Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

A highly efficient approach to vanillin starting from 4-cresol

Jian-An Jiang,[a] Cheng Chen,[a] Ying Guo,[a] Dao-Hua Liao,[a] Xian-Dao Pan[b] and Ya-Fei Ji*[a]

[a]School of Pharmacy, East China University of Science and Technology, Campus P. O. Box 363, 130 Meilong Road, Shanghai 200237, P. R. China. E-mail: jyf@ecust.edu.cn.
[b]Institute of Meteria Medica, Chinese Academy of Medical Sciences & Peking Union Medical College, 1 Xiannongtan Street, Beijing 100050, P. R. China.

Table of Contents

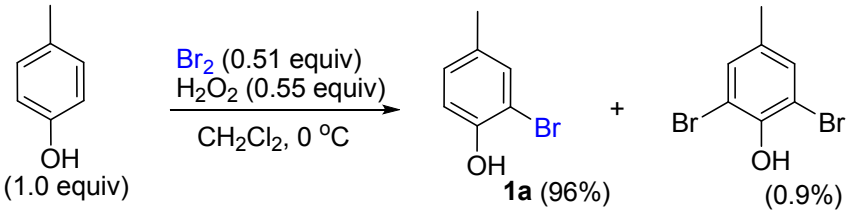
1. General Information

Unless otherwise indicated, all reagents were obtained from commercial sources and used as received without further purification. All reactions were carried out in oven-dried glassware and monitored by thin layer chromatography (TLC, pre-coated silica gel plates containing HF_{254}). Reaction products were purified *via* column chromatography on silica gel (300–400 mesh). Melting points were determined using an open capillaries and uncorrected. NMR spectra were determined on Bruker AV400 in $CDCl_3$ or DMSO-d_6 with TMS as internal standard for ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz), respectively. HRMS were carried out on a QSTAR Pulsar I LC/TOF MS mass spectrometer or Micromass GCTTM gas chromatograph-mass spectrometer. GC-MS were carried out on an Agilent 6890-5973N gas chromatograph-mass spectrometer.

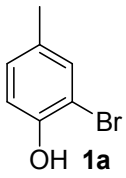
2. General preparation procedure and characterization data

2.1 Mild and eco-friendly oxybromination.

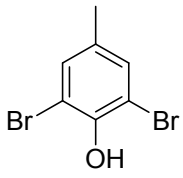
2.1.1 Oxybromination of 4-cresol into 1a.



General procedure: a three-necked flask was charged with 4-cresol (1.08 g, 10 mmol), CH_2Cl_2 (10 mL) and H_2O_2 (30%, 0.58 mL, d = 1.11 g/mL, 5.5 mmol), and then the solution was cooled to 0 °C. Under the temperature, to the solution was slowly added a solution of bromine (0.26 mL, d = 3.12 g/mL, 5.1 mmol) and CH_2Cl_2 (5 mL) over 4 h through a syringe pump. Afterwards, the mixture was further stirred for another 4 h. An aqueous $NaHSO_3$ (10 mL, 2%) was added to the mixture at 0 °C, and the reaction solution was allowed to stir for 1 h at room temperature. Furthermore, the solution was partitioned into two layers, and the aqueous phase was extracted with CH_2Cl_2 (5 mL × 3). Finally, the combined organic layers were dried over anhydrous Na_2SO_4, and concentrated to give a crude oil, which was purified *via* column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to provide the desired product **1a** (chromatographic separation can provide a more credible yield).

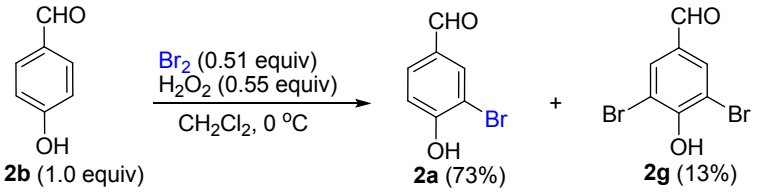


2-Bromo-4-methylphenol (1a): yellow oil, 1.80 g (96%); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28 (br d, J = 1.6 Hz, 1H), 7.02 (br d, J = 8.0, 1H), 6.92 (br d, J = 8.0 Hz, 1H), 5.40 (br s, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 150.0, 132.1, 131.4, 129.8, 115.8, 109.8, 20.2; HRMS (EI): m/z [M^+] calcd. for C_7H_7OBr 185.9680, found 185.9682.

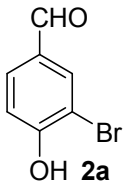


2,6-Dibromo-4-methylphenol:[1] yellow solid, 24 mg (0.9%), m.p. 44–46 °C (lit[1] m.p. 49–51 °C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.26 (br s, 2H), 5.71 (br s, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.1, 132.4 (4C), 109.4, 20.0; HRMS (EI): *m/z* [M^+] calcd. for $C_7H_6OBr_2$ 263.8785, found 263.8787.

2.1.2 Oxybromination of 4-hydroxybenzaldehyde into 2a.

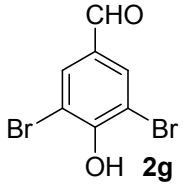


General procedure: a three-necked flask was charged with 4-hydroxybenzaldehyde (1.22 g, 10 mmol), CH_2Cl_2 (10 mL) and H_2O_2 (30%, 0.58 mL, *d* = 1.11 g/mL, 5.5 mmol), and then the solution was cooled to 0 °C. Under the temperature, to the solution was slowly added a solution of bromine (0.26 mL, *d* = 3.12 g/mL, 5.1 mmol) and CH_2Cl_2 (5 mL) over 4 h through a syringe pump. Afterwards, the mixture was further stirred for another 4 h. An aqueous $NaHSO_3$ (10 mL, 2%) was added to the mixture at 0 °C, and the reaction solution was allowed to stir for 1 h at room temperature. Furthermore, the solution was partitioned into two layers, and the aqueous phase was extracted with CH_2Cl_2 (5 mL × 3). Finally, the combined organic layers were dried over anhydrous Na_2SO_4, and concentrated to give a crude oil, which was purified *via* column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to provide the desired product **2a** and dibromination product **2g**.



2a

3-Bromo-4-hydroxybenzaldehyde (2a):[2] pale yellow solid, 1.46 g (73% yield), m.p. 130–132 °C (lit[2] m.p. 130–132 °C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.83 (br s, 1H), 8.04 (br s, 1H), 7.77 (br d, *J* = 8.4 Hz, 1H), 7.15 (br d, *J* = 8.4 Hz, 1H), 6.43 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 192.7, 151.8, 132.9, 130.3, 128.1, 127.5, 127.4; HRMS (EI): *m/z* [M^+] calcd. for $C_7H_5O_2Br$ 199.9473, found 199.9474.

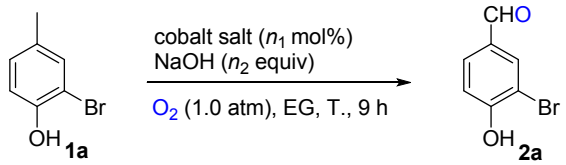


2g

3,5-Dibromo-4-hydroxybenzaldehyde (**2g**):[3] white solid, 0.36 g (13%), m.p. 182–184 °C (lit[3] m.p. 181–183 °C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.80 (br s, 1H), 8.00 (br s, 2H), 6.40 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ188.3, 154.5, 133.8 (2C), 131.5, 110.9 (2C); HRMS (ESI): *m/z* [M–H^+] calcd. for $C_7H_3Br_2O_2$ 276.8500, found 276.8517.

2.2 Oxidation of 1a into 2a.

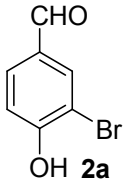
Table S1. Optimizations for the reaction conditions.[a]



Entry	Co salt (n_1 mol%)	NaOH (n_2 equiv)	T. (°C)	Yield (%)[b]
1	$CoCl_2$ (3.0)	2.0	50	trace
2	$CoBr_2$ (3.0)	2.0	50	trace
3	CoF_2 (3.0)	2.0	50	trace
4	Cobalt(II) acetylacetonate (3.0)	2.0	50	45
5	Cobalt tetramethoxyphenylporphyrin (3.0)	2.0	50	13
6	$Co(C_2O_4)\cdot 2H_2O$ (3.0)	2.0	50	27
7	$Co(OAc)_2\cdot 4H_2O$ (3.0)	2.0	50	53
8	$Co(OAc)_2\cdot 4H_2O$ (3.0)	2.0	60	59
9	$Co(OAc)_2\cdot 4H_2O$ (3.0)	2.0	70	68
10	$Co(OAc)_2\cdot 4H_2O$ (3.0)	2.0	80	76
11	$Co(OAc)_2\cdot 4H_2O$ (3.0)	0	80	0
12	$Co(OAc)_2\cdot 4H_2O$ (3.0)	3.0	80	90
13	$Co(OAc)_2\cdot 4H_2O$ (3.0)	4.0	80	90
14	$Co(OAc)_2\cdot 4H_2O$ (2.0)	4.0	80	90
15	$Co(OAc)_2\cdot 4H_2O$ (1.0)	**4.0**	**80**	90
16	$Co(OAc)_2\cdot 4H_2O$ (0.5)	4.0	80	79
17	$Co(OAc)_2\cdot 4H_2O$ (1.0)	4.0	80	trace[c]

[a]Reaction conditions: **1a** (5.0 mmol), cobalt salt (n_1 mol%), NaOH (n_2 equiv), EG (10 mL), O_2 (1.0 atm), 9 h. [b]Isolated yield. [c]Performed under argon atmosphere.

General procedure: a three-necked flask was charged with EG (10 mL), **1a** (0.94 g, 5.0 mmol), cobalt salt (*n* mol%), and solid NaOH (n_2 equiv), and then the solution was heated to 80 °C. The molecular oxygen was continuously supplied to the reaction through a top tube inlet for 9 h. Hydrochloric acid (10 mL, 10%) and methyl *tert*-butyl ether (MTBE, 15 mL) were successively added to the reaction mixture at room temperature. The MTBE phase was separated, and the aqueous phase was further extracted with MTBE (15 mL × 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a residue, which was purified *via* column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to provide the desired product **2a**.

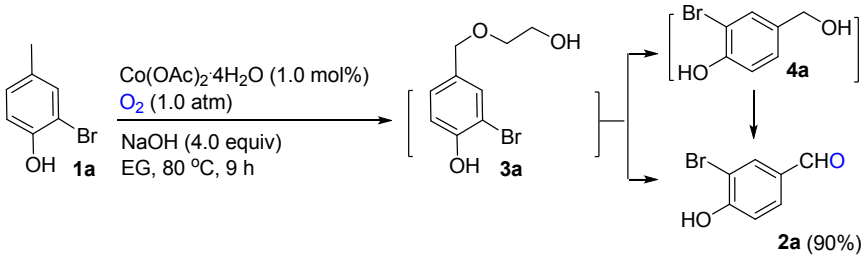


3-Bromo-4-hydroxybenzaldehyde (2a):[2] pale yellow solid, 0.90 g (as the best yield of 90%), m.p. 130–132 °C (lit[2] m.p. 130–132 °C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.83 (br s, 1H), 8.04 (br s, 1H), 7.77 (br d, J = 8.4 Hz, 1H), 7.15 (br d, J = 8.4 Hz, 1H), 6.43 (br s, 1H); ^{13}C

NMR (100 MHz, $CDCl_3$, ppm): δ 192.7, 151.8, 132.9, 130.3, 128.1, 127.5, 127.4; HRMS (EI): *m/z* [M^+] calcd. for $C_7H_5O_2Br$ 199.9473, found 199.9474.

2.3 Reaction process analysis for the oxidation of 1a.

2.3.1 The oxidation process of 1a in EG (Fig. 1 in the text).



Oxidation process analysis: a three-necked flask was charged with EG (10 mL), **1a** (0.94 g, 5.0 mmol), $Co(OAc)_2 \cdot 4H_2O$ (12.5 mg, 0.05 mmol) and solid NaOH (0.80 g, 20 mmol), and then the solution was heated to 80 °C. The molecular oxygen was continuously supplied to the reaction through a top tube inlet. About 0.2 mL of sample, withdrawn from the reaction mixture at the specified time (1.5, 3.0, 4.5, 6.0, 7.5 and 9.0 h), was acidified by hydrochloric acid (2.0 M) and was extracted with MTBE. The extracted sample was analyzed by GC-MS to evaluate the product distributions. It should be noted that the sample should be immediately analyzed after extraction.

Besides, another incomplete oxidation reaction (performed for 4 h) was worked up and purified *via* column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to provide the intermediates **3a** and **4a** for structure confirmation.

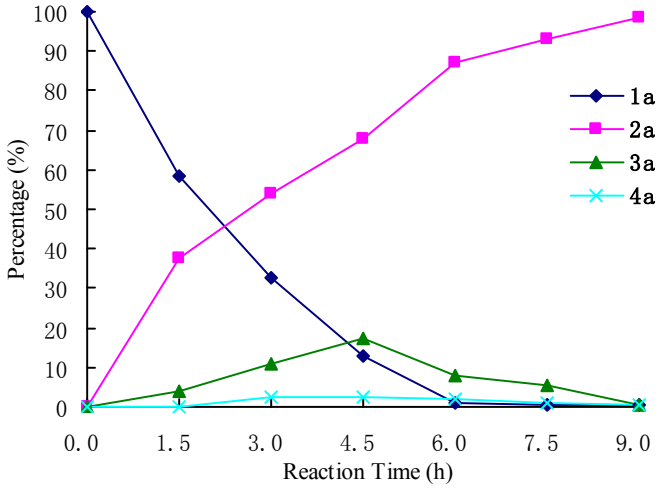
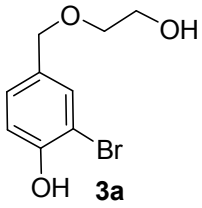
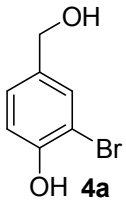


Fig. 1 Time-dependence curves for the oxidation **1a** to **2a** in EG (percentages as their respective ratios by area normalization method in the total ionization chromatography).



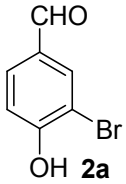
3a

2-Bromo-4-((2-hydroxyethoxy)methyl)phenol (3a): yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45 (br d, J = 2.0 Hz, 1H), 7.16 (dd, J = 8.0, 2.0 Hz, 1H), 6.95 (br d, J = 8.0 Hz, 1H), 4.44 (s, 2H), 3.76 (t, J = 4.8 Hz, 2H), 3.57 (t, J = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.4, 132.2, 131.2, 128.8, 116.2, 110.0, 72.2, 71.3, 61.7; HRMS (ESI): *m/z* [M-H$^+$] calcd. for $C_9H_{10}O_3Br$ 244.9813, found 244.9823.



4a

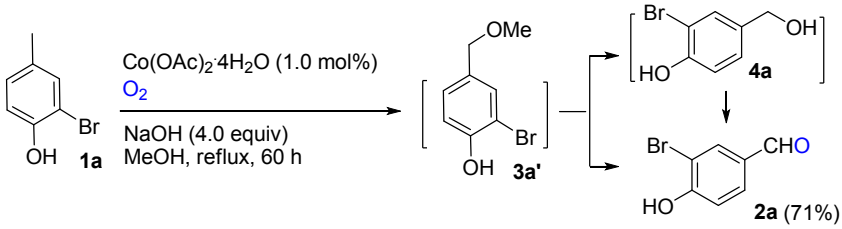
2-Bromo-4-(hydroxymethyl)phenol (4a):[4] white solid, m.p. 126–128 °C (lit[4] m.p. 127–129 °C); ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 7.41 (br d, J = 2.0 Hz, 1H), 7.11 (dd, J = 8.0, 2.0 Hz, 1H), 6.90 (br d, J = 8.4 Hz, 1H), 4.36 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ153.2, 135.3, 131.5, 127.5, 116.5, 109.3, 62.4; HRMS (EI): *m/z* [M$^+$] calcd. for $C_7H_7O_2Br$ 201.9629, found 201.9631.



2a

3-Bromo-4-hydroxybenzaldehyde (2a): the spectral data see 2.1 section.

2.3.2 The oxidation process of 1a in methanol (Fig. S1).



Oxidation process analysis: a three-necked flask was charged with MeOH (10 mL), **1a** (0.94 g, 5.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (12.5 mg, 0.05 mmol) and solid NaOH (0.8 g, 20 mmol). The mixture was heated to reflux (about 75 °C), and molecular oxygen was charged to the reaction solution. About 0.2 mL of sample, withdrawn from the reaction mixture at the specified time (12, 24, 36, 48 and 60 h), was acidified by hydrochloric acid (2.0 M) and was extracted with MTBE. The extracted sample was analyzed by GC-MS to evaluate the product distributions. It should be noted that the sample should be immediately analyzed after extraction.

Besides, an incomplete oxidation reaction (performed for 16 h) was worked up and purified *via* column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to provide the intermediates **3a'** and **4a** for structure confirmation.

Furthermore, a preparation reaction (performed for 60 h) was worked up and purified *via* column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to provide the desired product **2a**.

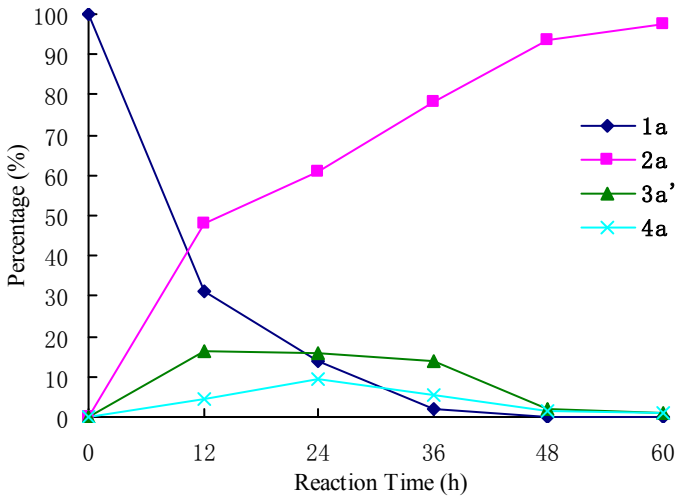
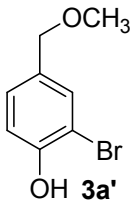
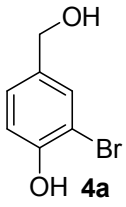


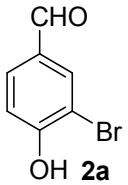
Fig. S1 Time-dependence curves for the oxidation of **1a** into **2a** in methanol (percentages as their respective ratios by area normalization method in the total ionization chromatography).



3a' **2-Bromo-4-(methoxymethyl)phenol (3a')**: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.39 (br s, 1H), 7.10 (br d, J = 8.0 Hz, 1H), 6.89 (br d, J = 8.0 Hz, 1H), 5.66 (br s, 1H), 4.29 (s, 2H), 3.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 150.8, 130.7, 130.6, 127.8, 114.9, 109.1, 72.5, 56.9; HRMS (EI): *m/z* [M^+] calcd. for $C_8H_9O_2Br$ 215.9786, found 215.9792.

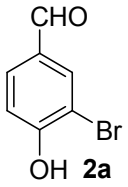


4a **2-Bromo-4-(hydroxymethyl)phenol (4a)**: the spectral data see 2.3.2 section.

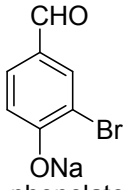


2a **3-Bromo-4-hydroxybenzaldehyde (2a)**: pale yellow solid, 0.71 g (71% yield); the spectral data see 2.1 section.

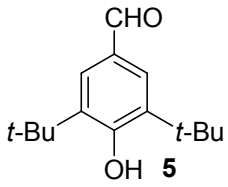
2.4 ^{1}H NMR spectra of compounds 2a and 5, in CD_3ONa/CD_3OD and CD_3OD, respectively.



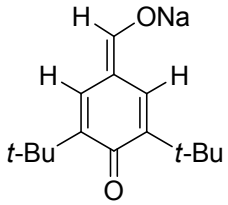
2a **3-Bromo-4-hydroxybenzaldehyde (2a)**: ^{1}H NMR (400 MHz, CD_3OD, ppm): δ 9.75 (br s, 1H), 8.03 (br d, J = 2.0 Hz, 1H), 7.74 (dd, J = 8.0, 2.0 Hz, 1H), 7.02 (br d, J = 8.0 Hz, 1H).



phenolate of **2a** **Sodium 2-bromo-4-formylphenolate**: ^{1}H NMR (400 MHz, CD_3OD, **2a** (6 mg) and CD_3ONa (7 mg) dissolved in 0.5 mL CD_3OD, ppm): δ 9.39 (br s, 1H), 7.89 (br d, J = 2.0 Hz, 1H), 7.51 (dd, J = 8.4, 2.0 Hz, 1H), 6.63 (br d, J = 8.4 Hz, 1H).

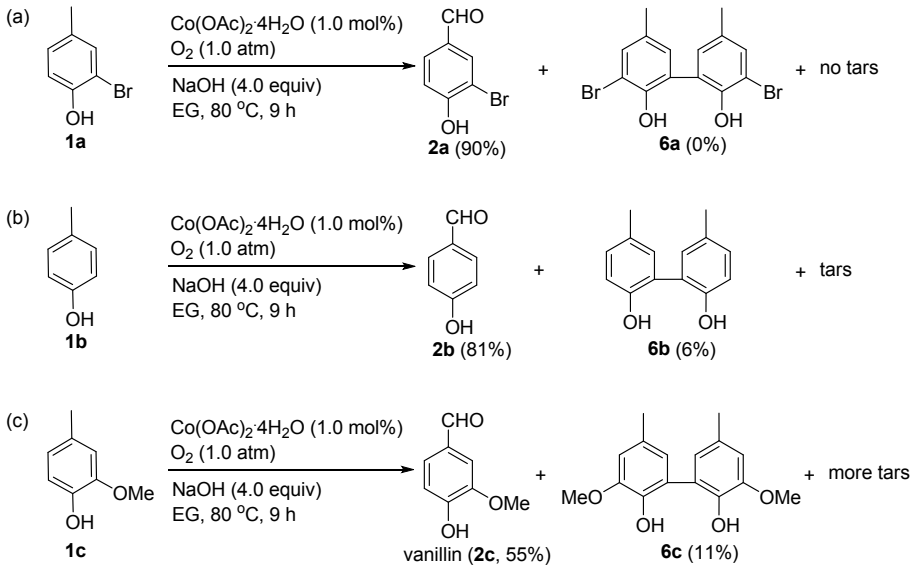


5 **3,5-Di-tert-butyl-4-hydroxybenzaldehyde (5)**: ^{1}H NMR (400 MHz, CD_3OD, ppm): δ 9.77 (br s, 1H), 7.75 (br s, 2H), 1.46 (s, 18H).



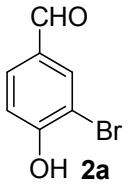
enolate of **5** **Sodium (3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methanolate**: ^{1}H NMR (400 MHz, CD_3OD, **5** (7 mg) and CD_3ONa (7 mg) dissolved in 0.5 mL CD_3OD, ppm): δ 9.02 (br s, 1H), 7.67 (br s, 1H), 7.25 (br s, 1H), 1.38 (s, 18H).

2.5 $Co(OAc)_2{\cdot}4H_2O$-catalyzed oxidation of 2-bromo-4-cresol (1a), 4-cresol (1b) and 2-methoxy-4-cresol (1c, Scheme 5 in the text).

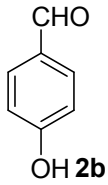


Scheme 5. Oxidations of **1a**, **1b** and **1c** under the standard conditions. Reaction performed with **1** (5.0 mmol), $Co(OAc)_2 \cdot 4H_2O$ (0.05 mmol), NaOH (20 mmol), EG (10 mL) and O_2 (1.0 atm) at 80 °C for 9 h.

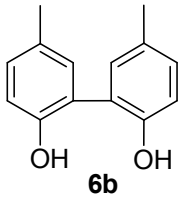
General procedure: a three-necked flask was charged with EG (10 mL), **1a**, **1b** or **1c** (5.0 mmol), $Co(OAc)_2 \cdot 4H_2O$ (12.5 mg, 0.05 mmol) and solid NaOH (0.80 g, 20 mmol), and then the solution was heated to 80 °C. The molecular oxygen was continuously supplied to the reaction through a top tube inlet for 9 h. Hydrochloric acid (10 mL, 10%) and methyl *tert*-butyl ether (MTBE, 15 mL) were successively added to the reaction mixture at room temperature. The MTBE phase was separated, and the aqueous phase was further extracted with MTBE (15 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo to give a residue, which was purified *via* column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to provide **2** and dimer **6**, respectively.



2a **3-Bromo-4-hydroxybenzaldehyde (2a)**: pale yellow solid, 0.90 g (90%); the spectral data see 2.1 section.

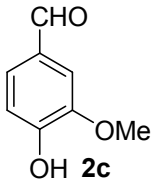


2b **4-Hydroxybenzaldehyde (2b)**:[5] yellow solid, 0.49 g (81% yield), m.p. 116–118 °C ((lit[5] m.p. 115–118 °C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.87 (br s, 1H), 7.83 (br d, J = 8.8 Hz, 2H), 7.98 (br d, J = 8.8 Hz, 2H), 6.29 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ191.2, 161.5, 132.5 (2C), 129.9, 116.0 (2C); HRMS (EI): *m/z* [M^+] calcd. for $C_7H_6O_2$ 122.0368, found 122.0367.



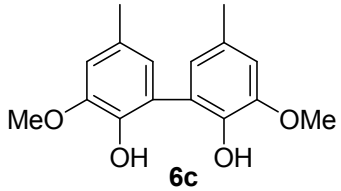
6b

5,5'-Dimethylbiphenyl-2,2'-diol (6b):[6] white solid, 32.1 mg (6% yield), m.p. 148–150 °C (lit[6] m.p. 155 °C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.11 (dd, J = 8.0, 1.6 Hz, 2H), 7.06 (br d, J = 1.6 Hz, 2H), 6.92 (br d, J = 8.0 Hz, 2H), 5.43 (br s, 2H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 150.6 (2C), 131.6 (2C), 130.8 (2C), 130.3 (2C), 123.7 (2C), 116.5 (2C), 20.5 (2C); HRMS (EI): *m/z* [M^+] calcd. for $C_{14}H_{14}O_2$ 214.0994, found 214.0992.



2c

Vanillin (2c):[7] white solid, 0.42 g (55%), m.p. 82–83 °C (lit[7] m.p. 80–81 °C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.82 (br s, 1H), 7.43–7.41 (m, 2H), 7.04 (br d, J = 8.8 Hz, 1H), 6.30 (br s, 1H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 191.1, 151.8, 147.2, 129.8, 127.6, 114.5, 108.9, 56.1; HRMS (ESI): *m/z* [M-H^+] calcd. for $C_8H_7O_3$ 151.0395, found 151.0400.

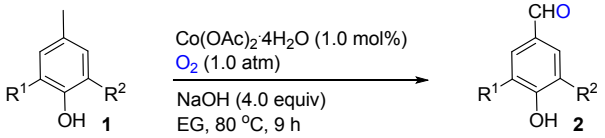


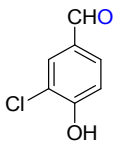
6c

3,3'-Dimethoxy-5,5'-dimethylbiphenyl-2,2'-diol (6c):[8] brown solid, 75.4 mg (11% yield), m.p. 132–134 °C (lit[8] m.p. 133–135 °C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.73 (br s, 2H), 6.72 (br s, 2H), 5.96 (br s, 2H), 3.91 (s, 6H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 147.1 (2C), 140.3 (2C), 129.6 (2C), 124.4 (2C), 123.4 (2C), 111.3 (2C), 56.0 (2C), 21.2 (2C); HRMS (ESI): *m/z* [M+H^+] calcd. for $C_{16}H_{19}O_4$ 275.1283, found 275.1283.

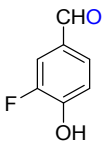
2.6 $Co(OAc)_2{\cdot}4H_2O$-catalyzed oxidation of 1 (Table 2 in the text).

Table 2. $Co(OAc)_2$-catalyzed oxidation of **1**.[a]

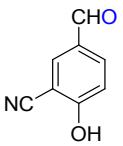




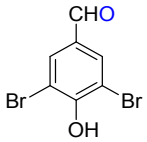
2d, 87%[b]



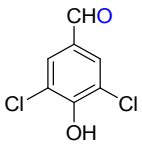
2e, 85%[b]



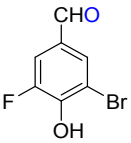
2f, 83%[b]



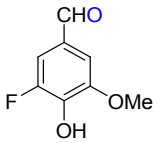
2g, 90%[b,c]



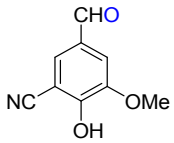
2h, 91%[b,c]



2i, 88%[b,c]



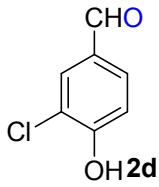
2j, 89%[b,c]



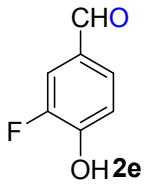
2k, 86%[b,c]

[a]Reaction conditions: substrates **1** (5.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (0.05 mmol), NaOH (20.0 mmol), EG (10 mL) and O_2 (1.0 atm) at 80 °C for 9 h. [b] Isolated yield *via* column chromatography. [c]Performed with NaOH (10.0 mmol).

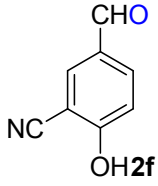
General procedure: a three-necked flask was charged with EG (10 mL), **1** (5.0 mmol), $Co(OAc)_2{\cdot}4H_2O$ (12.5 mg, 0.05 mmol) and solid NaOH (0.80 g, 20 mmol for **1d**, **1e**, **1f**; 0.40 g, 10 mmol for **2g**, **2h**, **2i**, **2j**, **2k**), and then the solution was heated to 80 °C. The molecular oxygen was continuously supplied to the reaction through a top tube inlet for 9 h. Hydrochloric acid (10 mL, 10%) and methyl *tert*-butyl ether (MTBE, 15 mL) were successively added to the reaction mixture at room temperature. The MTBE phase was separated, and the aqueous phase was further extracted with MTBE (15 mL × 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a residue, which was purified *via* column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to provide the desired products **2**.



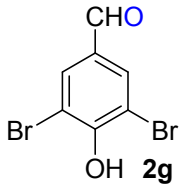
2d **3-Chloro-4-hydroxybenzaldehyde (2d)**: yellow oil, 0.68 g (87%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.85 (br s, 1H), 7.54 (br d, J = 2.4 Hz, 1H), 7.47 (dd, J = 8.8, 2.4 Hz, 1H), 6.96 (br d, J = 8.8 Hz, 1H), 5.98 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 195.6, 160.3, 137.1, 132.7, 124.8, 121.3, 119.6; HRMS (EI): *m/z* [M^+] calcd. for $C_7H_5ClO_2$ 155.9978, found 155.9977.



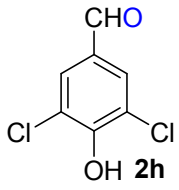
2e **3-Fluoro-4-hydroxybenzaldehyde (2e)**: yellow oil, 0.60 g (85%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.85 (br s, 1H), 7.67-7.61 (m, 2H), 7.15 (br d, J = 8.0 Hz, 1H), 5.98 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 190.2 (d, J = 2.2 Hz), 151.2 (d, J = 239.8 Hz), 149.6 (d, J = 14.7 Hz), 130.2 (d, J = 4.8 Hz), 128.6 (d, J = 2.8 Hz), 117.6 (d, J = 1.9 Hz), 115.8 (d, J = 18.3 Hz); HRMS (EI): *m/z* [M^+] calcd. for $C_7H_5FO_2$ 140.0274, found 140.0270.



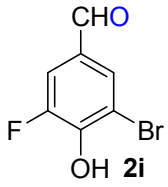
2f **5-Formyl-2-hydroxybenzonitrile (2f)**: yellow oil, 0.61 g (83%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 12.35 (br s, 1H), 9.83 (br s, 1H), 8.24 (br d, J = 2.4 Hz, 1H), 8.02 (dd, J = 8.8, 2.0 Hz, 1H), 7.18 (br d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 190.5, 165.4, 137.4, 135.3, 128.9, 117.3, 116.4, 100.1; HRMS (ESI): *m/z* [M–H $^+$] calcd. for $C_8H_4NO_2$ 146.0242, found 146.0258.



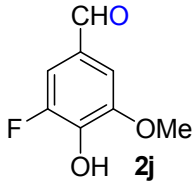
2g **3,5-Dibromo-4-hydroxybenzaldehyde** (**2g**): white solid, 1.26 g (90%); the spectra see 2.1 section.



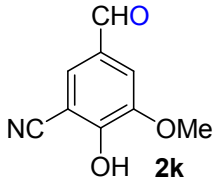
2h **3,5-Dichloro-4-hydroxybenzaldehyde (2h)**:[9] white solid, 0.87 g (91% yield), m.p. 158–160 °C (lit[9] m.p. 157 °C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.81 (br s, 1H), 7.83 (br s, 2H), 6.43 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 188.6, 153.1, 130.3 (2C), 129.9 (2C), 122.4; HRMS (ESI): *m/z* [M–H$^+$] calcd. for $C_7H_3Cl_2O_2$ 188.9510, found 188.9511.



2i **3-Bromo-5-fluoro-4-hydroxybenzaldehyde (2i)**: white solid, 0.96 g (88% yield), m.p. 138–140 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.74 (d, J = 2.0 Hz, 1H), 7.78 (t, J = 1.6 Hz, 1H), 7.54 (dd, J = 9.6, 1.6 Hz, 1H), 6.33 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 188.8, 151.2 (d, J = 247.3 Hz), 147.3 (d, J = 15.0 Hz), 130.7 (d, J = 2.7 Hz), 130.1 (d, J = 5.4 Hz), 115.7 (d, J = 18.8 Hz), 111.6 (d, J = 1.4 Hz); HRMS (ESI): *m/z* [M–H$^+$] calcd. for $C_7H_3BrFO_2$ 216.9300, found 216.9296.

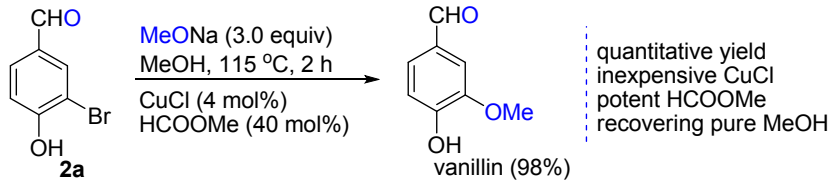


2j **3-Fluoro-4-hydroxy-5-methoxybenzaldehyde (2j)**: white solid, 0.76 g (89% yield), m.p. 116–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.81 (br s, 1H), 7.32–7.26 (m, 2H), 5.98 (br s, 1H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 190.2 (d, J = 2.3 Hz), 150.6 (d, J = 243.8 Hz), 148.8 (d, J = 5.3 Hz), 140.1 (d, J = 13.5 Hz), 128.2 (d, J = 6.3 Hz), 113.1 (d, J = 18.5 Hz), 106.1 (d, J = 1.7 Hz), 56.8; HRMS (ESI): *m/z* [M–H$^+$] calcd. for $C_8H_6FO_3$ 169.0301, found 169.0305.

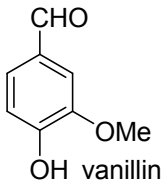


2k **5-Formyl-2-hydroxy-3-methoxybenzonitrile (2k)**: white solid, 0.76 g (86% yield), m.p. 196–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.83 (br s, 1H), 7.66 (br s, 1H), 7.58 (br s, 1H), 6.90 (br s, 1H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 190.2, 155.6, 148.5, 129.2, 128.7, 115.8, 113.1, 99.3, 56.4; HRMS (ESI): *m/z* [M–H$^+$] calcd. for $C_9H_6NO_3$ 176.0348, found 176.0361.

2.7 Methoxylation of 2a for preparing vanillin (Scheme 7 in the text).



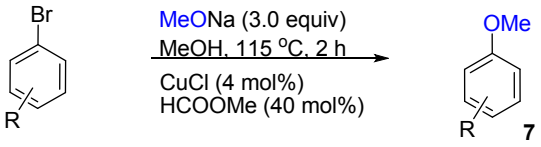
General procedure: the Teflon-lined autoclave (25 mL) was charged with **2a** (0.80 g, 4.0 mmol), MeOH (5 mL), MeONa (0.65 g, 12 mmol), CuCl (15.8 mg, 0.16 mmol) and HCOOMe (0.10 mL, d = 0.97 g/mL, 1.6 mmol). The autoclave was heated to 115 °C and stirred for 2 h. After the completion of reaction, the reactor was cooled to room temperature. The reaction mixture was stirred for 0.5 h in open system, and then concentrated to recover pure MeOH. To the residue was added MTBE (5 mL) and diluted hydrochloric acid (1.0 M, 8 mL) to adjust pH to 2.0–3.0. Furthermore, the solution was partitioned into two layers, and the aqueous phase was extracted with MTBE (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a solid, which was purified *via* column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 15:1) to provide the desired vanillin. Besides, the purity of the recovered MeOH was more than 99% measured by GC, and water content of the recovered MeOH was less than 0.12% measured by Karl Fischer method.

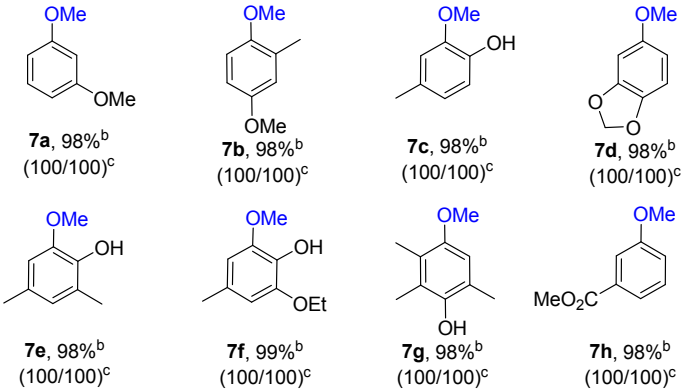


Vanillin: white solid, 596.4 mg (98% yield); the spectral data see 2.5 section.

2.8 CuCl/HCOOMe-catalyzed methoxylation (Table 3 in the text).

Table 3. CuCl/HCOOMe-catalyzed methoxylation.[a]

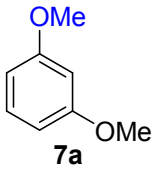




[a] Reaction conditions: aryl bromides (4.0 mmol), MeOH (5 mL), MeONa (0.65 g, 12 mmol), CuCl (15.8 mg, 0.16 mmol) and HCOOMe (0.10 mL, d = 0.97 g/mL, 1.6 mmol). [b] Isolated yield *via*

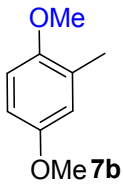
column chromatography. [c] Conv. (%)/Sele. (%) determined by GC-MS by area normalization method in the total ionization chromatography.

General procedure: the Teflon-lined (25 mL) was charged with the aryl bromides (4.0 mmol), MeOH (5 mL), freshly prepared MeONa (0.65 g, 12 mmol), CuCl (15.8 mg, 0.16 mmol) and HCOOMe (0.10 mL, d = 0.97 g/mL, 1.6 mmol). The autoclave was heated to 110 °C and stirred for 2 h. After the completion of reaction, the reactor was cooled to room temperature. The reaction mixture was stirred for 0.5 h in open system, and then concentrated to recover pure MeOH. To the residue was added MTBE (5 mL) and diluted hydrochloric acid (1.0 M, 8 mL) to adjust pH to 2.0–3.0. Furthermore, the solution was partitioned into two layers, and the aqueous phase was extracted with MTBE (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated to give a crude product, which was purified *via* column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 15:1) to provide the desired vanillin. Generally, the purity of the recovered MeOH was more than 99% measured by GC, and water content of the recovered MeOH was less than 0.12% measured by Karl Fischer method. In particular, the sample of the crude product was used to determine conversion and selectivity by GC-MS by area normalization method in the total ionization chromatography.



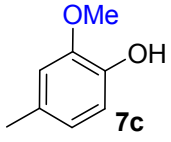
7a

1,3-Dimethoxybenzene (7a): colorless oil, 541.6 mg (98% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.19 (t, J = 8.0 Hz, 1H),6.52 (dd, J = 8.0, 2.0 Hz, 2H), 6.48 (t, J = 2.0 Hz, 1H), 3.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 160.9, 129.9, 106.2 (2C), 100.5 (2C), 55.2 (2C); HRMS (EI): m/z [M^+] calcd. for $C_8H_{10}O_2$ 138.0681, found 138.0680.



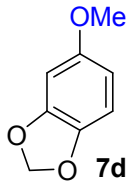
7b

1,4-Dimethoxy-2-methylbenzene (7b): colorless oil, 596.6 mg (98% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.76 (br d, J = 8.8 Hz, 2H), 6.69 (dd, J = 8.8, 3.2 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.5, 152.2, 127.8, 117.1, 110.9, 110.8, 55.8, 55.6, 16.4; HRMS (ESI): m/z [M+H^+] calcd. for $C_9H_{13}O_2$ 153.0916, found 153.0924.

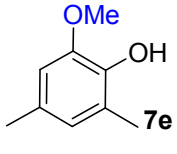


7c

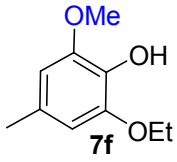
4-Methyl-2-methoxyphenol (7c): colorless oil, 541.6 mg (98% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.82 (br d, J = 8.0 Hz, 1H), 6.69 (br s, 1H), 6.68 (br d, J = 8.0 Hz, 1H), 5.50 (br s, 1H), 3.87 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.3, 143.4, 129.7, 121.6, 111.8, 55.9, 21.1; HRMS (EI): m/z [M^+] calcd. for $C_8H_{10}O_2$ 138.0681, found 138.0682.



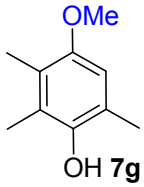
5-Methoxybenzo[d]1,3-dioxole (7d): pale yellow oil, 596.4 mg (98% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.71 (br d, J = 8.4 Hz, 1H), 6.49 (br s, 1H), 6.32 (br d, J = 8.4 Hz, 1H), 5.91 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.2, 148.3, 141.6, 107.9, 104.7, 101.1, 97.5, 56.0; HRMS (ESI): *m/z* [M+H$^+$] calcd. for $C_8H_9O_3$ 153.0552, found 153.0531.



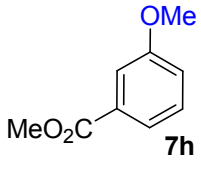
2-Methoxy-4,6-dimethylphenol (7e):[10] pale yellow solid, 596.6 mg (98% yield), m.p. 28–30 °C (lit[10] m.p. 34–35 °C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.57 (br s, 1H), 6.55 (br s, 1H), 5.53 (br s, 1H), 3.86 (s, 3H), 2.27 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.1, 141.5, 128.6 (2C), 123.6, 109.2, 56.0, 21.1, 15.4; HRMS (ESI): *m/z* [M+H$^+$] calcd. for $C_9H_{13}O_2$ 153.0916, found 153.0893.



2-Ethoxy-6-methoxy-4-methylphenol (7f): pale yellow oil, 721.6 mg (99% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.38 (br s, 2H), 5.36 (br s, 1H), 4.09 (q, J = 6.8 Hz, 2H), 3.87 (s, 3H), 2.28 (s, 3H), 1.43 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.9, 146.1, 132.7, 128.7, 106.7, 105.7, 64.7, 56.2, 21.6, 15.0; HRMS (ESI): *m/z* [M+H$^+$] calcd. for $C_{10}H_{15}O_3$ 183.1021, found 183.1023.



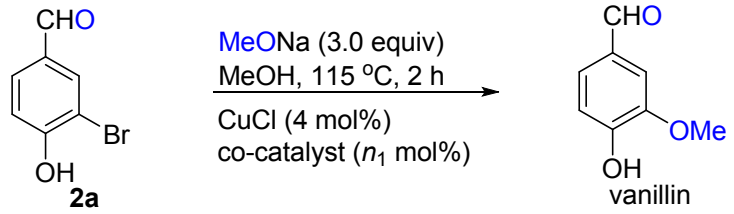
4-Methoxy-2,3,6-trimethylphenol (7g):[11] white solid, 651.6 mg (98% yield), m.p. 104–106 °C (lit[11] m.p. 101–102 °C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.52 (s, 1H), 4.26 (br s, 1H), 3.76 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 151.3, 145.9, 123.9, 123.6, 120.0, 110.9, 56.3, 16.3, 12.2, 11.9; HRMS (ESI): *m/z* [M+H$^+$] calcd. for $C_{10}H_{15}O_2$ 167.1072, found 167.1071.



Methyl 3-methoxybenzoate (7h): colorless oil, 651.4 mg (98% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.64 (dt, J = 8.0, 1.2 Hz, 1H), 7.56 (dd, J = 2.8, 1.6 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.10 (ddd, J = 8.0, 2.8 Hz, 2.4 Hz, 1H), 3.92 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.0, 159.5, 131.4, 129.4, 122.0, 119.5, 113.9, 55.4, 52.2; HRMS (ESI): *m/z* [M+H$^+$] calcd. for $C_9H_{11}O_3$ 167.0708, found 167.0719.

2.9 CuCl-catalyzed methoxylation of 2a with different co-catalysts (Table 4 in the text).

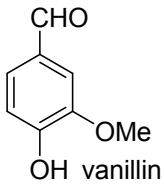
Table 4. CuCl-catalyzed methoxylation of **2a** with different co-catalysts.[a]



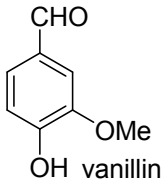
Entry	Co-catalyst	n_1 mol%	Conv./Sele. (%)[b]	Yield (%)[c]
1	HCOOMe	40	100/100	98
2	MeCOOMe	40	100/95	91
3	DMF	40	100/94	89

[a] Reaction conditions: **2a** (4.0 mmol), MeOH (5 mL), MeONa (0.65 g, 12 mmol), CuCl (15.8 mg, 0.16 mmol) and co-catalyst (n_1 mol%). [b] Determined by GC-MS. [c] Isolated yield *via* column chromatography.

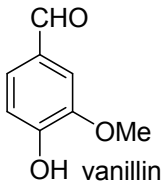
General procedure: the Teflon-lined autoclave (25 mL) was charged with **2a** (0.80 g, 4.0 mmol), MeOH (5 mL), MeONa (0.65 g, 12 mmol), CuCl (15.8 mg, 0.16 mmol) and co-catalyst (n_1 mol%). The autoclave was heated to 115 °C and stirred for 2 h. After the completion of reaction, the reactor was cooled to room temperature. The reaction mixture was stirred for 0.5 h in open system, and then concentrated to recover pure MeOH. To the residue was added MTBE (5 mL) and diluted hydrochloric acid (1.0 M, 8 mL) to adjust pH to 2.0–3.0. Furthermore, the solution was partitioned into two layers, and the aqueous phase was extracted with MTBE (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a crude product, which was purified *via* column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 15:1) to provide the desired vanillin. In particular, the sample of the crude product was used to determine conversion and selectivity with GC-MS by area normalization method in the total ionization chromatography.



Vanillin: white solid, 596.4 mg (98% yield with HCOOMe as co-catalyst); the spectral data see 2.5 section.



Vanillin: white solid, 553.8 mg (91% yield with MeCOOMe as co-catalyst); the spectral data see 2.5 section.



vanillin **Vanillin**: white solid, 541.6 mg (89% yield with DMF as co-catalyst); the spectral data see 2.5 section.

3. References

[1] S. Adimurthy, G. Ramachandraiah, A. V. Bedekar, S. Ghosh, B. C. Ranu and P. K. Ghosh, *Green Chem*., 2006, **8**, 916.

[2] J.-A. Jiang, C. Chen, J.-G. Huang, H.-W. Liu, S. Cao and Y.-F. Ji. *Green Chem*., DOI: 10.1039/C3GC41946K.

[3] L. He, L. Zhang, X. Liu, X. Li, M. Zheng, H. Li, K. Yu, K. Chen, X. Shen, H. Jiang and H. Liu, *J. Med. Chem.*, 2009, **52**, 2465.

[4] L. W. Woo Lawrence, C. Bubert, O. B. Sutcliffe, A. Smith, S. K. Chander, M. F. Mahon, A. Purohit, M. J. Reed and B. V. L. Potter, *J. Med. Chem.*, 2007, **50**, 3540.

[5] J. Magano, M. H. Chen, J. D. Clark and T. Nussbaumer, *J. Org. Chem.*, 2006, **71**, 7103.

[6] I. M. Malkowsky, C. E. Rommel, R. Froehlich, U. Griesbach, H. Puetter and S. R. Waldvogel, *Chem. Eur. J.*, 2006, **12**, 7482.

[7] J. KamLet and E. Conn, *US Pat*., 2640083, 1953.

[8] A. Alexakis, D. Polet, S. Rosset and S. March, *J. Org. Chem.*, 2004, **69**, 5660.

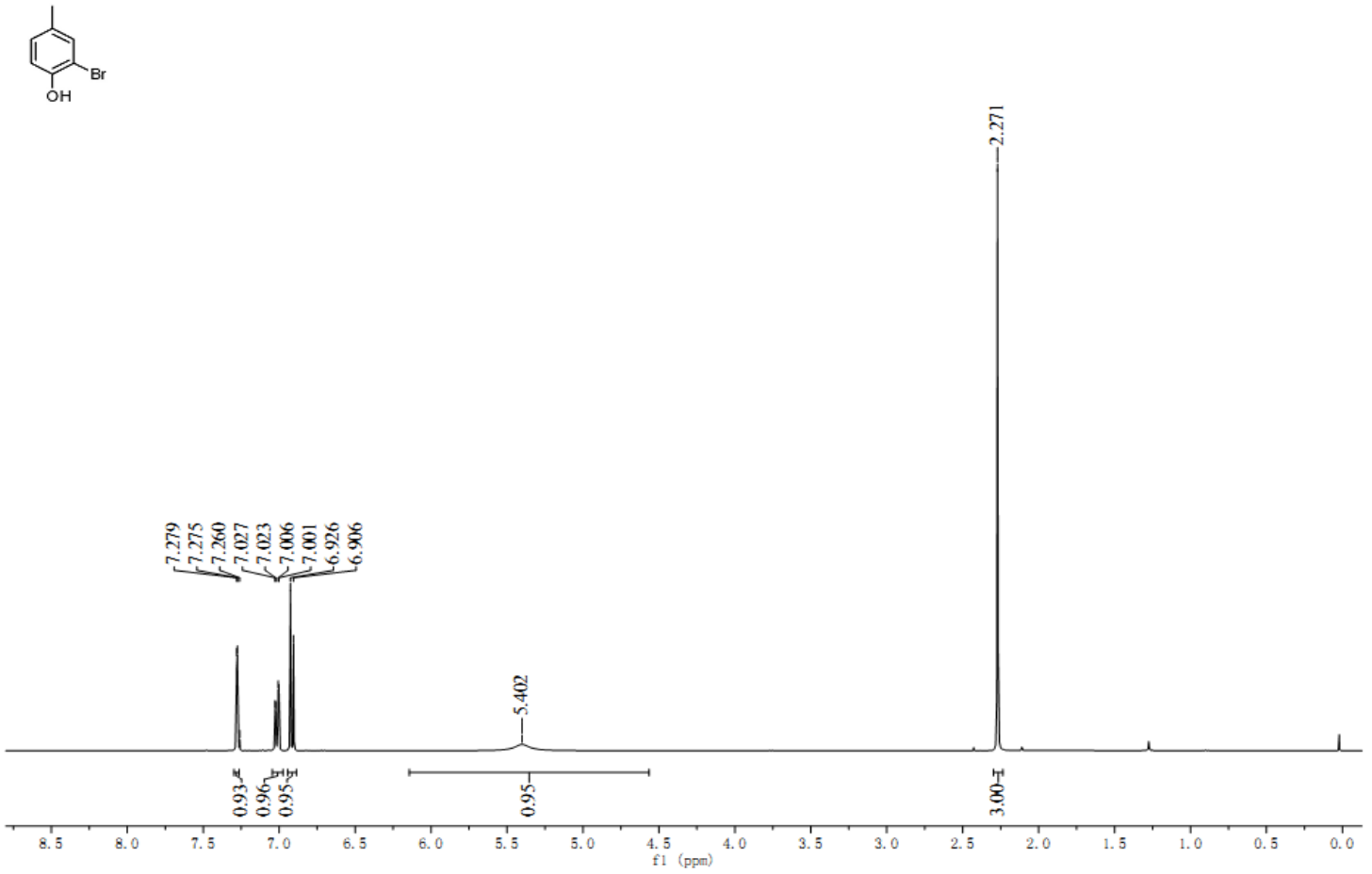
[9] M. Beller, M. Eckert and E. Holla Wolfgang, *J. Org. Chem.*, 1998, **63**, 5658.

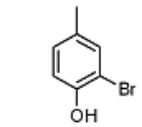
[10] D.-S. Hsu, C.-C. Liao, *Org. Lett*., 2007, **9**, 4563.

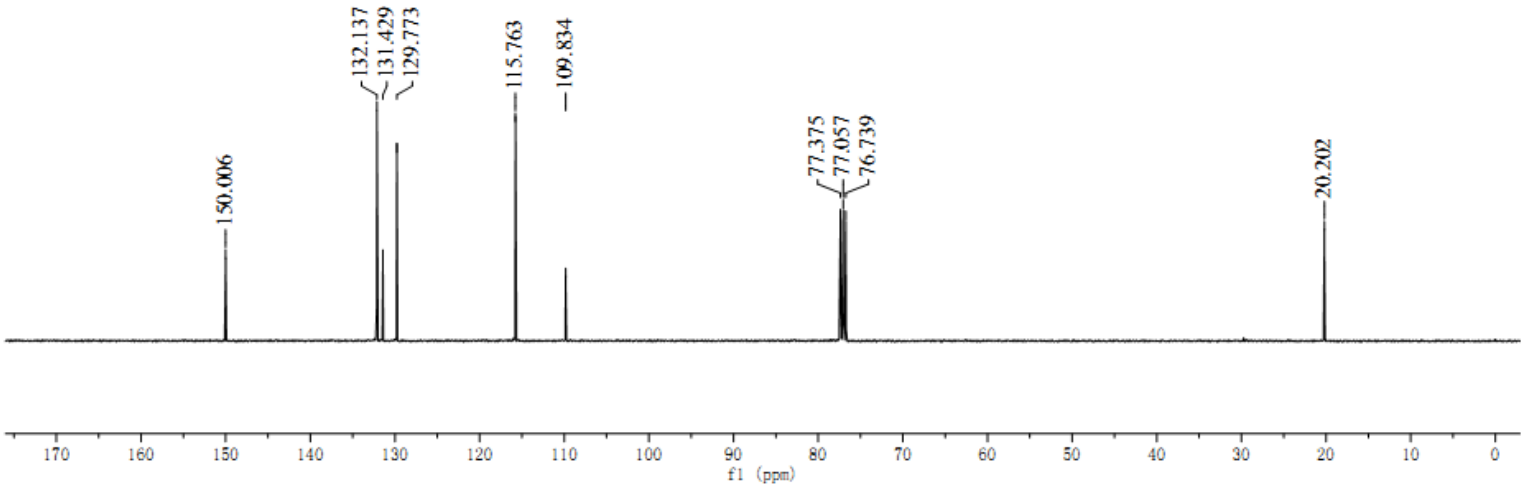
[11] K. A. Kun and H. G. Cassidy, *J. Org. Chem.*, 1962, **27**, 841.

4. Copies of Spectra

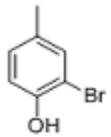
4.1 Copies of spectra for oxybromination of 4-cresol into 1a.




Br
OH


150.006
132.137
131.429
129.773
115.763
109.834
77.375
77.057
76.739
20.202
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

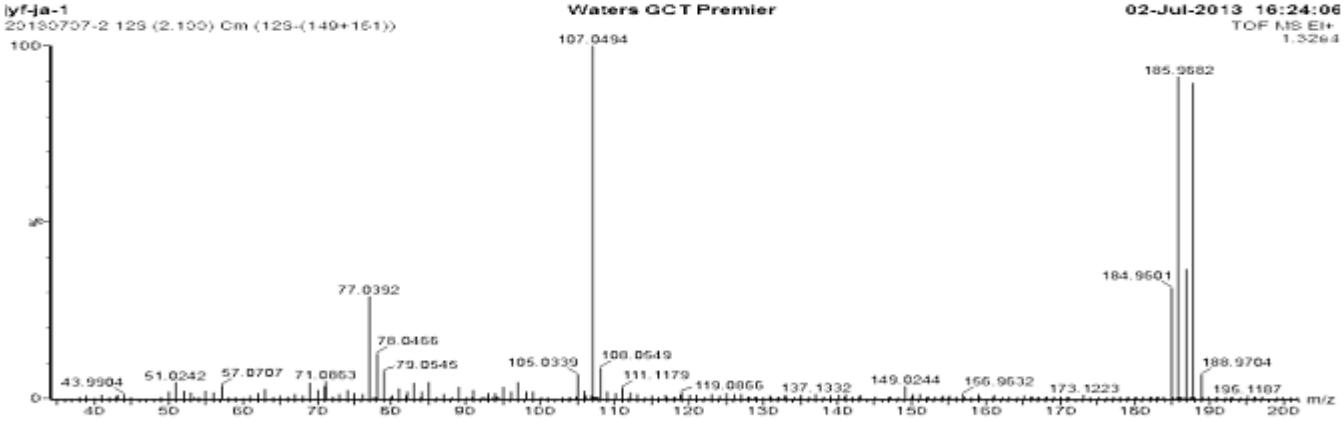
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

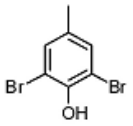
72 formula(e) evaluated with 11 results within limits (up to 50 closest results for each mass)

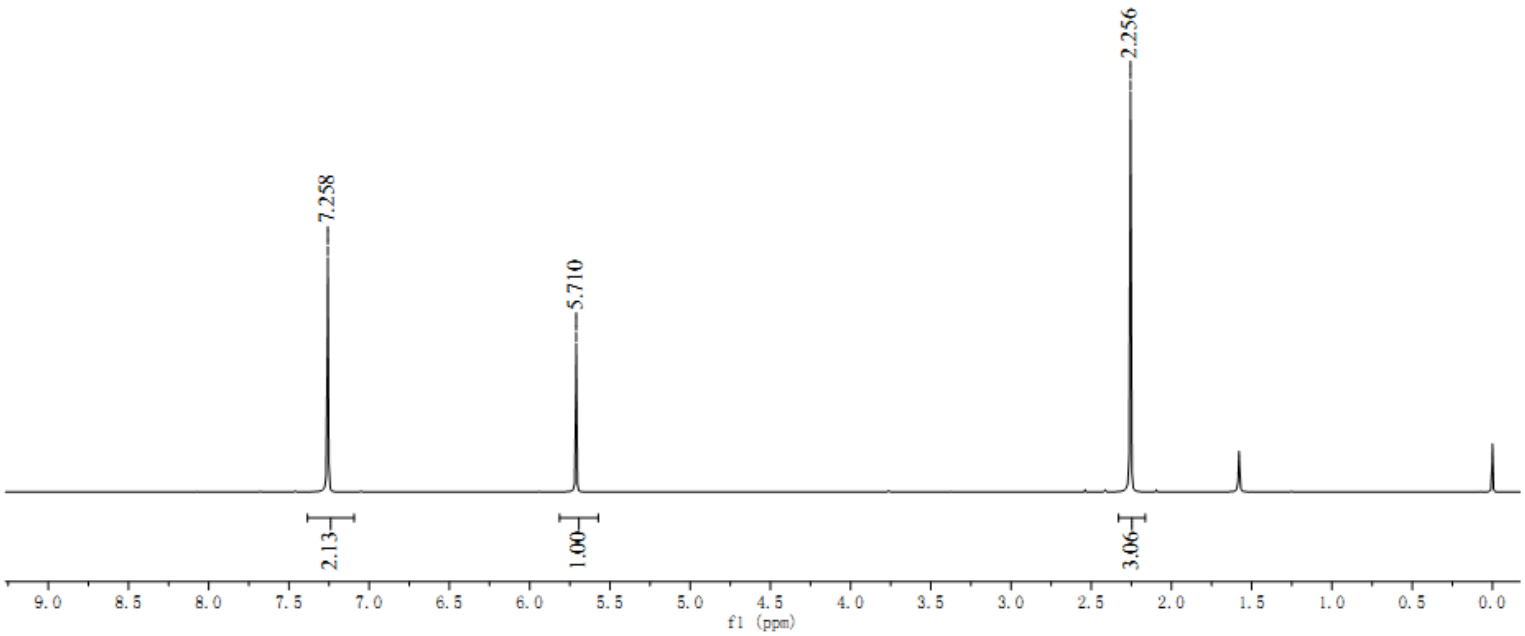
Elements Used:

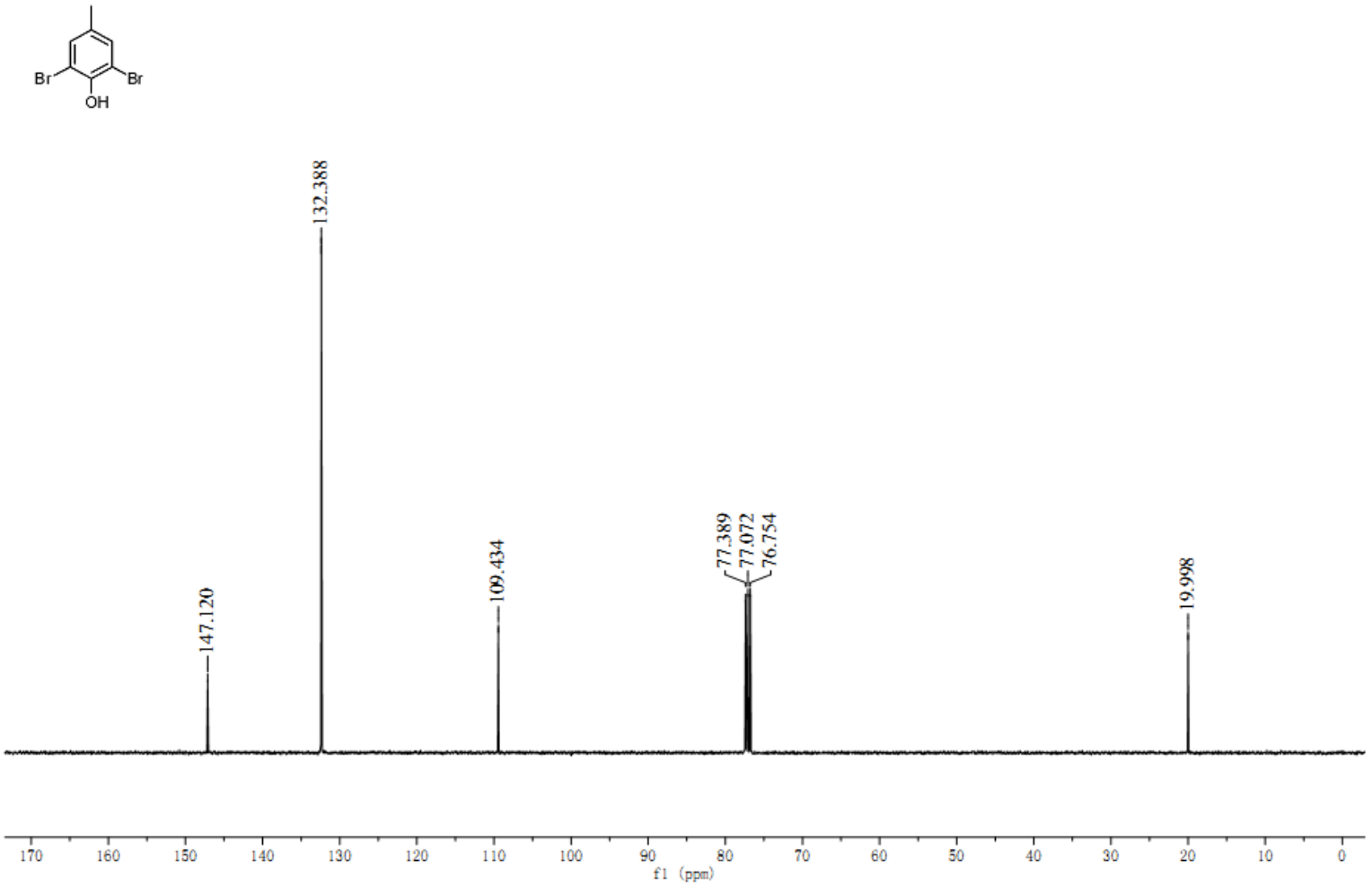
C: 0-7 H: 0-7 O: 0-1 79Br: 0-1 81Br: 0-1



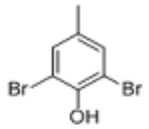
Minimum:	3.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
185.9682	91.31	185.9680	0.2	1.1	4.0	1594.1	C7 H7 O 79Br


Br
Br
OH


7.258
5.710
2.256
2.13
1.00
3.06
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)


Br
Br
OH
147.120
132.388
109.434
77.389
77.072
76.754
19.998
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



Single Mass Analysis

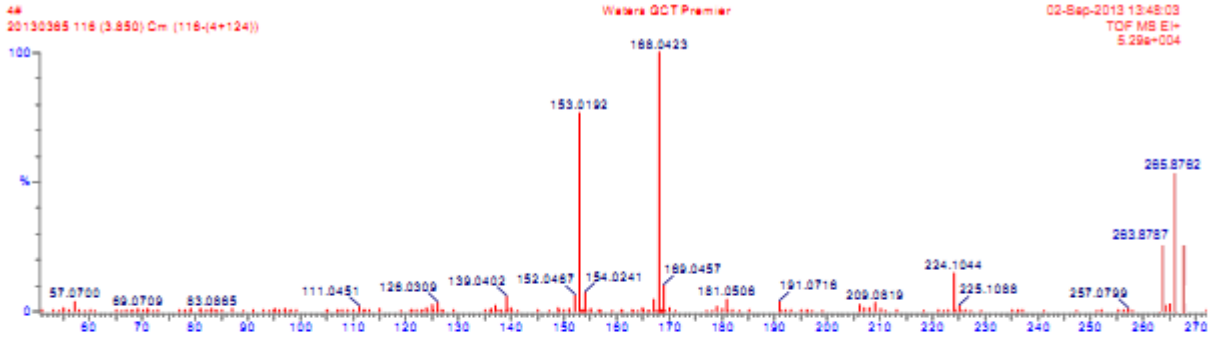
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Monoisotopic Mass, Odd and Even Electron Ions

19 formula(e) evaluated with 5 results within limits (up to 50 closest results for each mass)

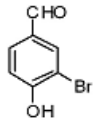
Elements Used:

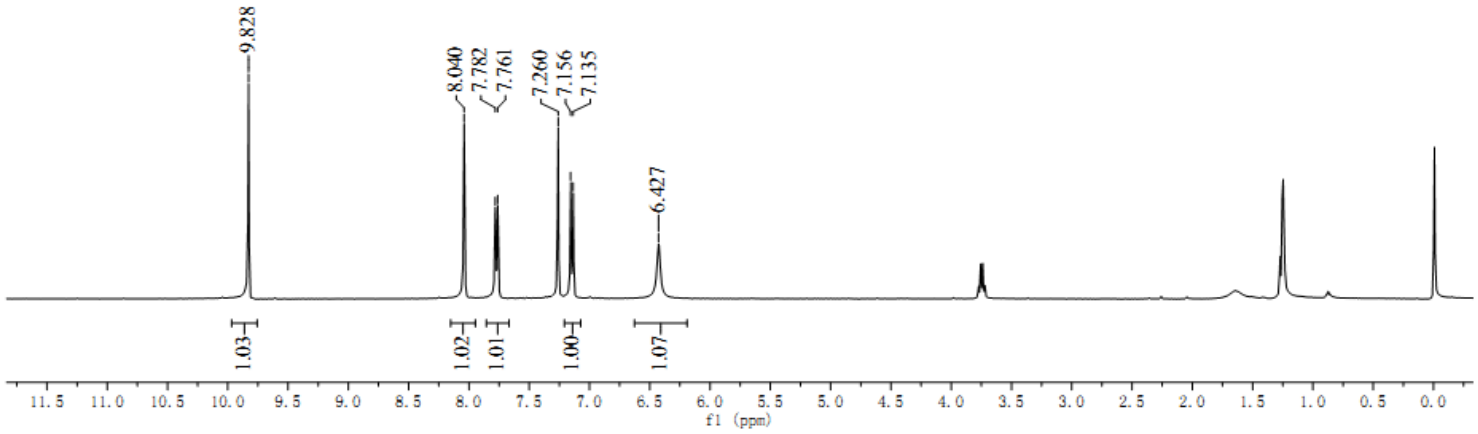
C: 0-7 H: 0-6 Br: 0-2 O: 0-4

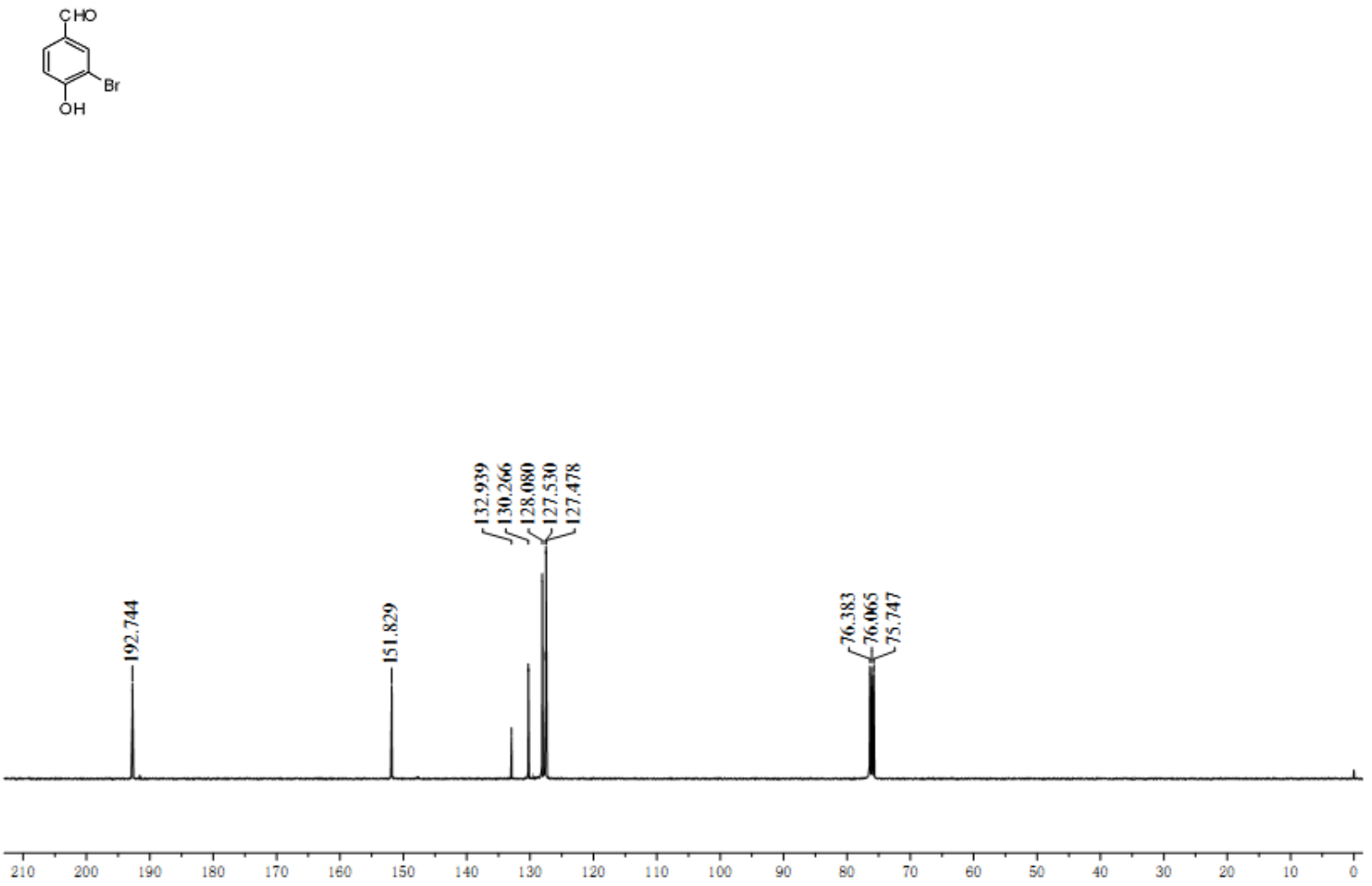


Minimum:					-1.5					
Maximum:		100.00		5.0	10.0	50.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula			
263.8787	25.00	263.8785	0.2	0.4	5.0	1	C7	H6	Br2	O4

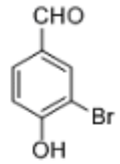
4.2 Copies of spectra for oxybromination of 4-hydroxybenzaldehyde into 2a.






CHO
Br
OH
192.744
151.829
132.939
130.266
128.080
127.530
127.478
76.383
76.065
75.747
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Elemental Composition Report



Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

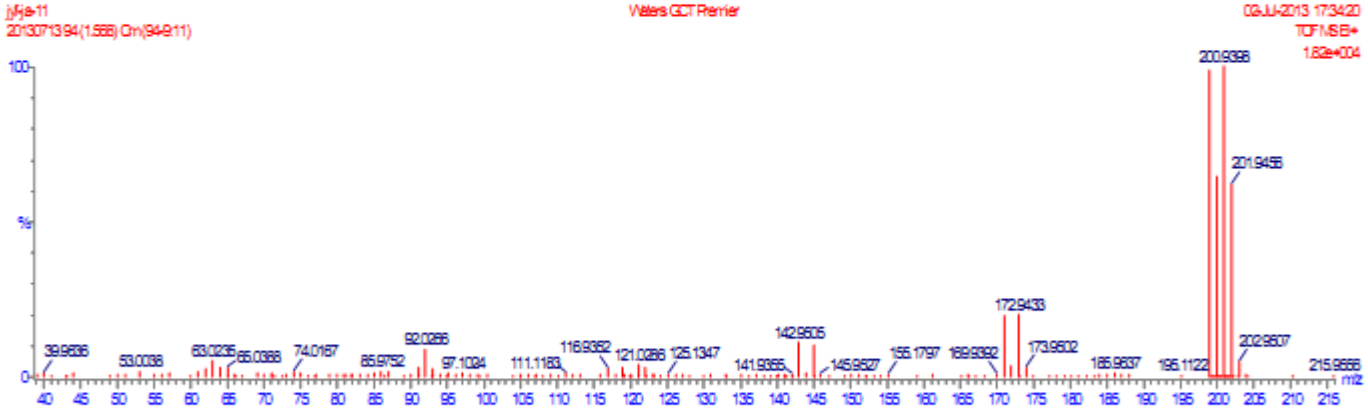
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

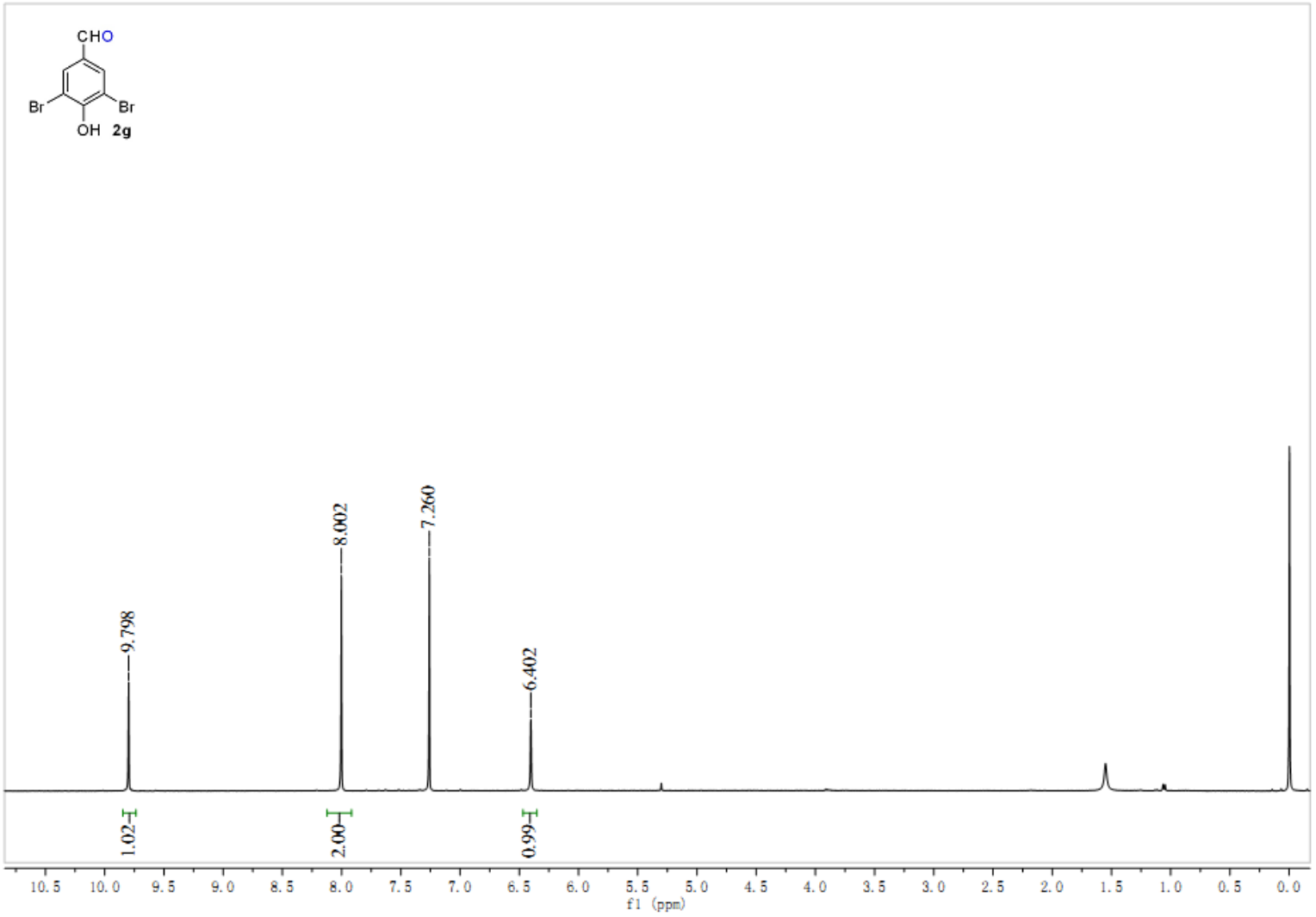
85 formula(e) evaluated with 12 results within limits (up to 50 closest results for each mass)

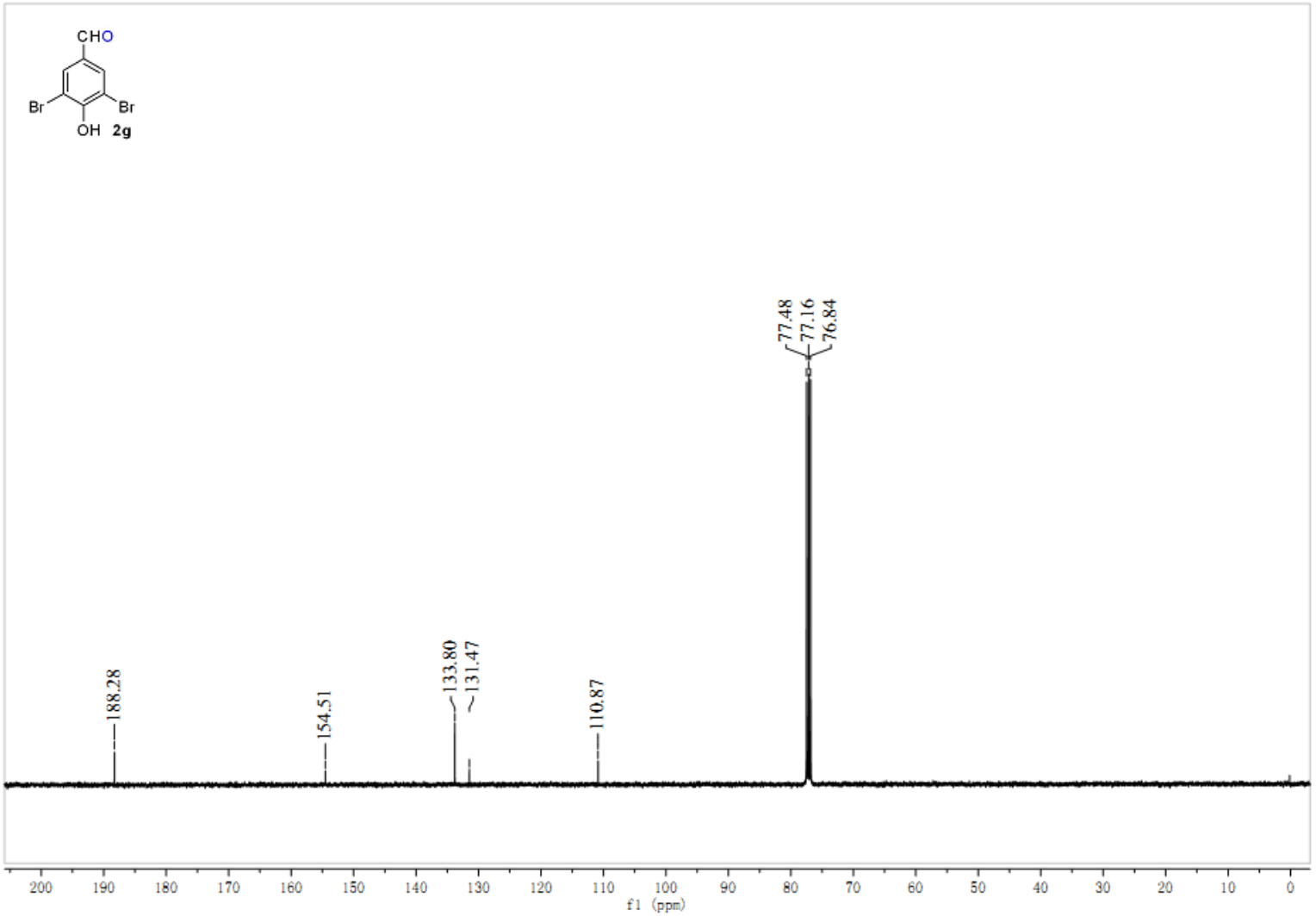
Elements Used:

C: 0-7 H: 0-5 O: 0-2 79Br: 0-1 81Br: 0-1

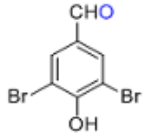


Minimum:	3.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
199.9474	64.49	199.9473	0.1	0.5	5.0	8332.2	C7 H5 O2 79Br


CHO
Br
Br
OH
2g
9.798
8.002
7.260
6.402
1.02
2.00
0.99
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)


CHO
Br
Br
OH
2g
188.28
154.51
133.80
131.47
110.87
77.48
77.16
76.84
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



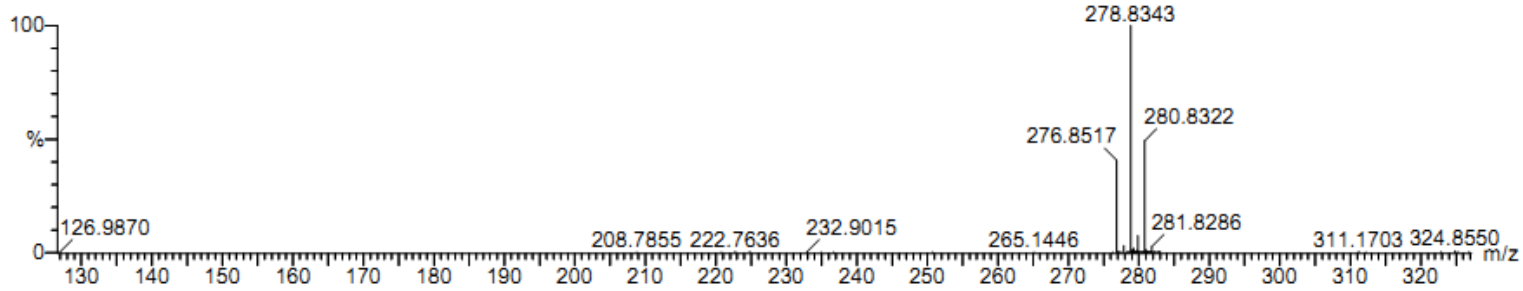
Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
28 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-45 H: 0-70 O: 0-2 Br: 0-2

YF-JI ECUST institute of Fine Chem 16-Dec-2013 21:30:33

JYF-JA-1 14 (0.541) Cm (14) 2: TOF MS ES- 6.84e+003

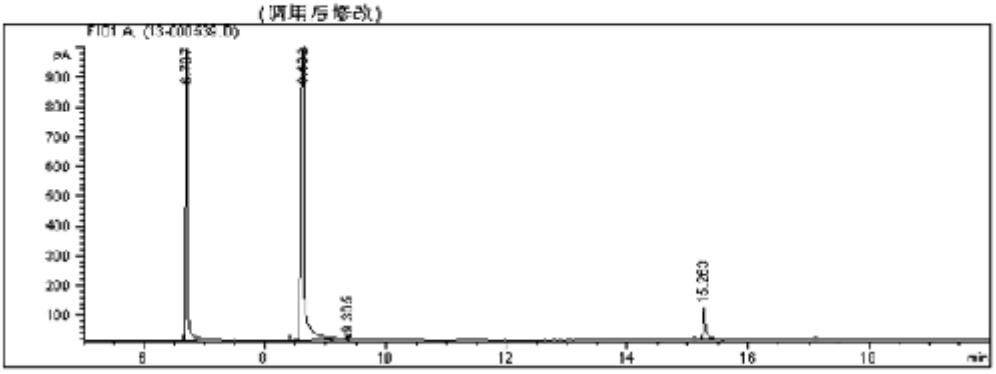


Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
276.8517	276.8500	1.7	6.1	5.5	46.5	0.0	C7 H3 O2 Br2

4.3 Copies of spectra for the oxidation process of 1a in EG.

数据文件: C:\CHEM32\1\DATA\13-000539.D
样品名称: 5#

操作者 :
仪器 : 仪器 1 位置 : 样品瓶 101
进样日期 : 12-Nov-13, 10:54:05 进样次数 : 1
进样量 : 手动
采集方法 : C:\CHEM32\1\METHODS\含溴化合物.M
最后修改 : 2013-11-12 10:50:36
分析方法 : C:\CHEM32\1\METHODS\含溴化合物.M
最后修改 : 2013-11-12 14:16:38
(调用后修改)



面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

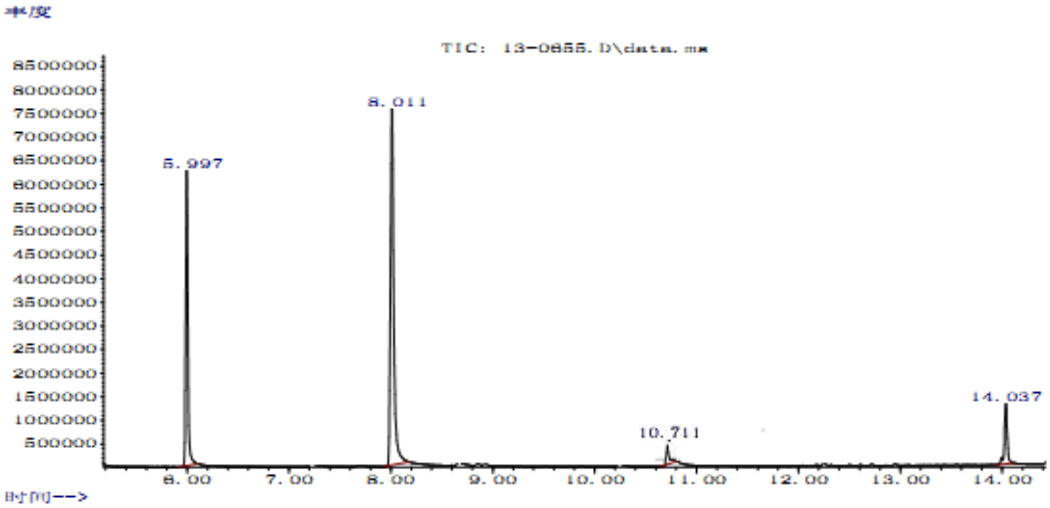
信号 1: FID1 A,

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	6.707	BV	0.0280	3085.84058	1715.18091	58.19582
2	8.632	BV	0.0525	4650.44141	1405.76208	37.56209
3	9.365	VV	0.0262	17.95808	10.39642	0.22228
4	15.263	VB	0.0437	324.76053	106.20811	4.01981

总量 : 8079.00059 3317.54752

*** 报告结束 ***

仪器 1 2013-11-12 14:17:05 页1/1



数据路径 : E:\2013-2\
数据文件 : 13-0655.D
采集 : 25 Oct 2013 14:54
样品 : 药学院

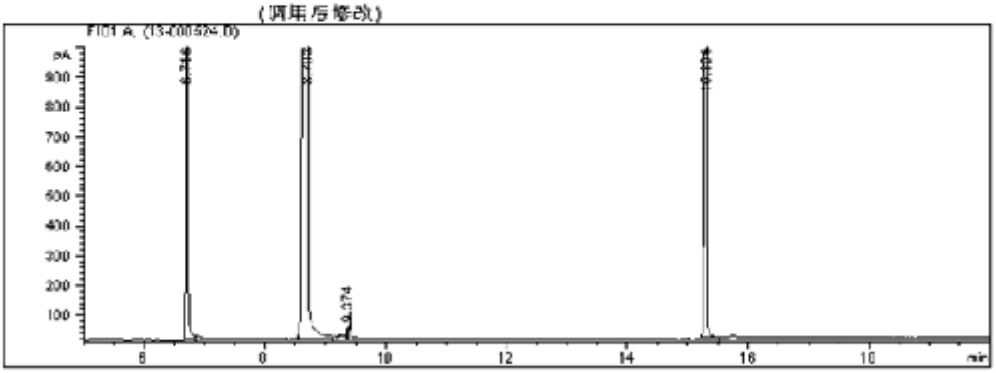
峰 #	R.T. 分钟	起始 扫描	TOP 扫描	截止 扫描	峰类型	峰高	修正面积 总面积	% 比总数
1	5.997	744	758	778	BB	6086961	93257278	32.515%
2	8.011	1134	1149	1181	BB	7613886	170161516	53.855%
3	10.711	1660	1672	1692	BB	1414163	28206104	2.927%
4	14.037	2298	2318	2332	BB	1278196	24336551	10.702%

修正后的面积和： 315961448

数据文件: C:\CHEM32\1\DATA\13-000524.D
样品名称: 1#

操作者 :
仪器 : 仪器 1 位置 : 样品瓶 101
进样日期 : 08-Nov-13, 09:33:15 进样次数 : 1
进样量 : 手动

采集方法 : C:\CHEM32\1\METHODS\含溴化合物.M
最后修改 : 2013-11-8 9:29:48
分析方法 : C:\CHEM32\1\METHODS\含溴化合物.M
最后修改 : 2013-11-12 14:14:43
(调用后修改)



面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: FID1 A,

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	6.716	BV	0.0274	3270.10156	1823.35535	12.87977
2	8.303	BV	0.0606	1.31134e4	2701.00024	67.67934
3	9.374	VV	0.0228	84.44823	42.31525	2.31296
4	15.306	BB	0.0355	4144.91748	1585.42542	17.12792

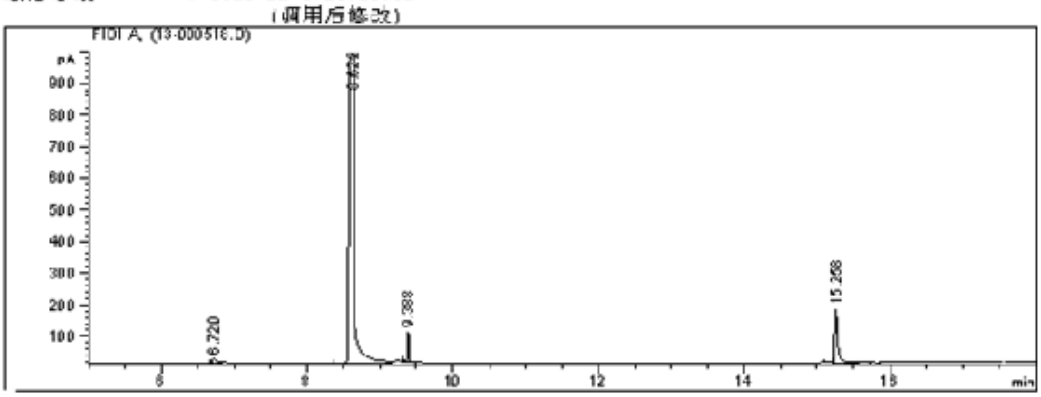
总量 : 2.08929e4 6152.09626

*** 报告结束 ***

数据文件: C:\CHEM32\1\DATA\13-000518.D

操作者 :
仪器 : 仪器 1 位置 : 样品瓶 101
进样日期 : 05-Nov-13, 14:06:02 进样次数 : 1
进样量 : 手动

采集方法 : C:\CHEM32\1\METHODS\含溴化合物.M
最后修改 : 2013-11-5 13:49:22
分析方法 : C:\CHEM32\1\METHODS\甲酯化.M
最后修改 : 2013-11-5 15:23:01
(调用后修改)



面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: FID1 A,

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	6.720	BV	0.0671	72.11262	15.27919	1.13594
2	8.622	BV	0.0507	5662.54443	1585.15845	89.19833
3	9.300	VB	0.0265	160.09092	96.40725	2.52145
4	15.258	VB	0.0394	452.71216	167.94901	7.13128

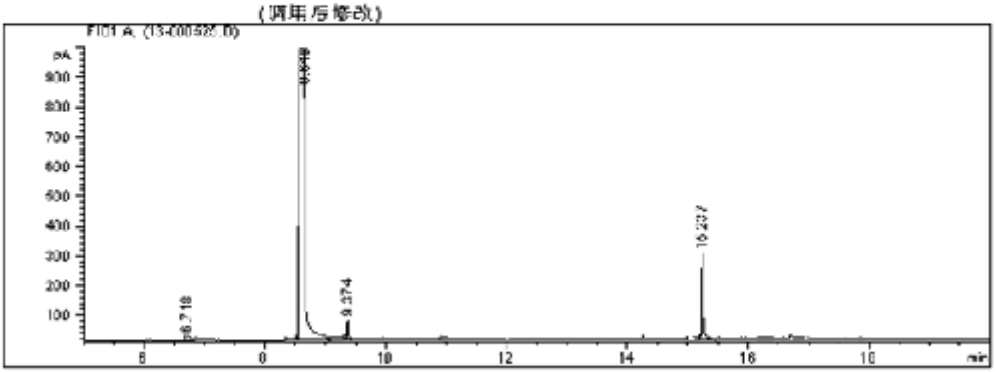
总量 : 6348.25313 1864.87390

*** 报告结束 ***

数据文件: C:\CHEM32\1\DATA\13-000525.D
样品名称: 4#

操作者 :
仪器 : 仪器 1 位置 : 样品瓶 101
进样日期 : 08-Nov-13, 10:13:02 进样次数 : 1
进样量 : 手动

采集方法 : C:\CHEM32\1\METHODS\含溴化合物.M
最后修改 : 2013-11-8 10:08:57
分析方法 : C:\CHEM32\1\METHODS\含溴化合物.M
最后修改 : 2013-11-12 14:13:18
(调用后修改)



面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: FID1 A,

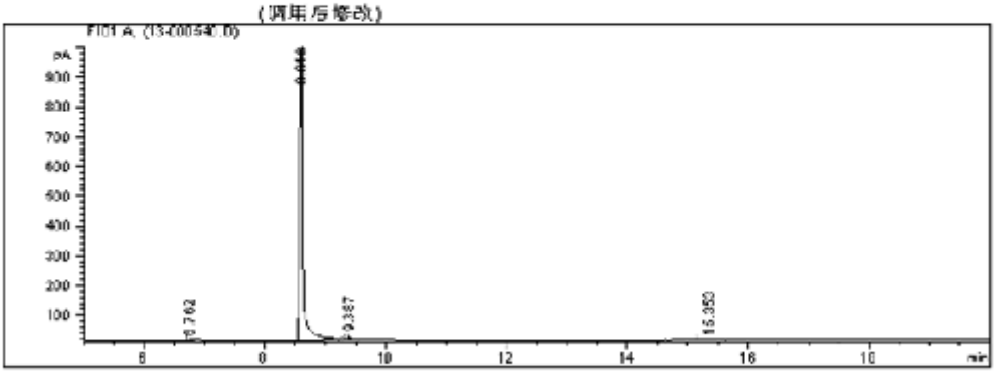
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	6.718	BV	0.0613	60.06580	13.40467	0.55385
2	8.640	BV	0.0573	1.01085e4	2290.81299	93.20000
3	9.374	VB	0.0243	96.72139	65.26938	0.89185
4	15.237	VB	0.0314	579.80878	288.46210	5.34630
总量 :				1.08450e4	2665.94913	

*** 报告结束 ***

数据文件: C:\CHEM32\1\DATA\13-000540.D
样品名称: 6#

操作者 :
仪器 : 仪器 1 位置 : 样品瓶 101
进样日期 : 12-Nov-13, 12:14:03 进样次数 : 1
进样量 : 手动

采集方法 : C:\CHEM32\1\METHODS\含溴化合物.M
最后修改 : 2013-11-12 11:29:51
分析方法 : C:\CHEM32\1\METHODS\含溴化合物.M
最后修改 : 2013-11-12 14:09:05
(调用后修改)



面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

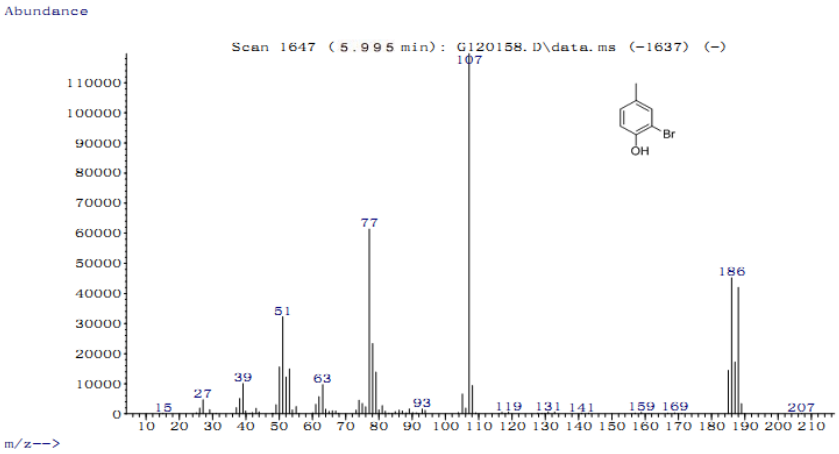
信号 1: FID1 A,

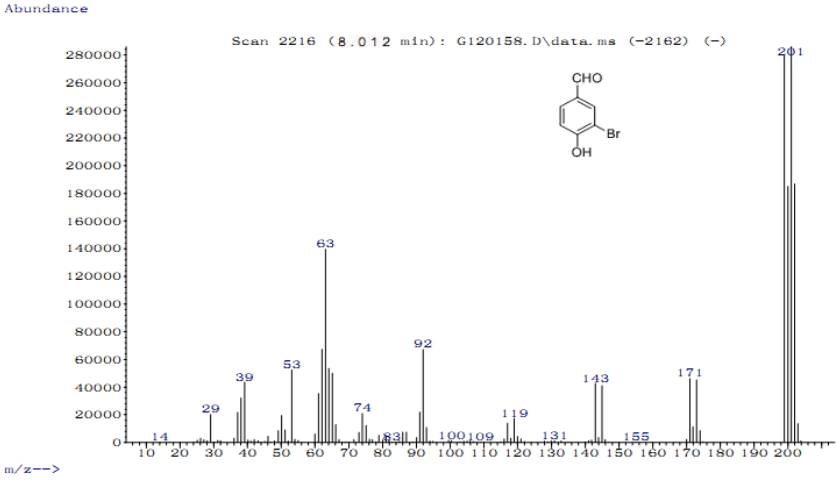
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	6.762	BV	0.0607	19.70951	4.62469	0.41266
2	8.610	BV	0.0459	4702.00604	1411.73096	98.44574
3	9.387	VB	0.0390	34.87370	12.33783	0.73015
4	15.353	BB	0.1298	19.65178	1.88251	0.41145

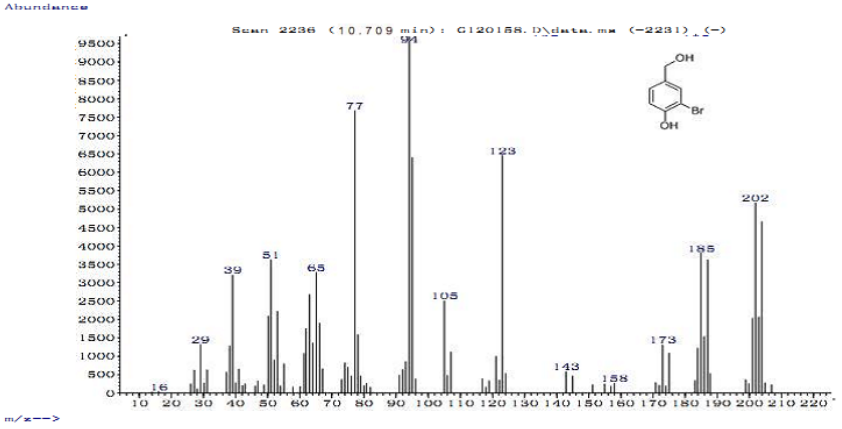
总量 : 4776.24183 1430.57598

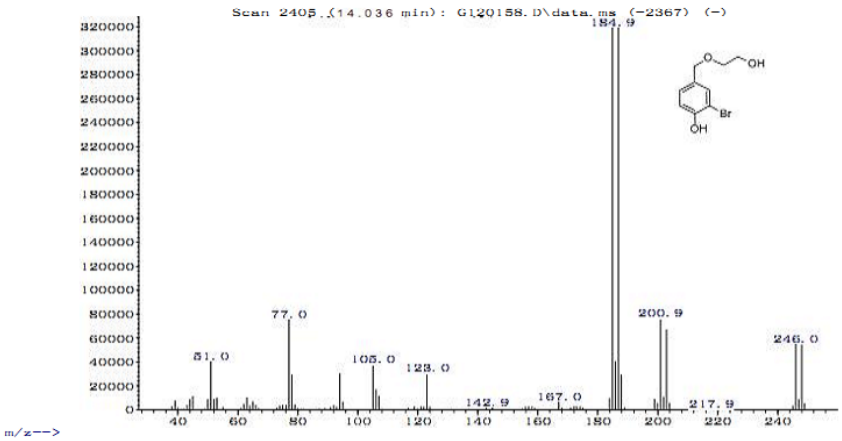
*** 报告结束 ***

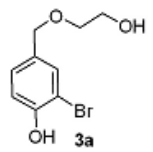
Agilent 5973N Mass Analysis & Research Center ECUST



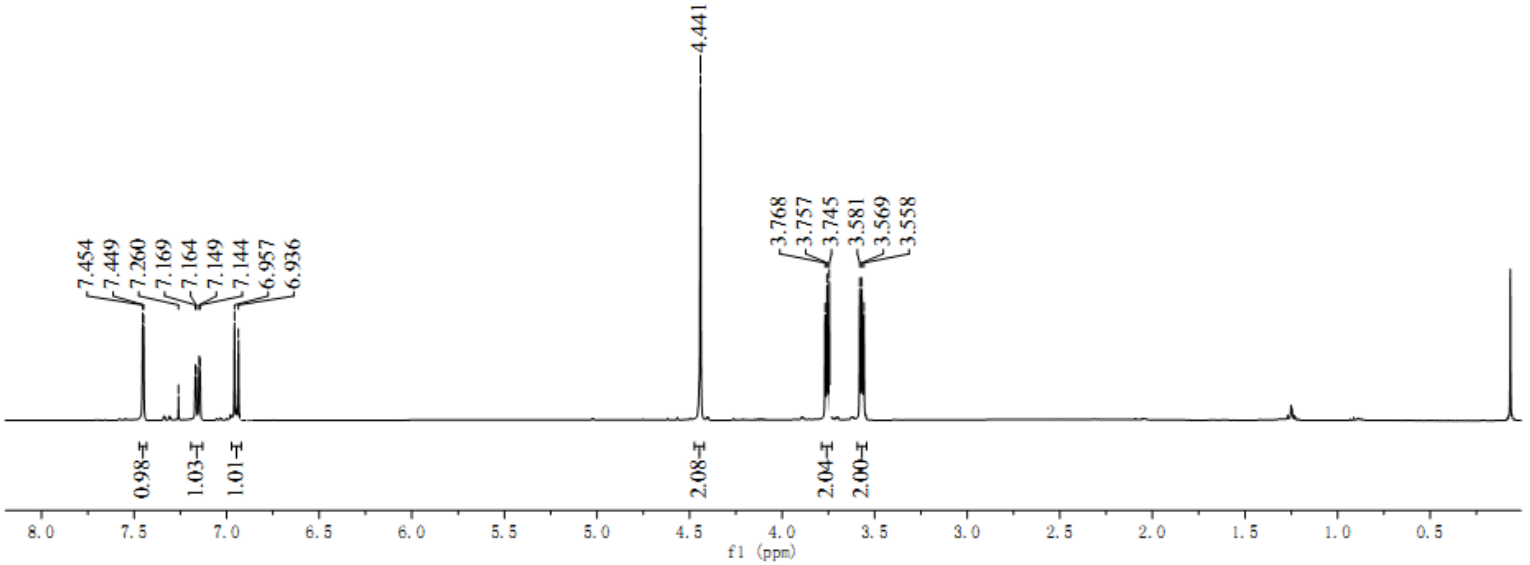


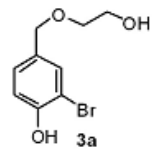

Abundance
Scan 2236 (10.709 min): G120158.D\data.ms (-2231) (-)
94
77
123
202
185
39
51
65
105
29
173
143
158
16
OH
Br
OH
m/z-->


Abundance
Scan 2405 (14.036 min): G120158.D\data.ms (-2367) (-)
184.9
77.0
200.9
246.0
51.0
105.0
123.0
142.9
167.0
217.9
O
OH
Br
OH
m/z-->

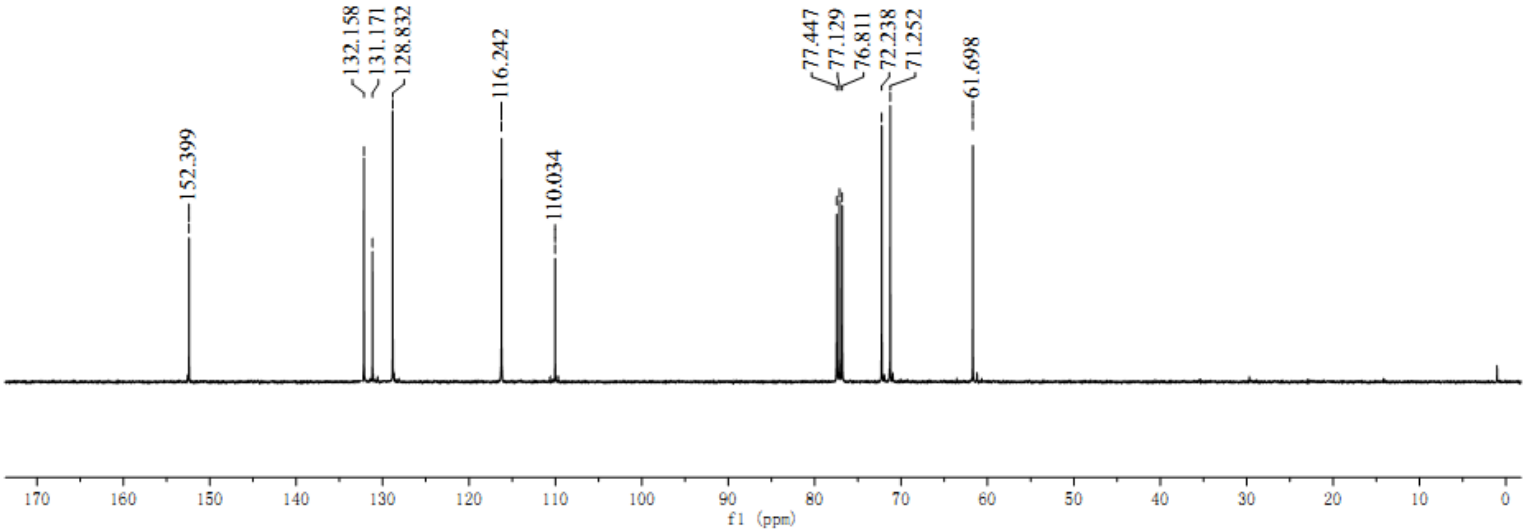

O
OH
Br
OH

3a


7.454
7.449
7.260
7.169
7.164
7.149
7.144
6.957
6.936
4.441
3.768
3.757
3.745
3.581
3.569
3.558
0.98
1.03
1.01
2.08
2.04
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
f1 (ppm)


O
OH
Br
OH

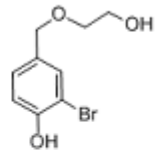
3a


152.399
132.158
131.171
128.832
116.242
110.034
77.447
77.129
76.811
72.238
71.252
61.698
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report

Single Mass Analysis

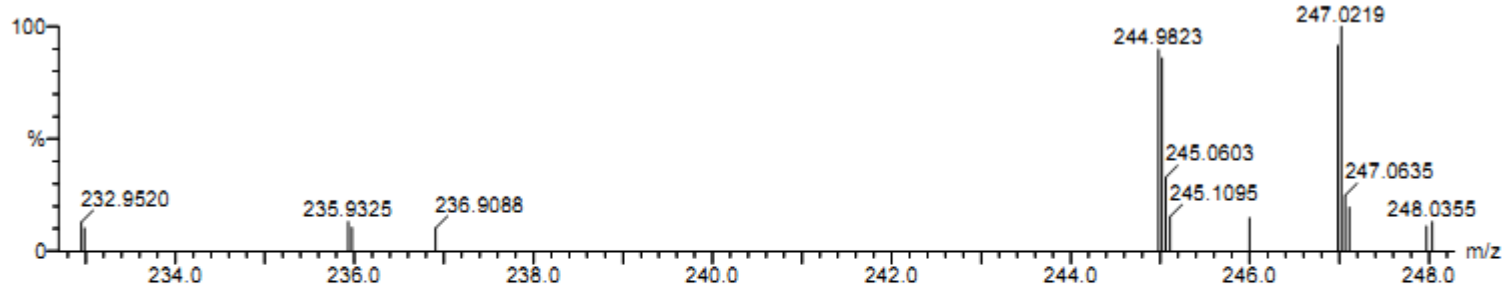
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2



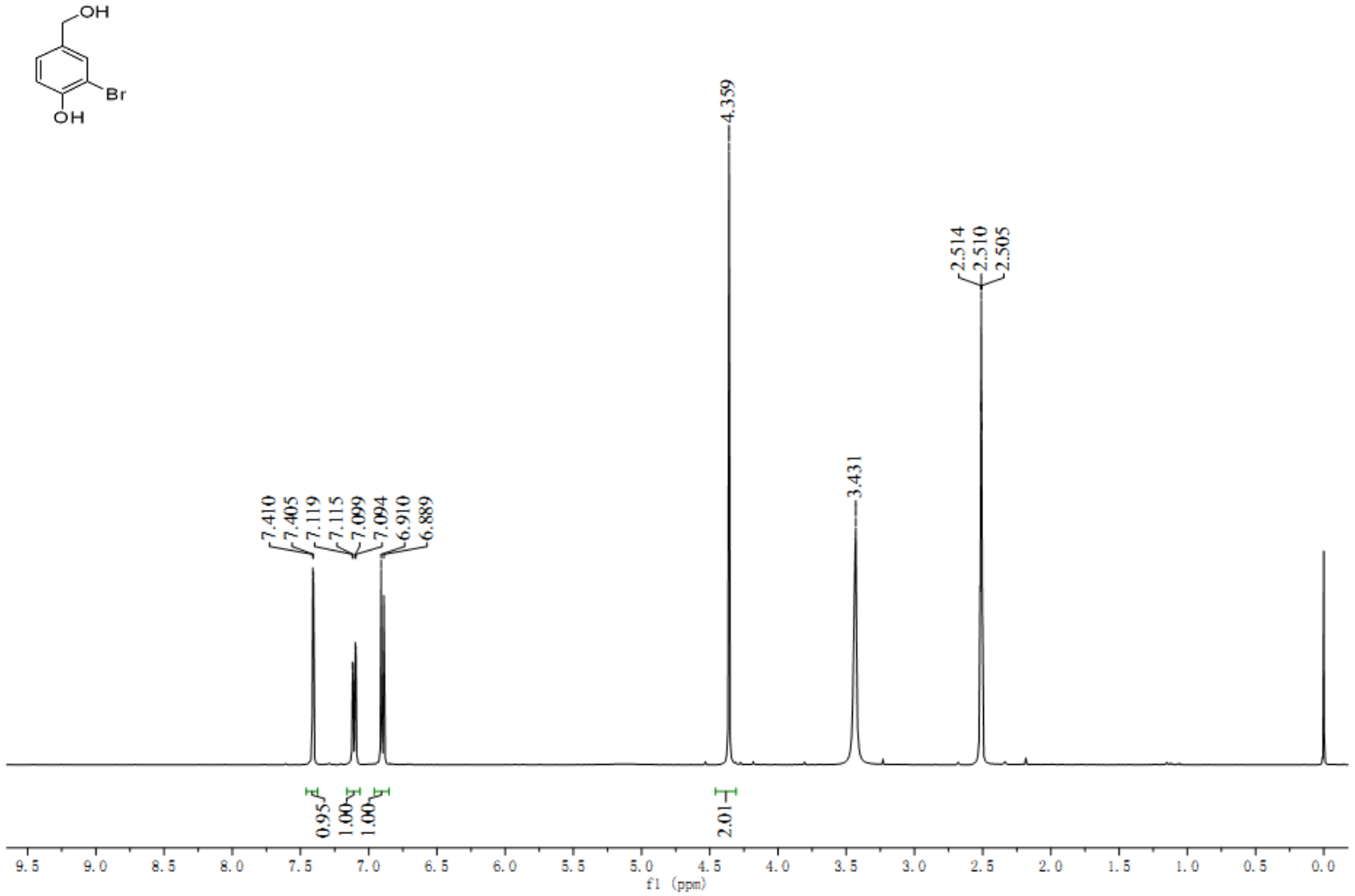
Monoisotopic Mass, Even Electron Ions
52 formula(e) evaluated with 11 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-35 H: 0-100 O: 0-10 Br: 0-1

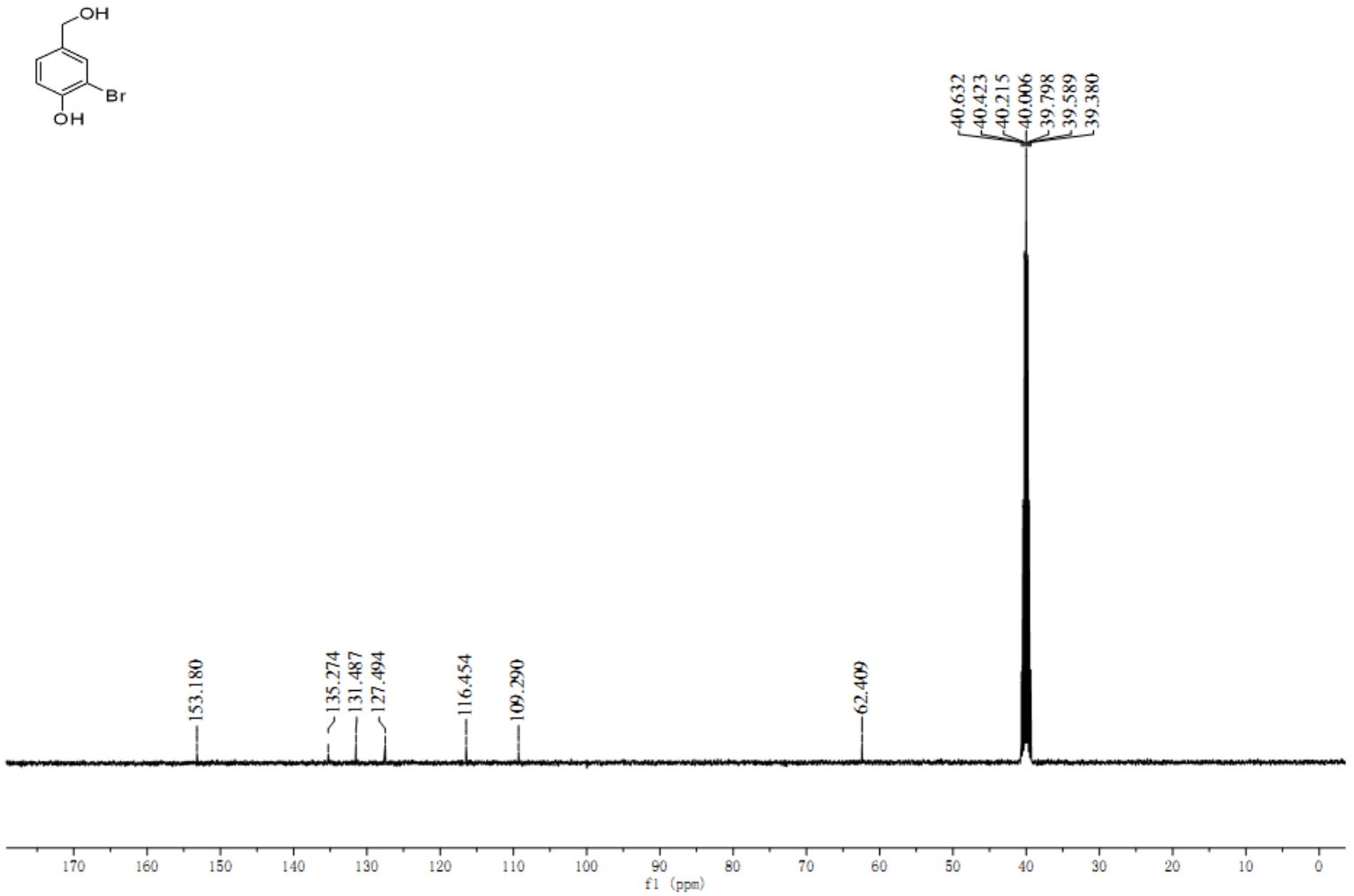
YF-JI ECUST institute of Fine Chem 13-Nov-2013 08:21:36

JYF-DJL-1 169 (1.169) Cm (166:173) 1: TOF MS ES- 8.71e+002

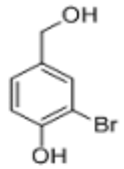


Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
244.9823	244.9813	1.0	4.1	4.5	49.6	0.0	C9 H10 O3 Br


OH
Br
OH
7.410
7.405
7.119
7.115
7.099
7.094
6.910
6.889
4.359
3.431
2.514
2.510
2.505
0.95
1.00
1.00
2.01
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)


OH
Br
OH
153.180
135.274
131.487
127.494
116.454
109.290
62.409
40.632
40.423
40.215
40.006
39.798
39.589
39.380
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

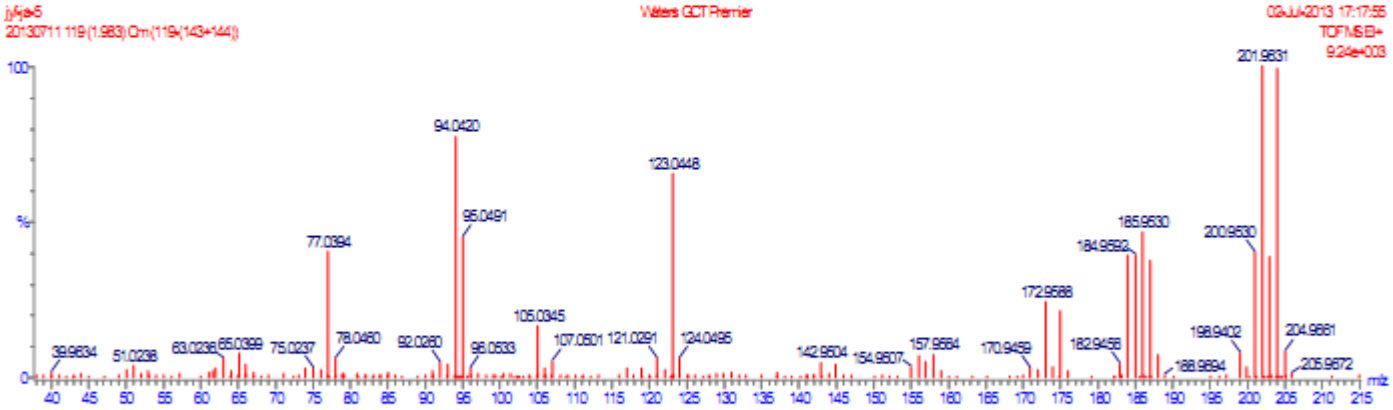
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

226 formula(e) evaluated with 35 results within limits (up to 50 closest results for each mass)

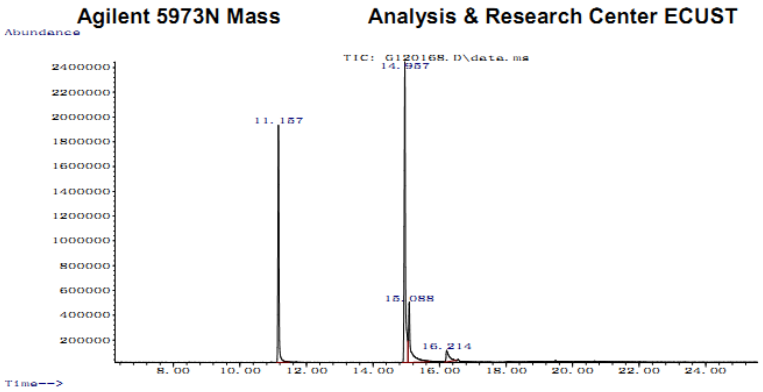
Elements Used:

C: 0-7 H: 0-7 O: 0-2 79Br: 0-1 81Br: 0-1



Minimum:	3.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
201.9631	100.00	201.9629	0.2	1.0	4.0	1133.7	C7 H7 O2 79Br

4.4 Copies of spectra for the oxidation process of 1a in methanol.



Data Path : E:/msdata / test /
Data File : G120168 .D
Acq On : 23 Apr 2012 14:21
Operator :
Sample : 1#
Misc :
ALS Vial : 1 Sample Multiplier: 1

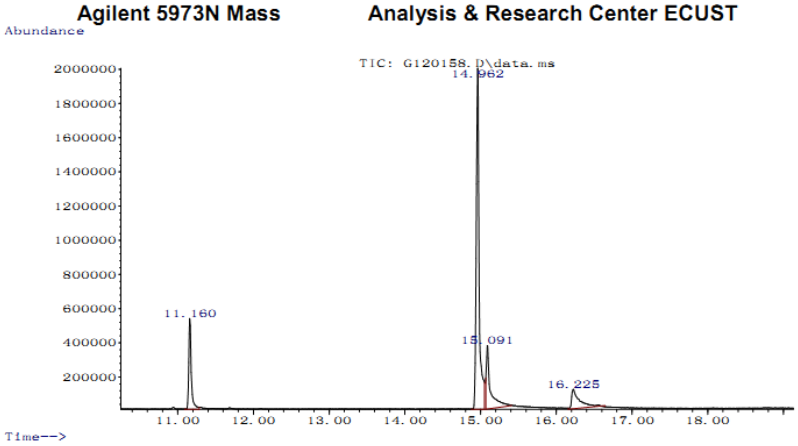
Integration Parameters : autointl.e
Integrator : ChemStation

Method : C: / msdchem / 1 / METHODS / 30 (3) – 8 – 280 . M
Title :

Signal : TIC: G120168 . D /data . ms

Peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	% of total
1	11.154	1350	1358	1398	M	1976767	40192866	64.78%	31.054%
2	14.956	1916	1927	1940	M	2445817	62047946	100.00%	47.939%
3	15.090	1941	1947	2028	M3	492810	21289685	34.31%	16.449%
4	16.212	2106	2115	2161	M6	92910	5900144	9.51%	4.559%

Agilent 5973N Mass **Analysis & Research Center ECUST**



Area Percent Report

Data Path : E:/msdata / test /
Data File : G120158 .D
Acq On : 19 Apr 2012 17:14
Operator :
Sample : 1#
Misc :
ALS Vial : 1 Sample Multiplier: 1

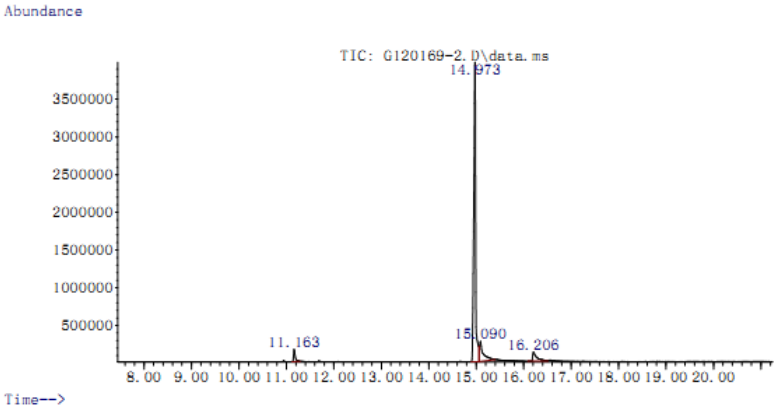
Integration Parameters : autointl.e
Integrator : ChemStation

Method : C: / msdchem / 1 / METHODS / 30 (3) – 8 – 280 . M
Title :

Signal : TIC: G120158 . D /data . ms

Peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	% of total
1	11.158	1637	1647	1666	M	533930	12111190	22.67%	13.808%
2	14.961	2204	2216	2230	M	2025628	53433483	100.00%	60.921%
3	15.087	2232	2235	2283	M2	378561	14038890	26.27%	16.006%
4	16.223	2395	2405	2467	M4	114203	8126268	15.21%	9.265%

Agilent 5973N Mass Analysis & Research Center ECUST



Area Percent Report

Data Path : E:/msdata / test /
Data File : G120169 . D
Acq On : 23 Apr 2012 16:16
Operator :
Sample : 2#
Misc :
ALS Vial : 1 Sample Multiplier: 1

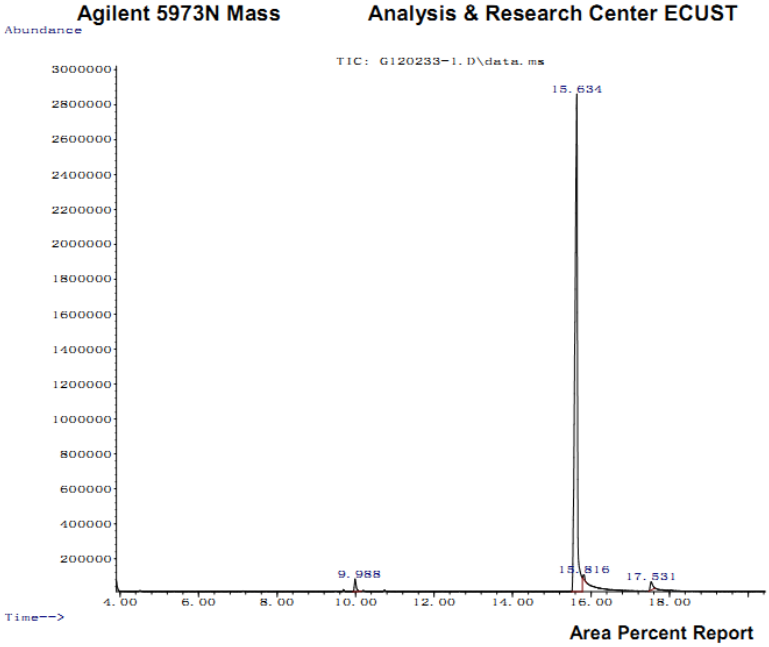
Integration Parameters : autointl.e
Integrator : ChemStation

Method : C: / msdchem / 1 / METHODS / 30 (3) – 8 – 280 . M
Title :

Signal : TIC: G120169 . D /data . ms

Peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	% of total
1	11.161	1352	13589	1377	M	166598	4051834	3.76%	2.937%
2	14.976	1917	1930	1943	M	4165701	107672228	100.00%	78.039%
3	15.090	1943	1947	2029	M5	273280	19040969	17.68%	13.801%
4	16.206	2104	2114	2158	M4	124498	7207699	6.69%	5.224%

Agilent 5973N Mass **Analysis & Research Center ECUST**



Area Percent Report

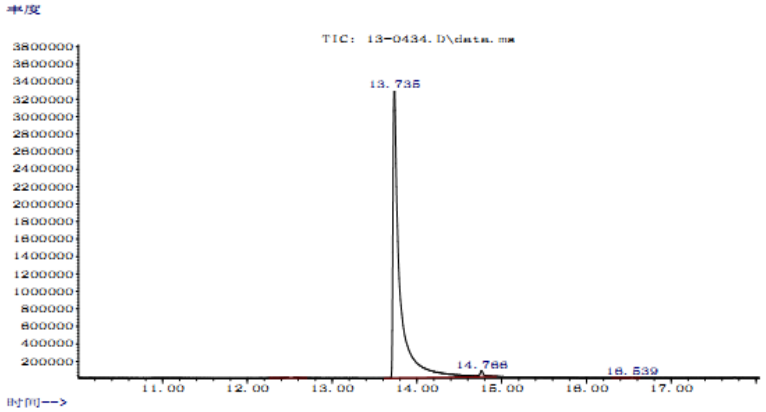
Data Path : E:/msdata / test /
Data File : G120233-1.D
Acq On : 11 May 2012 14:35
Operator :
Sample : 1#
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters : autointl.e
Integrator : ChemStation

Method : C: / msdchem / 1 / METHODS / 30 (3) – 8 – 280 . M
Title :

Signal : TIC: G120168 . D /data . ms

Peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	% of total
1	9.989	1461	1470	1398	M	73048	2302379	1.85%	1.782%
2	15.636	2295	2315	2336	M	2866806	124190818	100.00%	96.118%
3	15.816	2590	2599	2612	M5	48006	1941923	1.56%	1.503%
4	17.533	2337	2342	2353	M8	27555	771401	0.62%	0.597%



Area Percent Report

Data Path : E:/msdata / test /
Data File : 12-0445.D
Acq On : 12 May 2012 14:35
Operator :
Sample : 1#
Misc :
ALS Vial : 1 Sample Multiplier: 1

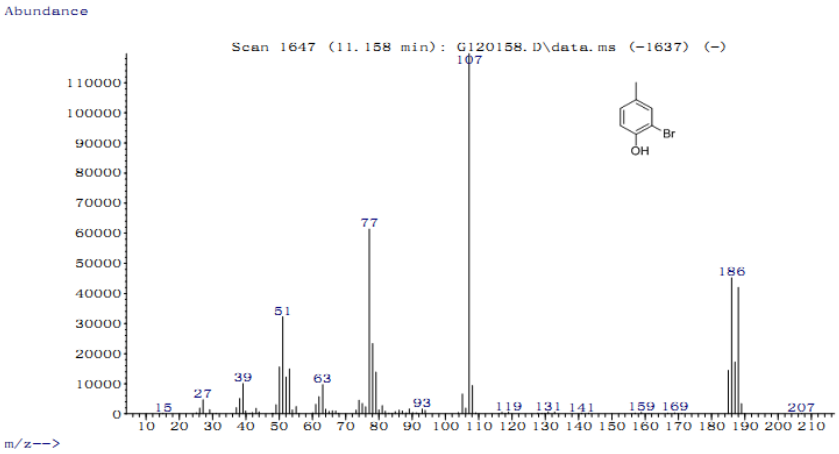
Integration Parameters : autointl.e
Integrator : ChemStation

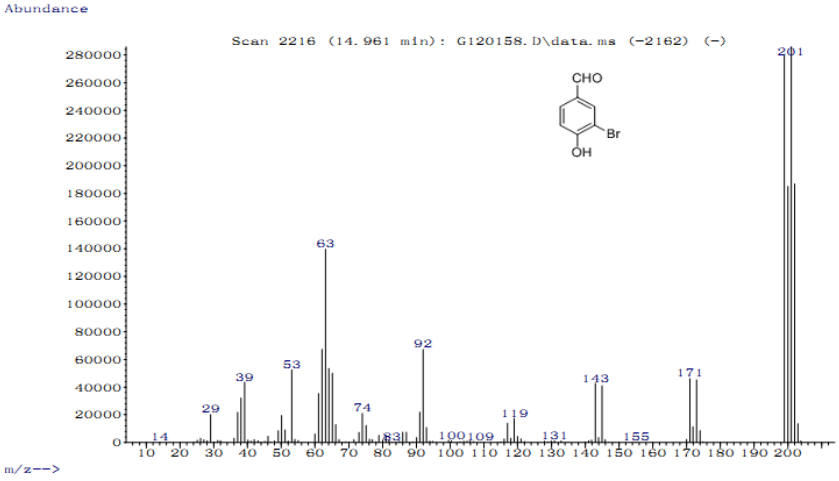
Method : C: / msdchem / 1 / METHODS / 30 (3) – 8 – 280 . M
Title :

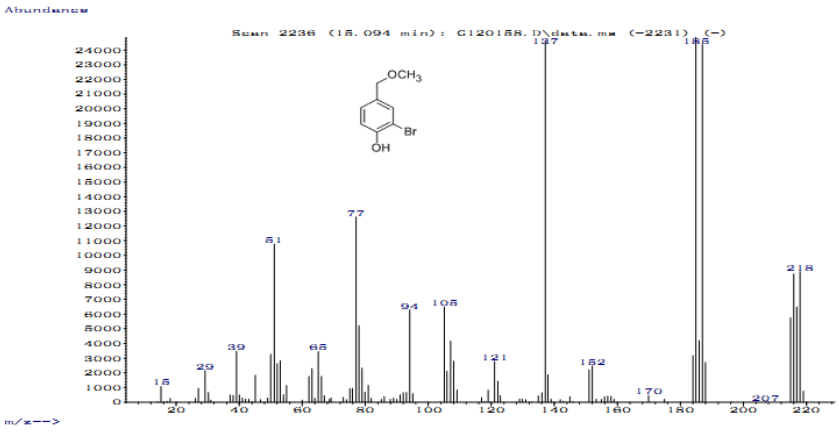
Signal : TIC: G120168 . D /data . ms

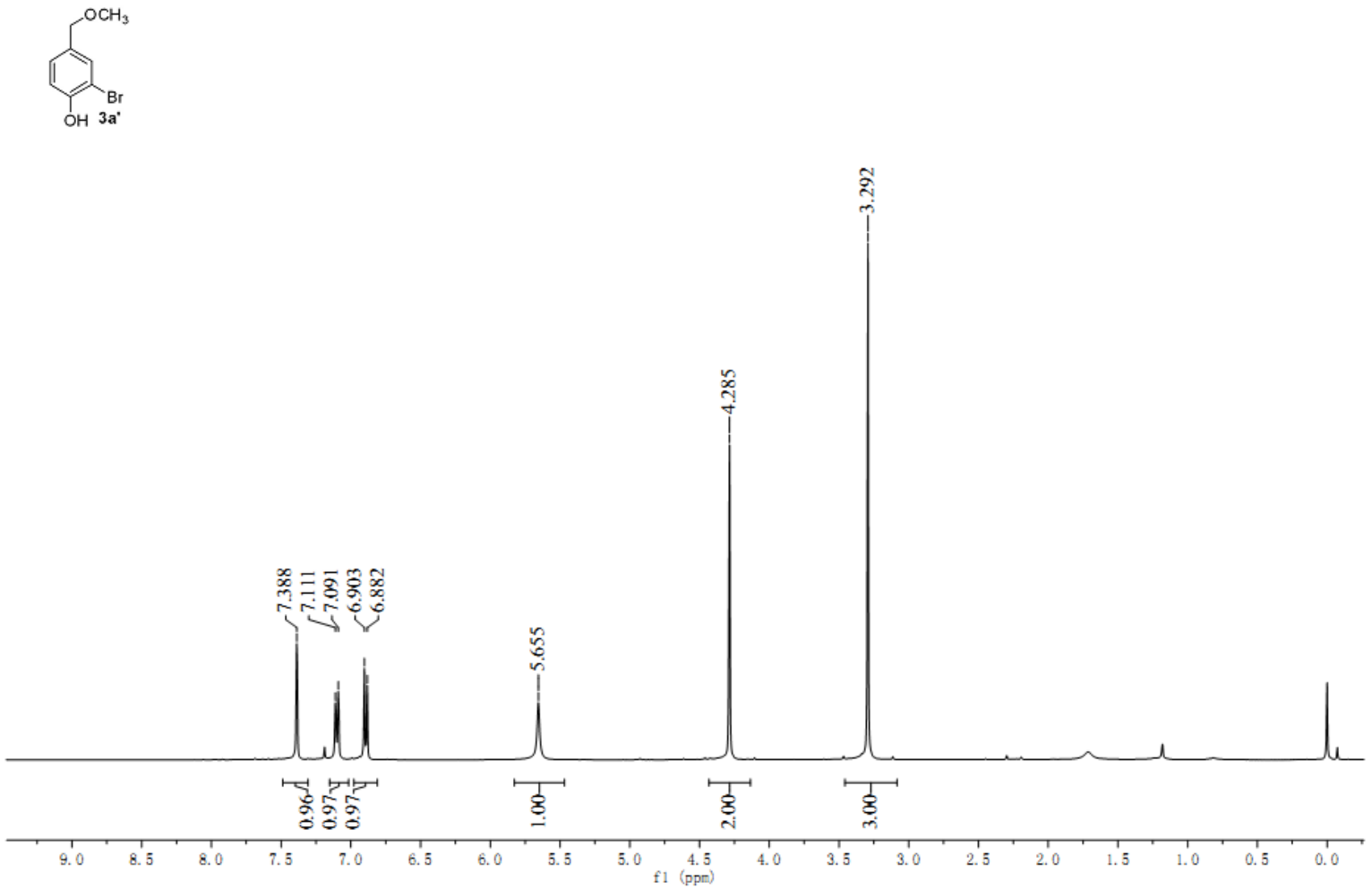
Peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max	% of total
1	13.735	1964	1983	2154	BB	3292515	181419490	100.00%	98.963%
2	16.539	2154	2175	2189	BB 2	65489	1525770	0.85%	0.832%
3	14.766	2485	2505	2514	BV	25086	375587	0.21%	0.205%

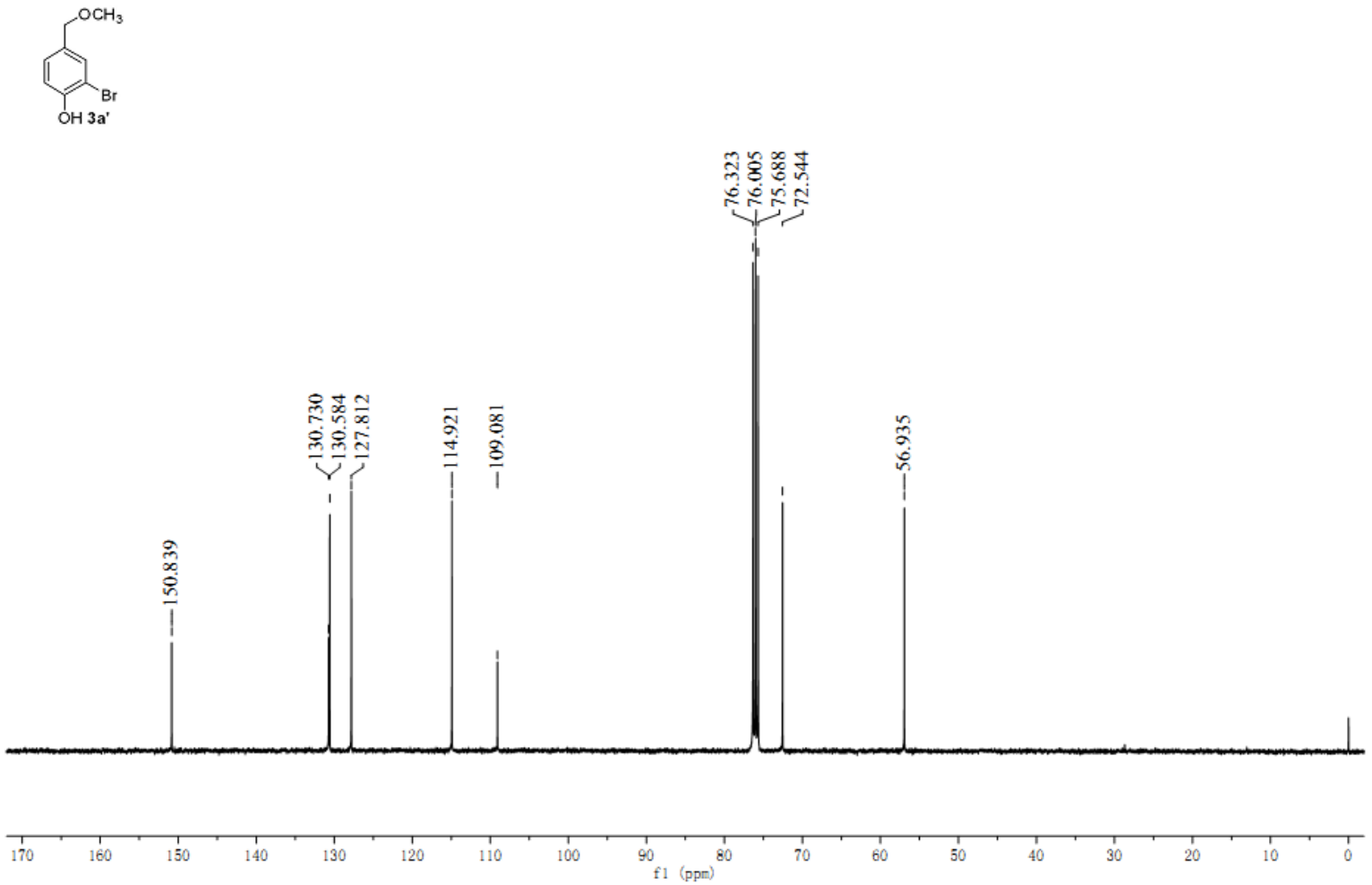
Agilent 5973N Mass Analysis & Research Center ECUST



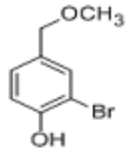



Abundance
Scan 2236 (15.094 min): G120158.D\data.ms (-2231) (-)
OCH3
Br
OH
m/z-->
Abundance
Scan 2405 (16.223 min): G120158.D\data.ms (-2367) (-)
OH
Br
OH
m/z-->


OCH3
Br
OH
3a'
7.388
7.111
7.091
6.903
6.882
5.655
4.285
3.292
0.96
0.97
0.97
1.00
2.00
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
f1 (ppm)


OCH3
Br
OH 3a'
150.839
130.730
130.584
127.812
114.921
109.081
76.323
76.005
75.688
72.544
56.935
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

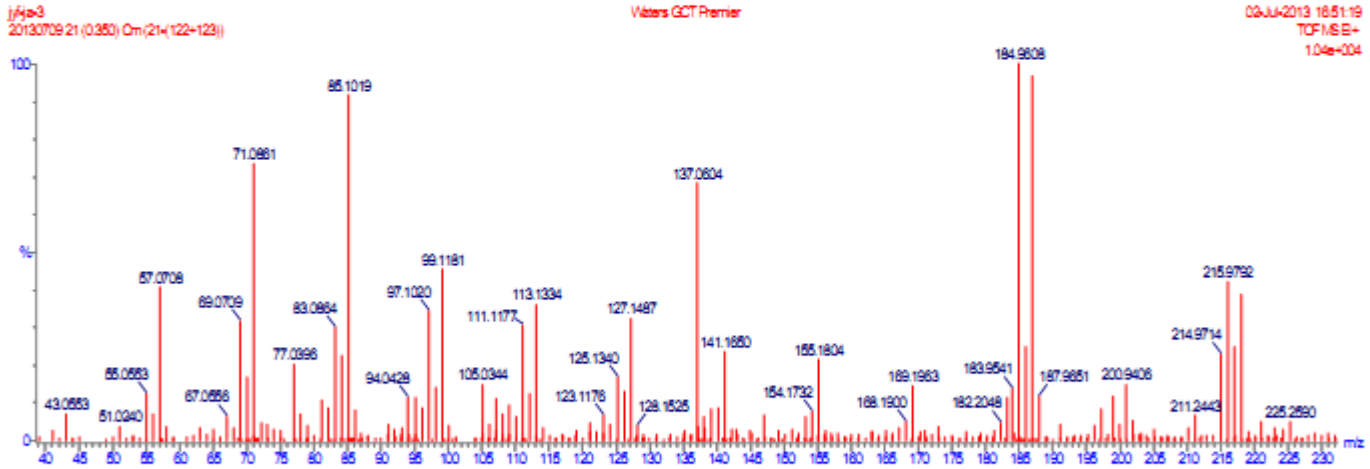
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

382 formula(e) evaluated with 25 results within limits (up to 50 closest results for each mass)

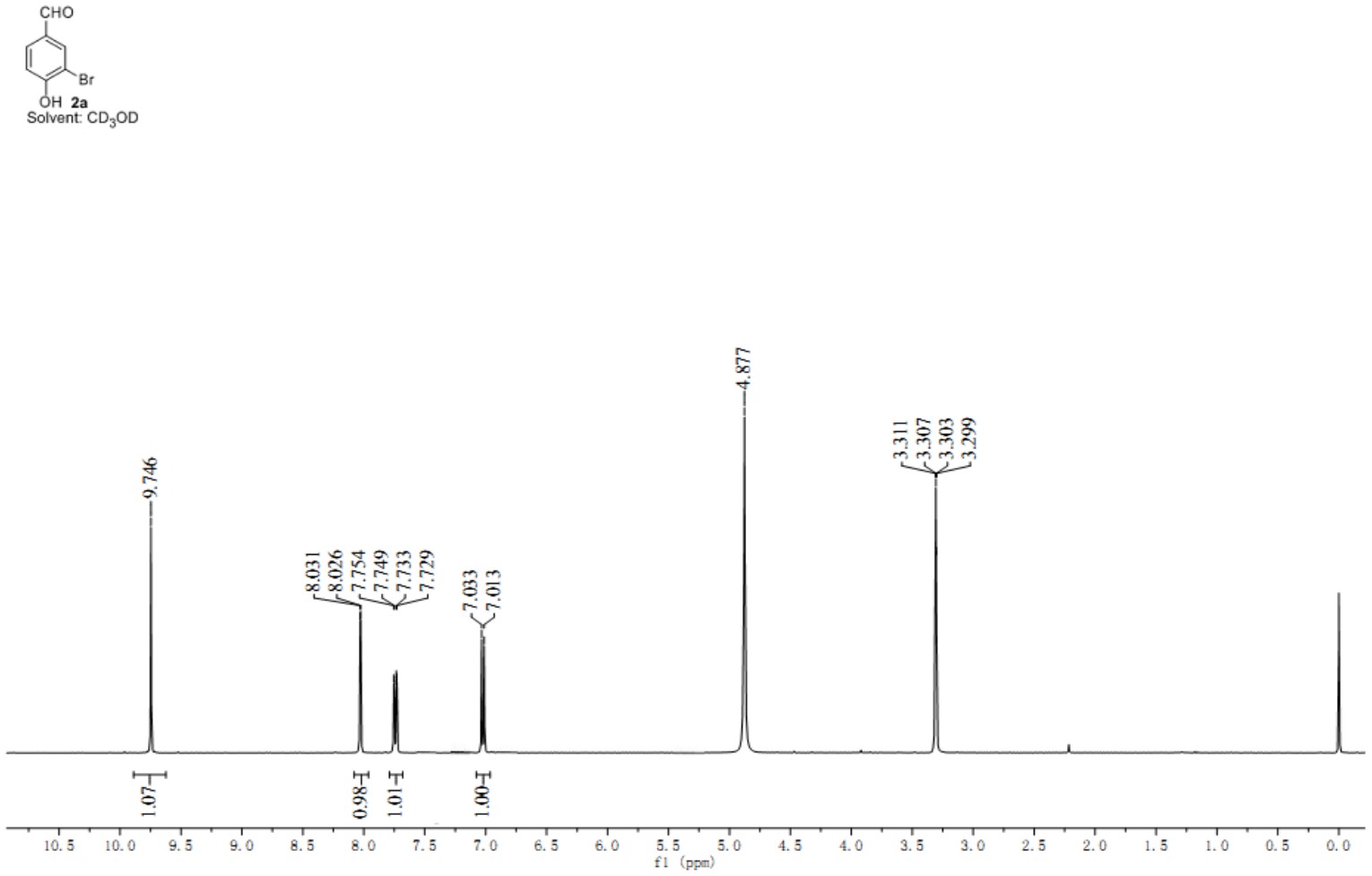
Elements Used:

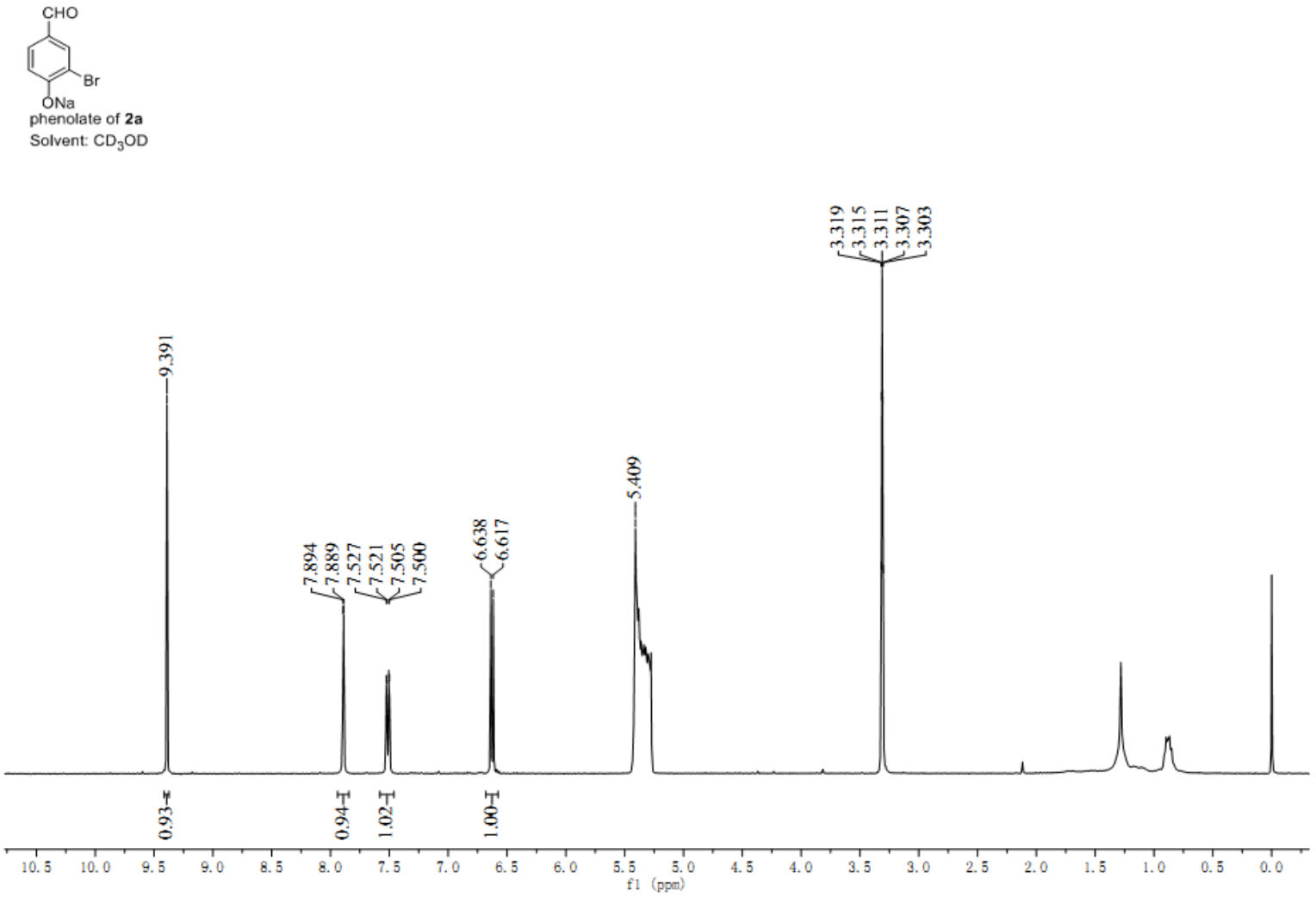
C: 0-8 H: 0-9 O: 0-2 79Br: 0-1 81Br: 0-1

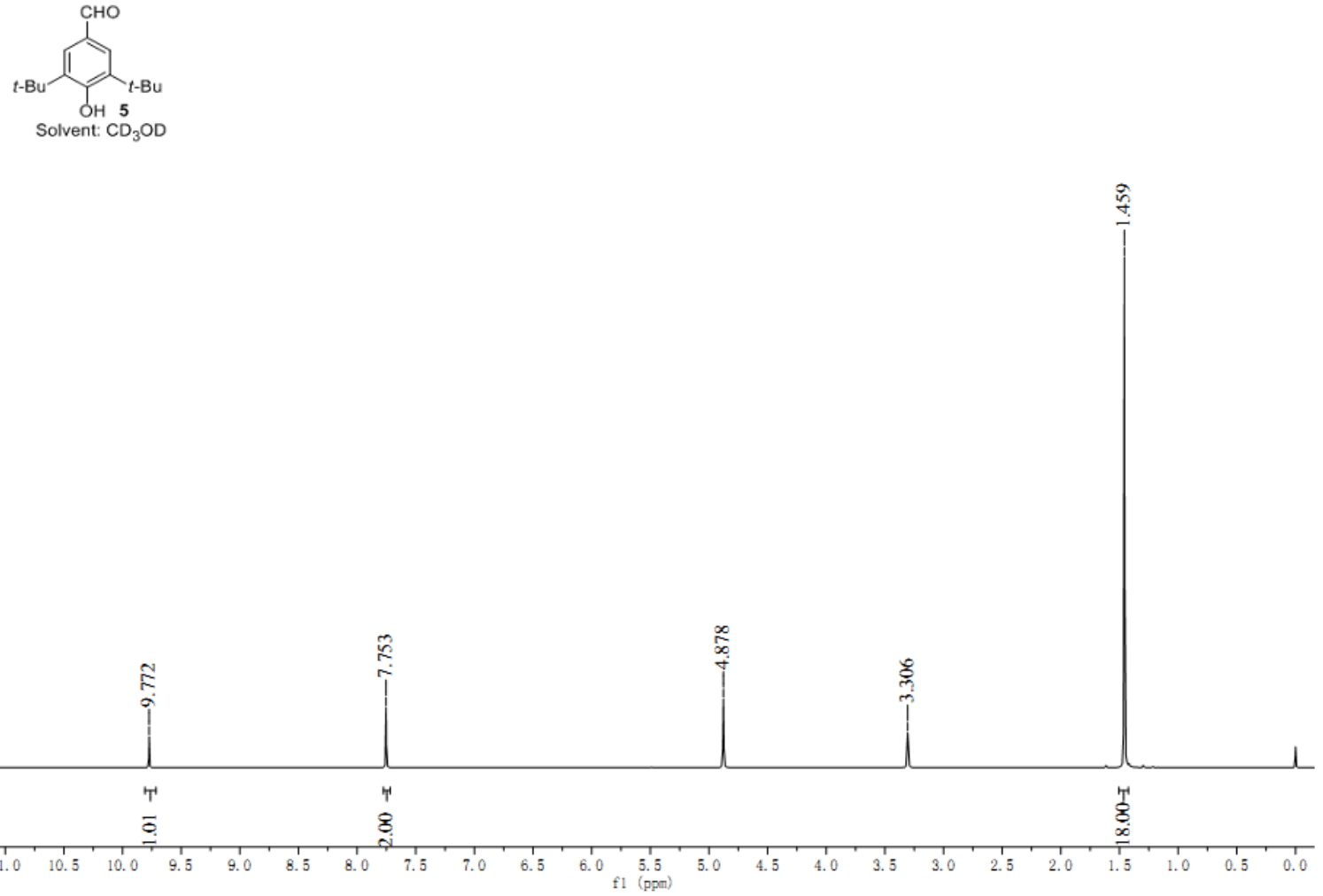


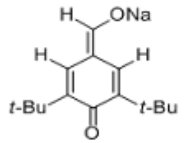
Minimum:					-1.5				
Maximum:		100.00	5.0	10.0	50.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula		
215.9792	41.98	215.9786	0.6	2.8	4.0	936.5	C8	H9	O2	79Br

4.5 Copies of ^{1}H NMR spectra for compounds 2a and 5, in CD3ONa/CD3OD and CD3OD, respectively.

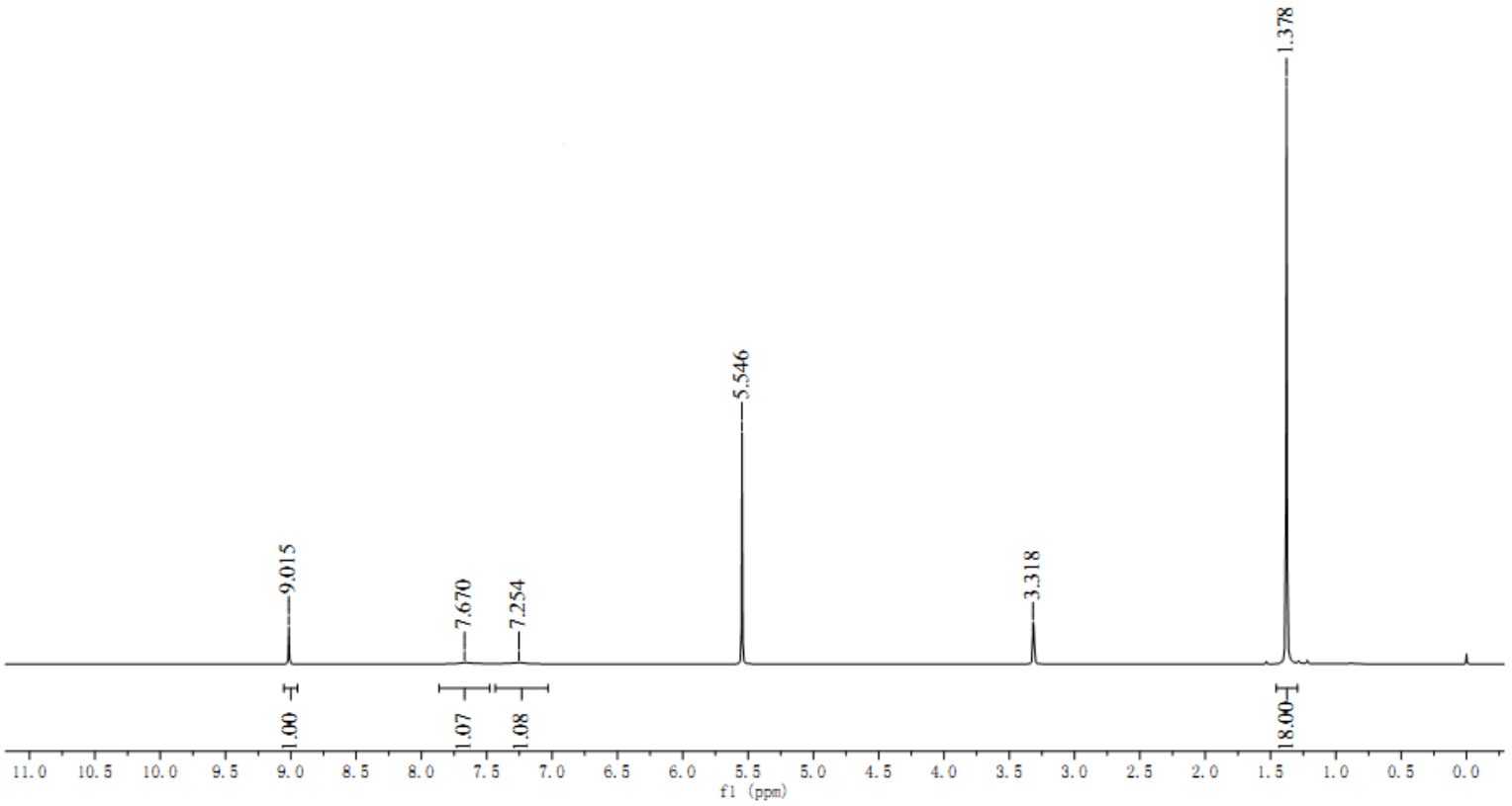



CHO
Br
ONa
phenolate of 2a
Solvent: CD3OD
9.391
7.894
7.889
7.527
7.521
7.505
7.500
6.638
6.617
5.409
3.319
3.315
3.311
3.307
3.303
0.93
0.94
1.02
1.00
f1 (ppm)

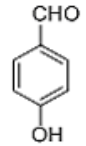

CHO
t-Bu
t-Bu
OH 5
Solvent: CD3OD
9.772
7.753
4.878
3.306
1.459
1.01
2.00
18.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

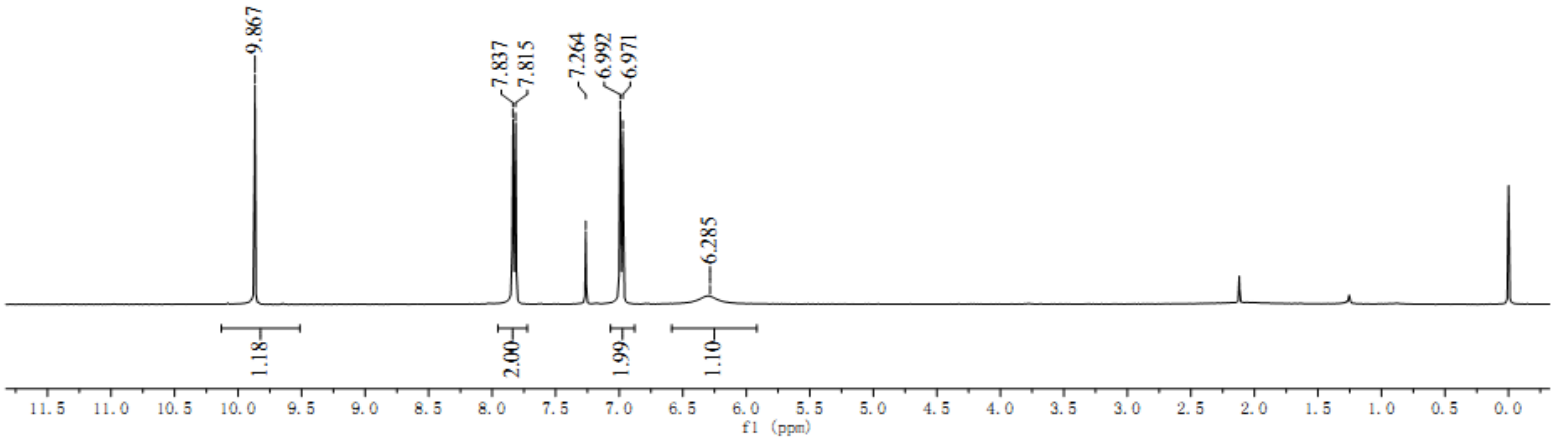


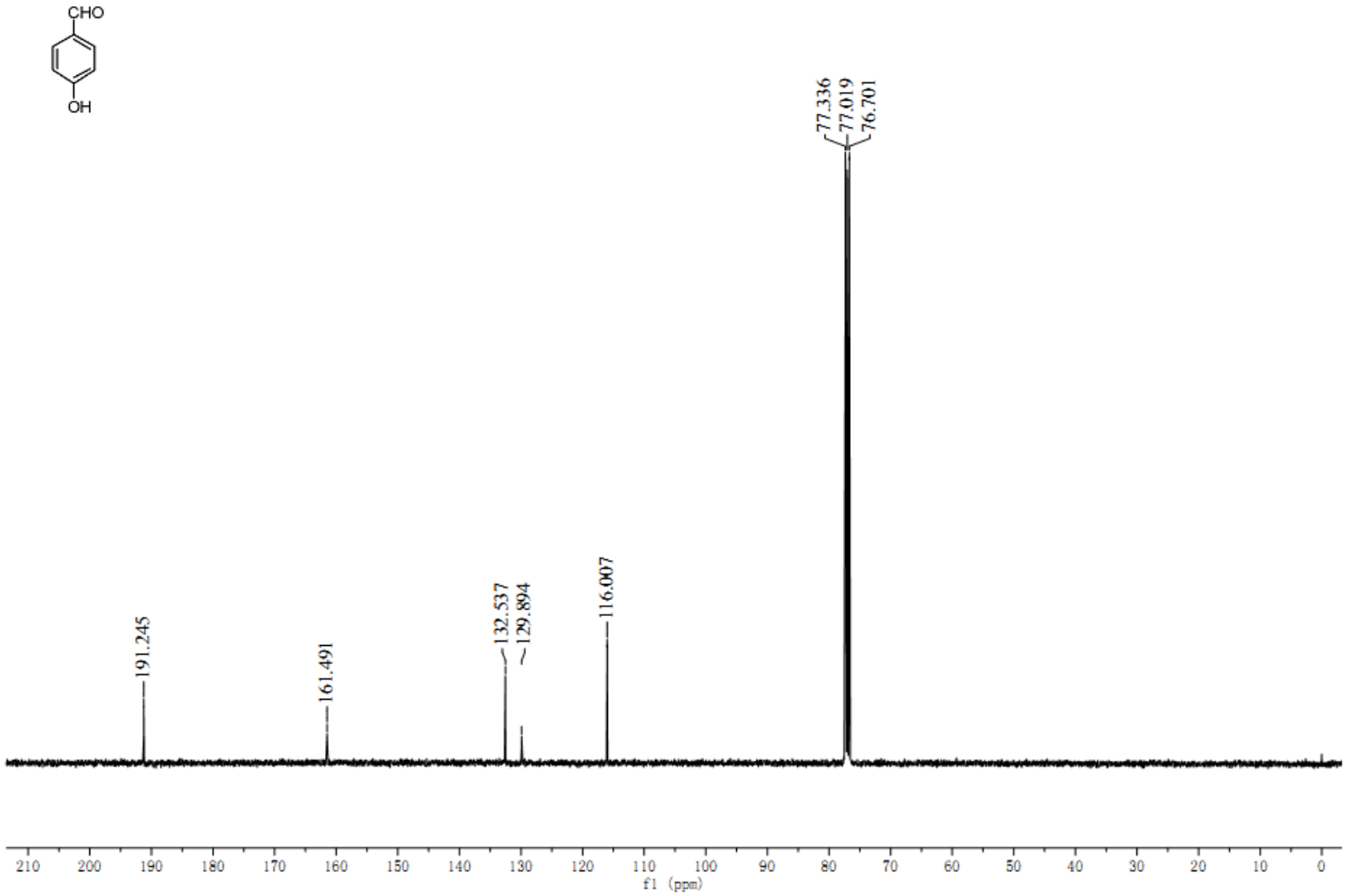
enolate of **5**
Solvent: CD_3OD



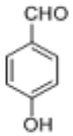
4.6 Copies of spectra for $Co(OAc)_2 \cdot 4H_2O$-catalyzed oxidation of 1a, 1b and 1c.






CHO
OH
191.245
161.491
132.537
129.894
116.007
77.336
77.019
76.701
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Elemental Composition Report



Single Mass Analysis

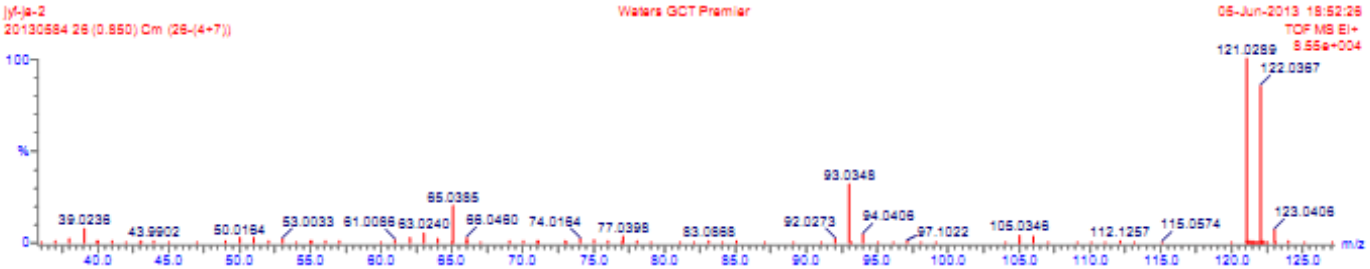
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Monoisotopic Mass, Odd and Even Electron Ions

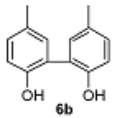
19 formula(e) evaluated with 9 results within limits (up to 50 closest results for each mass)

Elements Used:

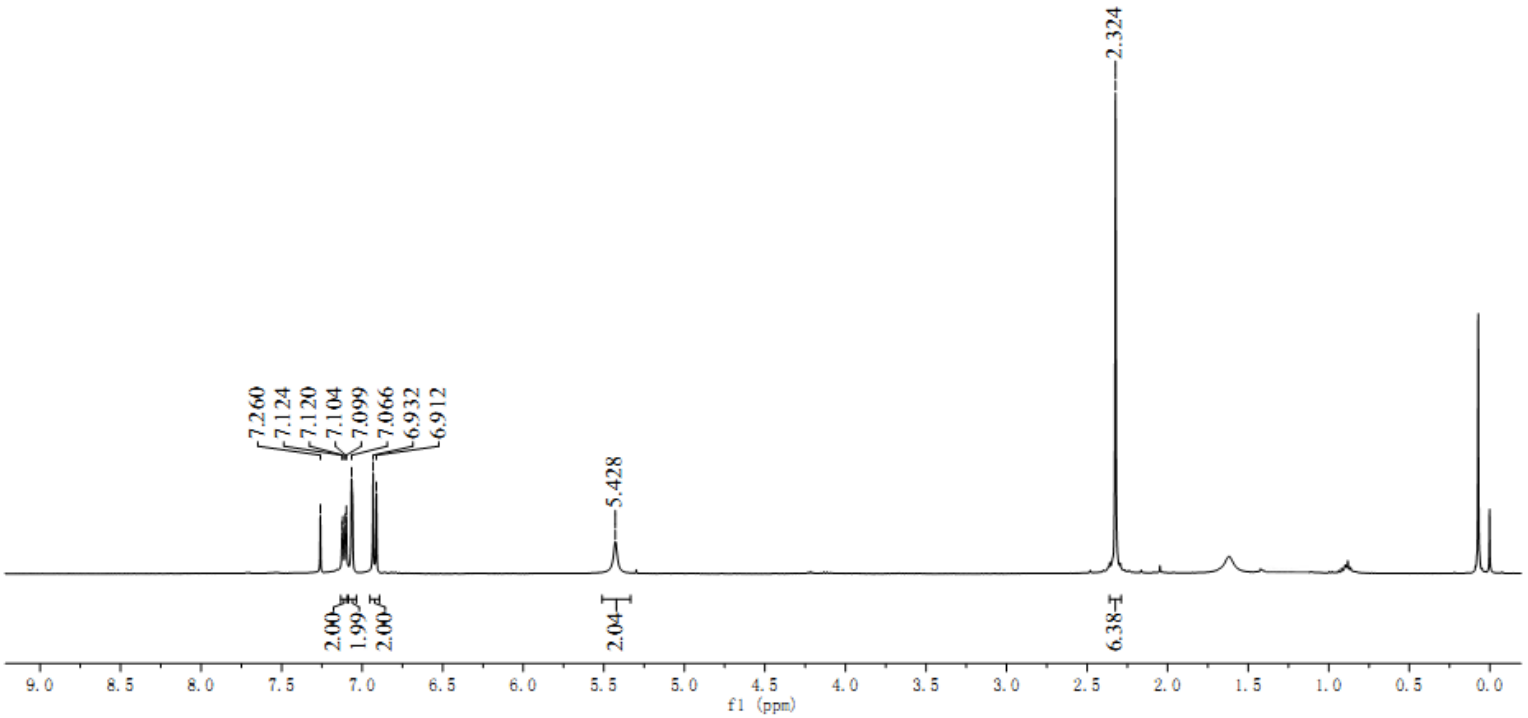
C: 0-7 H: 0-6 O: 0-2

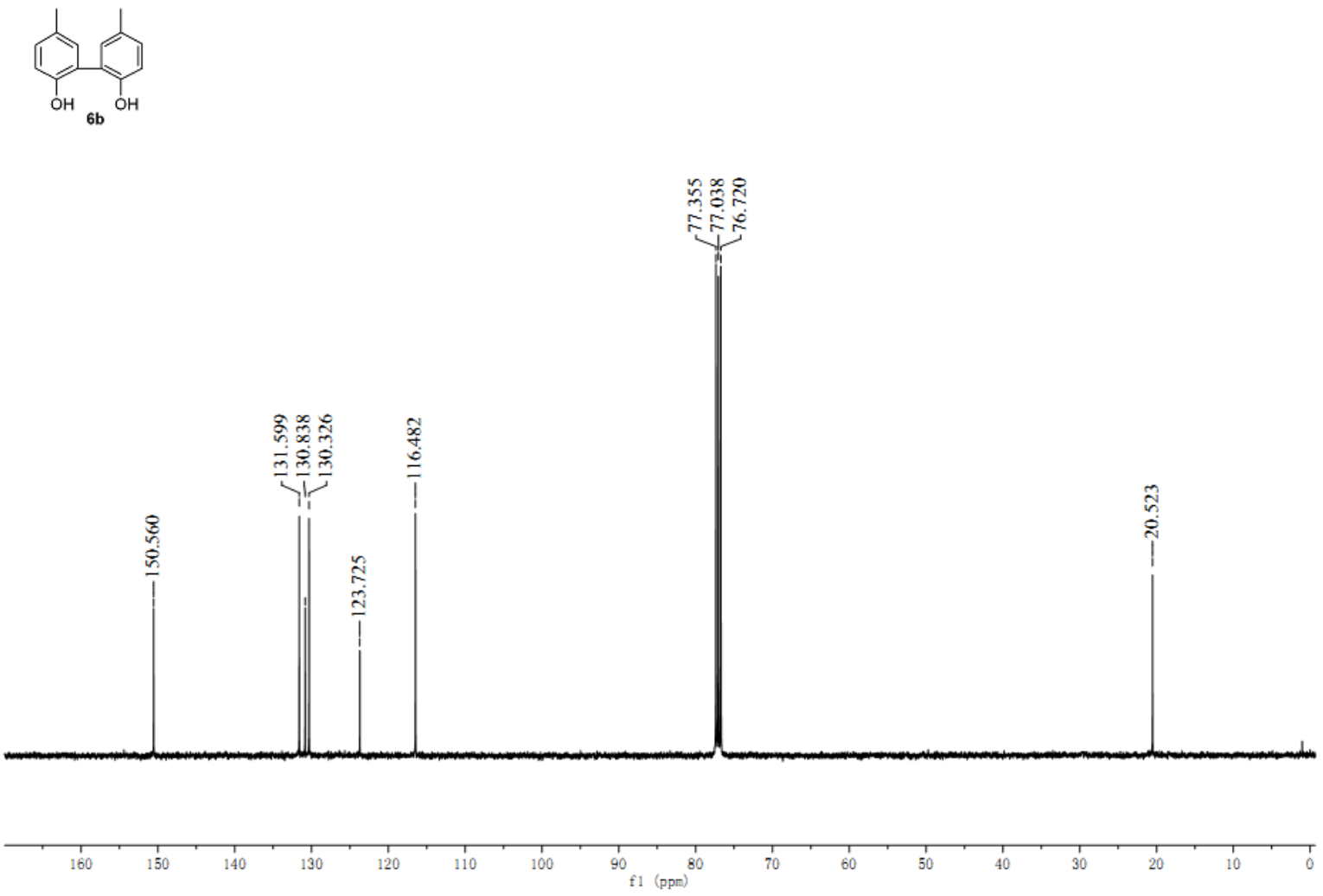


Minimum:	3.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
122.0367	84.79	122.0368	-0.1	-0.8	5.0	3.5	C7 H6 O2

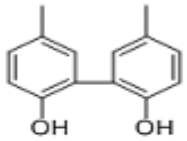

OH
OH

6b


7.260
7.124
7.120
7.104
7.099
7.066
6.932
6.912
5.428
2.324
2.00
1.99
2.00
2.04
6.38
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)


OH
OH
6b
150.560
131.599
130.838
130.326
123.725
116.482
77.355
77.038
76.720
20.523
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



Single Mass Analysis

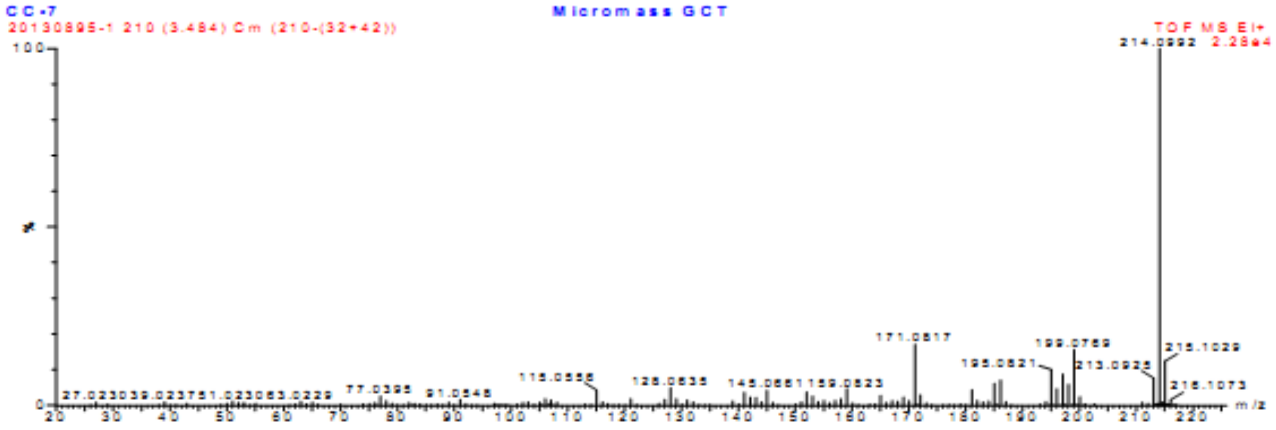
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Monoisotopic Mass, Odd and Even Electron Ions

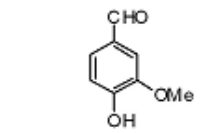
68 formula(e) evaluated with 20 results within limits (up to 50 closest results for each mass)

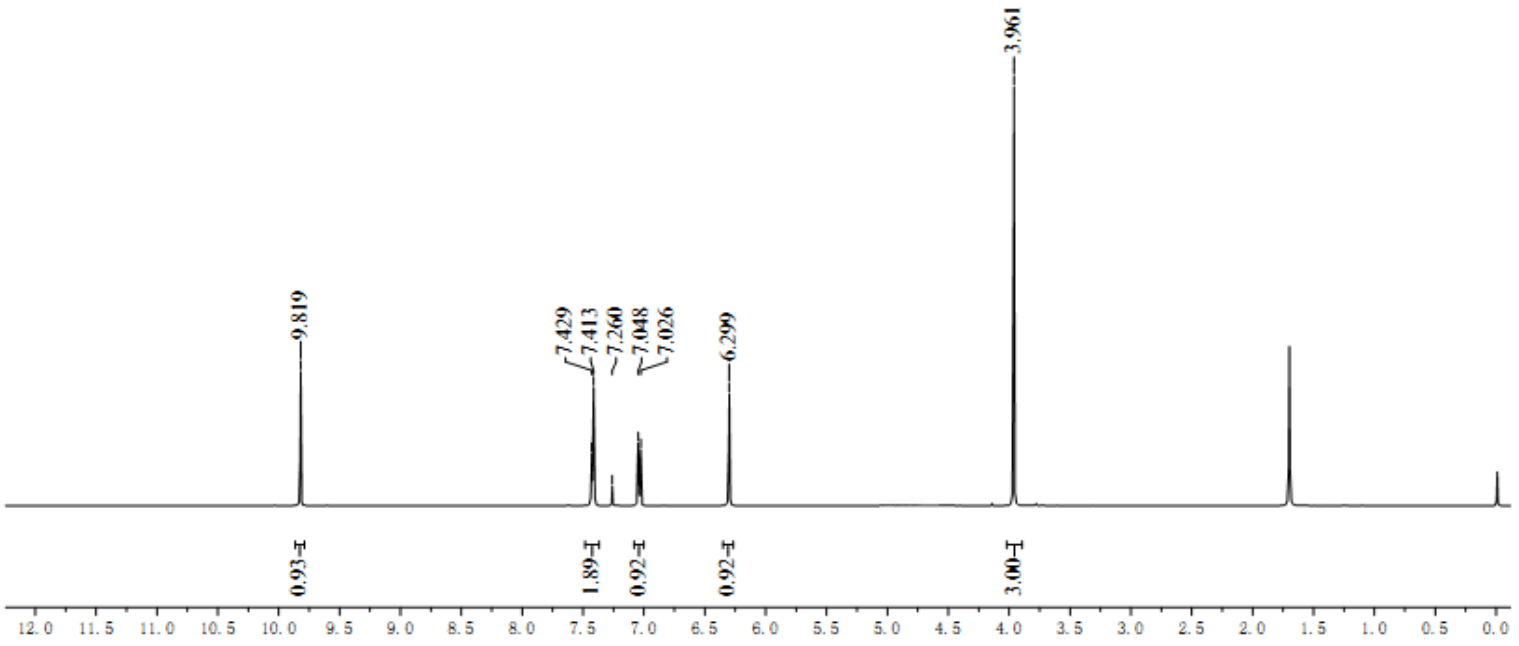
Elements Used:

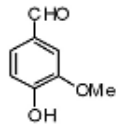
C: 0-14 H: 0-14 O: 0-2

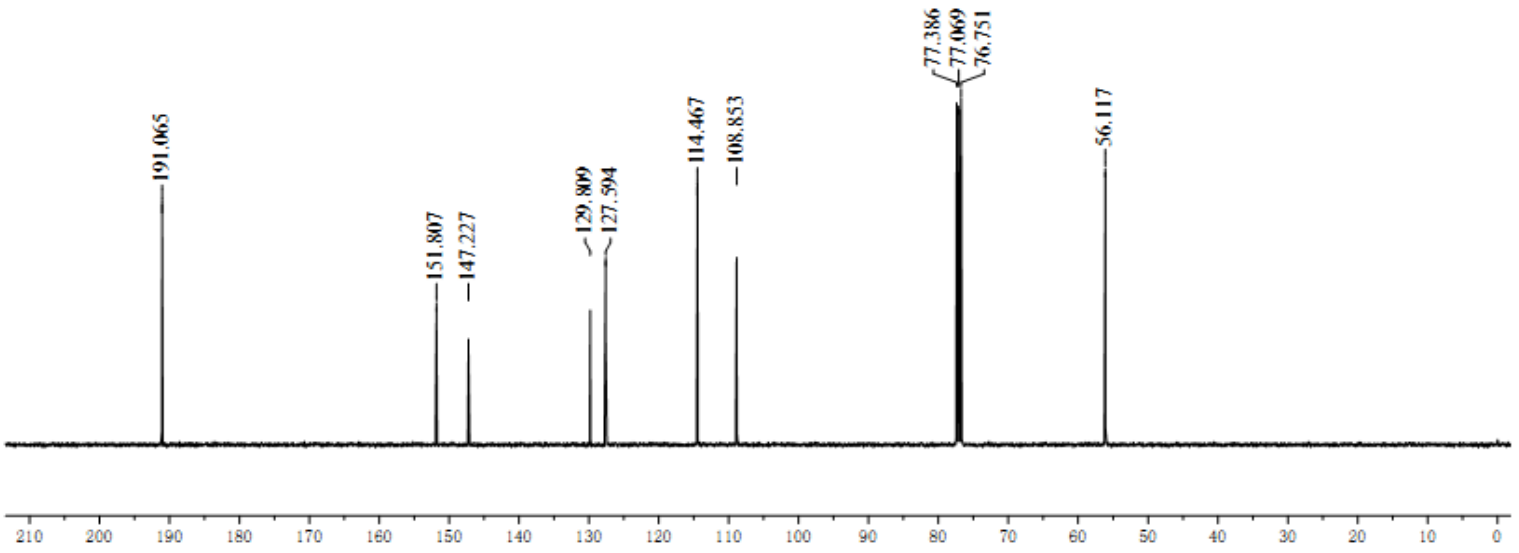


Minimum:		3.00			-1.5		
Maximum:		100.00	5.0	5.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
214.0992	100.00	214.0994	-0.2	-0.8	8.0	1	C14 H14 O2


CHO
OMe
OH


9.819
7.429
7.413
7.260
7.048
7.026
6.299
3.961
0.93
1.89
0.92
0.92
3.00
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

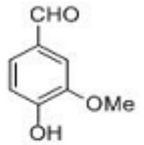

CHO
OMe
OH


191.065
151.807
147.227
129.809
127.594
114.467
108.853
77.386
77.069
76.751
56.117
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Elemental Composition Report

Single Mass Analysis

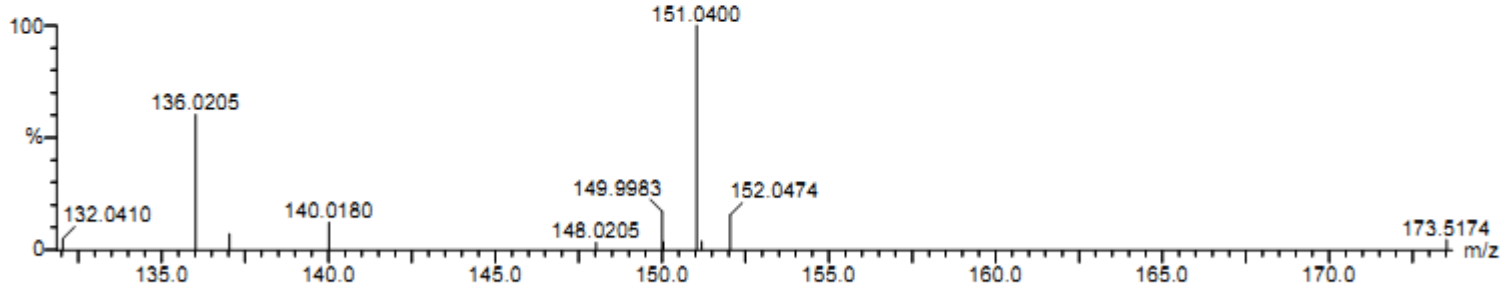
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2



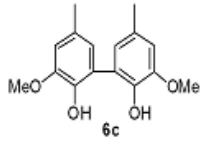
Monoisotopic Mass, Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-8 H: 0-30 O: 0-3

YF-JI ECUST institute of Fine Chem 16-May-2013 08:23:46

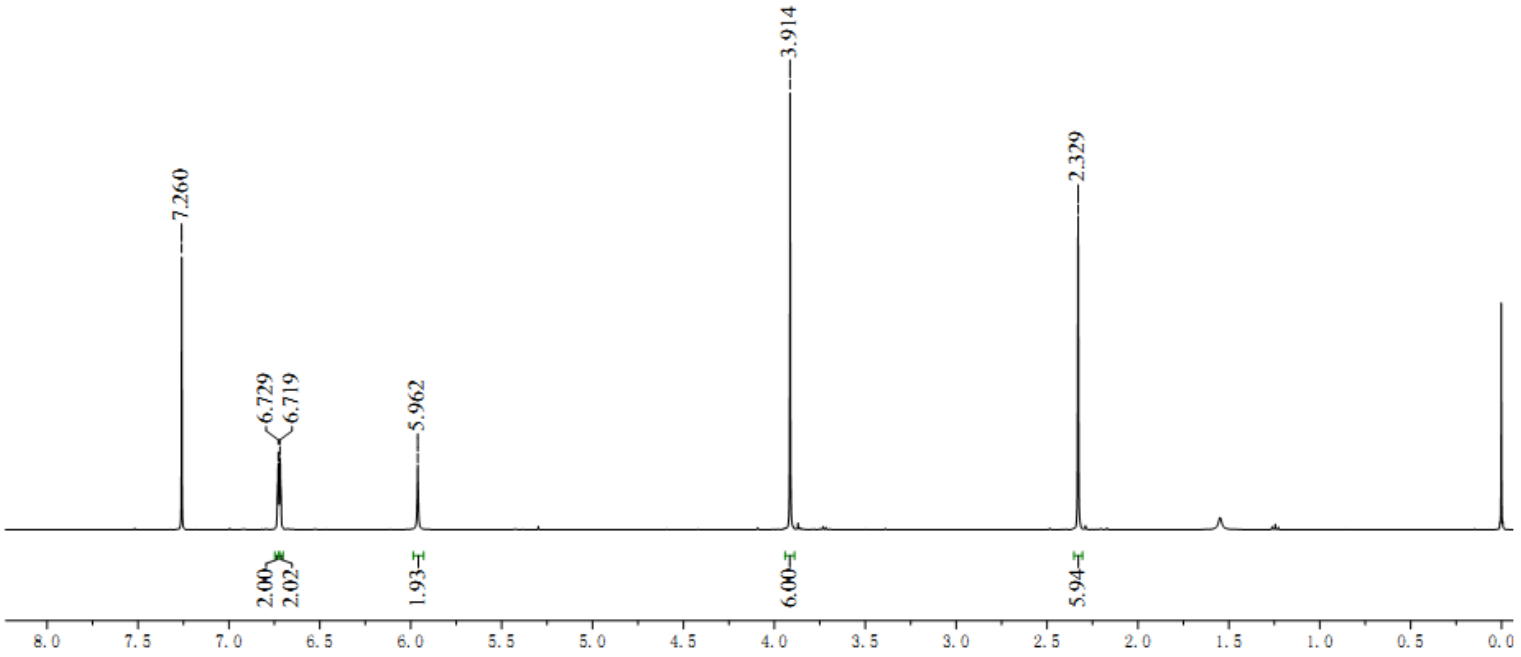
JYF-JA-6 29 (0.292) Cm (6:33) 1: TOF MS ES- 1.72e+004

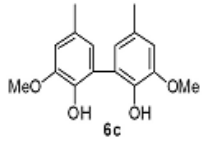


Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	**Calc. Mass**	**mDa**	**PPM**	**DBE**	**i-FIT**	**i-FIT (Norm)**	**Formula**
151.0400	151.0395	0.5	3.3	5.5	33.3	0.0	C8 H7 O3

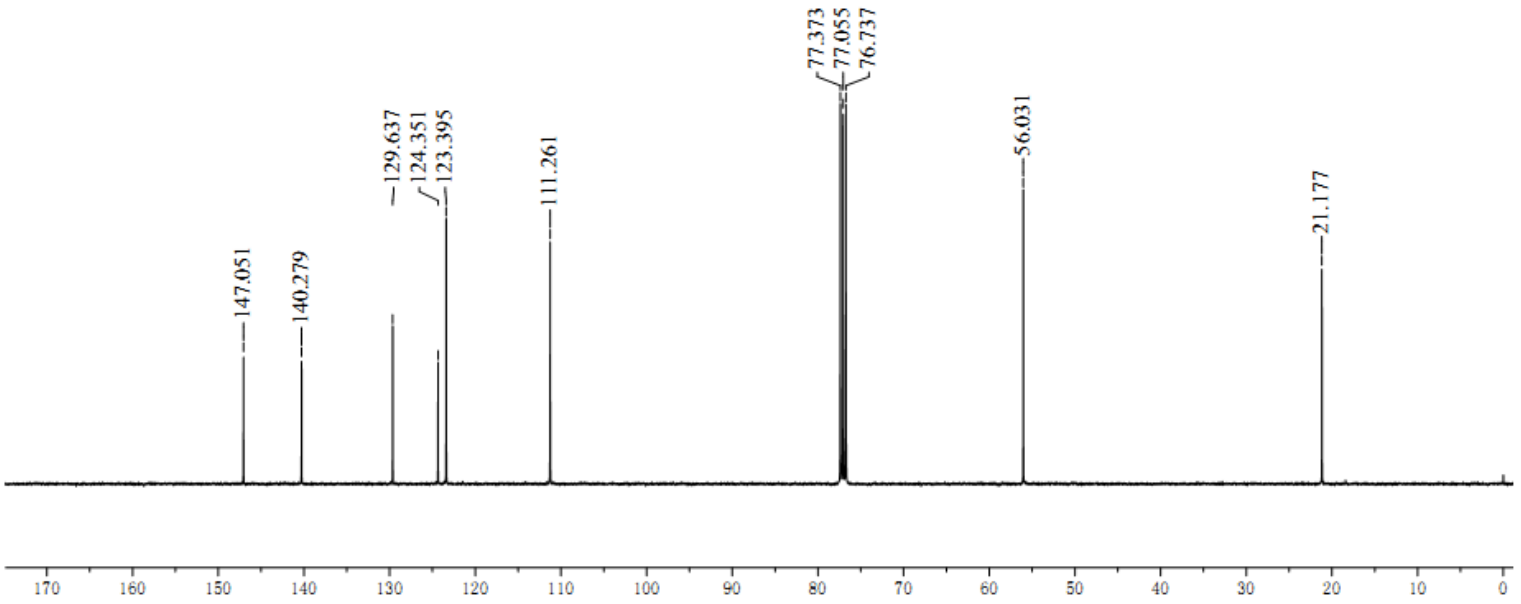

MeO
OH
OH
OMe

6c


7.260
6.729
6.719
5.962
3.914
2.329
2.00
2.02
1.93
6.00
5.94
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


MeO
OH
OH
OMe

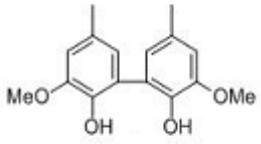
6c


147.051
140.279
129.637
124.351
123.395
111.261
77.373
77.055
76.737
56.031
21.177
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Elemental Composition Report

Single Mass Analysis

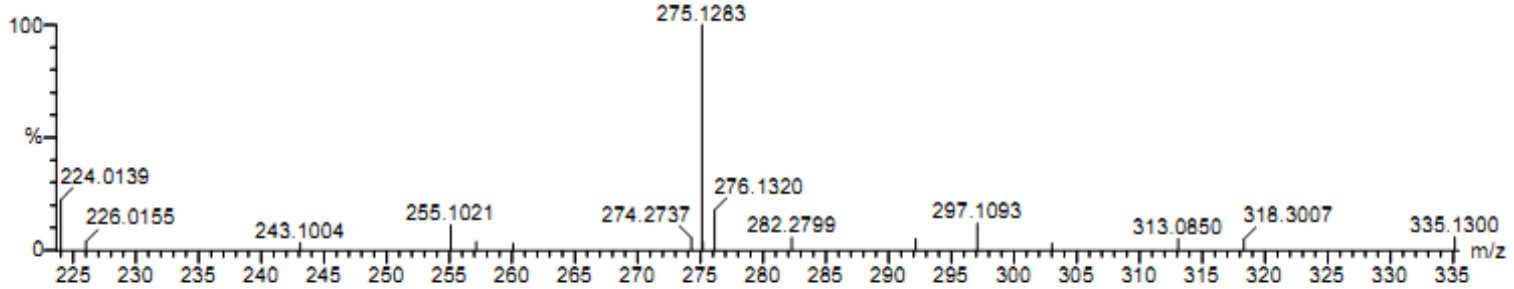
Tolerance = 100.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2



Monoisotopic Mass, Even Electron Ions
33 formula(e) evaluated with 17 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-39 H: 0-60 O: 0-8

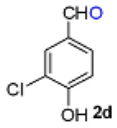
YF-JI ECUST institute of Fine Chem 02-Jan-2013 21:59:41

JYF-JA-105 16 (0.569) Cm (1:16) 1: TOF MS ES+ 9.57e+003

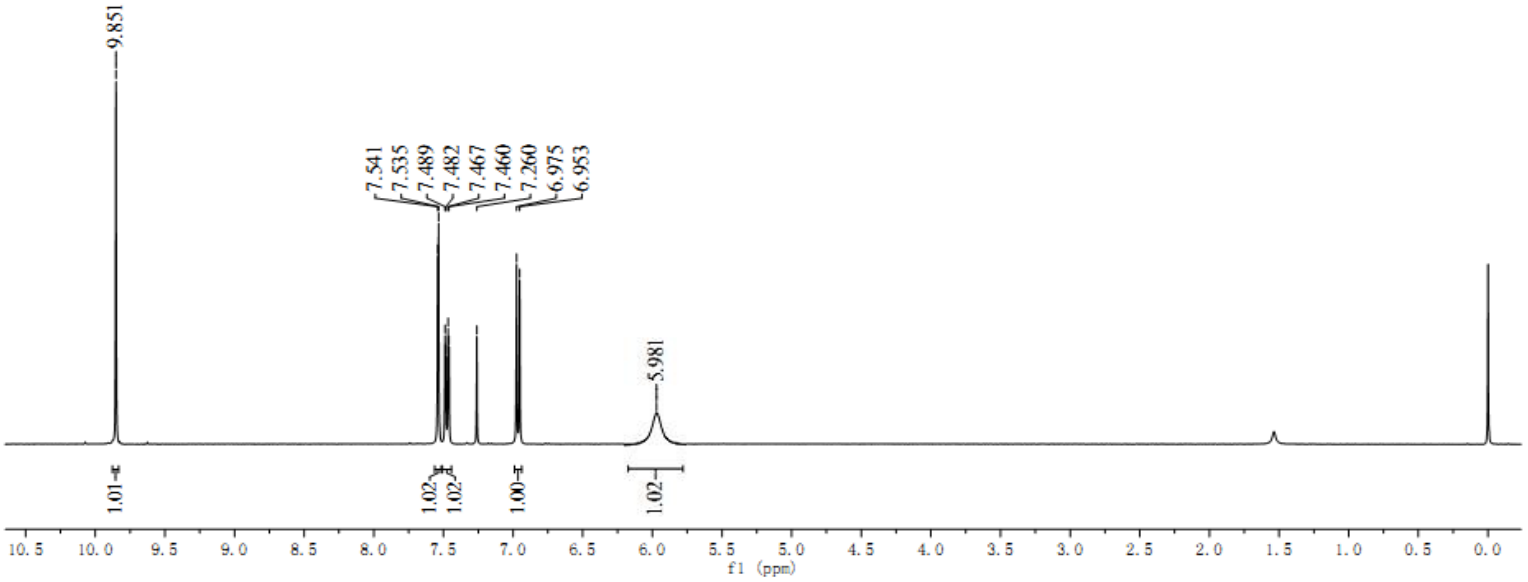


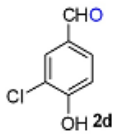
Minimum:				-1.5			
Maximum:		100.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
275.1283	275.1283	0.0	0.0	7.5	18.4	0.0	C16 H19 O4

4.7 Copies of spectra for $Co(OAc)_2{\cdot}4H_2O$-catalyzed oxidation of 1.

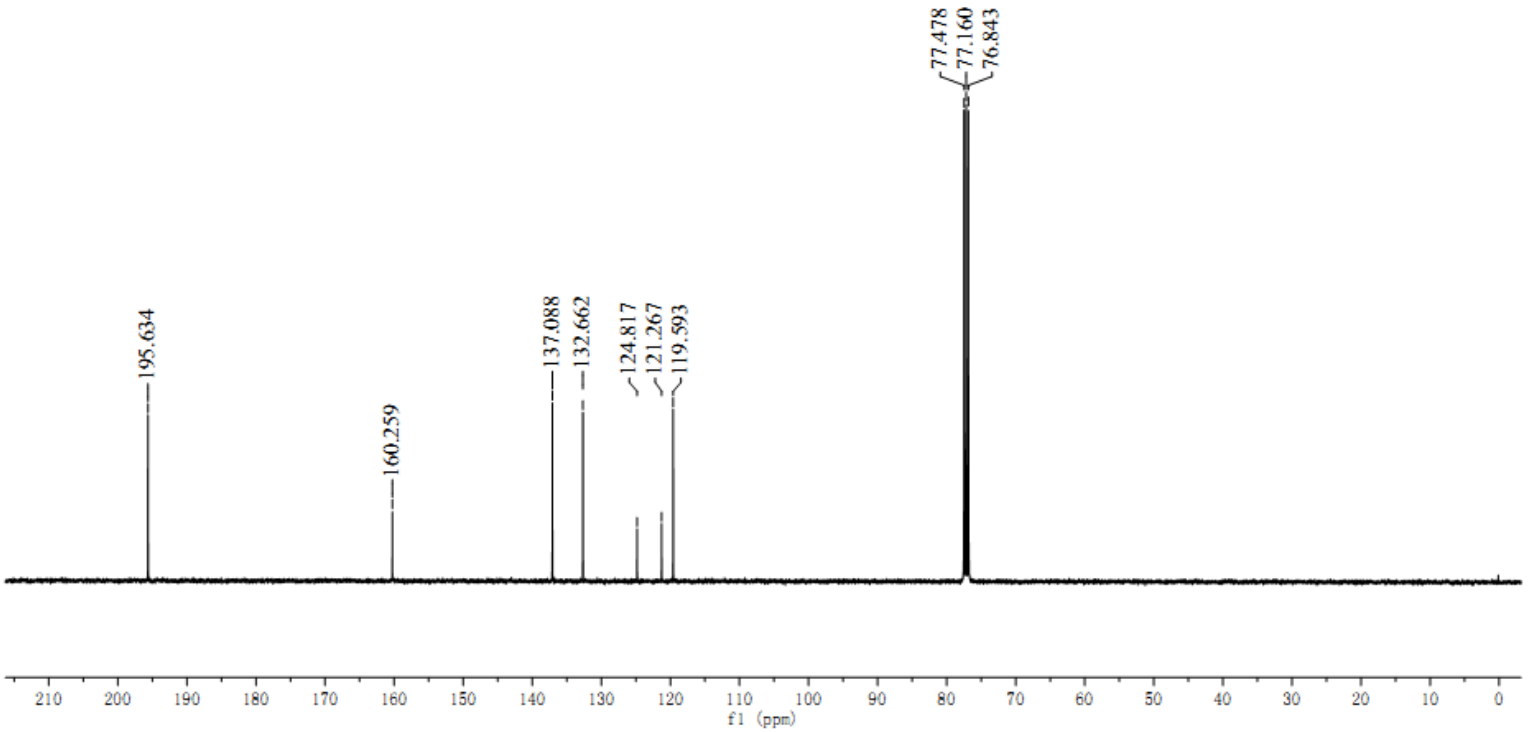


2d

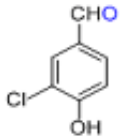



CHO
Cl
OH

2d


195.634
160.259
137.088
132.662
124.817
121.267
119.593
77.478
77.160
76.843
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Elemental Composition Report



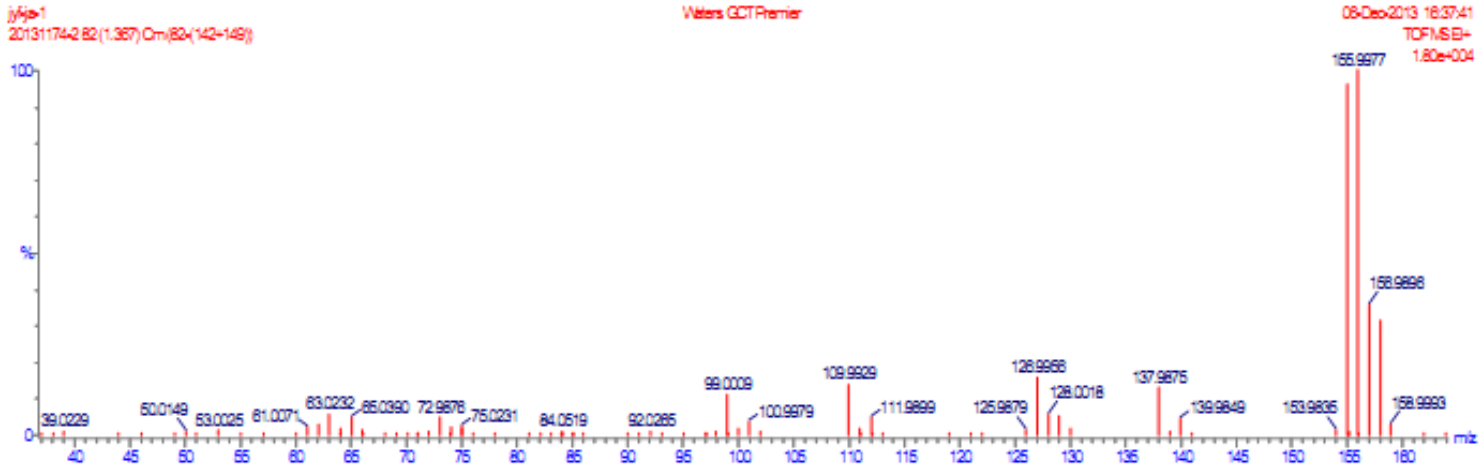
Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50

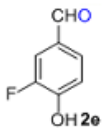
Monoisotopic Mass, Odd and Even Electron Ions

109 formula(e) evaluated with 19 results within limits (up to 50 closest results for each mass)

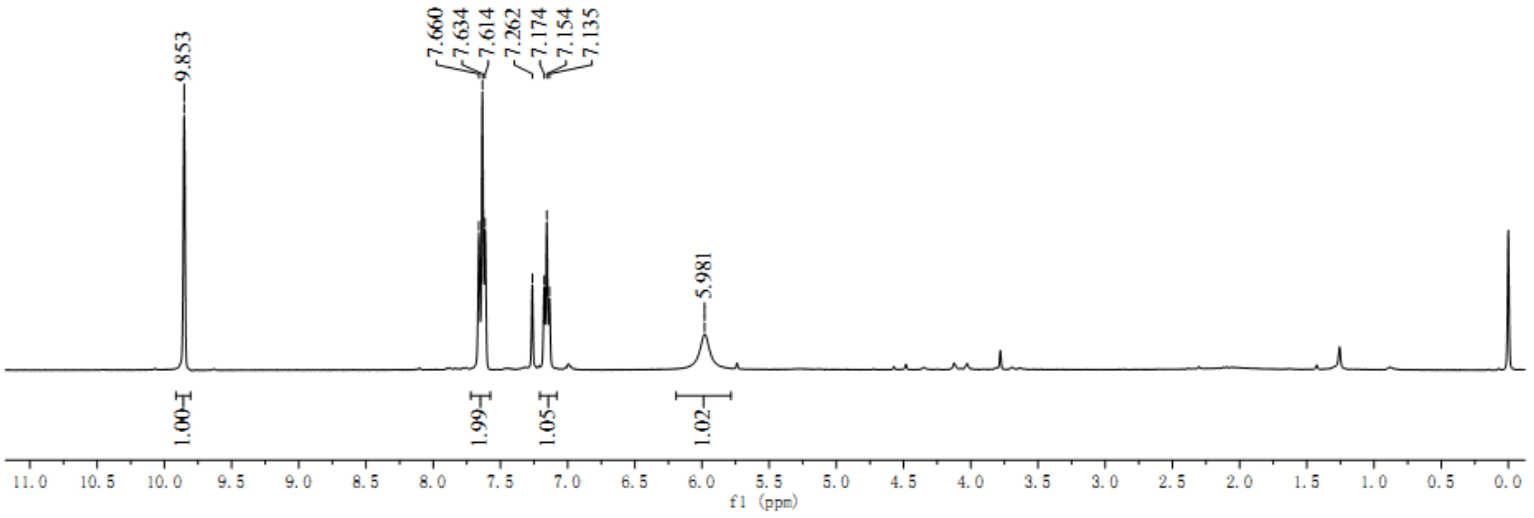
Elements Used: C: 0-7 H: 0-5 O: 0-2 35Cl: 0-1 37Cl: 0-1

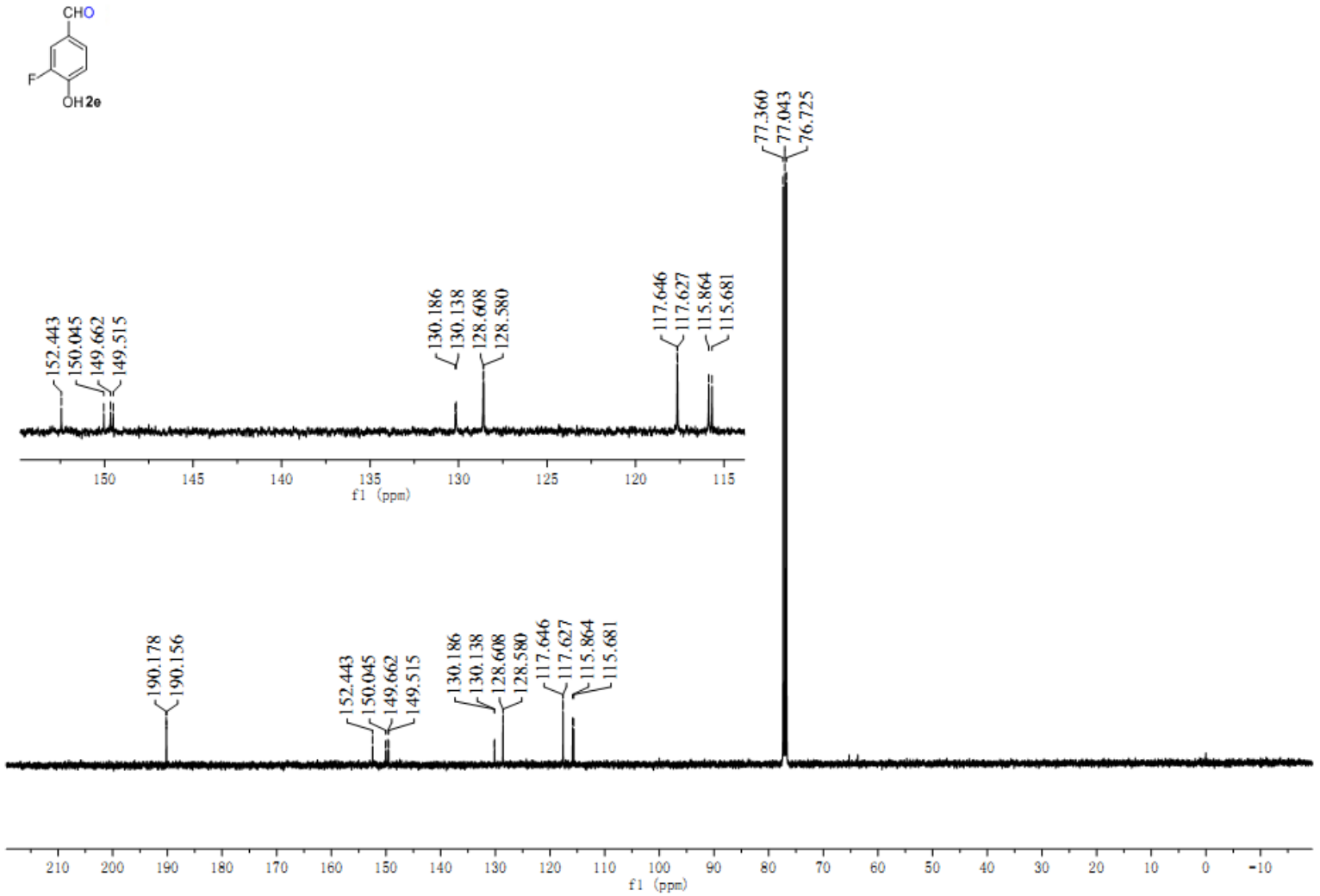


Minimum:		3.00					-1.5		
Maximum:		100.00			5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula		
155.9977	100.00	155.9978	-0.1	-0.6	5.0	2009.1	C7	H5	O2	35Cl

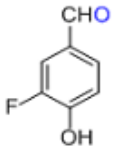

CHO
F
OH

2e


9.853
7.660
7.634
7.614
7.262
7.174
7.154
7.135
5.981
1.00
1.99
1.05
1.02
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
f1 (ppm)


CHO
F
OH 2e
77.360
77.043
76.725
152.443
150.045
149.662
149.515
130.186
130.138
128.608
128.580
117.646
117.627
115.864
115.681
190.178
190.156
f1 (ppm)

Elemental Composition Report

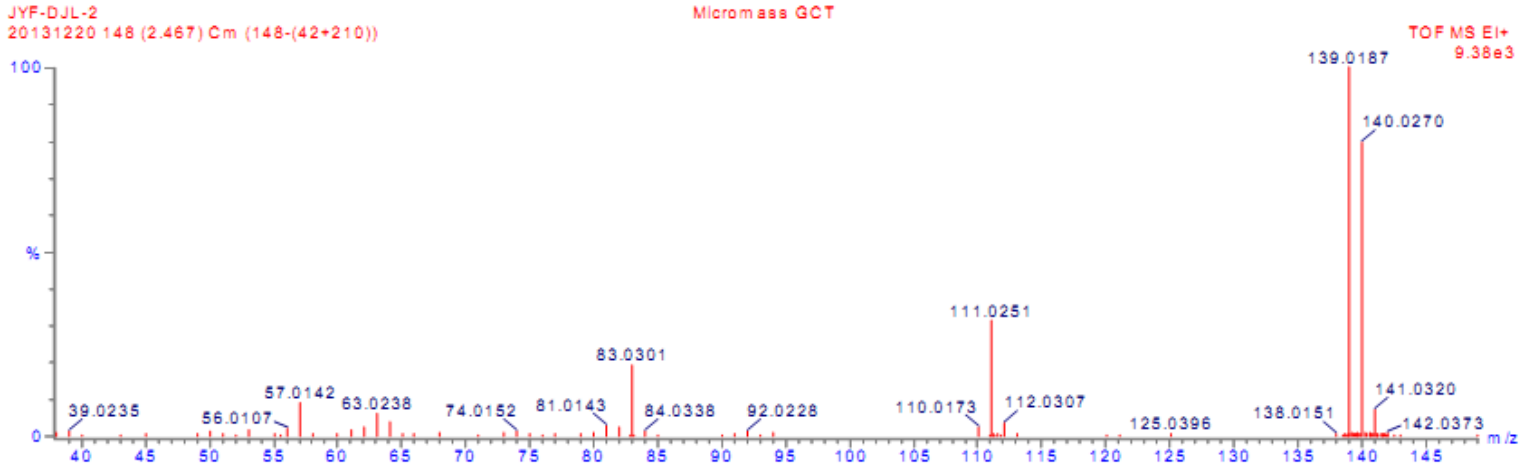


Single Mass Analysis

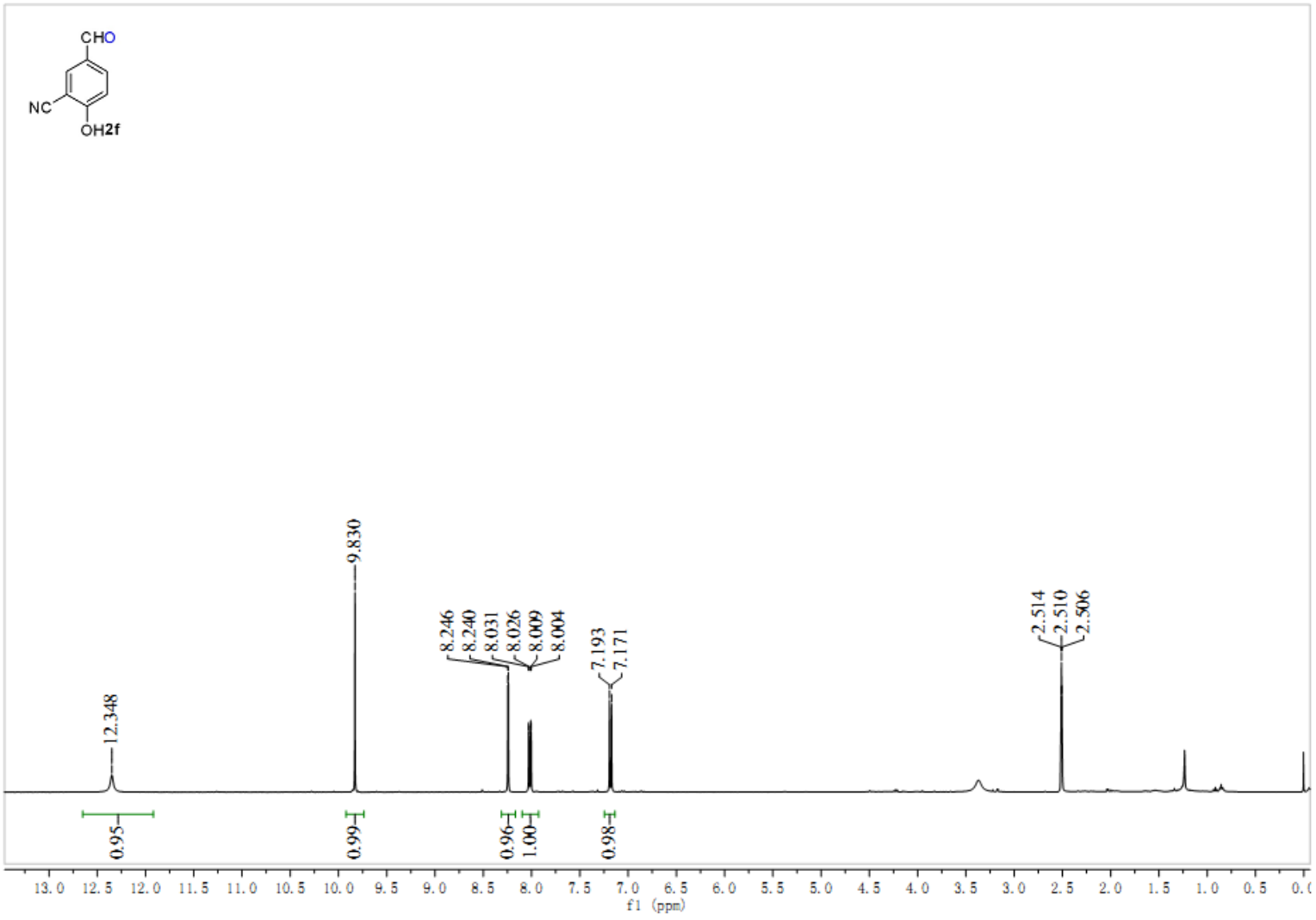
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50

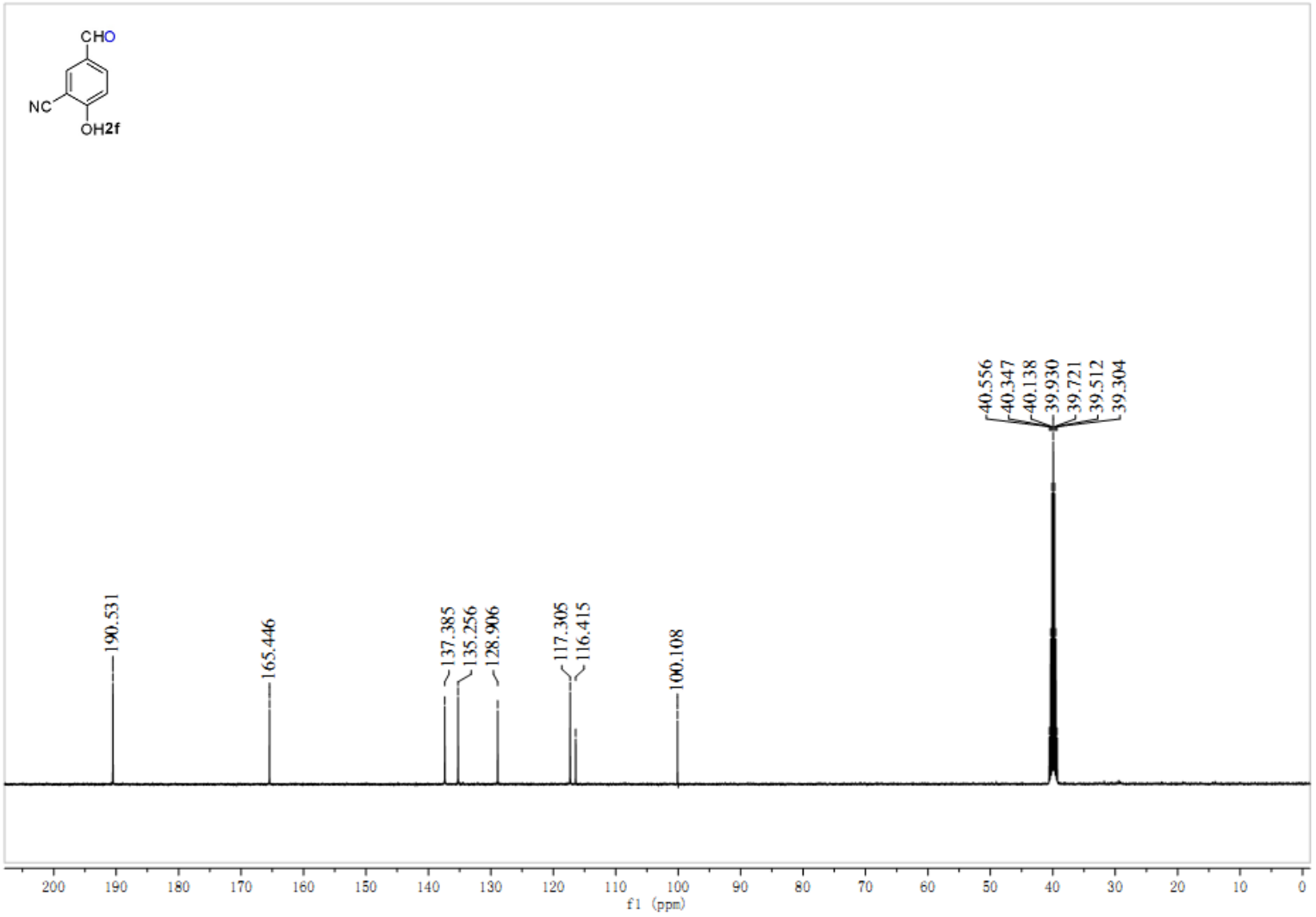
Monoisotopic Mass, Odd and Even Electron Ions

32 formula(e) evaluated with 10 results within limits (up to 50 closest results for each mass)

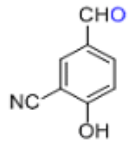


Minimum:	3.00				-1.5		
Maximum:	100.00		5.0		10.0		50.0
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
140.0270	79.65	140.0274	-0.4	-2.6	5.0	1	C7 H5 O2 F


CHO
NC
OH2f
12.348
9.830
8.246
8.240
8.031
8.026
8.009
8.004
7.193
7.171
2.514
2.510
2.506
0.95
0.99
0.96
1.00
0.98
f1 (ppm)


CHO
NC
OH2f
190.531
165.446
137.385
135.256
128.906
117.305
116.415
100.108
40.556
40.347
40.138
39.930
39.721
39.512
39.304
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



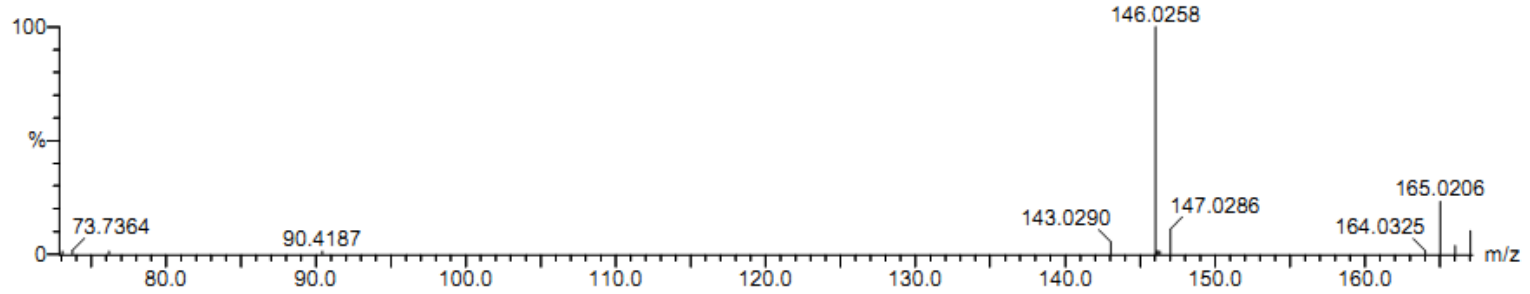
Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

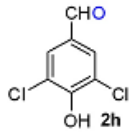
Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 4 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-45 H: 0-70 N: 0-3 O: 0-3

YF-JI ECUST institute of Fine Chem 16-Dec-2013 21:44:39

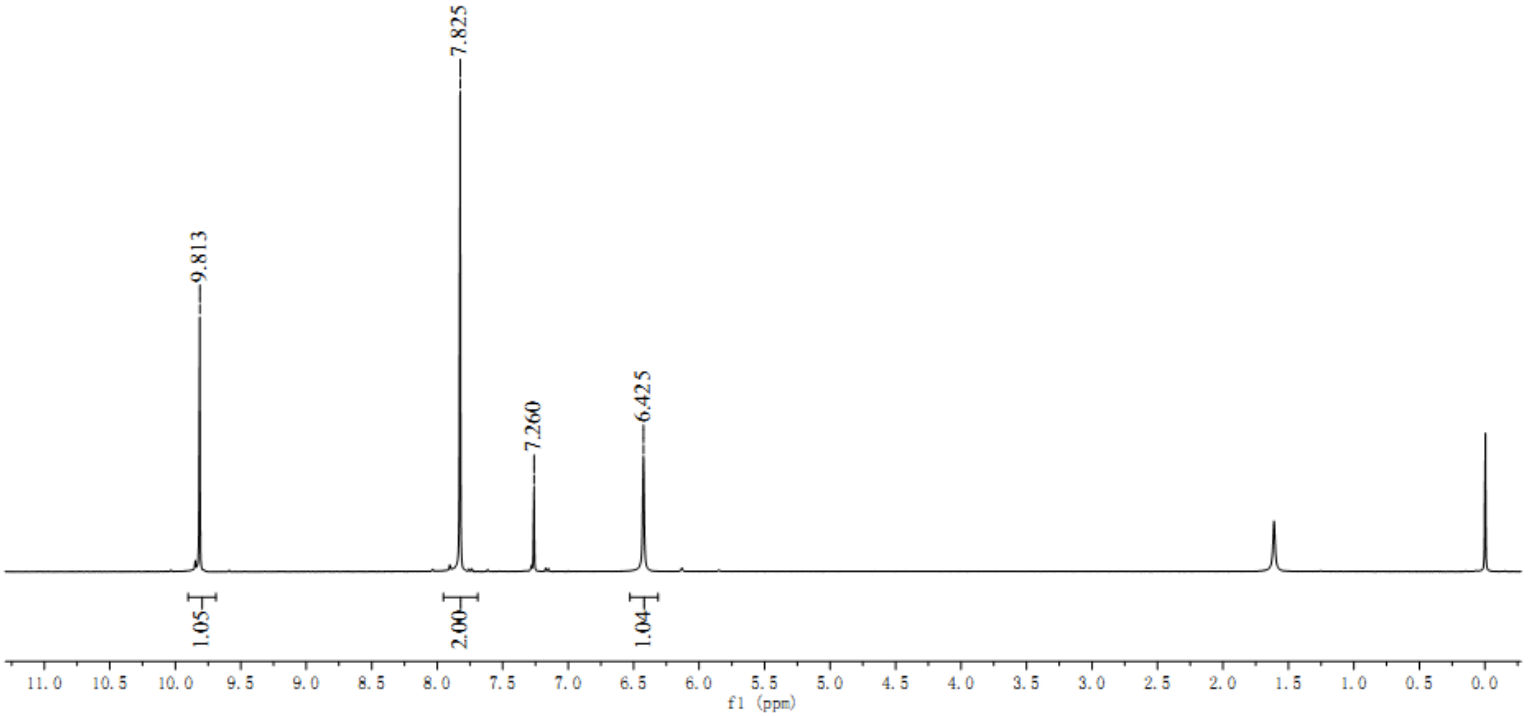
JYF-JA-6 27 (0.934) Cm (27:28) 2: TOF MS ES- 1.12e+003

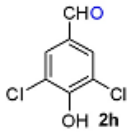


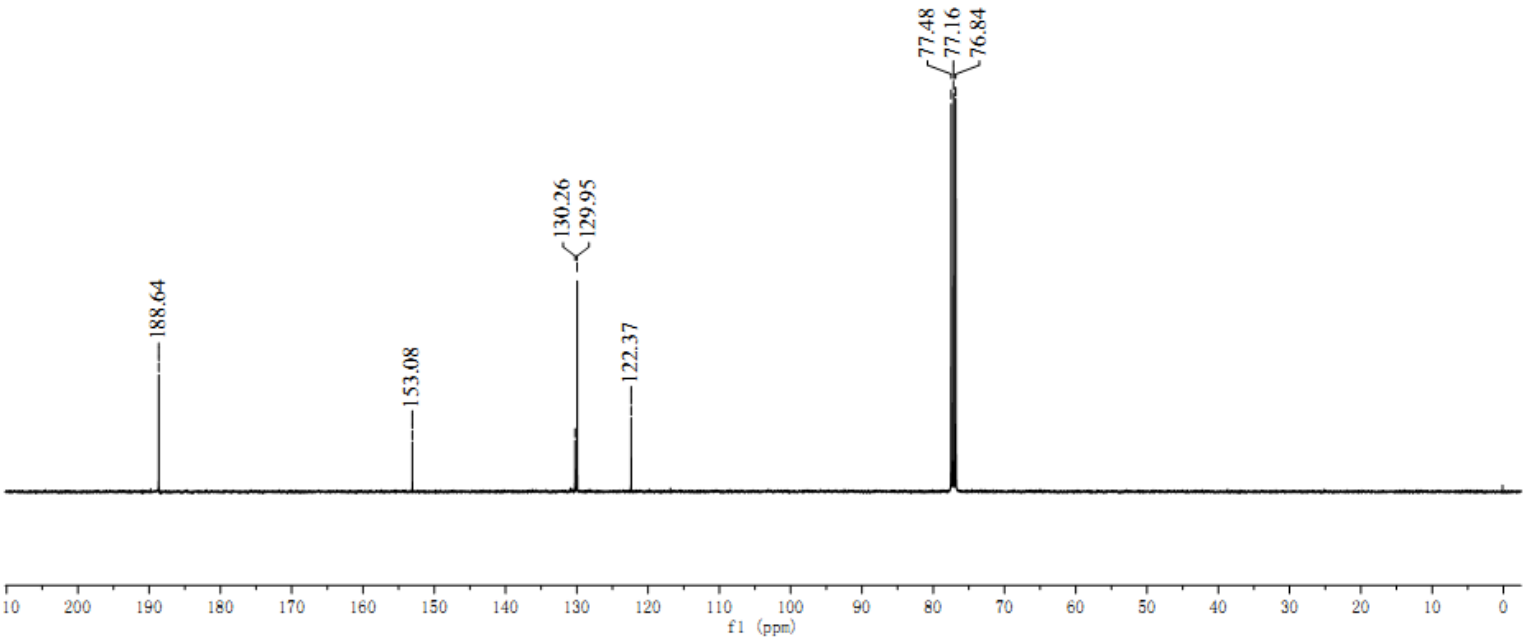
Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
146.0258	146.0242	1.6	11.0	7.5	22.0	0.0	C8 H4 N O2


CHO
Cl
Cl
OH

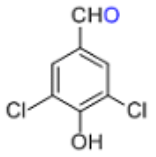
2h


9.813
7.825
7.260
6.425
1.05
2.00
1.04
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
f1 (ppm)


CHO
Cl
Cl
OH
2h


188.64
153.08
130.26
129.95
122.37
77.48
77.16
76.84
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



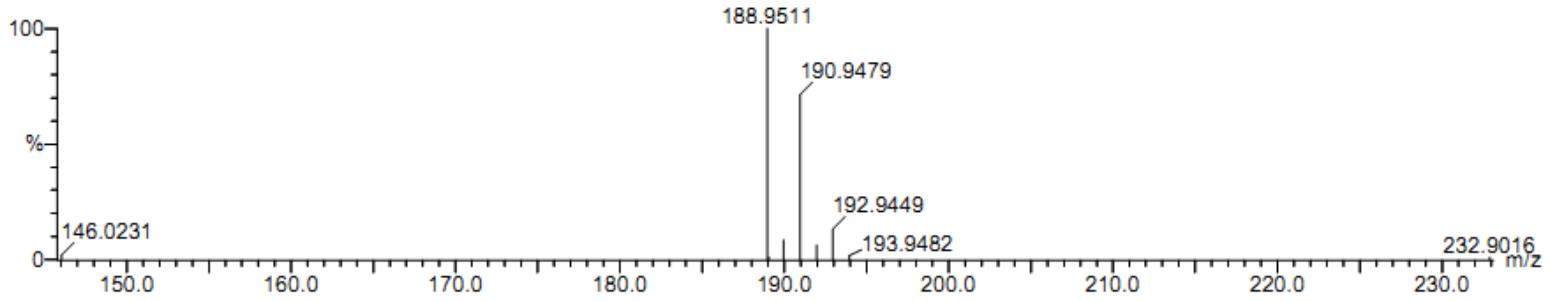
Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
23 formula(e) evaluated with 2 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-45 H: 0-70 O: 0-2 Cl: 0-2

YF-JI ECUST institute of Fine Chem 16-Dec-2013 21:34:38

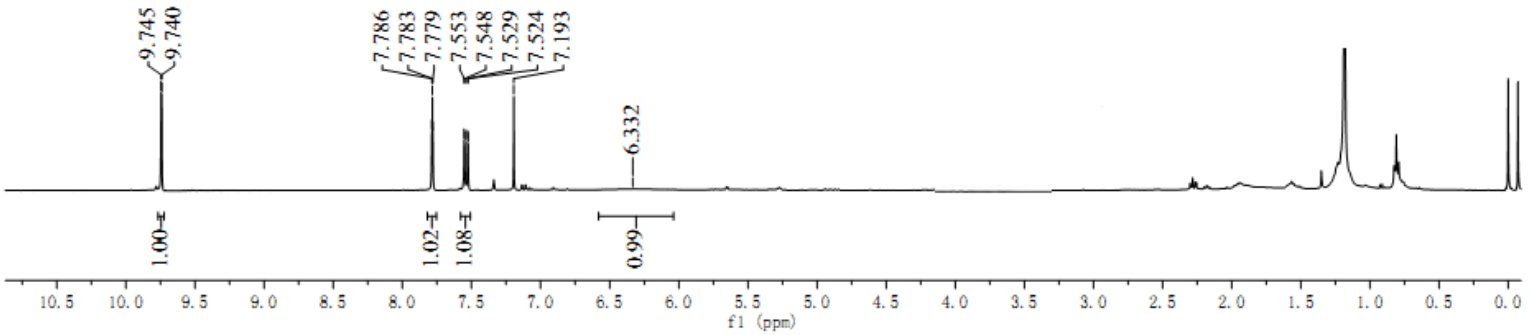
JYF-JA-2 5 (0.271) Cm (4:8) 2: TOF MS ES- 6.89e+003



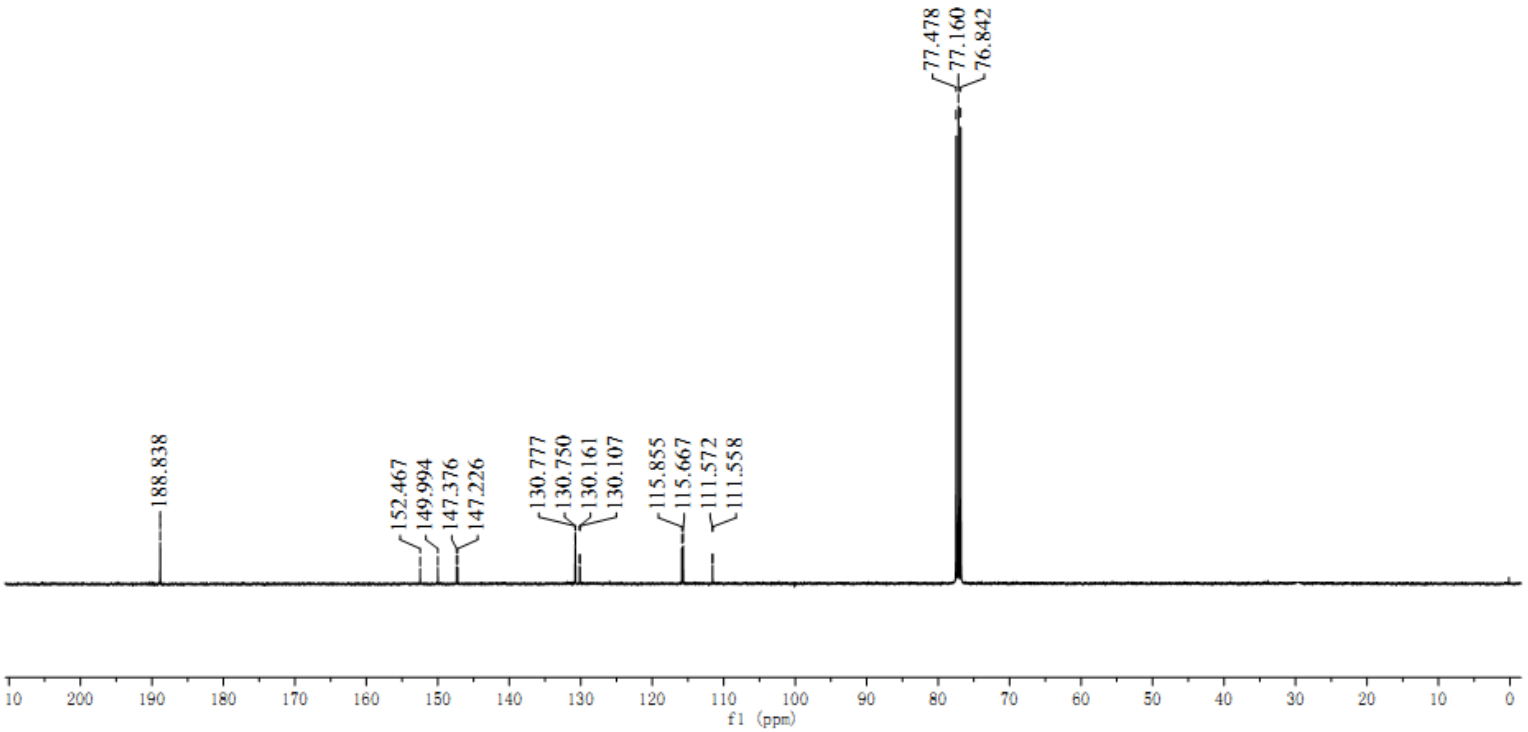
Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
188.9511	188.9510	0.1	0.5	5.5	14.8	0.0	C7 H3 O2 Cl2


CHO
F
Br
OH

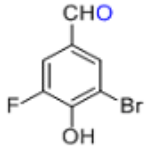
2i


9.745
9.740
7.786
7.783
7.779
7.553
7.548
7.529
7.524
7.193
6.332
1.00
1.02
1.08
0.99
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)


CHO
F
Br
OH
2i


188.838
152.467
149.994
147.376
147.226
130.777
130.750
130.161
130.107
115.855
115.667
111.572
111.558
77.478
77.160
76.842
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



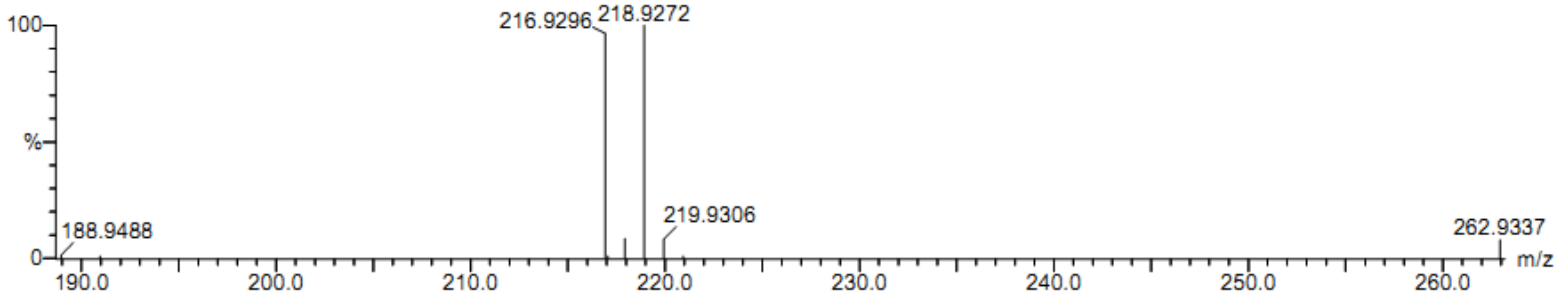
Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

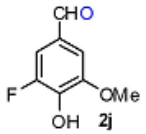
Monoisotopic Mass, Even Electron Ions
68 formula(e) evaluated with 7 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-45 H: 0-70 O: 0-2 Br: 0-2 F: 0-3

YF-JI ECUST institute of Fine Chem 16-Dec-2013 21:36:55

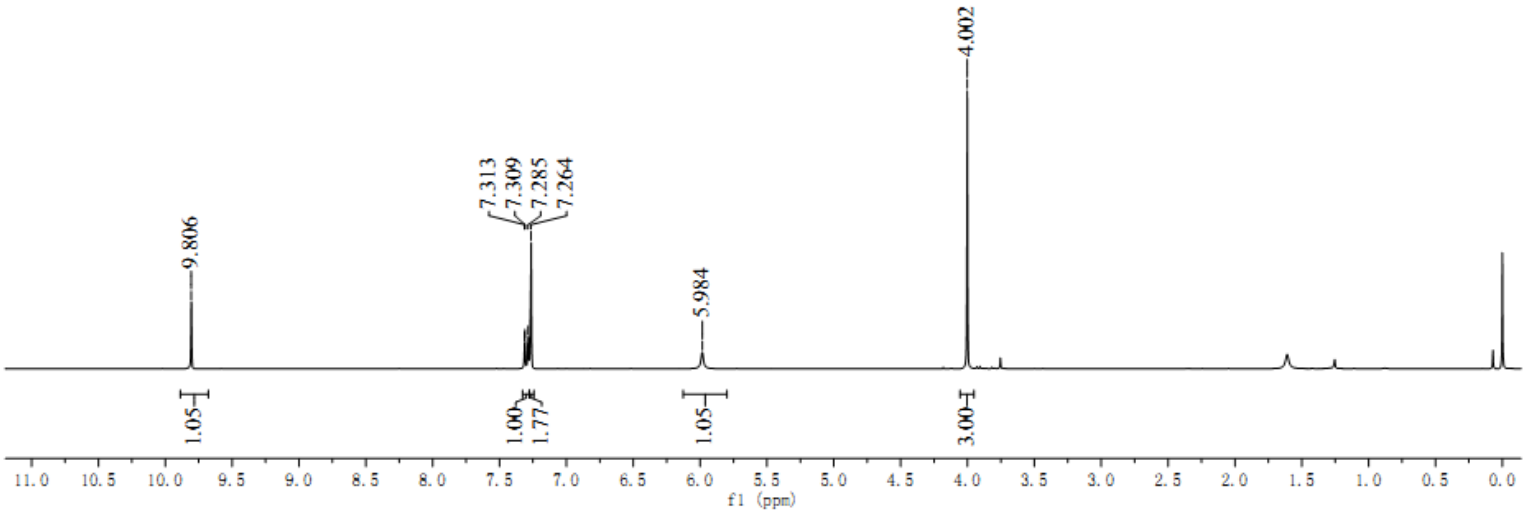
JYF-JA-3 10 (0.419) Cm (9:11) 2: TOF MS ES- 4.75e+003

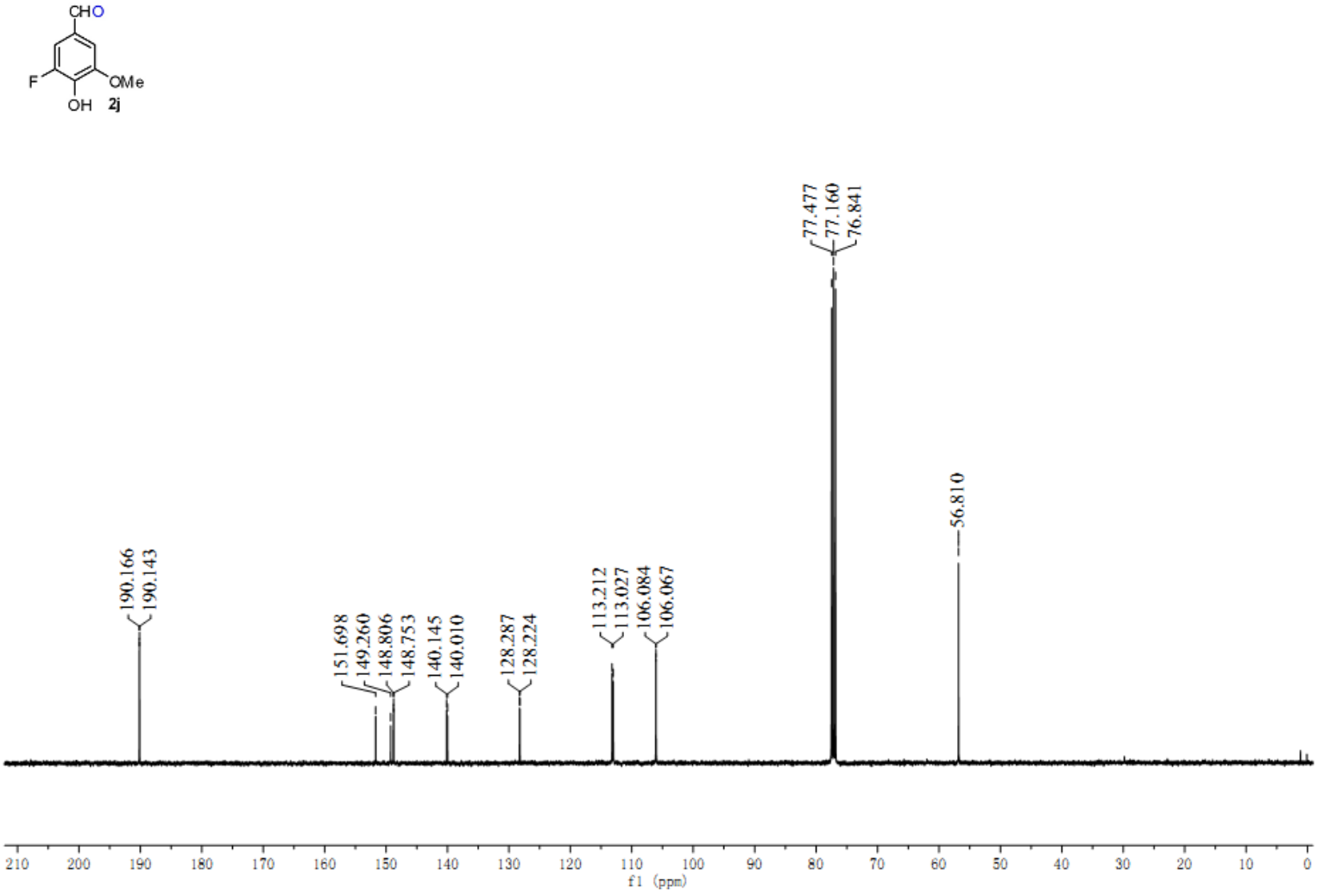


Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
216.9296	216.9300	-0.4	-1.8	5.5	13.8	0.0	C7 H3 O2 Br F

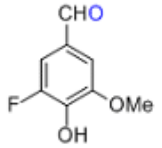

CHO
F
OMe
OH

2j


9.806
7.313
7.309
7.285
7.264
5.984
4.002
1.05
1.00
1.77
1.05
3.00
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
f1 (ppm)


CHO
F
OMe
OH
2j
190.166
190.143
151.698
149.260
148.806
148.753
140.145
140.010
128.287
128.224
113.212
113.027
106.084
106.067
77.477
77.160
76.841
56.810
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



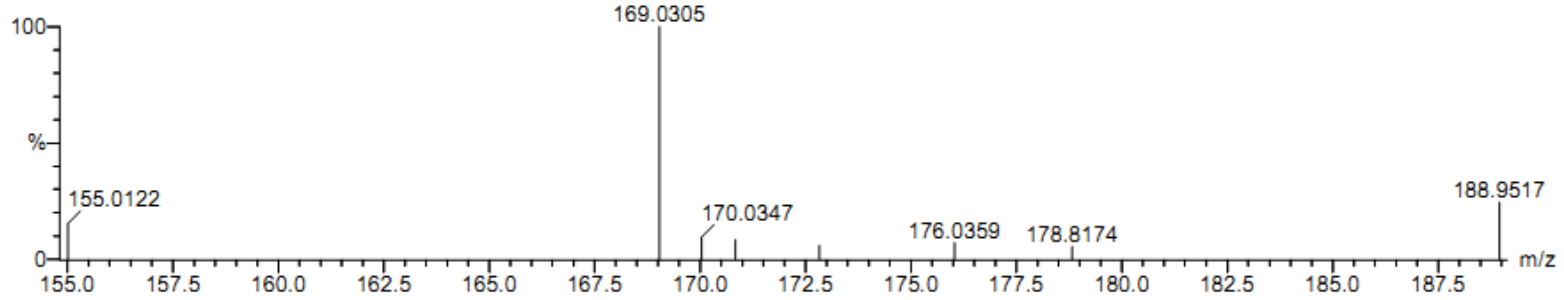
Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

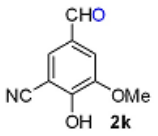
Monoisotopic Mass, Even Electron Ions
37 formula(e) evaluated with 10 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-45 H: 0-70 O: 0-3 F: 0-3

YF-JI ECUST institute of Fine Chem 16-Dec-2013 21:39:51

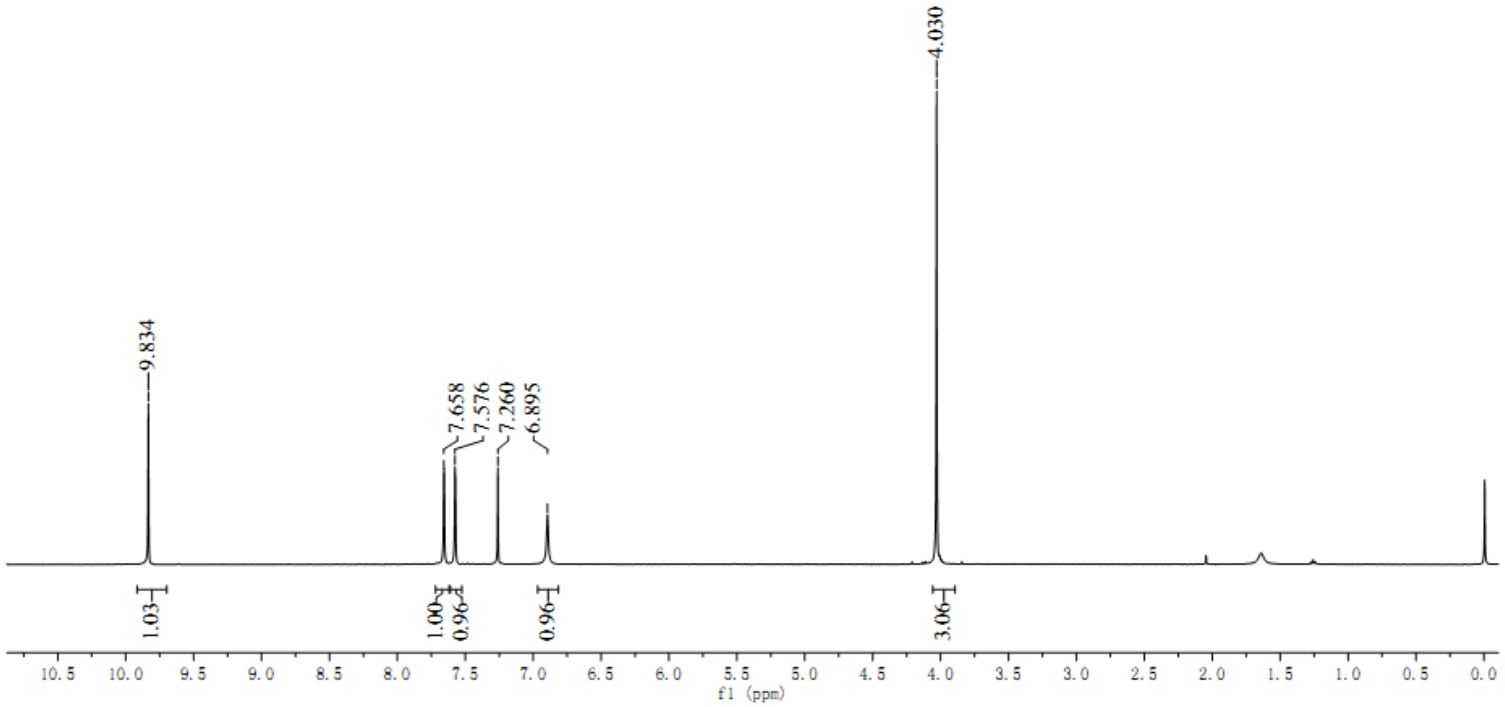
JYF-JA-4 12 (0.466) Cm (7:14) 2: TOF MS ES- 2.67e+003

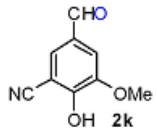


Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
169.0305	169.0301	0.4	2.4	5.5	5.4	0.0	C8 H6 O3 F

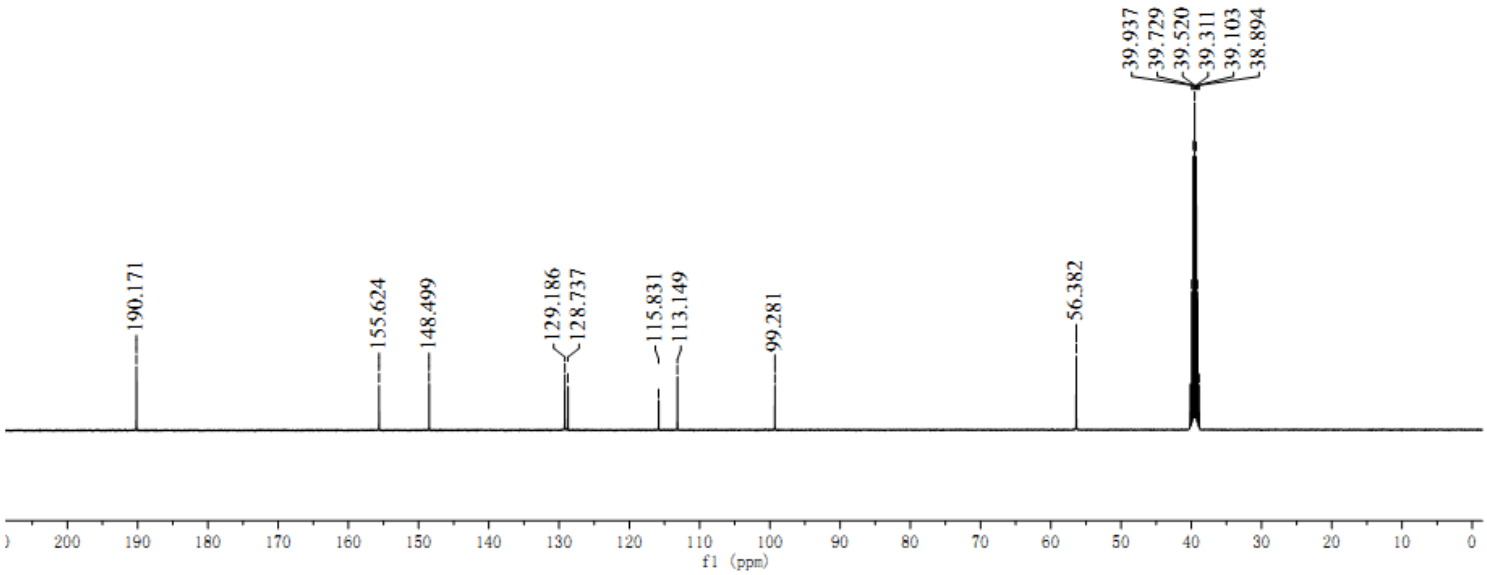

CHO
NC
OMe
OH

2k

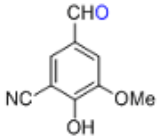

9.834
7.658
7.576
7.260
6.895
4.030
1.03
1.00
0.96
0.96
3.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CHO
NC
OMe
OH

2k


190.171
155.624
148.499
129.186
128.737
115.831
113.149
99.281
56.382
39.937
39.729
39.520
39.311
39.103
38.894
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



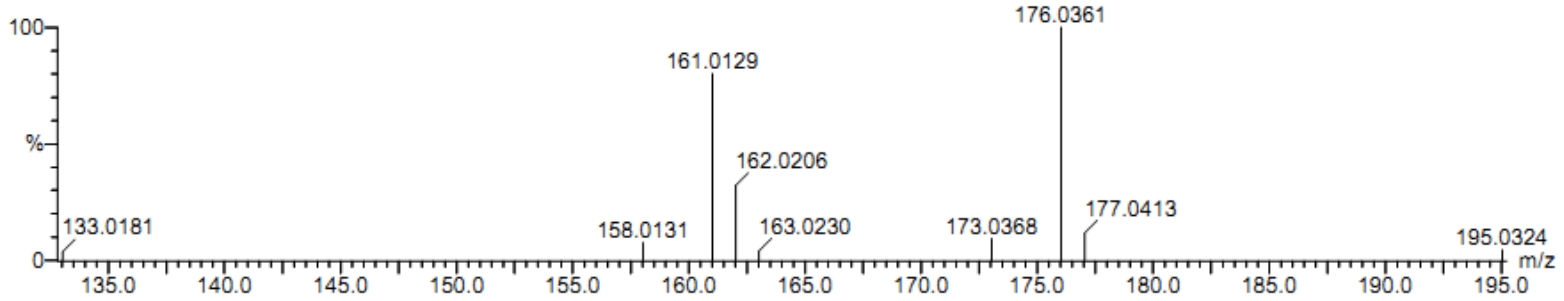
Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
40 formula(e) evaluated with 6 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-45 H: 0-70 N: 0-3 O: 0-3

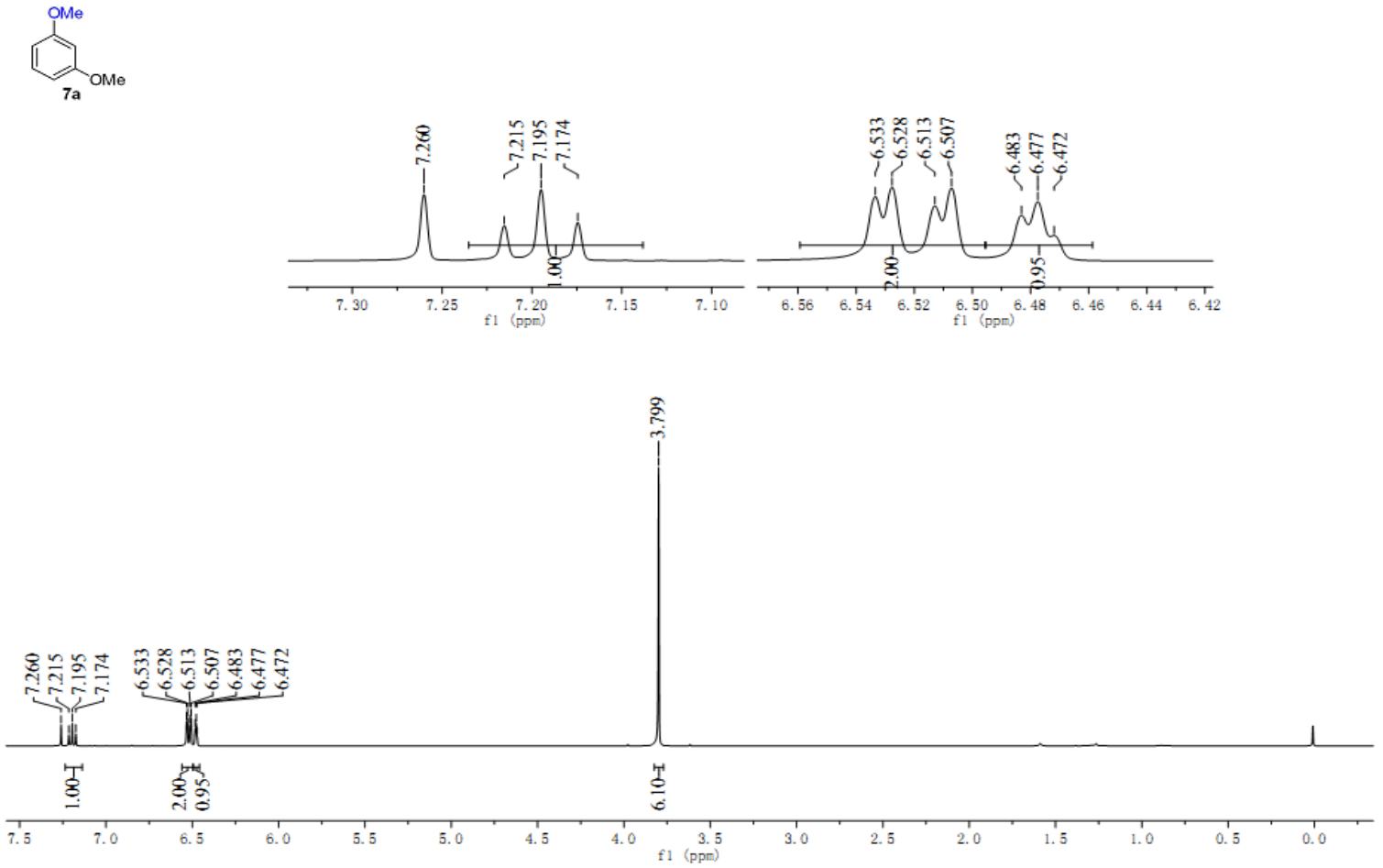
YF-JI ECUST institute of Fine Chem 16-Dec-2013 21:41:57

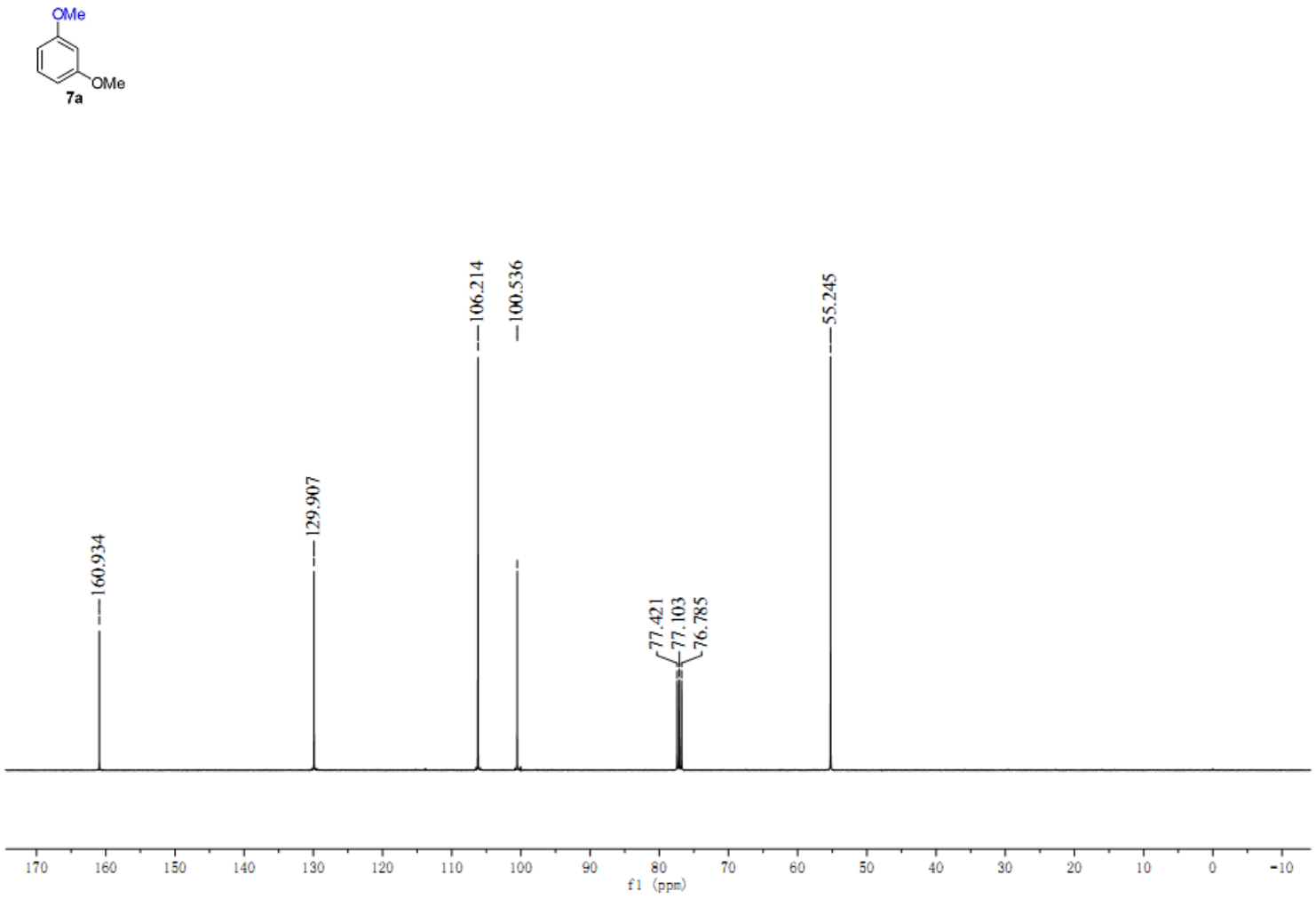
JYF-JA-5 17 (0.639) Cm (17:20) 2: TOF MS ES- 2.74e+003



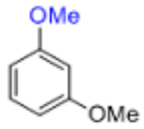
Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
176.0361	176.0348	1.3	7.4	7.5	8.3	0.0	C9 H6 N O3

4.8 Copies of spectra for CuCl/HCOOMe-catalyzed methoxylation.




OMe
OMe
7a
160.934
129.907
106.214
100.536
77.421
77.103
76.785
55.245
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Elemental Composition Report



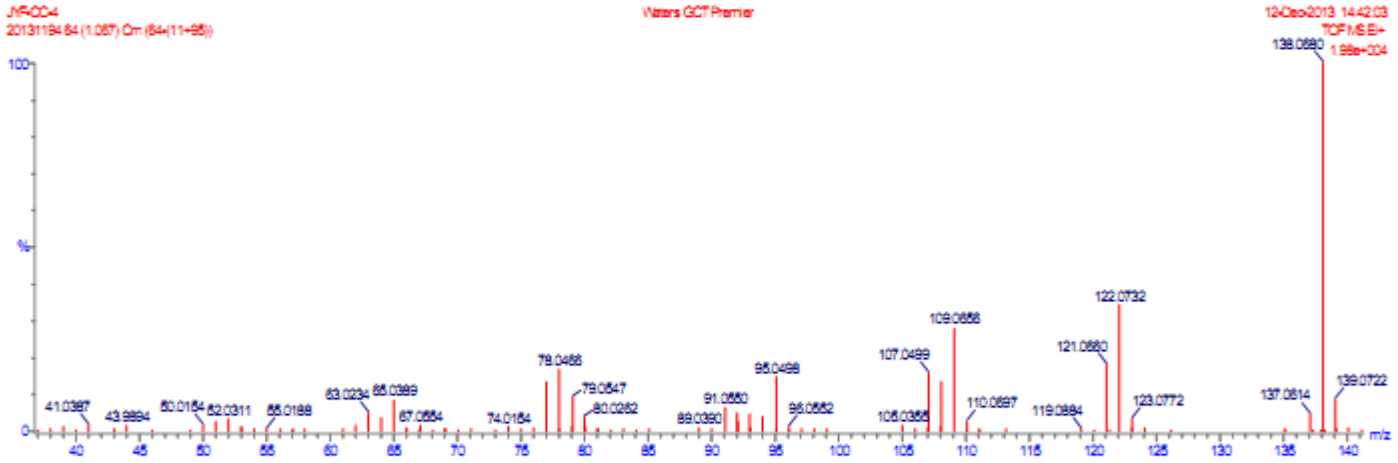
Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50

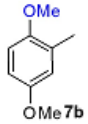
Monoisotopic Mass, Odd and Even Electron Ions

63 formula(e) evaluated with 23 results within limits (up to 50 closest results for each mass)

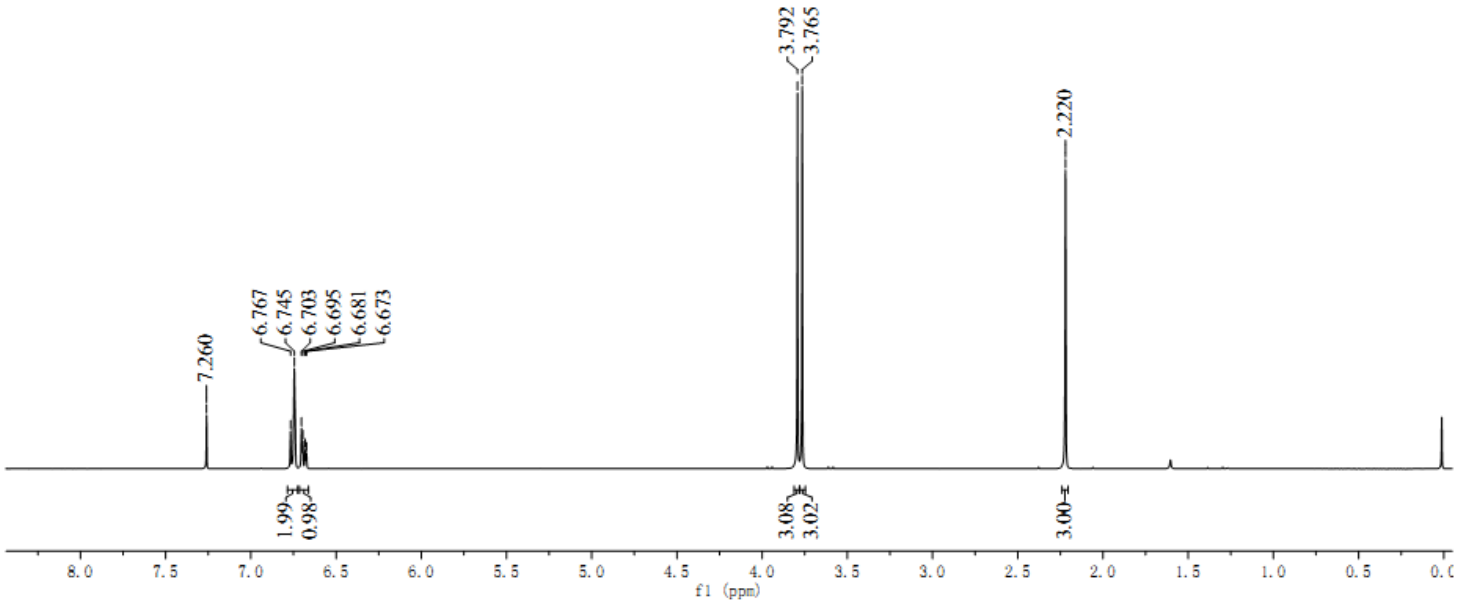
Elements Used: C: 0-8 H: 0-10 O: 0-2

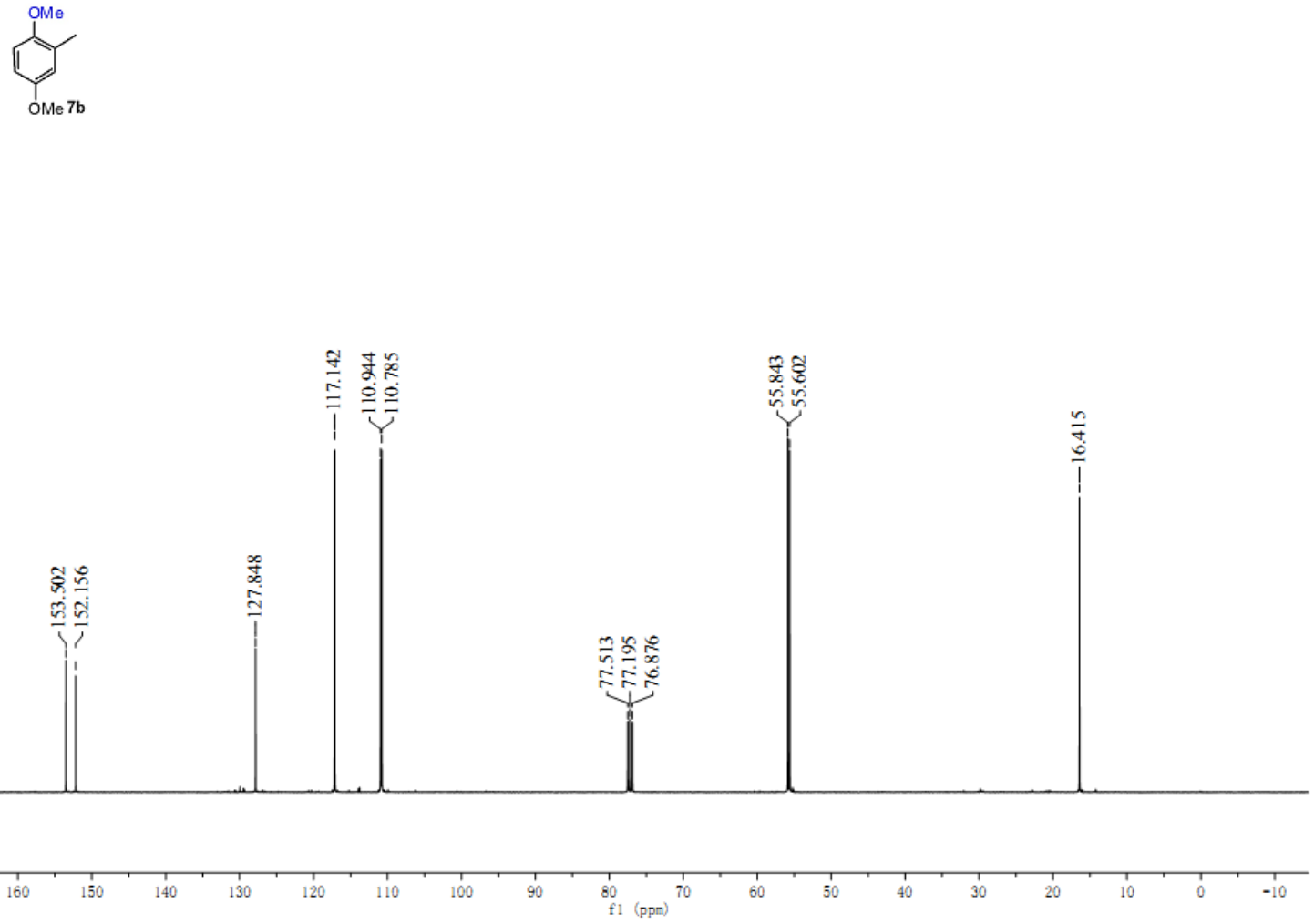


Minimum:	3.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
138.0680	100.00	138.0681	-0.1	-0.7	4.0	4.9	C8 H10 O2

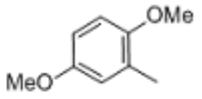

OMe
OMe

7b


7.260
6.767
6.745
6.703
6.695
6.681
6.673
3.792
3.765
2.220
1.99
0.98
3.08
3.02
3.00
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
f1 (ppm)


OMe
OMe
7b
153.502
152.156
127.848
117.142
110.944
110.785
77.513
77.195
76.876
55.843
55.602
16.415
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Elemental Composition Report



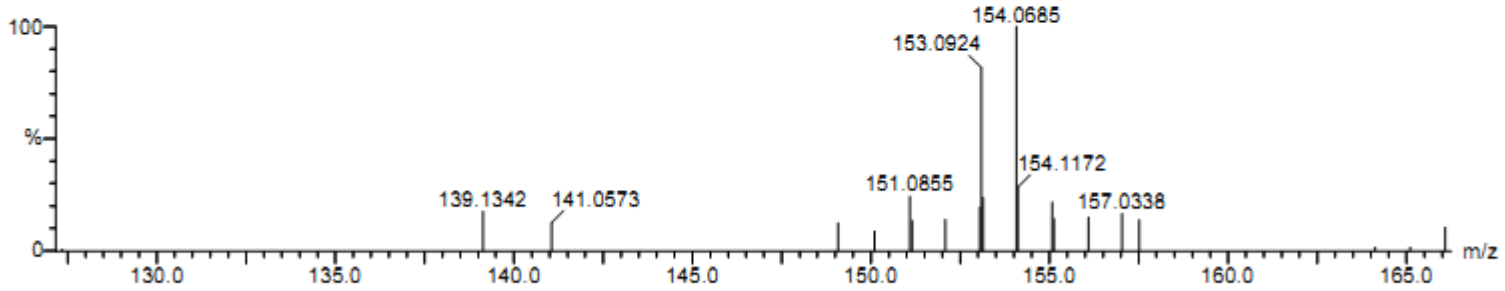
Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

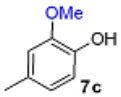
Monoisotopic Mass, Odd and Even Electron Ions
19 formula(e) evaluated with 4 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-35 H: 0-100 O: 0-10

YF-JI ECUST institute of Fine Chem 13-Nov-2013 16:19:07

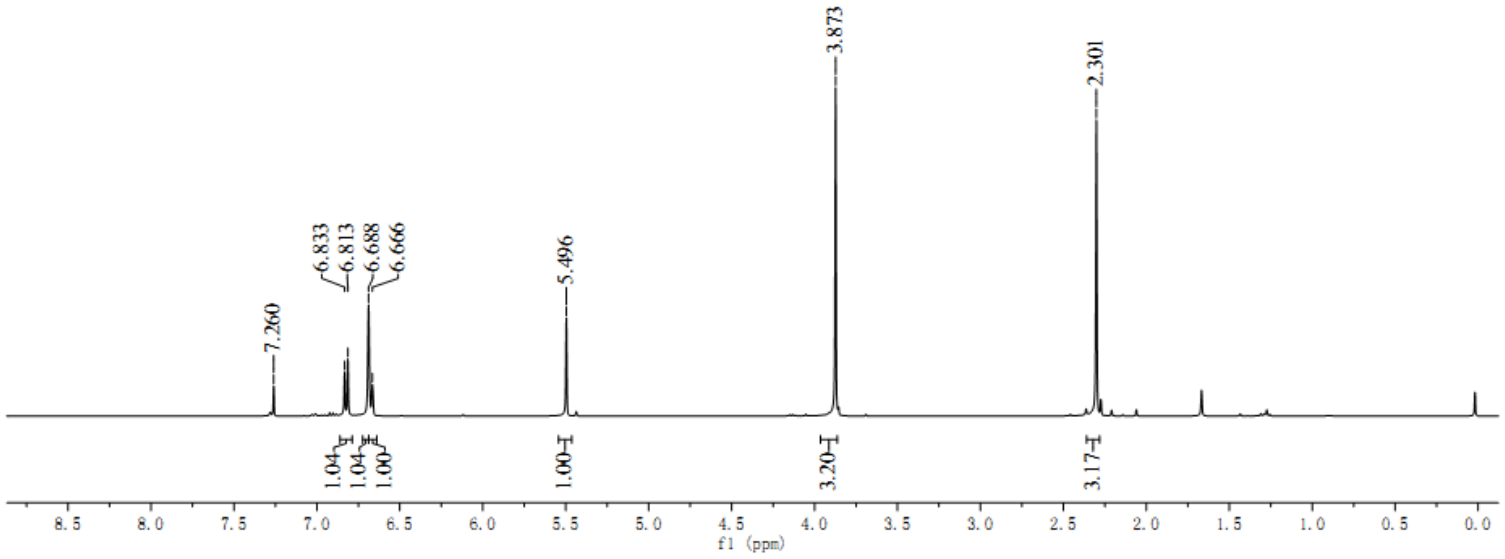
JYF-JA-1 110 (0.775) Cm (109:122) 1: TOF MS ES+ 5.82e+002

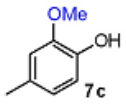


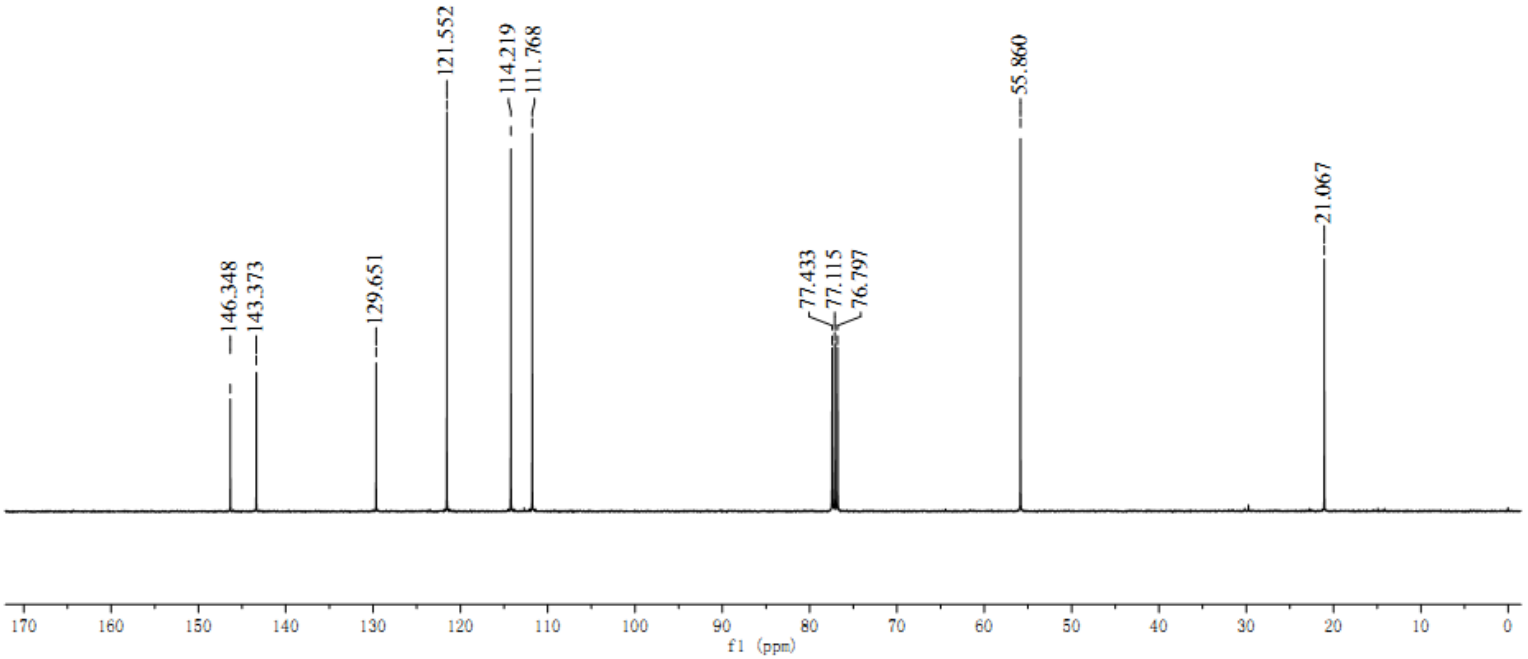
Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
153.0924	153.0916	0.8	5.2	3.5	42.0	0.0	C9 H13 O2


OMe
OH

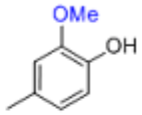
7c


7.260
6.833
6.813
6.688
6.666
5.496
3.873
2.301
1.04
1.04
1.00
1.00
3.20
3.17
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)


OMe
OH
7c


146.348
143.373
129.651
121.552
114.219
111.768
77.433
77.115
76.797
55.860
21.067
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



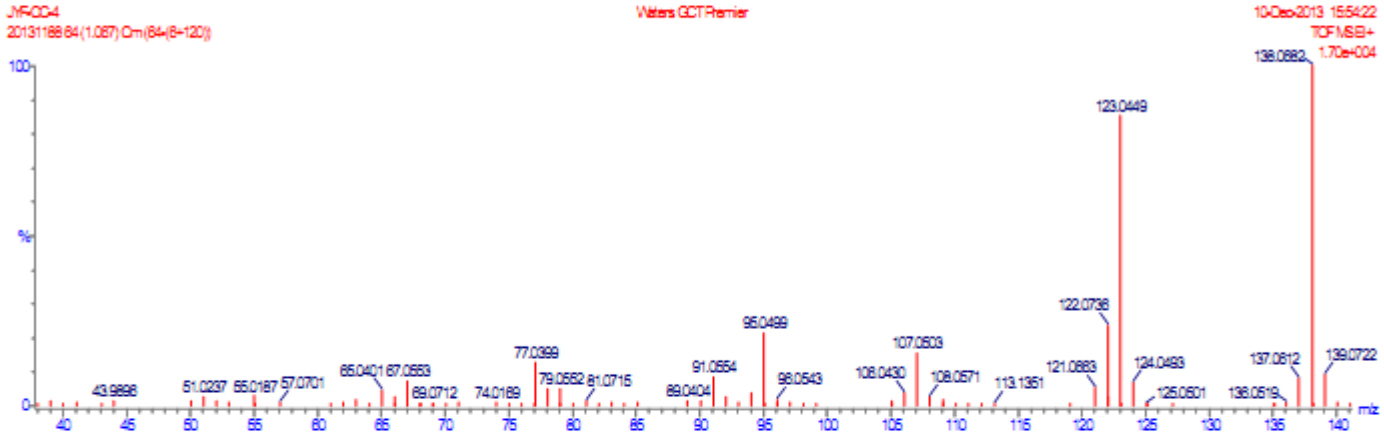
Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50

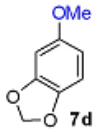
Monoisotopic Mass, Odd and Even Electron Ions

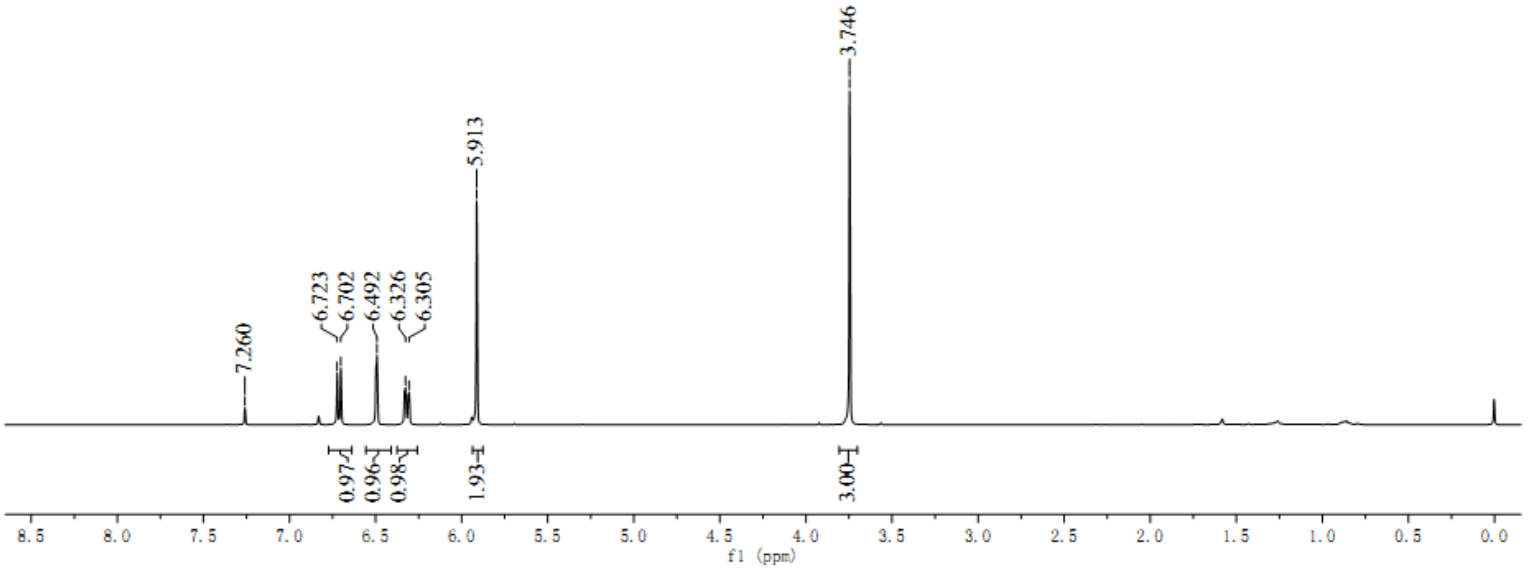
40 formula(e) evaluated with 16 results within limits (up to 50 closest results for each mass)

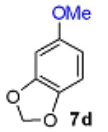
Elements Used: C: 0-8 H: 0-10 O: 0-2

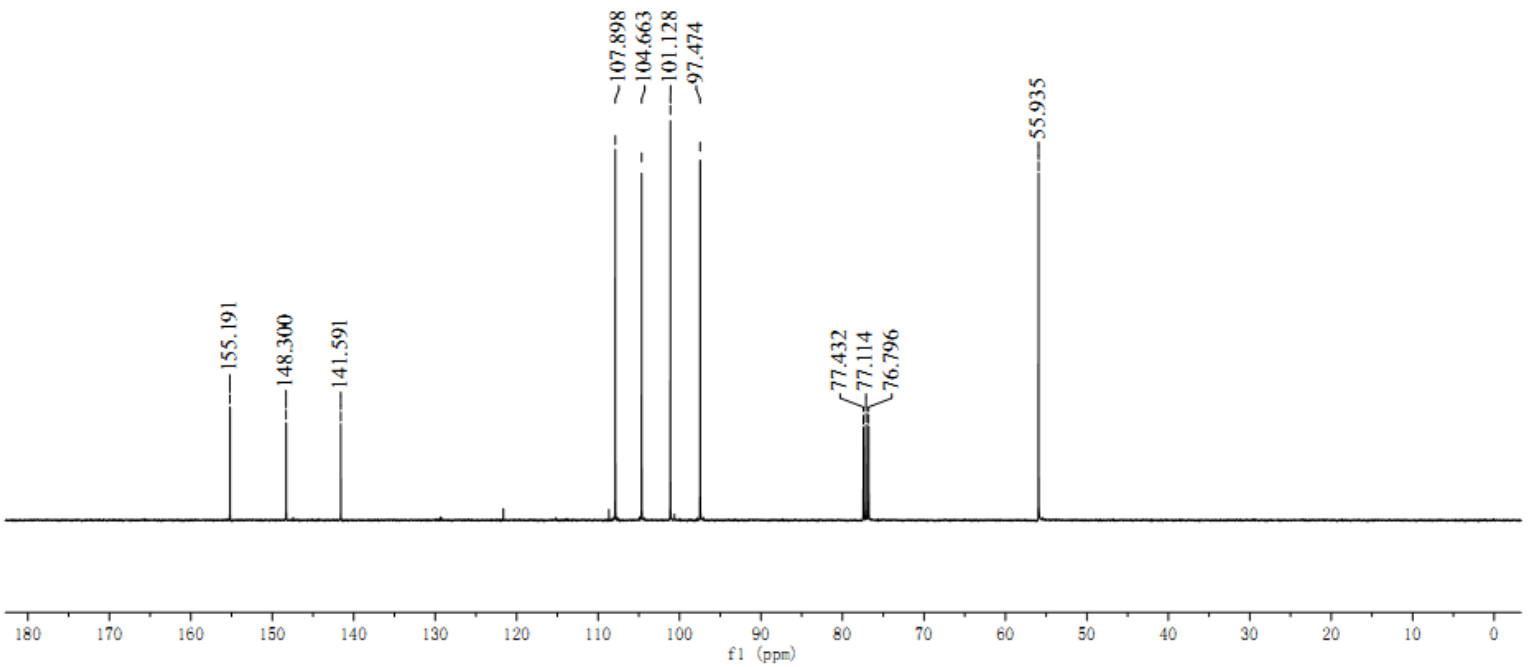


Minimum:	3.00				-1.5		
Maximum:	100.00		5.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
138.0682	100.00	138.0681	0.1	0.7	4.0	1.8	C8 H10 O2

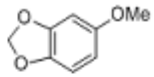

OMe
O
O
7d


7.260
6.723
6.702
6.492
6.326
6.305
5.913
3.746
0.97
0.96
0.98
1.93
3.00
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)


OMe
O
O
7d


155.191
148.300
141.591
107.898
104.663
101.128
97.474
77.432
77.114
76.796
55.935
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



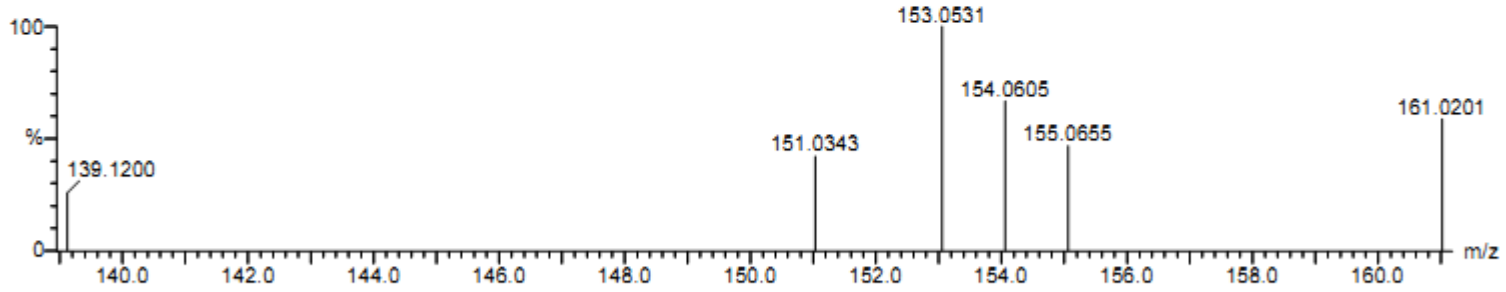
Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

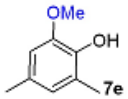
Monoisotopic Mass, Even Electron Ions
10 formula(e) evaluated with 3 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-35 H: 0-50 O: 0-3

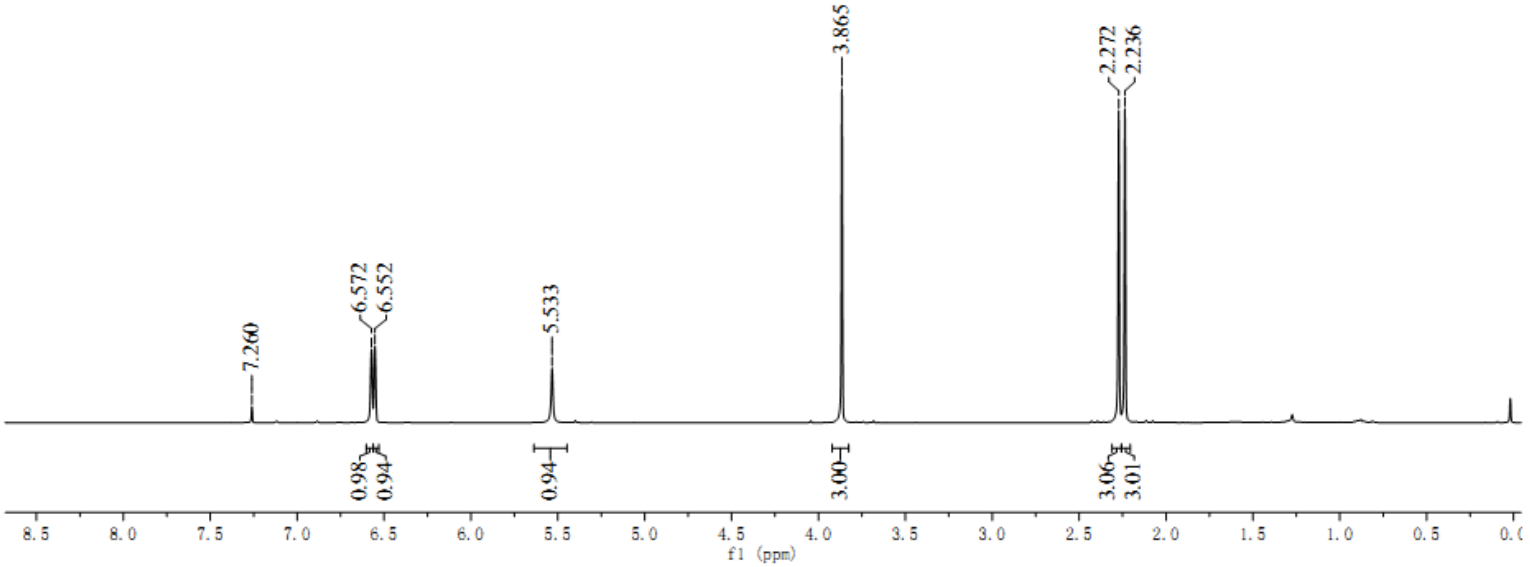
YF-JI ECUST institute of Fine Chem 15-Nov-2013 12:51:21

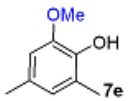
JYF-JA-4 2 (0.160) Cm (1:5) 1: TOF MS ES+ 8.68e+001

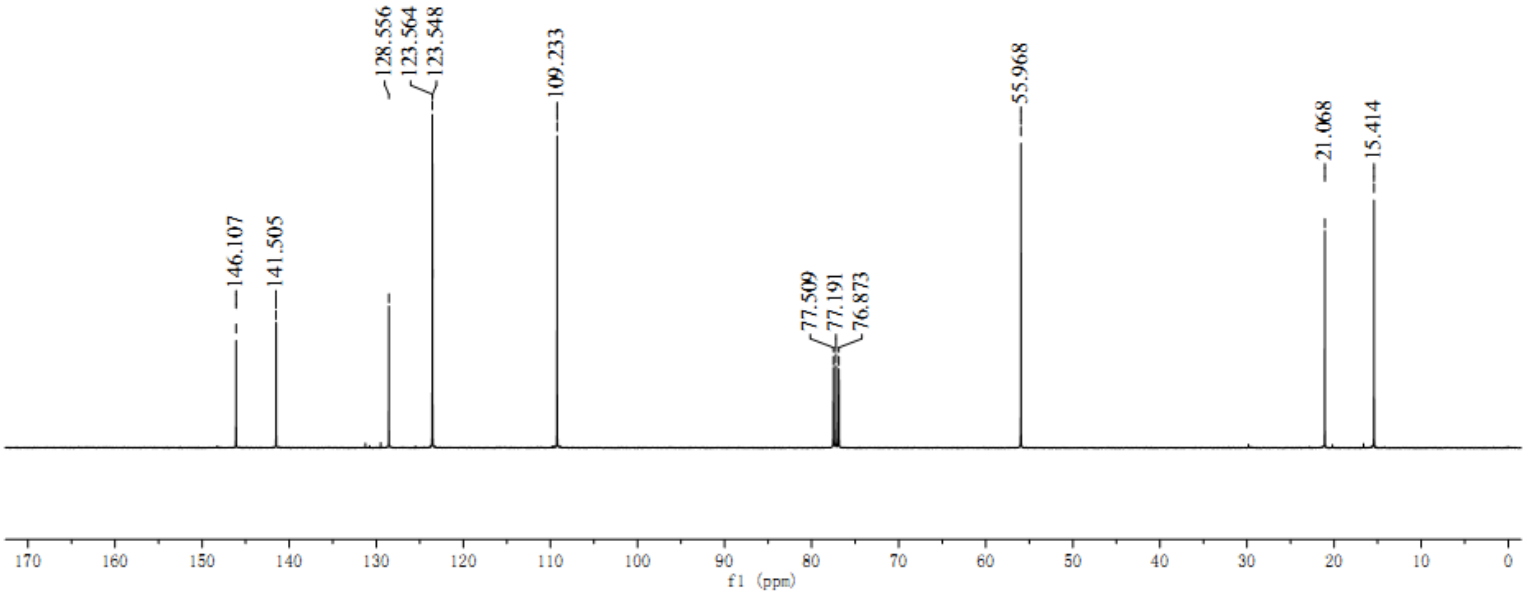


Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
153.0531	153.0552	-2.1	-13.7	4.5	11.8	0.0	C8 H9 O3

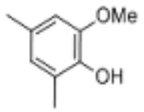

OMe
OH
7e


7.260
6.572
6.552
5.533
3.865
2.272
2.236
0.98
0.94
0.94
3.00
3.06
3.01
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
f1 (ppm)


OMe
OH
7e


146.107
141.505
128.556
123.564
123.548
109.233
77.509
77.191
76.873
55.968
21.068
15.414
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



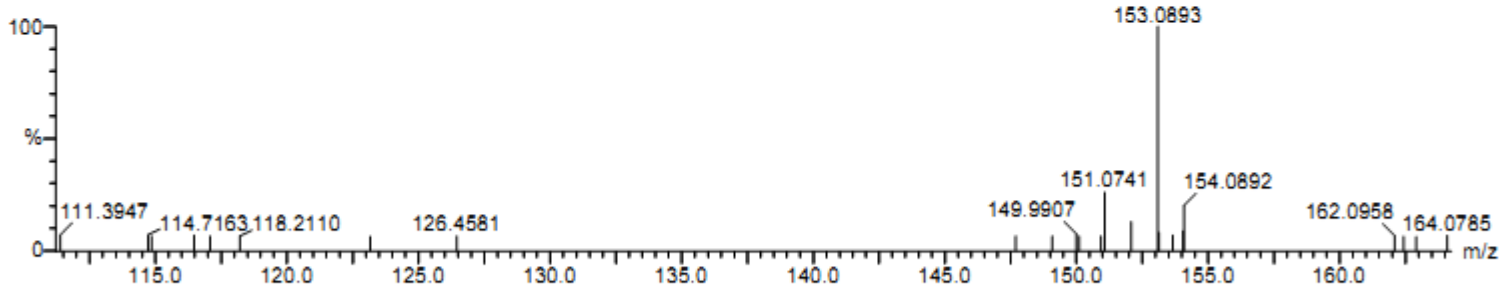
Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

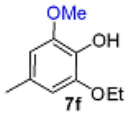
Monoisotopic Mass, Even Electron Ions
10 formula(e) evaluated with 2 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-35 H: 0-50 O: 0-3

YF-JI ECUST institute of Fine Chem 15-Nov-2013 13:06:17

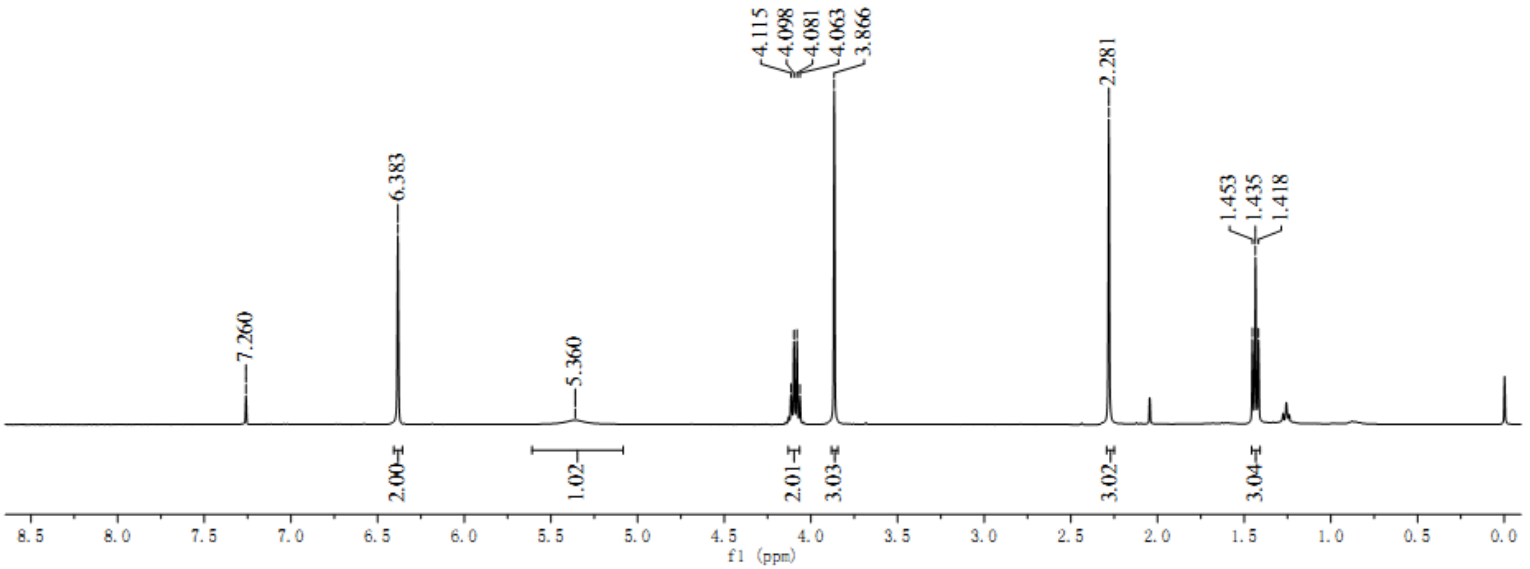
JYF-JA-5 52 (1.681) Cm (49:52) 1: TOF MS ES+ 2.37e+002

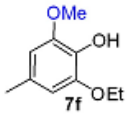


Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
153.0893	153.0916	-2.3	-15.0	3.5	27.2	0.0	C9 H13 O2

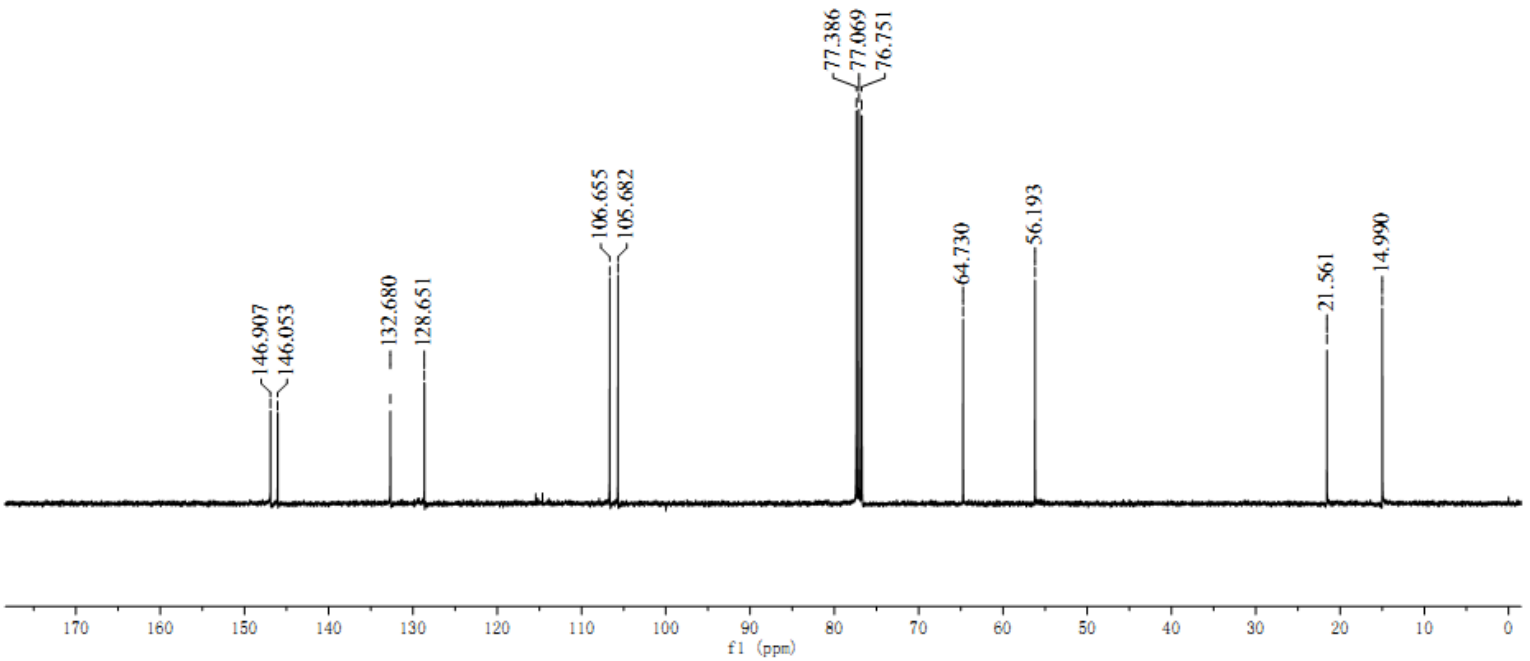

OMe
OH
OEt

7f

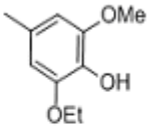

7.260
6.383
5.360
4.115
4.098
4.081
4.063
3.866
2.281
1.453
1.435
1.418
2.00
1.02
2.01
3.03
3.02
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OMe
OH
OEt

7f


146.907
146.053
132.680
128.651
106.655
105.682
77.386
77.069
76.751
64.730
56.193
21.561
14.990
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



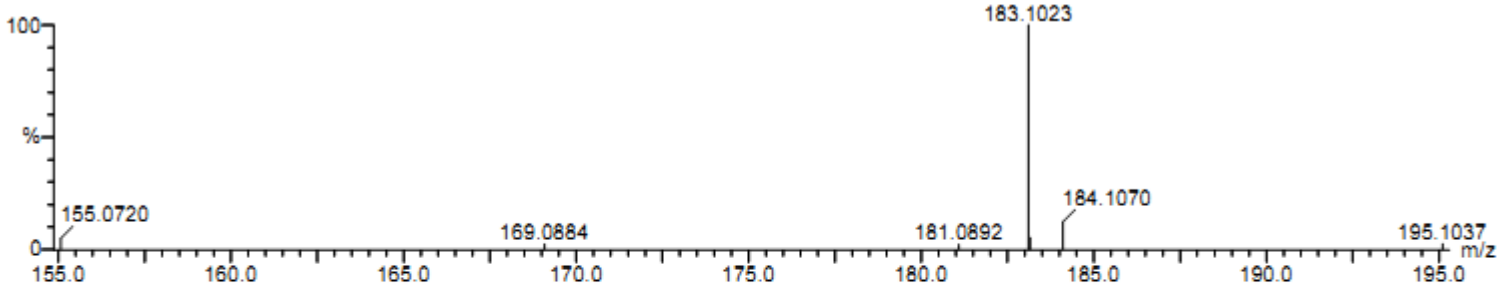
Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

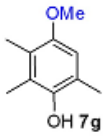
Monoisotopic Mass, Even Electron Ions
24 formula(e) evaluated with 5 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-37 H: 0-60 O: 0-9

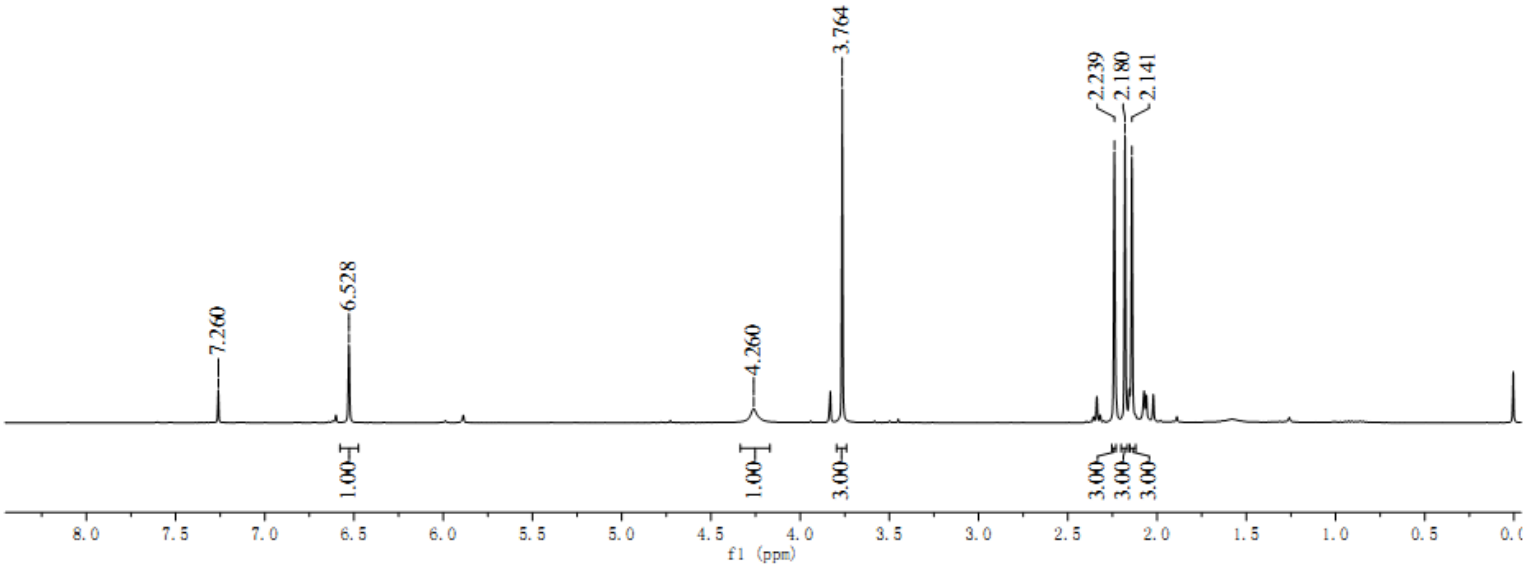
YF-JI ECUST institute of Fine Chem 15-Nov-2013 13:47:19

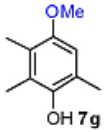
JYF-JA-6 24 (0.815) Cm (14:25) 1: TOF MS ES+ 8.59e+003



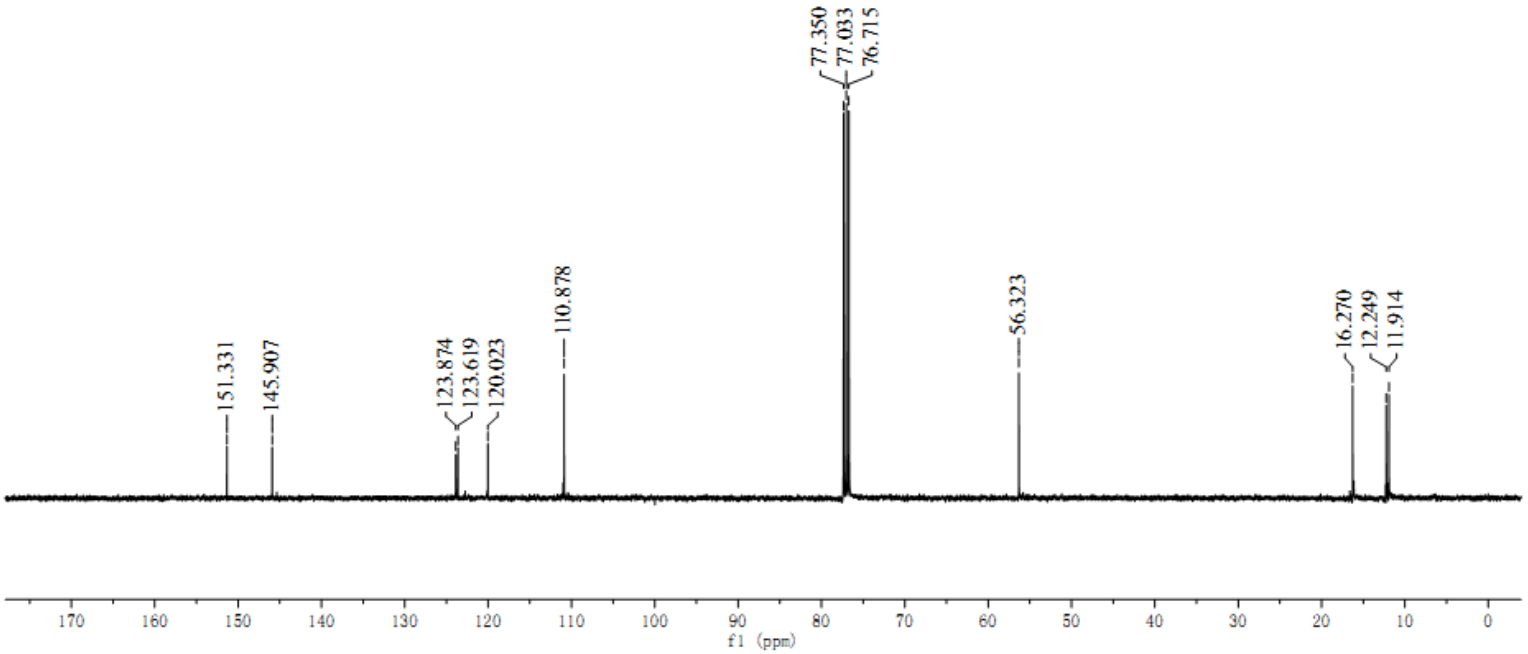
Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
183.1023	183.1021	0.2	1.1	3.5	21.1	0.0	C10 H15 O3


OMe
OH 7g


7.260
6.528
4.260
3.764
2.239
2.180
2.141
1.00
1.00
3.00
3.00
3.00
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
f1 (ppm)


OMe
OH

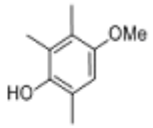
7g


151.331
145.907
123.874
123.619
120.023
110.878
77.350
77.033
76.715
56.323
16.270
12.249
11.914
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report

Single Mass Analysis

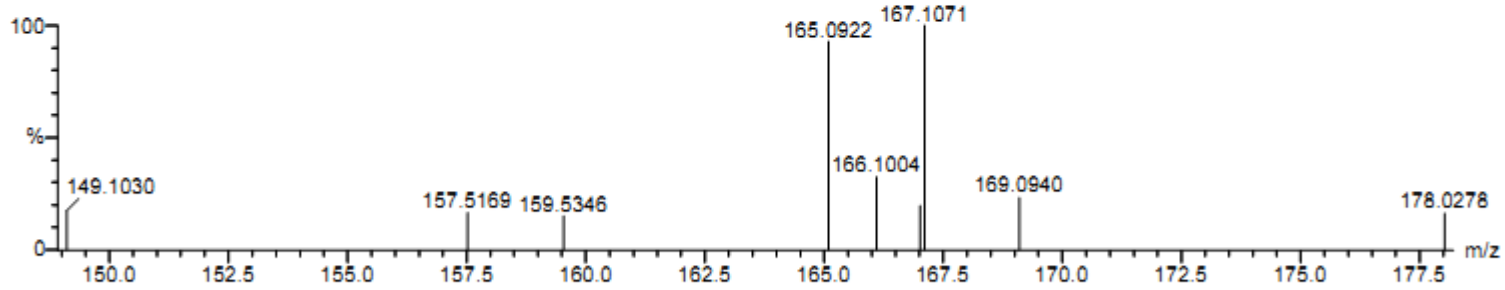
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2



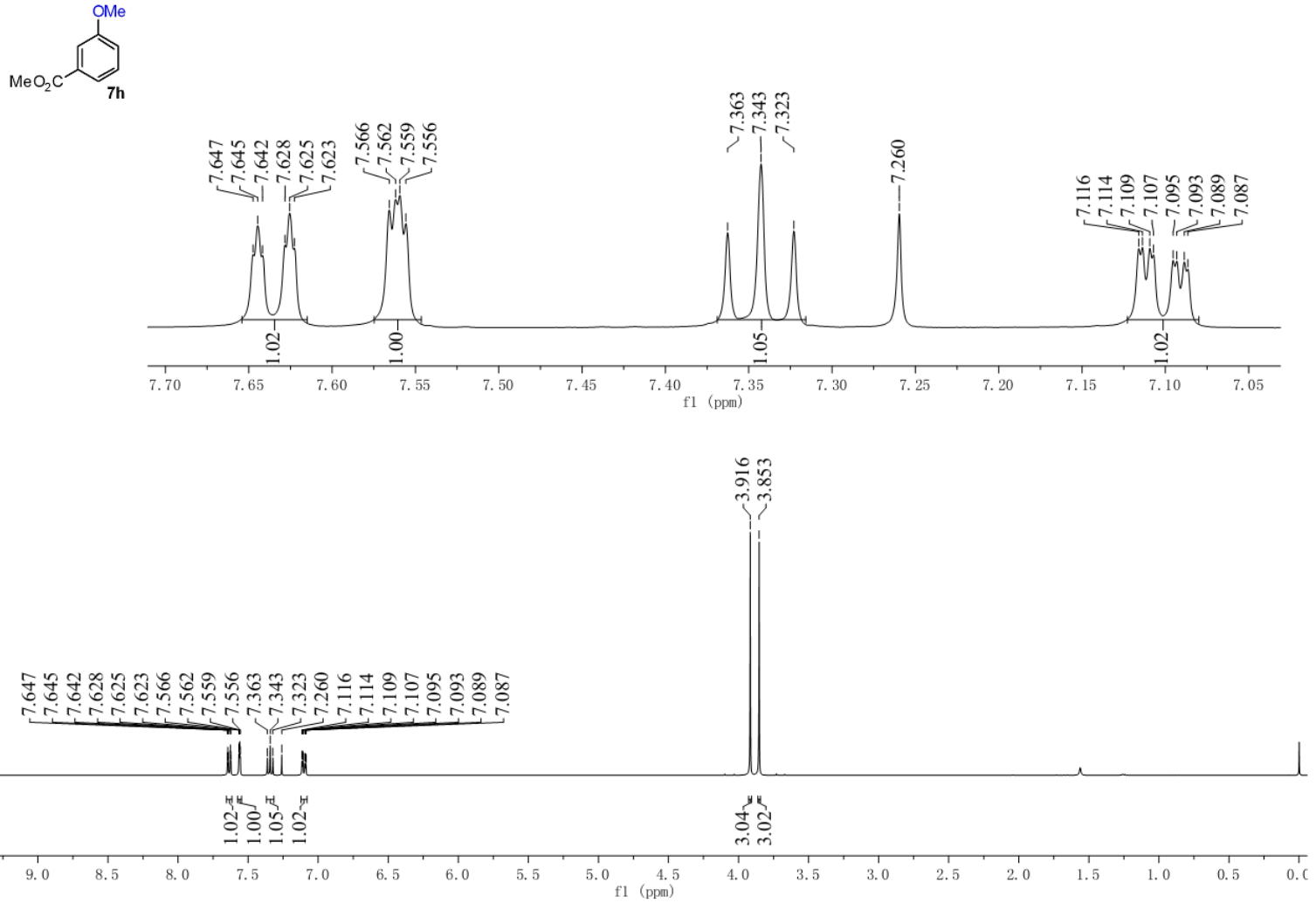
Monoisotopic Mass, Even Electron Ions
23 formula(e) evaluated with 4 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-37 H: 0-60 O: 0-9

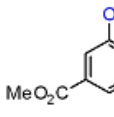
YF-JI ECUST institute of Fine Chem 15-Nov-2013 13:58:39

JYF-JA-8 27 (0.913) Cm (22:28) 1: TOF MS ES+ 2.55e+002

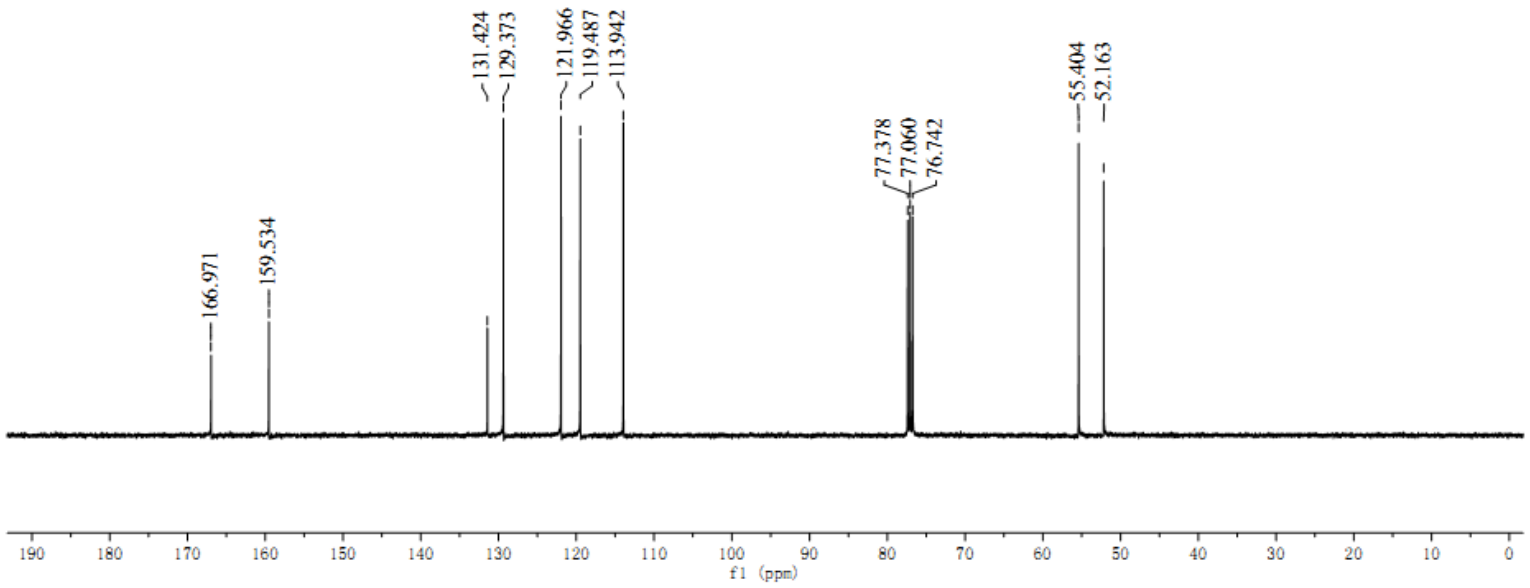


Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
167.1071	167.1072	-0.1	-0.6	3.5	15.4	0.0	C10 H15 O2

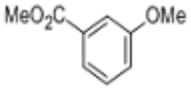

OMe
MeO2C
7h
7.647
7.645
7.642
7.628
7.625
7.623
7.566
7.562
7.559
7.556
7.363
7.343
7.323
7.260
7.116
7.114
7.109
7.107
7.095
7.093
7.089
7.087
1.02
1.00
1.05
1.02
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
f1 (ppm)
3.916
3.853
3.04
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


OMe
MeO2C

7h


166.971
159.534
131.424
129.373
121.966
119.487
113.942
77.378
77.060
76.742
55.404
52.163
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Elemental Composition Report



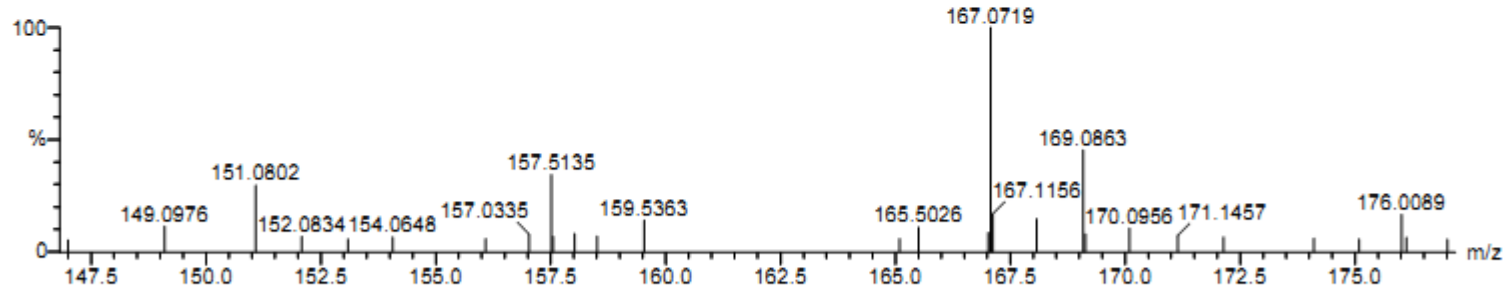
Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
23 formula(e) evaluated with 5 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-37 H: 0-60 O: 0-9

YF-JI ECUST institute of Fine Chem 15-Nov-2013 14:10:21

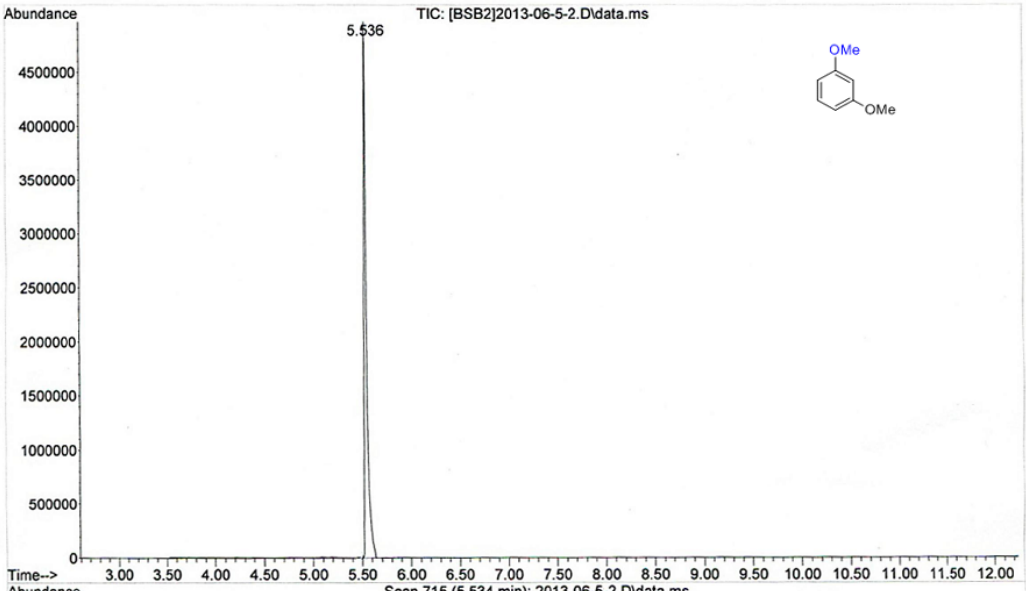
JYF-JA-11 2 (0.152) Cm (1:22) 1: TOF MS ES+ 1.22e+003

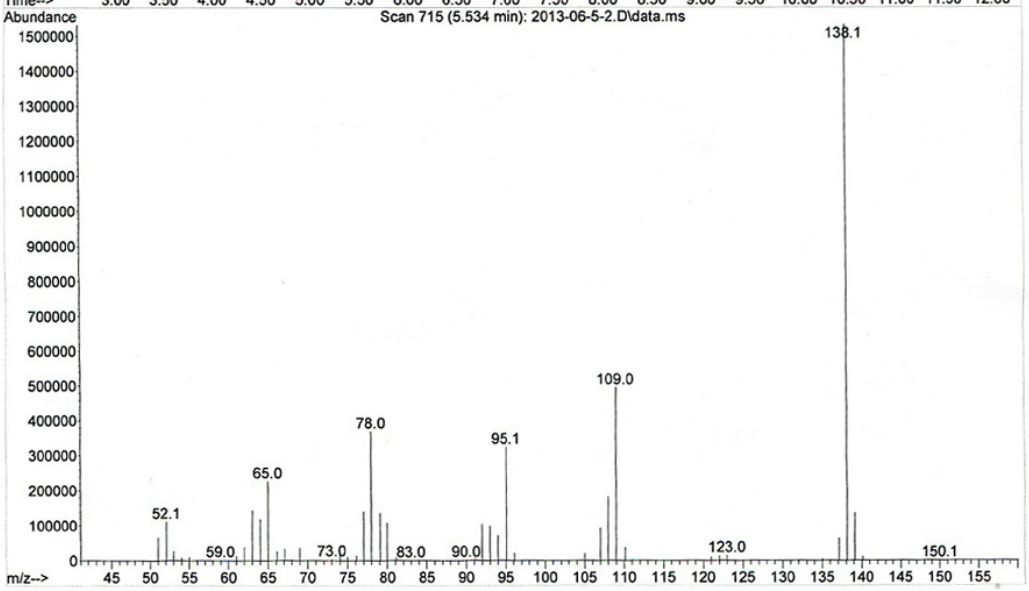


Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
167.0719	167.0708	1.1	6.6	4.5	18.2	0.0	C9 H11 O3

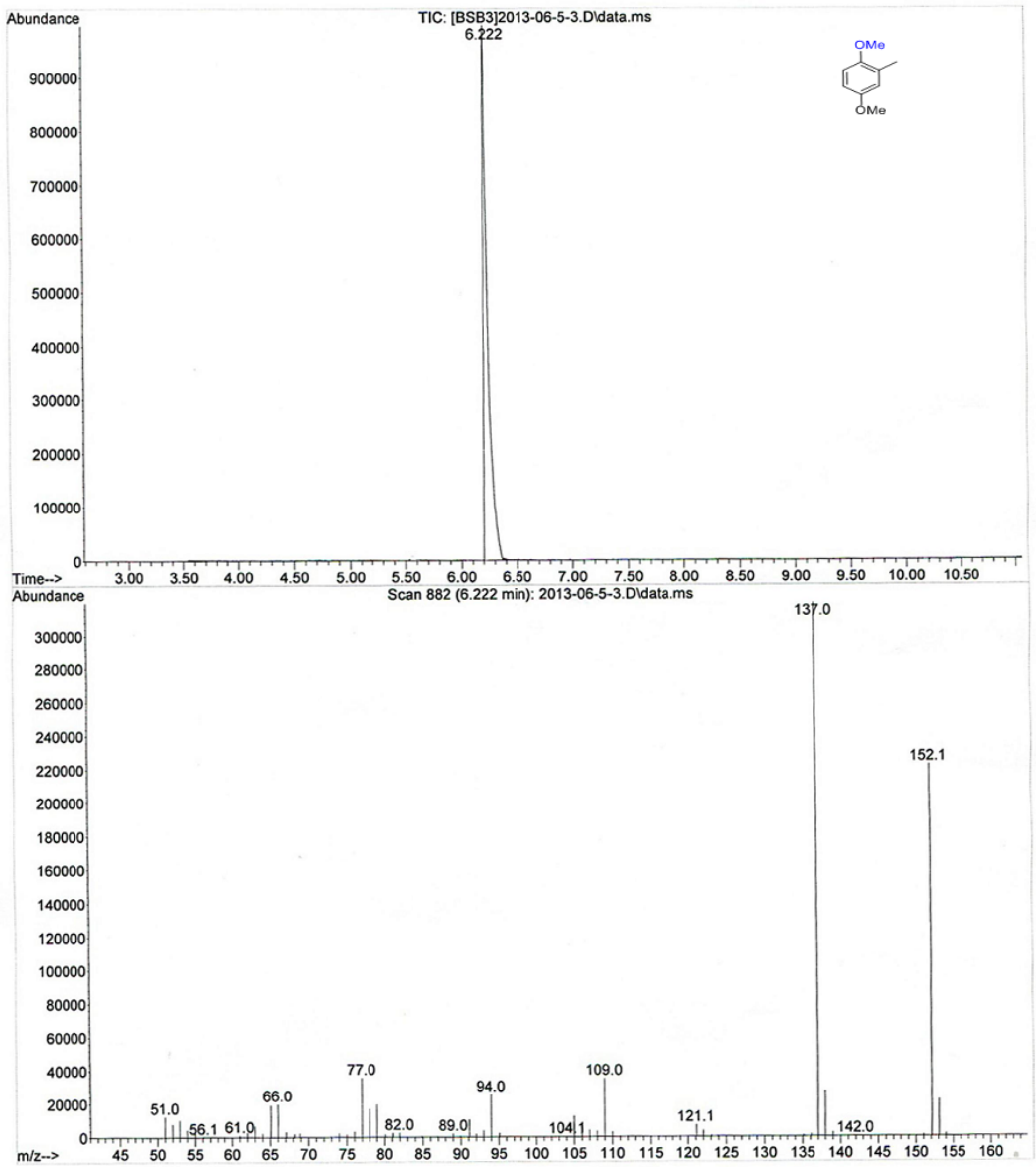
4.9 Copies of GC-MS for CuCl/HCOOMe-catalyzed methoxylation of aryl bromides.

```
ile       :D:\data\2013-06-5\BSB\2013-06-5-2.D
perator   : [BSB2]
cquired   :  5 Jun 2013  13:53     using AcqMethod METHOD-01.M
nstrument :    GC-MSD
ample Name: 2013-06-5-8
isc Info  :
ial Number: 18
```

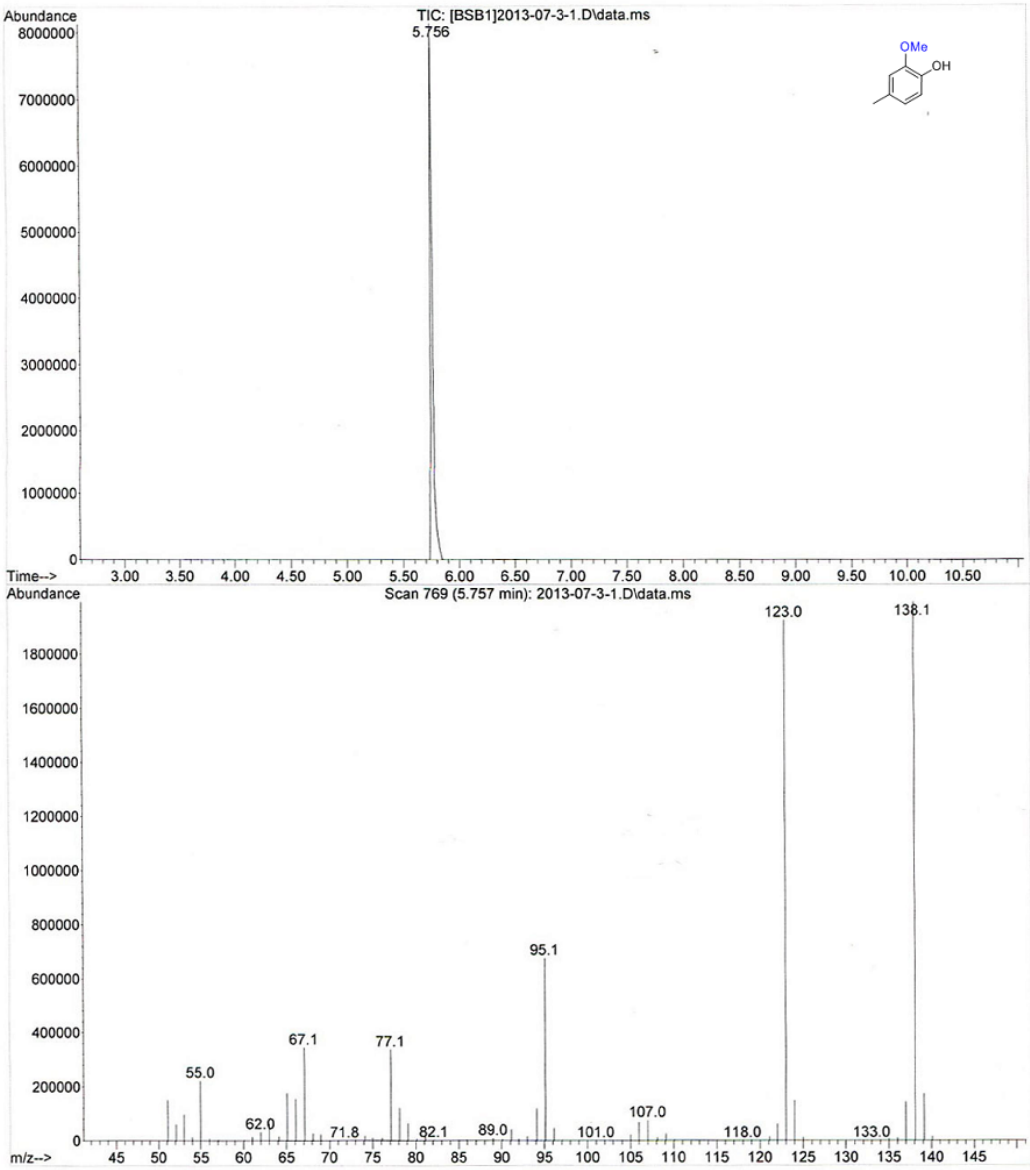




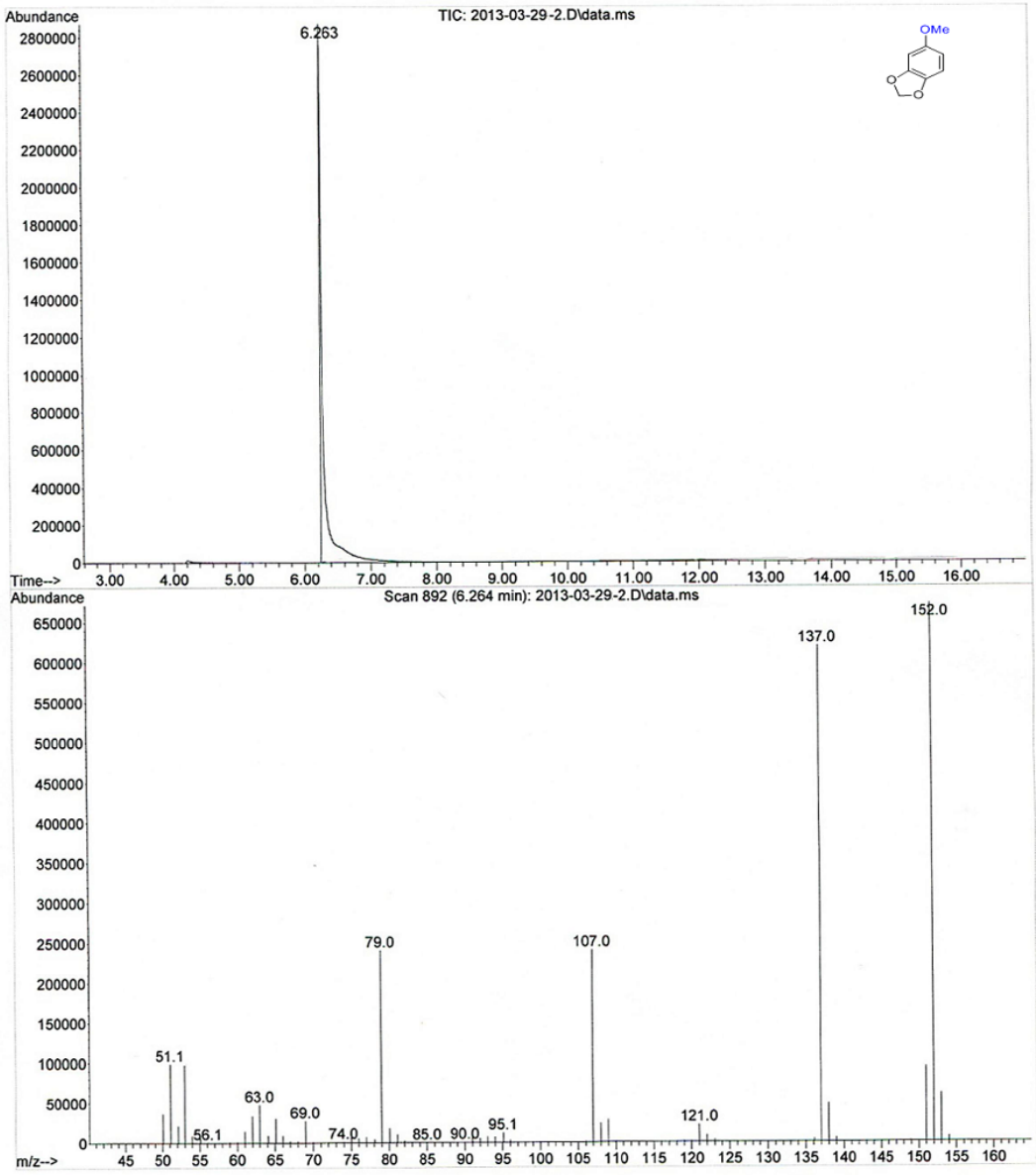
```
ile       :D:\data\2013-06-5\BSB\2013-06-5-3.D
perator   : [BSB3]
cquired   :  5 Jun 2013  14:09     using AcqMethod METHOD-01.M
nstrument :    GC-MSD
ample Name: 2013-06-5-9
isc Info  :
ial Number: 19
```



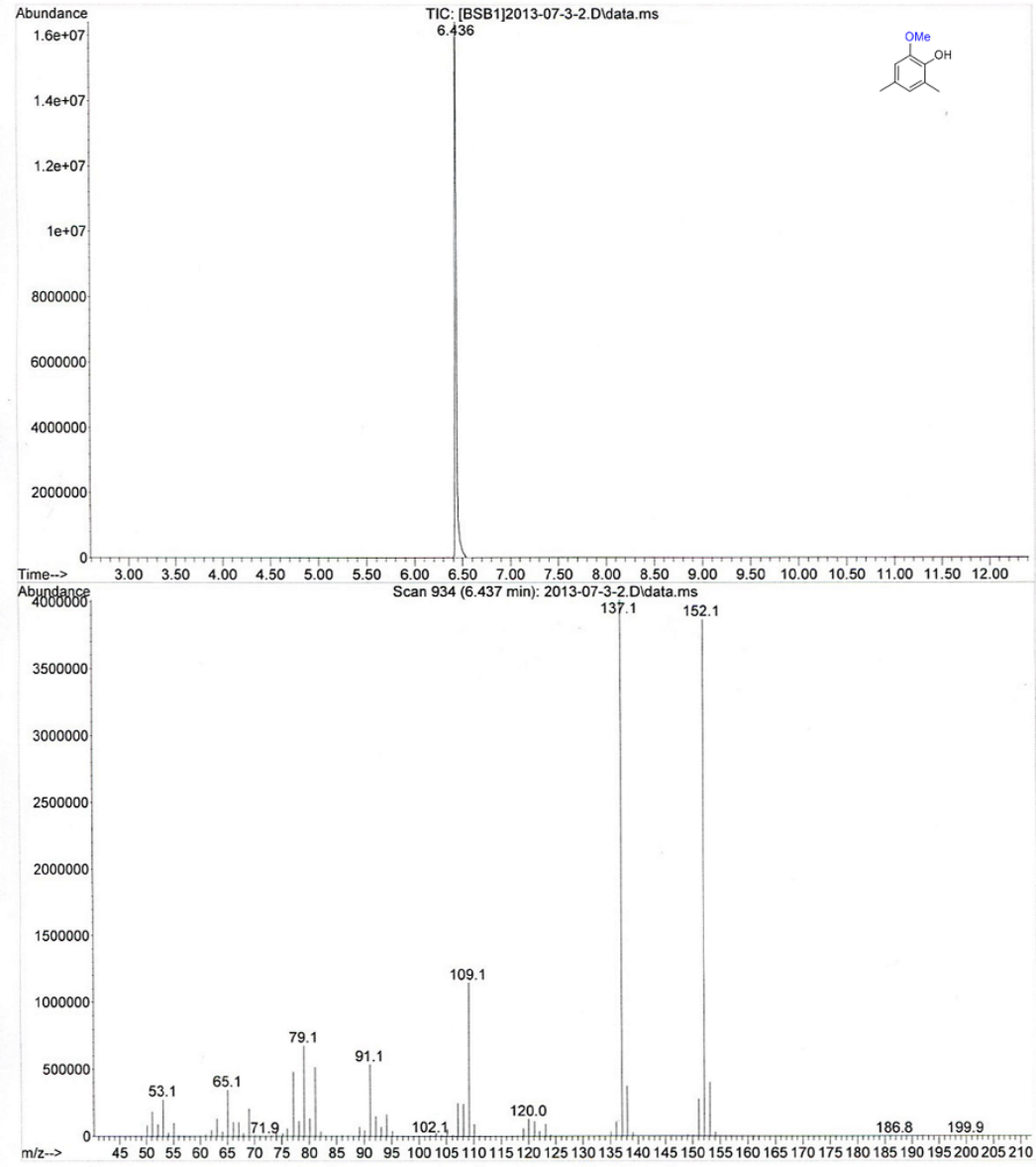
```
File       :D:\data\2013-07-3\BSB\2013-07-3-1.D
Operator   : [BSB1]
Acquired   :  3 Jul 2013  14:10     using AcqMethod METHOD-01.M
Instrument :    GC-MSD
Sample Name: 2013-07-3-8
Misc Info  :
Vial Number: 15
```



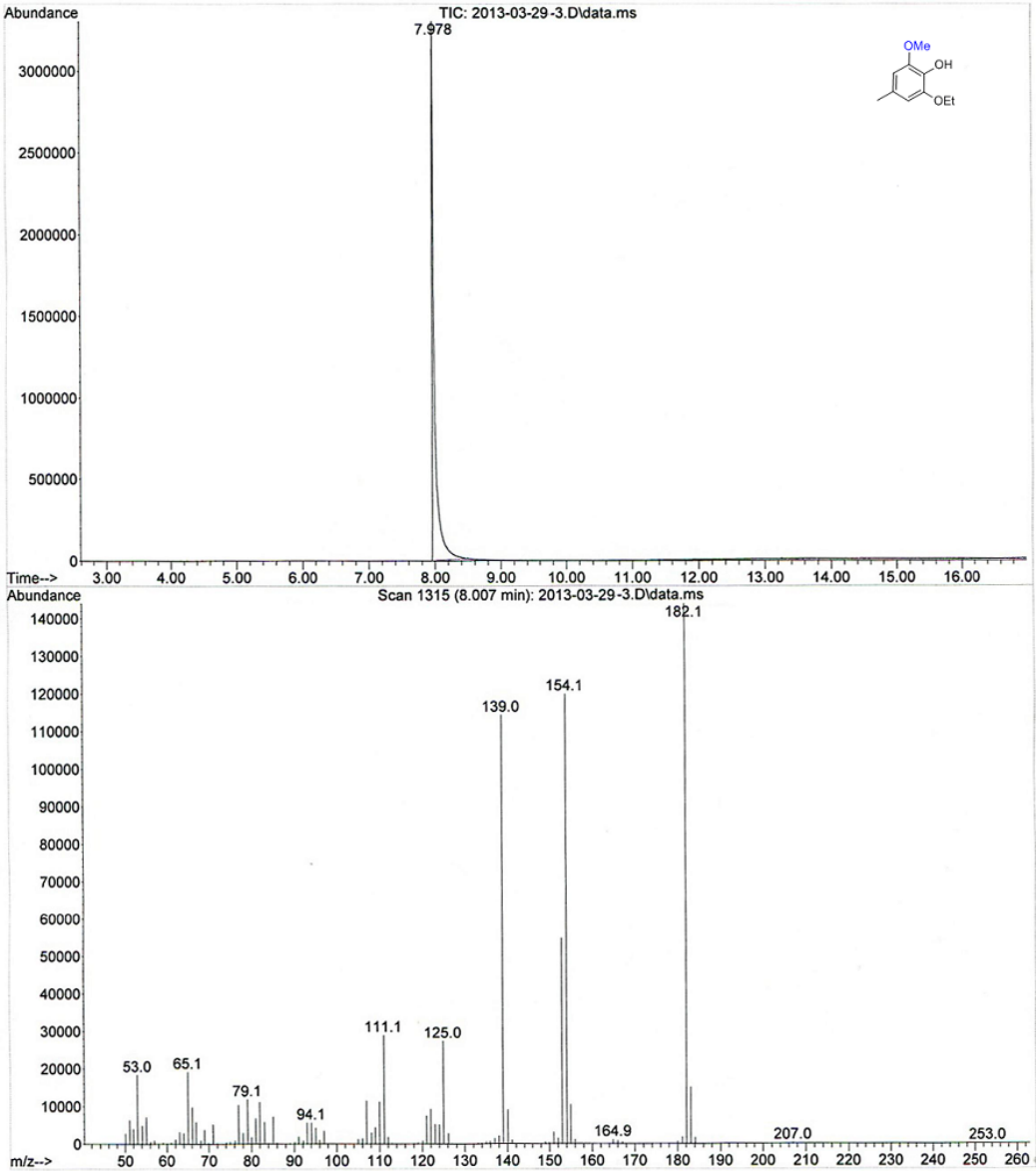
File :D:\data\2013-03-29\2013-03-29-2.D
Operator :
Acquired : 29 Mar 2013 13:46 using AcqMethod METHOD-01.M
Instrument : GC-MSD
Sample Name: 2013-03-29-5
Misc Info :
Vial Number: 15



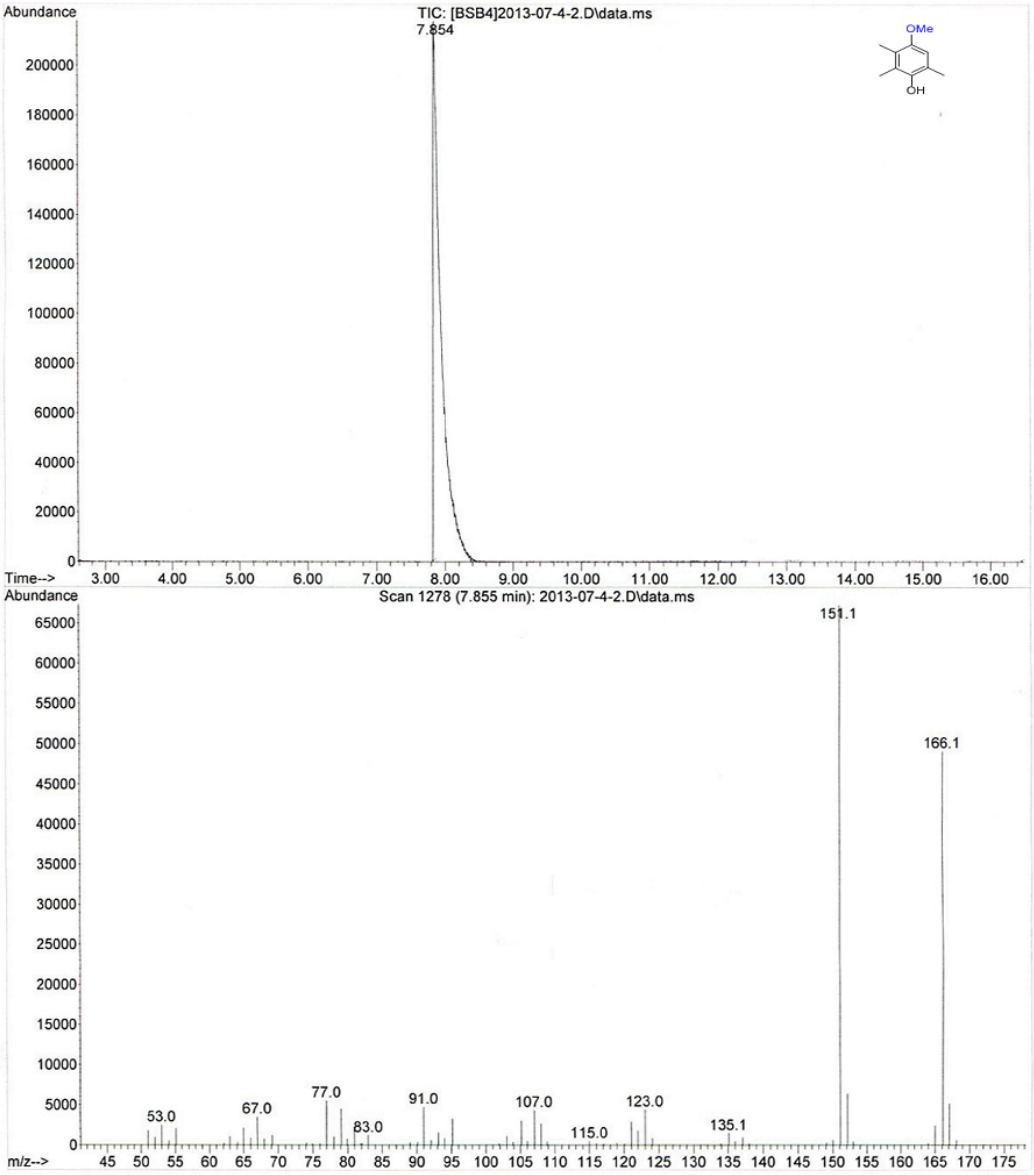
.le :D:\data\2013-07-3\BSB\2013-07-3-2.D
)erator : [BSB1]
:quired : 3 Jul 2013 14:24 using AcqMethod METHOD-01.M
ıstrument : GC-MSD
ımple Name: 2013-07-3-9
ısc Info :
ıal Number: 16



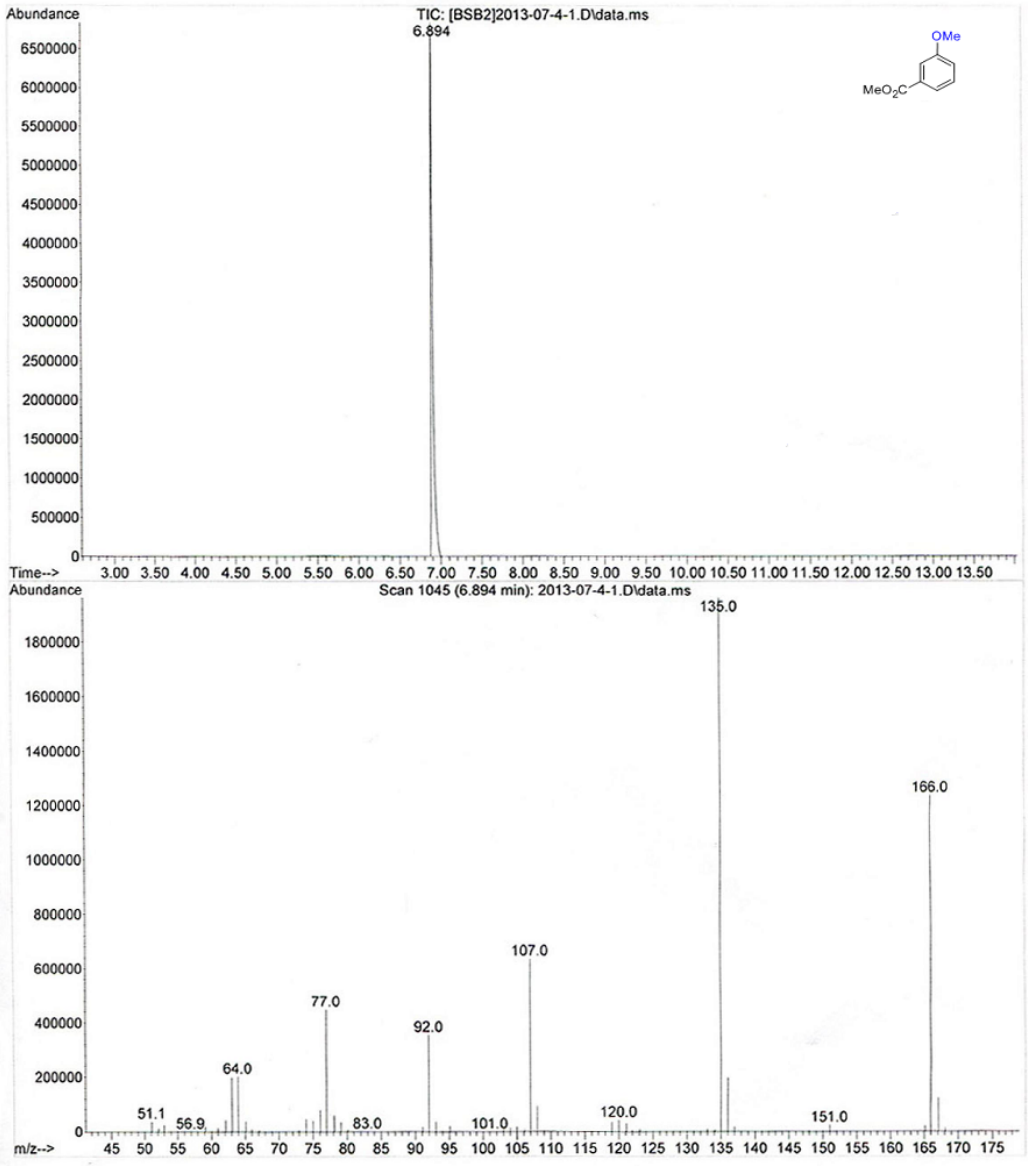
```
le       :D:\data\2013-03-29\2013-03-29-3.D
erator   :
quired   : 29 Mar 2013  14:06     using AcqMethod METHOD-01.M
strument :    GC-MSD
mple Name: 2013-03-29-6
sc Info  :
al Number: 16
```



ile :D:\data\2013-07-4\BSB\2013-07-4-2.D
perator : [BSB4]
cquired : 4 Jul 2013 12:00 using AcqMethod METHOD-01.M
nstrument : GC-MSD
ample Name: 2013-07-4-2
isc Info :
ial Number: 11

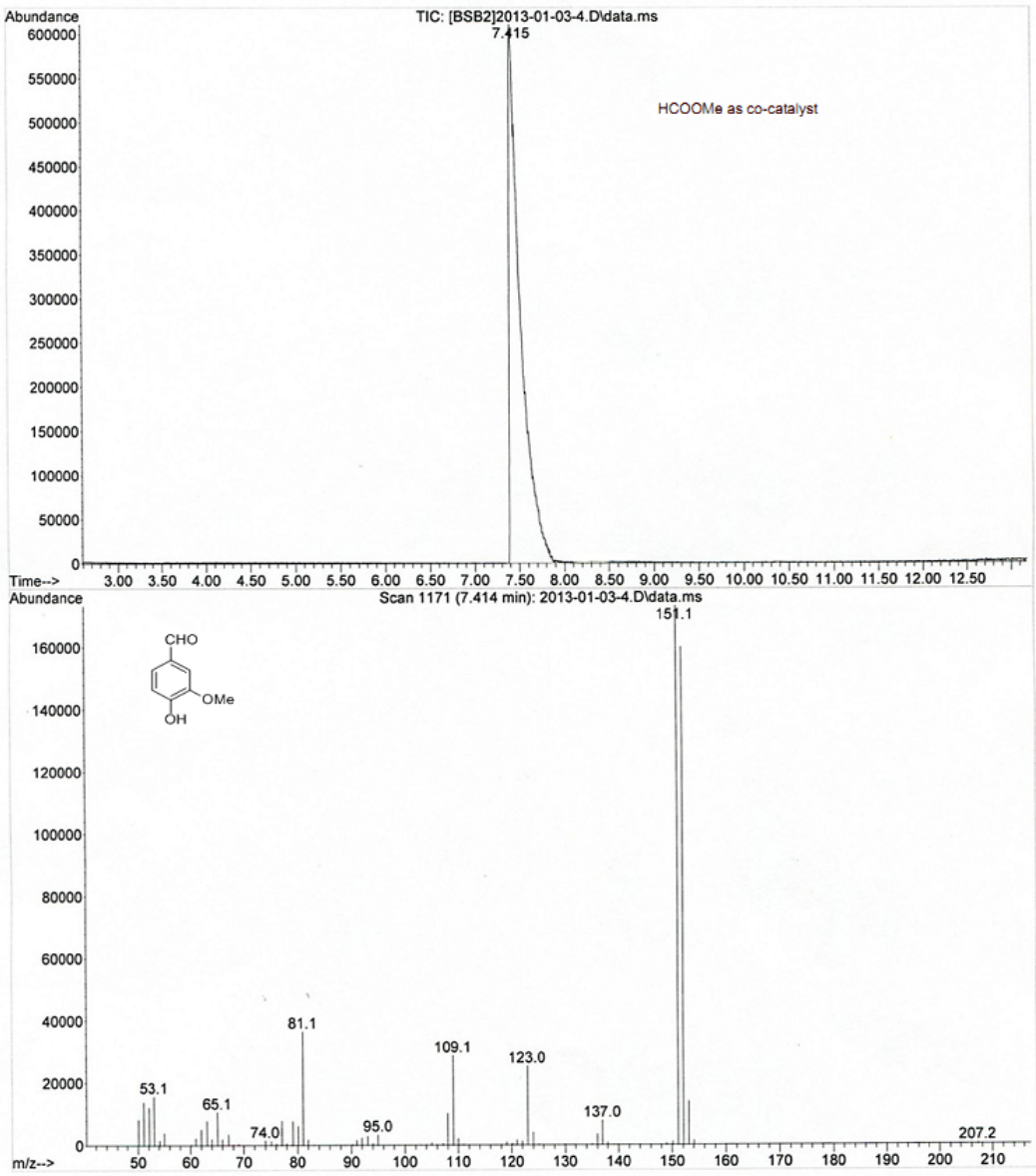


```
ile       :D:\data\2013-07-4\BSB\2013-07-4-1.D
perator   : [BSB2]
cquired   :  4 Jul 2013  11:42     using AcqMethod METHOD-01.M
nstrument :    GC-MSD
ample Name: 2013-07-4-1
lisc Info  :
ial Number: 10
```



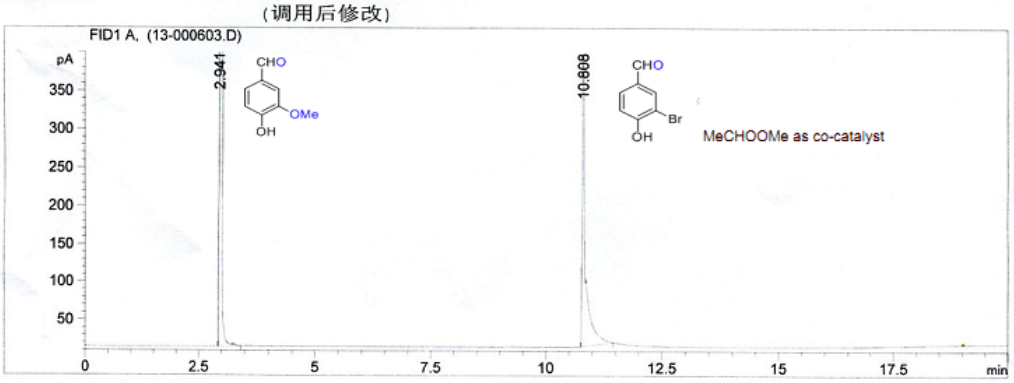
4.10 Copies of GC-MS for CuCl-catalyzed methoxylation of 2a with different co-catalysts.

```
File       :D:\data\2013-01-03\BSB\2013-01-03-4.D
Operator   : [BSB2]
Acquired   :  3 Jan 2013  12:25     using AcqMethod METHOD-01.M
Instrument :    GC-MSD
Sample Name: 2013-01-03-2
Misc Info  :
Vial Number: 12
```



数据文件：C:\CHEM32\1\DATA\13-000603.D
样品名称：JYF-CC-2

操作者 :
仪器 : 仪器 1 位置 : 样品瓶 101
进样日期 : 05-Dec-13, 14:51:52 进样次数 : 1
进样量 : 手动
采集方法 : C:\CHEM32\1\METHODS\JYF.M
最后修改 : 2013-12-5 14:48:00
分析方法 : C:\CHEM32\1\METHODS\气相条件.M
最后修改 : 2013-12-5 15:14:51
(调用后修改)



面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

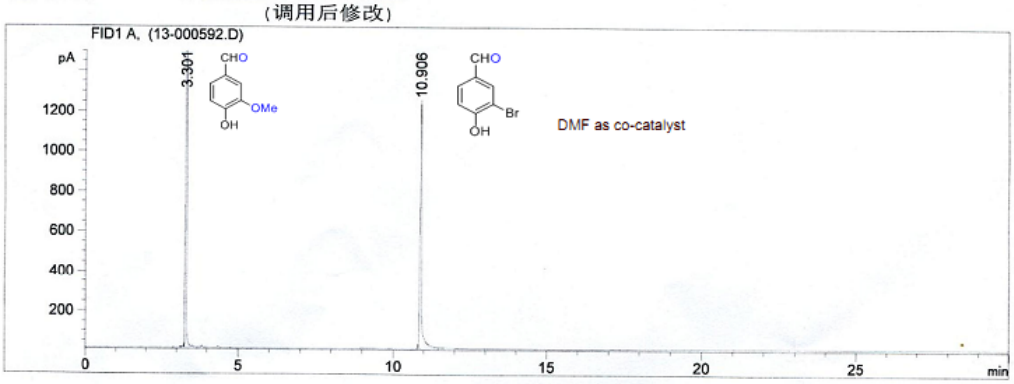
信号 1: FID1 A,

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	2.941	BB S	0.0286	4.14442e4	1.96233e4	95.15157
2	10.808	BB S	0.0449	2111.78394	649.31158	4.84843
总量 :				4.35560e4	2.02726e4	

*** 报告结束 ***

数据文件：C:\CHEM32\1\DATA\13-000592.D
样品名称：JFY-CC-1

操作者 :
仪器 : 仪器 1 位置 : 样品瓶 101
进样日期 : 02-Dec-13, 12:45:53 进样次数 : 1
进样量 : 手动
采集方法 : C:\CHEM32\1\METHODS\气相条件.M
最后修改 : 2013-11-20 17:09:12
分析方法 : C:\CHEM32\1\METHODS\气相条件.M
最后修改 : 2013-12-5 10:29:52
(调用后修改)



面积百分比报告

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: FID1 A,

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	3.301	VB S	0.0279	6.82191e4	4.10916e4	93.97011
2	10.906	BB	0.0512	4377.49268	1240.88257	6.02989
总量 :				7.25966e4	4.23324e4	

*** 报告结束 ***