

# **D-Glucosamine-derived copper catalyst for Ullmann-type C-N coupling reaction: theoretical and experimental study**

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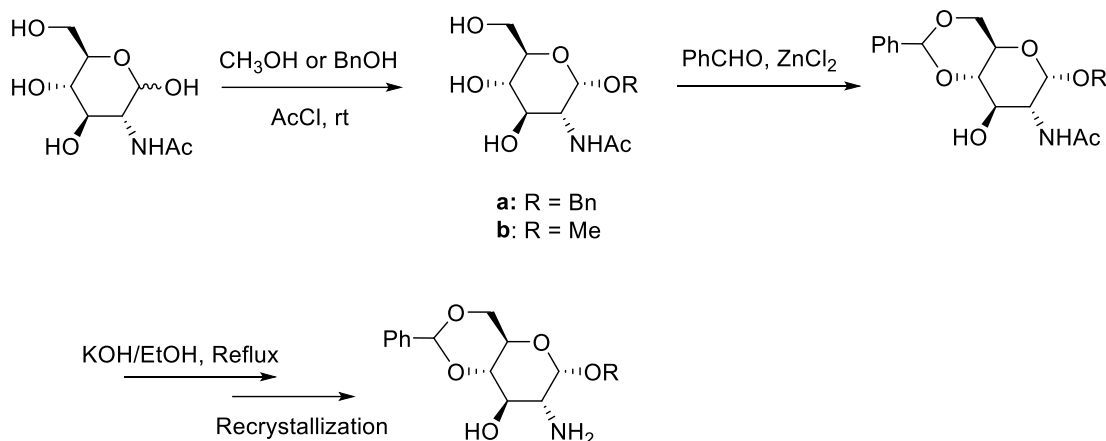
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## Experimental section

### The synthesis of L4-L9



The carbohydrate derived ligands L4-L9 were prepared by previously described methods.<sup>1-4</sup>

**L9** White solide. Mp 172.4-173.8 °C.  $[\alpha]_{\text{D}}^{20} = +59.7^\circ$  ( $c=1.05$ ,  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 – 6.91 (m, 10H), 5.53 (s, 1H), 4.90 (d,  $J = 3.6$  Hz, 1H), 4.75 (d,  $J = 11.7$  Hz, 1H), 4.52 (d,  $J = 11.8$  Hz, 1H), 4.24 (dd,  $J = 10.1, 4.8$  Hz, 1H), 3.88 (td,  $J = 9.9, 4.8$  Hz, 1H), 3.83 – 3.66 (m, 2H), 3.49 (t,  $J = 9.3$  Hz, 1H), 2.81 (dd,  $J = 9.7, 3.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.86, 137.67, 128.97, 128.42, 128.06, 127.89, 127.76, 126.62, 101.47, 99.58, 82.08, 71.70, 69.33, 68.74, 63.30, 57.06. MS (EI):  $m/z = 357$   $[\text{M}]^+$ .

**L8** White solide. M.p. 166 - 167 °C;  $[\alpha]_{\text{D}}^{20} = +103.1^\circ$  ( $c=0.905$ ,  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.41 (m, 2H), 7.41 – 7.35 (m, 3H), 5.61 (s, 1H), 4.62 (d,  $J = 3.6$  Hz, 1H), 4.18 (dd,  $J = 9.9, 4.8$  Hz, 1H), 3.76 3.56 (m, 3H), 3.48 (t,  $J = 9.2$  Hz, 1H), 3.29 (s, 3H), 2.81 (dd,  $J = 9.7, 3.6$  Hz, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.99, 134.09, 133.24, 131.63, 106.13, 103.97, 87.27, 73.27, 72.63, 67.68, 59.96, 59.35. MS (EI):  $m/z = 281$   $[\text{M}]^+$ .

**L7** White solide. M.p. 189-192 °C;  $[\alpha]_{\text{D}}^{20} = +56^\circ$  ( $c=0.21$ , MeOH);  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  8.00 (d,  $J = 8.2$  Hz, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.33 (m, 7H), 7.30 (ddd,  $J = 8.4, 3.6, 1.8$  Hz, 1H), 5.62 (s, 1H), 5.19 (d,  $J = 5.8$  Hz, 1H), 4.80 (d,  $J = 3.6$  Hz, 1H), 4.70 (d,  $J = 12.6$  Hz, 1H), 4.49 (d,  $J = 12.6$  Hz, 1H), 4.18 – 4.11 (m, 1H), 3.86 (ddd,  $J = 10.6, 8.3, 3.7$  Hz, 1H), 3.72 (ddd,  $J = 21.9, 12.6, 7.9$  Hz, 3H), 3.51 (t,  $J = 9.0$  Hz, 1H), 1.84 (d,  $J = 9.8$  Hz, 3H).  $^{13}\text{C NMR}$  (100 MHz, DMSO)  $\delta$  169.93, 138.19 (d,  $J = 3.3$  Hz), 129.34, 128.7, 128.49, 128.07 (d,  $J = 7.3$  Hz), 126.86, 101.34, 97.43, 69.06, 68.48, 67.73, 63.33 54.67, 23.00. MS (EI):  $m/z = 399$   $[\text{M}]^+$ .

**L6** White solide. M.p. 250 - 252 °C;  $[\alpha]_{\text{D}}^{20} = +90^\circ$  ( $c=0.11$ , MeOH);  $^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.90 (d,  $J = 8.4$  Hz, 1H), 7.46 (dd,  $J = 6.6, 3.2$  Hz, 2H), 7.41 – 7.35 (m, 3H), 5.61 (s, 1H), 4.62 (d,  $J = 3.6$  Hz, 1H), 4.18 (dd,  $J = 9.9, 4.8$  Hz, 1H), 3.89 – 3.80 (m, 1H), 3.74 (t,  $J = 10.1$  Hz, 1H), 3.69 – 3.63 (m, 1H), 3.63 – 3.56 (m, 1H), 3.48 (t,  $J = 9.2$  Hz, 1H), 3.29 (s, 3H), 1.85 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz, DMSO)  $\delta$  169.43, 137.74, 128.84, 127.99, 126.37, 100.87, 98.71, 82.01, 68.02, 67.37, 62.43, 54.71, 54.10, 22.57. MS (EI):  $m/z = 323$   $[\text{M}]^+$ .

## The spectral data of the products

**1-(4-Methoxyphenyl)-1H-imidazole 3a.**<sup>5</sup> Pale yellow solid, m.p.: 60-61 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (s, 1H), 7.30 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 6.7 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.00, 135.84, 130.67, 129.86, 123.25, 118.82, 114.93, 55.62. MS (EI): *m/z* = 174 [M]<sup>+</sup>.

**1-(4-Fluorophenyl)-1H-imidazole 3b.**<sup>6</sup> Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (d, *J* = 15.0 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.26 – 7.11 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.92, 160.46, 135.78, 133.61, 130.44, 123.51 (*J* = 8.5 Hz), 118.61, 116.76 (*J* = 23.0 Hz). MS (EI): *m/z* = 162 [M]<sup>+</sup>.

**1-(4-Chlorophenyl)-1H-imidazole 3c.**<sup>5</sup> Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (s, 1H), 7.52 – 7.42 (m, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.27 (s, 1H), 7.21 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.89, 135.53, 133.22, 130.67, 130.04, 122.72, 118.19. MS (EI): *m/z* = 178 [M]<sup>+</sup>.

**1-(4-(Trifluoromethoxy)phenyl)-1H-imidazole 3d.**<sup>7</sup> Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (s, 1H), 7.44 (d, *J* = 8.9 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.27 (s, 1H), 7.22 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.10, 135.90, 135.63, 130.79, 122.92, 122.54, 121.67, 119.10, 118.30. MS (EI): *m/z* = 228 [M]<sup>+</sup>.

**1-(4-(Trifluoromethyl)phenyl)-1H-imidazole 3e.**<sup>8</sup> Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (s, 1H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.25 (s, 1H), 7.20 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.48, 135.62, 134.99, 130.26 (*J* = 21.4 Hz), 121.45, 118.37. MS (EI): *m/z* = 212 [M]<sup>+</sup>.

**1-Phenyl-1H-imidazole 3f.**<sup>5</sup> Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87 (s, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.29 (s, 1H), 7.21 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.40, 135.60, 130.41, 129.89, 127.50, 121.51, 118.25. MS (EI): *m/z* = 144 [M]<sup>+</sup>.

**1-(4-Methoxyphenyl)-1H-benz[d]imidazole 3g.**<sup>9</sup> Yellow solid, m.p.: 96-97 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (s, 1H), 7.87 – 7.73 (m, 1H), 7.43 – 7.36 (m, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.24 (p, *J* = 7.2 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.37, 142.55, 129.12, 125.74, 123.56, 122.63, 120.43, 115.13, 110.36, 55.64. MS (EI): *m/z* = 224 [M]<sup>+</sup>.

**4-(4-Methoxyphenyl)morpholine 3h.**<sup>10</sup> White solid. m.p.: 72-73 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.97 – 6.77 (m, 4H), 3.90 – 3.82 (m, 4H), 3.77 (s, 3H), 3.11 – 3.00 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.00, 145.66, 117.84, 114.53, 67.06, 55.59, 50.84. MS (EI): *m/z* = 193 [M]<sup>+</sup>.

**1-(4-Methoxyphenyl)pyrrolidine 3i.**<sup>10</sup> Yellow solid. m.p.: 45-46 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.76 (d, *J* = 8.9 Hz, 2H), 6.45 (d, *J* = 8.9 Hz, 2H), 3.67 (s, 3H), 3.14 (t, *J* = 6.4 Hz, 4H), 1.99 – 1.79 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.75, 142.23, 114.00, 111.58, 54.98, 47.20, 24.35. MS (EI): *m/z* = 177 [M]<sup>+</sup>.

***N*-Benzyl-4-methoxybenzenamine 3j.**<sup>10</sup> White solid, m.p.: 49-50 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27 (q, *J* = 7.1 Hz, 3H), 7.18 (m, 1H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 8.7 Hz, 2H), 4.20 (s, 2H), 3.66 (d, *J* = 0.9 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 151.16, 141.43, 138.66, 127.56, 126.52, 126.14, 113.89, 113.08, 54.78, 48.22. MS (EI): *m/z* = 213 [M]<sup>+</sup>.

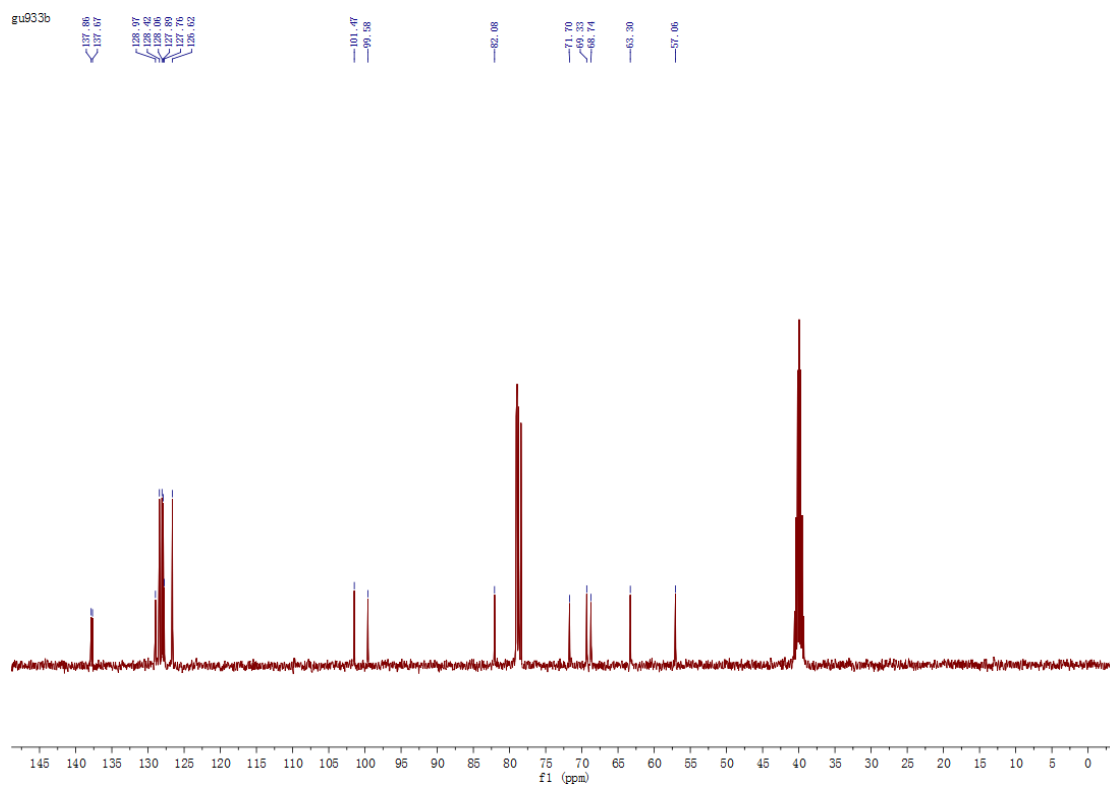
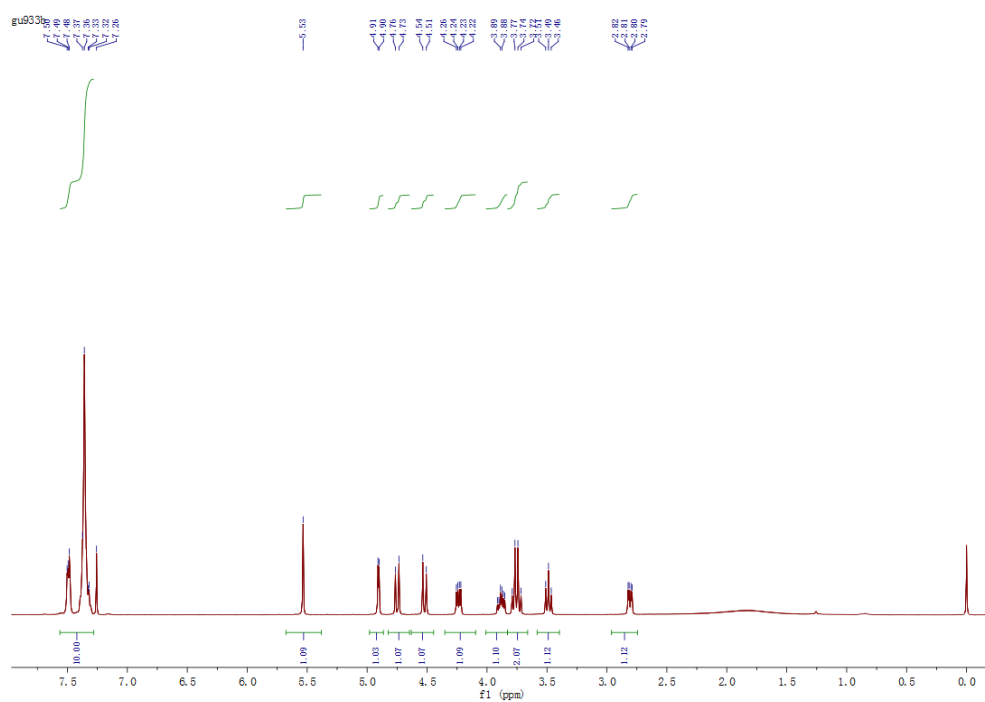
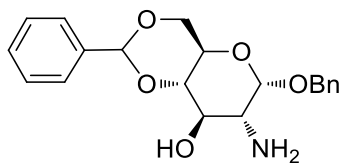
**4-Methoxy-*N*-phenylbenzenamine 3k.**<sup>11</sup> White solid, m.p.: 105-106 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.14 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.87 – 6.68 (m, 5H), 5.40 (s, 1H), 3.71 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.24, 144.14, 134.71, 128.27, 121.17, 118.53, 114.62, 113.64, 54.55. MS (EI): *m/z* = 199 [M]<sup>+</sup>.

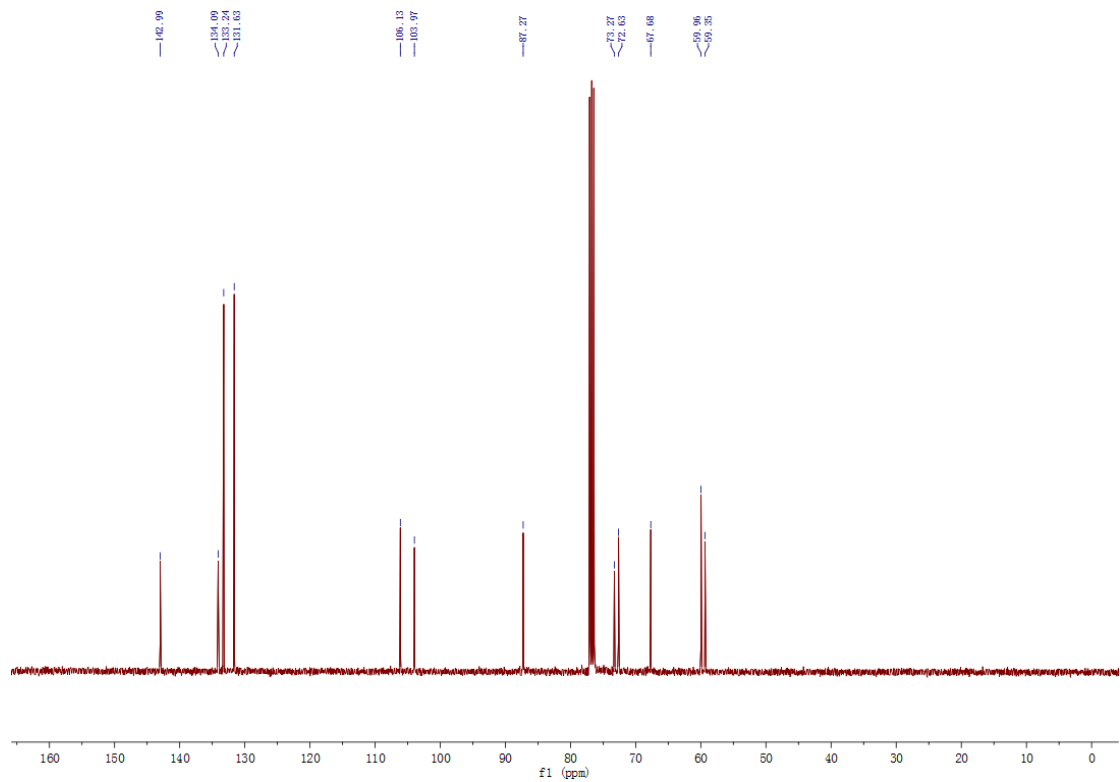
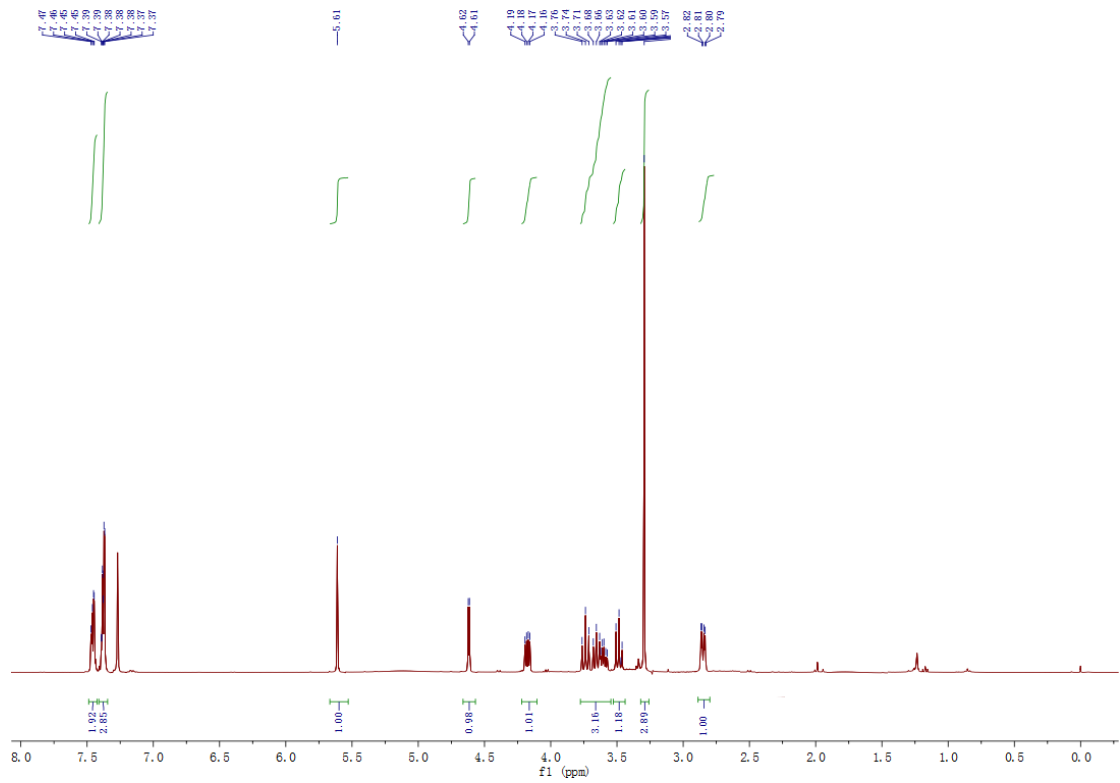
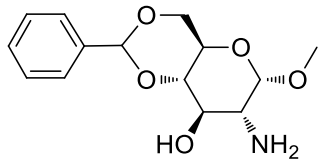
**Indoline.**<sup>12</sup> Pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.03 (d, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 7.6 Hz,

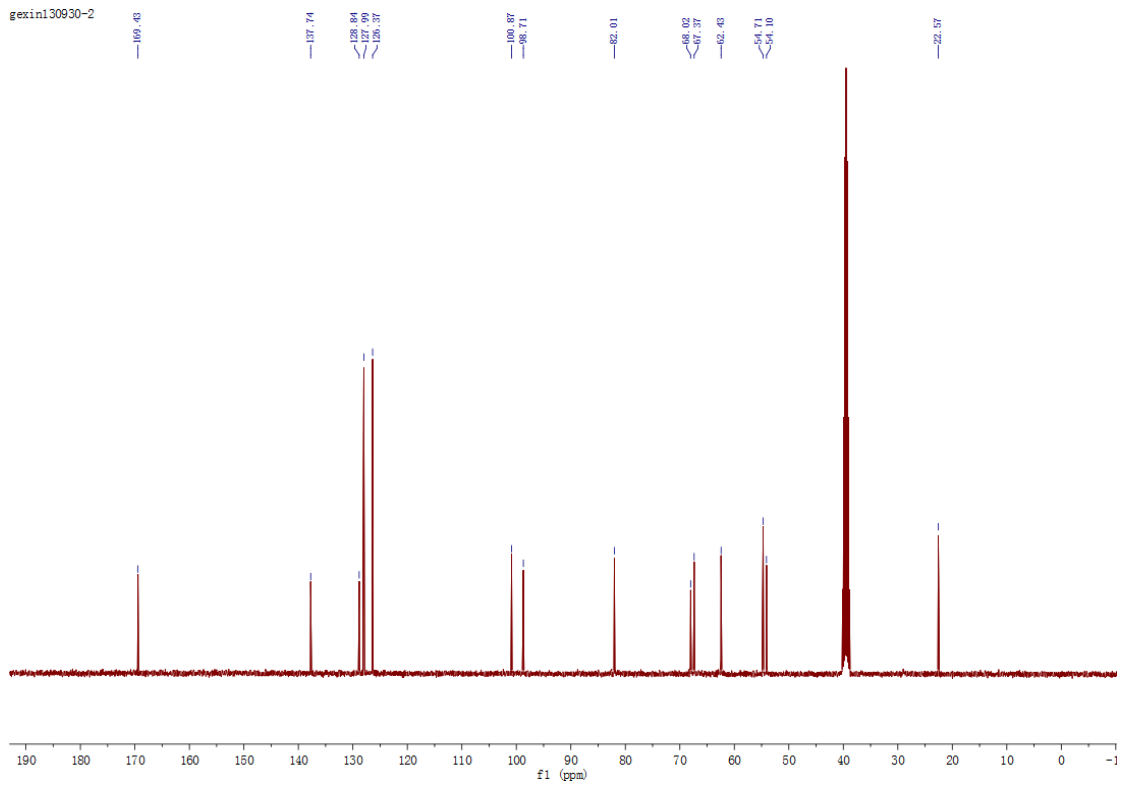
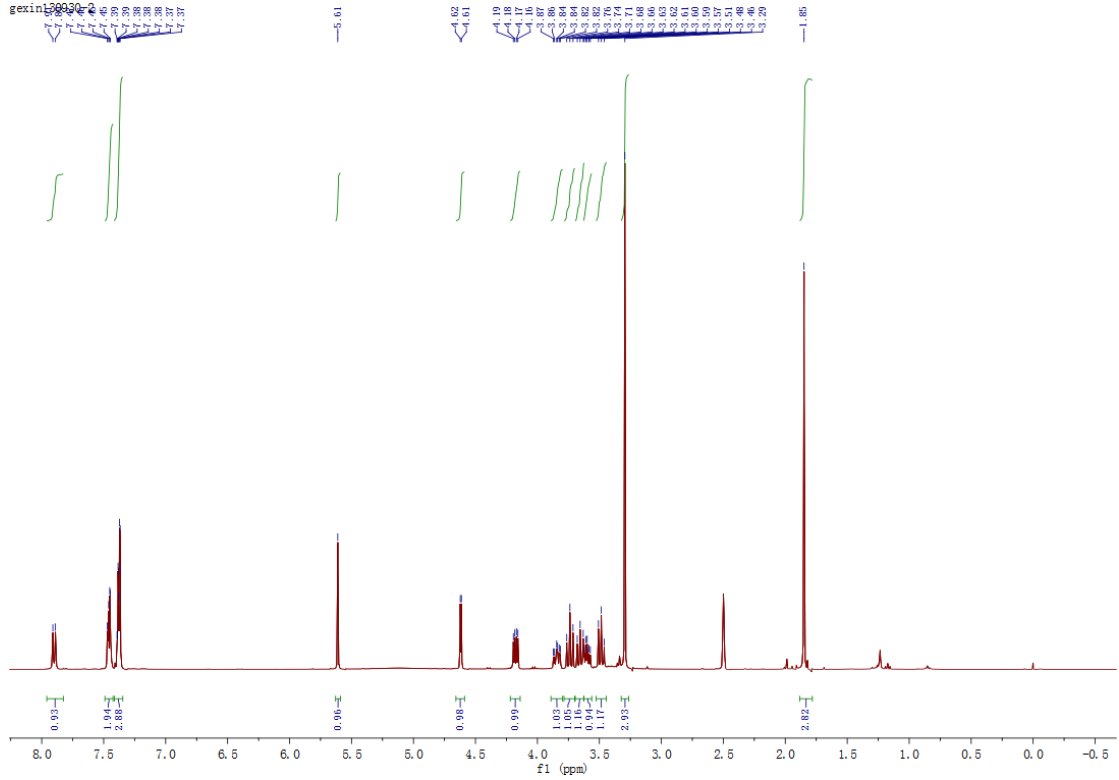
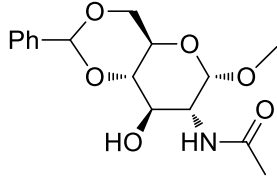
1H), 6.62 (t,  $J = 7.4$  Hz, 1H), 6.55 (d,  $J = 7.7$  Hz, 1H), 3.44 (t,  $J = 8.3$  Hz, 3H), 2.93 (t,  $J = 8.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.64, 129.37, 127.25, 124.68, 118.71, 109.51, 47.37, 29.89. MS (EI):  $m/z = 119$   $[\text{M}]^+$ .

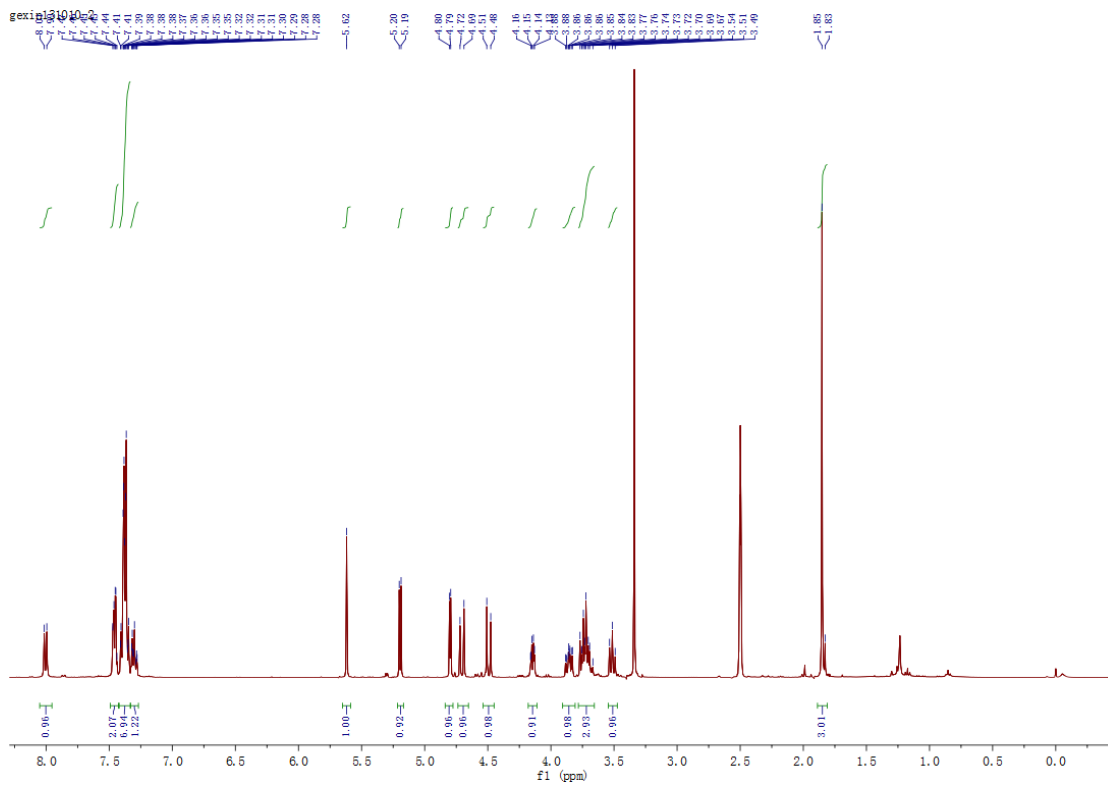
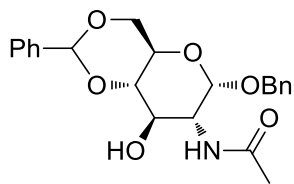
**1-(4-methoxyphenyl)indoline.**<sup>13</sup> Pale yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 8.9$  Hz, 1H), 7.11 (d,  $J = 9.0$  Hz, 2H), 7.06 (d,  $J = 7.1$  Hz, 1H), 6.95 (t,  $J = 7.6$  Hz, 1H), 6.82 (t,  $J = 8.0$  Hz, 3H), 3.79 (t,  $J = 8.4$  Hz, 2H), 3.73 (s, 3H), 3.03 (t,  $J = 8.4$  Hz, 2H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  138.22, 137.99, 130.67, 127.12, 124.88, 120.71, 118.17, 116.39, 114.57, 107.39, 55.60, 53.12, 28.33. MS (EI):  $m/z = 225$   $[\text{M}]^+$ .

# NMR Spectra of Ligand and Products

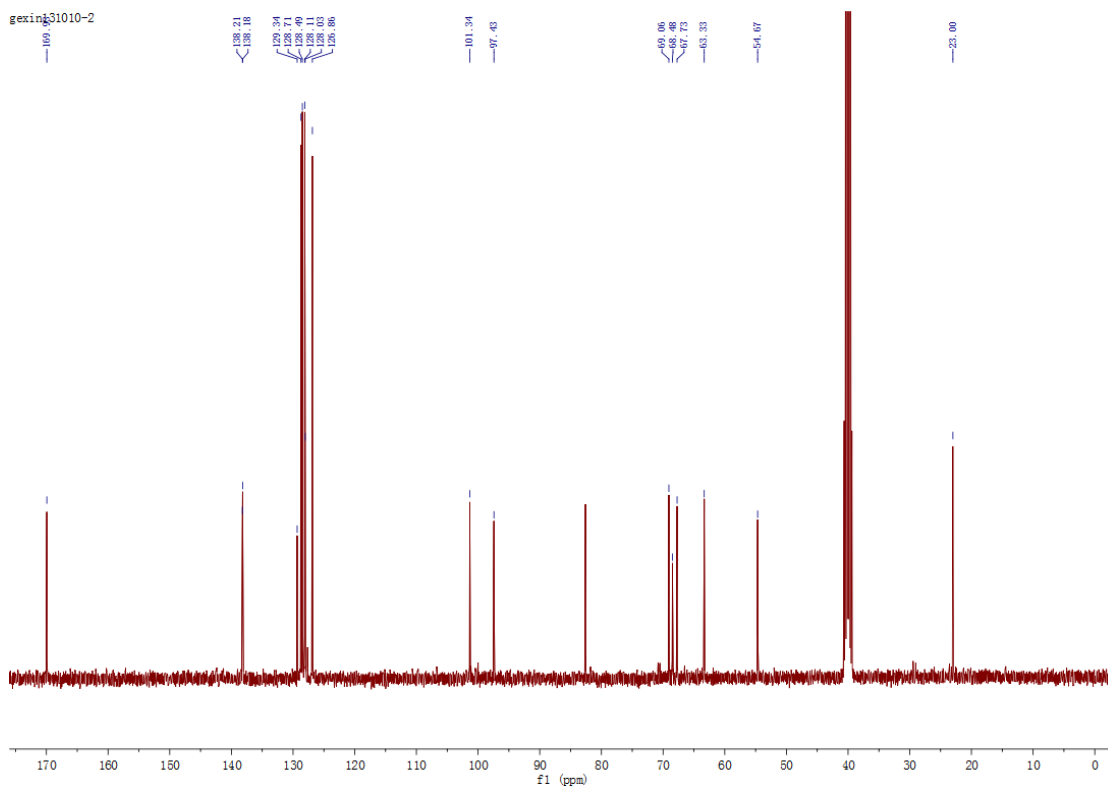




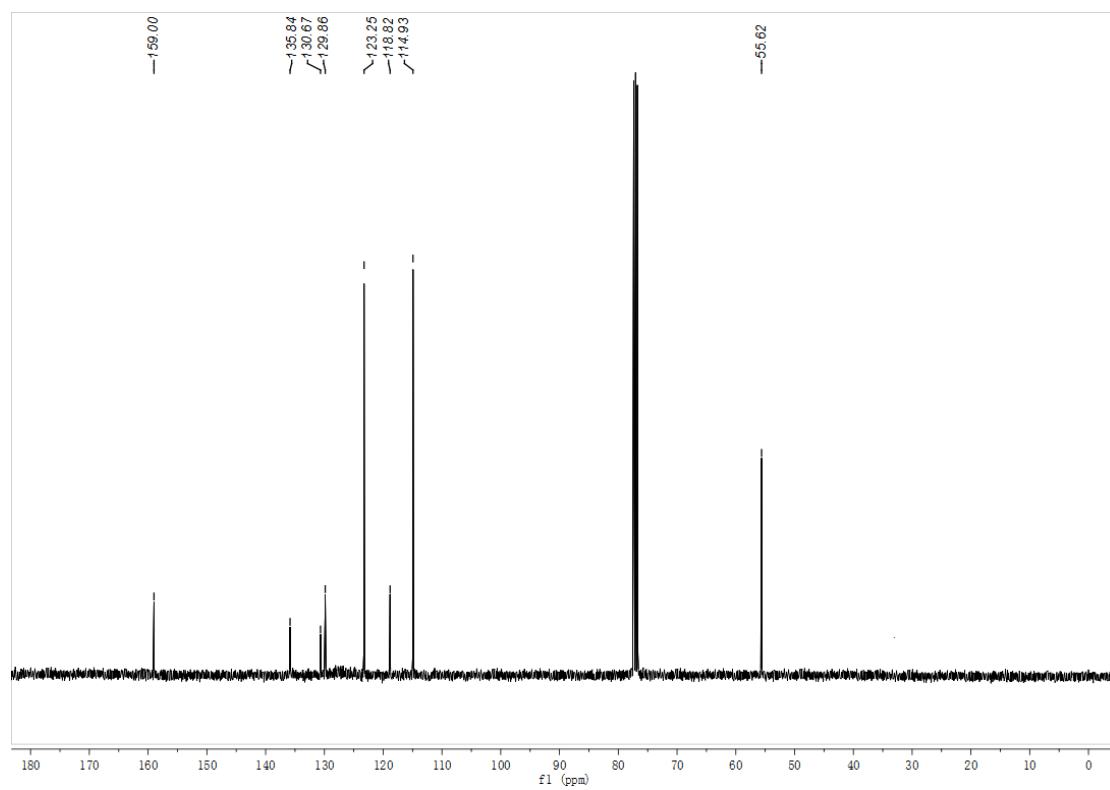
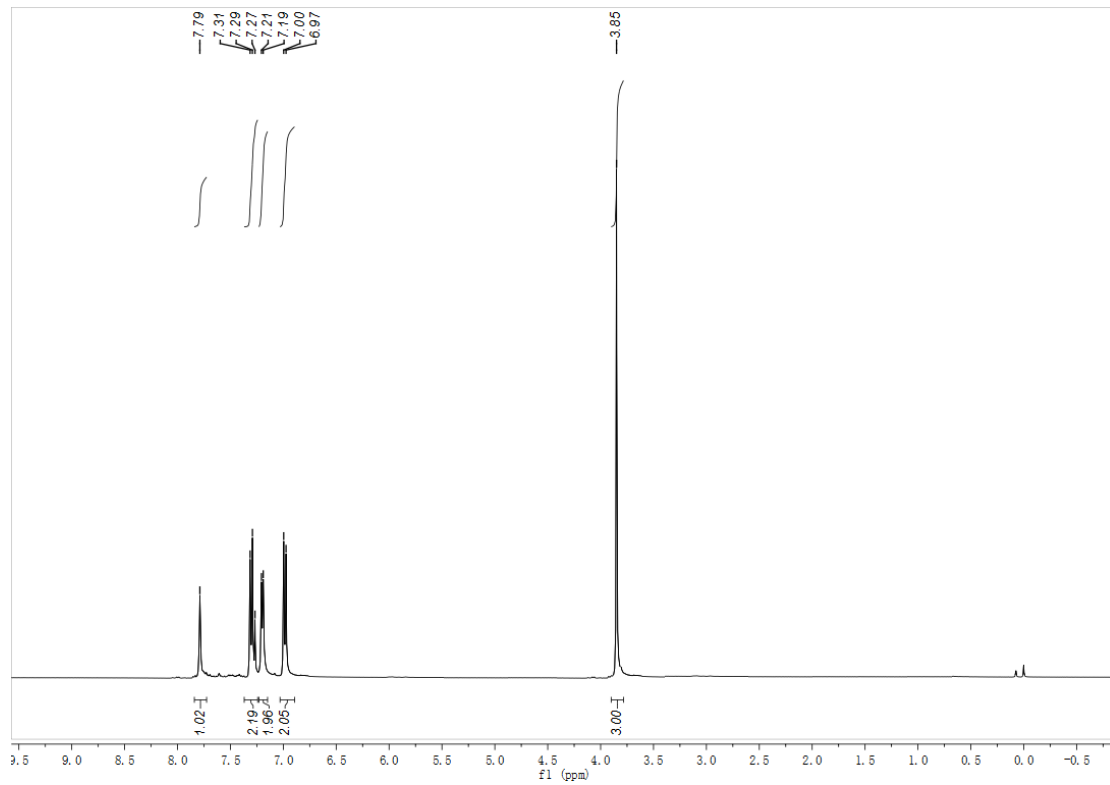
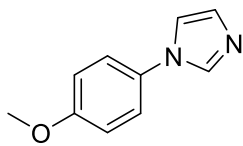


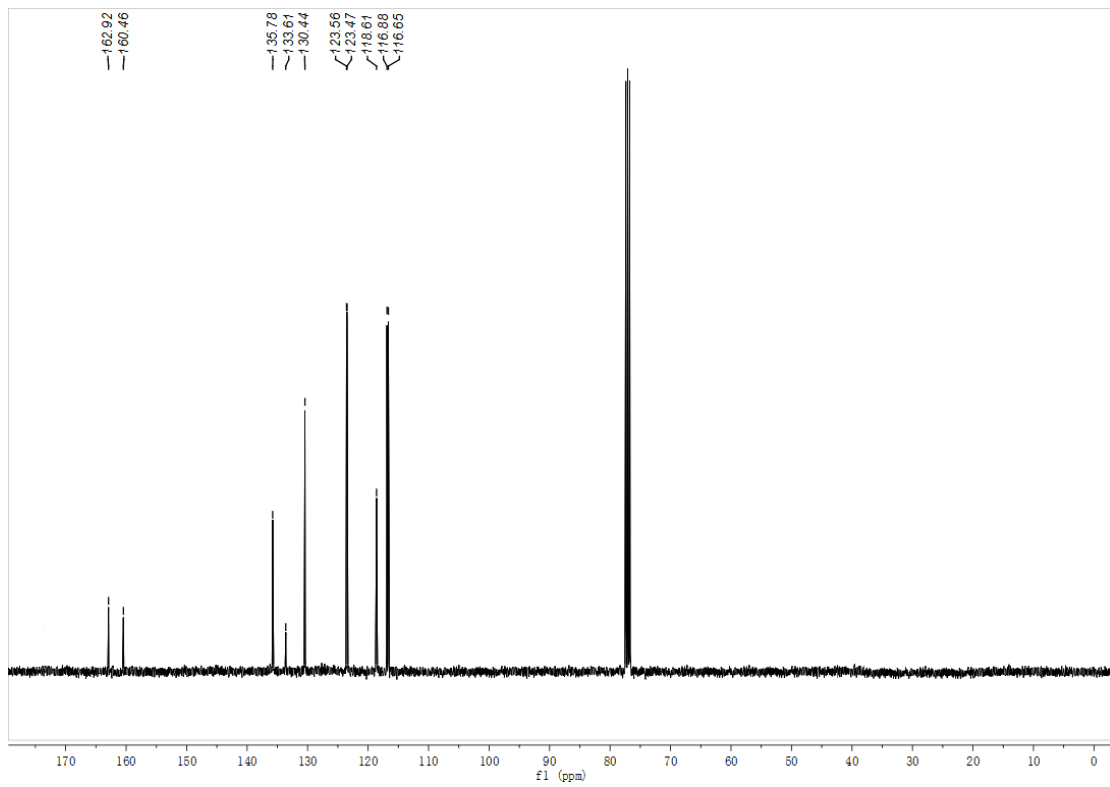
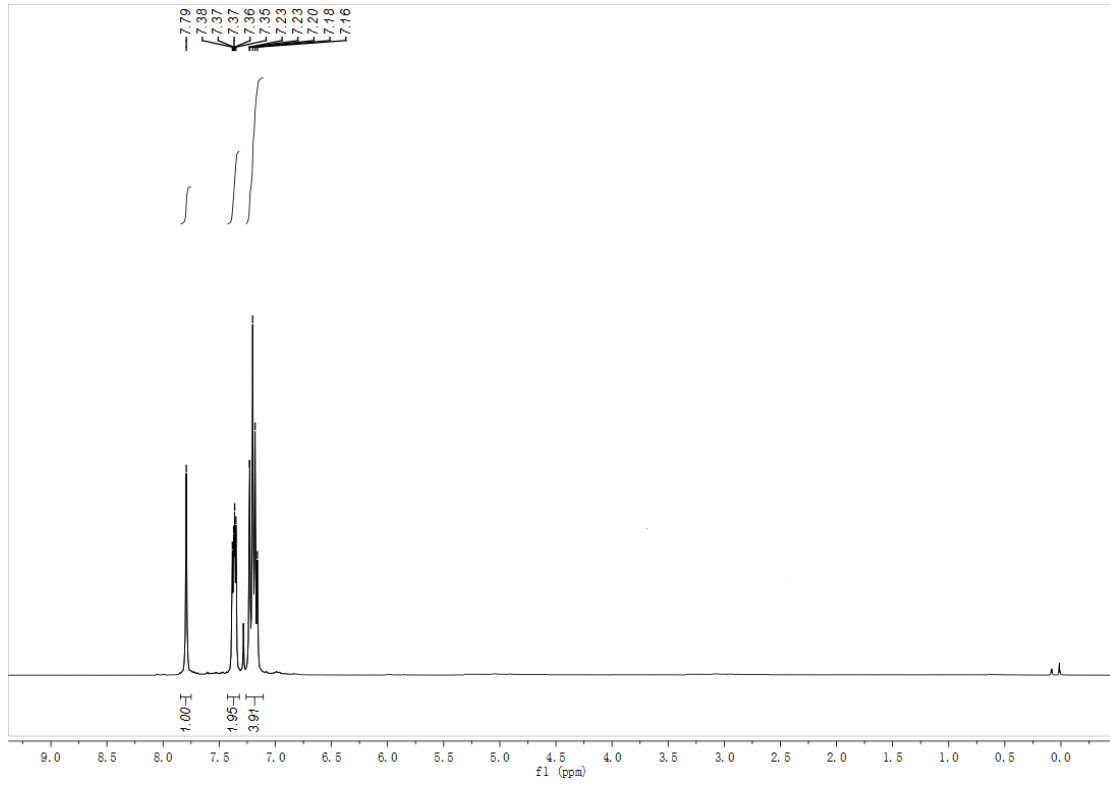
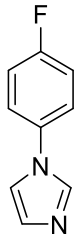


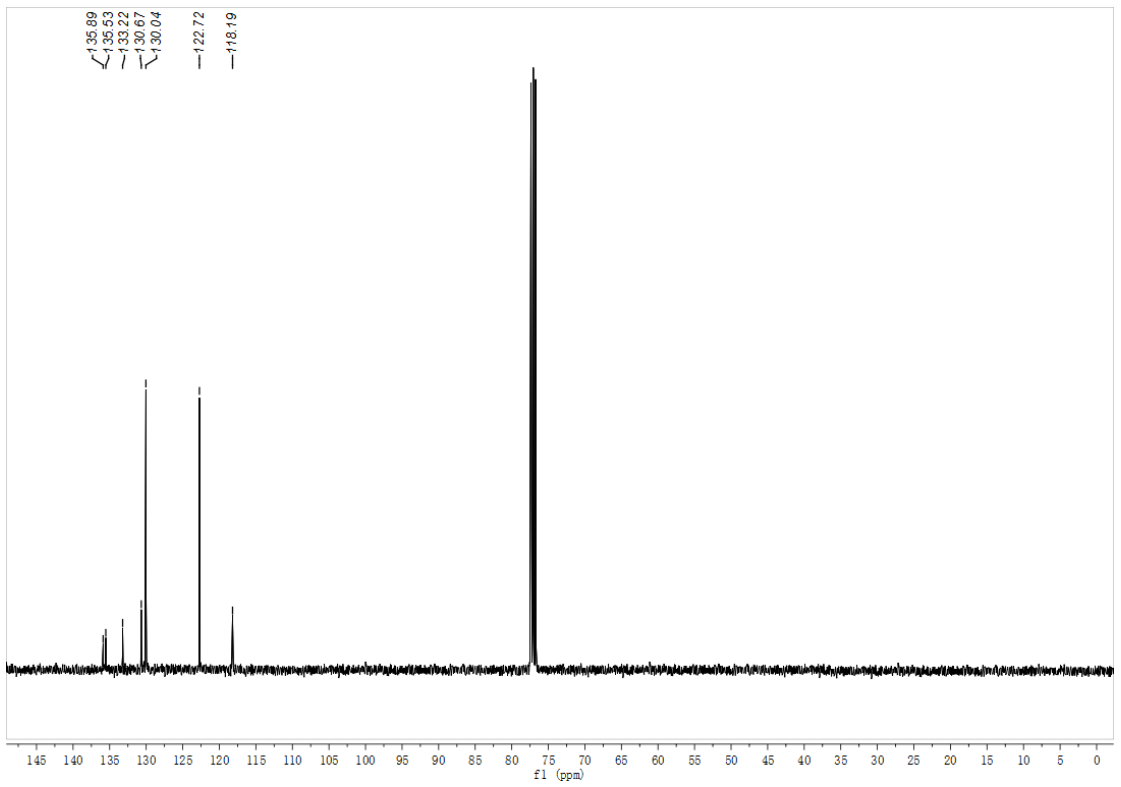
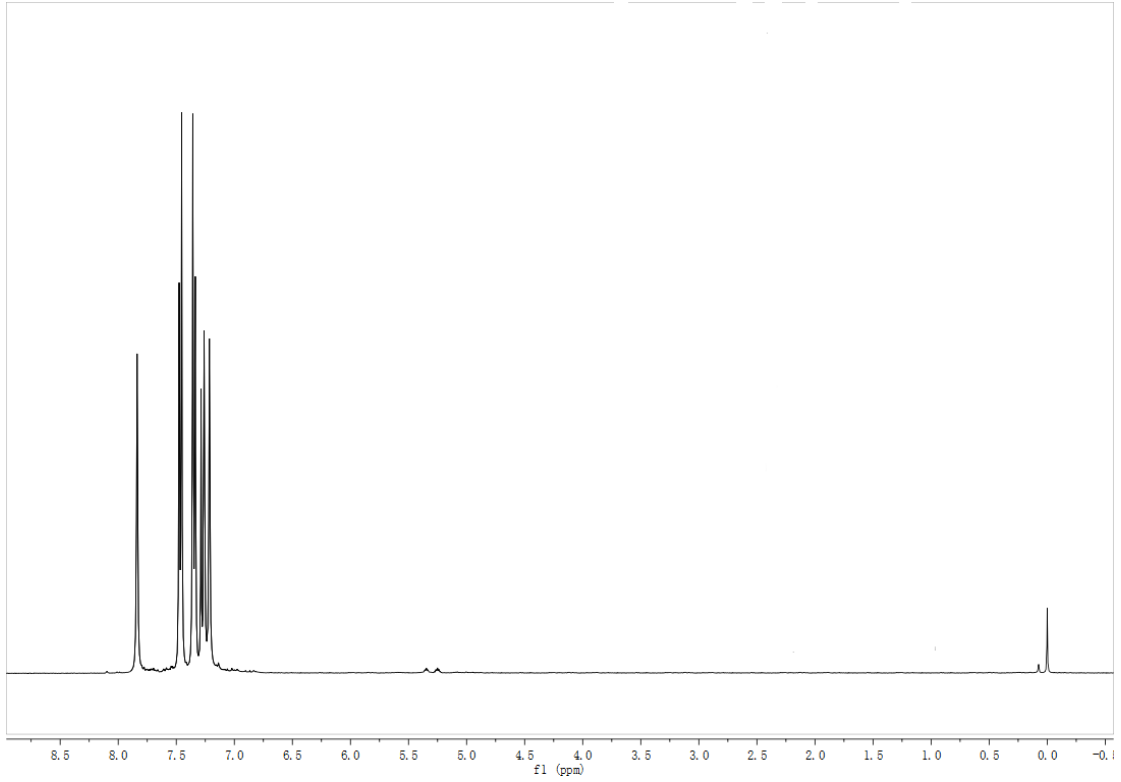
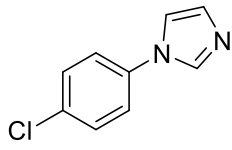
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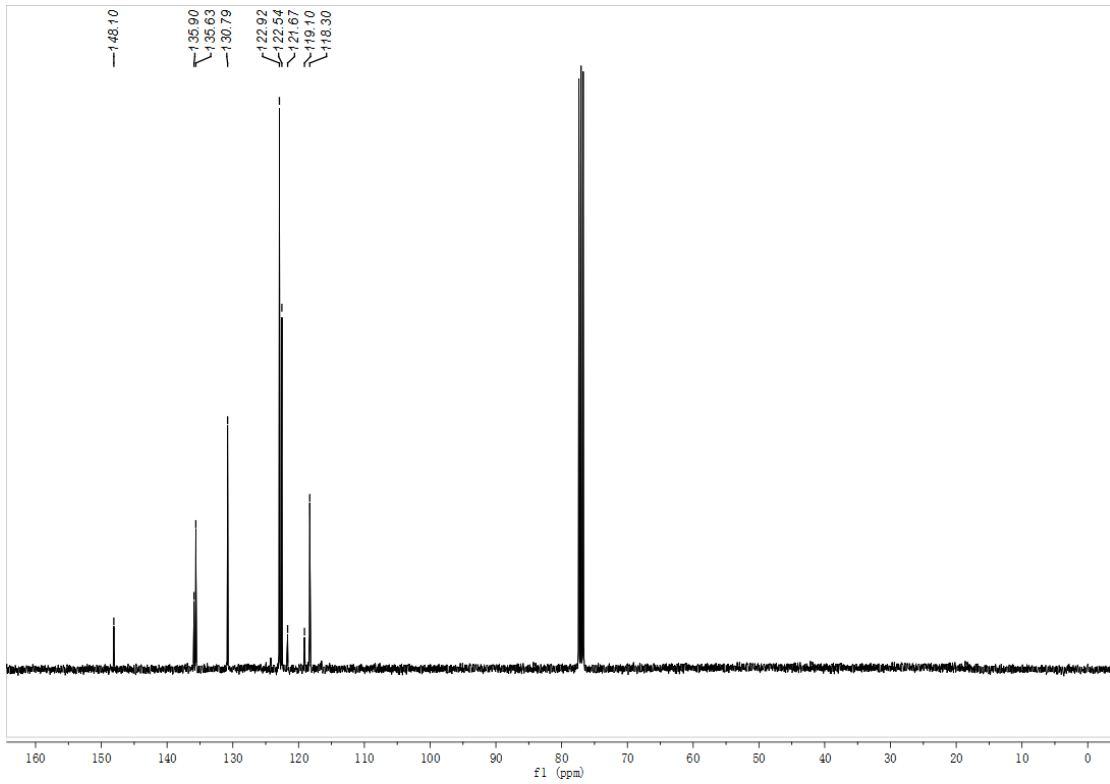
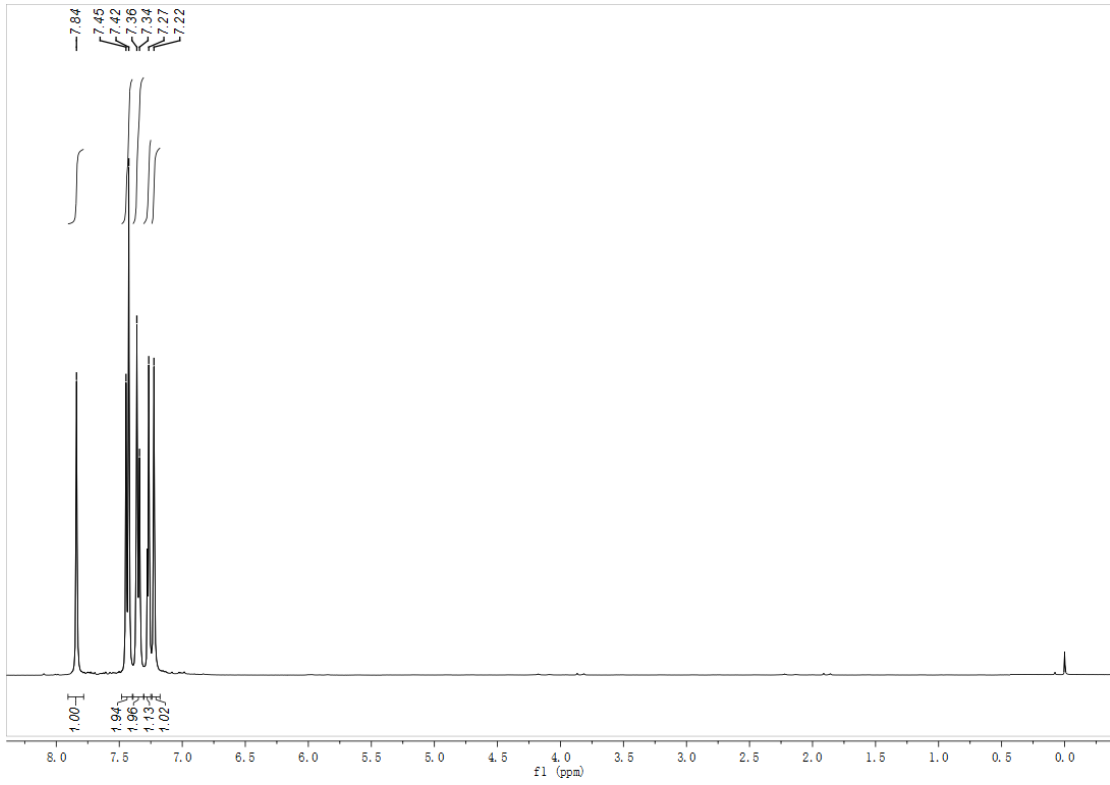
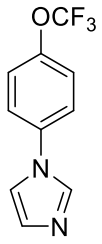


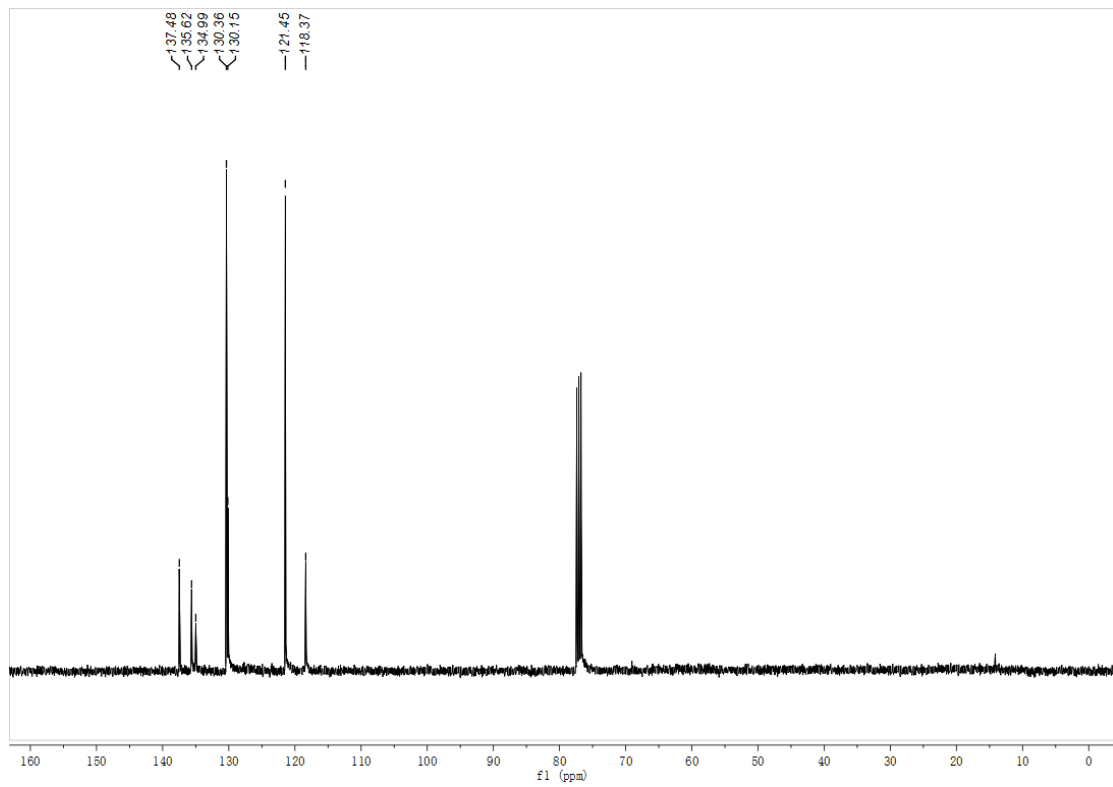
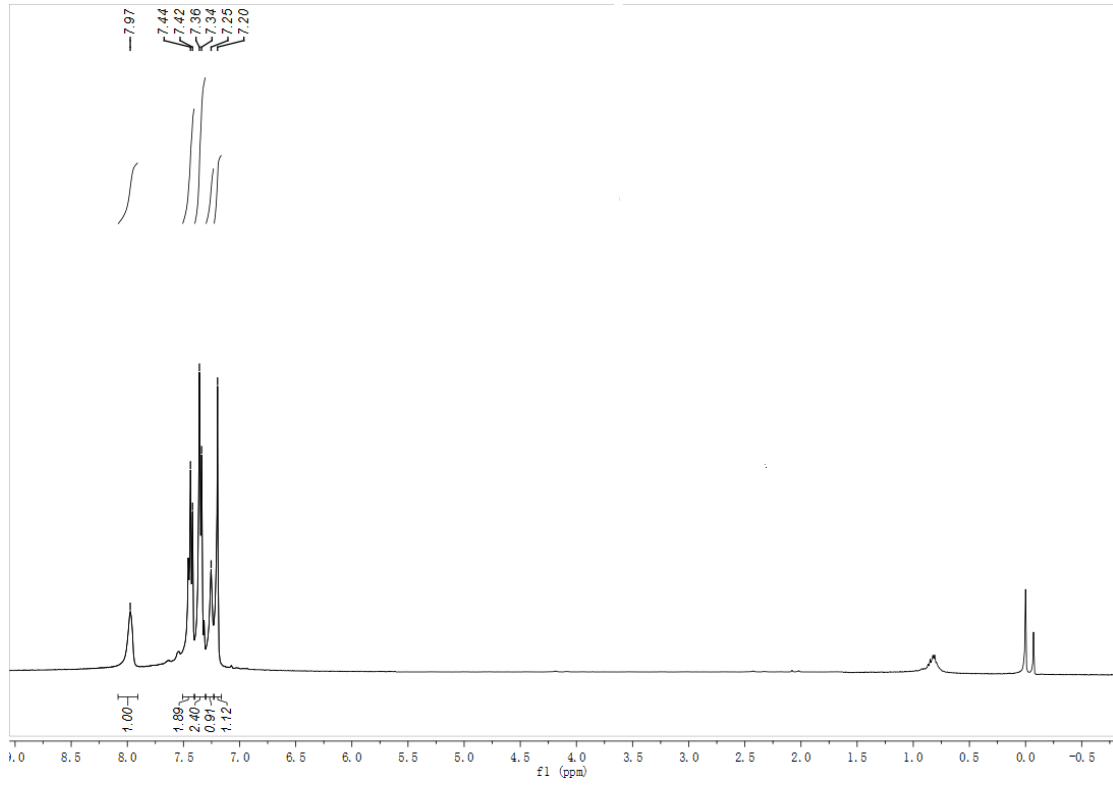
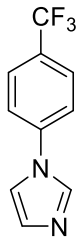


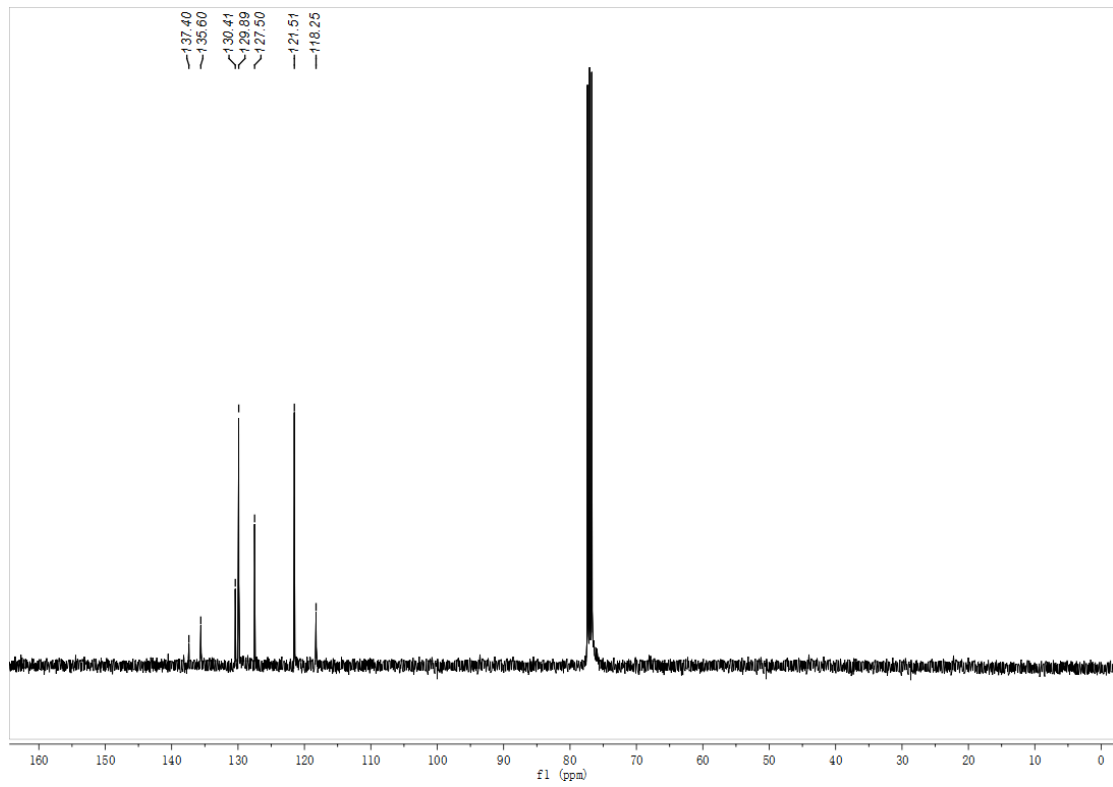
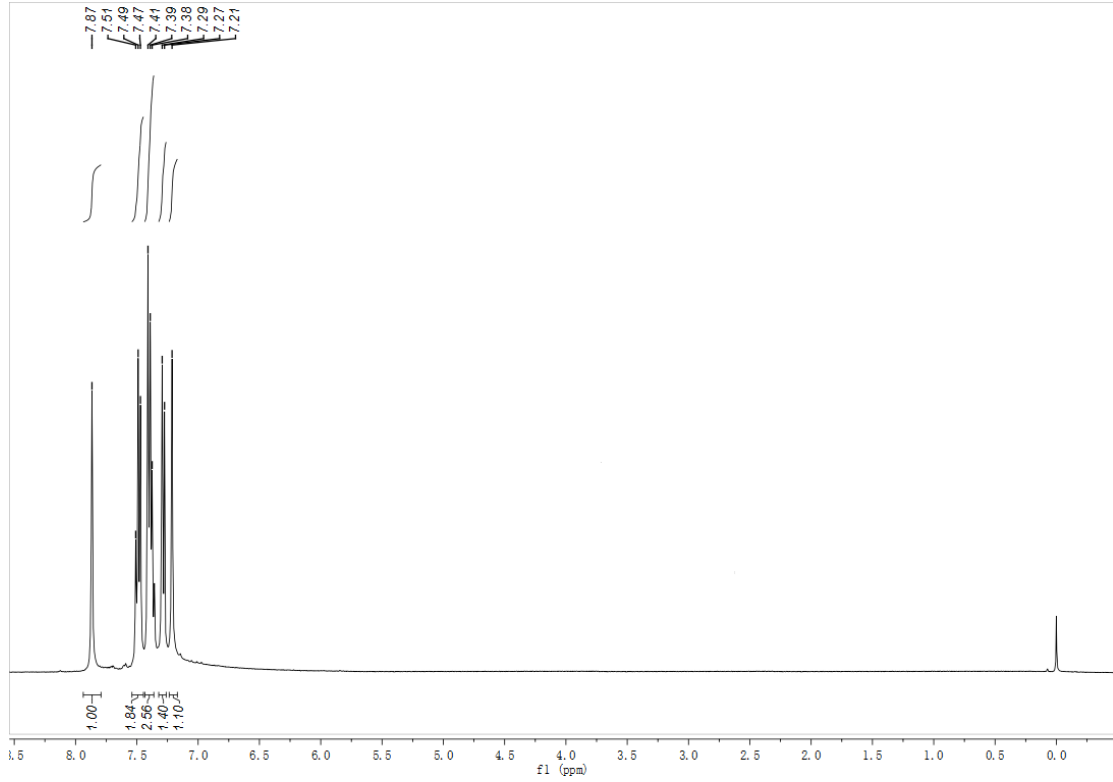
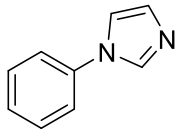


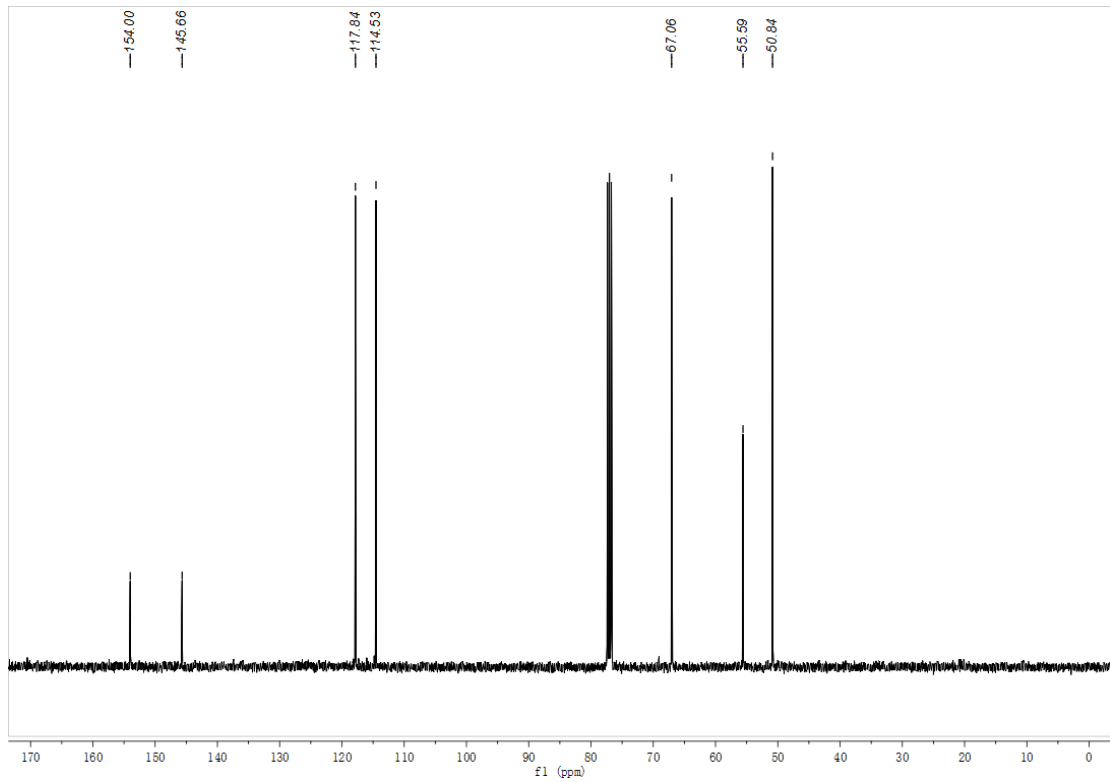
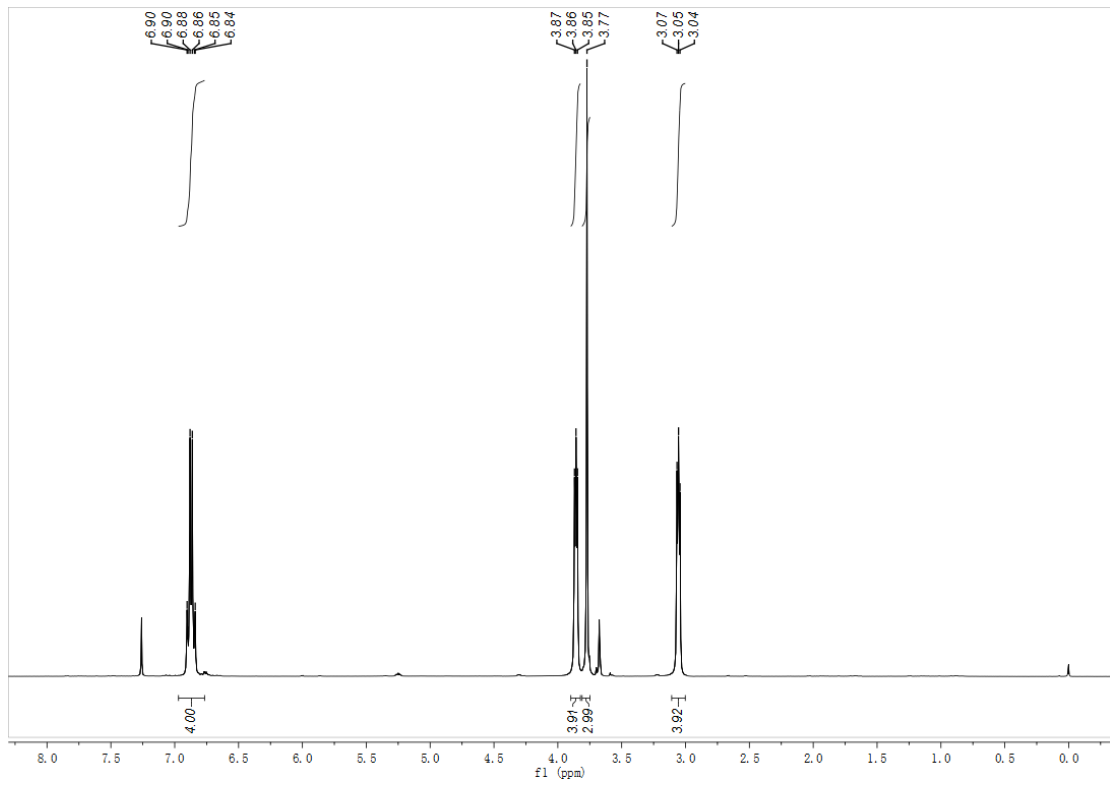
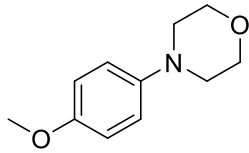


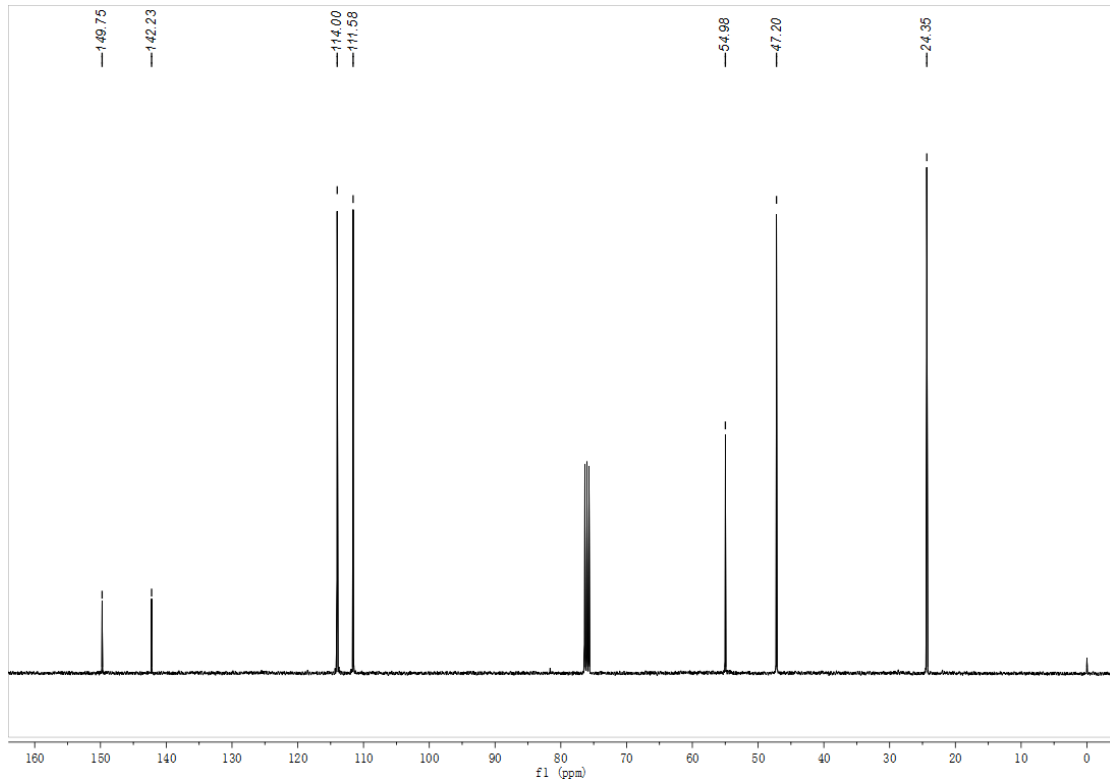
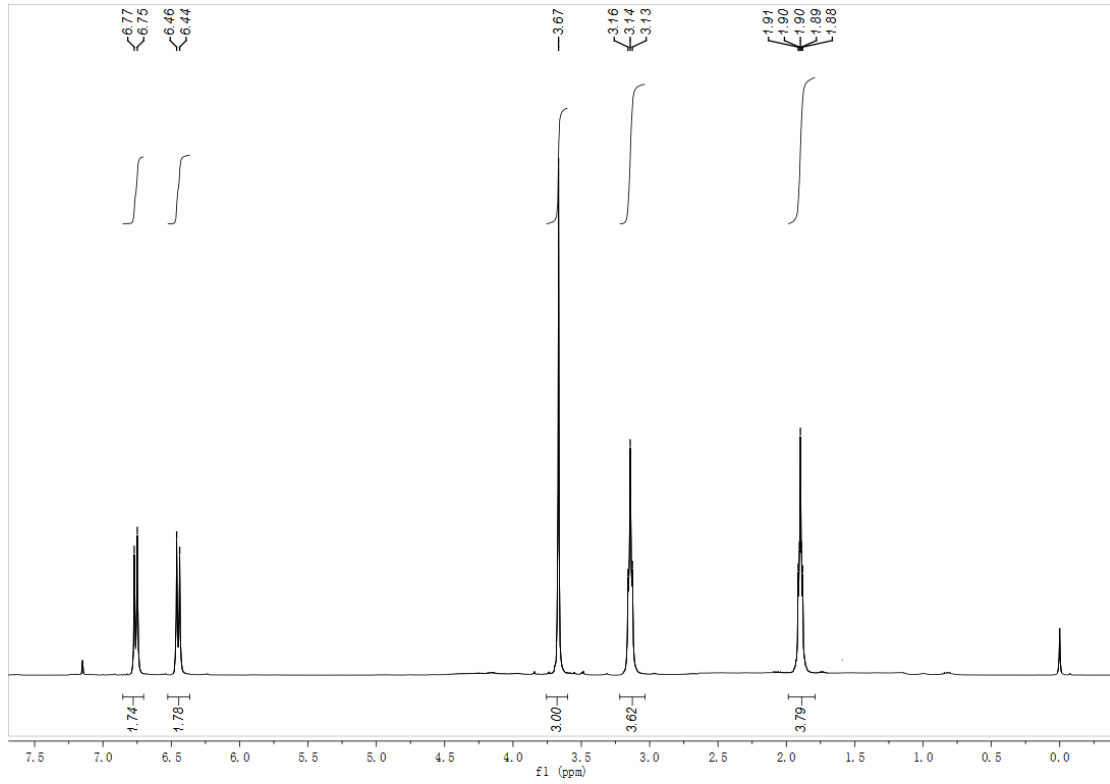
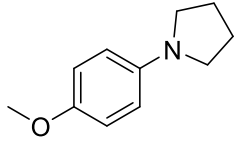




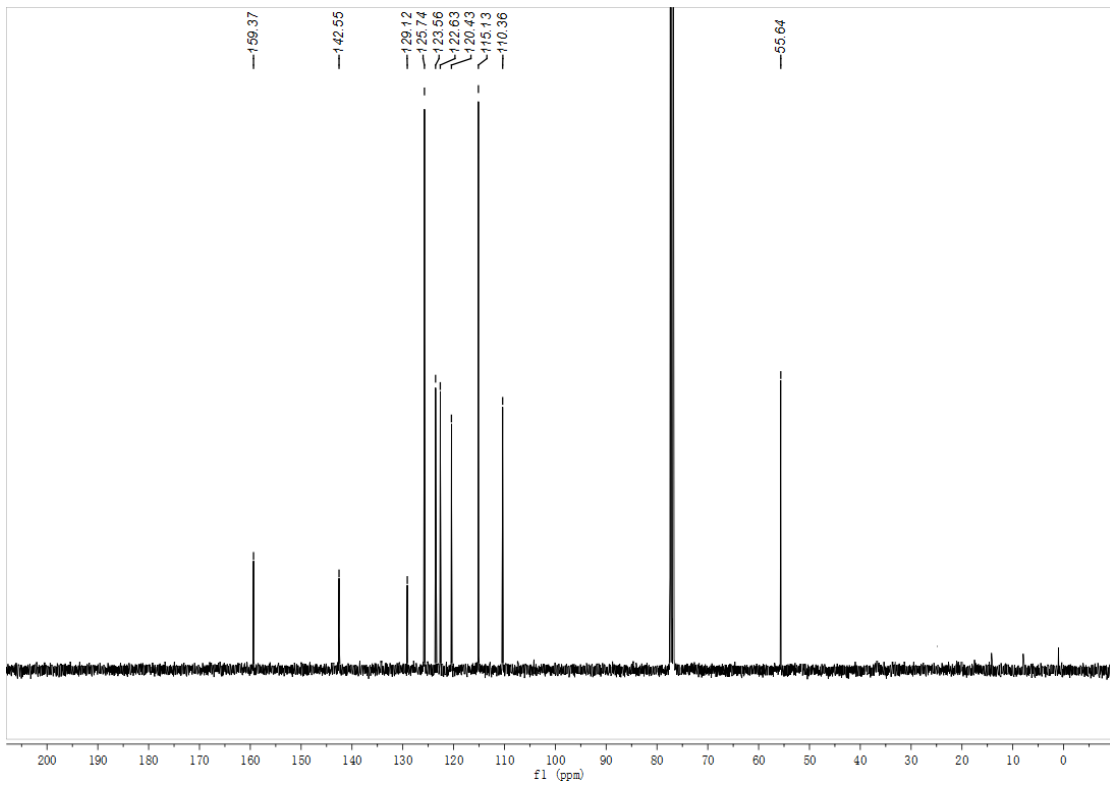
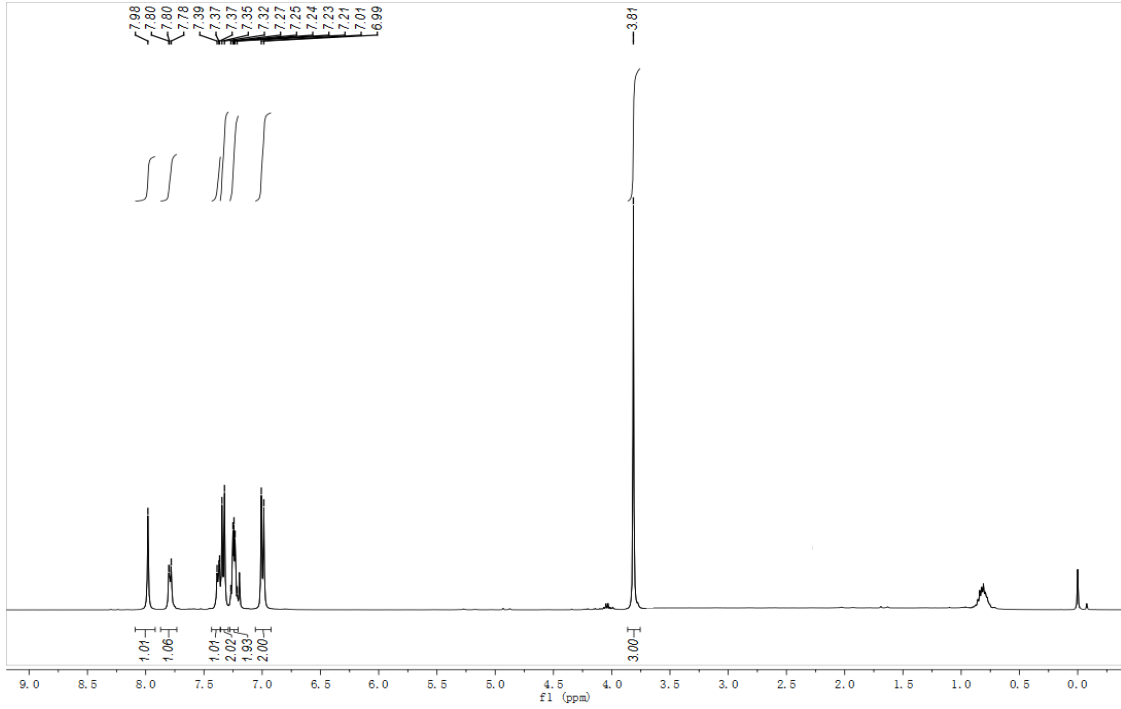
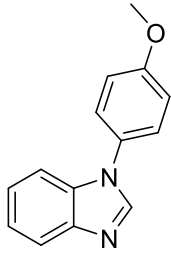


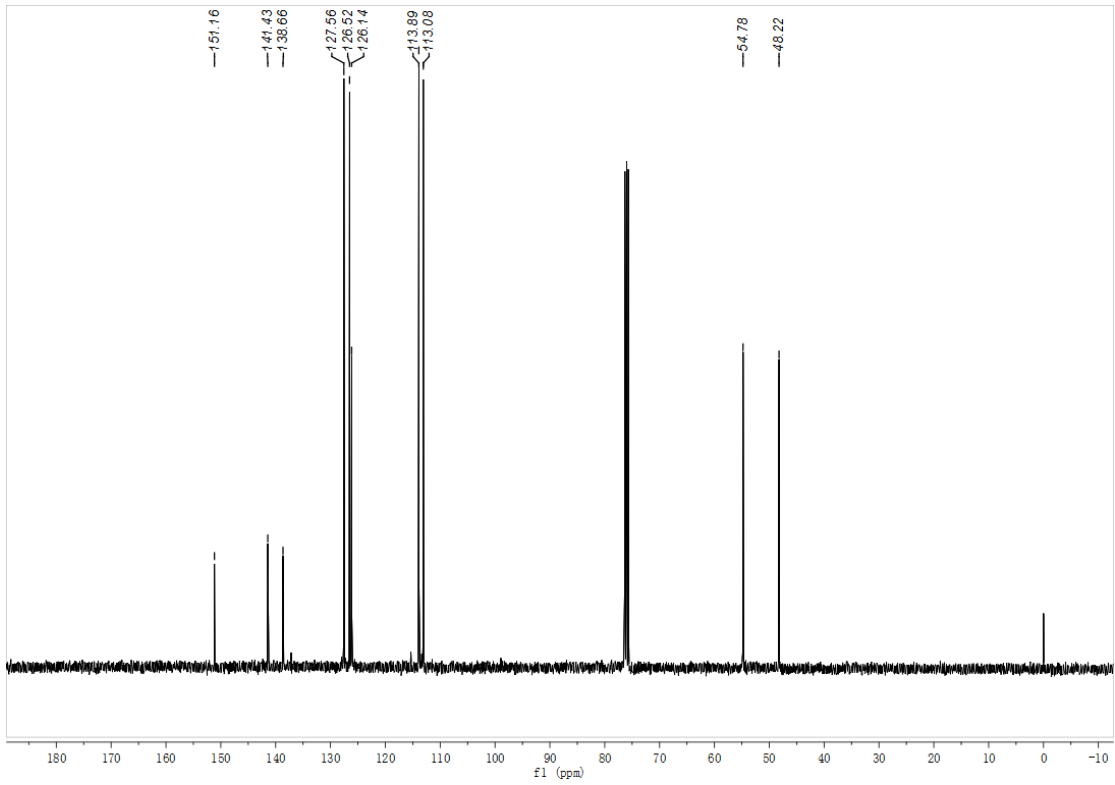
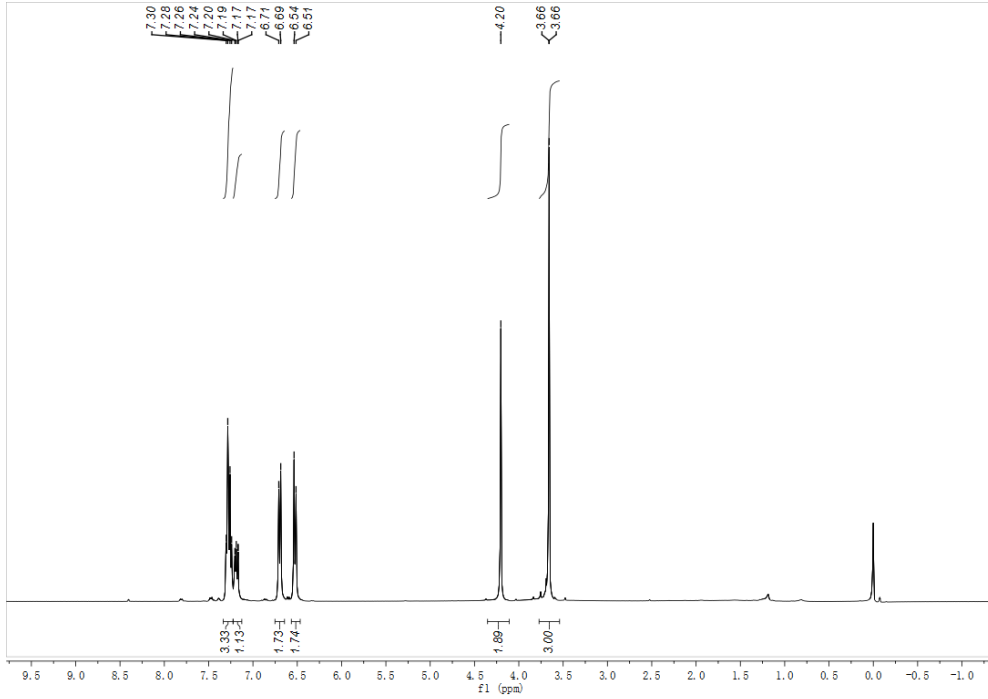
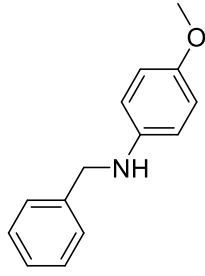


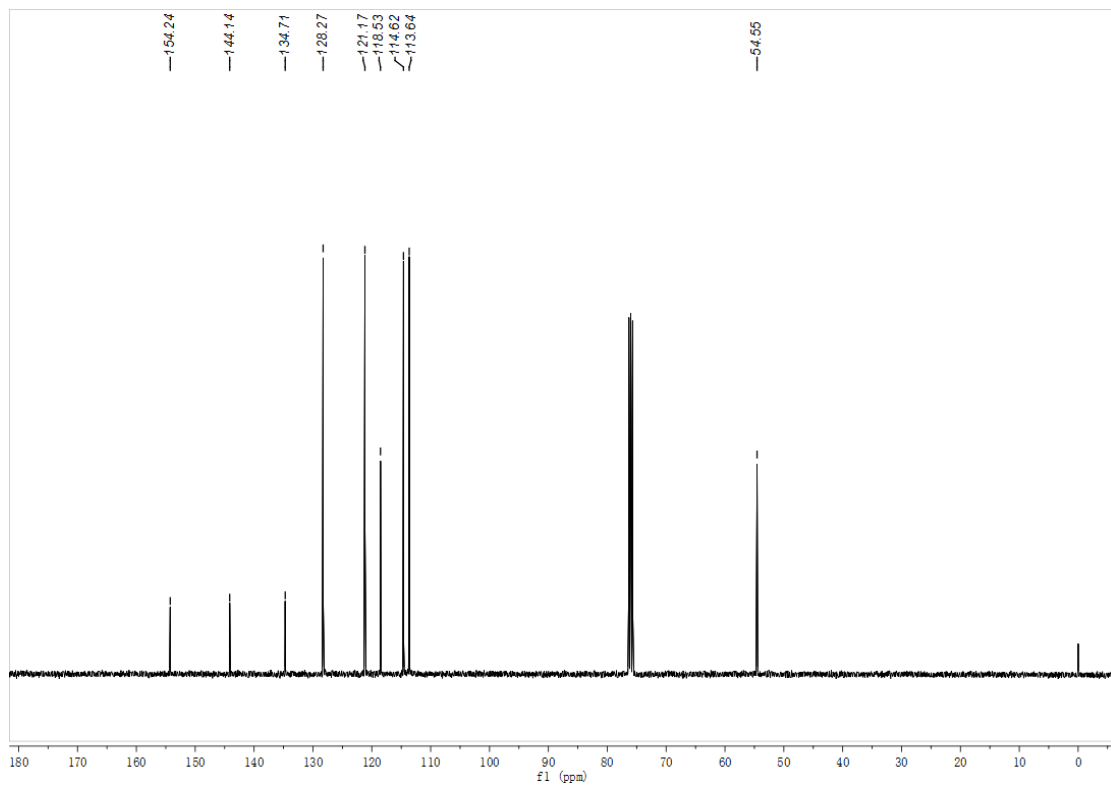
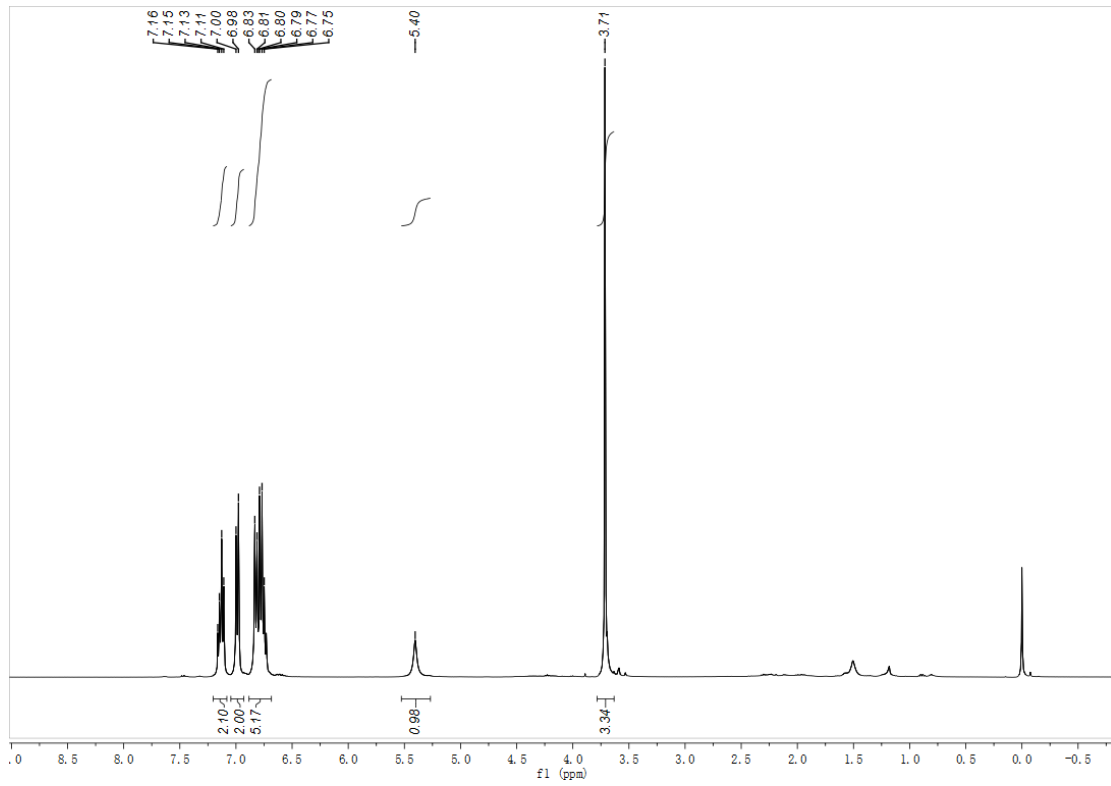
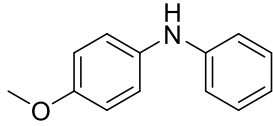


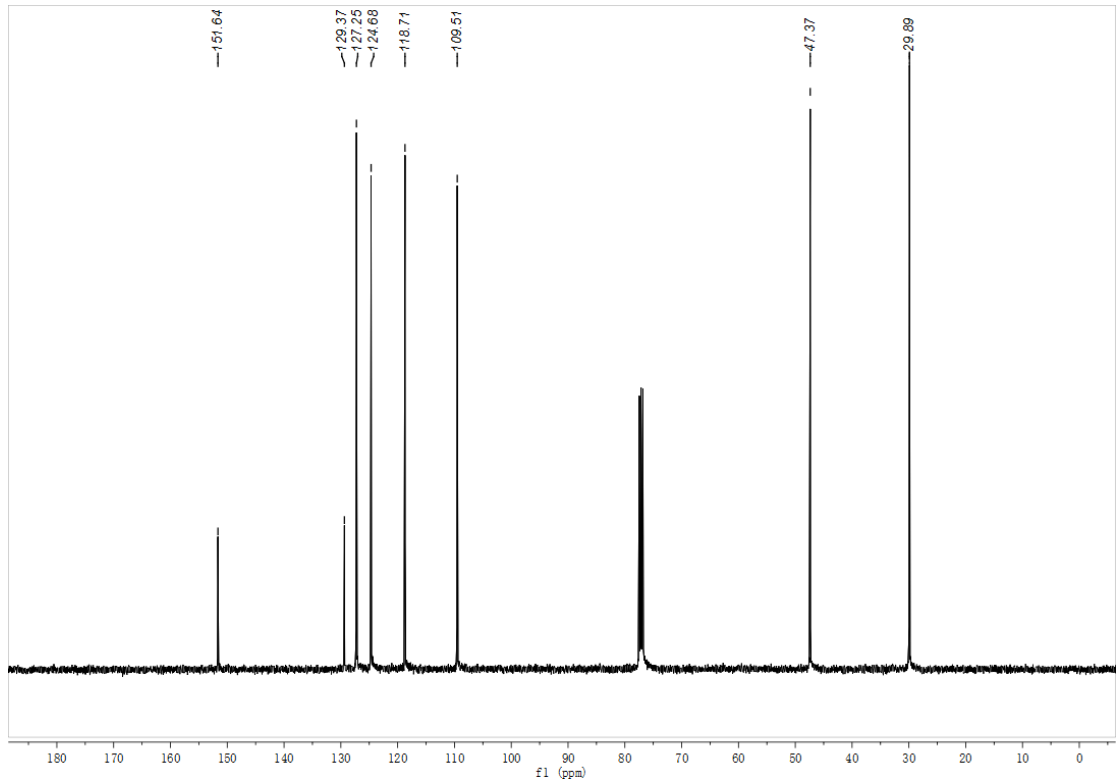
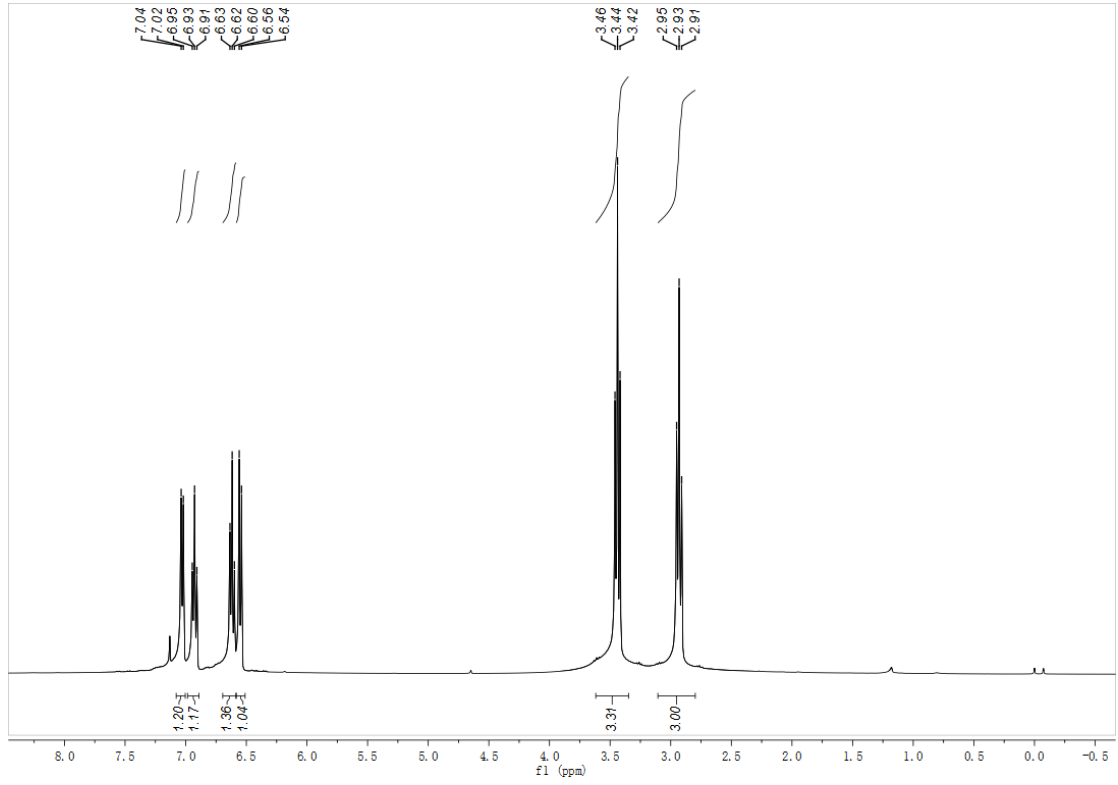
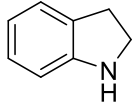


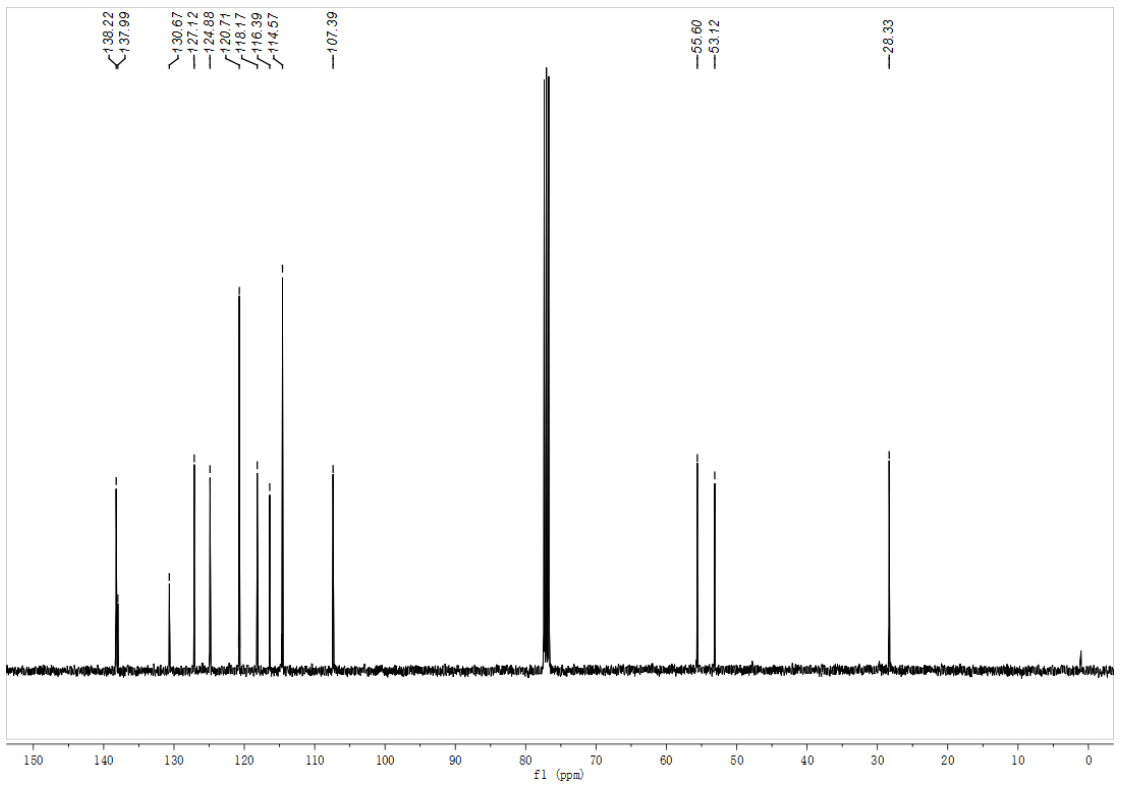
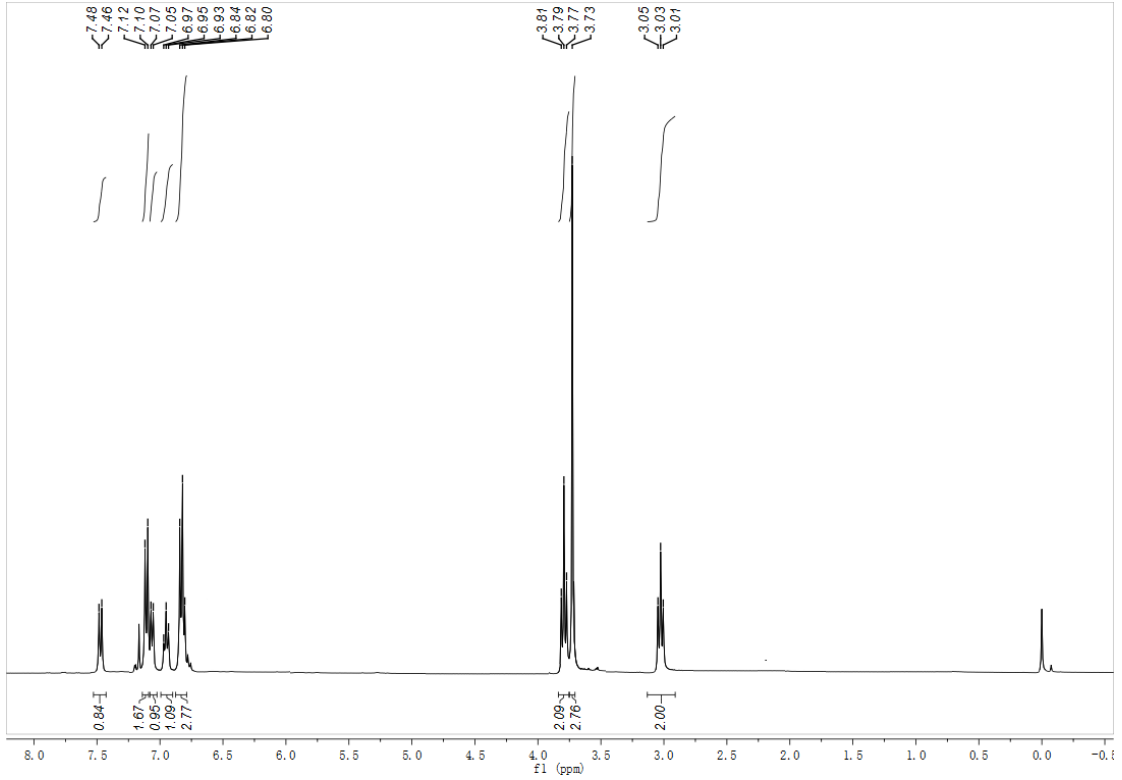
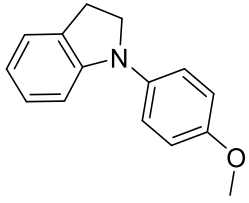






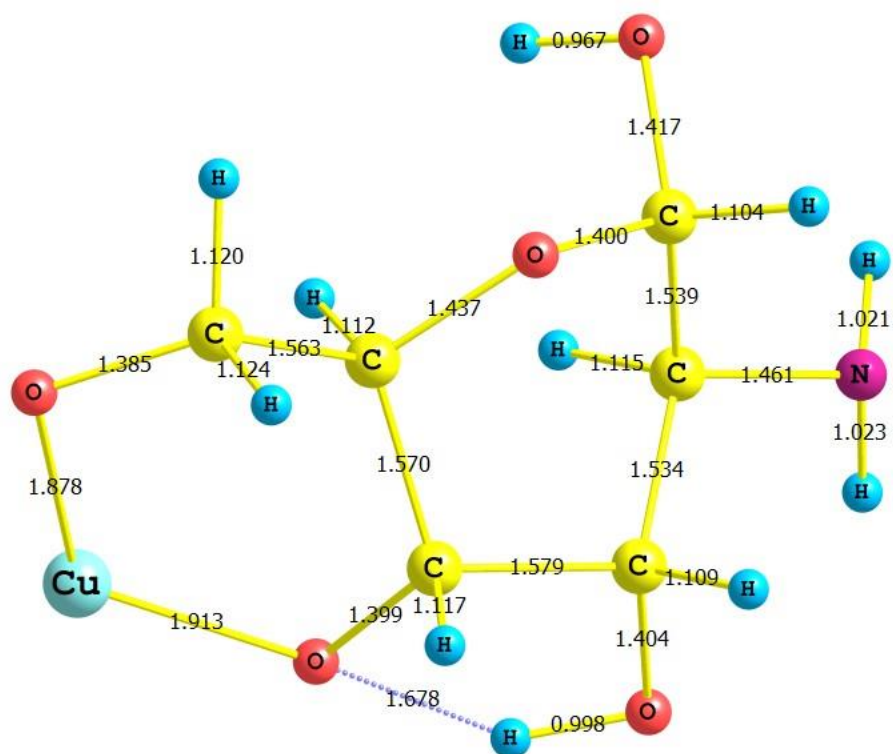




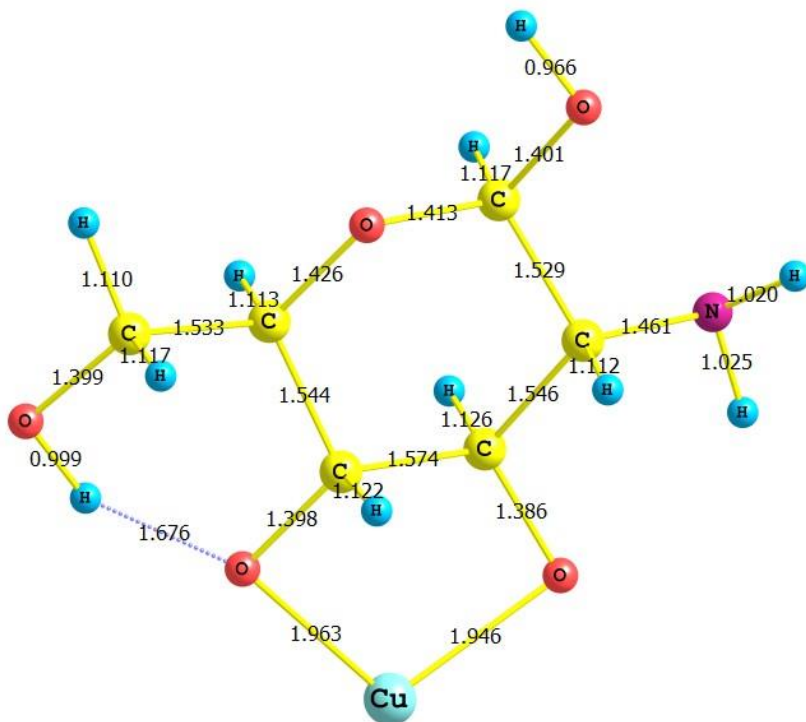


## Structural information of associated coordinates for the most favorable pathways

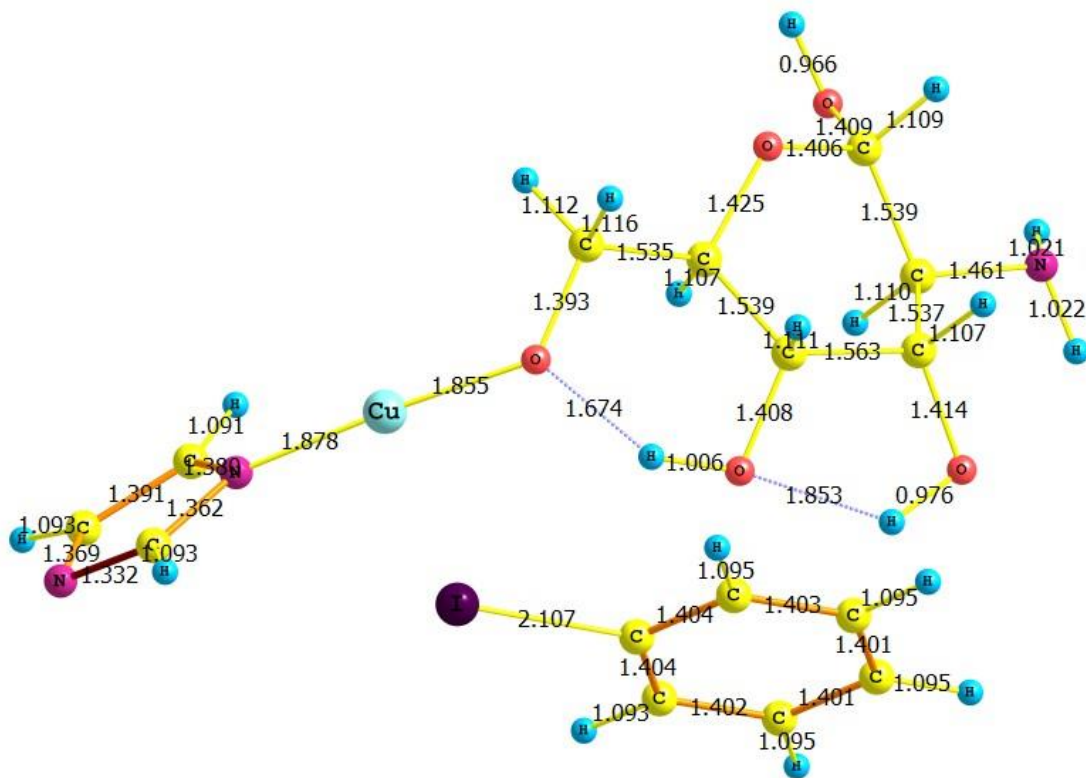
Selected bond lengths are in Å.



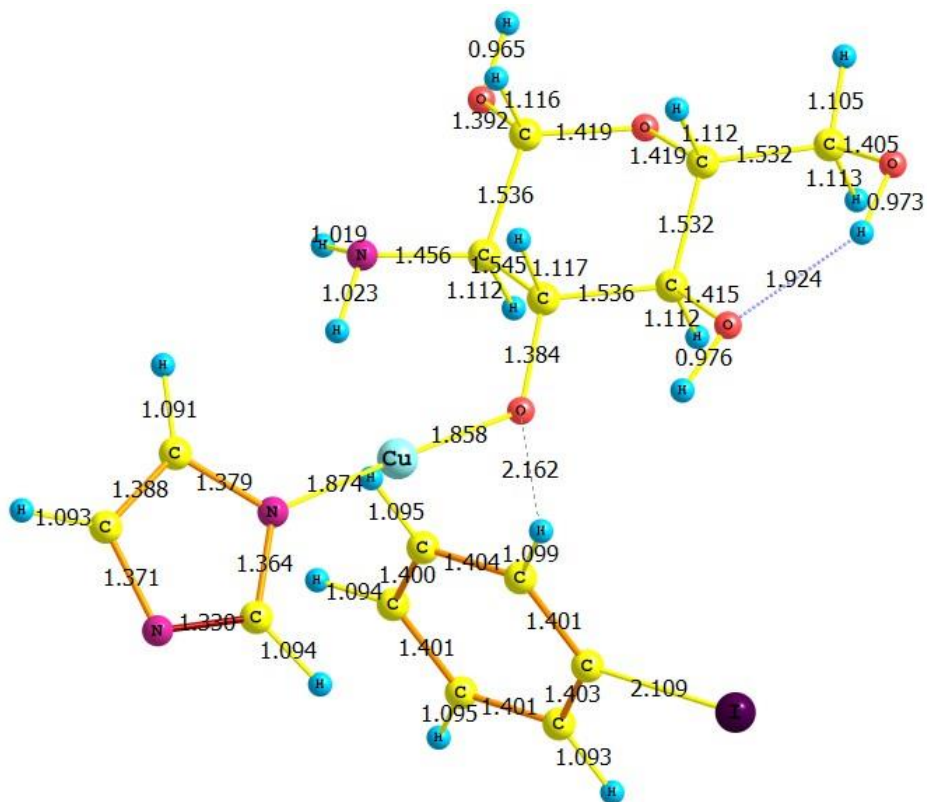
Cat. A



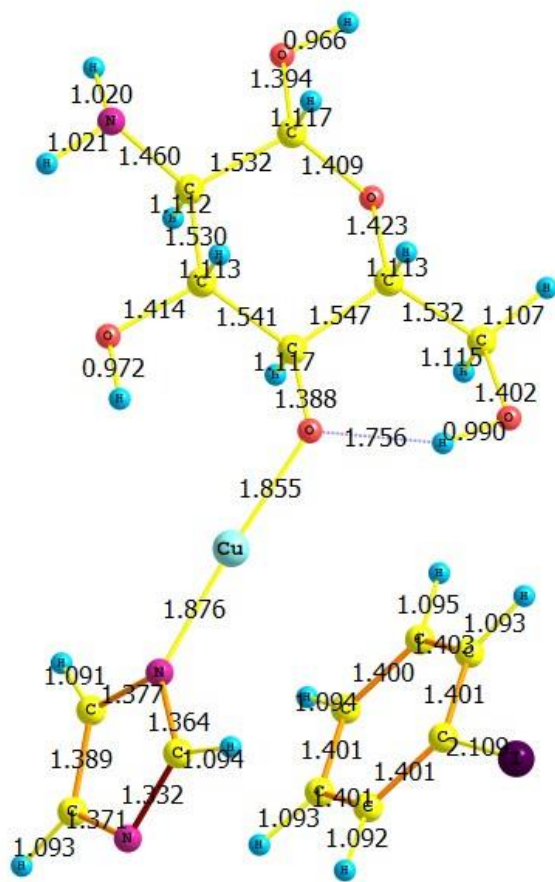
Cat. B



IM1a

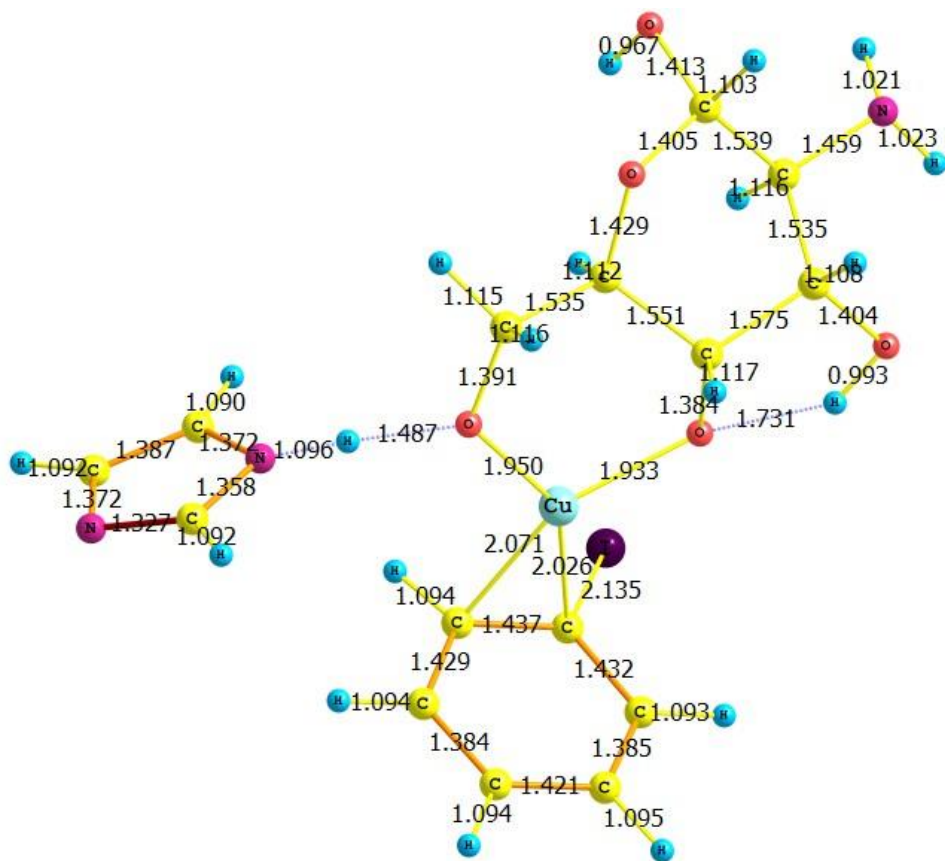


**IM1b**

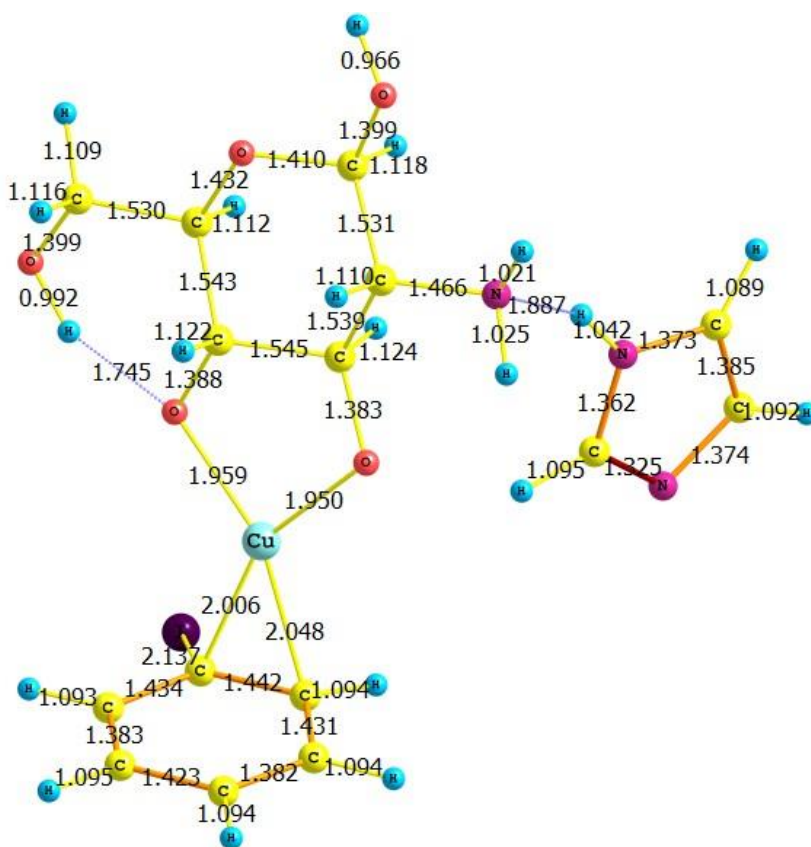


**IM1c**



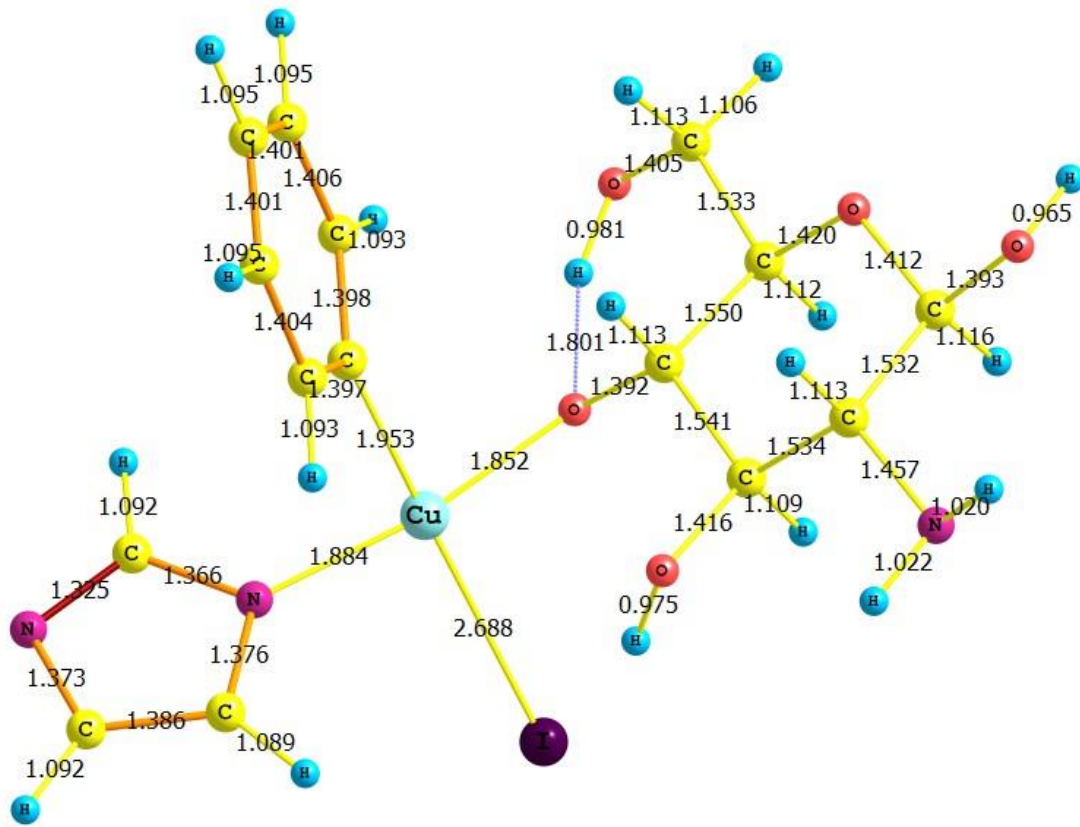


IM1d

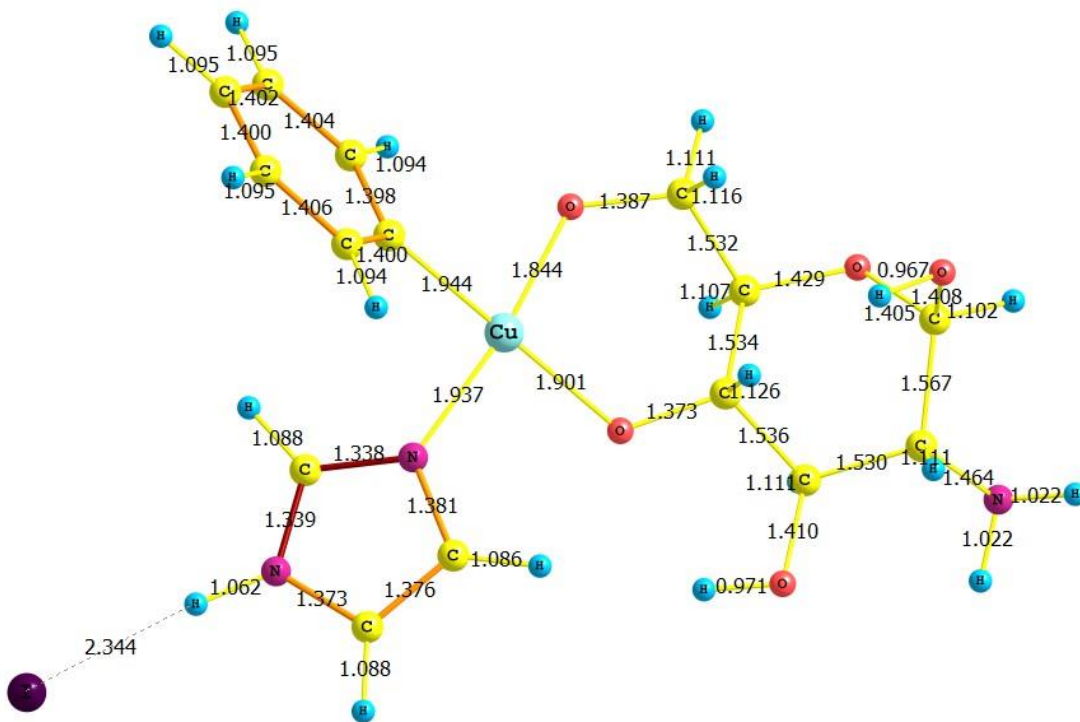


IM1e

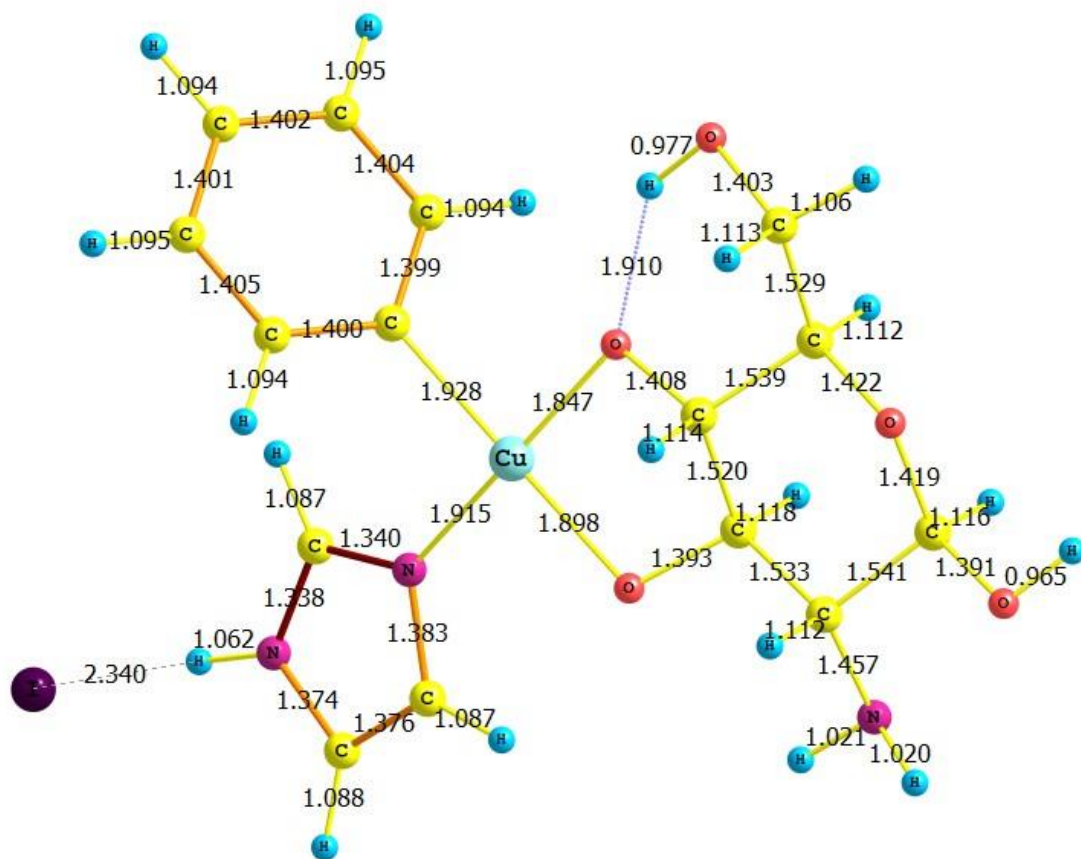




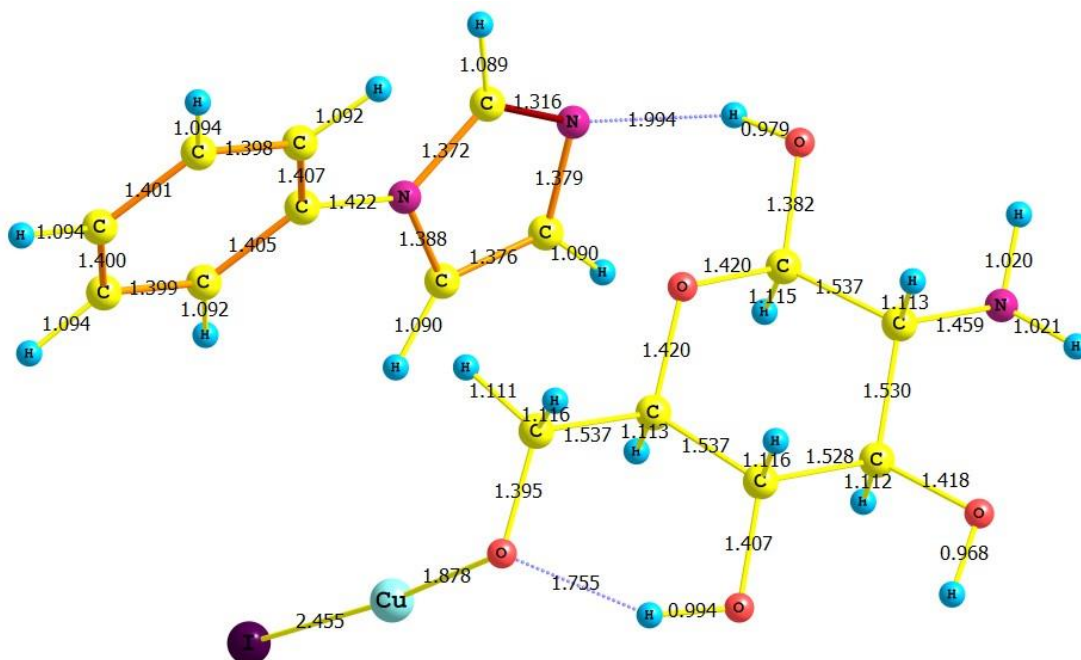
IM2c



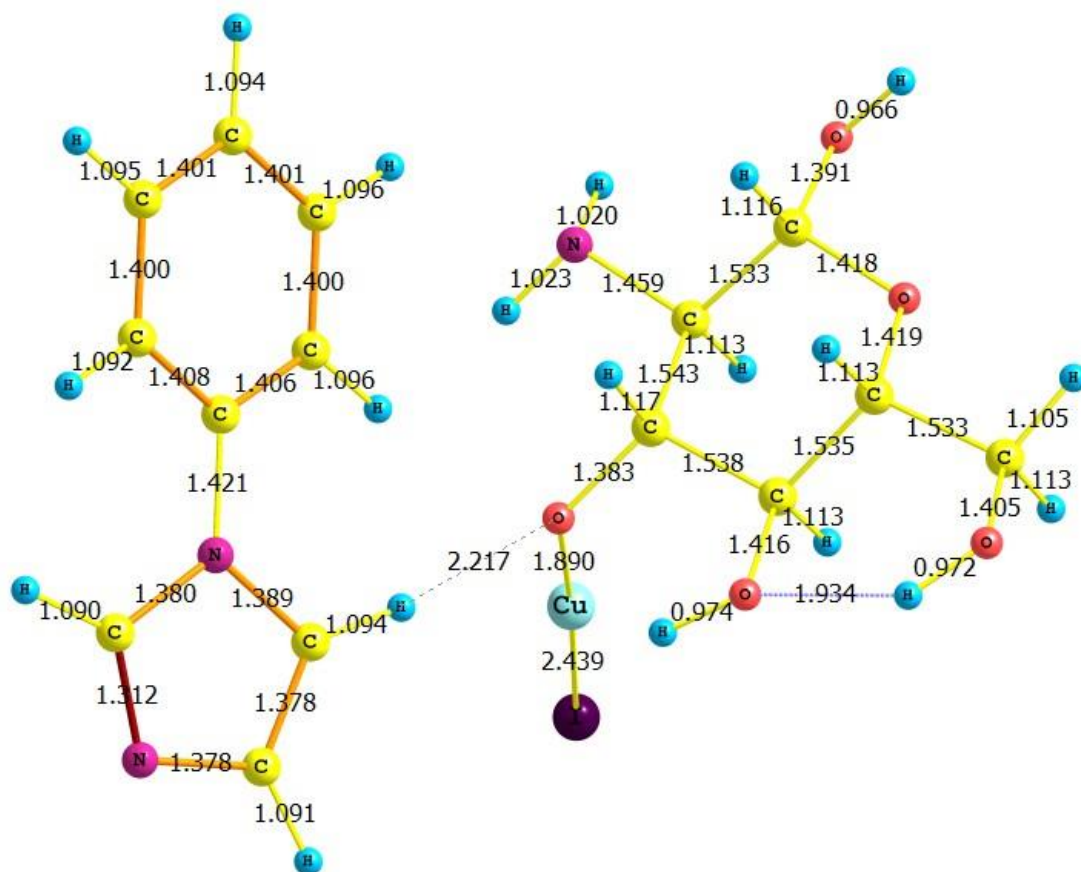
IM2d



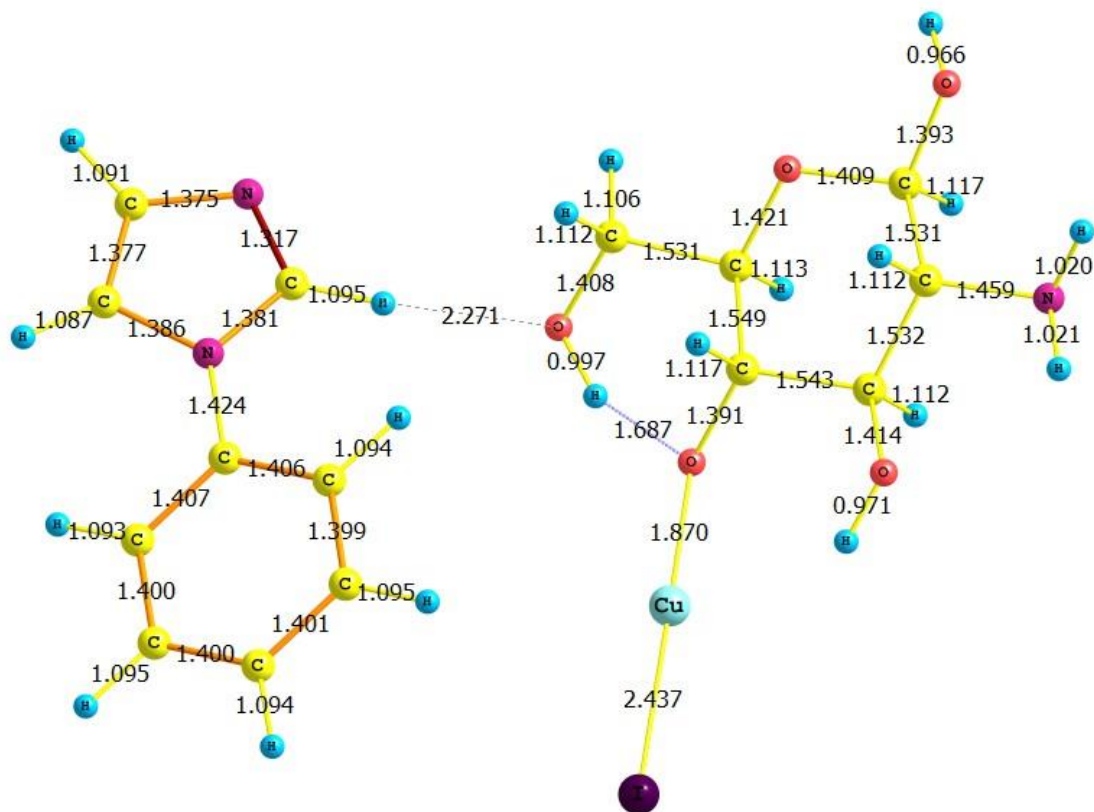
IM2e



IM3a

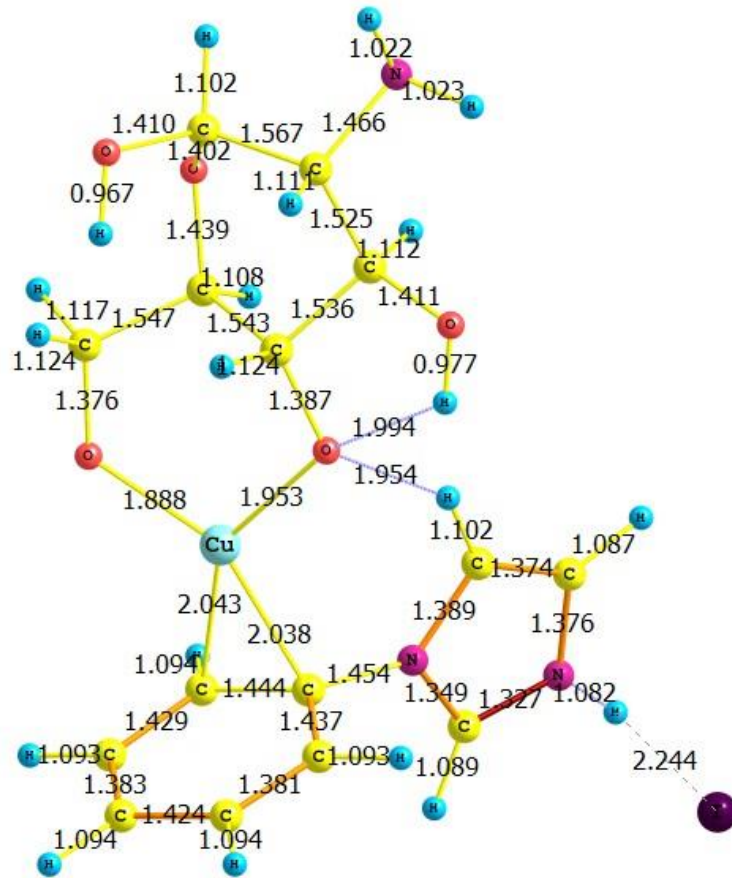


IM3b

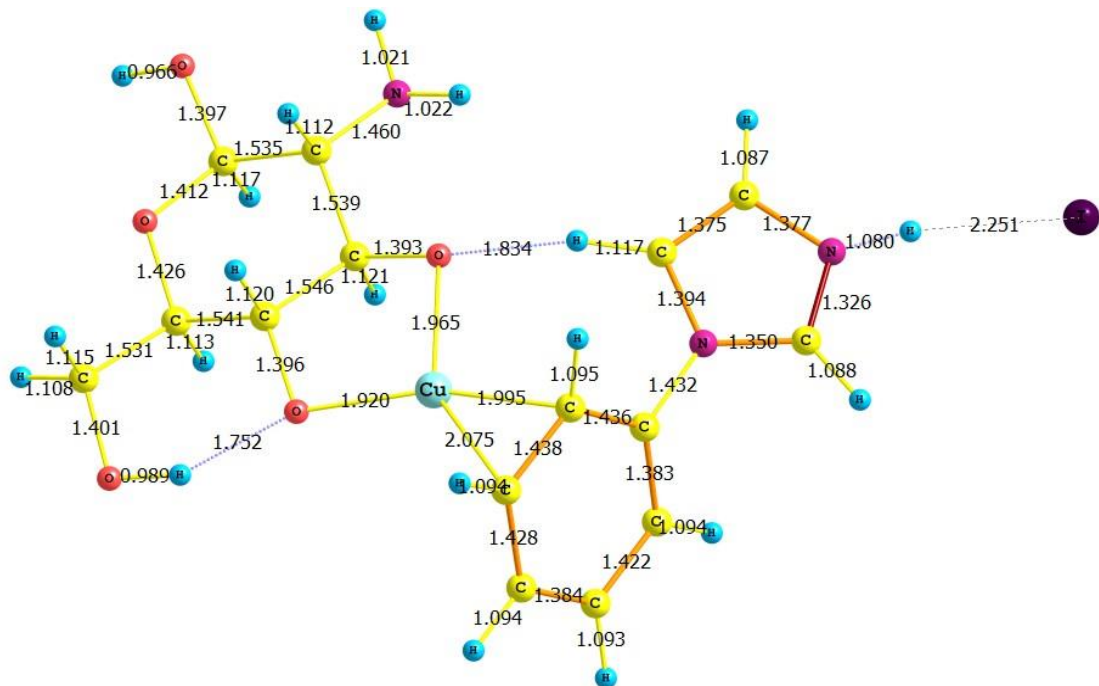


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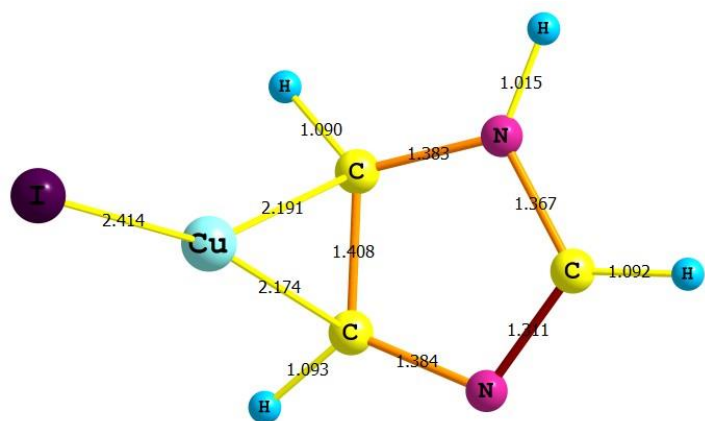




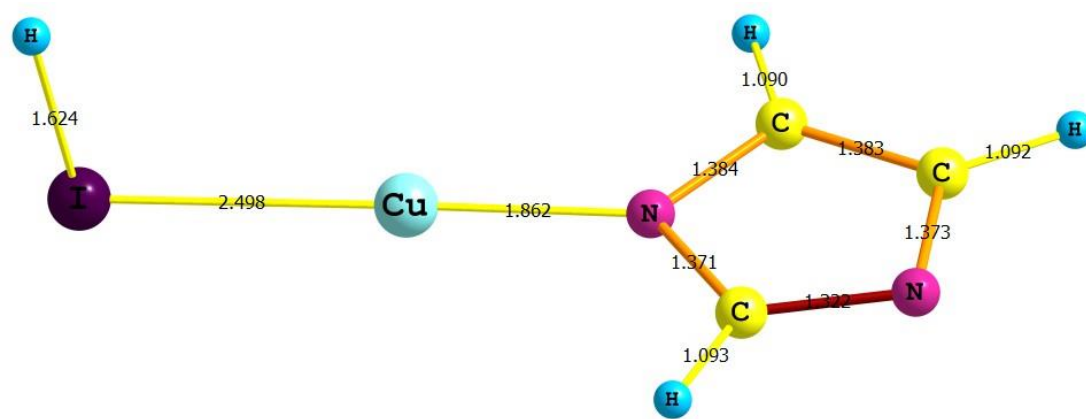
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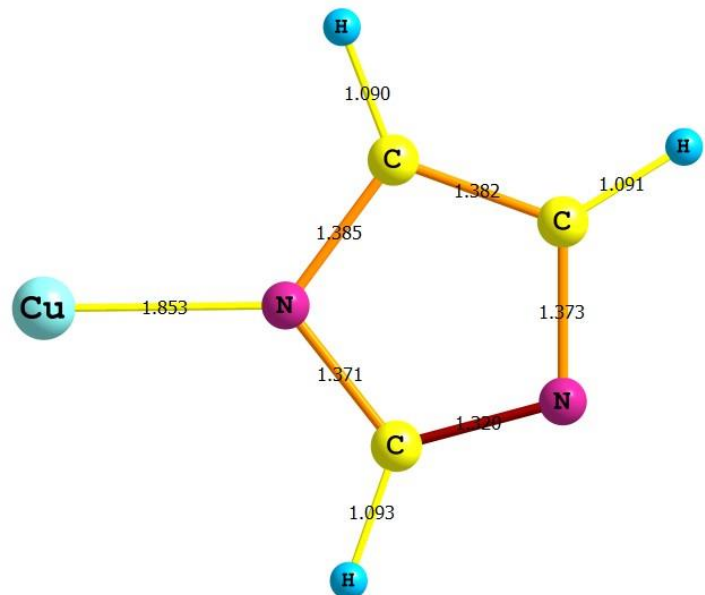
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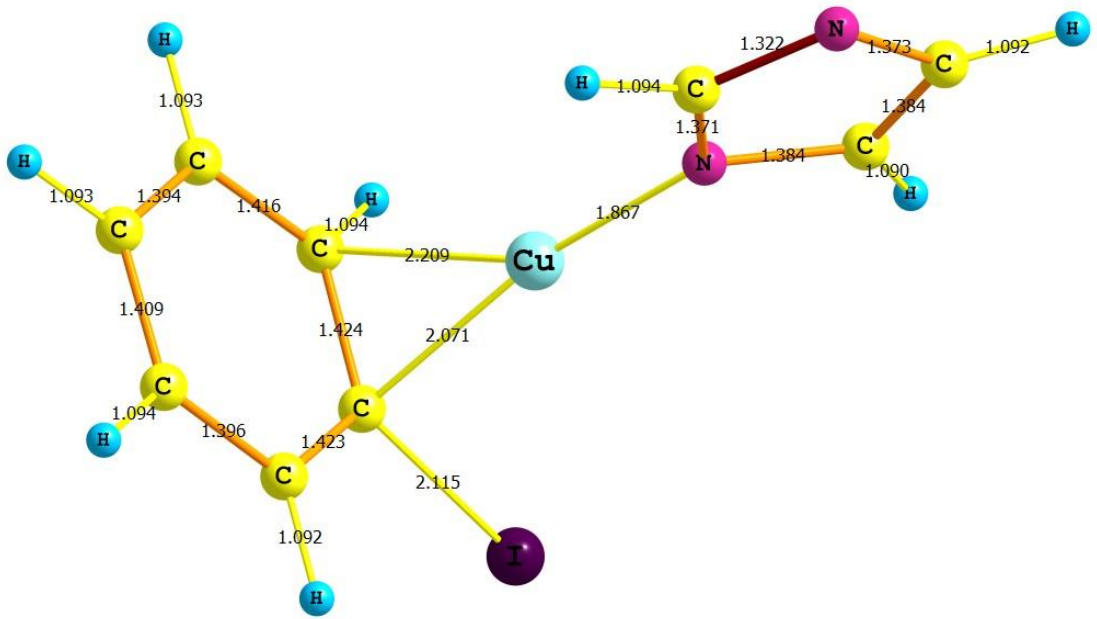
IM4



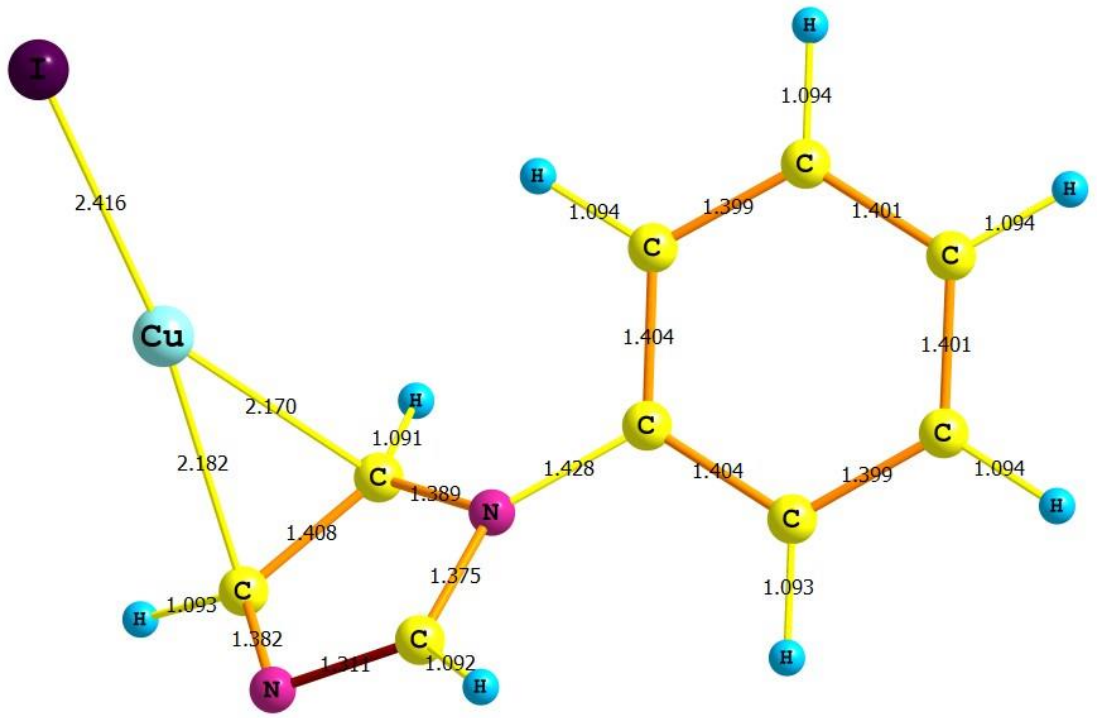
IM5



IM6

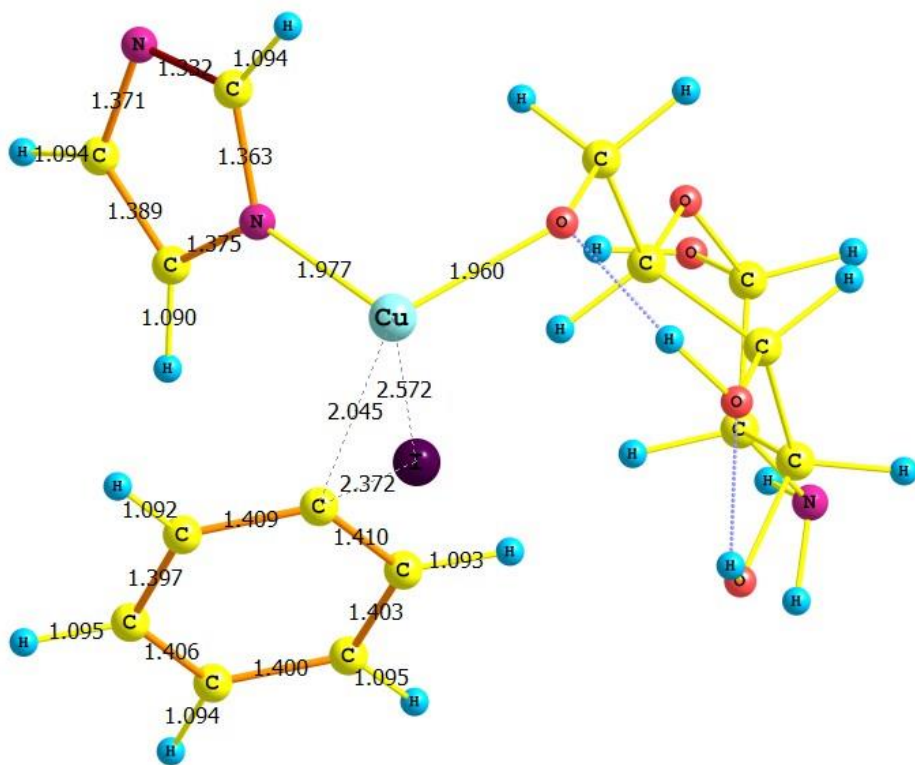


IM7

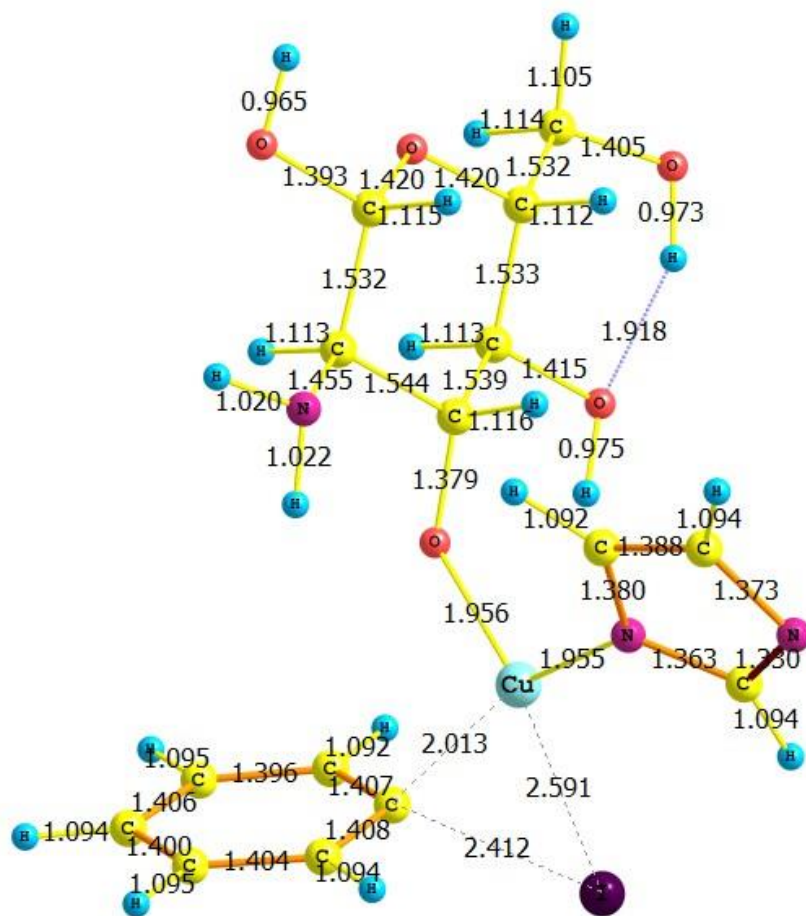


IM8

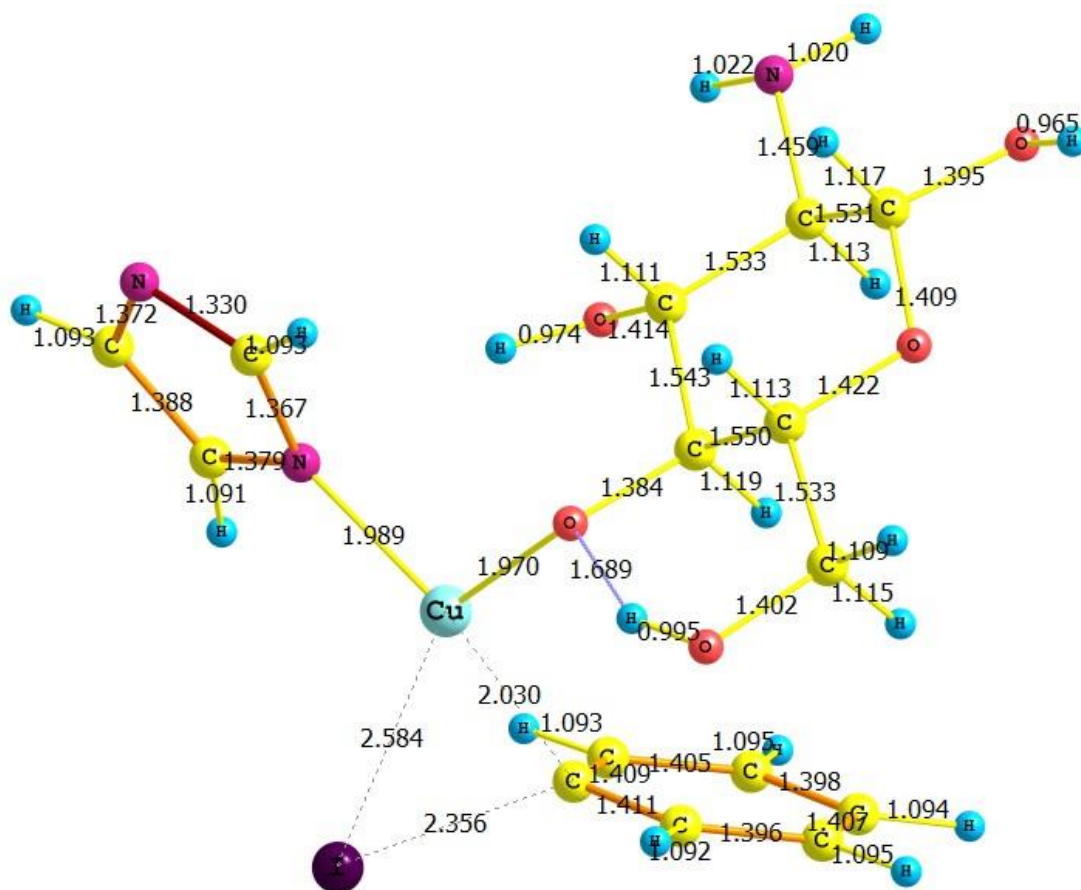




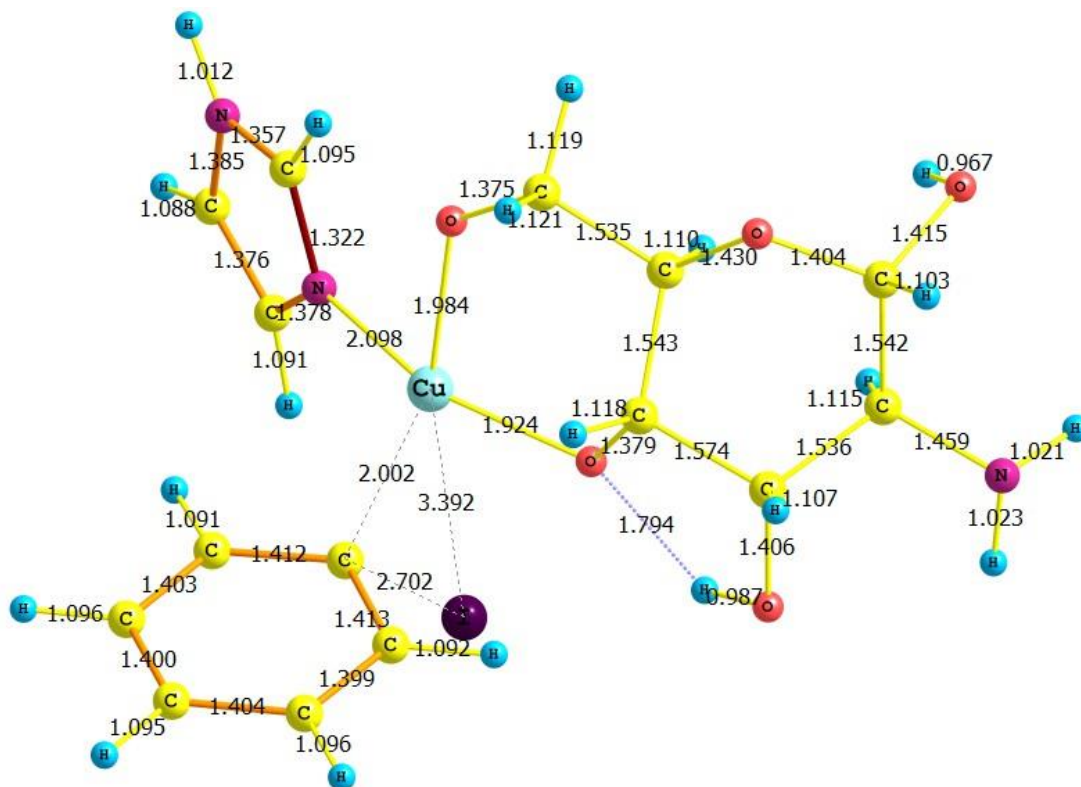
TS1/2a



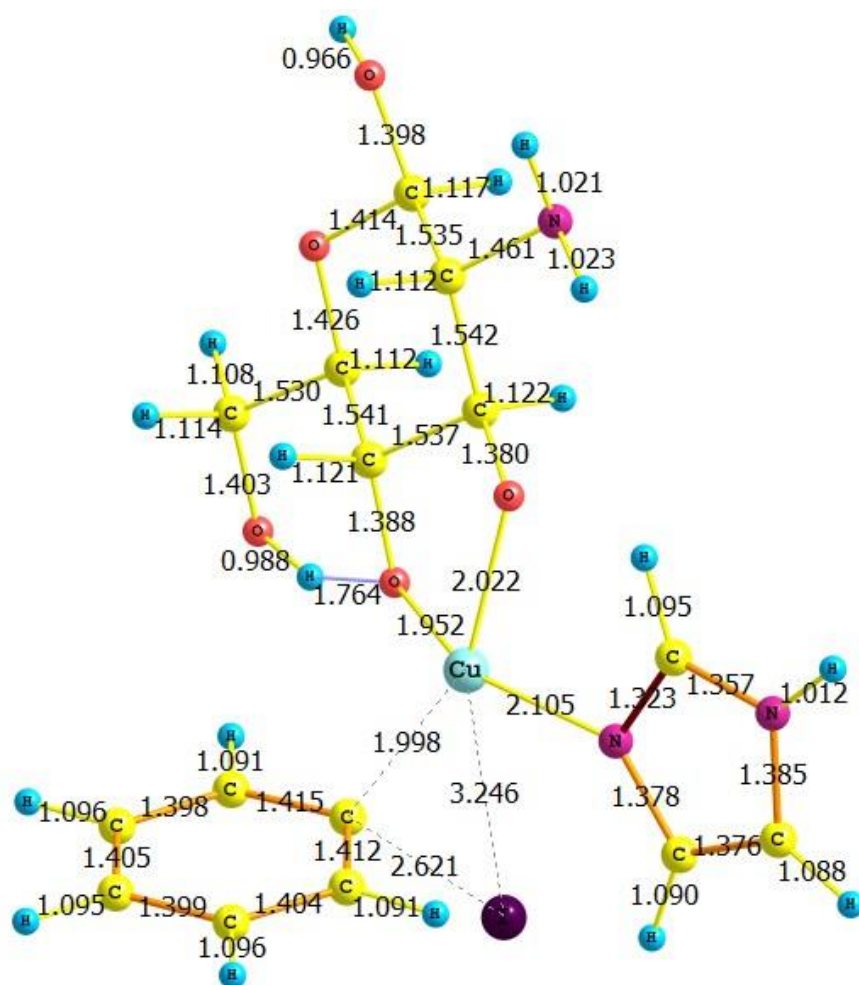
TS1/2b



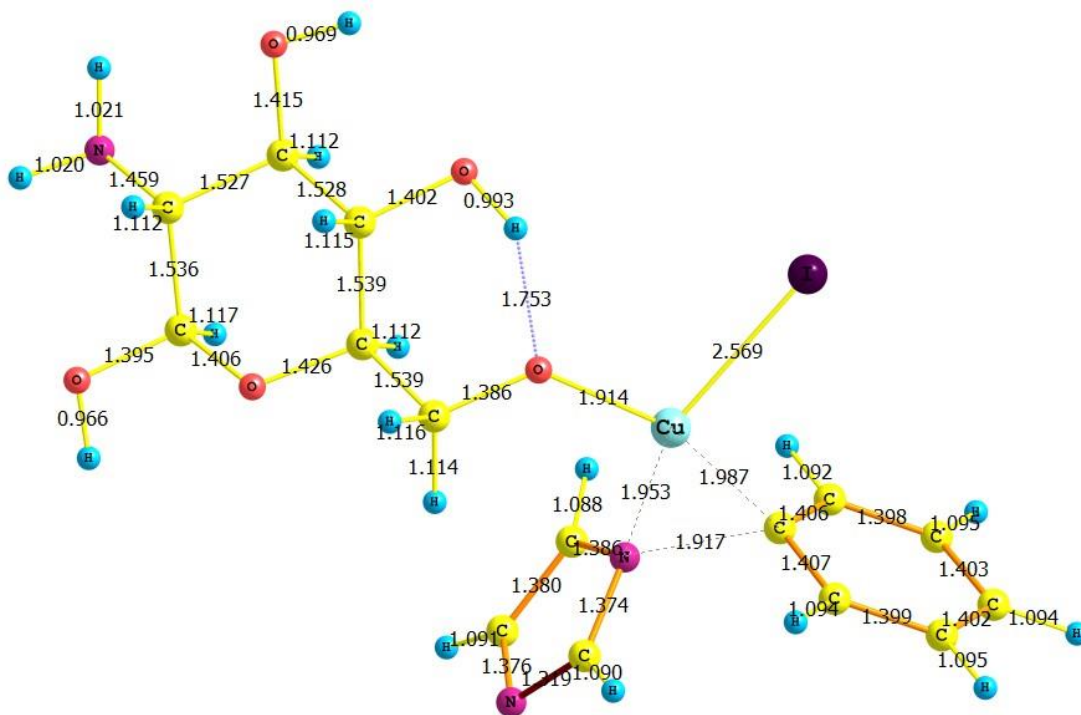
TS1/2c



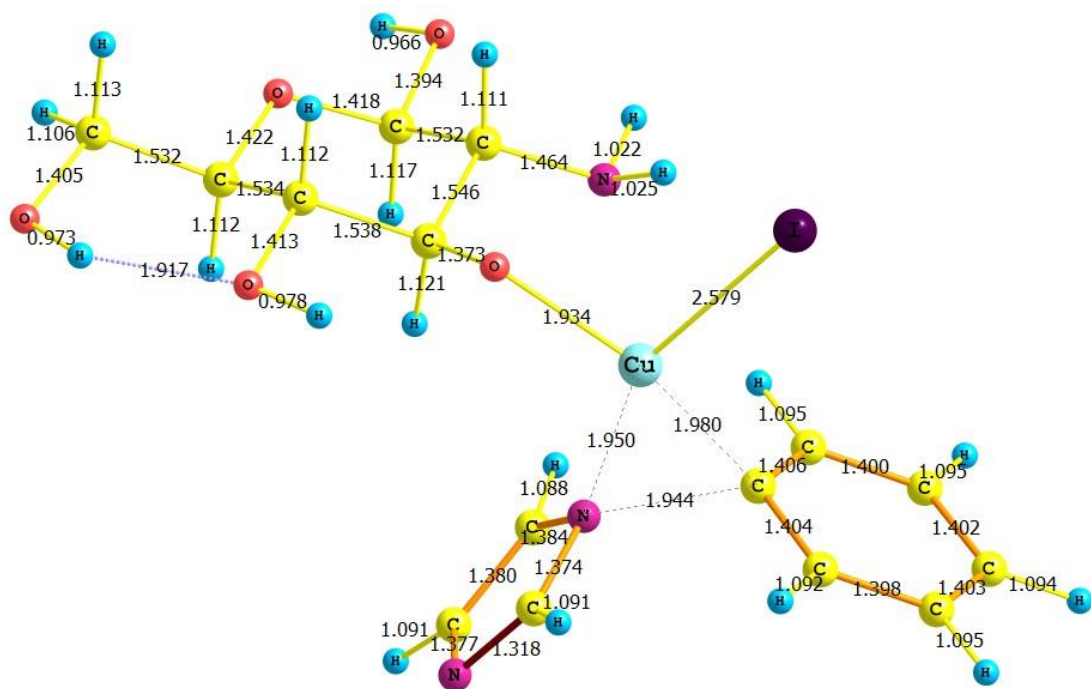
TS1/2d



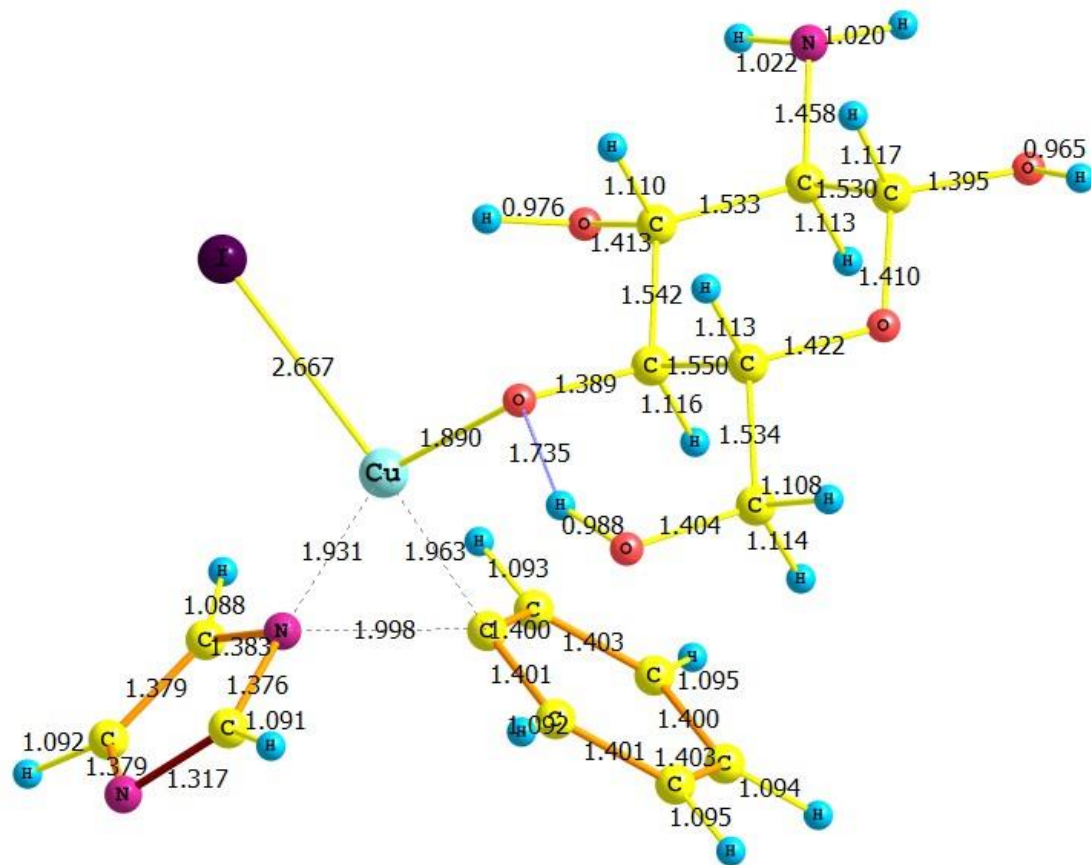
TS1/2e



TS2/3a



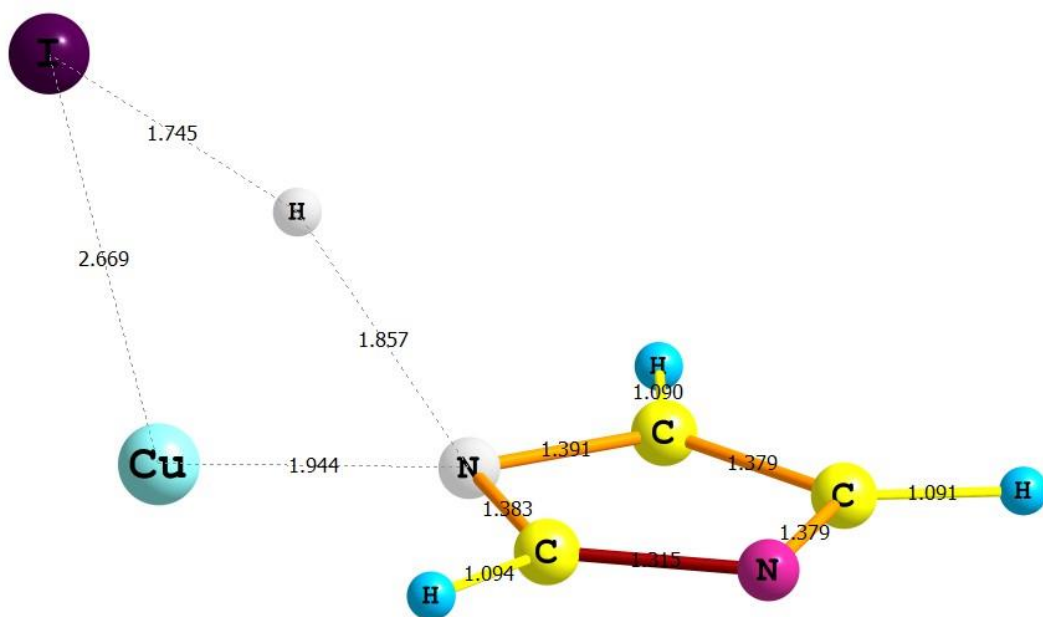
**TS2/3b**



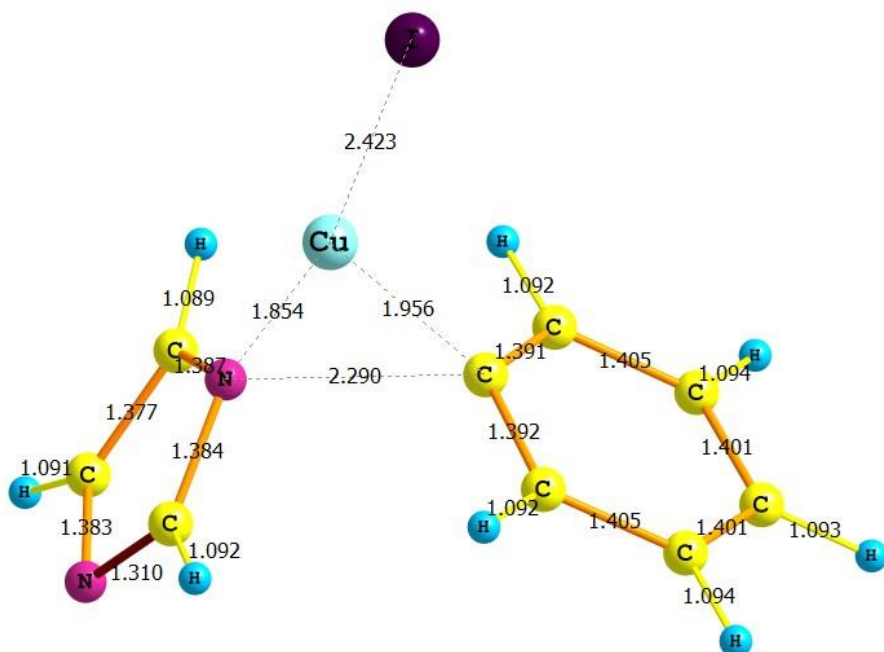
**TS2/3c**







TS4/5



TS7/8

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