

*Electronic Supplementary Information*

**Selective Aerobic Oxidation of Halides and Amines with an  
Inorganic-ligand Supported Zinc catalyst**

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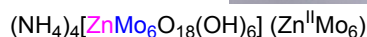
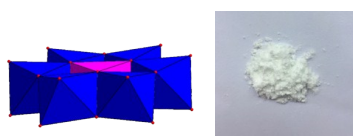
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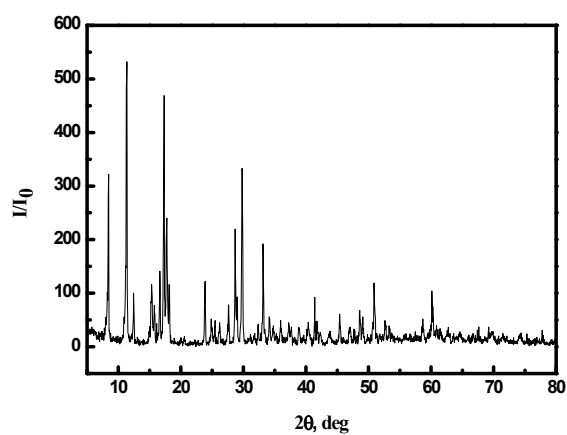
## I. General Information.

Zn-Anderson POM was prepared according to literature methods. All reagents obtained from Sigma-Aldrich and Admas-beta were used without further purification.  $^1\text{H}$  Nuclear Magnetic Resonance ( $^1\text{HNMR}$ ) spectra were recorded on Bruker AVANCE III 500 MHz (500 MHz for proton) spectrometer with tetramethylsilane as the internal reference using  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  as solvent in all cases, and chemical shifts were reported in parts per million (ppm,  $\delta$ ). FT-IR spectra were recorded on a Thermo fisher Nicolet 6700. Transmission Electron Microscope was performed on Bruker 200KV Tecnai G2 F30-TWIN. XRD were explored on D/max 2200PC of Japan. ESI-MS was made by Bruker. ICP-AES was performed on Optima 7000 DV of Perkinelmer. Cyclic voltammograms was tested on CHI660E A15409a of China. BET was performed in 3H-2000PM2 of China. GC analyses were performed on Shimadzu GC-2014 with a flame ionization detector equipped with an Rtx-1 capillary column (internal diameter = 0.25 mm, length = 30 m) or a Stabil wax capillary column (internal diameter = 0.25 mm, length = 30 m). GC mass spectra were recorded on Shimadzu GCMS-QP2010 with a capillary column (0.25 mm $\times$  30 m). Column chromatography was performed using 200-300 mesh base-washed silica gel.

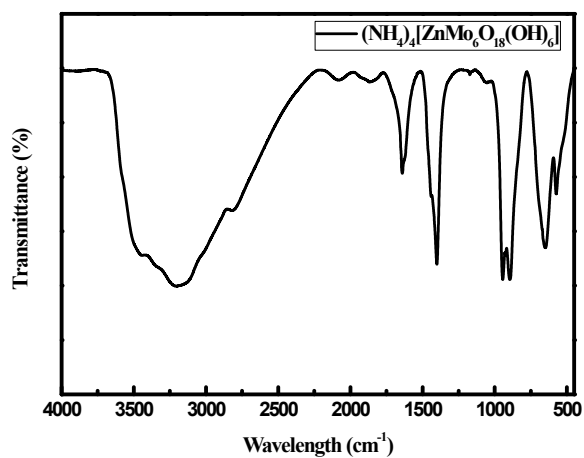
## II. Preparation and Characterizations of Catalyst



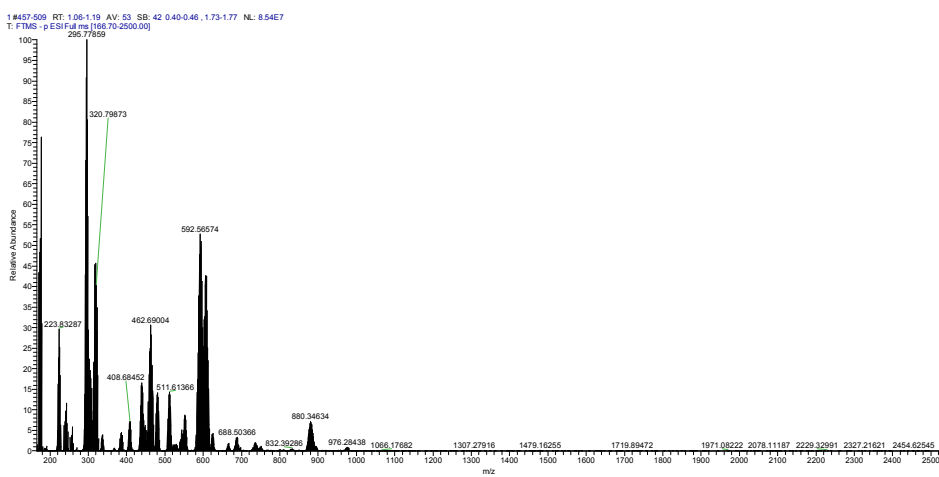
$(\text{NH}_4)_4[\text{ZnMo}_6\text{O}_{18}(\text{OH})_6]$  was synthesized via related reference and depicted in earlier works.<sup>1-5</sup>  $\text{Zn}^{\text{II}}\text{Mo}_6$  was prepared according to the following procedure: Firstly, 20 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  was dissolved in 300 mL water followed by heating to boiling. Second, 6.8 g  $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$  dissolved in 80mL water is added into the boiling aqueous solution. It is worth noting that drip must be vigorous stirring and dripping speed cannot be too fast. Further evaporating on oil bath at 100 °C almost 30 minutes, as a result of which it became clear and transparent. Third, the solution was filtered while hot and left at room temperature. After three days, the product was subjected to the first recrystallization in hot water (80 °C). After the seventh day, the product was subjected to a second recrystallization. Finally, we got white crystals. The crystals (12.6 g) was collected. The characterization include XRD (Fig. S1), FT-IR (Fig. S2), ESI-MS (Fig. S3), TEM (Fig. S4) and Cyclic voltammograms (Fig. S5),  $\text{N}_2$  adsorption–desorption isotherms (Fig. S6a) and Pore distribution curves (Fig. S6b).



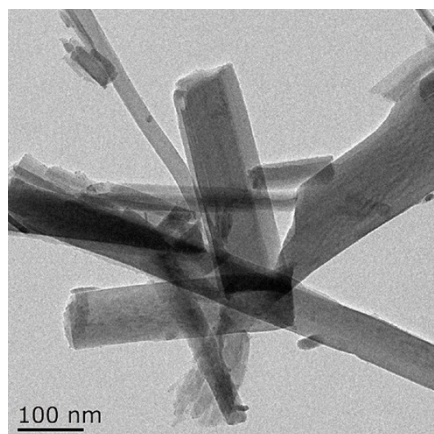
**Fig. S1** The XRD spectra of  $(\text{NH}_4)_4[\text{ZnMo}_6\text{O}_{18}(\text{OH})_6]$



**Fig. S2** The FT-IR spectra of  $(\text{NH}_4)_4[\text{ZnMo}_6\text{O}_{18}(\text{OH})_6]$



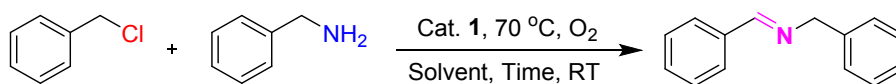
**Fig. S3** ESI-MS of  $(\text{NH}_4)_4[\text{ZnMo}_6\text{O}_{18}(\text{OH})_6]$



**Fig. S4** The TEM images of  $(\text{NH}_4)_4[\text{ZnMo}_6\text{O}_{18}(\text{OH})_6]$

### III. Reaction Optimization

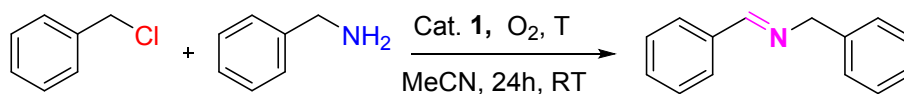
**Table S1** The solvents and time effects for the crossing-coupling of benzyl chloride and benzylamine <sup>a</sup>



Entry	Solvent (mL)	Time (h)	Yield (%) <sup>b</sup>	Sel. (%) <sup>b</sup>
1	Dioxane	24	32	47
2	Toluene	24	82	87
3	DMF	24	61	75
4	MeCN	24	89	90
5	EA	24	54	69
6	CH <sub>2</sub> Cl <sub>2</sub>	24	46	57
7	THF	24	65	87
8	Acetone	24	47	59
9	H <sub>2</sub> O	24	68	74
10	MeCN	12	84	86
11	MeCN	36	86	88

<sup>a</sup> Reaction condition: Cat. **1** (1.0 mol%), benzyl chloride (1.0 mmol), benzylamine (1.0 mmol), solvent (2 mL) under 70 °C with O<sub>2</sub> balloon, <sup>b</sup> Yields and selectivity were determined by GC and confirmed by GC-MS.

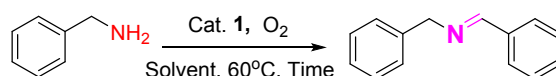
**Table S2** The temperature and the amount of catalyst for the crossing-coupling of benzyl chloride and benzylamine <sup>a</sup>



Entry	T (°C)	Cat. 1 (mol%)	Yield (%) <sup>b</sup>	Sel. (%) <sup>b</sup>
1	80	1	88	89
2	60	1	93	93
3	50	1	84	86
4	60	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	-	-
5	60	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> ·4H <sub>2</sub> O	-	-
6	60	-	-	-
7	60	0.5	84	88
8	60	2	87	89
9 <sup>c</sup>	60	1	18	34
10 <sup>d</sup>	60	1	<10	-

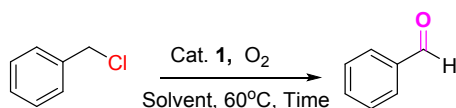
<sup>a</sup> Reaction condition: Benzyl chloride (1.0 mmol), benzylamine (1.0 mmol), MeCN (2 mL) with O<sub>2</sub> balloon, <sup>b</sup> Yields and selectivity were determined by GC and confirmed by GC-MS, <sup>c</sup> Under air atmosphere, <sup>d</sup> Under N<sub>2</sub> atmosphere.

**Table S3** The optimization condition for oxidative coupling reactions the self-coupling of amines <sup>a</sup>



Entry	Solvent (mL)	Cat. 1 (mol%)	Time (h)	Yield (%) <sup>b</sup>
1	MeCN	1	24	95
2	Toluene	1	24	74
3	Dioxane	1	24	64
4	CH <sub>2</sub> Cl <sub>2</sub>	1	24	36
5	H <sub>2</sub> O	1	24	57
6	Ethanol	1	24	84
7	MeCN	0.5	24	88
8	MeCN	2	24	92
9	MeCN	-	24	trace
10	MeCN	1	12	85
11	MeCN	1	36	93
12 <sup>c</sup>	MeCN	1	24	87
13 <sup>d</sup>	MeCN	1	24	95

<sup>a</sup> Reaction condition: Benzylamine (1.0 mmol), solvent (2 mL), 60 °C with O<sub>2</sub> balloon, <sup>b</sup> Yields and selectivity were determined by GC and confirmed by GC-MS, <sup>c</sup> 50 °C, <sup>d</sup> 70 °C.

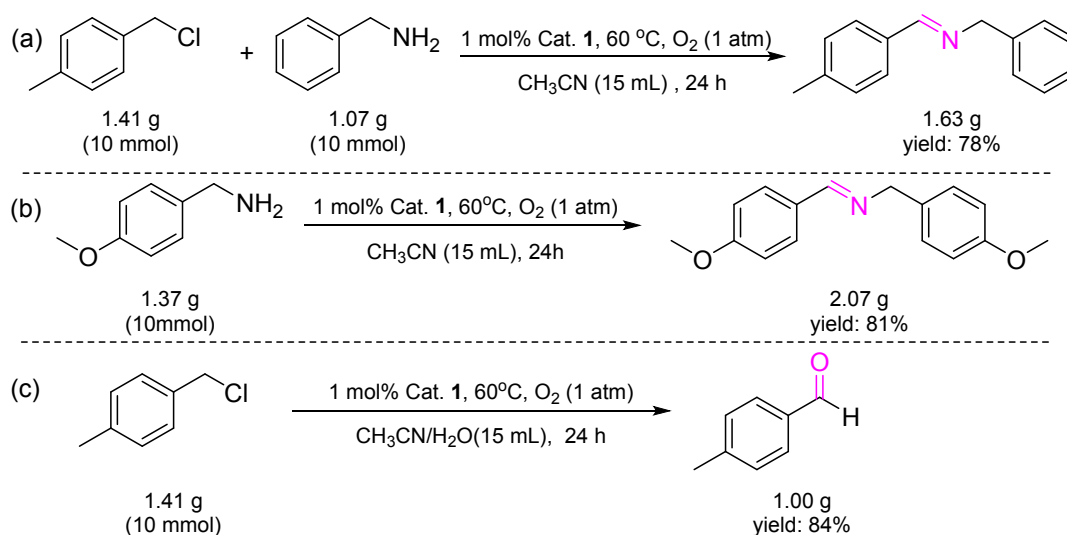
**Table S4** The optimization condition for the oxidation of benzyl chloride <sup>a</sup>

Entry	Solvent (mL)	Cat. 1 (mol%)	Time (h)	Yield (%) <sup>b</sup>
1	MeCN	1	24	89
2	Dioxane	1	24	67
3	DMF	1	24	54
4	Toluene	1	24	78
5	EA	1	24	45
6	CH <sub>2</sub> Cl <sub>2</sub>	1	24	71
7	H <sub>2</sub> O	1	24	87
8	MeCN/H <sub>2</sub> O	1	24	90
9	MeCN/H <sub>2</sub> O	0.5	24	83
10	MeCN/H <sub>2</sub> O	2	24	92
11	MeCN/H <sub>2</sub> O	-	24	Trace
12	MeCN/H <sub>2</sub> O	1	12	94
13	MeCN/H <sub>2</sub> O	1	36	94
14 <sup>c</sup>	MeCN/H <sub>2</sub> O	1	24	74
15 <sup>d</sup>	MeCN/H <sub>2</sub> O	1	24	93

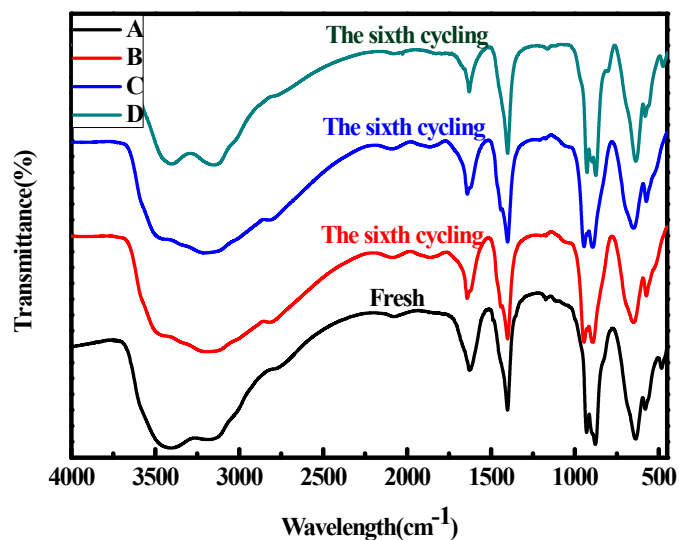
<sup>a</sup> Reaction condition: Benzyl chloride (1.0 mmol), solvent (2 mL), 60 °C with O<sub>2</sub> balloon, <sup>b</sup> Yields and selectivity were determined by GC and confirmed by GC-MS, <sup>c</sup> 50 °C, <sup>d</sup> 70 °C.

#### IV. Recycling and gram-scale experiments of the catalyst

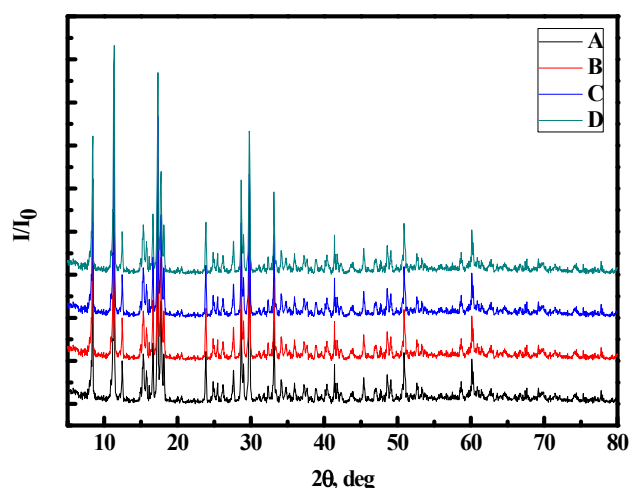
The gram-scale experiments of Zn-POM catalyst in the the cross-coupling of 4-methylbenzyl chloride and benzylamine, the self-coupling of (4-methoxyphenyl)methanamine and oxidation of 4-methylbenzyl chloride were investigated under the optimal reaction conditions, respectively (Schem S1). After the reaction is over, the catalyst can be precipitated by adding ethyl acetate or anhydrous ether to the reaction system, then filtered and dried at 80 °C for 12 h be further used for the next catalytic cycle. The recycled catalyst was characterized by FT-IR and XRD (Fig. S5 and Fig. S6).



**Schem. S1** Gram-scale experiments of the catalyst.



**Fig. S5** IR spectra of  $(\text{NH}_4)_4[\text{ZnMo}_6\text{O}_{18}(\text{OH})_6]$ : A is the fresh catalyst; B is the oxidation coupling of 4-methylbenzyl chloride and benzylamine; C is the self-oxidation coupling of (4-methoxyphenyl)methanamine; D is the oxidation of 4-methylbenzyl chloride.



**Fig. S6** XRD images of  $(\text{NH}_4)_4[\text{ZnMo}_6\text{O}_{18}(\text{OH})_6]$ : A is the fresh catalyst; B is the oxidation coupling of 4-methylbenzyl chloride and benzylamine; C is the self-oxidation coupling of (4-methoxyphenyl)methanamine; D is the oxidation of 4-methylbenzyl chloride.

**Table S5** Investigated the change of the content of molybdenum atom and zinc atom in the catalyst system before and after the reaction of 4-methylbenzyl chloride and benzylamine with ICP-AES.

Total mass/mg	m/n (Mo)/m g/mmol	m/n (Zn)/mg /mmol	Mo/%	Zn/%
12.00 <sup>a</sup>	$1.44/1.51 \times 10^{-2}$	$0.40/6.15 \times 10^{-3}$	12.04	3.30
11.40 <sup>b</sup>	$1.37/1.43 \times 10^{-2}$	$0.38/5.80 \times 10^{-3}$	12.04	3.30

<sup>a</sup> Before the reaction; <sup>b</sup> After the reaction.

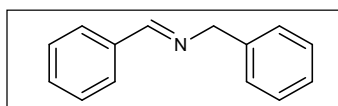
## V. References

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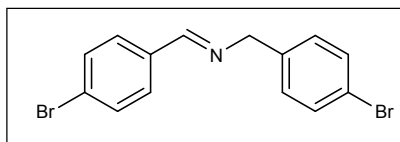


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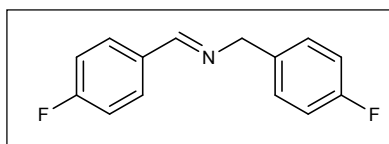
## VI. NMR Spectra



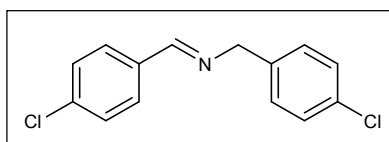
**N-benzyliden-1-phenylmethanamine (5a):** The reaction of benzylamine oxidation (107 mg, 1.0 mmol) under the optimized condition under 60 °C for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as yellow oil. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.48 (s, 1H), 7.91 (dd, J = 6.6, 2.9 Hz, 2H), 7.55 – 7.49 (m, 3H), 7.50 – 7.43 (m, 4H), 7.41 – 7.36 (m, 1H), 4.93 (s, 2H). Data in accordance with that previously published.<sup>6,7</sup>



**N-(3-fluorobenzyl)-1-(3-fluorophenyl)methanimine (5b):** The reaction of 4-bromobenzylamine oxidation (186 mg, 1.0 mmol) under the optimized condition under 60 °C for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as yellow oil. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.33 (s, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.46 (t, J = 8.5 Hz, 4H), 4.74 (s, 2H). Data in accordance with that previously published<sup>6,7</sup>.

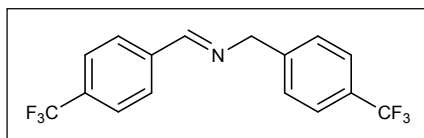


**1-phenyl-N-(1-phenylethyl)ethan-1-imine (5c):** The reaction of 4-fluorobenzylamine oxidation (125 mg, 1.0 mmol) under the optimized condition under 60 °C for 24h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as yellow oil. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.37 (s, 1H), 7.79 (dd, J = 8.5, 5.6 Hz, 2H), 7.32 (dd, J = 8.3, 5.8 Hz, 2H), 7.13 (t, J = 8.6 Hz, 2H), 7.05 (t, J = 8.1 Hz, 2H), 4.79 (s, 2H). Data in accordance with that previously published.<sup>6,7</sup>



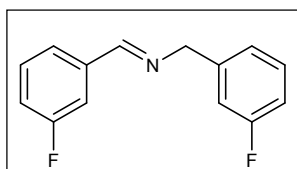
**N-(4-chlorobenzyl)-1-(4-**

**fluorophenyl)methanimine (5d):** The reaction of 4-chlorobenzylamine oxidation (142 mg, 1.0 mmol) under the optimized condition under 60 °C for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as yellow oil. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.37 (s, 1H), 7.79 (dd, J = 8.5, 5.6 Hz, 2H), 7.31 (dd, J = 8.6, 3.1 Hz, 2H), 7.12 (t, J = 8.6 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 4.79 (s, 2H). Data in accordance with that previously published.<sup>6,7</sup>



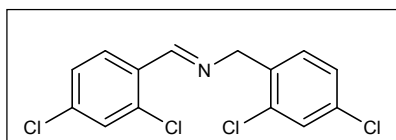
**N-(4-chlorobenzylidene)-1-(4-chlorophenyl)methanimine (5e):** The reaction of 4-(trifluoromethyl)benzylamine oxidation (175 mg, 1.0 mmol) under the optimized condition under 60

°C for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as a white solid. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.49 (s, 1H), 7.93 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 4.92 (s, 2H). Data in accordance with that previously published.<sup>6,7</sup>



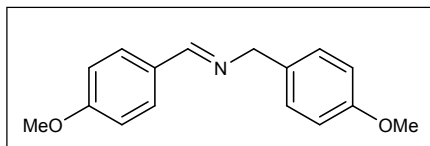
**N-(4-bromobenzylidene)-1-(4-bromophenyl)methanimine (5f):** The reaction of 3-fluorobenzylamine oxidation (125 mg, 1.0 mmol) under the optimized condition under 60 °C for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum

ether) gave the desired compound as a white solid. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.38 (s, 1H), 7.59 – 7.50 (m, 2H), 7.44 – 7.38 (m, 1H), 7.34 – 7.29 (m, 2H), 7.09 (s, 1H), 6.99 – 6.93 (m, 2H), 4.83 (s, 2H). Data in accordance with that previously published.<sup>6,7</sup>



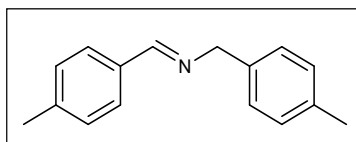
**N-(2,4-dichlorobenzylidene)-1-(2,4-dichlorophenyl)methanimine (5g):** The reaction of 2,4-dichlorobenzylamine oxidation (176 mg, 1.0 mmol) under the optimized condition under 60 °C

for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as yellow oil. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.79 (s, 1H), 8.05 (d, J = 8.5 Hz, 1H), 7.41 (dd, J = 3.8, 2.1 Hz, 2H), 7.36 (d, J = 2.2 Hz, 1H), 7.30 – 7.28 (m, 1H), 7.25 – 7.23 (m, 1H), 4.87 (s, 2H). Data in accordance with that previously published.<sup>6,7</sup>



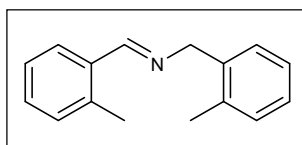
**N-(2-methylbenzylidene)-1-(o-tolyl)methanimine (5h):** The reaction of 4-methoxybenzylamine oxidation (137 mg, 1.0 mmol) under the optimized condition under 60 °C for 24 h. The crude

reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as yellow oil. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.32 (s, 1H), 7.74 (d, J = 8.7 Hz, 2H), 7.27 (s, 1H), 6.95 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.6 Hz, 3H), 4.75 (s, 2H), 3.83 (d, J = 18.5 Hz, 6H). Data in accordance with that previously published.<sup>6,7</sup>



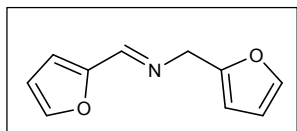
**N-(4-methylbenzylidene)-1-(p-tolyl)methanimine**

**(5i):** The reaction of 4-methylbenzylamine oxidation (121 mg, 1.0 mmol) under the optimized condition under 60 °C for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as a white solid. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.36 (s, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.23 (t, J = 8.1 Hz, 4H), 7.18 (s, 2H), 4.79 (s, 2H), 2.40 (s, 3H), 2.36 (s, 3H). Data in accordance with that previously published.<sup>6,7</sup>



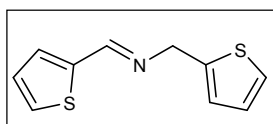
**N-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine**

**(5j):** The reaction of 2-methylbenzylamine oxidation (121 mg, 1.0 mmol) under the optimized condition under 60 °C for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow oil. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.72 (s, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.34 (t, J = 6.2 Hz, 3H), 7.29 (d, J = 6.5 Hz, 1H), 4.87 (s, 2H), 2.55 (s, 3H), 2.44 (s, 3H). Data in accordance with that previously published.<sup>6,7</sup>



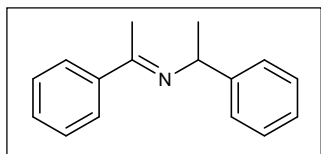
**1-(thiophen-2-yl)-N-(thiophen-2-ylmethyl)methanimine**

**(5k):** The reaction of 2-furfurylamine oxidation (97 mg, 1.0 mmol) under the optimized condition under 60 °C for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow oil. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.14 (s, 1H), 7.54 (s, 1H), 7.40 (s, 1H), 6.81 (d, J = 3.3 Hz, 1H), 6.50 (dd, J = 3.3, 1.7 Hz, 1H), 6.38 – 6.35 (m, 1H), 6.30 (d, J = 3.0 Hz, 1H), 4.78 (s, 2H). Data in accordance with that previously published.<sup>6,7</sup>



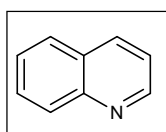
**N-(4-(trifluoromethyl)benzyl)-1-(4-**

**(trifluoromethyl)phenyl)methanimine (5l):** The reaction of 2-thiophenemethylamine oxidation (113 mg, 1.0 mmol) under the optimized condition under 60 °C for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow oil. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 8.13 (s, 1H), 7.53 (s, 1H), 7.39 (d, J = 1.0 Hz, 1H), 6.81 (d, J = 3.3 Hz, 1H), 6.49 (dd, J = 3.3, 1.7 Hz, 1H), 6.38 – 6.34 (m, 1H), 6.29 (d, J = 3.0 Hz, 1H), 4.77 (s, 2H). Data in accordance with that previously published.<sup>6,7</sup>



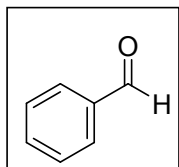
**1-(furan-2-yl)-N-(furan-2-ylmethyl)methanimine (5n):**

The reaction of α-methylbenzylamine oxidation (121 mg, 1.0 mmol) under the optimized condition under 60 °C for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as colourless oil. <sup>1</sup>H NMR (501 MHz, CDCl<sub>3</sub>) δ 7.87 (dd, J = 6.7, 3.0 Hz, 2H), 7.43 – 7.39 (m, 3H), 7.32 – 7.19 (m, 5H), 4.87 (q, J = 6.6 Hz, 1H), 2.30 (s, 3H), 1.58 (d, J = 6.6 Hz, 3H). Data in accordance with that previously published.<sup>6,7</sup>

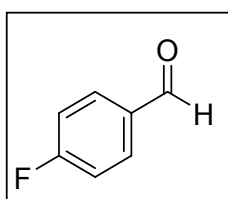


**Quinoline (5o):** The reaction of 1,2,3,4-tetrahydroquinoline oxidation (133 mg, 1.0 mmol) under the optimized condition under 60 °C for 24 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the

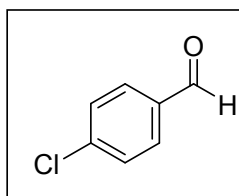
desired compound as colourless oil.  $^1\text{H}$  NMR (501 MHz,  $\text{CDCl}_3$ )  $\delta$  8.73 (dd,  $J = 4.1, 1.5$  Hz, 1H), 7.99 (d,  $J = 8.5$  Hz, 1H), 7.84 (d,  $J = 8.3$  Hz, 1H), 7.58 – 7.47 (m, 2H), 7.29 (t,  $J = 7.5$  Hz, 1H), 7.09 (dd,  $J = 8.3, 4.2$  Hz, 1H). Data in accordance with that previously published.<sup>6,7</sup>



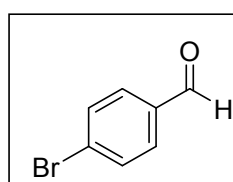
**Benzaldehyde (7a):** The reaction of benzyl chlorid oxidation (127 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.20 (s, 1H), 8.06 (d,  $J = 8.1$  Hz, 2H), 7.79 (dd,  $J = 28.6, 21.2$  Hz, 2H), 7.76 (dt,  $J = 50.1, 7.4$  Hz, 3H). Data in accordance with that previously published.<sup>8,9</sup>



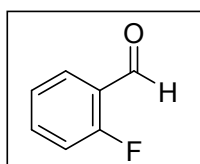
**4-Fluorobenzaldehyde (7b):** The reaction of 4-fluorobenzyl chloride oxidation (145 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as light yellow liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.12 (s, 1H), 8.07 (dd,  $J = 8.7, 5.5$  Hz, 2H), 7.37 (t,  $J = 8.5$  Hz, 2H). Data in accordance with that previously published.<sup>8,9</sup>



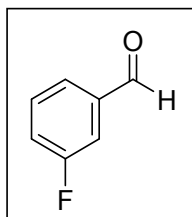
**4-Chlorobenzaldehyde (7c):** The reaction of 4-chlorobenzyl chloride oxidation (161 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as colorless flaky crystal.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.14 (s, 1H), 8.09 – 7.87 (m, 2H), 7.77 – 7.58 (m, 2H). Data in accordance with that previously published.<sup>8,9</sup>



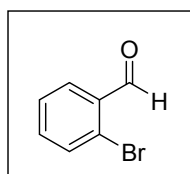
**4-Bromobenzaldehyde (7d):** The reaction of 4-bromobenzyl chloride oxidation (205 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as a yellow solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.14 (s, 1H), 7.91 (d,  $J = 8.4$  Hz, 2H), 7.85 (d,  $J = 8.3$  Hz, 2H). Data in accordance with that previously published.<sup>8,9</sup>



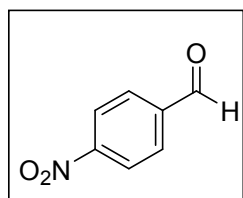
**2-Fluorobenzaldehyde (7e):** The reaction of 2-fluorobenzyl chloride oxidation (145 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetata and petroleum ether) gave the desired compound as yellow liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.55 (s, 1H), 8.05 (t,  $J = 8.0$  Hz, 1H), 7.79 (dd,  $J = 15.0, 7.7$  Hz, 1H), 7.45 (t,  $J = 7.5$  Hz, 1H), 7.39 – 7.31 (m, 1H). Data in accordance with that previously published.<sup>8,9</sup>



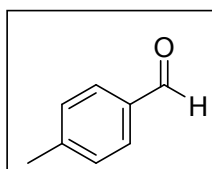
**3-Fluorobenzaldehyde (7f):** The reaction of 3-fluorobenzyl chloride oxidation (145 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.17 (d,  $J$  = 1.6 Hz, 1H), 7.86 (d,  $J$  = 7.6 Hz, 1H), 7.74 (dd,  $J$  = 10.0, 1.0 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.51 (ddd,  $J$  = 8.3, 5.0, 1.7 Hz, 1H). Data in accordance with that previously published.<sup>8,9</sup>



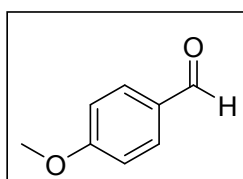
**2-Bromobenzaldehyde (7g):** The reaction of 2-bromobenzyl chloride oxidation (205 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as colorless liquid.  $^1\text{H}$  NMR (501 MHz,  $\text{CDCl}_3$ )  $\delta$  10.38 (s, 1H), 7.93 (dd,  $J$  = 7.1, 2.4 Hz, 1H), 7.69–7.65 (m, 1H), 7.48 – 7.44 (m, 2H). Data in accordance with that previously published.<sup>8,9</sup>



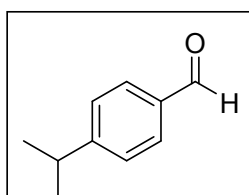
**4-Nitrobenzaldehyde (7h):** The reaction of 4-nitrobenzyl chloride oxidation (172 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as light yellow powder.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.33 (s, 1H), 8.55 (d,  $J$  = 8.6 Hz, 2H), 8.25 (d,  $J$  = 8.6 Hz, 2H). Data in accordance with that previously published.<sup>8,9</sup>



**p-Tolualdehyde (7i):** The reaction of 4-methylbenzyl chloride oxidation (141 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as light yellow liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.14 (s, 1H), 7.95 (d,  $J$  = 8.0 Hz, 2H), 7.51 (d,  $J$  = 7.8 Hz, 2H), 2.62 (s, 3H). Data in accordance with that previously published.<sup>8,9</sup>

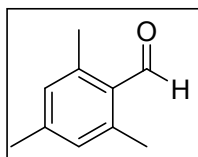


**4-Methoxybenzaldehyde (7j):** The reaction of 4-chloromethyl anisole oxidation (157 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.05 (s, 1H), 8.00 (d,  $J$  = 8.7 Hz, 2H), 7.17 (d,  $J$  = 8.6 Hz, 2H), 4.05 (s, 3H). Data in accordance with that previously published.<sup>8,9</sup>

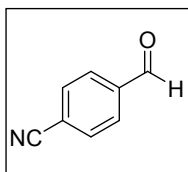


**4-Isopropylbenzaldehyde (7k):** The reaction of 4-isopropylbenzyl chloride oxidation (169 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave

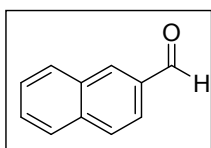
the desired compound as yellow liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.15 (s, 1H), 7.99 (d,  $J = 8.1$  Hz, 2H), 7.57 (d,  $J = 8.0$  Hz, 2H), 3.31 – 3.06 (m, 1H), 1.46 (d,  $J = 6.9$  Hz, 6H). Data in accordance with that previously published.<sup>8,9</sup>



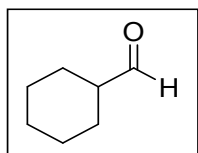
**2,4,6-Trimethylbenzaldehyde (7l):** The reaction of 2-(chloromethyl)-1,3,5-trimethylbenzene oxidation (169 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.74 (s, 1H), 7.08 (s, 2H), 2.76 (s, 6H), 2.50 (s, 3H). Data in accordance with that previously published.<sup>8,9</sup>



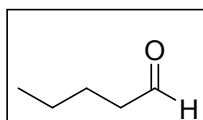
**4-Cyanobenzaldehyde (7m):** The reaction of 4-(chloromethyl)benzonitrile (152 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as light yellow powder.  $^1\text{H}$  NMR (501 MHz,  $\text{CDCl}_3$ )  $\delta$  10.11 (s, 1H), 8.02 (d,  $J = 8.2$  Hz, 2H), 7.87 (d,  $J = 8.1$  Hz, 2H). Data in accordance with that previously published.<sup>8,9</sup>



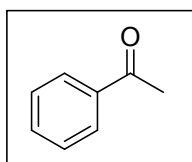
**2-Naphthaldehyde (7n):** The reaction of 2-(chloromethyl)naphthalene oxidation (177 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as a white crystals.  $^1\text{H}$  NMR (501 MHz,  $\text{CDCl}_3$ )  $\delta$  10.19 (s, 1H), 8.37 (s, 1H), 8.03 (d,  $J = 8.1$  Hz, 1H), 8.01 – 7.95 (m, 2H), 7.93 (d,  $J = 8.1$  Hz, 1H), 7.70 – 7.65 (m, 1H), 7.64 – 7.59 (m, 1H). Data in accordance with that previously published.<sup>8,9</sup>



**Cyclohexanecarboxaldehyde (7o):** The reaction of (chloromethyl)cyclohexane (132 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow liquid.  $^1\text{H}$  NMR (501 MHz,  $\text{CDCl}_3$ )  $\delta$  9.62 (s, 1H), 2.24 (ddd,  $J = 13.2, 7.2, 3.3$  Hz, 1H), 1.94 – 1.88 (m, 2H), 1.75 (dd,  $J = 8.9, 3.8$  Hz, 2H), 1.70 – 1.61 (m, 1H), 1.38 – 1.23 (m, 5H). Data in accordance with that previously published.<sup>8,9</sup>

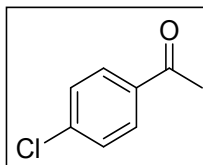


**Valeraldehyde (7p):** The reaction of 1-chloropentane oxidation (107 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.91 (d,  $J = 12.0$  Hz, 1H), 2.60 – 2.57 (m, 2H), 1.76 (d,  $J = 7.6$  Hz, 2H), 1.50 (d,  $J = 7.3$  Hz, 2H), 1.08 (s, 3H). Data in accordance with that previously published.<sup>8,9</sup>

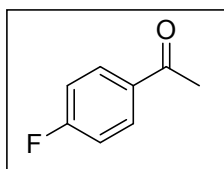


**Acetophenone (7q):** The reaction of 1-phenylethyl chloride oxidation

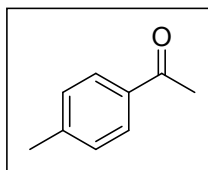
(141 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.97 (d, J = 7.4 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 2.61 (s, 3H). Data in accordance with that previously published.<sup>10</sup>



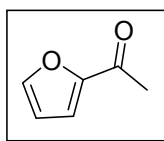
**4-Chloroacetophenone (7r):** The reaction of 1-chloro-4-(1-chloroethyl)benzene oxidation (175 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 2.58 (s, 3H). Data in accordance with that previously published.<sup>10</sup>



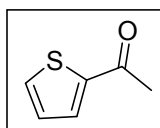
**4-Fluoroacetophenone (7s):** The reaction of 1-(1-chloroethyl)-4-fluorobenzene oxidation (159 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.15 – 7.77 (m, 2H), 7.13 (t, J = 8.5 Hz, 2H), 2.59 (s, 3H). Data in accordance with that previously published.<sup>10</sup>



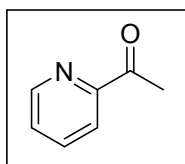
**4-Methylacetophenone (7t):** The reaction of 1-(4-methylphenyl)ethyl chloride oxidation (155 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.87 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 2.59 (s, 3H), 2.42 (s, 3H). Data in accordance with that previously published.<sup>10</sup>



**2-acetylfuran (7u):** The reaction of 2-(chloromethyl)furan oxidation (117 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.60 (s, 1H), 7.19 (d, J = 3.4 Hz, 1H), 6.55 (dd, J = 3.1, 1.4 Hz, 1H), 2.49 (s, 3H). Data in accordance with that previously published.<sup>10</sup>

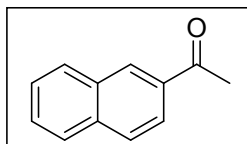


**2-Acetylthiophene (7v):** The reaction of 2-(chloromethyl)thiophene oxidation (133 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.70 (d, J = 3.5 Hz, 1H), 7.64 (d, J = 4.8 Hz, 1H), 7.13 (t, J = 4.3 Hz, 1H), 2.56 (s, 3H). Data in accordance with that previously published.<sup>10</sup>

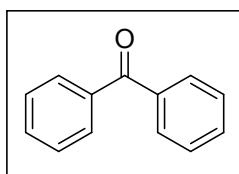


**2-Acetylpyridine (7w):** The reaction of 2-(1-chloroethyl)pyridine oxidation (155 mg, 1.0 mmol) under the optimized condition under

60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.67 (d, J = 4.5 Hz, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.82 (t, J = 7.7 Hz, 1H), 7.51–7.41 (m, 1H), 2.72 (s, 3H). Data in accordance with that previously published.<sup>10</sup>

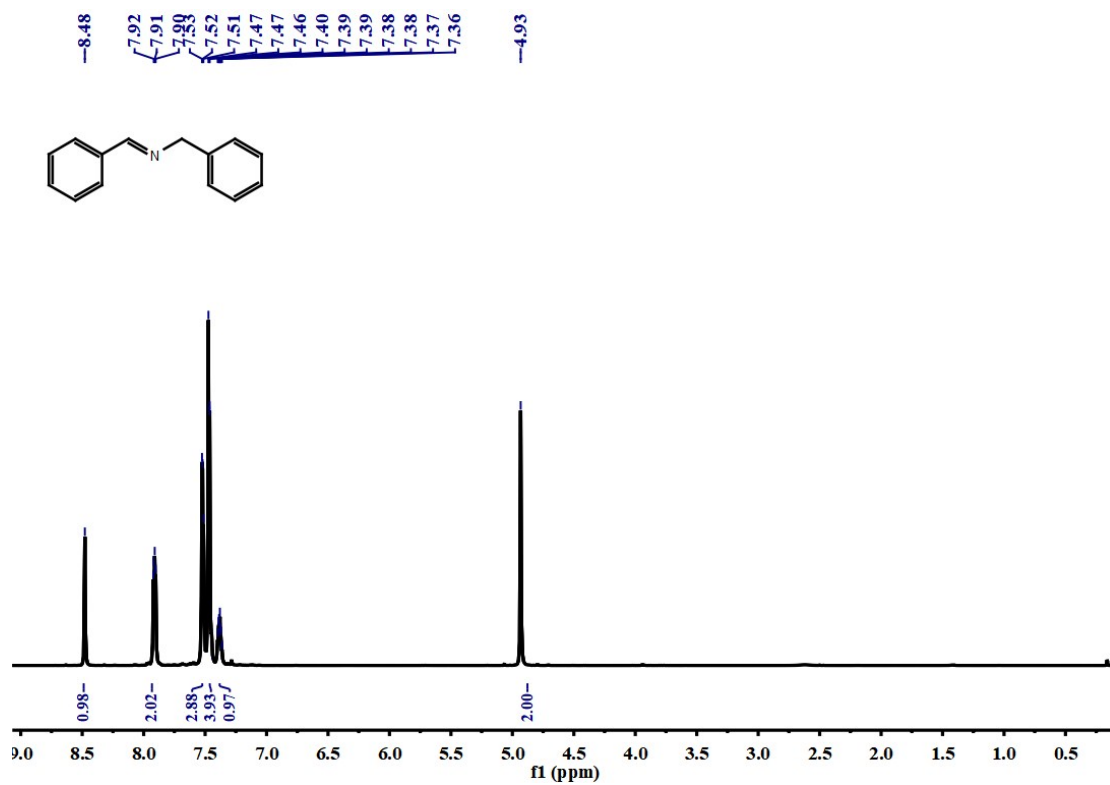


**2-Acetonaphthone (7x):** The reaction of 2-(chloromethyl)naphthalene oxidation (177 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as light yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.79 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 7.2 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 2.77 (s, 3H). Data in accordance with that previously published.<sup>10</sup>

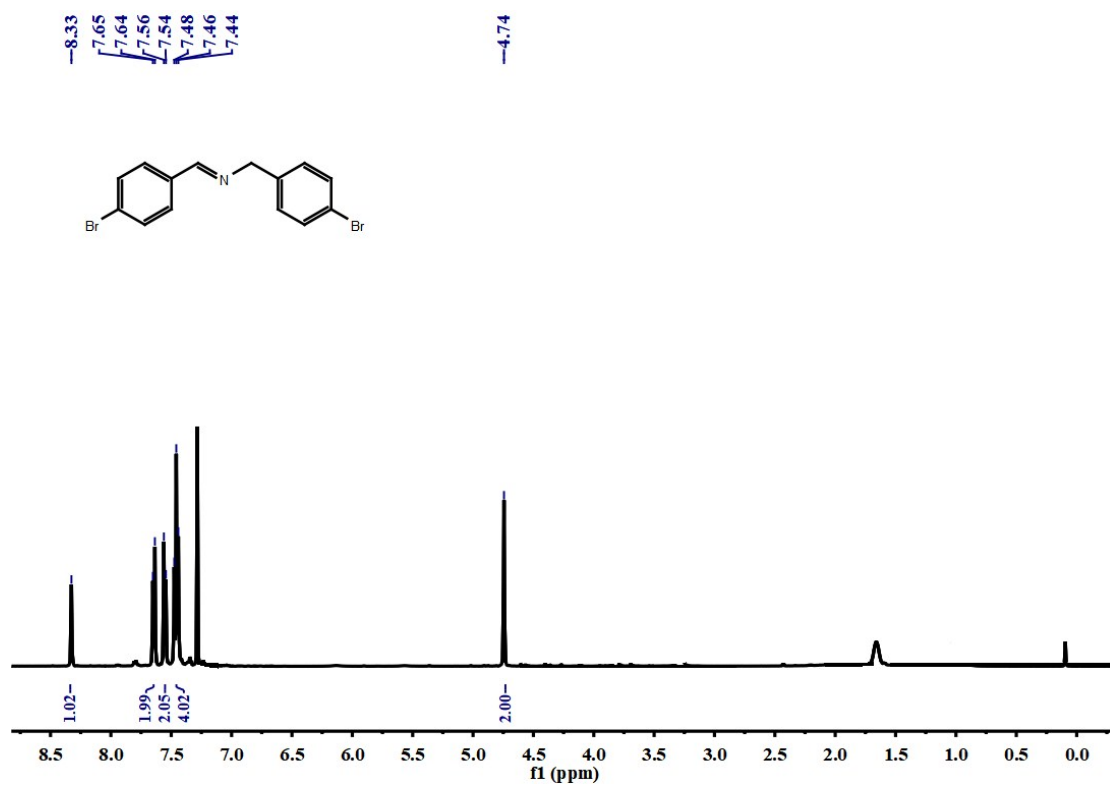


**Benzophenone (7y):** The reaction of chlorodiphenylmethane oxidation (203 mg, 1.0 mmol) under the optimized condition under 60 °C for 12 h. The crude reaction mixture followed by purification by column chromatography (with ethyl acetate and petroleum ether) gave the desired compound as an orange crystal. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.83 (d, J = 7.3 Hz, 4H), 7.62 (t, J = 7.4 Hz, 2H), 7.51 (t, J = 7.6 Hz, 4H). Data in accordance with that previously published.<sup>10</sup>

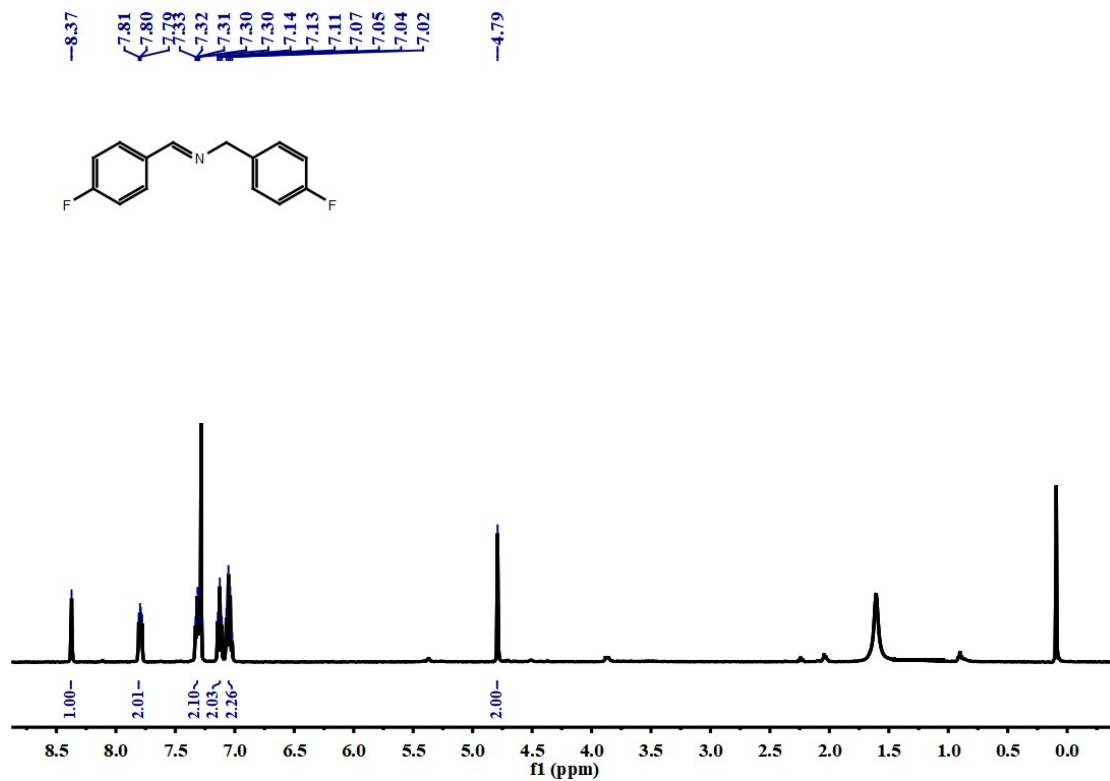




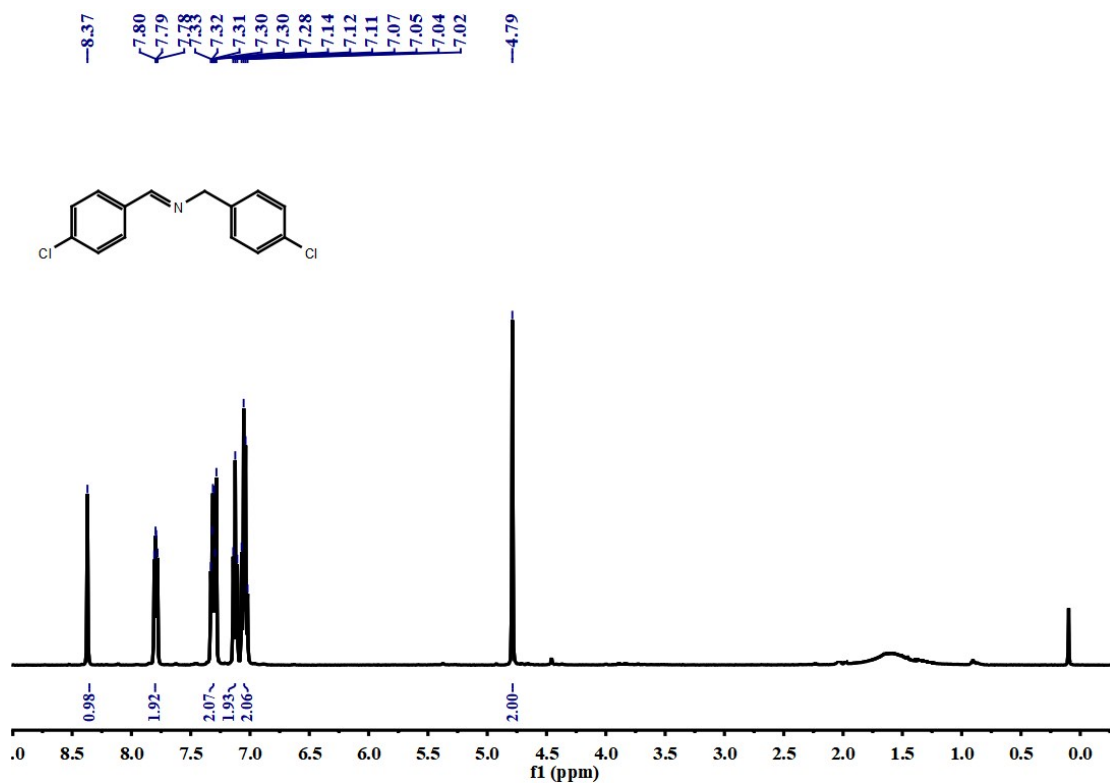
<sup>1</sup>H NMR spectra of 5a (500 MHz, CDCl<sub>3</sub>)



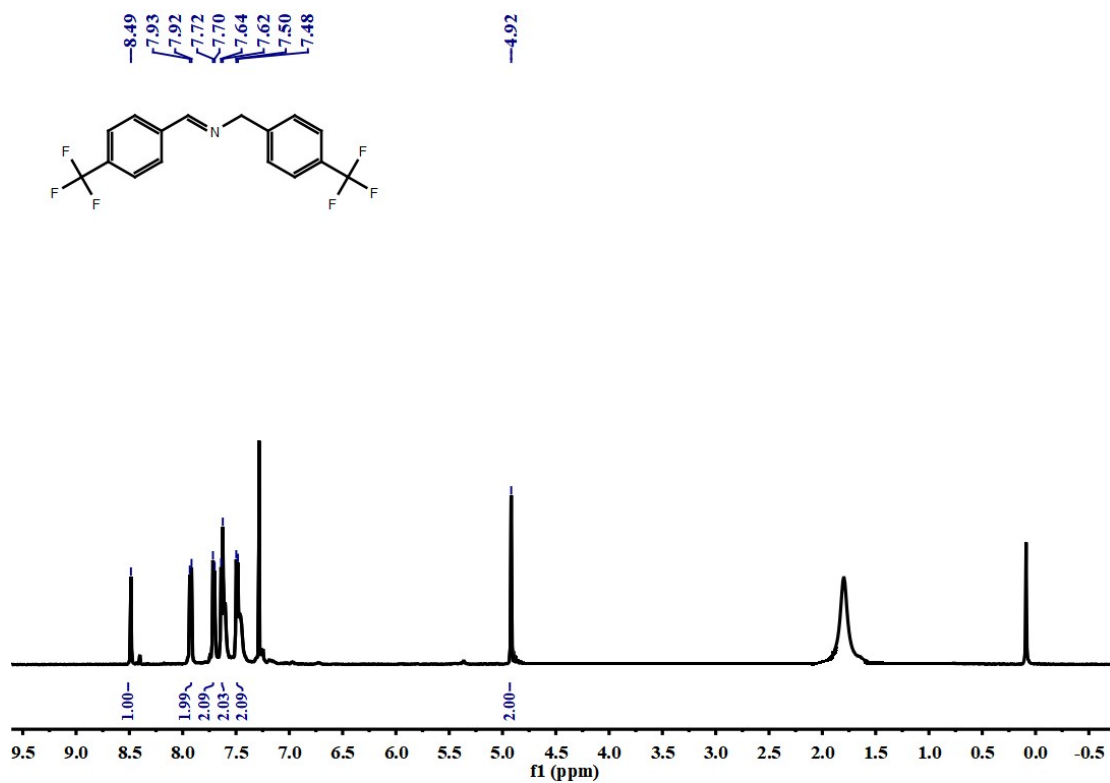
<sup>1</sup>H NMR spectra of 5b (500 MHz, CDCl<sub>3</sub>)



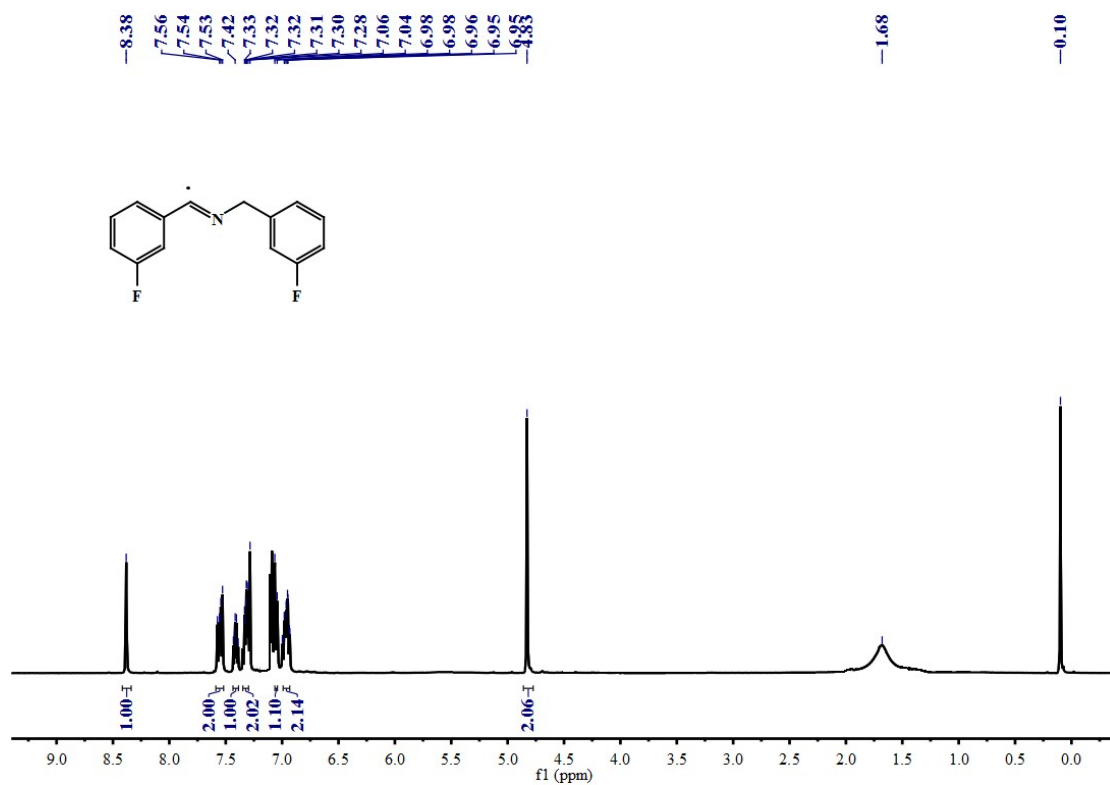
<sup>1</sup>H NMR spectra of 5c (500 MHz, CDCl<sub>3</sub>)



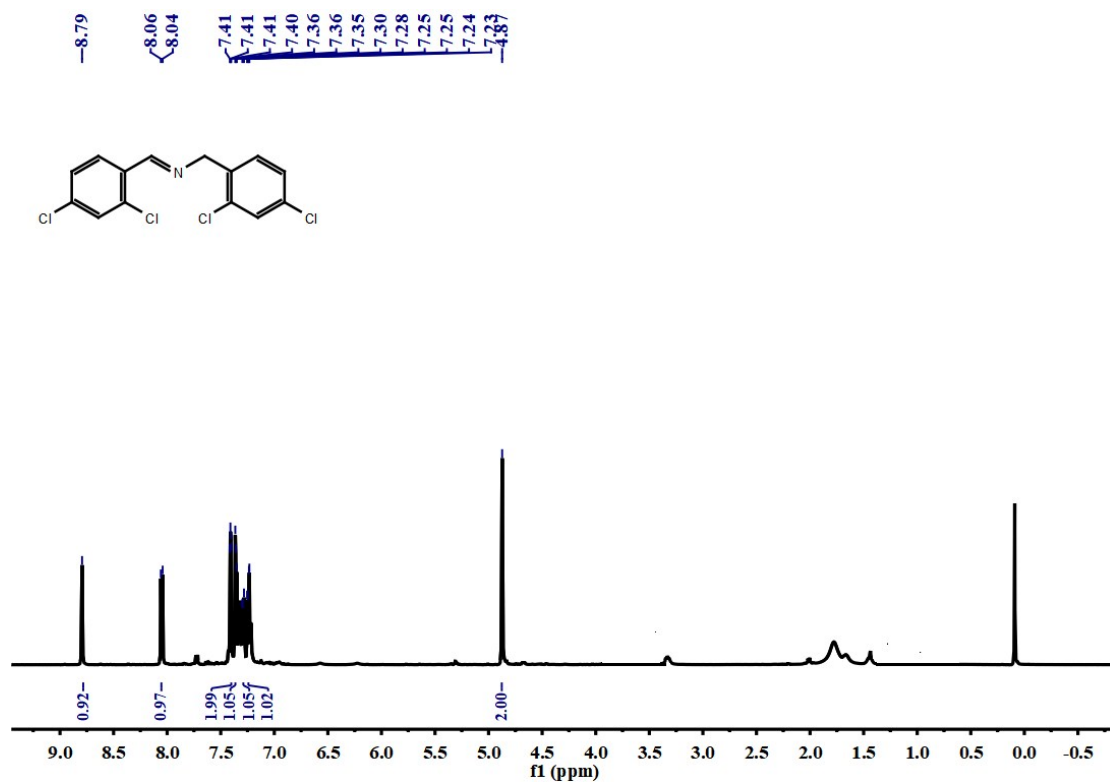
<sup>1</sup>H NMR spectra of 5d (500 MHz, CDCl<sub>3</sub>)



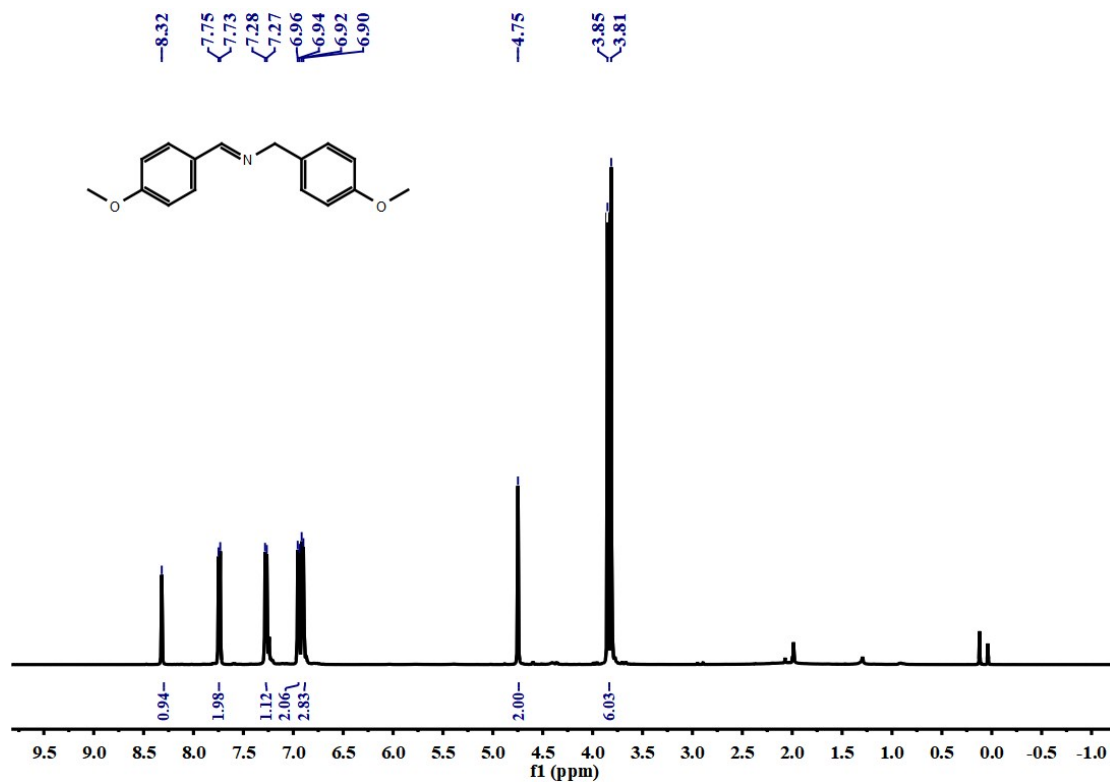
<sup>1</sup>H NMR spectra of 5e (500 MHz, CDCl<sub>3</sub>)



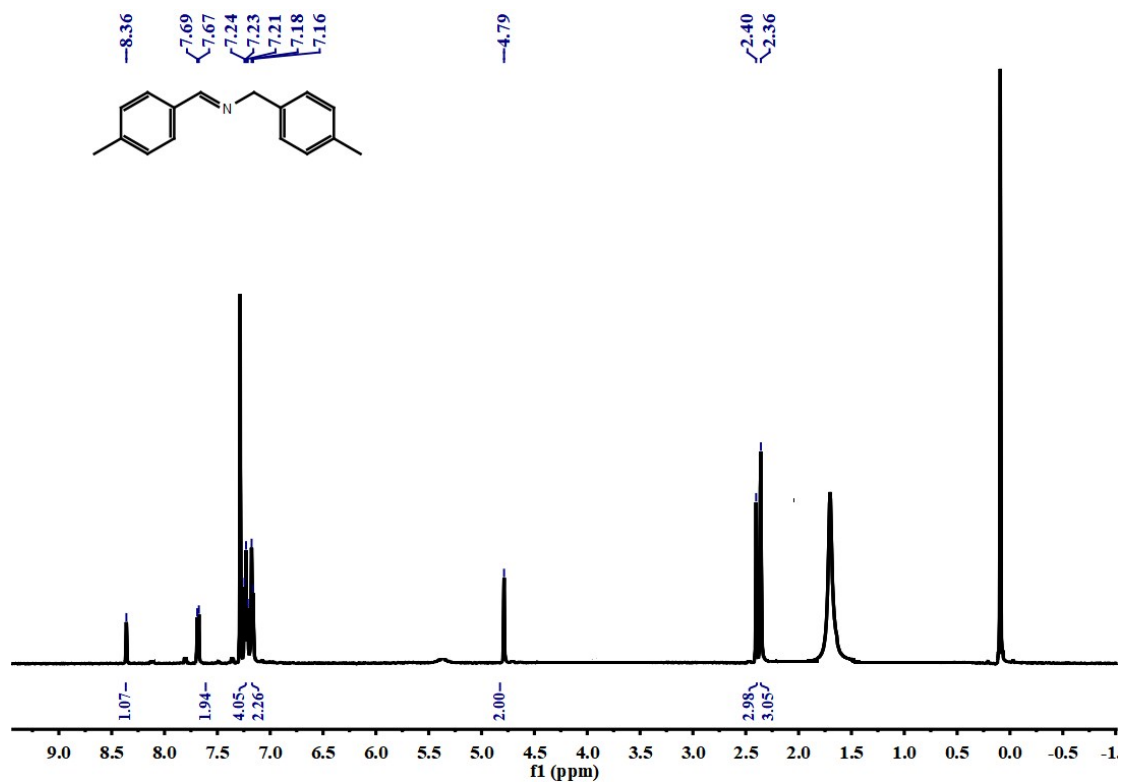
<sup>1</sup>H NMR spectra of 5f (500 MHz, CDCl<sub>3</sub>)



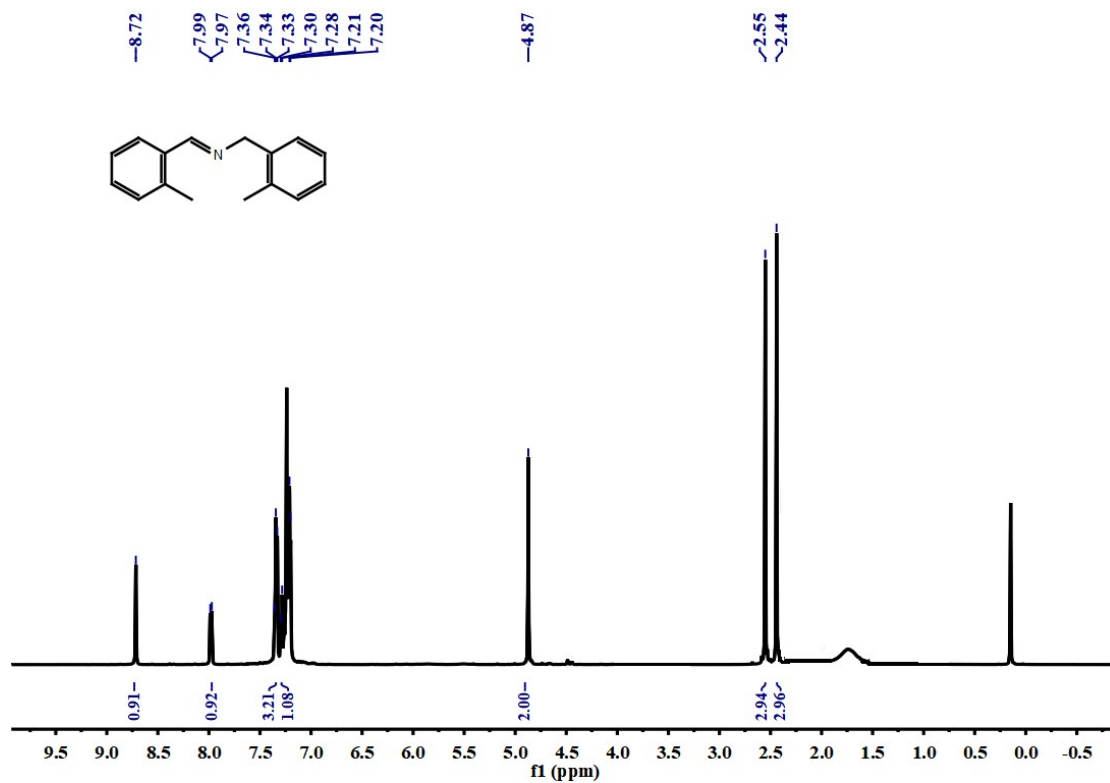
<sup>1</sup>H NMR spectra of 5g (500 MHz, CDCl<sub>3</sub>)



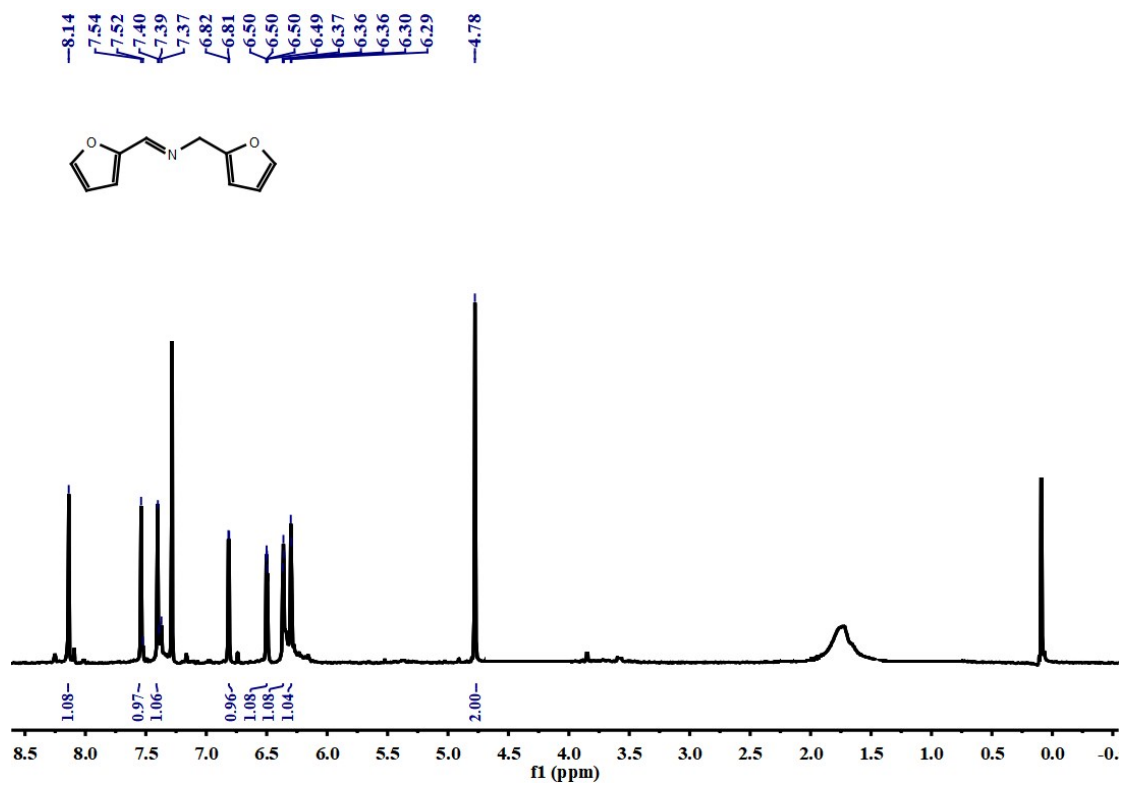
<sup>1</sup>H NMR spectra of 5h (500 MHz, CDCl<sub>3</sub>)



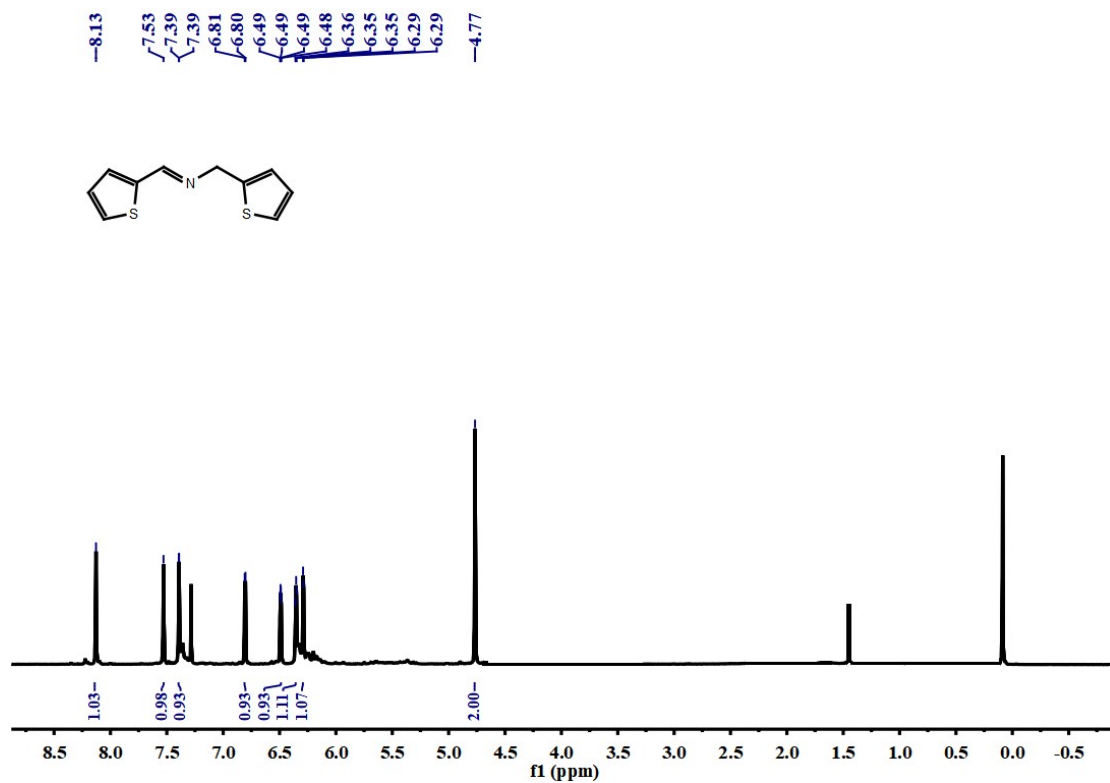
<sup>1</sup>H NMR spectra of **5i** (500 MHz, CDCl<sub>3</sub>)



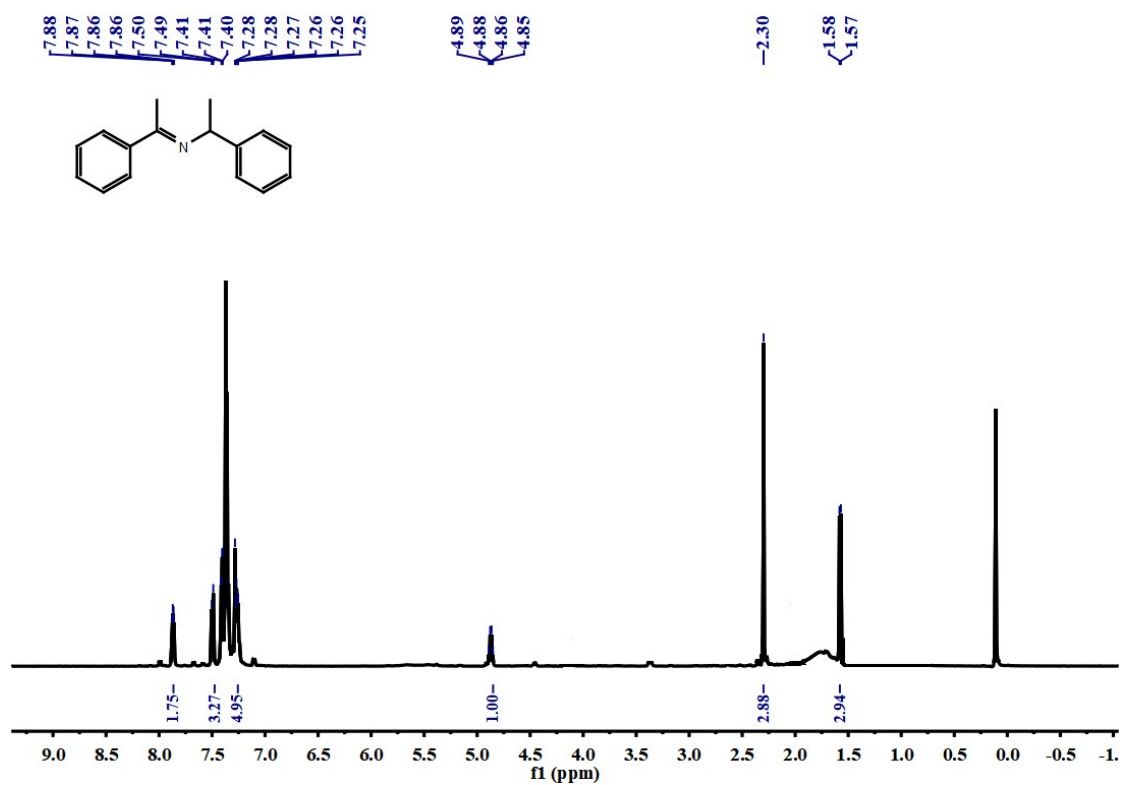
<sup>1</sup>H NMR spectra of **5j** (500 MHz, CDCl<sub>3</sub>)



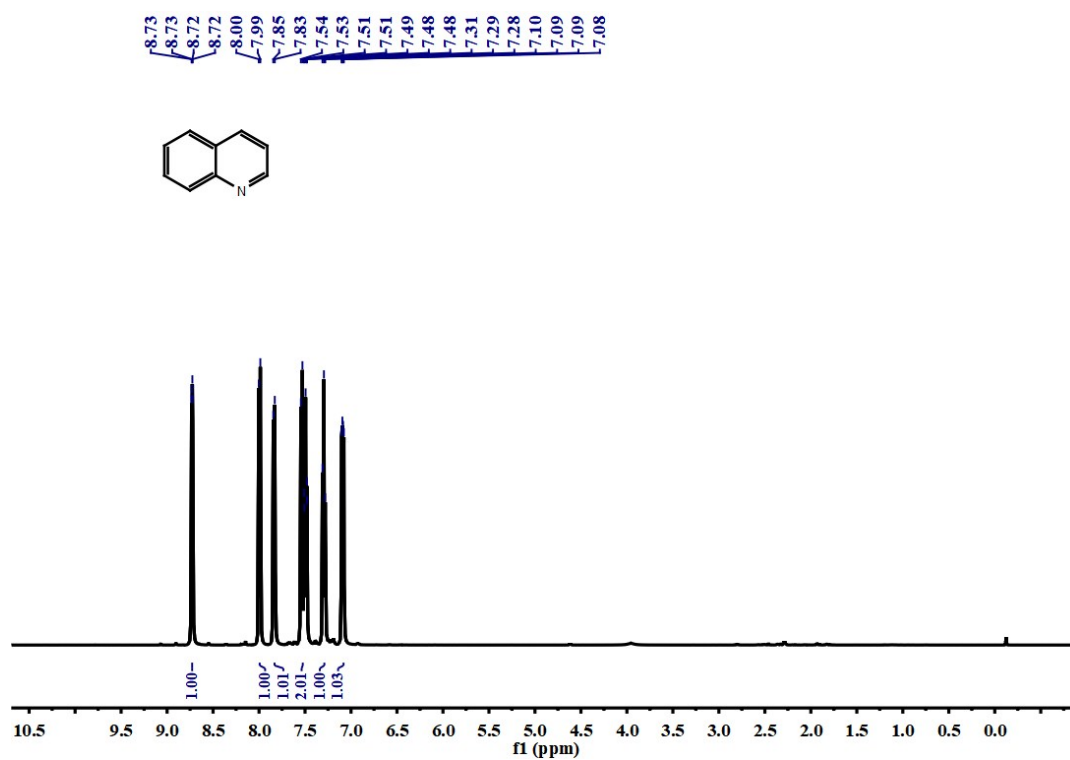
<sup>1</sup>H NMR spectra of 5k (500 MHz, CDCl<sub>3</sub>)



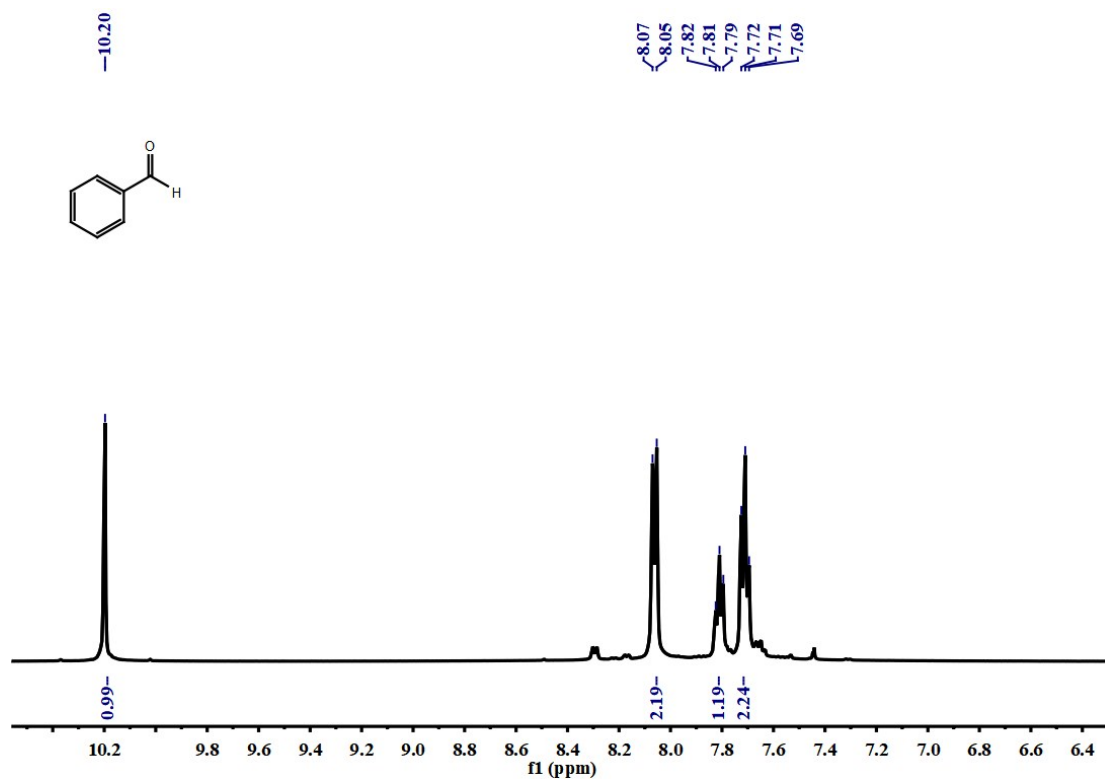
<sup>1</sup>H NMR spectra of 5l (500 MHz, CDCl<sub>3</sub>)



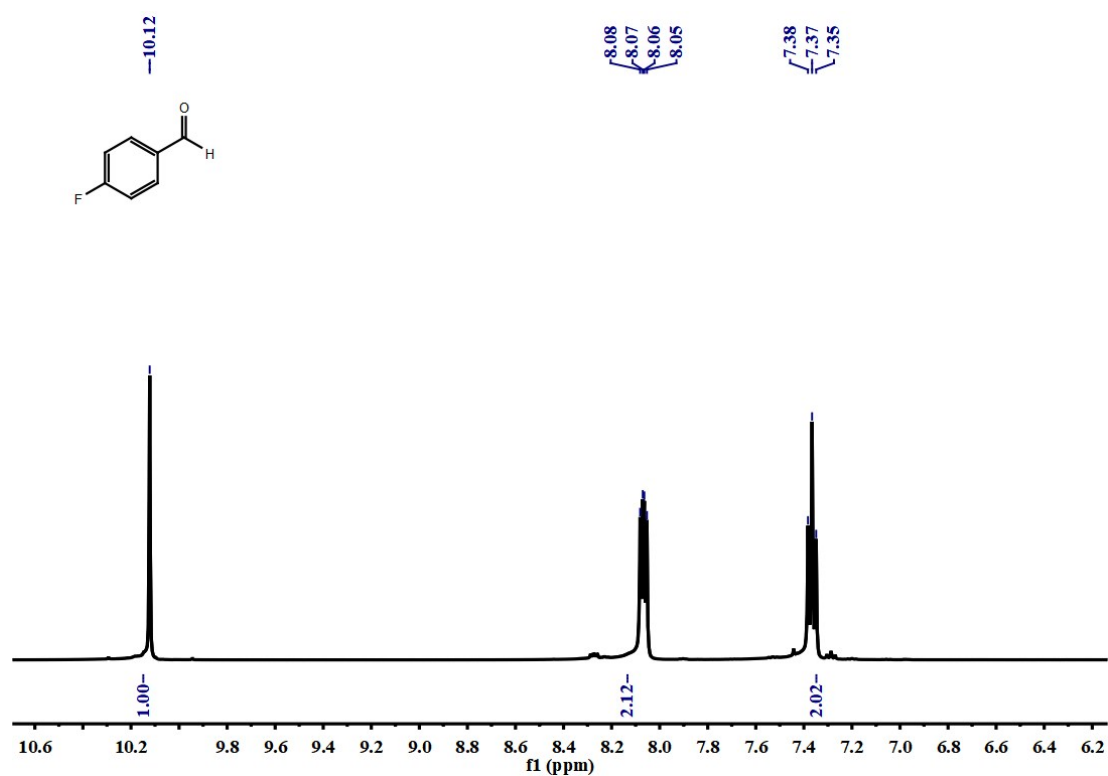
<sup>1</sup>H NMR spectra of 5n (500 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR spectra of 5o (500 MHz, CDCl<sub>3</sub>)

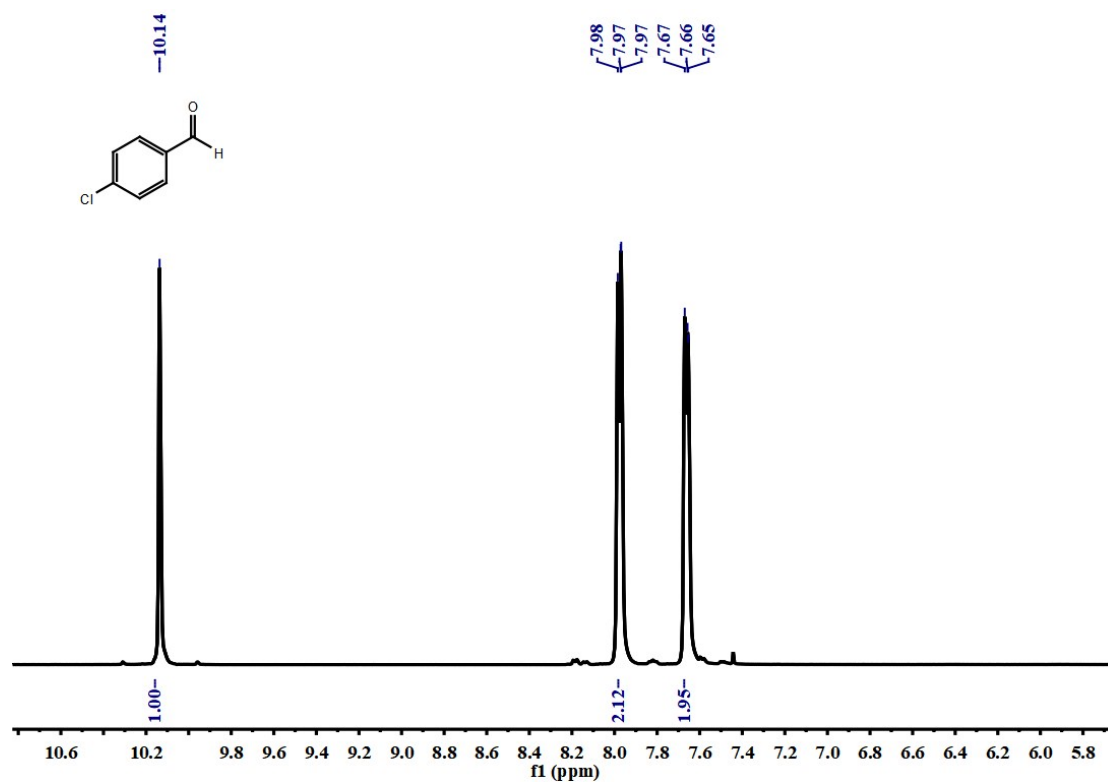


$^1\text{H}$  NMR spectra of 7a (500 MHz,  $\text{CDCl}_3$ )

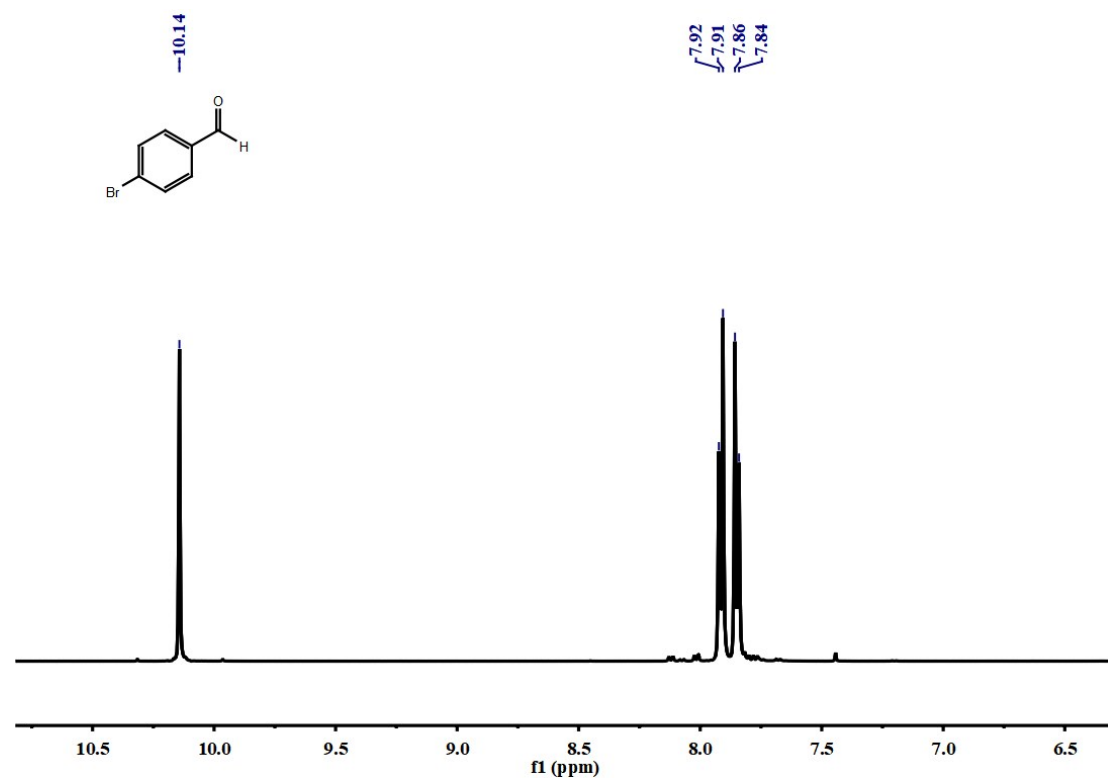


$^1\text{H}$  NMR spectra of 7b (500 MHz,  $\text{CDCl}_3$ )

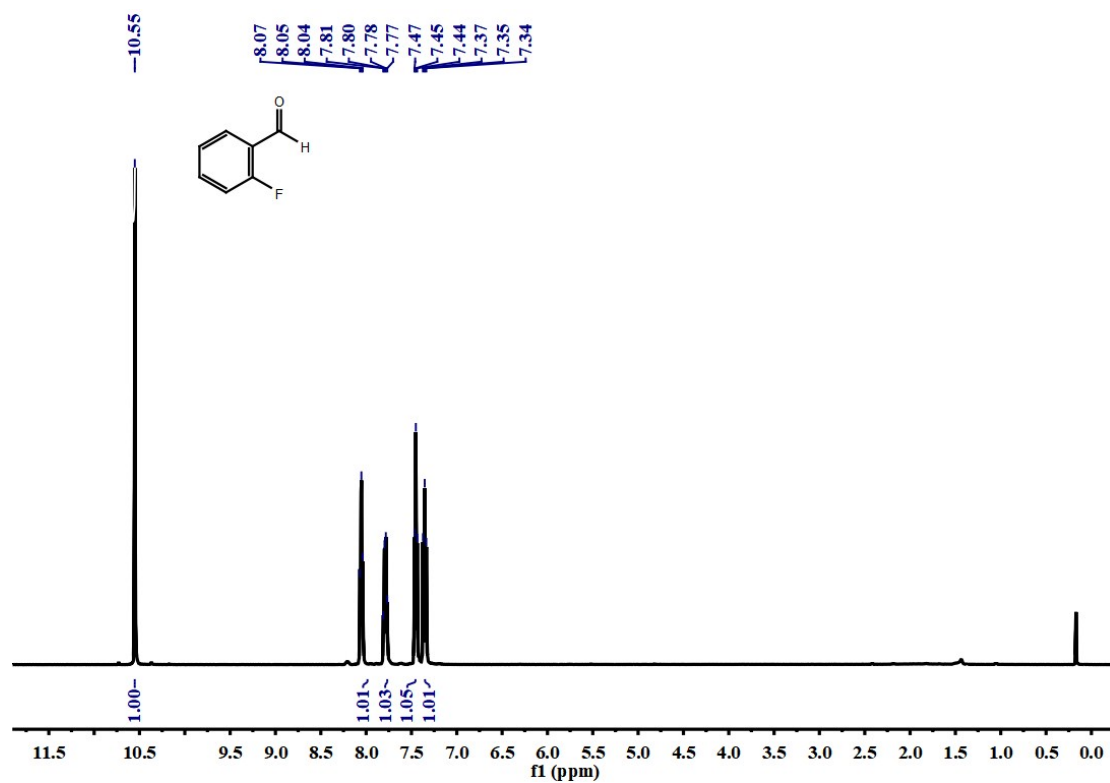




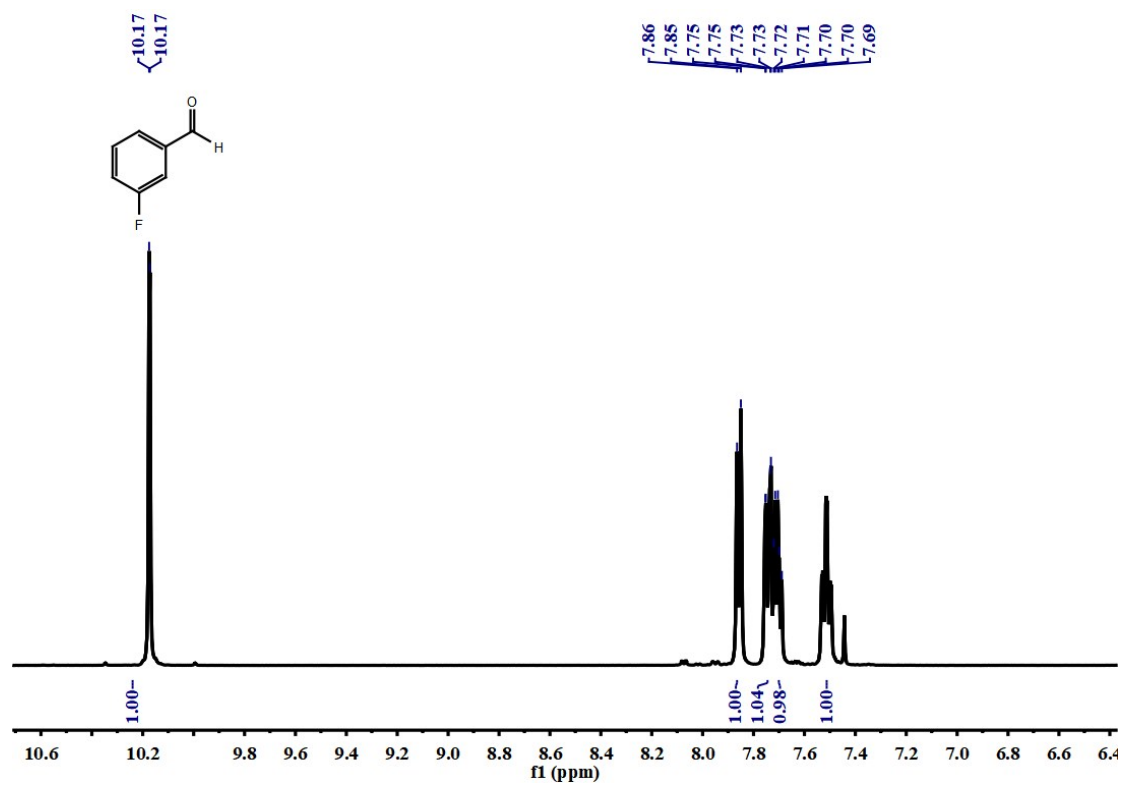
<sup>1</sup>H NMR spectra of 7c (500 MHz, CDCl<sub>3</sub>)



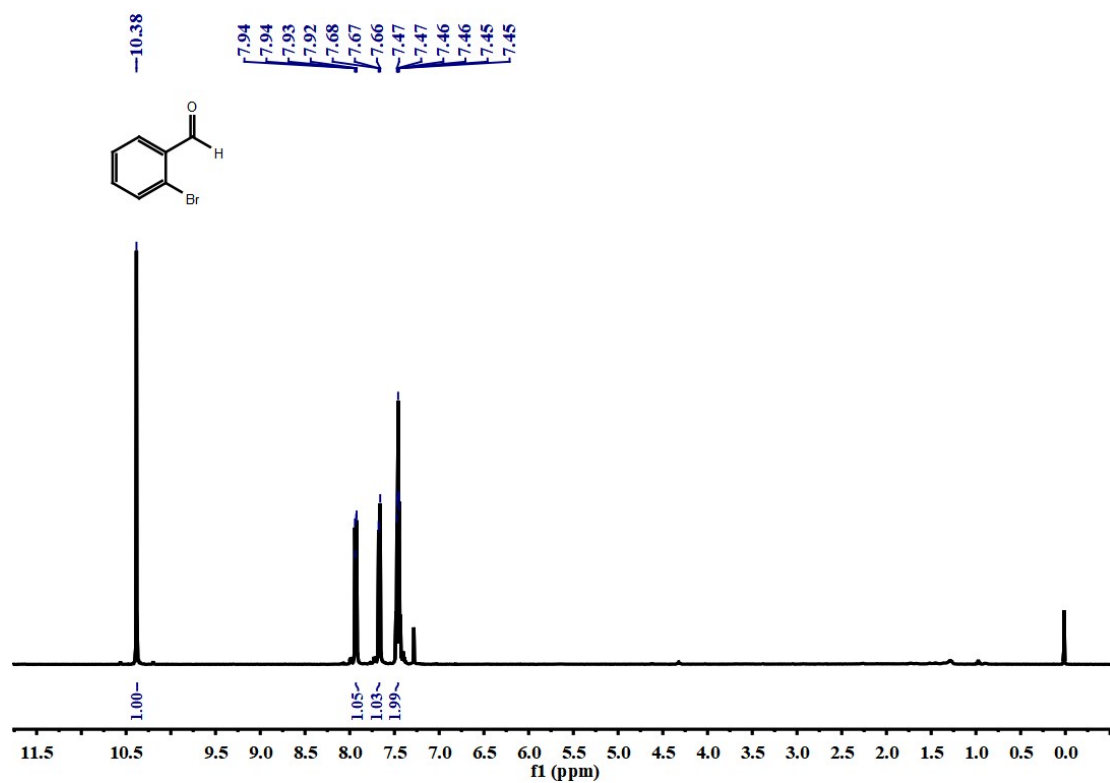
<sup>1</sup>H NMR spectra of 7d (500 MHz, CDCl<sub>3</sub>)



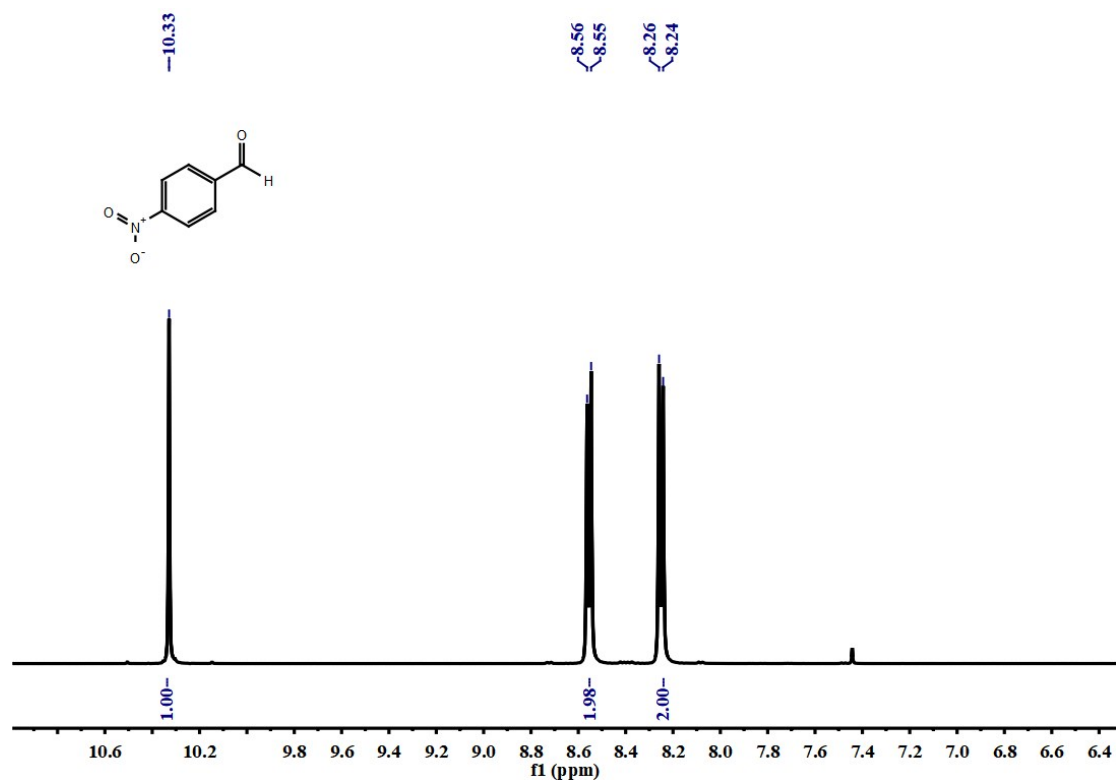
$^1\text{H}$  NMR spectra of 7e (500 MHz,  $\text{CDCl}_3$ )



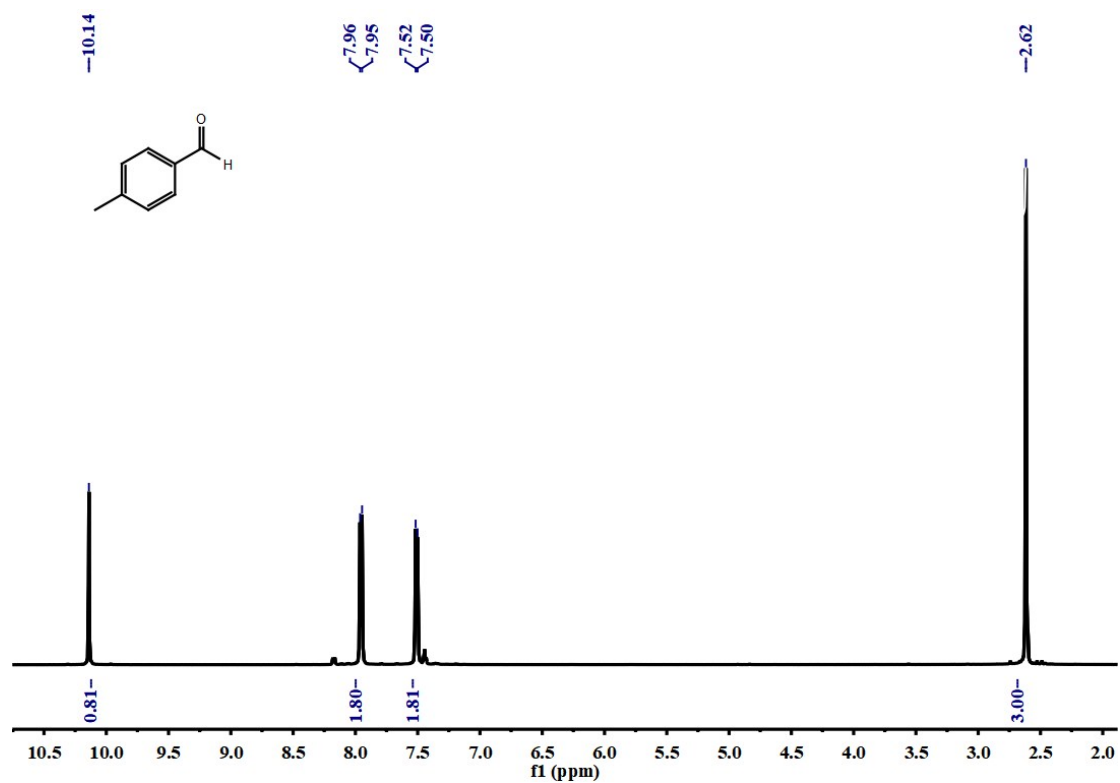
$^1\text{H}$  NMR spectra of 7f (500 MHz,  $\text{CDCl}_3$ )



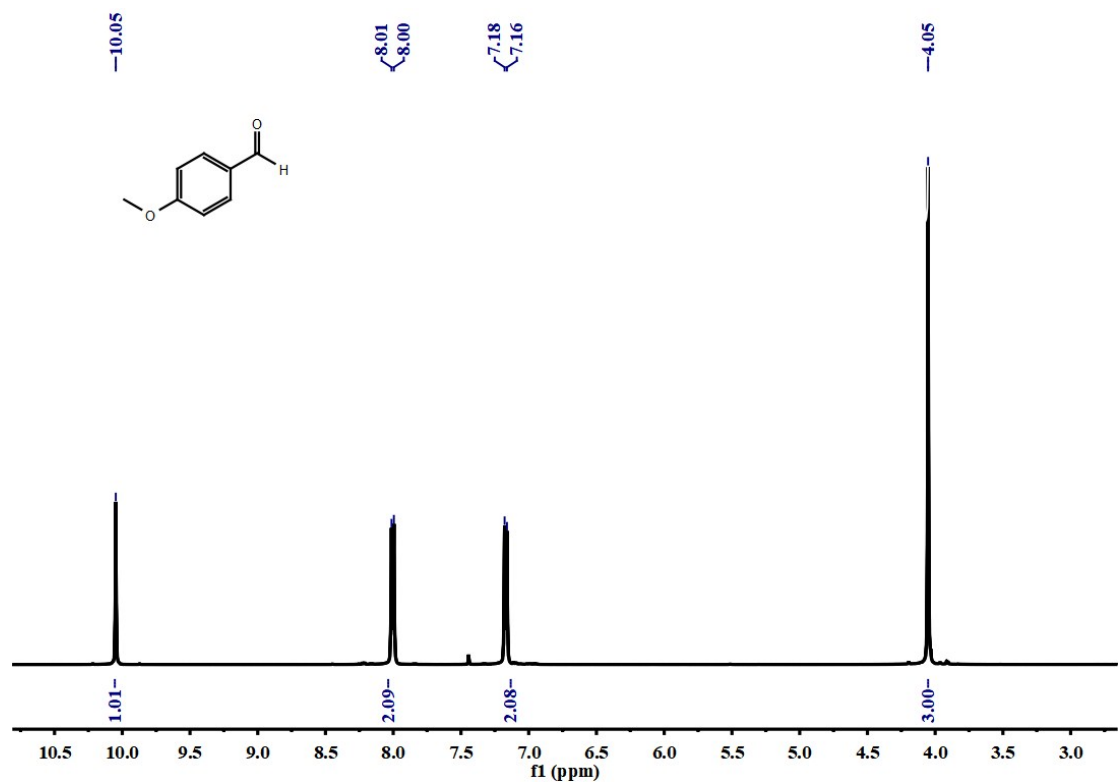
$^1\text{H}$  NMR spectra of 7g (500 MHz,  $\text{CDCl}_3$ )



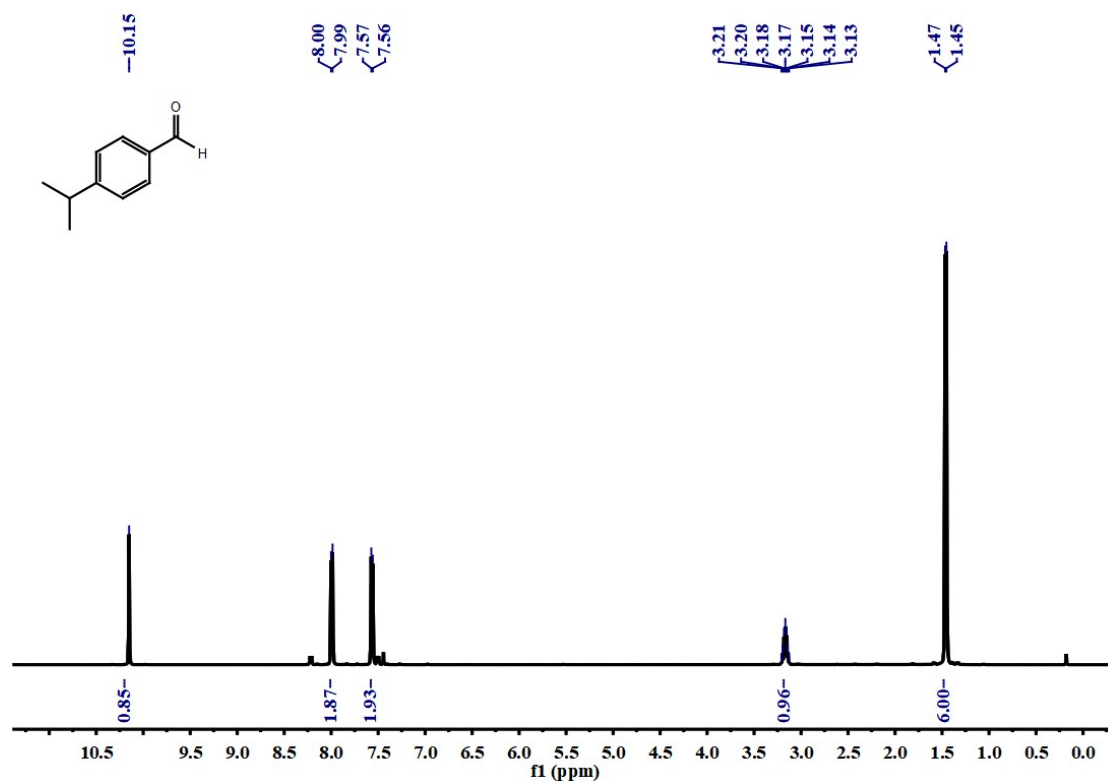
$^1\text{H}$  NMR spectra of 7h (500 MHz,  $\text{CDCl}_3$ )



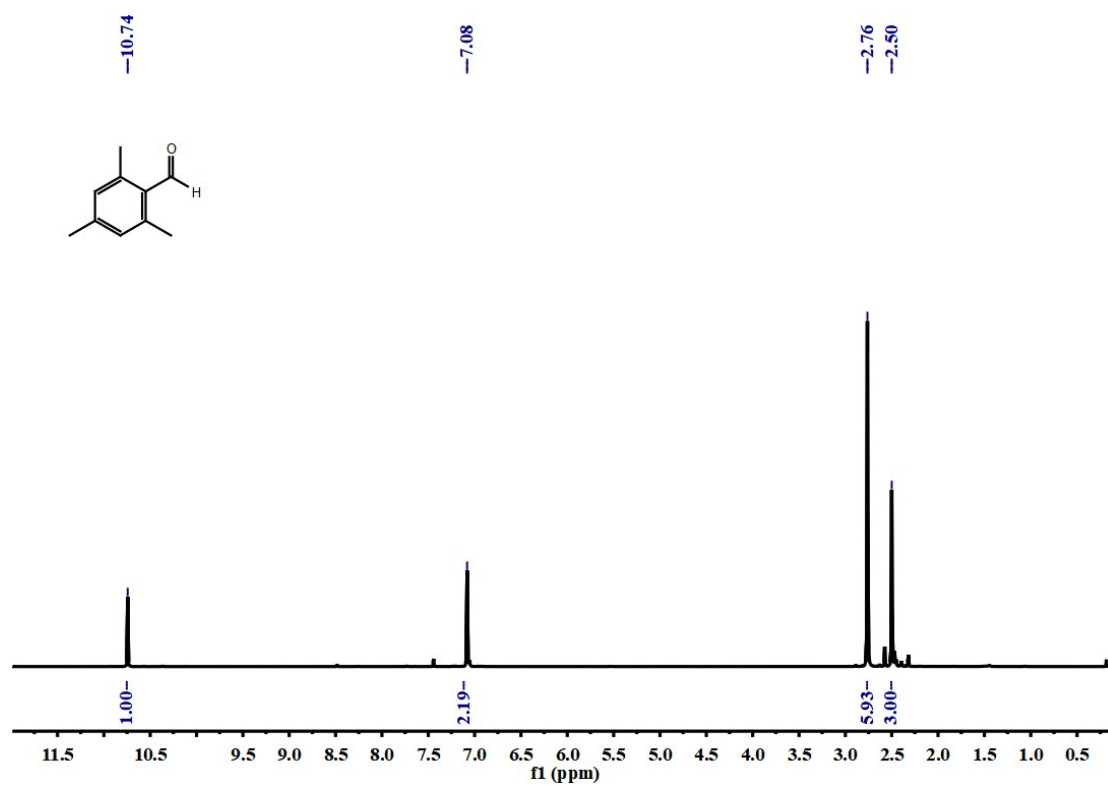
<sup>1</sup>H NMR spectra of 7i (500 MHz, CDCl<sub>3</sub>)



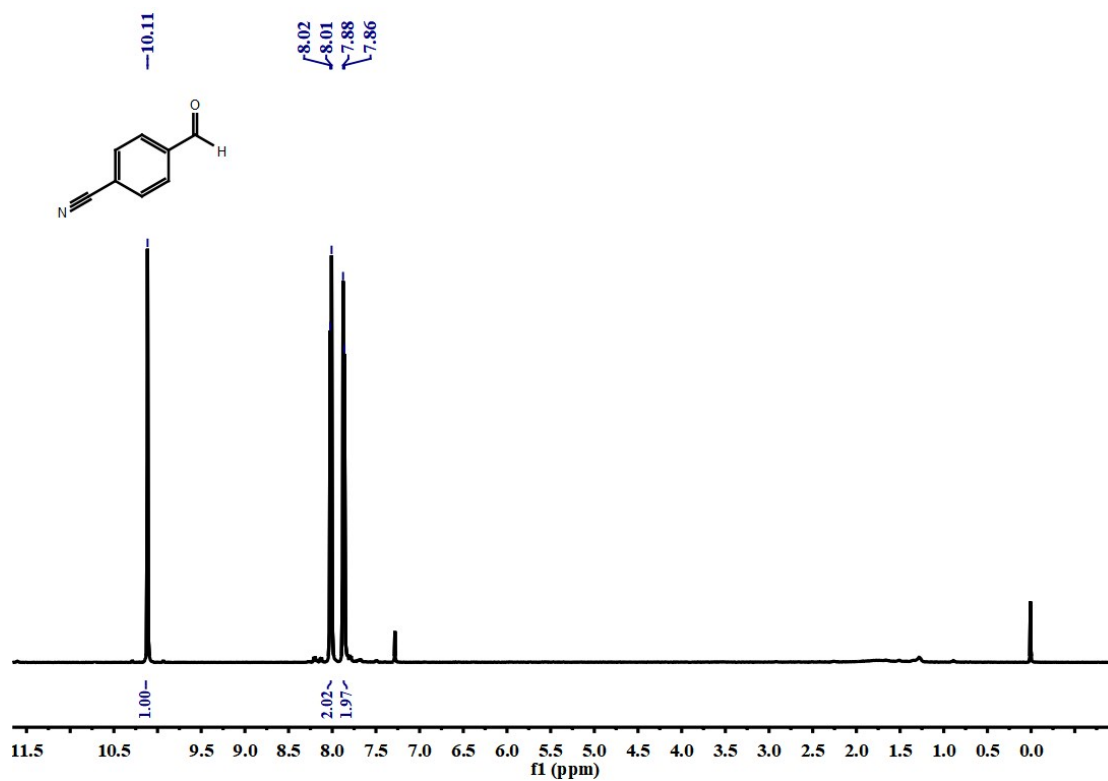
<sup>1</sup>H NMR spectra of 7j (500 MHz, CDCl<sub>3</sub>)



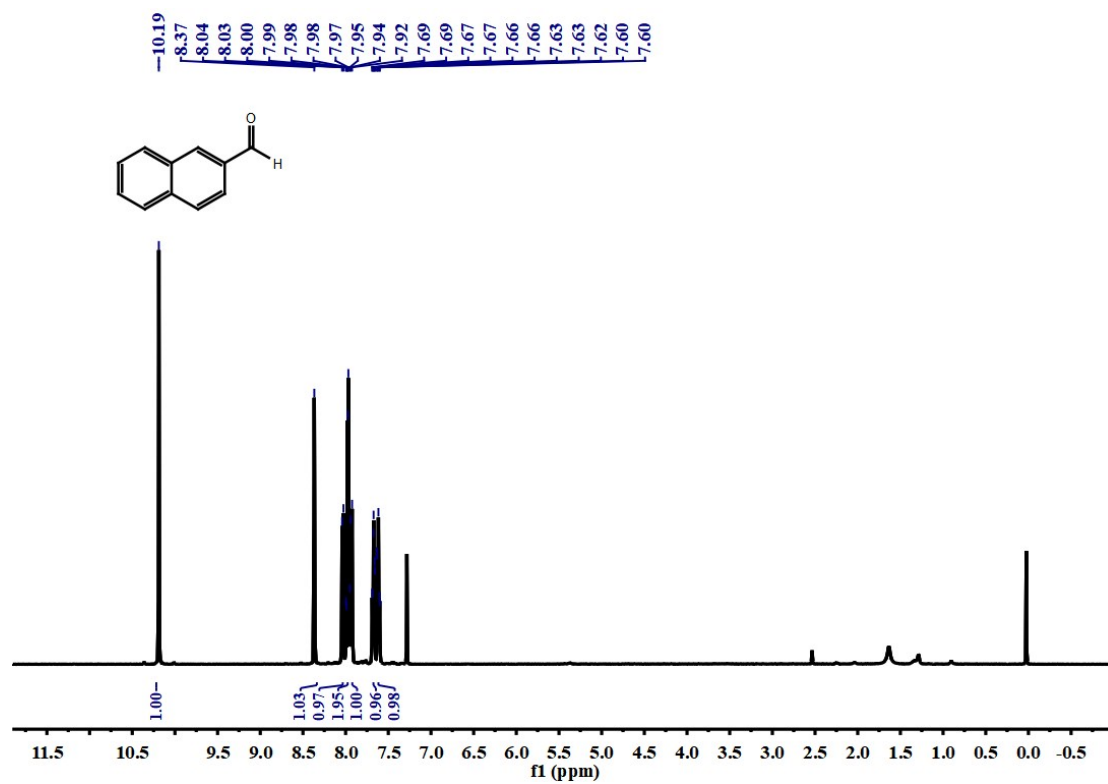
<sup>1</sup>H NMR spectra of 7k (500 MHz, CDCl<sub>3</sub>)



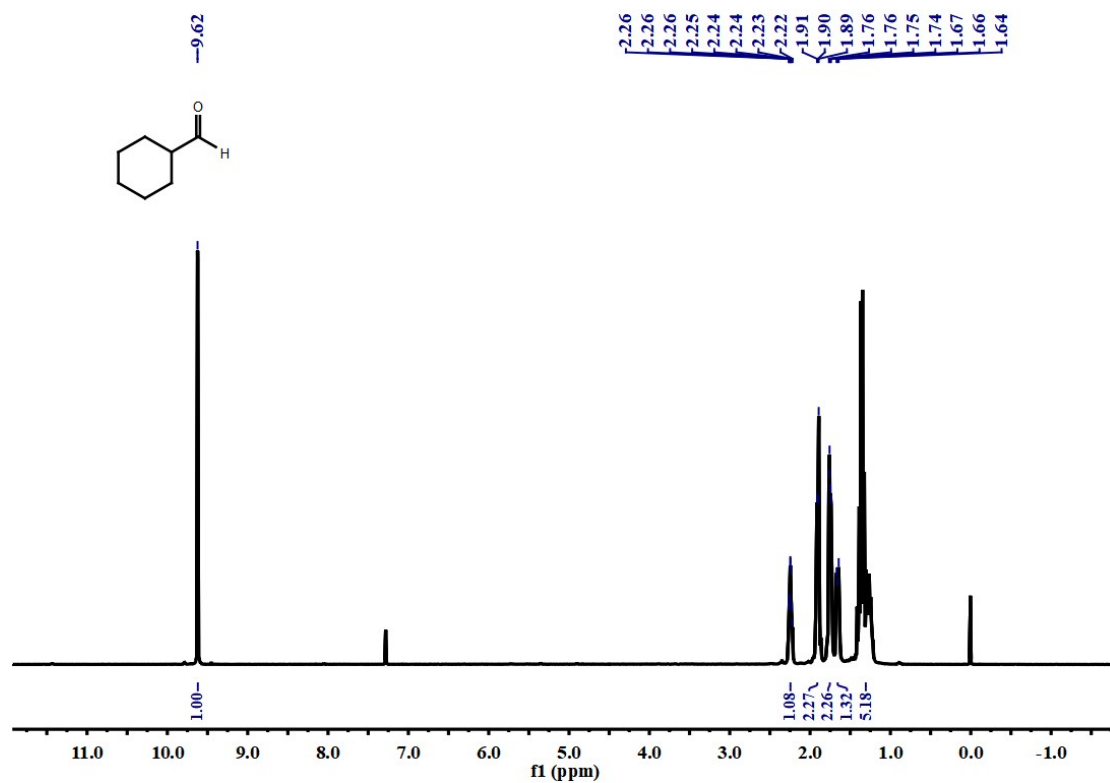
<sup>1</sup>H NMR spectra of 7l (500 MHz, CDCl<sub>3</sub>)



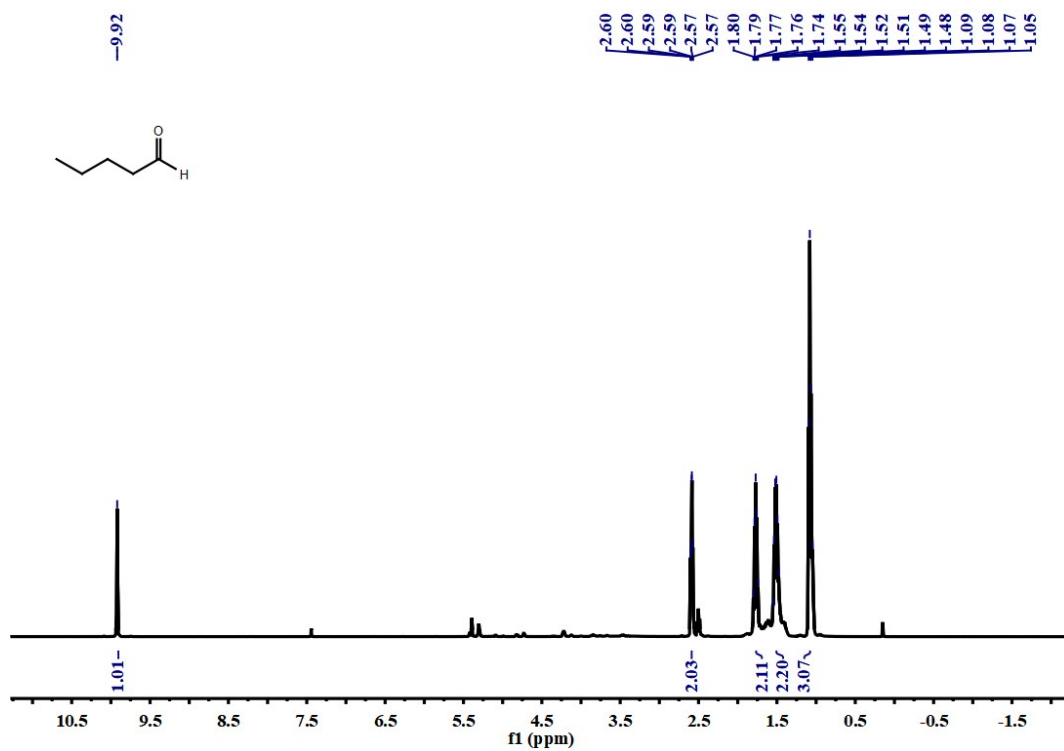
$^1\text{H}$  NMR spectra of 7m (500 MHz,  $\text{CDCl}_3$ )



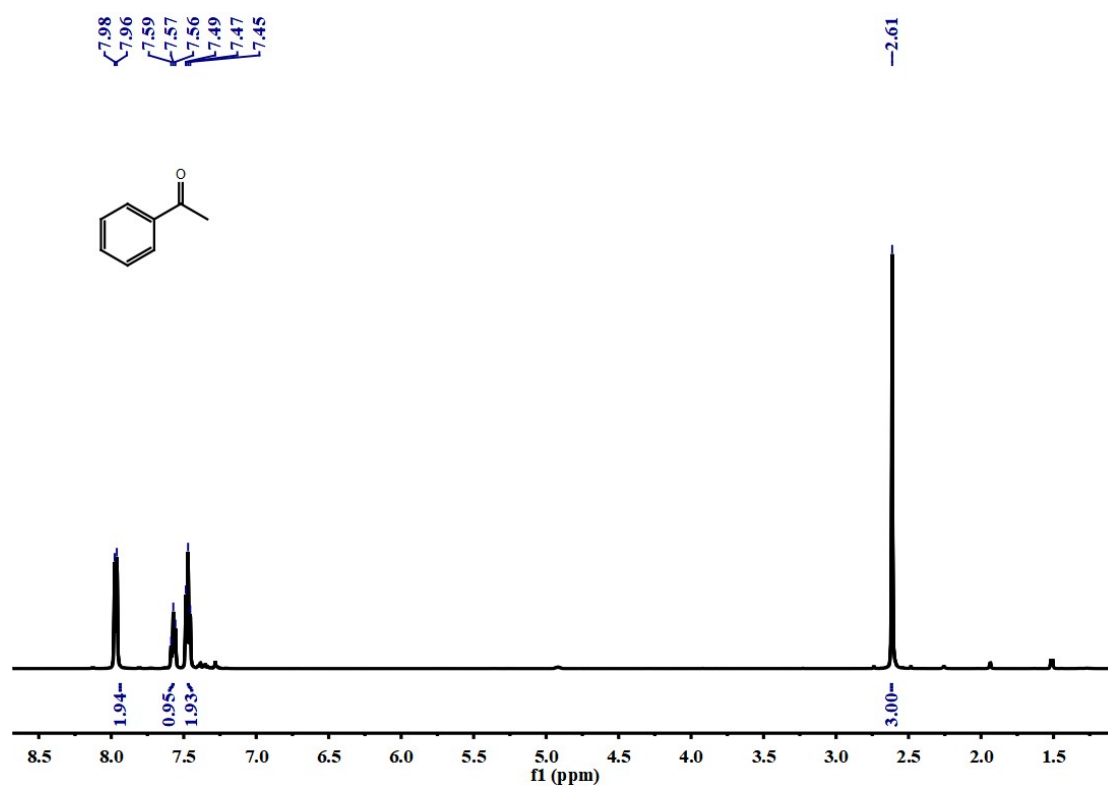
$^1\text{H}$  NMR spectra of 7n (500 MHz,  $\text{CDCl}_3$ )



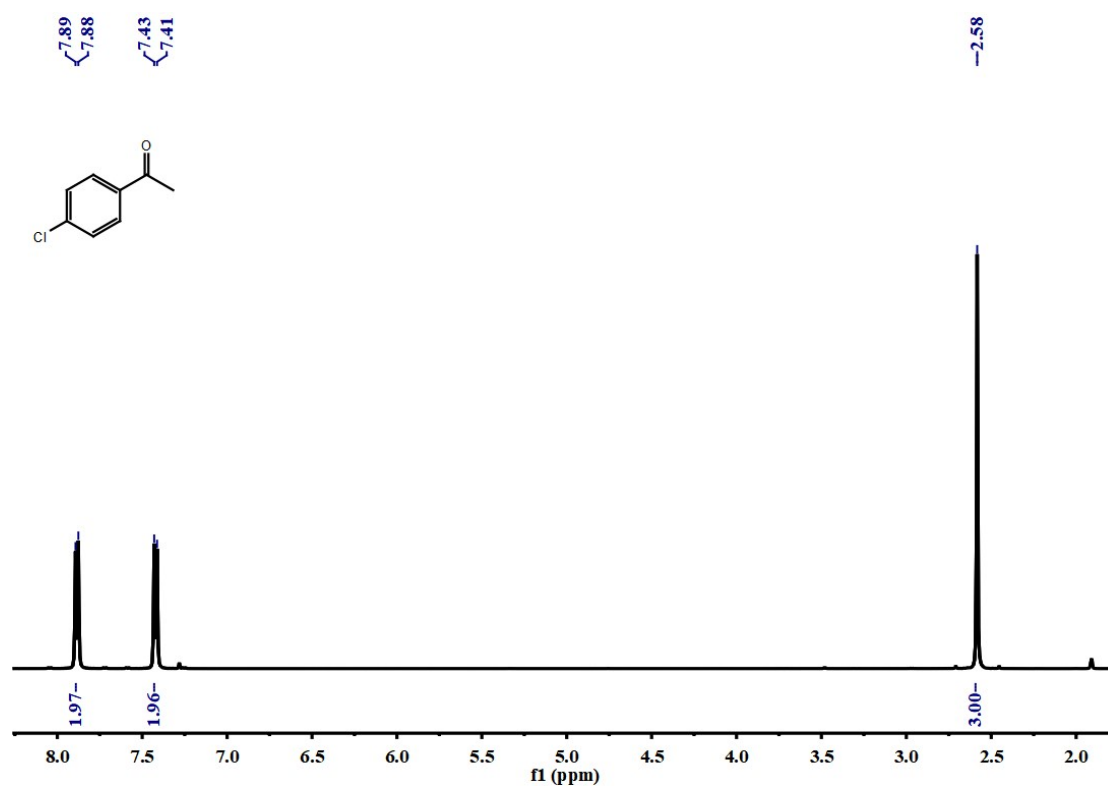
$^1\text{H}$  NMR spectra of 7o (500 MHz,  $\text{CDCl}_3$ )



$^1\text{H}$  NMR spectra of 7p (500 MHz,  $\text{CDCl}_3$ )

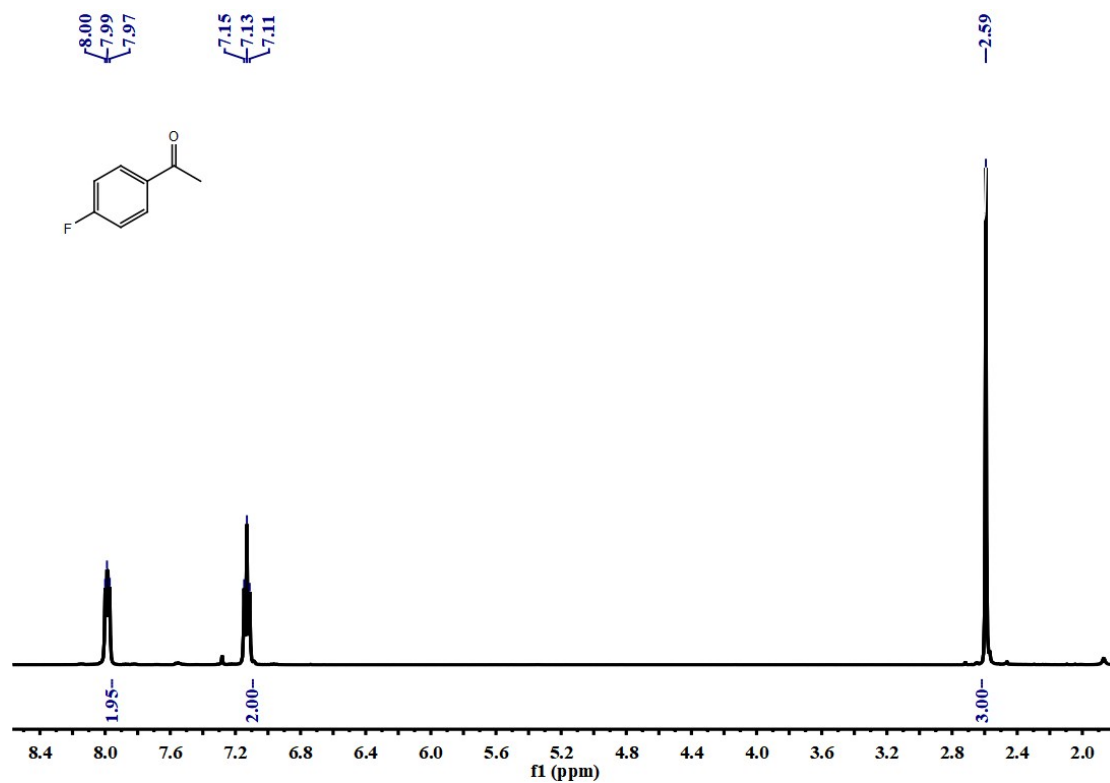


$^1\text{H}$  NMR spectra of 7q (500 MHz,  $\text{CDCl}_3$ )

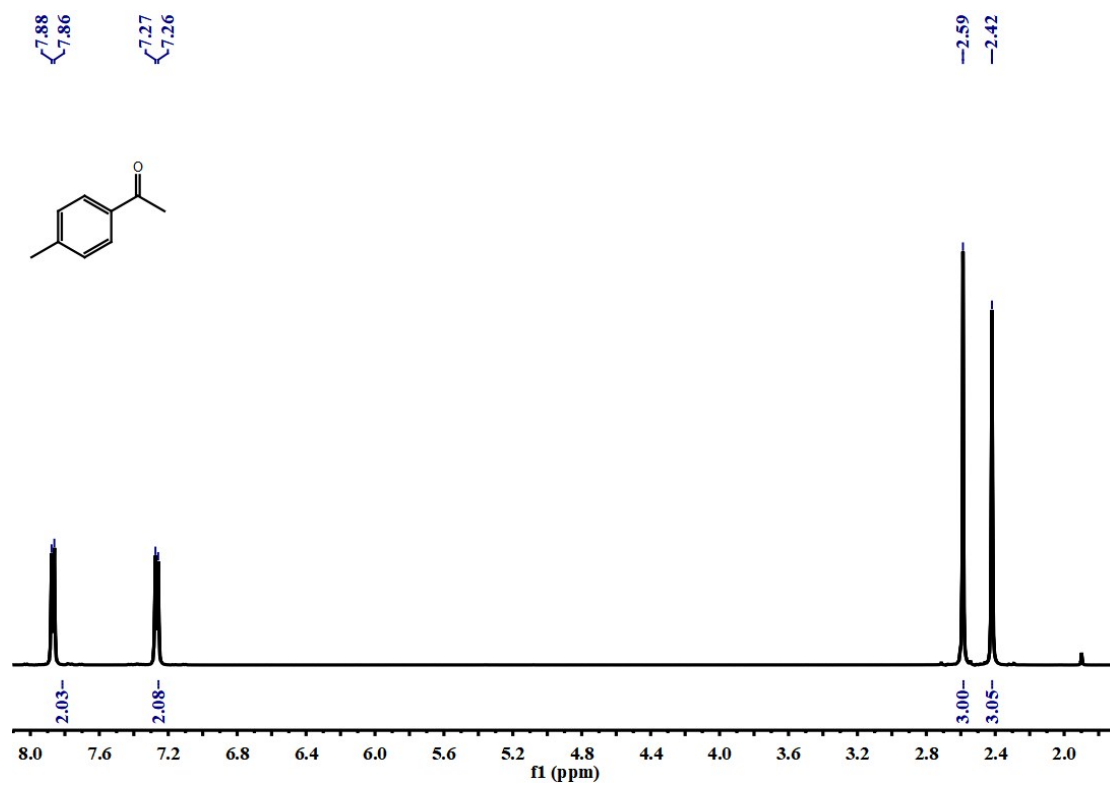


$^1\text{H}$  NMR spectra of 7r (500 MHz,  $\text{CDCl}_3$ )

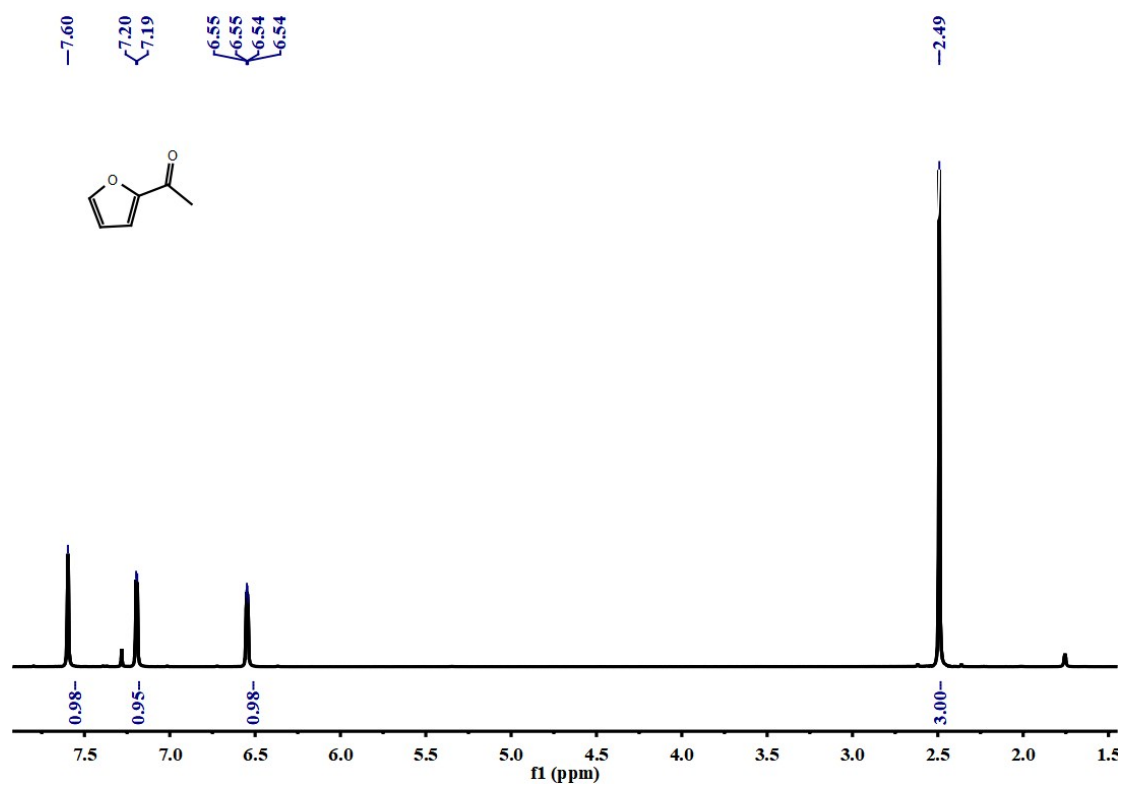




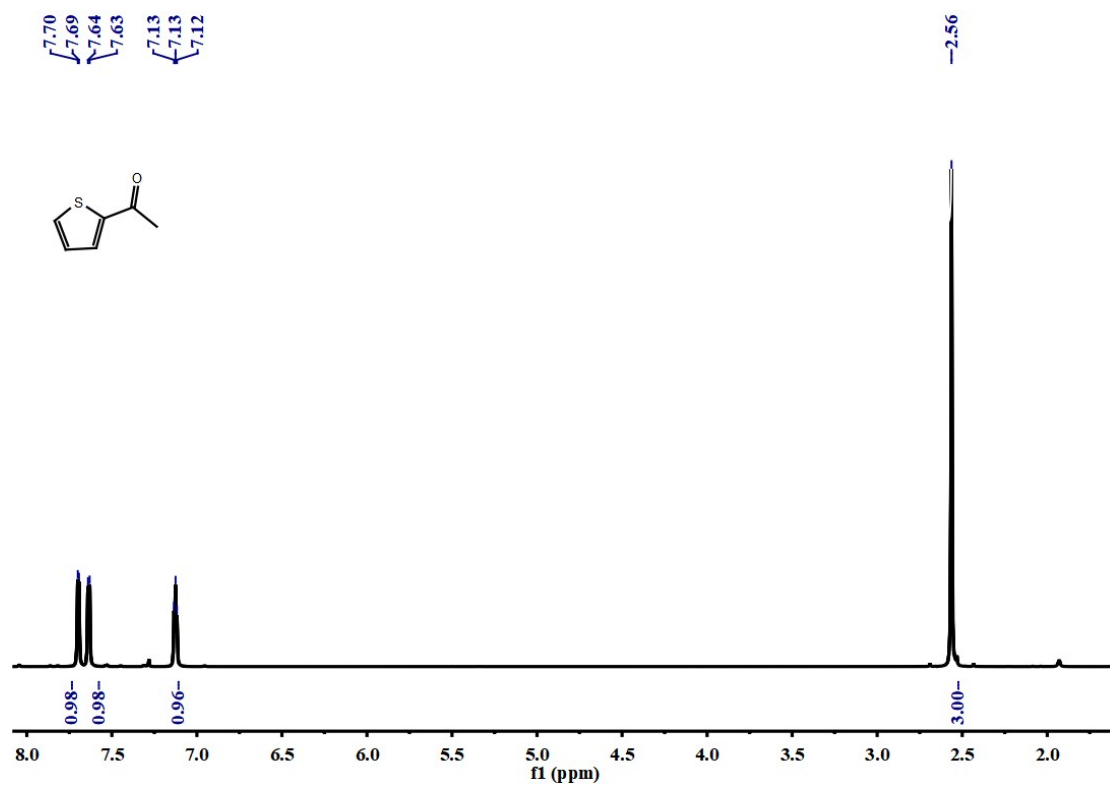
<sup>1</sup>H NMR spectra of 7s (500 MHz, CDCl<sub>3</sub>)



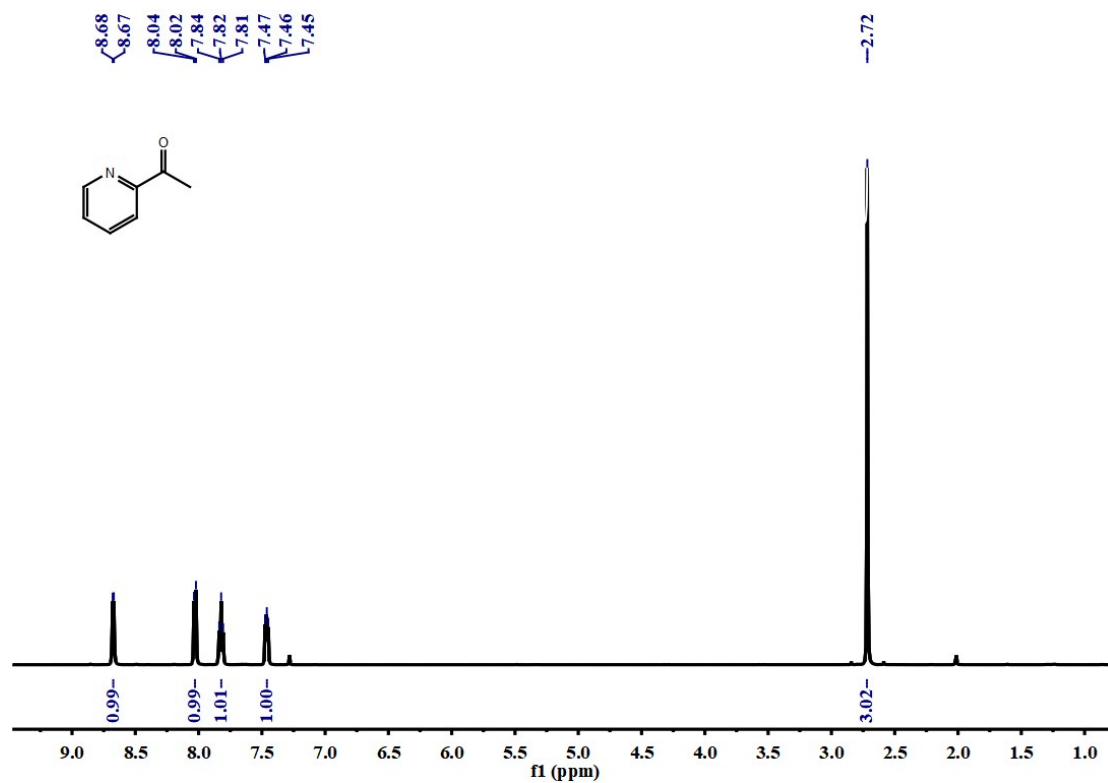
<sup>1</sup>H NMR spectra of 7t (500 MHz, CDCl<sub>3</sub>)



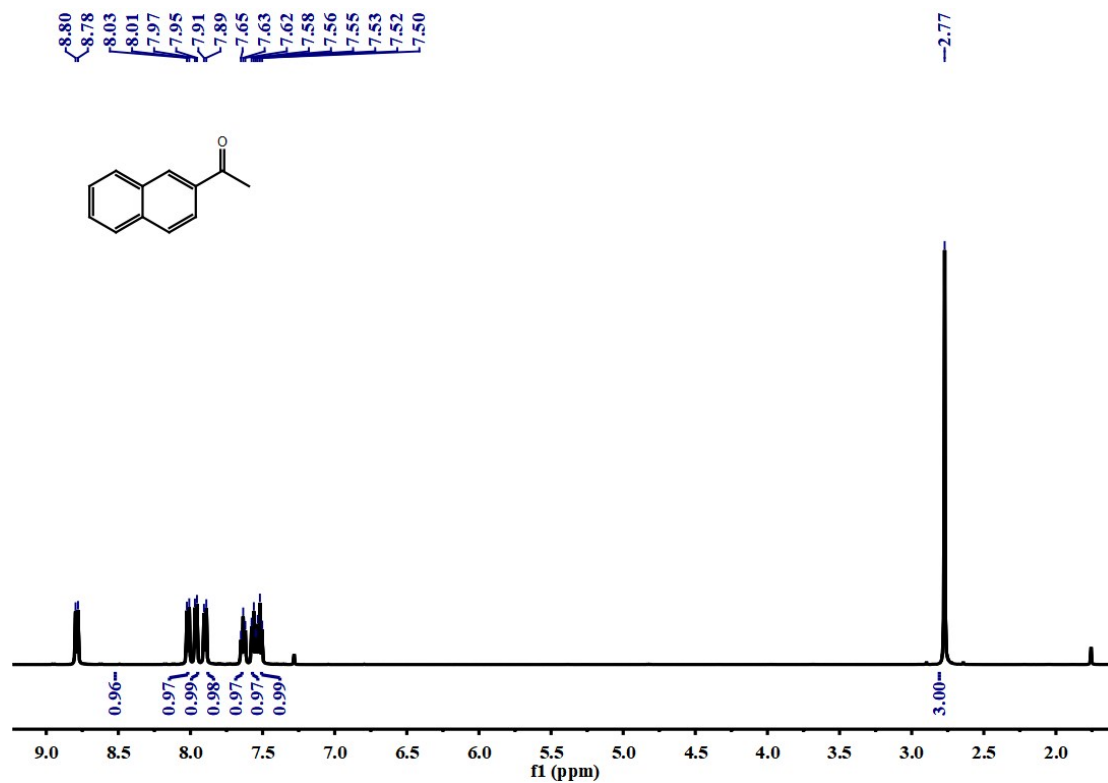
$^1\text{H}$  NMR spectra of 7u (500 MHz,  $\text{CDCl}_3$ )



$^1\text{H}$  NMR spectra of 7v (500 MHz,  $\text{CDCl}_3$ )

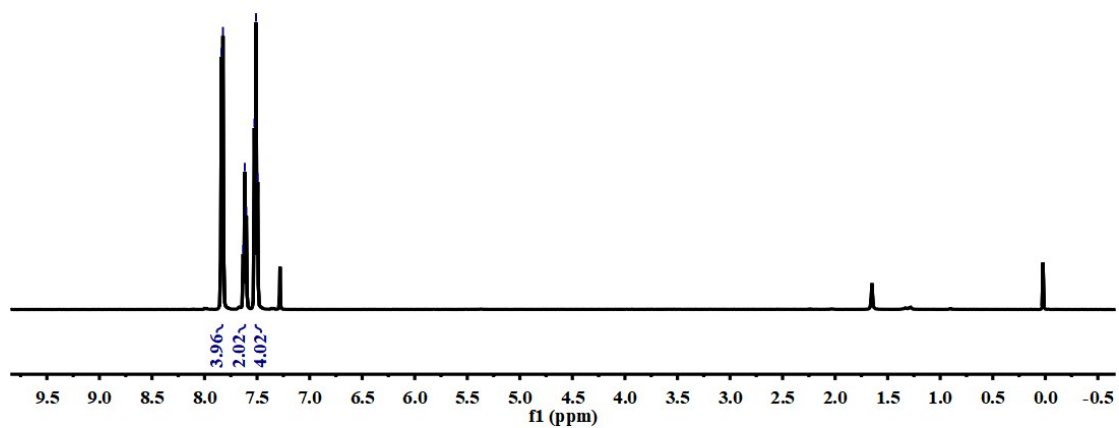
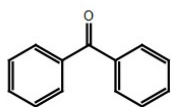


<sup>1</sup>H NMR spectra of 7w (500 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR spectra of 7x (500 MHz, CDCl<sub>3</sub>)

7.84  
7.82  
7.63  
7.62  
7.60  
7.53  
7.51  
7.49



<sup>1</sup>H NMR spectra of 7y (500 MHz, CDCl<sub>3</sub>)