Nickel-Catalyzed *Para*-Selective Carboxylation of Phenols with CBr_4/MeOH

Guangliang Tu,[†] Guodong Ju,[†] Zhibin Huang,[†] Shun-Jun Ji,[†*] and Yingsheng Zhao[†,‡*]

[†]Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science Soochow University, Suzhou 215123 (PR China).

[‡]School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453000 (PR China).

E-*mail:* shunjun@suda.edu.cn; yszhao@suda.edu.cn

Supporting Information

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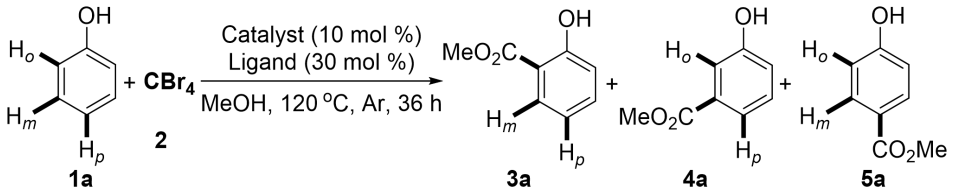
1. **Reagents:** Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Column chromatography purifications were performed using 200–300 mesh silica gel.

2. **Instruments:** NMR spectra were recorded on Varian Inova–400 MHz, Inova–300 MHz, Bruker DRX–400 or Bruker DRX–500 instruments and calibrated using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. HRMS analysis were carried out using a Bruker micrOTOF–Q instrument or a TOF–MS instrument. GC-MS analysis were carried out using a Bruker Scion SQ 436 instrument. The UV–visdiffuse reflection spectroscopy (DRS) were measured on a Shimadzu UV-3600 spectrophotometer at room temperature.

3. **Table S1. Optimization of reaction conditions**[a]



Entry	Catalyst	Ligand	**3a + 4a + 5a** yield (%)[b]	**5a/4a+3a** (*p*/others)[c]
1	$Co(acac)_2$	-	21	4.4/1
2	Fe(TPP)Cl	-	<5	-
3	$Pd(OAc)_2$	-	46	> 20/1
4	$Cu(acac)_2$	-	24	13/1
5	$Ni(dppf)Cl_2$	-	73	9.5/1
6	$Ni(PPh_3)_2Cl_2$	-	36	> 20/1
7	$Ni(dppp)Cl_2$	-	10	13/1
8	$Ni(dppe)Cl_2$	-	41	7.5/1
9	$Ni(bpy)Br_2$	-	16	19/1
10	$Ni(dppf)Cl_2$	PPh_3	70	7.5/1
11	$Ni(dppf)Cl_2$	dppp	74	8.8/1
12	$Ni(dppf)Cl_2$	Ac-Gly-OH	49	4.3/1
13	$Ni(dppf)Cl_2$	MesCOOH	48	6.7/1
14	$Ni(dppf)Cl_2$	bpy	58	23/1
15	$Ni(dppf)Cl_2$	L1	82(80)[d]	13/1
16	$Ni(dppf)Cl_2$	L2	51	4.5/1
17	$Ni(dppf)Cl_2$	L3	48	5.3/1
18	$Ni(dppf)Cl_2$	L4	62	5.5/1
19	$Ni(dppf)Cl_2$	L1	<5[e]	-
20	-	L1	<5	-

[a]Reaction performed on a 0.2 mmol scale with **2** (0.6 mmol) in dry MeOH (0.6 mL) under argon in a sealed tube. [b]GC yield with tridecane as the internal standard. [c]Selectivity ratio determined by ^{1}H NMR analysis. [d]Isolated yield. [e]Reaction performed on a 0.2 mmol scale with **2** (0.6 mmol) in dry MeOH (0.6 mL) under oxygen in a sealed tube. Key: 1,3-bis(diphenylphosphino)propane (dppp), N-acetylglycine (Ac-Gly-OH), 2,4,6-trimethylbenzoic acid (MesCOOH), 2,2'-bipyridine (bpy), 1,10-phenanthroline (L1), 3,4,7,8-tetramethyl-1,10-phenanthroline (L2), 2,9-diphenyl-1,10-phenanthroline (L3), and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (L4).

The ^{1}H NMR spectra of Entry 1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17 and 18.

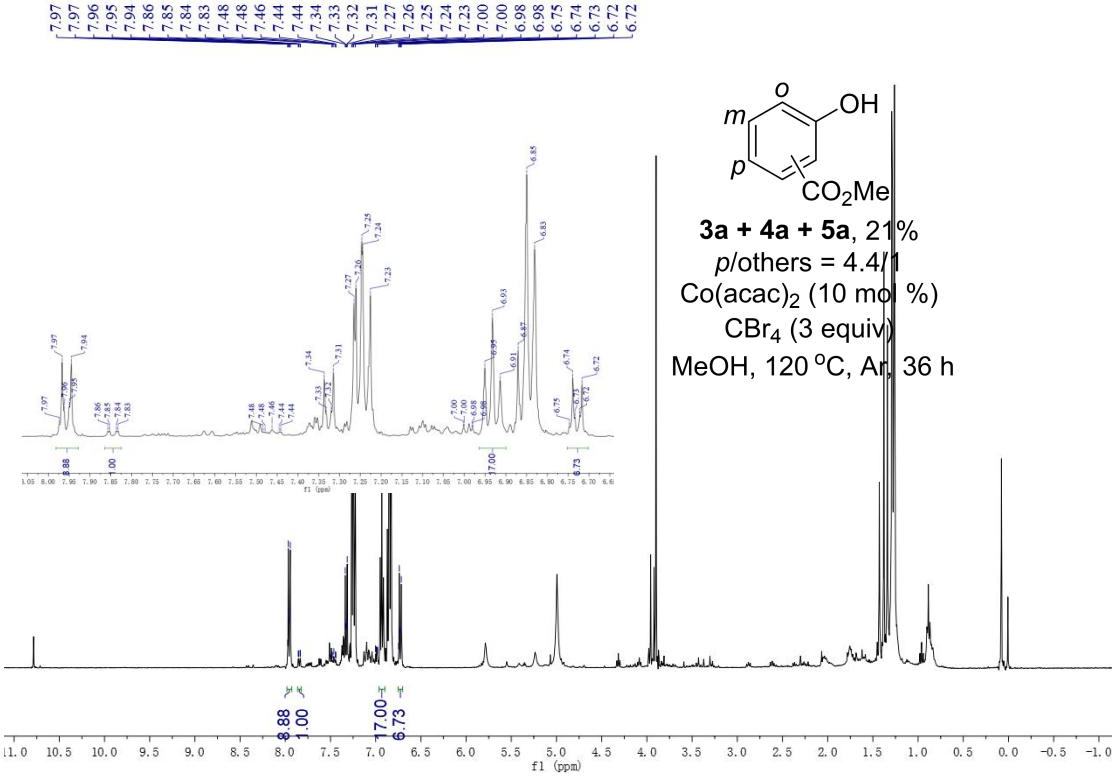


Figure S1. The ^{1}H NMR spectra of Entry 1

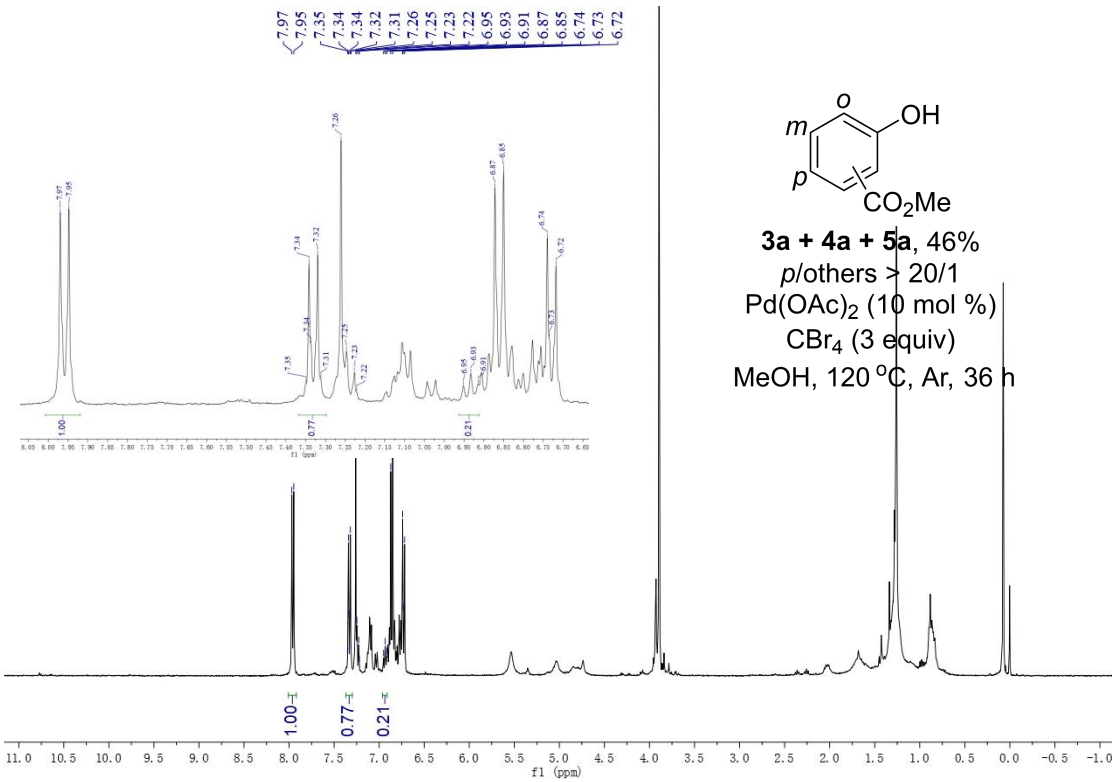


Figure S2. The ^{1}H NMR spectra of Entry 3

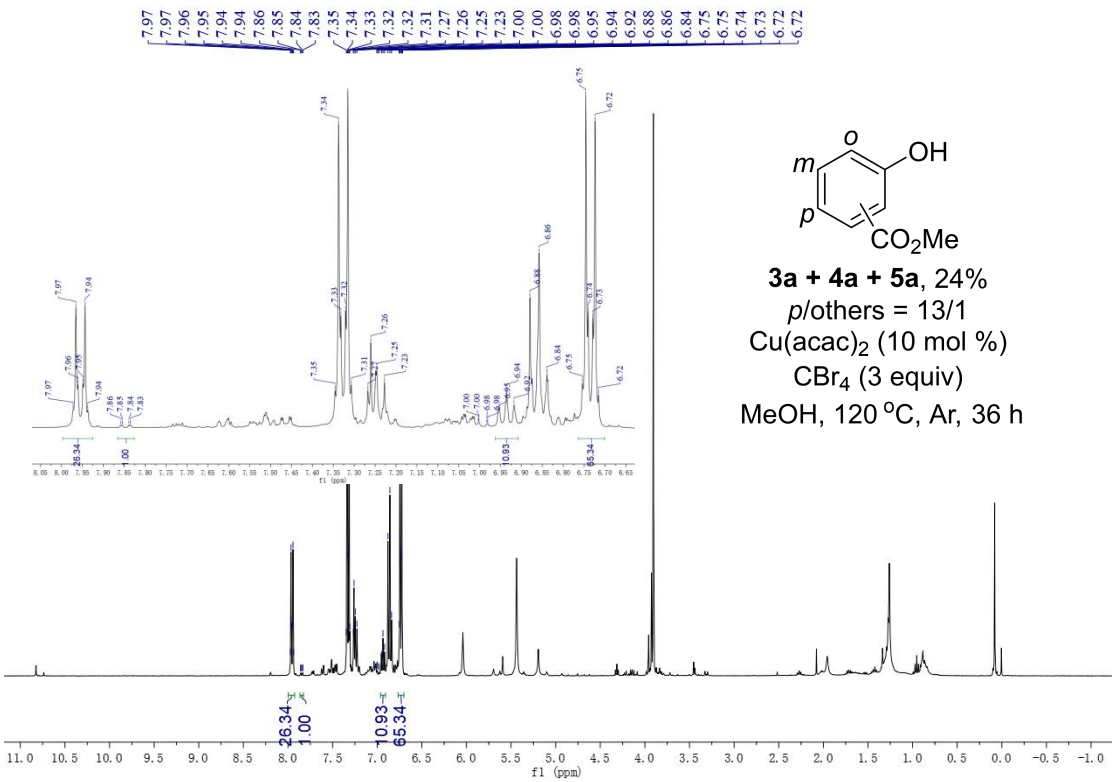


Figure S3. The ^{1}H NMR spectra of Entry 4

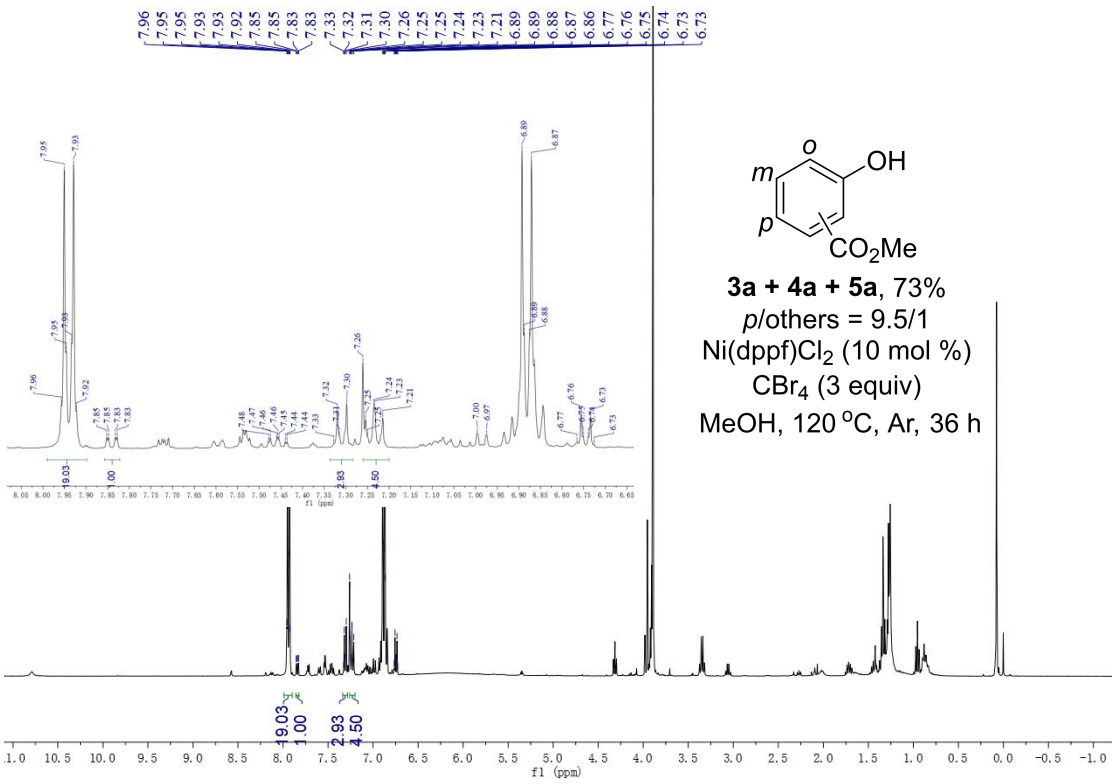


Figure S4. The ^{1}H NMR spectra of Entry 5

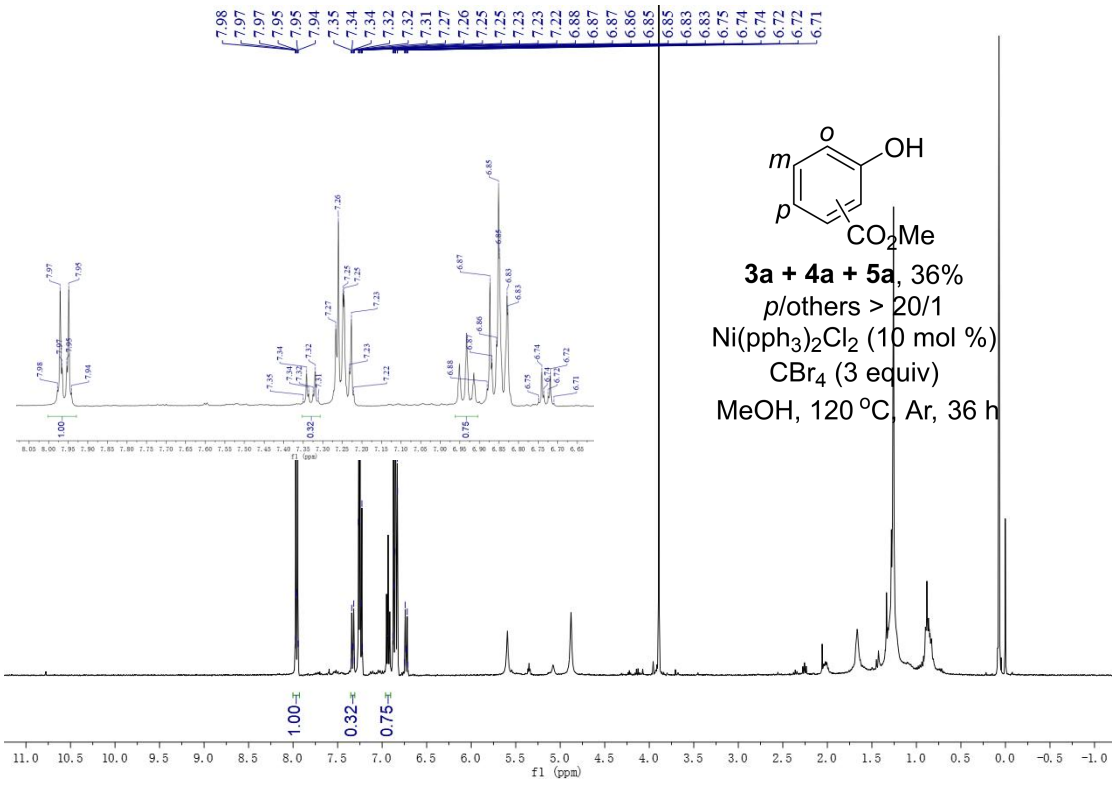


Figure S5. The ^{1}H NMR spectra of Entry 6

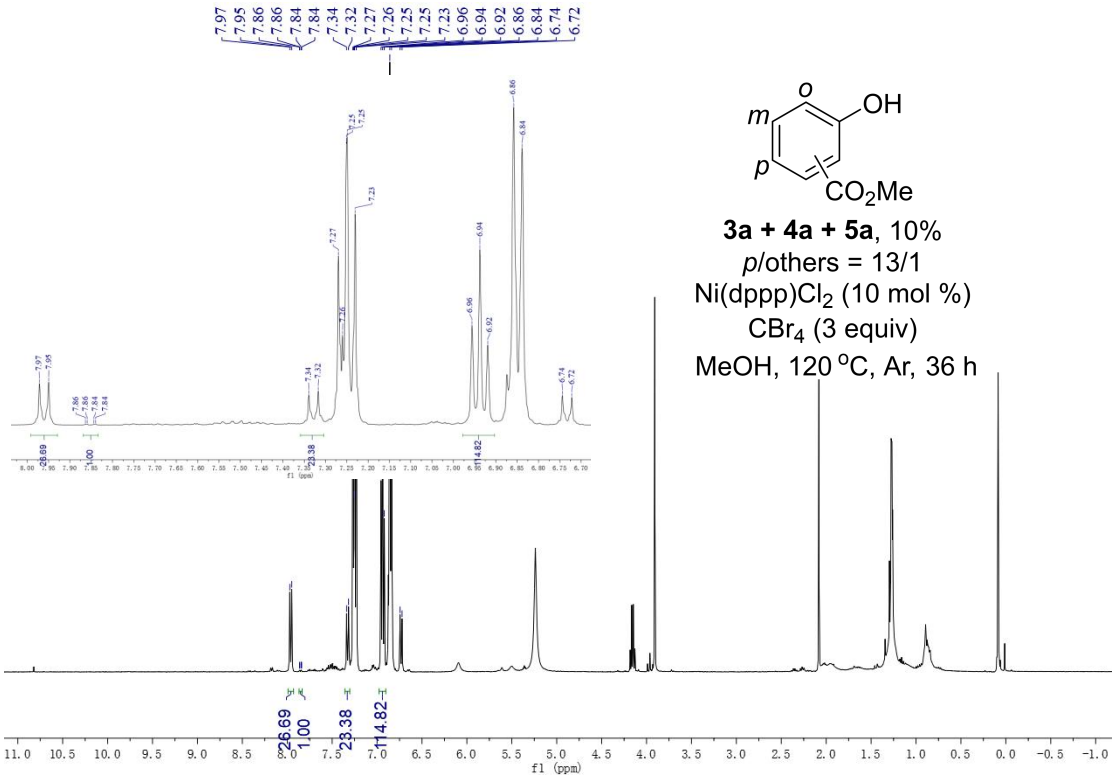


Figure S6. The ^{1}H NMR spectra of Entry 7

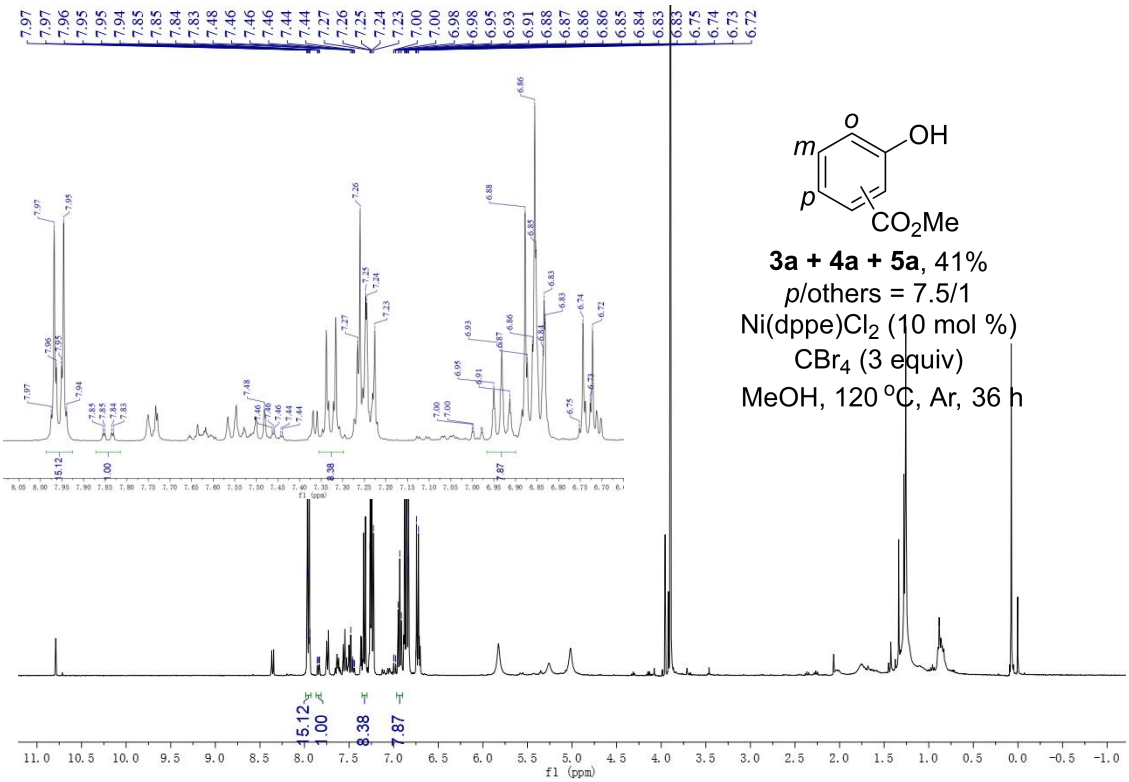


Figure S7. The ^{1}H NMR spectra of Entry 8

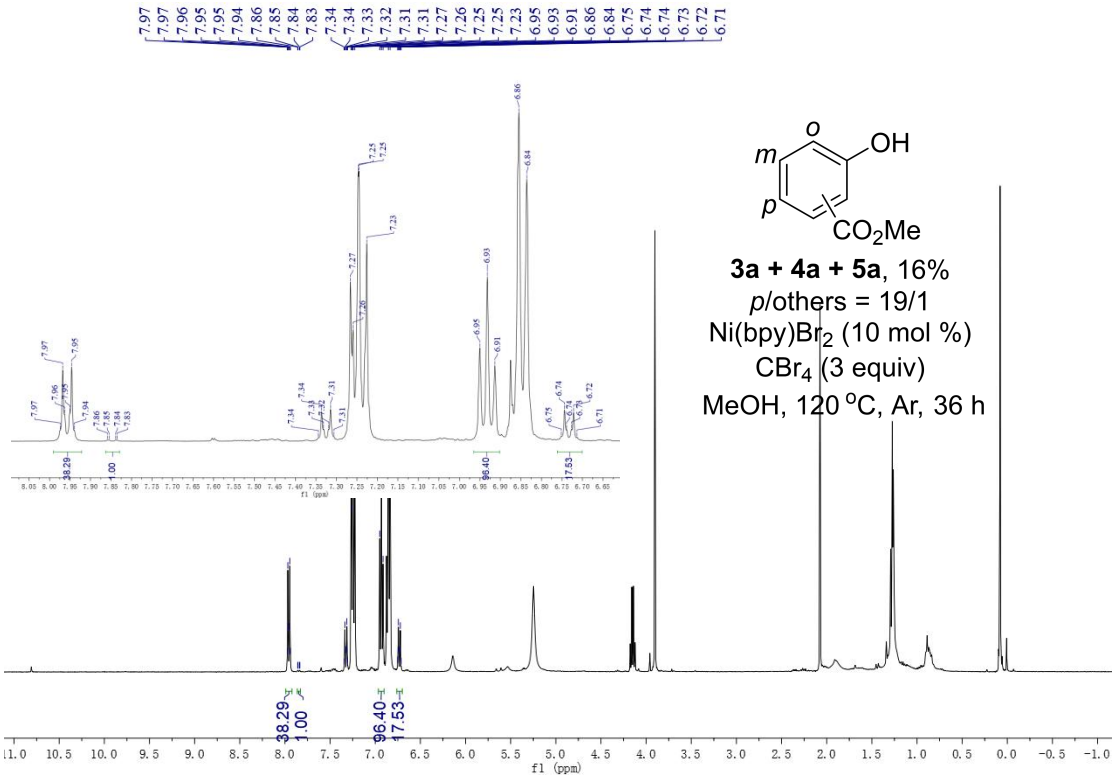


Figure S8. The ^{1}H NMR spectra of Entry 9

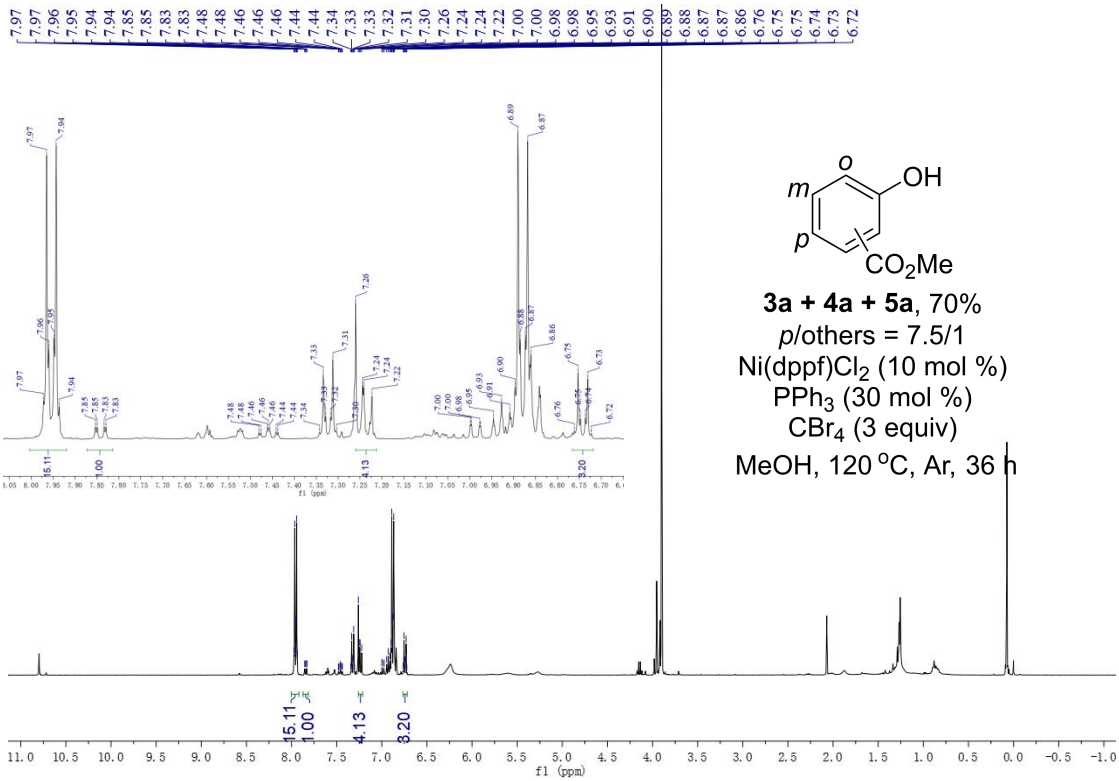


Figure S9. The ^{1}H NMR spectra of Entry 10

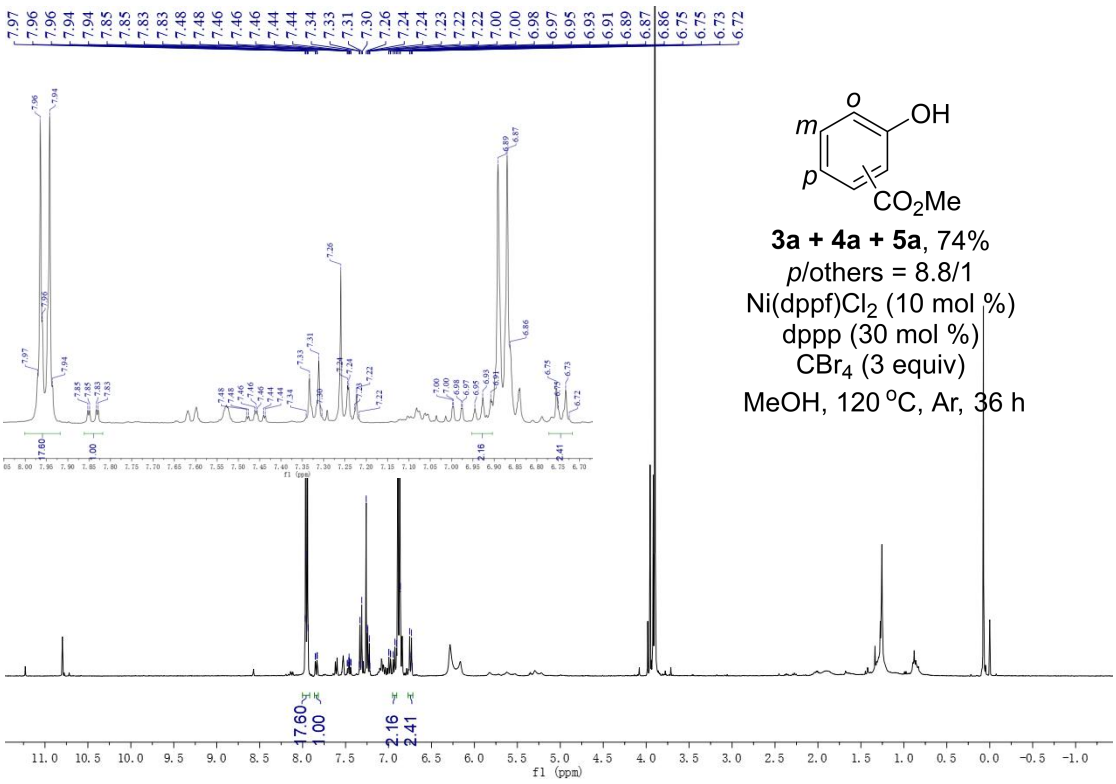


Figure S10. The ^{1}H NMR spectra of Entry 11.

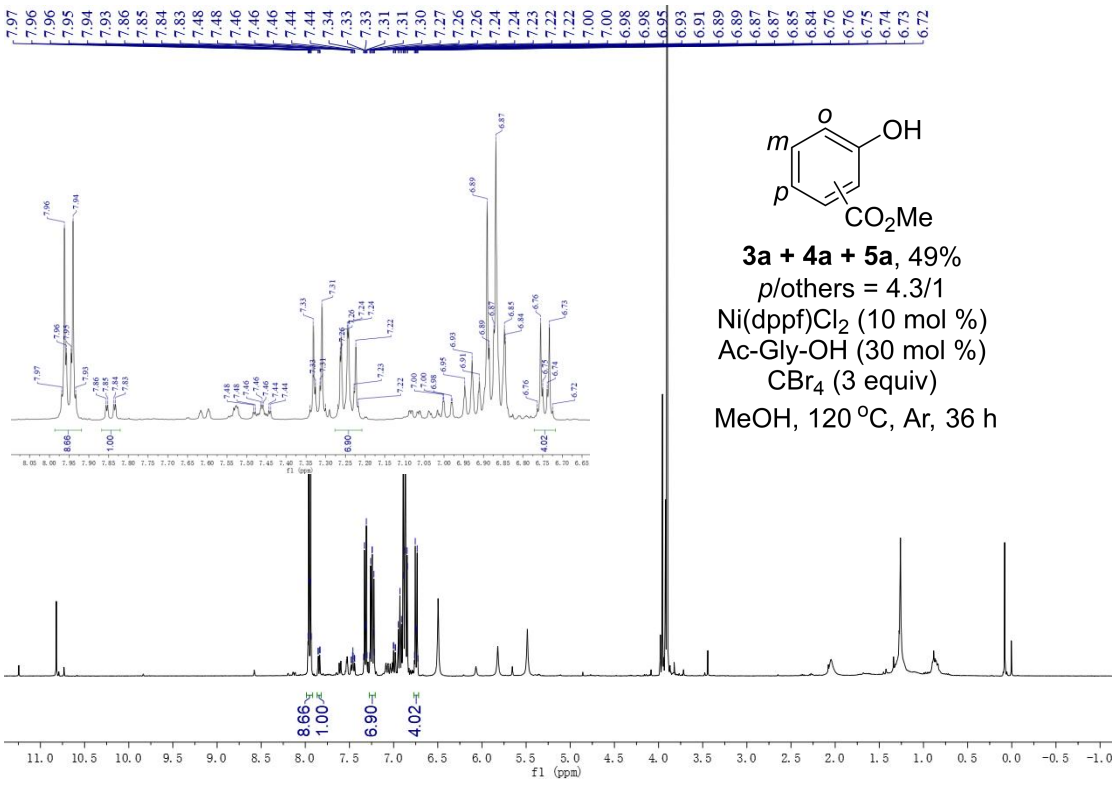


Figure S11. The ^{1}H NMR spectra of Entry 12.

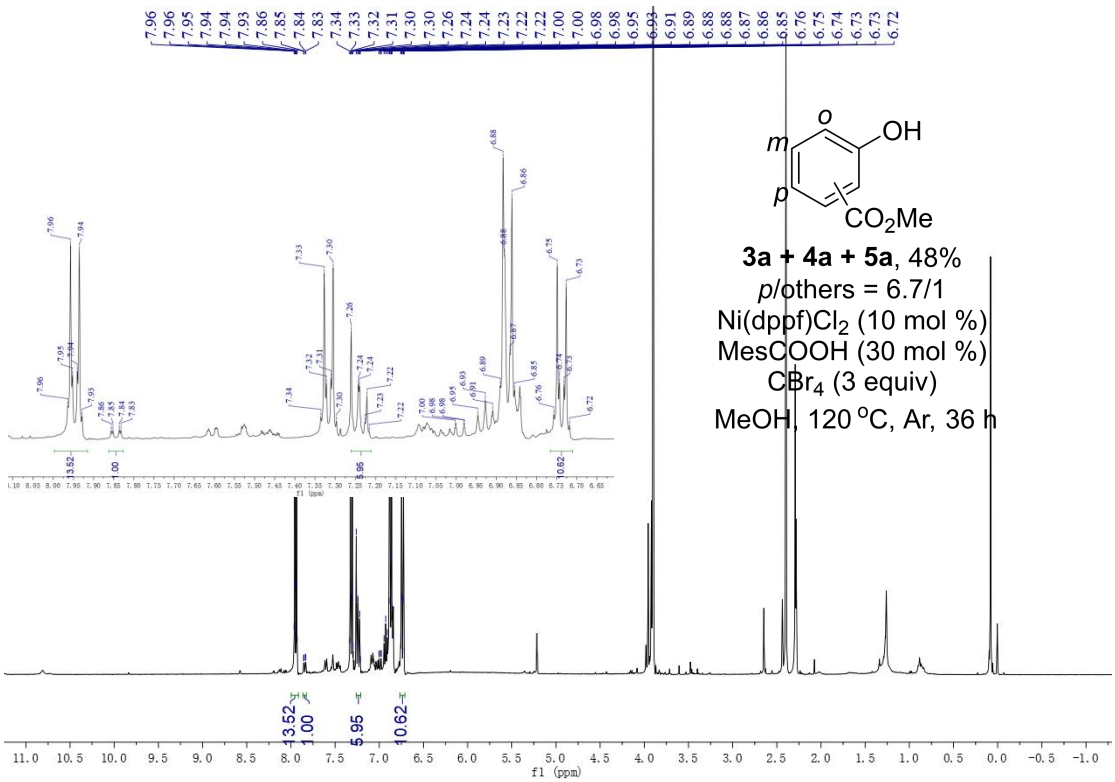


Figure S12. The ^{1}H NMR spectra of Entry 13.

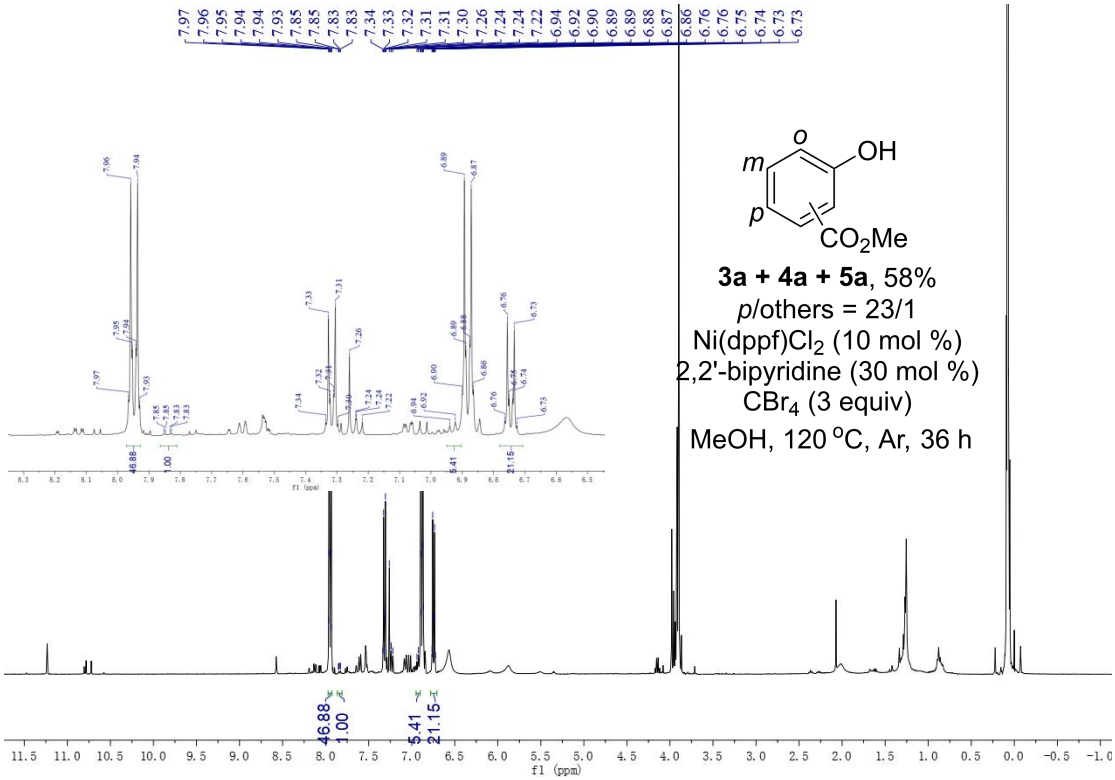


Figure S13. The ^{1}H NMR spectra of Entry 14.

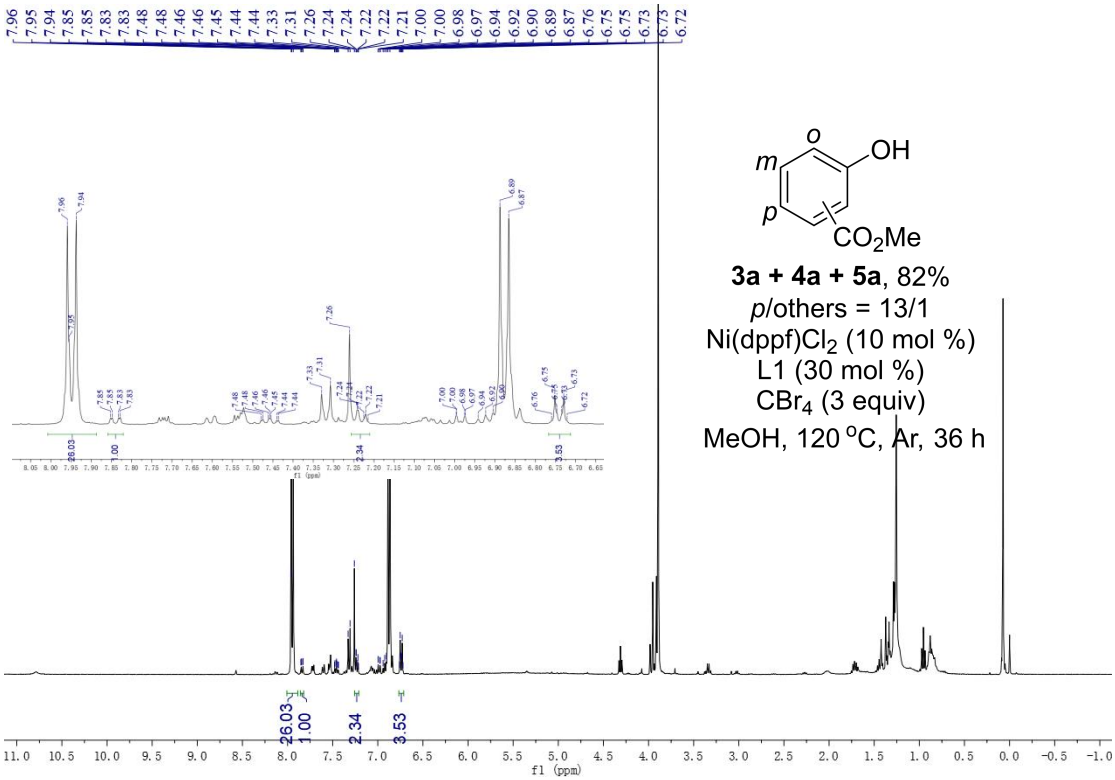


Figure S14. The ^{1}H NMR spectra of Entry 15. L1 = 1,10-phenanthroline

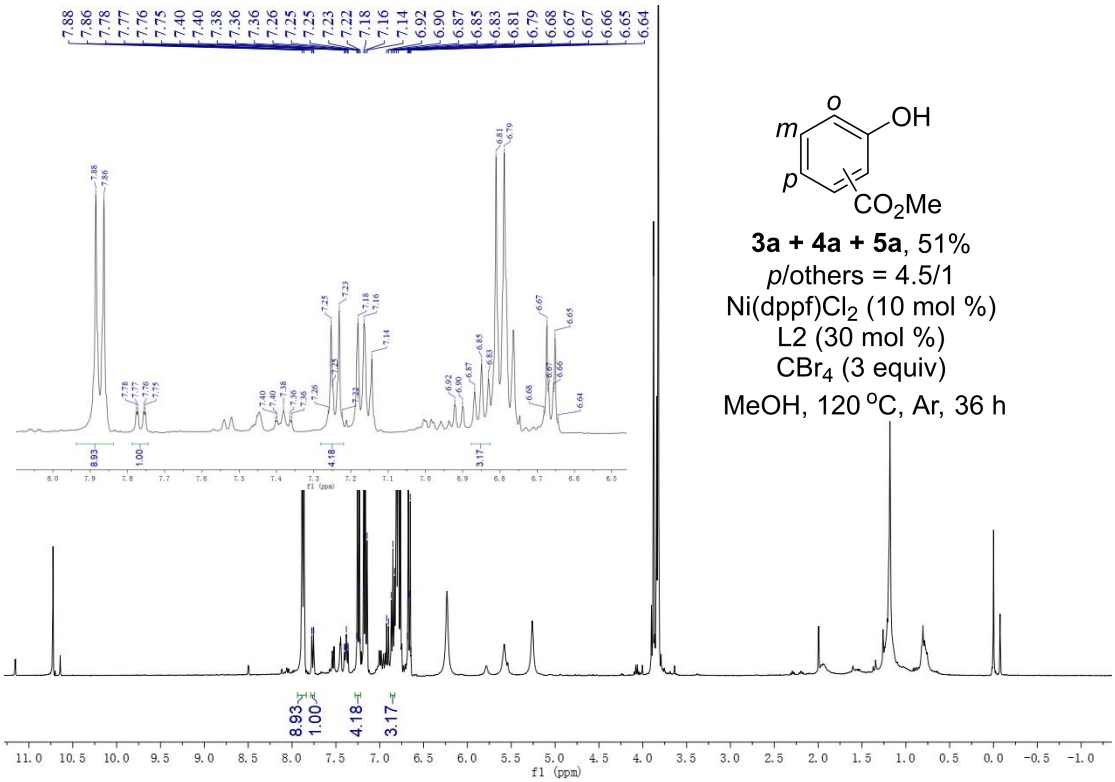


Figure S15. The ^{1}H NMR spectra of Entry 16. L2 = 3,4,7,8-tetramethyl-1,10-phenanthroline

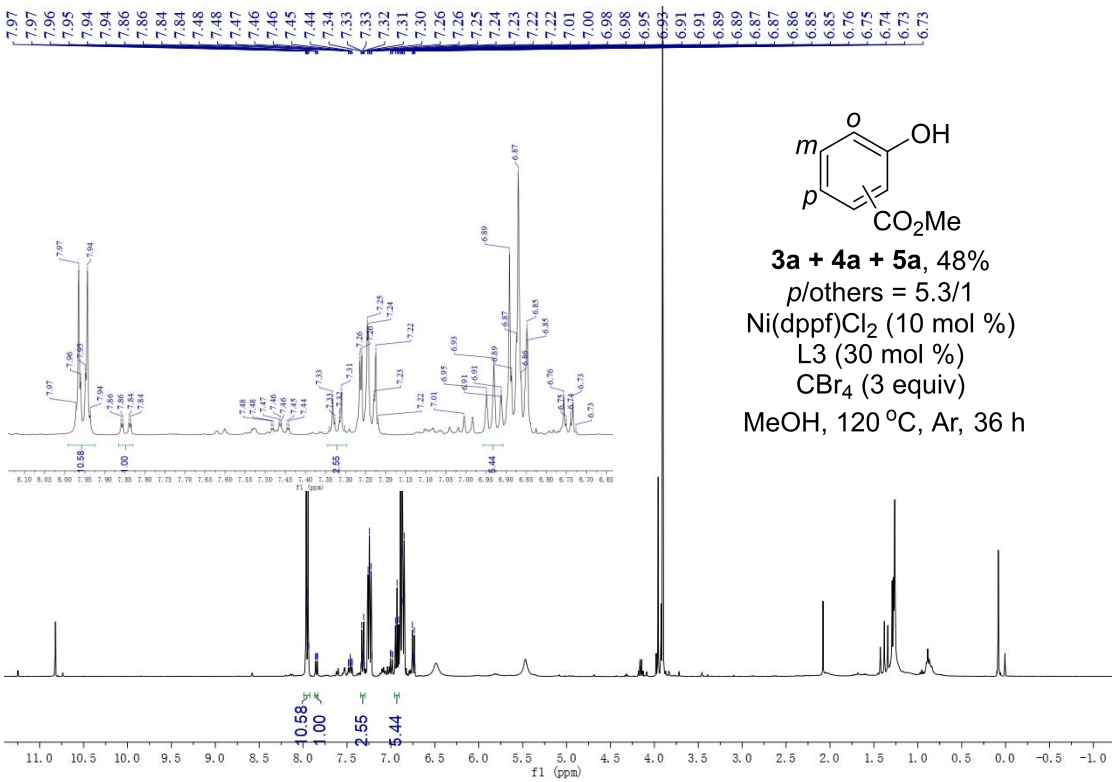


Figure S16. The ^{1}H NMR spectra of Entry 17. L3 = 2,9-dimethyl-1,10-phenanthroline

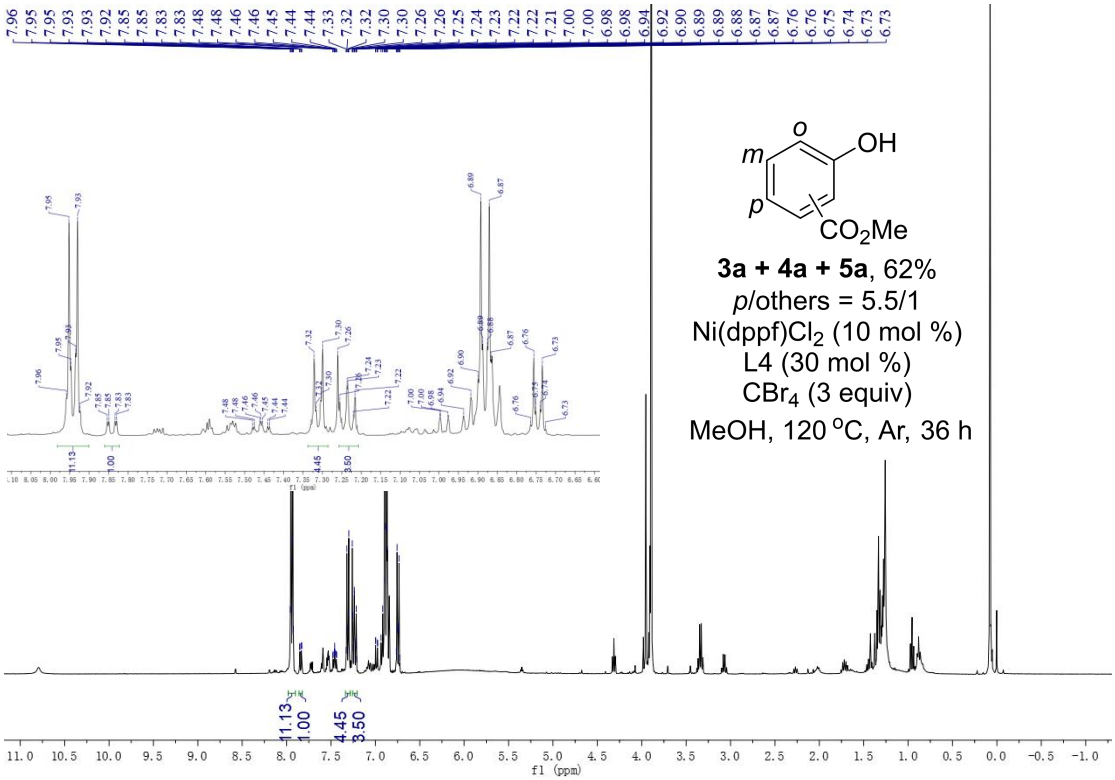
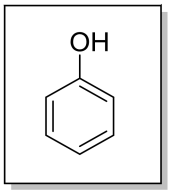


Figure S17. The ^{1}H NMR spectra of Entry 18. L4 = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline

^{1}H NMR (400 MHz, $CDCl_3$) of phenol and corresponding products under standard condition:
(These compounds were purchased from commercial sources and used without further purification)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.87 – 6.81 (m, 2H), 4.95 (s, 3H).

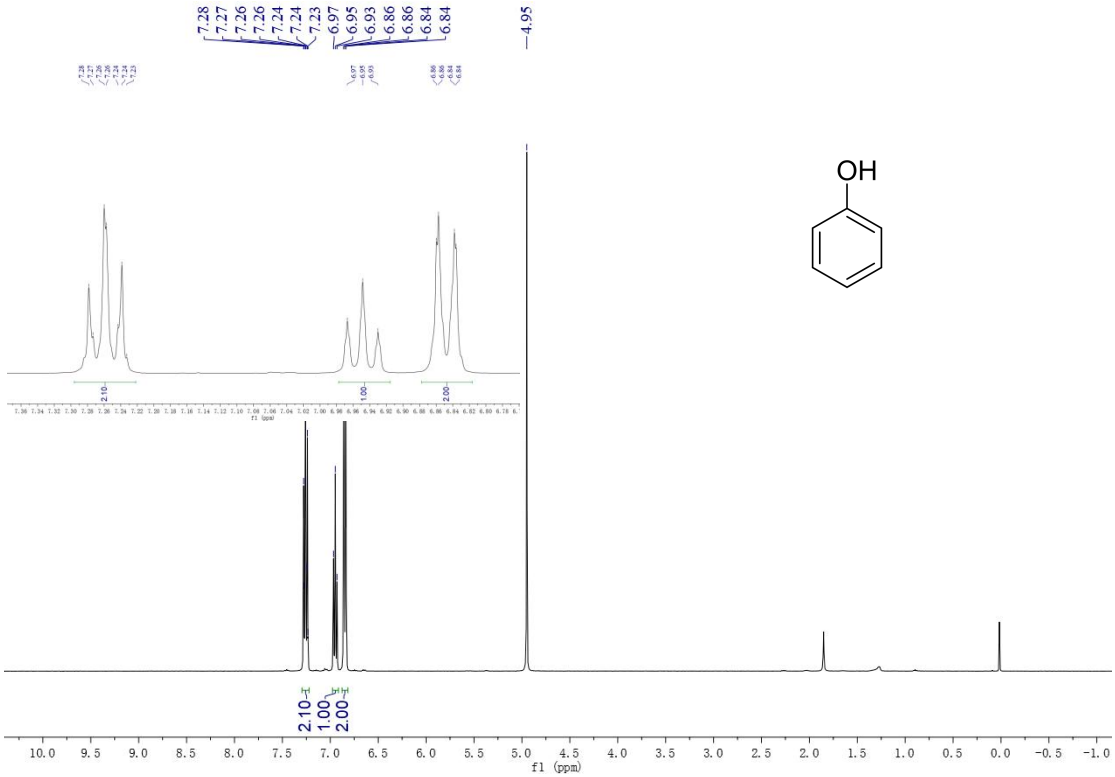
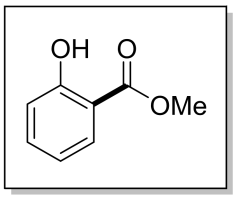


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) of phenol



^{1}H NMR (400 MHz, $CDCl_3$) δ 10.75 (s, 1H), 7.84 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.51 – 7.41 (m, 1H), 7.02 – 6.96 (m, 1H), 6.92 – 6.84 (m, 1H), 3.95 (s, 3H).

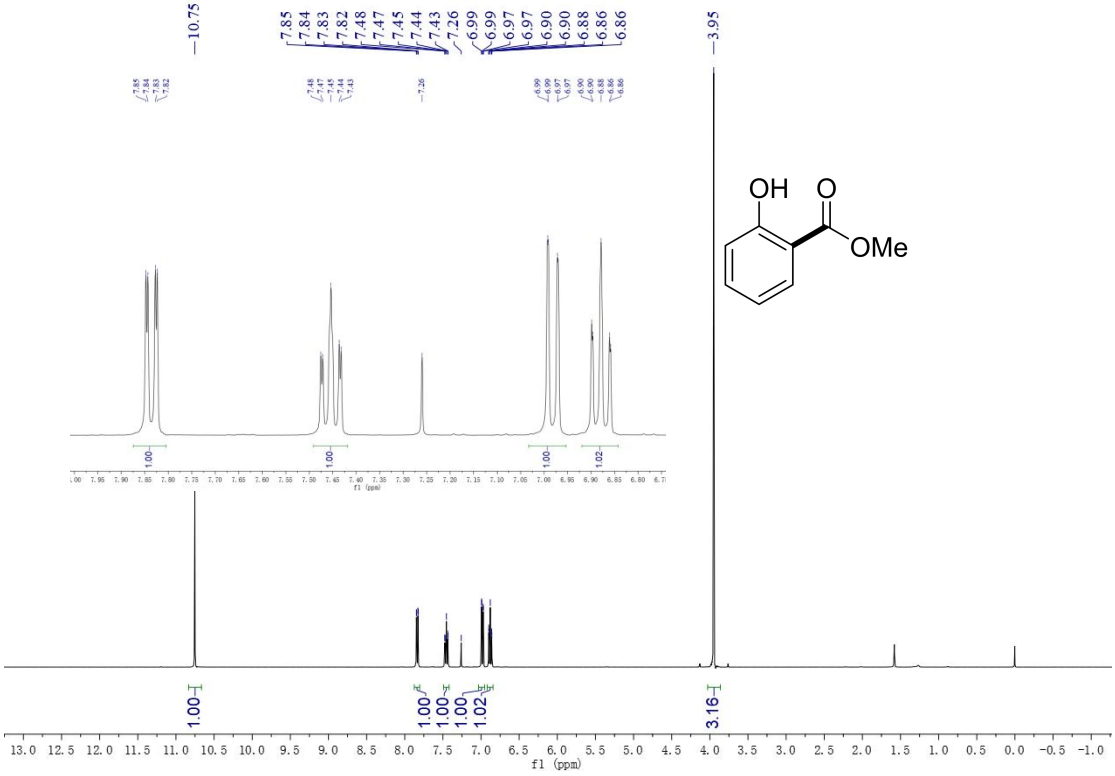
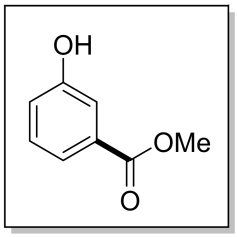


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2-hydroxybenzoate



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 1H), 7.61 – 7.57 (m, 1H), 7.32 – 7.28 (m, 1H), 7.10 – 7.07 (m, 1H), 6.51 (s, 1H), 3.92 (s, 3H).

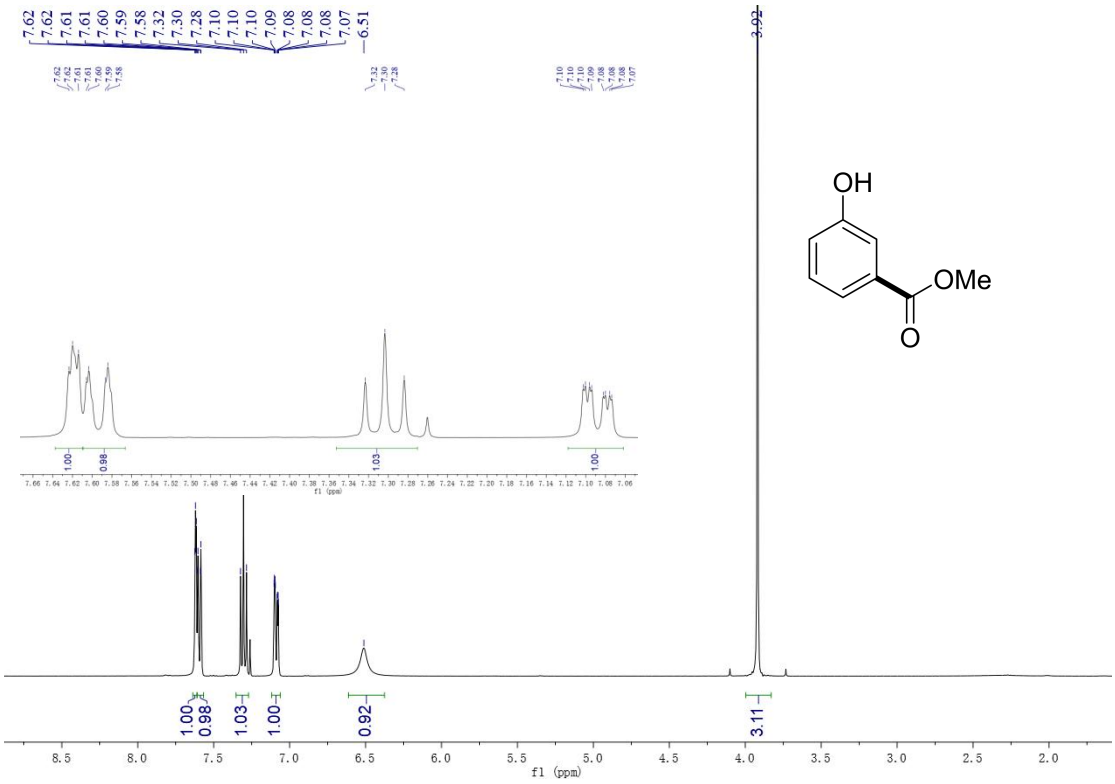
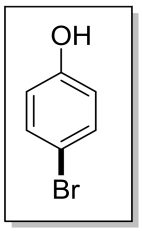


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) of methyl 3-hydroxybenzoate



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 6.77 – 6.69 (m, 2H), 4.90 (s, 1H).

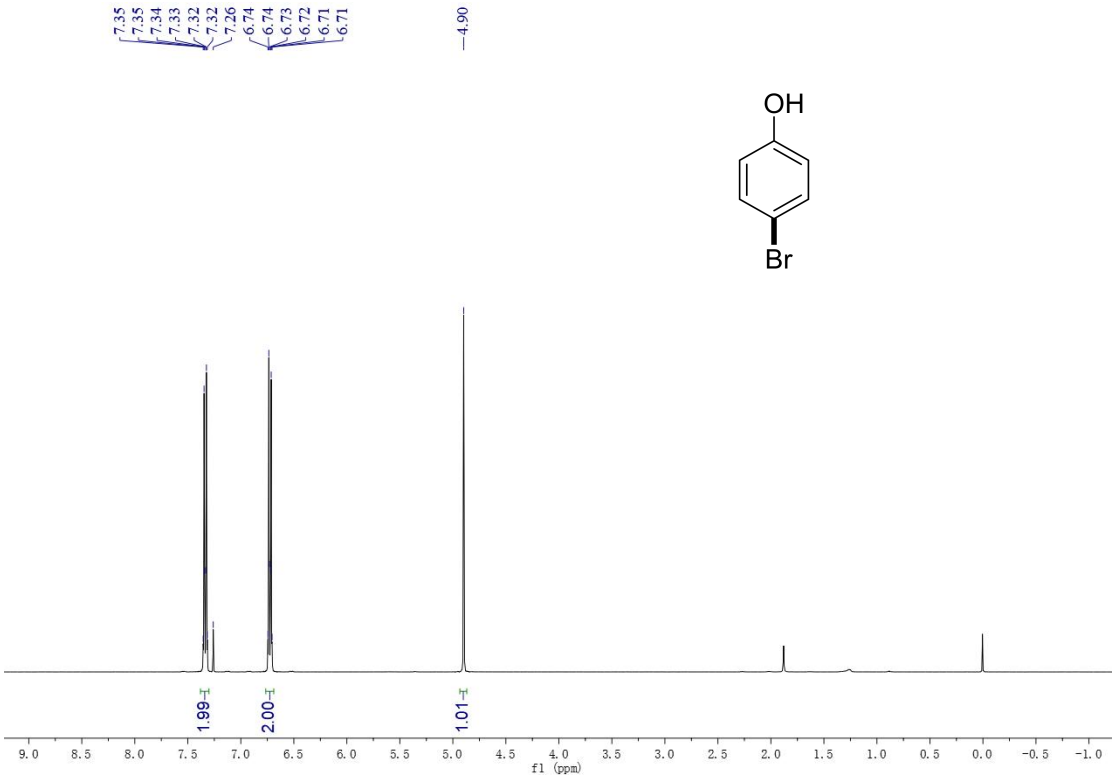
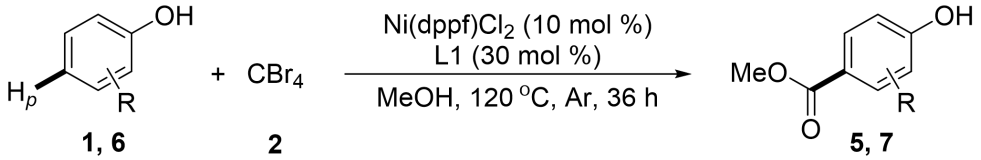


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of 4-bromophenol

4. Preparation of substrates

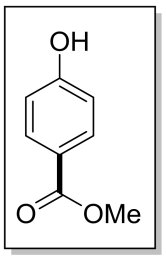
1a–1p, 6a-6j, 8, 1a-[D_5] were purchased from commercial sources and used without further purification.

5. General procedures for *para*-carboxylation of phenol derivatives



1, 6 **2** **5, 7**

A mixture of **1** or **6** (0.2 mmol, 1.0 equiv), CBr_4 (199.0 mg, 0.6 mmol, 3 equiv), $Ni(dppf)Cl_2$ (13.7 mg, 0.02 mmol, 0.1 equiv), 1,10-phenanthroline (L1, 10.8 mg, 0.06 mmol, 0.3 equiv) and dry MeOH (0.6 mL) in a 15.0 mL glass vial sealed under argon atmosphere was heated at 120 °C oil bath with vigorous stirring for 36 hours. The reaction mixture cooled to room temperature and concentrated in vacuo. The resulting residue was purified by column chromatography (PE / EA = 15 / 1 – 1 / 1) on silica gel to give the product **5** or **7**. These compound **5a**[1], **5b**[2], **5d**[3], **5f**[4], **5i**[5], **5j**[6], **5n**[7], **7a**[8], **7h**[9], **7i**[10] have been reported.



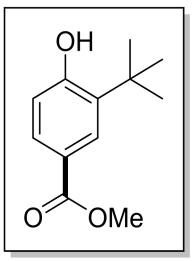
5a[1]

White solid, 24.3 mg, 80%, m.p. = 126-128 °C.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 6.88 – 6.84 (m, 2H), 5.70 (s, 1H), 3.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 159.9, 132.1, 122.9, 115.3, 52.1.



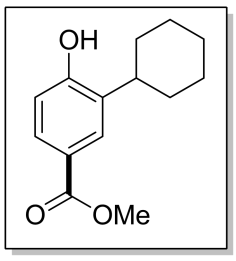
5b[2]

Yellow solid, 31.2 mg, 75%, m.p. = 149-150 °C.

Eluant : petroleum ether / ethyl acetate = 7 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 1.8 Hz, 1H), 7.78 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.43 (s, 1H), 3.90 (s, 3H), 1.42 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 159.5, 136.3, 129.5, 129.4, 121.8, 116.5, 52.2, 34.8, 29.5.



5c

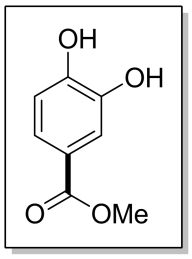
Yellow oil, 34.2 mg, 73%.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.0 Hz, 1H), 7.76 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.53 (s, 1H), 3.90 (s, 3H), 2.93 – 2.80 (m, 1H), 1.95 – 1.71 (m, 5H), 1.50 – 1.35 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 157.9, 134.1, 129.2, 129.0, 122.2, 115.2, 52.2, 37.1, 33.0, 27.0, 26.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}O_3Na$ 257.1148; Found: 257.1140.



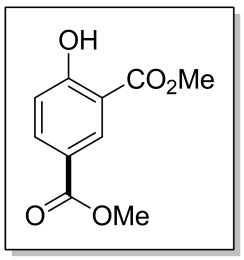
5d[3]

White solid, 28.9 mg, 86%, m.p. = 133-135 °C.

Eluant : petroleum ether / ethyl acetate = 1 / 1.

^{1}H NMR (400 MHz, DMSO) δ 9.60 (s, 2H), 7.34 (d, *J* = 2.1 Hz, 1H), 7.30 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR (100 MHz, DMSO) δ 166.3, 150.5, 145.2, 121.9, 120.6, 116.4, 115.4, 51.7.



5f[4]

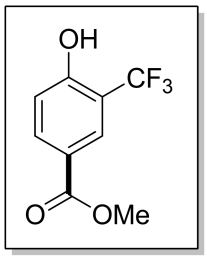
White solid, 22.3 mg, 53%, m.p. = 95-96 °C.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 8.57 (d, *J* = 2.1 Hz, 1H), 8.12 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 3.99 (s, 3H), 3.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 166.2, 165.3, 136.8, 132.7, 121.6, 118.0, 112.3, 52.8, 52.3.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{10}O_5Na$ 233.0420; Found: 233.0418.



5g

White solid, 23.3 mg, 53%, m.p. = 167-169 °C.

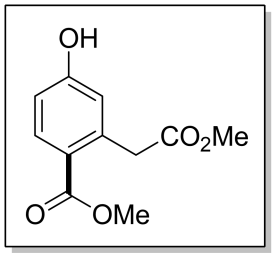
Eluant : petroleum ether / ethyl acetate = 15 / 1.

^{1}H NMR (400 MHz, DMSO) δ 11.63 (s, 1H), 8.08 – 8.02 (m, 2H), 8.04 (s, 1H), 7.13 (d, *J* = 9.3 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (100 MHz, DMSO) δ 165.1, 160.1 (q, J_{C-F} = 1.5 Hz), 135.0, 128.1 (q, J_{C-F} = 5.1 Hz), 123.5 (q, J_{C-F} = 272.4 Hz), 120.0, 117.3, 115.5 (q, J_{C-F} = 30.4 Hz), 52.1.

^{19}F NMR (376 MHz, DMSO) δ -61.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_7F_3O_3Na$ 243.0239; Found: 243.0245.



5h

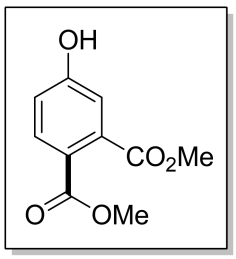
Yellow solid, 19.7 mg, 44%, m.p. = 110-112 °C.

Eluant : petroleum ether / ethyl acetate = 2 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 1H), 6.69 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.63 (d, *J* = 2.4 Hz, 1H), 6.54 (s, 1H), 3.95 (s, 2H), 3.83 (s, 3H), 3.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 167.3, 159.8, 138.4, 133.7, 121.3, 119.7, 114.6, 52.3, 51.9, 40.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{12}O_5Na$ 247.0577; Found: 247.0586.



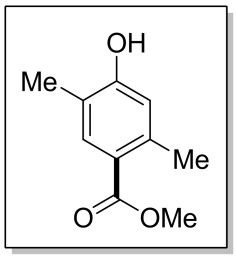
5i[5]

White solid, 17.6 mg, 42%, m.p. = 110-111 °C.

Eluant : petroleum ether / ethyl acetate = 15 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 167.0, 159.0, 136.0, 132.1, 122.3, 117.3, 115.5, 115.3, 53.0, 52.6.



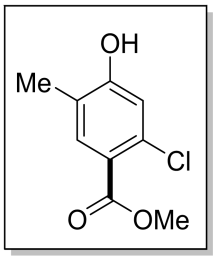
5j[6]

Yellow solid, 26.3 mg, 73%, m.p. = 85-87 °C.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 6.62 (s, 1H), 5.52 (s, 1H), 3.86 (s, 3H), 2.52 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 157.2, 140.9, 134.3, 121.5, 121.2, 118.0, 51.7, 21.8, 15.3.



5k

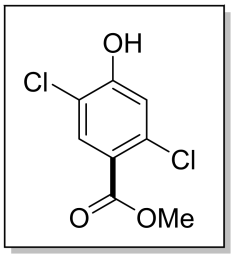
Yellow solid, 21.2 mg, 53%, m.p. = 108-110 °C.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 6.87 (s, 1H), 5.40 (s, 1H), 3.89 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 157.4, 134.7, 133.1, 122.9, 121.5, 117.6, 52.3, 15.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_{10}ClO_3$ 201.0318; Found: 201.0325.



5l

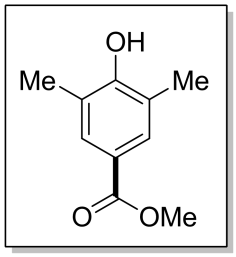
White solid, 19.4 mg, 44%, m.p. 122-123 °C.

Eluant : petroleum ether / ethyl acetate = 3 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.13 (s, 1H), 5.99 (s, 1H), 3.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 154.6, 134.8, 132.6, 122.6, 118.9, 118.5, 52.6.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_6Cl_2O_3Na$ 242.9586; Found: 242.9582.



5m

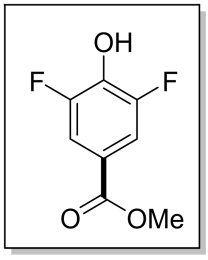
White solid, 27.4 mg, 76%, m.p. 130-132 °C.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 2H), 5.05 (s, 1H), 3.87 (s, 3H), 2.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 156.5, 130.6, 122.9, 122.1, 51.9, 15.9.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{12}O_3Na$ 203.0684; Found: 203.0679.



5n

White solid, 25.2 mg, 67%, m.p. 77-79 °C.

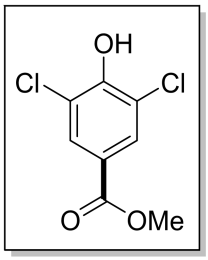
Eluant : petroleum ether / ethyl acetate = 3 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 5.99 (s, 1H), 3.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3 (t, $J_{C\text{-}F}$ = 3.3 Hz), 151.3 (dd, $J_{C\text{-}F}$ = 244.0, 5.5 Hz), 137.5 (t, $J_{C\text{-}F}$ = 16.0 Hz), 121.8 (t, $J_{C\text{-}F}$ = 7.9 Hz), 114.8 – 111.4 (m), 52.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -134.3.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_8H_7F_2O_3$ 189.0358; Found: 189.0357.



5o

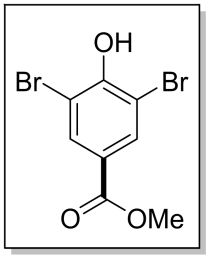
Yellow solid, 28.6 mg, 65%, m.p. 121-122 °C.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H), 6.27 (s, 1H), 3.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 151.7, 130.0, 123.8, 121.3, 52.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_8H_6Cl_2O_3Na$ 242.9586; Found: 242.9588.



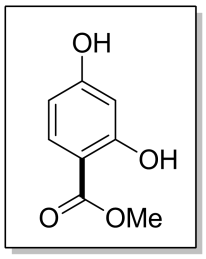
5p[7]

Yellow solid, 35.7 mg, 58%, m.p. 123-125 °C.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 2H), 6.29 (s, 1H), 3.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 153.3, 133.8, 124.9, 109.8, 52.6.



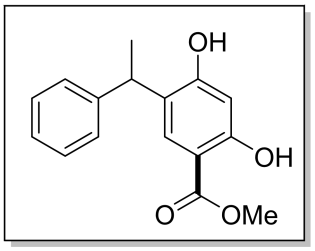
7a[8]

White solid, 22.2 mg, 66%, m.p. 116-118 °C.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.97 (s, 1H), 7.73 (d, J = 8.7 Hz, 1H), 6.40 (d, J = 2.3 Hz, 1H), 6.37 (dd, J = 8.7, 2.4 Hz, 1H), 5.63 (s, 1H), 3.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 163.8, 162.0, 132.1, 107.9, 106.1, 103.3, 52.2.



7b

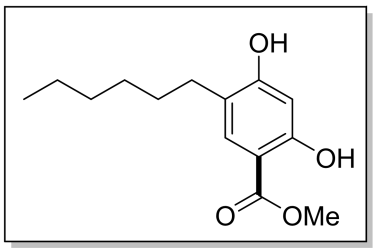
Colorless oil, 29.4 mg, 54%.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.84 (s, 1H), 7.74 (s, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 6.33 (s, 1H), 5.41 (s, 1H), 4.26 (q, *J* = 7.2 Hz, 1H), 3.92 (s, 3H), 1.61 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 162.3, 160.1, 145.3, 129.4, 128.9, 127.5, 126.7, 124.3, 105.6, 103.8, 52.2, 38.3, 21.5.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}O_4$ 273.1121; Found: 273.1127.



7c

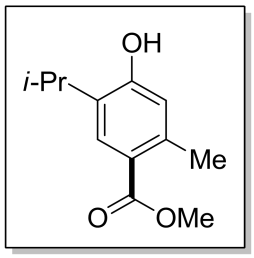
White solid, 23.2 mg, 46%. m.p. 86-87 °C.

Eluant : petroleum ether / ethyl acetate = 10 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.57 (s, 1H), 6.35 (s, 1H), 5.50 (s, 1H), 3.91 (s, 3H), 2.03 (t, *J* = 7.8 Hz, 2H), 1.61 – 1.52 (m, 2H), 1.39 – 1.27 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 161.9, 160.1, 131.4, 121.1, 105.6, 103.1, 52.1, 31.9, 29.9, 29.3, 29.2, 22.8, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}O_4Na$ 275.1254; Found: 275.1256.



7d

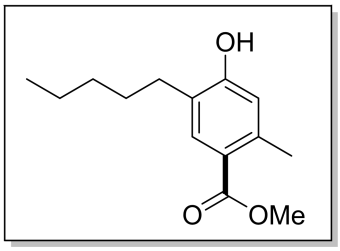
Yellow solid, 32.0 mg, 72%, m.p. 110-111 °C.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 6.60 (s, 1H), 5.12 (s, 1H), 3.86 (s, 3H), 3.21 – 3.11 (m, 1H), 2.53 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 156.0, 140.5, 131.8, 130.1, 122.0, 118.5, 51.7, 26.9, 22.6, 21.8.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{16}O_3Na$ 231.0997; Found: 231.0992.



7e

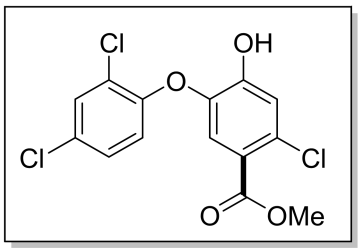
Yellow oil, 32.1 mg, 68%.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 6.61 (s, 1H), 5.25 (s, 1H), 3.85 (s, 3H), 2.57 (t, *J* = 7.8 Hz, 2H), 2.53 (s, 3H), 1.65 – 1.60 (m, 2H), 1.41 – 1.28 (m, 4H), 0.90 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 156.8, 140.8, 133.6, 126.1, 121.7, 119.8, 118.3, 51.7, 31.8, 29.6, 29.5, 22.7, 21.8, 14.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}O_3Na$ 259.1305; Found: 259.1307.



7f

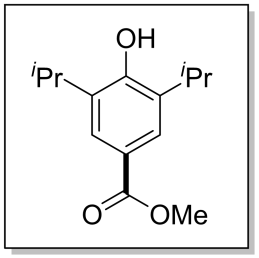
White solid, 23.5 mg, 34%, m.p. 55-56 °C.

Eluant : petroleum ether / ethyl acetate = 5 / 1.

^{1}H NMR (400 MHz, DMSO) δ 11.14 (s, 1H), 7.71 (s, 1H), 7.46 (s, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 7.11 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 3.76 (s, 3H).

^{13}C NMR (100 MHz, DMSO) δ 164.0, 152.9, 151.5, 140.9, 129.9, 129.9, 128.5, 127.2, 123.9, 123.5, 119.7, 119.2, 118.7, 52.2.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_9Cl_3O_4Na$ 368.9459; Found: 368.9459.



7g

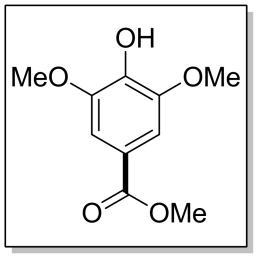
Yellow solid, 33.1 mg, 70%, m.p. 92-93 °C.

Eluant : petroleum ether / ethyl acetate = 15 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 2H), 5.58 (s, 1H), 3.89 (s, 3H), 3.26 – 3.12 (m, 2H), 1.28 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 154.6, 133.8, 125.8, 122.3, 52.0, 27.2, 22.7.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}O_3Na$ 259.1310; Found: 259.1316.



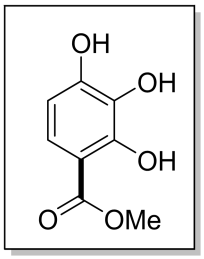
7h[9]

White solid, 31.0 mg, 73%, m.p. 105-107 ºC.

Eluant : petroleum ether / ethyl acetate = 2 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 2H), 5.93 (s, 1H), 3.94 (s, 6H), 3.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 146.8, 139.3, 121.2, 106.8, 56.6, 52.2.



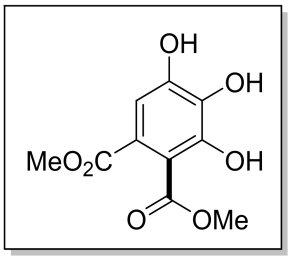
7i[10]

Yellow solid, 27.6 mg, 75%, m.p. 150-152 ºC.

Eluant : petroleum ether / ethyl acetate = 2 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 7.36 (d, J = 8.9 Hz, 1H), 6.51 (d, J = 8.9 Hz, 1H), 5.82 (s, 1H), 5.51 (s, 1H), 3.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 149.6, 149.3, 131.1, 122.1, 107.5, 105.8, 52.3.



7j

Yellow oil, 20.8 mg, 43%.

Eluant : petroleum ether / ethyl acetate = 1 / 1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 6.64 (s, 1H), 5.91 (s, 1H), 5.72 (s, 1H), 3.90 (s, 3H), 3.86 (s, 3H).

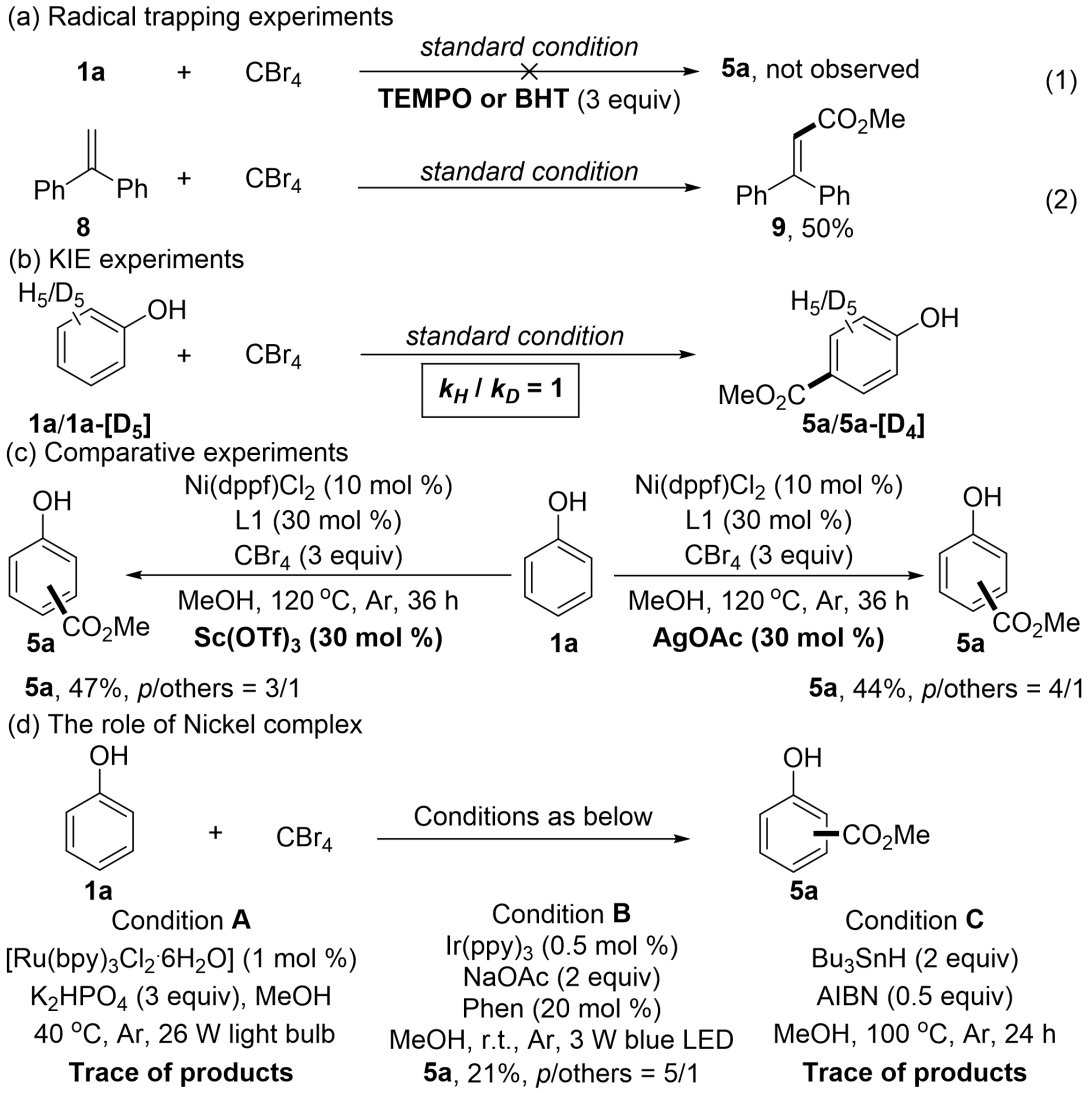
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.3, 149.5, 147.8, 132.7, 132.6, 127.9, 108.5, 103.6, 53.0, 52.8.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{11}O_7$ 243.0499; Found: 243.0494.

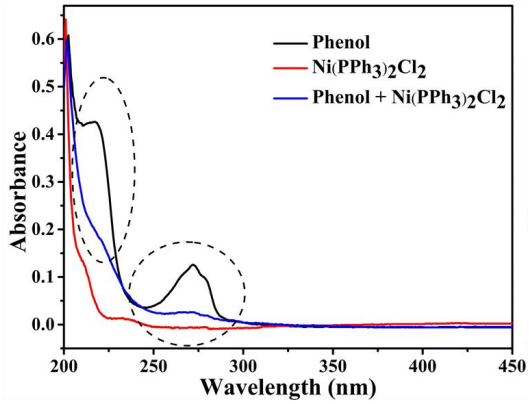
6. General Procedures for 10 mmol Scale Synthesis

A mixture of **6h** (1.5406 g, 10.0 mmol, 1.0 equiv), CBr_4 (9.9488 g, 30.0 mmol, 3 equiv), $Ni(dppf)Cl_2$ (686.0 mg, 1.0 mmol, 0.1 equiv), 1,10-phenanthroline (L1, 540.7 mg, 3.0 mmol, 0.3 equiv) and dry MeOH (20.0 mL) in a 100.0 mL explosion proof tube sealed under argon atmosphere was heated at 120 ^oC oil bath for 36 hours. The reaction mixture cooled to room temperature, open it carefully, filter with diatomite, and concentrated in vacuo. The resulting residue was purified by column chromatography (PE / EA = 2 / 1) on silica gel to give the product **7h** (White solid, 1.4209 g, 67% yield).

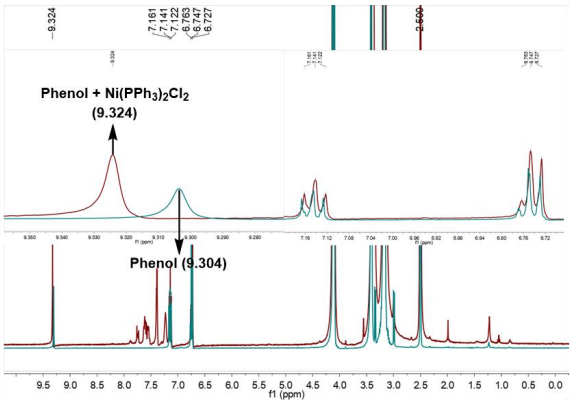
7. Scheme S1. Preliminary mechanistic studies



(e) UV-experiments and ^{1}H NMR analysis

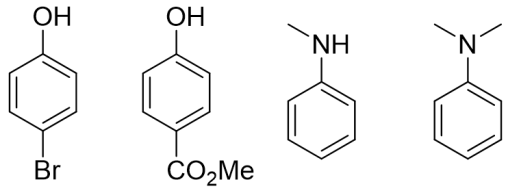


Absorption spectra of **1a** and $Ni(PPh_3)_2Cl_2$

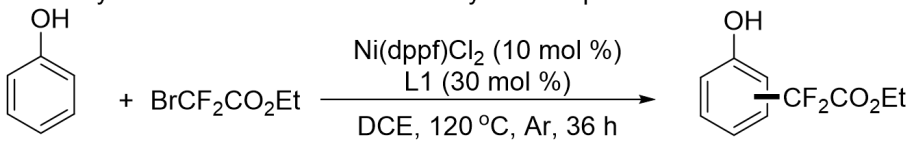


^{1}H NMR analysis of **1a** and $Ni(PPh_3)_2Cl_2$

(f) Ineffective Ni-catalyzed *para*-carboxylation of substrates



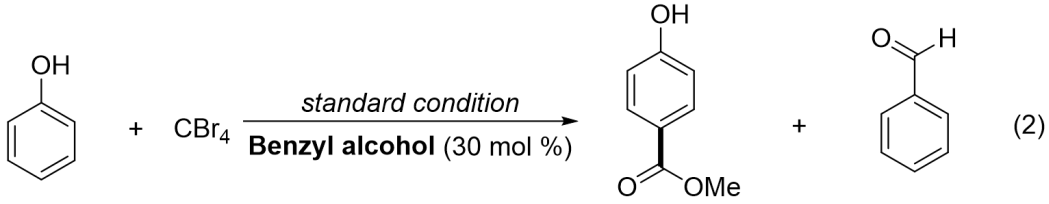
(g) Ni-catalyzed site selective difluoromethylation of phenol



1a **10**, 48%, *p*/*m* = 1.6/1

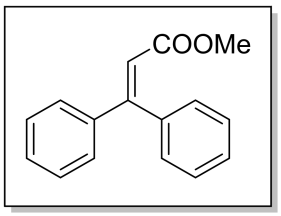
(h) Role of alcohol

1a **5a**, 80%, *p*/others = 13/1 **11**, GC-MS



1a **5a**, 66%, *p*/others = 14/1 **12**, 10%

General procedures for radical trapping experiments (a): (1) A mixture of **1a** (18.8 mg, 0.2 mmol, 1.0 equiv), CBr_4 (199.0 mg, 0.6 mmol, 3 equiv), $Ni(dppf)Cl_2$ (13.7 mg, 0.02 mmol, 0.1 equiv), 1,10-phenanthroline (L1, 10.8 mg, 0.06 mmol, 0.3 equiv), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 93.7 mg, 0.6 mmol, 3 equiv) or butylated hydroxytoluene (BHT, 132.2 mg, 0.6 mmol, 3equiv) and dry MeOH (0.6 mL) in a 15.0 mL glass vial sealed under argon atmosphere was heated at 120 ºC oil bath with vigorous stirring for 36 hours. The product **5a** is not detected.



9

Yellow liquid, 23.8 mg, 50%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 8H), 7.24 – 7.20 (m, 2H), 6.38 (s, 1H), 3.62 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 157.2, 140.9, 138.9, 129.6, 129.2, 128.5, 128.5, 128.3, 128.0, 116.9, 51.4.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{14}O_2Na$ 261.0891; Found: 261.0892.

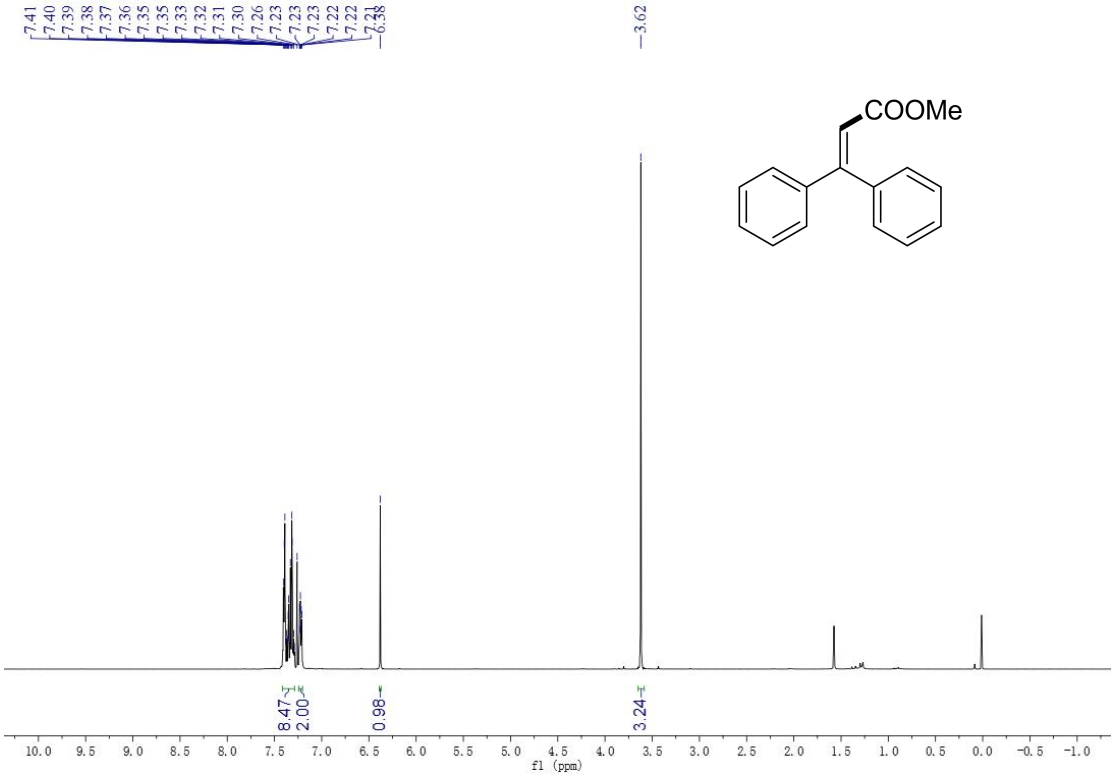


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) of 9

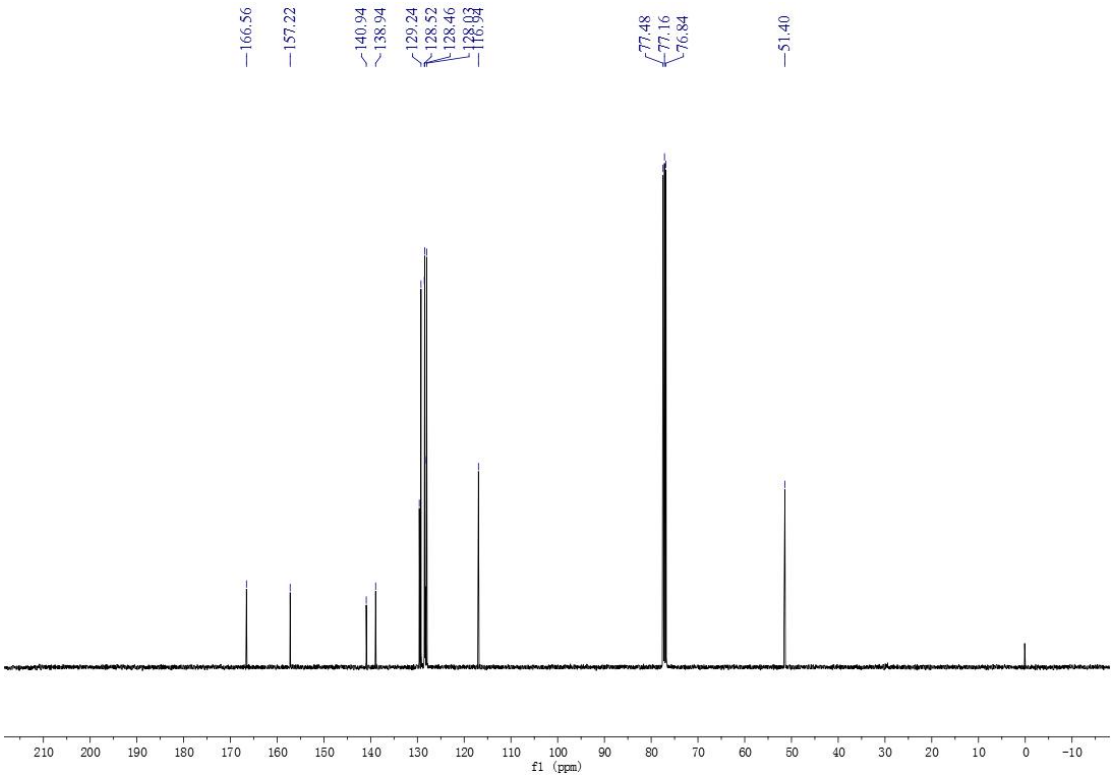


Figure S23. ^{13}C NMR (100 MHz, $CDCl_3$) of 9

General procedures for KIE experiments (b): A mixture of **1a** (18.8 mg, 0.2 mmol, 1.0 equiv) or **1a-[D_5]** (19.8 mg, 0.2 mmol, 1.0 equiv), CBr_4 (199.0 mg, 0.6 mmol, 3 equiv), Ni(dppf)Cl_2 (13.7 mg, 0.02 mmol, 0.1 equiv), 1,10-phenanthroline (L1, 10.8 mg, 0.06 mmol, 0.3 equiv) and dry MeOH (0.6 mL) in a 15.0 mL glass vial sealed under argon atmosphere was heated at 120 °C oil bath with vigorous stirring for a certain amount of time. The reaction mixture was cooled to room temperature, GC analysis using tridecane as an internal standard to provide the following conversions.

Time/(min)	60	90	120	150	180
3a/(%)	16.7	24	31.1	36.2	42.0
[D_1]-**3a**/(%)	6.9	14.3	20.8	25.4	31.3

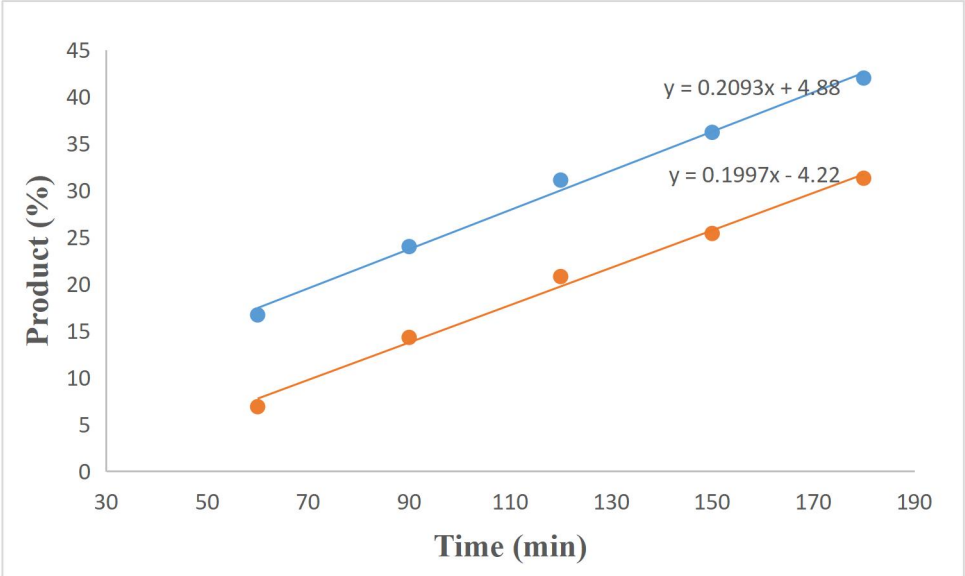


Figure S24. KIE experiments

KIE = 0.2093 / 0.1997 = 1.05

General procedures for comparative experiments:

(c, left) A mixture of **1a** (18.8 mg, 0.2 mmol, 1.0 equiv), Ni(dppf)Cl_2 (13.7 mg, 0.02 mmol, 0.1 equiv), 1,10-phenanthroline (L1, 10.8 mg, 0.06 mmol, 0.3 equiv), Sc(OTf)$_3$ (29.5 mg, 0.06 mmol, 0.3 equiv), CBr_4 (199.0 mg, 0.6 mmol, 3 equiv) and MeOH (0.6 mL) in a 15.0 mL glass vial sealed under argon atmosphere was heated at 120 °C oil bath with vigorous stirring for 36 hours. The reaction mixture cooled to room temperature and concentrated in vacuo. The resulting residue was purified by column chromatography (PE / EA = 3 / 1) on silica gel to give the product **5a**.

(c, right) A mixture of **1a** (18.8 mg, 0.2 mmol, 1.0 equiv), CBr_4 (199.0 mg, 0.6 mmol, 3 equiv), Ni(dppf)Cl_2 (13.7 mg, 0.02 mmol, 0.1 equiv), 1,10-phenanthroline (L1, 10.8 mg, 0.06 mmol, 0.3 equiv), AgOAc (10.0 mg, 0.06 mmol, 0.3 equiv) and MeOH (0.6 mL) in a 15.0 mL glass vial sealed under argon atmosphere was heated at 120 °C oil bath with vigorous stirring for 36 hours. The reaction mixture cooled to room temperature and concentrated in vacuo. The resulting residue was purified by column chromatography (PE / EA = 3 / 1) on silica gel to give the product **5a**.

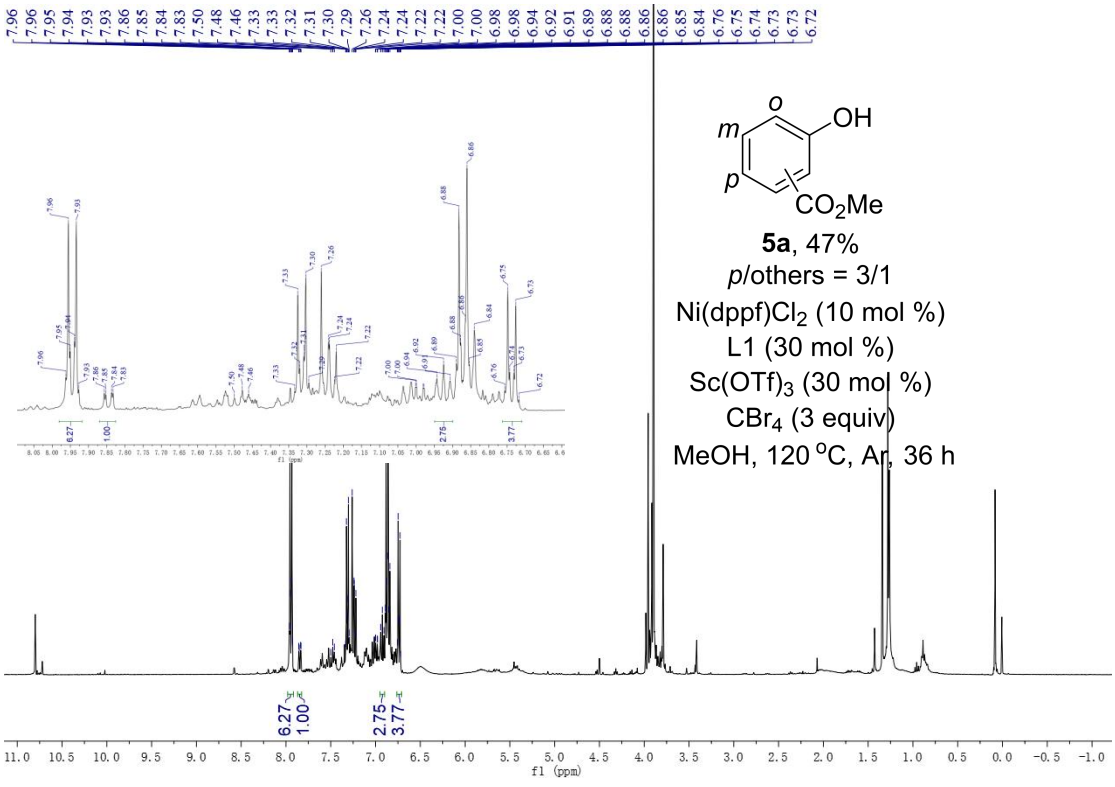


Figure S25. The ^{1}H NMR spectra analysis of comparative experiments (c, left)

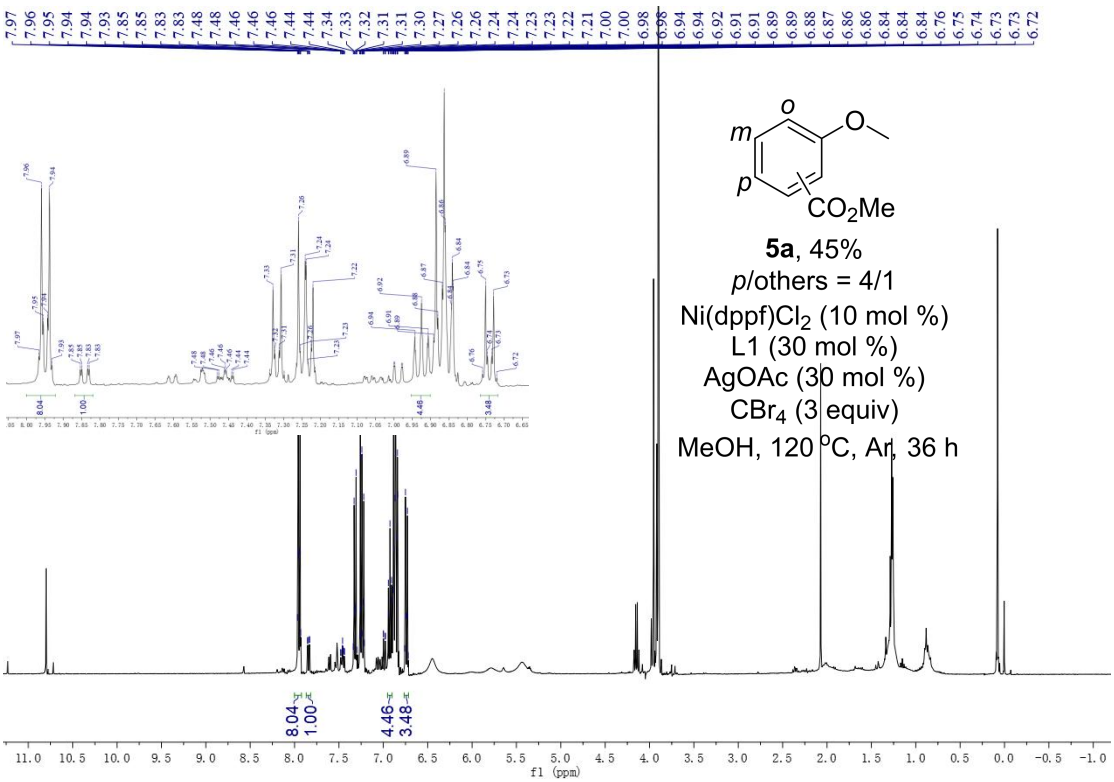


Figure S26. The ^{1}H NMR spectra analysis of comparative experiments (c, right)

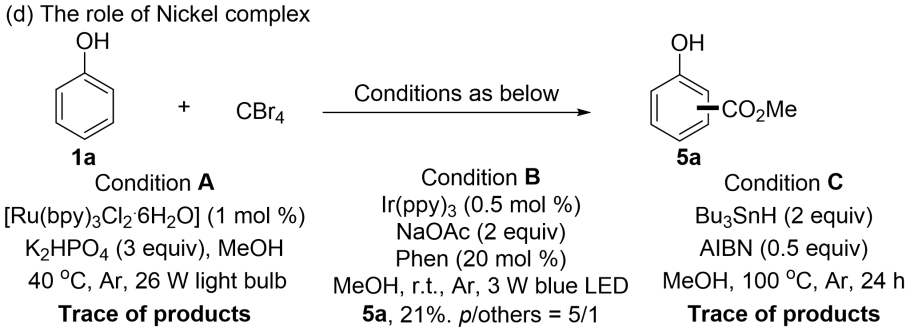


Figure S27. The role of Nickel complex (Scheme S1, d)

The formation of alkyl radicals initiated by alkyl halides under the conditions of Ru or Ir as a photocatalyst has been reported by Wang,[11a] Ackermann,[11b] and orthers.[12] In addition, extensive studies have shown that the combination of BuSnH and AIBN can obtain alkyl radicals.[13] Therefore, we applied substrates **1a** and **2** to these reported catalytic systems. Unfortunately, only poor yield and site selectivity are provided. These results also confirmed the above view.

General procedures for (d, condition B): A mixture of **1a** (18.8 mg, 0.2 mmol, 1.0 equiv), $Ir(ppy)_3$ (0.7 mg, 0.001 mmol, 0.005 equiv), NaOAc (32.8 mg, 0.4 mmol, 2 equiv), Phen (7.9 mg, 0.04 mmol, 0.2 equiv), CBr_4 (199.0 mg, 0.6 mmol, 3 equiv) and MeOH (0.6 mL) in a 15.0 mL glass vial sealed under argon atmosphere, stir vigorously for 24 hours under 3 W blue LED irradiation at room temperature. The reaction mixture concentrated in vacuo. The resulting residue was purified by column chromatography (PE / EA = 3 / 1) on silica gel to give the product **5a**.

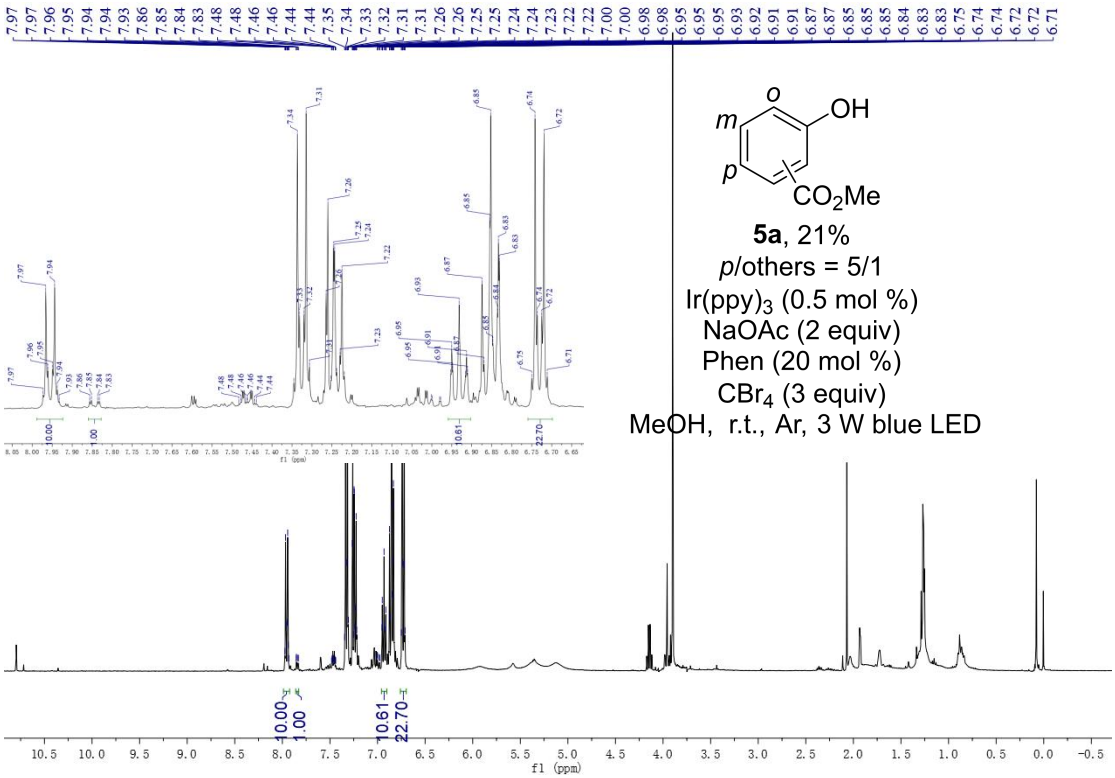


Figure S28. The ^{1}H NMR spectra analysis of (d, condition B)

General procedures for (e):

1. UV-experiments

UV spectra were obtained using 50 mol% catalyst. Compared with the standard UV spectra of phenol and $Ni(PPh_3)_2Cl_2$, the characteristic absorption band **E_2** of phenol almost disappeared at 217 nm. Moreover, the redshift of the characteristic **B** band at 272 nm was severely weakened. These results strongly suggest that phenol coordinated with the nickel catalyst, which reduced the aromaticity of phenol and activated the phenyl ring. The test methods and results are as follows.

(a) A mixture of phenol (18.8 mg, 0.2 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (65.4 mg, 0.1 mmol, 0.5 equiv), and MeOH (0.5 mL) in a 15.0 mL glass vial was stirred under argon atmosphere at 120 °C oil bath for 2 hours. The reaction mixture cooled to room temperature and transfer to a 50.0 mL volumetric flask for constant volume. The reaction mixture was further diluted and analyzed by UV.

(b) Phenol (18.8 mg, 0.2 mmol) was dissolved in MeOH (50.0 mL) in a 50.0 mL volumetric flask. The reaction mixture was further diluted and analyzed by UV.

(c) $Ni(PPh_3)_2Cl_2$ (65.4 mg, 0.1 mmol) was dissolved in MeOH (50.0 mL) in a 50.0 mL volumetric flask. The reaction mixture was further diluted and analyzed by UV.

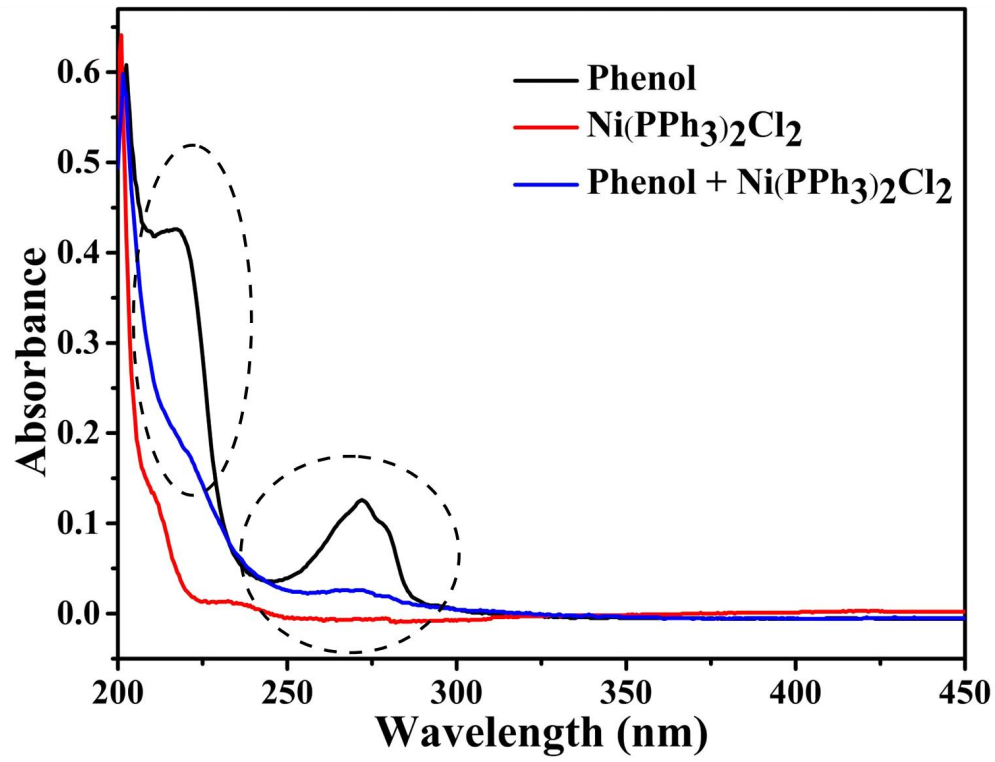


Figure S29. Absorption spectra of 1a and $Ni(PPh_3)_2Cl_2$ (Wavelength: 200-450 nm)

2. ^{1}H NMR analysis

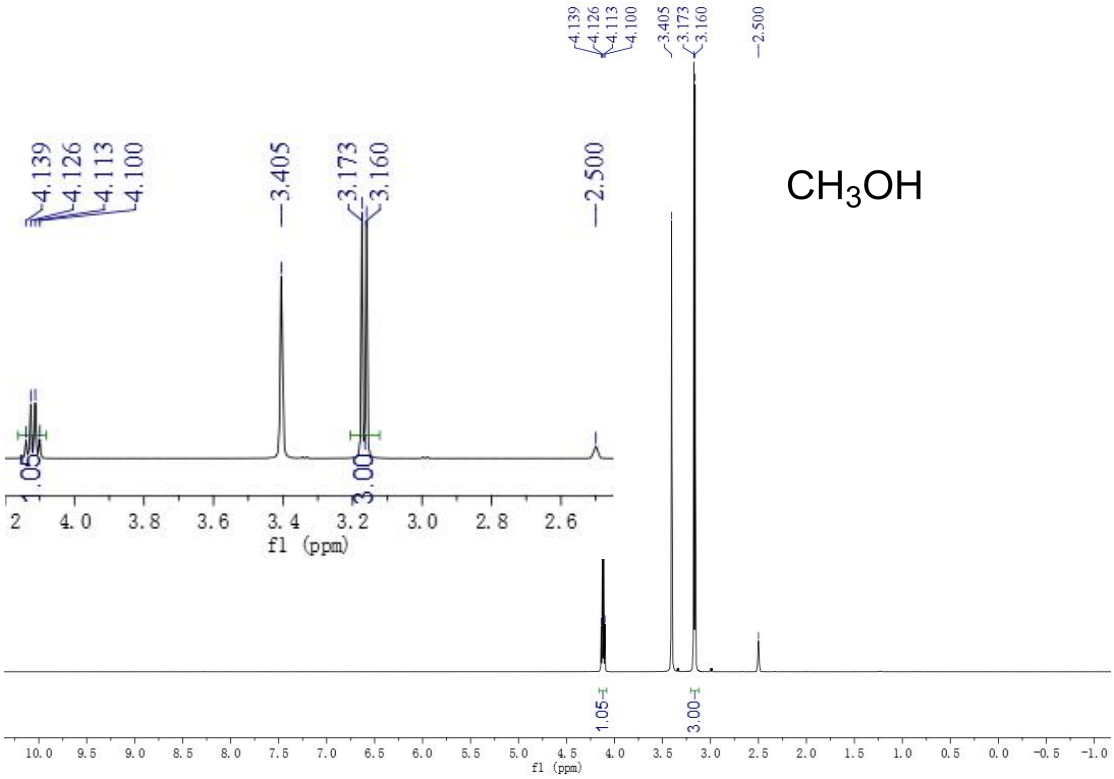


Figure S30. ^{1}H NMR (400 MHz, DMSO) of methanol

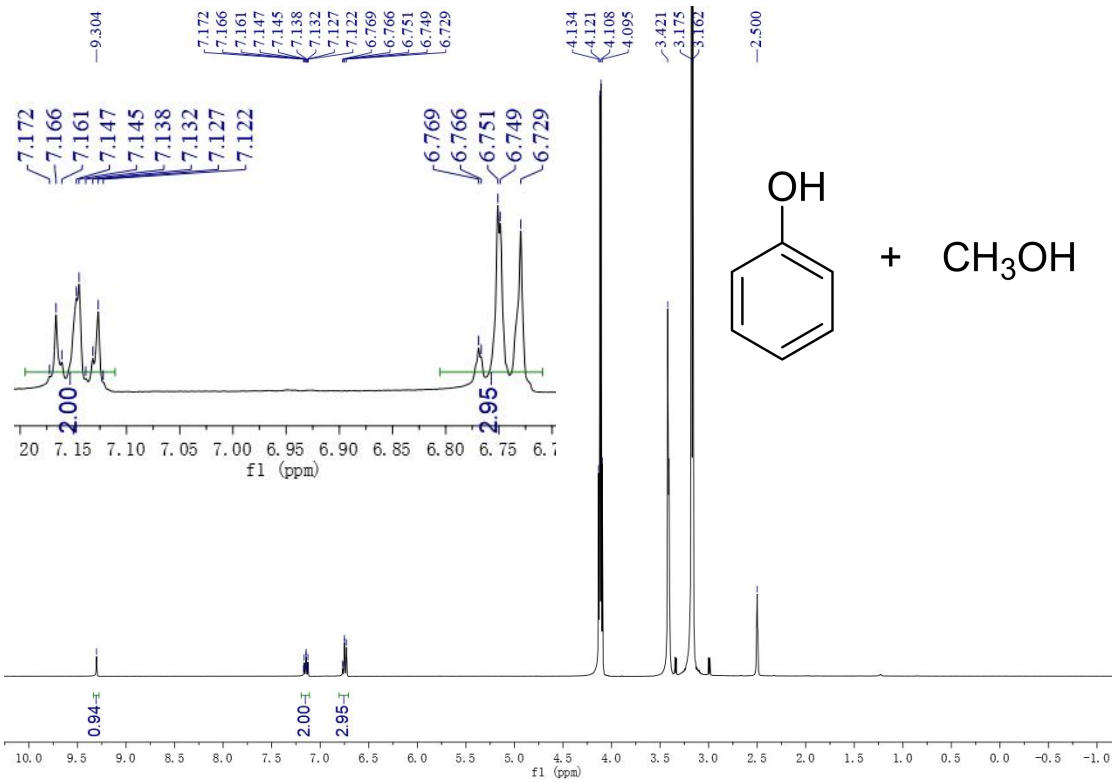


Figure S31. ^{1}H NMR (400 MHz, DMSO) of phenol and methanol

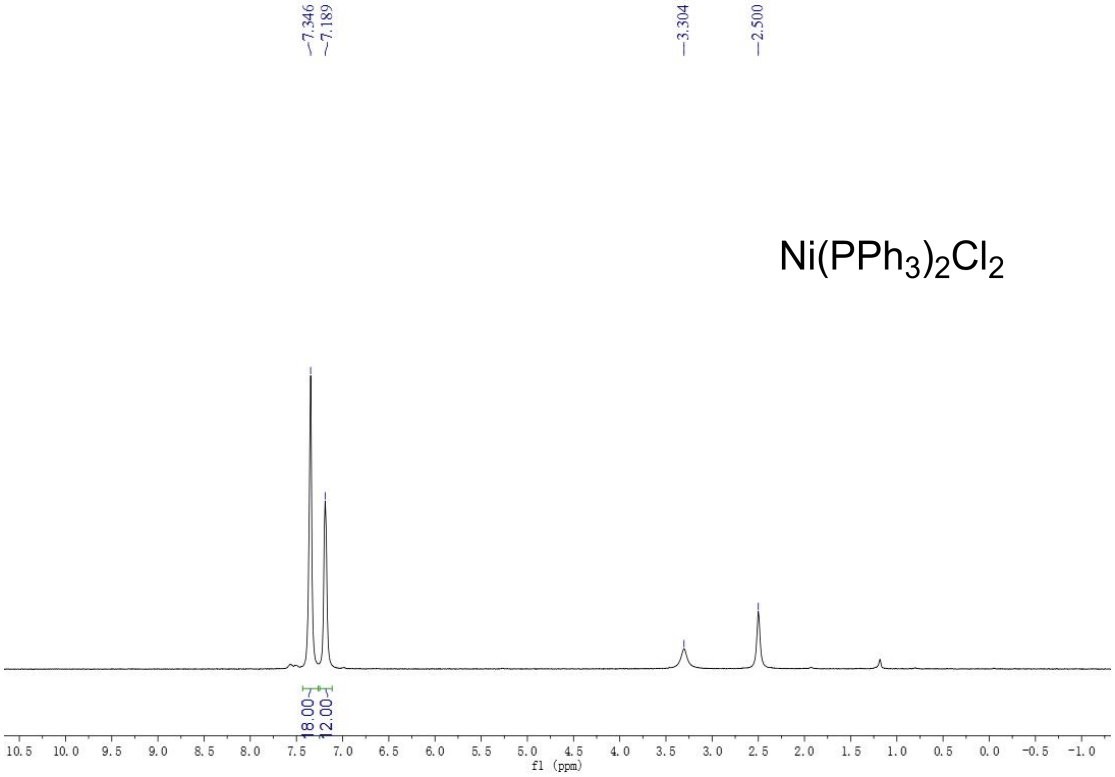


Figure S32. ^{1}H NMR (400 MHz, DMSO) of $Ni(PPh_3)_2Cl_2$

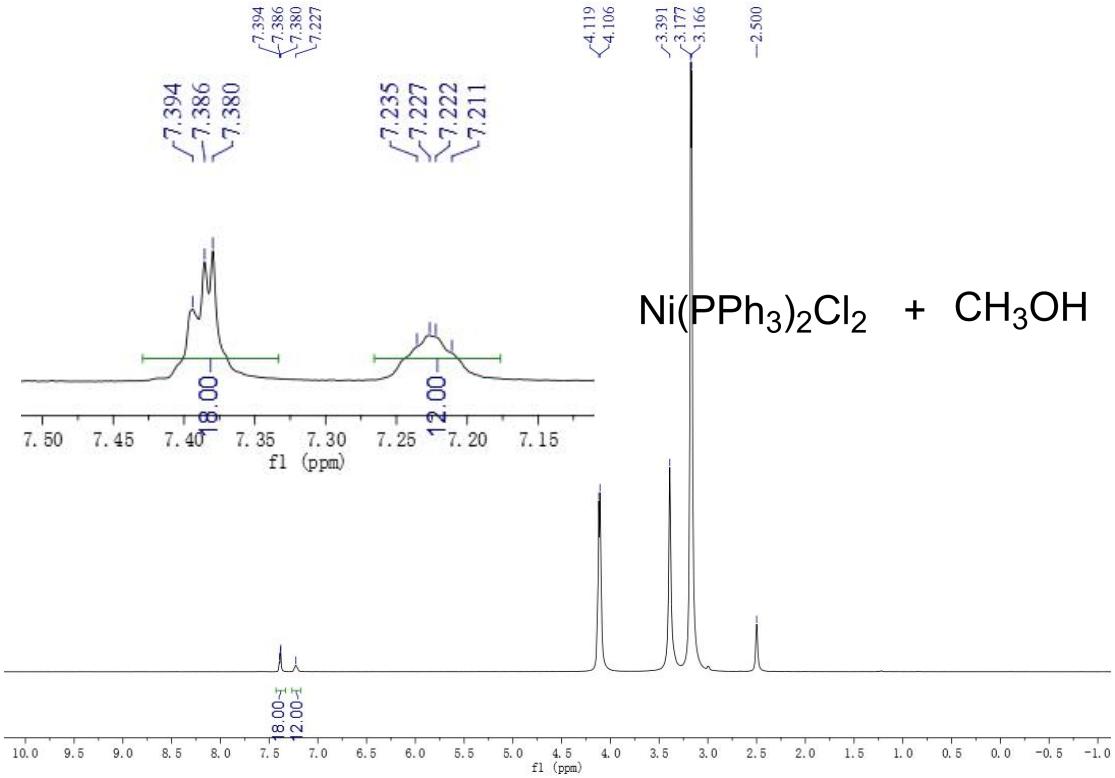


Figure S33. ^{1}H NMR (400 MHz, DMSO) of $Ni(PPh_3)_2Cl_2$ and methanol

A: A mixture of phenol (18.8 mg, 0.2 mmol, 1.0 equiv), $Ni(PPh_3)_2Cl_2$ (65.4 mg, 0.1 mmol, 0.5 equiv), and MeOH (0.5 mL) in a 15.0 mL glass vial was stirred under argon atmosphere at 120 °C oil bath for 2 hours. The reaction mixture cooled to room temperature and analyzed by ^{1}H NMR.

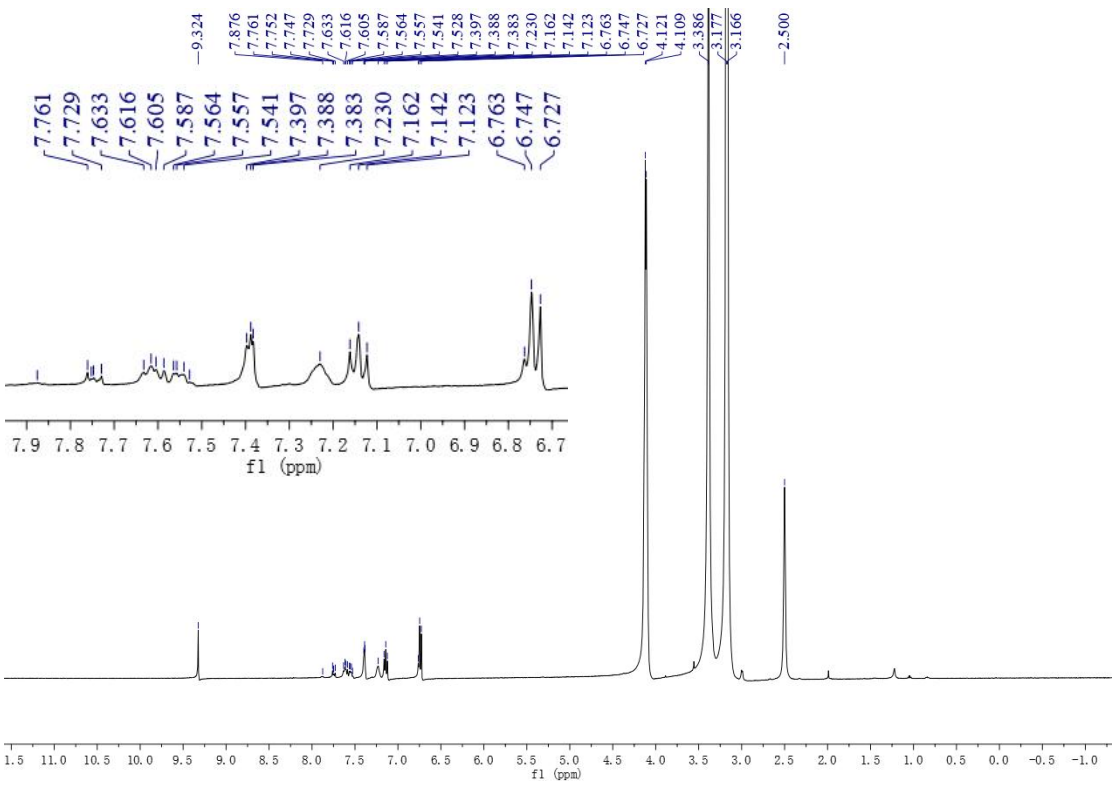


Figure S34. The ^{1}H NMR (400 MHz, DMSO) spectra analysis of A

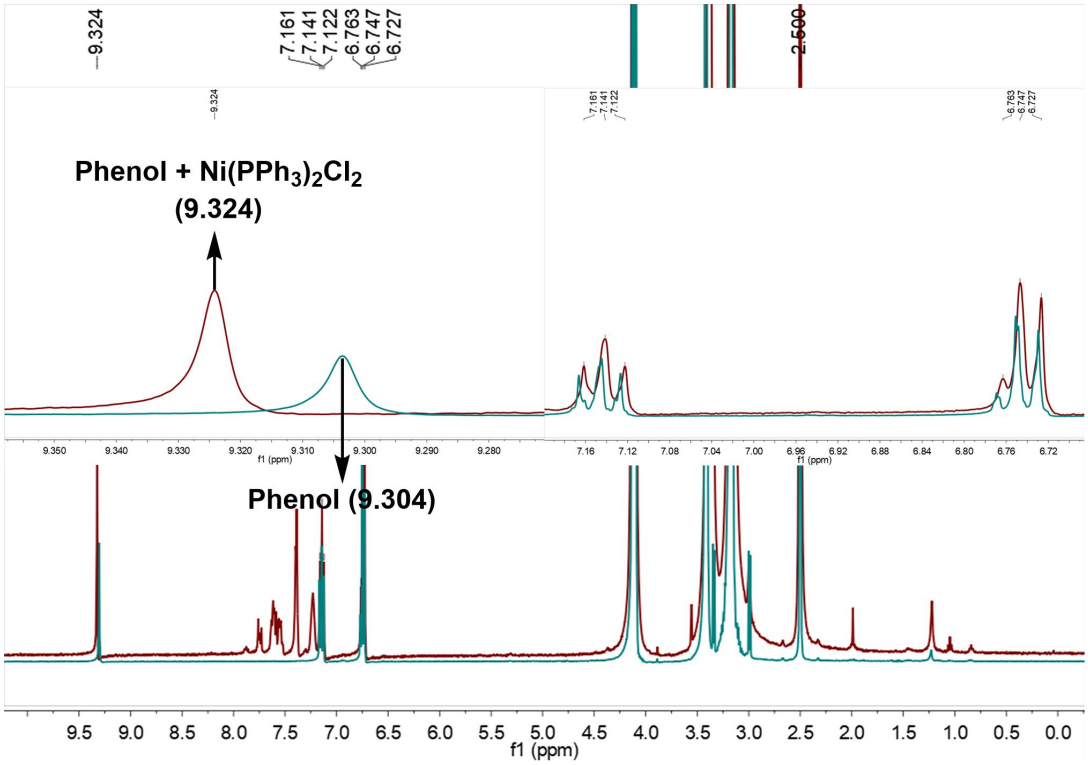


Figure S35. Superposition of ^{1}H NMR (400 MHz, DMSO) of A and (phenol + CH_3OH)

HCHO was purchased from commercial sources and used without further purification

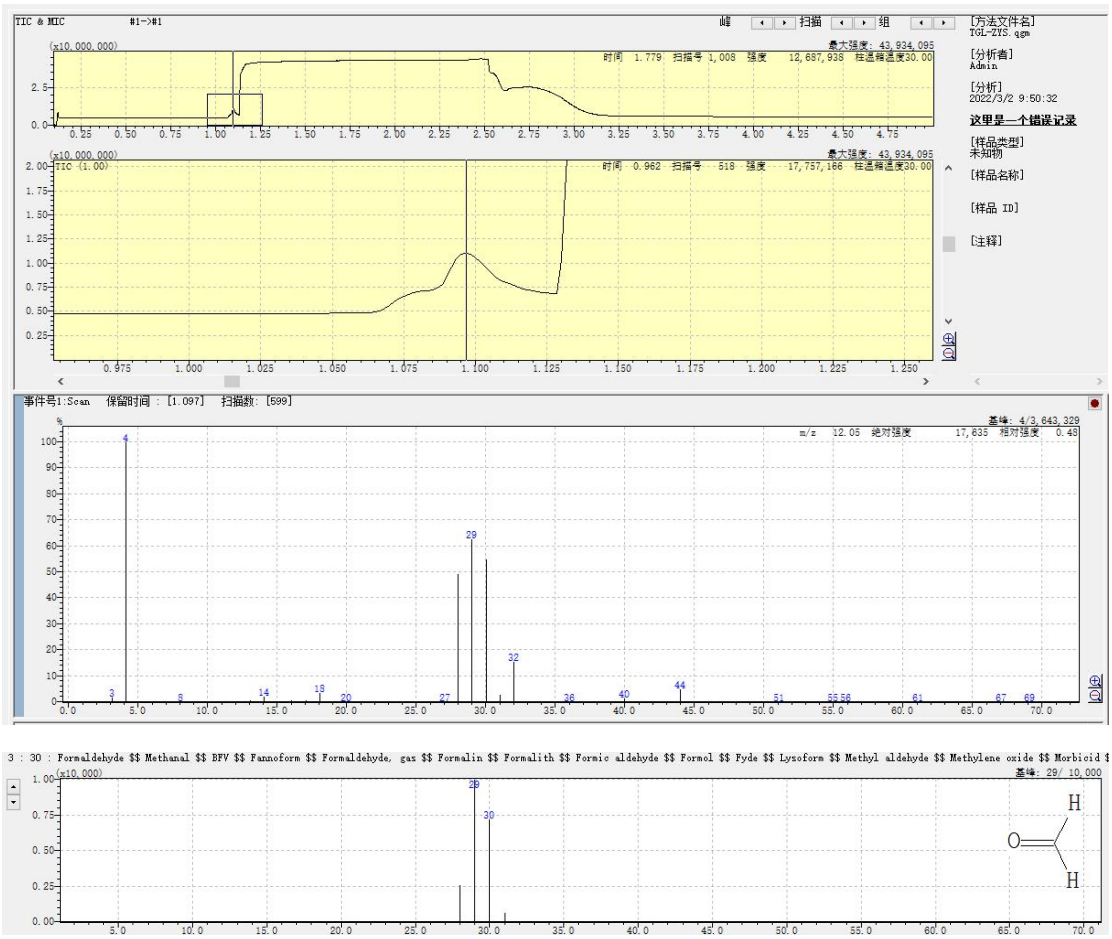
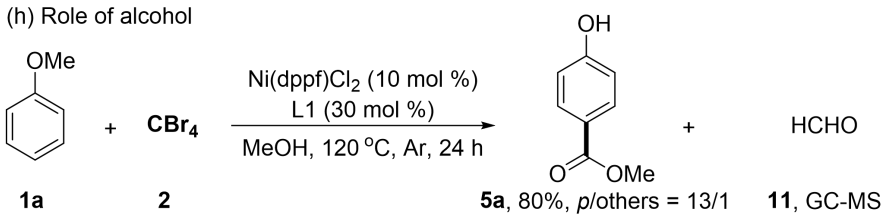


Figure S36. GC-MS analysis for HCHO



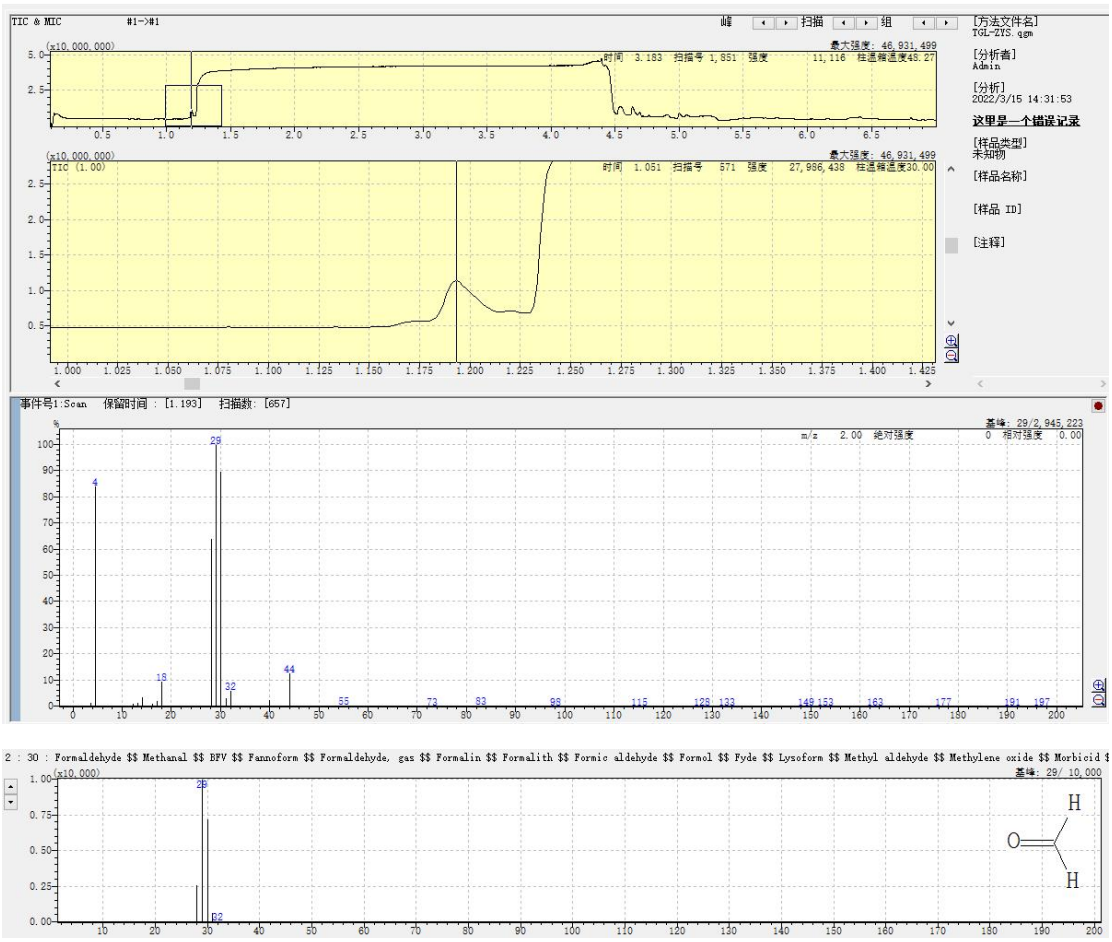


Figure S37. GC-MS analysis for (h)

General procedures for (h, 2): A mixture of **1a** (18.8 mg, 0.2 mmol, 1.0 equiv), CBr_4 (199.0 mg, 0.6 mmol, 3 equiv), $Ni(dppf)Cl_2$ (13.7 mg, 0.02 mmol, 0.1 equiv), 1,10-phenanthroline (L1, 10.8 mg, 0.06 mmol, 0.3 equiv), Benzyl alcohol (6.5 mg, 0.06 mmol, 0.3 equiv) and MeOH (0.6 mL) in a 15.0 mL glass vial sealed under argon atmosphere was heated at 120 ºC with vigorous stirring for 36 hours. The reaction mixture cooled to room temperature and concentrated in vacuo. The resulting residue was purified by column chromatography (PE / EA = 3 / 1) on silica gel to give the product.

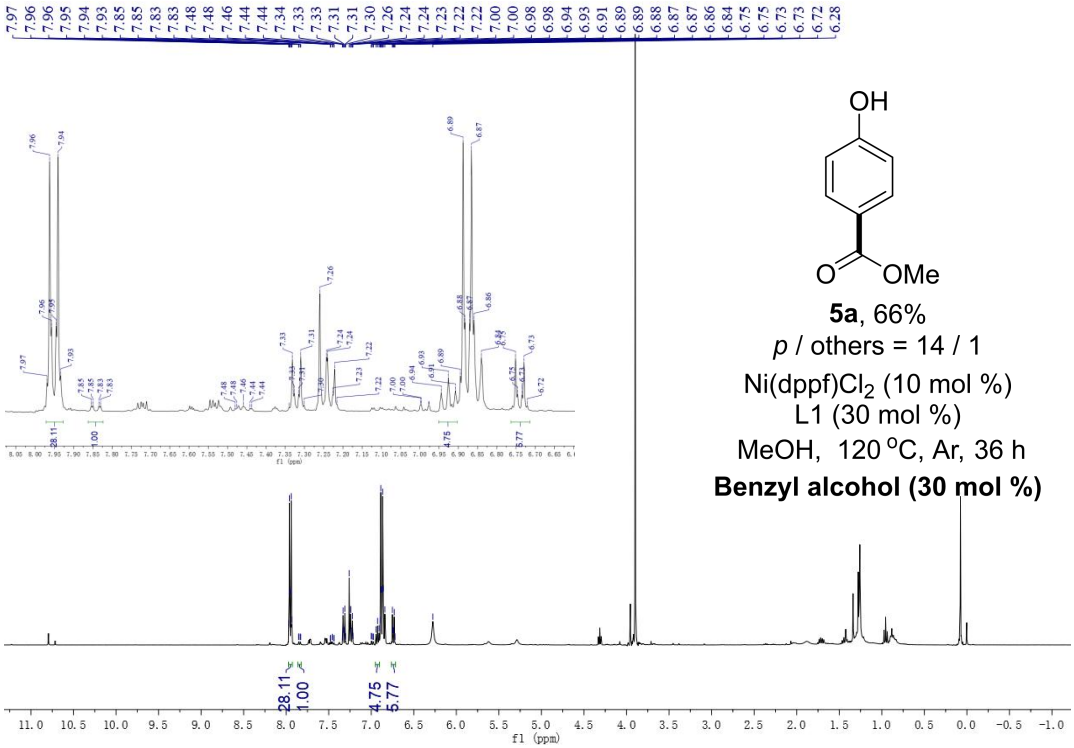


Figure S38. The ^{1}H NMR spectra analysis of (h, 5a)

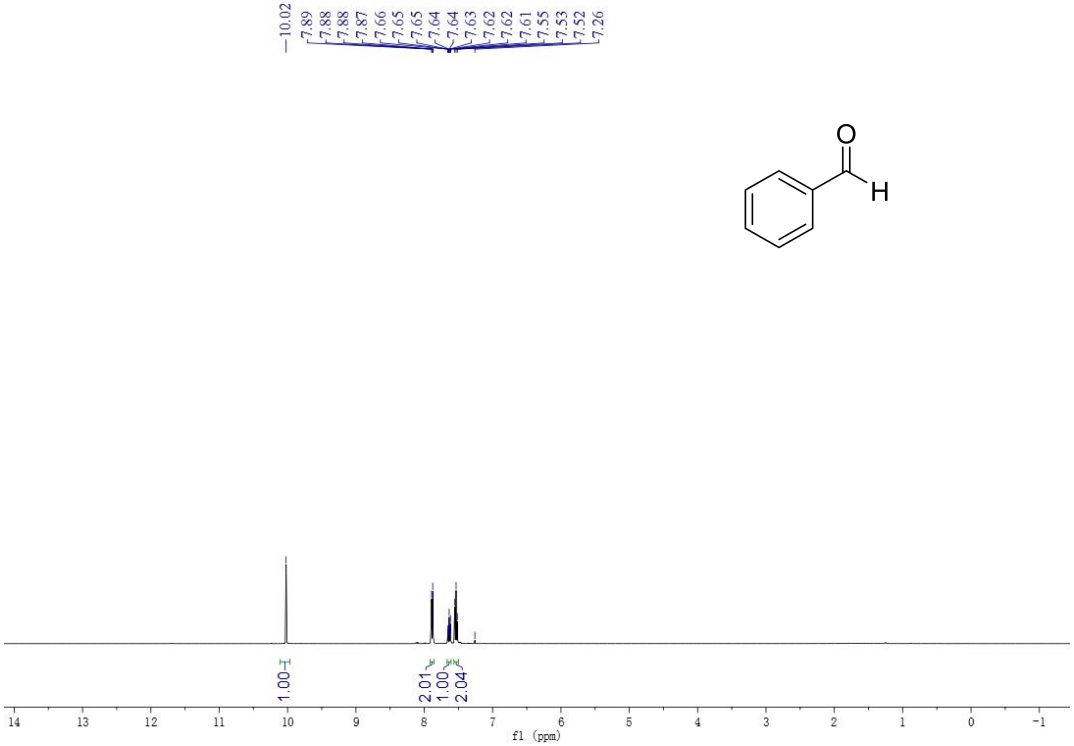


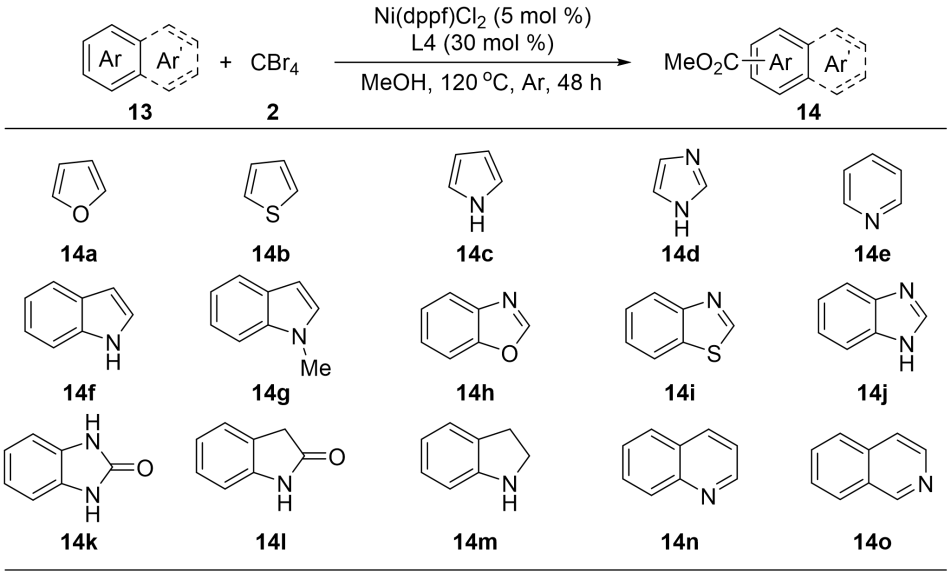
Figure S39. The ^{1}H NMR spectra analysis of (h, 12)

8. *para*-Carboxylation of aromatic heterocycles and benzocycloalkanes

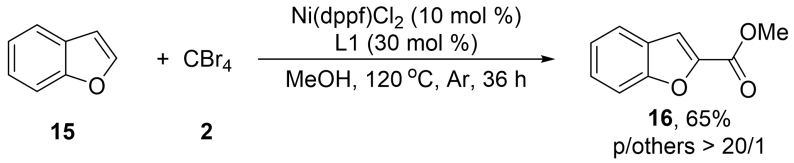
We systematically investigated the reactions of aromatic heterocycles and benzocycloalkanes under this standard conditions (Scheme S2). Unfortunately, this method is not compatible with simple

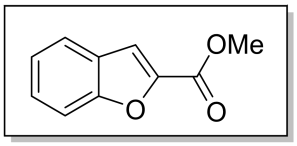
heterocyclic compounds and nitrogenous heterocyclic compound. Interestingly, the substrate benzofuran (**15**) can react with CBr_4 to provide methyl benzofuran-2-carboxylate in a 65% yield (Scheme S3). However, the site selectivity of carboxylated products was poor when benzothiophene was used as the substrate. This may be due to the interaction between nickel catalyst and sulfur atom, which leads to the change of its site activity.

Scheme S2. Ineffective Ni-catalyzed *para*-carboxylation of substrates



Scheme S3. effective Ni-catalyzed *para*-carboxylation of substrates





16[14]

Yellow oil, 22.9 mg, 65%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.59 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.53 (d, *J* = 0.8 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.34 – 7.28 (m, 1H), 3.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 155.8, 145.5, 127.8, 127.0, 124.0, 123.0, 114.2, 112.5, 52.5.

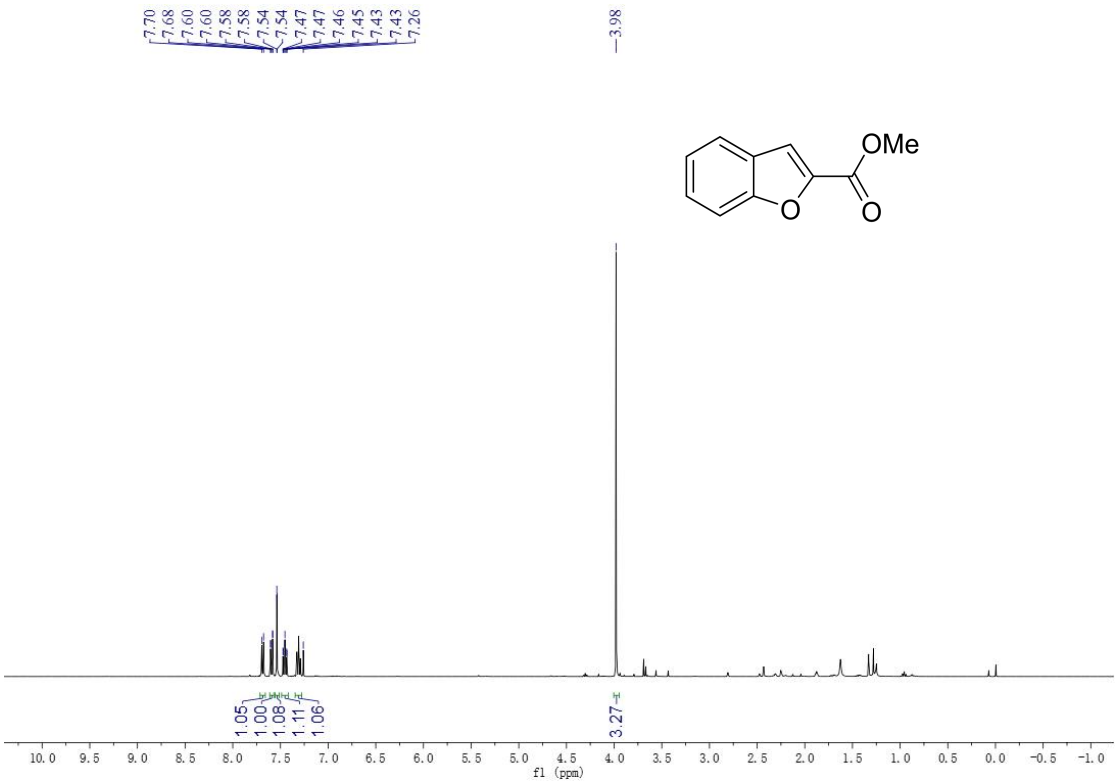


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) of 16

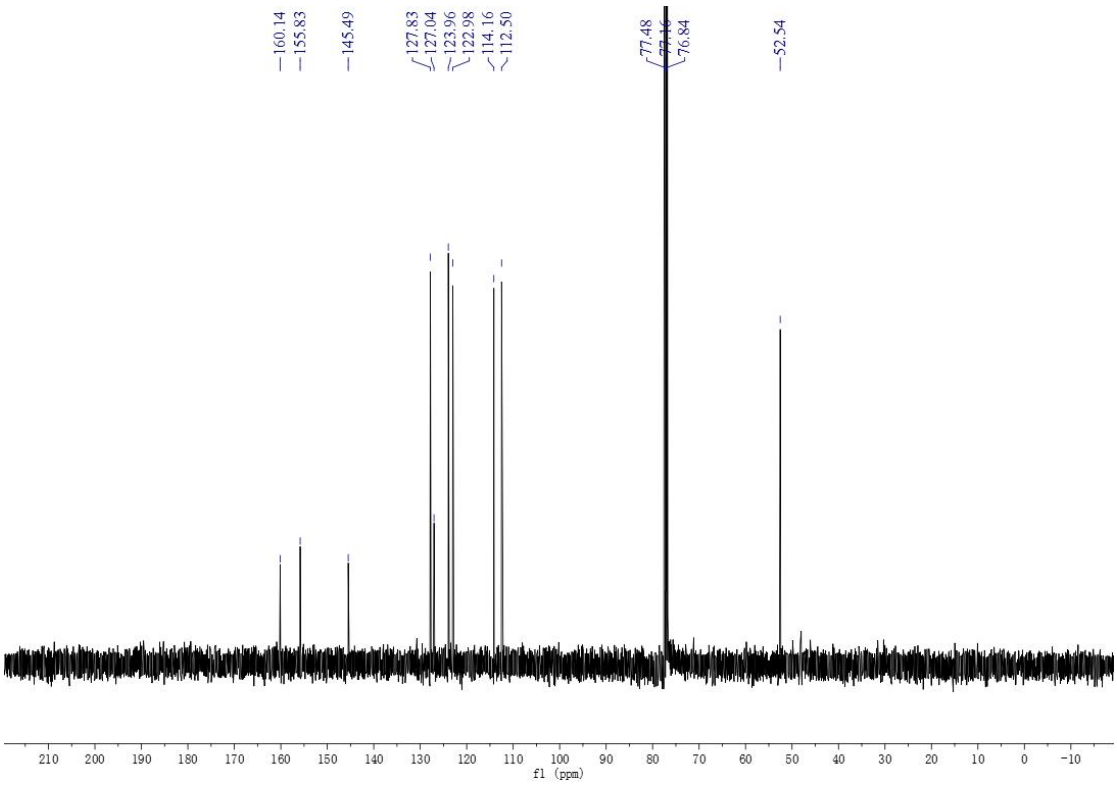
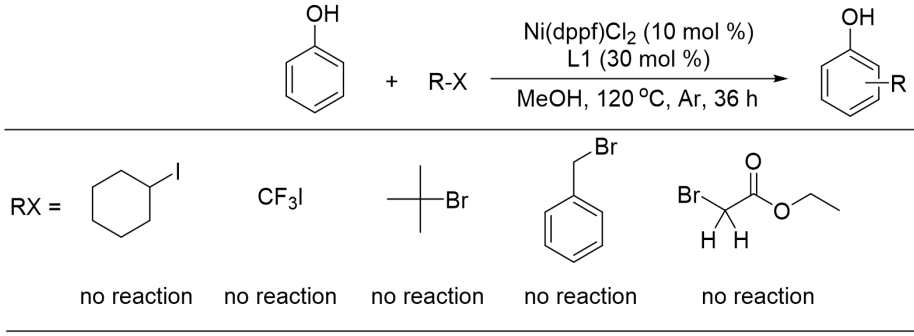


Figure S41. ^{13}C NMR (100 MHz, $CDCl_3$) of 16

9. Scheme S4. The influence of various C-radicals on nickel-catalyzed alkylation



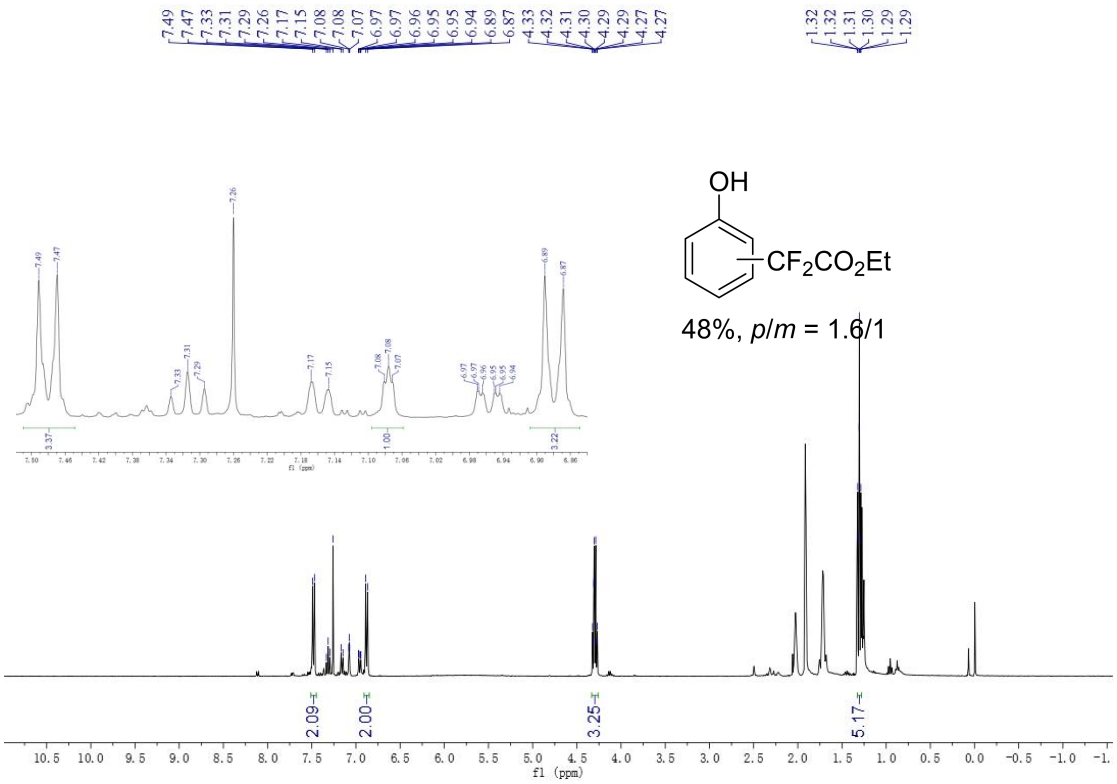


Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) of 10

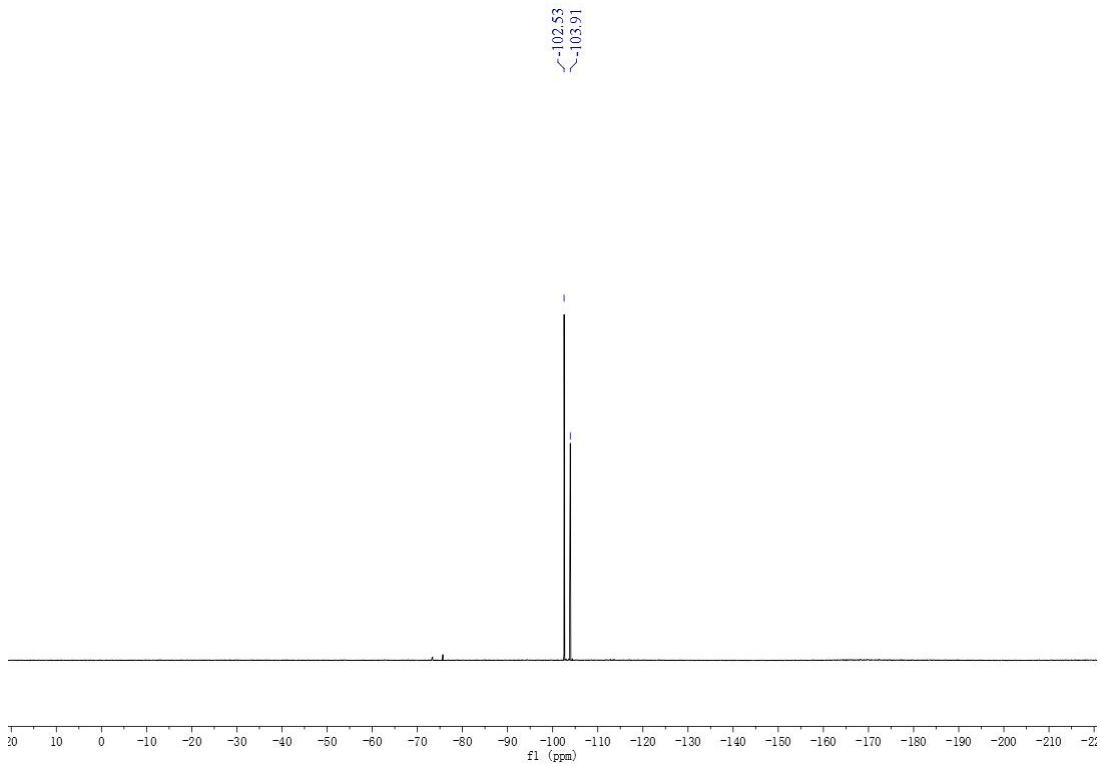


Figure S43. ^{19}F NMR (376 MHz, $CDCl_3$) of 10

10. ^{1}H NMR (400 MHz, DMSO) analysis of ligand coordination experiments

The following experiments were all carried out under 120 °C and argon atmosphere with stirring for 2 hours. The results show that the chemical shifts of aryl hydrogen are changed with the addition of 50% $NiCl_2$ or $Ni(dppf)Cl_2$ compared to the standard spectrum of phenol in methanol. In addition, when 1,10-Phen and $NiCl_2$ were added to the reaction at the same time, the chemical shift of aryl hydrogen shifted from 7.145 to 7.121 compared with the standard spectrum of phenol in methanol. However, when only $NiCl_2$ is added to the methanol solution of phenol, the chemical shift of the aryl hydrogen in the figure is 7.127. The above results indicate that 1,10-Phen may be involved in the coordination with the nickel catalyst, and then weakly interact with phenol. Unfortunately, the ligand 1,10-Phen did not show up in ^{1}H NMR for unknown reasons, and $Ni(dppf)Cl_2$ was poorly soluble in methanol.

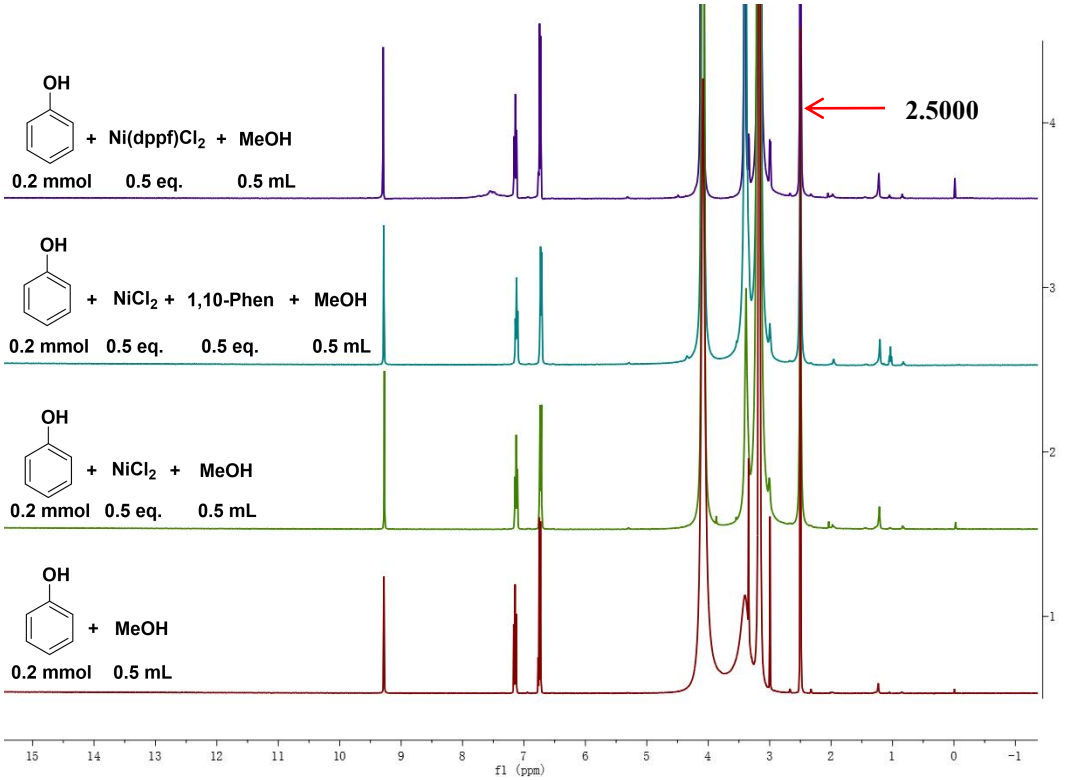


Figure S44. ^{1}H NMR (400 MHz, DMSO) analysis of ligand coordination experiments (1)

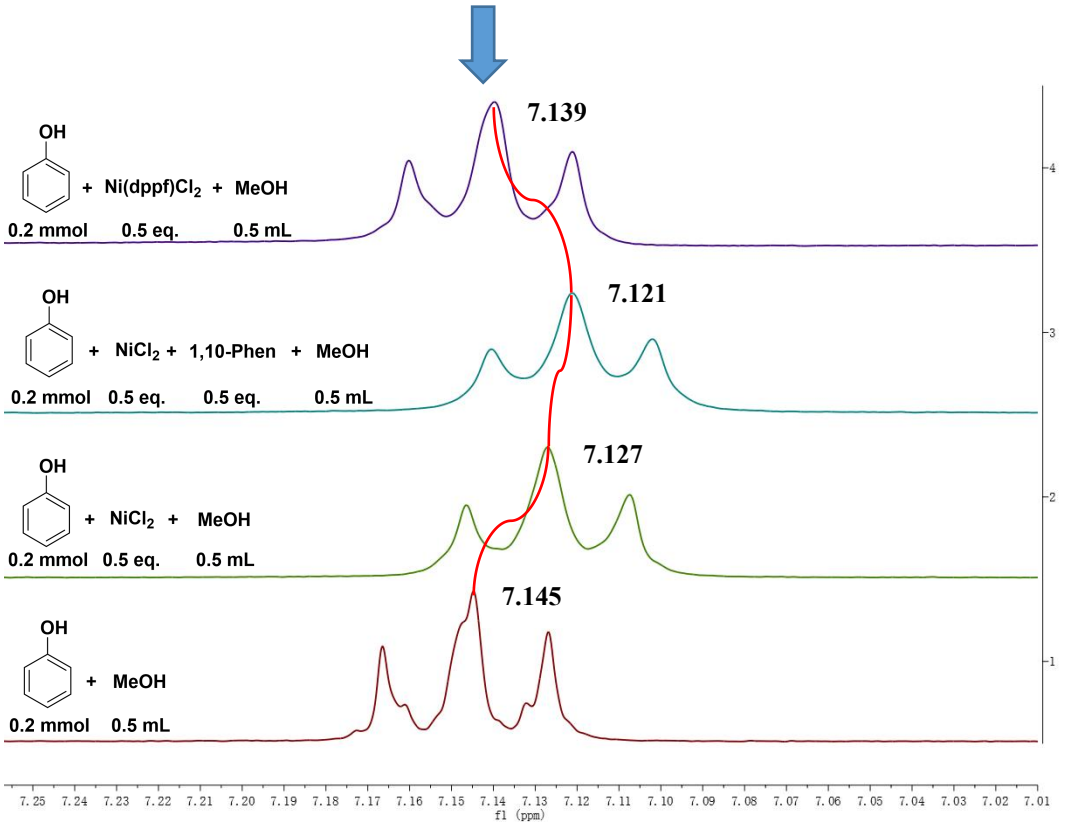


Figure S45. ^{1}H NMR (400 MHz, DMSO) analysis of ligand coordination experiments (2)

11. References

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12. NMR spectra

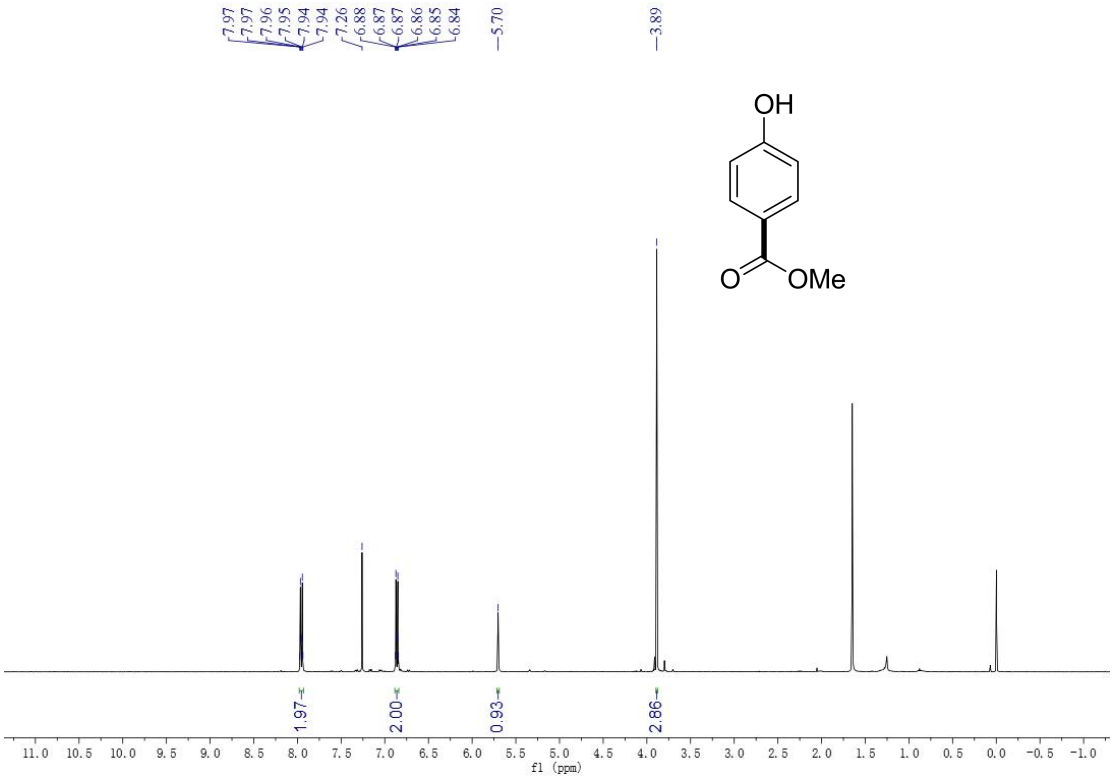

Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) of 5a

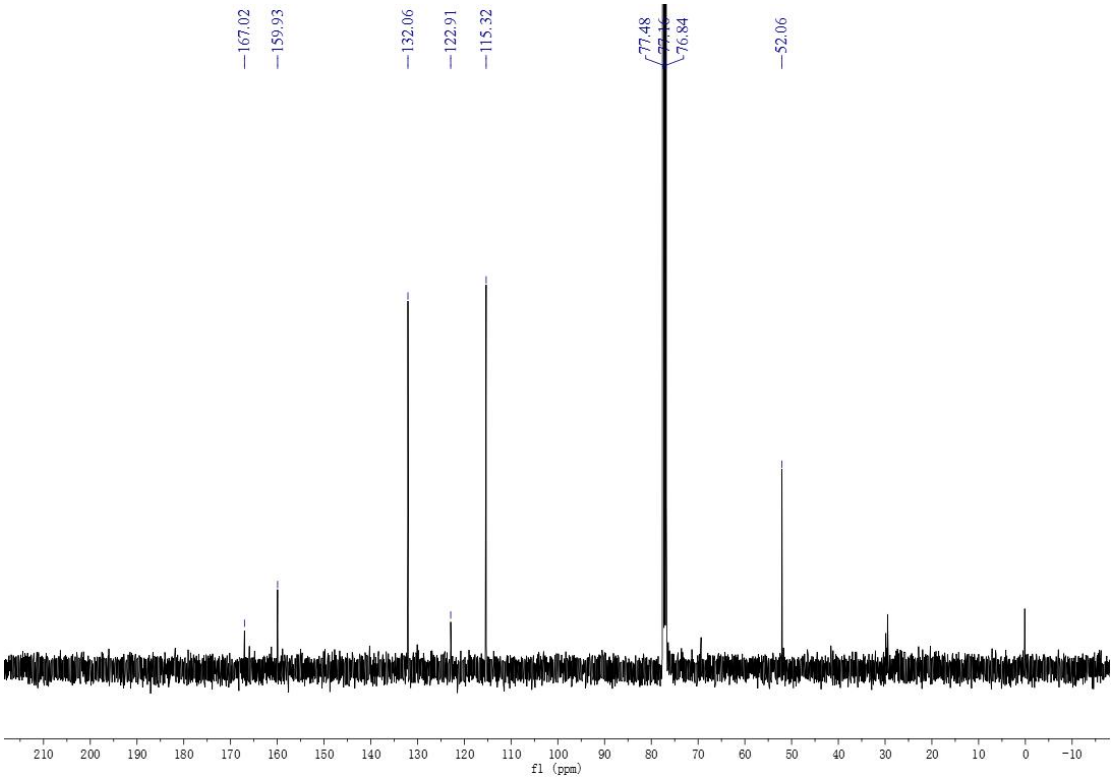

Figure S47. ^{13}C NMR (100 MHz, $CDCl_3$) of 5a

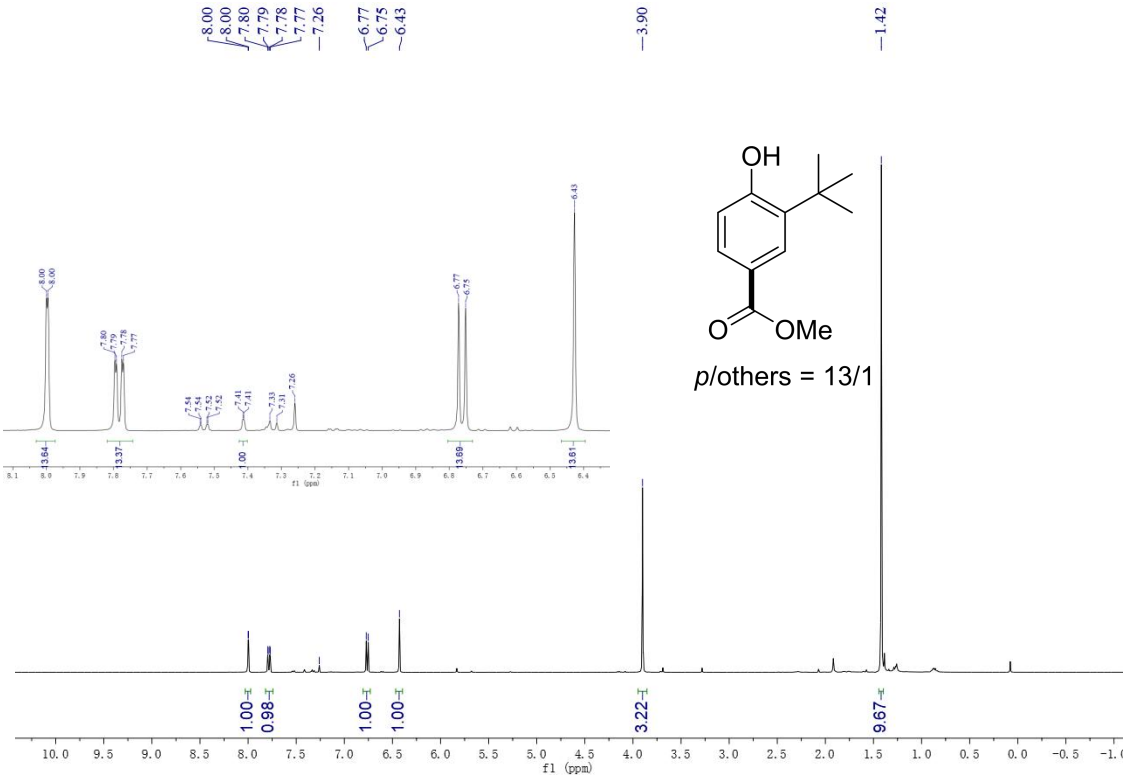

Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) of 5b

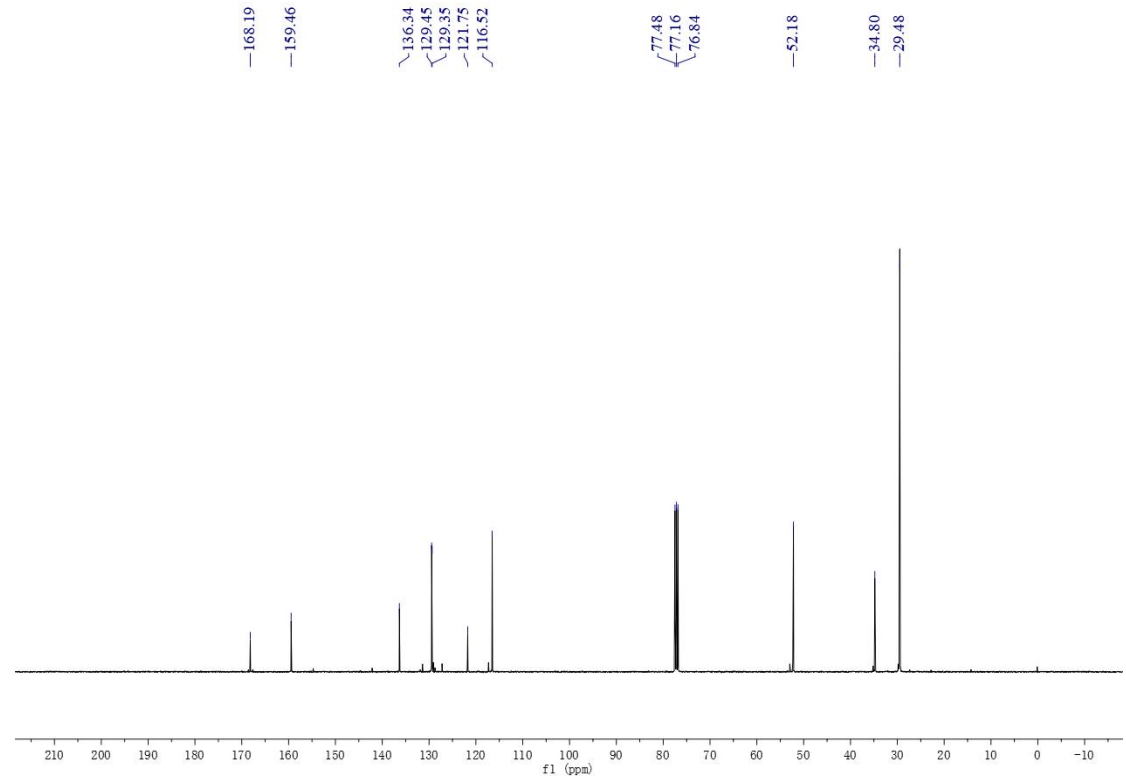

Figure S49. ^{13}C NMR (100 MHz, $CDCl_3$) of 5b

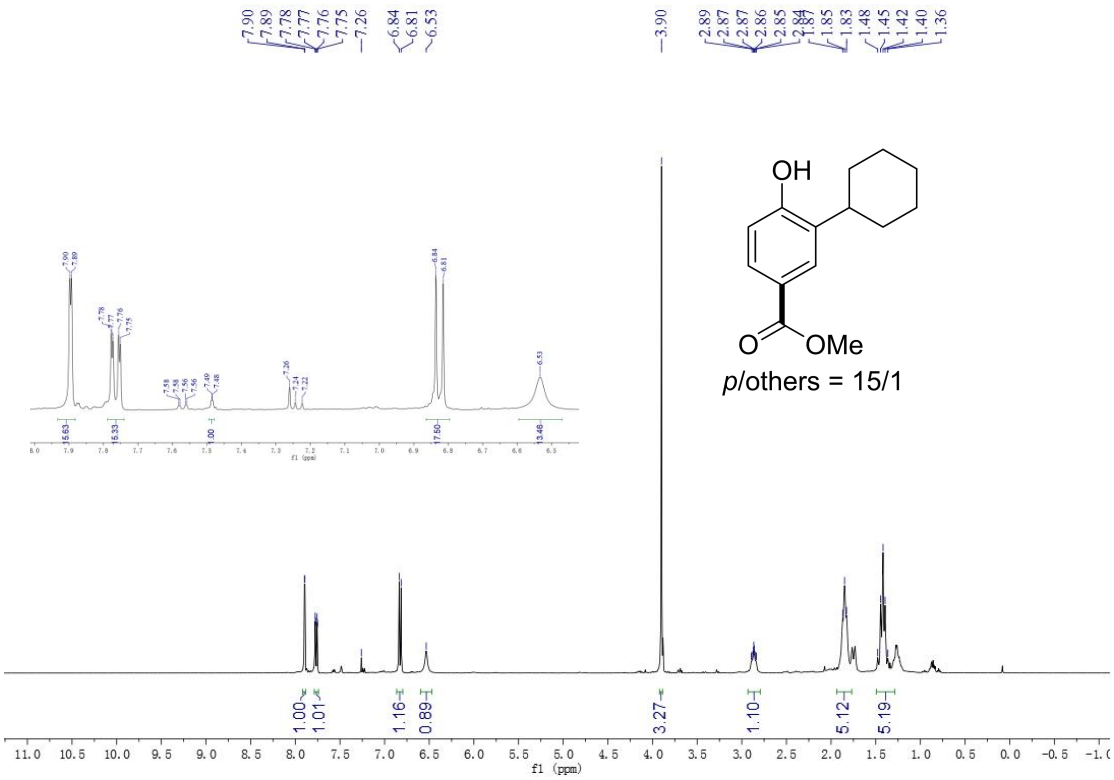

Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$) of 5c

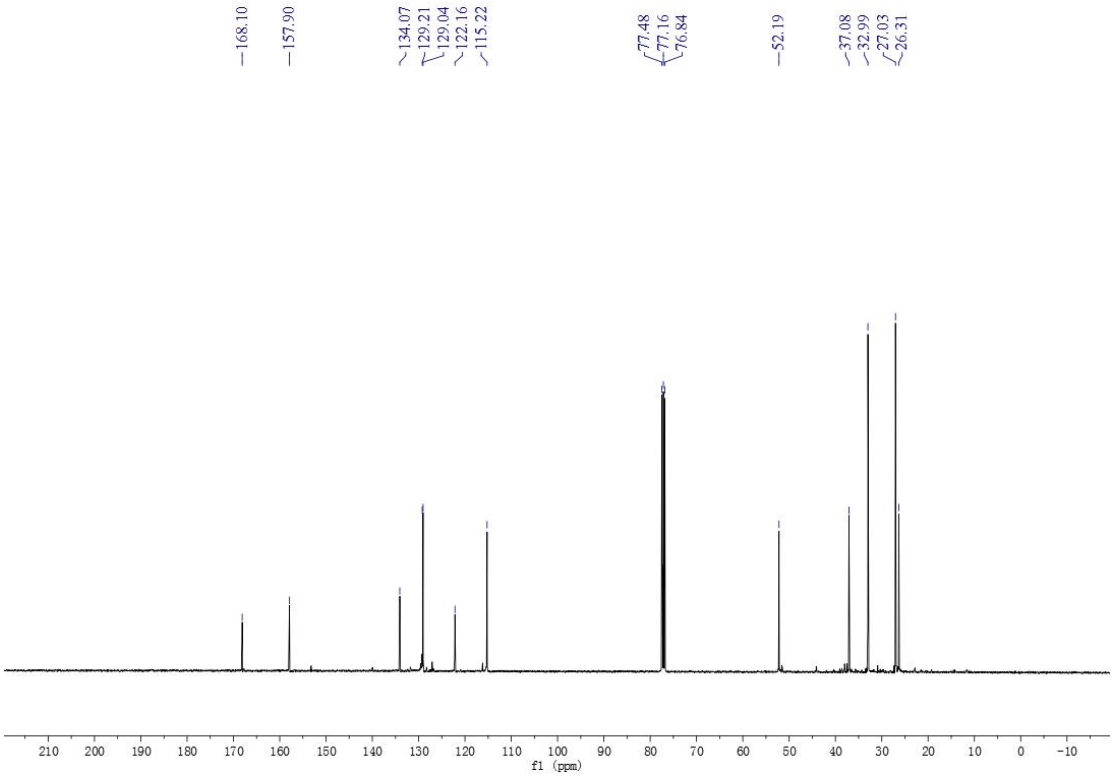

Figure S51. ^{13}C NMR (100 MHz, $CDCl_3$) of 5c

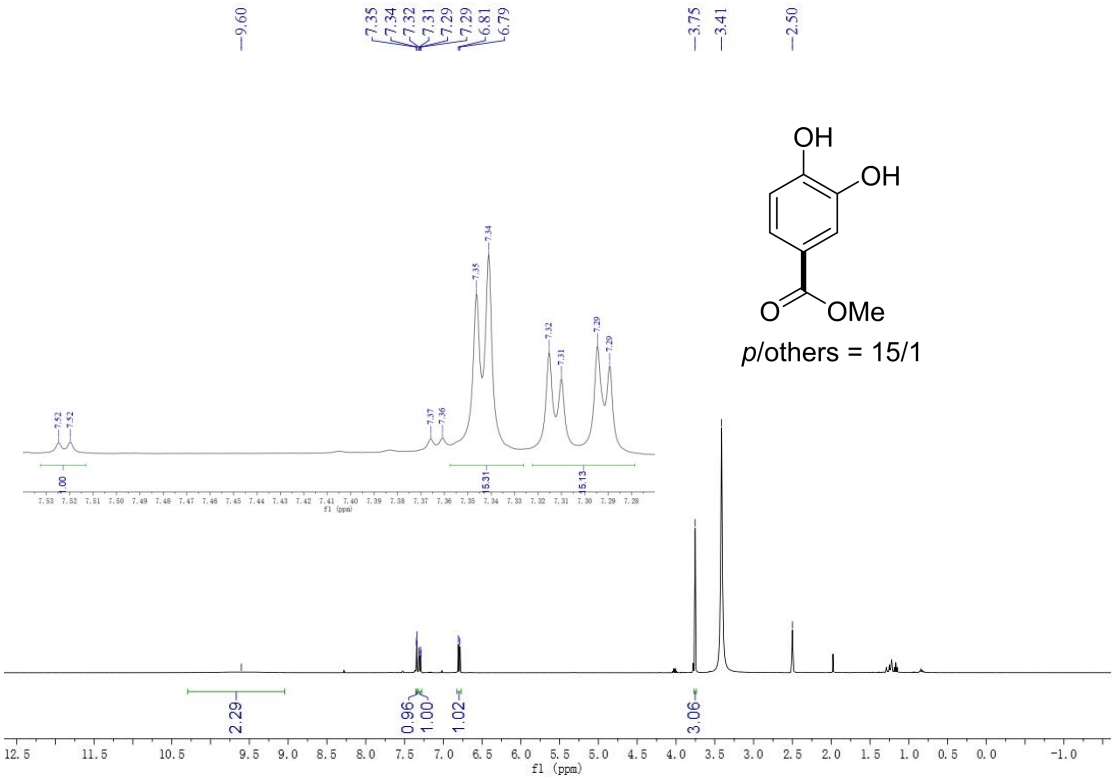

Figure S52. ^{1}H NMR (400 MHz, $CDCl_3$) of 5d

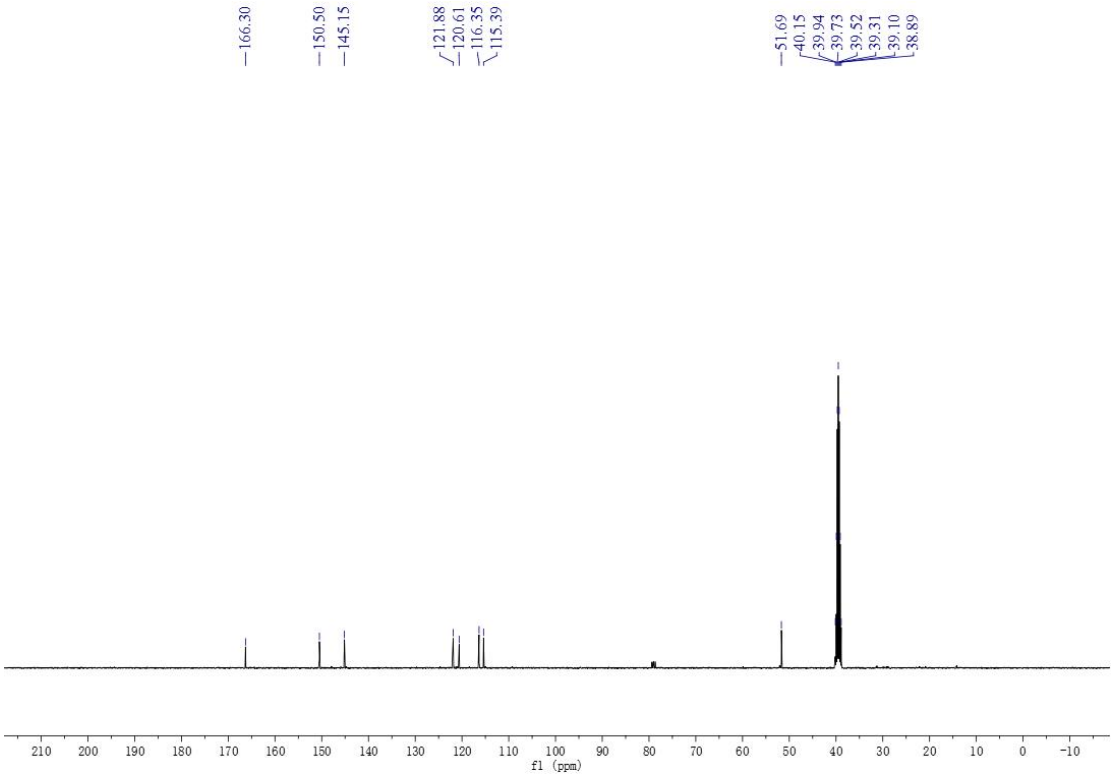

Figure S53. ^{13}C NMR (100 MHz, $CDCl_3$) of 5d

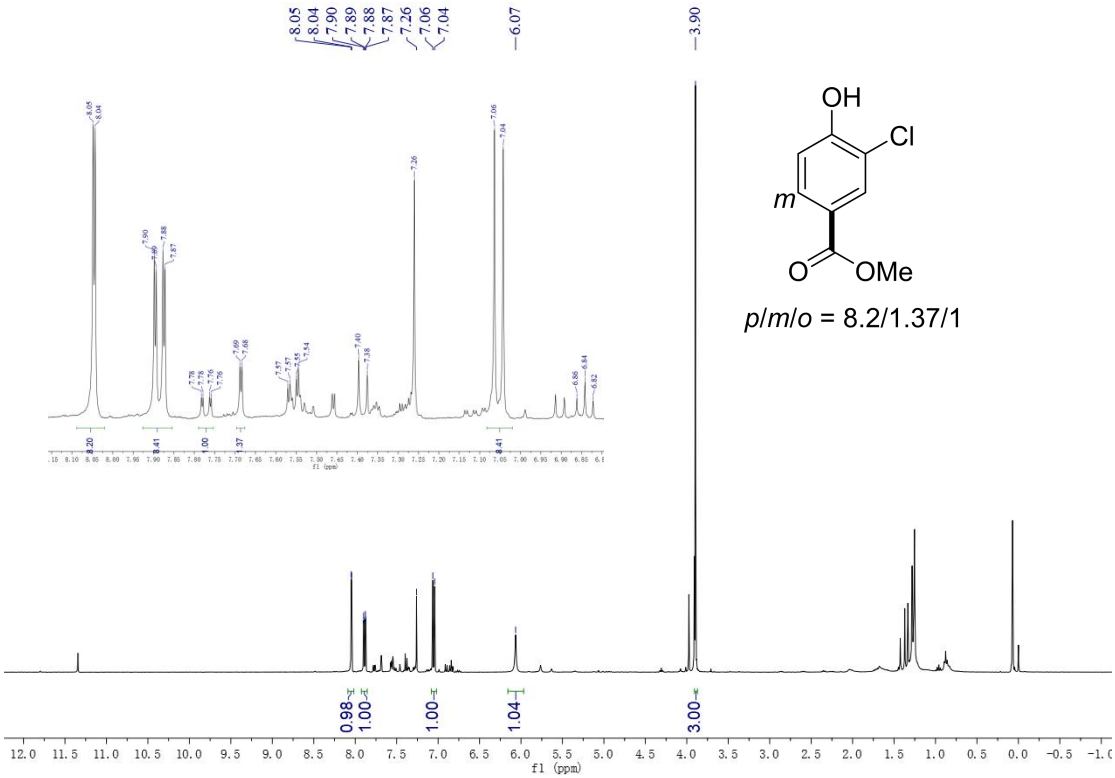

Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) of 5e

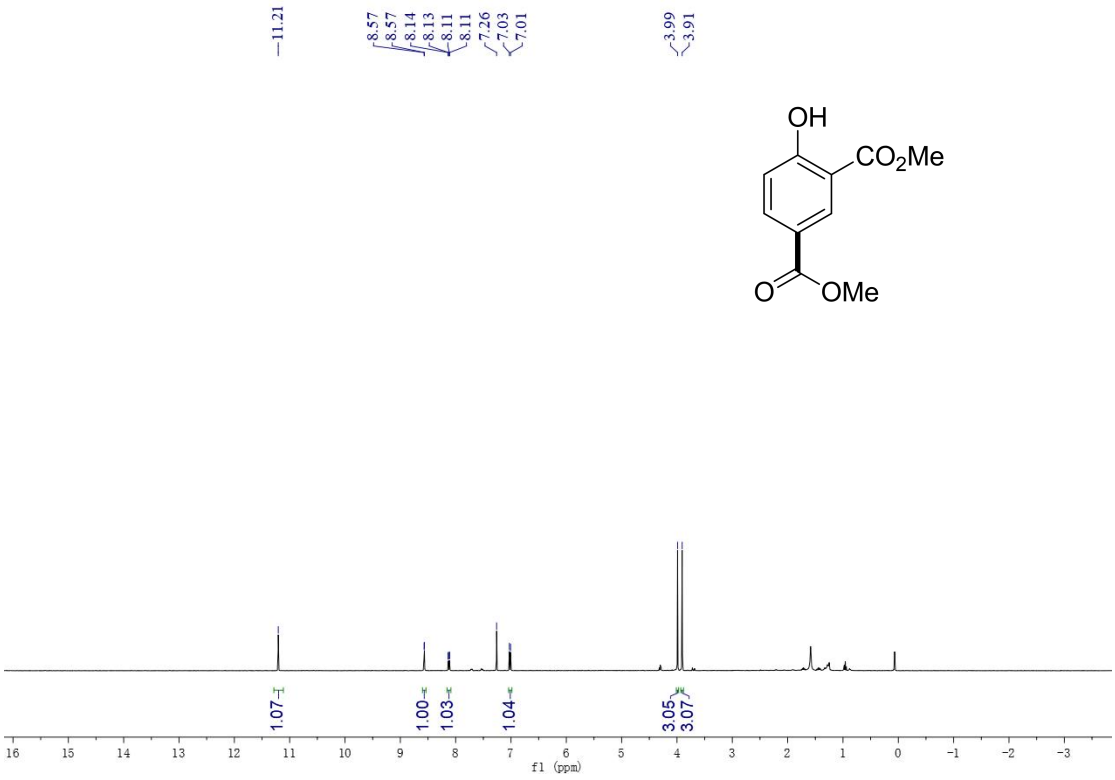

Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) of 5f

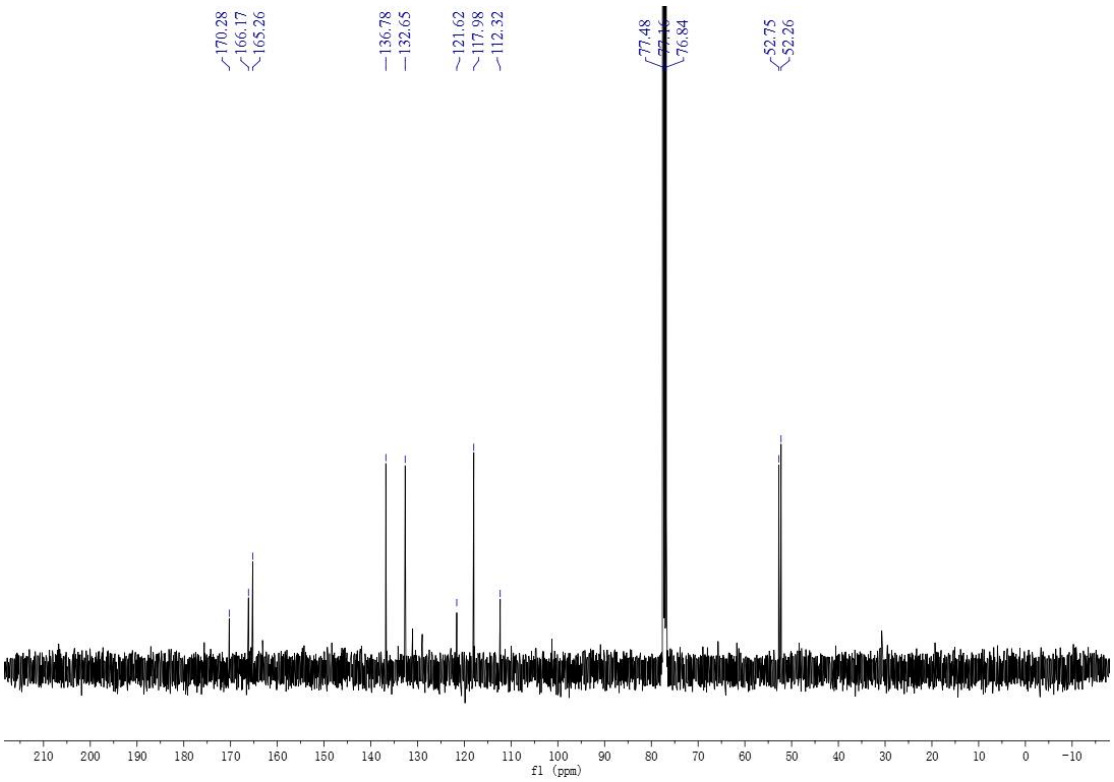

Figure S56. ^{13}C NMR (100 MHz, $CDCl_3$) of 5f

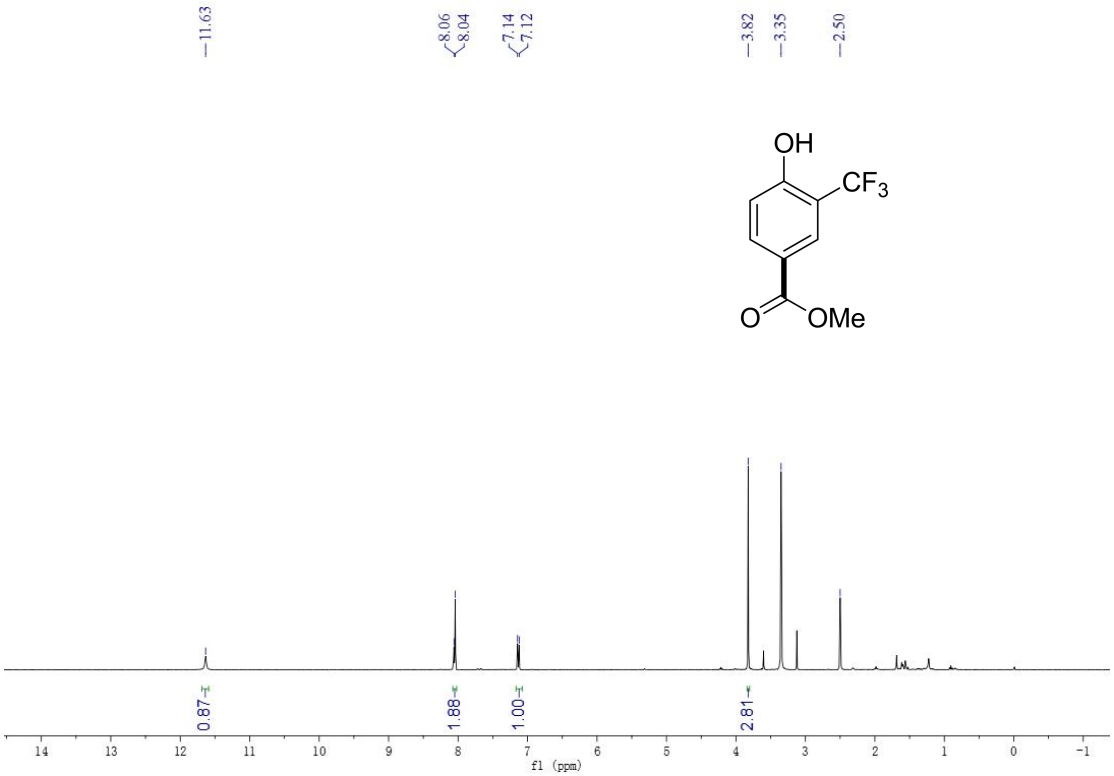

Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) of 5g

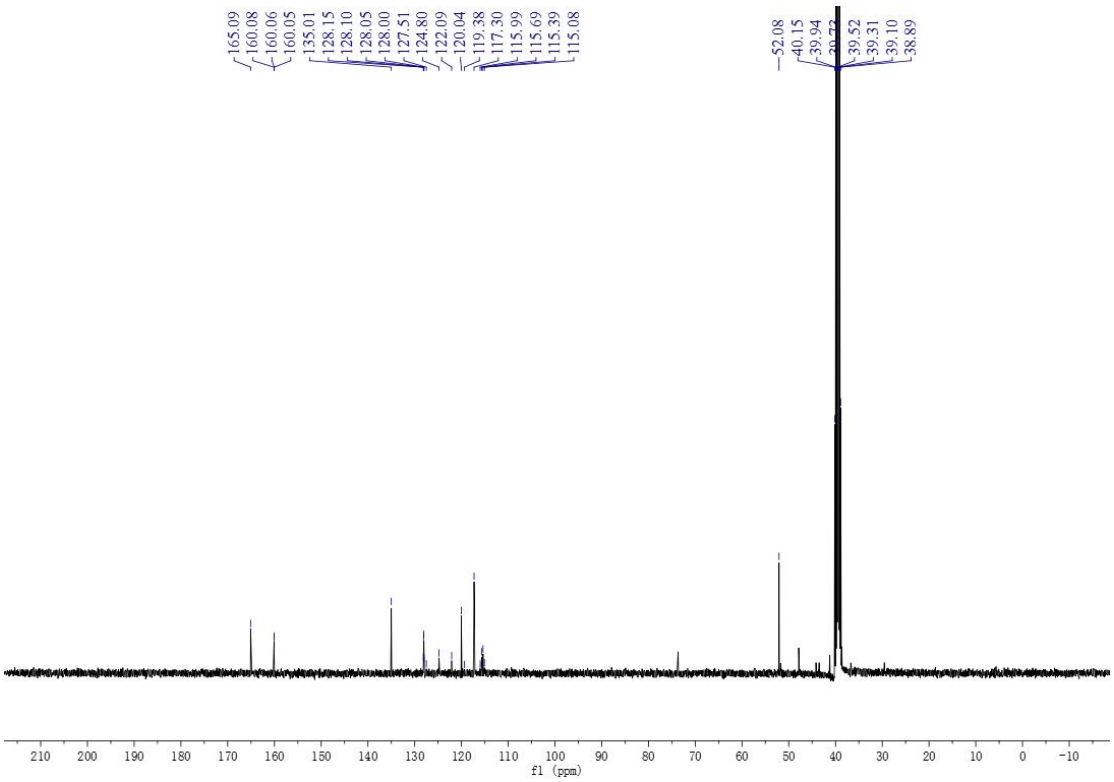

Figure S58. ^{13}C NMR (100 MHz, $CDCl_3$) of 5g

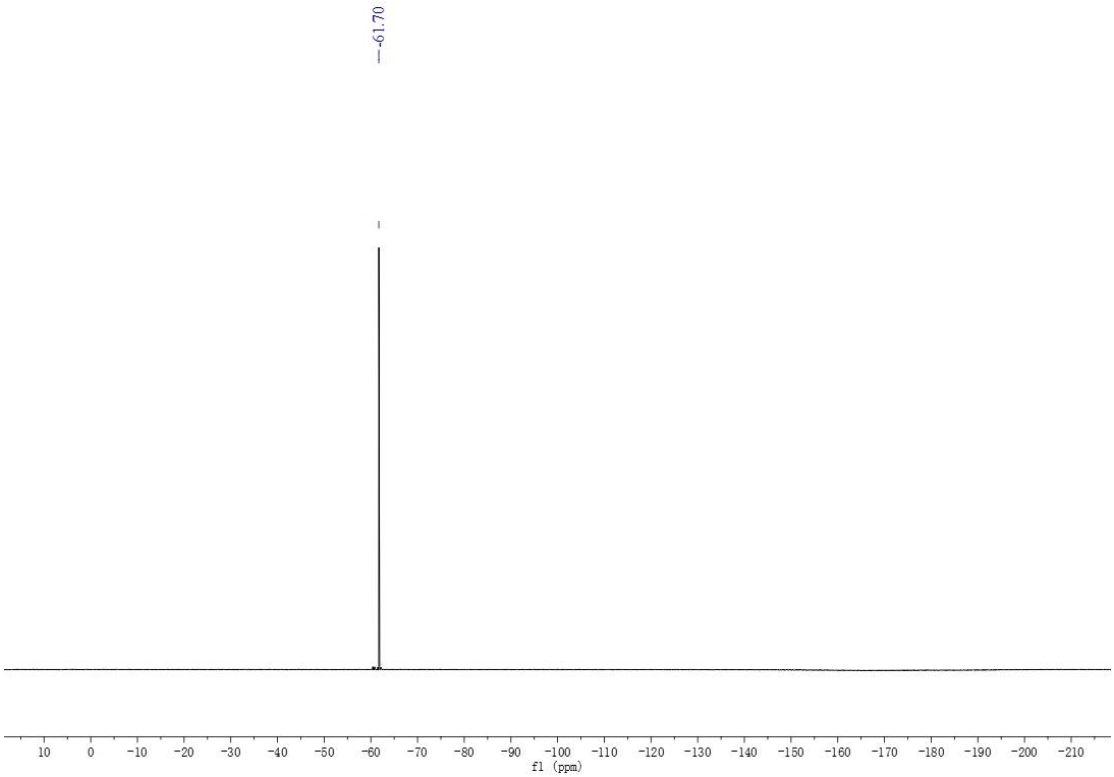

Figure S59. ^{19}F NMR (376 MHz, $CDCl_3$) of 5g

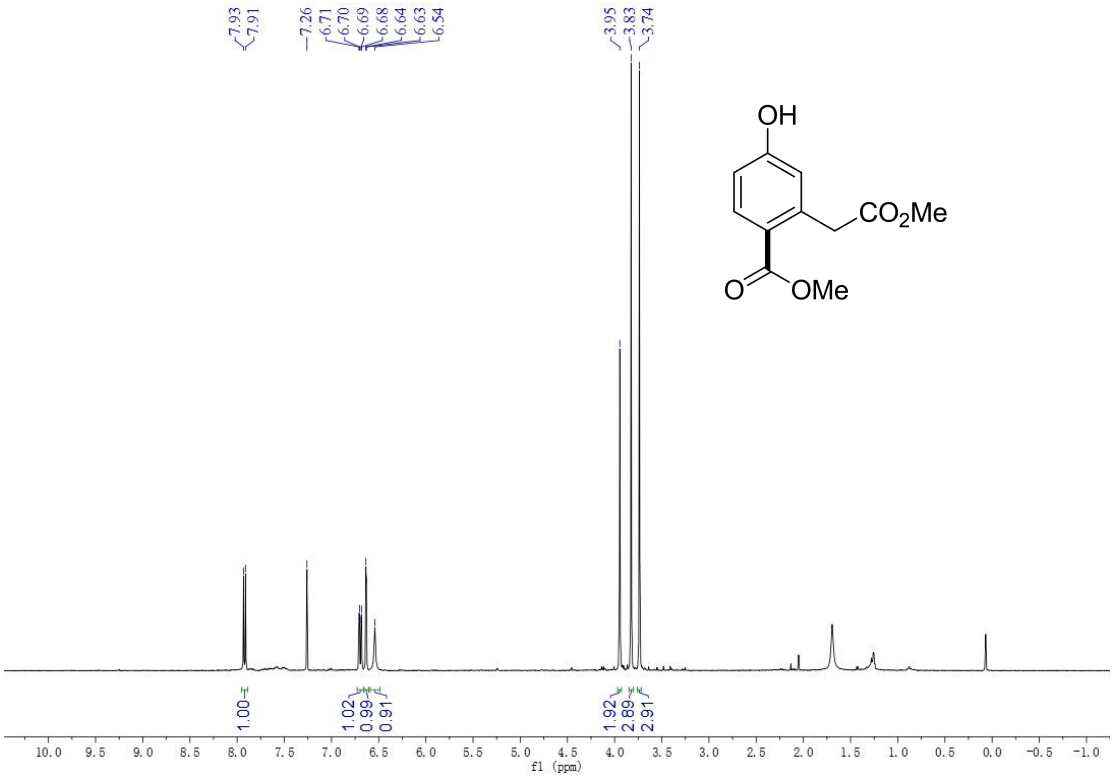

Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) of 5h

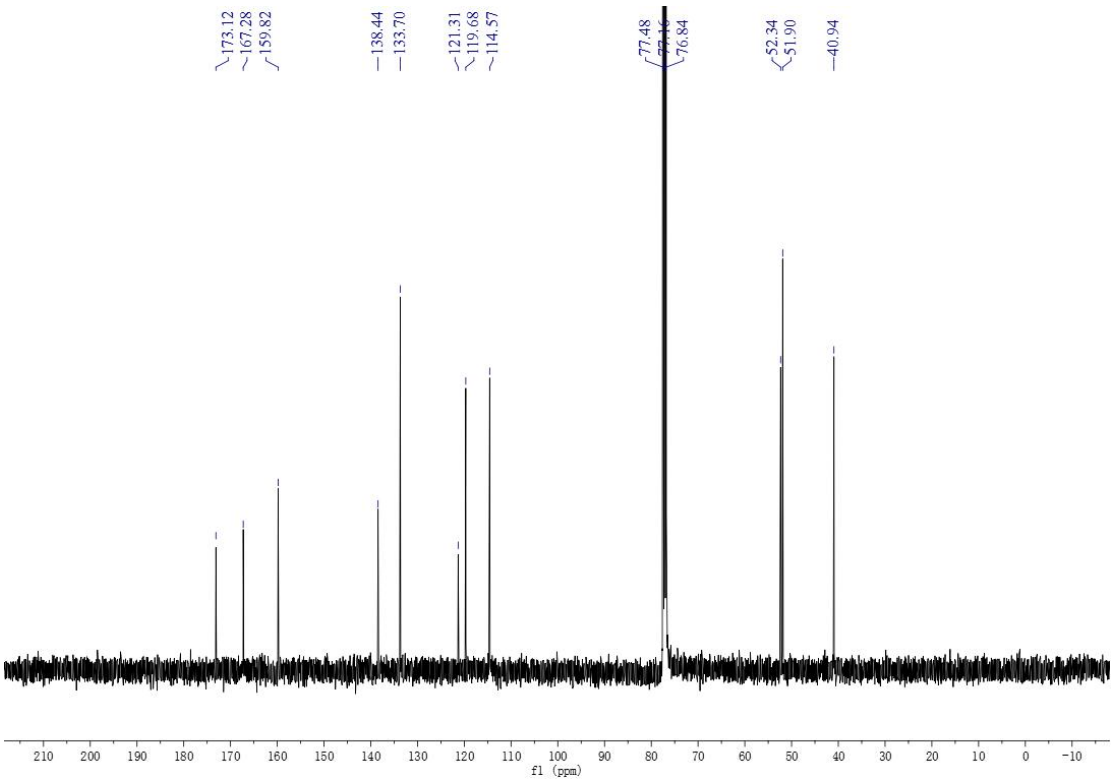

Figure S61. ^{13}C NMR (100 MHz, $CDCl_3$) of 5h

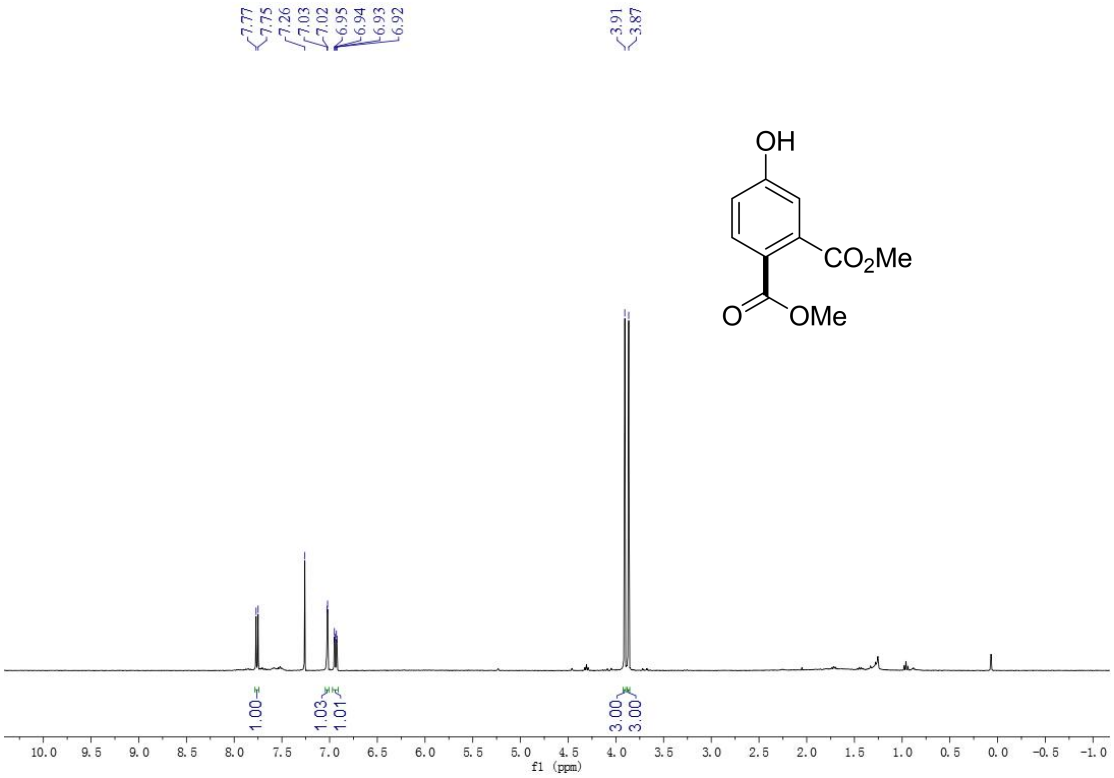

Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) of 5i

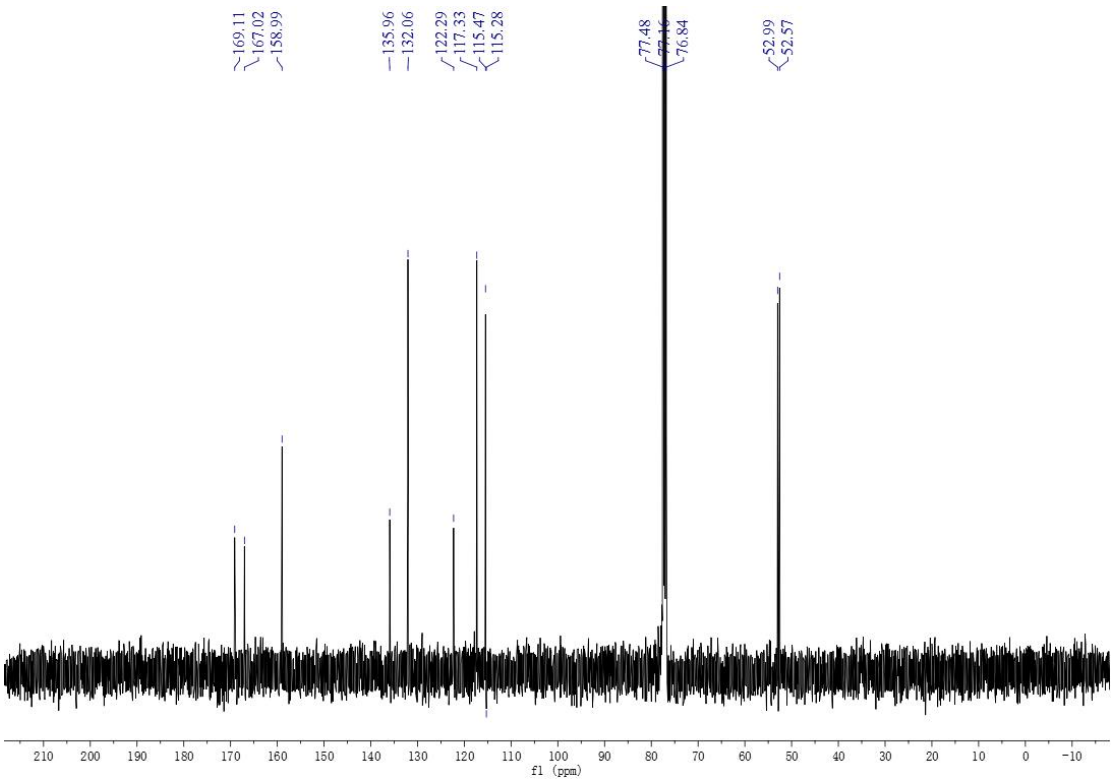

Figure S63. ^{13}C NMR (100 MHz, $CDCl_3$) of 5i

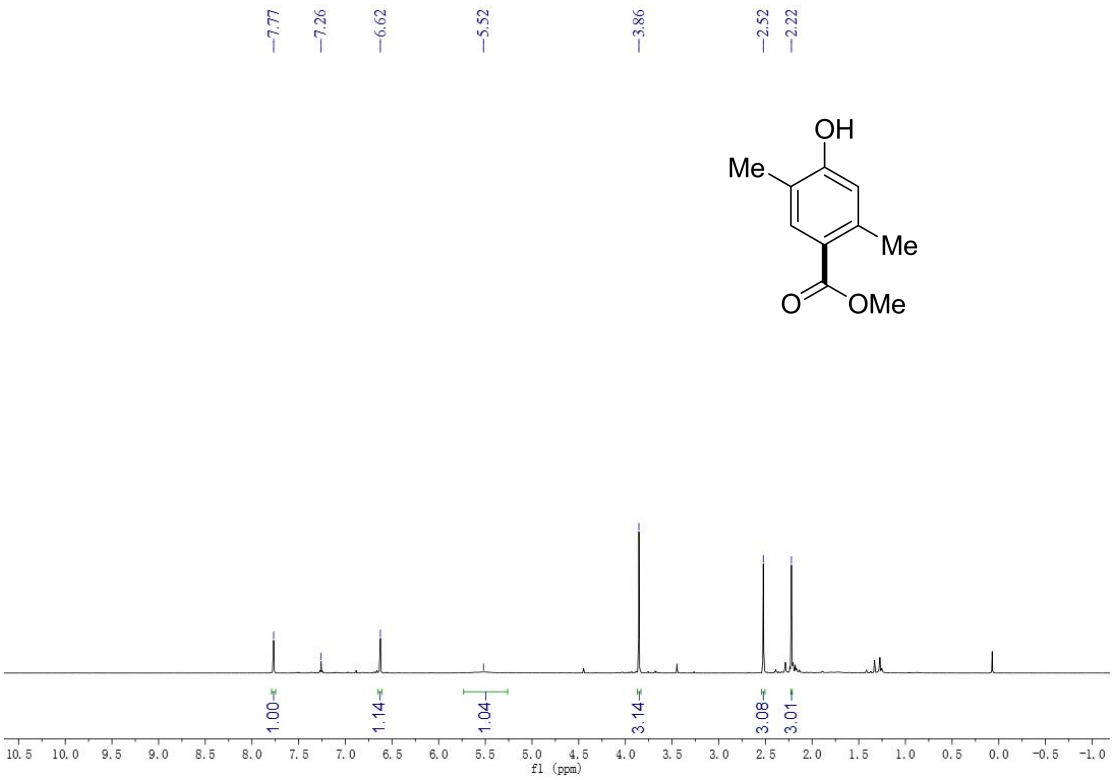

Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) of 5j

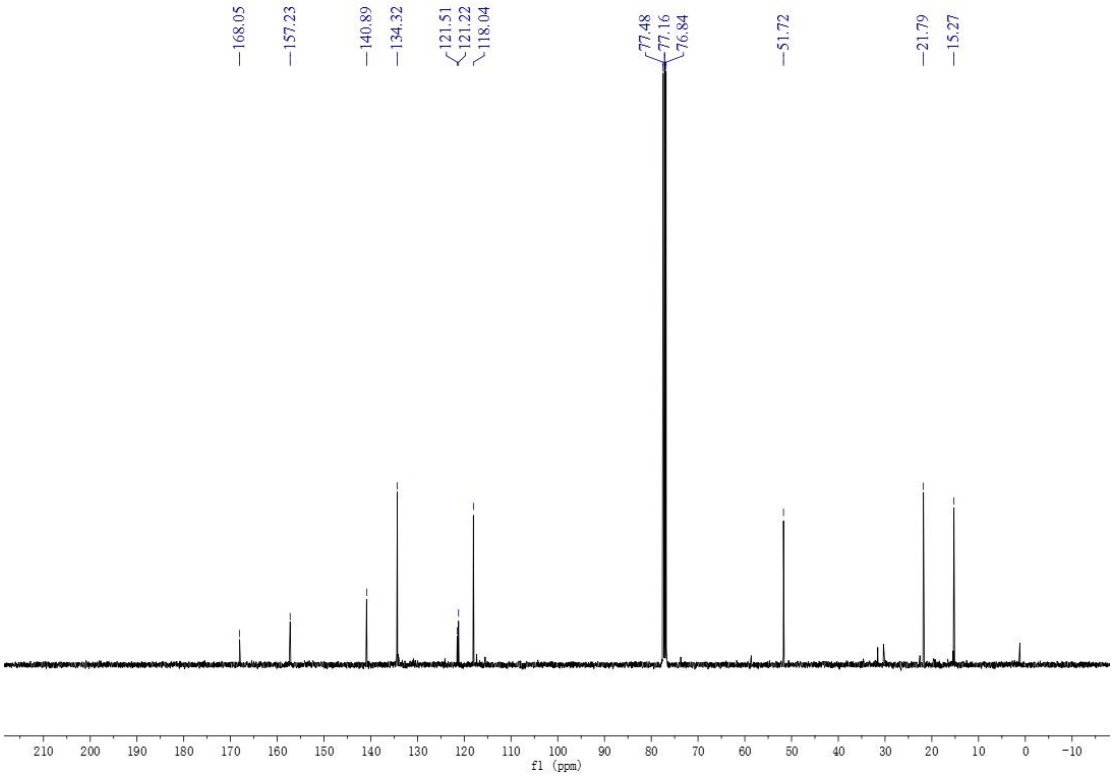

Figure S65. ^{13}C NMR (100 MHz, $CDCl_3$) of 5j

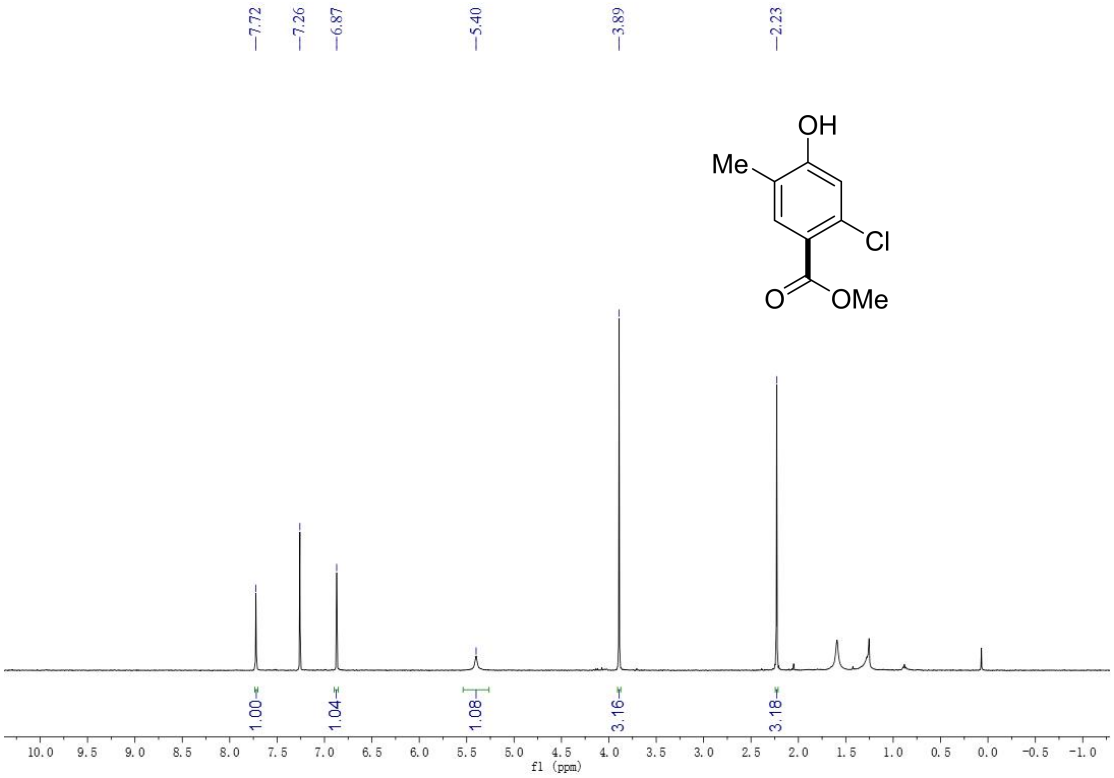

Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) of 5k

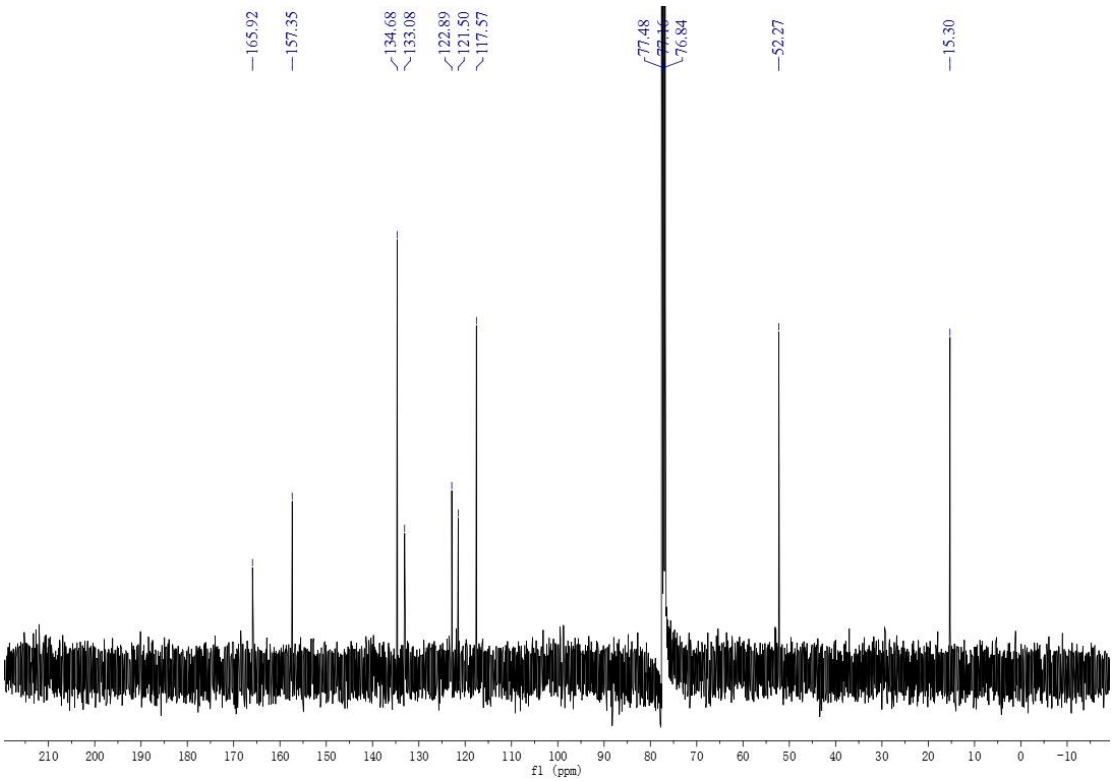

Figure S67. ^{13}C NMR (100 MHz, $CDCl_3$) of 5k

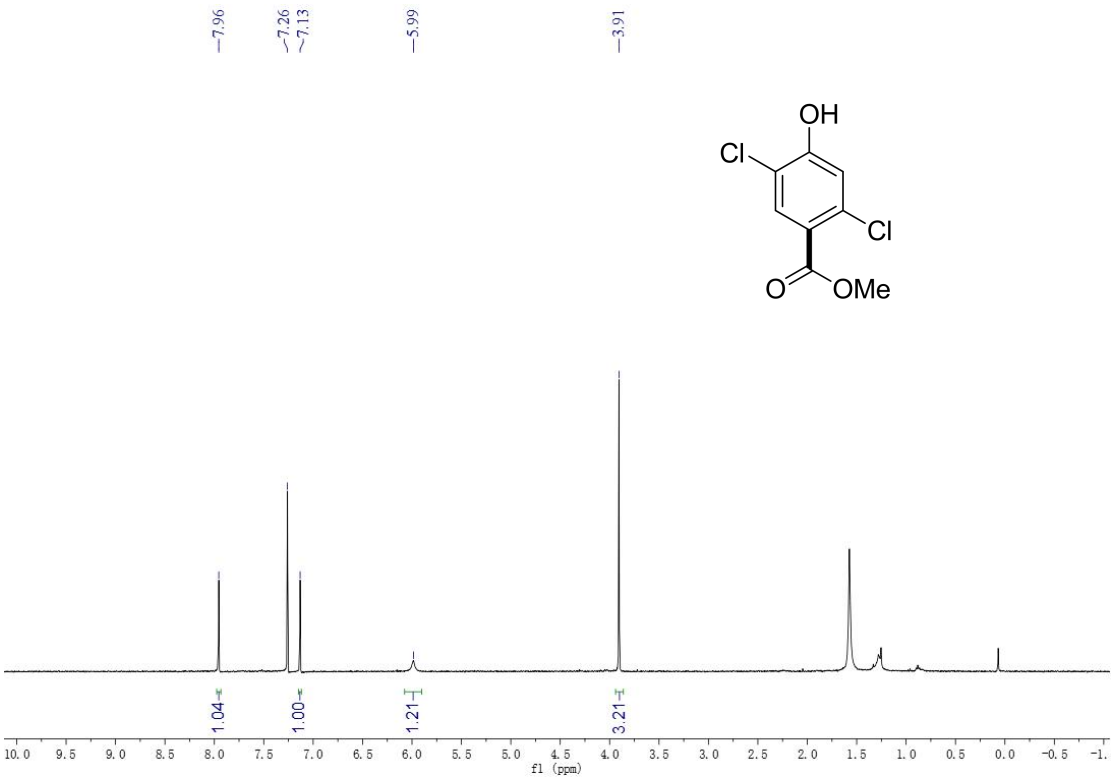

Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) of 5l

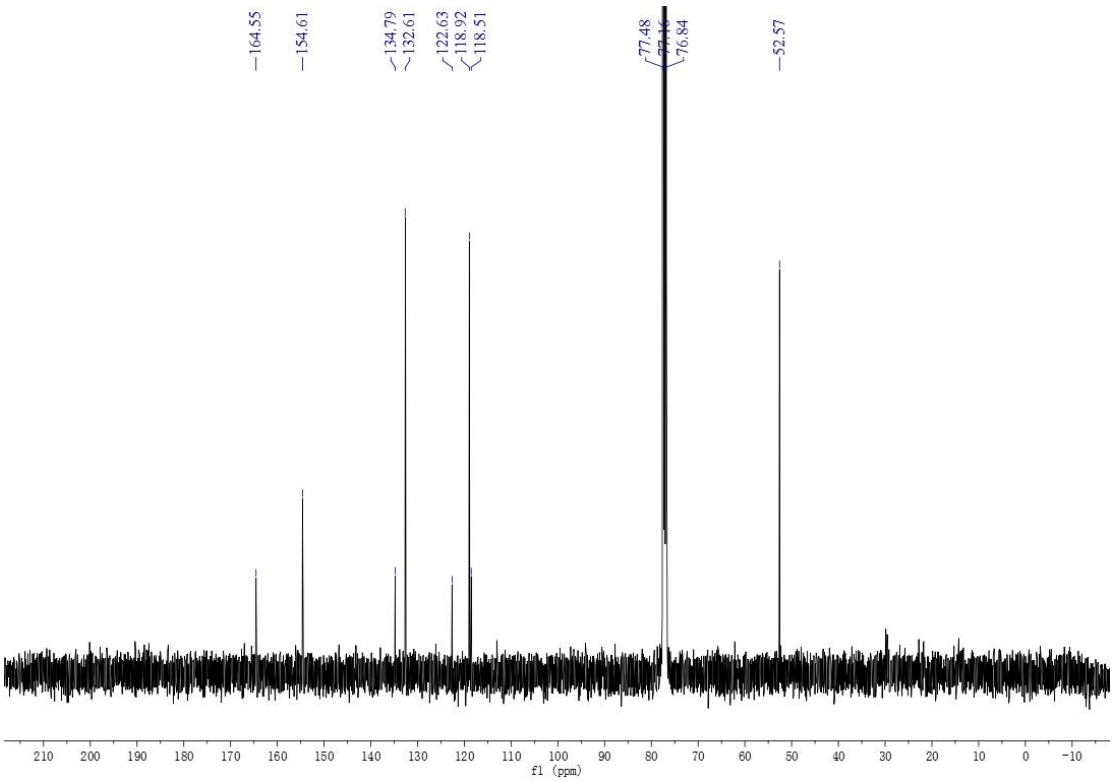

Figure S69. ^{13}C NMR (100 MHz, $CDCl_3$) of 5l

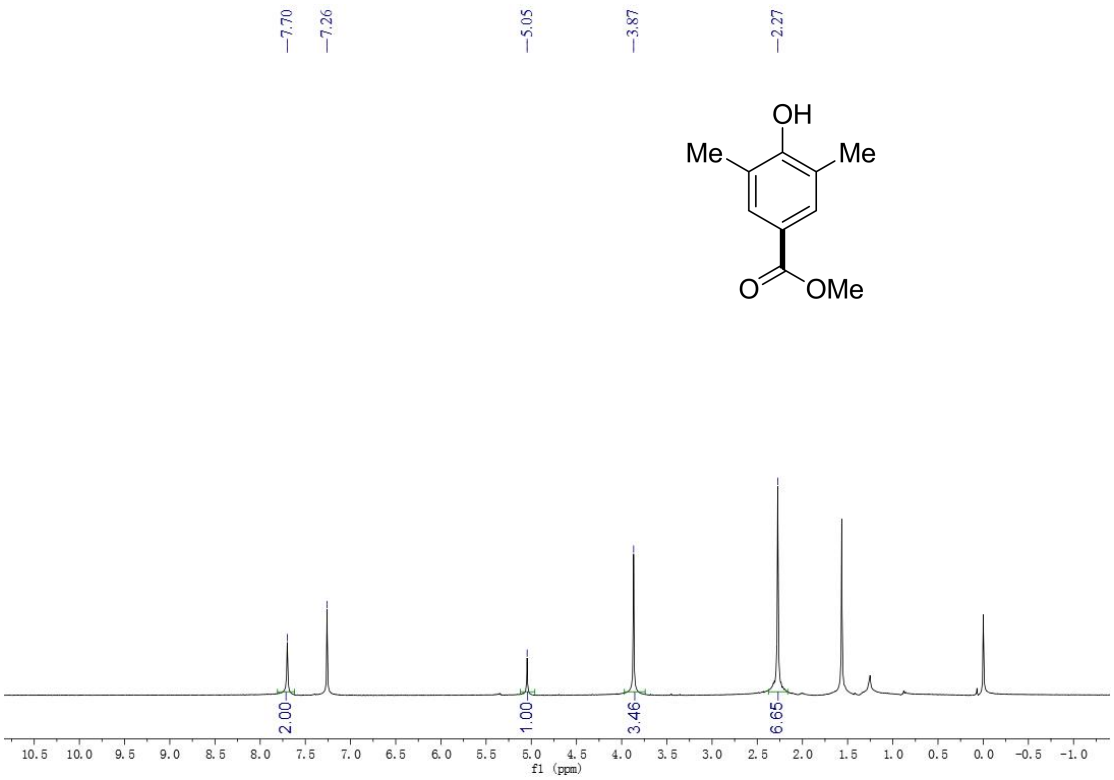

Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) of 5m

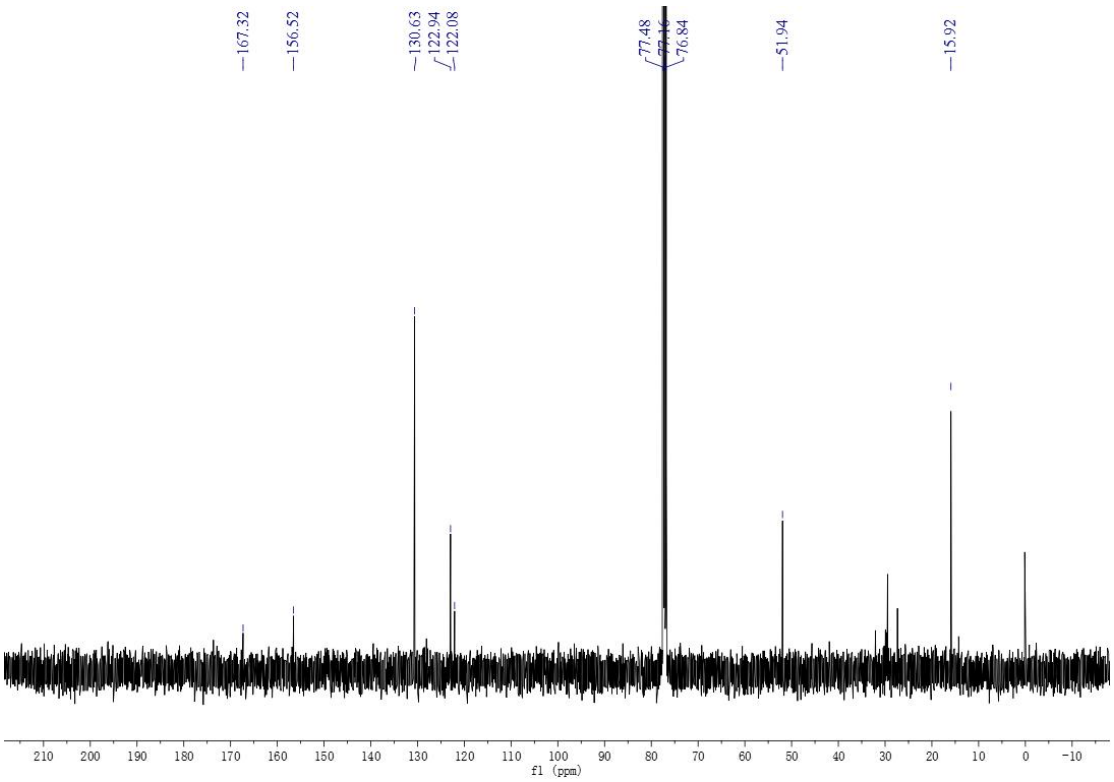

Figure S71. ^{13}C NMR (100 MHz, $CDCl_3$) of 5m

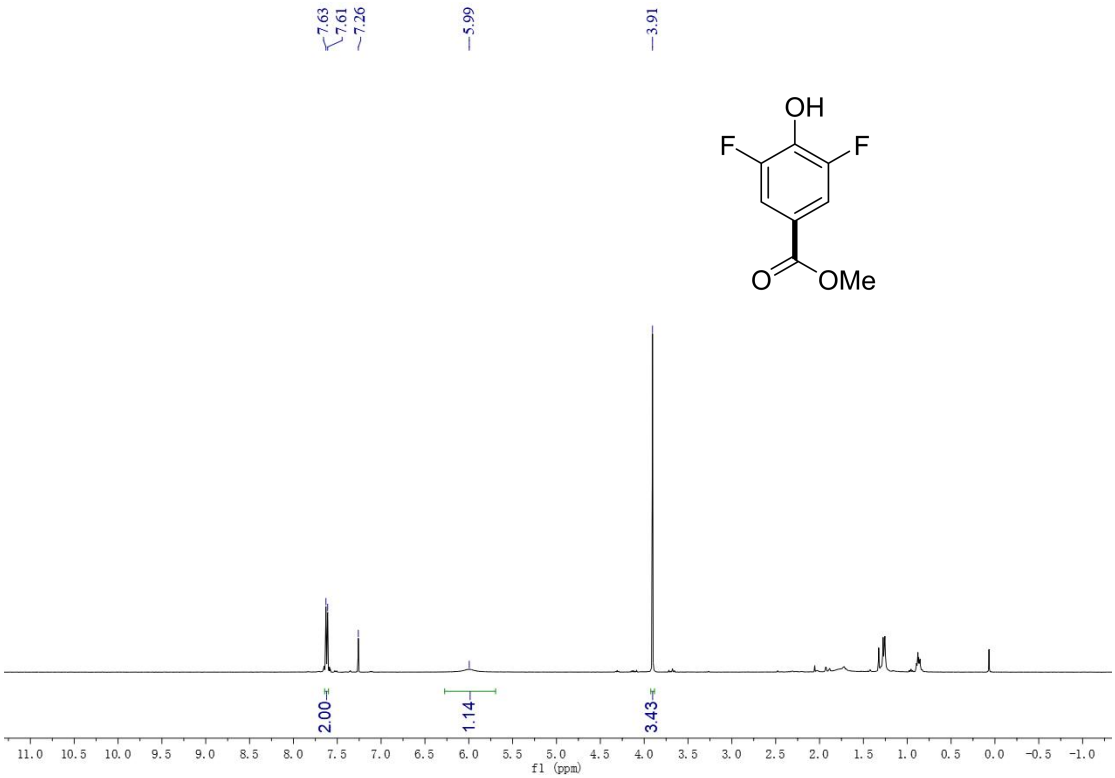

Figure S72. ^{1}H NMR (400 MHz, $CDCl_3$) of 5n

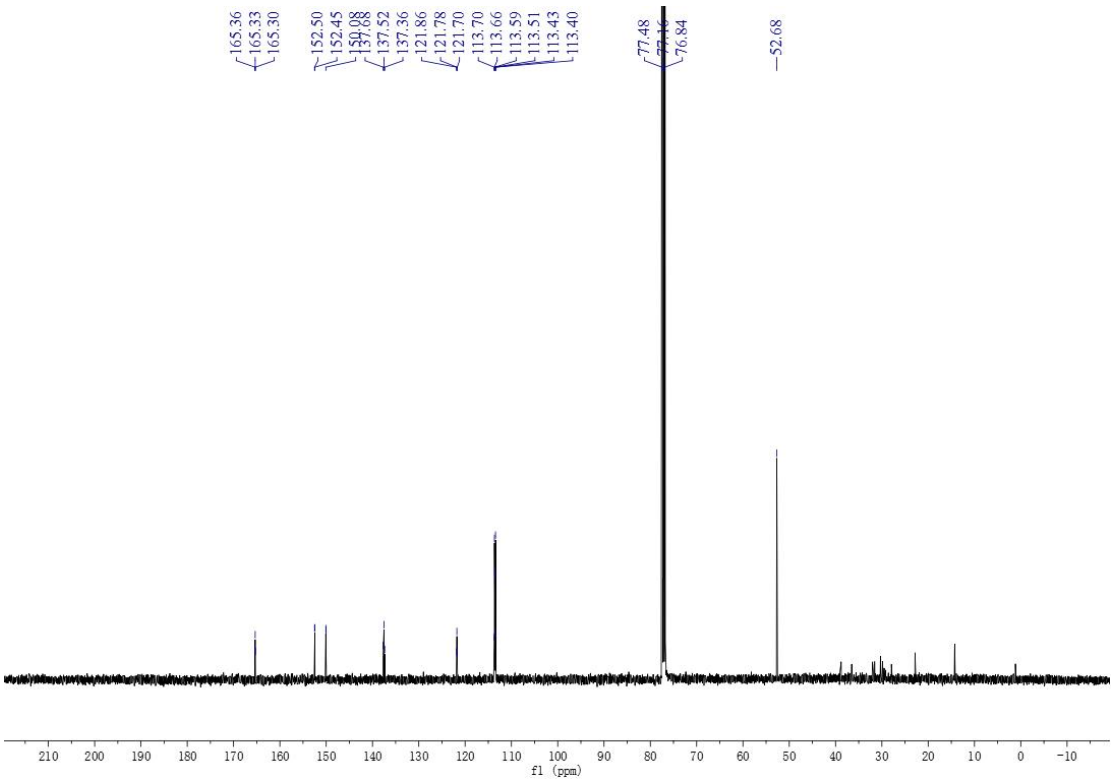

Figure S73. ^{13}C NMR (100 MHz, $CDCl_3$) of 5n

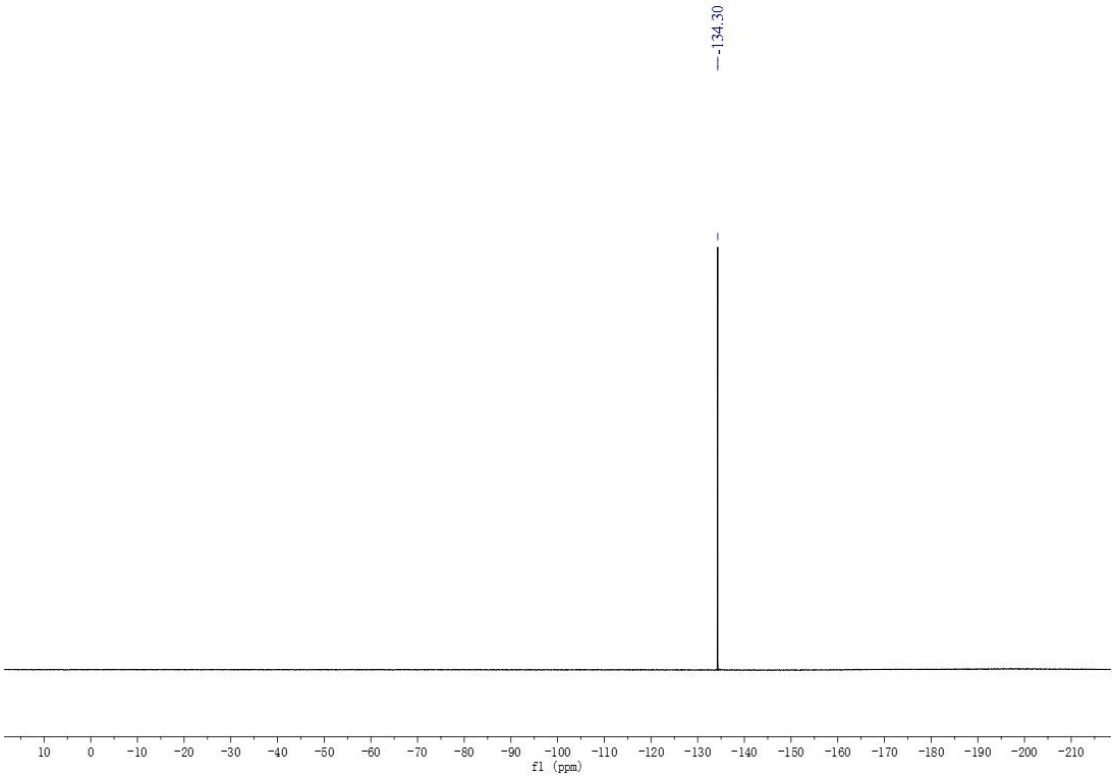

Figure S74. ^{19}F NMR (376 MHz, $CDCl_3$) of 5n

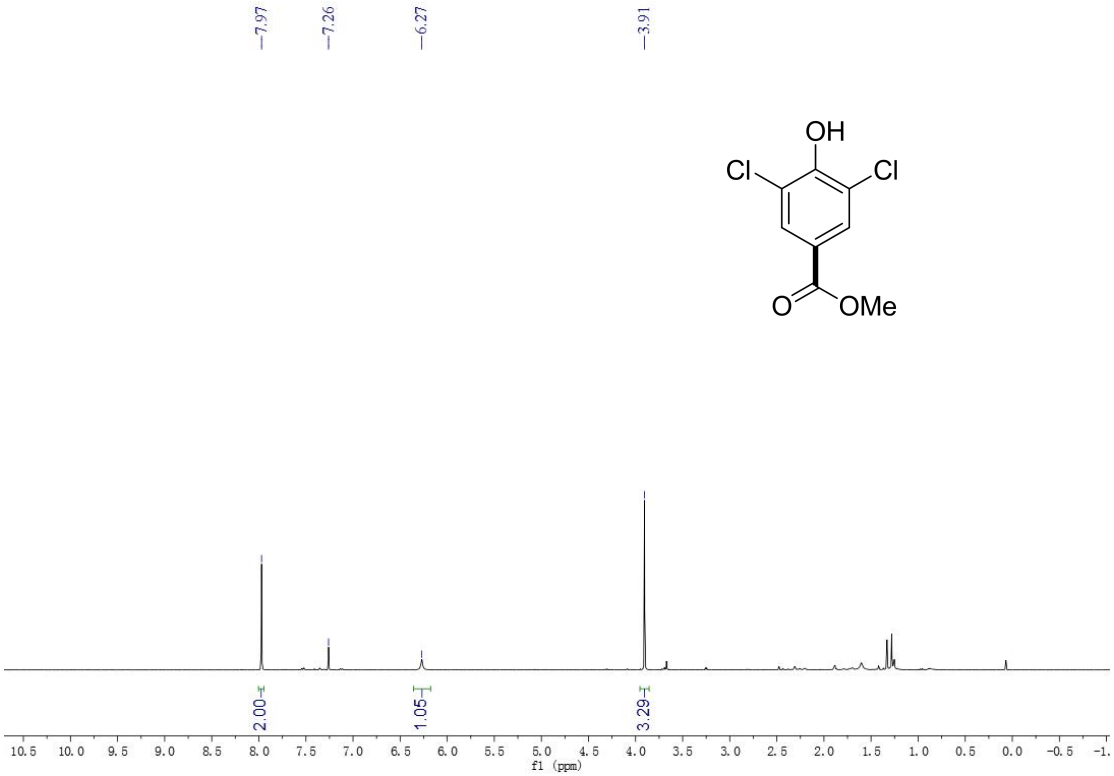

Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) of 5o

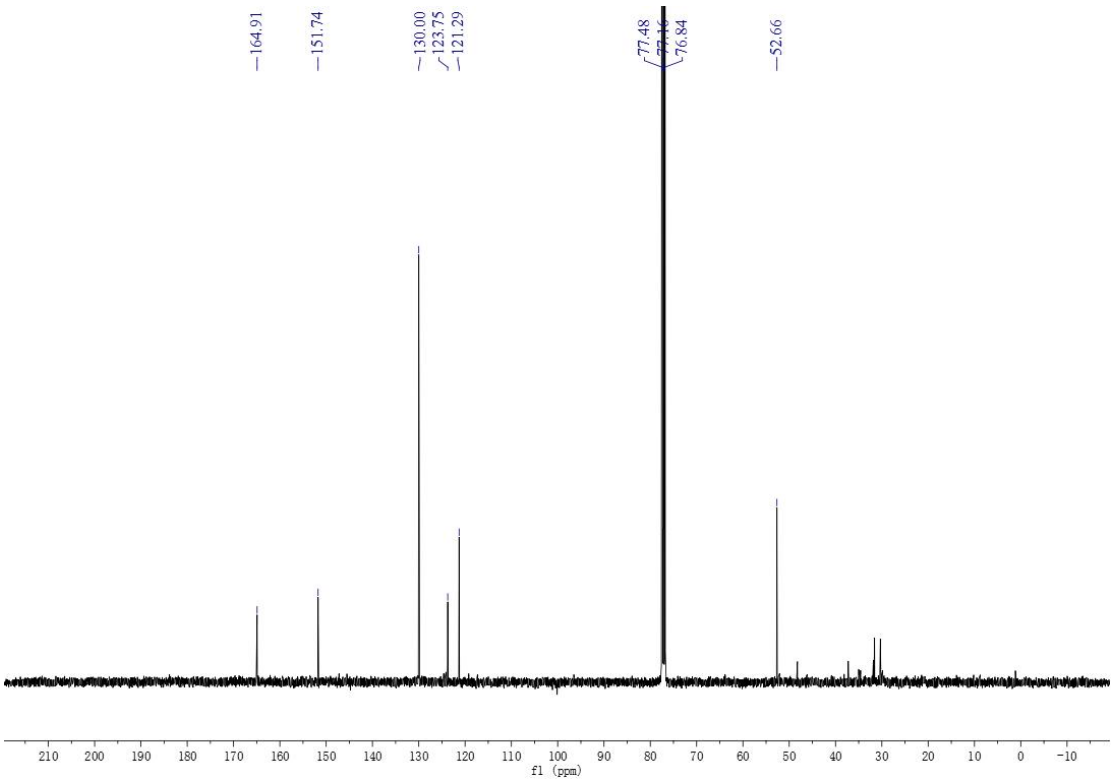

Figure S76. ^{13}C NMR (100 MHz, $CDCl_3$) of 5o

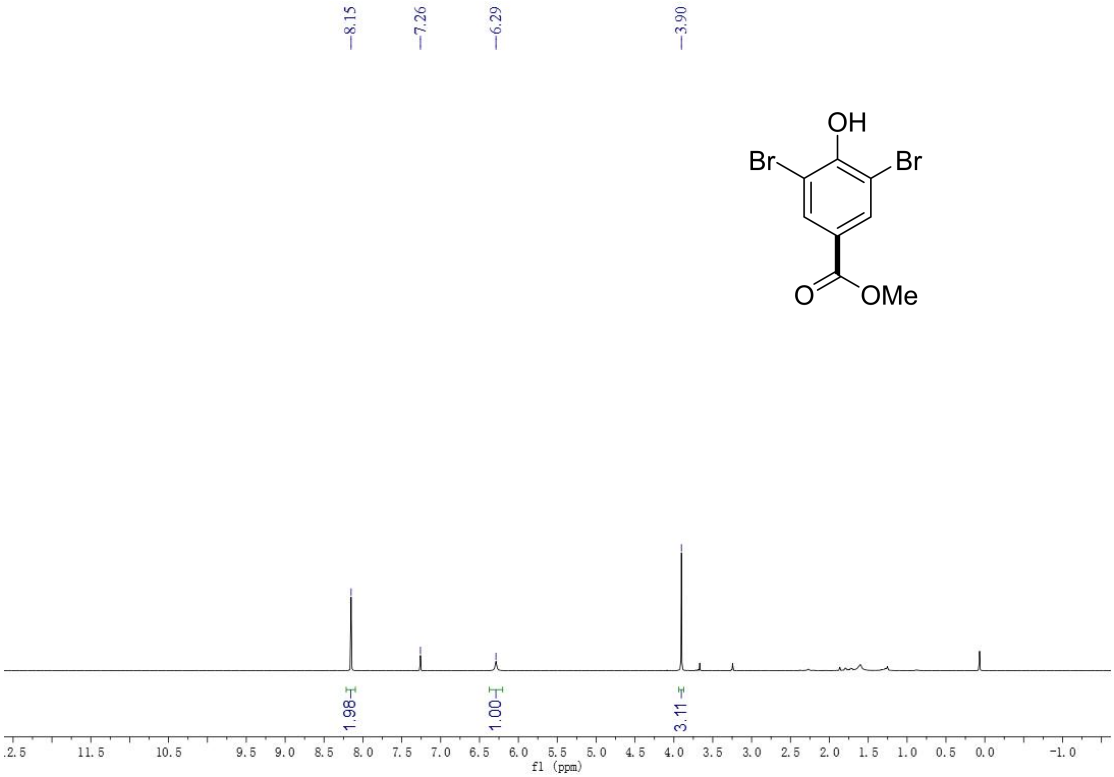

Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) of 5p

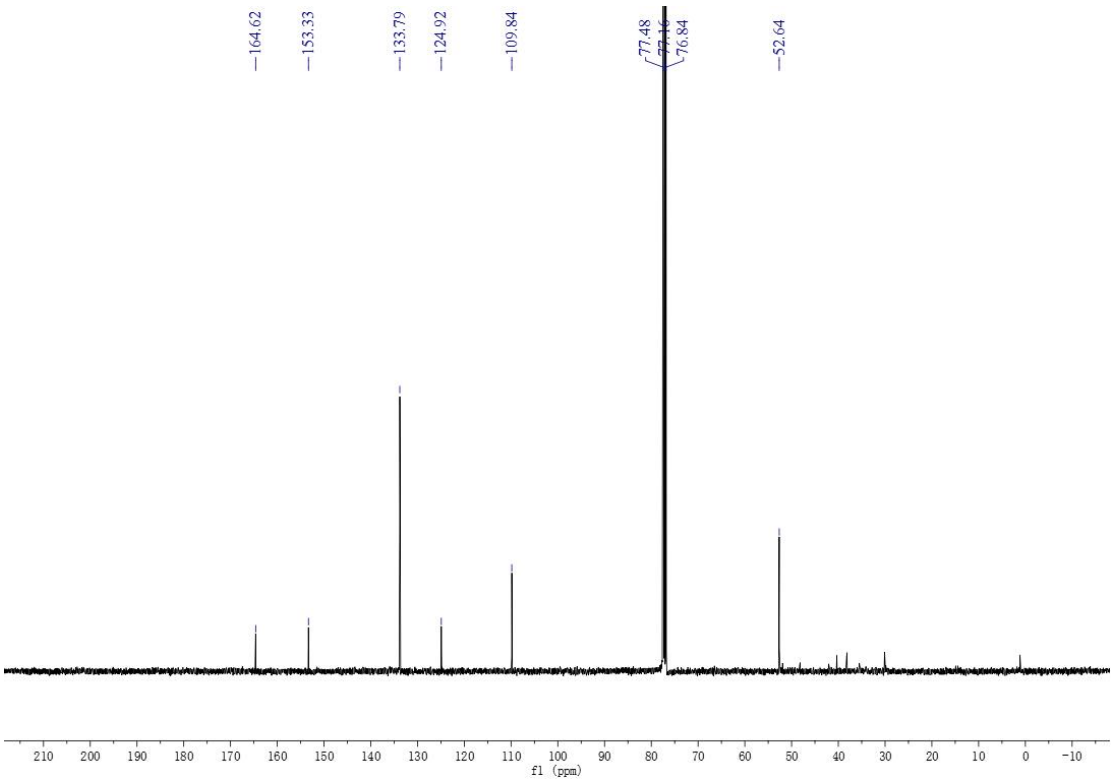

Figure S78. ^{13}C NMR (100 MHz, $CDCl_3$) of 5p

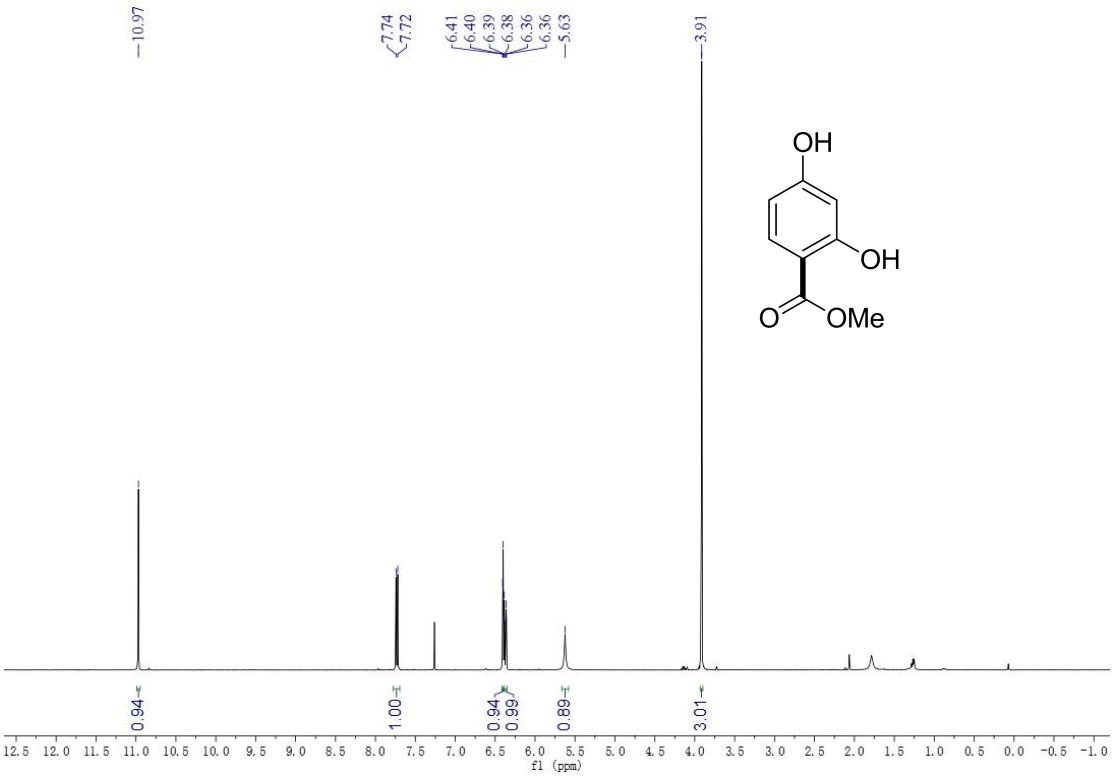

Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) of 7a

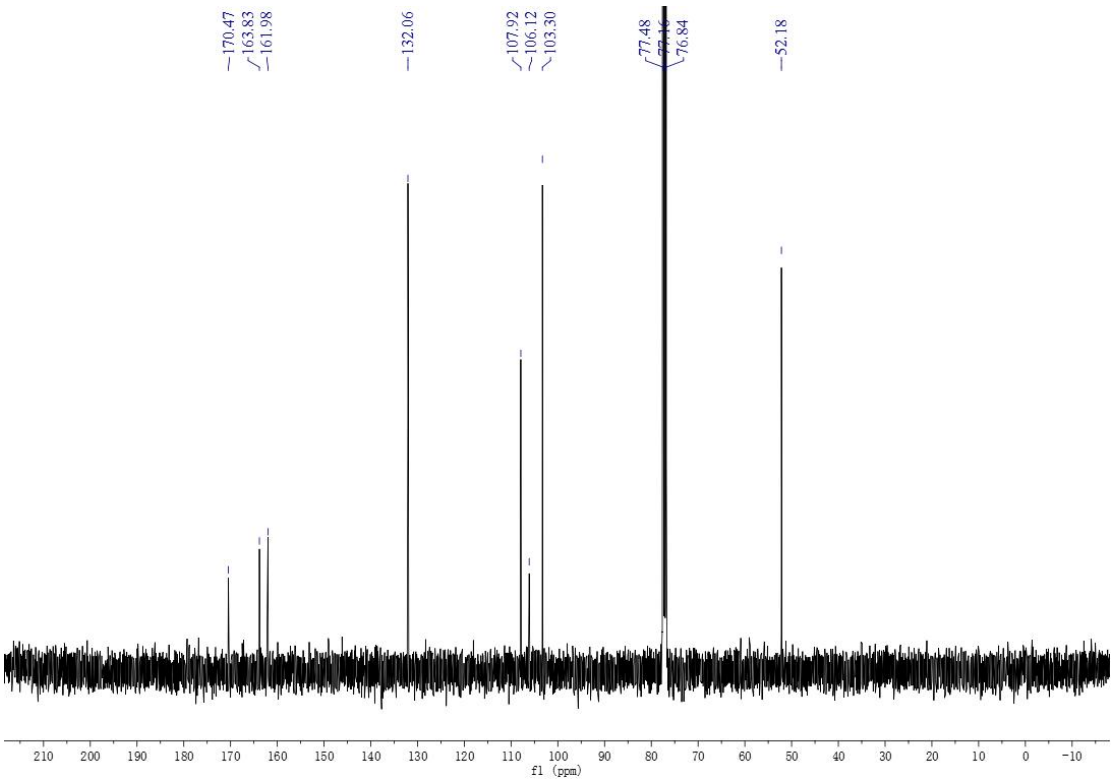

Figure S80. ^{13}C NMR (100 MHz, $CDCl_3$) of 7a

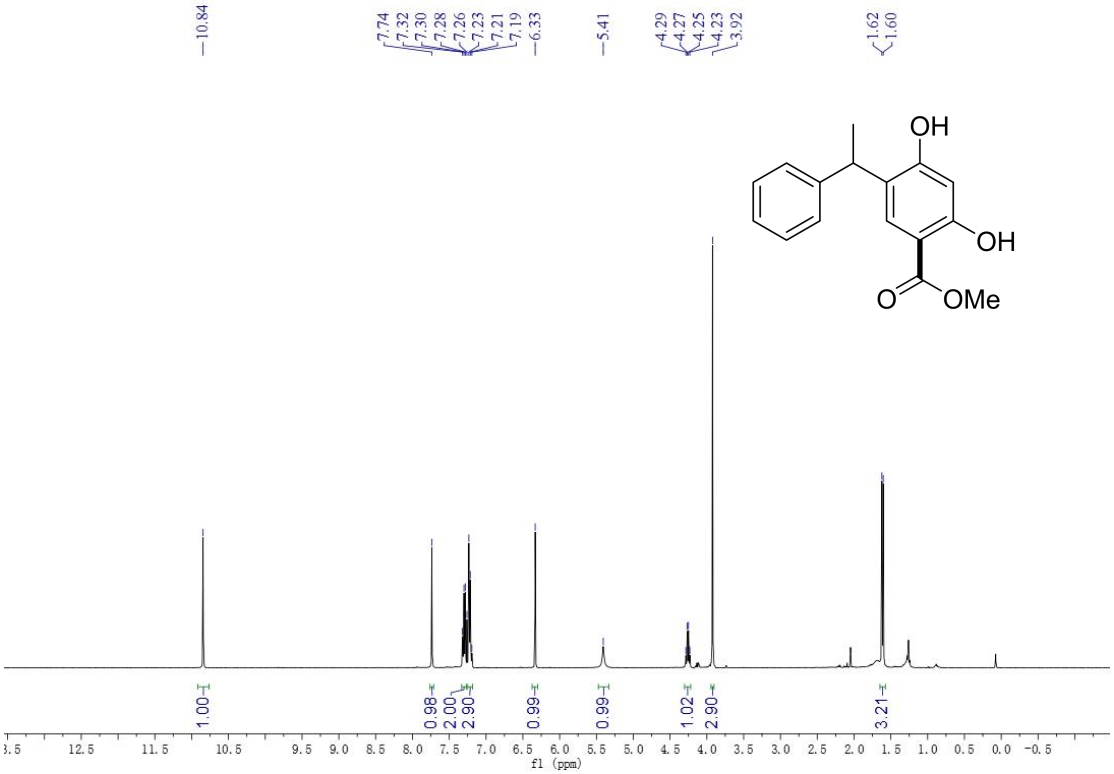

Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) of 7b

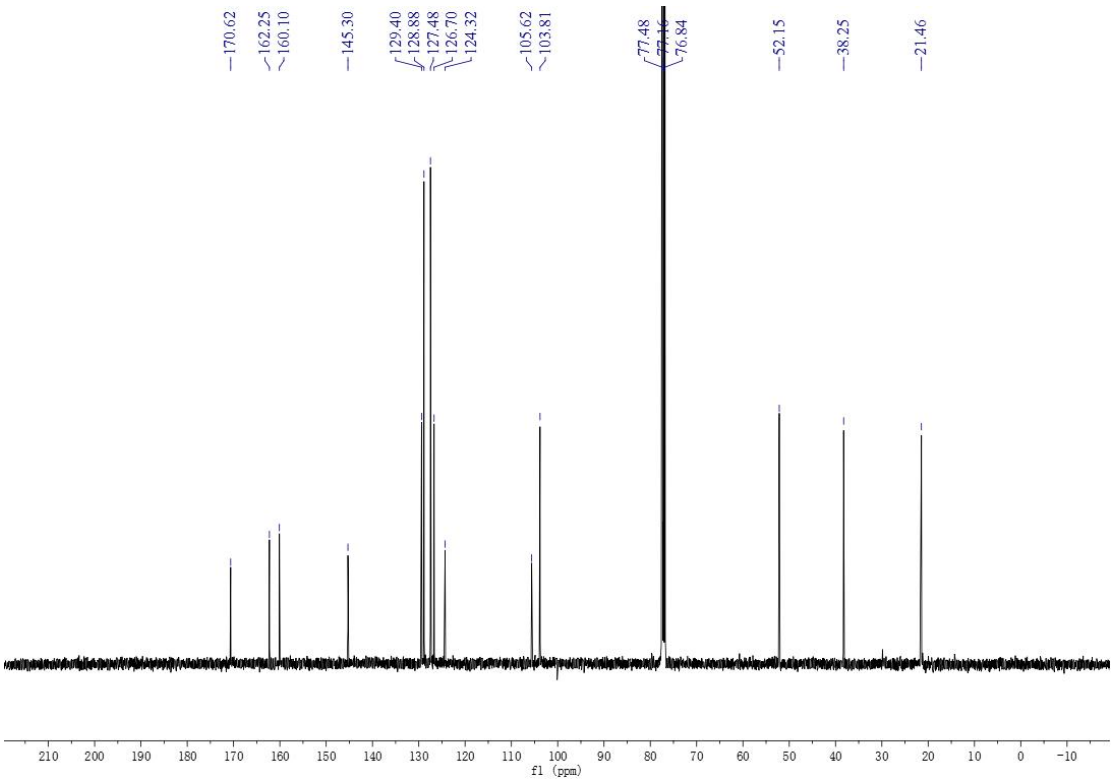

Figure S82. ^{13}C NMR (100 MHz, $CDCl_3$) of 7b

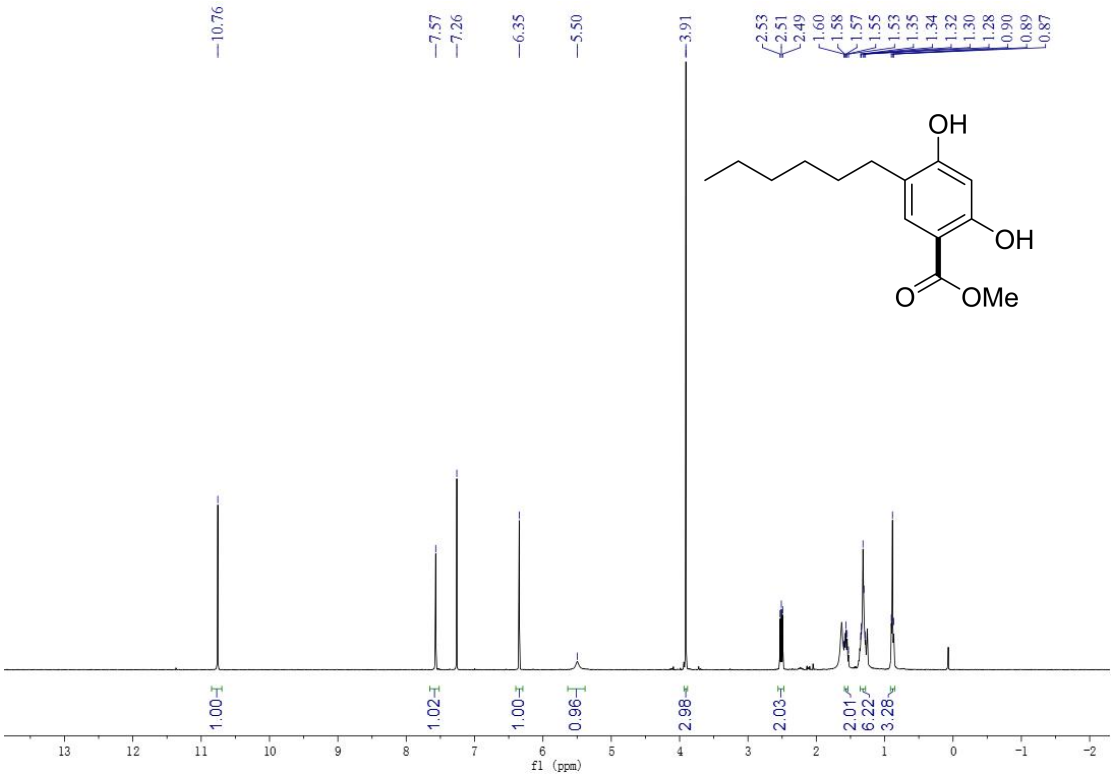

Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) of 7c

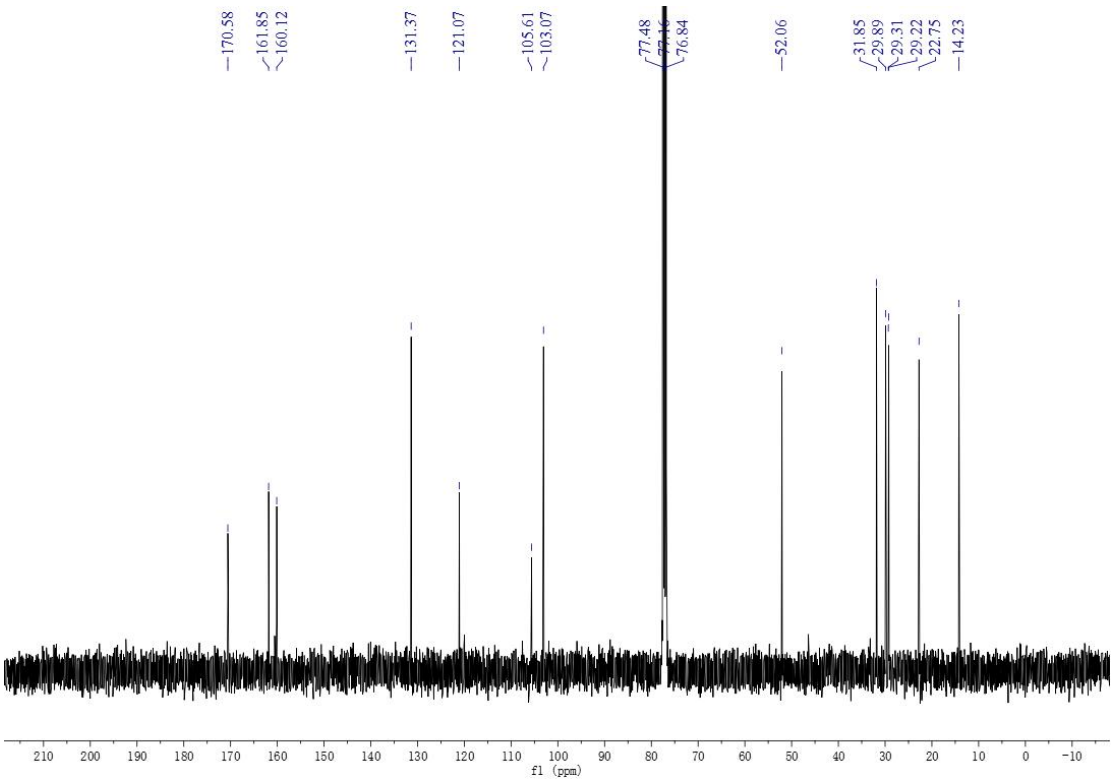

Figure S84. ^{13}C NMR (100 MHz, $CDCl_3$) of 7c

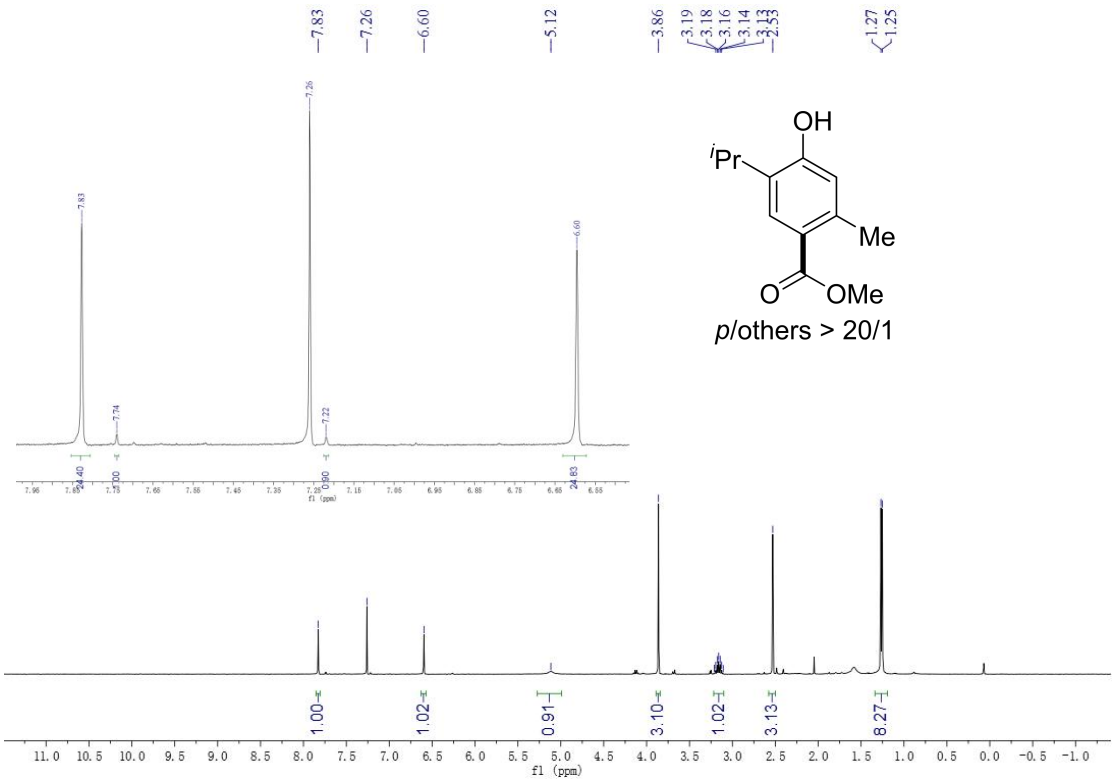

Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$) of 7d

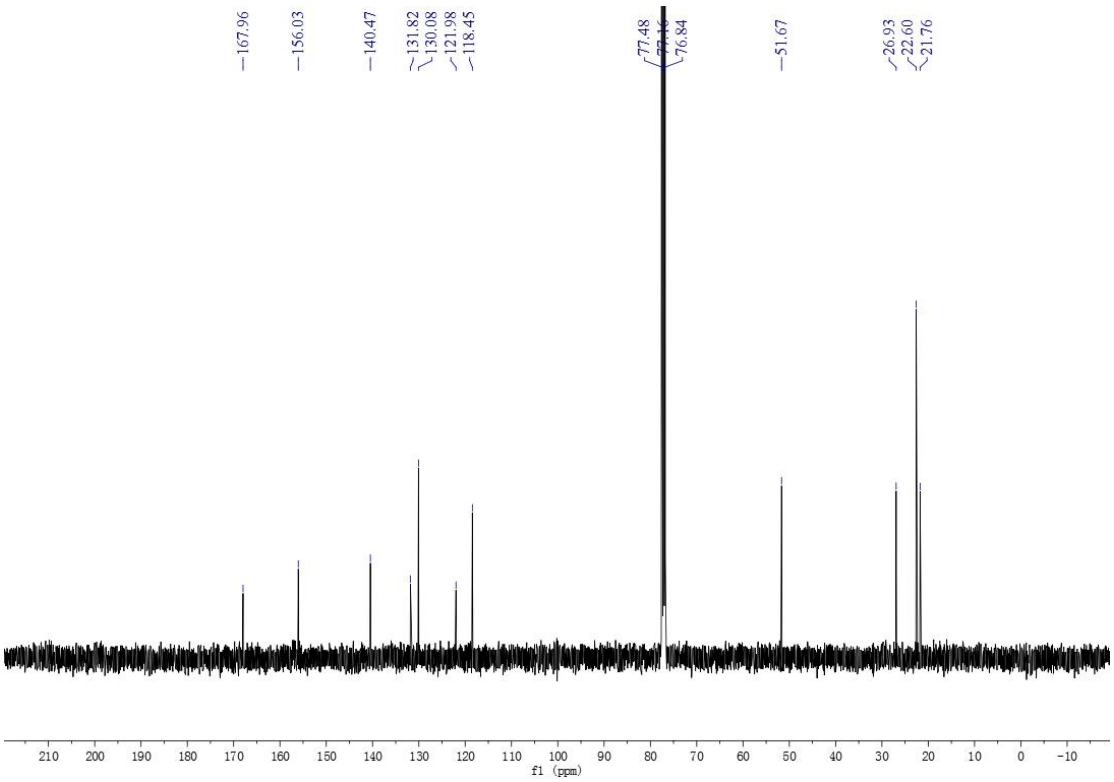

Figure S86. ^{13}C NMR (100 MHz, $CDCl_3$) of 7d

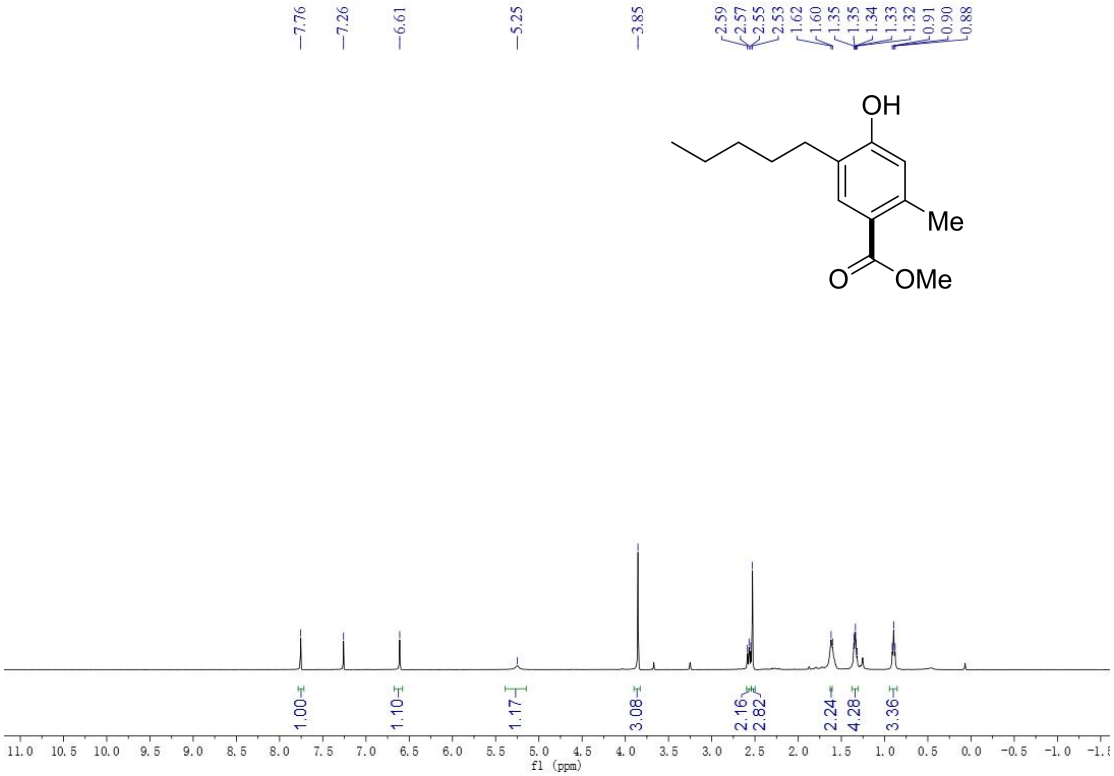

Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) of 7e

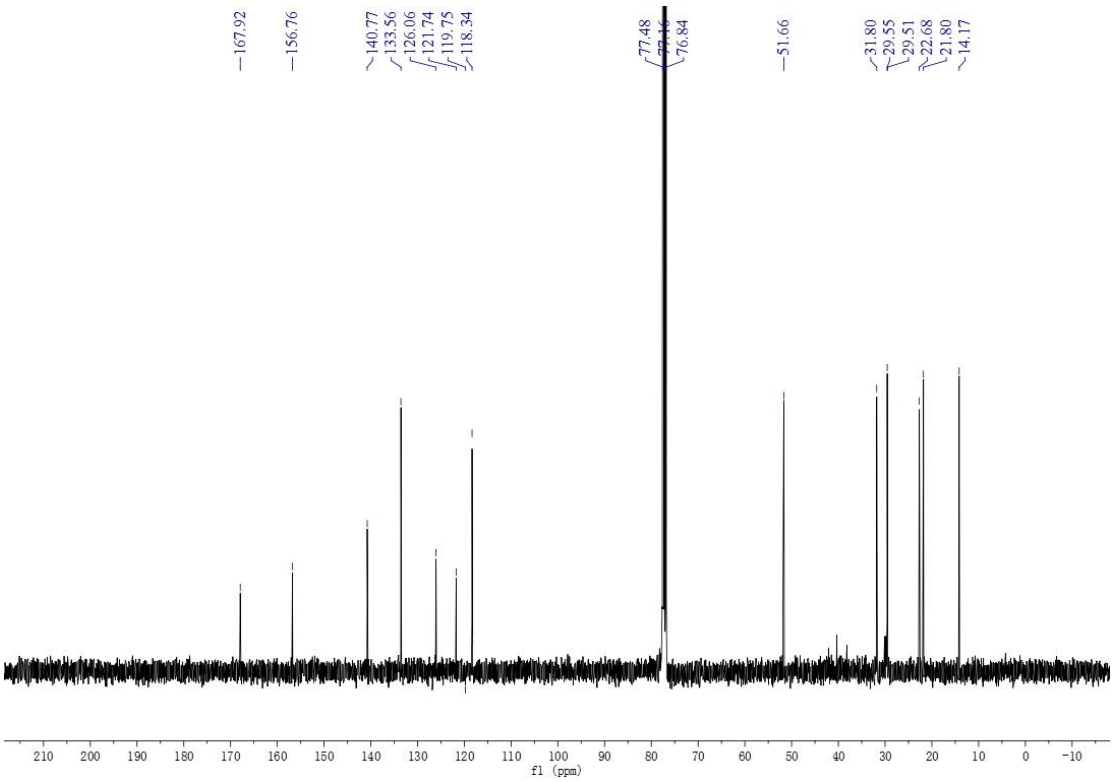

Figure S88. ^{13}C NMR (100 MHz, $CDCl_3$) of 7e

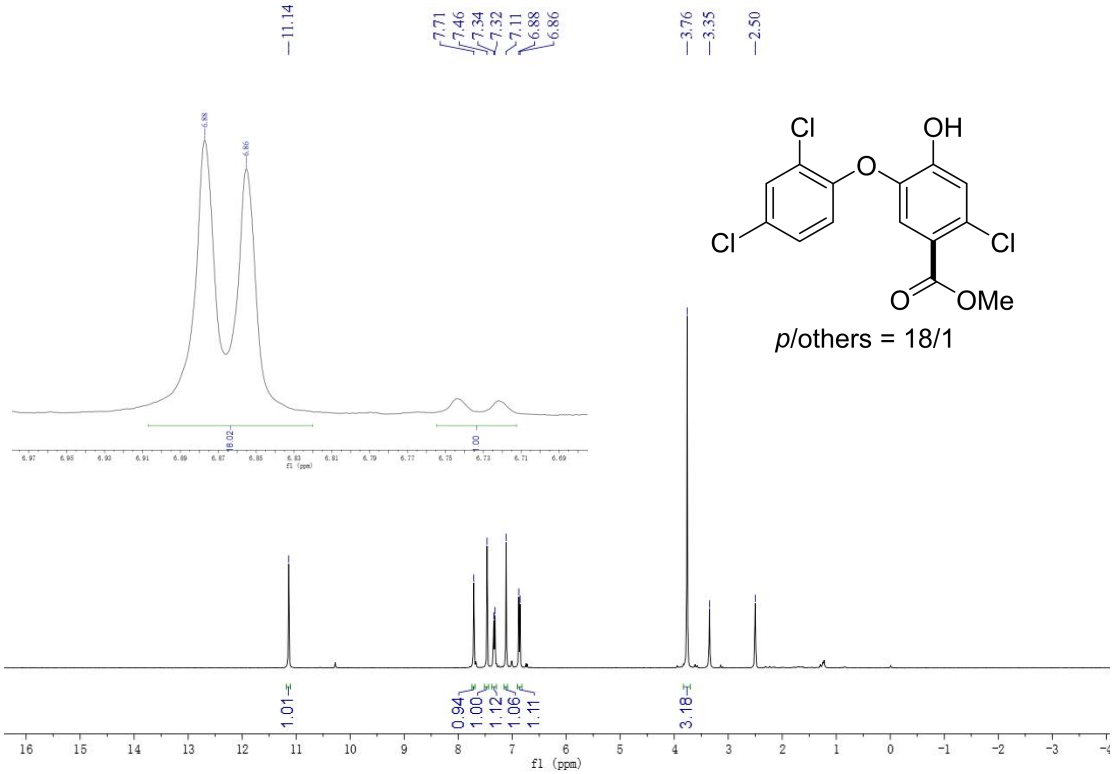

Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) of 7f

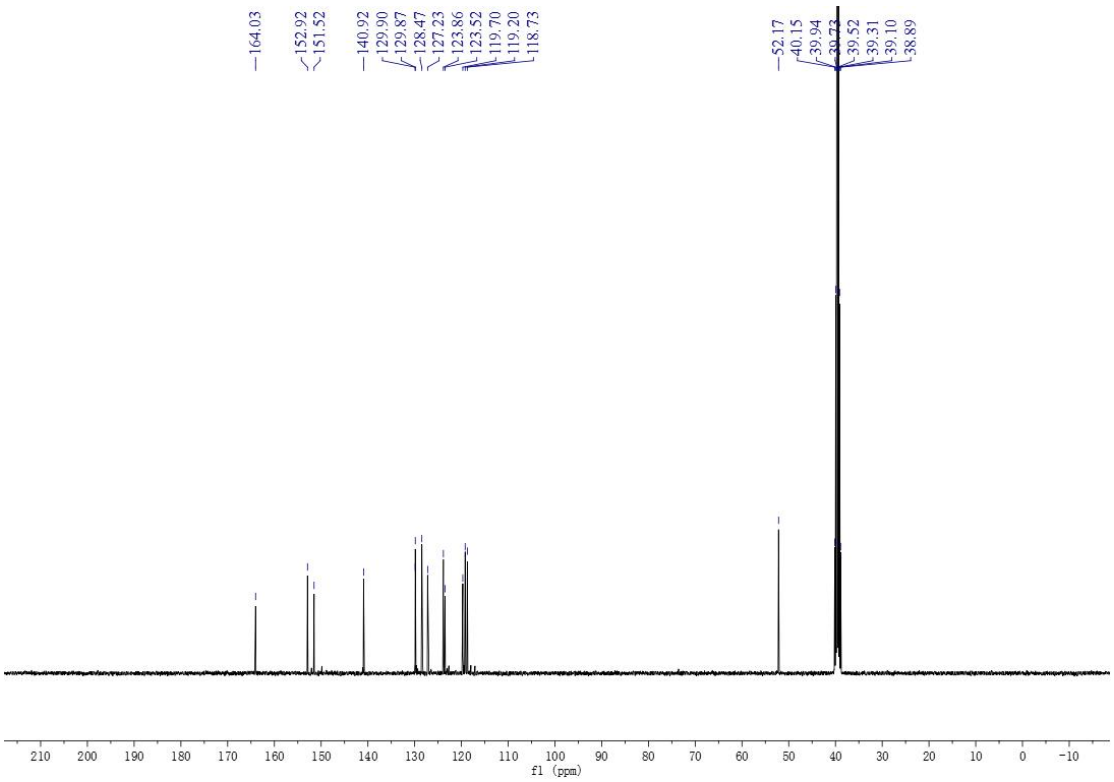

Figure S90. ^{13}C NMR (100 MHz, $CDCl_3$) of 7f

Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) of 7g

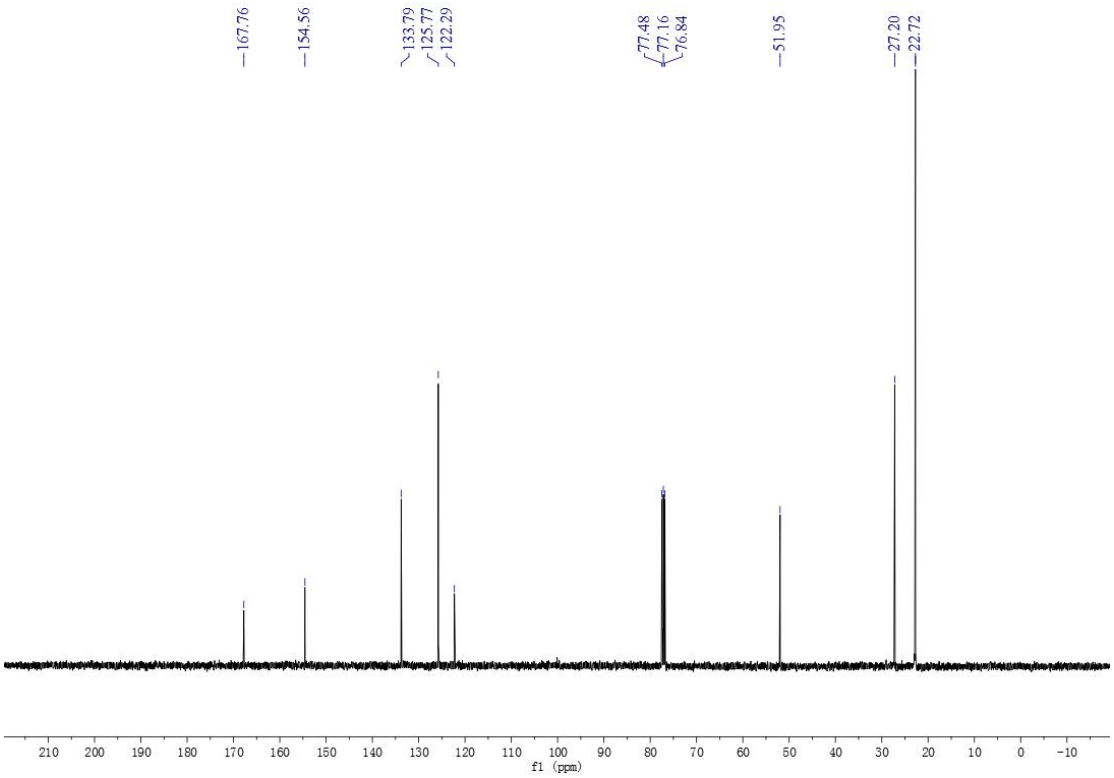

Figure S92. ^{13}C NMR (100 MHz, $CDCl_3$) of 7g

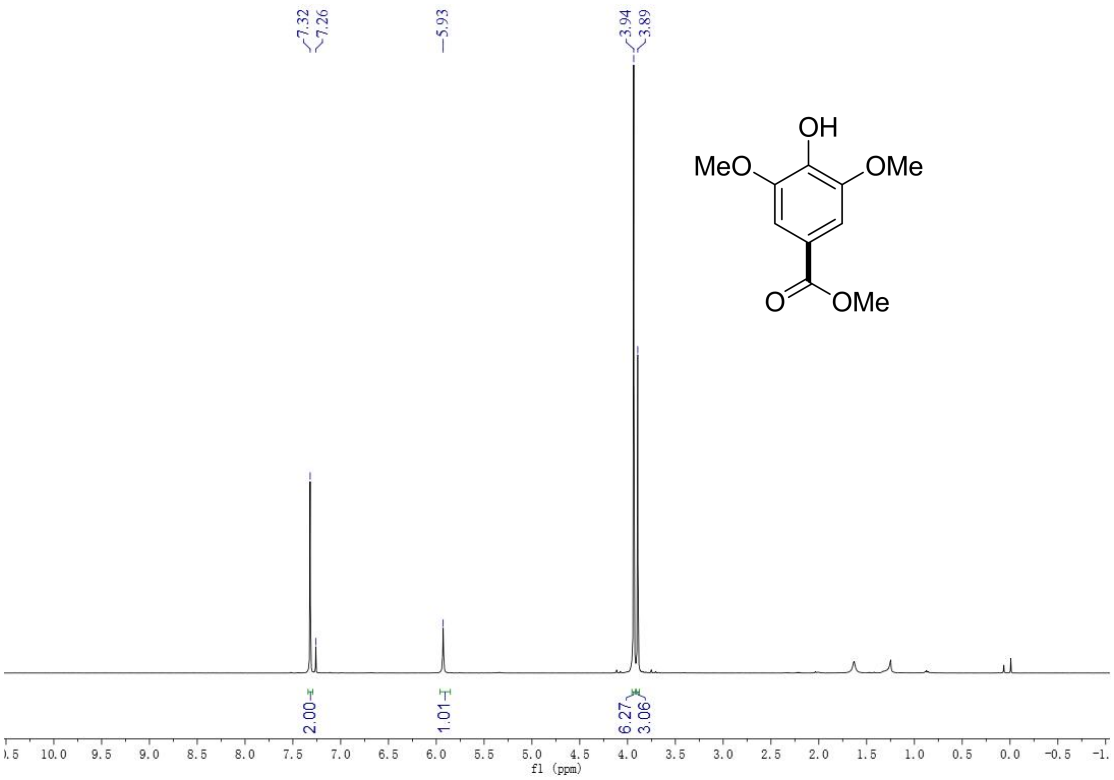

Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) of 7h

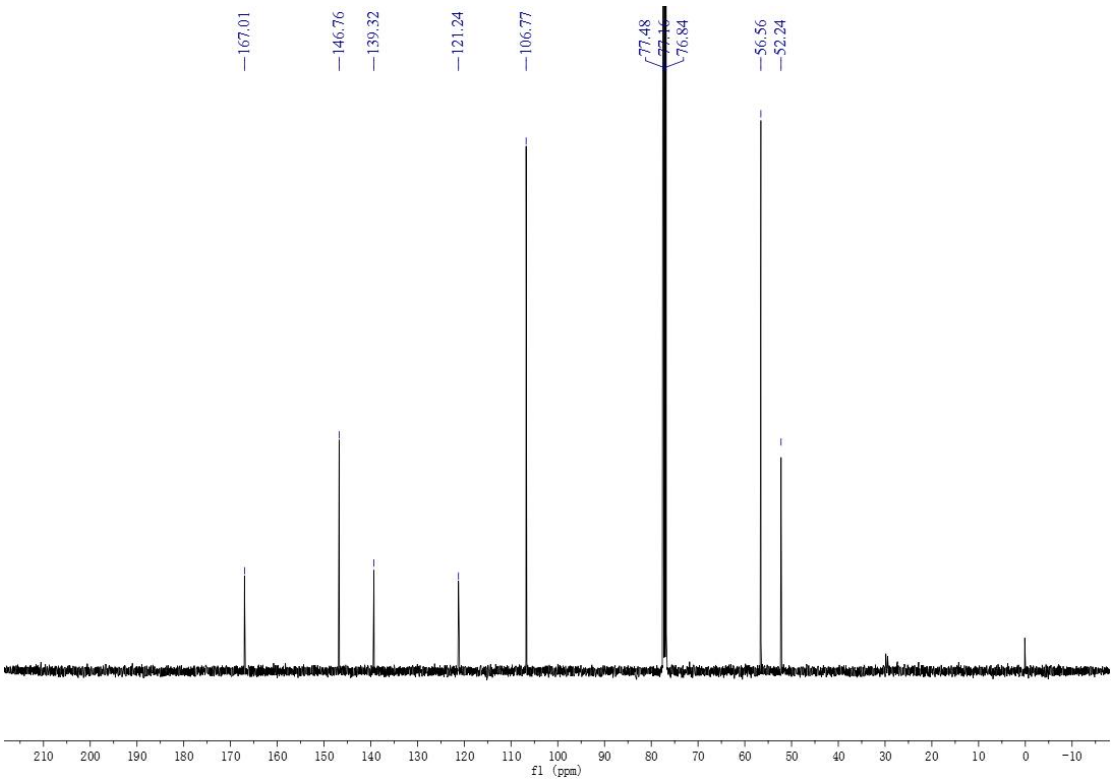

Figure S94. ^{13}C NMR (100 MHz, $CDCl_3$) of 7h

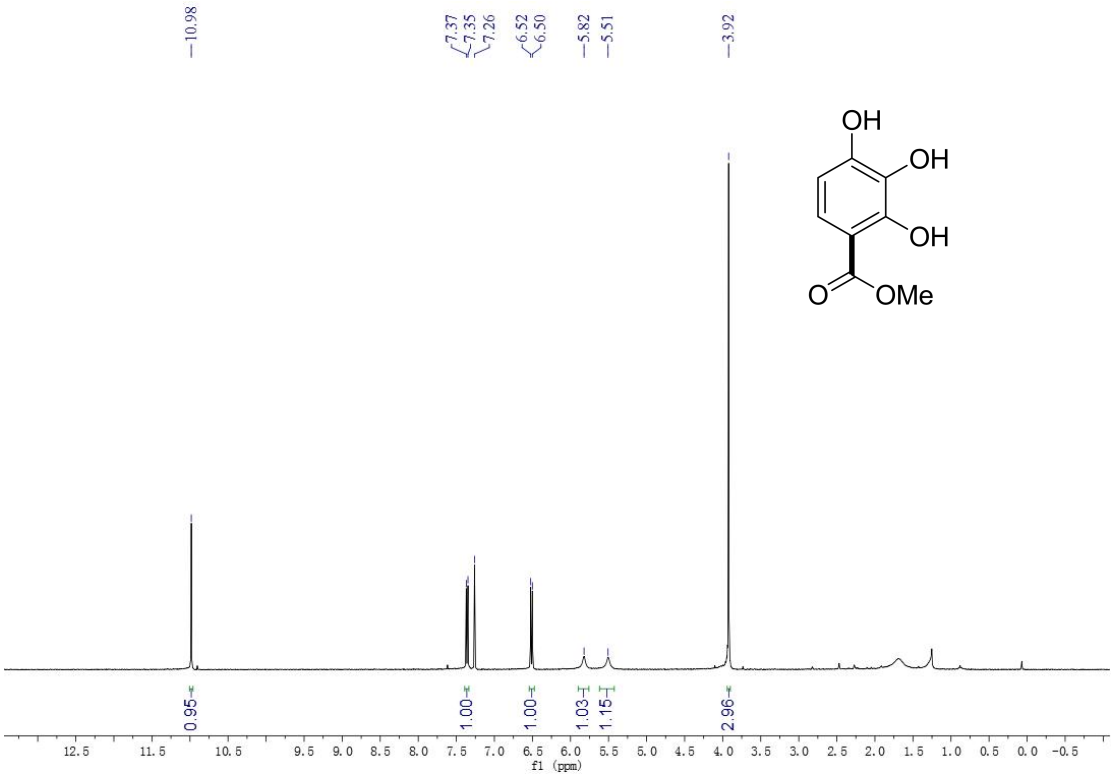

Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$) of 7i

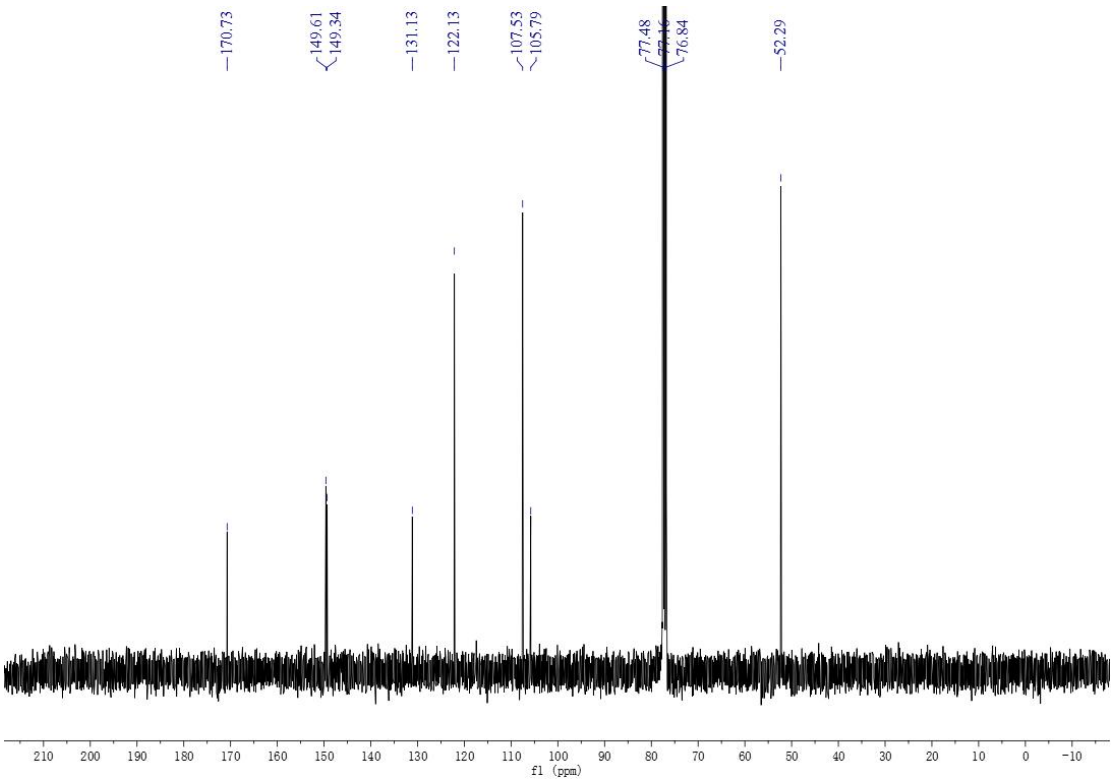

Figure S96. ^{13}C NMR (100 MHz, $CDCl_3$) of 7i

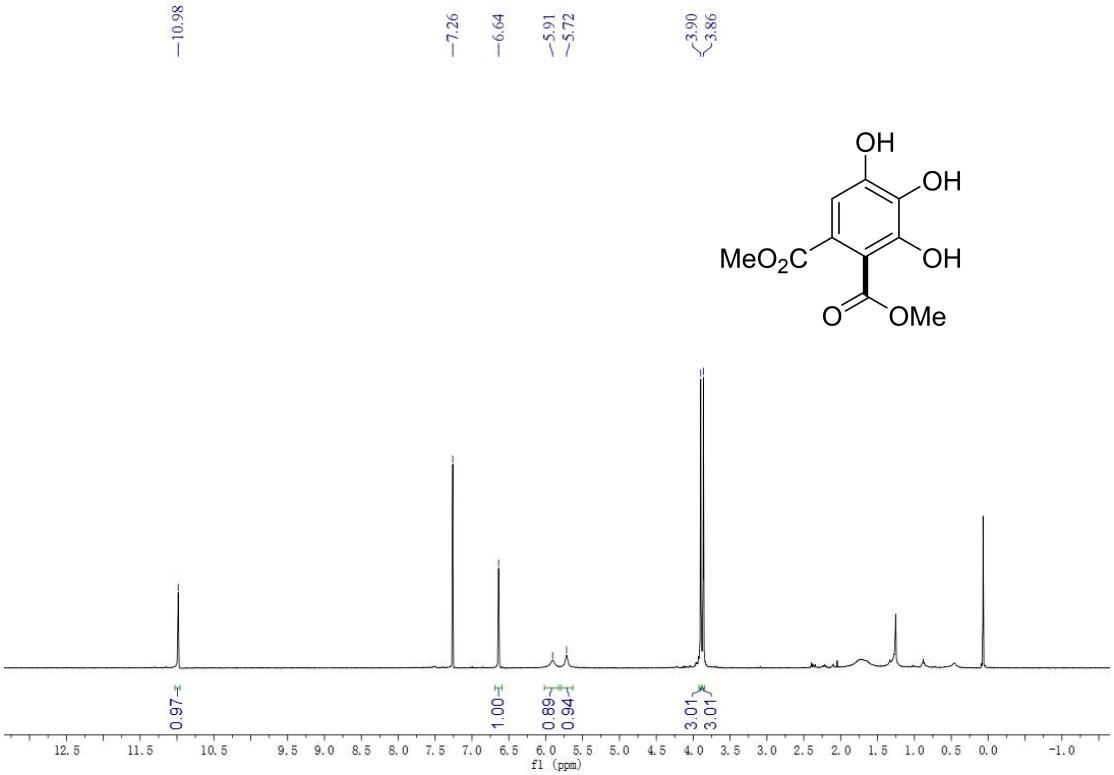

Figure S97. ^{1}H NMR (400 MHz, $CDCl_3$) of 7j

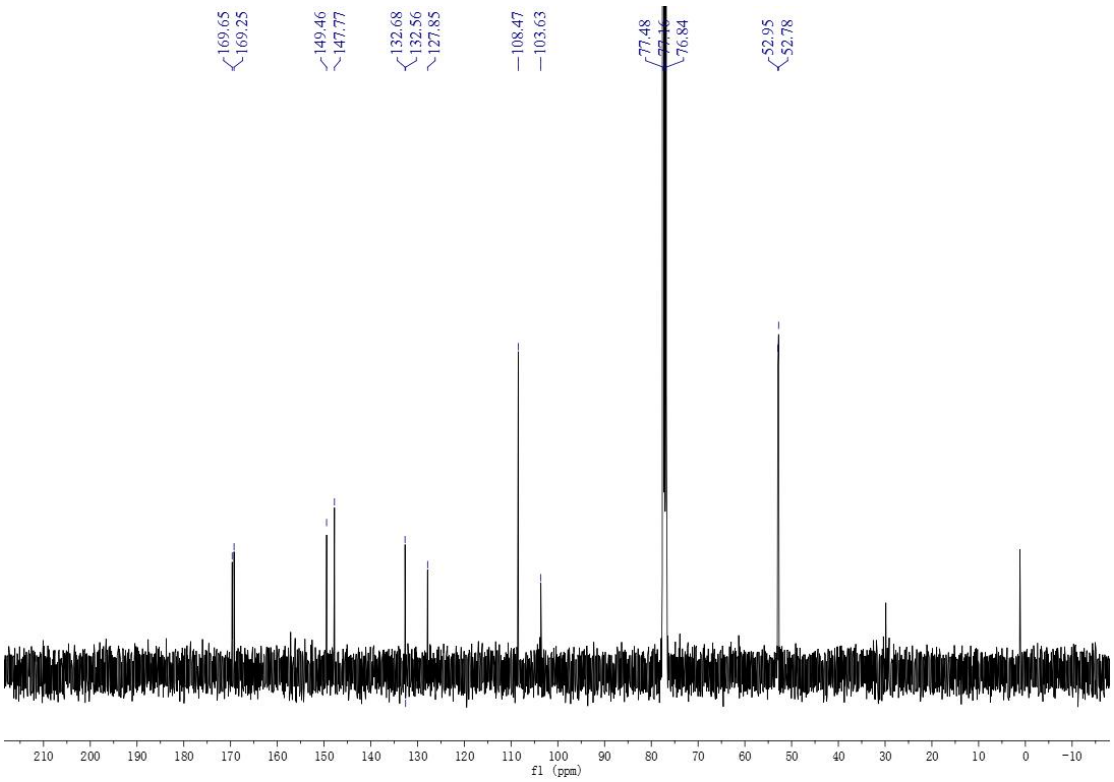

Figure S98. ^{13}C NMR (100 MHz, $CDCl_3$) of 7j