Supporting Information

Catalytic Asymmetric Bromochlorination of Aromatic Allylic Alcohols Promoted by Multifunctional Schiff Base Ligands

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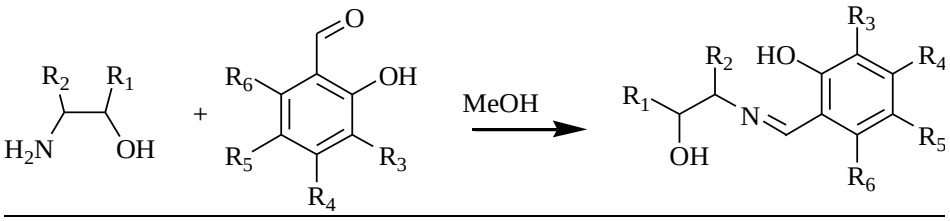
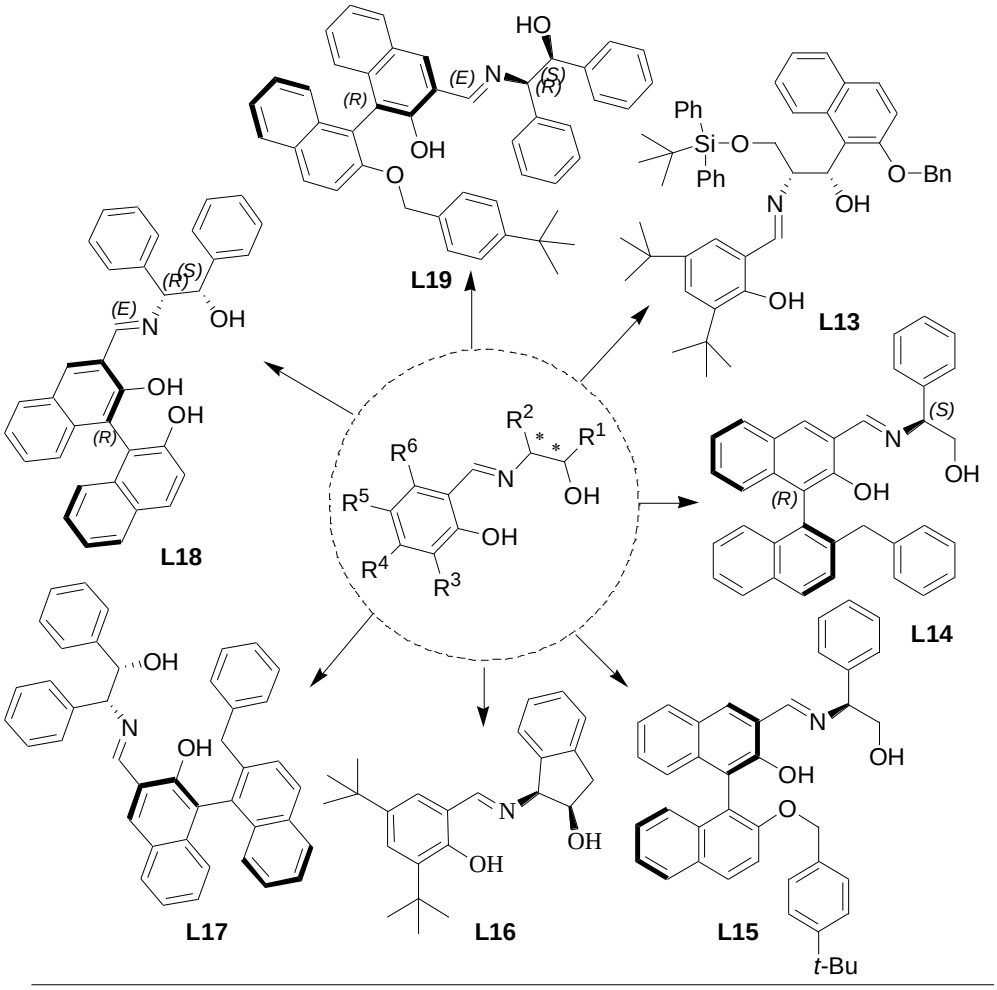
General Methods

All reactions and manipulations were performed using standard Schlenk techniques. All amino alcohols were commercially available and used without further purification. All the allyl alcohols were prepared according to the literature procedures. Flash column chromatography was performed over silica (200-300 mesh). **L1**[1], **L2-L6** [2], **L8** and **L9**[3], were prepared according to literature method or under the modified reaction conditions. ^{1}HNMR, ^{13}CNMR and ^{19}FNMR were respectively recorded at 400 or 500 MHz, 101 or 126 MHz, and 376 or 471 MHz respectively, and ^{31}P NMR were respectively recorded at 202 MHz respectively on Advance (Brucker). HPLC was carried out with a Agilent Technologies 1260 Infinity system equipped with a photodiode array detector. High Resolution Mass Spectra (ESI-HRMS) were operated on a micro TOF-Q II (Bruker). IR spectra were recorded using a FTIR apparatus (Nicolot 5700). Melting point was recorded by X-4 Optimelt (Shanghai optical instrument factory). Optical rotation was determined by SGW-3 Digital Automatic Polarimeter.

Preparation and Characterization of Ligands





L20: $R^1 = R^4 = R^6 = H$, $R^2 = Ph$, $R^3 = R^5 = t$-Bu

L21: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^3 = Si(i\text{-}Pr)_3$, $R^5 = Me$

L22: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^3 = TBS$, $R^5 = Me$

L23: $R^1 = R^2 = Ph$, $R^4 = R^6 = R^5 = H$, $R^3 = CH_2TMS$

L24: $R^1 = R^2 = Ph$, $R^3 = R^4 = R^6 = H$, $R^5 = F$

L25: $R^1 = R^2 = Ph$, $R^4 = R^6 = R^5 = H$, $R^3 = Me$

L26: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^5 = F$, $R^3 = Me$

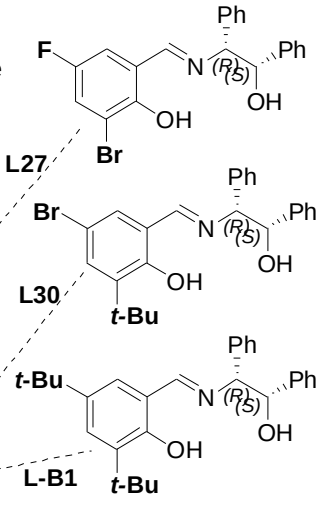
L27: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^5 = F$, $R^3 = Br$

L28: $R^1 = R^2 = Ph$, $R^3 = R^4 = R^5 = R^6 = H$

L29: $R^1 = R^2 = Ph$, $R^3 = R^4 = R^6 = H$, $R^5 = Cl$

L30: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^5 = Br$, $R^3 = t$-Bu

L-B1: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^5 = R^3 = t$-Bu



Aldehyde or its analogues (3.0 mmol) was added to a solution of commercial available amino alcohol (3.0 mmol) in MeOH (20 mL), and the solution was heated to 70 ℃ with stirring for 5 min. Then the solution was cooled to room temperature and stirred overnight. The mixture was washed with water and extracted with DCM, and the combined organic layers were dried over anhydrous Na_2SO_4, and was concentrated in vacuo and purified by flash column chromatography (silica gel, hexanes:EtOAc = 6:1) to afford a brittle yellow solid.

L-B1, yield: 76%; Orange solid; HRMS (ESI) Calcd for $[C_{29}H_{36}NO_2, M+H]^+$, 430.2741; Found: 430.2750 ;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 13.39 (s, 1H), 8.15 (s, 1H), 7.42–7.18 (m, 13H), 6.93 (d, J = 2.3 Hz, 1H), 5.08 (d, J = 6.6 Hz, 1H), 4.52 (d, J = 6.7 Hz, 1H), 2.13 (s, 1H), 1.45 (d, J = 1.5 Hz, 9H), 1.25 (d, J = 1.5 Hz, 9H).

^{13}C NMR (101 MHz, CDCl3) δ(ppm) = 167.1, 157.9, 140.3, 128.6, 128.2,127.8, 127.2, 126.3, 117.9, 80.0, 77.3, 76.7, 35.1, 34.1, 31.4, 29.4.

L7, yield: 76%; Orange solid; HRMS (ESI) Calcd for $[C_{25}H_{27}ClNO_2, M+H]^+$, 408.1725; Found: 408.1718;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =13.68 (s, 1H), 7.94 (s, 1H), 7.34 (d, *J* = 4.1 Hz, 4H), 7.29 (dd, *J* = 8.8, 4.6 Hz, 1H), 7.22 (dd, *J* = 7.2, 2.0 Hz, 4H), 7.18 (dd, *J* = 6.3, 3.5 Hz, 2H), 6.87 (d, *J* = 2.5 Hz, 1H), 4.97 (d, *J* = 6.8 Hz, 1H), 4.45 (d, *J* = 6.8 Hz, 1H), 2.20 (s, 1H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) = 165.5, 159.0, 140.1, 139.7, 139.2, 129.9, 128.8, 128.2, 127.3, 122.7, 119.3, 80.2, 78.4, 35.2, 29.2.

L13, yield: 75%; Orange solid; HRMS (ESI) Calcd for $[C_{51}H_{60}NO_4Si, M+H]^+$, 778.4281; Found:778.4286;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 8.23 (d, *J* = 8.1 Hz, 1H), 8.06 (s, 1H), 7.75 (dd, *J* = 21.1, 8.5 Hz, 2H), 7.51 (dd, *J* = 23.6, 7.4 Hz, 5H), 7.42 – 7.27 (m, 11H), 7.21 (dt, *J* = 18.7, 7.1 Hz, 6H), 6.94 (s, 1H), 6.05 (t, *J* = 6.5 Hz, 1H), 5.13 (dd, *J* = 35.3,

12.1 Hz, 2H), 3.96 (s, 1H), 3.89 (s, 1H), 3.75 (dd, *J* = 9.8, 6.4 Hz, 1H), 1.45 (s, 9H), 1.30 (s, 9H), 1.01 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) = 168.3, 158.2, 154.8, 136.8, 135.7, 133.3, 132.2, 130.1, 129.7, 128.9, 128.2, 127.7, 127.5, 127.1, 126.9, 124.0, 121.4, 118.3, 114.6, 75.5, 71.5, 69.5, 64.7, 35.2, 34.3, 31.6, 29.7, 26.9, 19.3.

L14, yield: 76%; Orange solid; HRMS (ESI) Calcd for $[C_{36}H_{29}NNaO_2, M+Na]^+$, 530.2062; Found: 530.2091;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 12.72 (s, 1H), 8.73 (s, 1H), 8.08 (s, 1H), 7.89 (t, *J* = 8.0 Hz, 3H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.18 (m, 12H), 7.10 – 7.04 (m, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 6.2 Hz, 3H), 4.56 (s, 1H), 3.88 (t, *J* = 7.6 Hz, 2H), 3.82 (s, 1H), 3.75 (s, 1H), 2.03 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ:166.4, 154.4, 141.1, 139.1, 138.4, 135.6, 133.9, 133.2, 132.7, 132.1, 129.4, 128.9, 128.7, 128.5, 127.9, 127.4, 126.3, 125.6, 125.4, 125.0, 123.6, 120.8, 119.8, 76.3, 67.7, 40.1.

L15, yield: 78%; Orange solid; HRMS (ESI) Calcd for $[C_{40}H_{38}NO_3, M+H]^+$, 580.2846; Found: 580.2841;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =12.90 (s, 1H), 8.70 (d, *J* = 7.0 Hz, 1H), 7.95 – 7.89 (m, 2H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 5.7 Hz, 1H), 7.39 – 7.19 (m, 12H), 7.16 – 7.09 (m, 3H), 6.92 (dd, *J* = 16.4, 5.5 Hz, 2H), 5.06 (d, *J* = 5.7 Hz, 2H), 4.48 (dd, *J* = 11.6, 5.1 Hz, 1H), 3.83 (dd, *J* = 11.7, 6.5 Hz, 2H), 1.27 – 1.18 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) = 166.7, 154.5, 150.5, 139.2, 135.9, 134.6, 134.0, 129.8, 129.0, 128.2, 127.6, 127.4, 126.9, 126.6, 125.7, 125.0, 124.0, 123.5, 120.9, 120.2, 117.7, 116.3, 76.5, 71.4, 67.7, 34.5, 31.4 .

L16, yield: 78%; Orange solid; HRMS (ESI) Calcd for $[C_{24}H_{32}NO_2, M+H]^+$, 366.2428; Found: 366.2439;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 13.13 (s, 1H), 8.60 (s, 1H), 7.42 (d, *J* = 2.3 Hz, 1H), 7.28 (d, *J* = 6.9 Hz, 2H), 7.24 – 7.12 (m, 3H), 4.78 (d, *J* = 5.3 Hz, 1H), 4.66 (q,

J= 5.3 Hz, 1H), 3.16 (ddd, *J* = 20.8, 15.9, 5.4 Hz, 2H), 2.22 (s, 1H), 1.41 (s, 9H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) =168.4, 158.2, 141.0, 140.6, 137.1, 128.6, 127.8, 127.2, 126.6, 125.6, 125.1, 118.0, 75.8, 75.3, 39.8, 35.2, 34.3, 31.6, 29.6.

L17, yield: 71%; Orange solid; HRMS (ESI) Calcd for $[C_{42}H_{33}NO_2, M+H]^+$, 584.2590; Found: 584.2653;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) = 12.80 (d, *J* = 2.0 Hz, 1H), 8.21 (s, 1H), 7.89 (dd, *J* = 8.5, 2.8 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.72 (s, 1H), 7.49 – 7.16 (m, 17H), 7.05 – 6.97 (m, 3H), 6.92 (dd, *J* = 13.8, 7.5 Hz, 3H), 4.94 (dd, *J* = 7.3, 1.9 Hz, 1H), 4.44 (d, *J* = 7.3 Hz, 1H), 3.73 (s, 2H), 2.06 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) = 165.7, 154.4, 141.0, 140.4, 139.4, 138.6, 135.6, 133.8, 133.2, 132.7, 132.1, 129.3, 128.9, 128.6, 128.5, 128.0, 127.4, 127.2, 126.2, 125.7, 125.4, 124.9, 123.5, 120.7, 119.6, 81.3, 78.5, 77.5, 77.2, 76.8, 40.0.

L18, yield: 76%; Orange solid; HRMS (ESI) Calcd for $[C_{35}H_{28}NO_3, M+H]^+$, 510.2064; Found: 510.2073 ;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =13.19 (s, 1H), 8.30 (s, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.77 (m, 2H), 7.48 – 7.39 (m, 3H), 7.35 – 7.17 (m, 12H), 7.06 (d, *J* = 8.5 Hz, 1H), 5.25 (s, 1H), 5.02 (d, *J* = 7.2 Hz, 1H), 4.54 (d, *J* = 7.2 Hz, 1H), 2.19 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) = 165.7, 155.4, 151.7, 140.2, 139.2, 135.6, 135.0, 133.7, 130.2, 129.4, 129.3,128.7, 128.5, 128.1, 127.8, 127.2, 126.6, 125.0, 124.1, 123.4, 120.9, 117.9, 114.6, 113.8, 81.1, 78.4.

L19, yield: 72%; Orange solid; HRMS (ESI) Calcd for $[C_{46}H_{41}NO_3, M+H]^+$, 656.3165; Found: 656.3258;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =12.87 (s, 1H), 8.23 (s, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.3 Hz, 1H), 7.69 (s, 1H), 7.43 (dd, *J* = 16.1, 8.3 Hz, 3H), 7.37 – 7.15 (m, 14H), 7.13 (s, 1H), 7.04 – 6.97 (m, 2H), 6.89 (d, *J* = 8.2

Hz, 2H), 5.00 (s, 2H), 4.96 (d, *J* = 6.7 Hz, 1H), 4.45 (d, *J* = 7.3 Hz, 1H), 2.08 (s, 1H), 1.17 (d, *J* = 3.2 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) = 165.98, 154.5, 150.2, 140.4, 139.4, 135.7, 134.5, 134.0, 133.7, 129.7, 128.8, 128.2, 127.4, 127.2, 126.8, 126.4, 125.5, 125.1, 123.9, 123.3, 120.7, 120.0, 117.5, 116.3, 81.3, 78.4, 71.3, 34.4, 31.4 .

L20, yield: 70 %; Orange thick liquid; HRMS (ESI) Calcd for $[C_{23}H_{32}NO_2, M+H]^+$, 354.2428; Found: 354.2437 ;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =13.50 (s, 1H), 8.50 (s, 1H), 7.45 – 7.24 (m, 6H), 7.12 (s, 1H), 4.45 (dd, *J* = 7.6, 5.4 Hz, 1H), 4.03 – 3.84 (m, 2H), 1.89 (s, 1H), 1.46 (d, *J* = 1.7 Hz, 9H), 1.30 (d, *J* = 1.8 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) =167.8, 158.1, 140.6, 136.9, 128.9, 128.0, 127.6, 127.3, 126.6, 118.0, 76. , 67.9, 35.2, 34.3, 31.6, 29.6.

L21, yield: 73%; Orange solid; HRMS (ESI) Calcd for $[C_{35}H_{28}NO_3, M+H]^+$, 488.2979; Found: 488.2980 ;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =12.83 (s, 1H), 8.07 (s, 1H), 7.40 – 7.26 (m, 5H), 7.22 (d, *J* = 10.1 Hz, 6H), 6.91 (s, 1H), 5.06 (d, *J* = 6.6 Hz, 1H), 4.50 (d, *J* = 6.7 Hz, 1H), 2.22 (s, 3H), 1.18 – 1.07 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) = 166.5, 164.2, 140.3, 133.2, 128.8, 128.2, 127.3, 117.5, 80.1, 78.4, 20.6, 19.2, 11.8.

L22, yield: 71%; Orange solid; HRMS (ESI) Calcd for $[C_{35}H_{28}NO_3, M+H]^+$, 446.2510; Found: 446.2501;

^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.84 (s, 1H), 8.05 (s, 1H), 7.46 – 7.13 (m, 12H), 6.89 (s, 1H), 5.04 (d, *J* = 6.7 Hz, 1H), 4.49 (d, *J* = 6.7 Hz, 1H), 2.21 (s, 3H), 0.93 (s, 9H), 0.33 (dd, *J* = 4.4, 2.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) =166.5, 163.9, 140.3, 133.4, 128.8, 128.1, 127.3, 127.0, 125.1, 117.5, 80.0, 78.4, 27.3, 20.5, 17.8, -4.6.

L23, yield: 71 %; Orange thick liquid; HRMS (ESI) Calcd for $[C_{25}H_{30}NO_2Si, M+H]^+$, 404.2040; Found: 404.2049;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =13.21 (s, 1H), 7.99 (s, 1H), 7.43 – 7.09 (m, 10H), 7.02 – 6.89 (m, 1H), 6.78 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 4.96 (d, *J* = 7.0 Hz, 1H), 4.42 (d, *J* = 7.0 Hz, 1H), 2.33 – 1.95 (m, 3H), -0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) =166.3 , 158.0, 140.3, 139.8, 132.4, 128.8, 128.1, 127.3, 118.1, 80.4, 78.6, 19.9, -1.4.

L24, yield: 71%; Orange solid; HRMS (ESI) Calcd for $[C_{21}H_{19}FNO_2, M+H]^+$, 336.1394; Found: 336.1418;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =12.85 (s, 1H), 7.97 (s, 1H), 7.37 (d, *J* = 4.0 Hz, 4H), 7.30 – 7.20 (m, 6H), 7.02 – 6.92 (m, 1H), 6.87 (dd, *J* = 9.0, 4.5 Hz, 1H), 6.76 (dd, *J* = 8.4, 3.1 Hz, 1H), 5.03 (d, *J* = 7.1 Hz, 1H), 4.51 (d, *J* = 7.1 Hz, 1H), 2.06 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) =165.0, 157.2, 156.7, 154.3, 140.2, 139.3, 129.0, 128.3, 127.3, 119.8, 119.6, 118.5, 118.1, 116.9, 116.7, 80.4, 78.5, 77.4.

L25, yield: 71%; Orange solid; HRMS (ESI) Calcd for $[C_{22}H_{22}NO_2, M+H]^+$, 332.1645; Found: 332.1655;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =13.34 (s, 1H), 8.02 (s, 1H), 7.37 (dt, *J* = 14.9, 7.5 Hz, 4H), 7.32 – 7.21 (m, 6H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 5.02 (d, *J* = 7.1 Hz, 1H), 4.47 (d, *J* = 7.1 Hz, 1H), 2.27 (s, 3H), 2.07 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) =166.3, 159.3, 140.4, 139.7, 133.7, 129.5, 128.9, 128.5, 128.1, 127.3, 126.0, 118.3, 118.1, 80.5, 78.5, 15.6.

L26, yield: 71%; Orange solid; HRMS (ESI) Calcd for $[C_{22}H_{21}FNO_2, M+H]^+$, 350.1551; Found: 350.1569;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =13.11 (s, 1H), 7.92 (s, 1H), 7.50 – 7.17 (m, 11H), 6.87 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.58 (dd, *J* = 8.3, 3.0 Hz, 1H), 4.99 (d, *J* = 7.1 Hz, 1H), 4.46 (d, *J* = 7.1 Hz, 1H), 2.25 (s, 3H), 2.12 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) =165.2, 156.2, 155.5, 153.8, 140.2, 139.4, 128.9, 128.5, 128.1, 127.9, 127.3, 120.8, 120.5, 117.5, 114.1, 113.9, 80.5, 78.4, 15.7.

L27, yield: 70%; Orange thick liquid; HRMS (ESI) Calcd for [$C_{21}H_{18}BrFNO_2$, M+H]$^+$, 414.0499; Found: 414.0524;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =13.92 (s, 1H), 7.89 (s, 1H), 7.46 – 7.20 (m, 12H), 6.75 (dd, *J* = 8.0, 2.9 Hz, 1H), 5.01 (d, *J* = 7.2 Hz, 1H), 4.50 (d, *J* = 7.2 Hz, 1H), 2.08 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) = 164.1, 154.5, 153.3, 139.8, 138.7, 128.9, 128.3, 128.0, 127.1, 123.3, 123.0, 118.4, 116.2, 116.0,115.8, 110.7, 80.1, 76.7 .

L28, yield: 72%; Orange solid; HRMS (ESI) Calcd for [$C_{21}H_{20}NO_2$, M+H]$^+$, 318.1489; Found: 318.1500 ;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =13.14 (s, 1H), 8.06 (s, 1H), 7.48 – 7.24 (m, 11H), 7.06 (s, 1H), 6.92 (s, 1H), 6.80 (t, *J* = 6.9 Hz, 1H), 5.03 (d, *J* = 6.9 Hz, 1H), 4.51 (d, *J* = 7.0 Hz, 1H), 2.11 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) =166.1, 161.0, 140.3, 132.7, 131.8, 128.9, 128.4, 128.0, 127.3, 118.8, 117.1, 80.3, 78.5 .

L29, yield: 75%; Orange solid; HRMS (ESI) Calcd for [$C_{21}H_{19}ClNO_2$, M+H]$^+$, 352.1099; Found: 352.1091;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =13.11 (s, 1H), 7.93 (s, 1H), 7.36 – 7.16 (m, 11H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 4.98 (d, *J* = 7.0 Hz, 1H), 4.48 (d, *J* = 7.1 Hz, 1H), 2.18 (s, 1H).

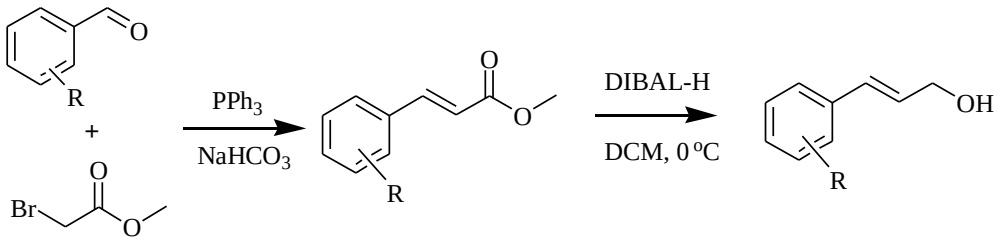
^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) = 164.8, 159.6, 140.1, 139.2, 132.4, 130.8, 128.9, 128.2, 127.2, 123.3, 119.5, 118.6, 80.1, 78.3 .

L30, yield: 73%; Orange solid; HRMS (ESI) Calcd for [$C_{25}H_{26}BrNO_2$, M+H]$^+$,452.1147; Found: 452.1239 ;

^{1}H NMR (400 MHz, $CDCl_3$): δ(ppm) =13.72 (s, 1H), 7.95 (s, 1H), 7.40 – 7.15 (m, 12H), 7.02 (d, *J* = 2.4 Hz, 1H), 5.00 (d, *J* = 6.9 Hz, 1H), 4.46 (d, *J* = 6.9 Hz, 1H), 2.30 – 1.95 (m, 1H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ(ppm) = 165.4, 159.5, 140.1, 139.2, 132.6, 131.9, 128.9, 128.2, 127.3, 119.9, 109.9, 80.2, 78.4, 35.2 .

General Procedure for the Preparation of allyl alcohols[4]



To a solution of triphenylphosphine (1.97g 7.5 mmol) in saturated $NaHCO_3$ (10 mL) at room temperature were added methyl bromacetate (737μL) and aldehyde (5.0 mmol) stirred 3h. The phases were separated and extracted with EtOAc (2 x 10 mL). The combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was dissolved in DCM (10 mL) in a 100 mL round-bottom flask and cooled to 0 ℃ Neat diisobutylaluminum hydride (10 mmol) was added dropwise and the reaction mixture was stirred for 3 h. an aqueous saturated solution of Rochelle's salt (20 mL) was slowly added followed by water (15 mL) and diethyl ether (20 mL). The emulsion was stirred vigorously overnight. The phases were separated and the aqueous phase was extracted with diethyl ether (2 x 20 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was then purified by flash chromatography to provide the desired allylic alcohol.

General Procedure for the Preparation of Bromochloroalcohols/Synthesis and Characterization of the Products[5]

General Procedure for the Preparation of Racemic Bromochlorides:

To an allylic alcohol substrate (0.1 mmol) in *n*-hexane (1 mL) is added $ClTi(Oi\text{-}Pr)_3$ (0.11 mmol, 1.10 equiv). To this solution is added solid *N*-bromosuccinimide (18.7 mg, 0.105 mmol, 1.05 equiv). The solution is stirred at room temperature and monitored by TLC. When judged complete, the reaction is quenched with saturation Na_2SO_3 solution (0.5 mL), and stirred vigorously for 15 min., then added 1M HCl (1 mL), the organic layer is separated and the aqueous layer is extracted with EtOAc (2 x 0.5 mL). The combine organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo to provide crude material, which is purified by flash column chromatography to provide the desired racemic bromochloride.

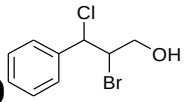
Synthesis and Characterization of Dihalide Products:

(Method A): To a solution of allylic alcohol substrate (0.5 mmol) in hexanes (3.0 mL) in reaction tube is added $ClTi(Oi\text{-}Pr)_3$ (0.55 mmol, 1.1 equiv) under nitrogen in at room temperature. To this solution is added a solution of **L-B1** (0.05mmol, 0.1 equiv) in hexanes (2 mL) dropwise over 1 min. then the solution is cooled to -20 ^oC. To this solution is added all at once solid N-bromosuccinimide (0.55 mmol,1.1 equiv). The reaction is stirred vigorously (700 rpm) over night. Reactions are monitored by TLC. The reaction mixture is quenched with saturation Na_2SO_3 solution (5 mL), diluted with 1M HCl (10 mL), and allowed to warm to room temperature with vigorous stirring for 10 min. The layers are separated and the aqueous layer is extracted with EtOAc (2 x 10 mL). The combined organic layers are washed with saturated aqueous NaCl (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to provide crude material, which is purified by flash column chromatography (EtOAc : hexane 17:1 to 10:1)to provide the desired bromochloride.

(Method B): To a solution of allylic alcohol substrate (0.5 mmol) and *t*-BuOH(0.5

mmol) in hexanes (3.0 mL) in reaction tube is cooled to -20 ^{o}C for 5 min then ClTi(Oi-Pr)$_3$ (0.55 mmol, 1.1 equiv) was added under nitrogen at -20 ^{o}C for 5 min. To this solution is added a solution of**L30** (0.05mmol, 0.1 equiv) in hexanes (2 mL) dropwise over 1 min at -20 ^{0}C for 30 min. To this solution is added all at once solid N-bromosuccinimide (0.55 mmol, 1.1 equiv). The reaction is stirred vigorously (700 rpm) over night. Reactions are monitored by TLC. The reaction mixture is quenched with saturation Na_2SO_3 solution (5 mL), diluted with 1M HCl (10 mL), and allowed to warm to room temperature with vigorous stirring for 15 min. The layers are separated and the aqueous layer is extracted with EtOAc (2 x 10 mL). The combined organic layers are washed with saturated aqueous NaCl (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to provide crude material, which is purified by flash column chromatography (EtOAc : hexane = 17:1 to 10:1)to provide the desired bromochloride.

If there is no special noted, the bromochlorides **2** was obtained from **method A**.

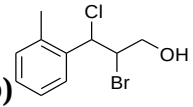
1. **(2a)** 

White waxy solid, m.p.= 69-70 ℃; **method A,** yield: 80%; cr: 33: 1; 86% *ee*; **method B,** yield: 75%; cr: 25:1; 92% *ee*; [HPLC condition: Chiralcel AS-H column, *n*-hexane/i-PrOH = 95:5,flow rate = 1.0 mL/min, t_R = 11.52 min, t_R = 13.68 min]; $[\alpha]_D^{20}$= –17.3(c = 3.7, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.34 (m, 5H), 5.21 (d, *J* = 10.1 Hz, 1H), 4.55 (ddd, *J* = 10.0, 4.7, 3.0 Hz, 1H), 4.27 (dd, *J* = 12, 4.0 Hz, 1H), 4.15 (dd, *J* =12.0,4.0Hz,1H), 2.42 (s, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 139.0, 129.1, 128.7, 127.8, 64.7, 61.6, 59.7 ppm;

IR (KBr)ν_{max}: 3418.8, 3067.2, 2930.9, 1955.4, 1618.0, 1495.8, 1455.6, 1388.5, 1280.0, 1232.6, 1167.5, 1071.3, 954.1, 824.9, 771.12, 700.5, 608.1cm^{-1}.

(2b) 

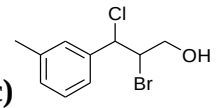
White waxy solid , m.p.= 89-90 ℃; **method A,** yield: 71% ; cr: 13:1; 70% *ee*;

method B, yield: 70% ; cr: 13: 1; 48% *ee*; [HPLC condition: Chiralcel OJ-H column, *n*-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, t_R = 26.23 min, t_R = 37.90 min]; $[\alpha]_D^{20}$= –5.90 (c = 4.5, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ:7.44-7.37 (m, 1H), 7.25 – 7.18 (m, 2H), 7.16 (s, 1H), 5.48 (d, *J* = 10.7 Hz, 1H), 4.58 (ddd, *J* = 10.7, 4.5, 2.6 Hz, 1H), 4.28 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.19 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.40 (d, *J* = 9.6 Hz, 3H), 2.31 (s, 1H) ppm ;

^{13}C NMR (101 MHz, $CDCl_3$) δ:137.6, 136.0, 130.7, 128.8, 126.8, 126.8, 64.8, 59.3, 57.2, 19.4 ppm ;

IR (KBr)ν_{max}: 3409.1, 3067.4, 2930.8, 2876.9, 1924.7, 1810.5, 1617.6, 1492.0, 1453.3, 1372.5, 1291.5, 1256.4, 1224.2, 1159.1, 1114.6, 1088.0, 1063.9, 969.9, 904.0, 866.5, 844.6, 764.5, 730.0, 704.2, 650.2cm^{-1}.

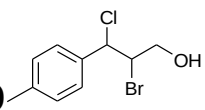
(2c) 

White waxy solid , m.p.= 49-50 ℃; **method A,** yield: 74% ; cr: 19:1; 85% *ee*; **method B,** yield: 72% ; cr: 17:1; 79% *ee*; [HPLC condition: Chiralcel OJ-H column, *n*-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, t_R = 25.15 min, t_R = 31.82 min]; $[\alpha]_D^{20}$ = –13.3(c = 3.7, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 – 7.21 (m, 1H), 7.15 (dd, *J* = 11.4, 8.1 Hz, 3H), 5.13 (d, *J* = 10.0 Hz, 1H), 4.51 (ddd, *J* = 10.0, 4.7, 3.0 Hz, 1H), 4.26 (dd, *J* = 12.0., 4.0 Hz, 1H), 4.16 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.37 (s, 1H), 2.35 (s, 3H) ppm ;

^{13}C NMR (101 MHz, $CDCl_3$) δ:138.9, 138.4, 129.8, 128.5, 128.5, 124.8, 64.7, 61.8, 59.7, 21.5 ppm ;

IR (KBr)ν_{max}: 3409.1, 3087.4, 2930.8, 2876.9, 1924.7, 1830.5, 1617.6, 1493.0, 1463.3, 1374.5, 1159.4, 1064.6, 790.9, 730.4, 699.2, 607.3cm^{-1}.

(2d) 

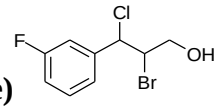
White waxy solid , m.p.= 96-97 ℃; **method A,** yield: 81%; cr: 24:1; 86% *ee*; **method B,** yield: 78%; cr: 24:1; 93% *ee*; [HPLC condition: Chiralcel IA-H column,

n-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, t_R = 14.83 min, t_R = 17.66 min]; $[\alpha]_D^{20}$= –15.3 (c = 3.3, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.19 (d, *J* = 10.0 Hz, 1H), 4.55 (ddd, *J* = 10.0, 4.7, 3.0 Hz, 1H),4.26 (dd, J = 12.0,4.0 Hz, 1H), 4.16 (dd, J = 12.0, 4.0 Hz, 1H), 2.45 (s, 1H), 2.38 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 139.0, 136.2, 129.4, 127.7, 64.7, 61.7, 59.8, 21.3 ppm;

IR (KBr)v_{max}: 3550.2, 3414.3, 2925.5, 1637.5, 1617.2, 1555.4, 1159.4, 1064.6, 780.9, 730.4, 689.2, 609.1 cm^{-1}.

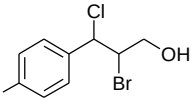
(2e) 

Colorless viscous liquid; **method B,** yield: 74%; cr: 8.2:1; 78% *ee*; **method B,** yield: 74%; cr: 13:1; 80% *ee*; [HPLC condition: Chiralcel OJ-H column, *n*-hexane/i-PrOH = 95:5,flow rate = 1.0 mL/min, t_R = 14.83min, t_R = 17.66 min]; $[\alpha]_D^{20}$= –7.85 (c = 3.2, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (td, *J* = 8.0, 5.8 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.07 (td, *J* = 8.4, 2.4 Hz, 1H), 5.20 (.d, *J* = 100 Hz, 1H), 4.49 (ddd, *J* = 10.0, 4.5, 3.1 Hz, 1H), 4.28 (dd, *J* =12.0, 4.0 Hz, 1H), 4.14 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.48 (s, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.9, 161.5, 141.4, 130.2, 123.7, 116.2, 116.0, 115.0, 114.8, 64.5, 60.6, 59.1 ppm;

IR (KBr)v_{max}: 3415.6, 2931.1, 2879.1, 1616.2, 1593.2, 1489.8, 1451.4, 1376.9, 1230.5, 1158.9, 1105.3,1058.5, 1014.1, 953.8, 904.3, 839.5, 787.5, 737.4, 696.2, 642.0, 613cm^{-1}.

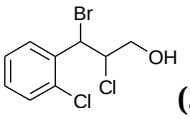
(2f) 

White waxy solid, m.p.= 64-65 ℃ ; **method A,** yield: 77% ; cr: 24:1; 80% *ee*; **method B,** yield: 78% ; cr: 18:1; 88% *ee*; [HPLC condition: Chiralcel OJ-H column, *n*-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, t_R = 32.84 min, t_R = 34.81 min]; $[\alpha]_D^{20}$= –9.89 (c = 4.1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.32 (m, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 5.18 (d, *J* = 10.0 Hz, 1H), 4.47 (ddd, *J* = 10.0, 4.5, 3.1 Hz, 1H), 4.24 (dd, *J* =12, 4.0 Hz, 1H), 4.11(dd, *J* =12, 4.0 Hz, 1H), 2.44 (s, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.1, 161.6, 135.0, 129.7, 115.8, 115.6, 64.6, 60.8, 59.7 ppm;

IR (KBr)ν_{max}: 3416.6, 2931.4, 1903.5, 1604.4, 1510.7, 1453.1, 1422.2, 1369.5, 1299.0, 1231.5, 1159.9, 1105.4,1058.7, 1014.5, 955.8, 904.4, 839.0, 787.8, 737.8, 696.4, 643.0, 623.1cm^{-1}.



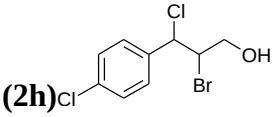
(2g)

White waxy solid, m.p.= 86-87 ℃; **method A,** yield: 72%; cr: 13:1; 80% *ee*; **method B,** yield: 78% ; cr: 10:1; 74% *ee*; [HPLC condition: Chiralcel OJ-H column, *n*-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, t_R = 25.71 min, t_R = 31.21 min]; $[\alpha]_D^{20}$= –6.89 (c = 2.3, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.36-7.27 (m, 2H), 5.77 (d, *J* = 10.1 Hz, 1H), 4.62 (ddd, *J* = 10.0, 4.7, 2.8 Hz, 1H), 4.25 (dd, *J* =12.0, 4.0 Hz, 1H), 4.18 (dd, *J* =12.0, 4.0 Hz, 1H), 2.33 (s, 1H) ppm ;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 136.8, 133.6, 130.0, 128.9, 127.5, 64.5, 58.5, 57.1 ppm ;

IR (KBr)ν_{max}: 3699.8, 3553.6, 3477.7, 3413.7, 3234.4, 2932.1, 1616.8, 1446.2, 1094.1, 741.1, 621.1cm^{-1}.



(2h)

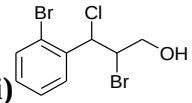
White waxy solid, m.p.= 86-87 ℃; **method A,** yield: 72%; cr: 10:1; 80% *ee*; **method**

B, yield: 83% ; cr: 14:1; 80% *ee*, [HPLC condition: Chiralcel IA-H column, n-hexane/i-PrOH = 95:5, low rate = 1.0 mL/min, t_R = 14.15 min, t_R = 17.89 min]; $[\alpha]_D^{20}$= –5.69 (c = 3.6, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38-7.31 (m, 4H), 5.17 (d, *J* = 10.0 Hz, 1H), 4.50-4.44 (m, 1H), 4.35 (dd, *J* =88.0, 4.0 Hz,1H), 4.11 (dd, *J* =16.0, 4.0 Hz,1H), 2.60 (s, 1H) ppm ;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 137.6, 134.9, 129.2, 128.9, 64.5, 60.6, 59.2 ppm ;

IR (KBr)ν_{max}: 3416.0, 2933.2, 1637.6, 1493.1, 1413.1, 1157.7, 1092.0,1013.8, 829.7, 733.2, 614.3 cm^{-1}.

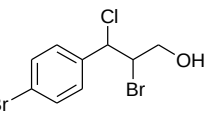
(2i) 

yield: 75%; White waxy solid, m.p.= 78-79 ℃; cr: 9:1; 82% *ee* [HPLC condition: Chiralcel OJ-H column, *n*-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, t_R = 29.11min, t_R = 39.41 min]; $[\alpha]_D^{20}$= –7.36 (c = 3.1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.52 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.41-7.32 (m, 1H), 7.22 – 7.15 (m, 1H), 5.77 (d, *J* = 10.0 Hz, 1H), 4.60 (ddd, *J* = 9.9, 4.7, 2.8 Hz, 1H), 4.21 (qd, *J* = 12.7, 3.9 Hz, 2H), 2.42 (s, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.4, 133.2, 130.3, 128.9, 128.2, 124.1, 64.4, 59.6, 58.6 ppm;

IR (KBr)ν_{max}: 3551.7, 3414.1, 1637.5, 1617.6, 1091.8, 737.6, 621.0 cm^{-1}.

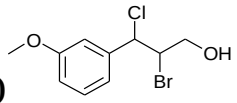
(2j) 

White waxy solid, m.p.= 69-70 ℃; **method A,** yield: 70% ; cr: 10:1; 75% *ee*; **method B,** yield: 75% ; cr: 11:1; 72% *ee*; [HPLC condition: Chiralcel IA-H column, *n*-hexane/i-PrOH = 95:5, flow rate = 1.0 mL/min, t_R = 15.06min, t_R = 20.17 min]; $[\alpha]_D^{20}$= –6.26 (c = 5.4, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ:7.47-7.39 (m, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 5.07 (d, *J* = 10.0 Hz, 1H), 4.37 (ddd, *J* = 10.0, 4.4, 3.1 Hz, 1H), 4.03 (dd, *J* = 16.0, 4.0 Hz, 1H), 3.88 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.57 (s, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ:138.0, 131.8, 129.5, 123.0, 64.4, 60.6, 59.1 ppm;

IR (KBr)ν_{max}: 3414.3, 2927.6, 1618.1, 1590.6, 1489.2, 1409.7, 1158.6, 1073.5, 1009.7,958.8, 826.4, 732.5, 676.8, 611.5 cm^{-1}.



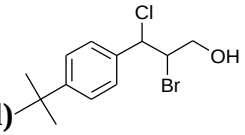
(2k)

yield: 22%; White waxy solid, m.p.= 53-54 ℃; cr: 12:1; 81% *ee* [HPLC condition: Chiralcel OJ-H column, *n*-hexane/i-PrOH = 85:15, flow rate = 1.0 mL/min, t_R = 24.05 min, t_R = 29.39 min]; $[\alpha]_D^{20}$= –7.26 (c = 2.4, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (t, *J* = 7.9 Hz, 1H), 7.01-6.87 (m, 3H), 5.14 (d, *J* = 10.0 Hz, 1H), 4.51 (ddd, *J* = 10.0, 4.7, 3.0 Hz, 1H), 4.24 (dd, *J* =12.0, 4.0 Hz, 1H), 4.13 (dd, *J* =12.0, 4.0 Hz, 1H), 3.83 (s, 3H), 2.14 (s, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.8, 140.5, 129.8, 120.2, 114.5, 113.8, 64.7, 61.5, 59.7, 55.5 ppm;

IR (KBr)ν_{max}: 3414.7, 3001.7, 2925.0, 2868.7, 1600.1, 1494.3, 1465.1, 1436.4, 1353.4, 1324.1, 1264.4, 1168.2, 1084.6, 1036.8, 995.7, 975.2, 855.8, 788.8, 751.0, 719.9, 691.0, 662.1, 629.5cm^{-1}.



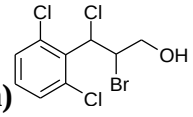
(2l)

White waxy solid , m.p.= 57-58 ℃ ; **method A,** yield: 69% ; cr: 32:1; 86% *ee*; **method B,** yield: 74 % ; cr: 50: 1; 90 % *ee*, [HPLC condition: Chiralcel OJ-H column, *n*-hexane/i-PrOH = 98:2, flow rate = 0.7 mL/min, t_R = 17.50 min, t_R = 20.02 min]; $[\alpha]_D^{20}$= –9.26 (c = 4.3, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33-7.27 (m, 2H), 7.25-7.20 (m, 2H), 5.10 (d, *J* = 9.8 Hz, 1H), 4.45 (ddd, *J* = 9.8, 4.8, 3.1 Hz, 1H), 4.24 (dd, *J* = 12.0,4.0 Hz, 1H), 4.13 (dd, *J* = 12.0,4.0 Hz, 1H), 2.32 (s, 1H), 1.23 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.1, 135.9, 127.4, 125.6, 64.7, 61.7, 59.8, 34.7, 31.4 ppm;

IR (KBr)ν_{max}: 409.1, 3087.4, 2930.8, 2876.9, 1924.5, 1820.5, 1616.6, 14935, 1463.2, 1373.5, 1159.4, 1064.6, 7919, 720.4, 698.2, 606.3cm^{-1}.



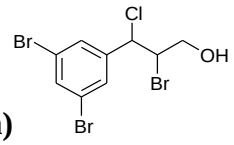
(2m)

yield: 60 % ; White waxy solid , m.p.= 45-46 ℃; cr: 3.2:1; 80% *ee* [HPLC condition: Chiralcel OD-H column, *n*-hexane/i-PrOH = 98:2, flow rate = 1.0 mL/min, t_R = 23.41min, t_R = 32.02 min]; $[\alpha]_D^{20}$ = –8.33 (c = 2.1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (ddd, *J* = 10.0, 5.4, 2.1 Hz, 2H), 7.20 (td, *J* = 8.1, 5.1 Hz, 1H), 6.25 (d, *J* = 11.6 Hz, 1H), 6.17 (d, *J* = 11.3 Hz, 1H), 5.49 (ddd, *J* = 11.6, 3.7, 2.4 Hz, 1H), 5.37 (ddd, *J* = 11.3, 3.8, 2.4 Hz, 1H), 4.27 (dd, *J* = 12.0,4.0 Hz, 1H), 4.18 (dd, *J* = 16.0,4.0 Hz, 1H), 2.19 (s, 1H) ppm ;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 130.6, 130.3, 128.7, 64.3, 55.8, 55.2 ppm;

IR (KBr)ν_{max}: 3412.7, 2926.8, 2874.4, 1617.6, 1580.1, 1562.0, 1437.2, 1347.8, 1210.5, 1186.2, 1149.8, 1092.2, 1071.8, 958.2, 907.4, 845.7, 781.2, 754.3, 713.5, 678.3, 615.5 cm^{-1}.



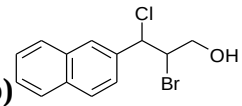
(2n)

yield: 74 % ; White waxy solid , m.p. = 101-102 ℃; cr: 6.3:1; **method A,** 82% *ee*; **method B,** 14% *ee*, [HPLC condition: Chiralcel OD-H column, *n*-hexane/i-PrOH = 98:2, flow rate = 1.0 mL/min, t_R =24.37 min, t_R = 26.89 min]; $[\alpha]_D^{20}$= –7.33 (c = 4.2, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (s, 1H), 7.48 (d, *J* = 1.6 Hz, 2H), 5.08 (d, *J* = 10.1 Hz, 1H), 4.48-4.36 (m, 1H), 4.24 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.08 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.23 (s, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.8, 134.8, 129.9, 123.1, 64.4, 59.6, 58.6 ppm;

IR (KBr)ν_{max}: 3414.2, 2925.4, 2854.2, 1730.1, 1638.0, 1617.7, 1585.3, 1560.7, 1430.8, 1351.0, 1197.6, 1157.4, 1099.2, 1065.7, 972.2, 919.5, 874.9, 855.9, 746.7, 687.1, 605.3 cm^{-1}.

(2o) 

White waxy solid, m.p.= 88-89 ℃ ; **method A** yield: 74%; cr: 11:1; 76% *ee*; **method B,** yield: 76%; cr: 10:1; 78% *ee*;[HPLC condition: Chiralcel AD-H column, *n*-hexane/i-PrOH = 98:2,flow rate = 0.8 mL/min, t_R = 53.8 min, t_R = 61.1 min]; $[\alpha]_D^{20}$= –18.33 (c = 4.2, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94-7.86 (m, 4H), 7.60-7.52 (m, 3H), 5.43 (d, *J* = 10.1 Hz, 1H), 4.69 (ddd, *J* = 10.1, 4.6, 3.0 Hz, 1H), 4.35 (dd, *J* = 12.0,4.0Hz, 1H), 4.25 (dd, *J* = 12.0,4.0Hz, 1H), 2.43 (s, 1H) ppm ;

^{13}C NMR (101 MHz, $CDCl_3$) δ: 136.2, 133.5, 132.9, 128.9, 128.3, 127.8, 126.8, 124.5, 64.7, 62.0, 59.5 ppm ;

IR (KBr)ν_{max}: 3415.6, 2931.1, 2879.1, 1616.2, 1593.1, 1489.8, 1451.4, 1376.9, 1261.7, 1144.4, 1064.0, 973.5, 947.0, 867.8, 786.7, 691.0, 658.5, 620.4 cm^{-1}.

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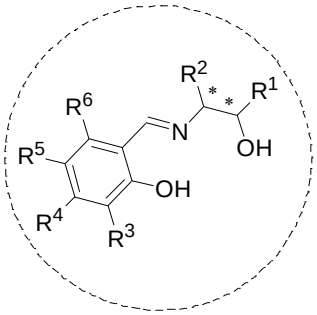
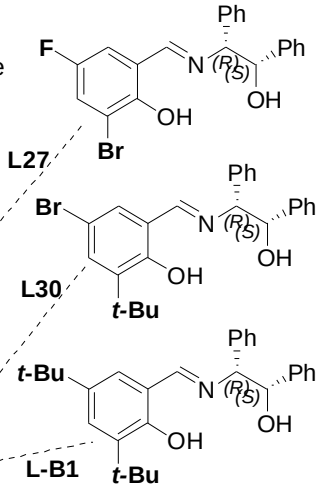
Table S1. Frontier orbital energy (in eV) calculated at B3LYP/6-31G(d,p) level of theory



L20: $R^1 = R^4 = R^6 = H$, $R^2 = Ph$, $R^3 = R^5 = t$-Bu
L21: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^3 = Si(i\text{-}Pr)_3$, $R^5 = Me$
L22: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^3 = TBS$, $R^5 = Me$
L23: $R^1 = R^2 = Ph$, $R^4 = R^6 = R^5 = H$, $R^3 = CH_2TMS$
L24: $R^1 = R^2 = Ph$, $R^3 = R^4 = R^6 = H$, $R^5 = F$
L25: $R^1 = R^2 = Ph$, $R^4 = R^6 = R^5 = H$, $R^3 = Me$
L26: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^5 = F$, $R^3 = Me$
L27: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^5 = F$, $R^3 = Br$
L28: $R^1 = R^2 = Ph$, $R^3 = R^4 = R^5 = R^6 = H$
L29: $R^1 = R^2 = Ph$, $R^3 = R^4 = R^6 = H$, $R^5 = Cl$
L30: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^5 = Br$, $R^3 = t$-Bu
L-B1: $R^1 = R^2 = Ph$, $R^4 = R^6 = H$, $R^5 = R^3 = t$-Bu



Ligand	LUMO	HOMO	Δ	*ee*% of product **2a**	R^1	R^3/R^5
L20	-1.030	-5.807	4.777	ND	H	*t*-Bu/*t*-Bu
L21	-0.939	-5.725	4.786	18	Ph	Si(*i*-Pr)$_3$/Me
L22	-0.947	-5.731	4.784	66	Ph	TBS/Me
L23	-0.903	-5.788	4.885	55	Ph	CH_2TMS/H
L24	-1.215	-5.951	4.736	78	Ph	H/F
L25	-1.220	-6.142	4.922	77	Ph	Me/H
L26	-1.147	-5.877	4.73	77	Ph	Me/F
L27	-1.450	-6.160	4.71	85	Ph	Br/F
L-B1	-0.862	-5.684	4.822	80	Ph	*t*-Bu/*t*-Bu
L28	-1.025	-6.000	4.975	57	Ph	H/H
L29	-1.308	-6.074	4.766	67	Ph	H/Cl

Figure S1. HOMO-LUMO structure of ligands **L20**-**L30**.

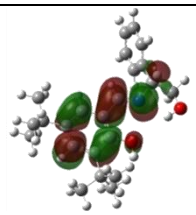
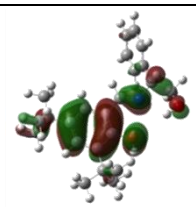
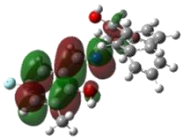
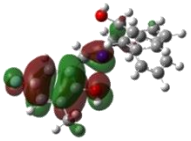
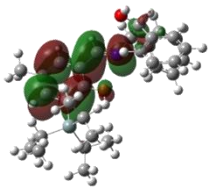
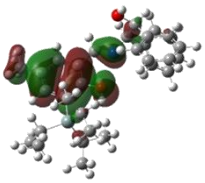
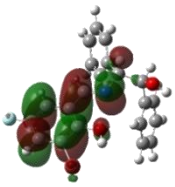
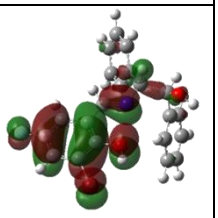
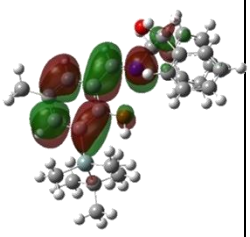
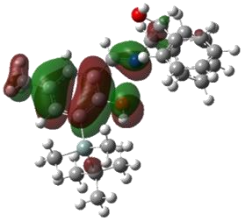
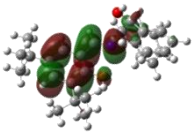
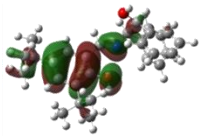
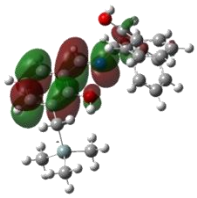
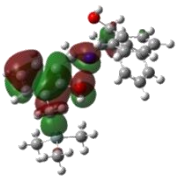
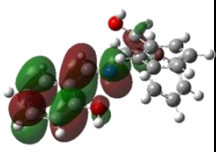
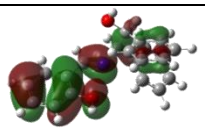
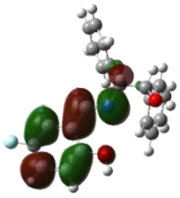
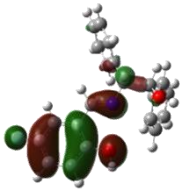
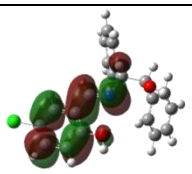
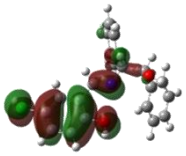
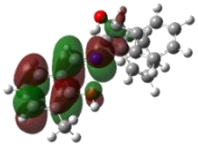
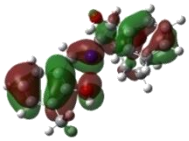
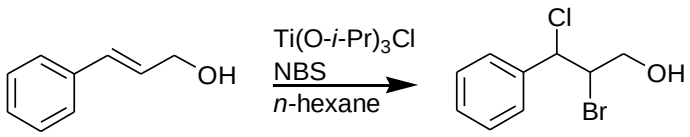
L	LUMO	HOMO	L	LUMO	HOMO
20	 -1.030	 -5.807	**26**	 -1.147	 -5.877
21	 -0.939	 -5.725	**27**	 -1.450	 -6.160
22	 -0.947	 -5.731	**B1**	 -0.862	 -5.684
23	 -0.903	 -5.788	**28**	 -1.025	 -6.000
24	 -1.215	 -5.951	**29**	 -1.308	 -6.074
25	 -1.220	 -6.142			

Figure S2. Nonlinear effects in Schiff base L-B1 -promoted bromochlorination of allylic alcohol 1a.



Entry	1	2	3	4	5
L(R.S)：L（S.R)	5 % : 5 %	4 % : 6 %	3 % 7 %	2 % : 8 %	0 : 10 %
Ee of L/%	0	20	40	60	100
Ee/%	0	35	55	70	86

Reaction conditions: 0.5 mmol ;*n*-hexane 5.0 mL ;Ti:0.55mmol ;L: 0.1 eq(0.05mmol) ;NBS:0.55 mmol; at -20°C.

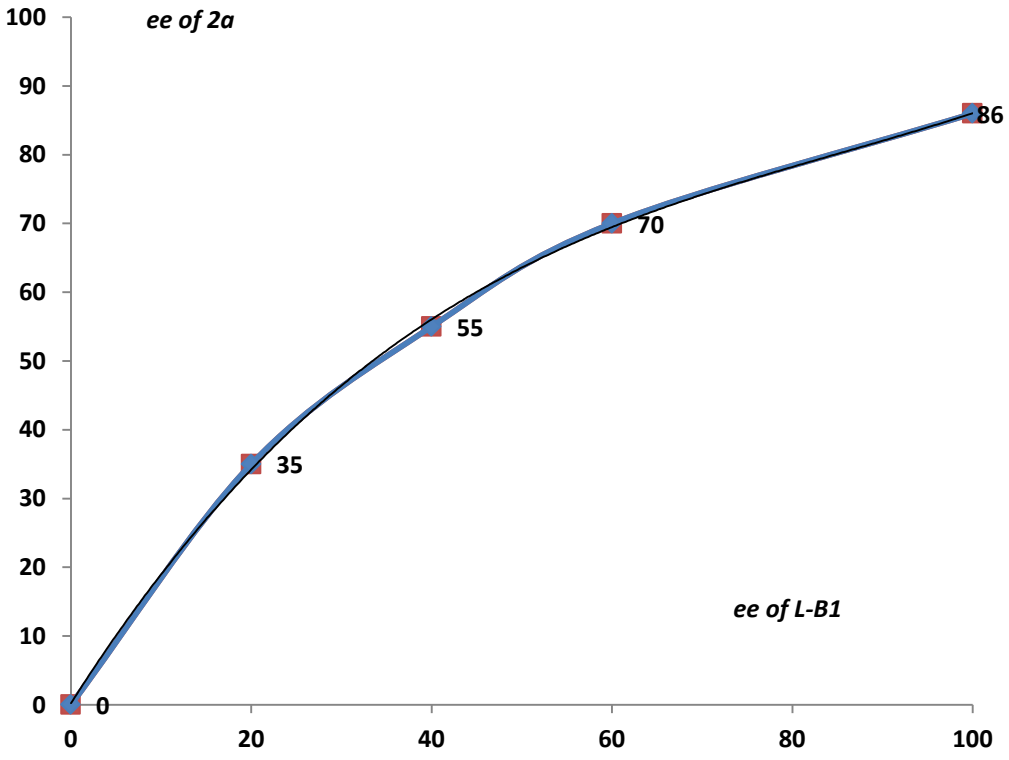
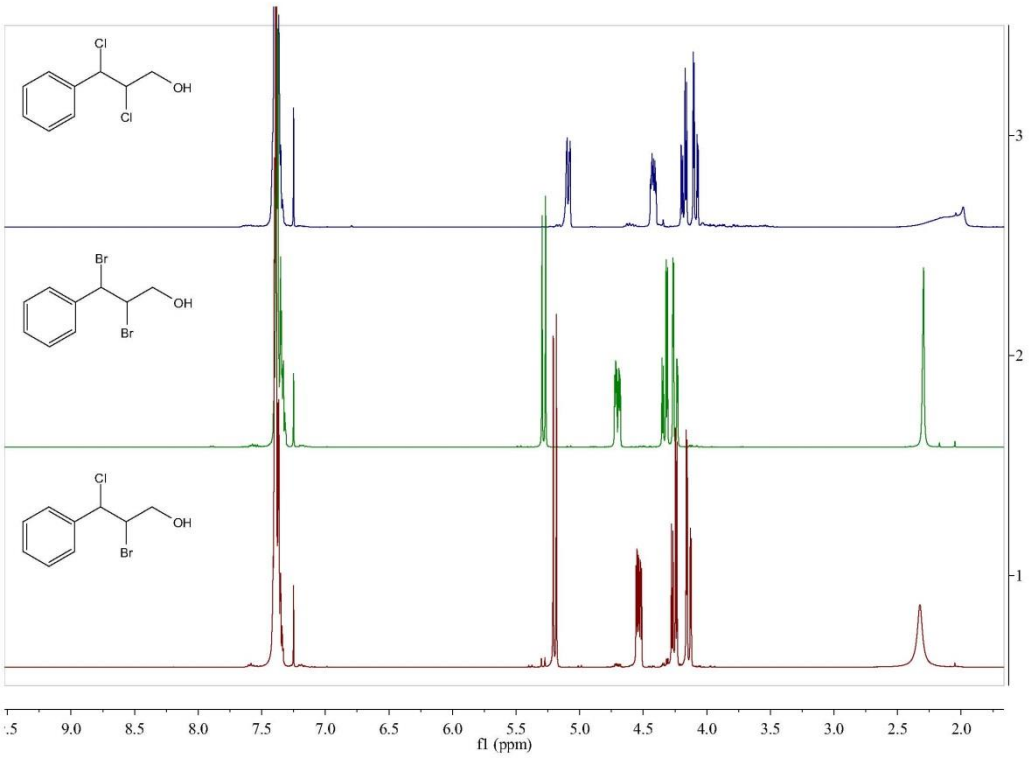
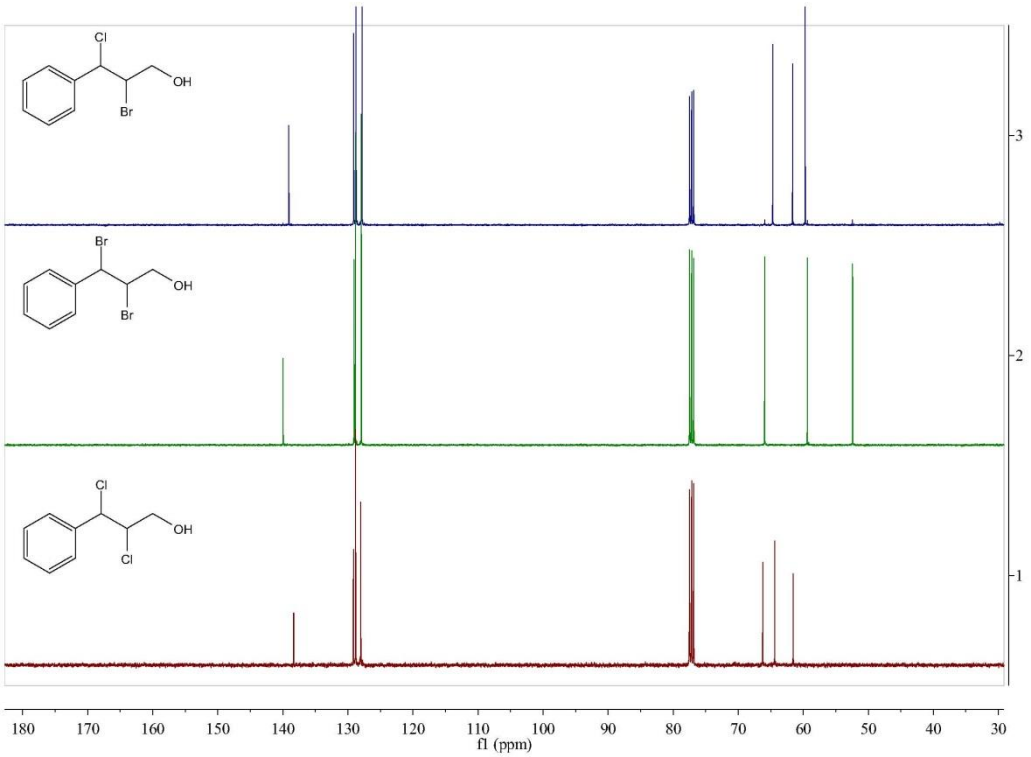


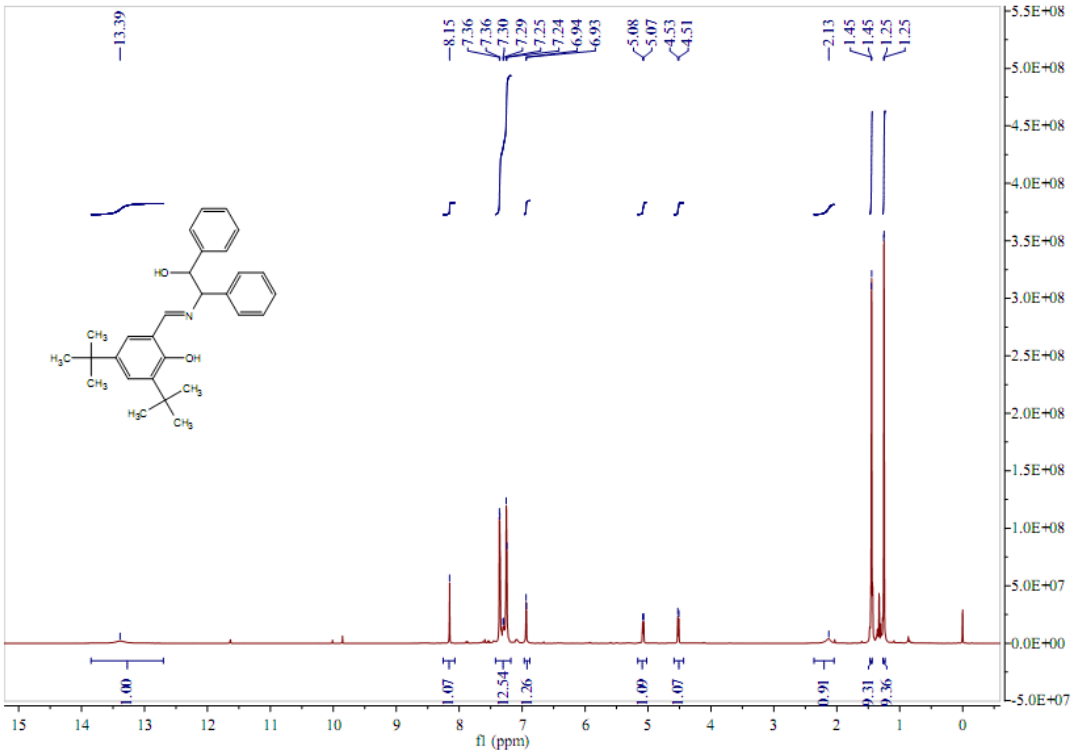
Figure S3. ^{1}H NMR and ^{13}C NMR spectrum for the comparison of dibromide, dichloride, and bromochloride.

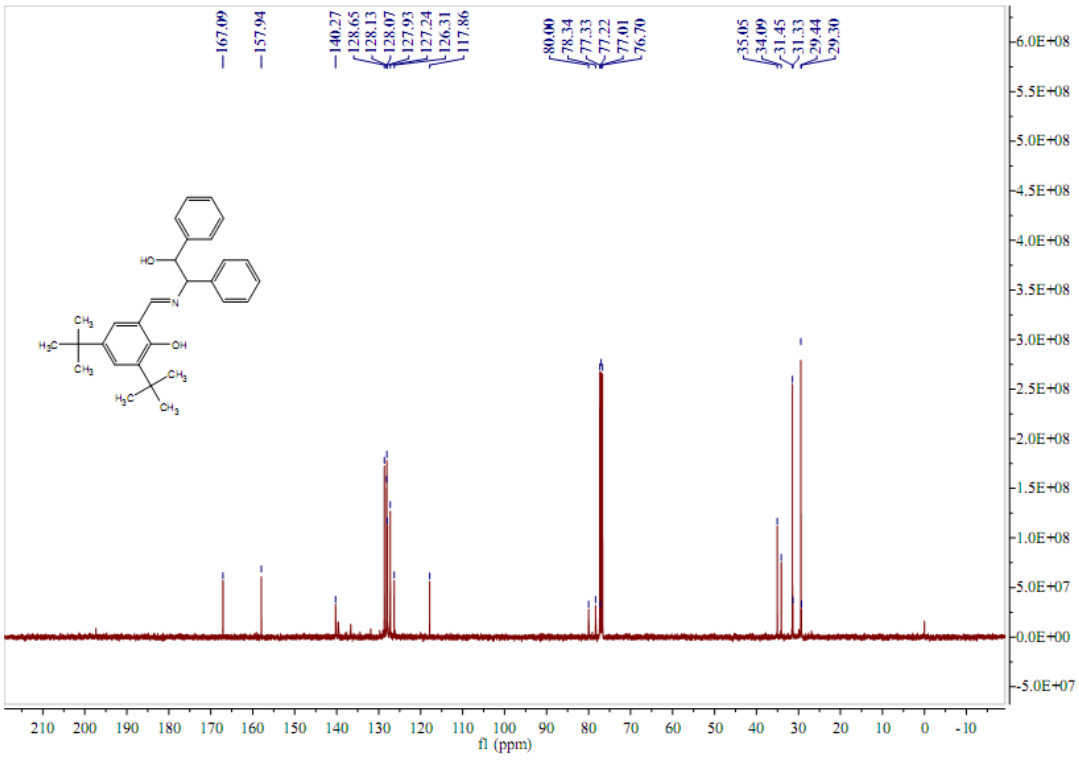




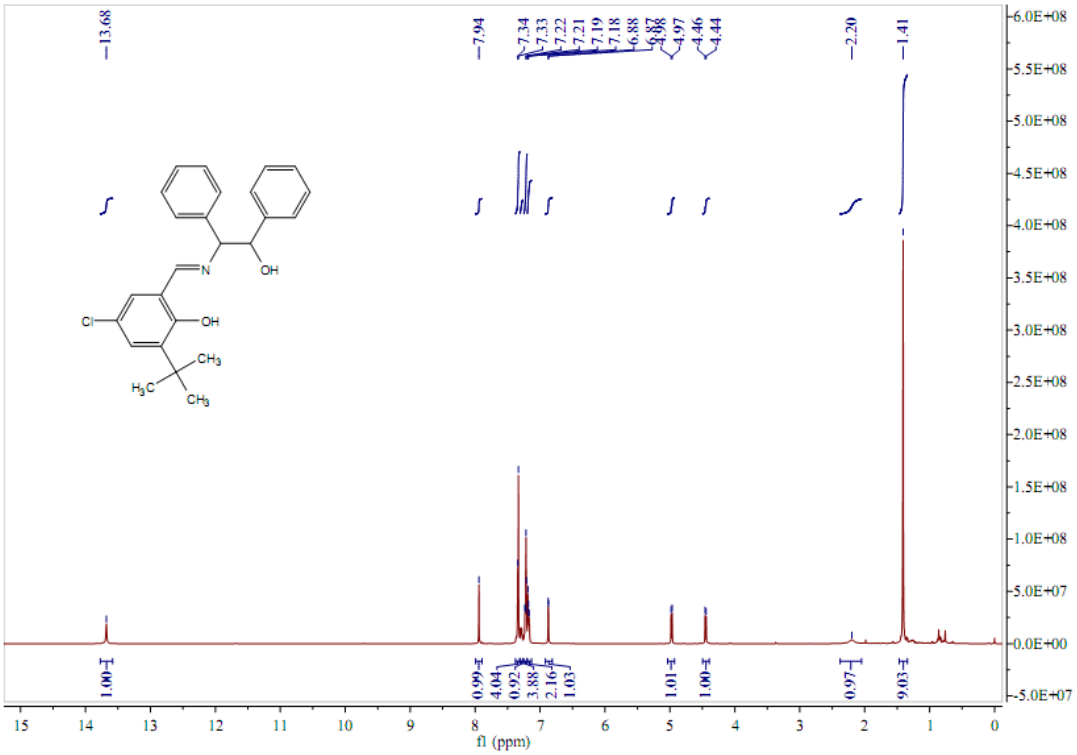
NMR spectra for Ligand

L-B1





L7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7.21
7.19
7.18
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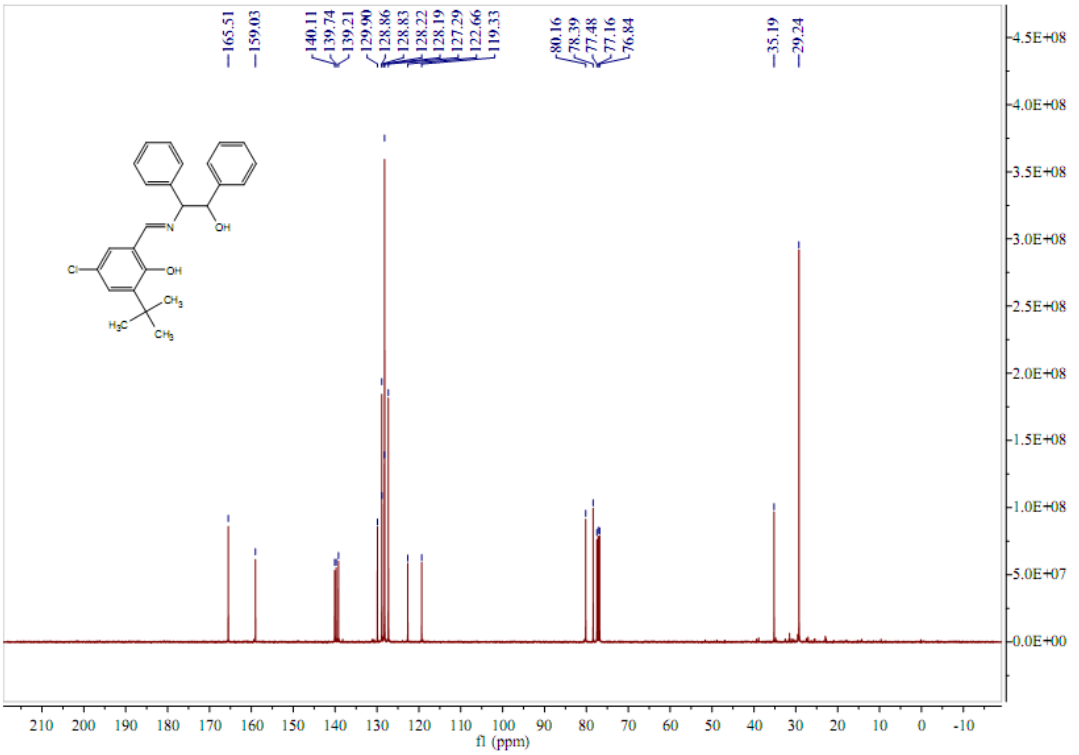
4.46
4.44
2.20
1.41
1.00
0.99
4.04
0.92
3.88
2.16
1.03
1.01
1.00
0.97
9.03
f1 (ppm)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128.86
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128.22
128.19
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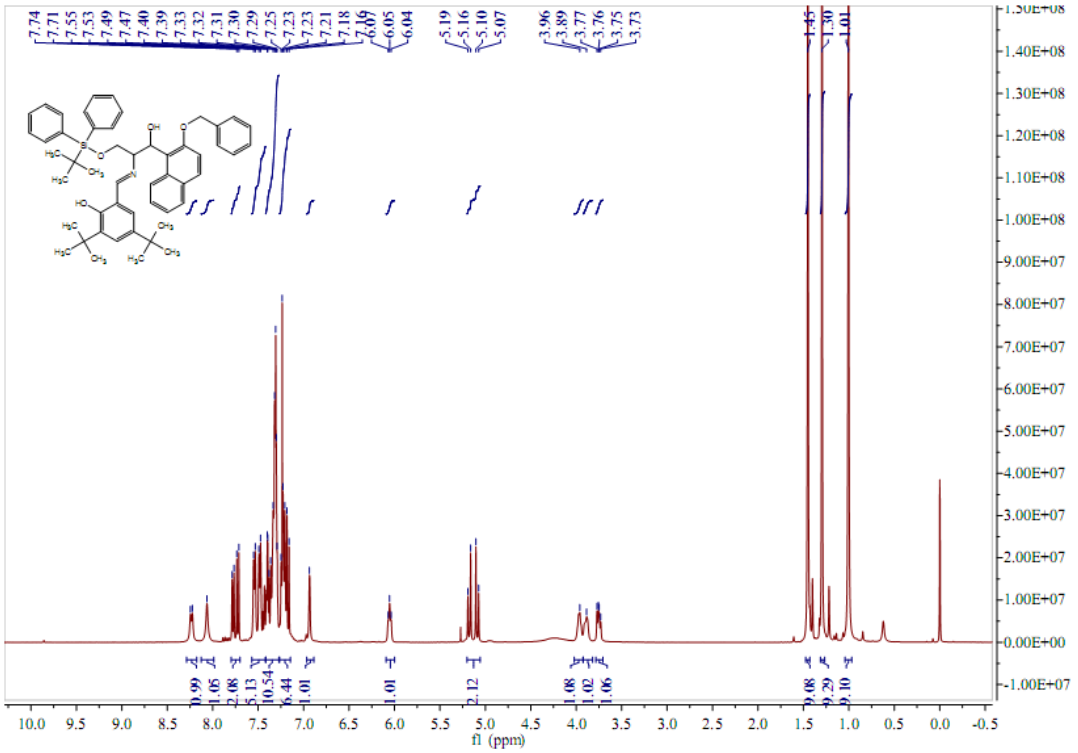
80.16
78.39
77.48
77.16
76.84
35.19
29.24
f1 (ppm)

L13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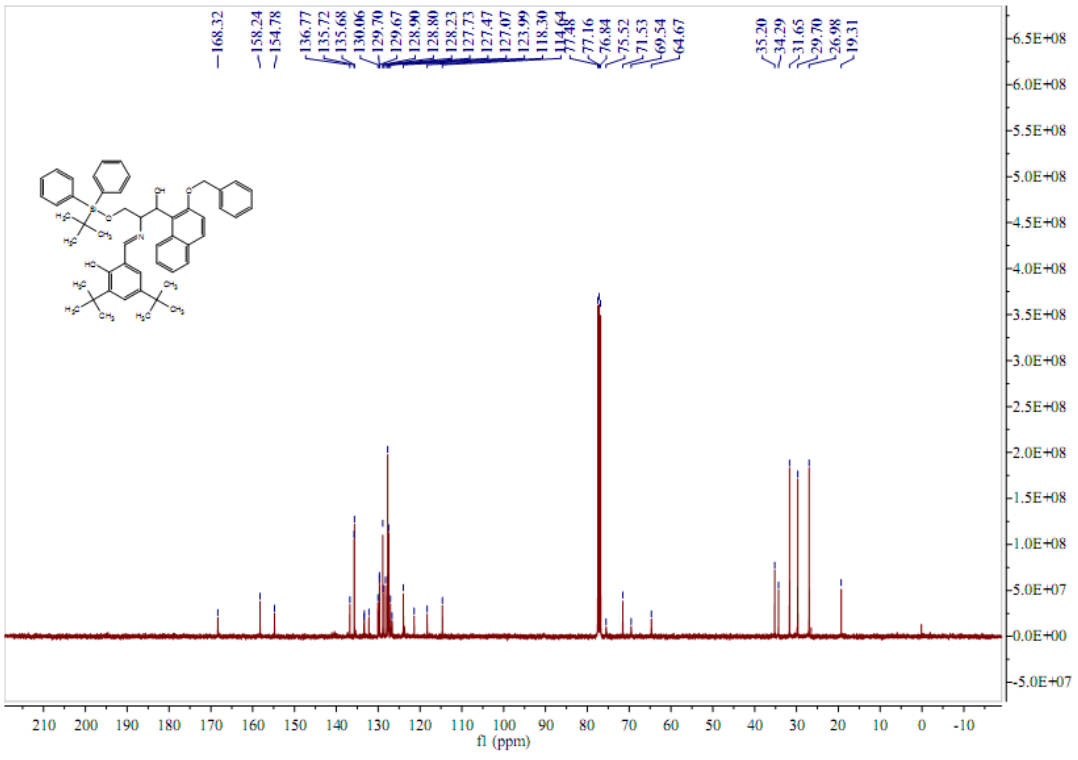
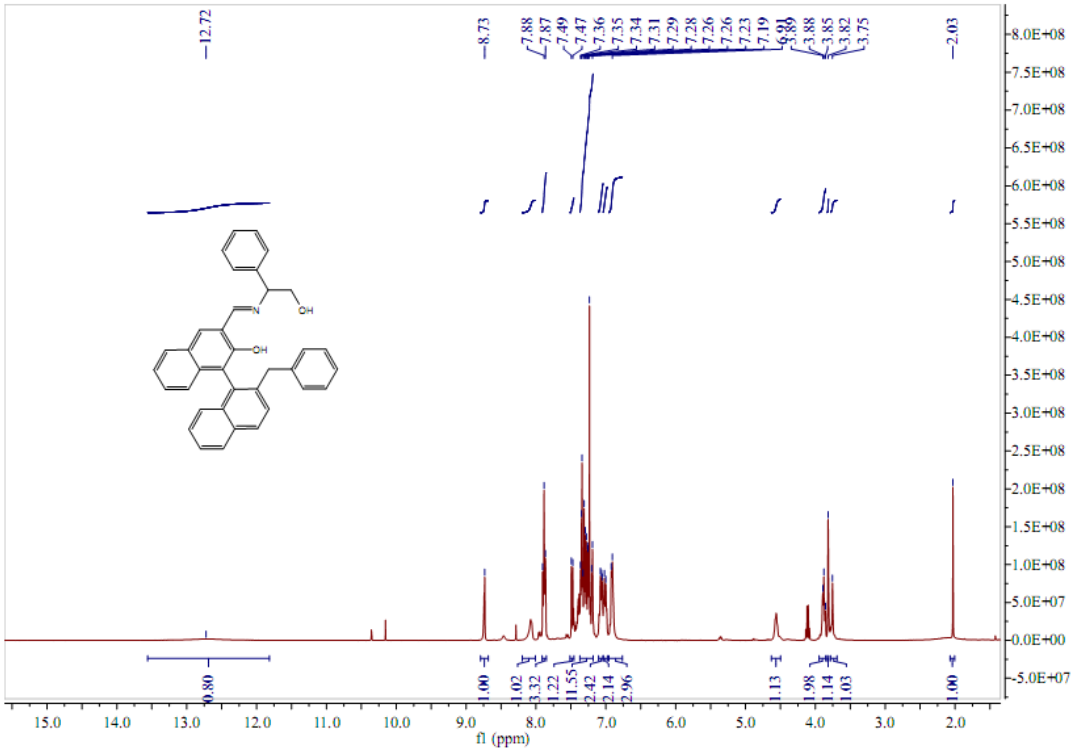
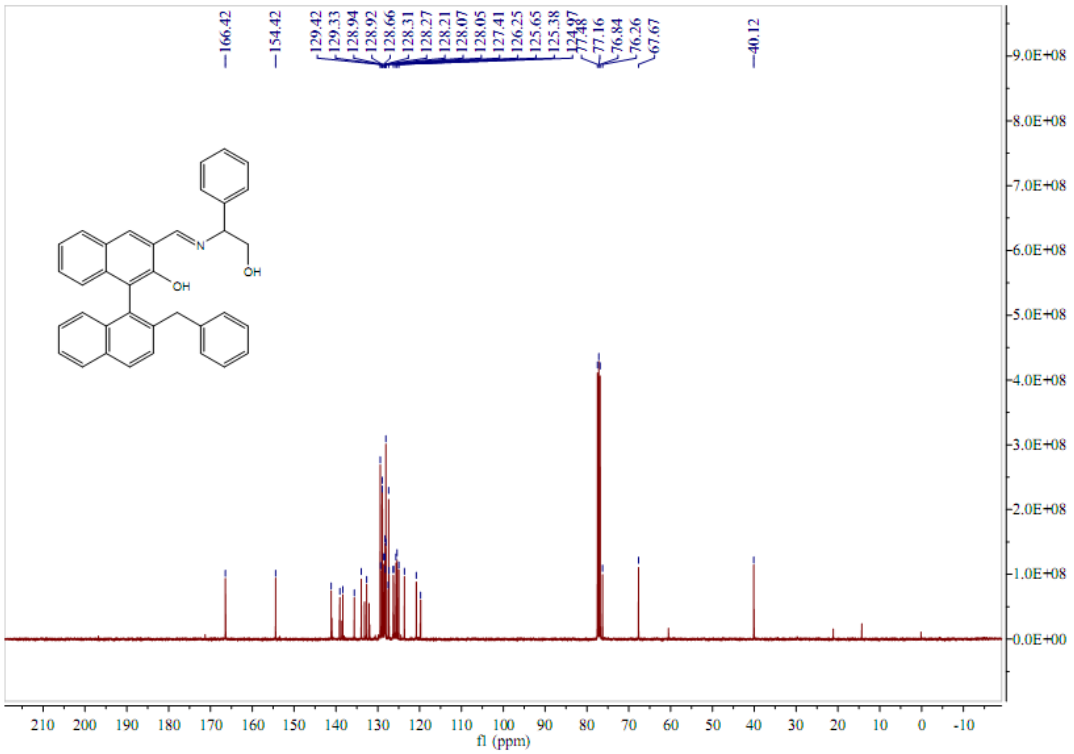
7.23
7.21
7.18
6.05
6.04
5.19
5.16
5.10
5.07
3.96
3.89
3.77
3.76
3.75
3.73
1.45
1.30
1.01
0.99
1.05
2.08
5.13
10.54
6.44
1.01
1.01
2.12
1.08
1.02
1.06
9.08
9.29
2.10
f1 (ppm)

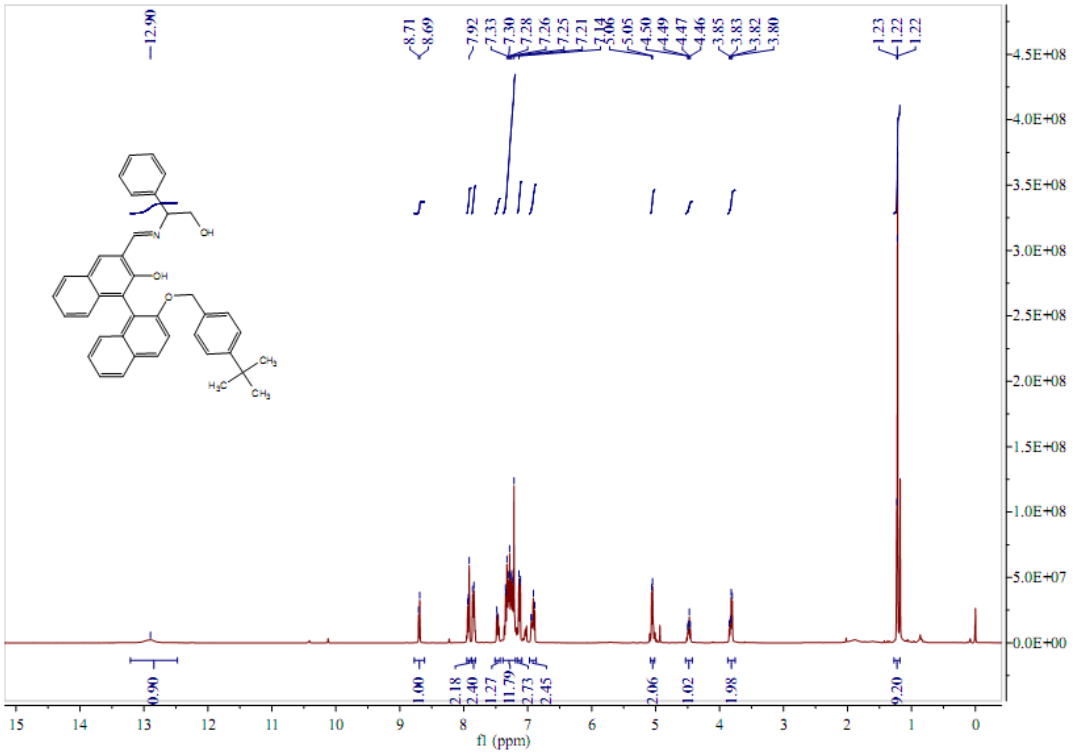

168.32
158.24
154.78
136.77
135.72
135.68
130.06
129.70
129.67
128.90
128.80
128.23
127.73
127.47
127.07
123.99
118.30
114.64
77.48
77.16
76.84
75.52
71.53
69.54
64.67
35.20
34.29
31.65
29.70
26.98
19.31
f1 (ppm)

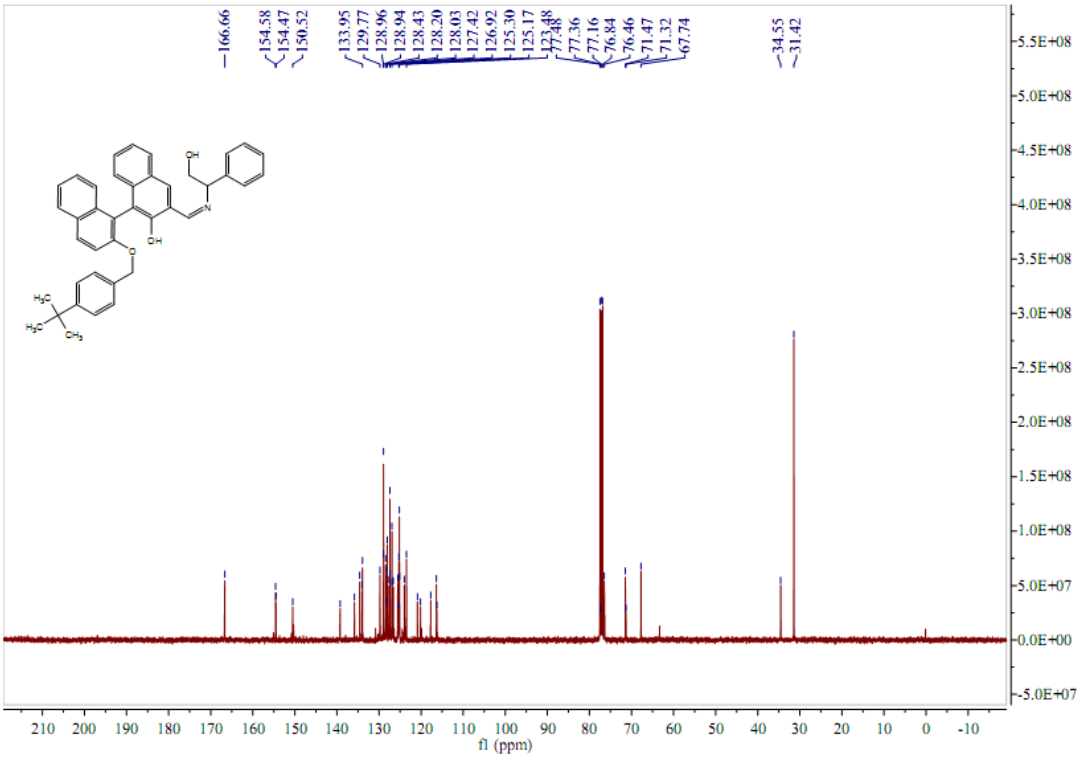
L14


12.72
8.73
7.88
7.87
7.49
7.47
7.36
7.35
7.34
7.31
7.29
7.28
7.26
7.26
7.23
7.19
6.91
6.89
3.88
3.85
3.82
3.75
2.03
OH
OH
0.80
1.00
1.02
3.32
1.22
11.55
2.42
2.14
2.96
1.13
1.98
1.14
1.03
1.00
f1 (ppm)

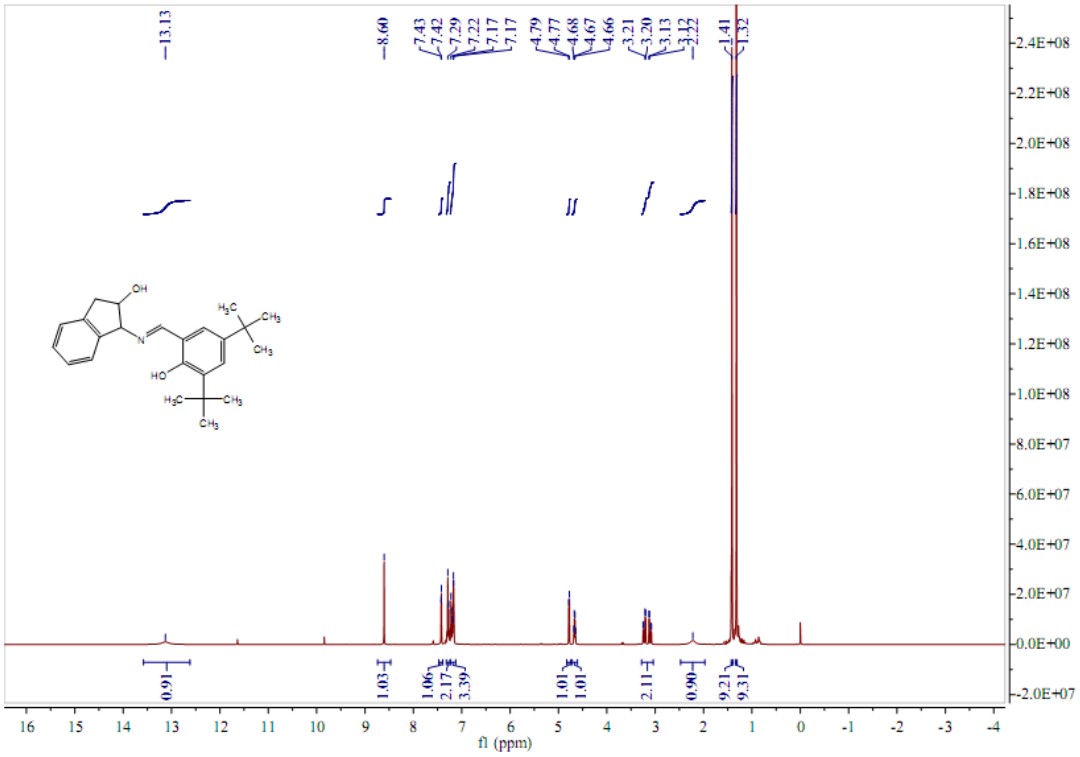

166.42
154.42
129.42
129.33
128.94
128.92
128.66
128.31
128.27
128.21
128.07
128.05
127.41
126.25
125.65
125.38
77.48
77.16
76.84
76.26
67.67
40.12
N
OH
OH
f1 (ppm)

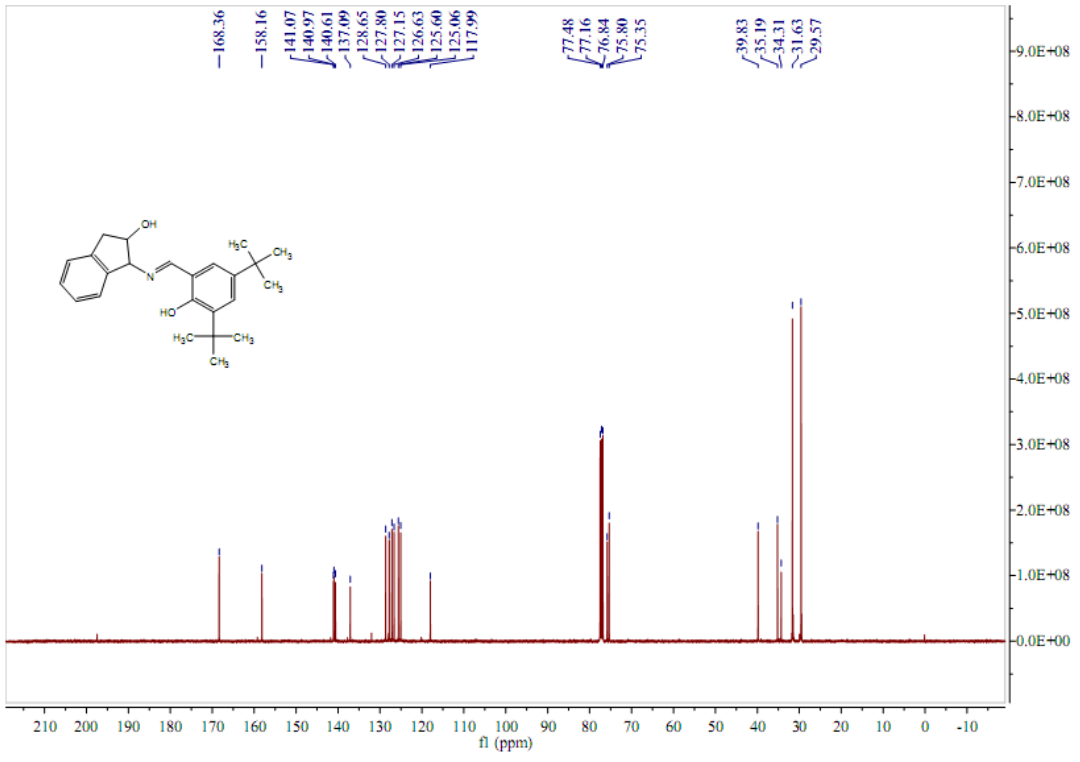
L15


12.90
8.71
8.69
7.92
7.33
7.30
7.28
7.26
7.25
7.21
5.05
4.50
4.49
4.47
4.46
3.85
3.83
3.82
3.80
1.23
1.22
1.22
0.90
1.00
2.18
2.40
1.27
11.79
2.73
2.45
2.06
1.02
1.98
9.20
f1 (ppm)

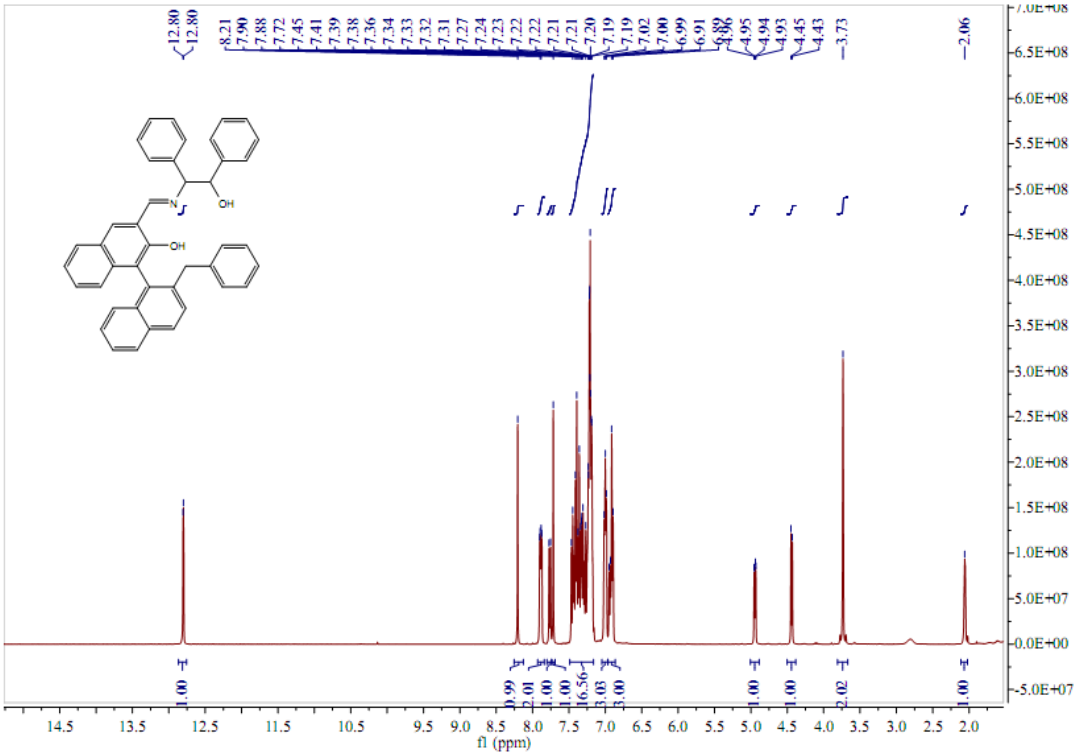

166.66
154.58
154.47
150.52
133.95
129.77
128.96
128.94
128.43
128.20
128.03
127.42
126.92
125.30
125.17
123.48
77.48
77.36
77.16
76.84
76.46
71.47
71.32
67.74
34.55
31.42
f1 (ppm)

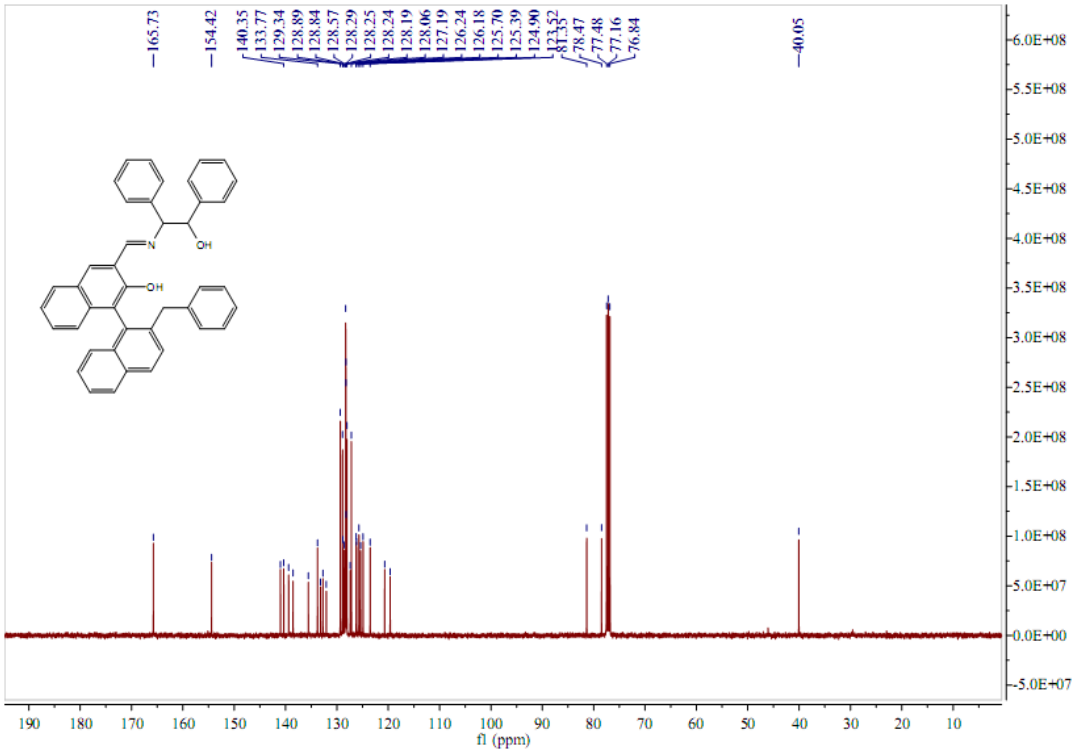
L16


13.13
8.60
7.43
7.42
7.29
7.22
7.17
7.17
4.79
4.77
4.68
4.67
4.66
3.21
3.20
3.13
3.12
2.22
1.41
1.32
0.91
1.03
1.06
2.17
3.39
1.01
1.01
2.11
0.90
9.21
9.31
f1 (ppm)

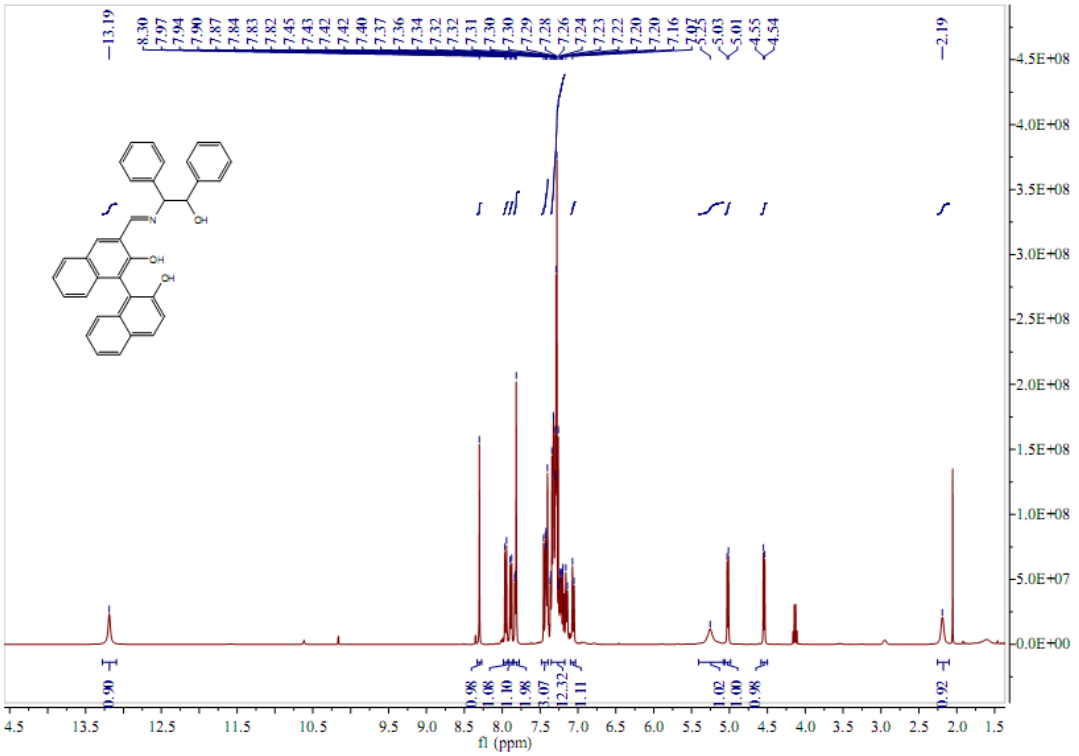

168.36
158.16
141.07
140.97
140.61
137.09
128.65
127.80
127.15
126.63
125.60
125.06
117.99
77.48
77.16
76.84
75.80
75.35
39.83
35.19
34.31
31.63
29.57
f1 (ppm)

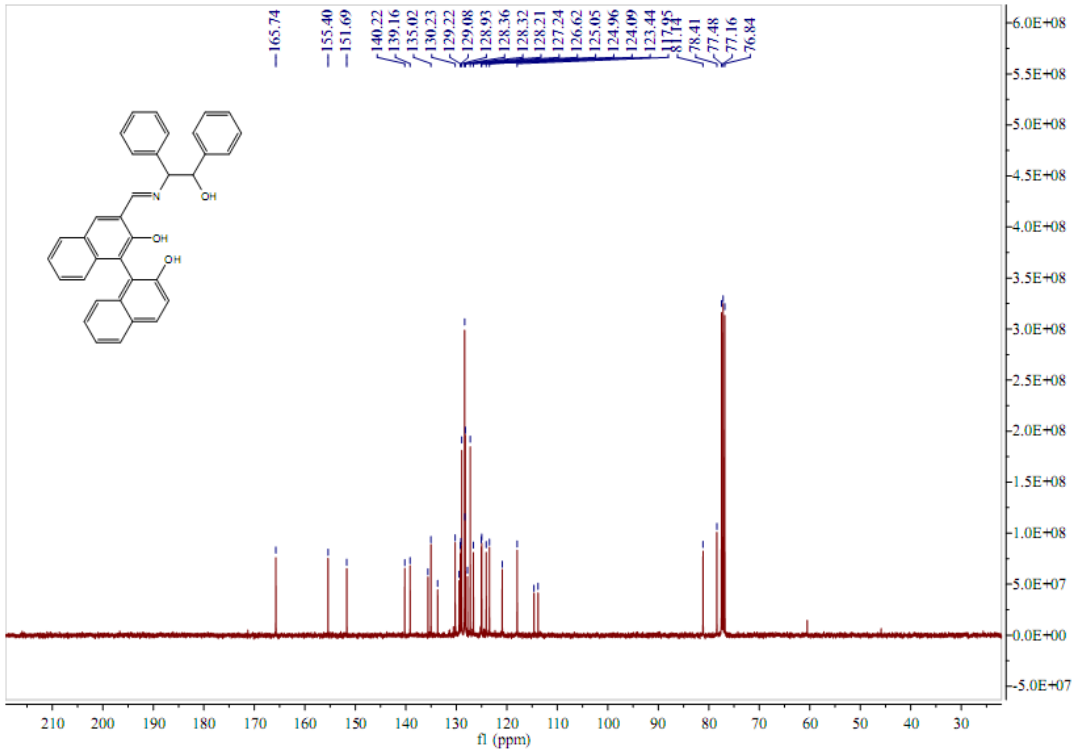
L17


12.80
12.80
8.21
7.90
7.88
7.72
7.45
7.41
7.39
7.38
7.36
7.34
7.33
7.32
7.31
7.27
7.24
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.02
7.00
6.99
6.91
6.89
6.86
4.95
4.94
4.93
4.45
4.43
3.73
2.06
OH
N
OH
1.00
0.99
2.01
1.00
1.00
16.56
3.03
3.00
1.00
1.00
2.02
1.00
f1 (ppm)

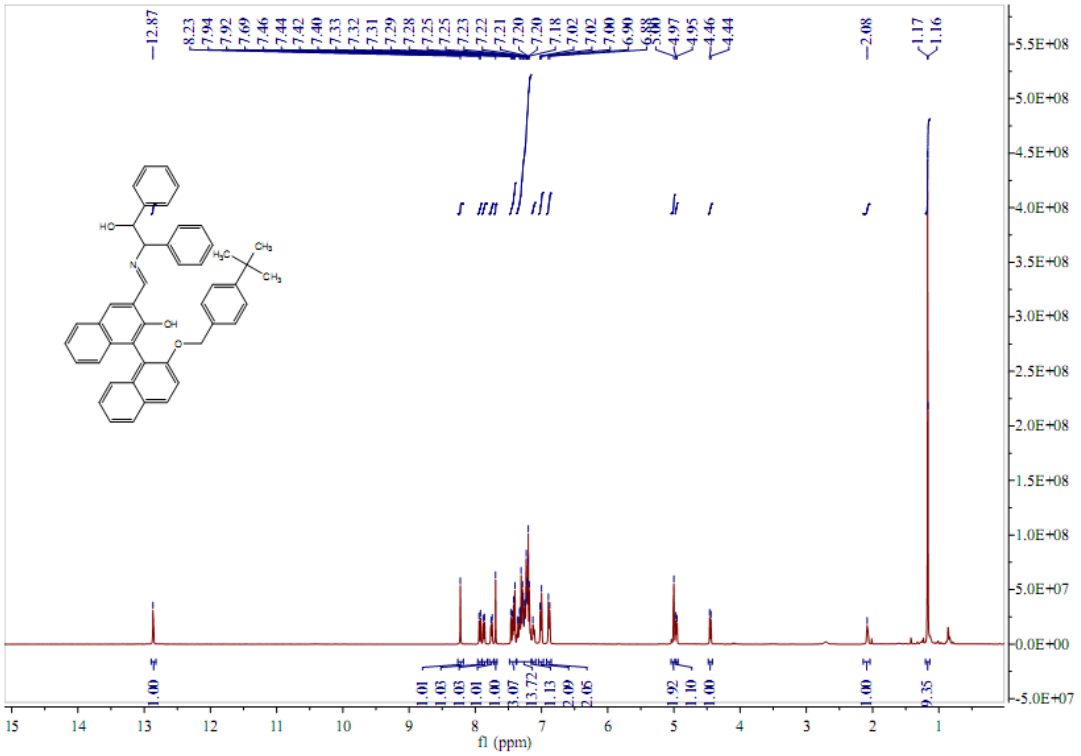

165.73
154.42
140.35
133.77
129.34
128.89
128.84
128.57
128.29
128.25
128.24
128.19
128.06
127.19
126.24
126.18
125.70
125.39
124.90
123.52
81.35
78.47
77.48
77.16
76.84
40.05
OH
N
OH
f1 (ppm)

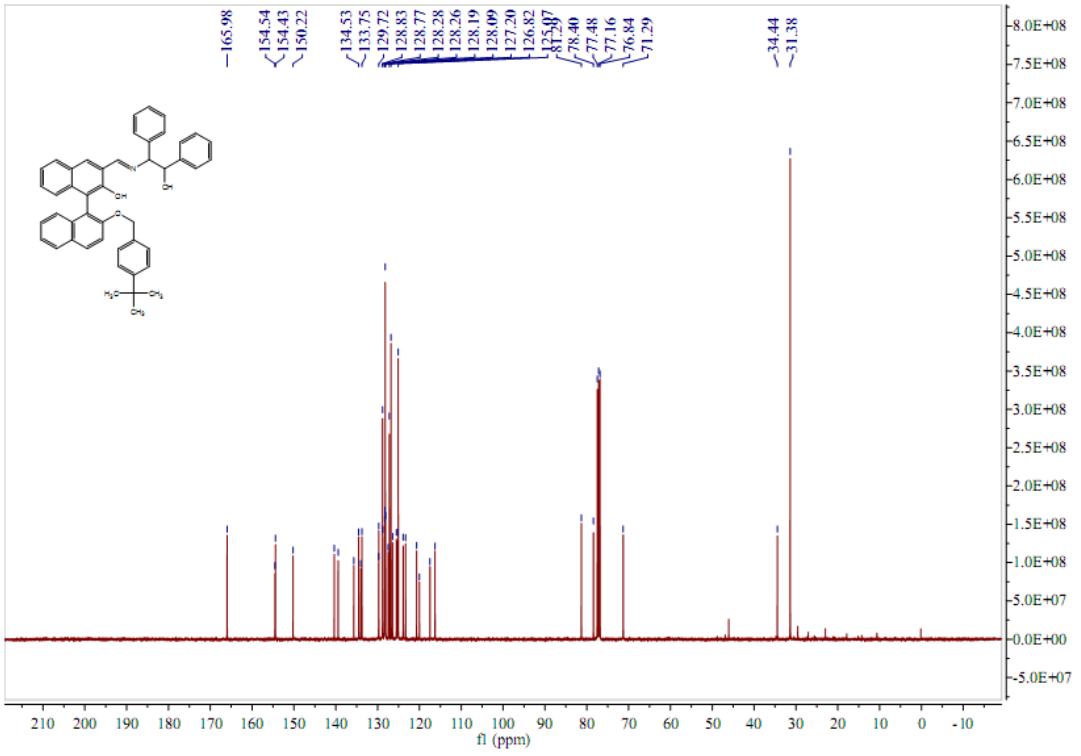
L18


13.19
8.30
7.97
7.94
7.90
7.87
7.84
7.83
7.82
7.45
7.43
7.42
7.42
7.40
7.37
7.36
7.34
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.26
7.24
7.23
7.22
7.20
7.20
7.16
5.03
5.01
4.55
4.54
2.19
OH
OH
OH
0.90
0.98
1.08
1.10
1.98
3.07
12.32
1.11
1.02
1.00
0.98
0.92
f1 (ppm)

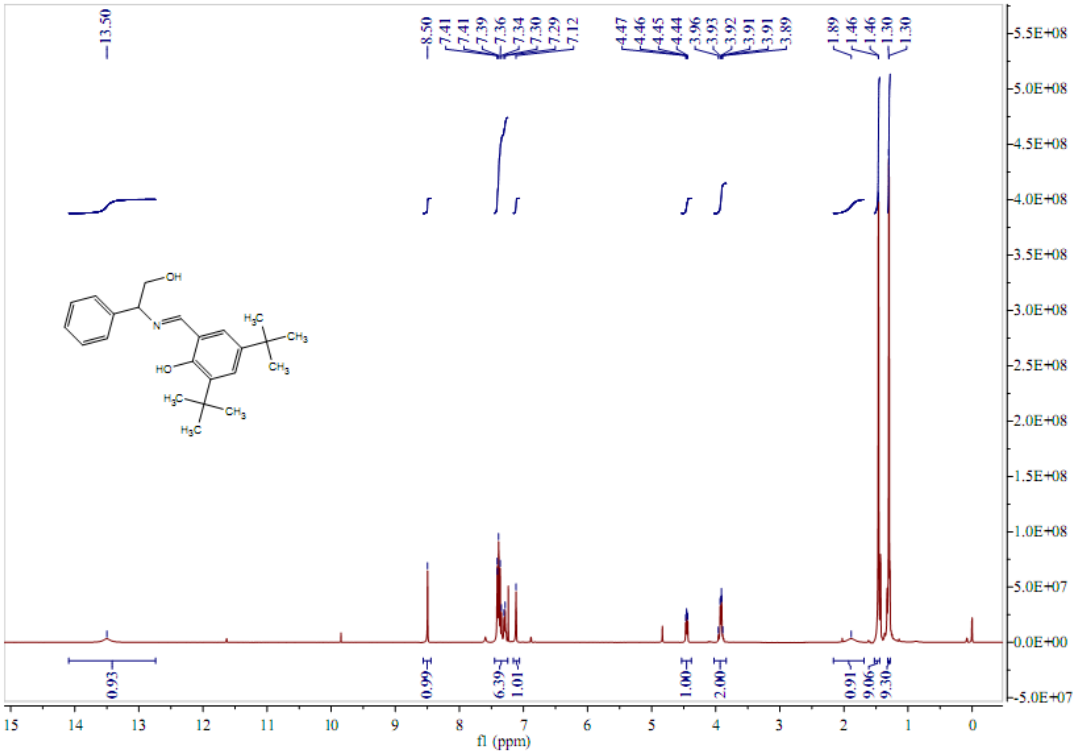

165.74
155.40
151.69
140.22
139.16
135.02
130.23
129.22
129.08
128.93
128.36
128.32
128.21
127.24
126.62
125.05
124.96
124.09
123.44
117.95
81.14
78.41
77.48
77.16
76.84
OH
OH
OH
f1 (ppm)

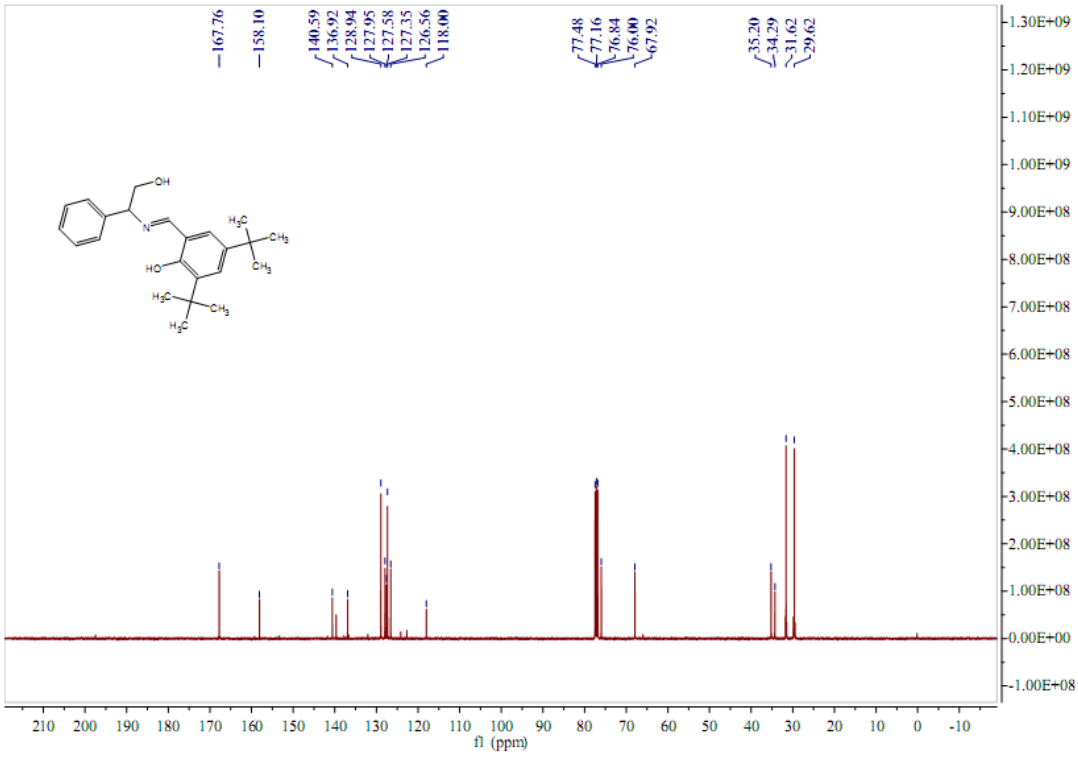
L19


12.87
8.23
7.94
7.92
7.69
7.46
7.44
7.42
7.40
7.33
7.32
7.31
7.29
7.28
7.25
7.25
7.23
7.22
7.21
7.20
7.20
7.18
7.02
7.02
7.00
6.90
4.97
4.95
4.46
4.44
2.08
1.17
1.16
f1 (ppm)

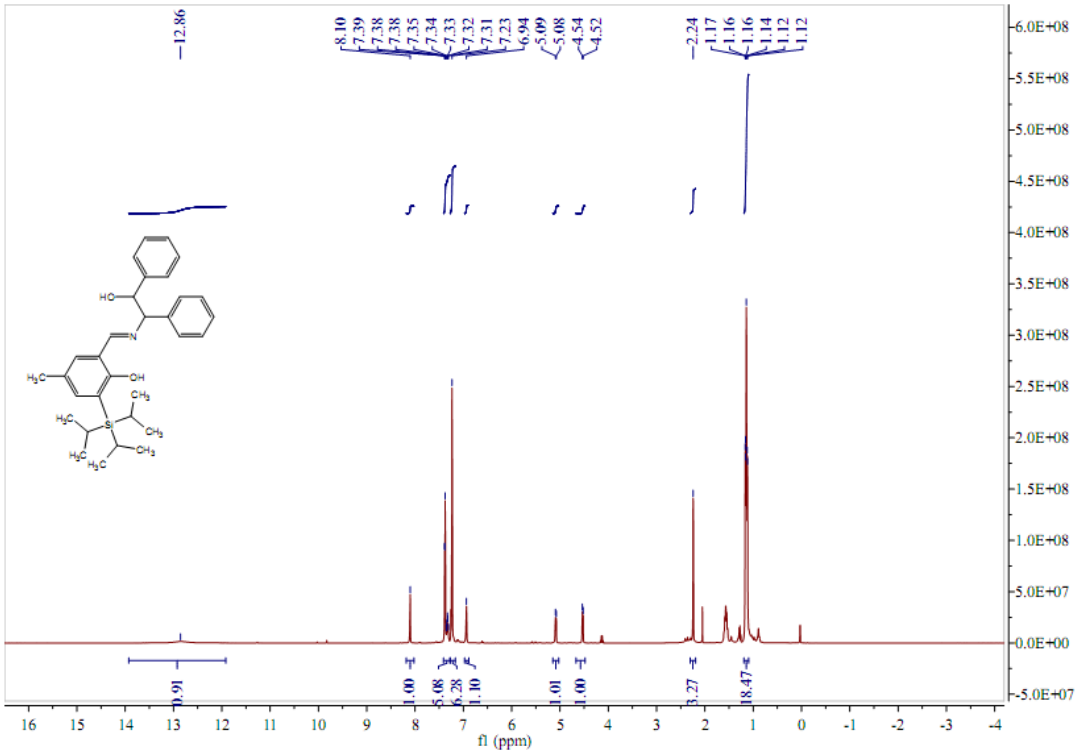

165.98
154.54
154.43
150.22
134.53
133.75
129.72
128.83
128.77
128.28
128.26
128.19
128.09
127.20
126.82
78.40
77.48
77.16
76.84
71.29
34.44
31.38
f1 (ppm)

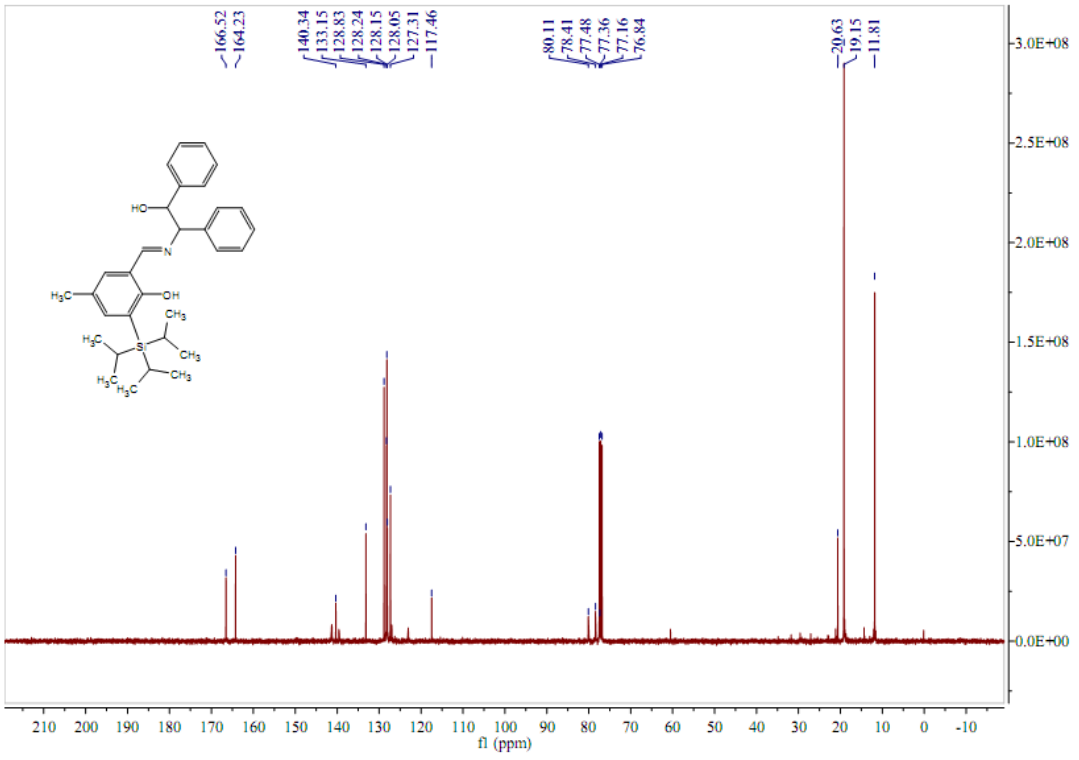
L20


13.50
8.50
7.41
7.41
7.39
7.36
7.34
7.30
7.29
7.12
4.47
4.46
4.45
4.44
3.96
3.93
3.92
3.91
3.91
3.89
1.89
1.46
1.46
1.30
1.30
0.93
0.99
6.39
1.01
1.00
2.00
0.91
9.06
9.30
f1 (ppm)

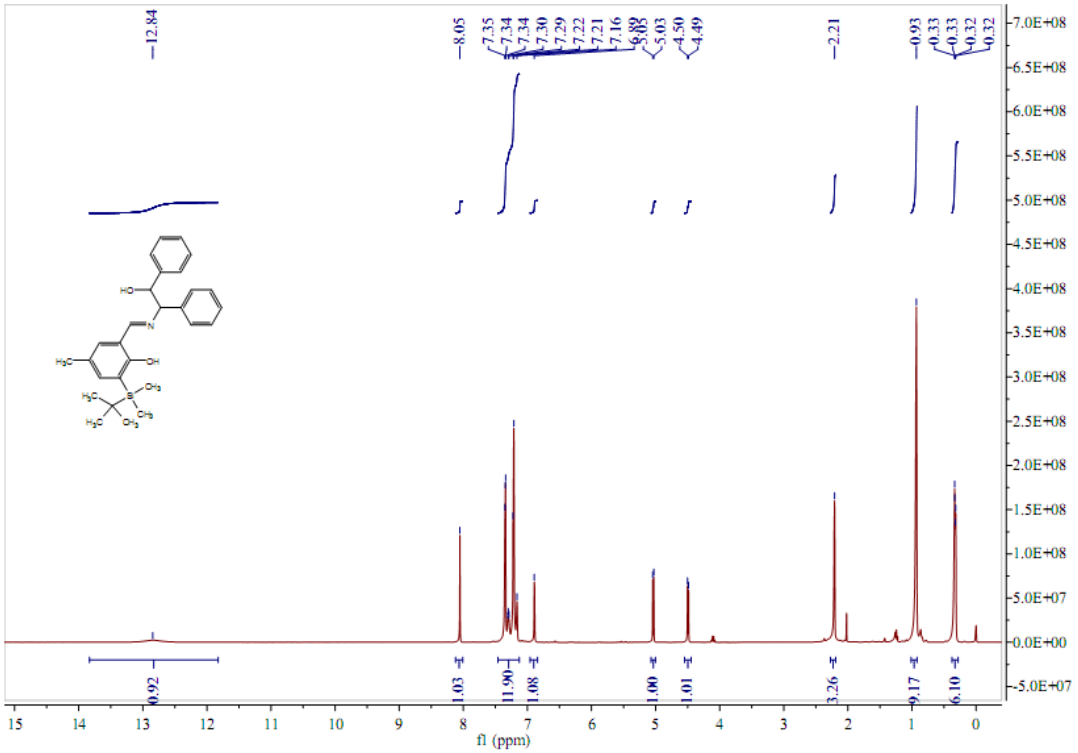

167.76
158.10
140.59
136.92
128.94
127.95
127.58
127.35
126.56
118.00
77.48
77.16
76.84
76.00
67.92
35.20
34.29
31.62
29.62
f1 (ppm)

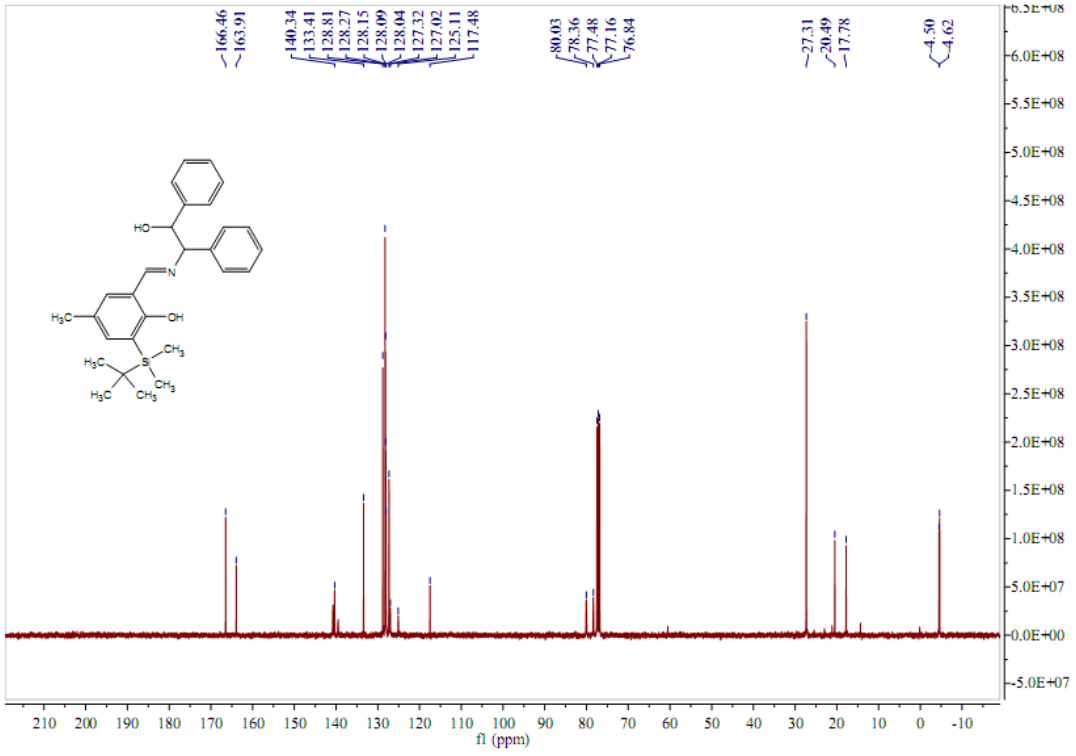
L21


12.86
8.10
7.39
7.38
7.38
7.35
7.34
7.33
7.32
7.31
7.23
6.94
5.09
5.08
4.54
4.52
2.24
1.17
1.16
1.16
1.14
1.12
1.12
HO
N
OH
H3C
CH3
Si
H3C
CH3
H3C
H3C
CH3
0.91
1.00
5.08
6.28
1.10
1.01
1.00
3.27
18.47
f1 (ppm)

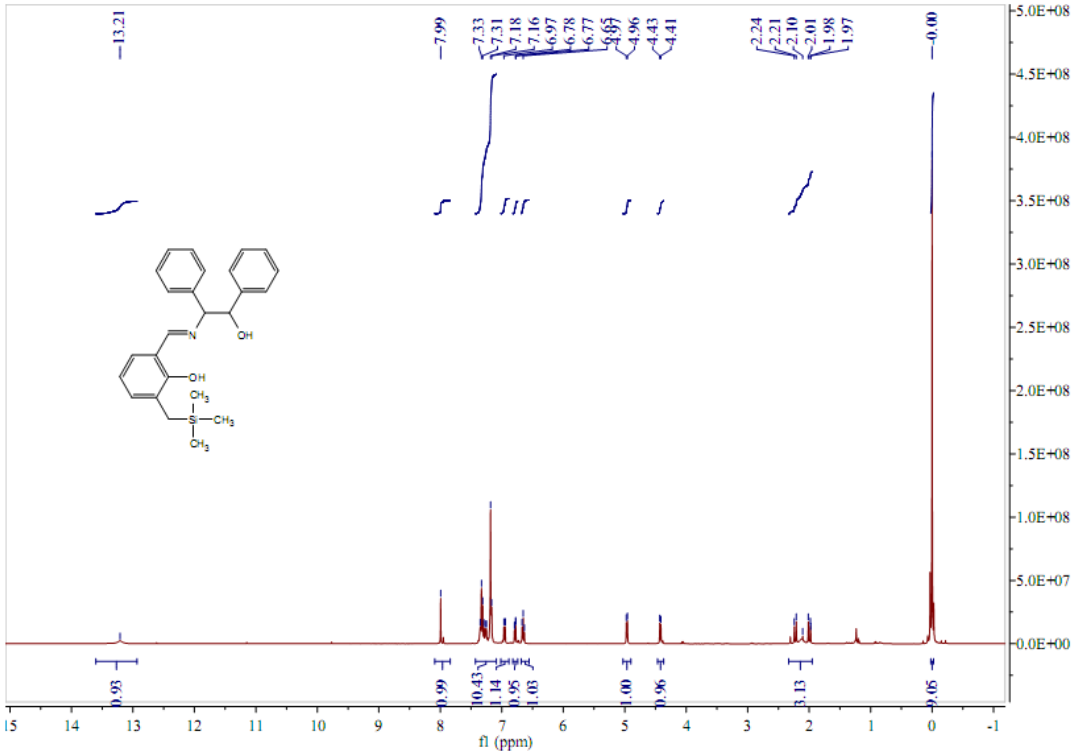

166.52
164.23
140.34
133.15
128.83
128.24
128.15
128.05
127.31
117.46
80.11
78.41
77.48
77.36
77.16
76.84
20.63
19.15
11.81
HO
N
OH
H3C
CH3
Si
H3C
CH3
H3C
H3C
CH3
f1 (ppm)

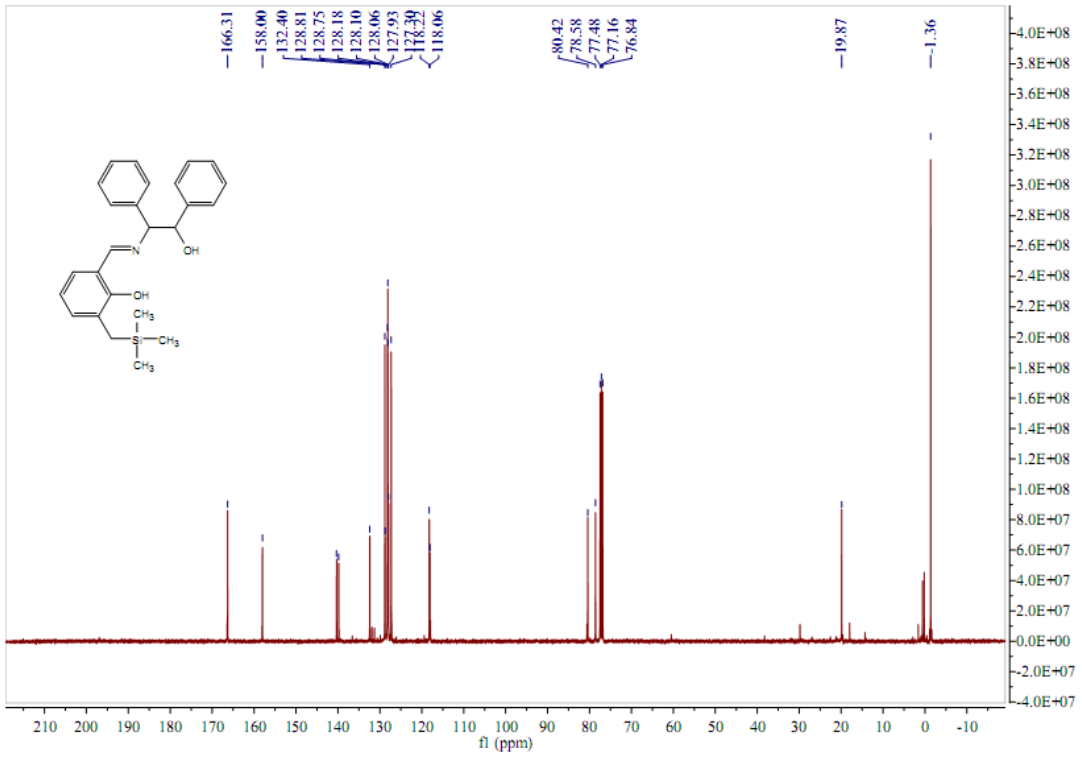
L22


12.84
8.05
7.35
7.34
7.34
7.30
7.29
7.22
7.21
7.16
6.89
6.85
5.03
4.50
4.49
2.21
0.93
0.33
0.33
0.32
0.32
0.92
1.03
11.90
1.08
1.00
1.01
3.26
9.17
6.10
f1 (ppm)

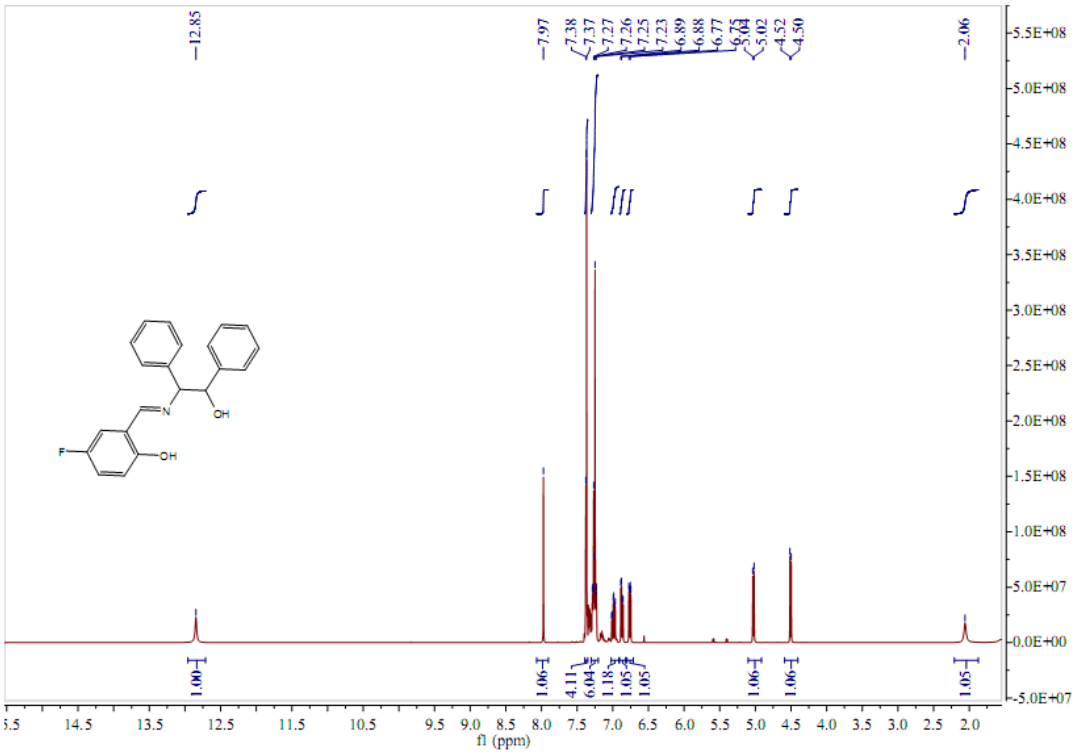

166.46
163.91
140.34
133.41
128.81
128.27
128.15
128.09
128.04
127.32
127.02
125.11
117.48
80.03
78.36
77.48
77.16
76.84
27.31
20.49
17.78
4.50
4.62
f1 (ppm)

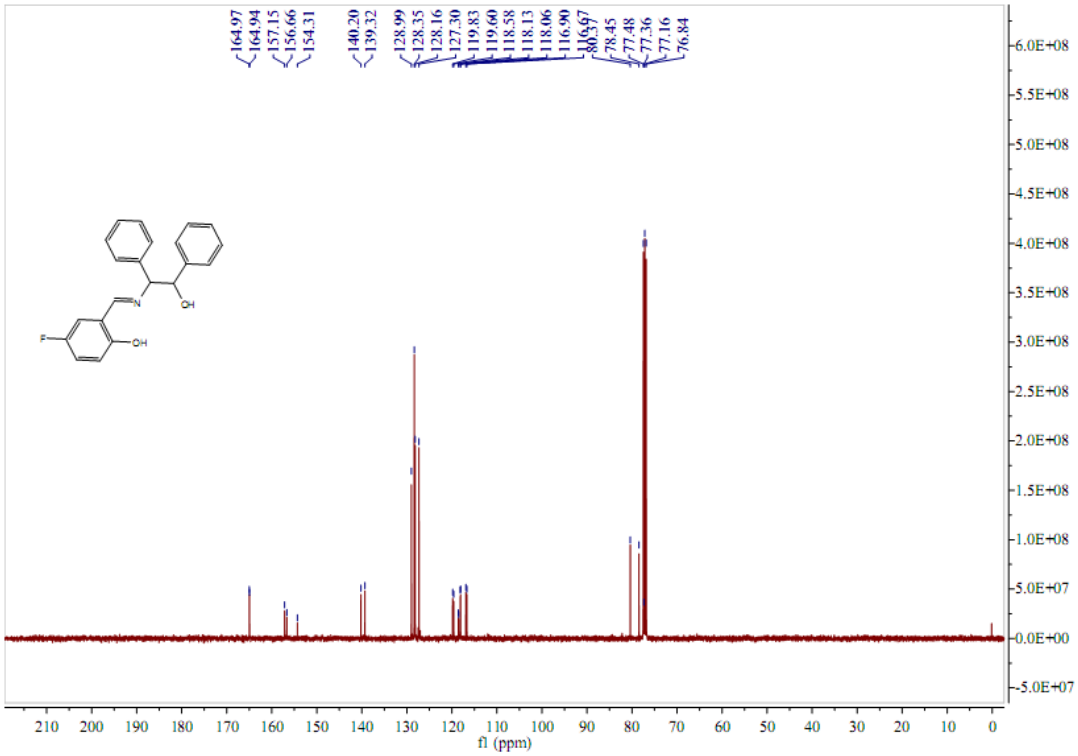
L23


13.21
7.99
7.33
7.31
7.18
7.16
6.97
6.78
6.77
4.96
4.43
4.41
2.24
2.21
2.10
2.01
1.98
1.97
0.00
0.93
0.99
10.43
1.14
0.95
1.03
1.00
0.96
3.13
9.05
f1 (ppm)

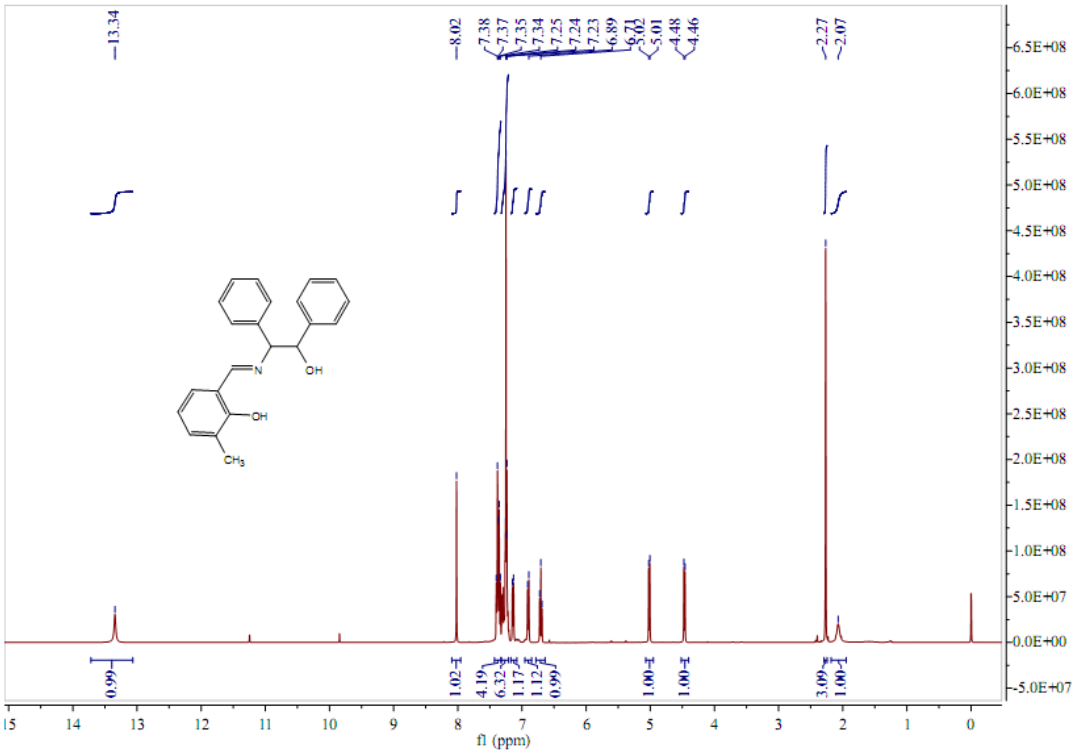

166.31
158.00
132.40
128.81
128.75
128.18
128.10
128.06
127.93
127.30
118.22
118.06
80.42
78.58
77.48
77.16
76.84
19.87
1.36
f1 (ppm)

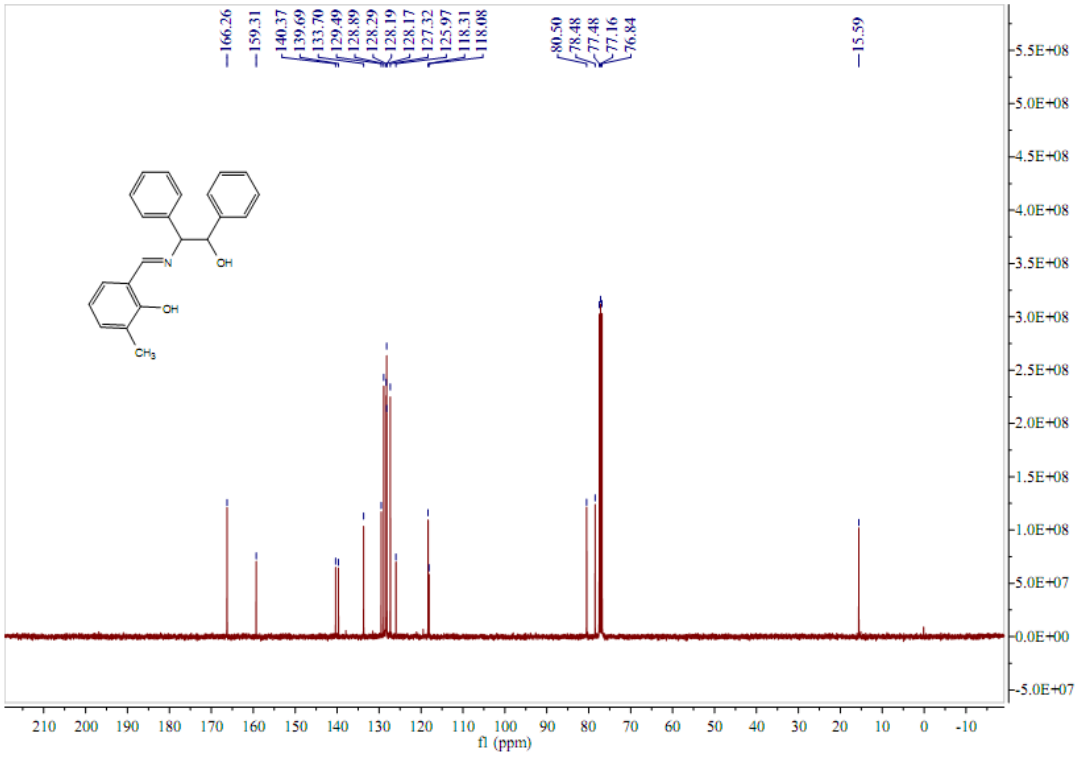
L24


12.85
7.97
7.38
7.37
7.27
7.26
7.25
7.23
6.89
6.88
6.77
6.75
5.04
5.02
4.52
4.50
2.06
1.00
1.06
4.11
6.04
1.18
1.05
1.05
1.06
1.06
1.05
f1 (ppm)

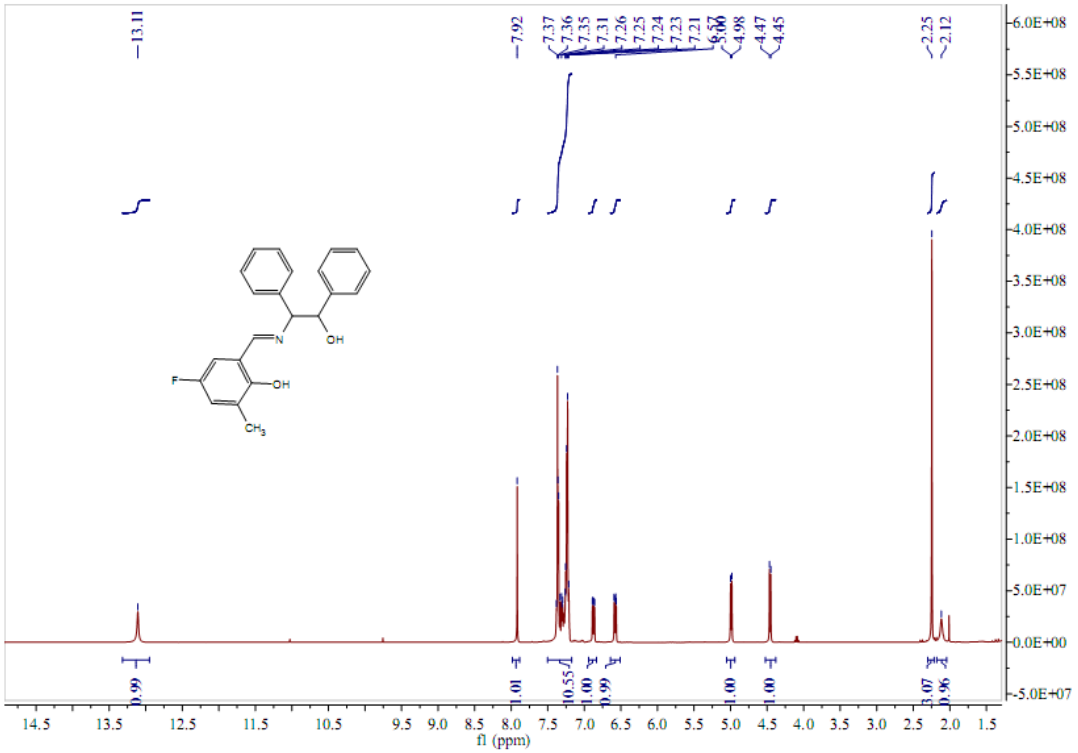

164.97
164.94
157.15
156.66
154.31
140.20
139.32
128.99
128.35
128.16
127.30
119.83
119.60
118.58
118.13
118.06
116.90
116.67
80.37
78.45
77.48
77.36
77.16
76.84
f1 (ppm)

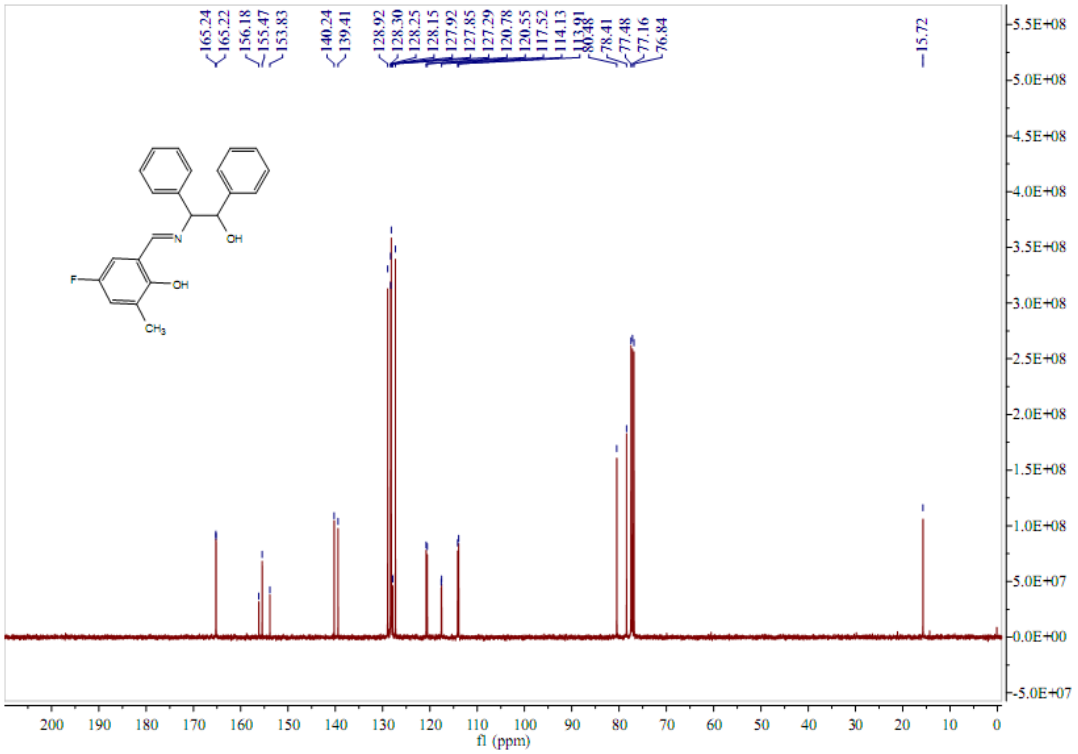
L25


13.34
8.02
7.38
7.37
7.35
7.34
7.25
7.24
7.23
6.89
6.71
5.02
5.01
4.48
4.46
2.27
2.07
0.99
1.02
4.19
6.32
1.17
1.12
0.99
1.00
1.00
3.09
1.00
f1 (ppm)

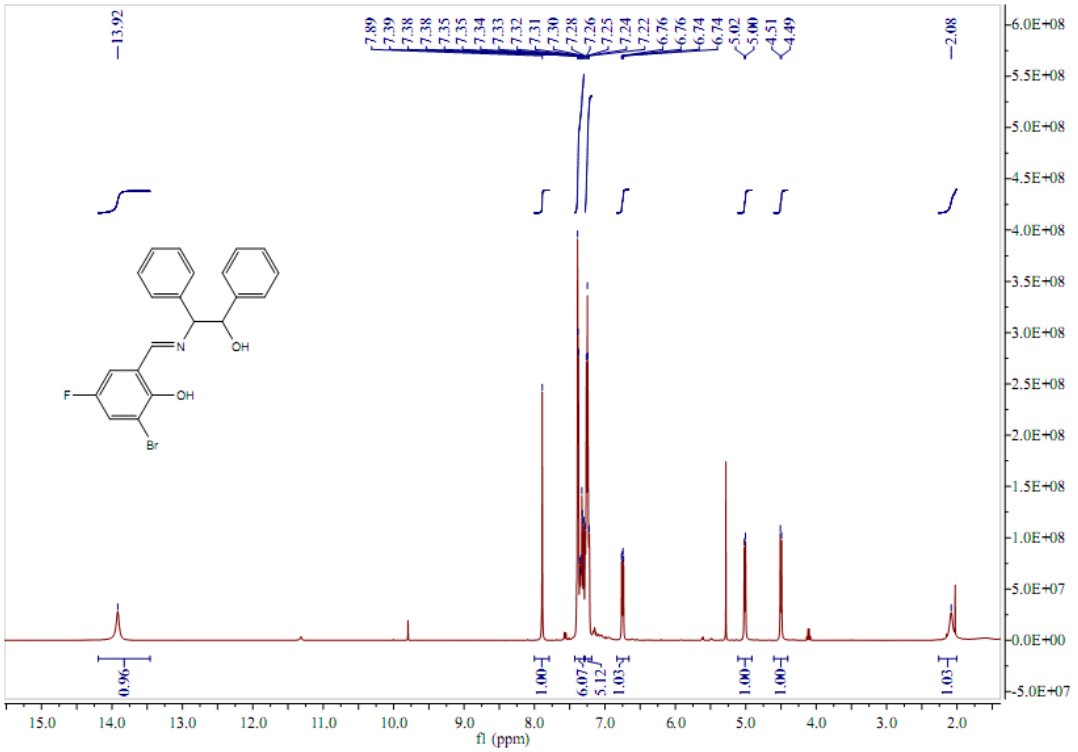

166.26
159.31
140.37
139.69
133.70
129.49
128.89
128.29
128.19
128.17
127.32
125.97
118.31
118.08
80.50
78.48
77.48
77.16
76.84
15.59
f1 (ppm)

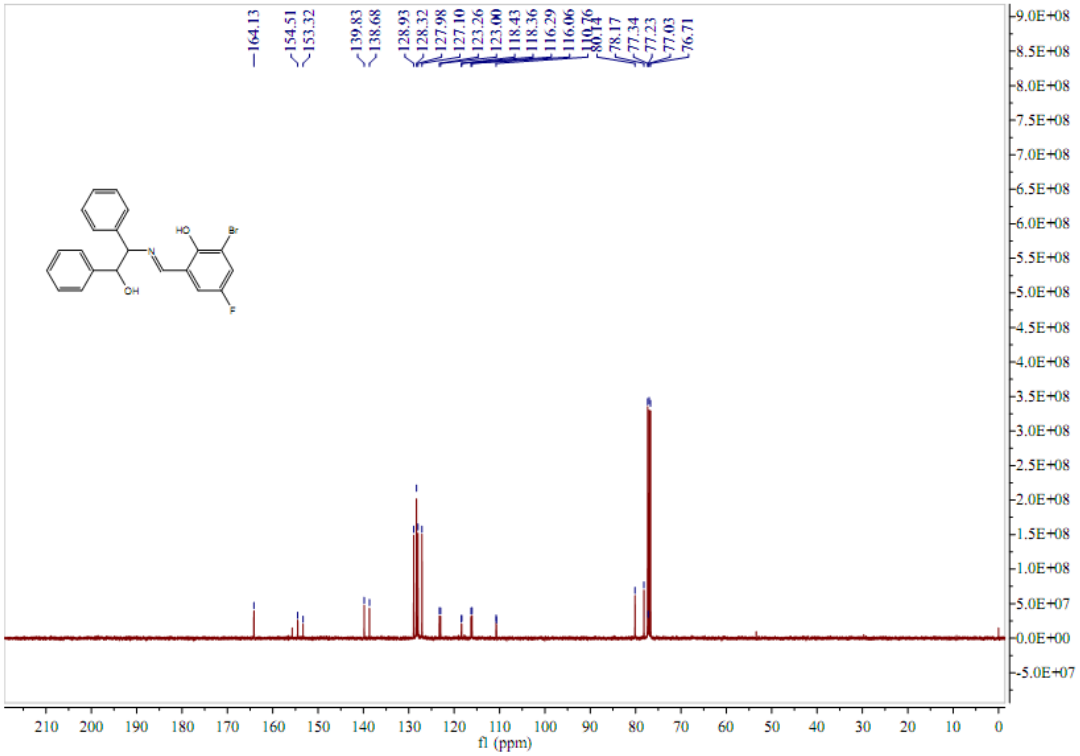
L26


13.11
7.92
7.37
7.36
7.35
7.31
7.26
7.25
7.24
7.23
7.21
6.67
5.00
4.98
4.47
4.45
2.25
2.12
F
OH
OH
N
CH3
f1 (ppm)

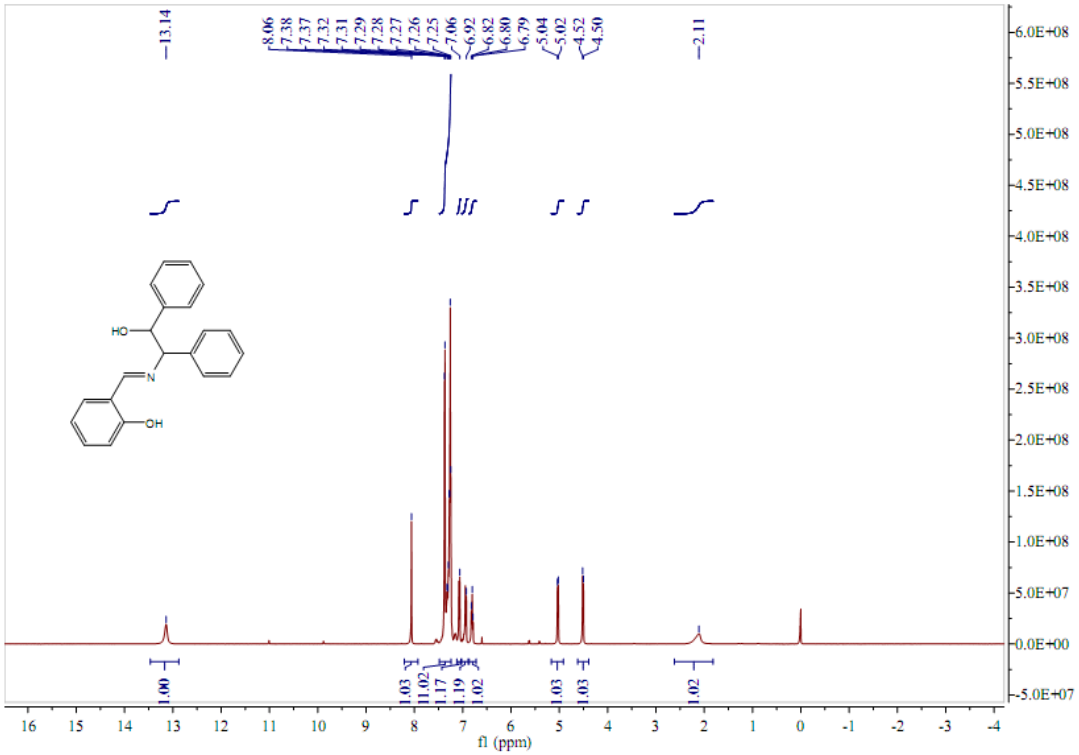

165.24
165.22
156.18
155.47
153.83
140.24
139.41
128.92
128.30
128.25
128.15
127.92
127.85
127.29
120.78
120.55
117.52
114.13
113.91
80.48
78.41
77.48
77.16
76.84
15.72
F
OH
OH
N
CH3
f1 (ppm)

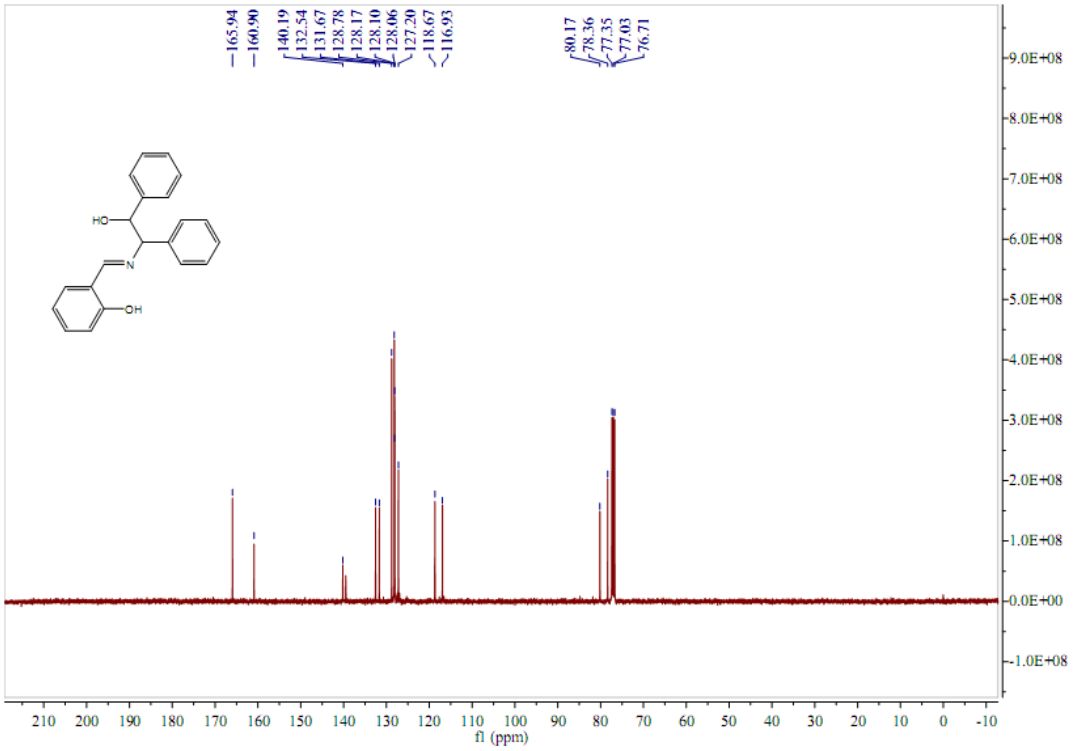
L27


13.92
7.89
7.39
7.38
7.38
7.35
7.35
7.34
7.33
7.32
7.31
7.30
7.28
7.26
7.25
7.24
7.22
6.76
6.76
6.74
6.74
5.02
5.00
4.51
4.49
2.08
N
OH
F
OH
Br
0.96
1.00
6.07
5.12
1.03
1.00
1.00
1.03
f1 (ppm)

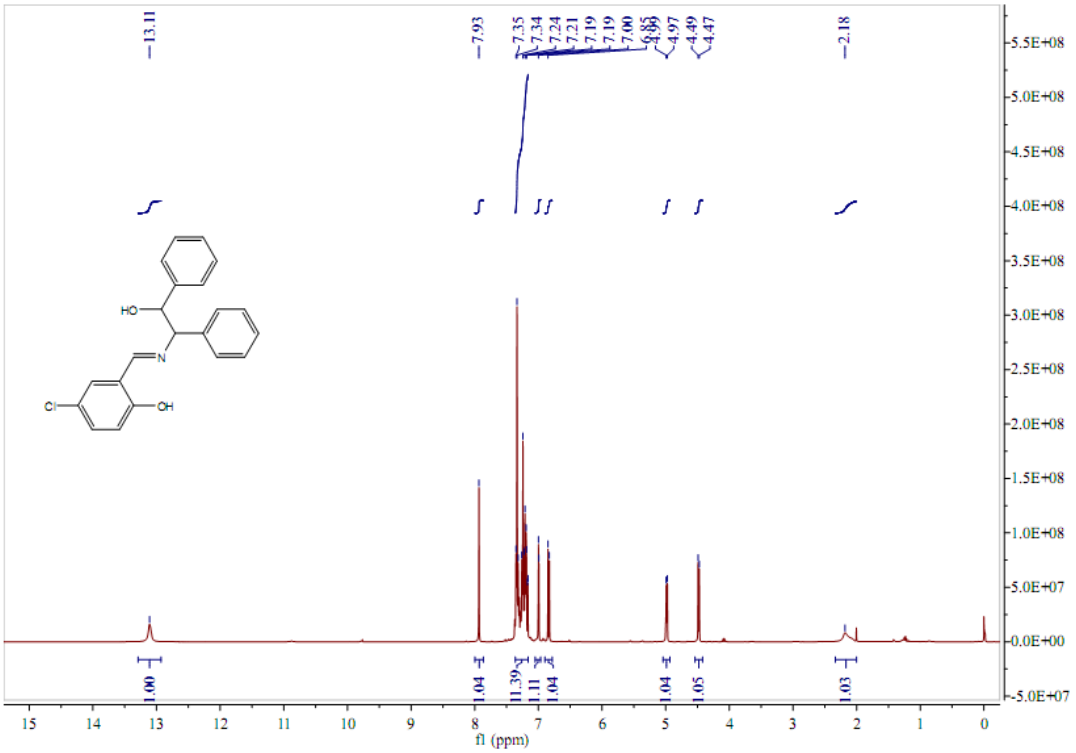

164.13
154.51
153.32
139.83
138.68
128.93
128.32
127.98
127.10
123.26
123.00
118.43
118.36
116.29
116.06
80.14
78.17
77.34
77.23
77.03
76.71
HO
Br
N
OH
F
f1 (ppm)

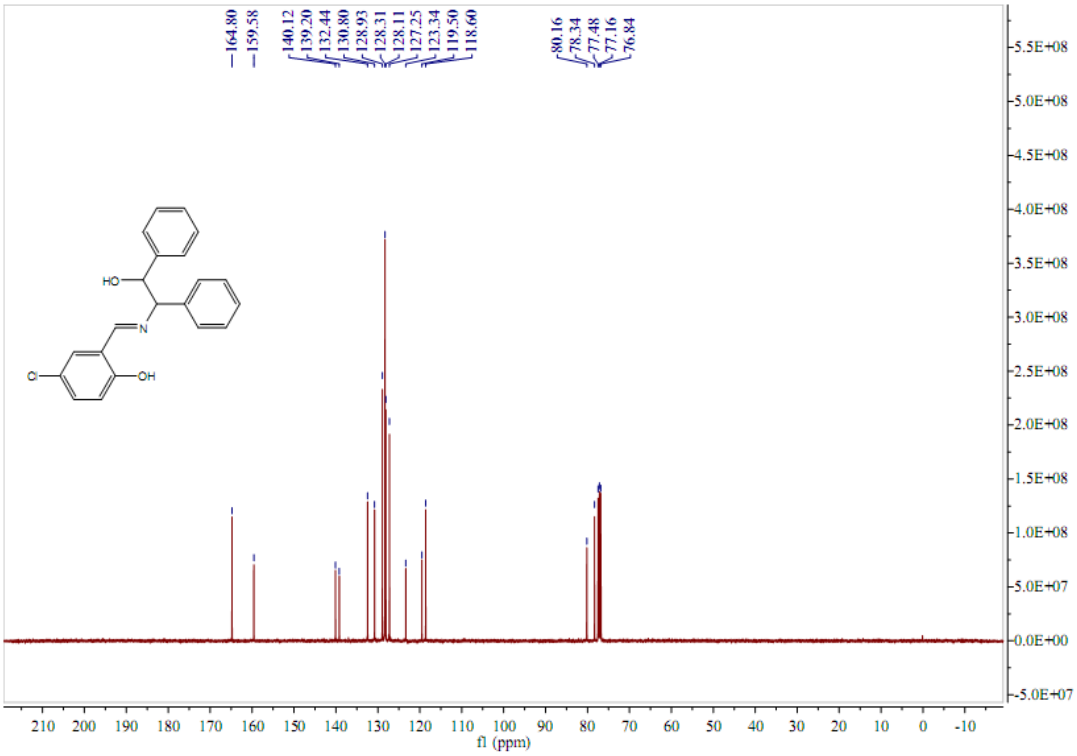
L28


13.14
8.06
7.38
7.37
7.32
7.31
7.29
7.28
7.27
7.26
7.25
7.06
6.92
6.82
6.80
6.79
5.04
5.02
4.52
4.50
2.11
HO
N
OH
1.00
1.03
1.02
1.17
1.19
1.02
1.03
1.03
1.02
f1 (ppm)

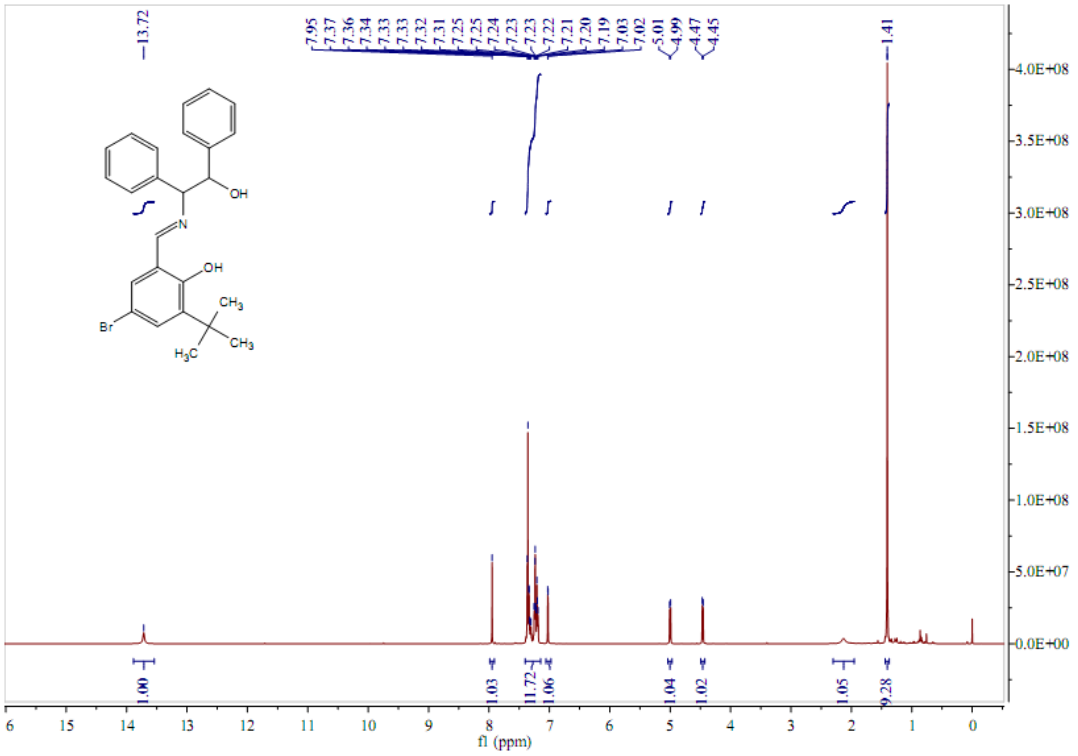

165.94
160.90
140.19
132.54
131.67
128.78
128.17
128.10
128.06
127.20
118.67
116.93
80.17
78.36
77.35
77.03
76.71
HO
N
OH
f1 (ppm)

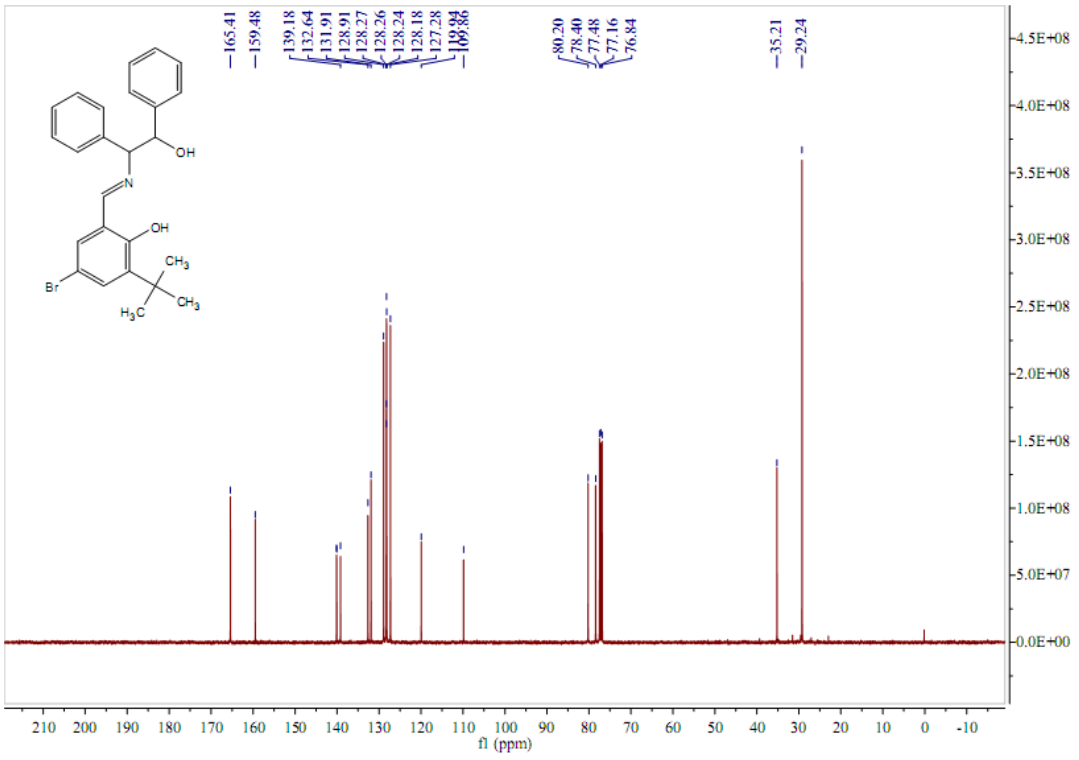
L29


13.11
7.93
7.35
7.34
7.24
7.21
7.19
7.19
7.00
6.85
4.97
4.49
4.47
2.18
HO
N
Cl
OH
1.00
1.04
11.39
1.11
1.04
1.04
1.05
1.03
f1 (ppm)


164.80
159.58
140.12
139.20
132.44
130.80
128.93
128.31
128.11
127.25
123.34
119.50
118.60
80.16
78.34
77.48
77.16
76.84
HO
N
Cl
OH
f1 (ppm)

L30


13.72
7.95
7.37
7.36
7.34
7.33
7.33
7.32
7.31
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.20
7.19
7.03
7.02
5.01
4.99
4.47
4.45
1.41
OH
N
OH
Br
CH3
H3C
CH3
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
1.00
1.03
11.72
1.06
1.04
1.02
1.05
9.28
6 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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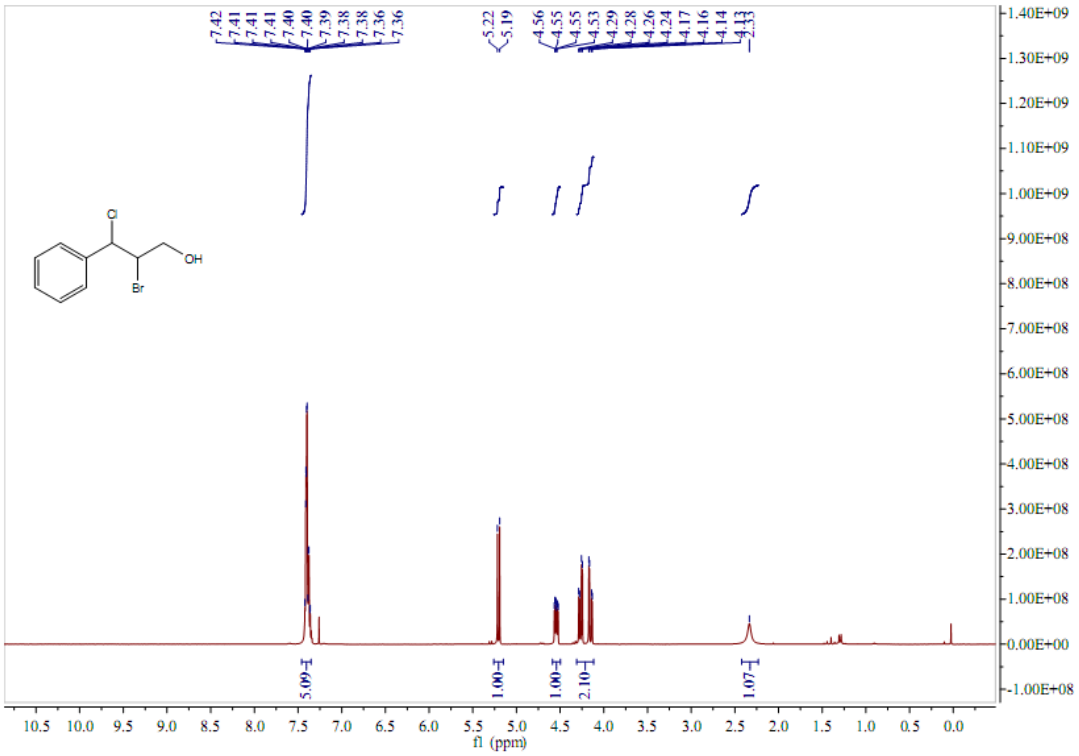
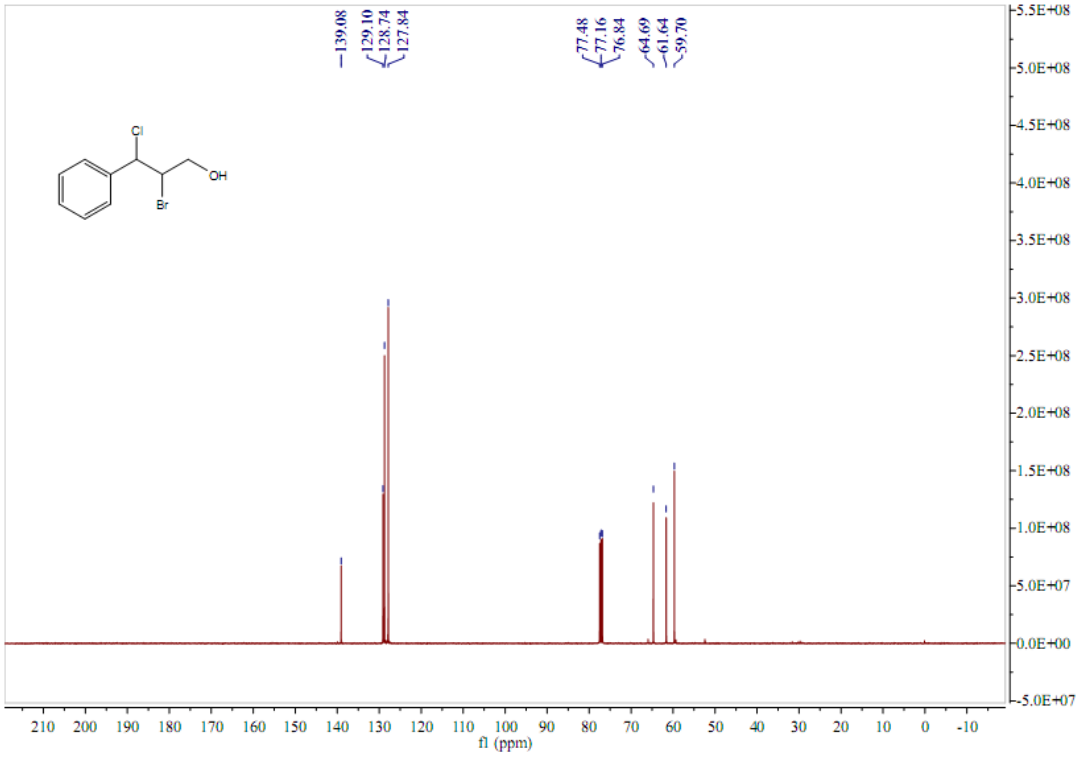
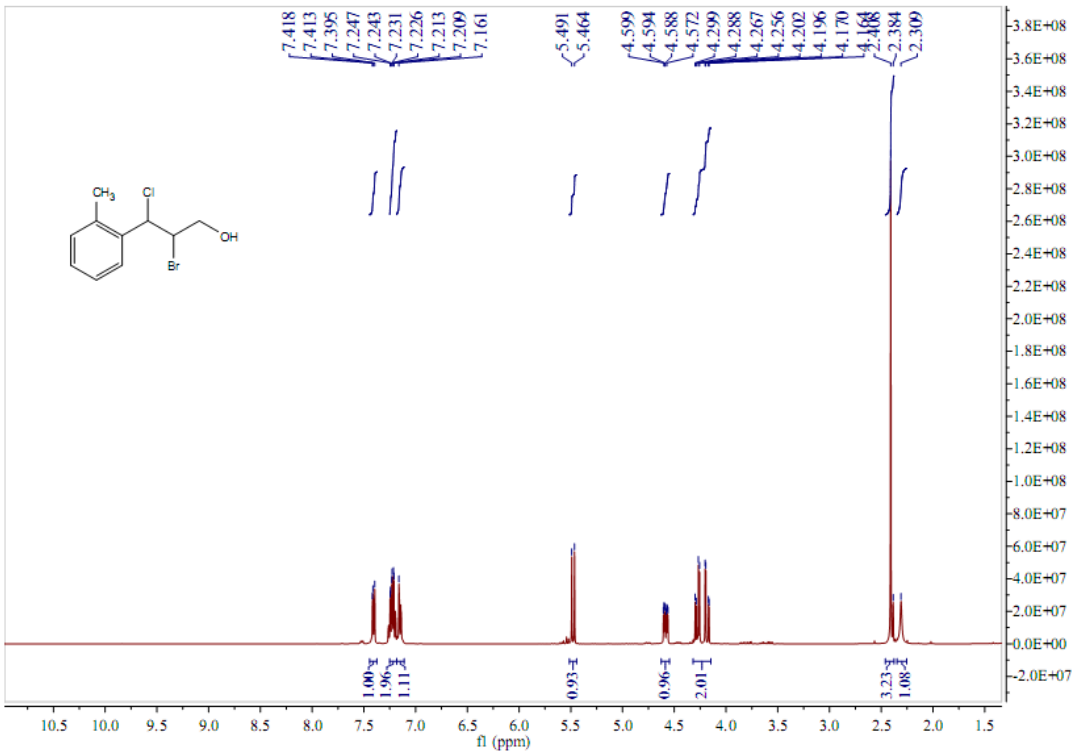
159.48
139.18
132.64
131.91
128.91
128.27
128.26
128.24
128.18
127.28
119.94
119.86
80.20
78.40
77.48
77.16
76.84
35.21
29.24
OH
N
OH
Br
CH3
H3C
CH3
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

NMR spectra for Di-halide Products.



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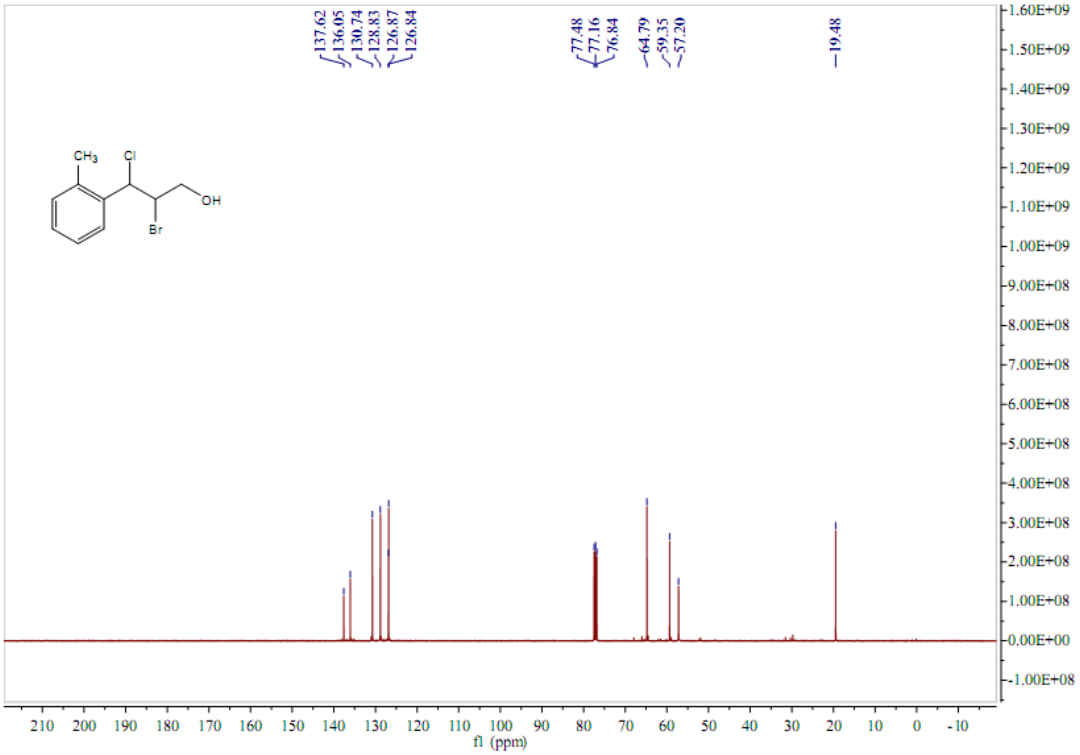
7.413
7.395
7.247
7.243
7.231
7.226
7.213
7.209
7.161
5.491
5.464
4.599
4.594
4.588
4.572
4.299
4.288
4.267
4.256
4.202
4.196
4.170
2.384
2.309
CH3
Cl
OH
Br
1.00
1.96
1.11
0.93
0.96
2.01
3.23
1.08
fl (ppm)


137.62
136.05
130.74
128.83
126.87
126.84
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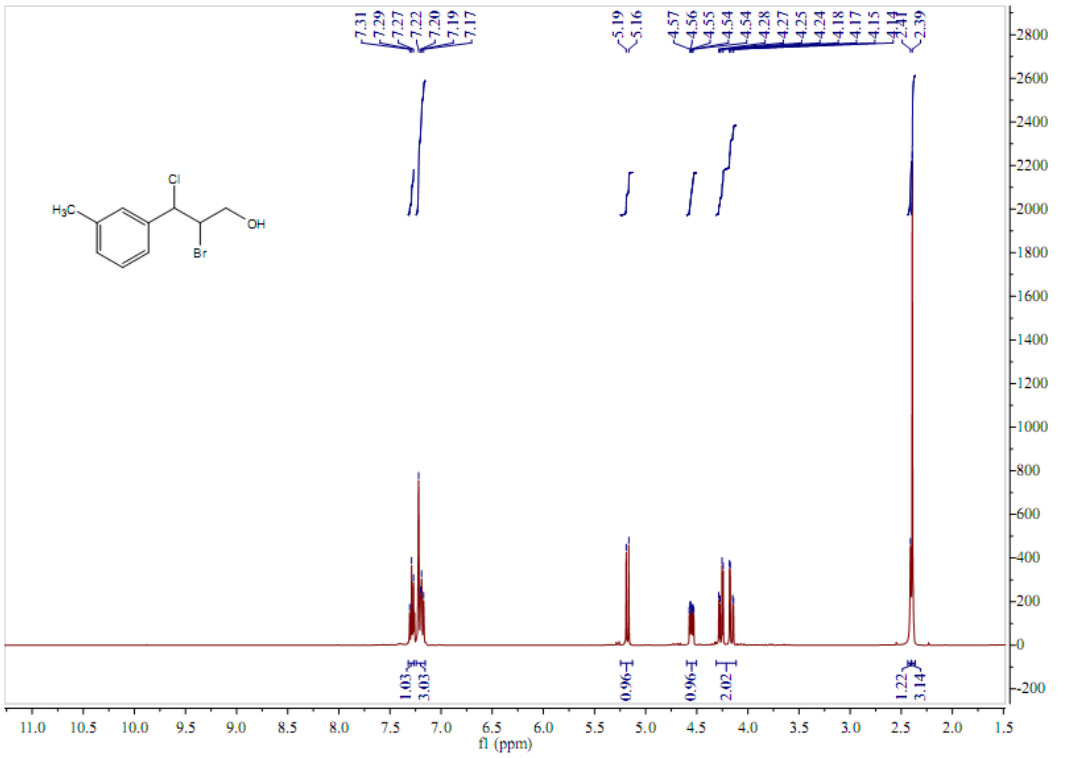
77.16
76.84
64.79
59.35
57.20
19.48
CH3
Cl
OH
Br
fl (ppm)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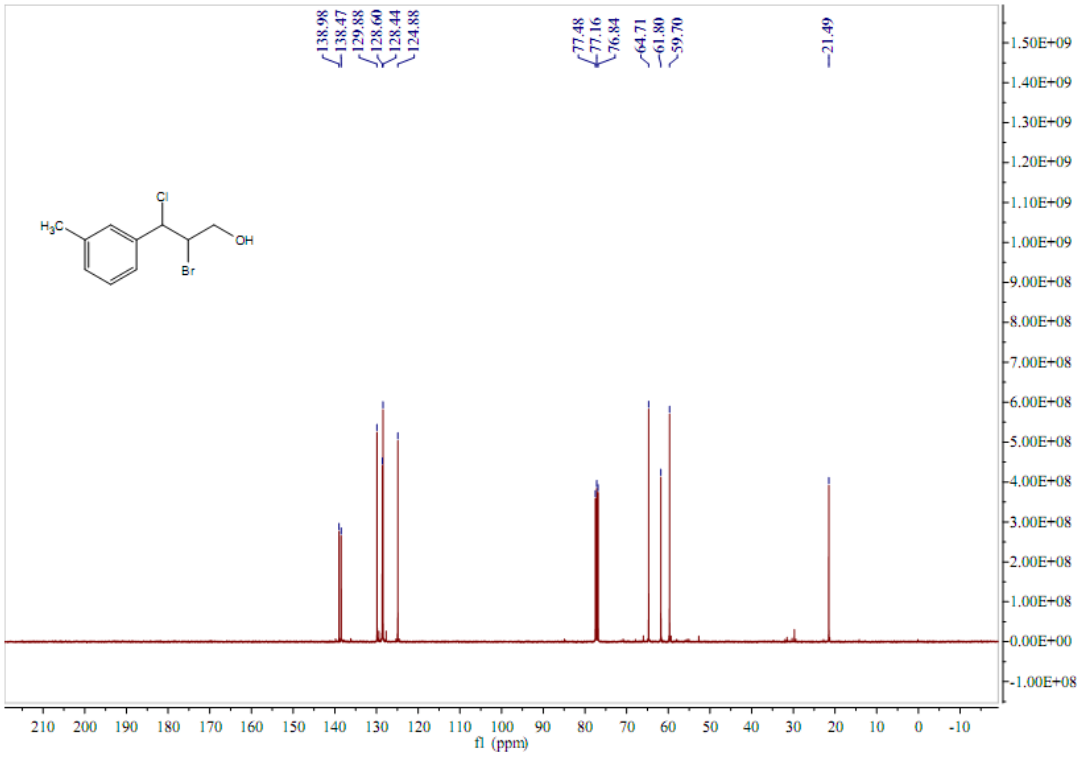
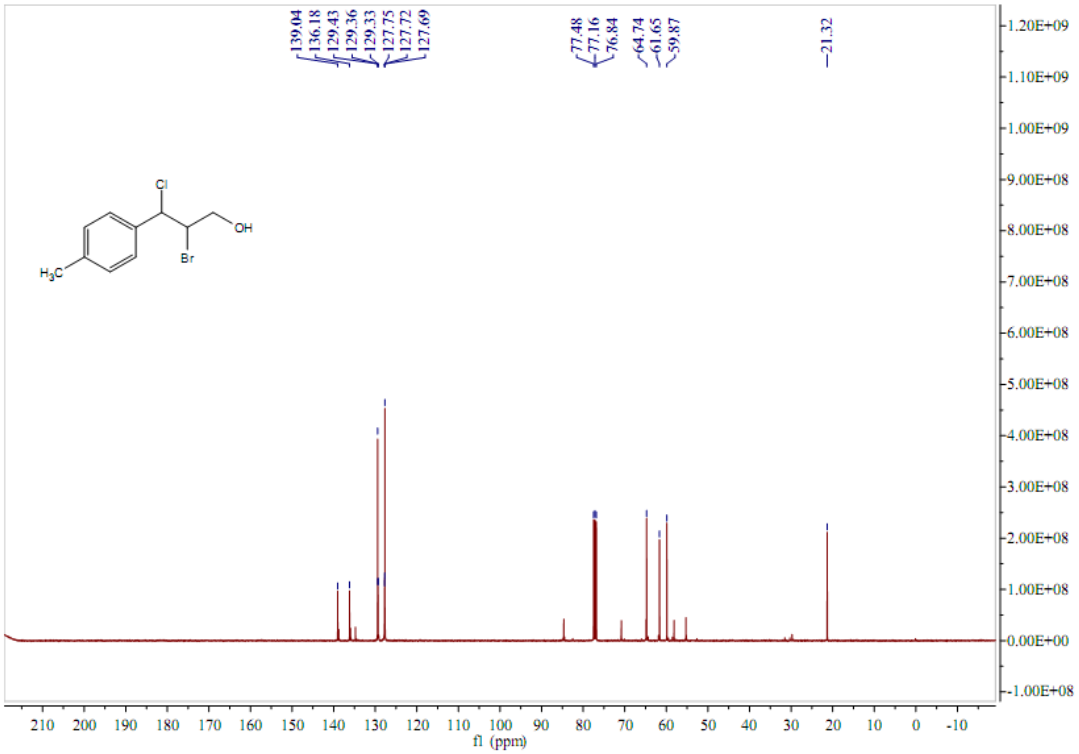
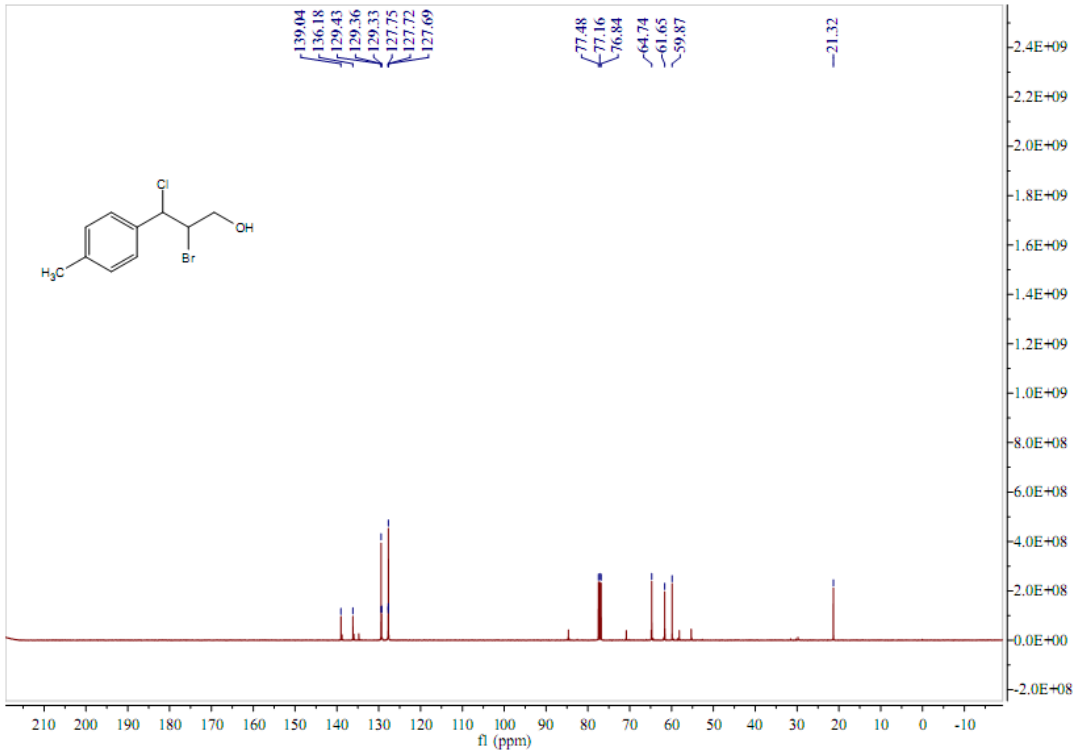
7.29
7.27
7.22
7.20
7.19
7.17
5.19
5.16
4.57
4.56
4.55
4.54
4.54
4.28
4.27
4.25
4.24
4.18
4.17
4.15
2.39
Cl
H3C
OH
Br
1.03
3.03
0.96
0.96
2.02
1.22
3.14
f1 (ppm)


138.98
138.47
129.88
128.60
128.44
124.88
77.48
77.16
76.84
64.71
61.80
59.70
21.49
Cl
H3C
OH
Br
f1 (ppm)


139.04
136.18
129.43
129.36
129.33
127.75
127.72
127.69
77.48
77.16
76.84
64.74
61.65
59.87
21.32
Cl
OH
Br
H3C
f1 (ppm)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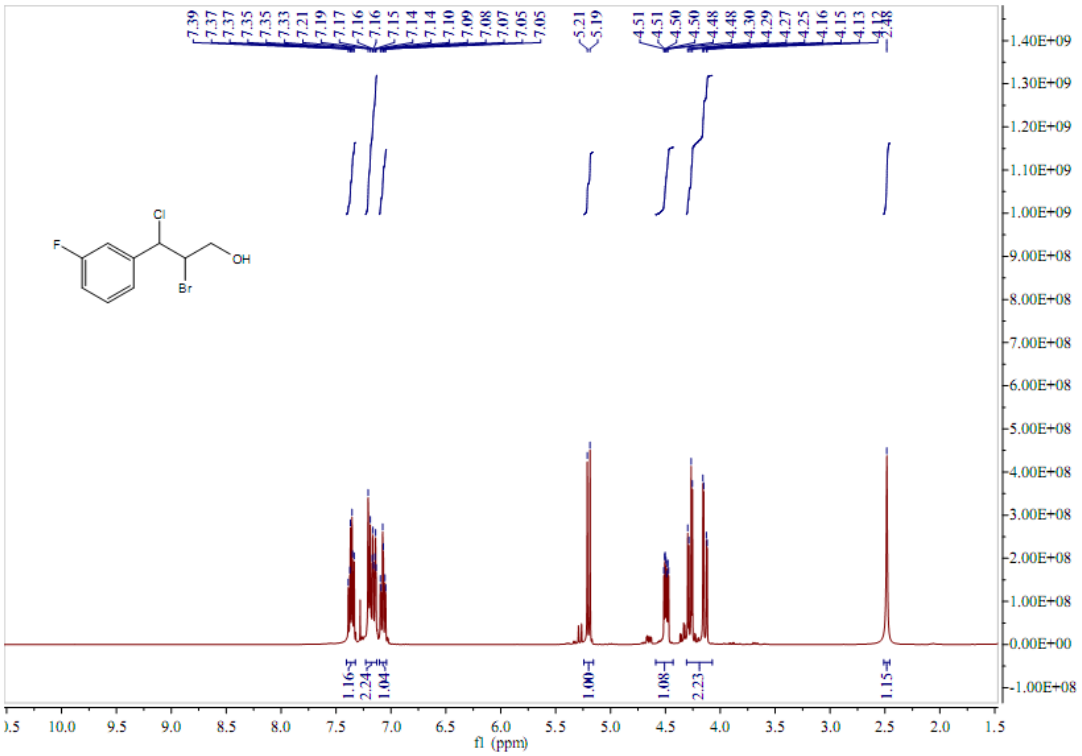
129.43
129.36
129.33
127.75
127.72
127.69
77.48
77.16
76.84
64.74
61.65
59.87
21.32
Cl
OH
Br
H3C
f1 (ppm)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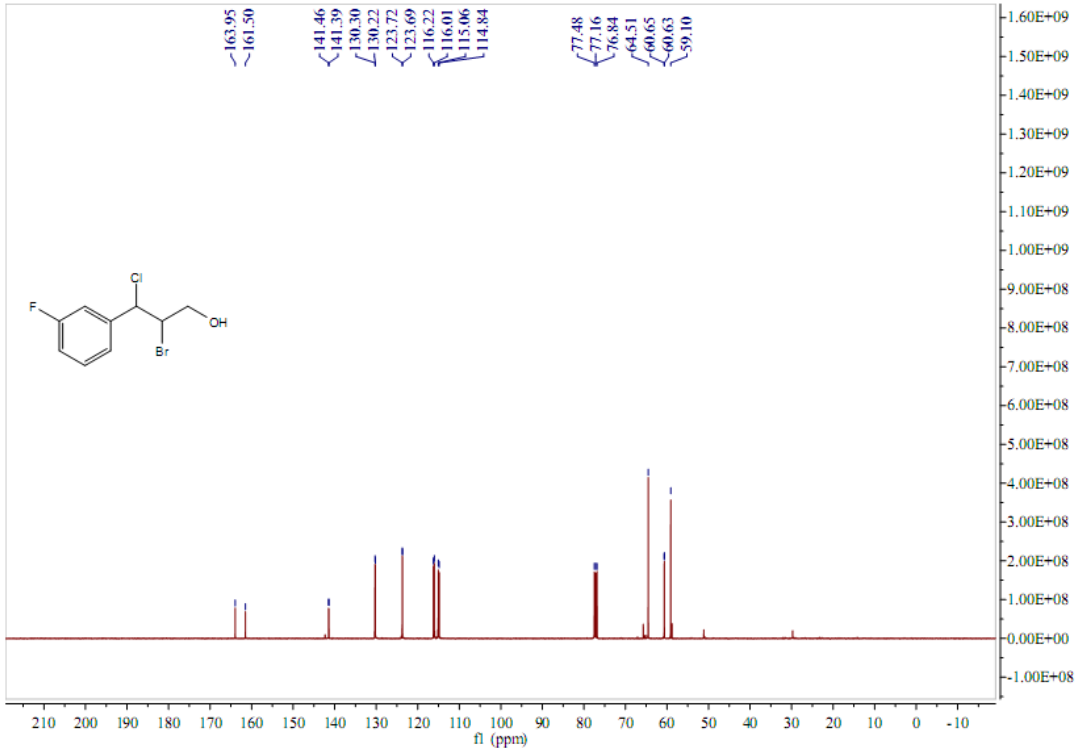
7.37
7.37
7.35
7.35
7.33
7.21
7.19
7.17
7.16
7.16
7.15
7.14
7.14
7.10
7.09
7.08
7.07
7.05
7.05
5.21
5.19
4.51
4.51
4.50
4.50
4.48
4.48
4.30
4.29
4.27
4.25
4.16
4.15
4.13
4.12
2.48
Cl
F
OH
Br
1.16
2.24
1.04
1.00
1.08
2.23
1.15
f1 (ppm)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161.50
141.46
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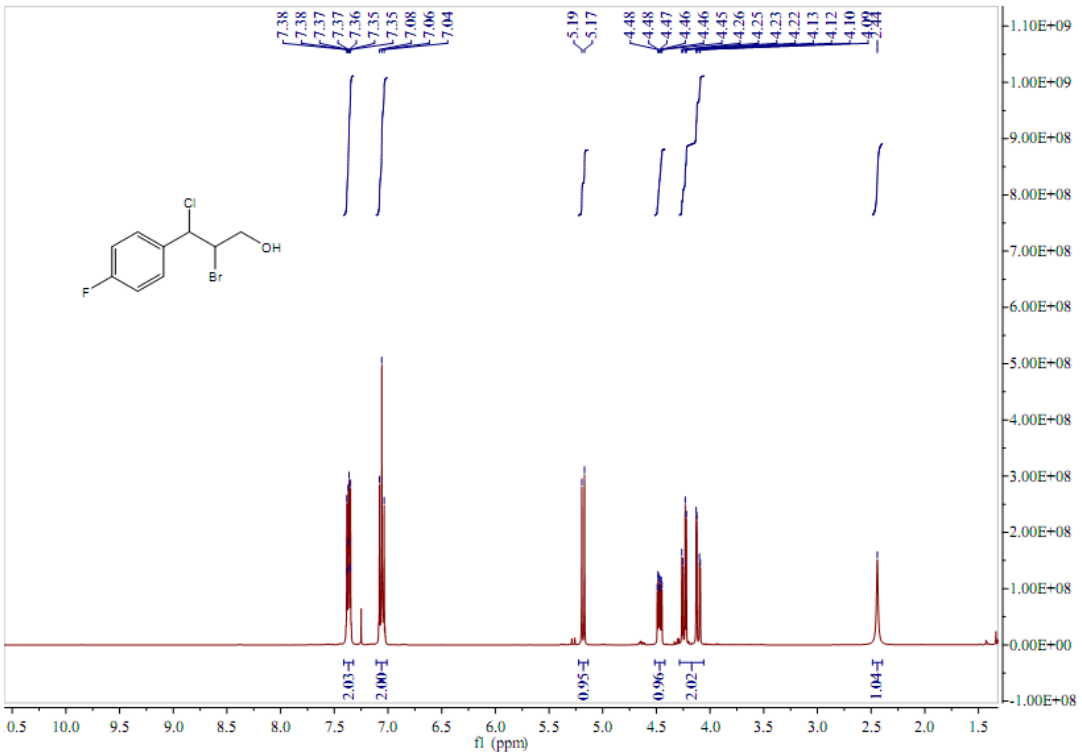
130.30
130.22
123.72
123.69
116.22
116.01
115.06
114.84
77.48
77.16
76.84
64.51
60.65
60.63
59.10
Cl
F
OH
Br
f1 (ppm)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7.38
7.37
7.37
7.36
7.35
7.35
7.08
7.06
7.04
5.19
5.17
4.48
4.48
4.47
4.46
4.46
4.45
4.26
4.25
4.23
4.22
4.13
4.12
4.10
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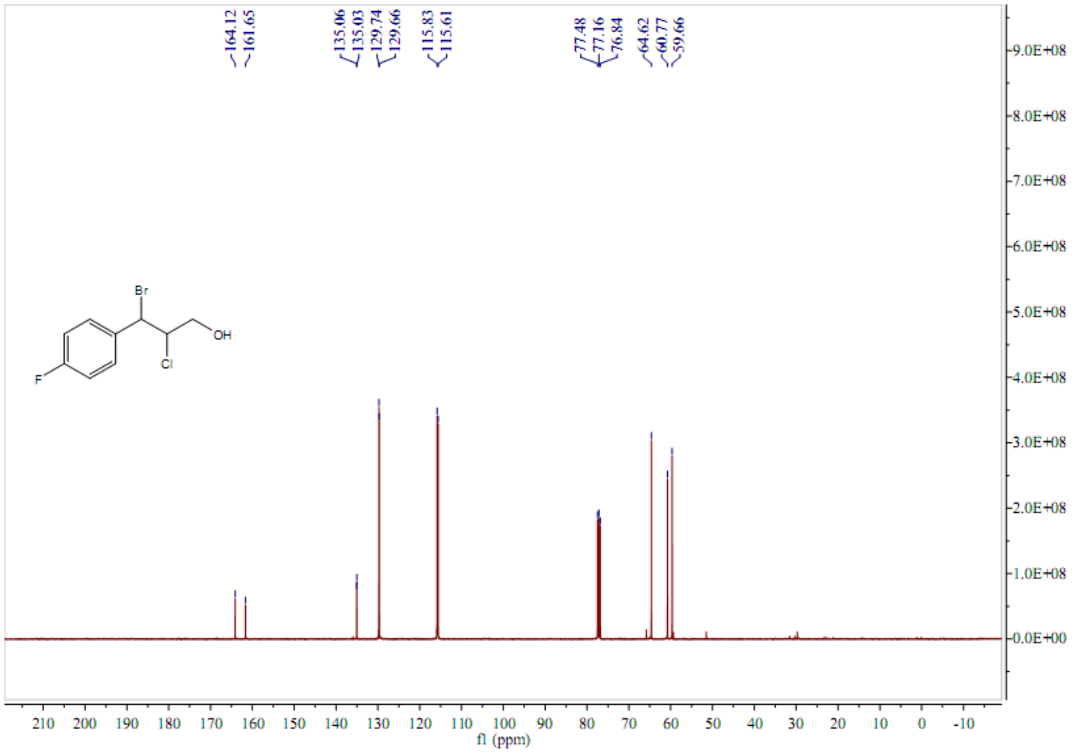
Cl
OH
Br
F
2.03
2.00
0.95
0.96
2.02
1.04
f1 (ppm)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77.16
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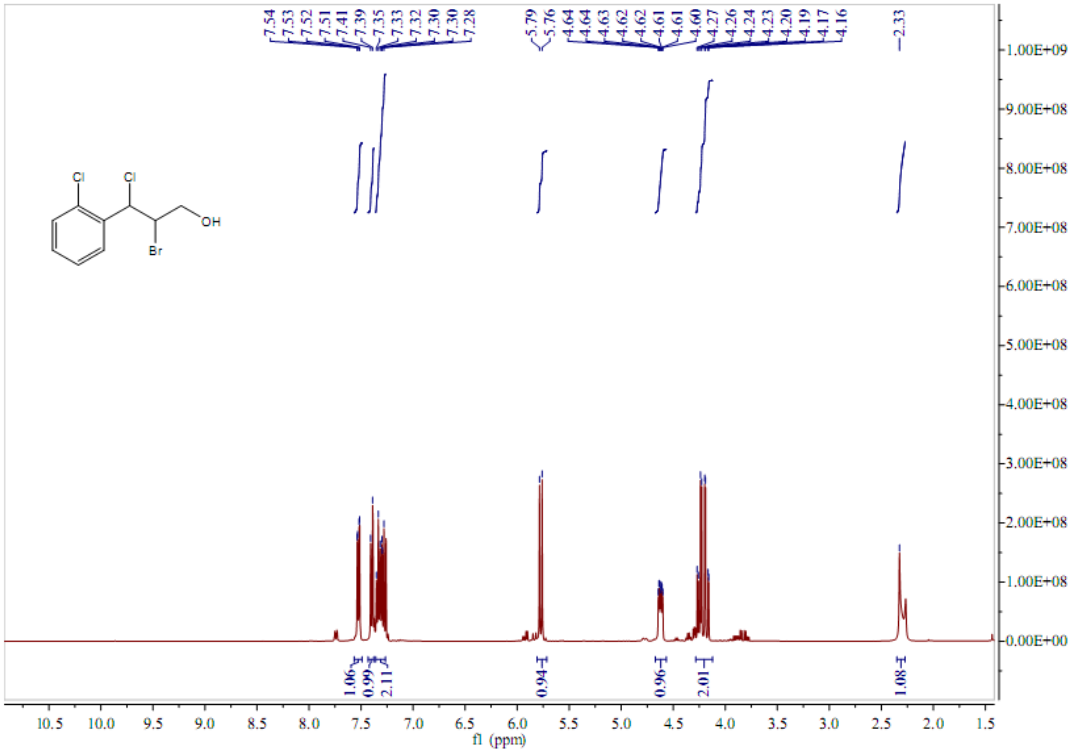
59.66
Br
OH
Cl
F
f1 (ppm)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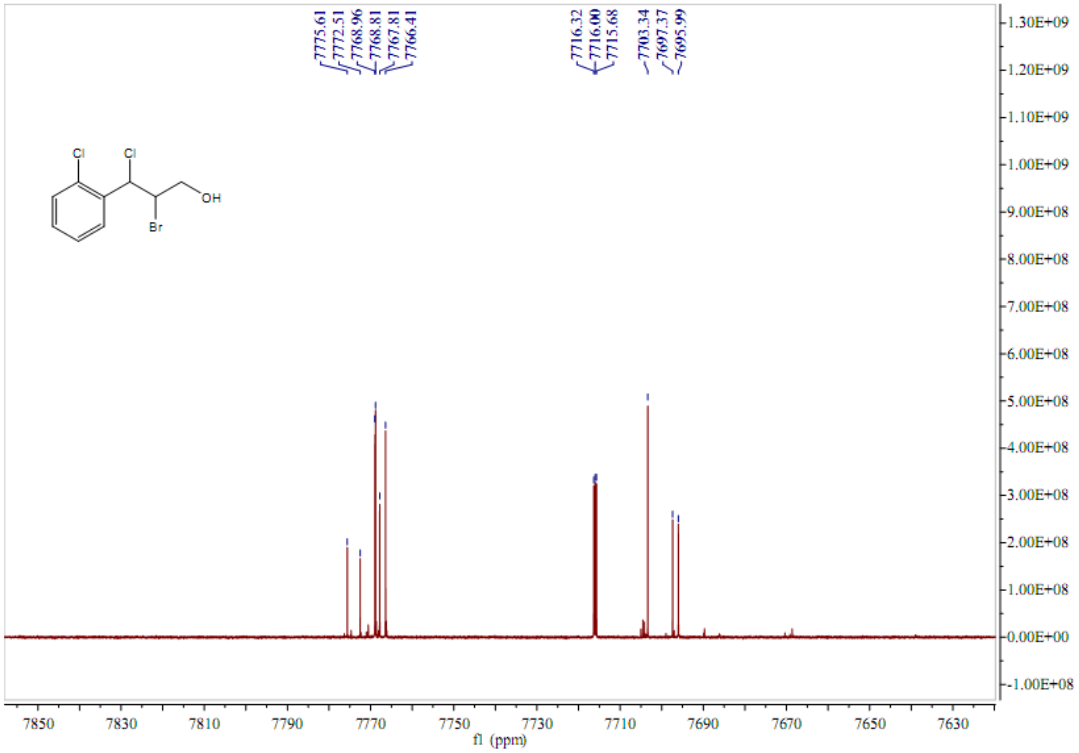
7.30
7.28
5.79
5.76
4.64
4.64
4.63
4.62
4.62
4.61
4.61
4.60
4.27
4.26
4.24
4.23
4.20
4.19
4.17
4.16
2.33
Cl
Cl
OH
Br
1.06
0.99
2.11
0.94
0.96
2.01
1.08
fl (ppm)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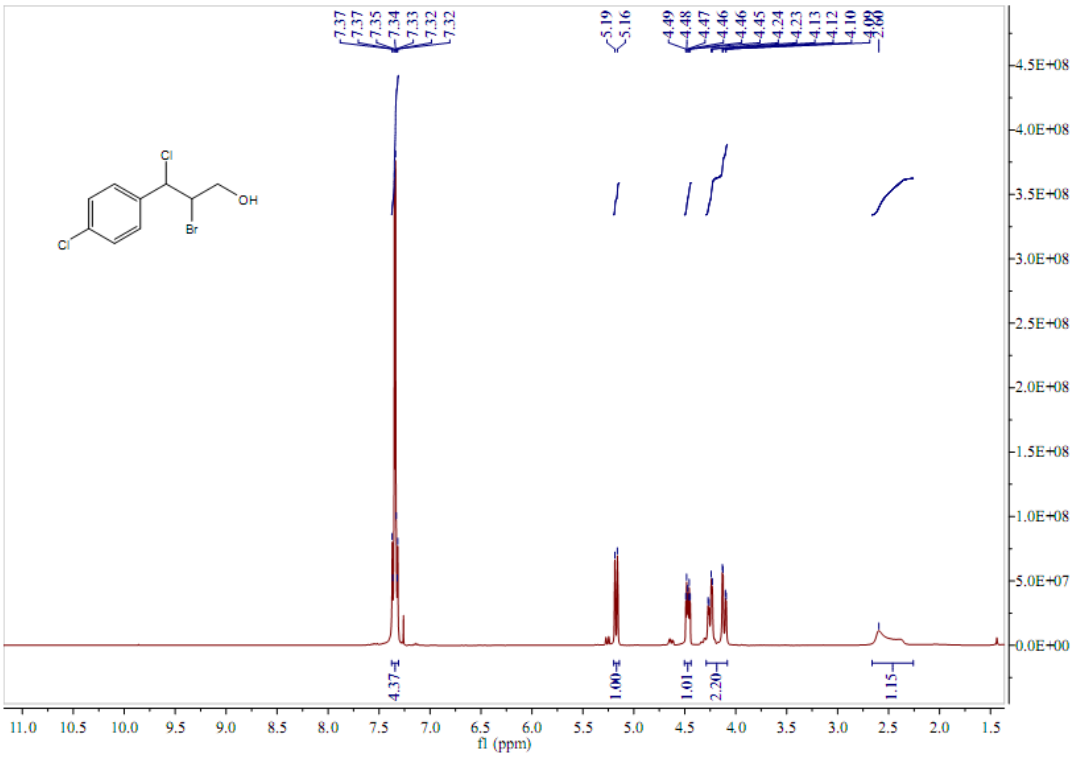
7695.99
Cl
Cl
OH
Br
fl (ppm)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5.19
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4.46
4.46
4.45
4.24
4.23
4.13
4.12
4.10
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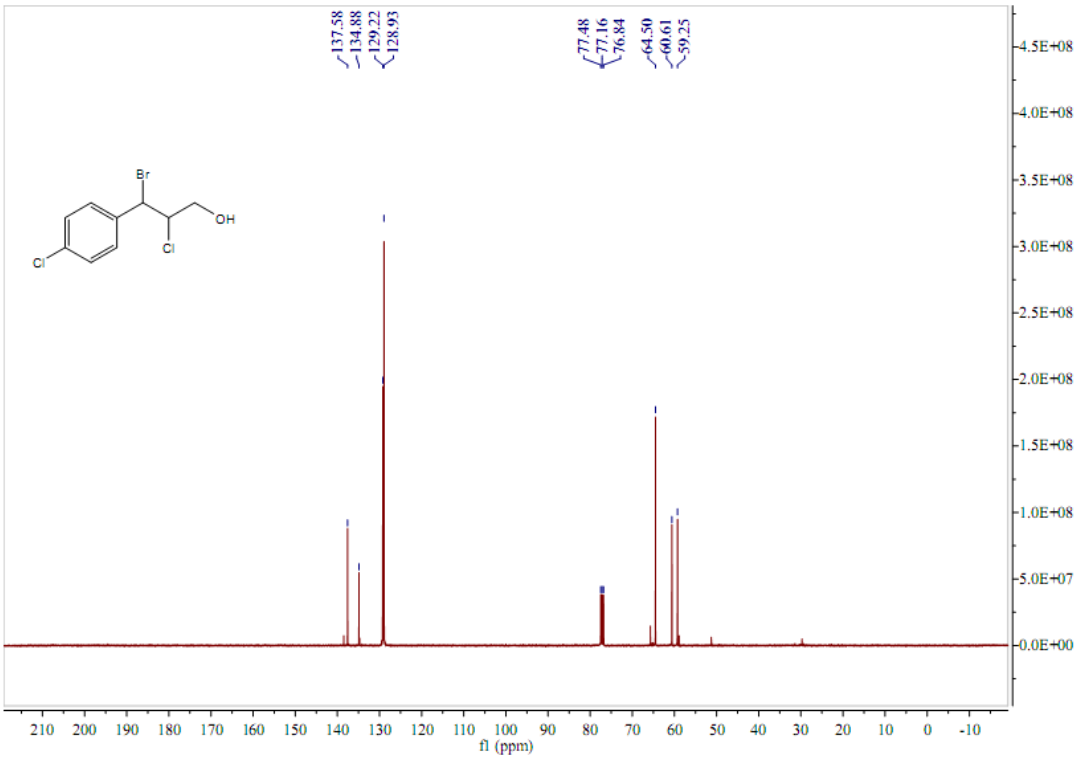
Cl
OH
Br
Cl
4.37
1.00
1.01
2.20
1.15
f1 (ppm)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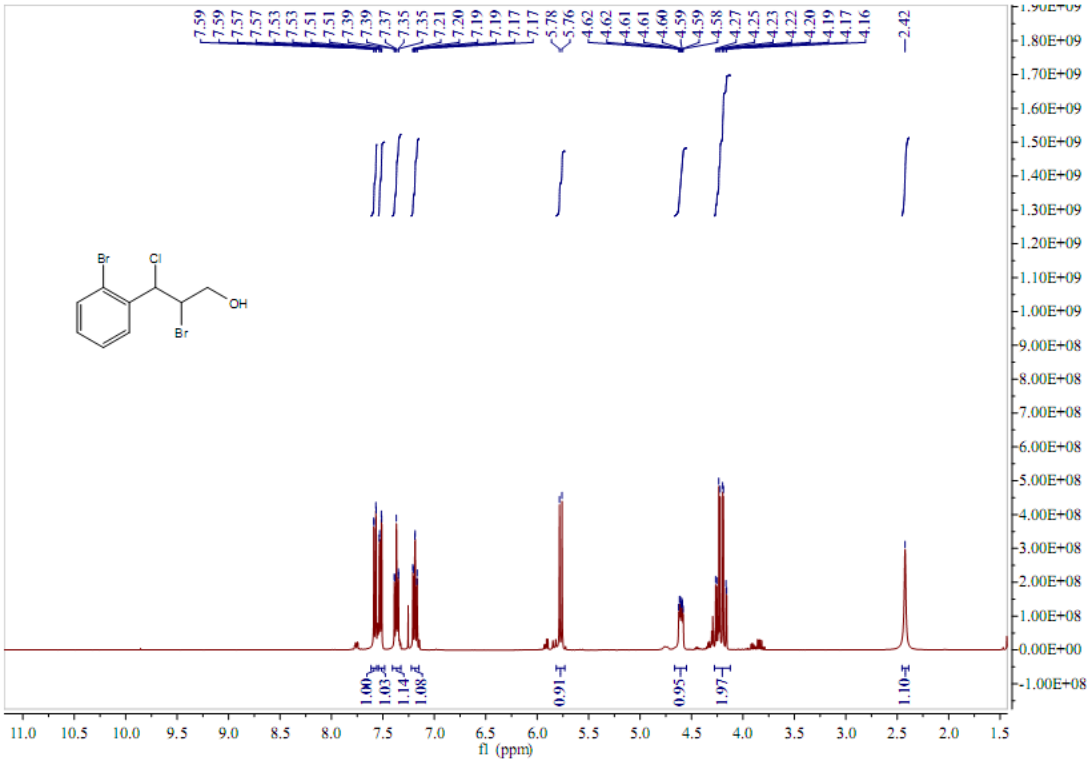
76.84
64.50
60.61
59.25
Br
OH
Cl
Cl
f1 (ppm)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7.57
7.53
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7.51
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7.37
7.35
7.35
7.21
7.20
7.19
7.19
7.17
7.17
5.78
5.76
4.62
4.62
4.61
4.61
4.60
4.59
4.59
4.58
4.27
4.25
4.23
4.22
4.20
4.19
4.17
4.16
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Br
Cl
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Br
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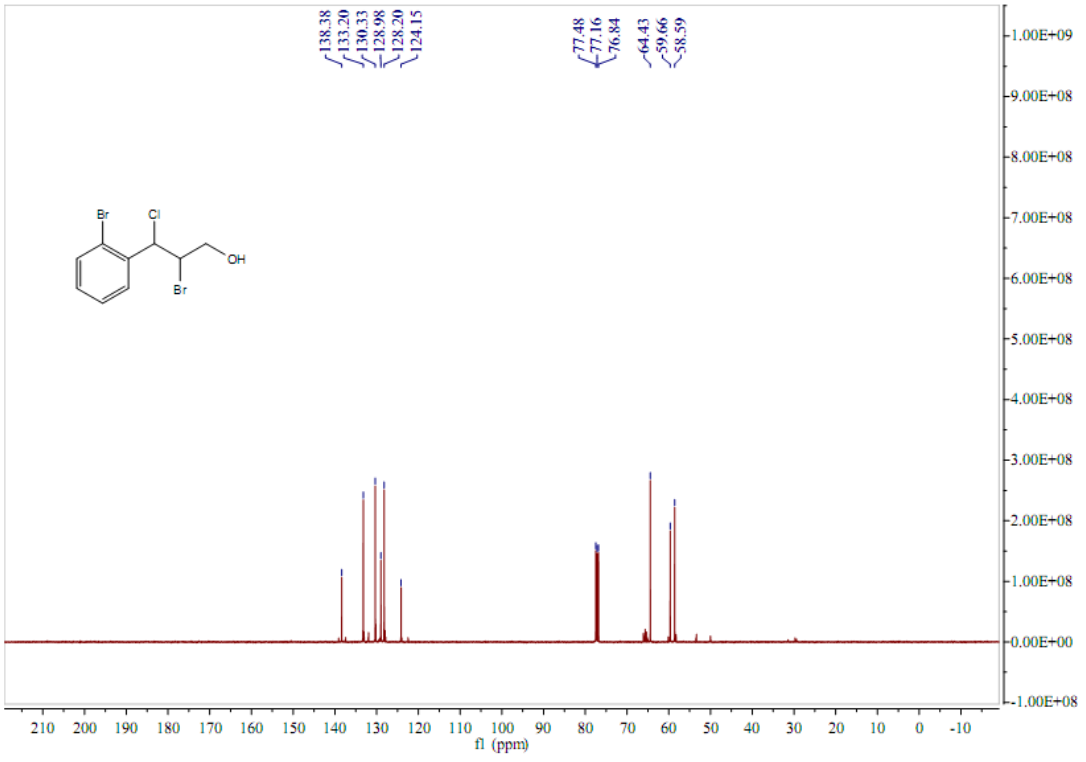
1.14
1.08
0.91
0.95
1.97
1.10
fl (ppm)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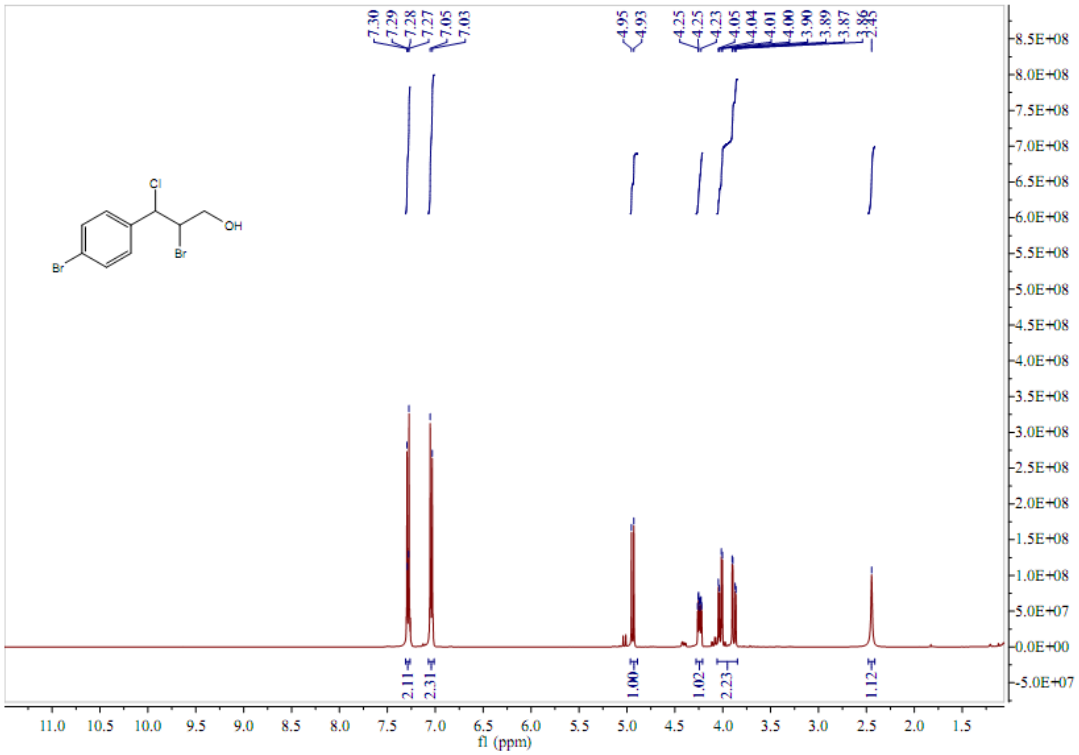
77.16
76.84
64.43
59.66
58.59
Br
Cl
OH
Br
fl (ppm)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7.03
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4.25
4.25
4.23
4.05
4.04
4.01
4.00
3.90
3.89
3.87
3.86
3.85
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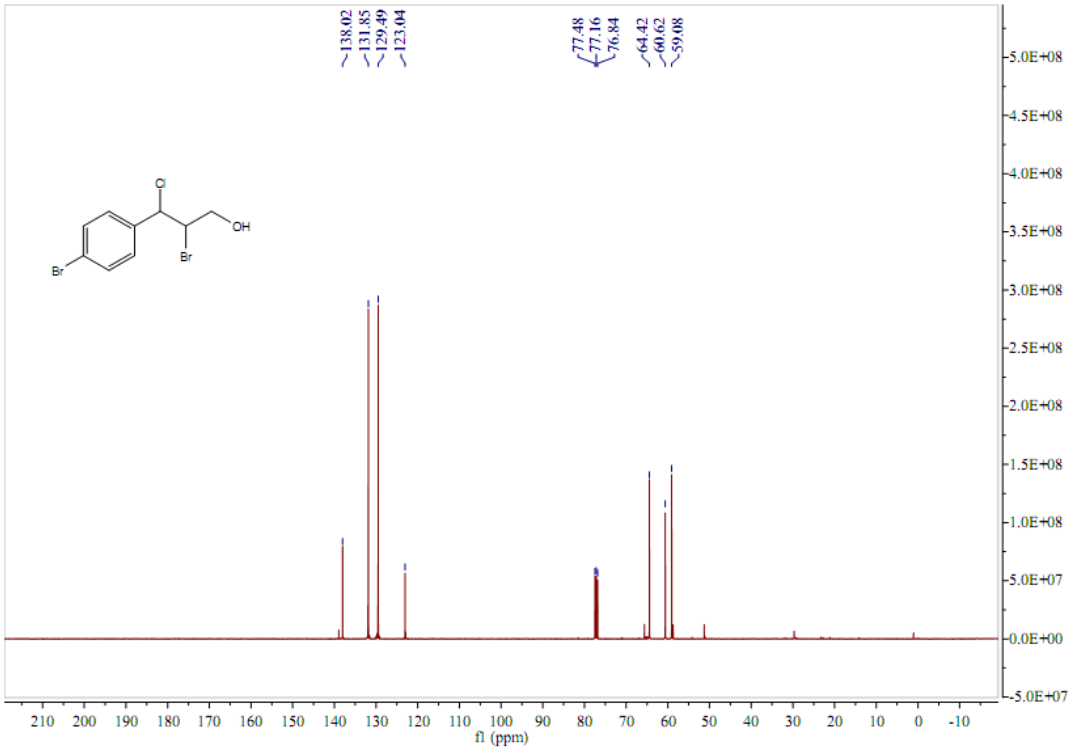
Cl
OH
Br
Br
2.11
2.31
1.00
1.02
2.23
1.12
fl (ppm)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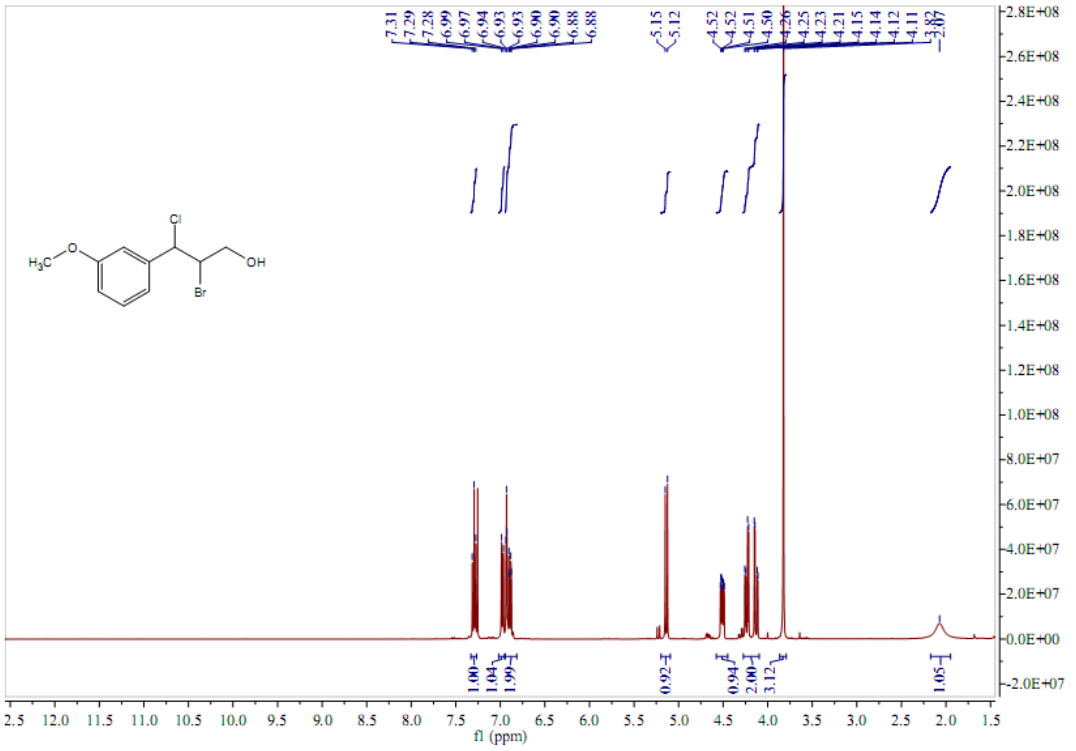
77.16
76.84
64.42
60.62
59.08
Cl
OH
Br
Br
fl (ppm)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6.90
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6.88
5.15
5.12
4.52
4.52
4.51
4.50
4.26
4.25
4.23
4.21
4.15
4.14
4.12
4.11
3.82
3.67
Cl
H3C
O
OH
Br
1.00
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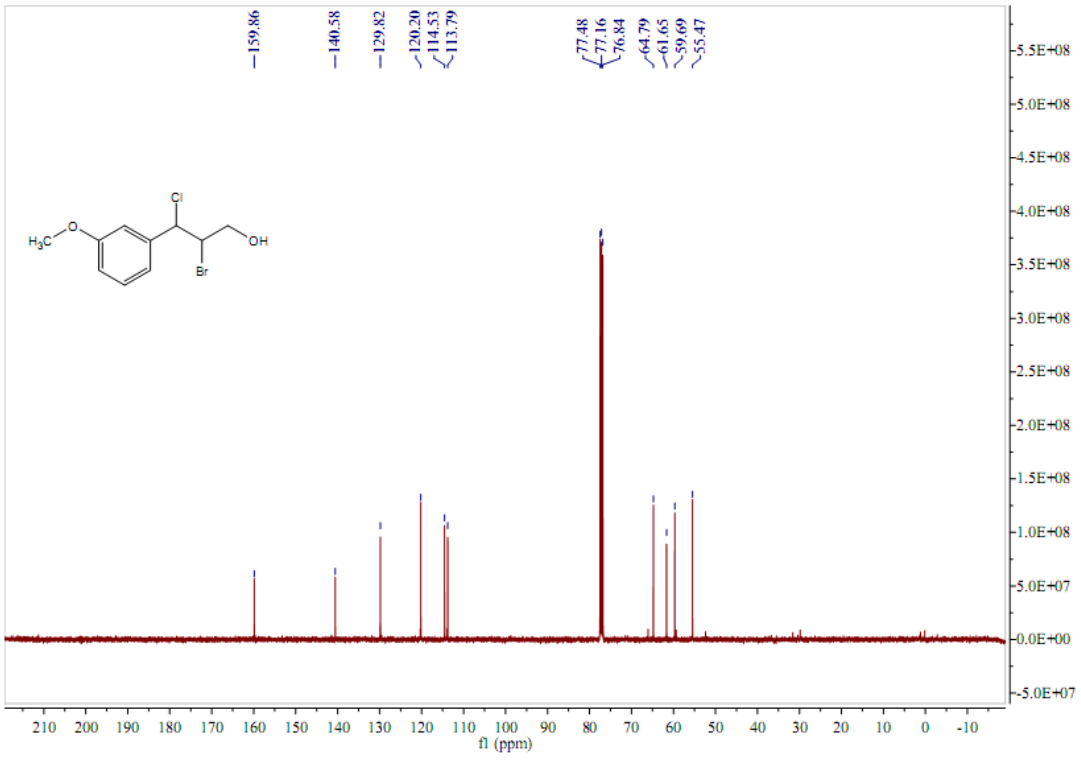
1.99
0.92
0.94
2.00
3.12
1.05
f1 (ppm)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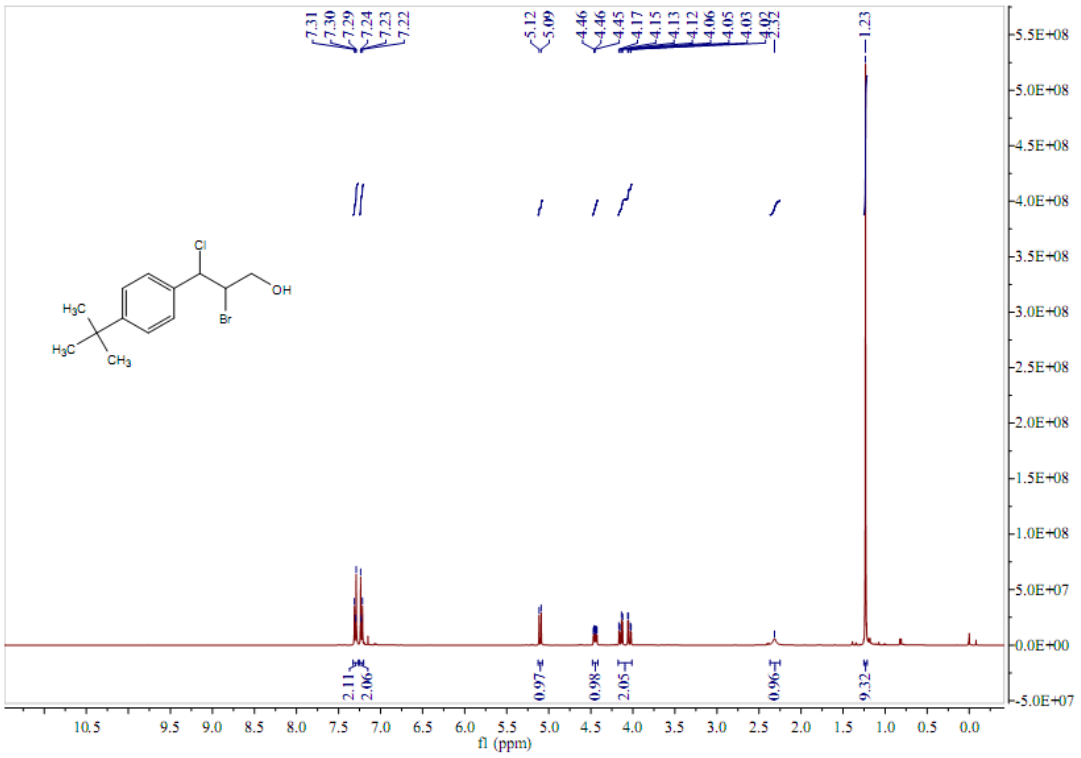
64.79
61.65
59.69
55.47
Cl
H3C
O
OH
Br
f1 (ppm)


7.31
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7.22
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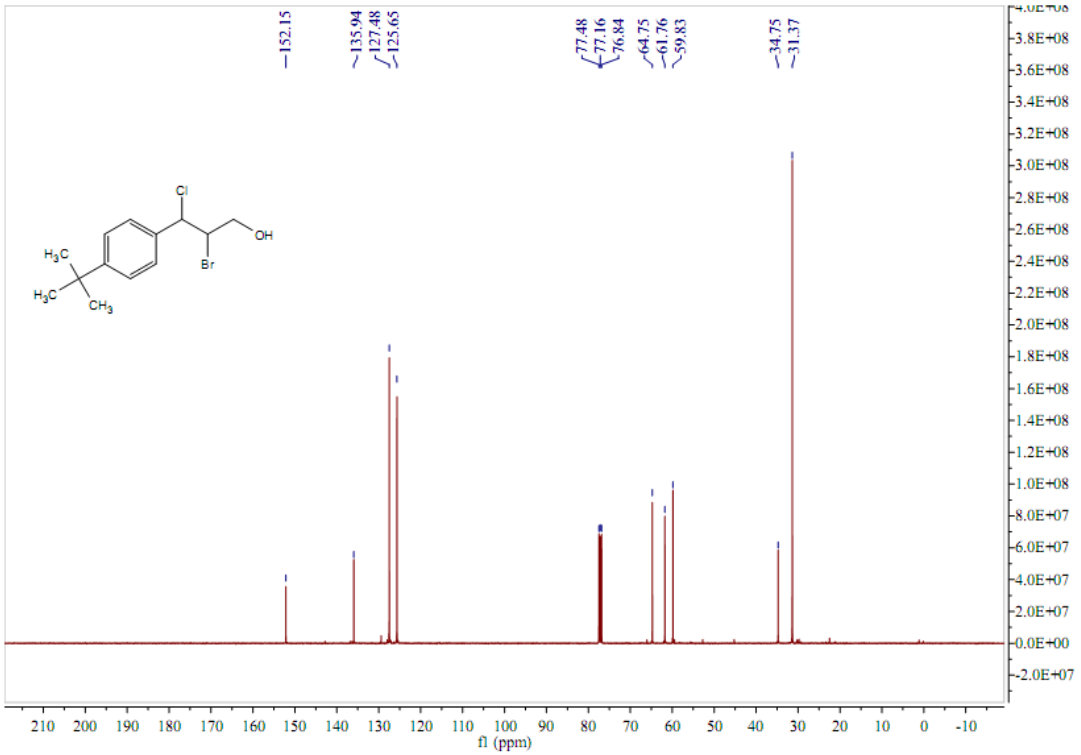
5.09
4.46
4.46
4.45
4.17
4.15
4.13
4.12
4.06
4.05
4.03
4.02
2.32
1.23
Cl
OH
Br
H3C
H3C
CH3
2.11
2.06
0.97
0.98
2.05
0.96
9.32
fl (ppm)


152.15
135.94
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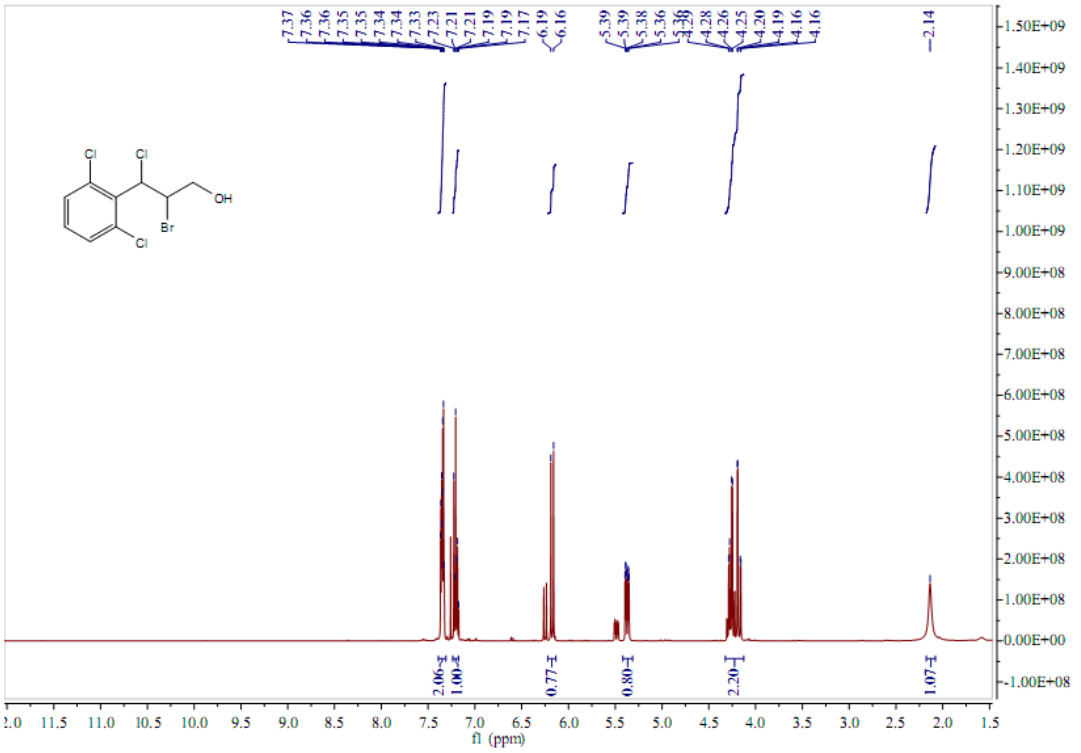
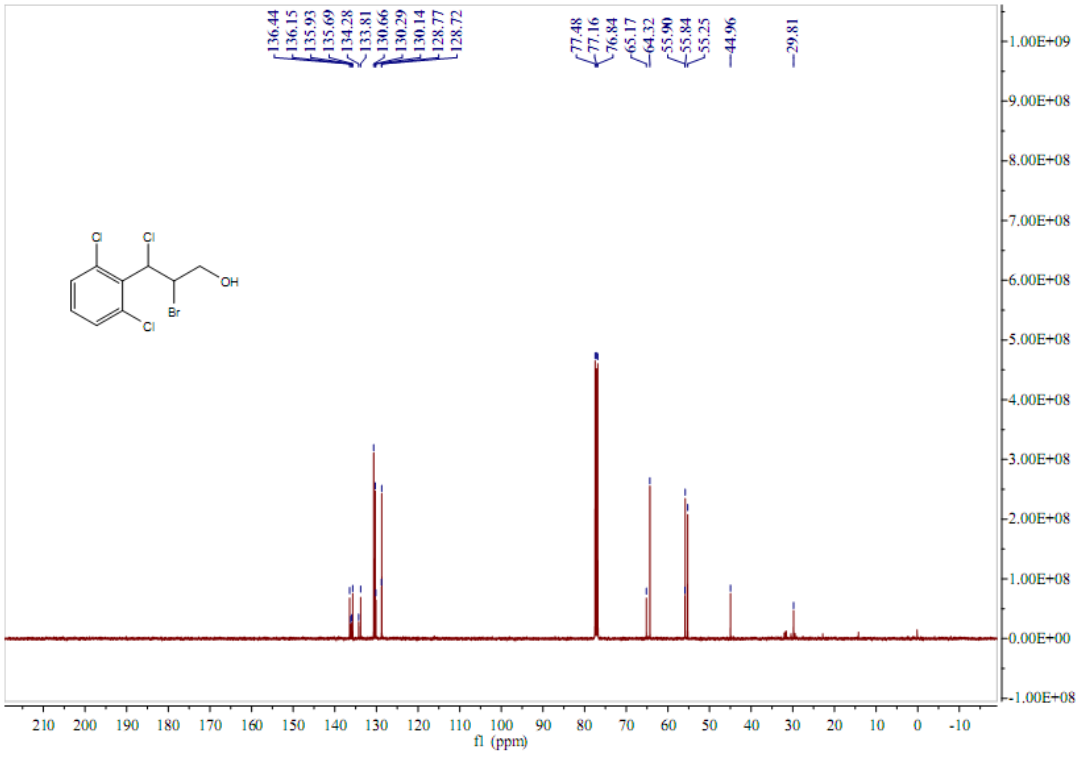
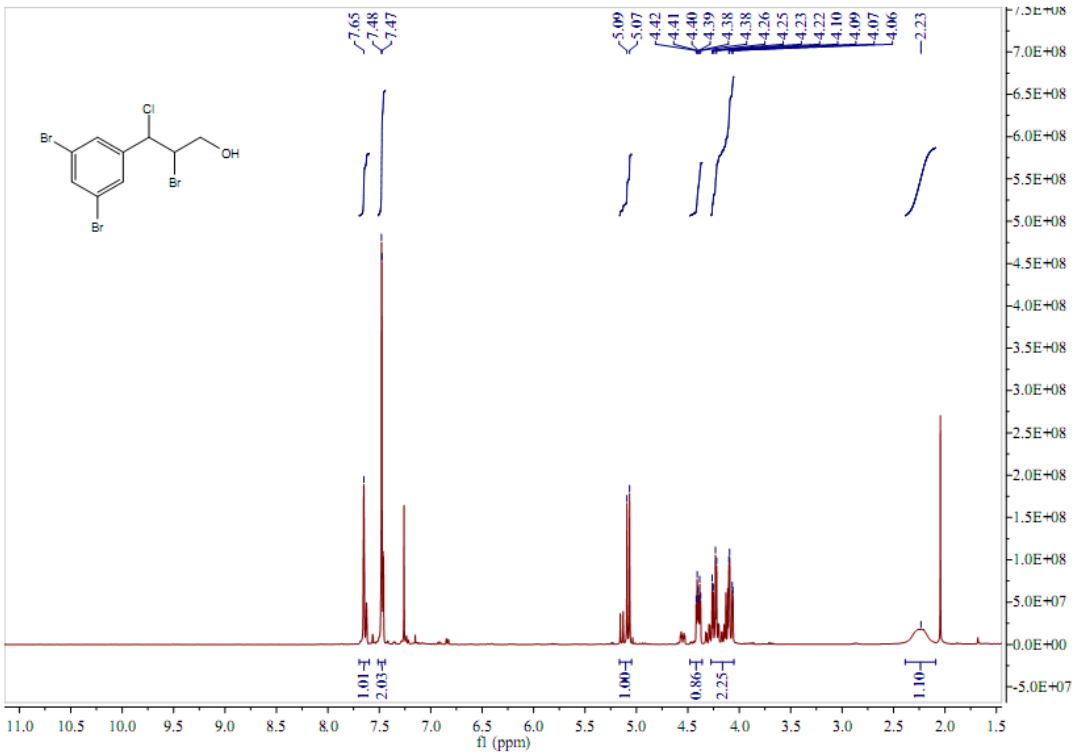
76.84
64.75
61.76
59.83
34.75
31.37
Cl
OH
Br
H3C
H3C
CH3
fl (ppm)


7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.23
7.21
7.21
7.19
7.19
7.17
6.19
6.16
5.39
5.39
5.38
5.36
4.28
4.26
4.25
4.20
4.19
4.16
4.16
2.14
Cl
Cl
OH
Br
Cl
2.06
1.00
0.77
0.80
2.20
1.07
f1 (ppm)


136.44
136.15
135.93
135.69
134.28
133.81
130.66
130.29
130.14
128.77
128.72
77.48
77.16
76.84
65.17
64.32
55.90
55.84
55.25
44.96
29.81
Cl
Cl
OH
Br
Cl
f1 (ppm)


Cl
Br
OH
Br
Br
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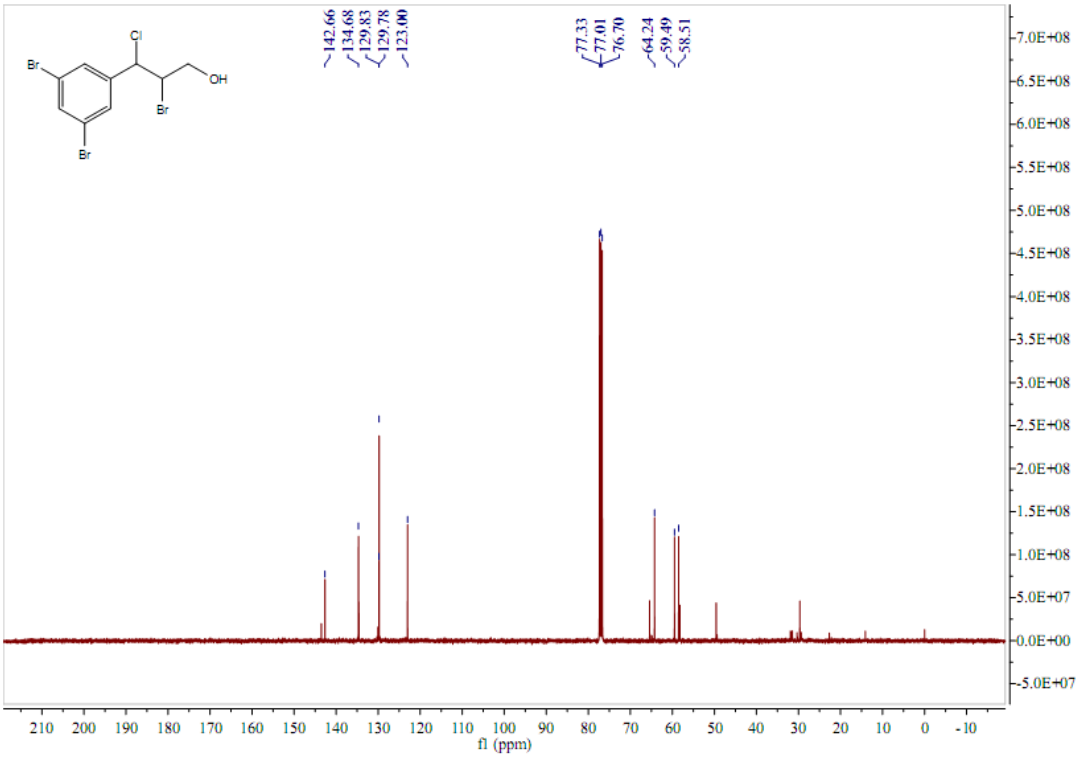
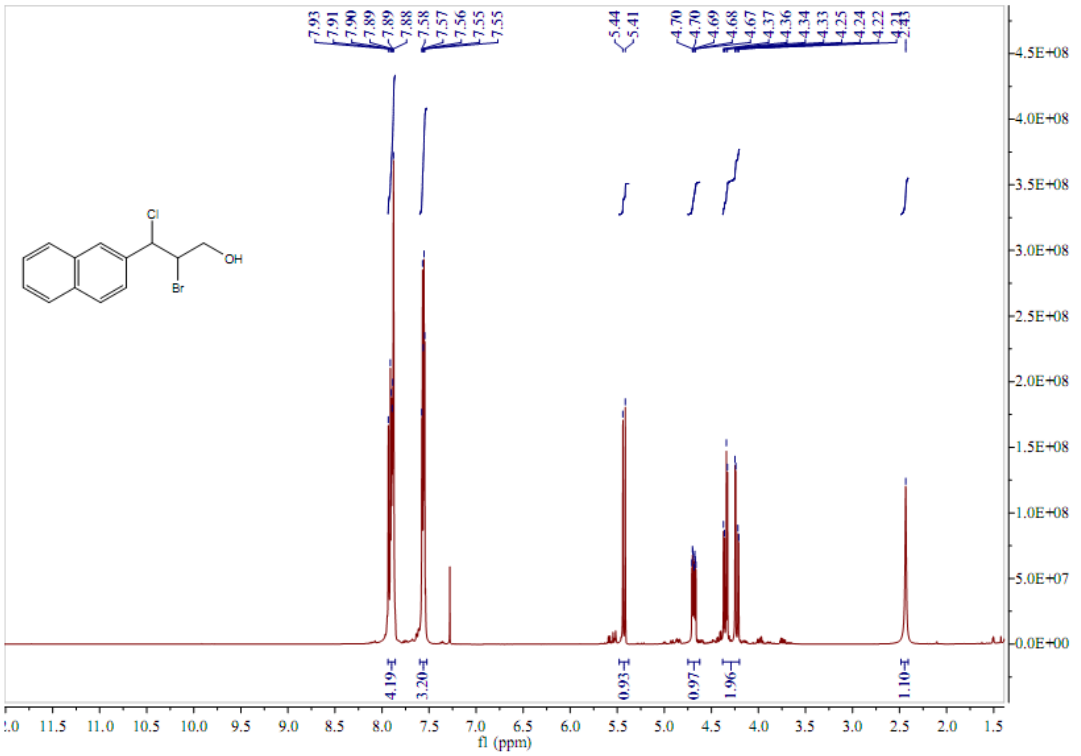
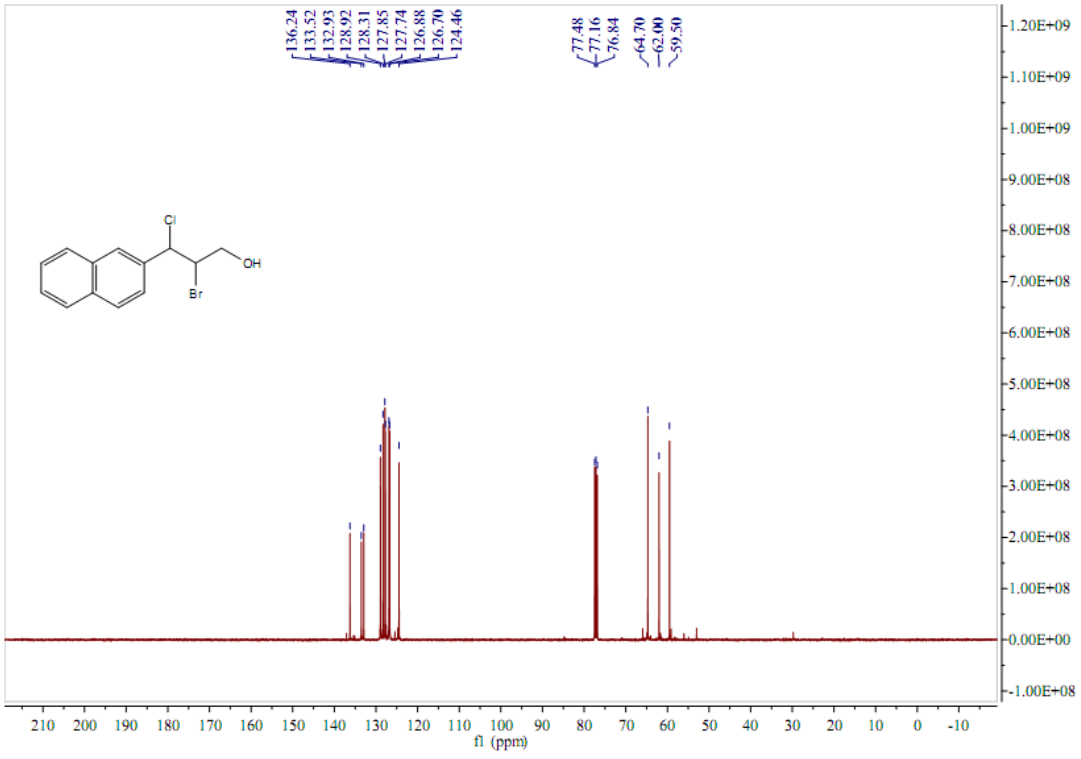
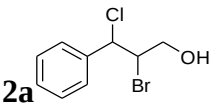
7.48
7.47
5.09
5.07
4.42
4.41
4.40
4.39
4.38
4.38
4.26
4.25
4.23
4.22
4.10
4.09
4.07
4.06
2.23
1.01
2.03
1.00
0.86
2.25
1.10
fl (ppm)


Cl
Br
OH
Br
Br
142.66
134.68
129.83
129.78
123.00
77.33
77.01
76.70
64.24
59.49
58.51
fl (ppm)

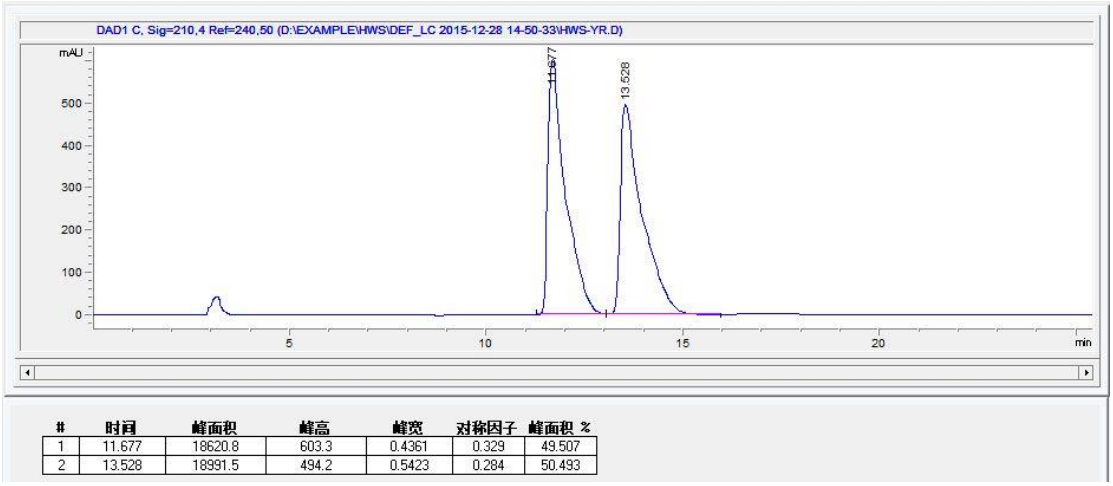

7.93
7.91
7.90
7.89
7.89
7.88
7.58
7.57
7.56
7.55
7.55
5.44
5.41
4.70
4.70
4.69
4.68
4.67
4.37
4.36
4.34
4.33
4.25
4.24
4.22
4.21
2.43
Cl
OH
Br
4.19
3.20
0.93
0.97
1.96
1.10
f1 (ppm)


136.24
133.52
132.93
128.92
128.31
127.85
127.74
126.88
126.70
124.46
77.48
77.16
76.84
64.70
62.00
59.50
Cl
OH
Br
f1 (ppm)

HPLC spectra



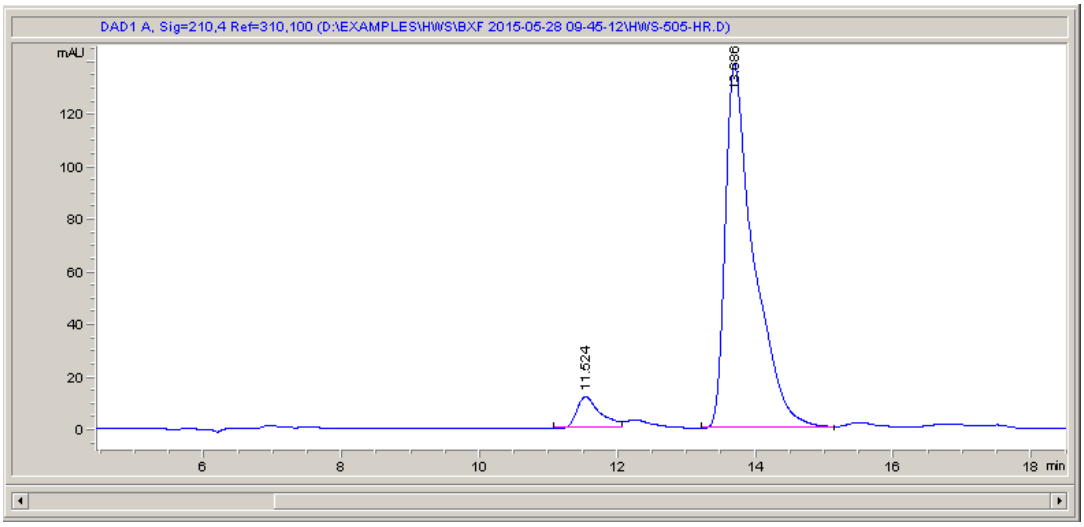
2a



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	11.677	18620.8	603.3	0.4361	0.329	49.507
2	13.528	18991.5	494.2	0.5423	0.284	50.493

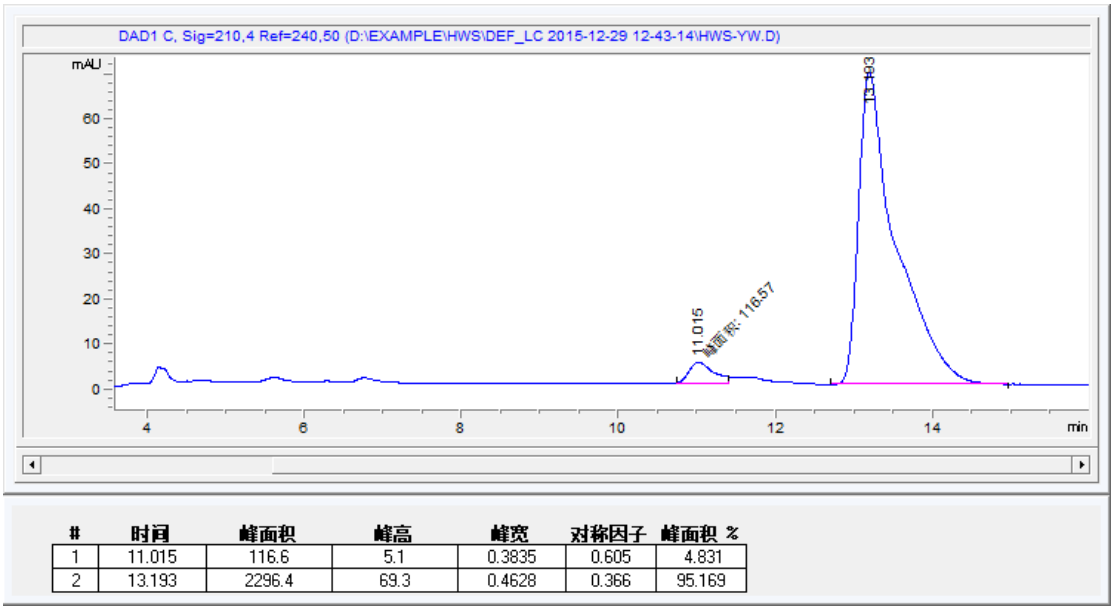
Ret Time	Area/mAU	Area/%
11.68	1322	49.601
13.82	1343.5	50.399

method A



Ret Time	Area/mAU	Area/%
11.52	286.5	6.704
13.68	3989.1	93.296

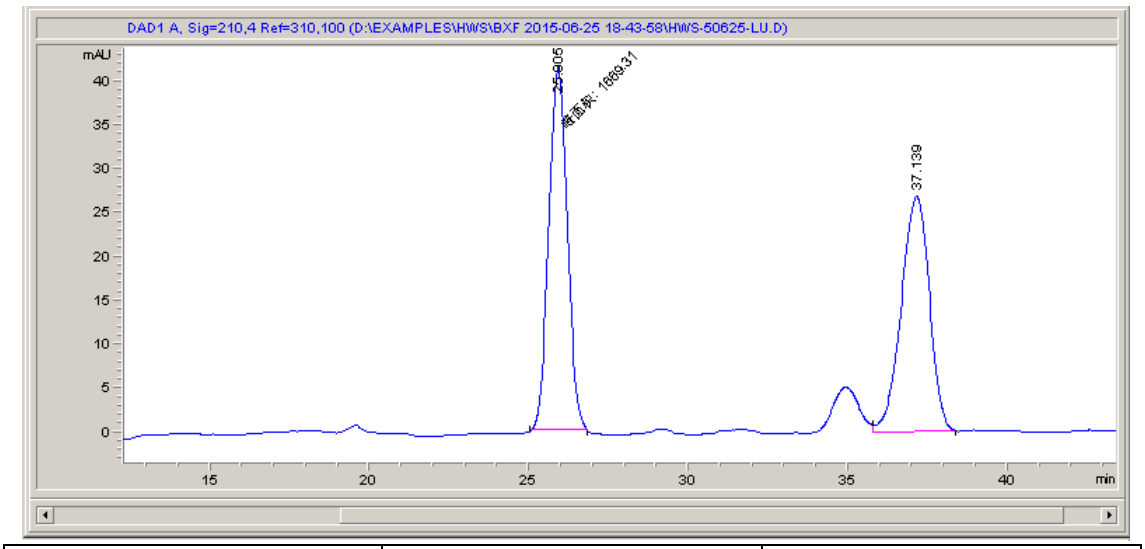
method B



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	11.015	116.6	5.1	0.3835	0.605	4.831
2	13.193	2296.4	69.3	0.4628	0.366	95.169

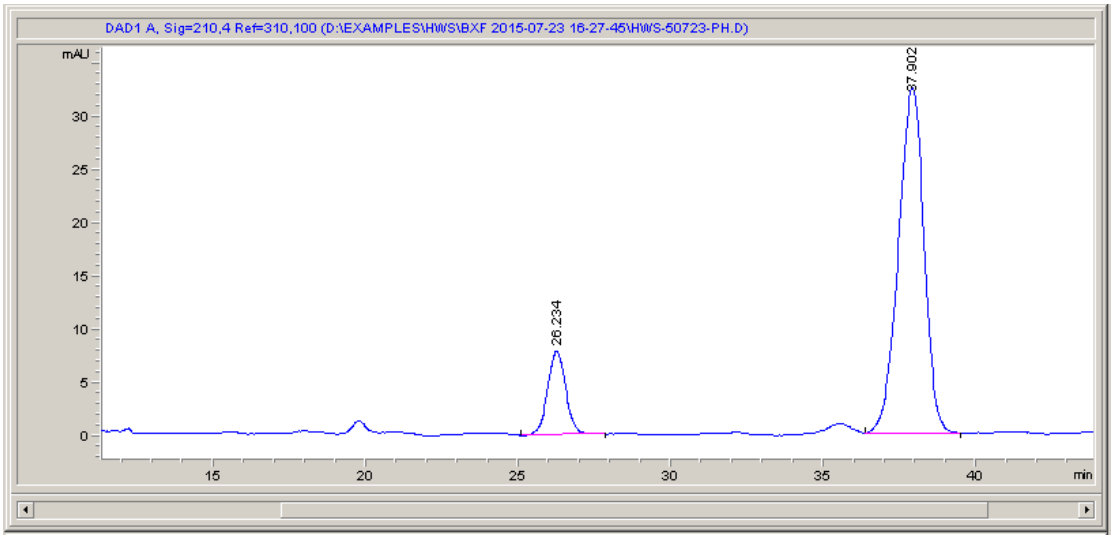
Ret Time	Area/mAU	Area/%
11..01	116.6	4.831
13.19	2296.4	95.169

2b



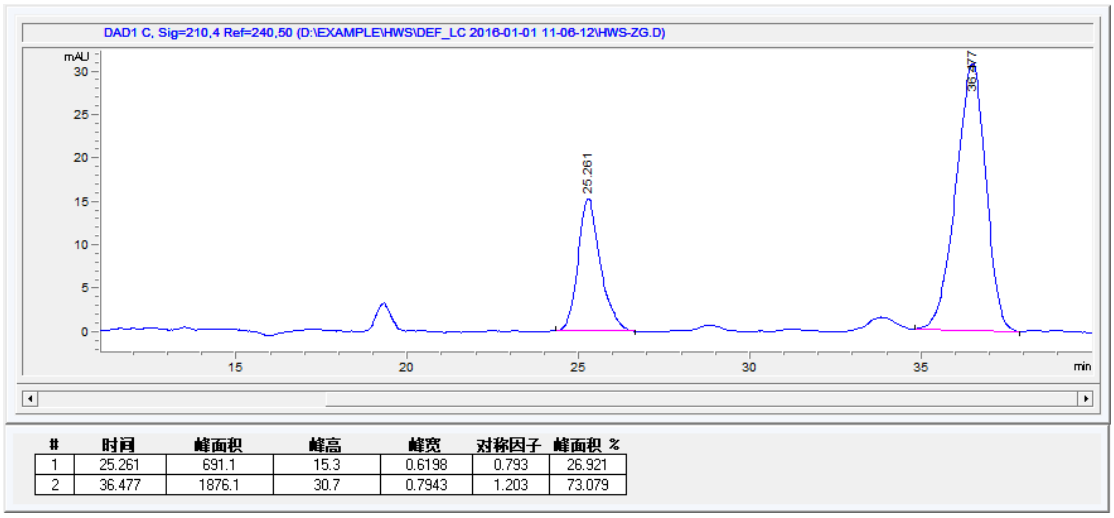
Ret Time	Area/mAU	Area/%
25.91	1669	50.185
37.14	1657	49.815

method A



Ret Time	Area/mAU	Area/%
26.23	355.5	15.047
37.90	1894.3	84.953

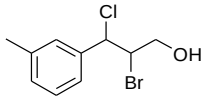
method B

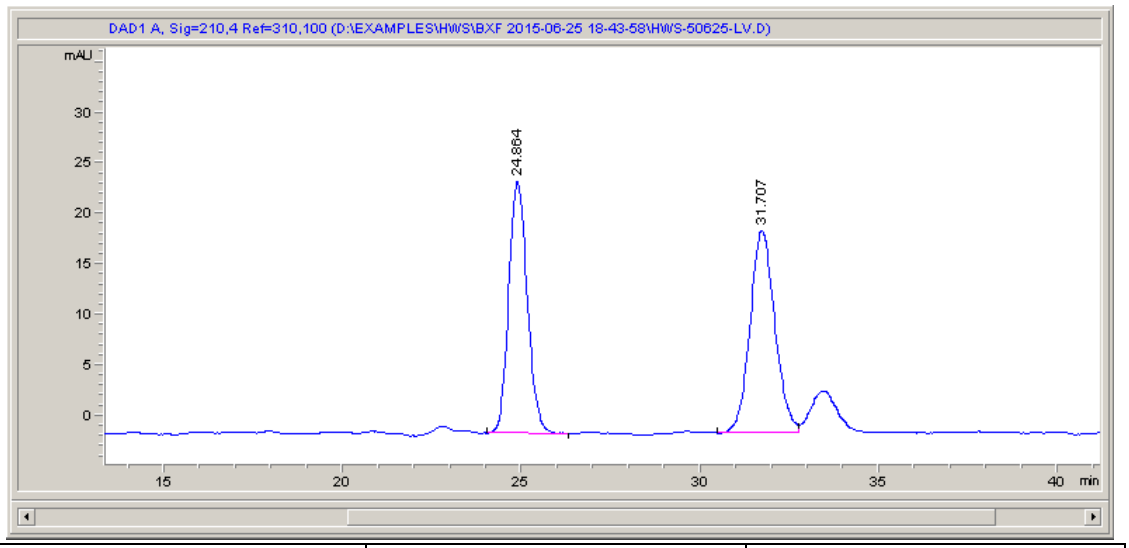


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	25.261	691.1	15.3	0.6198	0.793	26.921
2	36.477	1876.1	30.7	0.7943	1.203	73.079

Ret Time	Area/mAU	Area/%
25.26	691.1	26.921
36.48	1876.1	73.097

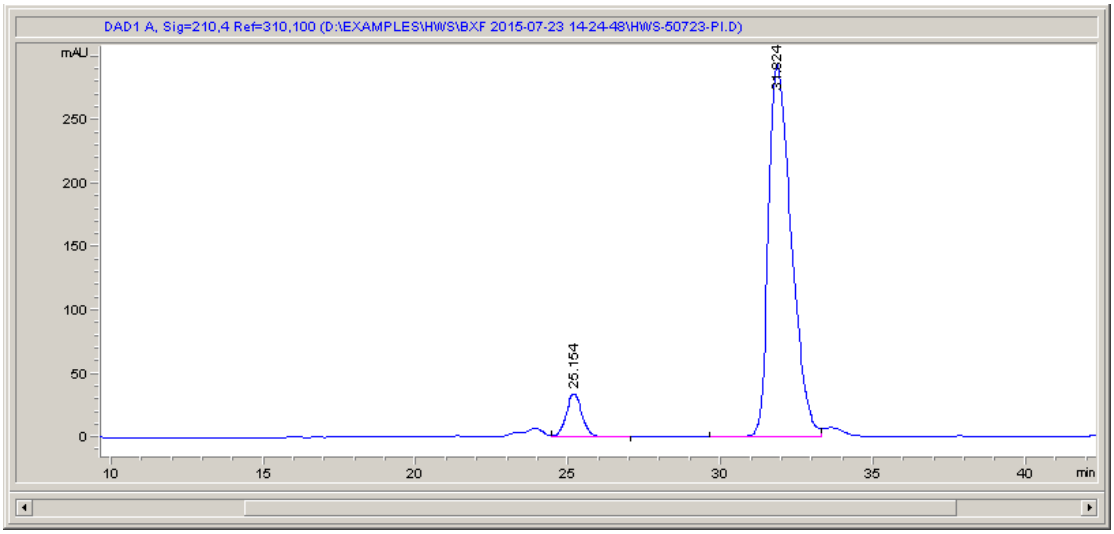
2c





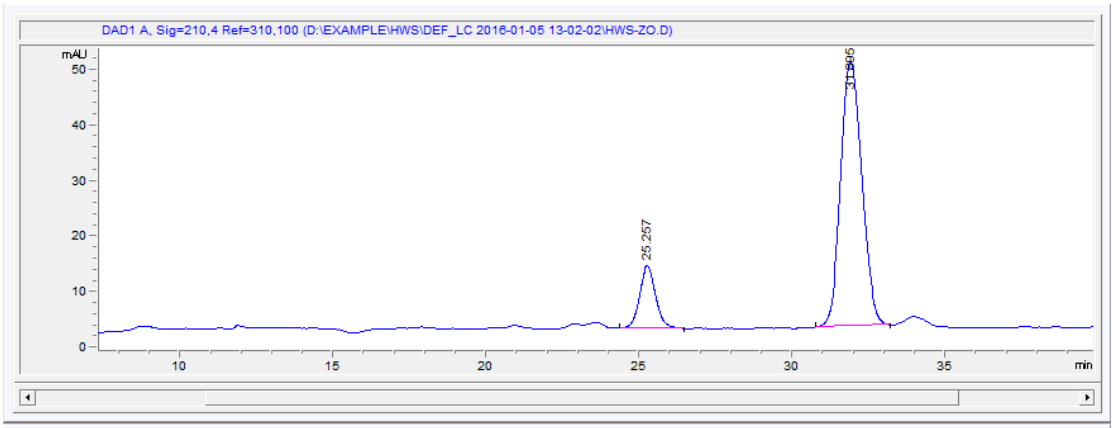
Ret Time	Area/mAU	Area/%
24.86	931.1	49.173
31.711	962.4	50.082

method A



Ret Time	Area/mAU	Area/%
25.15	1212.7	7.351
31.82	15285	92.649

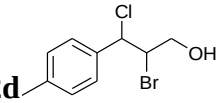
method B

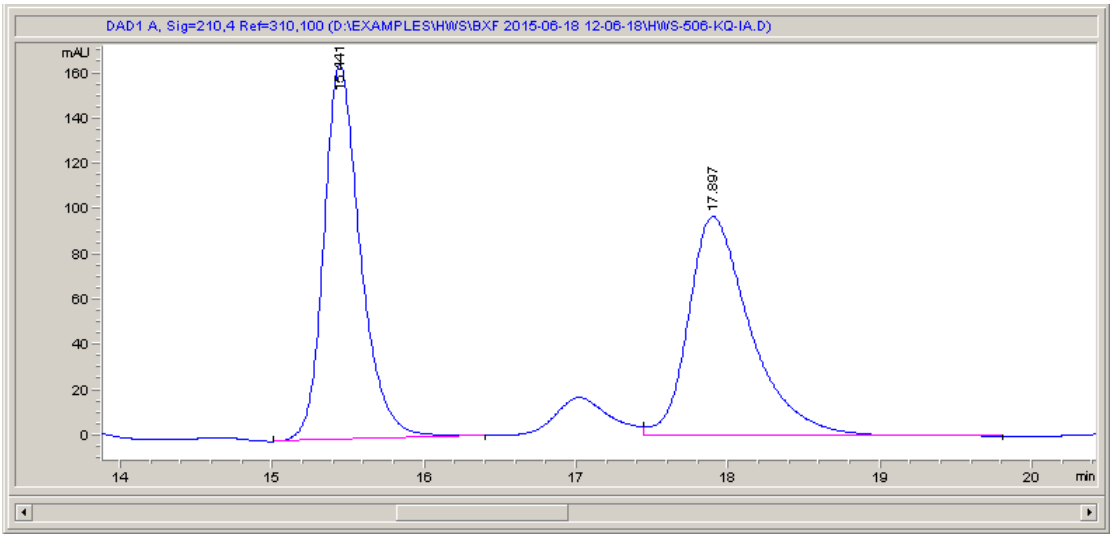


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	25.257	416.6	11.3	0.5353	0.922	15.493
2	31.895	2272.6	47.6	0.7369	0.84	84.507

Ret Time	Area/mAU	Area/%
25.25	416.6	15.49
31.89	2272.6	84.50

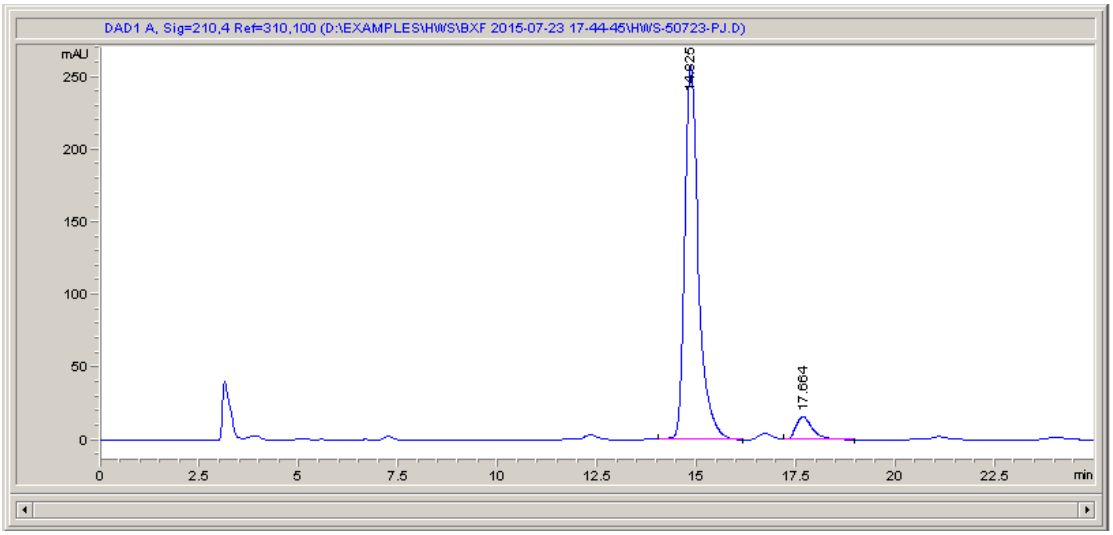
2d





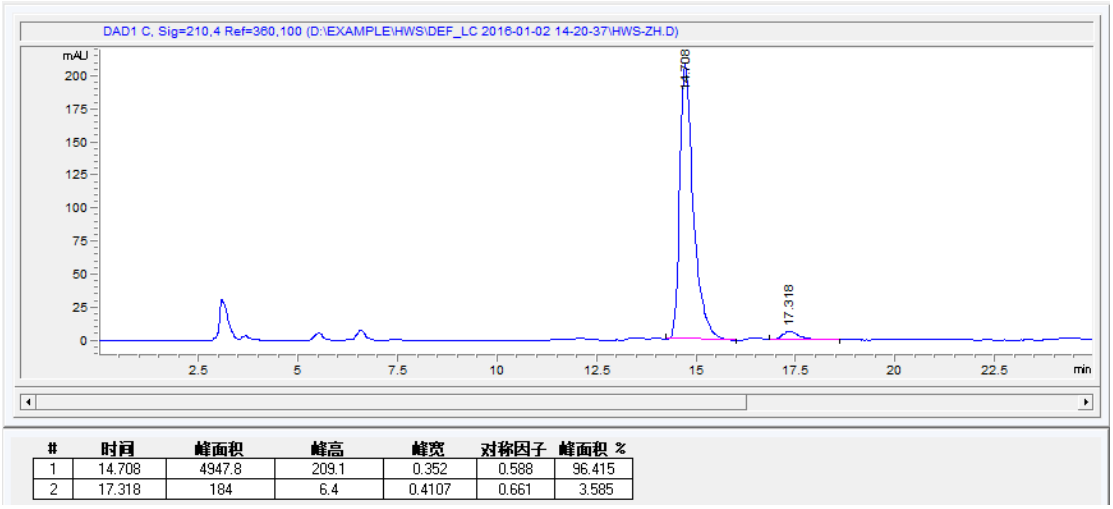
Ret Time	Area/mAU	Area/%
15.44	2658.2	50.01
17.89	2656.5	49.99

method A



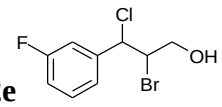
Ret Time	Area/mAU	Area/%
14.825	6343.8	93.077
17.664	471.9	6.923

method B

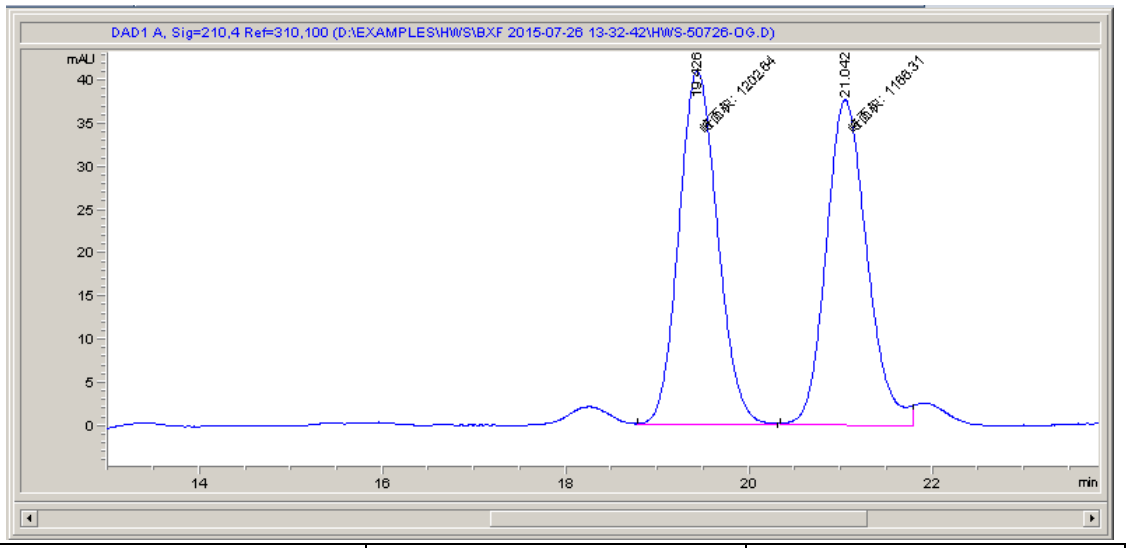


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	14.708	4947.8	209.1	0.352	0.588	96.415
2	17.318	184	6.4	0.4107	0.661	3.585

Ret Time	Area/mAU	Area/%
14.708	4947.8	96.415
17.318	184	3.585

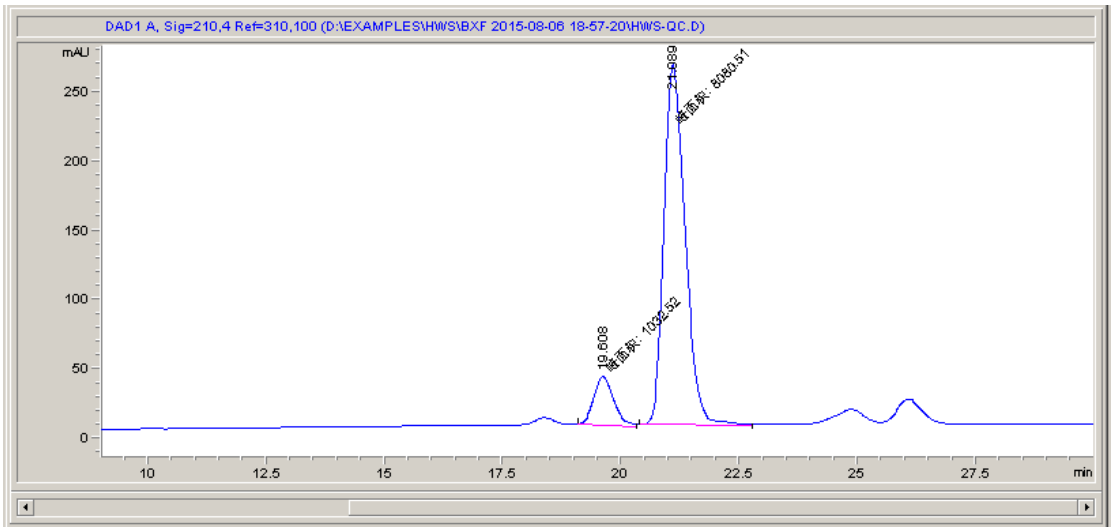


2e



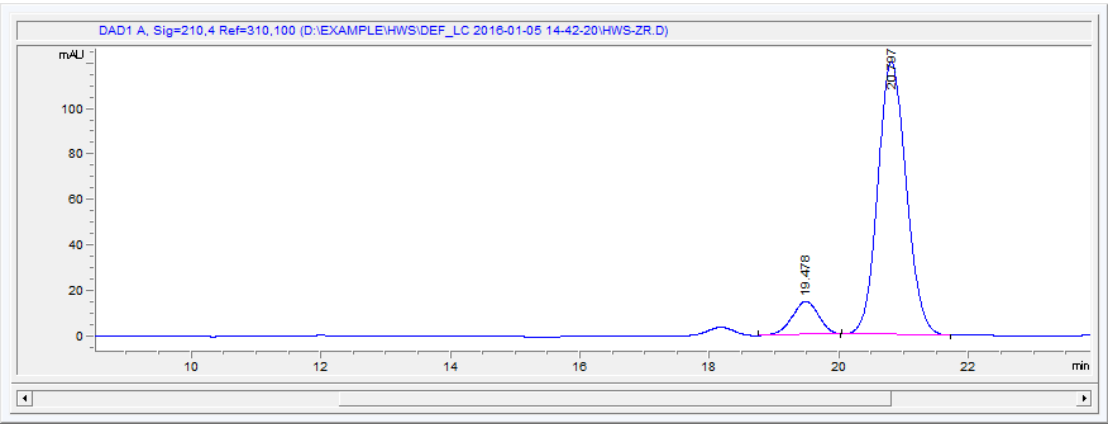
Ret Time	Area/mAU	Area/%
19.43	1200	50.82
21.04	1161	49.17

method A



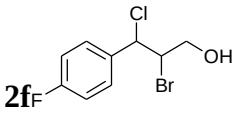
Ret Time	Area/mAU	Area/%
19.608	1012.6	10.844
21.089	8325.5	89.156

method B

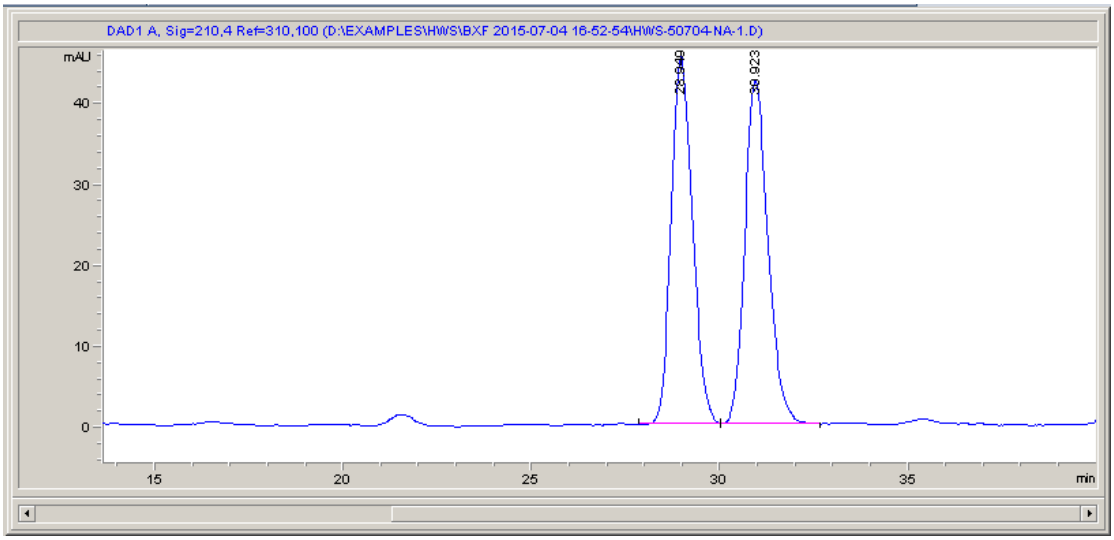


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	19.478	417.4	14.6	0.4344	1.084	10.256
2	20.797	3652.1	119.6	0.4781	0.861	89.744

Ret Time	Area/mAU	Area/%
19.478	417.4	10.256
20.797	3652.1	89.744

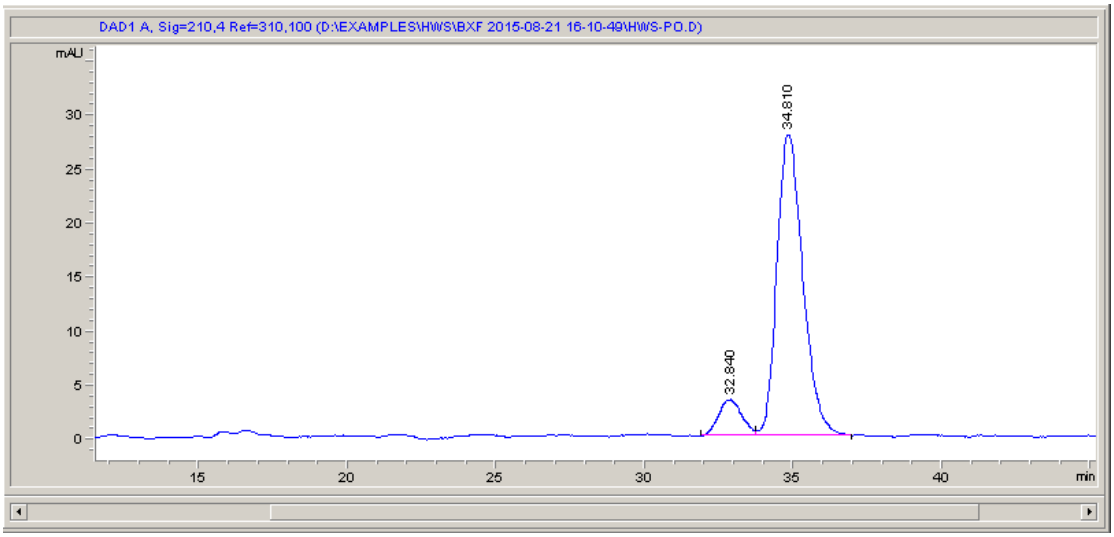


2f



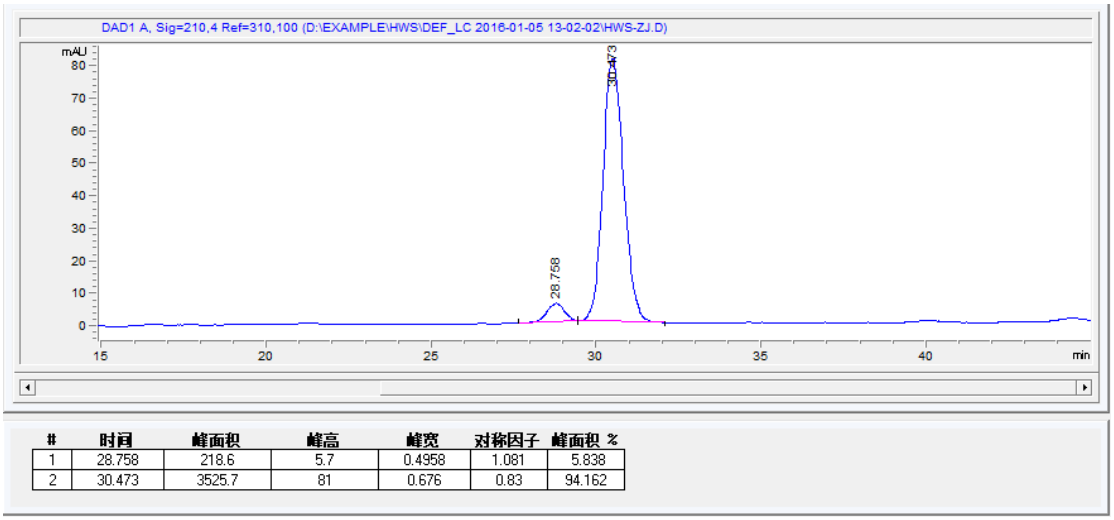
Ret Time	Area/mAU	Area/%
28.95	1790	49.638
30.923	1816	50.362

method A



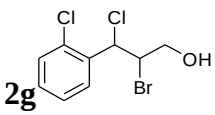
Ret Time	Area/mAU	Area/%
32.84	184.1	9.82
34.81	1690.5	90.18

method B

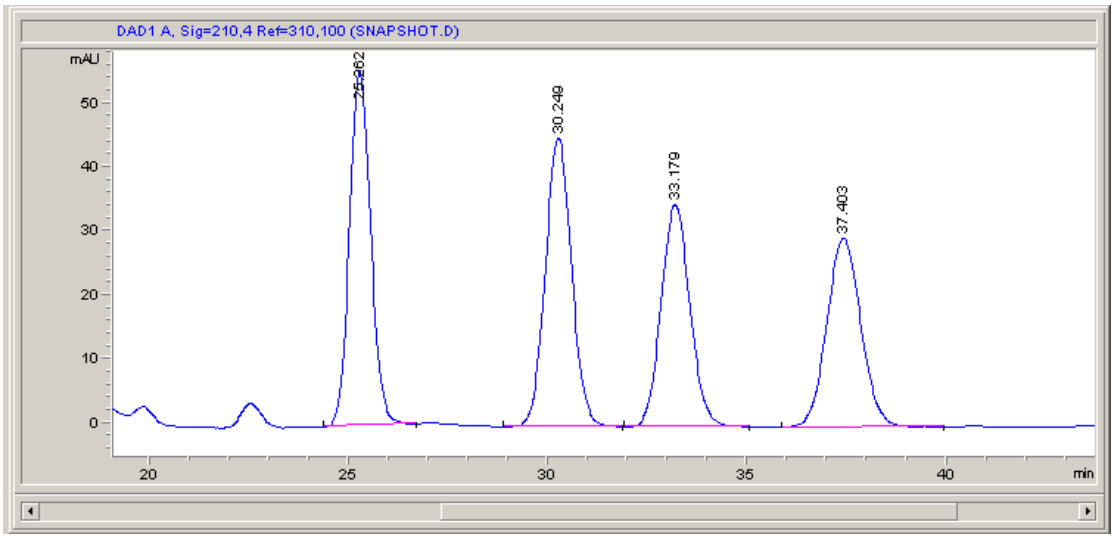


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	28.758	218.6	5.7	0.4958	1.081	5.838
2	30.473	3525.7	81	0.676	0.83	94.162

Ret Time	Area/mAU	Area/%
28.75	218.6	5.838
30.47	3525.7	94.162

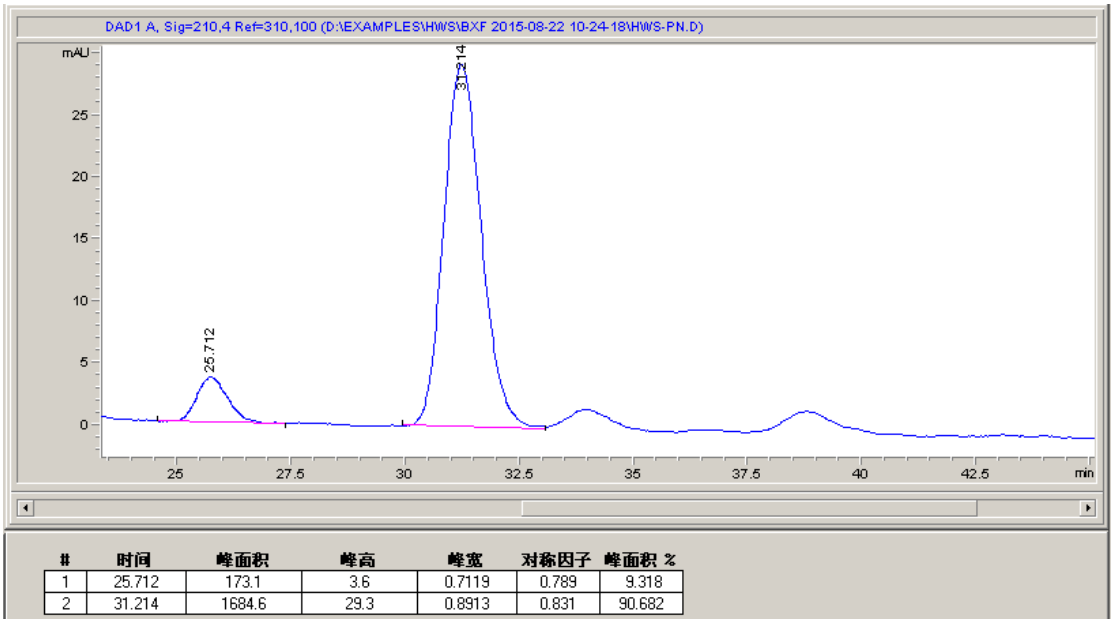


2g



Ret Time	Area/mAU	Area/%
25.26	2058.2	49.796
30.25	2075	50.02

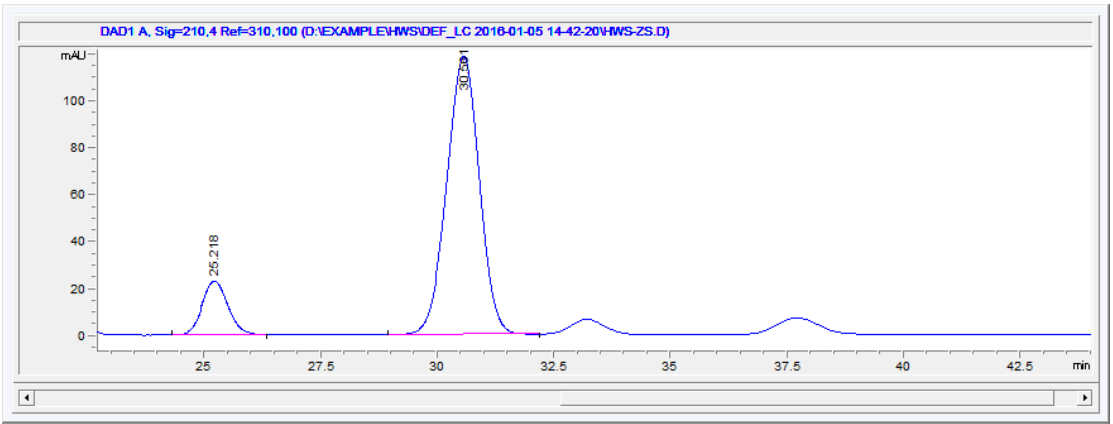
method A



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	25.712	173.1	3.6	0.7119	0.789	9.318
2	31.214	1684.6	29.3	0.8913	0.831	90.682

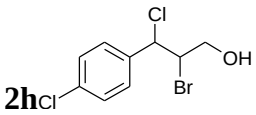
Ret Time	Area/mAU	Area/%
25.712	173.1	9.318
31.214	1684.6	90.682

method B

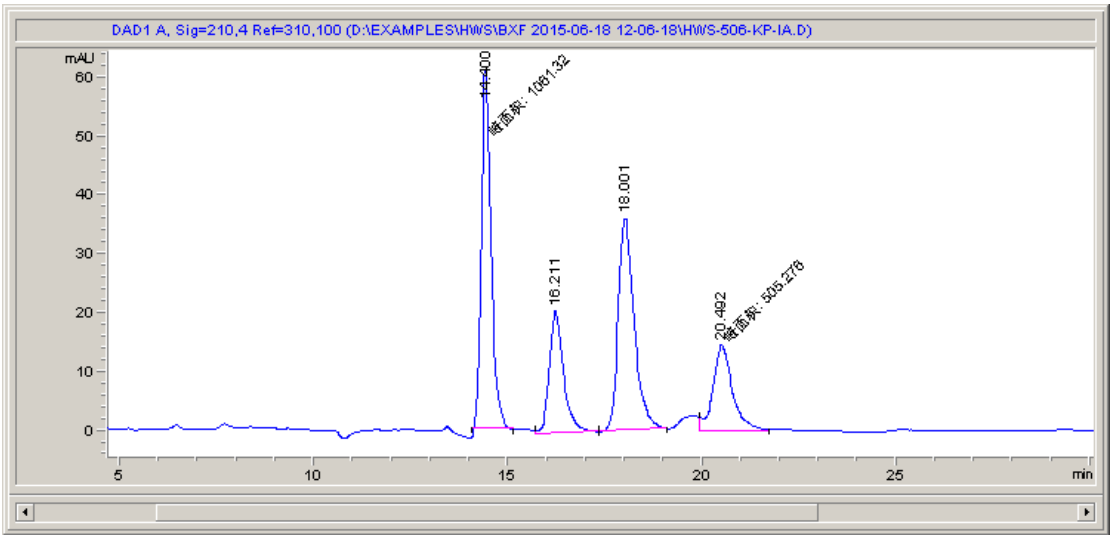


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	25.218	879.5	22.9	0.5724	0.916	13.315
2	30.561	5725.8	118.5	0.7278	1.07	86.685

Ret Time	Area/mAU	Area/%
25.218	879.5	13.313
31.561	5725.8	86.685

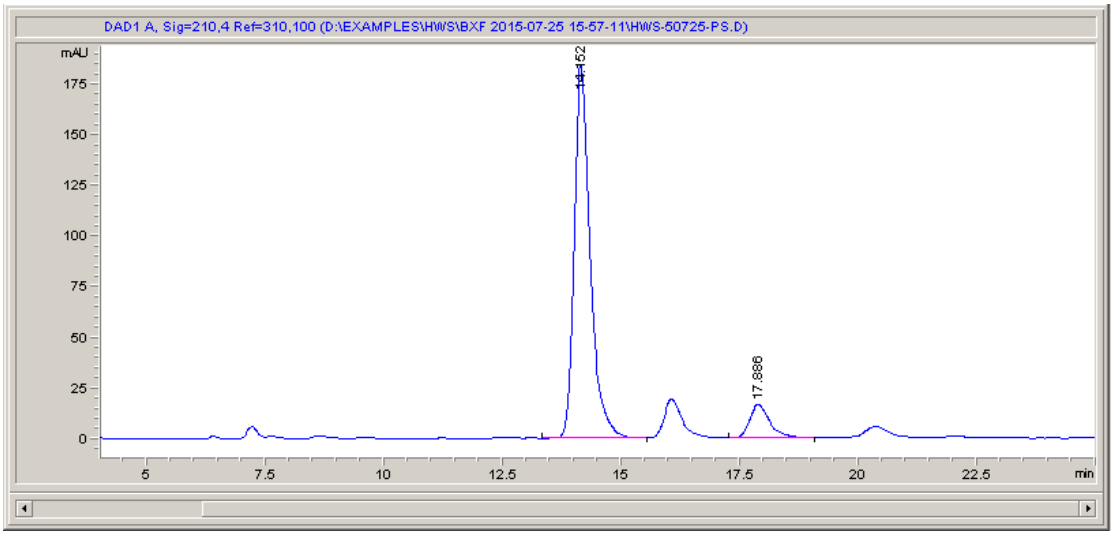


2h



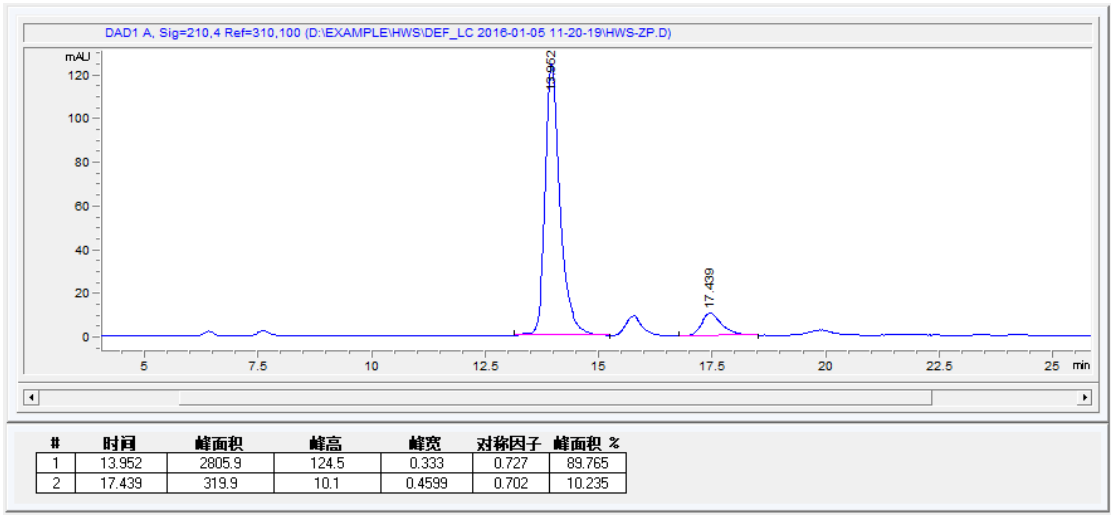
Ret Time	Area/mAU	Area/%
14.4	1061.3	50.67
18.0	1033.2	49.33

method A



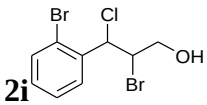
Ret Time	Area/mAU	Area/%
14.152	4328.4	89.786
17.886	492.4	10.214

method B

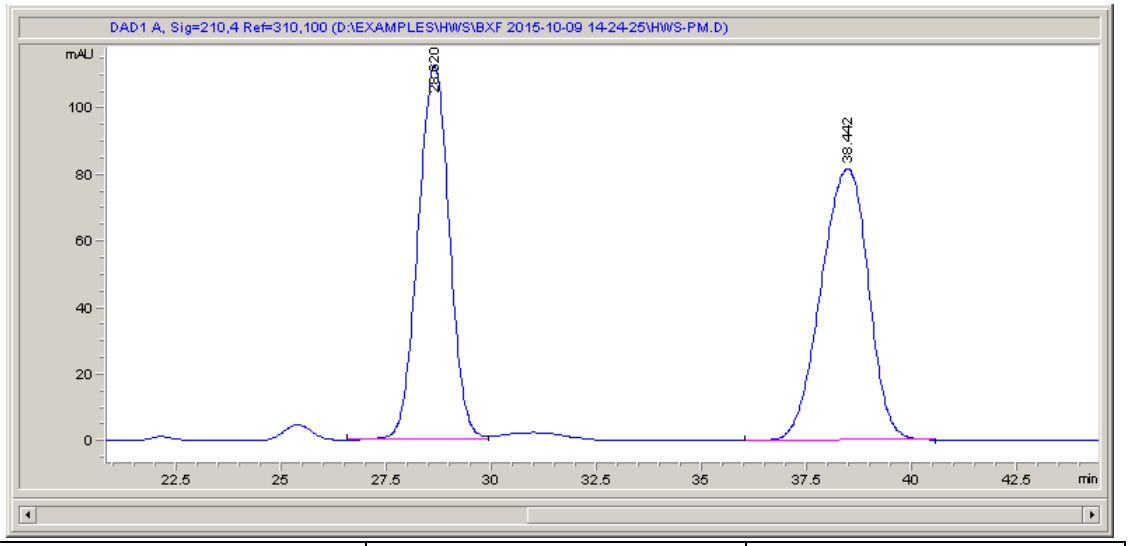


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	13.952	2805.9	124.5	0.333	0.727	89.765
2	17.439	319.9	10.1	0.4599	0.702	10.235

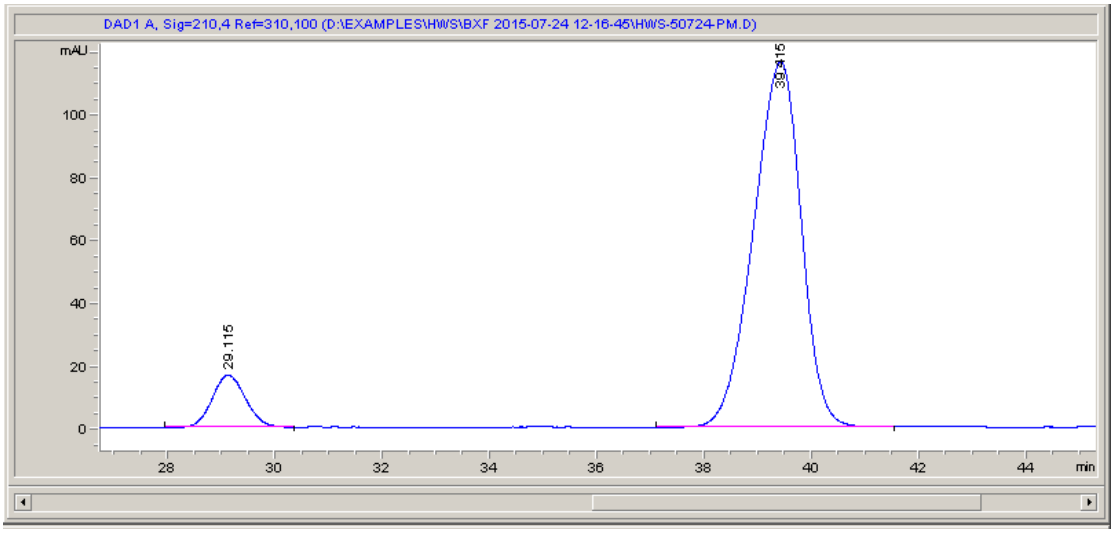
Ret Time	Area/mAU	Area/%
13.952	2805.9	89.765
17.439	319.9	10.235



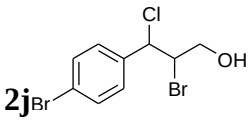
2i



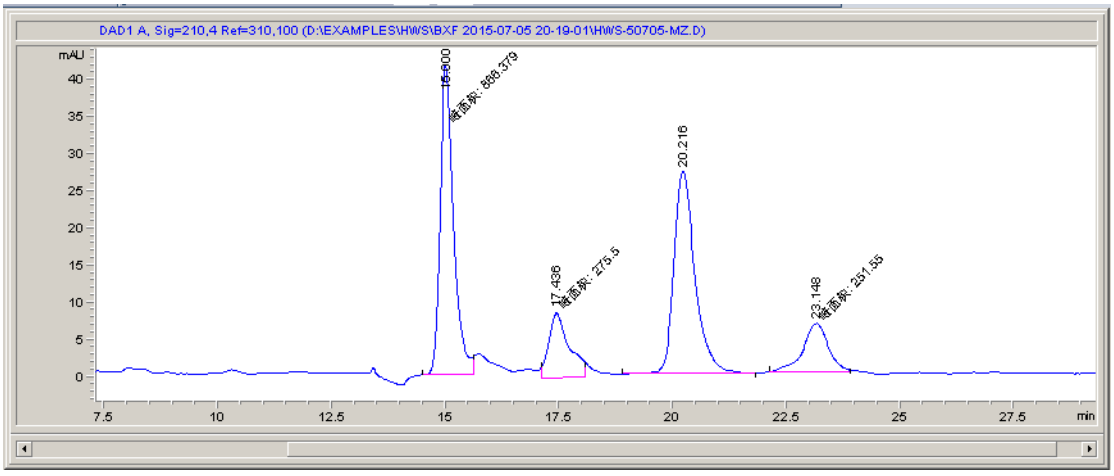
Ret Time	Area/mAU	Area/%
28.62	5830.3	47.728
38.44	6385.3	52.272



Ret Time	Area/mAU	Area/%
29.115	719.6	9.073
39.415	7211.9	90.927

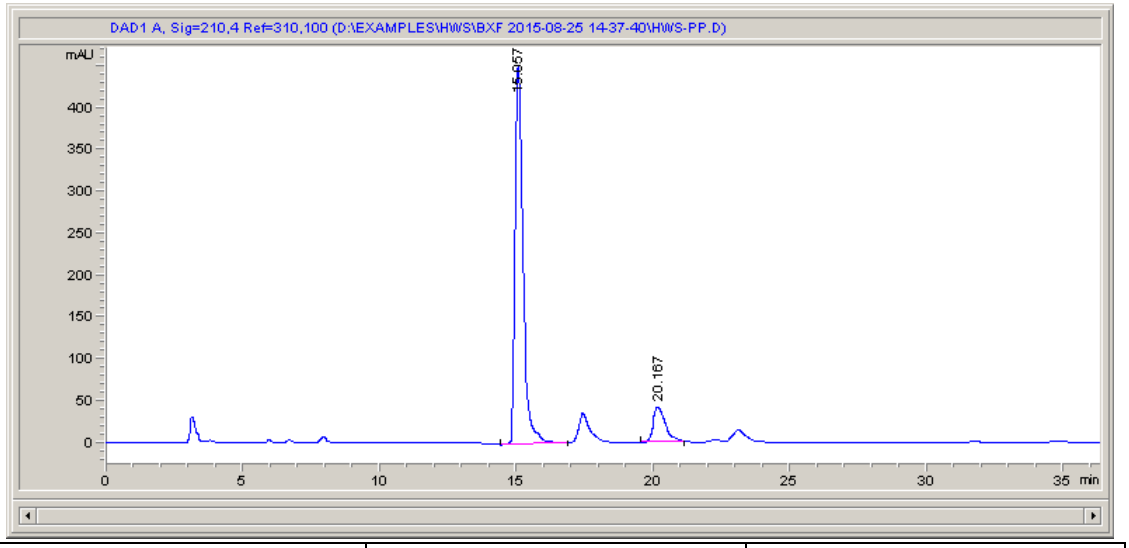


2j



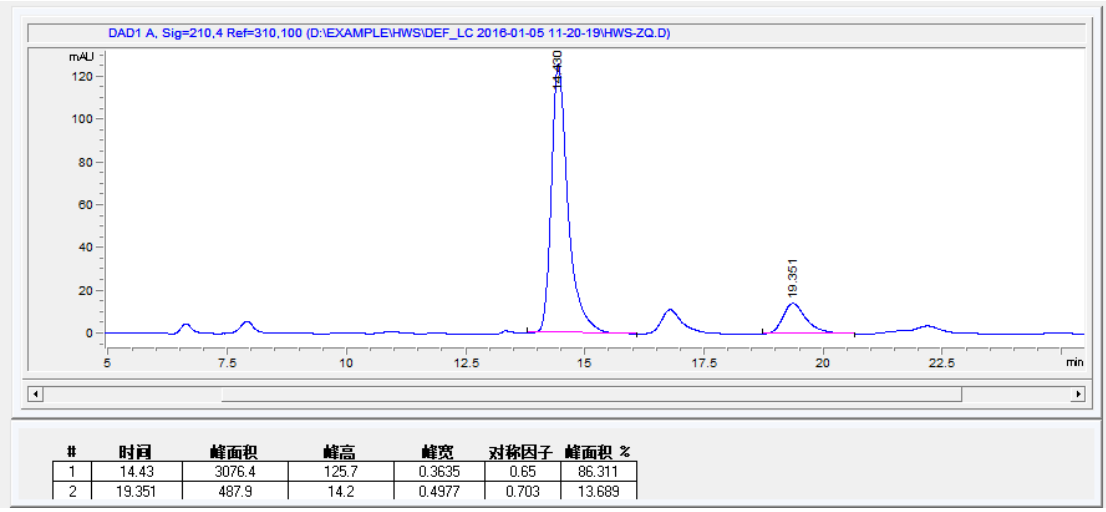
Ret Time	Area/mAU	Area/%
15.0	866.4	49.753
20.22	875	50.246

method A



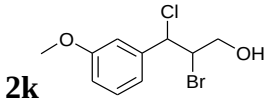
Ret Time	Area/mAU	Area/%
15.057	8914.7	87.451
20.167	1279.3	12.549

method B

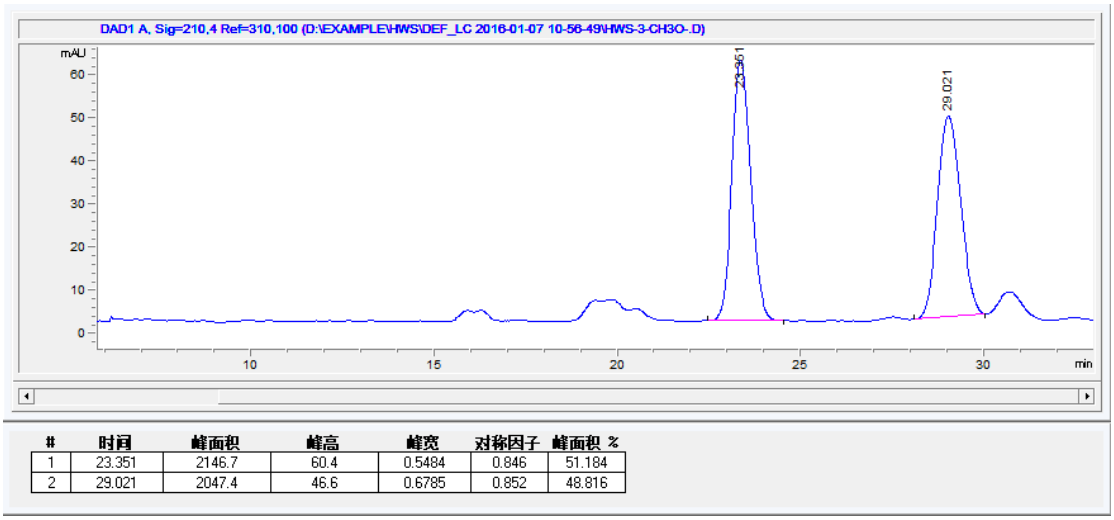


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	14.43	3076.4	125.7	0.3635	0.65	86.311
2	19.351	487.9	14.2	0.4977	0.703	13.689

Ret Time	Area/mAU	Area/%
14.43	3076.4	86.311
19.35	487.9	13.689

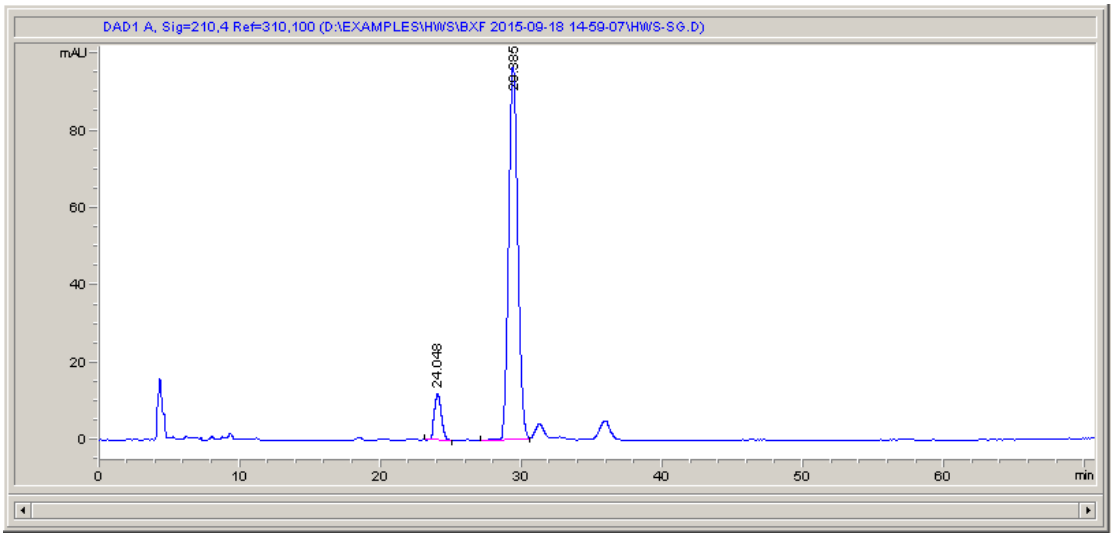


2k

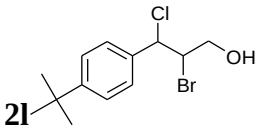


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	23.351	2146.7	60.4	0.5484	0.846	51.184
2	29.021	2047.4	46.6	0.6785	0.852	48.816

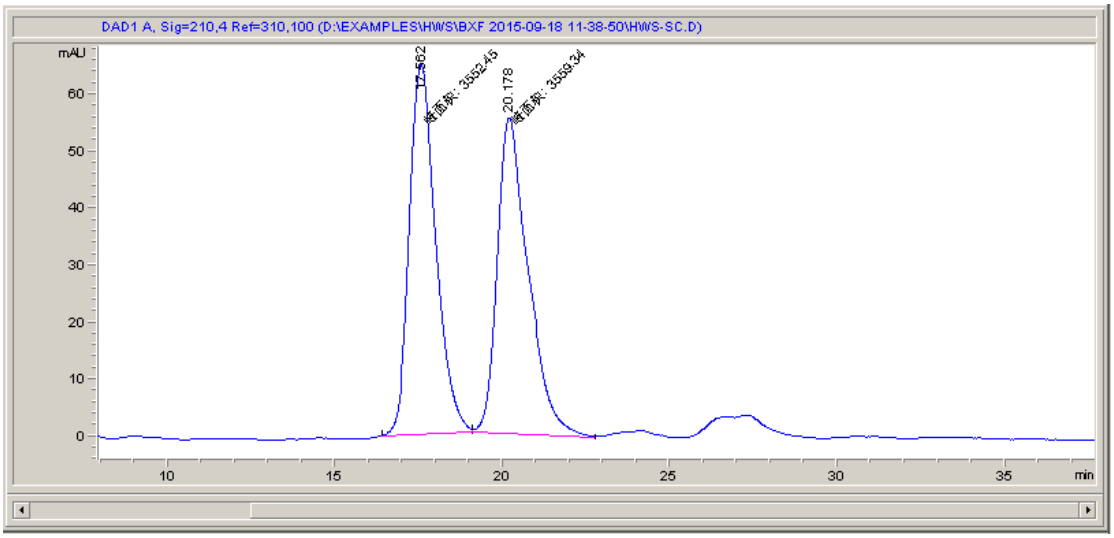
Ret Time	Area/mAU	Area/%
23.35	2146.7	51.184
29.02	2047.4	48.816



Ret Time	Area/mAU	Area/%
24.048	421.1	9.03
29.385	4242.4	90.97

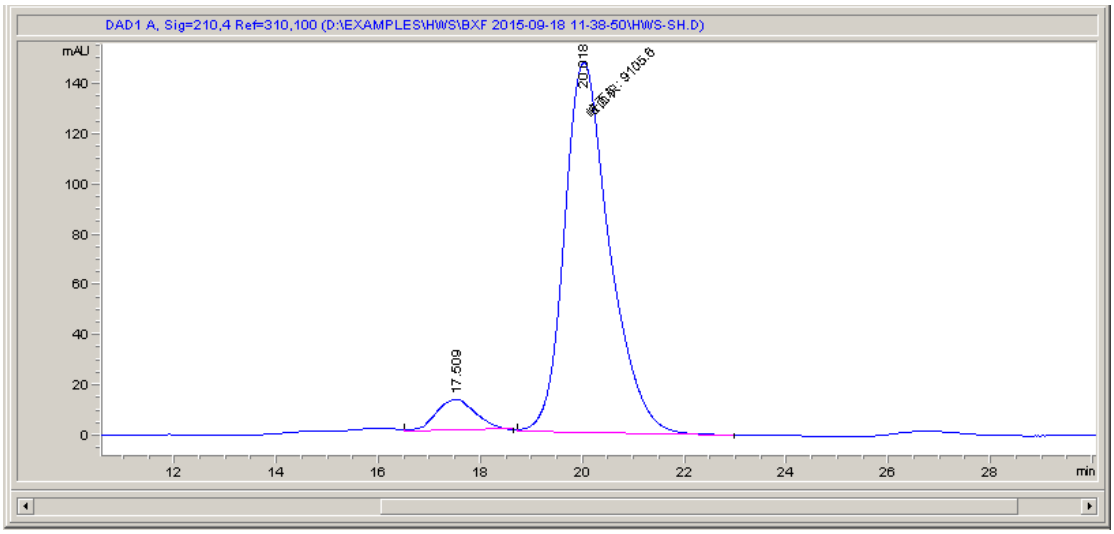


2l



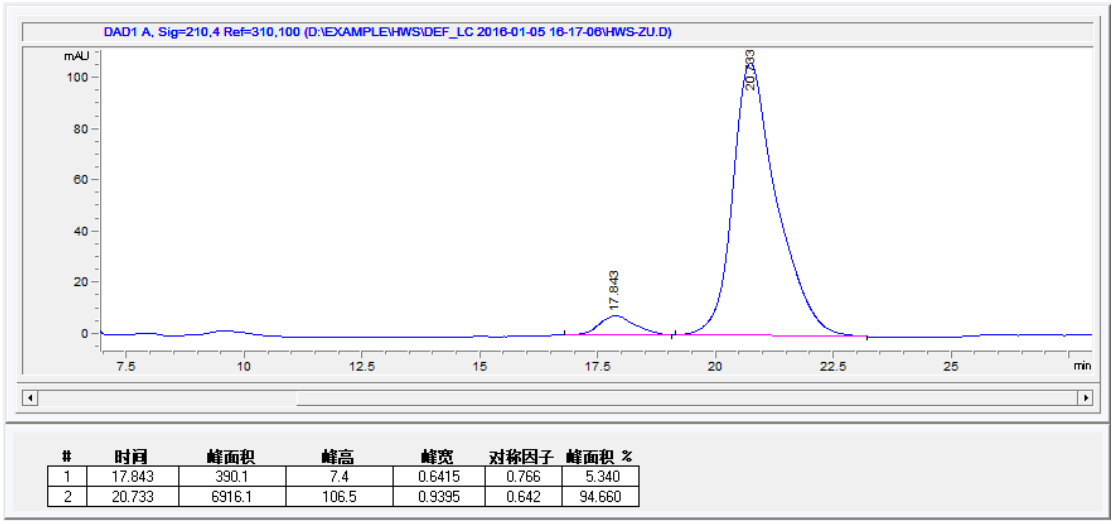
Ret Time	Area/mAU	Area/%
17.56	3552.4	49.952
20.17	3559.3	50.048

method A



Ret Time	Area/mAU	Area/%
17.509	693	7.073
20.018	9105.6	92.927

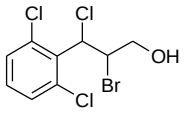
method B

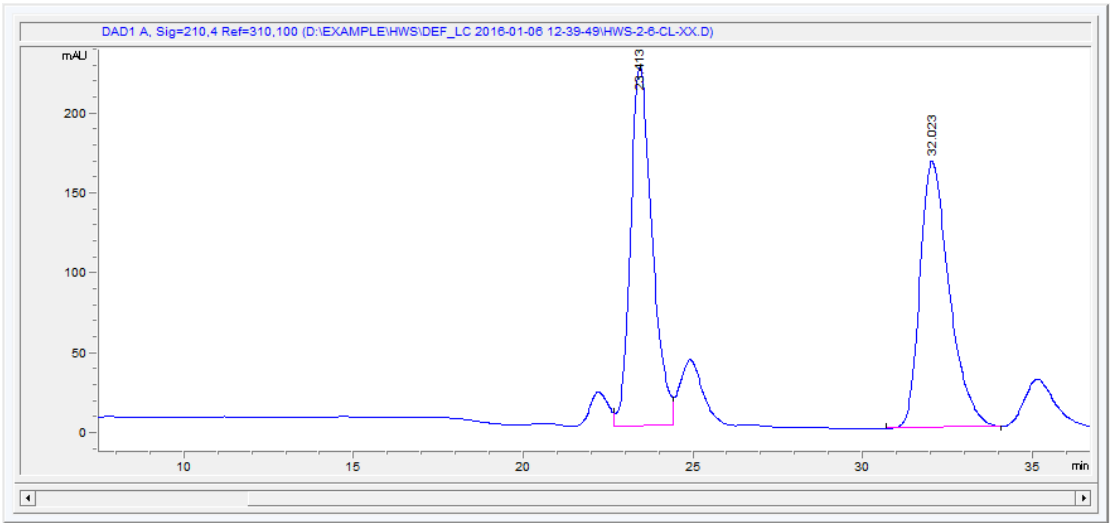


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	17.843	390.1	7.4	0.6415	0.766	5.340
2	20.733	6916.1	106.5	0.9395	0.642	94.660

Ret Time	Area/mAU	Area/%
17.843	390	5.34
20.733	6916.1	94.66

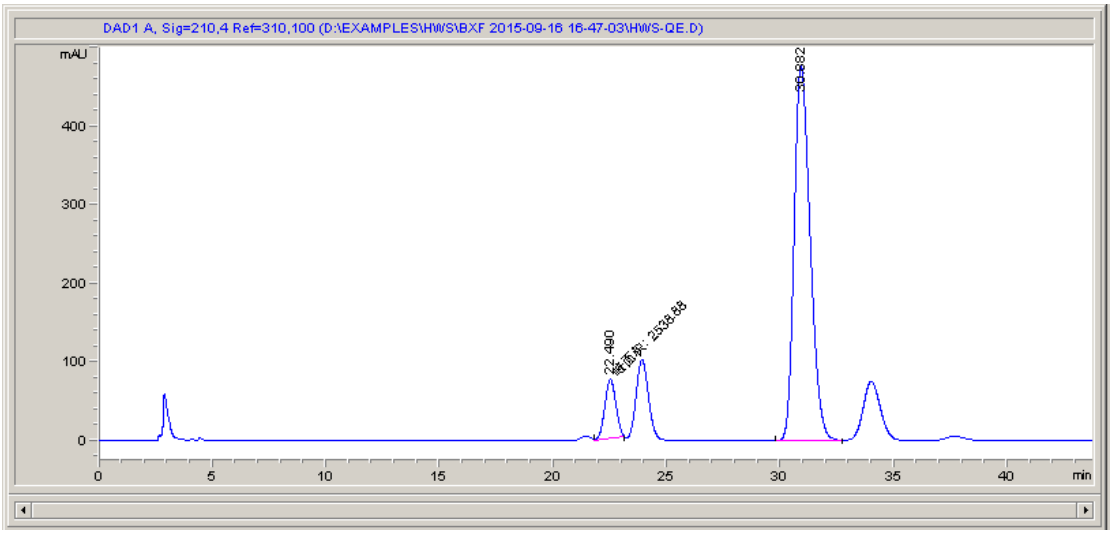
2m



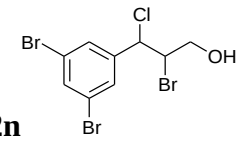


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	23.413	9995.6	224.6	0.6693	0.708	49.948
2	32.023	10016.2	166.7	0.9129	0.646	50.052

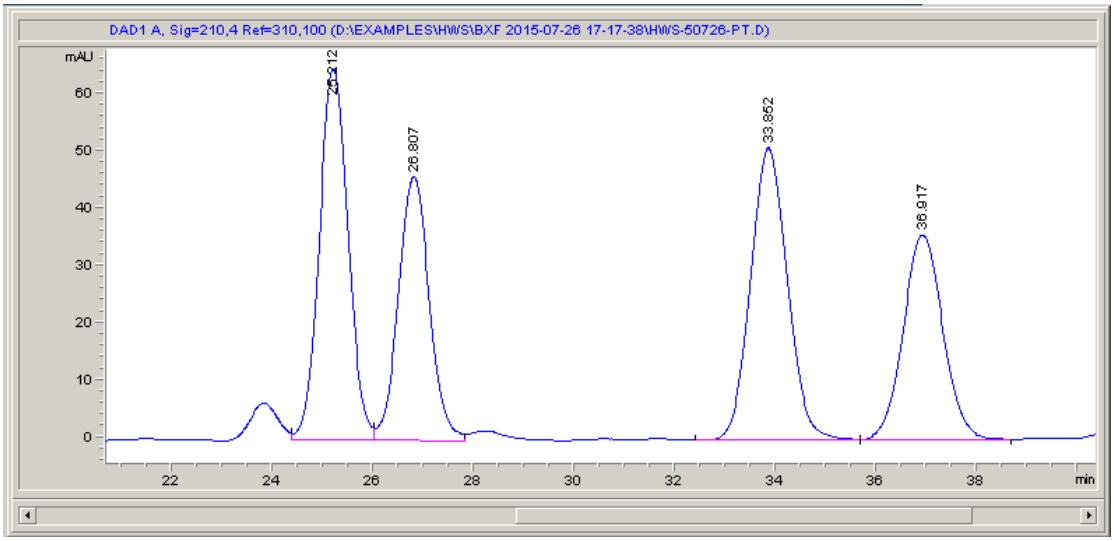
Ret Time	Area/mAU	Area/%
23.413	9995.6	49.94
32.023	10016.2	50.05



Ret Time	Area/mAU	Area/%
22.49	2538.9	9.794
30.882	23383.3	90.206

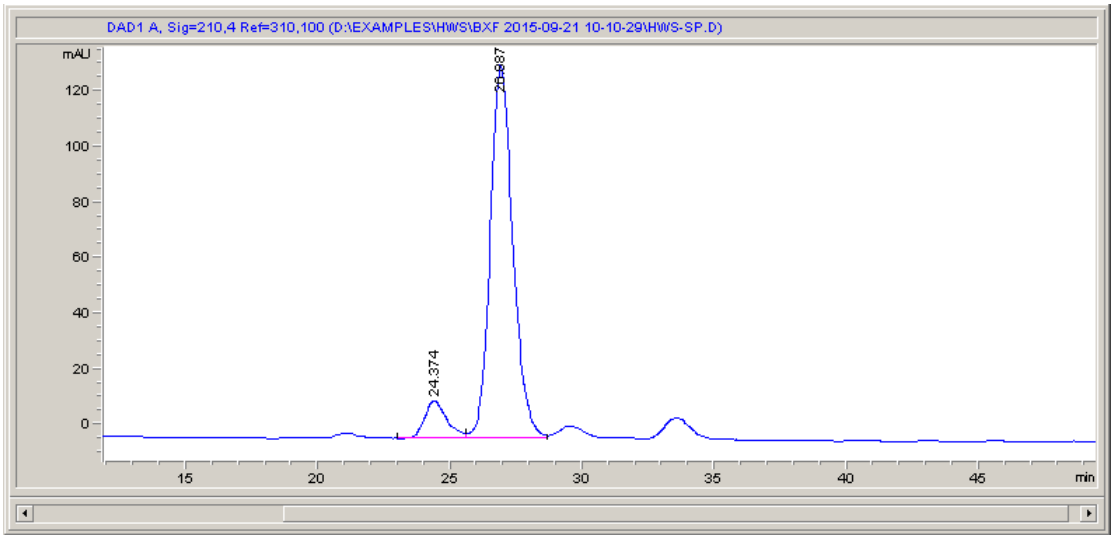


2n



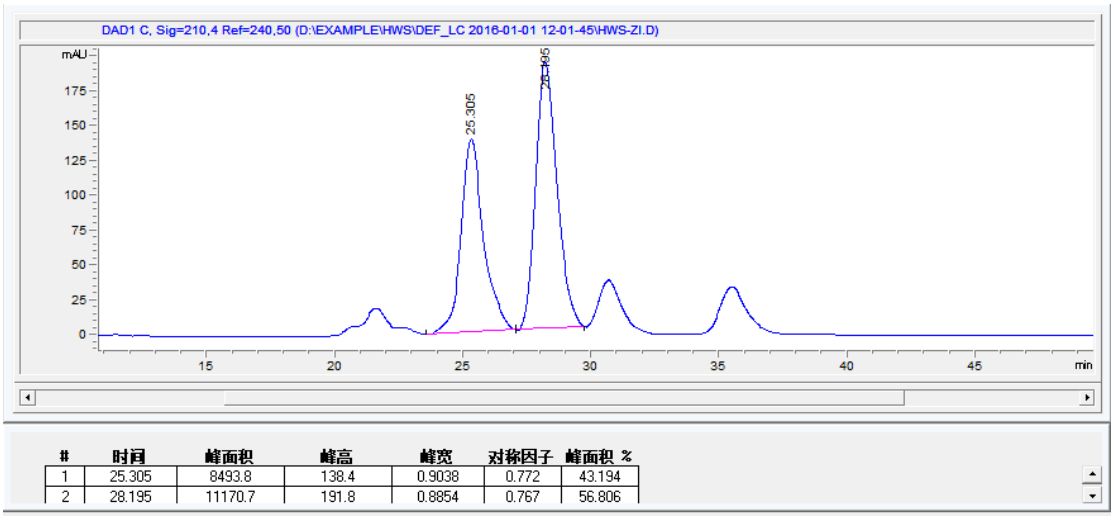
Ret Time	Area/mAU	Area/%
24.13	5752	49.93
26.80	5766	50.06

method A



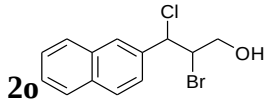
Ret Time	Area/mAU	Area/%
24.374	801.7	9.08
26.887	8027.6	90.92

method B

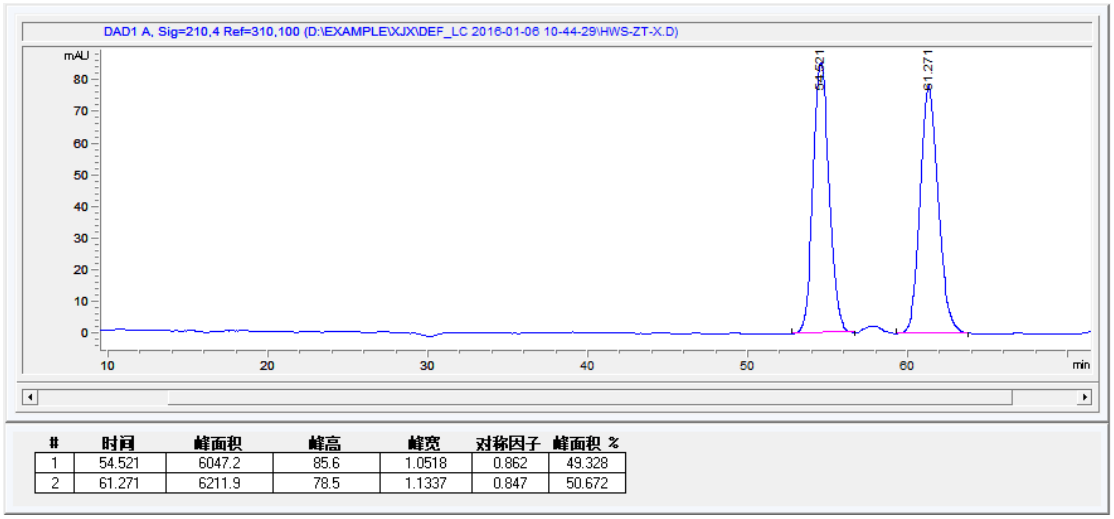


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	25.305	8493.8	138.4	0.9038	0.772	43.194
2	28.195	11170.7	191.8	0.8854	0.767	56.806

Ret Time	Area/mAU	Area/%
25.305	8493.8	43.194
28.195	11170.7	56.806



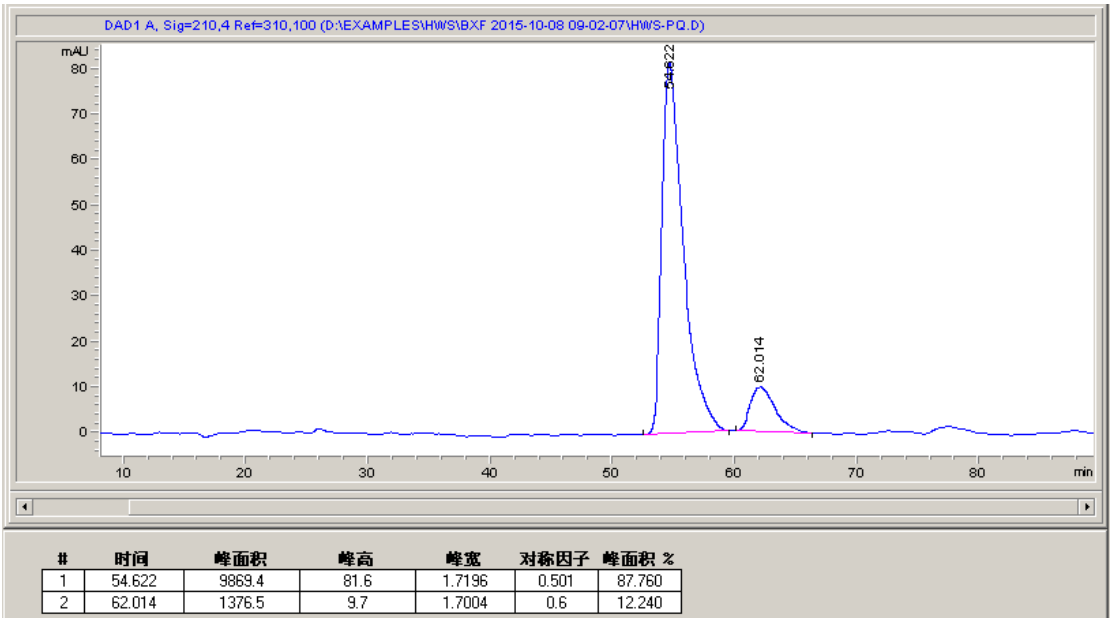
2o



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	54.521	6047.2	85.6	1.0518	0.862	49.328
2	61.271	6211.9	78.5	1.1337	0.847	50.672

Ret Time	Area/mAU	Area/%
54.521	6047.2	49.328
61.271	6211.9	50.672

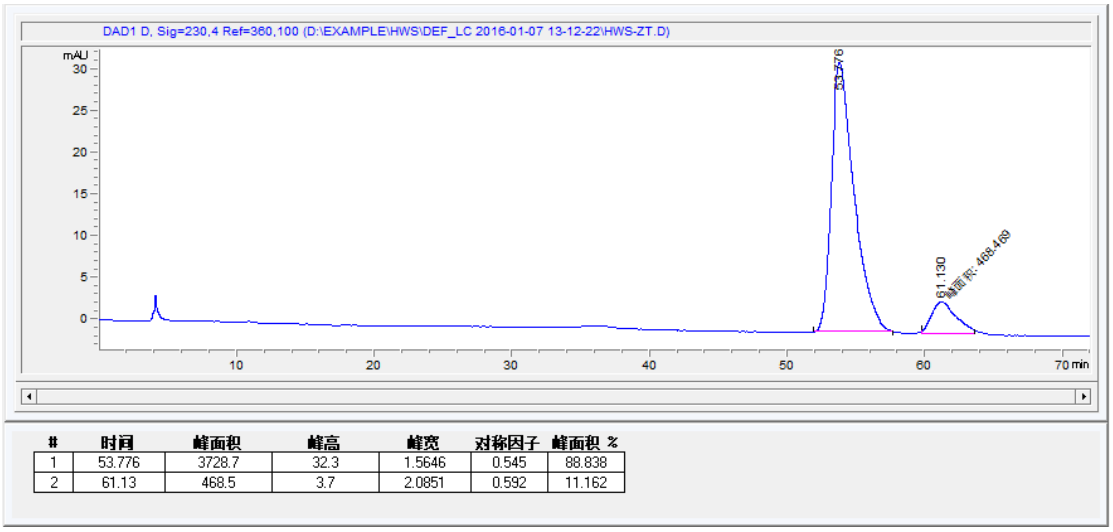
method A



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	54.622	9869.4	81.6	1.7196	0.501	87.760
2	62.014	1376.5	9.7	1.7004	0.6	12.240

Ret Time	Area/mAU	Area/%
54.622	9869.4	87.76
62.014	1376.5	12.24

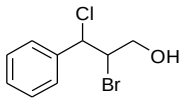
method B



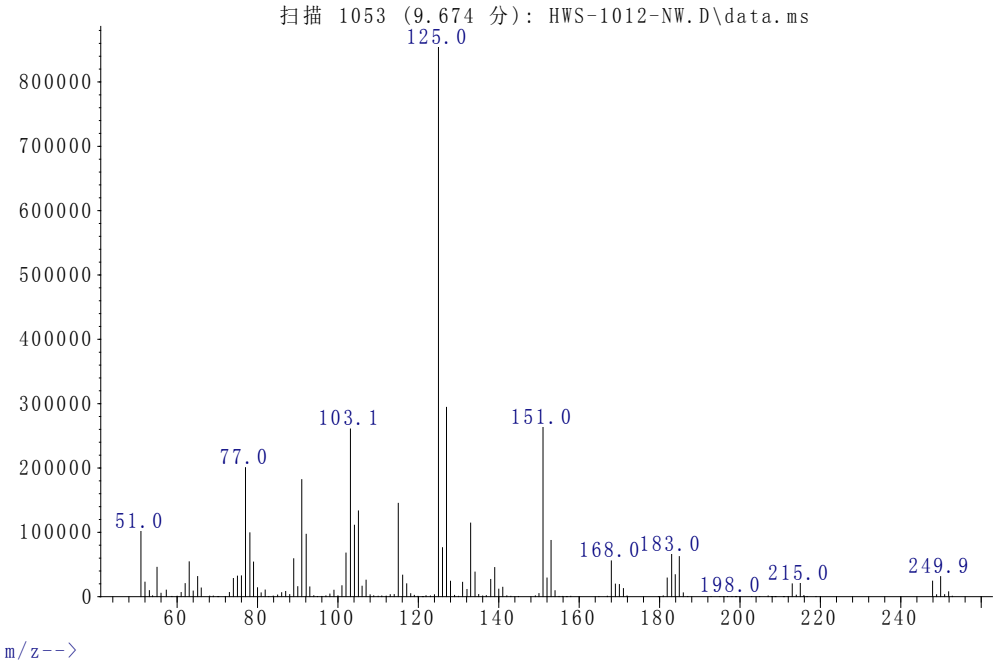
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	53.776	3728.7	32.3	1.5646	0.545	88.838
2	61.13	468.5	3.7	2.0851	0.592	11.162

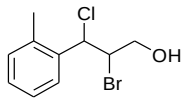
Ret Time	Area/mAU	Area/%
53.776	3728.7	88.838
61.13	468.5	11.162

Mass spectrum of Di-halide Products.



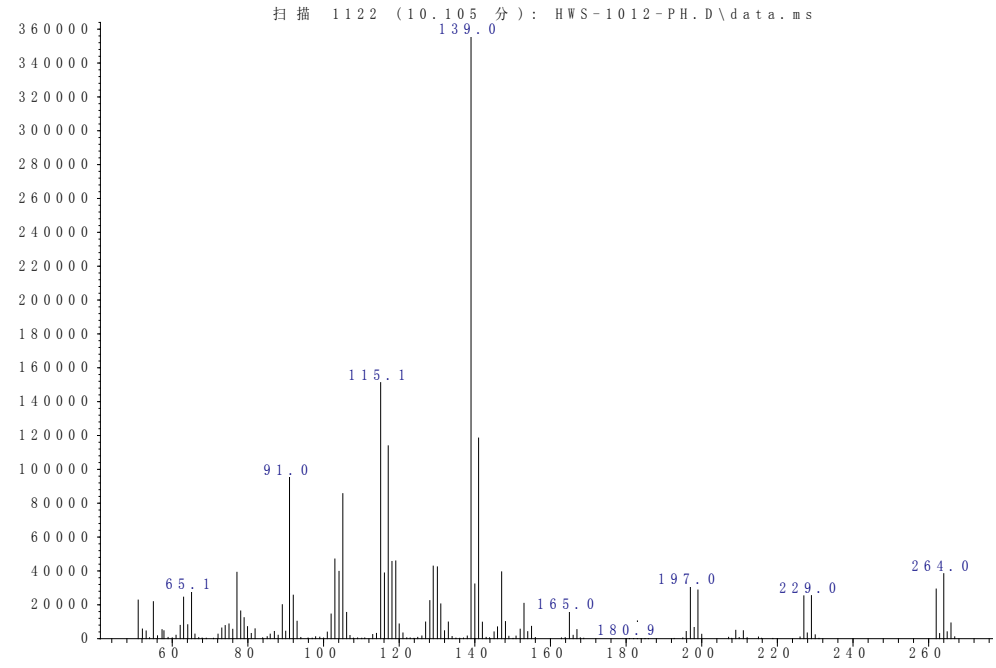
2a





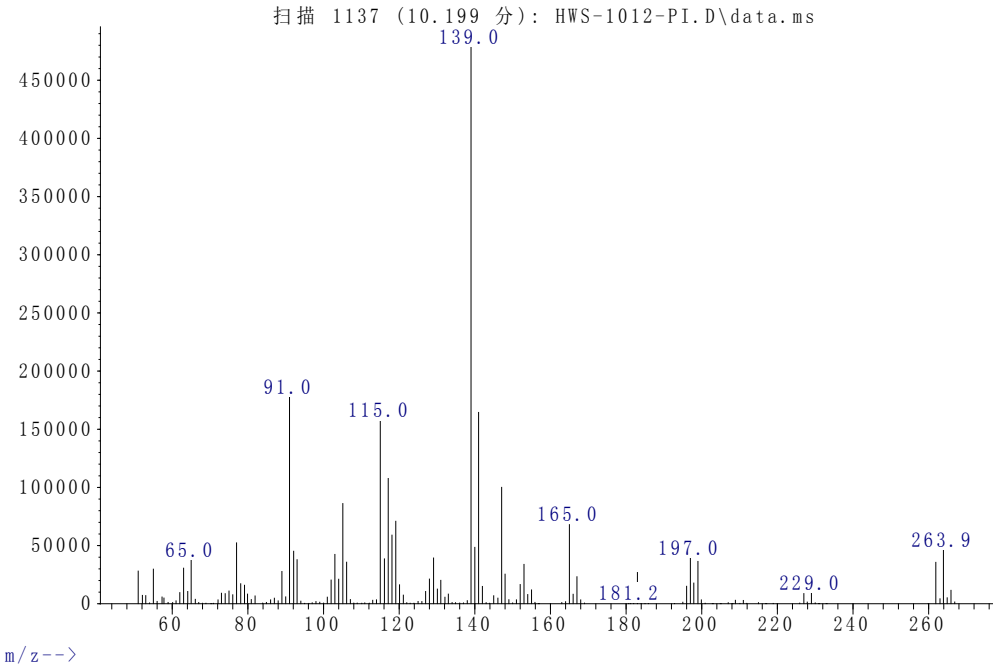
2b

丰 度


扫 描 1122 (10.105 分): HWS-1012-PH.D\data.ms
139.0
115.1
91.0
65.1
165.0
180.9
197.0
229.0
264.0
m/z-->
Cl
OH
Br

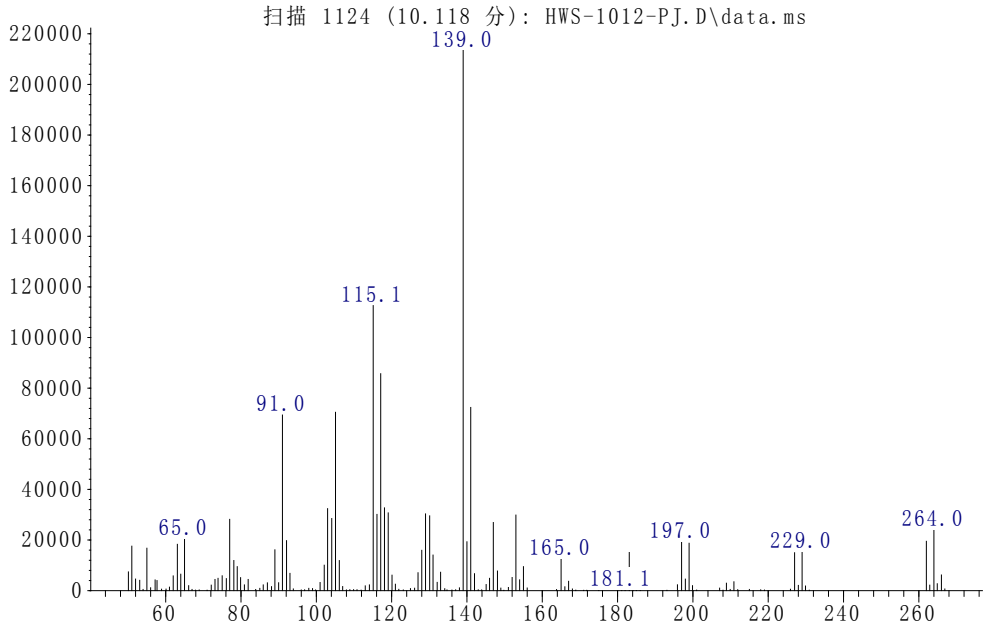
2c

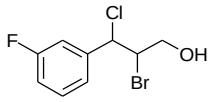
丰 度


扫描 1137 (10.199 分): HWS-1012-PI.D\data.ms
139.0
91.0
115.0
165.0
65.0
197.0
263.9
181.2
229.0
m/z-->
Cl
OH
Br

2d

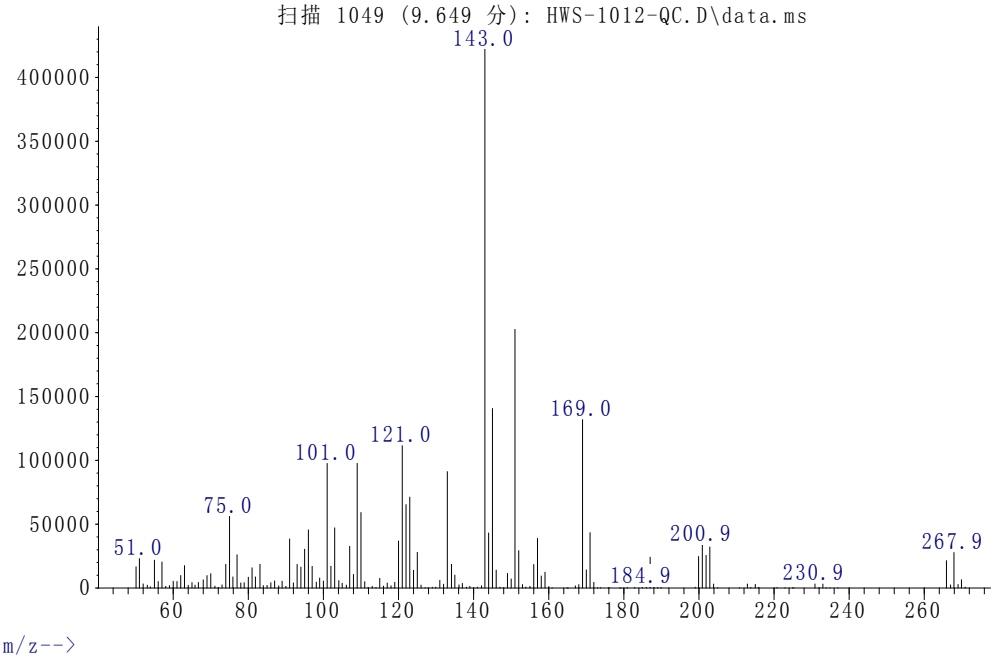
丰度

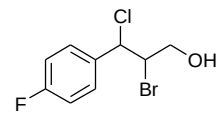

扫描 1124 (10.118 分): HWS-1012-PJ.D\data.ms
139.0
115.1
91.0
65.0
165.0
181.1
197.0
229.0
264.0
m/z-->


Cl
F
OH
Br

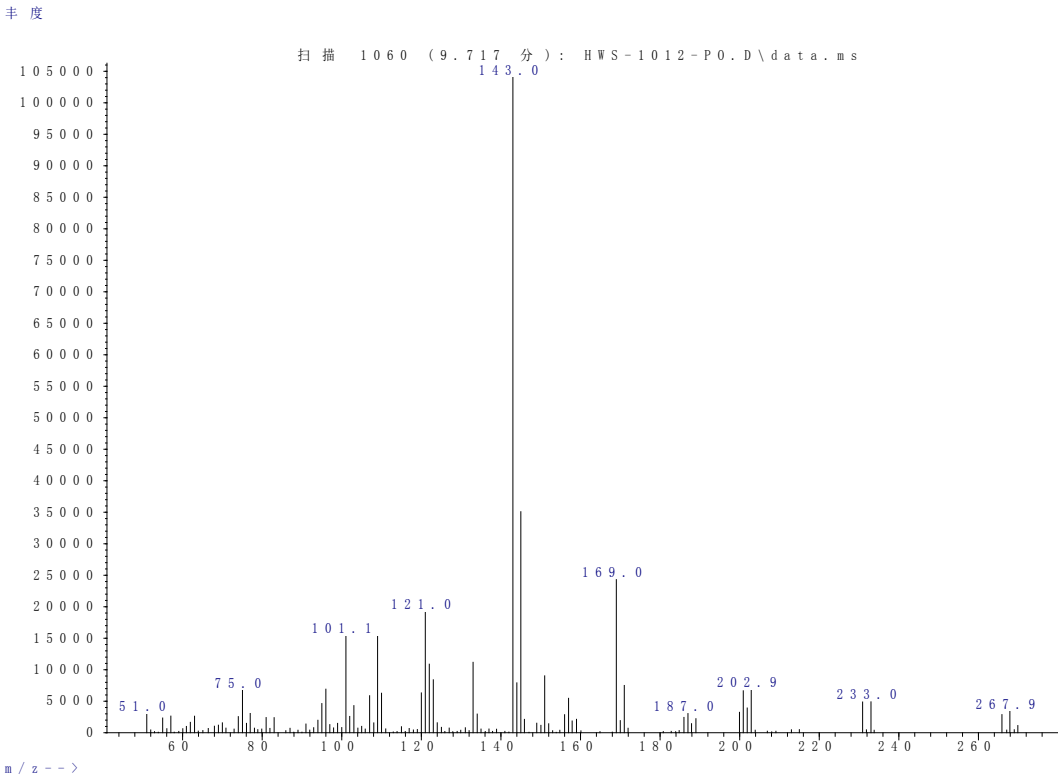
2e

丰度

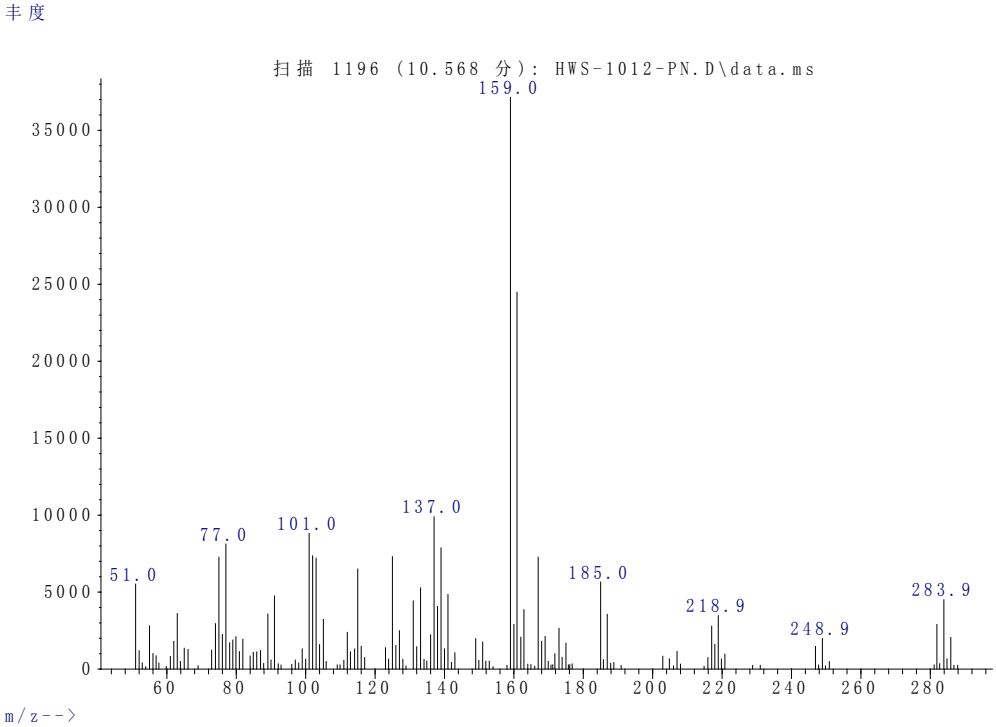

扫描 1049 (9.649 分): HWS-1012-QC.D\data.ms
143.0
169.0
121.0
101.0
75.0
51.0
200.9
184.9
230.9
267.9
m/z-->


Cl
OH
Br
F

2f

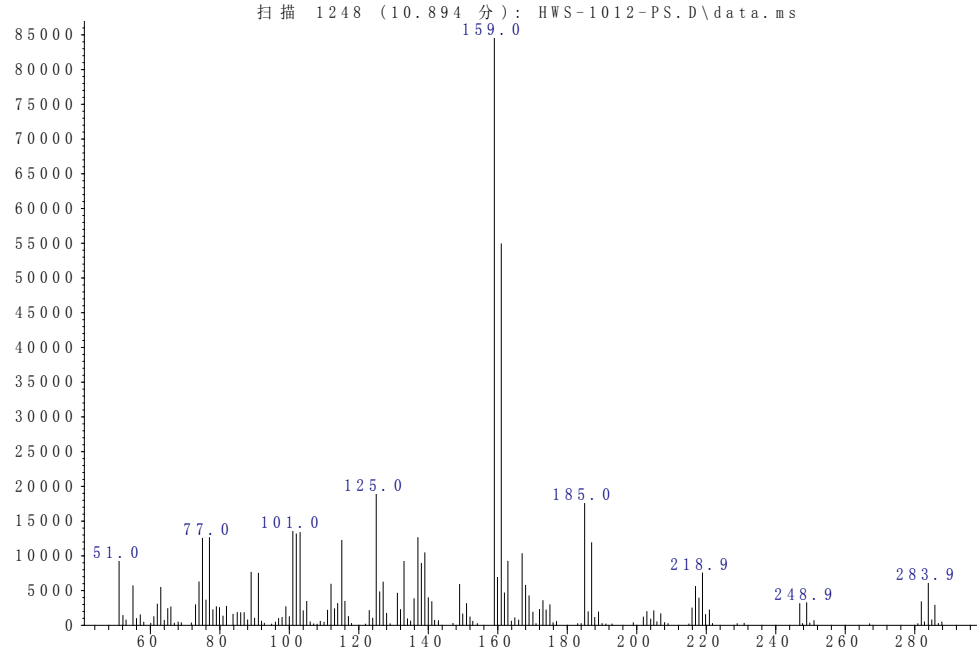

丰 度
扫 描 1060 (9.717 分): HWS-1012-P0.D\data.ms
143.0
169.0
121.0
101.1
75.0
51.0
187.0
202.9
233.0
267.9
m/z-->
Cl
Cl
OH
Br

2g


丰 度
扫 描 1196 (10.568 分): HWS-1012-PN.D\data.ms
159.0
137.0
101.0
77.0
51.0
185.0
218.9
248.9
283.9
m/z-->
Cl
OH
Br
Cl

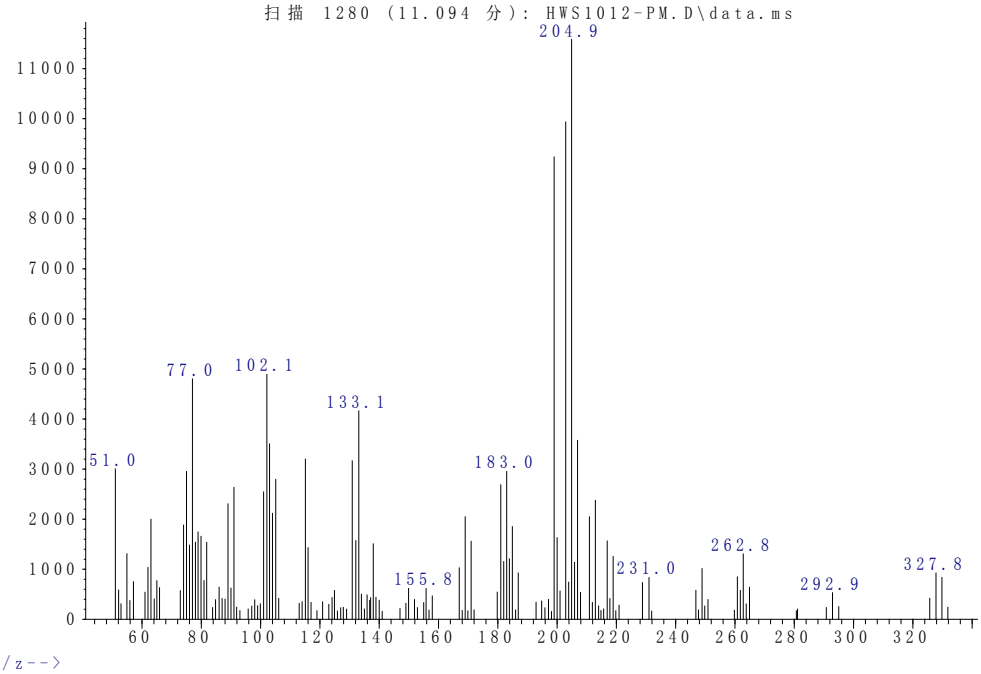
2h

丰度


扫描 1248 (10.894 分): HWS-1012-PS.D\data.ms
159.0
125.0
185.0
77.0
101.0
51.0
218.9
248.9
283.9
m/z-->
Br
Cl
OH
Br

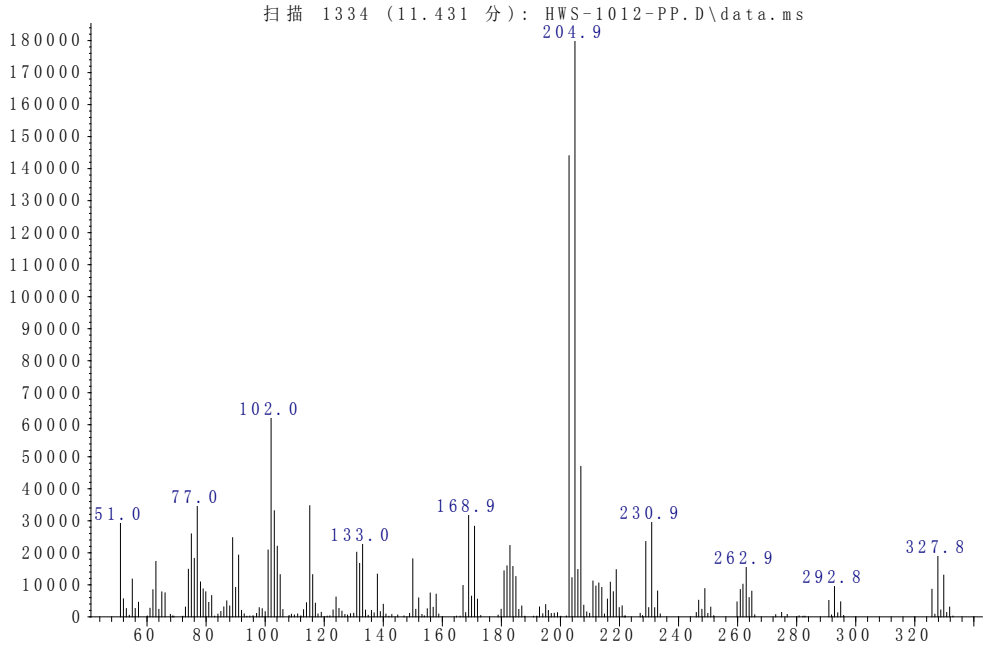
2i

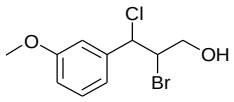
丰度


扫描 1280 (11.094 分): HWS1012-PM.D\data.ms
204.9
77.0
102.1
133.1
51.0
183.0
155.8
231.0
262.8
292.9
327.8
m/z-->
Cl
OH
Br
Br

2j

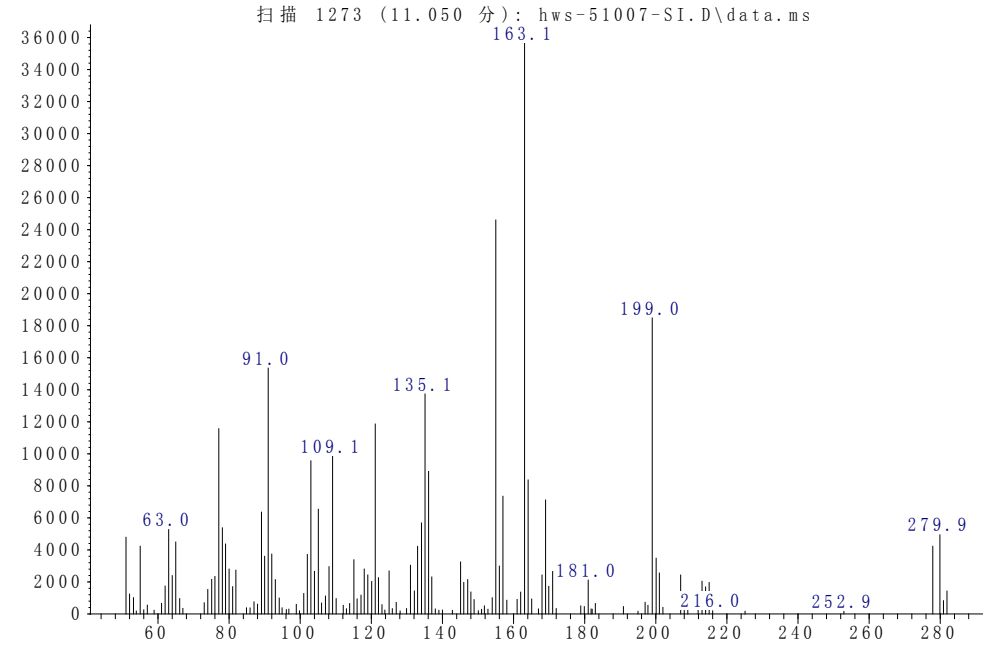
丰度

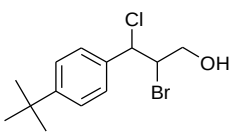

扫描 1334 (11.431 分): HWS-1012-PP.D\data.ms
204.9
102.0
77.0
51.0
168.9
133.0
230.9
262.9
292.8
327.8
m/z-->


Cl
O
OH
Br

2k

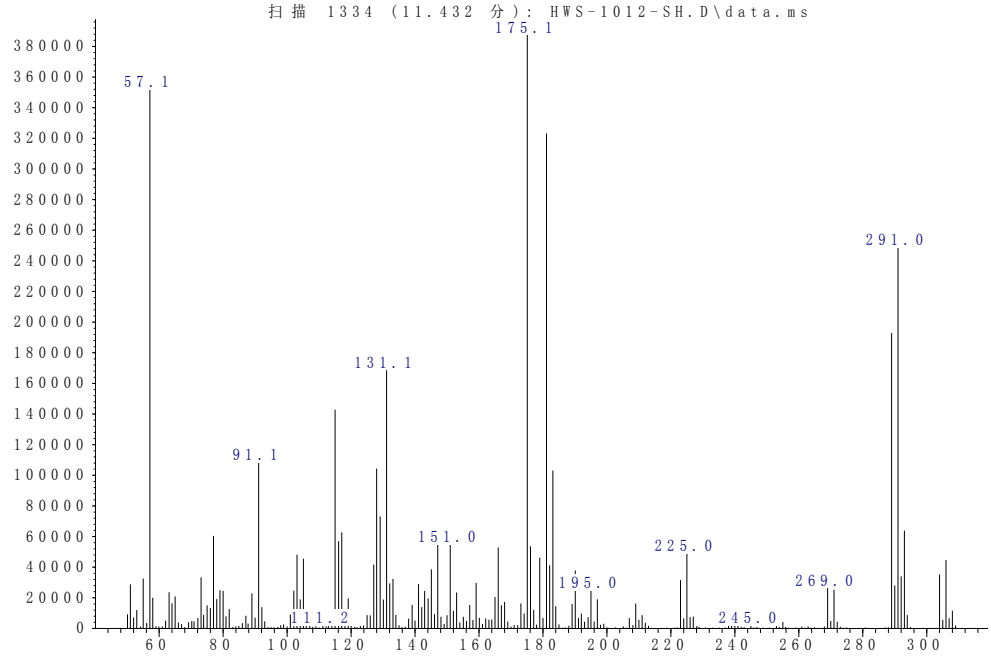
丰度


扫描 1273 (11.050 分): hws-51007-SI.D\data.ms
163.1
199.0
91.0
135.1
109.1
63.0
279.9
181.0
216.0
252.9
m/z-->


Cl
OH
Br

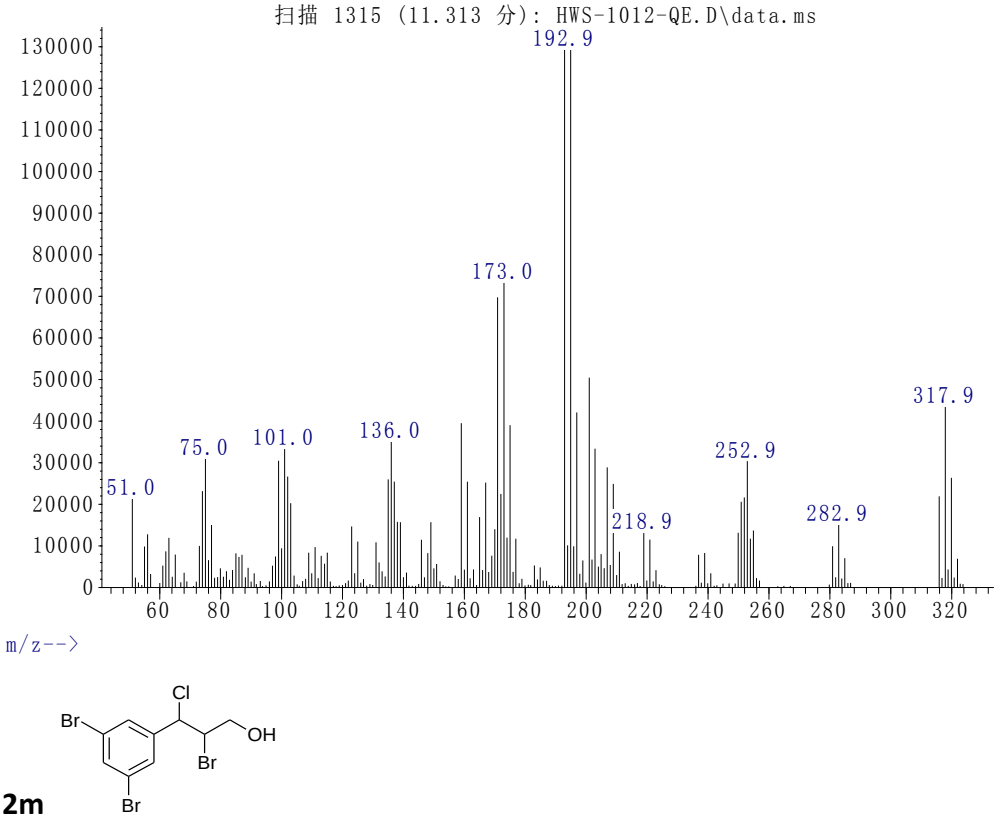
2l

丰 度


扫 描 1334 (11.432 分): HWS-1012-SH.D\data.ms
175.1
57.1
291.0
131.1
91.1
151.0
225.0
195.0
269.0
111.2
245.0
m/z-->
Cl
Cl
OH
Br
Cl

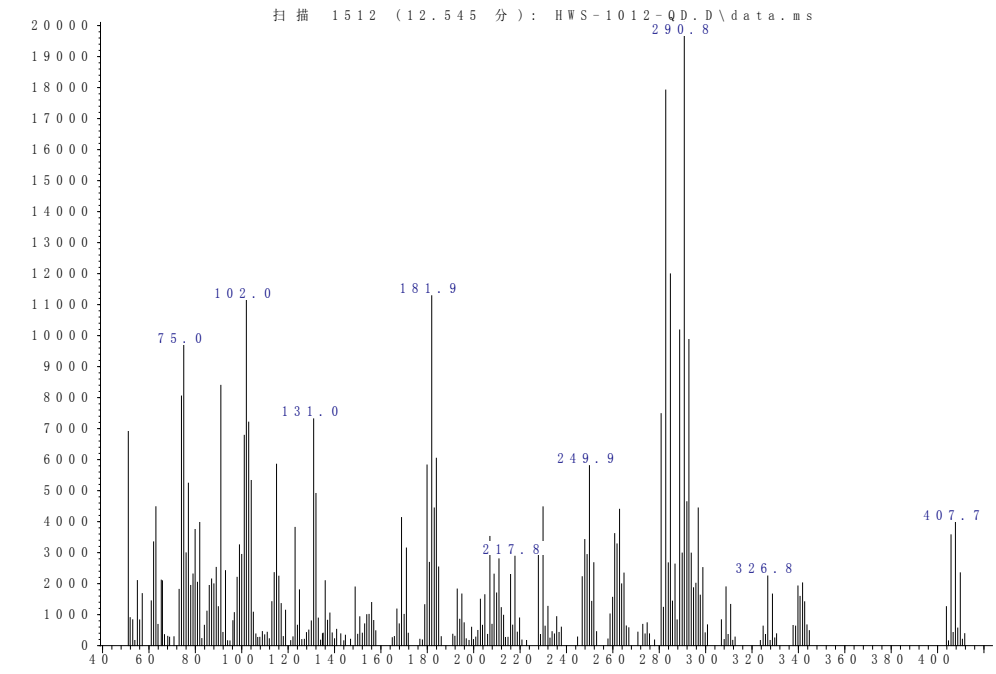
2m

丰度

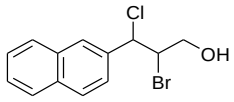

扫描 1315 (11.313 分): HWS-1012-QE.D\data.ms
192.9
173.0
317.9
75.0
101.0
136.0
252.9
51.0
218.9
282.9
m/z-->
Br
Cl
OH
Br
Br

2m

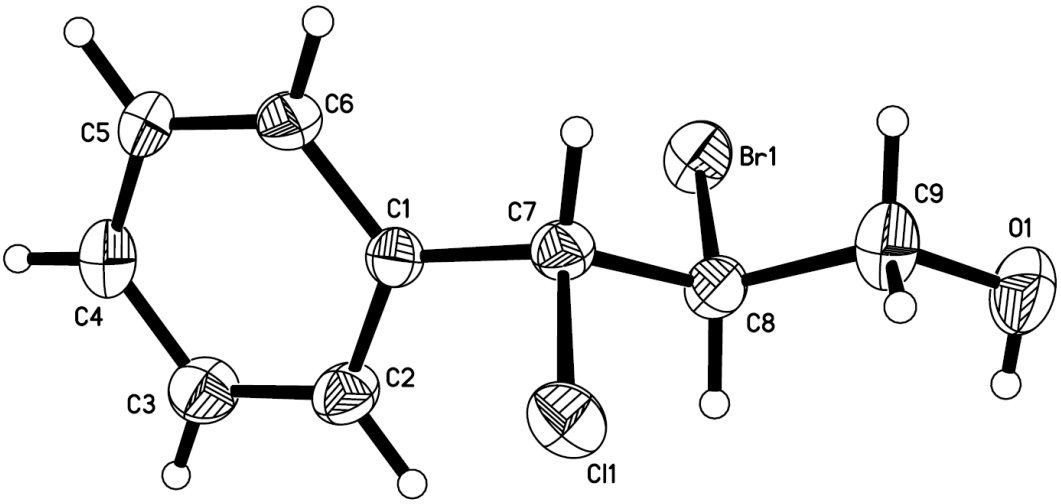
丰 度


扫 描 1512 (12.545 分): HWS-1012-QD.D\data.ms
290.8
181.9
102.0
75.0
131.0
249.9
217.8
326.8
407.7
m/z-->
丰度
扫描 1544 (12.745 分): hws-51008-NB.D\data.ms
175.0
141.0
115.0
76.0
55.0
94.9
199.0
219.0
239.0
263.0
299.9
m/z-->

2o


Cl
OH
Br

PS.



X-ray structure of product**2a**