Supporting Information

Electrochemical Decarboxylative Alkylation of β-Keto Acids with Phenol Derivatives

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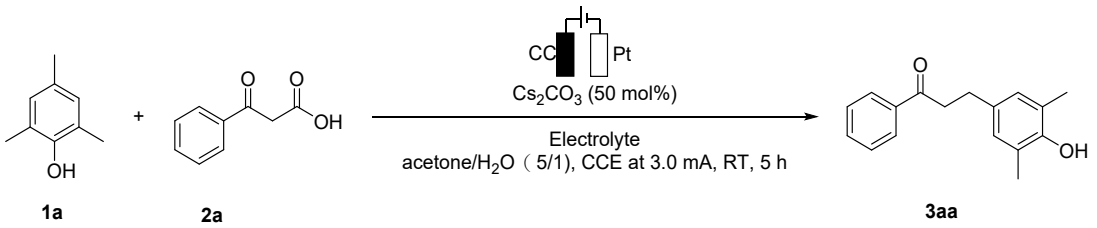
1. General information

^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded with solvent $CDCl_3$ on Bruker avance DPX 400 spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C). Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.16). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), td (doublet of triplet).

Exact ESI mass spectra were recorded on a Bruker Daltonics MicroTOF-Q. ESI-MS were obtained on a Thermo-ITQ. Mass spectral data (MS) was recorded using an Agilent-6110 mass spectrometer. For thin layer chromatography (TLC), pre-coated Qingdao Haiyang TLC plates (GF254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatographic separations were performed on 200-300 mesh silica gel (from Qingdao Haiyang Chem. Company, Ltd.). Unless otherwise noted, all reagents were purchased from commercial sources (Adamas, Energy, Aldrich) and used as received without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". The final cross-coupling reaction was carried out in an open vial under ambient condition.

2. Optimization of The Reaction Conditions

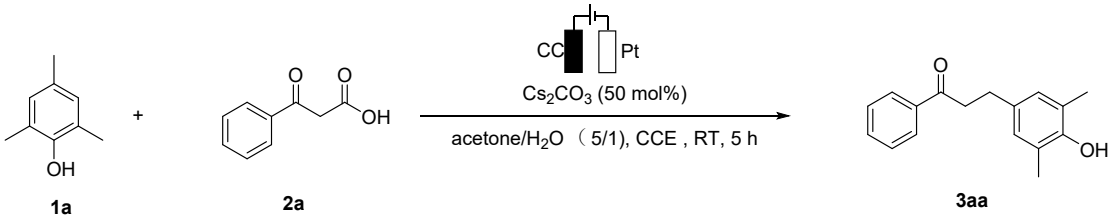
Table S1: Evaluation of electrolyte [a]



Entry	Electrolyte	Yield(%)[b]
1	*n*-Bu_4NPF_6	52%
2	*n*-Bu_4NBF_4	50%
3	none	**53%**

[a]Reaction conditions: undivided cell, Graphite anode, Pt cathode, **1a** (0.3 mmol), **2a** (0.6 mmol), Cs_2CO_3 (0.5 equiv.), electrolyte (0.1 M), acetone/H_2O (5/1, 6 mL), CCE = 3.0 mA, 5 h, RT, under air. [b]Yield is that of the isolated product. CCE = constant current electrolysis.

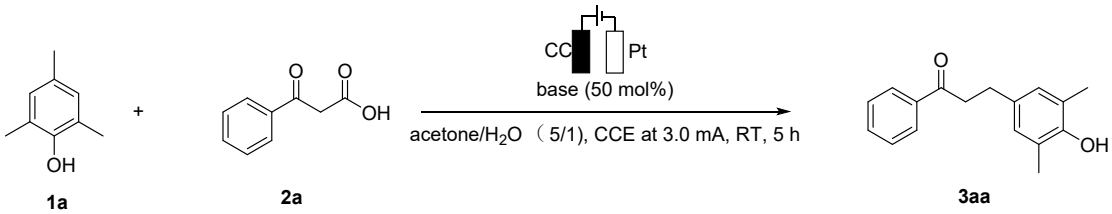
Table S2: Evaluation of f electric current[a]



Entry	Electric current (mA)	Yield (%) [b]
1	0	N.R
2	1.0	38
3	3.0	**53**
4	5.0	39
7	7.0	41

[a]Reaction conditions: undivided cell, Graphite anode, Pt cathode, **1a** (0.3 mmol), **2a** (0.6 mmol), Cs_2CO_3 (0.5 equiv.), acetone/H_2O (5/1, 6 mL), CCE, 5 h, RT, under air. [b] Yield is that of the isolated product. CCE = constant current electrolysis.

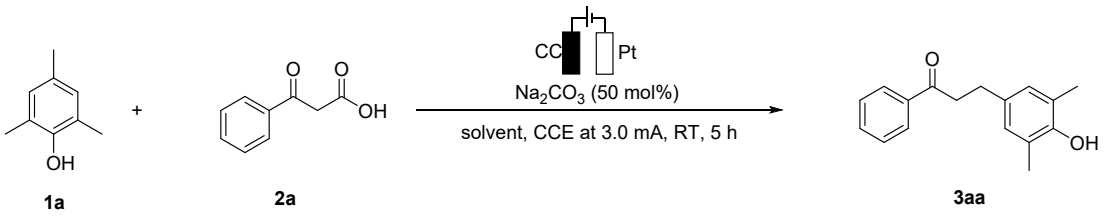
Table S3: Evaluation of base[a]



Entry	Base	Yield(%)[b]
1	Cs_2CO_3 as base	55
2	K_2CO_3 as base	46
3	Na_2CO_3 as base	**64**
4	NaOAc as base	35
5	$NaHCO_3$ as base	57
6	NaH_2PO_4 as base	33
7	DABCO as base	33
8	DBU as base	28
9	without base	45

[a]Reaction conditions: undivided cell, Graphite anode, Pt cathode, **1a** (0.3 mmol), **2a** (0.6 mmol), Base (0.5 equiv.), acetone/H_2O (5/1, 6 mL), CCE = 3.0 mA, 5 h, RT, under air. [b]Yield is that of the isolated product. CCE = constant current electrolysis.

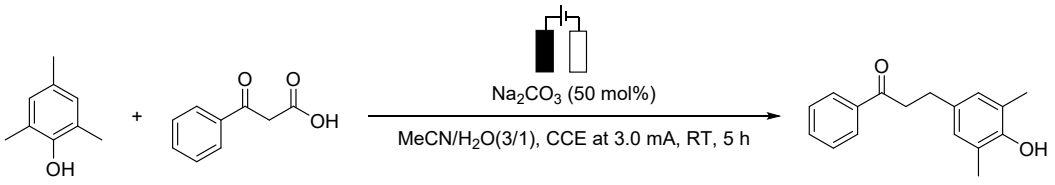
Table S4: Evaluation of solvents[a]



Entry	Solvent (mL)	Yield(%)[b]
1	acetone /H_2O (5/1)	65
2	acetone /H_2O (4/2)	60
3	acetone (6)	35
4	HFIP/H_2O (5/1)	45
5	THF/H_2O (5/1)	46
6	1,4-Dioxane/H_2O(5/1)	50
7	MeCN/H_2O (5/1)	65
8	MeCN/H_2O (4/1)	60
10	MeCN/H_2O (3/1)	**78**
12	MeCN/H_2O (2/1)	60
13	MeCN/H_2O (1/1)	60
14	MeCN (4)	42
15	H_2O (4)	N.R

[a]Reaction conditions: undivided cell, Graphite anode, Pt cathode, **1a** (0.3 mmol), **2a** (0.6 mmol), Na_2CO_3 (0.5 equiv.), Solvent (xx mL), CCE = 3.0 mA, 5 h, RT, under air. [b]Yield is that of the isolated product. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, CCE = constant current electrolysis.

Table S5: Evaluation of electrode[a]



Entry	Electrode	Yield(%)[b]
1	Graphite(+) , Pt(-)	**78**
2	Pt(+) , Pt(-)	65
3	Graphite (+) , Graphite (-)	62

[a]Reaction conditions: undivided cell, xx anode, xx cathode, **1a** (0.3 mmol), **2a** (0.6 mmol), Na_2CO_3 (0.5 equiv.), MeCN/H_2O (3/1, 4 mL), CCE = 3.0 mA, 5 h, RT, under air. [b]Yield is that of the isolated product. CCE = constant current electrolysis.

Table S6: Evaluation of the conductivity of different kind of solutions[a]

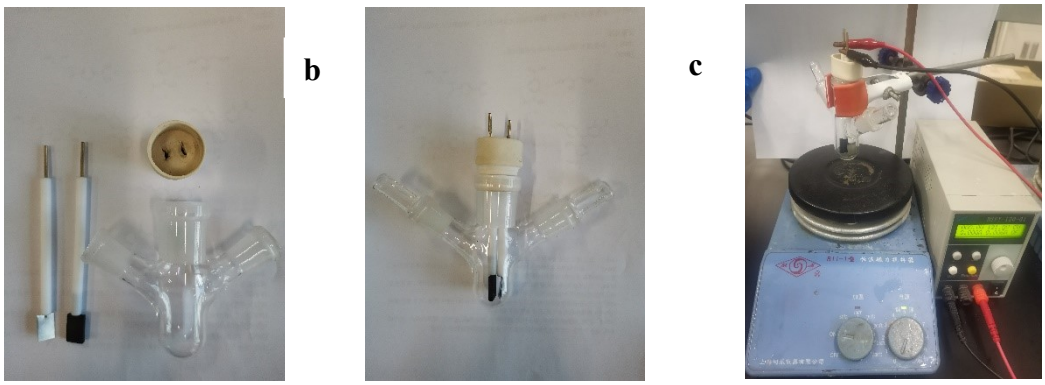
Entry	Variation of mixture	Description	Conductivity[b]
1	MeCN/H_2O	solvents	13.87 μS/cm
2	MeCN/H_2O + *n*-Bu_4NPF_6	with electrolyte	6250 μS/cm
3	MeCN/H_2O + Na_2CO_3	with Na_2CO_3	516 μS/cm
4	MeCN/H_2O + *n*-Bu_4NPF_6 + Na_2CO_3	with electrolyte and Na_2CO_3	9300 μS/cm
5	MeCN/H2O + 1a + 2a	without Na_2CO_3	225 μS/cm
6	MeCN/H_2O + 1a + 2a + Na_2CO_3	without electrolyte	1855 μS/cm
7	MeCN/H_2O + 1a + 2a + *n*-Bu_4NPF_6 + Na_2CO_3	with electrolyte and Na_2CO_3	10110 μS/cm

[a] Measure conditions: **1a** (0.8 mmol), **2a** (1.6 mmol), Na_2CO_3 (0.5 equiv.), MeCN /H_2O (3/1, 4 mL)，*n*-Bu_4NPF_6 (0.1 M). Conductivity was measured by DDSJ-308F Conductivity meter. [b] The data of each entry was measured three times and averaged.

3. General procedure

3.1 Graphical guide for the set-up

a b c



As experimental set-up, a graphite electrode (10 mm×15 mm×3 mm), a platinum plate electrode (10 mm×15mm×0.1 mm), rubber plugs, an undivided three-necked bottle and Hansheng Puyuan Programmable DC Power Supplies （HPYS-120-01）were used.

Figure S1. Setup for milligram scale photoelectrocatalytic reactions. a) Electrodes; b) Assembled reactor; c) Reaction in progress.

b

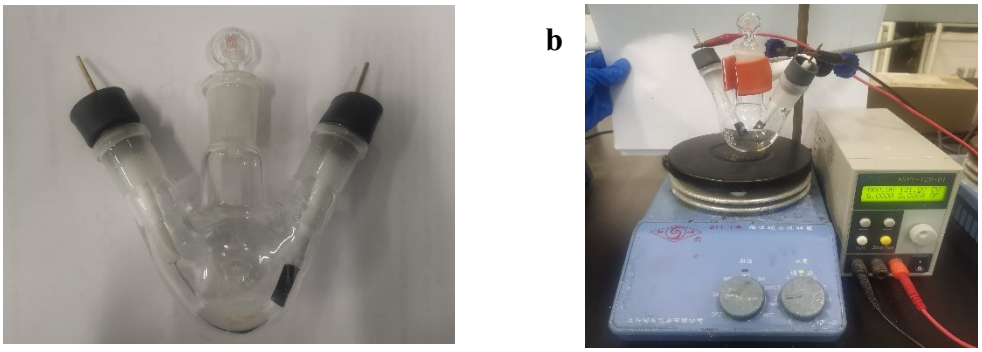
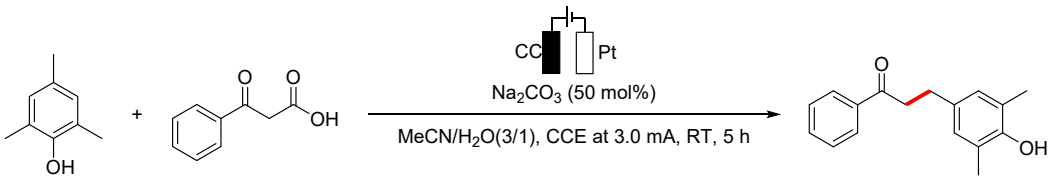


Figure S2. Setup for the gram scale synthesis of 3. a) Assembled reaction setup. b) Reaction in progress.

3.2 Substrate preparation

All the β-ketoacids derivatives [1-2] and phenol derivatives [3-4] are known compounds and prepared according to the reported procedure.

Electrochemical Decarboxylative Alkylation



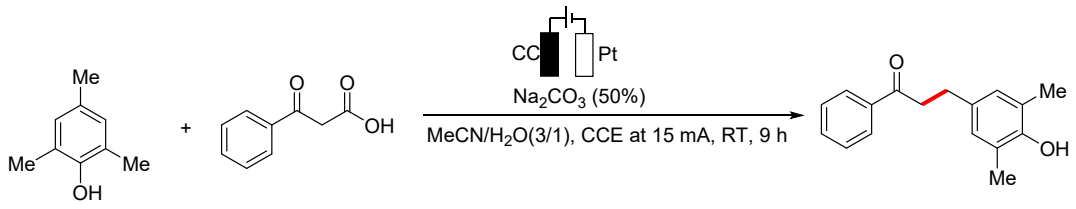
1a **2a** **3aa**

General procedure A:

Electrocatalysis was carried out in an undissociated cell with a Graphite (15 mm × 15 mm × 3 mm) as an anode and a platinum sheet (10 mm × 15 mm × 0.1 mm) as a cathode. 2,4,6-Trimethylphenol **1a** (54.48 mg, 0.4 mmol), 3-oxo-3-phenylpropionic acid **2a** (131.33 mg, 0.8 mmol), and anhydrous sodium carbonate (21.2 mg,0.2 mmol) were placed in a 10 mL three-necked flask and dissolved in acetonitrile/H_2O (3 mL/1 mL). Electrolysis was carried out continuously at a constant current of 3.0 mA for 5 h at room temperature. The electrodes were then cleaned with DCM, and then the combined solvents were dried with anhydrous sodium sulfate, and the solvents were removed by distillation under reduced pressure, followed by column chromatographic separation and purification (petroleum ether: ethyl acetate = 10:1) to obtain the desired product

4. Synthetic utility and comparison

A. Gram-Scale Synthesis

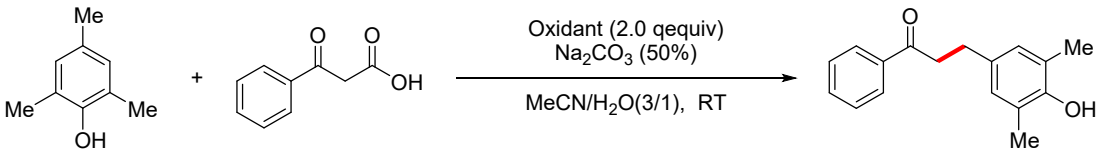


1a
5 mmol

2a

3aa
711 mg, 56%

B. Electrooxidation comparison with chemical methods



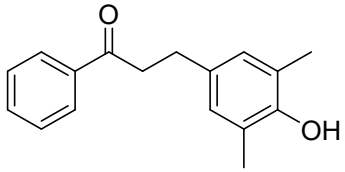
1a **2a** **3aa**

Entry	Oxidant	Yield[b](%)
1	DDQ	11
2	$Cu(OAc)_2$	13
3	TBHP	trace
4	Anode	78

[a]Reaction conditions: undivided cell, Graphite anode, Pt cathode, **1a** (0.3 mmol), **2a** (0.6 mmol), Na_2CO_3 (0.5 equiv.), MeCN/H_2O (3/1, 4 mL), CCE = 3.0 mA, 5 h, RT, under air. [b]Yield is that of the isolated product. CCE = constant current electrolysis. TBHP = tert-butyl hydroperoxide, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

5. Characterization data of products

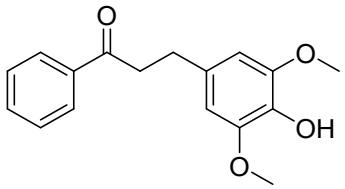
3-(4-hydroxy-3,5-dimethylphenyl)-1-phenylpropan-1-one(3aa)



3aa

Following the general procedure A. A yellow oily liquid. Isolated yield (PE/EA = 10:1), 79.3 mg, 78%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.97 (dd, J = 8.4, 1.3 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.46 (t, J = 7.5 Hz, 2H), 6.87 (s, 2H), 4.62 (s, 1H), 3.30 – 3.22 (m, 2H), 2.98 – 2.90 (m, 2H), 2.23 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 199.72, 150.64, 137.03, 133.16, 132.96, 128.72, 128.64, 128.20, 123.19, 41.08, 29.43, 16.05. **HR-MS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{18}NaO_2$ 277.1204, found 277.1216.

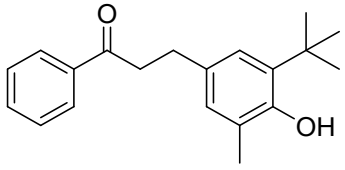
3-(4-hydroxy-3,5-dimethoxyphenyl)-1-phenylpropan-1-one（3ba）



3ba

Following the general procedure A. A yellow solid. Isolated yield (PE/EA = 10:1), 63 mg, 55%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.95 (dd, J = 8.5, 1.4 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.45 (t, J = 7.6 Hz, 2H), 6.46 (s, 2H), 5.43 (s, 1H), 3.86 (s, 6H), 3.31 – 3.24 (m, 2H), 3.00 (d, J = 8.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 199.56, 147.08, 136.97, 133.21, 133.08, 132.50, 128.72, 128.13, 105.10, 56.35, 40.95, 30.54. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}O_4$ 287.1283, found 287.1281.

3-(3-(tert-butyl)-4-hydroxy-5-methylphenyl)-1-phenylpropan-1-one (3ca)

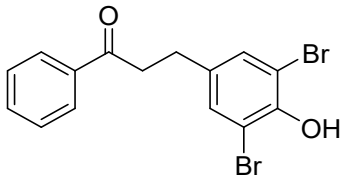


3ca

Following the general procedure A. A brownish yellow oily liquid. Isolated yield (PE/EA = 10:1), 81.7 mg, 69%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.98 (dd, J = 8.4, 1.4 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.47 (tt, J = 6.7, 1.4 Hz, 2H), 7.02 (d, J = 2.3 Hz, 1H), 6.91 (d, J = 2.1 Hz, 1H), 4.79 (s, 1H),

3.31 – 3.26 (m, 2H), 3.01 – 2.96 (m, 2H), 2.25 (s, 3H), 1.42 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 199.93, 151.13, 137.03, 135.85, 133.13, 132.42, 128.69, 128.57 – 128.31 (m), 128.20, 125.41 – 124.93 (m), 123.26, 41.16, 34.62, 29.90, 29.87, 16.15. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{25}O_2$ 297.1855, found 297.1856.

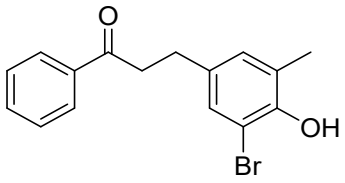
3-(3,5-dibromo-4-hydroxyphenyl)-1-phenylpropan-1-one (3da)



3da

Following the general procedure A. A light yellow solid. Isolated yield (PE/EA = 10:1), 62.6 mg, 41%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.98 – 7.91 (m, 2H), 7.59 – 7.54 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.34 (s, 2H), 5.84 (s, 1H), 3.26 (t, J = 7.5 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 198.60, 147.82, 136.72, 136.11, 133.43, 132.10, 128.82, 128.15, 109.81, 40.16, 28.60. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{13}Br_2O_4$ 382.9282, found 382.9279.

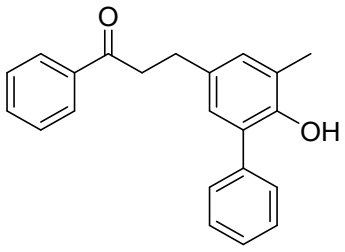
3-(3-bromo-4-hydroxy-5-methylphenyl)-1-phenylpropan-1-one (3ea)



3ea

Following the general procedure A. A yellow oily liquid. Isolated yield (PE/EA = 10:1), 67.4 mg, 53%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.50 – 7.39 (m, 2H), 7.19 (d, *J* = 1.3 Hz, 1H), 6.95 (d, *J* = 2.2 Hz, 1H), 5.46 (s, 1H), 3.29 – 3.19 (m, 2H), 2.99 – 2.90 (m, 2H), 2.27 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 199.20, 148.83, 136.86, 134.37, 133.29, 130.72, 129.05, 128.76, 128.16, 125.87, 110.04, 40.61, 29.01, 16.82. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}O_4$ 287.1283, found 287.1281.

3-(6-hydroxy-5-methyl-[1,1'-biphenyl]-3-yl)-1-phenylpropan-1-one (3fa)

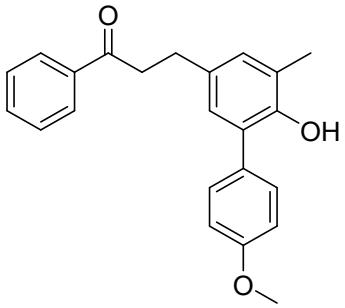


3fa

Following the general procedure A. A white solid. Isolated yield (PE/EA = 10:1 to 5:1), 68.7 mg, 54%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.52 – 7.39 (m, 7H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.98 (d, *J* = 3.0 Hz, 1H), 5.23 (s, 1H), 3.36 – 3.27 (m, 2H),

3.06 – 2.98 (m, 2H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 199.57, 149.03, 137.49, 136.93, 133.16, 132.93, 130.62, 129.42, 129.21, 128.69, 128.17, 127.93, 127.74, 127.64, 124.83, 40.91, 29.43, 16.37. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}O_2$ 317.1542, found 317.1544.

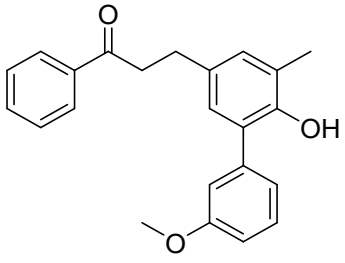
3-(6-hydroxy-4'-methoxy-5-methyl-[1,1'-biphenyl]-3-yl)-1-phenylpropan-1-one (3ga)



3ga

Following the general procedure A. A brownish yellow oily liquid. Isolated yield (PE/EA = 10:1), 76.2 mg, 55%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.60 – 7.51 (m, 1H), 7.50 – 7.41 (m, 2H), 7.41 – 7.31 (m, 2H), 7.05 – 6.97 (m, 3H), 6.95 – 6.90 (m, 1H), 5.15 (s, 1H), 3.86 (s, 4H), 3.34 – 3.25 (m, 2H), 3.03 – 2.95 (m, 2H), 2.28 (s,3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 199.65, 159.38, 149.13, 136.95, 133.16, 132.84, 130.40, 130.28, 129.53, 128.70, 128.17, 127.66, 127.43, 124.67, 114.83, 55.47, 40.95, 29.45, 16.35. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}O_3$ 347.1647, found 347.1645.

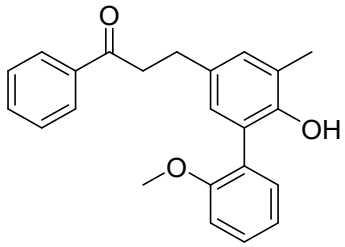
3-(6-hydroxy-3'-methoxy-5-methyl-[1,1'-biphenyl]-3-yl)-1-phenylpropan-1-one (3ha)



3ha

Following the general procedure A. A light yellow oily liquid. Isolated yield (PE/EA = 10:1), 69.2 mg, 50%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 – 7.95 (m, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.05 – 7.01 (m, 2H), 6.97 – 6.92 (m, 3H), 5.28 (s, 1H), 3.84 (s, 3H), 3.34 – 3.26 (m, 2H), 3.04 – 2.96 (m, 2H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 199.60, 160.46, 149.03, 138.86, 136.97, 133.20, 132.90, 130.73, 130.60, 128.74, 128.20, 127.56, 127.44, 124.89, 121.28, 114.55, 113.80, 55.47, 40.94, 29.84, 16.39. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}O_3$ 347.1647, found 347.1651.

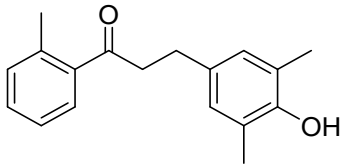
3-(6-hydroxy-2'-methoxy-5-methyl-[1,1'-biphenyl]-3-yl)-1-phenylpropan-1-one (3ia)



3ia

Following the general procedure A. A yellow oily liquid. Isolated yield (PE/EA = 10:1), 90 mg, 65%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 – 7.94 (m, 2H), 7.57 – 7.52 (m, 1H), 7.48 – 7.42 (m, 2H), 7.38 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.09 (td, *J* = 7.5, 1.1 Hz, 1H), 7.05 (td, *J* = 8.3, 7.9, 1.1 Hz, 2H), 6.99 – 6.94 (m, 1H), 6.11 (s, 1H), 3.90 (s, 3H), 3.34 – 3.26 (m, 2H), 3.03 – 2.98 (m, 2H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 199.70, 155.58, 150.31, 137.01, 133.16, 132.70, 130.75, 129.37, 128.86, 128.73, 128.20, 127.34, 126.38, 125.89, 122.19, 111.40, 56.17, 40.99, 29.54, 16.70. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}O_3$ 347.1647, found 347.1645.

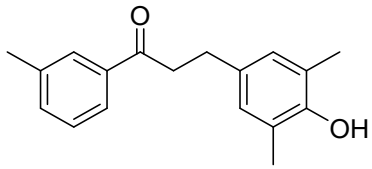
3-(4-hydroxy-3,5-dimethylphenyl)-1-(o-tolyl)propan-1-one (3ab)



3ab

Following the general procedure A. A brown oily liquid. Isolated yield (PE/EA = 10:1), 54.7 mg, 51%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.61 (dd, J = 8.0, 1.4 Hz, 1H), 7.36 (td, J = 7.5, 1.4 Hz, 1H), 7.24 (d, J = 5.0 Hz, 2H), 6.83 (s, 2H), 4.55 (s, 1H), 3.23 – 3.13 (t, 2H), 2.94 – 2.86 (t, 2H), 2.47 (s, 3H), 2.22 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 203.98, 150.61, 138.18, 138.09, 132.81, 132.06, 131.33, 128.62, 128.53, 125.77, 123.16, 43.87, 29.64, 21.37, 16.04. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{21}O_2$ 269.1542, found 269.1535.

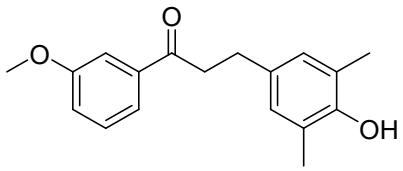
3-(4-hydroxy-3,5-dimethylphenyl)-1-(m-tolyl)propan-1-one (3ac)



3ac

Following the general procedure A. A brown solid. Isolated yield (PE/EA = 10:1), 72.9 mg, 68%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.75 (m, 2H), 7.43 – 7.31 (m, 2H), 6.89 (s, 2H), 4.89 (s, 1H), 3.31 – 3.22 (m, 2H), 2.99 – 2.91 (m, 2H), 2.42 (s,31H), 2.26 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 200.14, 150.73, 138.49, 137.01, 133.95, 132.92, 128.77, 128.62, 128.59, 125.44, 123.35, 41.17, 29.50, 21.48, 16.12. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{21}O_2$ 269.1542, found 269.1541.

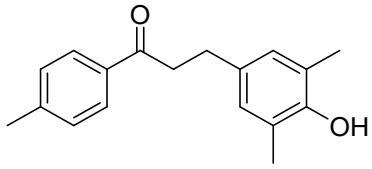
3-(4-hydroxy-3,5-dimethylphenyl)-1-(3-methoxyphenyl)propan-1-one (3ad)



3ad

Following the general procedure A. A brown oily liquid. Isolated yield (PE/EA = 10:1), 68.2 mg, 60%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.52 (m, 1H), 7.48 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.85 (s, 2H), 4.63 (s, 1H), 3.84 (s, 3H), 3.27 – 3.19 (m, 2H), 2.96 – 2.88 (m, 2H), 2.22 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 199.62, 159.91, 150.67, 138.35, 132.85, 129.69, 128.61, 123.24, 120.84, 119.69, 112.33 (d, *J* = 4.7 Hz), 55.55 (t, *J* = 4.1 Hz), 41.18, 29.47, 16.07. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}O_4$ 285.1491, found 285.1493.

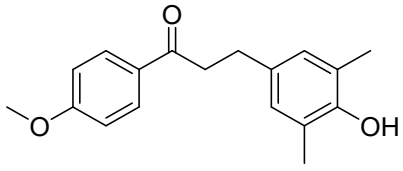
3-(4-hydroxy-3,5-dimethylphenyl)-1-(p-tolyl)propan-1-one (3ae)



3ae

Following the general procedure A. A white solid. Isolated yield (PE/EA = 10:1), 80.4 mg, 75%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.88 (d, J = 8.3 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 6.87 (s, 2H), 4.75 (s, 1H), 3.28 – 3.19 (m, 2H), 2.97 – 2.89 (m, 2H), 2.42 (s, 3H), 2.24 (s, 6H).**^{13}C NMR** (101 MHz, Chloroform-d) δ 199.47, 150.63, 143.92, 134.50, 132.99, 129.38, 128.60, 128.31, 123.22, 40.96, 29.51, 21.74, 16.06. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{21}O_2$ 269.1542, found 269.1542.

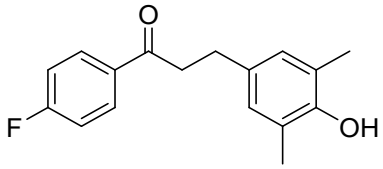
3-(4-hydroxy-3,5-dimethylphenyl)-1-(4-methoxyphenyl)propan-1-one (3af)



3af

Following the general procedure A. A yellow oily liquid. Isolated yield (PE/EA = 10:1), 87.51 mg, 77%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.95 (d, J = 9.0 Hz, H), 6.93 (d, J = 8.9 Hz, 2H), 6.86 (s, 2H), 4.62 (s, 1H), 3.87 (s, 3H), 3.24 – 3.16 (m, 2H), 2.96 – 2.88 (m, 2H), 2.23 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 198.33, 163.54, 150.61, 133.12, 130.47, 130.13, 128.63, 123.18, 113.83, 55.60, 40.76, 29.64, 16.06. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{121}O_3$ 285.1491, found 285.1491.

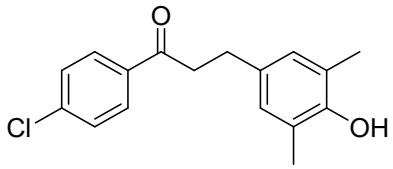
1-(4-fluorophenyl)-3-(4-hydroxy-3,5-dimethylphenyl)propan-1-one (3ag)



3ag

Following the general procedure A. A light yellow oily liquid. Isolated yield (PE/EA = 10:1), 59.9 mg, 55%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.99 (dd, J = 8.9, 5.4 Hz, 2H), 7.12 (t, J = 8.6 Hz, 2H), 6.86 (s, 2H), 4.63 (s, 1H), 3.25 – 3.20 (m, 2H), 2.96 – 2.90 (m, 2H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 197.98, 165.65 (d, *J* = 254.5 Hz) 150.52, 133.25 (d, J = 3.0 Hz), 132.58, 130.64 (d, *J* = 9.3 Hz), 128.44, 123.08, 115.63 (d, J = 21.8 Hz), 40.82, 29.22, 15.90. **^{19}F-NMR** (376 MHz, Chloroform-d) δ -105.25 (t, J = 6.6 Hz). **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{18}FO_2$ 273.1291, found 273.1283.

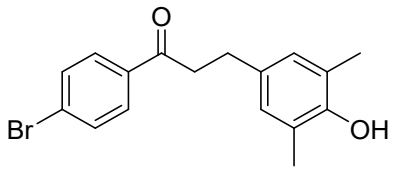
1-(4-chlorophenyl)-3-(4-hydroxy-3,5-dimethylphenyl)propan-1-one (3ah)



3ah

Following the general procedure A. A light yellow solid. Isolated yield (PE/EA = 10:1), 66.8 mg, 58%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.86 (m, 2H), 7.46 – 7.38 (m, 2H), 6.85 (s, 2H), 4.65 (s, 1H), 3.25 – 3.19 (m, 2H), 2.95 – 2.89 (m, 2H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.50, 150.69, 139.56, 135.27, 132.65, 129.59, 129.00, 128.59, 123.24, 41.02, 29.31, 16.05. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{18}ClO_2$ 289.0995, found 289.1004.

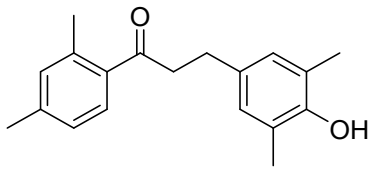
1-(4-bromophenyl)-3-(4-hydroxy-3,5-dimethylphenyl)propan-1-one (3ai)



3ai

Following the general procedure A. A brown solid. Isolated yield 69.1 mg, 52%.Purification by column chromatography on silica gel (petroleum ether/EtOAc: 15/1) **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.78 (m, 2H), 7.63 – 7.56 (m, 2H), 6.85 (s, 2H), 4.58 (s, 1H), 3.25 – 3.17 (m, 2H), 2.96 – 2.88 (m, 2H), 2.23 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 198.65, 150.70, 135.72, 132.68, 132.03, 129.73, 128.61, 128.31, 123.23, 41.03, 29.32, 16.06. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{18}BrO_2$ 333.0491, found 333.0496.

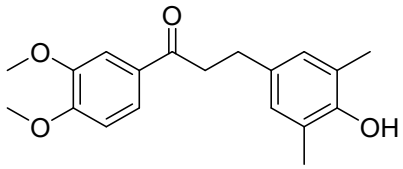
1-(2,4-dimethylphenyl)-3-(4-hydroxy-3,5-dimethylphenyl)propan-1-one (3aj)



3aj

Following the general procedure A. A brown solid. Isolated yield 79.0 mg, 70%.Purification by column chromatography on silica gel (petroleum ether/EtOAc: 10/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.84 (s, 2H), 4.67 (s, 1H), 3.23 – 3.13 (m, 2H), 2.96 – 2.86 (m, 2H), 2.49 (s, 3H), 2.36 (s, 3H), 2.23 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 203.21, 150.59, 141.96, 138.78, 134.95, 132.98, 132.92, 129.16, 128.60, 126.39, 123.16, 43.56, 29.80 (d, *J* = 5.7 Hz), 21.64, 21.46, 16.03. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}O_4$ 283.1698, found 283.1701.

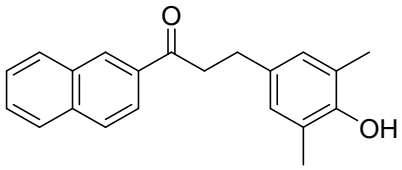
1-(3,4-dimethoxyphenyl)-3-(4-hydroxy-3,5-dimethylphenyl)propan-1-one (3ak)



3ak

Following the general procedure A. A white solid. Isolated yield 81.7 mg, 65%.Purification by column chromatography on silica gel (petroleum ether/EtOAc: 15/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 6.87 (s, 1H), 6.86 (s, 2H), 4.57 (s, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.23 – 3.16 (m, 2H), 2.95 – 2.87 (m, 2H), 2.22 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 198.36, 153.29, 150.63, 149.09, 133.08, 130.26, 128.63, 123.18, 122.79, 110.22 (d, J = 5.6 Hz), 110.08, 56.14, 40.66, 29.75, 16.06. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{23}O_4$ 315.1696, found 315.1600.

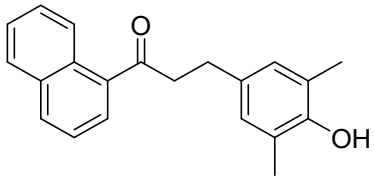
3-(4-hydroxy-3,5-dimethylphenyl)-1-(naphthalen-2-yl)propan-1-one (3al)



3al

Following the general procedure A. A yellow brown oily liquid. Isolated yield 86.4 mg, 71%.Purification by column chromatography on silica gel (petroleum ether/EtOAc: 15/1). **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.47 (s, 1H), 8.05 (dd, J = 8.6, 1.8 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.64 – 7.51 (m, 2H), 6.91 (s, 2H), 4.75 (s, 1H), 3.44 – 3.35 (m, 2H), 3.05 – 2.96 (m, 2H), 2.25 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 199.70, 150.69, 135.66, 134.29, 132.94, 132.62, 129.86, 129.65, 128.64, 128.54, 127.88, 126.86, 123.98, 123.27, 41.18, 29.56, 16.08. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}O_2$ 305.1542, found 305.1546.

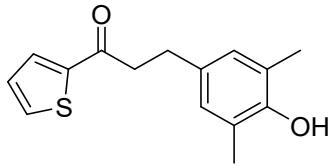
3-(4-hydroxy-3,5-dimethylphenyl)-1-(naphthalen-2-yl)propan-1-one (3am)



3am

Following the general procedure A. A light brown oily liquid. Isolated yield 76.6 mg, 63%.Purification by column chromatography on silica gel (petroleum ether/EtOAc: 15/1)**.** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 6.3 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.55 – 7.51 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 6.85 (s, 2H), 4.65 (s, 1H), 3.33 (t, *J* = 7.7 Hz, 2H), 3.00 (t, *J* = 7.7 Hz, 2H), 2.21 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 204.25, 150.64, 136.16, 134.04, 132.97 – 132.26 (m), 130.20, 128.80 (d, *J* = 11.6 Hz), 128.69 – 128.23 (m), 128.23 – 127.70 (m), 127.73 – 127.15 (m), 126.52, 126.02, 125.77, 124.82 – 123.99 (m), 123.19, 44.46, 29.96, 16.02 (d, *J* = 6.1 Hz). **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}O_2$ 305.1542, found 305.1548.

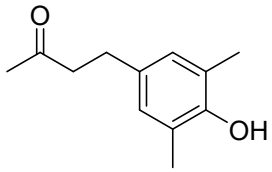
3-(4-hydroxy-3,5-dimethylphenyl)-1-(thiophen-2-yl)propan-1-one (3an)



3an

Following the general procedure A. A yellow oily liquid. Isolated yield 81.1 mg, 78%.Purification by column chromatography on silica gel (petroleum ether/EtOAc: 15/1)**.** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (dt, *J* = 3.8, 1.0 Hz, 1H), 7.63 (dt, *J* = 5.0, 1.0 Hz, 1H), 7.12 (ddd, *J* = 4.8, 3.8, 0.8 Hz, 1H), 6.86 (s, 2H), 4.73 (s, 1H), 3.22 – 3.15 (m, 2H), 2.97 – 2.91 (m, 2H), 2.23 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.73, 150.72, 144.31, 133.69, 132.58, 132.01, 128.61, 128.22, 123.27, 41.77, 29.72, 16.07. **HR-MS** (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}O_4$ 261.0949, found 261.0948.

4-(4-hydroxy-3,5-dimethylphenyl)butan-2-one（3ao）



3ao

Following the general procedure A. A light-yellow oily liquid. Isolated yield 23 mg, 31%. Purification by column chromatography on silica gel (petroleum ether/EtOAc: 15/1)**.** **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.79 (s, 2H), 4.86 (s, 1H), 2.81 – 2.67 (m, 4H), 2.22 (s, 6H), 2.14 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 208.89, 150.66, 132.48, 128.44, 123.26, 45.75, 30.18, 29.00, 16.05. **HR-MS** (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{16}O_2Na$ 215.1048, found 215.1056.

6. Cyclic voltammetry studies and control experiments

6.1 Cyclic voltammetry studies

Unless otherwise noted, the cyclic voltammograms were recorded on a CHI 760E instrument using a graphite sheet as the working electrode (10*15 *3 mm), a platinum sheet auxiliary electrode (10*15*0.1 mm) and a SCE as reference electrode,.Scan rate is 100 mV/s.

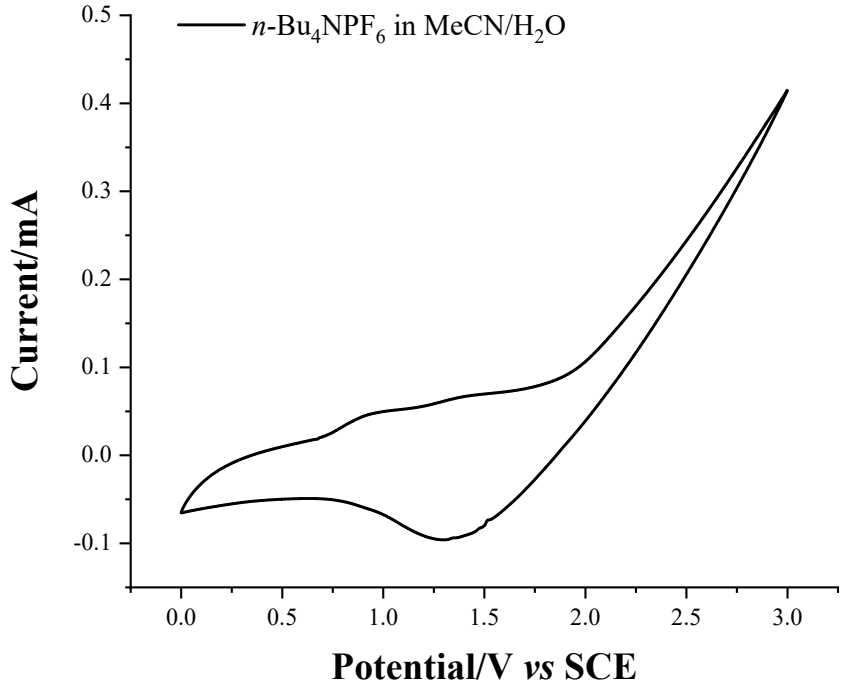


Figure S3. Cyclic voltammogram of *n*-Bu_4NPF_6 (0.1 M) in MeCN/H_2O (3/1).

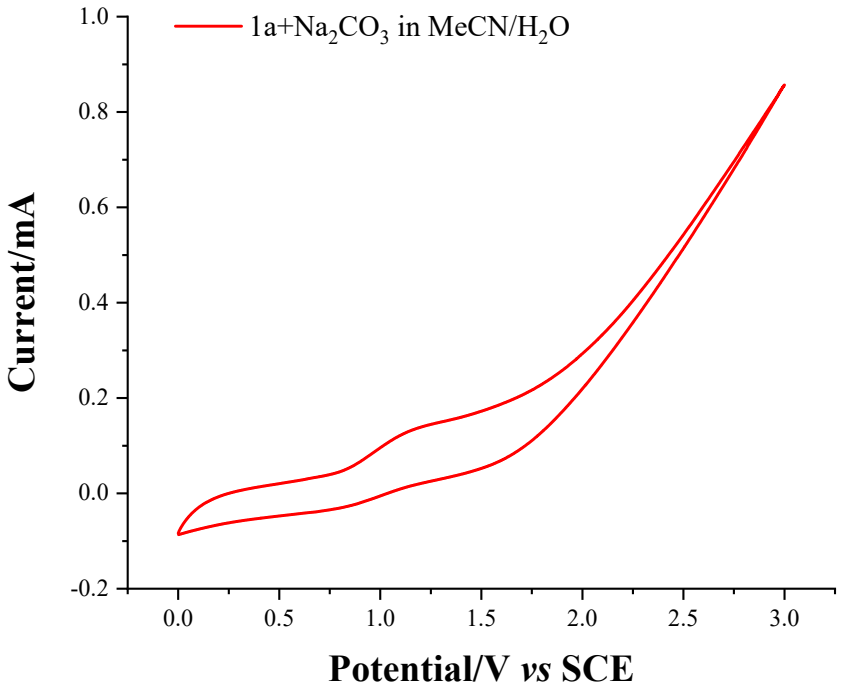


Figure S4. Cyclic voltammogram of **1a** (0.8 mmol) in an electrolyte of *n*-Bu_4NPF_6 (0.1 M) and Na_2CO_3 (0.4 mmol) in MeCN/H_2O (3/1). E_{oxi} = 1.18 V *vs.* SCE

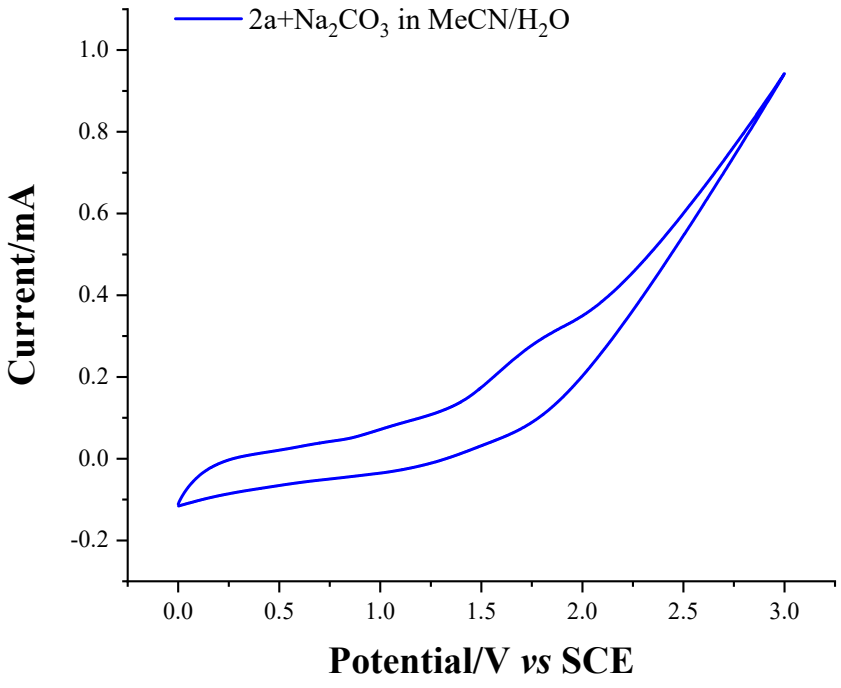


Figure S5. Cyclic voltammogram of **2a** (0.8 mmol) in an electrolyte of *n*-Bu_4NPF_6 (0.1 M) and Na_2CO_3 (0.4 mmol) in MeCN/H_2O (3/1). E_{oxi} = 1.76 V *vs.* SCE

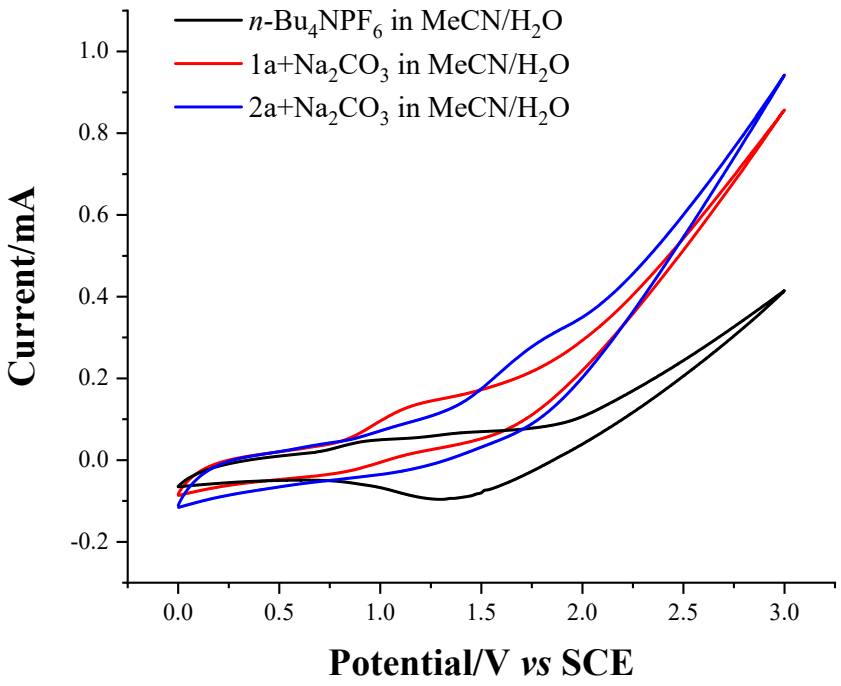
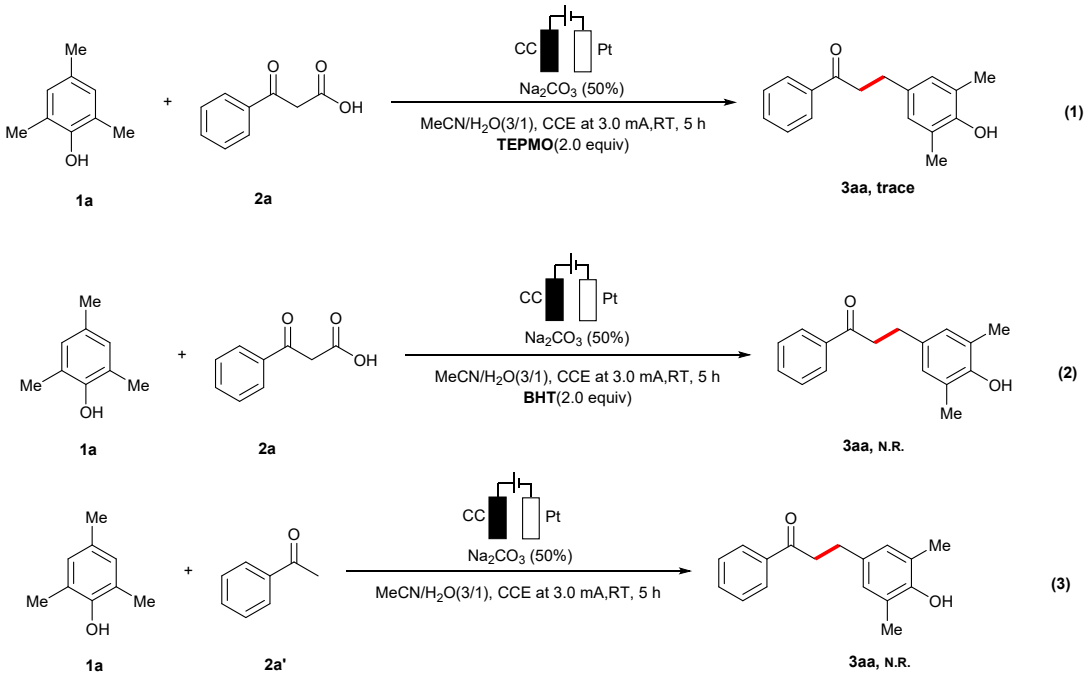


Figure S6. Cyclic voltammograms of *n*-Bu_4NPF_6 (0.1 M) in MeCN/H_2O (3/1) in (blank, black line), substrate **1a**+ Na_2CO_3 (red line), **2a**+ Na_2CO_3 (purple line),. Reference electrode: SCE, Scan rate = 100 mV/s.

Cyclic voltammetry experiments showed that in the presence of sodium carbonate, trimethylphenol **1a** exhibited a significant irreversible oxidation potential at 1.18 V (*vs.* SCE), whereas the oxidation potential of β-ketoacids **2a** was observed at a higher potential (E_{oxi} = 1.76 V *vs.* SCE). This result indicated that trimethylphenol **1a** was initially oxidized in a mixed solution of acetonitrile and H_2O. The mechanism of the reaction is also being further explored.



6.2 Control experiments

[a]Reaction conditions: undivided cell, Graphite anode, Pt cathode, **1a** (0.3 mmol), **2a** (0.6 mmol), Na_2CO_3 (0.5 equiv.), MeCN/H_2O (3/1, 4 mL), CCE = 3.0 mA, 5 h, RT, under air. CCE = constant current electrolysis.

In free radical validation experiments, only trace amount of the desired product were obtained when 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) was added, whereas when BHT (2,6-di-tert-butyl-4-methylphenol) was added as in radical trapping agent, the reaction did not take place. When we replaced β-phenylketo acid by acetophenone, target product could not be observed too, which indicates that acetophenone is not an intermediate product of β-phenylketo acid.

7. References

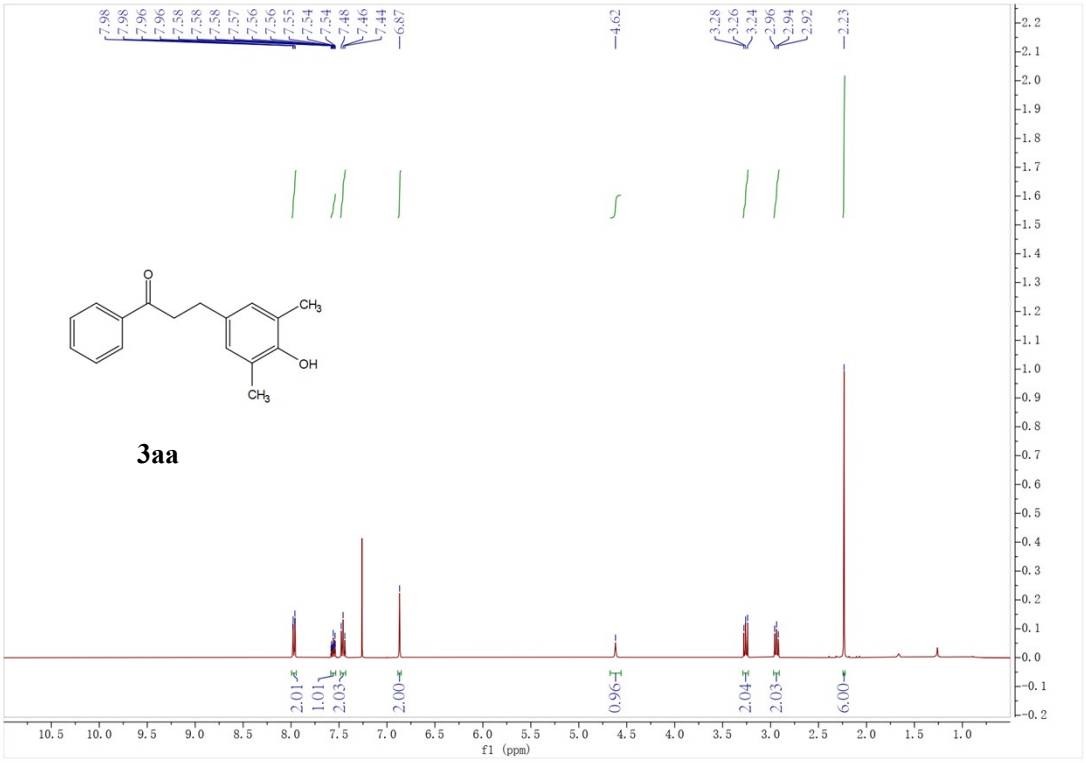
[1] Xu X, Chen H, He J, et al. Copper-Catalysed Decarboxylative Trifluoromethylation of β-Ketoacids[J]. Chinese Journal of Chemistry, 2017, 35(11): 1665-1668

[2] Jiang C, Chen Y, Huang G, et al. Scandium (III)-Catalysed Decarboxylative Addition of β-Ketoacids to para-Quinone Methides: Evidence for 1, 6-Addition and Base-Assisted Decarboxylation Tandem Process[J]. Asian Journal of Organic Chemistry, 2019, 8(2): 257-260.

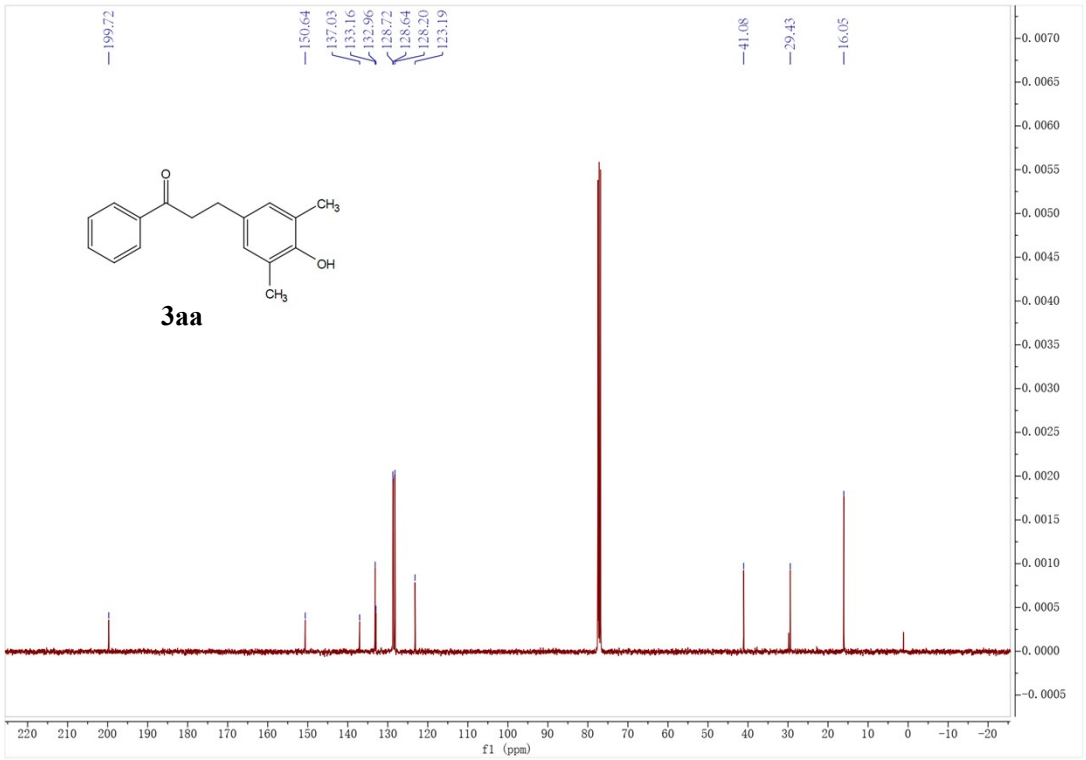
[3] Egami H, Ide T, Kawato Y, et al. Benzylic C–H trifluoromethylation of phenol derivatives[J]. Chemical Communications, 2015, 51(93): 16675-16678.

[4] Luo S, Luo F X, Zhang X S, et al. Synthesis of Dibenzopyranones through Palladium-Catalyzed Directed C–H Activation/Carbonylation of 2-Arylphenols[J]. Angewandte Chemie International Edition, 2013, 52(40): 10598-10601.

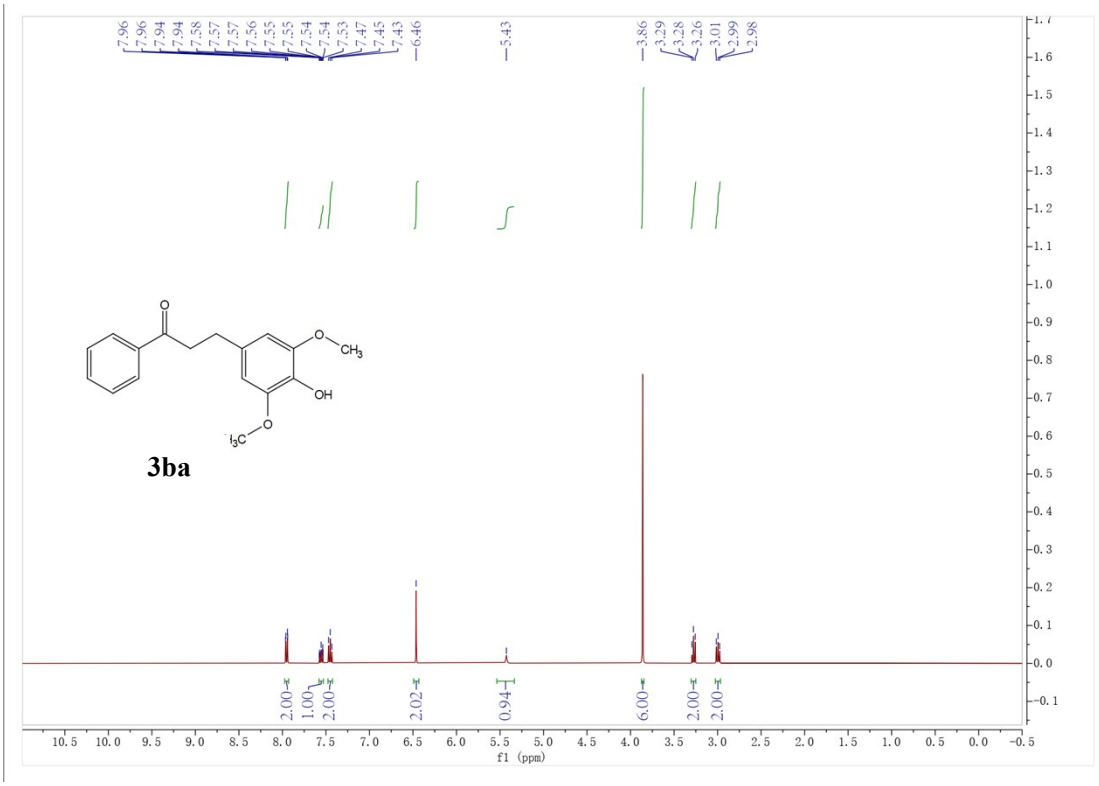
8. ^{1}H and ^{13}C-NMR spectra



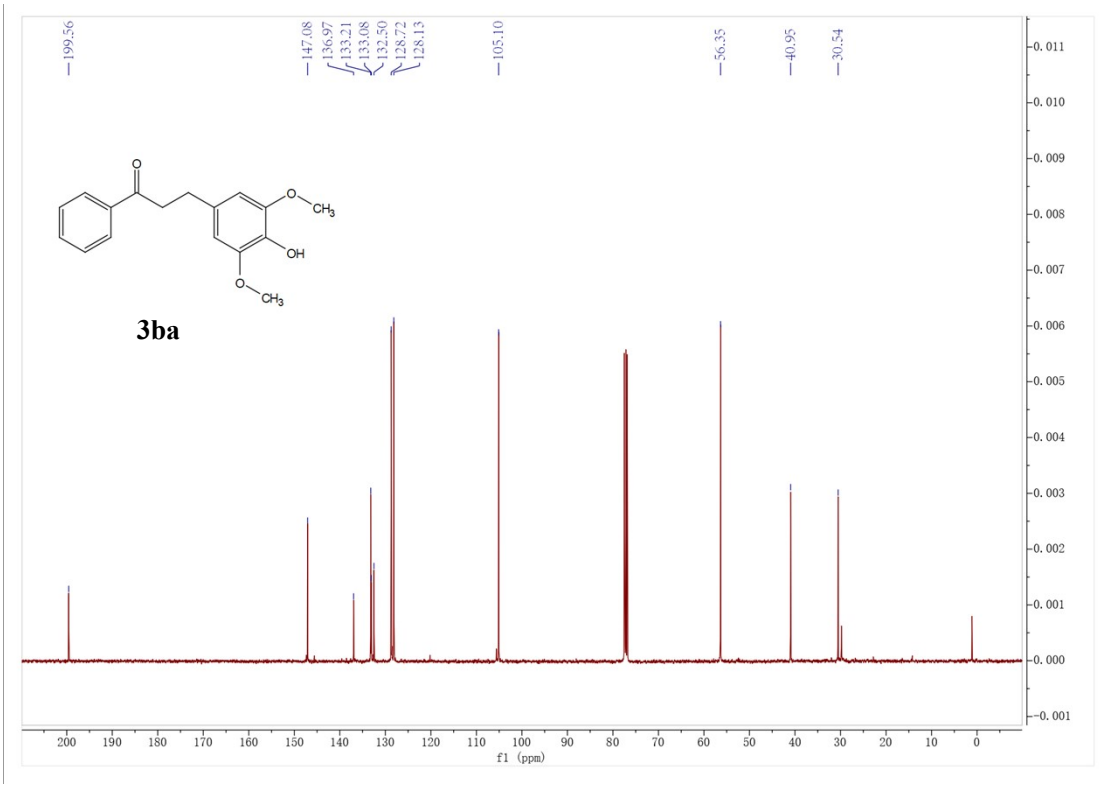
^{1}H NMR spectrum of **3aa** ($CDCl_3$, 400 MHz)



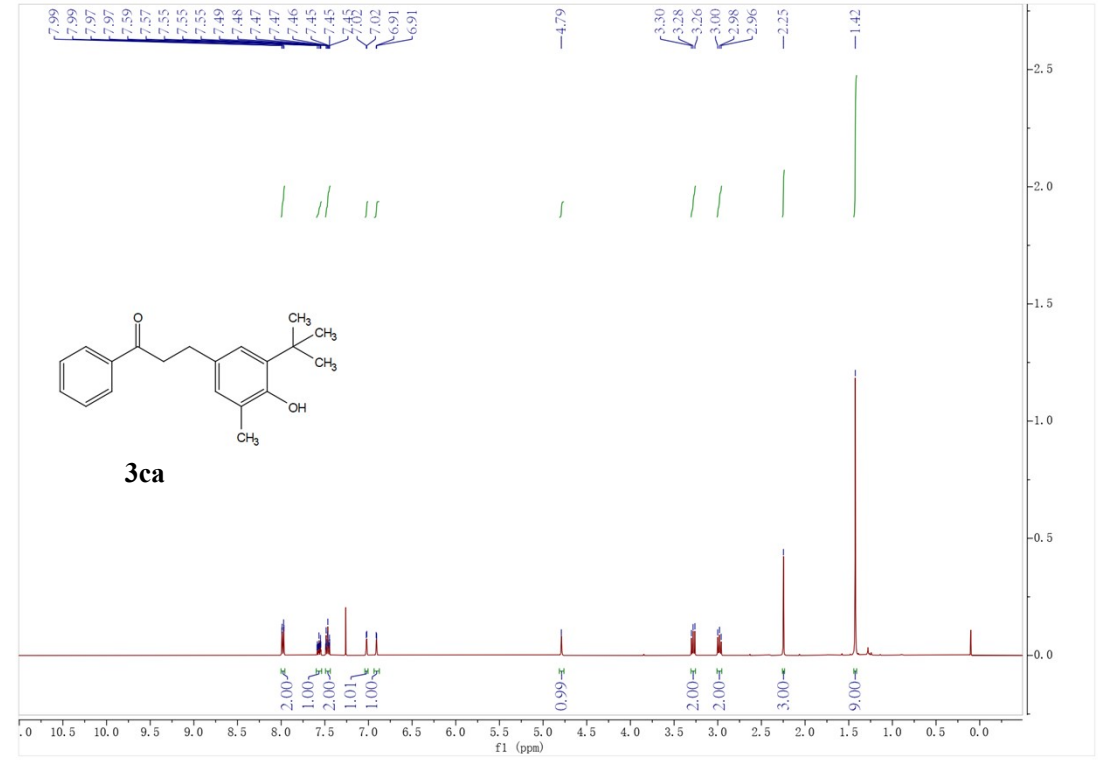
^{13}C NMR spectrum of **3aa** ($CDCl_3$, 101 MHz)



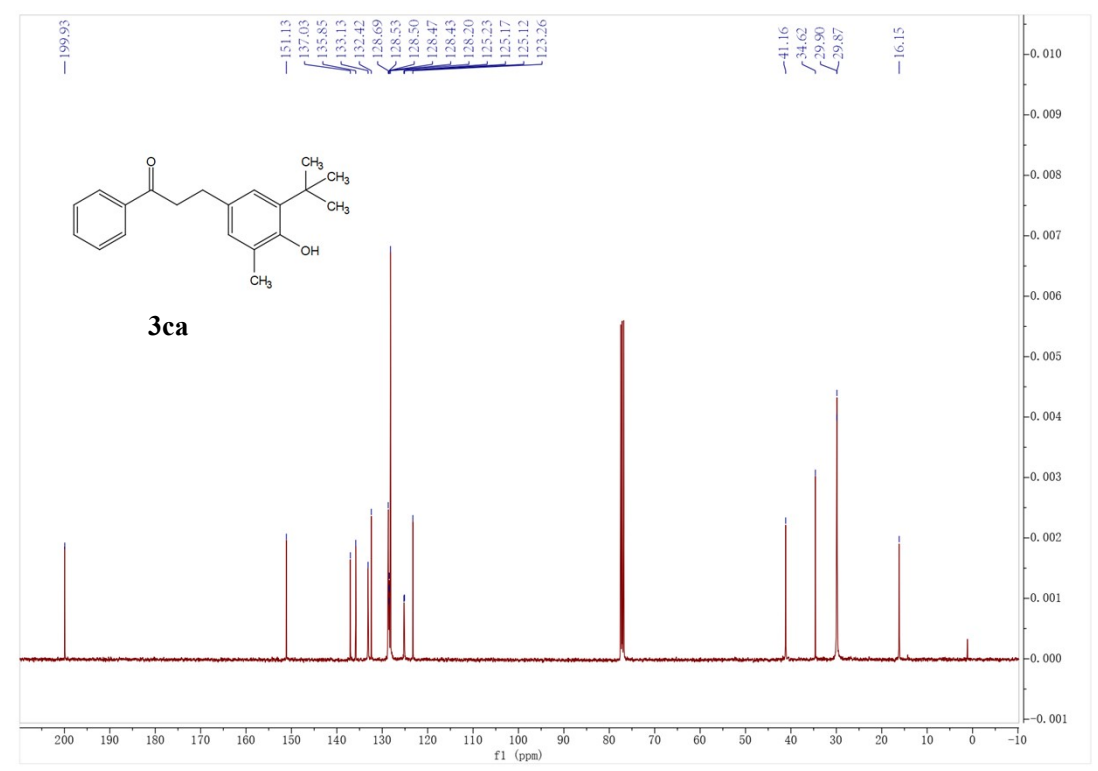
^{1}H NMR spectrum of **3ba** ($CDCl_3$, 400 MHz)



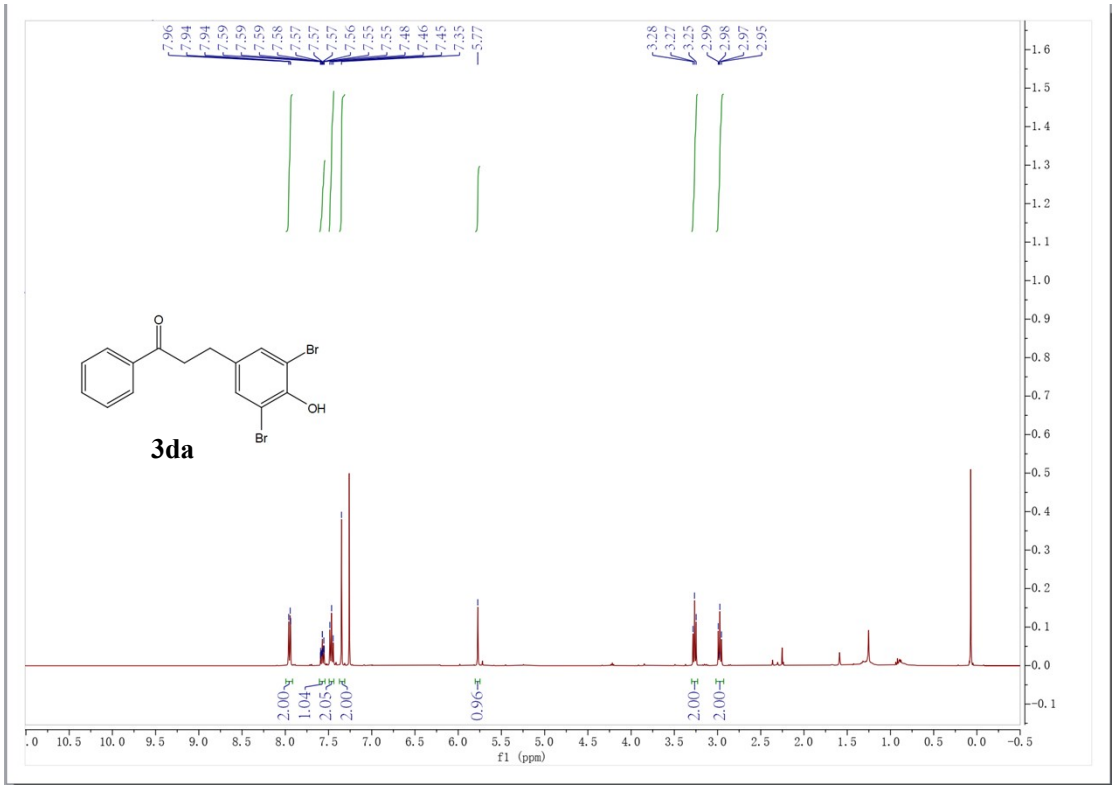
^{13}C NMR spectrum of **3ba** ($CDCl_3$, 101 MHz)



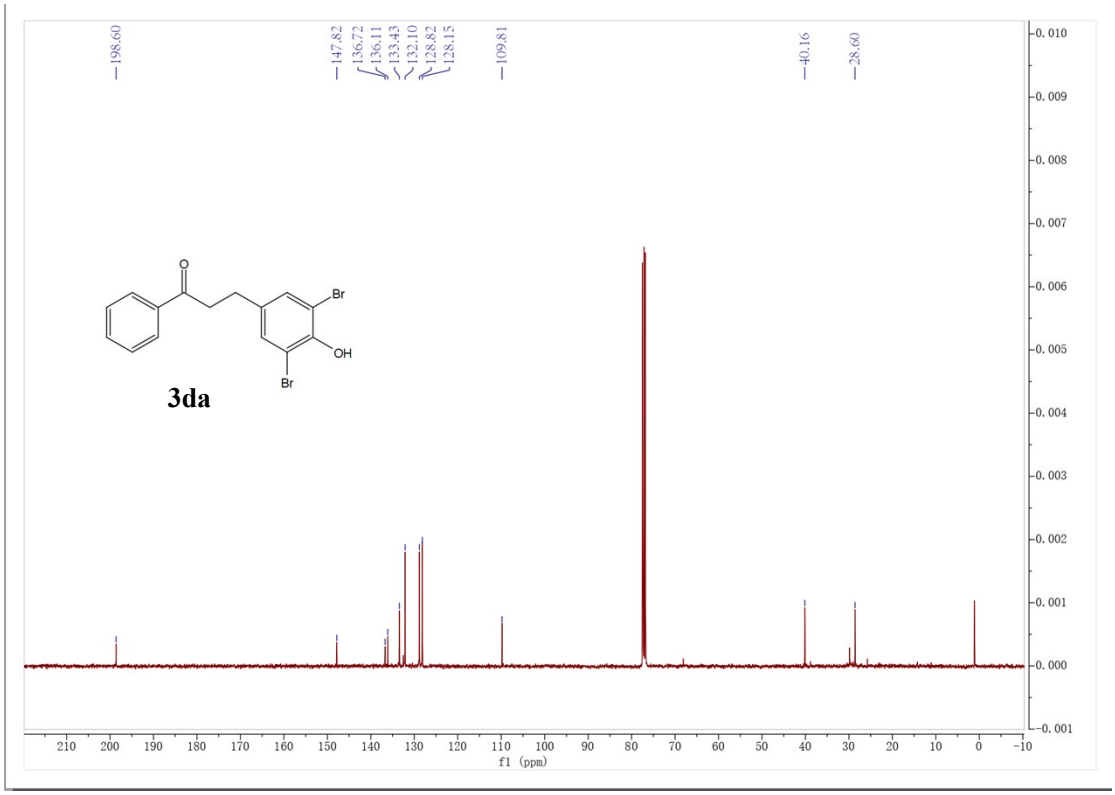
^{1}H NMR spectrum of **3ca** ($CDCl_3$, 400 MHz)



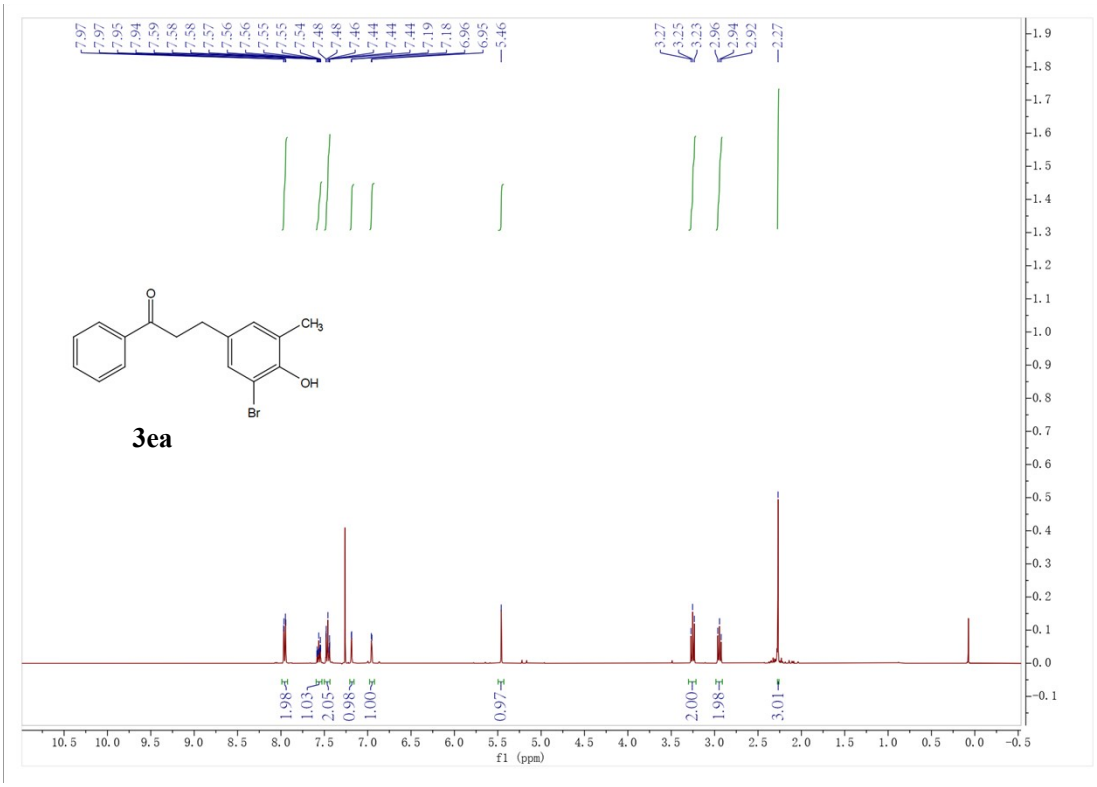
^{13}C NMR spectrum of **3ca** ($CDCl_3$, 101 MHz)



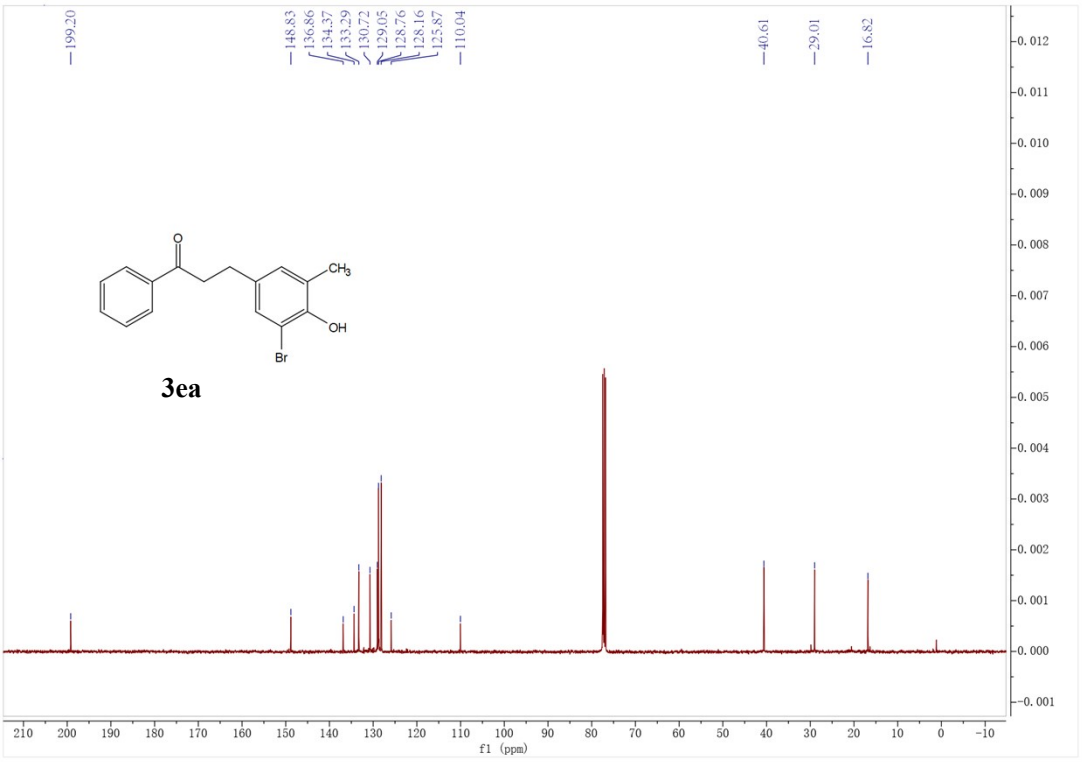
^{1}H NMR spectrum of **3da** ($CDCl_3$, 400 MHz)



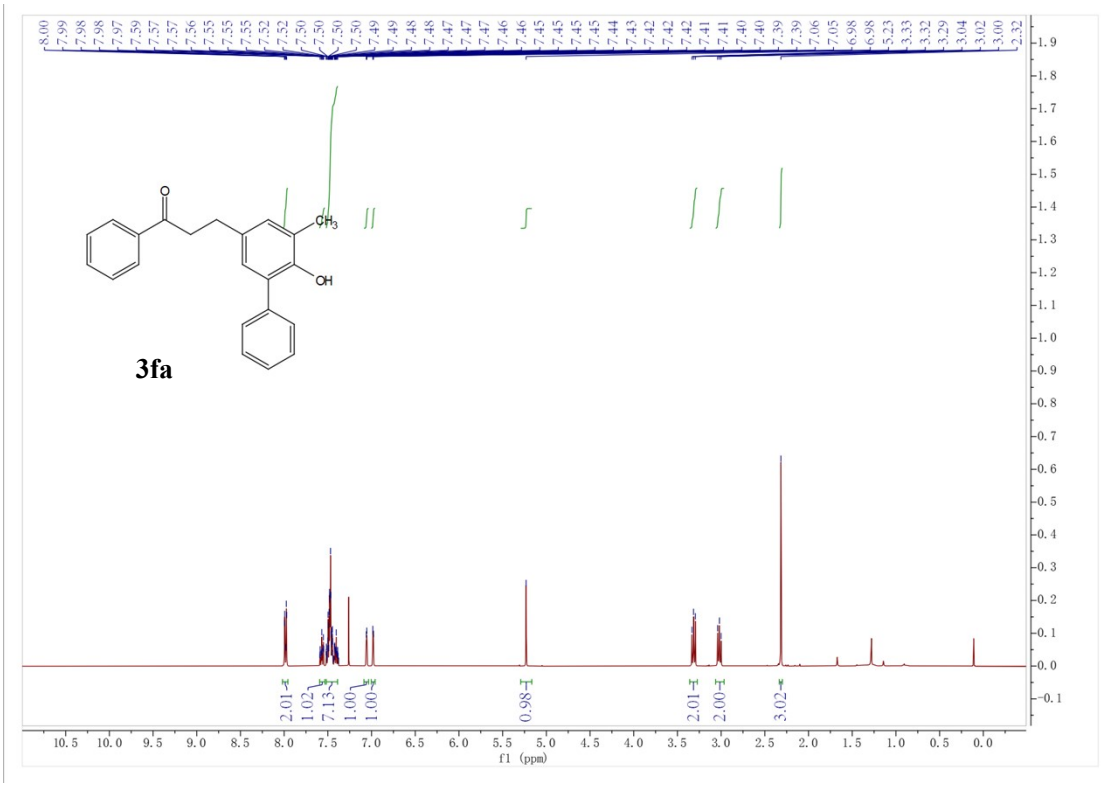
^{13}C NMR spectrum of **3da** ($CDCl_3$, 101 MHz)



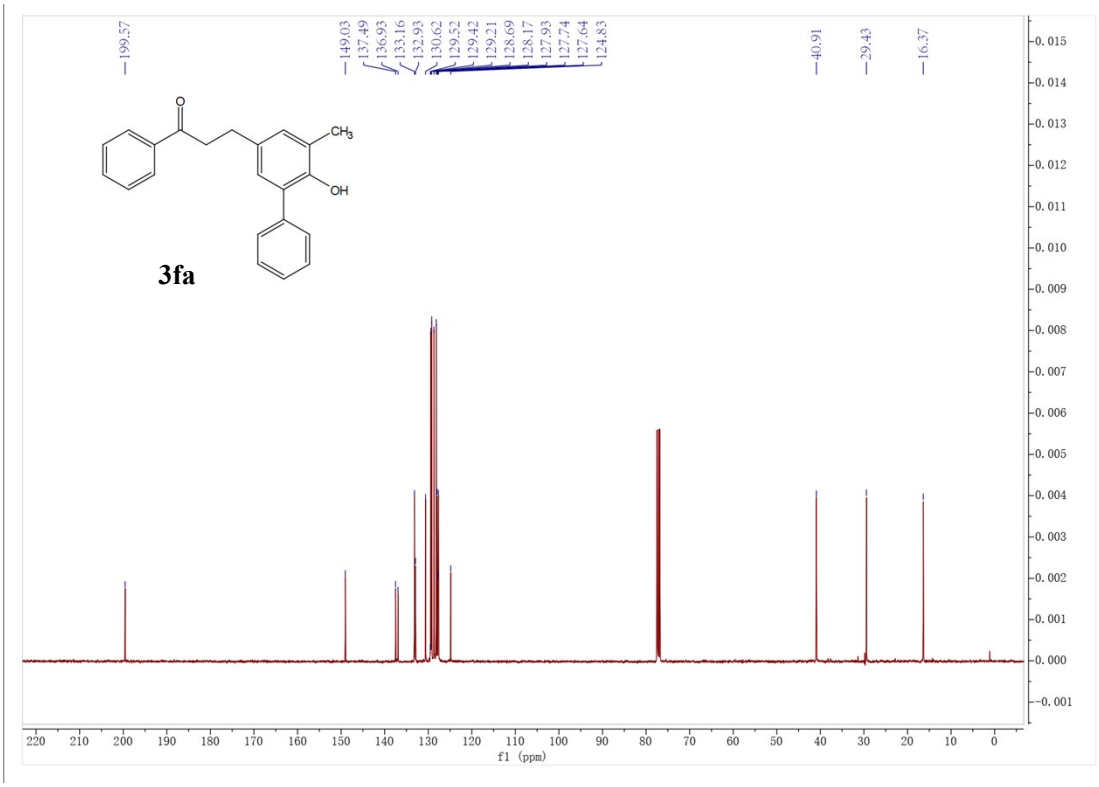
^{1}H NMR spectrum of **3ea** ($CDCl_3$, 400 MHz)



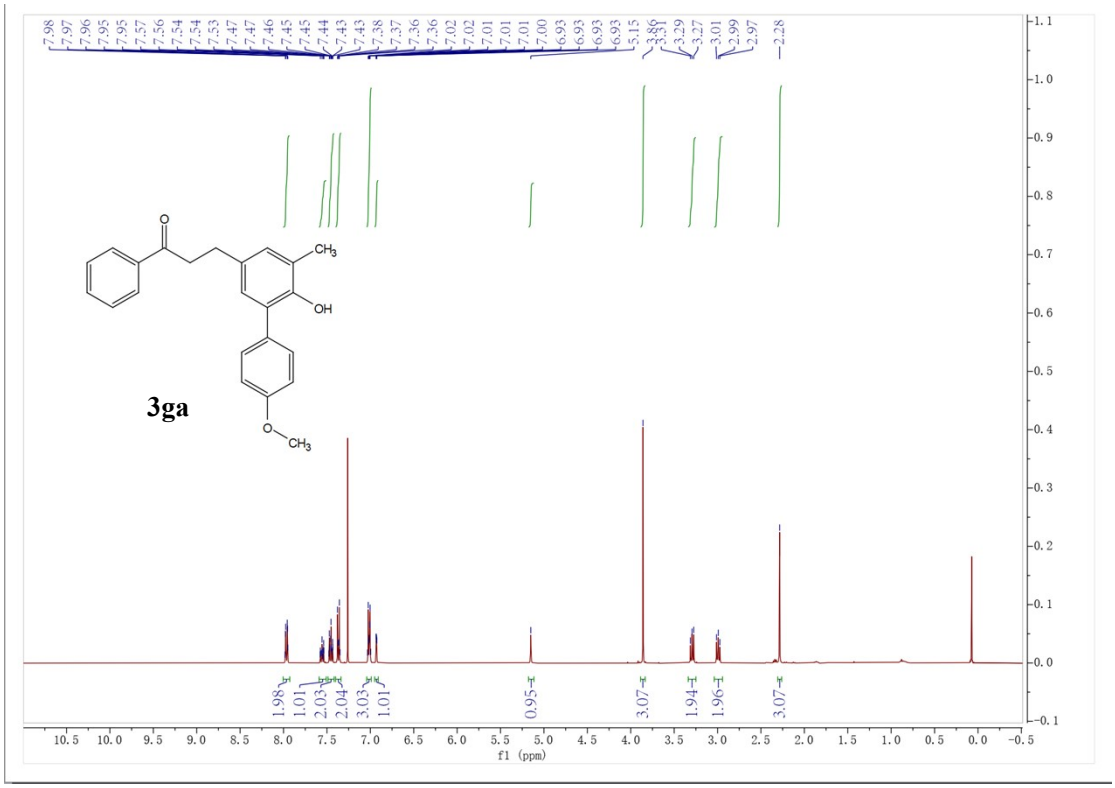
^{13}C NMR spectrum of **3ea** ($CDCl_3$, 101 MHz)



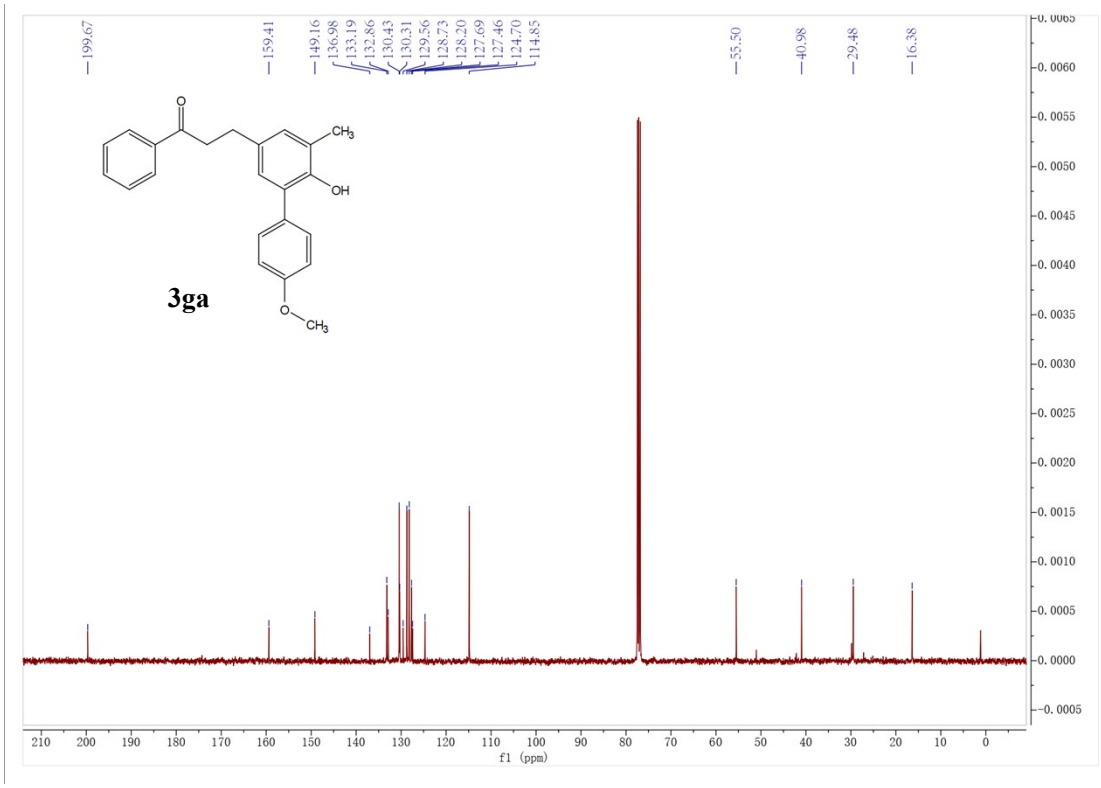
^{1}H NMR spectrum of **3fa** ($CDCl_3$, 400 MHz)



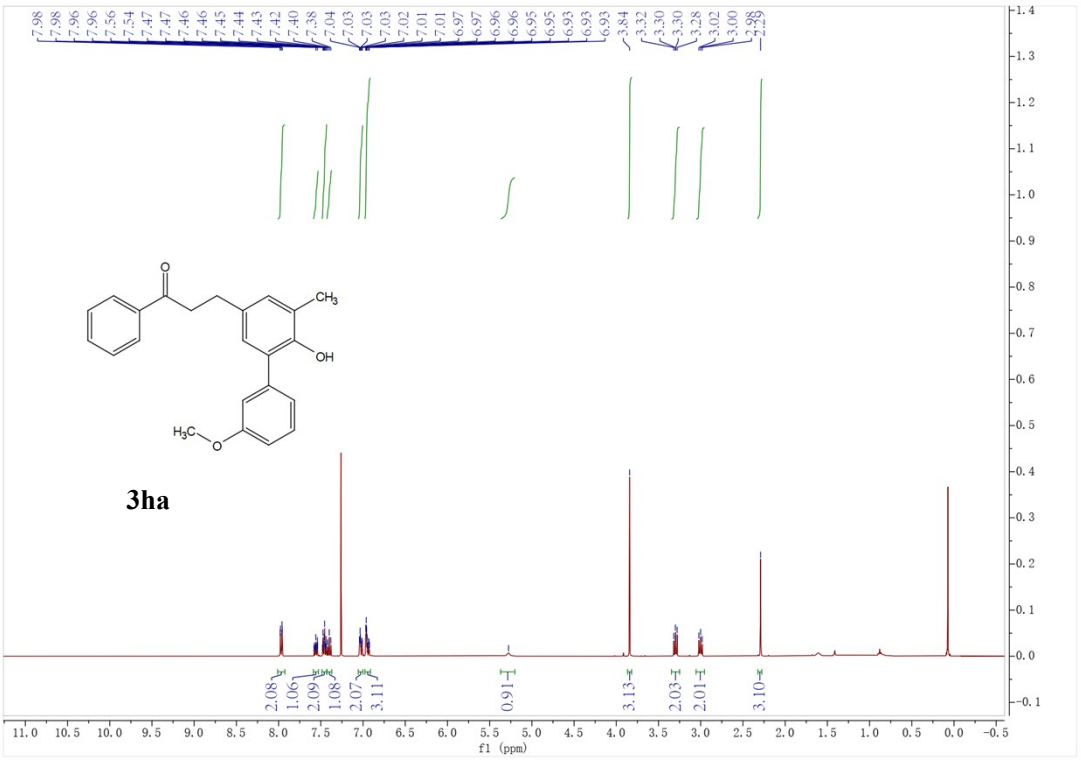
^{13}C NMR spectrum of **3fa** ($CDCl_3$, 101 MHz)



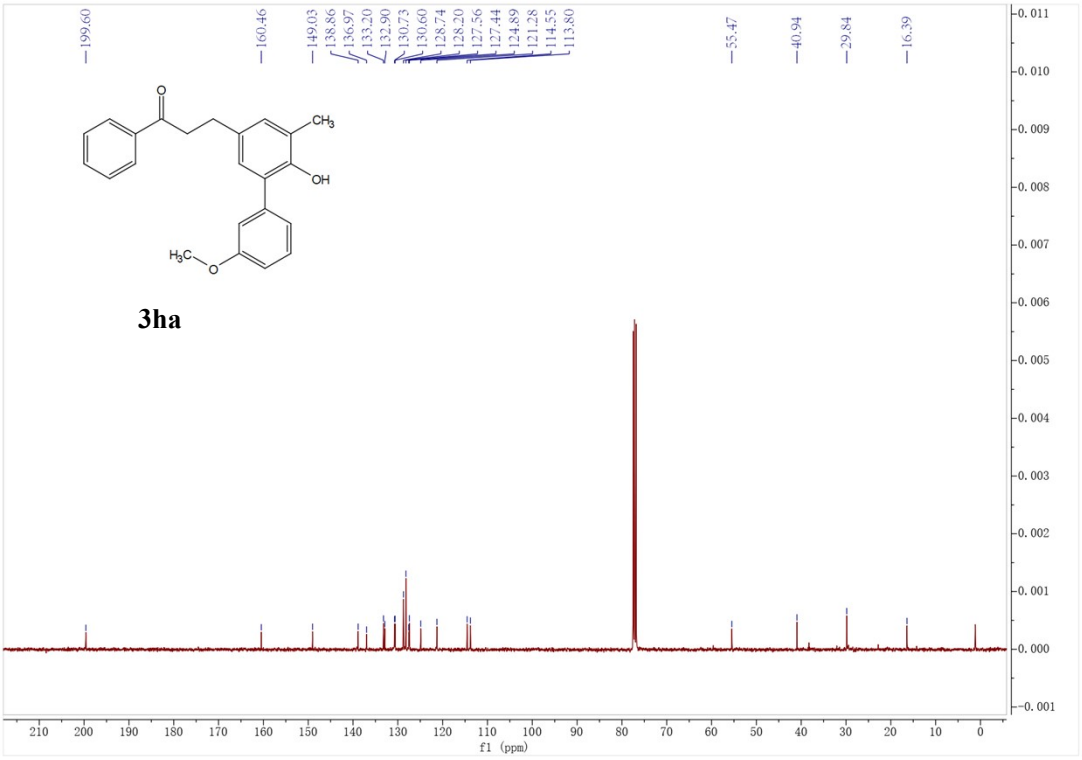
^{1}H NMR spectrum of **3ga** ($CDCl_3$, 400 MHz)



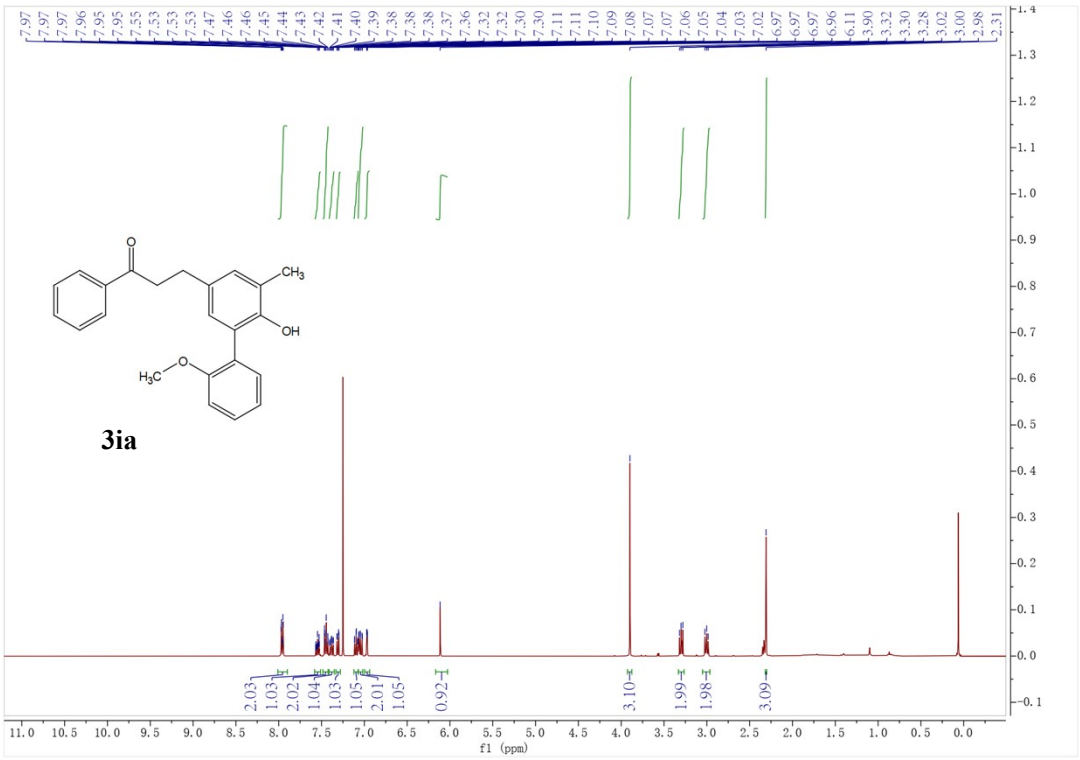
^{13}C NMR spectrum of **3ga** ($CDCl_3$, 101 MHz)



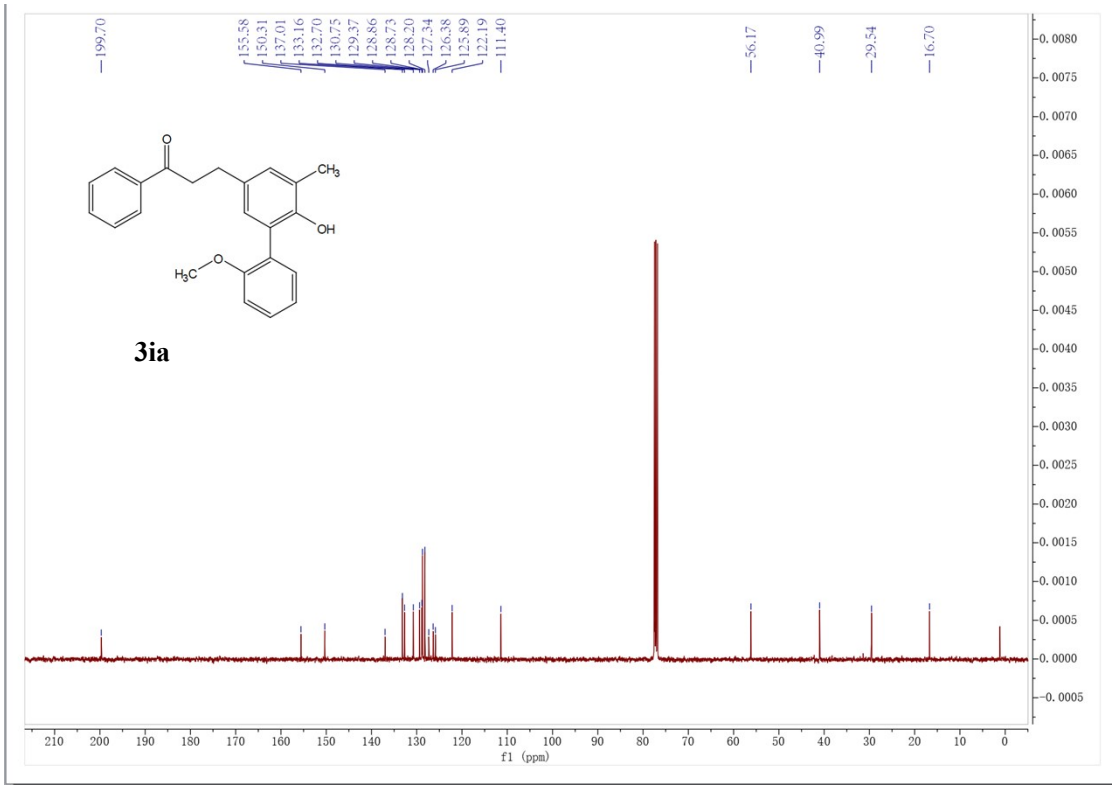
^{1}H NMR spectrum of **3ha** ($CDCl_3$, 400 MHz)



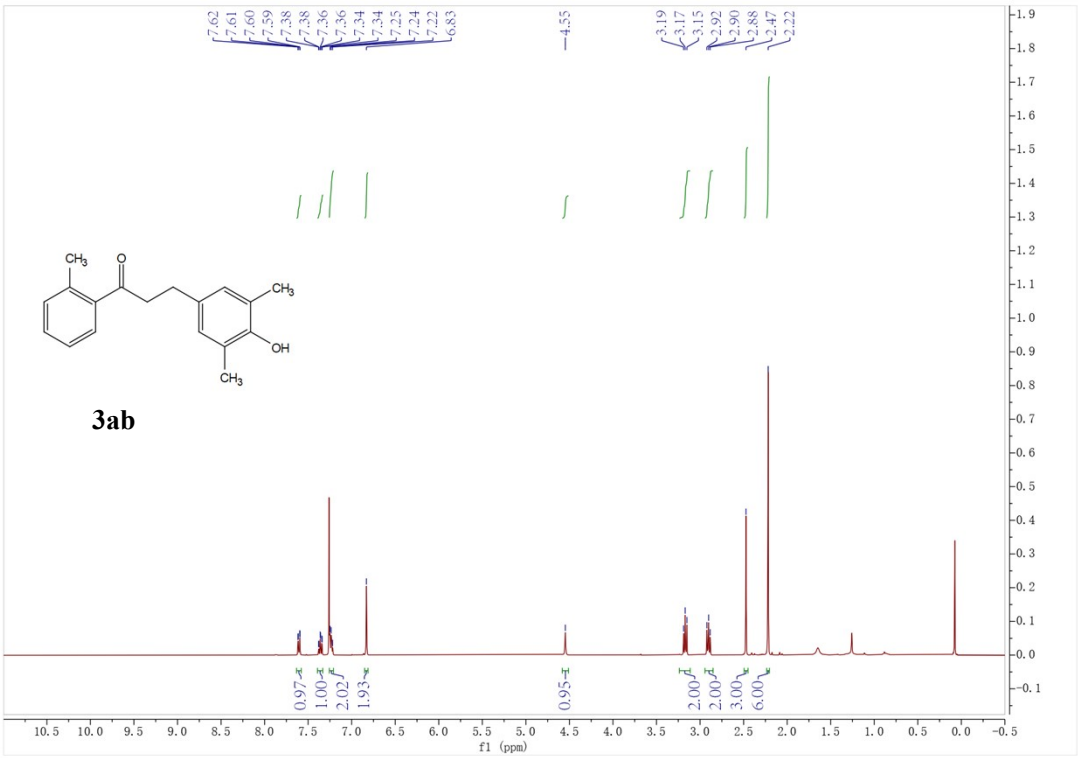
^{13}C NMR spectrum of **3ha** ($CDCl_3$, 101 MHz)



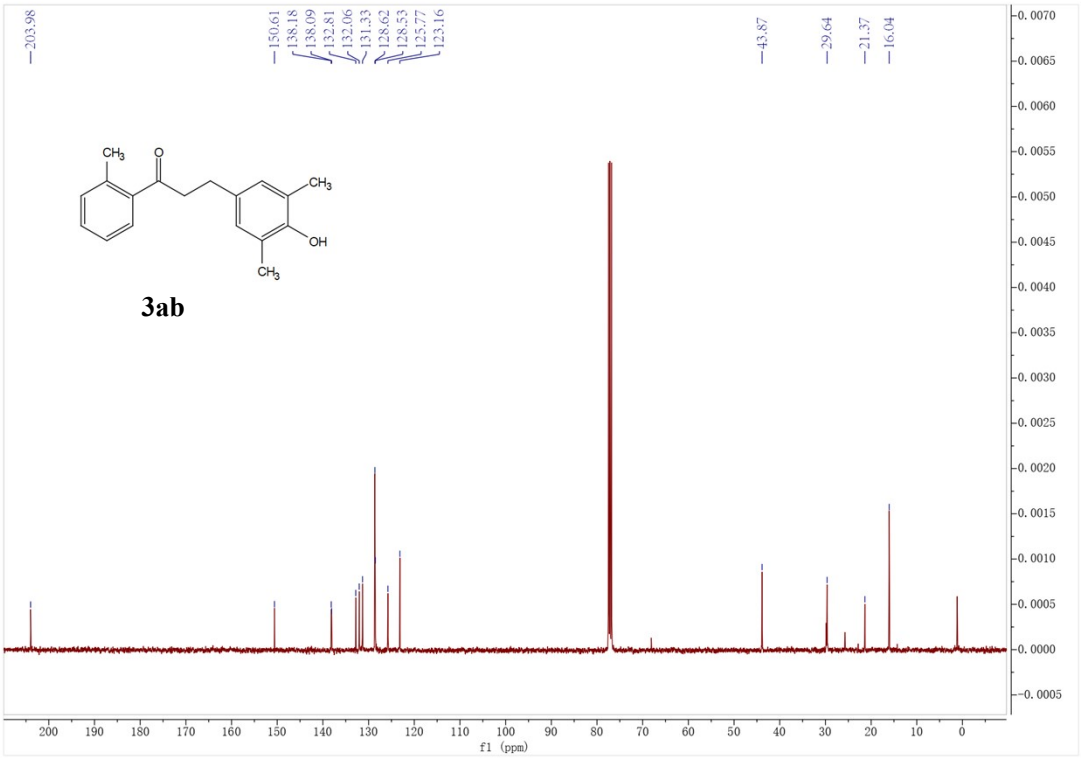
^{1}H NMR spectrum of **3ia** ($CDCl_3$, 400 MHz)



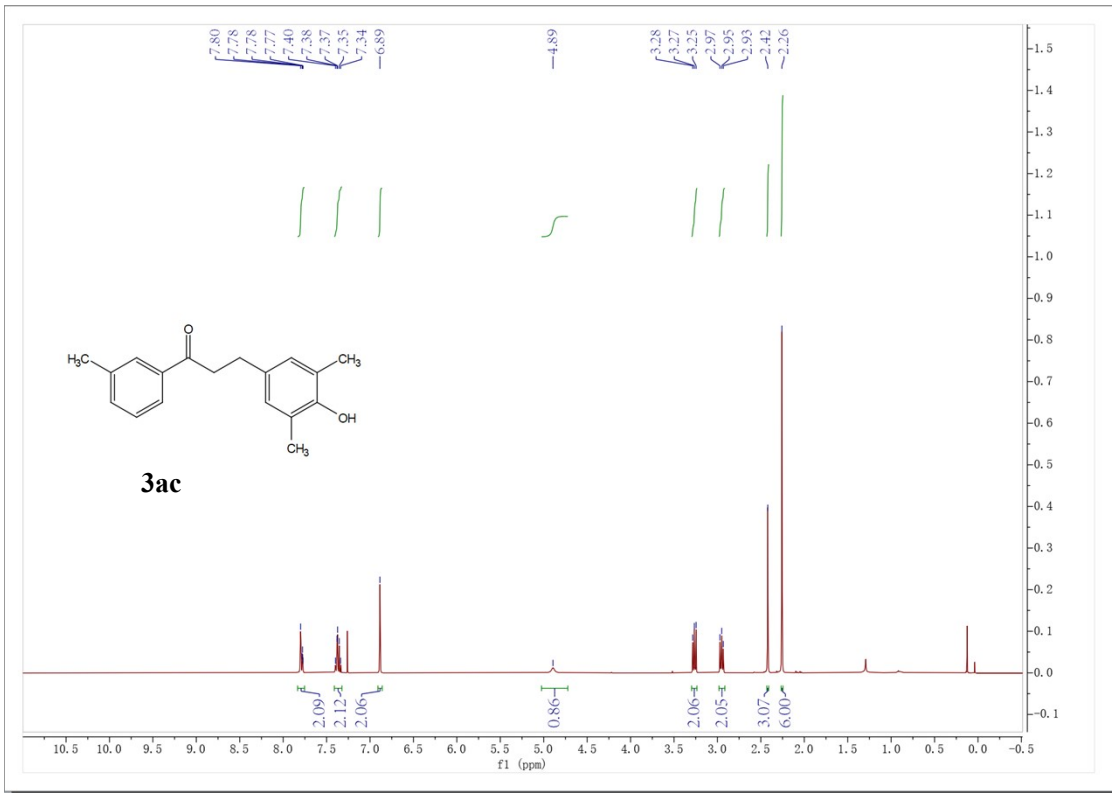
^{13}C NMR spectrum of **3ia** ($CDCl_3$, 101 MHz)



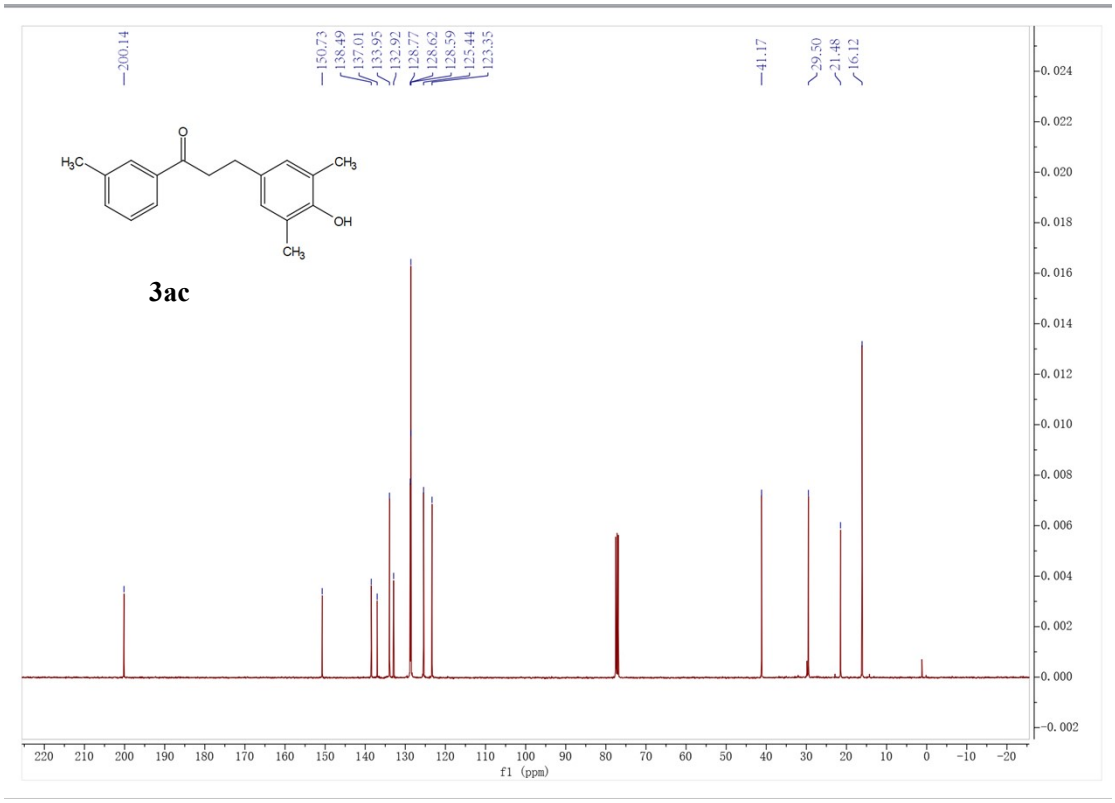
^{1}H NMR spectrum of **3ab** ($CDCl_3$, 400 MHz)



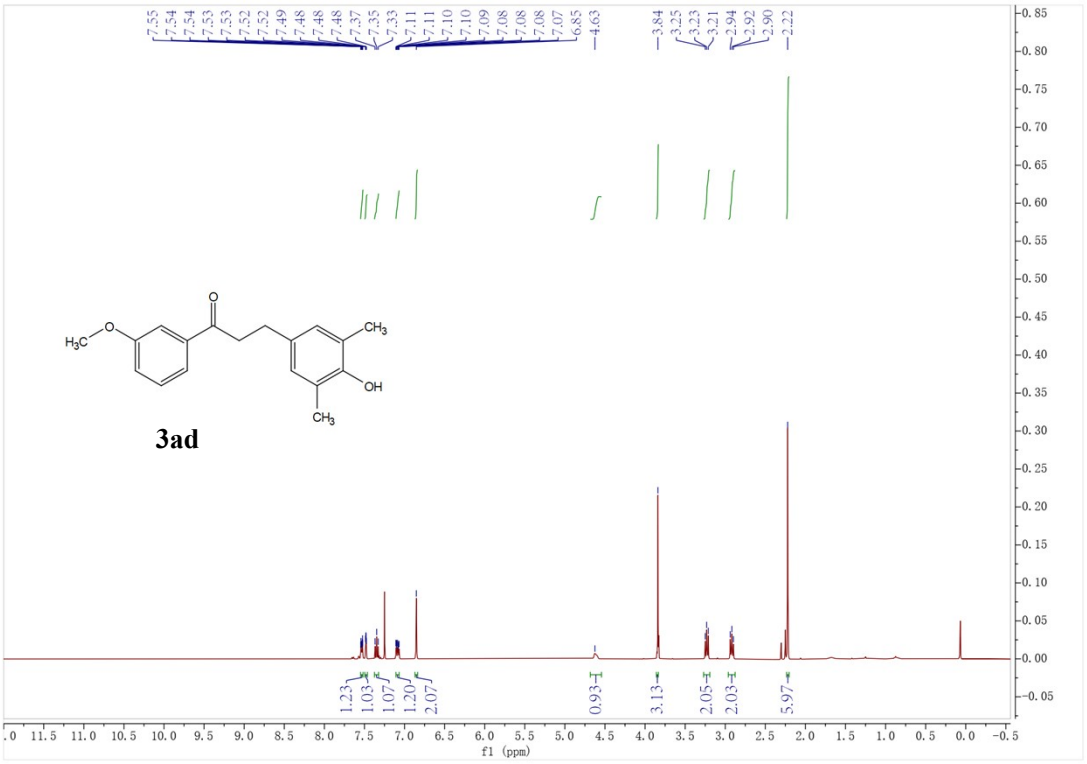
^{13}C NMR spectrum of **3ab** ($CDCl_3$, 101 MHz)



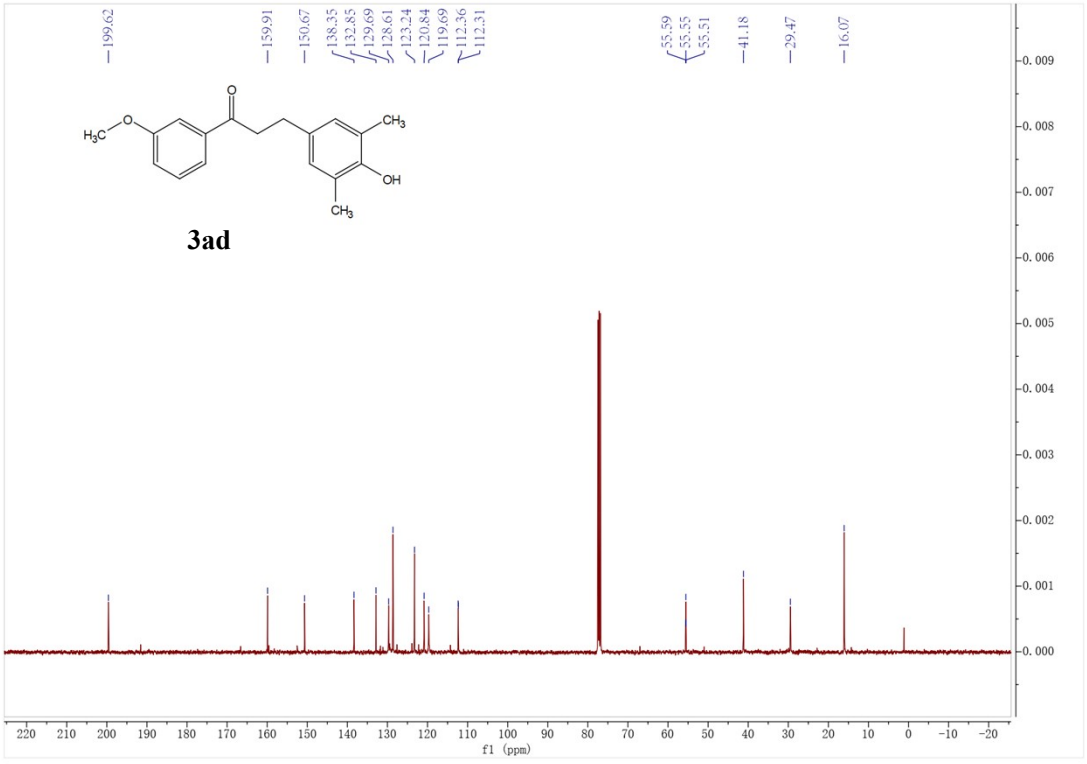
^{1}H NMR spectrum of **3ac** ($CDCl_3$, 400 MHz)



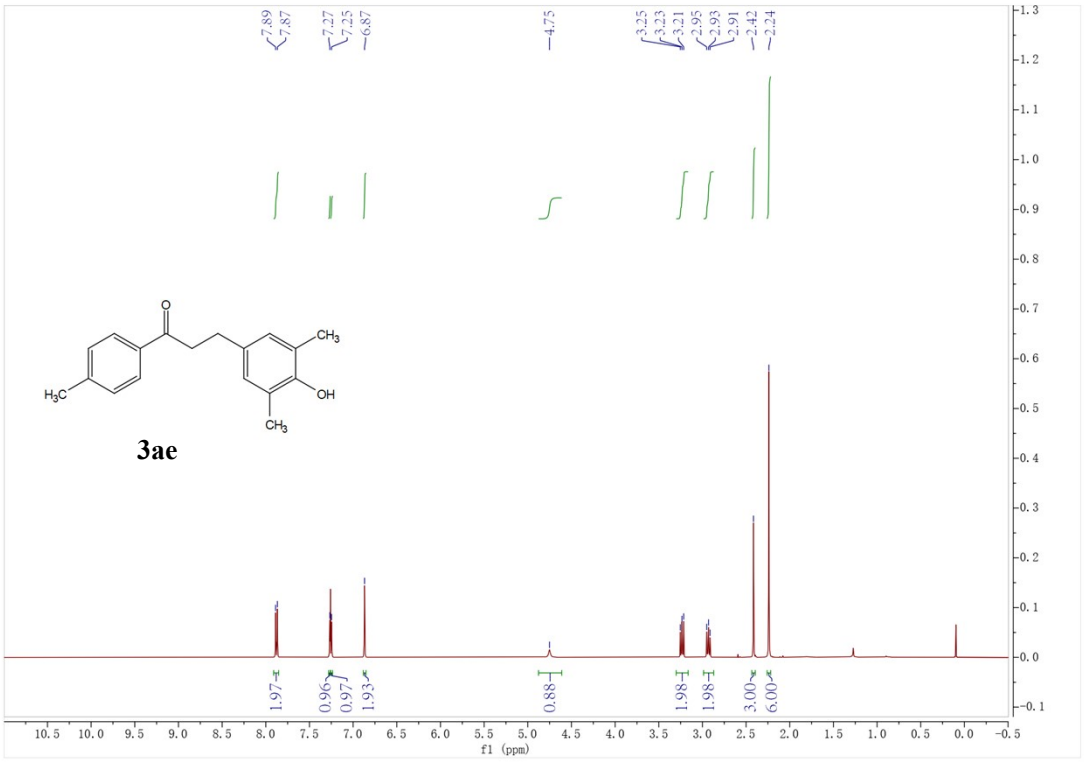
^{13}C NMR spectrum of **3ac** ($CDCl_3$, 101 MHz)



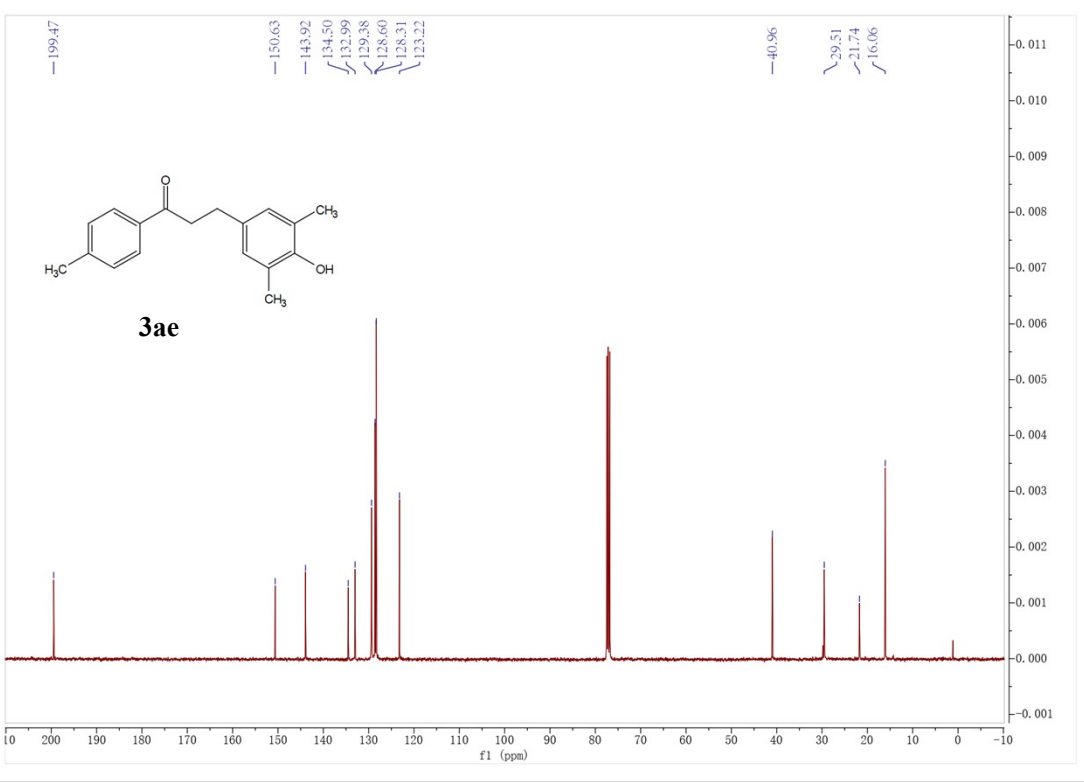
^{1}H NMR spectrum of **3ad** ($CDCl_3$, 400 MHz)



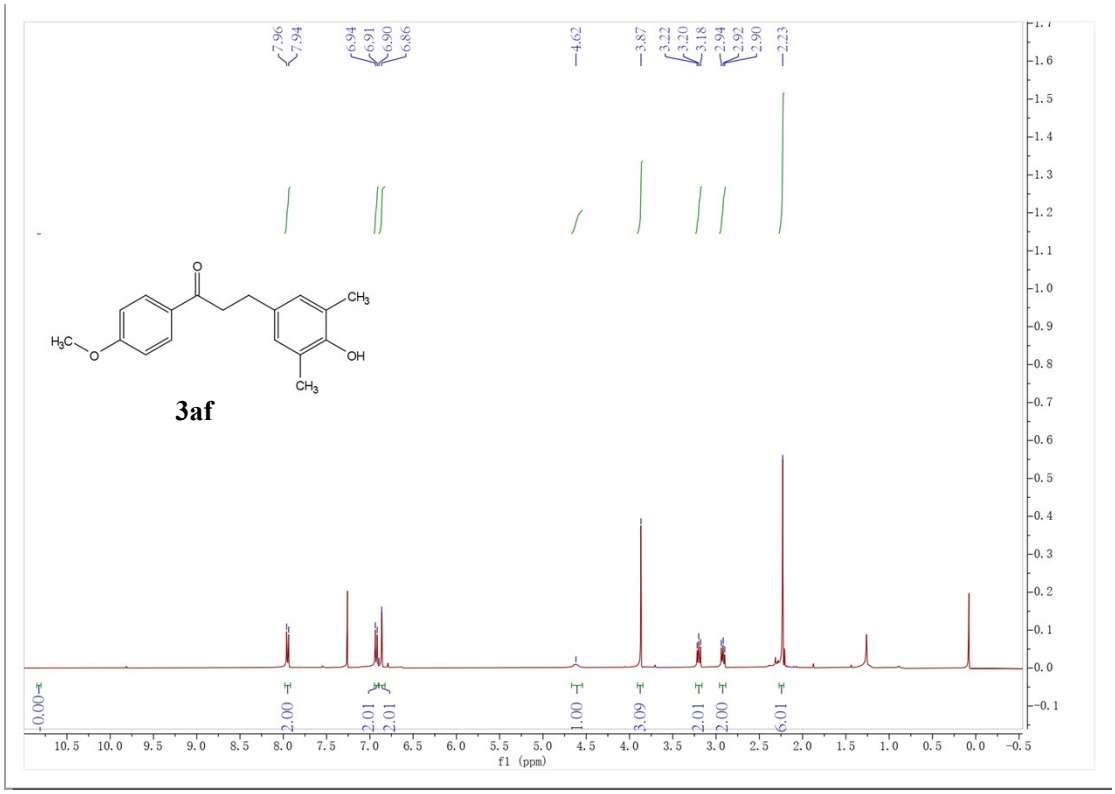
^{13}C NMR spectrum of **3ad** ($CDCl_3$, 101 MHz)



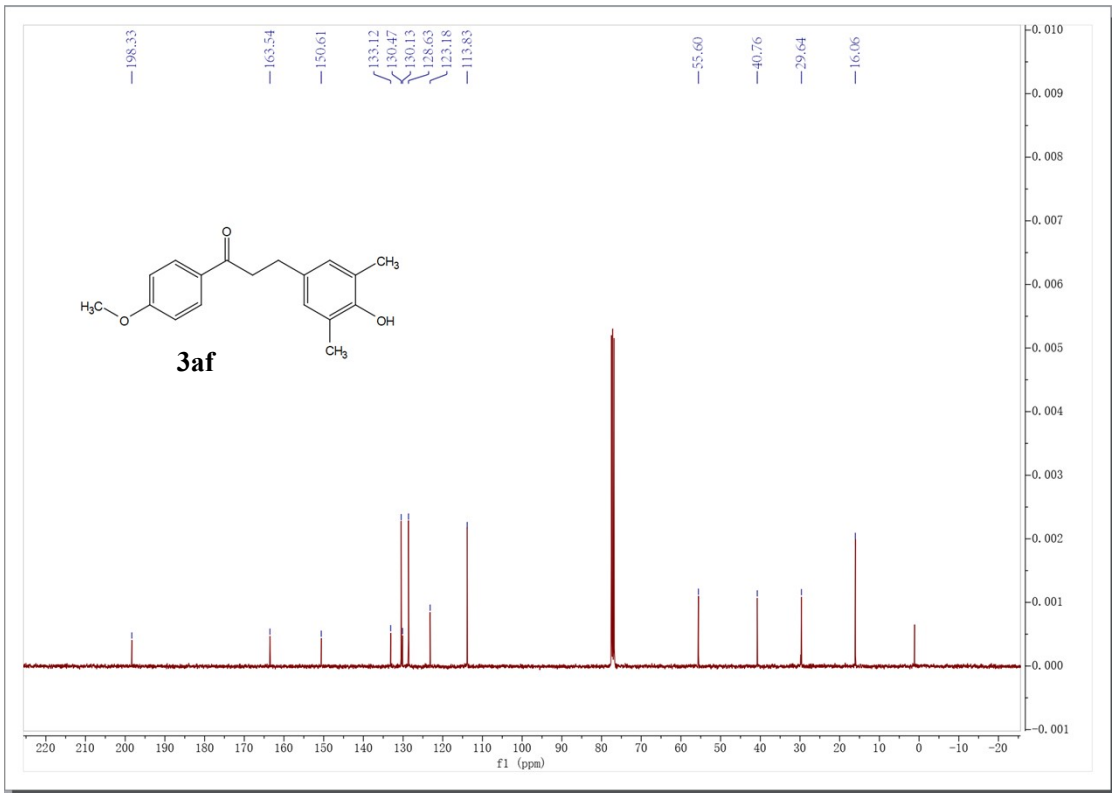
^{1}H NMR spectrum of **3ae** ($CDCl_3$, 400 MHz)



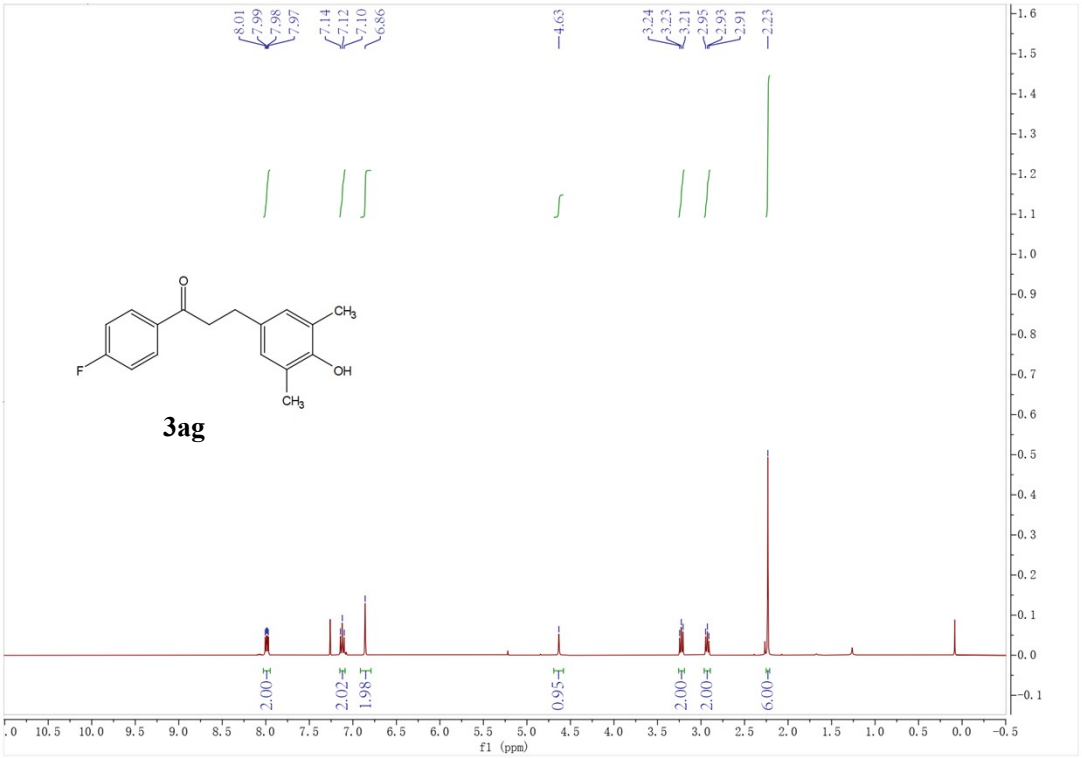
^{13}C NMR spectrum of **3ae** ($CDCl_3$, 101 MHz)



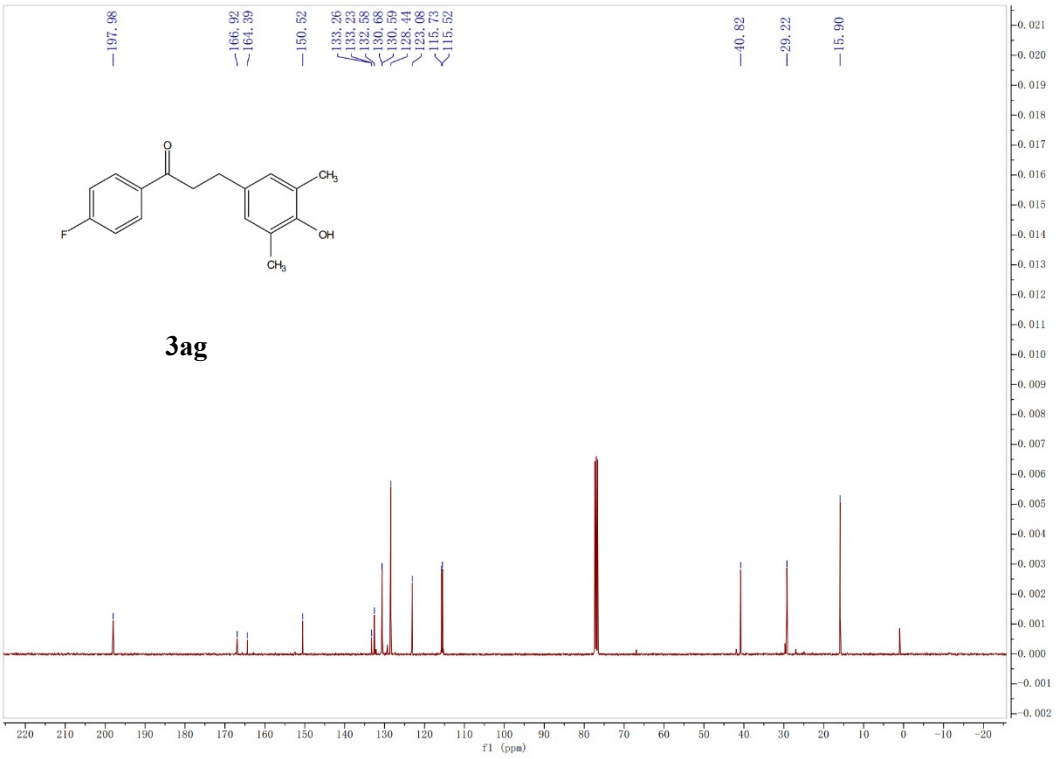
^{1}H NMR spectrum of **3af** ($CDCl_3$, 400 MHz)



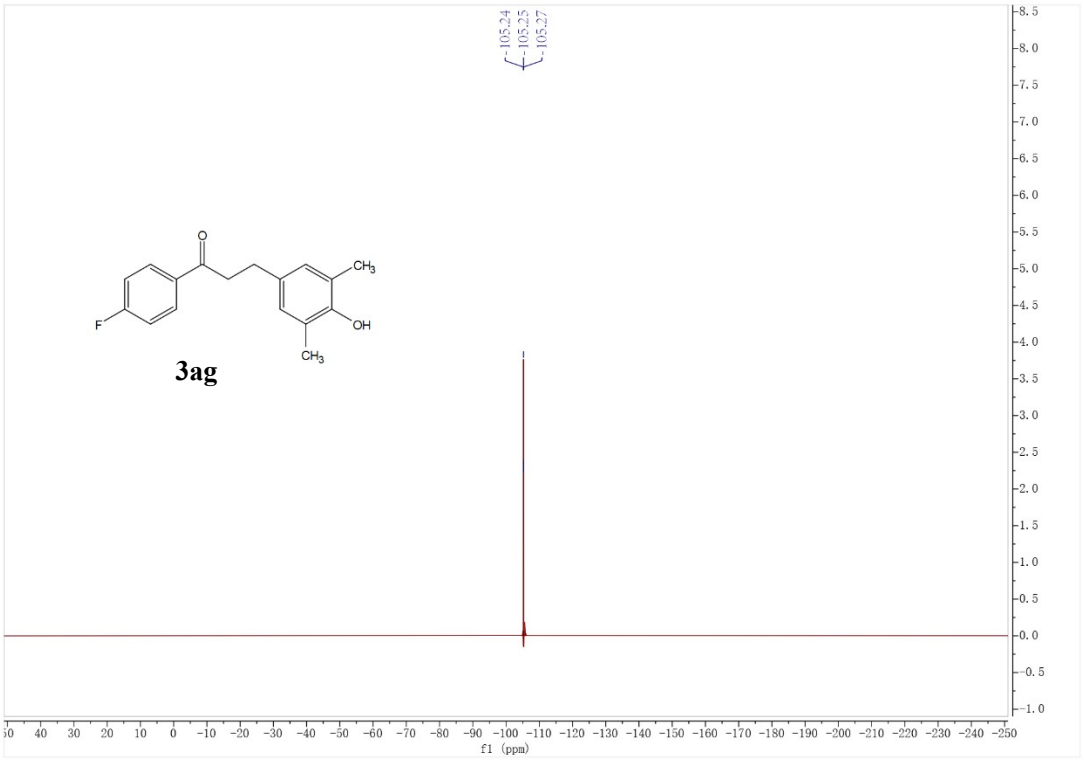
^{13}C NMR spectrum of **3af** ($CDCl_3$, 101 MHz)



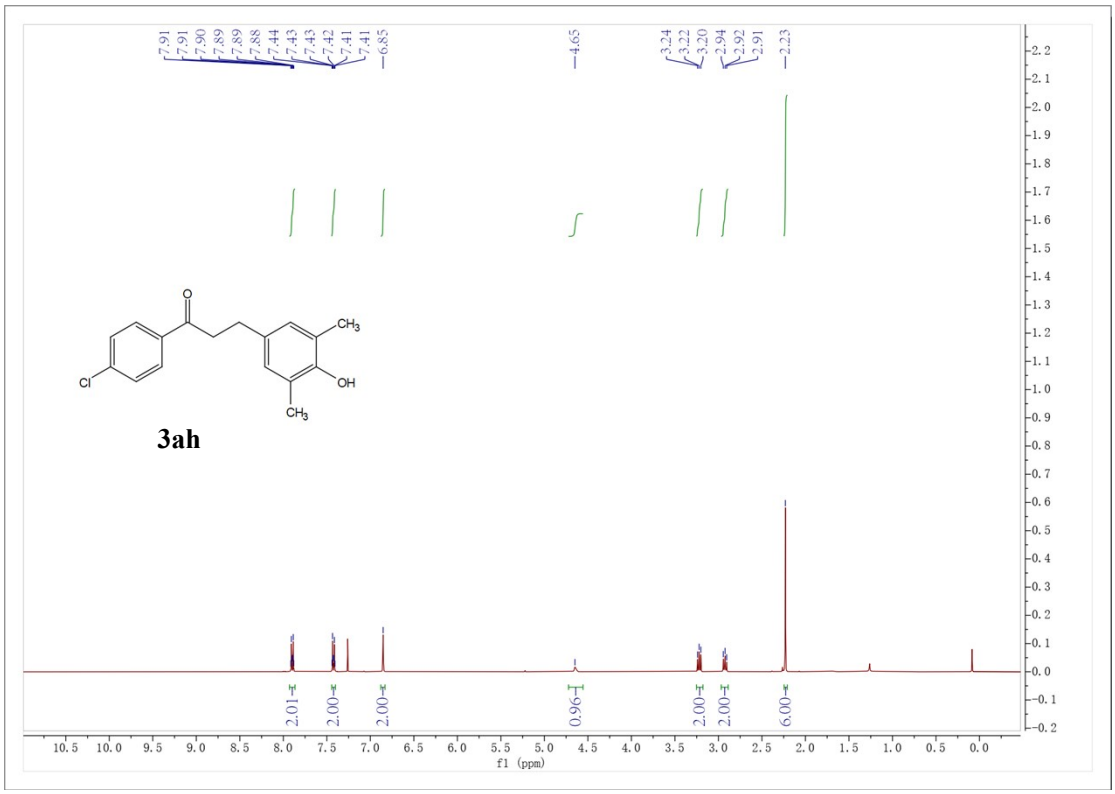
^{1}H NMR spectrum of **3ag** ($CDCl_3$, 400 MHz)



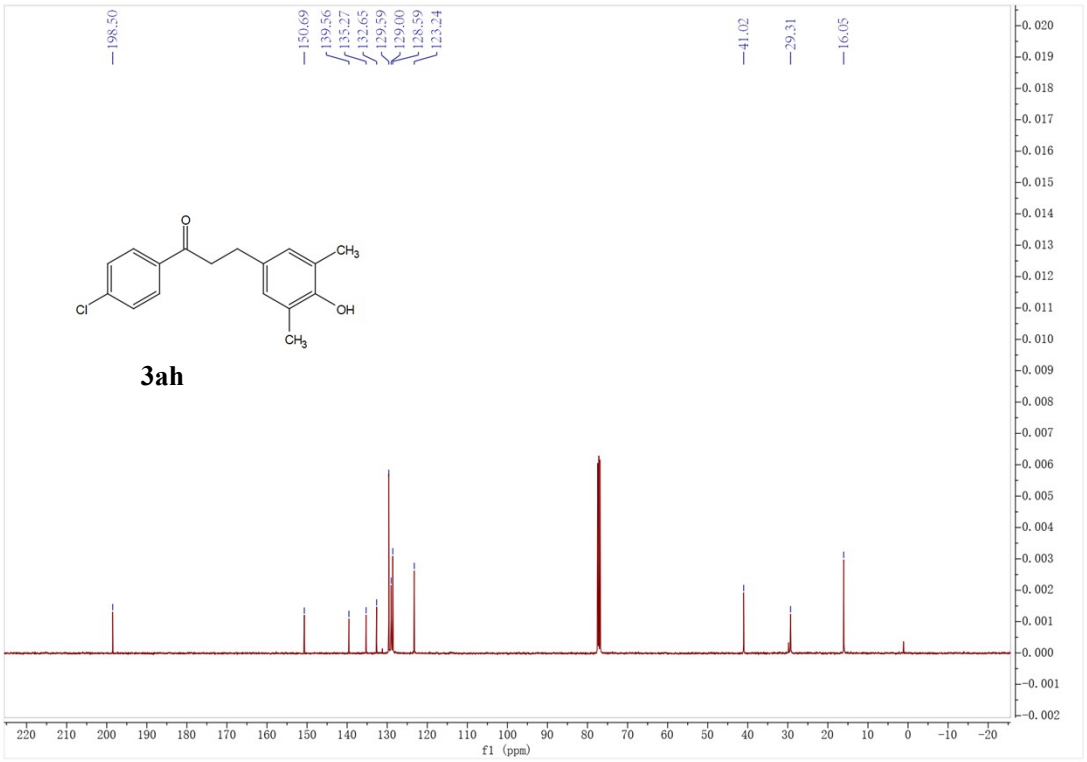
^{13}C NMR spectrum of **3ag** ($CDCl_3$, 101 MHz)



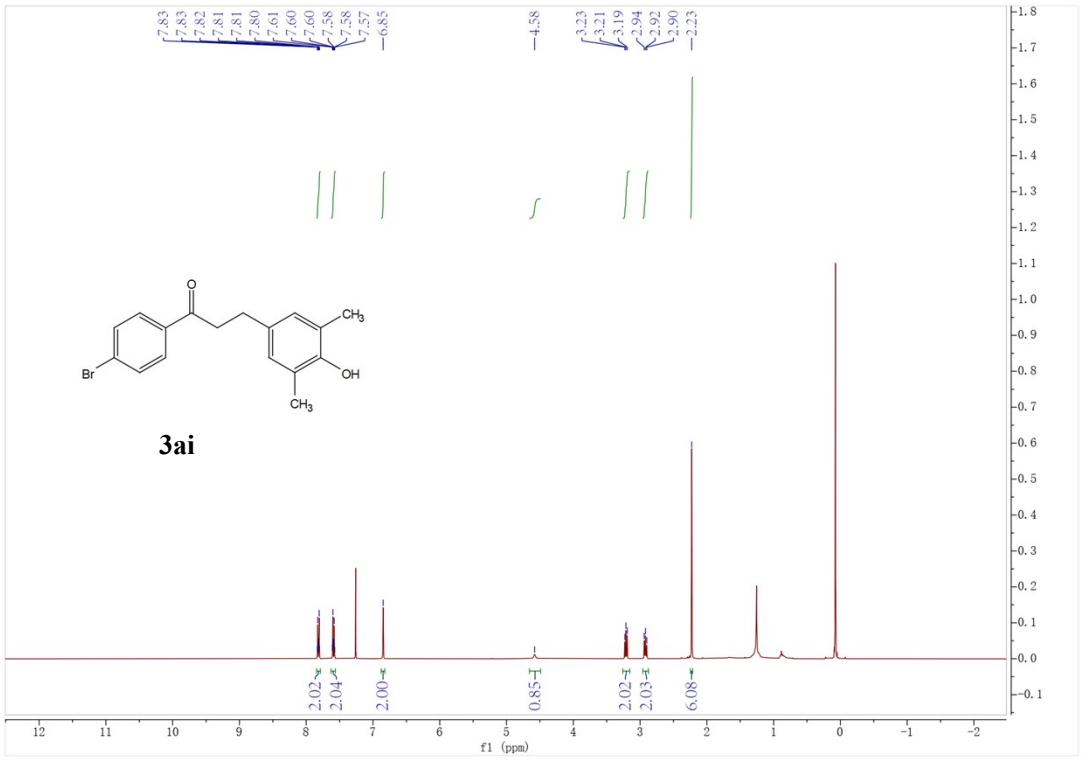
^{19}F NMR spectrum of **3ag** ($CDCl_3$, 376 MHz)



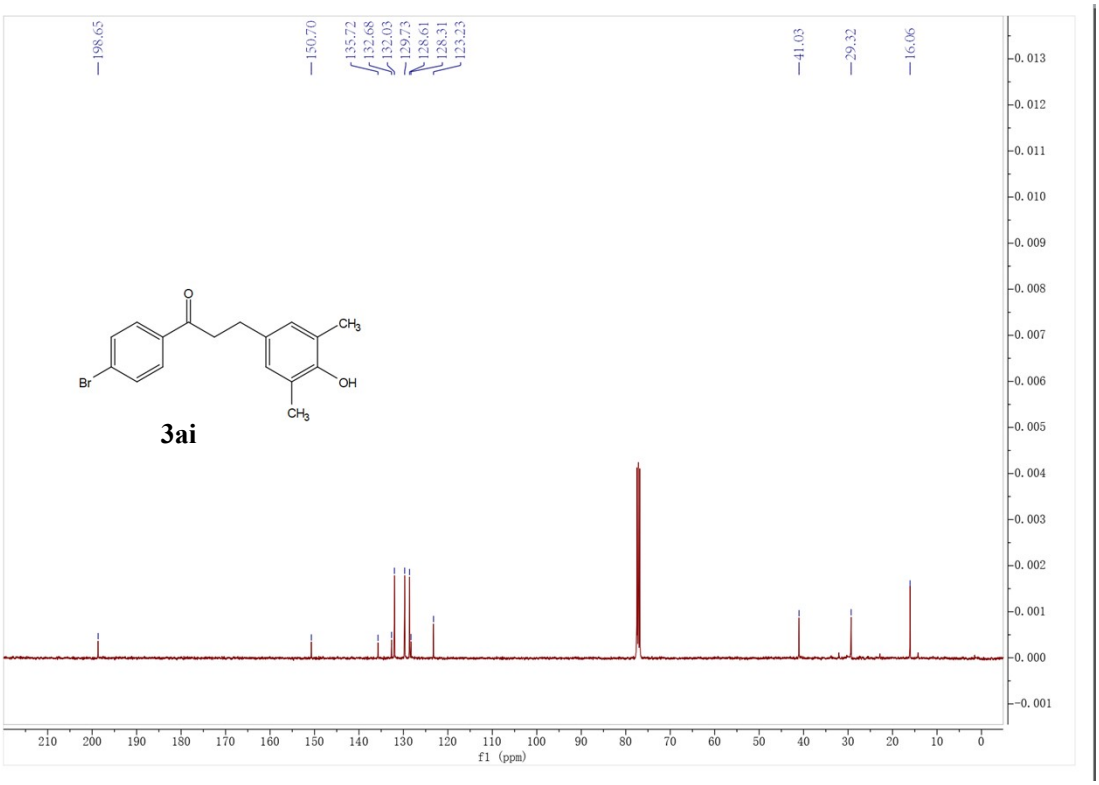
^{1}H NMR spectrum of **3ah** ($CDCl_3$, 400 MHz)



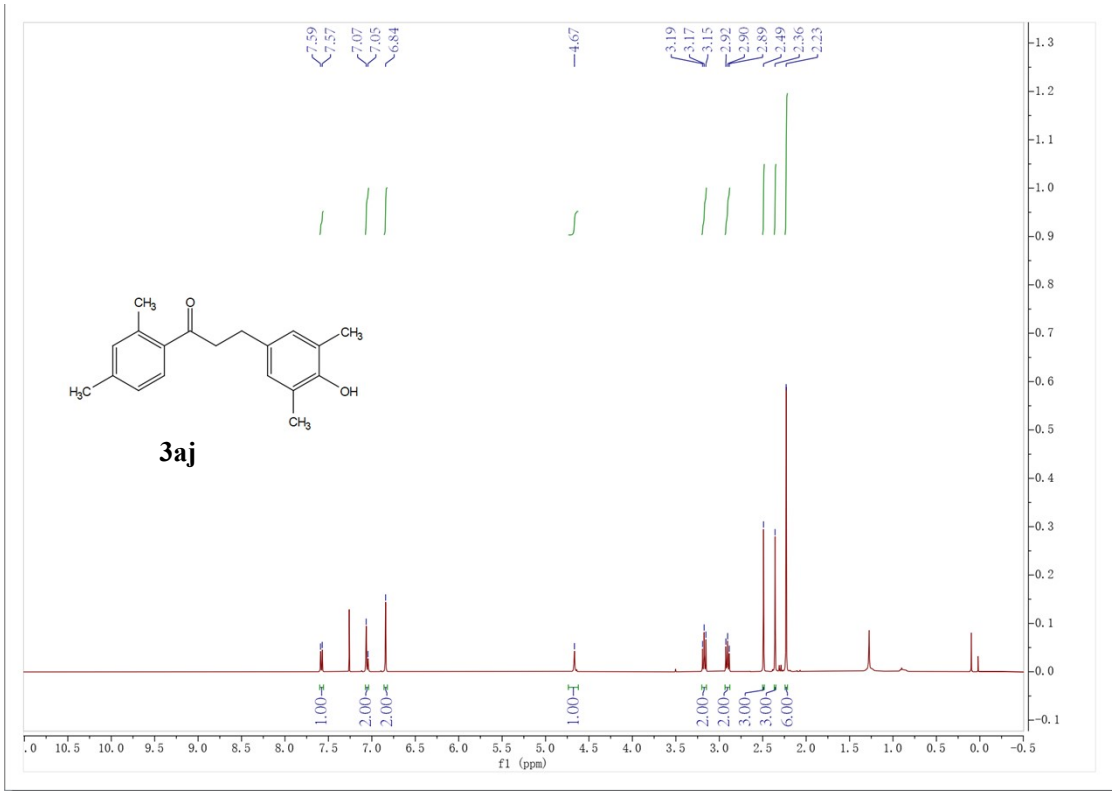
^{13}C NMR spectrum of **3ah** ($CDCl_3$, 101 MHz)



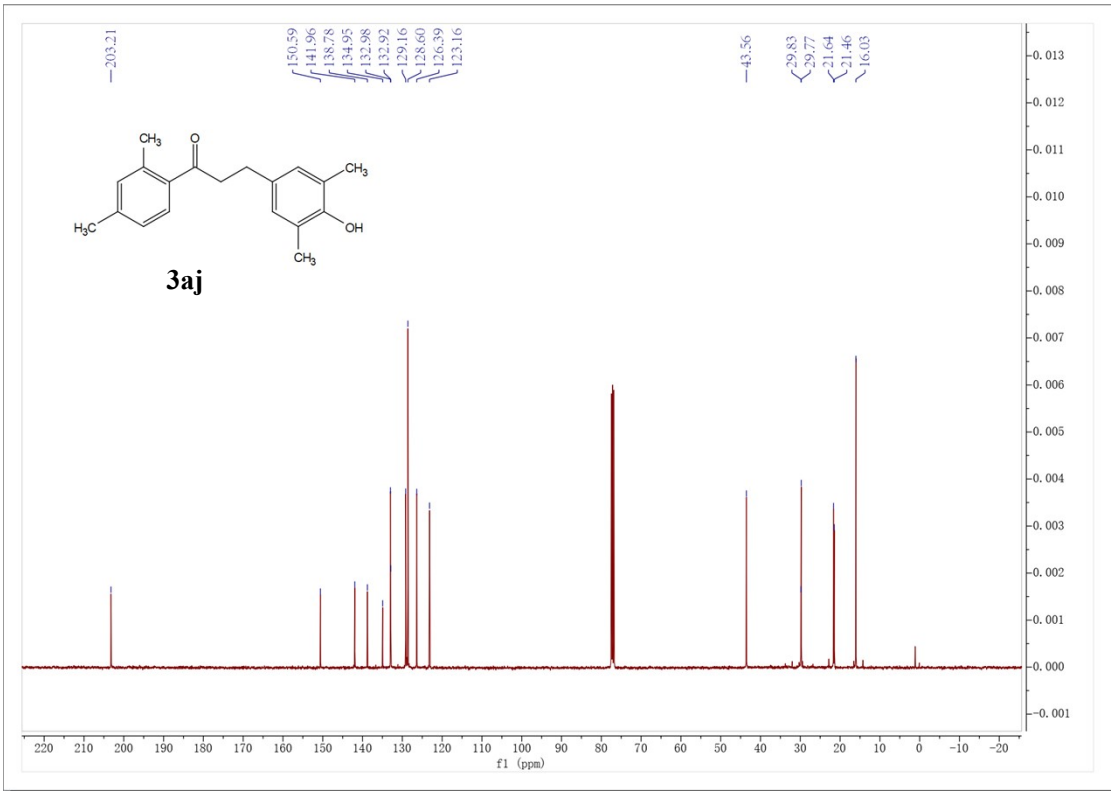
^{1}H NMR spectrum of **3ai** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **3ai** ($CDCl_3$, 101 MHz)



^{1}H NMR spectrum of **3aj** ($CDCl_3$, 400 MHz)



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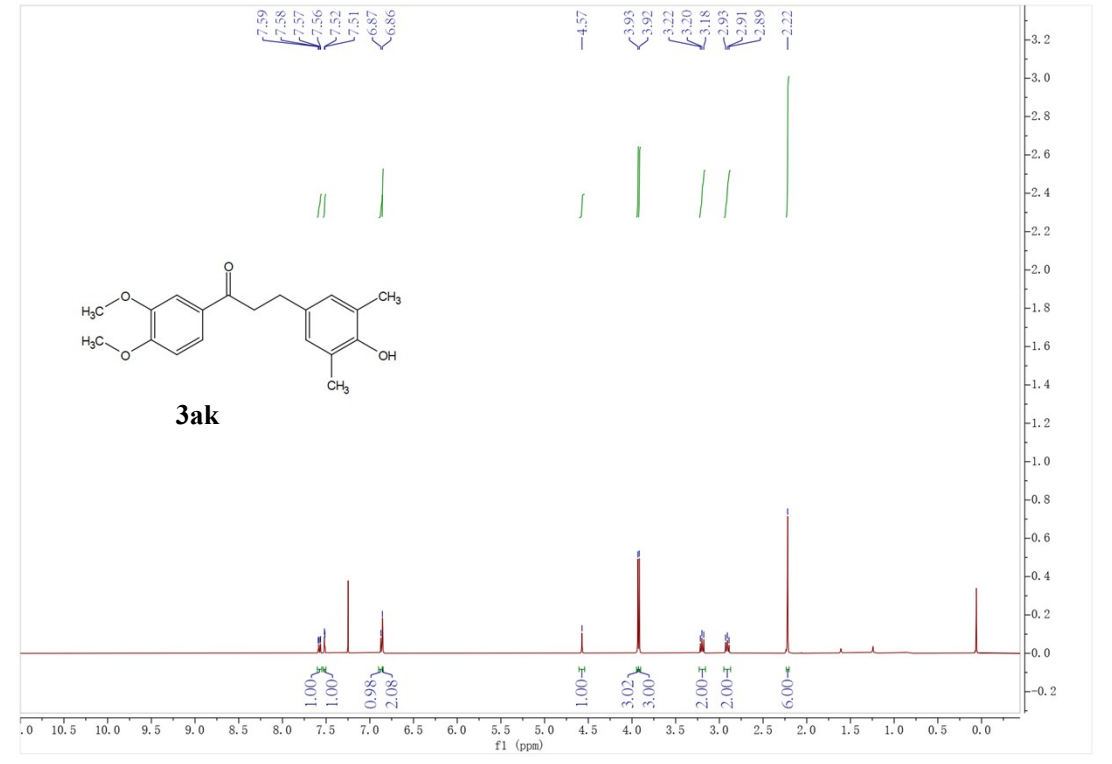
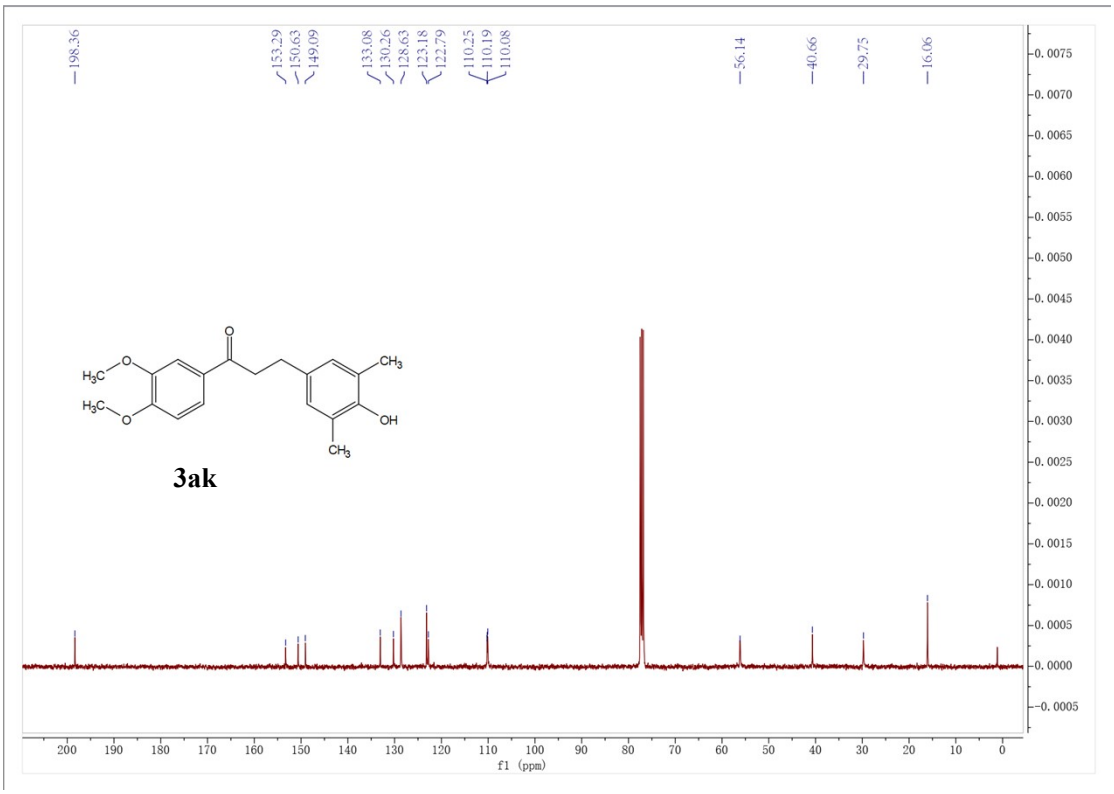
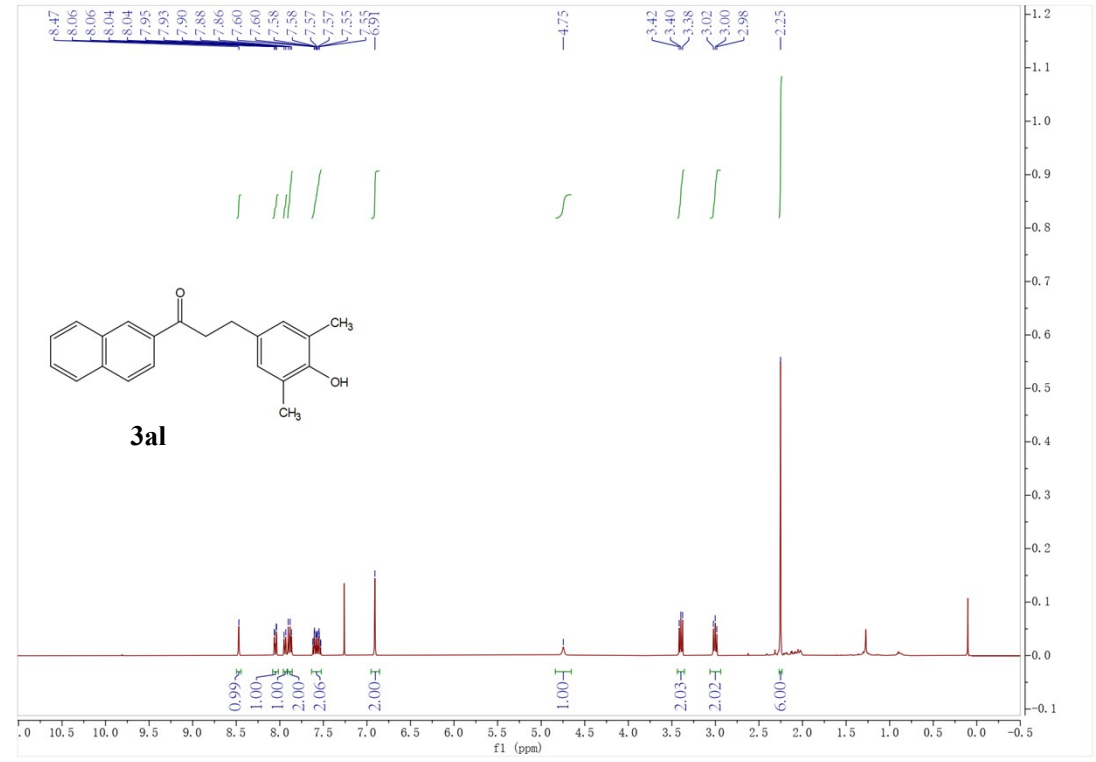


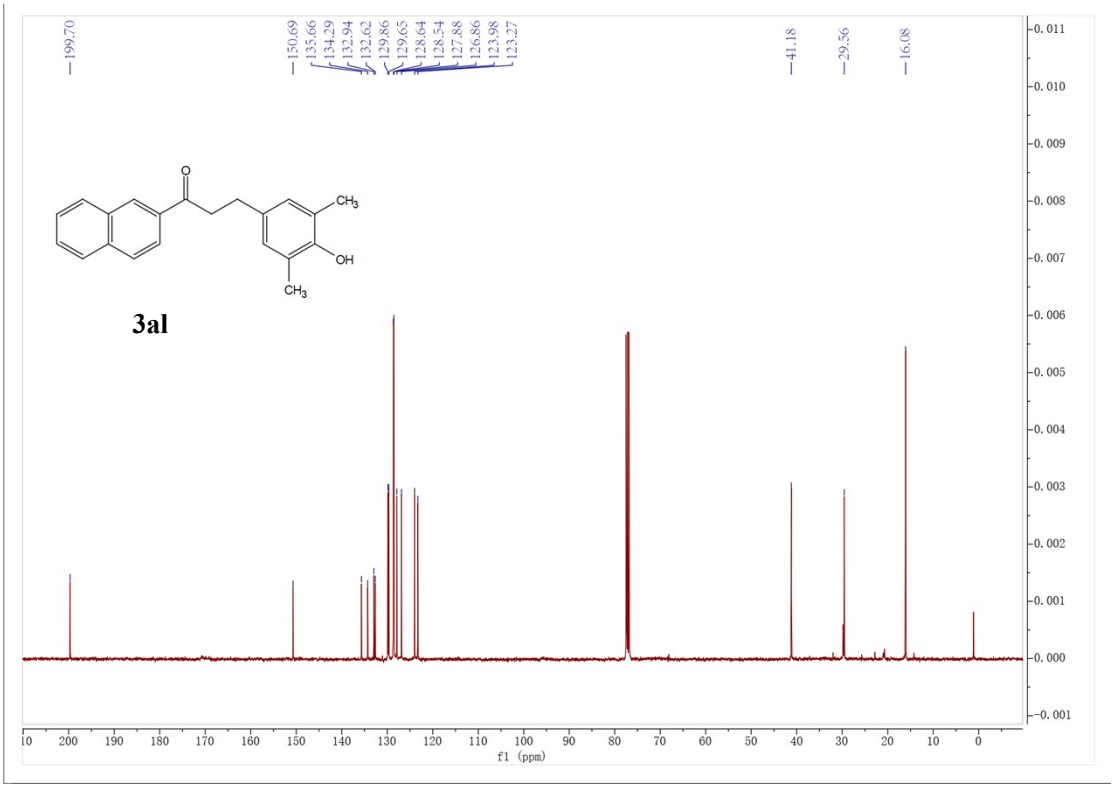
^{1}H NMR spectrum of **3ak** ($CDCl_3$, 400 MHz)



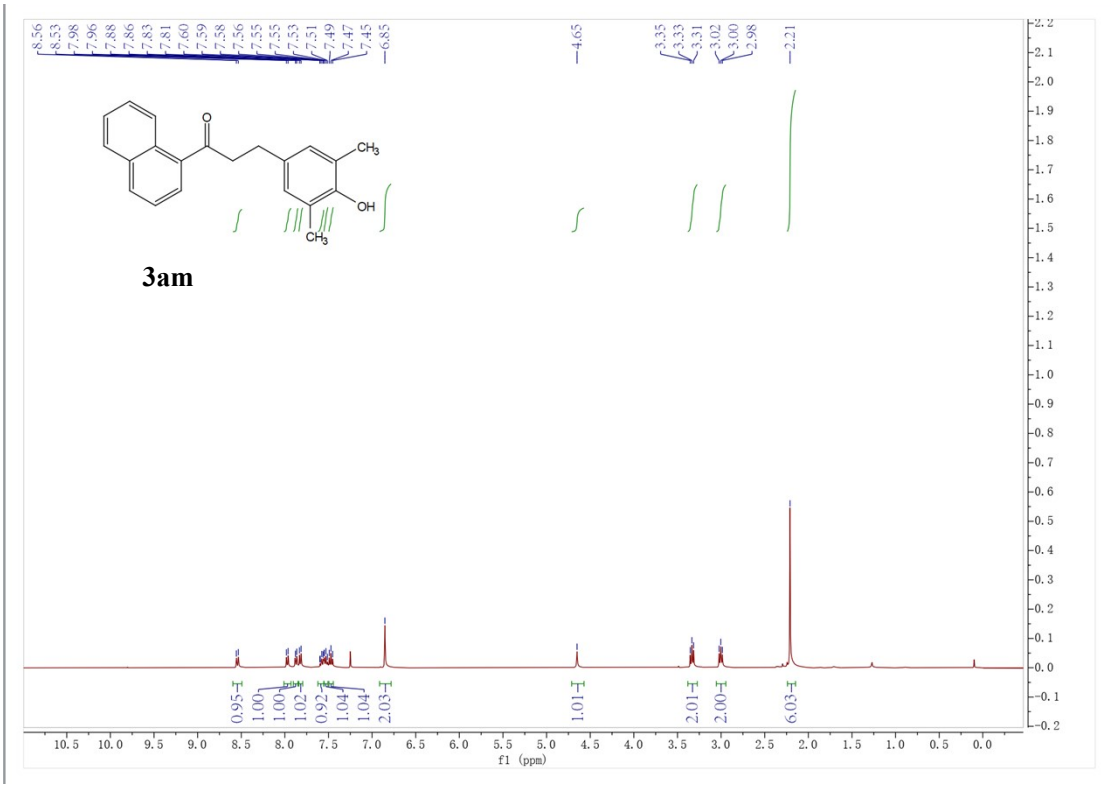
^{13}C NMR spectrum of **3ak** ($CDCl_3$, 101 MHz)



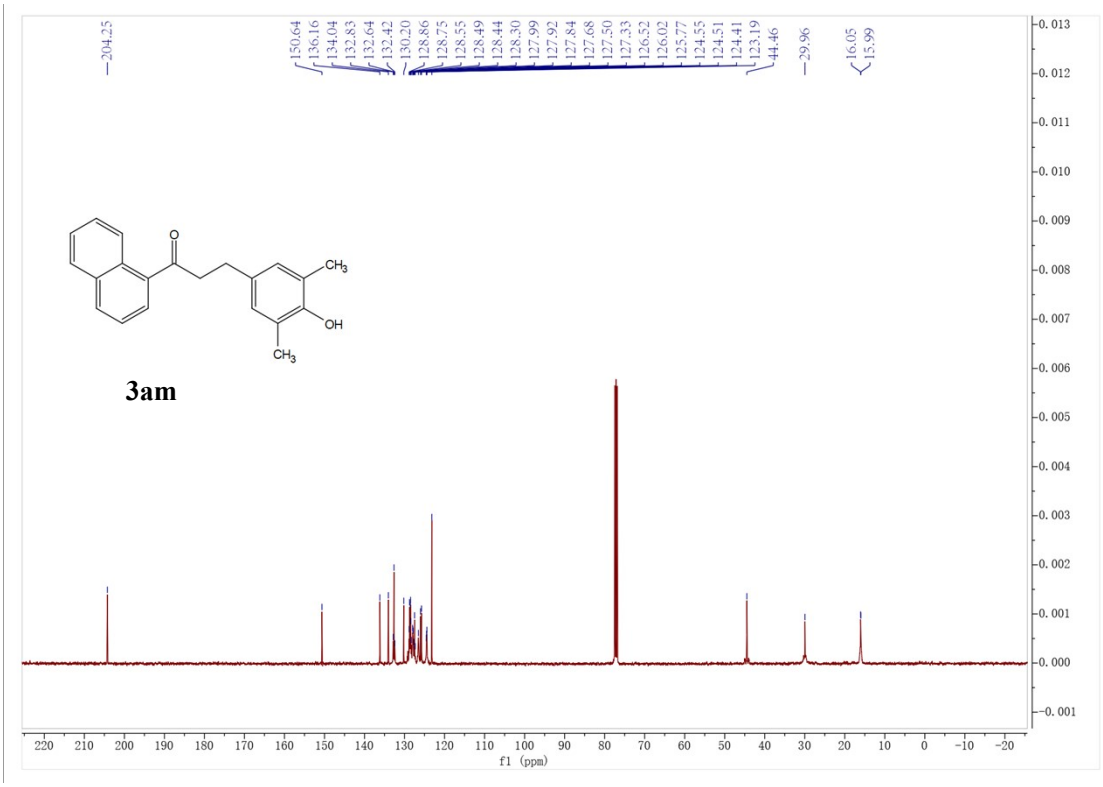
^{1}H NMR spectrum of **3al** ($CDCl_3$, 400 MHz)



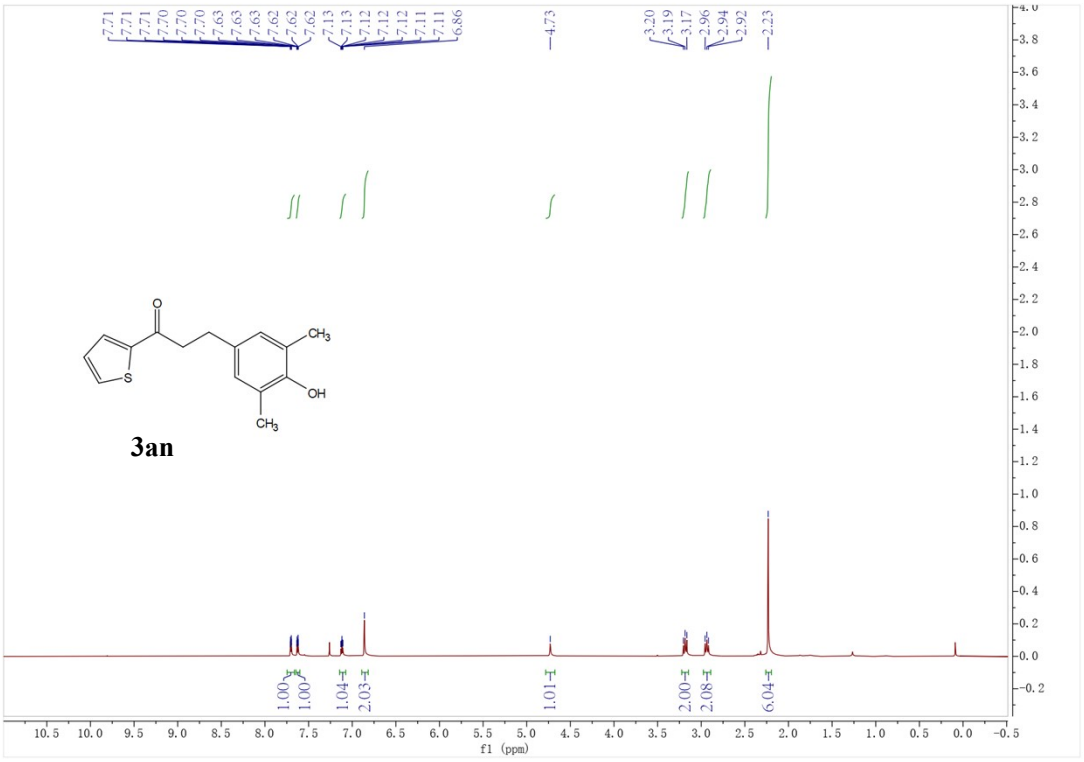
^{13}C NMR spectrum of **3al** ($CDCl_3$, 101 MHz)



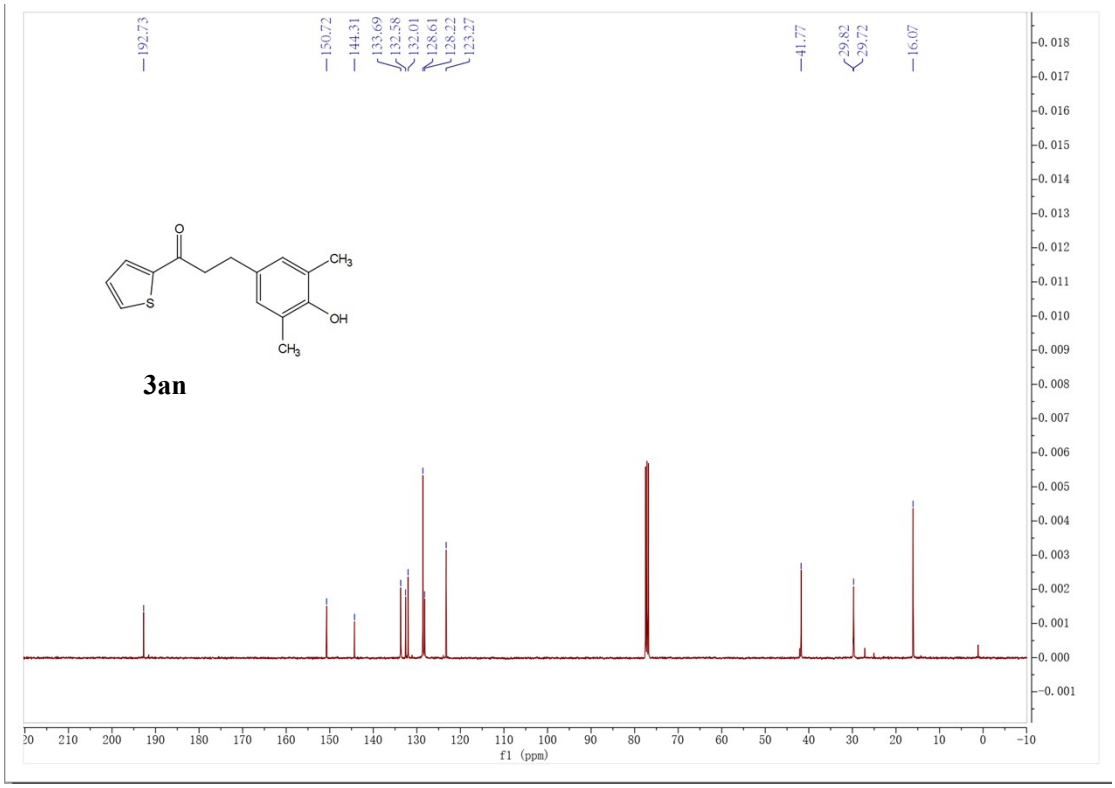
^{1}H NMR spectrum of **3am** ($CDCl_3$, 400 MHz)



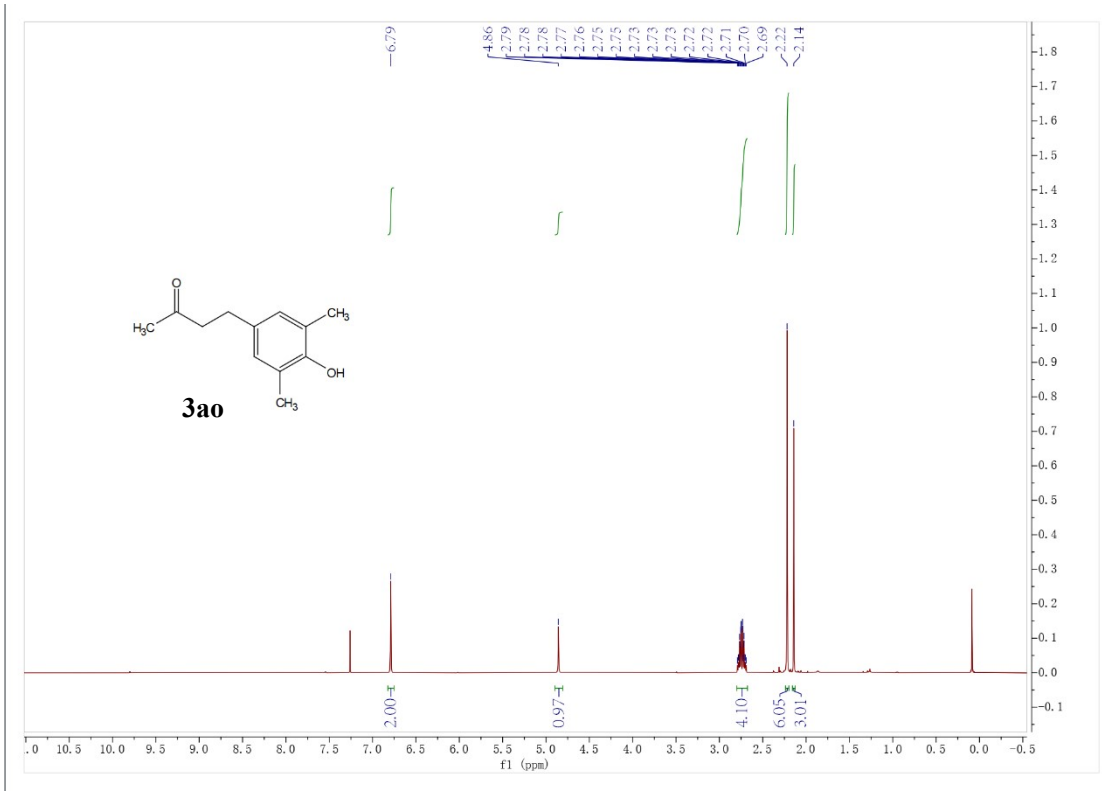
^{13}C NMR spectrum of **3am** ($CDCl_3$, 101 MHz)



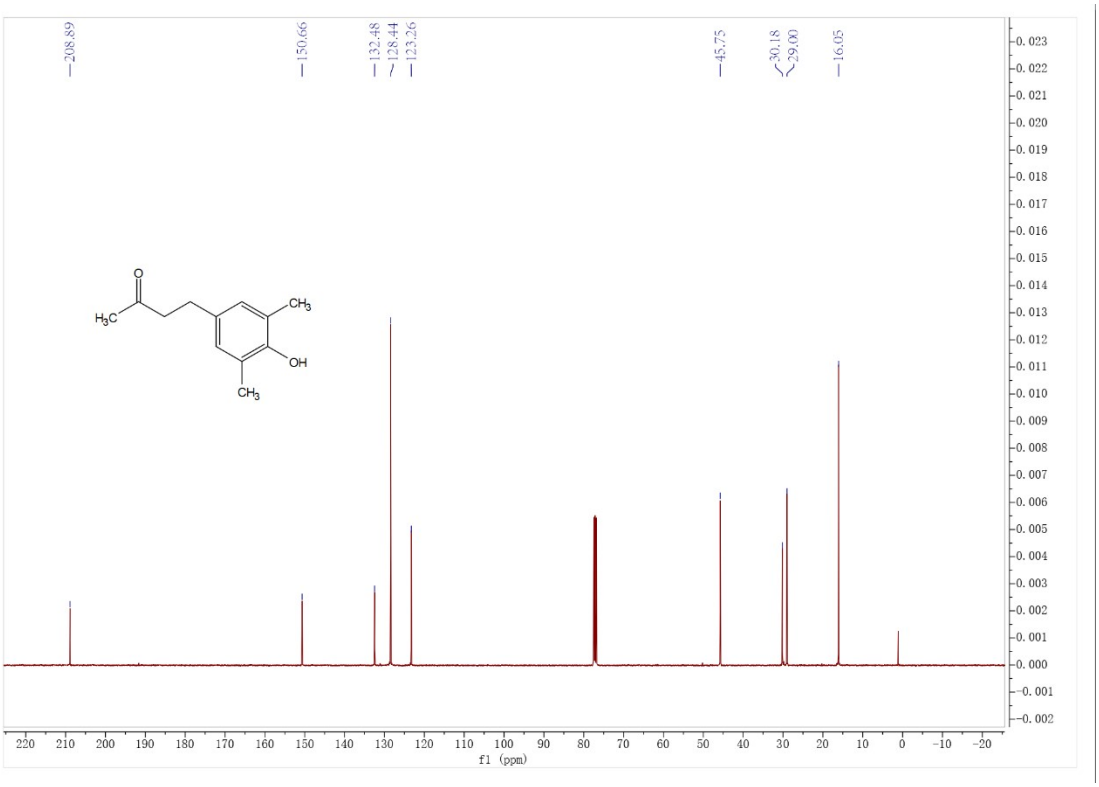
^{1}H NMR spectrum of **3an** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **3an** ($CDCl_3$, 101 MHz)



^{1}H NMR spectrum of **3ao** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **3ao** ($CDCl_3$, 101 MHz)