Supporting Information

An efficient approach for enhancing the catalytic activity of Ni-MOF-74 via a relay catalyst system for the selective oxidation of benzylic C–H bond under mild conditions

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1.General Information

1.1. Materials and Reagents

Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2$ $6H_2O$), 2,5-dihydroxyterephthalic acid (H_4dhtp), *N,N*-dimethylformamide (DMF), Ethanol (EtOH), diphenylmethane, 3-dihydro-1*H*-indene, ethyl benzene and its derivatives, toluene and its derivatives were purchased from Adamas-beta and Sigma-Aldrich. All chemicals were used without further purification.

1.2. Materials Characterization

XRD:

The product was characterized by XRD using a Rigaku D/max-ga X-ray diffractometer at a scan rate of 6 $^\circ$min^{-1} in 2 θ ranging from 5 $^\circ$ to 40 $^\circ$ with Cu Kα radiation (λ = 1.54178 Å).

SEM:

Scanning electron microscopy (SEM) was conducted on a Hitachi S-8010 with an accelerating voltage of 100 kV.

IR:

FT-IR spectra were obtained with a Bruker EQUINOX-55 spectrophotometer within the wavenumber interval of 400-4000 cm^{-1}.

Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-50 thermal analyzer from room temperature to 800 $^{\circ}$C at a heating rate of 10 $^{\circ}$C min^{-1} under an air atmosphere.

Gas chromatographic:

Gas chromatographic (GC) analyses were performed using a Shi-madzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis held samples at 100 $^{\circ}$C for 1 min, heated them from 100 to 280 $^{\circ}$C at 20 $^{\circ}$C /min, and held them at 280 $^{\circ}$C for 5 min. Inlet and detector temperatures were set constant at 280 $^{\circ}$C.

GC–MS:

GC–MS analyses were performed using a Shimadzu GCMS-QP2010 Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 µm). The temperature program for GC–MS analysis held samples at 100 ^{o}C for 1 min, heated samples from 100 to 250 ^{o}C at 20 ^{o}C /min and held them at 250 ^{o}C for 5 min. Inlet temperature was set constant at 250 ^{o}C. MS spectra were compared with the spectra gathered in the NIST library.
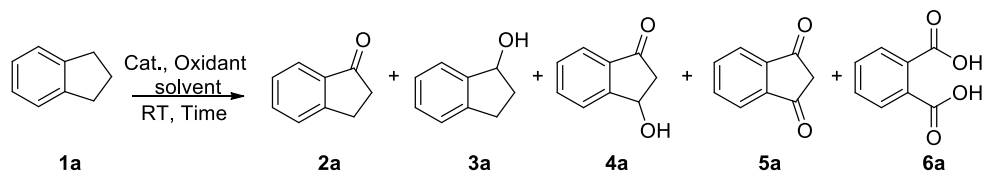
NMR spectrum:

^{1}H NMR spectra were collected on 400 MHz NMR spectrometers (Varian Inova-400) using CDCl$_3$ or DMSO-*d6*. Chemical shifts are reported in parts per million (ppm). Chemical shifts for protons are reported in parts per million downfield and are referenced to residual protium in the NMR solvent (CHCl$_3$ = δ 7.26). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

Chromatography:

Column chromatography was performed with silica gel (200-300 mesh ASTM).

2. Optimization of Reaction Conditions

Table S1 Optimization of reaction conditions.[a]

Entry	Catalyst	IL	Con. (%)	Yield (%)[b]				
				2a	3a	4a	5a	6a
1	—	[bmim]Br	31	24	6	nd[c]	nd	1
2	Ni-MOF-74	—	2	2	nd	nd	nd	nd
3	Ni-MOF-74	[bmim]Br	96	87	3	3	2	1
4	Co-MOF-74	—	54	32	10	1	1	nd
5	Co-MOF-74	[bmim]Br	92	75	9	2	3	3
6	Mn-MOF-74	—	80	61	14	1	2	2
7	Mn-MOF-74	[bmim]Br	94	85	4	3	1	1
8	Mg-MOF-74	—	1	1	nd	nd	nd	nd
9	Mg-MOF-74	[bmim]Br	74	65	9	nd	nd	nd
10	Zn-MOF-74	—	2	2	nd	nd	nd	nd
11	Zn-MOF-74	[bmim]Br	59	50	8	1	nd	nd
12	$Ni(NO_3)_2.6H_2O$	—	28	22	6	nd	nd	nd
13	$Ni(NO_3)_2.6H_2O$	[bmim]Br	95	90	1	1	2	1
14	$Ni(Ac)_2.4H_2O$	—	10	9	1	nd	nd	nd
15	$Ni(Ac)_2.4H_2O$	[bmim]Br	95	85	4	2	3	1
16	$NiCl_2.6H_2O$	—	21	17	4	nd	nd	nd
17	$Ni Cl_2.6H_2O$	[bmim]Br	81	70	7	1	1	2
18	Ni-MOF-74	[bbim]Br	82	73	6	1	2	nd
19	Ni-MOF-74	[emim]Br	91	80	5	2	3	1
20	Ni-MOF-74	[beim]Br	83	71	8	1	2	1
21	Ni-MOF-74	[bmim]Cl	4	4	nd	nd	nd	nd
22	Ni-MOF-74	[bmim]I	3	3	nd	nd	nd	nd
23	Ni-MOF-74	$[bmim]BF_4$	56	42	13	nd	nd	1
24	Ni-MOF-74	$[bmim]PF_6$	8	6	1	nd	1	nd

[a] Conditions: **1a** (0.2 mmol), cat. (5 mg), IL (50 μL), TBHP (0.8 mmol), room temperature, 12 h. [b] Conversion and yield are determined by GC. [c] nd = No detected.
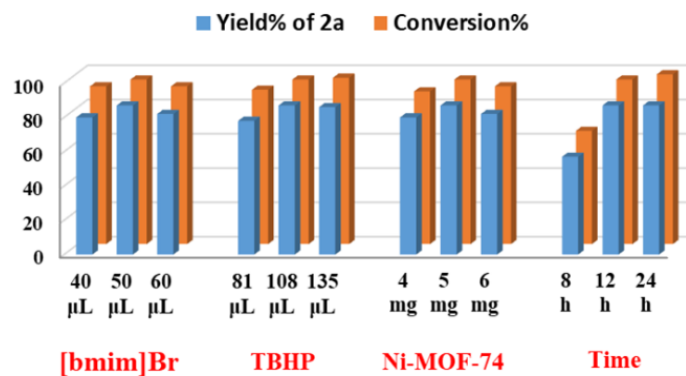
Fig. S1 Effect of the dosage of ILs, oxidant, catalyst and reaction time on the reaction.

3. Control Experiments

Table S2 Control experiments.

(a)

Entry	Oxidant	Atmosphere	Additive	Yield/%[a]
1	TBHP	N_2	-	92
2	Anhydrous TBHP	air	-	88
3	TBHP	air	TEMPO (4 equiv.)	Trace
4	TBHP	air	BHT (4 equiv.)	Trace
5	TBHP	air	DPE (4 equiv.)	36
6	t-BuOOt-Bu	air	-	Trace
7	CumOOCum	air	-	Trace
8	BPO	air	-	Trace
9	CumOOH	air	-	49
10[b]	TBHP	air	KBr (1 equiv.)	47

[a] Yield was determined by GC. [b] Without [bmim]Br.

(b)

(c)

(d)

4. Experimental section

4.1 Preparation of Ni-MOF-74

Ni-MOF-74 was synthesized according to the procedure reported by Matzger and co-workers.[1] In a typical procrdure, a solid mixture of H_4dhtp (0.48 g, 2.41 mmol) and $Ni(NO_3)_2$ $6H_2O$ (2.38 g, 8.18 mmol) was added to a 1:1:1 (v/v/v) mixture of DMF/EtOH/H_2O (50 mL) in a 100 mL screw cap jar. The suspension was mixed and stirred at room temperature until homogeneous. The reaction solution was then transferred to a 100 mL Teflon-sealed and placed in an oven at 100 °C for 24 h. After the reaction reached completion, the solid was isolated by centrifugation and washed with DMF three times, and then two more times with 20 mL of methanol. The solid product was kept immersed in methanol for 6 days, fresh solvent was added three times after solid decanting during this period. Methanol was finally removed under high vacuum at 150 °C, yielding the Ni-MOF-74 with headings as appropriate.

4.2 Catalytic studies

The catalytic oxidation was carried out in a glass tube equipped with a magnetic stirrer. In a typical reaction, the mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and benzyl hydrocarbons substrates (0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1 to ethyl acetate) to afford the desired product ketones or carboxylic acids. The product identity was further confirmed by ^{1}H NMR and GC–MS.

4.3 The Synthetic Procedure and Data for Products
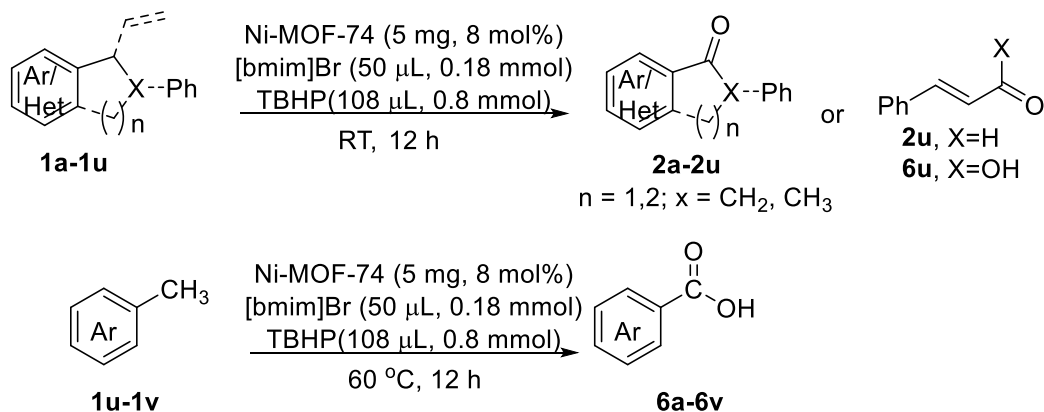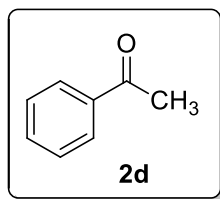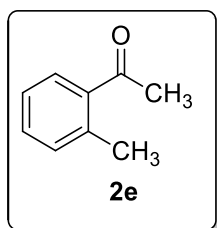

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and benzyl aromatic hydrocarbons substrates (0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1 to ethyl acetate) to afford the desired product ketones or carboxylic acids.

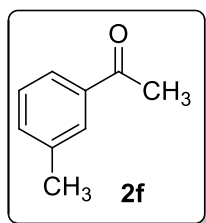A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 2,3-dihydro-1*H*-indene (23.6 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product 2,3-dihydro-*1H*-inden-1-one (**2a**), 84% isolated yield, colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.59-7.57 (m, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39-7.36 (m, 1H), 3.17-3.14 (m, 2H),
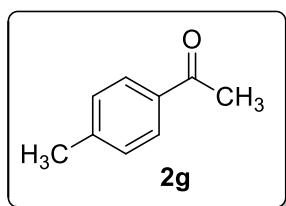
2.71-2.68 (m, 2H). MS: 132.
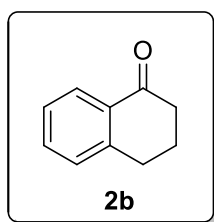
2b

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 µL, 0.8 mmol), [bmim]Br (50 µL, 0.18 mmol) and 1,2,3,4-tetrahydronaphthalene (26.4 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 50:1) to afford the desired product 3,4-dihydronaphthalen-1(2*H*)-one (**2b**), 75% isolated yield, colorless oil. ^{1}H NMR δ 8.04 (dd, *J*=8.0, 4.0 Hz, 1H), 7.47-7.45 (m, 1H), 7.33-7.24 (m, 2H), 2.97 (t, J=8 Hz, 2H), 2.66 (t, J=8 Hz, 2H), 2.18-2.11 (m, 2H). MS: 146.
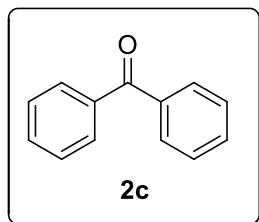
2c
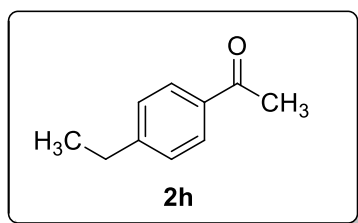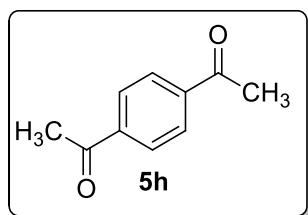
A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 µL, 0.8 mmol), [bmim]Br (50 µL, 0.18 mmol) and diphenylmethane (33.6 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product benzophenone (**2c**), 95% isolated yield, colorless oil. ^{1}H NMR δ 7.81-7.79 (m, 4H), 7.60-7.55 (m, 2H), 7.49-7.45 (m, 4H). MS: 182.

2d

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and ethylbenzene (21.2 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (hexane/ethyl acetate 100:1) to afford the desired product acetophenone (**2d**), 88% isolated yield, colorless oil. ^{1}H NMR (400 MHz, CDCl3) δ 7.97-7.95 (m, 2H), 7.58-7.51 (m, 1H), 7.48-7.44 (m, 2H), 2.61 (s, 3H). MS: 120.
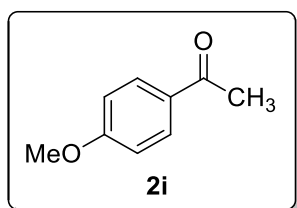

2e

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1-ethyl-2-methylbenzene (24.0 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (hexane/ethyl acetate 100:1) to afford the desired product 1-(*o*-tolyl)ethanone (**2e**), 85% isolated yield, colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.71 (dd, J = 8.0, 4.0 Hz, 1H), 7.43-7.37 (m, 1H), 7.29-7.27 (m, 1H), 7.25-7.24 (m, 1H), 2.99 (s, 3H), 2.54 (s, 3H). MS: 134.

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1-ethyl-3-methylbenzene (24.0 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (hexane/ethyl acetate 100:1) to afford the desired product 1-(*m*-tolyl)ethanone (**2f**), 86% isolated yield, colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74-7.71 (m, 2H), 7.37-7.34 (m, 2H), 2.59 (s, 3H), 2.41 (s, 3H). MS: 134.
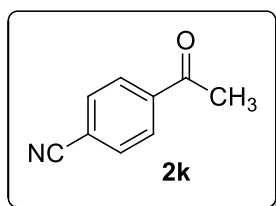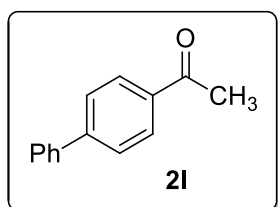

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1-ethyl-4-methylbenzene (24.0 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (hexane/ethyl acetate 100:1) to afford the desired product 1-(*p*-tolyl)ethanone (**2g**), 92% isolated yield, colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, *J*=8.0 Hz, 2H), 7.27-7.25 (m, 2H), 2.58 (s, 3H), 2.41 (s, 3H). MS: 134.
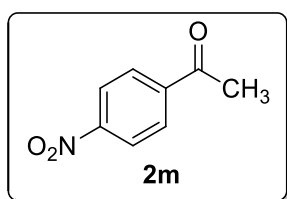
2h

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1,4-diethylbenzene (26.8 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (hexane/ethyl acetate 100:1) to afford the desired product 1-(4-ethylphenyl)ethanone (**2h**), 44% isolated yield, colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.71 (q, *J* = 8.0 Hz, 2H), 2.58 (s, 3H), 1.26 (t, *J* = 8.0 Hz, 3H). MS: 148.

5h

Byproduct 1,1'-(1,4-phenylene)diethanone (**5h**) was isolated by flash column chromatography (petroleum ether/ethyl acetate 20:1) with 22% isolated yield, white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03 (s, 4H), 2.65 (s, 6H). MS: 162.
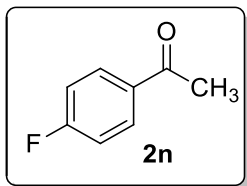

2i

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1-ethyl-4-methoxybenzene (27.2 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate

mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 50:1) to afford the desired product 1-(4-methoxyphenyl)ethanone (2i), 87% isolated yield, colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 2.56 (s, 3H). MS: 150.
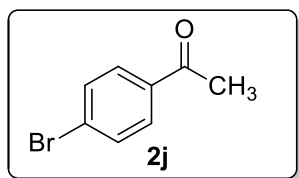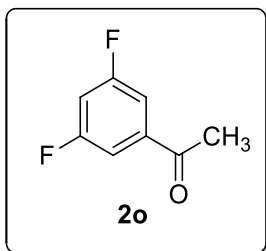

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1-bromo-4-ethylbenzene (37.0 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product 1-(4-bromophenyl)ethanone (2j), 75% isolated yield, colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8. 0 Hz, 2H), 2.59 (s, 3H). MS: 199.
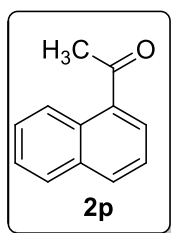

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 4-ethylbenzonitrile (26.2 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at 60 °C. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and

purified by flash column chromatography (petroleum ether/ethyl acetate 20:1) to afford the desired product 4-acetylbenzonitrile (**2k**), 70% isolated yield, white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 2.65 (s, 3H). MS: 145.
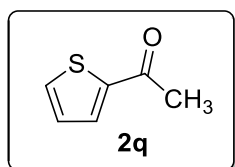

2l

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 4-ethyl-1,1'-biphenyl (36.4 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 50:1) to afford the desired product 1-([1,1'-biphenyl]-4-yl)ethanone (**2l**), 80% isolated yield, white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05-8.02 (m, 2H), 7.71-7.68 (m, 2H), 7.65-7.62 (m, 2H), 7.50-7.46 (m, 2H), 7.43-7.40 (m, 1H), 2.64 (s, 3H). MS: 196.
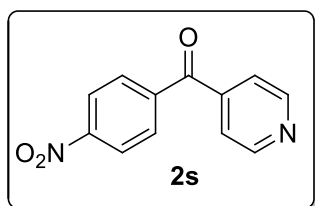

2m

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1-ethyl-4-nitrobenzene (30.2 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl

acetate 20:1) to afford the desired product 1-(4-nitrophenyl)ethanone (**2m**), 62% isolated yield, white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.32 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 8.0 Hz, 2H), 2.68 (s, 2H). MS: 165.
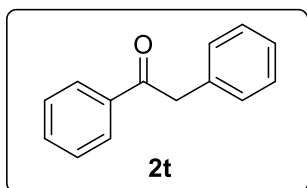

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1-ethyl-4-fluorobenzene (24.8 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. Isolated yield was difficult to obtain due to the low boiling point of the product 1-(4-fluorophenyl)ethanone (77-78 $^{\text{o}}$C). After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was analyzed using a GC-FID to get the GC yield. The product identity was further confirmed by GC-MS. 1-(4-fluorophenyl)ethanone (**2n**), 60% GC yield. MS: 138.
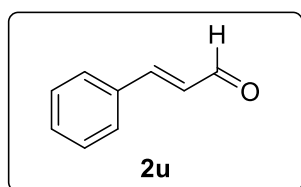

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1-ethyl-3,5-difluorobenzene (24.8 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (hexane/ethyl acetate 100:1) to afford the desired product 1-(3,5-difluorophenyl)ethanone (**2o**), colorless oil. The purification of the product is

difficult due to its low boiling point (94 °C), 90% yield (determined by GC), ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51-45 (m, 2H), 7.03-7.02 (m, 1H), 2.59 (s, 3H). MS: 156.

2p
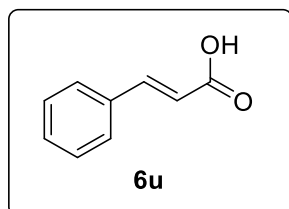
A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1-ethylnaphthalene (31.2 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product 1-(naphthalen-1-yl)ethanone (**2p**), 80% isolated yield, white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.75 (dd, *J* = 8.0, 0.8 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.89-7.87 (m, 1H), 7.63-7.59 (m, 1H), 7.56-7.49 (m, 2H), 2.76 (s, 3H). MS: 170.
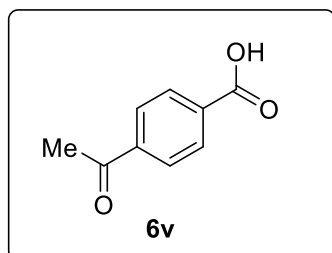

2q

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 2-ethylthiophene (22.4 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (hexane/ethyl acetate 100:1) to afford the desired product 1-(thiophen-2-yl)ethanone (**2q**), 95% isolated yield, colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.64 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.13 (dd, *J* = 4.9, 3.8 Hz, 1H), 2.57 (s, 3H). MS: 126.
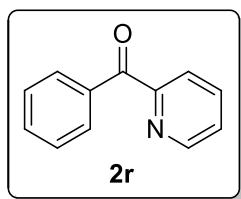
2r

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 µL, 0.8 mmol), [bmim]Br (50 µL, 0.18 mmol) and 2-benzylpyridine (33.8 mg, 0.2 mmol) were added into the tube, and stirred at 60 °C for 12 h. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 20:1) to afford the desired product phenyl(pyridin-2-yl)methanone (**2r**), 74% isolated yield, white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.72 (d, *J* = 4.0 Hz, 1H), 8.08-8.02 (m, 3H), 7.89 (td, *J* = 8.0, 2.0 Hz, 1H), 7.61-7.56 (m, 1H), 7.50-7.46 (m, 3H). MS: 183.

2s

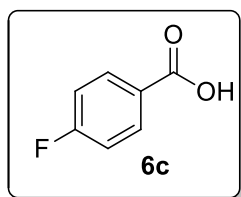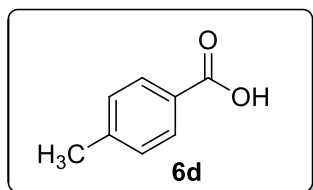A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 µL, 0.8 mmol), [bmim]Br (50 µL, 0.18 mmol) and 4-(4-nitrobenzyl)pyridine (42.8 mg, 0.2 mmol) were added into the tube, and stirred at 60 °C for 12 h. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 2:1) to afford the desired product (4-nitrophenyl)(pyridin-4-yl)methanone (**2s**), 83% isolated yield, white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.85 (d, *J* = 5.0 Hz, 2H), 8.36-8.32 (m, 2H), 7.97-7.94 (m, 2H), 7.58 (dd, *J* = 4.0, 1.5 Hz, 2H). MS: 228.
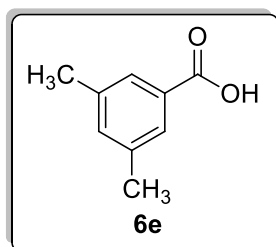

2t

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1,2-diphenylethane (36.4 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 50:1) to afford the desired product 1,2-diphenylethan-1-one (**2t**), 90% isolated yield, white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03-7.97 (m, 3H), 7.56-7.52 (m, 2H), 7.48-7.46 (m, 2H), 7.33-7.28 (m, 3H), 4.29 (s, 2H). MS: 196.

2u

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and allylbenzene (23.6 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 50:1) to afford the desired product cinnamaldehyde (**2u**), 60% isolated yield, colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.72 (d, J = 8.0, 1H), 7.59-7.57 (m, 2H), 9.49 (d, J = 16.0, 1H), 7.45-7.44 (m, 3H), 6.73 (q, J = 8.0, 1H). MS: 132.

6u

Byproduct 1,1'-(1,4-phenylene)diethanone (**6u**) was isolated by flash column chromatography (petroleum ether/ethyl acetate 1:1) with 23% isolated yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 7.96-7.93 (m, 1H), 7.69-7.67

17

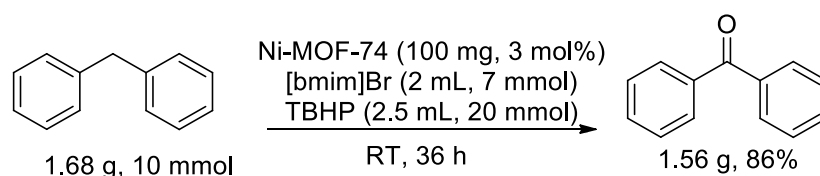(m, 1H), 7.59 (d, J = 16.0, 1H), 7.52-7.46 (m, 1H), 7.43-7.41 (m, 2H), 6.52 (d, J = 16.0, 1H). MS: 148.

6v

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 4-ethylbenzaldehyde (26.8 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (ethyl acetate) to afford the desired product 4-acetylbenzoic acid (**2u**), 58% isolated yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.30 (s, 1H), 8.04 (s, 4H), 2.61 (s, 3H). MS: 164.
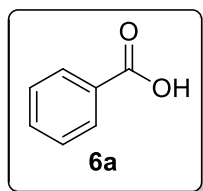
6a

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and toluene (18.4 mg, 0.2 mmol) were added into the tube, and stirred at 60 °C for 12 h. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (ethyl acetate) to afford the desired product benzoic acid (**6a**). 76% isolated yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.95 (s, 1H), 7.97-7.94 (m, 2H), 7.64-7.59 (m, 1H), 7.527.47 (m, 2H). MS: 122.
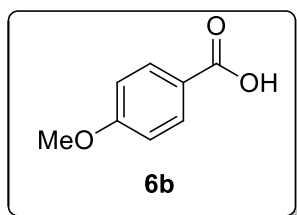
6b

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1-methoxy-4-methylbenzene (24.4 mg, 0.2 mmol) were added into the tube, and stirred at 60 ^{o}C for 12 h. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (ethyl acetate) to afford the desired product 4-methoxybenzoic acid (**6b**). 56% isolated yield, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.61 (s, 1H), 7.90-7.88 (m, 2H), 7.03-7.00 (m, 2H), 3.82 (s, 3H). MS: 152.

6c

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and 1-f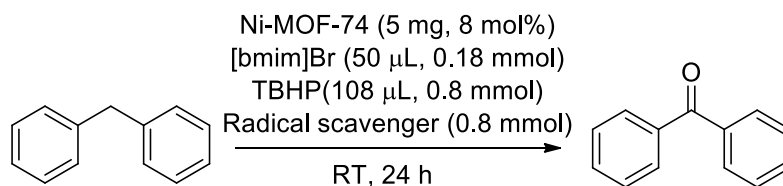luoro-4-methylbenzene (22.0 mg, 0.2 mmol) were added into the tube, and stirred at 60 ^{o}C for 12 h. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (ethyl acetate) to afford the desired product 4-fluorobenzoic acid (**6c**). 60% isolated yield, white solid.^{1}H NMR (400 MHz, DMSO-d_6) δ 13.03 (s, 1H), 8.00 (dd, *J* = 8.0, 5.7 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H). MS: 140.

6d

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and *p*-xylene (21.2 mg, 0.2 mmol) were added into the tube, and stirred at 60 °C for 12 h. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (ethyl acetate) to afford the desired product 4-methylbenzoic acid (**6d**). 62% isolated yield, white solid. ^{1}H NMR (400 MHz, DMSO) δ 12.75 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H). MS: 136.


6e

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and mesitylene (24.0 mg, 0.2 mmol) were added into the tube, and stirred at 60 °C for 12 h. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (ethyl acetate) to afford the desired product 3,5-dimethylbenzoic acid (**6e**). 70% isolated yield, white solid. ^{1}H NMR (400 MHz, DMSO) δ 12.73 (s, 1H), 7.56 (dd, *J* = 1.0, 0.6 Hz, 2H), 7.24 (t, *J* = 0.6 Hz, 1H), 2.32 (s, 6H). MS: 150.

4.4 Gram Scale Experiments

Gram Scale for Synthesis of Benzophenone

Ni-MOF-74 (100 mg, 3 mol%)
[bmim]Br (2 mL, 7 mmol)
TBHP (2.5 mL, 20 mmol)
RT, 36 h

1.68 g, 10 mmol

1.56 g, 86%

A mixture of Ni-MOF-74 (100 mg, 3 mol%), *tert*-butyl hydroperoxide 70% in water

(2.5 mL, 20 mmol), [bmim]Br (2 mL, 7 mmol) and diphenylmethane (1.68 g, 10 mmol) were added into a 25 mL flask, and stirred for 36 h at room temperature. After the reaction reached completion, 10 mL water was added to reaction mixture, extracted with ethyl acetate (10 mL×3) and then the solid catalyst was filtered. The filtrate mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product benzophenone (**2c**), 86% isolated yield, colorless oil.
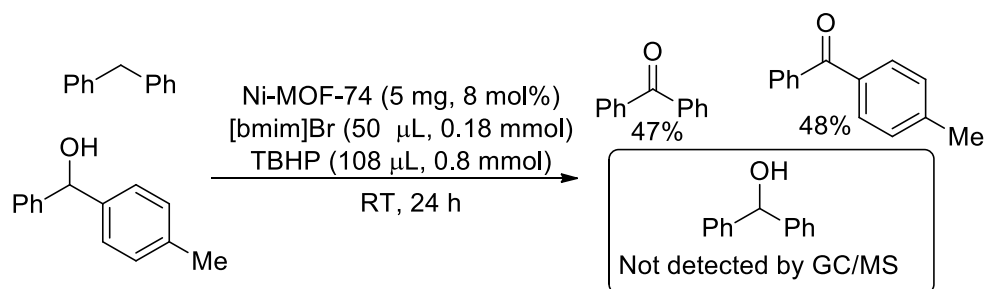
4.5 Recycling Experiment
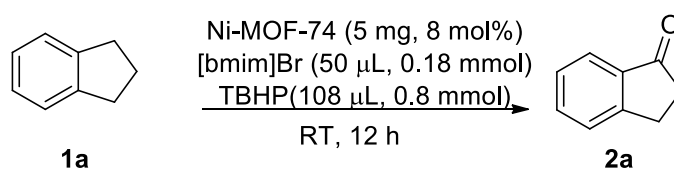
A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 µL, 0.8 mmol), [bmim]Br (50 µL, 0.18 mmol) and 2,3-dihydro-1*H*-indene (23.6 mg, 0.2 mmol) were added into the tube, and stirred for 12 h at room temperature. After the reaction reached completion, the mixture was extracted three times by ethyl acetate (5 mL×3), and then the remaining viscous aqueous mixture was concentrated and dried in vacuo. The catalyst system was recovered for use in the next run under the same conditions. The combined organic layer was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product **2a** (Table S1).
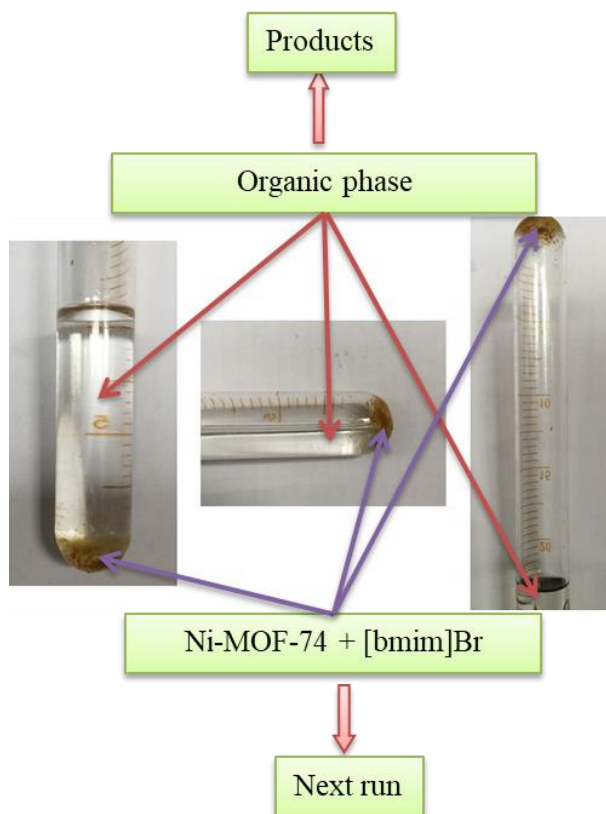
Fig. S2 The reaction mixture after addition ethyl acetate.

Table S3. Recycling Experiments.

Run	1	2	3	4
Yield (%)	87	78	73	72
Conversion (%)	96	88	84	84

4.6 Control Experiments on the Reaction Mechanism

4.6.1 The Influence of O_2 on the Reaction

$$1a \xrightarrow[\substack{N_2, \text{ RT, 12 h}}]{\substack{\text{Ni-MOF-74 (5 mg, 8 mol\%)} \\ \text{[bmim]Br (50 } \mu\text{L, 0.18 mmol)} \\ \text{TBHP(108 } \mu\text{L, 0.8 mmol)}}} 2a$$
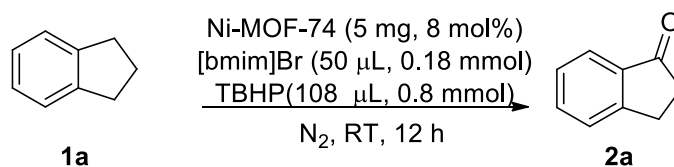
To a Schlenk tube were added Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 µL, 0.8 mmol), [bmim]Br (50 µL, 0.18 mmol) and diphenylmethane (33.6 mg, 0.2 mmol). The reaction tube was flushed with N_2 for 1.5 minutes and then equipped with a N_2 balloon. The system was stirred for 24 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was analyzed using a GC-FID to get the GC yield (92%). The product identity was further confirmed by GC-MS.

4.6.2 The Influence of H$_2$O on the Reaction

Ni-MOF-74 (5 mg, 8 mol%)
[bmim]Br (50 μL, 0.18 mmol)
Anhydrous TBHP (145 μL, 0.8 mmol)
RT, 24 h
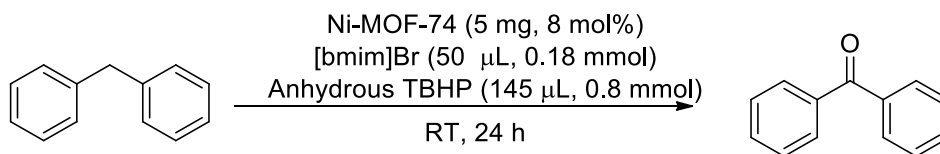
A miture of Ni-MOF-74 (5 mg, 8 mol%), 5.5 M tert-butyl hydroperoxide in decane (145 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and diphenylmethane (33.6 mg, 0.2 mmol) were added into the tube, and stirred for 24 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was analyzed using a GC-FID to get the GC yield (88%). The product identity was further confirmed by GC-MS.

4.6.3 Radical Trapping Experiments

Ni-MOF-74 (5 mg, 8 mol%)
[bmim]Br (50 μL, 0.18 mmol)
TBHP(108 μL, 0.8 mmol)
Radical scavenger (0.8 mmol)
RT, 24 h

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol), radical scavenger (0.8 mmol) and diphenylmethane (33.6 mg, 0.2 mmol) were added into the tube, and stirred for 24 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was analyzed using a GC-FID to get the GC yield.

Table S4. Radical Trapping experiments

Entry	Radical scavenger	Yield
1	2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)	Trace
2	BHT(2,6-di-tertbutyl-4-methylphenol)	Trace
3	DPE (1,1-diphenylethylene)	36

4.6.4 The Influence of Oxidants on the Reaction
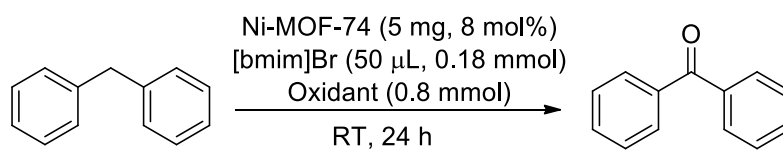
A mixture of Ni-MOF-74 (5 mg, 8 mol%), oxidant (0.8 mmol), [bmim]Br (50 μL, 0.18 mmol) and diphenylmethane (33.6 mg, 0.2 mmol) were added into the tube, and stirred for 24 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was analyzed using a GC-FID to get the GC yield.

Table S5. The Influence of Oxidants on the Reaction.

Entry	Oxidant	Atmosphere	IL	Additive	Yield
1	t-BuOOt-Bu	air	[bmim]Br	-	Trace
2	CumOOCum	air	[bmim]Br	-	Trace
3	BPO	air	[bmim]Br	-	Trace
4	CumOOH	air	[bmim]Br	-	49
5	TBHP	air	-	KBr	47

4.6.5 Phenyl(*p*-tolyl)methanol Oxidation Experiment
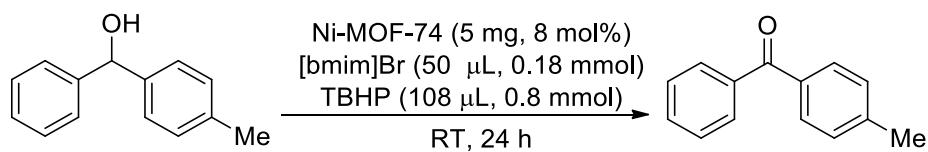
A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol), and phenyl(*p*-tolyl)methanol (39.8 mg, 0.2 mmol) were added into the tube, and stirred for 24 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was analyzed using a GC-FID to get the GC yield (98%), 95% isolated yield was afforded after purified by flash column chromatography (petroleum ether/ethyl acetate 100:1).

4.6.6 (Bromomethylene)dibenzene Oxidation Experiment
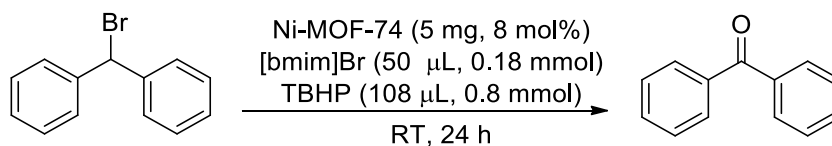
A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol), and (bromomethylene)dibenzene (49.4 mg, 0.2 mmol) were added into the tube, and stirred for 24 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was analyzed using a GC-FID, and no product was detected by TLC or GC-MS analysis.

4.6.7 Competition Experiments

A mixture of Ni-MOF-74 (5 mg, 8 mol%), *tert*-butyl hydroperoxide 70% in water (108 μL, 0.8 mmol), [bmim]Br (50 μL, 0.18 mmol), phenyl(*p*-tolyl)methanol (19.8 mg, 0.1 mmol) and diphenylmethane (16.8 mg, 0.1 mmol) were added into the tube, and stirred for 24 h at room temperature. After the reaction reached completion, the reaction mixture was extracted with ethyl acetate and then the solid catalyst was filtered. The filtrate mixture was analyzed using a GC-MS, no diphenylmethanol intermediate was detected throughout the reaction process.

5. Spectra of SEM, PXRD, TGA and FT-IR of NI-MOF-74
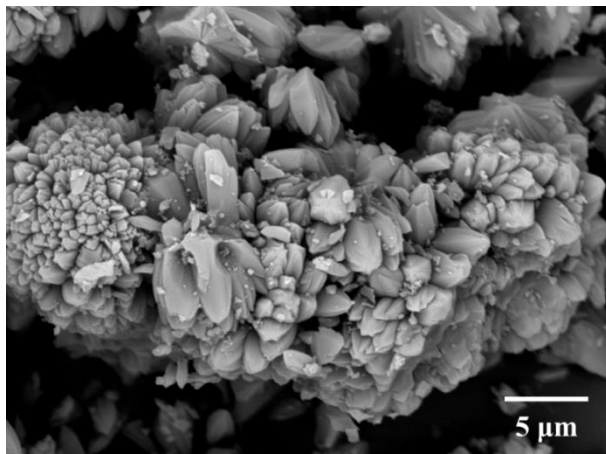
Fig. S3 SEM images of Ni-MOF-74.
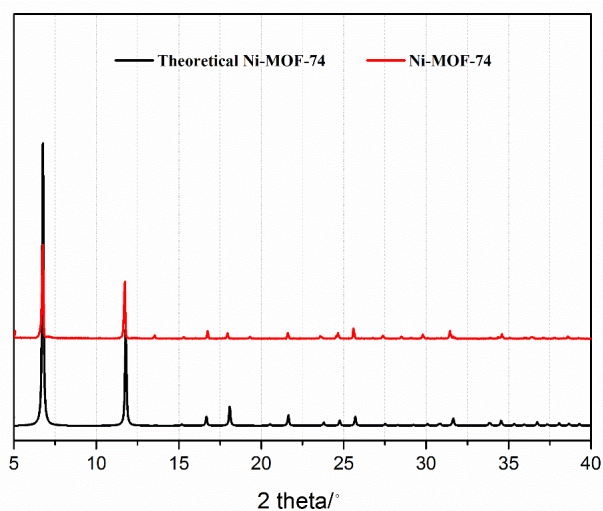
Fig. S4 PXRD images of theoretical simulation and synthesis of Ni-MOF-74.
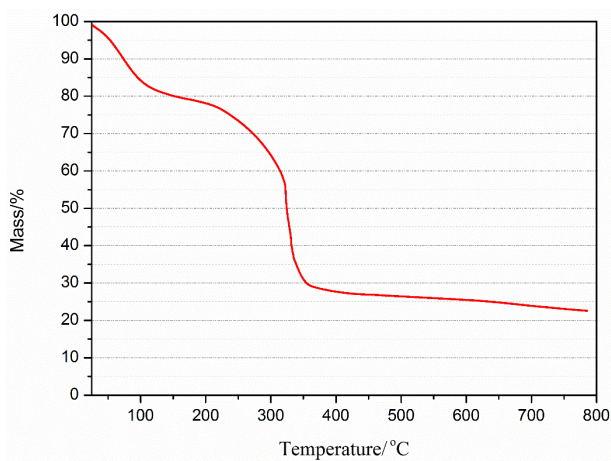
Fig. S5 The TGA images of Ni-MOF-74.
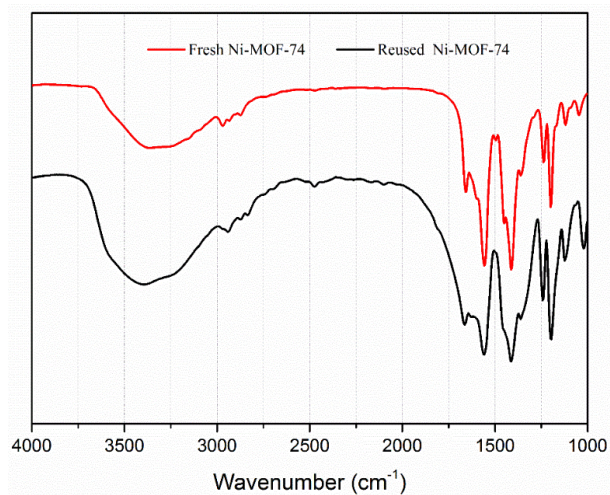
Fig. S6 FT-IR spectra of the fresh and reused Ni-MOF-74.
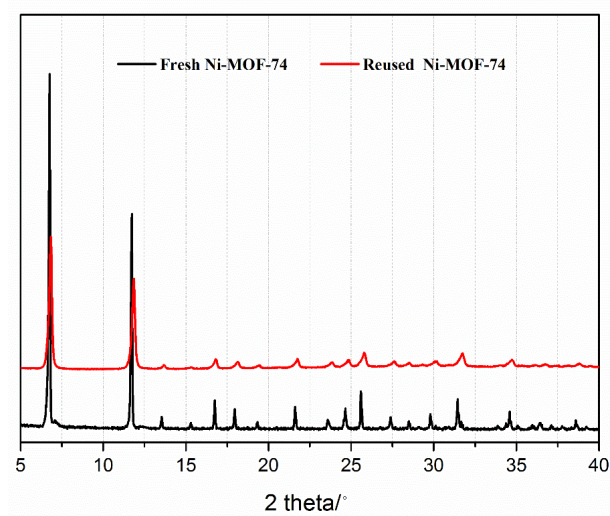
Fig. S7 PXRD of the fresh and reused Ni-MOF-74.

6. Copies of ^{1}H NMR and MS

^{1}H NMR spectra of compound **2a**
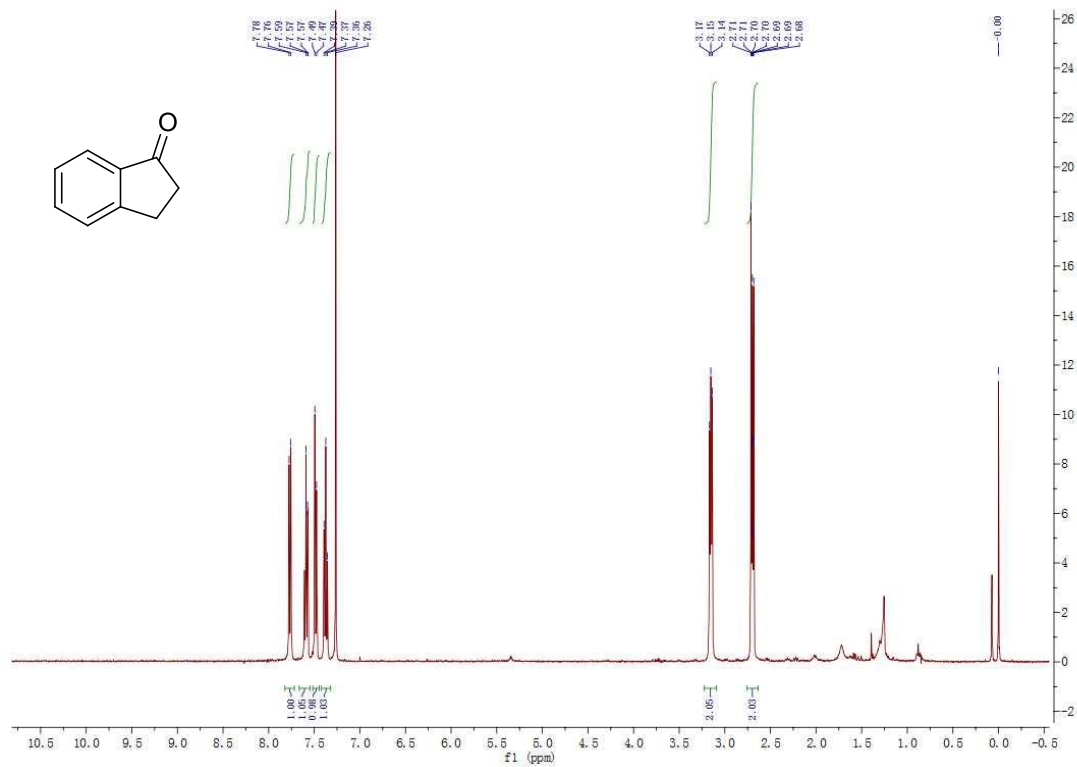
^{1}H NMR spectra of compound **2b**
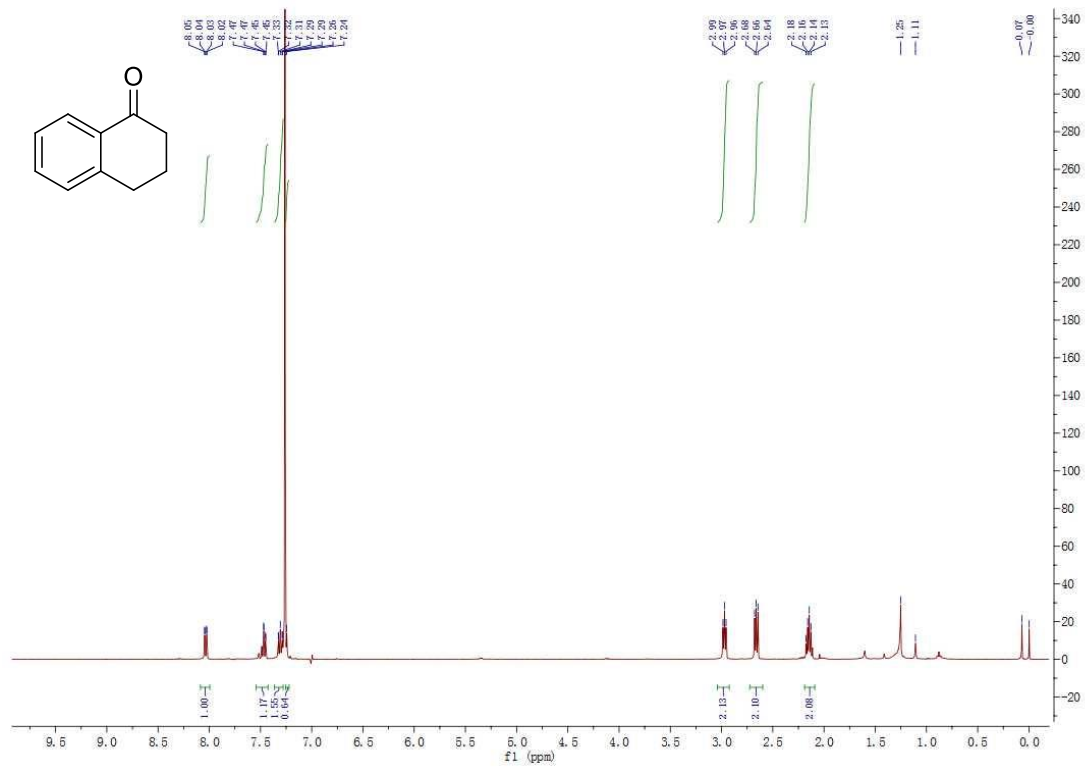
¹H NMR spectra of compound **2c**
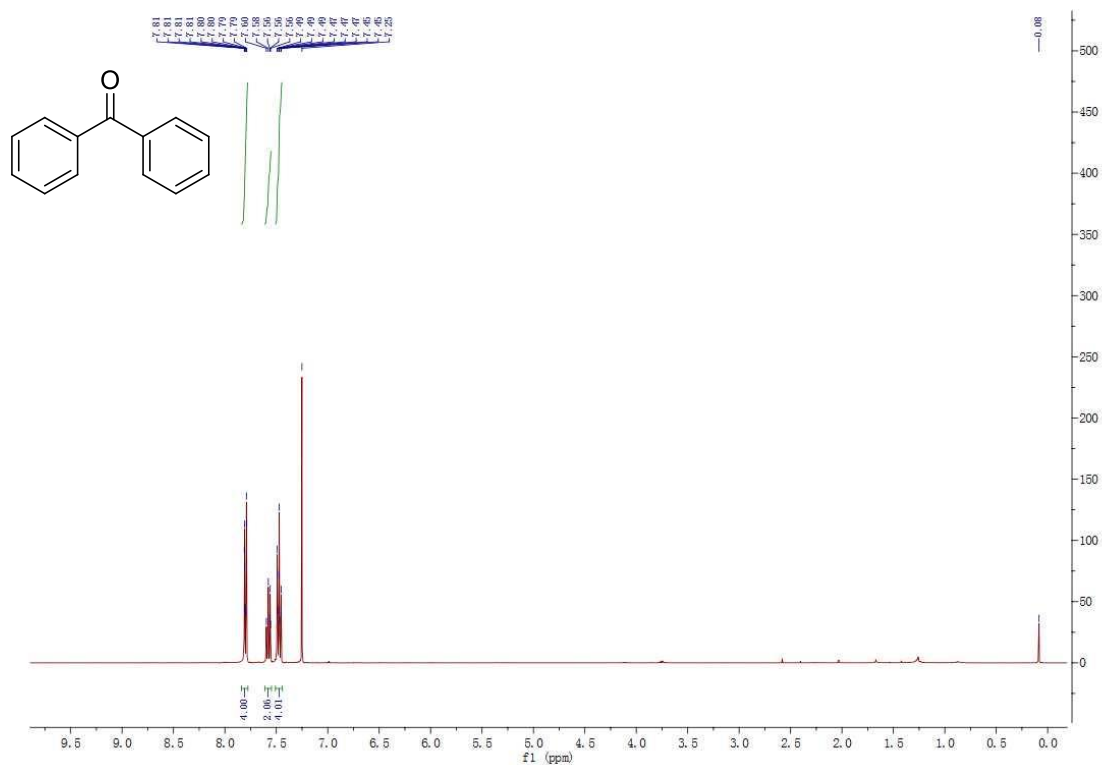
¹H NMR spectra of compound **2d**

^{1}H NMR spectra of compound **2e**

^{1}H NMR spectra of compound **2f**
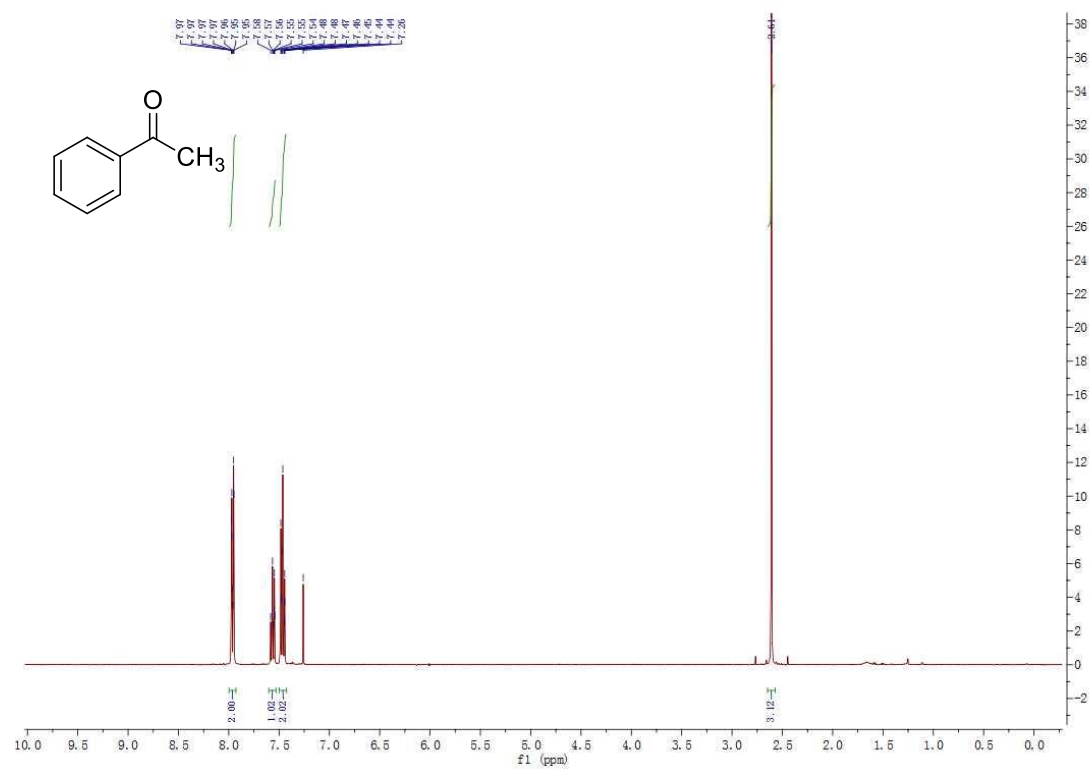
^{1}H NMR spectra of compound **2g**
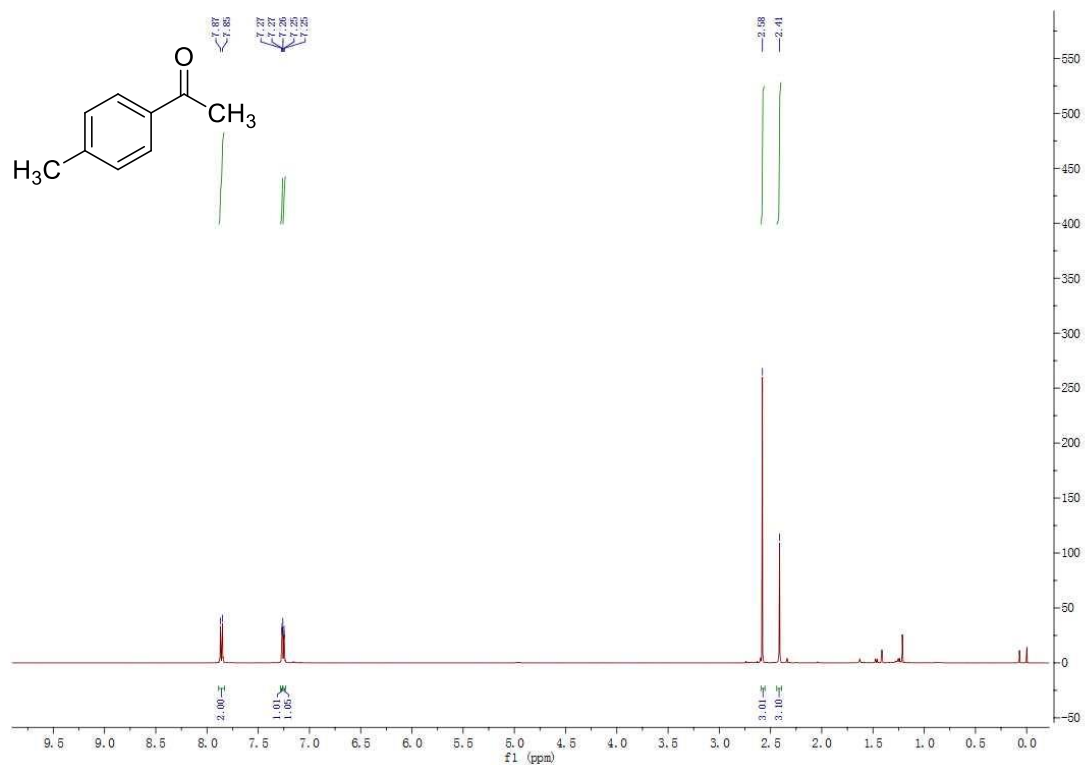
^{1}H NMR spectra of compound **2h**
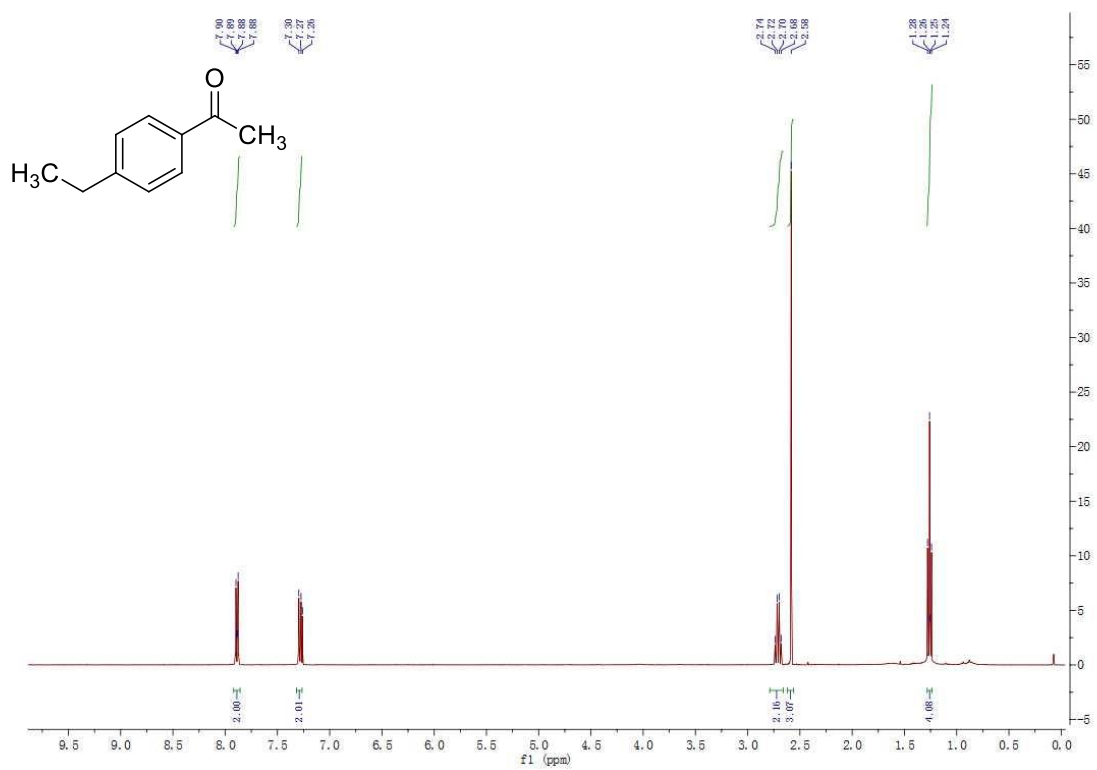
^{1}H NMR spectra of compound **5h**
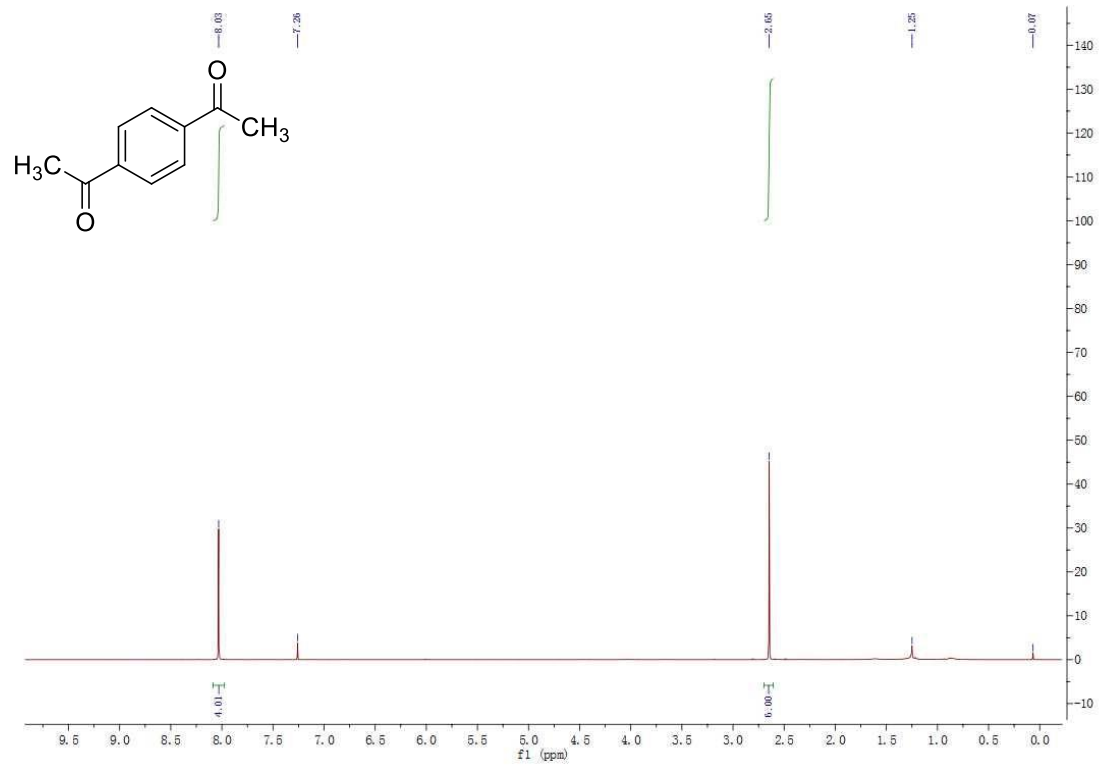
^{1}H NMR spectra of compound **2i**
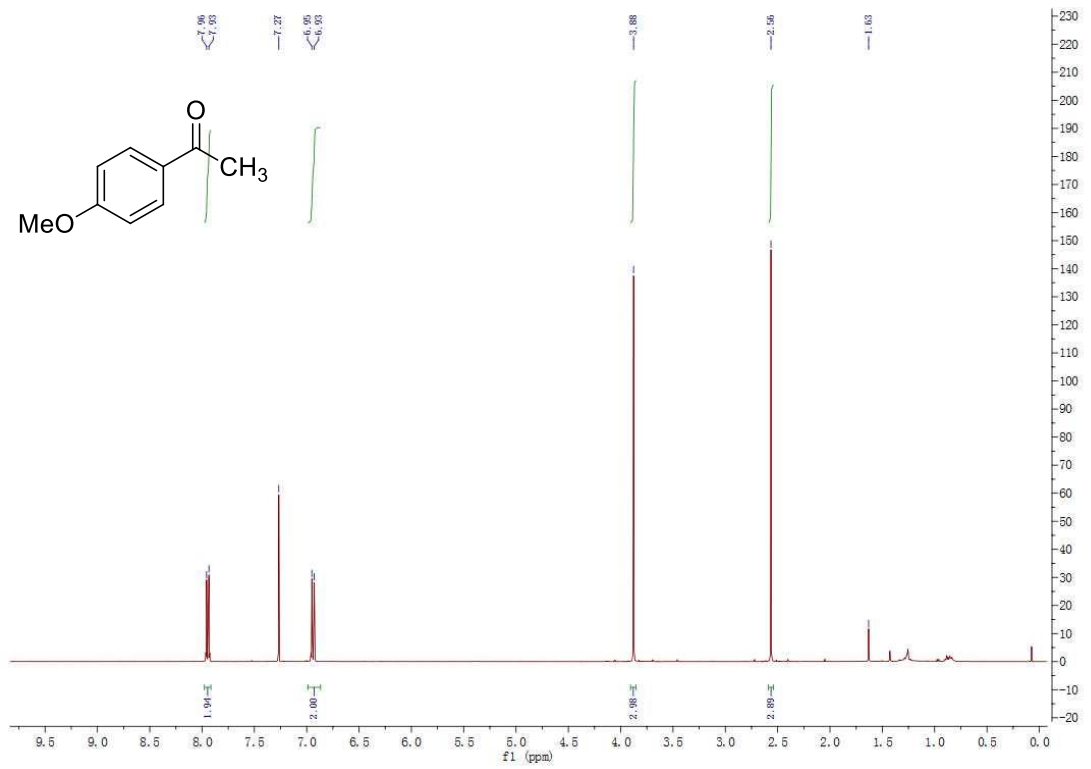
¹H NMR spectra of compound **2j**
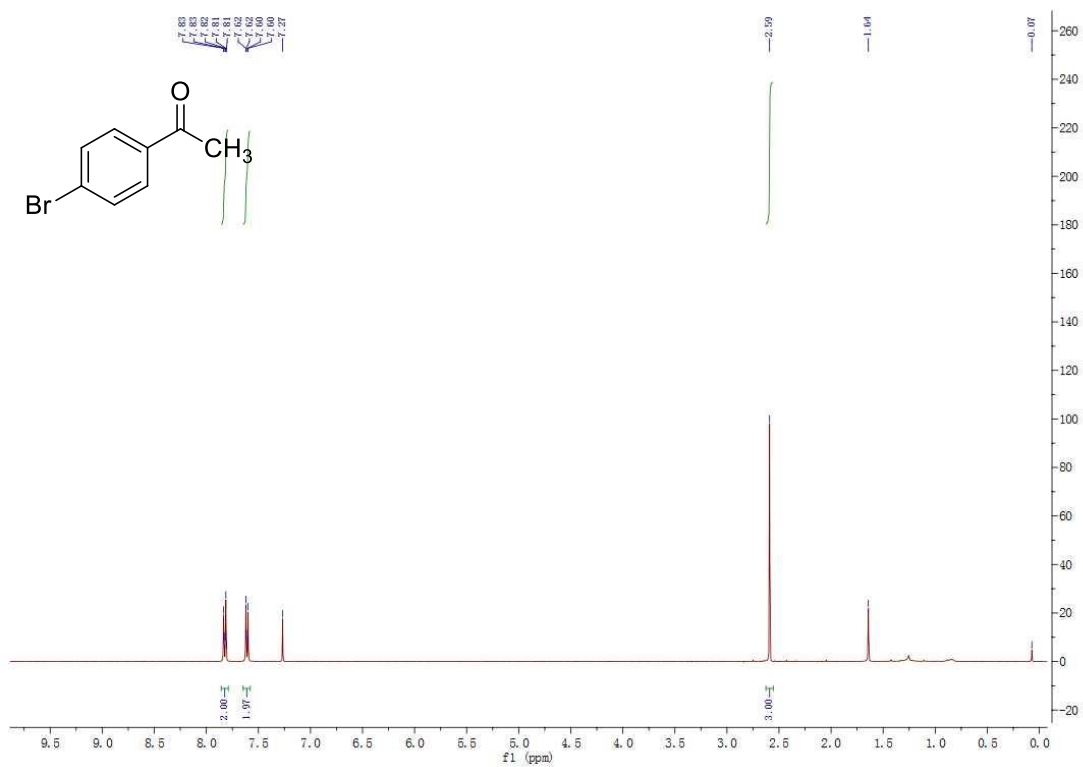
¹H NMR spectra of compound **2k**
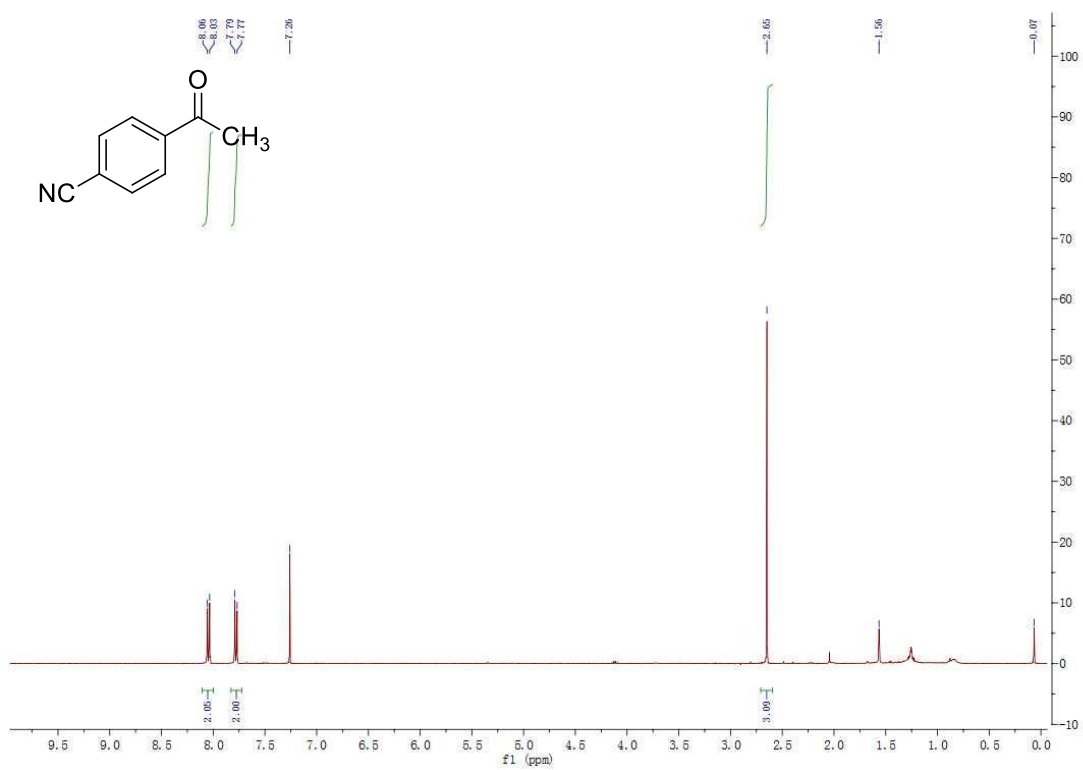
¹H NMR spectra of compound **2l**
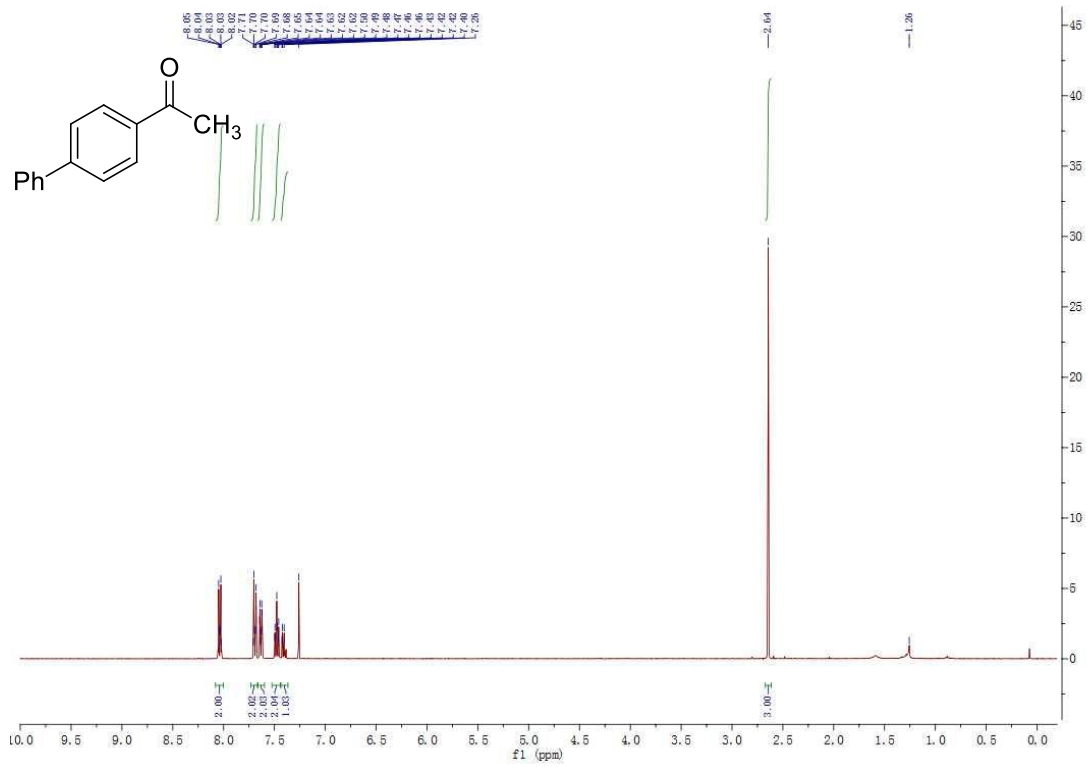
¹H NMR spectra of compound **2m**
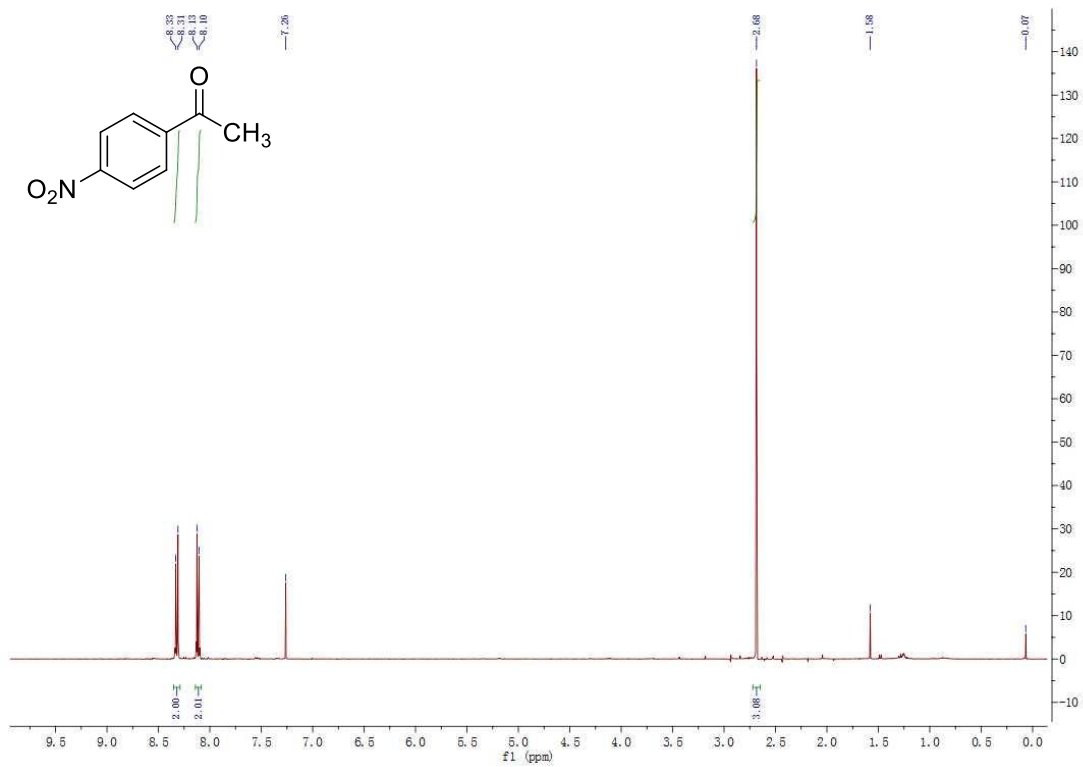
¹H NMR spectra of compound **2o**
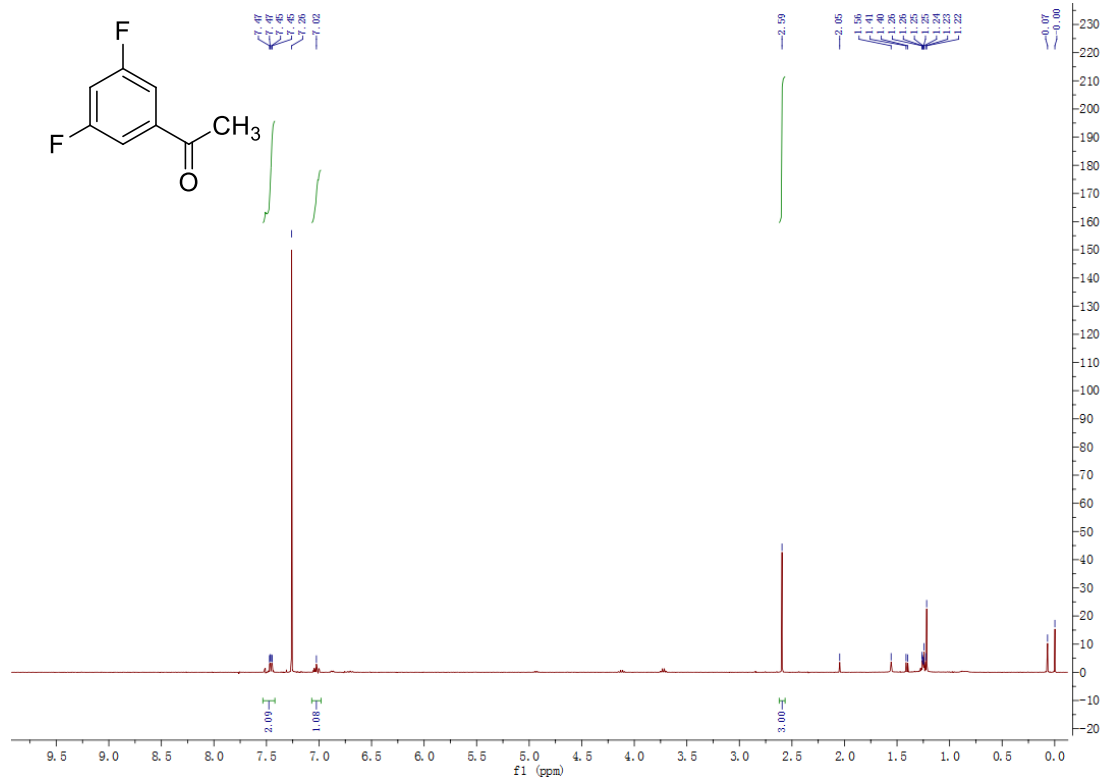
¹H NMR spectra of compound **2p**

39
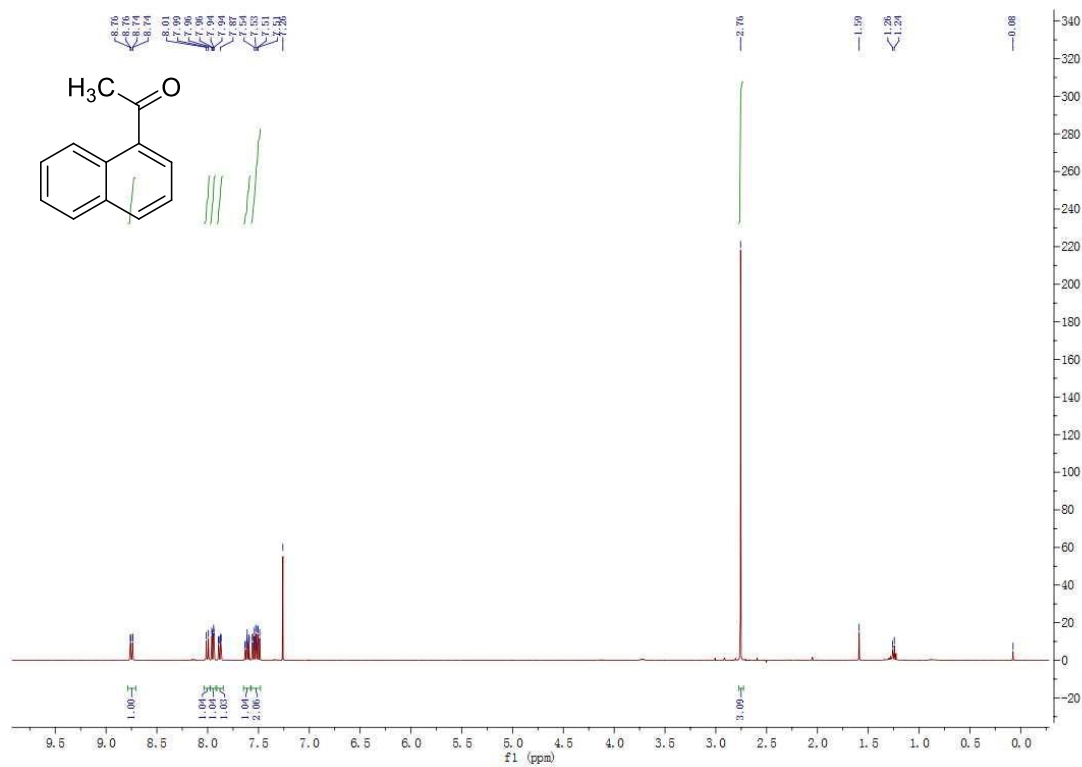
¹H NMR spectra of compound **2q**
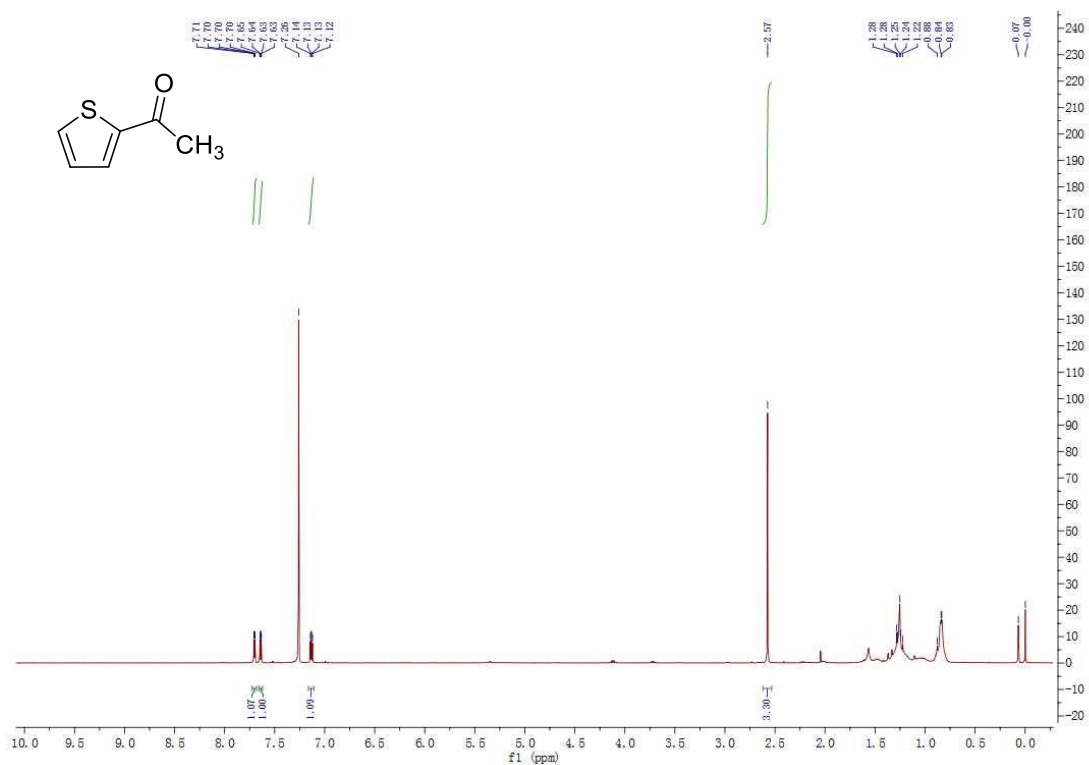
¹H NMR spectra of compound **2r**
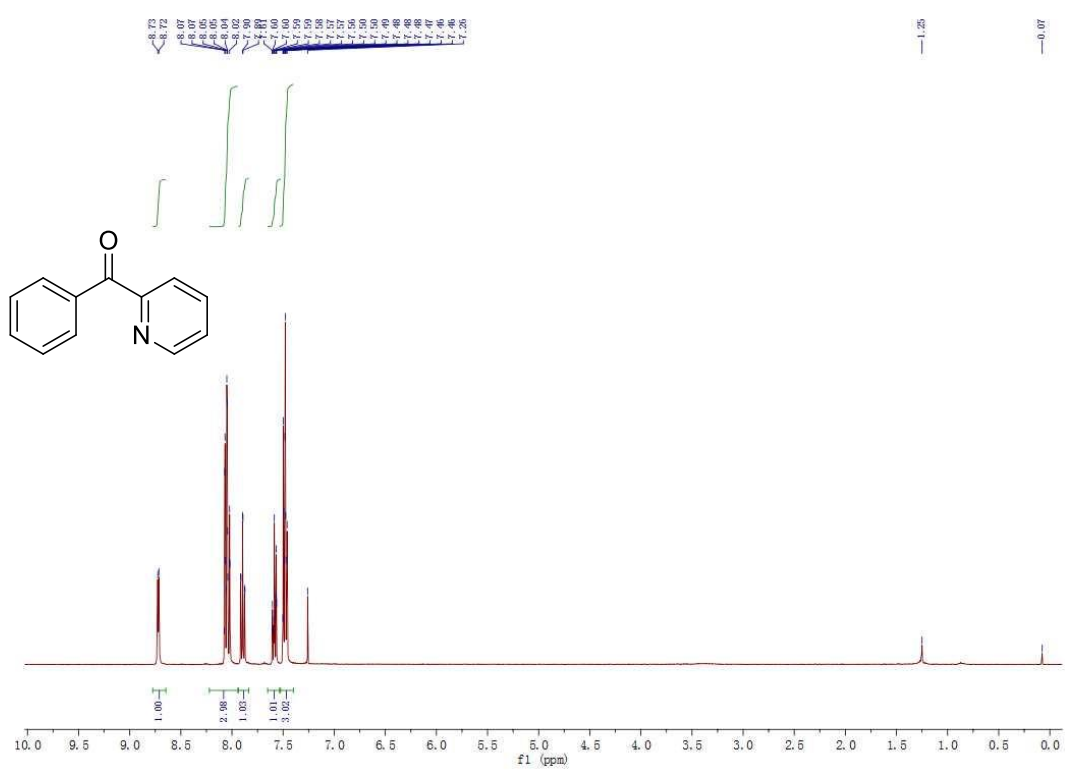
¹H NMR spectra of compound **2s**

¹H NMR spectra of compound **2t**

¹H NMR spectra of compound **2u**

¹H NMR spectra of compound **6a**

^{1}H NMR spectra of compound **6b**
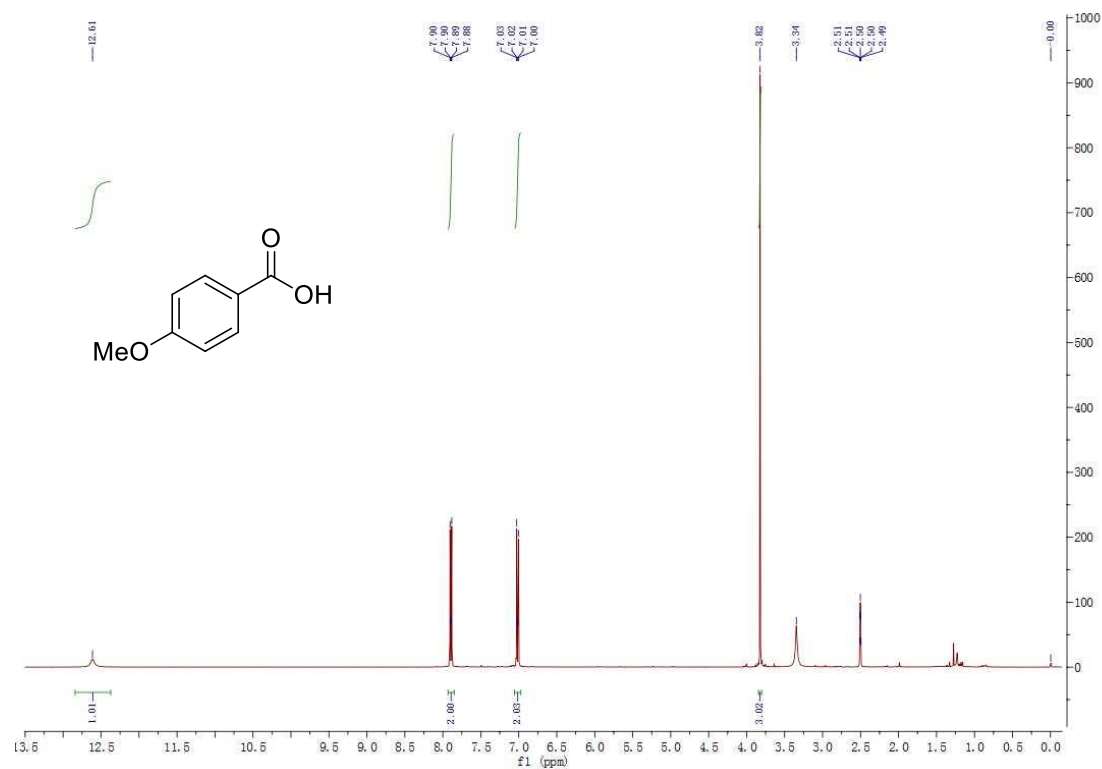
^{1}H NMR spectra of compound **6c**
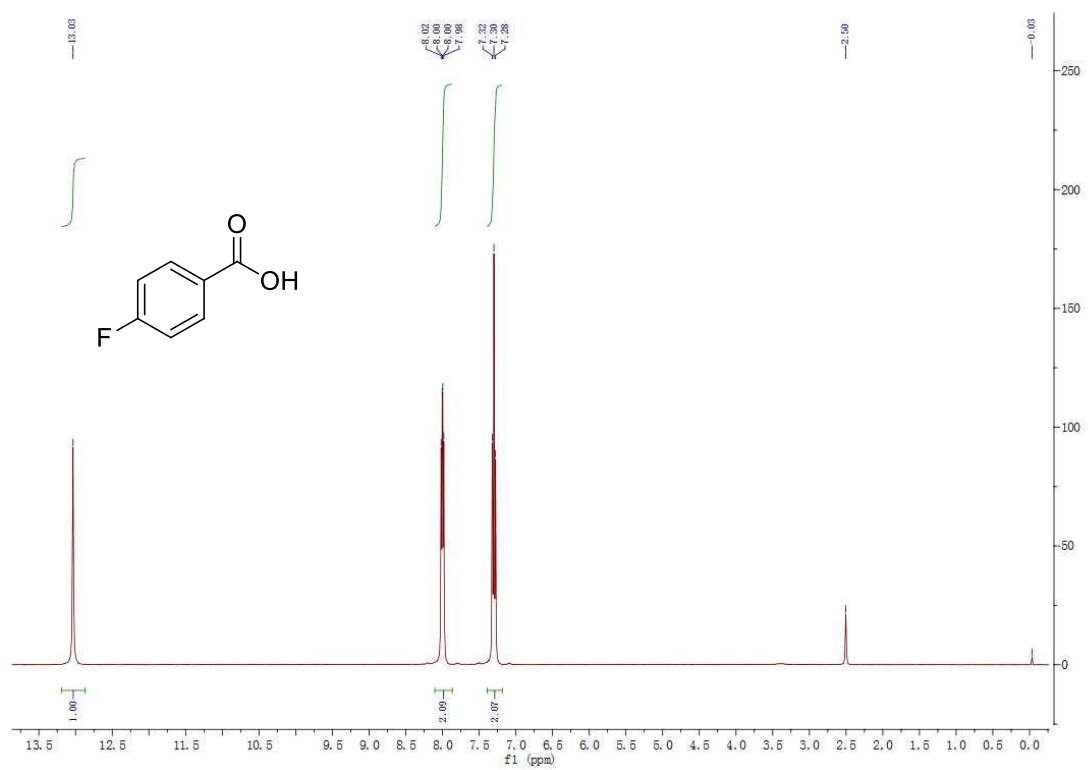
¹H NMR spectra of compound **6d**
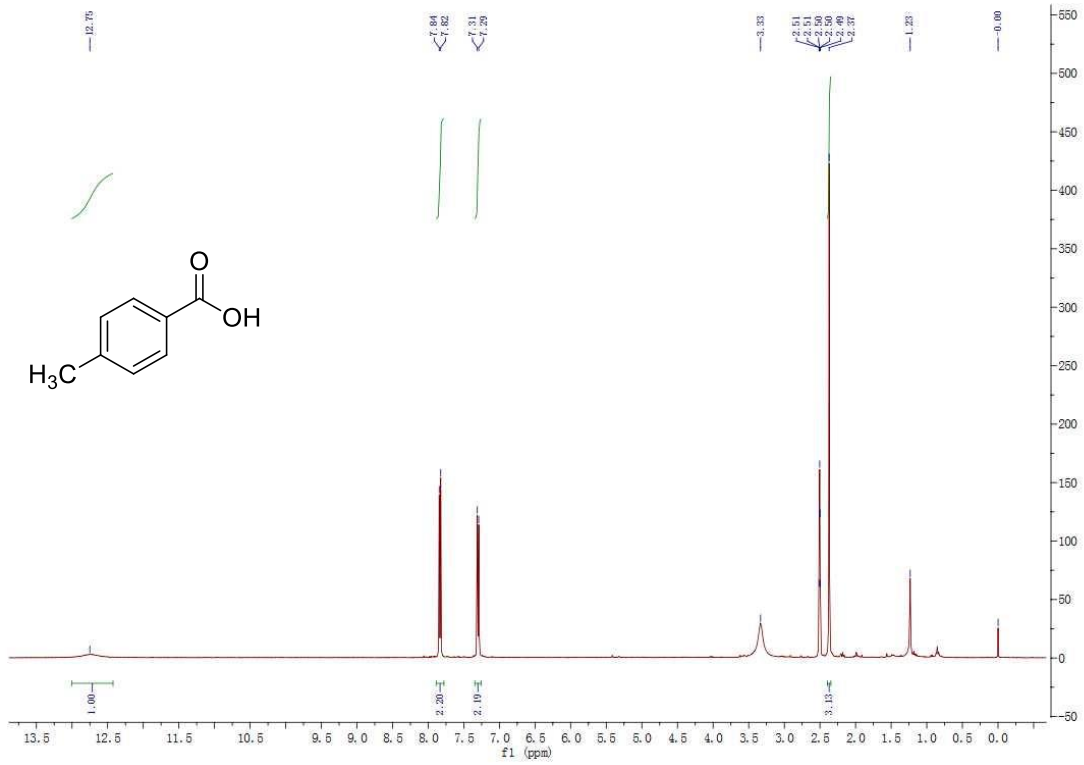
¹H NMR spectra of compound **6e**
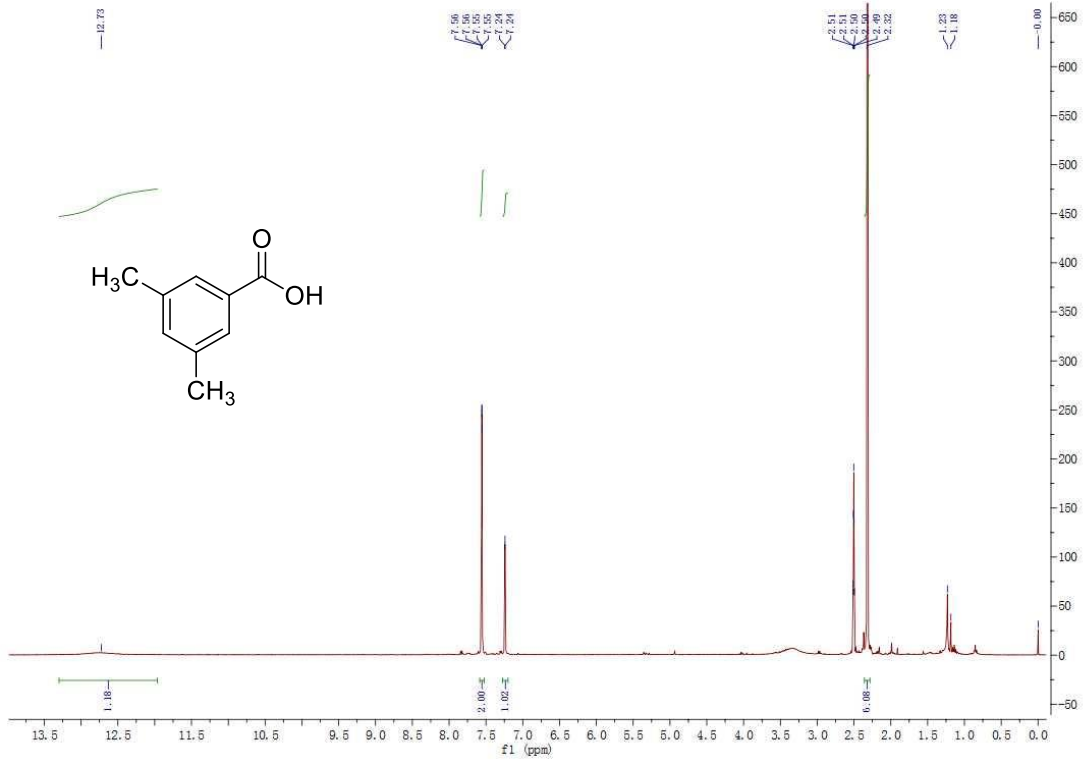
^{1}H NMR spectra of compound 6u
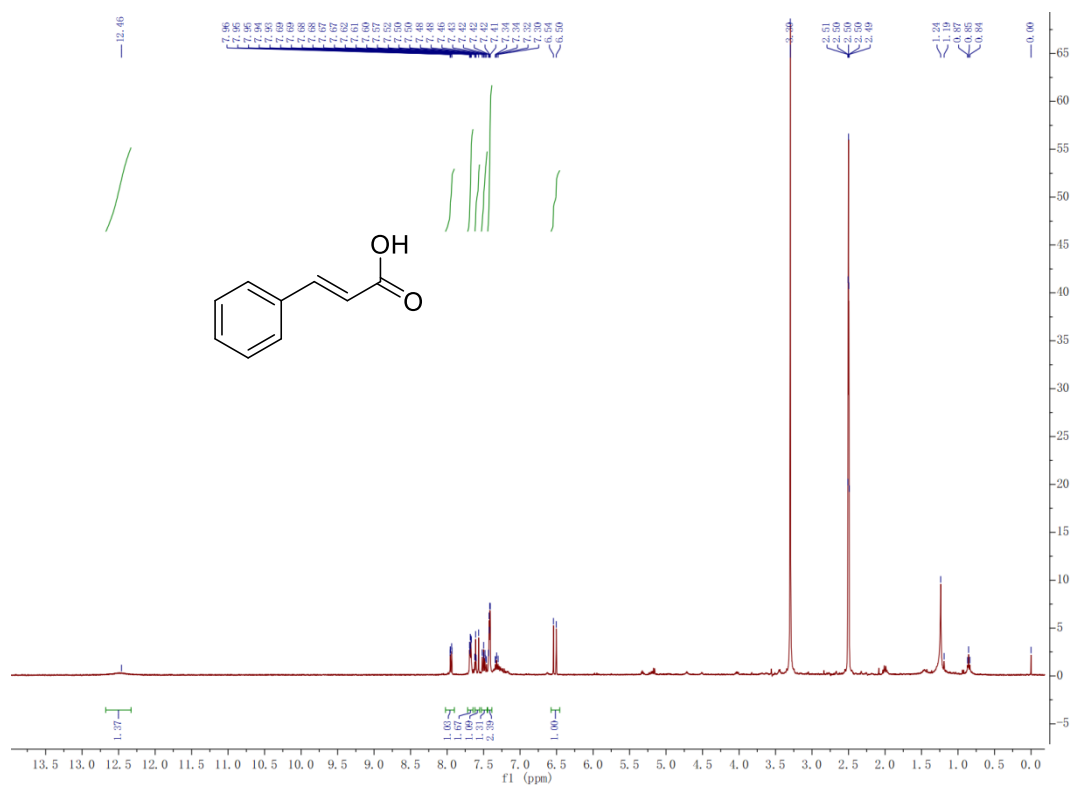
^{1}H NMR spectra of compound 6v

MS spectra of compound **2a**

MS spectra of compound **3a**

MS spectra of compound **4a**

MS spectra of compound **5a**
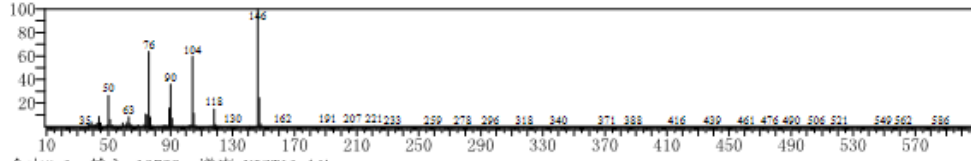
谱库
<< 目标组分 >>
行号#:1   保留时间:6.145(扫描数#:830)   质量峰:563
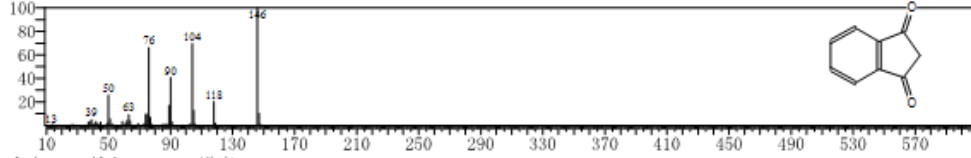原始模式:单个 6.145(830)   基峰:146.15(10000)
背景模式:无   组 1 - 事件 1   Scan

命中#:1   输入:13799   谱库:NIST11.lib
SI:96   分子式:C9H6O2   CAS:606-23-5   摩尔质量:146   保留指数:1389
组分名称:1H-Indene-1,3(2H)-dione $$ 1,3-Indandione $$ 1,3-Diketohydrindene $$ 1,3-Indanedione $$ 1,3-Indanone $$ Diketohydrindene $$ Indanedione-(1,3) $$ Indandione $$

MS spectra of compound **6a**
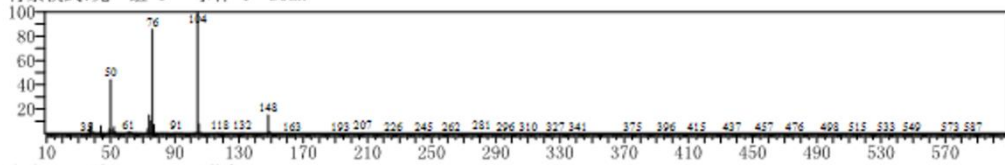
谱库
<< 目标组分 >>
行号#:1   保留时间:5.760(扫描数#:753)   质量峰:566
原始模式:单个 5.760(753)   基峰:104.10(10000)
背景模式:无   组 1 - 事件 1   Scan

命中#:2   输入:11893   谱库:NIST11s.lib
SI:96   分子式:C8H6O4   CAS:88-99-3   摩尔质量:166   保留指数:1620
组分名称:1,2-Benzenedicarboxylic acid $$ Phthalic acid $$ o-Benzenedicarboxylic acid $$ o-Dicarboxybenzene $$ Benzene-1,2-dicarboxylic acid $$ o-Phthalic acid $$ Acide phtalique $$ Kyselina ftalova $$ Sunftal 20 $$ Orthophthalic acid $$