Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A catalyst-free, facile and efficient approach to cyclic ester: synthesis of 4*H*-benzo[*d*][1,3]dioxin-4-ones

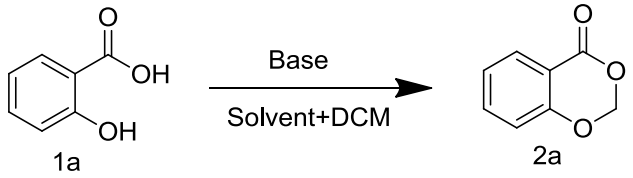
Feng Lin, Qiuling Song, Yuyu Gao and Xiuling Cui*

Table of Contents

I. General Remarks.

All manipulations were conducted with a reaction tube under air atmosphere. ^{1}H-NMR spectra were recorded on Bruker AVIII-400M spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard or calibrated with DMSO (δ = 2.54 ppm). ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm) and DMSO (δ = 40.45 ppm). High Resolution Mass spectra were recorded using Agilent 6450 spectrometer. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Table S1. Screening Different Reaction Conditions For the Formation of **4*H*-benzo[*d*][1,3]dioxin-4-one**.[a]



Entry	Base	Solvent	t(h)	T(^{o}C)	Yield%[b]
1	$K_3PO_4.3H_2O$	DMF	6	60	Trace
2	$K_3PO_4.3H_2O$	DMF	6	80	10
3	$K_3PO_4.3H_2O$	DMF	6	100	>99
4	$K_3PO_4.3H_2O$	DMSO	6	100	>99
5	$K_3PO_4.3H_2O$	1,4-Dioxane	6	100	NR
6	$K_3PO_4.3H_2O$	Toluene	6	100	NR
7	$K_3PO_4.3H_2O$	THF	6	100	NR
8	$K_2HPO_4.3H_2O$	DMF	6	100	15
9	$KHCO_3$	DMF	6	100	NR
10	K_2CO_3	DMF	6	100	Trace
11	Na_2CO_3	DMF	6	100	NR
12	$NaHCO_3$	DMF	6	100	NR
13	Pyridine	DMF	6	100	NR
14	Cs_2CO_3	DMF	6	100	Trace
15	NaOH	DMF	6	100	Trace
16	KOH	DMF	6	100	Trace
17	NaOEt	DMF	6	100	10%
18[c]	$K_3PO_4.3H_2O$	DMF	6	100	NR
19[d]	$K_3PO_4.3H_2O$	DMF	6	100	<5
20[e]	$K_3PO_4.3H_2O$	DMF	15	125	92
21[g]	$K_3PO_4.3H_2O$	DMF	15	125	71

[a] Reaction conditions: Salicylic acid (0.5 mmol), Bases (1 mmol), CH_2Cl_2 (0.6 mL), Solvent (1.5 mL). [b] Isolated yield based on **1a**, NR= no reaction.[c] The reaction was carried out with no CH_2Cl_2. [d] CH_2Cl_2 (0.25 mL), in sealed tube. [e] CH_2Cl_2 (0.25 mL), in sealed tube. [g] CH_2Cl_2 (0.1 mL), in sealed tube.

Table S2. Screening Different Reaction Conditions For the Formation of **2-Methyl-4*H*-benzo[*d*][1,3]dioxin-4-one**.[a]

Entry	Base	Solvent	t(h)	T(°)	Yield%[b]
1	$K_3PO_4.3H_2O$	DMF	10	100	trace
2	$K_3PO_4.3H_2O$	DMF	10	130	66
3	$K_3PO_4.3H_2O$	DMF	10	150	67
4[c]	$K_3PO_4.3H_2O$	DMF	10	130	<15
5[d]	$K_3PO_4.3H_2O$	DMF	10	150	62
6[e]	$K_3PO_4.3H_2O$	DMF	10	150	45

[a]Reaction conditions: Salicylic acid (0.5 mmol), Bases (1 mmol), 1,1-Dichloroethane (1,1-DCE) (1 mL), DMF (1.5 mL), reflux. [b] Isolated yields. [c] CH_3CHCl_2, (0.7 mL), in sealed tube. [d] CH_3CHCl_2 (0.7 mL), in sealed tube. [e] CH_3CHCl_2, (0.35 mL), in sealed tube.

III. Typical procedure:

Condition A:

Salicylic acid (69 mg, 0.5 mmol), $K_3PO_4.3H_2O$ (267 mg, 1 mmol), DCM (0.6 mL), and DMF (1.5 mL) were stirred in 100 ^oC oil bath under air for 6 hours. After cooling to r.t., the reaction solution was extracted with EtOAc and the resulting solution was washed with saturated $NaHCO_3$ solution (20 mL), water (20 mL x3) and brine. Then the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under vacuum. At last, the reaction affords 74.25 mg of the product as a white solid.

Condition B:

5-Chlorosalicylic acid (86 mg, 0.5 mmol), $K_3PO_4.3H_2O$ (267 mg, 1 mmol), DCM (0.6 mL), and DMF (1.5 mL) were stirred in 100 ^oC oil bath under air for 6 hours. After cooling to r.t., the reaction solution was extracted with EtOAc and the resulting solution was washed with saturated $NaHCO_3$ solution (20 mL), water (20 mL x3) and brine. Then the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was purified by flash chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1) to afford 88.32 mg of **2h** as a white solid.

Condition C:

Salicylic acid (69 mg, 0.5 mmol), $K_3PO_4.3H_2O$ (267 mg, 1 mmol), 1,1-Dichloroethane (1,1-DCE) (1 mL) , and DMF (1.5 mL) were stirred and refluxed in 130 ^oC oil bath under air for 10 hours. After cooling to r.t., the reaction solution was extracted with EtOAc and the resulting solution was washed with saturated $NaHCO_3$ solution (20 mL), water (20 mL x3) and brine. Then the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was purified by flash chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1) to afford 54 mg of **3a** as a white solid.

Large scale synthesis of 2a

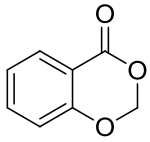
Salicylic acid (2.07 g, 15 mmol), $K_3PO_4.3H_2O$ (6.675 g, 25 mmol), DCM (6 mL) which was charged every other 3.3h, 2 mL once, and DMF (15 mL) were stirred in

100 ^{o}C oil bath under air for 10 hours. After cooling to r.t., the reaction solution was extracted with EtOAc and the resulting solution was washed with saturated $NaHCO_3$ solution (20 mL), water (20 mL x3) and brine. Then the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under vacuum. At last, the reaction affords **2a** in 98% yield as a white solid.

Large scale synthesis of 2n

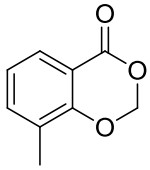
3,5-Ditert-butylsalicylic acid (3.75 g, 15 mmol), $K_3PO_4.3H_2O$ (6.675 g, 25 mmol), DCM (10 mL) which was charged every other 3h, 2 mL once, and DMF (15 mL) were stirred in 100 ^{o}C oil bath under air and reflux condition for 15 hours. After cooling to r.t., the reaction solution was extracted with EtOAc and the resulting solution was washed with saturated $NaHCO_3$ solution (20 mL), water (20 mL x3) and brine. Then the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was purified by flash chromatography on silica gel (eluent: petroleum ether / DCM= 3:1) to afford **3h** in 98% yield as colorless solid.

Analytical data for compounds 2&3:



4*H*-benzo[*d*][1,3]dioxin-4-one(2a):

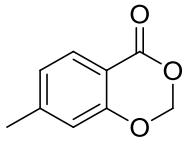
74.25 mg **(**>99%), white solid. Mp: 50-52 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.58 (dd, *J* = 12.2, 4.8 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 5.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.29, 158.39, 136.22, 130.30, 123.51, 116.63, 116.61, 116.59, 114.85, 91.05.



8-Methyl-4*H*-benzo[*d*][1,3]dioxin-4-one(2b):

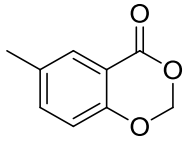
81.18 mg (99%), white solid. Mp: 45-47 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J*

= 7.8 Hz, 1H), 7.49 – 7.35 (m, 1H), 7.06 (t, *J* = 7.7 Hz, 1H), 5.65 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.70, 156.73, 137.18, 127.78, 126.23, 122.93, 114.49, 90.89, 14.82; HRMS calcd. for $C_9H_9O_3$ $[M+H]^+$ 165.0473, found 165.0545.



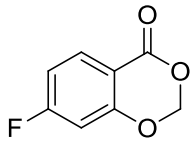
7-Methyl-4*H*-benzo[*d*][1,3]dioxin-4-one(2c):

81 mg **(**99%**),** white solid. Mp: 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.87 (s, 1H), 5.63 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.47, 158.43, 148.05, 130.14, 124.76, 116.73, 112.20, 91.03, 22.01; HRMS calcd. for $C_9H_9O_3$ $[M+H]^+$ 165.0473, found 165.0540.



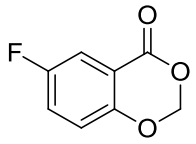
6-Methyl-4*H*-benzo[*d*][1,3]dioxin-4-one(2d):

80.3 mg **(**98%**)**, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 1.7, 0.5 Hz, 1H), 7.43 – 7.35 (m, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 5.63 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.51, 156.34, 137.13, 133.23, 129.92, 116.31, 114.46, 91.05, 20.45; HRMS calcd. for $C_9H_9O_3$ $[M+H]^+$ 165.0473, found 165.0545.



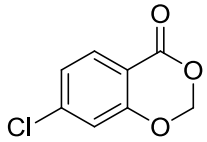
7-Fluoro-4*H*-benzo[*d*][1,3]dioxin-4-one(2e):

81.48 mg (97%)**,** white solid. Mp: 49-51 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, *J* = 8.8, 6.2 Hz, 1H), 6.92 (td, *J* = 8.5, 2.4 Hz, 1H), 6.78 (dd, *J* = 9.0, 2.4 Hz, 1H), 5.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.58, 166.01, 160.43, 160.05 (d, *J* = 13.6 Hz), 132.91 (d, *J* = 11.3 Hz), 111.93 (d, *J* = 22.8 Hz), 111.34 (d, *J* = 3.3 Hz), 104.19 (d, *J* = 25.3 Hz), 91.31; HRMS calcd. for $C_8H_6FO_3$ $[M+H]^+$ 169.0223, found 169.0301.



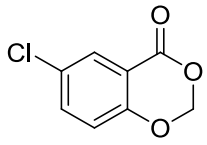
6-Fluoro-4*H*-benzo[*d*][1,3]dioxin-4-one(2f):

74.8 mg (89%), white solid. Mp: 99-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 7.7, 3.1 Hz, 1H), 7.36 – 7.26 (m, 1H), 7.07 (dd, *J* = 9.0, 4.1 Hz, 1H), 5.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.40 (d, *J* = 2.8 Hz), 159.31, 156.88, 154.65 (d, *J* = 2.2 Hz), 123.85 (d, *J* = 24.4 Hz), 118.42 (d, *J* = 7.7 Hz), 115.79 (d, *J* = 24.6 Hz), 104.95, 91.29; HRMS calcd. for $C_8H_6FO_3$ $[M+H]^+$ 169.0223, found 169.0299.



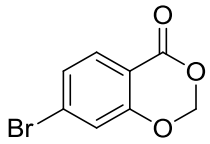
7-Chloro-4*H*-benzo[*d*][1,3]dioxin-4-one(2g):

87.4 mg (95%), white solid. Mp: 99-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.18 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.10 (d, *J* = 2.1 Hz, 1H), 5.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.50, 158.77, 142.35, 131.50, 124.39, 117.12, 113.32, 91.24; HRMS calcd. for $C_8H_7ClO_3$ $[M+H]^+$ 184.9927, found 185.0007.



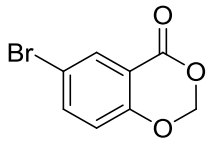
6-Chloro-4*H*-benzo[*d*][1,3]dioxin-4-one(2h):

88.32 mg (96%), white solid. Mp: 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 2.6 Hz, 1H), 7.53 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 5.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.14, 156.86, 136.29, 129.71, 129.69, 129.00, 118.34, 115.91, 91.19; HRMS calcd. for $C_8H_7ClO_3$ $[M+H]^+$ 184.9927, found 184.9994.



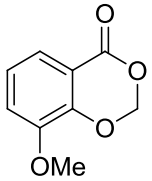
7-Bromo-4*H*-benzo[*d*][1,3]dioxin-4-one(2i):

102.6 mg (90%), white solid. Mp: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.28 (d, *J* = 1.7 Hz, 1H), 5.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.60, 158.62, 131.48, 130.72, 127.27, 120.13, 113.73, 91.22; HRMS calcd. for $C_8H_6BrO_3$ $[M+H]^+$ 228.9422, found 228.9503.



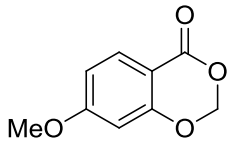
7-Bromo-4*H*-benzo[*d*][1,3]dioxin-4-one(2j):

104.88 mg (92%), white solid. Mp: 106-108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 2.5 Hz, 1H), 7.67 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 1H), 5.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.99, 157.33, 139.10, 132.75, 118.64, 116.33, 116.03, 91.15; HRMS calcd. for $C_8H_6BrO_3$ $[M+H]^+$ 228.9422, found 228.9485.



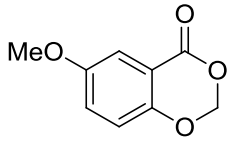
8-Methoxy-4*H*-benzo[*d*][1,3]dioxin-4-one(2k):

88.2 mg (98%), white solid. Mp: 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.21 – 7.08 (m, 2H), 5.70 (s, 2H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.08, 148.26, 147.68, 123.20, 121.21, 117.50, 115.57, 91.29, 56.31; HRMS calcd. for $C_9H_9O_4$ $[M+H]^+$ 181.0423, found 181.0499.



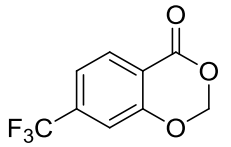
7-Methoxy-4*H*-benzo[*d*][1,3]dioxin-4-one(2l):

89.1 mg (99%), white solid. Mp: 74-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.8 Hz, 1H), 6.72 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.51 (d, *J* = 2.1 Hz, 1H), 5.63 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.09, 161.30, 160.30, 131.89, 111.44, 107.39, 100.35, 91.07, 55.80; HRMS calcd. for $C_9H_9O_4$ $[M+H]^+$ 181.0423, found 181.0492.



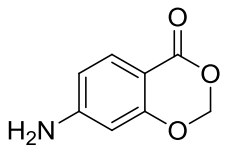
6-Methoxy-4*H*-benzo[*d*][1,3]dioxin-4-one(2m):

85.5 mg (95%), white solid. Mp: 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 3.1 Hz, 1H), 7.16 (dd, *J* = 9.1, 3.1 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 5.62 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.51, 155.48, 152.74, 124.89, 117.83, 114.97, 111.29, 91.23, 55.90, 55.88, 55.86; HRMS calcd. for $C_9H_9O_4$ $[M+H]^+$ 181.0423, found 181.0498.



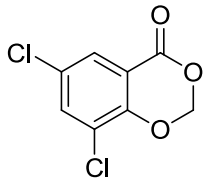
7-Trifluoromethyl-4*H*-benzo[*d*][1,3]dioxin-4-one(2n):

81.75 mg (75%), white solid. Mp: 67-69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.1 Hz, 1H), 7.45 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.36 (s, 1H), 5.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.98, 158.36, 137.82, 137.48, 131.39, 124.08, 121.36, 120.12 (q, *J* = 3.8 Hz), 117.65, 114.41 (d, *J* = 4.2 Hz), 91.36.



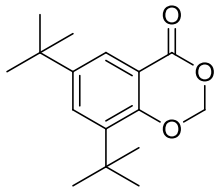
7-Amino-4*H*-benzo[*d*][1,3]dioxin-4-one(2o):

74.25 mg (90%), white solid. Mp: 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.6 Hz, 1H), 6.41 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.19 (d, *J* = 2.2 Hz, 1H), 5.58 (s, 2H), 4.42 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.90, 160.35, 154.13, 132.13, 110.65, 104.16, 99.43, 90.81; HRMS calcd. for $C_8H_8NO_3$ $[M+H]^+$ 166.0426, found 166.0501.



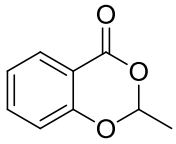
6,8-Dichloro-4*H*-benzo[*d*][1,3]dioxin-4-one(2p):

76.3 mg (70%), white solid. Mp: 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 2.5 Hz, 1H), 7.63 (d, *J* = 2.5 Hz, 1H), 5.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.16, 153.04, 136.03, 128.81, 128.25, 123.01, 116.76, 91.42.



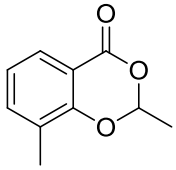
6,8-Ditert-butyl-4*H*-benzo[*d*][1,3]dioxin-4-one(2q):

128.4 mg (98%), white solid. Mp: 58-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.57 (ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H), 7.17 (td, *J* = 7.7, 1.0 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 5.75 (q, *J* = 5.2 Hz, 1H), 1.76 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.44, 155.30, 145.93, 137.69, 130.82, 124.43, 114.97, 90.43, 34.88, 34.70, 31.27, 29.62; HRMS calcd. for $C_{16}H_{23}O_3$ $[M+H]^+$ 263.1569, found 263.1642.



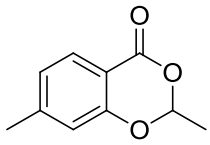
2-Methyl-4*H*-benzo[*d*][1,3]dioxin-4-one(3a):

54 mg (65%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.57 (ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H), 7.17 (td, *J* = 7.7, 1.0 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 5.75 (q, *J* = 5.2 Hz, 1H), 1.76 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.17, 158.33, 136.14, 130.17, 123.29, 116.54, 114.31, 98.96, 19.98; HRMS calcd. for $C_9H_9O_3$ $[M+H]^+$ 165.0473, found 165.0542.



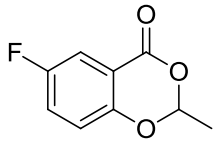
2,8-Dimethyl-4*H*-benzo[*d*][1,3]dioxin-4-one(3b):

43.6 mg (49%), white solid. Mp: 72-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 6.7 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 5.73 (d, *J* = 5.2 Hz, 1H), 2.26 (s, 3H), 1.78 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.64, 156.69, 137.10, 127.68, 126.12, 122.71, 113.97, 98.74, 20.08, 14.92; HRMS calcd. for $C_{10}H_{11}O_3$ $[M+H]^+$ 179.0630, found 179.0704.



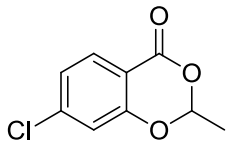
2,7-Dimethyl-4*H*-benzo[*d*][1,3]dioxin-4-one(3c):

47.2 mg (53%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.83 (s, 1H), 5.72 (q, *J* = 5.2 Hz, 1H), 2.40 (s, 3H), 1.74 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.36, 158.39, 147.91, 129.99, 124.53, 116.66, 111.66, 98.88, 22.03, 20.02; HRMS calcd. for $C_{10}H_{11}O_3$ $[M+H]^+$ 179.0630, found 179.0705.



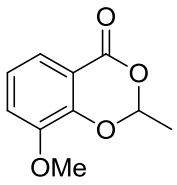
6-Fluoro-2-methyl-4*H*-benzo[*d*][1,3]dioxin-4-one(3d):

55 mg (55%), light yellow solid. Mp: 74-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 7.7, 3.1 Hz, 1H), 7.33 – 7.23 (m, 1H), 7.03 (dd, *J* = 9.0, 4.1 Hz, 1H), 5.73 (q, *J* = 5.2 Hz, 1H), 1.75 (dd, *J* = 4.6, 2.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.30, 159.21, 156.79, 154.58 (d, *J* = 2.1 Hz), 123.72 (d, *J* = 24.4 Hz), 118.29 (d, *J* = 7.7 Hz), 115.65 (d, *J* = 24.4 Hz), 104.98, 99.38, 19.93; HRMS calcd. for $C_9H_8FO_3$ $[M+H]^+$ 183.0379, found 183.0460.



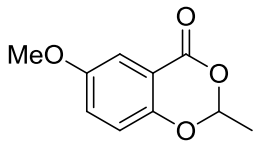
7-Chloro-2-methyl-4*H*-benzo[*d*][1,3]dioxin-4-one(3e):

42.57 mg (43%), white solid. Mp: 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.06 (d, *J* = 1.9 Hz, 1H), 5.75 (q, *J* = 5.2 Hz, 1H), 1.76 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.37, 158.74, 142.21, 131.33, 124.13, 117.04, 112.79, 99.32, 19.94; HRMS calcd. for $C_9H_8ClO_3$ $[M+H]^+$ 199.0084, found 199.0173.



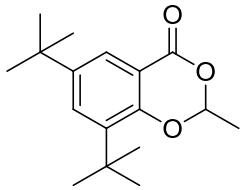
8-Methoxy-2-methyl-4*H*-benzo[*d*][1,3]dioxin-4-one(3f):

41.71 mg (43%), white solid. Mp: 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.16 – 7.05 (m, 2H), 5.77 (q, *J* = 5.2 Hz, 1H), 3.92 (s, 3H), 1.81 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.04, 148.23, 147.65, 122.93, 121.08, 117.41, 115.06, 99.25, 56.26, 20.02; HRMS calcd. for $C_{10}H_{11}O_4$ $[M+H]^+$ 195.0579, found 195.0651.



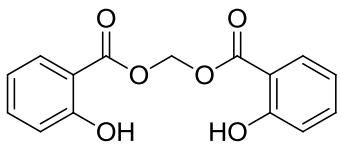
6-Methoxy-2-methyl-4*H*-benzo[*d*][1,3]dioxin-4-one(3g):

49.47 mg (51%), white solid. Mp: 87-89 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 3.1 Hz, 1H), 7.14 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 1H), 5.70 (q, *J* = 5.2 Hz, 1H), 3.82 (s, 3H), 1.74 (d, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.36, 155.28, 152.64, 124.74, 117.70, 114.37, 111.11, 99.13, 55.83; HRMS calcd. for $C_{10}H_{11}O_4$ $[M+H]^+$ 195.0579, found 195.0649.



6,8-Ditert-butyl-2-methyl-4*H*-benzo[*d*][1,3]dioxin-4-one(3h):

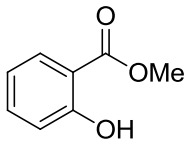
72.28 mg (52%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 2.5 Hz, 1H), 7.58 (d, *J* = 2.5 Hz, 1H), 5.68 (q, *J* = 5.2 Hz, 1H), 1.78 (d, *J* = 5.2 Hz, 3H), 1.39 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.31, 155.06, 145.60, 137.46, 130.64, 124.18, 114.38, 98.19, 34.77, 34.64, 31.26, 29.61, 20.21; HRMS calcd. for $C_{17}H_{25}O_3$ $[M+H]^+$ 277.1725, found 277.1804.



Methylene bis(2-hydroxybenzoate)(4)

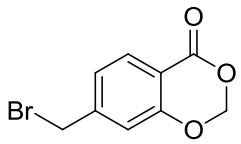
Salicylic acid (125 mg, 0.5 mmol), $K_2HPO_4.3H_2O$ (267 mg, 0.5 mmol), 1,1-Dichloromethane (1 mL) , and DMF (1.5 mL) were stirred in 100 ^{o}C oil bath under air and reflux condition for 10 hours. After cooling to r.t., the reaction solution was extracted with EtOAc and the resulting solution was washed with saturated $NaHCO_3$ solution (20 mL), water (20 mL x3) and brine. Then the organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was purified by flash chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 15:1) to afford

31.9 mg (28%) of **4** as a colorless solid. Mp: 104-106 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.37 (s, 2H), 7.89 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.50 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 2H), 7.00 (dd, *J* = 8.4, 1.0 Hz, 2H), 6.90 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 2H), 6.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.70, 162.13, 136.70, 130.26, 119.48, 117.78, 111.23, 79.57.



Methyl 2-hydroxybenzoate(5)

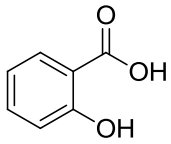
2a (75 mg, 0.5 mmol), K_2CO_3 (6.9 mg, 0.05 mmol), MeOH (2 mL) were stirred in 40 ℃ oil bath under air for 5 hours. After cooling to r.t., the reaction solution was quenched with saturated aqueous NH_4Cl and 1N aqueous HCl, and extracted with Et_2O. The organic layer was then washed with saturated $NaHCO_3$ solution (20 mL), water (20 mL x 3), brine, and dried over anhydrous $MgSO_4$. After filtration, the solvent was purified by flash chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1) to afford 73 mg (96%) of **5** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.74 (s, 1H), 7.83 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.48 – 7.41 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.90 – 6.84 (m, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.53, 161.56, 135.65, 129.86, 119.11, 117.53, 112.35, 52.21.



7-(Bromomethyl)-4*H*-benzo[*d*][1,3]dioxin-4-one(6)

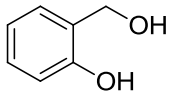
2c (82 mg, 0.5 mmol), *N*-bromosuccinimide (107 mg, 0.6 mmol), and benzoyl peroxide (12 mg, 0.05 mmol) in carbon tetrachloride (3 mL) was heated at reflux for 15h. The reaction mixture was then filtered, and the filtrate was concentrated. The crude product was dissolved in EtOAc, and the organic phase was washed with water and brine, dried over anhydrous Mg_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 8:1) to

afford 184 mg (76%) of **6** as white solid. Mp: 70-71 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.97 (d, *J* = 8.1 Hz, 1H), 7.21 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.11 (d, *J* = 1.4 Hz, 1H), 5.67 (s, 2H), 4.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.79, 158.48, 146.53, 130.94, 124.22, 117.06, 114.60, 91.18, 31.28.



Salicylic acid(1a)

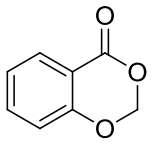
2a (75 mg, 0.5 mmol) in DMSO (3 mL) was treated with 48% aqueous KOH (0.5 mL) and the mixture was heated in 60 ℃ oil bath for 30 min. Upon cooling, the solution was acidified (10% HCI) and extracted three times with EtOAc, and these extracts were washed with water and brine and dried over anhydrous Na_2S0_4. Filtration and concentration left 100 mg of the crude acid as yellow solids, purified by HPLC afterwards to provide 66 mg (95%) of **1a**. Mp: 157-159 ℃. ^{1}H NMR (400 MHz, DMSO): δ 11.27 (s, 1H), 7.83 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.56 – 7.46 (m, 1H), 7.01 – 6.87 (m, 2H); ^{13}C NMR (100 MHz, DMSO): δ 173.01, 162.23, 136.63, 131.31, 120.16, 118.11, 113.94.

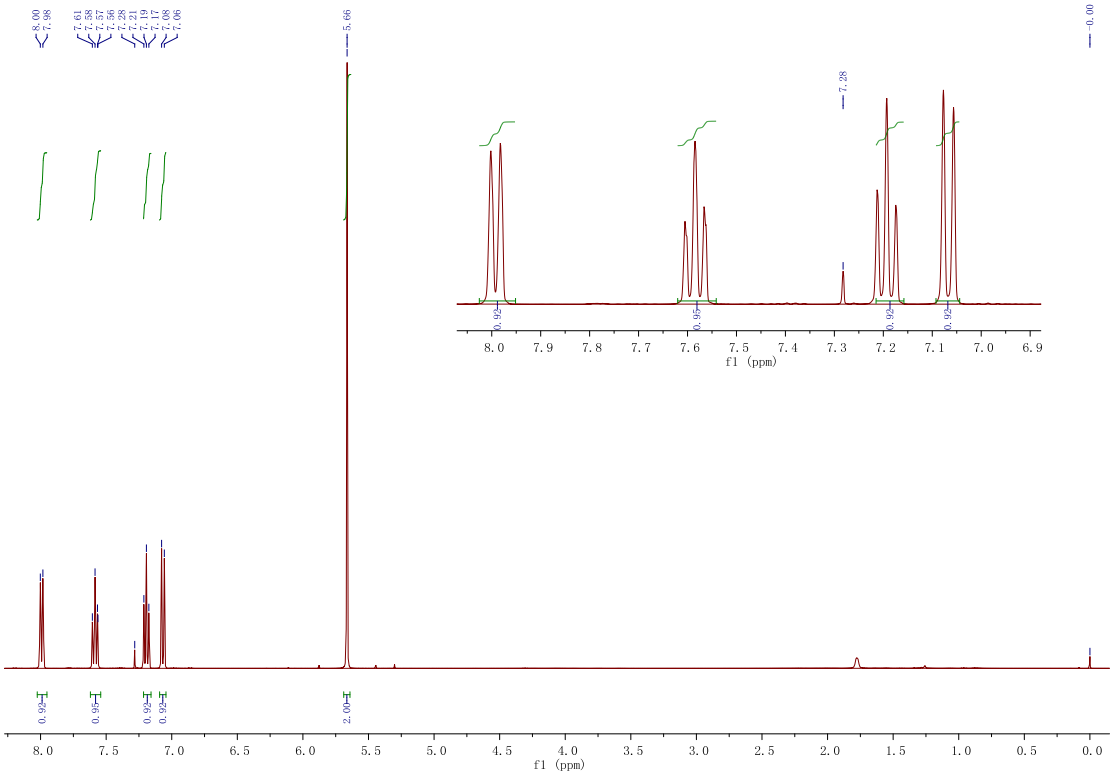


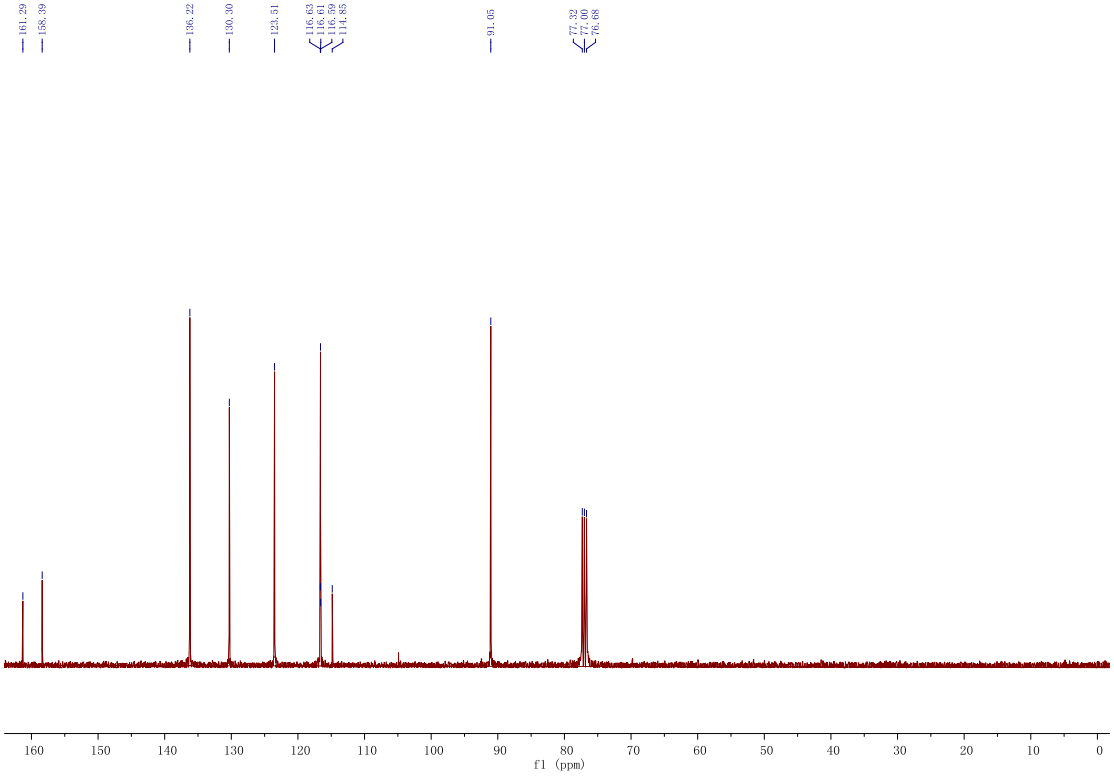
2-(Hydroxymethyl)phenol(7)

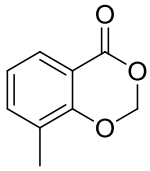
A solution of substituted **2a** (75mg, 0.5 mmol) in THF was treated with LAH (4 mmol, 152 mg). The reaction mixture was stirred at rt. until completion as determined by TLC. Then the reaction mixture was quenched with 1M HCl and MeOH followed by extraction of the aqueous layer with EtOAc. The combined organic layers were washed with water and brine, dried with anhydrous Mg_2SO_4 After filtration, the solvent was purified by flash chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1) to afford 50.82 mg (82%) of **7** as a white solid. Mp: 85-86 ℃. ^{1}H NMR (400 MHz, DMSO): δ 9.33 (s, 1H), 7.39 – 7.29 (m, 1H), 7.16 – 7.03 (m, 1H), 6.91 – 6.72 (m, 2H), 5.00 (s, 1H), 4.55 (s, 2H); ^{13}C NMR (100 MHz, DMSO): δ155.20, 129.50, 128.39, 119.72, 115.59, 59.36.

IV. ^{1}H NMR and ^{13}C NMR spectra of Products

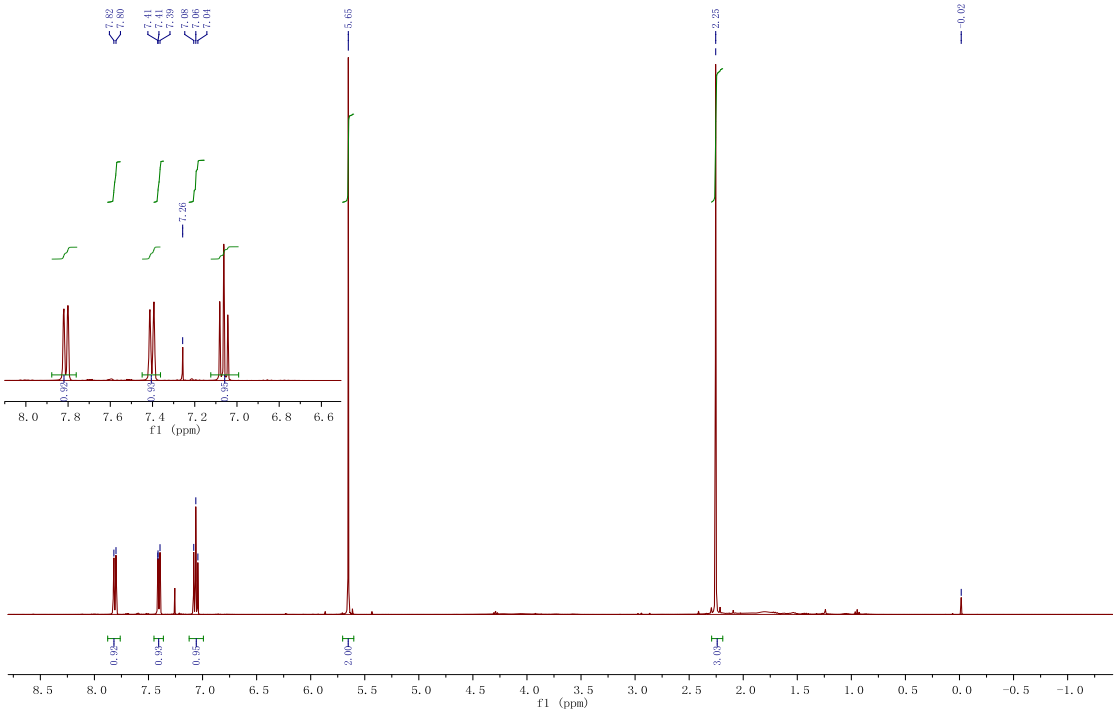


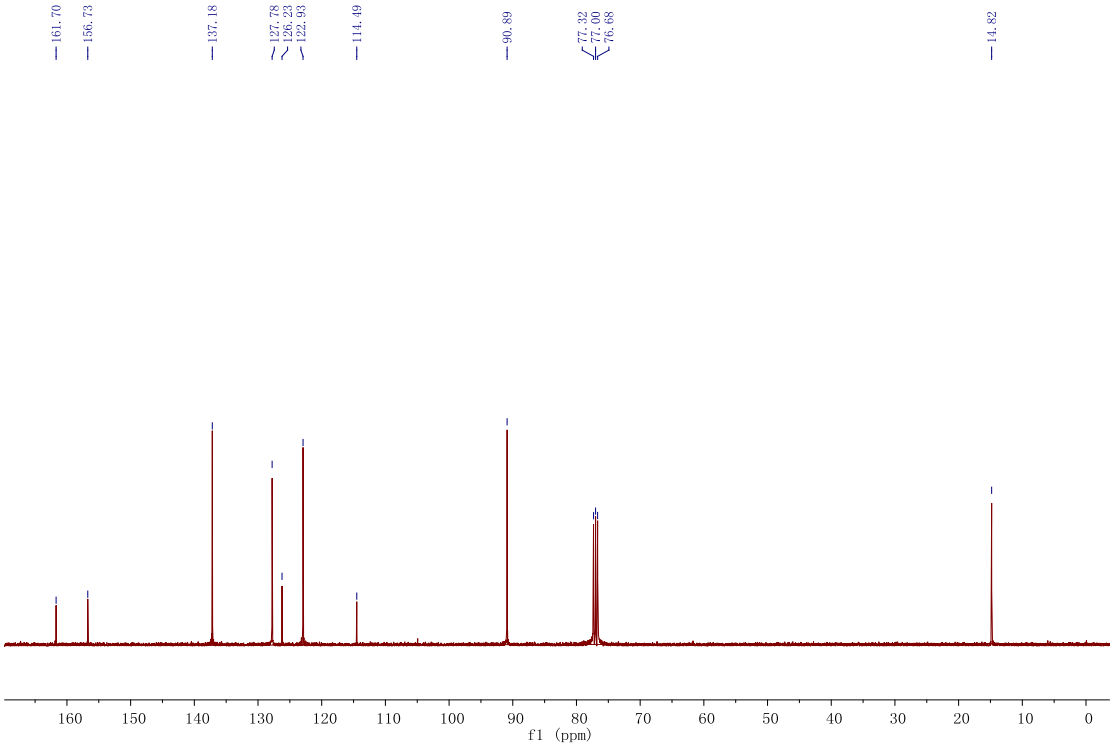


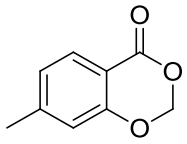




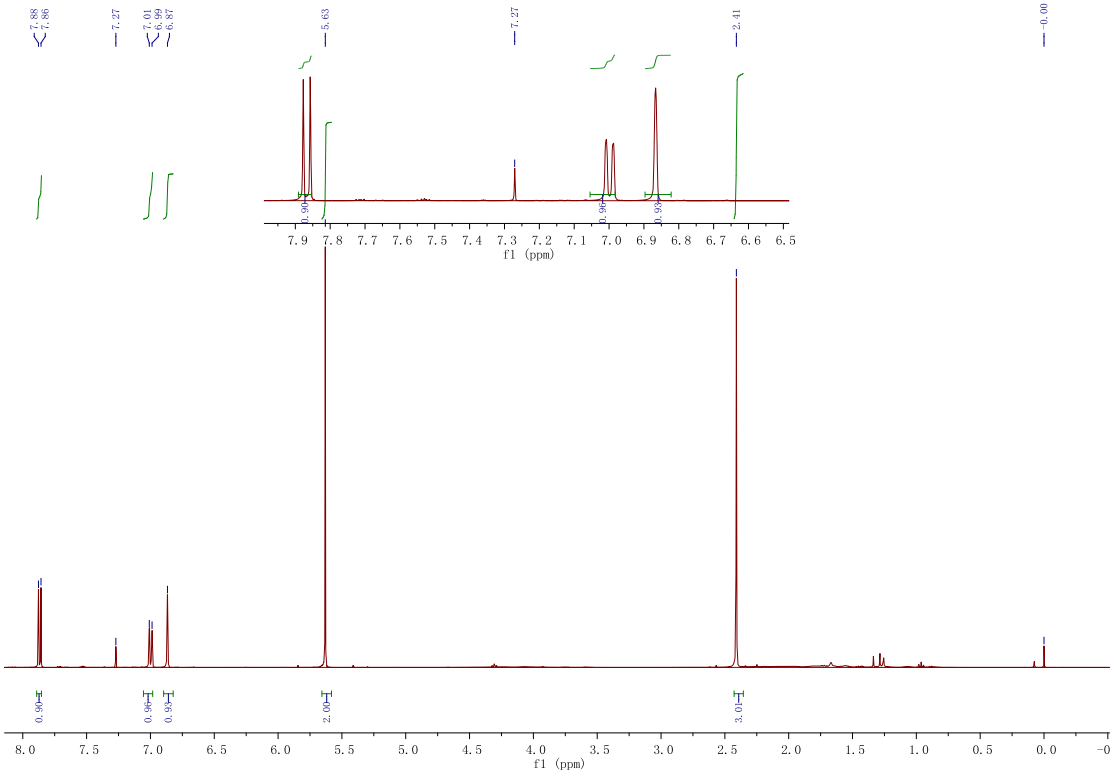
2b

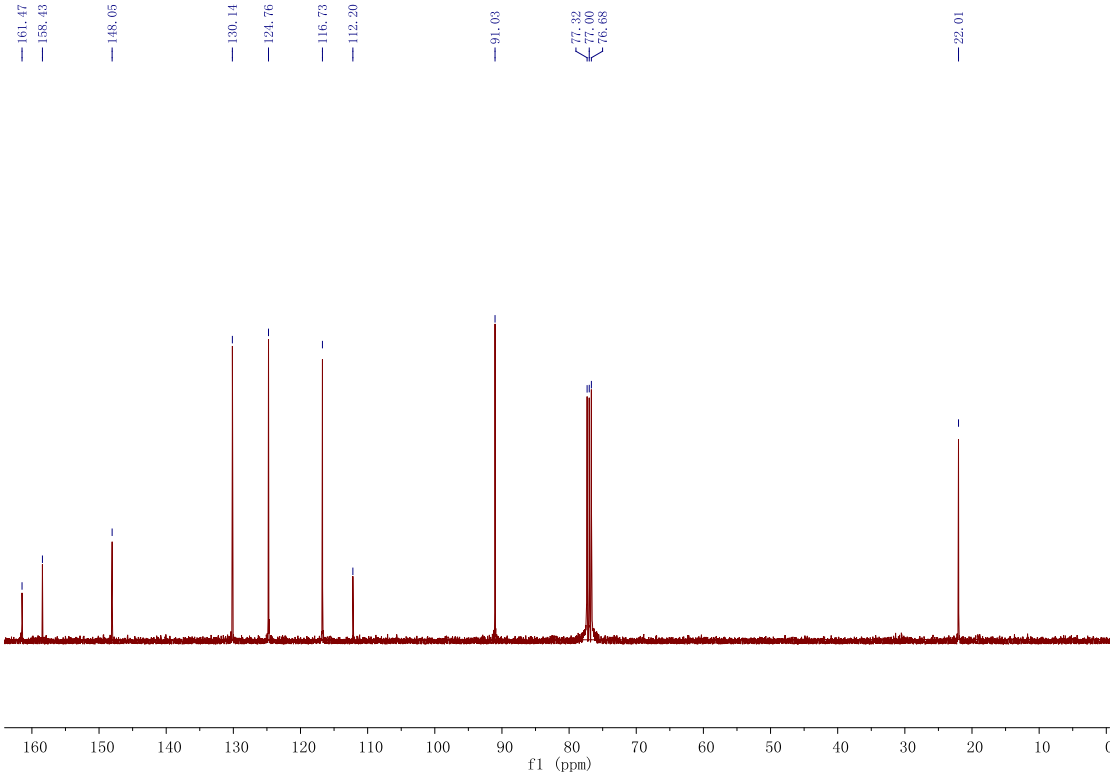

7.82
7.80
7.41
7.41
7.39
7.08
7.06
7.04
5.65
2.25
-0.02
7.26
f1 (ppm)

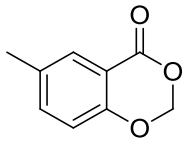

161.70
156.73
137.18
127.78
126.23
122.93
114.49
90.89
77.32
77.00
76.68
14.82
f1 (ppm)



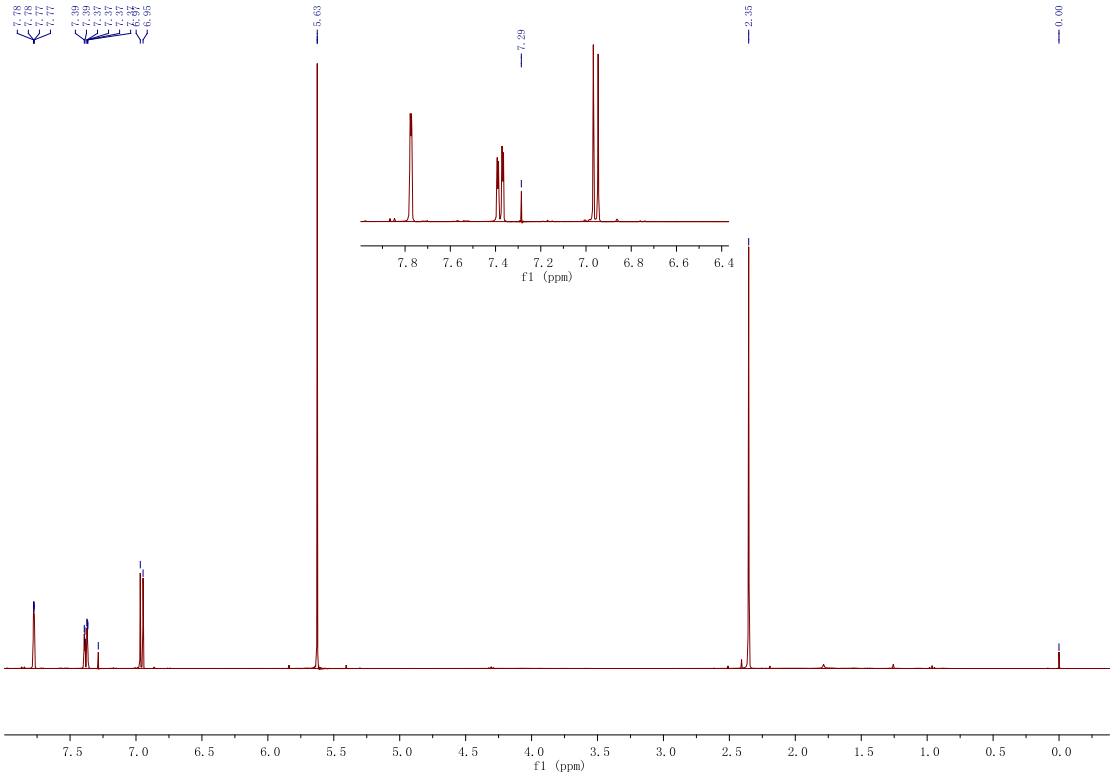
2c

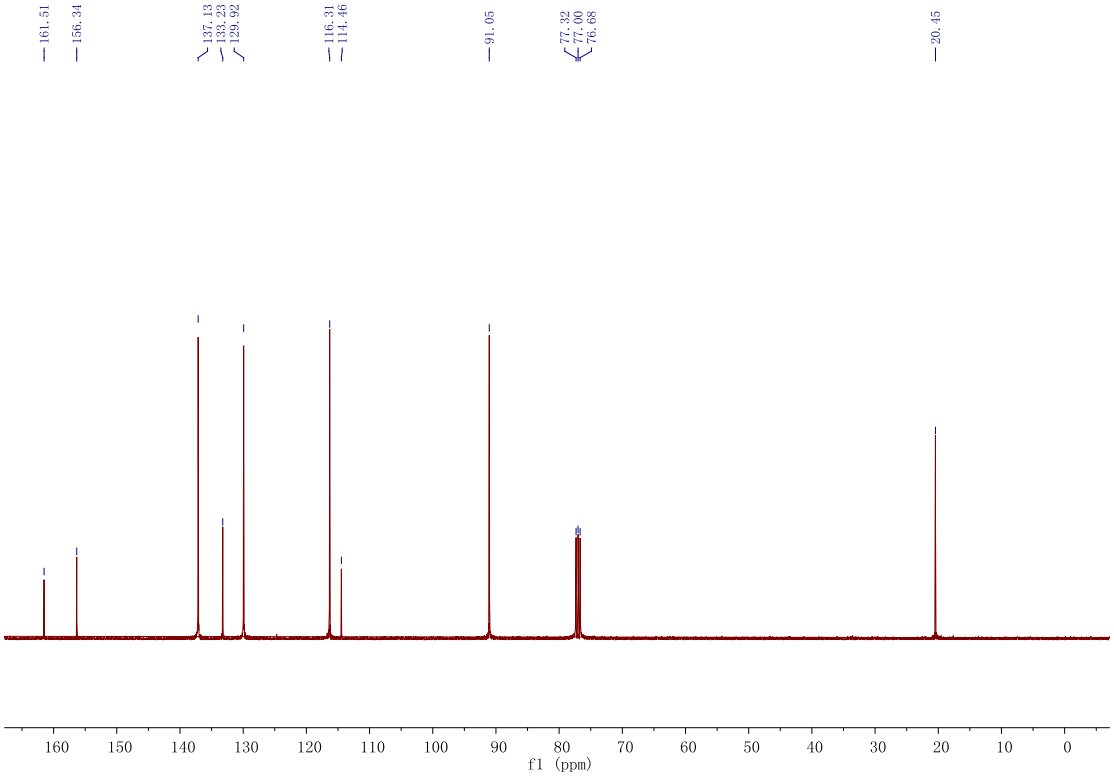

7.88
7.86
7.27
7.01
6.99
6.87
5.63
7.27
2.41
0.00
0.90
0.96
0.93
2.00
3.01
f1 (ppm)

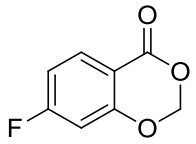

161.47
158.43
148.05
130.14
124.76
116.73
112.20
91.03
77.32
77.00
76.68
22.01
f1 (ppm)



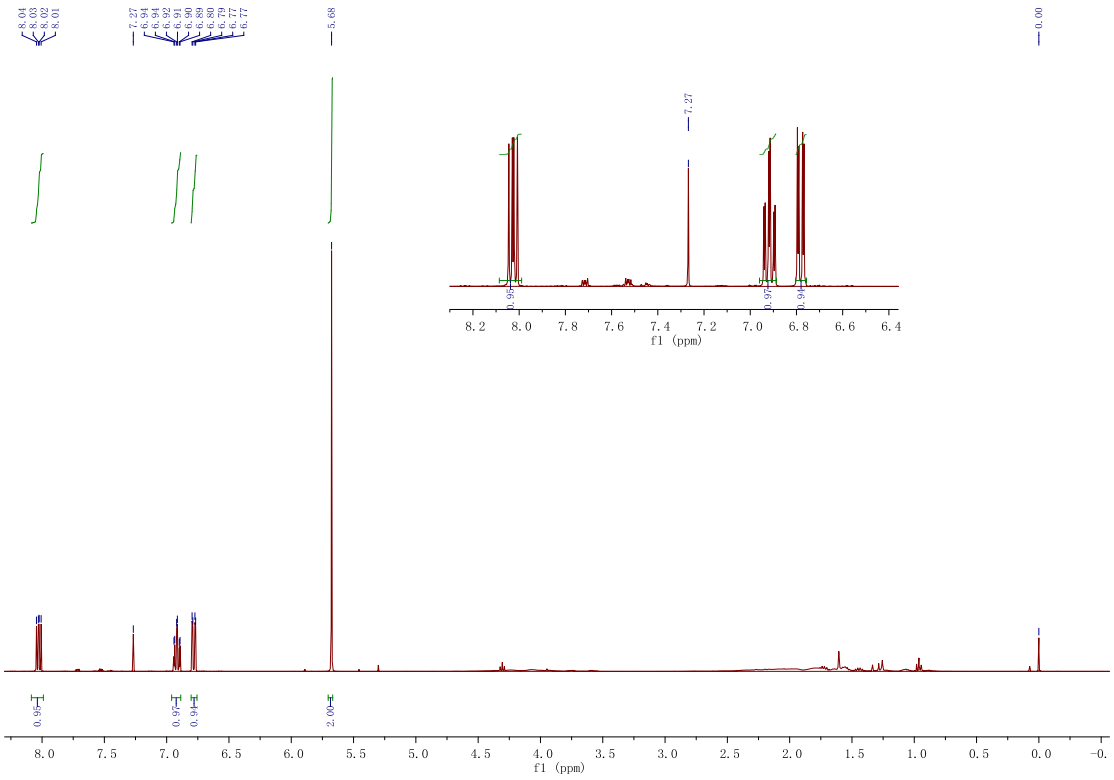
2d

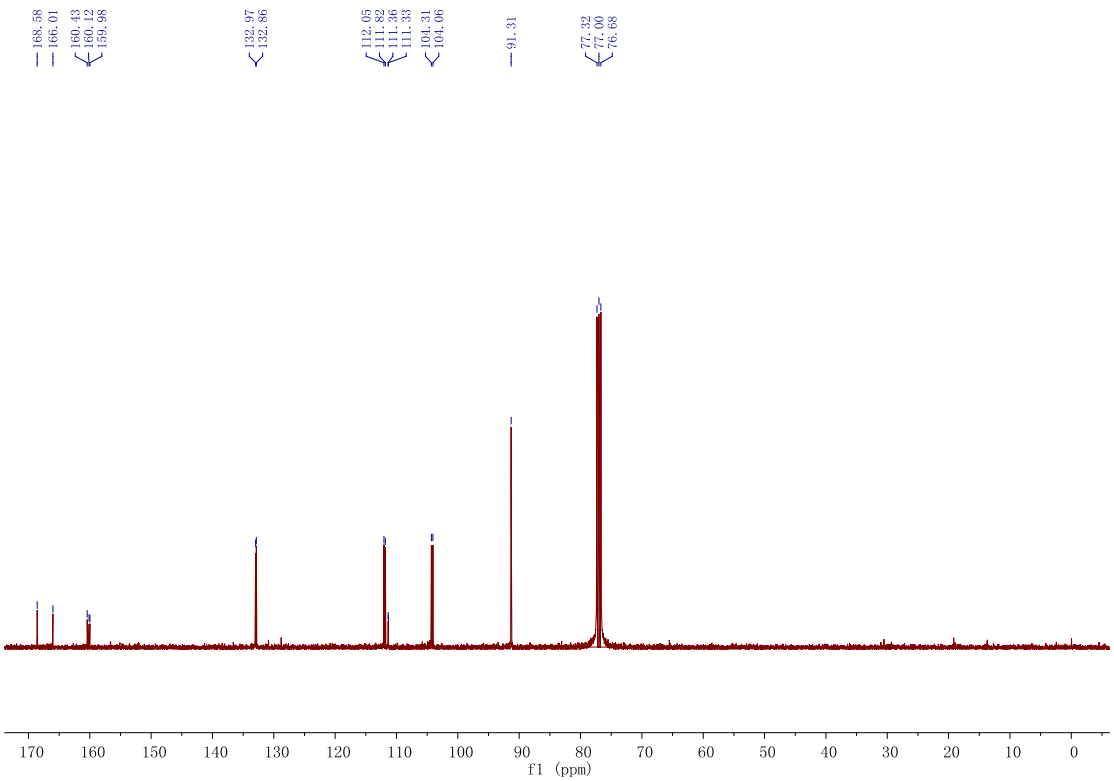

7.78
7.78
7.77
7.77
7.39
7.39
7.37
7.37
7.37
7.37
6.97
6.97
6.95
5.63
7.29
2.35
0.00
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
f1 (ppm)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

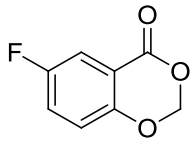

161.51
156.34
137.13
133.23
129.92
116.31
114.46
91.05
77.32
77.00
76.68
20.45
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
O
F

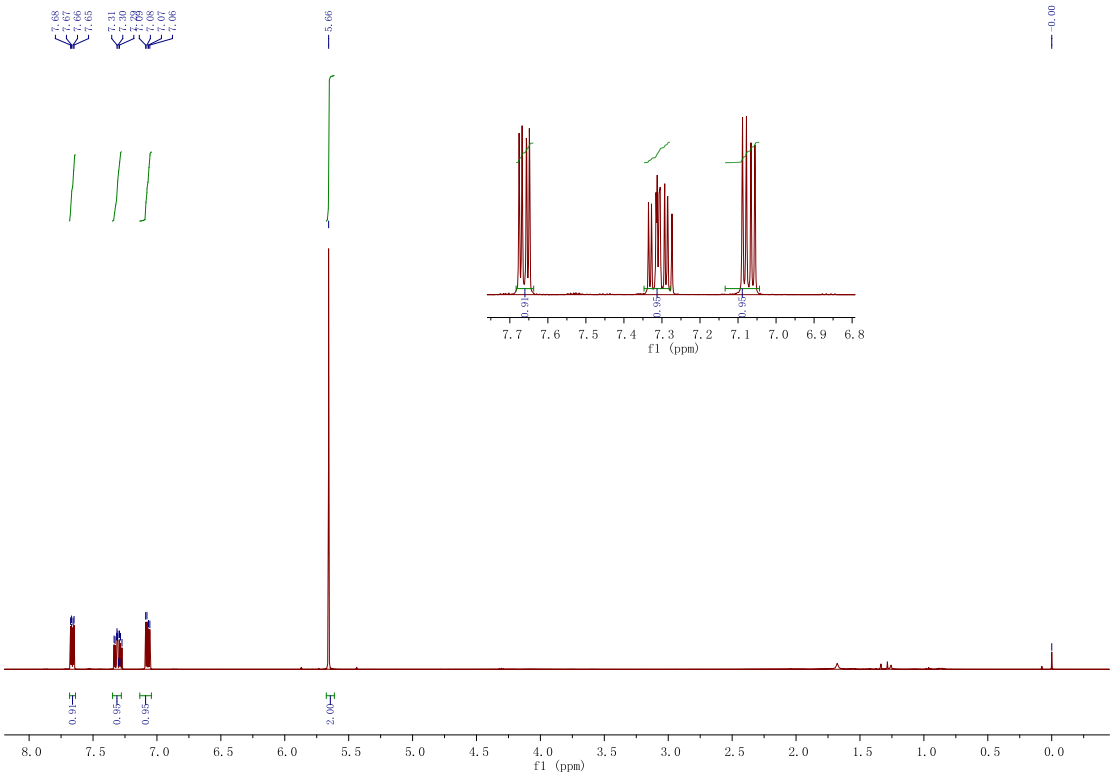
2e

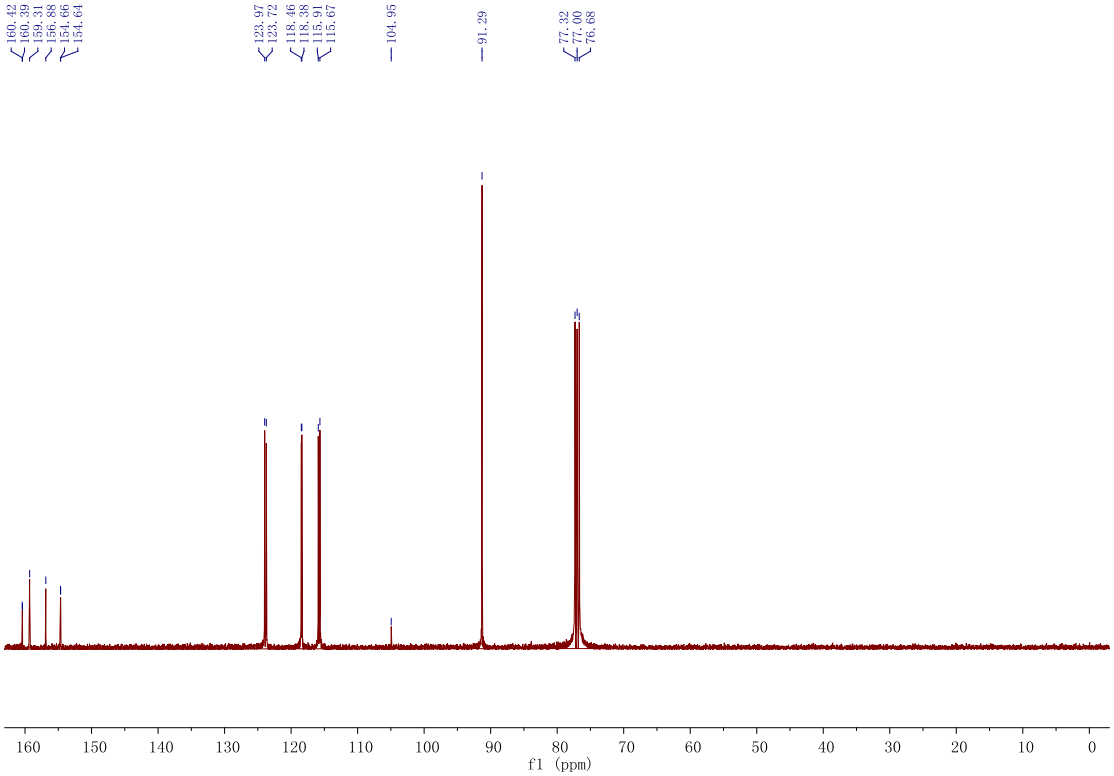

8.04
8.03
8.02
8.01
7.27
6.94
6.94
6.92
6.91
6.90
6.89
6.89
6.79
6.77
6.77
5.68
0.00
7.27
f1 (ppm)
f1 (ppm)

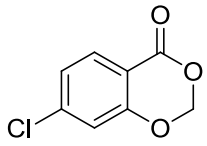

168.58
166.01
160.43
160.12
159.98
132.97
132.86
112.05
111.82
111.36
111.33
104.31
104.06
91.31
77.32
77.00
76.68
f1 (ppm)


O
F
O
O

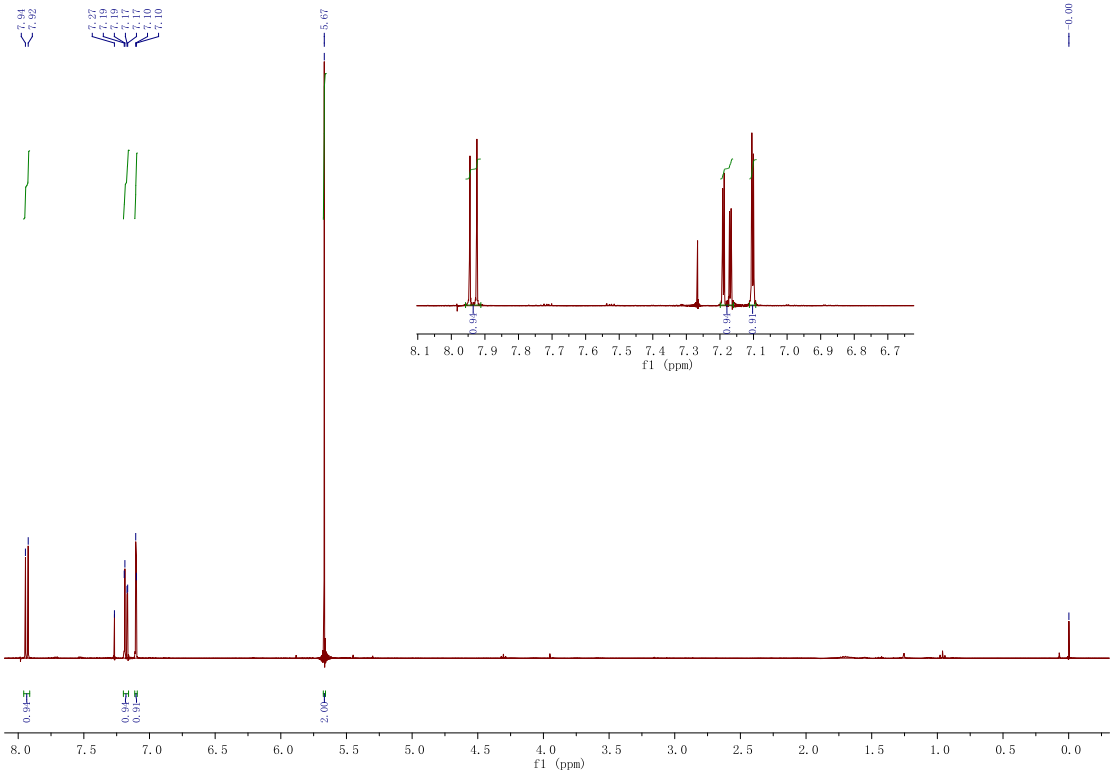
2f

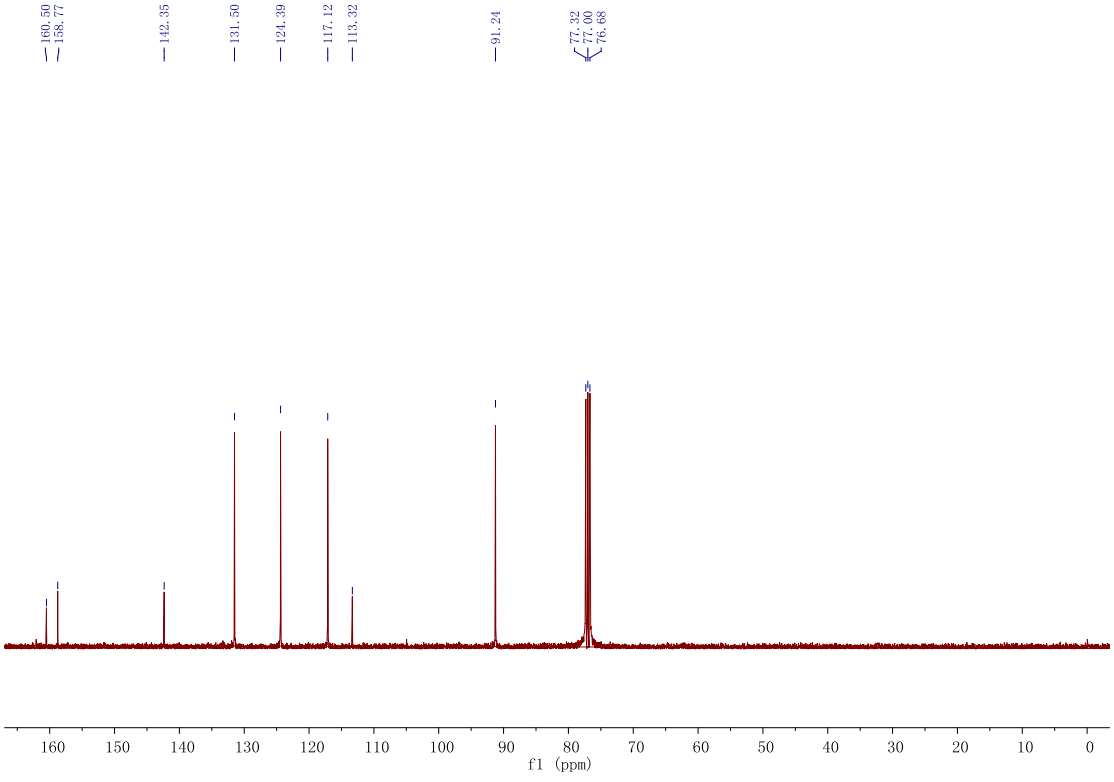

7.68
7.67
7.66
7.65
7.31
7.30
7.29
7.28
7.08
7.07
7.06
5.66
0.00
0.94
0.95
0.95
2.00
f1 (ppm)

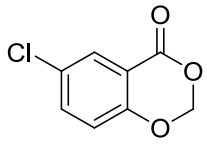

160.42
160.39
159.31
156.88
154.66
154.64
123.97
123.72
118.46
118.38
115.91
115.67
104.95
91.29
77.32
77.00
76.68
f1 (ppm)


O
O
O
Cl

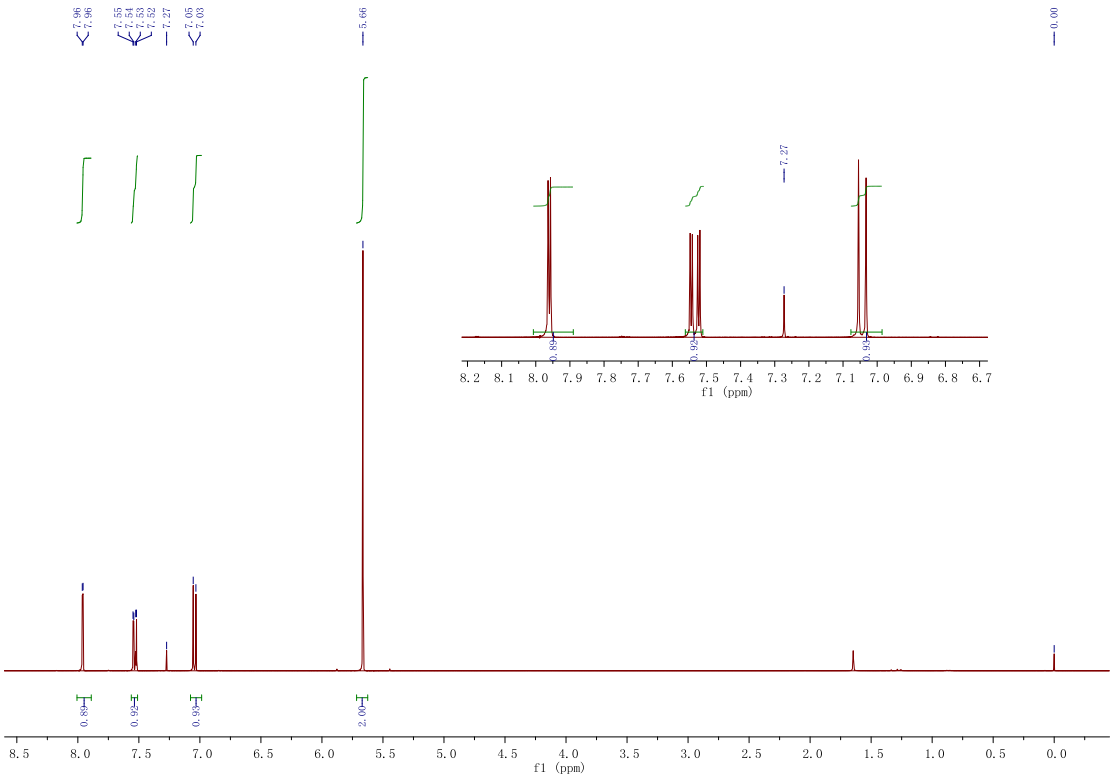
2g

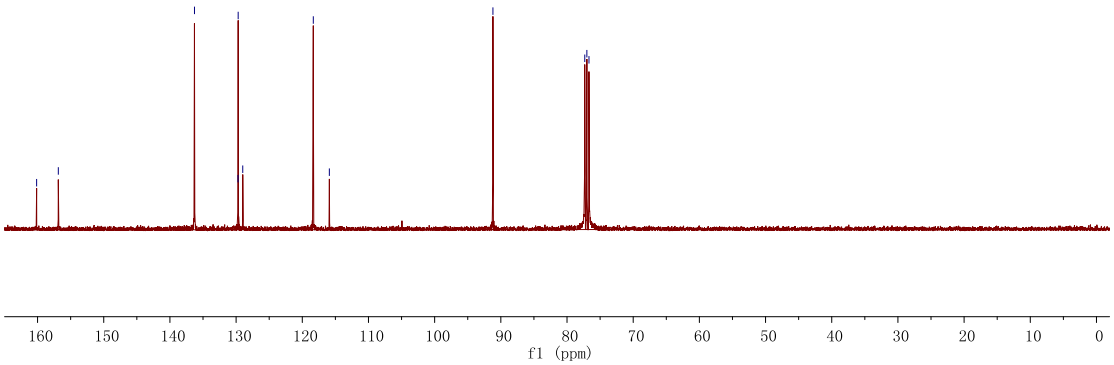

7.94
7.92
7.27
7.19
7.19
7.17
7.17
7.10
7.10
5.67
0.00
0.94
0.94
0.91
2.00
f1 (ppm)

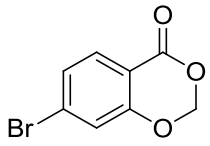

160.50
158.77
142.35
131.50
124.39
117.12
113.32
91.24
77.32
77.00
76.68
f1 (ppm)


Cl
O
O
O

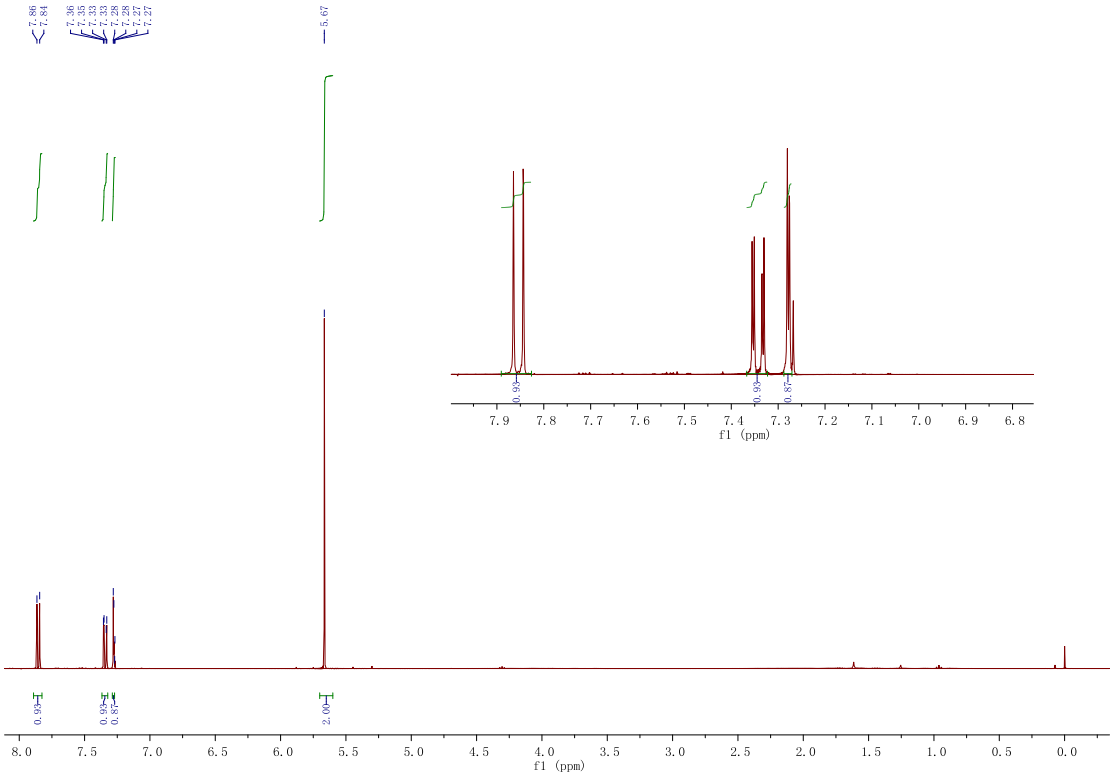
2h

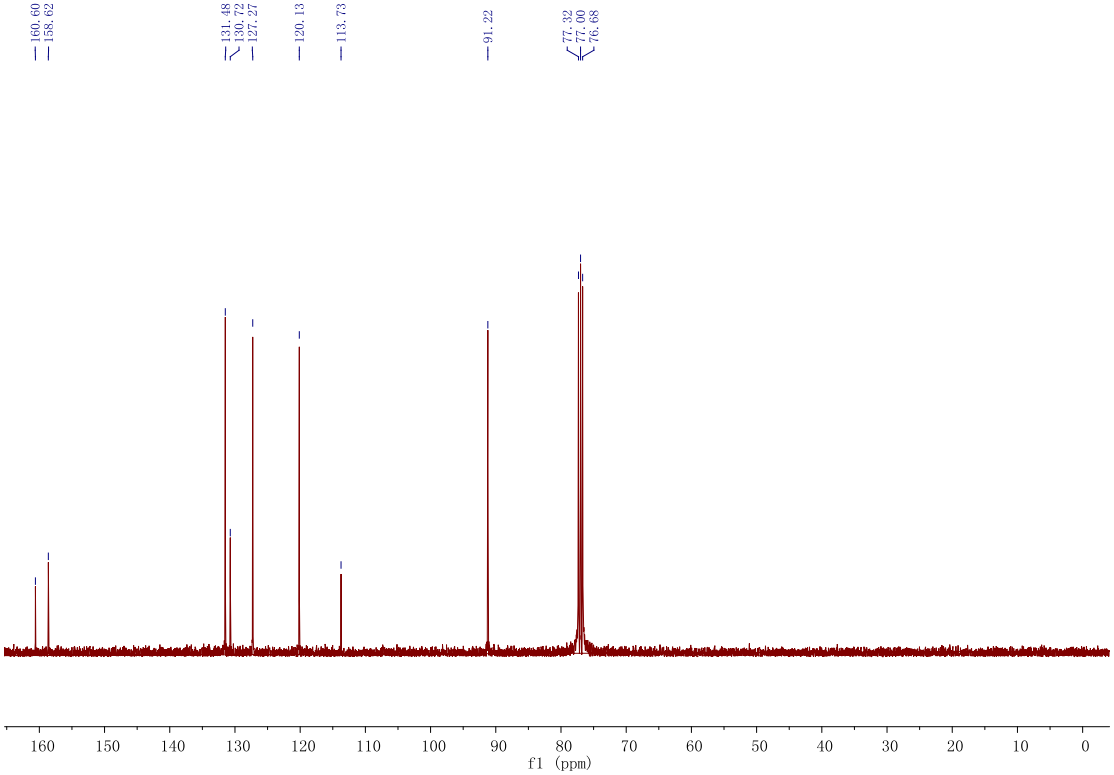

7.96
7.96
7.55
7.54
7.53
7.52
7.27
7.05
7.03
5.66
0.00
7.27
0.89
0.92
0.99
2.00
f1 (ppm)

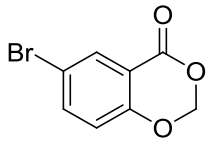

160.14
156.86
136.29
129.71
129.69
129.00
118.34
115.91
91.19
77.32
77.00
76.68
f1 (ppm)


O
O
O
Br

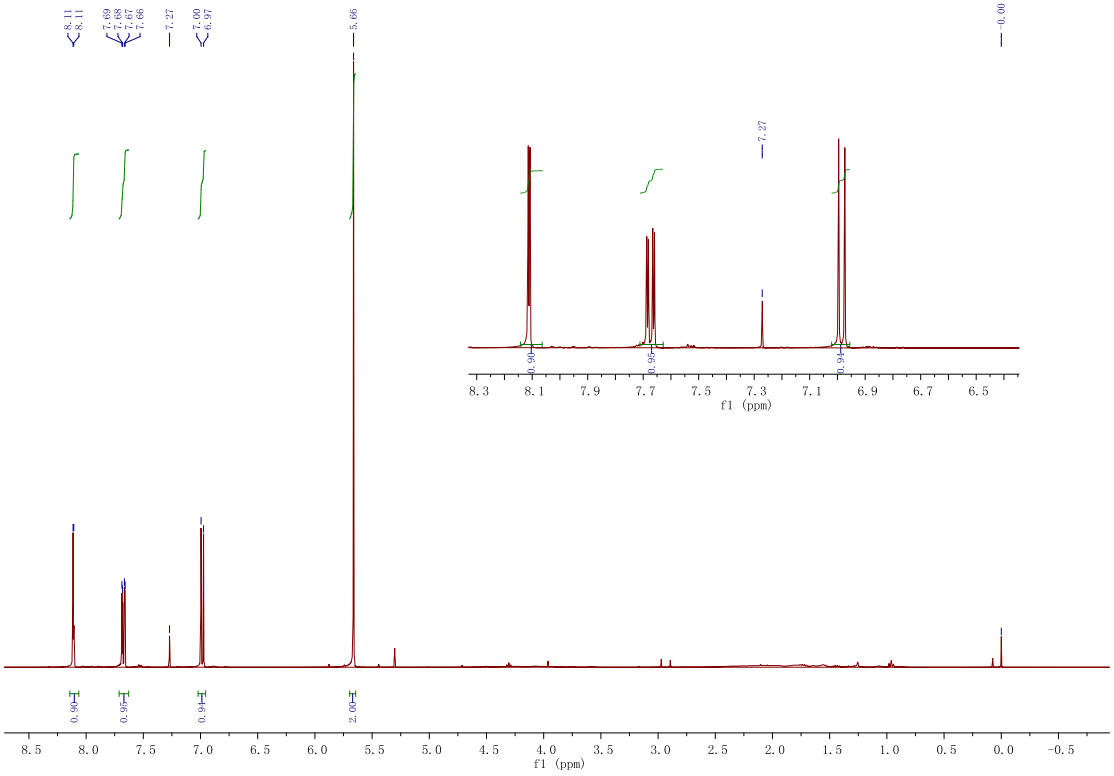
2i

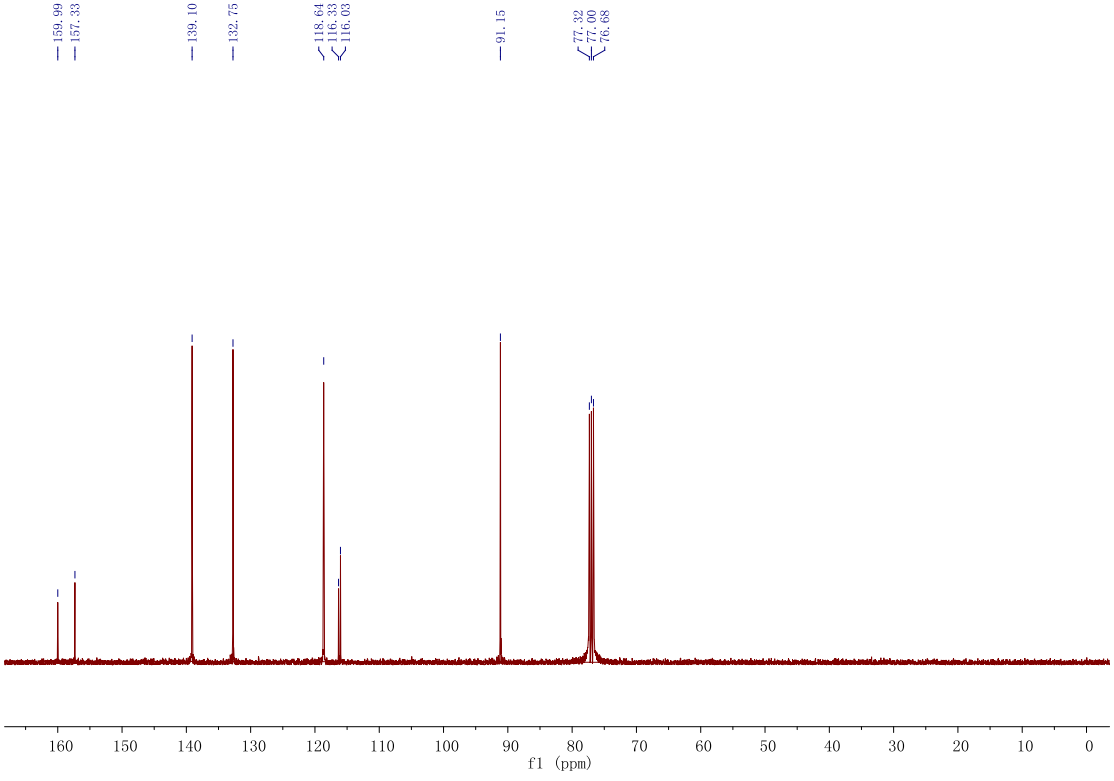

7.86
7.84
7.36
7.35
7.33
7.33
7.28
7.28
7.27
7.27
5.67
0.93
0.93
0.87
2.00
f1 (ppm)

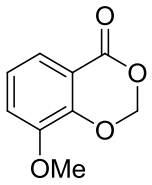

160.60
158.62
131.48
130.72
127.27
120.13
113.73
91.22
77.32
77.00
76.68
f1 (ppm)


Br
O
O
O

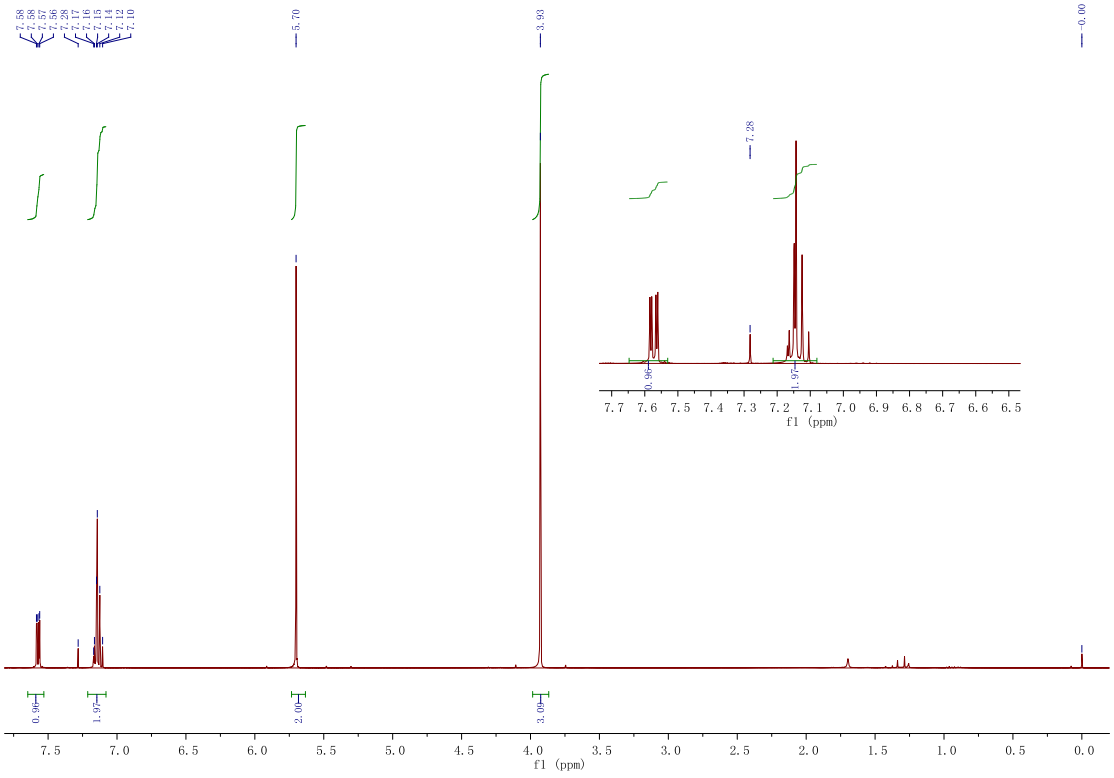
2j

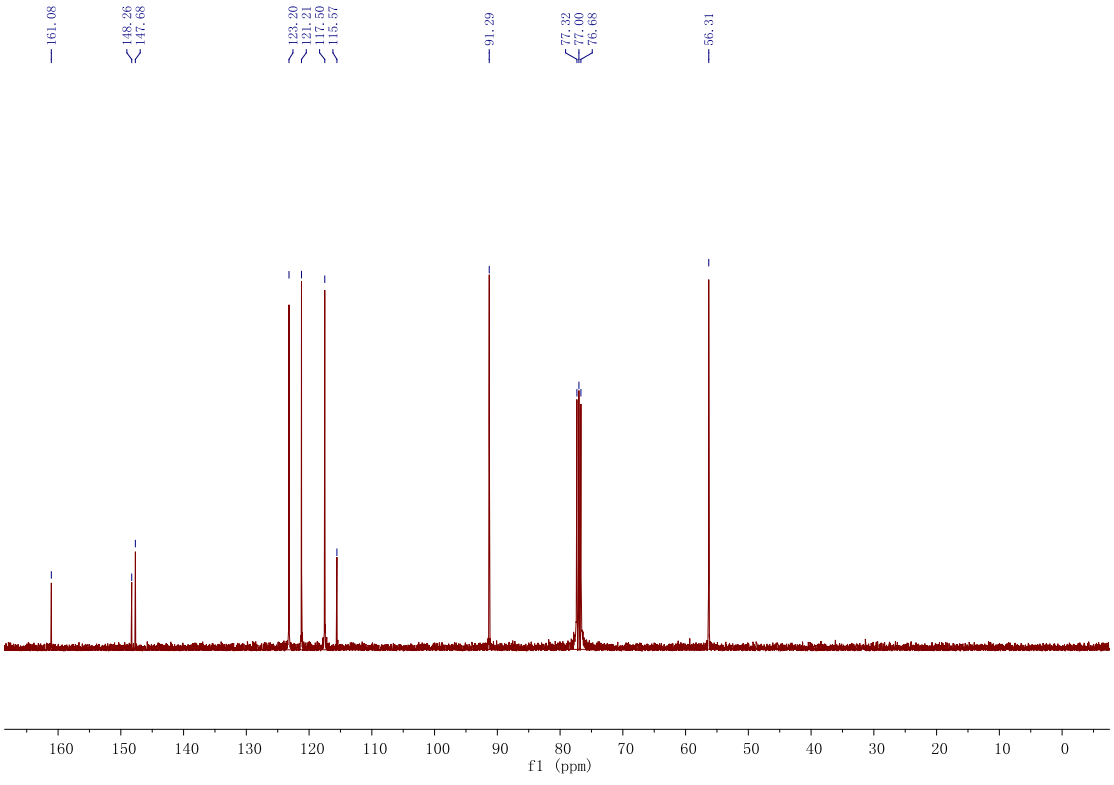

8.11
8.11
7.69
7.68
7.67
7.66
7.27
7.00
6.97
5.66
0.00
0.90
0.95
0.94
2.00
f1 (ppm)

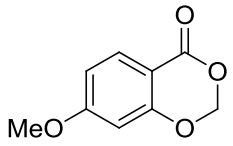

159.99
157.33
139.10
132.75
118.64
116.33
116.03
91.15
77.32
77.00
76.68
f1 (ppm)


O
O
O
OMe

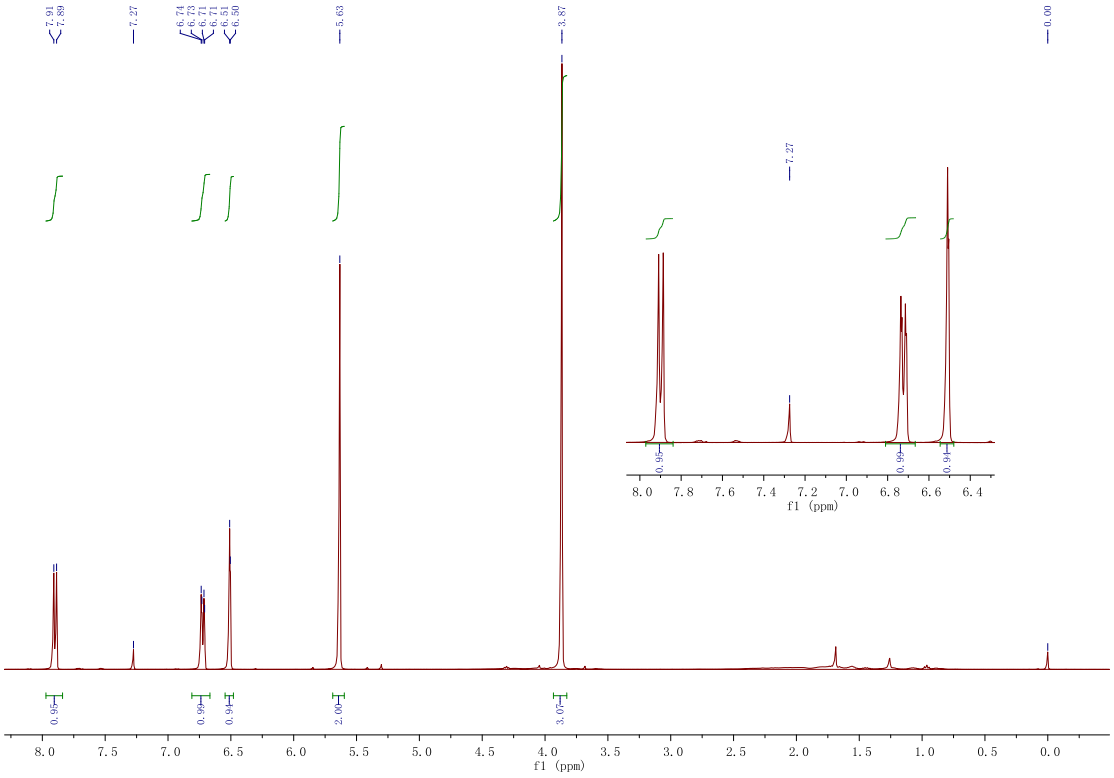
2k

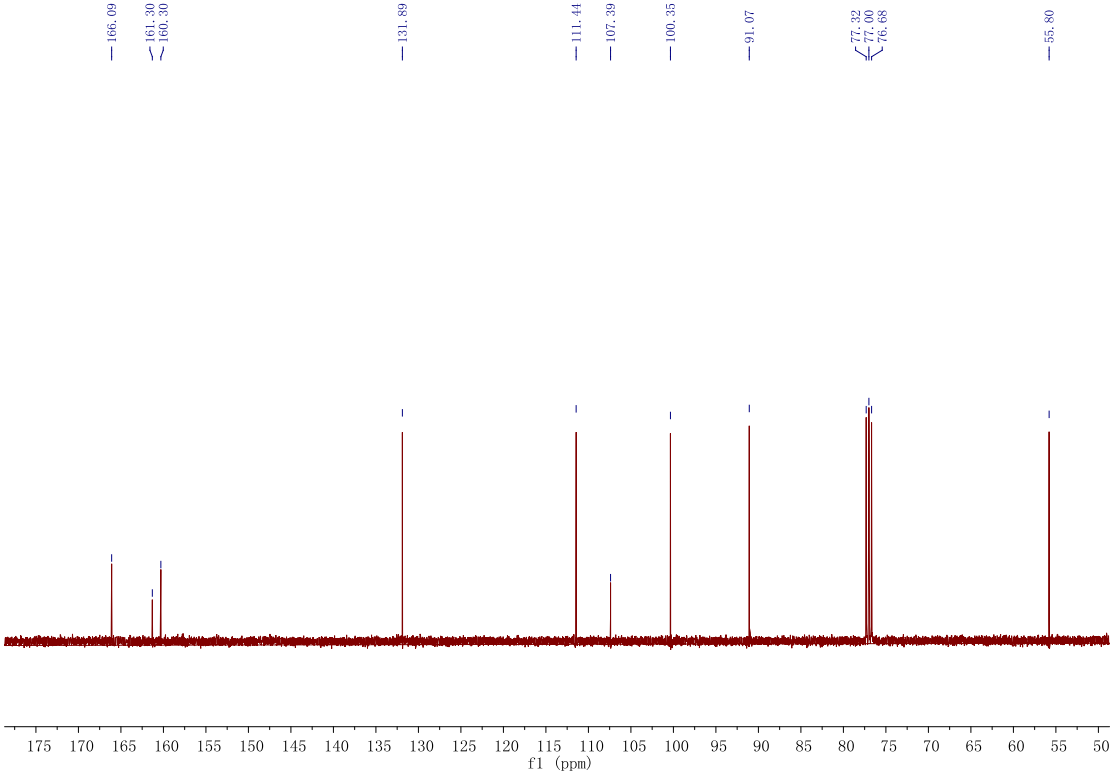

7.58
7.58
7.57
7.56
7.28
7.17
7.16
7.15
7.14
7.12
7.10
5.70
3.93
0.00
7.28
0.98
1.97
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
f1 (ppm)
0.90
1.97
2.00
3.09
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

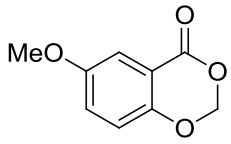

161.08
148.26
147.68
123.20
121.21
117.50
115.57
91.29
77.32
77.00
76.68
56.31
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
MeO
O

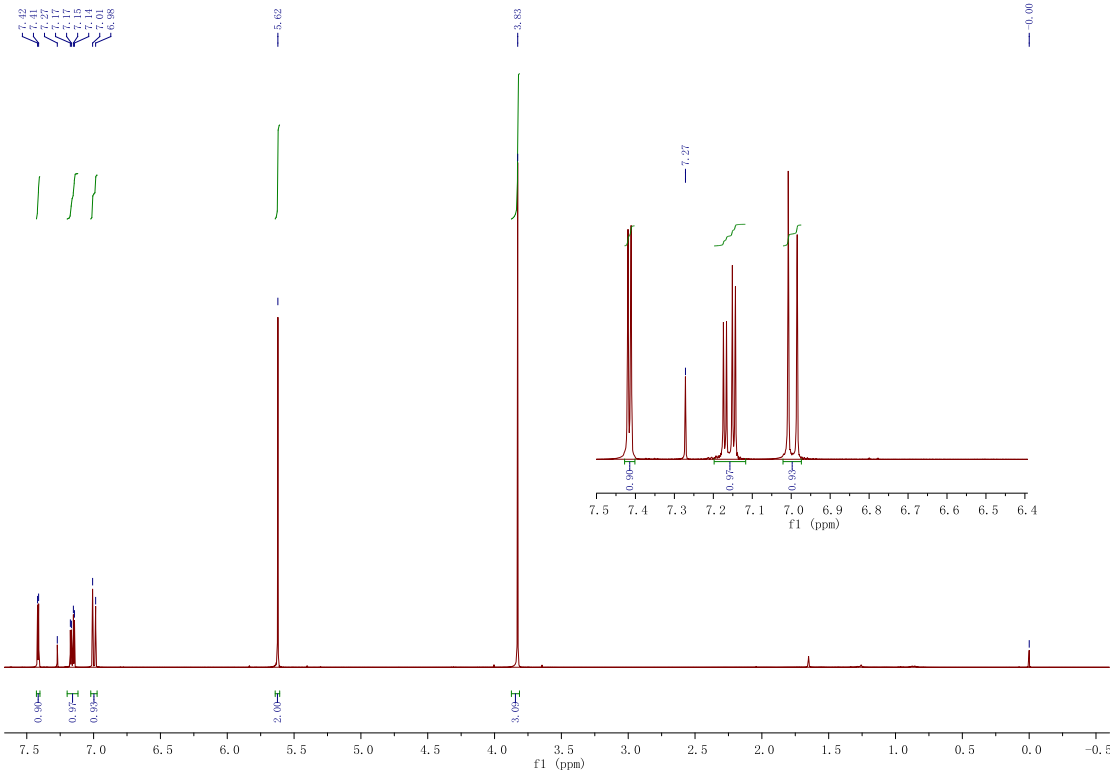
2l

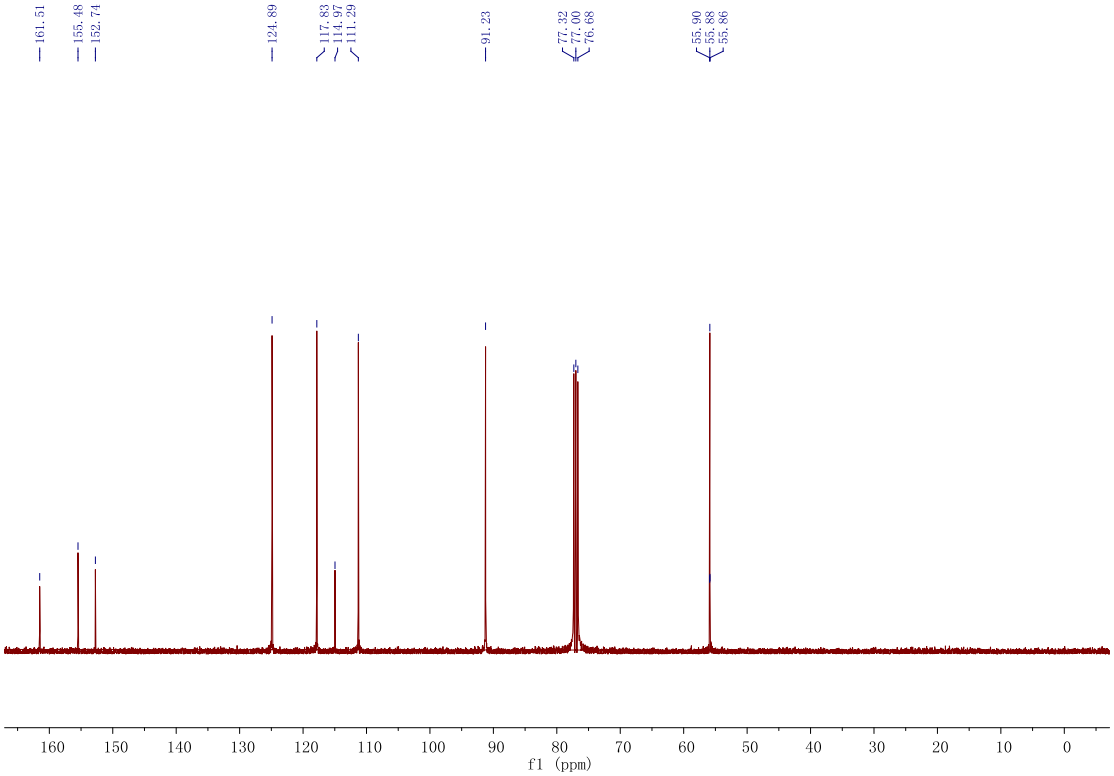

7.91
7.89
7.27
6.74
6.73
6.71
6.71
6.51
6.50
5.63
3.87
0.00
0.95
0.99
0.94
2.00
3.07
f1 (ppm)

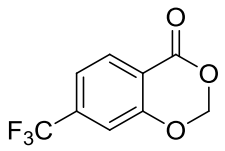

166.09
161.30
160.30
131.89
111.44
107.39
100.35
91.07
77.32
77.00
76.68
55.80
f1 (ppm)


MeO
O
O
O

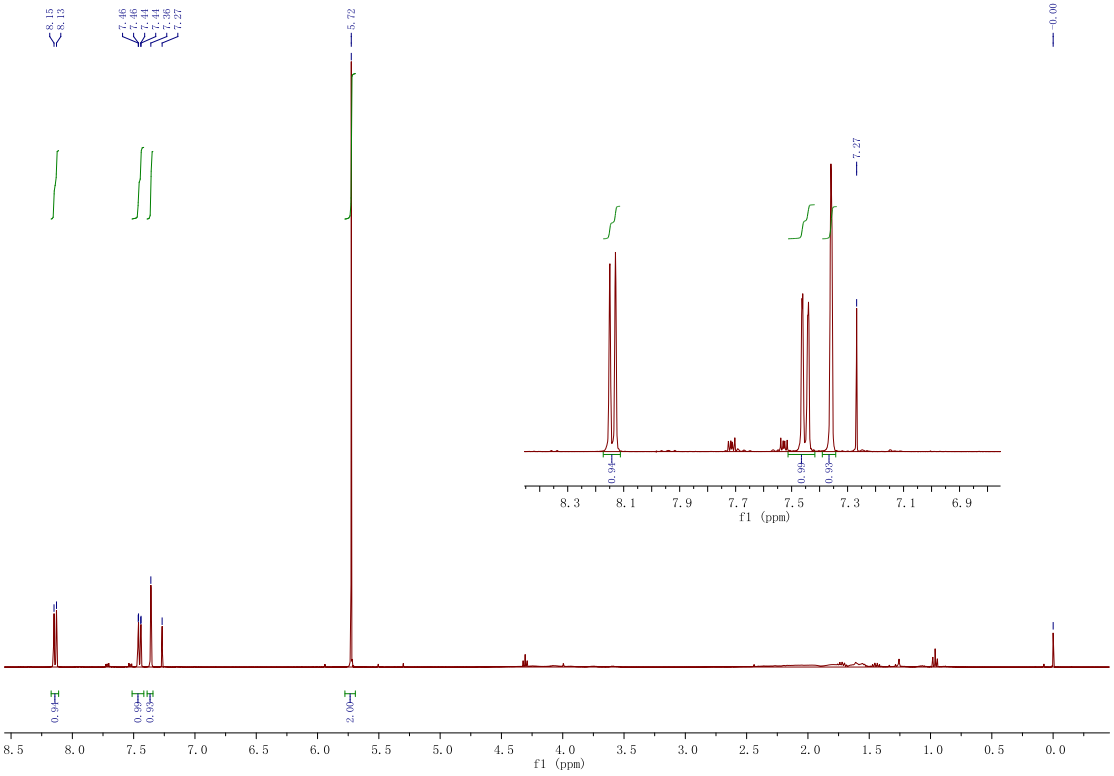
2m

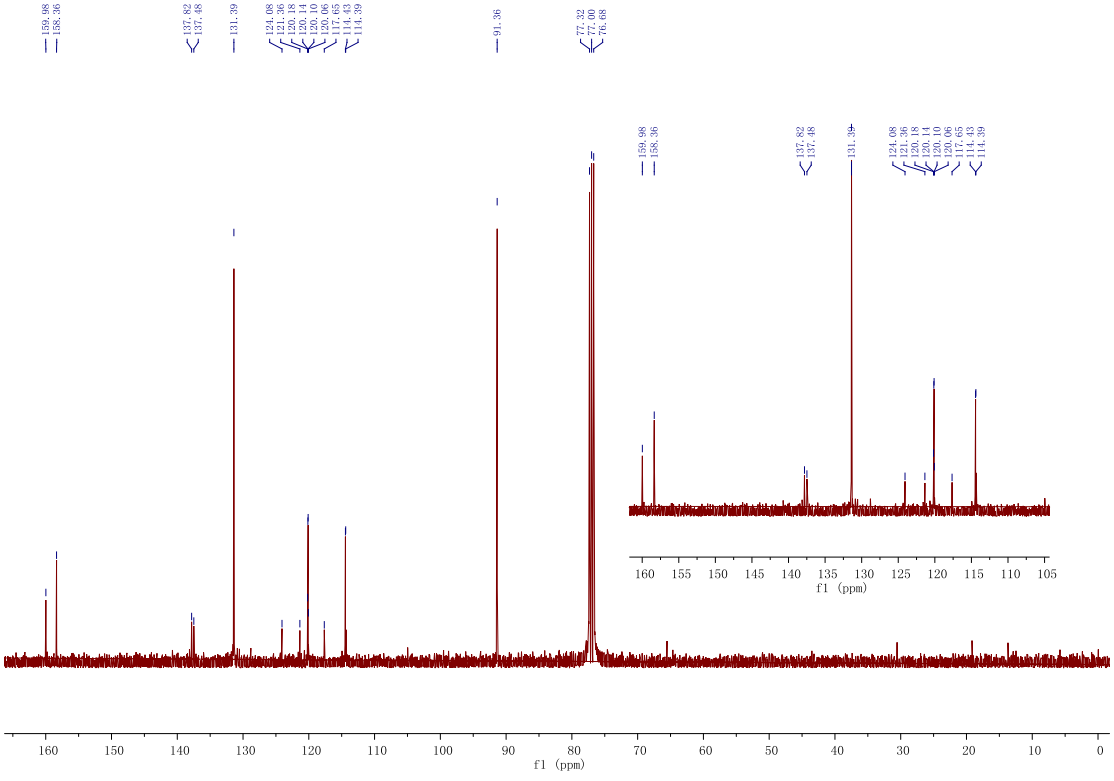

7.42
7.41
7.27
7.17
7.17
7.15
7.14
7.01
6.98
5.62
3.83
0.00
7.27
0.90
0.97
0.99
f1 (ppm)
0.90
0.97
0.99
2.00
3.09
f1 (ppm)

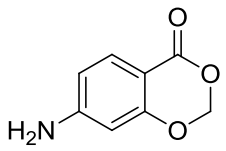

161.51
155.48
152.74
124.89
117.83
114.97
111.29
91.23
77.32
77.00
76.68
55.90
55.88
55.86
f1 (ppm)



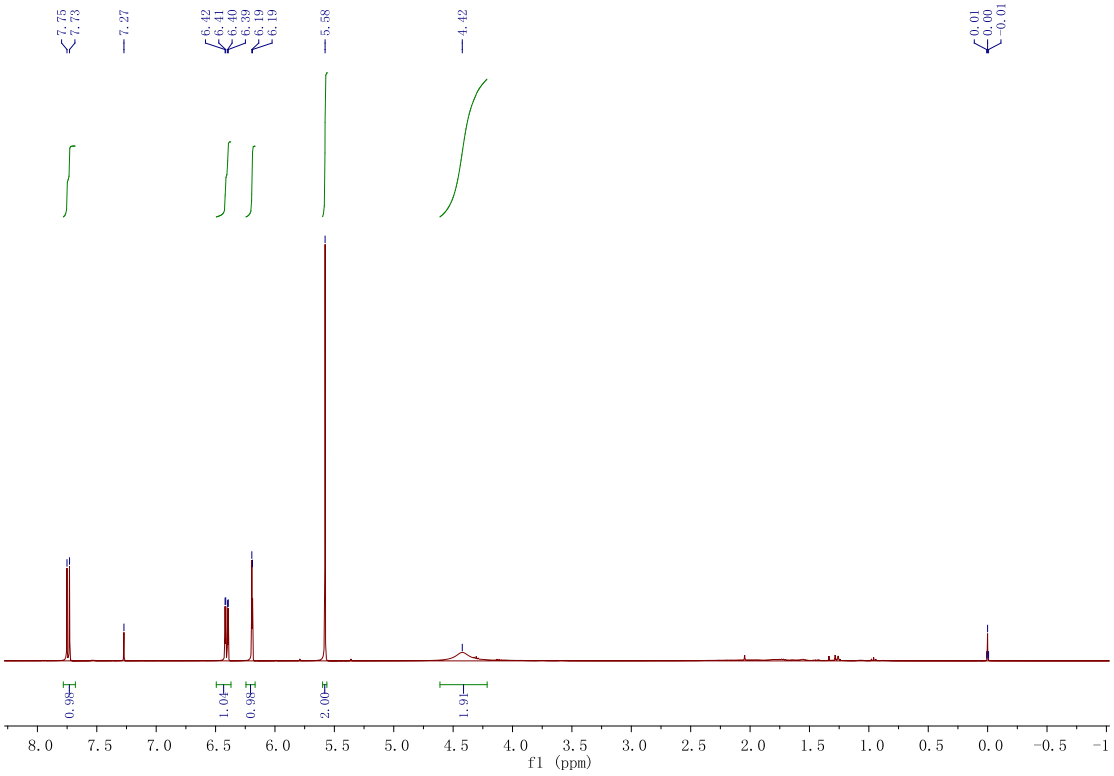
2n

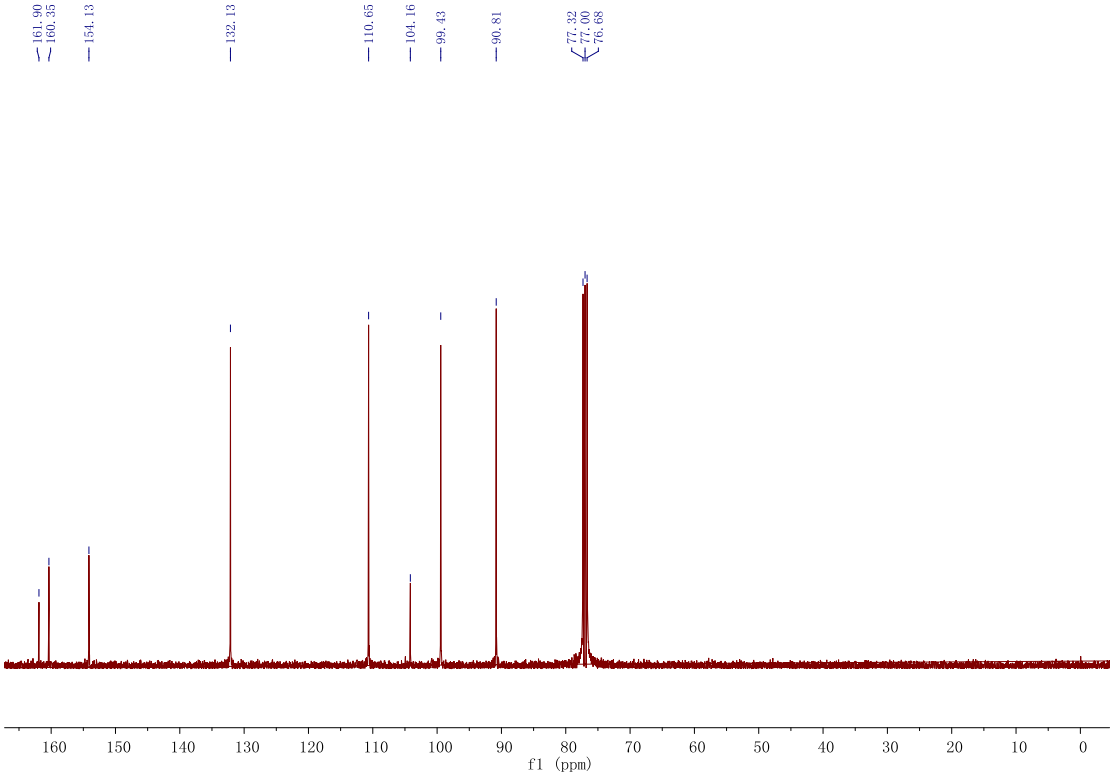


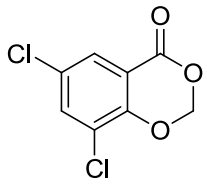




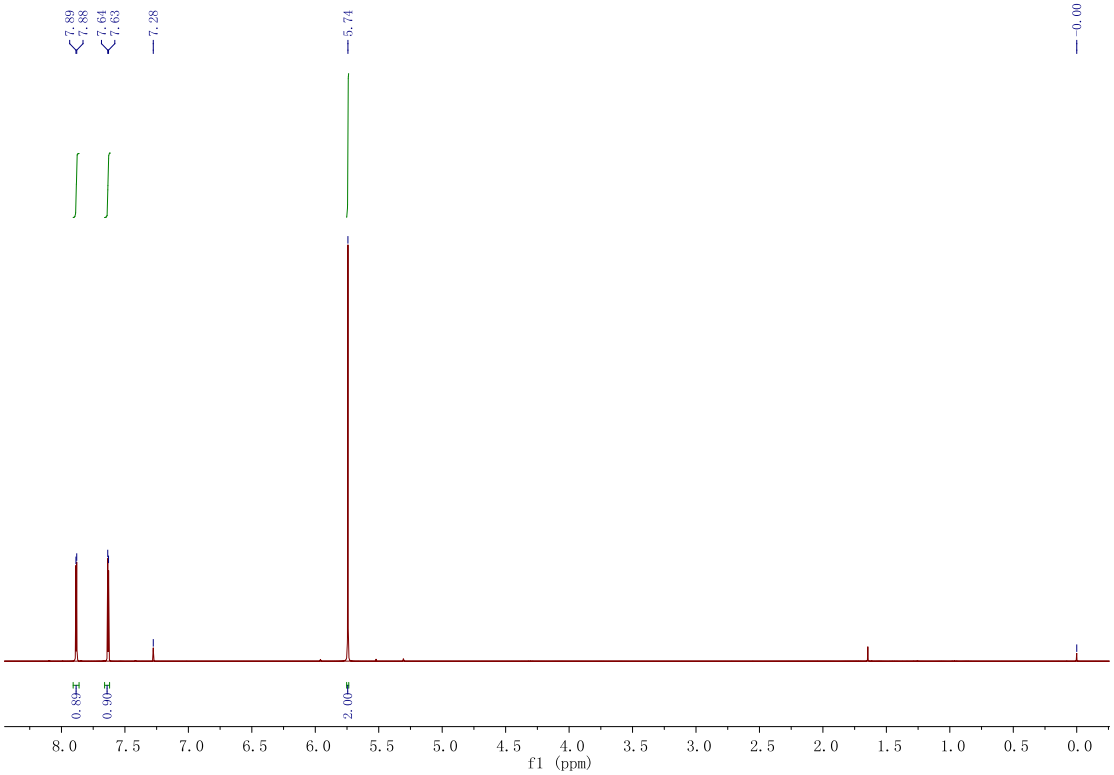
2o

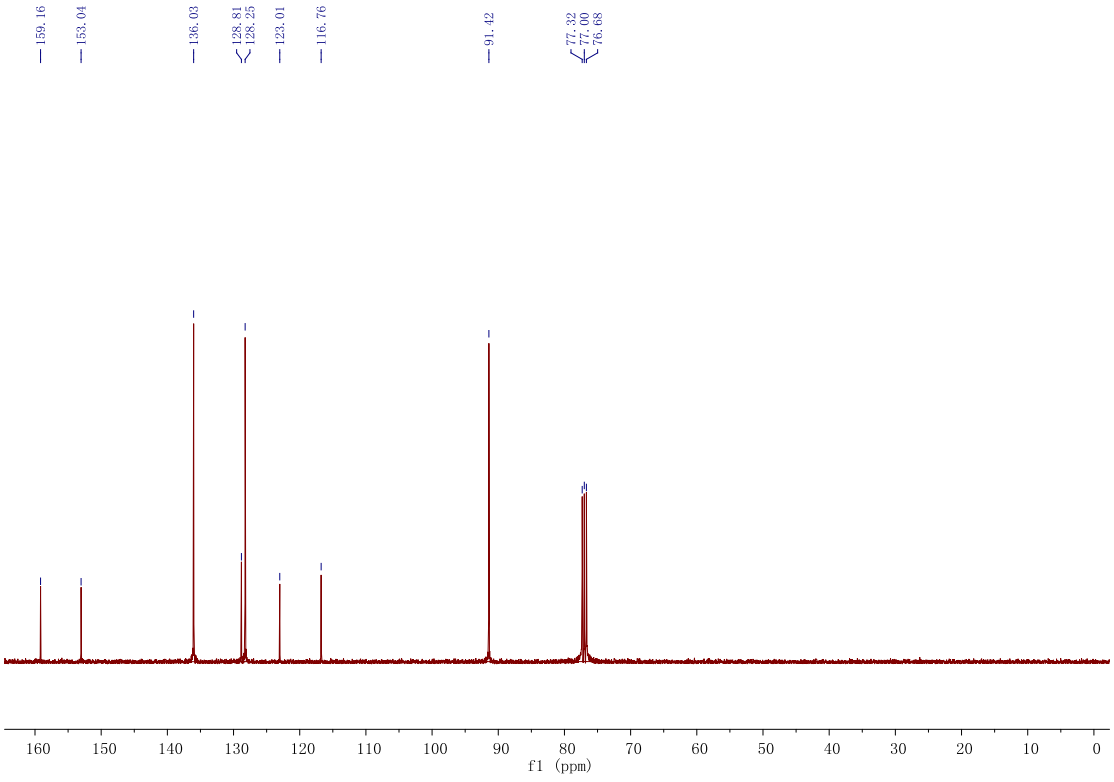

7.75
7.73
7.27
6.42
6.41
6.40
6.39
6.19
6.19
5.58
4.42
0.01
0.00
-0.01
0.99
1.04
0.99
2.00
1.91
f1 (ppm)

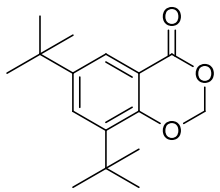

161.90
160.35
154.13
132.13
110.65
104.16
99.43
90.81
77.32
77.00
76.68
f1 (ppm)

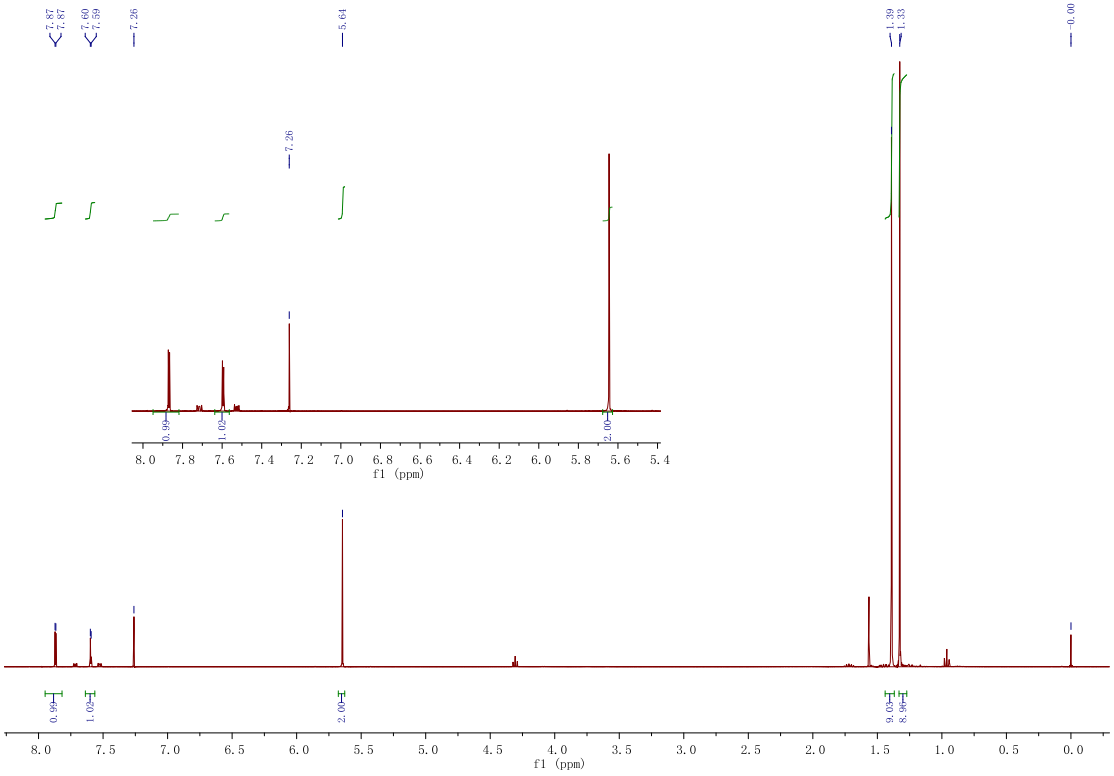

Cl
O
O
O
Cl

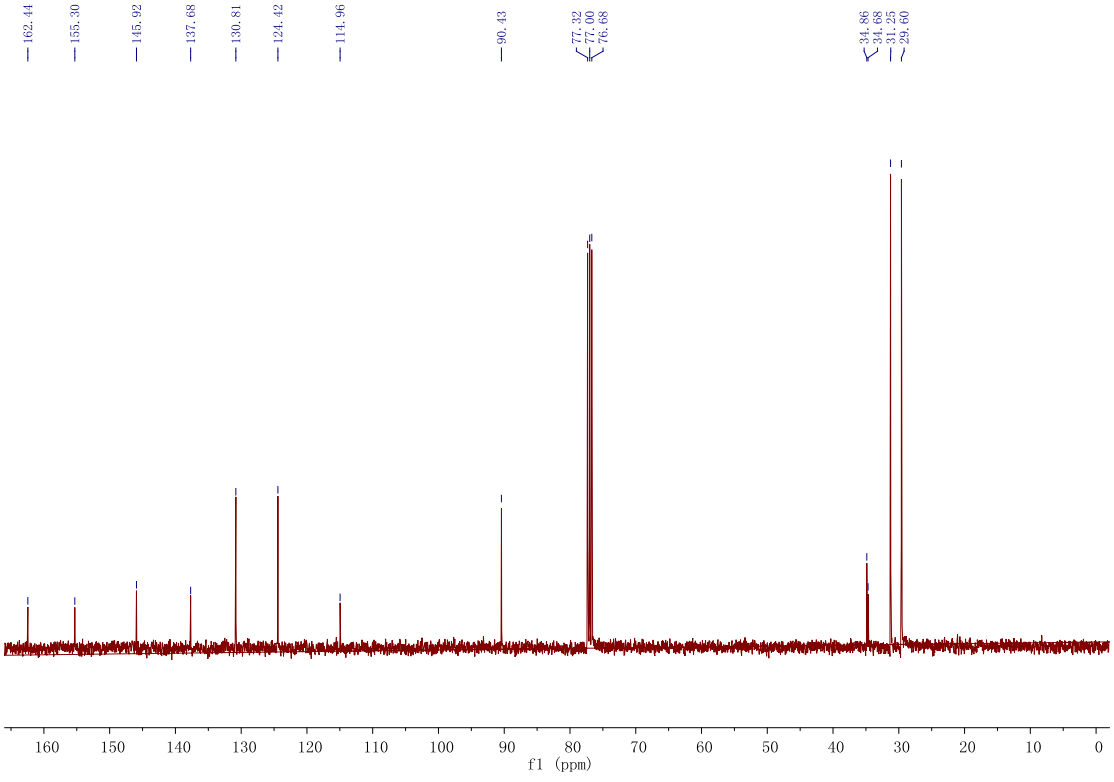
2p

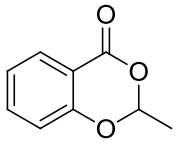

7.89
7.88
7.64
7.63
7.28
5.74
0.00
0.89
0.90
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.16
153.04
136.03
128.81
128.25
123.01
116.76
91.42
77.32
77.00
76.68
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

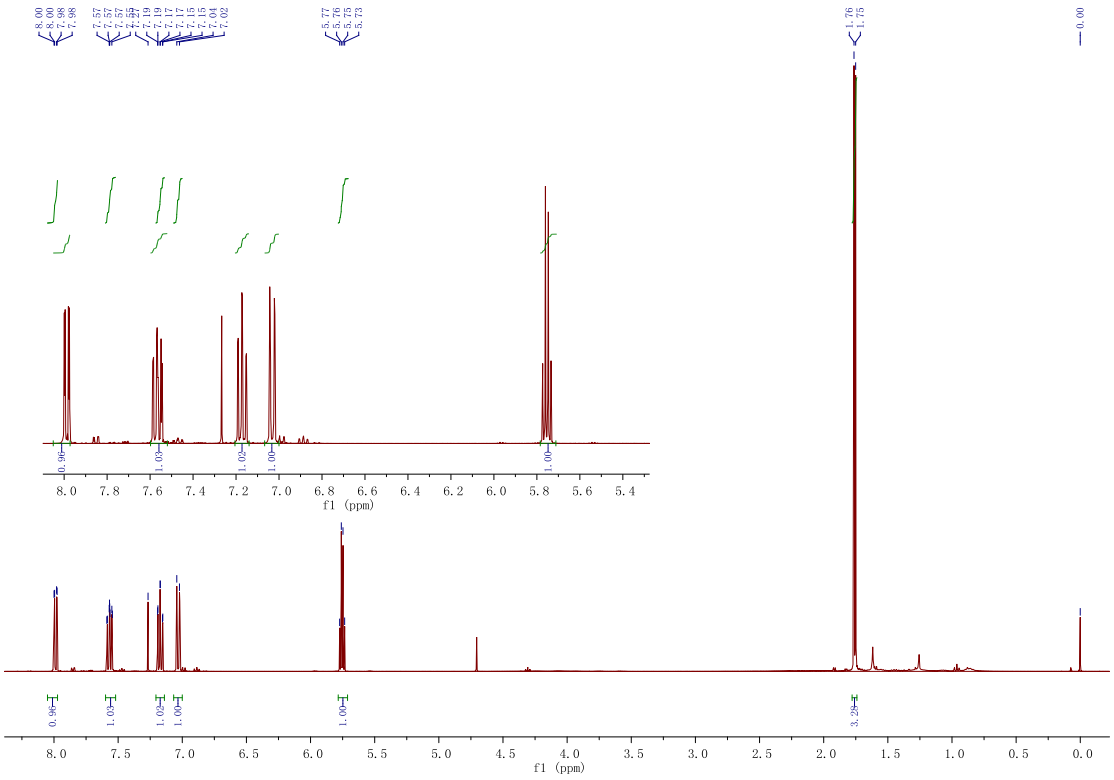

O
O
O

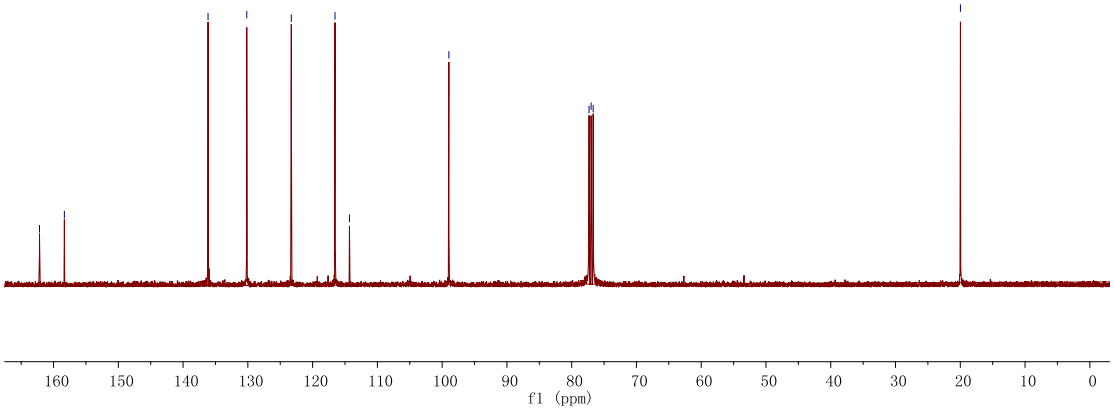

7.87
7.87
7.60
7.59
7.26
5.64
1.39
1.33
0.00
f1 (ppm)

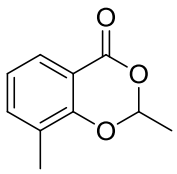

162.44
155.30
145.92
137.68
130.81
124.42
114.96
90.43
77.32
77.00
76.68
34.86
34.68
31.25
29.60
f1 (ppm)



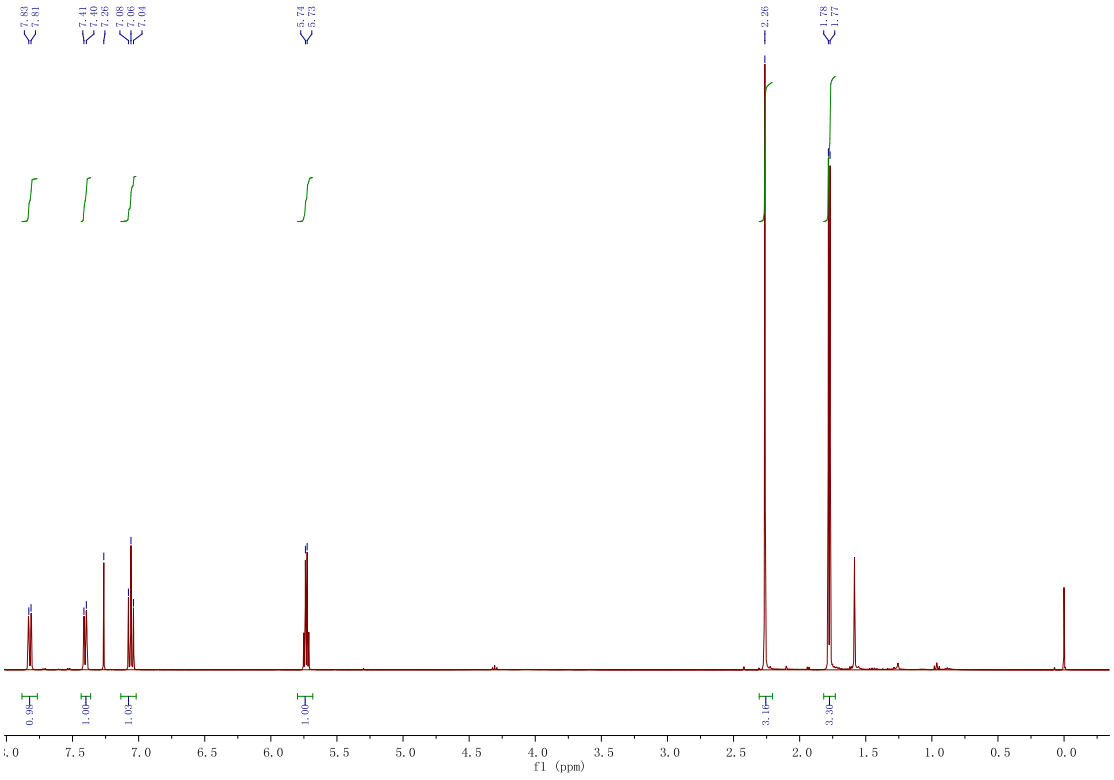
3a

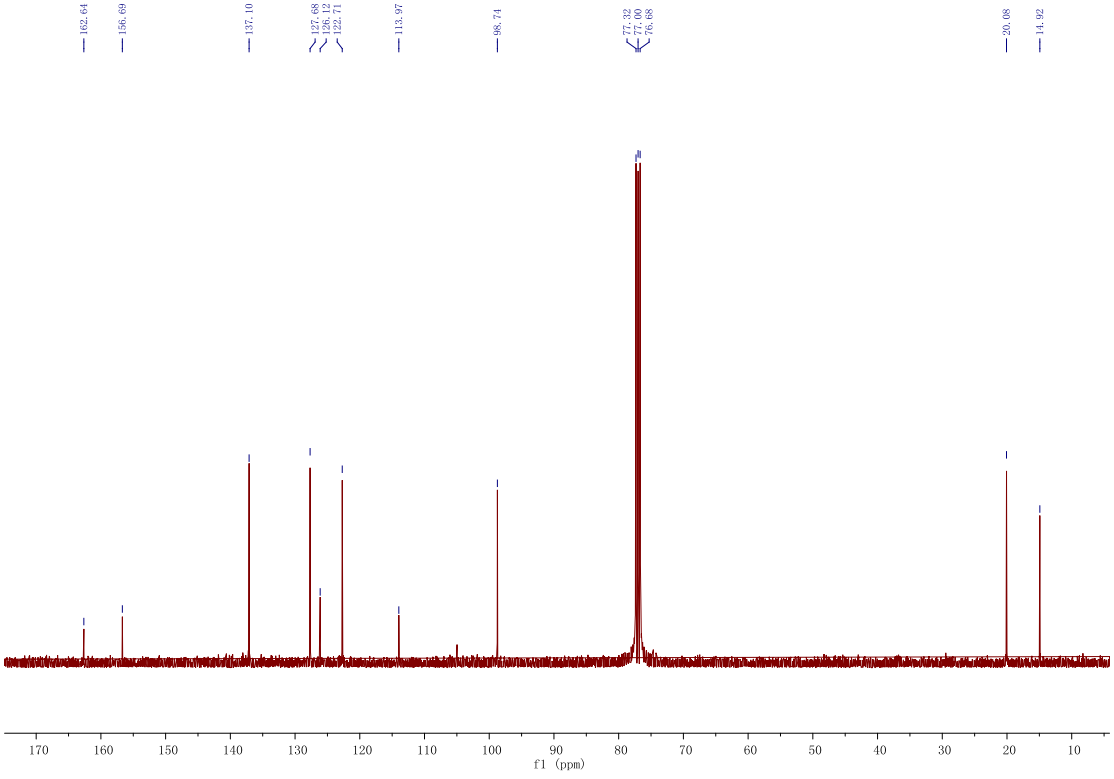

8.00
7.98
7.57
7.57
7.19
7.17
7.15
7.04
7.02
5.77
5.76
5.75
5.73
1.76
1.75
0.00
0.98
1.03
1.02
1.00
1.00
3.29
f1 (ppm)

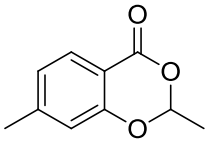

162.17
158.33
136.14
130.17
123.29
116.54
114.31
98.96
77.32
77.00
76.68
19.98
f1 (ppm)



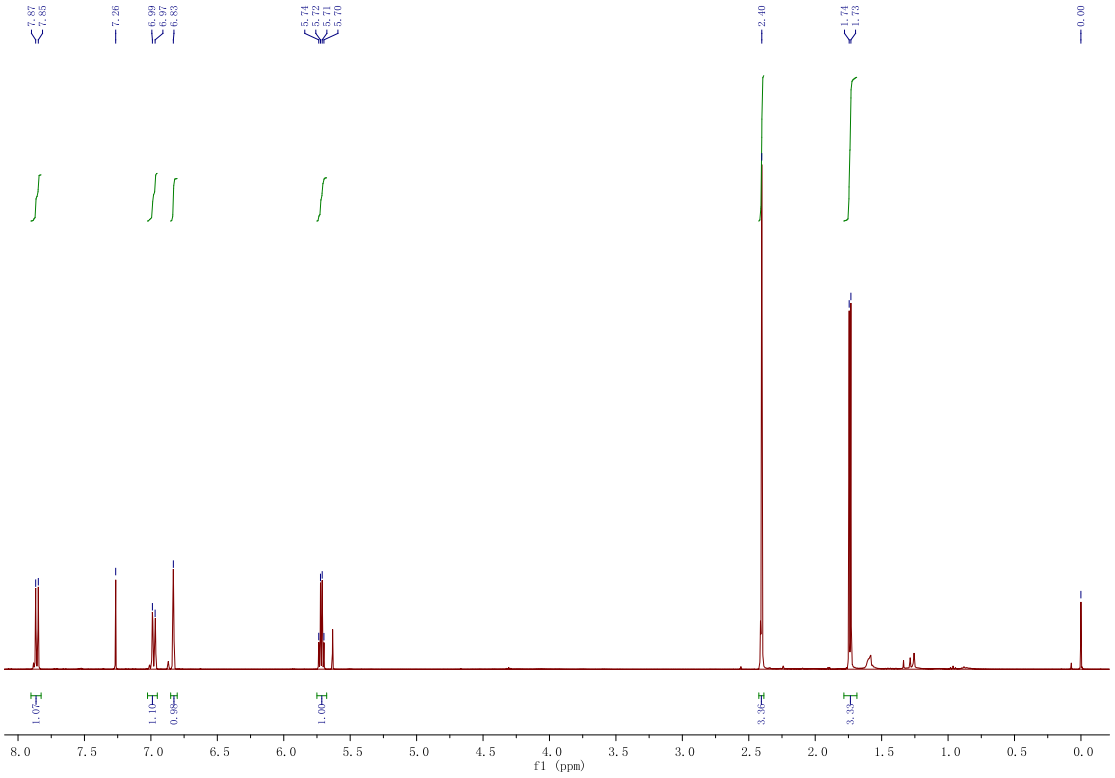
3b

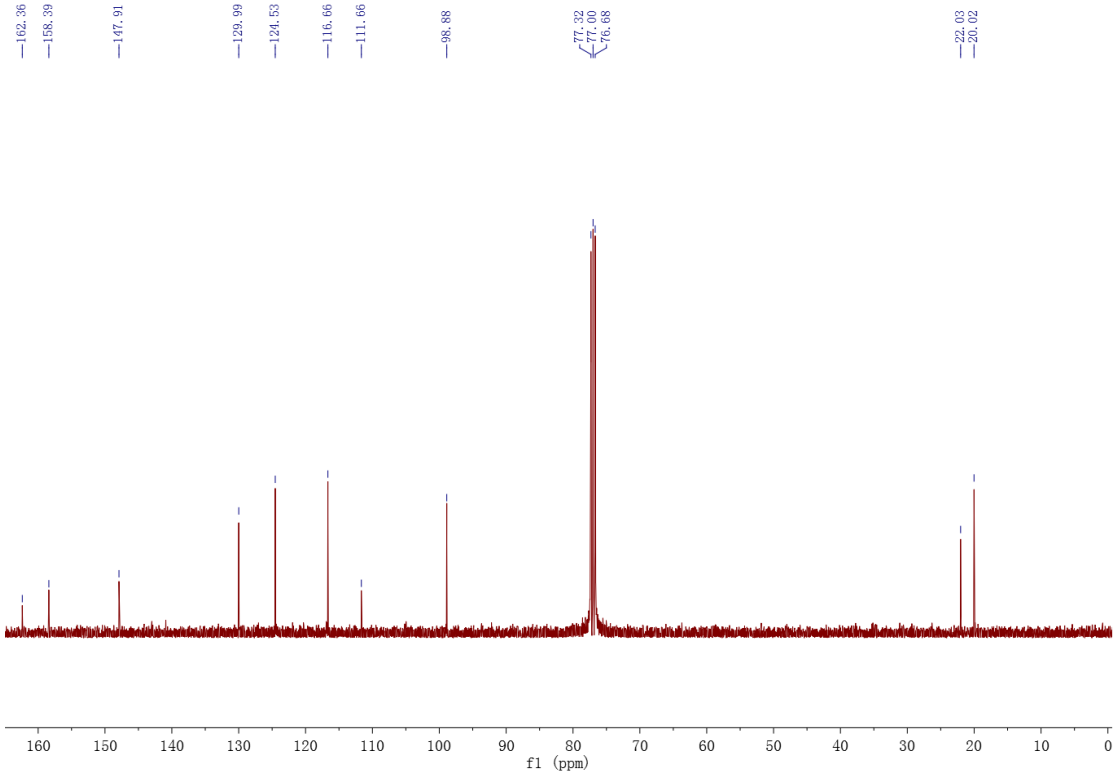

7.83
7.81
7.41
7.40
7.26
7.08
7.06
7.04
5.74
5.73
2.26
1.78
1.77
0.99
1.00
1.03
1.00
3.16
3.30
f1 (ppm)

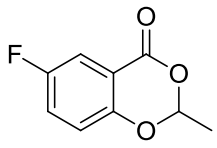

162.64
156.69
137.10
127.68
126.12
122.71
113.97
98.74
77.32
77.00
76.68
20.08
14.92
f1 (ppm)



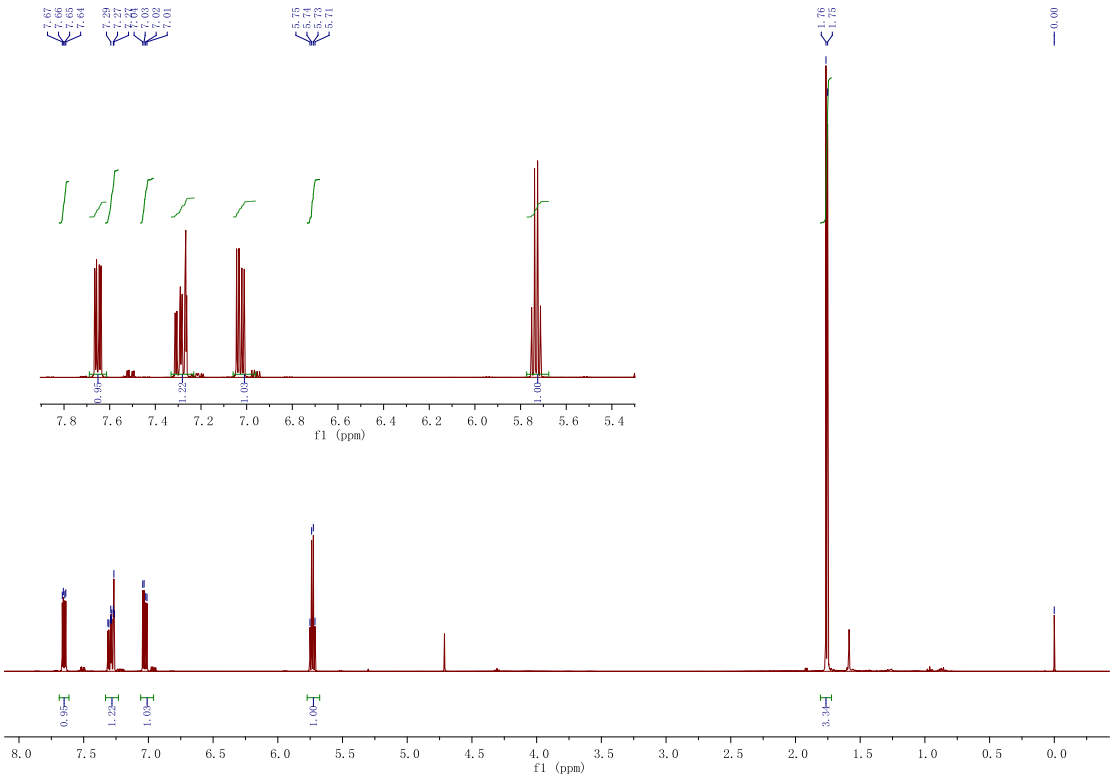
3c

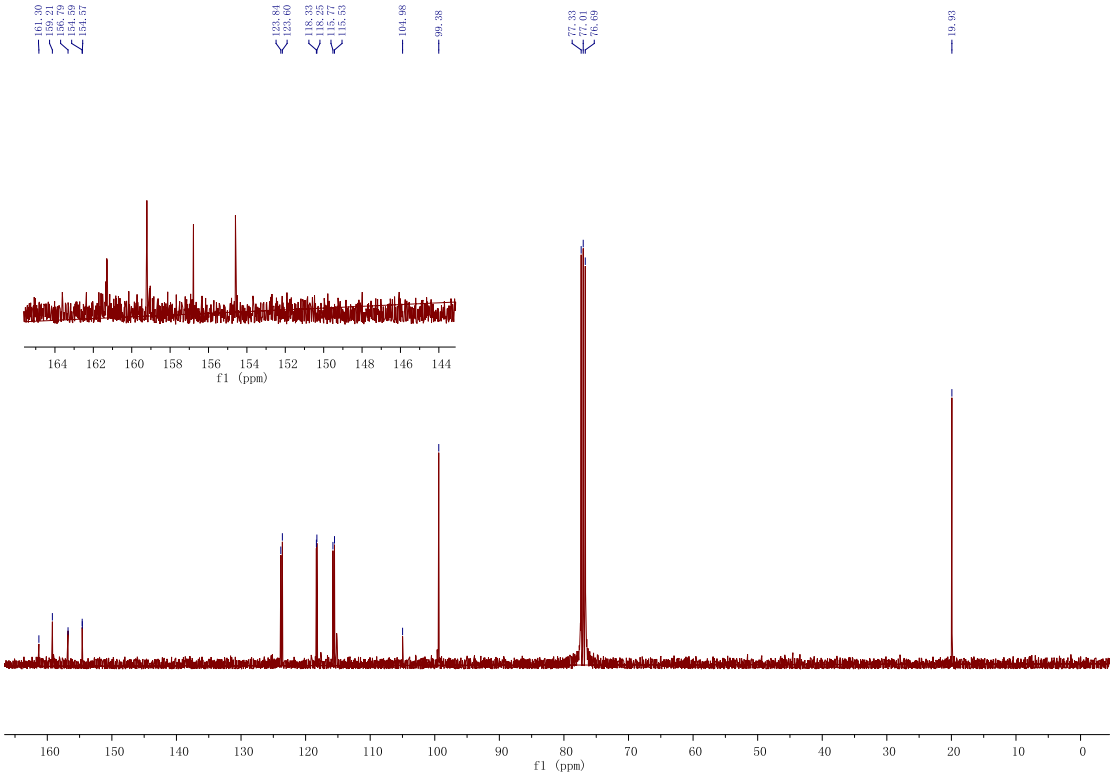

7.87
7.85
7.26
6.99
6.97
6.83
5.74
5.72
5.71
5.70
2.40
1.74
1.73
0.00
1.07
1.10
0.89
1.00
3.36
3.33
f1 (ppm)

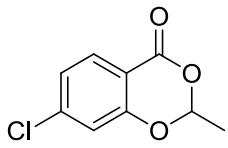

162.36
158.39
147.91
129.99
124.53
116.66
111.66
98.88
77.32
77.00
76.68
22.03
20.02
f1 (ppm)


O
F
O
O

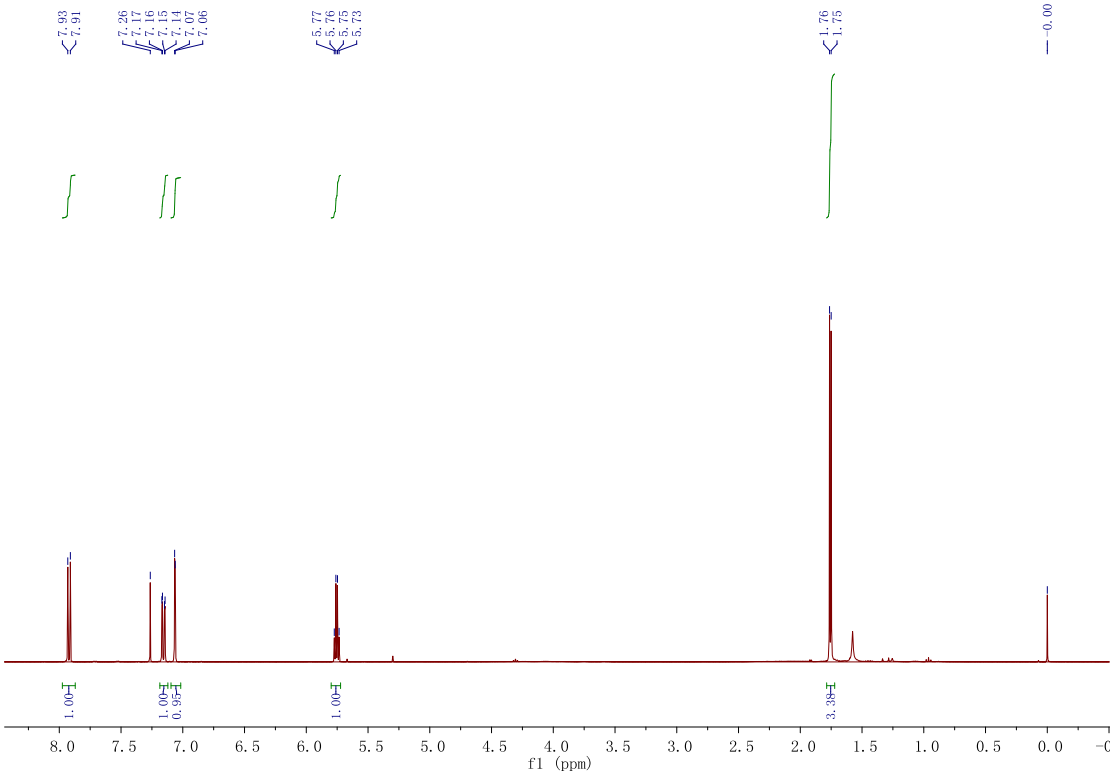
3d

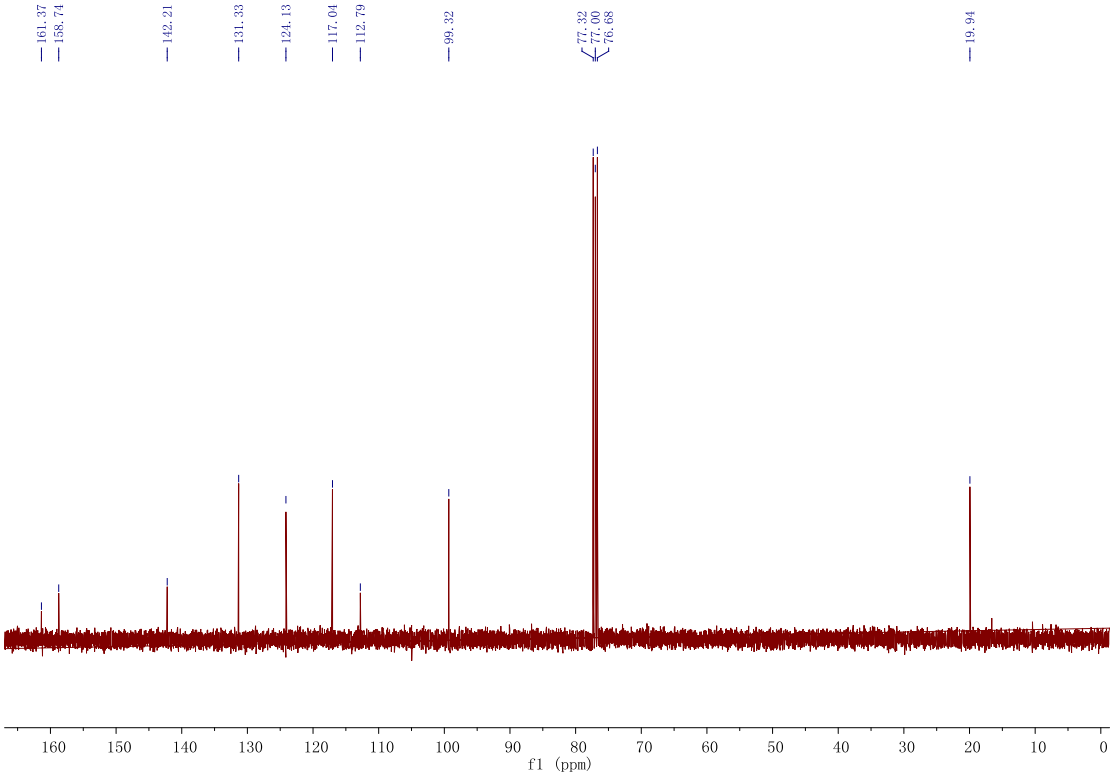

7.67
7.66
7.65
7.64
7.29
7.27
7.27
7.04
7.03
7.02
7.01
5.75
5.74
5.73
5.71
1.76
1.75
0.00
0.95
1.22
1.03
1.00
3.34
f1 (ppm)

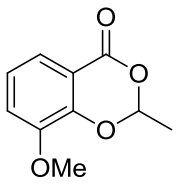

161.30
159.21
156.79
154.89
154.57
123.84
123.60
118.33
118.25
115.77
115.53
104.98
99.38
77.33
77.01
76.69
19.93
f1 (ppm)


O
O
Cl
O

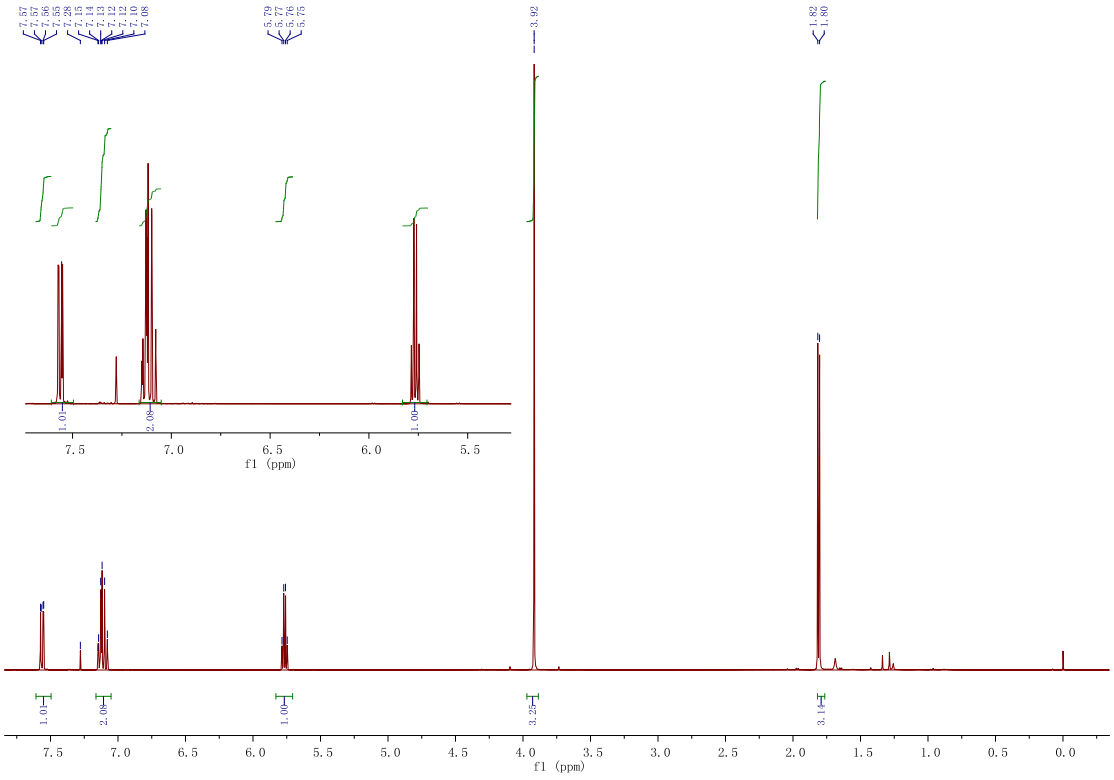
3e

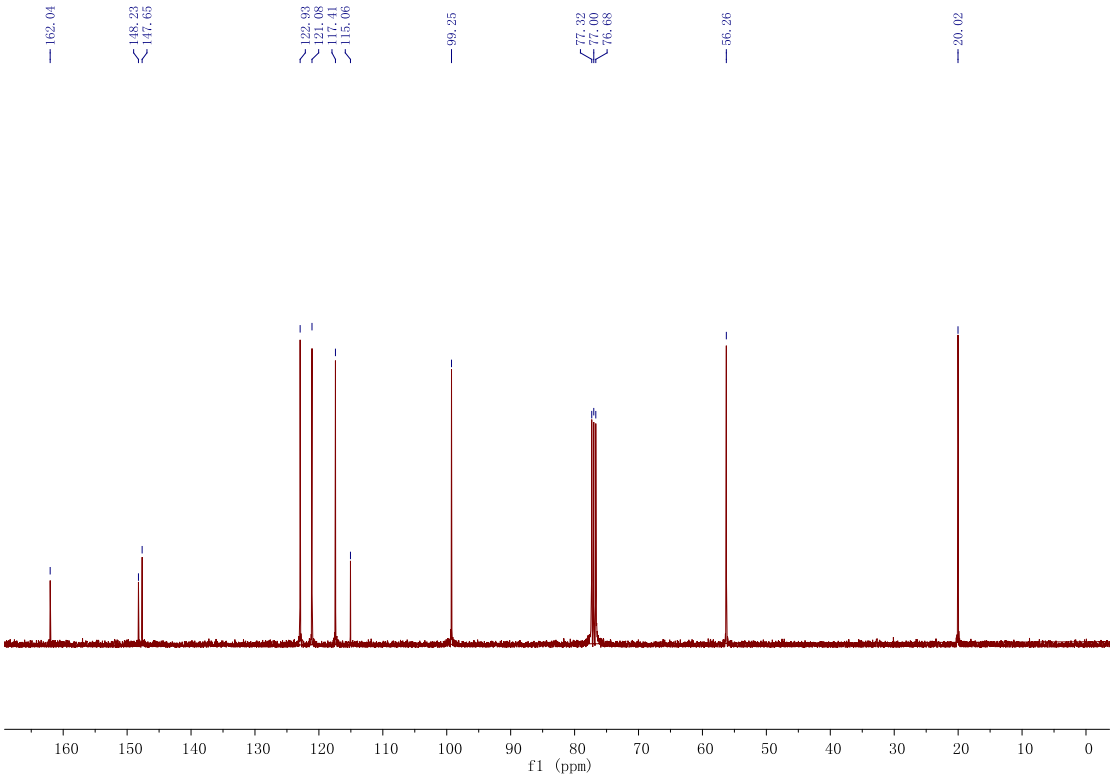

7.93
7.91
7.26
7.17
7.16
7.15
7.14
7.07
7.06
5.77
5.76
5.75
5.73
1.76
1.75
0.00
1.00
1.00
0.95
1.00
3.30
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

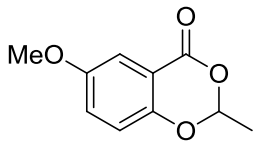

161.37
158.74
142.21
131.33
124.13
117.04
112.79
99.32
77.32
77.00
76.68
19.94
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
O
OMe

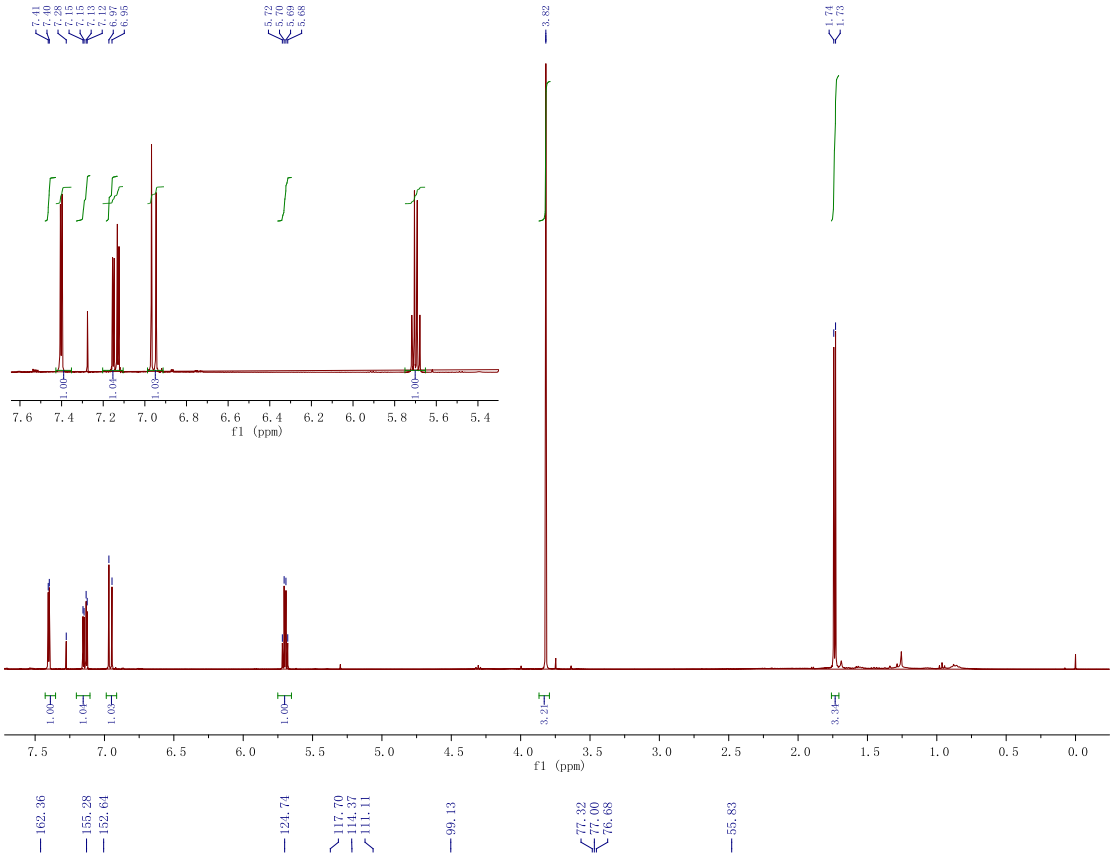
3f

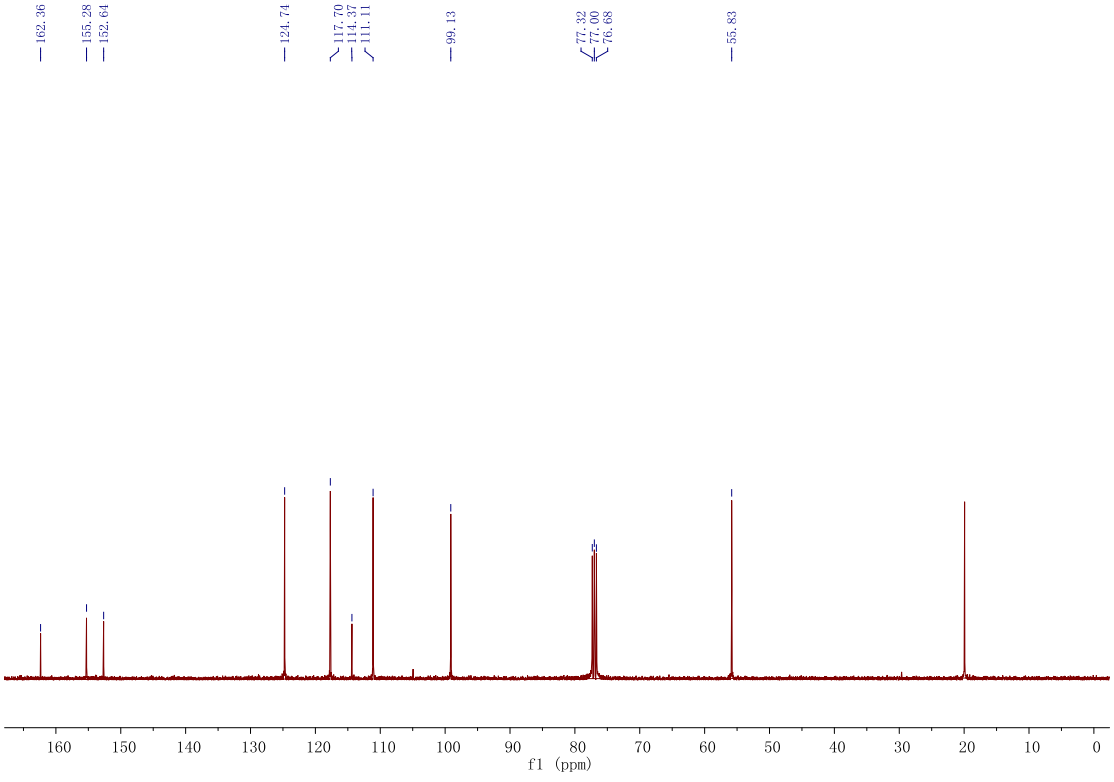

7.57
7.57
7.56
7.55
7.28
7.15
7.14
7.13
7.12
7.12
7.10
7.08
5.79
5.77
5.76
5.75
3.92
1.82
1.80
1.01
2.00
1.00
7.5
7.0
6.5
6.0
5.5
f1 (ppm)
1.01
2.00
1.00
3.25
3.14
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

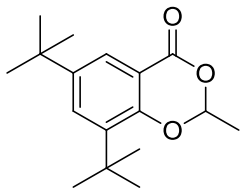

162.04
148.23
147.65
122.93
121.08
117.41
115.06
99.25
77.32
77.00
76.68
56.26
20.02
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
O
O
O

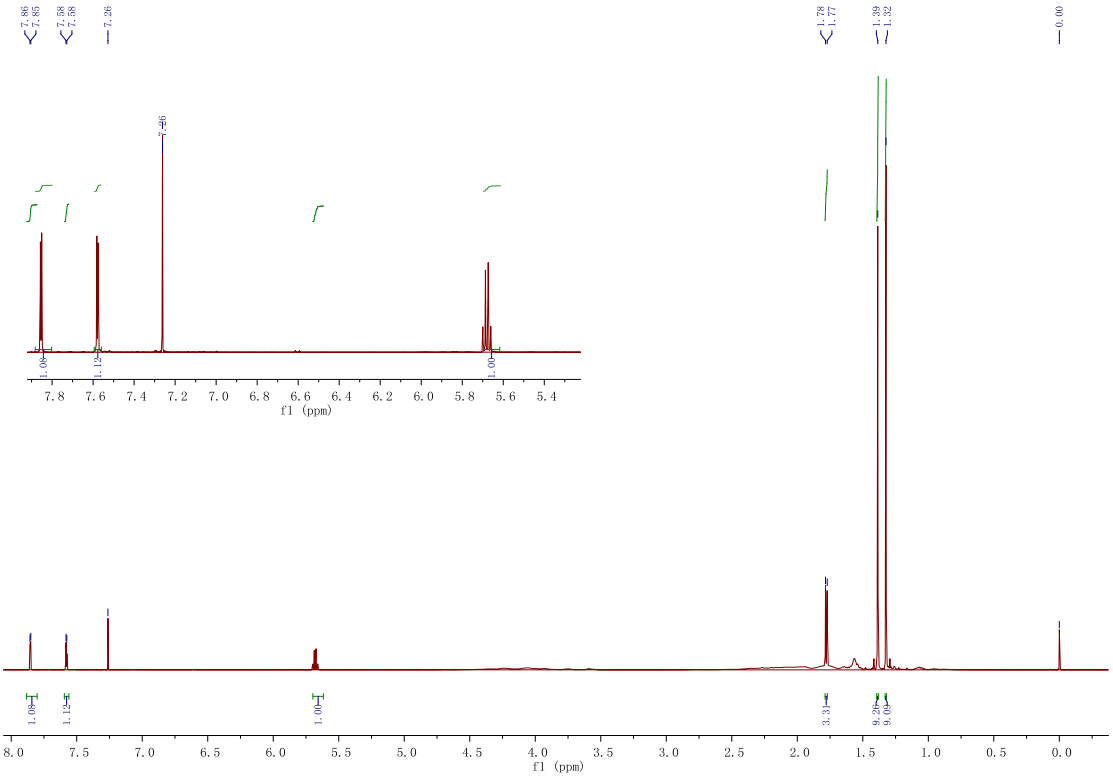
3g

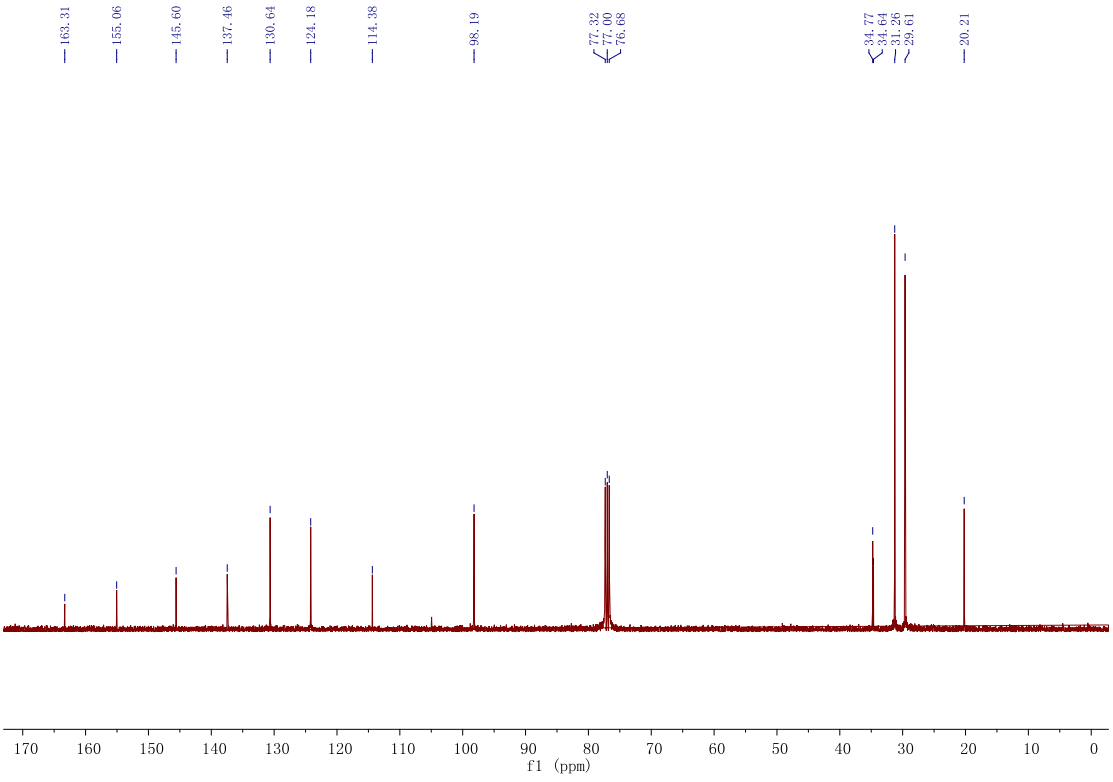

7.41
7.40
7.28
7.15
7.13
7.12
6.97
6.95
5.72
5.70
5.69
5.68
3.82
1.74
1.73
1.00
1.01
1.03
1.00
3.21
3.33
f1 (ppm)

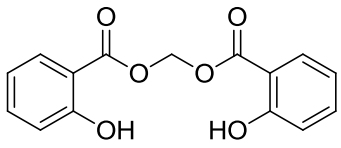

162.36
155.28
152.64
124.74
117.70
114.37
111.11
99.13
77.32
77.00
76.68
55.83
f1 (ppm)



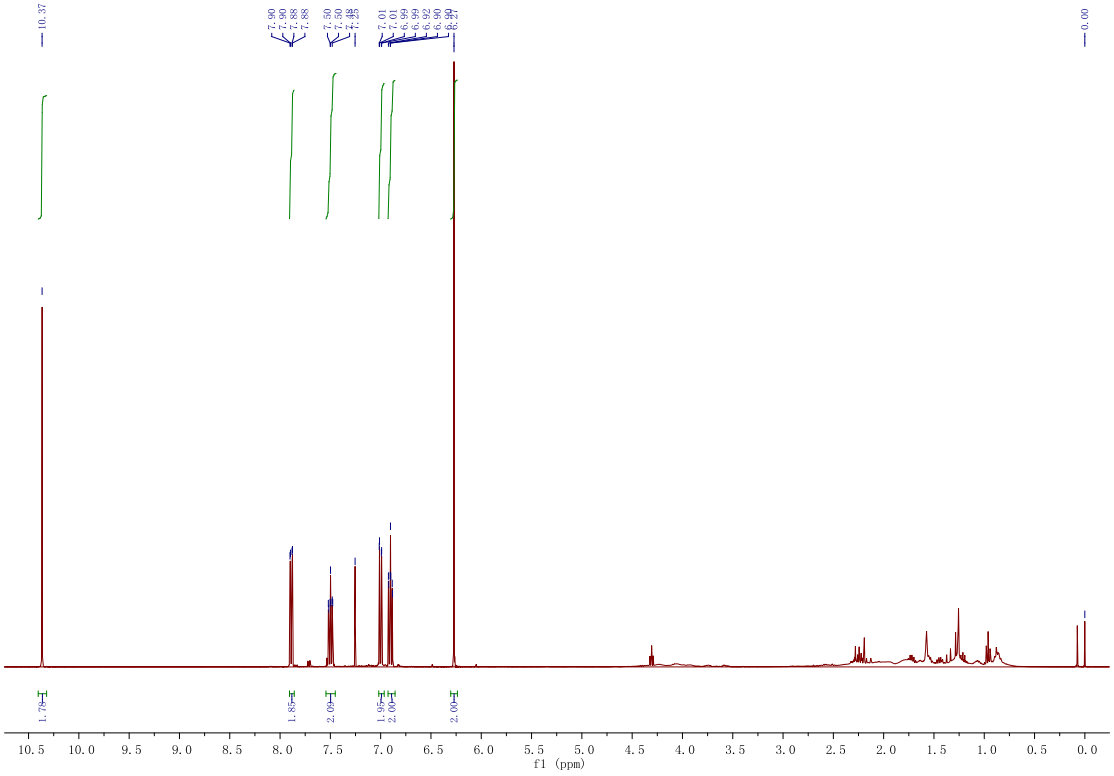
3h

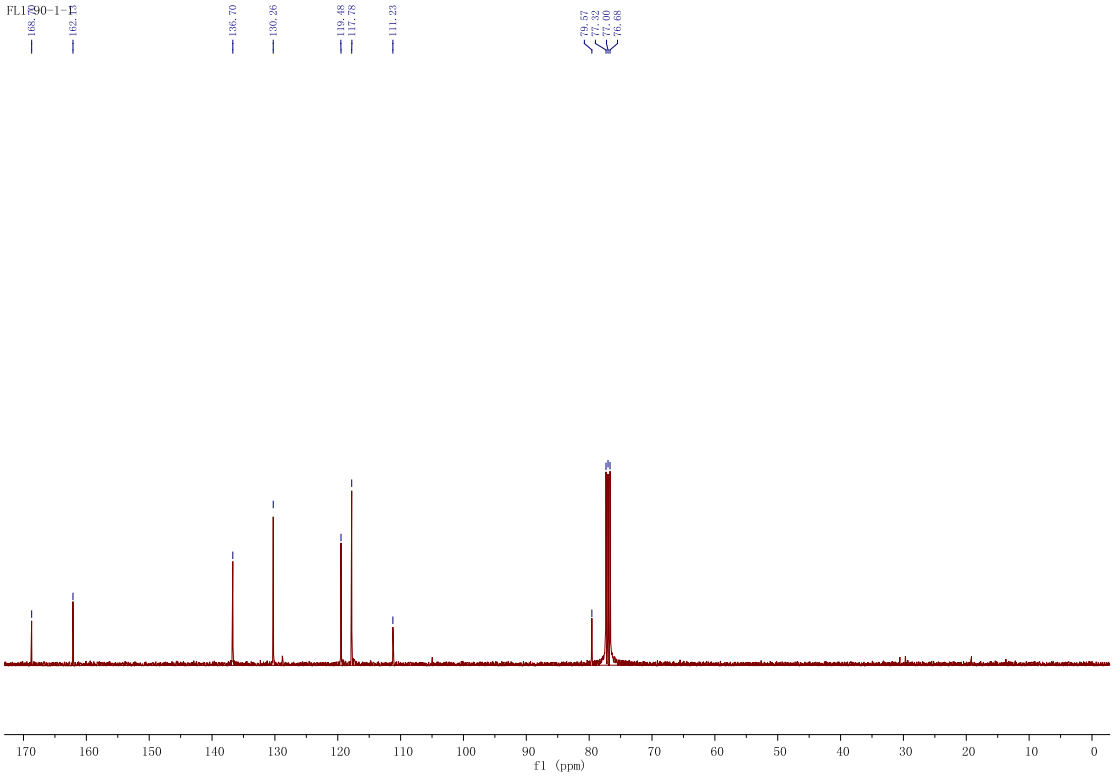

7.86
7.85
7.58
7.58
7.26
1.78
1.77
1.39
1.32
0.00
f1 (ppm)

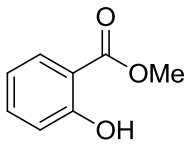

163.31
155.06
145.60
137.46
130.64
124.18
114.38
98.19
77.32
77.00
76.68
34.77
34.64
31.26
29.61
20.21
f1 (ppm)


O
O
O
O
OH
HO

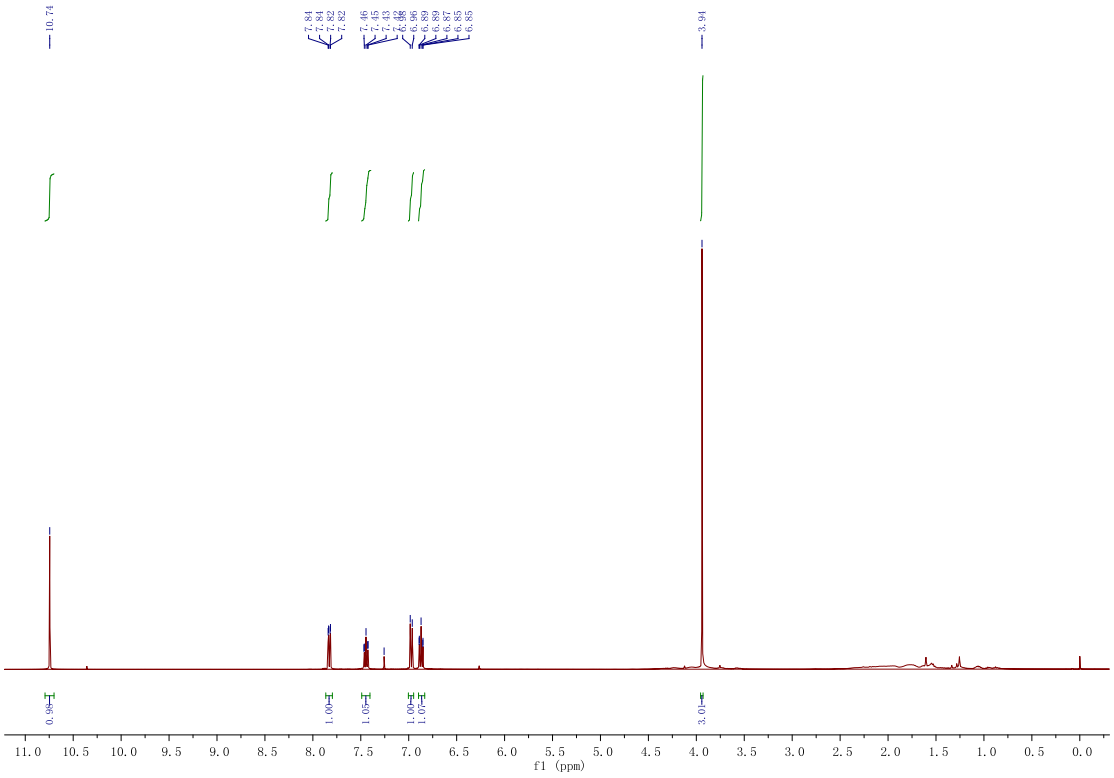
4

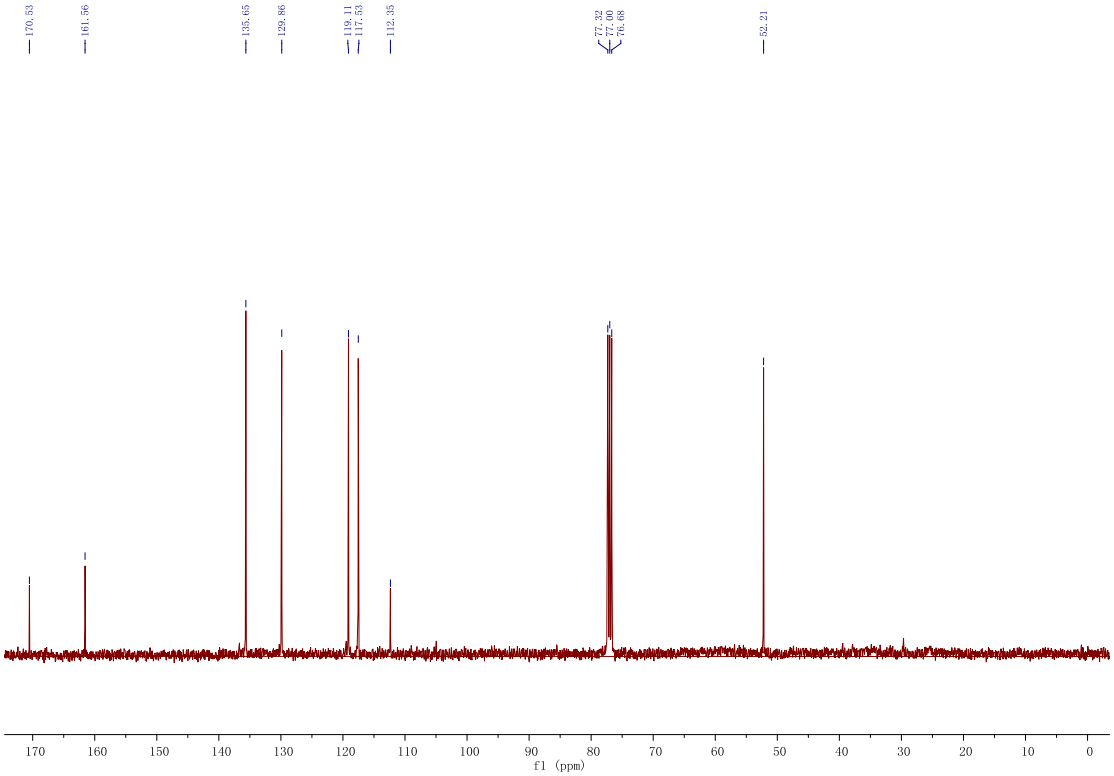

10.37
7.90
7.90
7.88
7.88
7.50
7.50
7.48
7.25
7.01
7.01
6.99
6.99
6.92
6.90
6.90
6.24
0.00
1.79
1.85
2.09
1.95
2.04
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

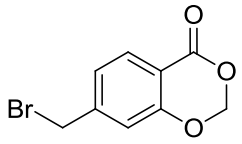

FL1F90-1-13
168.72
162.13
136.70
130.26
119.48
117.78
111.23
79.57
77.32
77.00
76.68
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
OMe
OH

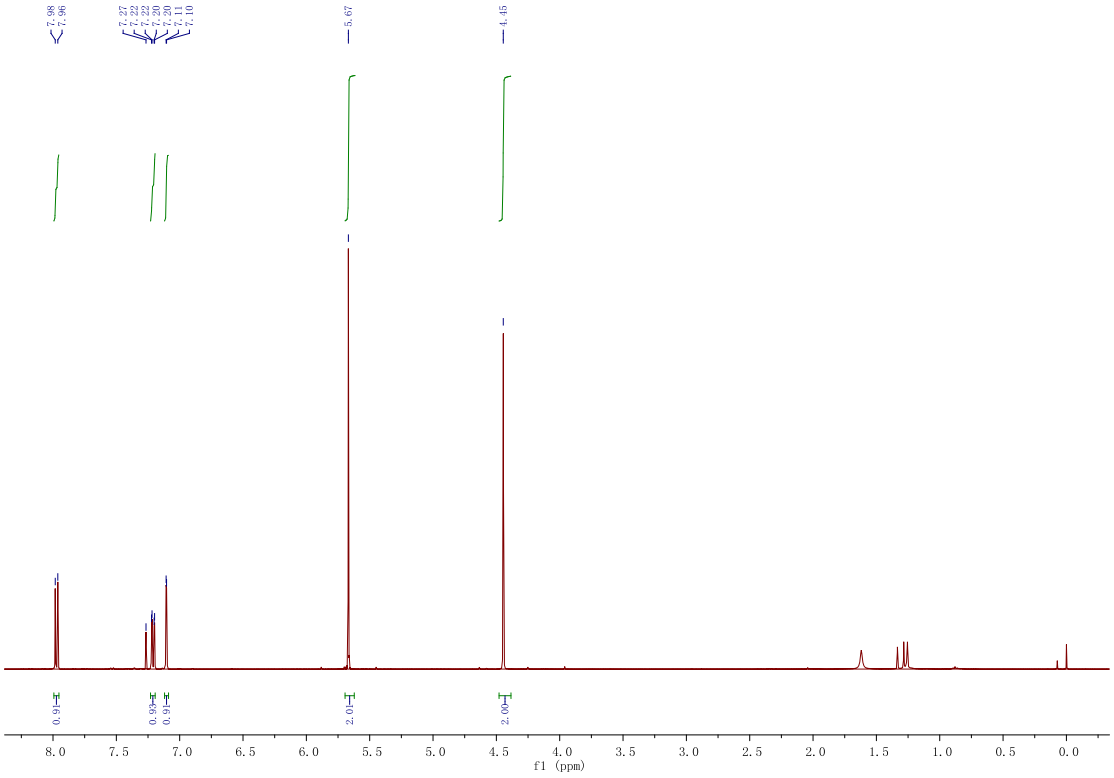
5

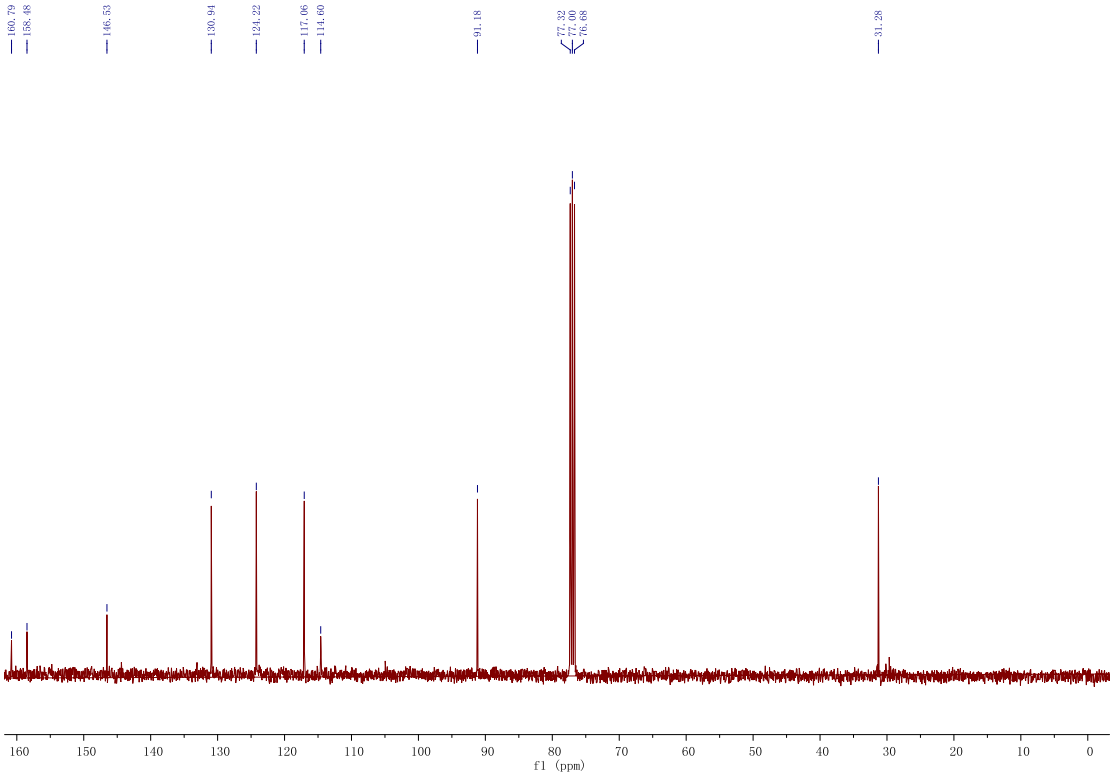

10.74
7.84
7.84
7.82
7.82
7.46
7.45
7.43
7.43
6.96
6.89
6.89
6.87
6.85
6.85
3.94
0.89
1.00
1.05
1.00
1.07
3.01
f1 (ppm)

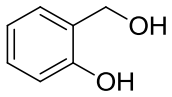

170.53
161.56
135.65
129.86
119.11
117.53
112.35
77.32
77.00
76.68
52.21
f1 (ppm)


O
O
Br
O

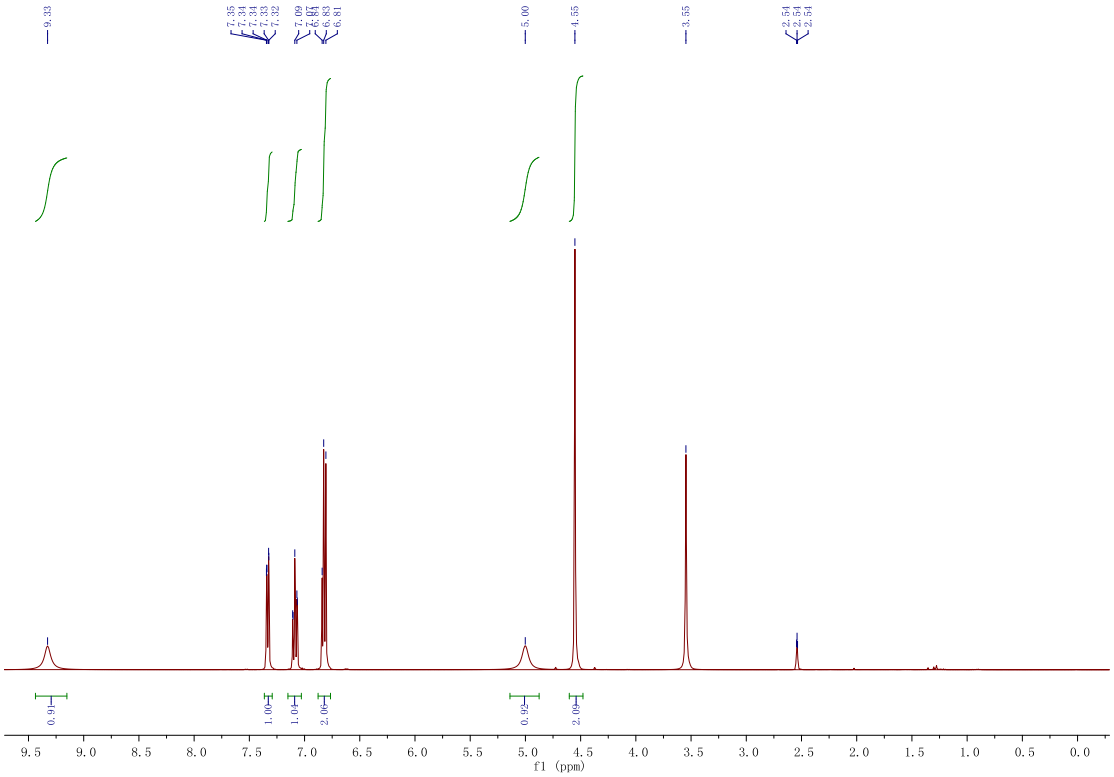
6

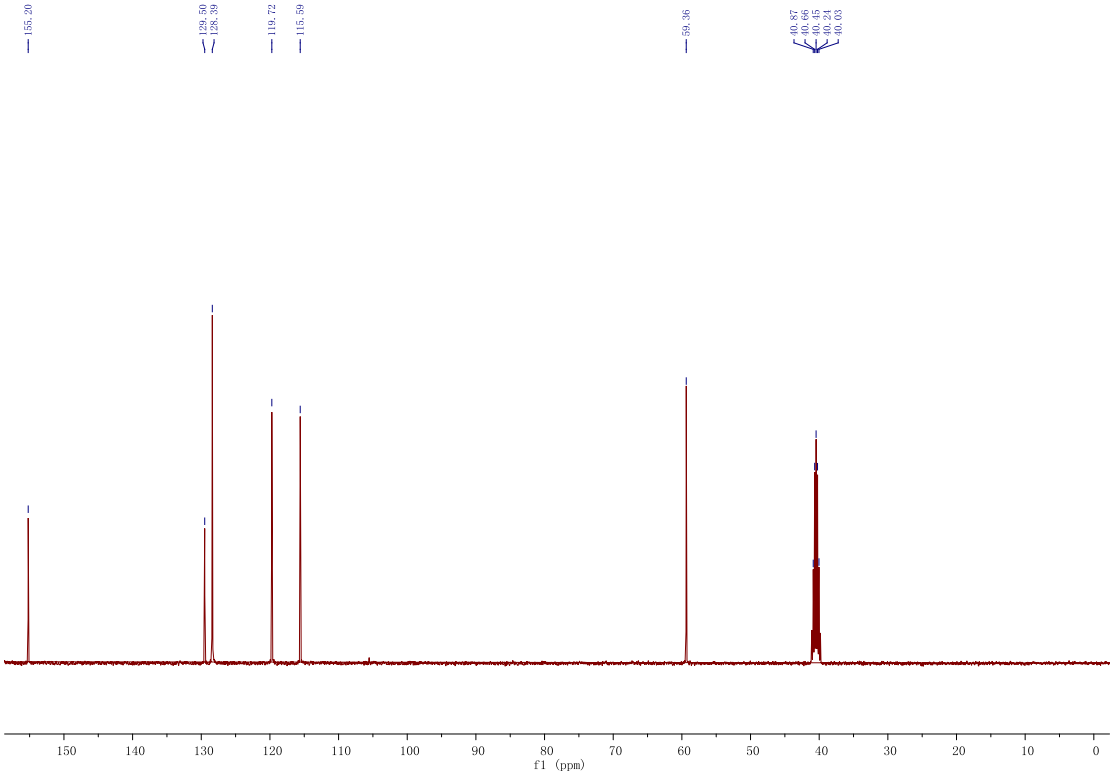

7.98
7.96
7.27
7.22
7.22
7.20
7.20
7.11
7.10
5.67
4.45
0.91
0.99
0.91
2.01
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

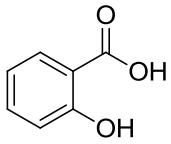

160.79
158.48
146.53
130.94
124.22
117.06
114.60
91.18
77.32
77.00
76.68
31.28
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
OH

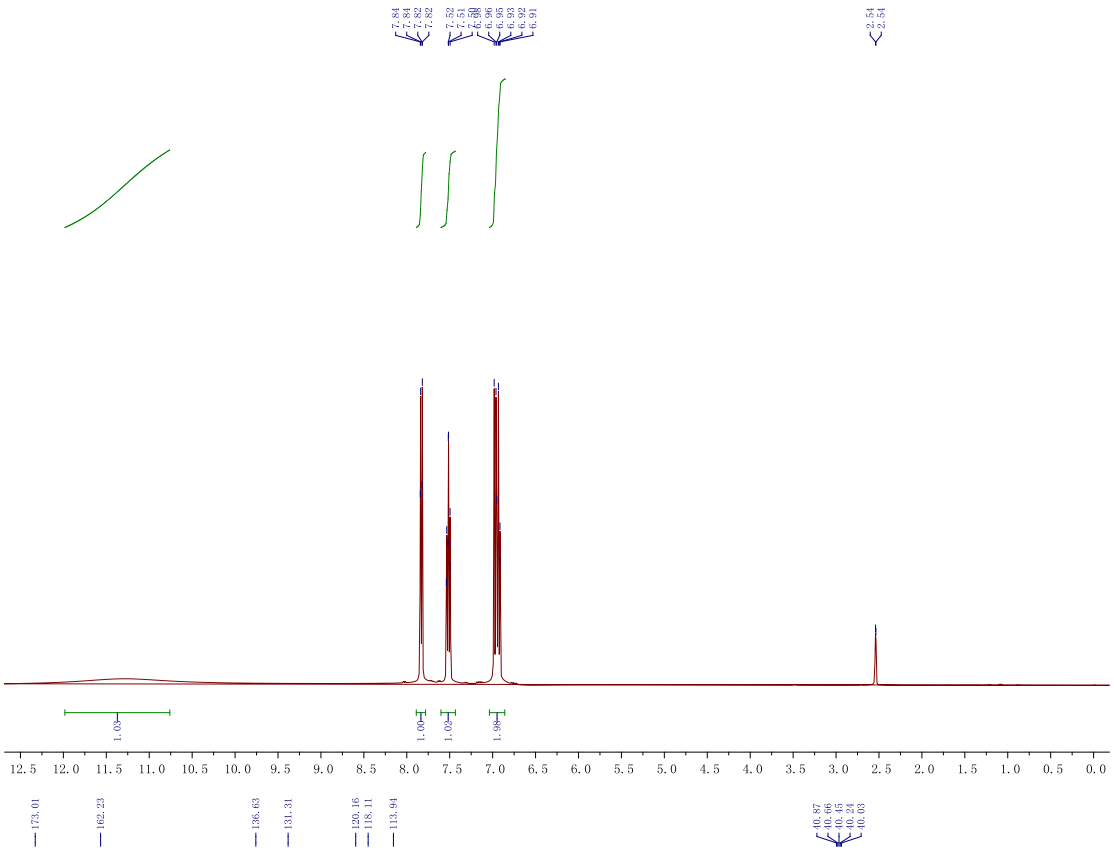
7

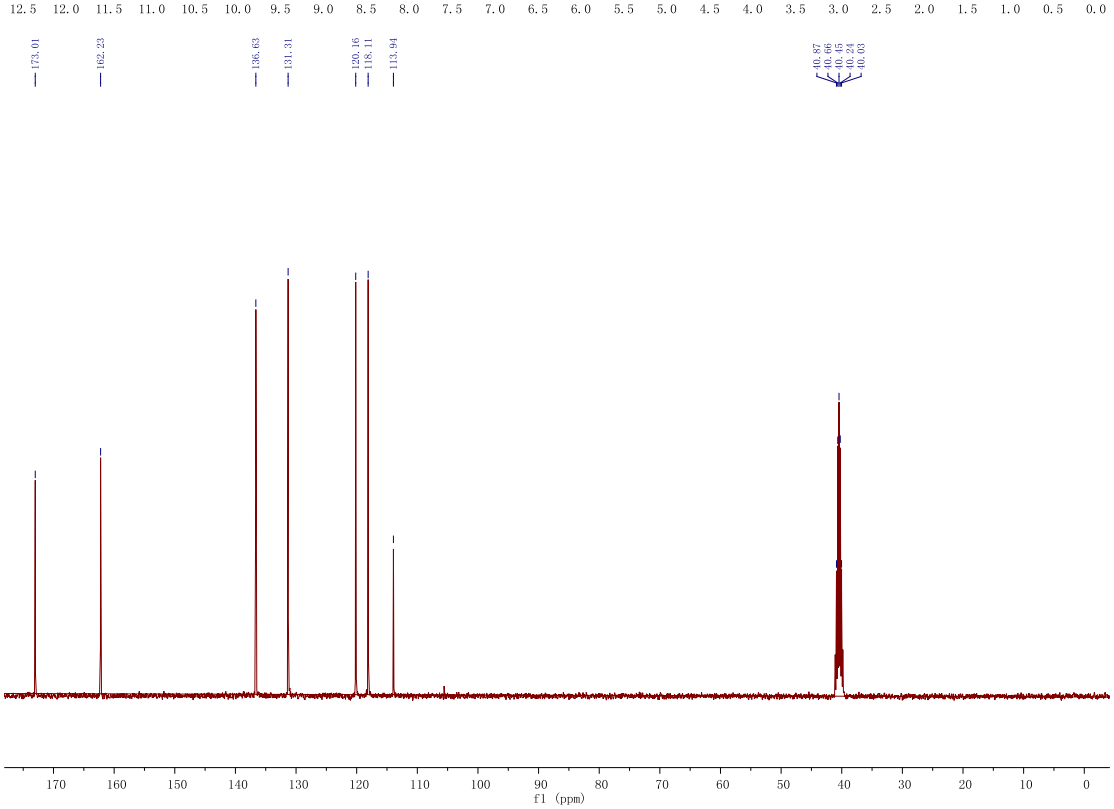

9.33
7.35
7.34
7.34
7.33
7.32
7.09
6.84
6.83
6.81
5.00
4.55
3.55
2.54
2.54
2.54
0.91
1.00
1.04
2.06
0.92
2.09
f1 (ppm)


155.20
129.50
128.39
119.72
115.59
59.36
40.87
40.66
40.45
40.24
40.03
f1 (ppm)


O
OH
OH

1a


7.84
7.84
7.82
7.82
7.52
7.51
6.96
6.95
6.93
6.92
6.91
2.54
2.54
1.03
1.00
1.02
1.98
12.5 12.0 11.5 11.0 10.5 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


173.01
162.23
138.63
131.31
120.16
118.11
113.94
40.87
40.66
40.45
40.24
40.03
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)