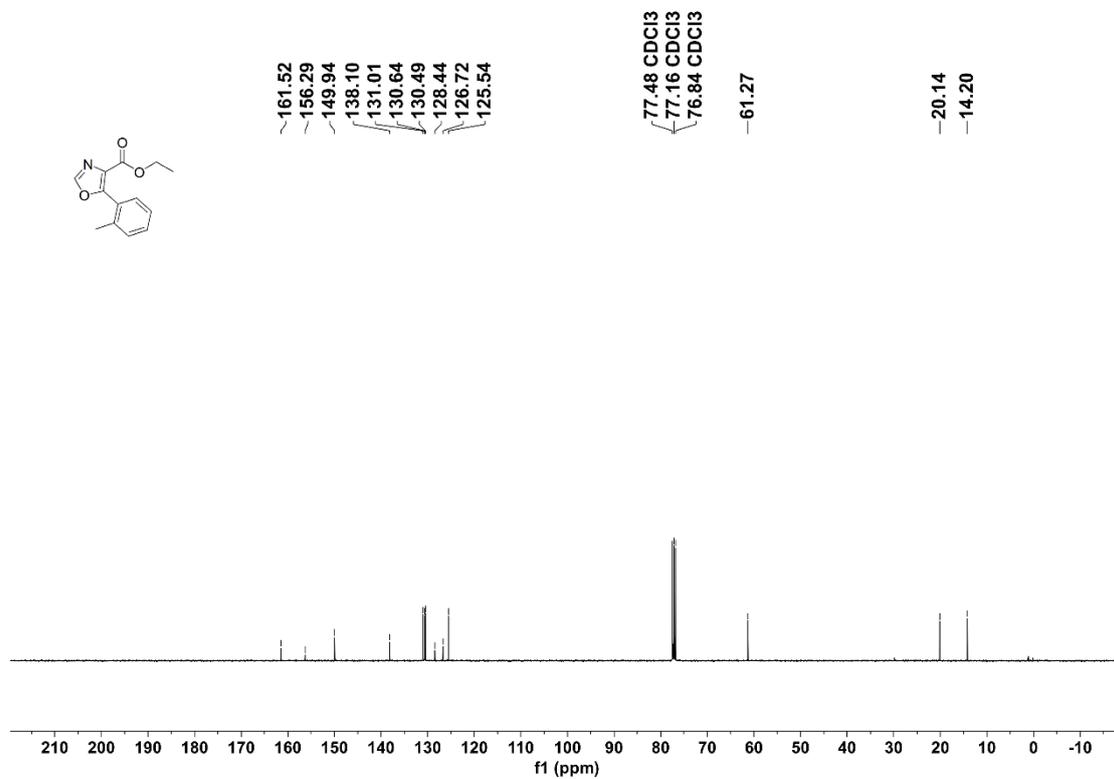
<sup>13</sup>C NMR spectrum of **3na**



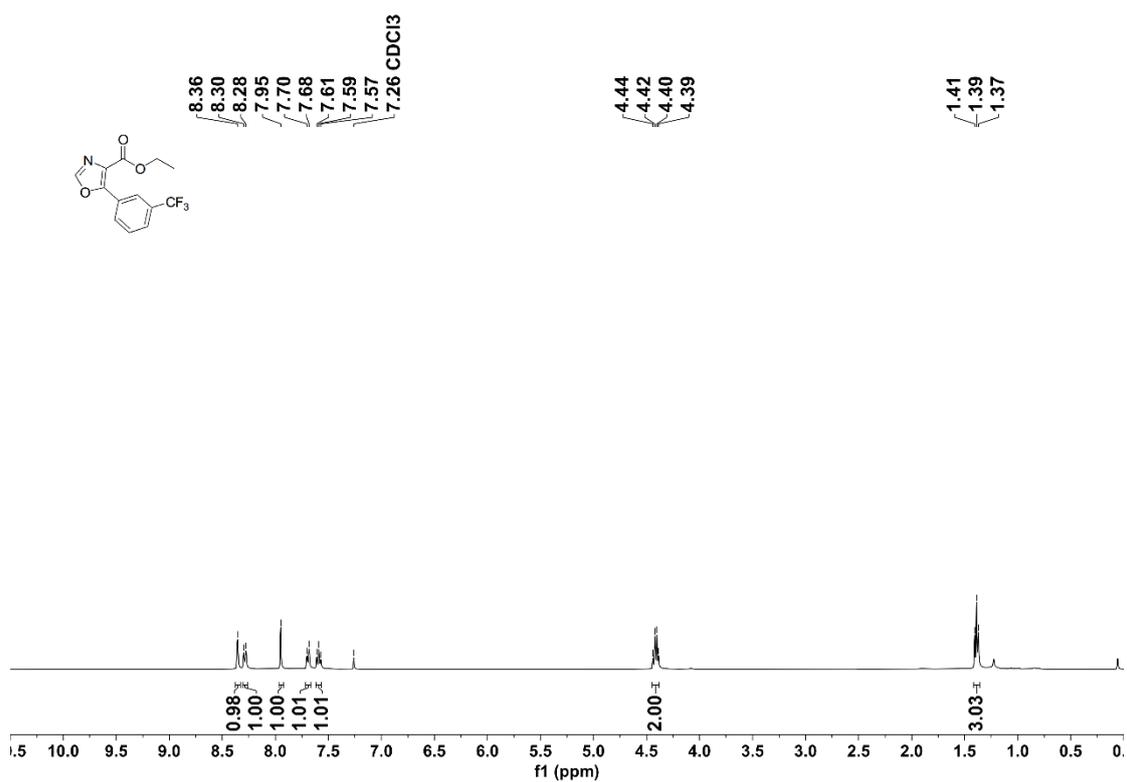
<sup>1</sup>H NMR spectrum of **30a**



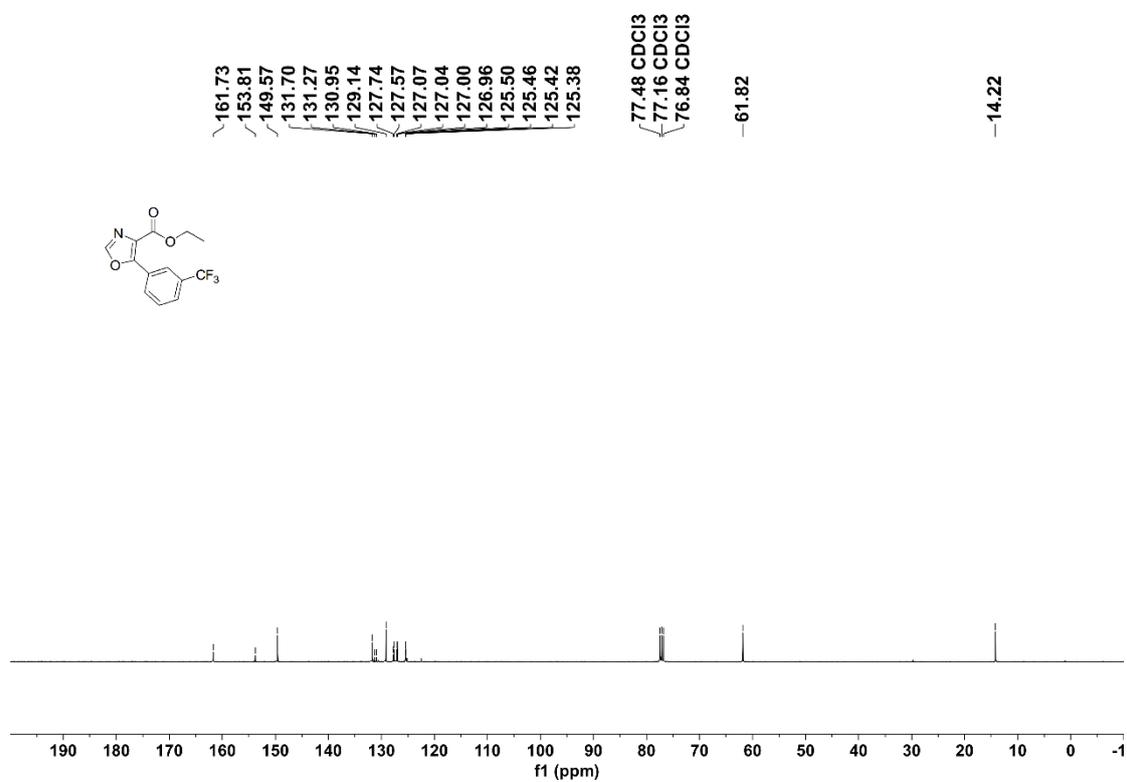
<sup>13</sup>C NMR spectrum of **30a**



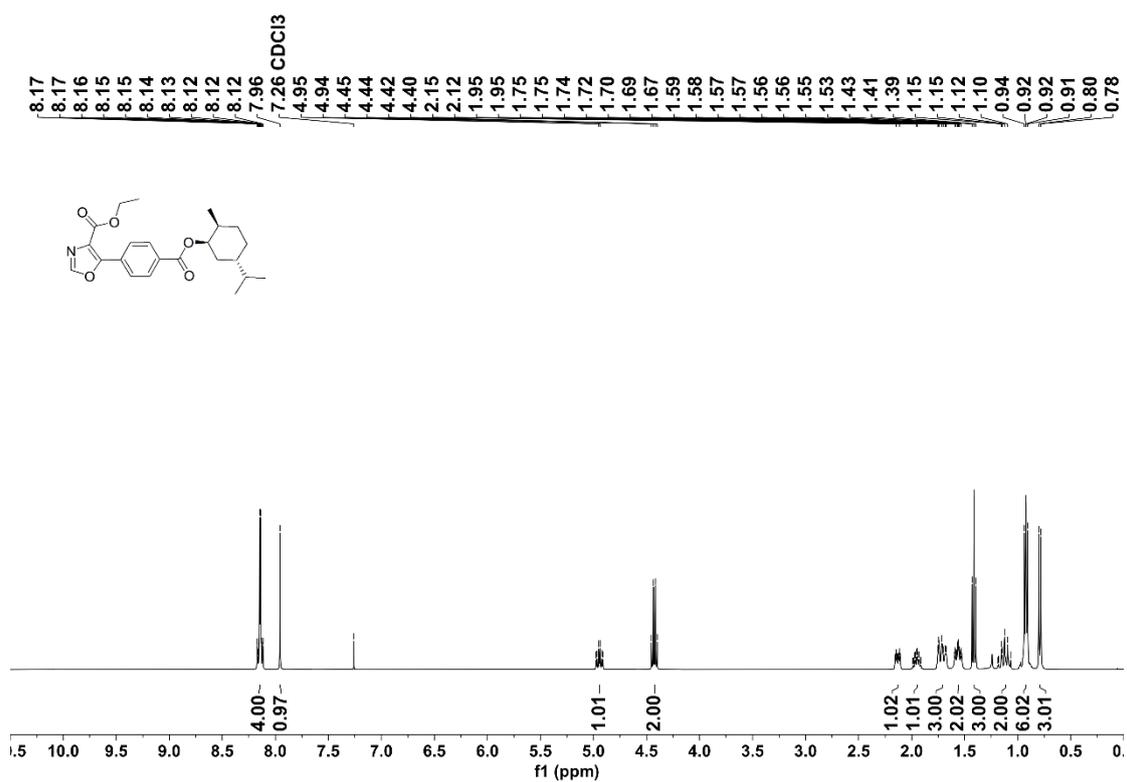
<sup>1</sup>H NMR spectrum of **3pa**



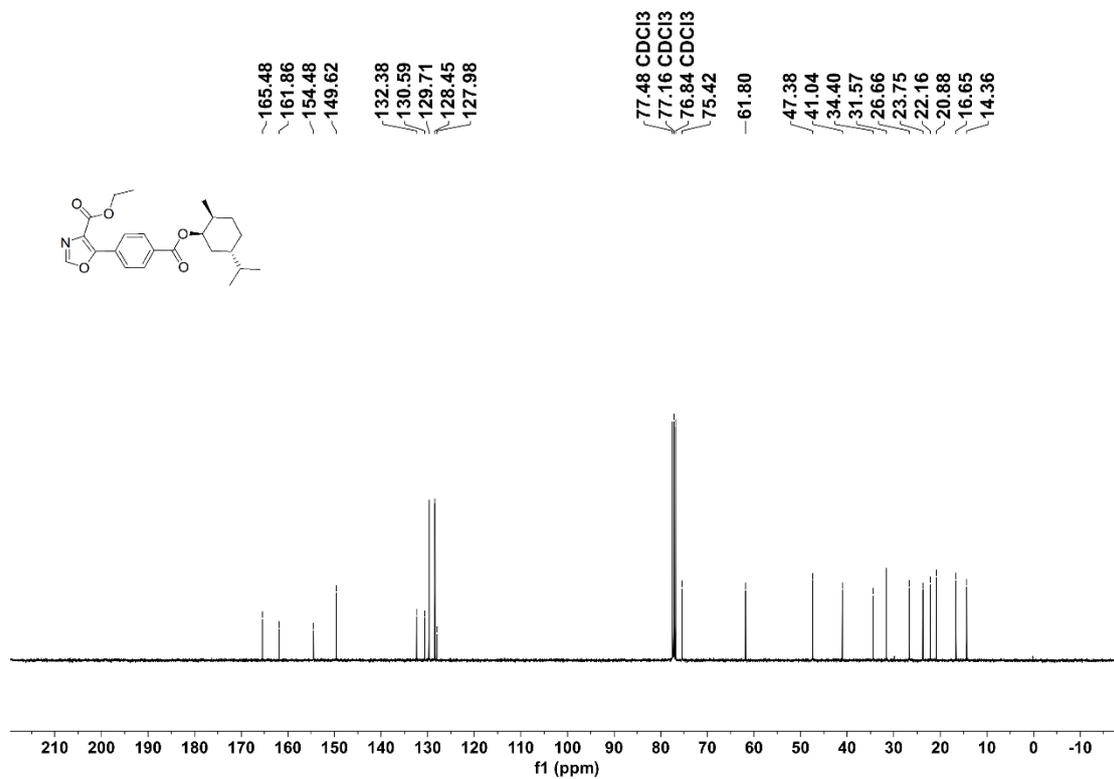
<sup>13</sup>C NMR spectrum of **3pa**



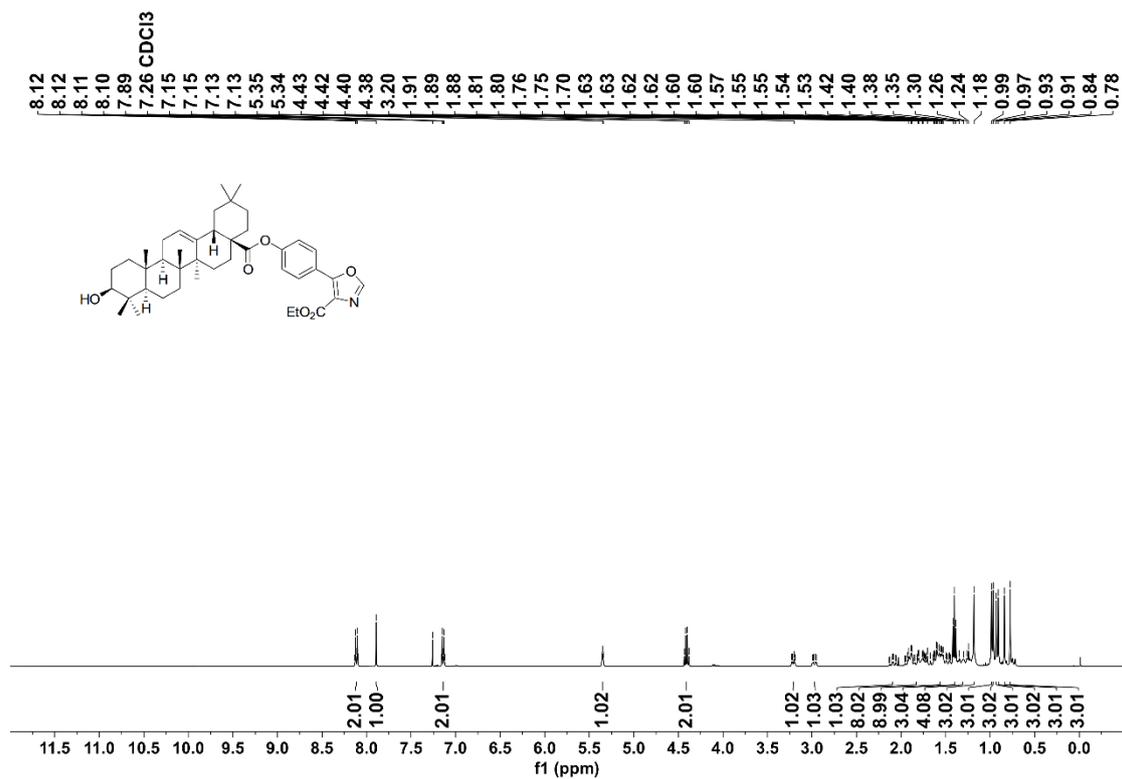
<sup>1</sup>H NMR spectrum of **3qa**



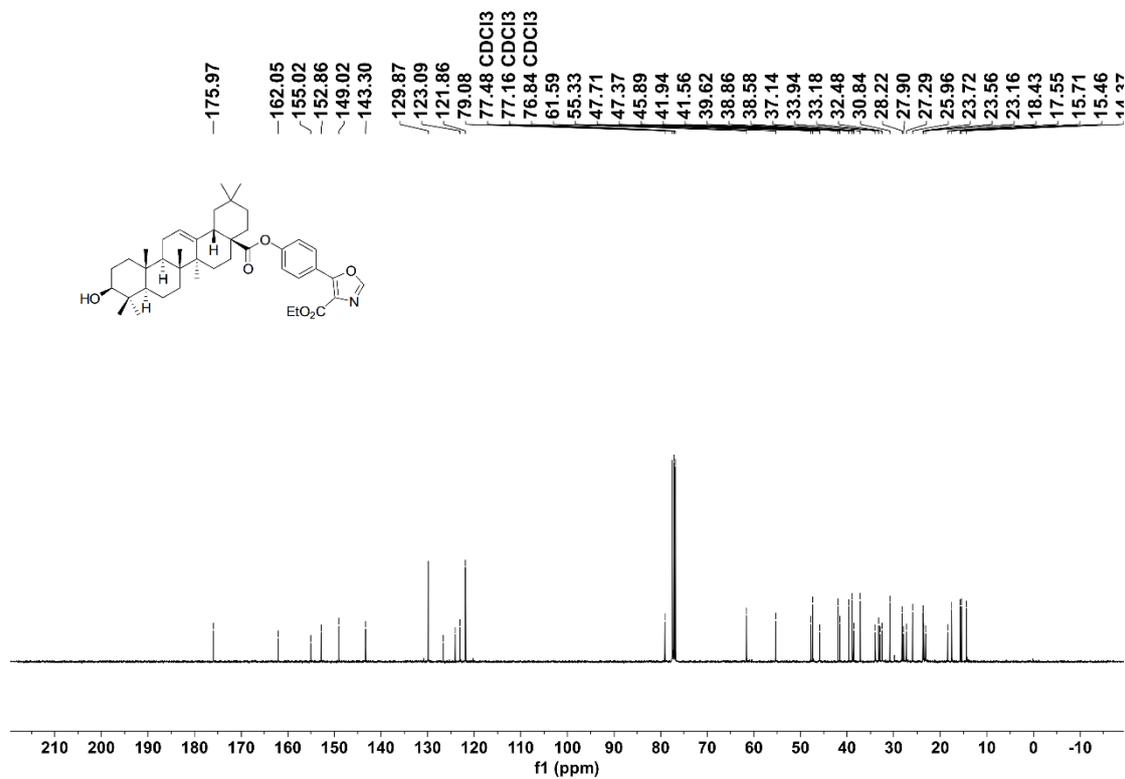
<sup>13</sup>C NMR spectrum of **3qa**



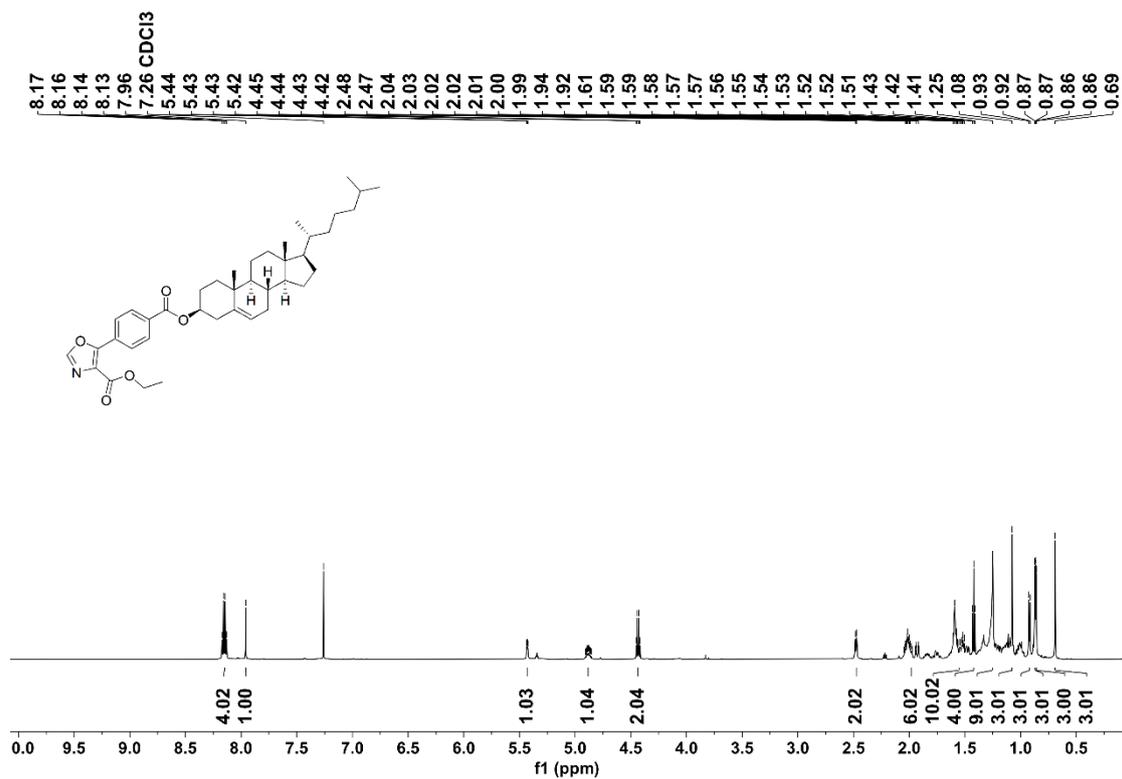
<sup>1</sup>H NMR spectrum of **3ra**



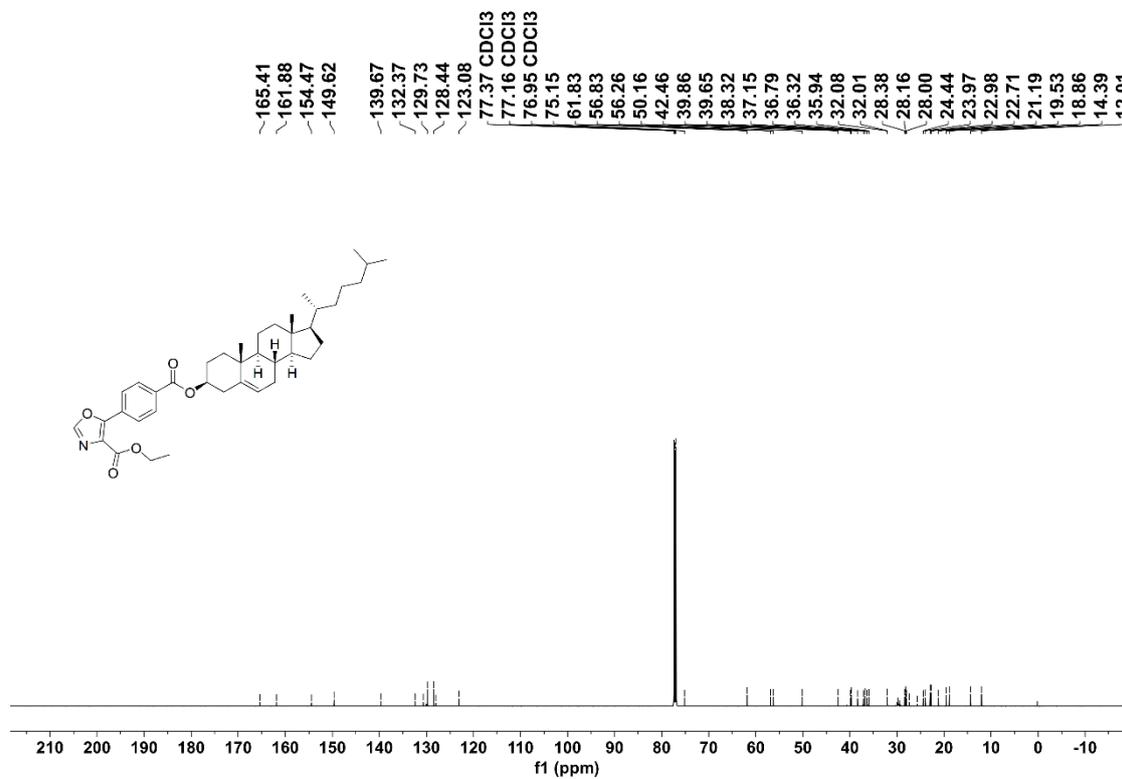
<sup>13</sup>C NMR spectrum of **3ra**



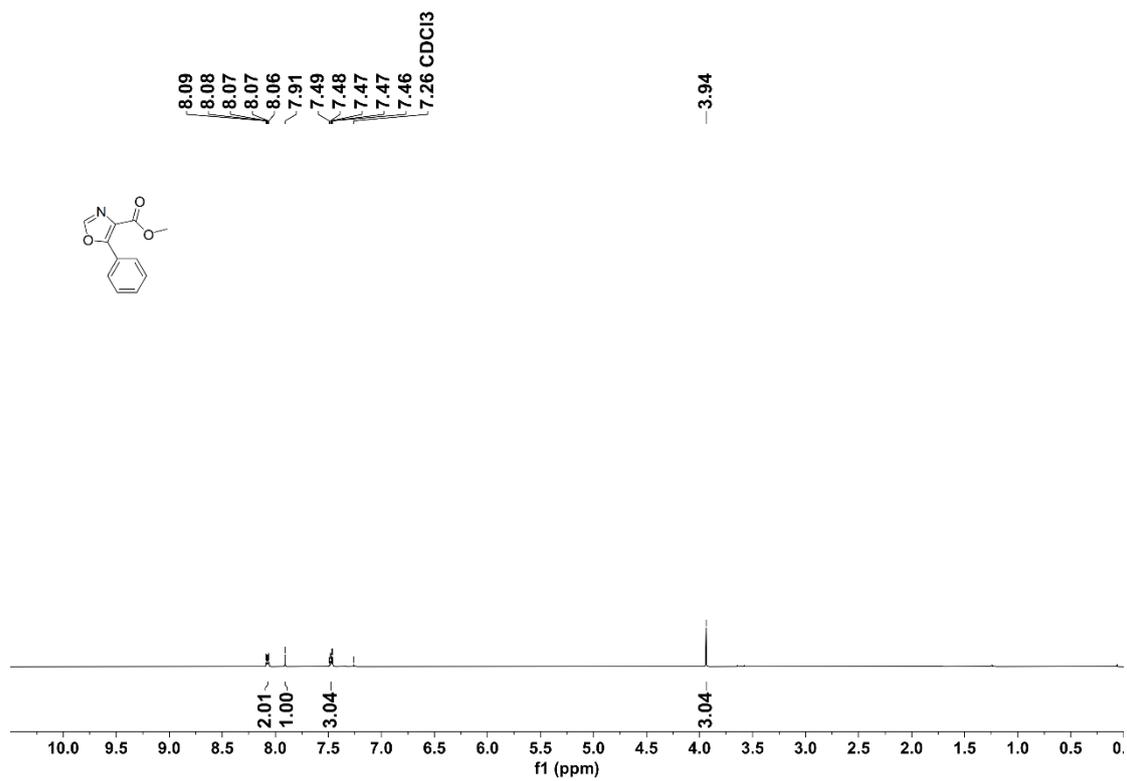
<sup>1</sup>H NMR spectrum of **3sa**



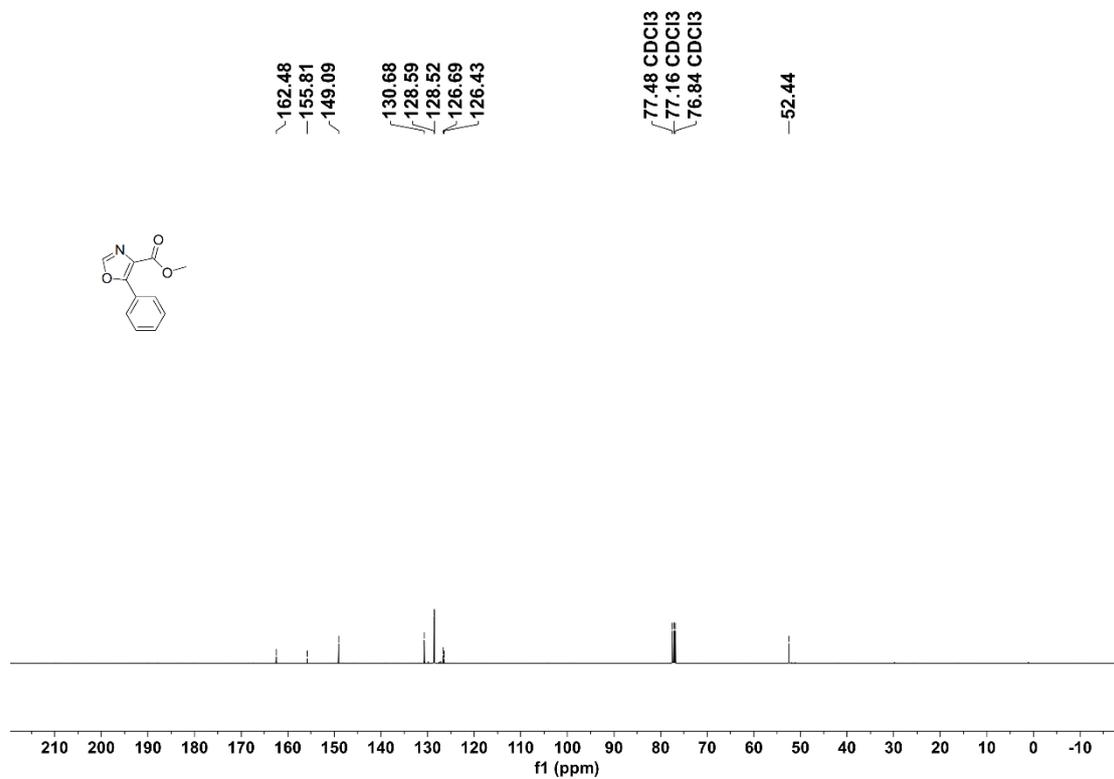
<sup>13</sup>C NMR spectrum of **3sa**



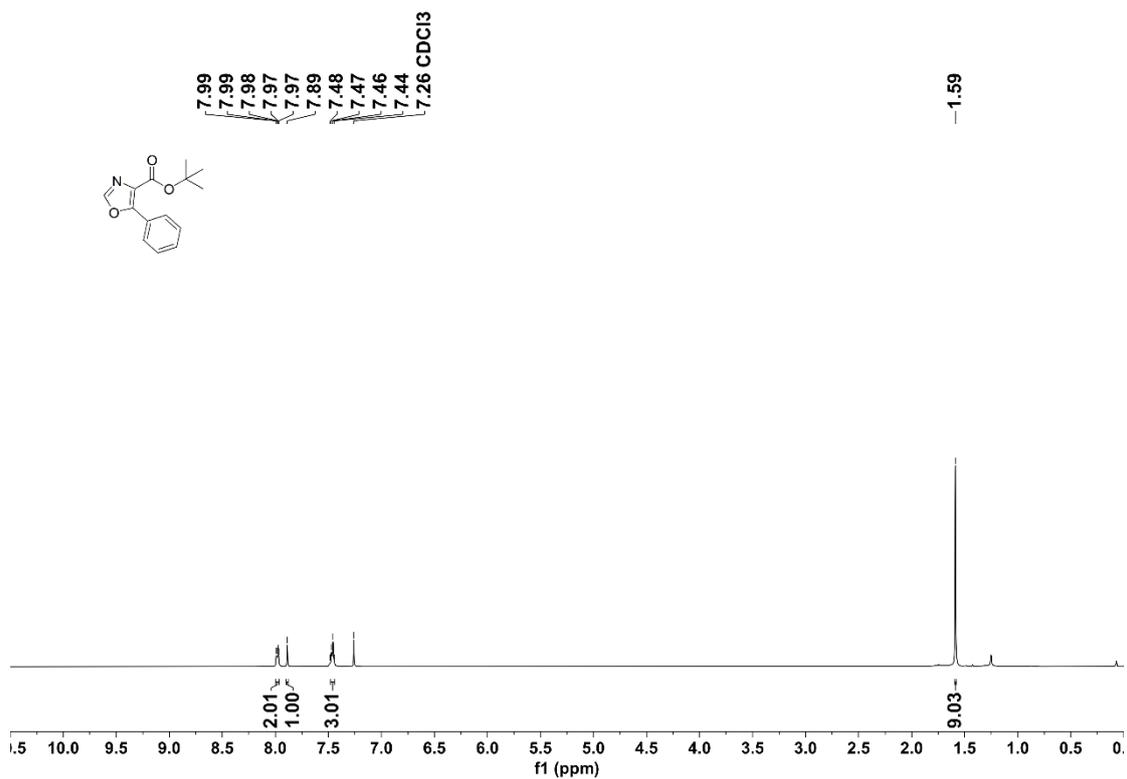
<sup>1</sup>H NMR spectrum of **3eb**



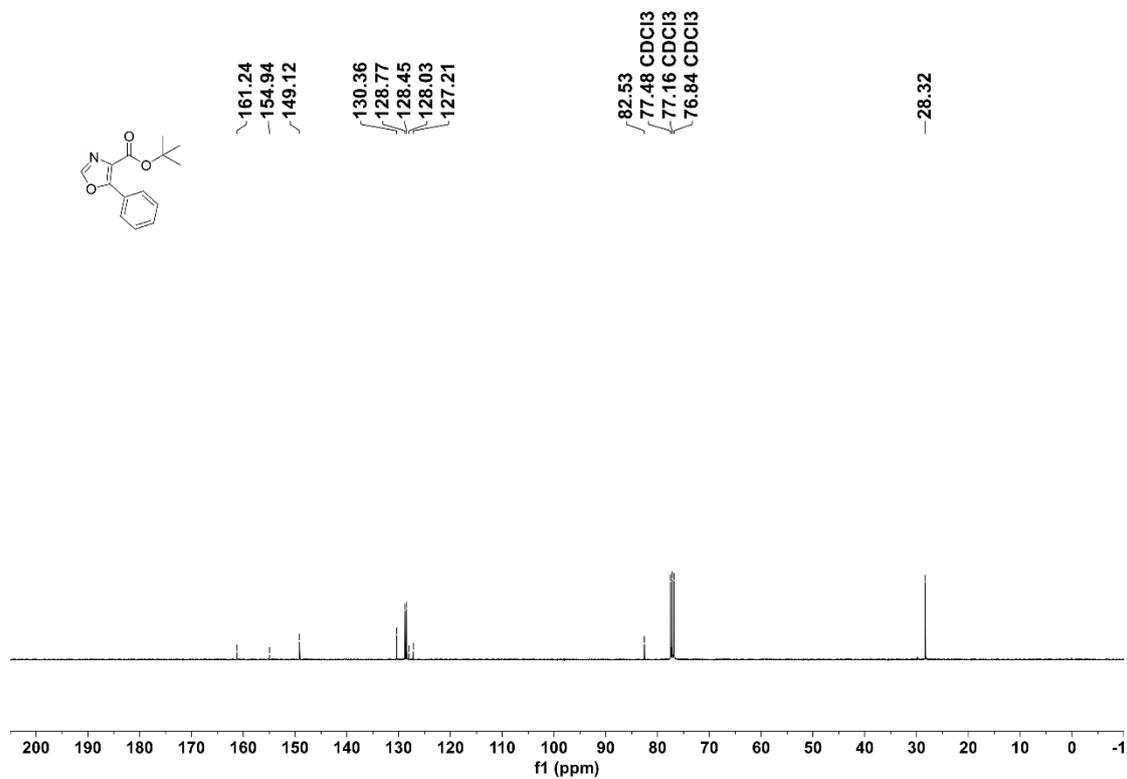
<sup>13</sup>C NMR spectrum of **3eb**



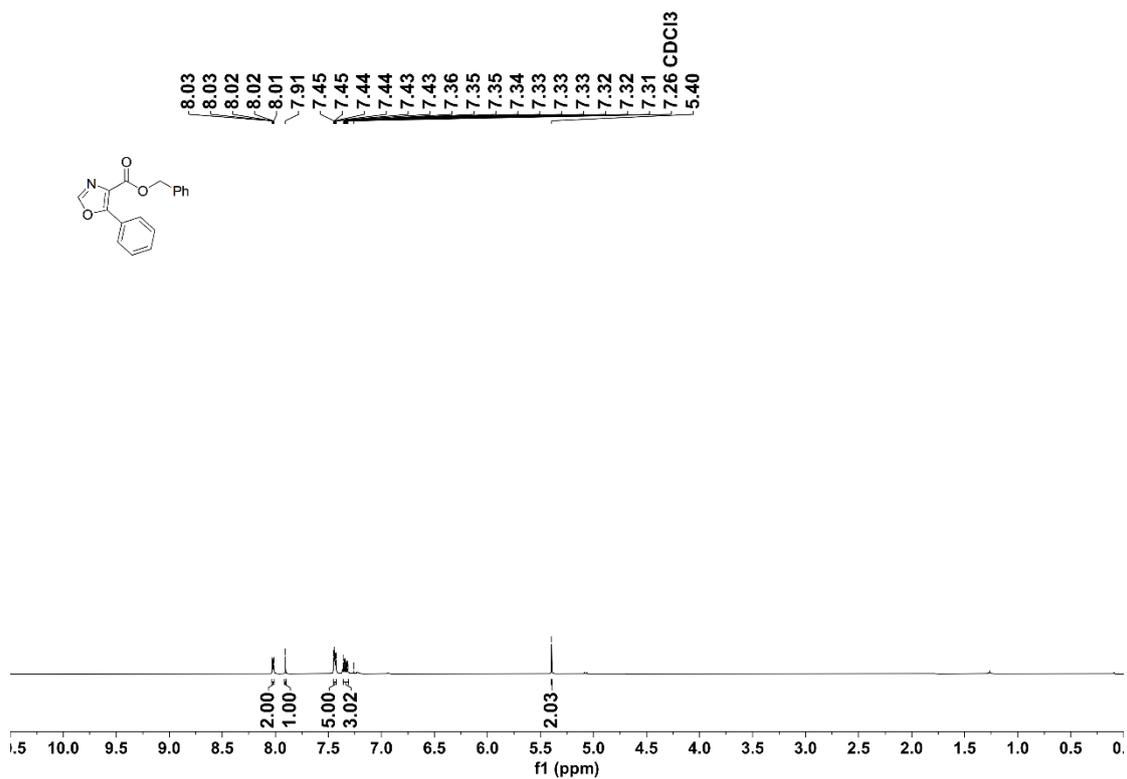
<sup>1</sup>H NMR spectrum of **3ec**



<sup>13</sup>C NMR spectrum of **3ec**



<sup>1</sup>H NMR spectrum of **3ed**



<sup>13</sup>C NMR spectrum of **3ed**

