Electronic Supplementary Information

Visible-light-driven C(sp^2)-H arylation of phenols with arylbromides enabled by electron donor-acceptor excitation

Da-Liang Zhu,[a,b] Shan Jiang,[a] David James Young,[c] Qi Wu,[a] Hai-Yan Li,[a] and Hong-Xi Li*[a]

[a]College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China.

[b]School of Chemistry and Environmental Engineering, Analysis and Testing Centre, Yancheng Teachers University, Yancheng 224007, China.

[c]College of Engineering, IT and Environment, Charles Darwin University, Darwin, NT 0909, Australia.

Email: lihx@suda.edu.cn

Table of Contents

General information

Compounds **1** and **2** and all reagents were commercially available and used without further purification. All solvents were obtained from commercial sources and were purified according to standard procedures. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at ambient temperature on a Varian UNITY plus-400 spectrometer. High-performance liquid chromatography (HPLC) was conducted on a LC-20AT with MeOH and H_2O as the mobile phase. High resolution mass spectra (HRMS) were obtained with a MICRO TOF-Q III. Infrared (IR) spectra were recorded on a VERTEX 70+HYPERION 2000 (4000-500 cm^{-1}).

General procedure for *ortho*-arylation of phenols

A 10 mL test tube was equipped with aryl bromide (0.2 mmol, 1.0 equiv), phenol (0.8 mmol, 4.0 equiv), Cs_2CO_3 (130 mg, 0.4 mmol, 2 equiv) and 0.5 mL degassed, anhydrous dimethyl sulfoxide (DMSO). The reaction was stirred under a nitrogen atmosphere and irradiated with blue LEDs (the maximum power density = 0.12 $mW \cdot cm^{-2}$) for 14 h, with fan cooling. After this period, the reaction was diluted with 3 mL of water and extracted with ethyl acetate (3 × 3 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Pure product was obtained by thin-layer chromatography (TLC) using petroleum ether (PE) and ethyl acetate (EA) as the eluent.

Gram scale reaction under the irradiation of blue LEDs or natural sunlight

1-(4-Bromophenyl)ethan-1-one (1.18 g, 6 mmol, 1.0 equiv), phenol (2.26 g, 24 mmol, 8.0 equiv), and Cs_2CO_3 (3.90 g, 12 mmol, 2 equiv) were weighed into a dried 50 mL flask and degassed, anhydrous DMSO (15 mL) was added. The reaction was stirred under a nitrogen atmosphere and irradiated by blue LEDs or natural sunlight (the maximum power density = 6.57 $mW \cdot cm^{-2}$) for 48 h or 10 h, respectively. After this period, the reaction was diluted with 50 mL of water and extracted with ethyl acetate (3 × 50 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel using PE and EA as the eluent: 0.75 g, 59% yield (blue LEDs soft rope light) or 0.74 g, 58% yield (natural sunlight).

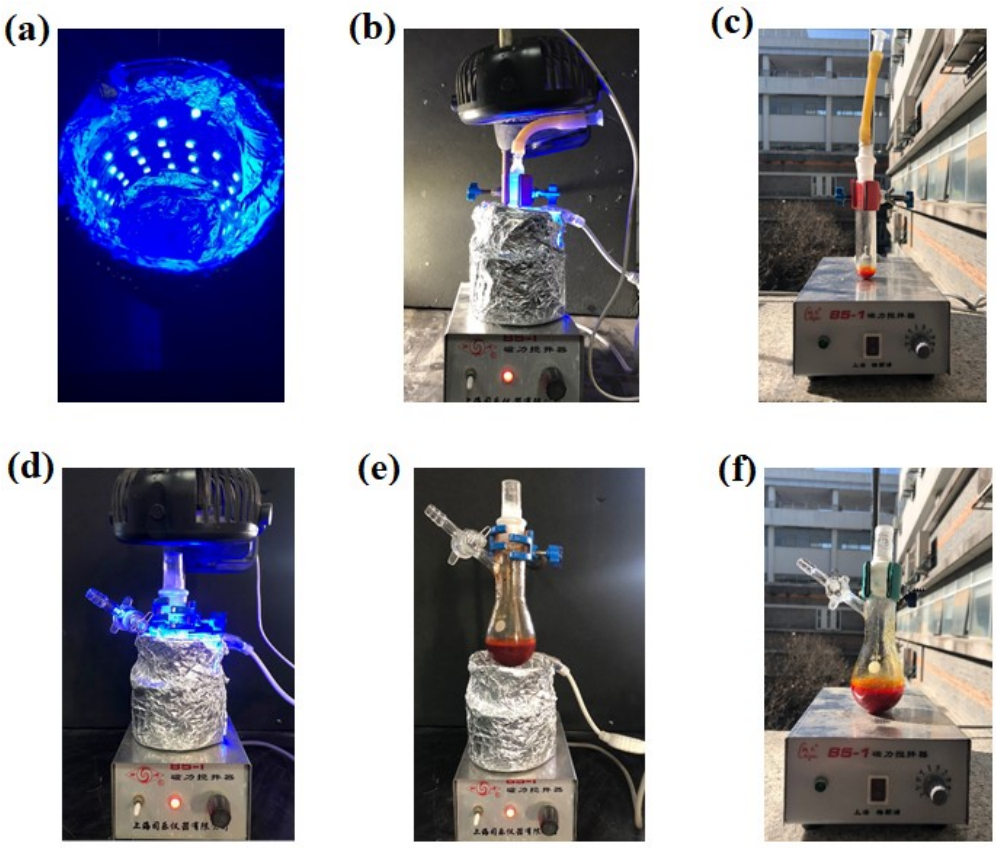


Figure S1. The reaction vessels (a, b, c) and gram scale reaction (d, e, f) with blue LEDs or natural sunlight irradiation.

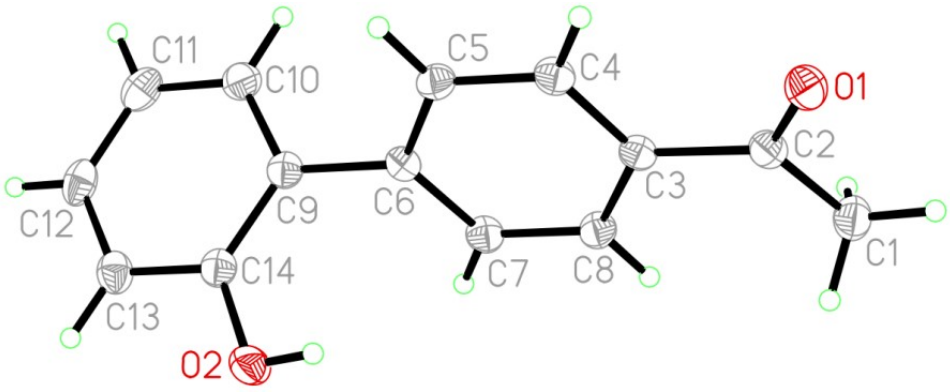
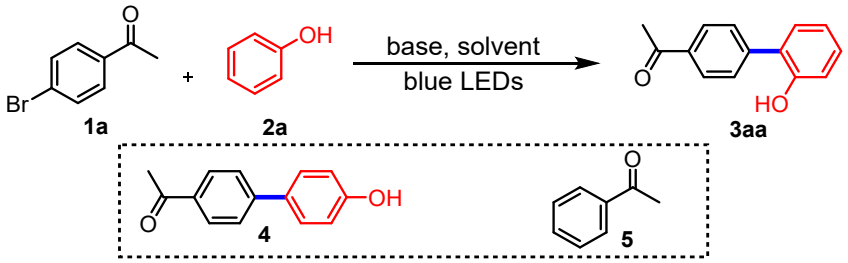


Figure S2. Molecular structure of **3aa** with 30% thermal probability ellipsoids.

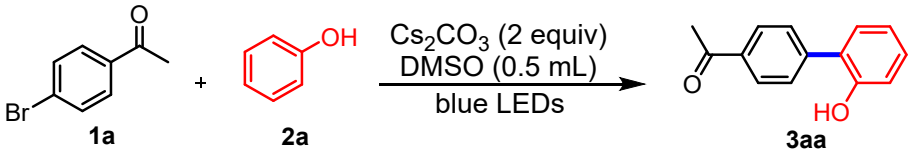
Table S1. Optimization of reaction conditions.[a]



Entry	**1a** (mmol)	**2a** (mmol)	Base (equiv)	Solvent (mL)	Yield (%)		
					3aa	**4**	**5**
1	0.2	0.8	Cs_2CO_3 (2)	DMSO (0.5)	61	10	10
2	0.2	0.8	Cs_2CO_3 (2)	DMF (0.5)	41	0	46
3	0.2	0.8	Cs_2CO_3 (2)	MeCN (0.5)	25	4	6
4	0.2	0.8	Cs_2CO_3 (2)	$CHCl_3$ (0.5)	0	0	0
5	0.2	0.4	K_2CO_3 (2)	DMSO (1)	22	7	19
6	0.2	0.4	K_3PO_4 (2)	DMSO (1)	27	6	19
7	0.2	0.4	CsF (2)	DMSO (1)	21	4	17
8	0.2	0.4	*t*-BuNH(*i*-Pr) (2)	DMSO (1)	0	0	0
9	0.2	0.4	Cs_2CO_3 (2)	DMSO (1)	40	9	14
10	0.2	0.8	-	DMSO (0.5)	0	0	0
11[b]	0.2	0.8	Cs_2CO_3 (2)	DMSO (0.5)	0	0	0
12[c]	0.2	0.8	Cs_2CO_3 (2)	DMSO (0.5)	55	11	6
13[d]	0.2	0.8	Cs_2CO_3 (2)	DMSO (0.5)	58	9	12
14[e]	0.2	0.8	Cs_2CO_3 (2)	DMSO (0.5)	26	0	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), Cs_2CO_3 (0.4 mmol), 0.5 mL DMSO, N_2, irradiation under blue LEDs for 14 h with fan cooling, HPLC yield. [b]In the dark. [c]Irradiation under a 300 W xenon lamp with a 420 nm cutoff filter for 5 h. [d]Under sunlight (the maximum power density was about 6.57 mW cm^{-2}) for 6 h. [e]The reaction was carried out in air.

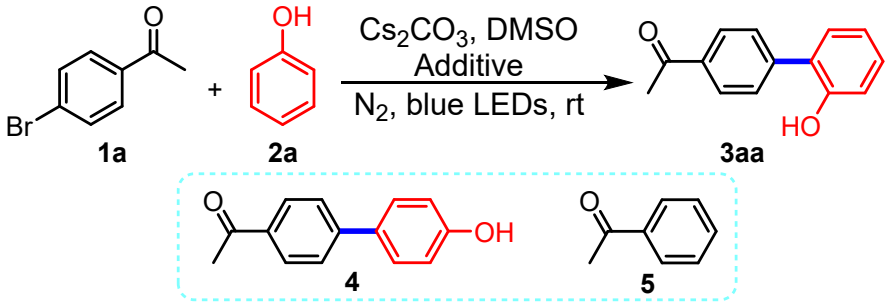
Table S2. Caesium carbonate purchased from different sources.[a]



Entry	Sources	Yield (%)
1	Energy Chemical (99.9%)	61
2	J&K (99%)	57
3	Damas-Beta (99.9%)	58
4	Aladdin (99.9%)	60
5	Alfa Aesar (>99.994%)	59

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), Cs_2CO_3 (0.4 mmol), 0.5 mL DMSO, N_2, irradiation under blue LEDs for 14 h with fan cooling, HPLC yield.

Table S3. Control experiments in the presence of transition metal ions.[a]



Entry	Additive (2 mol %)	Yield (%)		
		3aa	**4**	**5**
1	$FeSO_4$	56	11	10
2	$CoCl_2$	58	11	10
3	$NiBr_2$	55	10	8
4	$Pd(OAc)_2$	36	7	6

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), Cs_2CO_3 (0.4 mmol), Additive (2 mol %), 0.5 mL DMSO, N_2, irradiation under blue LEDs for 14 h with fan cooling, HPLC yield.

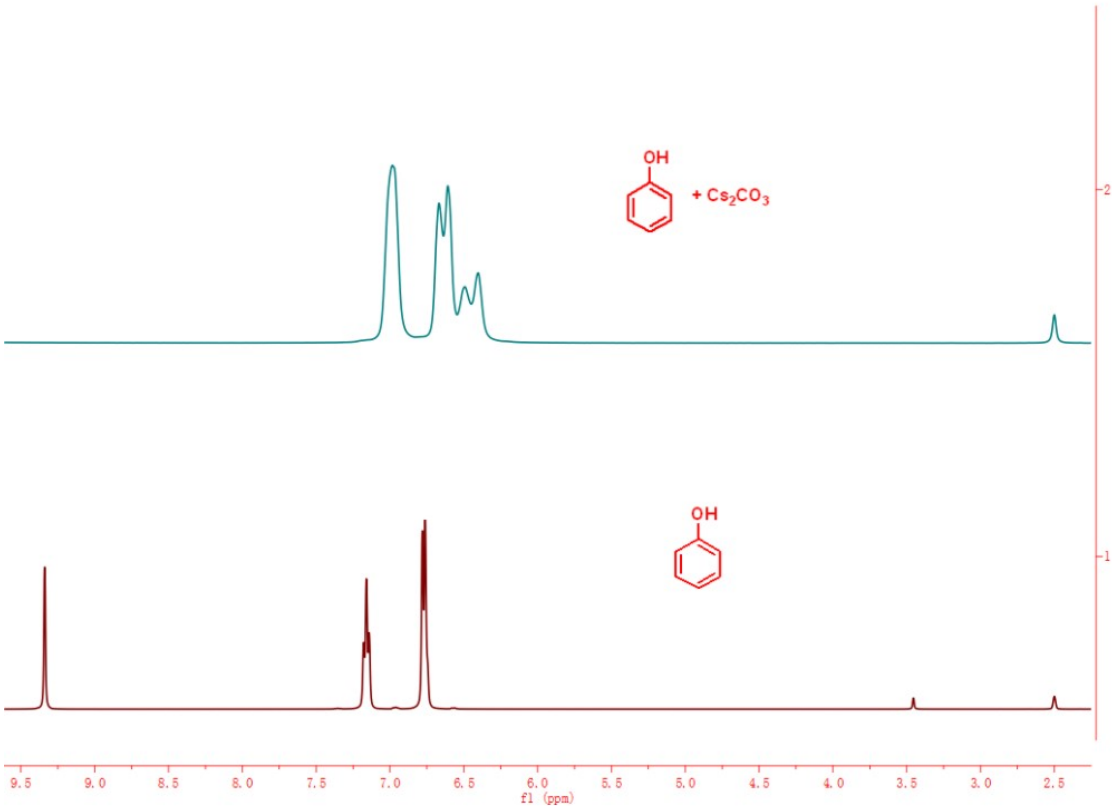


Figure S3. Comparison of ^{1}H NMR spectra of **2a** and the phenolate anion in d_6-DMSO

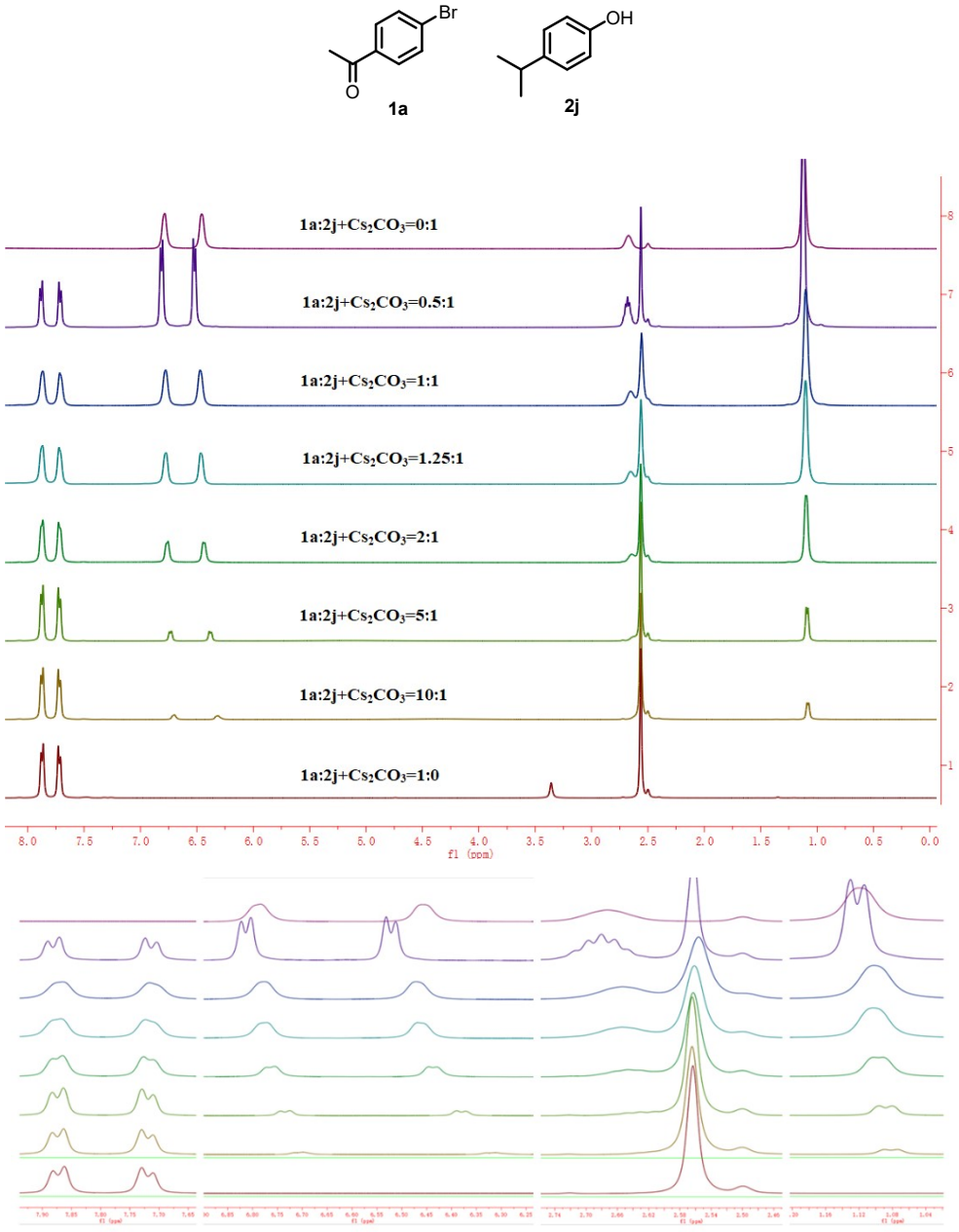


Figure S4. The ^{1}H NMR titration between **1a** and **2j** in d_6-DMSO.

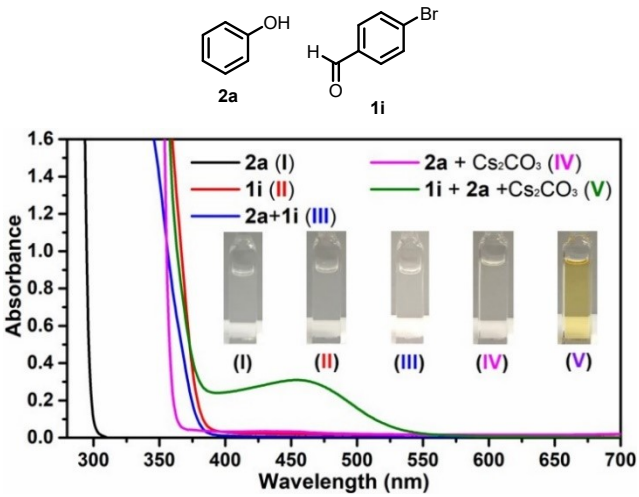


Figure S5. UV/Vis absorption spectra of DMSO solutions (0.1 M) of **2a** (I), **1i** (II), mixture of **2a** and **1i** (III), mixture of **2a** and Cs_2CO_3 (IV), and mixture of **2a**, **1i** and Cs_2CO_3 (V).

Stoichiometry of the EDA complex in solution

The stoichiometry of the EDA complex formed between 4-bromobenzaldehyde (**1i**) and phenol (**2a**) in DMSO with excess Cs_2CO_3 was measured using the Job's plot method.[S1] The Job's plot was recorded by measuring the absorption at 525 nm of different ratios of **1i** and **2a** in DMSO with excess Cs_2CO_3, and the total concentration of the two components remained constant at 0.1 M. The maximum absorbance was observed at 50% molar fraction, suggesting that the stoichiometry of the EDA complex is 1:1.

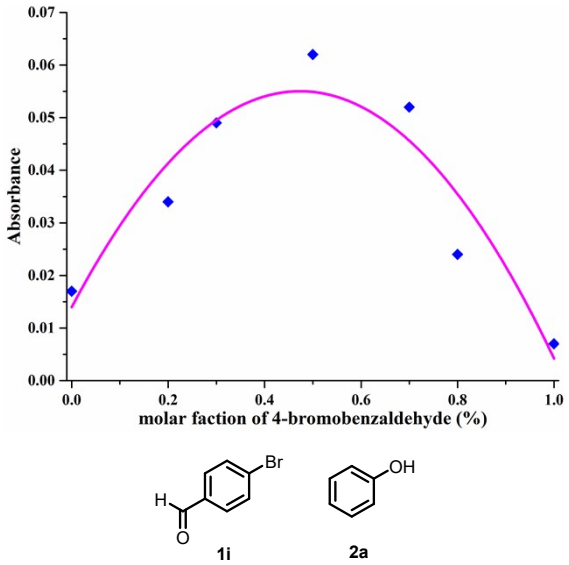


Figure S6. Job's plot for ratio between **1i** and **2a** in DMSO with excess Cs_2CO_3 with UV/vis absorption spectrometry.

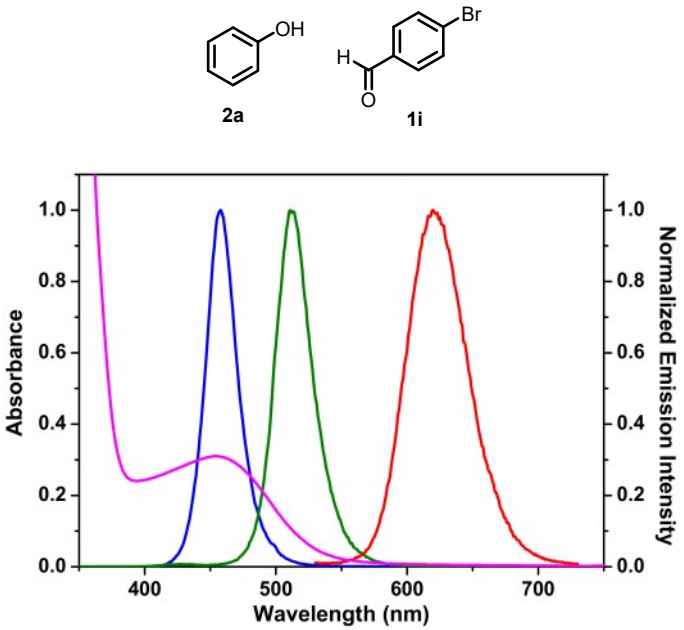


Figure S7. The absorption spectrum of the solution of **1i**, **2a** and Cs_2CO_3 in DMSO (0.1 M) (pink line) under N_2 and the emission spectra of blue LEDs (blue line), green LEDs (green line) and red LEDs (red line).

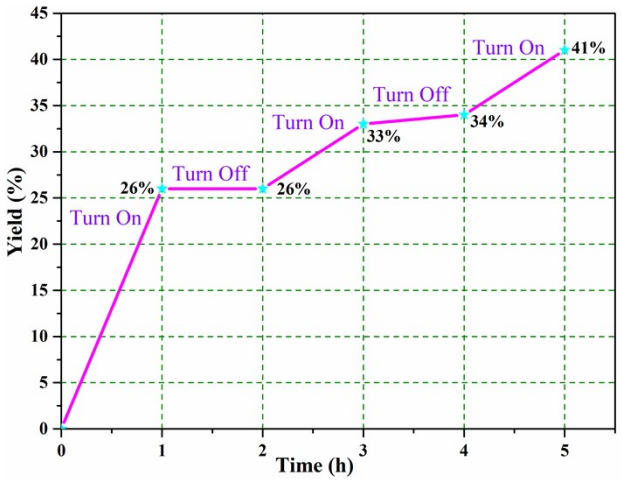
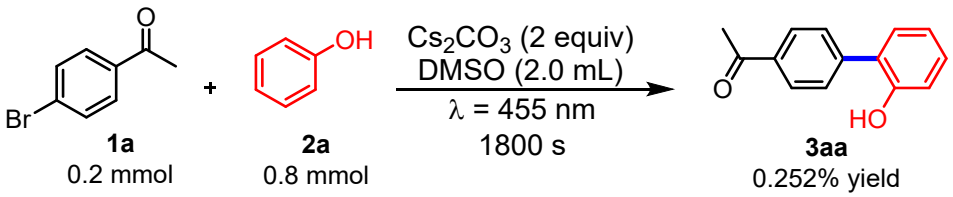


Figure S8. The light on/off experiments.

Determination of quantum yield[S2]

Under the optimized reaction conditions, the yield of **3aa** reached 47% when the volume of the solvent was changed to 2 mL, because the measurement of quantum yield cannot be performed when the volume of the DMSO was 0.5 mL. Therefore, we used the 2 mL of DMSO to measure the quantum yield of the catalytic system.



1a 0.2 mmol + **2a** 0.8 mmol → **3aa** 0.252% yield

A cuvette was equipped with **1a** (0.2 mmol, 1.0 equiv), **2a** (0.8 mmol, 4.0 equiv), Cs_2CO_3 (130 mg, 0.4 mmol, 2 equiv) and 2.0 mL degassed, anhydrous DMSO. The reaction was irradiated (λ = 455 nm, 0.14 $mW \cdot cm^{-2}$) for 1800 s. After that, the yield of product was determined by HPLC. The quantum yield was determined as follows:

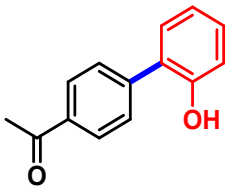
ϕ = Mole number for product/Mole number for absorption of photons = 0.654

$$\phi = \frac{nN_A/t}{fP\lambda/hc}$$

n: the mole number of the product **3aa**; t: reaction time (1800 s); N_A: 6.02×10^{23}/mol; f: $1\text{-}10^{-A}$ (455 nm, A = 0.708); P: P = E*S (E: illumination intensity, E = 0.14 mW/cm^2; S: the area of irradiation S = 1 cm^2); λ: wavelength (λ = 4.55×10^{-7} m); h: planck constant (h = 6.626×10^{-34} J*s); c: velocity of light (c = 3×10^8 m/s).

NMR data of products

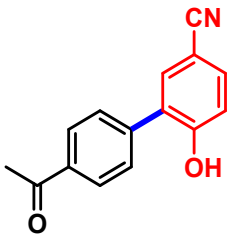
1-(2'-hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (3aa)[S3]



The general procedure was followed using1-(4-bromophenyl)ethan-1-one (0.2 mmol) and phenol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3aa** (25.0 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.06 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.24 (m, 2H), 7.09 – 6.94 (m, 2H), 5.40 (s, 1H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.0, 152.7, 142.7, 136.3, 130.5, 130.0, 129.6, 129.2, 127.4, 121.4, 116.5, 26.9. m.p. = 146.3-146.2 °C. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{12}O_2Na^+$ 235.0730; Found 235.0703.

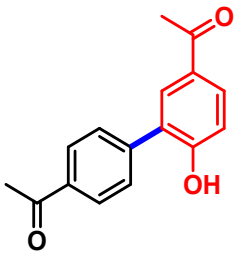
4'-acetyl-6-hydroxy-[1,1'-biphenyl]-3-carbonitrile (3ab)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-hydroxybenzonitrile (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ab** (33.7 mg, 71%).

^{1}H NMR (400 MHz, d_6-DMSO, ppm) δ = 11.00 (s, 1H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.79 (s, 1H), 7.70 (dd, *J* = 16.7, 8.0 Hz, 3H), 7.11 (d, *J* = 8.4 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO, ppm) δ = 197.6, 158.8, 141.1, 135.6, 134.6, 133.7, 129.4, 128.0, 127.9, 119.3, 117.1, 101.8, 26.8. m.p. = 180.9-181.5 °C. IR (ATR, cm^{-1}): 3386, 2977, 2922, 2225, 1662, 1599, 1557, 1508, 1496, 1420, 1395, 1347, 1298, 1279, 1175, 1134, 1113, 957, 847, 825, 776, 738, 718, 675, 603. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{11}NO_2Na^+$ 260.0682; Found 260.0670.

1,1'-(6-hydroxy-[1,1'-biphenyl]-3,4'-diyl)bis(ethan-1-one) (3ac)

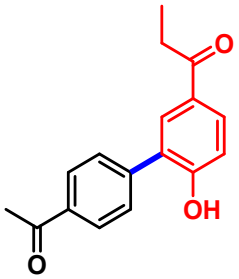


The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 1-(4-

hydroxyphenyl)ethan-1-one (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ac** (34.5 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.05 (d, *J* = 7.8 Hz, 2H), 7.98 – 7.87 (m, 2H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 2.64 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.2, 197.2, 157.5, 141.8, 136.6, 131.6, 130.8, 130.7, 129.7, 129.2, 127.5, 116.5, 26.9, 26.6. m.p. = 132.3-132.9 °C. IR (ATR, cm^{-1}): 3400, 2964, 2923, 1679, 1651, 1573, 1509, 1462, 1398, 1356, 1314, 1277, 1241, 1186, 1144, 1082, 1049, 959, 838, 818, 768, 734, 711, 666, 619, 593. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{14}O_3Na^+$ 277.0835; Found 277.0826.

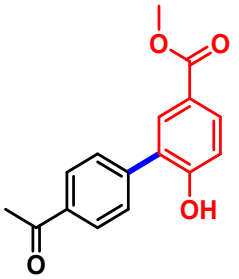
1-(4'-acetyl-6-hydroxy-[1,1'-biphenyl]-3-yl)propan-1-one (3ad)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 1-(4-hydroxyphenyl)propan-1-one (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ad** (35.9 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.04 (d, *J* = 8.0 Hz, 2H), 7.95 (s, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.99 (s, 1H), 2.99 (q, *J* = 7.2 Hz, 2H), 2.64 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 200.2, 198.5, 157.6, 142.1, 136.3, 131.3, 130.4, 130.3, 129.7, 129.1, 127.5, 116.5, 31.7, 26.9, 8.7. m.p. = 110.3-110.9 °C. IR (ATR, cm^{-1}): 3351, 2974, 2937, 2905, 1664, 1588, 1515, 1460, 1427, 1401, 1343, 1288, 1271, 1195, 1145, 1086, 1051, 1010, 966, 856, 836, 796, 751, 680, 641, 604. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{16}O_3Na^+$ 291.0992; Found 291.0978.

methyl 4'-acetyl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (3ae)

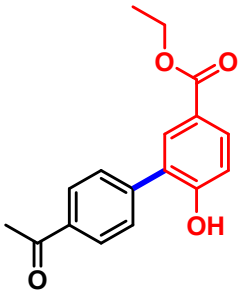


The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and methyl 4-hydroxybenzoate (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the yellowish solid **3ae** (37.8 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.06 (d, *J* = 7.6 Hz, 2H), 8.01 (s, 1H), 7.97 (d, *J* = 8.4 Hz,

1H), 7.64 (d, J = 7.4 Hz, 2H), 7.04 (d, J = 8.3 Hz, 1H), 6.45 (s, 1H), 3.91 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.3, 167.0, 157.1, 141.8, 136.5, 132.6, 131.7, 129.6, 129.2, 127.3, 123.2, 116.5, 52.3, 26.9. m.p. = 147.1-147.8 °C. IR (ATR, cm^{-1}): 3332, 2957, 2918, 2848, 1691, 1679, 1602, 1495, 1451, 1427, 1397, 1358, 1318, 1308, 1272, 1254, 1190, 1142, 1119, 1079, 1026, 959, 908, 875, 839, 823, 806, 766, 745, 722, 697, 640, 599. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{14}O_4Na^+$ 293.0784; Found 293.0779.

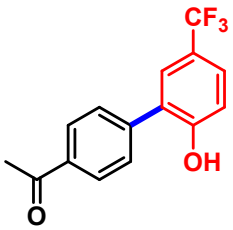
ethyl 4'-acetyl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (3af)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and ethyl 4-hydroxybenzoate (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3af** (41.5 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.02 (d, J = 9.0 Hz, 3H), 7.95 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 7.7 Hz, 2H), 7.06 (s, 1H), 7.04 (d, J = 8.2 Hz, 1H), 4.36 (q, J = 6.7 Hz, 2H), 2.63 (s, 3H), 1.38 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.5, 166.7, 157.3, 142.1, 136.3, 132.6, 131.7, 129.7, 129.1, 127.3, 123.3, 116.4, 61.2, 26.8, 14.6. m.p. = 147.6-148.5 °C. IR (ATR, cm^{-1}): 3358, 2976, 2930, 2901, 1682, 1597, 1514, 1496, 1393, 1354, 1300, 1233, 1135, 1049, 1035, 960, 855, 838, 764, 744, 726, 687, 636. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{16}O_4Na^+$ 307.0941; Found 307.0943.

1-(2'-hydroxy-5'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (3ag)

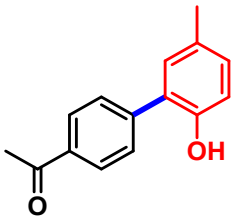


The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-(trifluoromethyl)phenol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ag** (37.0 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.05 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.7 Hz, 2H), 7.53 (d, J = 10.3 Hz, 2H), 7.09 (d, J = 8.2 Hz, 1H), 6.60 (s, 1H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.7, 155.7, 141.6, 136.5, 129.7, 129.3, 127.9 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 127.7, 127.1 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.5 (q, $^1J_{C\text{-}F}$ = 271.3 Hz), 123.6 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 116.8, 26.9. ^{19}F NMR (377 MHz,

$CDCl_3$, ppm) δ = -61.5. m.p. = 141.3-142.0 °C. IR (ATR, cm^{-1}): 3360, 2954, 2923, 1667, 1656, 1619, 1598, 1555, 1520, 1433, 1400, 1359, 1329, 1270, 1253, 1206, 1152, 1126, 1099, 1083, 1027, 960, 909, 827, 773, 754, 685, 648, 625. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{11}F_3O_2Na^+$ 303.0603; Found 303.0625.

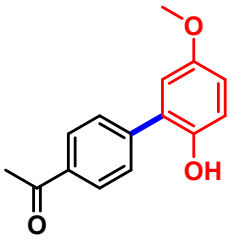
1-(2'-hydroxy-5'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (3ah)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and *p*-cresol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ah** (18.1 mg, 40%).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.05 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.08 (s, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.03 (s, 1H), 2.65 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.0, 150.4, 142.9, 136.2, 130.9, 130.6, 130.5, 129.5, 129.2, 127.1, 116.3, 26.9, 20.7. m.p. = 110.3-110.7 °C. IR (ATR, cm^{-1}): 3373, 2956, 2921, 2851, 1665, 1602, 1492, 1456, 1424, 1396, 1375, 1356, 1324, 1271, 1189, 1168, 1088, 1051, 962, 882, 841, 820, 778, 754, 726, 680, 636. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{14}O_2Na^+$ 249.0886; Found 249.0863.

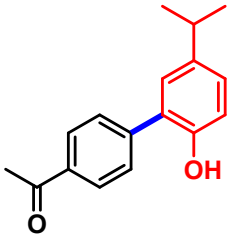
1-(2'-hydroxy-5'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one (3ai)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-methoxyphenol (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ai** (18.4 mg, 38%).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.06 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.88 – 6.80 (m, 2H), 4.91 (s, 1H), 3.80 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.0, 154.1, 146.6, 142.7, 136.4, 129.5, 129.2, 127.9, 117.3, 115.5, 115.4, 56.1, 26.9. m.p. = 137.1-137.9 °C. IR (ATR, cm^{-1}): 3331, 2993, 2924, 2847, 1665, 1600, 1487, 1467, 1441, 1423, 1400, 1350, 1327, 1261, 1217, 1168, 1108, 1032, 955, 884, 849, 836, 828, 783, 752, 738, 720, 675, 636, 607. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{14}O_3Na^+$ 265.0835; Found 265.0826.

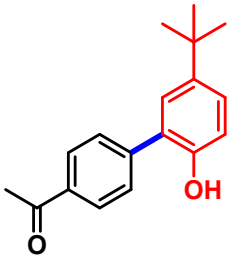
1-(2'-hydroxy-5'-isopropyl-[1,1'-biphenyl]-4-yl)ethan-1-one (3aj)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-isopropylphenol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3aj** (21.3 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.06 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.10 (m, 2H), 6.91 (d, *J* = 8.2 Hz, 1H), 5.13 (s, 1H), 2.90 (dt, *J* = 13.7, 6.8 Hz, 1H), 2.65 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.0, 150.6, 143.1, 141.9, 136.2, 129.6, 129.2, 128.4, 127.9, 127.0, 116.3, 33.6, 26.9, 24.4. m.p. = 100.9-101.7 °C. IR (ATR, cm^{-1}): 3385, 2954, 2919, 2850, 1671, 1604, 1496, 1461, 1430, 1401, 1378, 1358, 1291, 1271, 1250, 1187, 1116, 1082, 1052, 961, 883, 836, 823, 775, 738, 722, 691, 642, 624, 604; QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{17}H_{18}O_2Na^+$ 277.1199; Found 277.1184.

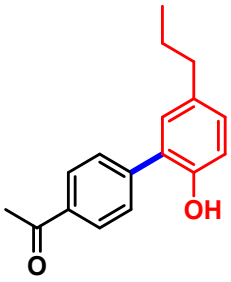
1-(5'-(tert-butyl)-2'-hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (3ak)[S4]



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-(*tert*-butyl)phenol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ak** (21.4 mg, 40%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.05 (d, *J* = 7.4 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.34 – 7.26 (m, 2H), 6.92 (d, *J* = 8.2 Hz, 1H), 5.39 (s, 1H), 2.64 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.2, 150.5, 144.1, 143.5, 143.4, 136.1, 129.6, 129.1, 127.4, 126.9, 126.7, 116.0, 34.4, 31.7, 26.9. m.p. = 135.4-136.2 °C. QTOF-MS *m/z* [M + Na]$^+$ Calcd for $C_{18}H_{20}O_2Na^+$ 291.1356; Found 291.1358.

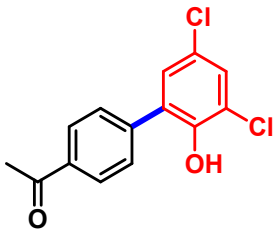
1-(2'-hydroxy-5'-propyl-[1,1'-biphenyl]-4-yl)ethan-1-one (3al)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-propylphenol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3al** (21.8 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.05 (d, *J* = 7.5 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.09 (s, 2H), 6.89 (d, *J* = 7.7 Hz, 1H), 5.11 (s, 1H), 2.65 (s, 3H), 2.57 (t, *J* = 7.3 Hz, 2H), 1.64 (dd, *J* = 14.2, 7.0 Hz, 2H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.0, 150.6, 143.0, 136.2, 135.6, 130.4, 129.9, 129.6, 129.2, 127.0, 116.3, 37.4, 26.9, 25.0, 14.0. m.p. = 86.8-87.2 °C. IR (ATR, cm^{-1}): 3375, 2960, 2918, 2849, 1672, 1657, 1601, 1556, 1513, 1499, 1464, 1428, 1398, 1356, 1270, 1179, 1133, 1116, 1092, 1049, 1014, 961, 899, 880, 842, 819, 787, 746, 720, 676, 633, 611. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{18}O_2Na^+$ 277.1199; Found 277.1190.

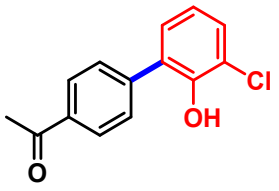
1-(3',5'-dichloro-2'-hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (3am)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 2,4-dichlorophenol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3am** (24.1 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.02 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 5.91 (s, 1H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.0, 147.6, 141.0, 136.6, 129.7, 129.6, 129.4, 128.7, 128.5, 125.8, 121.7, 26.9. m.p. = 138.5-139.7 °C. IR (ATR, cm^{-1}): 3363, 2973, 2919, 1676, 1606, 1493, 1462, 1393, 1350, 1309, 1270, 1220, 1150, 1091, 1054, 959, 883, 854, 842, 821, 753, 745, 721, 709, 641, 606. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{10}Cl_2O_2Na^+$ 302.9950; Found 302.9962.

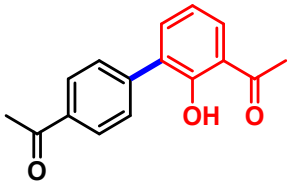
1-(3'-chloro-2'-hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (3an)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 2-chlorophenol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3an** (19.7 mg, 40%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.03 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 6.4 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 5.85 (s, 1H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.0, 148.7, 142.3, 136.2, 129.6, 129.6, 129.1, 128.7, 128.6, 121.5, 121.1, 26.9. m.p. = 143.2-143.9 °C. IR (ATR, cm^{-1}): 3360, 2973, 2926, 1661, 1605, 1552, 1453, 1402, 1354, 1306, 1272, 1225, 1185, 1158, 1126, 1088, 1049, 1012, 960, 882, 849, 826, 811, 799, 785, 745, 718, 648, 618. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{11}ClO_2Na^+$ 269.0340; Found 269.0341.

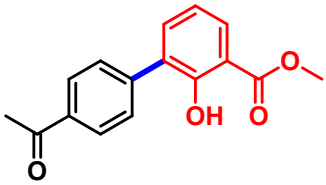
1,1'-(2-hydroxy-[1,1'-biphenyl]-3,4'-diyl)bis(ethan-1-one) (3ao)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 1-(2-hydroxyphenyl)ethan-1-one (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ao** (22.9 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 12.92 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 2.70 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 205.1, 198.1, 160.0, 142.1, 137.3, 136.1, 131.1, 130.1, 129.8, 128.4, 120.2, 119.1, 27.2, 26.9. m.p. = 80.6-81.5 °C. IR (ATR, cm^{-1}): 3363, 2976, 2934, 2899, 1669, 1603, 1512, 1492, 1448, 1398, 1380, 1352, 1272, 1228, 1204, 1182, 1091, 1052, 1004, 948, 880, 861, 831, 798, 745, 721, 701, 634. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{14}O_3Na^+$ 277.0835; Found 277.0821.

methyl 4'-acetyl-2-hydroxy-[1,1'-biphenyl]-3-carboxylate (3ap)

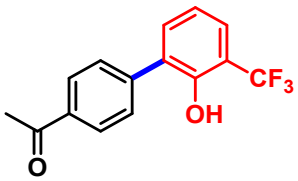


The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and methyl 2-hydroxybenzoate (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ap** (23.8 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 11.37 (s, 1H), 8.03 (d, *J* = 7.4 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 1H), 6.99 (t, *J* = 7.3 Hz, 1H), 3.98 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.0, 171.1, 159.1, 142.3, 136.6, 136.1, 130.3,

129.8, 129.4, 128.4, 119.4, 113.0, 52.8, 26.9. m.p. = 145.0-145.8 °C. IR (ATR, cm^{-1}): 3367, 2957, 2926, 1676, 1664, 1606, 1427, 1400, 1330, 1305, 1291, 1263, 1245, 1195, 1148, 1079, 1058, 956, 927, 908, 879, 844, 828, 813, 756, 728, 704, 601. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{14}O_4Na^+$ 293.0784; Found 293.0796.

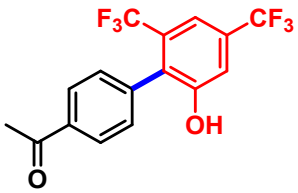
1-(2'-hydroxy-3'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (3aq)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 2-(trifluoromethyl)phenol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3aq** (26.9 mg, 48%).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.05 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 3H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 5.89 (s, 1H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 197.8, 150.8 (q, $^4J_{C\text{-}F}$ = 1.5 Hz), 140.9, 136.9, 134.2, 129.8, 129.4, 129.4, 127.3 (q, $^3J_{C\text{-}F}$ = 5.0 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 120.8, 117.8 (q, $^2J_{C\text{-}F}$ = 30.7 Hz), 26.8. ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ = -61.6. m.p. = 143.3-144.1 °C. IR (ATR, cm^{-1}): 3223, 2978, 2925, 1667, 1596, 1560, 1511, 1467, 1430, 1403, 1365, 1331, 1272, 1242, 1179, 1129, 1109, 1078, 1051, 1035, 960, 921, 882, 859, 831, 818, 798, 750, 688, 646, 621, 608. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{11}F_3O_2Na^+$ 303.0603; Found 303.0602.

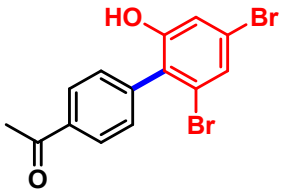
1-(2'-hydroxy-4',6'-bis(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (3ar)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 3,5-bis(trifluoromethyl)phenol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ar** (34.1 mg, 49%).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.07 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.48 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 5.93 (s, 1H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.2, 154.8, 137.7, 137.0, 132.3 (q, $^2J_{C\text{-}F}$ = 33.9 Hz), 131.0 (q, $^2J_{C\text{-}F}$ = 30.9 Hz), 130.7, 129.4, 129.1, 123.3 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 123.1 (q, $^1J_{C\text{-}F}$ = 274.4 Hz), 116.8 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 115.1 (qd, $^3J_{C\text{-}F}$ = 7.5, 3.7 Hz), 26.8. ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ = -58.0, -63.2. m.p. = 173.4-174.8 °C. IR (ATR, cm^{-1}): 3378, 2954, 2918, 2850, 1670, 1604, 1487, 1448, 1380, 1312, 1273, 1163, 1115, 1092, 1052, 1023, 1003, 956, 880, 855, 837, 768, 726, 692, 668, 641, 623, 598. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{10}F_6O_2Na^+$ 371.0477; Found 371.0482.

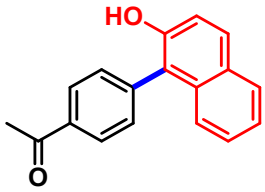
1-(2',4'-dibromo-6'-hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (3as)



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 3,5-dibromophenol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3as** (34.5 mg, 47%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.10 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 3H), 7.15 (s, 1H), 5.19 (s, 1H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 197.7, 154.3, 139.6, 137.5, 130.9, 129.4, 127.7, 127.6, 124.0, 123.0, 118.6, 26.9. m.p. = 191.1-191.8 °C. IR (ATR, cm^{-1}): 3356, 2954, 2914, 2849, 1728, 1664, 1602, 1568, 1462, 1404, 1382, 1357, 1331, 1267, 1234, 1181, 1097, 1050, 1017, 1001, 956, 909, 881, 860, 844, 831, 786, 748, 728, 640, 618, 602. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{14}H_{10}Br_2O_2Na^+$ 390.8940; Found 390.8959.

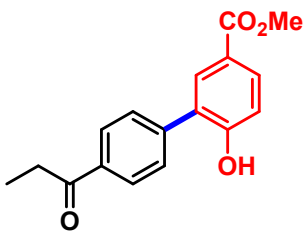
1-(4-(2-hydroxynaphthalen-1-yl)phenyl)ethan-1-one (3at)[S5]



The general procedure was followed using 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and naphthalen-2-ol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3at** (26.7 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.16 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.36 (s, 3H), 7.26 (d, *J* = 6.3 Hz, 1H), 5.27 (s, 1H), 2.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.0, 150.2, 140.1, 137.1, 133.1, 131.8, 130.3, 129.6, 129.1, 128.4, 127.0, 124.5, 123.8, 120.3, 117.8, 26.9. m.p. = 200.3-200.7 °C. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{18}H_{14}O_2Na^+$ 285.0886; Found 285.0867.

methyl 6-hydroxy-4'-propionyl-[1,1'-biphenyl]-3-carboxylate (3be)

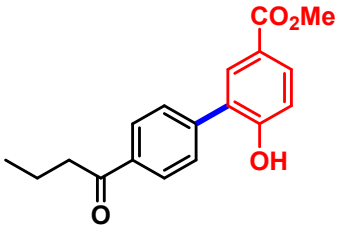


The general procedure was followed using 1-(4-bromophenyl)propan-1-one (0.2 mmol) and methyl 4-hydroxybenzoate (0.8 mmol). The crude product was purified by preparative TLC, using

PE and EA (v/v = 2/1) as eluent, to yield the white solid **3be** (40.3 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.07 – 7.99 (m, 3H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.67 (s, 1H), 3.90 (s, 3H), 3.03 (dd, *J* = 13.1, 6.2 Hz, 2H), 1.24 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 201.0, 167.1, 157.2, 141.6, 136.2, 132.6, 131.7, 129.6, 128.8, 127.4, 123.1, 116.5, 52.3, 32.1, 8.5. m.p. = 145.3-146.0 °C. IR (ATR, cm^{-1}): 3374, 2985, 2895, 1686, 1602, 1507, 1437, 1349, 1311, 1226, 1127, 960, 849, 796, 765, 729, 645, 633. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{16}O_4Na^+$ 307.0941; Found 307.0932.

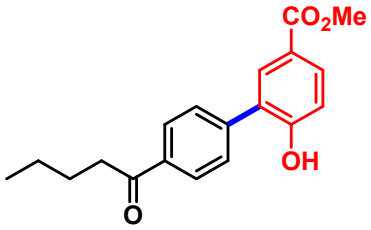
methyl 4'-butyryl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (3ce)



The general procedure was followed using 1-(4-bromophenyl)butan-1-one (0.2 mmol) and methyl 4-hydroxybenzoate (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ce** (43.5 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.07 (d, *J* = 6.6 Hz, 2H), 7.99 (d, *J* = 14.8 Hz, 2H), 7.62 (d, *J* = 6.5 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 1H), 3.90 (s, 3H), 2.99 (s, 2H), 1.80 (d, *J* = 6.1 Hz, 2H), 1.04 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 200.3, 166.9, 156.8, 141.2, 136.7, 132.5, 131.8, 129.6, 129.1, 127.4, 123.4, 116.4, 52.3, 40.9, 18.0, 14.1. m.p. = 96.5-97.2 °C. IR (ATR, cm^{-1}): 3355, 2922, 2848, 1712, 1667, 1602, 1411, 1369, 1306, 1234, 1114, 1005, 971, 904, 832, 766, 732, 637. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{18}H_{18}O_4Na^+$ 321.1097; Found 321.1088.

methyl 6-hydroxy-4'-pentanoyl-[1,1'-biphenyl]-3-carboxylate (3de)

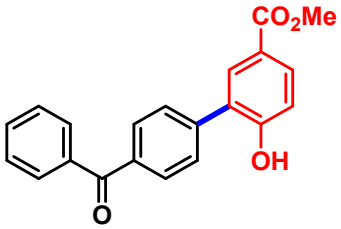


The general procedure was followed using 1-(4-bromophenyl)pentan-1-one (0.2 mmol) and methyl 4-hydroxybenzoate (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3de** (43.7 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.08 – 7.99 (m, 3H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.80 (s, 1H), 3.90 (s, 3H), 2.99 (t, *J* = 7.0 Hz, 2H), 1.72 (dd, *J* = 13.9, 6.8 Hz, 2H), 1.42 (dd, *J* = 14.4, 7.2 Hz, 2H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 200.9, 167.1, 157.3, 141.6, 136.3, 132.6, 131.7, 129.6, 128.9, 127.4, 123.0, 116.5, 52.3, 38.7, 26.8, 22.7, 14.1. m.p. = 116.6-117.4 °C. IR (ATR, cm^{-1}): 3324, 2989, 2899,

1700, 1665, 1605, 1399, 1365, 1301, 1261, 1241, 1213, 1140, 1113, 977, 848, 768, 742, 726, 665. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{19}H_{20}O_4Na^+$ 335.1254; Found 335.1267.

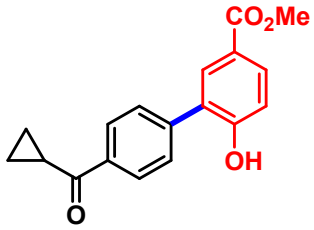
methyl 4'-benzoyl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (3ee)



The general procedure was followed using (4-bromophenyl)(phenyl)methanone (0.2 mmol) and methyl 4-hydroxybenzoate (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ee** (45.8 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.04 (d, *J* = 1.9 Hz, 1H), 7.99 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.63 (dd, *J* = 12.6, 7.8 Hz, 3H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.00 (s, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 196.5, 166.9, 156.9, 140.8, 137.6, 137.3, 132.9, 132.6, 131.8, 131.1, 130.3, 129.3, 128.6, 127.4, 123.4, 116.5, 52.3. m.p. = 165.3-165.8 °C. IR (ATR, cm^{-1}): 3253, 2985, 2887, 1687, 1651, 1601, 1428, 1386, 1320, 1280, 1205, 1129, 967, 946, 928, 845, 762, 729, 691, 633. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{21}H_{16}O_4Na^+$ 355.0941; Found 355.0929.

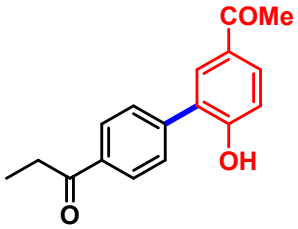
methyl 4'-(cyclopropanecarbonyl)-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (3fe)



The general procedure was followed using (4-bromophenyl)(cyclopropyl)methanone (0.2 mmol) and methyl 4-hydroxybenzoate (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3fe** (42.6 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.11 (d, *J* = 7.3 Hz, 2H), 8.02 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.37 (s, 1H), 3.90 (s, 3H), 2.71 (s, 1H), 1.28 (s, 2H), 1.09 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 200.7, 167.0, 157.1, 141.2, 137.4, 132.6, 131.7, 129.5, 129.0, 127.4, 123.2, 116.4, 52.3, 17.6, 12.2. m.p. = 122.4-123.2 °C. IR (ATR, cm^{-1}): 3156, 2973, 2895, 1724, 1632, 1601, 1432, 1405, 1384, 1303, 1291, 1227, 1138, 1115, 1032, 994, 870, 844, 762, 732, 642. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{18}H_{16}O_4Na^+$ 319.0941; Found 319.0946.

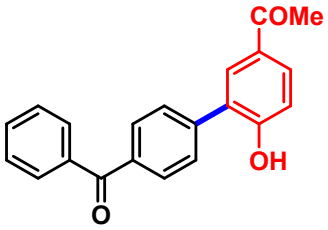
1-(5'-acetyl-2'-hydroxy-[1,1'-biphenyl]-4-yl)propan-1-one (3bc)



The general procedure was followed using 1-(4-bromophenyl)propan-1-one (0.2 mmol) and 1-(4-hydroxyphenyl)ethan-1-one (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3bc** (38.6 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.07 (d, *J* = 8.3 Hz, 2H), 7.96 – 7.89 (m, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.45 (s, 1H), 3.05 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 200.8, 197.2, 157.4, 141.4, 136.4, 131.5, 130.8, 129.6, 128.9, 127.5, 116.5, 32.1, 26.6, 8.5. m.p. = 105.1-105.9 °C. IR (ATR, cm^{-1}): 3294, 3192, 3063, 2963, 2920, 2851, 2362, 2335, 1665, 1594, 1510, 1458, 1399, 1354, 1280, 1223, 1135, 1078, 1012, 952, 850, 821, 798, 674, 643. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{16}O_3Na^+$ 291.0992; Found 291.0997.

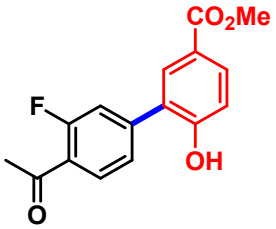
1-(4'-benzoyl-6-hydroxy-[1,1'-biphenyl]-3-yl)ethan-1-one (3ec)



The general procedure was followed using (4-bromophenyl)(phenyl)methanone (0.2 mmol) and 1-(4-hydroxyphenyl)ethan-1-one (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ec** (42.3 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.97 (d, *J* = 2.2 Hz, 1H), 7.92 (dd, *J* = 8.4, 1.9 Hz, 3H), 7.85 (s, 1H), 7.84 (t, *J* = 1.6 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.61 (dt, *J* = 2.5, 1.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.47 (s, 1H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 197.1, 196.6, 157.4, 140.9, 137.5, 137.2, 132.9, 131.6, 131.0, 130.8, 130.8, 130.3, 129.3, 128.6, 127.5, 116.5, 26.6. m.p. = 73.2-74.1 °C. IR (ATR, cm^{-1}): 3188, 2955, 2922, 2853, 2367, 2336, 2255, 1648, 1594, 1511, 1427, 1395, 1359, 1278, 1240, 1131, 1079, 922, 848, 827, 696, 640. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{21}H_{16}O_3Na^+$ 339.0992; Found 339.0983.

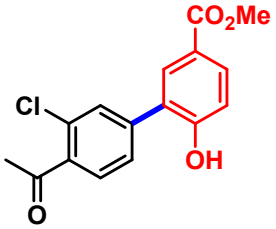
methyl 4'-acetyl-3'-fluoro-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (3ge)



The general procedure was followed using 1-(4-bromo-2-fluorophenyl)ethan-1-one (0.2 mmol) and methyl 4-hydroxybenzoate (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ge** (34.0 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.07 – 7.90 (m, 3H), 7.40 (dd, *J* = 16.4, 10.3 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.59 (s, 1H), 3.91 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 196.1 (d, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 166.9, 162.5 (d, $^{1}J_{C\text{-}F}$ = 255.7 Hz), 157.1, 144.0 (d, $^{3}J_{C\text{-}F}$ = 9.2 Hz), 132.3 (d, $^{2}J_{C\text{-}F}$ = 46.8 Hz), 131.3 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 126.2, 126.2, 125.3 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 124.8 (d, $^{3}J_{C\text{-}F}$ = 12.8 Hz), 123.3, 117.7 (d, $^{2}J_{C\text{-}F}$ = 24.9 Hz), 116.7, 52.4, 31.7 (d, $^{4}J_{C\text{-}F}$ = 7.3 Hz). ^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ = -108.0, -108.5. m.p. = 154.9-155.8 °C. IR (ATR, cm^{-1}): 3273, 2954, 2924, 1689, 1677, 1621, 1605, 1433, 1390, 1360, 1325, 1272, 1260, 1191, 1127, 964, 930, 872, 835, 769, 740, 724, 693, 656. QTOF-MS *m/z* [M + Na]$^{+}$ Calcd for $C_{16}H_{13}FO_4Na^{+}$ 311.0690; Found 311.0698.

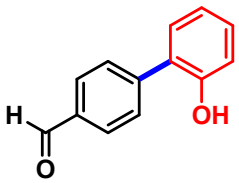
methyl 4'-acetyl-3'-chloro-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (3he)



The general procedure was followed using 1-(4-bromo-2-chlorophenyl)ethan-1-one (0.2 mmol) and methyl 4-hydroxybenzoate (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3he** (35.3 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.99 (s, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.62 (s, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 5.85 (s, 1H), 3.91 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 200.2, 166.7, 156.7, 140.9, 138.3, 132.5, 132.3, 132.0, 131.5, 130.3, 127.9, 126.1, 123.6, 116.5, 52.3, 31.0. m.p. = 135.3-136.1 °C. IR (ATR, cm^{-1}): 3273, 1685, 1604, 1510, 1432, 1380, 1316, 1260, 1138, 1041, 974, 876, 828, 752, 737, 688, 636. QTOF-MS *m/z* [M + Na]$^{+}$ Calcd for $C_{16}H_{13}ClO_4Na^{+}$ 327.0395; Found 327.0379.

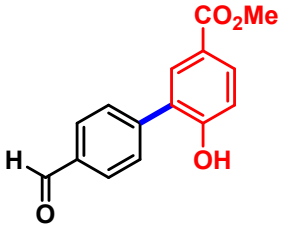
2'-hydroxy-[1,1'-biphenyl]-4-carbaldehyde (3ia)



The general procedure was followed using 4-bromobenzaldehyde (0.2 mmol) and phenol (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ia** (22.6 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 10.05 (s, 1H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 6.8 Hz, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 5.43 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 192.3, 152.7, 144.3, 135.4, 130.7, 130.5, 130.2, 130.1, 127.2, 121.4, 116.6. m.p. = 107.7-108.3 °C. IR (ATR, cm^{-1}): 3378, 2978, 2923, 2844, 1668, 1600, 1559, 1451, 1410, 1378, 1300, 1276, 1256, 1214, 1168, 1091, 1051, 1002, 881, 846, 835, 822, 756, 722, 710, 662. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{13}H_{10}O_2Na^+$ 221.0573; Found 221.0570.

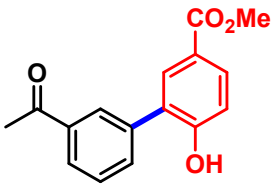
methyl 4'-formyl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (3ie)



The general procedure was followed using 4-bromobenzaldehyde (0.2 mmol) and methyl 4-hydroxybenzoate (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3ie** (34.8 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 10.06 (s, 1H), 8.02 (s, 1H), 7.99 (d, *J* = 7.7 Hz, 3H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.07 (s, 1H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 192.1, 166.9, 156.9, 143.1, 135.9, 132.7, 131.9, 130.5, 130.1, 127.2, 123.5, 116.5, 52.3. m.p. = 142.3-143.1 °C. IR (ATR, cm^{-1}): 3258, 2985, 2891, 1690, 1600, 1424, 1387, 1317, 1283, 1251, 1208, 1129, 967, 838, 799, 731, 690, 645. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{12}O_4Na^+$ 279.0628; Found 279.0615.

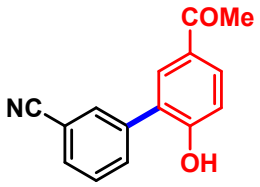
methyl 3'-acetyl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (3je)



The general procedure was followed using 1-(3-bromophenyl)ethan-1-one (0.2 mmol) and methyl 4-hydroxybenzoate (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3je** (25.4 mg, 47%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.09 (s, 1H), 7.98 (d, *J* = 9.8 Hz, 3H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 5.76 (s, 1H), 3.90 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 198.1, 166.9, 156.8, 138.1, 137.1, 134.0, 132.6, 131.6, 129.7, 129.3, 128.2, 127.5, 123.4, 116.3, 52.2, 27.0. m.p. = 73.7-74.5 °C. IR (ATR, cm^{-1}): 3327, 2955, 2925, 2852, 1718, 1688, 1665, 1602, 1510, 1434, 1399, 1356, 1318, 1263, 1202, 1113, 1043, 981, 892, 832, 795, 767, 735, 688, 622. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{14}O_4Na^+$ 293.0784; Found 293.0796.

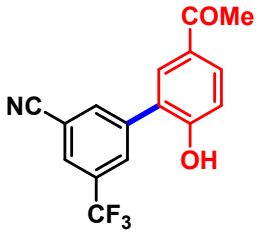
5'-acetyl-2'-hydroxy-[1,1'-biphenyl]-3-carbonitrile (3kc)



The general procedure was followed using 3-bromobenzonitrile (0.2 mmol) and 1-(4-hydroxyphenyl)ethan-1-one (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3kc** (22.8 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.91 (dd, *J* = 9.5, 7.3 Hz, 3H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 6.8 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 1H), 6.50 (s, 1H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 197.0, 157.3, 138.3, 133.9, 133.2, 131.7, 131.5, 131.0, 130.9, 129.8, 126.5, 118.8, 116.5, 113.1, 26.6. m.p. = 89.7-90.2 °C. IR (ATR, cm^{-1}): 3169, 3060, 2928, 2769, 2225, 1642, 1583, 1430, 1400, 1363, 1269, 1131, 1083, 963, 898, 823, 791, 689, 639. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{11}NO_2Na^+$ 260.0682; Found 260.0676.

5'-acetyl-2'-hydroxy-5-(trifluoromethyl)-[1,1'-biphenyl]-3-carbonitrile (3lc)

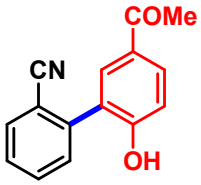


The general procedure was followed using 3-bromo-5-(trifluoromethyl)benzonitrile (0.2 mmol) and 1-(4-hydroxyphenyl)ethan-1-one (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3lc** (31.7 mg, 52%).

^{1}H NMR (400 MHz, d_6-DMSO, ppm) δ = 11.01 (s, 1H), 8.38 (s, 1H), 8.29 (d, *J* = 12.6 Hz, 2H), 8.02 (d, *J* = 2.2 Hz, 1H), 7.90 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO, ppm) δ = 196.2, 158.9, 139.9, 136.7, 131.8, 130.8, 130.3 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 130.1 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 129.2, 127.7 (q, $^3J_{C\text{-}F}$ = 3.4 Hz), 123.9, 123.3 (q, $^1J_{C\text{-}F}$ = 273.0 Hz), 117.6, 116.2, 112.8, 26.5. ^{19}F NMR (376 MHz, d_6-DMSO, ppm) δ = -61.4. m.p. = 117.7-118.5 °C. IR (ATR, cm^{-1}): 3067, 2928, 2759, 2361, 2336, 2234, 1648, 1585, 1445, 1401, 1372,

1344, 1283, 1220, 1164, 1129, 1062, 968, 892, 836, 727, 695, 647. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{16}H_{10}F_3NO_2Na^+$ 328.0556; Found 328.0565.

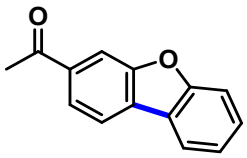
5'-acetyl-2'-hydroxy-[1,1'-biphenyl]-2-carbonitrile (3mc)



The general procedure was followed using 2-bromobenzonitrile (0.2 mmol) and 1-(4-hydroxyphenyl)ethan-1-one (0.8 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 2/1) as eluent, to yield the white solid **3mc** (19.4 mg, 41%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.74 (d, *J* = 2.0 Hz, 1H), 8.43 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.07 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.68 – 7.63 (m, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 196.7, 160.7, 154.5, 135.5, 134.3, 133.7, 131.0, 130.7, 129.8, 123.8, 122.3, 121.4, 118.5, 118.3, 26.9. m.p. = 121.3-122.0 °C. IR (ATR, cm^{-1}): 3077, 2921, 2851, 2361, 2336, 2224, 1749, 1672, 1604, 1567, 1490, 1416, 1356, 1251, 1214, 1089, 1028, 959, 895, 829, 769, 727, 683, 628. QTOF-MS *m/z* $[M + Na]^+$ Calcd for $C_{15}H_{11}NO_2Na^+$ 260.0682; Found 260.0699.

1-(dibenzo[*b*,*d*]furan-3-yl)ethan-1-one[S3]



In a nitrogen filled glove box, **3aa** (0.20 mmol), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol, 10 mol %), 3-nitropyridine (2.5 mg, 0.020 mmol, 10 mol %), C_6F_6 (0.3 mL), DMI (0.2 mL) and BzOO*t*Bu (76 μL, 0.40 mmol, 2.0 equiv) were added into 15 mL tube. The resulting solution was stirred at 90 °C for 4 h. After cooling to room temperature, the crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as eluent, to yield the white solid 1-(dibenzo[*b*,*d*]furan-2-yl)ethan-1-one (19.7 mg, 47%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.17 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 3H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 197.6, 157.8, 156.2, 136.3, 128.9, 128.8, 123.5, 123.4, 123.4, 121.7, 120.7, 112.3, 112.0, 27.1. QTOF-MS *m/z* $[M + H]^+$ Calcd for $C_{14}H_{11}O_2^+$ 211.0754; Found 211.0751.

X-ray diffraction crystallography

The crystal structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques with the *SHELXL-2018/3* program.[S6] Crystallographic data are summarized in Table S4. Additionally, complete data have been deposited with the Cambridge Crystallographic Data Centre under the number CCDC 2108994. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S4. Crystal data and structure refinement parameters.

Compound	**3aa**
CCDC number	2108994
formula	$C_{14}H_{12}O_2$
F*w*	212.24
crystal system	monoclinic
space group	$P2_1/n$
a (Å)	6.8356(3)
b (Å)	22.7724(11)
c (Å)	7.0408(3)
α (°)	90
β (°)	101.861(5)
γ (°)	90
V (Å^3)	1072.59(9)
Z	4
D_c/g cm^{-3}	1.314
F(000)	448
μ/mm^{-1}	0.699
Total reflections	2265
Unique reflections	1751
R_{int}	0.0411
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0654
$wR_2{}^b$[$I > 2\sigma(I)$]	0.1660
GOF^c	1.058

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. ^{c}GOF $= \{\Sigma w((F_o^2 - F_c^2)^2)/(n-p)\}^{1/2}$,

where n = number of reflections and p = total numbers of parameters refined.

References

S1 P. Job, *Ann. Chim.*, 1928, **9***,* 113.

S2 (a) K. Zhang, L.-Q. Lu, Y. Jia, Y. Wang, F.-D. Lu, F. Pan, and W.-J. Xiao, *Angew. Chem. Int. Ed.* 2019, **58**, 13375–13379; (b) M. A. Cismesia and T. P. Yoon, *Chem. Sci.*, 2015, **6**, 5426–5434.

S3 Y. Wei and N. Yoshikai, *Org. Lett.*, 2011, **13**, 5504–5507.

S4 Z. Zuo, X. Yang, J. Liu, J. Nan, L. Bai, Y. Wang and X. Luan, *J. Org. Chem.*, 2015, **80**, 3349–3356.

S5 J. Nan, Z. Zuo, L. Luo, L. Bai, H. Zheng, Y. Yuan, J. Liu, X. Luan and Y. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 17306−17309.

S6 G. M. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **C71**, 3–8.

NMR spectra

Figure S9. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(2'-hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (**3aa**) in $CDCl_3$

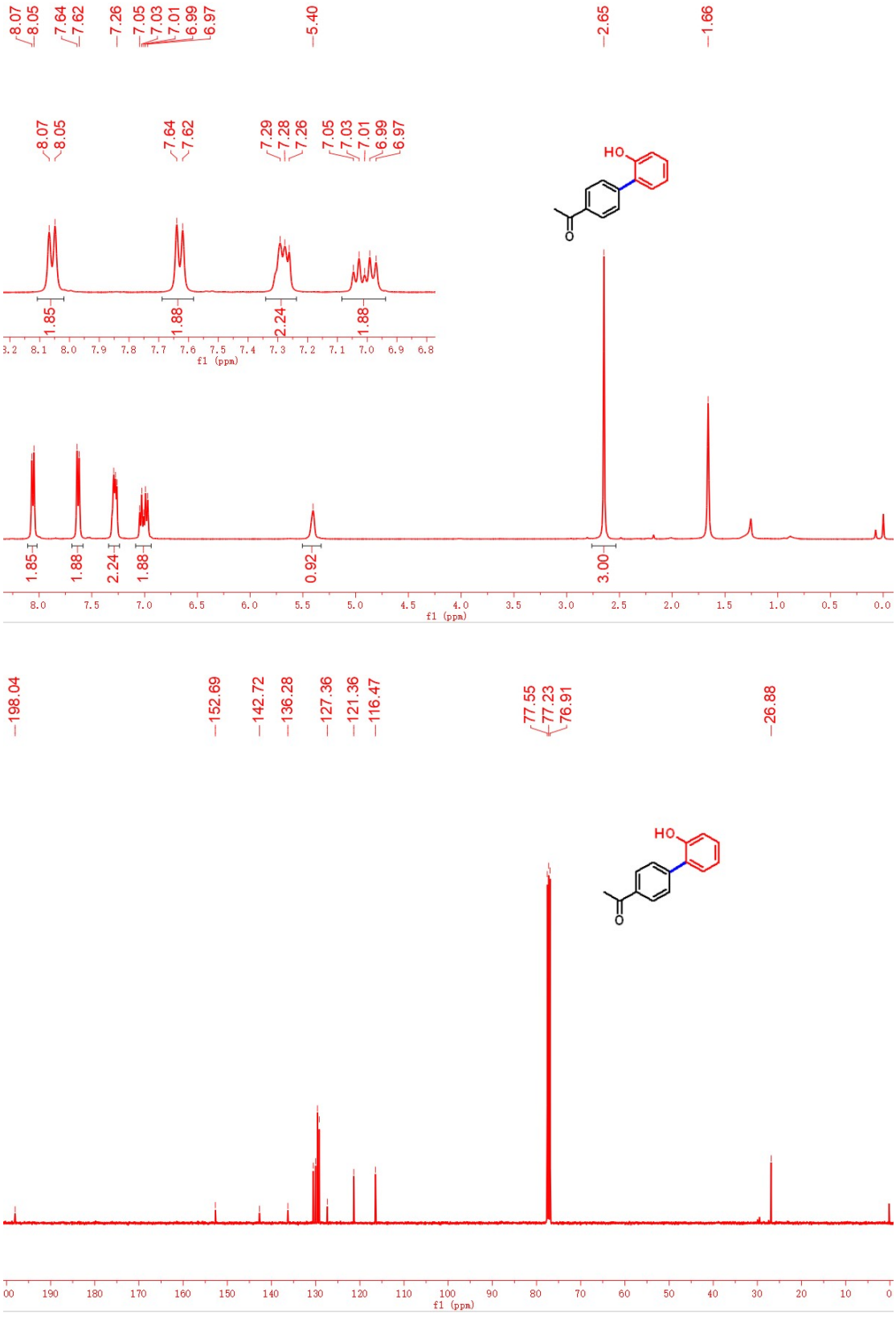


Figure S10. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 4'-acetyl-6-hydroxy-[1,1'-biphenyl]-3-carbonitrile (**3ab**) in d_6-DMSO

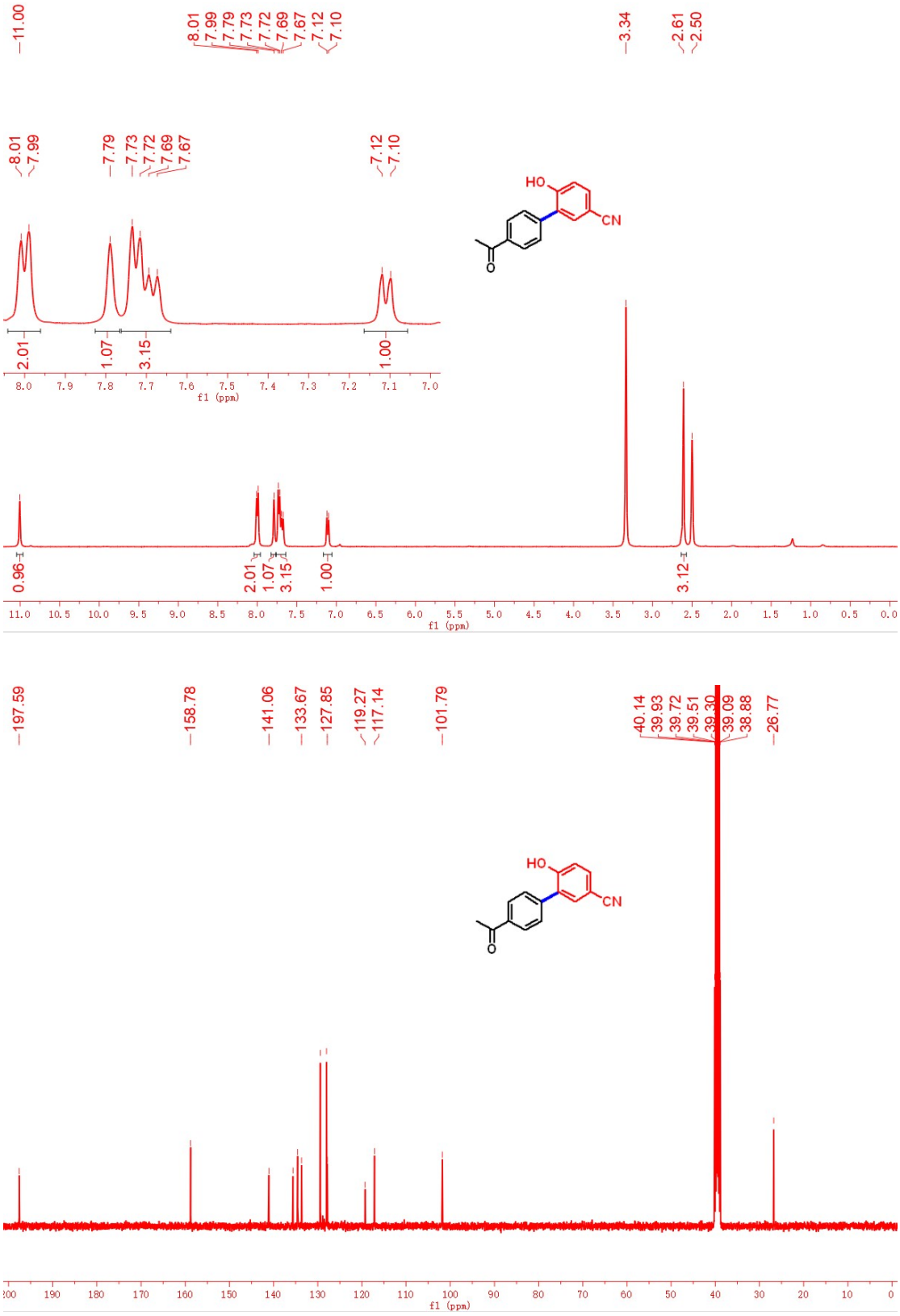


Figure S11. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1,1'-(6-hydroxy-[1,1'-biphenyl]-3,4'-diyl)bis(ethan-1-one) (**3ac**) in $CDCl_3$

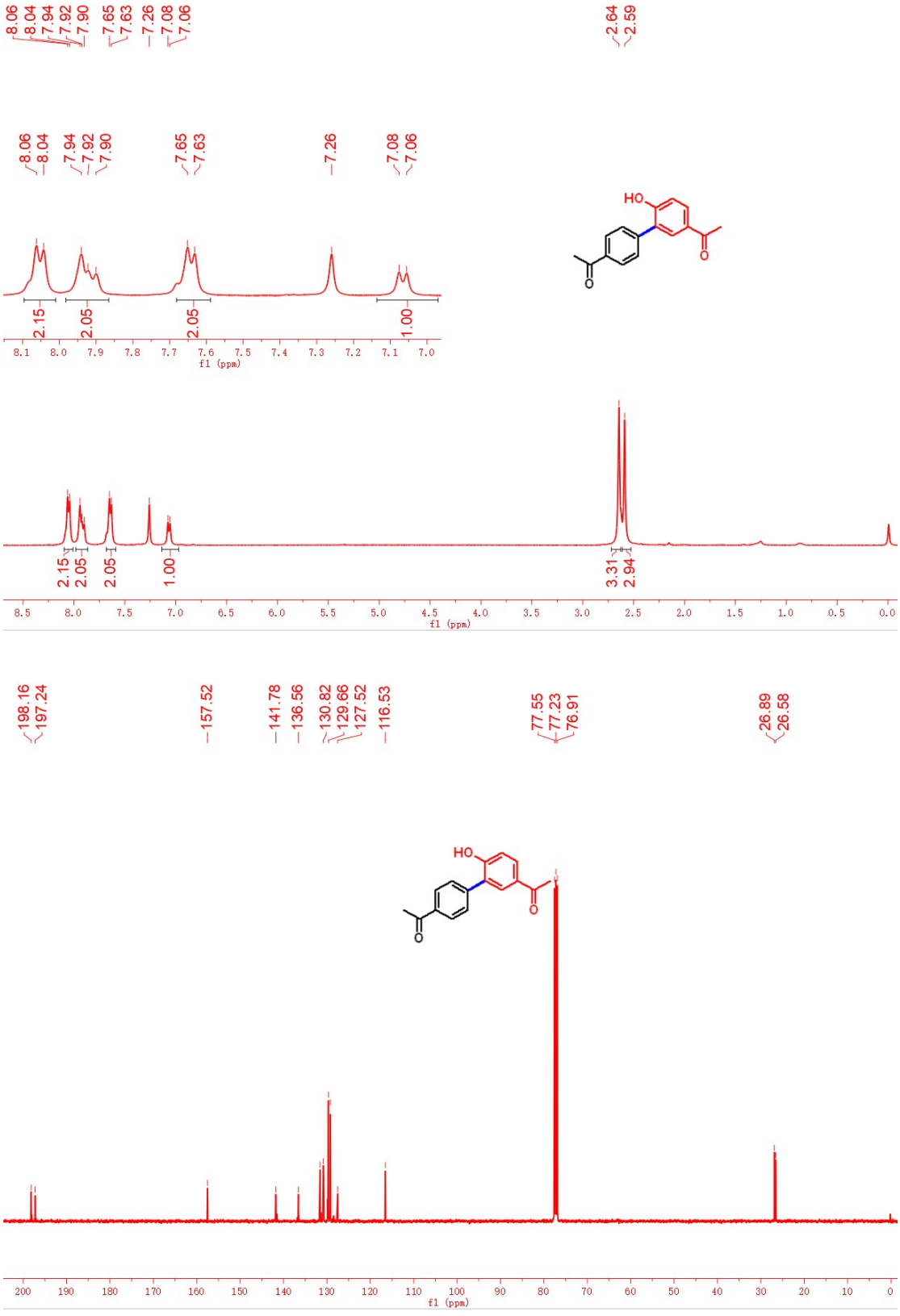


Figure S12. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(4'-acetyl-6-hydroxy-[1,1'-biphenyl]-3-yl)propan-1-one (**3ad**) in $CDCl_3$

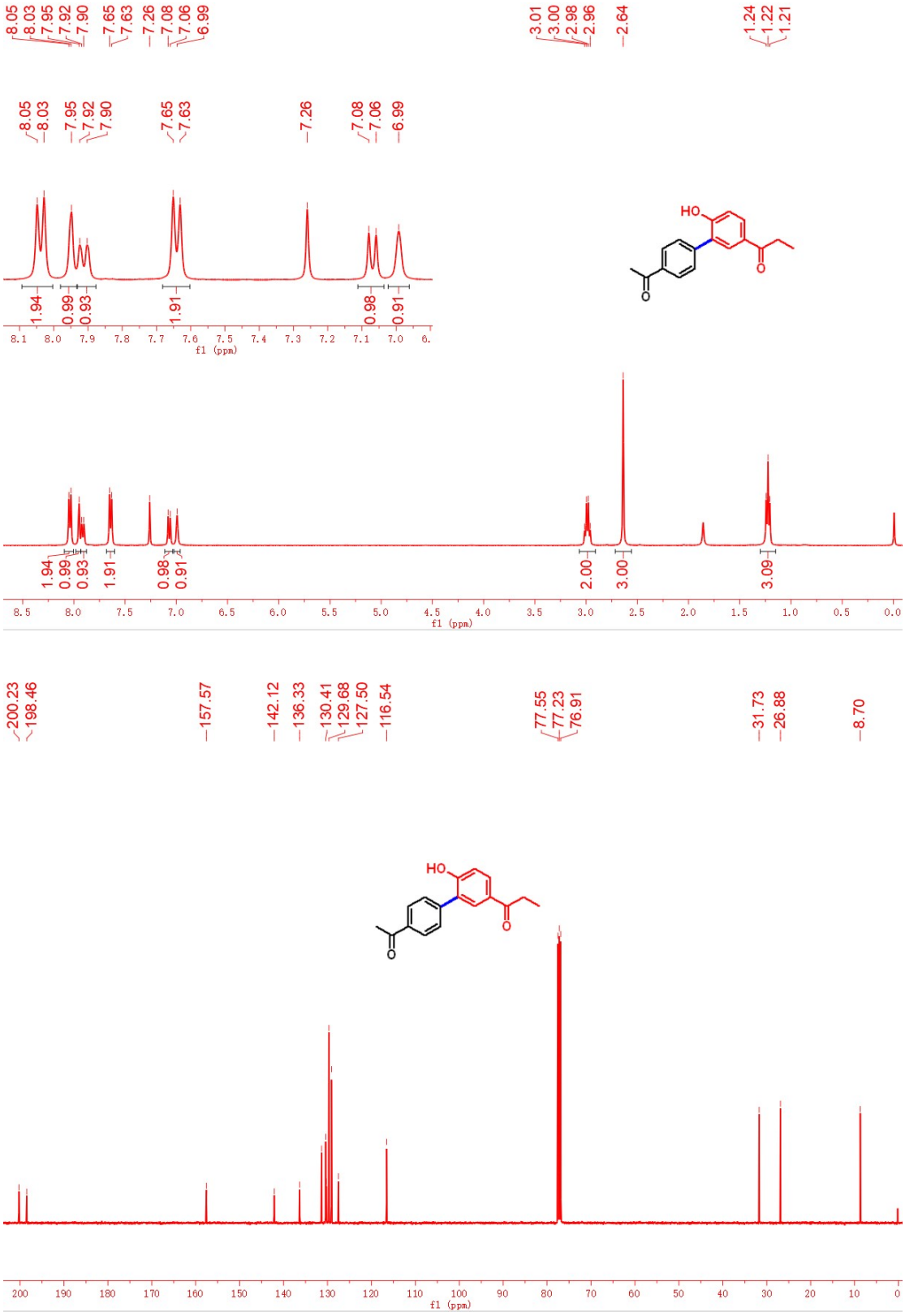


Figure S13. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 4'-acetyl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (**3ae**) in $CDCl_3$

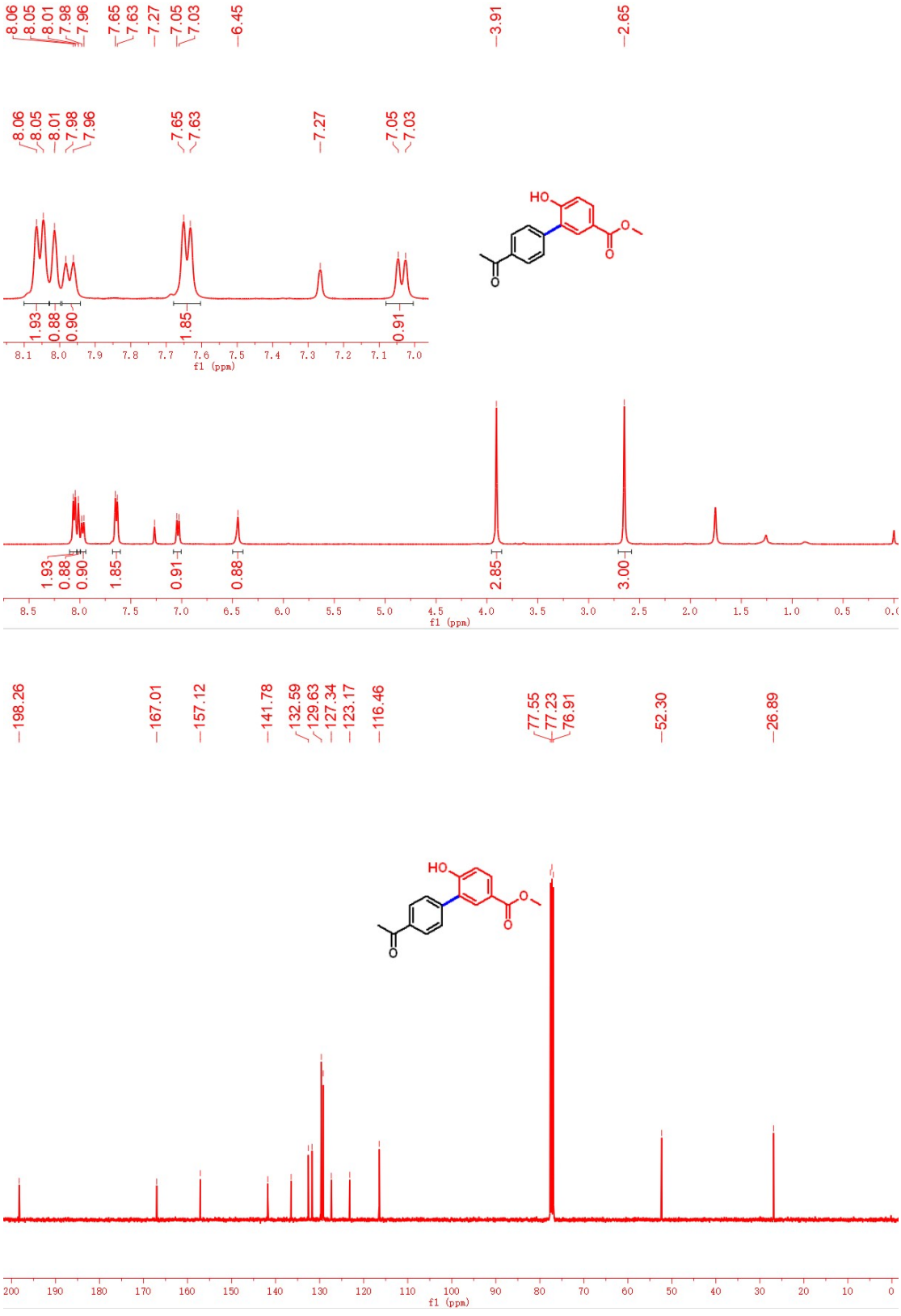


Figure S14. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for ethyl 4'-acetyl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (**3af**) in $CDCl_3$

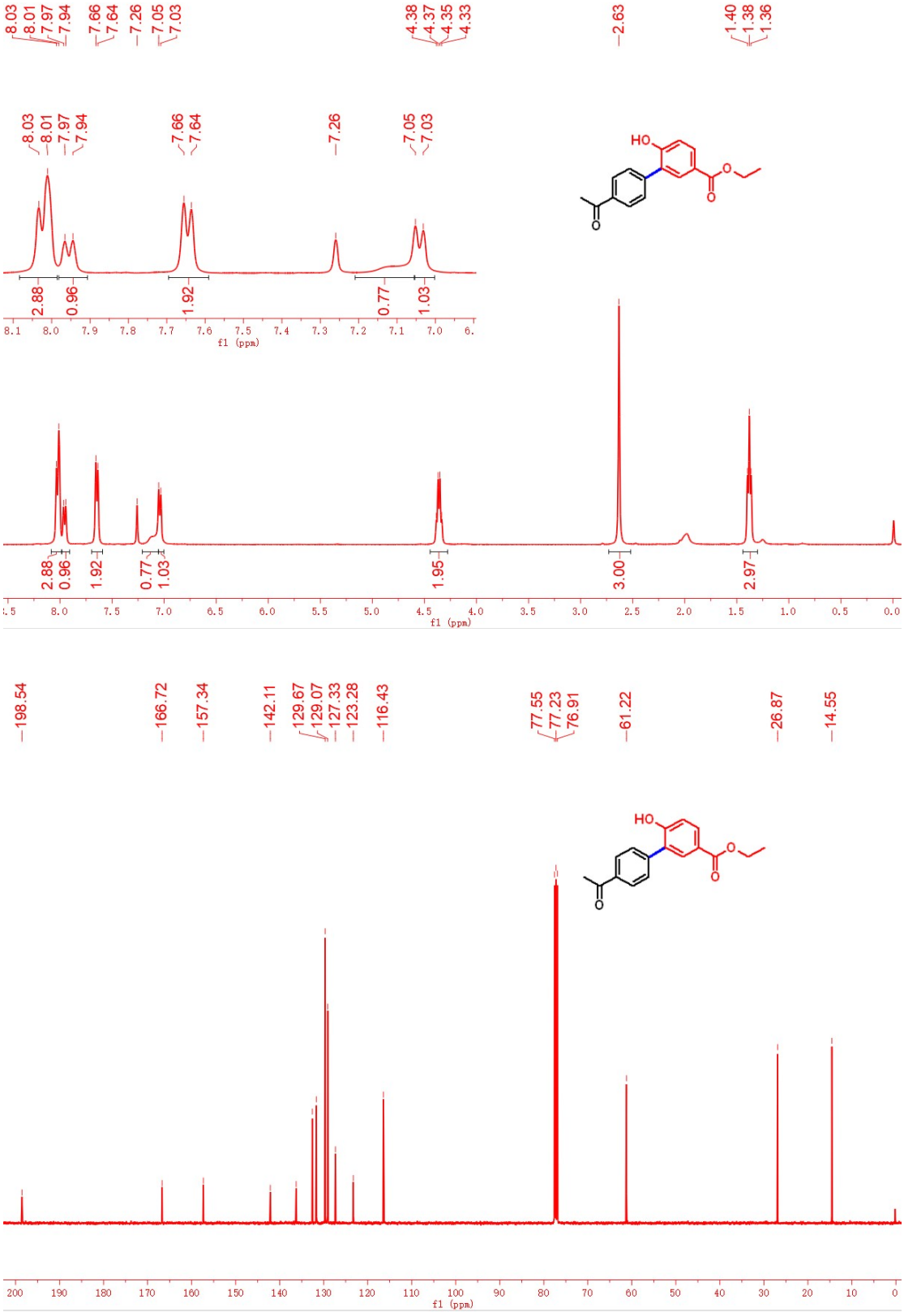
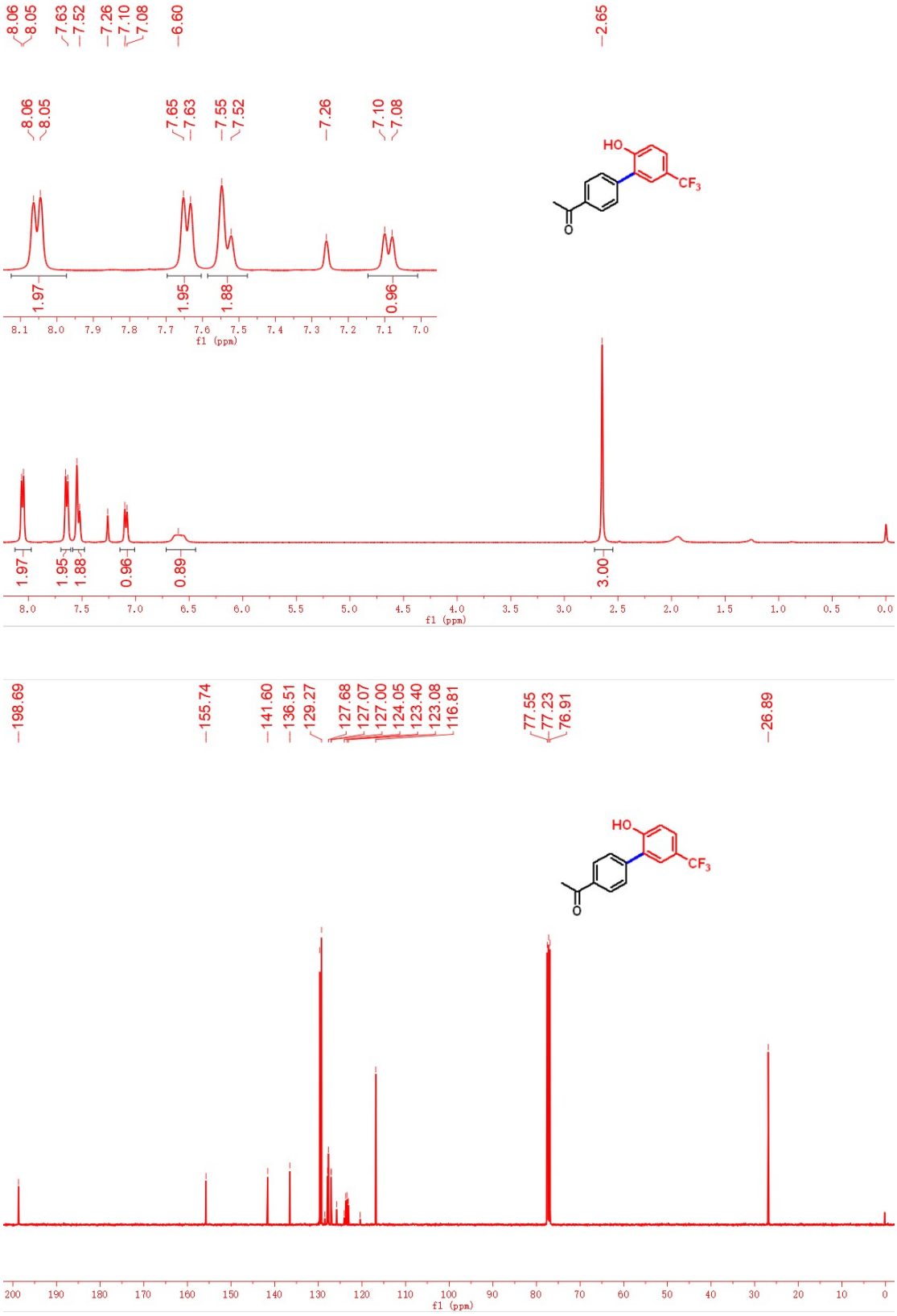


Figure S15. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F NMR (377 MHz) NMR spectra for1-(2'-hydroxy-5'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (**3ag**) in $CDCl_3$



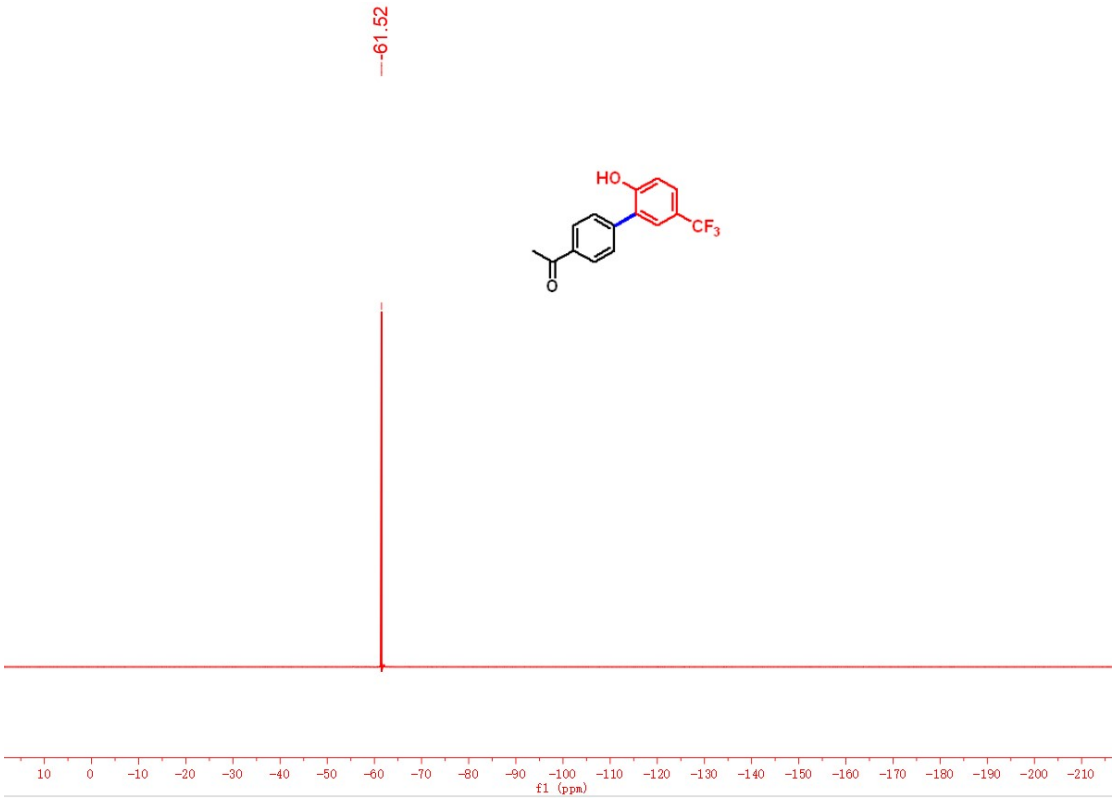

-61.52
HO
CF3
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Figure S16. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(2'-hydroxy-5'-methyl-[1,1'-biphenyl]-4-yl)ethan-1-one (**3ah**) in $CDCl_3$

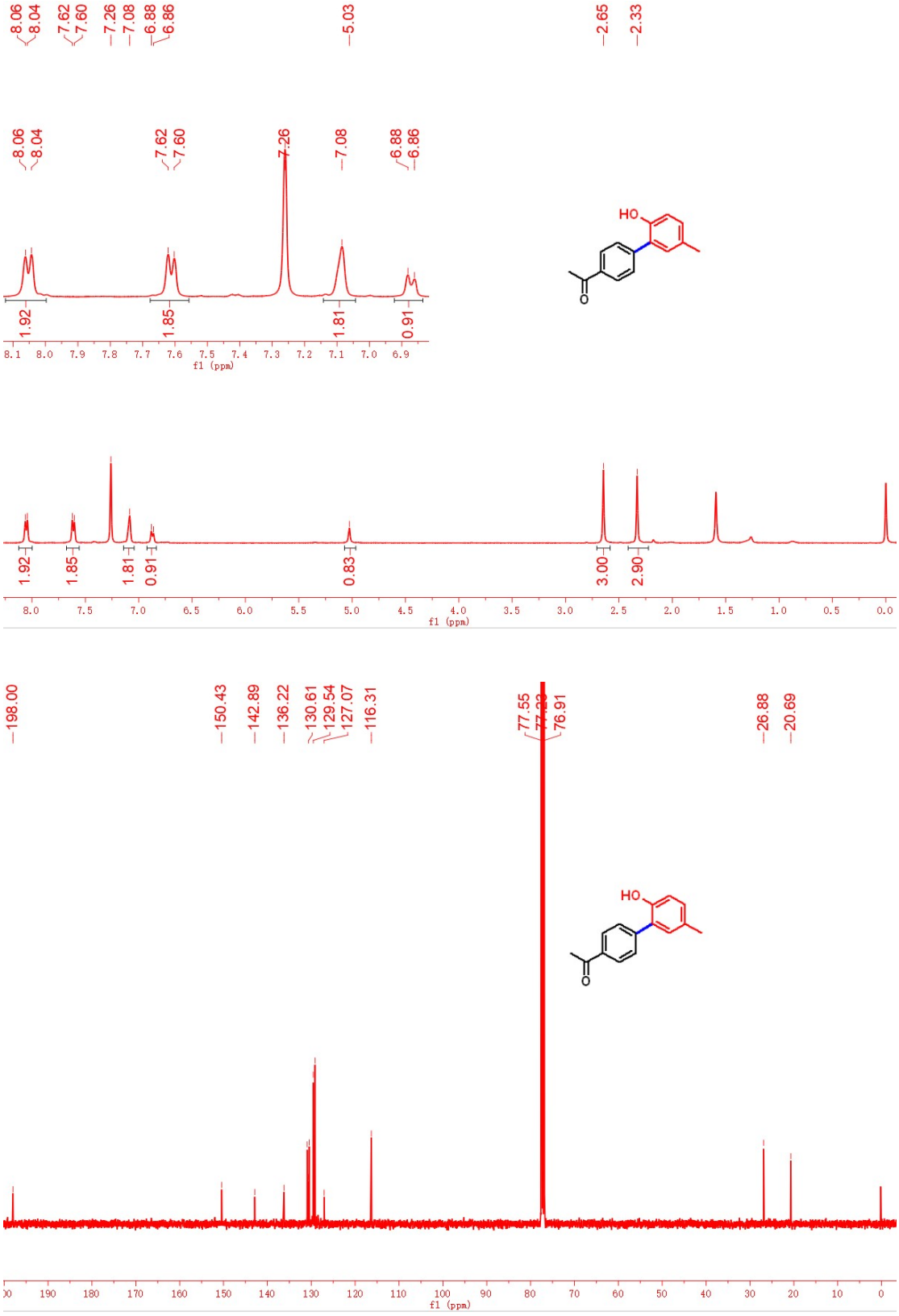


Figure S17. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(2'-hydroxy-5'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one (**3ai**) in $CDCl_3$

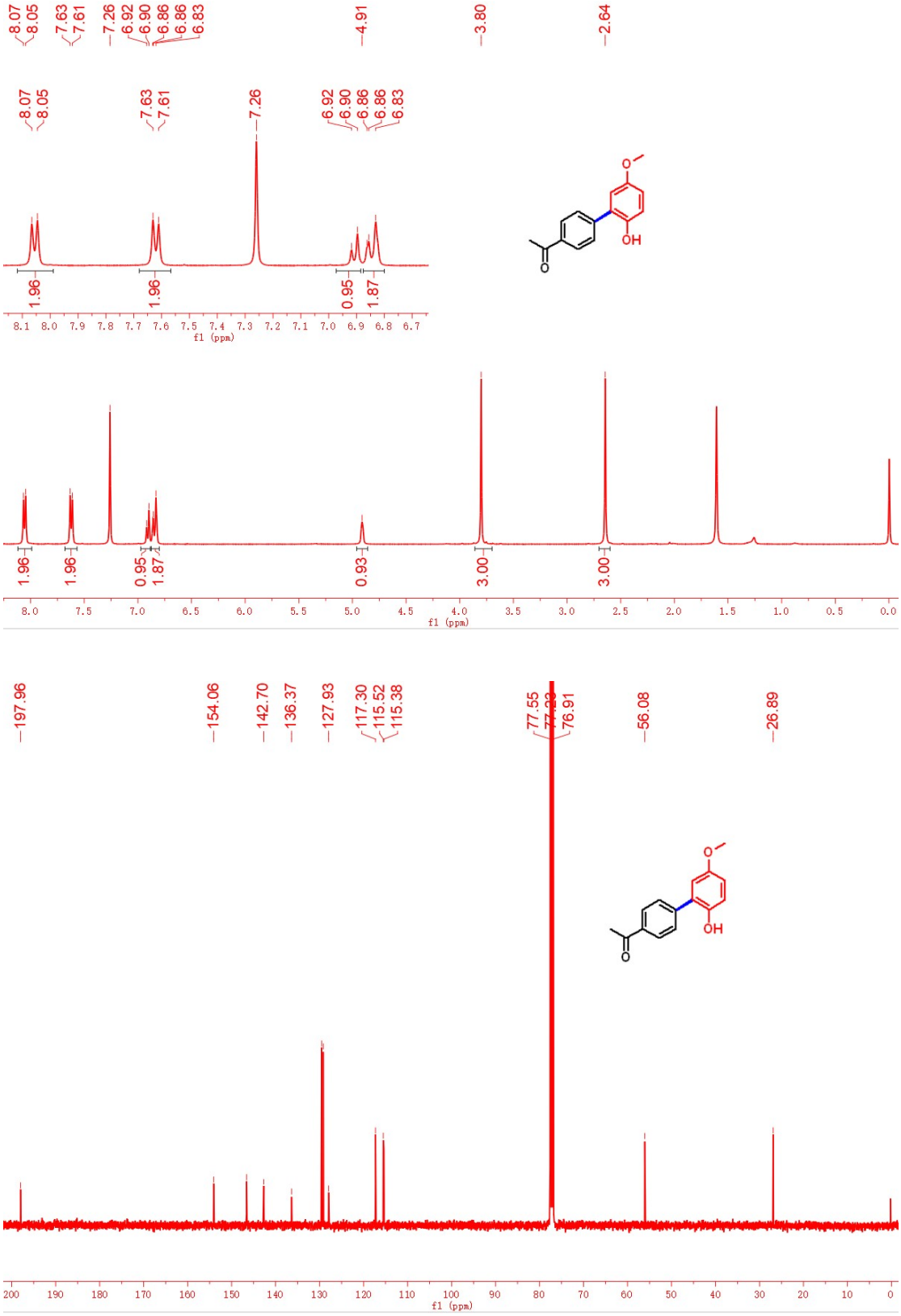


Figure S18. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(2'-hydroxy-5'-isopropyl-[1,1'-biphenyl]-4-yl)ethan-1-one (**3aj**) in $CDCl_3$

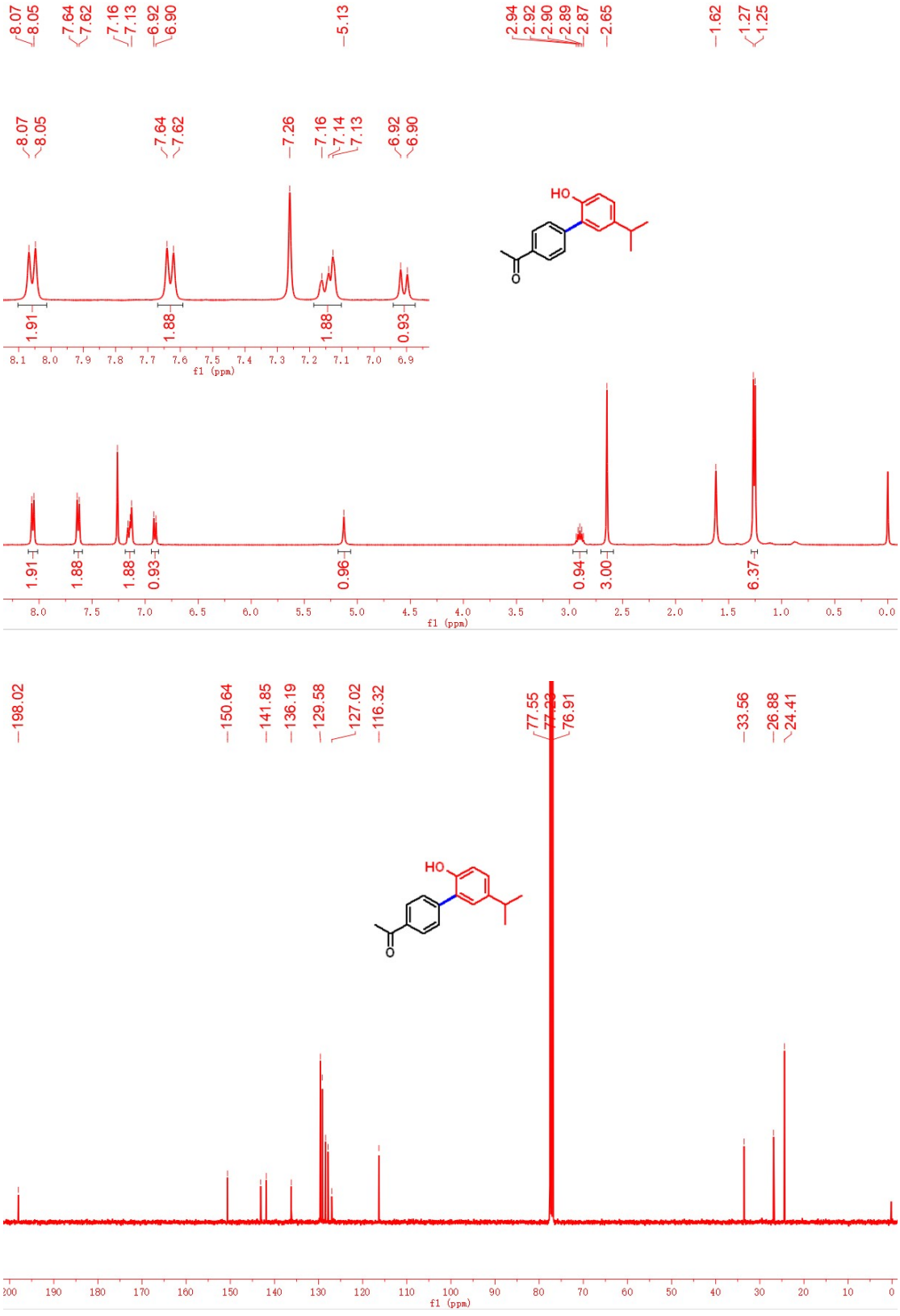


Figure S19. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(5'-(*tert*-butyl)-2'-hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (**3ak**) in $CDCl_3$

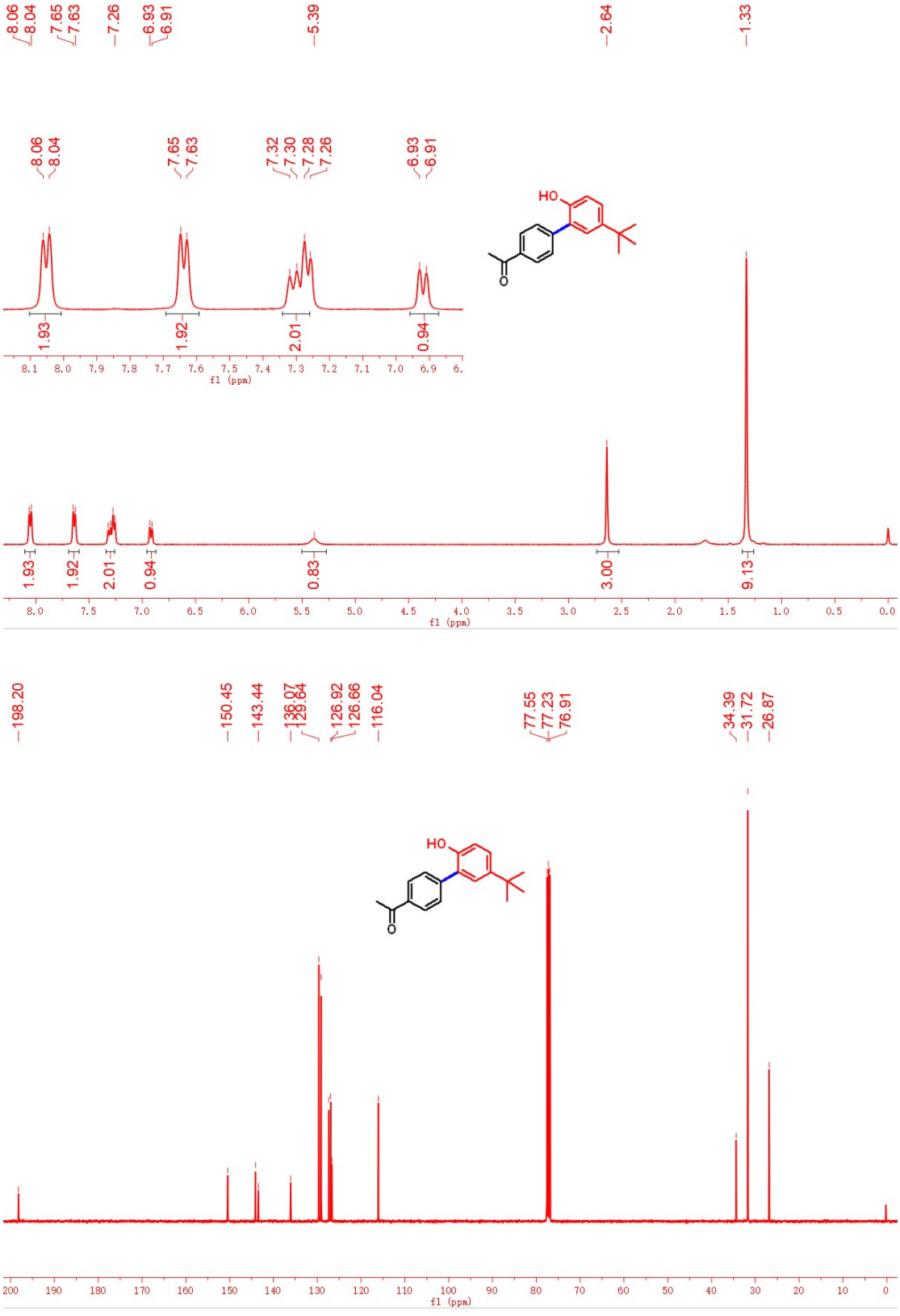


Figure S20. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(2'-hydroxy-5'-propyl-[1,1'-biphenyl]-4-yl)ethan-1-one (**3al**) in $CDCl_3$

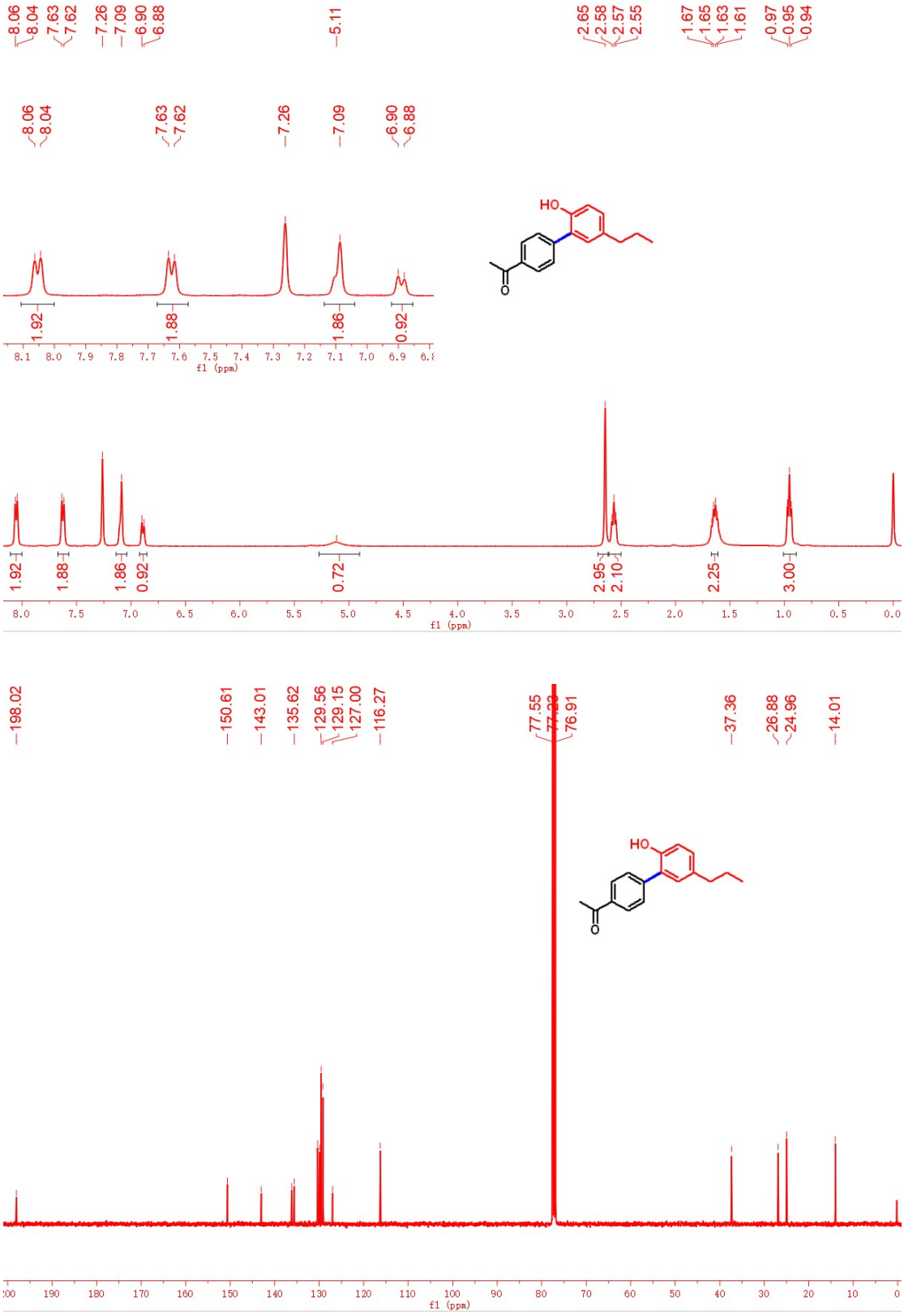


Figure S21. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(3',5'-dichloro-2'-hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (**3am**) in $CDCl_3$

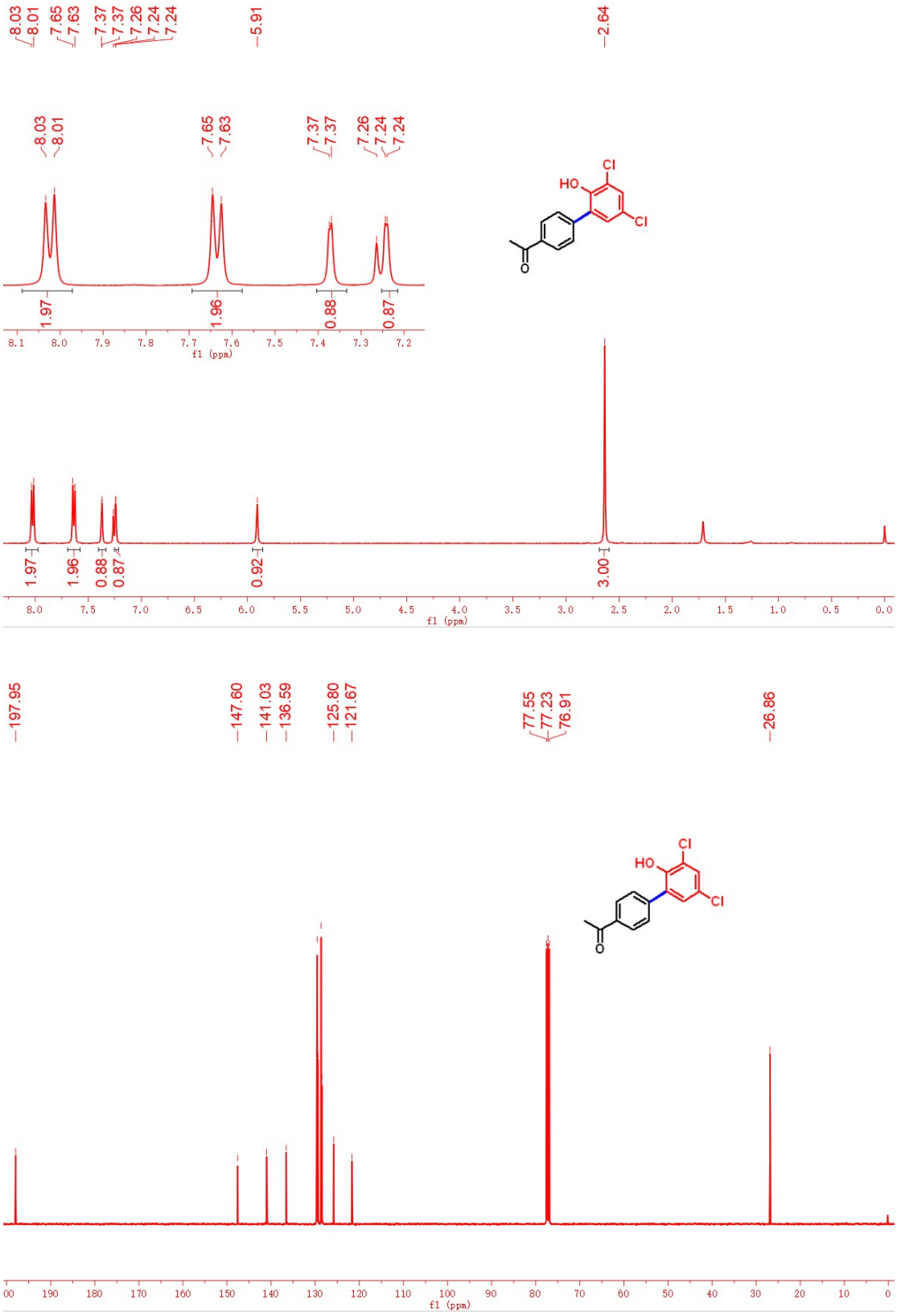


Figure S22. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(3'-chloro-2'-hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (**3an**) in $CDCl_3$

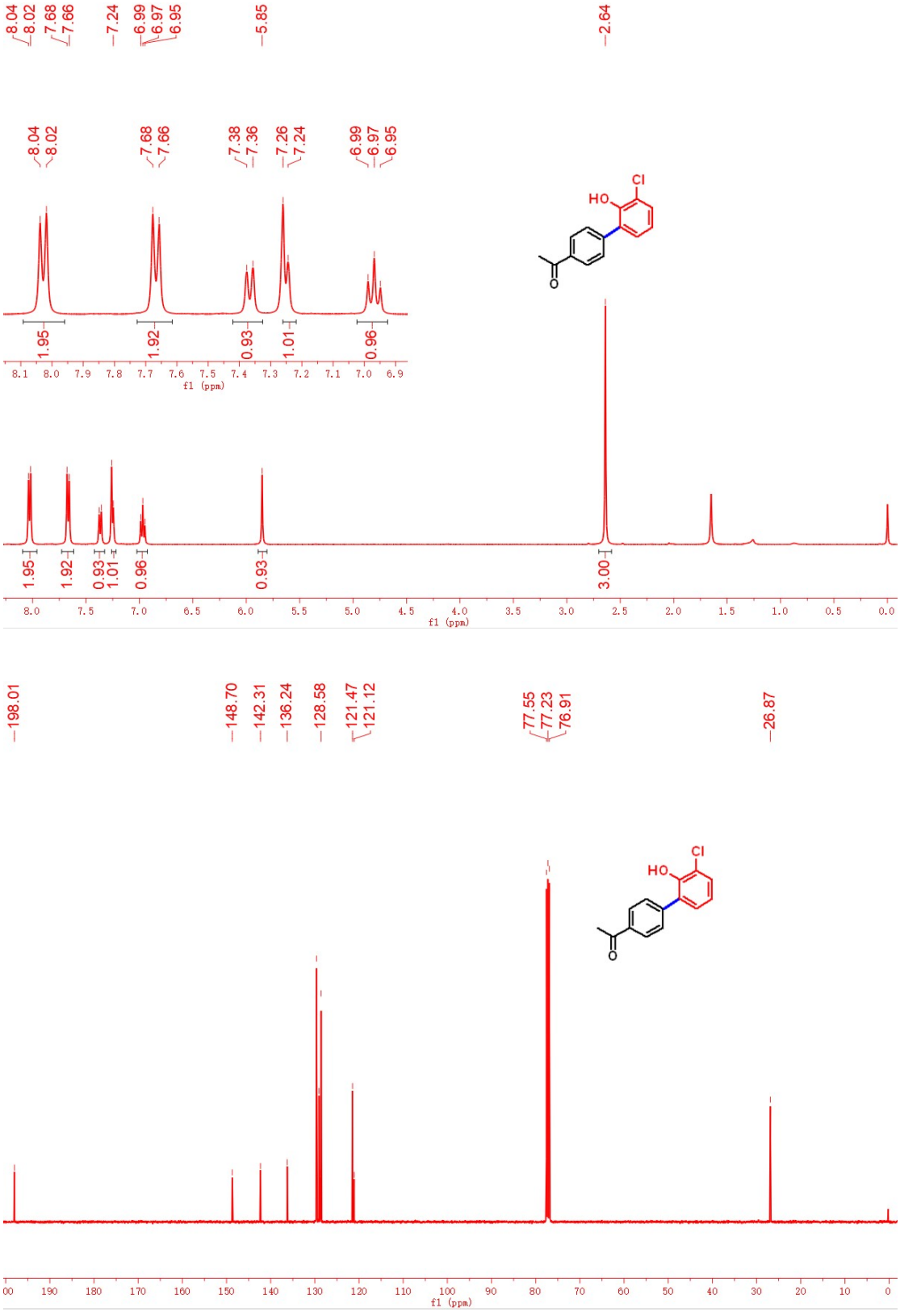


Figure S23. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1,1'-(2-hydroxy-[1,1'-biphenyl]-3,4'-diyl)bis(ethan-1-one) (**3ao**) in $CDCl_3$

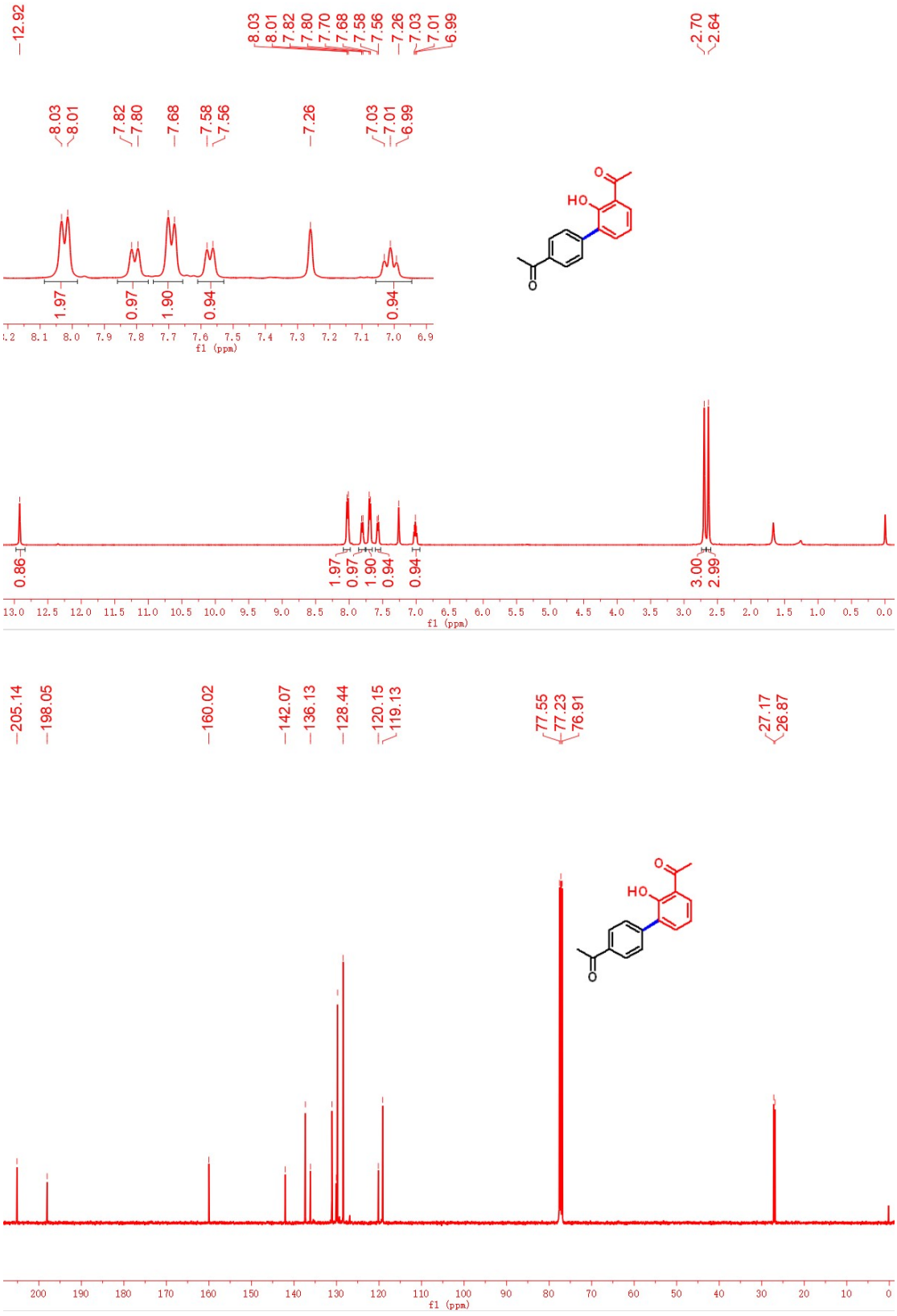


Figure S24. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 4'-acetyl-2-hydroxy-[1,1'-biphenyl]-3-carboxylate (**3ap**) in $CDCl_3$

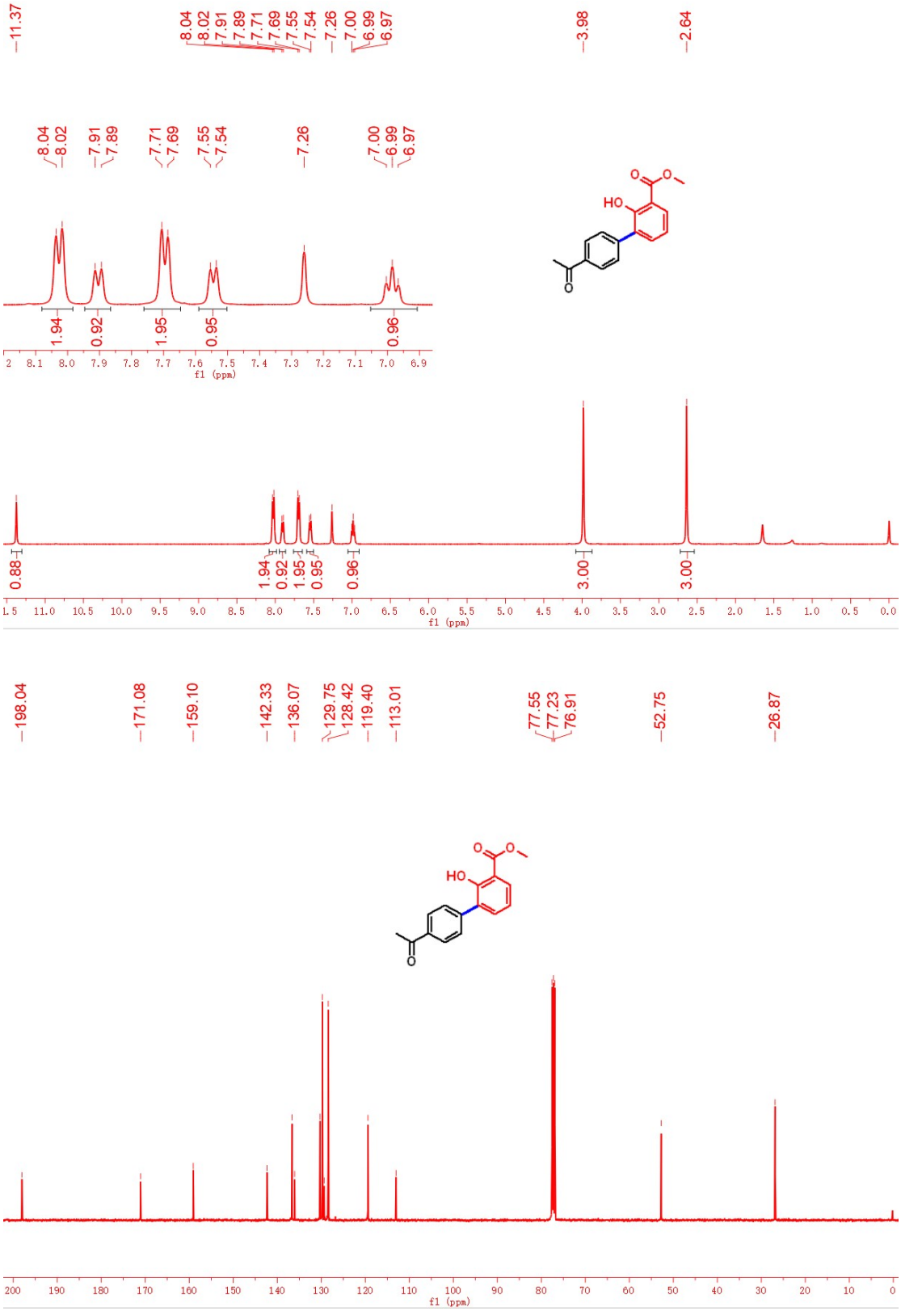
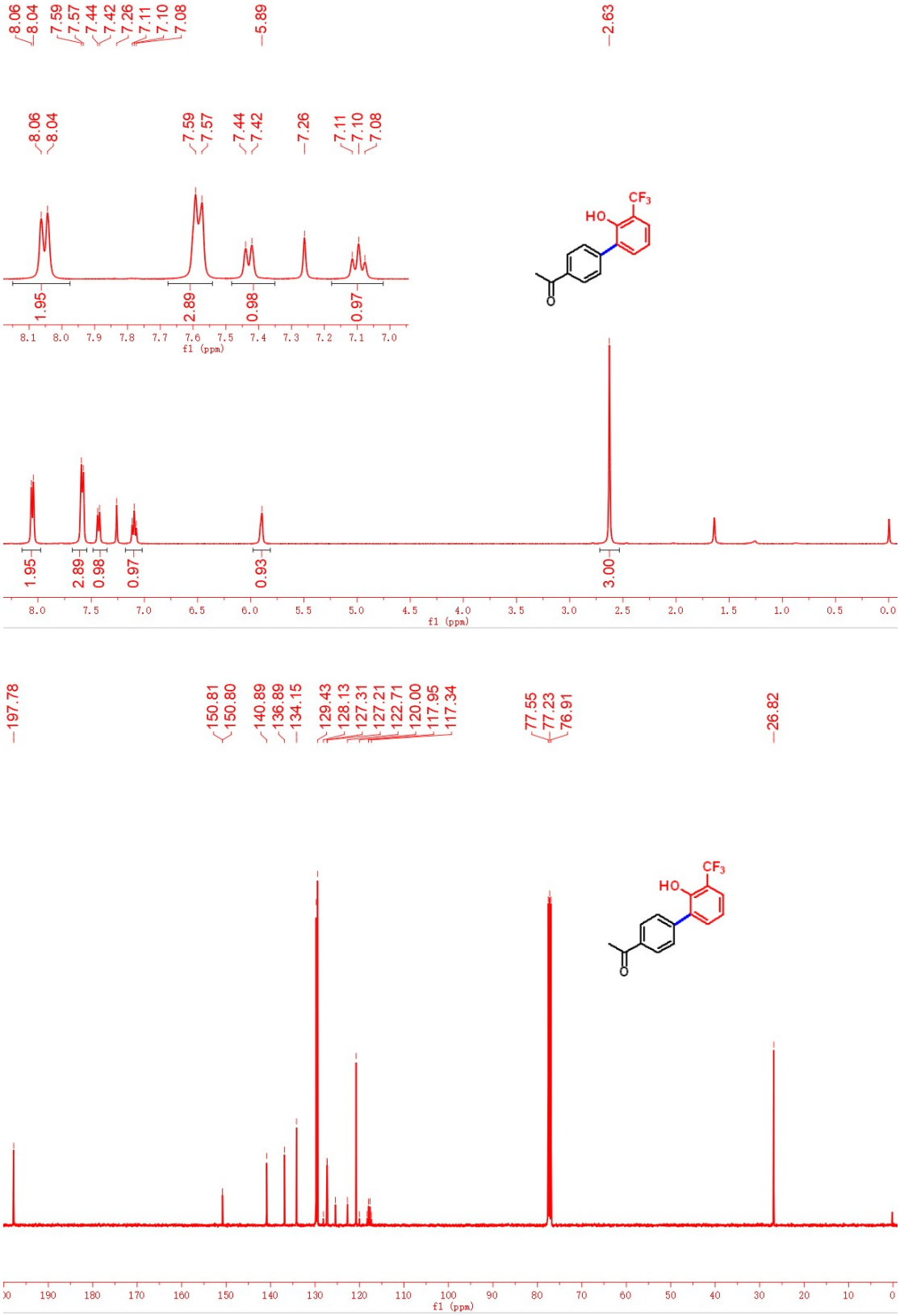


Figure S25. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F NMR (377 MHz) NMR spectra for 1-(2'-hydroxy-3'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (**3aq**) in $CDCl_3$



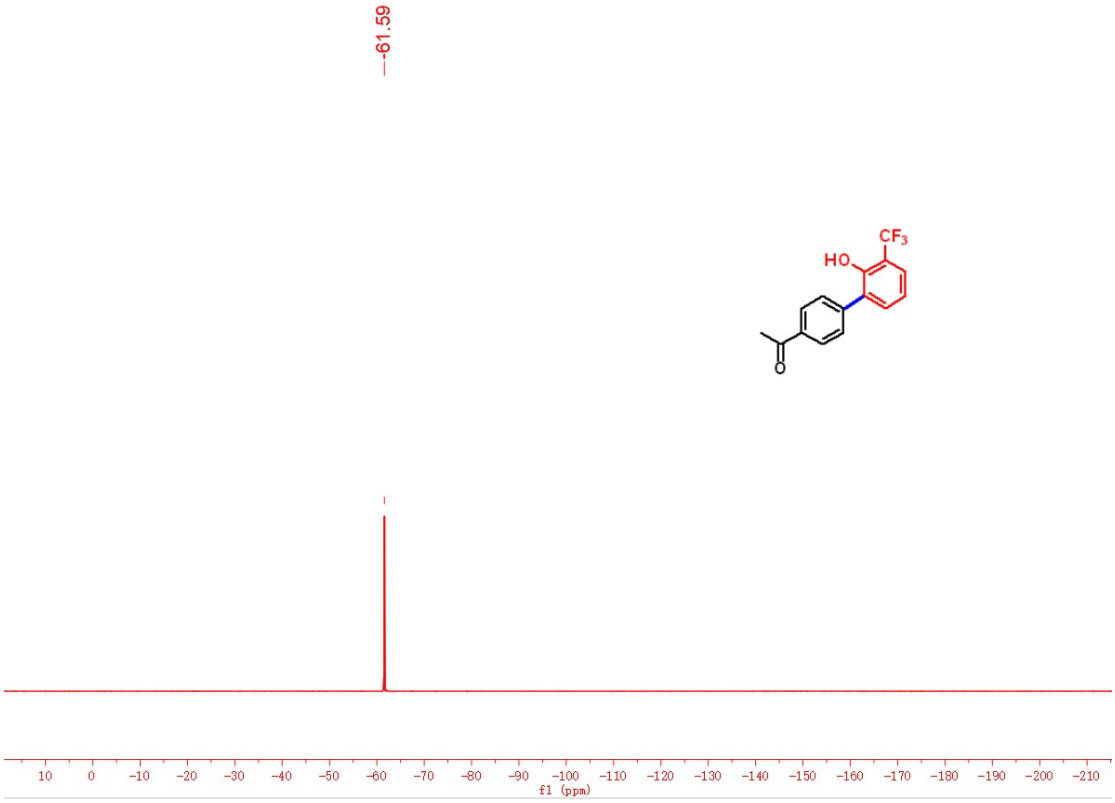
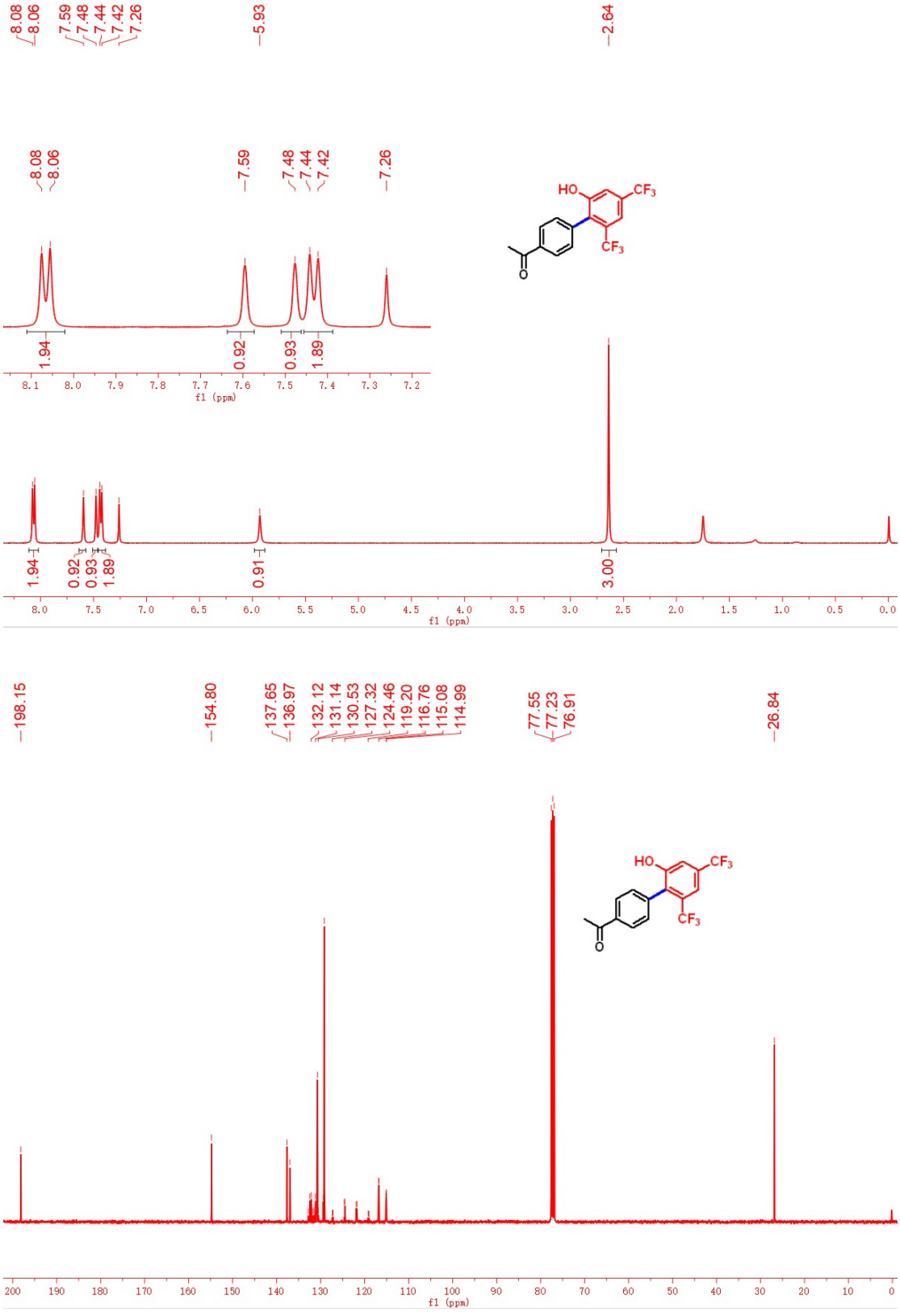

-61.59
CF3
HO
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Figure S26. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F NMR (377 MHz) NMR spectra for 1-(2'-hydroxy-4',6'-bis(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethan-1-one (**3ar**) in $CDCl_3$



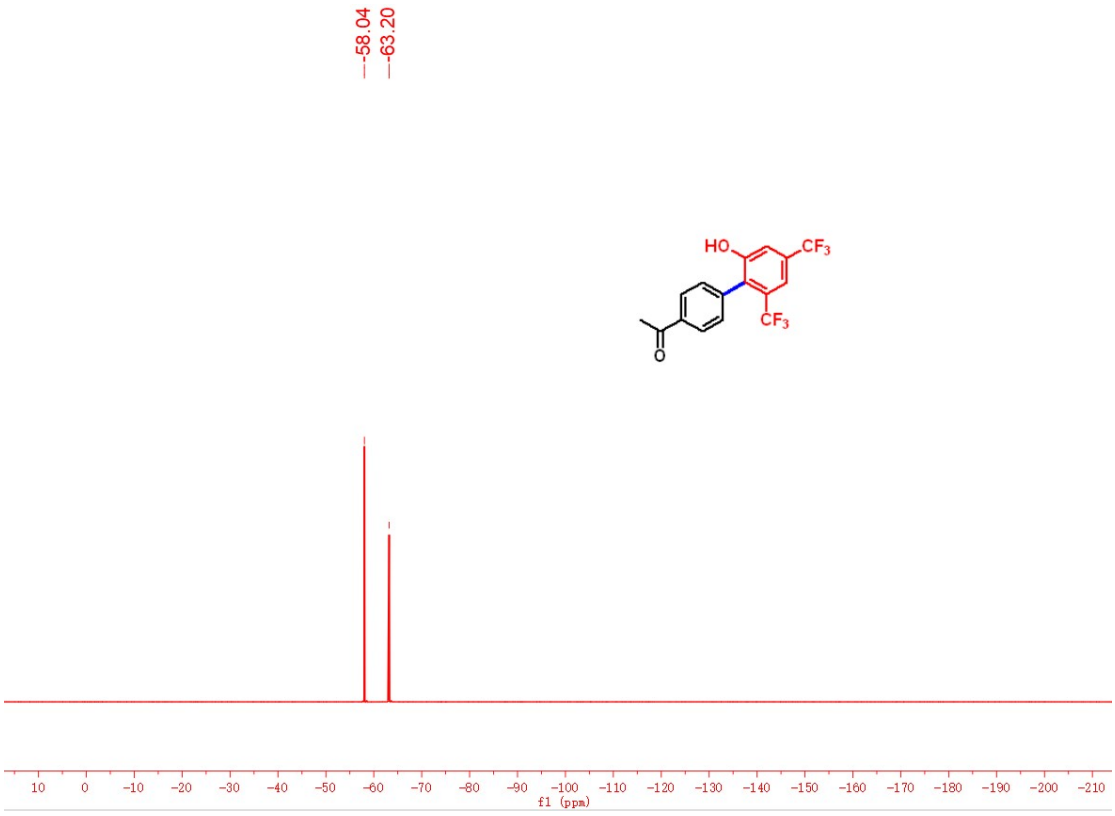

-58.04
-63.20
HO
CF3
CF3
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Figure S27. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(2',4'-dibromo-6'-hydroxy-[1,1'-biphenyl]-4-yl)ethan-1-one (**3as**) in $CDCl_3$

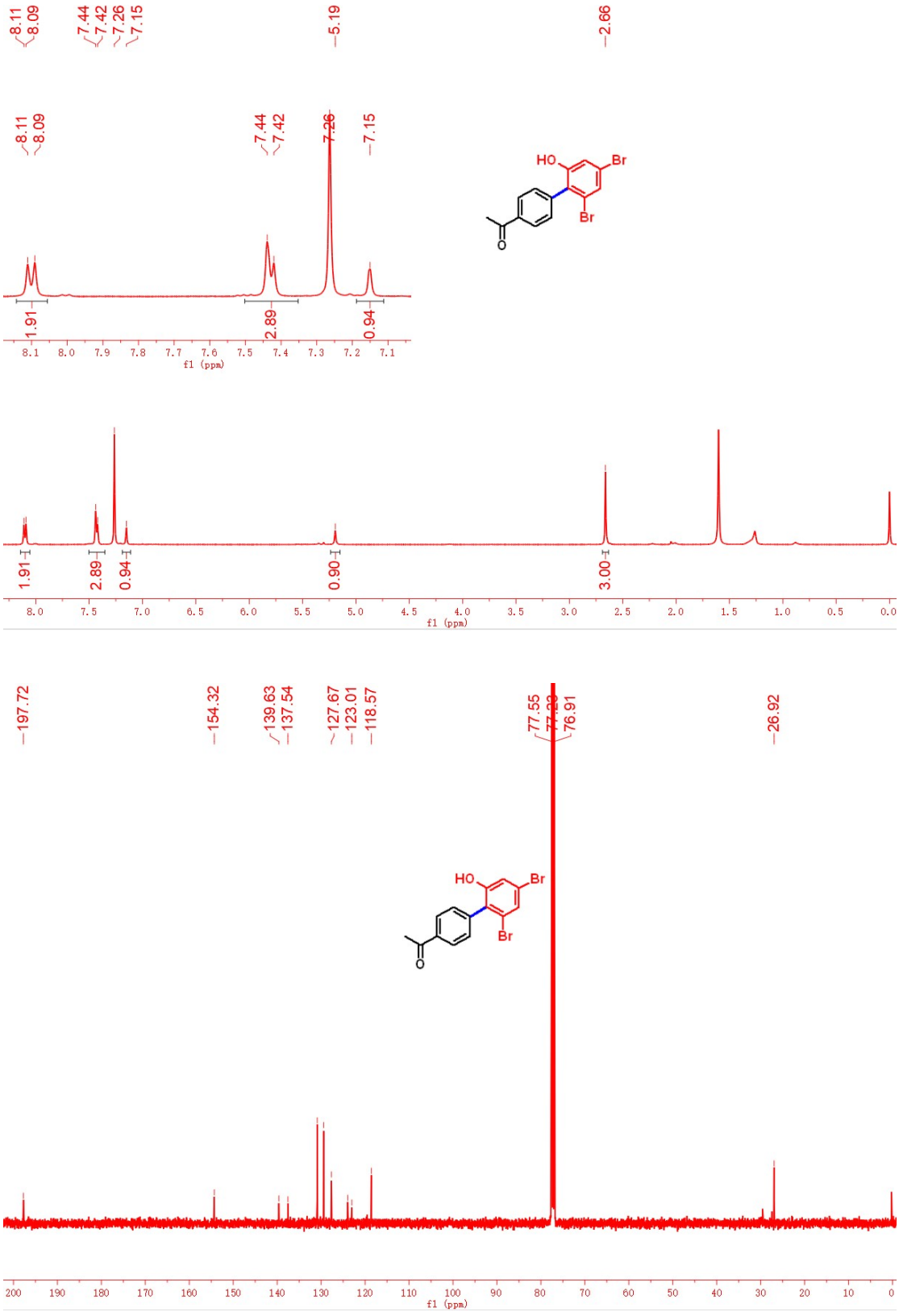


Figure S28. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(4-(2-hydroxynaphthalen-1-yl)phenyl)ethan-1-one (**3at**) in $CDCl_3$

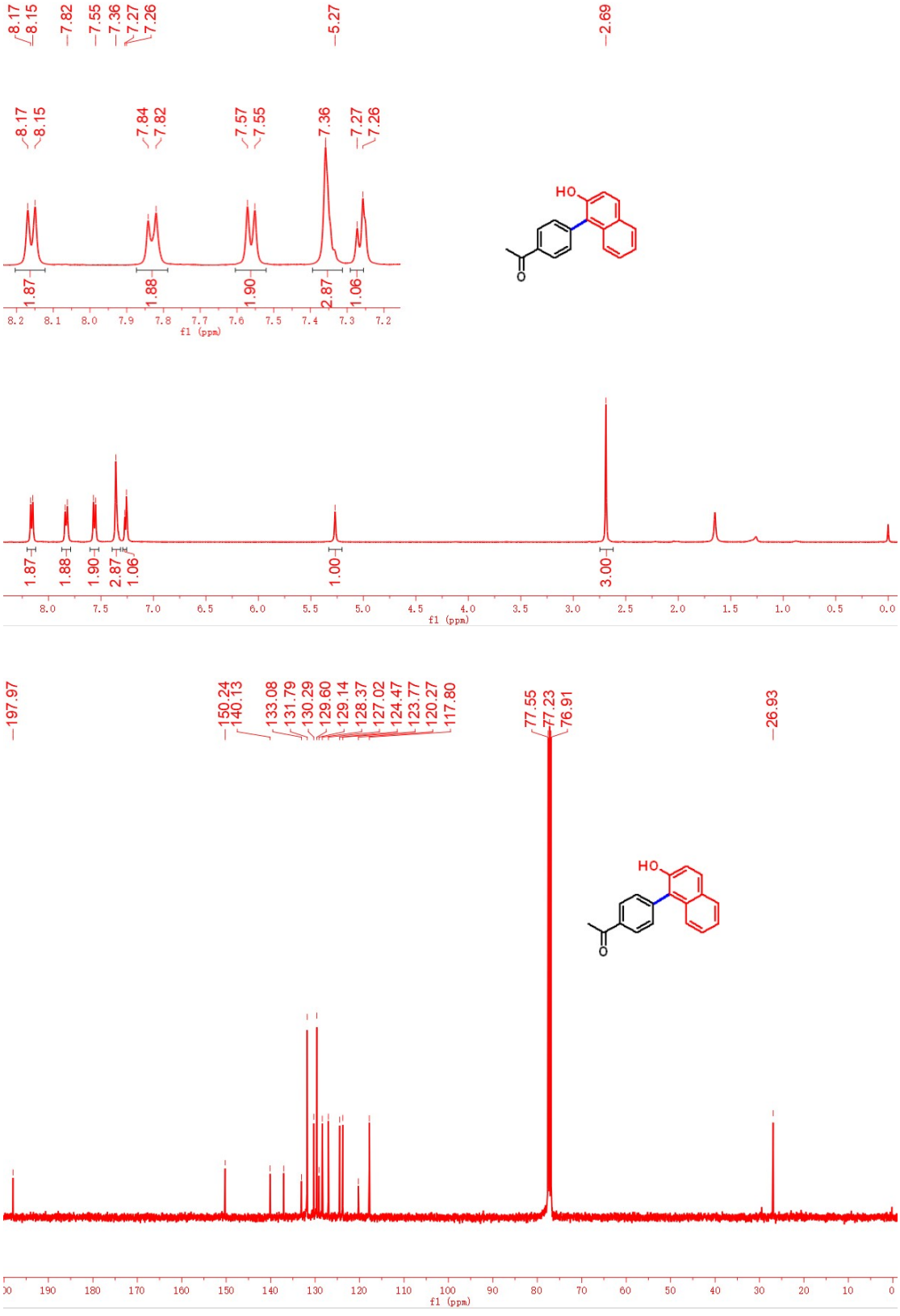


Figure S29. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 6-hydroxy-4'-propionyl-[1,1'-biphenyl]-3-carboxylate (**3be**) in $CDCl_3$

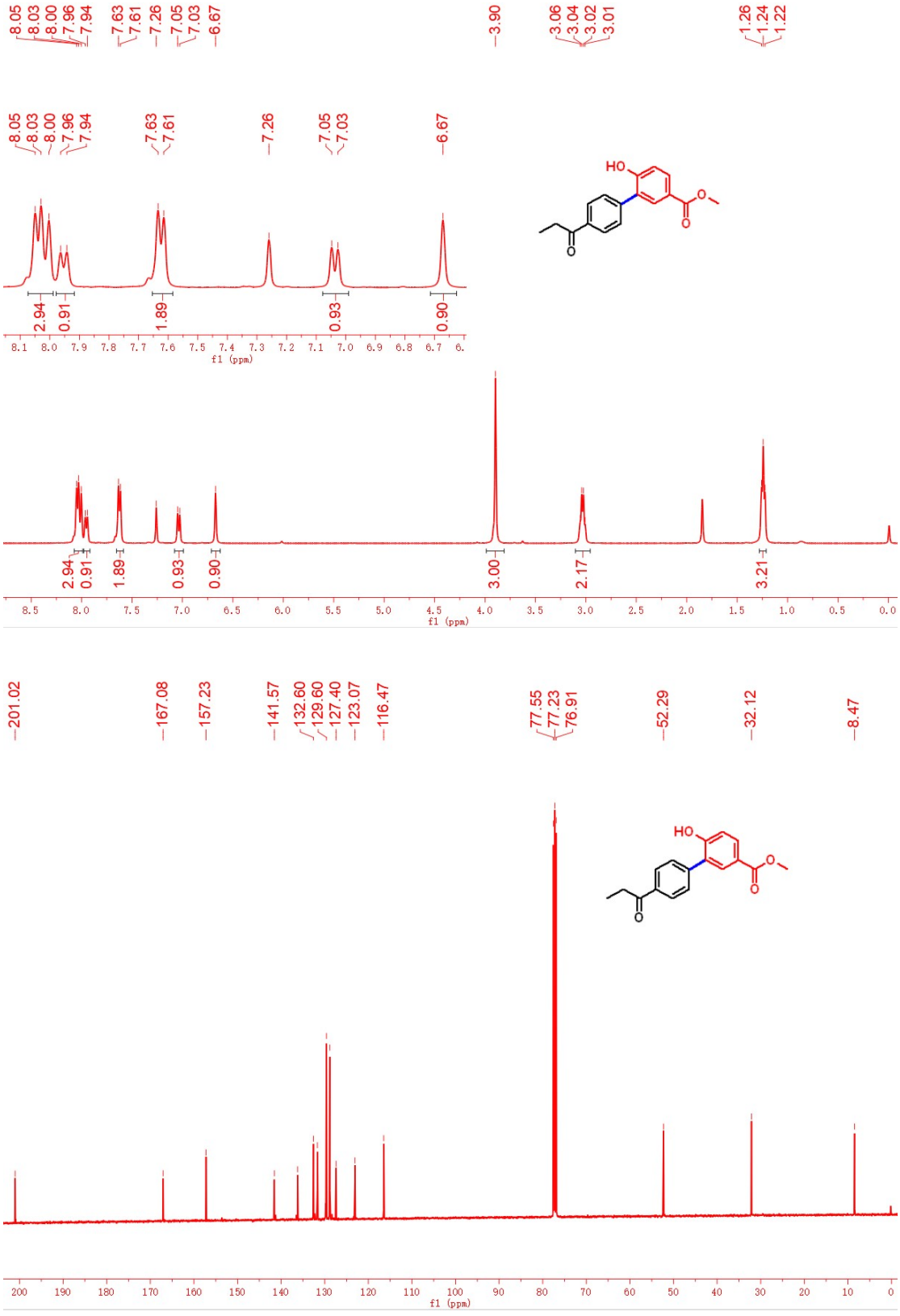


Figure S30. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 4'-butyryl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (**3ce**) in $CDCl_3$

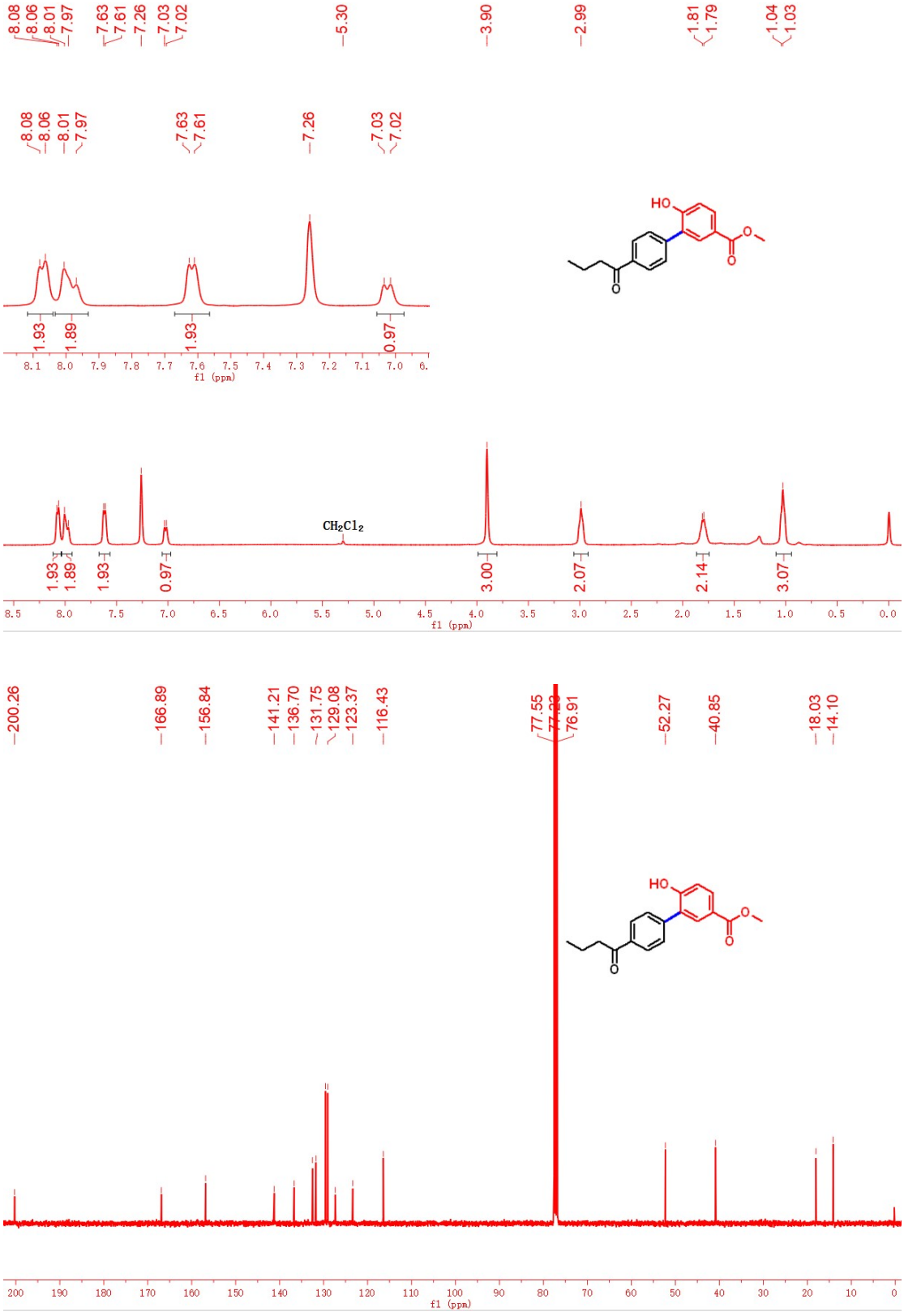


Figure S31. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 6-hydroxy-4'-pentanoyl-[1,1'-biphenyl]-3-carboxylate (**3de**) in $CDCl_3$

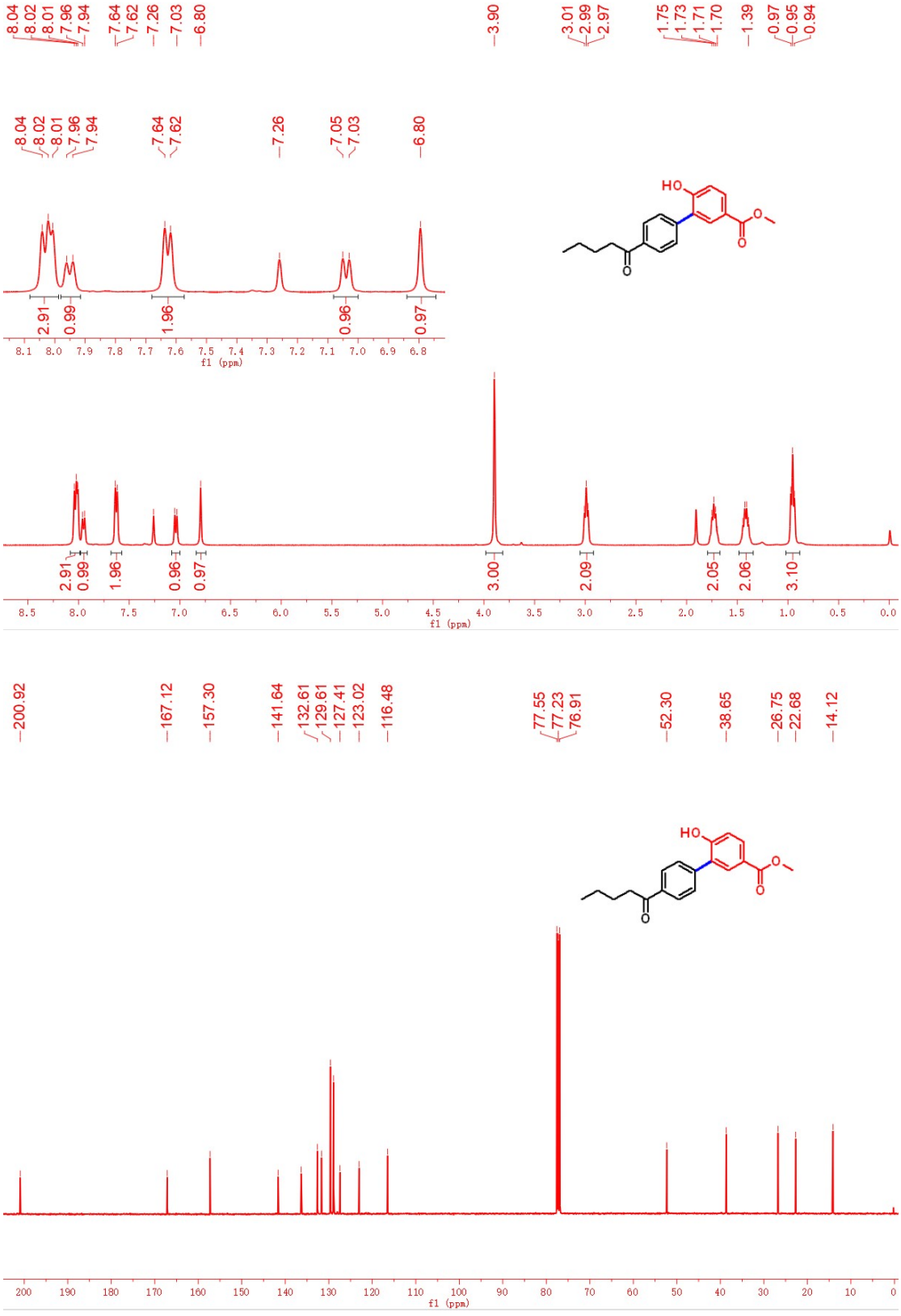


Figure S32. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 4'-benzoyl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (**3ee**) in $CDCl_3$

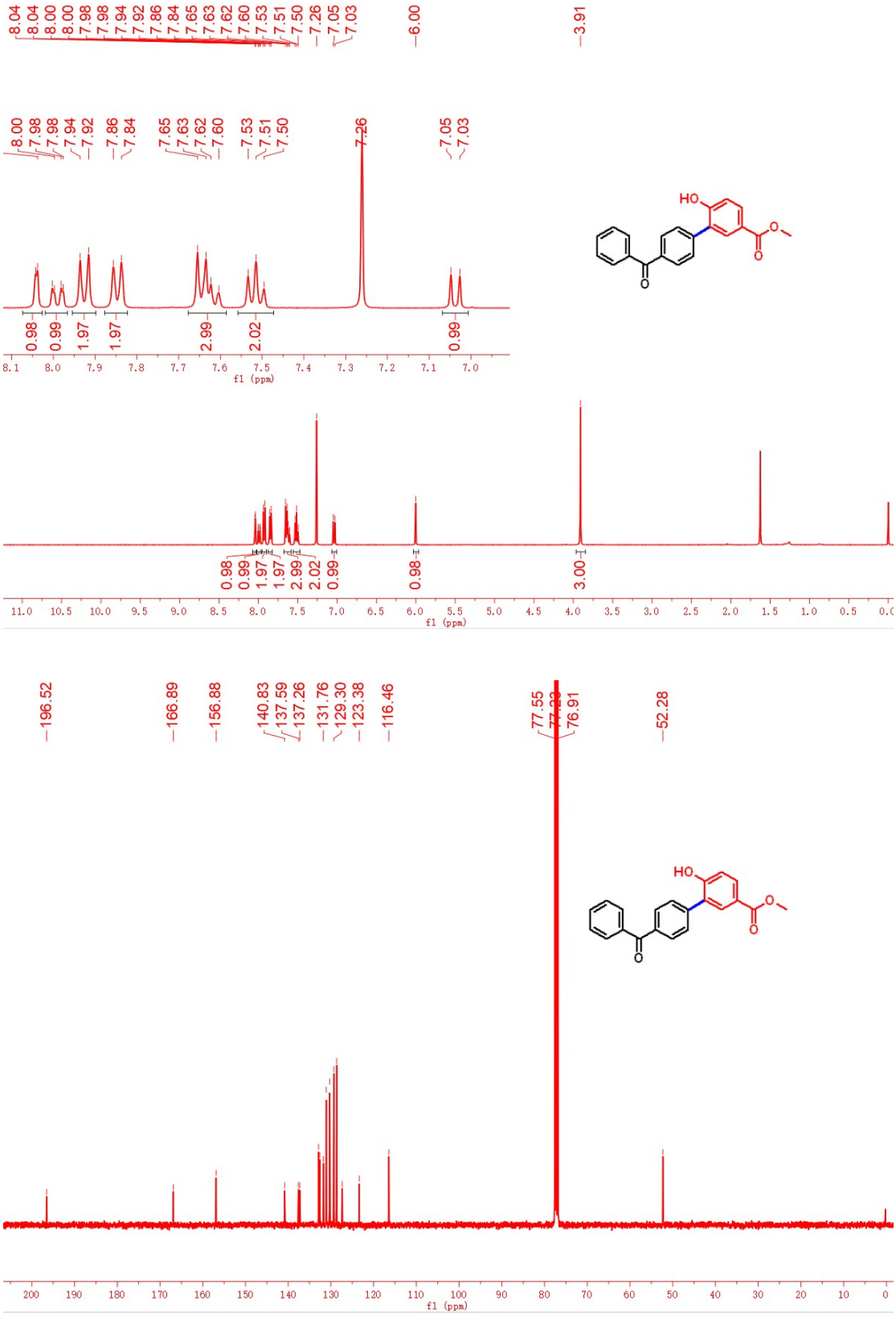


Figure S33. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 4'-(cyclopropanecarbonyl)-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (**3fe**) in $CDCl_3$

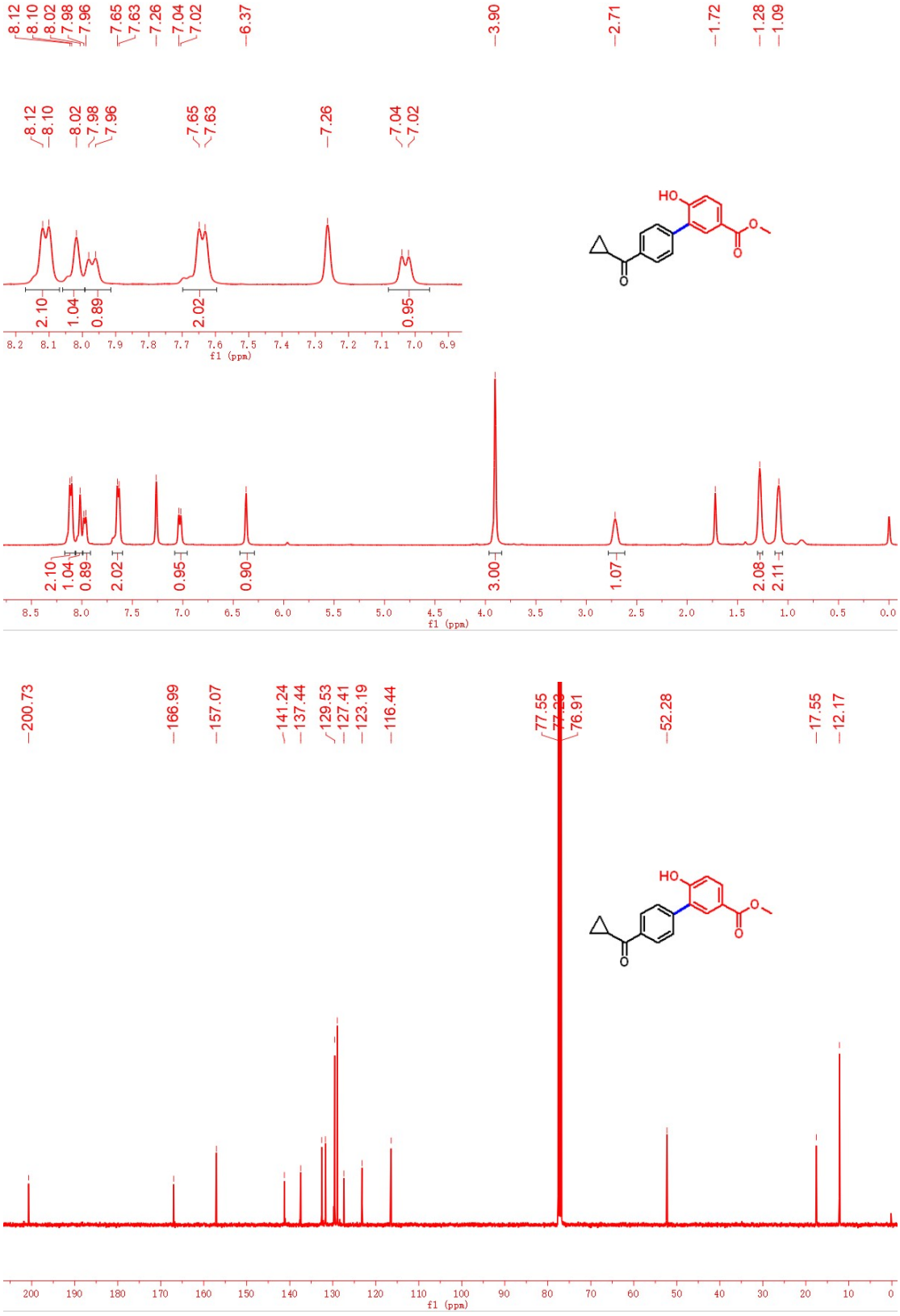


Figure S34. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(5'-acetyl-2'-hydroxy-[1,1'-biphenyl]-4-yl)propan-1-one (**3bc**) in $CDCl_3$

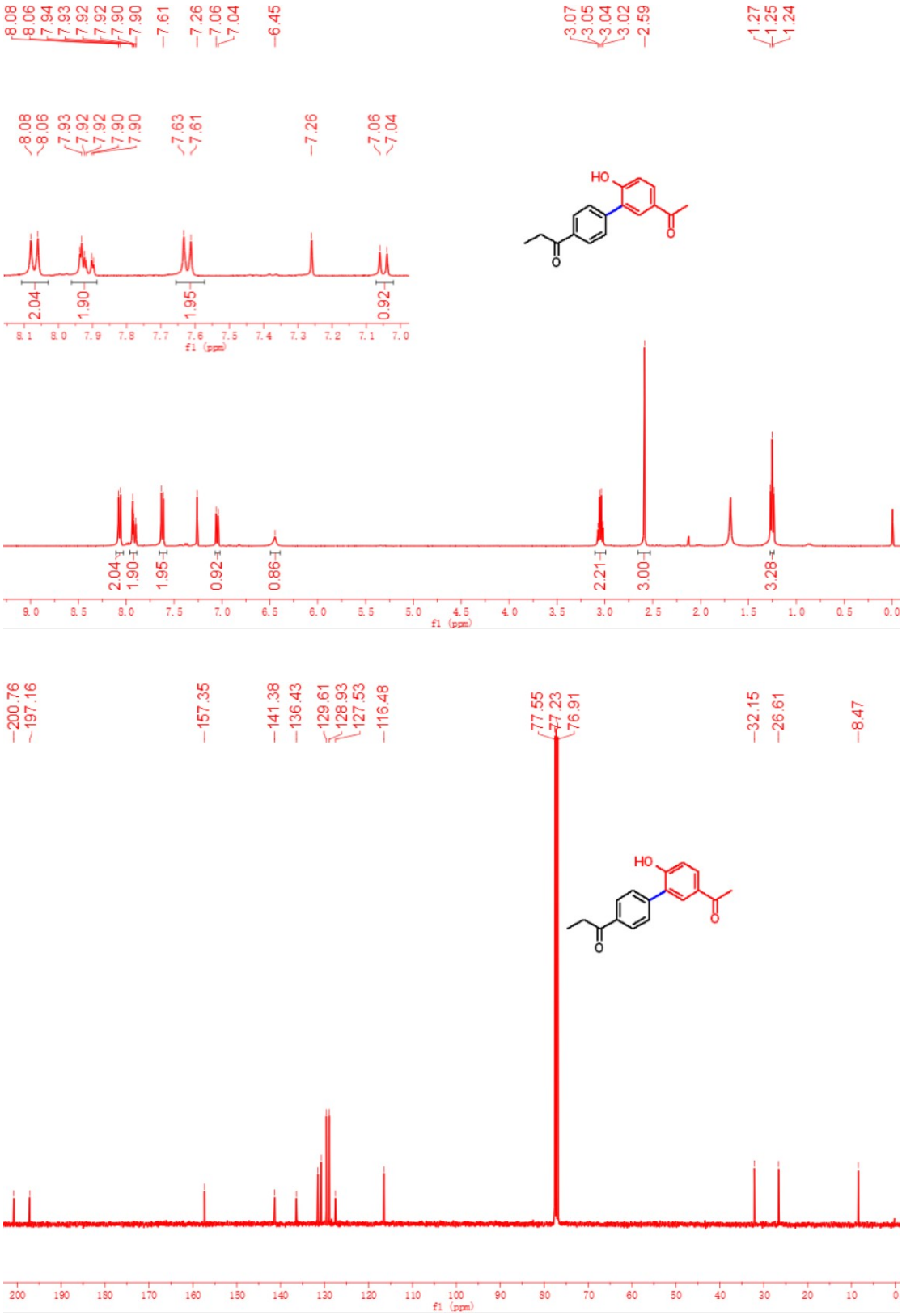


Figure S35. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(4'-benzoyl-6-hydroxy-[1,1'-biphenyl]-3-yl)ethan-1-one (**3ec**) in $CDCl_3$

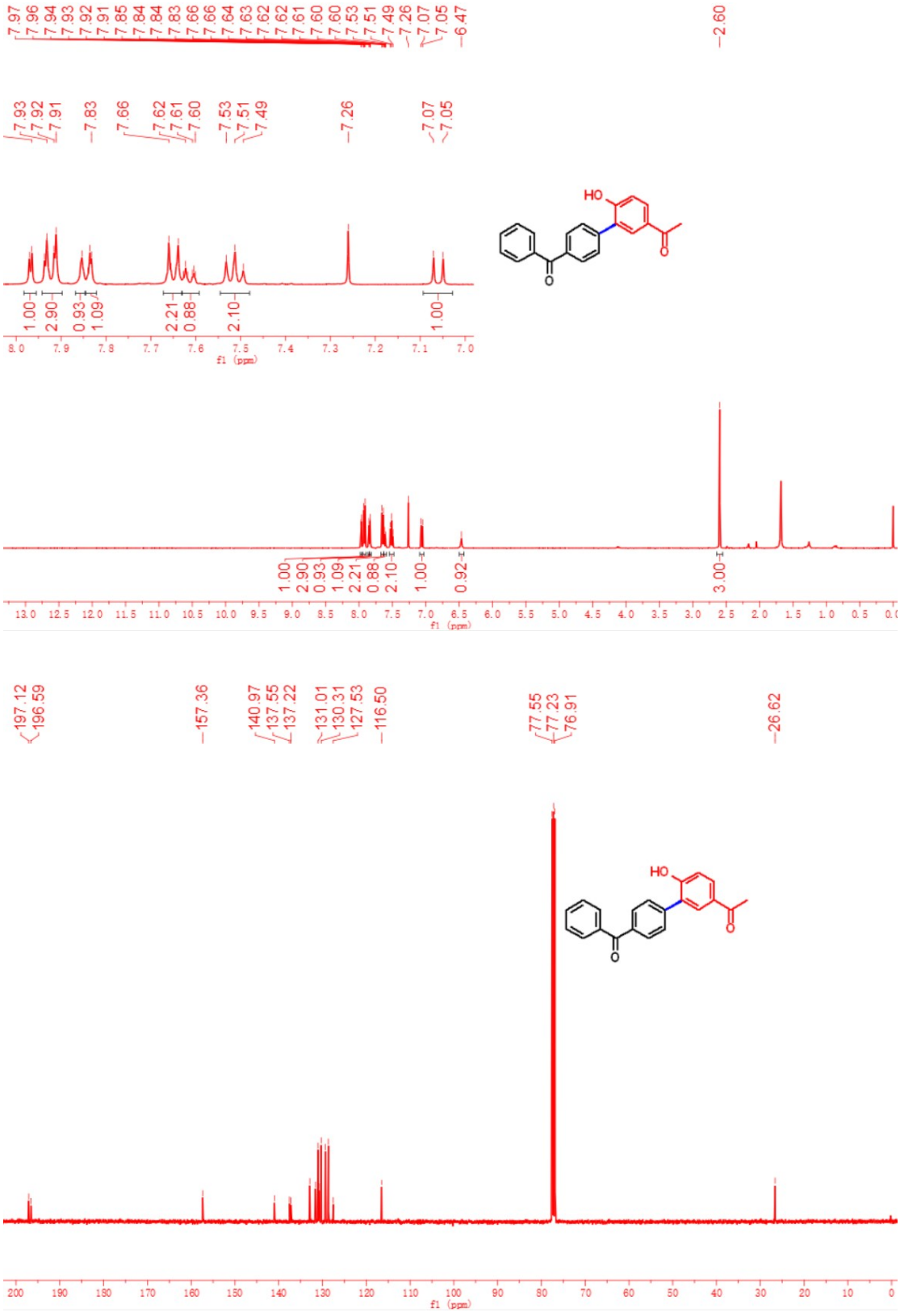
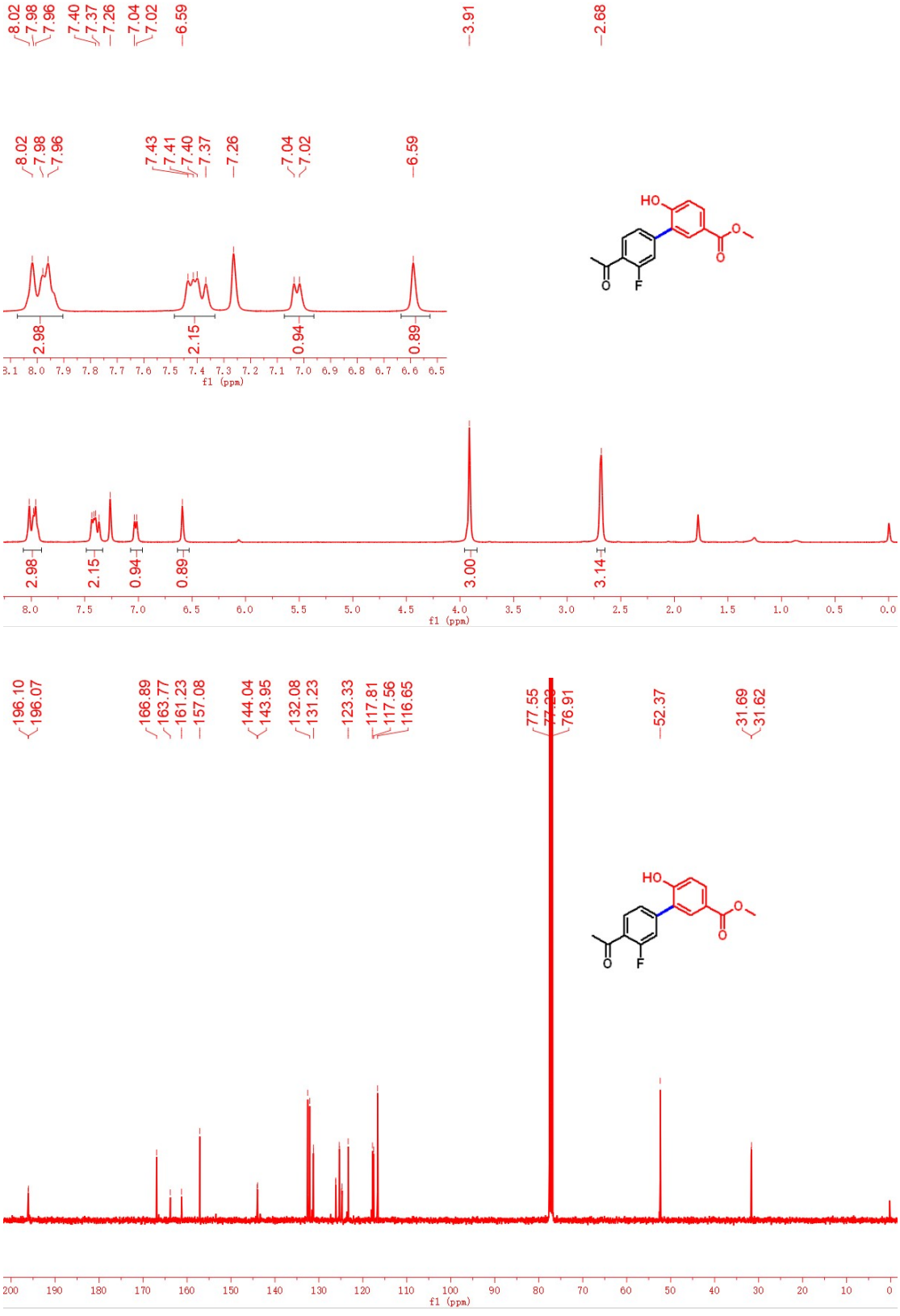


Figure S36. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F (377 MHz) NMR spectra for methyl 4'-acetyl-3'-fluoro-6-hydroxy-[1,1'-biphenyl]-3-carboxylate **(3ge)** in $CDCl_3$



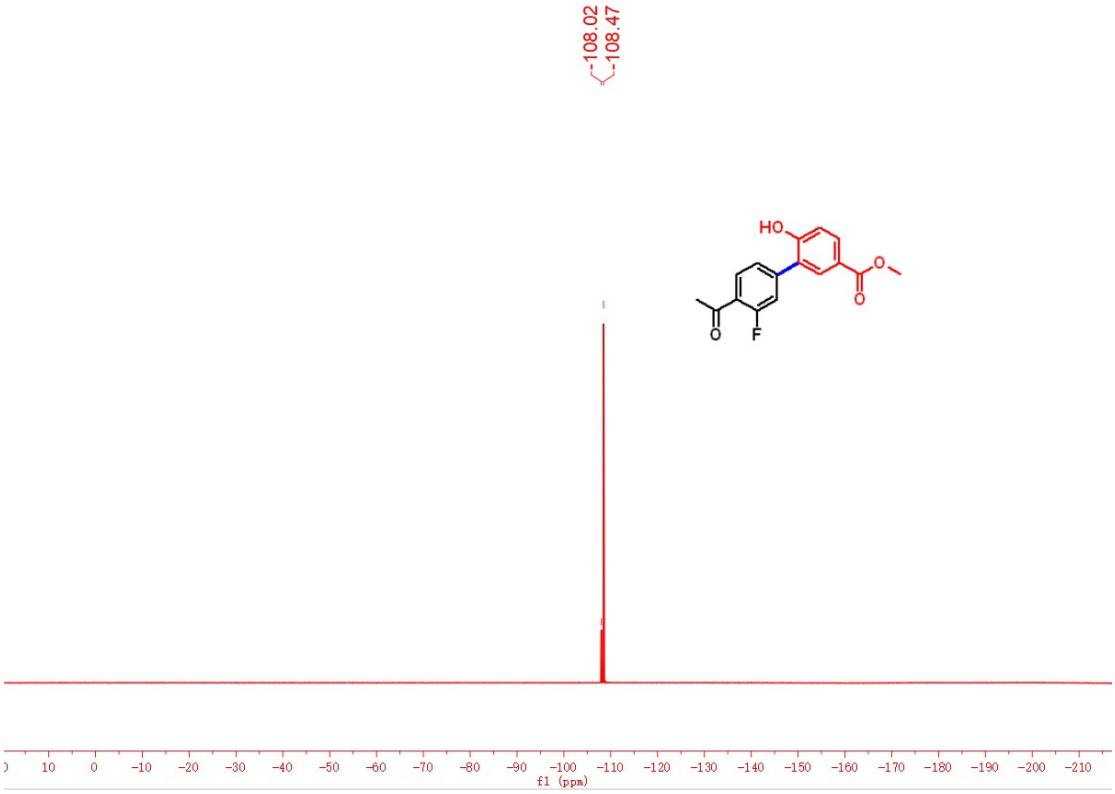

-108.02
-108.47
HO
O
O
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

Figure S37. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 4'-acetyl-3'-chloro-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (**3he**) in $CDCl_3$

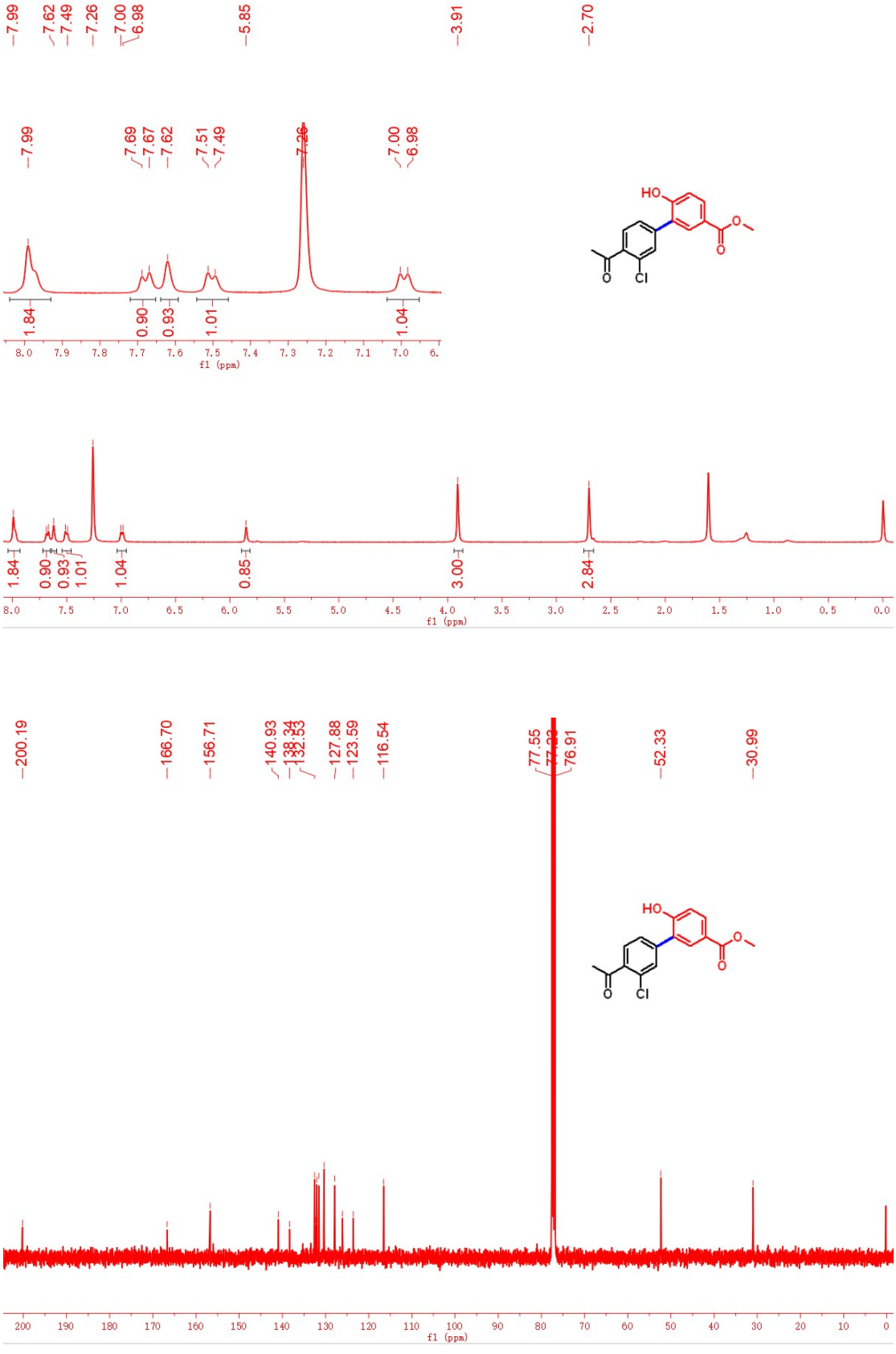


Figure S38. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 2'-hydroxy-[1,1'-biphenyl]-4-carbaldehyde (**3ia**) in $CDCl_3$

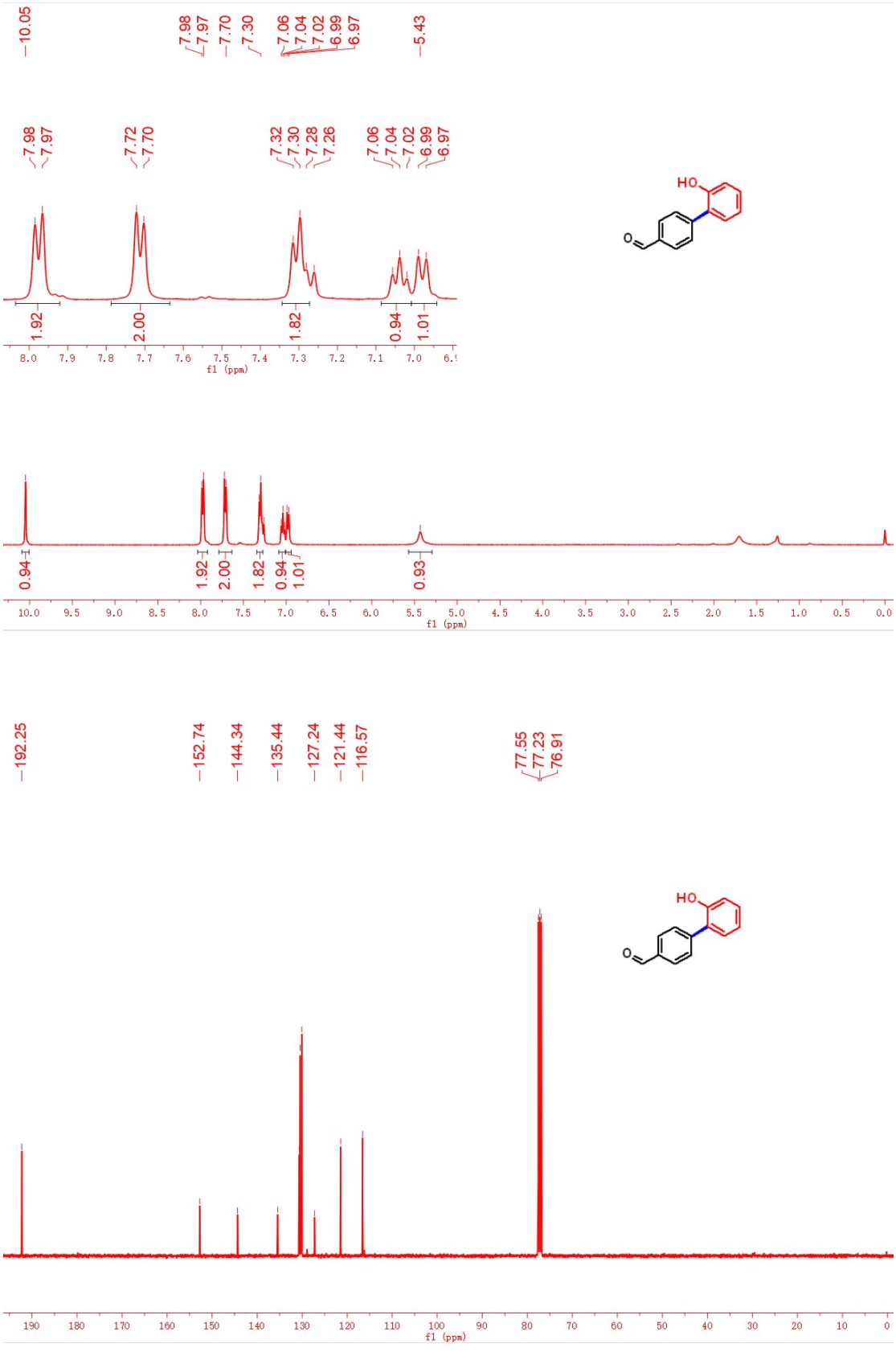


Figure S39. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 4'-formyl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (**3ie**) in $CDCl_3$

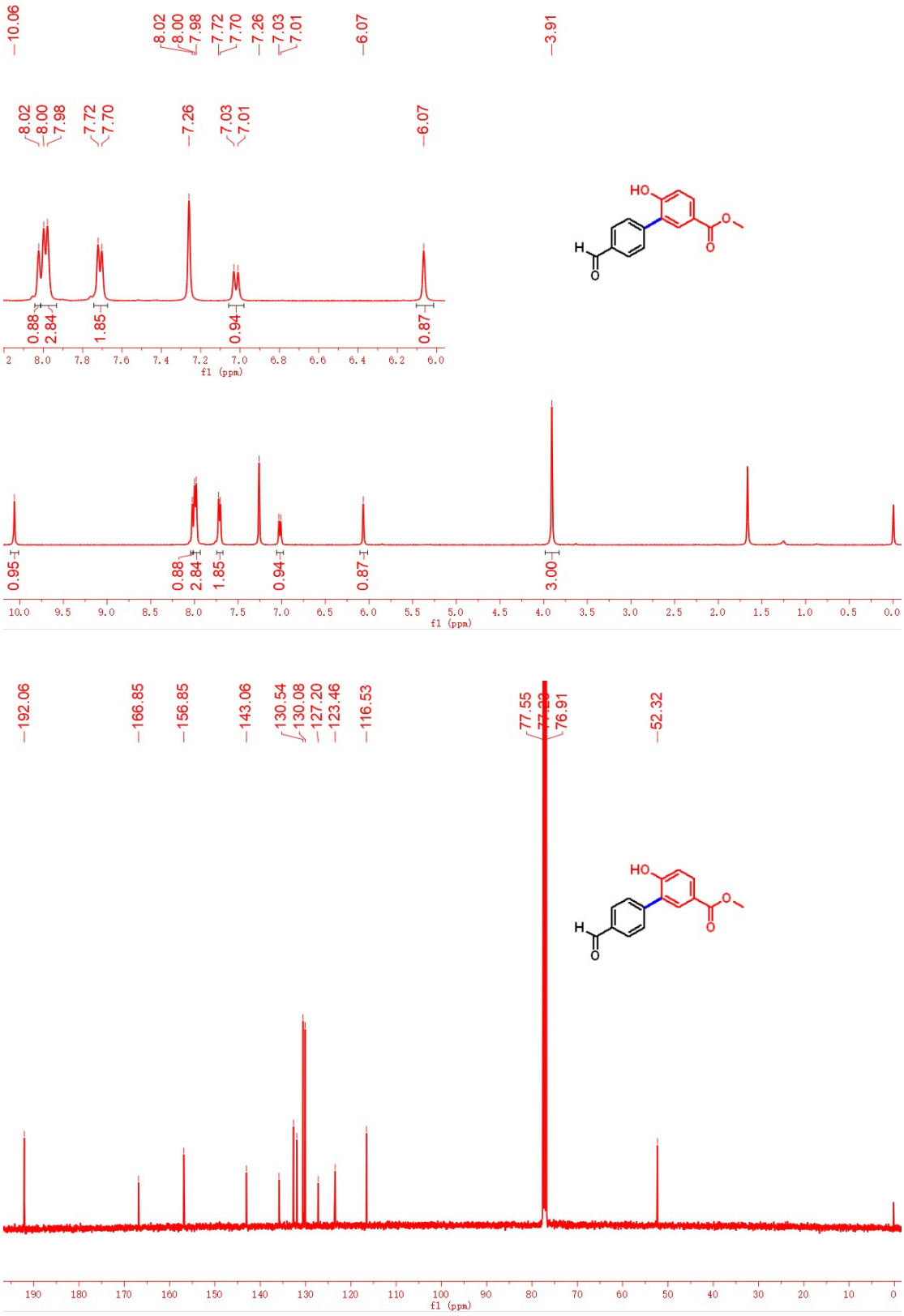


Figure S40. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for methyl 3'-acetyl-6-hydroxy-[1,1'-biphenyl]-3-carboxylate (**3je**) in $CDCl_3$

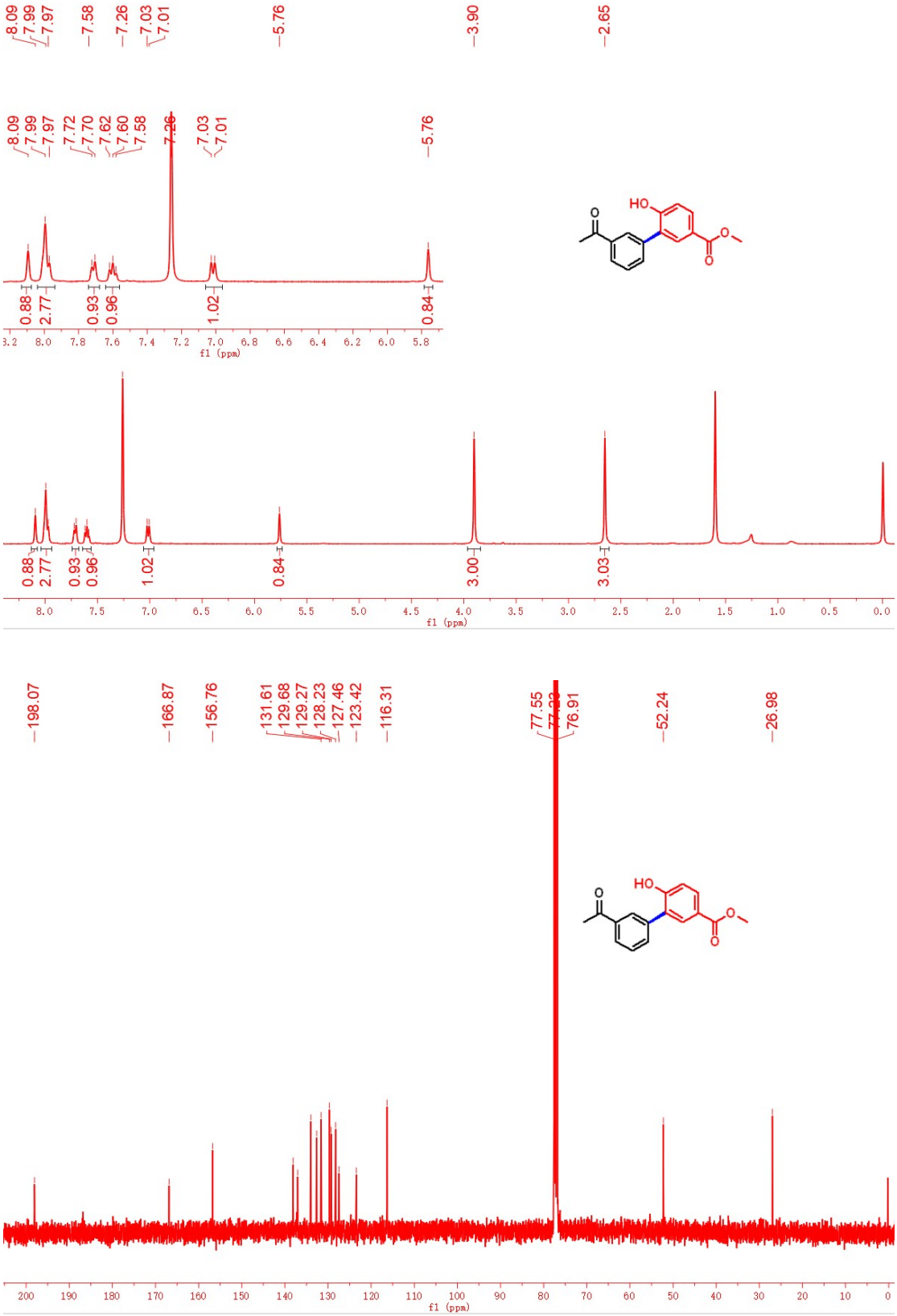


Figure S41. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 5'-acetyl-2'-hydroxy-[1,1'-biphenyl]-3-carbonitrile (**3kc**) in $CDCl_3$

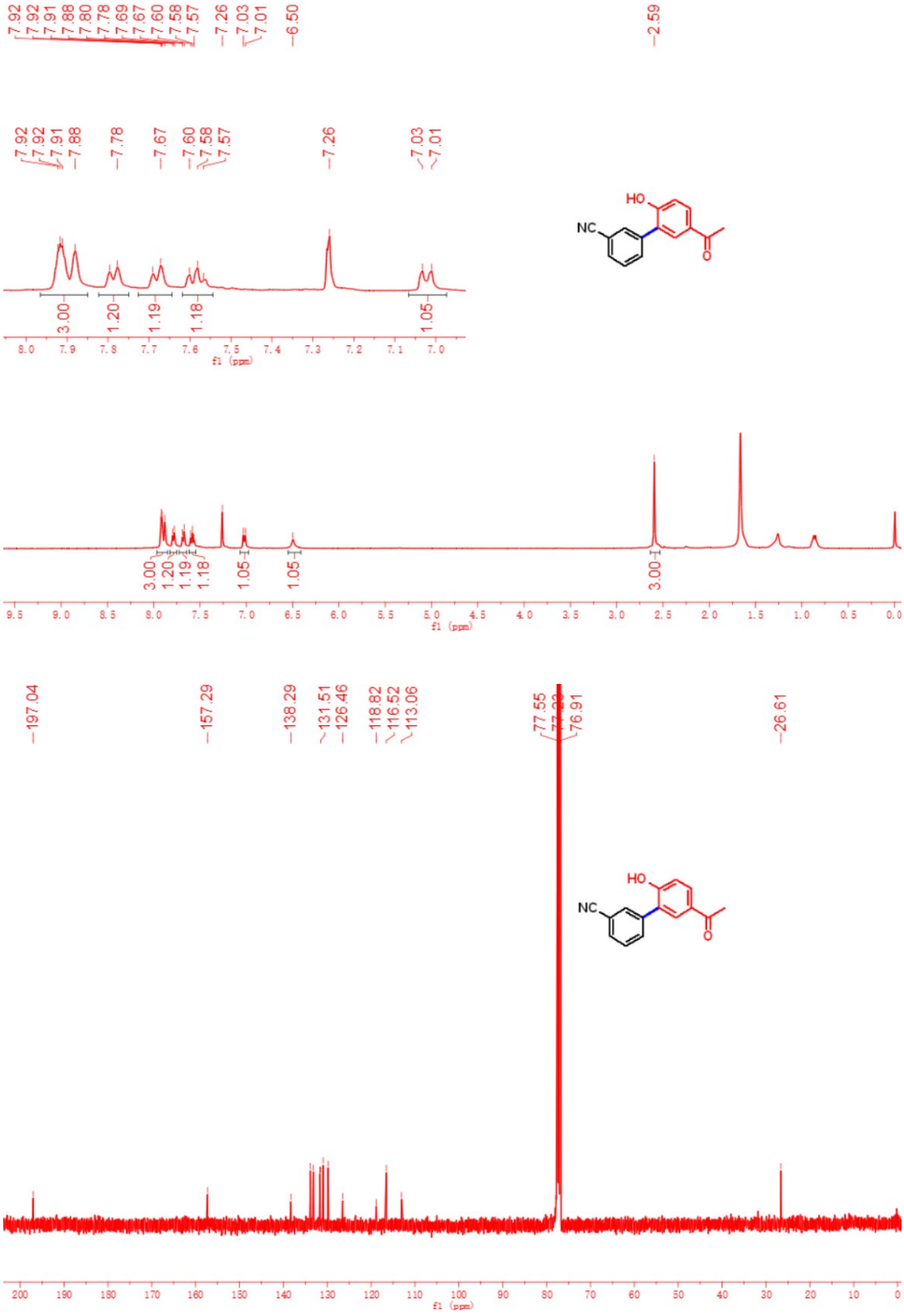
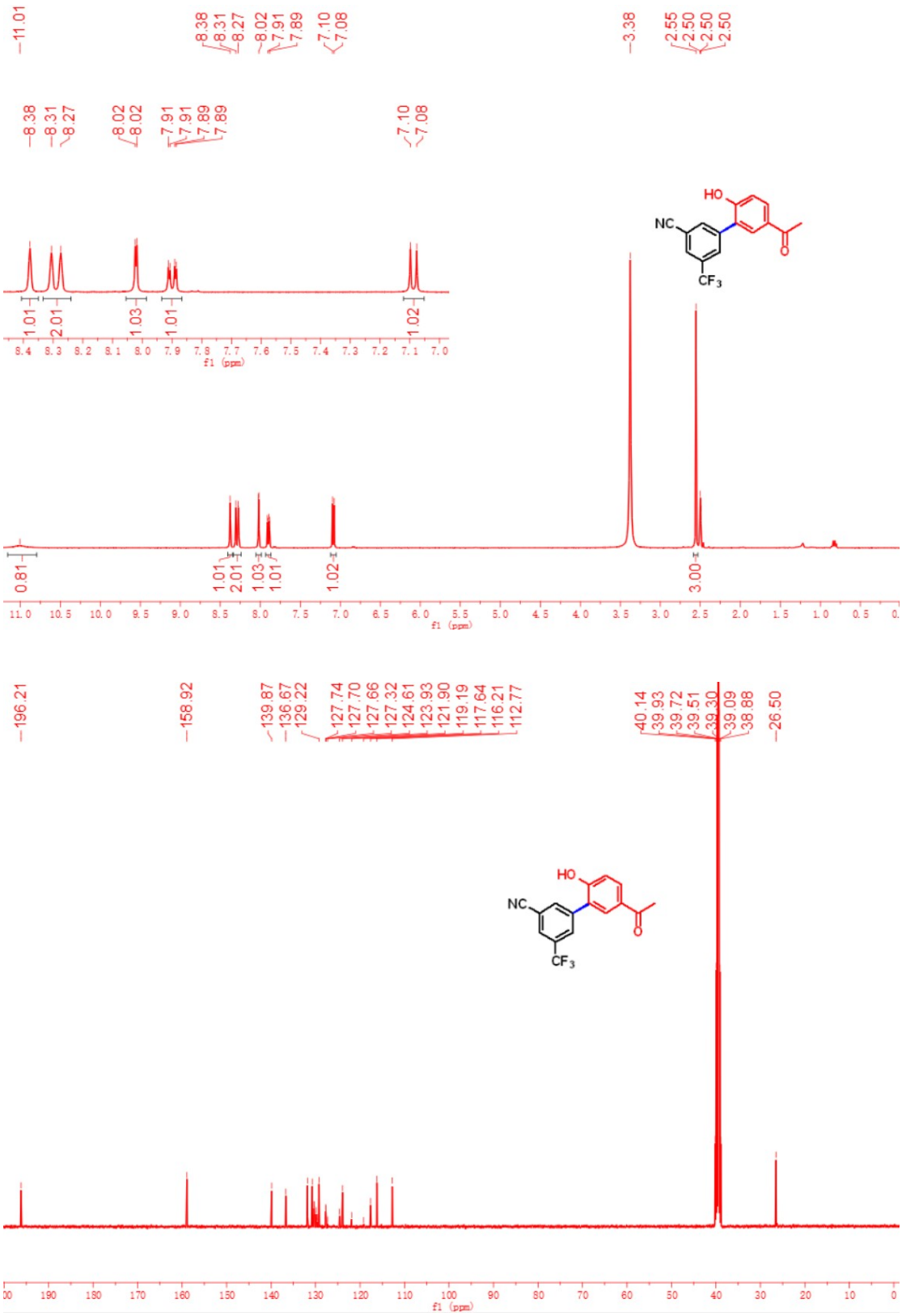


Figure S42. The ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{19}F (376 MHz) NMR spectra for 5'-acetyl-2'-hydroxy-5-(trifluoromethyl)-[1,1'-biphenyl]-3-carbonitrile (**3lc**) in d_6-DMSO



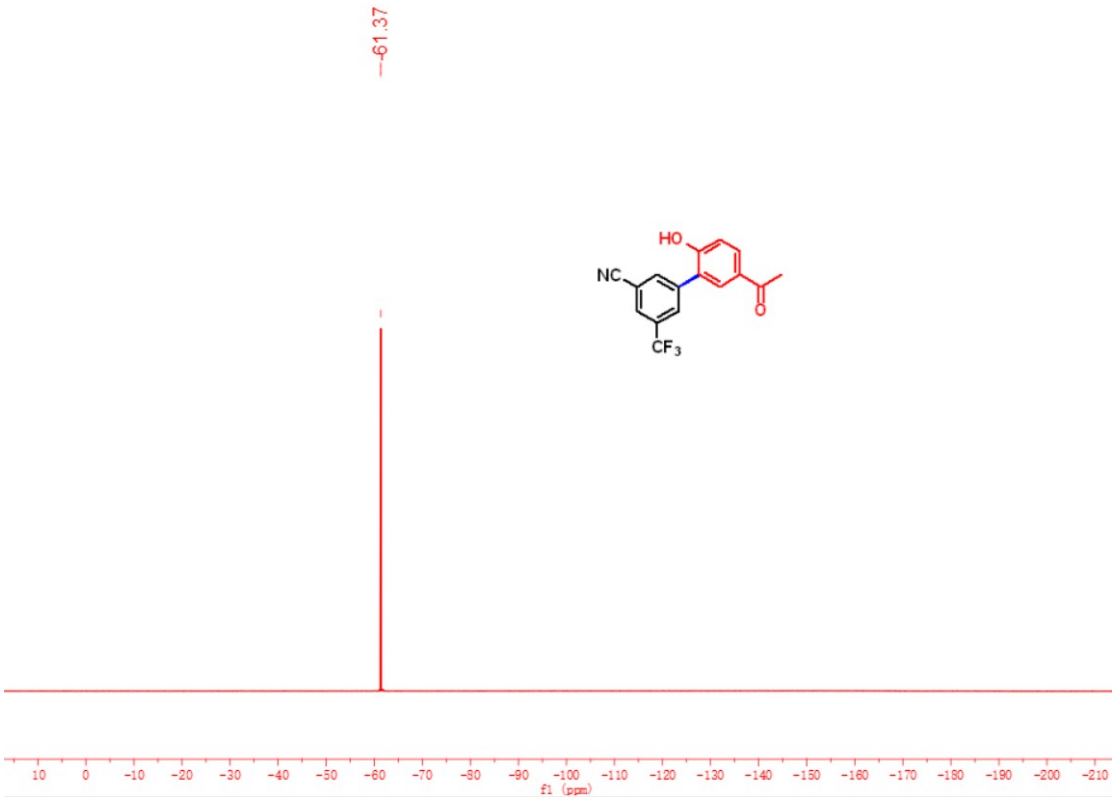

-61.37
HO
NC
O
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Figure S43. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 5'-acetyl-2'-hydroxy-[1,1'-biphenyl]-2-carbonitrile (**3mc**) in $CDCl_3$

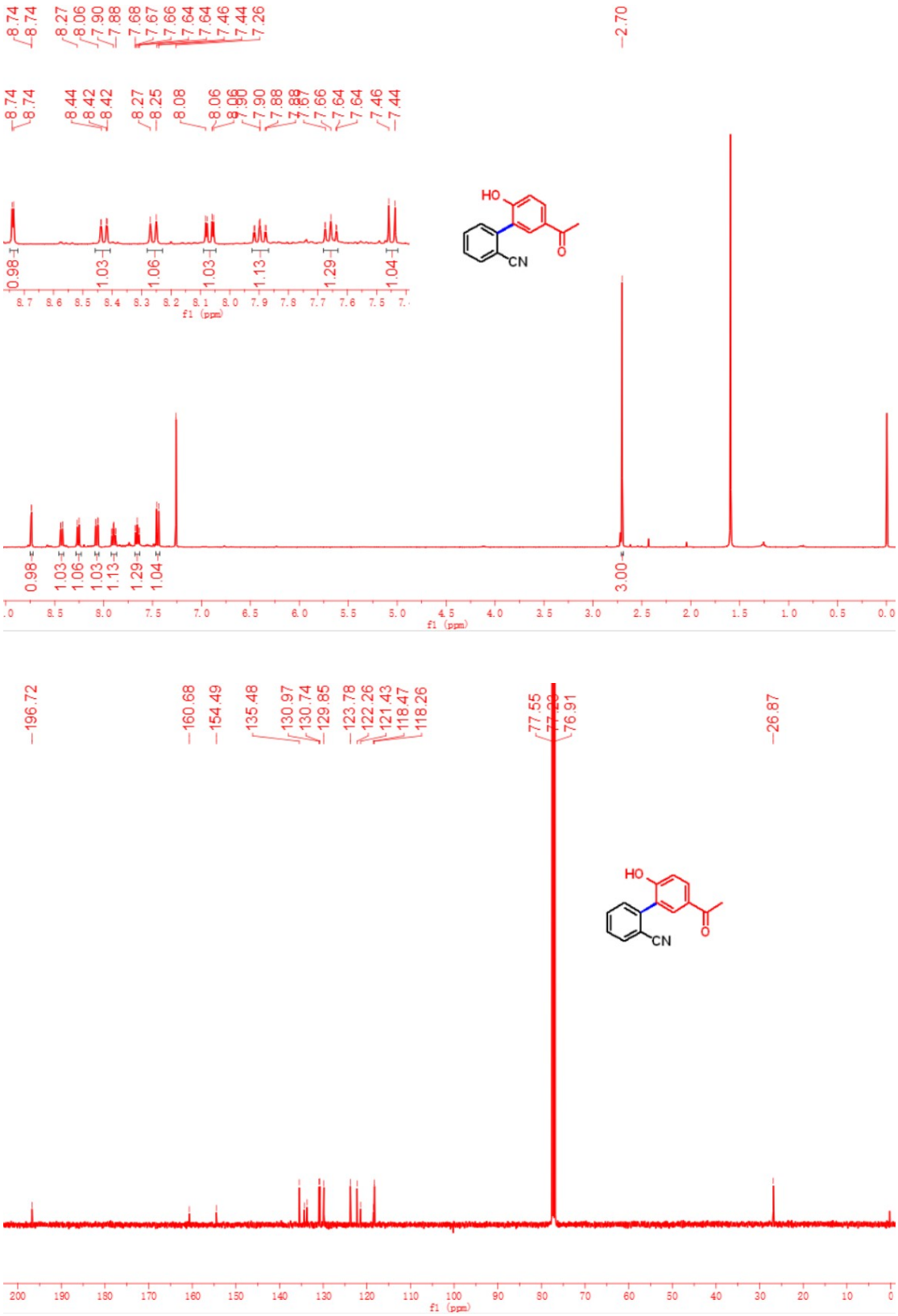


Figure S44. The ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra for 1-(dibenzo[*b*,*d*]furan-3-yl)ethan-1-one in $CDCl_3$