Supporting Information

BINOL-Salen Metal Catalysts Incorporating a Bifunctional Design

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General. Unless otherwise noted, all non-aqueous reactions were carried out under an atmosphere of dry N_2 in dried glassware. When necessary, solvents and reagents were dried prior to use. Toluene and CH_2Cl_2 were de-oxygenated by purging with N_2 and then dried by passing through activated alumina. CH_3CN and EtOH were distilled from CaH_2. DMF was distilled from $MgSO_4$. TMEDA was distilled from Na. THF used in the catalytic Michael reactions was distilled from Na/benzophenone ketyl. $Ni(OAc)_2{\cdot}4H_2O$, $Cu(OAc)_2$ and $Pd(OAc)_2$, were purchased from Strem and were used without further purification. Cyclohexenone and benzyl malonate were purchased from Aldrich and cyclohexenone was distilled prior to use. $ZnEt_2$ was used as a freshly prepared 1M solution in toluene. NaO^tBu, KO^tBu, LiO^tBu and Cs_2CO_3 were dried with gentle heating on a high vacuum and stored in the glove box. All salen complexes were dried thoroughly with gentle heating on a high vacuum for several hours prior to use. 2,2'-Bis(methoxymethyloxy)-1,1'-binaphthalene-3-carboxyaldehyde,[1] 2'-methoxy-1,1'-binaphthyl-2-ol (**28**),[2] (-)-*(1R,2R)*-cyclohexanediamine and (+)-*(1S,2S)*-cyclohexanediamine were prepared according to established procedures.[3]

Analytical thin layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica-gel 60-F plates. Preparative thin layer chromatography was performed on EM Reagents 1.00 mm silica-gel plates. Visualization was accomplished with UV light. Chromatography on silica gel was performed using a forced flow of the indicated solvent system on EM Reagents Silica Gel 60 (230-400 mesh).[4] Analytical high performance liquid chromatography (HPLC) was performed on a Waters 600 HPLC with UV detection at 254 nm. Analytical Chiralpak AD and Chiralpak AS columns (0.46 cm X 25 cm) from Daicel were used. ^{1}H NMR spectra were recorded on Bruker AM-500 (500 MHz), AM-250 (250 MHz), or AM-200 (200 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane (0 ppm) or from the solvent resonance ($CDCl_3$ 7.26 ppm, DMSO-d_6 2.49 ppm, D_2O 4.80 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants, and number of protons. Mass spectra were obtained on a low resonance Micromass Platform LC in electron spray mode and high resonance VG autospec with an ionization mode of either CI or ES. IR spectra were taken on a Perkin-Elmer FT-IR spectrometer using a thin film on NaCl plates. Melting points were obtained on Thomas Scientific Unimelt apparatus and are uncorrected. Optical rotations were measured on a

Perkin-Elmer Polarimeter 341 with a sodium lamp and are reported as follows $[\alpha]^{T}_{\lambda}$, (c = g/100 mL, solvent).

(-)-*(S)*-1,1'-Binaphthalene-3-carboxyaldehyde. Concentrated HCl (44 mL of a 12M soln) was added dropwise to a solution of (-)-(*S*)-2,2'-bis(methoxymethyloxy)-1,1'-binaphthalene-3-carboxyaldehyde (4.0 g, 9.94 mmol) in THF cooled to 0 °C. After stirring for 3 h at rt, the solution was extracted with EtOAc, washed with water, saturated $NaHCO_3$, and brine. After drying over Na_2SO_4 and removal of solvent the diol was obtained in quantitative yield (3.12 g, 9.94 mmol) as a yellow solid: mp 208-210 °C; $[\alpha]^{20}_{D}$ -58 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.63 (br s, 1H), 10.19 (s, 1H), 8.36 (s, 1H), 8.02 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.82 (d, *J* = 8.14 Hz, 1H), 7.4-7.15 (m, 11 Hz), 7.1 (d, *J* = Hz, 1H), 4.9 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4 (C=O), 139.1, 137.0, 133.3, 131.2, 130.5, 130.0, 129.3, 128.3, 127.8, 126.7, 125.1, 124.9, 124.4, 123.5, 122.2, 117.7; IR (film) 3417 (br), 2357, 1651 (C=O), 1504, 1386, 1338, cm^{-1}.

(-)-*(S,S)*-Ethylenediamine-BINOL-salen (9). (-)-*(S)*-1,1'-Binaphthalene-3-carboxyaldehyde (300 mg, 0.954 mmol) was dissolved completely in EtOH (4 mL) with heating. The yellow solution was then allowed to cool to rt and ethylenediamine (32 µL, 0.477 mmol) was added dropwise. During this addition, the product precipitated out of solution. The pale orange slurry was then allowed to stir at rt for at least 24 h or with intermittent heating and cooling for approximately 12 h. The precipitate was collected by filtration, washed with cold EtOH, and dried with gentle heating *in vacuo* to provide **9** in 88% yield (275 mg, 0.421 mmol) as a pale orange powder: mp 183-186 °C; $[\alpha]^{20}_{D}$ -95 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.3 (br s, 2H), 8.59 (s, 2H, HC=N), 7.85 (m, 8H), 7.4-7.0 (m, 14H), 5.05 (br s, 2H), 3.95 (m, 4H, H_2C-N); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7 (C=N), 155.4, 151.5, 135.3, 134.7, 133.5, 130.0, 129.2, 129.0, 128.9, 128.2, 127.6, 126.4, 124.7, 124.6, 123.9, 123.2, 120.6, 117.7, 59.4 (C-N); IR (film) 3423 (br), 2358, 1647 (C=N), 1506, 1339 cm^{-1}; MS (ES) *m/z* 653 (MH^+), 675 (MNa^+), 676 ($MHNa^+$).

(-)-*(S,S)*-Diaminobenzene-BINOL-salen (10). (-)-*(S)*-1,1'-Binaphthalene-3-carboxyaldehyde (300 mg, 0.954 mmol) was dissolved completely in EtOH (4 mL) with heating. The yellow solution was then allowed to cool to rt and 1,2-diaminobenzene (51.6 mg, 0.477 mmol) was added. The dark red solution was allowed to stir at rt for 24 h which caused the continuous formation of a yellow precipitate. The precipitate was collected by filtration, washed with cold EtOH, and dried with gentle heating *in vacuo* to provide **10** in 93% yield (210 mg, 0.443 mmol) as a bright yellow powder: mp 196-200 °C; $[\alpha]^{20}_{D}$ -118 (*c* 0.5, THF); ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.95 (br s, 2H), 8.88 (s, 2H, HC=N), 7.80 (d, *J* = 8.5 Hz, 6H), 7.36-7.32 (m, 6H), 7.28-7.24 (m, 5H), 7.17-7.01 (m, 7H), 5.49 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6 (C=N), 155.8, 151.6, 141.6, 136.0, 135.9, 133.5, 129.9, 129.4, 129.3, 129.2, 128.1, 127.9, 126.3, 125.0, 124.8, 124.0, 123.2, 121.1, 121.0, 119.6, 114.7, 114.5; IR (film) 3386 (br), 3054, 2358, 1618 (C=N), 1506, 1343 cm^{-1}; MS (ES) *m/z* 701 (MH^+), 741 ($M{\cdot}CH_3CN^+$).

(-)-*(S,S,S,S)*-Diaminocyclohexane-BINOL-salen (11). (-)-(*S*)-1,1'-Binaphthalene-3-carboxy-aldehyde (400 mg, 1.273 mmol) was dissolved completely in EtOH (5 mL) with heating. The yellow solution was then allowed to cool to rt and (+)-(*1S,2S*)-diaminocyclohexane (76 µL, 0.636 mmol) was added dropwise. During this addition, the product precipitated out of solution. The orange slurry

was then allowed to stir at rt for 24 h. The precipitate was collected by filtration, washed with cold EtOH and dried with gentle heating *in vacuo* to provide **11** in 85% yield (380 mg, 0.538 mmol) as a pink-orange powder: mp 193-196 °C; $[\alpha]_D^{20}$ +270 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.52 (br s, 2H), 8.52 (s, 2H, HC=N), 7.97 (d, *J* = 8.9 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.87 (s, 2H), 7.81 (d, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 2H), 7.36-7.29 (m, 6H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), *5*.11 (br s, 2H), 3.38 (d, *J* = 8.9 Hz, 2H) (HC-N), 2.0 (d, *J* = 13.4 Hz, 2H), 1.9 (d, *J* = 9.3 Hz, 2H), 1.74 (d, *J* = 9.3 Hz, 2H), 1.47 (t, *J* = 10.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3 (C=N), 155.9, 151.8, 135.6, 135.0, 133.9, 130.5, 129.7, 129.6, 129.5, 128.7, 128.1, 126.9, 125.1, 125.0, 124.3, 123.7, 121.0, 118.1, 114.8, 113.7, 73.3 (C-N), 33.2, 24.4; IR (film) 3507 (br), 3423 (br), 3057, 2933, 2859, 1631 (C=N), 1510, 1344 cm^{-1}; MS (ES) *m/z* 729 (MNa^+); HRMS (ES) calcd *m/z* 707.290983 ($C_{48}H_{39}N_2O_4$, MH^+), found *m/z* 707.290854.

(-)-*(S,R,R,S)*-Diaminocyclohexane-BINOL-salen (12). Diastereomer **12** was prepared similarly to **11** using (-)-(*1R, 2R)*-diaminocyclohexane in 89% yield: mp 185-188 °C; $[\alpha]_D^{20}$ -342 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.43 (br s, 2H), 8.56 (s, 2H, C=N), 7.90 (m, 8H), 7.37-7.10 (m, 14H), 5.05 (br s, 2H), 3.36 (m, 2H) (CH-N), 2.0-1.43 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0 (C=N), 155.5, 151.5, 135.3, 134.7, 133.5, 130.0, 129.3, 129.2, 129.0, 128.2, 127.8, 126.5, 124.8, 124.6, 123.9, 123.3, 120.6, 117.7, 114.4, 113.4, 72.2 (C-N), 32.7, 24.1; IR (film) 3414 (br), 3055, 2931, 2858, 1628 (C=N), 1506, 1344 cm^{-1}; MS (ES) *m/z* 729 (MNa^+), 747 ($M{\cdot}CH_3CN^+$); HRMS (ES) calcd *m/z* 707.2910 ($C_{48}H_{39}N_2O_4$, MH^+), found *m/z* 707.2913.

(-)-*(S,S)-cis*-Diaminocyclohexane-BINOL-salen (13). Diastereomer **13**, a pale orange powder, was prepared similarly to **11** using *cis*-diaminocyclohexane in 92% yield: mp 192-196 °C; $[\alpha]_D^{20}$ -72 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.58 (br s, 1H), 13.26 (br s, 1H) 8.61 (s, 1H), 8.58 (s, 1H), 7.96 (s, 1H), 7.87-7.79 (m, 5H), 7.72 (br s, 1H), 7.31-7.26 (m, 7H), 7.11-7.04 (m, 5H), 5.27 (br s, 1H), 5.15 (br s, 1H) 3.78 (br s, 2H), 1.97 (m, 2H), 1.81 (m, 4H), 1.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8 (C=N), 164.5 C=N), 156.0, 152.8, 135.3, 135.2, 133.9, 133.8, 130.3, 130.2, 129.7, 129.6, 129.5, 129.4, 129.35, 129.3, 129.2, 128.6, 128.5, 128.2, 126.75, 126.7, 125.5, 125.24, 125.2, 124.2, 124.0, 123.6, 123.5, 121.3, 118.3, 118.2, 115.0, 114.8, 114.1, 113.9, 69.7, 69.4, 58.9, 31.3, 18.8; IR (film) 3382 (br), 3056, 2935, 2859, 1631 (C=N), 1511, 1346 cm^{-1}; MS (ES) *m/z* 729 (MNa^+), 747 ($M{\cdot}CH_3CN^+$); HRMS (ES) calcd *m/z* 707.2910 ($C_{48}H_{39}N_2O_4$, MH^+), found *m/z* 707.2910.

(-)-*(S,R,R,S)*-Diphenylethylenediamine-BINOL-salen (14). (-)-(*S)*-1,1'-Binaphthalene-3-carboxy-aldehyde (300 mg, 0.955 mmol) was dissolved completely in EtOH (5 mL) with heating and (+)-(*1R,2R*)-diphenylethylenediamine (101 mg, 0.477 mmol) was added at once to the warm yellow solution. During this addition, a yellow-orange precipitate was formed. The slurry was then allowed to stir at rt for 24 h. The precipitate was collected by filtration, washed with cold EtOH and dried with gentle heating *in vacuo* to provide **14** in 93% yield (357 mg, 0.444 mmol) as a pale-orange powder: mp 204-206 °C; $[\alpha]_D^{20}$ -222 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.28 (br s, 2H), 8.71 (s, 2H, HC=N), 7.97 (s, 2H), 7.87 (t, *J* = 9 Hz, 6H), 7.33-7.05 (m, 24H), 2H), *5*.14 (br s, 2H), 4.78 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7 (C=N), 155.5, 151.9, 139.0, 136.0, 135.7, 133.9, 132.2, 130.4, 129.7, 129.68, 129.6, 128.9, 128.6, 128.4, 128.3, 126.9, 125.3, 125.2, 124.4, 123.7, 121.0, 118.2, 114.7, 114.2, 80.8

(C-N); IR (film) 3530 (br), 3058, 2868, 1628 (C=N), 1511, 1346 cm^{-1}; MS (ES) *m/z* 827 (MNa^+); HRMS (ES) calcd *m/z* 827.2886 ($C_{56}H_{40}N_2O_4Na$, MNa+), found *m/z* 827.2908.

(-)-*(S,S)*-Ni(II)-Ethylenediamine-BINOL-salen (15). Two methods could be used interchangeably.

Method A: BINOL-salen **9** (100 mg, 0.153 mmol) and $Ni(OAc)_2{\cdot}4H_2O$ (27 mg, 0.153 mmol) were combined in a flask with EtOH (3 mL). After heating at reflux for 1 h, the dark yellow slurry became dark orange. The mixture was allowed to cool slowly to rt and then stored at 0 °C for 1 h. The fine red precipitate was collected by vacuum filtration, washed with cold EtOH and dried *in vacuo* with gentle heating for several hours to provide **15** in 65% yield (70 mg, 0.099 mmol) as a red solid.

Method B: (-)-*(S)*-1,1'-Binaphthalene-3-carboxyaldehyde (105 mg, 0.33 mmol) was dissolved completely in EtOH (3 mL) with heating. The yellow solution was then allowed to cool to rt and ethylenediamine (11 µL, 0.17 mmol) was added dropwise. During this addition, the product precipitated out of solution. The pale orange slurry was then allowed to stir at rt for 24 h. $Ni(OAc)_2{\cdot}4H_2O$ (31 mg, 0.17 mmol) was added and the slurry was heated at reflux for 2 h then allowed to cool slowly to rt and stored at 0 °C for 1 h. The fine red precipitate was collected by vacuum filtration and washed with cold EtOH then dried *in vacuo* with gentle heating for several hours to provide **15** in 68% yield (80 mg, 0.11 mmol): mp > 300 °C (dec.); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.0 (d, *J* = 8.1 Hz, 2H), 7.84-7.79 (m, 6H), 7.69 (d, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.12-7.05 (m, 5H), 6.6 (m, 3H), 6.47 (d, *J* = 8.7 Hz, 2H), 3.46 (dd, *J* = 38, 8 Hz, 4H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 164.7 (C=N), 156.3, 153.5, 137.9, 136.4, 134.3, 129.7, 129.5, 129.3, 128.8, 128.4, 126.3, 126.2, 125.8, 125.7, 124.1, 123.0, 122.5, 120.8, 118.3, 118.0, 59.4 (C-N); IR (film) 3429 (br), 1638 (C=N), 1512, 1427 cm^{-1}; MS (ES) *m/z* 731 (MNa^+), 749 ($M{\cdot}CH_3CN^+$); HRMS (ES) calcd *m/z* 709.1637 ($C_{44}H_{31}N_2O_4Ni$, MH^+), found *m/z* 709.1629

(-)-*(S,S)*-Cu(II)-Ethylenediamine-BINOL-salen (16). BINOL-salen **9** (300 mg, 0.459 mmol) and $Cu(OAc)_2$ (83.5 mg, 0.459 mmol) were combined in a flask with EtOH (11 mL) and water (1.1 mL). The mixture was heated at reflux for 2.5 h, stirred at rt for 1 h and stored at 0 °C for 1 h. The fine brown precipitate was collected by gravity filtration, washed with Et_2O, and dried *in vacuo* with gentle heating for several hours to provide **16** in 92% yield (303 mg, 0.424 mmol) as a brown solid: mp > 300 °C (dec.); IR (film) 3442.0 (br), 2368, 2338, 1640 (C=N), 1512, 1437 cm^{-1}; MS (ES) *m/z* 714 (MH^+); HRMS (ES) calcd *m/z* 714.157982 ($C_{44}H_{31}N_2O_4Cu$, MH^+); found *m/z* 714.60403.

(-)-*(S,S)*-Pd(II)-Ethylenediamine-BINOL-salen (18). BINOL-salen **9** (100 mg, 0.150 mmol) and MeONa (19.8 mg, 0.360 mmol) were combined in a flask with MeOH (11.5 mL). The orange solution was stirred at rt for 15 min and $Pd(OAc)_2$ (33.7 mg, 0.150 mmol) was added at once. The orange-brown slurry was stirred for 3 h then stored at 0 °C for 1 h. The precipitate was collected by vacuum filtration, washed with cold MeOH, then Et_2O, and dried *in vacuo* with gentle heating for several hours to provide **18** in 87% yield (99.1 mg, 0.131 mmol) as a brown-orange solid: mp > 300 °C (dec.); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.60 (s, 2H), 8.21 (s, 2H), 7.92(d, *J* = 8.6 Hz, 4H), 7.79 (d, *J* = 8.5 Hz, 4H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.06 (m, 4H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.2 Hz, 2H), 3.99 (br s); ^{13}C NMR (125 MHz, THF-d_8) δ 161.4 (C=N), 156.9, 154.3, 138.0, 137.4, 134.6, 129.8, 129.3, 128.6, 128.3, 127.8, 126.5, 126.0, 125.9, 125.8, 125.3, 122.5, 121.3, 119.1, 118.7, 60.1; IR (film)

3499 (br), 3049, 2918, 1614 (C=N), 1580, 1344, 1310 cm^{-1}; MS (ES) *m/z* 779 (MNa^+); HRMS (ES) calcd *m/z* 779.1138 ($C_{44}H_{30}N_2O_4PdNa$, MNa^+); found *m/z* 779.1168.

(-)-*(S,S)*-Ni(II)-Diaminobenzene-BINOL-salen (19). BINOL-salen **10** (257 mg, 0.367 mmol) and $Ni(OAc)_2{\cdot}4H_2O$ (65 mg, 0.367 mmol) were combined in a flask with EtOH (6 mL). After heating at reflux for 1 h, the dark yellow slurry became dark red. The mixture was allowed to cool slowly to rt and then stored at 0 °C for 1 h. The reaction mixture was concentrated, washed with cold EtOH and dried *in vacuo* with gentle heating for several hours to provide **19** in 88% yield (240 mg, 0.318 mmol) as a dark red solid: mp > 300 °C (dec.); ^1H NMR (500 MHz, CD_2Cl_2) δ 8.8-6.7 (m, 24H), 6.6-6.3 (m, 3H), 6.05 (bs, 1H); IR (film) 3250 (br), 3049, 1604 (C=N), 1574, 1327 cm^{-1}; MS (ES) *m/z* 779 (MNa^+); HRMS (ES) calcd *m/z* 779.1457 ($C_{48}H_{30}N_2O_4Ni$, MH^+), found *m/z* 779.1479.

(-)-*(S,S,S,S)*-Ni(II)-Diaminocyclohexane-BINOL-salen (20). Compound **11** (90 mg, 0.127 mmol) and $Ni(OAc)_2{\cdot}4H_2O$ (22.5 mg, 0.127 mmol) were combined in a flask with EtOH (2.7 mL). After heating at reflux for 1 h, the reaction was allowed to cool slowly to rt and then stored at 0 °C for 1 h. The red-orange precipitate was collected by gravity filtration, washed with cold EtOH, and dried *in vacuo* with gentle heating for several hours to provide **20** in 83% yield (80 mg, 0.105 mmol) as an orange solid: mp > 300 °C (dec.); ^1H NMR (500 MHz, CD_2Cl_2) δ 8.06 (s, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.93 (s, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.15-7.06 (m, 6H), 6.78 (br s, 2H), 6.58 (d, *J* = 8.6 Hz, 2H), 6.18 (d, *J* = 8.7 Hz, 2H), 3.31 (br s, 2H), 2.63 (d, *J* = 10.9 Hz, 2H), 2.05 (d, *J* = 8.3 Hz, 2H), 1.46 (m, 4H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 160.5 (C=N), 156.2, 153.2, 137.9, 136.8, 134.3, 129.6, 129.3, 129.2, 128.7, 128.4, 126.4, 126.2, 125.8, 125.7, 124.2, 123.0, 122.4, 120.5, 118.3, 118.0, 70.9 (C-N), 29.3, 24.6; IR (film) 3215 (br), 3052, 2930, 1612 (C=N), 1583, 1347, 1323 cm^{-1}; MS (ES) *m/z* 785 (MNa^+); HRMS (ES) calcd *m/z* 763.210680 ($C_{48}H_{37}N_2O_4Ni$, MH^+), found 763.210049.

(-)-*(S,S,S,S)*-Cu(II)-Diaminocyclohexane-BINOL-salen (21). Compound **11** (60 mg, 0.085 mmol) and $Cu(OAc)_2$ (15.4 mg, 0.085 mmol) were combined in a flask with EtOH (2.0 mL) and water (0.2 mL). The mixture was heated at reflux for 2.5 h, stirred at rt for 15 min and stored at 0 °C for 1 h. The green-brown precipitate was collected by gravity filtration, washed with cold EtOH, and dried *in vacuo* with gentle heating for several hours to provide **21** in 86% yield (56 mg, 0.073 mmol) as a green-brown solid: mp > 300 °C (dec.); IR (film) 3472 (br), 3053, 2935, 1613 (C=N), 1582, 1348, 1324 cm^{-1}; MS (ES) *m/z* 790 (MNa^+); HRMS (ES) calcd *m/z* 768.202959 ($C_{48}H_{37}N_2O_4Cu$, MH^+); found *m/z* 768.204932.

(-)-*(S,R,R,S)*-Ni(II)-Diaminocyclohexane-BINOL-salen (22). Compound **22** was prepared from **12** in 85% yield following the procedure for the preparation of **20**: X-ray quality crystals of **22** were grown in CH_2Cl_2 layered with hexanes: mp > 300 °C (dec.); ^1H NMR (500 MHz, CD_2Cl_2) δ 8.03-7.78 (m, 10H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 2H), 7.12-7.06 (m, 4H), 6.64 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 6.32 (s, 2H), 3.22 (m, 2H), 2.60 (m, 2H), 2.04 (m, 2H), 1.45 (m, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 160.5 (C=N), 156.6, 153.3, 138.0, 136.9, 134.4, 129.6, 129.3, 129.2, 128.7, 128.3, 126.3, 126.2, 125.7, 125.6, 124.2, 122.9, 122.3, 120.7, 118.0, 117.9, 70.6 (C-N), 29.3, 24.6; IR (film) 3427 (br), 3055, 2941, 2859, 1613 (C=N), 1584, 1347, 1323 cm^{-1}; MS (ES) *m/z* 785 (MNa^+); HRMS (ES) calcd *m/z* 785.192625 ($C_{48}H_{36}N_2O_4NiNa$, MNa^+); found *m/z* 785.194218.

(-)-*(S,R,R,S)*-Cu(II)-Diaminocyclohexane-BINOL-salen (23). Compound **23** was prepared from **12** in 85% yield following the procedure for the preparation of **21**: mp > 300 °C (dec.); IR (film) 3438 (br), 3054, 2937, 2859, 1613 (C=N), 1582, 1348, 1319 cm^{-1}; MS (ES) *m/z* 768 (M^+), 791 (MNa^+); HRMS (ES) calcd *m/z* 768.204932 ($C_{48}H_{37}N_2O_4Cu$, MH^+); found *m/z* 768.208454; calcd *m/z* 790.186877 ($C_{48}H_{36}N_2O_4CuNa$, MNa^+), found 790.185549.

(-)-*(S,S)*-Ni(II)-*cis*-Diaminocyclohexane-BINOL-salen (24). Compound **24**, a red solid, was prepared from **13** in 74% yield following the procedure for the preparation of **20**: mp > 300 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.68 (s, 1H), 7.59 (m, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.32 (m, 3H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.12-7.01 (m, 6H) 6.80 (br s, 2H), 6.67 (d, *J* = 8.7 Hz, 1H), 6.63 (m, 2H), 6.49 (m, 1H), 3.55 (m, 1H), 3.26 (m, 1H), 2.22 (m, 2H), 1.35-1.00 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (C=N), 162.1, (C=N) 155.5, 155.3, 153.8, 152.6, 137.7, 137.5, 136.1, 135.9, 134.2, 133.8, 129.5, 129.3, 129.1, 129.0, 128.9, 128.6, 128.43, 128.4, 128.3, 127.8, 126.5, 126.4, 126.1, 125.9, 125.8, 125.6, 125.4, 125.2, 123.9, 123.8, 122.8, 122.5, 122.4, 122.0, 121.5, 120.2, 118.5, 118.1, 117.7, 68.2 (C-N), 66.6 (C-N); IR (film) 3255 (br), 3054, 2934, 2857, 1611 (C=N), 1584, 1350, 1329 cm^{-1}; MS (ES) *m/z* 785 (MNa^+), 825 ($MNaCH3CN^+$); HRMS (ES) calcd *m/z* 785.1926 ($C_{48}H_{36}N_2O_4NiNa$, MNa^+); found *m/z* 785.1920.

(-)-*(S,R,R,S)*-Ni(II)-Diphenylethylenediamine-BINOL-salen (25). Compound **25**, a red solid, was prepared from **14** in 84% yield following the procedure for the preparation of **20**: mp > 300 °C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 7.93-6.98 (m, 30H), 6.60 (d, *J* = 6.0 Hz, 4H), 6.44 (d, *J* = 7.2 Hz, 2H), 4.71 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8 (C=N), 156.1, 153.1, 138.2, 137.9, 136.4, 134.1, 129.7, 129.4, 129.1, 128.72, 128.70, 127.8, 127.6, 126.4, 126.1, 126.0, 125.3, 122.6, 122.3, 120.7, 119.0, 117.7, 79.6 (C-N); IR (film) 3511 (br), 3055, 1607 (C=N), 1584, 1347, 1323 cm^{-1}; MS (ES) *m/z* 883 (MNa^+); HRMS (ES) calcd *m/z* 883.2083 ($C_{56}H_{38}N_2O_4NiNa$, MNa^+); found *m/z* 883.2059.

General Procedure for the Michael reaction of cyclohexenone and benzyl malonate. M^1-BINOL-salen **15-25** (0.028 mmol) and base (0.056 mmol) were combined in a 10 mL flask in an inert atmosphere glovebox. After the flask was sealed, removed from the glovebox, and placed under N_2, THF (5 mL) was added. The mixture was allowed to stir at rt for 2.5 h and then cooled to the reaction temperature as necessary. Cyclohexenone (0.282 mmol) and benzyl malonate (0.282 mmol) were successively added. After stirring for 48 h, the reaction mixture was quenched with H_2O, extracted with EtOAc, dried over $MgSO_4$, and concentrated. The Michael adduct was isolated from the crude residue by preparative TLC (SiO_2; 50% EtOAc / hexanes). ^1H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra for 3-[bis(benzyloxycarbonyl)methyl]cyclohexanone (**27**) were identical to those previously reported.[5]

Enantiomeric purity of the Michael adduct was determined by HPLC: Daicel Chiralpak AS, 10% 2-propanol / hexane, 0.9 mL / min; $t_R(+)$ = 29 min, $t_R(-)$ = 38 min. The absolute configuration of **27** has been determined.[6]

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