

## Supporting Information

for

### **Catalytic asymmetric Henry reaction using copper chiral tridentate Schiff-base complexes and their polymer-supported complexes**

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#### **Experimental details and characterization data for all compounds**

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## 1. General remarks

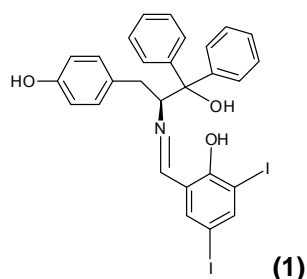
All solvents were dried by standard method. Unless otherwise noted, commercially available reagents were used without further purification. All reactions were monitored by TLC with Haiyang GF254 silica gel coated plates. Column chromatography was carried out using 100-200 mesh silica gel. Liquid aldehydes were freshly distilled before use. Melting points were recorded on X-4 melting point apparatus and the thermometer was uncorrected. NMR spectra were recorded on a Bruker Advance III at 500 MHz for <sup>1</sup>H and 126 MHz for <sup>13</sup>C using CDCl<sub>3</sub> or CD<sub>3</sub>SOCD<sub>3</sub> as solvent (with TMS as an internal standard). IR spectra (film) were recorded on a NEXUS FI/IR spectrometer. Mass spectra (MS) were carried out on VARIAN1200 and measured by the EI method. The ee value determination was carried out using chiral HPLC with a Daicel Chiracel AD-H or OD-H column.

## 2. General procedure for the preparation for 4-(2-amino-3-hydroxy-3,3-diphenyl-propyl)-phenol [1a]

L-Tyrosine methyl ester hydrochloride (2.31 g, 10 mmol) was added portionwise to freshly prepared Grignard reagent of PhMgBr (80 mmol) in diethyl ether under an argon atmosphere at 0 °C. Then the mixture was stirred at ambient temperature overnight, and a cold saturated NH<sub>4</sub>Cl was added into it under vigorous stirring. The mixture was extracted with ethyl acetate (50 mL × 3). The combined organic layer was washed with brine and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then concentrated in a vacuum. This residue was recrystallized with diethyl ether and gave compound **1a** as a colorless crystal. Yield: 65.3%; mp: 215 °C (reference [1] m.p. 215~217 °C); [α]<sub>D</sub><sup>20</sup> = -81.58 (c 0.076, CH<sub>2</sub>Cl<sub>2</sub>) (reference [1] [α]<sub>D</sub><sup>20</sup> = -90.8 (c 0.1184, THF)); IR (KBr): 3506, 3357, 3027, 1583, 1511, 1447, 822, 768, 703 cm<sup>-1</sup>; MS (EI, 70 eV): m/z = 320(M<sup>+</sup>, 1), 212(10), 167(17), 136(100), 91(17).

### 3. General procedure for the preparation for Schiff-base ligands 1-14 [2]

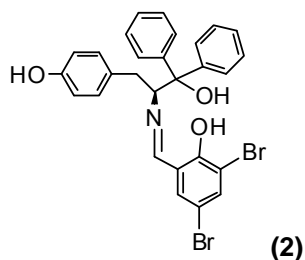
To a solution of 4-(2-amino-3-hydroxy-3,3-diphenyl-propyl)-phenol [**1a**] (2 mmol) in 10 mL 95% EtOH was added substituted salicylaldehyde [**2a-f**] (2 mmol). The resulting solution was vigorously stirred for 24 h at room temperature, then the reaction was vacuum filtered to to remove the solvent. The crude product was purified by silica gel flash column chromatography or recrystallized to give, the resulting chiral Schiff-base(1-14) as a yellow solid, in high yield (>98%).



#### **2-(((S)-1-hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-4,6-diiodo-phenol (1):**

Yellow solid; mp: 129~130 °C;  $[\alpha]_D^{20} = -115.38$  ( $c = 0.0468$  g/mL,  $\text{CH}_2\text{Cl}_2$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3417, 3057, 1630, 1510, 1444, 1384, 1226, 826, 768, 701;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 14.24 (br, 1H, Ph-OH), 7.99 (d,  $J = 2.1$  Hz, 1H, Ph-H), 7.62 (d,  $J = 7.5$  Hz, 2H, Ph-H), 7.45~7.37 (m, 4H, Ph-H), 7.34 (s, 1H, CH=N), 7.30 (t,  $J = 6.7$  Hz, 1H, Ph-H), 7.25 (d,  $J = 8.0$  Hz, 2H, Ph-H), 7.23~7.07 (m, 2H, Ph-H), 6.82 (d,  $J = 8.4$  Hz, 2H, Ph-H), 6.68 (d,  $J = 8.4$  Hz, 2H, Ph-H), 5.04 (br, 1H, Ph-OH), 4.33 (dd,  $J = 10.3, 1.6$  Hz, 1H, C\*H), 2.92 (br, 1H, OH), 2.97 (dd,  $J = 14.0, 1.3$  Hz, 1H, Ph- $\text{CH}_2$ ), 2.80 (dd,  $J = 14.0, 10.4$  Hz, 1H, Ph- $\text{CH}_2$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 164.1, 162.2, 154.4, 149.2, 144.7, 143.7, 140.0, 130.7, 130.2, 128.6, 127.3, 125.9, 118.9, 115.6, 88.9, 79.6, 78.3, 77.7, 77.3, 77.0, 76.8, 36.4; MS (EI, 70 eV)  $m/z$ : 676( $\text{M}^+$ , 2%),

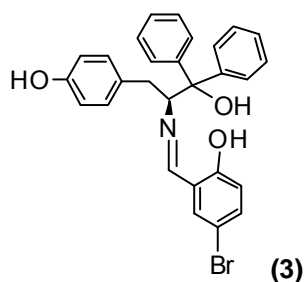
493(100%), 386(30%), 374(52%), 183(48%), 105 (61%), 77(50%); Anal. Calcd for  $C_{28}H_{23}I_2NO_3$ : C, 49.80; H, 3.43; N, 2.07. Found: C, 49.77; H, 3.41; N, 2.05.



**2,4-Dibromo-6-(((S)-2-hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-p**

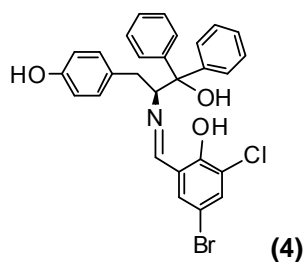
**henol (2):**

Yellow solid; mp: 105~107 °C;  $[\alpha]_D^{20} = -126.25$  ( $c = 0.0800$  g/mL,  $CH_2Cl_2$ ). IR (KBr,  $cm^{-1}$ ): 3385, 3024, 2931, 1631, 1482, 1383, 1273, 824, 767, 702;  $^1H$  NMR (500 MHz,  $CDCl_3$ , ppm)  $\delta$ : 12.86 (br, 1H, Ph-OH), 7.63 (d,  $J = 7.6$  Hz, 2H, Ph-H), 7.53 (s, 1H, CH=N), 7.47 (d,  $J = 7.6$  Hz, 2H, Ph-H), 7.41 (t,  $J = 7.8$  Hz, 2H, Ph-H), 7.31 (m, 3H, Ph-H), 7.16 (t,  $J = 7.4$  Hz, 1H, Ph-H), 7.01 (d,  $J = 2.5$  Hz, 1H, Ph-H), 6.80 (m, 3H, Ph-H), 6.67 (d,  $J = 8.4$  Hz, 2H, Ph-H), 5.54 (br, 1H, Ph-OH), 4.30 (dd,  $J = 10.3, 1.8$  Hz, 1H, C\*H), 3.00 (dd,  $J = 14.0, 1.4$  Hz, 1H, Ph- $CH_2$ ), 2.90 (br, 1H, OH), 2.77 (dd,  $J = 14.0, 10.3$  Hz, 1H, Ph- $CH_2$ );  $^{13}C$  NMR (126 MHz,  $CDCl_3$ , ppm)  $\delta$ : 165.1, 160.0, 154.2, 145.1, 144.0, 135.2, 133.53, 130.7, 128.5, 127.2, 126.1, 119.7, 119.0, 115.4, 110.1, 79.7, 78.9, 77.3, 77.0, 76.8, 36.5; MS (EI, 70 eV)  $m/z$ : 542( $M^+$ , 1%), 399(34%), 275(25%), 183(65%), 136(42%), 105(100%), 77(57%); Anal. Calcd for  $C_{28}H_{23}Br_2NO_3$ : C, 57.85; H, 3.99; N, 2.41. Found: C, 57.83; H, 3.96; N, 2.40.



**4-Bromo-2-(((S)-2-hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-phenol (3):**

Yellow solid; mp: 114~116 °C;  $[\alpha]_D^{20} = -123.08$  ( $c = 0.0520$  g/mL,  $\text{CH}_2\text{Cl}_2$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3355, 3024, 2933, 1632, 1450, 1446, 1222, 831, 768, 699;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 14.16 (br, 1H, Ph-OH), 9.81 (s, 1H, CH=N), 7.62 (m, 3H, Ph-H), 7.42 (m, 5H, Ph-H), 7.28 (m, 3H, Ph-H), 7.15 (t,  $J = 7.3$  Hz, 1H, Ph-H), 6.94 (d,  $J = 2.3$  Hz, 1H, Ph-H), 6.82 (d,  $J = 8.3$  Hz, 2H, Ph-H), 6.68 (d,  $J = 8.4$  Hz, 2H, Ph-H), 5.53 (br, 1H, Ph-OH), 4.33 (dd,  $J = 10.3, 1.6$  Hz, 1H, C\*H), 3.00 (br, 1H, OH), 2.98 (d, br,  $J = 14.0$  Hz, 1H, Ph-CH<sub>2</sub>), 2.79 (dd,  $J = 14.0, 10.5$  Hz, 1H, Ph-CH<sub>2</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 164.4, 159.1, 154.4, 144.7, 143.7, 138.1, 132.9, 130.7, 130.2, 128.6, 127.3, 125.9, 119.1, 115.5, 112.9, 108.9, 79.6, 77.9, 77.3, 77.0, 76.8, 36.4; MS (EI, 70 eV)  $m/z$ : 504( $\text{M}^+$ , 2%), 321(68%), 319(100%), 277(30%), 183(75%), 105(87%), 77(44%); Anal. Calcd for  $\text{C}_{28}\text{H}_{24}\text{BrNO}_3$ : C, 66.94; H, 4.82; N, 2.79. Found: C, 66.92; H, 4.79; N, 2.75.

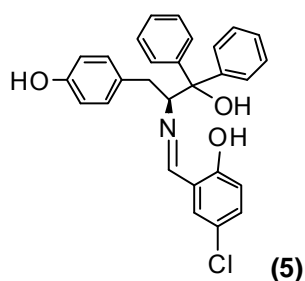


**2,4-Dichloro-6-(((S)-2-hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-phenol (4):**

Yellow solid; mp: 96~98 °C;  $[\alpha]_D^{20} = -132.28$  ( $c = 0.0756$  g/mL,  $\text{CH}_2\text{Cl}_2$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3356, 3026, 2966, 1634, 1505, 1448, 1217, 855, 749, 701;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 13.97 (br, 1H, Ph-OH), 7.62 (d,  $J = 7.5$  Hz, 2H, CH=N, Ph-H), 7.46~7.39 (m, 5H, Ph-H), 7.34 (d,  $J = 2.4$  Hz, 1H, Ph-H), 7.31 (d,  $J = 7.3$  Hz, 1H, Ph-H), 7.26 (d,  $J = 8.0$  Hz, 2H, Ph-H), 7.16 (t,  $J =$

7.3 Hz, 1H, Ph-H), 6.83 (d,  $J = 8.4$  Hz, 2H, Ph-H), 6.77 (d,  $J = 2.4$  Hz, 1H, Ph-H), 6.68 (d,  $J = 8.4$  Hz, 2H, Ph-H), 5.43 (br, 1H, Ph-OH), 4.31 (s, 1H, C\*H), 2.99 (d, br,  $J = 14.0$  Hz, 1H, Ph-CH<sub>2</sub>), 2.98 (br, 1H, OH), 2.79 (dd,  $J = 14.0, 10.5$  Hz, 1H, Ph-CH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 164.6, 158.5, 154.6, 144.6, 143.6, 132.9, 130.7, 129.9, 129.6, 129.2, 128.6, 128.3, 127.4, 126.0, 123.5, 121.7, 118.3, 115.6, 79.6, 77.6, 77.3, 77.0, 76.8, 36.3; MS (EI, 70 eV)  $m/z$ : 493(M<sup>+</sup>, 1%), 309(67%), 267(39%), 183(57%), 107(37%), 105 (100%), 77(70%);

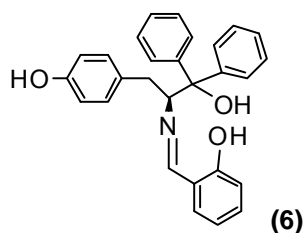
Anal. Calcd for C<sub>28</sub>H<sub>23</sub>Cl<sub>2</sub>NO<sub>3</sub>: C, 68.30; H, 4.71; N, 2.84. Found: C, 68.28; H, 4.69; N, 2.82.



**4-Chloro-2-(((S)-2-hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-phenol (5):**

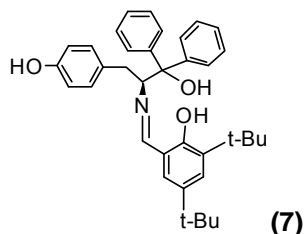
Yellow solid; mp: 98~101 °C;  $[\alpha]_D^{20} = -152.63$  ( $c = 0.0760$  g/mL, CH<sub>2</sub>Cl<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 3415, 3028, 1634, 1519, 1479, 1249, 854, 757, 706; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 12.85 (br, 1H, Ph-OH), 7.63 (d,  $J = 7.4$  Hz, 2H, Ph-H), 7.53 (s, 1H, CH=N), 7.49~7.45 (m, 2H, Ph-H), 7.41 (t,  $J = 7.8$  Hz, 2H, Ph-H), 7.36~7.28 (m, 2H, Ph-H), 7.26 (s, 1H, Ph-H), 7.21~7.13 (m, 2H, Ph-H), 6.88 (d,  $J = 2.6$  Hz, 1H, Ph-H), 6.83 (d,  $J = 8.6$  Hz, 3H, Ph-H), 6.72~6.61 (m, 2H, Ph-H), 5.54 (s, 1H, Ph-OH), 4.30 (dd,  $J = 10.3, 1.9$  Hz, 1H, C\*H), 3.00 (dd,  $J = 14.0, 1.5$  Hz, 1H, Ph-CH<sub>2</sub>), 2.94 (br, 1H, OH), 2.77 (dd,  $J = 14.0, 10.3$  Hz, 1H, Ph-CH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 165.1, 159.5, 154.2, 145.1, 143.9, 132.3, 130.9, 130.4, 128.5, 128.3, 127.2, 126.1, 123.2, 119.0, 118.5, 115.3, 79.7, 78.9, 77.3, 77.0, 76.7, 36.5; MS (EI, 70 eV)  $m/z$ :

459(M<sup>+</sup>, 2%), 275(100%), 233(29%), 183(63%), 167(21%), 105 (84%), 77(50%); Anal. Calcd for C<sub>28</sub>H<sub>24</sub>ClNO<sub>3</sub>: C, 73.44; H, 5.28; N, 3.06. Found: C, 73.41; H, 5.26; N, 3.04.



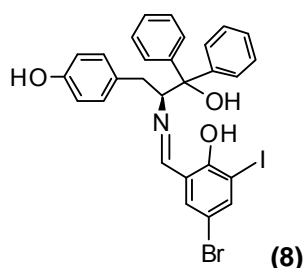
**2-(((S)-2-hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-phenol (6):**

Yellow solid; mp: 237 °C;  $[\alpha]_D^{20} = -66.67$  ( $c = 0.0636$  g/mL, CH<sub>2</sub>Cl<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 3561, 3054, 2970, 2559, 1628, 1456, 1385, 1284, 836, 755, 701; <sup>1</sup>H NMR(500 MHz, DMSO, ppm)  $\delta$ : 13.22 (s, 1H, Ph-OH), 9.12 (s, 1H, Ph-OH), 7.80 (s, 1H, CH=N), 7.70 (d,  $J = 7.7$  Hz, 2H, Ph-H), 7.56 (d,  $J = 7.7$  Hz, 2H, Ph-H), 7.38 (t,  $J = 7.7$  Hz, 2H, Ph-H), 7.22 (m, 4H, Ph-H), 7.07 (t,  $J = 7.3$  Hz, 1H, Ph-H), 7.01 (dd,  $J = 7.5, 1.0$  Hz, 1H, Ph-H), 6.81 (d,  $J = 8.3$  Hz, 2H, Ph-H), 6.77~6.67 (m, 2H, Ph-H), 6.58 (d,  $J = 8.3$  Hz, 2H, Ph-H), 6.03 (s, 1H, OH), 4.54 (d,  $J = 9.9$  Hz, 1H, C\*H), 2.85 (d, br,  $J = 13.9$  Hz, 1H, Ph-CH<sub>2</sub>), 2.69 (dd,  $J = 13.9, 10.6$  Hz, 1H, Ph-CH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, DMSO, ppm)  $\delta$ : 165.6, 160.6, 155.4, 146.1, 146.0, 131.9, 131.4, 130.2, 128.9, 128.0, 127.5, 126.4, 126.3, 126.2, 126.0, 118.3, 117.9, 116.4, 114.9, 79.0, 77.2, 35.9; MS (EI, 70 eV)  $m/z$ : 424 (M<sup>+</sup>, 7%), 241(100%), 199 (20%), 105(25%), 77(7%); Anal. Calcd for C<sub>28</sub>H<sub>25</sub>NO<sub>3</sub>: C, 79.41; H, 5.95; N, 3.31. Found: C, 79.40; H, 5.94; N, 3.29.



**2,4-Di-tert-butyl-6-(((S)-2-hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-phenol (7):**

Yellow solid; mp: 88~90 °C;  $[\alpha]_D^{20} = -128.91$  ( $c = 0.0768$  g/mL,  $\text{CH}_2\text{Cl}_2$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3420, 2959, 1623, 1513, 1440, 1361, 1250, 829, 769, 702;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 12.91 (br, 1H, Ph-OH), 7.69 (s, 1H, CH=N), 7.59 (d,  $J = 7.6$  Hz, 2H, Ph-H), 7.52 (d,  $J = 7.7$  Hz, 2H, Ph-H), 7.40 (t,  $J = 7.7$  Hz, 2H, Ph-H), 7.34 (d,  $J = 2.3$  Hz, 1H, Ph-H), 7.29 (d,  $J = 5.8$  Hz, 1H, Ph-H), 7.27~7.21 (m, 2H, Ph-H), 7.14 (t,  $J = 7.3$  Hz, 1H, Ph-H), 6.85 (d,  $J = 8.4$  Hz, 2H, Ph-H), 6.75 (t,  $J = 7.6$  Hz, 1H, Ph-H), 6.66 (d,  $J = 8.4$  Hz, 2H, Ph-H), 5.56 (br, 1H, Ph-OH), 4.32 (d,  $J = 8.4$  Hz, 1H, C\*H), 3.06 (br, 1H, OH), 2.95 (d, br,  $J = 13.9$  Hz, 1H, Ph- $\text{CH}_2$ ), 2.82 (dd,  $J = 13.9$ , 10.0 Hz, 1H, Ph- $\text{CH}_2$ ), 1.42 (s, 9H,  $-\text{CH}_3$ ), 1.26 (s, 9H,  $-\text{CH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 167.7, 157.6, 154.0, 145.7, 144.3, 140.0, 136.4, 131.3, 130.9, 128.4, 127.2, 126.6, 126.4, 126.0, 117.7, 115.2, 79.9, 78.6, 77.2, 76.8, 76.7, 36.7, 35.0, 34.1, 31.5, 29.4; MS (EI, 70 eV)  $m/z$ : 535( $\text{M}^+$ , 7%), 353(100%), 219(20%), 105(23%), 77(14%), 57(11%); Anal. Calcd for  $\text{C}_{28}\text{H}_{25}\text{NO}_3$ : C, 80.71; H, 7.71; N, 2.61. Found: C, 80.69; H, 7.69; N, 2.60.

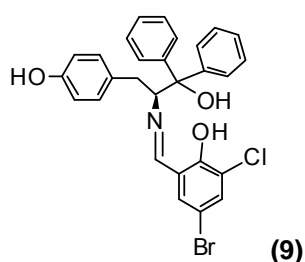


**4-Bromo-2-(((S)-2-hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-6-iodo-phenol (8):**

Yellow solid; mp: 118~120 °C;  $[\alpha]_D^{20} = -128.75$  ( $c = 0.0800$  g/mL,  $\text{CH}_2\text{Cl}_2$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3450, 3058, 1632, 1509, 1445, 1369, 1223, 827, 769, 702;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 14.19 (br, 1H, Ph-OH), 7.83 (d,  $J = 2.3$  Hz, 1H, Ph-H), 7.64~7.60 (m, 2H, Ph-H), 7.46~7.39 (m, 4H, Ph-H), 7.35 (s, 1H, CH=N), 7.30 (d,  $J = 7.3$  Hz, 1H, Ph-H), 7.25 (d,  $J = 8.0$  Hz, 2H, Ph-H), 7.17 (s, 1H, Ph-H), 6.97 (t,  $J = 6.9$  Hz, 1H, Ph-H), 6.81 (d,  $J = 8.4$  Hz, 2H, Ph-H), 6.67 (d,  $J =$



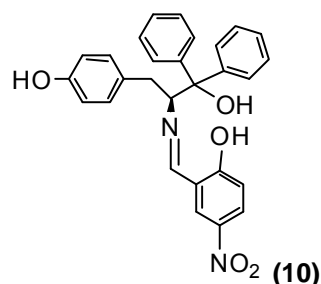
8.4 Hz, 2H, Ph-H), 5.03 (br, 1H, Ph-OH), 4.34 (dd,  $J = 10.4, 1.8$  Hz, 1H, C\*H), 2.97 (dd,  $J = 14.0, 2.7$  Hz, 2H, Ph-CH<sub>2</sub>, OH), 2.80 (dd,  $J = 14.0, 10.4$  Hz, 1H, Ph-CH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 164.3, 161.3, 154.4, 144.8, 143.8, 133.9, 130.7, 130.2, 128.6, 127.3, 125.2, 118.0, 115.3, 109.6, 88.2, 79.6, 77.8, 77.3, 77.0, 76.8, 36.4; MS (EI, 70 eV)  $m/z$ : 629(M<sup>+</sup>, 1%), 445(35%), 353(67%), 183(41%), 105 (100%), 77(69%); Anal. Calcd for C<sub>28</sub>H<sub>23</sub>BrINO<sub>3</sub>: C, 53.53; H, 3.69; N, 2.23. Found: C, 53.51; H, 3.66; N, 2.22.



**4-Bromo-2-chloro-6-(((S)-2-hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-phenol (9):**

Yellow solid; mp: 115~117 °C;  $[\alpha]_D^{20} = -134.18$  ( $c = 0.0708$  g/mL, CH<sub>2</sub>Cl<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 3059, 1636, 1508, 1448, 1383, 1221, 848, 769, 703 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 14.05 (br, 1H, Ph-OH), 7.62 (m, 2H, Ph-H), 7.46 (m, 2H, Ph-H), 7.44 (d,  $J = 0.6$  Hz, 1H, Ph-H), 7.43 (s, 1H, CH=N), 7.41 (d,  $J = 8.0$  Hz, 1H, Ph-H), 7.31 (d,  $J = 7.4$  Hz, 2H, Ph-H), 7.26 (d,  $J = 8.0$  Hz, 2H, Ph-H), 7.17 (d,  $J = 7.3$  Hz, 1H, Ph-H), 6.90 (d,  $J = 2.4$  Hz, 1H, Ph-H), 6.83 (d,  $J = 8.4$  Hz, 2H, Ph-H), 6.71~6.64 (m, 2H, Ph-H), 5.14 (s, 1H, Ph-OH), 4.32 (dd,  $J = 10.4, 1.9$  Hz, 1H, C\*H), 2.99 (dd,  $J = 14.0, 1.6$  Hz, 1H, Ph-CH<sub>2</sub>), 2.94 (s, 1H, OH), 2.79 (dd,  $J = 14.0, 10.5$  Hz, 1H, Ph-CH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 164.4, 157.7, 154.4, 144.7, 143.7, 135.1, 132.0, 130.7, 130.3, 128.5, 127.3, 126.0, 123.4, 119.2, 115.5, 108.6, 79.7, 78.2, 77.2, 77.0, 76.7, 36.4; MS (EI, 70 eV)  $m/z$ : 537(M<sup>+</sup>, 1%), 335(80%), 313 (53%), 312(30%), 183(75%),

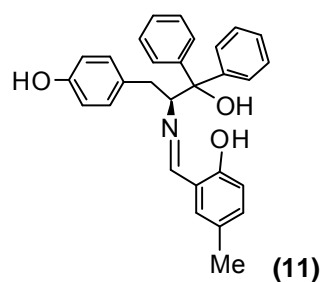
105 (100%), 77(56%); Anal. Calcd for  $C_{28}H_{23}BrClNO_3$ : C, 62.64; H, 4.32; N, 2.61. Found: C, 62.58; H, 4.29; N, 2.60.



**2-(((S)-2-Hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-4-nitro-phenol**

**(10):**

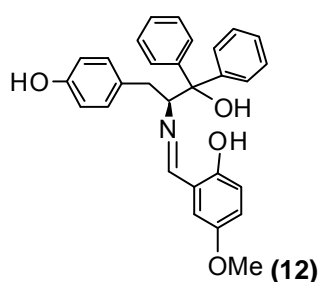
Yellow solid; mp: 127~129 °C;  $[\alpha]_D^{20} = -123.13$  ( $c = 0.134$  g/mL,  $CH_2Cl_2$ ). IR (KBr,  $cm^{-1}$ ): 3480, 3059, 1613, 1512, 1447, 1323, 1233, 837, 769, 702;  $^1H$  NMR(500 MHz, DMSO, ppm)  $\delta$ : 14.37 (br, 1H, Ph-OH), 9.23 (br, 1H, Ph- OH), 8.06 (d,  $J = 3.0$  Hz, 1H, Ph-H), 8.02 (s, 1H, CH=N), 7.95 (m, 1H, Ph-H), 7.73 (d,  $J = 7.7$  Hz, 2H, Ph-H), 7.57 (d,  $J = 7.7$  Hz, 2H, Ph-H), 7.44 (t,  $J = 7.7$  Hz, 2H, Ph-H), 7.23 (t,  $J = 7.7$  Hz, 2H, Ph-H), 7.09 (t,  $J = 7.3$  Hz, 1H, Ph-H), 6.93 (d,  $J = 8.4$  Hz, 2H, Ph-H), 6.62 (d,  $J = 8.4$  Hz, 3H, Ph-H), 6.53 (d,  $J = 9.7$  Hz, 1H, Ph-H), 4.94 (t,  $J = 6.7$  Hz, 1H, C\*H), 3.39 (br, 1H, OH), 2.85 (d, br,  $J = 6.7$  Hz, 2H, Ph-H);  $^{13}C$  NMR (126 MHz, DMSO, ppm)  $\delta$ : 177.1, 166.2, 155.9, 144.9, 144.7, 133.9, 131.7, 130.2, 129.1, 128.3, 127.9, 127.1, 126.9, 126.5, 126.0, 125.8, 122.5, 115.3, 113.1, 78.8, 71.4, 35.1; MS (EI, 70 eV)  $m/z$ : 468( $M^+$ , 1%), 269(24%), 182(40%), 136 (39%), 105(100%), 77(66%); Anal. Calcd for  $C_{28}H_{24}N_2O_5$ : C, 71.78; H, 5.16; N, 5.98. Found: C, 71.69; H, 5.15; N, 5.97.



**2-(((S)-2-Hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-4-methyl-phen**

**ol (11):**

Yellow solid; mp: 196~198 °C;  $[\alpha]_D^{20} = -161.49$  ( $c = 0.0644$  g/mL,  $\text{CH}_2\text{Cl}_2$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3582, 3030, 2967, 1634, 1498, 1447, 1240, 834, 755, 702;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 11.35 (br, 1H, Ph-OH), 7.67~7.63 (m, 2H, Ph-H), 7.60 (s, 1H, CH=N), 7.49 (d,  $J = 7.4$  Hz, 2H, Ph-H), 7.39 (d,  $J = 8.0$  Hz, 2H, Ph-H), 7.29 (s, 1H, Ph-H), 7.25 (d,  $J = 8.0$  Hz, 2H, Ph-H), 7.14 (t,  $J = 7.4$  Hz, 1H, Ph-H), 7.06 (m, 1H, Ph-H), 6.84 (d,  $J = 8.4$  Hz, 2H, Ph-H), 6.79 (d,  $J = 8.4$  Hz, 1H, Ph-H), 6.71 (d,  $J = 1.7$  Hz, 1H, Ph-H), 6.66 (d,  $J = 8.4$  Hz, 2H, Ph-H), 5.55 (br, 1H, Ph-OH), 4.30 (dd,  $J = 10.2, 1.7$  Hz, 1H, C\*H), 2.99 (dd,  $J = 13.9, 1.5$  Hz, 1H, Ph- $\text{CH}_2$ ), 2.96 (br, 1H, OH), 2.79 (dd,  $J = 13.9, 10.3$  Hz, 1H, Ph- $\text{CH}_2$ ), 2.21 (s, 3H, - $\text{CH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ : 166.5, 158.5, 154.0, 145.4, 144.1, 133.3, 131.6, 130.8, 128.3, 127.7, 127.0, 126.2, 126.0, 118.0, 116.6, 115.3, 79.8, 78.9, 77.3, 77.0, 76.8, 36.5, 20.2; MS (EI, 70 eV)  $m/z$ : 438( $\text{M}^+$ , 2%), 255(100%), 183(30%), 105(45%), 77(31%); Anal. Calcd for  $\text{C}_{29}\text{H}_{27}\text{NO}_3$ : C, 79.61; H, 6.22; N, 3.20. Found: C, 79.58; H, 6.19; N, 3.19.

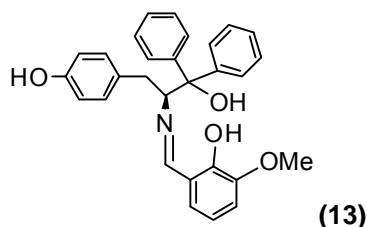


**2-(((S)-2-Hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-4-methoxy-phe**

**nol (12):**

Yellow solid; mp: 97~99 °C;  $[\alpha]_D^{20} = -130$  ( $c = 0.120$  g/mL,  $\text{CH}_2\text{Cl}_2$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3358, 3026, 2929, 1635, 1494, 1448, 1384, 1269, 824, 753, 702;  $^1\text{H}$  NMR (500 MHz, DMSO, ppm)  $\delta$ : 12.55 (s, 1H, Ph-OH), 9.13 (d,  $J = 6.3$  Hz, 1H, Ph-OH), 7.77 (s, 1H, CH=N), 7.63 (m, 5H, Ph-H), 7.54

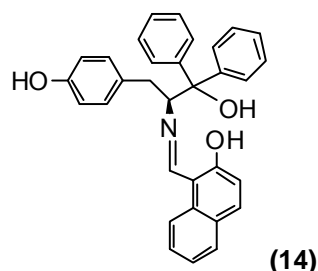
(d,  $J = 7.5$  Hz, 2H, Ph-H), 7.37 (t,  $J = 7.7$  Hz, 2H, Ph-H), 7.26~7.19 (m, 3H, Ph-H), 7.08 (t,  $J = 7.3$  Hz, 1H, Ph-H), 6.88~6.76 (m, 3H, Ph-H), 6.00 (s, 1H, Ph-H), 5.39 (s, 1H, OH), 4.48 (d,  $J = 9.7$  Hz, 1H, C\*H), 2.83 (d, br,  $J = 13.9$  Hz, 1H, Ph-CH<sub>2</sub>), 2.65 (dd,  $J = 13.9, 10.5$  Hz, 1H, Ph-CH<sub>2</sub>), 2.53~2.48 (m, 3H, -OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, DMSO, ppm)  $\delta$ : 165.3, 155.4, 154.2, 151.2, 146.1, 130.2, 129.9, 128.9, 128.0, 127.5, 126.3, 126.2, 126.0, 125.4, 118.7, 118.2, 117.0, 114.9, 79.5, 79.0, 77.5, 58.6, 55.4, 36.3, 22.0; MS (EI, 70 eV)  $m/z$ : 453(M<sup>+</sup>, 2%), 271(21%), 182(27%), 136(100%), 105(60%), 77 (50%); Anal. Calcd for C<sub>29</sub>H<sub>27</sub>NO<sub>4</sub>: C, 76.80; H, 6.00; N, 3.09. Found: C, 76.73; H, 5.98; N, 3.07.



**2-(((S)-2-Hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-6-methoxyphenol (13):**

Yellow solid; mp: 106~109 °C;  $[\alpha]_D^{20} = -168.42$  ( $c = 0.133$  g/mL, CH<sub>2</sub>Cl<sub>2</sub>). IR (KBr, cm<sup>-1</sup>): 3405, 3057, 1629, 1510, 1449, 1384, 1251, 838, 738, 702; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 13.37 (br, 1H, Ph-OH), 7.66~7.62 (m, 2H, Ph-H), 7.57 (s, 1H, CH=N), 7.51~7.46 (m, 2H, Ph-H), 7.39 (t,  $J = 7.8$  Hz, 2H, Ph-H), 7.25 (m, 3H, Ph-H), 7.12 (t,  $J = 7.4$  Hz, 1H, Ph-H), 6.85 (m, 3H, Ph-H), 6.71~6.62 (m, 3H, Ph-H), 6.53 (d,  $J = 7.8$  Hz, 1H, Ph-H), 5.55 (br, 1H, Ph-OH), 4.30 (dd,  $J = 10.2, 1.9$  Hz, 1H, C\*H), 3.86 (s, 3H, -OCH<sub>3</sub>), 2.99 (br, 1H, OH), 2.97 (dd,  $J = 14.0, 1.6$  Hz, 1H, Ph-CH<sub>2</sub>), 2.80 (dd,  $J = 14.0, 10.3$  Hz, 1H, Ph-CH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 166.5, 154.2, 148.3, 145.2, 144.0, 130.8, 128.4, 127.1, 127.0, 126.1, 126.0, 123.1, 118.1, 117.8, 115.3, 114.0, 79.7, 78.5, 77.3, 77.0, 76.8, 56.0, 36.6; MS (EI, 70 eV)  $m/z$ : 453(M<sup>+</sup>, 7%),

271(100%), 229 (34%), 152(44%), 105(68%), 77(48%); Anal. Calcd for C<sub>29</sub>H<sub>27</sub>NO<sub>4</sub>: C, 76.80; H, 6.00; N, 3.09. Found: C, 76.72; H, 5.99; N, 3.07.



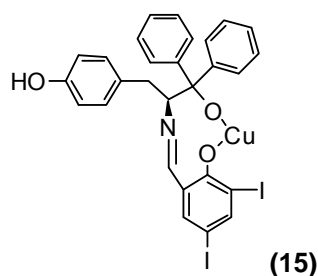
**1-(((S)-2-Hydroxy-1-(4-hydroxy-benzyl)-2,2-diphenyl-ethylimino)-methyl)-naphthalen-2-ylidene**

**1(14):**

Yellow solid; mp: 245 °C;  $[\alpha]_D^{20} = -178.12$  ( $c = 0.141$  g/mL, CH<sub>2</sub>Cl<sub>2</sub>). IR (KBr): 3581, 3081, 3030, 1626, 1444, 1340, 1280, 842, 752, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO, ppm)  $\delta$ : 13.77~13.64 (m, 1H, naphthyl-OH), 9.12 (s, 1H, Ph-OH), 8.34 (d,  $J = 10.9$  Hz, 1H, CH=N), 7.74 (d,  $J = 7.5$  Hz, 2H, Ph-H), 7.68 (d,  $J = 7.5$  Hz, 2H, Ph-H), 7.59 (d,  $J = 9.4$  Hz, 1H, Ph-H), 7.54~7.41 (m, 4H, Ph-H), 7.33~7.26 (m, 2H, Ph-H), 7.19 (t,  $J = 7.8$  Hz, 2H, Ph-H), 7.09 (t,  $J = 7.3$  Hz, 1H, Ph-H), 7.01 (t,  $J = 7.3$  Hz, 1H, Ph-H), 6.94 (d,  $J = 8.4$  Hz, 2H, Ph-H), 6.58 (m, 3H, Ph-H), 6.43 (s, 1H, OH), 5.04 (m, 1H, C\*H), 2.85~2.65 (m, 2H, Ph-CH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, DMSO, ppm)  $\delta$ : 177.7, 158.2, 155.7, 145.5, 136.8, 134.3, 130.2, 128.7, 128.3, 127.9, 127.7, 126.7, 126.2, 126.1, 125.4, 124.8, 121.7, 117.6, 115.1, 104.8, 79.3, 69.7, 39.5, 35.9; MS (EI, 70 eV)  $m/z$ : 474 (M<sup>+</sup>, 2%), 291 (71%), 241(31%), 184(100%), 105(81%), 77(60%); Anal. Calcd for C<sub>32</sub>H<sub>27</sub>NO<sub>3</sub>: C, 81.16; H, 5.75; N, 2.96. Found: C, 81.14; H, 5.74; N, 2.95.

**4. Preparation and characterization of copper Schiff-base complex 15**

General procedure for the preparation of copper Schiff-base complex **15** was consulted the literature[3] method.



**Compound 15:** Elemental Anal. Found: C, 45.61; H, 2.86; N, 1.89. IR (KBr,  $\text{cm}^{-1}$ ): 3374, 3012, 2935, 1629, 1439, 1145, 1052, 746, 704, 592, 564, 503, 454.

To a mixture of complex 15 (0.051 g) in Milli-Q water (2 mL) was added  $\text{HNO}_3$  (20 ml, 69.2%).

The mixture was heated at  $150^\circ\text{C}$  and the digested solution was diluted to 25 ml with Milli-Q water. Heavy metal Cu concentrations in the prepared solutions were determined using atomic absorption spectrometry (AA-800, Perkin-Elmer Inc.). Metal Cu concentrations were 5.541 mg/L and 5.570 mg/L (panel data which were diluted to 30 times). Metal concentrations had a  $n(\text{ligand 1})$ -to- $n(\text{Cu})$  ratio of 1.065.

$$m(\text{Cu}) = \frac{1}{2} \times (5.541 + 5.570) \times 30 = 166.665 \text{ mg / L}$$

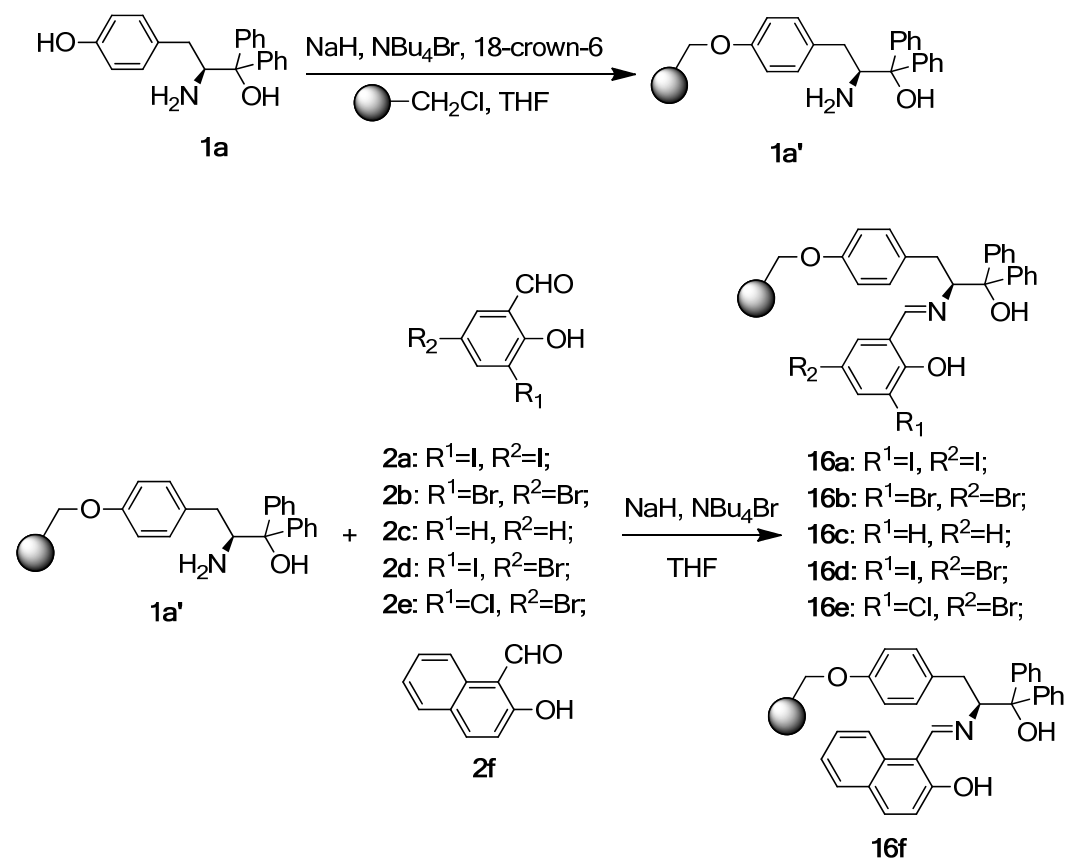
$$n(\text{Cu}) = \frac{m(\text{Cu})}{M(\text{Cu})} = \frac{166.665}{64} = 2.604 \text{ mmol / L}$$

$$m(\text{ligand 1}) = m(\text{complex 15}) - m(\text{Cu}) = \frac{0.051 \times 1000}{25 \times 0.001} - 166.665 = 1873.335 \text{ mg / L}$$

$$n(\text{ligand 1}) = \frac{m(\text{ligand 1})}{M(\text{ligand 1})} = \frac{1873.335}{675.30} = 2.774 \text{ mmol / L}$$

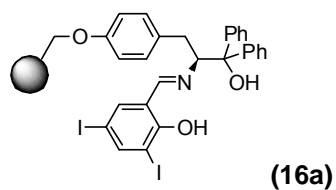
$$n(\text{Cu}) : n(\text{ligand 1}) = 2.604 : 2.774 = 1 : 1.065$$

## 5. Preparation of polymer-supported chiral tridentate Schiff-base ligands 16a-f, 17 [4]

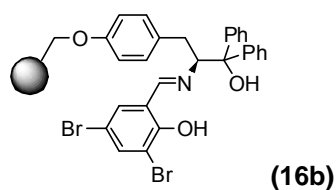


To a stirred mixture of **1a** (0.957 g, 3 mmol) in anhydrous THF (100 mL) was added NaH (0.120g, 3mmol), NBu<sub>4</sub>Br (0.115g, 0.3mmol) and 18-crown-6 (0.079g, 0.3mmol). The mixture was stirred for 30 min at room temperature. Then the Merrifield resin (3g, 100~200 mesh, 1.0~1.2 mmol/g) was added and the solution was heated under reflux for 60 h. The solvent was evaporated and washed by THF, THF/H<sub>2</sub>O, THF/MeOH, MeOH, CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O to give **1a'**.

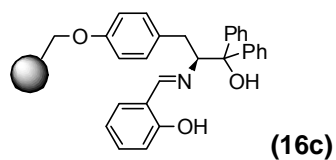
Next, to a stirred mixture of **1a'** (1.29 g, 1 mmol) in anhydrous THF (50 mL) was added NaH (0.040g, 1mmol), NBu<sub>4</sub>Br (0.038g, 0.1mmol) and 18-crown-6 (0.026g, 0.1mmol). The mixture was stirred for 30 min at room temperature. Then the salicylaldehyde(**2a-2f**) (1 mmol) was added and then the solution was heated under reflux overnight. And the reaction was vacuum filtered and washed by THF. At last, the solution was dried to provide the polymer-supported chiral tridentate Schiff-base ligands **16a-f** and catalyst **17**.



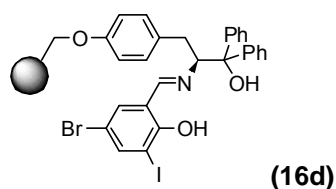
**Compound 16a:** Elemental Anal. Found: C, 51.21; H, 3.86; N, 1.97. IR (KBr,  $\text{cm}^{-1}$ ): 3424, 3058, 3024, 2920, 2848, 1942, 1691, 1600, 1492, 1450, 1383, 1264, 1028, 905, 837, 756, 697, 538.



**Compound 16b:** Elemental Anal. Found: C, 59.12; H, 4.42; N, 2.29. IR (KBr,  $\text{cm}^{-1}$ ): 3440, 3058, 3024, 2921, 1943, 1802, 1721, 1600, 1492, 1450, 1370, 1265, 1027, 906, 838, 756, 697, 536.

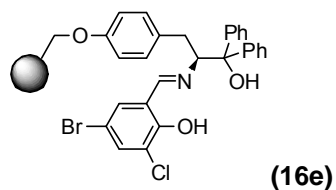


**Compound 16c:** Elemental Anal. Found: C, 79.78; H, 6.46; N, 3.09. IR (KBr,  $\text{cm}^{-1}$ ): 3420, 3059, 3025, 2921, 1944, 1803, 1666, 1601, 1492, 1451, 1383, 1028, 906, 826, 756, 698, 539.

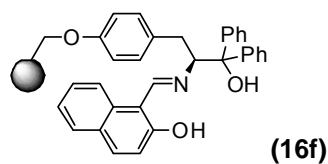


**Compound 16d:** Elemental Anal. Found: C, 54.89; H, 4.14; N, 2.12. IR (KBr,  $\text{cm}^{-1}$ ): 3421, 3058, 3024, 2920, 1943, 1802, 1600, 1492, 1450, 1365, 1265, 1027, 906, 821, 756, 697, 538.

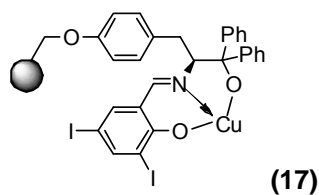




**Compound 16e:** Elemental Anal. Found: C, 63.77; H, 4.81; N, 2.47. IR (KBr,  $\text{cm}^{-1}$ ): 3059, 3025, 2922, 1943, 1802, 1722, 1601, 1492, 1450, 1369, 1265, 1027, 906, 822, 756, 697, 538.



**Compound 16f:** Elemental Anal. Found: C, 81.40; H, 6.22; N, 2.78. IR (KBr,  $\text{cm}^{-1}$ ): 3394, 3058, 3024, 2921, 1943, 1723, 1601, 1492, 1450, 1242, 1076, 1028, 906, 820, 756, 698, 538.



**Compound 17:** Elemental Anal. Found: C, 52.55; H, 4.27; N, 1.92. IR (KBr,  $\text{cm}^{-1}$ ): 3377, 3024, 2922, 1604, 1492, 1442, 1384, 1032, 905, 757, 696, 627, 539.

To a mixture of polymers complex 17 (0.052 g) in Milli-Q water (2 mL) was added  $\text{HNO}_3$  (20 ml, 69.2%). The mixture was heated at  $150^\circ\text{C}$  and the digested solution was diluted to 25 ml with Milli-Q water. Heavy metal Cu concentrations in the prepared solutions were determined using atomic absorption spectrometry. Metal Cu concentrations were 2.651 mg/L and 2.663 mg/L (panel data which were diluted to 30 times ). We assumed that the metal coordination of polymers complex 17 work on the same mechanism like complex 15. The amount of chlorobenzyl groups which have been substituted was 79.38%.

$$n(\text{Cu}) = \frac{m(\text{Cu})}{M(\text{Cu})} = \frac{\frac{1}{2} \times (2.651 + 2.663) \times 30}{64} = 1.245 \text{ mmol} / L$$

$$\therefore n(\text{Cu}) : n(\text{ligand 1}) = 1 : 1.065$$

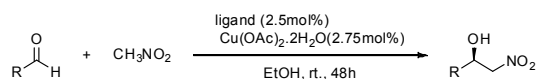
$$\therefore n(\text{ligand 1}) = 1.065 \times n(\text{Cu}) = 1.065 \times 1.245 = 1.651 \text{ mmol} / L$$

$$n(\text{Cl-phenyl}) = n(\text{ligand 1}) = 1.651 \text{ mmol} / L$$

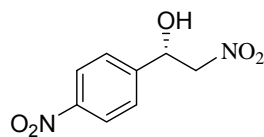
$$n(\text{actual Cl-phenyl}) = 0.052 \times \frac{1000}{25} = 2.08 \text{ mmol} / L$$

$$\left( \frac{\text{Cl-phenyl}}{\text{actual Cl-phenyl}} \right) \% = \frac{n(\text{Cl-phenyl})}{n(\text{actual Cl-phenyl})} \times 100\% = \frac{1.651}{2.08} \times 100\% = 79.38\%$$

## 6. Typical procedure for the asymmetric Henry reaction[5]

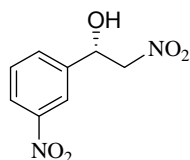


The chiral ligand (0.005 mmol) and metal-salt (0.0055 mmol) were placed in a 10 mL round-bottomed flask. Ethanol (2.0 mL) was added and the mixture was stirred for 3 h at room temperature. Subsequently, aldehyde (0.2 mmol) and nitromethane (0.3 mL, 7.5 mmol) were added. The reaction was stirred at room temperature for 24 h. Purification was obtained by TLC. The ee value was determined by HPLC on Chiralcel AD-H or OD-H column.



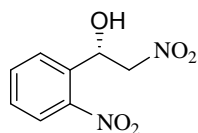
**2-Nitro-1-(4-nitro-phenyl)-ethanol:** Chiralcel AD-H column, Hex: *i*-Pro

=85:15, 1.0 mL/min, 254nm.  $t_{\text{minor}} = 6.590 \text{ min}$ ,  $t_{\text{major}} = 8.707 \text{ min}$ .



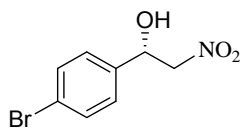
**2-Nitro-1-(3-nitro-phenyl)-ethanol:** Chiralcel AD-H column, Hex: *i*-Pro

=85:15, 1.0 mL/min, 254nm.  $t_{\text{major}} = 11.732 \text{ min}$ ,  $t_{\text{minor}} = 13.840 \text{ min}$ .



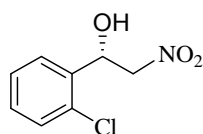
**2-Nitro-1-(2-nitro-phenyl)-ethanol:** Chiralcel AD-H column, Hex: *i*-Pro

=85:15, 1.0 mL/min, 254nm.  $t_{\text{minor}} = 38.000$  min,  $t_{\text{major}} = 43.832$  min.



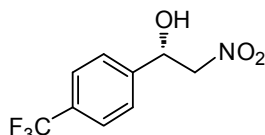
**(S)-1-(4-bromophenyl)-2-nitroethanol:** Chiralcel OD-H column, Hex:

*i*-Pro =85:15, 1.0 mL/min, 215nm.  $t_{\text{minor}} = 12.6$  min,  $t_{\text{major}} = 16.8$  min.



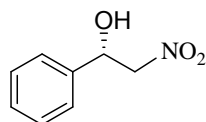
**(S)-1-(2-Chlorophenyl)-2-nitroethanol:** Chiralcel OD-H column, Hex:

*i*-Pro =95:5, 0.5 mL/min, 215nm.  $t_{\text{minor}} = 34.9$  min,  $t_{\text{major}} = 36.5$  min.



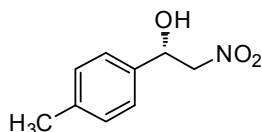
**2-Nitro-1-(4-trifluoromethyl-phenyl)-ethanol:** Chiralcel AD-H column,

Hex: *i*-Pro =95:5, 1.0 mL/min, 254nm.  $t_{\text{minor}} = 19.515$  min,  $t_{\text{major}} = 29.287$  min.



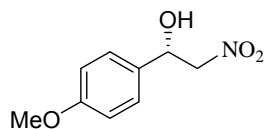
**(S)-2-Nitro-1-phenylethanol:** Chiralcel OD-H column, Hex: *i*-Pro =90:10,

1.0 mL/min, 210 nm.  $t_{\text{minor}} = 12.6$  min,  $t_{\text{major}} = 14.2$  min.



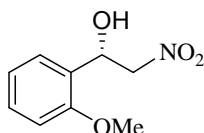
**2-Nitro-1-p-tolyl-ethanol:** Chiralcel OD-H column, Hex: *i*-Pro =90:10,

1.0mL/min, 215nm.  $t_{\text{minor}} = 16.475$ ,  $t_{\text{major}} = 22.813$  min.



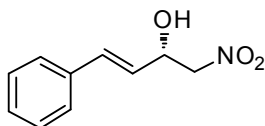
**(S)-1-(4-Methoxyphenyl)-2-nitroethanol:** Chiralcel OD-H column,

Hex: *i*-Pro =90:10, 0.5 mL/min, 232nm.  $t_{\text{major}} = 34.7$ min,  $t_{\text{minor}} = 49.5$  min.



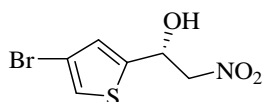
**(S)-1-(2-Methoxyphenyl)-2-nitroethanol:** Chiralcel OD-H column, Hex:

*i*-Pro =90:10, 1.0 mL/min, 215nm.  $t_R = 14.528$  min,  $t_R = 18.086$  min.



**1-Nitro-4-phenyl-but-3-en-2-ol:** Chiralcel OD-H column, Hex: *i*-Pro

=90:10, 1.0 mL/min, 254 nm.  $t_{major} = 45.2$  min,  $t_{minor} = 52.1$  min.



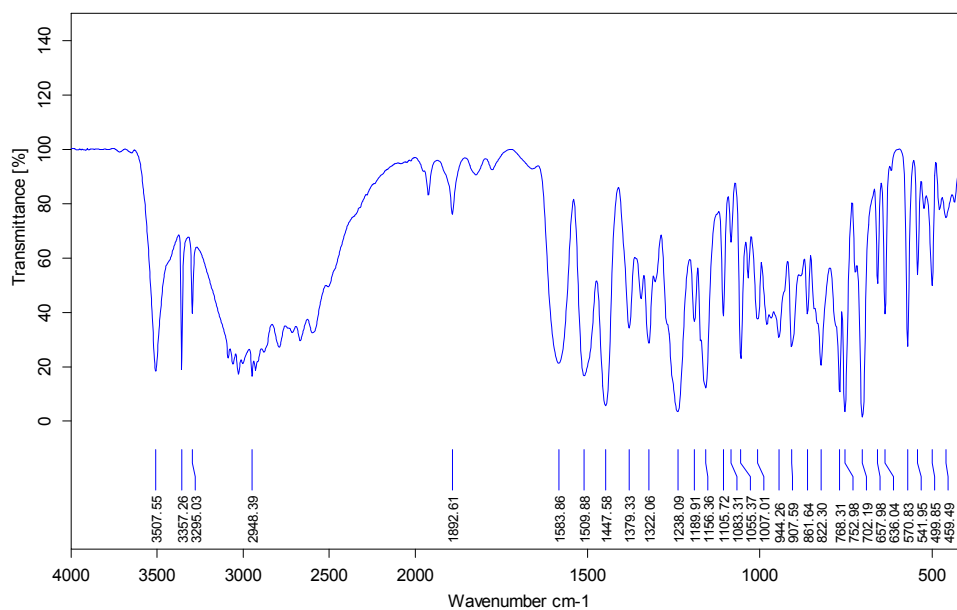
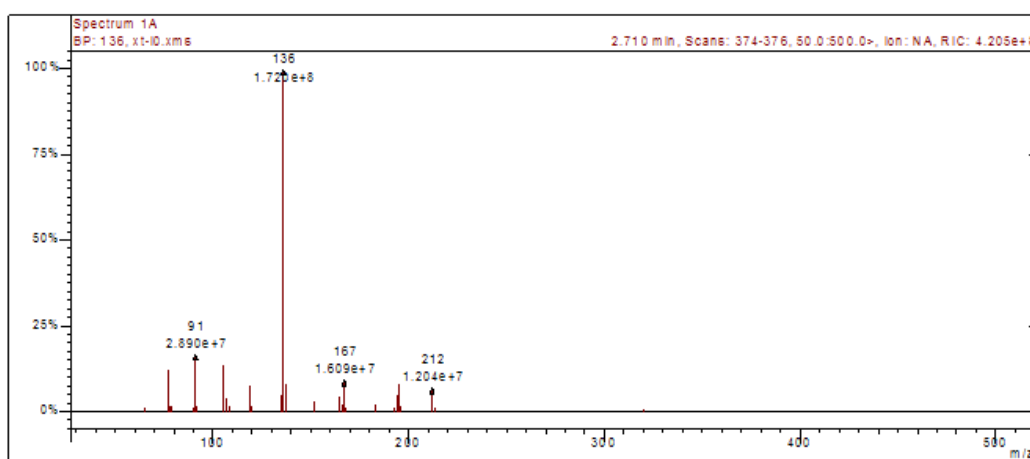
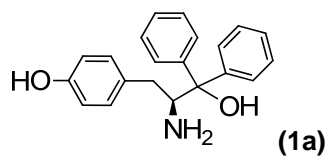
**1-(4-Bromo-thiophen-2-yl)-2-nitro-ethanol:** Chiralcel AD-H column,

Hex: *i*-Pro =95:5, 1.0 mL/min, 254nm.  $t_{major} = 27.387$  min,  $t_{minor} = 32.633$  min.

## References

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2. (a)S. -P. Xu, H. -L. Zhu, Z. -P. Xiao, W. -D. Wan, CN 101161620, 2008-4-16; (b) A. Vibhute, S. Mogle, K. Karamunge, V. Gurav, Y. Vibhute, Chin. Chem. Lett. 21 (2010) 914–918; (c) X. -J. Liu, Qu Fu Normal University. Master's Thesis 2002 20; (d) A. -X. Hu, Z. Qin, Chen, P. CN 101602761, 2009-12-16; (e) A. -Y. Vibhute, et al. J. Chem. Pharm. Res. 2 (2010) 620-625; (f) S. -S. Mogle, B. -S. Dawane, M. -A. Sayyed, Y. -B. Vibhute, J. Chem. Res. 2006 101.
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5. W. Mansawat, I. Saengswang, P. U-prasitwong, Tetrahedron Lett. 48 (2007) 4151-4308.

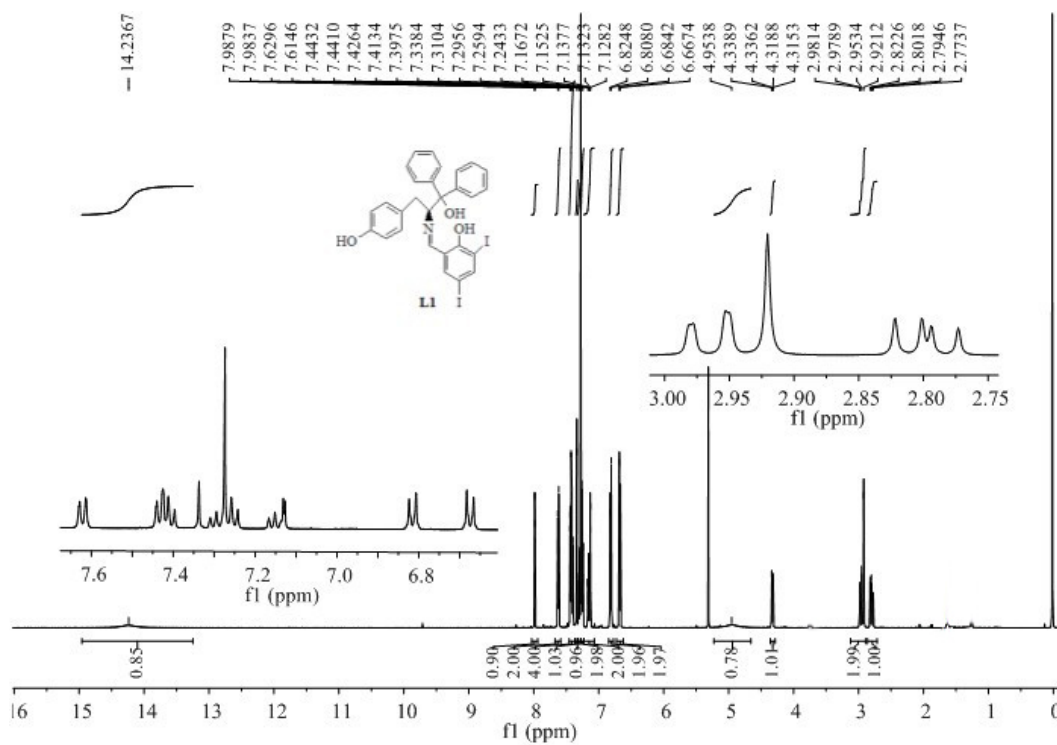
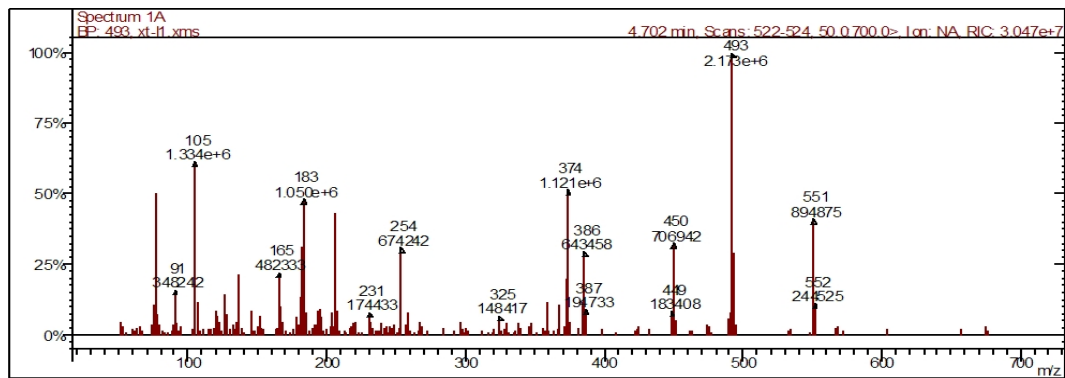
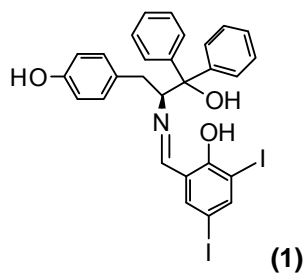
MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR and IR spectra for all compounds

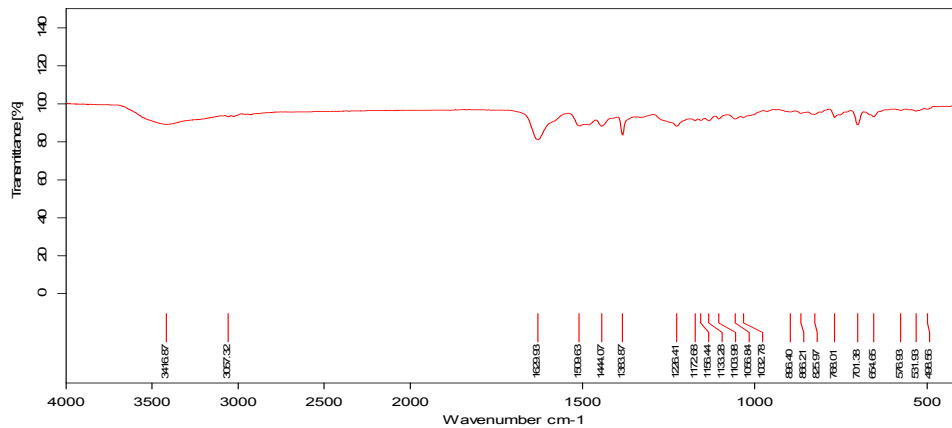
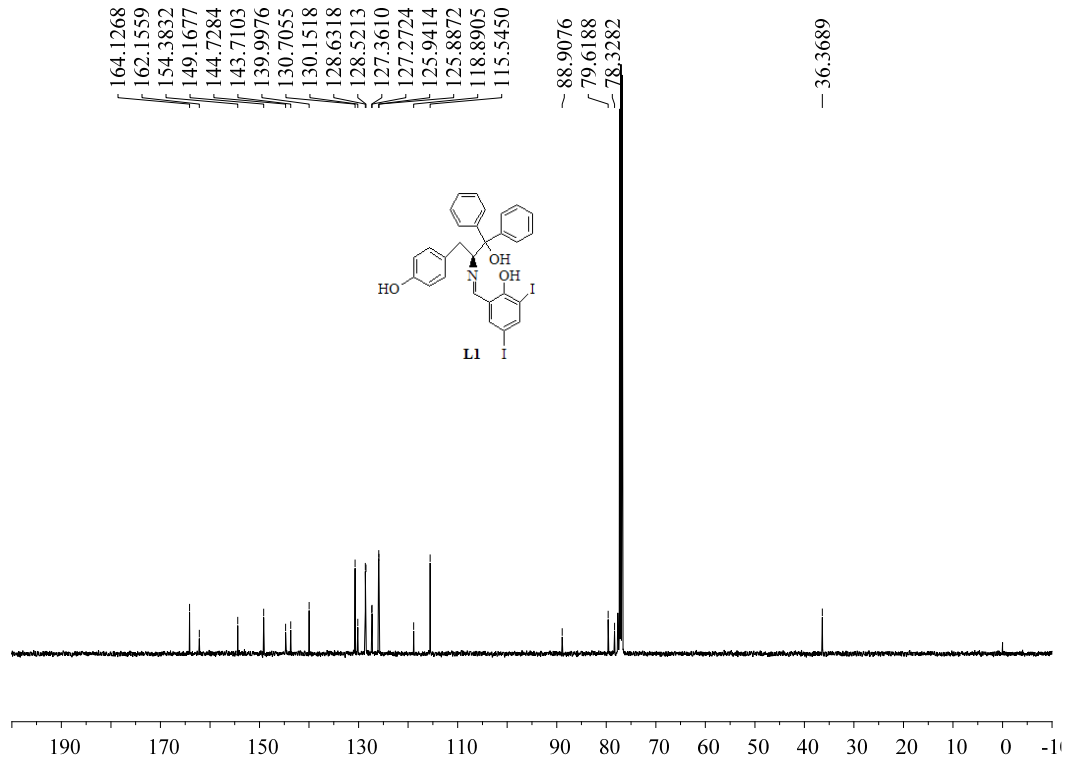


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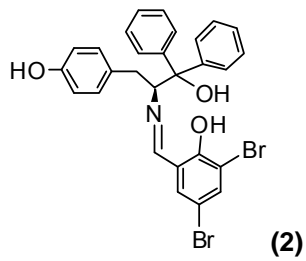
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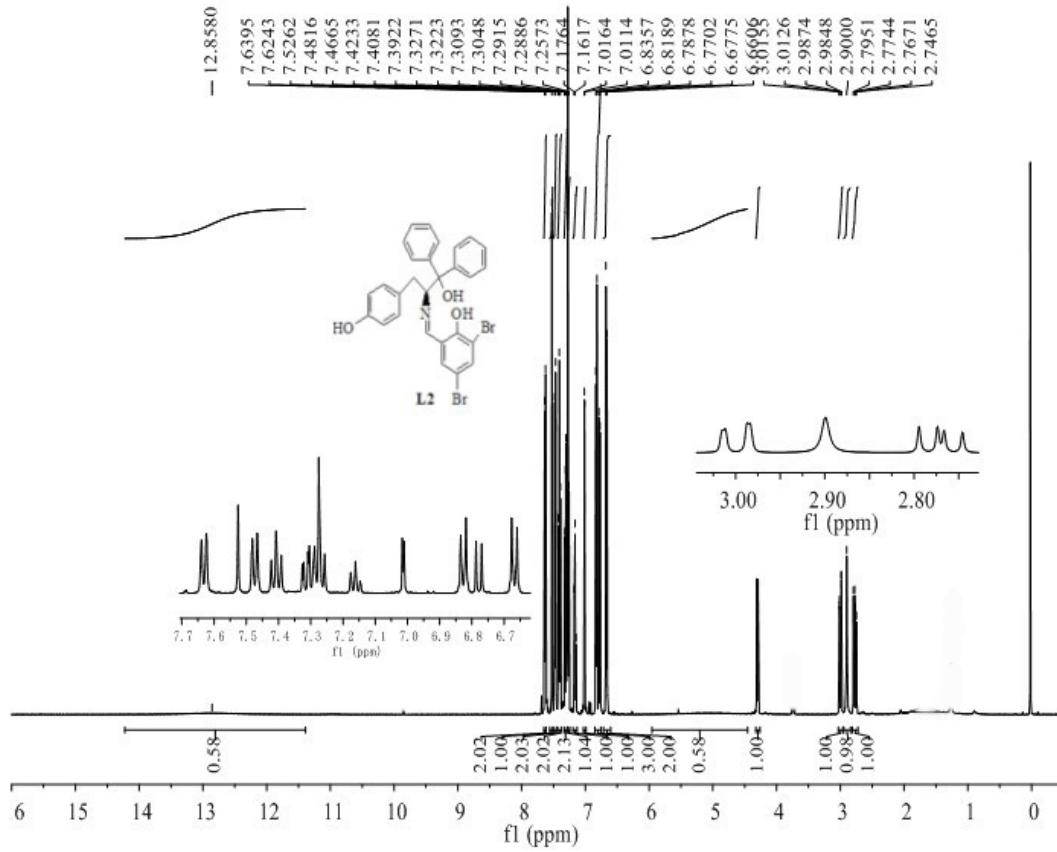
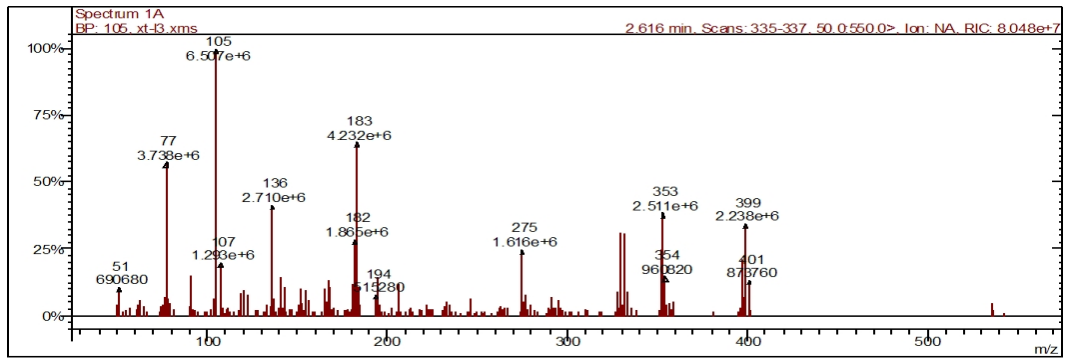
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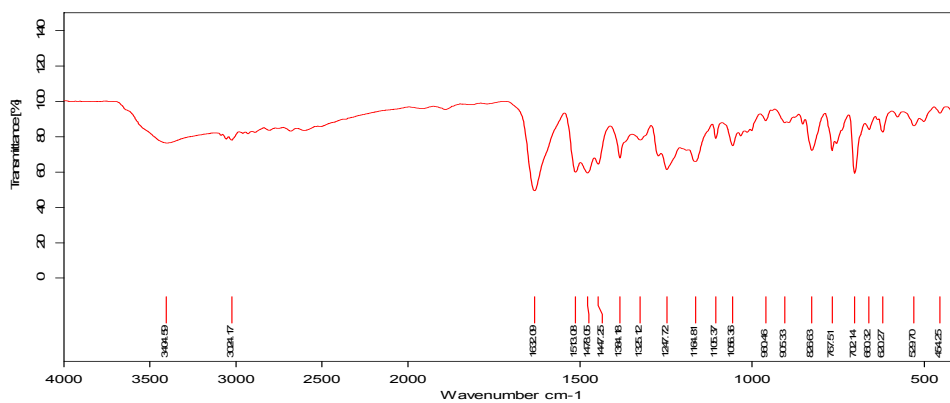
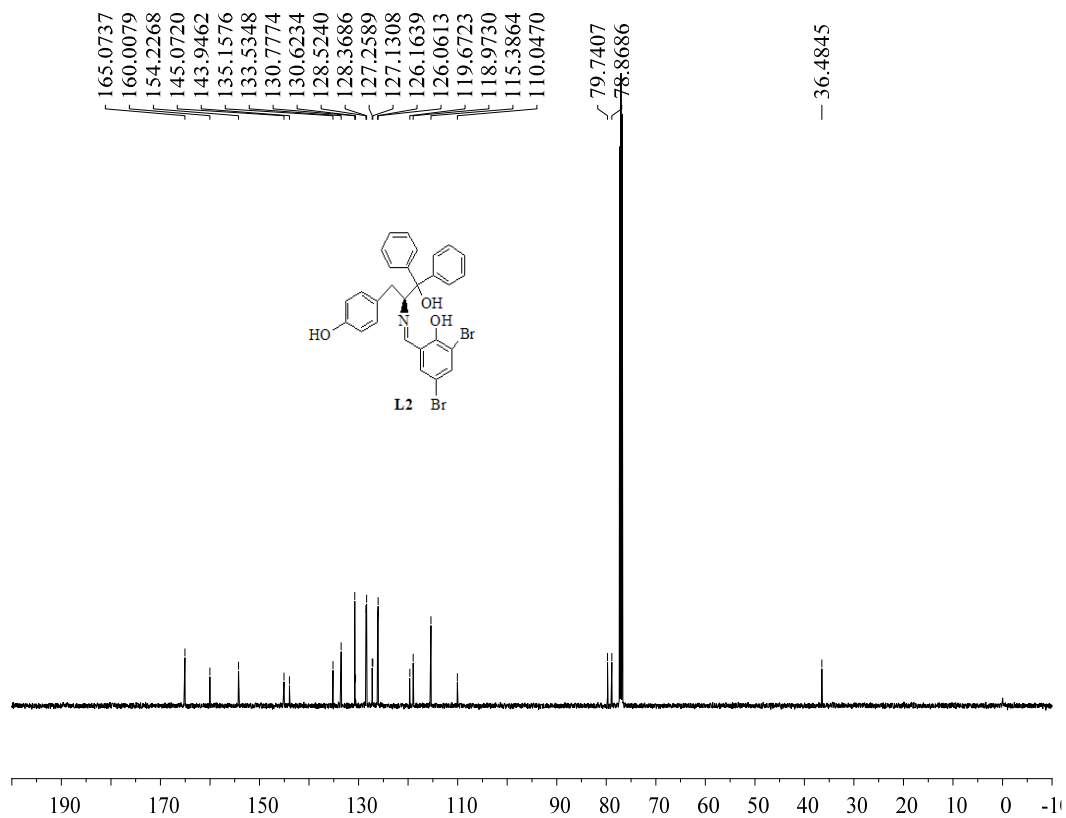


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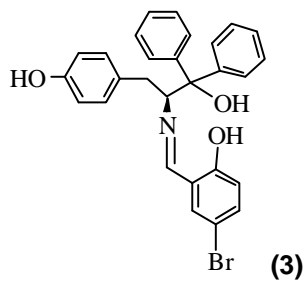


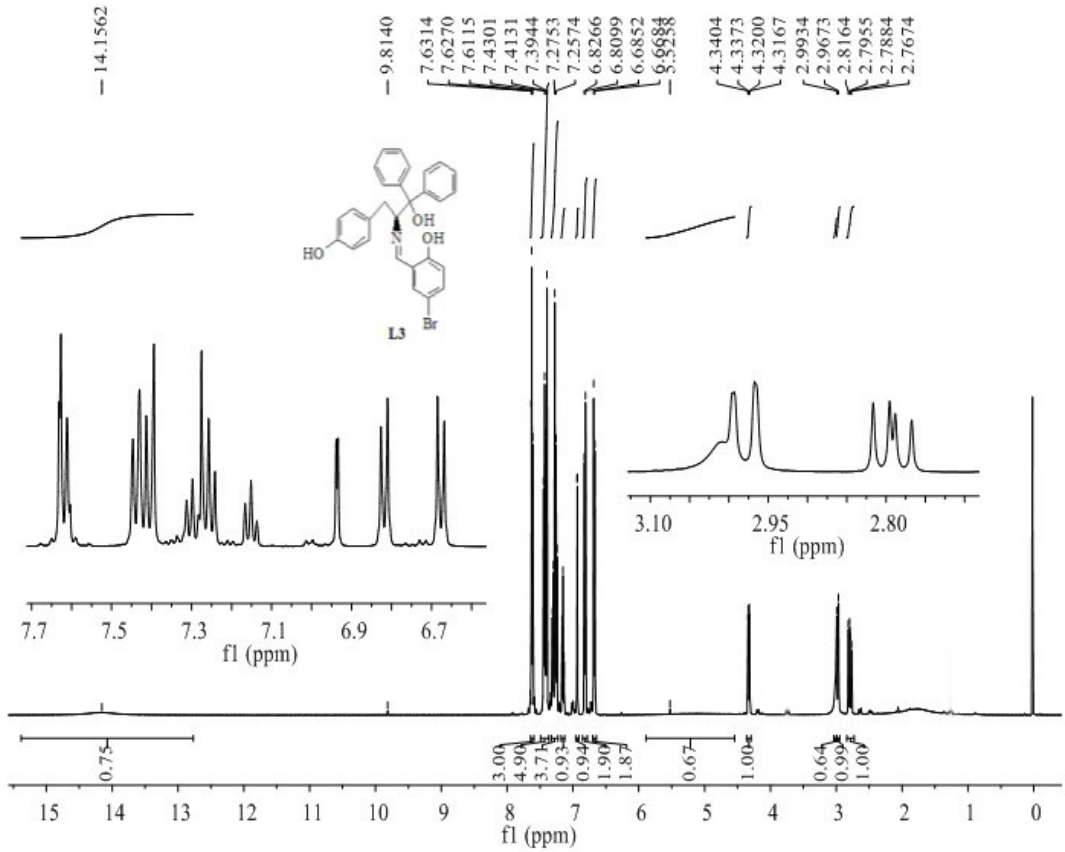
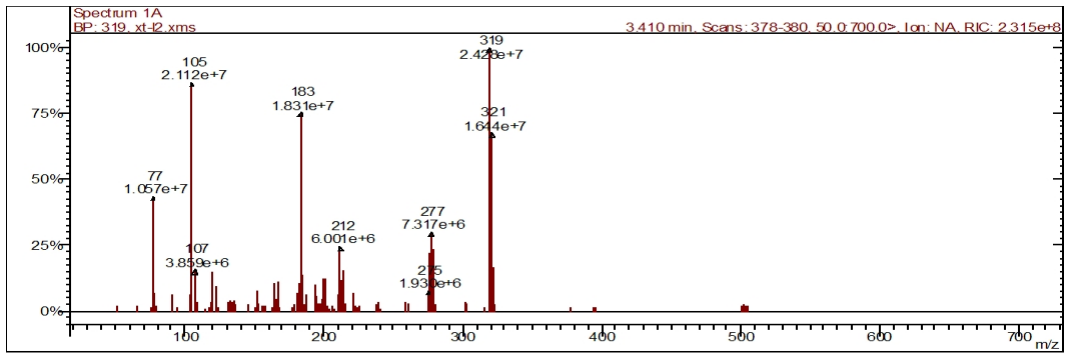


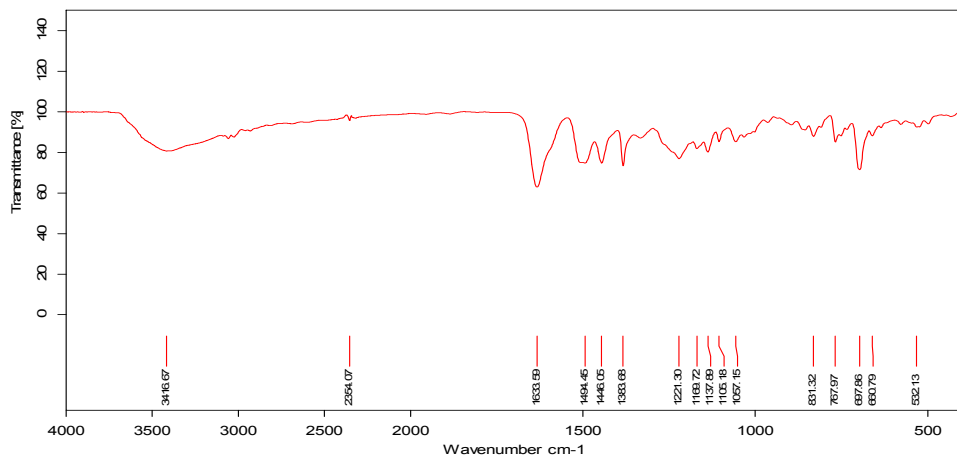
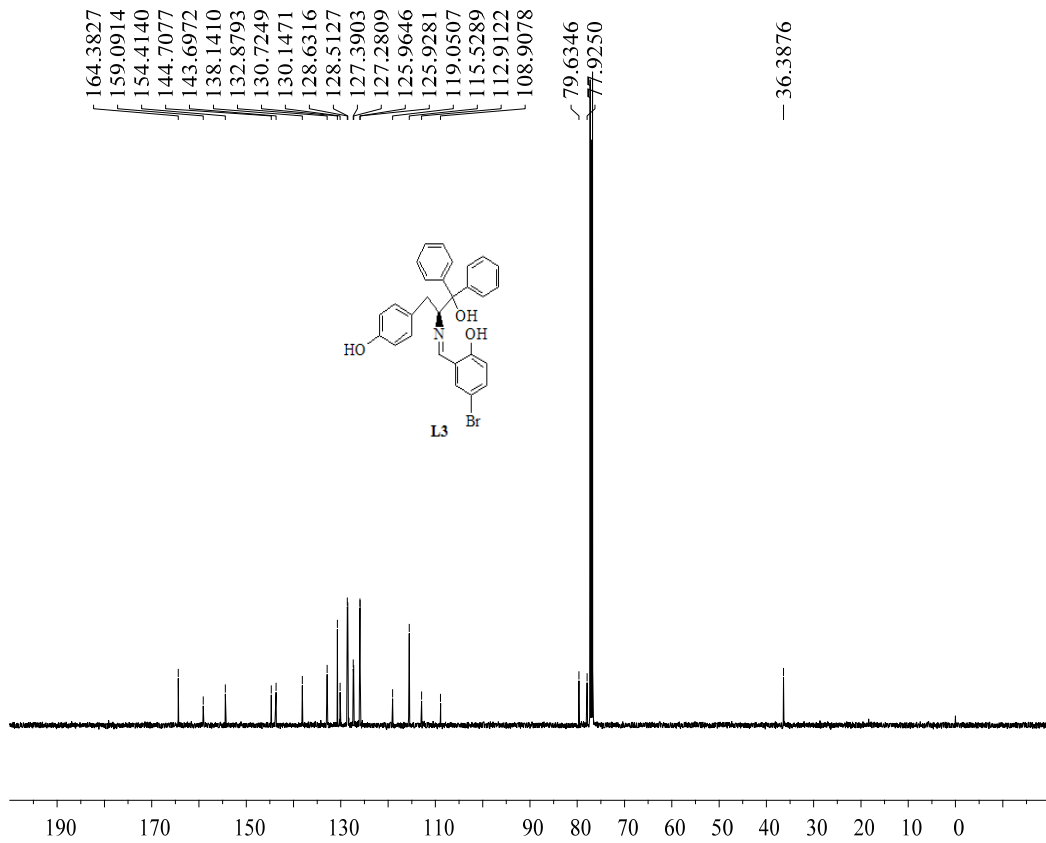




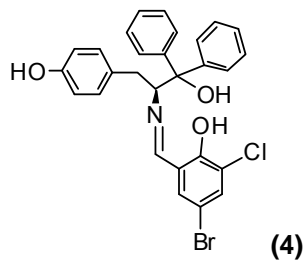
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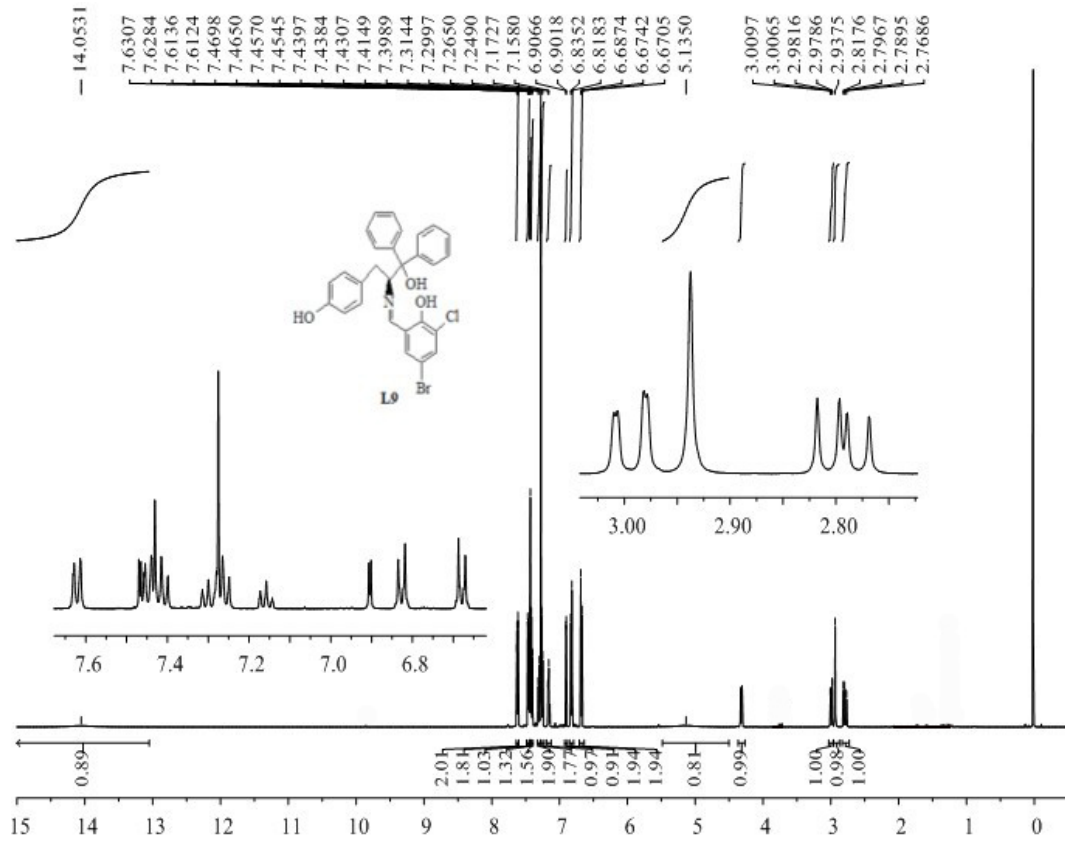
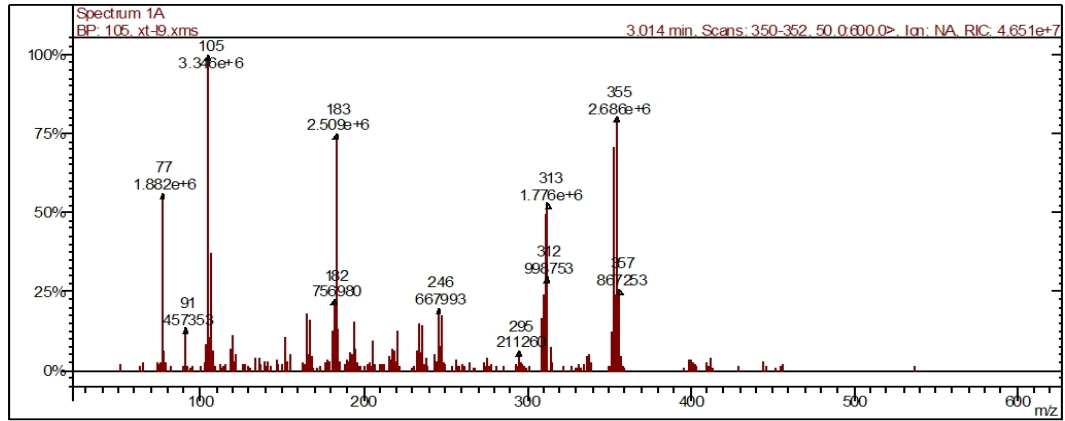




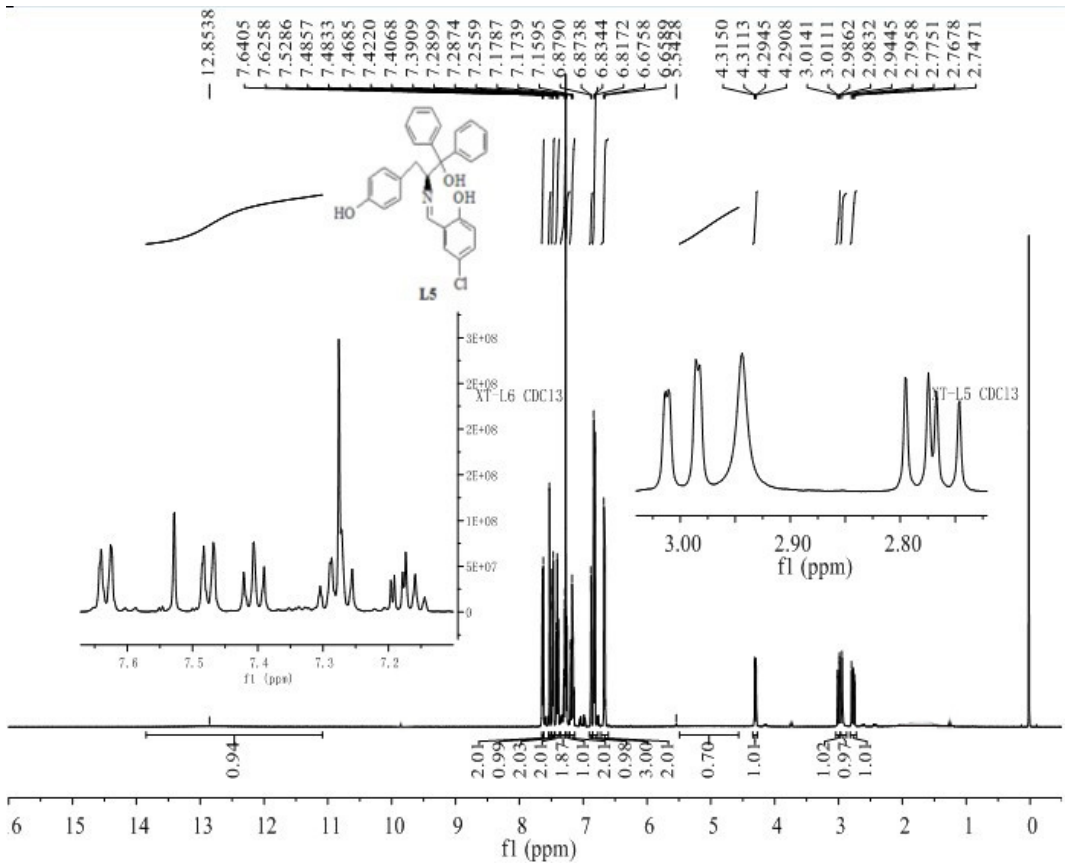
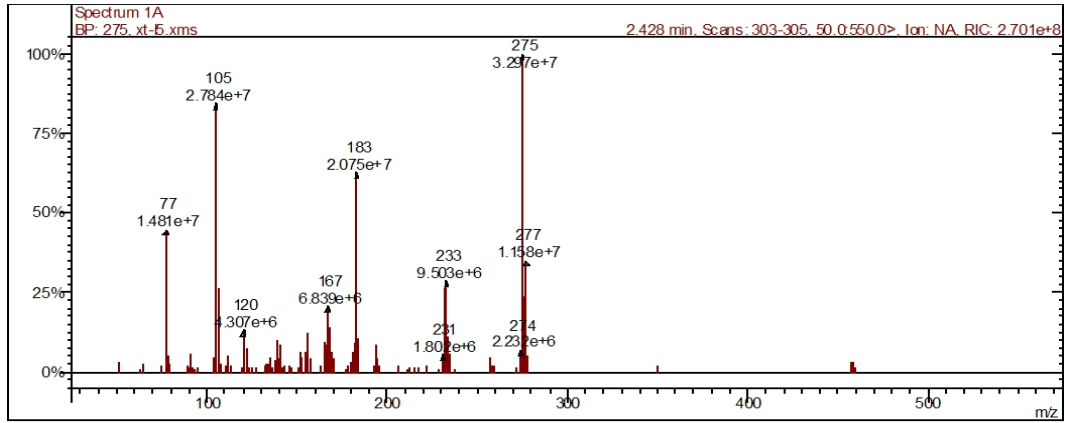


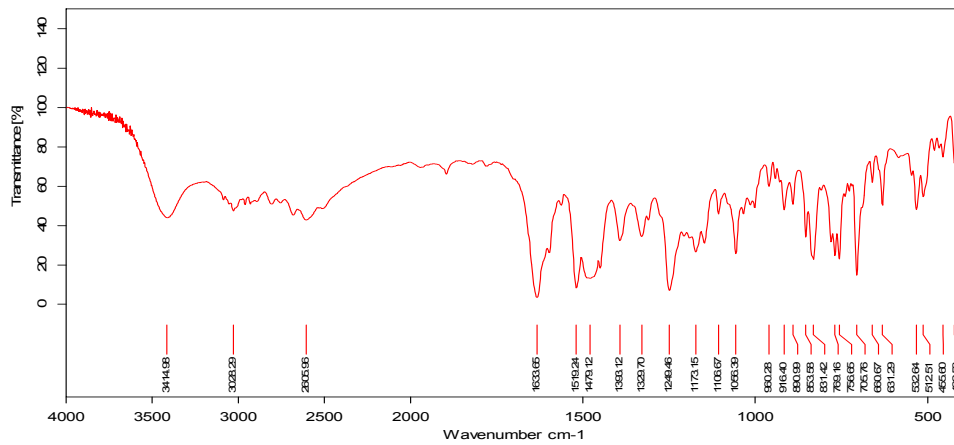
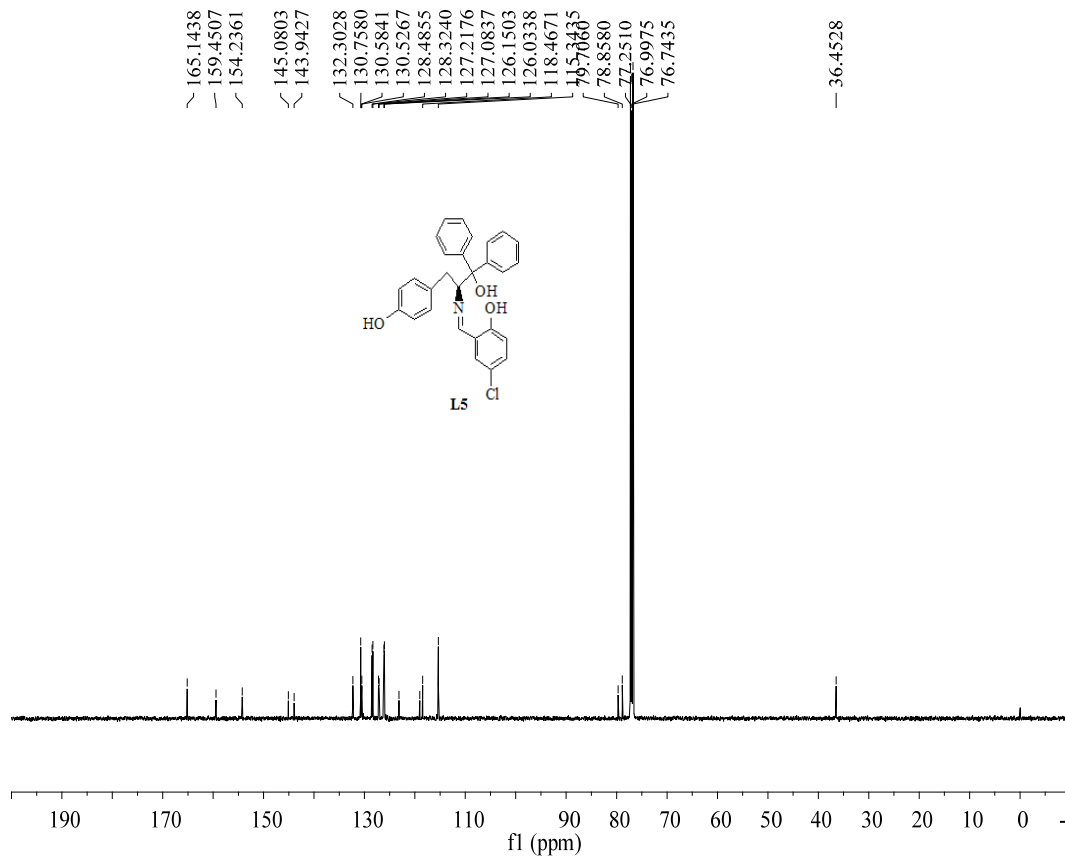
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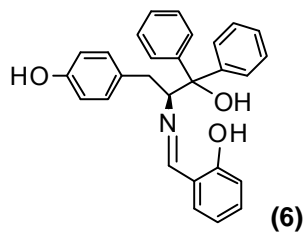


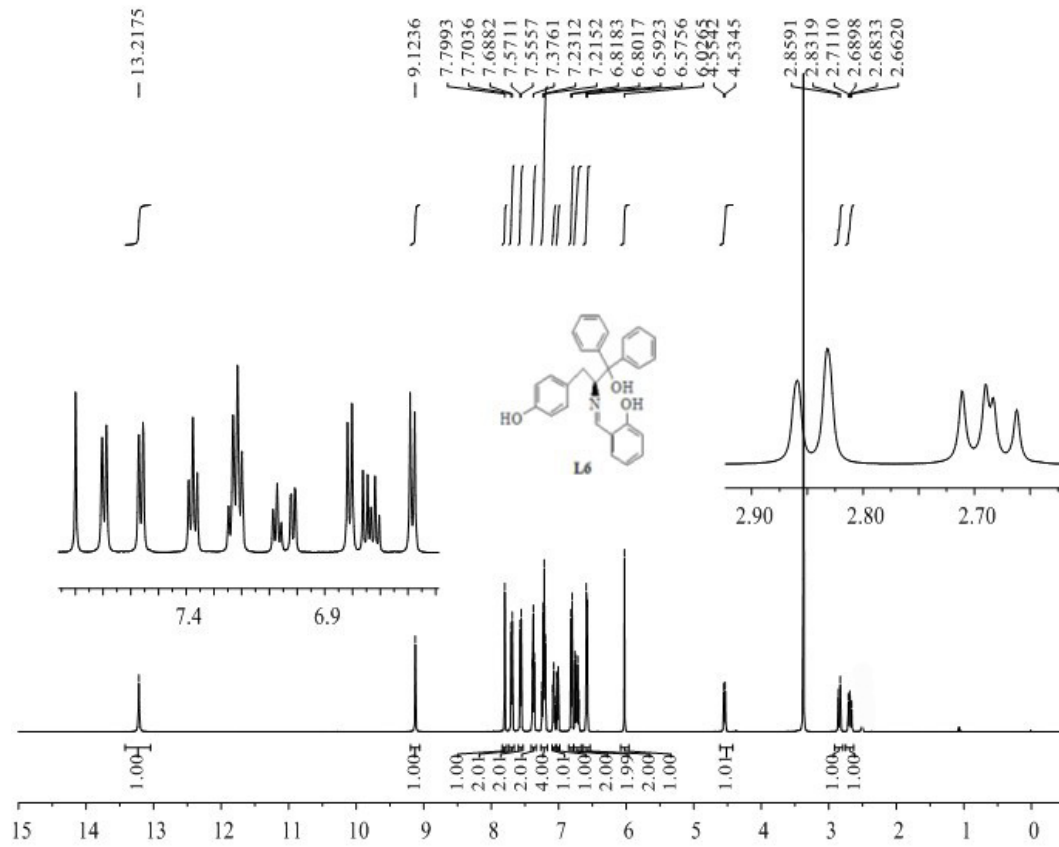
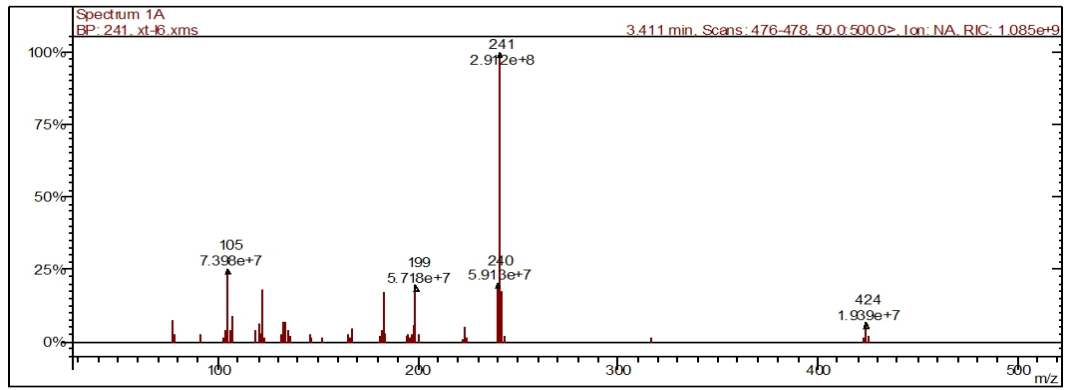




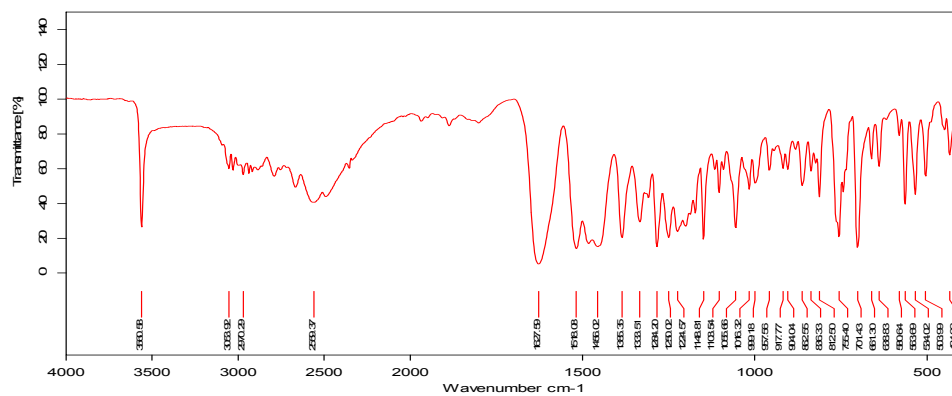
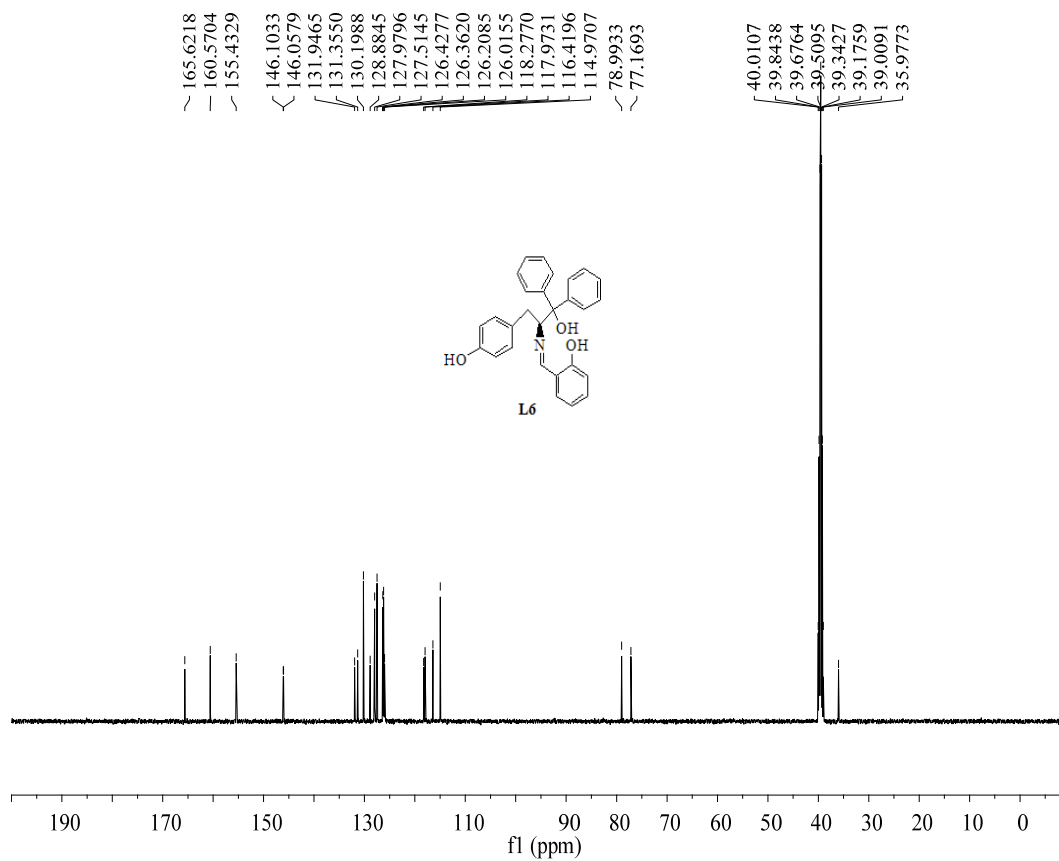


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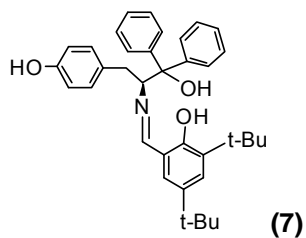


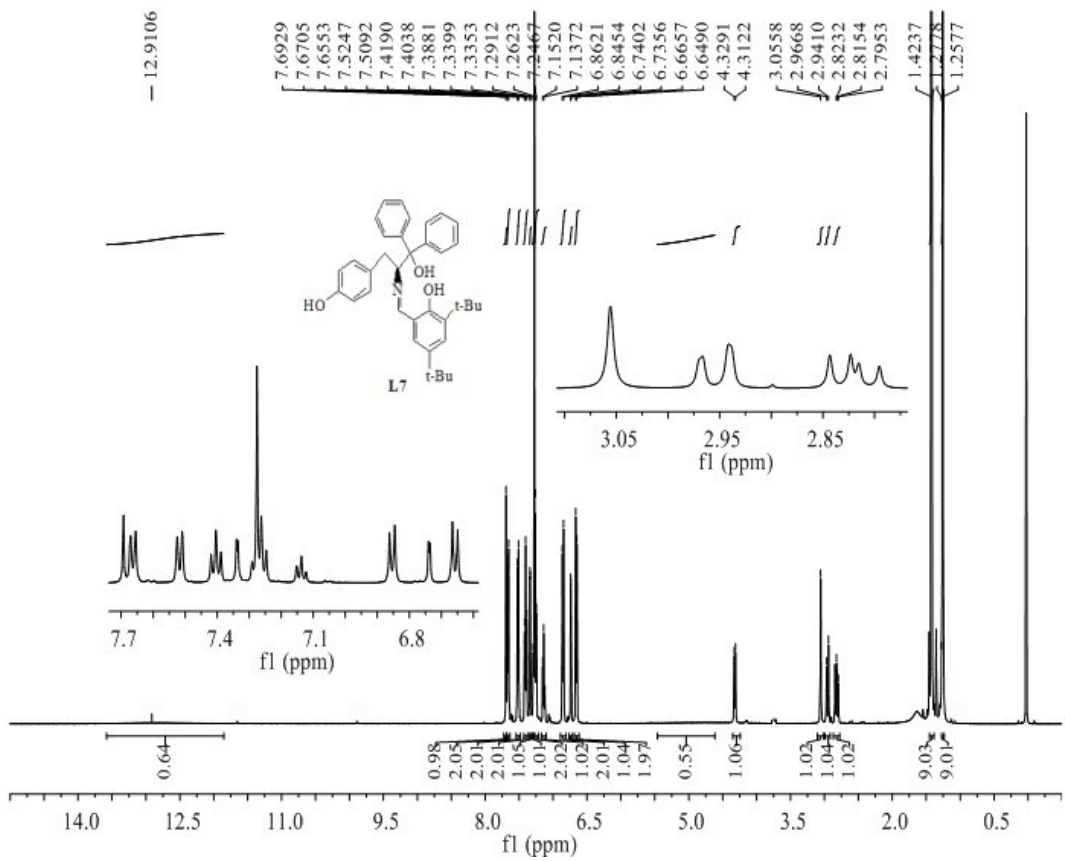
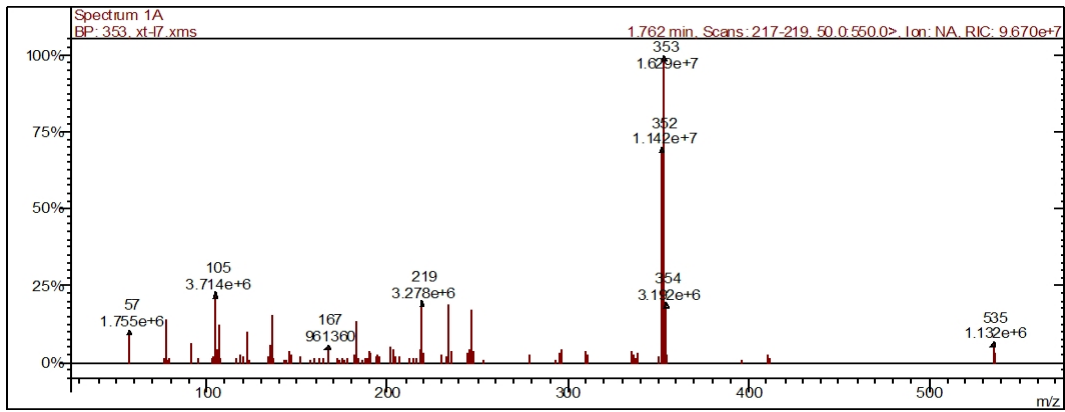


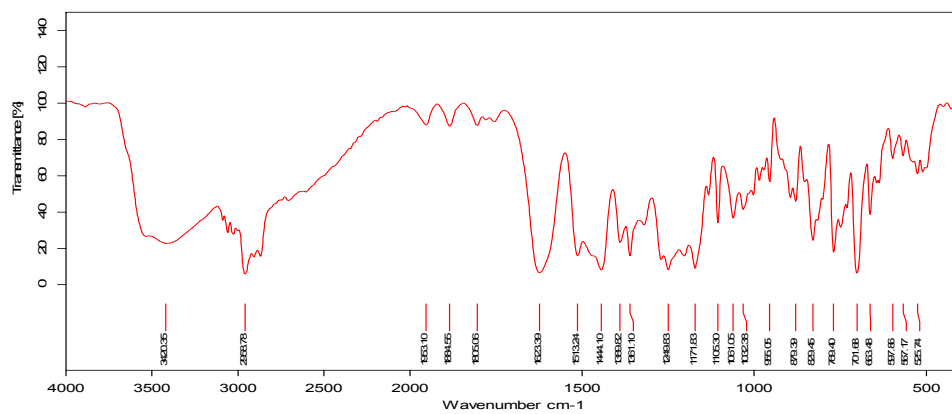
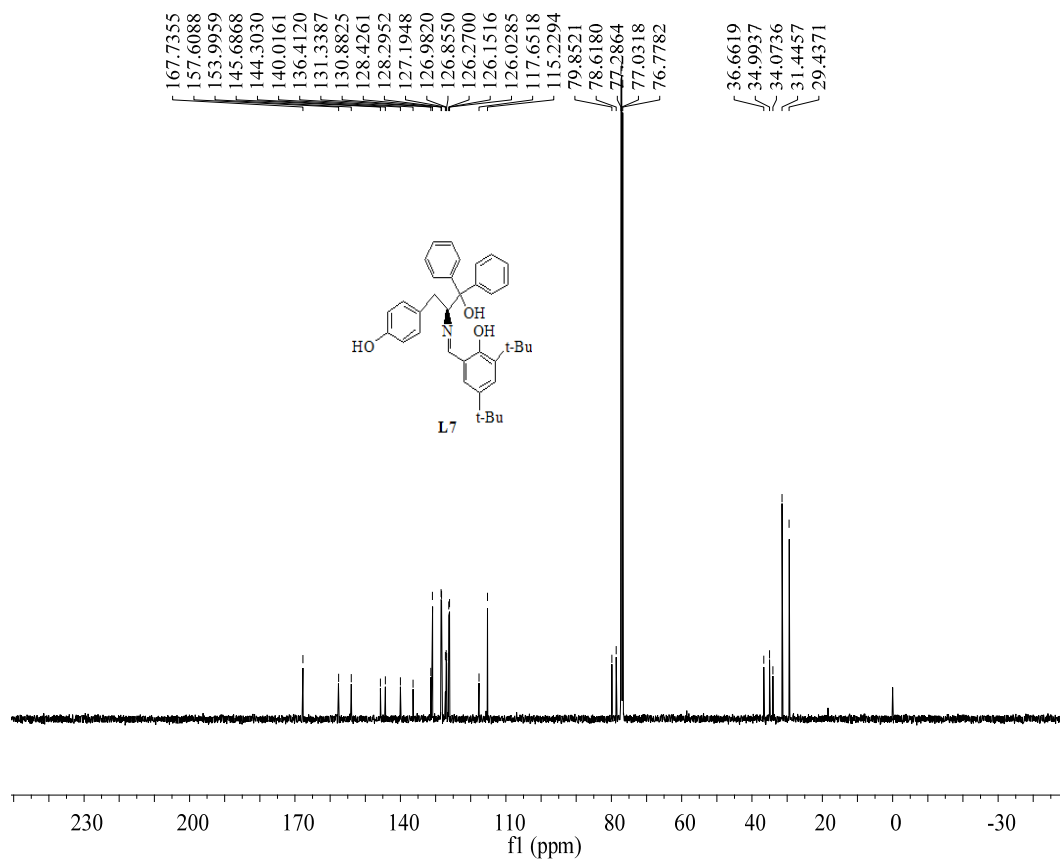




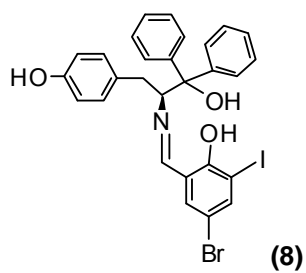
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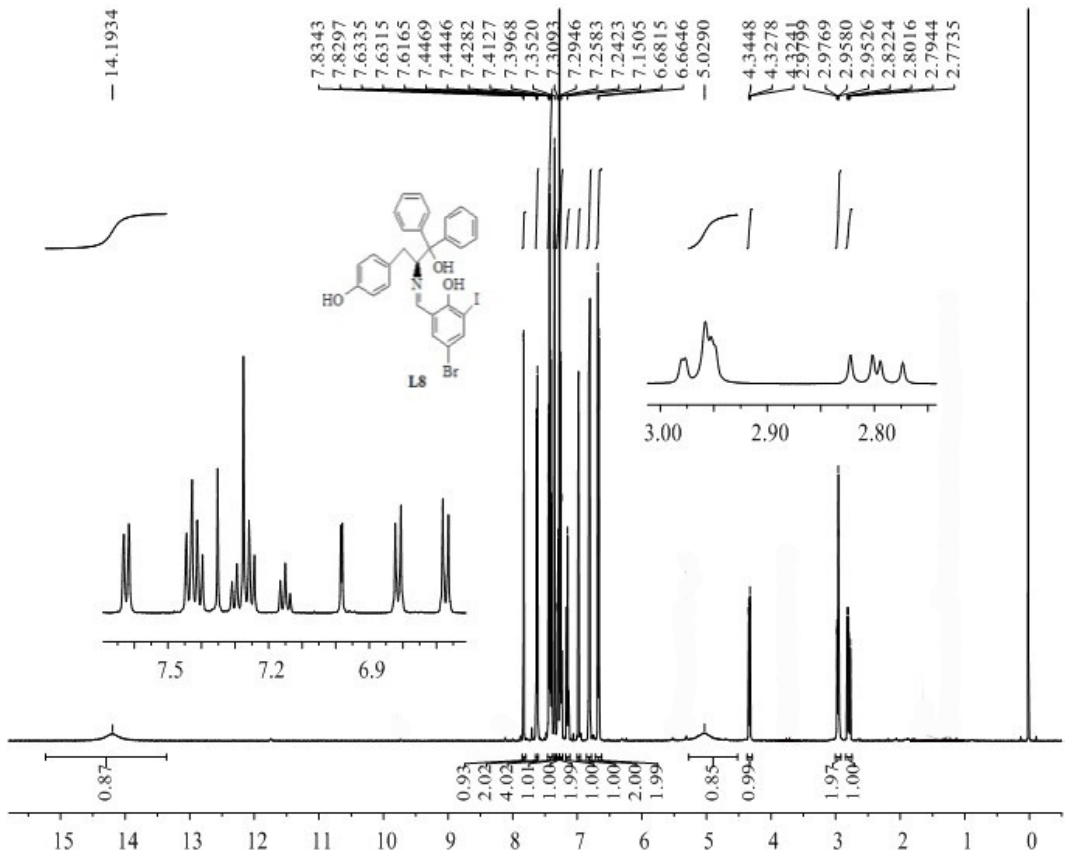
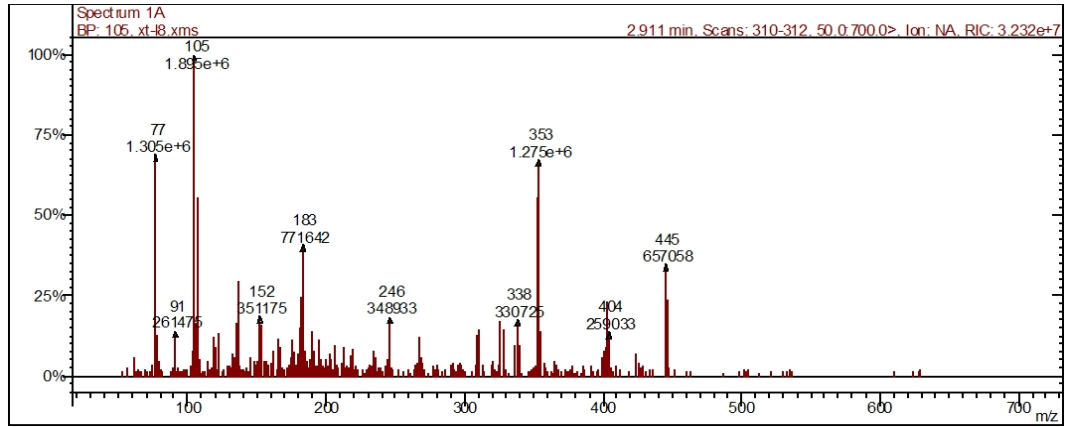


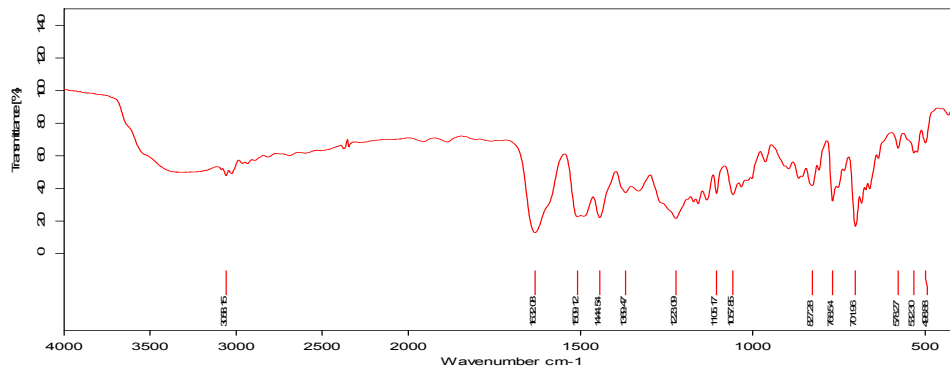
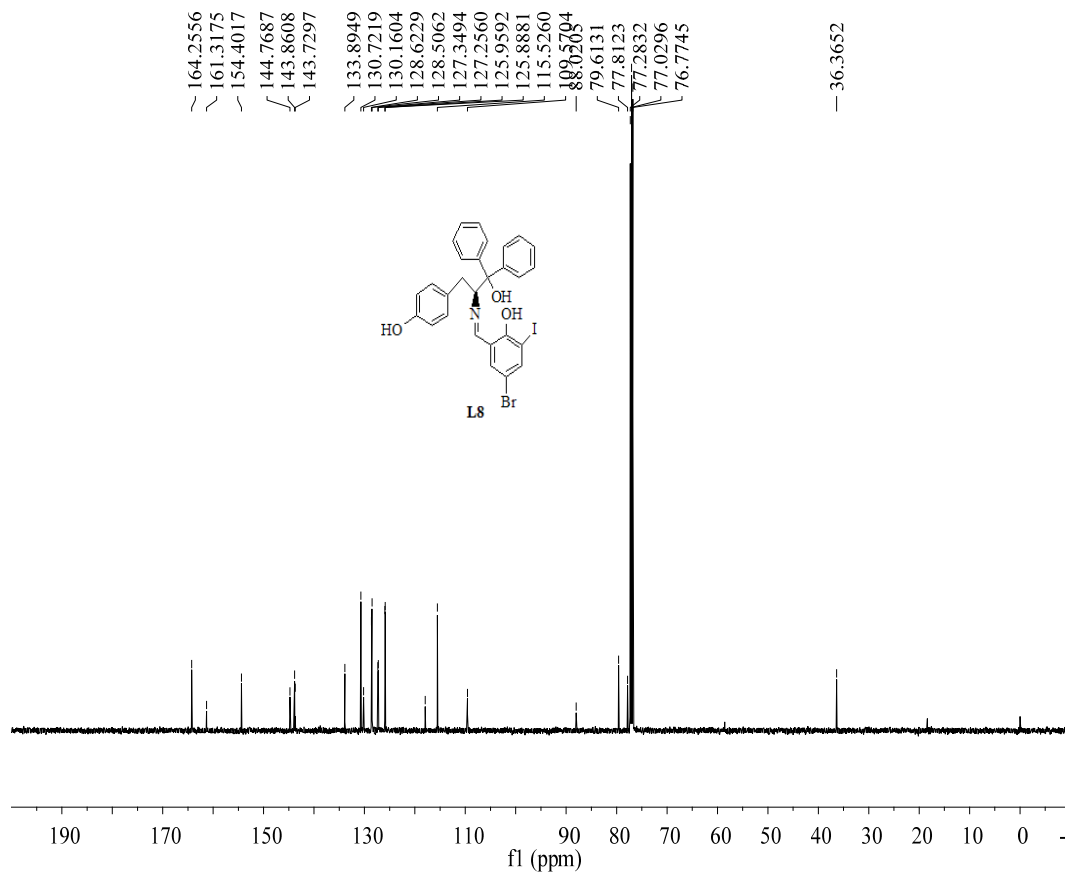




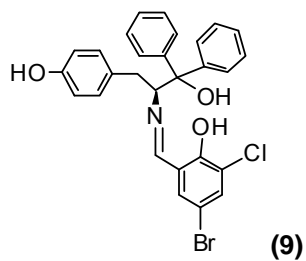
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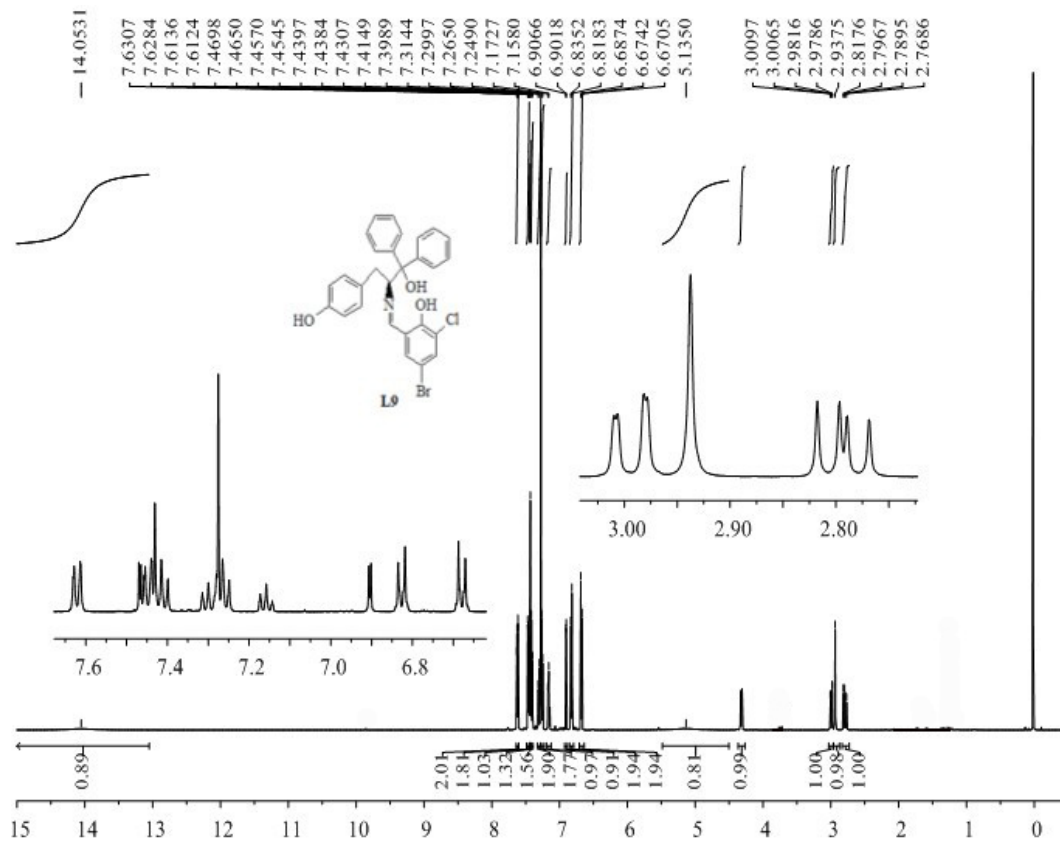
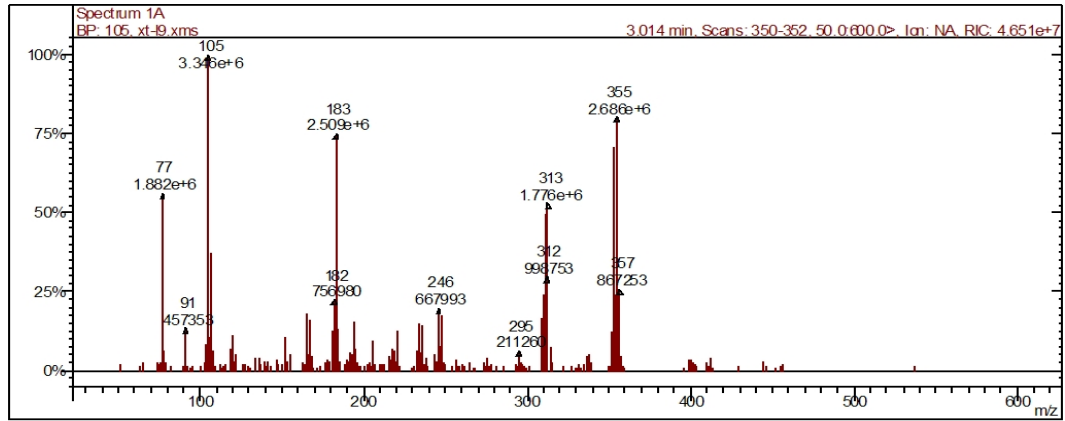


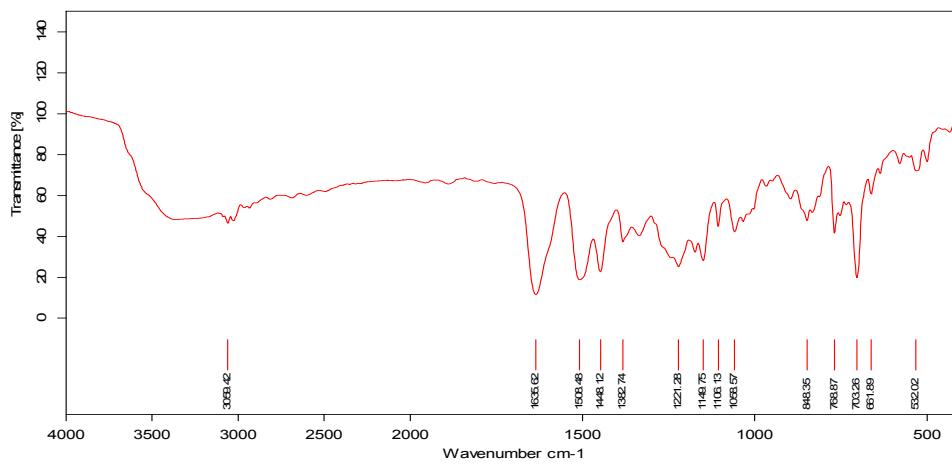
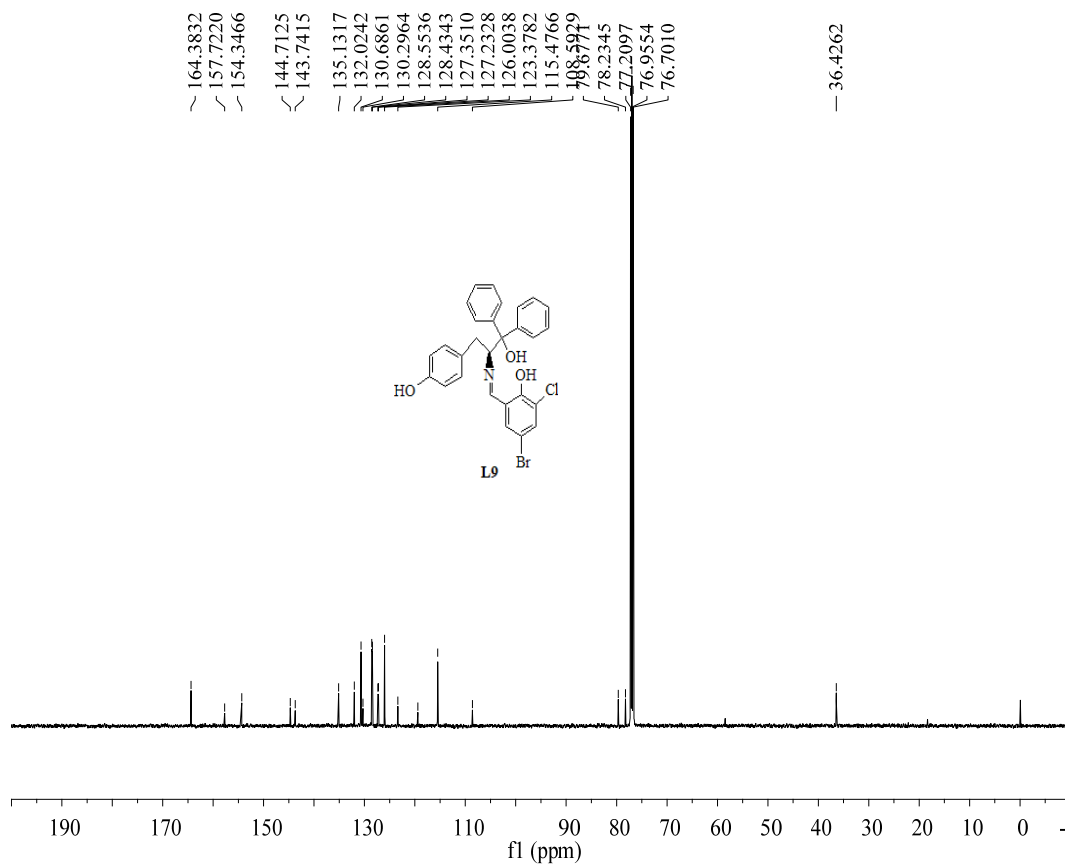




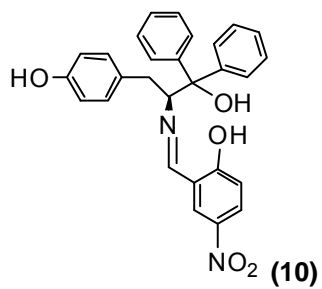
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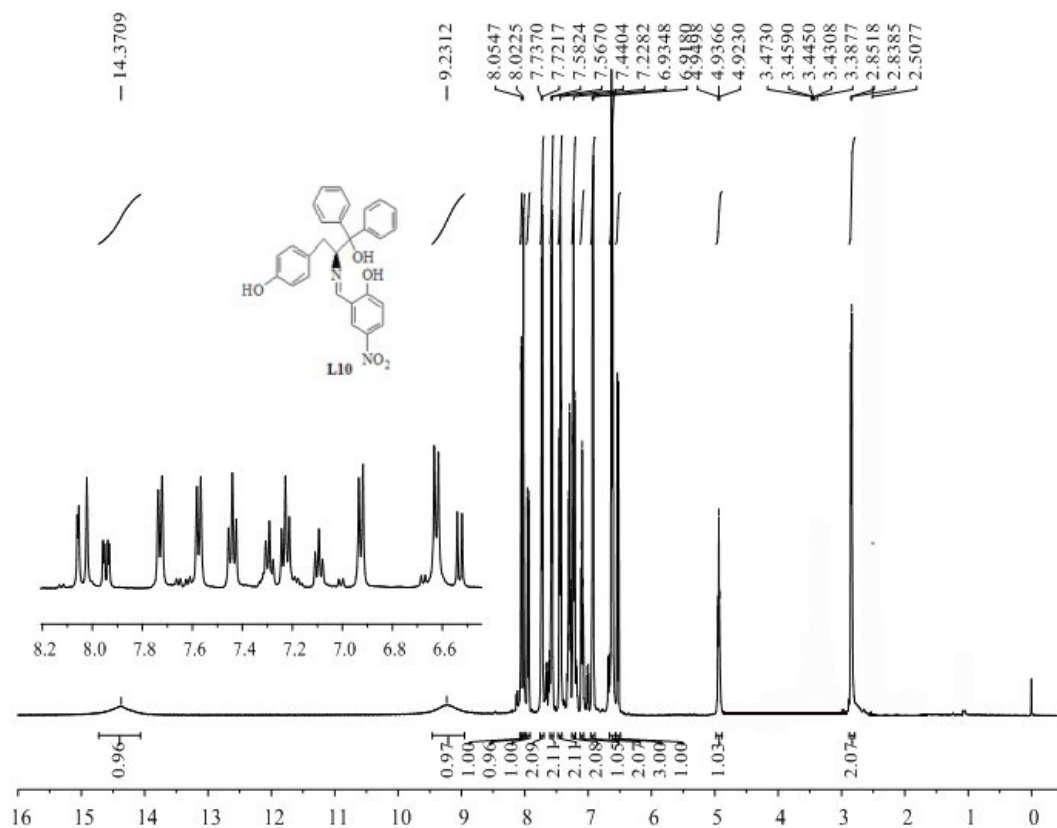
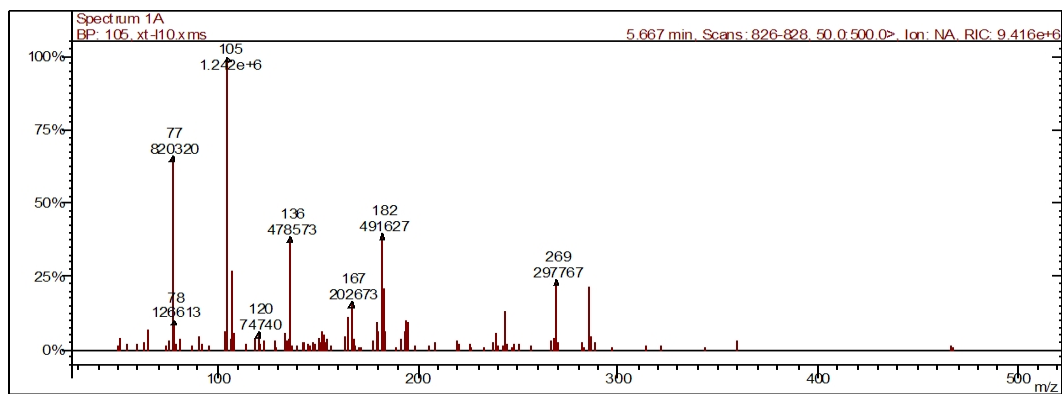




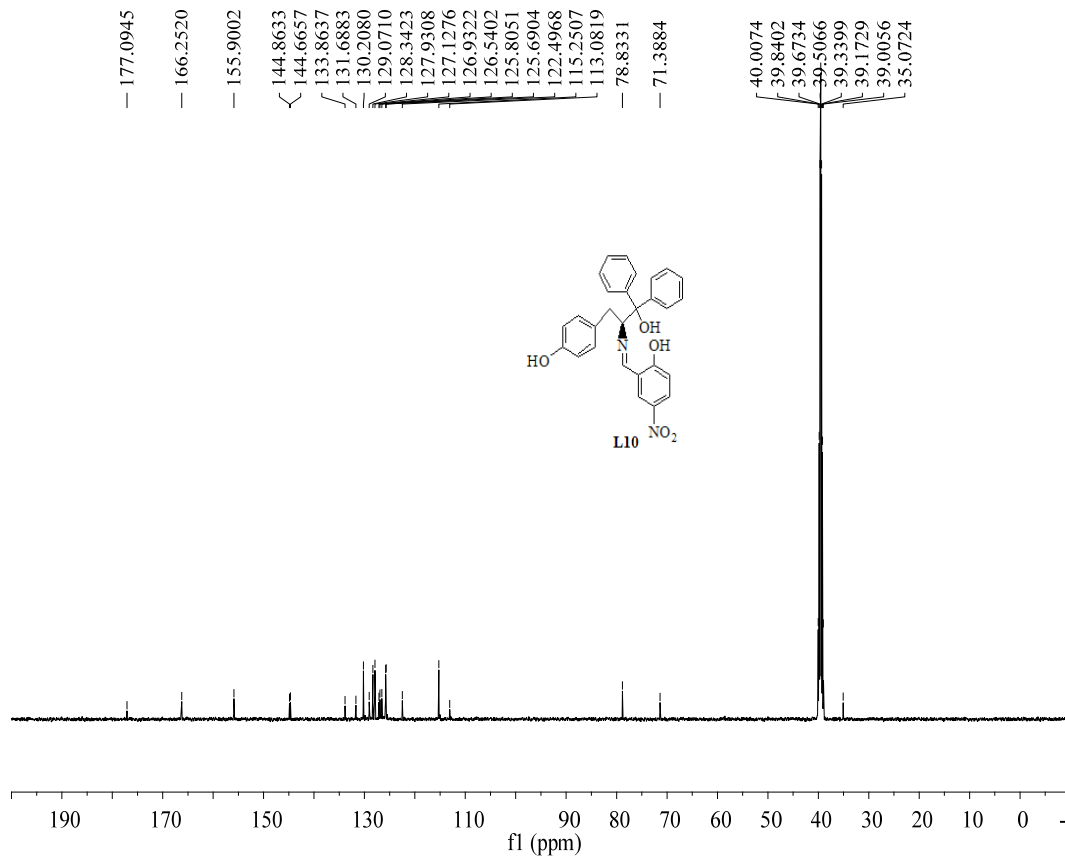


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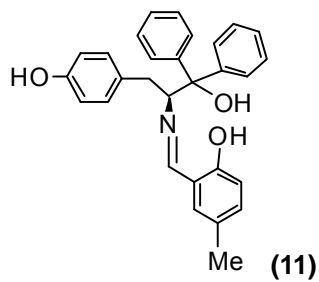


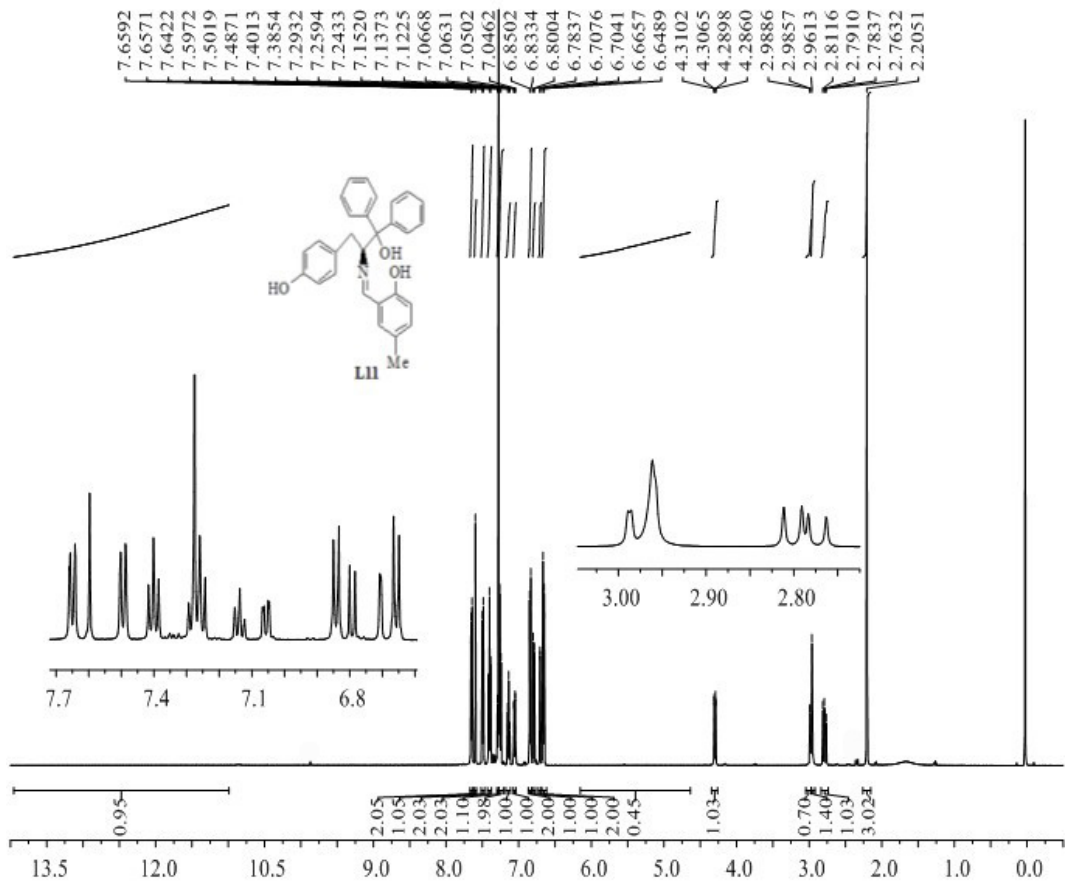
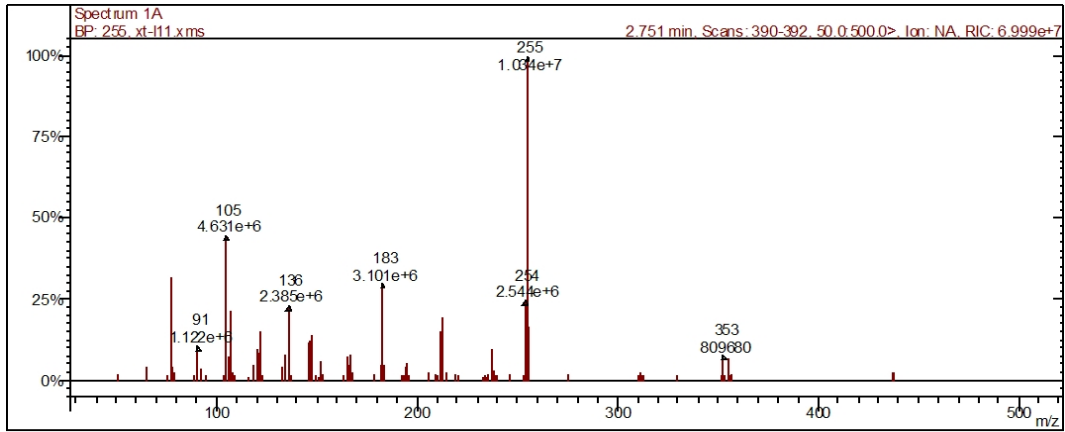


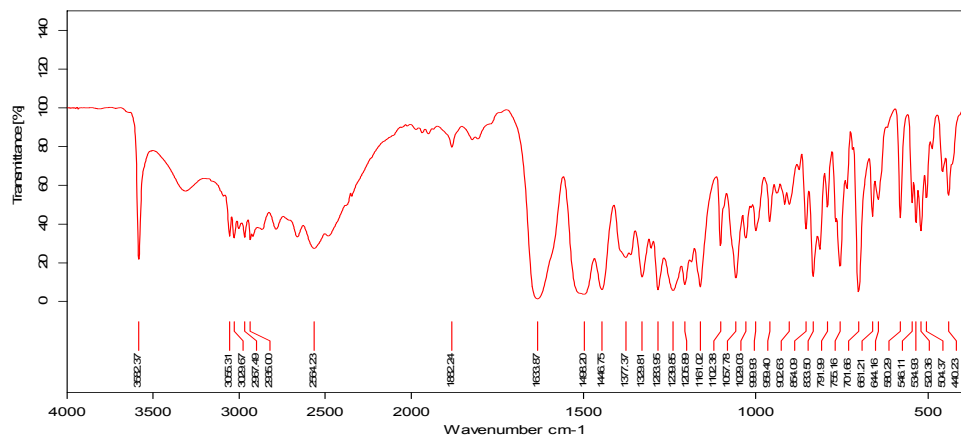
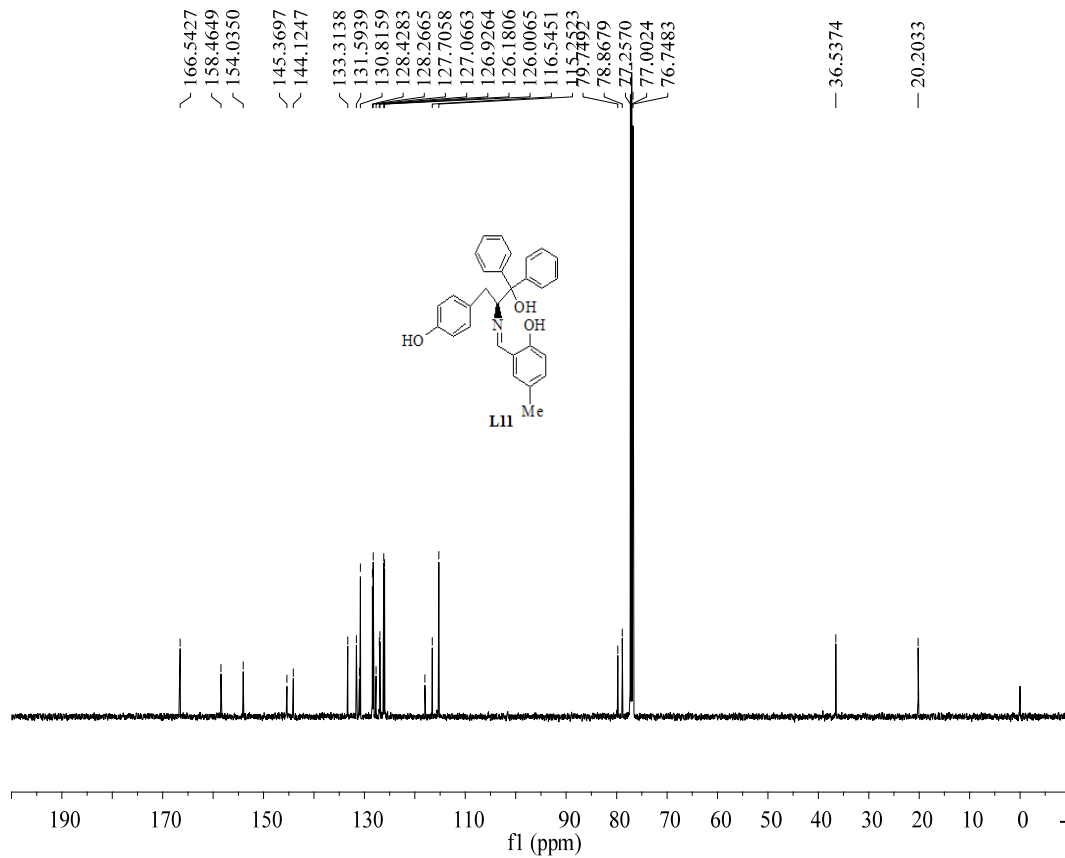




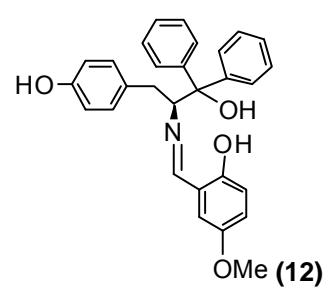
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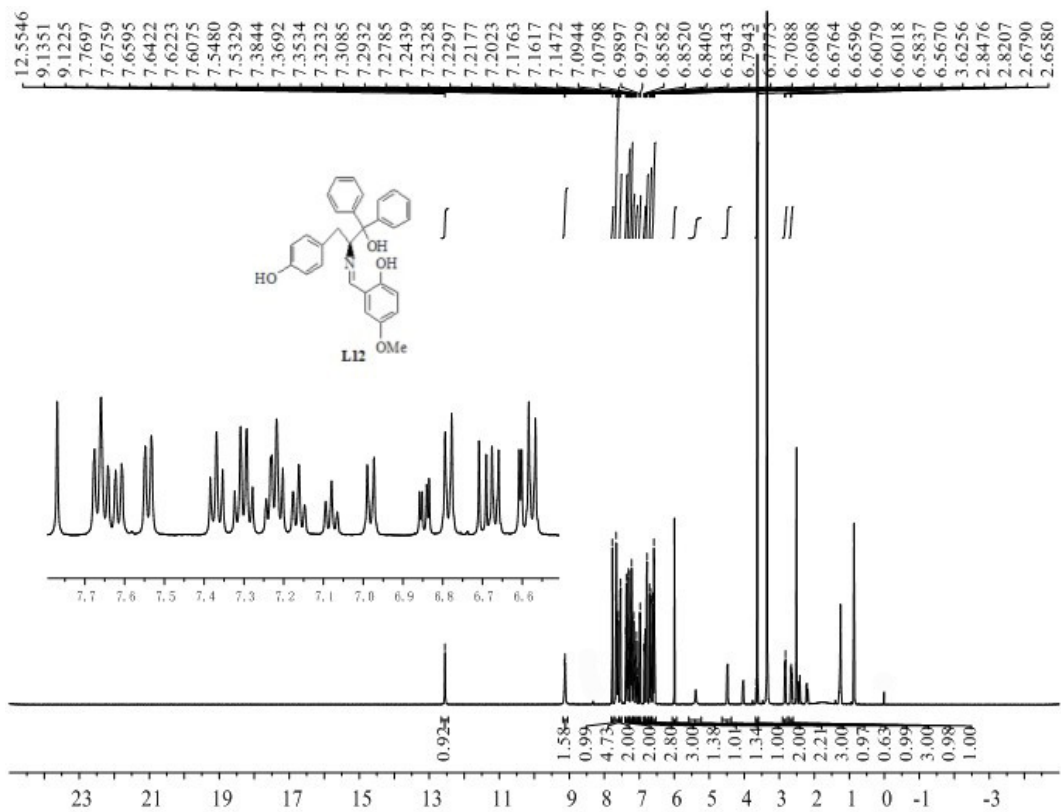
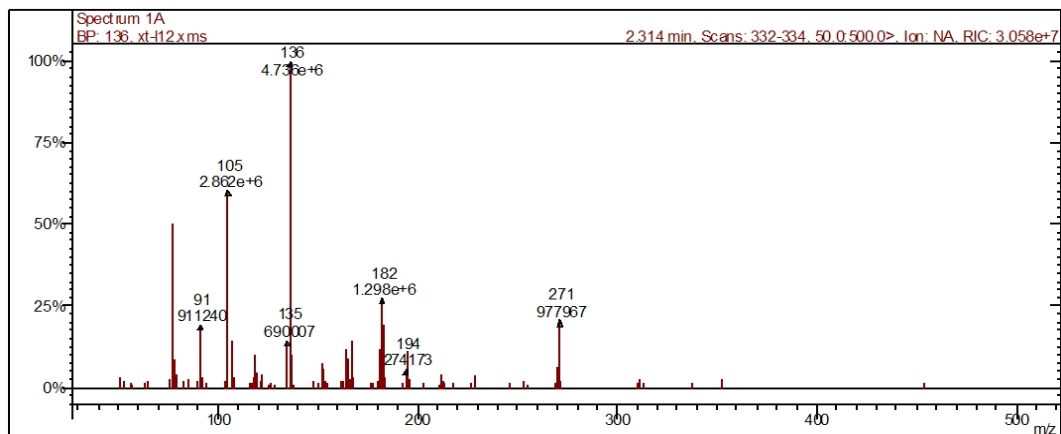


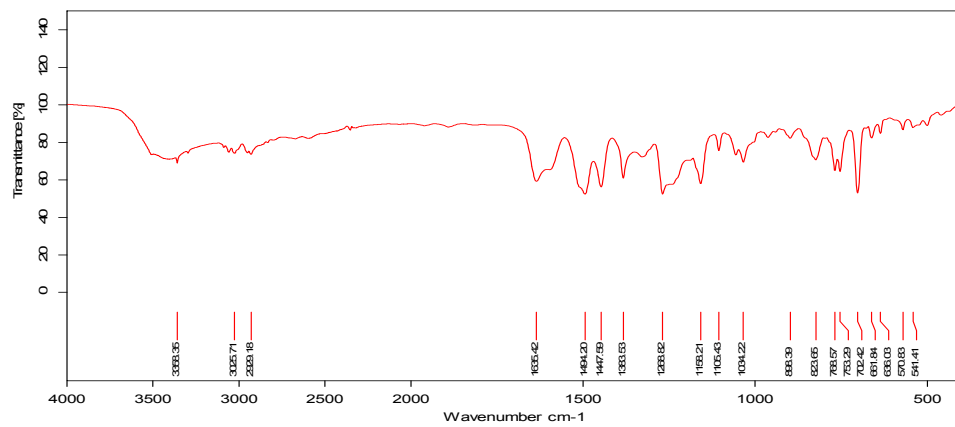
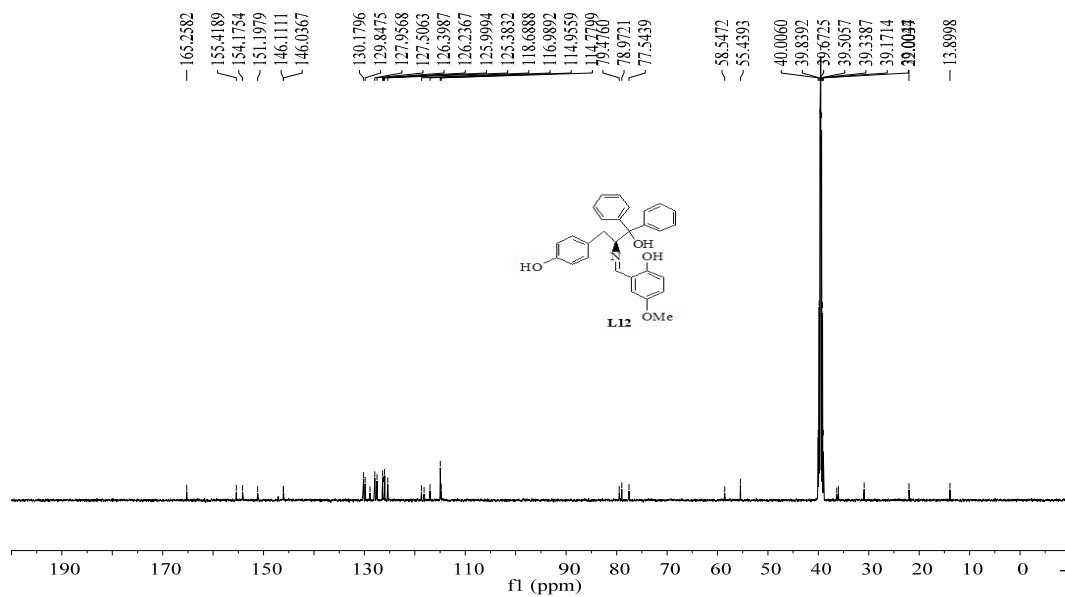




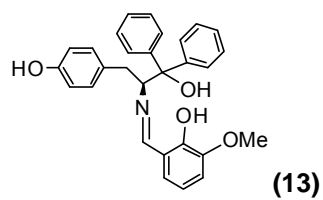
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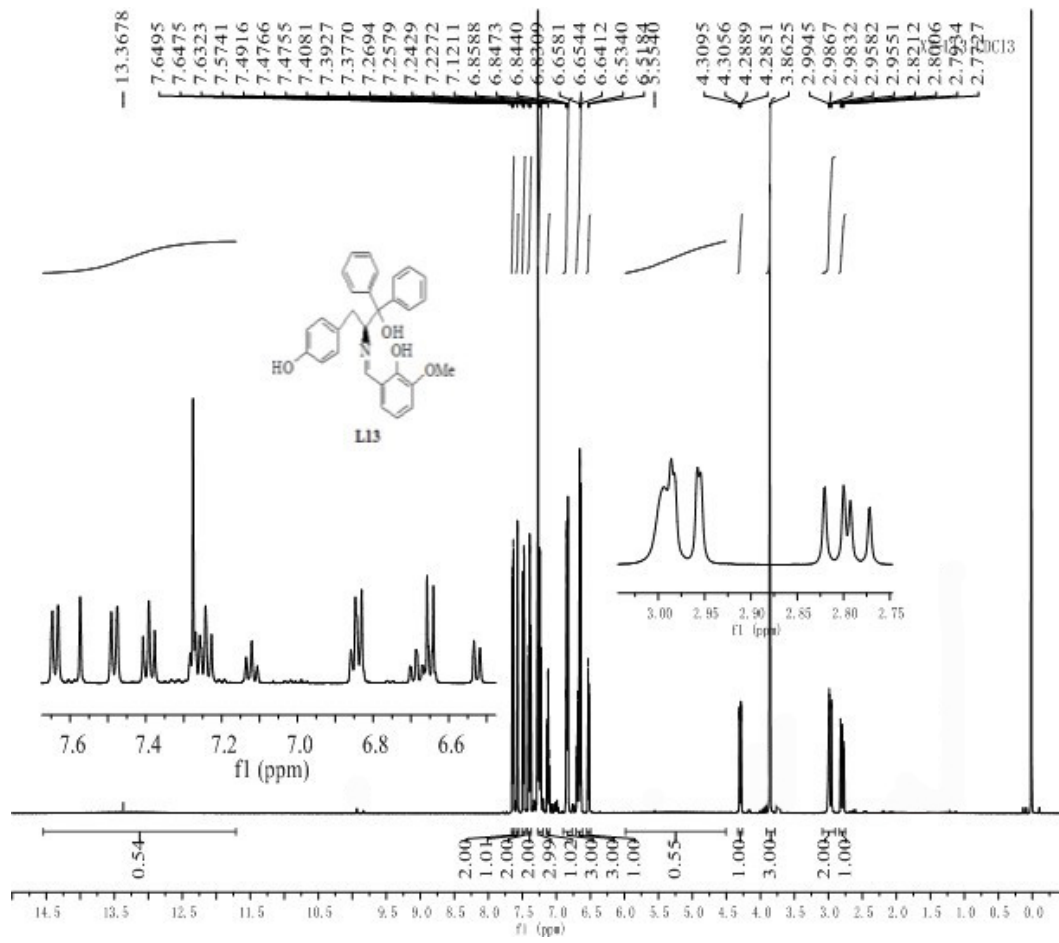
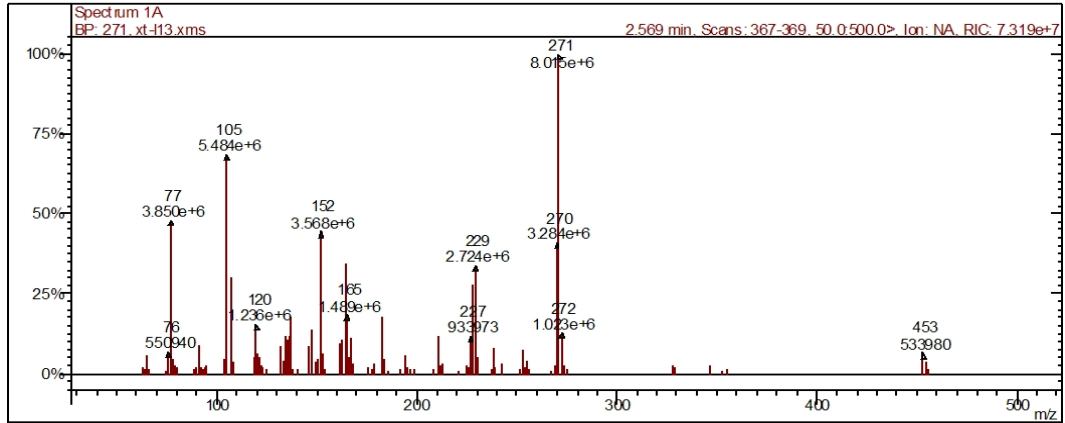


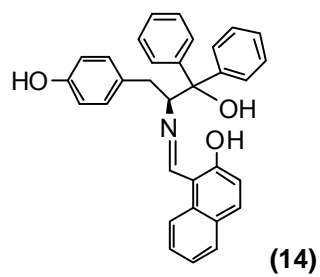
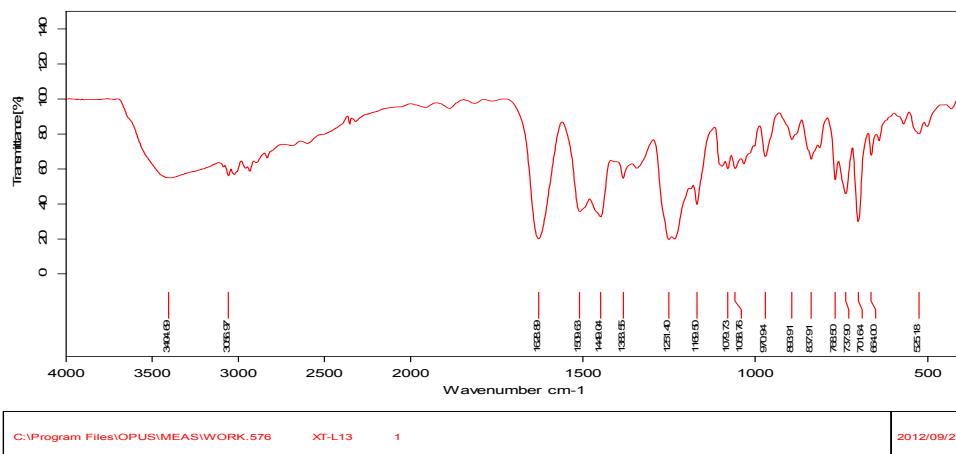
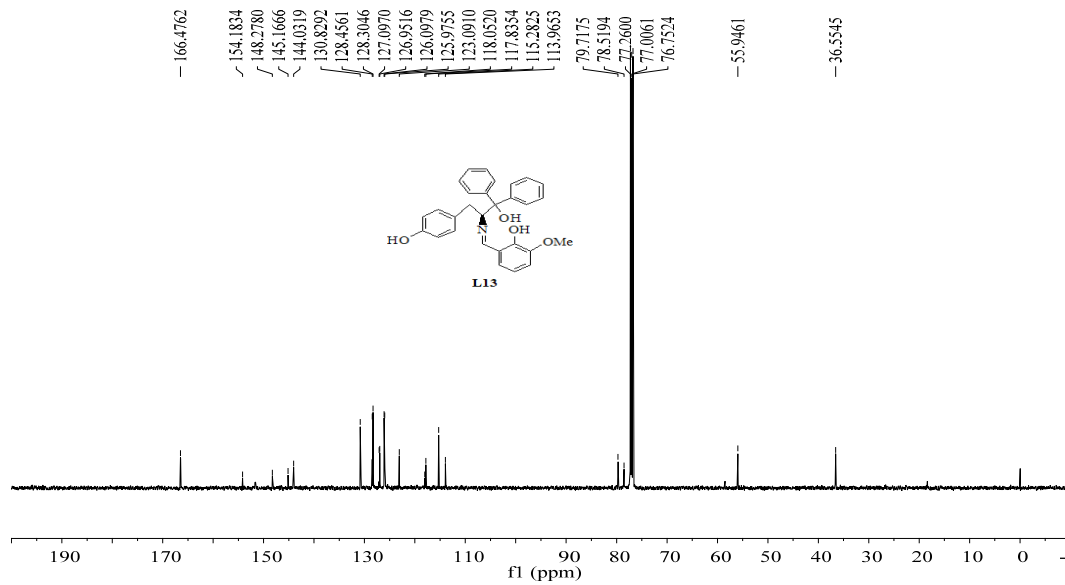


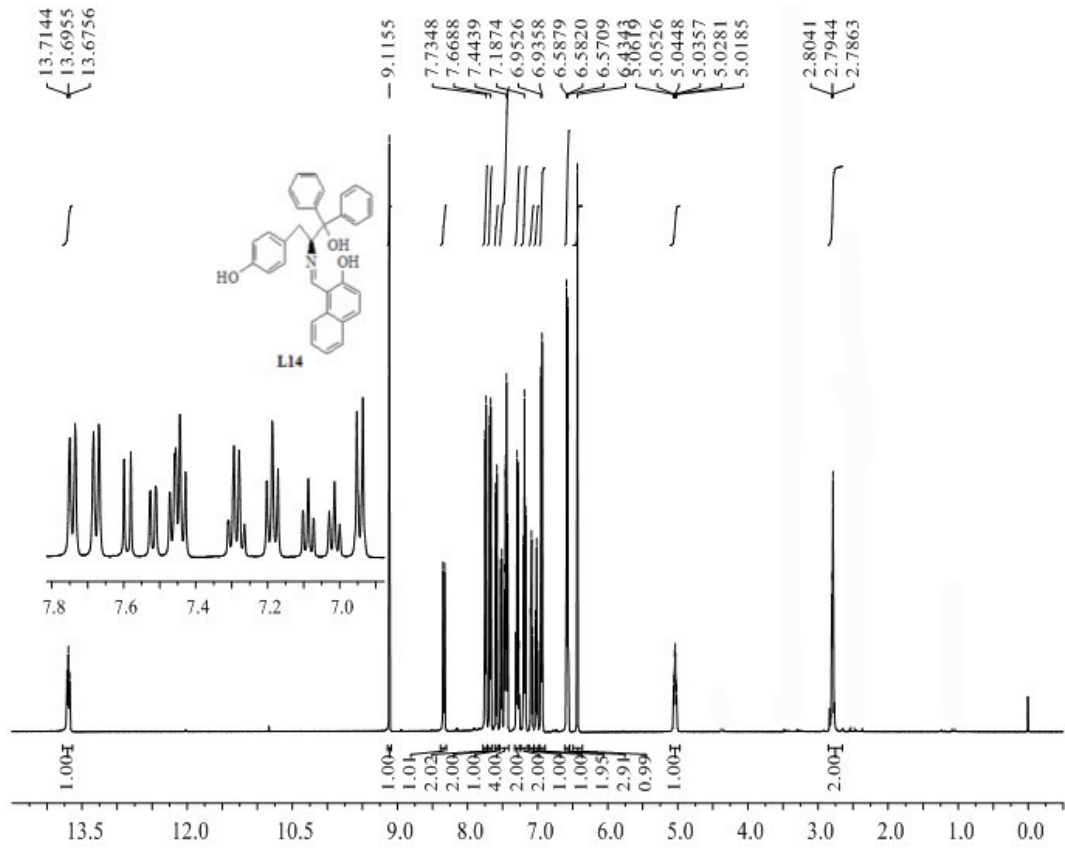
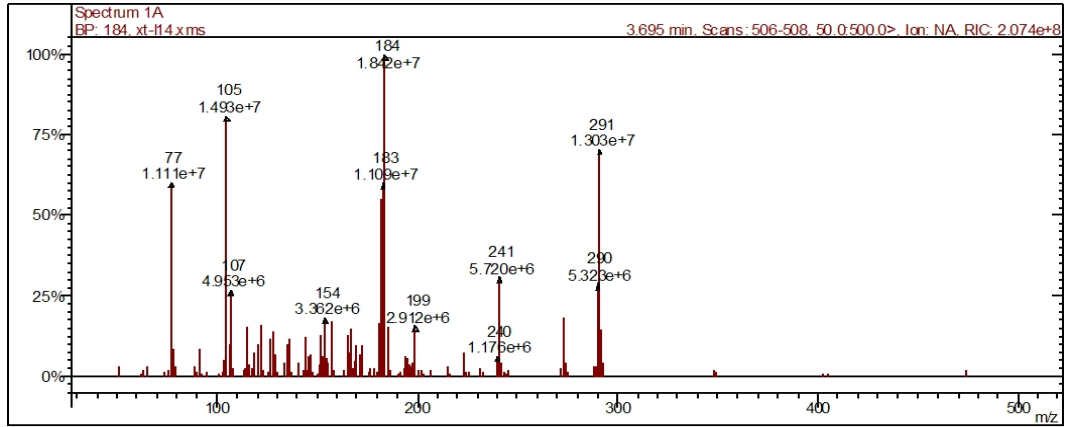


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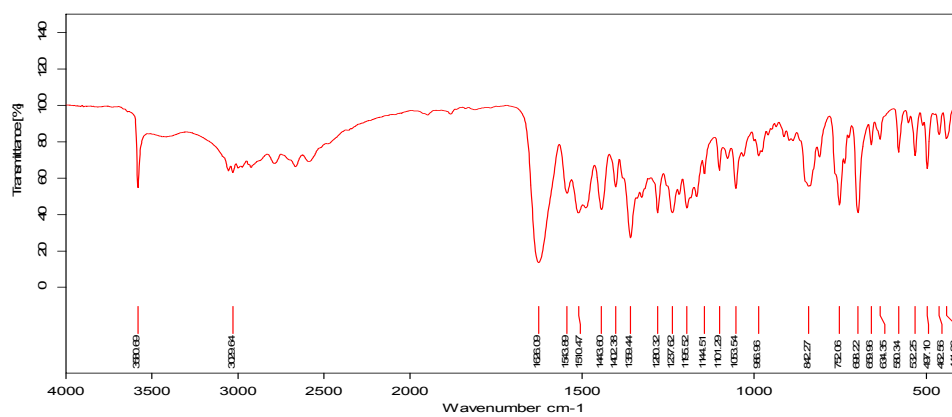
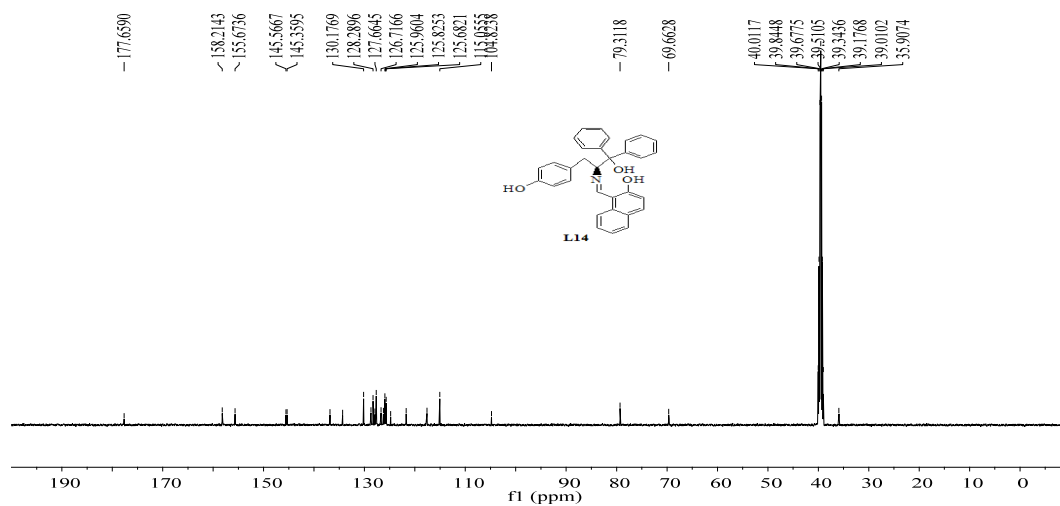




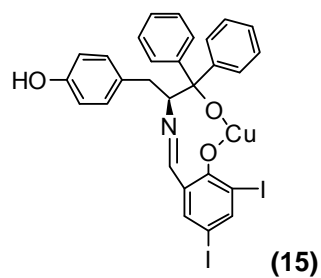


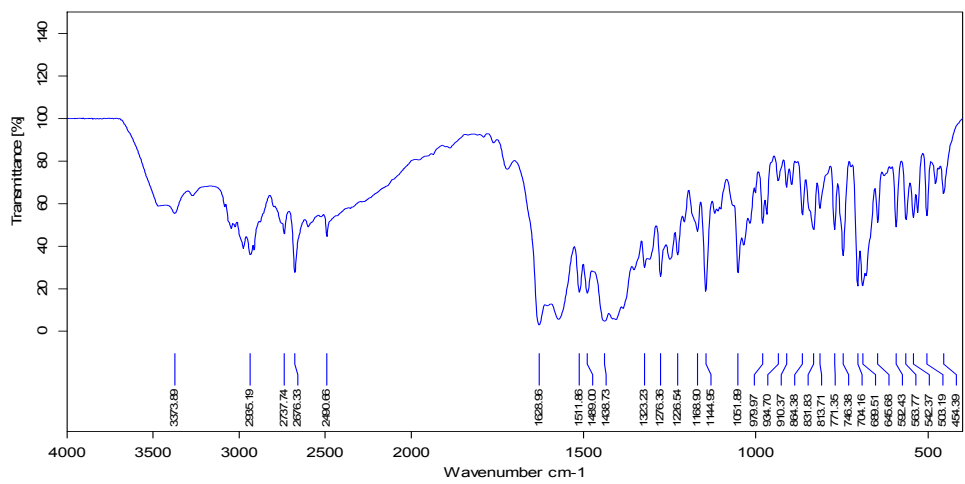




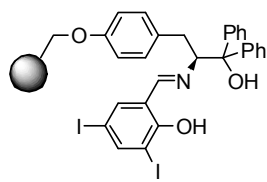


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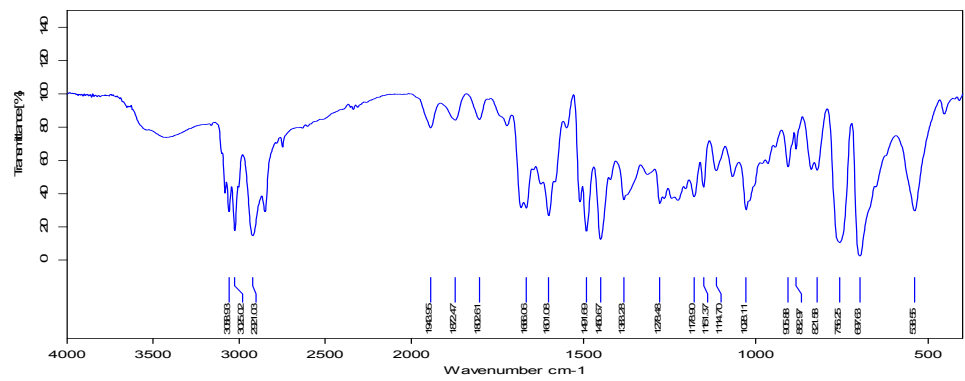




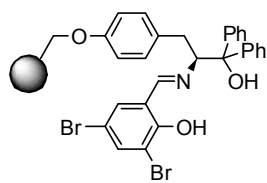
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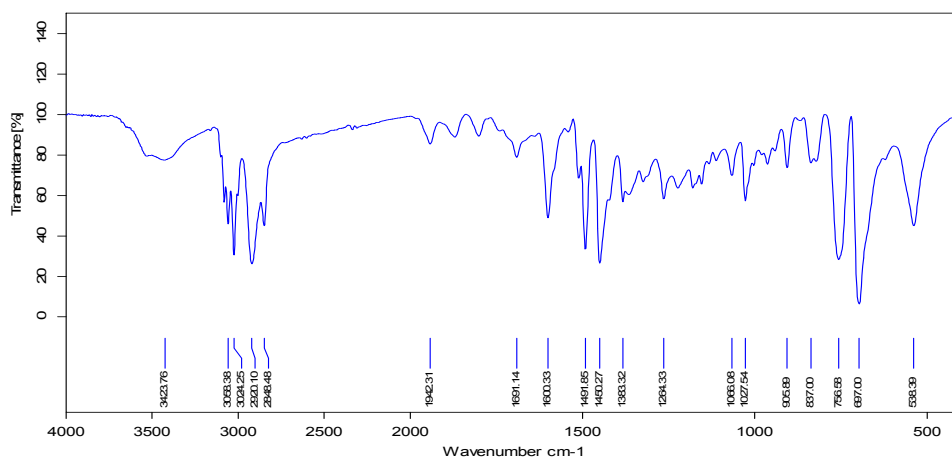
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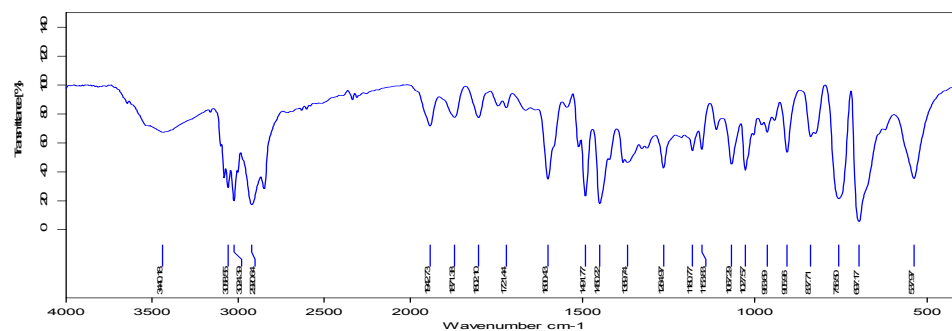
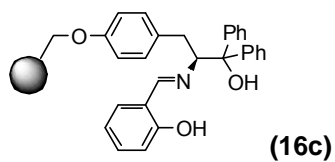
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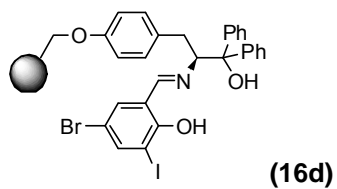
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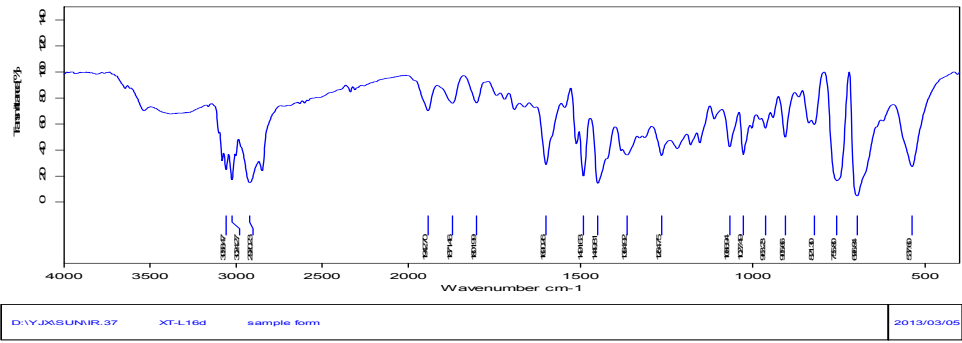


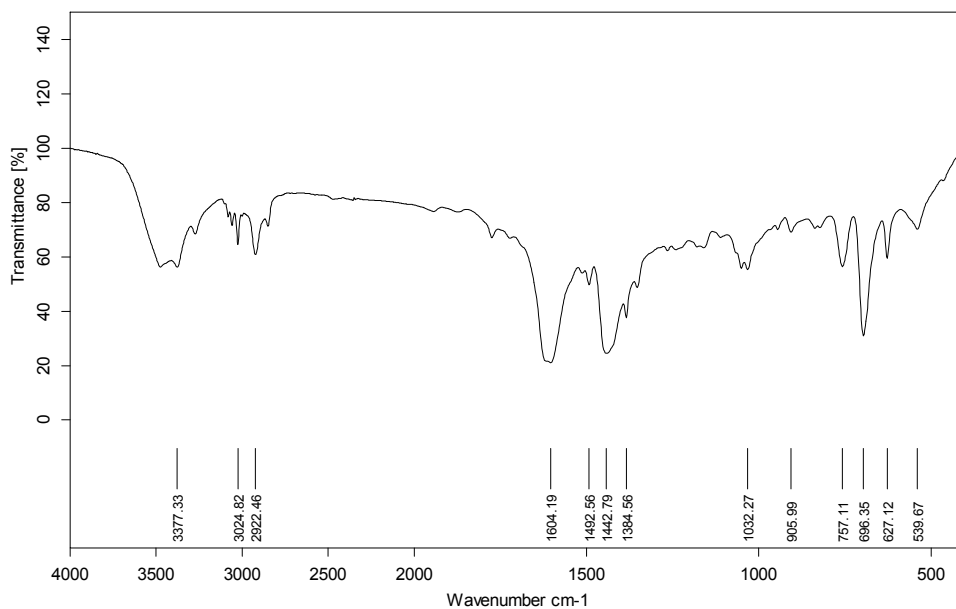
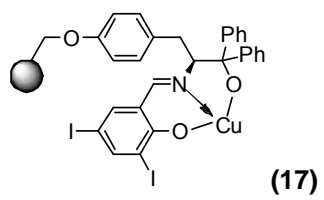
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