Directed o-Acylation of Acyloxacetamide with Alkynes: A Rh-Cu Bimetallic Catalyzed Relay Race

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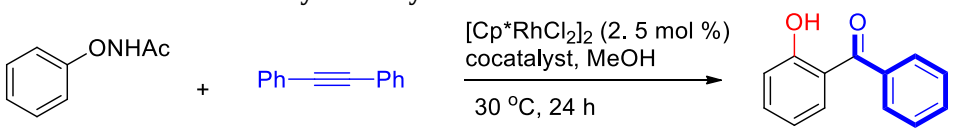
1. General experimental information

1.1. General methods

All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. All reagents were purchased from TCI, Acros or Strem. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (40-63 mm). Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. ^{1}H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance DPX 600 fourier Transform spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using a Waters HPLC/ZQ4000 Mass Spectrometer. High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer. Crystal data were collected on a Bruker D8 Advance employing graphite monochromated Mo - Kα radiation (λ = 0.71073 Å) at 293 (2) K and operating in the φ-ωscan mode. The structure was solved by direct methods SHELXS-97.

1.1. Table 1. The effect of the co-catalyst on the directed o-acylation of acyloxacetamide with alkynes: Rh-Cu bimetallic catalyzed relay race [a]



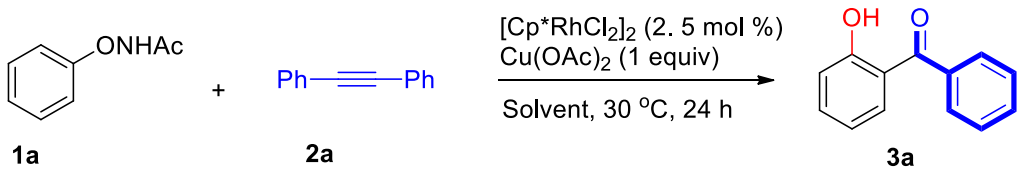
1a **2a** **3a**

Entry	Cocatalyst	Yield (%) [b]
1	NHPI	nr
2	AgOAc	trace
3	$CuSO_4$	8
4	$Cu(CN)_2$	12
5	CuO	18

6	$CuCl_2$	20
7	$CuBr_2$	32
8	$Cu(OAc)_2$	54

[a] The reactions were carried out using *N*-phenoxyacetamide **1a** (0.1 mmol), alkyne **2a** (0.15 mmol) $[Cp^*RhCl_2]_2$ (1.6 mg, 2.5 mol %) in the presence of co-catalyst in MeOH (1.0 mL) at 30 °C for 24 h in a sealed reaction tube , followed by flash chromatography on SiO_2. [b] Isolated yield

1.2. Table 2. The effect of the solvent on the directed o-acylation of acyloxacetamide with alkynes: Rh-Cu bimetallic catalyzed relay[a]

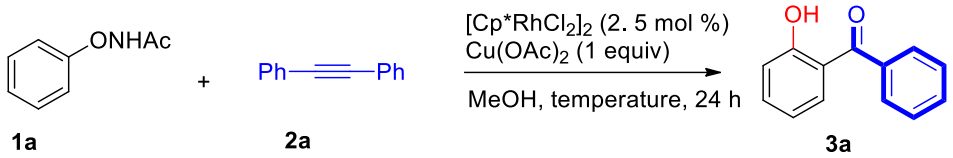


1a **2a** **3a**

Entry	Solvent	Yield (%) [b]
1	t-AmOH	trace
2	i-PrOH	12
3	EtOH	45
4	MeOH	54

[a] The reactions were carried out using *N*-phenoxyacetamide **1a** (0.1 mmol), alkyne **2a** (0.15 mmol) $[Cp^*RhCl_2]_2$ (1.6 mg, 2.5 mol %) in the presence of $Cu(OAc)_2$ (0.1 mmol) in solvent (1.0 mL) at 30 °C for 24 h in a sealed reaction tube , followed by flash chromatography on SiO_2. [b] Isolated yield.

1.3. Table 3. The effect of the reaction temperature on the directed o-acylation of acyloxacetamide with alkynes: Rh-Cu bimetallic catalyzed relay race [a]



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

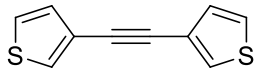
Entry	Temp. (℃)	Yield (%) [b]
1	30	54
2	50	86
3	80	80

[a] The reactions were carried out using *N*-phenoxyacetamide **1a** (0.1 mmol), alkyne **2a** (0.15 mmol) $[Cp^*RhCl_2]_2$ (1.6 mg, 2.5 mol %) in the presence of $Cu(OAc)_2$ (0.1 mmol) in MeOH (1.0 mL) at the given temperature for 24 h in a sealed reaction tube , followed by flash chromatography on

SiO_2. [b] Isolated yield.

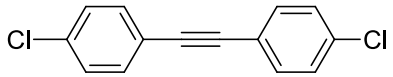
1.4. General procedure for the synthesis of alkyne

$[Pd(PPh_3)Cl_2]_2$ (2 mol%), CuI (4 mol%), Et_3N (2.0 equiv) and Ary iodide (0.1 mmol, 1.1 equiv) were dissolved in 10.0 mL DMF and heated to 80 °C. Subsequently, terminal alkyne (1.0 equiv) was added to resulting mixture by syringe, and the reaction was stirred under argon atmosphere for 10 h. After cooling to room temperature, the solvent was removed and extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure to give the crude product. The residue was purified by silica gel flash chromatography using petroleum ether to afford the desired product **2**.



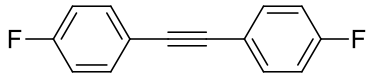
2b

1,2-di(thiophen-3-yl)ethyne (2b)[1]**:** white solid; 15 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 7.32 (d, J = 1.1 Hz, 2H), 7.24 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.87, 128.57, 125.43, 122.27, 84.12.



2c

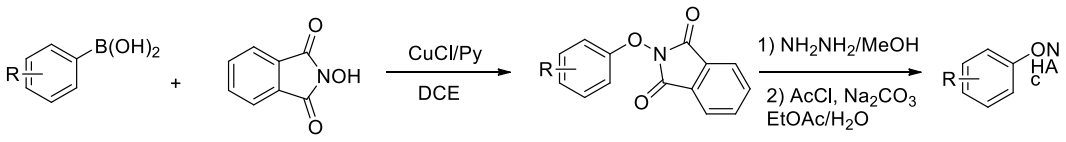
1,2-bis(4-chlorophenyl)ethyne (2c)[1]**:** white solid; 17 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.9 Hz, 4H), 7.32 (d, J = 7.9 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.54, 132.80, 128.76, 121.46, 89.18.



2d

1,2-bis(4-fluorophenyl)ethyne (2d)[1]: white solid; 15 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 4H), 7.04 (t, J = 8.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 1162.56 (d, J = 249.7 Hz, J_{CF}), 133.44 (d, J = 20 Hz, J_{CF}), 119.20, 115.68 (d, J = 22.2 Hz, J_{CF}), 87.97.

1.5 General procedure for synthesis of substrates 1:



5 1

N-Aryoxyacetamides were prepared following a published procedure reported by Lu[2]:

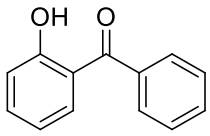
The mixture of *N*-hydroxyphthalimide (1 eq), arylboronic acid (2 eq), CuCl (1 eq), freshly activated 4-Å molecular sieves and pyridine (1 eq) in DCE were stirred at rt for 48 h. Then silica gel was added to the flask and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the corresponding products.

Hydrazine monohydrate (3 eq) was added to the solution of *N*-aryloxyphthalimide **5** in $CHCl_3$. The reaction was stirred at RT for overnight and filtered off. The filtrate was concentrated and resulting oil was purified by column chromatography on silical gel using 30% ethyl acetate in petroleum ether as eluent to afford the *N*-aryoxyamine.

Na_2CO_3 (1.2 eq) was added to the mixture of *N*-aryoxyamine (1 eq) in a 2:1 mixture of EA:H_2O. The resulting solution was cooled to 0 °C followed by dropwise addition of acyl chloride (1 eq). After stirring at RT for 2 h, The reaction was quenched with sat. $NaHCO_3$ and diluted with EA. The organic phase was dried and concentrated. The *N*-aryoxyacetamide was obtained by recrystaion form EA/PE.

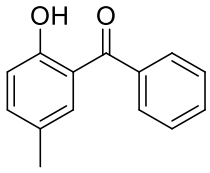
1.6 General procedure for synthesis of orth-acylphenols (3a-3p)

To the solution of *N*-phenoxyacetamide 1 (0.1 mmol) and alkyne 2 (0.15 mmol) in dry MeOH (1.0 mL) were added $[Cp^*RhCl_2]_2$ (2.0 mg, 2.5 mol %), $Cu(OAc)_2$ (18 mg, 0.1 mmol) under air atmosphere, and then the corresponding reaction mixture was stirred in a sealed tube at 50 °C for 24 h. After the starting materials were disappeared, then the mixture was cooled down to room temperature and concentrated under vacuum, and the resulting crude products were purified by flash chromatography on silical gel using 10% (v/v) ethyl acetate in petroleum ether as eluent to afford the desired orth-Acylphenols **3**.



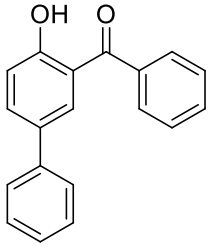
3a

(2-hydroxyphenyl)(phenyl)methanone (3a)[3]: oil; 17 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.03 (s, 1H), 7.68 (d, J = 7.7 Hz, 2H), 7.59 (d, J = 6.3 Hz, 2H), 7.51 (t, J = 7.4 Hz, 3H), 7.08 (d, J = 8.4 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 201.67, 163.25, 137.93, 136.35, 133.63, 131.94, 129.17, 128.36, 119.15, 118.66, 118.43. MS (ESI): m/z = 197.97 $[M]^+$.



3b

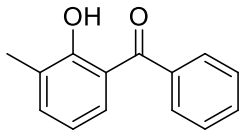
(2-hydroxy-5-methylphenyl)(phenyl)methanone (3b)[4]: white solid; 19 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.83 (s, 1H), 7.67 (d, J = 7.5 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.51 (t, J = 7.2 Hz, 2H), 7.39 – 7.29 (m, 2H), 6.98 (d, J = 8.3 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.60, 161.19, 138.12, 137.38, 133.22, 131.79, 129.11, 128.33, 127.79, 118.85, 118.18, 20.47. MS (ESI): m/z = 211.98 $[M]^+$.



3c

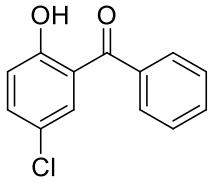
(4-hydroxy-[1,1'-biphenyl]-3-yl)(phenyl)methanone (3c)[5]: white solid; 22 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.00 (s, 1H), 7.81 (s, 1H), 7.75 (t, J = 9.2 Hz, 3H), 7.60 (d, J = 5.8 Hz, 1H),

7.54 (d, J = 6.8 Hz, 2H), 7.43 (d, J = 9.2 Hz, 2H), 7.41 (d, J = 7.0 Hz, 2H), 7.32 (d, J = 6.2 Hz, 1H), 7.17 (d, J = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.64, 162.65, 139.85, 137.88, 135.11, 132.10, 132.03, 131.73, 129.92, 129.24, 128.89, 128.48, 127.14, 126.64, 119.26, 118.89. MS (ESI): m/z = 273.99 $[M]^+$.



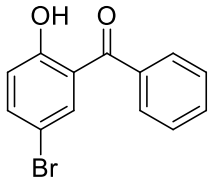
3d

(2-hydroxy-3-methylphenyl)(phenyl)methanone (3d)[5]: white solid; 10 mg, 44% yield; m.p. 160.2-161.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.32 (s, 1H), 7.66 (s, 2H), 7.57 (d, *J* = 2.7 Hz, 1H), 7.49 (s, 2H), 7.42 (d, *J* = 6.5 Hz, 1H), 7.37 (s, 1H), 6.77 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.95, 161.69, 138.25, 137.13, 131.75, 131.30, 129.15, 128.27, 127.47, 118.44, 117.95, 15.57. MS (ESI): m/z = 211.98 $[M]^+$.



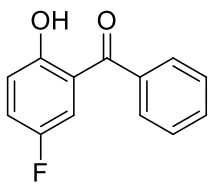
3e

(5-chloro-2-hydroxyphenyl)(phenyl)methanone (3e)[4]: white solid; 18 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.89 (s, 1H), 7.68 (d, J = 7.1 Hz, 2H), 7.62 (d, J = 7.3 Hz, 1H), 7.58 – 7.49 (m, 3H), 7.46 (d, J = 8.7 Hz, 1H), 7.04 (d, J = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.62, 161.72, 137.26, 136.18, 132.40, 129.13, 128.59, 123.41, 120.10, 119.79. MS (ESI): m/z = 231.93 $[M]^+$.



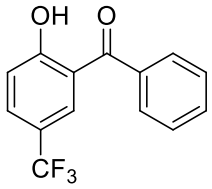
3f

(5-bromo-2-hydroxyphenyl)(phenyl)methanone (3f)[4]: white solid; 22 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.91 (s, 1H), 7.72 – 7.66 (m, 3H), 7.64 – 7.48 (m, 4H), 6.99 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.54, 162.17, 138.96, 137.23, 135.40, 132.41, 129.15, 128.61, 120.50, 120.43, 110.27. MS (ESI): m/z = 275.88 $[M]^+$.



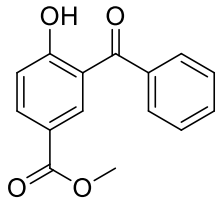
3g

(5-fluoro-2-hydroxyphenyl)(phenyl)methanone (3g)[6]: white solid; 13 mg, 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 7.68 (d, J = 7.2 Hz, 2H), 7.65 – 7.58 (m, 1H), 7.53 (t, J = 7.2 Hz, 2H), 7.32 – 7.21 (m, 2H), 7.04 (d, J = 8.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.64, 154.56 (d, J = 238.7 Hz, J_{CF}), 137.36, 132.31, 129.08, 128.54, 123.86 (d, J = 23.7 Hz, J_{CF}), 119.74 (d, J = 7.2 Hz, J_{CF}), 118.29 (d, J = 23.7 Hz, J_{CF}). MS (ESI): m/z = 215.96 $[M]^+$.



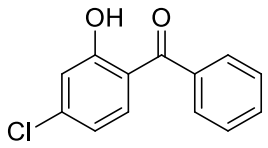
3h

(2-hydroxy-5-(trifluoromethyl)phenyl)(phenyl)methanone (3h)[4]: white solid; 19 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.30 (s, 1H), 7.89 (s, 1H), 7.76 – 7.62 (m, 4H), 7.55 (t, J = 7.3 Hz, 2H), 7.18 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.89, 165.57, 136.98, 132.66, 132.61, 132.58, 130.82, 130.78, 129.19, 128.70, 119.34, 118.52. MS (ESI): m/z = 265.96 $[M]^+$



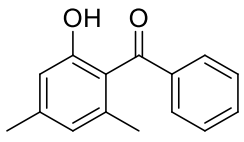
3i

methyl 3-benzoyl-4-hydroxybenzoate (3i)[4]: white solid; 17 mg, 67% yield; m.p.202.3-203.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.45 (s, 1H), 8.36 (s, 1H), 8.17 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 6.9 Hz, 2H), 7.63 (d, J = 6.9 Hz, 1H), 7.55 (t, J = 7.1 Hz, 2H), 7.11 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.31, 166.84, 165.95, 137.24, 137.04, 135.83, 132.50, 129.30, 128.63, 120.95, 118.68, 118.55, 52.14. MS (ESI): m/z = 256.13 $[M]^+$



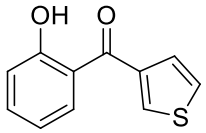
3j

(4-chloro-2-hydroxyphenyl)(phenyl)methanone (3j)[4]: white solid; 15 mg, 65% yield. m.p. 232.3-234 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.18 (s, 1H), 7.66 (d, J = 7.5 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.52 (t, J = 7.5 Hz, 3H), 7.10 (s, 1H), 6.86 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.83, 163.91, 142.26, 137.60, 134.49, 132.19, 129.07, 128.49, 119.37, 118.56, 117.72. MS (ESI): m/z = 231.93 $[M]^+$



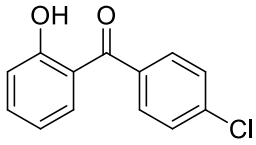
3k

(2-hydroxy-4,6-dimethylphenyl)(phenyl)methanone (3k)[7]: white solid; 17 mg, 76% yield. m.p.262.2-263.6 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 1H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.1 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 6.71 (s, 1H), 6.56 (s, 1H), 2.32 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.35, 159.44, 144.63, 140.47, 138.81, 132.59, 128.79, 128.63, 124.01, 120.29, 115.45, 22.58, 21.61. MS (ESI): m/z = 226.16 $[M]^+$



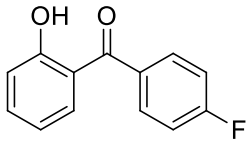
3l

(2-hydroxyphenyl)(thiophen-3-yl)methanone (3l)[3]: yellow oil; 13 mg, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 7.93 (s, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.51 (s, 2H), 7.43 (s, 1H), 7.06 (d, J = 8.3 Hz, 1H), 6.92 (t, J = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.38, 162.90, 140.28, 136.14, 132.50, 132.41, 128.43, 126.34, 119.88, 118.82, 118.40. MS (ESI): m/z = 203.92 $[M]^+$.



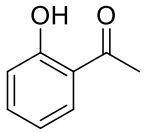
3m

(4-chlorophenyl)(2-hydroxyphenyl)methanone (3m)[5]: white solid; 18 mg, 76% yield. m.p.222.3-223.8 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.87 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 3H), 7.56 – 7.45 (m, 6H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.23, 163.23, 138.43, 136.57, 136.20, 133.21, 130.64, 128.72, 118.95, 118.79, 118.59. MS (ESI): m/z = 231.93 $[M]^+$.



3n

(4-fluorophenyl)(2-hydroxyphenyl)methanone (3n)[5]: white solid; 16 mg, 74% yield. m.p.152.3-153 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.88 (s, 1H), 7.72 (dd, *J* = 7.6, 5.9 Hz, 2H), 7.58 – 7.48 (m, 2H), 7.19 (t, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.89 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.02, 165.04 (d, *J* = 252.3 Hz, J_{CF}), 163.79, 163.17, 136.43, 134.10, 133.26, 131.81 (d, *J* = 6.8 Hz, J_{CF}) , 119.06, 118.65 (d, *J* = 20.5 Hz, J_{CF}), 115.60 (d, *J* = 21.9 Hz, J_{CF}), MS (ESI): m/z = 215.96 $[M]^+$

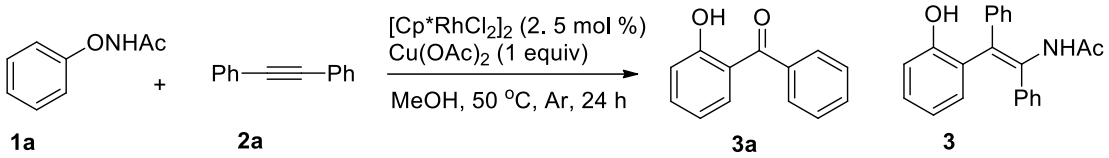


3p

1-(2-hydroxyphenyl)ethanone (3p): oil; 9 mg, 68% yield. m.p.162.3-163.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.25 (s, 1H), 7.73 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 – 7.44 (m, 1H), 6.97 (dd, *J* = 8.4, 0.7 Hz, 1H), 6.93 – 6.87 (m, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.52, 162.40, 136.45, 130.71, 119.74, 118.92, 118.42, 26.60. MS (ESI): m/z = 135.95 $[M]^+$

2. Controlled experiments for mechanism studies

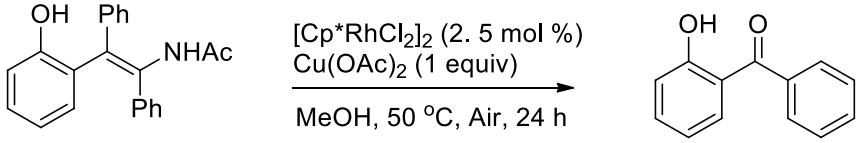
(a) Rh-Cu bimetallic catalyzed acylation Csp^2-H of *N*-phenoxyacetamideand alkyne under Ar conditions.



1a **2a** **3a** (not observed) **3**

To the solution of *N*-phenoxyacetamide **1a** (0.1 mmol) and alkyne **2a** (0.15 mmol) in MeOH (1.0 mL) were added $[Cp^*RhCl_2]_2$ (2.0 mg, 2.5 mol %), $Cu(OAc)_2$ (18 mg, 0.1 mmol) under Ar atmosphere, and then the corresponding reaction mixture was stirred in a sealed tube at 50 ℃ for 24 h. After the reaction was cooled down to room temperature and concentrated under vacuum, and the resulting crude products were purified by flash chromatography on silical gel using petroleum ether as eluent to afford the product **3**.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 6H), 7.15 (s, 3H), 7.06 (dd, *J* = 20.1, 12.2 Hz, 3H), 6.79 – 6.71 (m, 3H), 1.89 (s, 3H).

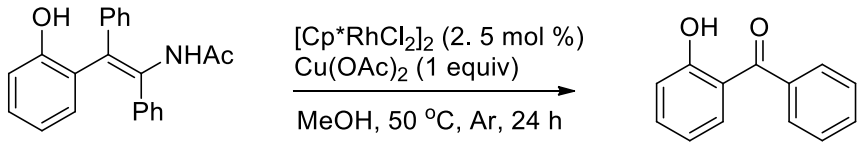
(b) *N*-(2-(2-hydroxyphenyl)-1,2-diphenylvinyl)acetamide was treated under conditions



3 **3a (83%)**

To the solution of **3** (0.1 mmol) in MeOH (1.0 mL) were added $[Cp^*RhCl_2]_2$ (2.0 mg, 2.5 mol %), $Cu(OAc)_2$ (18 mg, 0.1 mmol) under air atmosphere. The reaction mixture was stirred in sealed tube at 50 °C for 24 h. Then the transformation was obtained**3a** (16mg, 83%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.03 (s, 1H), 7.68 (d, J = 7.7 Hz, 2H), 7.59 (d, J = 6.3 Hz, 2H), 7.51 (t, J = 7.4 Hz, 3H), 7.08 (d, J = 8.4 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 201.67, 163.25, 137.93, 136.35, 133.63, 131.94, 129.17, 128.36, 119.15, 118.66, 118.43.

(c): *N*-(2-(2-hydroxyphenyl)-1,2-diphenylvinyl)acetamide was treated under conditions except air



3 **3a** (not observed)

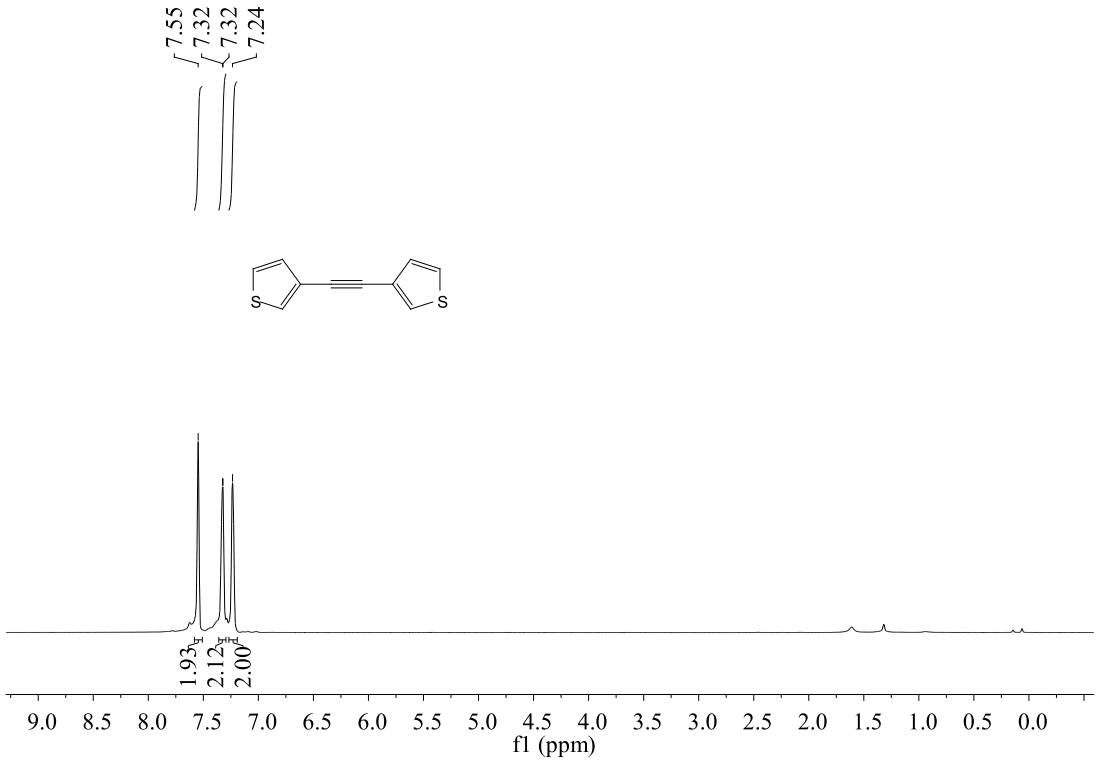
To the solution of **3** (0.1 mmol) in MeOH (1.0 mL) were added $[Cp^*RhCl_2]_2$ (2.0 mg, 2.5 mol %), $Cu(OAc)_2$ (18 mg, 0.1 mmol) under Ar atmosphere. The reaction mixture was stirred in sealed tube at 50 °C for 24 h. The **3a** was not observed by the TLC and the **3** was recovered 80% yield.

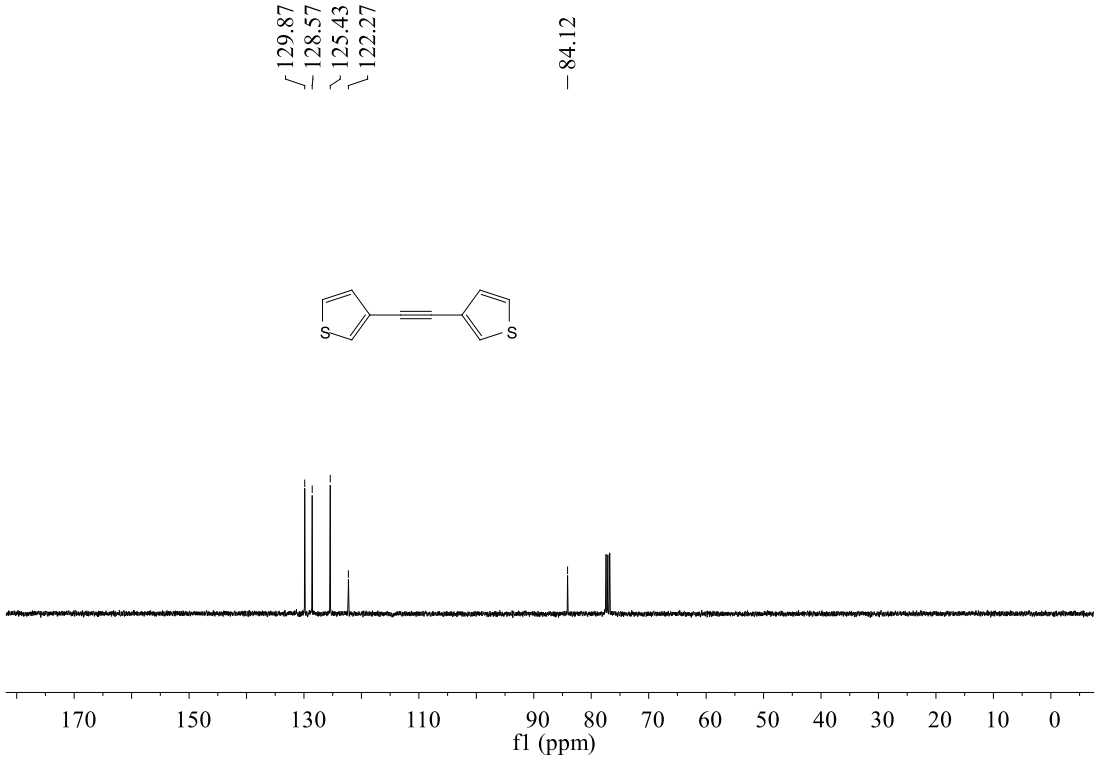
3. References

1. Yan, H.; Wang, H.; Li, X.; Xin, X.; Wang, C.; Wan, B. *Angew. Chem. Int. Ed.* **2015,** *54*, 10613.
2. Li, B.; Lan, J.; Wu, D.; You, J. *Angew. Chem. Int. Ed.* **2015,** *54*, 14008.
3. Nowrouzi, N.; Zarei, M.; Roozbin, F. *RSC Adv.* **2015,** *5*, 102448.
4. Wang, D.; Cui, S. *Tetrahedron.* **2015,** *71*, 8511.
5. Weng, F.; Wang, C.; Xu, B. *Tetrahedron. Lett.* **2010,** *51*, 2593.
6. Gao, Z.; Lim, Y. H.; Tredwell, M.; Li, L.; Verhoog, S.; Hopkinson, M.; Kaluza, W.; Collier, T. L.; Passchier, J.; Huiban, M.; Gouverneur, V. *Angew. Chem. Int. Ed.* **2012,** *51*, 6733.
7. Harjani, J. R.; Nara, S. J.; Salunkhe, M. M. *Tetrahedron. Lett.* **2001,** *42*, 1979.

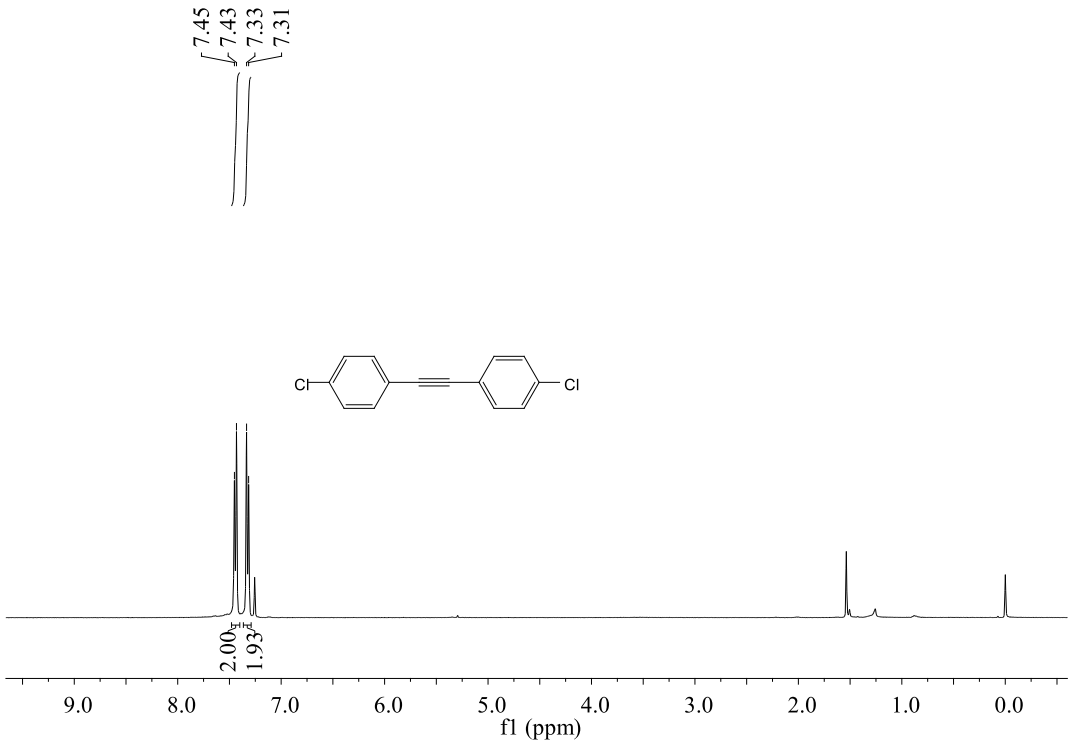
4. ^{1}H NMR and ^{13}C NMR spectrum for all isolated products.

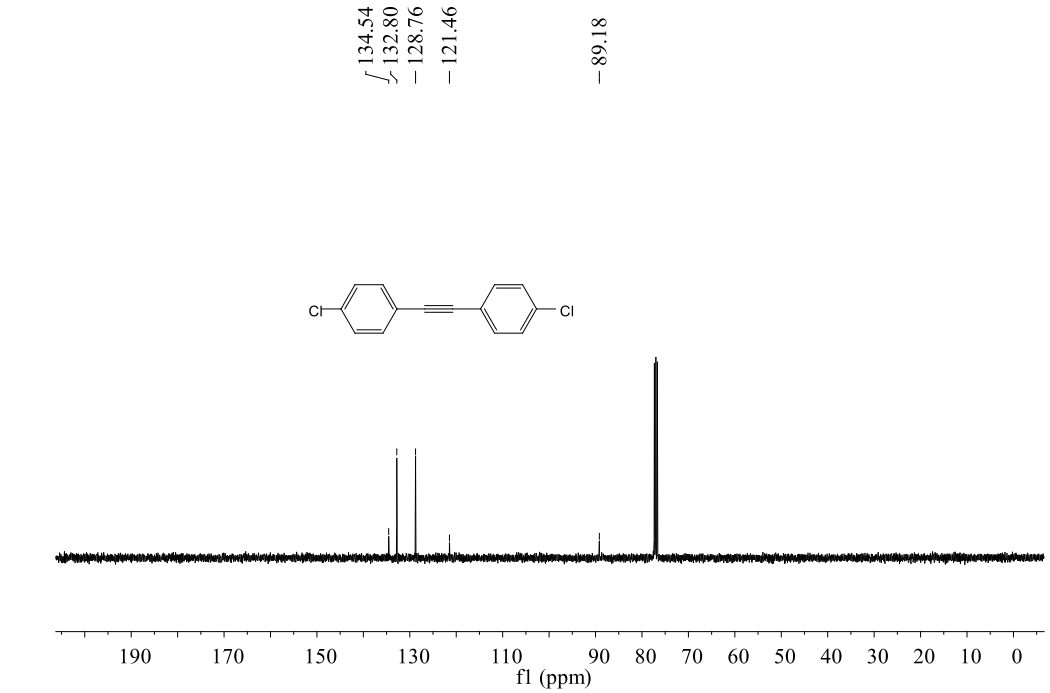
1) 1,2-di(thiophen-3-yl)ethyne (**2b**) (Using $CDCl_3$ as solvent)



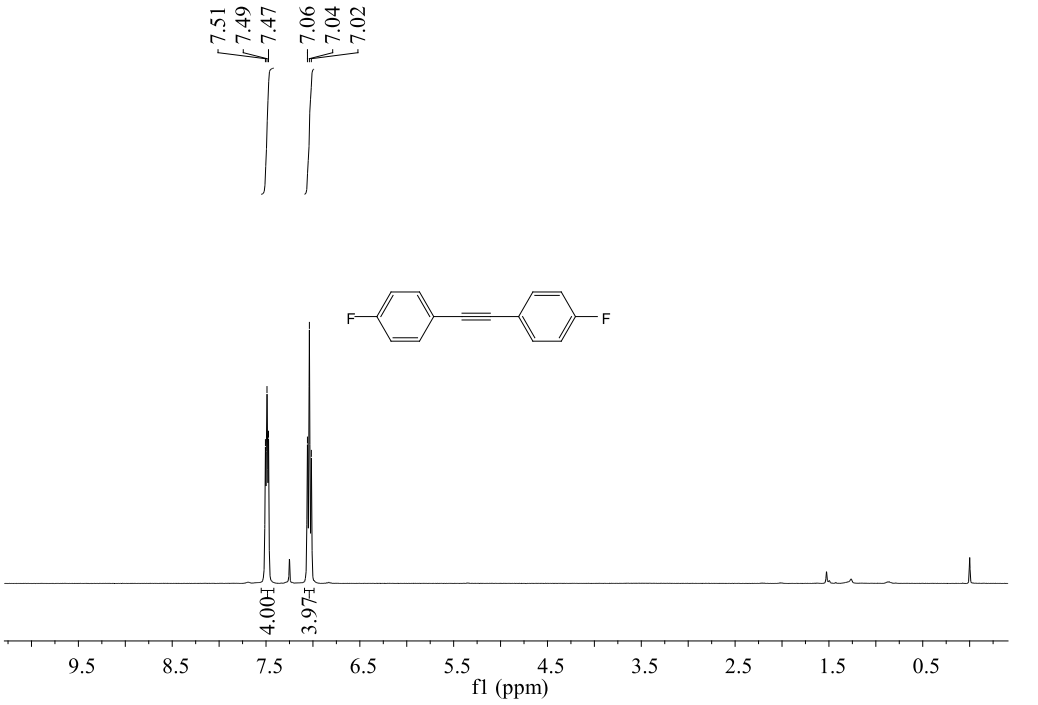


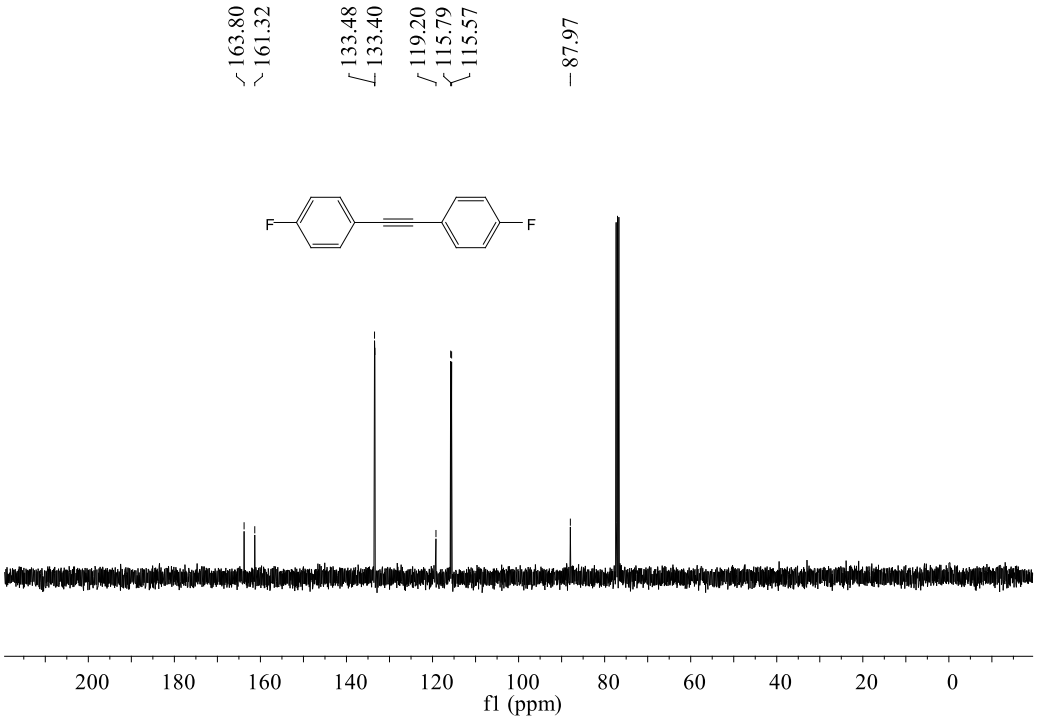
2) 1,2-bis(4-chlorophenyl)ethyne (**2c**) (Using $CDCl_3$ as solvent)



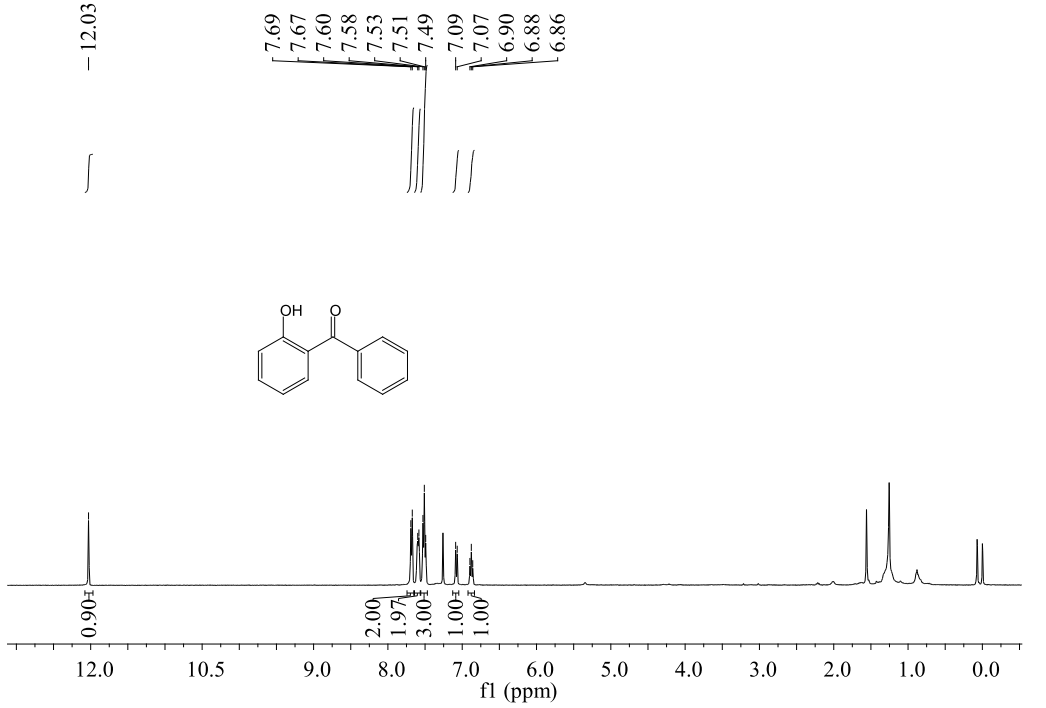


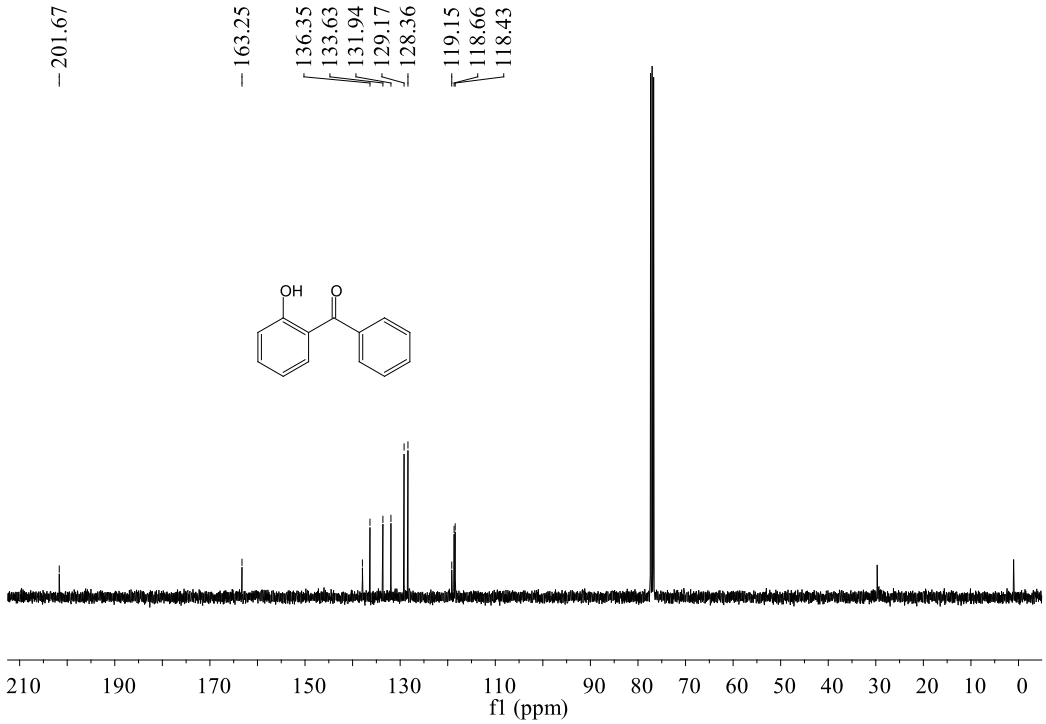
3) 1,2-bis(4-fluorophenyl)ethyne (**2d**) (Using $CDCl_3$ as solvent)



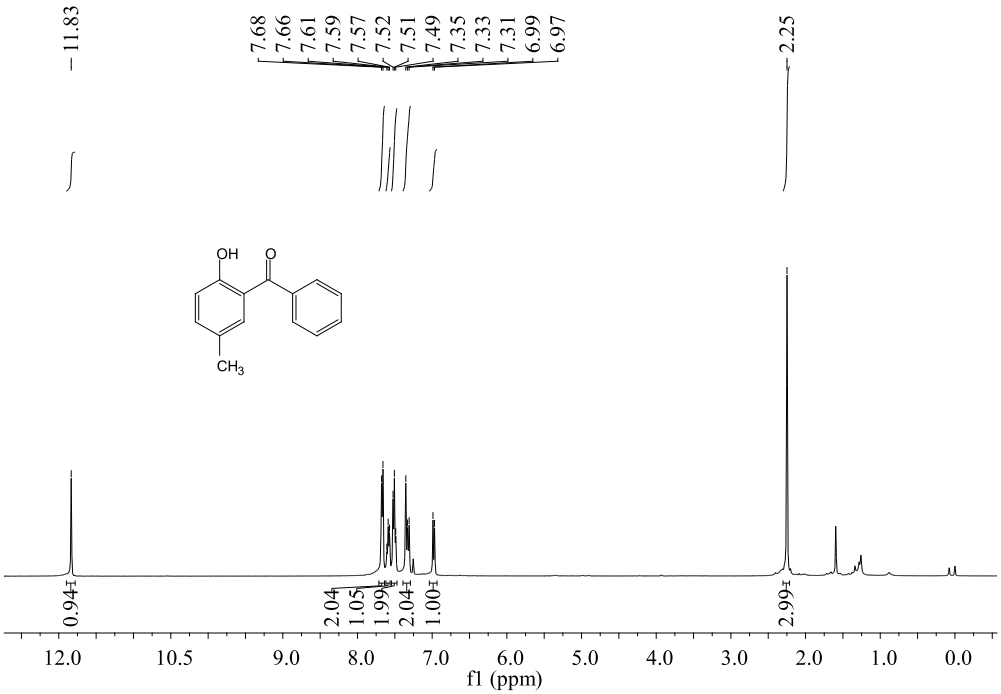


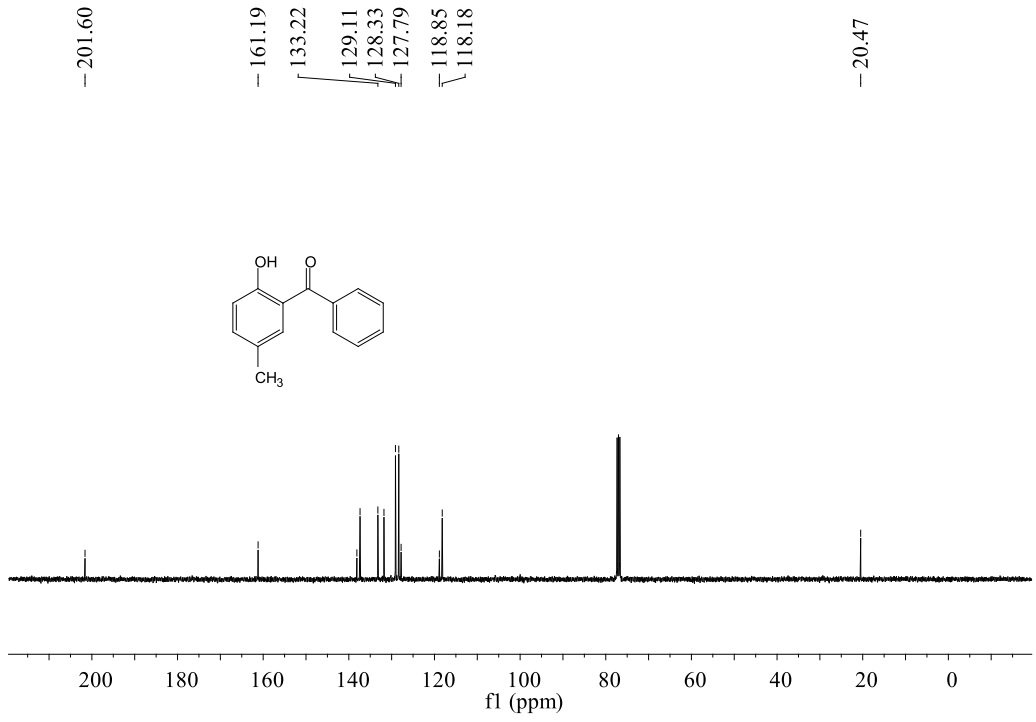
4) (2-hydroxyphenyl)(phenyl)methanone (3a) (Using $CDCl_3$ as solvent)



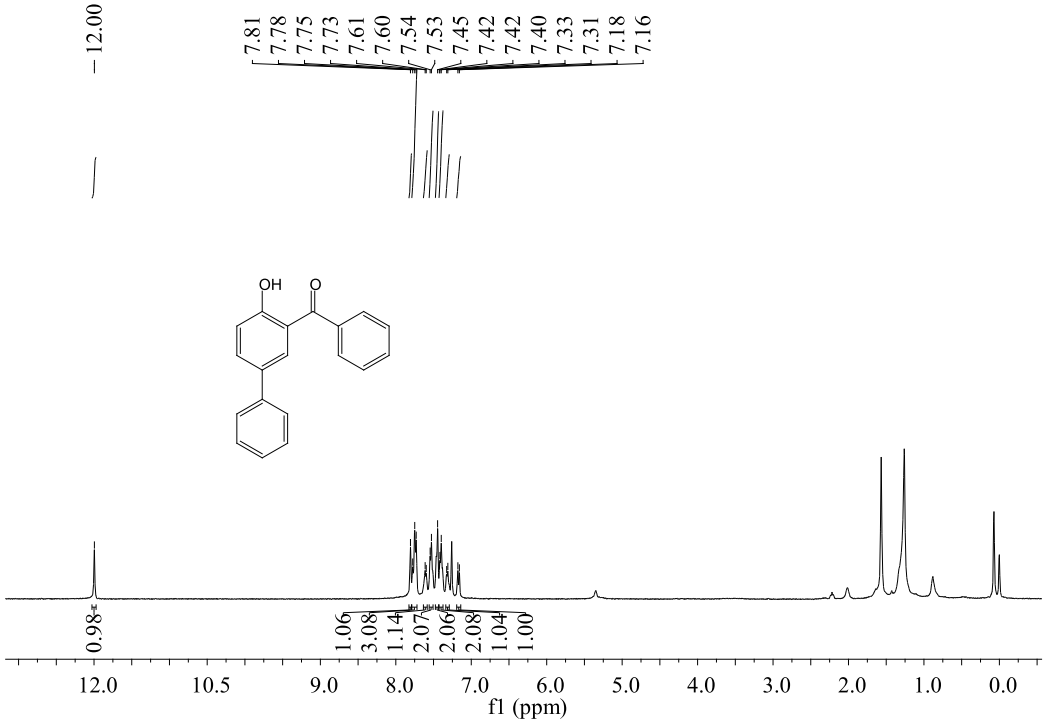


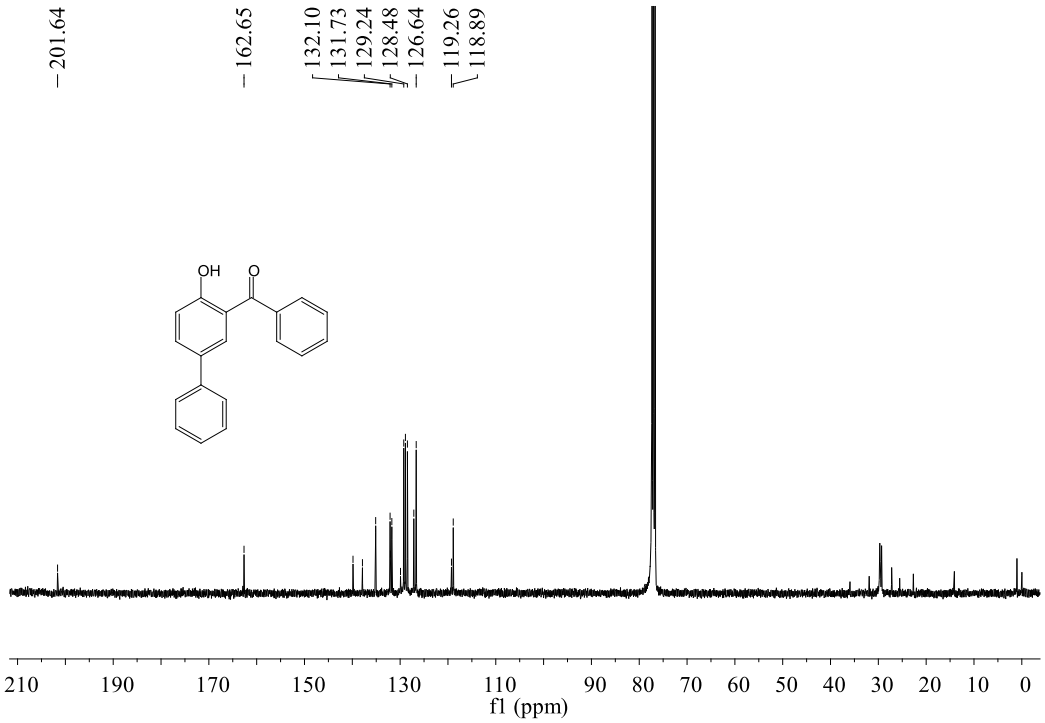
5) (2-hydroxy-5-methylphenyl)(phenyl)methanone (3b) (Using $CDCl_3$ as solvent)



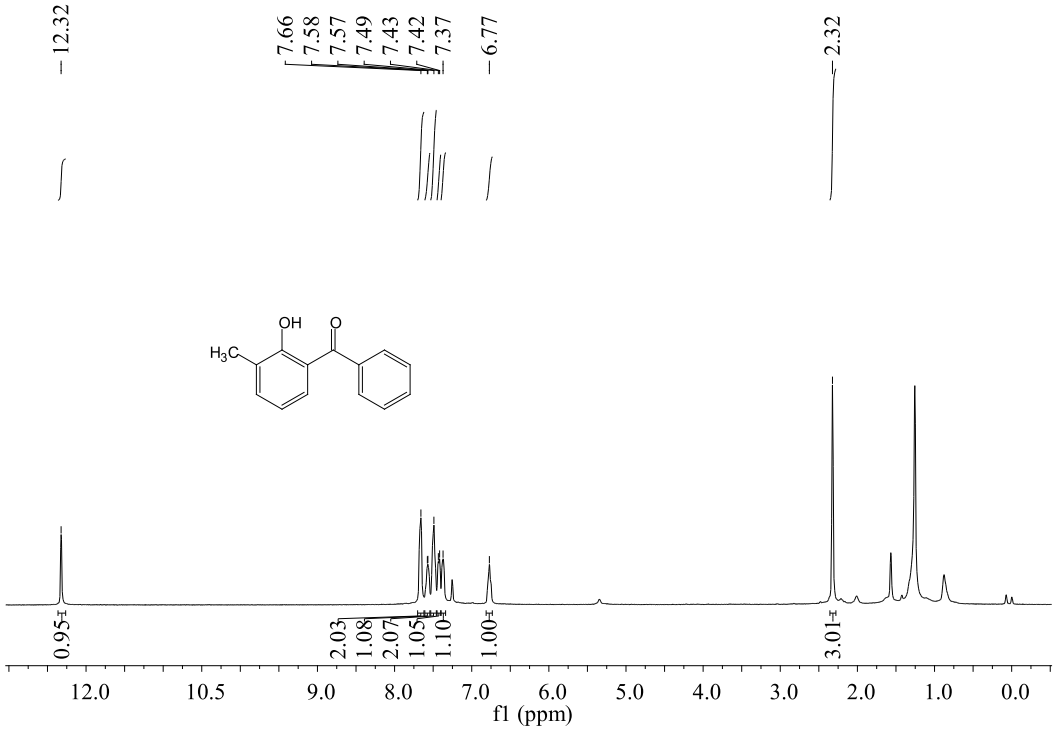


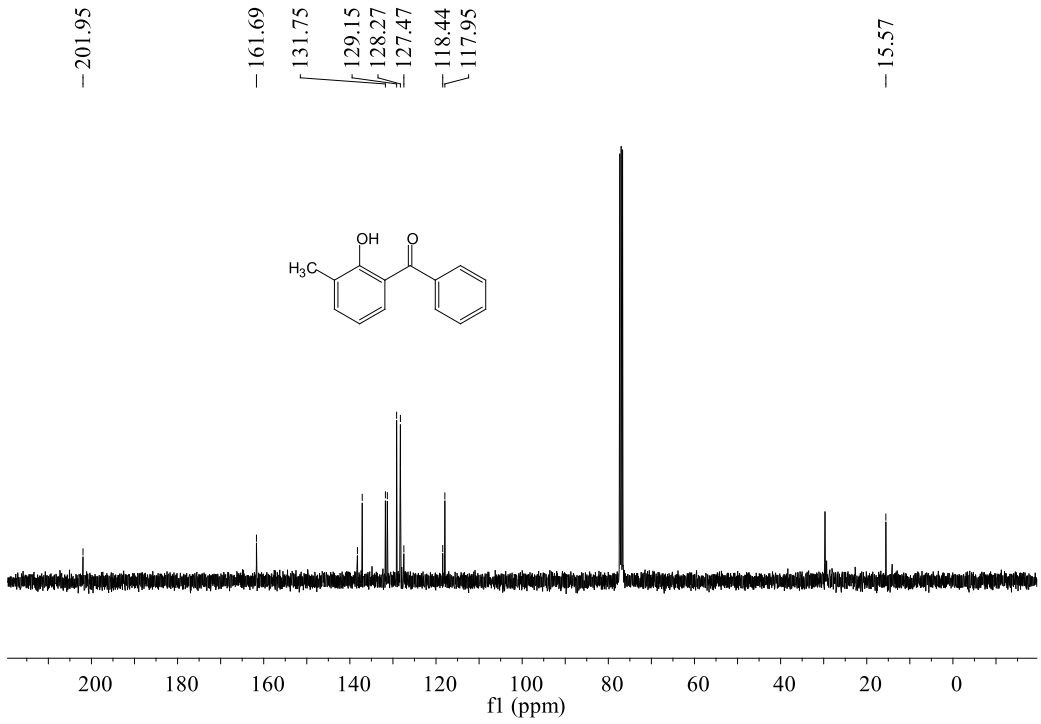
6) (4-hydroxy-[1,1'-biphenyl]-3-yl)(phenyl)methanone (3c) (Using $CDCl_3$ as solvent)



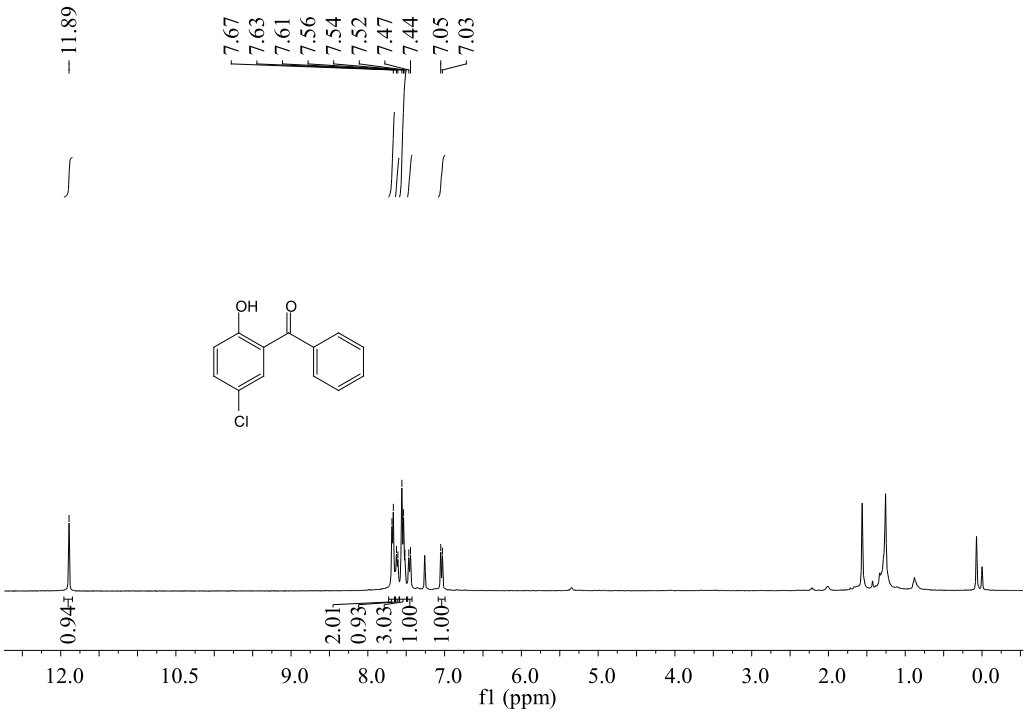


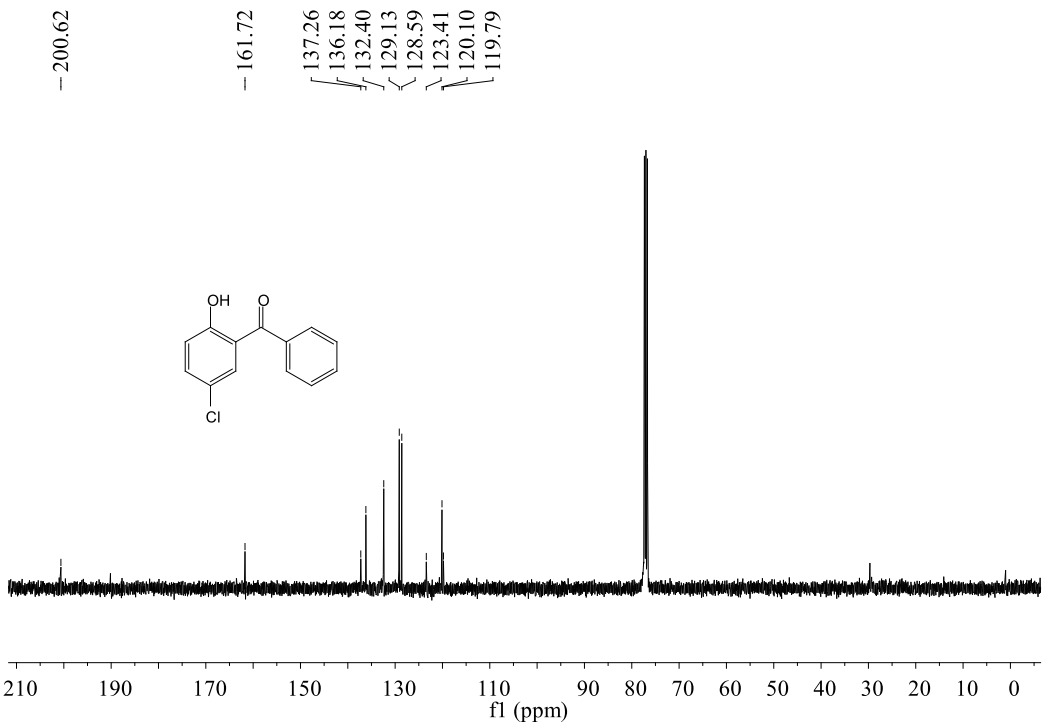
7) (2-hydroxy-3-methylphenyl)(phenyl)methanone (3d) (Using $CDCl_3$ as solvent)



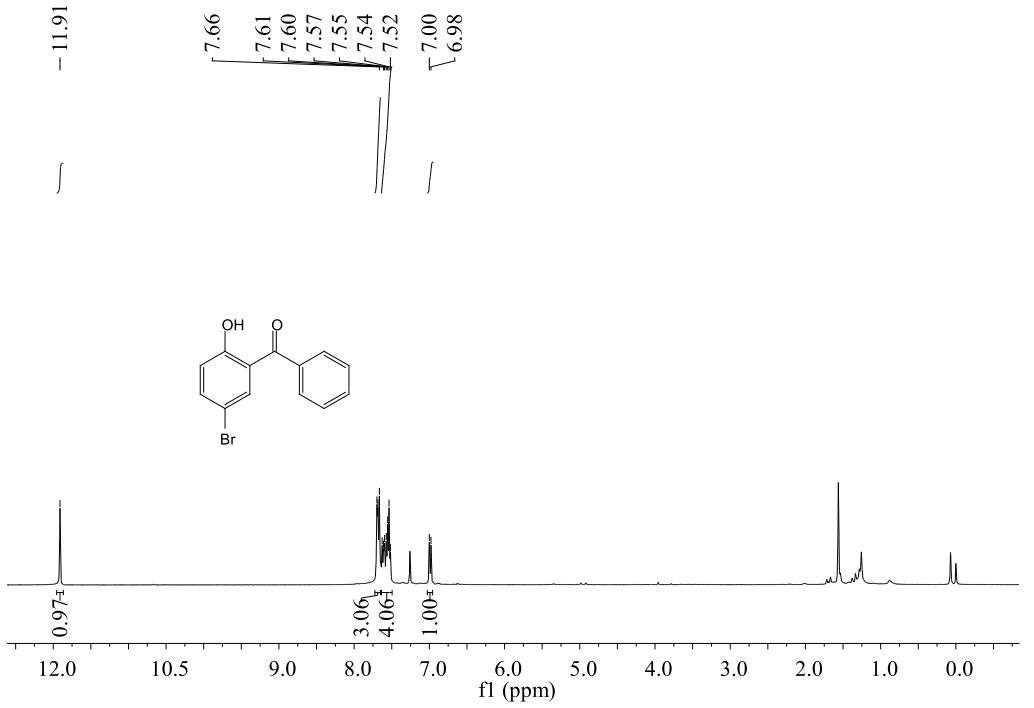


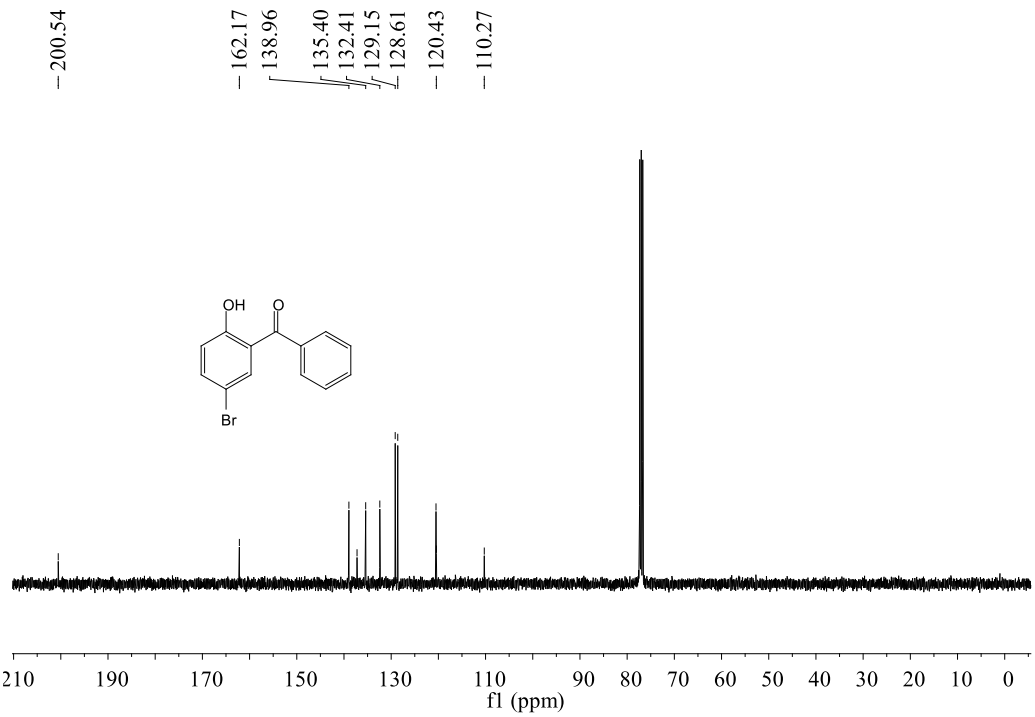
8) (5-chloro-2-hydroxyphenyl)(phenyl)methanone (3e) (Using $CDCl_3$ as solvent)



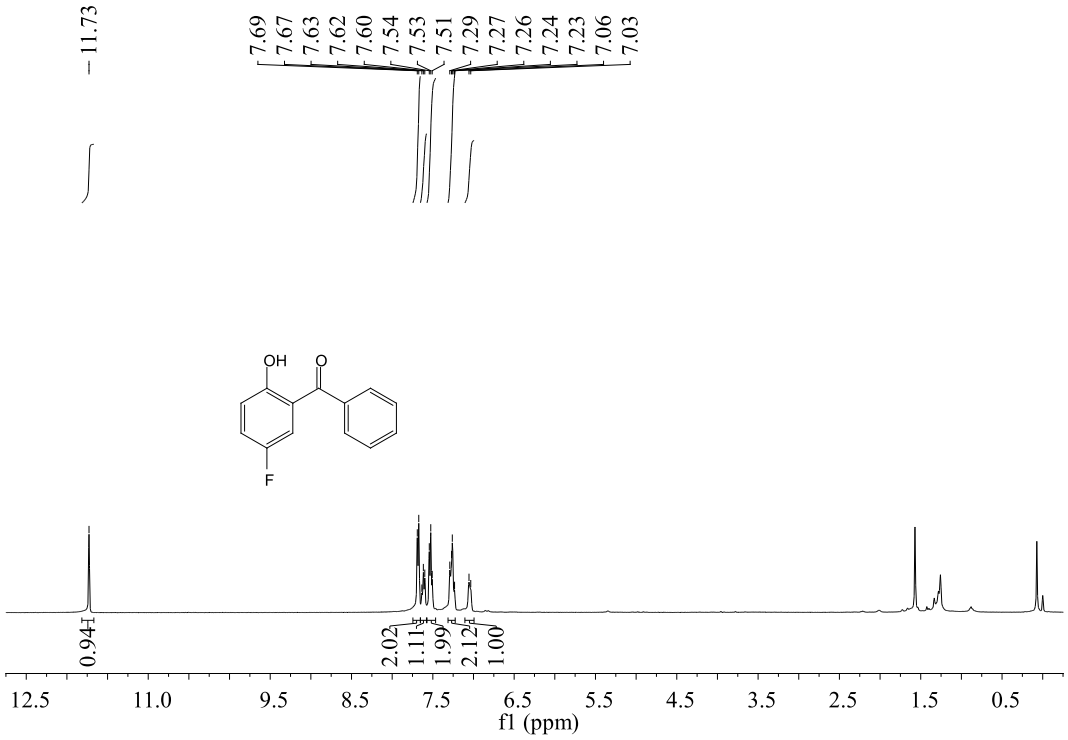


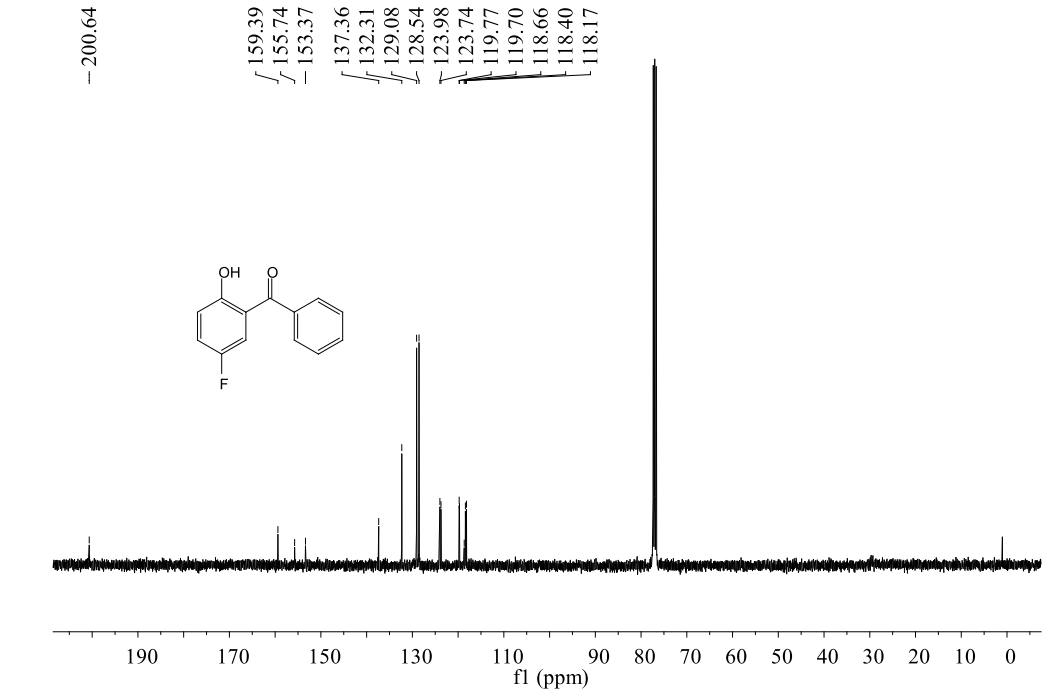
9) (5-bromo-2-hydroxyphenyl)(phenyl)methanone (3f) (Using $CDCl_3$ as solvent)



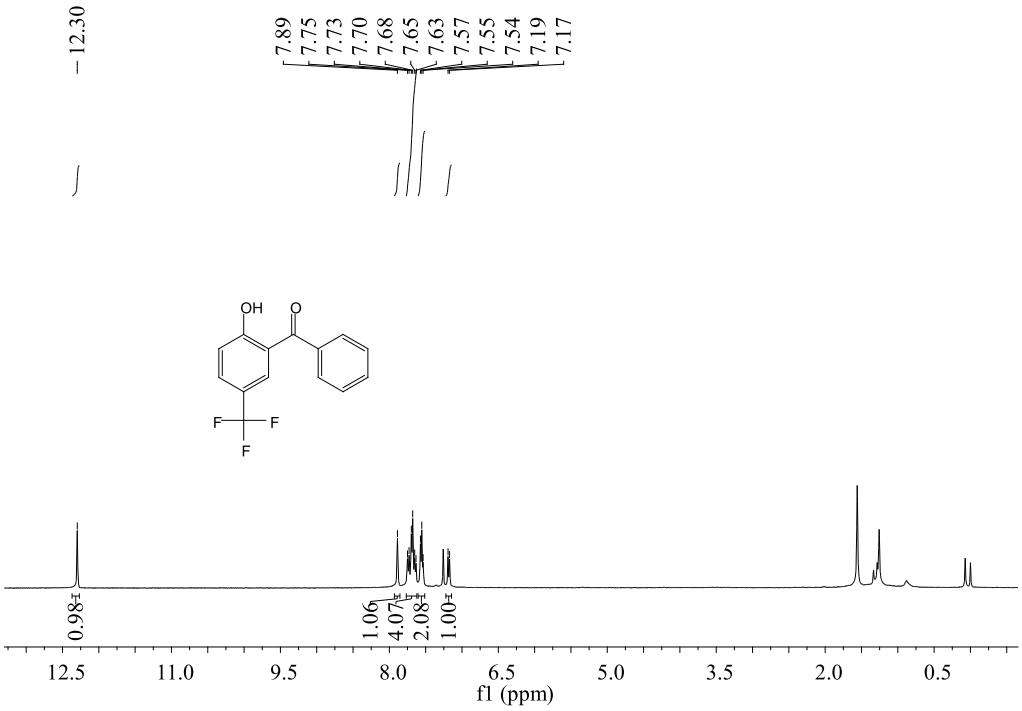


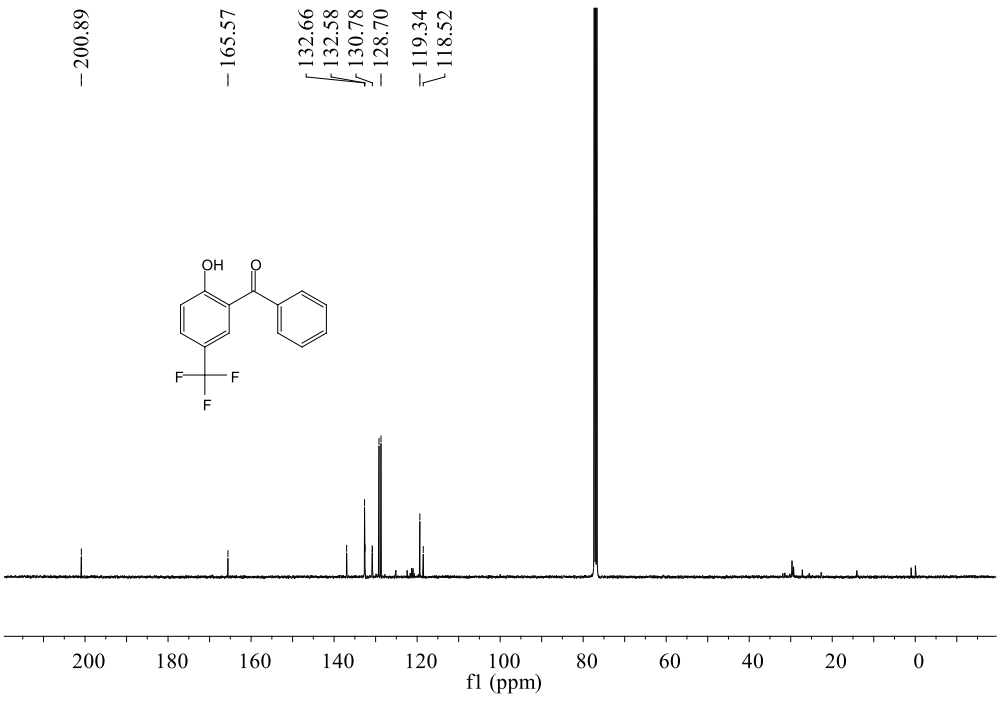
10) (5-fluoro-2-hydroxyphenyl)(phenyl)methanone (3g) (Using $CDCl_3$ as solvent)



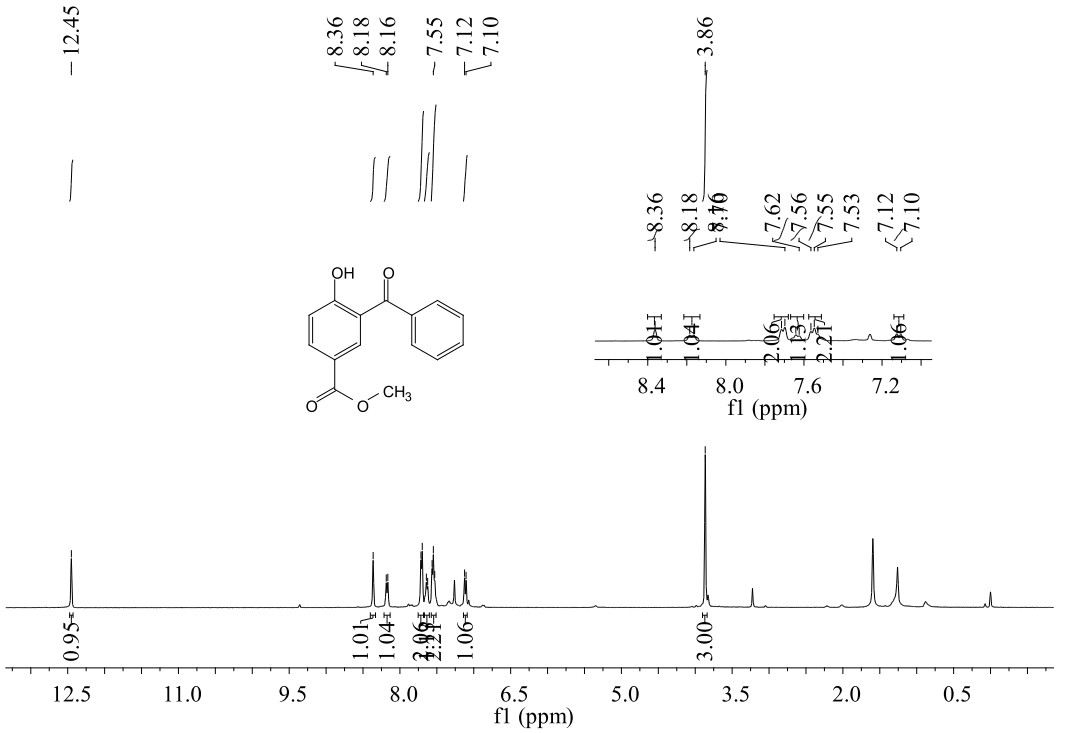


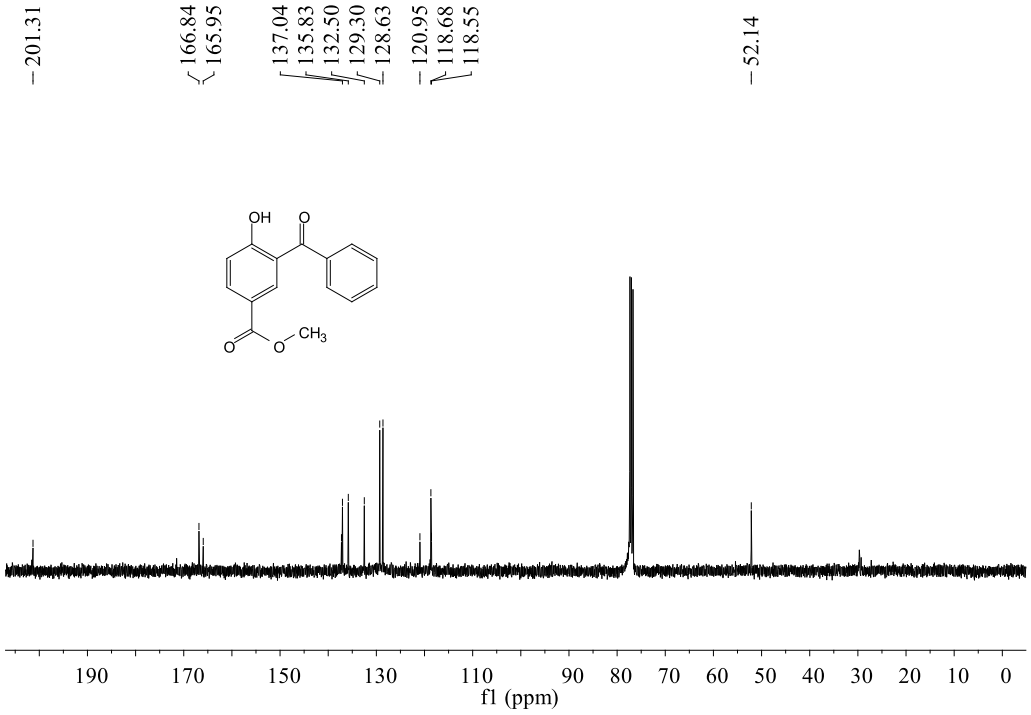
11) (2-hydroxy-5-(trifluoromethyl)phenyl)(phenyl)methanone (3h) (Using $CDCl_3$ as solvent)



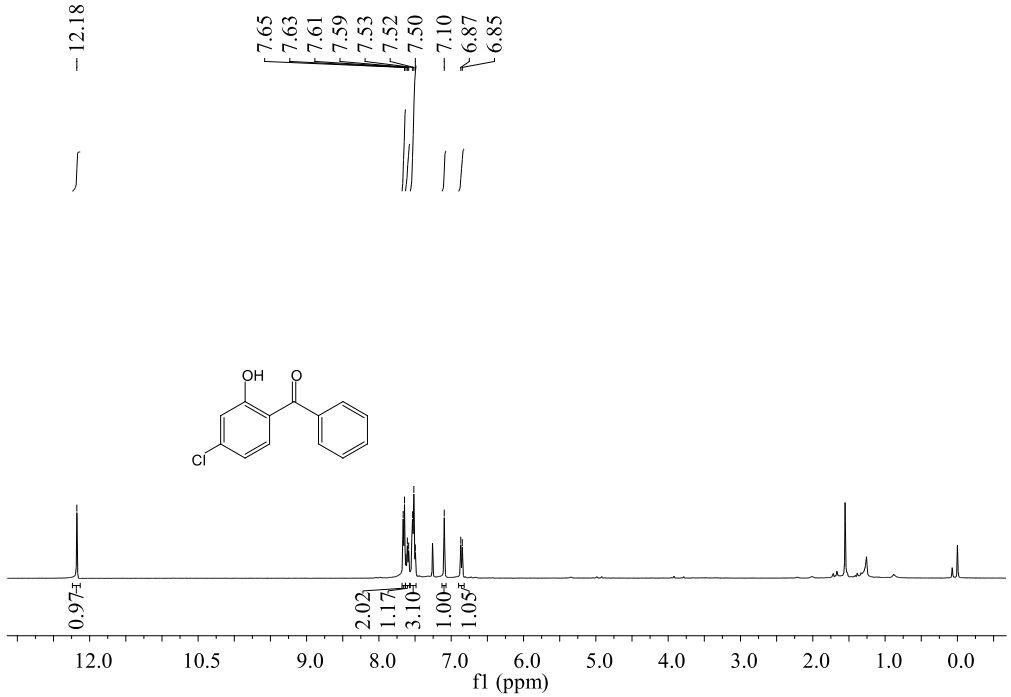


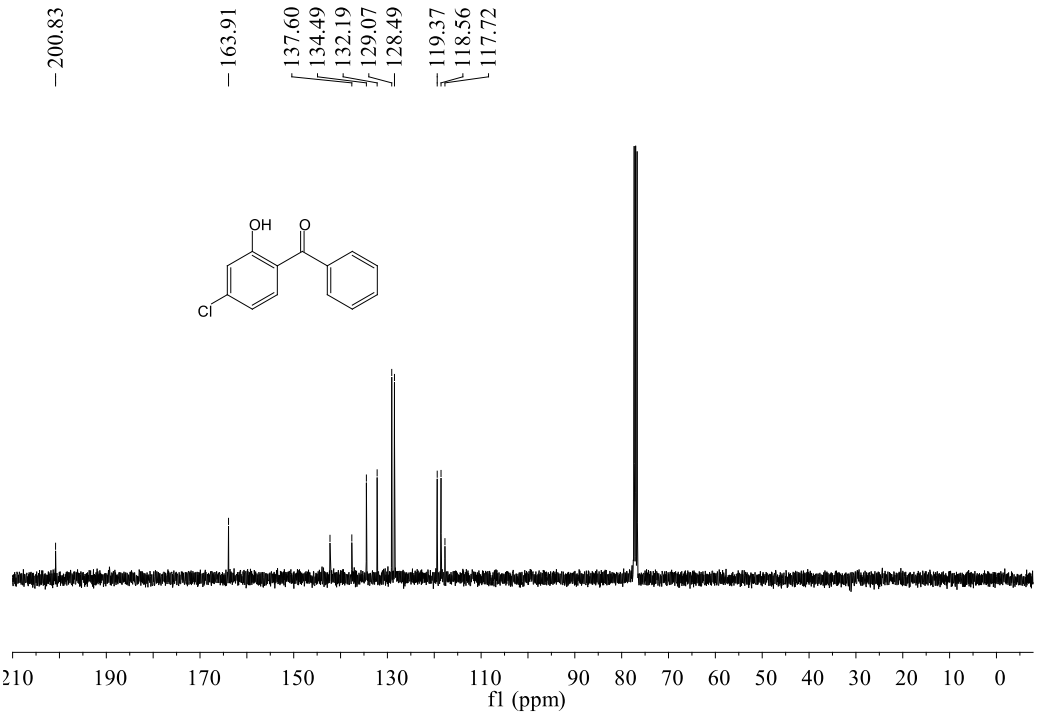
12) methyl 3-benzoyl-4-hydroxybenzoate (3i) (Using $CDCl_3$ as solvent)



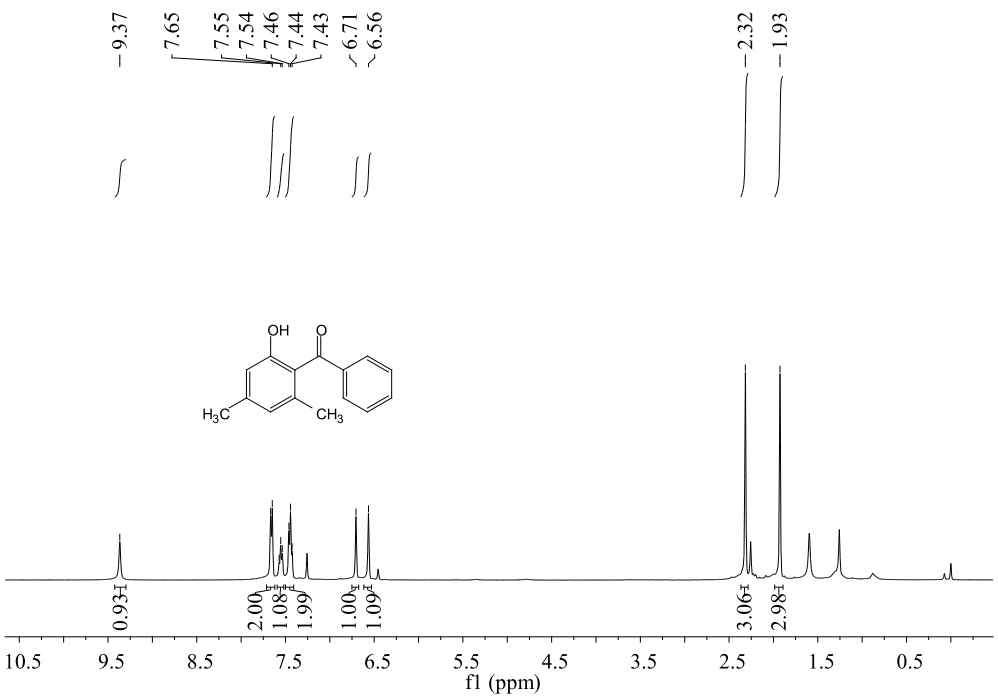


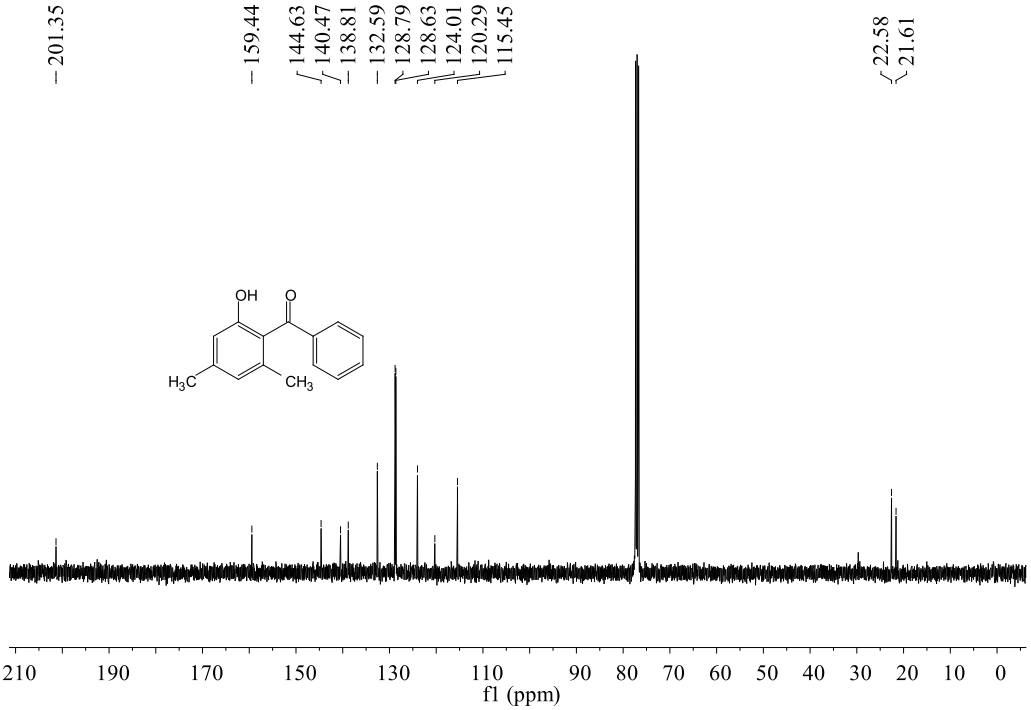
13) (4-chloro-2-hydroxyphenyl)(phenyl)methanone (3j) (Using $CDCl_3$ as solvent)



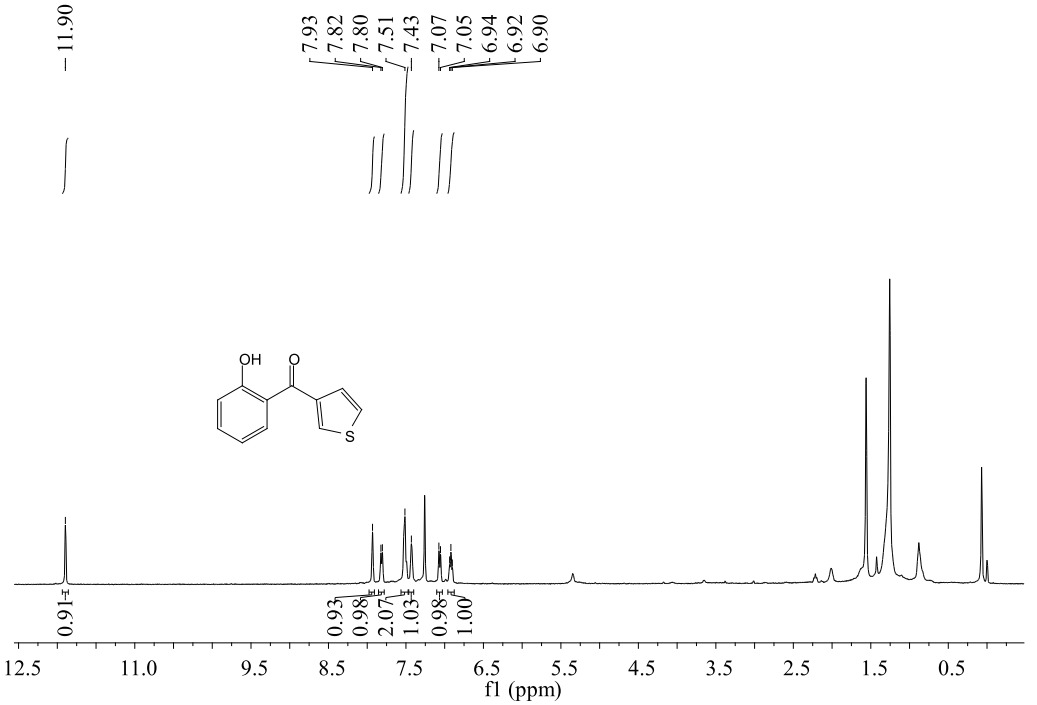


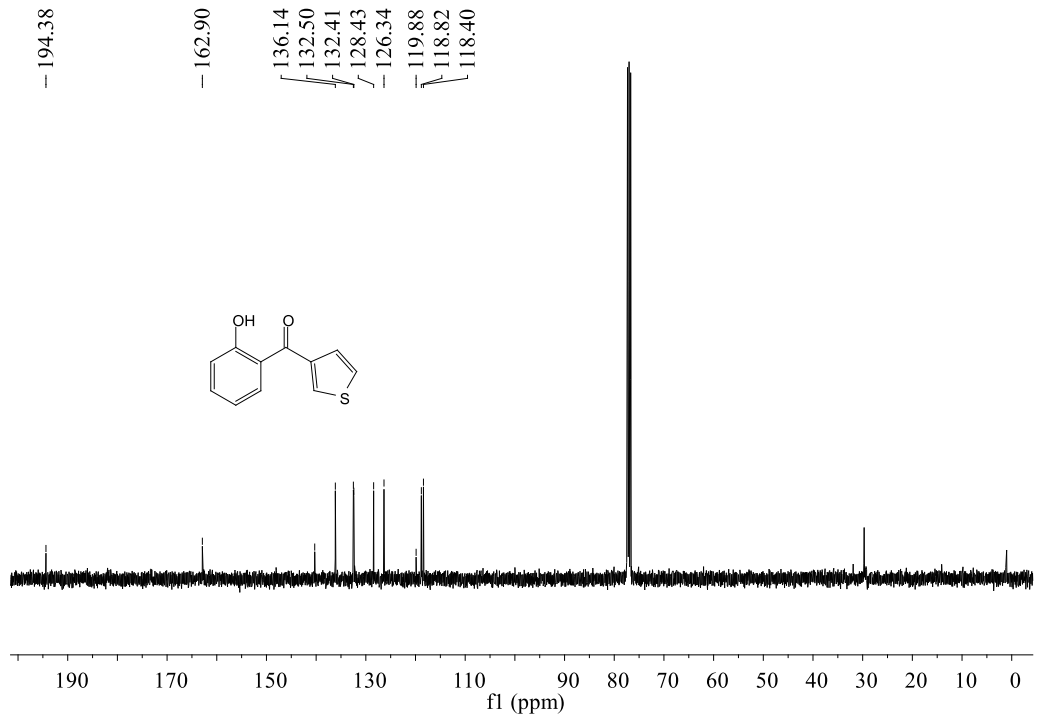
14) (2-hydroxy-4,6-dimethylphenyl)(phenyl)methanone (3k) (Using $CDCl_3$ as solvent)



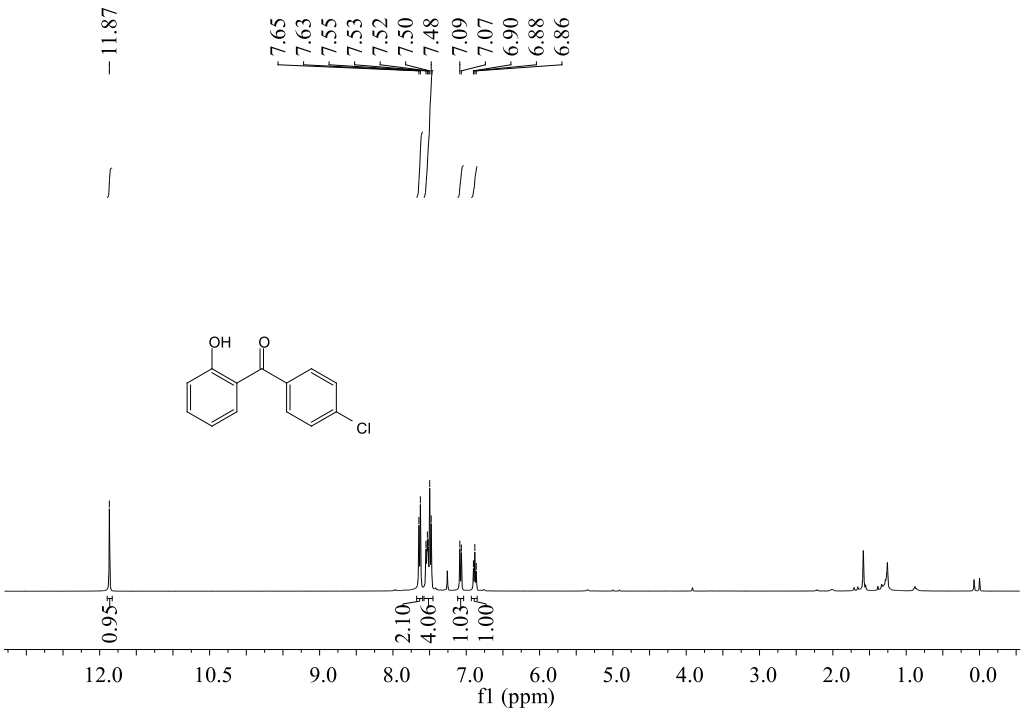


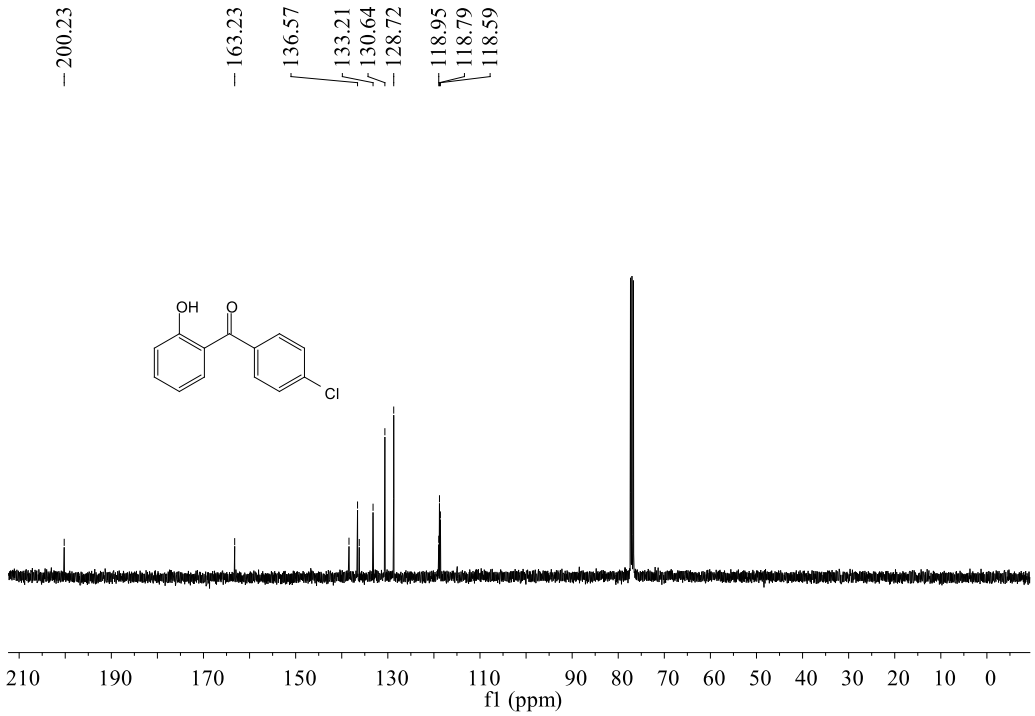
15) (2-hydroxyphenyl)(thiophen-3-yl)methanone (3l) (Using $CDCl_3$ as solvent)



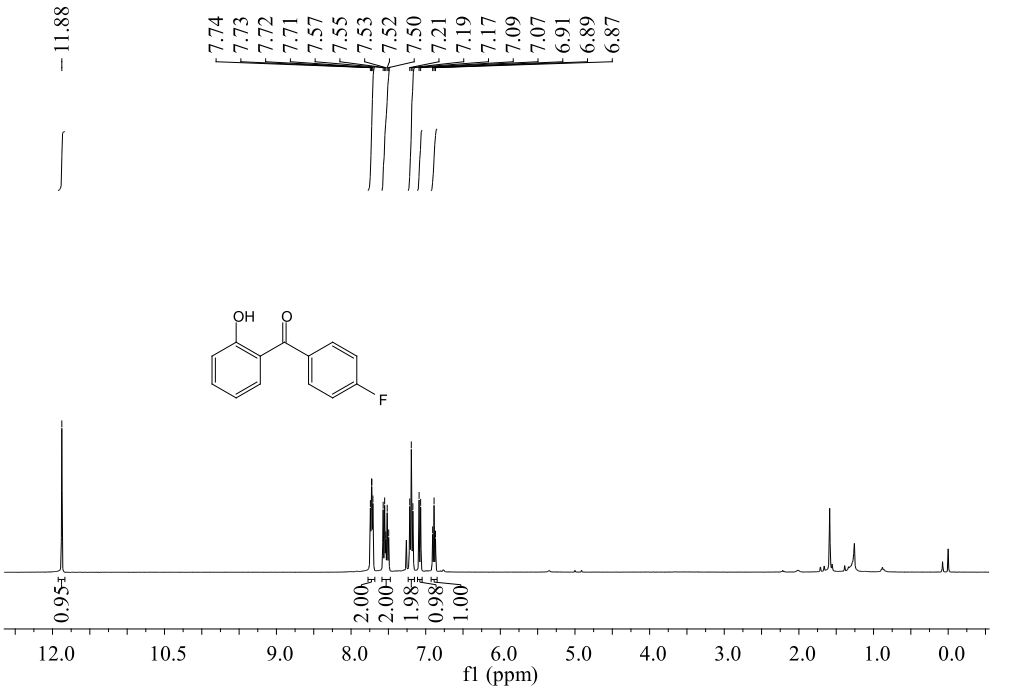


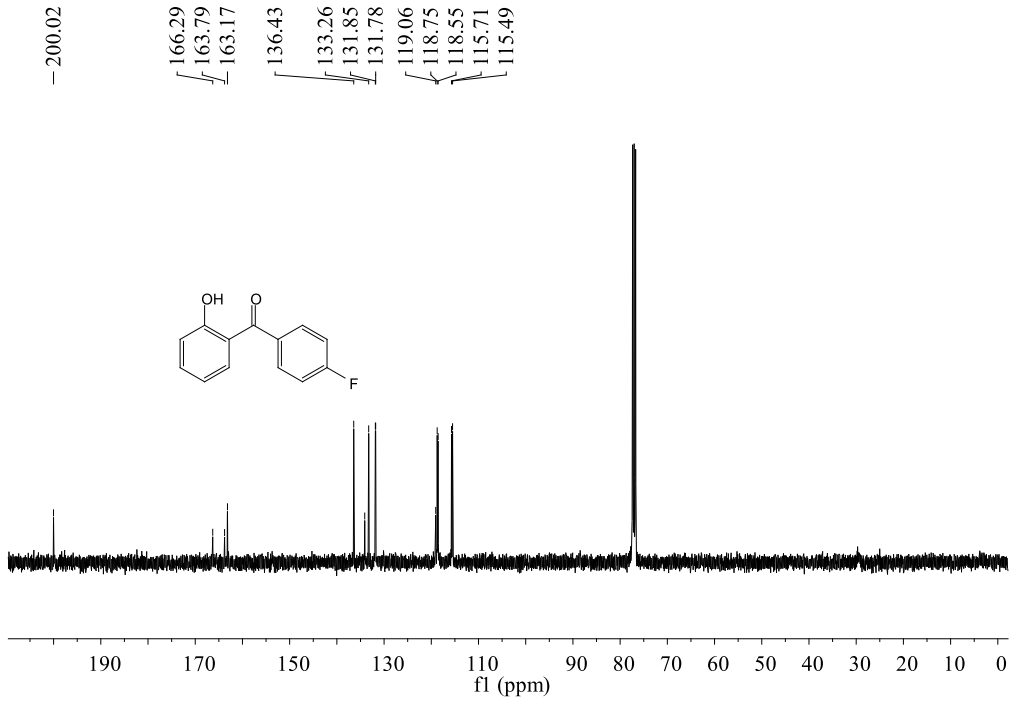
16) (4-chlorophenyl)(2-hydroxyphenyl)methanone (3m) (Using $CDCl_3$ as solvent)



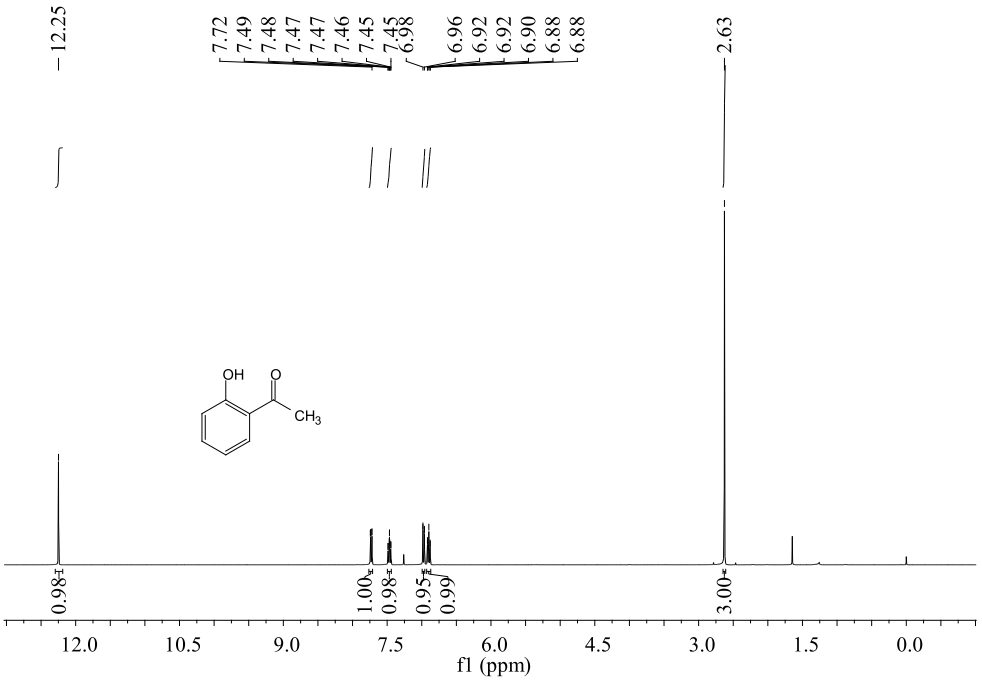


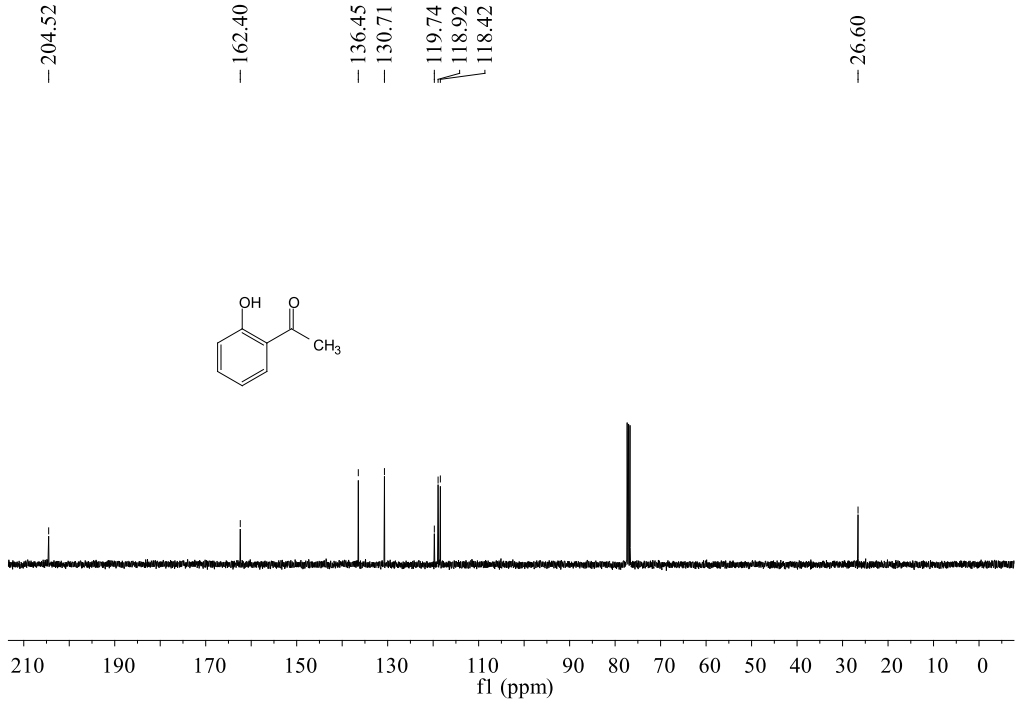
17) (4-fluorophenyl)(2-hydroxyphenyl)methanone (3n) (Using $CDCl_3$ as solvent)





18) 1-(2-hydroxyphenyl)ethanone (3p) (Using $CDCl_3$ as solvent)





19) (E)-N-(2-(2-hydroxyphenyl)-1,2-diphenylvinyl)acetamide (3) (Using $CDCl_3$ as solvent)