Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

An Efficient Protocol for the Preparation of Aldehydes/Ketones and Imines from Aerobic Oxidation of Organic Halides and Amines by Inorganic-ligand Supported Iron catalyst

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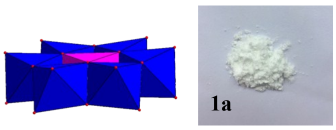
1. General experimental conditions.

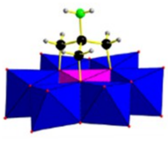
Fe-Anderson POM was prepared according to literature methods[1,2]. All reagents obtained from Sigma-Aldrich and Admas-beta were used without further purification. ^1H Nuclear Magnetic Resonance (^1HNMR) spectra were recorded on Bruker AVANCE III 500 MHz (500 MHz for proton) spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ or DMSO-d_6 as solvent in all cases, and chemical shifts were reported in parts per million (ppm, δ). FT-IR spectra were recorded on a Thermo fisher Nicolet 6700. 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× 30 m). Column chromatography was performed using 200-300 mesh base-washed silica gel.

2. Synthesis and characterizations of the catalyst.



1a: $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ ($Fe^{III}Mo_6$)

Figure S1 $(NH_4)_3[FeMo_6O_{18}(OH)_6]$



$[[N(C_4H_9)_4]_3[FeMo_6O_{18}(OH)_3\{(OCH_2)_3CR\}]$

1b: R=CH_3; **1c**: R=NH_2;

1d: R=NO_2; **1e**: R=CH_2OH

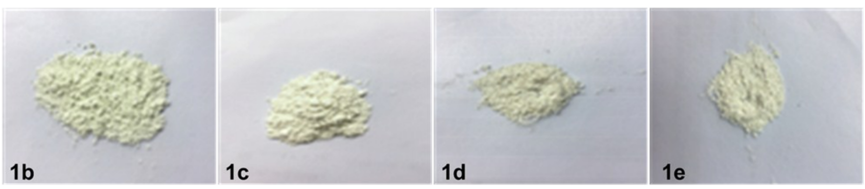


Figure S2 $[N(C_4H_9)_4]_3[FeMo_6O_{18}(OH)_3\{(OCH_2)_3CR\}]$

1b $[N(C_4H_9)_4]_3[FeMo_6O_{18}(OH)_3\{(OCH_2)_3CCH_3\}]$ was synthesized according to our previous report and the literature procedure[3-5]: $(NH_4)_3[FeMo_6O_{18}(OH)_6]\cdot 7H_2O$ (2.5g, 2.0mmol), $CH_3C(CH_2OH)_3$ (0.36g, 3.0mmol) and H_2O (20mL) was refluxed for 24h. After the solution was cooled down to room temperature, tetrabutyl ammonium bromide (2.0 g, 6.1 mmol) was added and still stirred for 1h. Then the large white solid (3.0 g) appeared and filtered off for use.

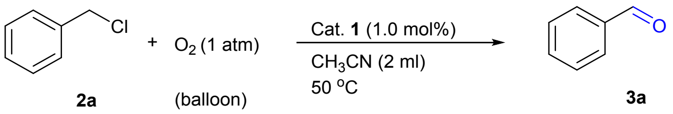
1c $[N(C_4H_9)_4]_3[FeMo_6O_{18}(OH)_3\{(OCH_2)_3CNH_2\}]$ was synthesized according to our previous report and the literature procedure[3-5]: $(NH_4)_3[FeMo_6O_{18}(OH)_6]\cdot 7H_2O$ (2.5g, 2.0mmol), $NH_2C(CH_2OH)_3\cdot HCl$ (0.47g, 3.0mmol) and H_2O (20mL) was refluxed for 24h. After the solution was cooled down to room temperature, tetrabutyl ammonium bromide (2.0 g, 6.1 mmol) was added and still stirred for 1h. Then the large white solid (2.8 g) appeared and filtered off for use.

1d $[N(C_4H_9)_4]_3[FeMo_6O_{18}(OH)_3\{(OCH_2)_3CNO_2\}]$ was synthesized according to our previous report and the literature procedure[3-5]: $(NH_4)_3[FeMo_6O_{18}(OH)_6]\cdot 7H_2O$ (2.5g, 2.0mmol), $NO_2C(CH_2OH)_3$ (0.45g, 3.0mmol) and H_2O (20mL) was refluxed for 24h. After the solution was cooled down to room temperature, tetrabutyl ammonium bromide (2.0 g, 6.1 mmol) was added and still stirred for 1h. Then the large white solid (2.5 g) appeared and filtered off for use.

1e $[N(C_4H_9)_4]_3[FeMo_6O_{18}(OH)_3\{(OCH_2)_3CCH_2OH\}]$ was synthesized according to our previous report and the literature procedure[3-5]: $(NH_4)_3[FeMo_6O_{18}(OH)_6]\cdot 7H_2O$ (2.5g, 2.0mmol), $CH_2OHC(CH_2OH)_3$(0.41g, 3.0mmol) and H_2O (20mL) was refluxed for 24h. After the solution was cooled down to room temperature, tetrabutyl ammonium bromide (2.0 g, 6.1 mmol) was added and still stirred for 1h. Then the large white solid (3.1 g) appeared and filtered off for use.

3. Optimization of reaction conditions

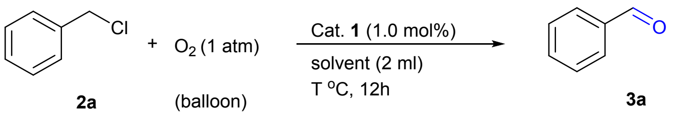
Table S1 Investigation of catalysts 1[a]



Entry	Cat.	Time(h)	Yield(%)[b]
1	-	24	<5
2	**1a**	12	93
3	**1b**	12	90
4	**1c**	12	85
5	**1d**	12	91
6	**1e**	12	90

[a] Reaction conditions: Cat. **1** (1.0 mol%), benzyl chloride (0.5 mmol), O_2 (1 atm), and CH_3CN (2 mL) at 50°C. [b] Yields were determined by GC and confirmed by GC-MS.

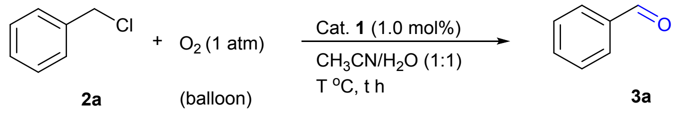
Table S2 Optimization of solvents [a]



Entry	Solvent	Temperature	Yield(%)[b]
1	MeCN	60°C	93
2	CH_2Cl_2	35°C	28
3	Toluene	60°C	33
4	Cyclohexane	60°C	15
5	Acetone	50°C	55
6	THF	60°C	68
7	Dioxane	60°C	82
8	DMF	60°C	63
9	H_2O	60°C	87
10	MeCN:H_2O=1:1	60°C	99

[a] Reaction conditions: Cat. **1** (1.0 mol%), benzyl chloride (0.5 mmol), O_2 (1 atm), and solvent (2 mL), 12h. [b] Yields were determined by GC and confirmed by GC-MS.

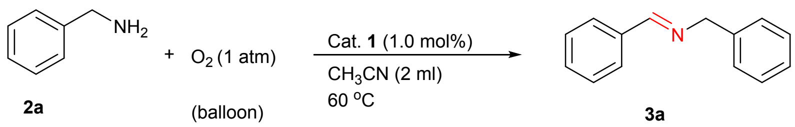
Table S3 Optimization of reaction conditions



Entry	Temperature	Time(h)	Yield(%)[b]
1	r.t.	24	<5
2	40	12	79
3	50	12	90
4	60	12	99
5	70	12	99

[a] Reaction conditions: Cat. **1** (1.0 mol%), benzyl chloride (0.5 mmol), O_2 (1 atm), and CH_3CN (1 mL), H_2O (1 mL). [b] Yields were determined by GC and confirmed by GC-MS.

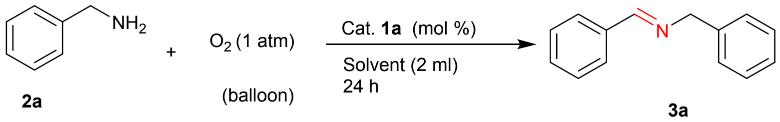
Table S4 Investigation of catalysts 1[a]



Entry	Cat.	Time(h)	Sel.(%)[b]	Yield(%)[b]
1	-	48	-	-
2	**1a**	24	99	92
3	**1b**	24	94	91
4	**1c**	24	88	86
5	**1d**	24	98	90
6	**1e**	24	97	90
7	**$Fe_2(SO_4)_3$**	48	-	-
8	**$(NH_4)_6Mo_7O_{24}$**	48	-	-

[a] Reaction conditions: Cat. **1** (1.0 mol%), amine (0.5 mmol), O_2 (1 atm), and CH_3CN (2 mL) at 60°C. [b] Selectivity and yields were determined by GC and confirmed by GC-MS.

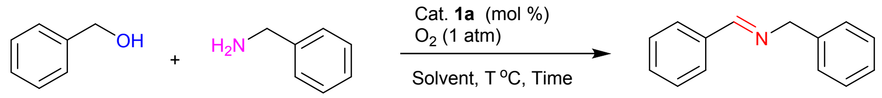
Table S5 Optimization of reaction conditions[a]



Entry	Solvent	Cat. (mol %)	Sel. (%)[b]	Yield(%)[b]
1	MeCN	1	96	95
2	Toluene	1	69	55
3	CH_2Cl_2	1	68	63
4	MeOH	1	85	81
5	THF	1	90	82
6	EA	1	87	79
7	dioxane	1	92	88
8	MeCN	0.1	80	78
9	MeCN	0.5	88	82
10	MeCN	2	90	88
11[c]	MeCN	1	94	85
12[d]	MeCN	1	99	98
13[e]	MeCN	1	93	90
14[f]	MeCN	1	-	-
15[g]	MeCN	1	95	92

[a] Reaction conditions: amines (0.5 mmol), cat. **1a** (1.0 mol%), O_2 balloon (1 atm), and solvent (2.0 mL). [b] Yield and selectivity were determined by GC and confirmed by GC-MS. [c] at 50 °C. [d] at 70 °C. [e] Reactions were carried out under atmospheric air. [f] Reactions were carried out under N_2 atmosphere. [g] Reactions were carried out with H_2O_2 as the sole oxidant.

Table S6 Optimization of reaction conditions[a]



Entry	Solvent	Cat. (mol %)	Time (h)	T (°C)	Yield (%)[b]
1	CH_3CN	1	12	50	95
2	Toluene	1	12	50	76
3	CH_2Cl_2	1	12	50	60
5	THF	1	12	50	78
6	EA	1	12	50	55
7	dioxane	1	12	50	82
8	CH_3CN	0.1	12	50	66
9	CH_3CN	0.5	12	50	89
11	CH_3CN	1	12	60	88
12	CH_3CN	1	12	30	53
13	CH_3CN	1	6	50	70
14	CH_3CN	1	24	50	90
15	CH_3CN	1	36	50	72

[a] Reaction conditions: Cat **1a** (1.0 mol%), amine (0.5 mmol), alcohol (0.5 mmol), O_2 balloon (1 atm), CH_3CN (3 mL).[b] Conversion and selectivity were determined by GC and confirmed by GC-MS.

4. Recycling experiments of the catalyst for oxidative coupling reaction

After the oxidative coupling experiment, the iron catalyst **1a** were precipitated by adding diethyl ether to the reaction system, and then recovered for reuse. The recovered catalyst was characterized by IR (Fig. S3).

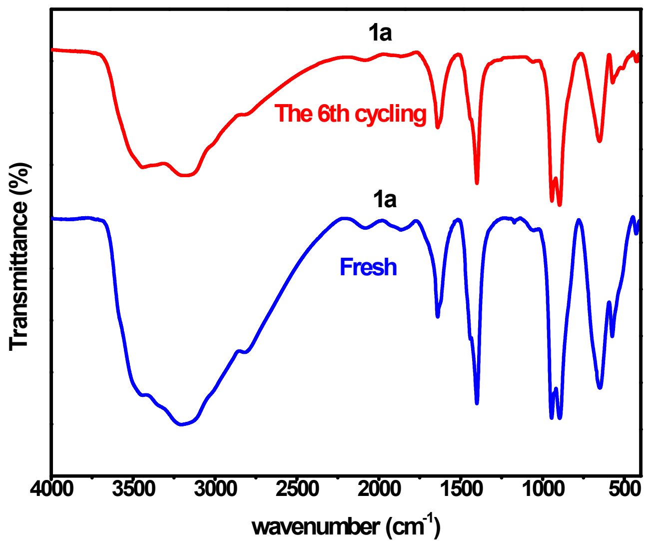


Figure S3 IR spectra of the catalyst before and after reaction

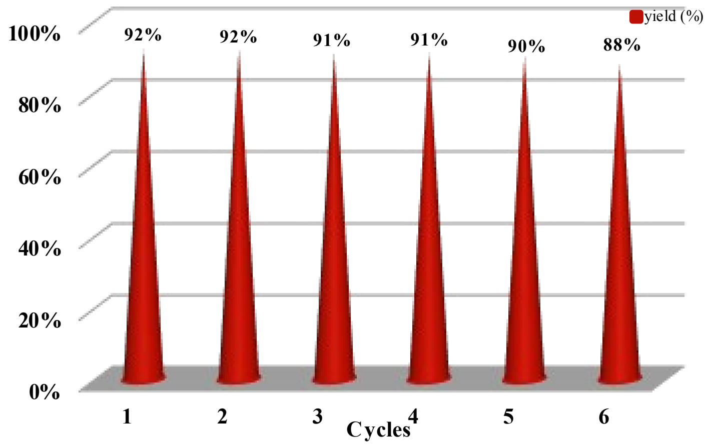


Figure S4 Recycling experiments of catalyst, the first time reaction condition: Cat. **1a** (1.0 mol%), amine (20 mmol), O_2 balloon (1.0 atm), CH_3CN (10 mL) at 70 ^{o}C for 24h.

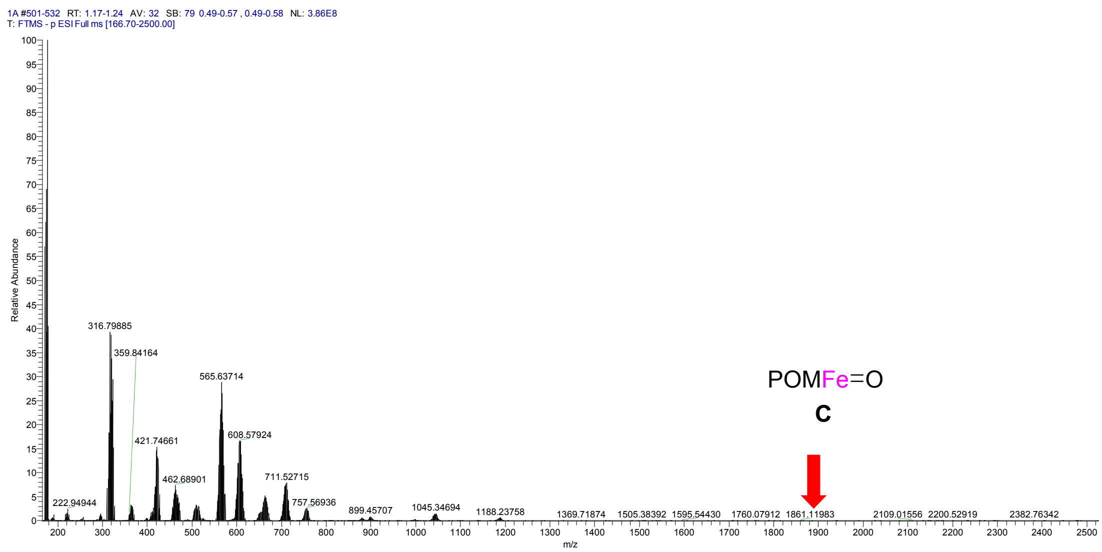
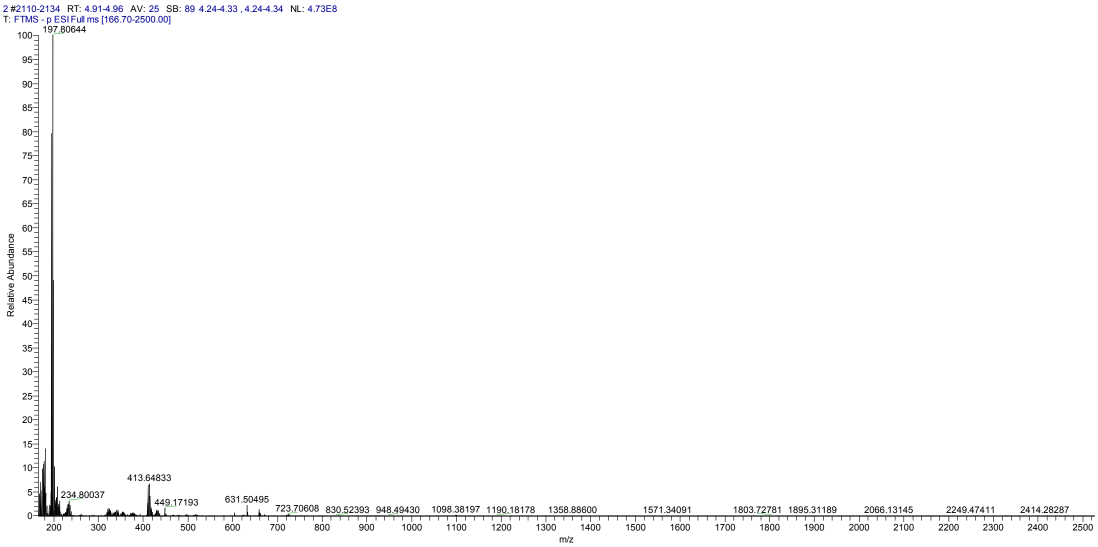
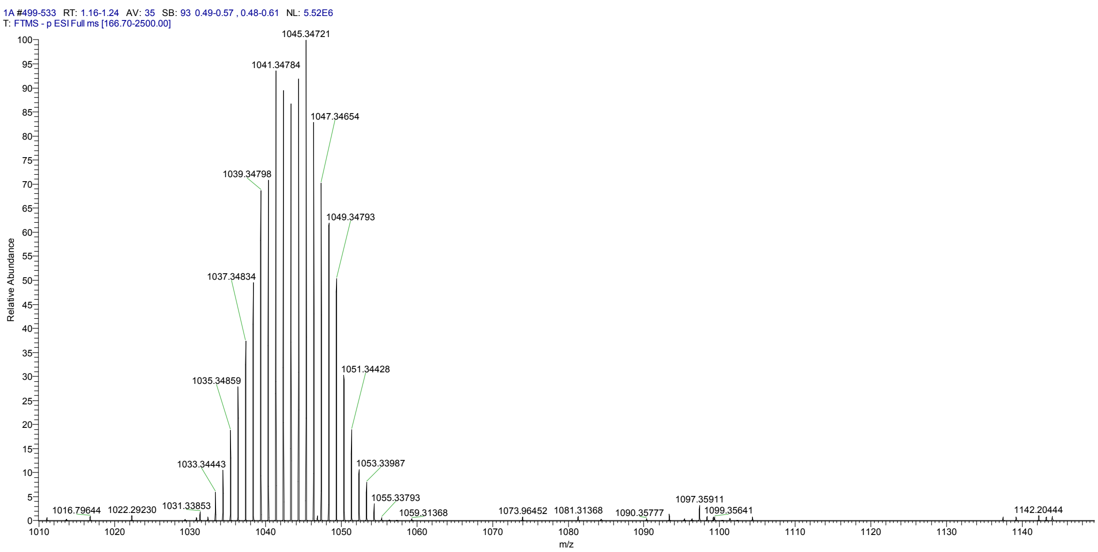


Figure S5 ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$



FigureS6 ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$ + H_2O_2



FigureS7 Zoom the area of ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$, (m/z =1010-1500, $\{NH_4H[FeMo_6O_{24}H_6]\}^{1-}$ = 1043.34 g/mol)

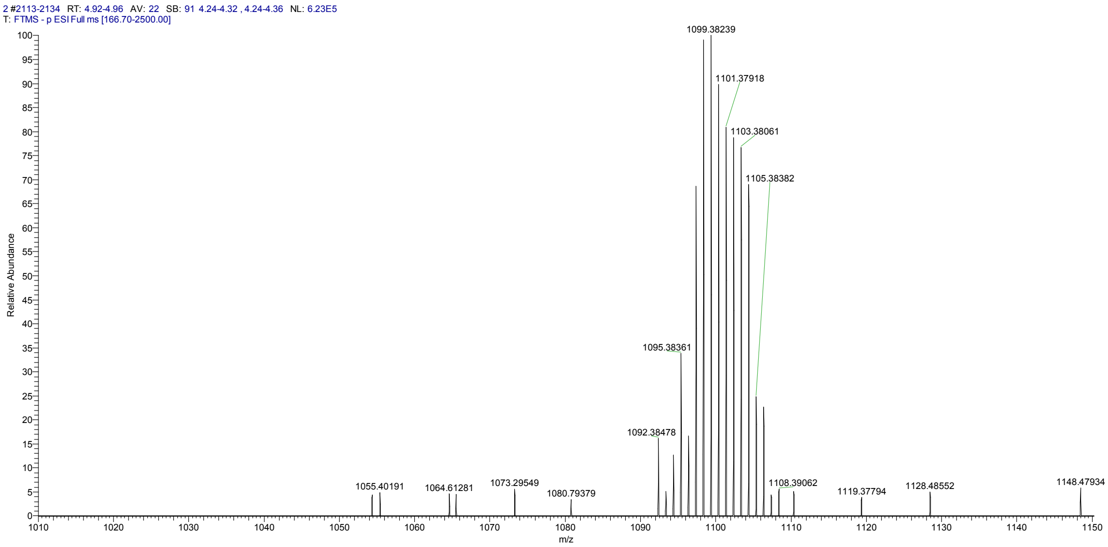
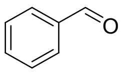
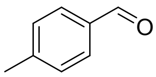


Figure S8 Zoom the area of ESI-MS of $(NH_4)_3[FeMo_6O_{18}(OH)_6]$+$O_2$, (m/z = 1010-1500, $\{Na_2[FeMo_6O_{24}H_6]+O\}^{1-}\cdot H_2O$ = 1100.61 g/mol)

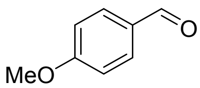
5. Characterizations of typical products



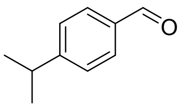
Benzaldehyde (3a): Light yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.15 (s, 1H), 8.05 – 7.98 (m, 2H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 2H).



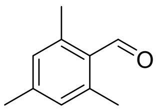
4-methylbenzaldehyde (3b): Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 2.49 (s, 3H).



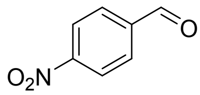
4-methoxybenzaldehyde (3c): Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 3.98 (s, 3H).



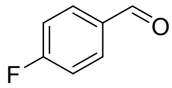
4-isopropylbenzaldehyde (3d): Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.54 (t, *J* = 15.2 Hz, 2H), 3.16 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 6H).



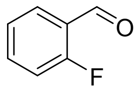
4-isopropylbenzaldehyde (3e): Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.73 (s, 1H), 7.07 (s, 2H), 2.76 (s, 6H), 2.49 (s, 3H).



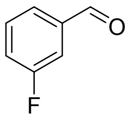
4-nitrobenzaldehyde (3f): White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.41 (d, *J* = 8.6 Hz, 2H), 8.09 (d, *J* = 8.7 Hz, 2H).



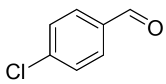
4-nitrobenzaldehyde (3g): Light yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.02 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.32 (t, *J* = 8.5 Hz, 2H).



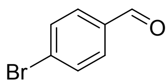
2-fluorobenzaldehyde (3h): Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.51 (d, *J* = 1.8 Hz, 1H), 8.11 – 7.93 (m, 1H), 7.85 – 7.68 (m, 1H), 7.52 – 7.21 (m, 2H).



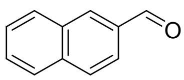
3-fluorobenzaldehyde (3i): Yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.14 (d, *J* = 1.7 Hz, 1H), 7.93 – 7.79 (m, 1H), 7.69 (ddd, *J* = 13.0, 7.9, 6.3 Hz, 2H), 7.58 – 7.41 (m, 1H).



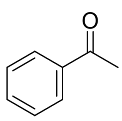
4-chlorobenzaldehyde (3j): Light yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H).



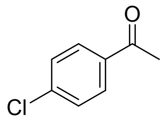
4-bromobenzaldehyde (3k): White soild. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.72 (dd, *J* = 32.8, 8.4 Hz, 4H).



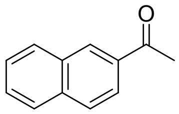
2-naphthaldehyde (3l): Light yellow soild. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 8.35 (s, 1H), 8.09 – 7.83 (m, 4H), 7.62 (dt, *J* = 28.2, 7.4 Hz, 2H).



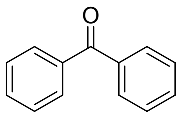
Acetophenone (3n): Light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.05 (m, 2H), 7.78 – 7.50 (m, 3H), 2.83 – 2.68 (m, 3H).



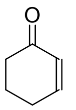
1-(4-chlorophenyl)ethan-1-one (3o): Light yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 – 7.84 (m, 2H), 7.67 – 7.50 (m, 2H), 2.73 (d, *J* = 1.1 Hz, 3H).



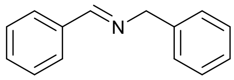
1-(naphthalen-2-yl)ethan-1-one (3p): White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 – 8.90 (m, 1H), 8.20 – 7.95 (m, 3H), 7.84 – 7.51 (m, 3H), 3.08 – 2.59 (m, 3H).



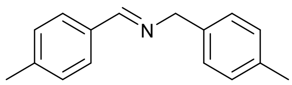
Benzophenone (3q): White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.4 Hz, 4H), 7.78 (t, *J* = 7.4 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 4H).



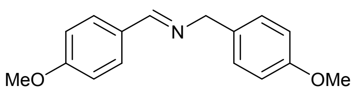
Cyclohex-2-en-1-one (3r): Light yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.03 (m, 1H), 6.14 – 6.05 (m, 1H), 2.49 (ddd, *J* = 27.6, 7.1, 4.2 Hz, 4H), 2.19 – 1.99 (m, 2H).



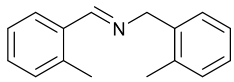
***N*-benzyliden-1-phenylmethanamine (5a):** Yellow oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.91 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.56 – 7.50 (m, 3H), 7.49 – 7.42 (m, 4H), 7.38 (td, *J* = 5.1, 3.0 Hz, 1H), 4.93 (s, 2H). Data in accordance with that previously published[6-11].



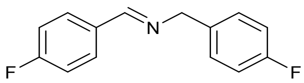
N-(4-methylbenzylidene)-1-(p-tolyl)methanamine (5b): White solid.^{1}H NMR (500MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 4H), 7.18 (s, 2H), 4.79 (s, 2H), 2.40 (s, 3H), 2.36 (s, 3H).Data in accordance with that previously published[6-11].



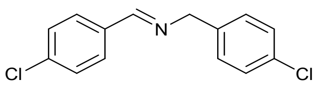
N-(2-methylbenzylidene)-1-(o-tolyl)methanamine (5c): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.34 (d, J = 7.1 Hz, 3H), 7.29 (d, J = 6.5 Hz, 1H), 7.21 (d, J = 4.6 Hz, 3H), 4.87 (s, 2H), 2.55 (s, 3H), 2.44 (s, 3H). Data in accordance with that previously published[6-11].



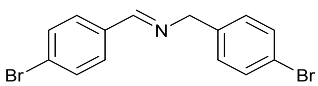
N-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (5d): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.23 – 7.19 (m, 1H), 6.96 – 6.79 (m, 5H), 4.71 (s, 2H), 3.81 (s, 3H), 3.77 (s, 3H).Data in accordance with that previously published[6-11].



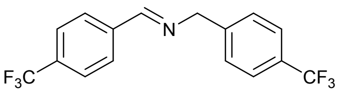
1-phenyl-N-(1-phenylethyl)ethan-1-imine (5e): Yellow oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.31 – 7.29 (m, 3H), 7.19 – 7.12 (m, 5H), 4.76 (q, *J* = 6.6 Hz, 1H), 2.19 (d, *J* = 5.8 Hz, 3H), 1.47 (d, *J* = 6.6 Hz, 3H). Data in accordance with that previously published[6-11].



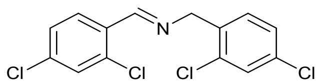
N-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (5f): Yellow oil. ^{1}H NMR (501 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.70 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.22 (dd, *J* = 8.6, 5.7 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 6.96 – 6.92 (m, 2H), 4.69 (s, 2H). Data in accordance with that previously published[6-11].



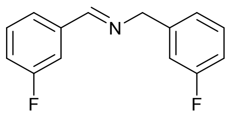
N-(3-fluorobenzyl)-1-(3-fluorophenyl)methanimine (5g): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.59 – 7.52 (m, 2H), 7.41 (dt, *J* = 13.5, 6.8 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.04 (s, 1H), 6.96 (td, *J* = 8.3, 4.3 Hz, 2H), 4.83 (s, 2H). Data in accordance with that previously published[6-11].



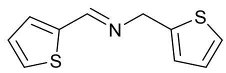
N-(4-chlorobenzylidene)-1-(4-chlorophenyl)methanamine (5h): White solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.79 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.32 (dd, *J* = 8.6, 5.7 Hz, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 7.05 – 7.02 (m, 2H), 4.79 (s, 2H). Data in accordance with that previously published[6-11].



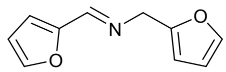
N-(2, 4-dichlorobenzyl)-1-(2,4-dichlorophenyl)methanimine (5i): Yellow oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.41 (dd, *J* = 3.8, 2.1 Hz, 2H), 7.36 (d, *J* = 2.2 Hz, 1H), 7.30 (d, *J* = 3.9 Hz, 1H), 7.23 (d, *J* = 1.8 Hz, 1H), 4.87 (s, 2H).Data in accordance with that previously published[6-11].



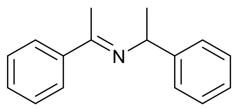
N-(4-bromobenzyl)-1-(4-bromophenyl)methanimine (5j): White solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 8.5 Hz, 4H), 4.74 (s, 2H). Data in accordance with that previously published[6-11].



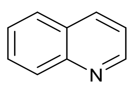
N-(4-(trifluoromethyl)benzyl)-1-(4-(trifluoromethyl)phenyl)methanimine (5K): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.54 (s, 2H), 7.39 (d, *J* = 6.9 Hz, 2H), 4.83 (s, 2H). Data in accordance with that previously published[6-11].



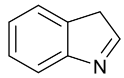
1-(thiophen-2-yl)-N-(thiophen-2-ylmethyl)methanimine (5l): Yellow oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.44 (s, 1H), 7.30 (t, *J* = 8.5 Hz, 1H), 6.72 (d, *J* = 3.3 Hz, 1H), 6.40 (dd, *J* = 3.3, 1.7 Hz, 1H), 6.28 – 6.24 (m, 1H), 6.20 (d, *J* = 3.0 Hz, 1H), 4.68 (s, 2H).Data in accordance with that previously published[6-11].



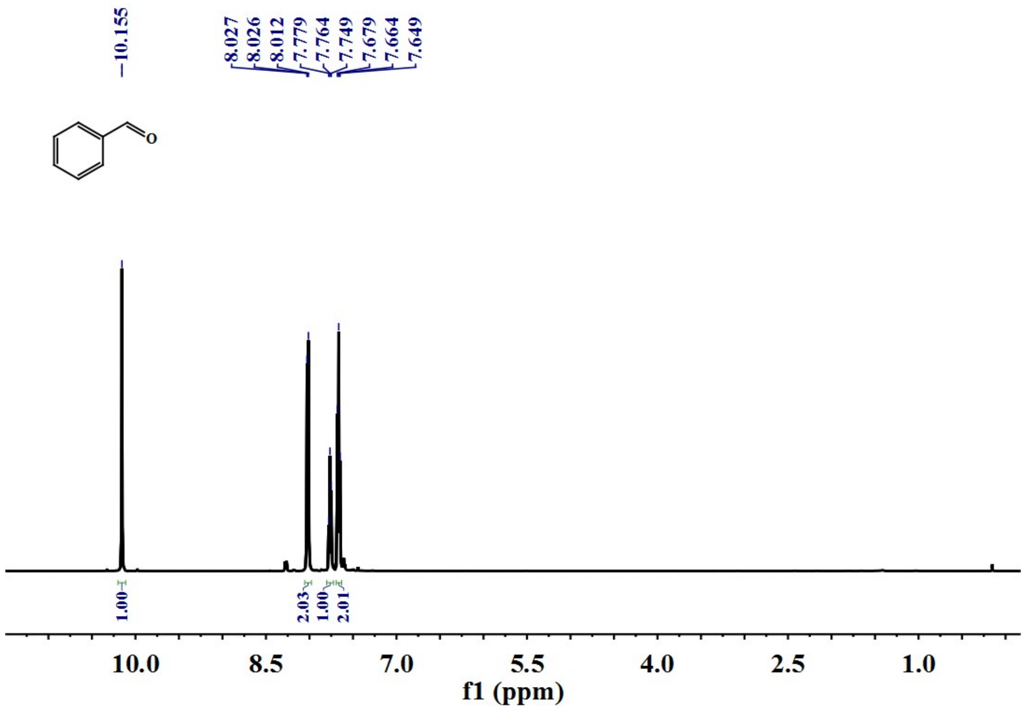
1-(furan-2-yl)-N-(furan-2-ylmethyl)methanimine (5m): Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.31 (s, 1H), 6.72 (d, *J* = 3.3 Hz, 1H), 6.41 (dd, *J* = 3.3, 1.7 Hz, 1H), 6.28 – 6.24 (m, 1H), 6.23 – 6.16 (m, 1H), 4.69 (s, 2H).Data in accordance with that previously published[6-11].



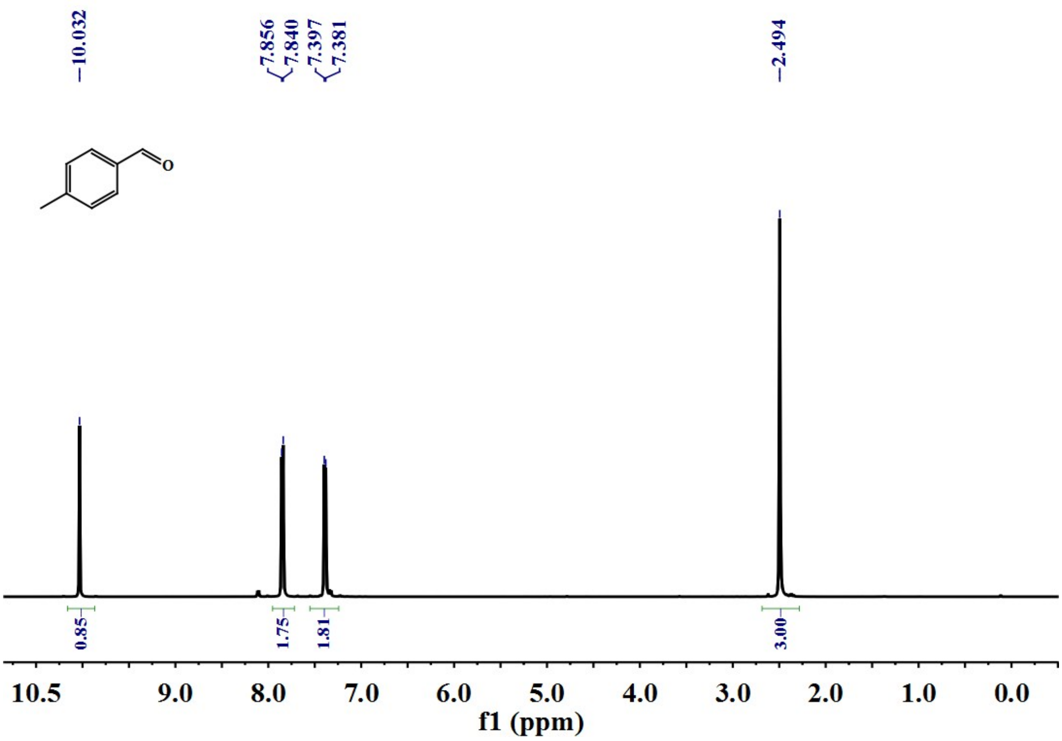
Quinoline (5n): Colourless oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 4.1, 1.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.58 – 7.45 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 8.3, 4.2 Hz, 1H).Data in accordance with that previously published[6-11].



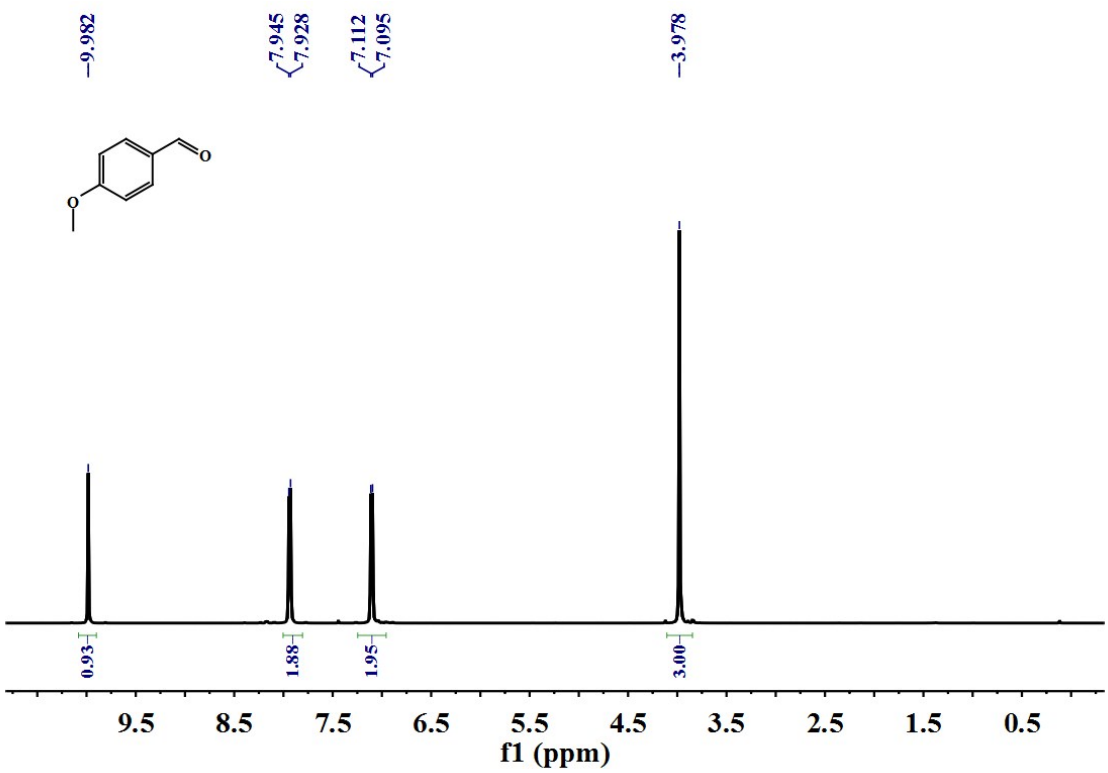
3H-indole (5o): white solid.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.14 (m, 3H), 6.63 (s, 1H).Data in accordance with that previously published[6-11].



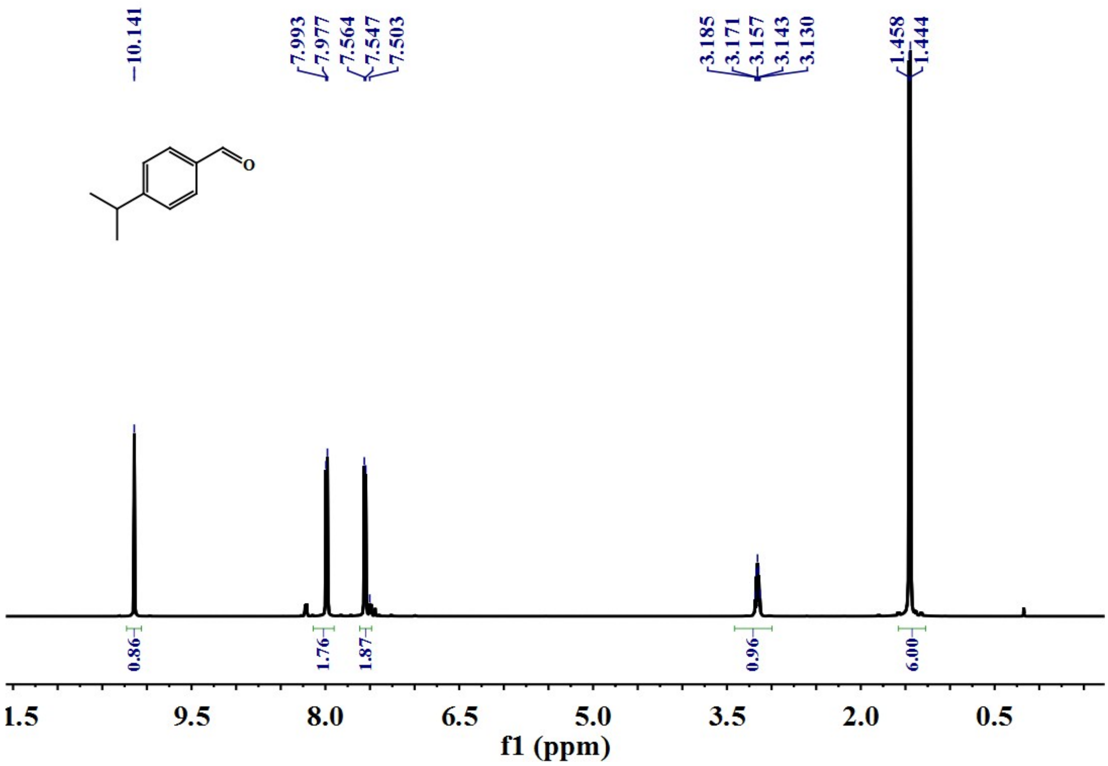
^{1}H NMR spectra of 3a (500 MHz, $CDCl_3$)



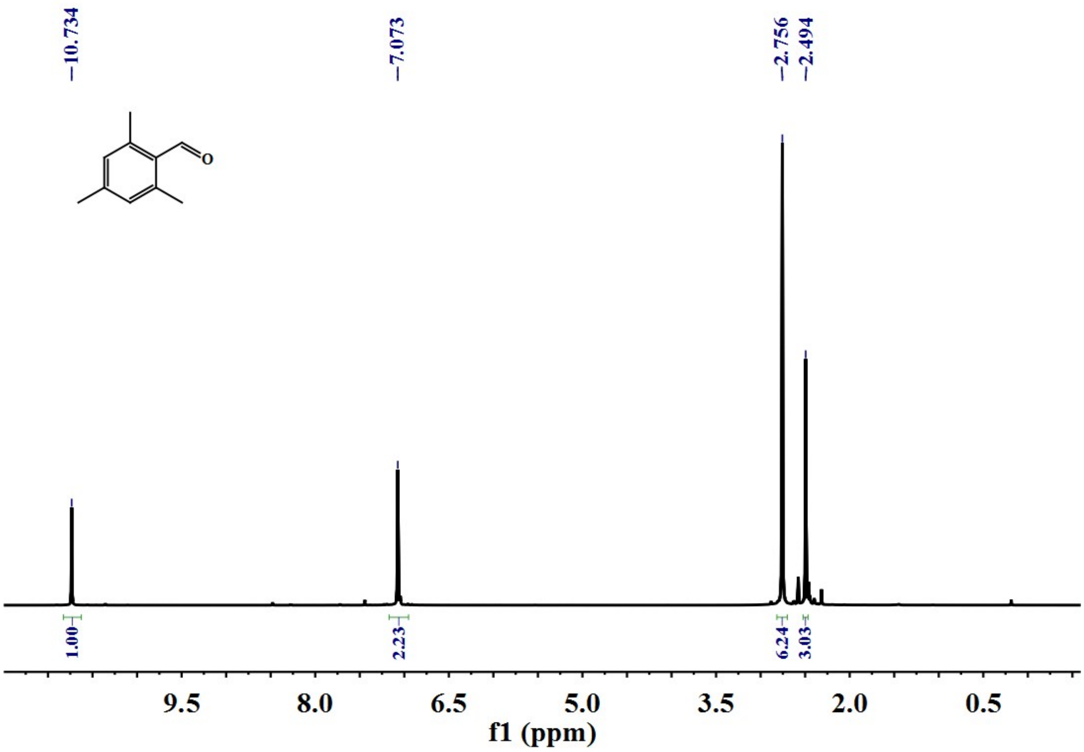
^{1}H NMR spectra of **3b** (500 MHz, $CDCl_3$)



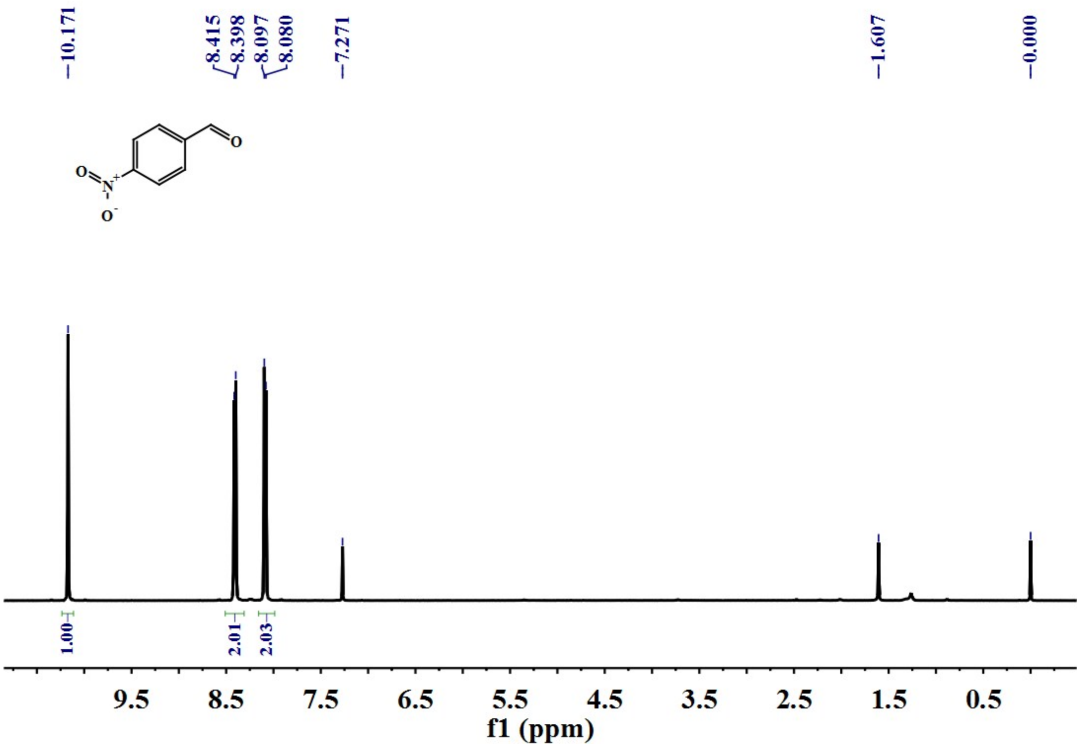
^{1}H NMR spectra of **3c** (500 MHz, $CDCl_3$)



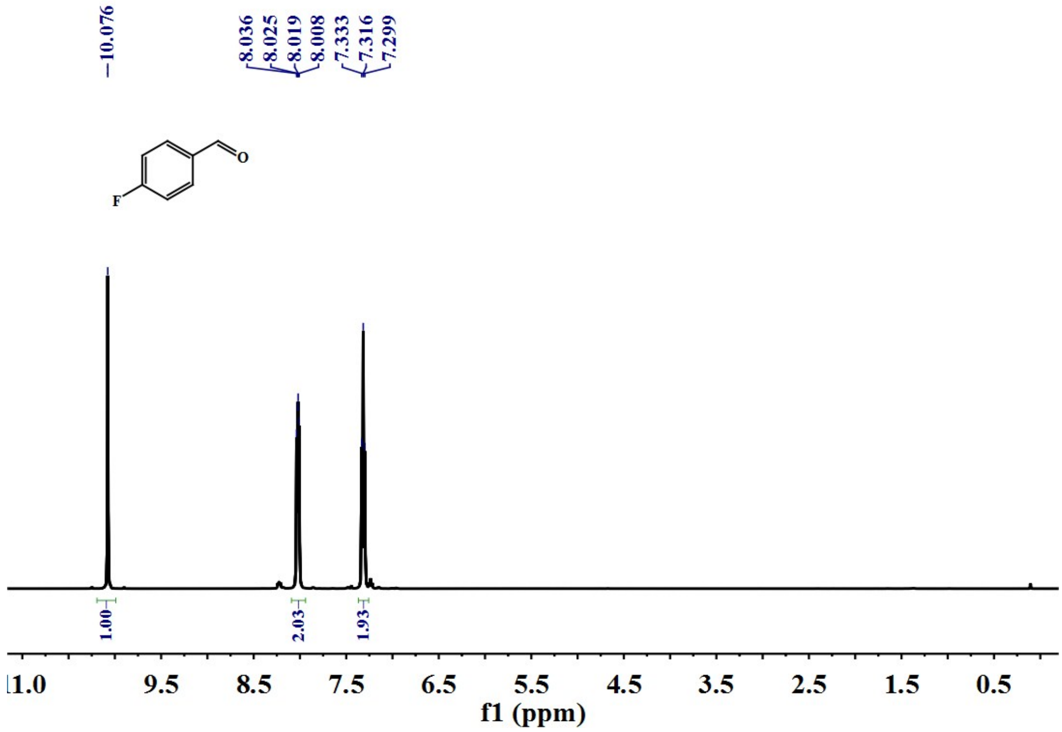
[1]H NMR spectra of **3d** (500 MHz, $CDCl_3$)



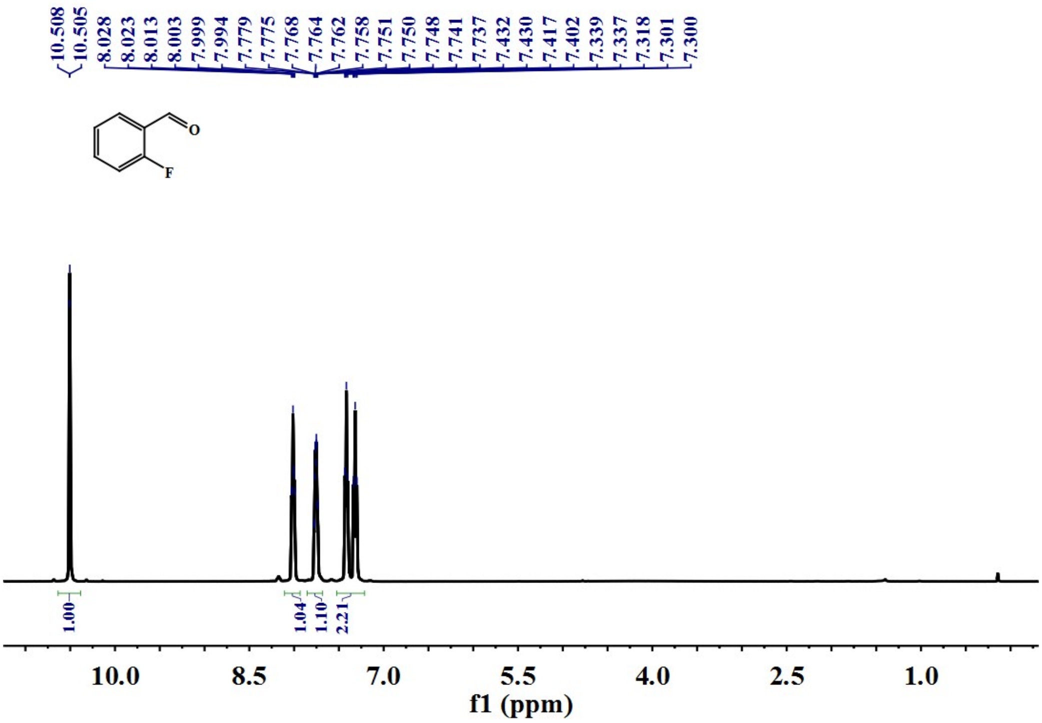
[1]H NMR spectra of **3e** (500 MHz, $CDCl_3$)



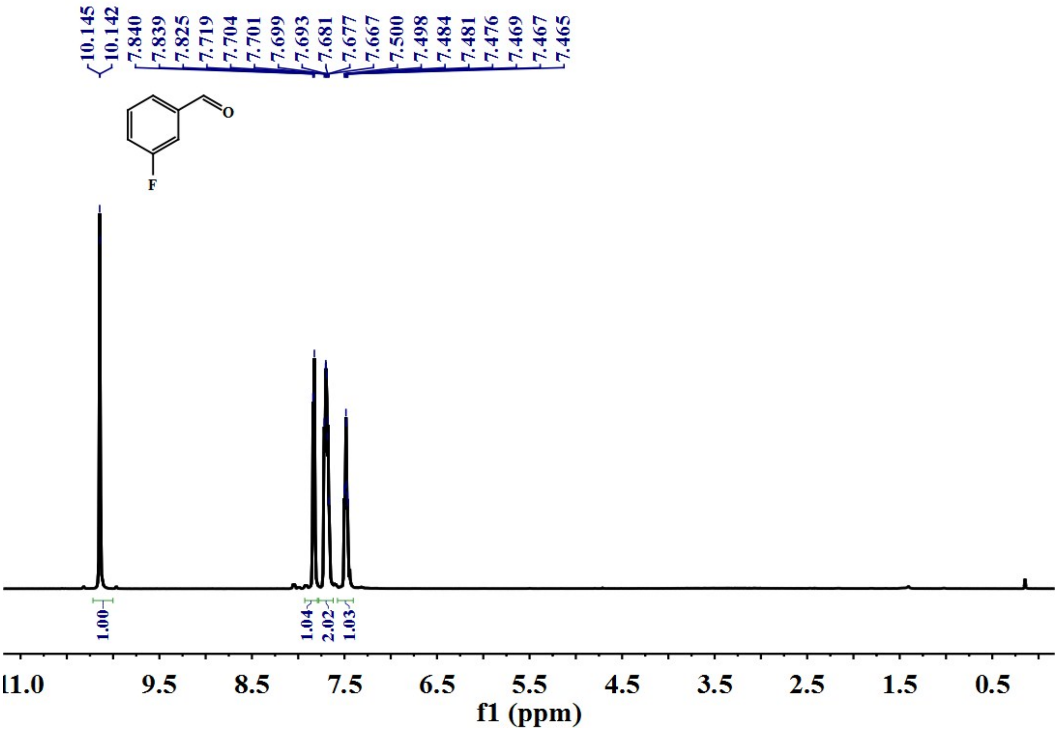
^{1}H NMR spectra of 3f (500 MHz, $CDCl_3$)



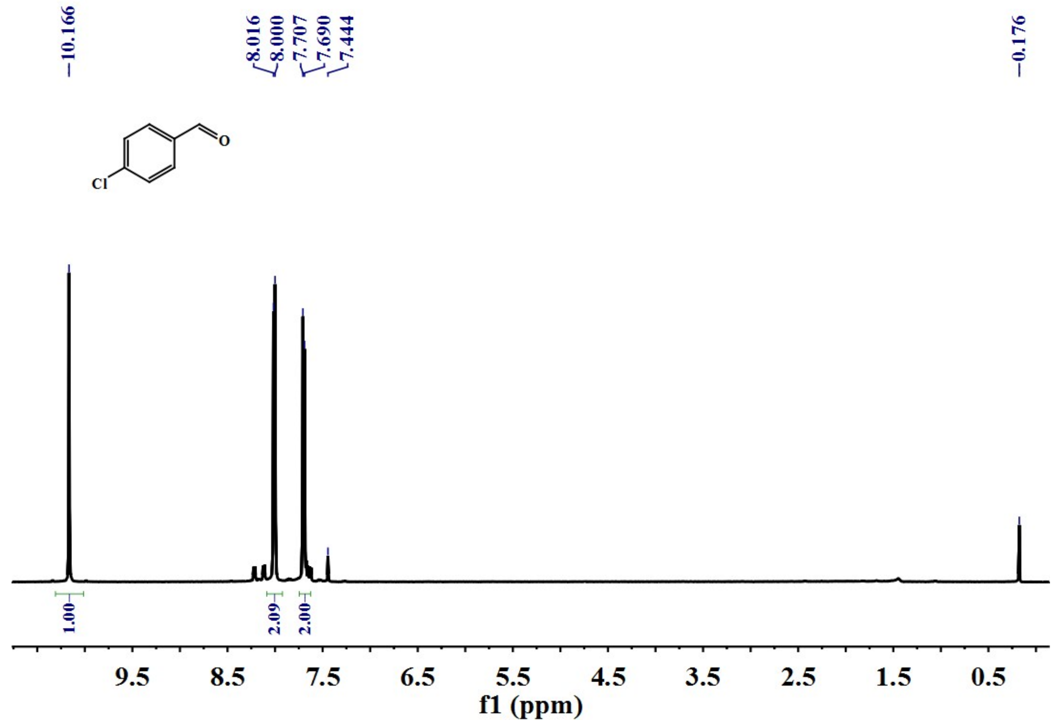
^{1}H NMR spectra of 3g (500 MHz, $CDCl_3$)



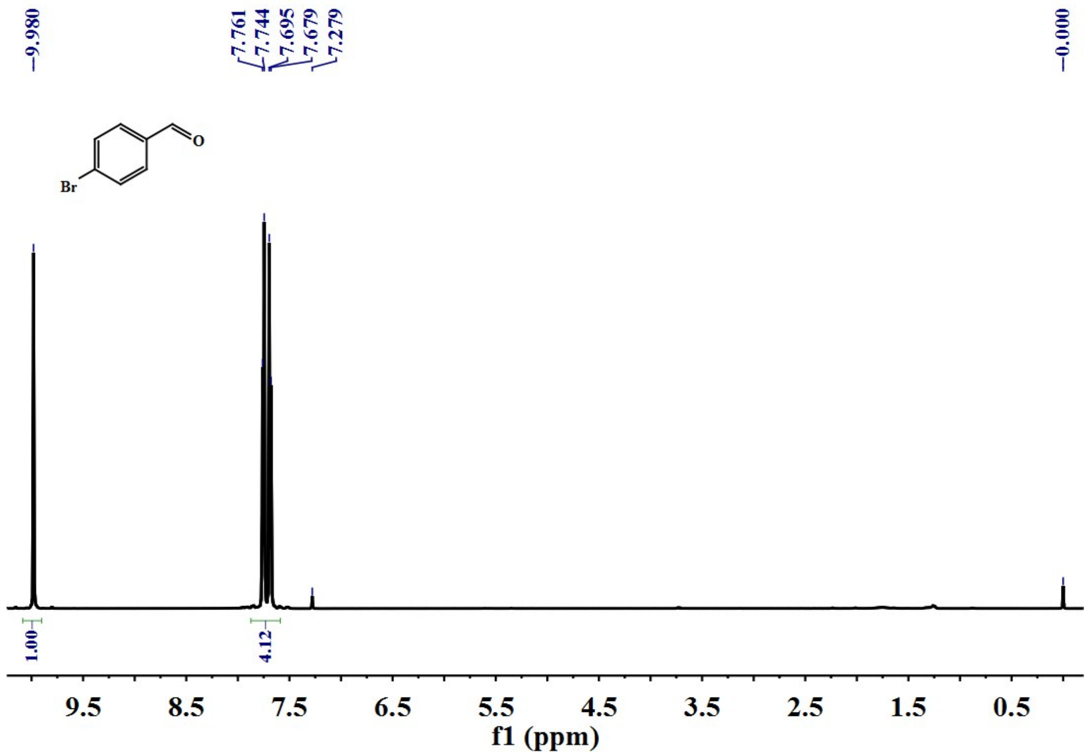
^{1}H NMR spectra of **3h** (500 MHz, $CDCl_3$)



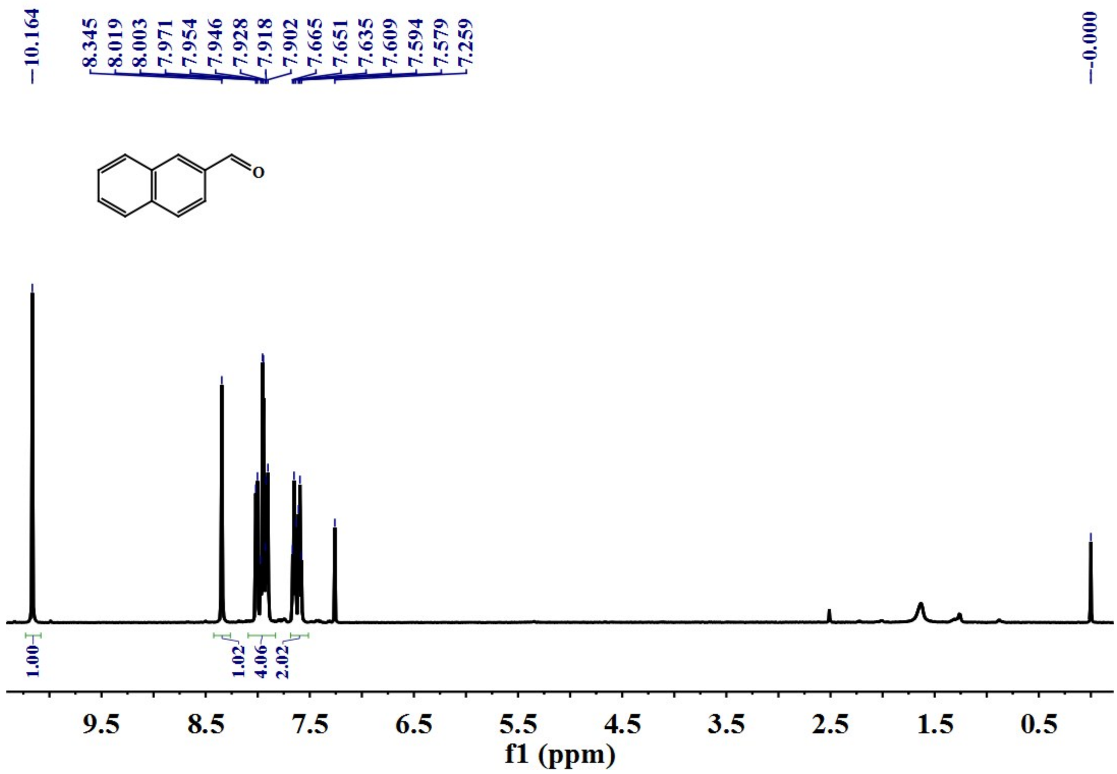
^{1}H NMR spectra of **3i** (500 MHz, $CDCl_3$)



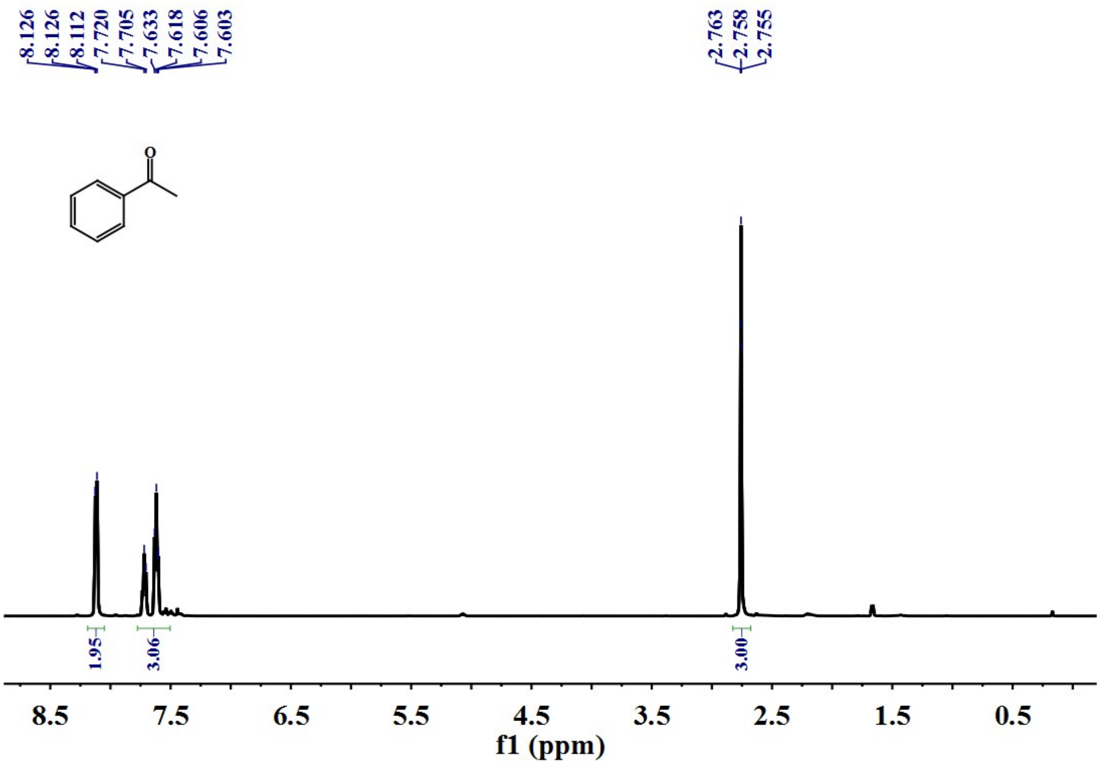
¹H NMR spectra of 3j (500 MHz, $CDCl_3$)



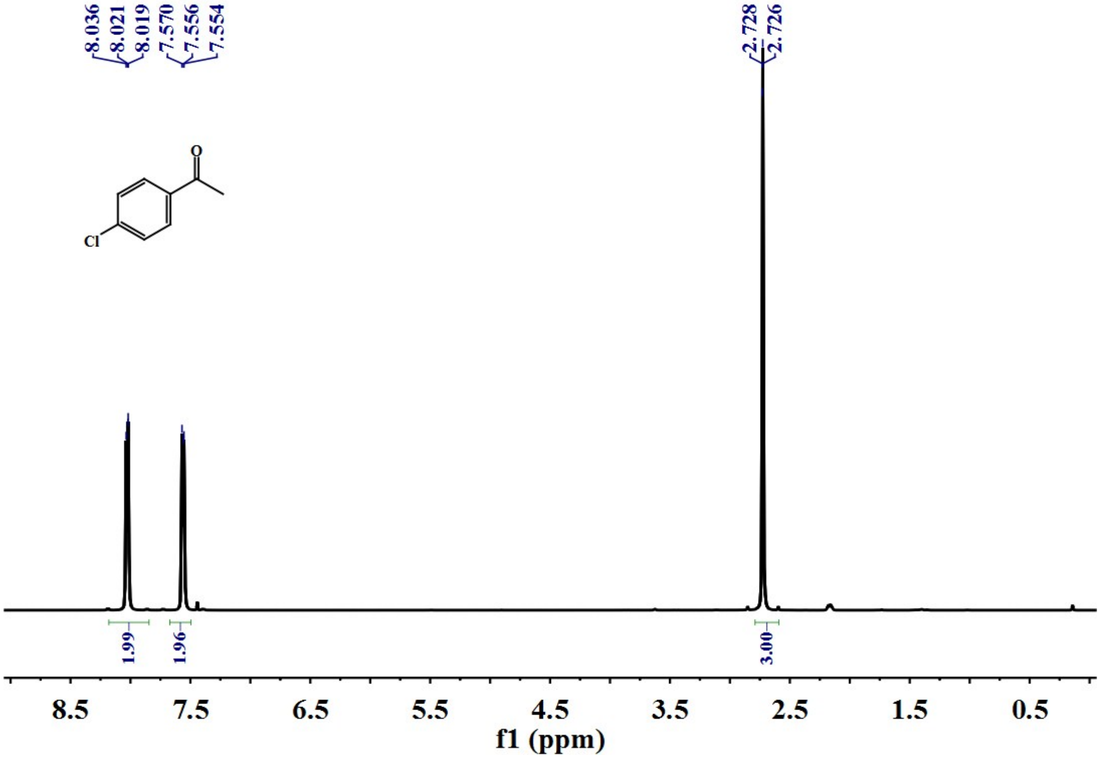
¹H NMR spectra of 3k (500 MHz, $CDCl_3$)



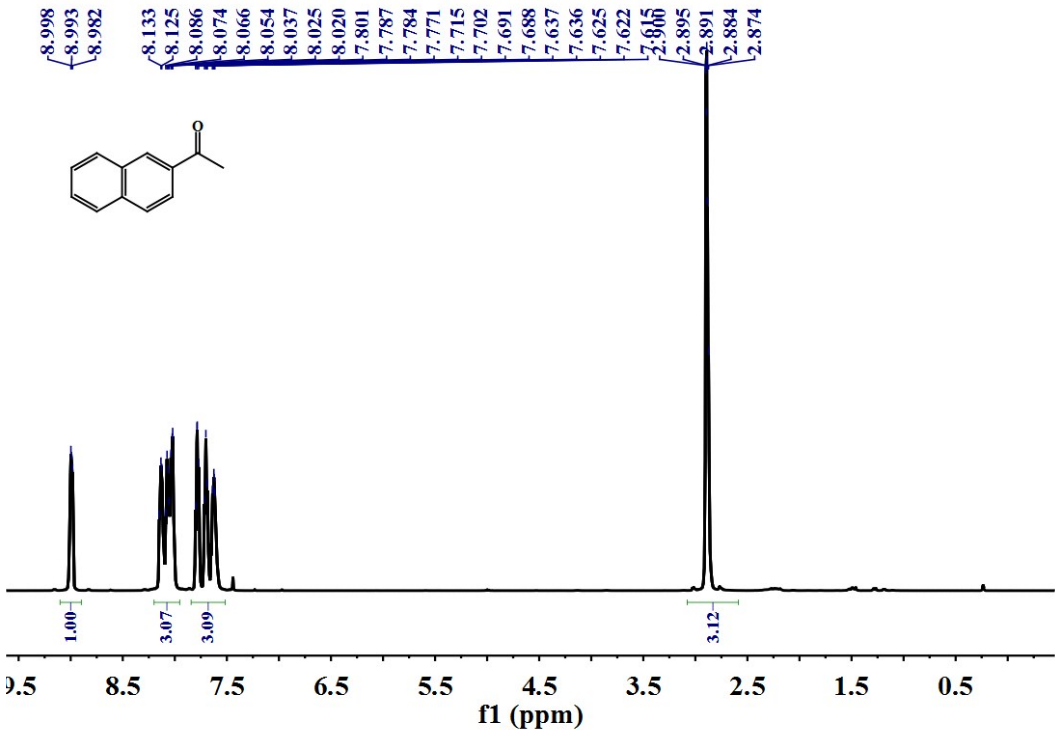
^{1}H NMR spectra of **3l** (500 MHz, $CDCl_3$)



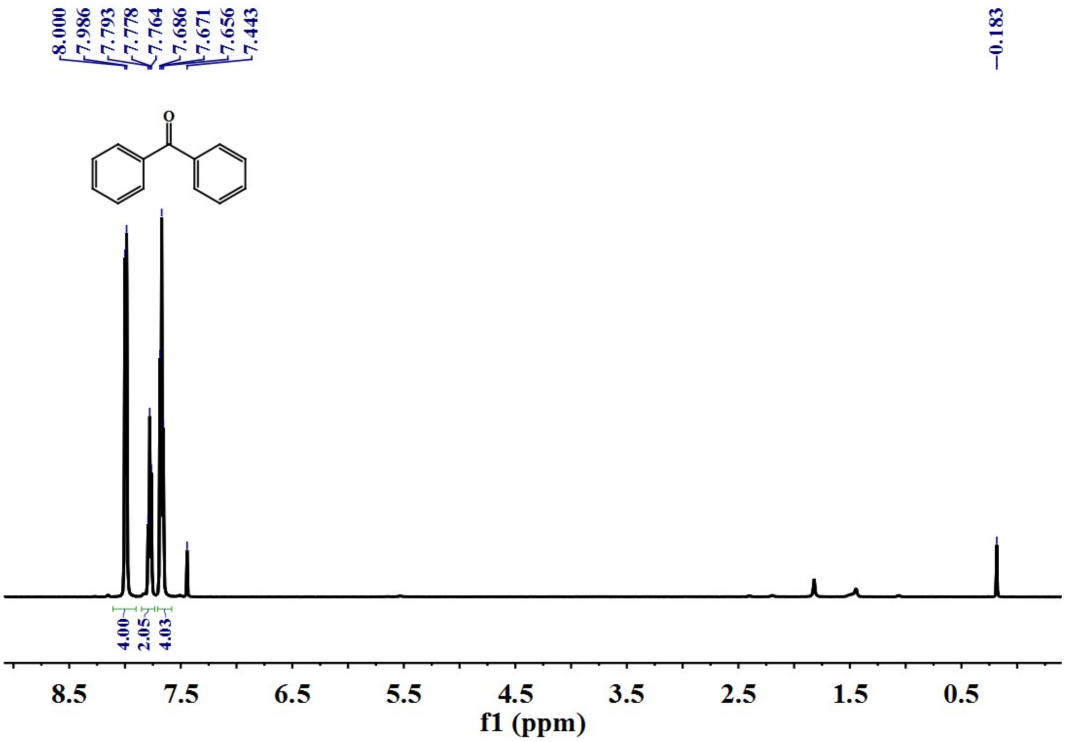
^{1}H NMR spectra of **3n** (500 MHz, $CDCl_3$)



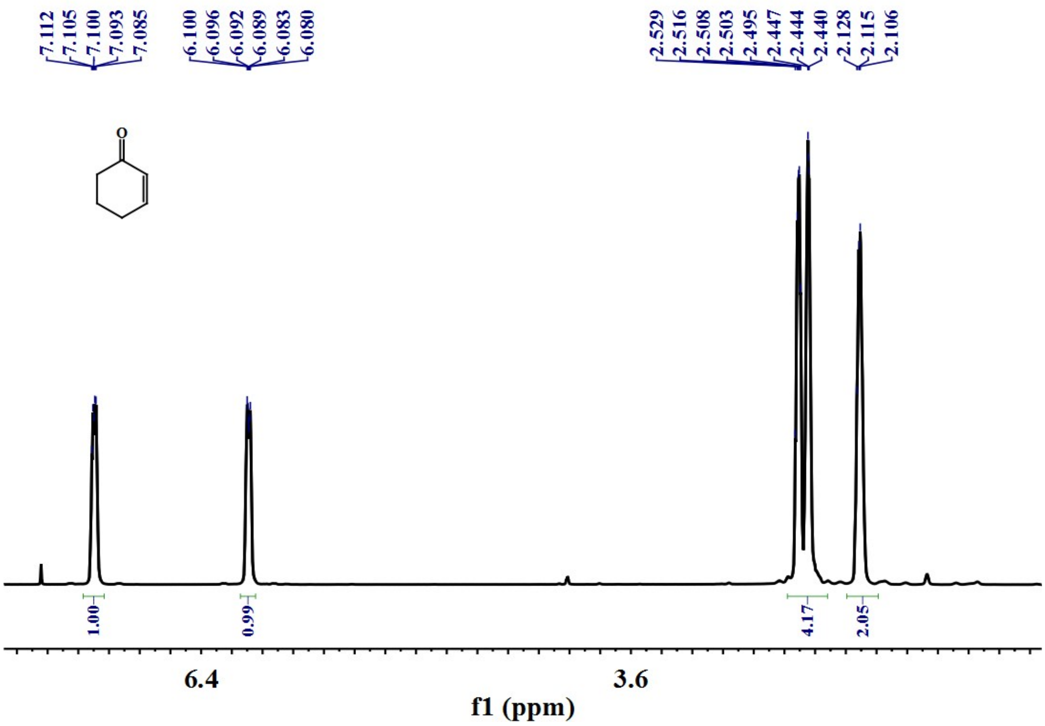
^{1}H NMR spectra of **3o** (500 MHz, $CDCl_3$)



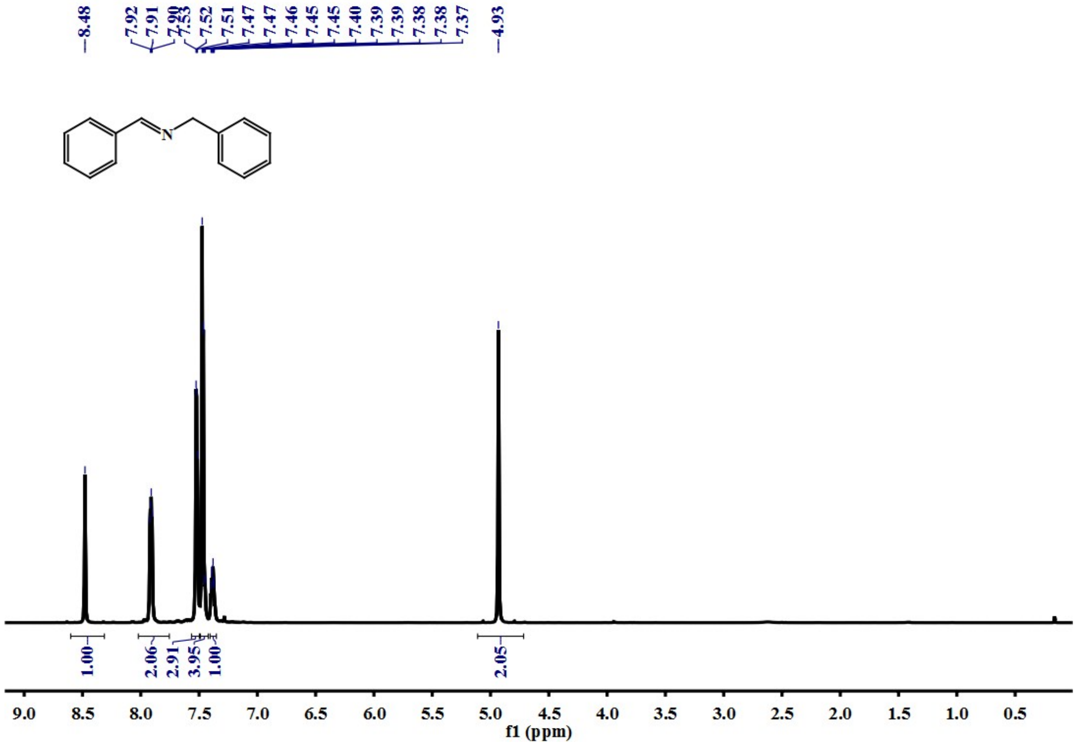
^{1}H NMR spectra of **3p** (500 MHz, $CDCl_3$)



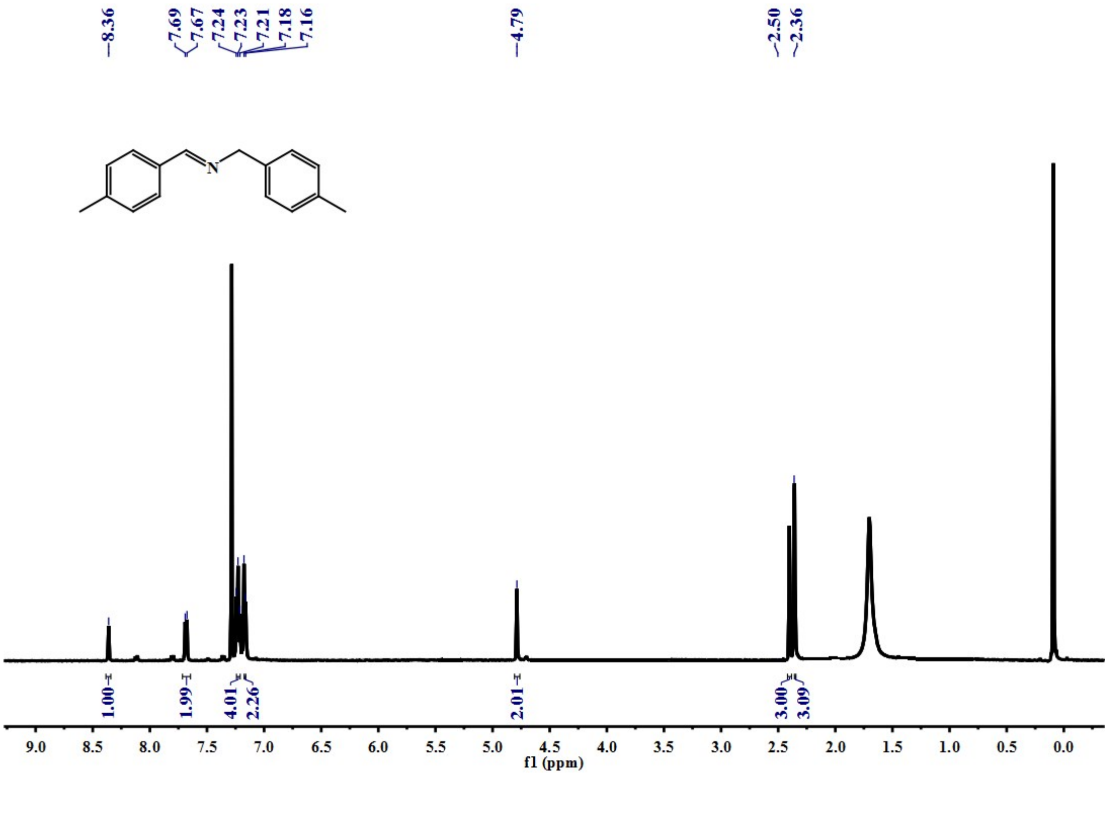
[1]H NMR spectra of 3q (500 MHz, $CDCl_3$)



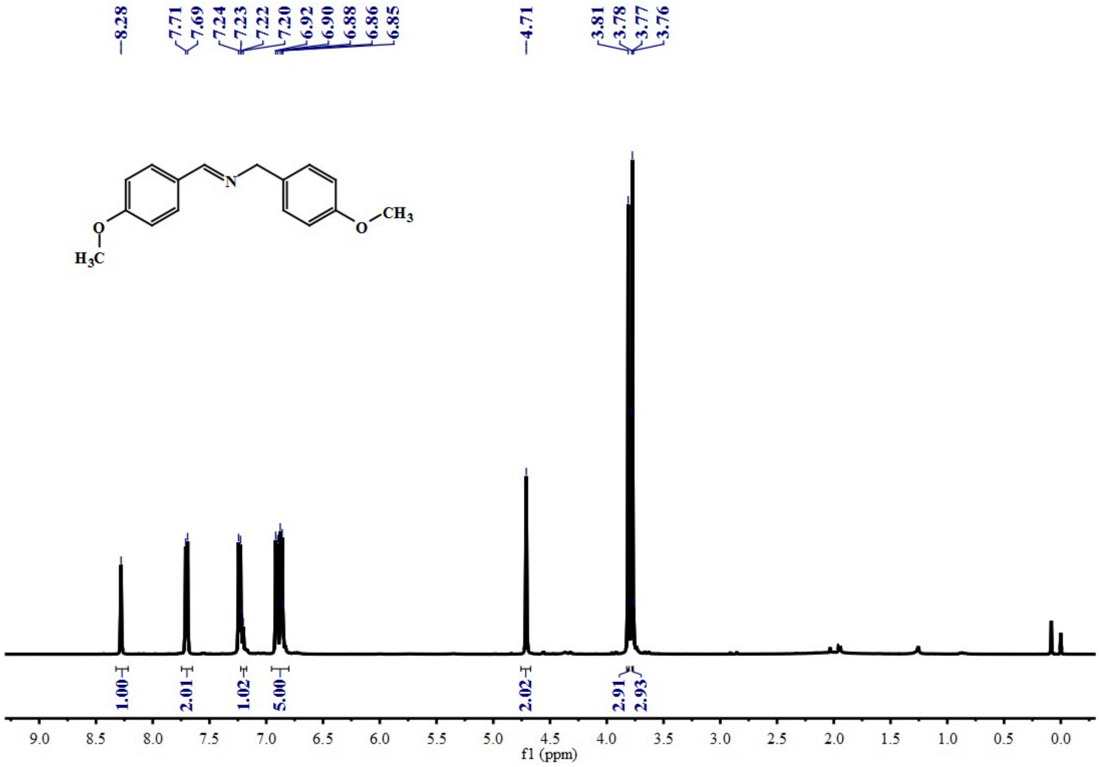
[1]H NMR spectra of 3r (500 MHz, $CDCl_3$)



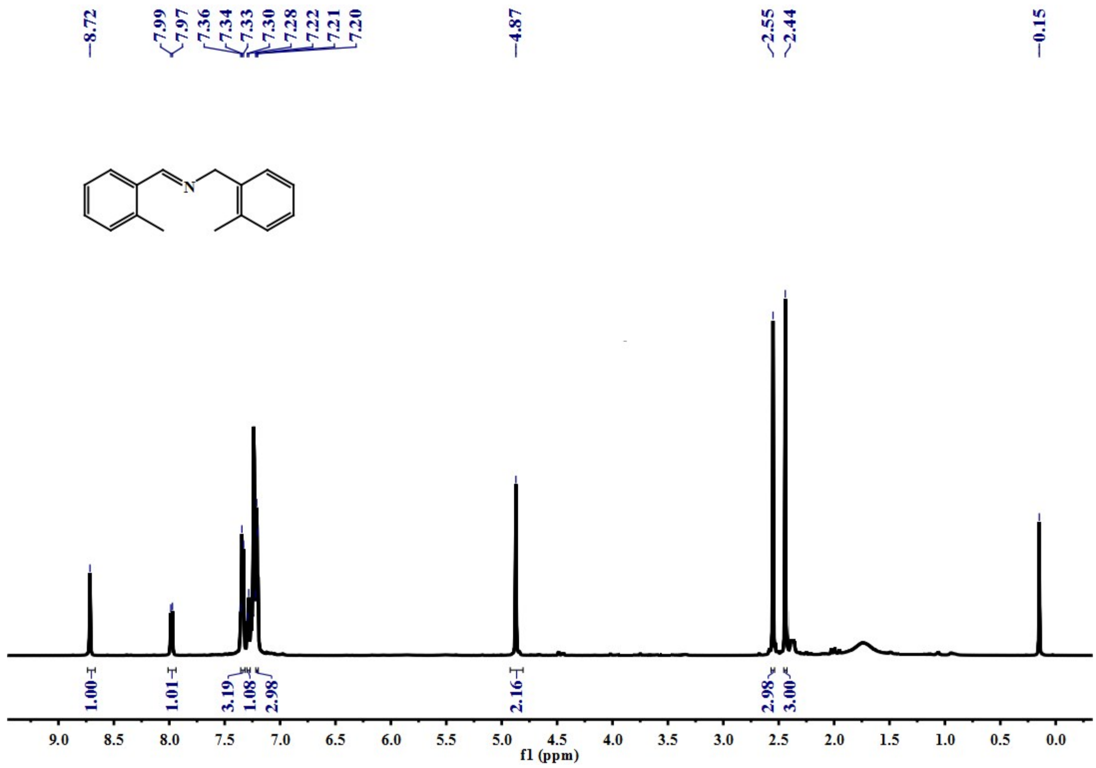
^{1}H NMR spectra of **5a** (500 MHz, $CDCl_3$)



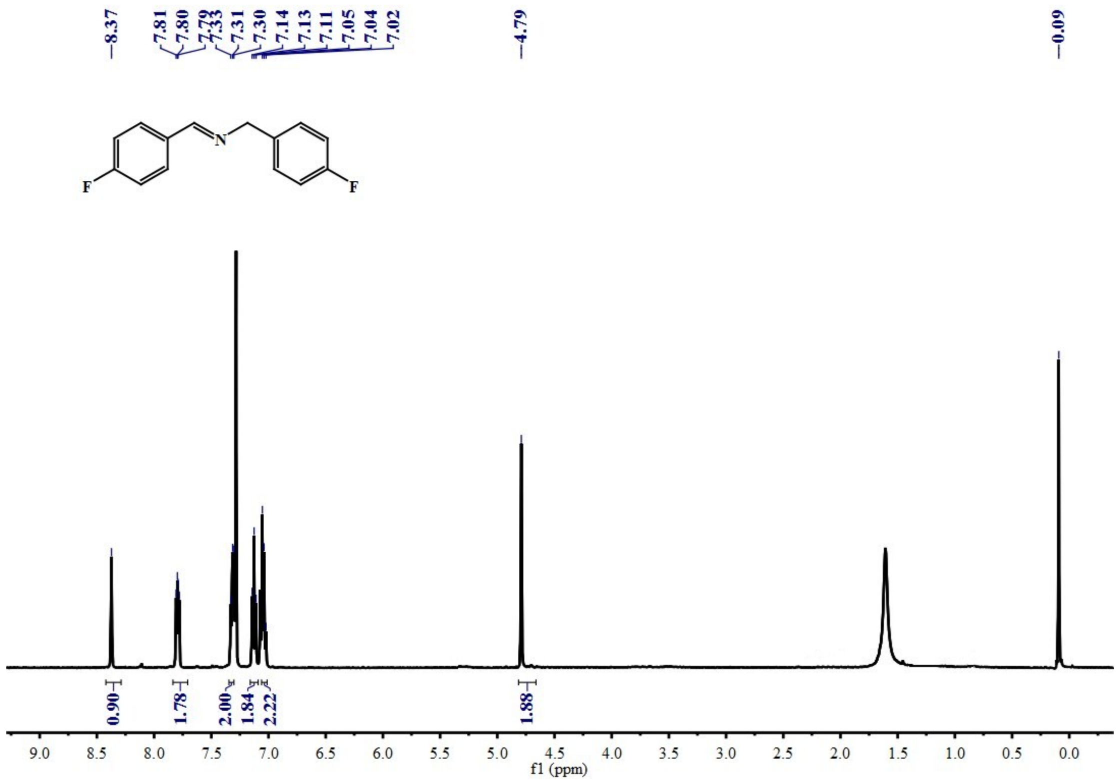
^{1}H NMR spectra of **5b** (500 MHz, $CDCl_3$)



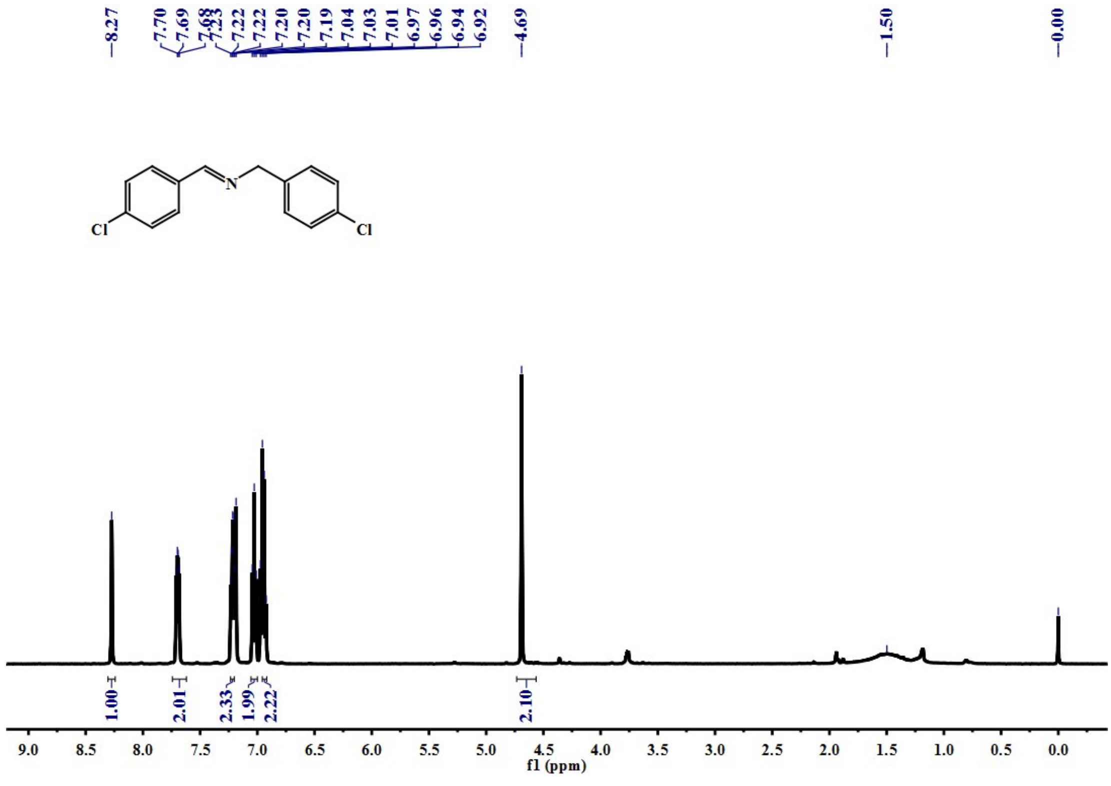
^{1}H NMR spectra of 5c (500 MHz, $CDCl_3$)



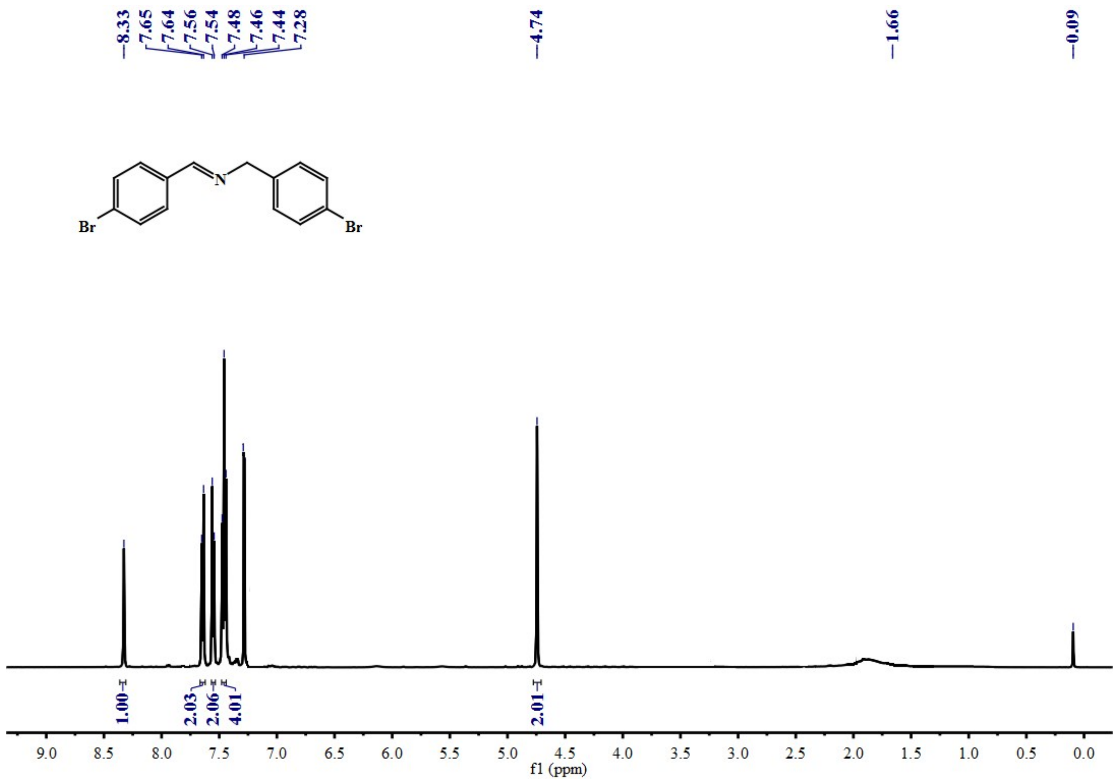
^{1}H NMR spectra of 5d (500 MHz, $CDCl_3$)



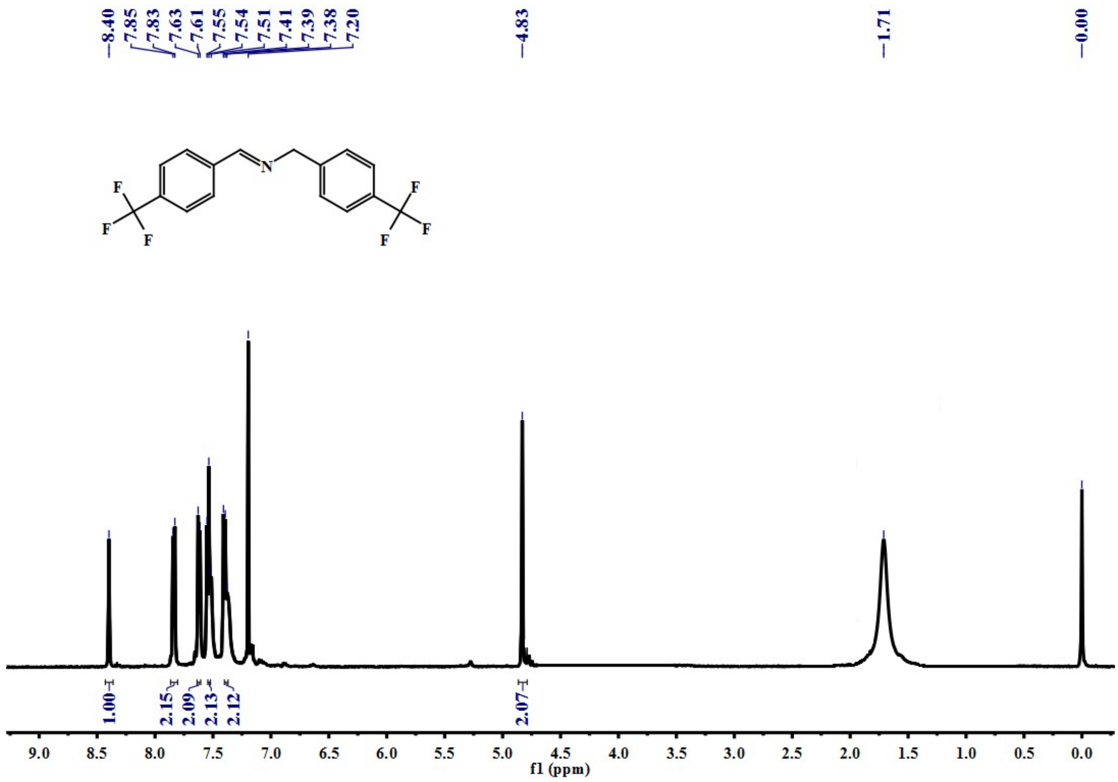
[1]H NMR spectra of 5e (500 MHz, $CDCl_3$)



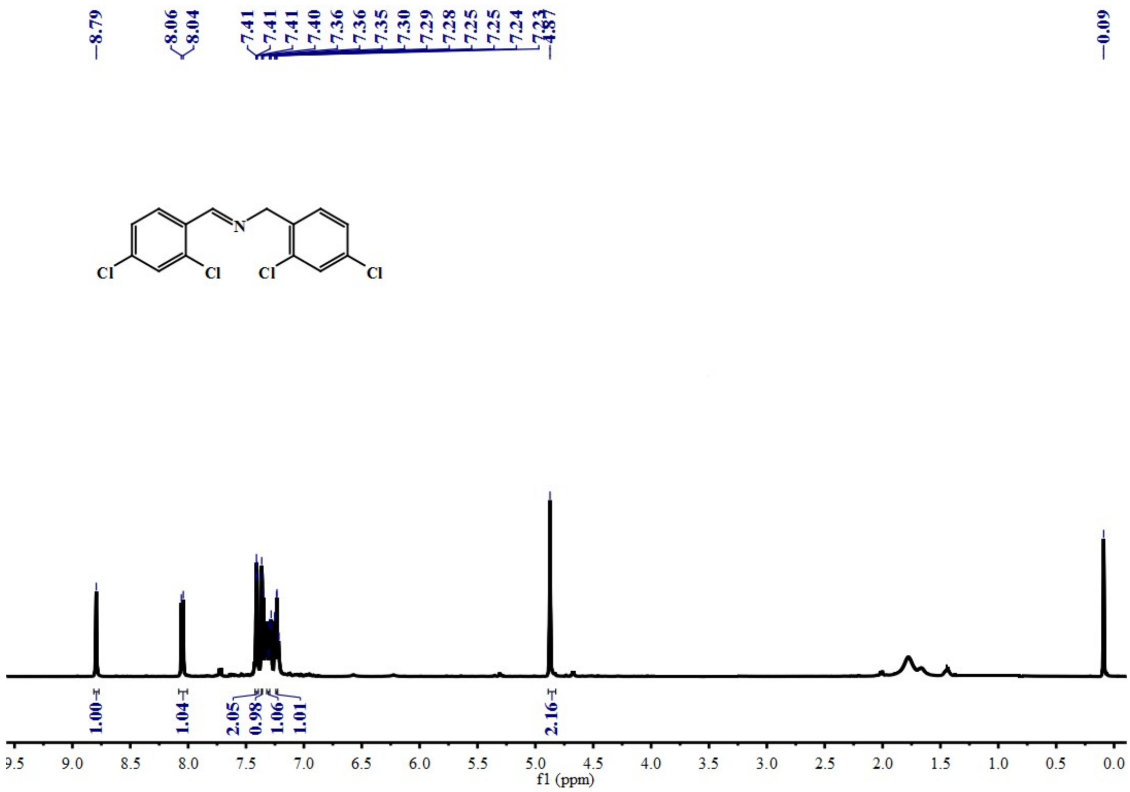
[1]H NMR spectra of 5f (500 MHz, $CDCl_3$)



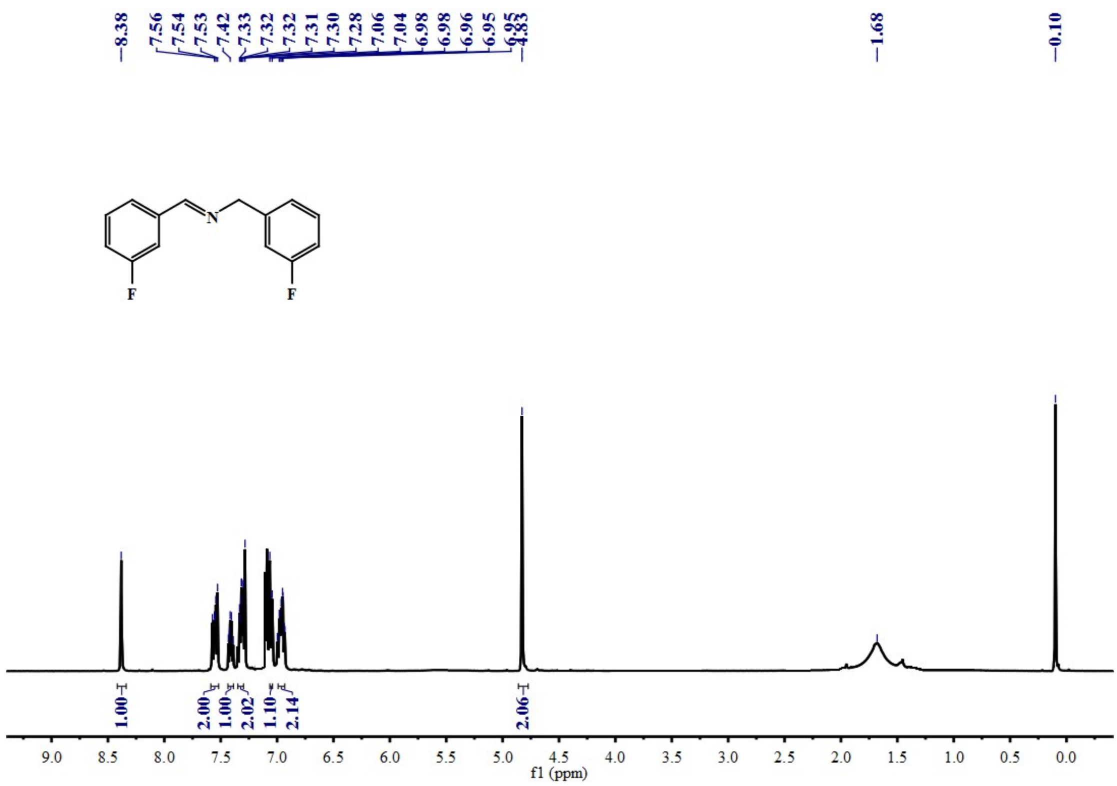
^{1}H NMR spectra of 5g (500 MHz, $CDCl_3$)



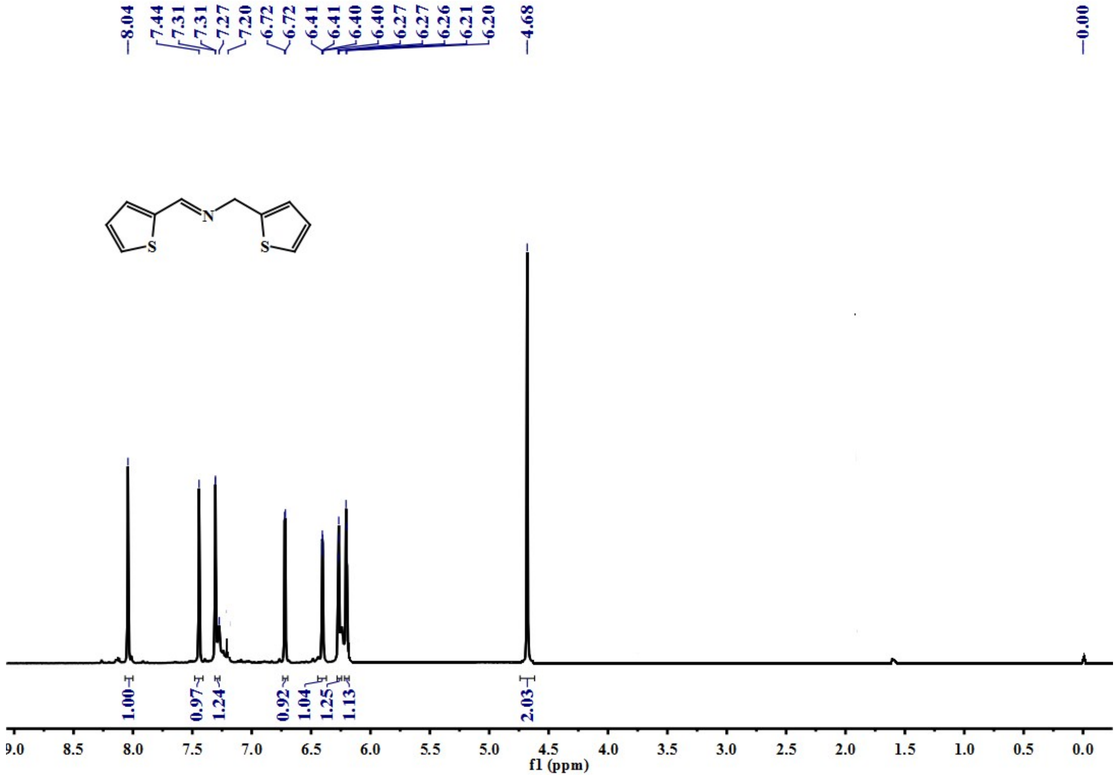
^{1}H NMR spectra of 5h (500 MHz, $CDCl_3$)



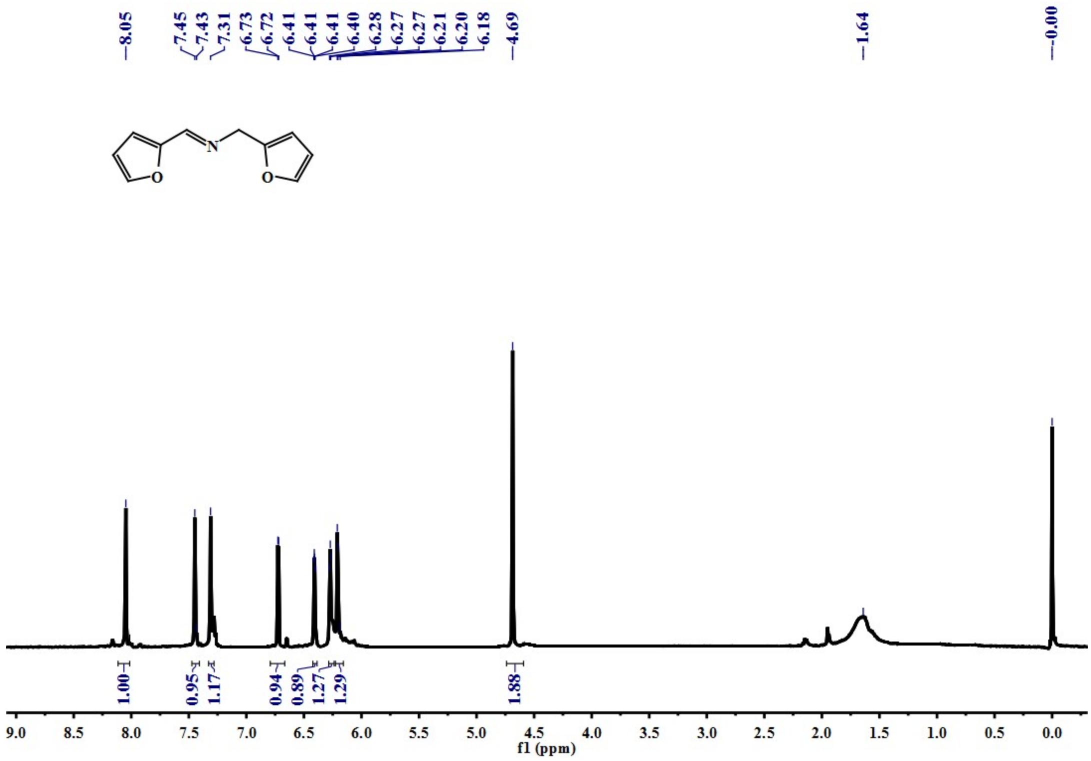
^{1}H NMR spectra of **5i** (500 MHz, $CDCl_3$)



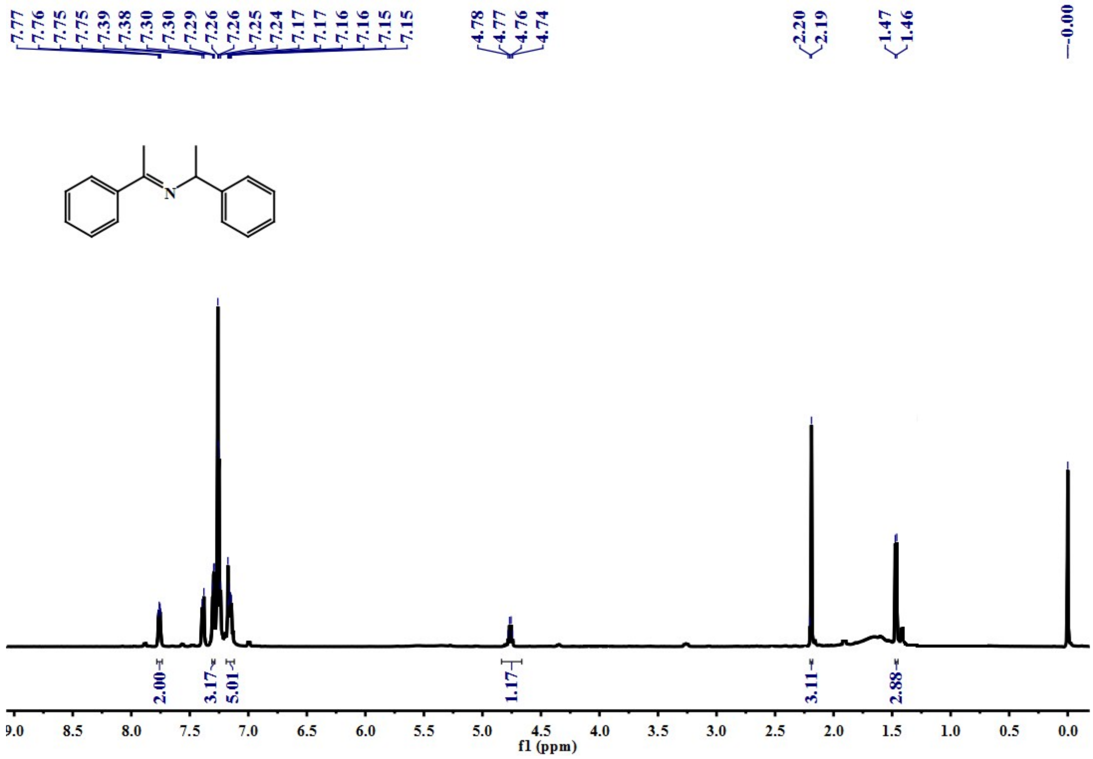
^{1}H NMR spectra of **5j** (500 MHz, $CDCl_3$)



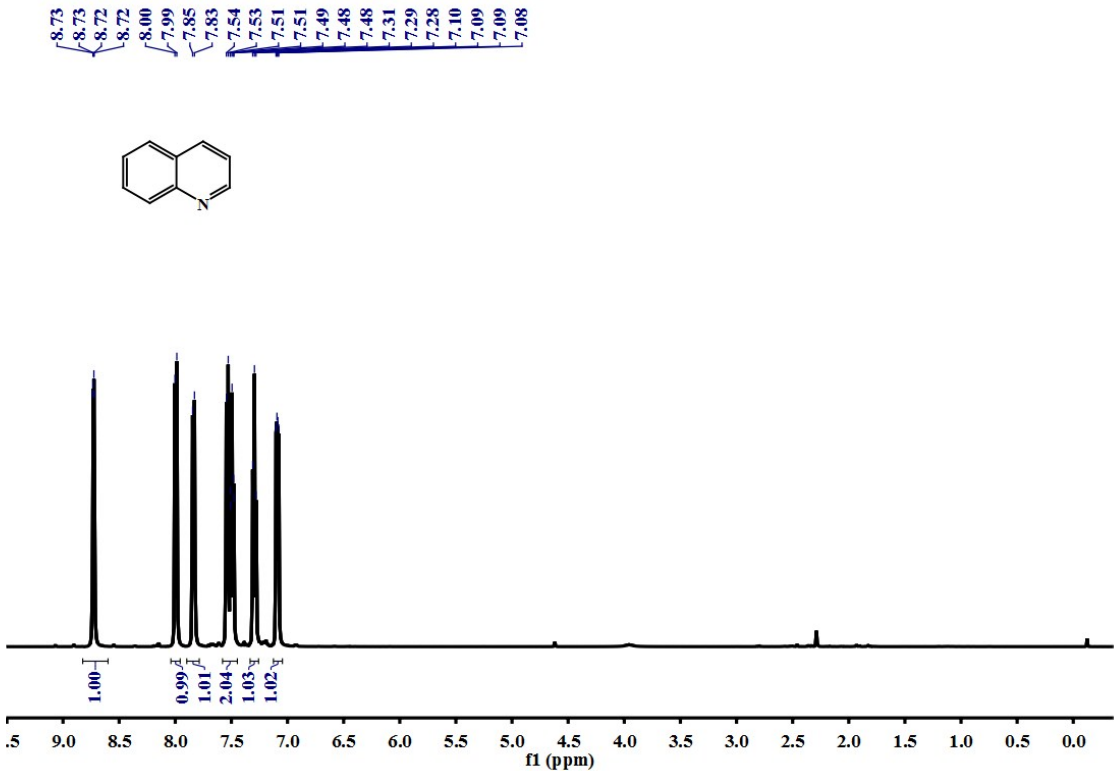
^{1}H NMR spectra of **5k** (500 MHz, $CDCl_3$)



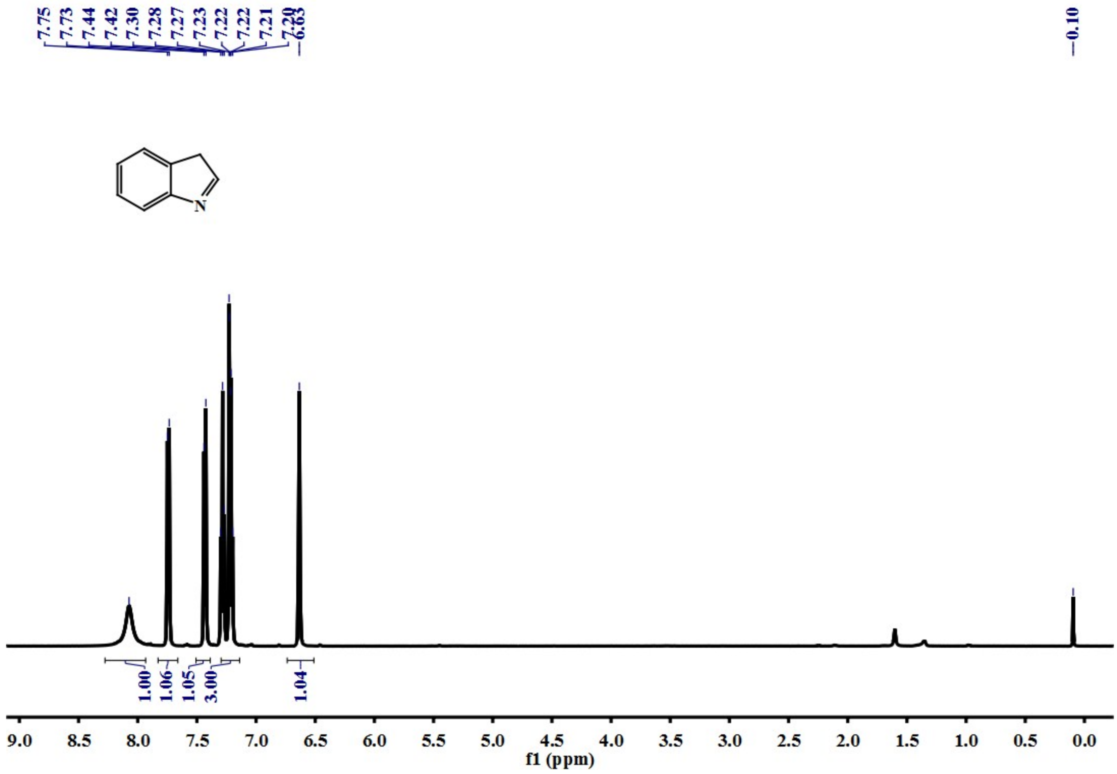
^{1}H NMR spectra of **5l** (500 MHz, $CDCl_3$)



^{1}H NMR spectra of 5m (500 MHz, CDCl$_3$)



^{1}H NMR spectra of 5n (500 MHz, CDCl$_3$)



^{1}H NMR spectra of 5o (500 MHz, $CDCl_3$)

Reference

1 K. Nomiya, T. Takahashi, T. Shirai and M. Miwa, *Polyhedron,* 1987, **6**, 213-218.

2 F. Ito, T. Ozeki, H. Ichida, H. Miyamae and Y. Sasaki, *Acta Cryst.,* 1989, **45**, 946-947.

3 A. Blazevic, E. Al-Sayed, A. Roller, G. Giester and Rompel, A. *Chemistry,* 2015, **21**, 4762-4771.

4 H.Ai, Y. Wang, B. Li and L.-X. Wu, *Eur. J. Inorg. Chem.,* 2014, **17**, 2766-2772.

5 P.-F. Wu, P.-C. Yin, Z. Jin, H. Jian, Z.-C. Xiao and Wei,Y.-G. *Chemistry,* 2011, **17**, 12002-12005.

6 S. Biswas, B. Dutta, K. Mullick and C.-H. Kuo, *ACS Catal.,* 2015, **5**, 4394-4403.

7 B. Chen, S.-S. Shang, L.-Y. Wang, Y. Zhang and S. Gao, *Chem.Commun.,* 2016, **52**, 481-484.

8 W.-P. Deng, J.-S. Chen, J.-C. Kang, Q.-H. Zhang and Y. Wang, *Chem. Commun.,* 2016, **52**, 6805-6808.

9 A. Kumar, P. Kumar, C. Joshi, S. Ponnada, A. K.Pathak, A. B. Sreedhar Ali, and S. L. Jain, *Green Chem.,* 2016, **18**, 2514-2521.

10 M. Largeron, M. B. Fleury, *Angew. Chem. Int. Ed.,* 2012, **51**, 5409–5412.

11 K. Suzuki, F. Tang, Y. Kikukawa, K. Yamaguchi and N. Mizuno, *Angew. Chem. Int. Ed.,* 2014, **53**, 5356-5360.