

# Enantioselective Oxidation of Racemic Secondary Alcohols Catalyzed by Chiral Mn(III)-Salen Complex with N-Bromosuccinimide as a Powerful Oxidant

Daqian Xu,<sup>a,b</sup> Shoufeng Wang,<sup>a</sup> Zhiqiang Shen,<sup>a</sup> Chungu Xia<sup>a</sup> and Wei Sun<sup>\*a</sup>

<sup>a</sup> State key laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academic of Sciences, Lanzhou 730000, China

<sup>b</sup> Graduate School of the Chinese Academy of Sciences, Beijing, China.

## 1. Instruments

NMR spectra were obtained on a BRUKER Avance III 400 MHz spectrometer operating at 400MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR in CDCl<sub>3</sub>. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectra (HRMS) were recorded by Bruker micrOTOFQ-II (ESI). GC-MS was recorded by a Agilent 7890A/5975C. UV-vis spectra were obtained on a PE Lambda 35 spectrometer. Enantiomeric excesses (ee) were determined by GC analysis on an Agilent 7890A with a Varian CP-Chirasil-Dex CB capillary column or HPLC analysis on a Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak OD-H, OJ columns were purchased from Daicel Chemical Industries, LTD. Column chromatography was generally performed on silica gel (200-300 mesh) and TLC inspections were on silica gel GF<sub>254</sub> plates.

## 2. Materials:

NBS (N-bromosuccinimide), diacetoxyiodobenzene and potassium acetate were purchased from Aldrich and used as received. N-Bromophthalimide was purchased from Tokyo Chemical Industry Co. LTD and used as received. 1-(2,3-Difluorophenyl)ethanol, 1-(2,6-difluorophenyl)ethanol were prepared by reduction of ketone with NaBH<sub>4</sub> and then purified by silica gel column chromatography. (±)-1-(2-Fluorophenyl)ethanol, (±)-1-(4-trifluoromethylphenyl)ethanol were prepared from the corresponding aldehyde with CH<sub>3</sub>MgI and purified by column chromatography on silica gel. Others racemic secondary alcohols were purchased from Alfa Aesar, ACROS or Aldrich and used as received. Mn(III)-salen complex **1a** (Jacobsen catalyst) was purchased from ACROS and was used as received. Mn(III)-salen complexes **1b-1e** were prepared in accordance with literature procedures and were identified by HRMS.<sup>1</sup>

## 3. OKR procedure

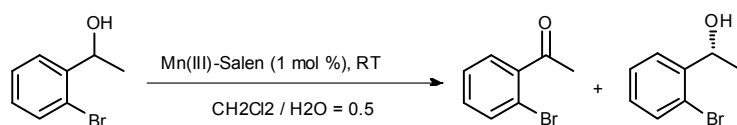
### 3.1. General procedure for asymmetric oxidation with PhI(OAc)<sub>2</sub>:

The 5 ml round-bottom tube charged with ( $\pm$ )-1-(2-bromophenyl)ethanol (50 mg, 0.25 mmol), (*R,R*)-Mn-complex **1a** (1.6 mg, 0.0025 mmol) and KBr (2.38 mg, 0.020 mmol), then H<sub>2</sub>O (1.00 ml) and CH<sub>2</sub>Cl<sub>2</sub> (500  $\mu$ l) was added. The biphasic mixture was allowed to stir for five minutes before PhI(OAc)<sub>2</sub> (56.7 mg, 0.175 mmol) was added. After 4h, the reaction was quenched with saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The mixture was then extracted with Et<sub>2</sub>O (3 x 2 mL) and then combined the organic extracts. The conversion of the substrate was determined by GC measurement. Enantiomeric excess of the product was determined by GC analysis. The absolute configuration of the products was determined by comparison of literature procedures.

### 3.2. General OKR procedure with NBS:

The 5 ml round-bottom tube charged with secondary alcohol (0.25 mmol), (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol) and KOAc (19.6mg, 0.2 mmol), then H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500  $\mu$ L) was added. The biphasic mixture was allowed to stir for five minutes before NBS (28.9 mg, 0.1625 mmol) was added. After desired reaction time indicated in the tables 1-3, the mixture was then extracted with Et<sub>2</sub>O (3 x 2 ml) and then combined organic extracts. The conversion of the substrate was determined by GC measurement. Enantiomeric excess of the products was determined by GC analysis or HPLC analysis. The absolute configuration of the products was determined by comparison of literature procedures.

**Table 1 Conditions screen <sup>a</sup>**



entry	oxidant	cat (1%)	time	Add	Conv(%) <sup>b</sup>	ee(%) <sup>b</sup>	<i>k</i> <sub>rel</sub> <sup>d</sup>
1	PhI(OAc) <sub>2</sub>	<b>1a</b>	4h	KBr (8mol%)	<3	0	-
2	NBS	<b>1a</b>	40min	KOAc(0.8eq)	40	48	10
3	NBS	<b>1a</b>	4h	KOAc(0.8eq)	63	94	12
4	NBS	<b>1b</b>	4h	KOAc(0.8eq)	64	99	17
5	NBS	<b>1c(1%)</b>	4h	KOAc(0.8eq)	61	85	9
6	NBS	<b>1d(1%)</b>	4h	KOAc(0.8eq)	64	93	10
7	NBS	<b>1e(1%)</b>	4h	KOAc(0.8eq)	62	91	11
8	NBS	<b>1b(0.5%)</b>	4h	KOAc(0.8eq)	63	93	11
9	NBS	<b>1b(2%)</b>	4h	KOAc(0.8eq)	64.8	99	16
10	NBP <sup>e</sup>	<b>1b(1%)</b>	4h	KOAc(0.8eq)	63.5	95	11
11	NCS <sup>f</sup>	<b>1b(1%)</b>	4h	KOAc(0.8eq)	14	2	-
12	NIS <sup>g</sup>	<b>1b(1%)</b>	4h	KOAc(0.8eq)	26	12	-

<sup>a</sup> Condition: 1.0 mol % of Mn(III)-salen complex, 0.25 mmol of (±)-1-(2-bromophenyl)ethanol, 1 mL of H<sub>2</sub>O, 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub>, 0.163 mmol of NBS (0.65 equiv.), 0.2 mmol of KOAc (0.80 equiv.), RT for 4 h. <sup>b</sup> Determined by GC. <sup>c</sup> Determined by GC with a chiral column. <sup>d</sup>  $k_{rel} = \ln[(1 - conv)(1 - ee)] / \ln[(1 - conv)(1 + ee)]$  <sup>f</sup> 0.163 mmol of NBP (0.65 equiv.), NBP= N-Bromophthalimine. <sup>g</sup> 0.163 mmol of NCS (0.65 equiv.), NCS= N-Chlorosuccinimide. <sup>h</sup> 0.163 mmol of NIS (0.65 equiv.), NIS= N-Iodosuccinimide.

### 3.3. Asymmetric oxidation of alcohols

**(±)-1-(2-Bromophenyl)ethanol (1a):**<sup>2</sup> Conditions: (±)-1-(2-Bromophenyl)ethanol (50 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 4 h. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 80 °C, hold 2 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R = 10.537$  min, minor enantiomer  $t_R = 11.048$  min; Conversion= 64%; ee= 99% of (*R*)-isomer. C<sub>8</sub>H<sub>9</sub>BrO: Calcd: 199.98, EI-MS found: 200.0. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.49 (dt, *J* = 11.4, 5.7 Hz, 1H), 7.39 – 7.27 (m, 1H), 7.12 (td, *J* = 7.7, 1.7 Hz, 1H), 5.22 (q, *J* = 6.4 Hz, 1H), 2.20 (s, 1H), 1.47 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 144.64, 132.62, 128.76, 127.86, 126.68, 121.66, 69.14, 23.60.

**(±)-1-(2-Chlorophenyl)ethanol (1b):**<sup>2</sup> Conditions: (±)-1-(2-Chlorophenyl)ethanol (39 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 4 h. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R = 2.649$  min, minor enantiomer  $t_R = 3.109$  min; Conversion= 60%; ee= 93% of (*R*)-isomer. C<sub>8</sub>H<sub>9</sub>ClO: Calcd: 156.0, EI-MS found: 156.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.30 (ddd, *J* = 15.2, 7.8, 1.2 Hz, 2H), 7.19 (tt, *J* = 6.9, 3.4 Hz, 1H), 5.28 (q, *J* = 6.4 Hz, 1H), 2.15 (s, 1H), 1.48 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 143.06, 131.59, 129.38, 128.40, 127.22, 126.40, 66.92, 23.51.

**(±)-1-(2-Fluorophenyl)ethanol (1c):**<sup>2</sup> Conditions: (±)-1-(2-Fluorophenyl)ethanol (35 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 4 h. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 80 °C, hold 2 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R = 7.492$  min, minor enantiomer  $t_R = 7.758$  min; Conversion= 59%; ee= 94% of (*R*)-isomer. C<sub>8</sub>H<sub>9</sub>FO: Calcd: 140.1, EI-MS found: 140.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (t, *J* = 7.6 Hz, 1H), 7.23 (m, 1H), 7.14 (m, 1H), 7.07 – 6.92 (m, 1H), 5.19 (m, 1H), 2.18 (s, 1H), 1.55 – 1.42 (m, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.66 (d, *J* = 245.2 Hz), 132.74 (d, *J* = 13.3 Hz), 128.69 (d, *J* = 8.3 Hz), 126.63 (d, *J* = 4.6 Hz), 124.28 (d, *J* = 3.5 Hz), 115.23 (d, *J* = 21.8 Hz), 64.36 (d, *J* = 3.1 Hz), 24.05 (s).

**(±)-1-(2-Methylphenyl)ethanol (2d):**<sup>2</sup> Conditions: (±)-1-(2'-Methylphenyl)ethanol (34 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 4 h. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub>

(flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 80 °C, hold 2 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 8.667 min, minor enantiomer  $t_R$  = 9.109 min; Conversion= 58%; ee= 94% of (*R*)-isomer.  $C_9H_{12}O$ : Calcd: 136.1, EI-MS found: 136.1.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.51 (d,  $J$  = 7.6 Hz, 1H), 7.23 (d,  $J$  = 7.6 Hz, 1H), 7.19 – 7.09 (m, 2H), 5.13 (q,  $J$  = 6.4 Hz, 1H), 2.34 (s, 3H), 1.71 (s, 1H), 1.46 (d,  $J$  = 6.4 Hz, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  143.84, 134.23, 130.37, 127.19, 126.40, 124.44, 66.81, 23.95, 18.95.

**(±)-1-(2-Methoxyphenyl)ethanol (2e):**<sup>2</sup> Conditions: (±)-1-Phenylethanol (38 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6mg, 0.2 mmol);  $H_2O$  (1.00 mL) and  $CH_2Cl_2$  (500  $\mu$ L); NBS (28.9 mg, 0.1625 mmol); room temperature; 4 h. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas,  $N_2$  (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 80 °C, hold 2 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 20.137 min, minor enantiomer  $t_R$  = 20.474 min; Conversion= 58%; ee= 56% of (*R*)-isomer.  $C_9H_{12}O_2$ : Calcd: 152.1, EI-MS found: 152.1.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.34 (dd,  $J$  = 7.5, 1.6 Hz, 1H), 7.28 – 7.21 (m, 1H), 6.96 (m, 1H), 6.88 (dd,  $J$  = 8.2, 0.7 Hz, 1H), 5.09 (q,  $J$  = 6.5 Hz, 1H), 3.86 (s, 3H), 1.50 (d,  $J$  = 6.5 Hz, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  156.50, 133.40, 128.30, 126.09, 120.78, 110.38, 66.48, 55.25, 22.86.

**(±)-1-(2,3-Difluorophenyl)ethanol (2f):**<sup>2c</sup> Conditions: (±)-1-(2,3-Difluorophenyl) ethanol (39.5 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol);  $H_2O$  (1.00 mL) and  $CH_2Cl_2$  (500  $\mu$ L); NBS (28.9 mg, 0.1625 mmol); room temperature; 4 h. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas,  $N_2$  (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; minor enantiomer  $t_R$  = 7.805 min, major enantiomer  $t_R$  = 7.952 min; Conversion= 62%; ee= 99.4% of (*R*)-isomer. Colourless oil,  $C_8H_8F_2O$ : Calcd: 158.0, EI-MS found: 158.1.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  1.48 (d,  $J$  = 4.0 Hz, 3H), 2.51 (s, 1H), 5.18 (q,  $J$  = 8.0 Hz, 1H), 7.06 (m, 2H), 7.22 (m, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  150.3 (dd,  $J$  = 247.8, 12.9 Hz), 147.5 (dd,  $J$  = 247.1, 13.0 Hz), 135.1 (d,  $J$  = 10.3 Hz), 124.2 (dd,  $J$  = 6.8, 4.6 Hz), 121.2 (t,  $J$  = 3.4 Hz), 115.8 (d,  $J$  = 17.1 Hz), 64.1 (t,  $J$  = 2.9 Hz), 24.0 (s).

**(±)-1-(2,6-Difluorophenyl)ethanol (2g):**<sup>2a</sup> Conditions: (±)-1-(2,6-Difluorophenyl) ethanol (39.5 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol);  $H_2O$  (1.00 mL) and  $CH_2Cl_2$  (500  $\mu$ L); NBS (28.9 mg, 0.1625 mmol); room temperature; 4 h. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas,  $N_2$  (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; minor enantiomer  $t_R$  = 6.782 min, major enantiomer  $t_R$  = 6.562 min; Conversion= 56%; ee= 95% of (*R*)-isomer. Colourless oil,  $C_8H_8F_2O$ : Calcd: 158.0, EI-MS found: 158.1.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.19 (tt,  $J$  = 8.4, 6.4 Hz, 1H), 6.93 – 6.78 (m, 2H), 5.24 (q,  $J$  = 6.5 Hz, 1H), 2.55 (s, 1H), 1.61 (d,  $J$  = 6.8 Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  160.8 (dd,  $J$  = 247.6, 8.8 Hz), 128.9 (t,  $J$  = 10.7 Hz), 120.5 (t,  $J$  = 16.6 Hz), 112.5 – 110.7 (m), 62.3 (t,  $J$  = 3.3 Hz), 23.3 (s).

**(±)-1-(3-Methylphenyl)ethanol (2h):** Conditions: (±)-1-(3-Methylphenyl)ethanol (34 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol);  $H_2O$  (1.00 mL) and  $CH_2Cl_2$  (500  $\mu$ L);

NBS (28.9 mg, 0.1625 mmol); room temperature; 20 min. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 8.222 min, minor enantiomer  $t_R$  = 8.430 min; Conversion = 63%; ee = 98.7 % of (*R*)-isomer. C<sub>9</sub>H<sub>12</sub>O: Calcd: 136.1, EI-MS found: 136.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 (t,  $J$  = 5.9 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.08 (d,  $J$  = 7.4 Hz, 1H), 2.36 (s, 3H), 1.92 (s, 1H), 1.48 (d,  $J$  = 6.5 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 145.81, 138.16, 128.42, 128.21, 126.13, 122.45, 70.41, 25.14, 21.50.

**(±)-1-(3-Fluorophenyl)ethanol (2i):** Conditions: (±)-1-(3-Fluorophenyl)ethanol (35 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 20 min. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 7.693 min, minor enantiomer  $t_R$  = 8.026 min; Conversion = 62%; ee = 98.6% of (*R*)-isomer. C<sub>8</sub>H<sub>9</sub>FO: Calcd: 140.1, EI-MS found: 140.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 (m, 1H), 7.09 (dd,  $J$  = 12.1, 9.3 Hz, 2H), 6.94 (m, 1H), 4.87 (q,  $J$  = 6.4 Hz, 1H), 2.16 (s, 1H), 1.46 (dd,  $J$  = 6.5, 0.6 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 162.95 (d,  $J$  = 245.7 Hz), 148.53 (d,  $J$  = 6.6 Hz), 129.97 (d,  $J$  = 8.2 Hz), 120.96 (d,  $J$  = 2.8 Hz), 114.17 (d,  $J$  = 21.2 Hz), 112.30 (d,  $J$  = 21.8 Hz), 69.71 (d,  $J$  = 1.7 Hz), 25.19 (s).

**(±)-1-phenylethanol (2j):**<sup>2</sup> Conditions: (±)-1-Phenylethanol (30.5 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 20 min. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 80 °C, hold 2 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 7.265 min, minor enantiomer  $t_R$  = 7.569 min; Conversion = 63%; ee = 97% of (*R*)-isomer. C<sub>8</sub>H<sub>10</sub>O: Calcd: 122.0, EI-MS found: 122.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.31 (m, 4H), 7.29 – 7.23 (m, 1H), 4.95 – 4.79 (m, 1H), 2.08 (d,  $J$  = 54.4 Hz, 1H), 1.53 – 1.41 (m, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 145.85, 128.50, 127.45, 125.43, 70.35, 25.18.

**(±)-1-(4-Fluorophenyl)ethanol (2k):**<sup>2</sup> Conditions: (±)-1-(4-Fluorophenyl)ethanol (35 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 20 min. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 7.588 min, minor enantiomer  $t_R$  = 7.986 min; Conversion = 63%; ee = 97.5% of (*R*)-isomer. C<sub>8</sub>H<sub>9</sub>FO: Calcd: 140.1, EI-MS found: 140.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.28 (m, 2H), 7.05 – 6.97 (m, 2H), 4.85 (q,  $J$  = 6.4 Hz, 1H), 2.19 (s, 1H), 1.45 (d,  $J$  = 6.5 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 162.06 (d,  $J$  = 245.0 Hz), 141.51 (d,  $J$  = 3.1 Hz), 127.05 (d,  $J$  = 8.1 Hz), 115.23 (d,  $J$  = 21.3 Hz), 69.71 (s), 25.27 (s).

**(±)-1-(4-Methylphenyl)ethanol (2l):**<sup>2</sup> Conditions: (±)-1-(4-Methylphenyl)ethanol (34 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 20 min. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier

gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 8.982 min, minor enantiomer  $t_R$  = 8.309 min; Conversion = 62%; ee = 94.5% of (*R*)-isomer. C<sub>9</sub>H<sub>12</sub>O: Calcd: 136.1, EI-MS found: 136.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 4.83 (q, *J* = 6.4 Hz, 1H), 2.33 (s, 3H), 2.02 (s, 1H), 1.46 (d, *J* = 6.5 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 142.93, 137.10, 129.16, 125.40, 70.19, 25.12, 21.14.

**(±)-1-(4-Trifluoromethylphenyl)ethanol (2m)**:<sup>2</sup> Conditions: (±)-1-(4-Trifluoromethylphenyl)ethanol (47.5 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 20 min. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 130 °C, hold 4 min, ramp 5 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 3.526 min, minor enantiomer  $t_R$  = 4.093 min; Conversion = 60%; ee = 94 % of (*R*)-isomer. C<sub>9</sub>H<sub>9</sub>F<sub>3</sub>O: Calcd: 190.1, EI-MS found: 190.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 4.97 (q, *J* = 6.5 Hz, 1H), 1.91 (s, 1H), 1.51 (d, *J* = 6.5 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 149.68 (s), 125.95 (s), 125.64 (s), 125.48 (s), 125.43 (s), 69.84 (s), 25.43 (s).

**(±)-1-(4-Chlorophenyl)ethanol (2n)**:<sup>2</sup> Conditions: (±)-1-(4-Chlorophenyl)ethanol (39 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 20 min. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 9.756 min, minor enantiomer  $t_R$  = 10.038 min; Conversion = 61%; ee = 94% of (*R*)-isomer. C<sub>8</sub>H<sub>9</sub>ClO: Calcd: 156.0, EI-MS found: 156.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.26 (m, 4H), 4.85 (q, *J* = 6.5 Hz, 1H), 2.13 (s, 1H), 1.45 (d, *J* = 6.5 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 144.26, 132.98, 128.56, 126.82, 69.65, 25.25.

**(±)-1-Indanol (2o)**:<sup>2c</sup> Conditions: (±)-1-indanol (33.5 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 2 h. Conversion was determined GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane: isopropanol = 90:10, 0.8 mL/min, 254 nm); major enantiomer  $t_R$  = 13.917 min, minor enantiomer  $t_R$  = 13.530 min; Conversion = 61%; ee = 99.9% of (*R*)-isomer. C<sub>9</sub>H<sub>10</sub>O: Calcd: 134.1, EI-MS found: 134.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 6.8 Hz, 1H), 7.25 – 7.16 (m, 3H), 5.17 (d, *J* = 5.2 Hz, 1H), 3.07 – 2.92 (m, 1H), 2.85 – 2.69 (m, 1H), 2.49 – 2.36 (m, 1H), 1.97 – 1.78 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 145.06, 143.32, 128.22, 126.67, 124.87, 124.33, 76.19, 35.77, 29.82.

**(±)-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-ol (2p)**:<sup>2</sup> Conditions: (±)-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-5-ol (40.5 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 2 h. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 11.704 min, minor enantiomer  $t_R$  = 12.416 min; Conversion = 55%; ee = 94% of (*R*)-isomer.

$C_{11}H_{14}O$ : Calcd: 162.1, EI-MS found: 162.0.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.43 (d,  $J = 7.4$  Hz, 1H), 7.20 (td,  $J = 7.4$ , 1.5 Hz, 1H), 7.15 (td,  $J = 7.3$ , 1.5 Hz, 1H), 7.09 (dd,  $J = 7.3$ , 1.1 Hz, 1H), 4.92 (d,  $J = 7.5$  Hz, 1H), 2.91 (dd,  $J = 14.0$ , 8.4 Hz, 1H), 2.70 (ddd,  $J = 14.1$ , 10.6, 1.3 Hz, 1H), 2.11 – 1.99 (m, 1H), 1.95 (dd,  $J = 8.8$ , 7.5 Hz, 2H), 1.86 – 1.69 (m, 3H), 1.56 – 1.36 (m, 1H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  144.29, 140.81, 129.51, 126.99, 126.12, 124.55, 73.98, 36.58, 35.75, 27.86, 27.60.

**(±)-Menthol (2q)**:<sup>2c</sup> Conditions: (±)-Menthol (39 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol);  $H_2O$  (1.00 mL) and  $CH_2Cl_2$  (500  $\mu$ L); NBS (28.9 mg, 0.1625 mmol); room temperature; 2 h. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas,  $N_2$  (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R = 16.217$  min, minor enantiomer  $t_R = 15.965$  min; Conversion = 64%; ee = 98.7% of (*S*)-isomer.  $C_{10}H_{20}O$ : Calcd: 156.1, EI-MS found: 156.0.  $^1H$  NMR (400 MHz,  $CDCl_3$ ) 3.41 (m, 1H), 2.25 – 2.09 (m, 1H), 1.96 (dd,  $J = 9.3$ , 2.7 Hz, 1H), 1.63 (ddd,  $J = 12.9$ , 11.5, 2.4 Hz, 2H), 1.52 – 1.35 (m, 2H), 1.32 – 1.18 (m, 1H), 1.16 – 1.04 (m, 1H), 0.98 (m, 1H), 0.94 (m, 1H), 0.91 (tt,  $J = 8.4$ , 3.3 Hz, 6H), 0.84 – 0.75 (m, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  71.48, 50.06, 44.98, 34.51, 31.62, 25.74, 23.03, 22.24, 21.04, 16.02.

**(±)-1,1-Diphenyl-2-propanol (2r)**:<sup>2c</sup> Conditions: (±)-1,1-Diphenyl-2-propanol (53 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol);  $H_2O$  (1.00 mL) and  $CH_2Cl_2$  (500  $\mu$ L); NBS (28.9 mg, 0.1625 mmol); room temperature; 2 h. Conversion was determined GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas,  $N_2$  (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, rap 10 °C/min to 170 °C, then hold 10 min; Enantiomeric excess was determined by HPLC with a Chiralcel OJ column (hexane: isopropanol = 75:25, 1 mL/min, 254 nm); major enantiomer  $t_R = 50.581$  min, minor enantiomer  $t_R = 40.608$  min; Conversion = 59%; ee = 99.9% of (*R*)-isomer.  $C_{15}H_{16}O$ : Calcd: 212.1, EI-MS found: 212.1.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.39 (d,  $J = 7.9$  Hz, 2H), 7.33 (t,  $J = 7.5$  Hz, 2H), 7.30 – 7.26 (m, 4H), 7.24 (dd,  $J = 6.9$ , 5.2 Hz, 1H), 7.21 – 7.15 (m, 1H), 4.55 (dq,  $J = 8.7$ , 6.1 Hz, 1H), 3.81 (d,  $J = 8.8$  Hz, 1H), 1.68 (s, 1H), 1.20 (dd,  $J = 6.1$ , 0.8 Hz, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  142.51, 141.54, 128.93, 128.66, 128.20, 126.96, 126.60, 70.08, 60.64, 21.43.

**(±)-1-(2-Naphthyl)ethanol (2s)**:<sup>2c</sup> Conditions: (±)-1-(2'-Naphthyl)ethanol (43 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol);  $H_2O$  (1.00 mL) and  $CH_2Cl_2$  (500  $\mu$ L); NBS (28.9 mg, 0.1625 mmol); room temperature; 2 h. Conversion was determined GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas,  $N_2$  (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 10 min, ramp 10 °C/min to 170 °C, then hold 10 min; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (hexane: isopropanol = 90:10, 1 mL/min, 254 nm) major enantiomer  $t_R = 14.530$  min, minor enantiomer  $t_R = 13.917$  min; Conversion = 58%; ee = 99.8% of (*R*)-isomer.  $C_{12}H_{12}O$ : Calcd: 172.1, EI-MS found: 172.1.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.94 – 7.70 (m, 4H), 7.62 – 7.38 (m, 3H), 5.06 (q,  $J = 6.4$  Hz, 1H), 1.78 (s, 1H), 1.58 (d,  $J = 6.5$  Hz, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  143.20, 133.29, 132.89, 128.33, 127.95, 127.69, 126.17, 125.82, 123.84, 123.81, 70.53, 25.17.

**(±)-1-phenyl-2-propanol (2t)**:<sup>2d</sup> Conditions: (±)-1-phenyl-2-propanol (31.5 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol);  $H_2O$  (1.00 mL) and  $CH_2Cl_2$  (500  $\mu$ L); NBS (28.9 mg, 0.1625

mmol); room temperature; 2 h. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 100 °C, hold 5 min, ramp 5 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 9.065 min, minor enantiomer  $t_R$  = 8.919 min; Conversion = 64%; ee = 98% of (*R*)-isomer. C<sub>8</sub>H<sub>12</sub>O: Calcd: 136.1, EI-MS found: 136.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.25 (m, 2H), 7.24 – 7.14 (m, 3H), 4.05 – 3.89 (m, 1H), 2.71 (qd,  $J$  = 13.4, 6.4 Hz, 2H), 1.83 (s, 1H), 1.21 (d,  $J$  = 6.2 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 138.61, 129.46, 128.56, 126.49, 68.90, 45.80, 22.79.

**(±)-3,3dimethyl-2-propanol (2u)**:<sup>2c</sup> Conditions: (±)-3,3dimethyl-2-propanol (25.5 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 20min. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 50 °C, hold 2 min, ramp 4 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 7.656 min, minor enantiomer  $t_R$  = 7.944 min; Conversion = 63%; ee = 86% of (*R*)-isomer. C<sub>6</sub>H<sub>14</sub>O: Calcd: 102.1, EI-MS found: 102.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.48 (q,  $J$  = 6.4 Hz, 1H), 1.45 (s, 1H), 1.12 (d,  $J$  = 6.4 Hz, 3H), 0.89 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 75.65, 34.89, 25.40, 17.86.

**(±)-1-cyclopropylethanol (2v)**:<sup>2c</sup> Conditions: (±)-1-cyclopropylethanol (21.5 mg, 0.25 mmol); (*R,R*)-Mn-complex **1b** (1.3 mg, 0.0025 mmol); KOAc (19.6 mg, 0.2 mmol); H<sub>2</sub>O (1.00 mL) and CH<sub>2</sub>Cl<sub>2</sub> (500 μL); NBS (28.9 mg, 0.1625 mmol); room temperature; 20min. GC (Varian Capillary Column CP-Chirasil-Dex CB): carrier gas, N<sub>2</sub> (flow 20 mL/min); injection temp, 250 °C; detector temperature, 280 °C; column temperature, 50 °C, hold 2 min, ramp 4 °C/min to 170 °C, then hold 10 min; major enantiomer  $t_R$  = 5.798 min, minor enantiomer  $t_R$  = 6.013 min; Conversion = 62%; ee = 67% of (*R*)-isomer. C<sub>5</sub>H<sub>10</sub>O: Calcd: 86.0, EI-MS found: 86.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.05 (dq,  $J$  = 8.3, 6.2 Hz, 1H), 1.85 (s, 1H), 1.25 (d,  $J$  = 6.2 Hz, 3H), 0.88 (m, 1H), 0.54 – 0.40 (m, 2H), 0.30 – 0.21 (m, 1H), 0.19 – 0.09 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 72.98, 22.39, 19.16, 3.01, 2.21.

#### 3.4. Studies of the reaction between NBS and water.



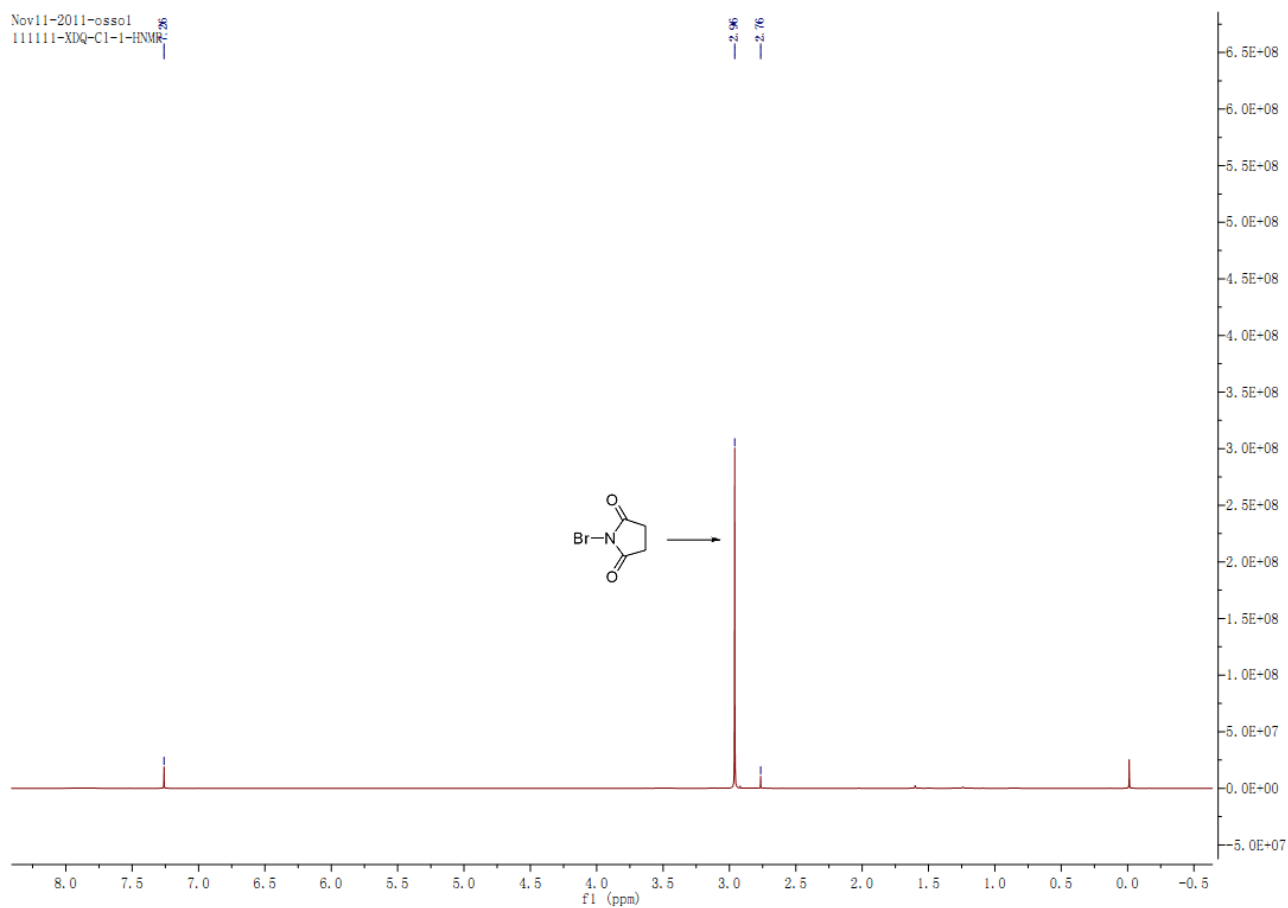


Figure S1.  $^1\text{H}$  NMR of NBS in  $\text{CDCl}_3$

Nov11-2011-ossol  
1111111-1DQ-C-1-HNMR

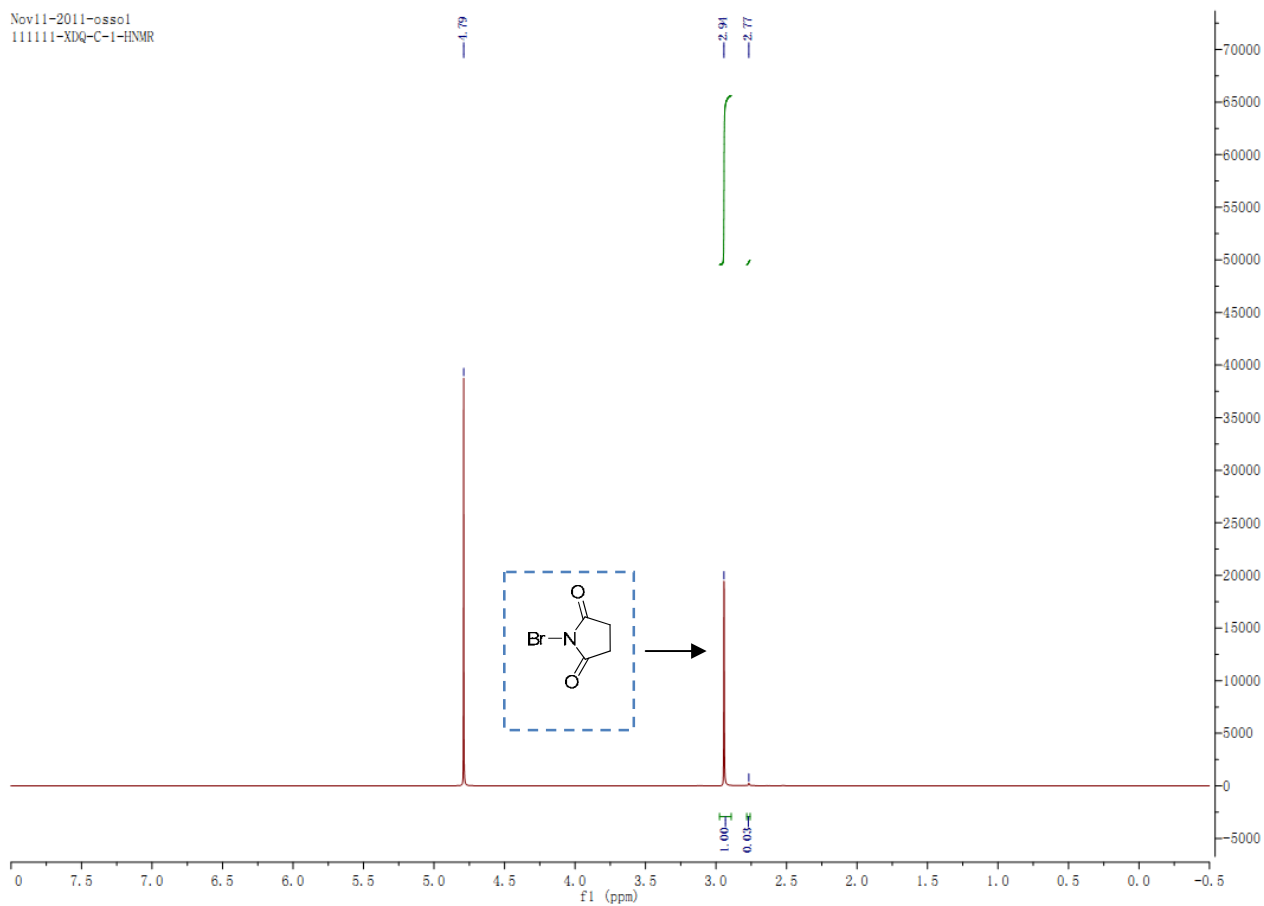


Figure S2.  $^1\text{H}$  NMR of NBS in  $\text{D}_2\text{O}$

Nov11-2011-ossol  
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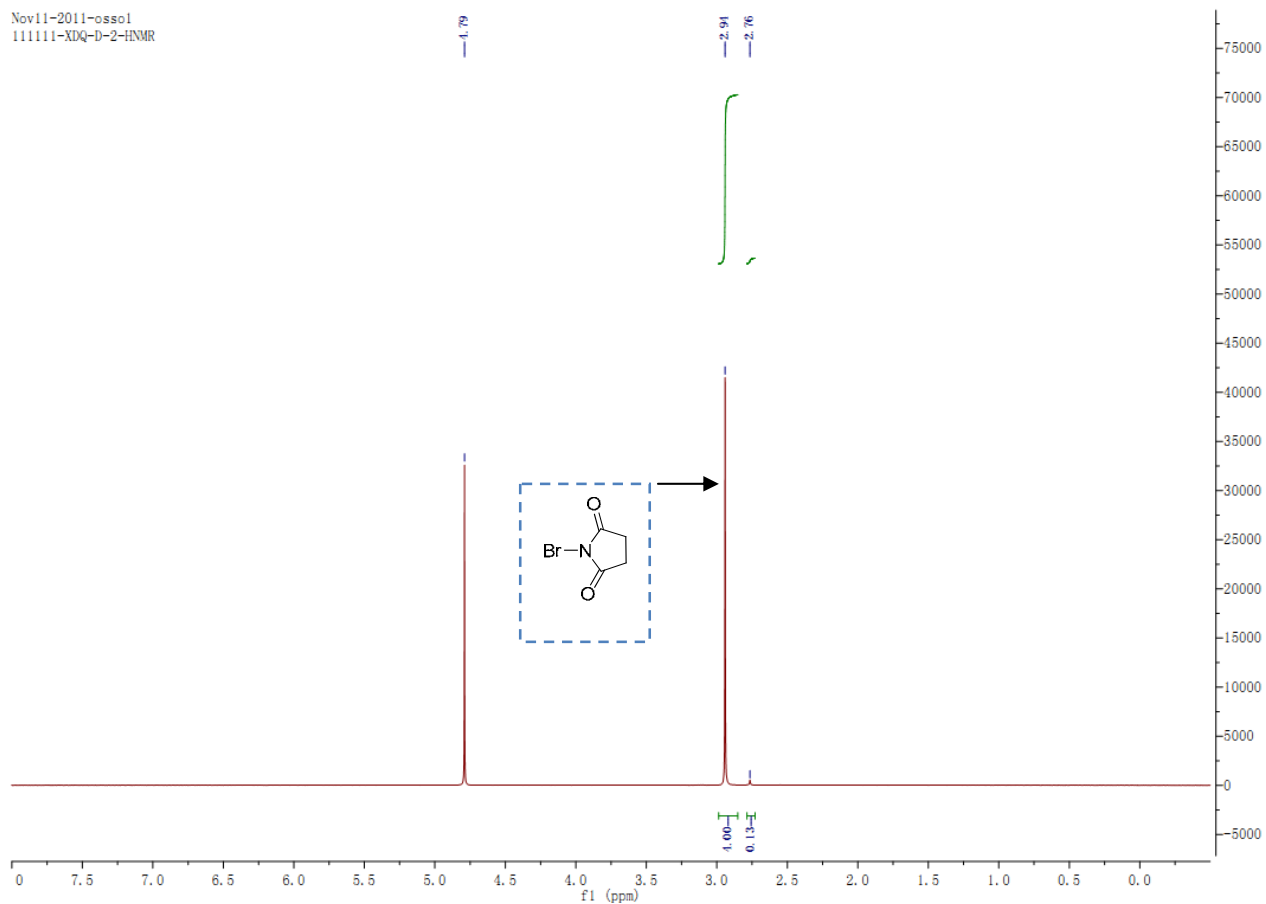


Figure S3.  $^1\text{H}$  NMR of NBS in  $\text{D}_2\text{O}$  after 1 h.

Nov11-2011-0ssol  
111111-XDQ-D-3-HNMR

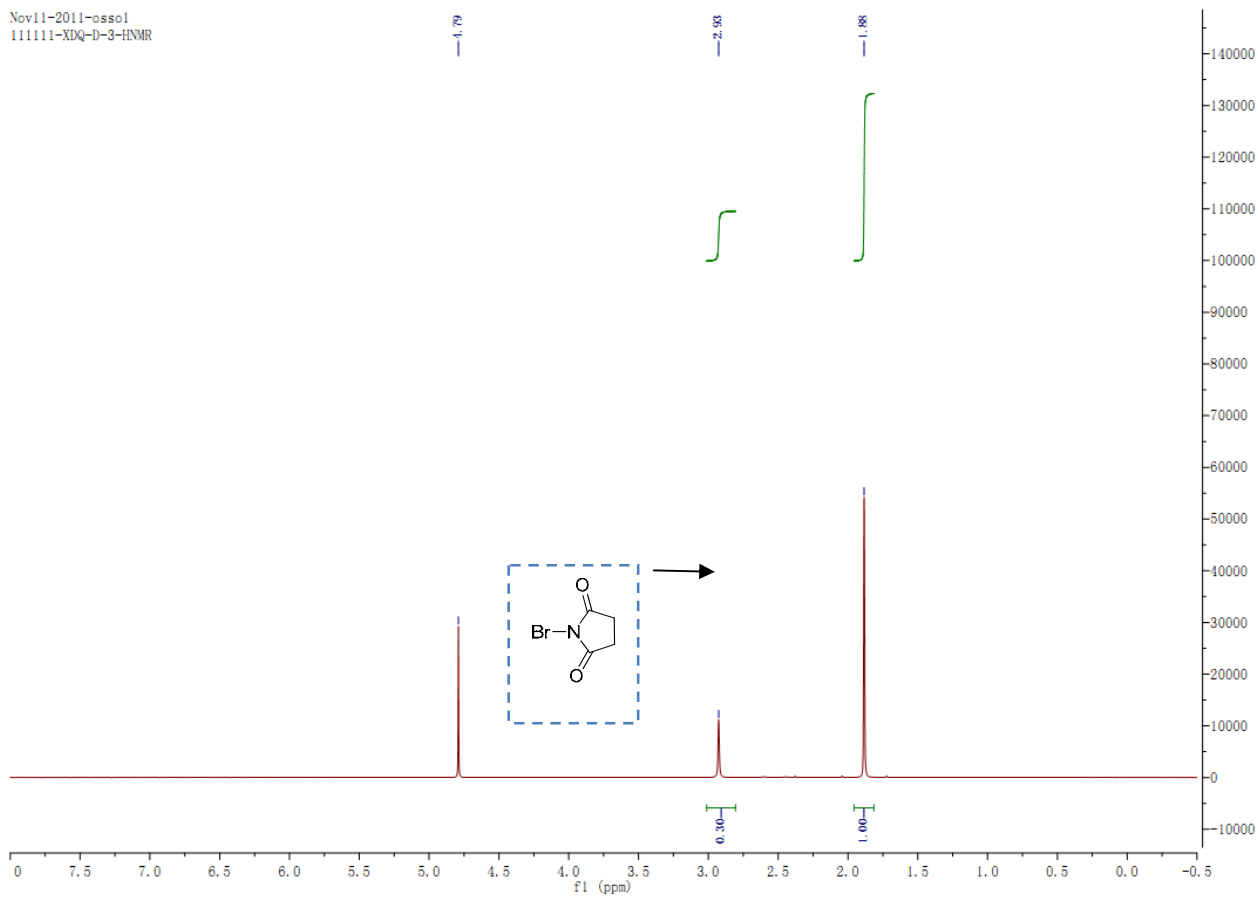


Figure S4.  $^1\text{H}$  NMR of NBS in  $\text{D}_2\text{O}$  in the presence of KOAc.

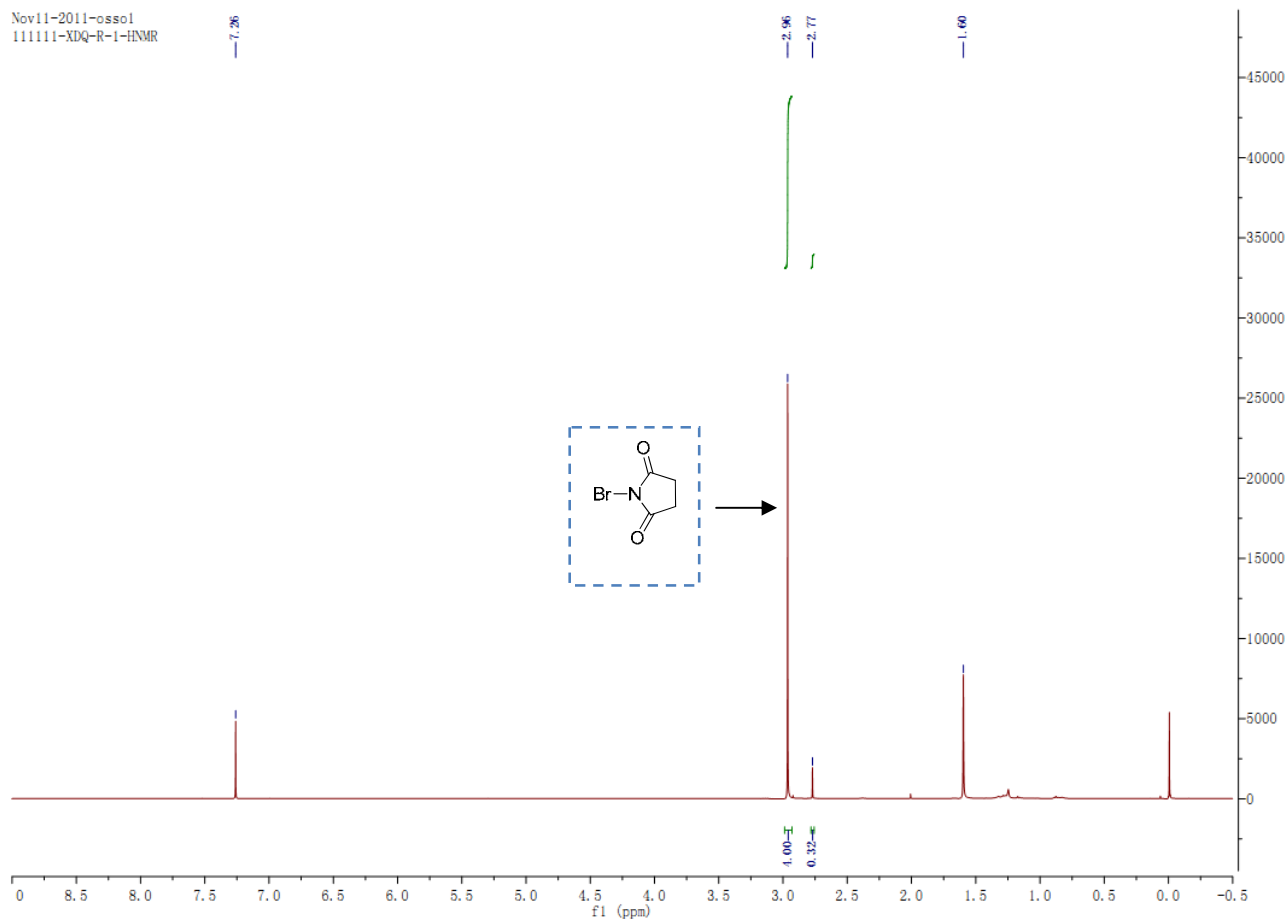


Figure S5.  $^1\text{H}$  NMR in  $\text{CDCl}_3$  (NBS was stirred in water in the presence of KOAc for 1 h, then the mixture was extracted with  $\text{CDCl}_3$ ).

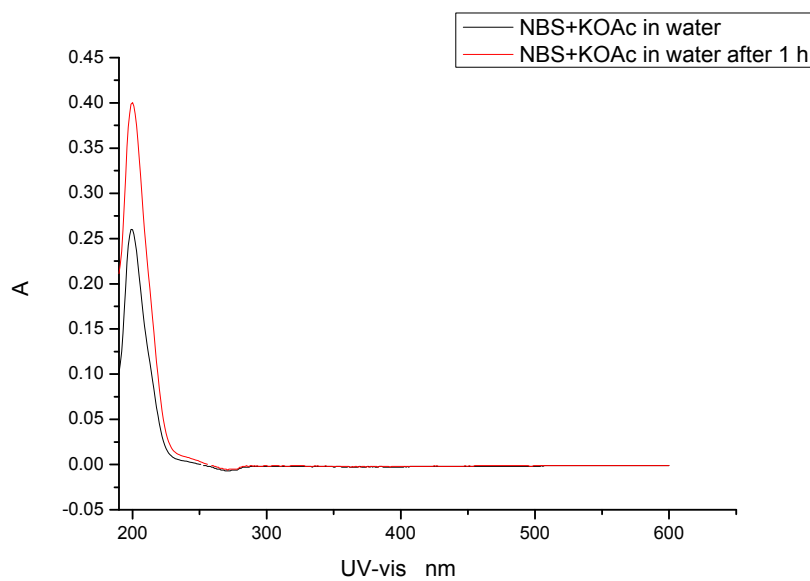
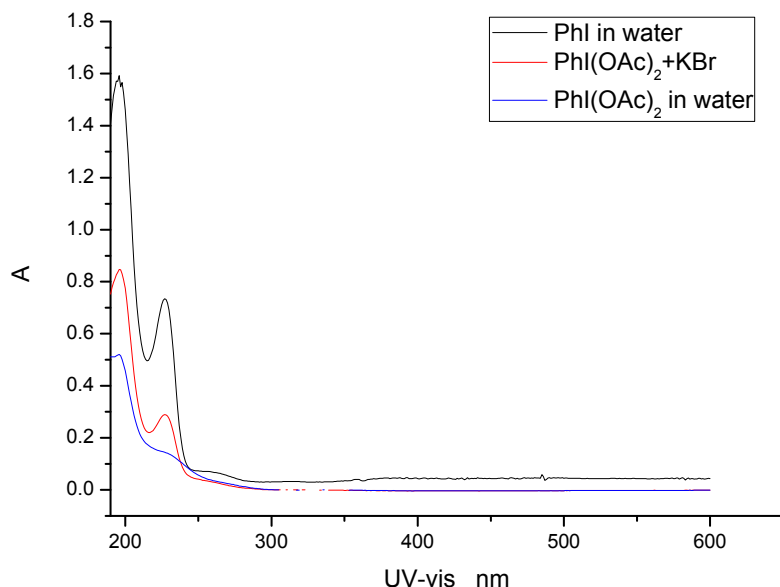


Figure S6. UV-visible absorbance spectra of NBS in water in the presence of KOAc.

The UV-visible spectra also indicate that the reaction between NBS and water in the presence of KOAc is slow.



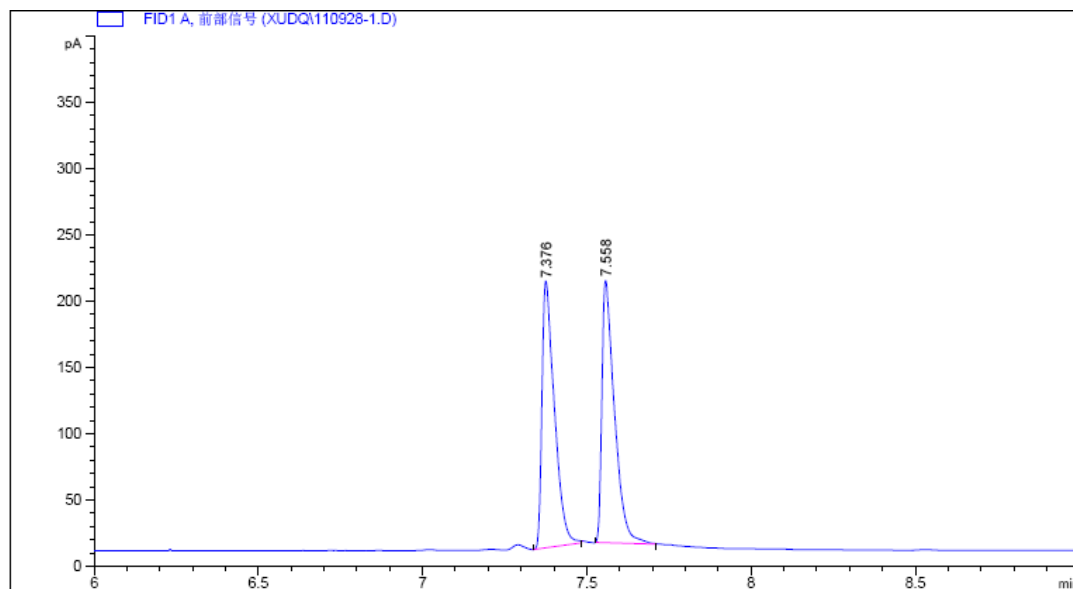
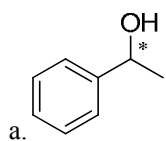
**Figure S7. UV-visible absorbance spectra of PhI(OAc)<sub>2</sub> and KBr in water in the presence of KOAc.**

The UV-visible spectra indicate that the reaction between PhI(OAc)<sub>2</sub> and KBr in water is rapid. Once PhI(OAc)<sub>2</sub> and KBr are added together in water, iodobenzene is observed. The finding is also confirmed by GC-MS spectrum. It is well in accordance with the observation by Corey. This results reveal that the forming HOBr is rapid, and the real oxidant species in the PhI(OAc)<sub>2</sub>/KBr/H<sub>2</sub>O OKR system is HOBr.<sup>3</sup>

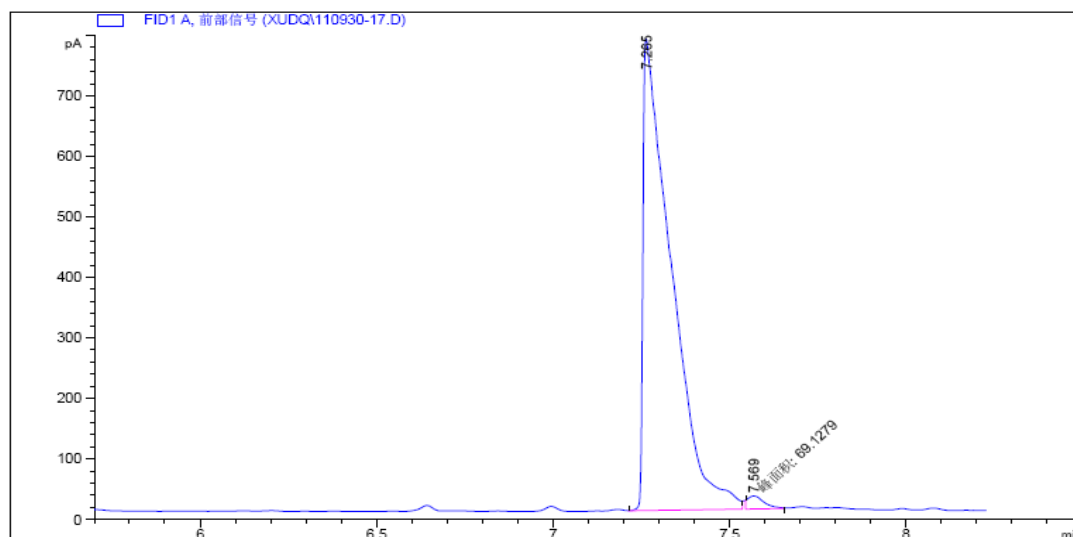
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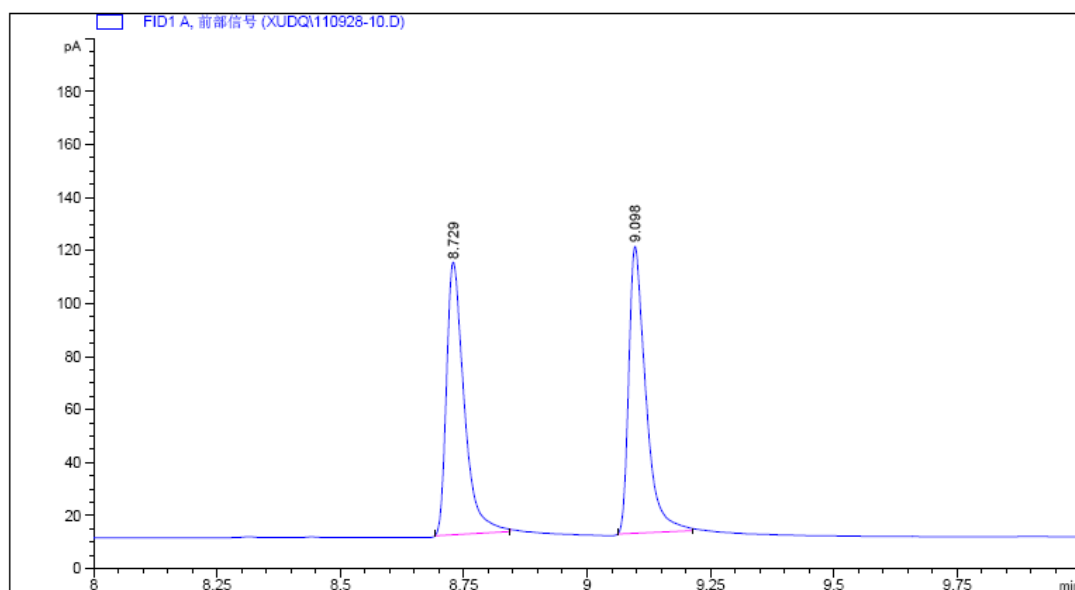
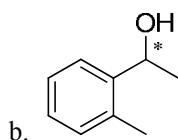
## 6. Copies of GS or HPLC Spectra



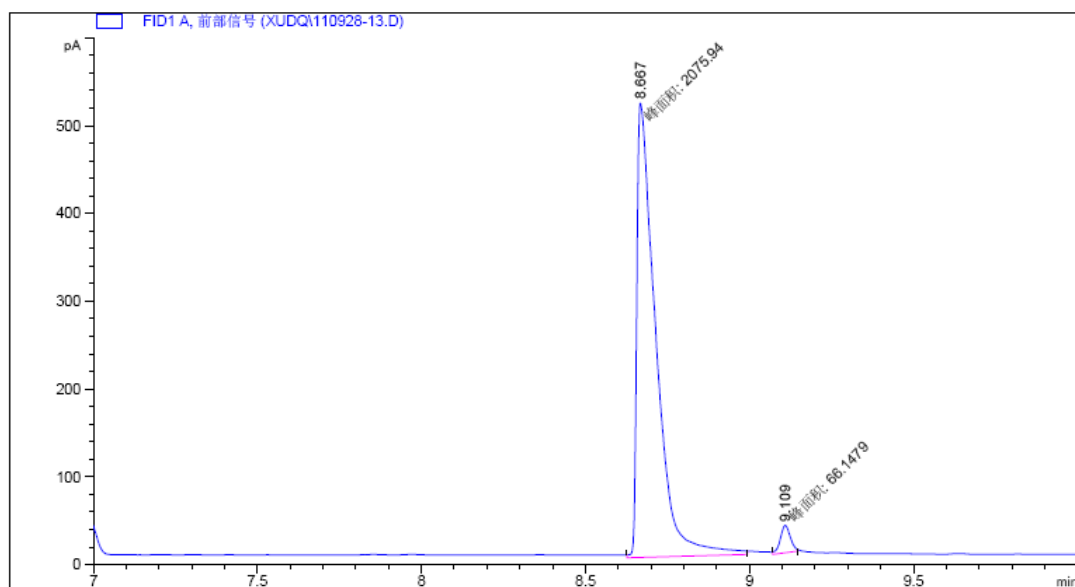
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.376	VB	0.0377	526.71918	199.95245	50.11043
2	7.558	BB	0.0390	524.39777	197.47047	49.88957



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.265	VV	0.0727	4324.63184	780.40967	98.42668
2	7.569	MF	0.0543	69.12794	21.21583	1.57332



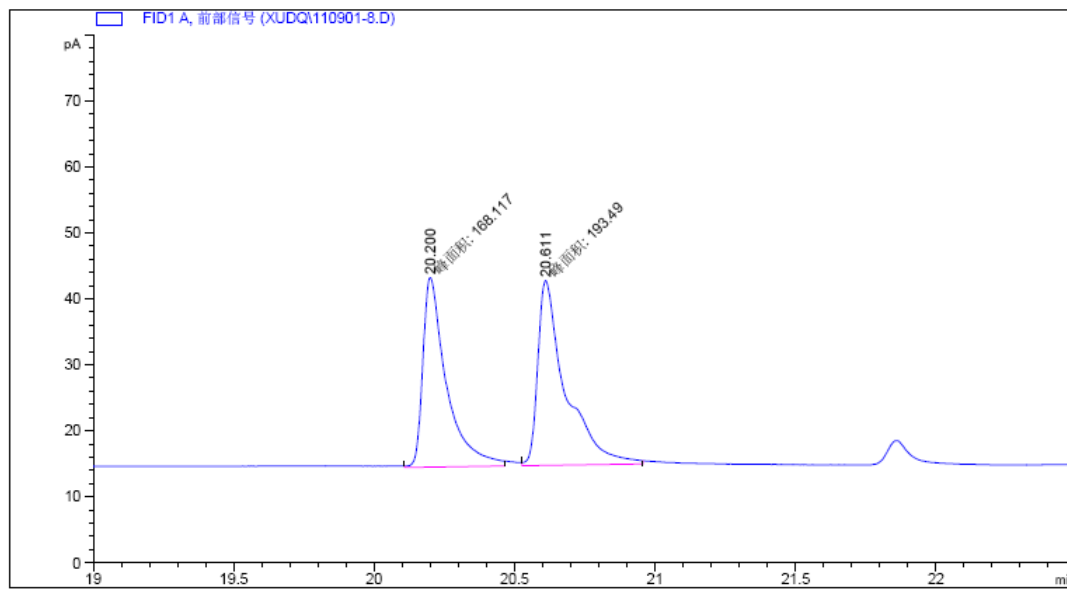
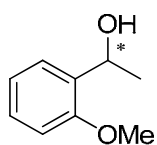
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	8.729	BB	0.0372	256.11530	102.48384	49.67957
2	9.098	BB	0.0350	259.41913	108.19790	50.32043



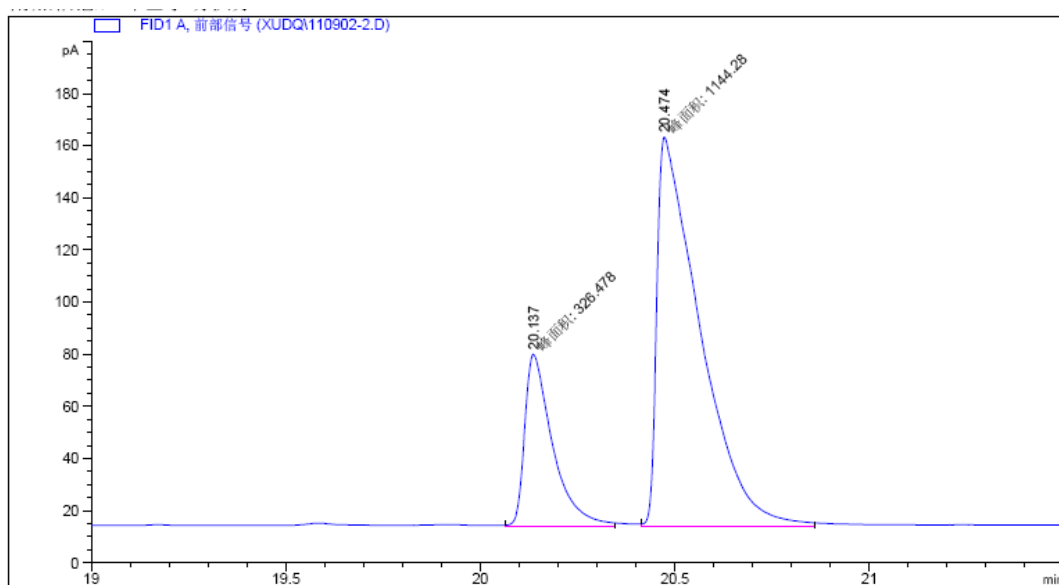
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	8.667	MM	0.0668	2075.93921	518.05951	96.91199
2	9.109	MM	0.0353	66.14785	31.26530	3.08801



c.

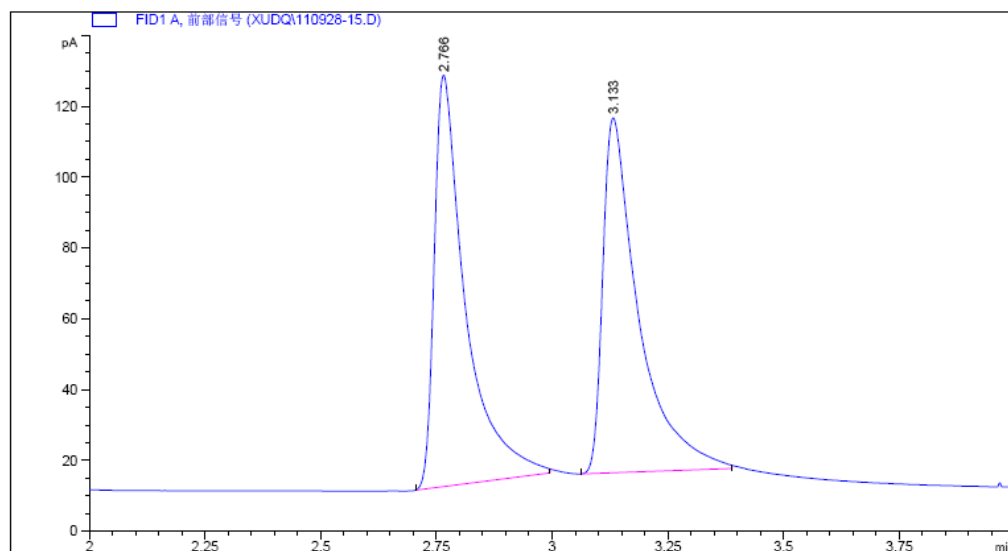
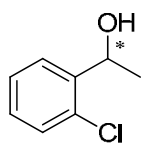


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	20.200	MF	0.0976	168.11693	28.71748	46.49166
2	20.611	FM	0.1150	193.48969	28.04255	53.50834

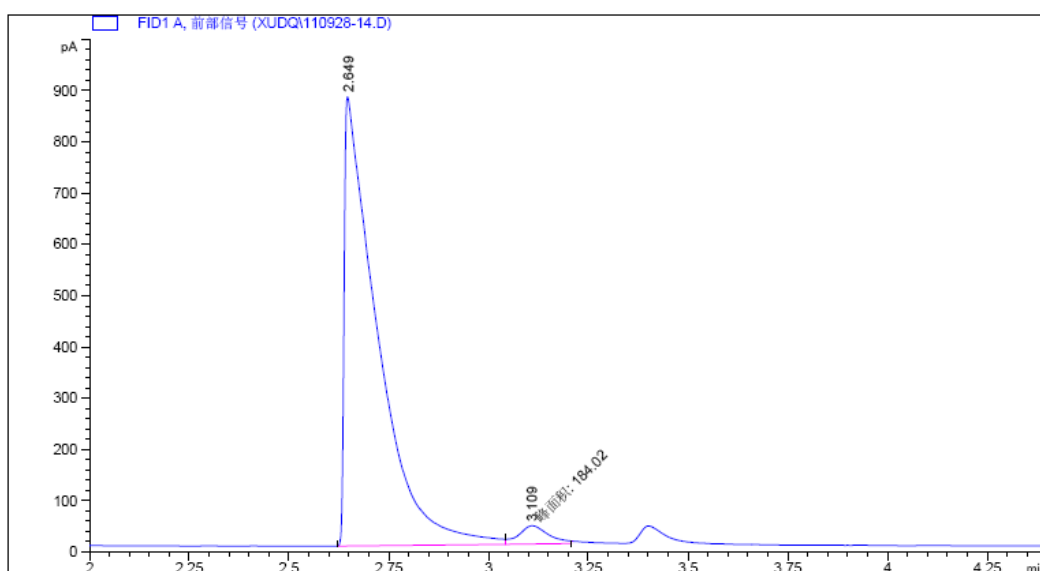


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	20.137	MF	0.0826	326.47781	65.84028	22.19798
2	20.474	FM	0.1278	1144.27649	149.19771	77.80202

d.

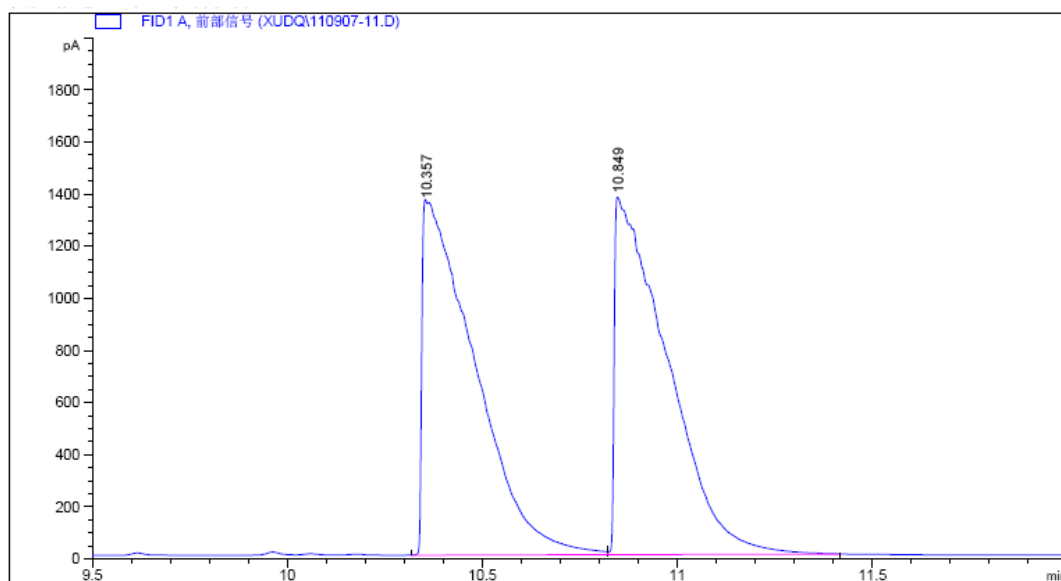
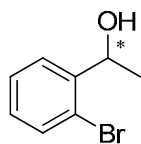


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	2.766	BB	0.0678	545.18372	116.10116	50.33560
2	3.133	BB	0.0757	537.91400	100.13499	49.66440

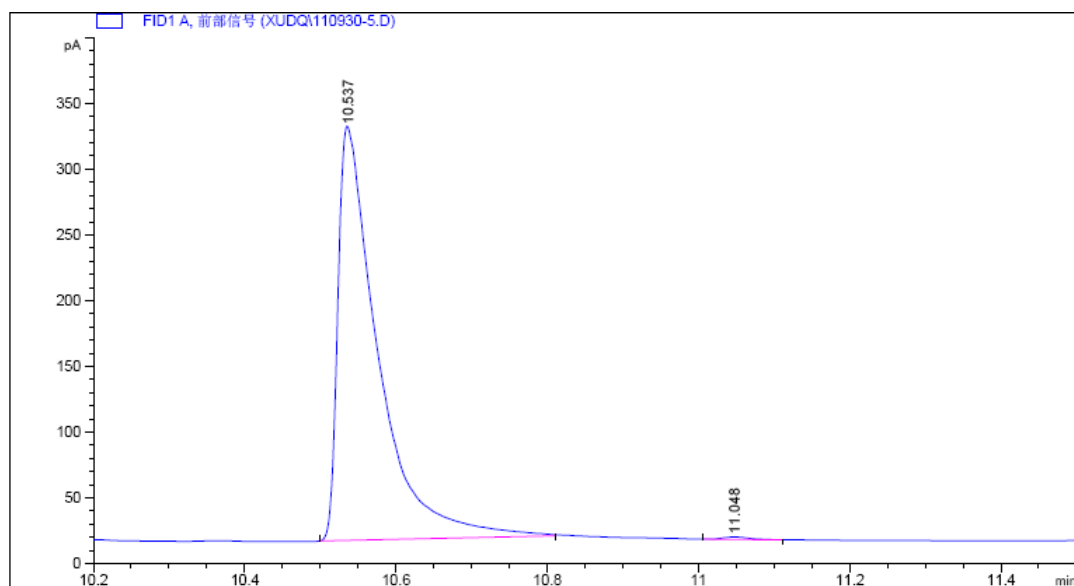


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	2.649	BV	0.0730	5035.42383	877.13080	96.47433
2	3.109	MF	0.0866	184.02020	35.42723	3.52567

e.

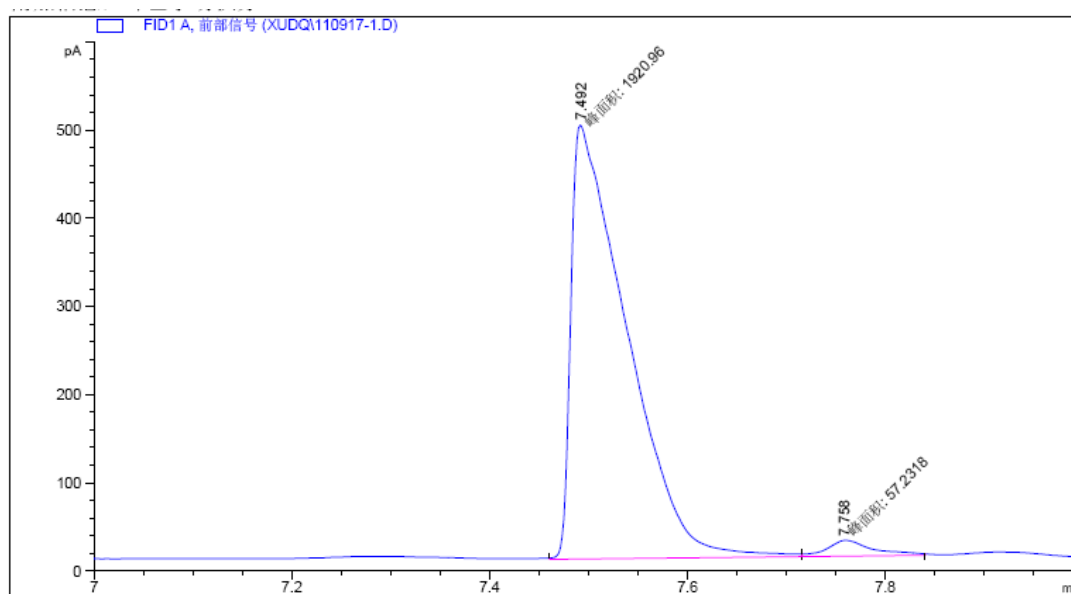
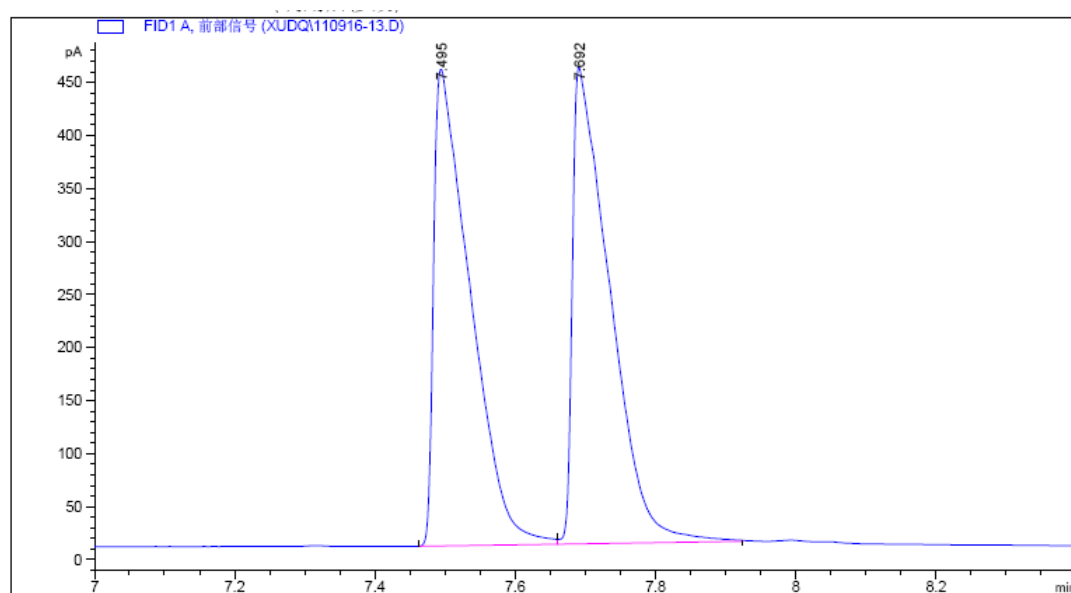
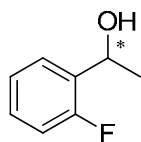


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	10.357	BV	0.1140	1.27539e4	1353.21326	49.85124
2	10.849	VB	0.1138	1.28300e4	1375.98450	50.14876



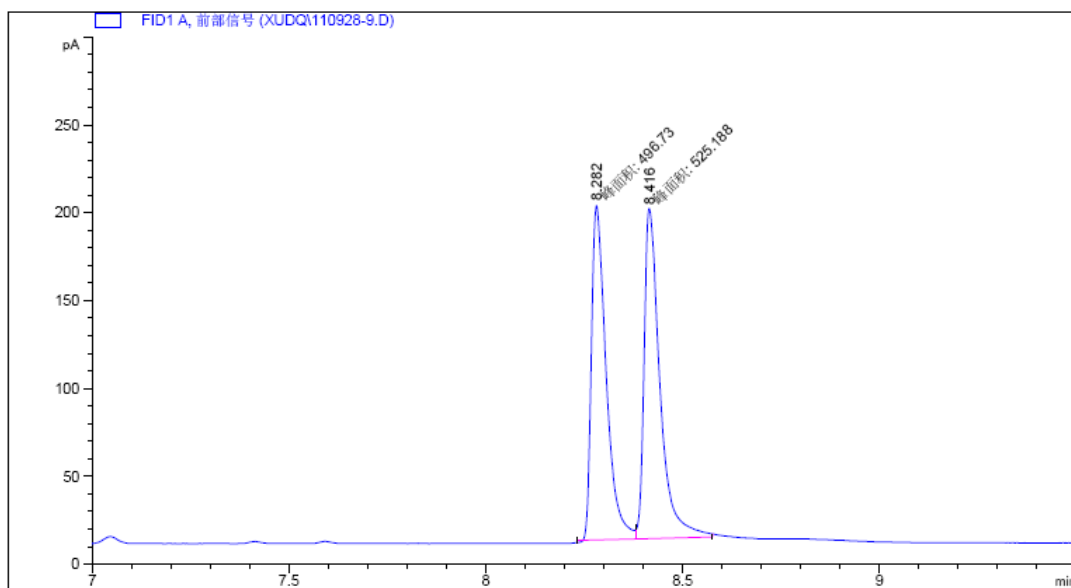
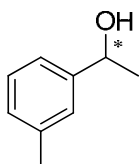
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	10.537	BB	0.0533	1161.47424	313.22836	99.63171
2	11.048	BB	0.0354	4.29339	1.89529	0.36829

f.

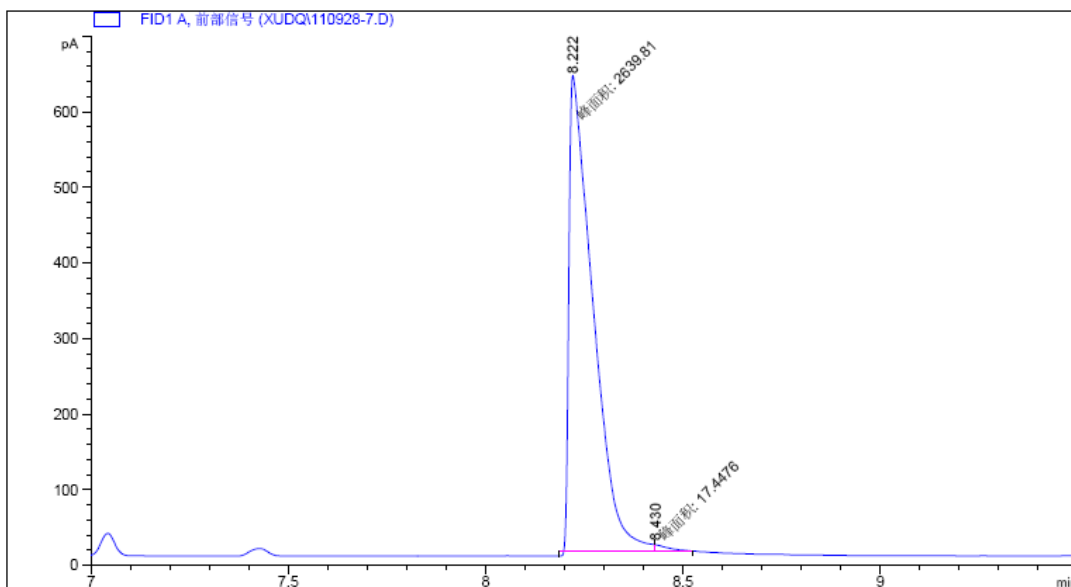


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.492	MF	0.0649	1920.96411	493.57233	97.10687
2	7.758	FM	0.0538	57.23181	17.74626	2.89313

g.

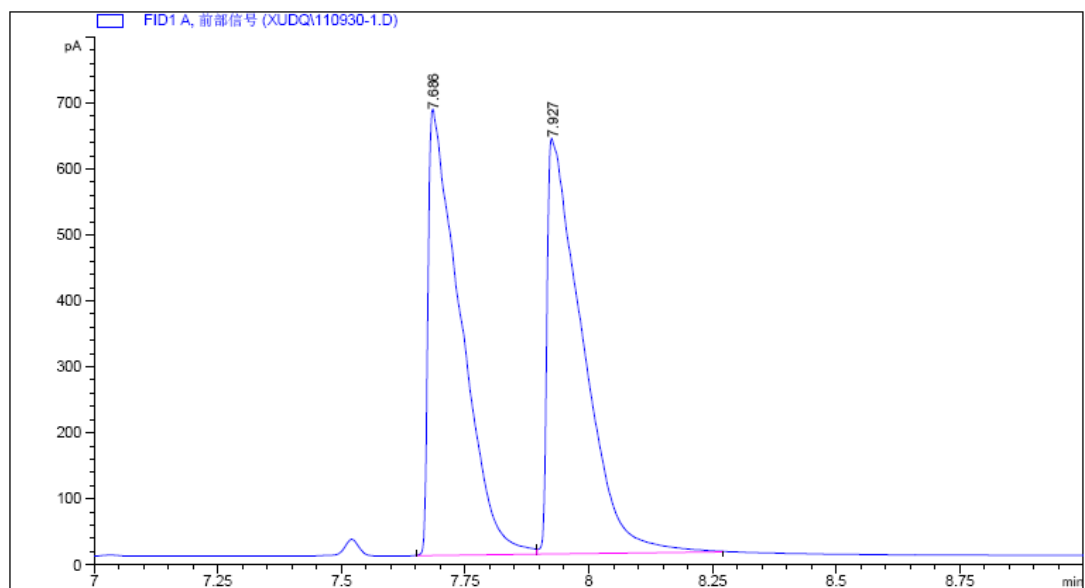
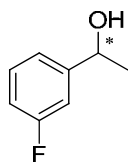


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	8.282	MF	0.0434	496.72961	190.67015	48.60761
2	8.416	FM	0.0465	525.18787	188.05725	51.39239

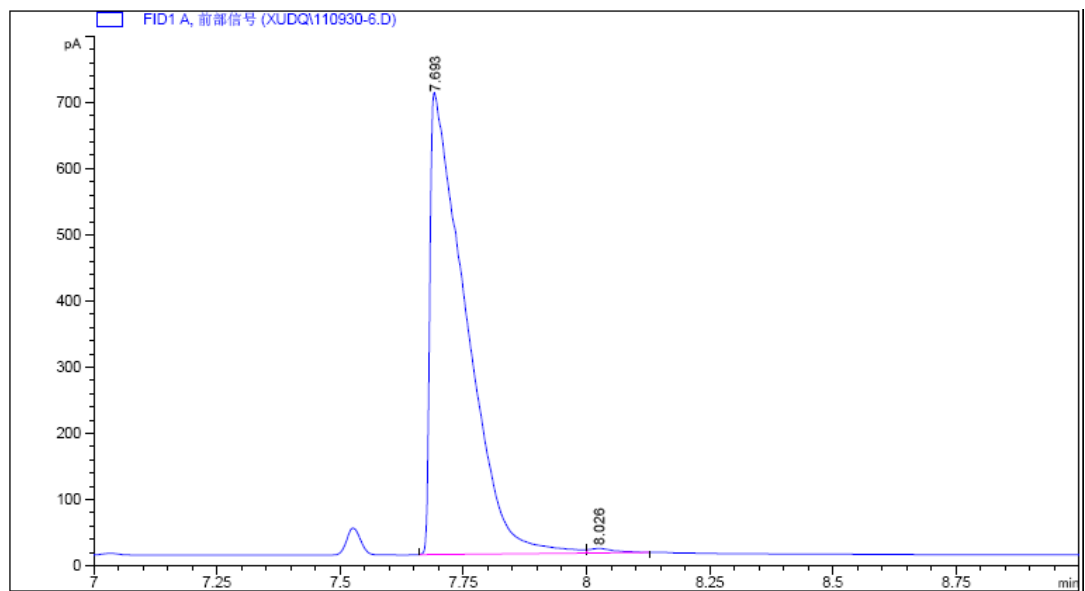


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	8.222	MF	0.0699	2639.81323	629.36322	99.34340
2	8.430	FM	0.0355	17.44763	8.19494	0.65660

h.

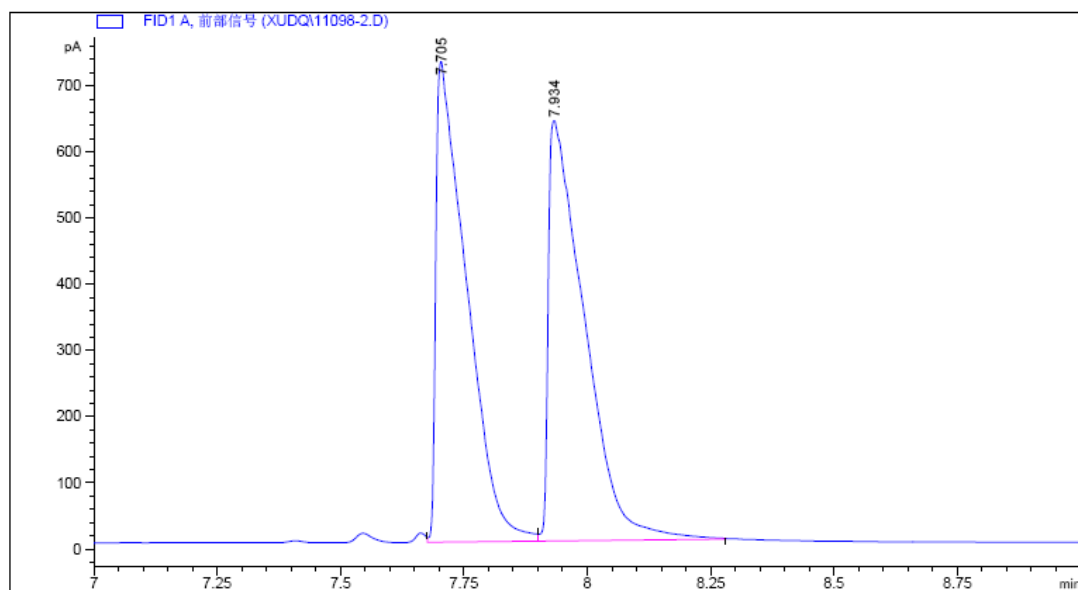
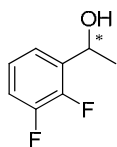


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.686	BV	0.0604	3063.68140	669.82086	49.52985
2	7.927	VB	0.0683	3121.84448	625.10767	50.47015

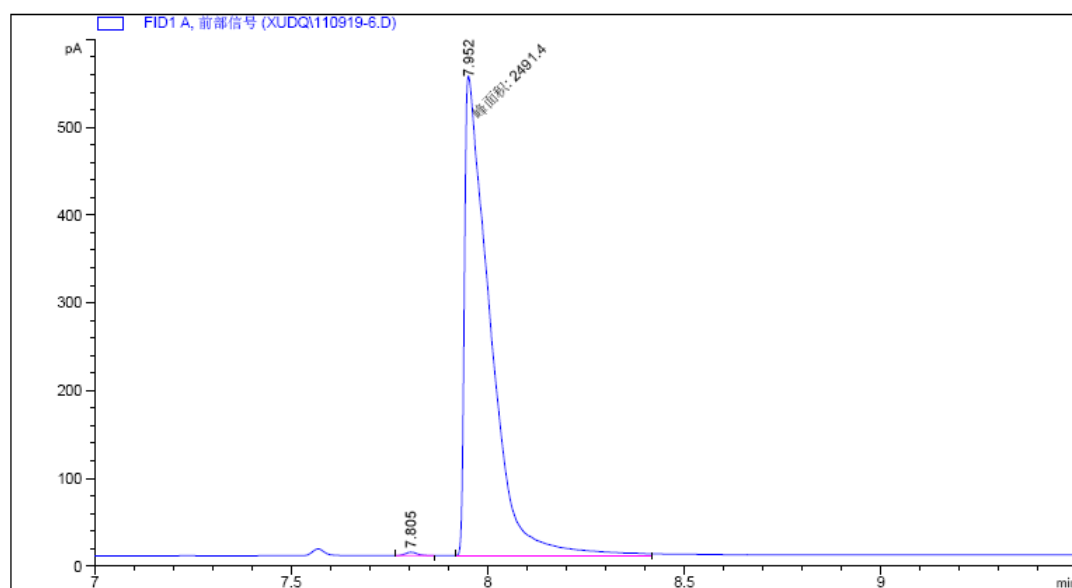


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.693	BB	0.0639	3495.27002	692.06354	99.29864
2	8.026	BB	0.0534	24.68774	6.78842	0.70136

i.

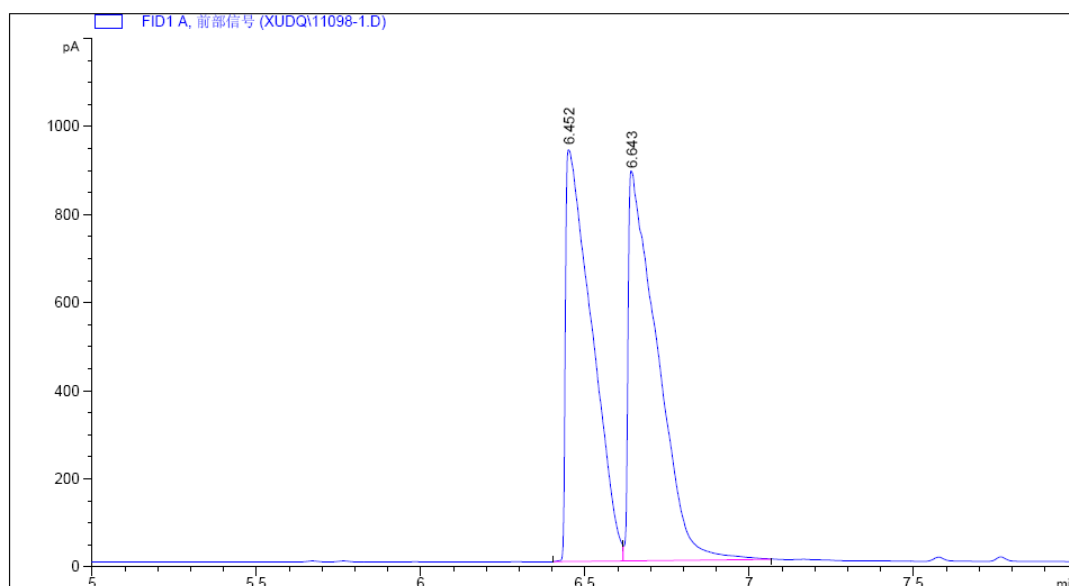
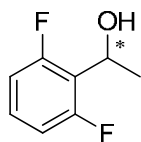


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.705	VV	0.0554	3135.75879	726.07245	49.29120
2	7.934	VB	0.0683	3225.94165	634.42914	50.70880

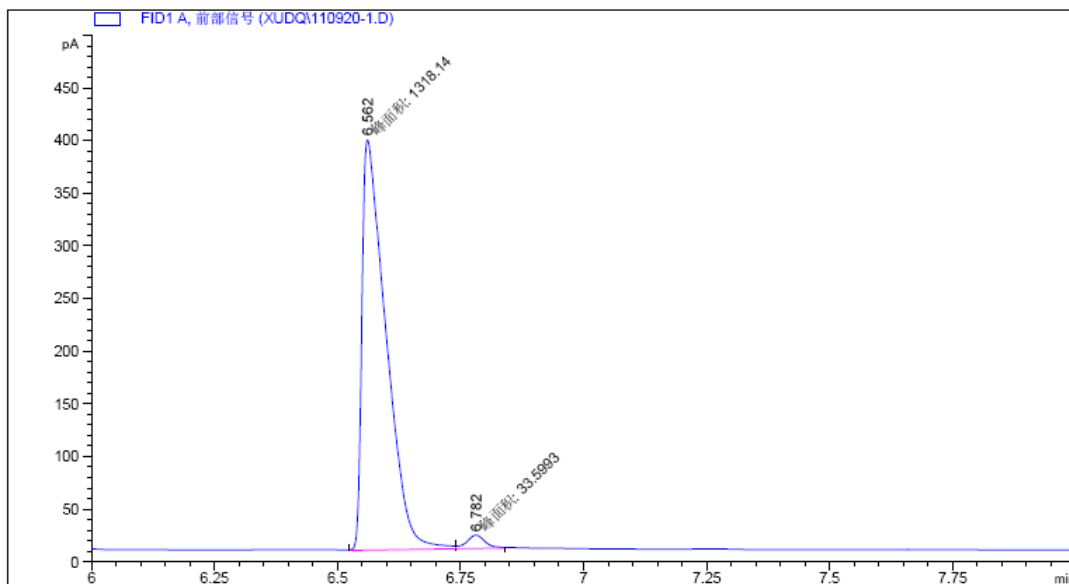


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.805	BB	0.0317	7.77264	3.81967	0.31101
2	7.952	MM	0.0757	2491.40234	548.85846	99.68899

j.



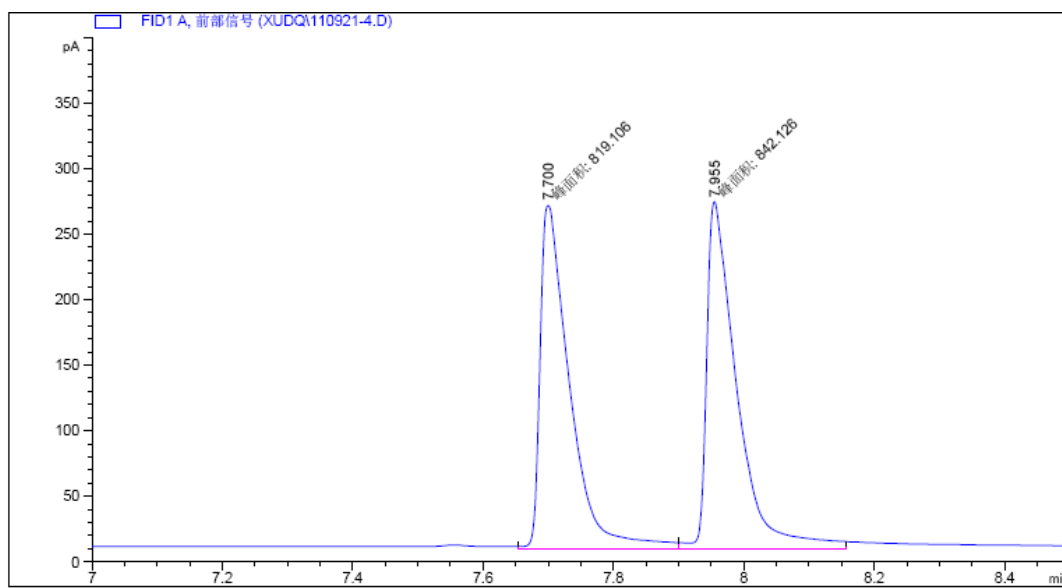
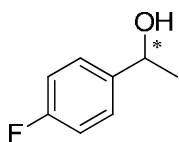
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	6.452	BV	0.0734	5174.88574	937.08588	48.79681
2	6.643	VB	0.0768	5430.08057	882.31976	51.20319



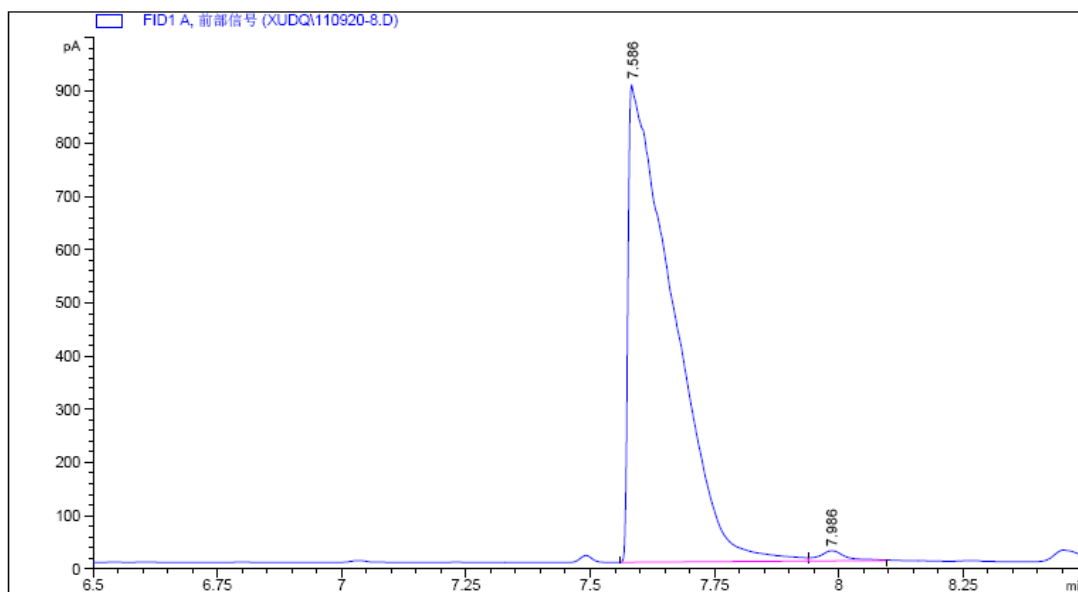
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	6.562	MF	0.0563	1318.13525	389.91962	97.51436
2	6.782	FM	0.0434	33.59927	12.88979	2.48564

k.



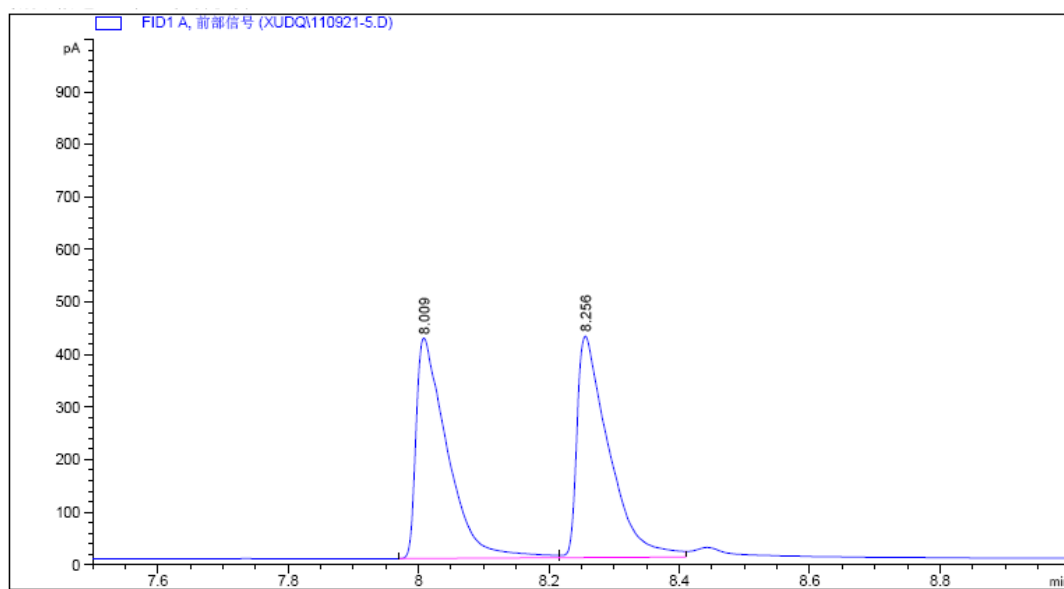
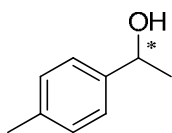


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.700	MF	0.0520	819.10571	262.69031	49.30712
2	7.955	FM	0.0530	842.12646	265.02542	50.69288

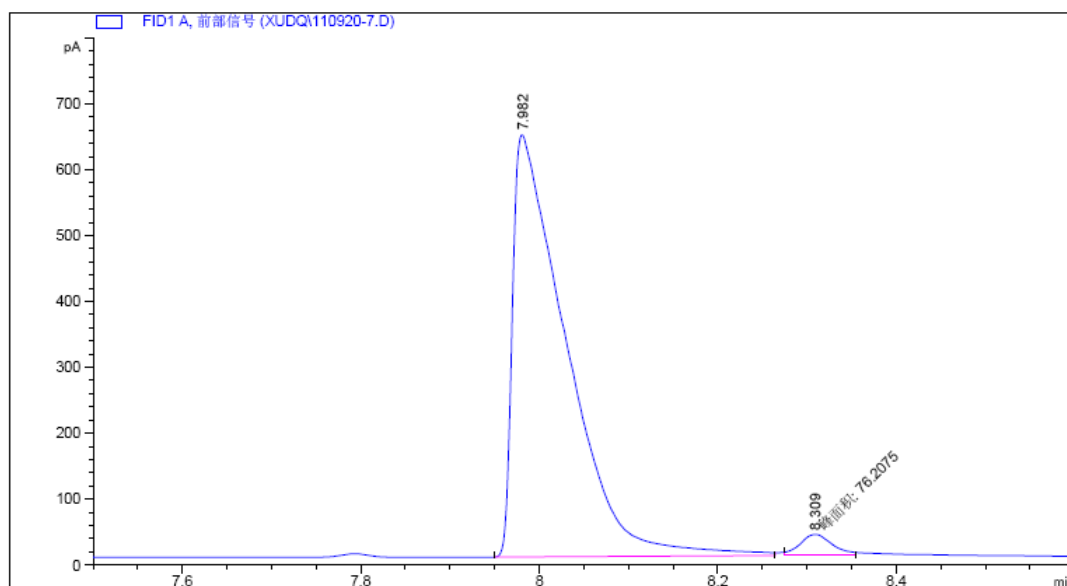


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.586	BV	0.0782	5591.35205	902.99298	98.77791
2	7.986	VB	0.0519	69.17697	18.82023	1.22209

1.

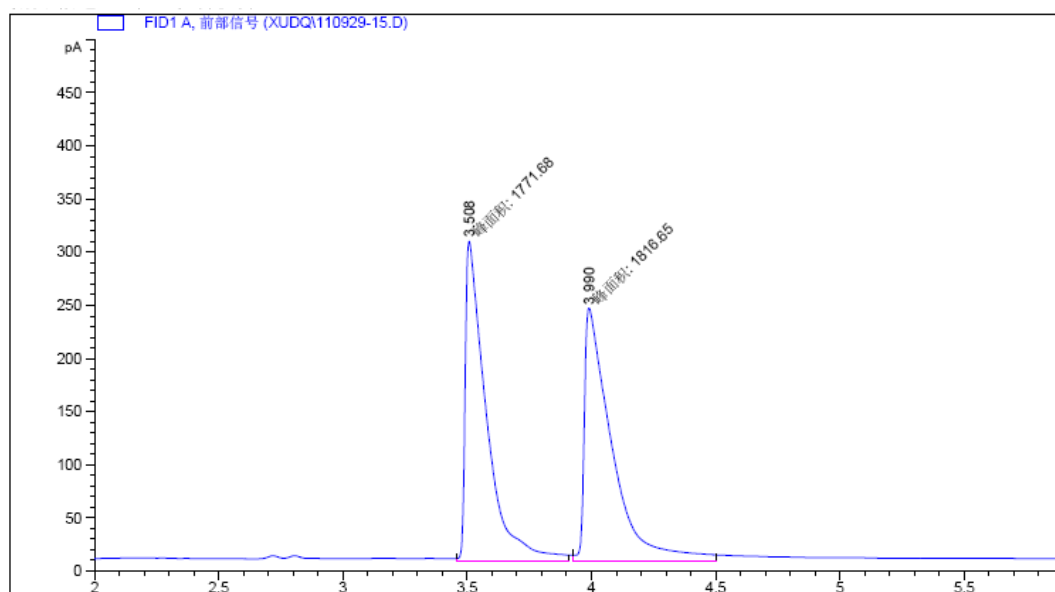
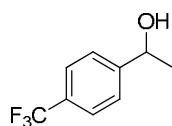


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	8.009	BV	0.0459	1395.99414	418.55594	49.49392
2	8.256	VV	0.0474	1424.54260	421.35721	50.50608

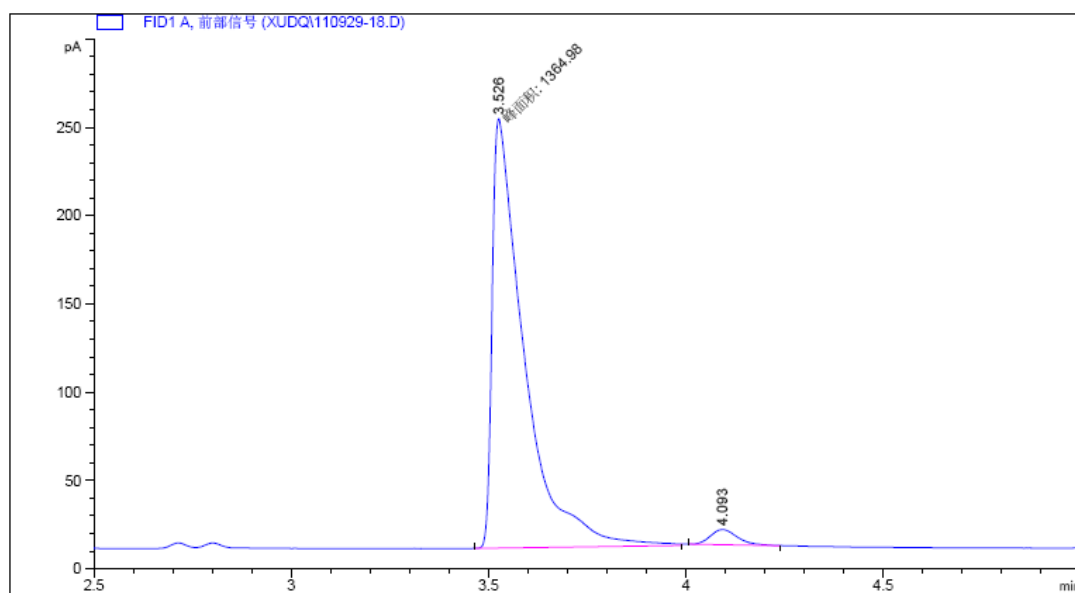


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.982	BB	0.0565	2665.38989	641.23517	97.22033
2	8.309	MM	0.0407	76.20746	31.20559	2.77967

m.

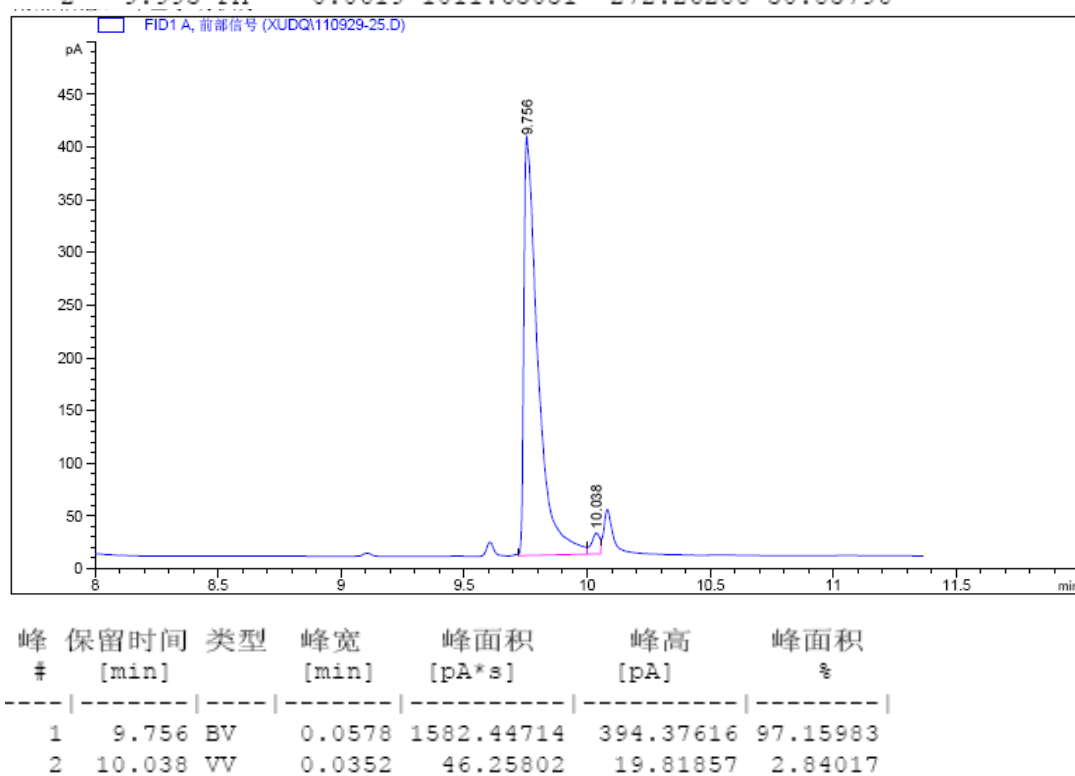
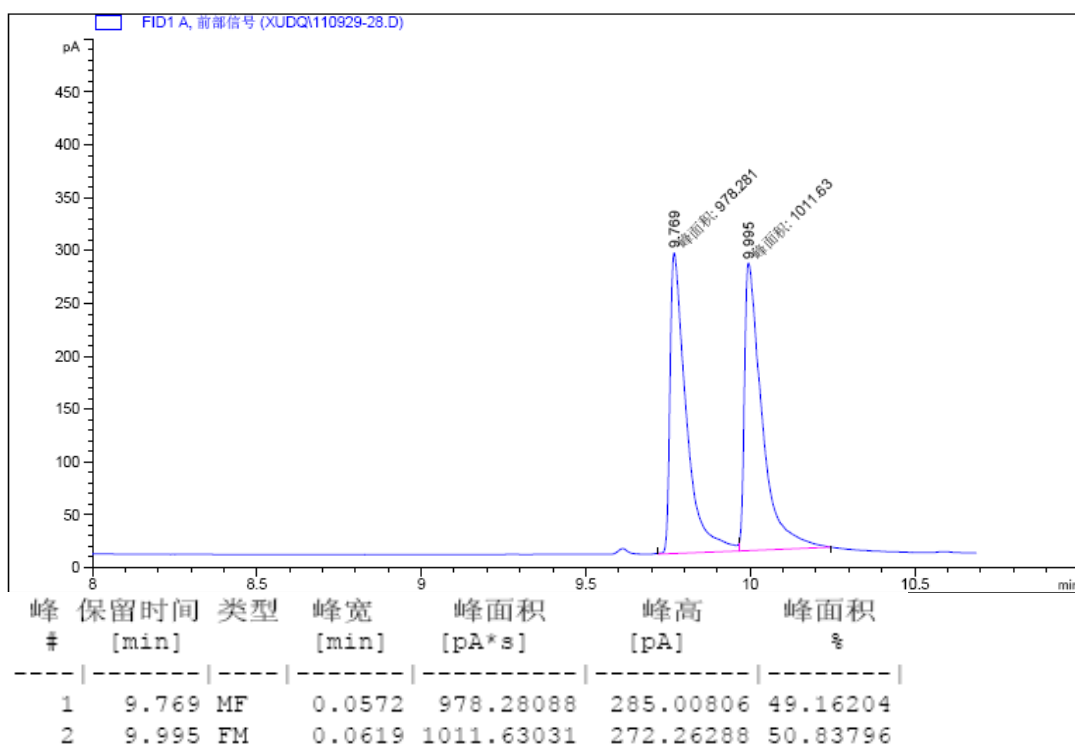
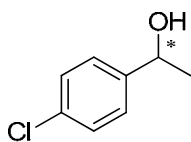


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	3.508	MF	0.0982	1771.67651	300.65964	49.37339
2	3.990	FM	0.1274	1816.64624	237.73053	50.62661

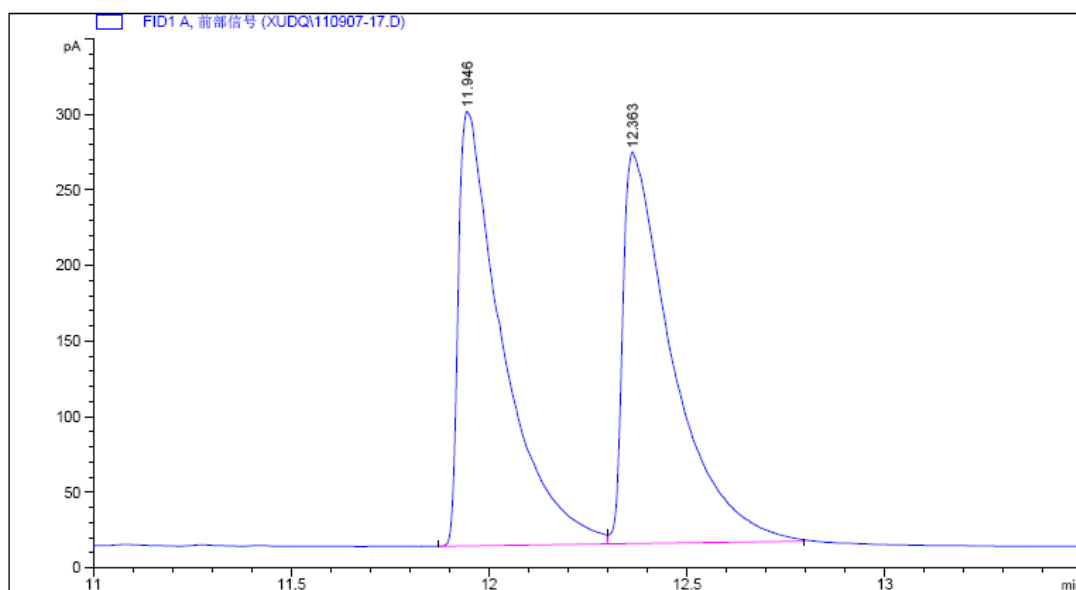
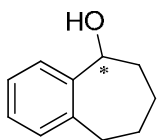


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	3.526	MM	0.0935	1364.97949	243.18668	97.07622
2	4.093	BB	0.0748	41.11093	8.58982	2.92378

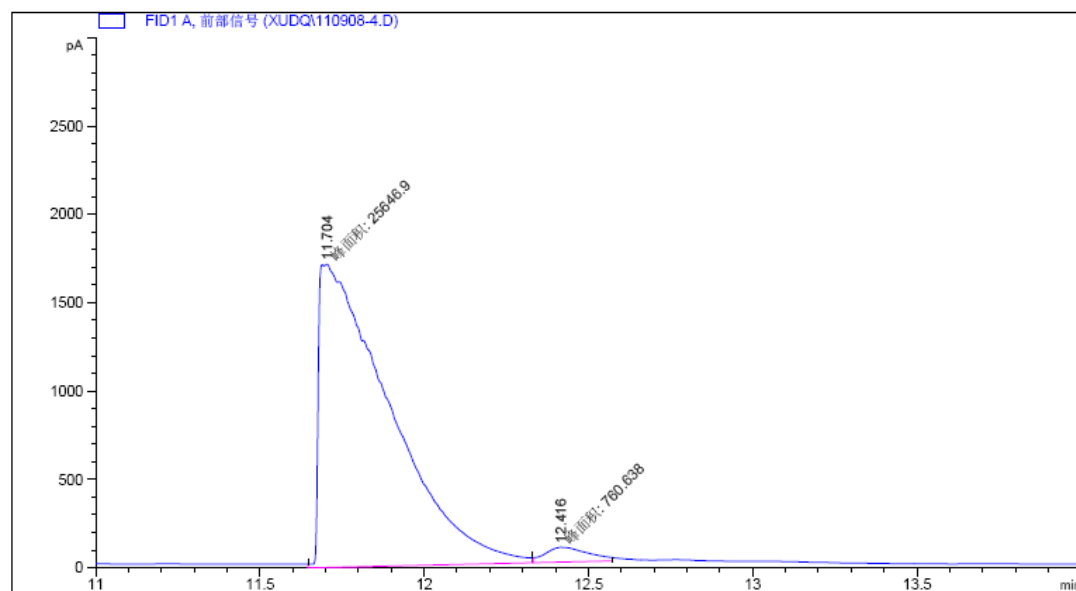
n.



0.

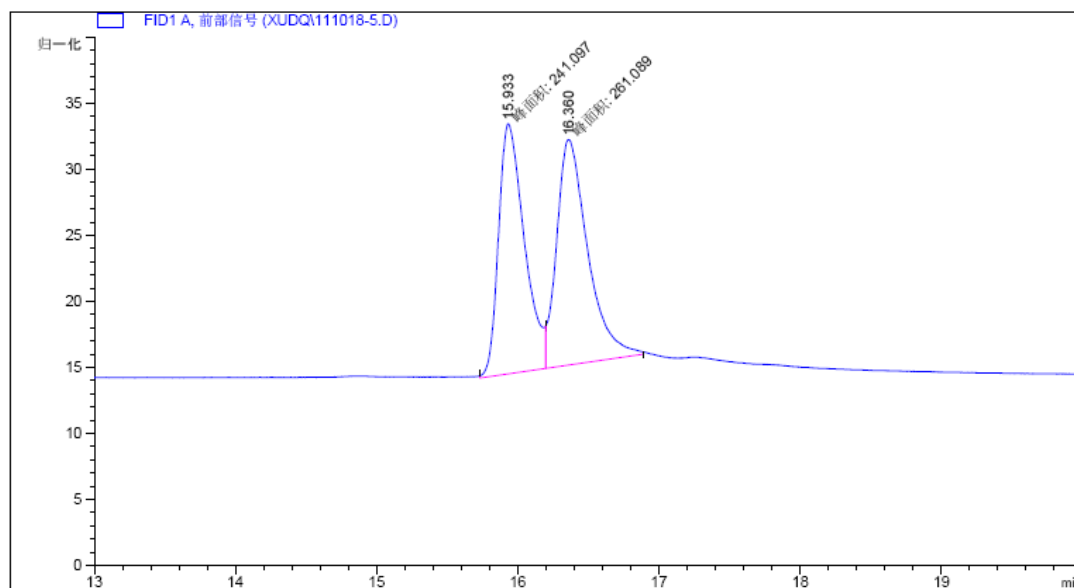
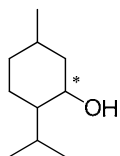


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	11.946	BV	0.1033	2226.39087	287.51370	49.80019
2	12.363	VB	0.1132	2244.25635	258.67844	50.19981

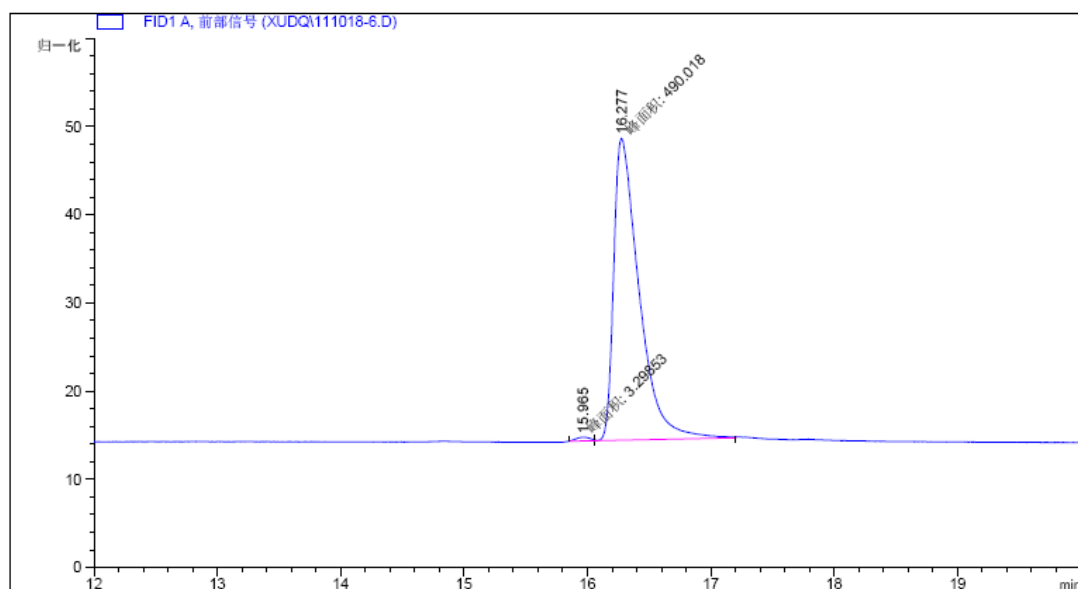


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	11.704	MF	0.2491	2.56469e4	1715.69470	97.11962
2	12.416	FM	0.1520	760.63751	83.40169	2.88038

p

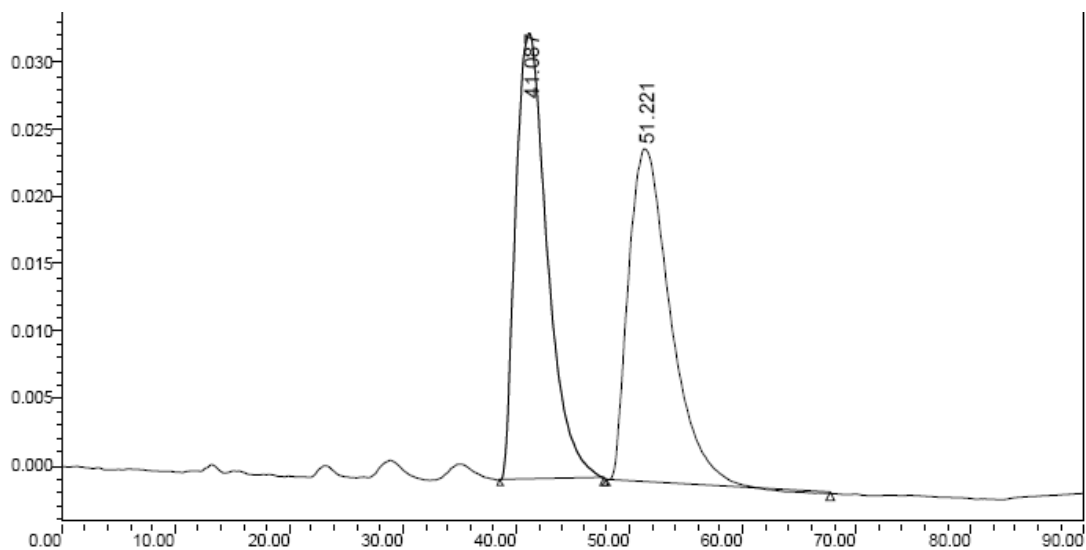
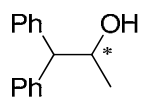


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	15.933	MF	0.2121	241.09747	18.94121	48.00959
2	16.360	FM	0.2550	261.08856	17.06714	51.99041

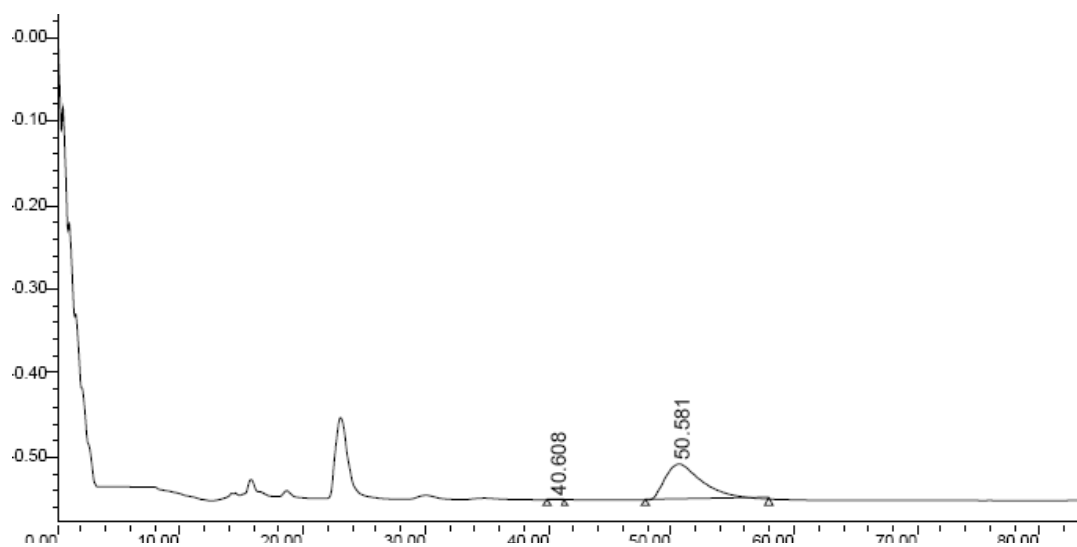


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	15.965	MF	0.1262	3.29853	4.35644e-1	0.66864
2	16.277	FM	0.2385	490.01843	34.24429	99.33136

9

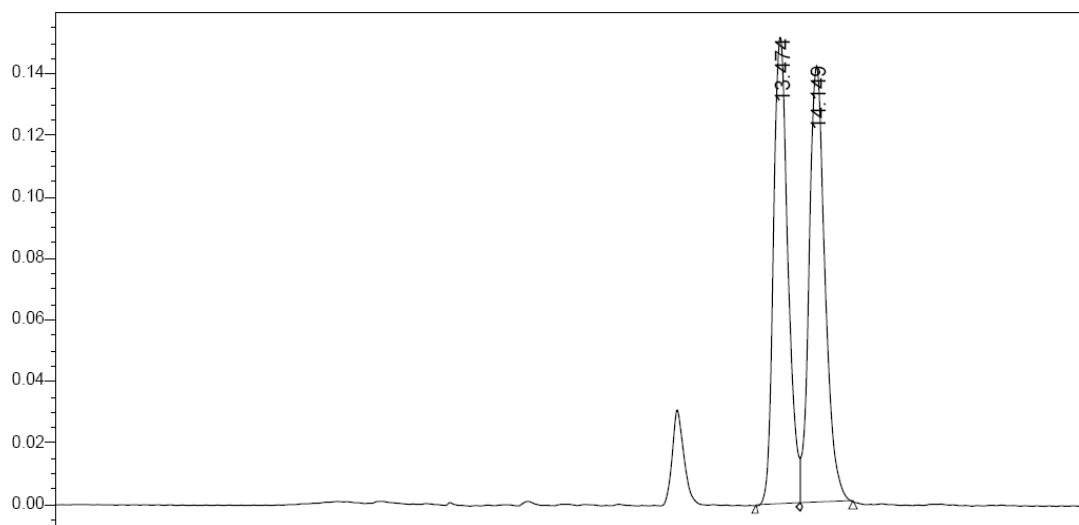
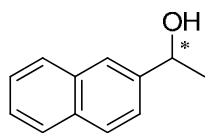


RT (min)	Area (V*sec)	%Area	Heigh (V)	% Heigh
41.081	432509	50.07	33220	57.27
51.221	414313	49.93	24788	42.73

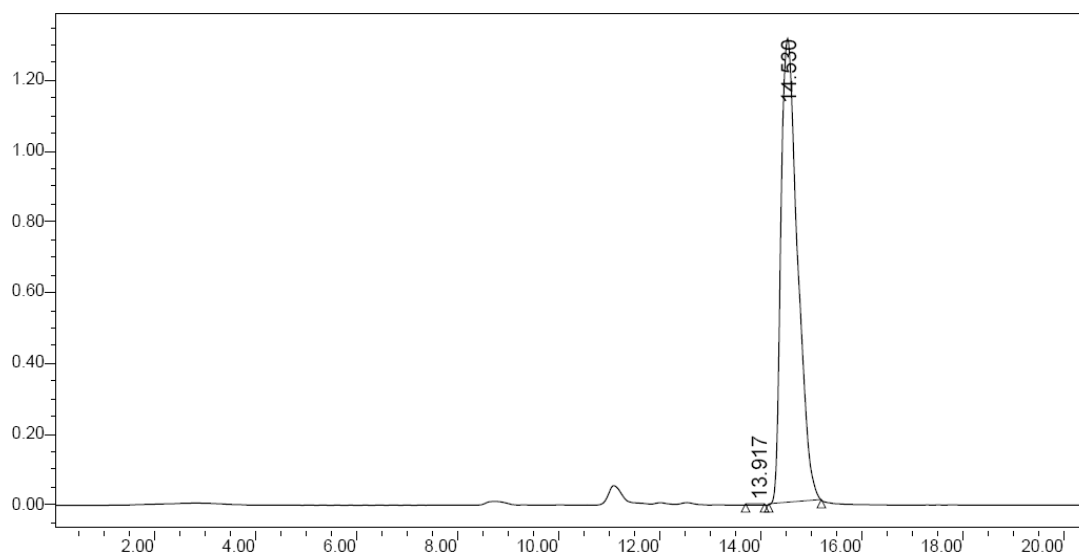


RT (min)	Area (V*sec)	%Area	Heigh (V)	% Heigh
40.608	3838	0.04	72	0.17
50.581	122547	99.96	42378	99.83

I.



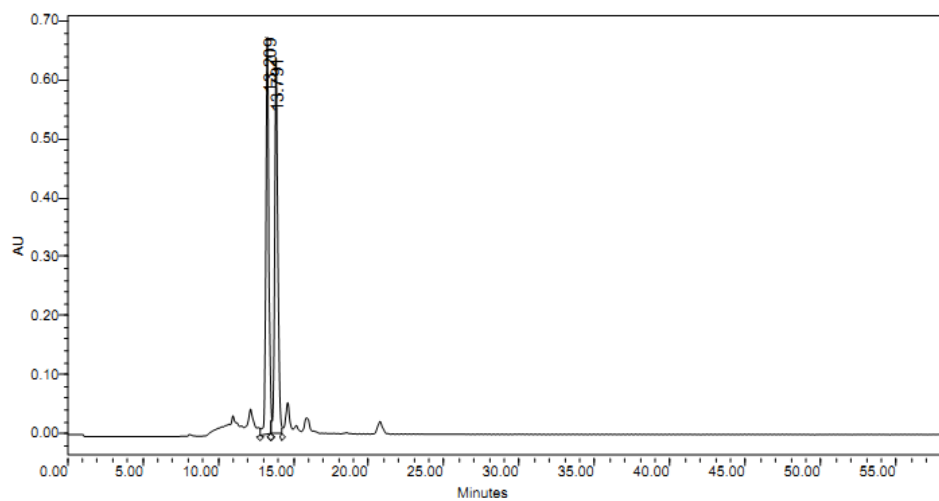
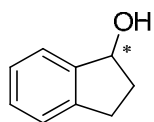
RT (min)	Area (V*sec)	%Area	Height (V)	% Height
13.474	2862315	49.361	52230	51.69
14.149	2936678	50.641	42260	48.31



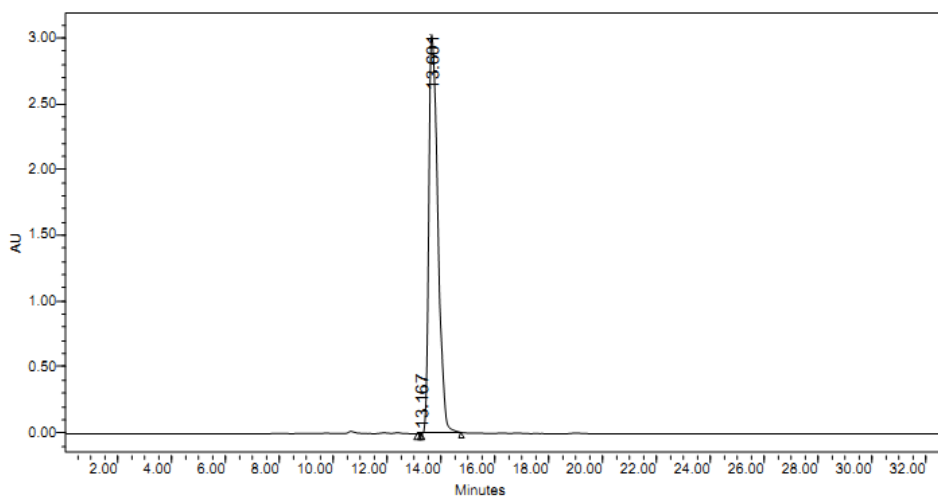
RT (min)	Area (V*sec)	%Area	Height (V)	% Height
13.917	417	0.00	46	0.00
14.530	30216764	100.00	315793	100.00

s.



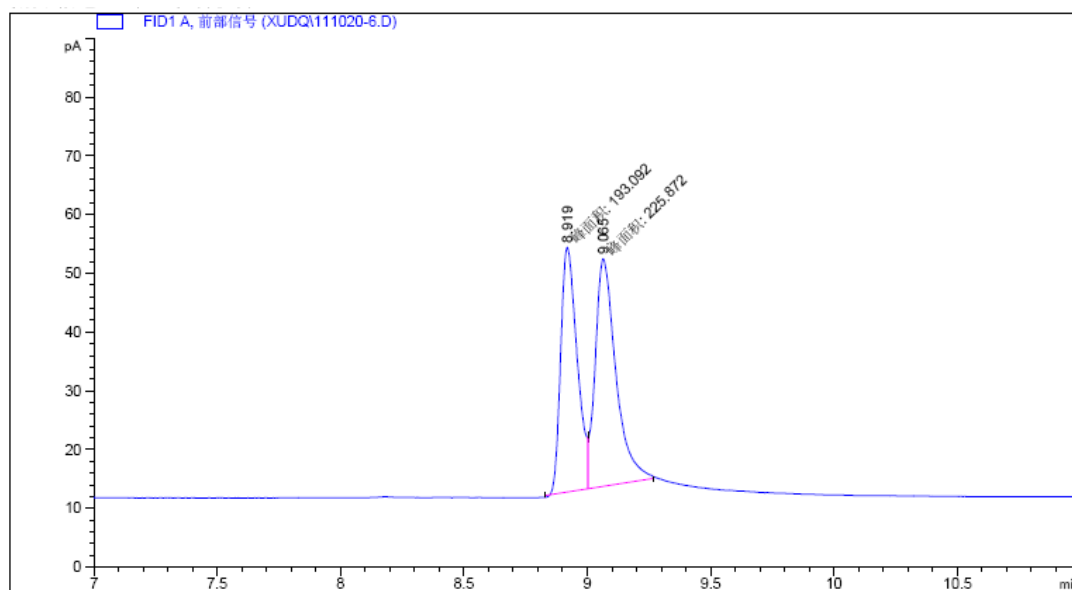
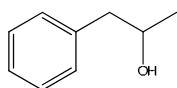


RT (min)	Area (Vsec)	%Area	Height (V)	% Height
113.2099	190580	50.076	77683	51.29
213.7919	164655	49.936	43708	48.71

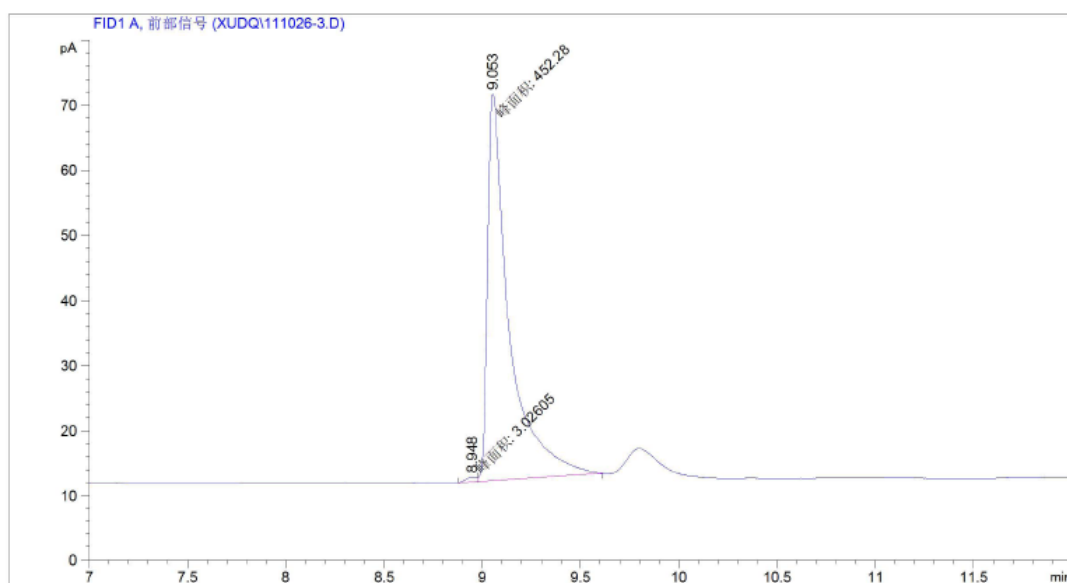


RT (min)	Area (Vsec)	%Area	Height (V)	% Height
113.167	604	0.00	-161	0.01
213.6017	638258	100.00	27292	99.99

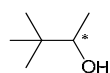
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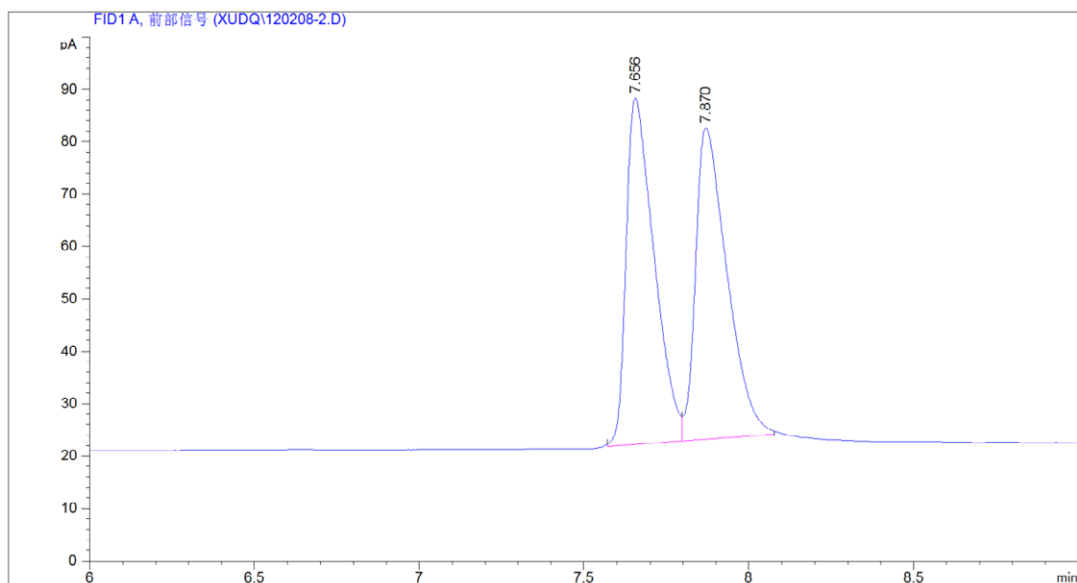


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	8.919	MF	0.0772	193.09190	41.68716	46.08792
2	9.065	FM	0.0972	225.87234	38.73124	53.91208

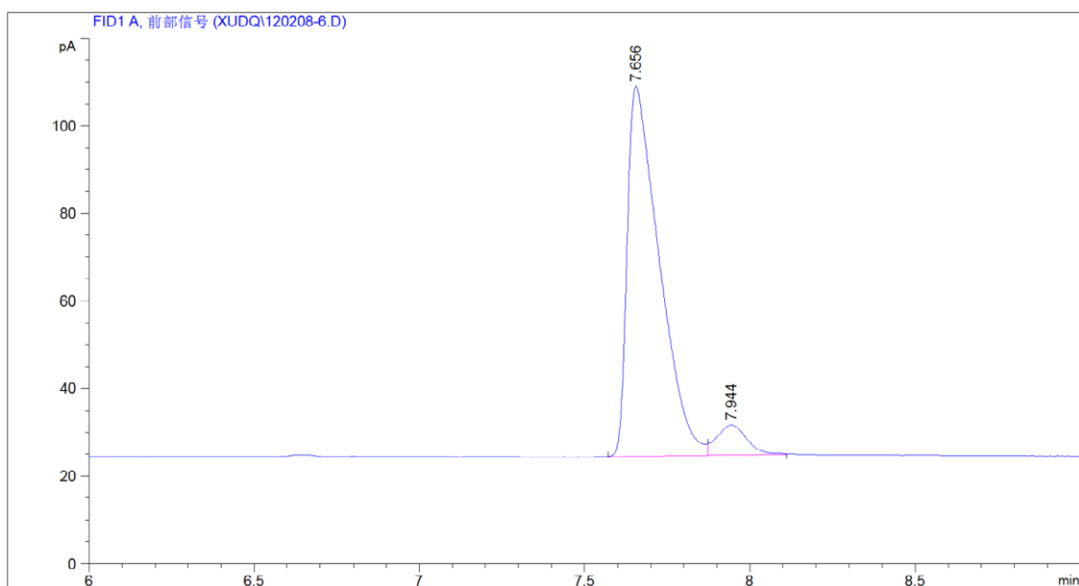


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	8.948	MF	0.0642	3.02605	7.85034e-1	0.66462
2	9.053	FM	0.1271	452.27972	59.32846	99.33538

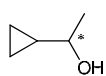


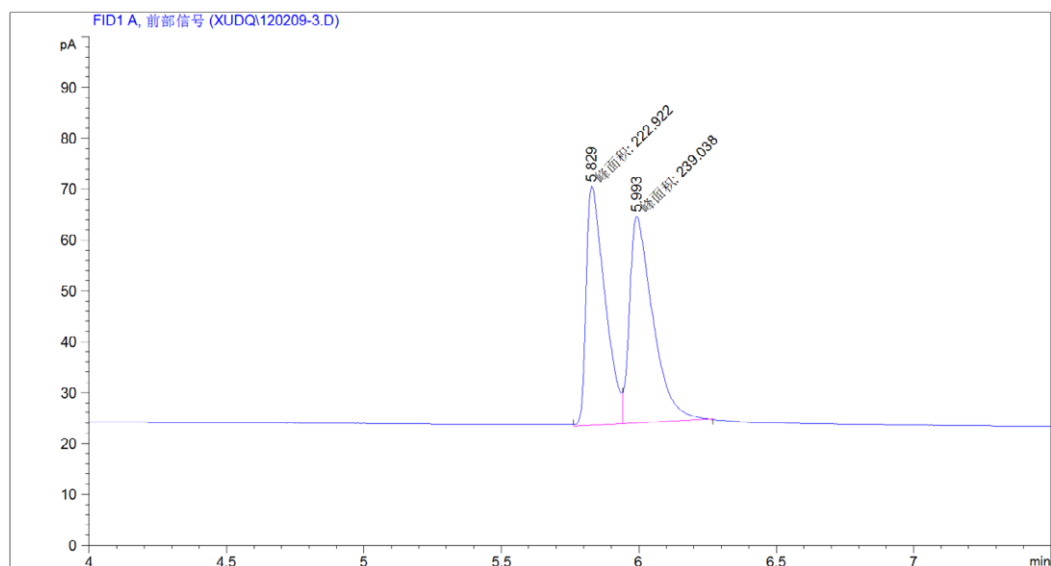


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.656	BV	0.0857	389.11649	66.10107	49.64502
2	7.870	VB	0.0954	394.68115	59.48867	50.35498

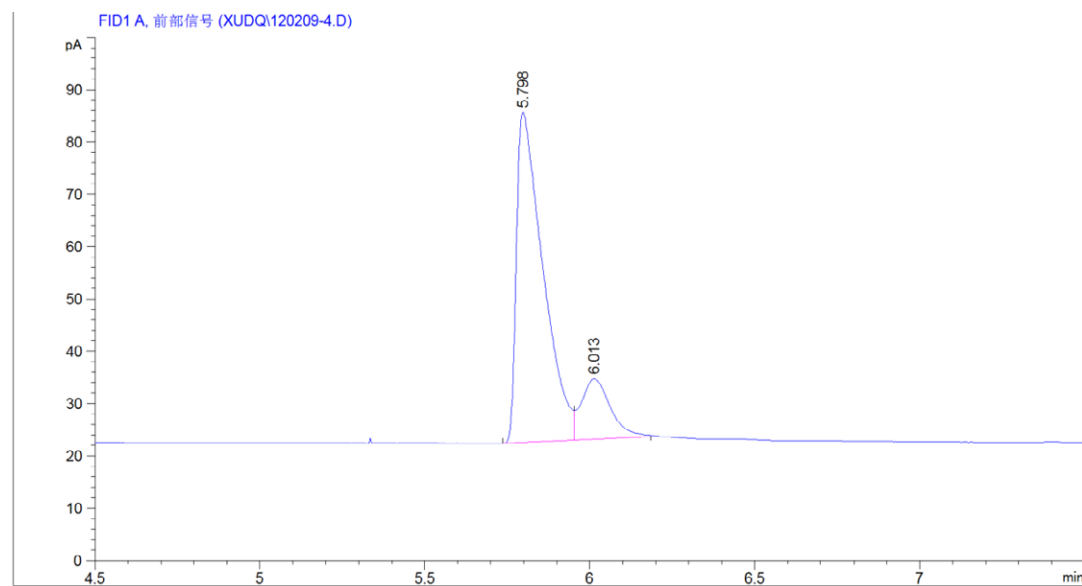


峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	7.656	BB	0.0924	567.68628	84.44694	93.03597
2	7.944	BB	0.0958	42.49307	6.81270	6.96403





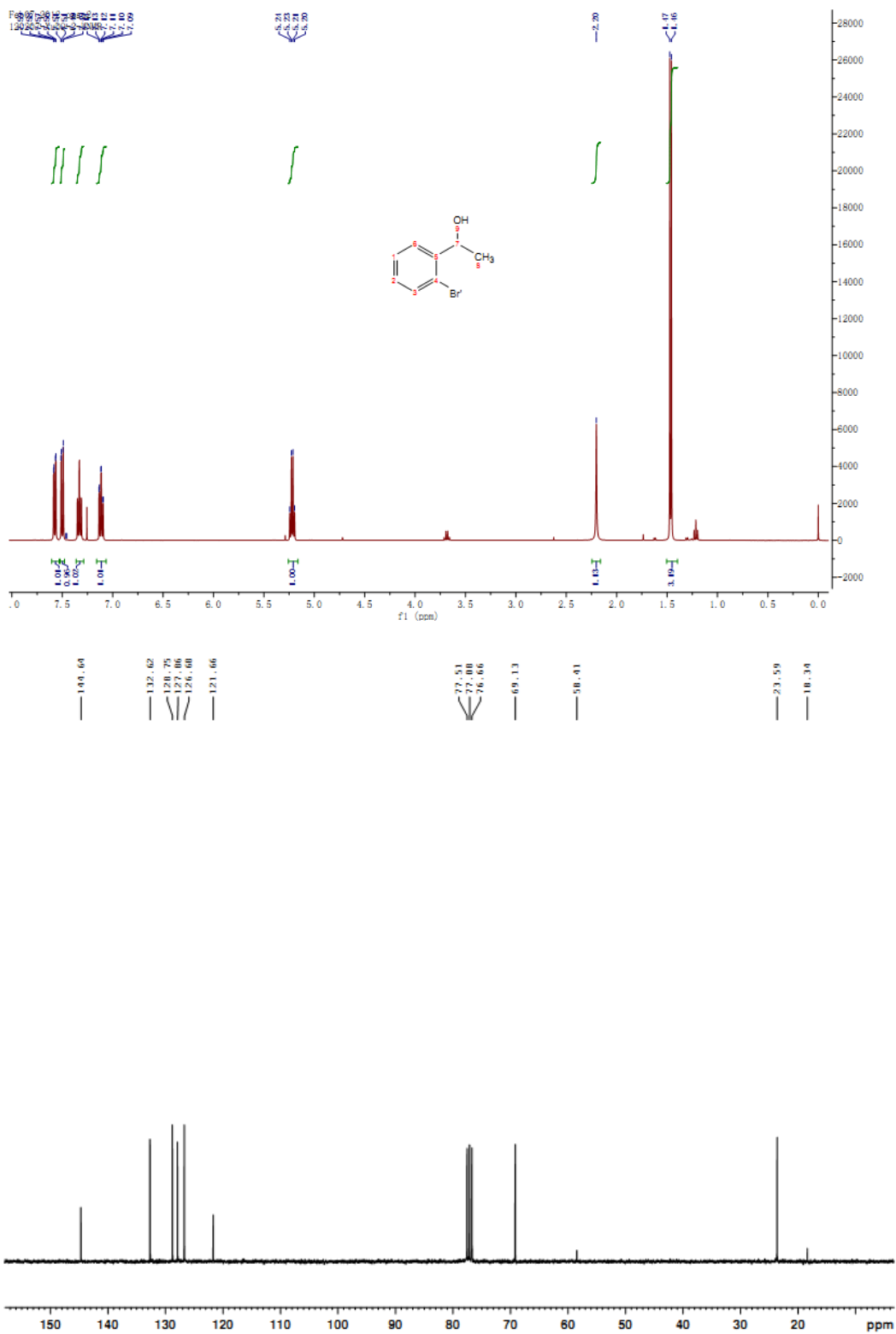
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	5.829	MF	0.0790	222.92249	47.04689	48.25574
2	5.993	FM	0.0980	239.03812	40.63602	51.74426



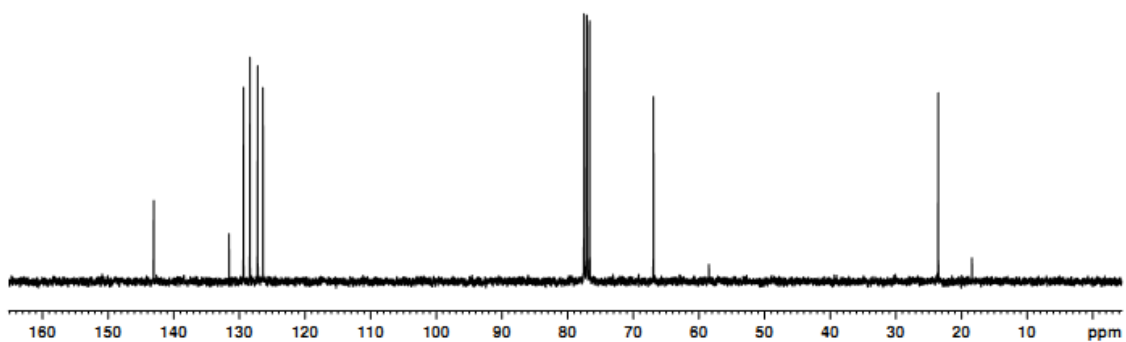
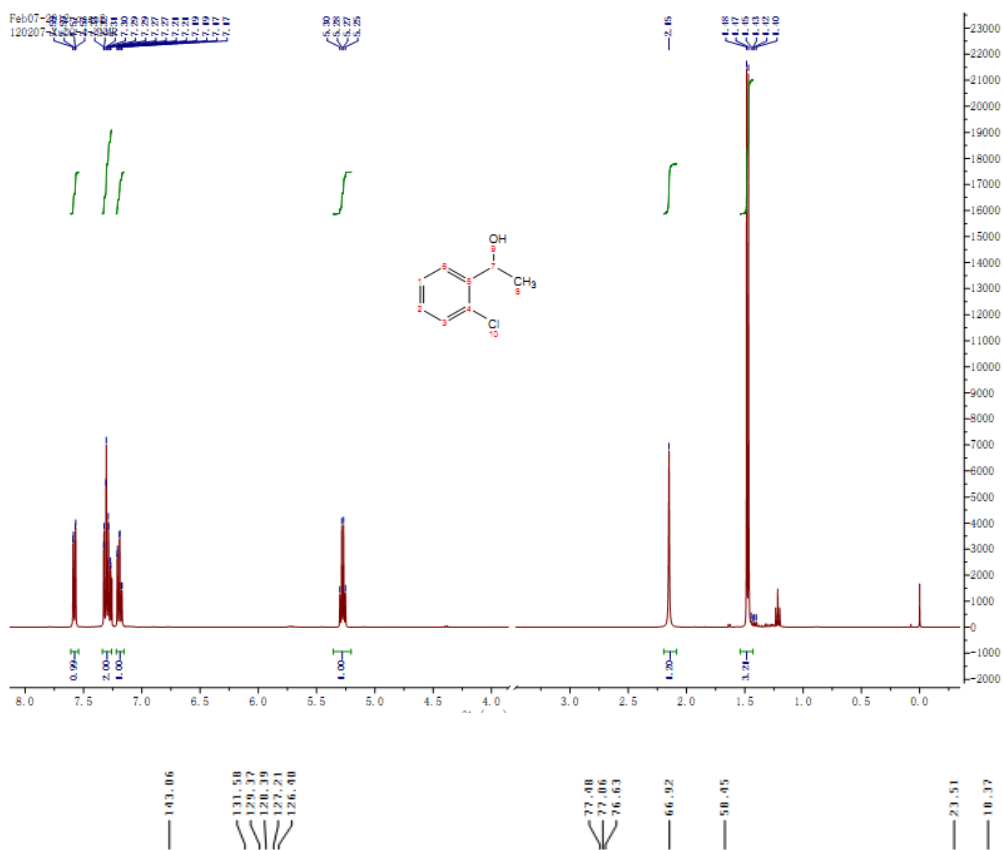
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	5.798	BV	0.0770	351.78360	63.13416	83.22714
2	6.013	VB	0.0929	70.89536	11.49612	16.77286

#### 4. NMR chart of substituents.

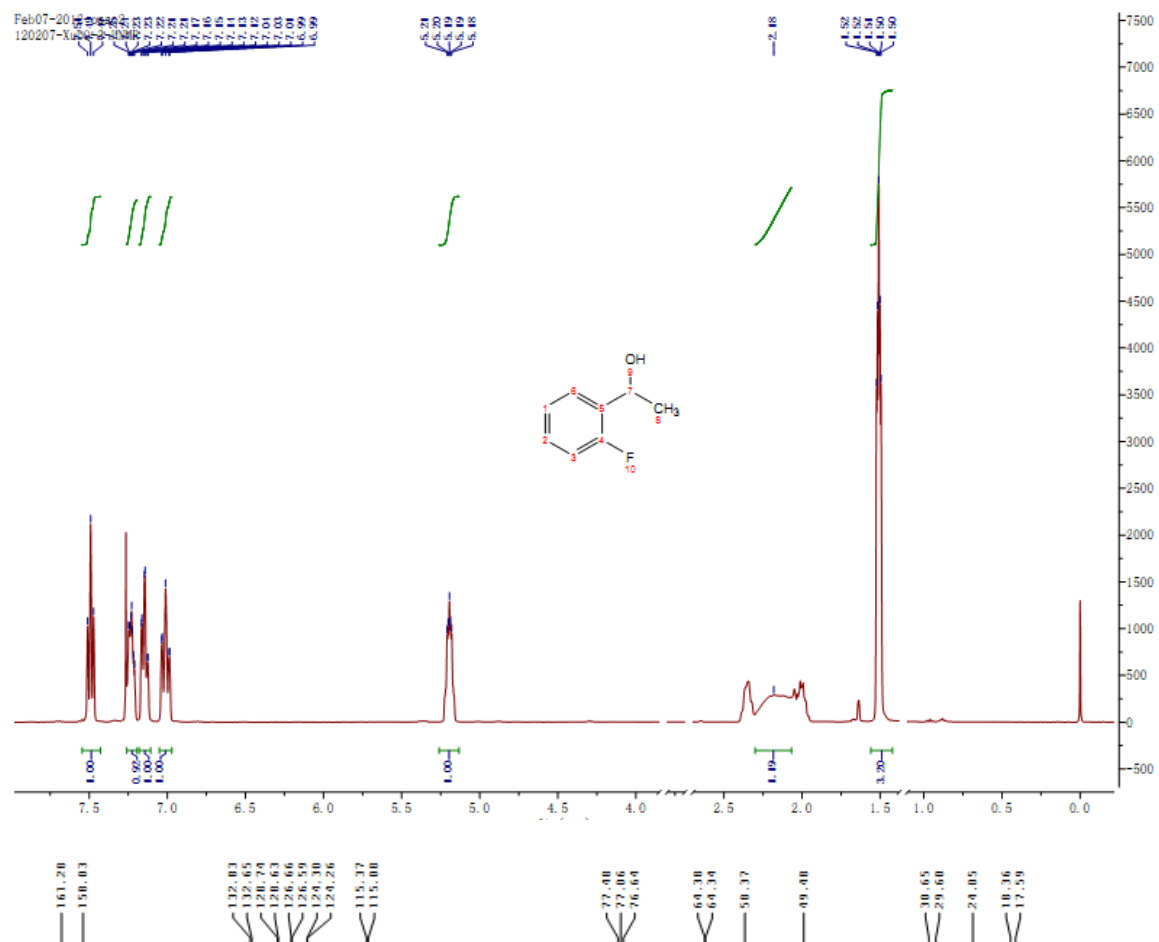
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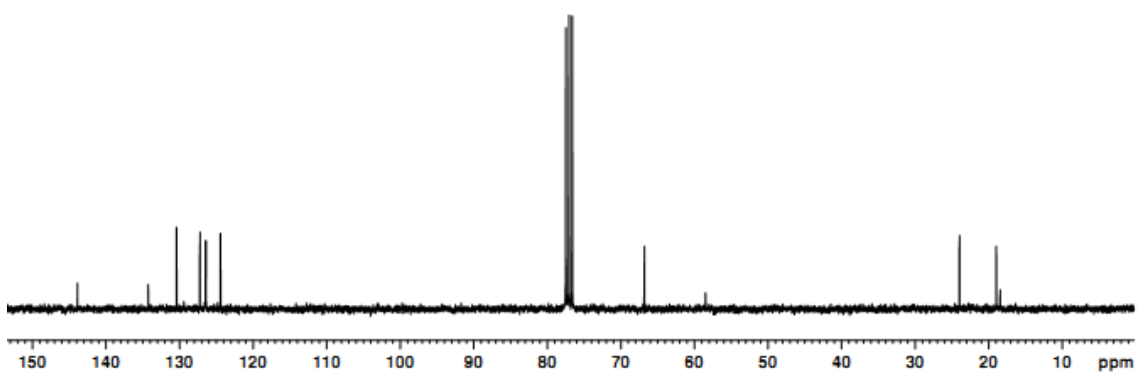
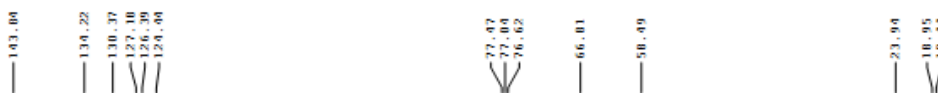
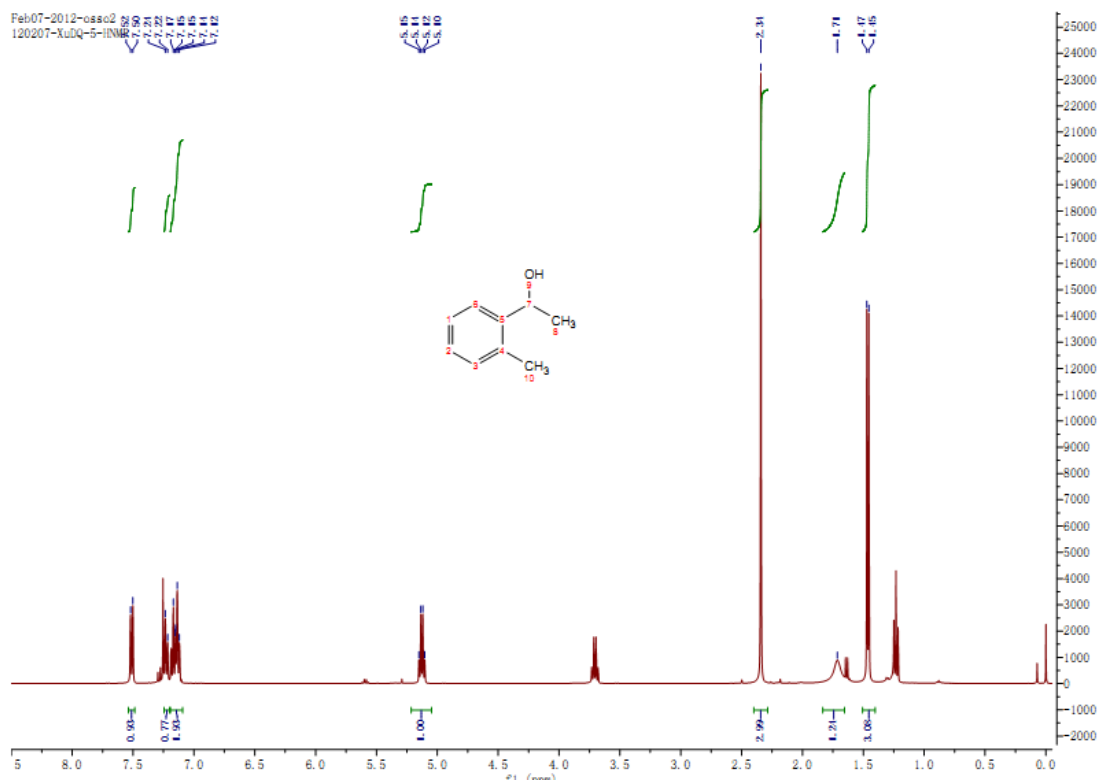
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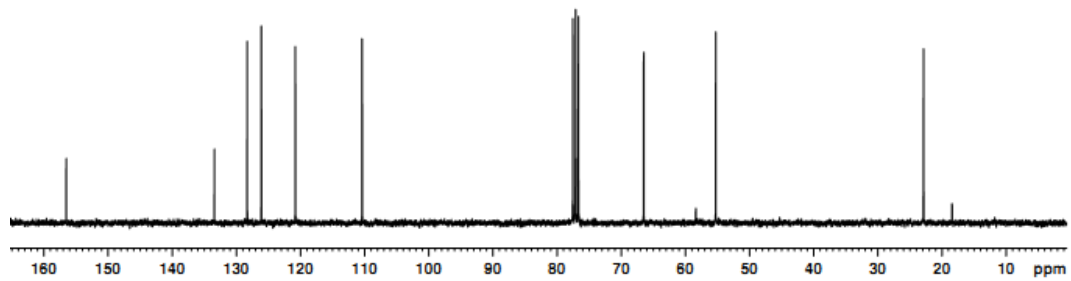
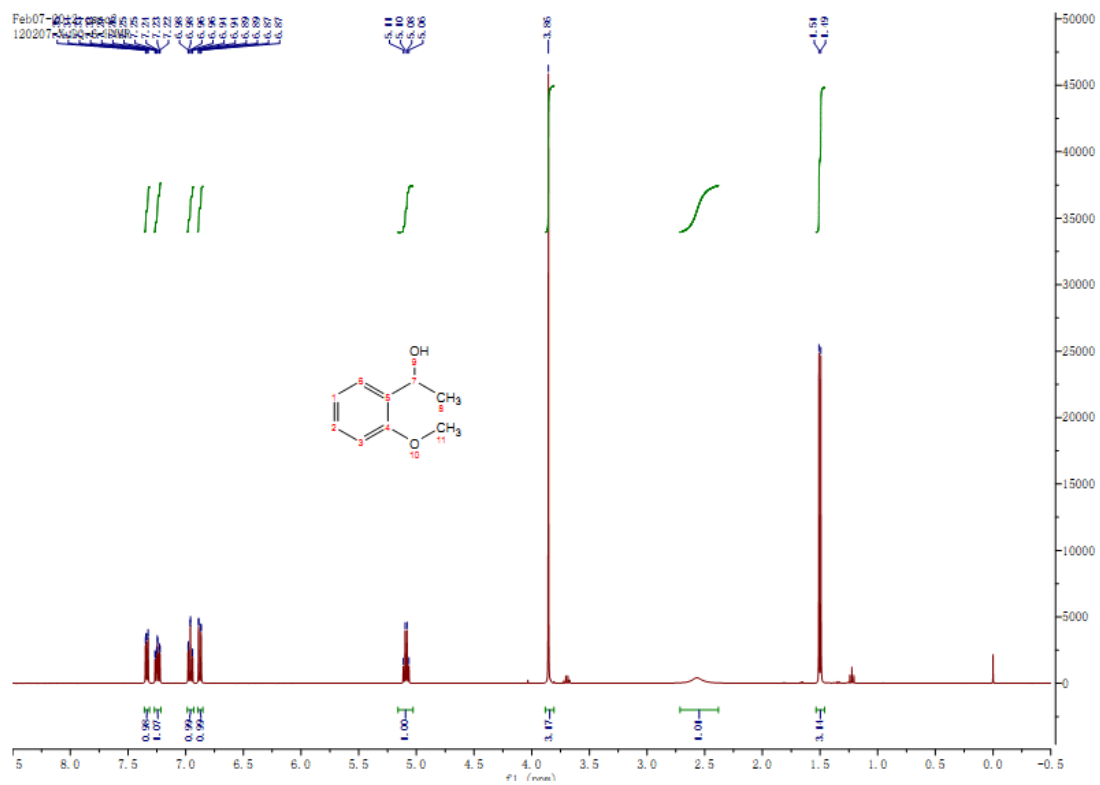


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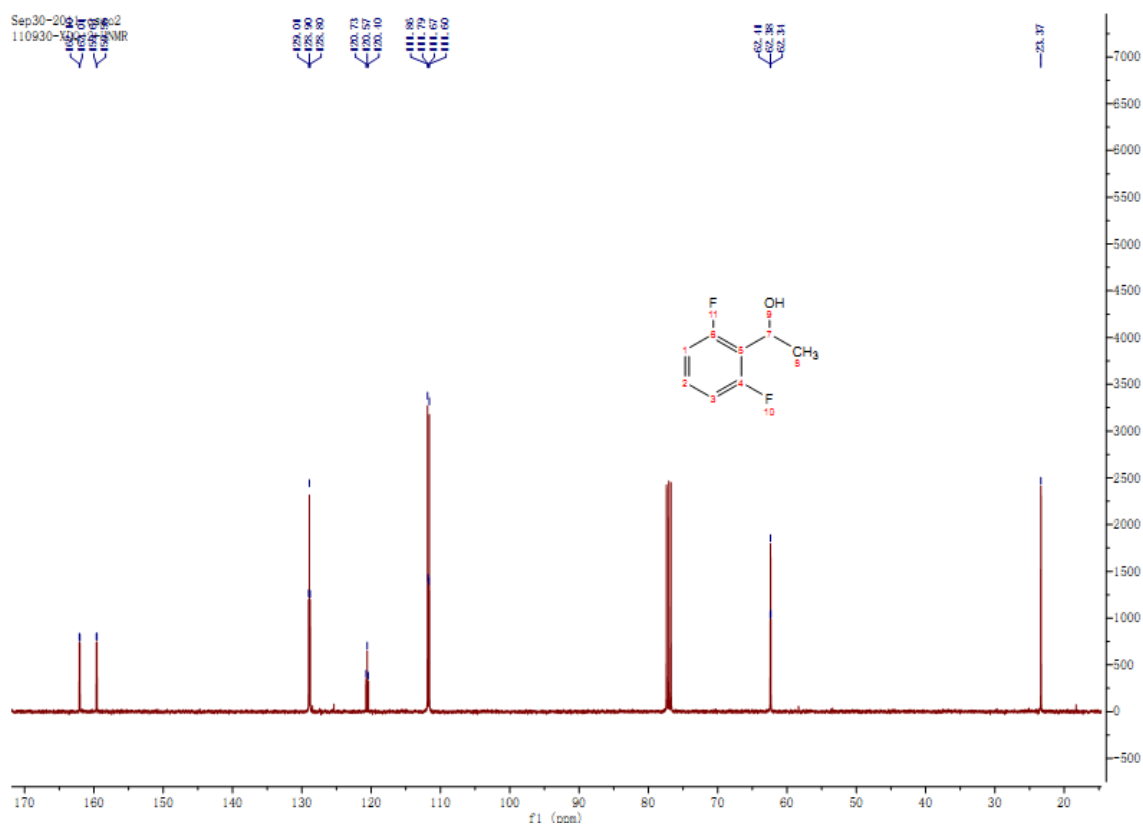
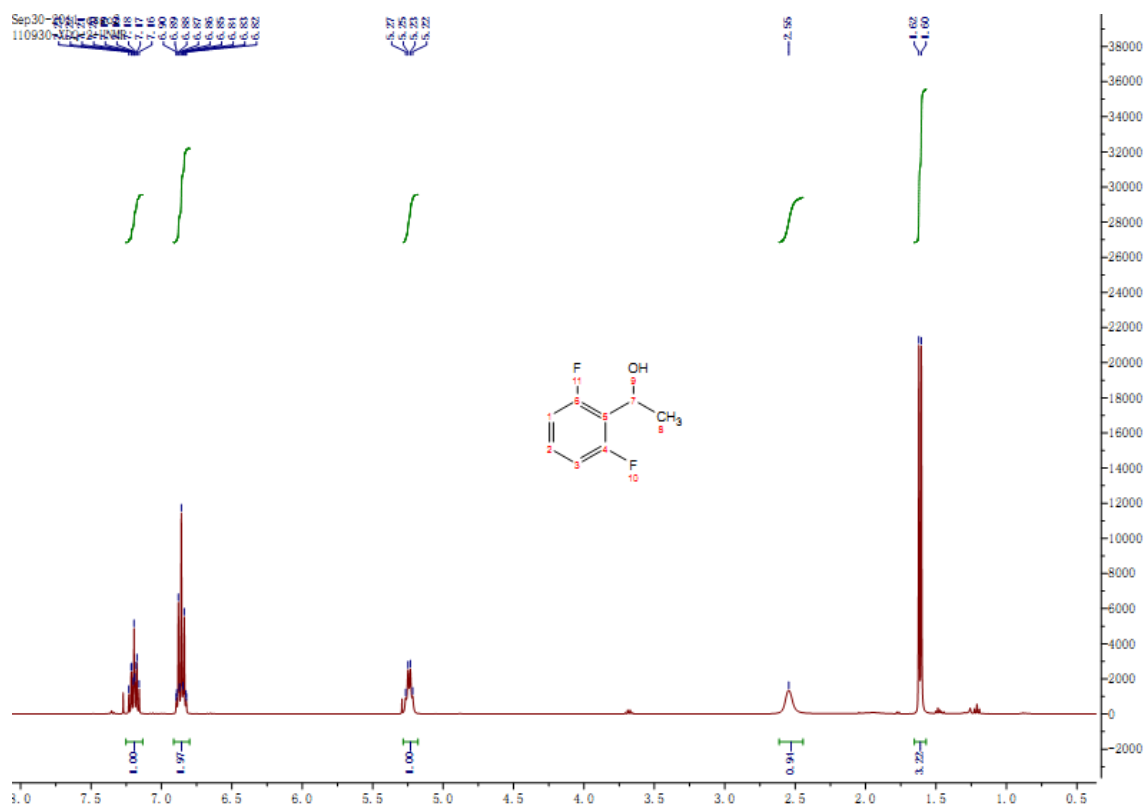
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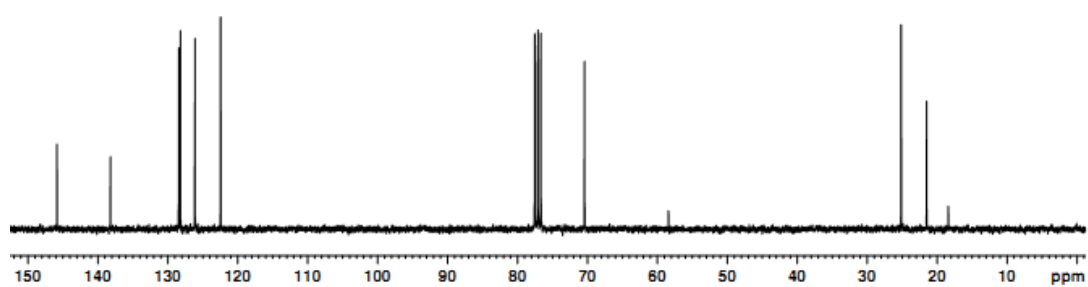
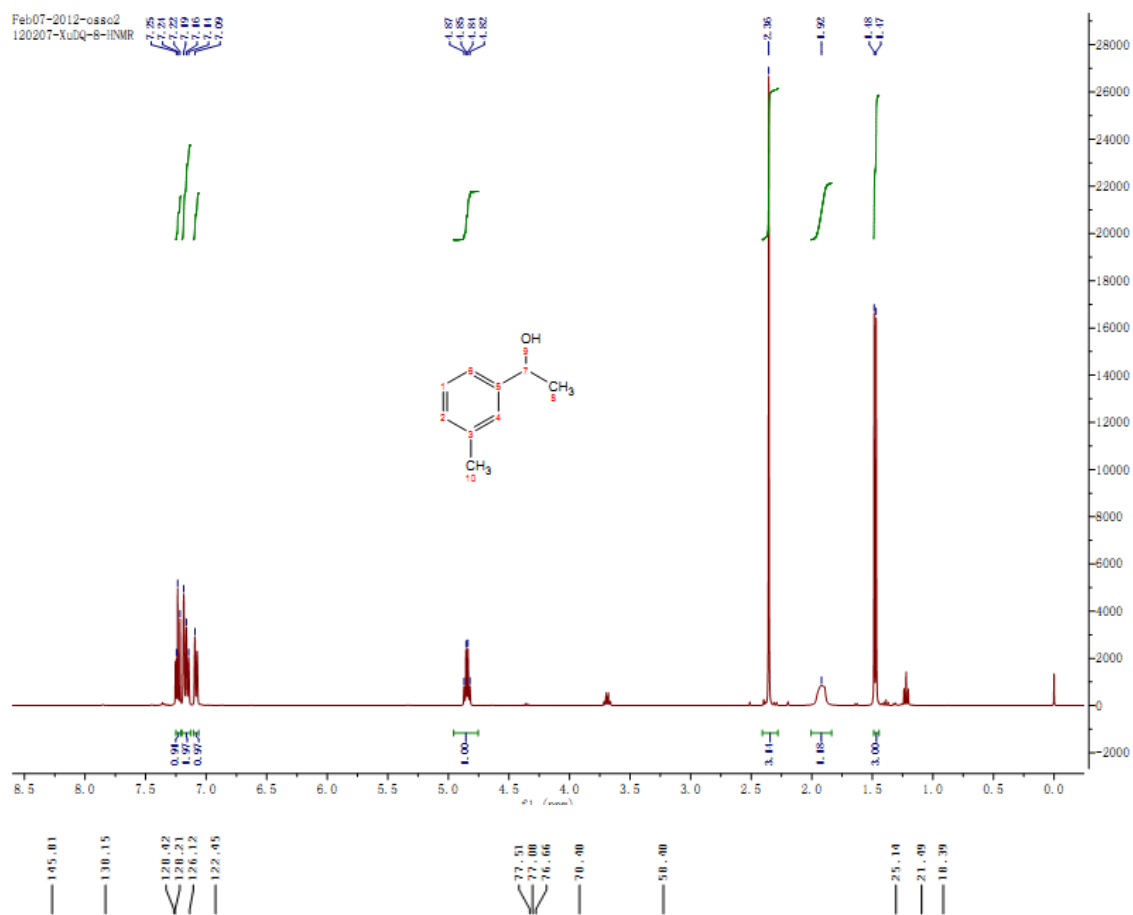


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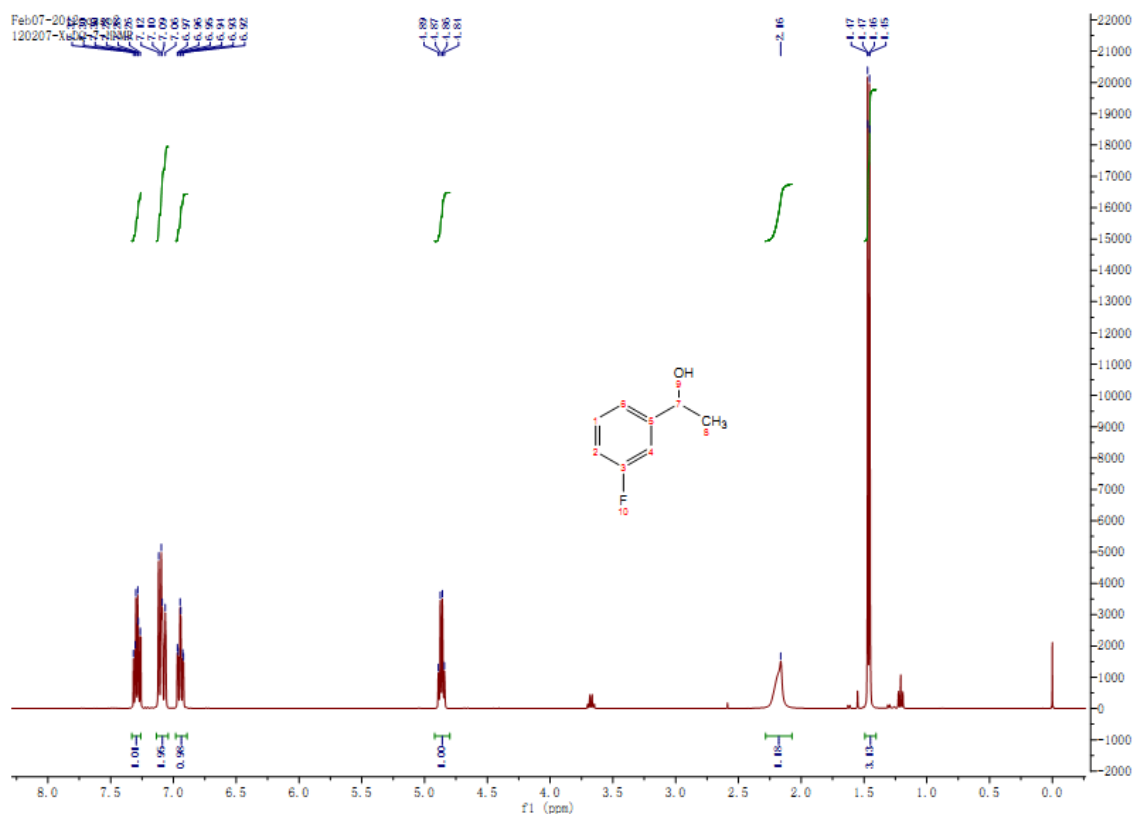




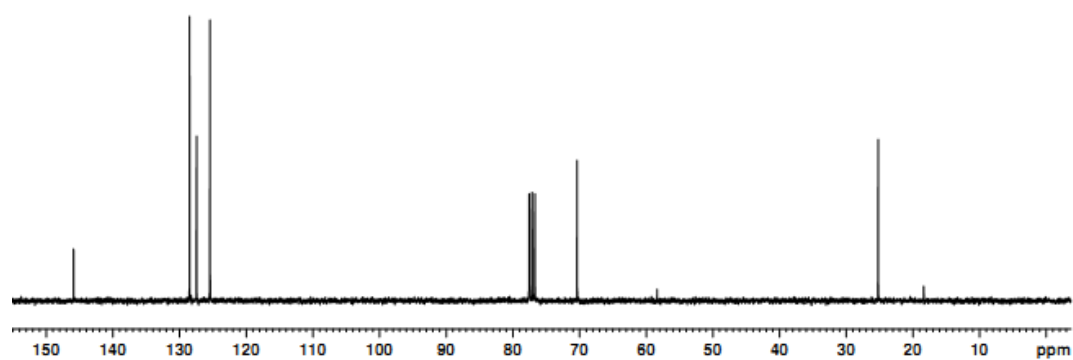
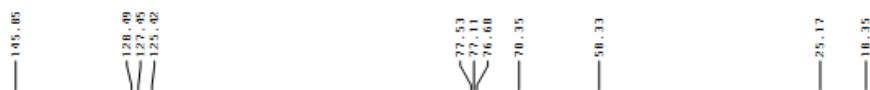
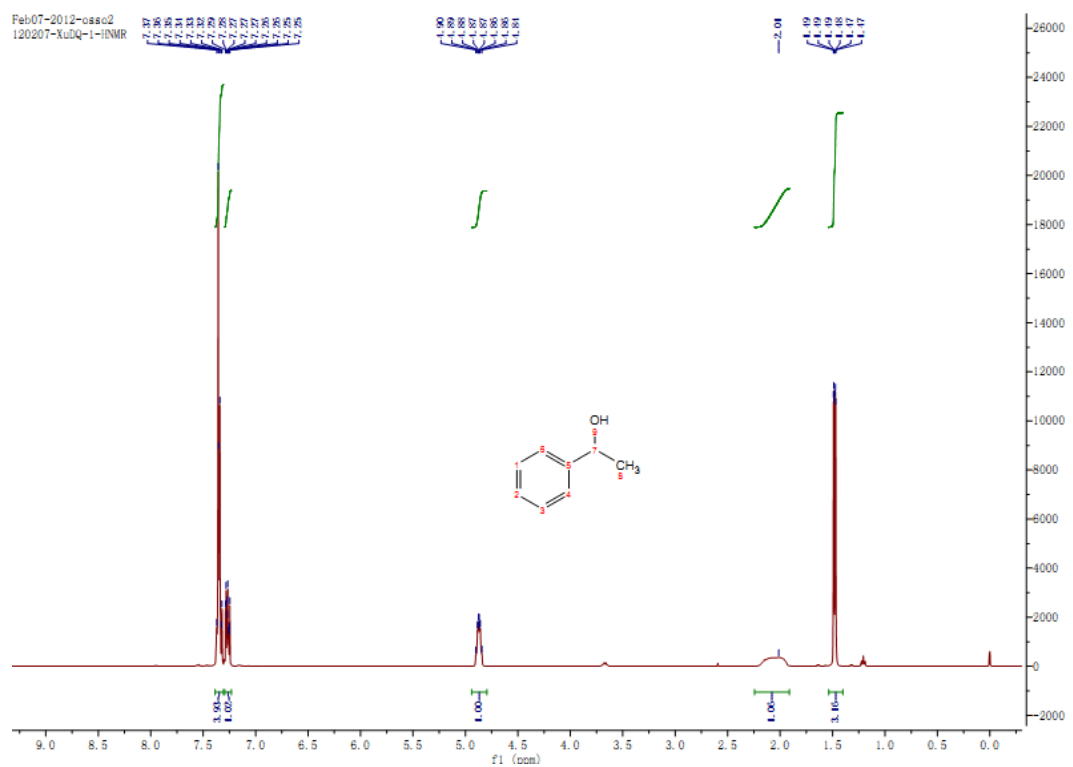
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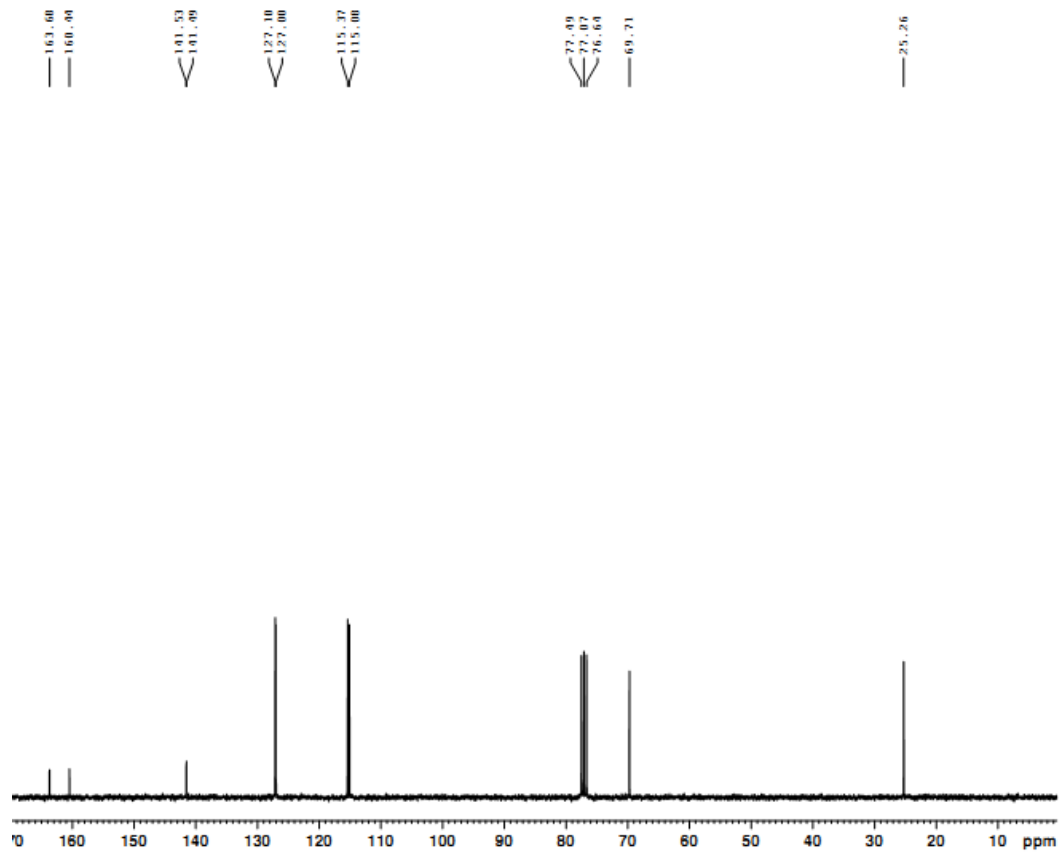
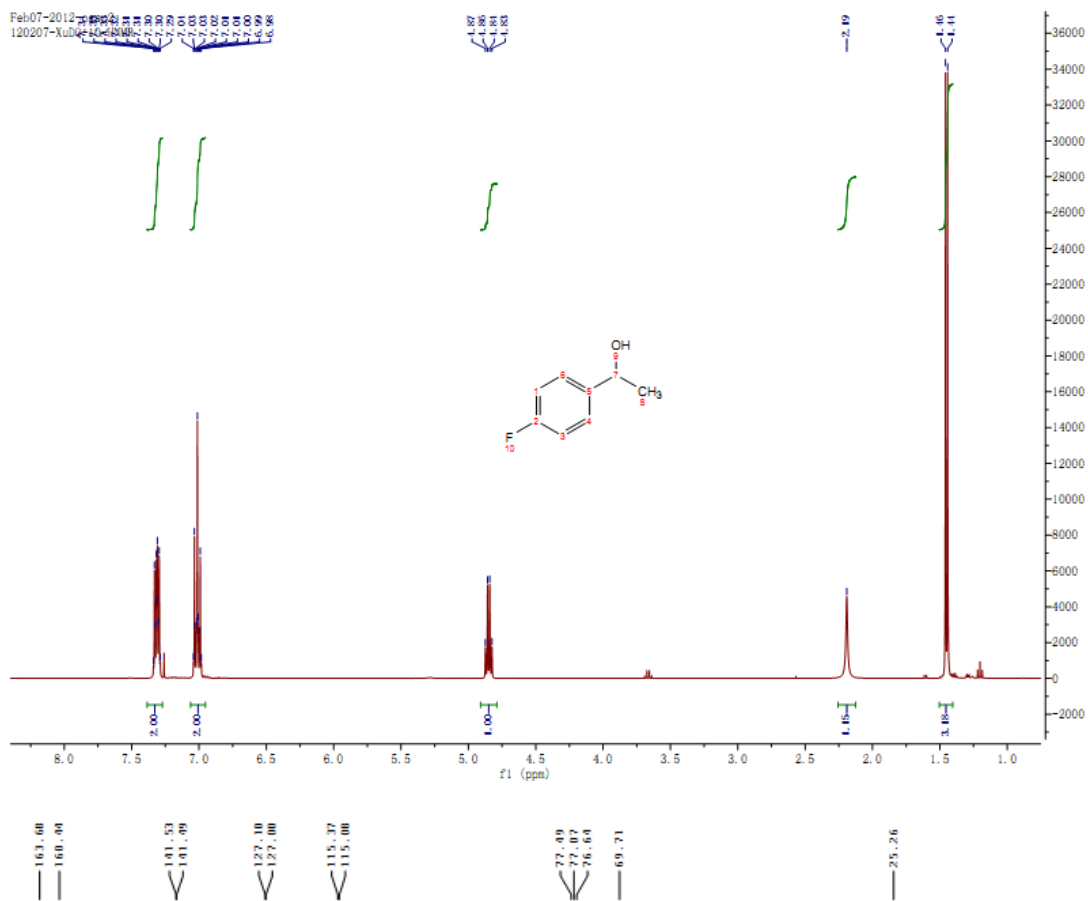
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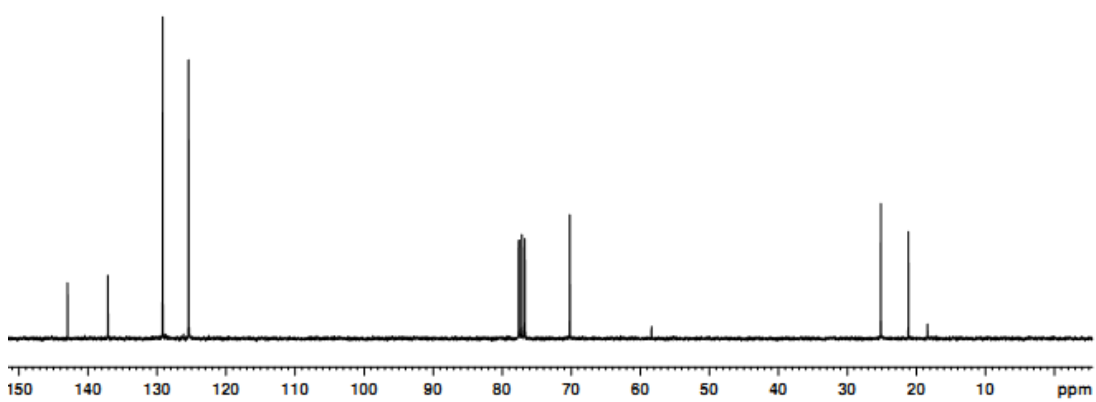
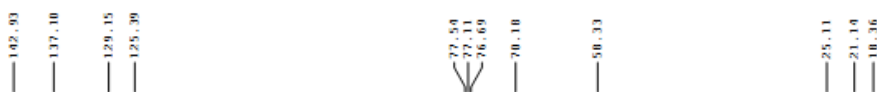
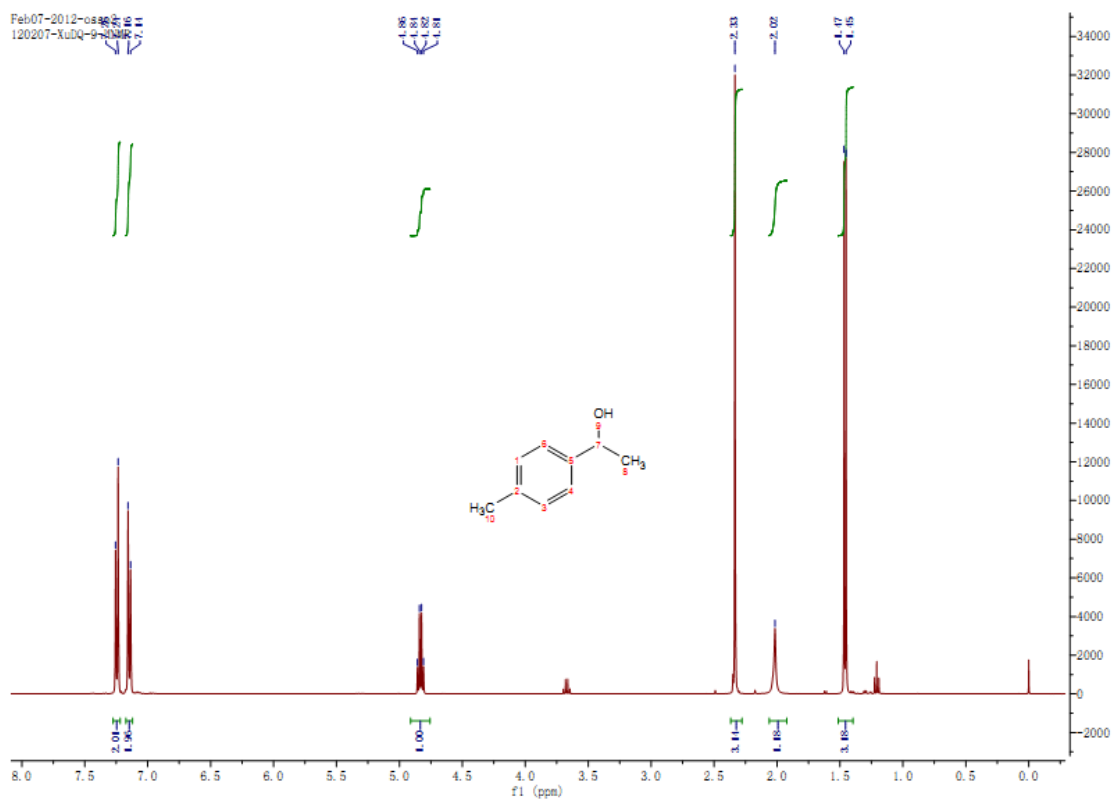


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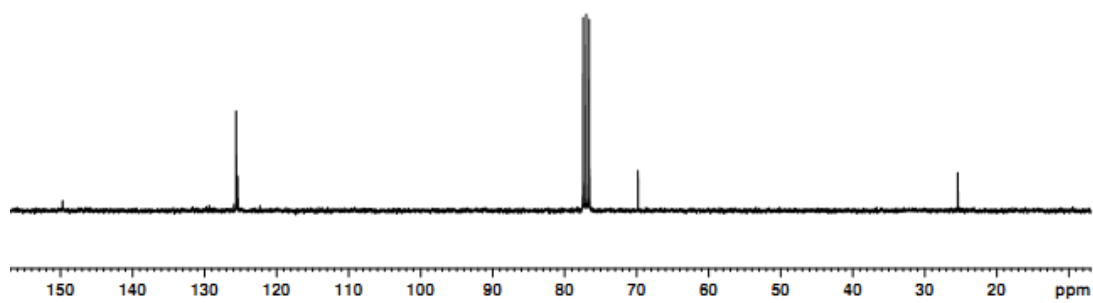
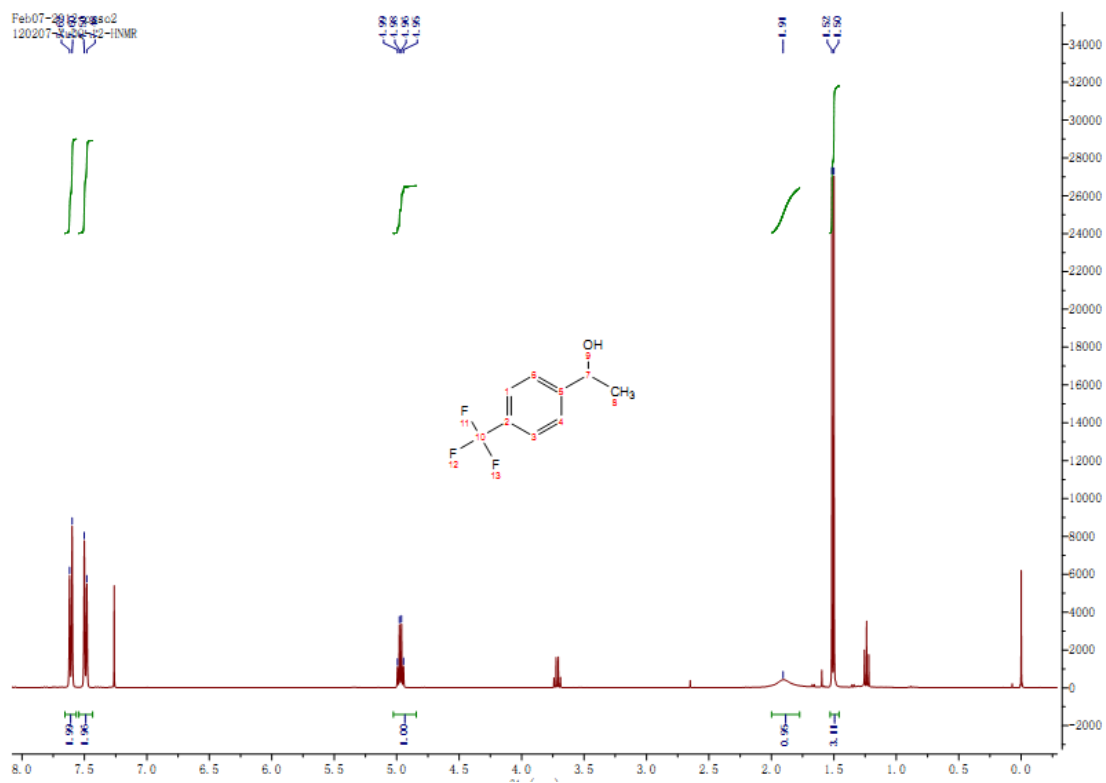
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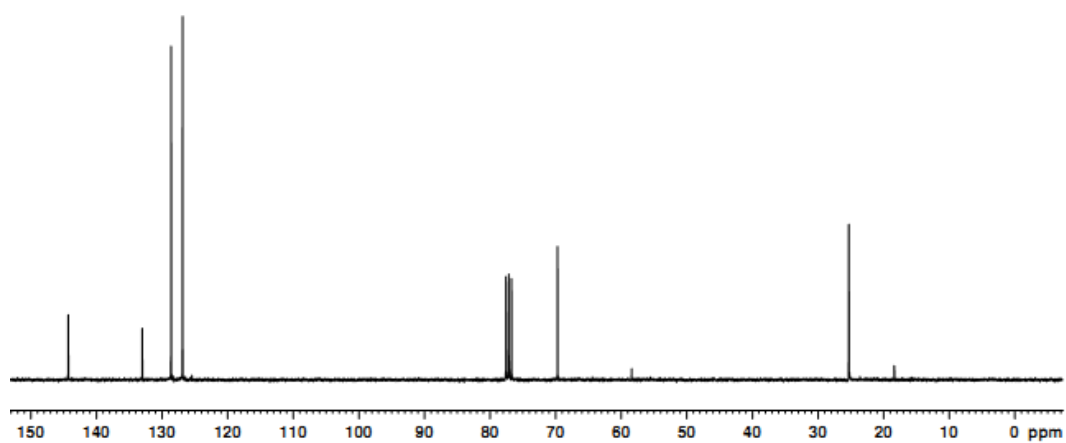
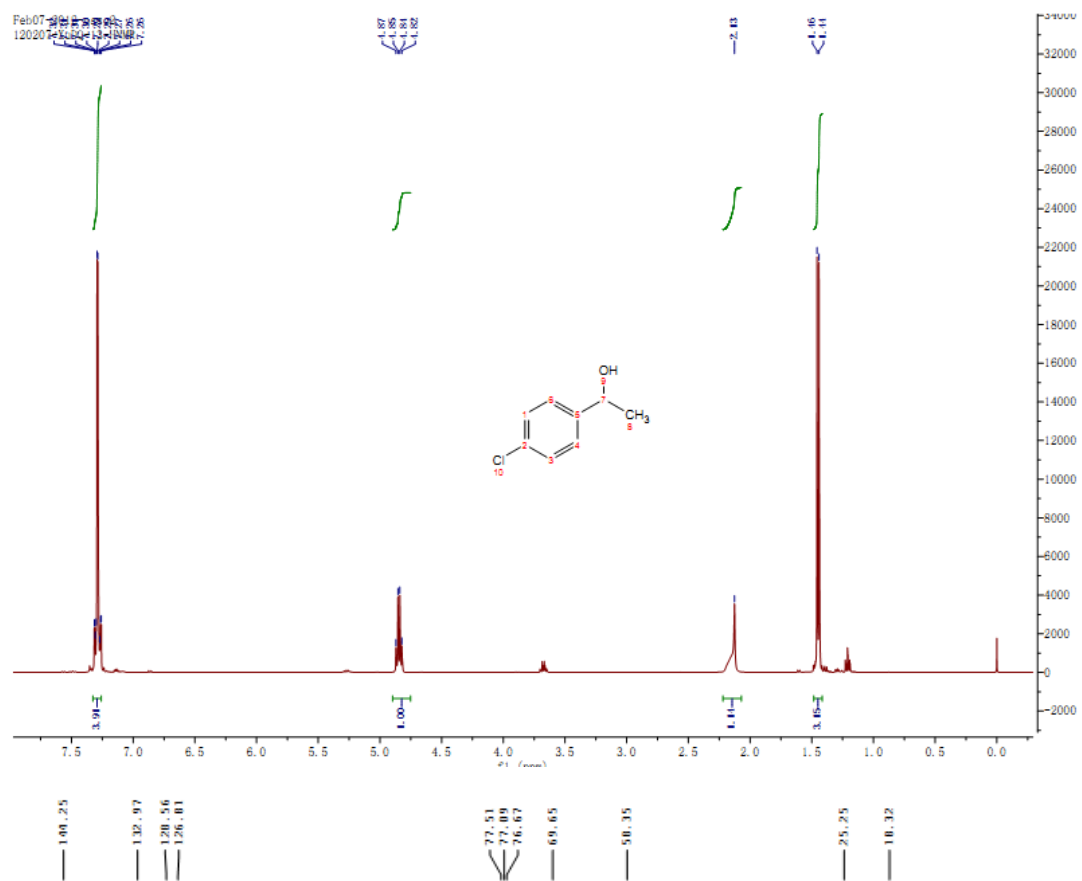


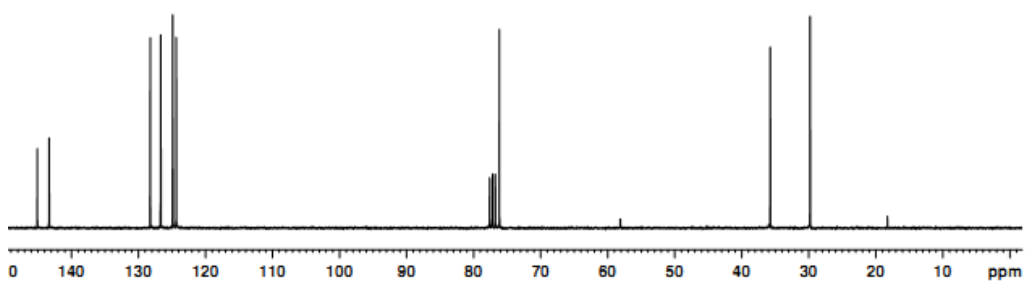
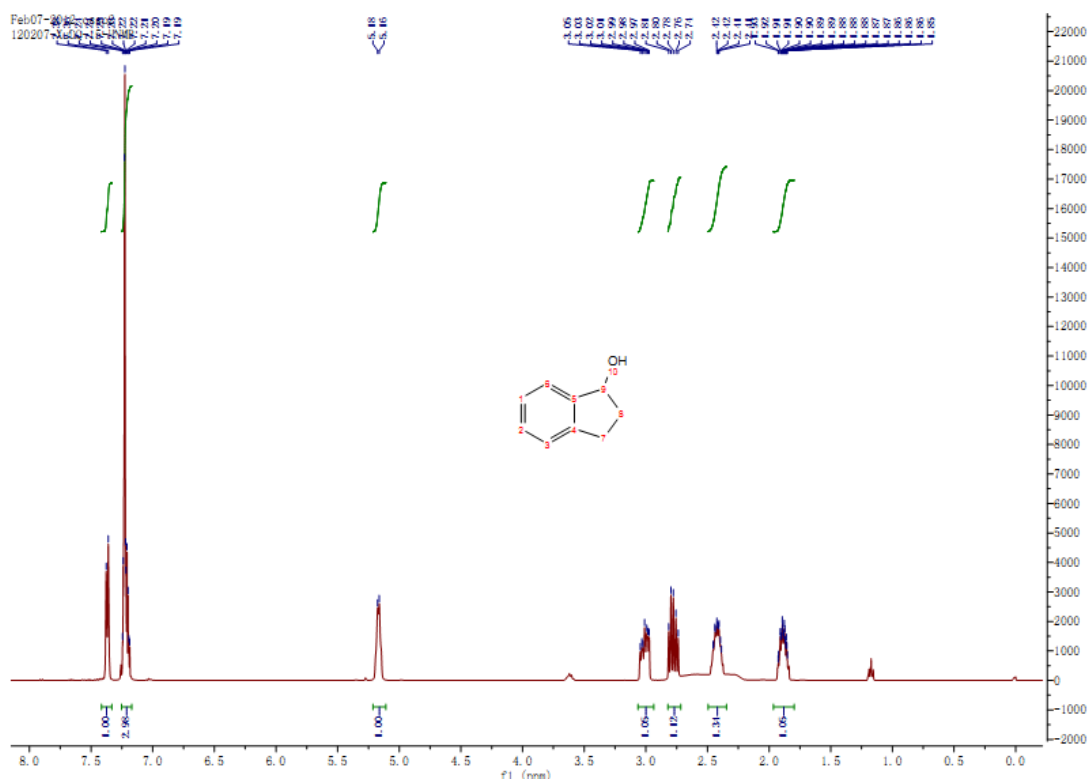
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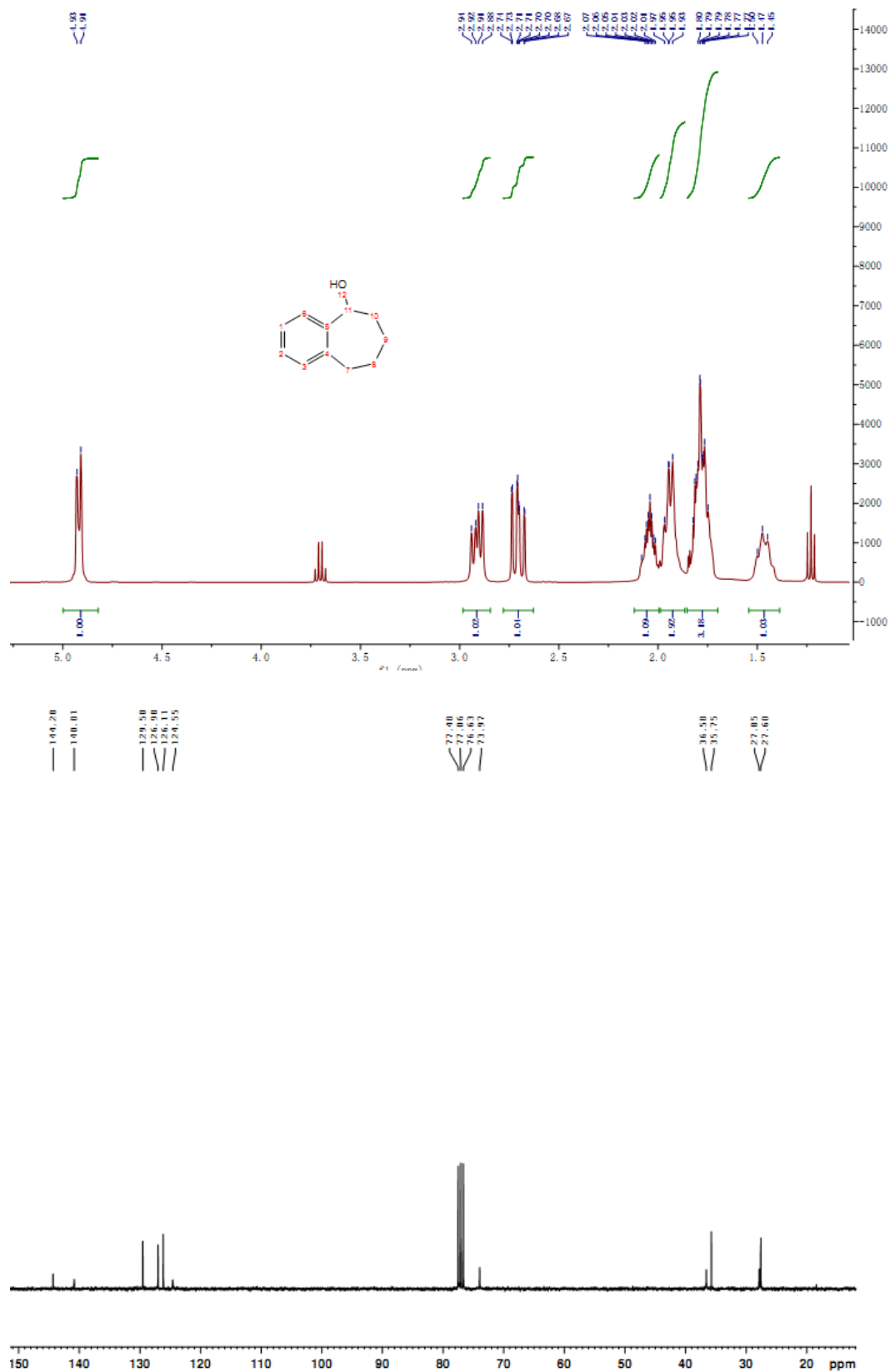


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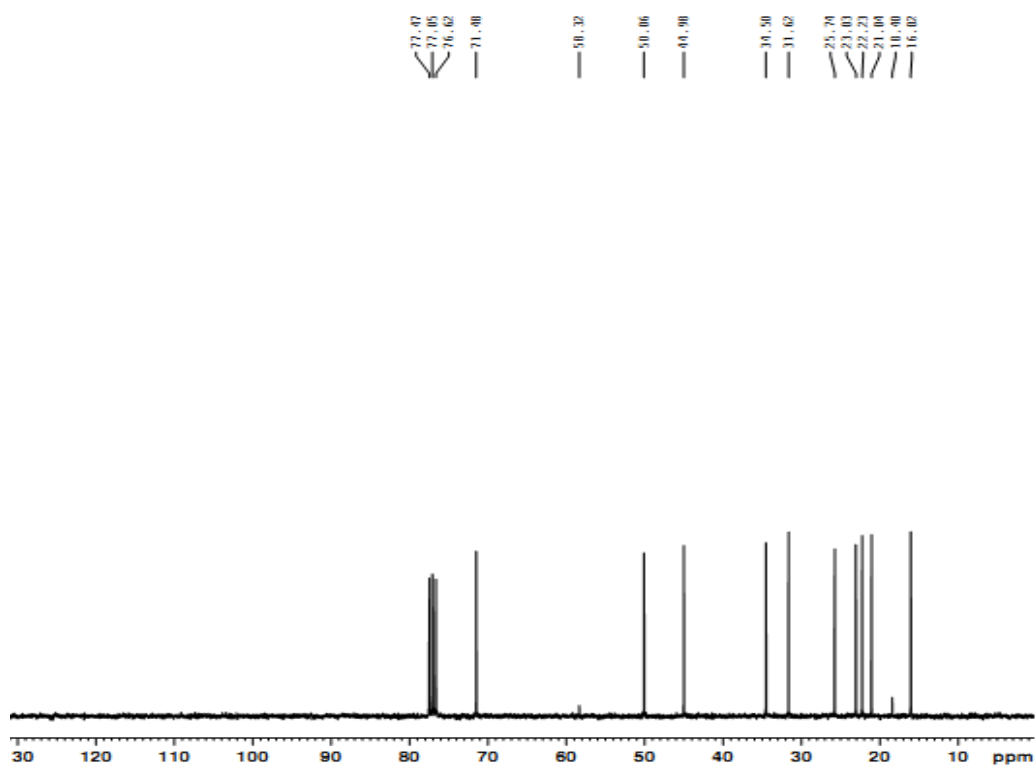
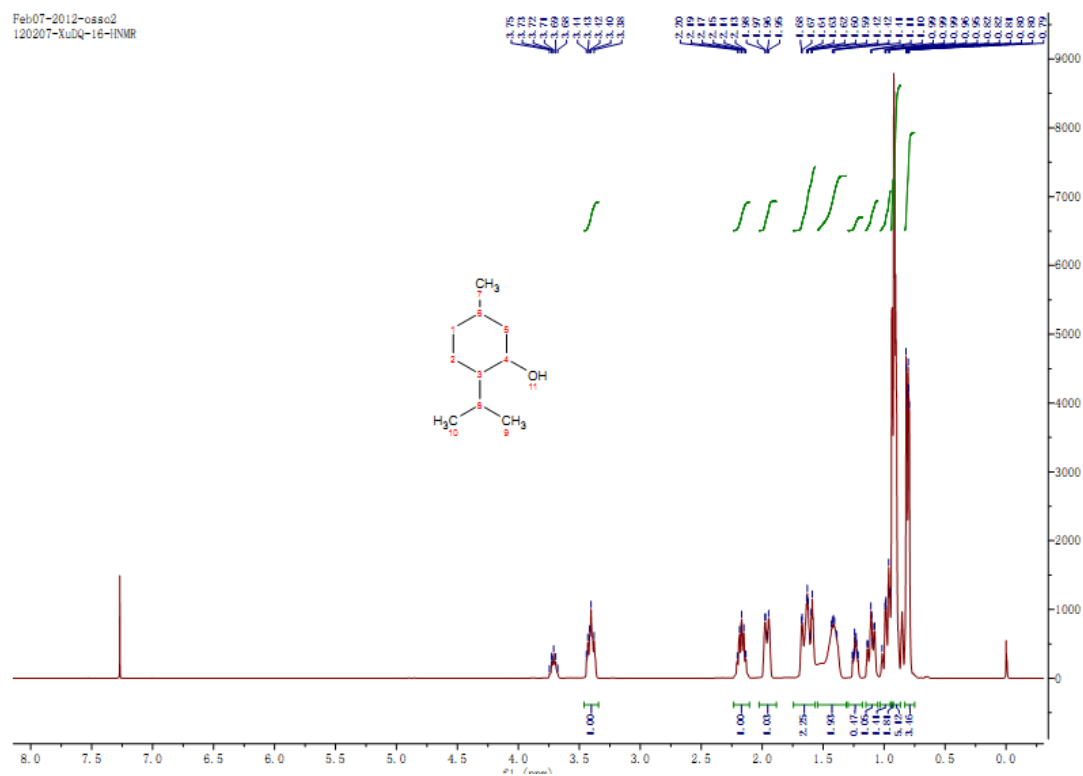


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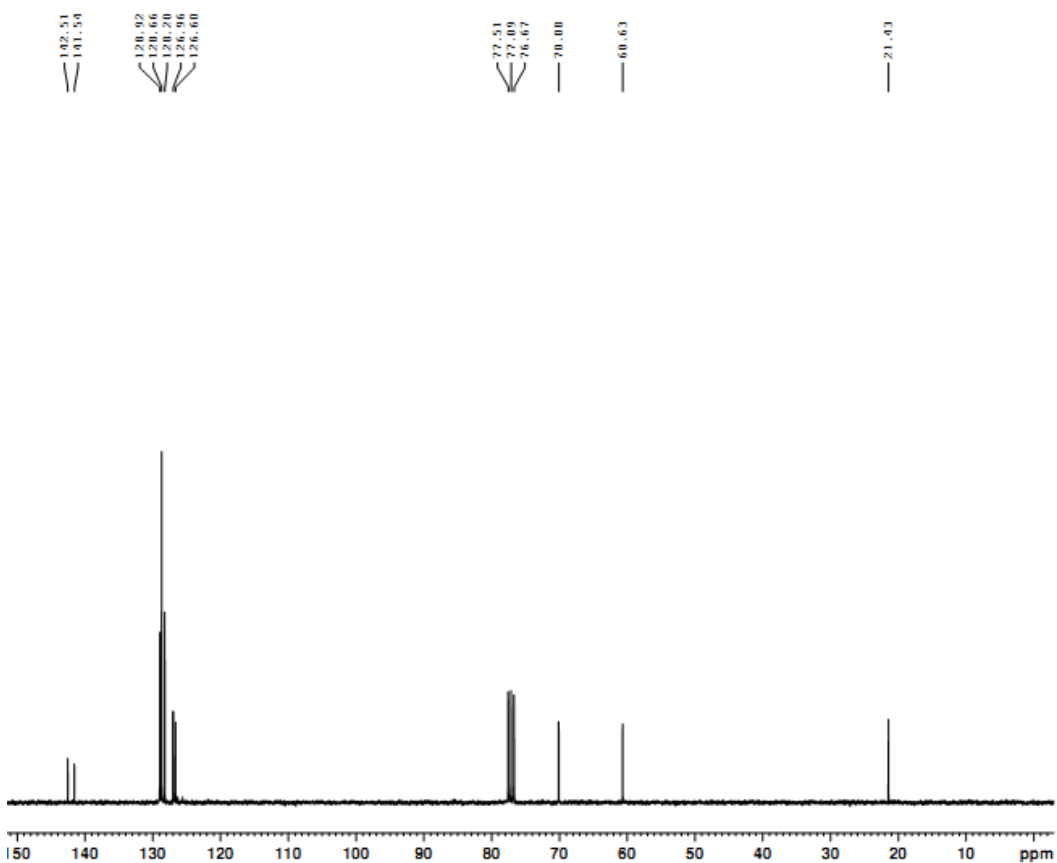
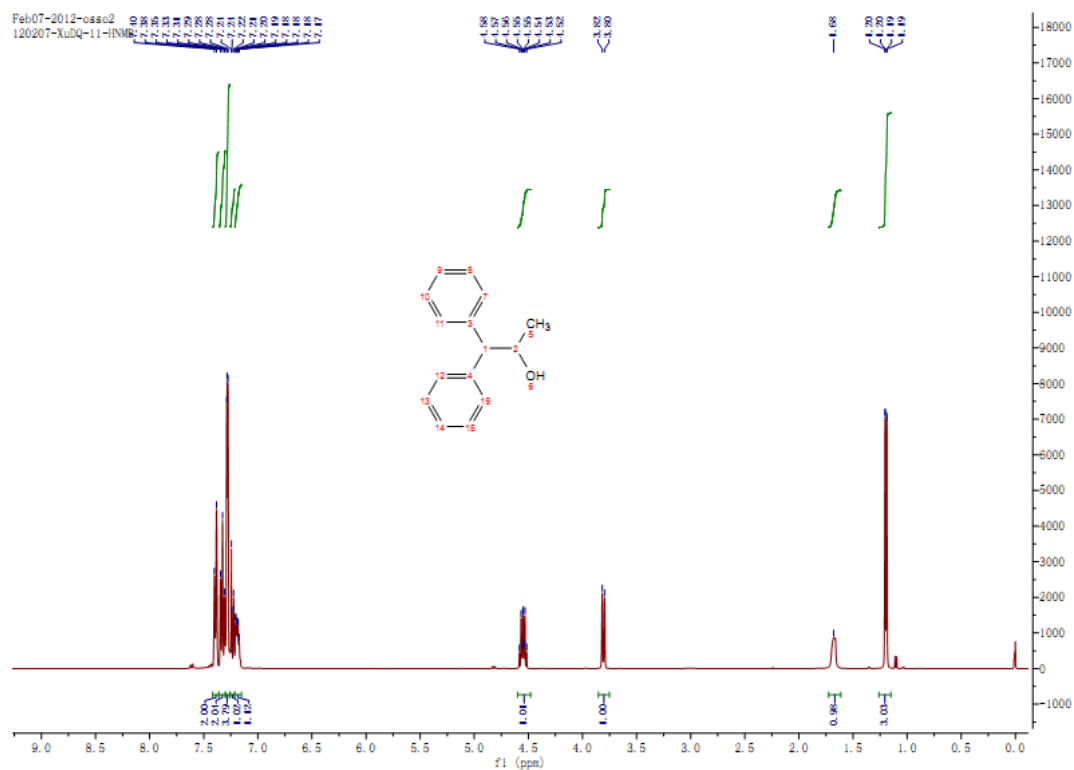


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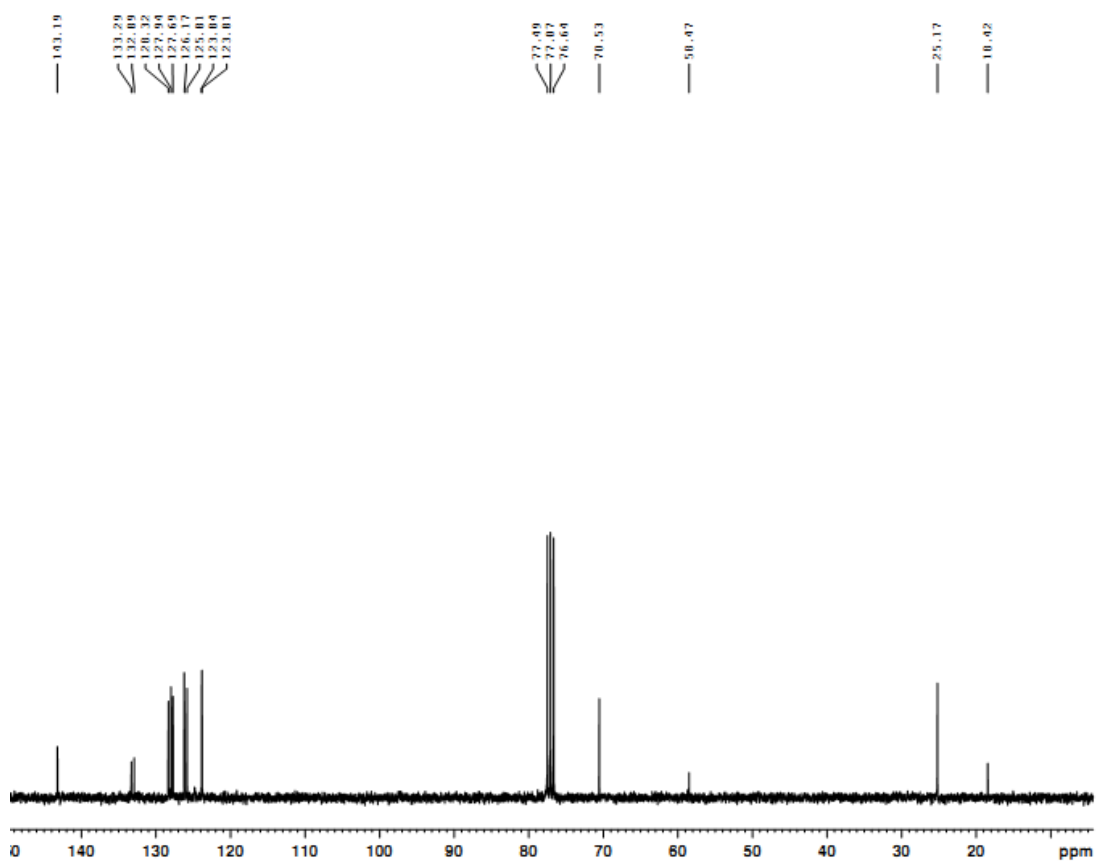
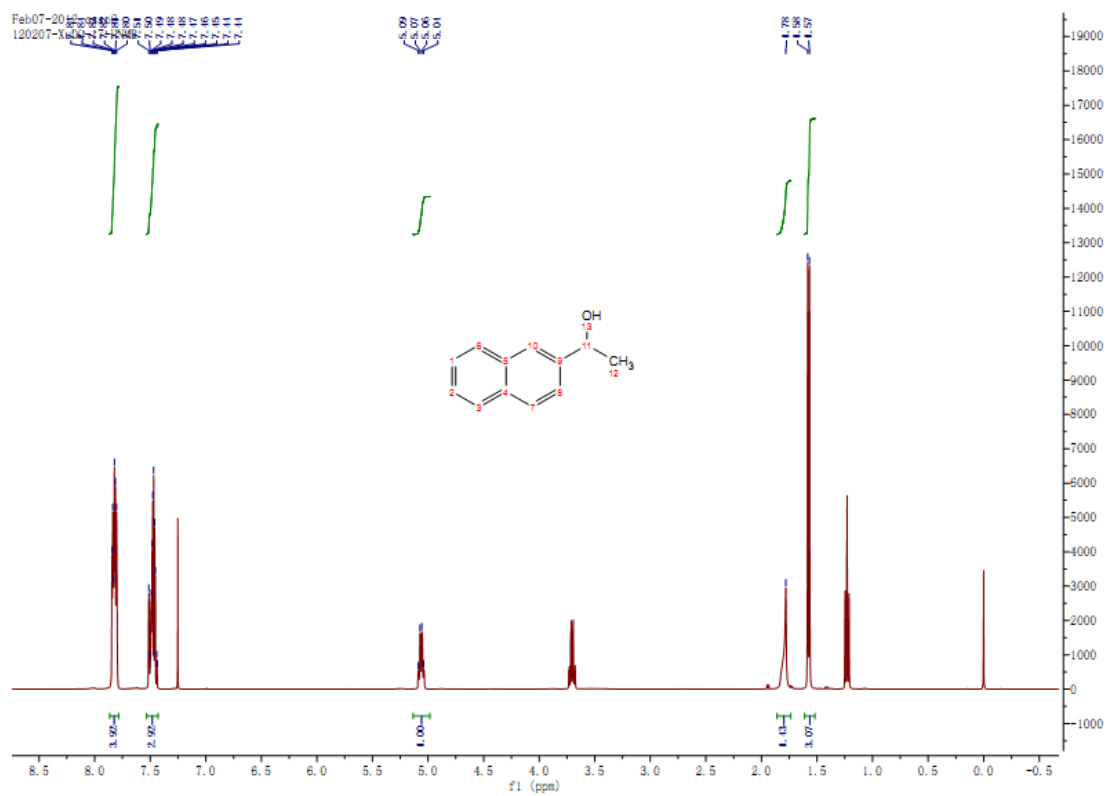
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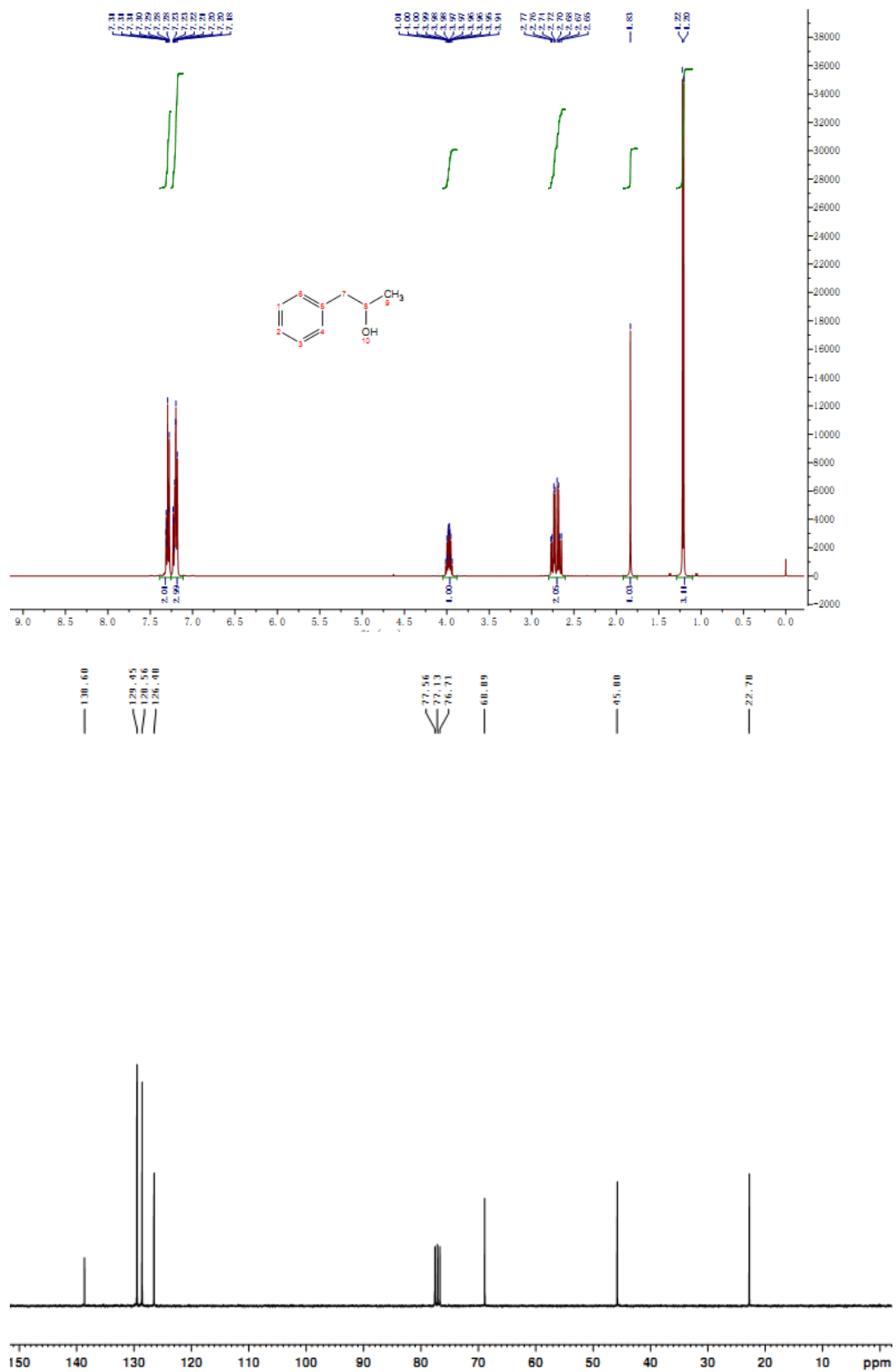
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2s



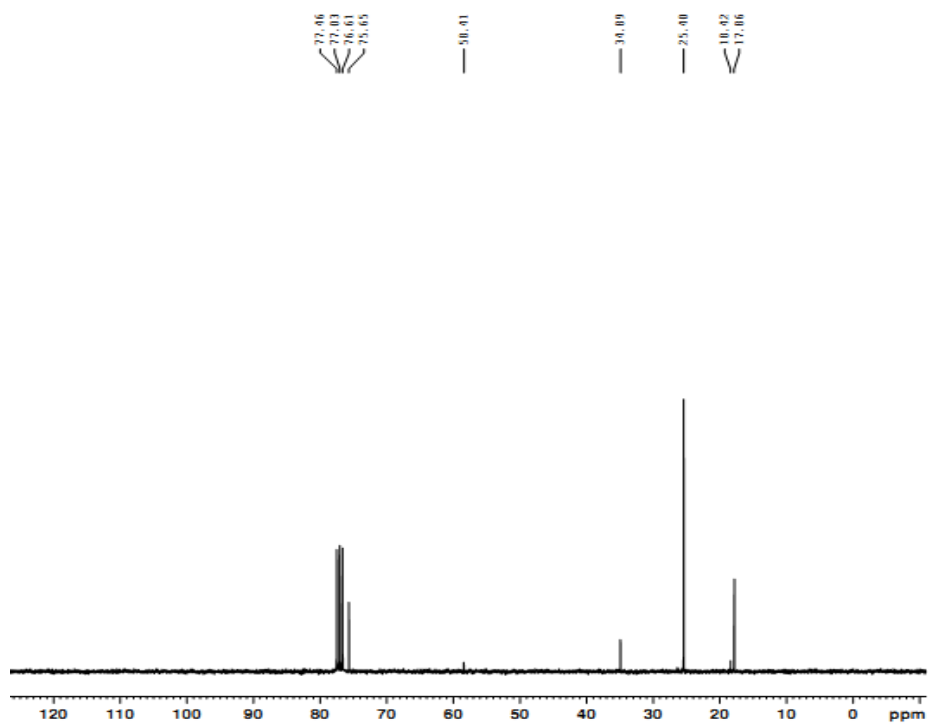
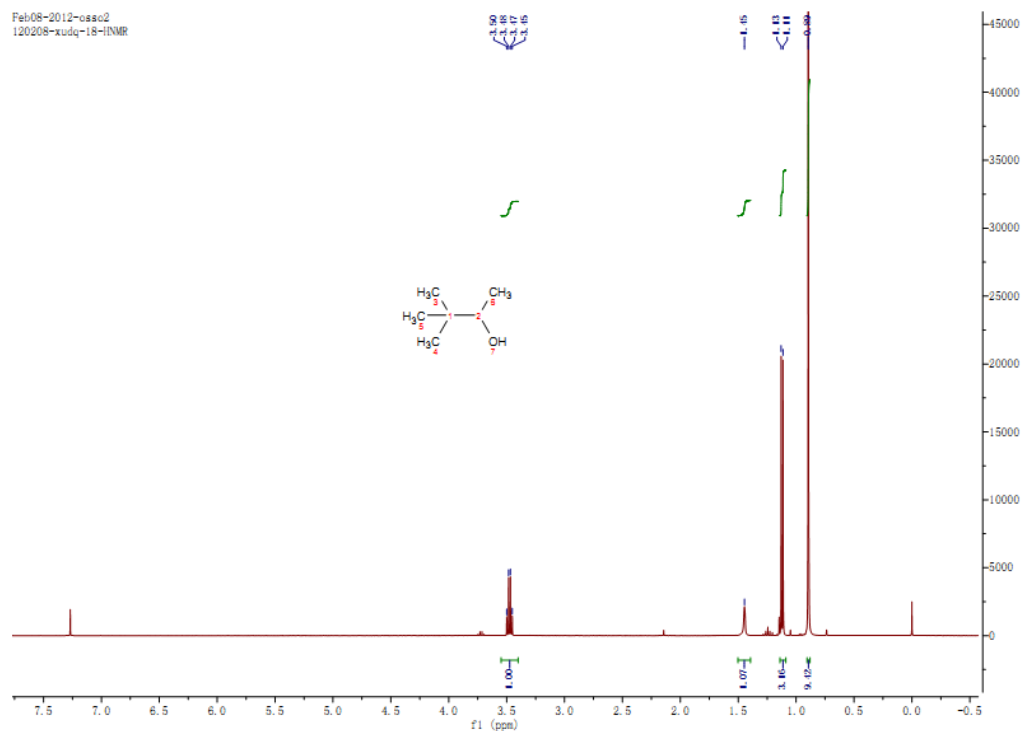
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2u



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2v

