Supporting Information

Rhodium-catalyzed Regiospecific C–H *ortho*-Phenylation of Benzoic Acids with Cu/Air as Oxidant

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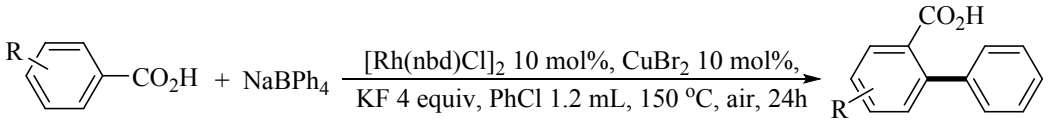
Part I: Experimental section

General Information:

All reactions were carried out in air and all reagents were weighed and handled in air unless otherwise stated. All reagents were obtained from commercial sources and used without further purification unless otherwise stated. Column chromatography was performed on silica gel (200-300 mesh) and visualized with ultraviolet light. Ethyl acetate and petroleum ether was used as eluents. ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded on a 400 MHz, 100 MHz and 377 MHz NMR spectrometer respectively. NMR spectrometer as solutions in $CDCl_3$ unless otherwise stated. IR spectra were recorded on a New Fourier transform infrared spectroscopy. HRMS were made by means of ESI. Melting points (mp) were measured on micro melting point apparatus and uncorrected.

Typical procedure for the synthesis of 2a (Table 2):



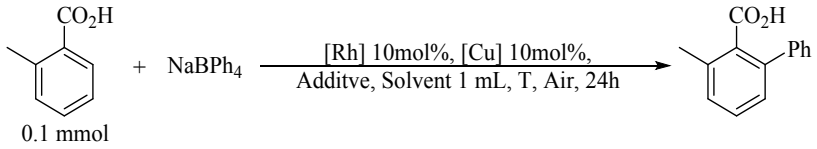
A solution of aromatic acid **1a** (27.2 mg, 0.2 mmol), $NaBPh_4$ (0.27 g, 0.8 mmol), KF (46 mg, 0.8 mmol), $[Rh(nbd)Cl]_2$ (9.2 mg, 0.02 mmol) and $CuBr_2$ (4.5 mg, 0.02 mmol) in chlorobenzene (1.2 mL) was stirred in a sealed tube under air at 150 °C for 24 h. The reaction mixture was then cooled to room temperature and acidified by dilute aqueous HCl to pH<3, and then the solvent was evaporated in vacuo. The residue was purified by preparative thin-layer chromatography (TLC) on silica gel with petroleum ether and ethyl acetate as eluent to give the pure product **2a**.

Half-gram-scale synthesis of 2a:

A solution of o-Toluic acid (3.7 mmol), $[Rh(nbd)Cl]_2$ (27 mg, 1.6 mol%), Sodium tetraphenylboron (14.8 mmol), $CuBr_2$ (4.5 mg, 0.37 mmol)and activated KF (46.4 mg, 14.8 mmol) in distilled 4-chlorotoluene (20 mL) was stirred in a sealed tube at 150 °C for 72 h under an atmosphere of air. The reaction mixture was then cooled to room temperature and acidified by dilute HCl to PH<3, and then the solvent was evaporated in vacuo. The residue was purified by preparative thin-layer chromatography (TLC) on silica gel with ethyl acetate and petroleum ether containing appropriate quantity of acetic acid to give the pure product.

Optimization results of Rh-catalyzed *ortho*-phenylation:

Table 1S Optimization of Rh-catalyzed *ortho*-phenylation of benzoic acid[a]



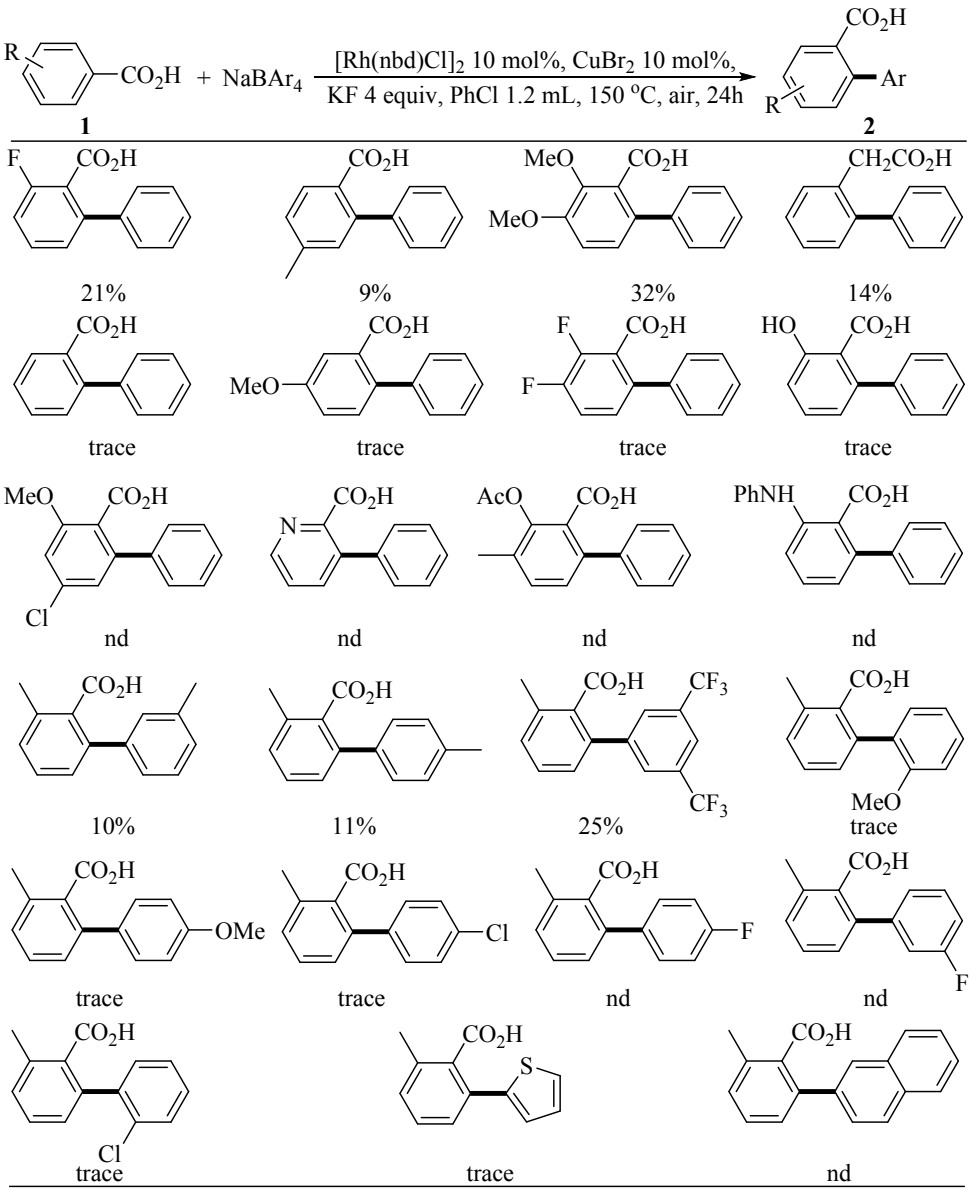
0.1 mmol **1a** **2a**

Entry	Catalyst	Cu-salt	Solvent	$NaBPh_4$ /equiv.	Additive	T /°C	Yield /%
1[b]	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	4	KF	150	75
2[b]	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	4	KF	130	20
3[c]	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	4	KF	150	82
4	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	4	KF	150	82(71)[d]
5[e]	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	4	KF	150	46
6	$(Ph_3P)_3RhCl$	$CuBr_2$	PhCl	4	KF	150	22
7	$RhCl_3·3H_2O$	$CuBr_2$	PhCl	4	KF	150	8
8	$Rh(CO)_2acac$	$CuBr_2$	PhCl	4	KF	150	54
9	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	3	KF	150	57
10	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	0	KF	150	trace
11	$[Rh(nbd)Cl]_2$	CuI	PhCl	4	KF	150	41
12	$[Rh(nbd)Cl]_2$	CuCl	PhCl	4	KF	150	30
13	$[Rh(nbd)Cl]_2$	$CuCl_2·2H_2O$	PhCl	4	KF	150	64
14	$[Rh(nbd)Cl]_2$	CuO	PhCl	4	KF	150	22
15	$[Rh(nbd)Cl]_2$	$CuSO_4·5H_2O$	PhCl	4	KF	150	42
16	$[Rh(nbd)Cl]_2$	$Cu(OAc)_2$	PhCl	4	KF	150	35
17	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	4	LiF	150	19
18	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	4	NaF	150	28
19	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	4	NaOAc	150	10
20	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	4	KOAc	150	43
21	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	4	K_3PO_4	150	31
22	$[Rh(nbd)Cl]_2$	$CuBr_2$	H_2O	4	KF	150	5
23	$[Rh(nbd)Cl]_2$	$CuBr_2$	Toluene	4	KF	150	27
24	$[Rh(nbd)Cl]_2$	$CuBr_2$	DMF	4	KF	150	33
25	$[Rh(nbd)Cl]_2$	$CuBr_2$	DMSO	4	KF	150	46
26	$[Rh(nbd)Cl]_2$	$CuBr_2$	NMP	4	KF	150	42
27	——	$CuBr_2$	PhCl	4	KF	150	trace
28	$[Rh(nbd)Cl]_2$	——	PhCl	4	KF	150	14
29	$[Rh(nbd)Cl]_2$	$CuBr_2$	PhCl	4	——	150	25

[a] Unless otherwise noted, all reactions were carried out using 0.1 mmol **1a**, 10 mol% [Rh], 10 mol % [Cu] and 1 mL solvent in a sealed tube under air for 24h. Yields are based on ^1H NMR using CH_3NO_2 as internal standard. [b] 4 equiv. of $CuBr_2$ was used and reaction was carried out under Argon. [c] 20 mol % $CuBr_2$ was used. [d] Isolated yield.[e] 5 mol % $[Rh(nbd)Cl]_2$ was used.

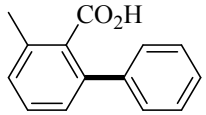
Some failures coupling reactions

Table 2S Some failures coupling reactions[a]

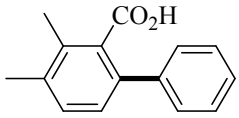


[a] All reactions were carried out with aromatic acid (0.2 mmol), $NaBPh_4$ (4 equiv.), $[Rh(nbd)Cl]_2$ (10 mol %), $CuBr_2$ (10 mol %), KF (4 equiv.) and 1.2 mL PhCl in a sealed tube under air at 150 °C for 24 h. All yields are detected by GC-MS.

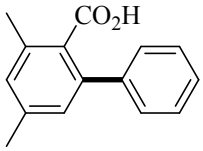
Characterization of products:



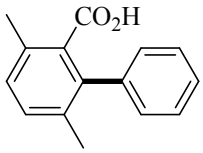
2a White solid; Yield 86%; Mp 132-134 °C [lit[1] mp 133-135°C]; IR (neat) ν_{max} 3057, 2917, 2849, 2627, 1682, 1461, 1133, 1064, 1000, 759, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.40 (m, 6H), 7.23 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.5, 140.7, 140.2, 135.5, 132.2, 129.7, 129.2, 128.4 (2C), 127.6, 127.5, 20.0; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}O_2$ 213.0910, found $[M+H]^+$ 213.0912.



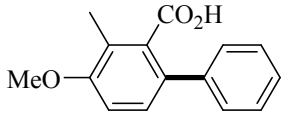
2b White solid; Yield 85%; Mp 143-146 °C; IR (neat) ν_{max} 3057, 2921, 2852, 2644, 2360, 1687, 1566, 1417, 1289, 1163, 769, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.45-7.33 (m, 5H), 7.25 (d, *J* = 3 Hz, 1H), 7.13 (d, *J* = 8 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.6, 140.7, 137.5, 136.2, 133.2, 132.7, 131.0, 128.4, 128.3, 127.3, 127.2, 20.0, 16.7; HRMS (ESI) *m/z* calcd for $C_{15}H_{15}O_2$ 227.1067, found $[M+H]^+$ 227.1061.



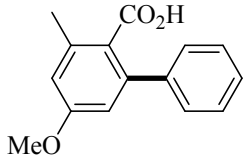
2c White solid; Yield 83%; Mp 133-135 °C [lit[2] mp 134-135°C]; IR (neat) ν_{max} 3029, 2972, 2853, 2645, 2361, 1676, 1605, 1576, 1301, 976, 850, 783, 730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.33 (m, 5H), 7.04 (s, 1H), 7.02 (s, 1H), 2.41 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.4, 140.9, 140.5, 139.9, 135.8, 130.1, 129.3, 128.4, 128.3, 127.5, 21.3, 20.0; HRMS (ESI) *m/z* calcd for $C_{15}H_{15}O_2$ 227.1067, found $[M+H]^+$ 227.1061.



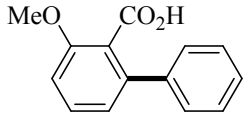
2d White solid; Yield 81%; Mp 141-143 °C [lit[3] mp 145°C]; IR (neat) ν_{max} 3059, 2919, 2854, 2619, 2525, 1682, 1442, 1425, 1289, 994, 774, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.33 (m, 3H), 7.23 (m, 3H), 7.13 (d, *J* = 8 Hz, 1H), 2.37 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.5, 139.1, 139.0, 133.7, 133.3, 131.9, 131.2, 129.2, 129.1, 128.1, 127.3, 77.4, 77.1, 76.7, 20.2, 19.5; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}O_2$ 225.0921, found $[M-H]^-$ 225.0921.



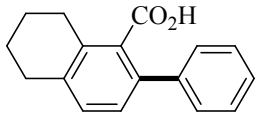
2e White solid; Yield 88%; Mp 186-187 °C; IR (neat) ν_{max} 3008, 2844, 2545, 2359, 2341, 1683, 1597, 1457, 1293, 930, 813, 771, 709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.45-7.32 (m, 5H), 7.20 (d, *J* = 8 Hz, 1H), 6.96 (d, *J* = 8 Hz, 1H), 3.89 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ = 172.2, 156.8, 140.7, 135.6, 131.2, 128.2, 127.9, 127.8, 126.6, 122.4, 110.4, 54.8, 11.7; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}O_3$ 241.0870, found $[M-H]^-$ 241.0871.



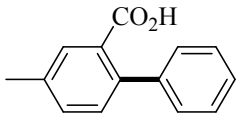
2f White solid; Yield 78%; Mp 164-166 °C; IR (neat) ν_{max} 2978, 2846, 2646, 2541, 2359, 1673, 1598, 1451, 1336, 1280, 1045, 940, 768, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.41-7.34 (m, 5H), 6.75 (s, 1H), 6.72 (d, *J* = 2 Hz, 1H), 3.84 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ = 172.65, 159.9, 141.6, 141.0, 136.7, 128.1, 127.9, 127.1, 126.8, 114.0, 112.4, 54.4, 18.8; HRMS (ESI) *m/z* calcd for $C_{15}H_{15}O_3$ 243.1016, found $[M+H]^+$ 243.1009.



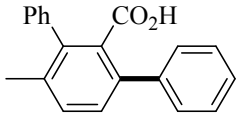
2g White solid; Yield 87%; Mp 106-107 °C [lit[4] mp 108.5-109.5°C]; IR (neat) ν_{max} 3196, 2965, 2839, 2659, 2365, 1692, 1587, 1466, 1255, 1114, 1015, 755, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.37 (m, 6H), 6.96-7.01 (m, 2H), 3.92 (s, 3H).^{13}C NMR (100 MHz, CD_3OD) δ = 173.0, 156.5, 141.4, 139.9, 130.9, 128.4, 128.4, 127.7, 122.3, 122.2, 110.0, 56.2; HRMS (ESI) *m/z* calcd for $C_{14}H_{12}NaO_3$ 251.0679, found $[M+Na]^+$ 251.0677.



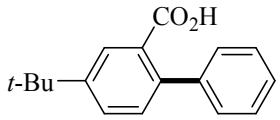
2h White solid; Yield 75%; Mp 134-135 °C; IR (neat) ν_{max} 3026, 2943, 2863, 2360, 2342, 1696, 1522, 1428, 1225, 1152, 1074, 1031, 819, 769, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.43-7.31 (m, 5H), 7.19 (d, *J* = 8 Hz, 1H), 7.13 (d, *J* = 8 Hz, 1H), 2.83 (m, 4H), 1.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.4, 140.6, 137.2, 136.8, 133.9, 132.2, 130.8, 128.4, 128.4, 127.4, 127.0, 29.7, 26.9, 22.9, 22.6; HRMS (ESI) *m/z* calcd for $C_{17}H_{17}O_2$ 253.1223, found $[M+H]^+$ 253.1222.



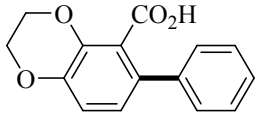
2ia White solid; Yield 60%; Mp 150-151 °C [lit[5] mp 140-147°C]; IR (neat) ν_{max} 3029, 2850, 2566, 2360, 1696, 1466, 1292, 829, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.75 (s, 1H), 7.31 (m, 7H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.1, 141.0, 140.5, 137.1, 132.9, 131.1, 129.1, 128.6, 128.1, 127.2, 20.9; HRMS (ESI) *m/z* calcd for $C_{14}H_{11}O_2$ 211.0765, found $[M-H]^-$ 211.0765.



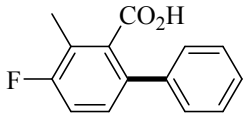
2ic White solid; Yield 70%; Mp 81-84 °C; IR (neat) ν_{max} 3056, 2921, 2360, 2341, 1696, 1292, 760, 698, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.38 (m, 10H), 7.28 (d, *J* = 8 Hz, 1H), 7.24 (m, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.2, 140.3, 139.4, 138.8 137.2, 135.6, 132.9, 131.2, 129.2, 128.8, 128.4, 128.4, 128.1, 127.4, 20.4; HRMS (ESI) *m/z* calcd for $C_{20}H_{16}NaO_2$ 311.1043, found $[M+Na]^+$ 311.1041.



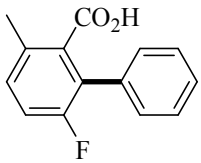
2j White solid; Yield 81%; mp 182 °C; IR (neat) ν_{max} 2961, 2867, 2650, 2536, 1678, 1583, 1442, 1406, 1287, 1176, 1086, 950, 823, 763, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): ^1H NMR (400 MHz, $CDCl_3$) δ = 7.98 (s, 1H), 7.60 (dd, *J* = 8, 2 Hz, 1H), 7.35 (m, 6H), 1.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.00, 150.40, 141.11, 140.57, 131.07, 129.29, 128.96, 128.61, 128.09, 127.69, 127.21, 34.72, 31.29; HRMS (ESI) *m/z* calcd for $C_{17}H_{17}O_2$ 253.1234, found $[M-H]^-$ 253.1230.



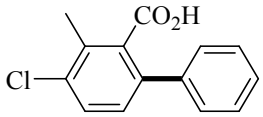
2k White solid; Yield 58%; Mp 168-170 °C; IR (neat) ν_{max} 2921, 2361, 2342, 1697, 1478, 1307, 1251, 902, 956, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.36 (m, 5H), 7.00 (d, *J* = 8 Hz, 1H), 6.89 (d, *J* = 8 Hz, 1H), 4.41-4.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 142.9, 141.0, 139.8, 133.8, 128.4, 128.3, 127.4, 122.8, 121.5, 118.8, 64.7, 64.2; HRMS (ESI) *m/z* calcd for $C_{15}H_{12}NaO_4$ 279.0628, found $[M+Na]^+$ 279.0629.



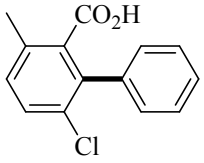
2l White solid; Yield 69%; Mp 139-141 °C; IR (neat) ν_{max} 2920, 2359, 2341, 1691, 1449, 1291, 1241, 913, 828, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.37 (m, 5H), 7.22-7.13 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.7 , 160.3 (d, *J* = 244 Hz), 139.8 , 136.0 (d, *J* =4 Hz), 134.0 (d, *J* = 4 Hz), 128.9 (d, *J* = 8 Hz), 128.4, 128.3, 127.6, 122.7 (d, *J* = 19 Hz), 116.5 (d, *J* = 23 Hz), 11.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ = -117.4; HRMS (ESI) *m/z* calcd for $C_{14}H_{10}FO_2$ 229.0670, found $[M-H]^-$ 229.0671.



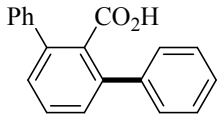
2m White solid; Yield 68%; Mp 140-141 °C; IR (neat) ν_{max} 3191, 2360, 2341, 1687, 1445, 1277, 1196, 949, 823, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.45-7.38 (m, 5H), 7.24-7.20 (m, 1H), 7.15 (t, *J* = 9 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.1, 157.7 (d, *J* = 243 Hz), 135.7, 134.3 (d, *J* = 3 Hz),133.2, 130.8 (t, *J* = 4 Hz), 129.5, 128.3, 128.2, 127.5 (d, *J* = 18 Hz), 117.1 (d, *J* = 23 Hz), 19.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ = -119.5; HRMS (ESI) *m/z* calcd for $C_{14}H_{15}FNO_2$ 248.1081, found $[M+NH_4]^+$ 248.1086.



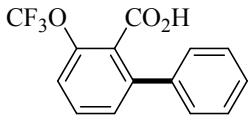
2n White solid; Yield 66%; Mp 165-168 °C; IR (neat) ν_{max} 2922, 2629, 2359, 2342, 1691, 1447, 1279, 1114, 908, 823, 767 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 8 Hz, 1H), 7.38 (s, 5H), 7.17 (d, *J* = 8 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.2, 139.6, 138.5, 134.2, 134.0, 133.0, 130.5, 128.6, 128.5, 128.3, 127.9, 17.5; HRMS (ESI) *m/z* calcd for $C_{14}H_{10}ClO_2$ 245.0375, found $[M-H]^-$ 245.0373.



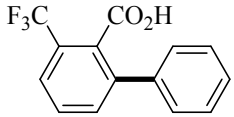
2o White solid; Yield 43%; Mp 157-163 °C; IR (neat) ν_{max} 2919, 2625, 2360, 2342, 1683, 1439, 1274, 943, 847, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, *J* = 8 Hz, 1H), 7.41-7.37 (m, 3H), 7.28 (m, 2H), 7.16 (d, *J* = 8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.9, 137.9, 137.0, 135.0, 133.5, 131.1, 130.6, 130.5, 129.5, 128.1, 128.0, 19.4; HRMS (ESI) *m/z* calcd for $C_{14}H_{10}ClO_2$ 245.0375, found $[M-H]^-$ 245.0374.



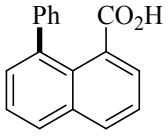
2p White solid; Yield 84% (*ortho*-phenylbenzoic acid used as substrate); 64% (*ortho*-chlorobenzoic acid used as substrate); Mp 189-191 °C [lit[6] mp 188-189 °C]; IR (neat) ν_{max} 2360, 1691, 1458, 1297, 1134, 916, 815, 757, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.52 (t, *J* = 8 Hz, 1H), 7.38 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.7, 140.3, 131.8, 129.7, 129.0, 128.5, 128.4, 127.7; HRMS (ESI) *m/z* calcd for $C_{19}H_{13}O_2$ 273.0921, found $[M-H]^-$ 273.0919.



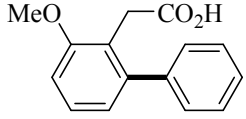
2q White solid; Yield 75%; Mp 78-82 °C; IR (neat) ν_{max} 2926, 1706, 1462, 1166, 1065, 760, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.59-7.48 (m, 1H), 7.46-7.34 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.4, 146.1, 142.4, 138.8, 131.0, 128.6, 128.3, 128.3, 127.1, 121.7 (q, *J* = 170 Hz), 119.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ = -57.17; HRMS (ESI) *m/z* calcd for $C_{14}H_{10}F_3O_3$ 283.0577, found $[M+H]^+$ 283.0588.



2r White solid; Yield 81%; Mp 153-156 °C; IR (neat) ν_{max} 2919, 3850, 2360, 2341, 1700, 1326, 1292, 1170, 1118, 938, 762, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.1 Hz, 1H), 7.60 (q, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 4.7 Hz, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.2, 140.0 (d, *J* = 245 Hz), 133.7, 130.4, 129.8, 128.6, 128.5, 128.3, 127.5 (q, *J* = 32 Hz), 125.1 (q, *J* = 5 Hz), 123.4 (q, *J* = 272 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ = -59.34; HRMS (ESI) *m/z* calcd for $C_{14}H_8F_3O_2$ 265.0482, found $[M-H]^-$ 265.0479.



2s White solid; Yield 54%; Mp 203-217 °C [lit[7] mp 223-224 °C]; IR (neat) ν_{max} 2919, 1287, 1240, 1072, 759, 745, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, *J* = 8 Hz, 1H), 7.99 (d, *J* = 8 Hz, 1H), 7.92 (d, *J* = 8 Hz, 1H), 7.64-7.52 (m, 5H), 7.49-7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.8, 140.7, 138.4, 132.3, 130.4, 129.7, 128.8, 128.7, 128.6, 128.3, 127.9, 127.7, 127.6, 126.5, 125.1; HRMS (ESI) *m/z* calcd for $C_{17}H_{13}O_2$ 249.0910, found $[M+H]^+$ 249.0904.



2t White solid; Yield 57%; Mp 146-148 °C; IR (neat) ν_{max} 2924, 2360, 2341, 1715, 1636, 1259, 1368, 1259, 1118, 1017, 858, 758, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.45-7.33 (m, 6H), 6.95 (d, *J* =

8 Hz, 2H), 3.91 (s, 3H), 3.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 157.9, 144.0, 140.9, 129.2, 128.3, 128.1, 127.3, 122.4, 120.7, 109.3, 55.8, 33.3; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}O_3$ 241.0870, found $[M-H]^-$ 241.0868.

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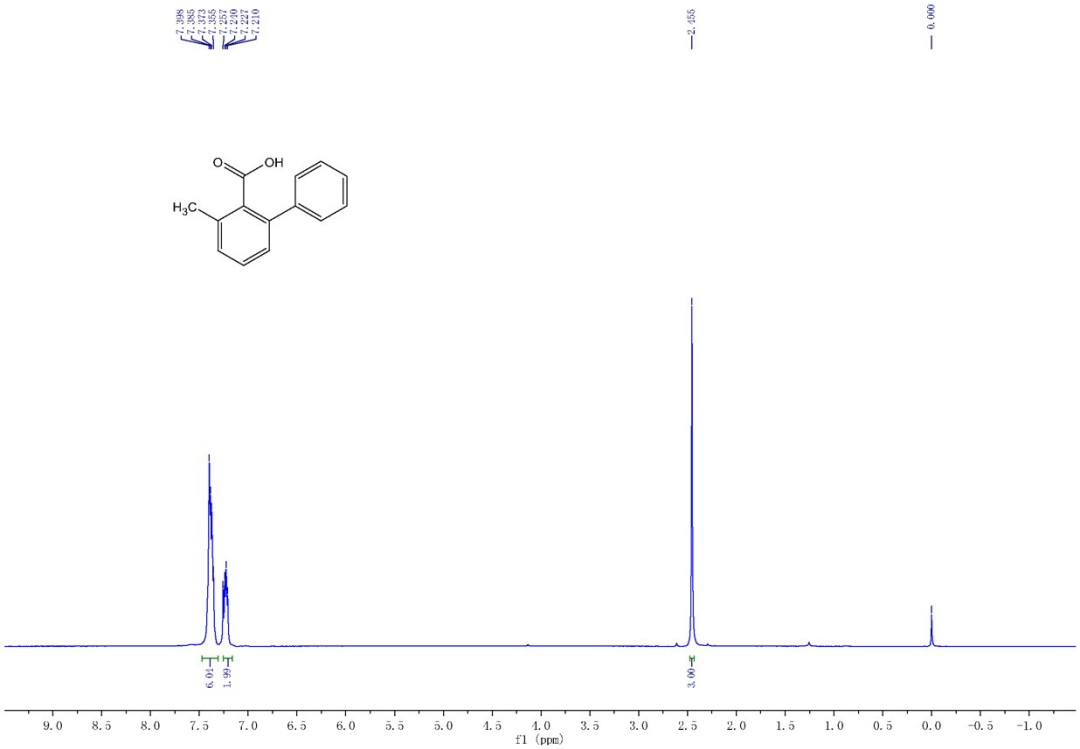
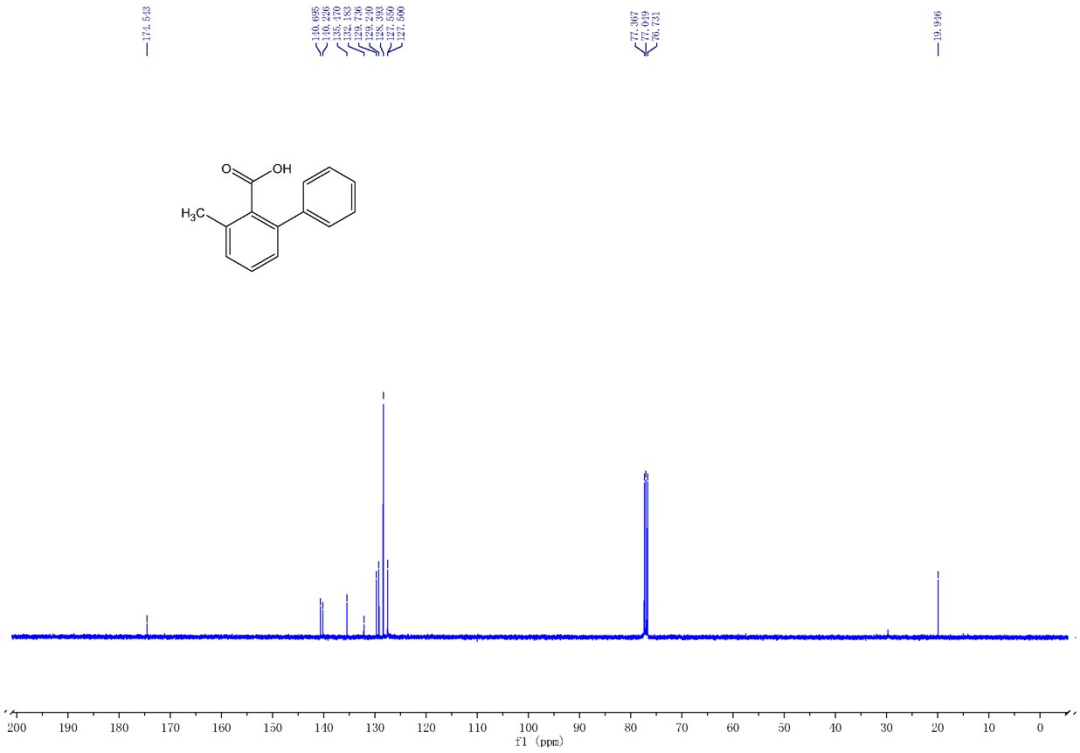
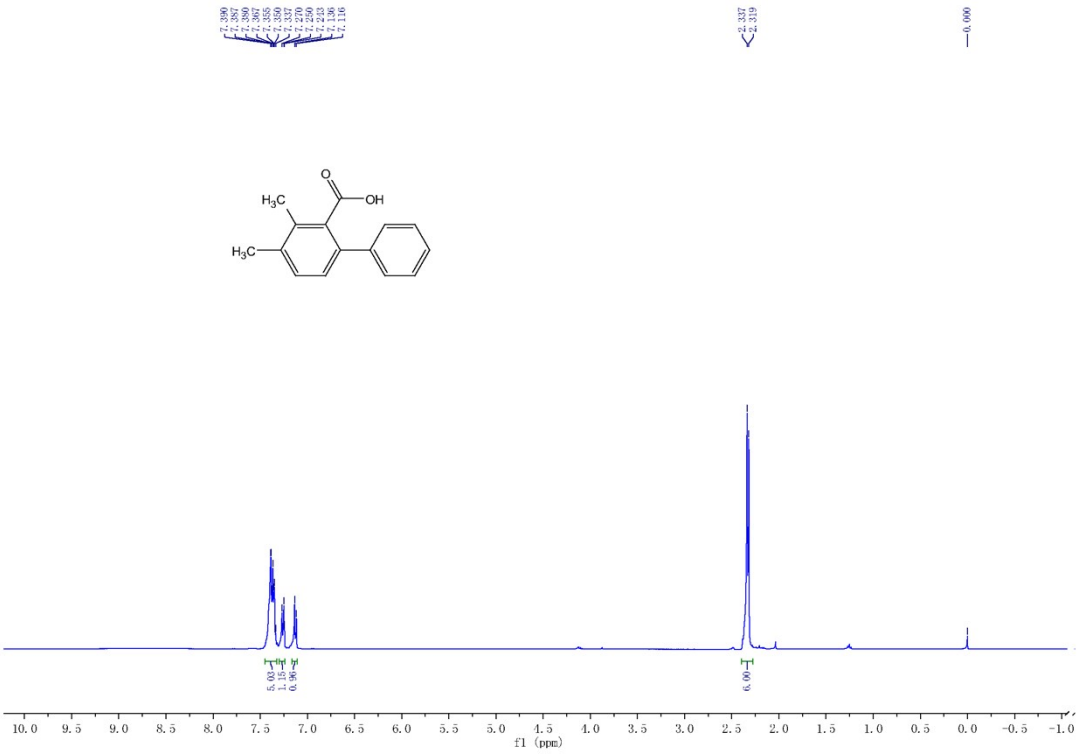
Part II: NMR spectra



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7.136
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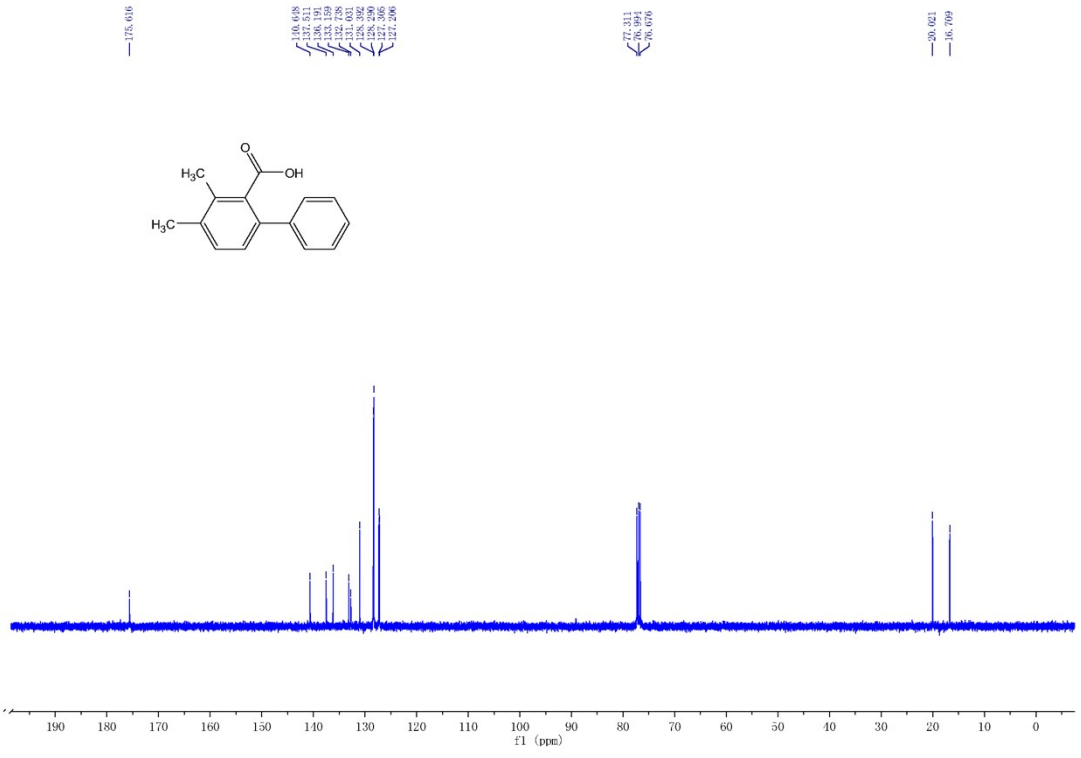
2.337
2.319
0.000
O
OH
H3C
H3C
5.03
1.15
0.96
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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131.031
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76.994
76.676
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16.709
O
OH
H3C
H3C
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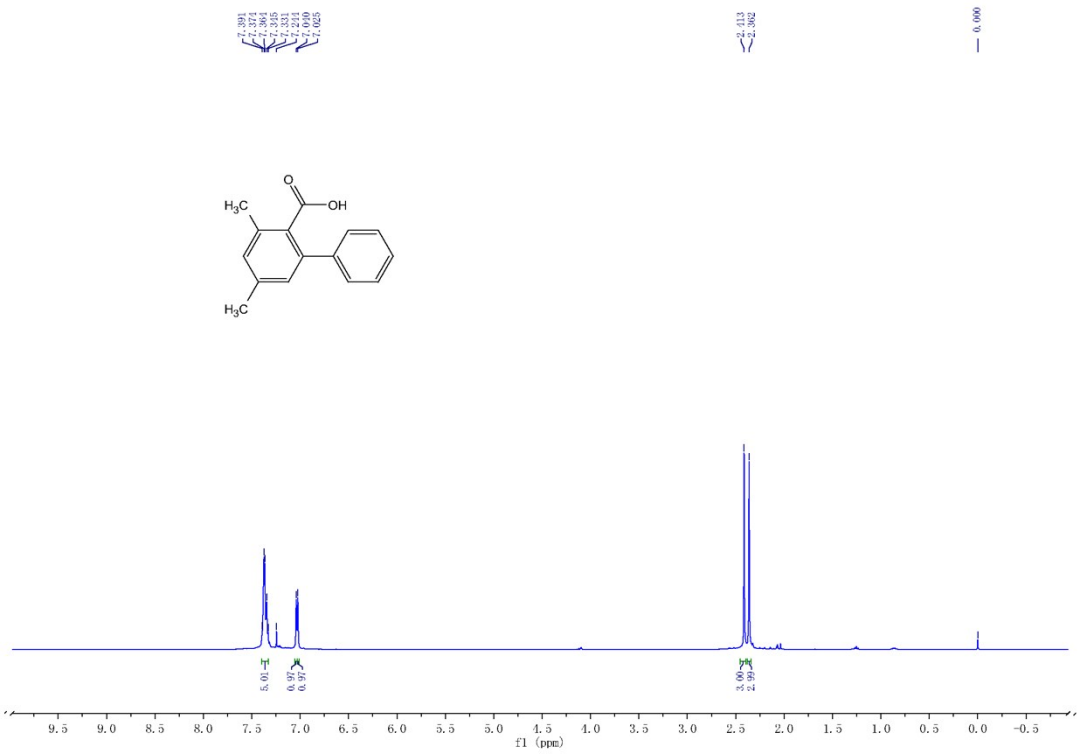
f1 (ppm)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OH
H3C
H3C
5.01
0.97
0.97
3.00
2.99
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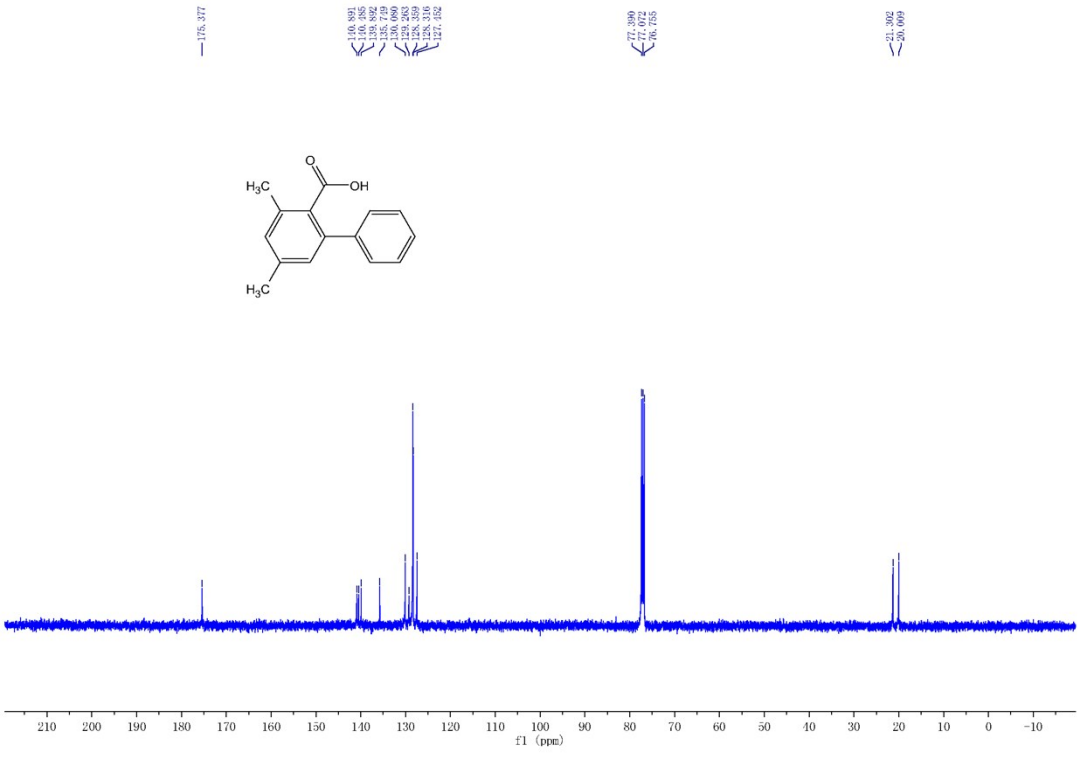
f1 (ppm)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127.152
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76.755
21.302
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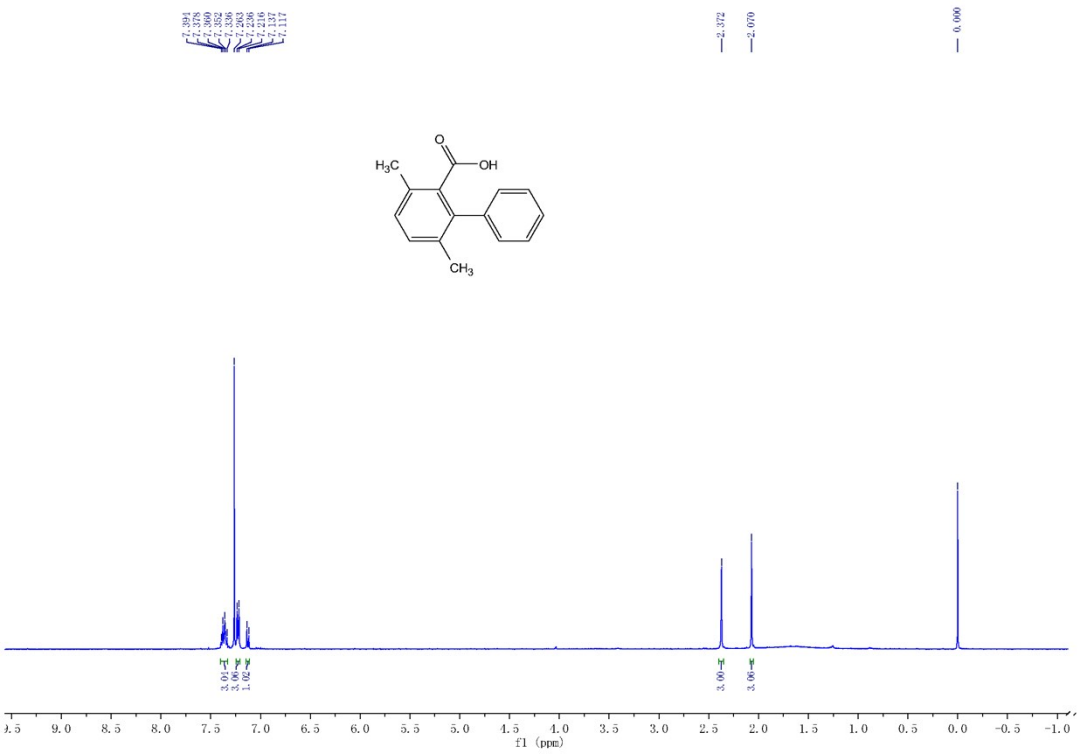
O
OH
H3C
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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H3C
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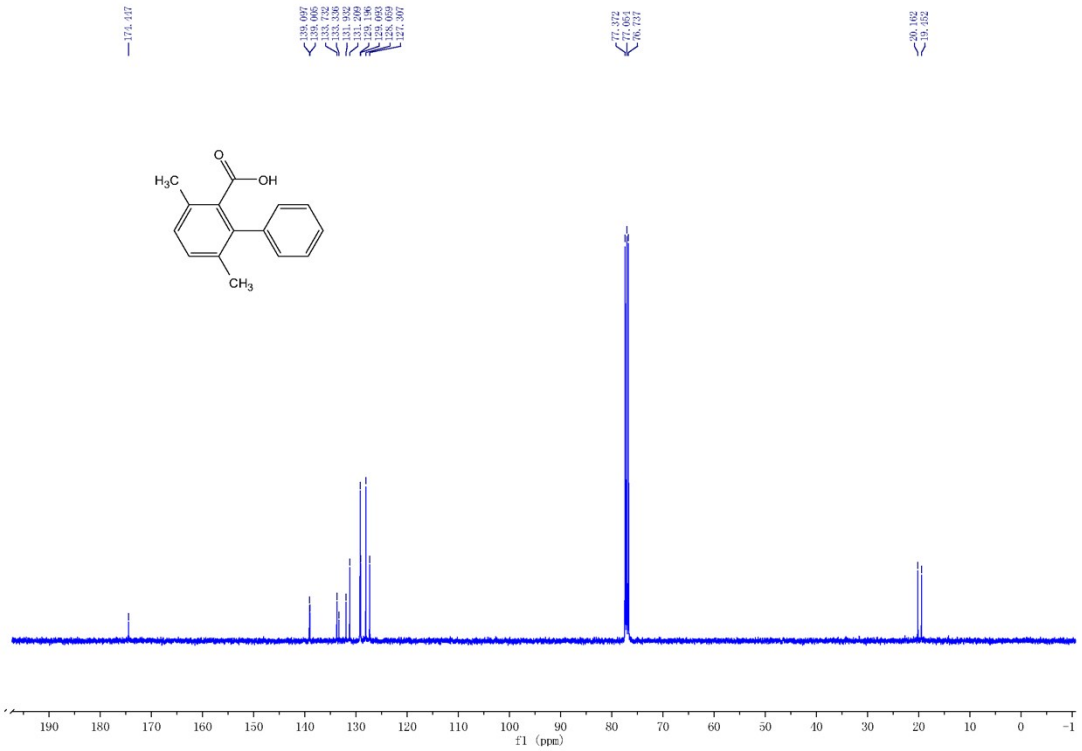
3.00
1.02
3.00
3.06
f1 (ppm)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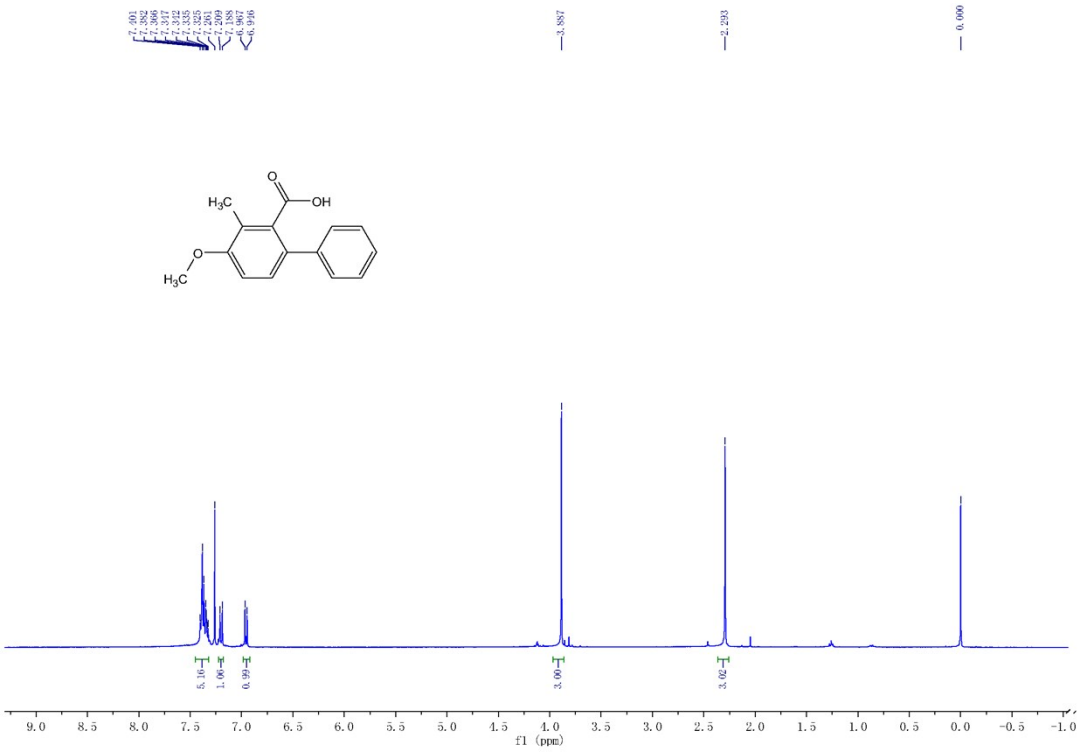
CH3
f1 (ppm)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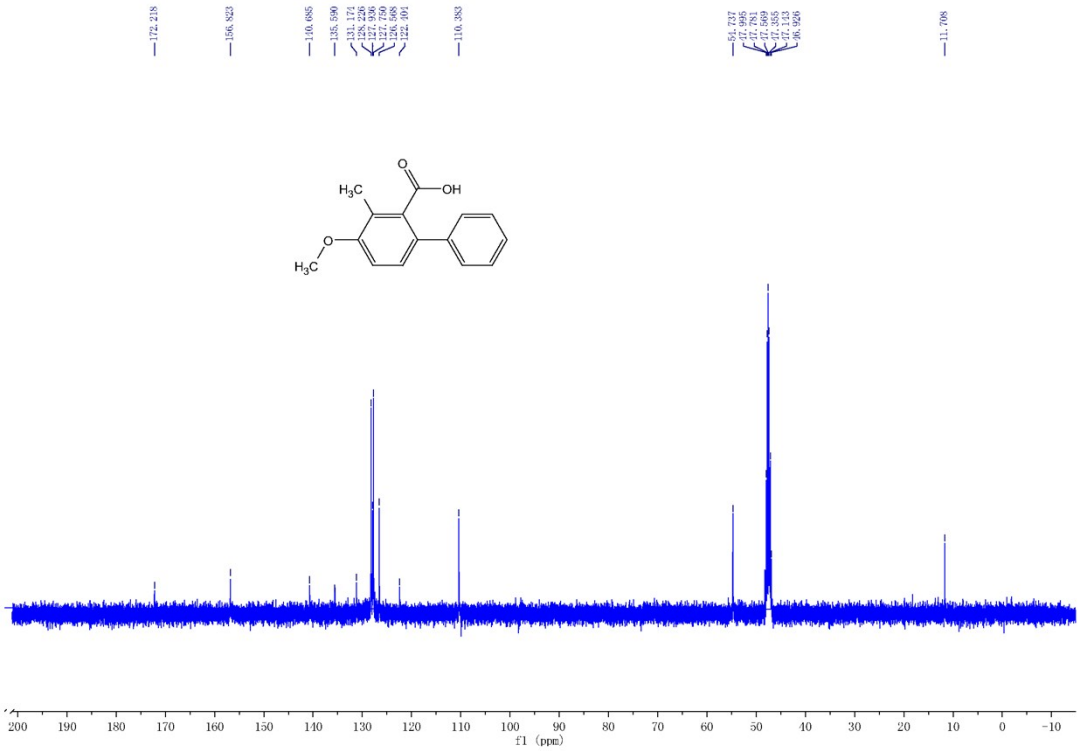
0.000
O
OH
H3C
O
H3C
5.16
1.06
0.99
3.00
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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64.737
47.995
47.793
47.569
47.355
47.143
46.926
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OH
H3C
O
H3C
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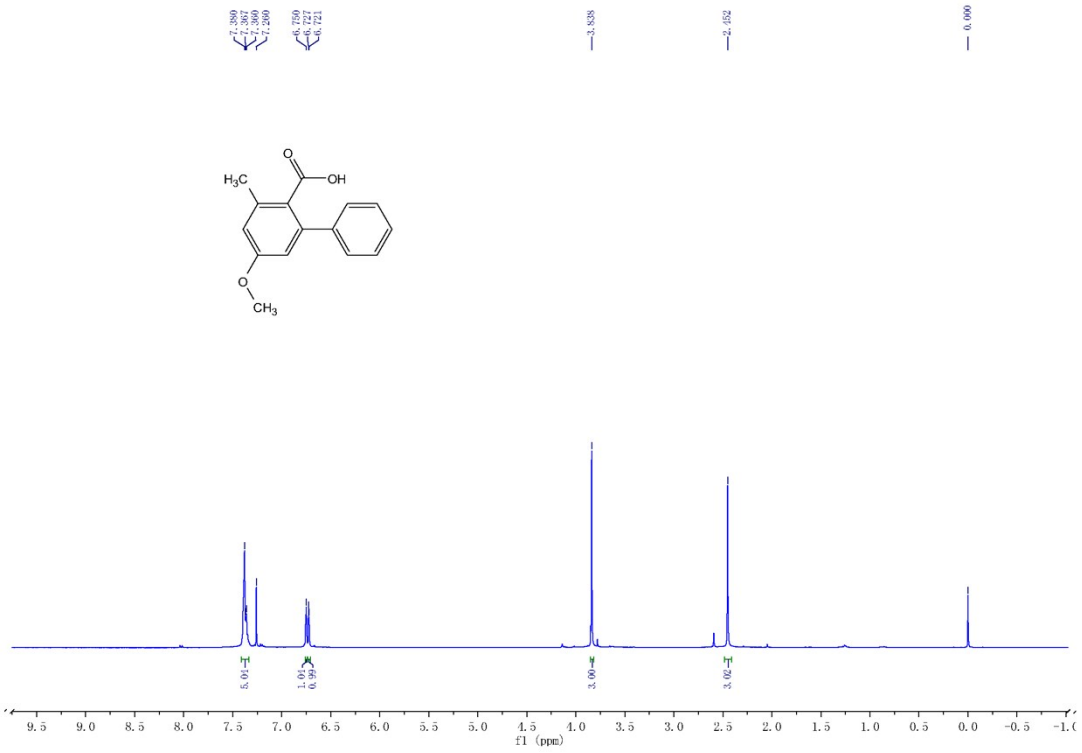
f1 (ppm)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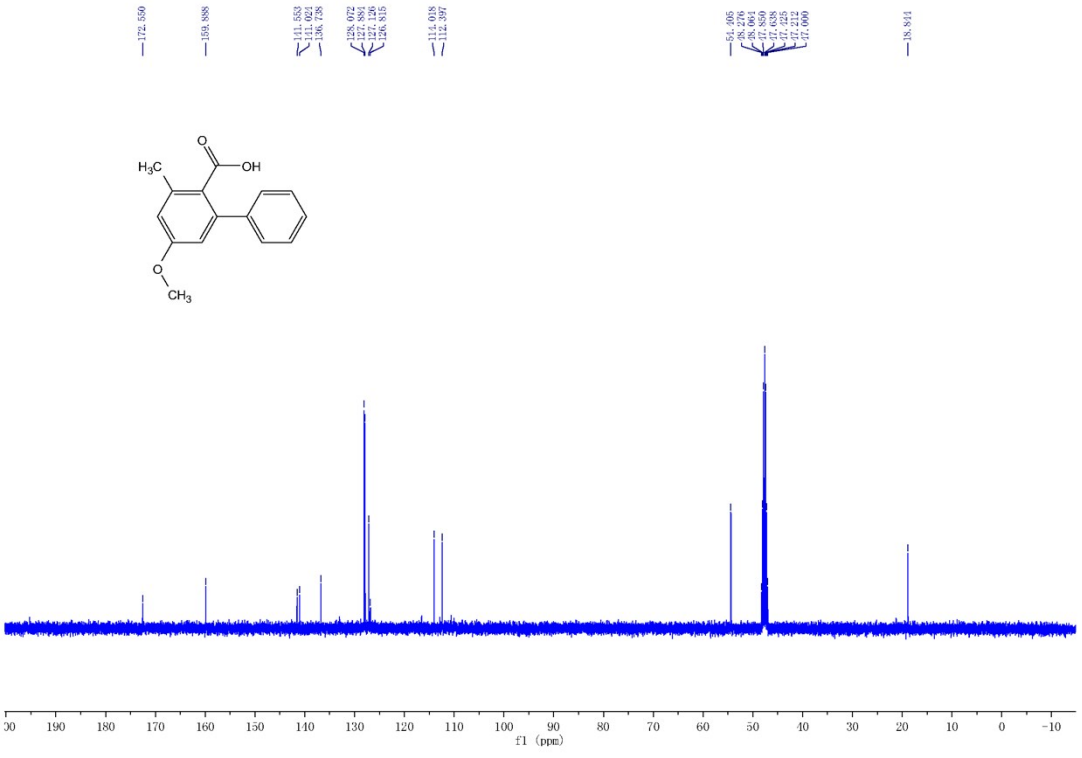
f1 (ppm)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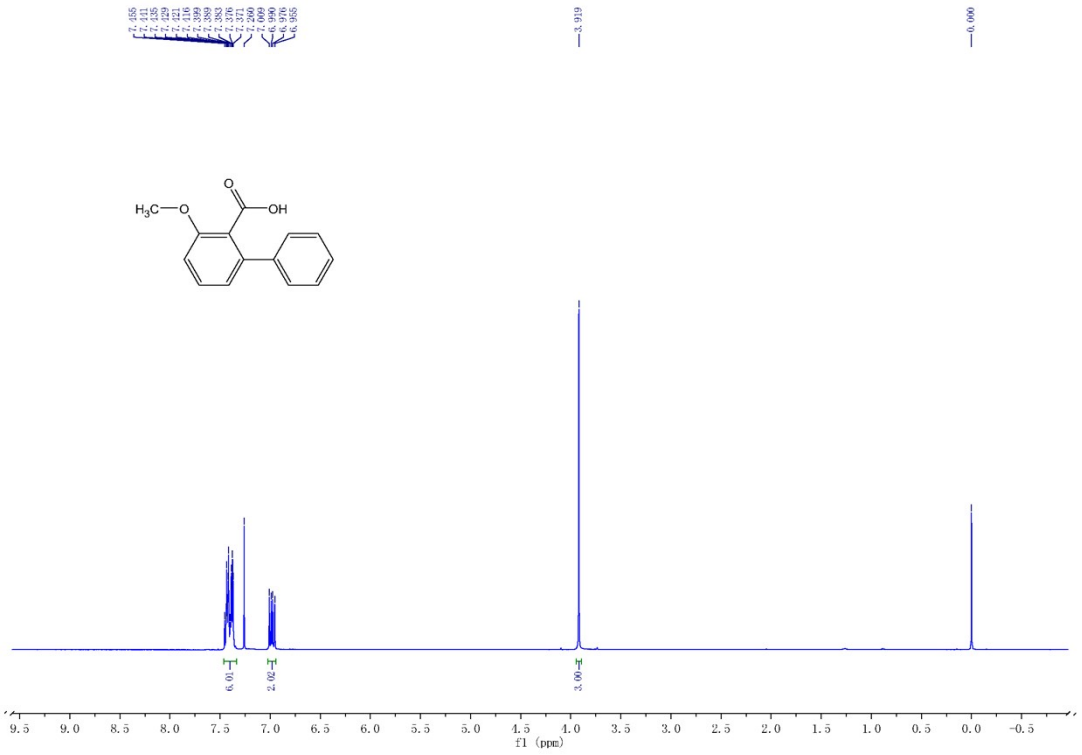
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OH
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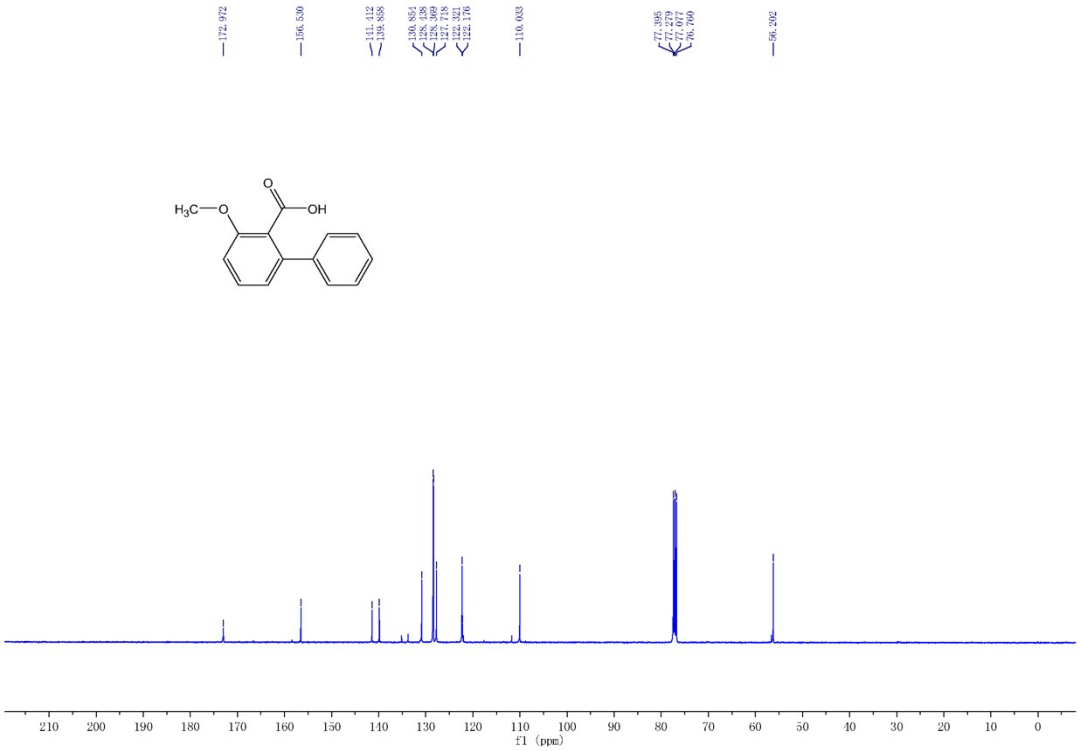
2.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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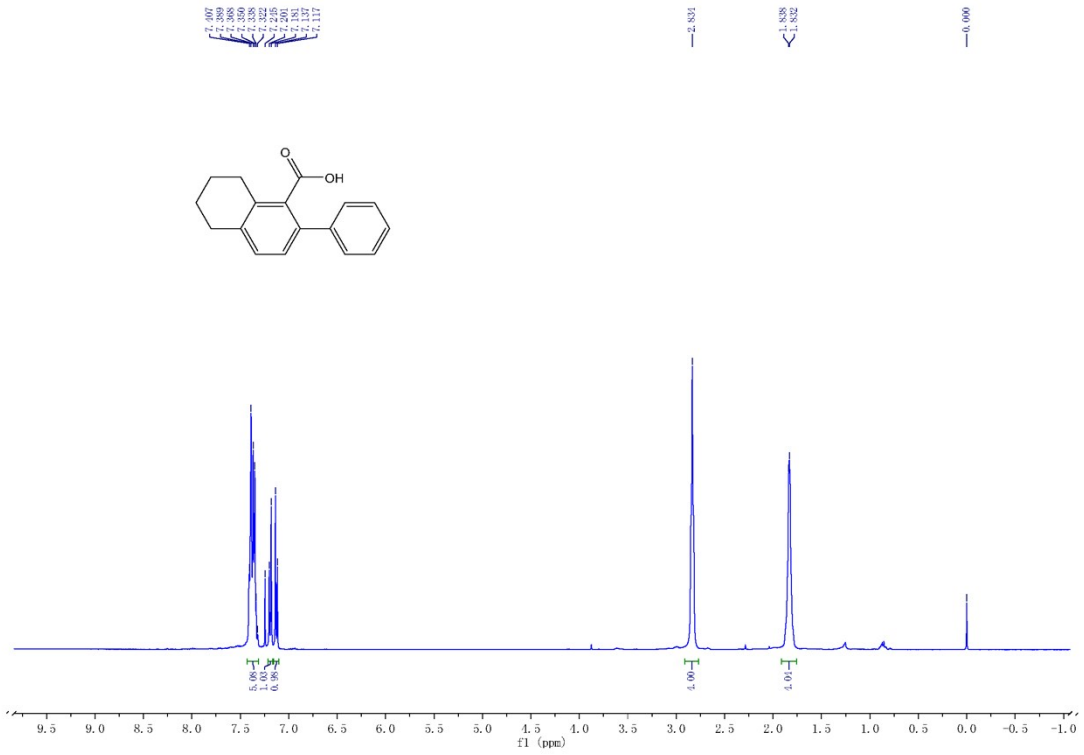
f1 (ppm)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4.01
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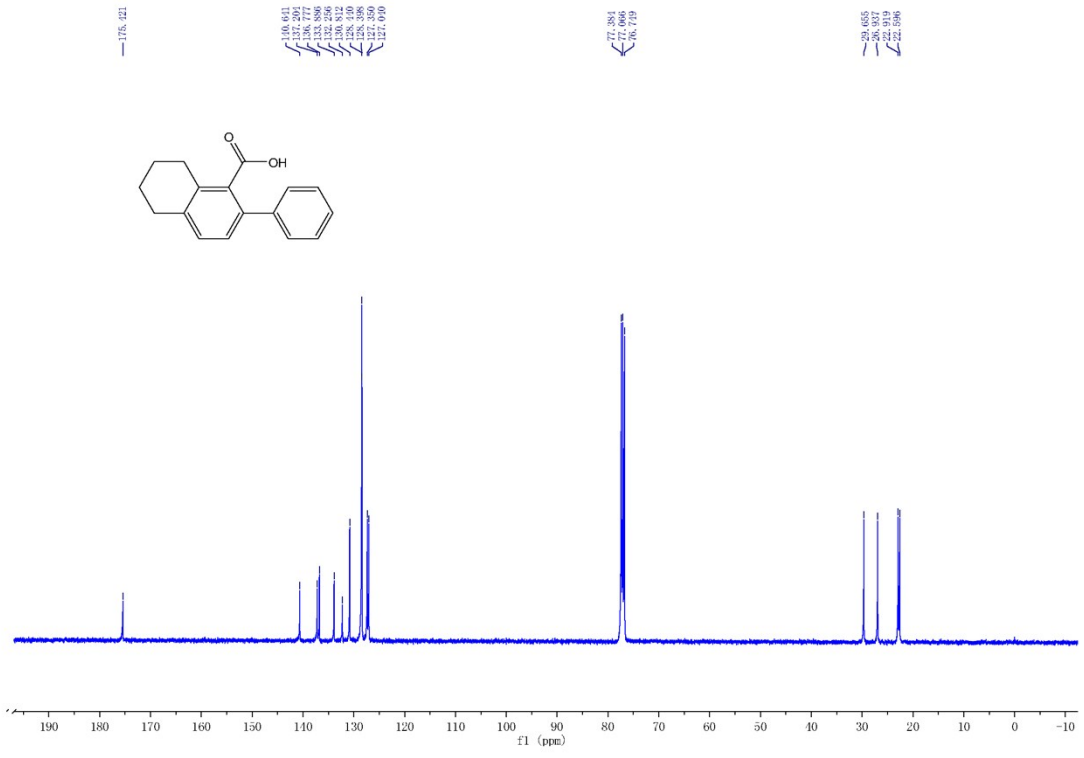
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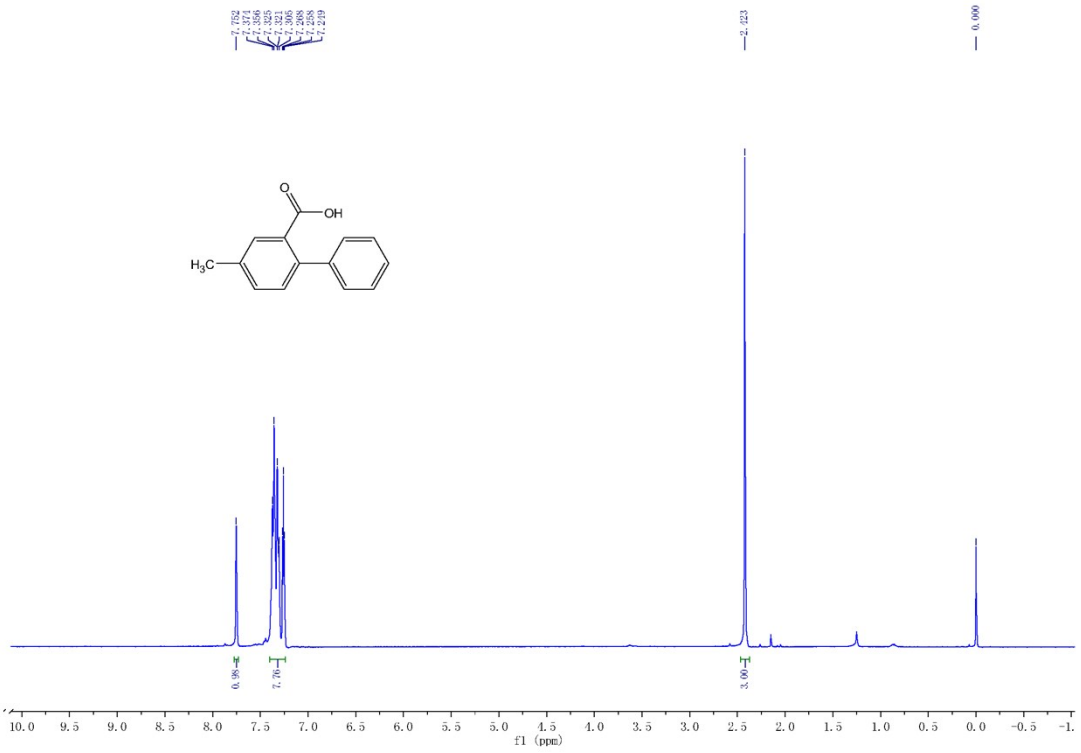
f1 (ppm)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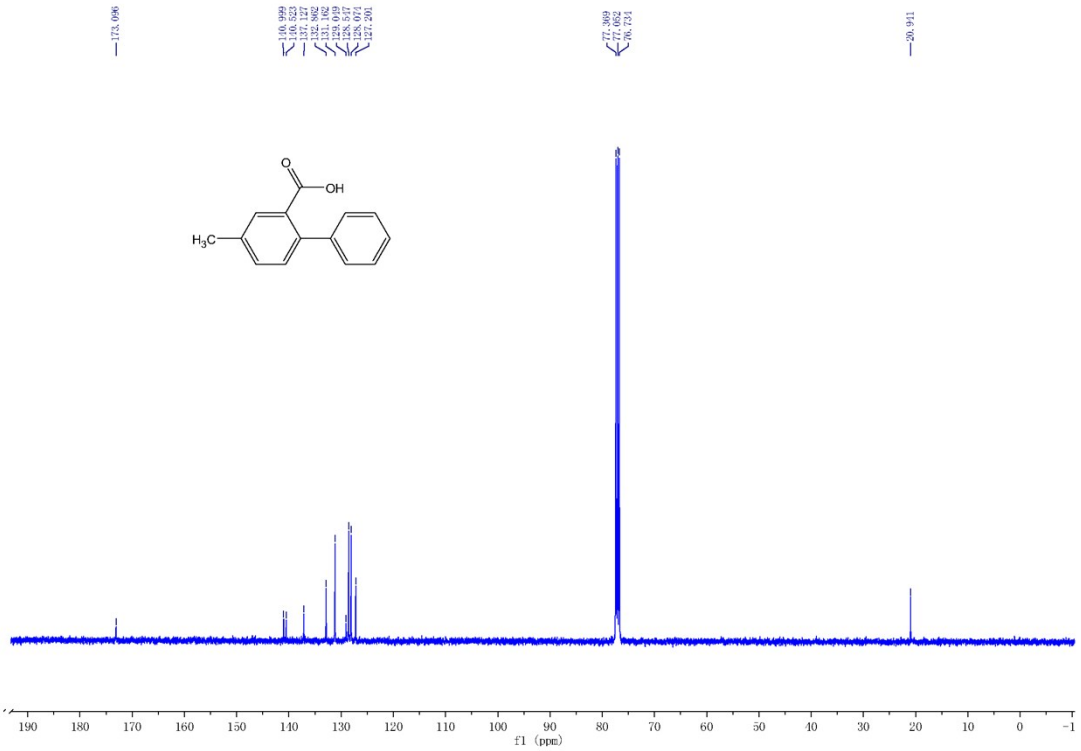
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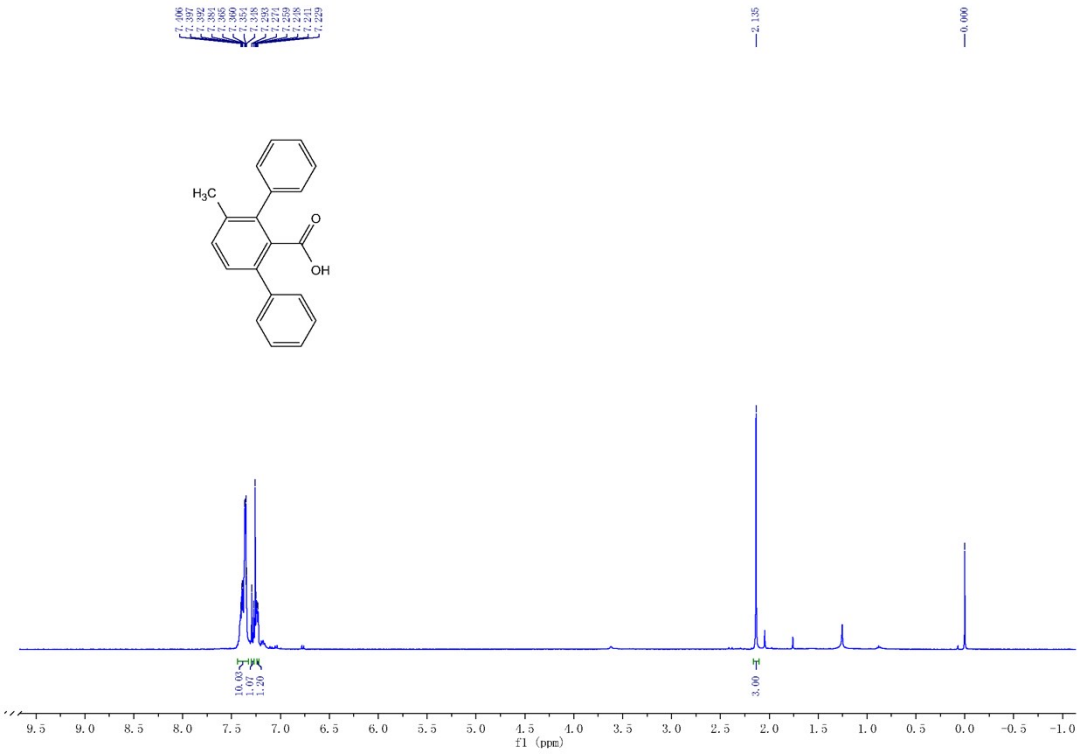
f1 (ppm)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7.229
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H3C
O
OH
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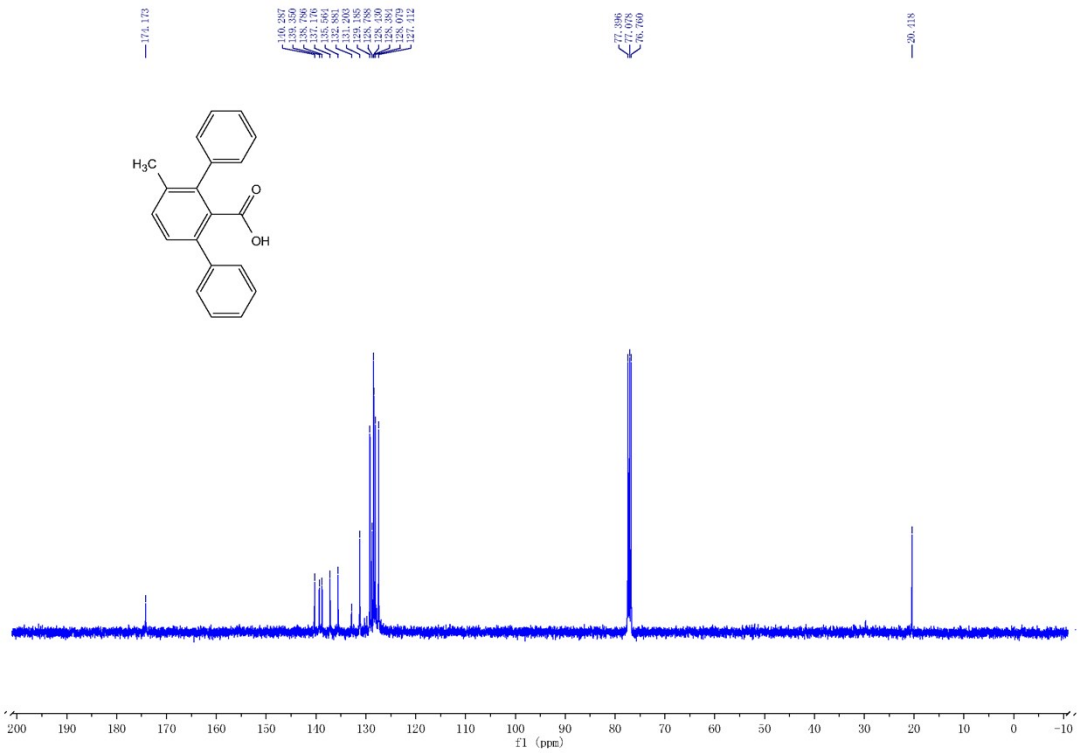
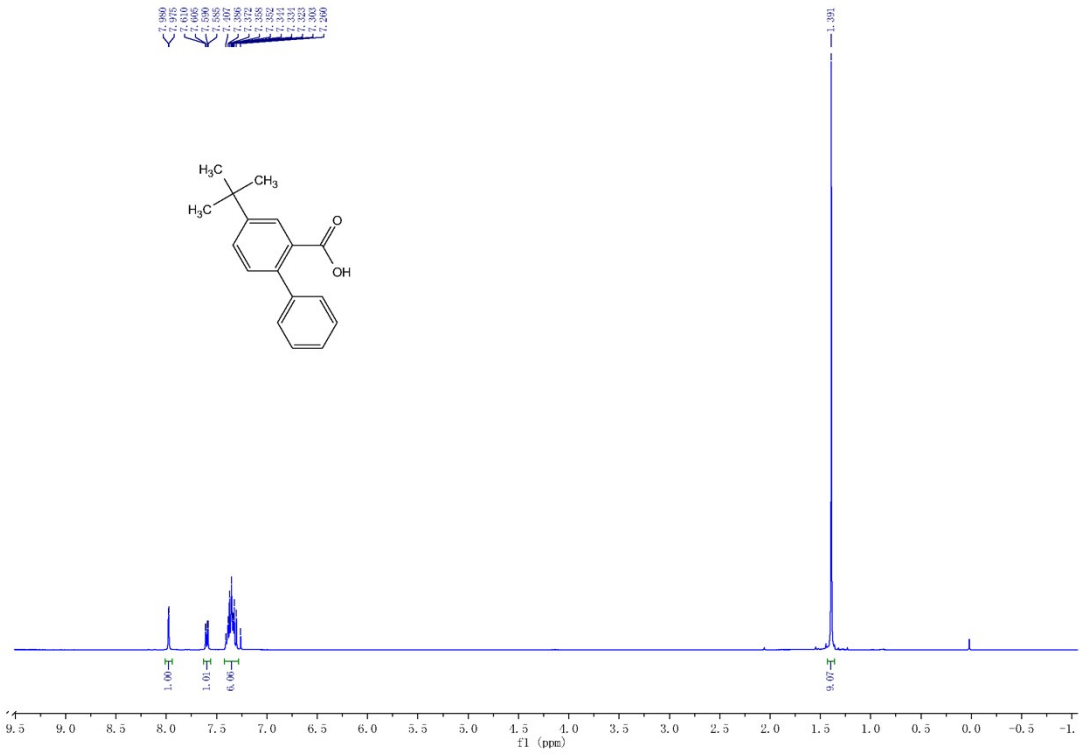
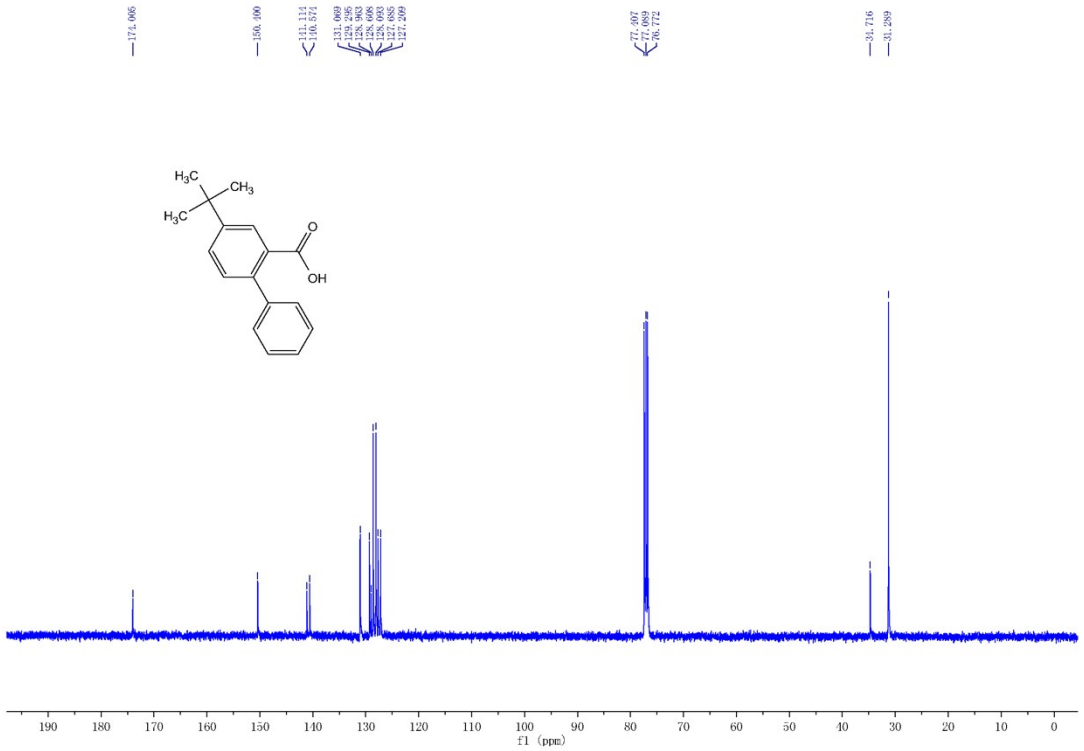
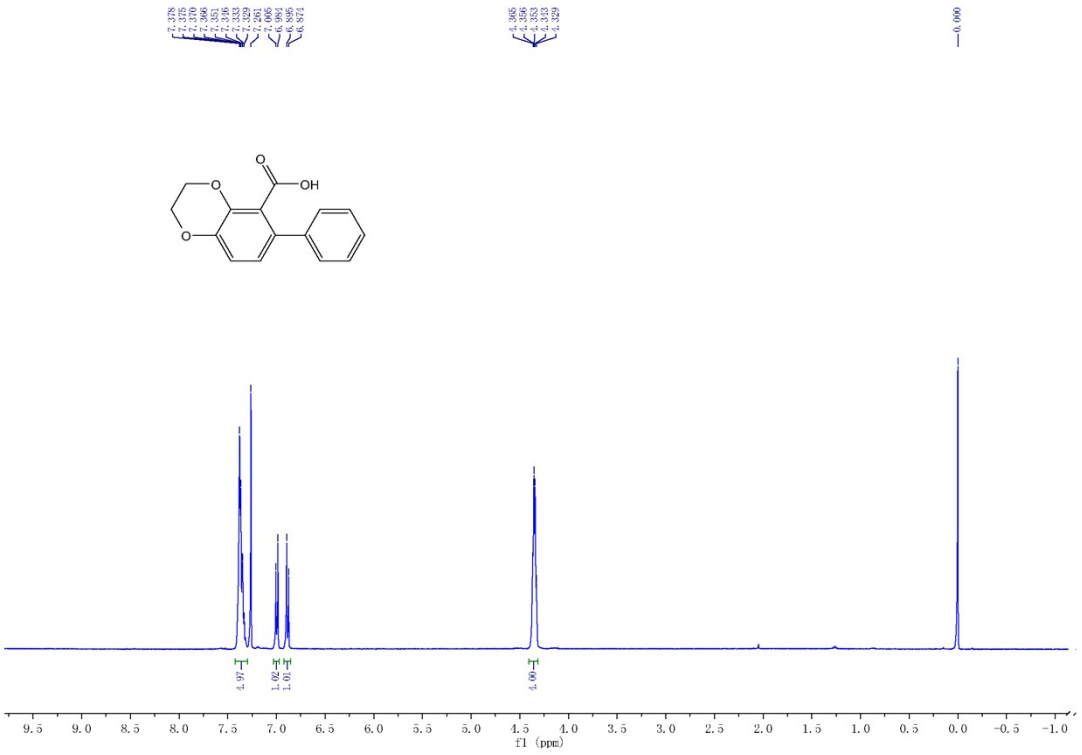
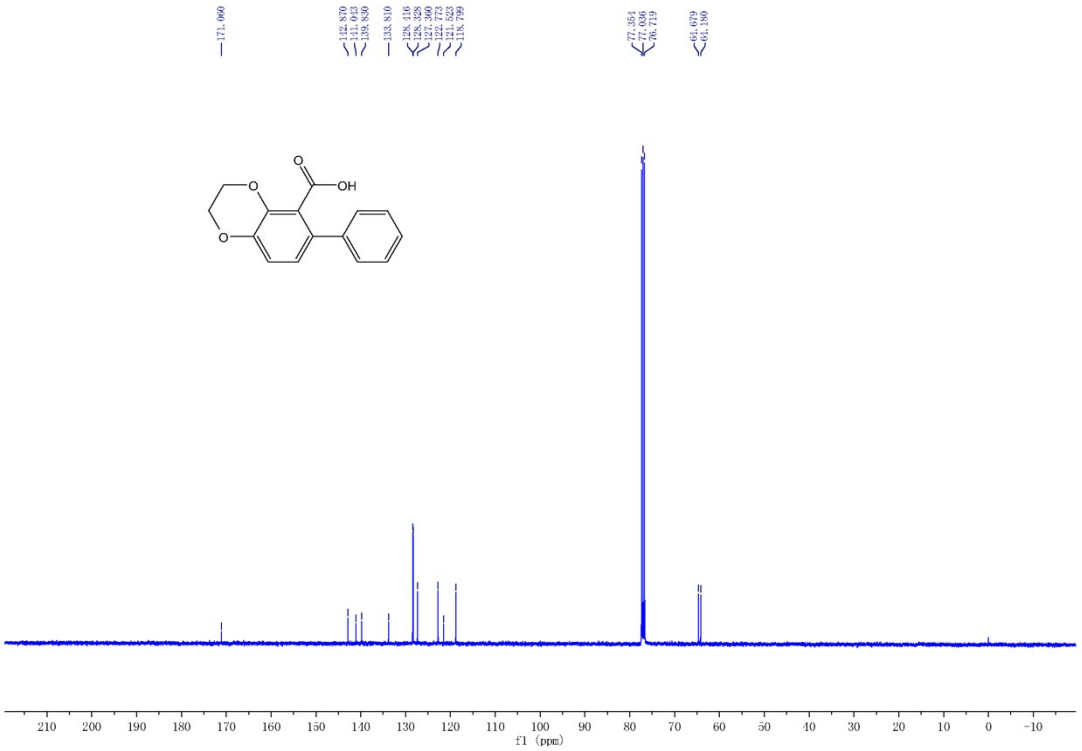
1.97
1.50
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

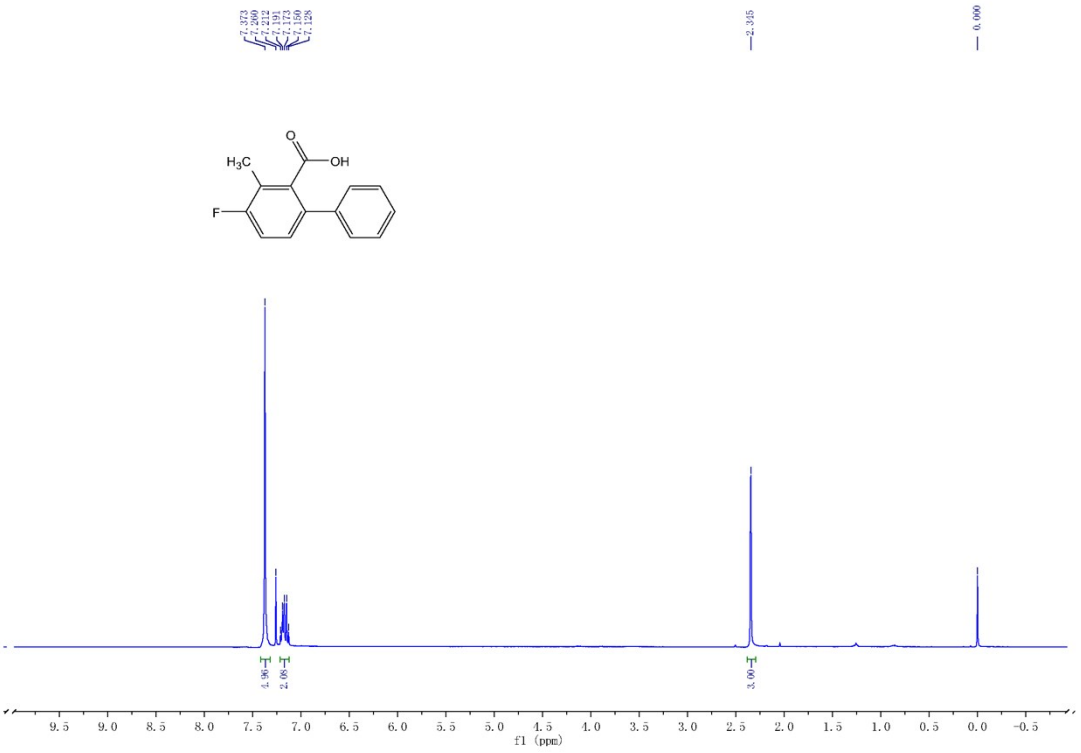

174.173
140.287
139.956
138.790
137.176
135.961
132.981
132.808
129.185
128.788
128.330
128.165
128.079
127.312
77.396
77.078
76.760
20.418
H3C
O
OH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

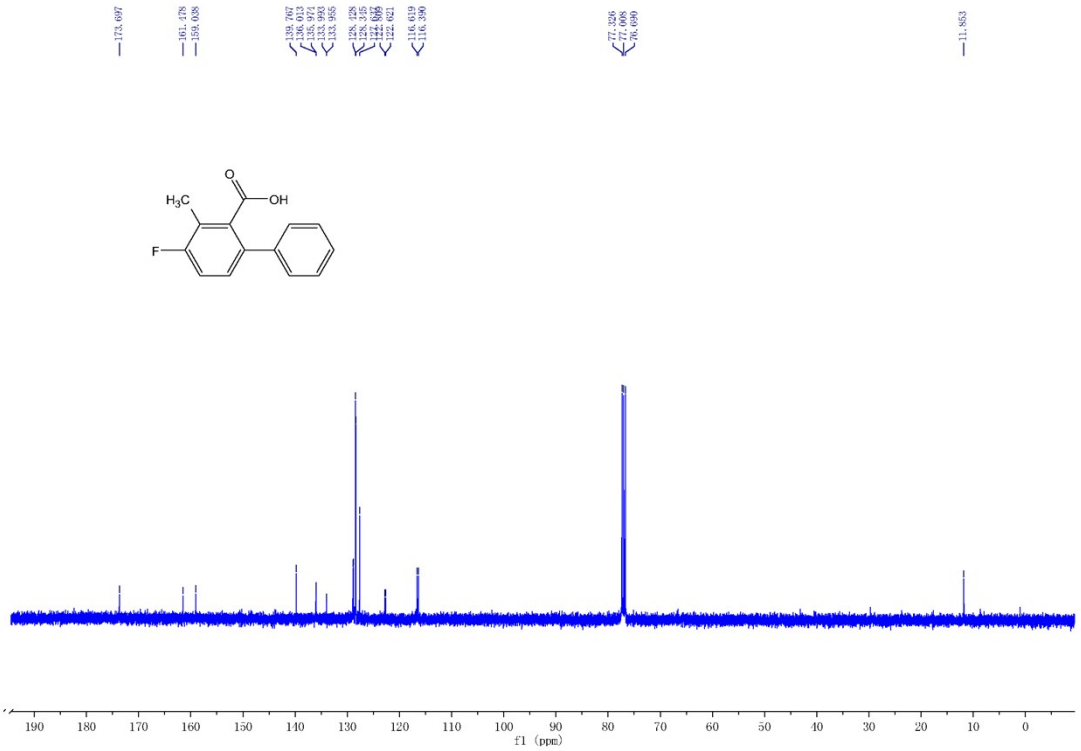

7.980
7.975
7.610
7.606
7.590
7.585
7.397
7.393
7.372
7.358
7.352
7.344
7.334
7.323
7.303
7.260
1.391
H3C
CH3
H3C
O
OH
1.00
1.01
6.06
9.07
f1 (ppm)

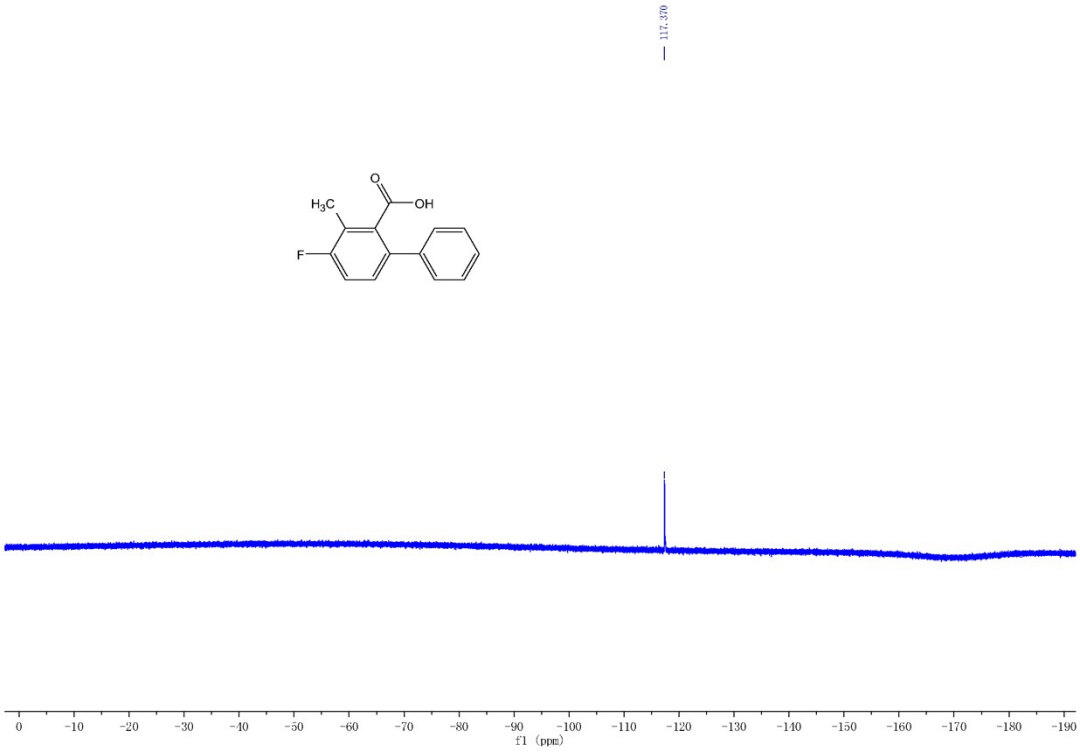

174.066
150.400
141.114
140.574
131.089
129.395
128.983
128.698
128.093
127.695
127.209
77.407
77.099
76.772
35.716
31.269
H3C
CH3
H3C
O
OH
f1 (ppm)

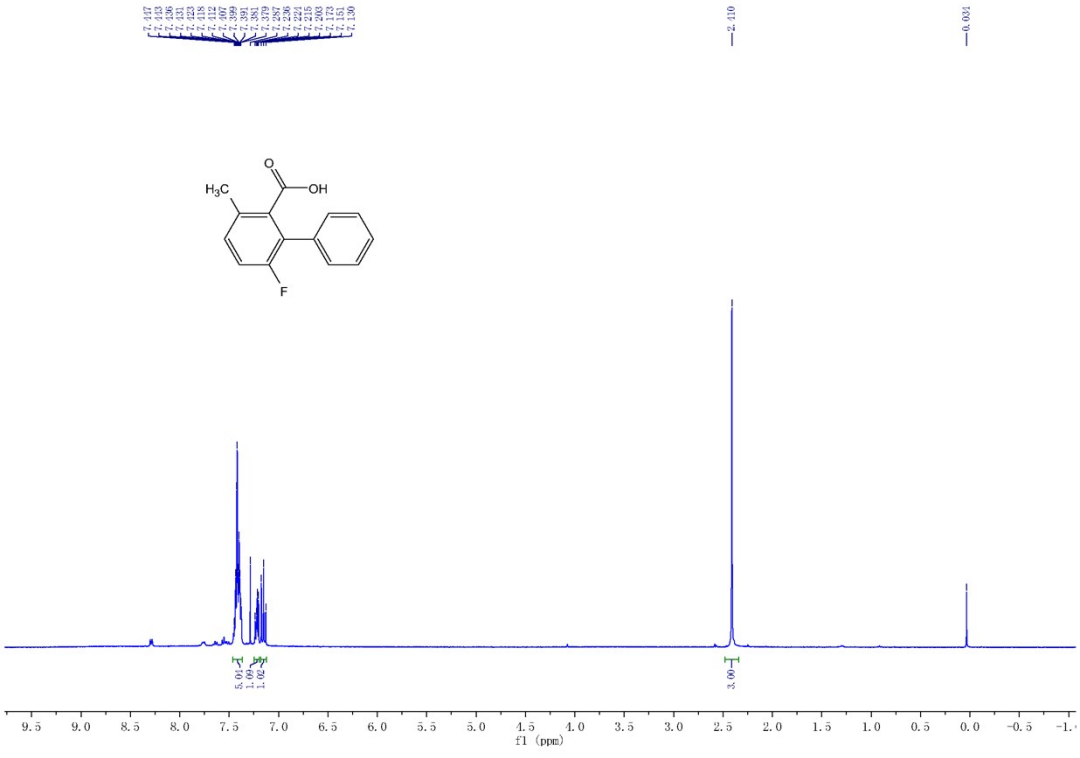

7.378
7.375
7.370
7.366
7.351
7.336
7.333
7.329
7.261
7.006
6.894
6.896
6.874
4.365
4.356
4.353
4.333
4.329
0.000
O
OH
O
O
4.97
1.02
1.01
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

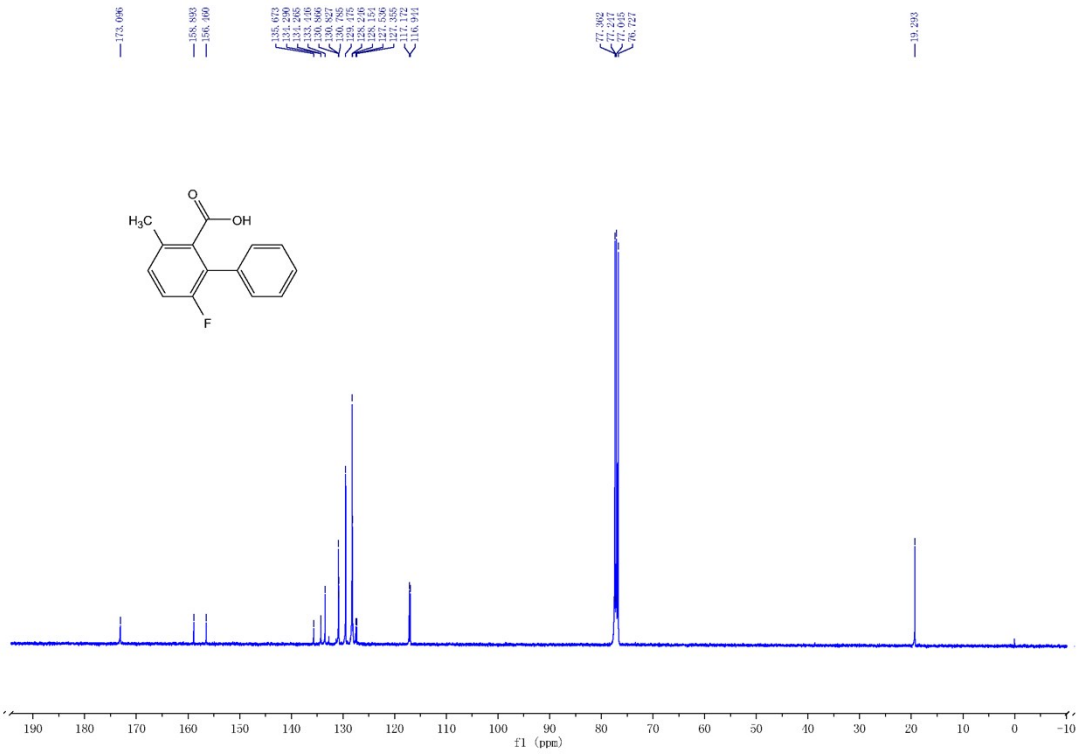

171.060
142.870
141.933
139.830
133.810
128.216
128.208
127.360
122.773
121.523
118.199
77.354
77.054
76.719
61.679
61.180
O
OH
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

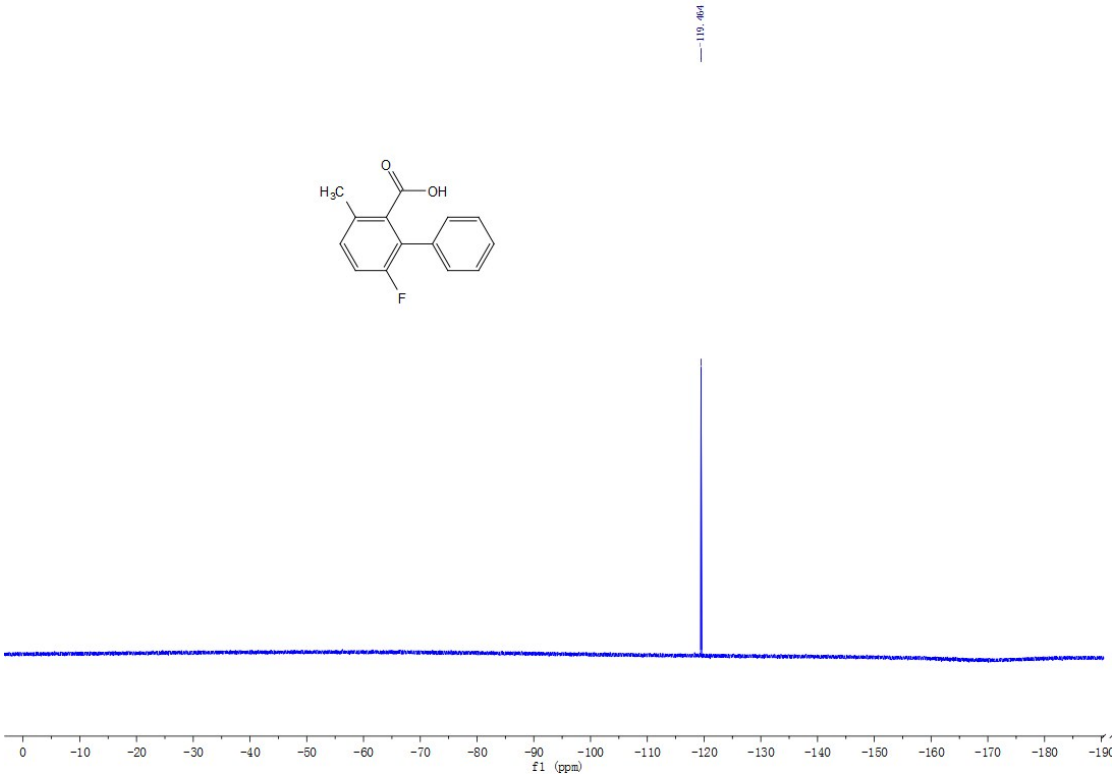

7.373
7.209
7.212
7.191
7.173
7.150
7.128
2.335
0.000
O
OH
H3C
F
4.96
2.08
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

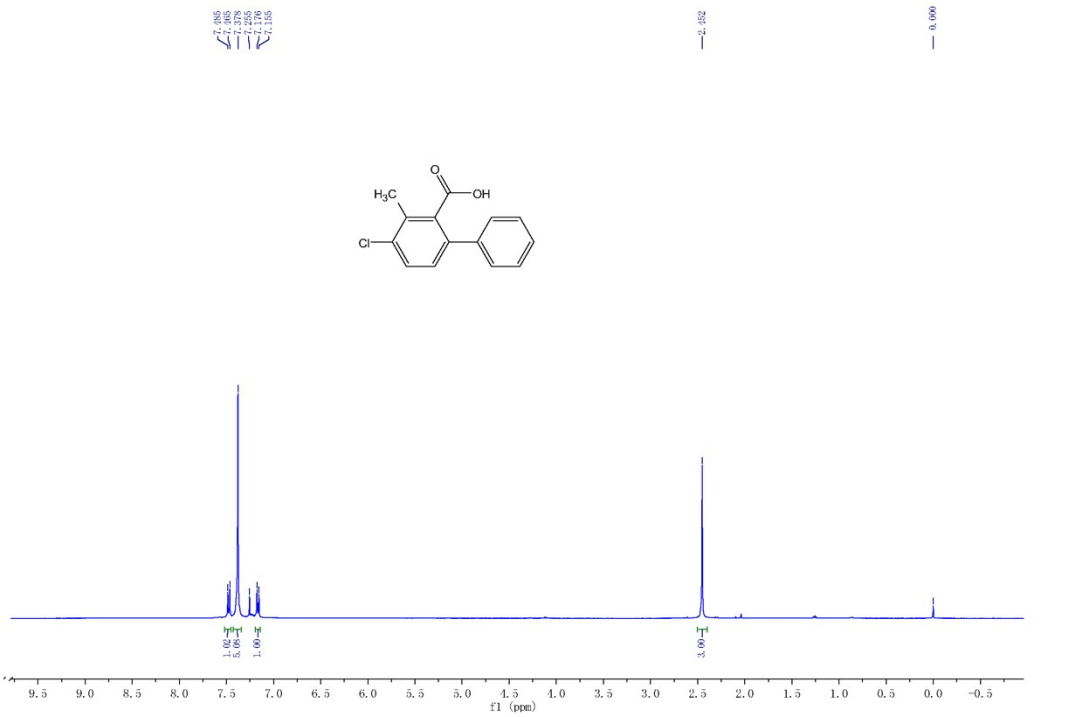

173.697
161.278
159.038
139.767
136.613
135.971
133.993
133.955
128.428
128.335
125.657
122.621
116.619
116.390
77.326
77.008
76.690
11.853
O
OH
H3C
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

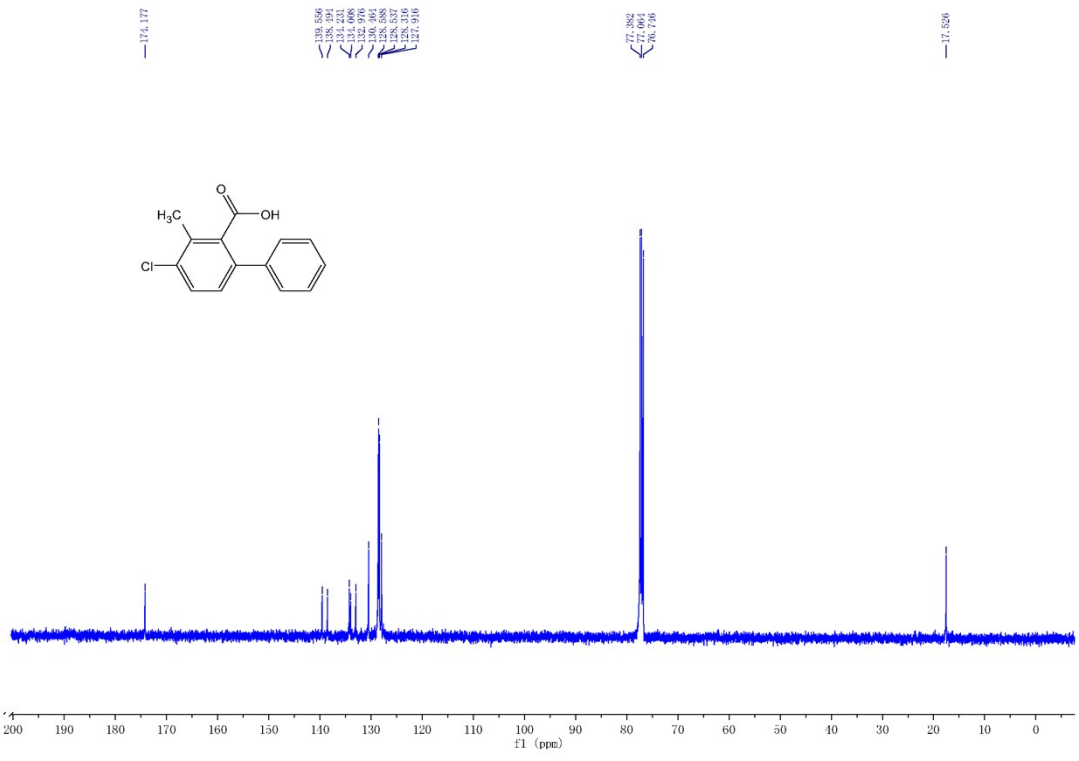

117.370
O
OH
H3C
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

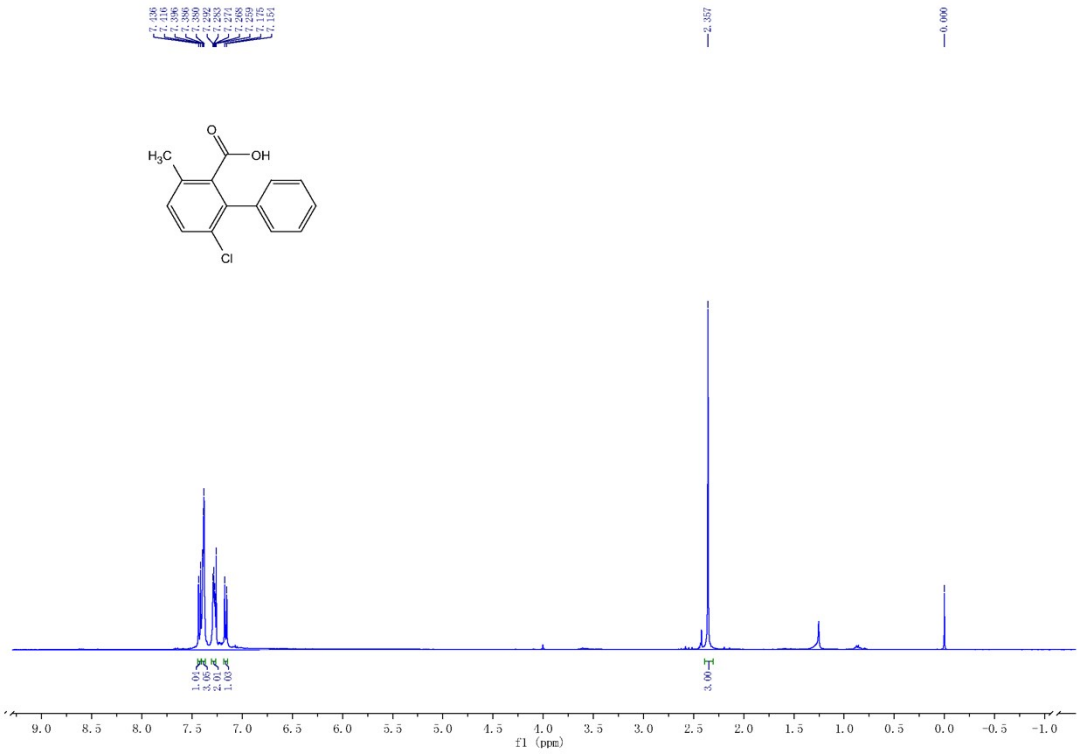

7.417
7.413
7.136
7.131
7.423
7.418
7.412
7.407
7.399
7.391
7.381
7.379
7.367
7.236
7.224
7.215
7.203
7.173
7.151
7.130
2.410
6.031
O
OH
H3C
F
5.01
1.00
1.02
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

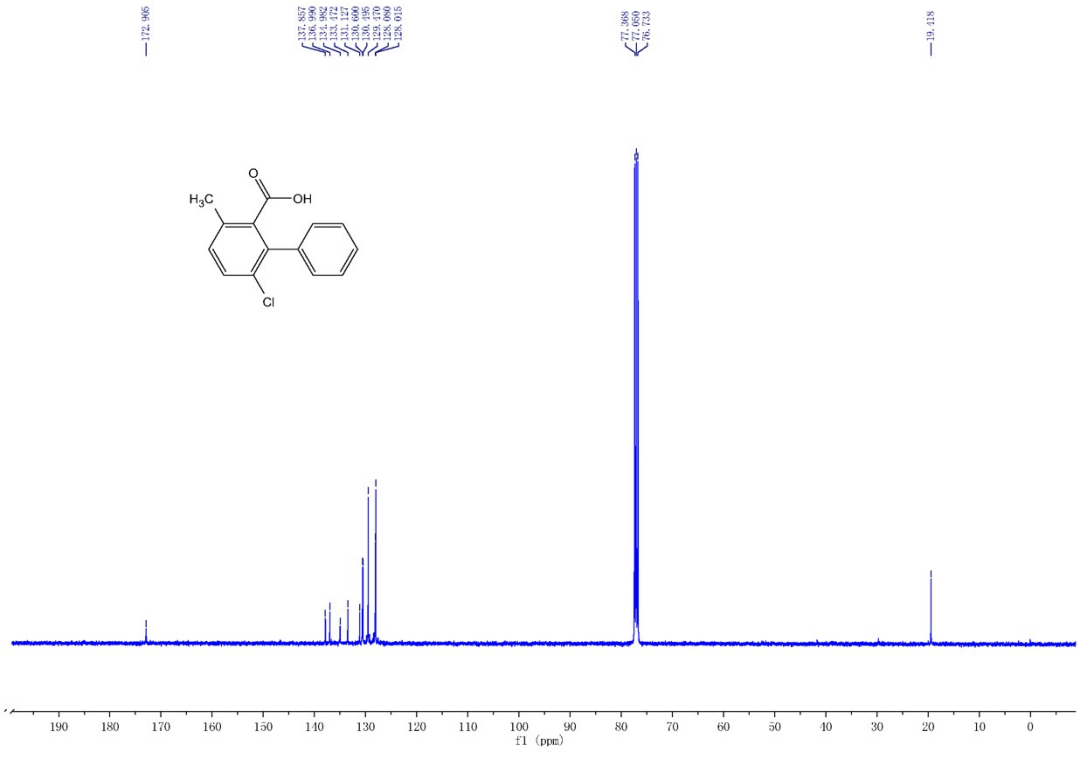

173.096
158.883
156.060
135.673
133.290
133.265
133.036
130.966
130.827
130.785
129.175
129.045
128.159
127.536
127.385
117.172
116.941
77.382
77.070
77.017
76.727
19.293
O
OH
H3C
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

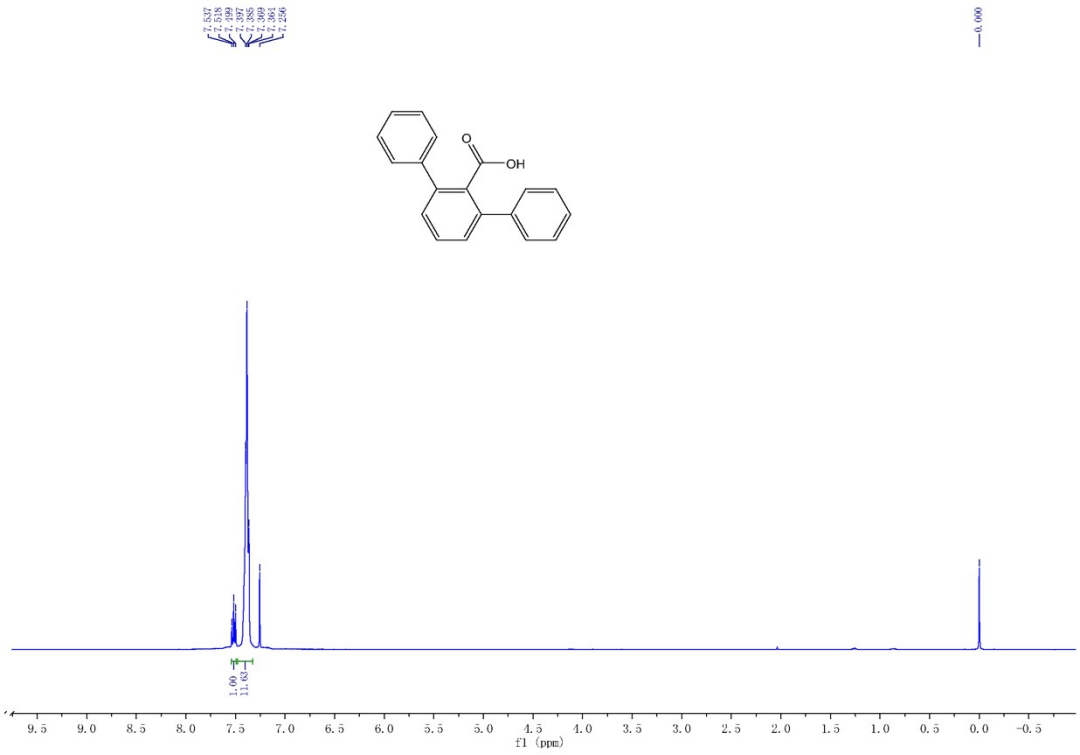

119.464
O
OH
H3C
F
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

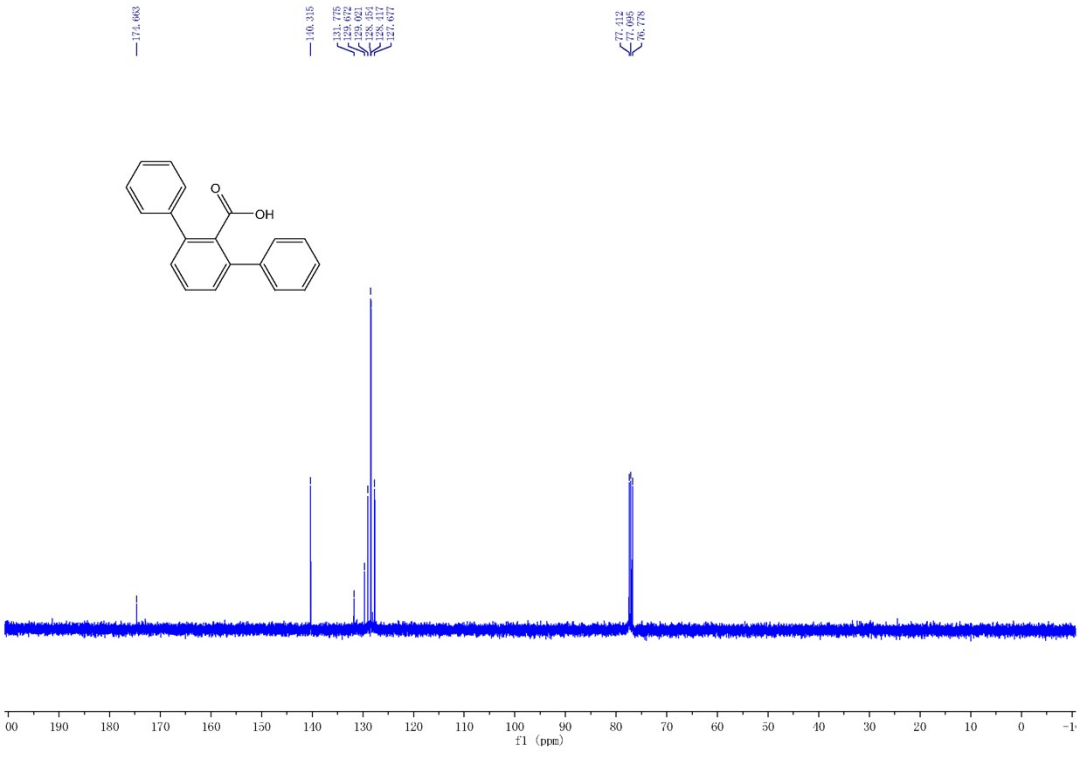

7.385
7.365
7.378
7.358
7.176
7.155
2.552
0.000
O
OH
H3C
Cl
1.02
5.08
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

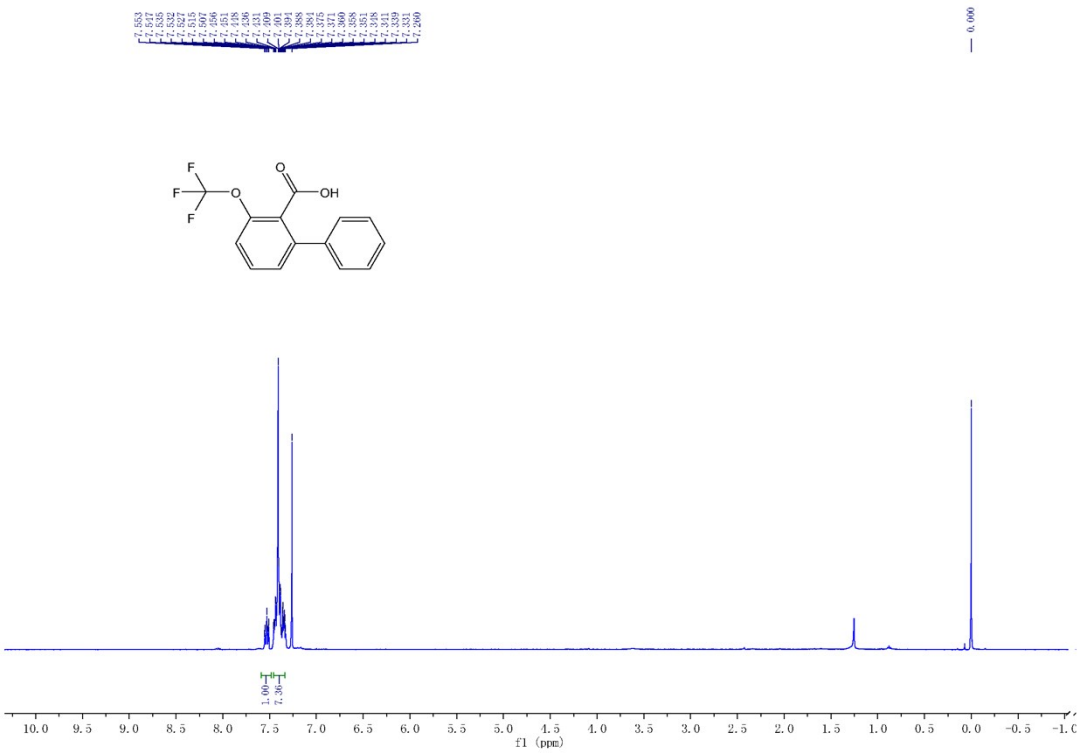

174.177
139.656
138.199
134.231
134.008
132.975
130.960
128.588
128.537
128.316
127.916
77.382
77.064
76.746
17.526
O
OH
H3C
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

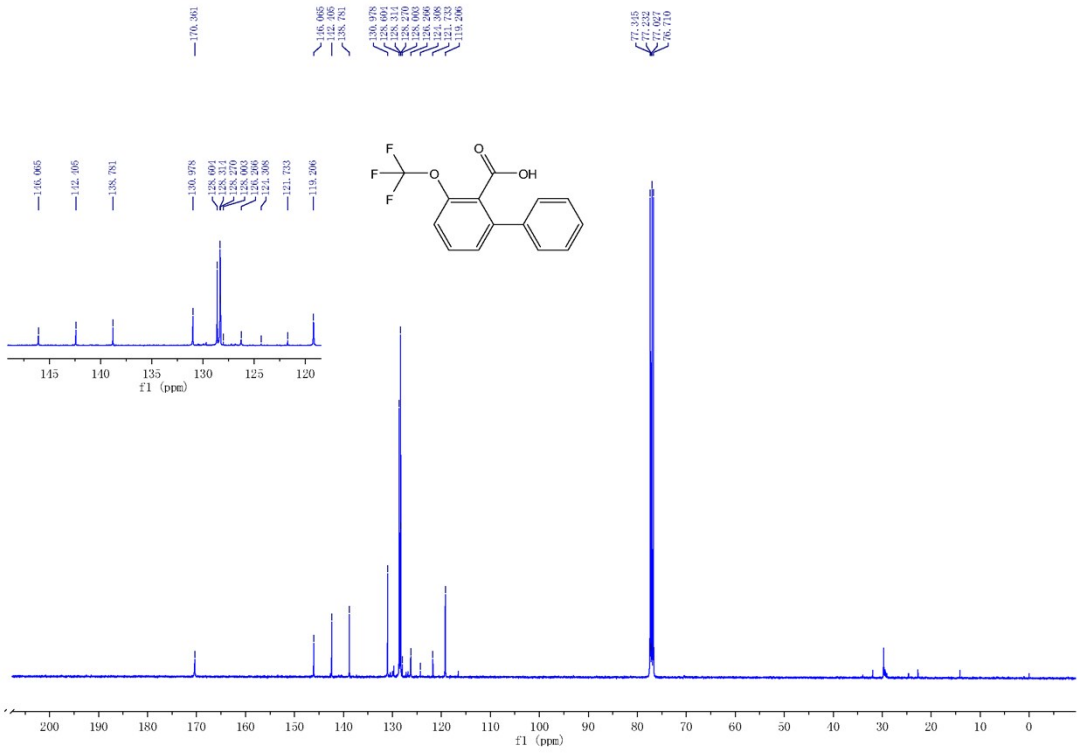

7.436
7.414
7.396
7.386
7.380
7.292
7.283
7.271
7.268
7.259
7.175
7.154
2.357
0.000
O
OH
H3C
Cl
1.04
1.05
2.01
1.03
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

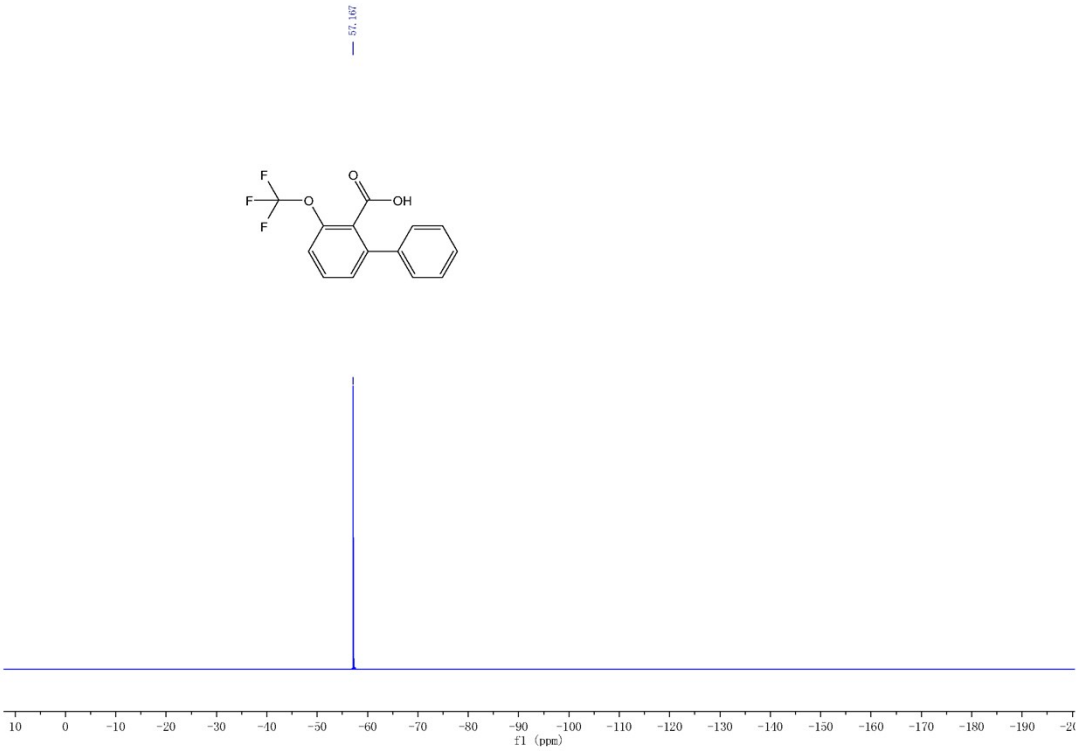

172.906
137.857
136.990
131.982
131.772
131.127
130.600
130.195
129.970
128.699
128.015
77.388
77.069
76.733
19.418
O
OH
H3C
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.547
7.518
7.499
7.397
7.385
7.369
7.364
7.256
0.000
O
OH
1.00
11.63
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.663
140.315
131.775
129.872
129.021
128.554
128.417
127.677
77.412
77.095
76.778
O
OH
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.553
7.537
7.535
7.532
7.527
7.515
7.507
7.496
7.491
7.488
7.436
7.431
7.399
7.391
7.391
7.388
7.381
7.375
7.371
7.360
7.358
7.351
7.339
7.331
7.269
0.000
1.00
7.36
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


170.361
146.005
142.005
138.781
130.978
128.691
128.311
128.270
128.003
126.206
121.308
121.733
119.206
77.345
77.232
77.027
76.710
145 140 135 130 125 120
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


57.167
F
F
F
O
O
OH
10
0
-10
-20
-30
-40
-50
-60
-70
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-100
-110
-120
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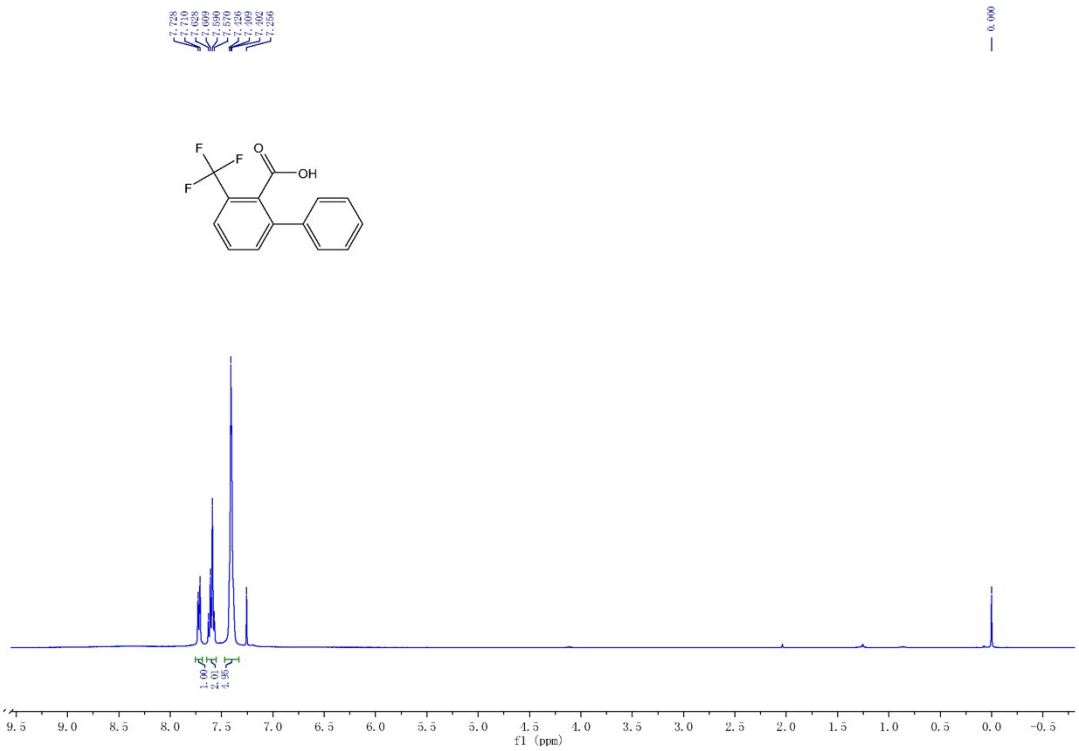
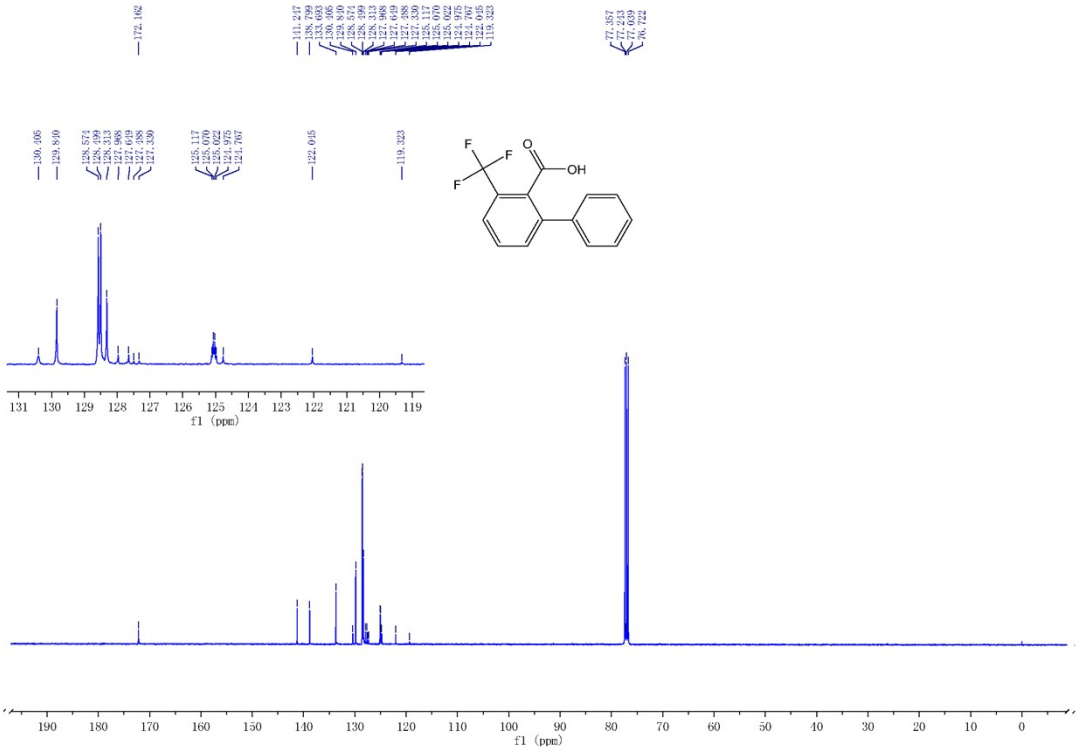
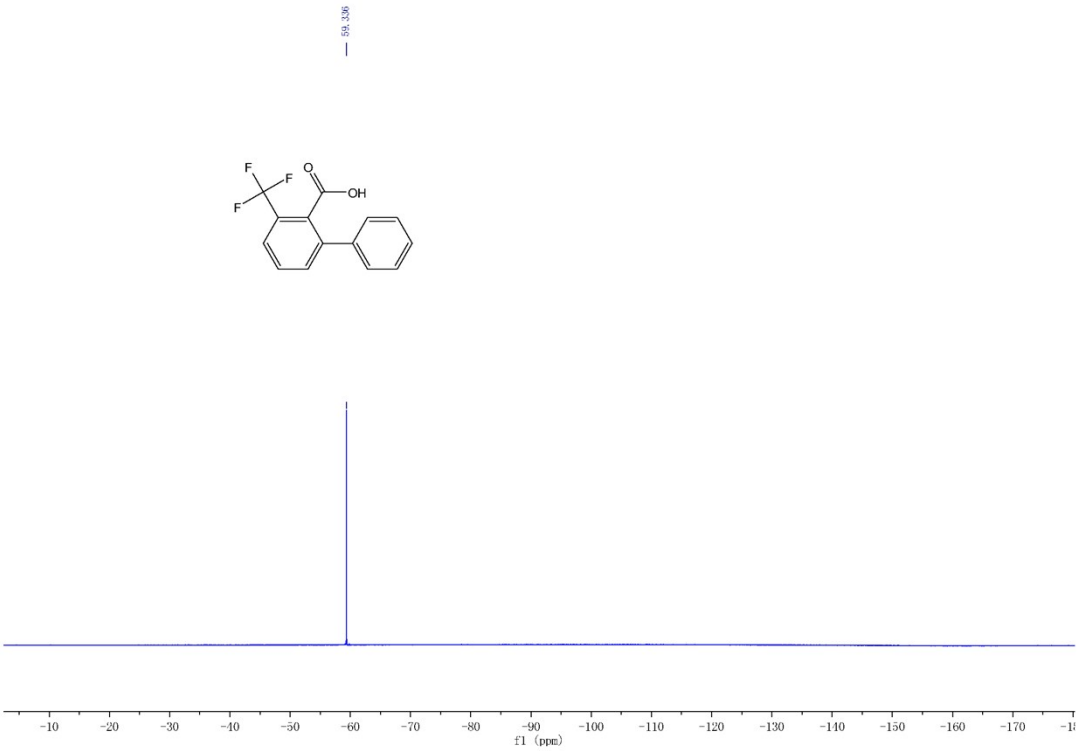
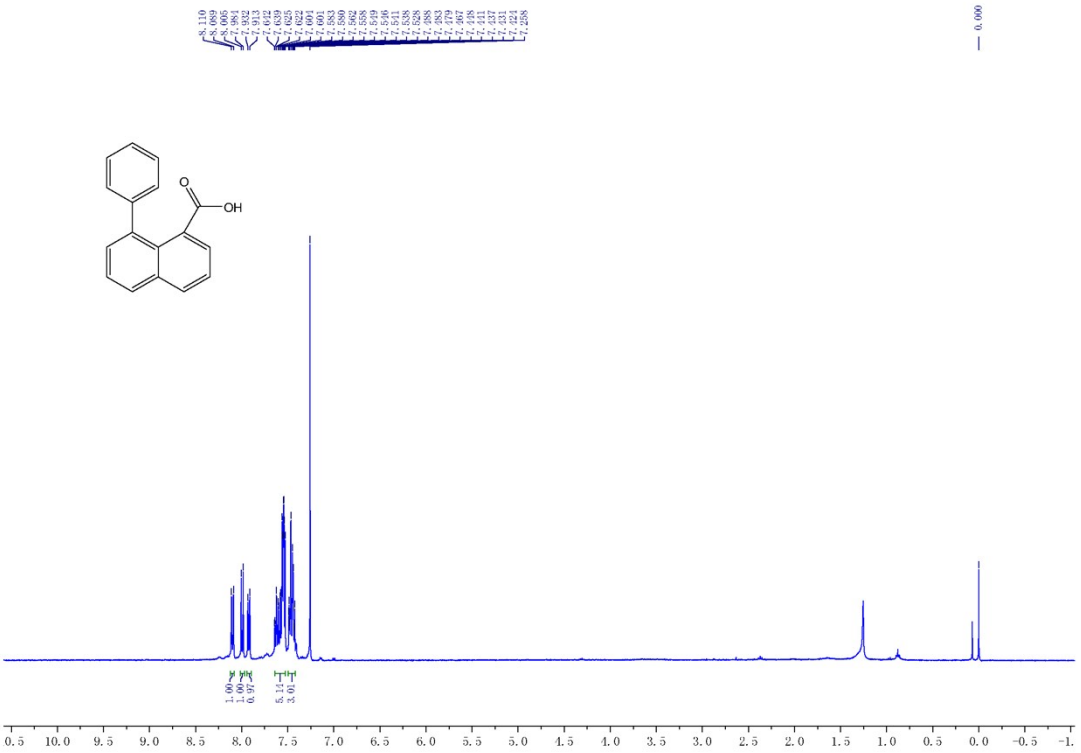
-140
-150
-160
-170
-180
-190
f1 (ppm)


7.728
7.710
7.628
7.609
7.599
7.570
7.426
7.409
7.402
7.256
6.000
F
F
F
O
OH
1.00
2.01
2.40
4.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


172.162
111.247
138.799
133.668
130.005
129.830
128.571
128.359
128.313
127.968
127.649
127.398
127.300
125.117
125.070
125.022
124.975
121.767
122.045
119.323
77.357
77.243
77.039
76.722
F
F
F
O
OH
131 130 129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-59.336
F
F
F
O
OH
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)


8.110
8.089
8.066
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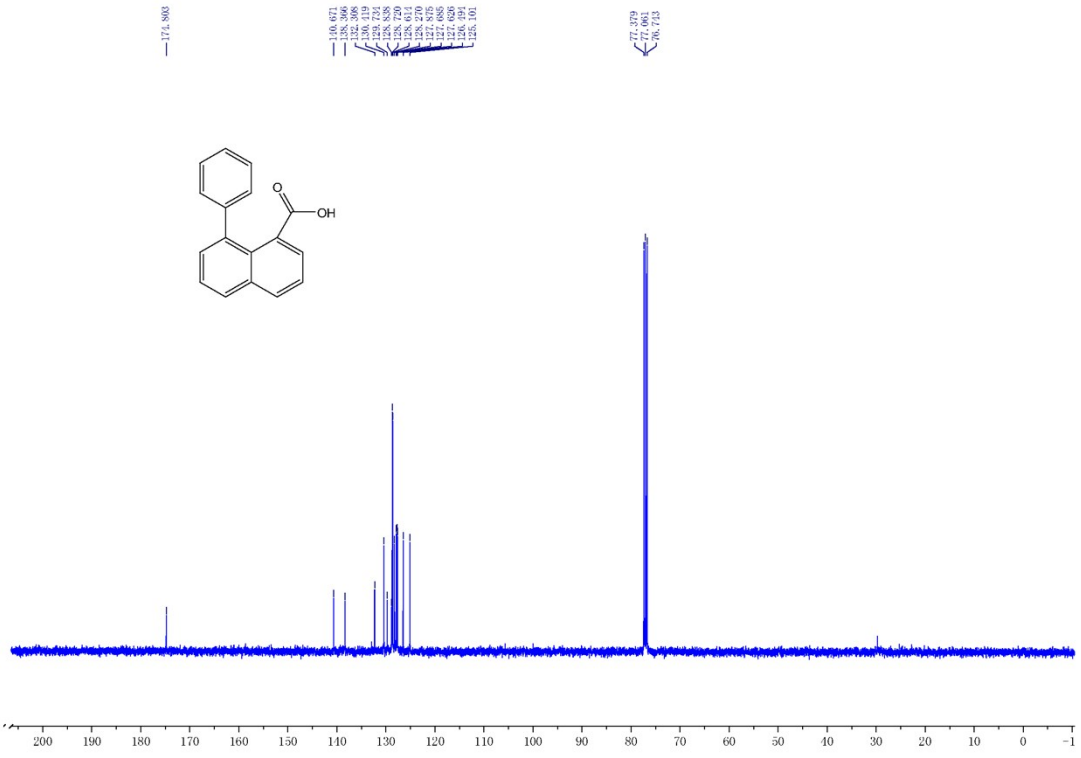
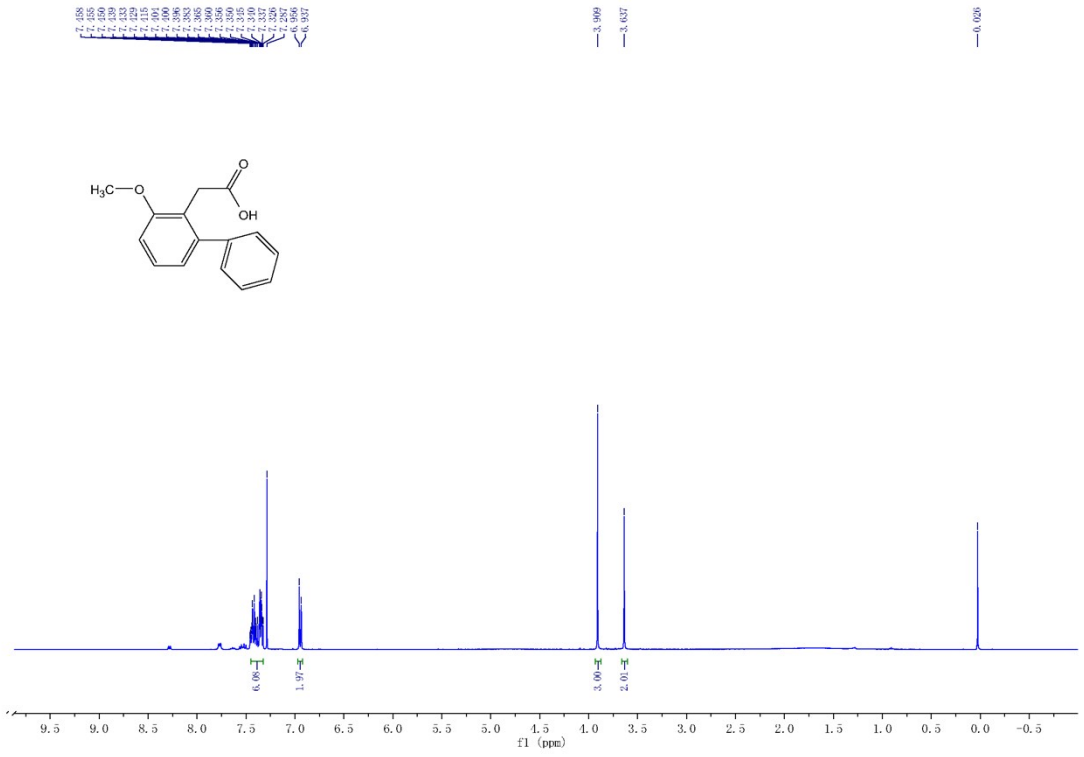
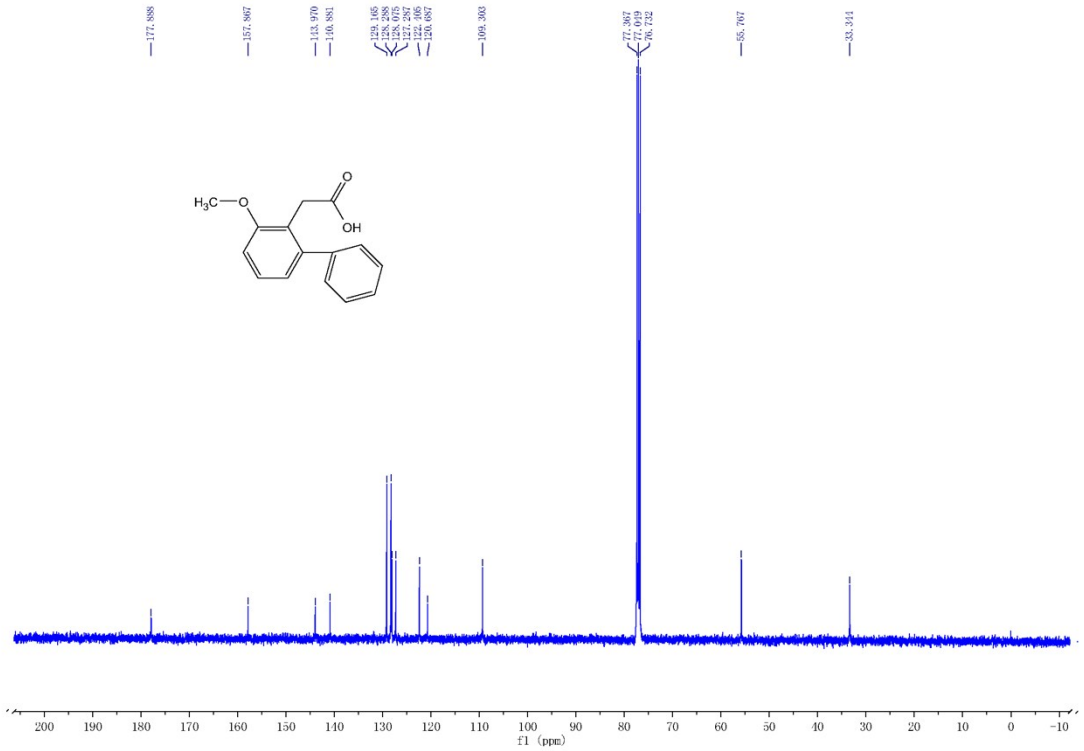
7.932
7.913
7.612
7.609
7.625
7.622
7.604
7.601
7.583
7.580
7.562
7.558
7.549
7.546
7.541
7.538
7.528
7.383
7.479
7.476
7.456
7.441
7.137
7.131
7.261
7.258
0.000
O
OH
1.00
1.00
0.97
5.14
3.01
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.


171.903
140.671
138.966
132.308
130.219
129.732
128.958
128.720
128.614
128.270
127.885
127.626
126.091
125.101
77.379
77.061
76.743
O
OH
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1


7.458
7.455
7.450
7.439
7.433
7.429
7.115
7.091
7.069
7.396
7.383
7.365
7.360
7.356
7.350
7.335
7.319
7.317
7.326
7.287
6.956
6.937
3.909
3.637
0.026
H3C—O
O
OH
6.08
1.97
3.00
2.01
f1 (ppm)


177.888
157.867
143.970
140.881
129.185
128.288
128.075
127.257
124.495
120.687
109.303
77.367
77.019
76.732
55.767
33.344
H3C—O
O
OH
f1 (ppm)