Supporting Information

Synthesis, Characterization of New Chiral Cu(II)-N_4 Complexes and Their Application In The Asymmetric Aza-Henry Reaction

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Characterization data of aza-Henry product:

1. (*S*)-2-Nitro-1-phenyl-*N*-Tosylethanamine

White solid, Yield 75%; ee 76%; $[\alpha]_D^{20}$ = +34.56 (c 1.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm) δ = 7.65 (d, 2H, *J* = 8.0 Hz), 7.26-7.19 (m, 5H), 7.11-7.09 (d, 2H), 5.36-5.35 (d, 1H, *J*= 7.2 Hz), 4.97 (q, 1H, *J* = 6.6 Hz), 4.85 (dd,1H, *J*= 13, 6.4 Hz), 4.68 (dd, 1H, *J*= 13, 6.4 Hz), 2.3 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm) δ = 144.0, 136.4, 135.2, 129.7, 129.1, 127.1, 126.4, 78.9, 55.4, 21.5; HPLC (Chiralcel OD-H, hexane/2-propanol = 90/10, flow 0.80 mL/min, λ =240 nm) $t_{(major)}$ = 32.1 min and $t_{(minor)}$ = 45.6 min.

2. (*S*)-2-Nitro-1-(2'-methoxyphenyl)-*N*-Tosylethanamine

White solid, Yield 65%; ee 80%; $[\alpha]_D^{20}$ = +46.56 (c 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) δ = 7.81-7.80 (d,1H, *J* = 8.0 Hz), 7.55-7.54 (d, 2H, *J* = 8.0 Hz), 7.20-7.17 (m, 1H), 7.11-7.09 (d, 2H, *J* = 8.0 Hz), 6.93-6.92 (d, 1H, *J* = 7.5 Hz), 6.77-6.72 (m, 2H), 5.87-5.85 (d, 1H, *J* = 10 Hz), 5.12 (q, 1H, *J* = 7 Hz), 4.82-4.81 (dd, 1H, *J* = 12.5, 7.5 Hz), 4.65-4.64 (dd, 1H, *J* = 12.5, 6.5 Hz), 3.80 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ =

156.0, 143.1, 136.5, 129.8, 129.4, 129.0, 126.6, 122.2, 120.7, 110.5, 77.4, 55.1, 54.4, 21.1; HPLC (Chiralcel OD-H, hexane/2-propanol = 70/30, flow 0.60 mL/min, λ= 220 nm) $t_{(major)}$ = 22.2 min and $t_{(minor)}$ = 32.4 min.

3. (*S*)-2-Nitro-1-(4'-methoxyphenyl)-*N*-Tosylethanamine

White solid, Yield 68%; ee 78%; $[\alpha]_D^{20}$ = +26.52 (c 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ ppm) δ = 7.65 (d, 2H, *J* = 8.0 Hz), 7.25-7.23 (m, 2H), 7.00-6.98 (d, 2H, *J* = 8.5 Hz), 6.76-6.74 (m, 2H), 5.28-5.26 (d, 1H, *J* = 7.0 Hz), 4.91 (q, 1H, *J* = 6.5 Hz), 4.84 (dd, 1H, *J*= 13, 6.5 Hz), 4.66 (dd, 1H, *J* = 13, 6.5 Hz), 3.74 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ = 160.2, 144.2, 136.6, 129.9, 127.9, 127.4, 114.7, 79.1, 55.5, 55.1, 21.7; HPLC (Chiralcel OD-H, hexane/2-propanol = 85/15, flow 0.80 mL/min, λ= 220 nm) $t_{(major)}$ = 34.6 min and $t_{(minor)}$ = 38.6 min.

4. (*S*)-2-Nitro-1-(2-methylphenyl)-*N*-Tosylethanamine

White solid, Yield 58%; ee 82%; $[\alpha]_D^{20}$ = +42.25 (c 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ ppm) δ = 7.64 (d, 2H, *J* = 8.5 Hz), 7.24 (d, 2H, *J*= 8.0 Hz), 7.16-7.11 (m, 3H), 7.07 (d, 1H, *J* = 7.0 Hz), 5.23 (q, 1H, *J* = 6.5 Hz), 5.06-5.05 (d, 1H, *J* = 6.0 Hz), 4.89-4.88 (dd,1H, *J* = 13, 6.5 Hz), 4.70-4.69 (dd,1H, *J* = 13, 7.0 Hz), 2.40 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ = 145.8, 136.7, 135.48, 131.55, 130.8, 129.0, 128.8, 127.4, 80.3, 53.2, 23.3, 20.6; HPLC (Chiralcel AD-H, hexane/2-propanol = 90/10, flow 0.80 mL/min, λ= 230 nm) $t_{(major)}$ = 24.4 min and $t_{(minor)}$ = 29.4 min.

5. (*S*)-2-Nitro-1-(4-methylphenyl)-*N*-Tosylethanamine

White solid, Yield 56%; ee 75%; $[\alpha]_D^{20}$ = +16.24 (c 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ ppm) δ = 7.65 (d, 2H, *J* = 8.0 Hz), 7.25-7.23 (m, 2H), 7.06 (d, 2H, *J* = 8.0 Hz), 6.96 (d, 2H, *J* = 8.0 Hz), 5.25 (d, 1H, *J* = 7.0 Hz), 4.93 (q, 1H, *J* = 7.0 Hz), 4.85-4.83 (dd, 1H, *J* = 13, 6.5

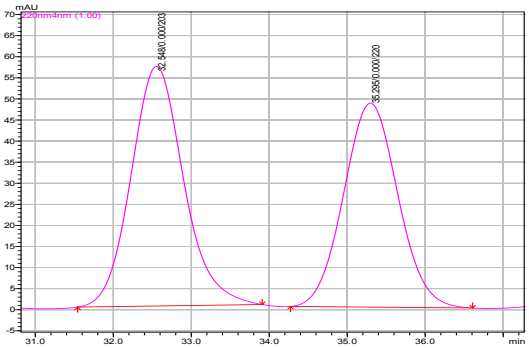
Hz), 4.67-4.66 (dd, 1H, *J* = 13, 6.5 Hz), 2.42 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ = 144.2, 139.3, 136.6, 132.5, 130.1, 129.9, 127.4, 126.5, 79.1, 55.3, 21.7, 21.2; HPLC (Chiralcel OD-H, hexane/2-propanol = 90/10, flow 1.0 mL/min, λ=220 nm) $t_{(major)}$ = 32.3 min and $t_{(minor)}$= 38.7 min.

6. (*S*)-2-Nitro-1-(2'-fluorophenyl)-*N*-Tosylethanamine

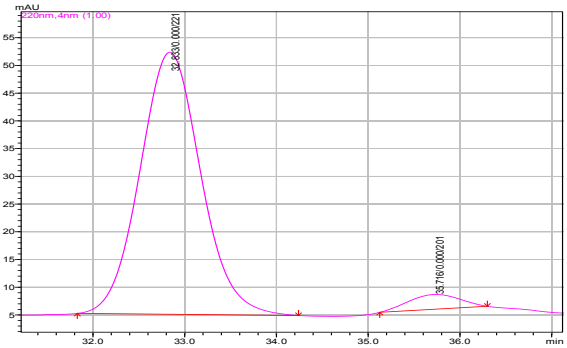
White solid, Yield 78%; ee 85%; $[\alpha]_D^{20}$ = +45.25 (c 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) δ = 7.61 (d, 2H, *J* = 8.5 Hz), 7.25 (m, 1H), 7.16 (d, 2H, *J* = 8.0 Hz), 7.12 (m, 1H), 7.00-6.91 (m, 1H), 5.77 (d, 1H, *J*= 9.5 Hz), 5.26 (q, 1H, *J*= 6.5 Hz), 4.80-4.77 (dd, 1H, *J*= 13.5, 7.5 Hz), 4.66-4.63 (dd, 1H, *J*= 13, 6.0 Hz), 2.35 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ = 159.5, 141.4, 136.5, 130.7, 129.6, 128.0, 128.2, 127.6, 127.0, 126.5, 124.7, 116.0, 115.9, 83.7, 51.5, 20.1; HPLC (Chiralcel OD-H, hexane/2-propanol = 90/10, flow 0.80 mL/min, λ=220 nm) $t_{(major)}$ = 24.4 min and $t_{(minor)}$= 28.4 min.

7. (*S*)-2-Nitro-1-(4'-fluorophenyl)-*N*-Tosylethanamine

White solid, Yield 75%; ee 90%; $[\alpha]_D^{20}$ = +20.22 (c 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) δ = 7.81 (d, 1H, *J* = 8.5 Hz), 7.63 (d, 2H, *J*= 8.5 Hz), 7.24 (d, 2H, *J*= 8.5 Hz), 7.08-7.06 (m, 2H), 6.95-6.91 (m, 2H), 5.49 (d, 1H, *J* = 7.0 Hz), 5.1 (q, 1H, *J*= 7.0 Hz), 4.80-4.79 (dd, 1H, *J* = 13, 6.5 Hz), 4.64-4.63 (dd, 1H, *J* = 13, 6.0 Hz), 2.40 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ = 163.1, 146.0, 138.2, 131.6, 130.2 (d, *J*= 3.3 Hz), 129.0, 128.3, 118.1 (d, *J* = 8.7 Hz), 80.7, 56.6, 23.4; HPLC (Chiralcel IC, hexane/2-propanol = 80/20, flow 0.70 mL/min, λ = 220 nm) $t_{(major)}$ = 32.8 min and $t_{(minor)}$ = 36.7 min.



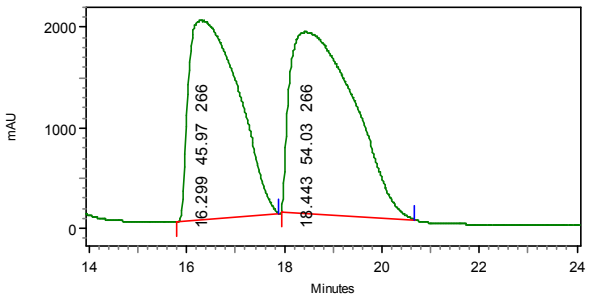
Racemic



Chiral

8. (*S*)-2-Nitro-(1-naphtyl)-*N*-Tosylethanamine

White solid, Yield 62%; ee 65 %; $[\alpha]_D^{20}$ = +24.24 (c 1.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ ppm) δ = 7.81 (d, 1H, *J* = 8.0 Hz), 7.75 (d, 2H, *J* = 8.0 Hz), 7.54 (d, 2H, *J* = 8.0 Hz), 7.50-7.44 (m, 2H), 7.35-7.29 (m, 2H), 7.06 (d, 2H, *J*= 8.0 Hz), 5.87-5.82 (q, 1H, *J* = 6.5 Hz), 5.75 (d, 1H, *J*= 7.5 Hz), 4.97-4.96 (dd, 1H, *J*= 13.0, 7.5 Hz), 4.86-4.85 (dd, 1H, *J*= 13.0, 6.0 Hz), 2.31 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ = 143.8, 136.1, 133.8, 130.7, 129.8, 129.7, 129.5, 129.2, 127.2, 127.1, 126.2, 125.1, 124.5, 121.5, 78.6, 51.7, 21.4; HPLC (Chiralcel OD-H, hexane/2-propanol = 80/20, flow 1.0 mL/min, λ =240 nm) $t_{(minor)}$ = 16.8 min and $t_{(major)}$ = 19.0 min.



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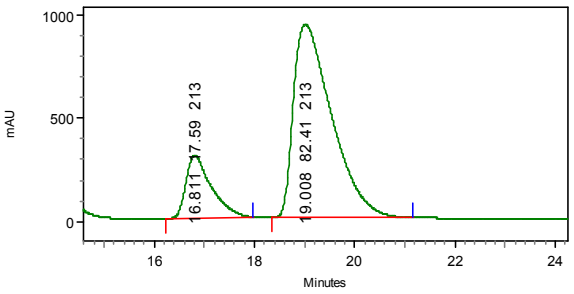
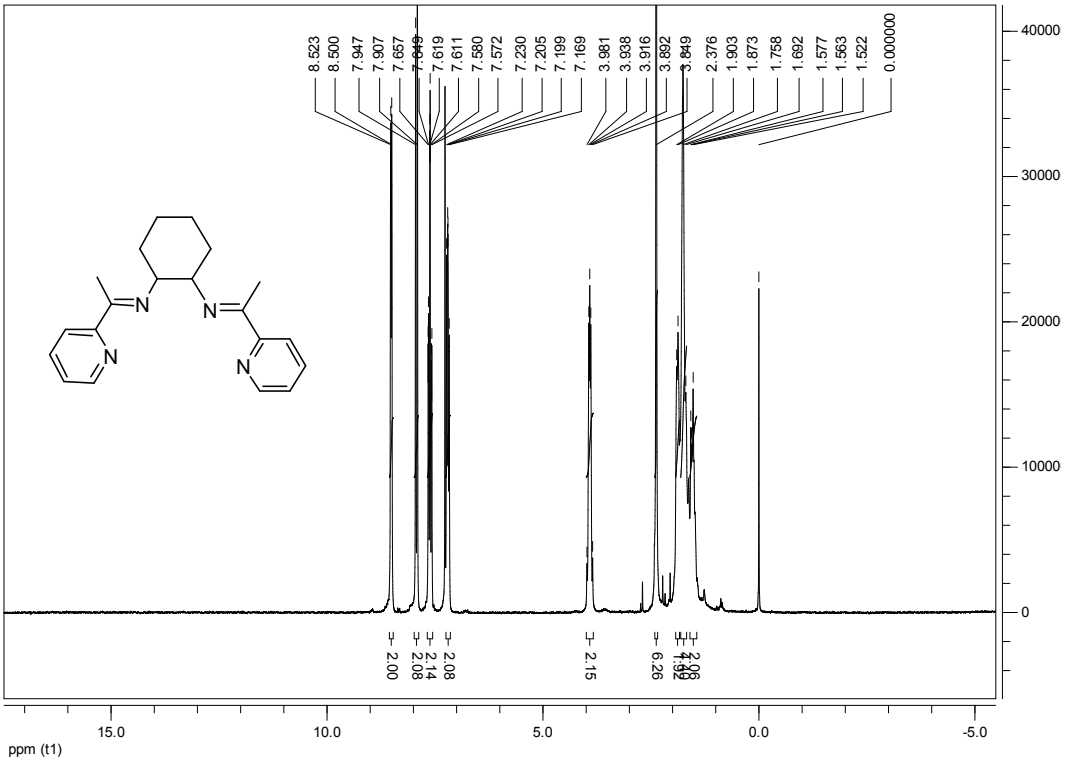
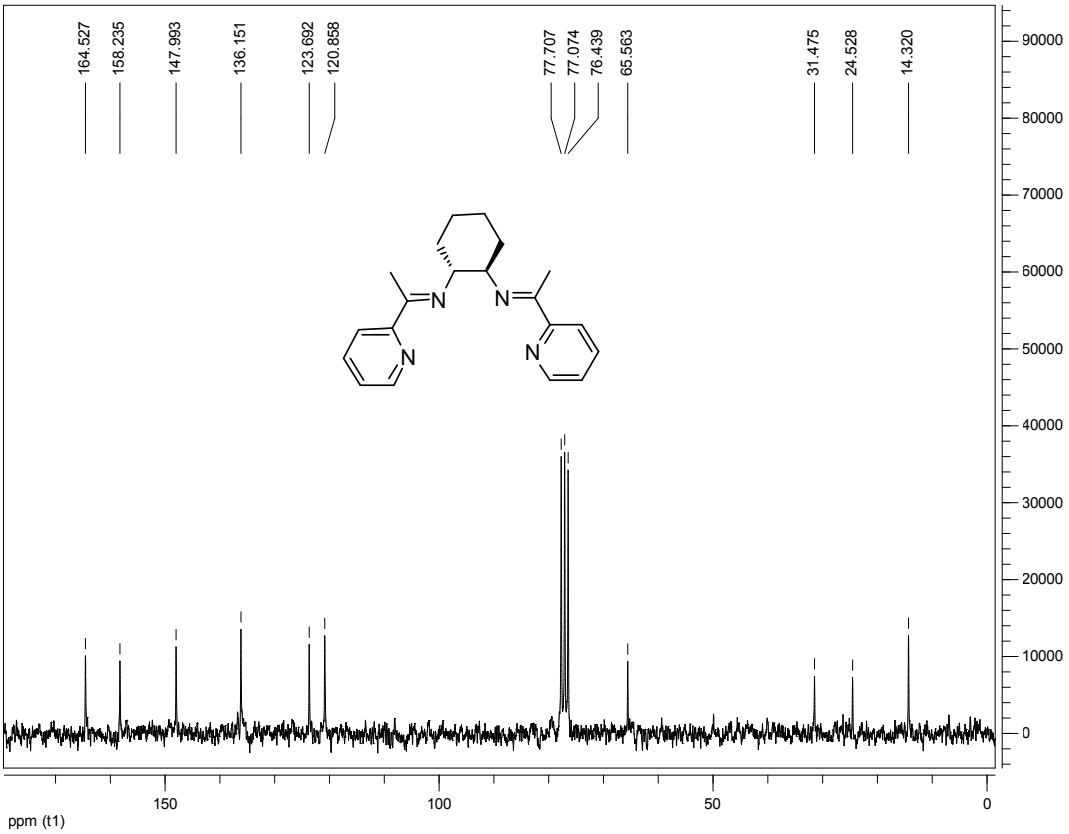


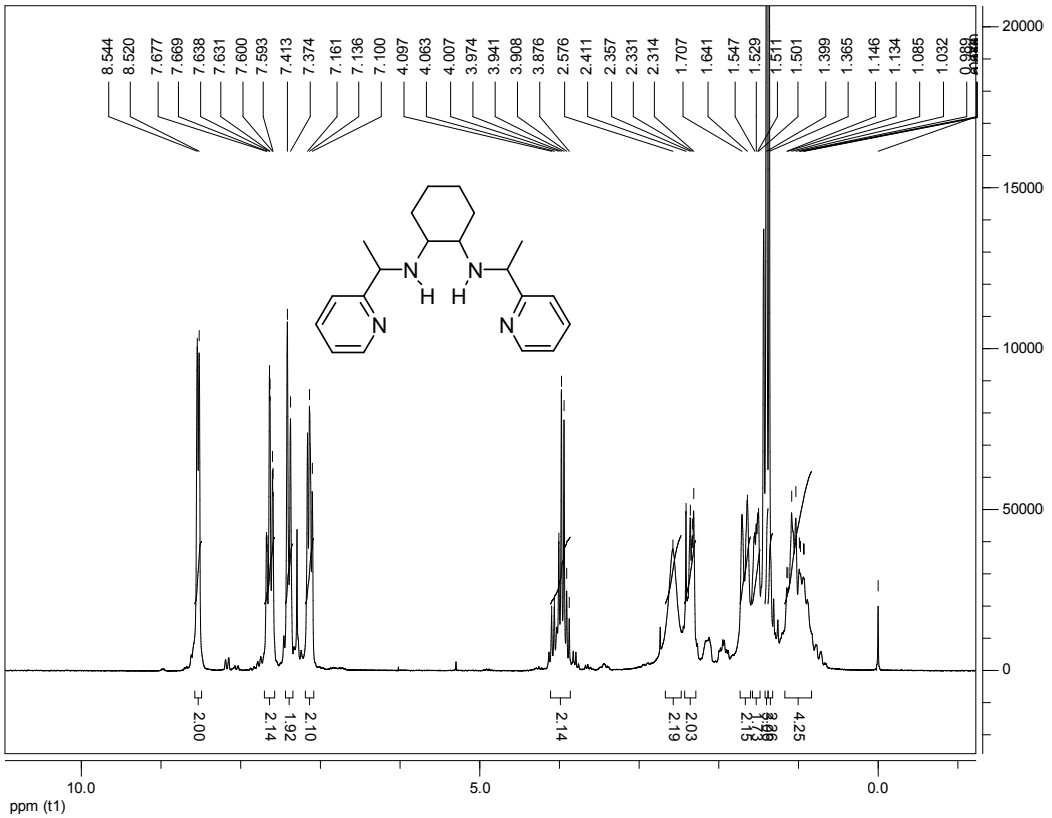
Chiral

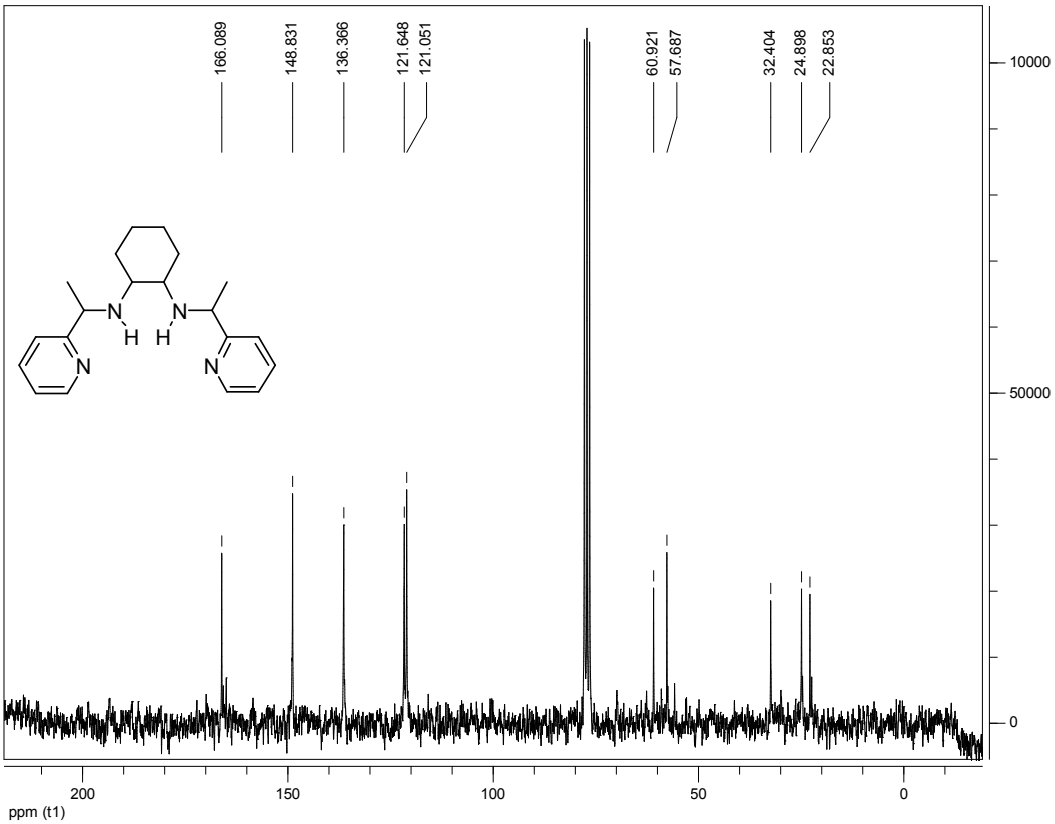
^{1}H & ^{13}C-NMR spectra of ligands **1**

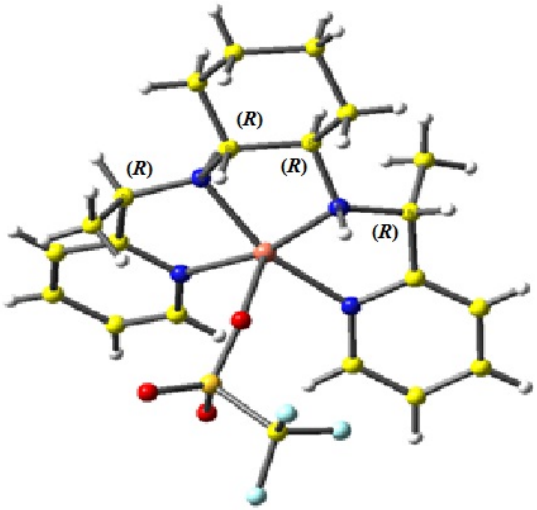




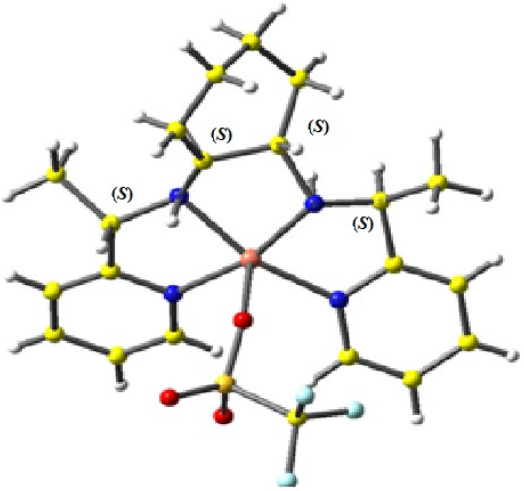
^{1}H & ^{13}C-NMR spectra of ligands **2**







Complex **Cu(II)-2**



Complex **Cu(II)-4**