Supporting Information

Selective α-oxidation of amides via visible-light-driven Iron-catalysis

*Shu-Hong Liu, Zhi-Chao Dong, Zhong-Lin Zang, Cheng-He Zhou and Gui-Xin Cai**

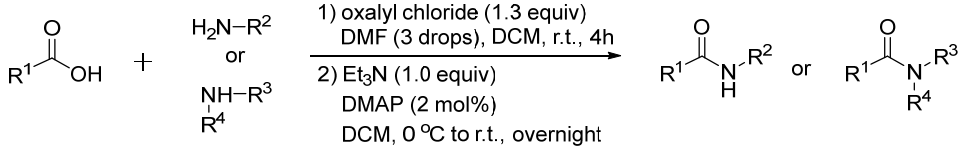
Contents

1. General Information

Reagents and solvents were obtained from commercial suppliers and used without further purification unless otherwise indicated. The reactions were detected by analytical thin layer chromatography (TLC) on Yinlong silica gel HSGF254 plates (0.2 ± 0.03 mm), appeared by ultraviolet light or by appropriate staining with alkaline potassium permanganate solutions. ^{1}H NMR spectra were obtained on Bruker Avance 600MR spectrometer at ambient temperature. The data marking mode as follows: chemical shift on the δ scale using residual proton solvent as internal standard [δ 7.26 ($CDCl_3$) ppm; TMS: 0.00 ppm], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), integration, and coupling constant (*J*) in hertz (Hz). The photochemical reactions were performed with 30 W blue LEDs (Leishi lighting). High resolution mass spectra were obtained on a Bruker impact II spectrometer. Mettler toledo electronic balance is used for reaction feeding, which model is ME204E/02 produced by Shanghai Mettler-Toledo Instrument Co., Ltd. Its maximum weighing is 220 g, and the actual scale is 0.1 mg. Electron paramagnetic Resonance Spectrometer is used for mechanistic study, which model is EMXplus-9.5/12 produced by Bruker. UV spectra were recorded at room temperature on a TU-2450 spectrophotometer (Puxi Analytic Instrument Ltd. of Beijing, China) equipped with 1.0 cm quartz cells.

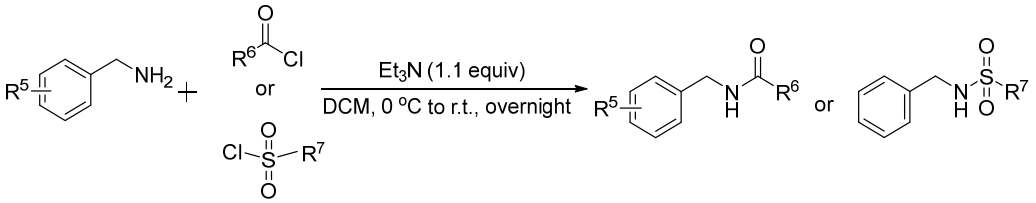
2. Synthesis of Starting Materials

2.1 General procedure A for amide synthesis[1]



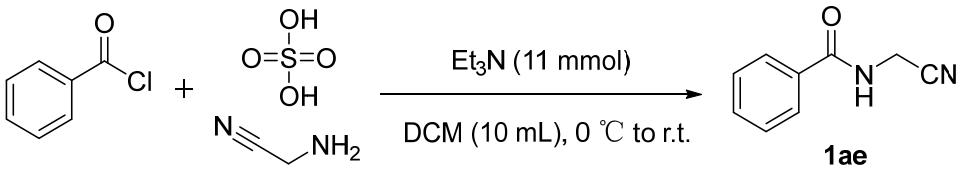
To a 100 mL oven-dried round-bottom flask equipped with a Teflon-coated magnetic stir bar was added benzoic acid (1.0 equiv.). The flask was backfilled with N_2 three times before adding DCM (0.2 M) and cooling to 0 ºC in an ice bath. Oxalyl chloride (1.3 equiv.) was then added followed by DMF (3-5 drops). The reaction was then allowed to warm to room temperature and stirred for 4 hours. The reaction was then concentrated under reduced pressure and the residue was then taken up in fresh DCM (0.2 M) and cooled to 0 ºC. Et_3N (1.0 equiv.) was added dropwise followed by amine (1.0 equiv.) and DMAP (0.02 equiv.). The reaction was then allowed to warm to room temperature and stirred overnight. The reaction was quenched with 10 mL H_2O and 25 mL DCM and the organics were washed with 1M HCl (25 mL × 2), 1M NaOH (25 mL × 2) and 25 mL brine, then dried with anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by silica gel chromatography, eluting with petroleum ether/EtOAc.

2.2 General procedure B for amide synthesis[2]



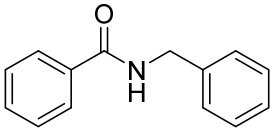
To a stirring of benzylamine (1.0 equiv.), Et_3N (1.1 equiv.) in CH_2Cl_2 (45 mL), was added acid chloride (1.1 equiv.) at 0 °C (ice/water bath). The reaction mixture was stirred at 0 °C for 10 minutes. Then, the reaction mixture was stirred at room temperature overnight. After the completion, the mixture was washed with saturated $NaHCO_3$ solution (3 times) and brine, and dried with anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by silica gel chromatography, eluting with petroleum ether/EtOAc.

2.3 General procedure C for amide synthesis[3]



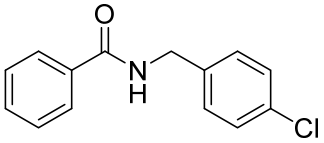
1ae

To a stirring of aminoacetonitrile sulfate (5 mmol) and triethylamine (11 mmol) in CH_2Cl_2 (10 mL), was added benzoyl chloride (11 mmol) at 0 ℃ (ice/water bath). The reaction mixture was stirred at 0 ℃ for 1h. Then, the reaction mixture was stirred at room temperature for 2 h. After the completion, the solvent was removed by rotary evaporation and the crude reaction mixture was purified by silica gel chromatography, eluting with petroleum ether/EtOAc.



1a

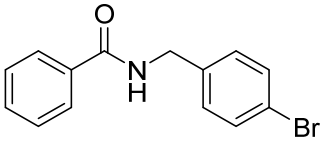
***N*-benzylbenzamide (1a) [1485-70-7]: 1a** was purchased from Bide Pharmaceutical.



1b

***N*-(4-chlorobenzyl)benzamide (1b)[4] :** According to the procedure **A**, the title compound **1b** was obtained as white solid (0.55 g, isolated yield: 55%). R_f = 0.50 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point:142-144 ºC (reported melting point: 142-143 ºC).

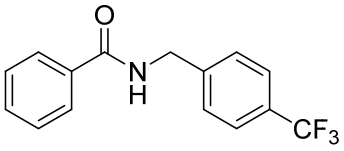
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 6.78 (s, 1H), 4.46 (d, J = 4.9 Hz, 2H).



1c

***N*-(4-bromobenzyl)benzamide (1c)[4] :** According to the procedure **A**, the title compound **1c** was obtained as white solid (0.65 g, isolated yield: 56%). R_f = 0.30 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 141-143 ºC (reported melting point: 141-142 ºC).

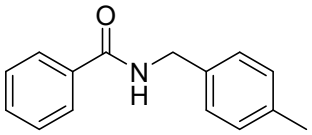
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.45 – 7.35 (m, 4H), 7.17 (d, J = 8.0 Hz, 2H), 6.86 (s, 1H), 4.53 (d, J = 5.7 Hz, 2H).



1d

***N*-(4-(trifluoromethyl)benzyl)benzamide (1d)[5] :** According to the procedure **A**, the title compound **1d** was obtained as white solid (0.55 g, isolated yield: 48%). R_f = 0.30 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 132-133 ºC (reported melting point: 132-134 ºC).

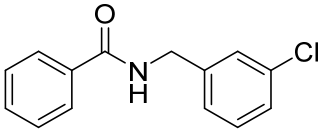
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.3 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.8 Hz, 4H), 6.86 (s, 1H), 4.65 (d, J = 5.9 Hz, 2H).



1e

***N*-(4-methylbenzyl)benzamide (1e)[4] :** According to the procedure **A**, the title compound **1e** was obtained as white solid (0.65 g, isolated yield: 72%). R_f = 0.55 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 137-139 ºC (reported melting point: 137-138 ºC).

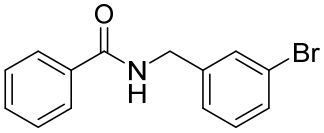
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.46 (s, 1H), 4.59 (d, *J* = 5.4 Hz, 2H), 2.35 (s, 3H).



1f

***N*-(3-chlorobenzyl)benzamide (1f)**[6] **:** According to the procedure **A**, the title compound **1f** was obtained as white solid (1.17 g, isolated yield: 48%). R_f = 0.45 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 140-141 ºC (reported melting point: 139-140 ºC).

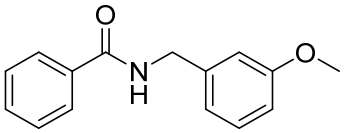
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.34 (s, 1H), 7.28 (d, *J* = 4.6 Hz, 2H), 7.23 (d, *J* = 4.1 Hz, 1H), 7.17 (s, 1H), 4.59 (d, *J* = 5.9 Hz, 2H).



1g

***N*-(3-bromobenzyl)benzamide (1g)**[7] **:** According to the procedure **A**, the title compound **1g** was obtained as white solid (0.71 g, isolated yield: 65%). R_f = 0.45 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 117-119 ºC (reported melting point: 117-118 ºC).

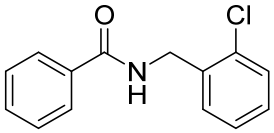
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.46 (s, 1H), 7.40 (t, *J* = 8.5 Hz, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.83 (s, 1H), 4.56 (d, *J* = 5.7 Hz, 2H)



1h

***N*-(3-methoxybenzyl)benzamide (1h)**[7] **:** According to the procedure **A**, the title compound **1h** was obtained as white solid (1.95 g, isolated yield: 81%). R_f = 0.50 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 137-139 ºC (reported melting point: 137-138 ºC).

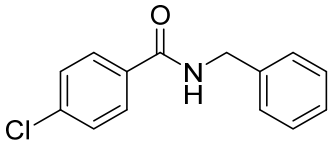
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.81 (s, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.49 (s, 1H), 4.52 (d, *J* = 5.6 Hz, 2H), 3.71 (s, 3H).



1i

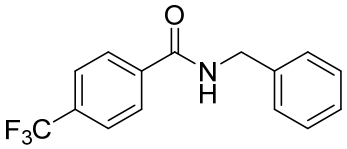
***N*-(2-chlorobenzyl)benzamide (1i)**[6] **:** According to the procedure **A**, the title compound **1i** was obtained as white solid (2.01 g, isolated yield: 82%). R_f = 0.40 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 140-141 ºC (reported melting point: 140-142 ºC).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.34 (m, 4H), 7.24 – 7.19 (m, 2H), 6.89 (s, 1H), 4.69 (d, *J* = 6.0 Hz, 2H).



1j

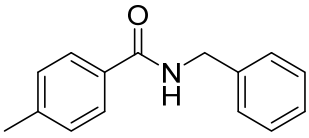
***N*-benzyl-4-chlorobenzamide (1j)**[13] **: 1j** was obtained from Cai′s group.



1k

***N*-benzyl-4-(trifluoromethyl)benzamide (1k)**[7] **:** According to the procedure **A**, the title compound **1k** was obtained as white solid (1.49 g, isolated yield: 89%). R_f = 0.25 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 169-172 ºC (reported melting point: 167-168 ºC).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.1 Hz, 2H), 7.65 (d, *J* = 6.7 Hz, 2H), 7.33 (s, 5H), 6.76 (s, 1H), 4.62 (s, 2H).

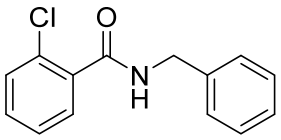


1l

***N*-benzyl-4-methylbenzamide (1l)**[6] **:** According to the procedure **A**, the title compound **1l** was obtained as white solid (0.90 g, isolated yield: 80%). R_f = 0.45 (silica

gel, petroleum ether/EtOAc = 3:1). Melting Point: 133-134 °C (reported melting point: 134-135 °C).

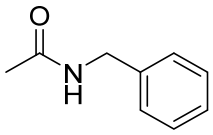
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 4.4 Hz, 4H), 7.27 (dq, *J* = 8.7, 4.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 1H), 4.60 (d, *J* = 5.7 Hz, 2H), 2.37 (s, 3H).



1m

***N*-benzyl-2-chlorobenzamide (1m)[8] :** According to the procedure **A**, the title compound **1m** was obtained as white solid (1.71 g, isolated yield: 86%). R_f = 0.45 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 104-105 °C (reported melting point: 104-105 °C).

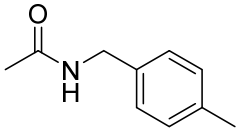
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.37 – 7.32 (m, 5H), 7.31 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.29 – 7.25 (m, 2H), 6.66 (s, 1H), 4.60 (d, *J* = 5.7 Hz, 2H).



1n

***N*-benzylacetamide (1n)[4] :** According to the procedure **B**, the title compound **1n** was obtained as white solid (0.67 g, isolated yield: 91%). R_f = 0.25 (silica gel, petroleum ether/EtOAc = 5:1). Melting Point: 60-61 °C (reported melting point: 67-68 °C).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 6.8 Hz, 3H), 6.21 (s, 1H), 4.38 (d, *J* = 5.7 Hz, 2H), 1.98 (s, 3H).

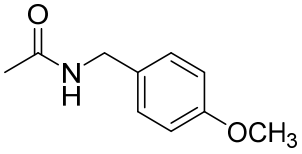


1o

***N*-(4-methylbenzyl)acetamide (1o)[9] :** According to the procedure **B**, the title compound **1o** was obtained as white solid (0.47 g, isolated yield: 58%). R_f = 0.25 (silica

gel, petroleum ether/EtOAc = 5:1). Melting Point: 110-111 ºC (reported melting point: 110-113 ºC).

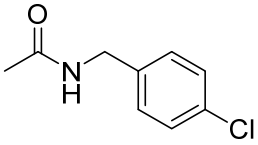
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (q, *J* = 8.0 Hz, 4H), 6.30 (s, 1H), 4.31 (d, *J* = 5.6 Hz, 2H), 2.31 (s, 3H), 1.95 (s, 3H).



1p

***N*-(4-methoxybenzyl)acetamide (1p)[9] :** According to the procedure **B**, the title compound **1p** was obtained as white solid (0.50 g, isolated yield: 28%). R_f = 0.60 (silica gel, petroleum ether/EtOAc = 5:1). Melting Point: 96-97 ºC (reported melting point: 96-97 ºC).

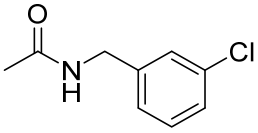
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.36 (s, 1H), 4.27 (d, *J* = 5.2 Hz, 2H), 3.74 (s, 3H), 1.93 (s, 3H).



1q

***N*-(4-chlorobenzyl)acetamide (1q)[9] :** According to the procedure **B**, the title compound **1q** was obtained as white solid (1.04 g, isolated yield: 71%). R_f = 0.10 (silica gel, petroleum ether/EtOAc = 5:1). Melting Point: 106-108 ºC (reported melting point: 107-108 ºC).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.50 (s, 1H), 4.30 (d, *J* = 5.8 Hz, 2H), 1.95 (s, 3H).

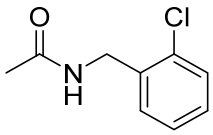


1r

***N*-(3-chlorobenzyl)acetamide (1r)[9] :** According to the procedure **B**, the title compound **1r** was obtained as white solid (1.27 g, isolated yield: 69%). R_f = 0.10 (silica gel,

petroleum ether/EtOAc = 5:1). Melting Point: 128-129 ºC (reported melting point: 127-128 ºC).

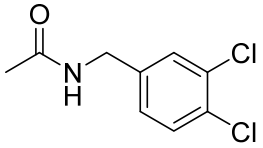
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, *J* = 5.9 Hz, 3H), 7.10 (d, *J* = 5.7 Hz, 1H), 6.52 (s, 1H), 4.32 (d, *J* = 5.9 Hz, 2H), 1.97 (s, 3H).



1s

***N*-(2-chlorobenzyl)acetamide (1s)[9] :** According to the procedure **B**, the title compound **1s** was obtained as white solid (0.54 g, isolated yield: 37%). R_f = 0.10 (silica gel, petroleum ether/EtOAc = 5:1). Melting Point: 72-73 ºC (reported melting point: 72-73 ºC).

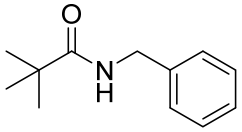
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (q, *J* = 4.7 Hz, 2H), 7.23 – 7.18 (m, 2H), 6.21 (s, 1H), 4.48 (d, *J* = 6.0 Hz, 2H), 1.98 (s, 3H).



1t

***N*-(3,4-dichlorobenzyl)acetamide (1t)[10] :** According to the procedure **B**, the title compound **1t** was obtained as white solid (1.21 g, isolated yield: 70%). R_f = 0.10 (silica gel, petroleum ether/EtOAc = 5:1). Melting Point: 95-96 ºC (reported melting point: 97-98 ºC).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.07 – 7.03 (m, 1H), 6.61 (s, 1H), 4.29 (d, *J* = 6.0 Hz, 2H), 1.97 (s, 3H).

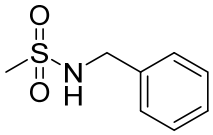


1u

***N*-benzylpivalamide (1u)[8] :** According to the procedure **B**, the title compound **1u** was obtained as white solid (0.96 g, isolated yield: 50%). R_f = 0.55 (silica gel,

petroleum ether/EtOAc = 5:1). Melting Point: 81-82 ºC (reported melting point: 81-83 ºC).

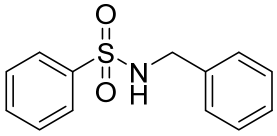
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 5.7 Hz, 3H), 5.93 (s, 1H), 4.35 (d, *J* = 5.1 Hz, 2H), 1.15 (s, 9H).



1v

***N*-benzylmethanesulfonamide (1v)**[11] **:** According to the procedure **B**, the title compound **1v** was obtained as white solid (0.64 g, isolated yield: 43%). R_f = 0.45 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 62-63 ºC (reported melting point: 62-63ºC).

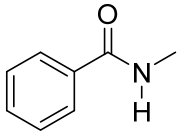
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 6.5 Hz, 4H), 7.31 (d, *J* = 6.5 Hz, 1H), 5.08 (s, 1H), 4.29 (s, 2H), 2.82 (s, 3H).



1w

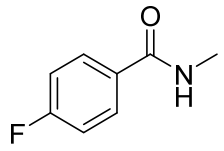
***N*-benzylbenzenesulfonamide (1w)**[4] **:** According to the procedure **B**, the title compound **1w** was obtained as white solid (1.81 g, isolated yield: 92%). R_f = 0.45 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 85-86 ºC (reported melting point: 85-87 ºC).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.21 (q, *J* = 6.3 Hz, 3H), 7.17 – 7.13 (m, 2H), 5.29 (t, *J* = 6.3 Hz, 1H), 4.09 (d, *J* = 6.3 Hz, 2H).



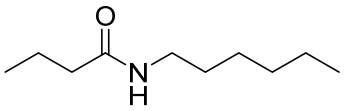
1x

***N*-methylbenzamide (1x) [613-93-4]: 1x** was purchased from Bide Pharmaceutical.



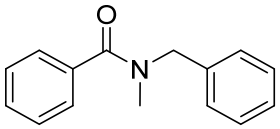
1y

4-fluoro-*N*-methylbenzamide (1y) [701-49-5]: 1y was purchased from Bide Pharmaceutical.



1z

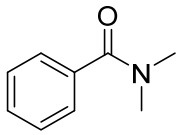
***N*-butyrylhexanamide (1z)**[13] **: 1z** was obtained from Cai′s group.



1aa

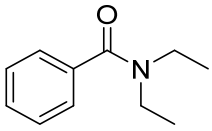
***N*-hexylbutyramide (1aa)**[12] **:** According to the procedure **A**, the title compound **1aa** was obtained as colorless oil (0.72 g, isolated yield: 35%). R_f = 0.40 (silica gel, petroleum ether/EtOAc = 3:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.11 (m, 10H), 4.63 (d, J = 152.1 Hz, 2H), 2.94 (d, J = 104.0 Hz, 3H).



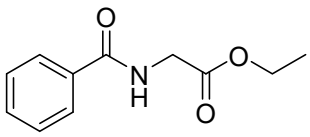
1ab

***N*, *N*-dimethylbenzamide (1ab) [611-74-5]: 1ab** was purchased from Bide Pharmaceutical.



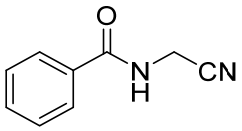
1ac

***N*, *N*-dimethylbenzamide (1ac)**[13] **: 1ac** was obtained from Cai′s group.



1ad

ethyl benzoylglycinate (1ad) [1499-53-2]: 1ad was purchased from Bide Pharmaceutical.



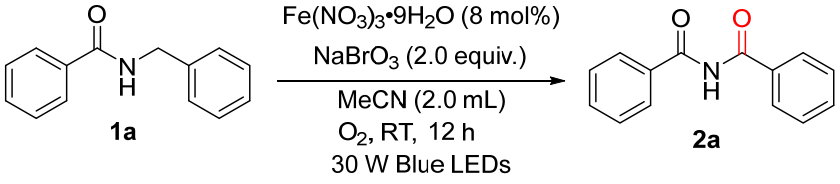
1ae

***N*-(cyanomethyl)benzamide (1ae)**[3] **:** According to the procedure **C**, the title compound **1ae** was obtained as colorless solid (0.56 g, isolated yield: 70%). R_f = 0.10 (silica gel, petroleum ether/EtOAc = 3:1). Melting Point: 81-82 ºC (reported melting point: 81-83 ºC).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.59 (s, 1H), 4.40 (d, J = 5.8 Hz, 2H).

3. Optimization of Reaction Conditions

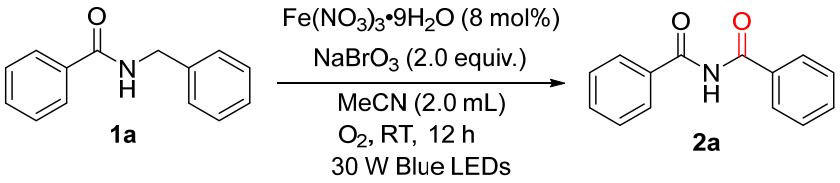
3.1 Screening of catalyst



Entry	Variation from the standard conditions[a]	Yield (%)[b]
1	None	94
2	$Fe(acac)_3$ instead of $Fe(NO_3)_3 \cdot 9H_2O$	trace
3	$Fe(OTf)_3$ instead of $Fe(NO_3)_3 \cdot 9H_2O$	54
4	$Fe_2(SO_4)_3$ instead of $Fe(NO_3)_3 \cdot 9H_2O$	56
5	$FeBr_3$ instead of $Fe(NO_3)_3 \cdot 9H_2O$	58
6	$CuBr_2$ instead of $Fe(NO_3)_3 \cdot 9H_2O$	30
7	$Cu(NO_3)_2 \cdot H_2O$ instead of $Fe(NO_3)_3 \cdot 9H_2O$	71

[a]Reaction conditions: **1a** (0.2 mmol), $Fe(NO_3)_3 \cdot 9H_2O$ (0.016 mmol, 8 mol%), $NaBrO_3$ (0.4 mmol, 2.0 equiv.) in CH_3CN (2.0 mL) in the presence of O_2 at room temperature with 30 W blue LEDs (λ = 455 nm, at a distance of 4-5 cm) irradiation for 12 h. [b]Isolated yield.

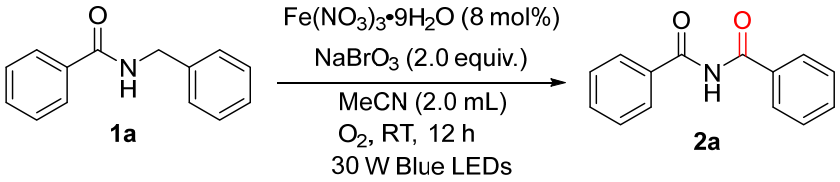
3.2 Screening of solvents



Entry	Variation from the standard conditions[a]	Yield (%)[b]
1	None	94
2	H_2O: MeCN =1:1	91
3	DCM instead of MeCN	16
4	MeOH instead of MeCN	n.p.[c]
5	Acetone instead of MeCN	29
6	CCl_4 instead of MeCN	28

[a]Reaction conditions: **1a** (0.2 mmol), $Fe(NO_3)_3 \cdot 9H_2O$ (0.016 mmol, 8 mol%), $NaBrO_3$ (0.4 mmol, 2.0 equiv.) in CH_3CN (2.0 mL) in the presence of O_2 at room temperature with 30 W blue LEDs (λ = 455 nm, at a distance of 4-5 cm) irradiation for 12 h. [b]Isolated yield. [c]n.p. = no product.

3.3 Screening of oxidant



Entry	Variation from the standard conditions[a]	Yield (%)[b]
1	None	94
2	1 eq. $NaBrO_3$	88
3	Air instead of O_2	55

[a]Reaction conditions: **1a** (0.2 mmol), $Fe(NO_3)_3 \cdot 9H_2O$ (0.016 mmol, 8 mol%), $NaBrO_3$ (0.4 mmol, 2.0 equiv.) in CH_3CN (2.0 mL) in the presence of O_2 at room temperature with 30 W blue LEDs (λ = 455 nm, at a distance of 4-5 cm) irradiation for 12 h. [b]Isolated yield.

4. Experimental Procedures

4.1 The photos of the photochemical reactor

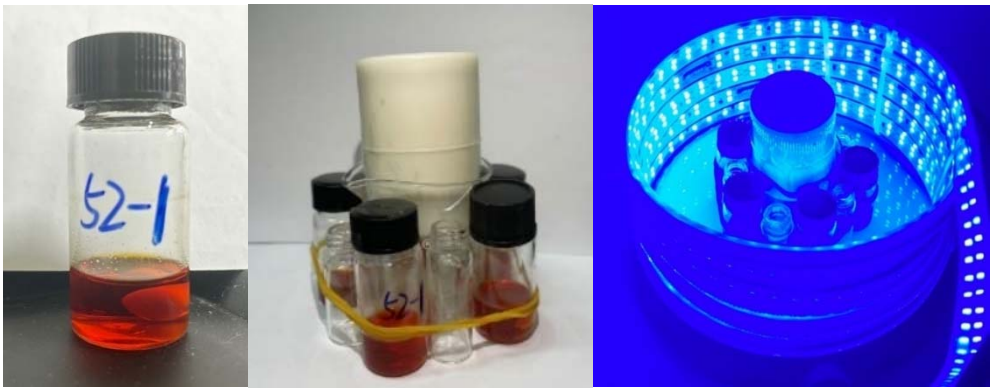
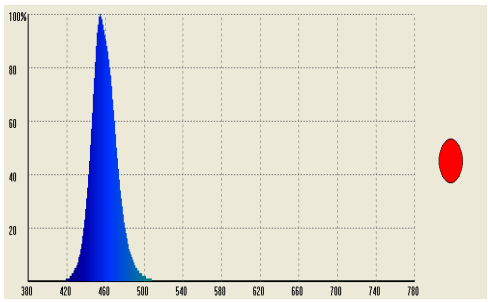
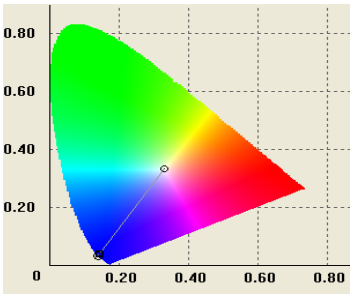


Figure S1. Reaction setup for standard conditions (0.2 mmol scale)

4.2 Report of spectroradiometric analysis for light source

Basic Information			
Sample	30W Blue Light source		
Sample Information	Blue light source	Testing Date	2023.07.22
Tester	Shu-Hong Liu	Amblent Temperature	25℃
Testing Result			
Setup photo	 Spectrum distribution	 Chromaticity diagram	
Chromaticity Coordinates	x=0.1440 y=0.0381 u=0.1818 v=0.1082		
Temperature	>25000K	Peak Wavelength	455nm
SDCM	0	Main Wavelength	461nm
Color Shift	0.000000 duv	Wavelength Width	0nm
Red Ratio	0	Color Purty	98.00%
Luminous Flux	1.661e3lux	Radiant Flux	3.489e4w/m2
Rendering Flux	Ra=53.0 R1=23.0 R2=56.0 R3=99.0 R4=86.0 R5=6.0 R6=67.0 R7=52.0 R8=38.0 R9=99.0 R10=99.0 R11=99.0 R12=99.0 R13=45.0 R14=34.0		

4.3 General procedure for α-oxidation of amide

Amide (0.2 mmol, 1.0 equiv.), $Fe(NO_3)_3 \cdot 9H_2O$ (0.016 mmol, 8 mol%, 6.2 mg), $NaBrO_3$ (0.4 mmol, 2.0 equiv. 60.3 mg) and CH_3CN (2.0 mL) were placed in a dry 10 mL reaction flask in an air atmosphere. The reaction mixture was irradiated with 30W blue LEDs (λ = 455 nm, at a distance of 4-5 cm, 1000 rpm stir rate) at room temperature in the presence of O_2 for 12 h. After completion of the reaction, the organic solvent was removed under vacuum, the mixture was purified directly by silica gel column chromatography (petroleum ether/EtOAc) to give the desired products **2a-2aa**.

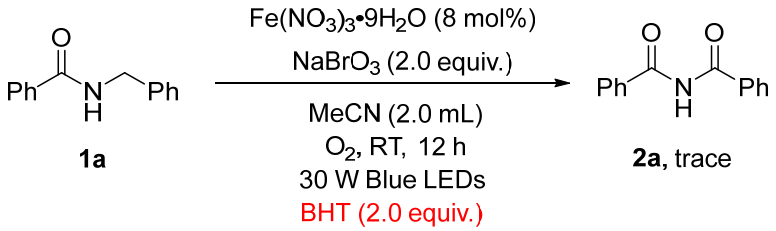
5. Mechanistic Studies

5.1 Other functional groups exploration

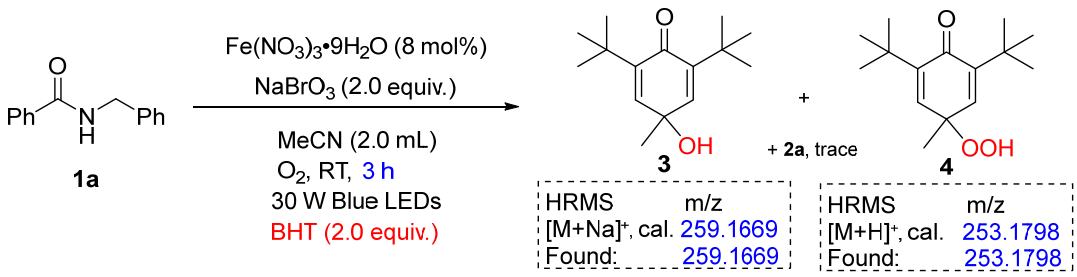
$R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = R^2 = Me$

Other substrates including benzylamine, *N*-methylbenzylamine and *N*,*N*-dimethylbenzylamine were tested (0.2 mmol, 1.0 equiv.), $Fe(NO_3)_3 \cdot 9H_2O$ (0.016 mmol, 8 mol%, 6.2 mg), $NaBrO_3$ (0.4 mmol, 2.0 equiv. 60.3 mg) and CH_3CN (2.0 mL) were placed in a dry 10 mL reaction flask in an air atmosphere. The reaction mixture was irradiated with 30W blue LEDs (λ = 455 nm, at a distance of 4-5 cm, 1000 rpm stir rate) at room temperature in the presence of O_2 for 12 h. After completion of the reaction, the organic solvent would be monitored by TLC and all the substrates were not tolerated.

5.2 Radical inhibition and trapping experiments



N-benzoylbenzamide (0.2 mmol, 1.0 equiv. 42.2 mg), $Fe(NO_3)_3 \cdot 9H_2O$ (0.016 mmol, 8 mol%, 6.2 mg), $NaBrO_3$ (0.4 mmol, 2.0 equiv. 60.3 mg), (2,6-di-tert-butyl-4-methylphenol) BHT (0.4 mmol, 2.0 equiv. 44.0 mg) and CH_3CN (2.0 mL) were placed in a dry 10 mL reaction flask in an air atmosphere. The reaction mixture was irradiated with 30W blue LEDs (λ = 455 nm, at a distance of 4-5 cm, 1000 rpm stir rate) at room temperature in the presence of O_2 for 12 h. After completion of the reaction, the organic solvent would be monitored by TLC and the product **2a** was only given trace amount.



N-benzoylbenzamide (0.2 mmol, 1.0 equiv. 42.2mg), $Fe(NO_3)_3 \cdot 9H_2O$ (0.016 mmol, 8 mol%, 6.2 mg), $NaBrO_3$ (0.4 mmol, 2.0 equiv. 60.3mg), 2,6-di-tert-butyl-4-methylphenol (BHT) (0.4 mmol, 2.0 equiv. 44.0 mg) and CH_3CN (2.0 mL) were placed in a dry 10 mL reaction flask in an air atmosphere. The reaction mixture was irradiated with 30W blue LEDs (λ = 455 nm, at a distance of 4-5 cm, 1000 rpm stir rate) at room temperature in the presence of O_2 for 3 h. After completion of the reaction, the organic solvent would be monitored by Mass spectrometry (HRMS) and the hydroxyl radical (HO·) intermediate **3** and the hydroperoxyl radical (HOO·) intermediate **4** were verified.

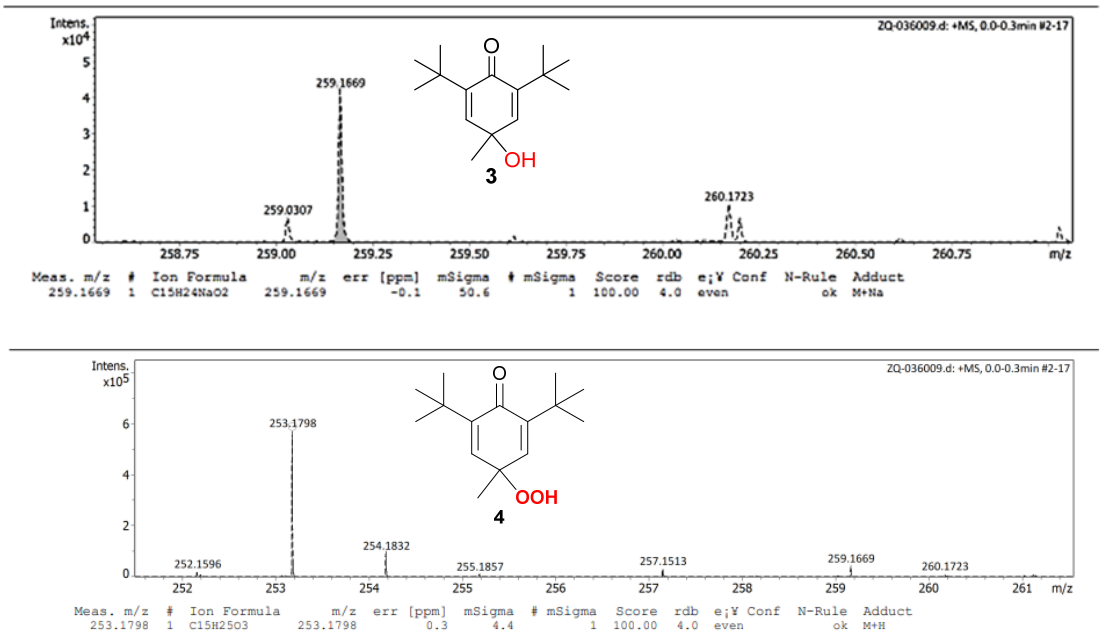
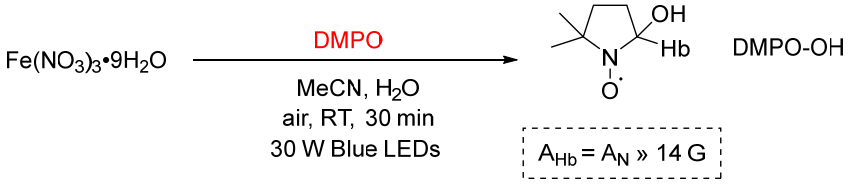


Figure S2. Mass spectrometry (HRMS) data of the radical trapping experiment (with BHT).

5.3 Electron paramagnetic resonance (EPR) experiments



$Fe(NO_3)_3 \cdot 9H_2O$ (0.04 mmol, 16.2 mg), H_2O (1.0 mL) and CH_3CN (1.0 mL) were placed in a 10 mL reaction flask and the mixture solution was stirred well. 1 mL of the mixture solution was transferred into another 10 mL dry reaction flask and DMPO (5,5-Dimethyl-1-pyrroline-*N*-oxide, 10 μL) was added as radical capturer. The mixture was irradiated with blue LEDs at room temperature for 30 min. Then the organic solvent would be monitored by electron paramagnetic resonance (EPR) instrument and the result showed that the hydroxyl radical was captured.

5.4 UV-vis absorption experiments

According to the test condition 1(Fe cat. + **1a** + $NaBrO_3$ + MeCN + O_2 + irr. 30 min.), $Fe(NO_3)_3 \cdot 9H_2O$ (0.2 mmol, 80.2 mg), *N*-benzoylbenzamide **1a** (0.2 mmol, 42.2 mg), $NaBrO_3$ (0.2 mmol, 30.1 mg) and CH_3CN (2.0 mL) were placed in a dry 10 mL reaction flask and the reaction mixture (c = 0.1 mol/L) was irradiated with 30W blue LEDs (λ = 455 nm, at a distance of 4-5 cm, 1000 rpm stir rate) at room temperature in the presence of O_2 for 30 min. Then 20 μL of the stirred mixture was transferred to the colorimetrical cylinder followed the 10 mL isochoric process using additional CH_3CN. The solvent (c = 0.02 mmol/L) would be monitored by UV-vis absorption spectrophotometer. Other test conditions were operated similarly.

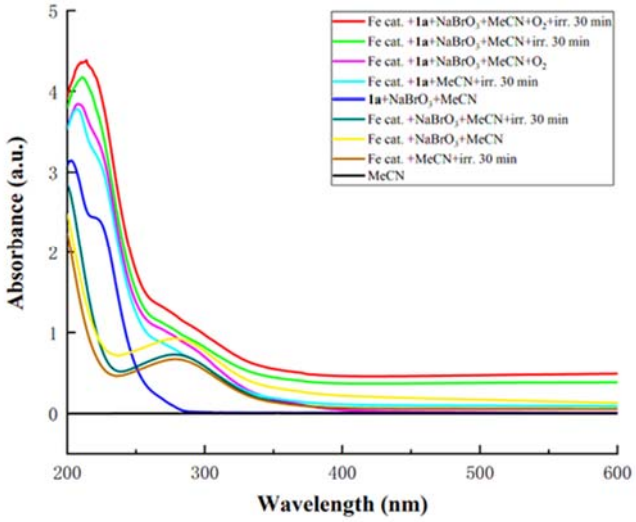


Figure S3. UV-vis absorption spectra

6. References

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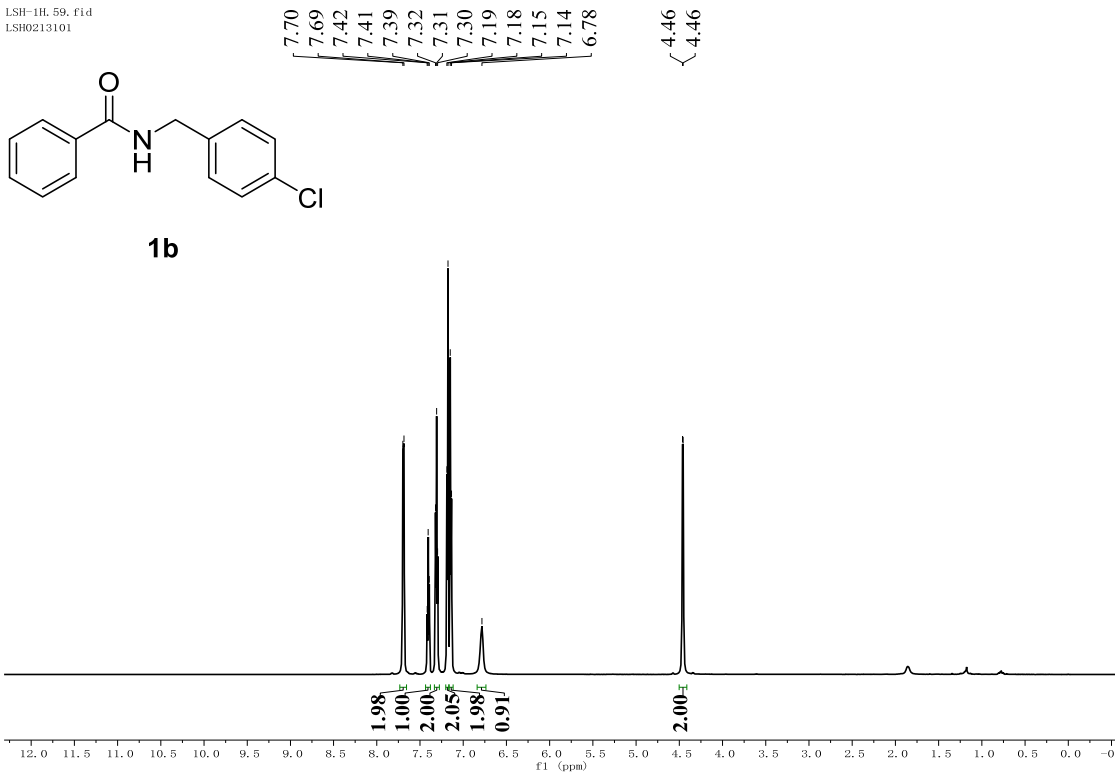
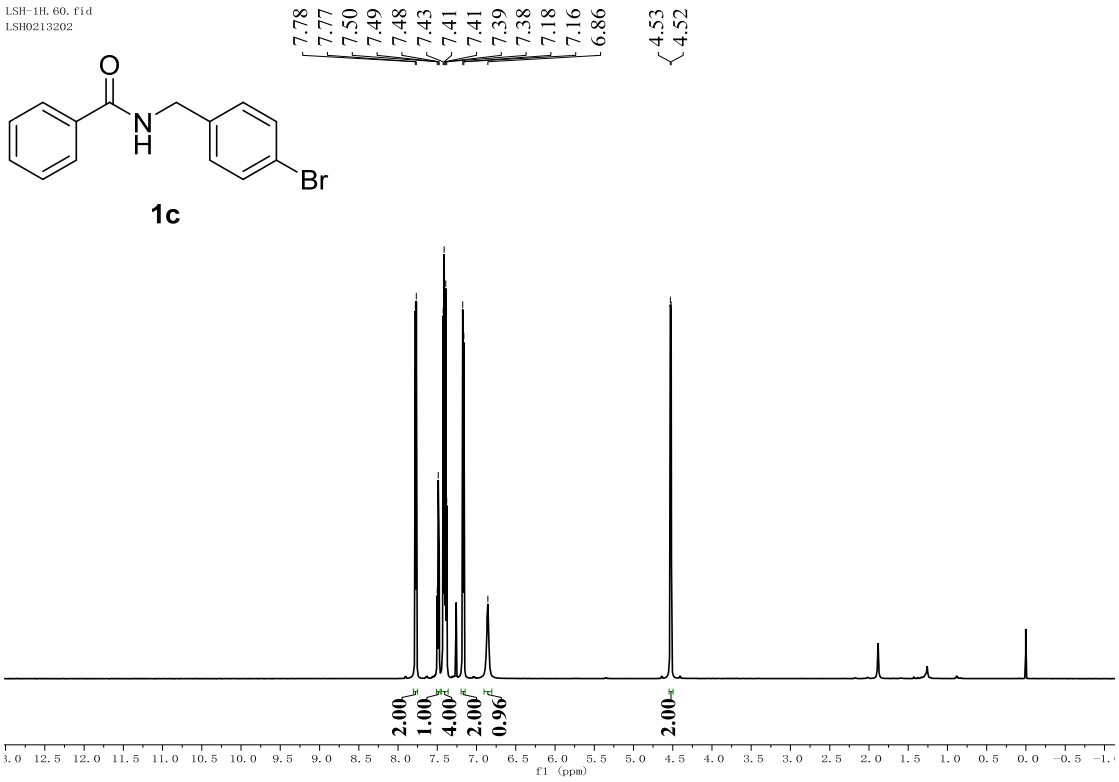
7. Experimental Spectra

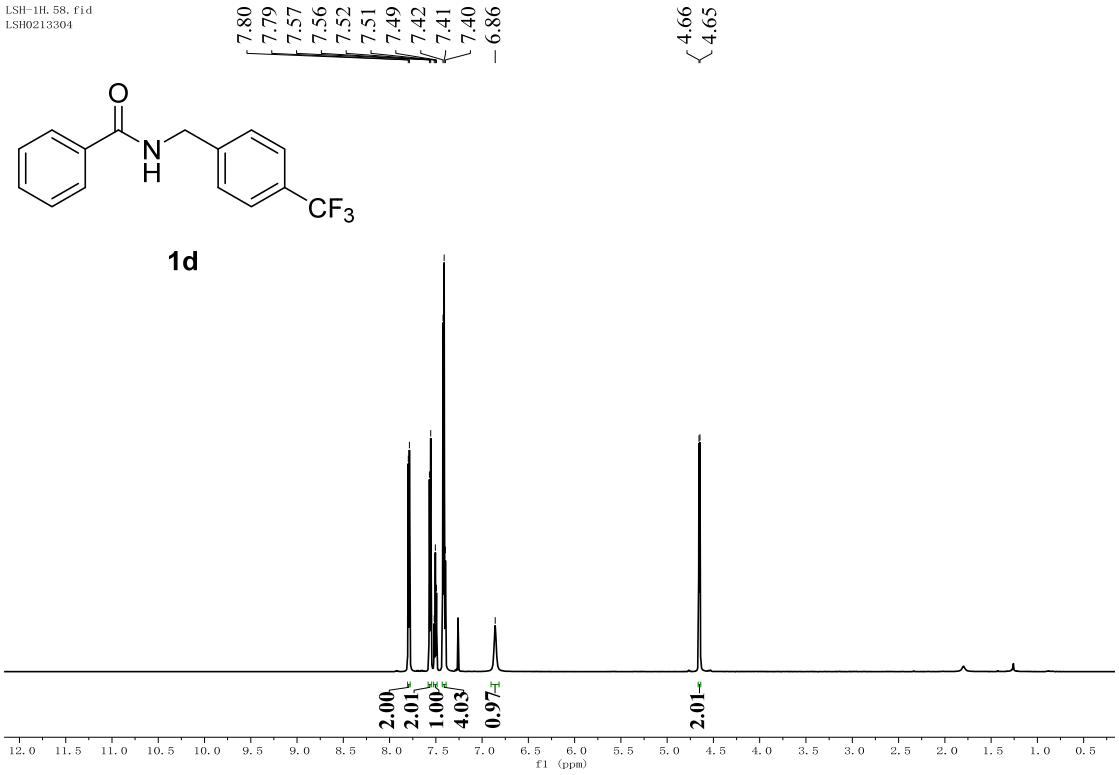
***N*-(4-chlorobenzyl)benzamide (1b) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



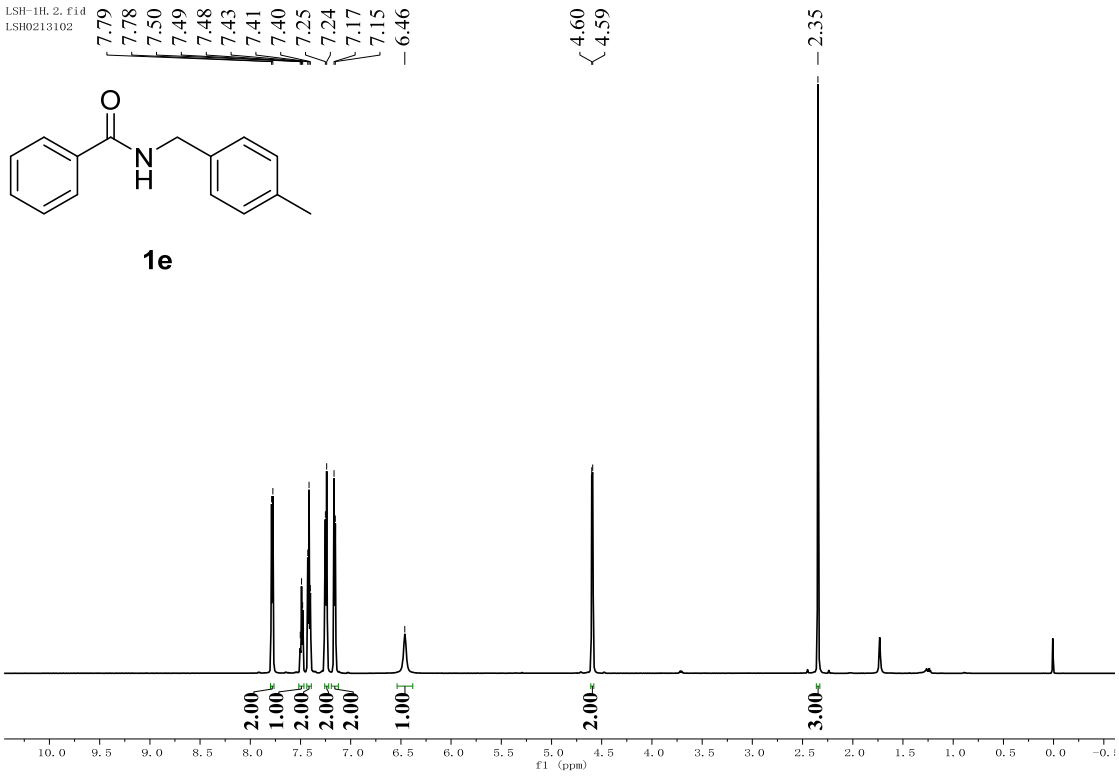
***N*-(4-bromobenzyl)benzamide (1c) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



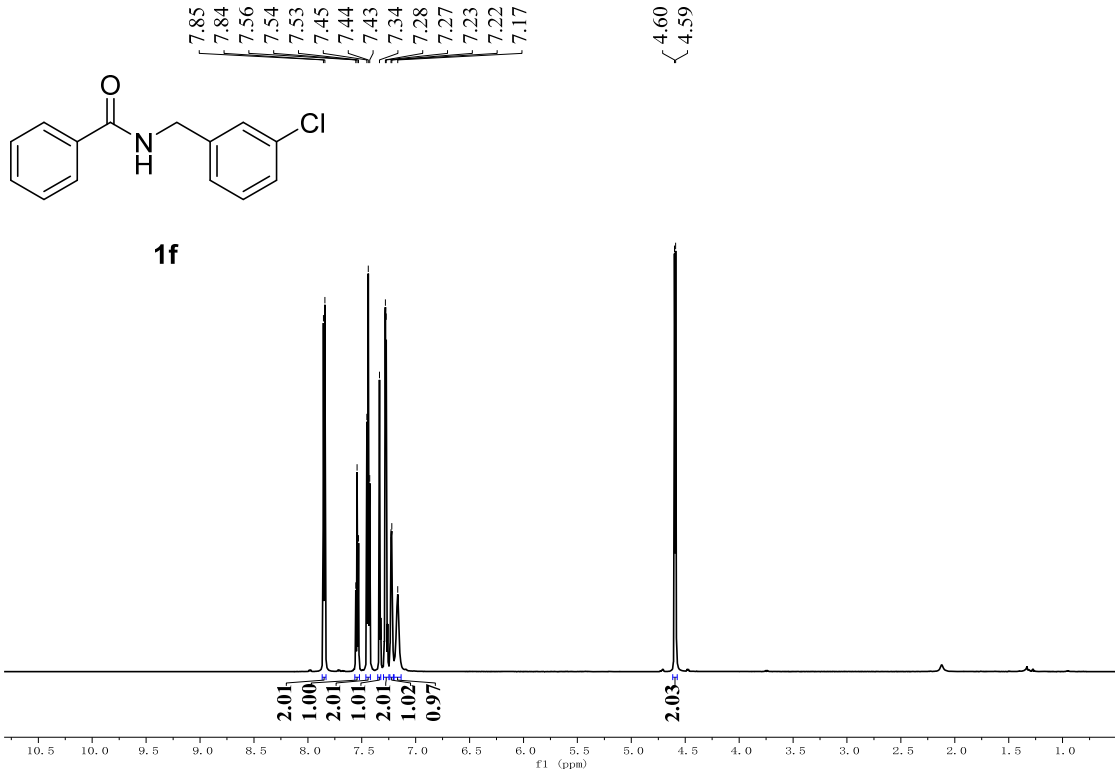
***N*-(4-(trifluoromethyl)benzyl)benzamide (1d) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



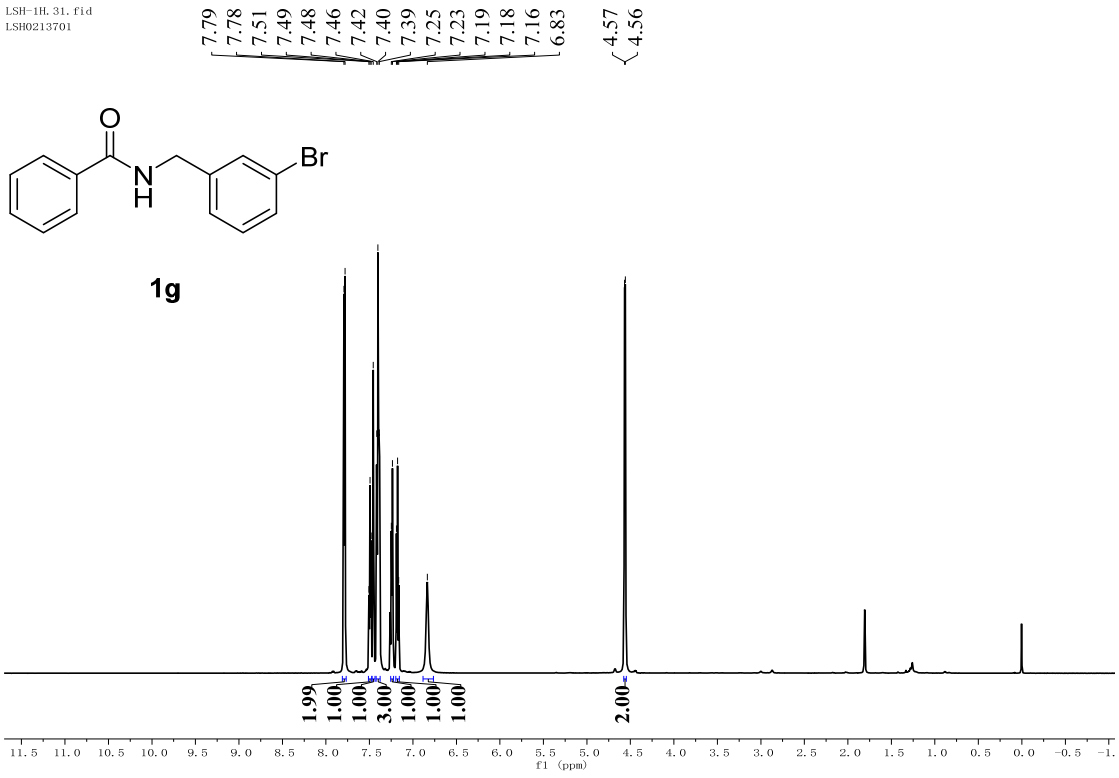
***N*-(4-methylbenzyl)benzamide (1e) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



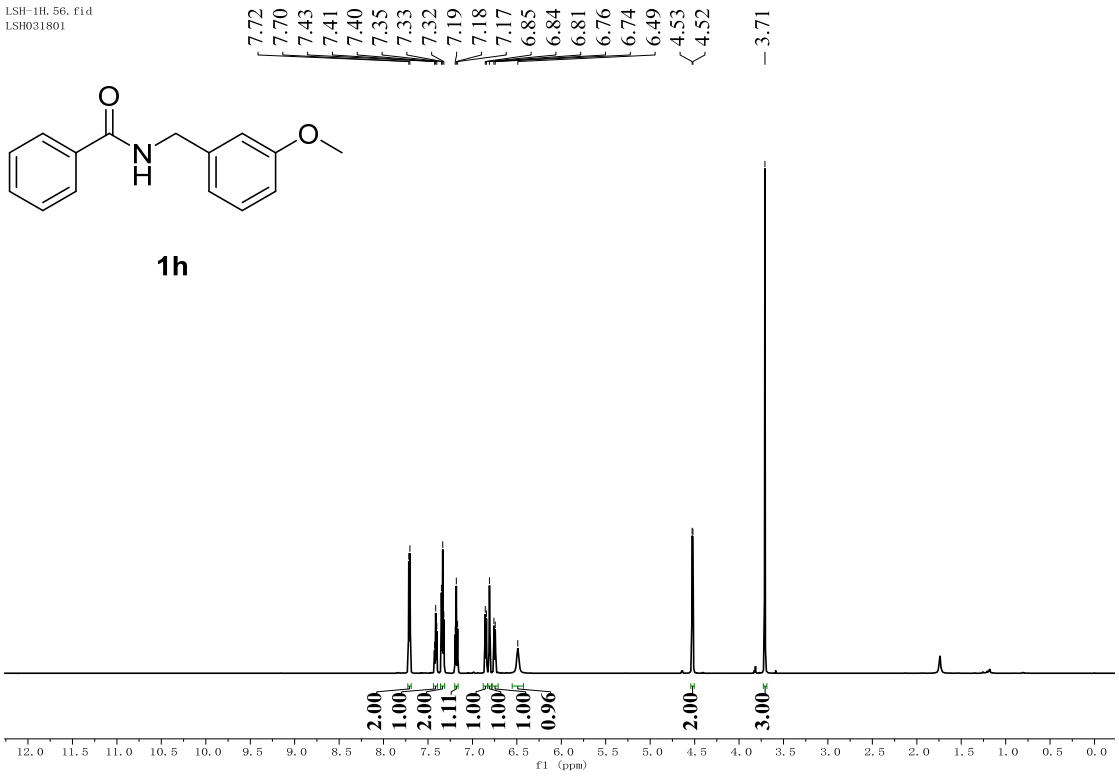
***N*-(3-chlorobenzyl)benzamide (1f) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



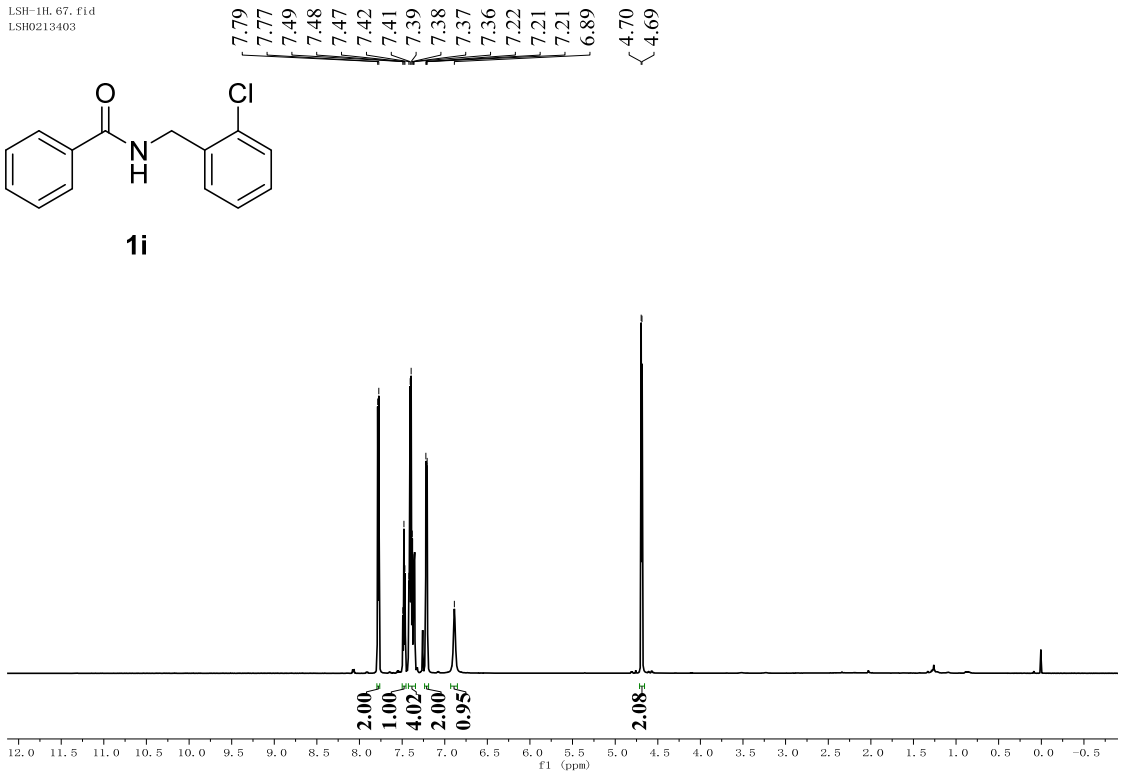
***N*-(3-bromobenzyl)benzamide (1g) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



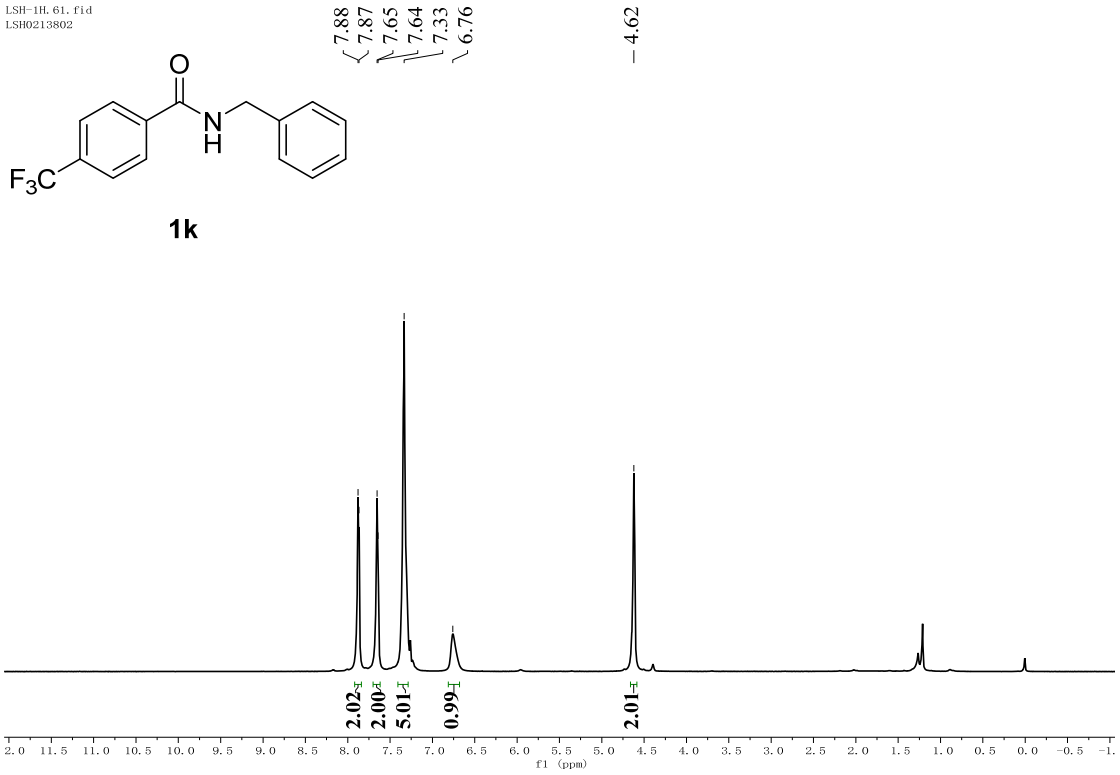
***N*-(3-methoxybenzyl)benzamide (1h) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



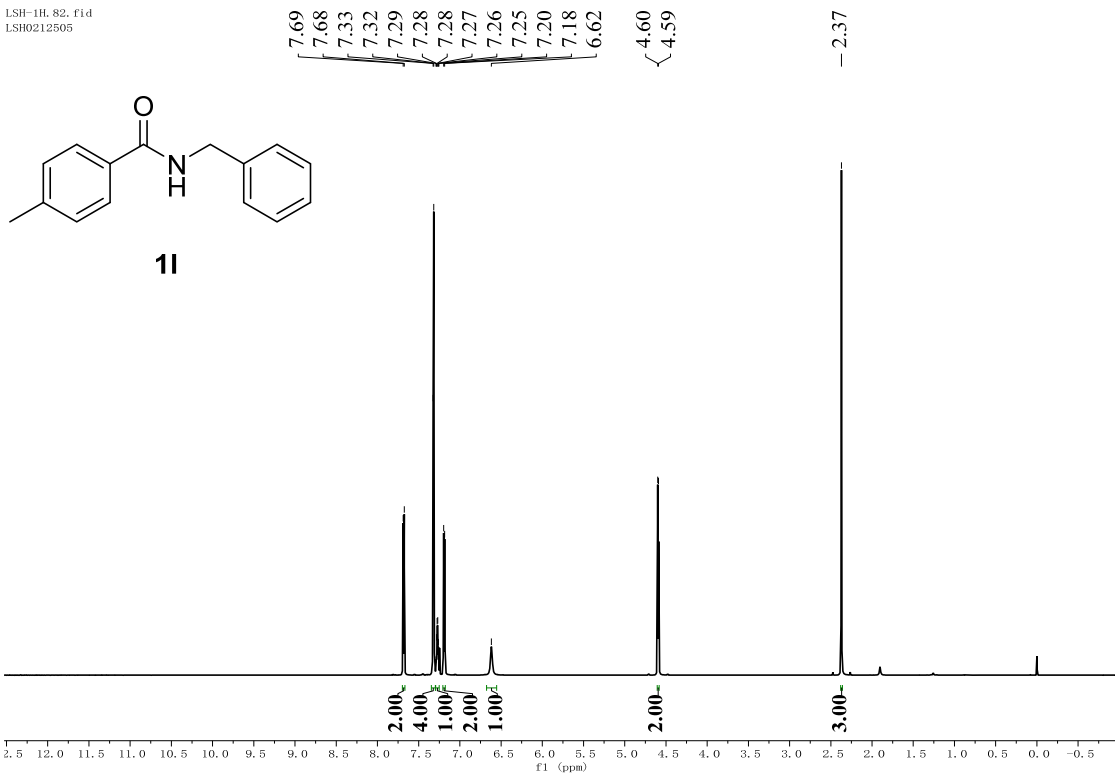
***N*-(2-chlorobenzyl)benzamide (1i) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



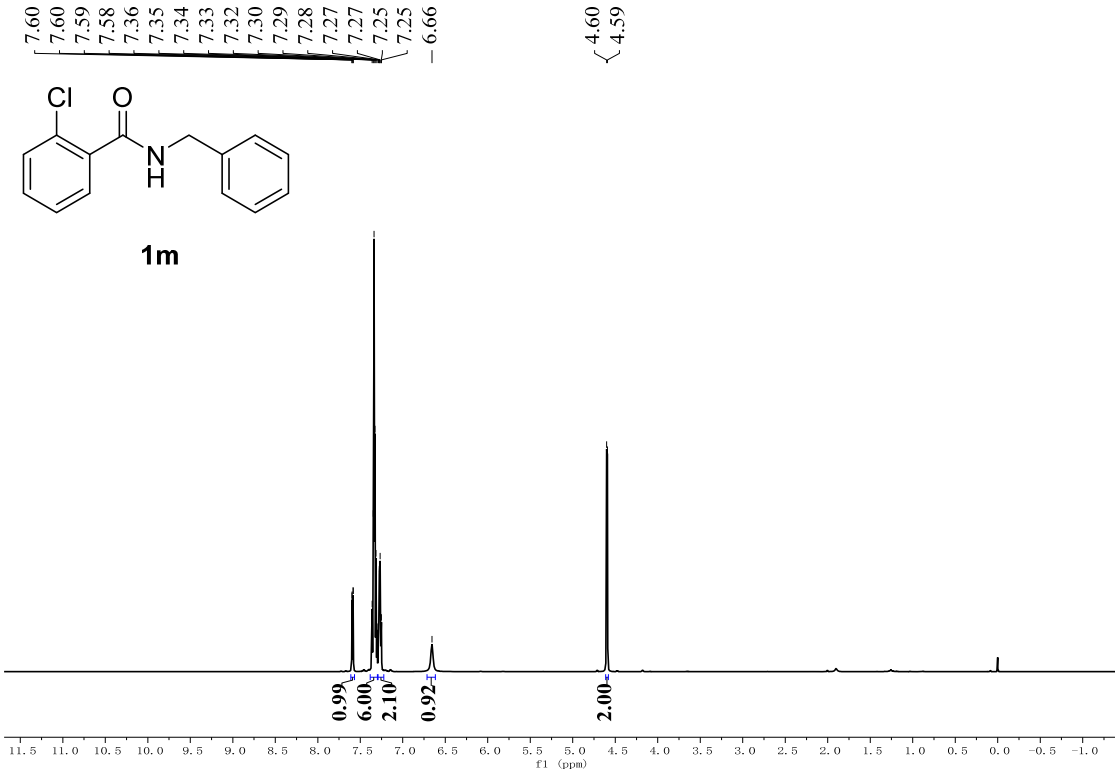
***N*-benzyl-4-(trifluoromethyl)benzamide (1k) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



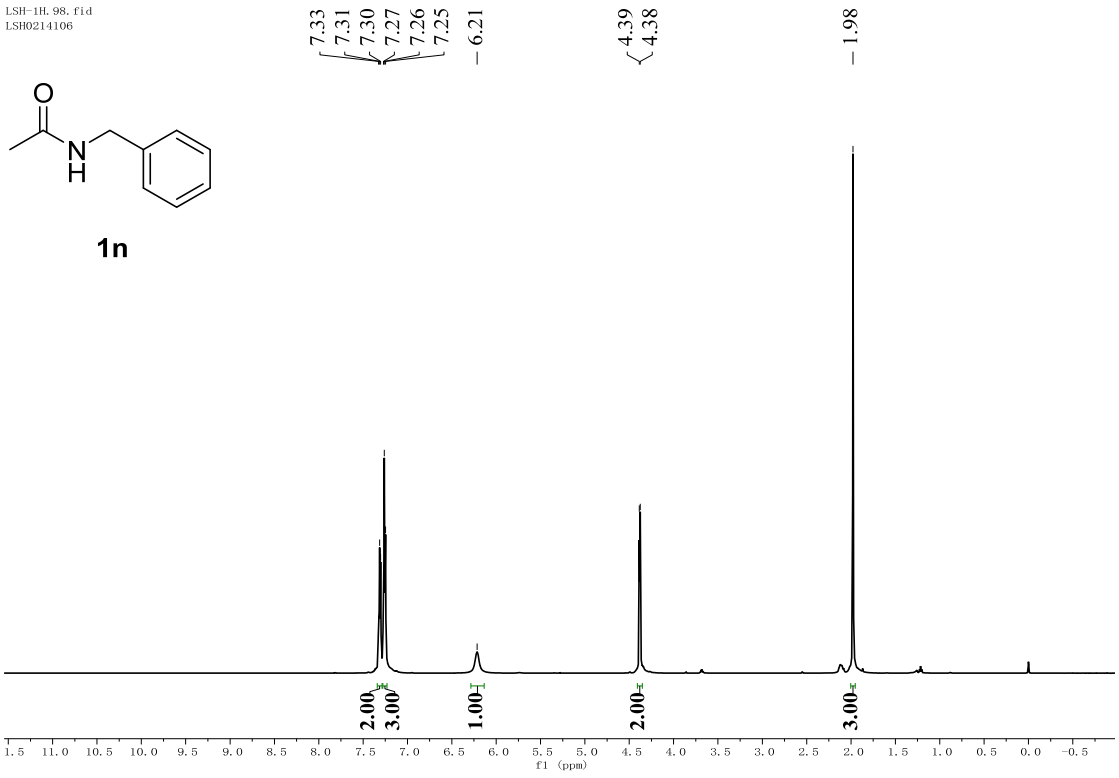
***N*-benzyl-4-methylbenzamide (1l) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



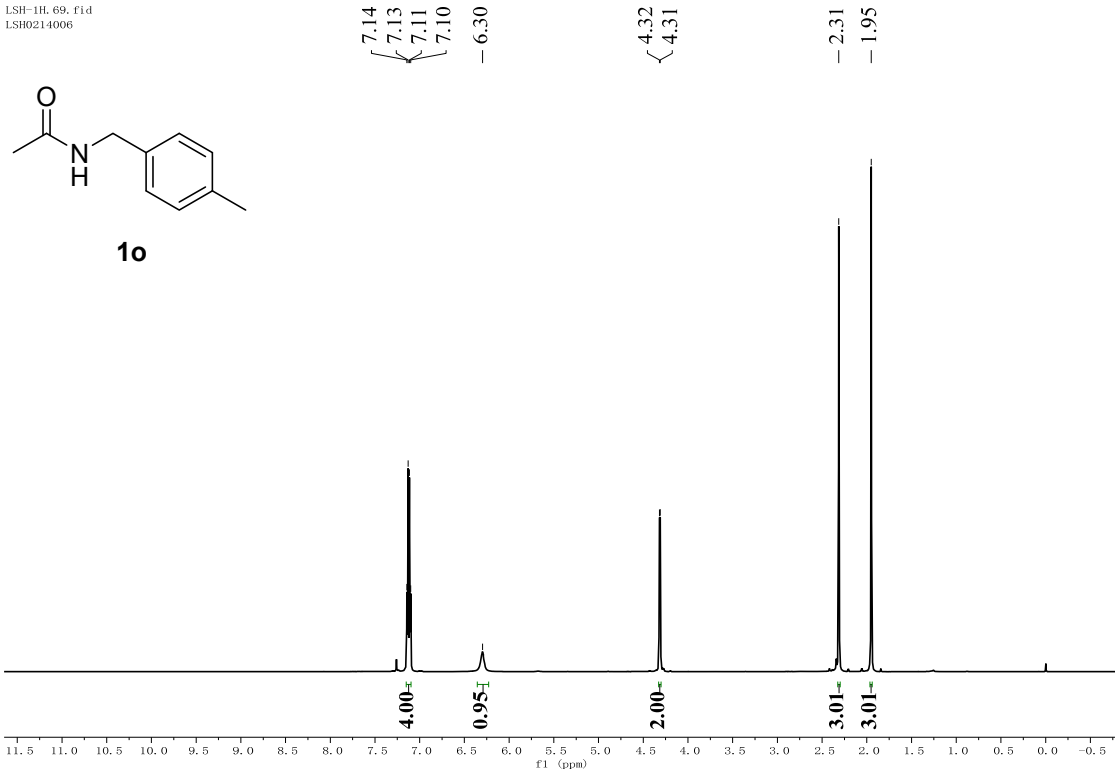
***N*-benzyl-2-chlorobenzamide (1m) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



***N*-benzylacetamide (1n) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**

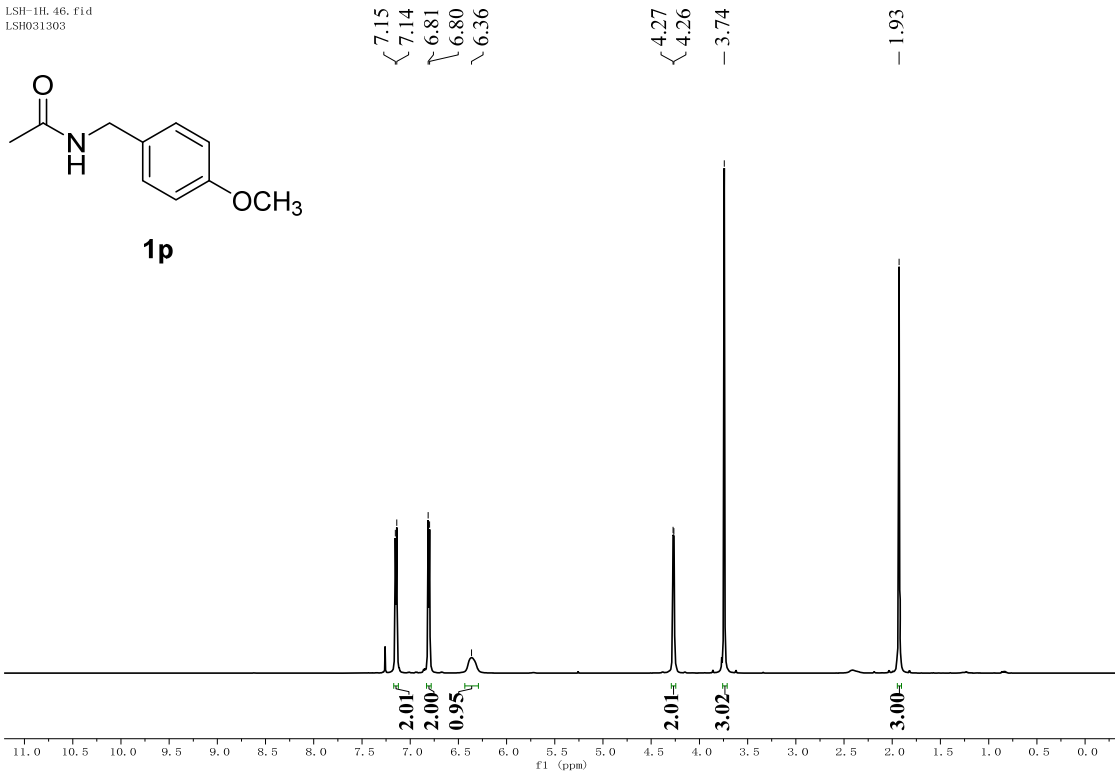


***N*-(4-methylbenzyl)acetamide (1o) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



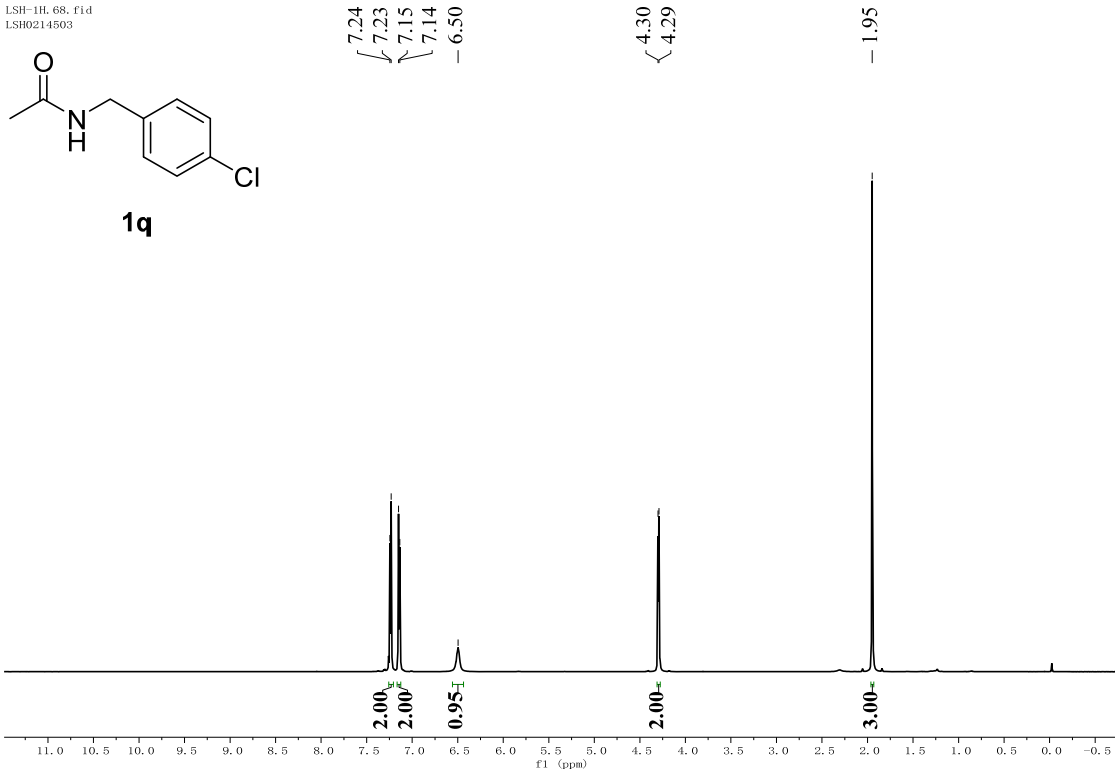
1o

***N*-(4-methoxybenzyl)acetamide (1p) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**

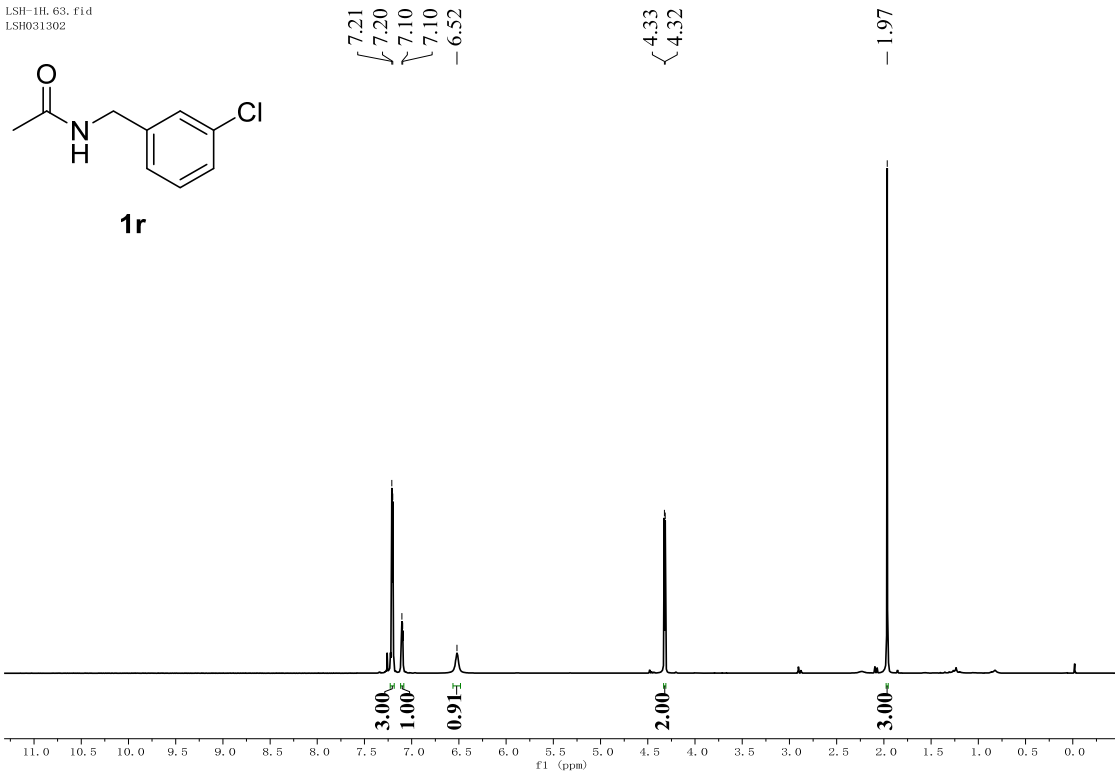


1p

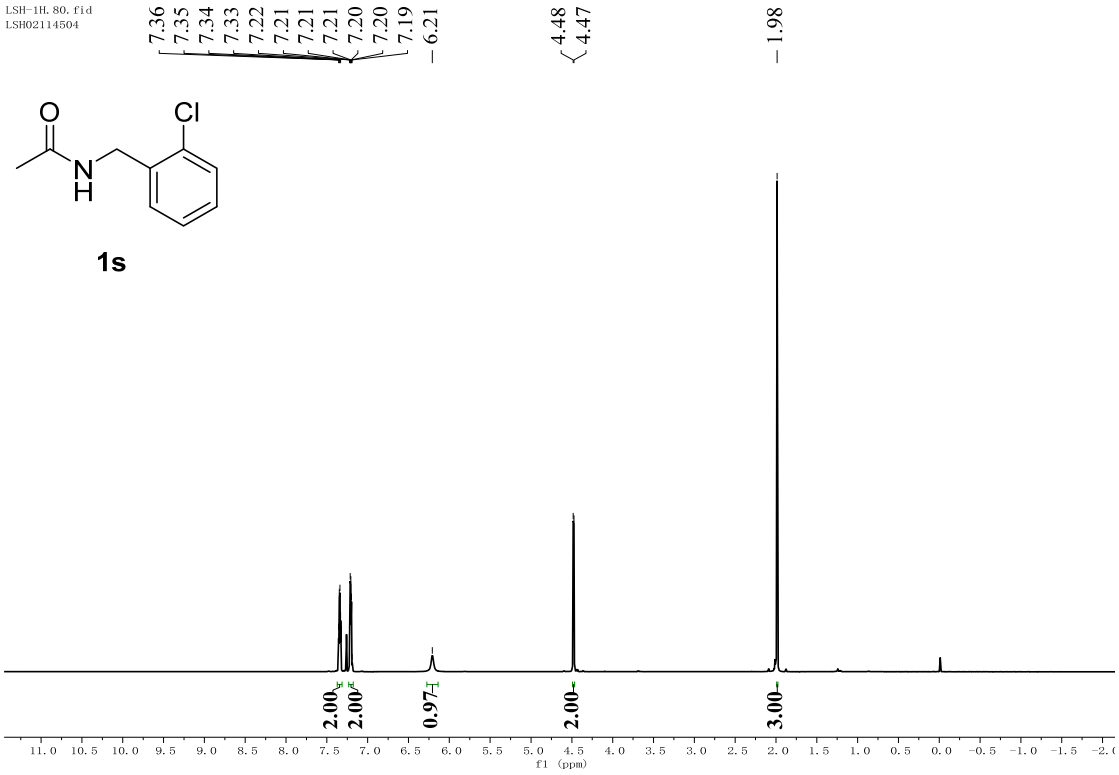
***N*-(4-chlorobenzyl)acetamide (1q) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



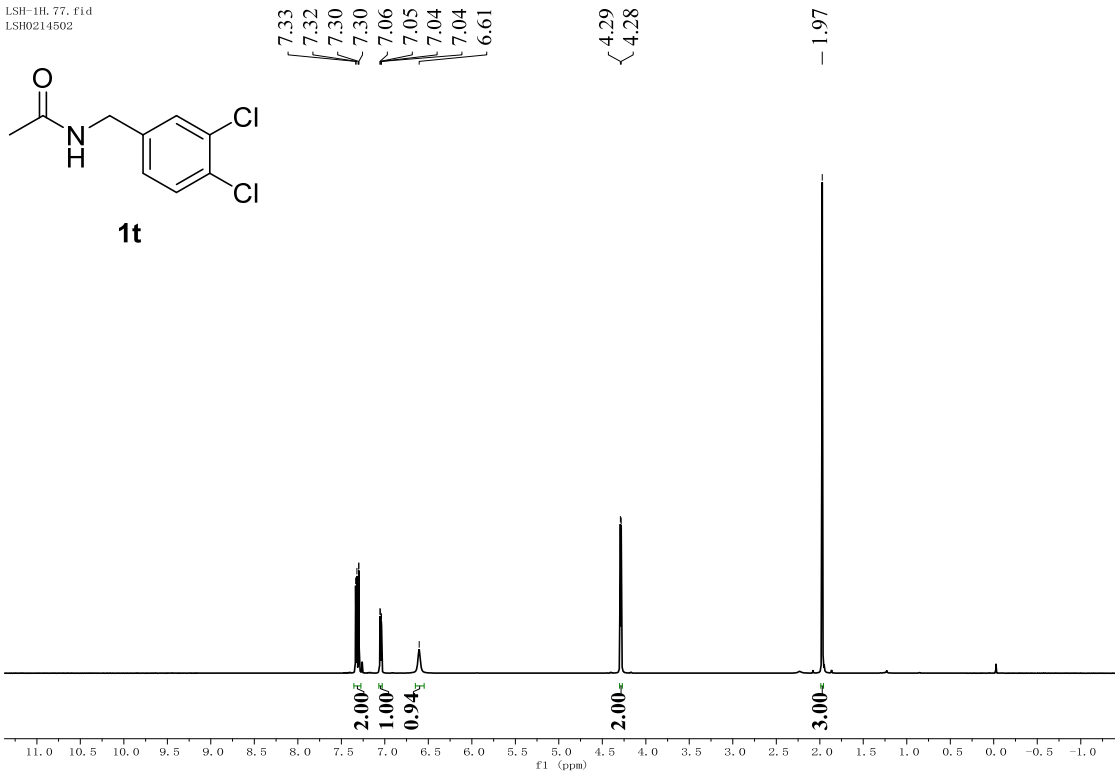
***N*-(3-chlorobenzyl)acetamide (1r) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



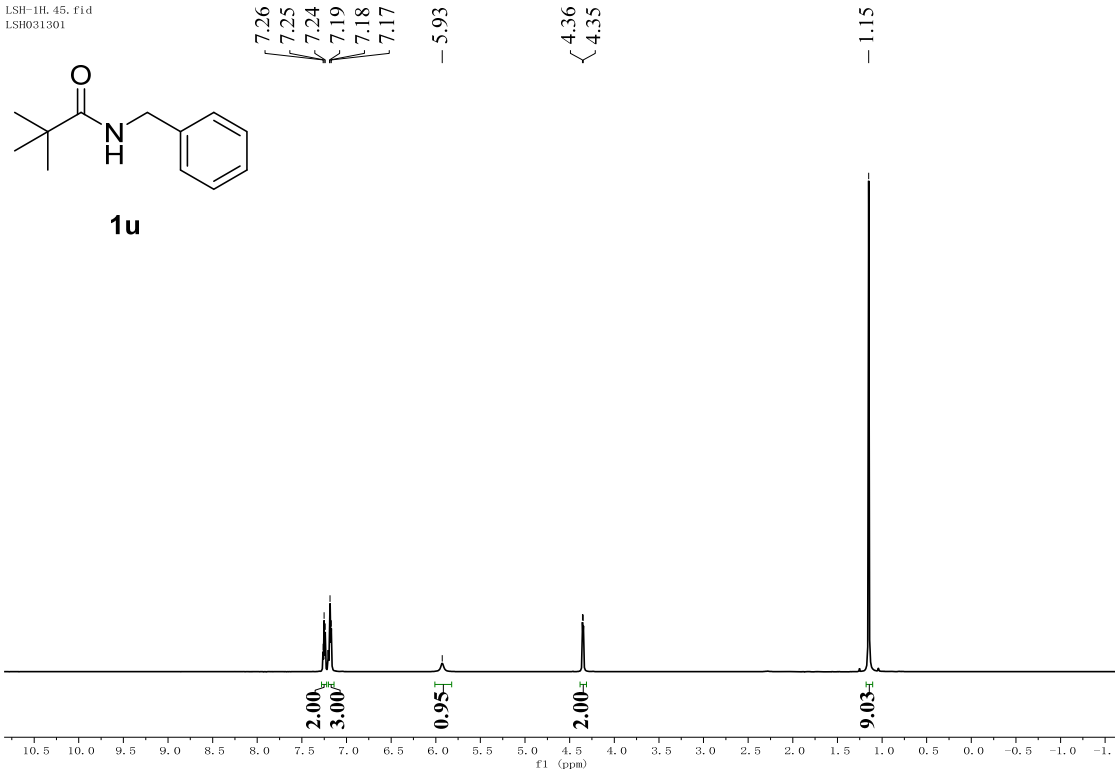
***N*-(2-chlorobenzyl)acetamide (1s) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



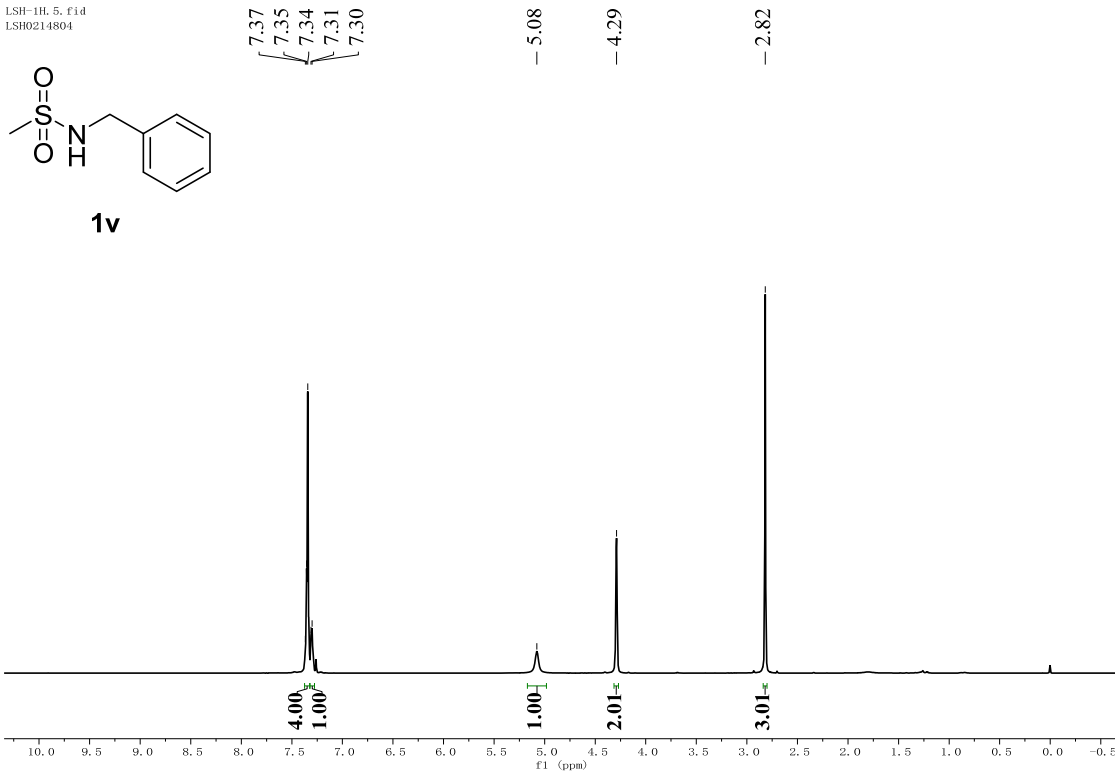
***N*-(3,4-dichlorobenzyl)acetamide (1t) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



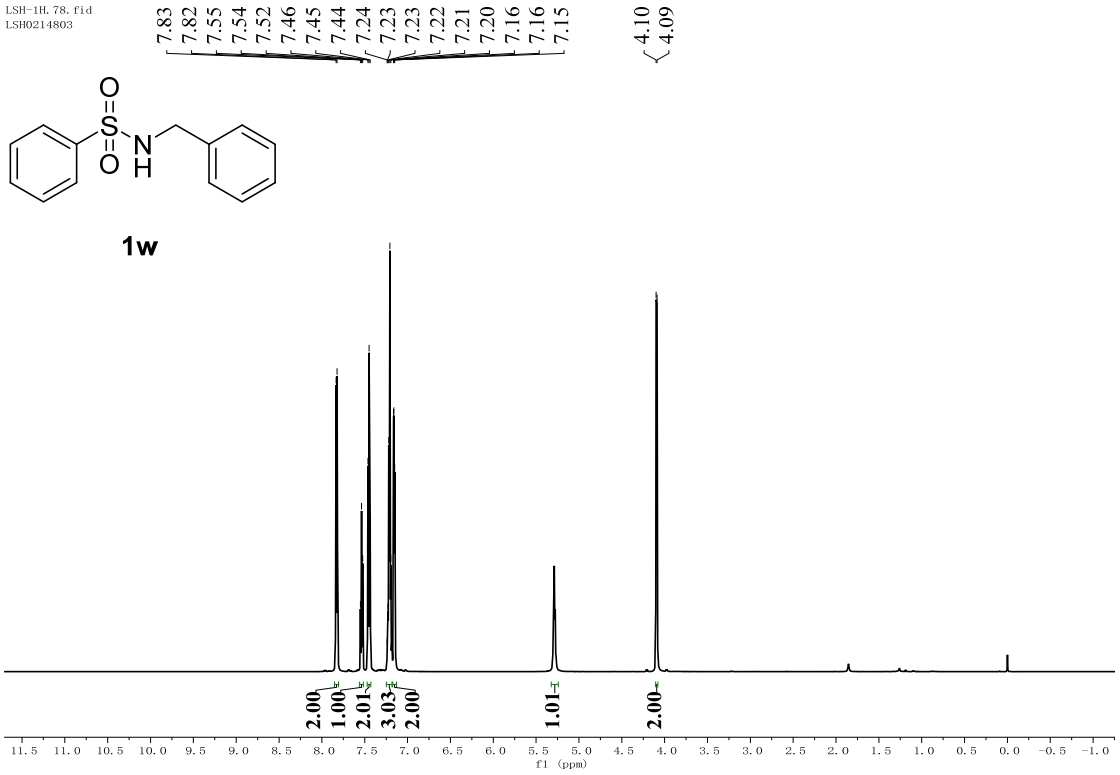
***N*-benzylpivalamide (1u) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



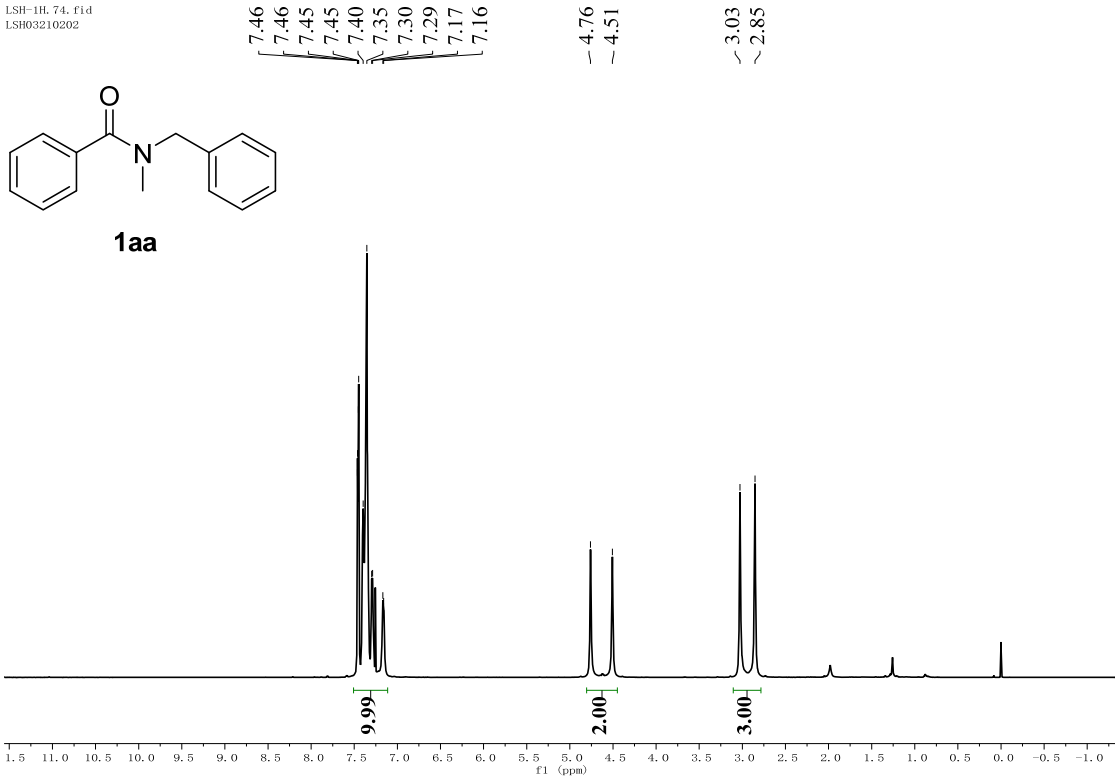
***N*-benzylmethanesulfonamide (1v) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



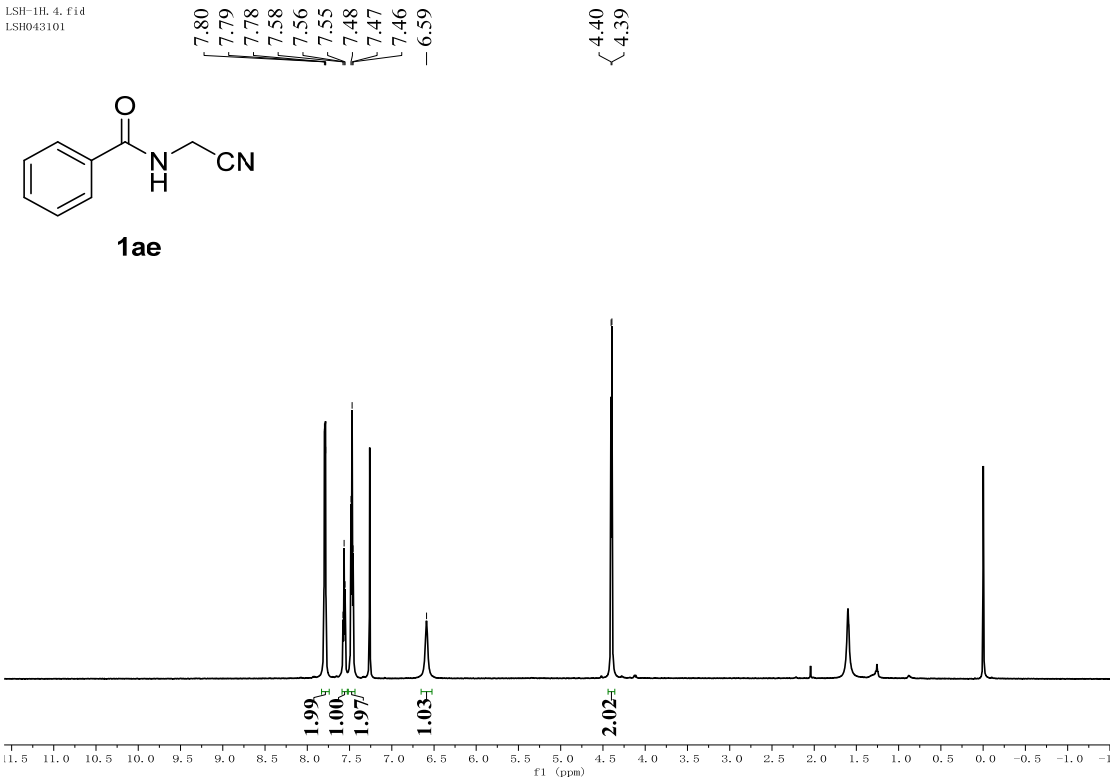
_N_-benzylbenzenesulfonamide (1w) ^{1}H NMR (600 MHz, $CDCl_3$)**:**



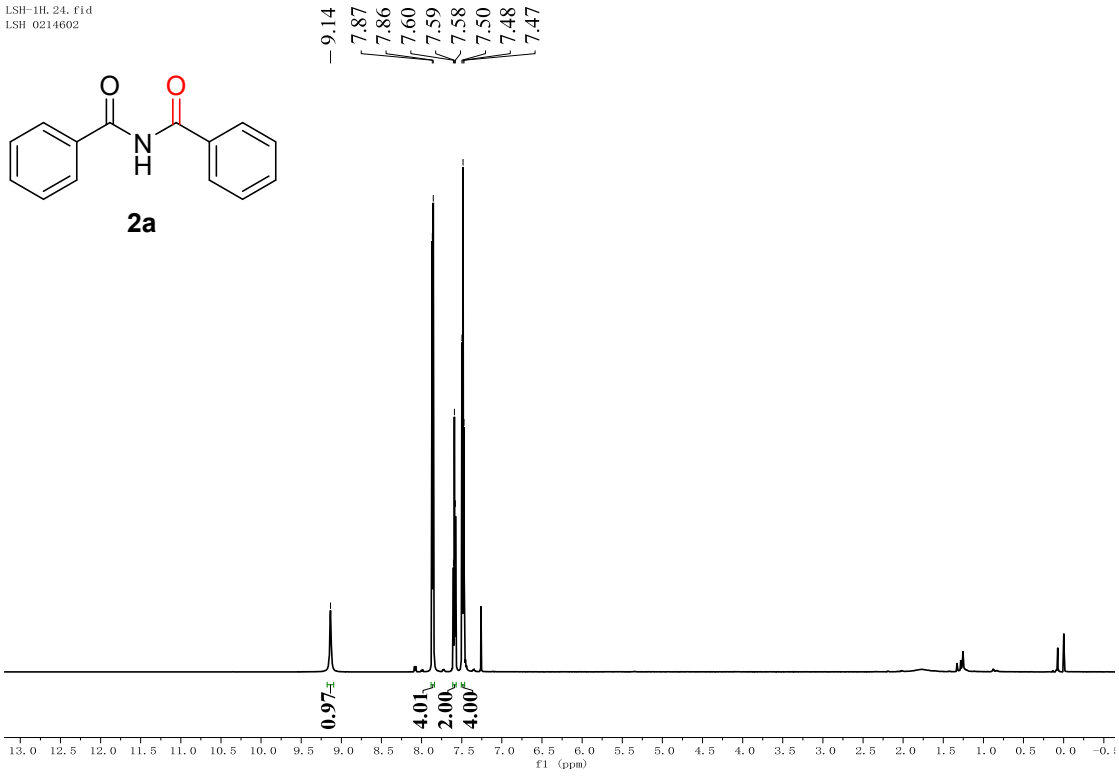
_N_-hexylbutyramide (1aa) ^{1}H NMR (600 MHz, $CDCl_3$):



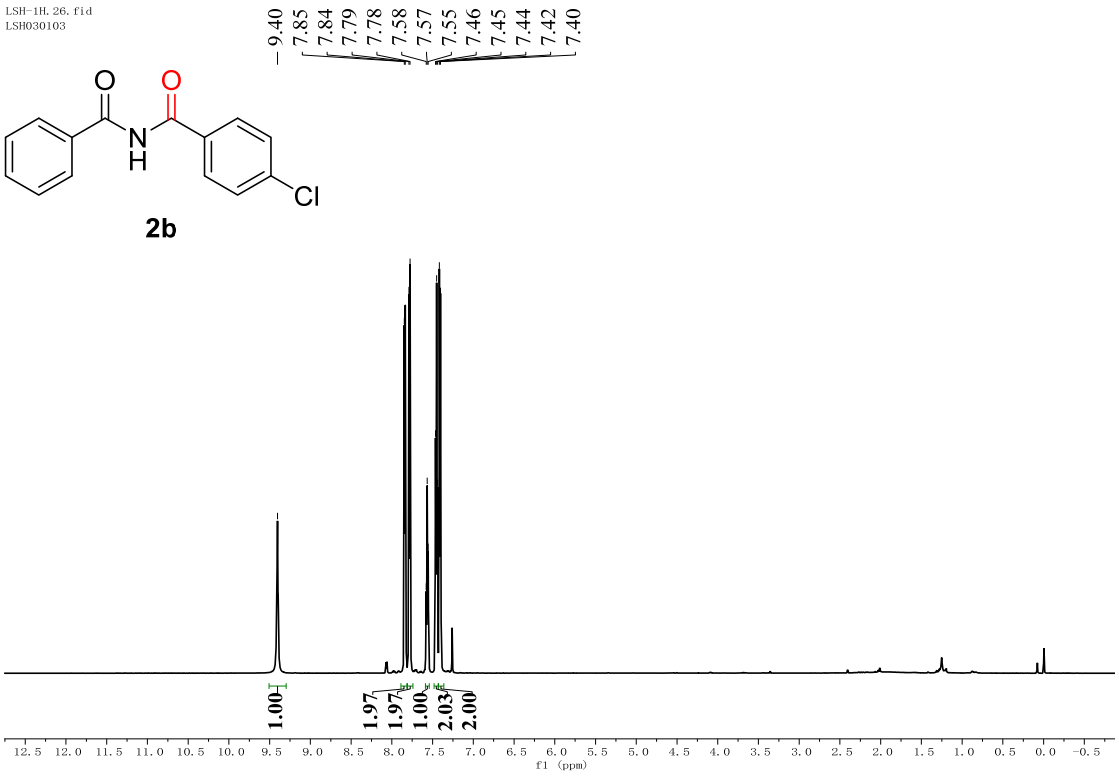
***N*-(cyanomethyl)benzamide (1 ae) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



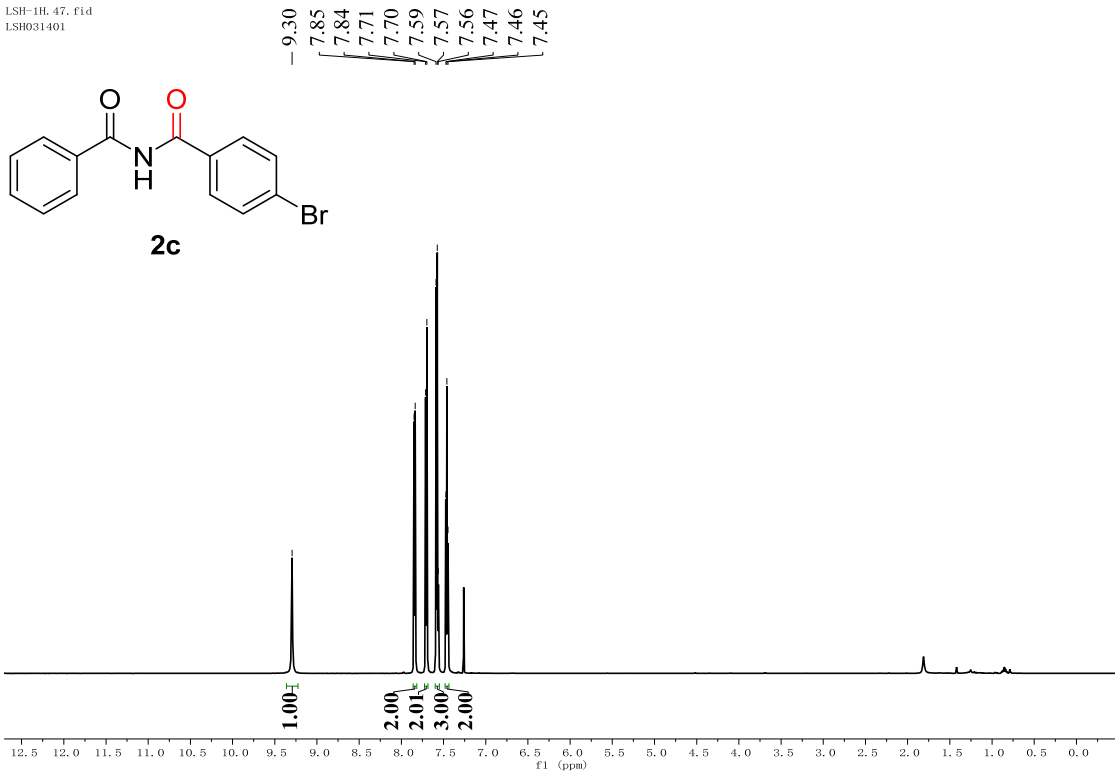
***N*-benzoylbenzamide (2a) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



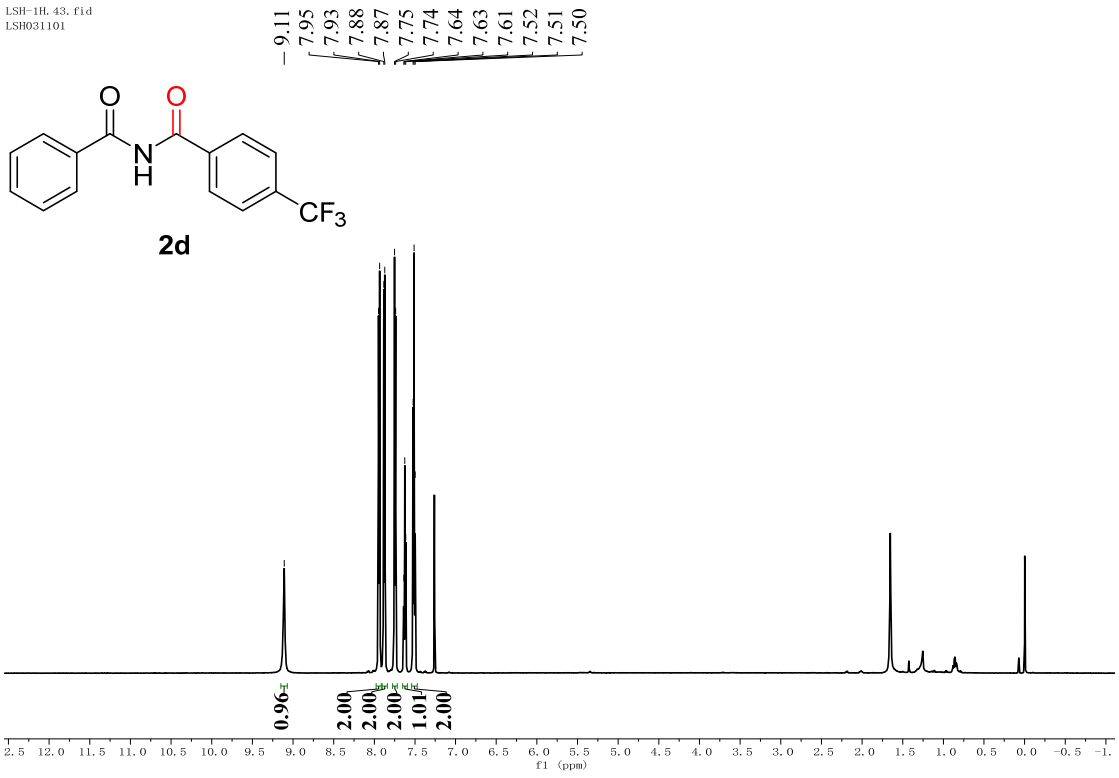
***N*-benzoyl-4-chlorobenzamide (2b) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



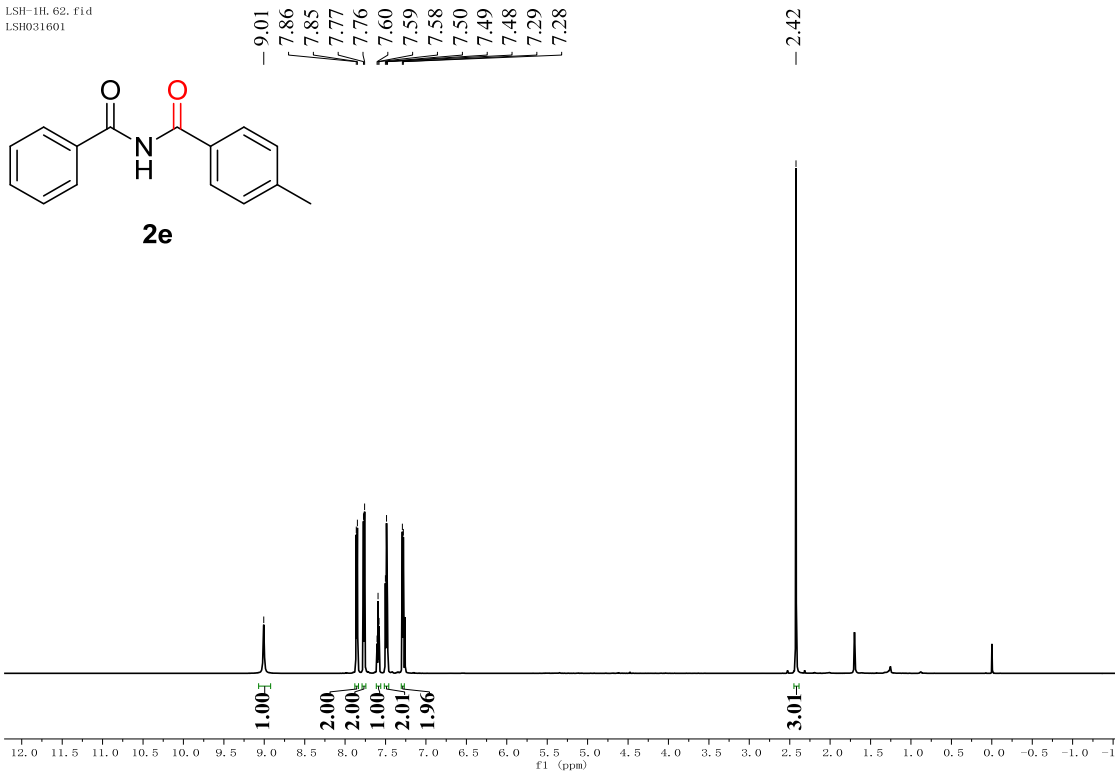
***N*-benzoyl-4-bromobenzamide (2c) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



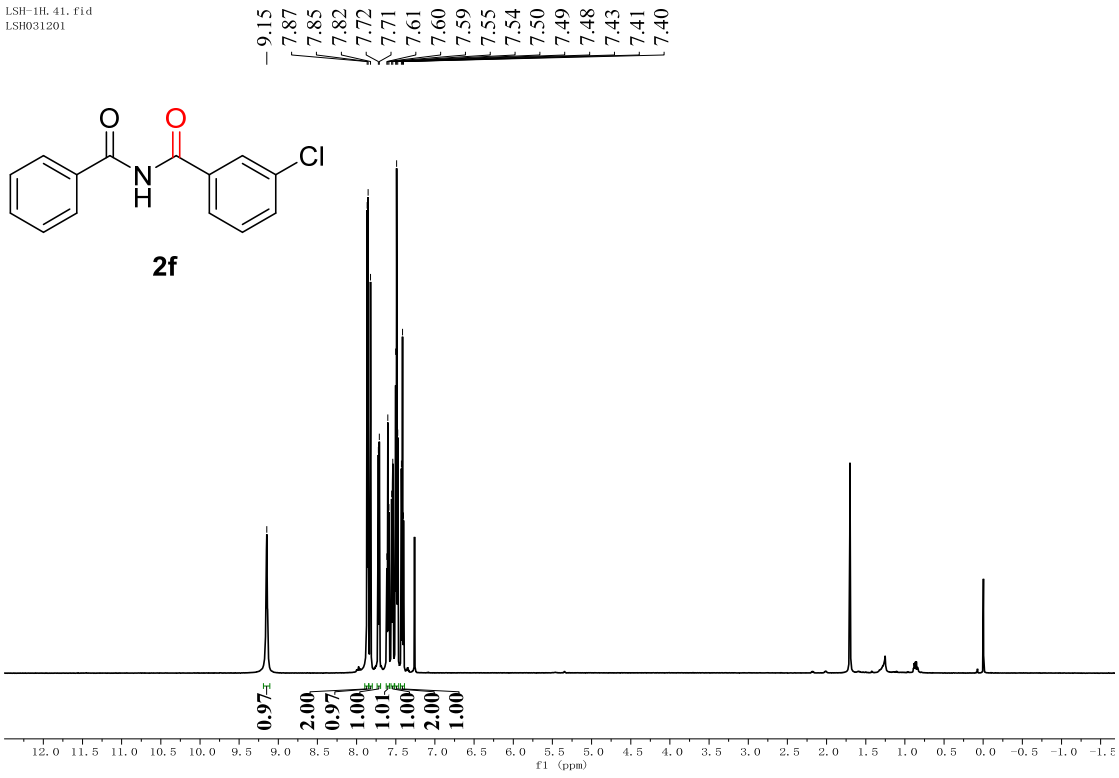
***N*-benzoyl-4-(trifluoromethyl)benzamide (2d) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



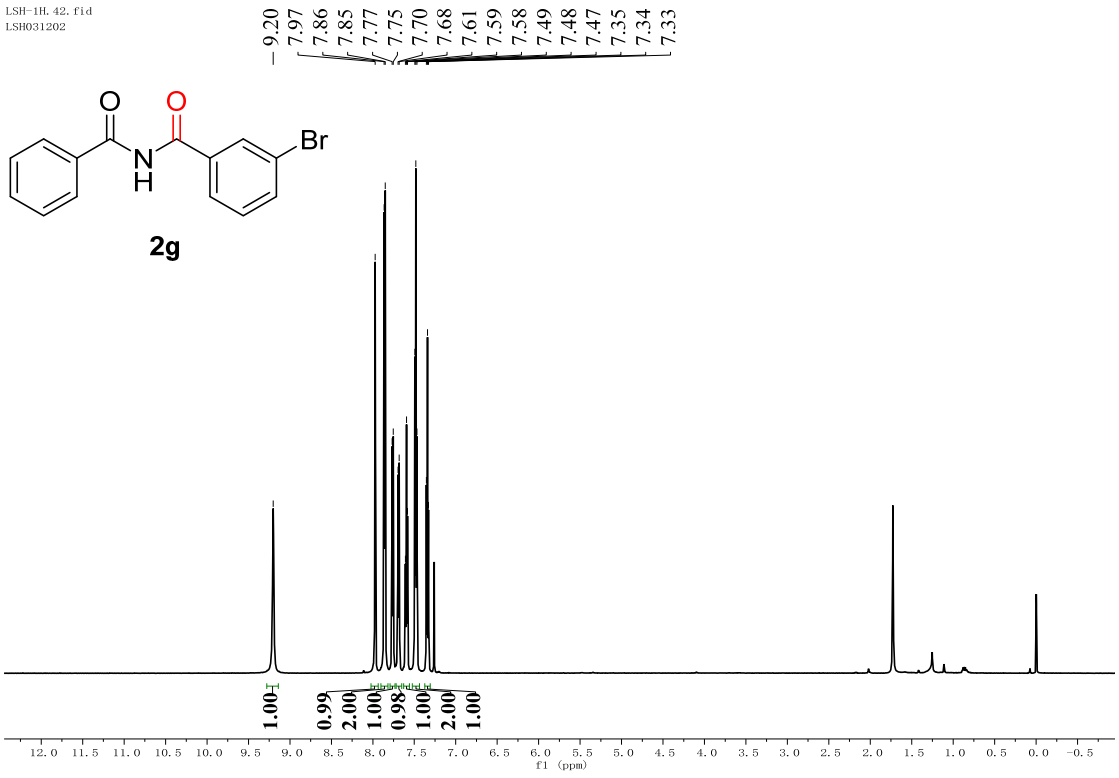
***N*-benzoyl-4-methylbenzamide (2e) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



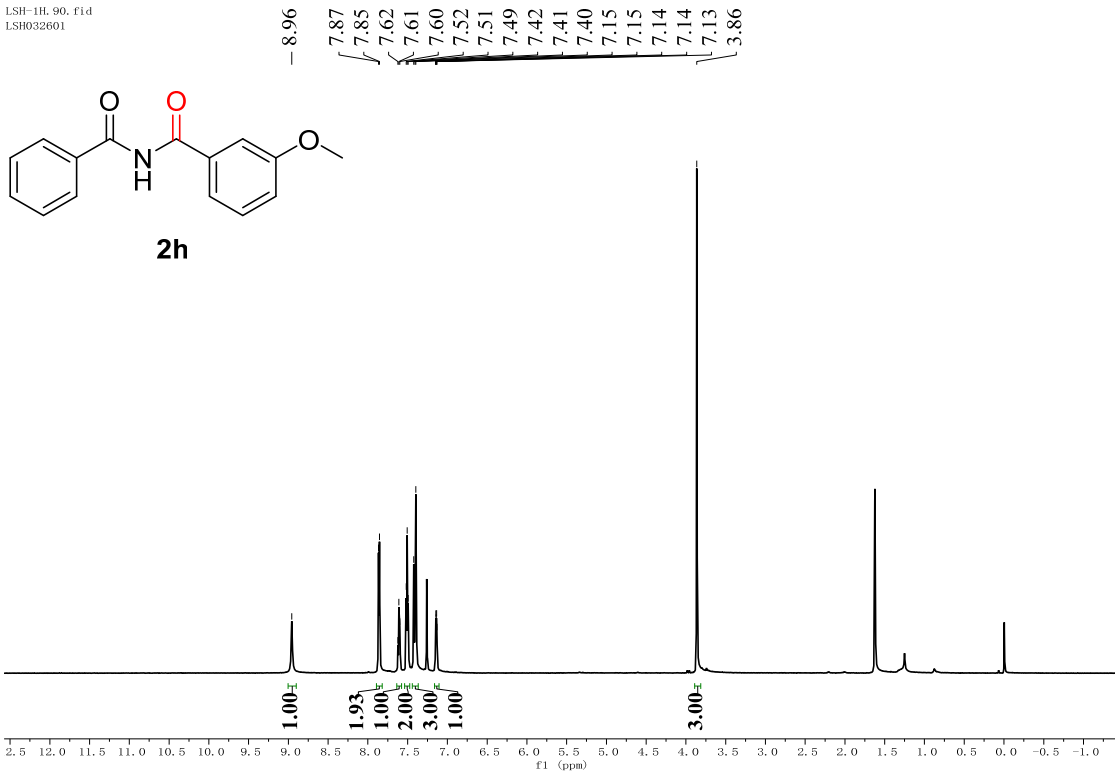
***N*-benzoyl-3-chlorobenzamide (2f) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



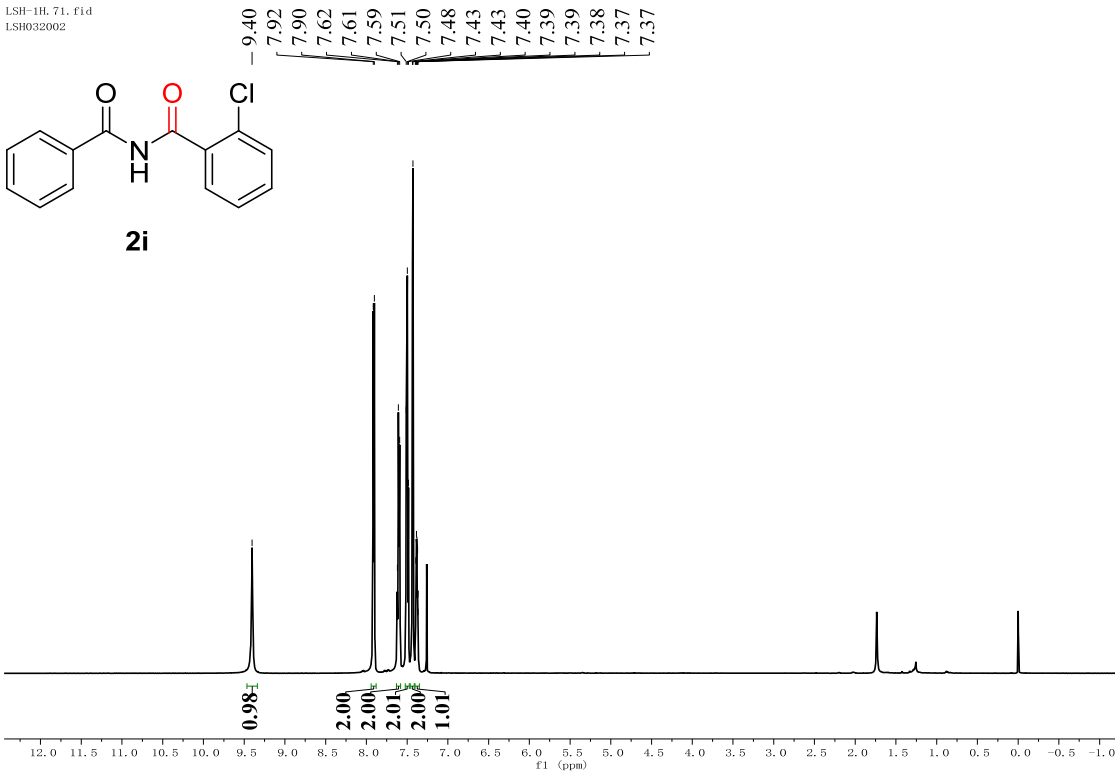
***N*-benzoyl-3-bromobenzamide (2g) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



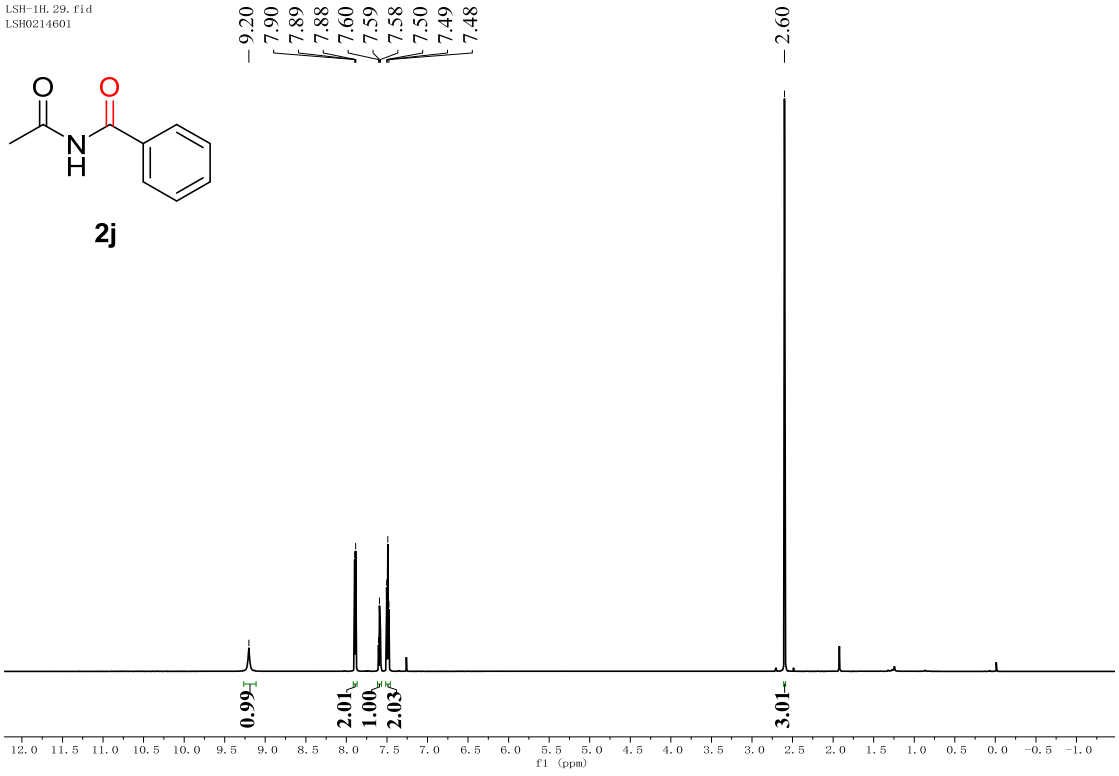
***N*-benzoyl-3-methoxybenzamide (2h) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



***N*-benzoyl-2-chlorobenzamide (2i) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**

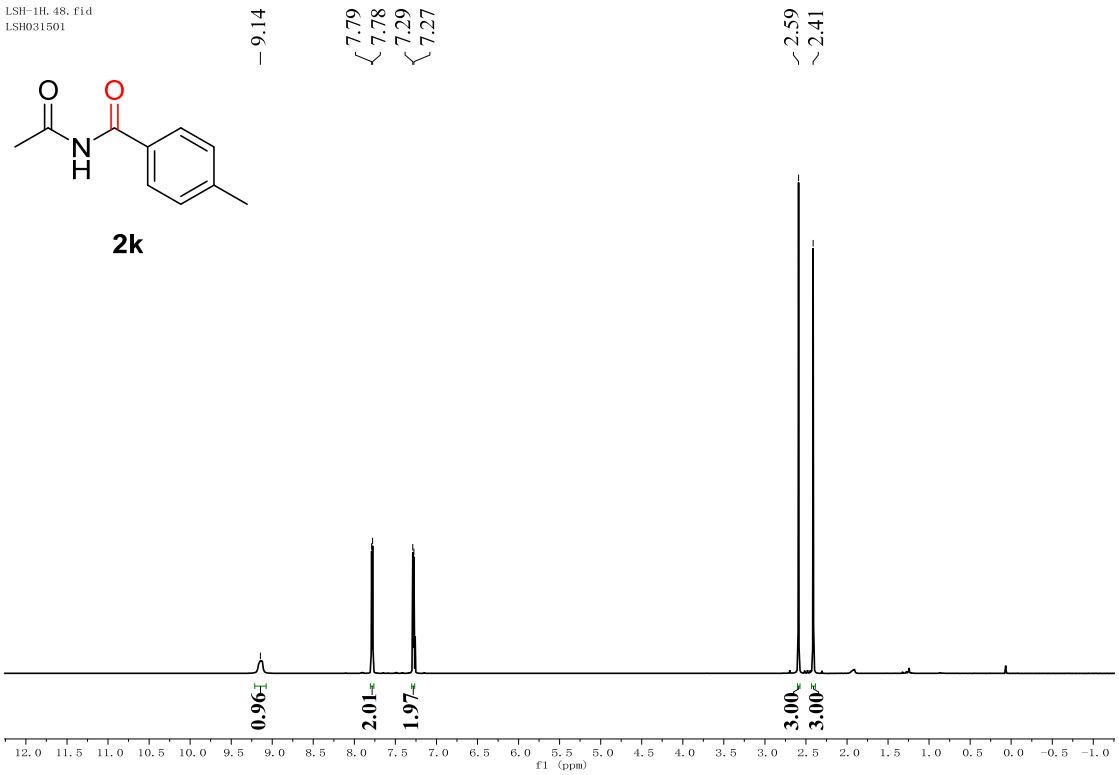


***N*-acetylbenzamide (2j) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



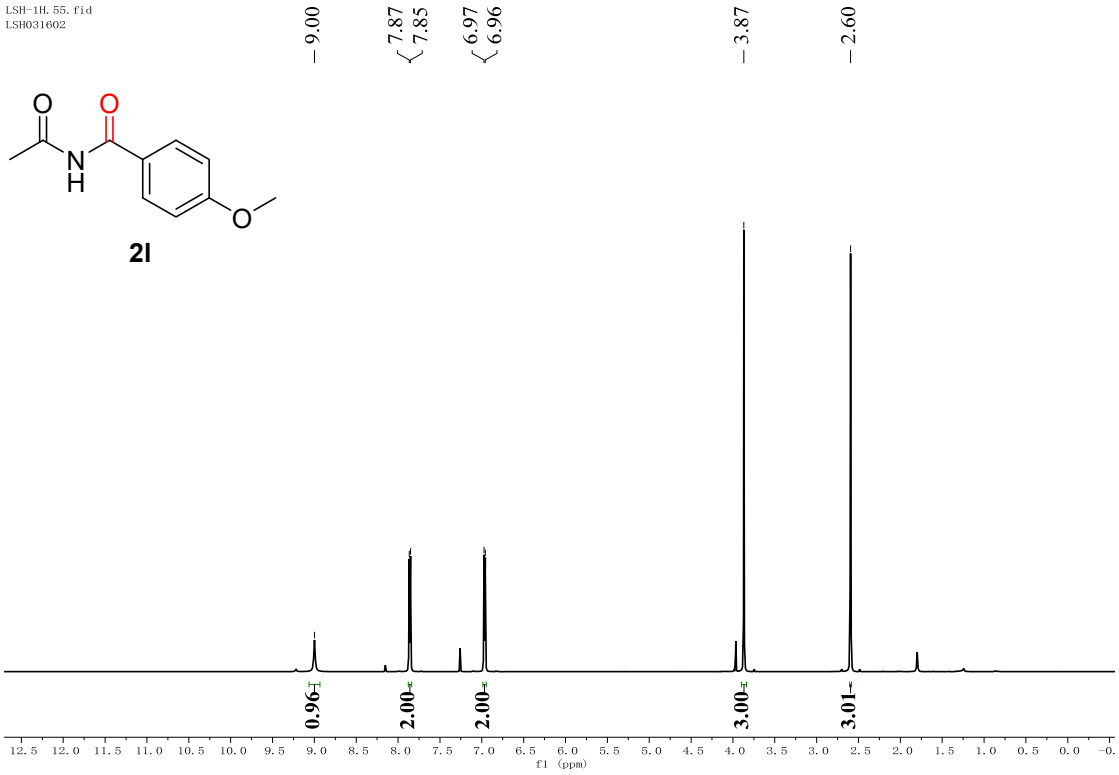
2j

***N*-acetyl-4-methylbenzamide (2k) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**

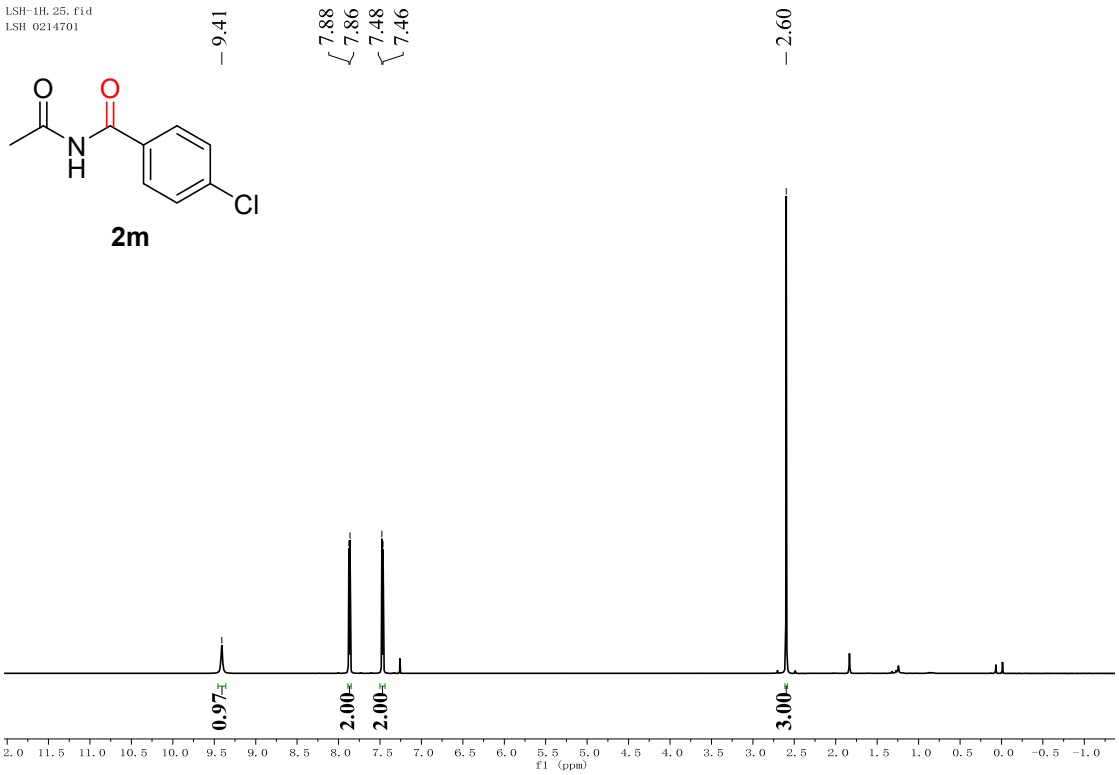


2k

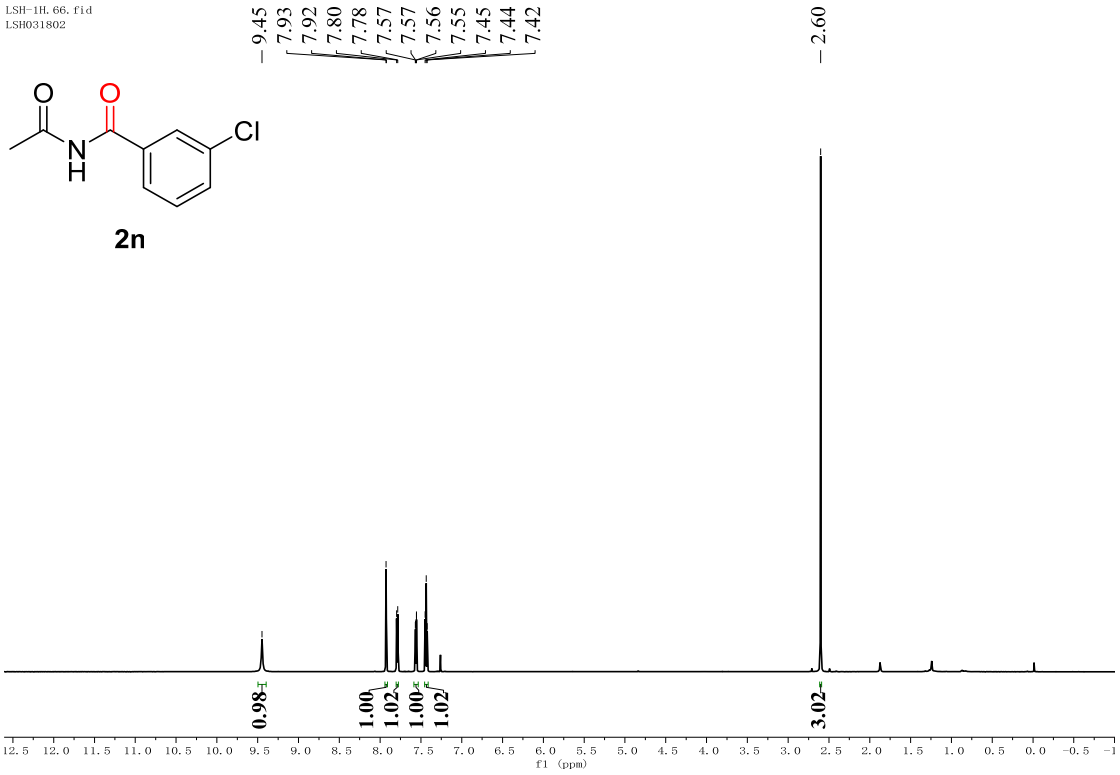
***N*-acetyl-4-methoxybenzamide (2l) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



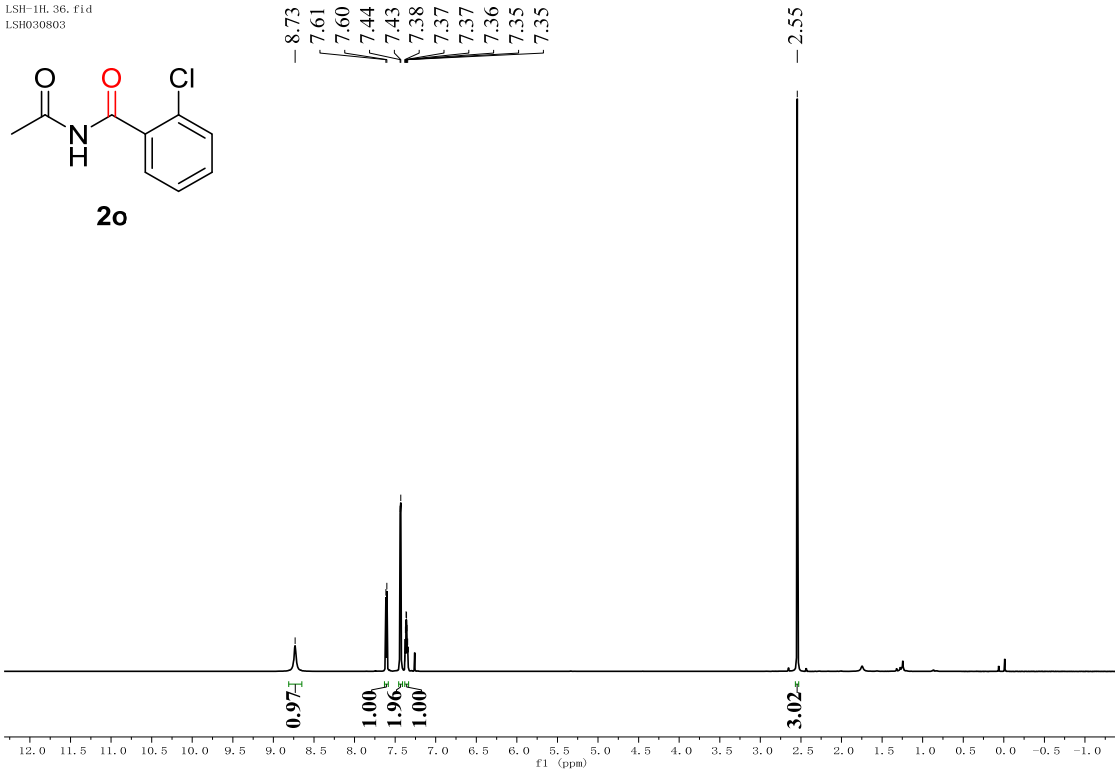
***N*-acetyl-4-chlorobenzamide (2m) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



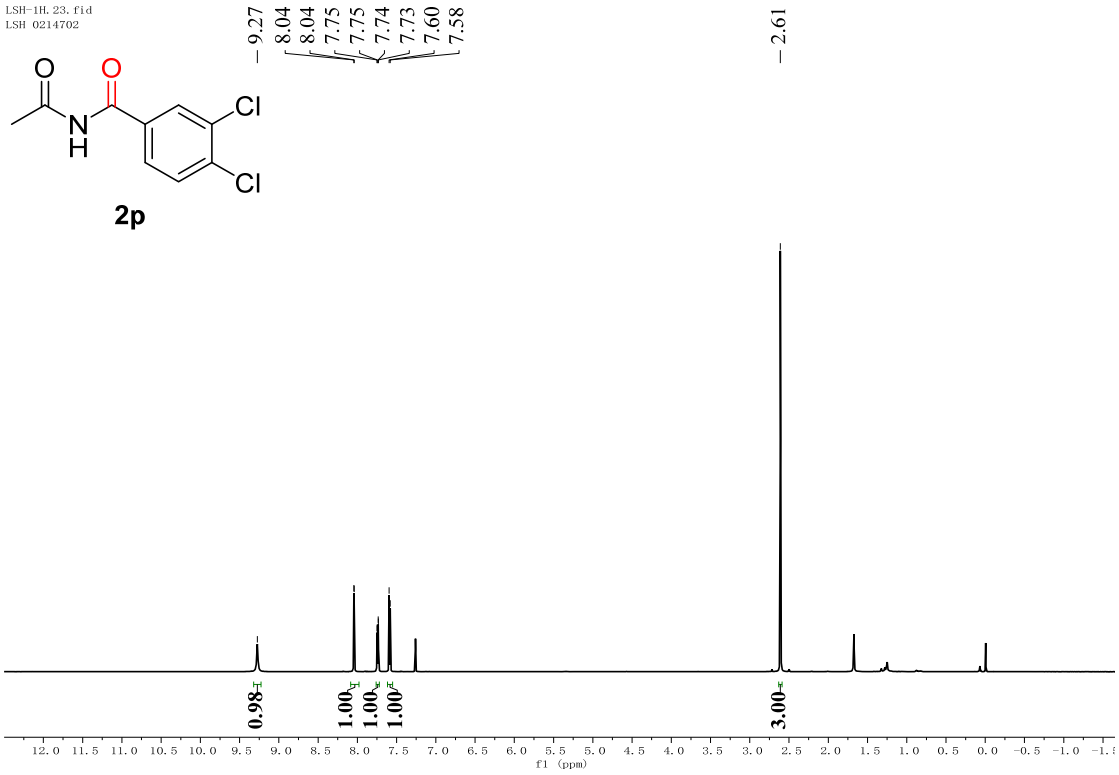
***N*-acetyl-3-chlorobenzamide (2n) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



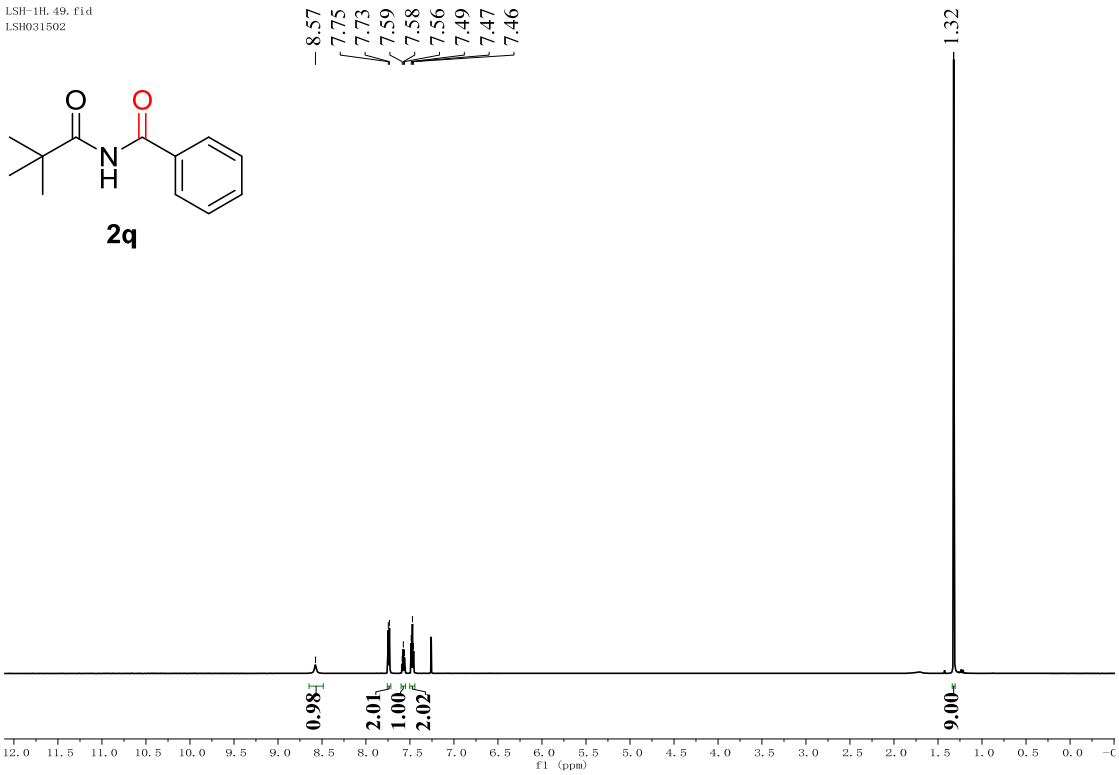
***N*-acetyl-2-chlorobenzamide (2o) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



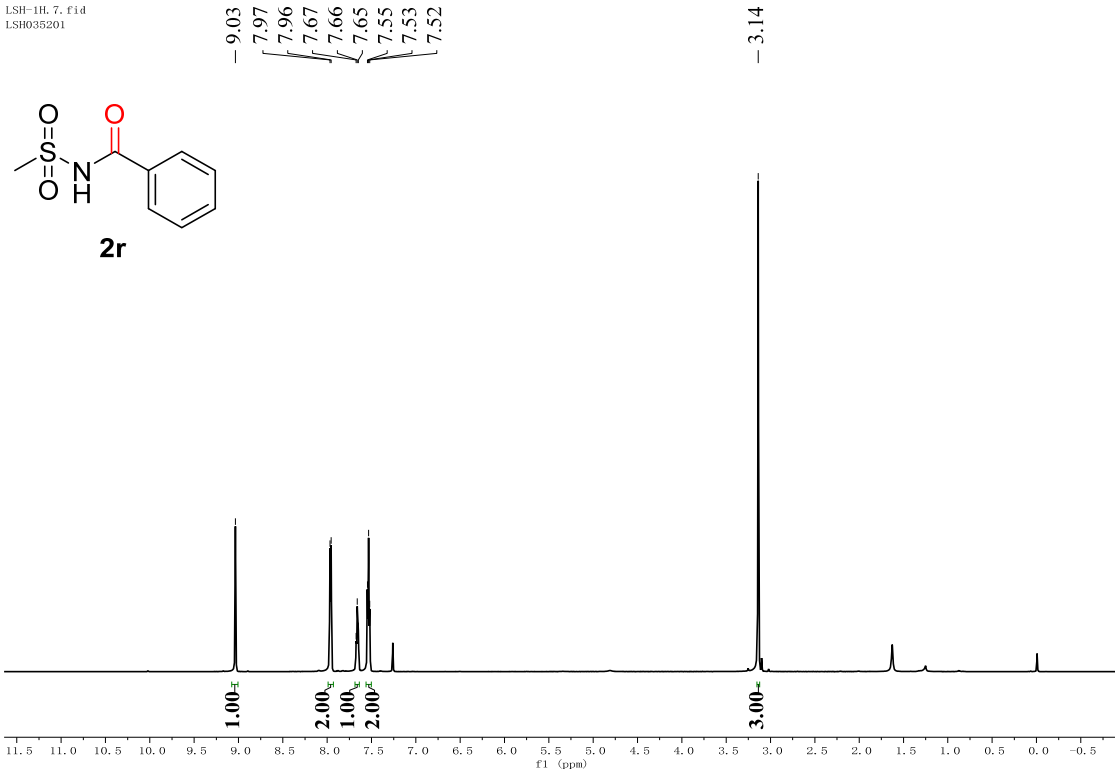
***N*-acetyl-3,4-dichlorobenzamide (2p) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



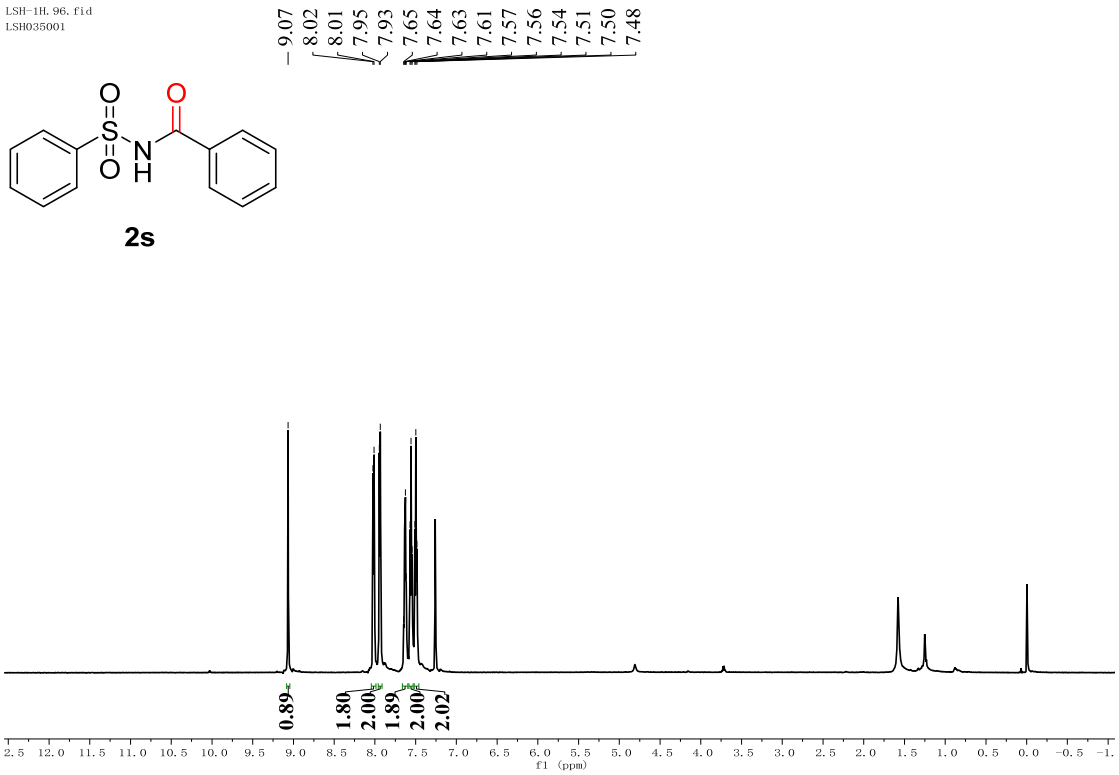
***N*-pivaloylbenzamide (2q) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



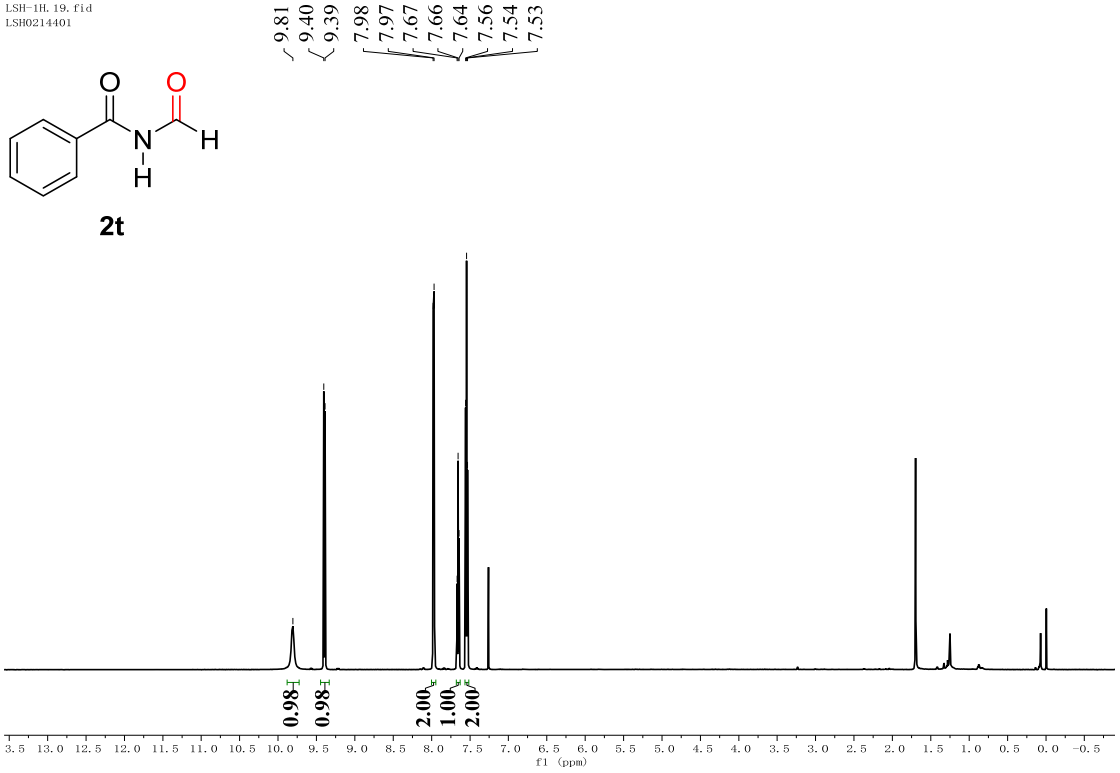
***N*-(methylsulfonyl)benzamide (2r) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**



***N*-(phenylsulfonyl)benzamide (2s) ^{1}H NMR** (600 MHz, $CDCl_3$)**:**

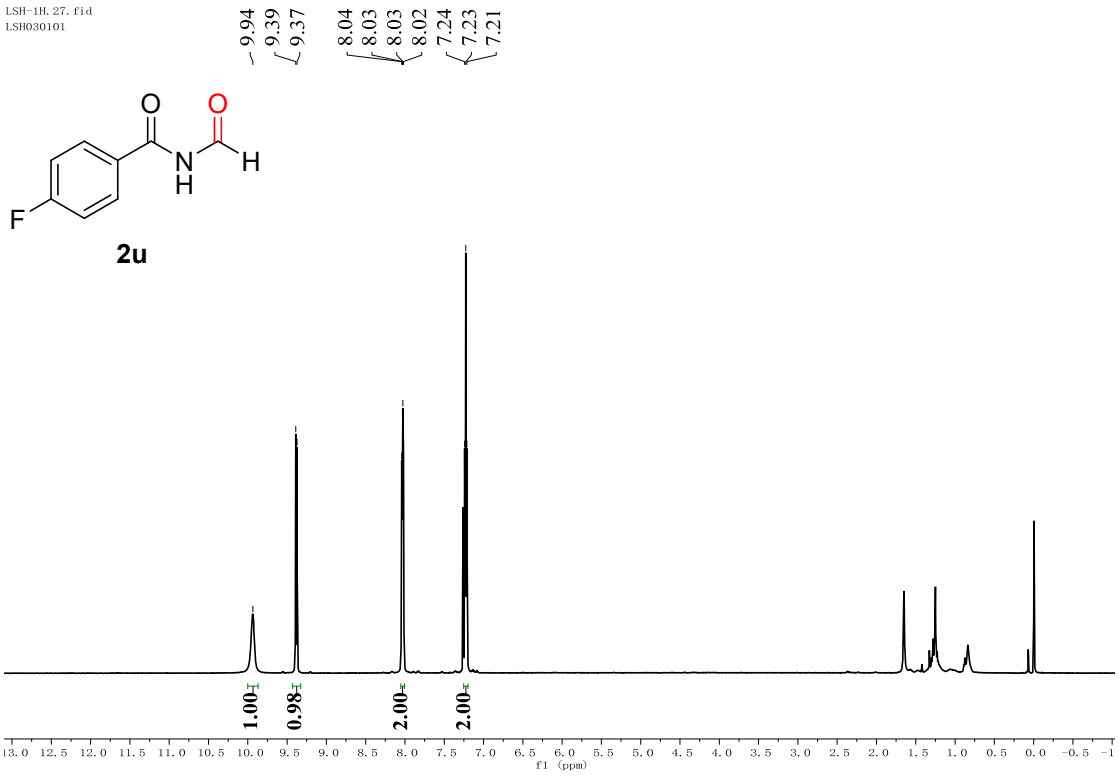


_N_-formylbenzamide (2t) ^{1}H NMR (600 MHz, $CDCl_3$)**:**



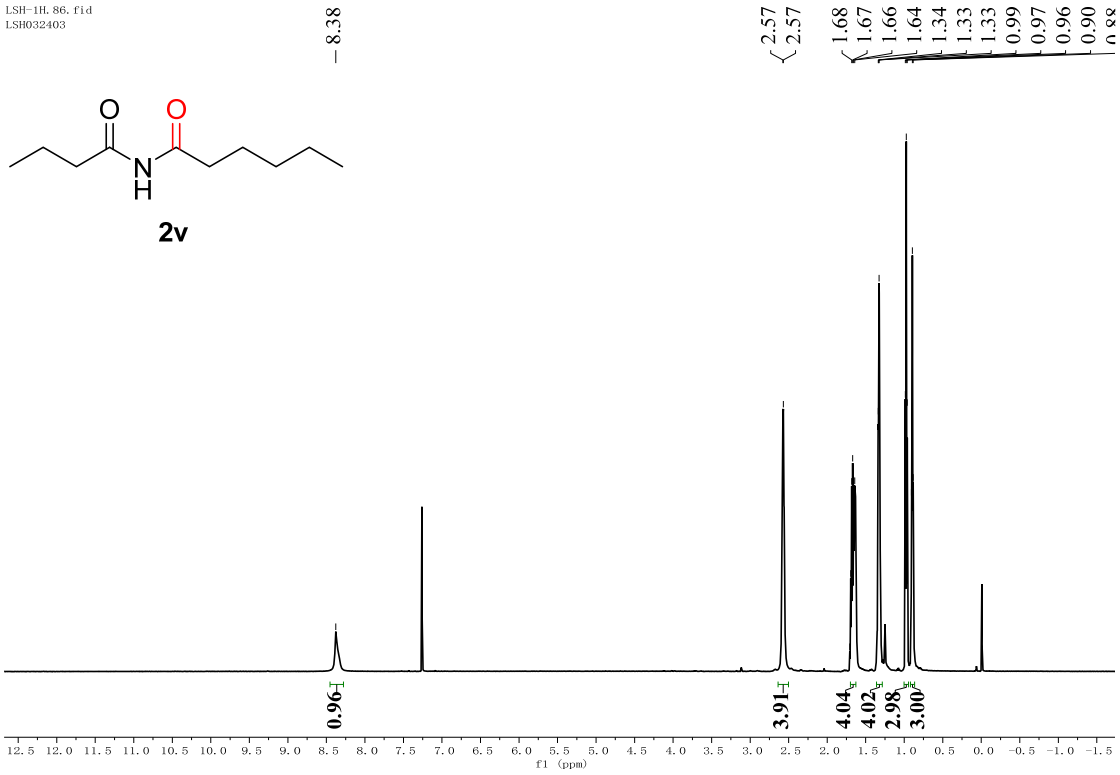
2t

4-fluoro-_N_-formylbenzamide (2u) ^{1}H NMR (600 MHz, $CDCl_3$)**:**



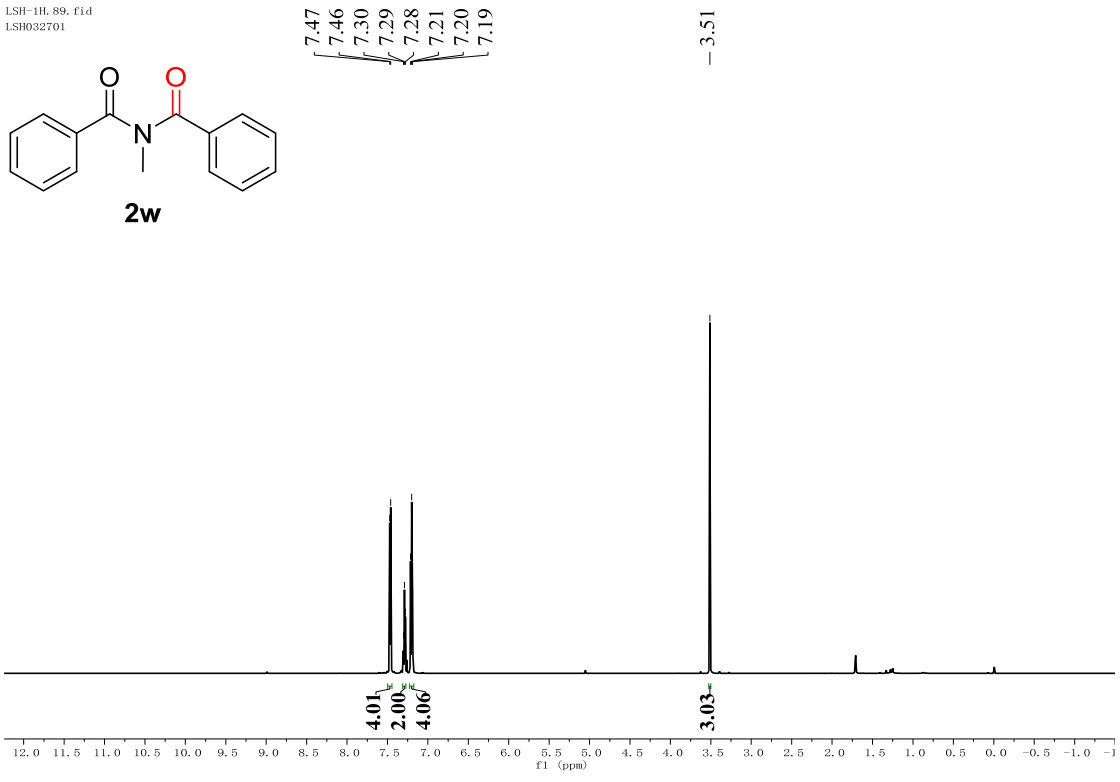
2u

_N_-butyrylhexanamide (2v) ^{1}H NMR (600 MHz, $CDCl_3$)**:**



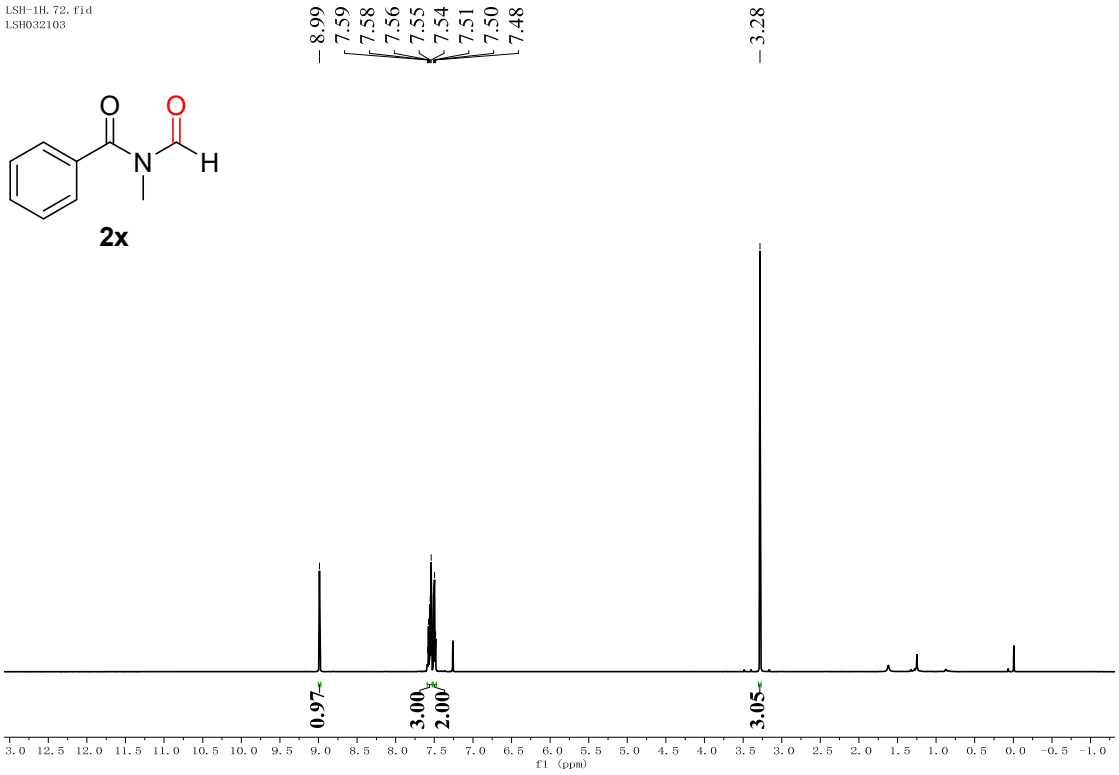
2v

_N_-benzoyl-_N_-methylbenzamide (2w) ^{1}H NMR (600 MHz, $CDCl_3$)**:**

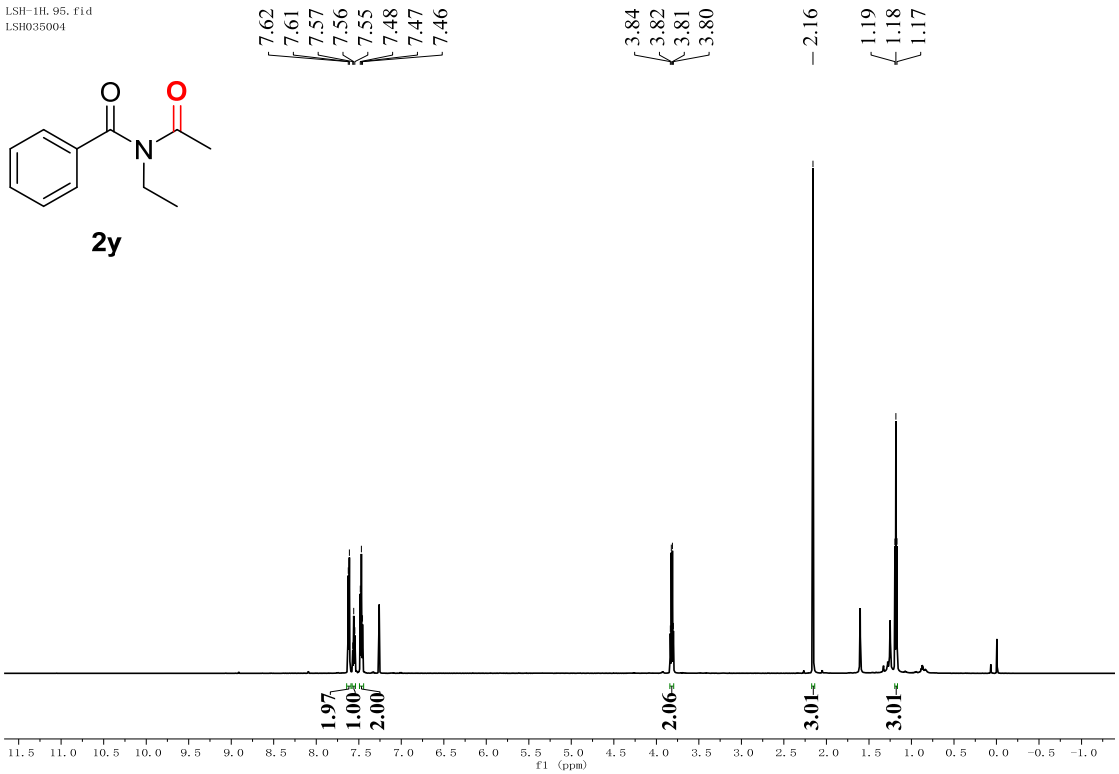


2w

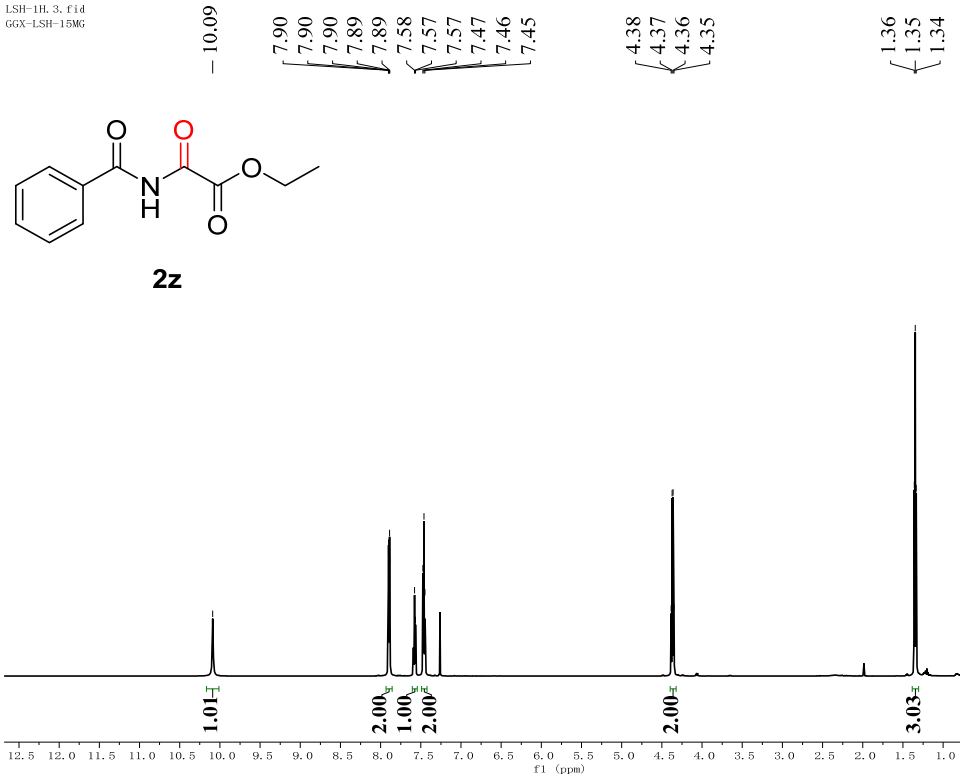
_N_-formyl-_N_-methylbenzamide (2x) ^{1}H NMR (600 MHz, $CDCl_3$)**:**



_N_-acetyl-_N_-ethylbenzamide (2y) ^{1}H NMR (600 MHz, $CDCl_3$)**:**

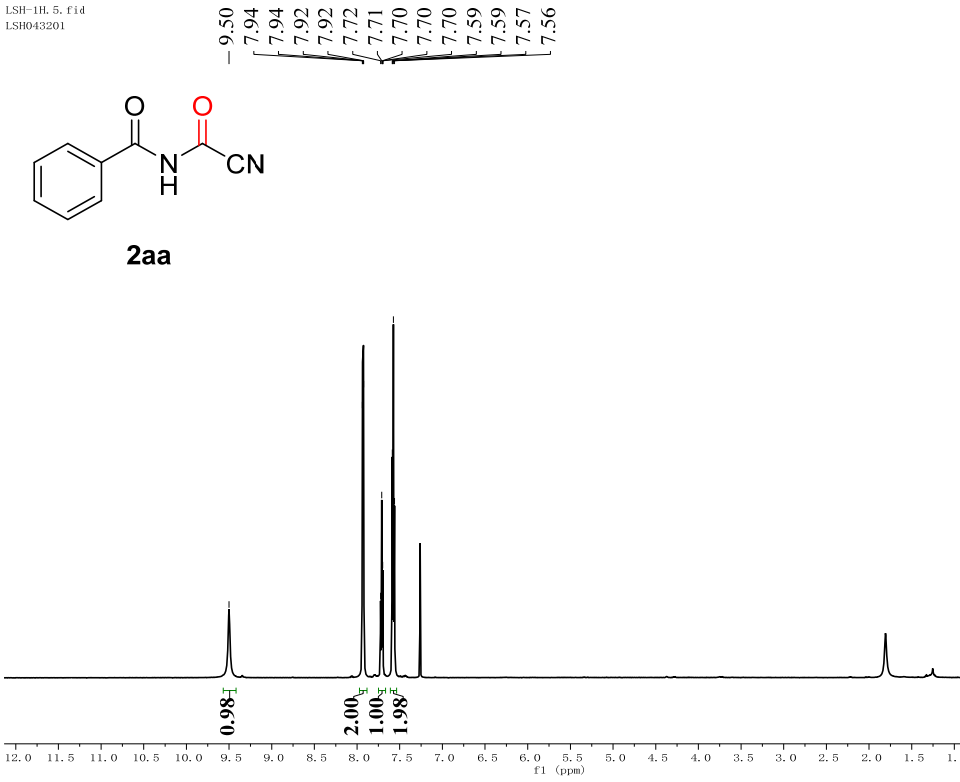


ethyl 2-benzamido-2-oxoacetate (2z) ^{1}H NMR (600 MHz, $CDCl_3$):



2z

benzoylcarbamoyl cyanide (2aa) ^{1}H NMR (600 MHz, $CDCl_3$):



2aa