

## Electronic Supporting Information for **One-Pot Synthesis of Acyloxycarbonyl compounds from ketones using Pybox-Copper(II) catalysts**

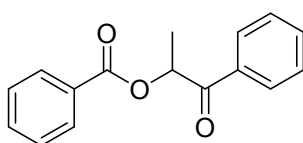
Wei-Guo Jia,\* Hui Zhang, Dan-Dan Li, Li-Qin Yan\*

**1. General Information.** Commercial reagents were analytical grade and used as received from Aladdin and Alfa aesar. All reactions were performed in oven-dried or flame-dried glassware, and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). All solvent were purified and degassed by standard procedures. The starting materials, [(Dm-Pybox)Cu(II)Br<sub>2</sub>] was synthesized according to the procedures described in the literature.<sup>1</sup> <sup>1</sup>H and <sup>13</sup>C NMR were recorded on a 300 MHz or 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to CDCl<sub>3</sub> (7.26 ppm for <sup>1</sup>H and 77 ppm for <sup>13</sup>C) or internal TMS. High-resolution mass spectra (HRMS) were obtained using APCI-TOF in positive mode. IR spectra were recorded on a Niciolet AVATAR-360IR spectrometer. Element analyses were performed on an Elementar III vario EI Analyzer.

### **General procedure for the synthesis $\alpha$ -acyloxylation of ketones**

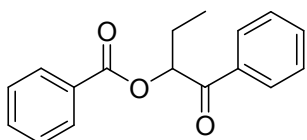
[(Dm-Pybox)Cu(II)Br<sub>2</sub>] (25 mg, 0.05 mmol, 0.1 equiv) was dissolved in DMF (1 mL), then appropriate ketone (0.5 mmol, 1.0 equiv) was added. This was stirred for 10 minutes at room temperature before the addition of potassium hexacyanoferrate (II) trihydrate (84.5 mg, 0.2 mmol, 2.4 equiv). The reaction was stirred at 110°C for 9 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the desired products.

### **Experimental Data for Products of $\alpha$ -acyloxylation of ketones**



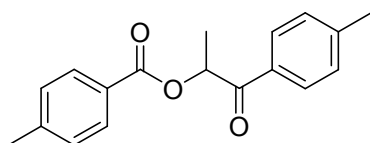
1-oxo-1-phenylpropan-2-yl benzoate (**1a**)

Pale yellow solid (72 mg, 90% Yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.10 (d, J = 7.38 Hz, 2H), 8.00 (d, J = 7.38 Hz, 2H), 7.60 (m, 2H), 7.48 (m, 4H), 6.21 (q, J = 6.90 Hz, 1H), 1.68 (d, J = 6.90 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 196.72, 165.97, 134.44, 133.57, 133.27, 129.86, 129.47, 128.79, 128.51, 128.38, 71.85, 17.18. HRMS (ESI) Calcd. for C<sub>16</sub>H<sub>14</sub>O<sub>3</sub> [M + H]<sup>+</sup> 255.1016, found 255.1020.



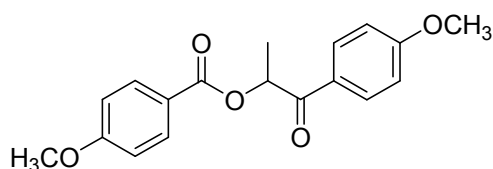
1-oxo-1-phenylbutan-2-yl benzoate (**2a**)

Pale yellow solid (84 mg, 97% Yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.10 (d, J = 7.20 Hz, 2H), 8.00 (d, J = 7.20 Hz, 2H), 7.58 (m, 2H), 7.48 (m, 4H), 6.05 (q, J = 4.50 Hz, 1H), 2.06 (m, 2H), 1.12 (t, J = 7.20 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 196.37, 166.19, 134.95, 133.50, 133.24, 129.85, 129.60, 128.78, 128.43, 128.39, 24.92, 9.96. HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>16</sub>O<sub>3</sub> [M + H]<sup>+</sup> 269.1172, found 269.1173.



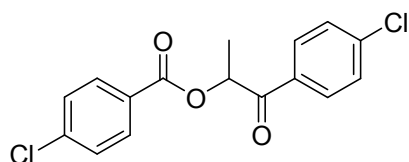
1-oxo-1-p-tolylpropan-2-yl 4-methylbenzoate (**3a**)

Yellow solid (81 mg, 94% Yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.97 (d, J = 8.10 Hz, 2H), 7.90 (d, J = 8.10 Hz, 2H), 7.26 (t, J = 8.10 Hz, 4H), 6.16 (q, J = 6.90 Hz, 1H), 2.41 (s, 3H), 1.64 (d, J = 6.90 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 196.39, 166.02, 144.44, 143.95, 131.98, 129.91, 129.46, 129.08, 128.66, 126.85, 71.63, 21.69, 17.27. HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>3</sub> [M + H]<sup>+</sup> 283.1329, found 283.1327.



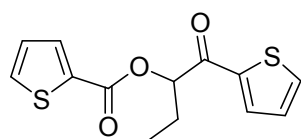
1-(4-methoxyphenyl)-1-oxopropan-2-yl 4-methoxybenzoate (**4a**)

Yellow solid (88 mg, 93% Yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.04 (d, J = 9.00 Hz, 2H), 8.00 (d, J = 9.00 Hz, 2H), 6.95 (d, J = 8.50 Hz, 2H), 6.91 (d, J = 8.50 Hz, 2H), 6.14 (q, J = 7.00 Hz, 1H), 3.86 (s, 6H), 1.64 (d, J = 7.00 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 195.32, 165.68, 163.82, 163.60, 131.94, 130.88, 127.41, 122.00, 113.97, 113.62, 71.31, 55.47, 17.34. HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>5</sub> [M + H]<sup>+</sup> 315.1227, found 315.1226.



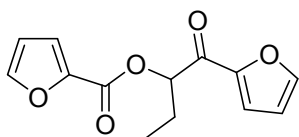
1-(4-chlorophenyl)-1-oxopropan-2-yl 4-chlorobenzoate (**5a**)

Pale yellow solid (70 mg, 73% Yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.01 (d, J = 8.70 Hz, 2H), 7.93 (d, J = 8.70 Hz, 2H), 7.45 (m, 4H), 6.11 (q, J = 6.90 Hz, 1H), 1.65 (d, J = 6.90 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 195.43, 165.12, 140.21, 139.94, 132.69, 131.25, 129.89, 129.21, 128.82, 127.78, 71.96, 17.08. HRMS (ESI) Calcd. for C<sub>16</sub>H<sub>12</sub>Cl<sub>2</sub>O<sub>3</sub> [M + H]<sup>+</sup> 323.0236, found 323.0238.



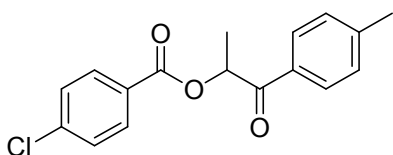
1-oxo-1-(thiophen-2-yl)butan-2-yl thiophene-2-carboxylate (**6a**)

Pale yellow solid (78 mg, 87% Yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (m, 2H), 7.68 (m, 1H), 7.60 (m, 1H), 7.15 (m, 1H), 7.12 (m, 1H), 5.75 (q, J = 5.50 Hz, 1H), 2.09 (m, 2H), 1.11 (t, J = 7.50 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 189.08, 161.63, 140.96, 134.42, 134.17, 133.06, 132.72, 128.23, 127.87, 78.00, 25.51, 9.85. HRMS (ESI) Calcd. for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>S<sub>2</sub> [M + H]<sup>+</sup> 281.0301, found 281.0303.



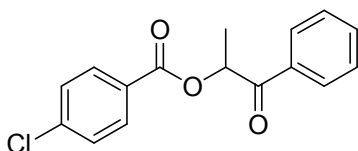
1-(furan-2-yl)-1-oxobutan-2-yl furan-2-carboxylate (**7a**)

Yellow solid (60 mg, 79% Yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (m, 2H), 7.35 (m, 1H), 7.28 (m, 1H), 6.57 (m, 1H), 6.53 (m, 1H), 5.80 (q,  $J = 4.50$  Hz, 1H), 2.05 (m, 2H), 1.09 (t,  $J = 7.50$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  184.68, 157.98, 150.73, 146.92, 146.74, 144.05, 118.83, 118.78, 112.47, 111.94, 24.78, 9.74. HRMS (ESI) Calcd. for  $\text{C}_{13}\text{H}_{12}\text{O}_5$   $[\text{M} + \text{H}]^+$  249.0757, found 249.0758.



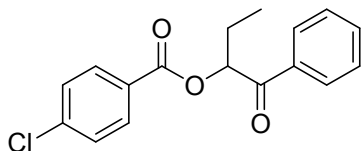
1-oxo-1-p-tolylpropan-2-yl 4-chlorobenzoate (**8a**)

$[(\text{Dm-Pybox})\text{Cu}(\text{II})\text{Br}_2]$  (25 mg, 0.05 mmol, 0.2 equiv) was dissolved in DMF (1.0 mL), then 4-chloropropiophenone (42 mg, 0.25 mmol, 1.0 equiv) and 4-Methylpropiophenone (38  $\mu\text{L}$ , 0.25 mmol, 1.0 equiv) were added. This was stirred for 10 minutes at room temperature before the addition of potassium hexacyanoferrate (II) trihydrate (84.5 mg, 0.2 mmol, 4.8 equiv). The reaction was stirred at  $100^\circ\text{C}$  for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the pale yellow solid (132 mg, 88% Yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (m, 2H), 7.35 (m, 1H), 7.28 (m, 1H), 6.57 (m, 1H), 6.53 (m, 1H), 5.80 (q,  $J = 4.50$  Hz, 1H), 2.06 (m, 2H), 1.09 (t,  $J = 7.50$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  196.01, 165.12, 144.65, 139.73, 131.76, 131.26, 129.52, 128.74, 128.62, 128.03, 72.03, 21.71, 17.31. HRMS (ESI) Calcd. for  $\text{C}_{13}\text{H}_{12}\text{O}_5$   $[\text{M} + \text{H}]^+$  249.0757, found 249.0758.



### 1-oxo-1-phenylpropan-2-yl 4-chlorobenzoate (**9a**)

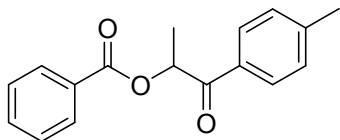
[(Dm-Pybox)Cu(II)Br<sub>2</sub>] (25 mg, 0.05 mmol, 0.2 equiv) was dissolved in DMF (1.0 mL), then 4-chloropropiophenone (42 mg, 0.25 mmol, 1.0 equiv) and propiophenone (34  $\mu$ L, 0.25 mmol, 1.0 equiv) were added. This was stirred for 10 minutes at room temperature before the addition of potassium hexacyanoferrate (II) trihydrate (84.5 mg, 0.2 mmol, 4.8 equiv). The reaction was stirred at 100°C for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the yellow solid (102 mg, 71% Yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d, J = 8.50 Hz, 2H), 7.98 (d, J = 8.50 Hz, 2H), 7.60 (t, J = 8.00 Hz, 1H), 7.49 (t, J = 8.00 Hz, 2H), 7.42 (d, J = 8.00 Hz, 2H), 6.20 (q, J = 7.00 Hz, 1H), 1.67 (d, J = 7.00 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  196.49, 165.13, 139.79, 134.39, 133.65, 131.25, 128.83, 128.76, 128.49, 127.98, 72.09, 17.20. HRMS (ESI) Calcd. for C<sub>13</sub>H<sub>12</sub>O<sub>5</sub> [M + H]<sup>+</sup> 249.0757, found 249.0758.



### 1-oxo-1-phenylbutan-2-yl 4-chlorobenzoate (**10a**)

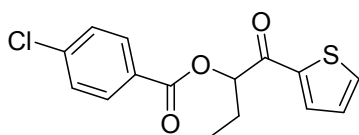
[(Dm-Pybox)Cu(II)Br<sub>2</sub>] (25 mg, 0.05 mmol, 0.2 equiv) was dissolved in DMF (1.0 mL), then 4-chloropropiophenone (42 mg, 0.25 mmol, 1.0 equiv) and Butyrophenone (38  $\mu$ L, 0.25 mmol, 1.0 equiv) were added. This was stirred for 10 minutes at room temperature before the addition of potassium hexacyanoferrate (II) trihydrate (84.5 mg, 0.2 mmol, 4.8 equiv). The reaction was stirred at 100°C for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the pale yellow solid (134 mg, 89% Yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (d, J = 8.00 Hz, 2H), 7.99 (d, J = 8.00 Hz, 2H), 7.61 (t, J = 7.50 Hz, 1H), 7.50 (t, J = 7.50 Hz, 2H), 7.46(d, J = 7.50 Hz, 2H), 6.05 (q, J = 4.50 Hz, 1H), 2.05

(m, 2H), 1.11 (t, J = 7.00 Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  196.15, 165.34, 139.74, 134.78, 133.62, 131.23, 129.88, 129.21, 128.82, 128.77, 128.40, 128.03, 24.90, 9.95. HRMS (ESI) Calcd. for  $\text{C}_{13}\text{H}_{12}\text{O}_5$   $[\text{M} + \text{H}]^+$  249.0757, found 249.0758.



1-oxo-1-p-tolylpropan-2-yl benzoate (**11a**)

[PyboxCu(**II**)Br<sub>2</sub>](25 mg, 0.05 mmol, 0.2 equiv) was dissolved in DMF (1.0 mL), then propiophenone (34  $\mu\text{L}$ , 0.25 mmol, 1.0 equiv) and 4-Methylpropiophenone (38  $\mu\text{L}$ , 0.25 mmol, 1.0 equiv) were added. This was stirred for 10 minutes at room temperature before the addition of Potassium hexacyanoferrate(**II**) trihydrate(84.5 mg, 0.2 mmol, 0.8 equiv). The reaction was stirred at 100°C for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the pale yellow solid (61 mg, 91% Yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (m, 1H), 7.97 (m, 2H), 7.91 m, 1H), 7.56 (m, 1H), 7.44(m, 2H), 7.25(m, 2H) 6.19 (q, J = 4.50 Hz, 1H), 2.41 (s, 3H), 1.66 (d, J = 4.50 Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  196.33, 166.05, 144.60, 144.04, 133.66, 133.31, 131.99, 129.99, 129.95, 129.57, 128.74, 128.46, 71.90, 21.17, 17.37. HRMS (ESI) Calcd. for  $\text{C}_{17}\text{H}_{16}\text{O}_3$   $[\text{M} + \text{H}]^+$  269.1172, found 269.1170.



1-oxo-1-(thiophen-2-yl)butan-2-yl 4-chlorobenzoate (**12a**)

[PyboxCu(**II**)Br<sub>2</sub>](25 mg, 0.05 mmol, 0.2 equiv) was dissolved in DMF (1.0 mL), then 4-chloropropiophenone (42 mg, 0.25 mmol, 1.0 equiv) and 2-Butyrylthiophene (36  $\mu\text{L}$ , 0.25 mmol, 1.0 equiv) were added. This was stirred for 10 minutes at room temperature before the addition of

Potassium hexacyanoferrate(II) trihydrate(84.5 mg, 0.2 mmol, 0.8 equiv). The reaction was stirred at 100°C for 10 hours, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the pale yellow solid (51 mg, 67% Yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.04 (m, 2H), 7.87 (d, J = 8.00 Hz, 1H), 7.69 (d, J = 8.00 Hz, 1H), 7.43 (m, 2H), 7.16(d, J = 7.50 Hz, 1H), 5.80 (q, J = 4.50 Hz, 1H), 2.12 (m, 2H), 1.12 (t, J = 7.00 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 189.13, 165.39, 140.02, 134.63, 132.77, 131.41, 128.97, 128.43, 78.01, 25.65, 10.07. HRMS (ESI) Calcd. for C<sub>15</sub>H<sub>13</sub>ClO<sub>3</sub>S [M + H]<sup>+</sup> 309.0347, found 309.0348.

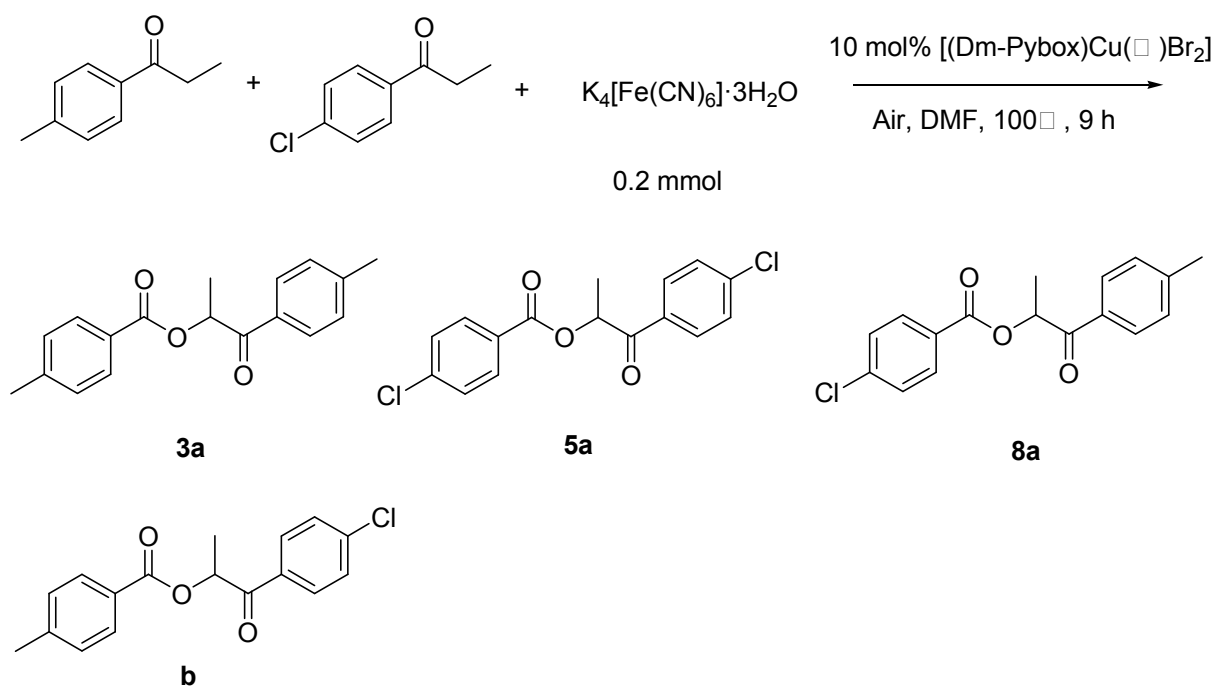
X-ray crystallography for **1a** and **8a**:

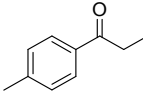
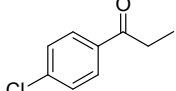
Diffraction data of **1a** and **8a** were collected on a Bruker Smart CCD diffractometer with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All the data were collected at room temperature and the structures were solved by direct methods and subsequently refined on F<sup>2</sup> by using full-matrix least-squares techniques (SHELXL)<sup>2</sup>, and SADABS absorption corrections<sup>3</sup> applied to the data.

## References

1. W.-G. Jia, D.-D. Li, Y.-C. Dai, H. Zhang, L.-Q. Yan, E.-H. Sheng, Y. Wei, X.-L. Mu and K.-W. Huang, *Org. Biomol. Chem.*, 2014, **12**, 5509-5516.
2. G. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, 1997.
3. G. Sheldrick, *SADABS v. 2.01, Bruker/Siemens area detector absorption correction program*, 1998.

**Table S1. Studying the reaction selectivity toward  $\alpha$ -oxyacylation of ketones**

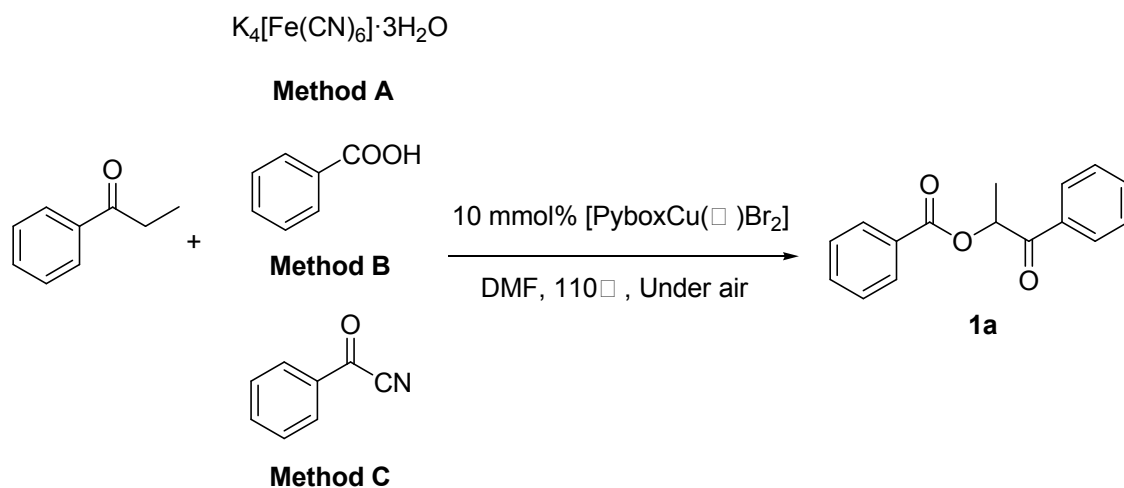


Entry	 (mmol)	 (mmol)	3a (yield%) <sup>a,b</sup>	5a (yield%) <sup>a,b</sup>	8a (yield%) <sup>a,b</sup>	b (yield%) <sup>a,b</sup>
1	0.25	0.25	/	/	88	/
2	0.25	0.30	/	5	85	/
3	0.30	0.25	3	/	86	/

a: Isolated yield; b: reaction condition: 1mL DMF as solvent, 0.2 mmol  $K_4[Fe(CN)_6] \cdot 3H_2O$ , under air, 100°C.

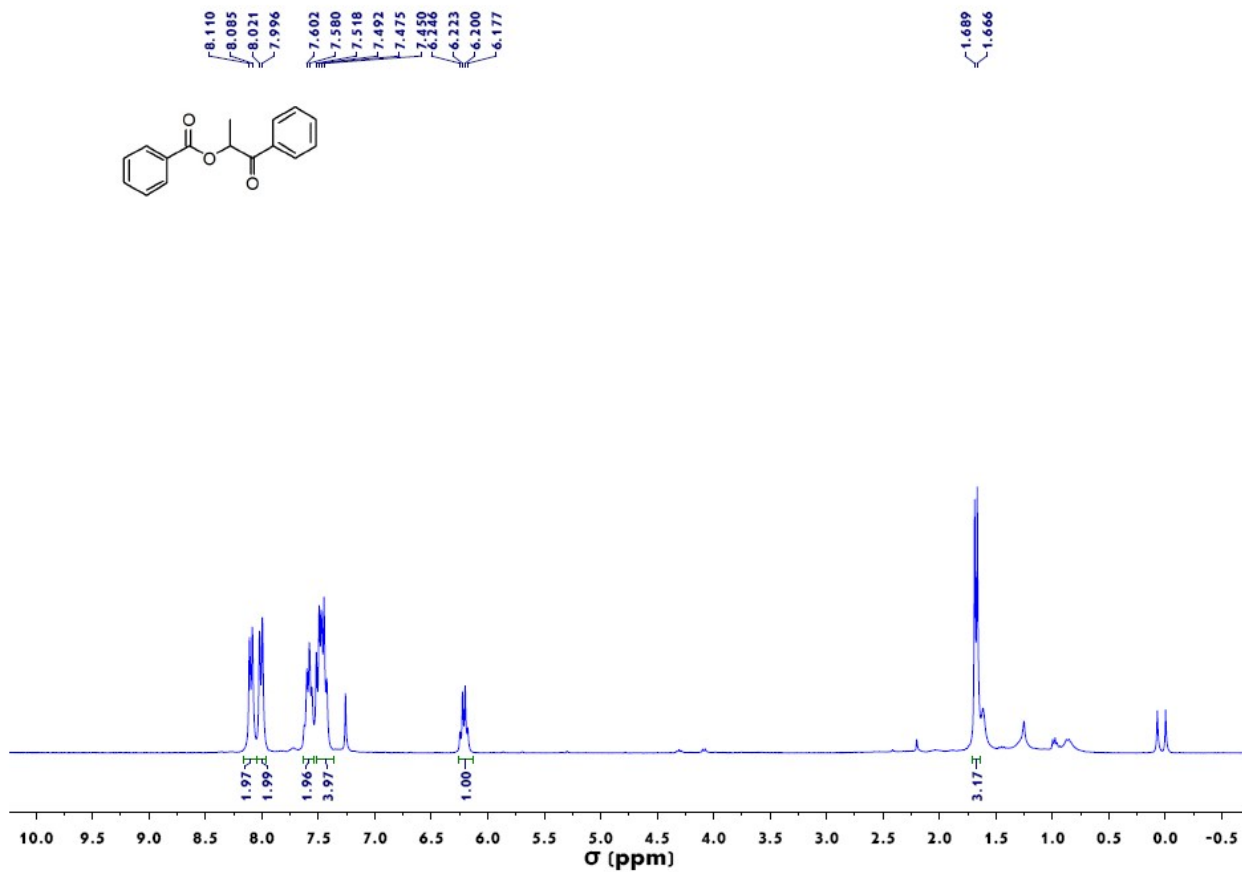


**Table S2. Studying the catalytic mechanism toward  $\alpha$ -oxyacylation of ketones**

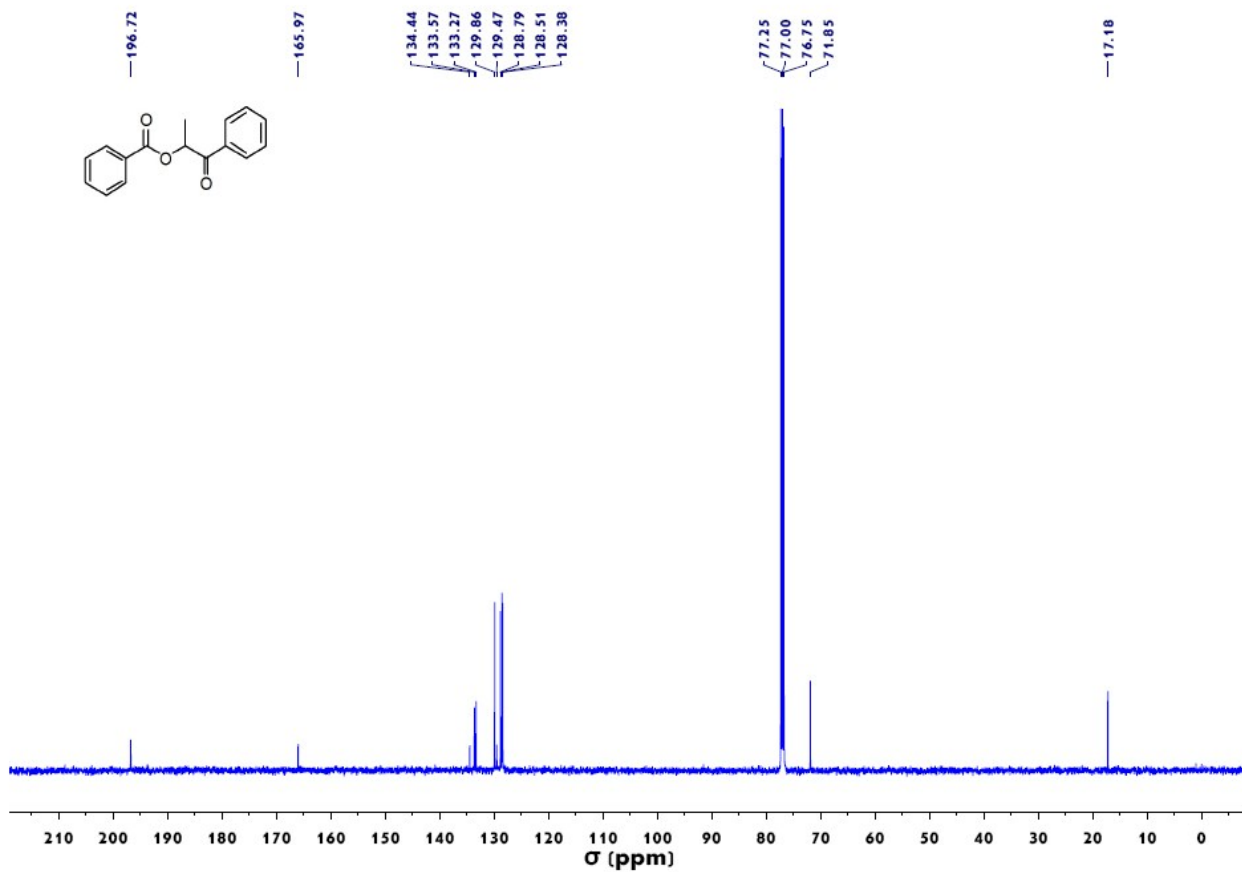


Entry	[PyboxCu(II)Br <sub>2</sub> ] (mol%)	$K_4[Fe(CN)_6] \cdot 3H_2O$ (mmol)	Benzoic acid (mmol)	benzoyl cyanide (mmol)	Product 1a (%) <sup>a,b</sup>
1		0.2			NR
2	10	0.2			90
3	10				NR
4			1.2		NR
5	10		1.2		21
6				1.2	NR
	10			1.2	15

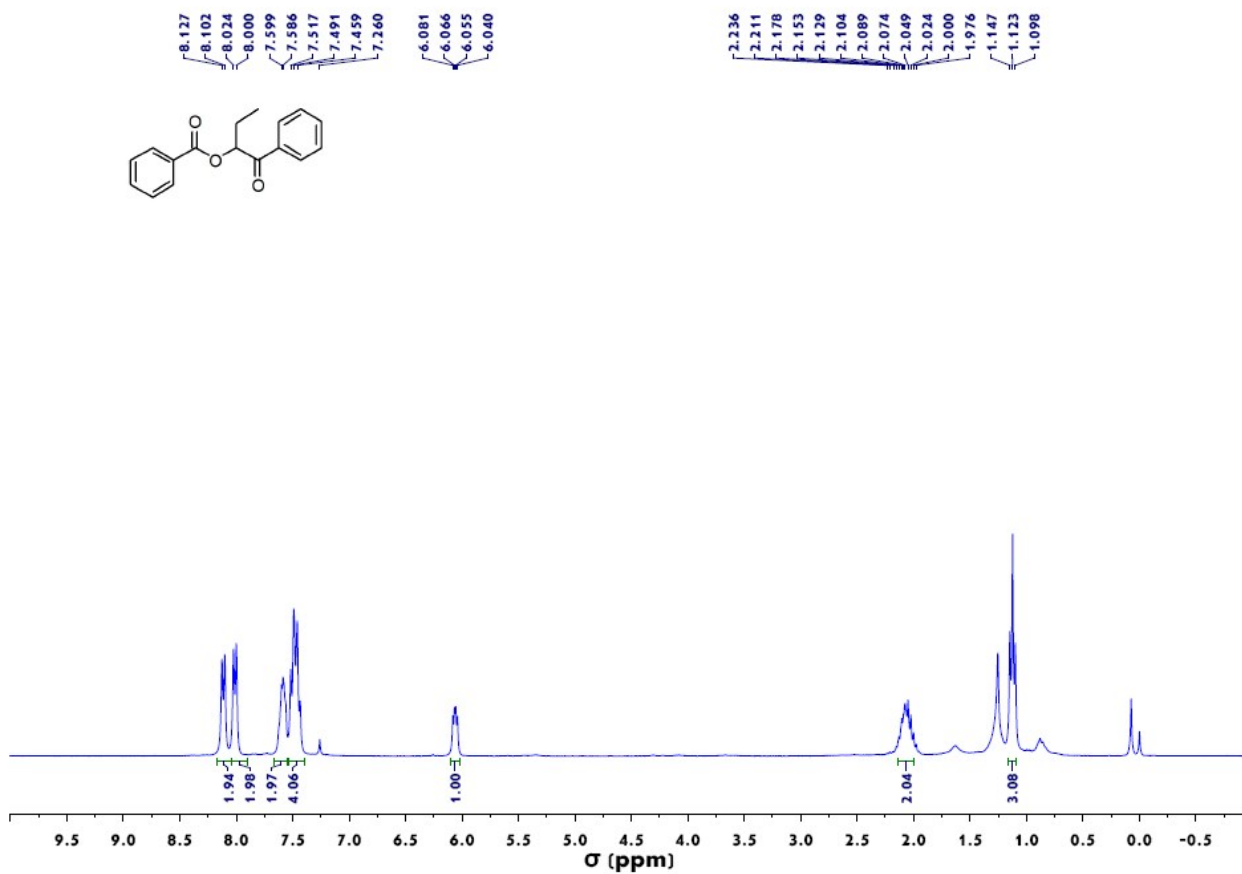
a: Isolated yield; b: reaction condition: 0.5 mmol propiophenone, 1mL DMF as solvent, 9 h, under air, 110°C;



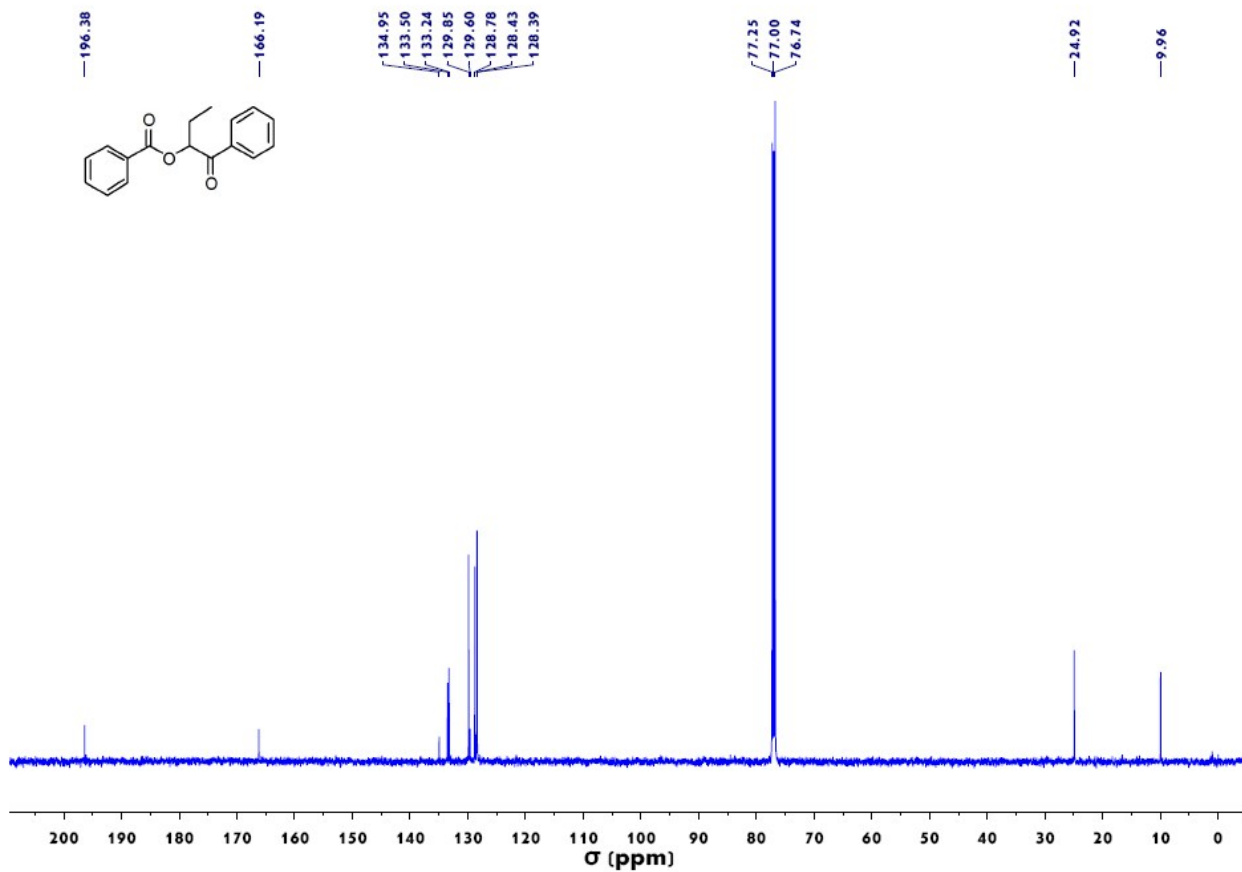
<sup>1</sup>H NMR spectrum of 1a



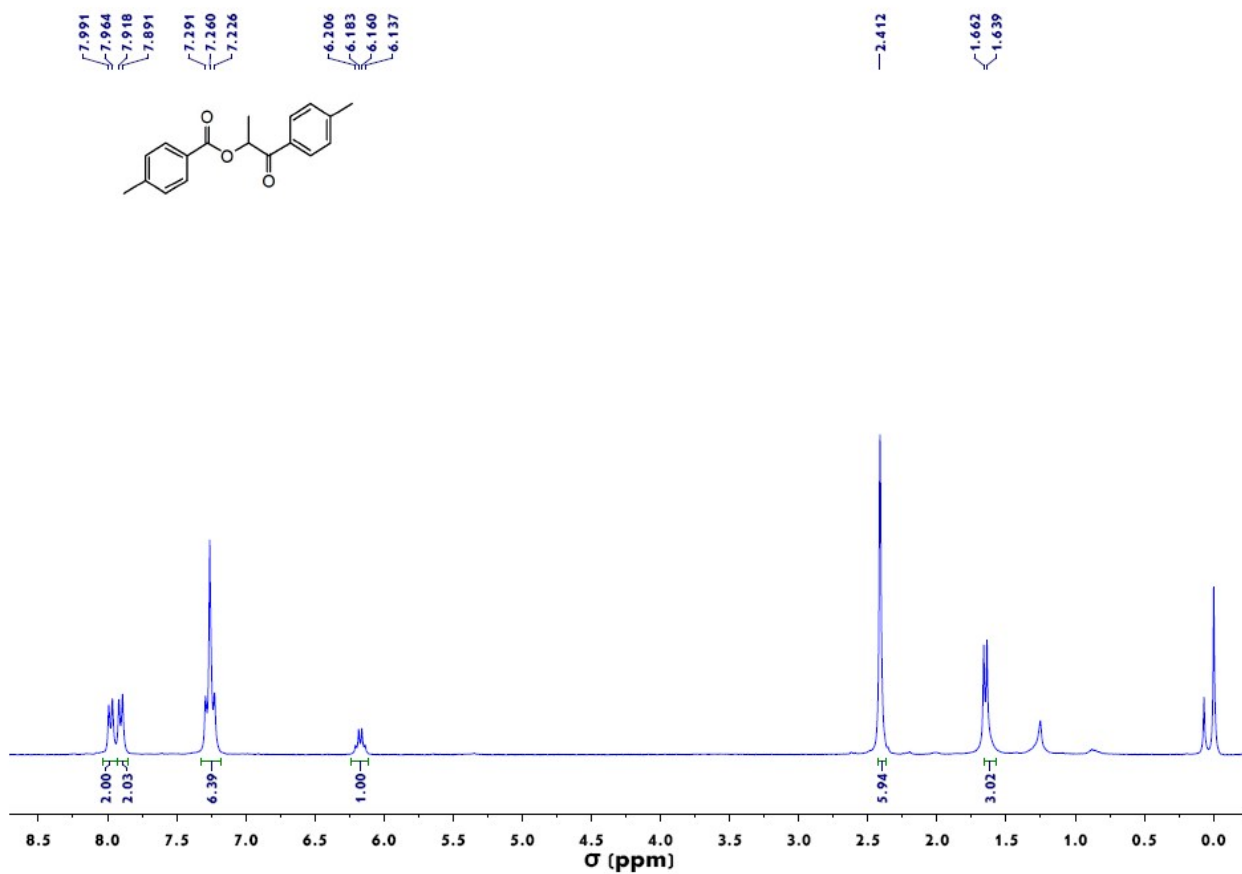
<sup>13</sup>C NMR spectrum of 1a



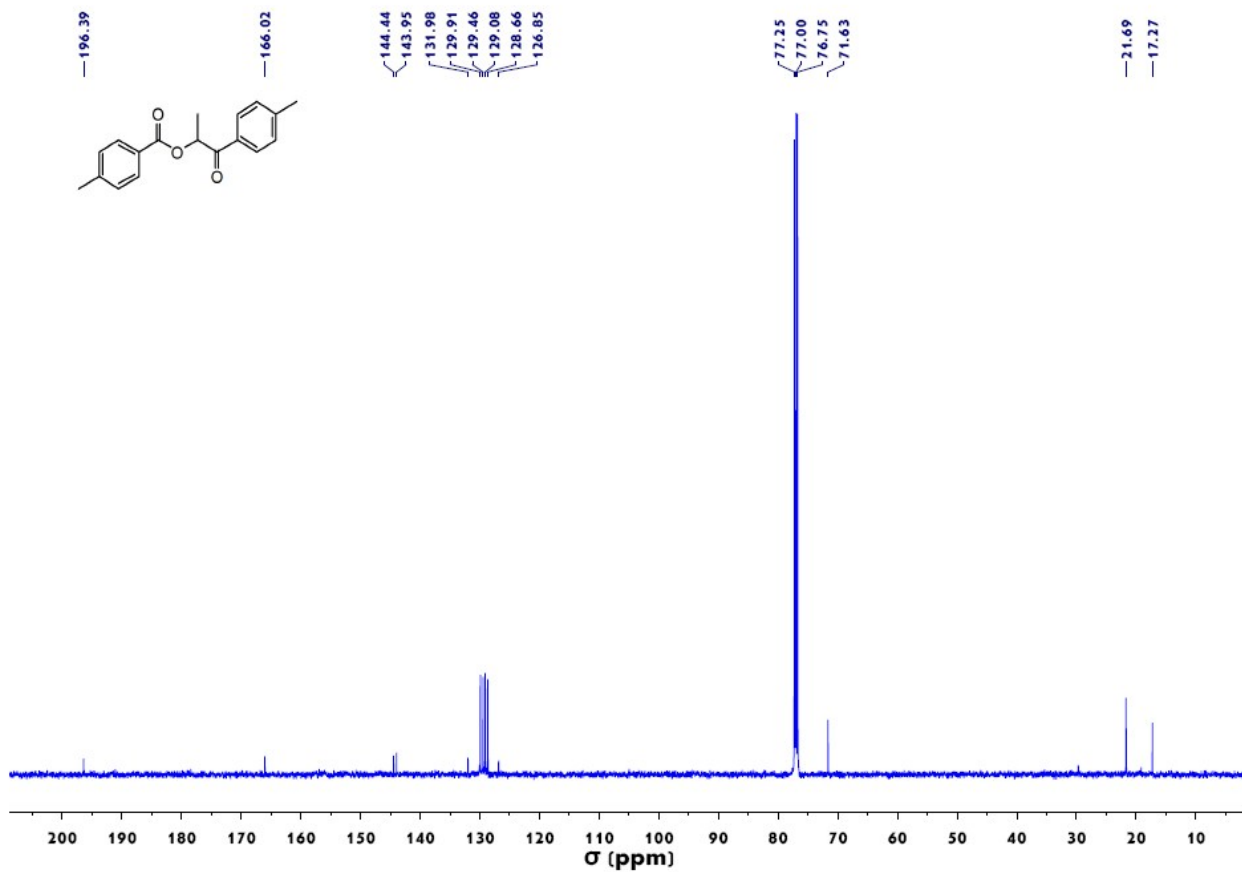
<sup>1</sup>H NMR spectrum of **2a**



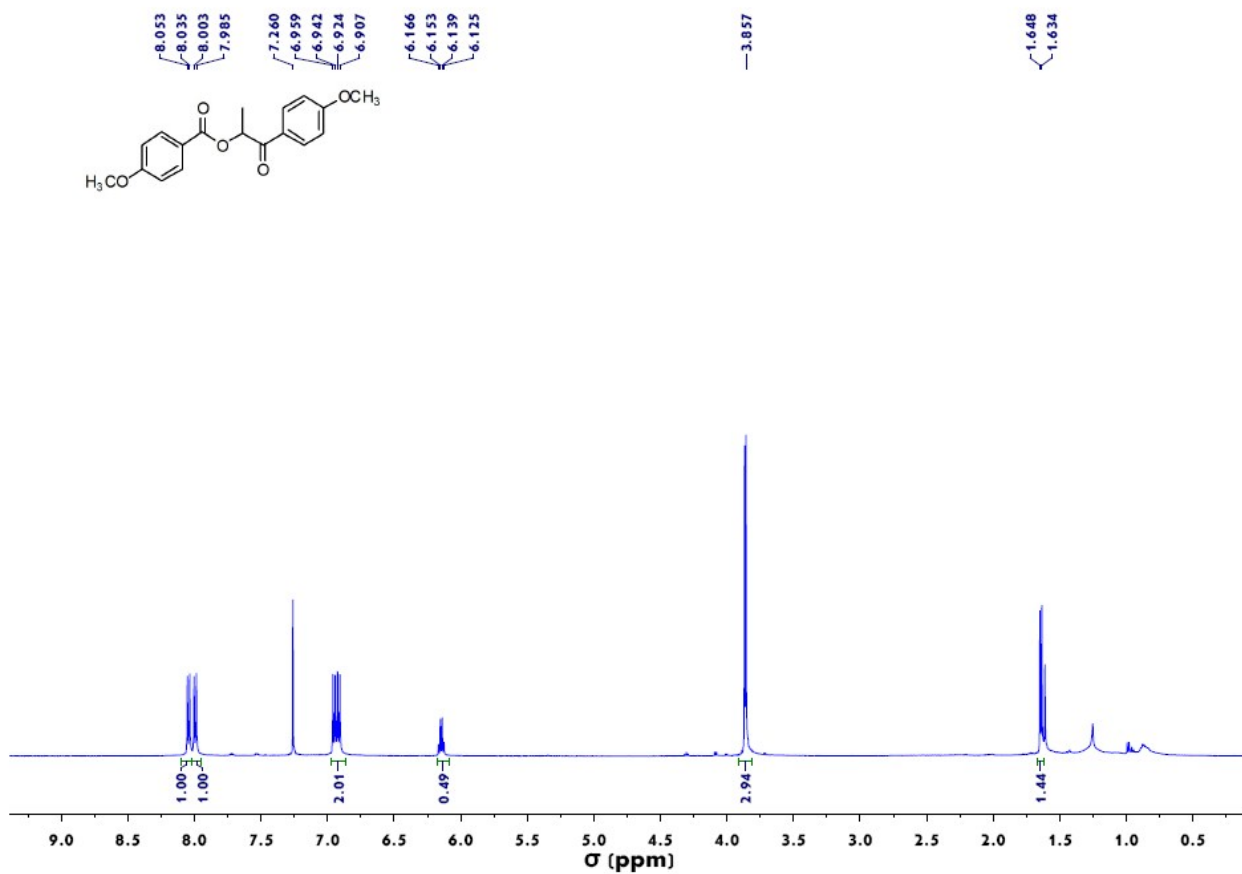
<sup>13</sup>C NMR spectrum of **2a**



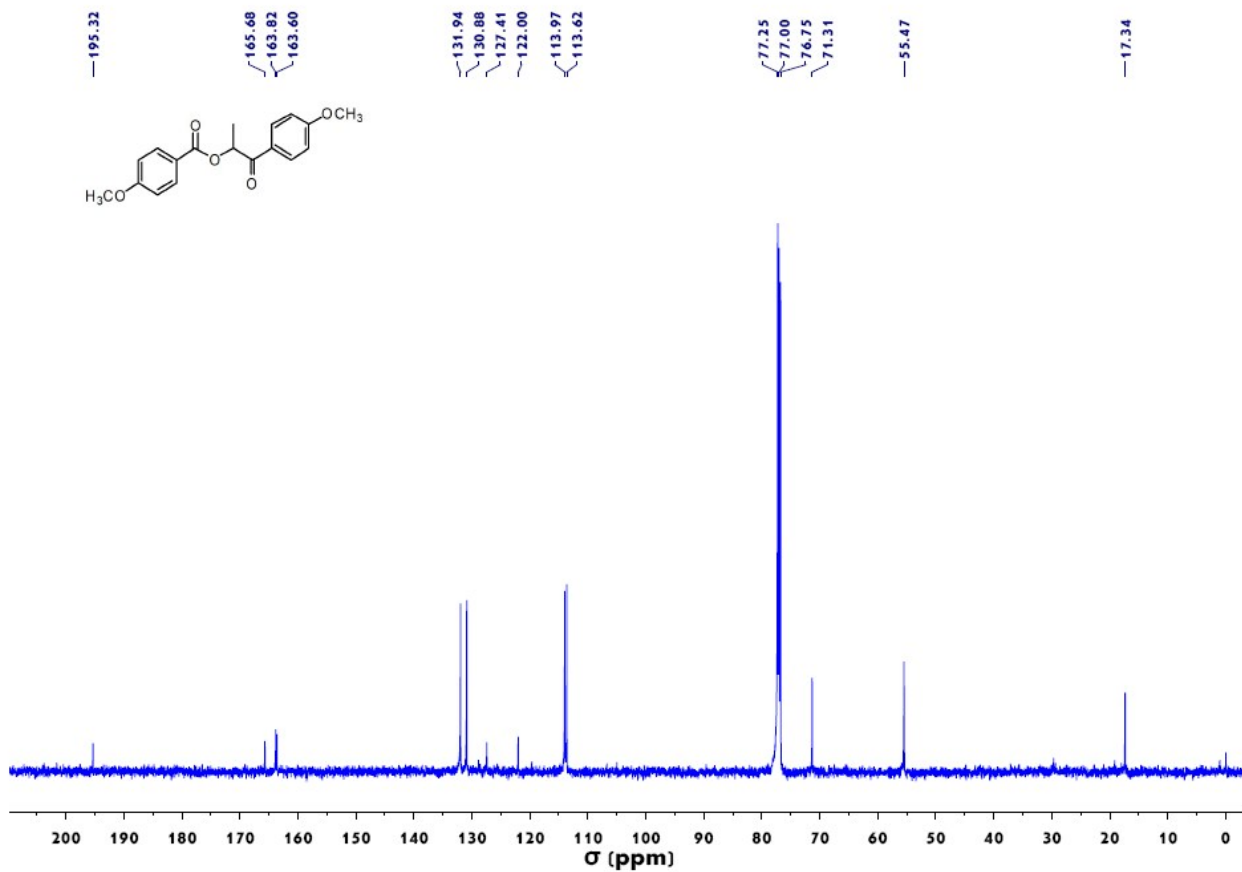
<sup>1</sup>H NMR spectrum of 3a



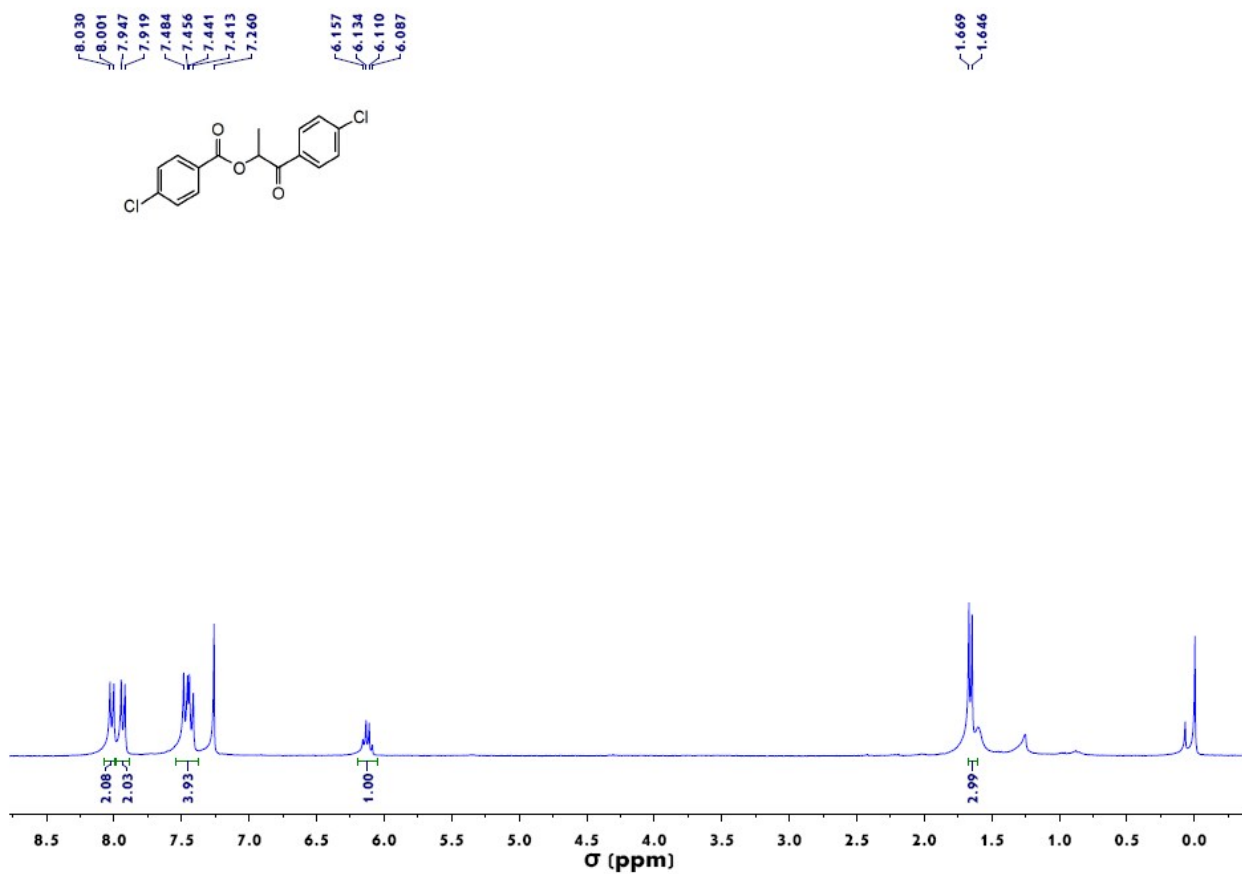
<sup>13</sup>C NMR spectrum of 3a



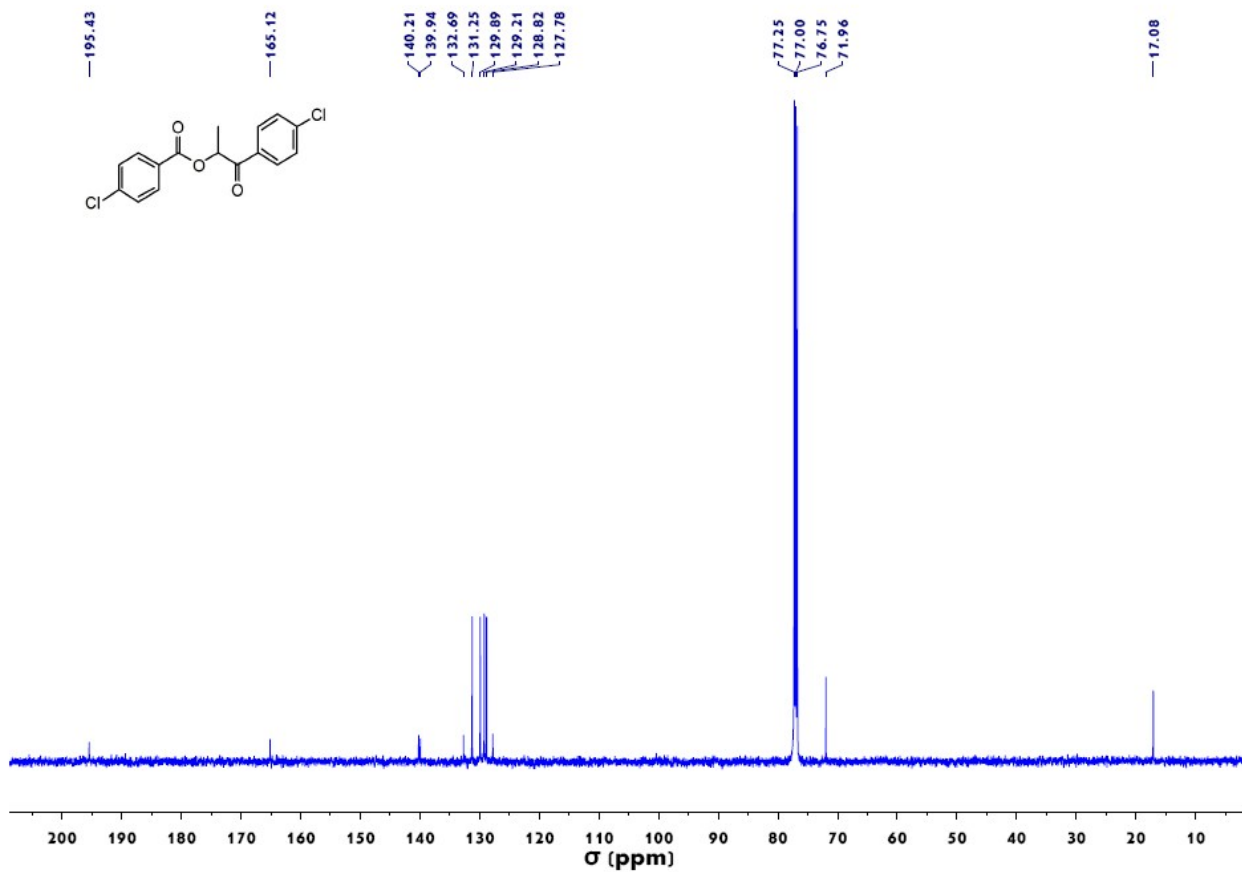
<sup>1</sup>H NMR spectrum of 4a



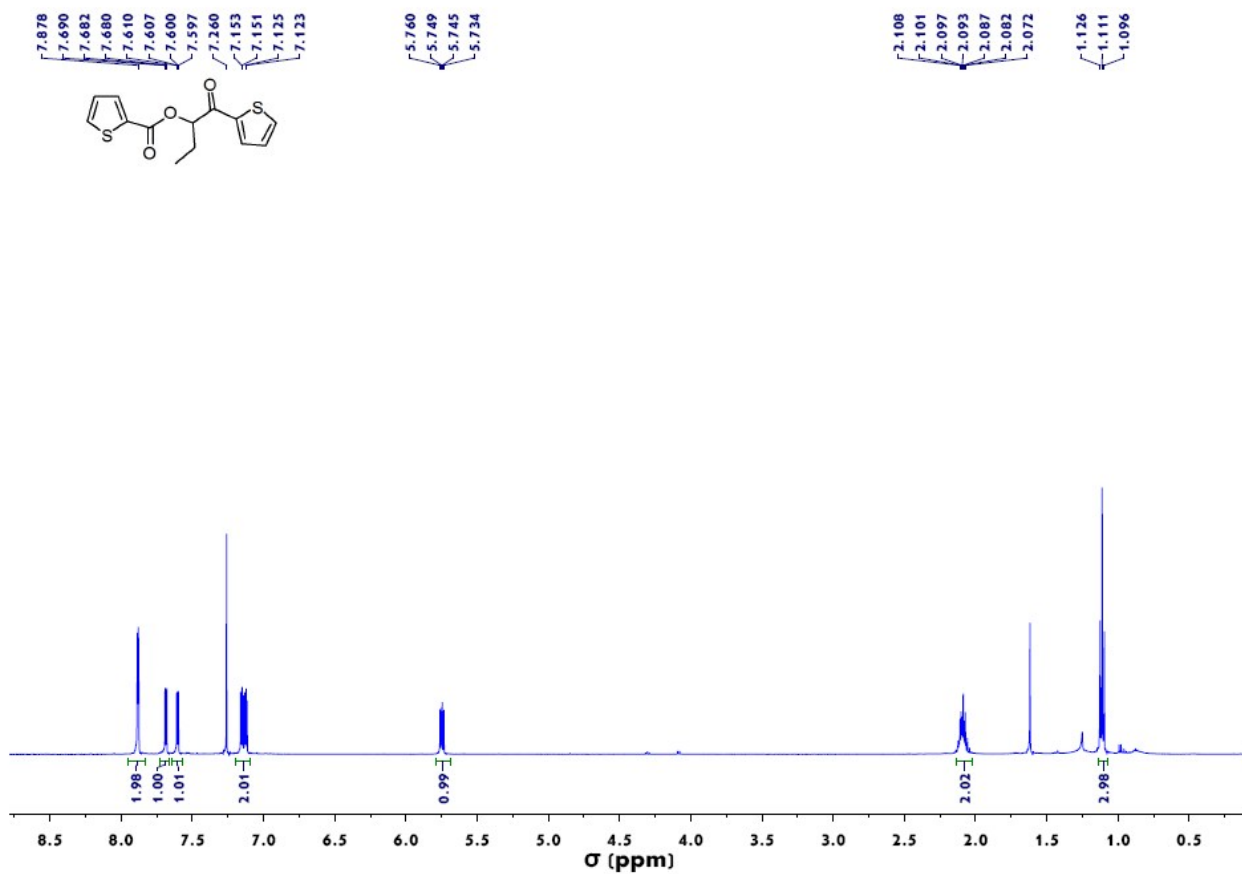
<sup>13</sup>C NMR spectrum of 4a



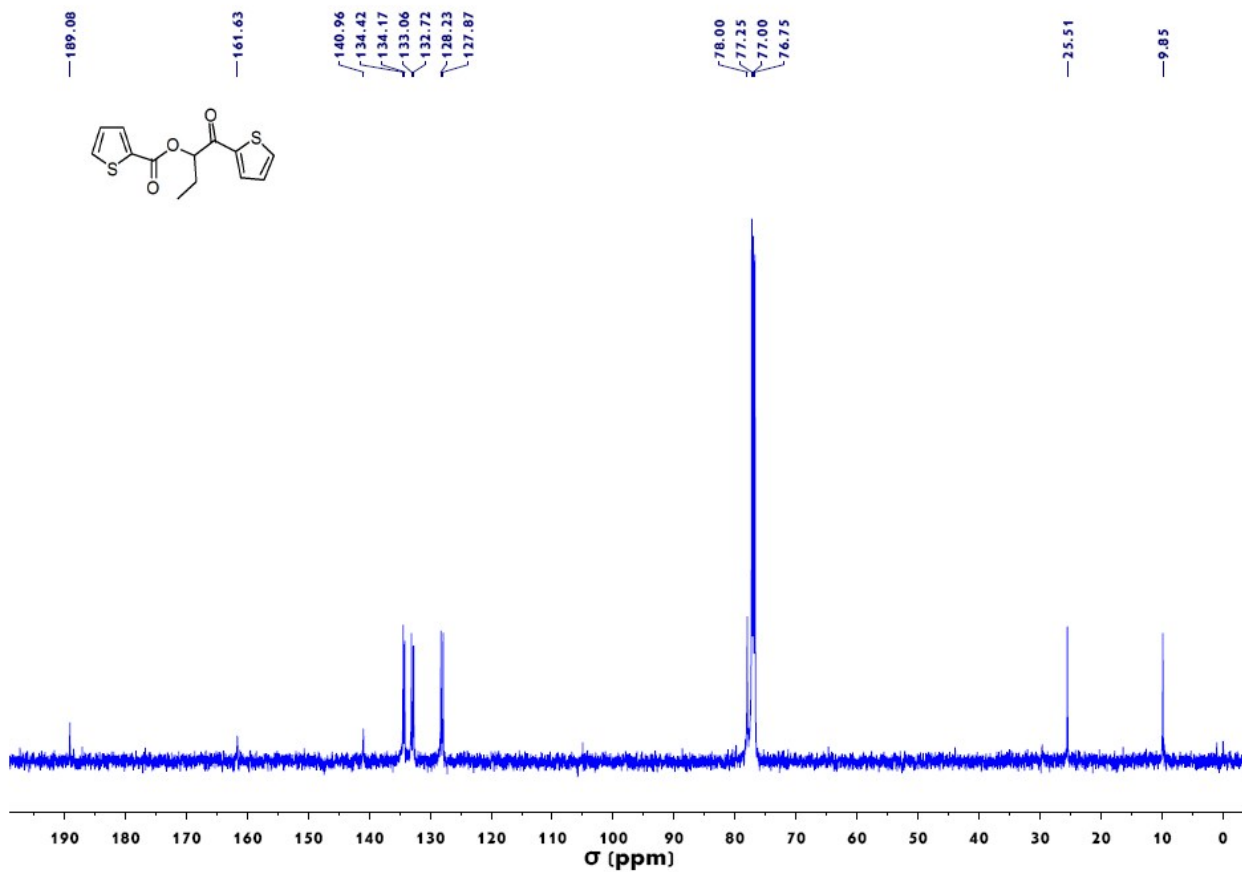
<sup>1</sup>H NMR spectrum of 5a



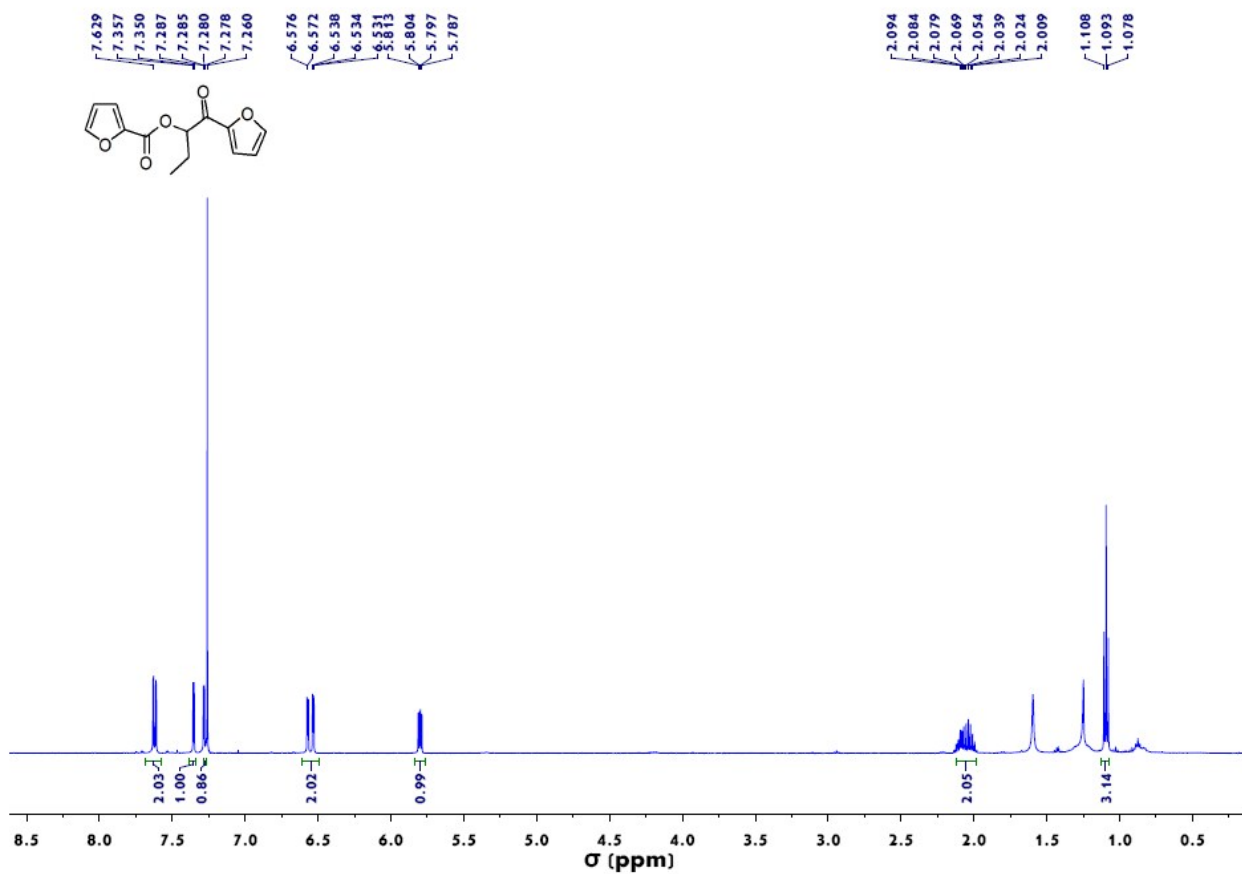
<sup>13</sup>C NMR spectrum of 5a



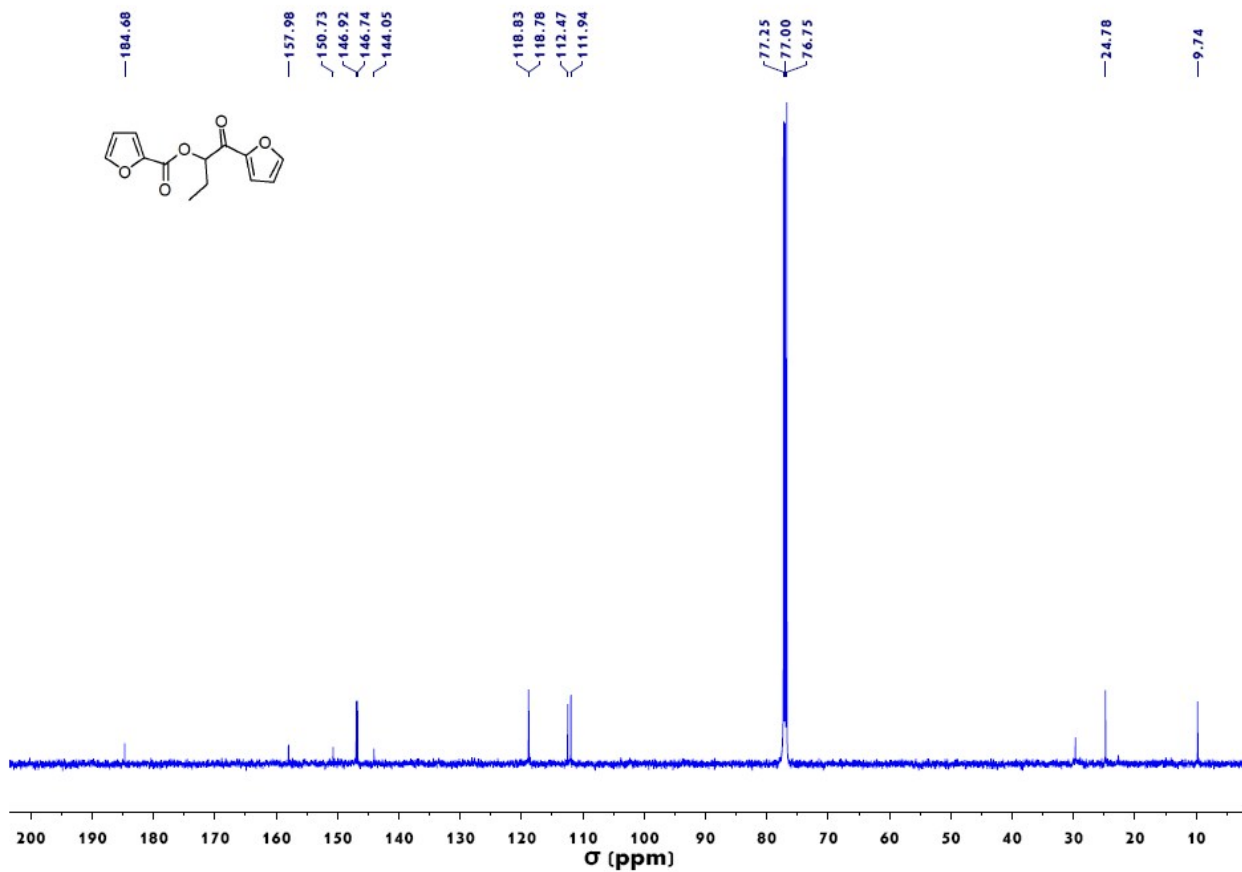
<sup>1</sup>H NMR spectrum of 6a



<sup>13</sup>C NMR spectrum of 6a

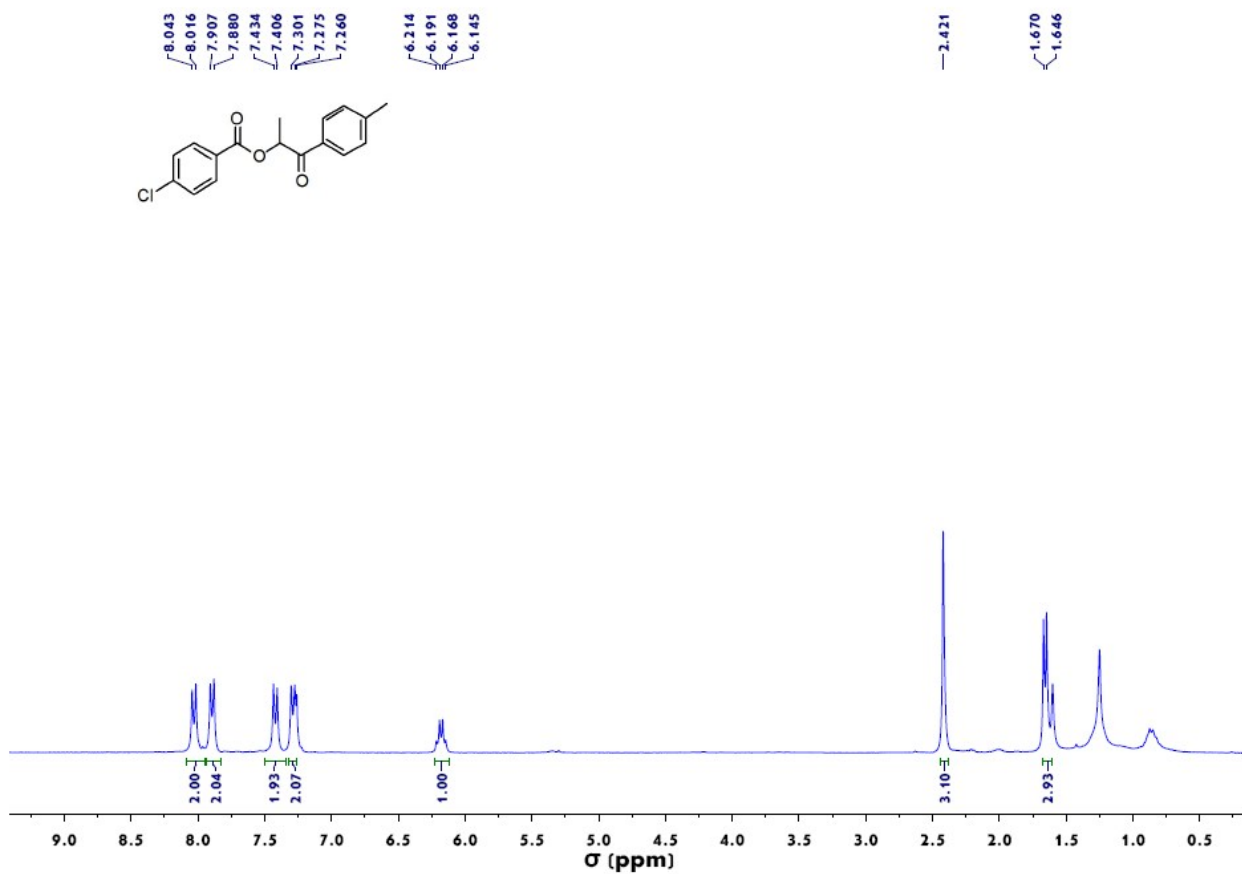


<sup>1</sup>H NMR spectrum of 7a

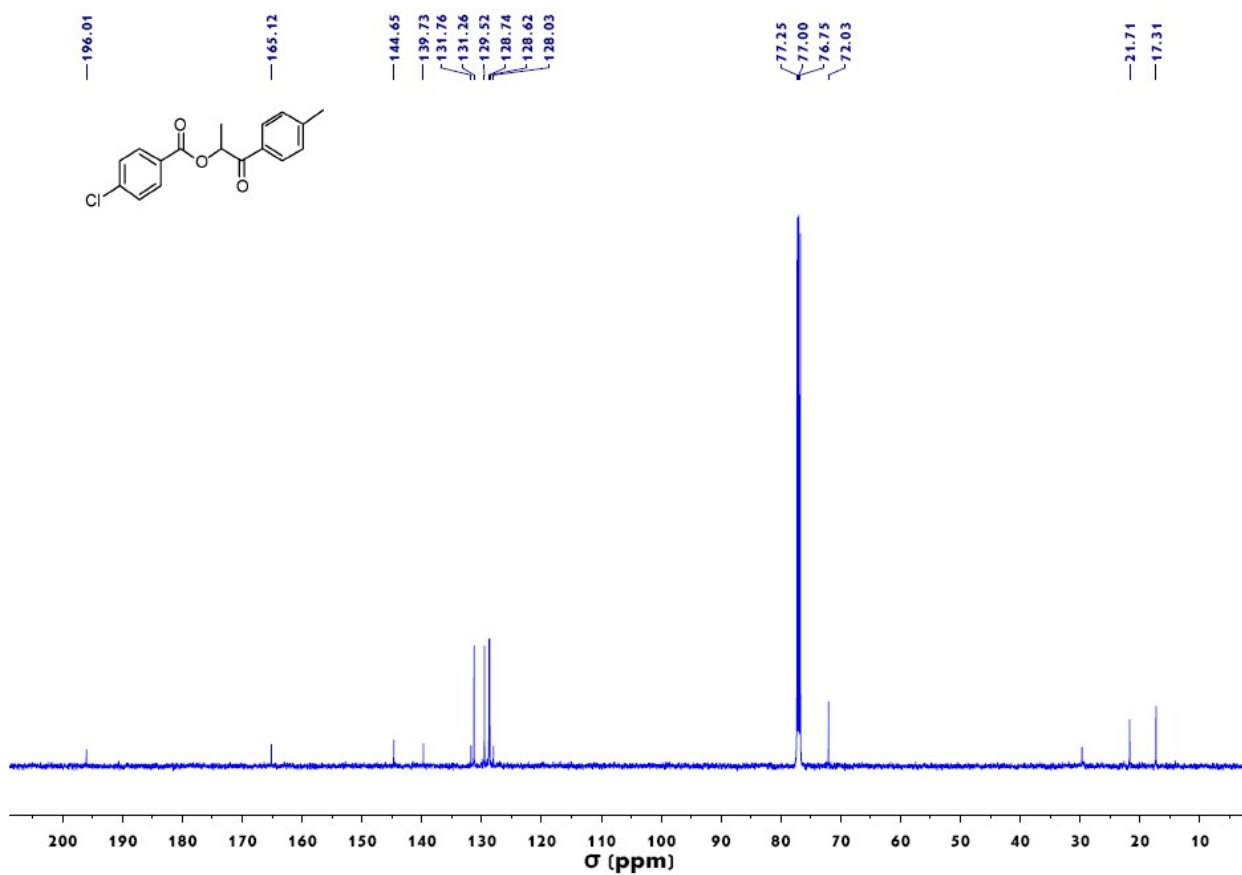


<sup>13</sup>C NMR spectrum of 7a

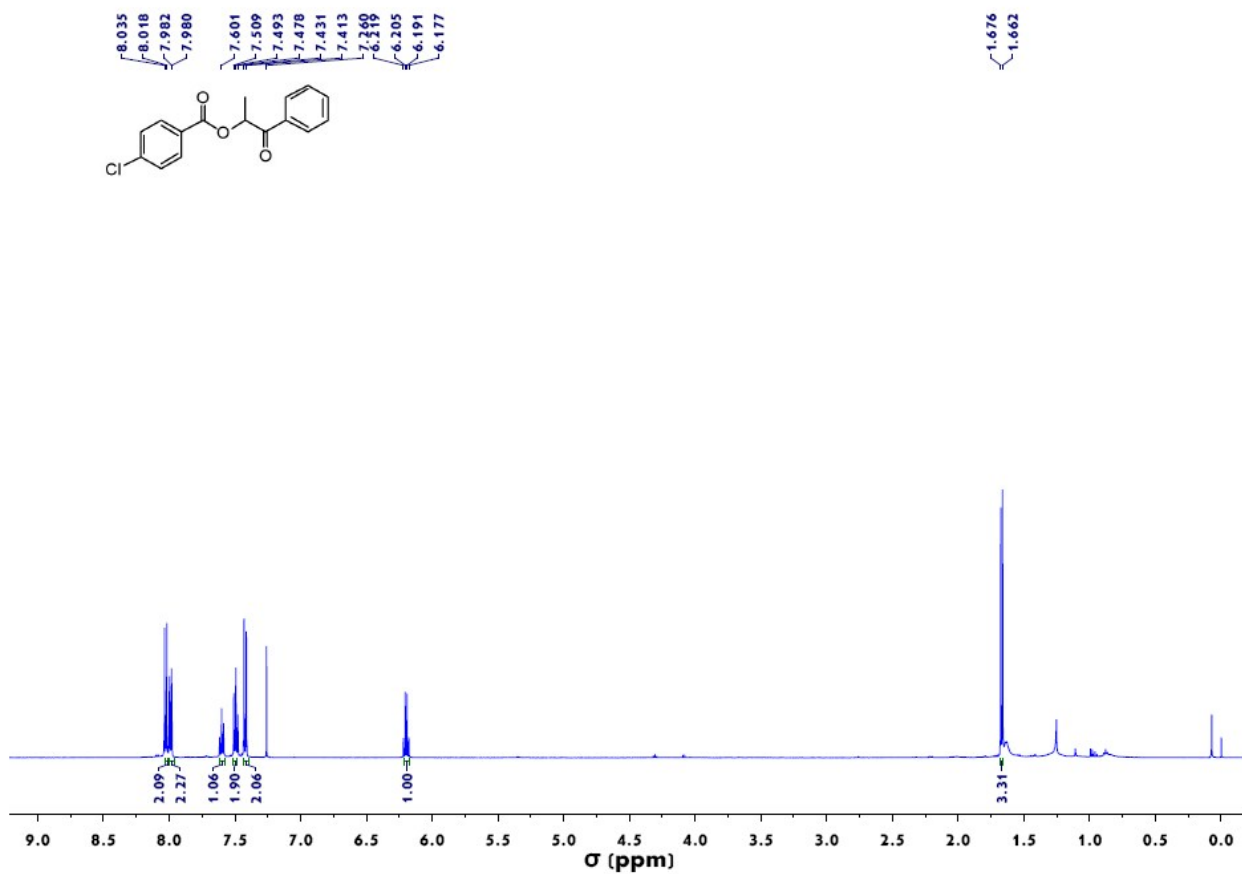




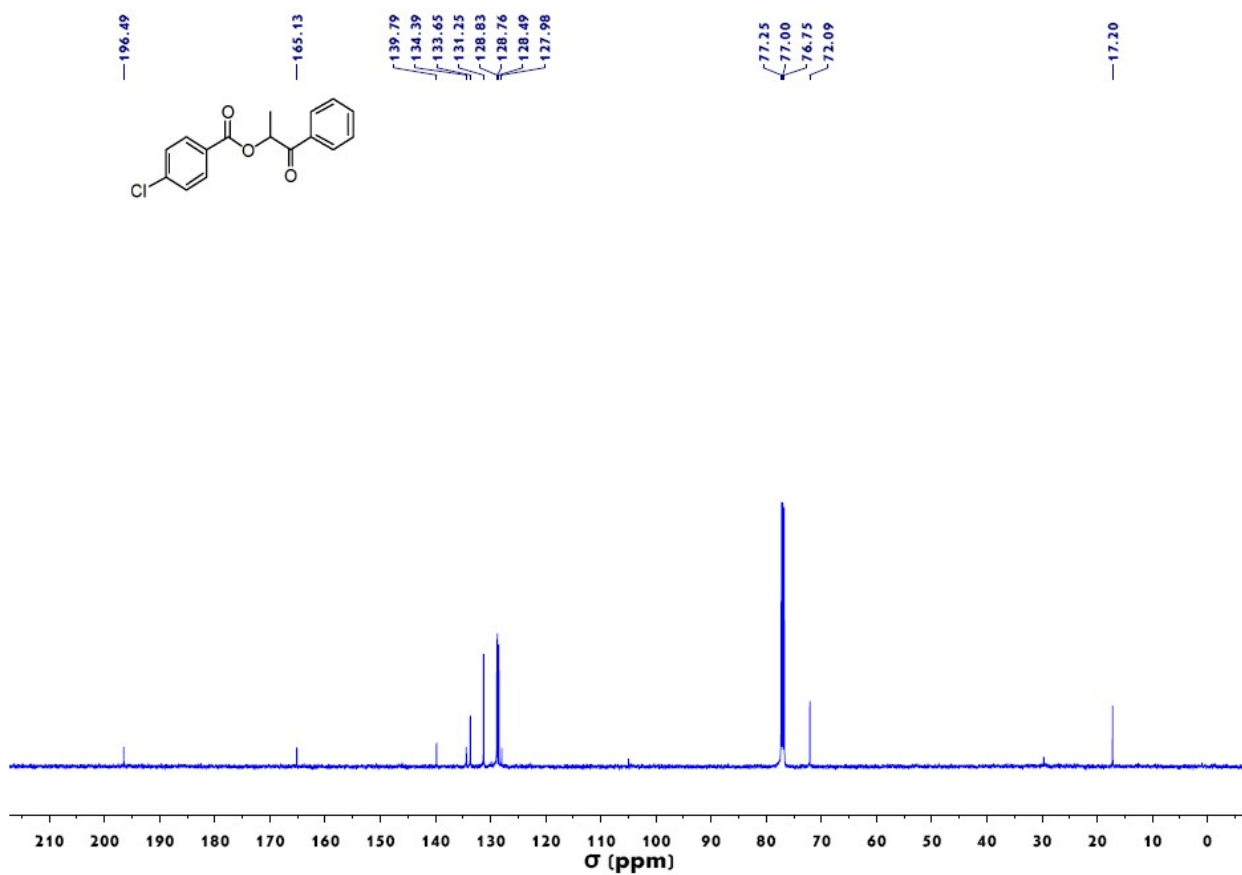
<sup>1</sup>H NMR spectrum of **8a**



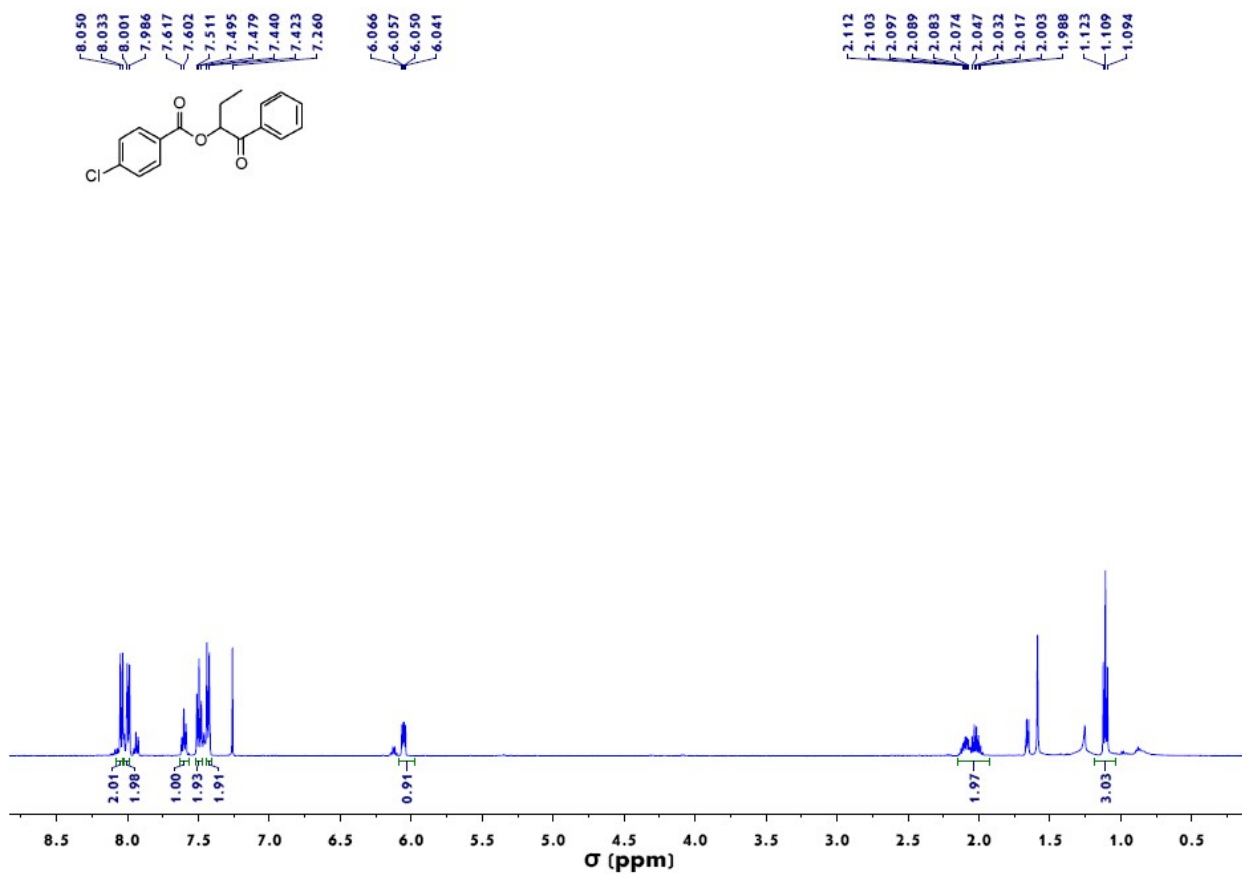
<sup>13</sup>C NMR spectrum of **8a**



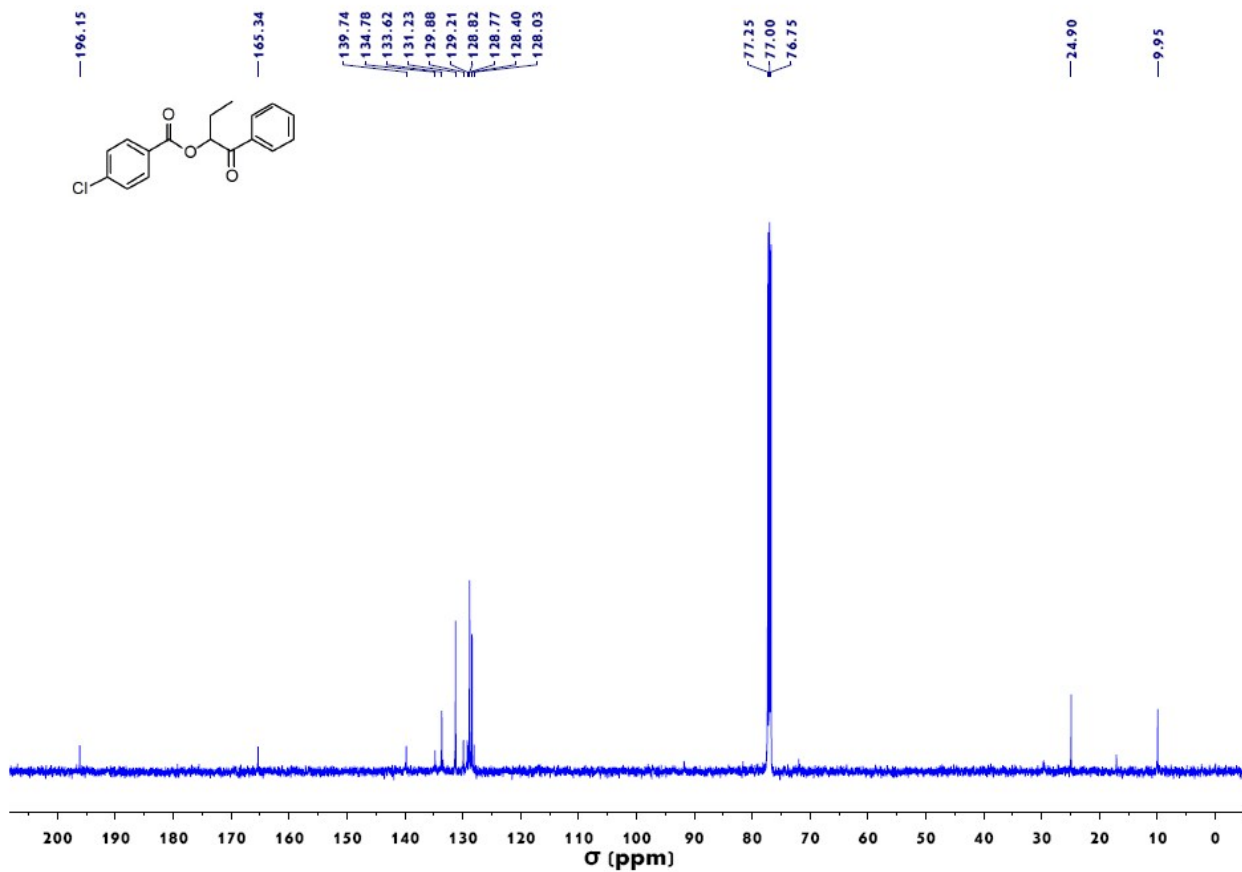
<sup>1</sup>H NMR spectrum of 9a



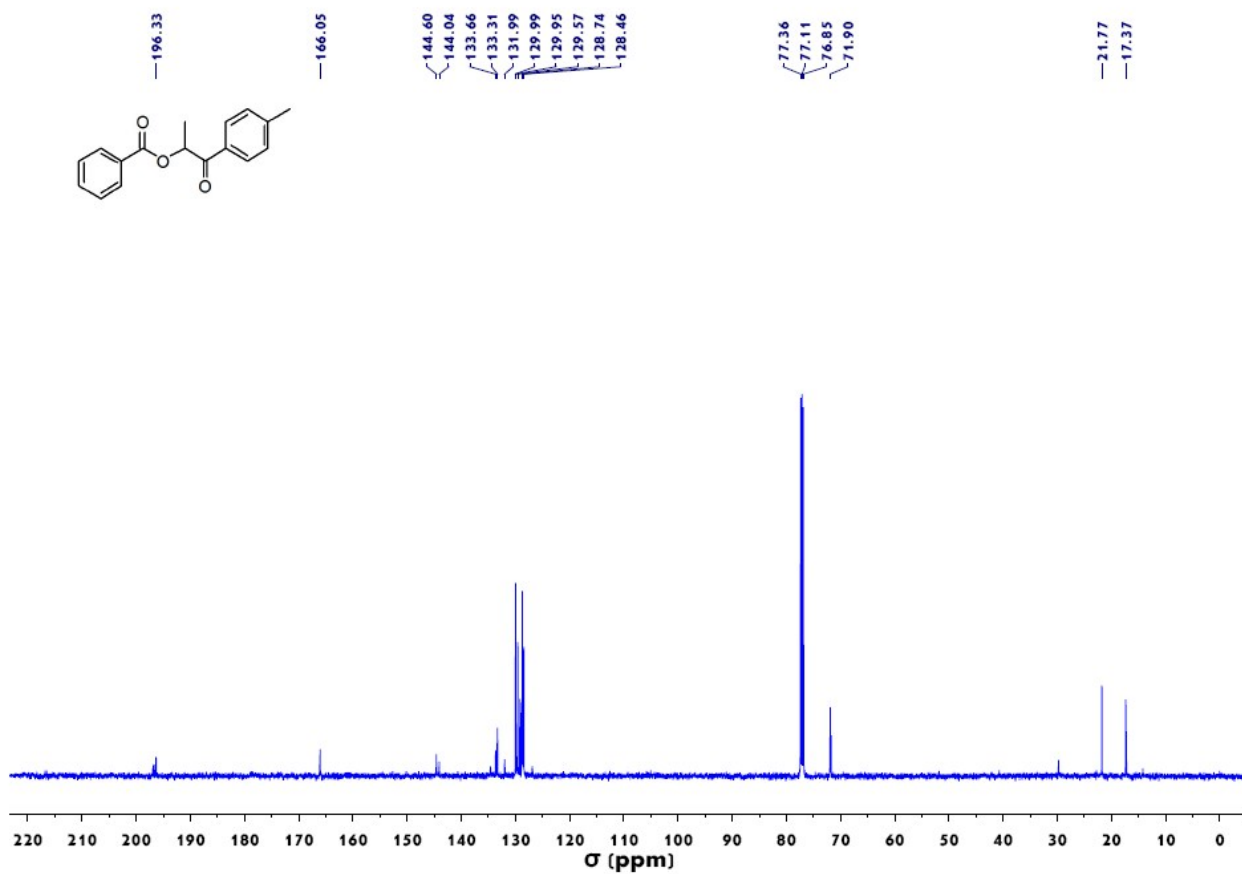
<sup>13</sup>C NMR spectrum of 9a



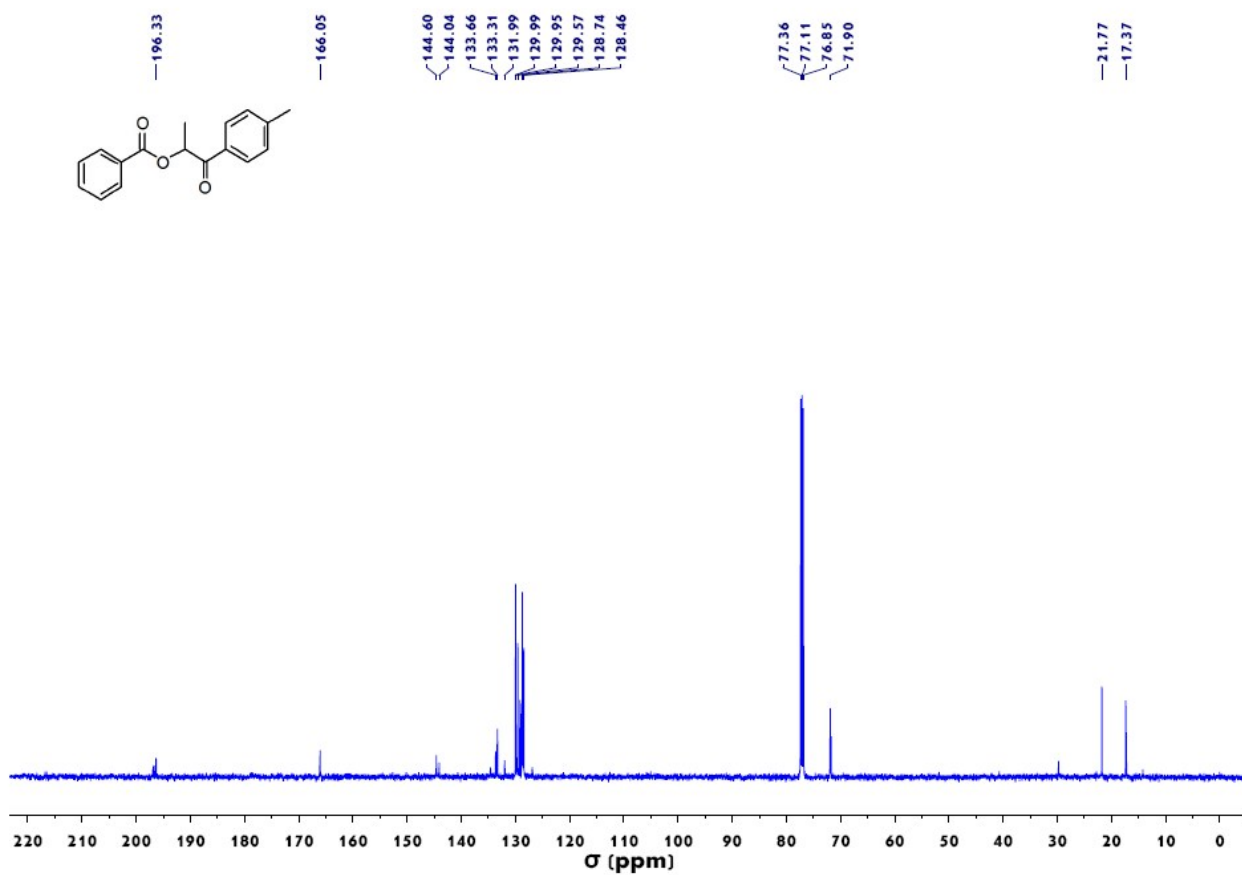
<sup>1</sup>H NMR spectrum of 10a



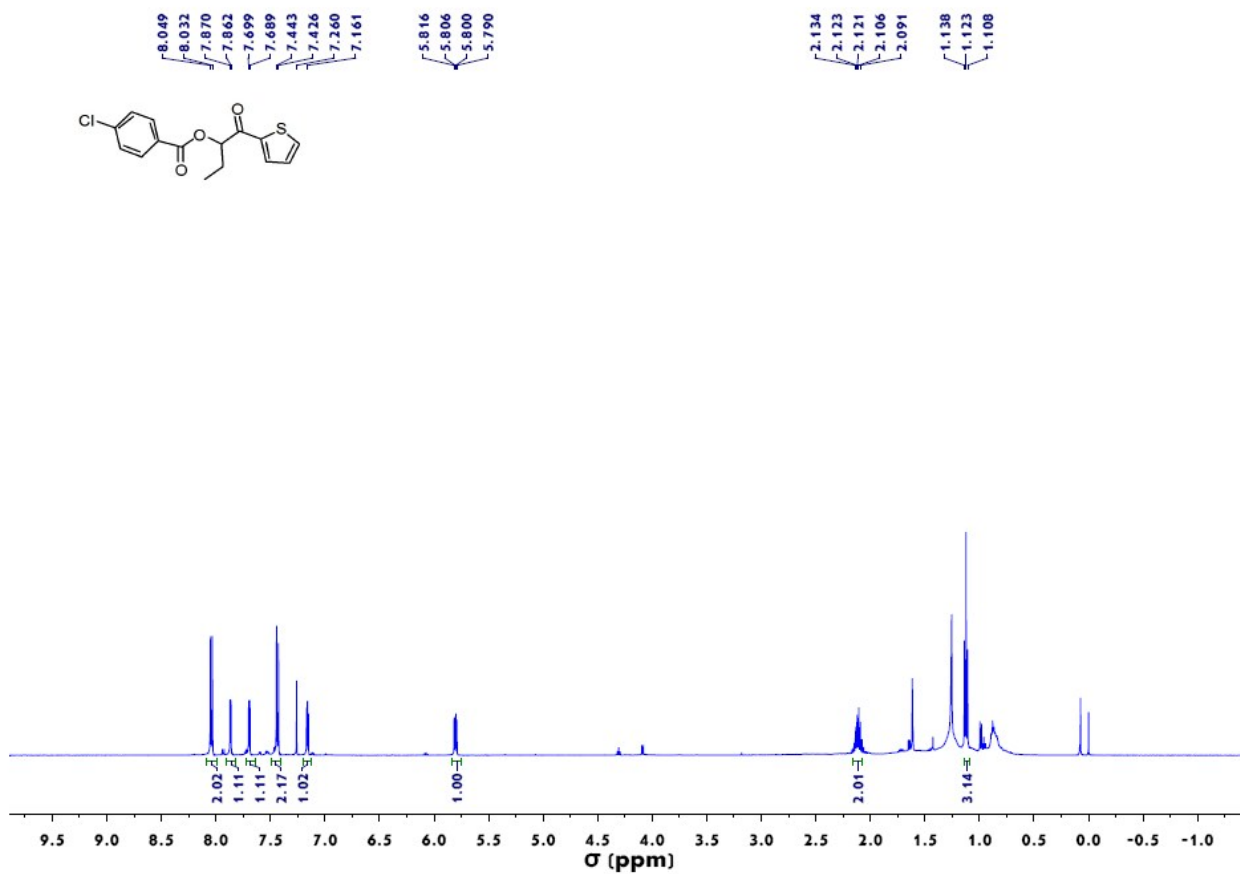
<sup>13</sup>C NMR spectrum of 10a



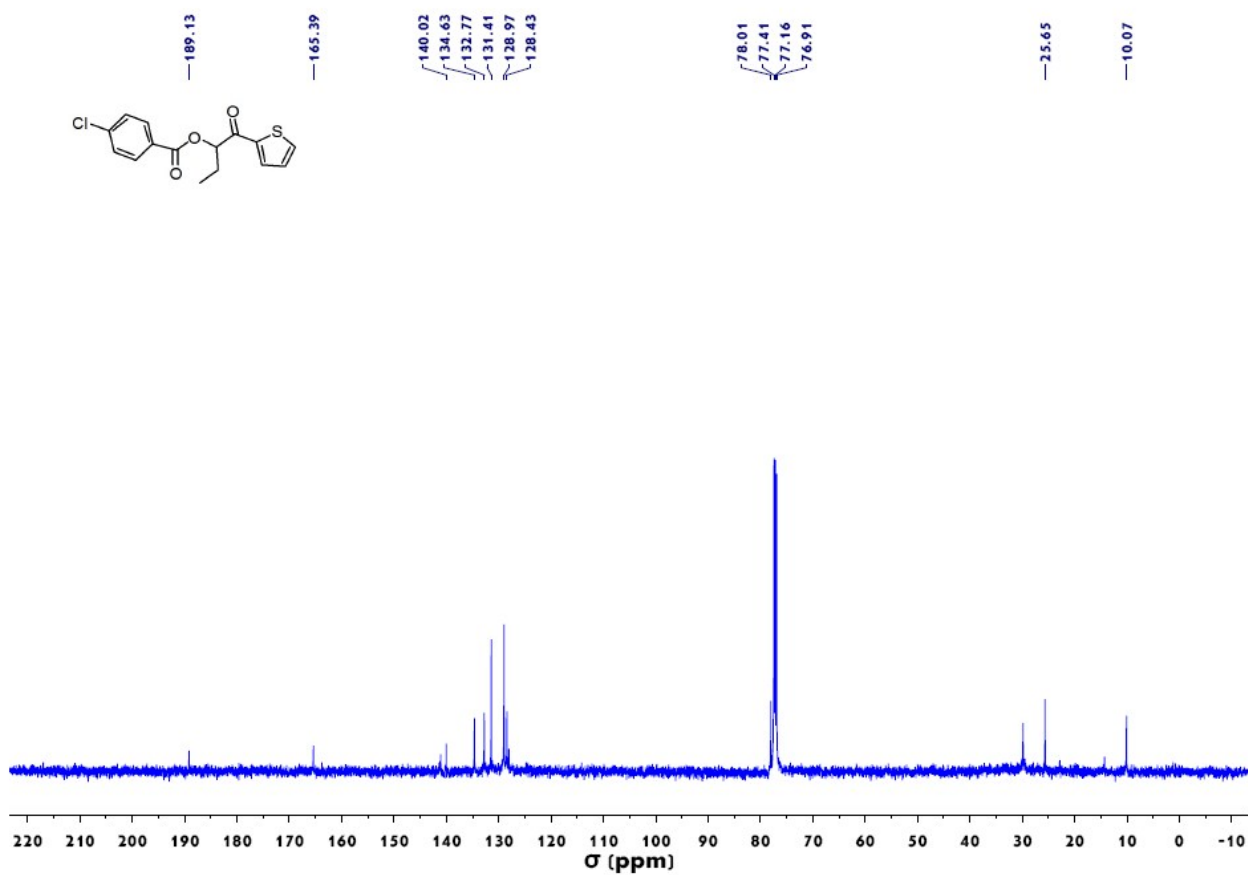
$^1\text{H}$  NMR spectrum of 11a



$^{13}\text{C}$  NMR spectrum of 11a



<sup>1</sup>H NMR spectrum of 12a



<sup>13</sup>C NMR spectrum of 12a