Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Efficient β-Alkylation of Secondary Alcohols to α-Substituted Ketones Catalyzed by Functionalized Ir Complexes via Borrowing Hydrogen in Water

Xin Liu,[ab] Wen-Zhe Dong,[ab] Yang Li,[ab] Xiaoqiang Yu,[b] Wan-Hui Wang,[ab,*] Yuichiro Himeda,[c] Ming Bao[ab,*]

[a] School of Chemical Engineering, Dalian University of Technology, Liaodongwan New District, Panjin, China

[b] State Key Laboratory of Fine Chemicals, Dalian University of Technology, Ganjingzi District, Dalian China

[c] National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

Contents

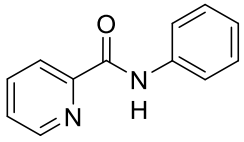
1. General Information

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a glovebox. All aqueous solutions were degassed before use. Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE III HD 500 spectrometers using tetramethylsilane (TMS) as an internal standard. Gas chromatography (GC) analyses were performed on an Agilent Technologies 7820A GC instrument with a HP-5 Agilent 19091J-413 column.

2. Synthesis of Ligands and Ir Complexes

2.1 Synthesis of Ligands

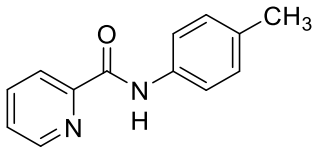
a) *N*-Phenylpicolinamide (L1)



Under nitrogen atmosphere, 2-picolinic acid (2.0 mmol, 246.22 mg), *N*,*N*′-carbonyl diimidazole (CDI, 2.2 mmol, 356.73 mg), and dry THF (8 mL) were added into a 25 mL two necks round bottom flask and the solution was stirred and refluxed for 2 h at 50℃. After cooling to room temperature, aniline (2.0 mmol, 186.34 mg) and dry THF (5 mL) were added to the solution and monitored the solution by TLC until the reaction finished. The resulting mixture was dried under a vacuum and dissolved with CH_2Cl_2. Then the CH_2Cl_2 solution was washed with water (3×10 mL) and dried over Na_2SO_4. The solvent of the filtrate was evaporated and the residue was purified by column chromatography on silica gel to give **L1** as a white solid (63% yield, 249.48 mg, 1.26 mmol).

^{1}H NMR (500 MHz, Chloroform-d) δ 9.96 (s, 1H), 8.55 (d, *J* = 4.7 Hz, 1H), 8.24 (d, *J* = 7.9 Hz, 1H), 7.85 (td, *J* = 7.7, 1.7 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.42 (ddd, *J* = 7.7, 4.7, 1.2 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H).

b) *N*-(*p*-Tolyl)picolinamide (L2)

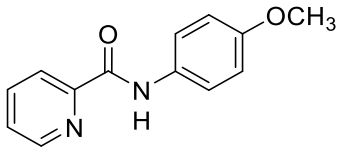


Under nitrogen atmosphere, 2-picolinic acid (2.0 mmol, 246.22 mg), *N*,*N*′-carbonyl diimidazole (CDI, 2.2 mmol, 356.73 mg), and dry THF (8 mL) were added into a 25 mL two necks round bottom flask and the solution was stirred and refluxed for 2 h at 50℃. After cooling to room temperature, *p*-methylaniline (2.0 mmol, 214.30 mg) and dry THF

(5 mL) were added into the solution and monitored the solution by TLC until the reaction finished. The resulting mixture was dried under a vacuum and dissolved with CH_2Cl_2. Then the CH_2Cl_2 solution was washed with water (3×10 mL) and dried over Na_2SO_4. The solvent of the filtrate was evaporated and the residue was purified by column chromatography on silica gel to give **L2** as a white solid (66% yield, 279.84 mg, 1.32 mmol).

^{1}H NMR (500 MHz, Chloroform-d) δ 9.96 (s, 1H), 8.61 (d, *J* = 4.1 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 7.90 (td, *J* = 7.7, 1.7 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.49-7.45 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 2.35 (s, 3H).

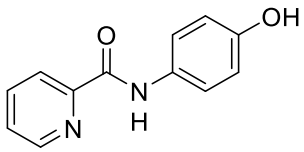
c) *N*-(4-Methoxyphenyl)-2-pyridinecarboxamide (L3)



Under nitrogen atmosphere, 2-picolinic acid (2.0 mmol, 246.22 mg), *N*,*N*′-carbonyl diimidazole (CDI, 2.2 mmol, 356.73 mg), and dry THF (8 mL) were added into a 25 mL two necks round bottom flask and the solution was stirred and refluxed for 2 h at 50℃. After cooling to room temperature, *p*-methoxyaniline (2.0 mmol, 246.30 mg) and dry THF (5 mL) were added to the solution and monitored the solution by TLC until the reaction finished. The resulting mixture was dried under a vacuum and dissolved with CH_2Cl_2. Then the CH_2Cl_2 solution was washed with water (3×10 mL) and dried over Na_2SO_4. The solvent of the filtrate was evaporated and the residue was purified by column chromatography on silica gel to give **L3** as a white solid (58% yield, 264.48 mg, 1.16 mmol).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.52 (s, 1H), 8.73 (d, *J* = 4.7 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 8.06 (t, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 9.1 Hz, 2H), 7.71-7.61 (m, 1H), 6.94 (d, *J* = 9.1 Hz, 2H), 3.75 (s, 3H).

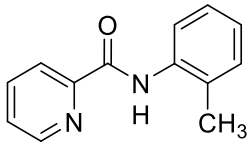
d) *N*-(4-Hydroxyphenyl)picolinamide (L4)



Under nitrogen atmosphere, 2-picolinic acid (2.0 mmol, 246.22 mg), *N*,*N*′-carbonyl diimidazole (CDI, 2.2 mmol, 356.73 mg), and dry THF (8 mL) were added into a 25 mL two necks round bottom flask and the solution was stirred and refluxed for 2 h at 50℃. After cooling to room temperature, *p*-hydroxyaniline (2.0 mmol, 218.26 mg) and dry THF (5 mL) were added into the solution and monitored the solution by TLC until the reaction finished. The resulting mixture was dried under a vacuum and dissolved with CH_2Cl_2. Then the CH_2Cl_2 solution was washed with water (3×10 mL) and dried over Na_2SO_4. The solvent of the filtrate was evaporated and the residue was purified by column chromatography on silica gel to give **L4** as a white solid (65% yield, 278.20 mg, 1.30 mmol).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.39 (s, 1H), 9.29 (s, 1H), 8.74-8.68 (m, 1H), 8.17-8.10 (m, 1H), 8.04 (td, *J* = 7.6, 1.7 Hz, 1H), 7.74-7.60 (m, 3H), 6.75 (d, *J* = 8.9 Hz, 2H).

e) *N*-*o*-Tolyl-2-pyridinecarboxamide (L5)

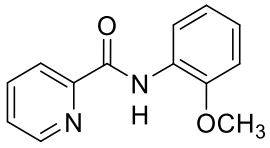


Under nitrogen atmosphere, 2-picolinic acid (2.0 mmol, 246.22 mg), *N*,*N*′-carbonyl diimidazole (CDI, 2.2 mmol, 356.73 mg), and dry THF (8 mL) were added into a 25 mL two necks round bottom flask and the solution was stirred and refluxed for 2 h at 50℃. After cooling to room temperature, *o*-toluidine (2.0 mmol, 214.30 mg) and dry THF (5 mL) were added to the solution and monitored the solution by TLC until the reaction finished. The resulting mixture was dried under a vacuum and dissolved with CH_2Cl_2. Then the CH_2Cl_2 solution was washed with water (3×10 mL) and dried over Na_2SO_4. The solvent of

the filtrate was evaporated and the residue was purified by column chromatography on silica gel to give **L5** as a white solid (64% yield, 271.36 mg, 1.28 mmol).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.27 (s, 1H), 8.75 (d, *J* = 4.8 Hz, 1H), 8.17 (d, *J* = 7.7 Hz, 1H), 8.09 (td, *J* = 7.7, 1.7 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.71-7.67 (m, 1H), 7.33-7.21 (m, 2H), 7.13 (t, *J* = 7.1 Hz, 1H), 2.32 (s, 3H).

f) *N*-(2-Methoxyphenyl)pyridine-2-carboxamide (L6)

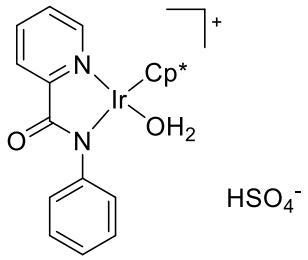


Under nitrogen atmosphere, 2-picolinic acid (2.0 mmol, 246.22 mg), *N*,*N*′-carbonyl diimidazole (CDI, 2.2 mmol, 356.73 mg), and dry THF (8 mL) were added into a 25 mL two necks round bottom flask and the solution was stirred and refluxed for 2 h at 50°C. After cooling to room temperature, 2-methoxy-phenylamine (2.0 mmol, 246.30 mg) and dry THF (5 mL) were added to the solution and monitored the solution by TLC until the reaction finished. The resulting mixture was dried under a vacuum and dissolved with CH_2Cl_2. Then the CH_2Cl_2 solution was washed with water (3×10 mL) and dried over Na_2SO_4. The solvent of the filtrate was evaporated and the residue was purified by column chromatography on silica gel to give **L6** as a white solid (71% yield, 323.76 mg, 1.42 mmol).

^{1}H NMR (500 MHz, Chloroform-d) δ 10.58 (s, 1H), 8.68-8.64 (m, 1H), 8.62 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.30 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.90 (td, *J* = 7.7, 1.7 Hz, 1H), 7.49-7.44 (m, 1H), 7.10 (td, *J* = 7.8, 1.7 Hz, 1H), 7.03 (td, *J* = 7.7, 1.4 Hz, 1H), 6.94 (dd, *J* = 8.1, 1.5 Hz, 1H), 3.98 (s, 3H).

2.2 Synthesis of Ir Complexes

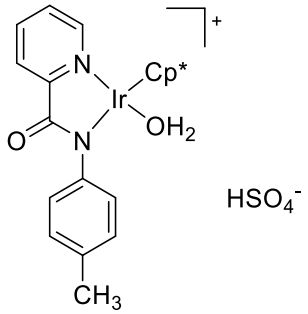
a) Synthesis of Complex **1a**



A 50 mL round bottom flask was charged with **L1** (0.052 mmol, 10.31 mg) and $[Cp^*Ir(OH_2)_3]SO_4$ (0.052 mmol, 30.00 mg) under a nitrogen atmosphere. Then deionized water (10 mL) was added and the solution was stirred until all the ligand was dissolved. The solution was filtered out of the undissolved substance and dried under a vacuum. Then the mixture was recrystallized from a mixture solution of isopropanol and *n*-hexane to give the luminous yellow product (43% yield, 14.08 mg, 0.022 mmol). The NMR data are consistent with the previous report.[1]

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.52 (br, 1H), 8.76 (d, *J* = 5.5 Hz, 1H), 8.37 (t, *J* = 7.7 Hz, 1H), 8.13 (d, *J* = 7.6 Hz, 1H), 7.92 (t, *J* = 6.9 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 1.44 (s, 15H). ESI-MS (m/z): $[M-HSO_4-H_2O]^+$ calcd for $C_{22}H_{24}IrN_2O^+$, 525.15124; found, 525.14966.

b) Synthesis of Complex **1b**

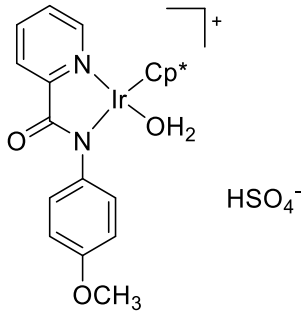


A 50 mL round bottom flask was charged with **L2** (0.052 mmol, 11.04 mg) and $[Cp^*Ir(OH_2)_3]SO_4$ (0.052 mmol, 30.00 mg) under a nitrogen atmosphere. Then deionized water (10 mL) was added and the solution was stirred until all the ligand was dissolved. The solution was filtered out of the undissolved substance and dried under a vacuum. Then

the mixture was recrystallized from a mixture solution of isopropanol and *n*-hexane to give the luminous yellow product (58% yield, 19.62 mg, 0.030 mmol).

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.59 (br, 1H), 8.75 (d, *J* = 2.8 Hz, 1H), 8.36 (t, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.91 (t, *J* = 6.1 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 2.31 (s, 3H), 1.49-1.41 (m, 15H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 172.33, 153.48, 151.04, 143.48, 141.05, 136.09, 129.51, 125.96, 125.58, 87.22, 20.14, 7.60. ESI-MS (m/z): $[M-HSO_4-H_2O]^+$ calcd for $C_{23}H_{26}IrN_2O^+$, 539.16689; found, 539.16614.

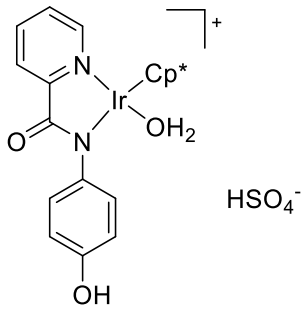
c) Synthesis of Complex **1c**



A 50 mL round bottom flask was charged with **L3** (0.052 mmol, 11.87 mg) and $[Cp^*Ir(OH_2)_3]SO_4$ (0.052 mmol, 30.00 mg) under a nitrogen atmosphere. Then deionized water (10 mL) was added and the solution was stirred until all the ligand was dissolved. The solution was filtered out of the undissolved substance and dried under a vacuum. Then the mixture was recrystallized from a mixture solution of isopropanol and *n*-hexane to give the luminous yellow product (62% yield, 21.44 mg, 0.032 mmol).

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.61 (br, 1H), 8.73 (d, *J* = 5.5 Hz, 1H), 8.38-8.32 (m, 1H), 8.13-8.09 (m, 1H), 7.92-7.87 (m, 1H), 7.48 (d, *J* = 9 Hz, 2H), 6.95 (d, *J* = 9 Hz, 2H), 3.77 (s, 3H), 1.45 (s, 14H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.99, 156.41, 154.14, 152.57, 142.11, 139.52, 130.95, 128.00, 113.72, 95.76, 55.75, 8.22. ESI-MS (m/z): $[M-HSO_4-H_2O]^+$ calcd for $C_{23}H_{26}IrN_2O_2^+$, 555.16180; found, 555.16089.

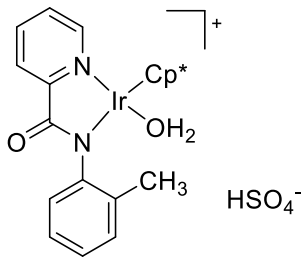
d) Synthesis of Complex **1d**



A 50 mL round bottom flask was charged with **L4** (0.052 mmol, 11.14 mg) and $[Cp^*Ir(OH_2)_3]SO_4$ (0.052 mmol, 30.00 mg) under a nitrogen atmosphere. Then deionized water (10 mL) was added and the solution was stirred until all the ligand was dissolved. The solution was filtered out of the undissolved substance and dried under a vacuum. Then the mixture was recrystallized from a mixture solution of isopropanol and *n*-hexane to give the luminous yellow product (54% yield, 18.37 mg, 0.028 mmol).

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.61 (br, 1H), 9.38 (s, 1H), 8.73 (d, *J* = 5.5 Hz, 1H), 8.34 (t, *J* = 7.6 Hz, 1H), 8.09 (d, *J* = 7.3 Hz, 1H), 7.89 (t, *J* = 6.1 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 1.45 (s, 15H). ^{1}H NMR (500 MHz, Deuterium Oxide) δ 8.82 (d, *J* = 5.5 Hz, 1H), 8.10 (t, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.69 (t, *J* = 6.6 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 1.30 (s, 15H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.89, 154.56, 154.28, 152.55, 142.08, 138.07, 130.86, 128.00, 127.89, 114.96, 95.74, 8.21. ESI-MS (m/z): $[M-HSO_4-H_2O]^+$ calcd for $C_{22}H_{24}IrN_2O_2^+$, 541.14615; found 541.14752.

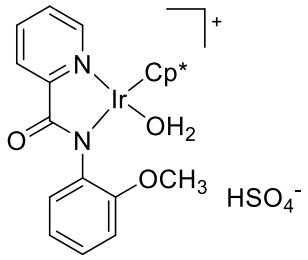
e) Synthesis of Complex **1e**



A 50 mL round bottom flask was charged with **L5** (0.052 mmol, 11.04 mg) and $[Cp^*Ir(OH_2)_3]SO_4$ (0.052 mmol, 30.00 mg) under a nitrogen atmosphere. Then deionized water (10 mL) was added and the solution was stirred until all the ligand was dissolved. The solution was filtered out of the undissolved substance and dried under a vacuum. Then the mixture was recrystallized from a mixture solution of isopropanol and *n*-hexane to give the luminous yellow product (55% yield, 18.97 mg, 0.029 mmol).

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.60 (br, 1H), 8.79 (d, *J* = 5.4 Hz, 1H), 8.37 (t, *J* = 7.7 Hz, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.92 (t, *J* = 6.6 Hz, 1H), 7.30-7.24 (m, 3H), 7.14 (t, *J* = 7.3 Hz, 1H), 2.13 (s, 3H), 1.44 (s, 15H). ^{1}H NMR (500 MHz, Deuterium Oxide) δ 8.94 (d, *J* = 5.6 Hz, 1H), 8.17 (t, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.75 (t, *J* = 6.7 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 2.08 (s, 3H), 1.30 (s, 15H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 171.86, 153.18, 150.93, 144.90, 141.10, 134.19, 130.48, 129.28, 126.85, 126.31, 126.03, 125.27, 87.57, 17.60, 7.72. ESI-MS (m/z): $[M-HSO_4-H_2O]^+$ calcd for $C_{23}H_{26}IrN_2O^+$, 539.16689; found, 539.16632.

f) Synthesis of Complex **1f**



A 50 mL round bottom flask was charged with **L6** (0.052 mmol, 11.87 mg) and $[Cp^*Ir(OH_2)_3]SO_4$ (0.052 mmol, 30.00 mg) under a nitrogen atmosphere. Then deionized water (10 mL) was added and the solution was stirred until all the ligand was dissolved. The solution was filtered out of the undissolved substance and dried under a vacuum. Then the mixture was recrystallized from a mixture solution of isopropanol and *n*-hexane to give the luminous yellow product (61% yield, 21.44 mg, 0.032 mmol).

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.60 (br, 1H), 8.79 (d, *J* = 5.3 Hz, 1H), 8.35 (t, *J* = 7.7 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.90 (t, *J* = 6.7 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 3.75 (s, 3H), 1.43 (s, 14H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 172.46, 153.36, 152.90, 151.13, 141.10, 134.50, 129.42, 127.52, 126.74, 125.98, 121.20, 111.85, 87.37, 55.24, 7.56. ESI-MS (m/z): $[M-HSO_4-H_2O]^+$ calcd for $C_{23}H_{26}IrN_2O_2^+$, 555.16180; found, 555.16150.

2.3 Comparison of ^{1}H NMR spectra of L4 and Cat. 1d

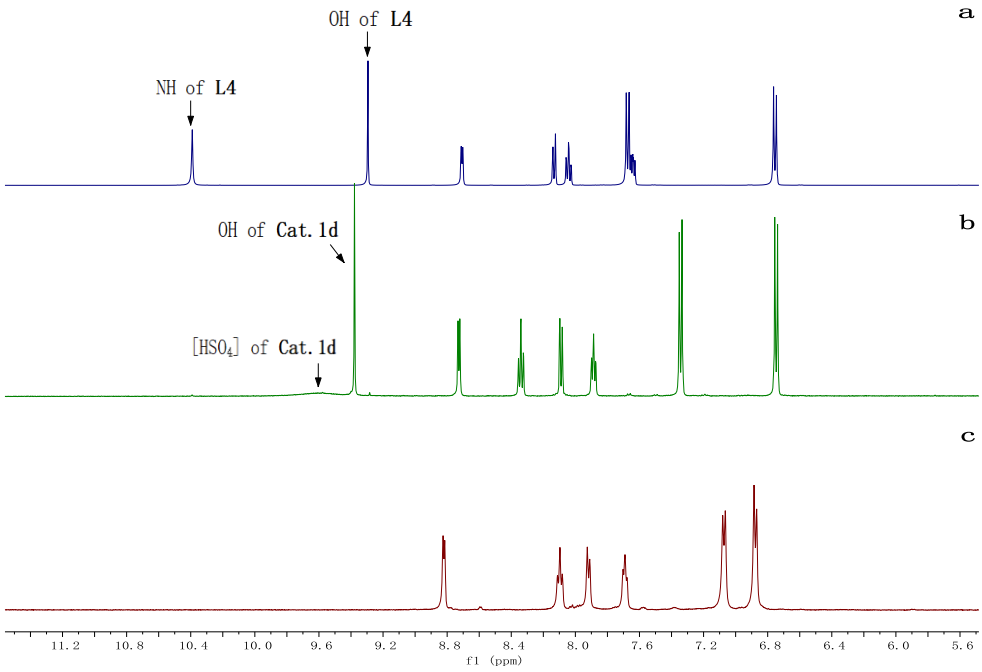


Fig. S1 Partial ^{1}H NMR spectra of (**a**) **L4** in DMSO-d_6, (**b**) Cat. **1d** in DMSO-d_6, (**c**) Cat. **1d** in D_2O.

2.4 Comparison of ^{1}H NMR spectra of L5 and Cat. 1e

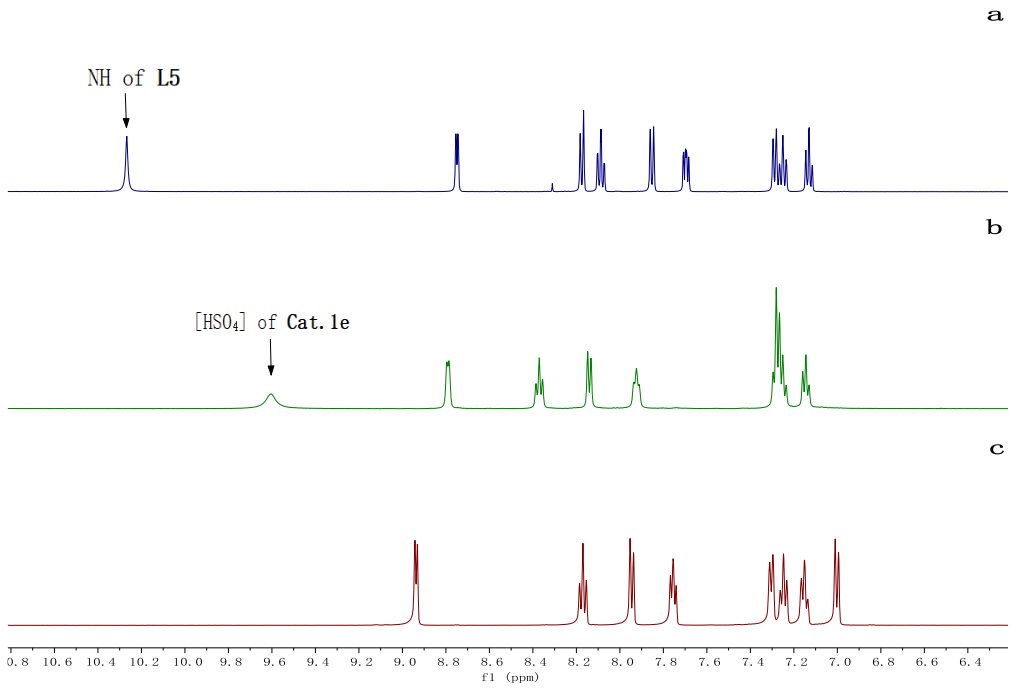


Fig. S2 Partial ^{1}H NMR spectra of (**a**) **L5** in DMSO-d_6, (**b**) Cat. **1e**. in DMSO-d_6, (**c**) Cat. **1e** in D_2O.

3. Single Crystal X-ray Diffraction Data of Complex 1d−H_2O

Table S1 Crystal data and structure refinement for complex 1d−H_2O.

Empirical formula	$C_{22}H_{25}IrN_2O_6S$
CCDC number	2122399
Formula weight	637.70
Temperature/K	299(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.3763(3)
b/Å	13.3112(4)
c/Å	16.7527(5)
α/°	90
β/°	96.3810(10)
γ/°	90
Volume/$Å^3$	2299.56(12)
Z	4
$\rho_{calc}g/cm^3$	1.842
μ/mm^{-1}	5.938
θ range for data collection/°	5.754 to 52.154
Reflections collected	17701
Independent reflections	4496 [R_{int} = 0.0178, R_{sigma} = 0.0154]
Data/restraints/parameters	4496/0/297

Goodness-of-fit on F^2	1.128
Final R indexes [I>=2σ (I)]	R_1 = 0.0151, wR_2 = 0.0324
Final R indexes [all data]	R_1 = 0.0181, wR_2 = 0.0377

Table S2. Comparison of select bond lengths (Å) and angles (°) in complex 1d−H_2O.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C(1)	C(2)	1.378(4)	C(13)	Ir(1)	2.180(3)
C(1)	N(1)	1.340(3)	C(14)	C(15)	1.437(5)
C(2)	C(3)	1.369(5)	C(14)	C(19)	1.505(5)
C(3)	C(4)	1.382(5)	C(14)	Ir(1)	2.156(3)
C(4)	C(5)	1.380(4)	C(15)	C(16)	1.439(5)
C(5)	C(6)	1.481(4)	C(15)	C(20)	1.505(4)
C(5)	N(1)	1.347(3)	C(15)	Ir(1)	2.122(3)
C(6)	N(2)	1.317(3)	C(16)	C(17)	1.433(4)
C(6)	O(1)	1.248(3)	C(16)	C(21)	1.502(5)
C(7)	C(8)	1.381(4)	C(16)	Ir(1)	2.144(3)
C(7)	C(12)	1.385(4)	C(17)	C(22)	1.490(4)
C(7)	N(2)	1.433(3)	C(17)	Ir(1)	2.177(3)
C(8)	C(9)	1.388(4)	Ir(1)	N(1)	2.096(2)
C(9)	C(10)	1.386(4)	Ir(1)	N(2)	2.092(2)
C(10)	C(11)	1.380(4)	Ir(1)	O(4)	2.1653(18)
C(10)	O(2)	1.365(3)	O(3)	S(1)	1.550(2)

C(11)	C(12)	1.378(4)	O(4)	S(1)	1.4777(19)
C(13)	C(14)	1.422(5)	O(5)	S(1)	1.434(2)
C(13)	C(17)	1.429(4)	O(6)	S(1)	1.414(2)
C(13)	C(18)	1.499(4)			

Table S3 Bond Angles for complex 1d−H_2O.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N(1)	C(1)	C(2)	121.9(3)	C(13)	C(17)	Ir(1)	70.98(15)
C(3)	C(2)	C(1)	119.7(3)	C(16)	C(17)	C(22)	127.4(3)
C(2)	C(3)	C(4)	118.9(3)	C(16)	C(17)	Ir(1)	69.39(16)
C(5)	C(4)	C(3)	119.0(3)	C(22)	C(17)	Ir(1)	128.3(2)
C(4)	C(5)	C(6)	122.4(3)	C(14)	Ir(1)	C(13)	38.27(12)
N(1)	C(5)	C(4)	122.0(3)	C(14)	Ir(1)	C(17)	65.08(12)
N(1)	C(5)	C(6)	115.7(2)	C(14)	Ir(1)	O(4)	110.80(11)
N(2)	C(6)	C(5)	114.0(2)	C(15)	Ir(1)	C(13)	64.64(12)
O(1)	C(6)	C(5)	118.7(3)	C(15)	Ir(1)	C(14)	39.24(13)
O(1)	C(6)	N(2)	127.3(3)	C(15)	Ir(1)	C(16)	39.42(13)
C(8)	C(7)	C(12)	119.0(3)	C(15)	Ir(1)	C(17)	65.57(12)
C(8)	C(7)	N(2)	121.1(2)	C(15)	Ir(1)	O(4)	149.77(12)
C(12)	C(7)	N(2)	119.8(2)	C(16)	Ir(1)	C(13)	64.20(12)
C(7)	C(8)	C(9)	120.3(3)	C(16)	Ir(1)	C(14)	65.44(13)
C(10)	C(9)	C(8)	120.2(3)	C(16)	Ir(1)	C(17)	38.71(11)

C(11)	C(10)	C(9)	119.4(3)	C(16)	Ir(1)	O(4)	149.18(10)
O(2)	C(10)	C(9)	123.6(3)	C(17)	Ir(1)	C(13)	38.28(11)
O(2)	C(10)	C(11)	117.0(3)	N(1)	Ir(1)	C(13)	143.79(10)
C(12)	C(11)	C(10)	120.3(3)	N(1)	Ir(1)	C(14)	161.91(11)
C(11)	C(12)	C(7)	120.8(3)	N(1)	Ir(1)	C(15)	122.83(12)
C(14)	C(13)	C(17)	109.7(3)	N(1)	Ir(1)	C(16)	98.59(11)
C(14)	C(13)	C(18)	125.6(3)	N(1)	Ir(1)	C(17)	108.35(10)
C(14)	C(13)	Ir(1)	69.93(17)	N(1)	Ir(1)	O(4)	87.25(8)
C(17)	C(13)	C(18)	124.6(3)	N(2)	Ir(1)	C(13)	139.05(10)
C(17)	C(13)	Ir(1)	70.74(16)	N(2)	Ir(1)	C(14)	106.33(11)
C(18)	C(13)	Ir(1)	124.4(2)	N(2)	Ir(1)	C(15)	101.74(11)
C(13)	C(14)	C(15)	107.2(3)	N(2)	Ir(1)	C(16)	130.03(11)
C(13)	C(14)	C(19)	125.8(3)	N(2)	Ir(1)	C(17)	167.23(10)
C(13)	C(14)	Ir(1)	71.80(16)	N(2)	Ir(1)	N(1)	76.82(8)
C(15)	C(14)	C(19)	126.9(3)	N(2)	Ir(1)	O(4)	80.79(8)
C(15)	C(14)	Ir(1)	69.09(17)	O(4)	Ir(1)	C(13)	93.50(10)
C(19)	C(14)	Ir(1)	128.2(2)	O(4)	Ir(1)	C(17)	110.74(9)
C(14)	C(15)	C(20)	126.6(4)	C(1)	N(1)	C(5)	118.6(2)
C(14)	C(15)	Ir(1)	71.67(17)	C(1)	N(1)	Ir(1)	125.82(19)
C(16)	C(15)	C(14)	107.9(3)	C(5)	N(1)	Ir(1)	115.56(17)
C(16)	C(15)	C(20)	125.4(4)	C(6)	N(2)	C(7)	117.0(2)
C(16)	C(15)	Ir(1)	71.13(16)	C(6)	N(2)	Ir(1)	117.77(17)

C(20)	C(15)	Ir(1)	126.5(3)	C(7)	N(2)	Ir(1)	125.16(17)
C(15)	C(16)	C(21)	125.8(3)	S(1)	O(4)	Ir(1)	129.76(11)
C(15)	C(16)	Ir(1)	69.45(17)	O(4)	S(1)	O(3)	102.24(12)
C(17)	C(16)	C(15)	108.4(3)	O(5)	S(1)	O(3)	107.95(16)
C(17)	C(16)	C(21)	125.8(3)	O(5)	S(1)	O(4)	109.78(13)
C(17)	C(16)	Ir(1)	71.90(15)	O(6)	S(1)	O(3)	107.34(16)
C(21)	C(16)	Ir(1)	126.1(3)	O(6)	S(1)	O(4)	113.62(14)
C(13)	C(17)	C(16)	106.9(3)	O(6)	S(1)	O(5)	114.95(18)
C(13)	C(17)	C(22)	125.5(3)				

4. General Procedure for the Catalytic Reaction and Product Characterization

4.1 General Procedure for Catalytic Reaction

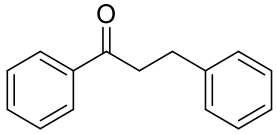
A mixture of 1-phenylethanol (0.5 mmol), benzyl alcohol (0.8 mmol), catalyst **1d** (0.01 mmol), and KOH (0.75 mmol) in 1 mL H_2O were added in a 10 mL Schlenk tube and stirred in an oil-bath (100 °C) for 24 hours. Upon completion of the reaction, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic layer was directly detected by GC with the addition of *n*-decane as an internal standard to determine the GC yield. To determine the isolated yield, the combined organic solvent was evaporated and the residue was purified by column chromatography over silica gel using ethyl acetate/hexane mixture (1:10) as an eluent to provide the products.

4.2 Procedure for the Reuse of the Catalyst 1d for Catalytic Reaction

A mixture of 1-phenylethanol (1 mmol), benzyl alcohol (1.6 mmol), catalyst **1d** (0.02 mmol), and KOH (1.5 mmol) in 2 mL H_2O were added in a 10 mL Schlenk tube and stirred in an oil-bath (100 °C) for 24 hours. The organic product was extracted with *n*-hexane (3×10 mL) and the aqueous phase containing catalyst **1d** was recovered. The combined organic layer was directly detected by GC with the addition of *n*-decane as an internal standard to determine the yield (99%). The pH of reaction solution before and after reaction was found to be 13.60 and 13.59, respectively. After replenishing small amount of KOH (0.04 mmol) to the aqueous phase, 1-phenylethanol (1 mmol) and benzyl alcohol (1.6 mmol) were added and the mixture was stirred in an oil-bath (100 °C) for 24 hours. The organic product was extracted with *n*-hexane (3×10 mL). *n*-Decane was added to the combined organic phase as an internal standard, and the GC detection indicated a yield of 56%.

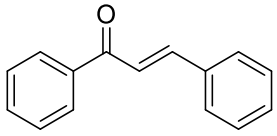
4.3 Product Characterization

1,3-Diphenylpropan-1-one (4a) [2]



Yield: 99% (104 mg, 0.49 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 6.5 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 3.31 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.7 Hz, 2H).

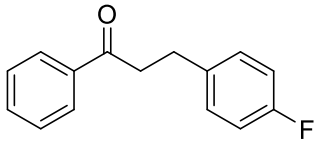
Chalcone (4a') [3]



Yield: 89% (93 mg, 0.45 mmol).

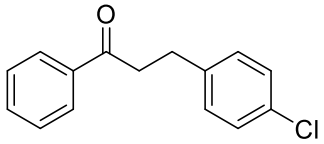
^{1}H NMR (500 MHz, Chloroform-d) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 15.7 Hz, 1H), 7.68-7.63 (m, 2H), 7.61-7.49 (m, 4H), 7.42 (d, *J* = 4.7 Hz, 3H).

3-(4-Fluorophenyl)-1-phenylpropan-1-one (4b) [2]



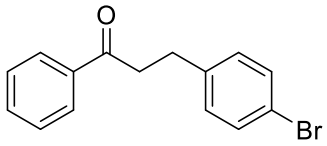
Yield: 73% (83 mg, 0.37 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.23-7.17 (m, 2H), 6.97 (t, *J* = 8.4 Hz, 2H), 3.27 (t, *J* = 7.5 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H).

3-(4-Chlorophenyl)-1-phenylpropan-1-one (4c) [2]



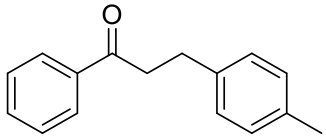
Yield: 88% (108 mg, 0.44 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 3.18 (t, *J* = 7.5 Hz, 2H), 2.94 (t, *J* = 7.5 Hz, 2H).

3-(4-Bromophenyl)-1-phenylpropan-1-one (4d) [2]



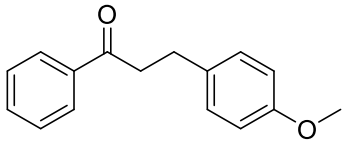
Yield: 86% (124 mg, 0.43 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 3.28 (t, *J* = 7.5 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H).

1-Phenyl-3-(p-tolyl)propan-1-one (4e) [2]



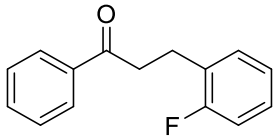
Yield: 80% (90 mg, 0.40 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.88 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.09-7.02 (m, 4H), 3.21 (t, *J* = 7.7 Hz, 2H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.25 (s, 3H).

3-(4-Methoxyphenyl)-1-phenylpropan-1-one (4f) [2]



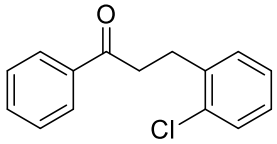
Yield: 75% (90 mg, 0.38 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 3.79 (s, 3H), 3.27 (t, *J* = 7.6 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H).

3-(2-Fluorophenyl)-1-phenylpropan-1-one (4g) [4]



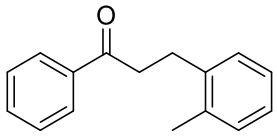
Yield: 84% (96 mg, 0.42 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.18 (q, *J* = 7.0 Hz, 1H), 7.09-6.97 (m, 2H), 3.29 (t, *J* = 7.6 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H).

3-(2-Chlorophenyl)-1-phenylpropan-1-one (4h) [5]



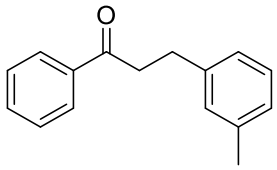
Yield: 80% (98 mg, 0.40 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.21-7.17 (m, 2H), 3.31 (t, *J* = 7.6 Hz, 2H), 3.18 (t, *J* = 7.6 Hz, 2H).

1-Phenyl-3-(o-tolyl)propan-1-one (4i) [2]



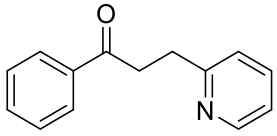
Yield: 85% (95 mg, 0.43 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.11-7.03 (m, 4H), 3.17 (t, *J* = 7.6 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.27 (s, 3H).

1-Phenyl-3-(m-tolyl)propan-1-one (4j) [2]



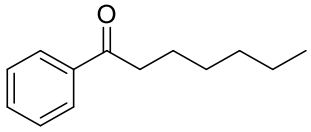
Yield: 74% (83 mg, 0.37 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.09-7.00 (m, 3H), 3.29 (t, *J* = 7.8 Hz, 2H), 3.03 (t, *J* = 7.8 Hz, 2H), 2.33 (s, 3H).

1-Phenyl-3-(pyridin-2-yl)propan-1-one (4k) [6]



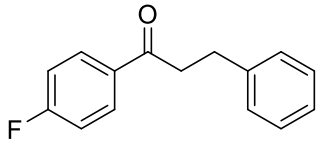
Yield: 70% (74 mg, 0.35 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 8.52 (d, *J* = 4.7 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 2H), 7.61-7.52 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.14-7.08 (m, 1H), 3.51 (t, *J* = 7.3 Hz, 2H), 3.24 (t, *J* = 7.3 Hz, 2H).

1-Phenylheptan-1-one (4l) [7]



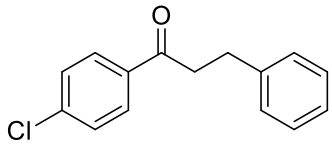
Yield: 49% (47 mg, 0.25 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.98-7.94 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.74 (p, *J* = 7.4 Hz, 2H), 1.43-1.28 (m, 6H), 0.89 (t, *J* = 6.3 Hz, 3H).

1-(4-Fluorophenyl)-3-phenylpropan-1-one (4m) [2]



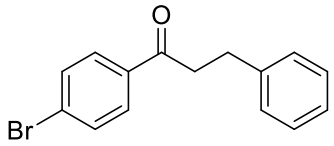
Yield: 74% (84 mg, 0.37 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.95-7.86 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.16 (d, *J* = 7.3 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 8.4 Hz, 2H), 3.19 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H).

1-(4-Chlorophenyl)-3-phenylpropan-1-one (4n) [2]



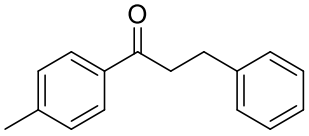
Yield: 90% (110 mg, 0.45 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.26-7.18 (m, 3H), 3.26 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H).

1-(4-Bromophenyl)-3-phenylpropan-1-one (4o) [2]



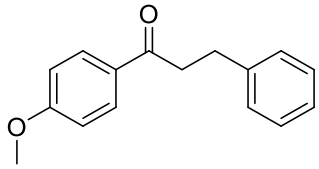
Yield: 90% (130 mg, 0.45 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.72 (d, *J* = 7.7 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.15 (dt, *J* = 19.4, 7.6 Hz, 3H), 3.18 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H).

3-Phenyl-1-(p-tolyl)propan-1-one (4p) [2]



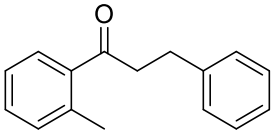
Yield: 86% (96 mg, 0.43 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.86 (d, *J* = 7.7 Hz, 2H), 7.32-7.18 (m, 7H), 3.27 (t, *J* = 7.7 Hz, 2H), 3.06 (t, *J* = 7.7 Hz, 2H), 2.40 (s, 3H).

1-(4-Methoxyphenyl)-3-phenylpropan-1-one (4q) [2]



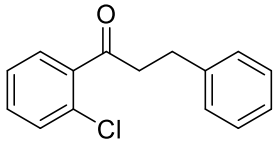
Yield: 82% (98 mg, 0.41 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.17 (d, *J* = 7.3 Hz, 2H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 2H), 3.78 (s, 3H), 3.17 (t, *J* = 7.7 Hz, 2H), 2.98 (t, *J* = 7.7 Hz, 2H).

3-Phenyl-1-(o-tolyl)propan-1-one (4r) [2]



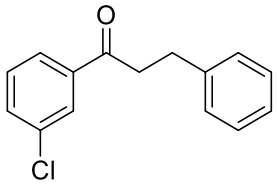
Yield: 32% (36 mg, 0.16 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.21 (dd, *J* = 13.7, 6.4 Hz, 5H), 3.22 (t, *J* = 7.6 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.46 (s, 3H).

1-(2-Chlorophenyl)-3-phenylpropan-1-one (4s) [10]



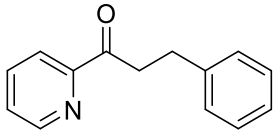
Yield: 41% (50 mg, 0.21 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.41-7.35 (m, 3H), 7.31-7.27 (m, 3H), 7.23-7.18 (m, 3H), 3.27 (t, *J* = 7.7 Hz, 2H), 3.05 (t, *J* = 7.7 Hz, 2H).

1-(3-Chlorophenyl)-3-phenylpropan-1-one (4t) [8]



Yield: 86% (105 mg, 0.43 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 7.91 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.26-7.17 (m, 3H), 3.27 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H).

3-Phenyl-1-(pyridin-2-yl)propan-1-one (4u) [9]



Yield: 62% (65 mg, 0.31 mmol).
^{1}H NMR (500 MHz, Chloroform-d) δ 8.59 (d, *J* = 4.3 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.43-7.35 (m, 1H), 7.20 (d, *J* = 4.2 Hz, 4H), 7.15-7.08 (m, 1H), 3.50 (t, *J* = 7.6 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H).

5. Mechanistic Studies

5.1 ^{1}H NMR investigation of catalyst 1d under basic conditions

Catalyst **1d** (0.005 mmol) was dissolved in 1 mL methanol solution of 2 eq NEt_3 (0.01 mmol) and 15 eq NEt_3 (0.075 mmol), respectively. The thoroughly mixed solutions were then evaporated under reduced pressure and the residues were dissolved in DMSO-d_6 for NMR testing. The ^{1}H NMR spectra are shown in Fig. S3-S6.

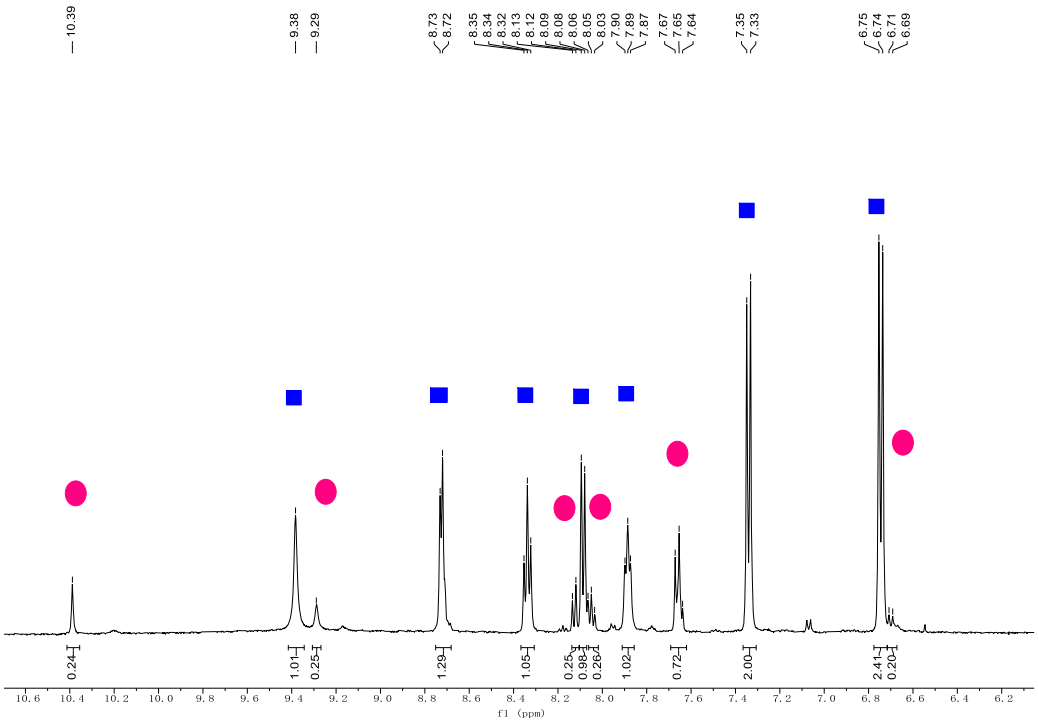


Fig. S3 Enlarged partial ^{1}H NMR spectrum of Cat. **1d** treated with 2 eq NEt_3 in DMSO-d_6. Blue squares indicate the peaks of Cat. **1d** and Red circles indicate the peaks of **L4**.

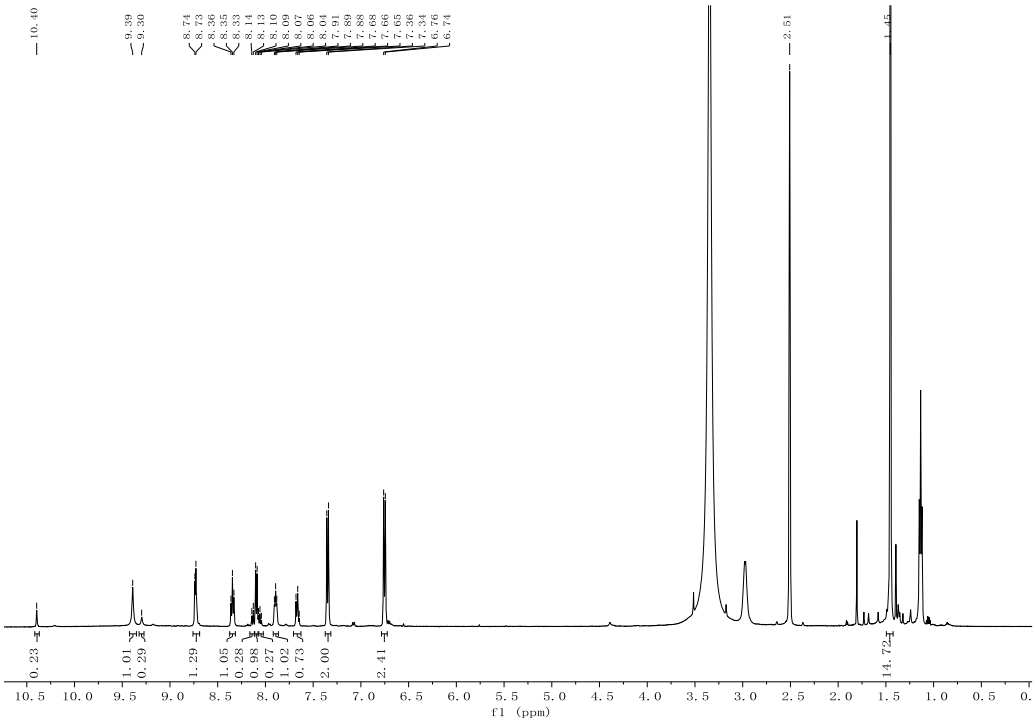


Fig. S4 The ^{1}H NMR spectrum of Cat. **1d** treated with 2 eq NEt_3 in DMSO-d_6.

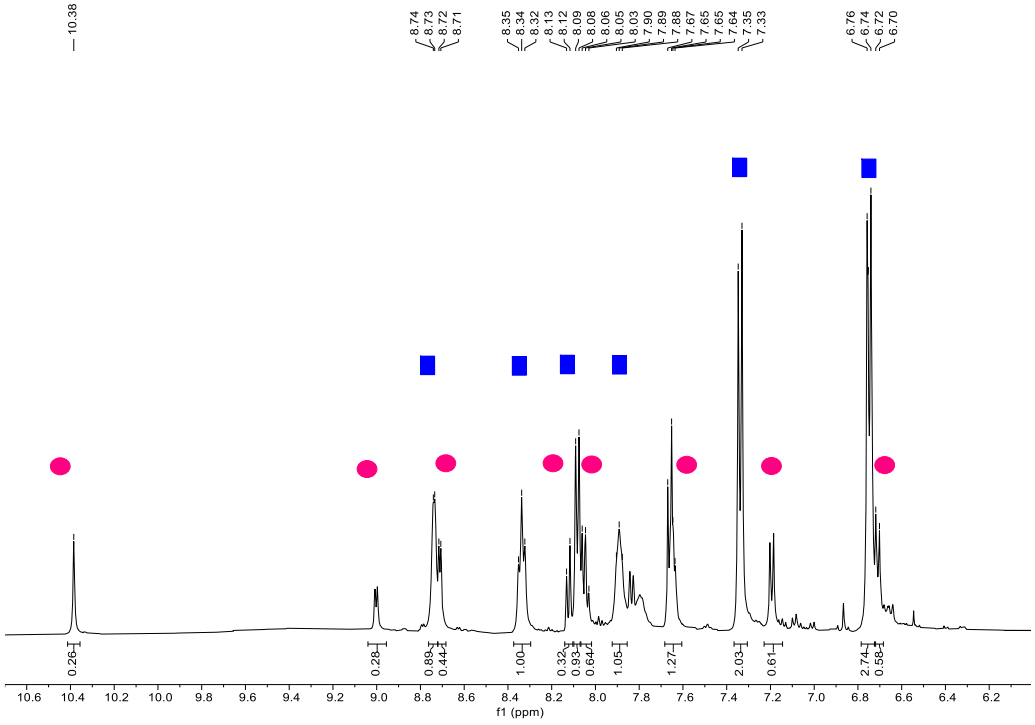


Fig. S5 Enlarged partial ^{1}H NMR spectrum of Cat. **1d** treated with 15 eq NEt_3 in DMSO-d_6. Blue squares indicate the peaks of Cat. **1d** and Red circles indicate the peaks of **L4**.

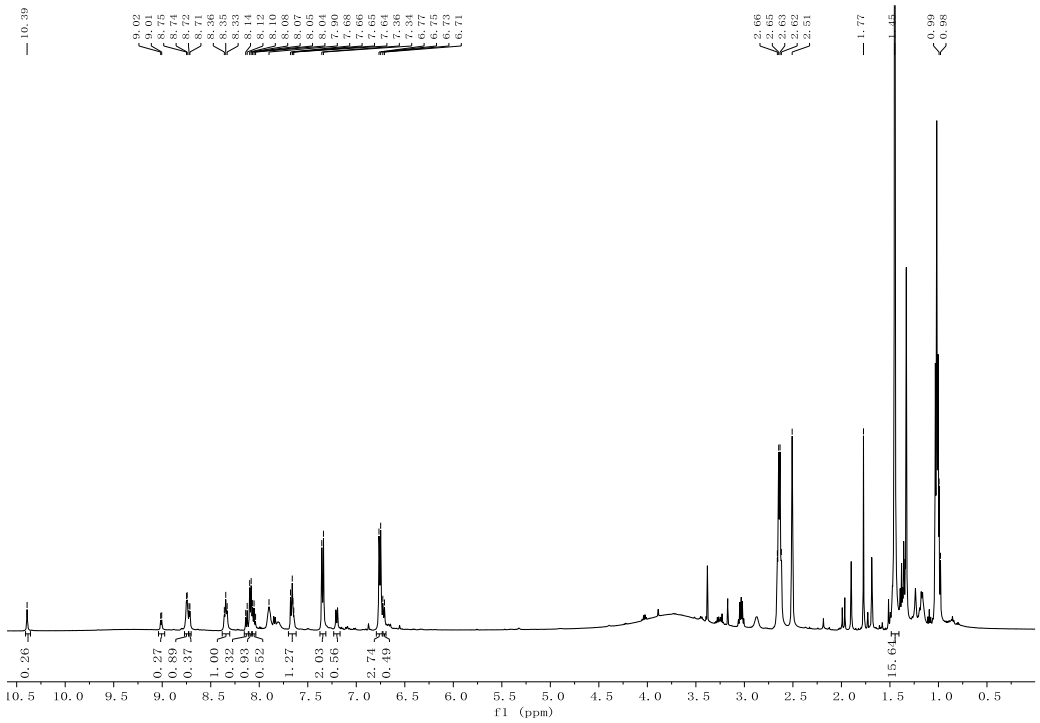


Fig. S6 The ^{1}H NMR spectrum of Cat. **1d** treated with 15 eq NEt_3 in DMSO-d_6.

5.2 Control Experiments

a) A mixture of 1-phenylethanol (0.5 mmol), benzaldehyde (0.8 mmol), catalyst **1d** (0.01 mmol), and KOH (0.75 mmol) in 1 mL H_2O were added in a 10 mL Schlenk tube and stirred in an oil-bath (100 °C) for 24 hours. Upon completion of the reaction, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic layers were evaporated and the residue was purified by column chromatography over silica gel using ethyl acetate/hexane mixture (1:10) as an eluent to provide the product.

b) A mixture of acetophenone (0.5 mmol), benzyl alcohol (0.8 mmol), catalyst **1d** (0.01 mmol), and KOH (0.75 mmol) in 1 mL H_2O were added in a 10 mL Schlenk tube and stirred in an oil-bath (100 °C) for 24 hours. Upon completion of the reaction, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic layers were evaporated and the residue was purified by column

chromatography over silica gel using ethyl acetate/hexane mixture (1:10) as an eluent to provide the product.

c) A mixture of acetophenone (0.5 mmol), benzaldehyde (0.8 mmol), and KOH (0.75 mmol) in 1 mL H_2O were added in a 10 mL Schlenk tube and stirred in an oil bath (100 °C) for 24 hours. Upon completion of the reaction, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic layers were evaporated and the residue was purified by column chromatography over silica gel using ethyl acetate/hexane mixture (1:10) as an eluent to provide the product.

d) A mixture of chalcone (0.5 mmol), benzyl alcohol (0.8 mmol), catalyst **1d** (0.01 mmol), and KOH (0.75 mmol) in 1 mL H_2O were added in a 10 mL Schlenk tube and stirred in an oil-bath (100 °C) for 24 hours. Upon completion of the reaction, the reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic layers were evaporated and the residue was purified by column chromatography over silica gel using ethyl acetate/hexane mixture (1:10) as an eluent to provide the product.

5.3 *In-situ* FT-IR Experiments

A mixture of 1-phenylethanol (0.5 mmol), benzyl alcohol (0.8 mmol), catalyst **1d** (0.01 mmol), and KOH (0.75 mmol) in 1 mL H_2O was added in a 10 mL Schlenk tube. The IR probe was inserted into the solution through an adapter. After the Schlenk tube was put into an oil bath (100°C), data collection was started. The collected spectra are shown in **Fig. 4** and **Fig. 5**.

6. NMR Spectra

6.1 NMR Spectra of the ligands

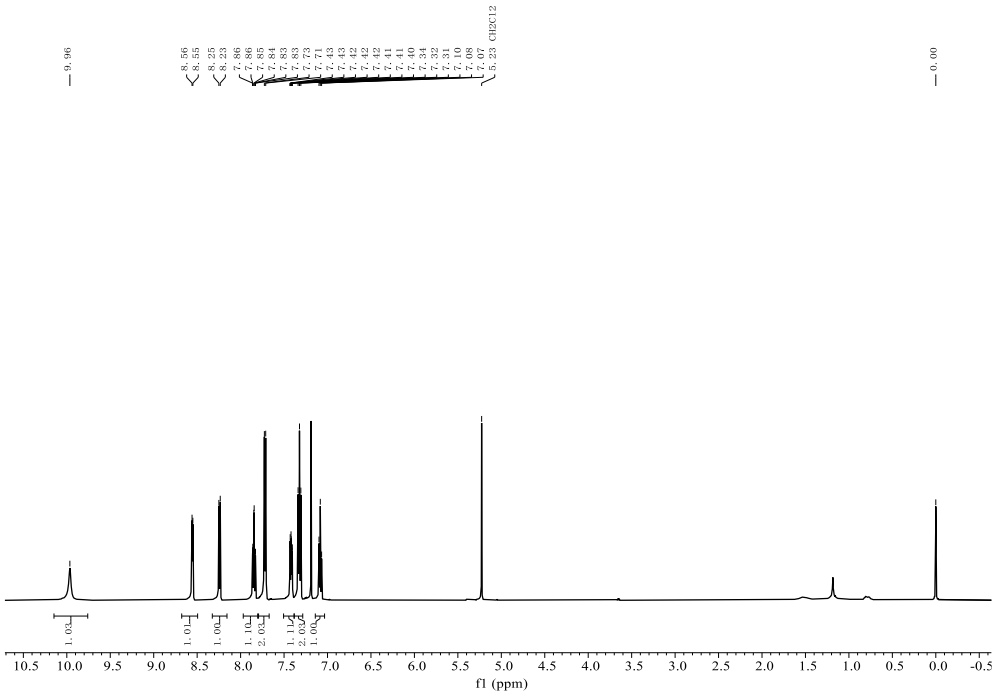


Fig. S7 ^{1}H NMR spectrum of **L1** in $CDCl_3$.

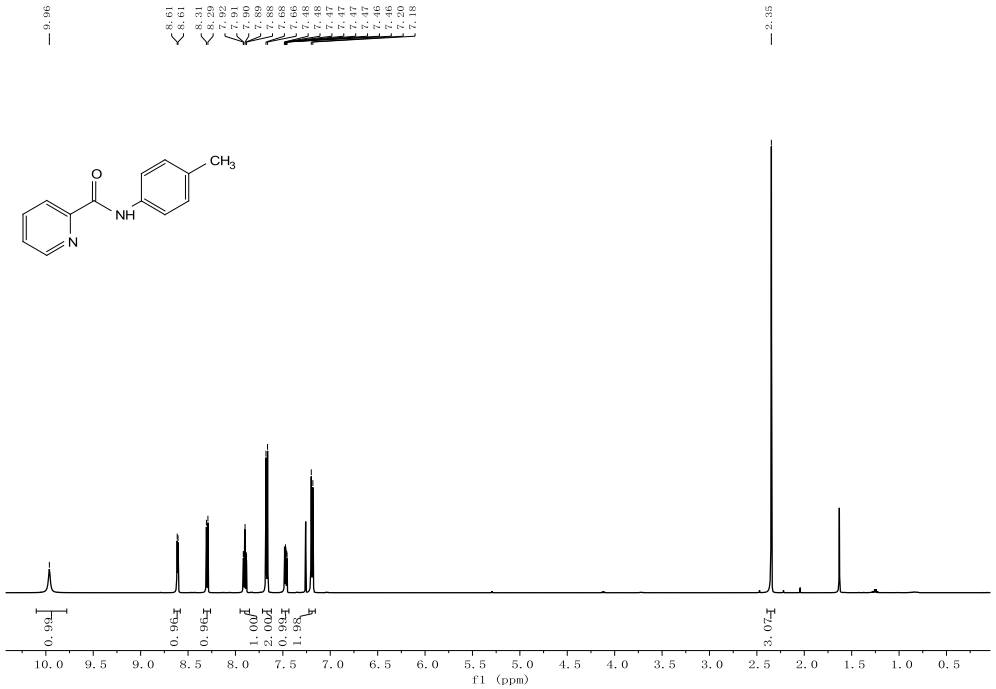


Fig. S8 ^{1}H NMR spectrum of **L2** in $CDCl_3$.

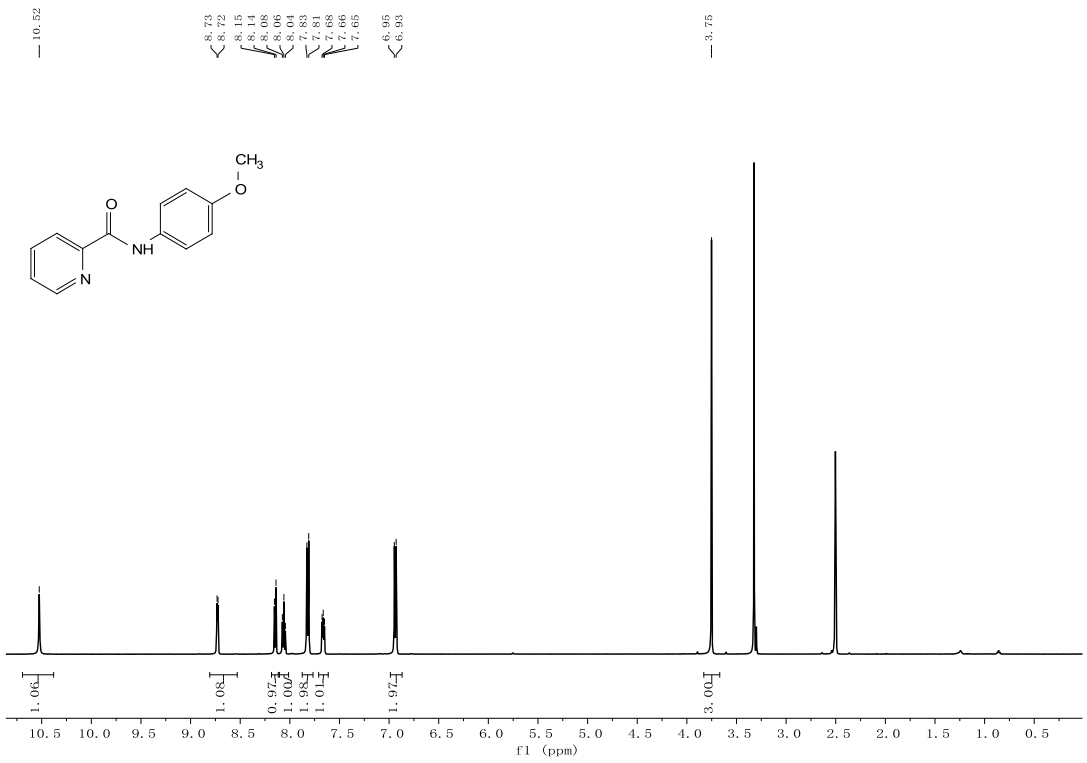


Fig. S9 ^{1}H NMR spectrum of **L3** in DMSO-d_6.

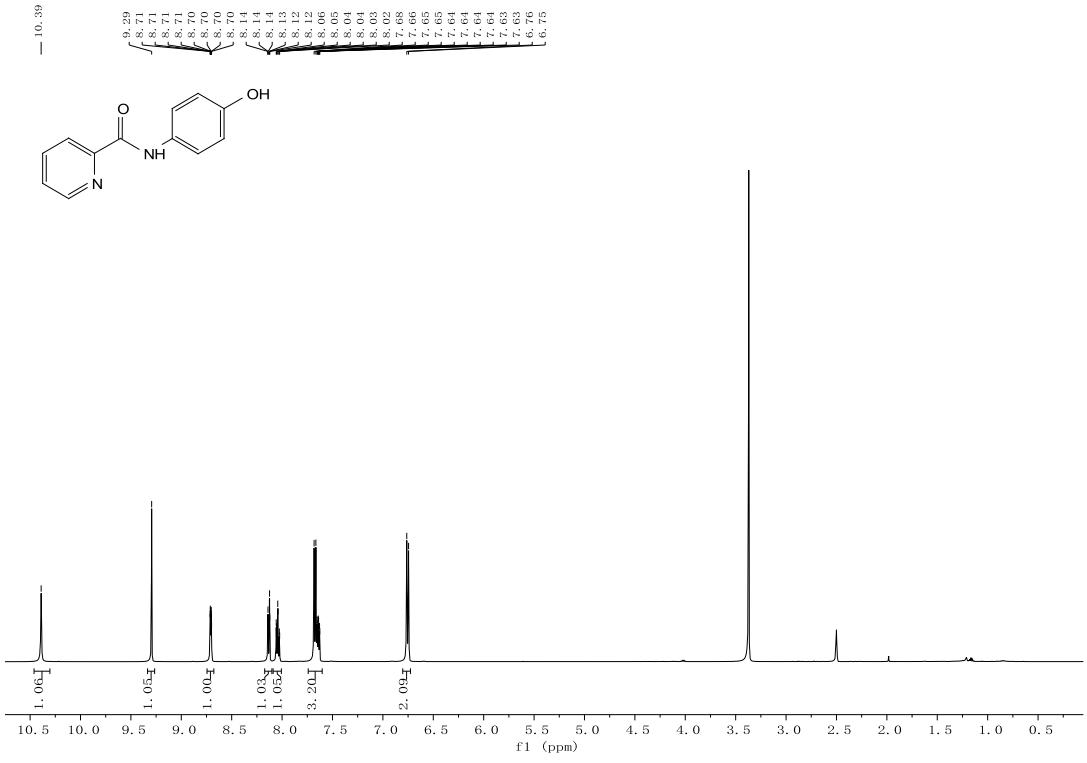


Fig. S10 ^{1}H NMR spectrum of **L4** in DMSO-d_6.

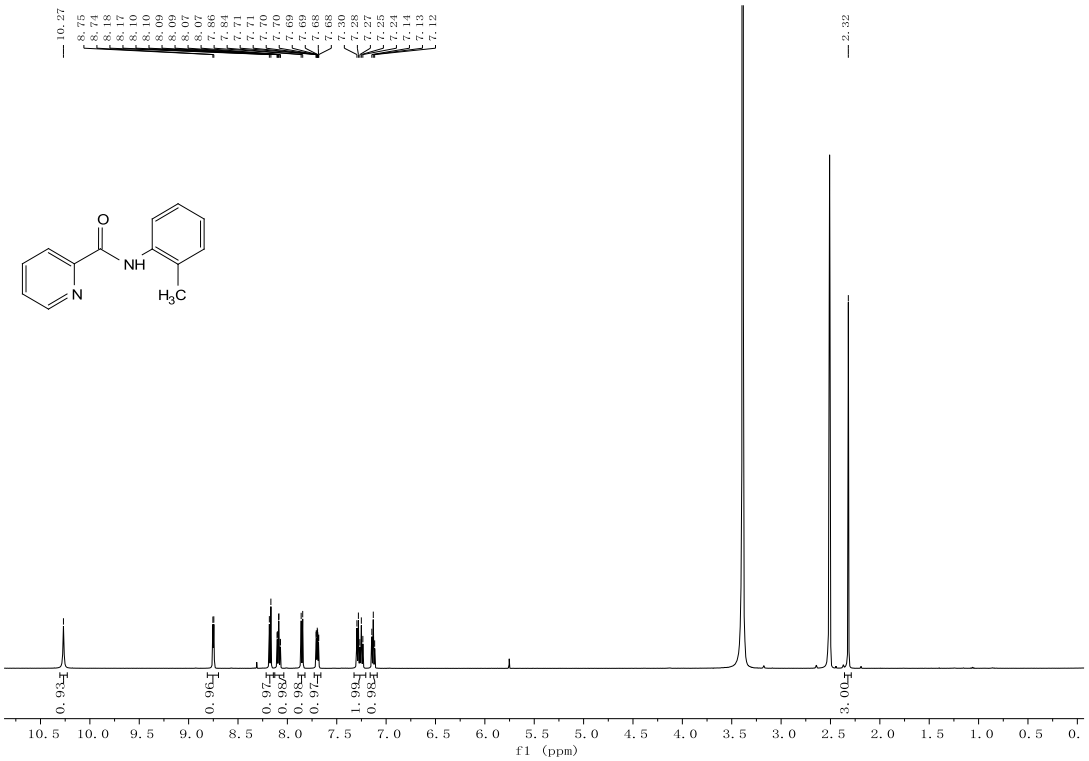


Fig. S11 ^{1}H NMR spectrum of **L5** in DMSO-d_6.

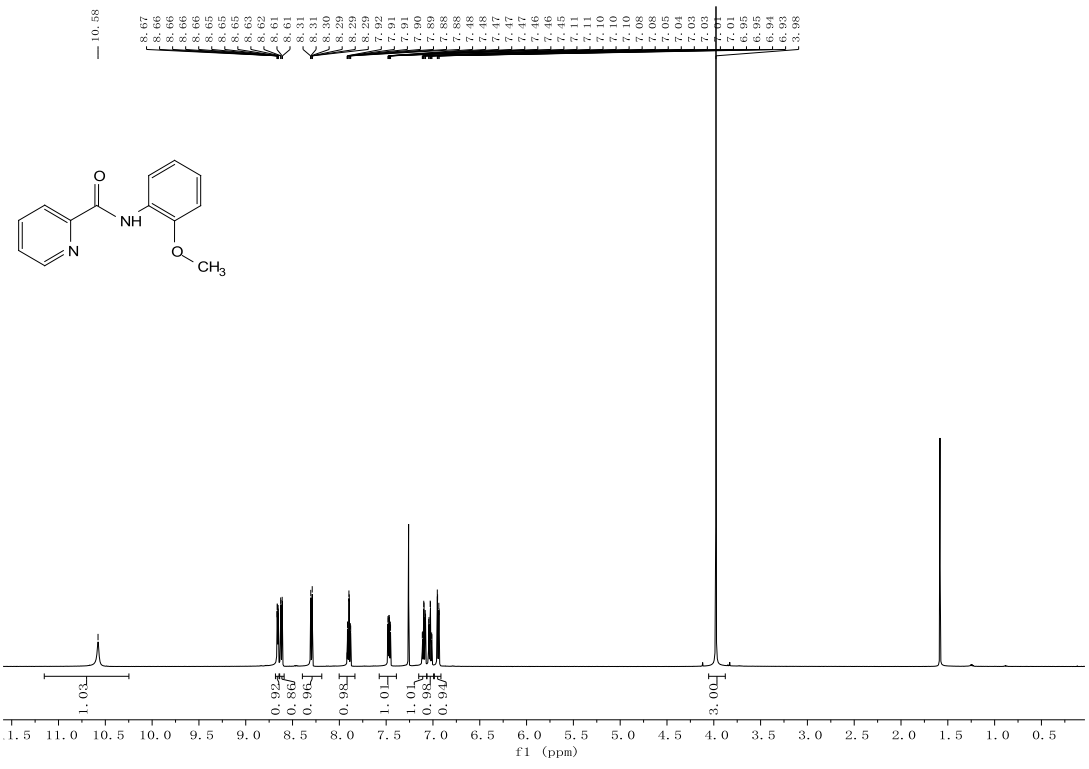


Fig. S12 ^{1}H NMR spectrum of **L6** in $CDCl_3$.

6.2 NMR Spectra of the Ir Complexes

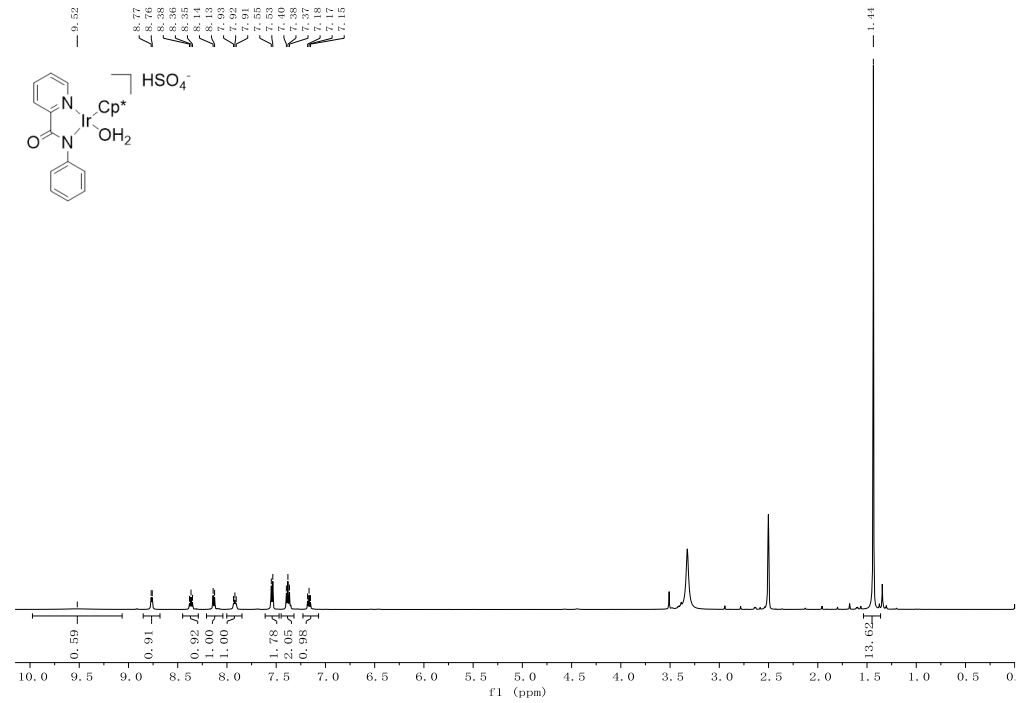


Fig. S13 ^{1}H NMR spectrum of **Cat. 1a** in DMSO-d_6.

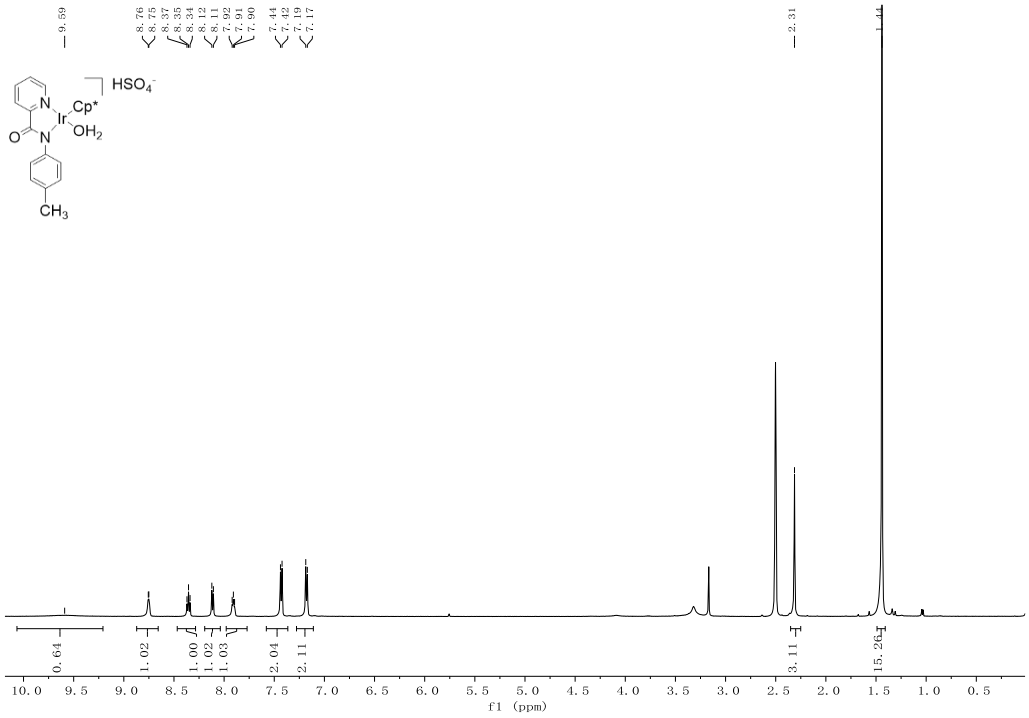


Fig. S14 ^{1}H NMR spectrum of **Cat. 1b** in DMSO-d_6.

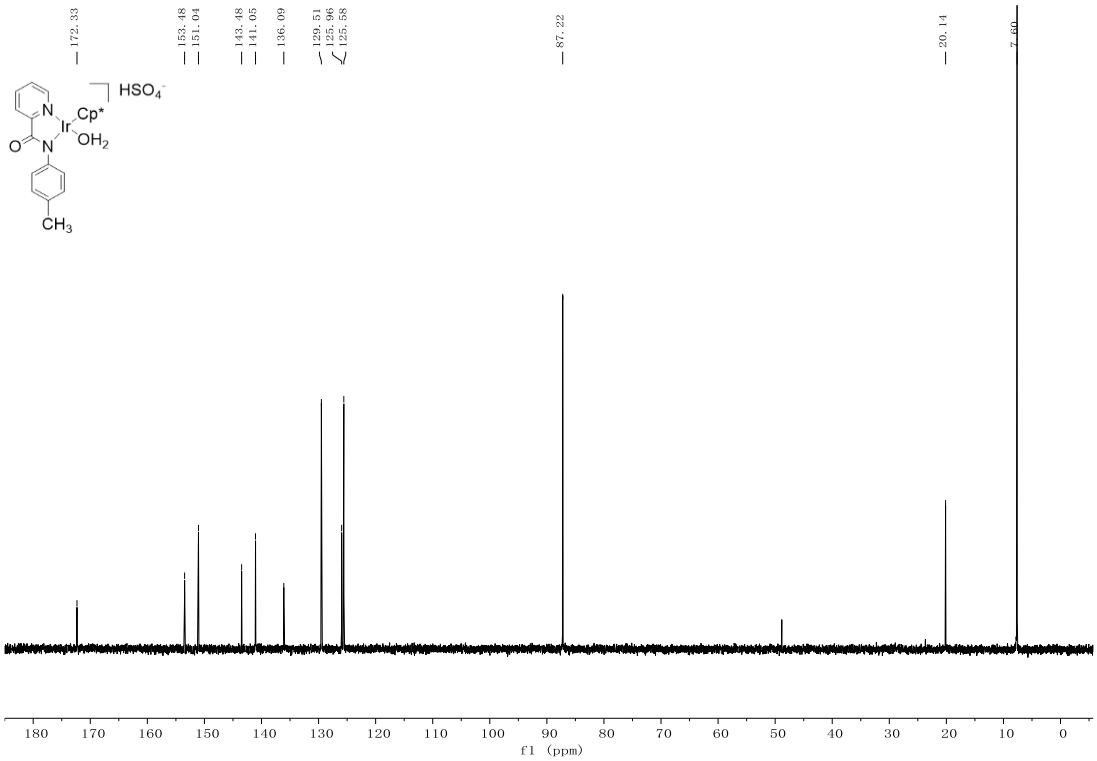


Fig. S15 ^{13}C NMR spectrum of **Cat. 1b** in DMSO-d_6.

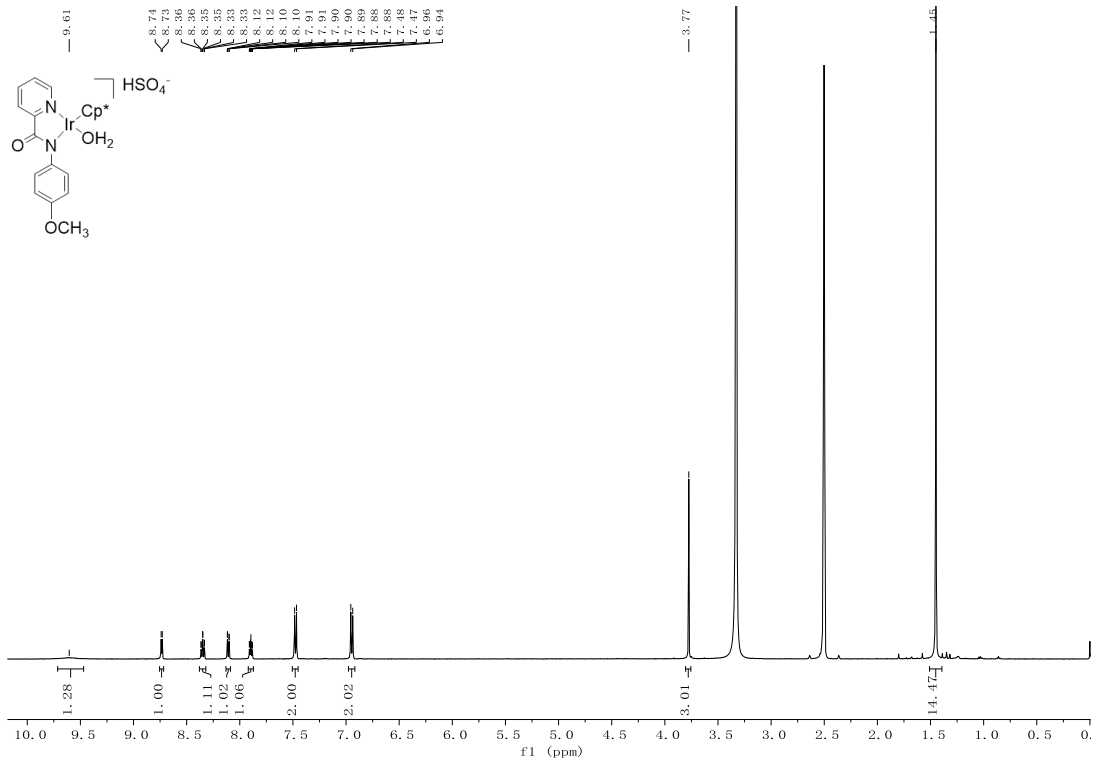


Fig. S16 ^{1}H NMR spectrum of **Cat. 1c** in DMSO-d_6.

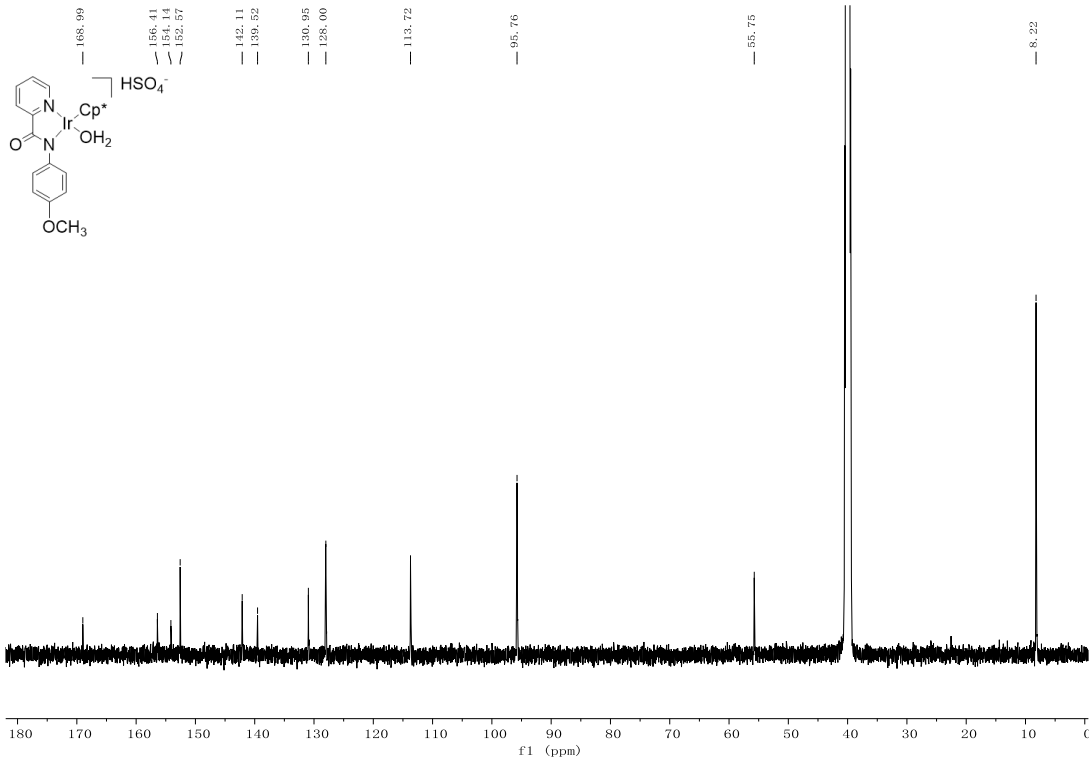


Fig. S17 ^{13}C NMR spectrum of **Cat. 1c** in DMSO-d_6.

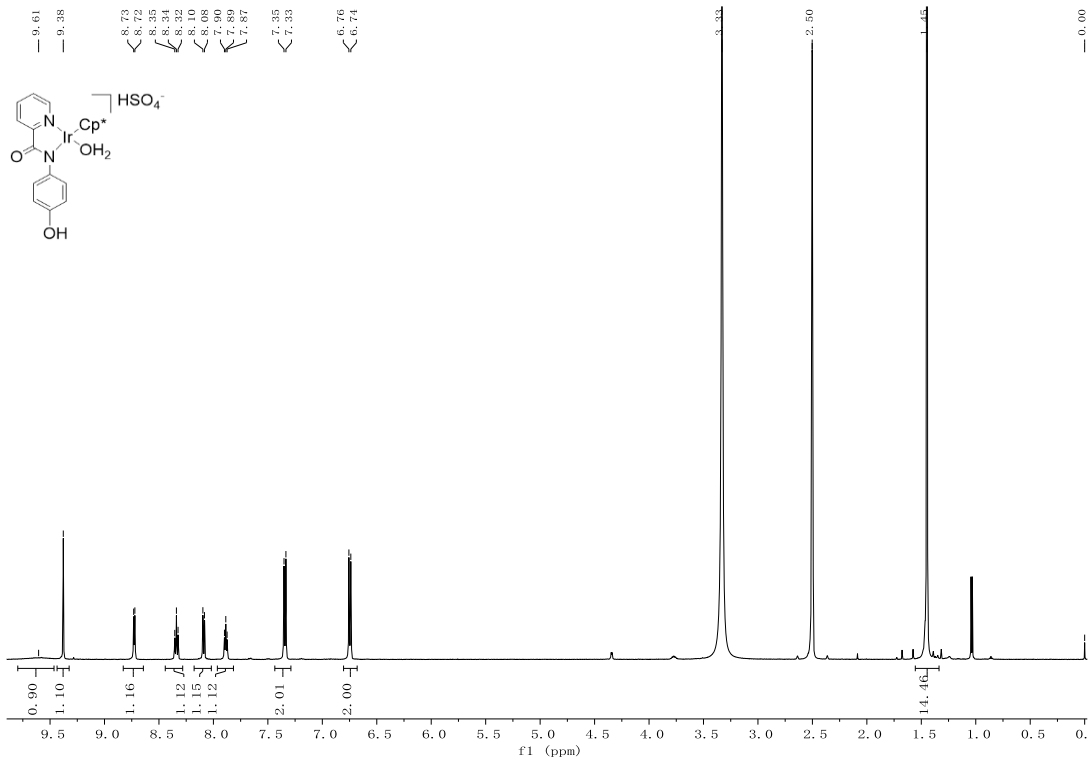


Fig. S18 ^{1}H NMR spectrum of **Cat. 1d** in DMSO-d_6.

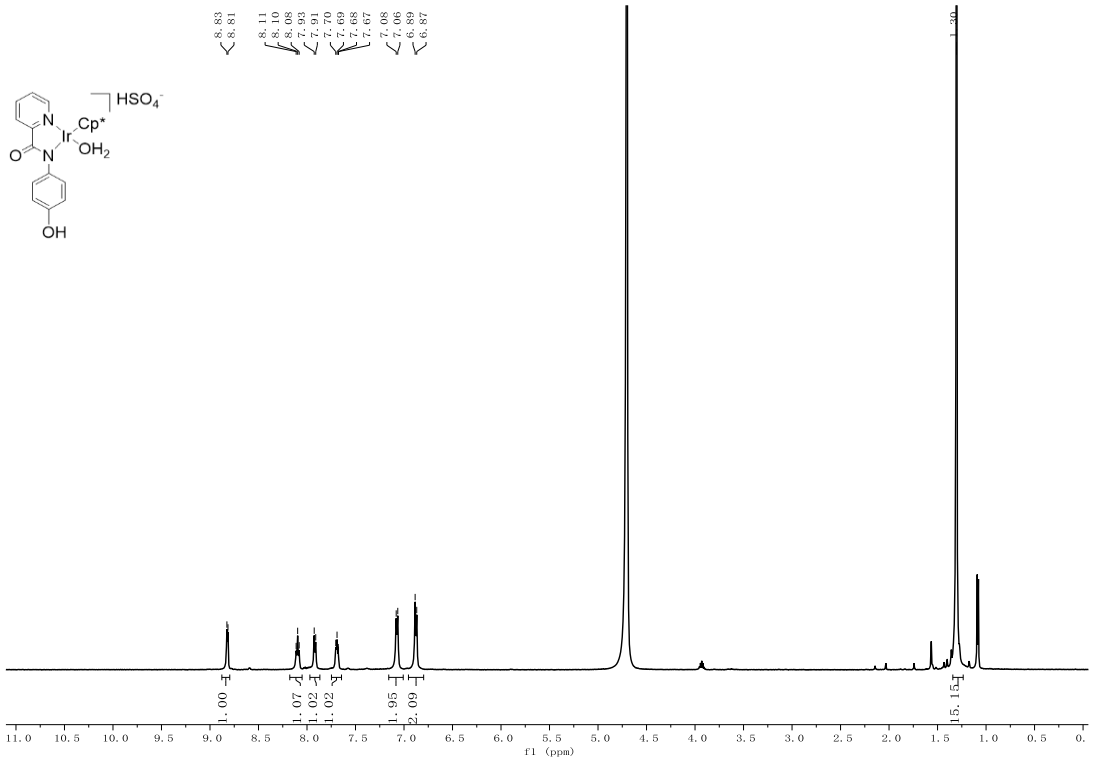


Fig. S19 ^{1}H NMR spectrum of **Cat. 1d** in D_2O.

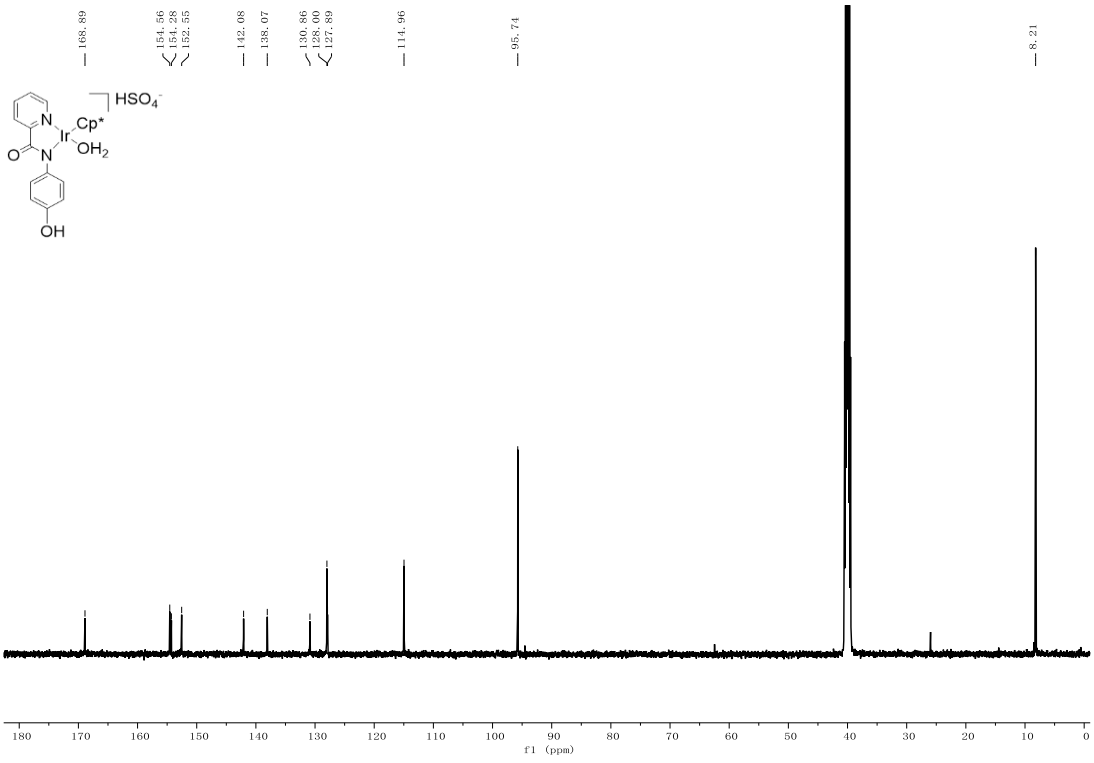


Fig. S20 ^{13}C NMR spectrum of **Cat. 1d** in DMSO-d_6.

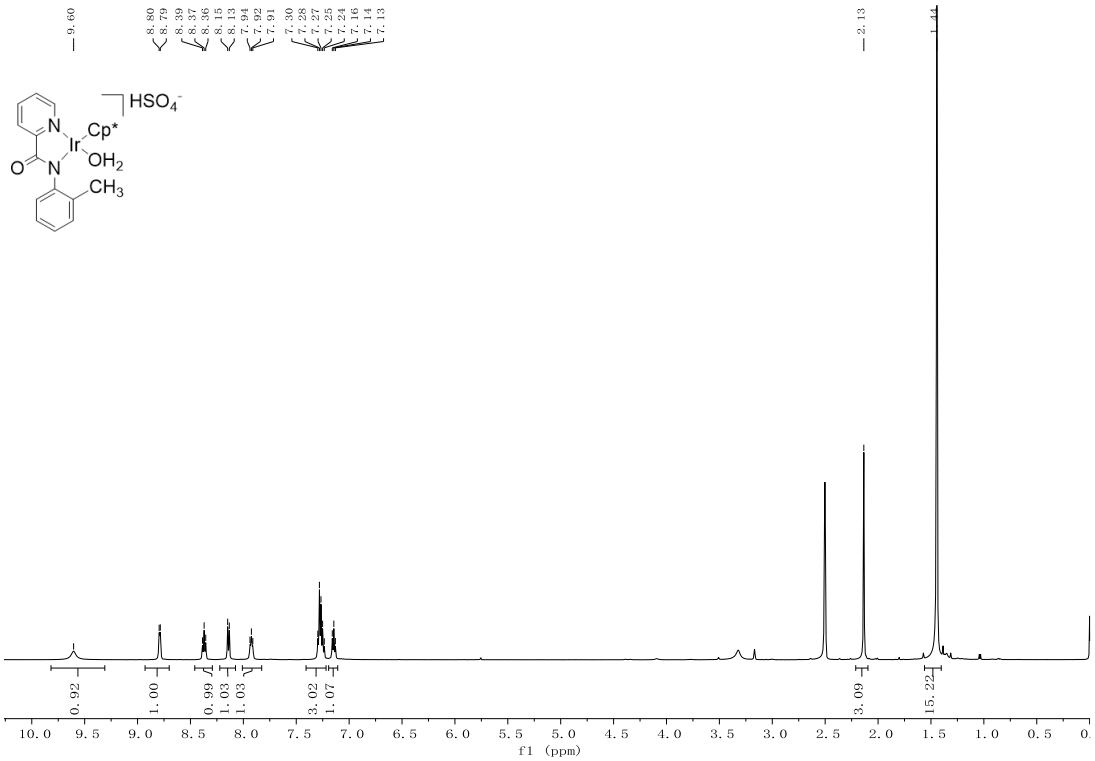


Fig. S21 ^{1}H NMR spectrum of **Cat. 1e** in DMSO-d_6.

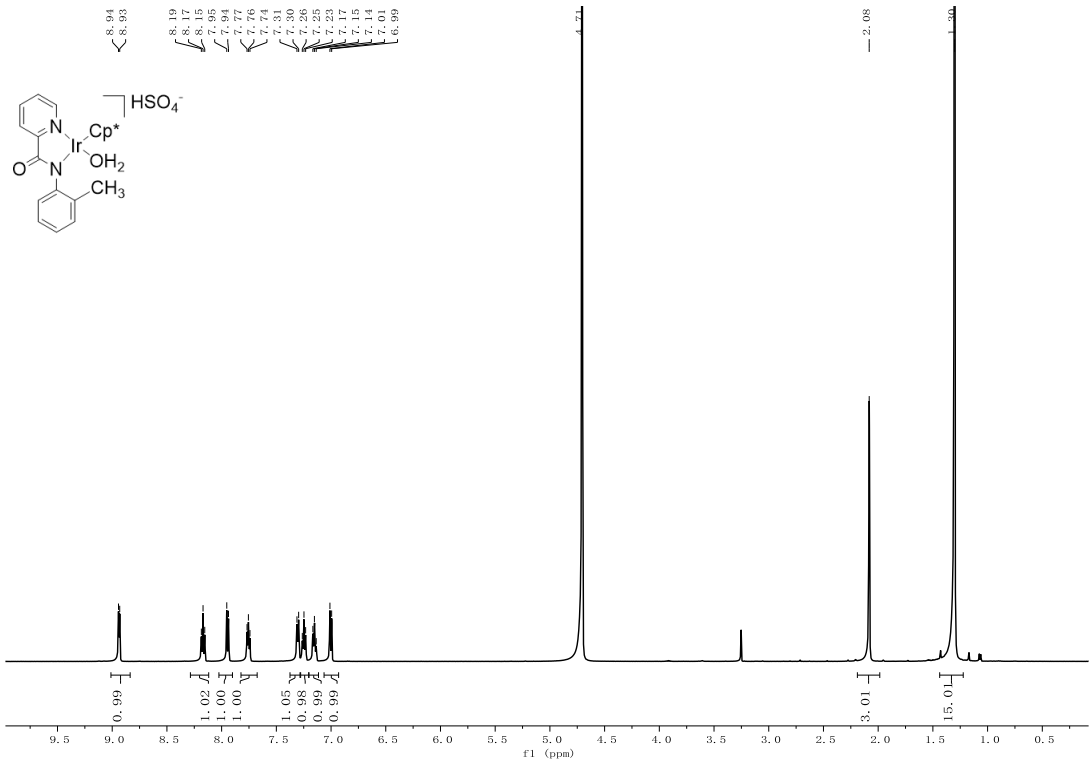


Fig.S22 ^{1}H NMR spectrum of **Cat. 1e** in D_2O.

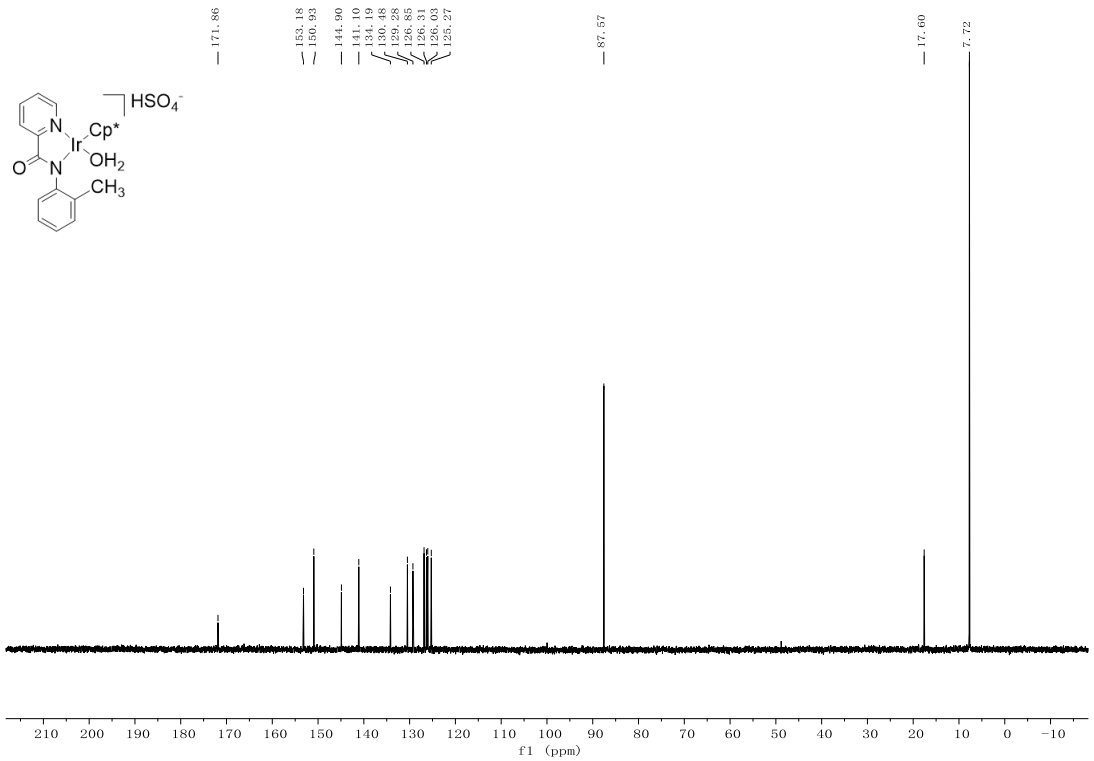


Fig. S23 ^{13}C NMR spectrum of **Cat. 1e** in DMSO-d_6.

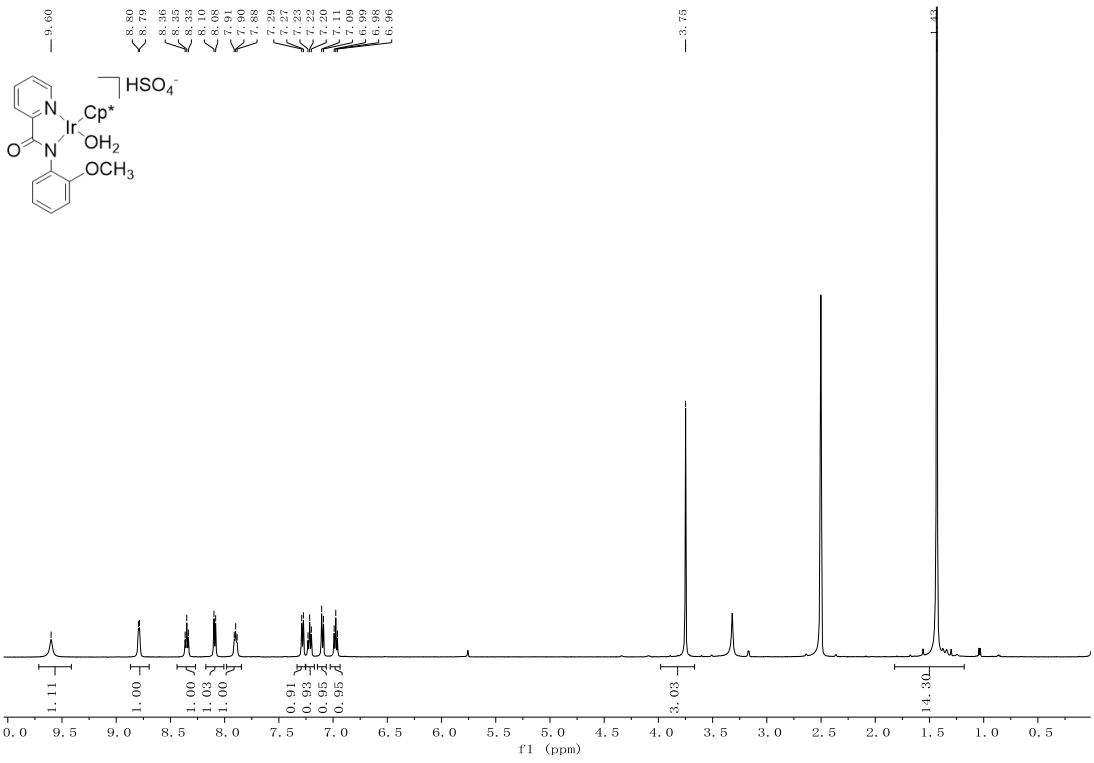


Fig. S24 ^{1}H NMR spectrum of **Cat. 1f** in DMSO-d_6.

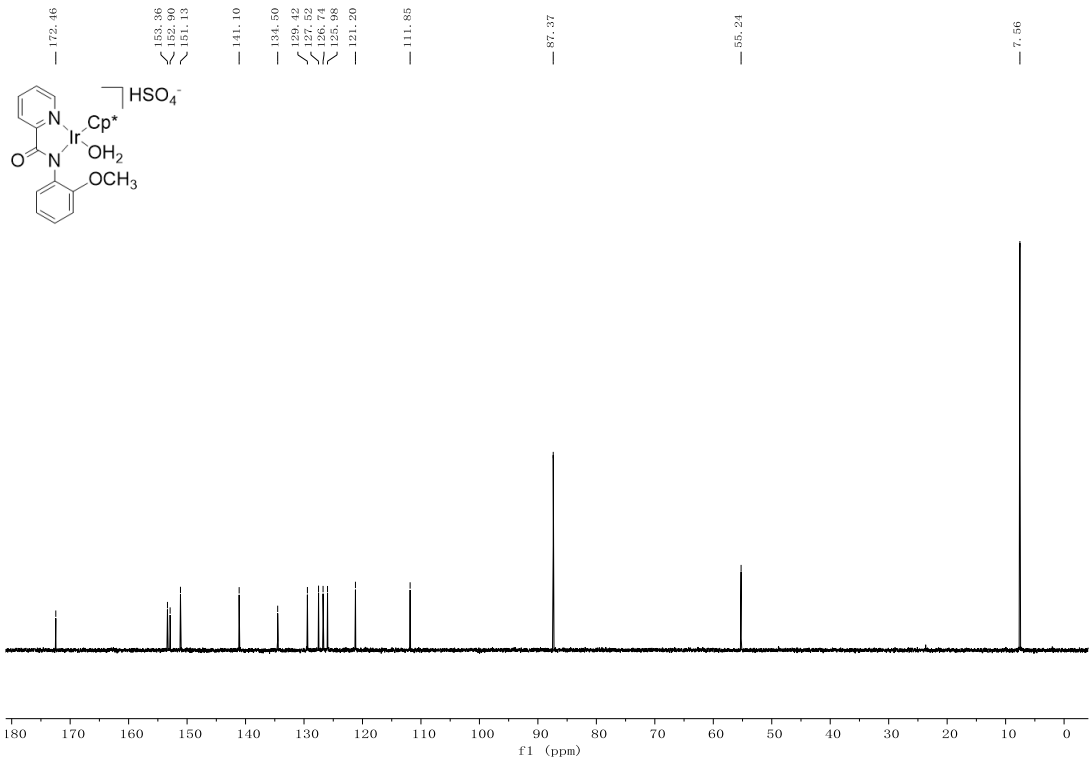


Fig. S25 ^{13}C NMR spectrum of **Cat. 1f** in DMSO-d_6.

6.3 NMR Spectra of the products

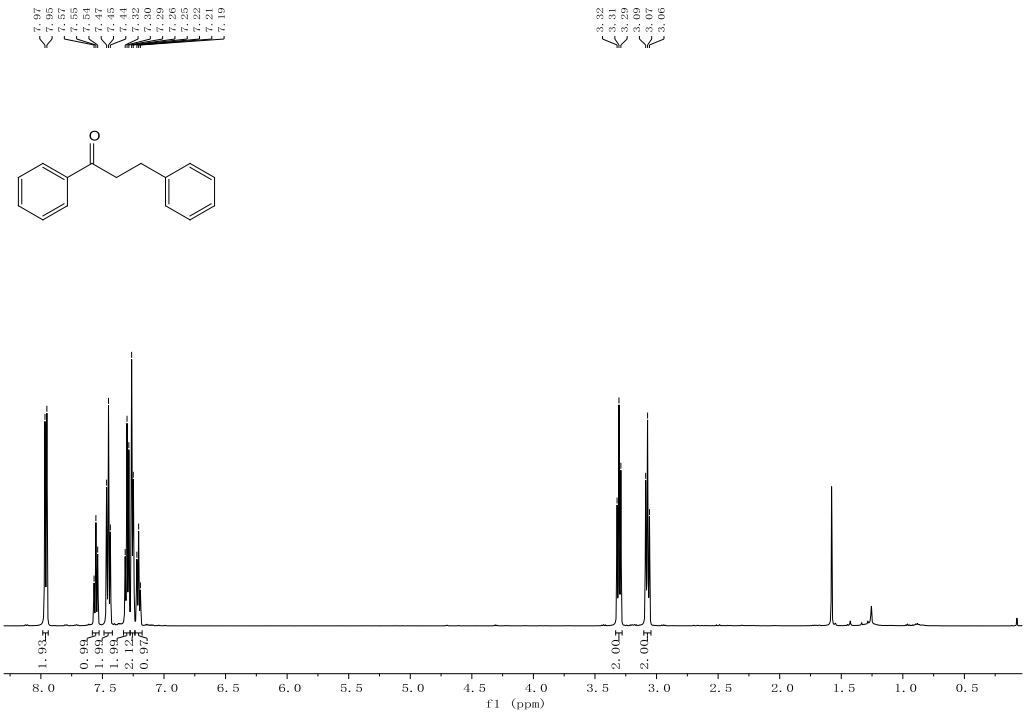


Fig. S26 ^{1}H NMR spectrum of **4a** in $CDCl_3$.

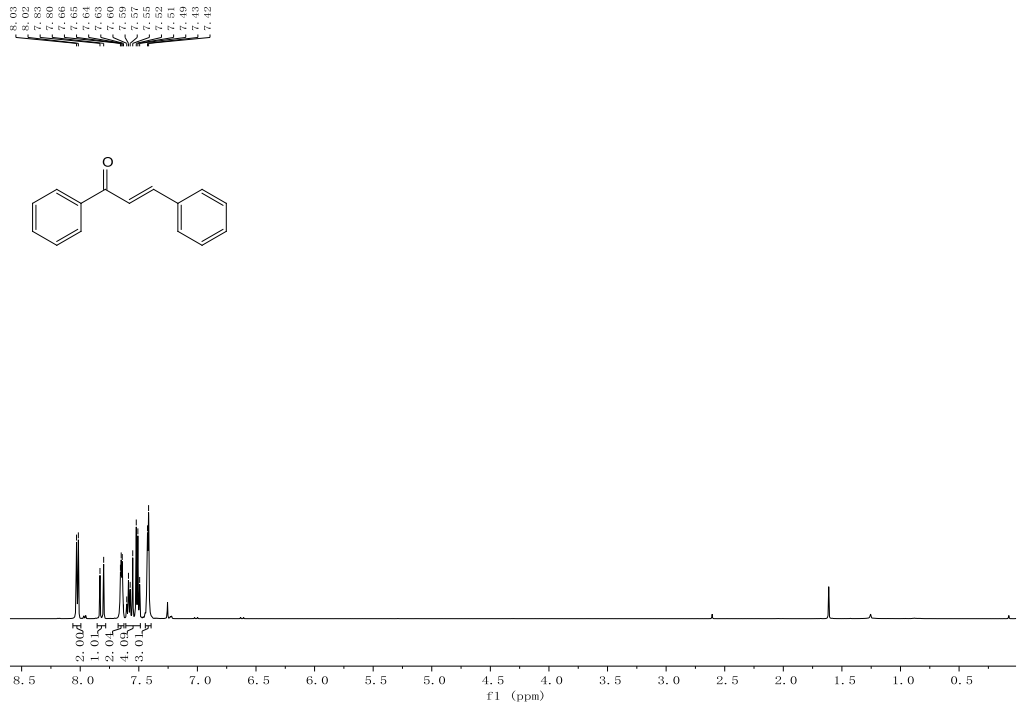


Fig. S27 ^{1}H NMR spectrum of **Chalcone** in $CDCl_3$.

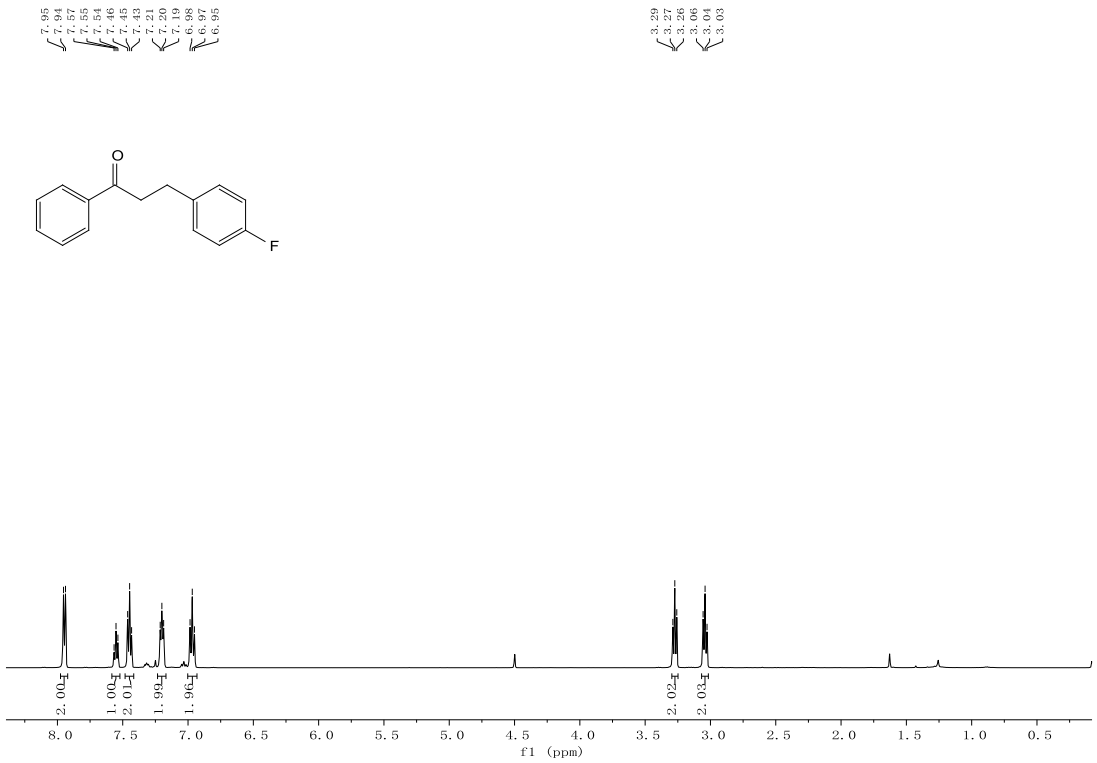


Fig. S28 ^{1}H NMR spectrum of **4b** in $CDCl_3$.

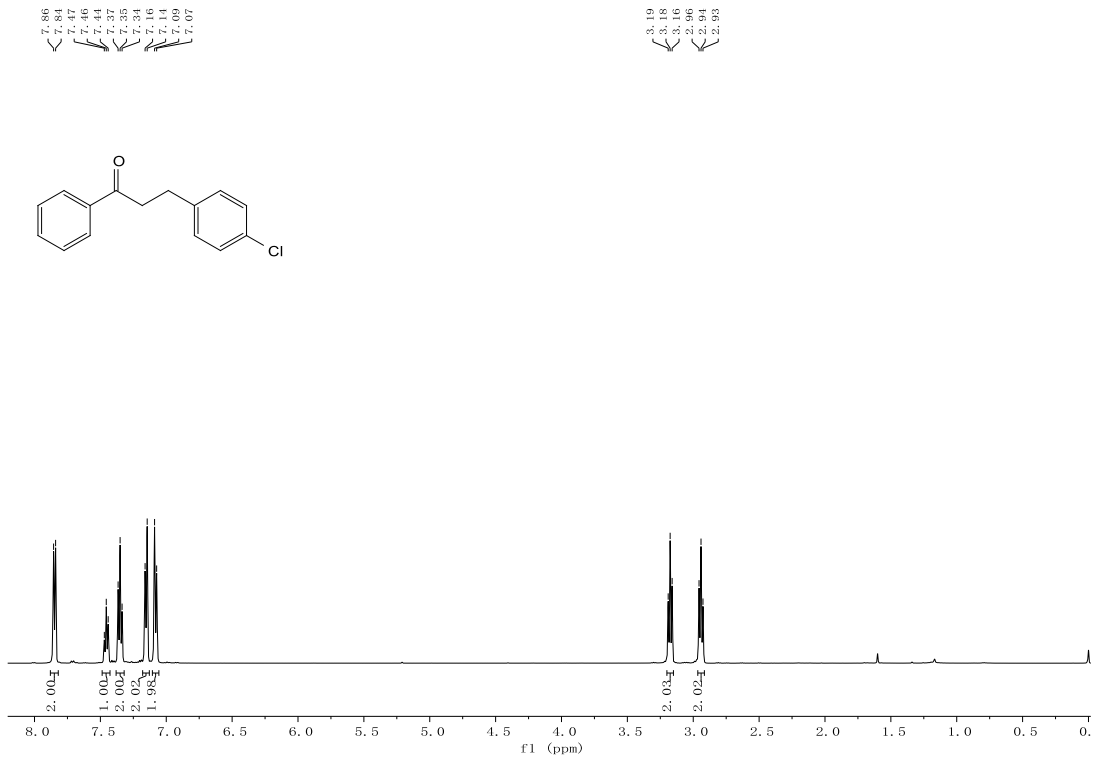


Fig. S29 ^{1}H NMR spectrum of **4c** in $CDCl_3$.

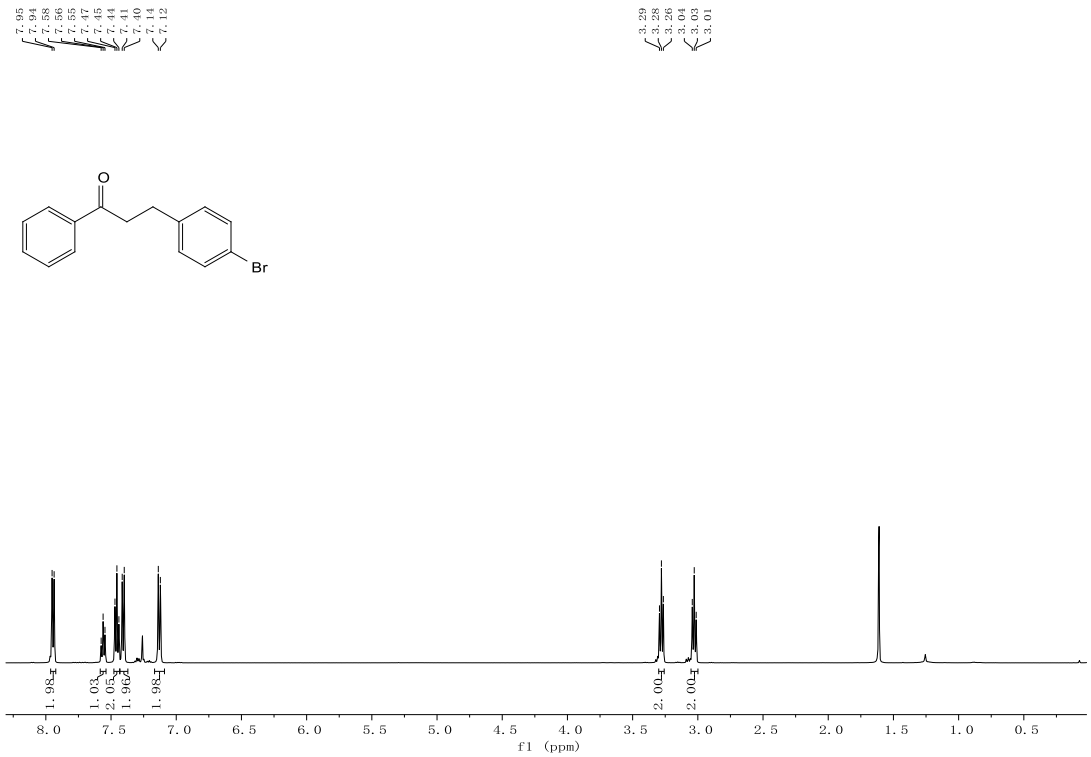


Fig. S30 ^{1}H NMR spectrum of **4d** in $CDCl_3$.

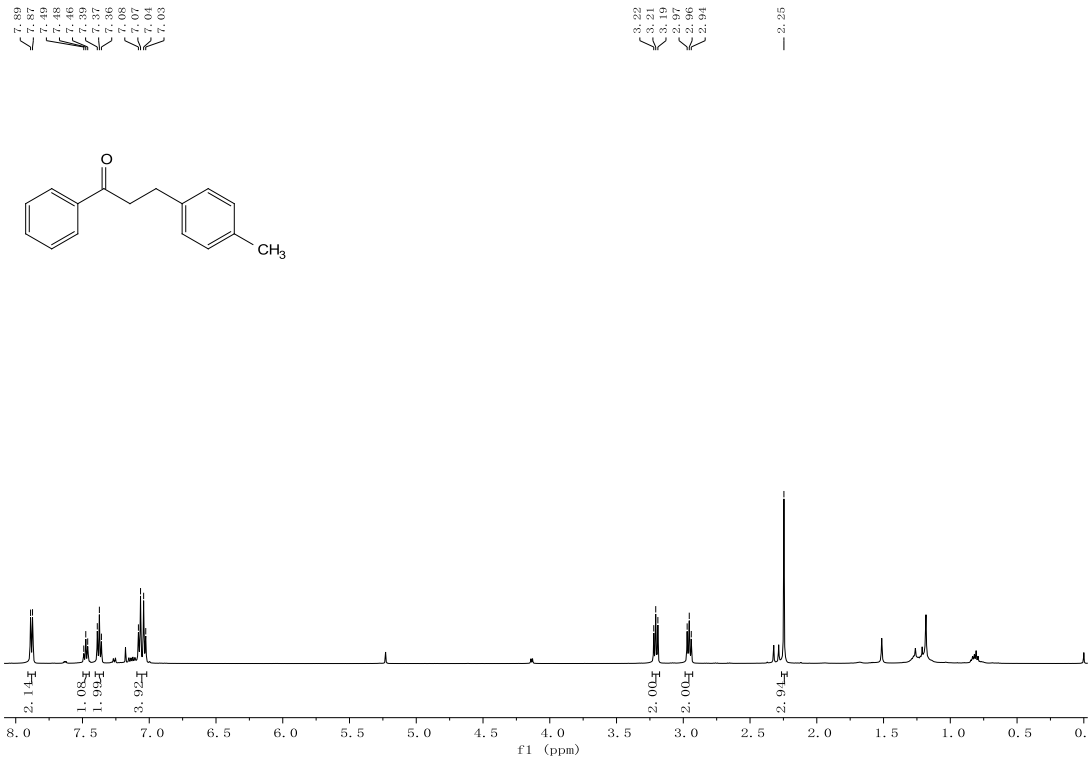


Fig. S31 ^{1}H NMR spectrum of **4e** in $CDCl_3$.

Fig. S32 ^{1}H NMR spectrum of **4f** in $CDCl_3$.

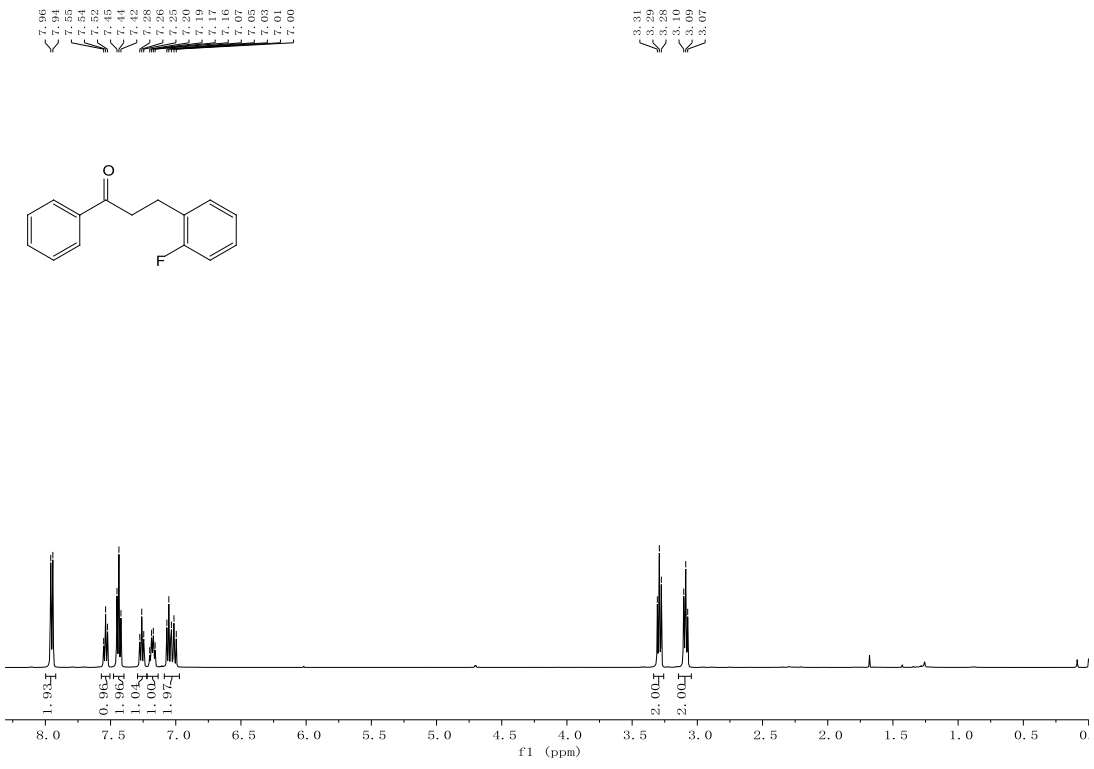


Fig. S33 ^{1}H NMR spectrum of **4g** in $CDCl_3$.

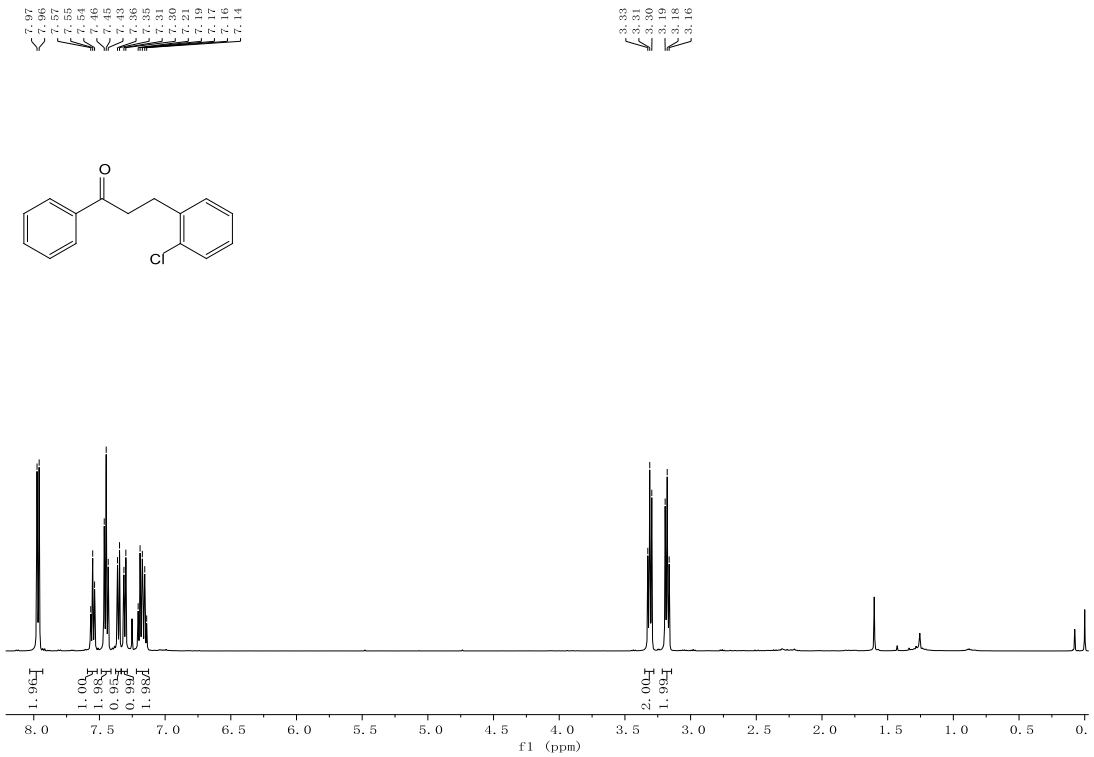


Fig. S34 ^{1}H NMR spectrum of **4h** in $CDCl_3$.

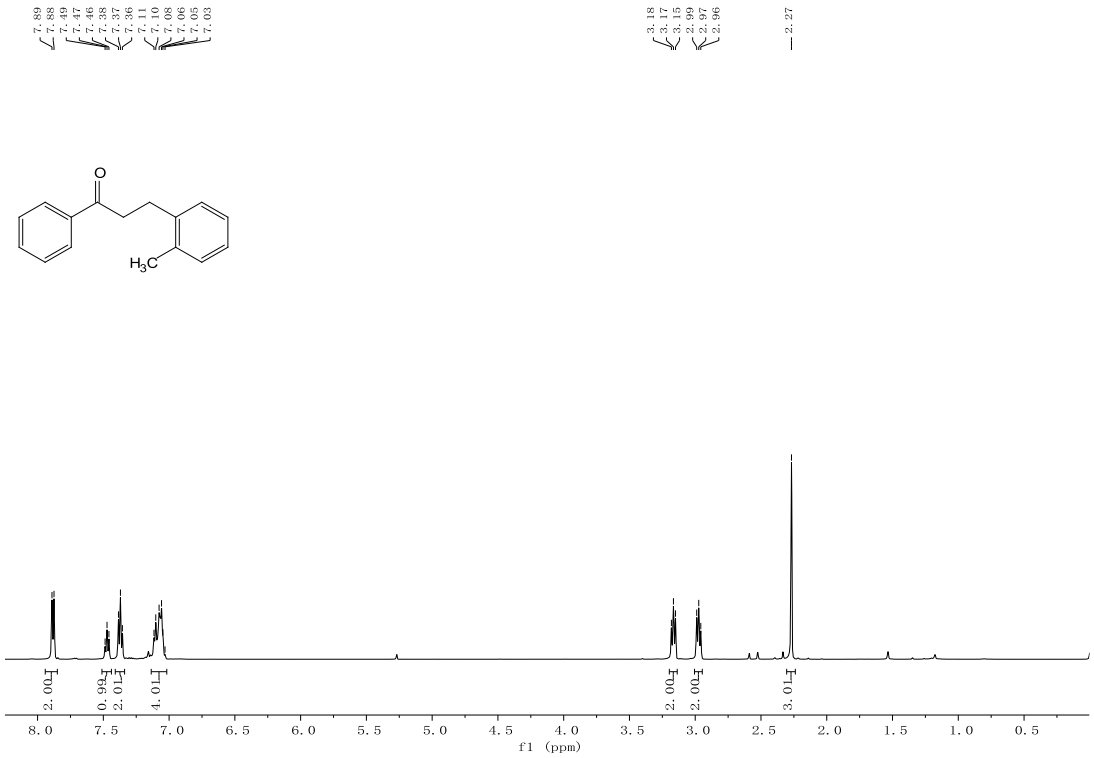


Fig. S35 ^{1}H NMR spectrum of **4i** in $CDCl_3$.

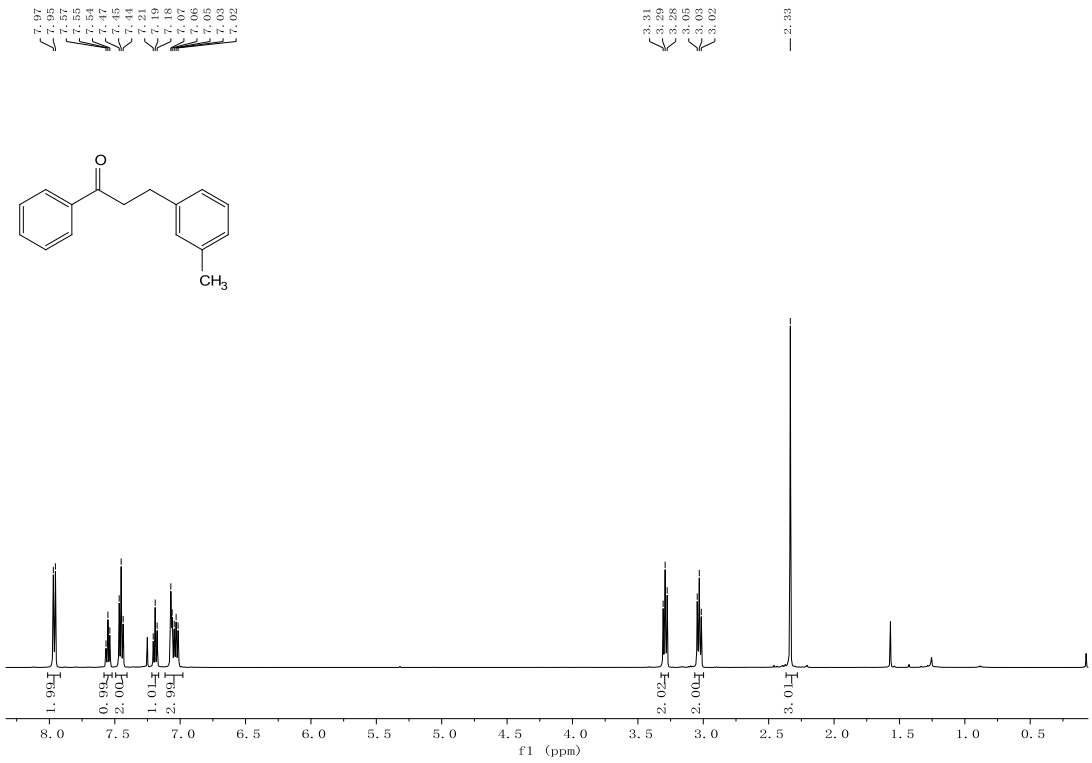


Fig. S36 ^{1}H NMR spectrum of **4j** in $CDCl_3$.

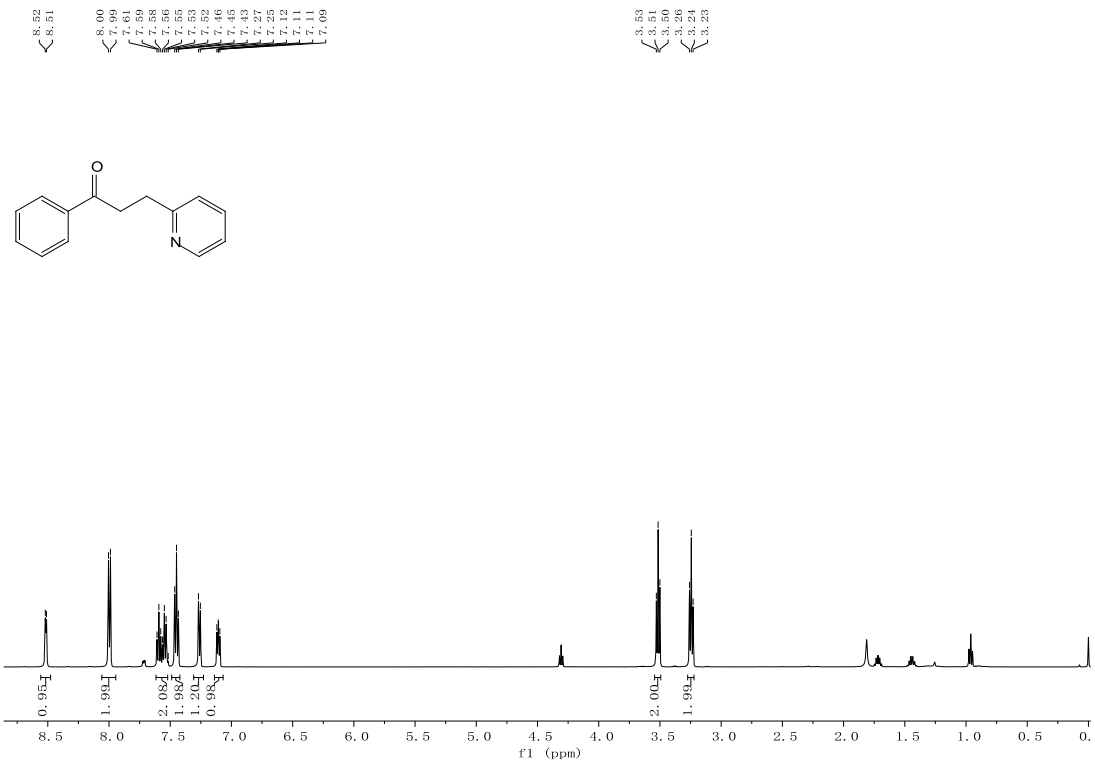


Fig. S37 ^{1}H NMR spectrum of **4k** in $CDCl_3$.

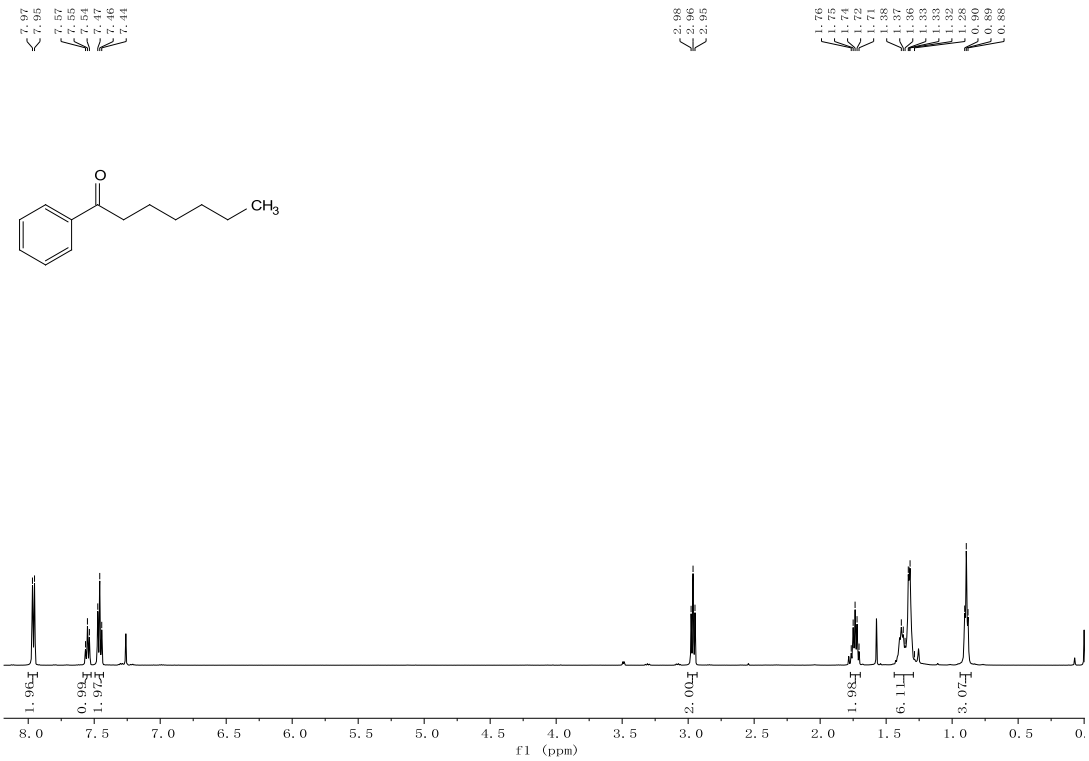


Fig. S38 ^{1}H NMR spectrum of **4l** in $CDCl_3$.

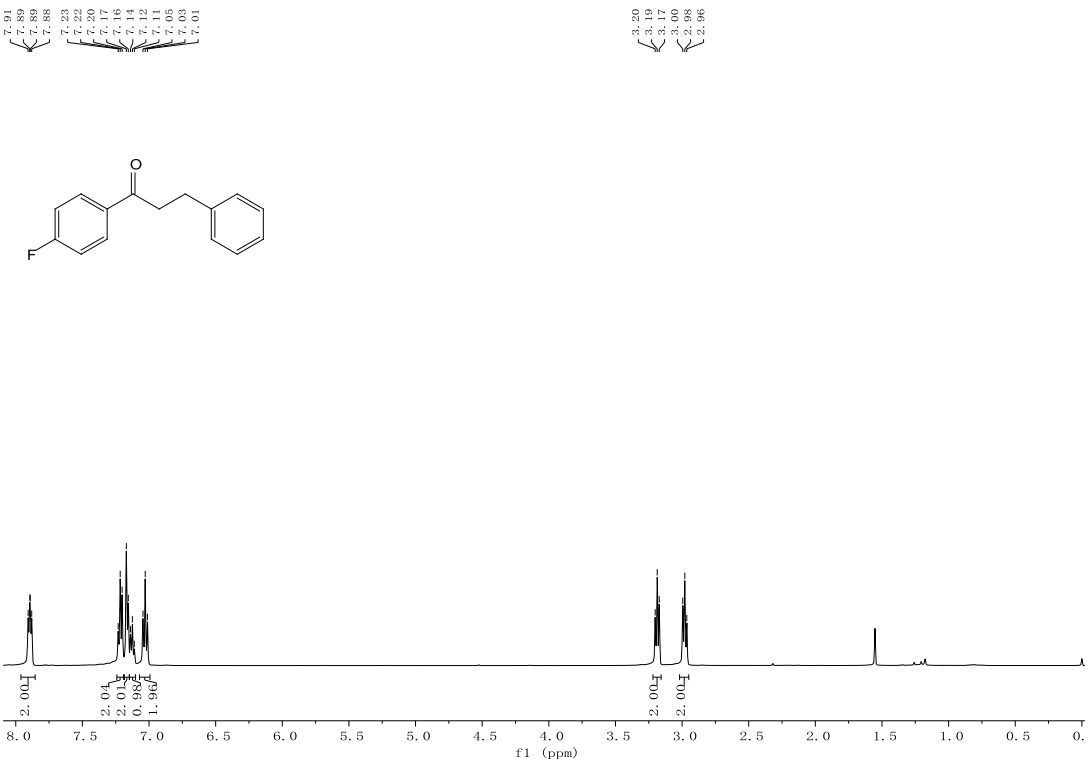


Fig. S39 ^{1}H NMR spectrum of **4m** in $CDCl_3$.

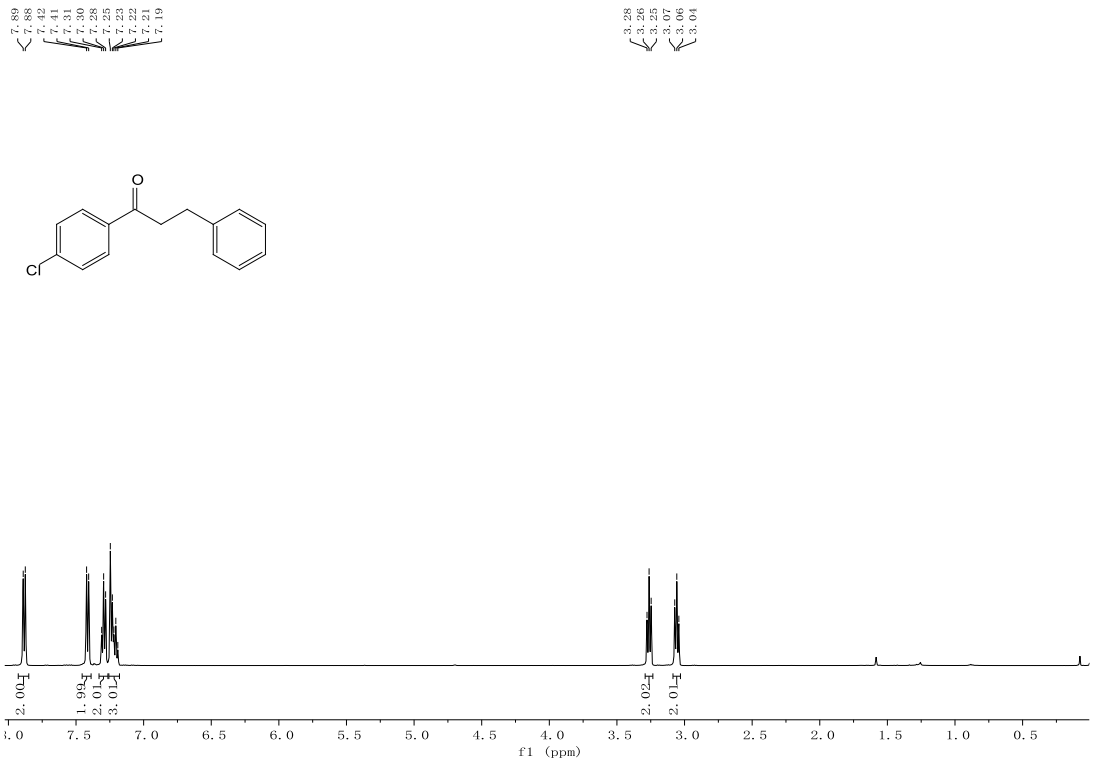


Fig. S40 ^{1}H NMR spectrum of **4n** in $CDCl_3$.

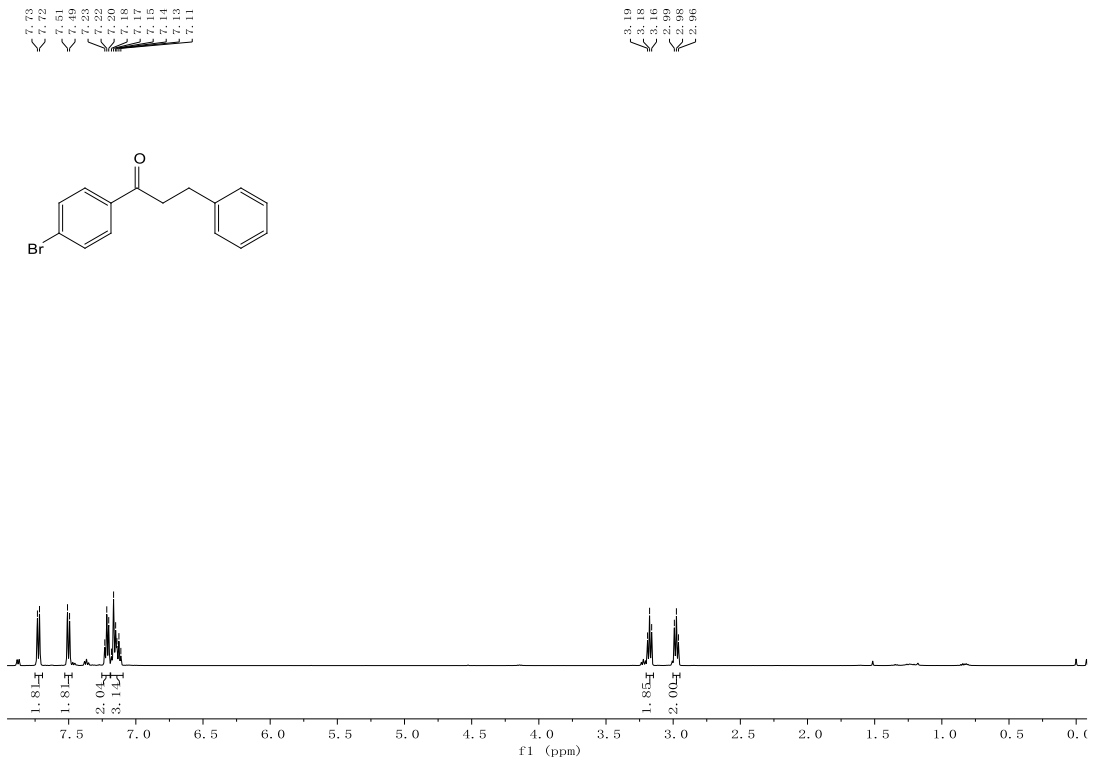


Fig. S41 ^{1}H NMR spectrum of **4o** in $CDCl_3$.

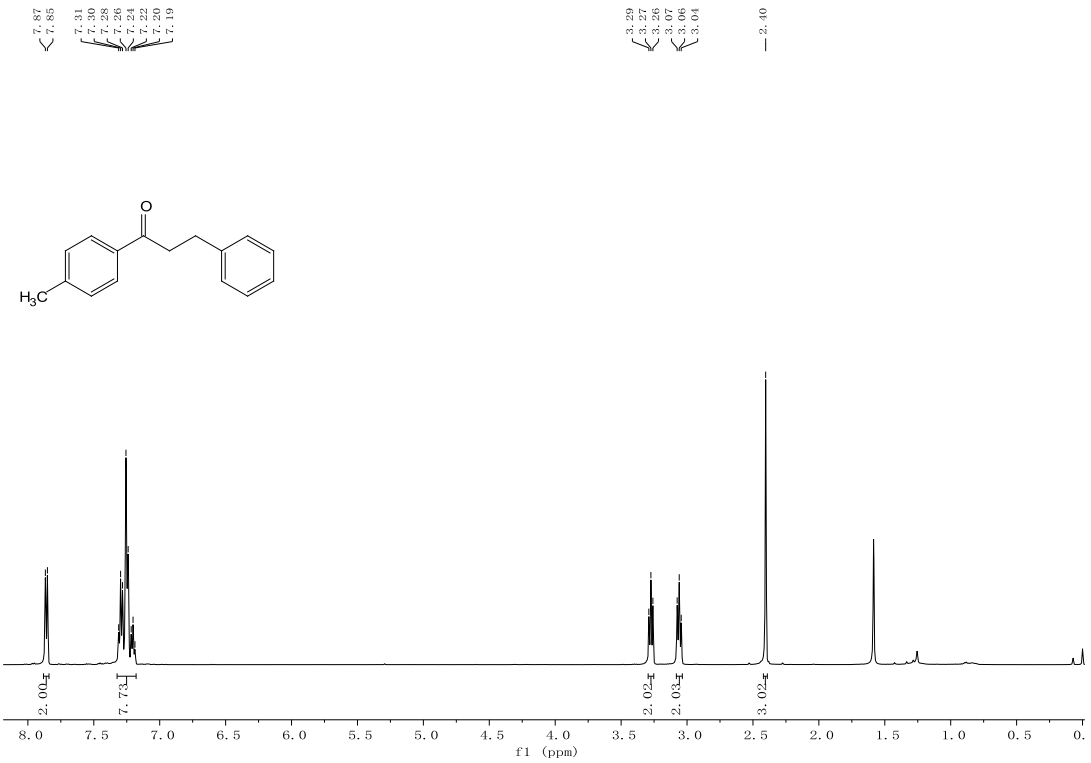


Fig. S42 ^{1}H NMR spectrum of **4p** in $CDCl_3$.

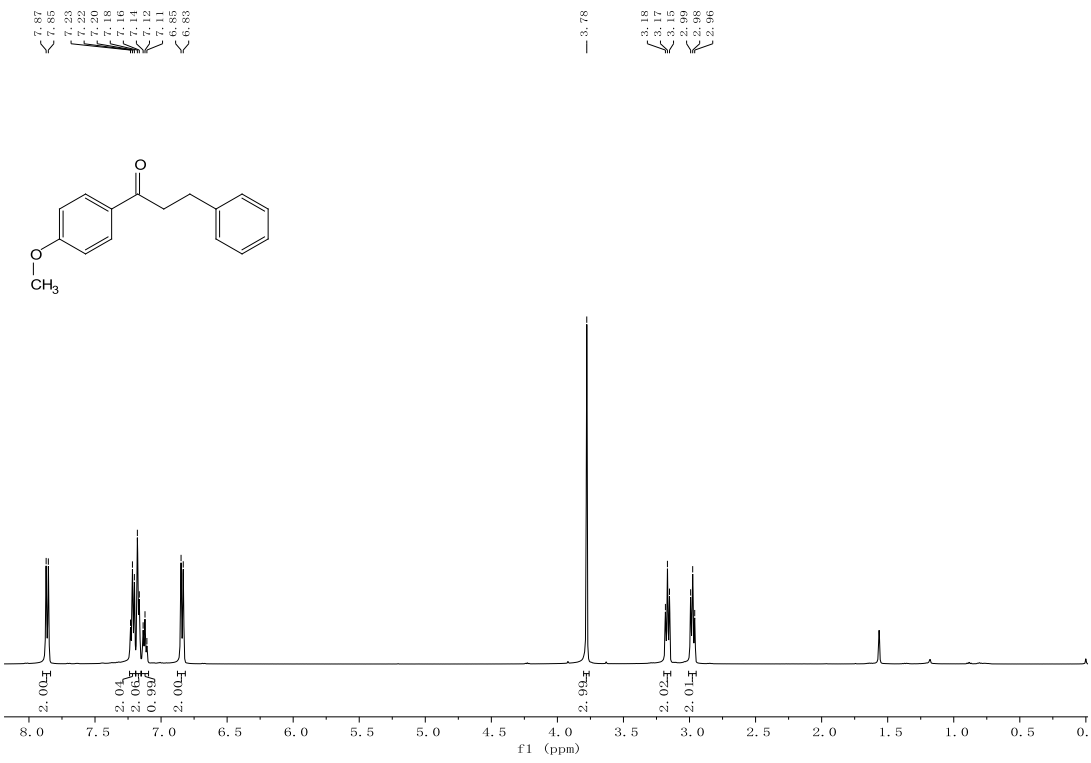


Fig. S43 ^{1}H NMR spectrum of **4q** in $CDCl_3$.

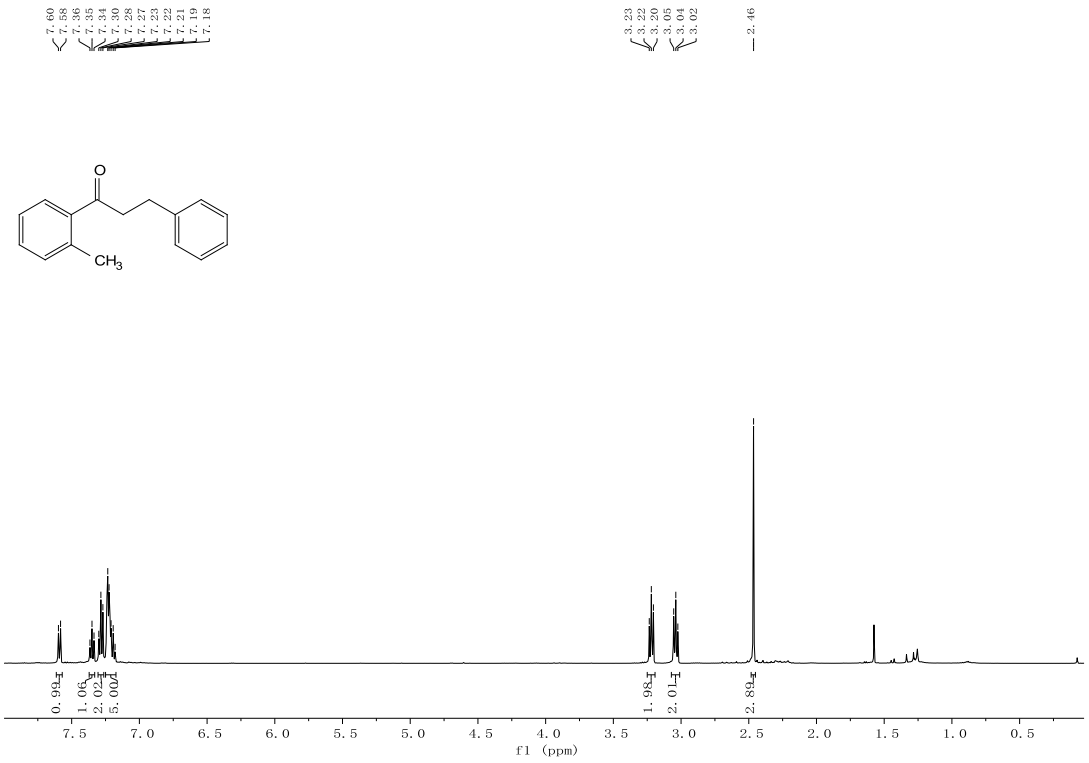


Fig. S44 ^{1}H NMR spectrum of **4r** in $CDCl_3$.

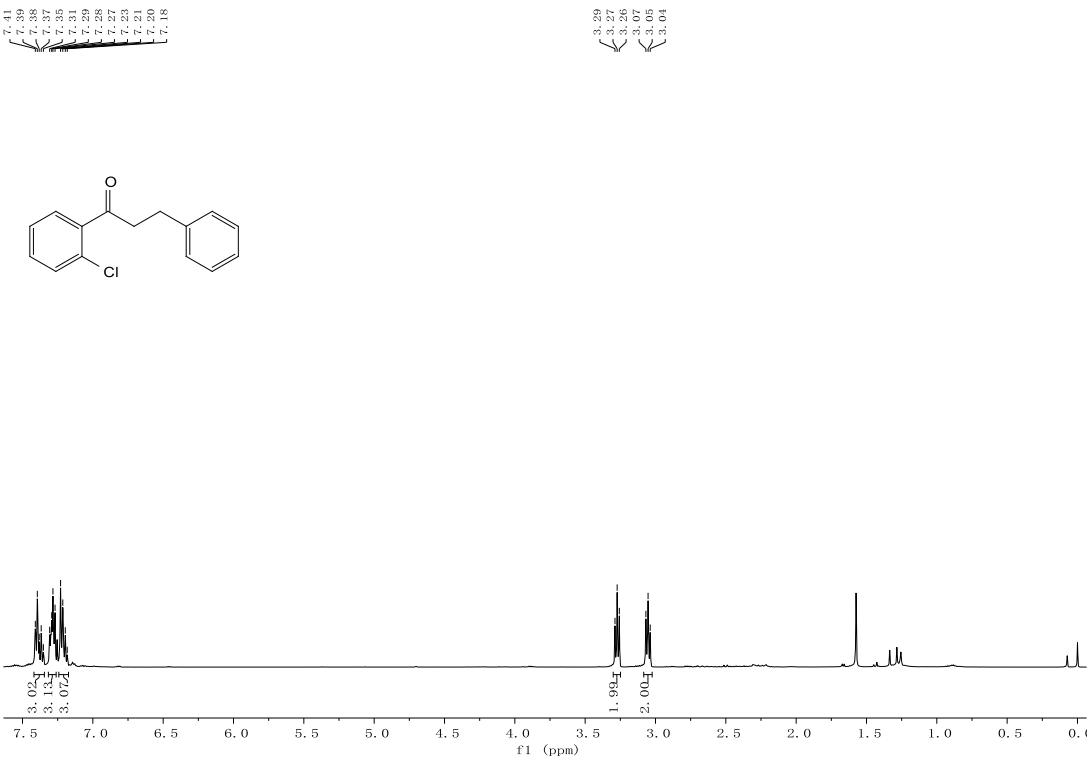


Fig. S45 ^{1}H NMR spectrum of **4s** in $CDCl_3$.

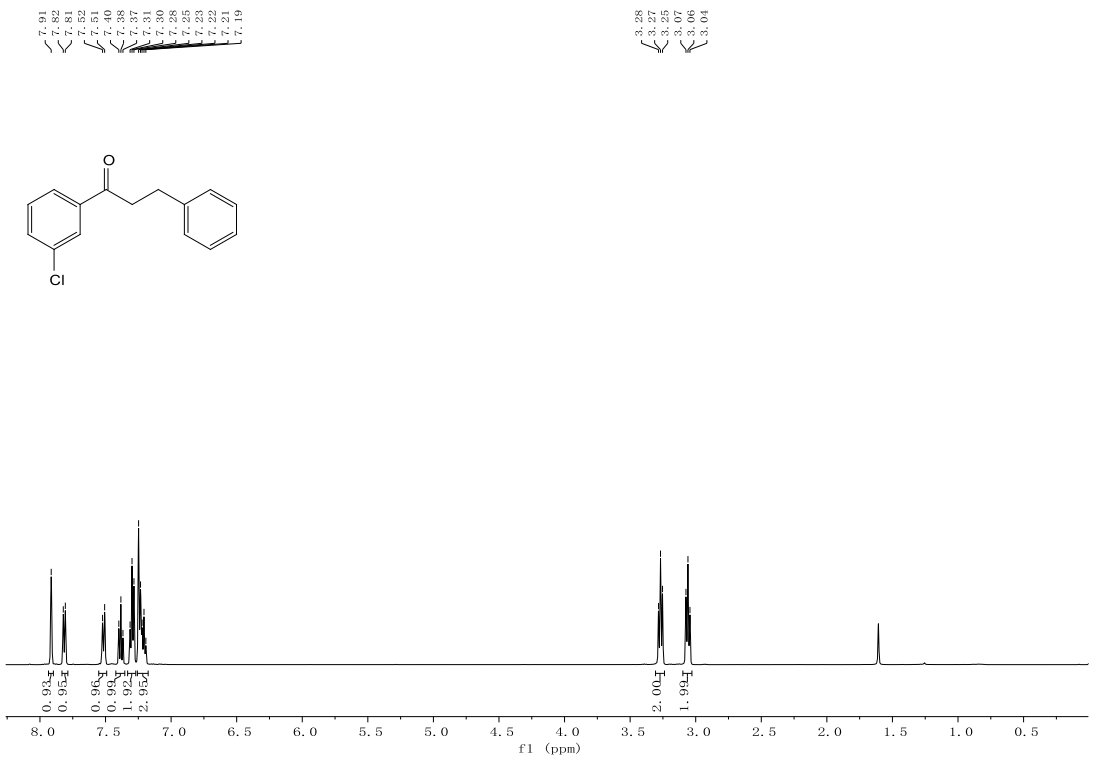


Fig. S46 ^{1}H NMR spectrum of **4t** in $CDCl_3$.

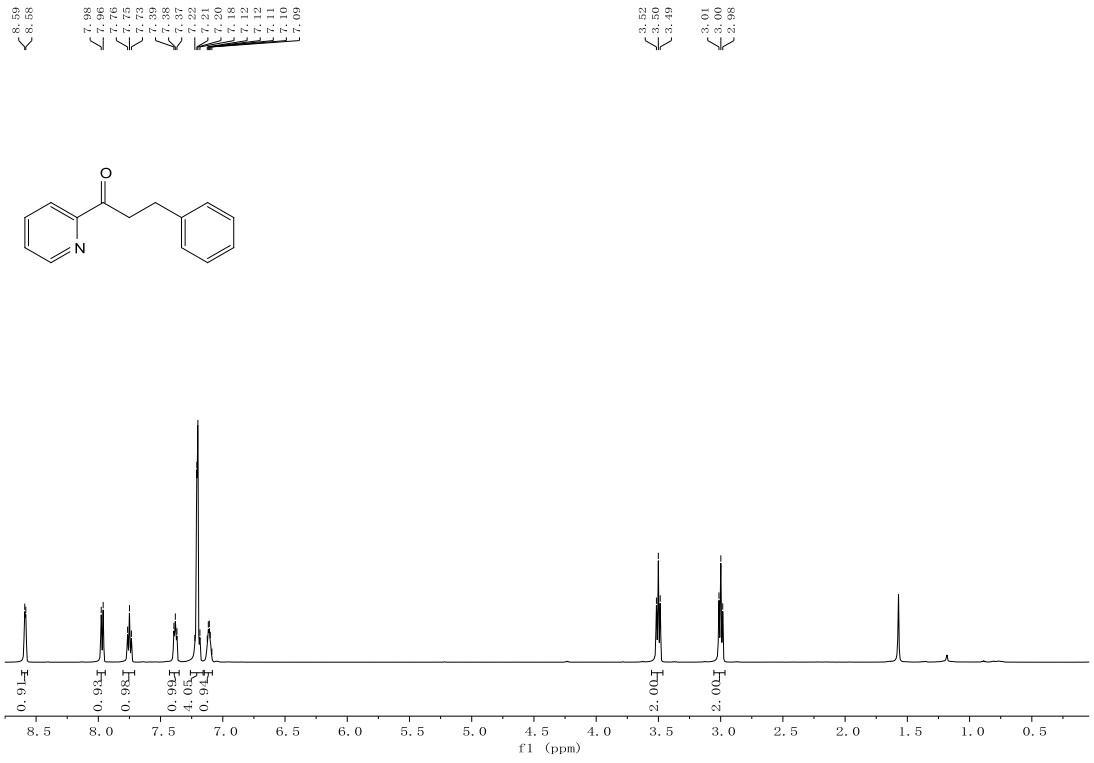


Fig. S47 ^{1}H NMR spectrum of **4u** in $CDCl_3$.

7. References

[1] R. Kanega, N. Onishi, L. Wang, K. Murata, J. Muckerman, E. Fujita, and Y. Himeda, Picolinamide-Based Iridium Catalysts for Dehydrogenation of Formic Acid in Water: Effect of Amide N Substituent on Activity and Stability, *Chem. Eur. J.*, 2018, **24**, 18389–18392.

[2] X.-B. Lan, Z. Ye, J. Liu, M. Huang, Y. Shao, X. Cai, Y. Liu, and Z. Ke, Sustainable and Selective Alkylation of Deactivated Secondary Alcohols to Ketones by Non-bifunctional Pincer N-heterocyclic Carbene Manganese, *ChemSuschem*, 2020, **13**, 2557-2563.

[3] Y. Cao, L. Liu, T. Huang and T. Chen, Iodine-catalyzed *α,β*-dehydrogenation of ketones and aldehydes generating conjugated enones and enals, *New J. Chem.*, 2020, **44**, 8697-8701.

[4] P. Liu, R. Liang, L. Lu, Z. Yu, and F. Li, Use of a Cyclometalated Iridium(III) Complex Containing a N^C^N Coordinating Terdentate Ligand as a Catalyst for the *α*-Alkylation of Ketones and N-Alkylation of Amines with Alcohols, *J. Org. Chem.*, 2017, **82**, 1943-1950.

[5] C. Zhang, J.-P. Zhao, B. Hu, J. Shi, and D. Chen, Ruthenium-Catalyzed *β*-Alkylation of Secondary Alcohols and *α*-Alkylation of Ketones via Borrowing Hydrogen: Dramatic Influence of the Pendant N-Heterocycle, *Organometallics*, 2019, **38**, 654-664.

[6] J. Das, M. Vellakkaran, and D. Banerjee, Nickel-Catalyzed Alkylation of Ketone Enolates: Synthesis of Monoselective Linear Ketones, *J. Org. Chem.*, 2019, **84**, 769-779.

[7] N. F. Nikitas, D. I. Tzaras, I. Triandafillidi and C. G. Kokotos, Photochemical oxidation of benzylic primary and secondary alcohols utilizing air as the oxidant, *Green Chem.*, 2020, **22**, 471-477.

[8] R. Wang, J. Ma, and F. Li, Synthesis of *α*-Alkylated Ketones via Tandem Acceptorless Dehydrogenation/*α*-Alkylation from Secondary and Primary Alcohols Catalyzed by

Metal-Ligand Bifunctional Iridium Complex [Cp*Ir(2,2′-bpyO)(H_2O)], *J. Org. Chem.*, 2015, **80**, 10769-10776.

[9] R. I. Rodríguez, L. Mollari, J. Alemán, Light-Driven Enantioselective Synthesis of Pyrroline Derivatives by a Radical/Polar Cascade Reaction, *Angew. Chem. Int. Ed.*, 2021, **60**, 4555-4560.

[10] H. Qin, J. Yang, K. Yan, Y. Xue, M. Zhang, X. Sun, J. Wen and H. Wang, Electrochemical-Induced Hydrogenation of Electron-Deficient Internal Olefins and Alkynes with CH_3OH as Hydrogen Donor, *Adv. Syn. Catal.*, 2021, **363**, 2104-2109.