Supporting Information

Catalysis of the Michael Addition Reaction by Late Transition Metal Complexes of BINOL-Derived Salens

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General. Unless otherwise noted, all non-aqueous reactions were carried out under an atmosphere of dry N₂ in glassware that had been either flame dried in a stream of N₂ or dried in an oven (90 °C) for at least 6 h. When necessary, solvents and reagents were dried prior to use. Toluene and CH₂Cl₂ were de-oxygenated by purging with N₂ and then dried by passing through activated alumina. CH₃CN and EtOH were distilled from CaH₂. DMF was distilled from MgSO₄. TMEDA was distilled from Na. THF used in the catalytic Michael reactions was distilled from Na/benzophenone ketyl. 95% LiH, purchased from Aldrich and stored under N₂ atmosphere in a dry box, was used in the catalytic Michael additions with the BINOL-Salen complexes. Ni(OAc)₂·4H₂O was purchased from Strem and used without further purification. Cyclohexenone was distilled prior to use. NaO^tBu, KO^tBu, LiO^tBu and Cs₂CO₃ 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(methoxymethoxy)-1,1'-binaphthalene-3-carboxyaldehyde,¹ (-)-(1*R*,2*R*)-cyclohexanediamine,² and (+)-(1*S*,2*S*)-cyclohexanediamine² were prepared according to established procedures. The synthesis and characterization of compounds **12-13**, **15-16**, **19**, **21-22**, and **30** have previously been reported.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 a UV detection. Analytical Chiralpak AD and Chiralpak AS columns (0.46 cm X 25 cm) from Daicel were used. ¹H NMR and ¹³C 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 (CDCl₃ 7.26 ppm, DMSO-*d*₆ 2.49 ppm, D₂O 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. ¹³C NMR chemical shifts are reported in ppm from tetramethylsilane (0 ppm) or from solvent resonance (CDCl₃ 77.3 ppm). 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. An ASI ReactIR 1000 equipped with Si-Comp probe was used for the kinetic analyses. 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 [α]_D²⁰ (c = g/100mL, solvent).

(-)-(R,R)-Diaminocyclohexane-biphenol-salen (10). **10** was prepared in a manner analogous to compounds **13-18**.³ 78% yield; yellow solid; [α]_D²⁰ -1013 (c 0.32, CH₂Cl₂); ¹H NMR (500 MHz, CD₂Cl₂)

δ 8.32 (s, 2H, C=N), 7.40 (dd, J = 1.6, 5.9 Hz, 2H), 7.28-7.24 (m, 6H), 6.99 (d, J = 7.6 Hz, 4H), 6.89 (t, J = 7.6 Hz, 4H), 3.49 (d, J = 9.7 Hz, 2H), 2.10 (d, J = 14.5 Hz, 2H), 1.93 (d, J = 9.7 Hz, 2H), 1.76 (d, J = 9.2 Hz, 2H), 1.50 (m, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 166.3 (C=N), 162.9, 155.4, 136.7, 132.4, 131.3, 129.5, 129.3, 126.7, 120.9, 118.8, 118.6, 117.7, 70.2, 32.9, 24.3; IR (film) 3051, 2933, 2864, 1632 (C=N), 1491, 1448, 1399 cm^{-1} ; MS (ES) m/z 507 (MH^+); HRMS (ES) calcd m/z 507.2284 ($\text{C}_{32}\text{H}_{30}\text{N}_2\text{O}_4$, MH^+), found m/z 707.2288.

(-)-(R,R)-Ni(II)-Diaminocyclohexane-biphenol-salen (11). **11** was prepared in a manner analogous to compounds **19-24**.³ 70% yield; yellow-brown solid; mp > 300 °C (dec.); ^1H NMR (500 MHz, CD_2Cl_2) δ 8.01 (s, 2H), 7.40 (d, J = 5.9 Hz, 2H), 7.28 (d, J = 6.5 Hz, 4H), 7.14 (t, J = 7.9 Hz, 2H), 6.95 (t, J = 7.6 Hz, 2H), 6.81 (t, J = 7.5 Hz, 2H), 6.16 (d, J = 7.8 Hz, 2H), 3.16 (m, 2H), 2.46 (d, J = 10 Hz, 2H), 1.94 (m, 2H), 1.33 (m, 4H); IR (film) 3052, 3013, 2918, 2856, 1625 (C=N), 1487, 1432, 1380, 1320 cm^{-1} ; MS (ES) m/z 563 (MH^+), 585 (MNa^+); HRMS (ES) calcd m/z 585.1300 ($\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_4\text{NiNa}$, MNa^+); found m/z 585.1319.

(-)-(S,S)-Diaminobenzene-BINOL-salen (14). (-)-(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 room temperature 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 **14** in 93% yield (210 mg, 0.443 mmol) as a bright yellow powder: mp 196-200 °C; $[\alpha]_{\text{D}}^{20}$ -118 (c 0.5, THF); ^1H 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 ($\text{M}\cdot\text{CH}_3\text{CN}^+$).

(-)-(S,S)-cis-Diaminocyclohexane-BINOL-salen (17). (-)-(S)-1,1'-Binaphthalene-3-carboxyaldehyde (400 mg, 1.273 mmol) was dissolved completely in EtOH (5 mL) with heating. The yellow solution was then allowed to cool to room temperature and *cis*-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 room temperature for 24 h. The precipitate was collected by filtration, washed with cold EtOH and dried with gentle heating *in vacuo* to provide **17** in 92% yield (380 mg, 0.538 mmol) as a pale orange powder: mp 192-196 °C; $[\alpha]_{\text{D}}^{20}$ -72 (c 1.0, CHCl_3); ^1H 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 (18). (-)-(S)-1,1'-Binaphthalene-3-carboxyaldehyde (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 **18** in 93% yield (357 mg, 0.444 mmol) as a pale-orange powder: mp 204-206 °C; $[\alpha]_D^{20}$ -222 (c 1.0, $CHCl_3$); 1H 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), 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)-Diaminobenzene-BINOL-salen (20). BINOL-salen **14** (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 **20** 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)-Ni(II)-cis-Diaminocyclohexane-BINOL-salen (23). Compound **17** (1 equiv) and $Ni(OAc)_2 \cdot 4H_2O$ (1 equiv) were combined in a flask with EtOH (0.05 M). 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 **23** in 74% yield as a red solid: 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 ($MNaCH_3CN^+$); 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 (24). Compound **24**, a red solid, was

prepared from **18** in 84% yield following the procedure for the preparation of **23**: mp > 300 °C (dec.); ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (125 MHz, CDCl₃) 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 (C₅₆H₃₈N₂O₄NiNa, MNa⁺); found *m/z* 883.2059.

General Procedure for the Michael reaction between enones and malonates. Ni-BINOL-salen **19-24** (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 and removed from the glovebox, the appropriate solvent (5 mL) was added. The slurry was allowed to stir at rt for 2 h and then cooled to the reaction temperature as necessary. The enone (0.282 mmol) and malonate (0.282 mmol) were added successively. After stirring for 2-5 days (see main text for specific reaction times) the reaction mixture was quenched with H₂O, extracted with EtOAc, dried over MgSO₄, and concentrated. The Michael adduct was isolated from the crude residue by preparative TLC (SiO₂; 50% EtOAc/hexanes) or flash column chromatography.

3-[bis(Benzyloxycarbonyl)methyl]cyclohexanone (28). Prepared by the Michael reaction between cyclohexenone and benzyl malonate and isolated by preparative TLC (SiO₂; 50% EtOAc/hexanes). NMR spectra are identical to those previously reported.⁵ Enantiomeric purity was determined by HPLC: Daicel Chiralpak AS, 10% 2-propanol/hexane, 0.9 mL/min, 254 nm; *t*_R(+) = 29 min, *t*_R(-) = 38 min. The absolute configuration was established by comparison to the literature.⁵

3-[bis(Methoxycarbonyl)methyl]cyclohexanone (Entry 5, Table 5). Prepared by the Michael reaction between cyclohexenone and dimethyl malonate and isolated by flash column chromatography (10% acetone/hexanes to 20% acetone/hexanes). NMR spectra are identical to those previously reported.⁵ Enantiomeric purity was determined by HPLC: Daicel Chiralpak AS, 10% 2-propanol/hexanes, 0.5 mL/min, 210 nm; *t*_R(+) = 48 min, *t*_R(-) = 64 min. The absolute configuration was established by comparison to the literature.⁵

3-[bis(Benzyloxycarbonyl)methyl]cycloheptanone (Entry 6, Table 5). Prepared by the Michael reaction between cycloheptenone and benzyl malonate and isolated by preparative TLC (SiO₂; 20% EtOAc/hexanes). NMR spectra are identical to those previously reported.⁵ Enantiomeric excess was determined by ¹H NMR after forming the diastereomeric ketals from the Michael product and (*R,R*)-butanediol: The integrations of the ¹H NMR peaks at 2.45 ppm and 2.55 ppm were compared. The absolute configuration was not determined.

3-[bis(Benzyloxycarbonyl)methyl]cyclopentanone (Entries 7 and 8, Table 5). Prepared by the Michael reaction between cyclopentenone and benzyl malonate and isolated by preparative TLC (SiO₂; 20% EtOAc/hexanes). NMR spectra are identical to those previously reported.⁵ Enantiomeric excess was determined by ¹H NMR after forming the diastereomeric ketals from the Michael product

and (*R,R*)-butanediol: The integrations of the ^1H NMR peaks at 3.38 ppm and 3.41 ppm were compared. The absolute configuration was not determined.

(3-oxo-1,3-diphenyl-propyl)-malonic acid dimethyl ester (Entries 9 and 10, Table 5). Prepared by the Michael reaction between *trans*-chalcone and dimethyl malonate and isolated by flash column chromatography (10-20% acetone/hexanes). NMR spectra are identical to those previously reported.⁶ Enantiomeric excess was determined by HPLC: Daicel Chiralpak AS, 10% 2-propanol/hexanes, 0.5 mL/min, 254 nm; $t_{\text{R}}(+)$ = 22 min, $t_{\text{R}}(-)$ = 26 min. The absolute configuration was established by comparison to the literature.⁶

Methyl 2-carbomethoxy-4-nitro-3-phenylbutyrate (Entry 11, Table 5). Prepared by the Michael reaction between nitrostyrene and dimethyl malonate and isolated by flash column chromatography (10-20% acetone/hexanes). NMR spectra are identical to those previously reported.⁷ Enantiomeric excess was determined by HPLC: Daicel Chiralpak AD, 5% 2-propanol/hexanes, 0.5 mL/min, 254 nm; $t_{\text{R}}(+)$ = 31 min, $t_{\text{R}}(-)$ = 45 min. The absolute configuration was established by comparison to the literature.

Non-linear effects. A 9.5 mM solution of (-)-(*S,R,R,S*)-Ni(II)-cyclohexanediamine-BINOL-salen and a 4.8 mM solution of (+)-(*R,S,S,R*)-Ni(II)-cyclohexanediamine-BINOL-salen [the (+) enantiomer made in a manner exactly analogous to the (-) enantiomer⁴] were made by weighing out the appropriate amount of Ni(II)-BINOL-salen (0.1447 g and 0.0544 g respectively) into two separate Schlenk flasks in an inert atmosphere glove box. Each Ni(II)-BINOL-salen was then dissolved with the appropriate amount of dry THF (20 mL and 15 mL respectively). Also, four flame dried test tubes were charged with Cs_2CO_3 (18.4 mg, 0.056 mmol) in an inert atmosphere glove box. The test tubes were then sealed, removed from the glove box, and purged with N_2 . Each of the four test tubes was then charged with the necessary amount of (-)-(*S,R,R,S*)-Ni(II)-cyclohexanediamine-BINOL-salen and (+)-(*R,S,S,R*)-Ni(II)-cyclohexanediamine-BINOL-salen solutions so as to make the catalyst in 0% ee, 50% ee, 75% ee, and 100% ee. THF was then added to bring each reaction to 5.6 mM in total catalyst. The mixtures were allowed to stir at rt for 2.5 h and then cooled to -20 °C. Cyclohexenone (0.282 mmol) and benzyl malonate (0.282 mmol) were then successively added to each reaction. After stirring for 5 days, each reaction was quenched as described in the General Procedure. The 3-[bis(benzyloxycarbonyl)methyl]cyclohexanone was then isolated and the enantiomeric excess was determined as described above.

Table S1: Results of non-linear effects experiments

catalyst ee (%)	(-) catalyst soln (mL)	(+) catalyst soln (mL)	THF (mL)	Michael adduct yield	Michael adduct ee (%)
0	1.49	2.96	0.55	1%	3 (R)
50	2.23	1.48	1.29	5%	70 (R)
75	2.60	0.74	1.66	13%	77 (R)
100	2.97	0	2.03	14%	84 (R)

Kinetic analyses: Method A. In an inert atmosphere glove box, a Schlenk flask was charged with (-)-(S,R,R,S)-Ni(II)-BINOL-salen. The flask was then sealed, removed from the glove box, and purged with N₂. Dry THF was added to make the catalyst solution. A two neck flask with a 24/40 and 14/20 joint was flame dried and charged with the appropriate amount of Cs₂CO₃ (depending on the concentration of catalyst) in an inert atmospheres glove box. The two neck flask was then sealed, removed from the glove box, connected to the probe of an ASI ReactIR 1000, and purged with N₂. The appropriate amount of catalyst solution was added to the two neck flask followed by the appropriate amount of THF to bring the total volume in the flask to 3 mL. The reaction was allowed to stir for 2.5 h at rt, after which time a background IR spectrum was taken of the reaction mixture. The ASI ReactIR 1000 was then prompted to start collecting spectra. Cyclohexenone (0.060 mL, 0.622 mmol) was added to the reaction via syringe. After the cyclohexenone appeared in the display window, the benzyl malonate (0.15 mL, 0.622 mmol) and THF (2 mL) were added successively. Data collection with the ASI ReactIR 1000 was continued until the cyclohexenone consumption stopped. A profile for the decomposition of the cyclohexenone carbonyl peak at 1687 or 1691 cm⁻¹ was then generated and transferred to Microsoft Excel. The initial rate for the reaction was found by plotting a tangent for the initial portion of the reaction curve. The reaction was found to be first order in catalyst as determined by a best fit to a ln[cat] vs rate plot (see main text) or from the slope of a ln[cat] vs ln[rate] plot (see below).

Kinetic analyses: Method B. In an inert atmosphere glove box, a two neck flask with a 24/40 and 14/20 joint was flame dried and charged with the appropriate amount of (-)-(S,R,R,S)-Ni(II)-BINOL-salen and Cs₂CO₃ (depending on the concentration of catalyst needed for the run). The two neck flask was then sealed, removed from the glove box, connected to the probe of an ASI ReactIR 1000, and purged with N₂. THF (3 mL) was then added and the reaction was allowed to stir for 2.5 h at rt, after which time a background was taken of the reaction mixture. The ASI ReactIR 1000 was then prompted to start collecting spectra and the remainder of the experiment was identical to that of Method A.

Table S2: Kinetics results.

mol% catalyst	Method	[catalyst soln] (mM)	vol catalyst soln (mL)	[catalyst] in reaction (mM)	rate x 10 ⁵ (abs/min)
1	A	9.40	0.66	1.19	-1.33
1	B	NA	NA	1.22	-1.45
2	A	0.94	1.32	2.39	-2.35
2	B	NA	NA	2.39	-3.02
3	B	NA	NA	3.58	-4.56
4	A	13.0	2.57	4.77	-4.52
6	B	NA	NA	7.16	7.90

Figure S1: Representative reaction profile for a Michael reaction from the ASI ReactIR 1000.

Figure S2: Catalyst rate order analysis: ln[rate] vs ln[cat] plot (slope = catalyst rate order).

(-)-(S)-2'-Methoxy-[1,1']-Binaphthalenyl-2-ol (35). **35** was prepared in 86% yield following the procedure for the synthesis of 2'-methoxy-biphenyl-2-ol.⁸ **35** has previously been synthesized by similar methods.⁹

(-)-(S)-2'-Methoxy-2-methoxymethyl-[1,1']binaphthalenyl (36). A slurry of NaH (392 mg, 60% dispersion in mineral oil, 3.99 mmol) in THF (30 mL) and DMF (10 mL) was purged with N₂ and cooled to 0 °C. **35** (1.8 g, 5.99 mmol) was added as a solution in THF (11 mL). The pale yellow anion was stirred for 1.5 h at 0 °C. MOMCl (0.68 mL, 8.99 mmol) was added dropwise and the solution was allowed to warm to ambient. After stirring for 4 h, the reaction was quenched with water, extracted with EtOAc, dried over MgSO₄ and concentrated. Purification by flash chromatography on SiO₂ (5% EtOAc:hexanes) afforded the bisether in 92% yield (1.9 g, 5.51 mmol) as a white solid. (+/-)-**36** has previously been synthesized by similar methods.¹⁰

(-)-(S)-2-Hydroxy-2'-methoxy-[1,1']binaphthalenyl-3-carbaldehyde (37). (-)-**37** was prepared from **36** in 81% yield following the procedure for the synthesis of (+/-)-**37**.¹⁰

(-)-(S,S)-Ethylenediamine-MeO-BINOL-salen (38). **38** was prepared from **37** in a manner analogous to compounds **13-18**.³ 92% yield; off white powder; mp 172-176 °C (dec.); [α]_D²⁰ -167 (*c* 0.33, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 12.88 (brs, 2H), 8.58 (s, 2H, HC=N), 7.99-7.79 (m, 8H), 7.46 (d, *J* = 9 Hz, 2H), 7.30-7.14 (m, 12H), 3.99-3.93 (m, 4H, H₂C-N), 3.72 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 167.2 (C=N), 155.5, 154.8, 136.0, 134.2, 133.8, 130.1, 129.8, 129.2, 128.5, 128.4, 127.7, 126.8, 125.5, 125.2, 124.0, 123.6, 121.0, 120.0, 127.8, 126.8, 125.5, 125.2, 124.0, 123.6, 121.0, 120.0, 117.5, 114.8,

60.1, 57.4 (C-N); IR (film) 3060-2500 (br), 3054, 2835, 1633 (C=N), 1506, 1344 cm^{-1} ; MS (ES) m/z 1361 ($\text{M}\cdot\text{MH}^+$); HRMS (ES) calcd m/z 703.2573 ($\text{C}_{46}\text{H}_{36}\text{N}_2\text{O}_4\text{Na}$, MNa^+), found m/z 703.2604.

(-)-(S,S)-Ni(II)-Ethylenediamine-MeO-BINOL-salen (31). **31** was prepared from **38** or **37** in a manner analogous to compounds **19-24**.³ 74% yield; light brown solid; mp > 300 °C (dec.); ^1H NMR (500 MHz, CDCl_3) δ 7.96-7.92 (dd, J = 4.2, 8.2 Hz, 4H); 7.45 (d, J = 6.9 Hz, 2H), 7.36 (s, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.17 (s, 2H), 7.14 (d, J = 7.4 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 6.9 (m, 4H), 6.85 (d, J = 8.8 Hz, 2H), 6.50 (d, J = 8.0 Hz, 2H), 3.23 (d, J = 7.1 Hz, 2H), 3.09 (d, J = 7.5 Hz, 2H), 3.02 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.4, 155.5, 137.4, 133.9, 129.4, 129.0, 128.7, 127.9, 127.7, 125.8, 125.5, 124.7, 124.5, 123.8, 123.2, 122.2, 120.9, 118.4, 117.2, 116.9, 58.4, 57.6; IR (film) 2359, 2338, 1612 (C=N), 1583, 1427, 1335, 1263 cm^{-1} ; MS (ES) m/z 737 (MH^+), 759 (MNa^+); HRMS (ES) calcd m/z 759.1770 ($\text{C}_{46}\text{H}_{34}\text{N}_2\text{O}_4\text{Ni}$, MNa^+), found m/z 759.1776.

Michael reaction with Cs-naphthoxide (33). A round bottom flask was flame dried and charged with Cs_2CO_3 (9.2 mg, 0.028 mmol) in an inert atmospheres glove box. The flask was sealed, removed from the glove box and charged with 1-naphthol (81 mg, 0.056 mmol). A reflux condenser was then attached, and the system was purged with N_2 . THF (4.4 mL) was added, and the reaction was heated to reflux overnight (~12 h). The reflux condenser was removed and the brownish solution was allowed to cool to room temperature. Cyclohexenone (0.282 mmol, 0.0273 mL) followed by a 0.47 M solution of benzyl malonate in THF (0.282 mmol, 0.60 mL) were added to the reaction. The reaction was monitored by ^1H NMR spectroscopy (500 MHz) as follows: 0.10 mL aliquots were removed from the reaction at 2 h, 10 h, 24 h, and 48 h. The aliquots were quenched by passage through a plug of silica. After concentration, the ^1H NMR sepctrum of each aliquot was taken. Peaks at 6.05 ppm (cyclohexenone) and 3.45 ppm (**28**) were integrated and used to determine conversion.

Equation 3. **25d** was made in a manner analogous to **33**. The Michael reaction was then carried out between cyclohexenone and benzyl malonate in the usual manner.

Competing reaction pathways. The reactions referred to in **Figure 9** were carried out between cyclohexenone and benzyl malonate in the usual manner using Cs_2CO_3 or CsHCO_3 . Conversions were determined by ^1H NMR spectroscopy as described above.

X-Ray Methods and Data for (-)-(S,S)-Ni(II)-Ethylenediamine-BINOL-salen (19). X-ray quality crystals were grown from THF.

Compound **19**, $\text{NiC}_{60}\text{H}_{62}\text{N}_2\text{O}_8$, crystallizes in the triclinic space group P1 with $a=16.4690(8)\text{\AA}$, $b=16.5978(8)\text{\AA}$, $c=9.0916(5)\text{\AA}$, $\alpha=90.114(3)^\circ$, $\beta=101.520(4)^\circ$, $\gamma=107.967(3)^\circ$, $V=2311.0(2)\text{\AA}^3$, $Z=2$ and $d_{\text{calc}}=1.434\text{ g/cm}^3$. X-ray intensity data were collected on a Rigaku R-Axis IIC area detector employing graphite-monochromated Mo- K_α radiation ($\lambda=0.71069\text{ \AA}$) at a temperature of 200 K. Indexing was performed from a series of 1° oscillation images with exposures of 200 seconds per frame. A hemisphere of data was collected using 4° oscillation angles with exposures of 1200 seconds per frame and a crystal-to-detector distance of 82 mm. Oscillation images were processed using *bioteX*¹¹, producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the *teXsan*¹² program package for further processing and structure solution on a Silicon Graphics O2 computer. A total of 17363 reflections were measured over the ranges $5.02 \leq 2\theta \leq 50.7^\circ$, $-18 \leq h \leq 19$, $-19 \leq k \leq 19$, $-10 \leq l \leq 10$ yielding 12491 unique reflections ($R_{\text{int}} = 0.0485$). The intensity data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods (*SIR92*¹³). The asymmetric unit includes four molecules of disordered tetrahydrofuran solvent. The data were corrected for the presence of disordered solvent using *SQUEEZE*.¹⁴ Refinement was by full-matrix least squares based on F^2 using *SHELXL-93*¹⁵. All reflections were used during refinement (F^2 's that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w=1 / [\sigma^2(F_o^2) + 0.0766P^2 + 2.3428P]$ where $P = (F_o^2 + 2F_c^2) / 3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged to $R_1=0.0663$ and $wR_2=0.1596$ for 10724 reflections for

which $F > 4\sigma(F)$ and $R_1=0.0774$, $wR_2=0.1694$ and $GOF = 1.096$ for all 12491 unique, non-zero reflections and 923 variables¹⁶. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.292 and -0.583 e/Å³.

Table S1 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Table S2. Anisotropic thermal parameters are in Table S3. Tables S4 and S5 list bond distances and bond angles. Figures S3 and S4 are ORTEP¹⁷ representations of the molecule with 30% probability thermal ellipsoids displayed.

Figure S3. ORTEP drawing of molecule no. 1 of the asymmetric unit with 30% probability thermal ellipsoids.

Figure S4. ORTEP drawing of molecule no. 2 of the asymmetric unit with 30% probability thermal ellipsoids.

Table S1. Summary of Structure Determination of Compound **19**

Formula:	NiC ₆₀ H ₆₂ N ₂ O ₈
Formula weight:	997.83
Crystal class:	triclinic
Space group:	P1 (#1)
Z	2
Cell constants:	
a	16.4690(8)Å
b	16.5978(8)Å
c	9.0916(5)Å
α	90.114(3)°
β	101.520(4)°
γ	107.967(3)°
V	2311.0(2)Å ³
μ	4.84 cm ⁻¹
crystal size, mm	0.40 x 0.12 x 0.04

D_{calc}	1.434 g/cm ³
F(000)	1056
Radiation:	Mo-K $_{\alpha}$ ($\lambda=0.71069\text{\AA}$)
2 θ range	5.02 – 50.7 °
hkl collected:	-18 $\leq$ h $\leq$ 19; -19 $\leq$ k $\leq$ 19; -10 $\leq$ l $\leq$ 10
No. reflections measured:	17363
No. unique reflections:	12491 ($R_{\text{int}}=0.0485$)
No. observed reflections	10724 ($F>4\sigma$)
No. reflections used in refinement	12491
No. parameters	923
R indices ($F>4\sigma$)	$R_1=0.0663$ $wR_2=0.1596$
R indices (all data)	$R_1=0.0774$ $wR_2=0.1694$
GOF:	1.096
Final Difference Peaks, e/ $\text{\AA}^3$	+0.292, -0.583

Table S2. Refined Positional Parameters for Compound 19

Atom	x	y	z	U _{eq} , Å ²
Ni	0.75790(5)	0.96601(5)	0.70310(8)	0.0445(2)
O1	0.7367(3)	1.0617(3)	0.7703(6)	0.0477(12)
O2	0.8470(4)	1.0435(3)	0.6340(6)	0.0494(13)
O3	0.7249(4)	1.1695(3)	0.5595(5)	0.0643(14)
H3	0.709(6)	1.185(2)	0.4760(14)	0.096
O4	0.9537(4)	1.1630(3)	0.8445(5)	0.0649(13)
H4	0.921(5)	1.117(2)	0.8062(5)	0.097
N1	0.6733(4)	0.8907(3)	0.7824(7)	0.048(2)
N2	0.7777(4)	0.8730(3)	0.6302(6)	0.0439(14)
C1	0.6632(5)	1.0626(5)	0.8116(9)	0.049(2)
C2	0.6475(4)	1.1431(4)	0.8230(8)	0.045(2)
C3	0.5659(5)	1.1440(4)	0.8441(9)	0.055(2)
C4	0.5046(6)	1.0676(5)	0.8764(10)	0.070(2)
C5	0.5262(5)	0.9924(4)	0.8835(10)	0.061(2)
H5	0.4888(5)	0.9436(4)	0.9127(10)	0.081
C6	0.6011(5)	0.9907(4)	0.8481(9)	0.052(2)
C7	0.6139(5)	0.9072(5)	0.8388(10)	0.055(2)
H7	0.5758(5)	0.8624(5)	0.8768(10)	0.073
C8	0.6790(6)	0.8035(4)	0.7791(8)	0.051(2)
H8a	0.7193(6)	0.7965(4)	0.8679(8)	0.068
H8b	0.6221(6)	0.7623(4)	0.7766(8)	0.068
C9	0.7096(5)	0.7913(4)	0.6448(8)	0.050(2)
H9a	0.6619(5)	0.7781(4)	0.5574(8)	0.066
H9b	0.7344(5)	0.7451(4)	0.6542(8)	0.066
C10	0.8396(6)	0.8710(4)	0.5686(9)	0.052(2)
H10	0.8380(6)	0.8185(4)	0.5299(9)	0.069
C11	0.9126(6)	0.9437(4)	0.5533(8)	0.049(2)
C12	0.9835(5)	0.9309(4)	0.5122(8)	0.052(2)
H12	0.9811(5)	0.8757(4)	0.4871(8)	0.069
C13	1.0594(5)	0.9972(5)	0.5066(9)	0.058(2)
C14	1.0609(5)	1.0822(4)	0.5435(9)	0.056(2)
C15	0.9860(5)	1.0977(4)	0.5723(8)	0.045(2)
C16	0.9133(5)	1.0289(4)	0.5852(8)	0.047(2)
C17	0.7154(4)	1.2240(4)	0.7967(7)	0.044(2)
C18	0.7444(5)	1.2355(5)	0.6662(9)	0.056(2)
C19	0.7935(5)	1.3150(5)	0.6290(10)	0.062(2)
H19	0.8078(5)	1.3220(5)	0.5348(10)	0.082
C20	0.8204(6)	1.3828(5)	0.7349(10)	0.069(2)
H20	0.8526(6)	1.4360(5)	0.7107(10)	0.092
C21	0.8008(5)	1.3736(4)	0.8753(9)	0.056(2)
C22	0.8330(5)	1.4420(5)	0.9875(10)	0.067(2)
H22	0.8658(5)	1.4948(5)	0.9633(10)	0.089
C23	0.8182(6)	1.4332(5)	1.1233(12)	0.078(3)

H23	0.8437(6)	1.4787(5)	1.1951(12)	0.104
C24	0.7638(6)	1.3552(5)	1.1633(9)	0.075(2)
H24	0.7527(6)	1.3496(5)	1.2597(9)	0.099
C25	0.7277(5)	1.2878(4)	1.0547(8)	0.056(2)
H25	0.6904(5)	1.2371(4)	1.0779(8)	0.075
C26	0.7468(5)	1.2951(4)	0.9100(7)	0.049(2)
C27	0.9863(5)	1.1869(4)	0.5971(9)	0.052(2)
C28	0.9764(5)	1.2169(5)	0.7318(10)	0.059(2)
C29	0.9927(6)	1.3042(5)	0.7679(10)	0.070(2)
H29	0.9929(6)	1.3236(5)	0.8640(10)	0.093
C30	1.0084(6)	1.3600(5)	0.6560(12)	0.075(3)
H30	1.0200(6)	1.4177(5)	0.6782(12)	0.099
C31	1.0070(5)	1.3312(4)	0.5091(10)	0.063(2)
C32	1.0128(6)	1.3850(5)	0.3865(12)	0.083(3)
H32	1.0189(6)	1.4421(5)	0.4029(12)	0.110
C33	1.0097(7)	1.3542(6)	0.2475(12)	0.088(3)
H33	1.0115(7)	1.3899(6)	0.1687(12)	0.117
C34	1.0039(7)	1.2710(6)	0.2203(11)	0.085(3)
H34	1.0031(7)	1.2516(6)	0.1237(11)	0.113
C35	0.9994(5)	1.2163(5)	0.3321(9)	0.063(2)
H35	0.9969(5)	1.1605(5)	0.3119(9)	0.083
C36	0.9983(5)	1.2443(4)	0.4818(9)	0.057(2)
C37	0.4222(6)	1.0699(6)	0.8985(14)	0.100(4)
H37	0.3835(6)	1.0213(6)	0.9258(14)	0.133
C38	0.3986(7)	1.1425(6)	0.881(2)	0.148(6)
H38	0.3438(7)	1.1432(6)	0.891(2)	0.197
C39	0.4585(7)	1.2137(6)	0.846(2)	0.111(4)
H39	0.4431(7)	1.2631(6)	0.838(2)	0.148
C40	0.5388(5)	1.2181(5)	0.8231(12)	0.078(3)
H40	0.5752(5)	1.2678(5)	0.7944(12)	0.104
C41	1.1370(7)	0.9823(6)	0.4865(12)	0.090(3)
H41	1.1363(7)	0.9271(6)	0.4667(12)	0.120
C42	1.2111(6)	1.0466(6)	0.4957(13)	0.096(3)
H42	1.2610(6)	1.0362(6)	0.4787(13)	0.128
C43	1.2134(6)	1.1300(6)	0.5312(12)	0.084(3)
H43	1.2657(6)	1.1741(6)	0.5408(12)	0.112
C44	1.1415(5)	1.1473(5)	0.5514(9)	0.067(2)
H44	1.1447(5)	1.2034(5)	0.5709(9)	0.089
Ni'	0.70109(5)	0.93411(4)	0.27113(8)	0.0412(2)
O1'	0.7559(3)	0.8536(3)	0.2554(5)	0.0413(11)
O2'	0.6127(3)	0.8469(3)	0.3195(6)	0.0460(12)
O3'	0.6652(3)	0.6905(3)	0.2134(6)	0.0566(12)
H3'	0.6787(12)	0.7413(11)	0.200(9)	0.085
O4'	0.5175(3)	0.6490(3)	0.5789(5)	0.0537(12)
H4'	0.552(4)	0.624(5)	0.6159(10)	0.080
N1'	0.7843(4)	1.0185(4)	0.2073(7)	0.048(2)
N2'	0.6507(4)	1.0165(3)	0.3004(7)	0.0429(14)

C1'	0.8133(5)	0.8538(4)	0.1706(8)	0.044(2)
C2'	0.8389(4)	0.7824(4)	0.1580(7)	0.041(2)
C3'	0.8866(5)	0.7770(4)	0.0444(7)	0.048(2)
C4'	0.9220(4)	0.8489(4)	-0.0329(7)	0.048(2)
C5'	0.9069(5)	0.9257(4)	0.0043(8)	0.051(2)
H5'	0.9347(5)	0.9756(4)	-0.0363(8)	0.068
C6'	0.8522(5)	0.9276(4)	0.0985(8)	0.045(2)
C7'	0.8379(5)	1.0087(5)	0.1286(9)	0.048(2)
H7'	0.8699(5)	1.0564(5)	0.0877(9)	0.064
C8'	0.7834(5)	1.1058(4)	0.2414(9)	0.054(2)
H8a'	0.8074(5)	1.1439(4)	0.1690(9)	0.072
H8b'	0.8175(5)	1.1273(4)	0.3414(9)	0.072
C9'	0.6896(5)	1.0983(4)	0.2317(8)	0.048(2)
H9a'	0.6599(5)	1.0967(4)	0.1277(8)	0.064
H9b'	0.6847(5)	1.1461(4)	0.2870(8)	0.064
C10'	0.5898(5)	1.0108(4)	0.3758(8)	0.046(2)
H10'	0.5780(5)	1.0601(4)	0.3989(8)	0.061
C11'	0.5403(5)	0.9324(4)	0.4245(9)	0.048(2)
C12'	0.4755(5)	0.9378(4)	0.4988(8)	0.052(2)
H12'	0.4732(5)	0.9903(4)	0.5298(8)	0.069
C13'	0.4131(5)	0.8616(4)	0.5266(8)	0.053(2)
C14'	0.4162(4)	0.7841(4)	0.4722(7)	0.046(2)
C15'	0.4836(4)	0.7782(4)	0.4013(7)	0.040(2)
C16'	0.5472(5)	0.8522(4)	0.3805(8)	0.044(2)
C17'	0.8214(4)	0.7128(4)	0.2619(7)	0.0432(14)
C18'	0.7378(4)	0.6712(4)	0.2857(9)	0.048(2)
C19'	0.7218(5)	0.6039(4)	0.3798(9)	0.056(2)
H19'	0.6652(5)	0.5769(4)	0.3918(9)	0.075
C20'	0.7896(5)	0.5777(4)	0.4547(9)	0.060(2)
H20'	0.7773(5)	0.5310(4)	0.5127(9)	0.080
C21'	0.8774(5)	0.6192(4)	0.4462(8)	0.050(2)
C22'	0.9486(5)	0.5958(4)	0.5234(8)	0.055(2)
H22'	0.9377(5)	0.5499(4)	0.5831(8)	0.073
C23'	1.0307(5)	0.6359(4)	0.5155(8)	0.057(2)
H23'	1.0761(5)	0.6187(4)	0.5690(8)	0.076
C24'	1.0476(5)	0.7050(4)	0.4243(8)	0.056(2)
H24'	1.1049(5)	0.7343(4)	0.4187(8)	0.074
C25'	0.9812(4)	0.7296(4)	0.3440(7)	0.0432(14)
H25'	0.9945(4)	0.7761(4)	0.2859(7)	0.057
C26'	0.8933(4)	0.6873(3)	0.3460(7)	0.0403(13)
C27'	0.4796(4)	0.6959(4)	0.3367(8)	0.042(2)
C28'	0.4969(4)	0.6336(4)	0.4274(7)	0.045(2)
C29'	0.4870(4)	0.5514(4)	0.3659(8)	0.049(2)
H29'	0.4945(4)	0.5093(4)	0.4297(8)	0.066
C30'	0.4666(5)	0.5339(4)	0.2128(8)	0.056(2)
H30'	0.4622(5)	0.4805(4)	0.1744(8)	0.074
C31'	0.4522(5)	0.5941(4)	0.1138(8)	0.053(2)

C32'	0.4316(5)	0.5783(5)	-0.0431(8)	0.058(2)
H32'	0.4285(5)	0.5256(5)	-0.0833(8)	0.077
C33'	0.4163(6)	0.6371(5)	-0.1377(9)	0.072(2)
H33'	0.4004(6)	0.6240(5)	-0.2410(9)	0.096
C34'	0.4248(5)	0.7204(5)	-0.0771(8)	0.060(2)
H34'	0.4179(5)	0.7621(5)	-0.1422(8)	0.080
C35'	0.4431(5)	0.7388(4)	0.0754(8)	0.055(2)
H35'	0.4451(5)	0.7918(4)	0.1124(8)	0.073
C36'	0.4590(4)	0.6771(4)	0.1791(8)	0.045(2)
C37'	0.9707(5)	0.8440(5)	-0.1421(8)	0.056(2)
H37'	0.9968(5)	0.8929(5)	-0.1867(8)	0.075
C38'	0.9802(5)	0.7683(5)	-0.1839(9)	0.067(2)
H38'	1.0112(5)	0.7655(5)	-0.2577(9)	0.089
C39'	0.9418(6)	0.6941(5)	-0.1121(8)	0.068(2)
H39'	0.9473(6)	0.6423(5)	-0.1394(8)	0.091
C40'	0.8964(5)	0.6991(4)	-0.0025(8)	0.053(2)
H40'	0.8713(5)	0.6500(4)	0.0426(8)	0.071
C41'	0.3462(5)	0.8670(5)	0.5997(9)	0.060(2)
H41'	0.3454(5)	0.9197(5)	0.6336(9)	0.080
C42'	0.2820(5)	0.7938(5)	0.6206(10)	0.071(2)
H42'	0.2387(5)	0.7957(5)	0.6709(10)	0.094
C43'	0.2850(5)	0.7165(5)	0.5629(9)	0.061(2)
H43'	0.2418(5)	0.6669(5)	0.5749(9)	0.081
C44'	0.3461(4)	0.7106(4)	0.4923(8)	0.051(2)
H44'	0.3436(4)	0.6576(4)	0.4546(8)	0.068

$$U_{eq}=1/3[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha]$$

Table S3. Refined Thermal Parameters (U's) for Compound **19**

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Ni	0.0511(5)	0.0377(4)	0.0429(5)	0.0007(3)	0.0068(4)	0.0134(4)
O1	0.047(3)	0.046(3)	0.051(3)	-0.002(2)	0.011(3)	0.015(2)
O2	0.063(3)	0.040(3)	0.049(3)	0.001(2)	0.013(3)	0.021(2)
O3	0.096(4)	0.063(3)	0.036(3)	-0.002(2)	0.013(3)	0.029(3)
O4	0.076(4)	0.070(3)	0.044(3)	-0.009(2)	0.013(3)	0.016(3)
N1	0.062(4)	0.033(3)	0.041(4)	-0.004(2)	0.002(3)	0.011(3)
N2	0.043(3)	0.045(3)	0.036(3)	0.000(2)	-0.001(3)	0.011(2)
C1	0.046(4)	0.048(4)	0.051(5)	-0.001(3)	0.004(4)	0.013(3)
C2	0.045(4)	0.037(3)	0.052(4)	0.001(3)	0.007(3)	0.014(3)
C3	0.053(4)	0.040(3)	0.077(5)	0.001(3)	0.032(4)	0.009(3)
C4	0.062(5)	0.065(5)	0.083(6)	-0.003(4)	0.024(5)	0.014(4)
C5	0.064(5)	0.045(4)	0.074(6)	0.004(3)	0.025(4)	0.012(3)
C6	0.055(5)	0.043(4)	0.052(5)	0.007(3)	0.011(4)	0.010(3)
C7	0.053(5)	0.054(5)	0.061(5)	0.001(4)	0.011(4)	0.022(4)
C8	0.068(5)	0.035(3)	0.039(4)	0.004(3)	0.006(4)	0.004(3)
C9	0.058(4)	0.042(3)	0.052(4)	0.004(3)	0.013(4)	0.018(3)
C10	0.067(5)	0.041(4)	0.043(4)	0.003(3)	0.005(4)	0.014(3)
C11	0.072(5)	0.044(4)	0.041(4)	0.007(3)	0.014(4)	0.030(4)
C12	0.069(5)	0.054(4)	0.040(4)	-0.004(3)	0.009(4)	0.031(4)
C13	0.063(5)	0.062(4)	0.059(5)	0.003(3)	0.031(4)	0.025(4)
C14	0.056(5)	0.054(4)	0.055(5)	0.000(3)	0.009(4)	0.013(3)
C15	0.054(4)	0.041(3)	0.044(4)	-0.003(3)	0.015(3)	0.017(3)
C16	0.064(5)	0.040(4)	0.040(4)	0.002(3)	0.005(4)	0.022(3)
C17	0.053(4)	0.042(3)	0.035(3)	0.010(2)	0.007(3)	0.014(3)
C18	0.067(5)	0.051(4)	0.049(4)	0.001(3)	0.009(4)	0.017(3)
C19	0.069(5)	0.065(5)	0.065(5)	0.022(4)	0.030(4)	0.030(4)
C20	0.078(6)	0.052(4)	0.082(6)	0.025(4)	0.027(5)	0.021(4)
C21	0.068(5)	0.031(3)	0.064(5)	-0.003(3)	0.001(4)	0.017(3)
C22	0.067(5)	0.052(4)	0.075(6)	-0.001(4)	0.000(5)	0.018(3)
C23	0.080(6)	0.046(4)	0.095(7)	-0.016(4)	-0.007(5)	0.018(4)
C24	0.103(7)	0.062(5)	0.052(5)	-0.012(4)	-0.001(5)	0.029(4)
C25	0.073(5)	0.041(3)	0.051(4)	0.000(3)	0.004(4)	0.019(3)
C26	0.057(4)	0.045(3)	0.047(4)	-0.001(3)	0.009(3)	0.020(3)
C27	0.054(4)	0.050(4)	0.050(4)	0.001(3)	0.014(4)	0.010(3)
C28	0.045(4)	0.069(5)	0.073(6)	0.004(4)	0.027(4)	0.021(3)
C29	0.077(6)	0.054(5)	0.077(6)	-0.019(4)	0.014(5)	0.018(4)
C30	0.063(5)	0.048(4)	0.105(8)	-0.013(4)	0.006(5)	0.015(4)
C31	0.056(4)	0.048(4)	0.085(6)	0.003(4)	0.017(4)	0.015(3)
C32	0.083(6)	0.061(5)	0.106(8)	0.027(5)	0.022(6)	0.025(4)
C33	0.103(8)	0.074(6)	0.086(7)	0.020(5)	0.031(6)	0.020(5)
C34	0.100(7)	0.085(6)	0.066(6)	0.025(4)	0.026(5)	0.018(5)
C35	0.064(5)	0.068(5)	0.054(5)	0.007(3)	0.019(4)	0.013(4)
C36	0.050(4)	0.051(4)	0.073(5)	0.021(3)	0.021(4)	0.013(3)
C37	0.062(6)	0.072(6)	0.176(12)	0.011(6)	0.046(7)	0.020(4)

C38	0.069(7)	0.078(7)	0.31(2)	-0.010(9)	0.087(10)	0.015(5)
C39	0.077(7)	0.061(5)	0.207(13)	-0.008(6)	0.048(8)	0.027(5)
C40	0.056(5)	0.055(4)	0.123(8)	-0.003(4)	0.006(5)	0.025(4)
C41	0.103(8)	0.084(6)	0.112(8)	0.005(5)	0.053(7)	0.052(6)
C42	0.060(6)	0.100(7)	0.132(10)	-0.009(6)	0.034(6)	0.020(5)
C43	0.063(5)	0.085(6)	0.105(8)	-0.011(5)	0.027(5)	0.019(4)
C44	0.070(5)	0.062(4)	0.074(6)	-0.004(4)	0.020(4)	0.026(4)
Ni'	0.0453(5)	0.0378(4)	0.0408(5)	0.0037(3)	0.0070(4)	0.0146(3)
O1'	0.041(3)	0.043(2)	0.042(3)	-0.002(2)	0.010(2)	0.015(2)
O2'	0.044(3)	0.048(3)	0.052(3)	0.004(2)	0.012(3)	0.020(2)
O3'	0.040(3)	0.052(3)	0.076(4)	0.004(2)	0.009(2)	0.014(2)
O4'	0.064(3)	0.051(3)	0.042(3)	0.008(2)	0.007(2)	0.015(2)
N1'	0.059(4)	0.039(3)	0.045(4)	0.003(3)	0.004(3)	0.020(3)
N2'	0.046(4)	0.035(3)	0.046(3)	0.009(2)	0.002(3)	0.014(2)
C1'	0.047(4)	0.051(4)	0.034(4)	0.003(3)	0.002(3)	0.021(3)
C2'	0.041(4)	0.049(4)	0.032(3)	-0.001(3)	0.006(3)	0.014(3)
C3'	0.054(4)	0.057(4)	0.037(4)	0.006(3)	0.008(3)	0.023(3)
C4'	0.050(4)	0.064(4)	0.038(4)	0.003(3)	0.016(3)	0.026(3)
C5'	0.046(4)	0.059(4)	0.048(4)	0.013(3)	0.017(4)	0.012(3)
C6'	0.047(4)	0.050(4)	0.039(4)	0.003(3)	0.004(3)	0.021(3)
C7'	0.053(5)	0.044(4)	0.037(4)	0.007(3)	-0.006(4)	0.010(3)
C8'	0.063(5)	0.044(4)	0.058(5)	0.003(3)	0.007(4)	0.022(3)
C9'	0.070(5)	0.036(3)	0.042(4)	0.009(3)	0.013(3)	0.022(3)
C10'	0.044(4)	0.049(4)	0.047(4)	0.002(3)	0.011(4)	0.019(3)
C11'	0.046(4)	0.051(4)	0.050(4)	0.009(3)	0.013(4)	0.017(3)
C12'	0.060(5)	0.046(4)	0.058(5)	0.009(3)	0.013(4)	0.029(3)
C13'	0.056(4)	0.061(4)	0.051(4)	0.007(3)	0.019(4)	0.028(3)
C14'	0.050(4)	0.046(4)	0.041(4)	0.005(3)	-0.005(3)	0.021(3)
C15'	0.037(3)	0.051(4)	0.038(4)	-0.002(3)	0.015(3)	0.017(3)
C16'	0.049(4)	0.040(3)	0.043(4)	-0.010(3)	-0.004(3)	0.021(3)
C17'	0.050(4)	0.041(3)	0.040(4)	-0.002(2)	0.007(3)	0.018(3)
C18'	0.037(4)	0.038(3)	0.069(5)	-0.001(3)	0.003(4)	0.017(3)
C19'	0.047(4)	0.050(4)	0.078(5)	0.011(3)	0.022(4)	0.017(3)
C20'	0.053(4)	0.060(4)	0.069(5)	0.018(3)	0.018(4)	0.017(3)
C21'	0.058(4)	0.046(3)	0.046(4)	0.003(3)	0.006(3)	0.022(3)
C22'	0.058(4)	0.060(4)	0.051(4)	0.018(3)	0.011(4)	0.026(3)
C23'	0.049(4)	0.061(4)	0.061(5)	0.011(3)	-0.003(4)	0.025(3)
C24'	0.048(4)	0.059(4)	0.063(5)	0.002(3)	0.008(4)	0.023(3)
C25'	0.036(3)	0.046(3)	0.051(4)	-0.003(3)	0.008(3)	0.017(3)
C26'	0.045(4)	0.041(3)	0.037(3)	0.000(2)	0.001(3)	0.021(2)
C27'	0.037(3)	0.043(3)	0.043(4)	0.001(3)	0.006(3)	0.010(3)
C28'	0.045(4)	0.048(3)	0.037(4)	0.009(3)	0.007(3)	0.008(3)
C29'	0.043(4)	0.043(4)	0.059(5)	0.013(3)	0.004(3)	0.013(3)
C30'	0.057(4)	0.052(4)	0.054(5)	-0.009(3)	0.000(4)	0.018(3)
C31'	0.057(4)	0.044(4)	0.053(4)	-0.003(3)	0.008(4)	0.014(3)
C32'	0.065(5)	0.068(4)	0.044(4)	-0.004(3)	0.013(4)	0.024(4)
C33'	0.083(6)	0.079(5)	0.045(5)	-0.014(4)	0.012(4)	0.014(4)

C34'	0.060(5)	0.068(5)	0.041(4)	0.013(3)	-0.001(4)	0.009(3)
C35'	0.053(4)	0.053(4)	0.048(4)	0.010(3)	-0.002(3)	0.009(3)
C36'	0.042(4)	0.050(4)	0.042(4)	-0.002(3)	0.007(3)	0.014(3)
C37'	0.054(4)	0.079(5)	0.046(4)	0.012(3)	0.017(4)	0.031(4)
C38'	0.063(5)	0.102(6)	0.058(5)	0.020(4)	0.025(4)	0.050(4)
C39'	0.088(6)	0.089(5)	0.042(4)	-0.002(4)	0.012(4)	0.049(5)
C40'	0.068(5)	0.057(4)	0.047(4)	0.002(3)	0.023(4)	0.029(3)
C41'	0.049(4)	0.075(5)	0.059(5)	-0.005(3)	0.012(4)	0.025(3)
C42'	0.041(4)	0.102(6)	0.064(5)	0.000(4)	0.006(4)	0.020(4)
C43'	0.053(5)	0.068(5)	0.059(5)	-0.003(3)	0.008(4)	0.018(3)
C44'	0.039(4)	0.060(4)	0.050(4)	0.002(3)	0.006(3)	0.013(3)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)].$$

Table S4. Bond Distances (Å) in Compound 19

Ni-N2	1.823(6)	Ni-N1	1.832(7)	Ni-O2	1.846(5)
Ni-O1	1.855(5)	O1-C1	1.342(9)	O2-C16	1.345(9)
O3-C18	1.377(8)	O4-C28	1.393(9)	N1-C7	1.287(10)
N1-C8	1.480(9)	N2-C10	1.265(10)	N2-C9	1.496(8)
C1-C6	1.401(11)	C1-C2	1.443(10)	C2-C3	1.399(10)
C2-C17	1.514(8)	C3-C4	1.430(10)	C3-C40	1.433(10)
C4-C5	1.399(10)	C4-C37	1.422(12)	C5-C6	1.344(11)
C6-C7	1.469(10)	C8-C9	1.447(10)	C10-C11	1.447(11)
C11-C12	1.370(11)	C11-C16	1.438(9)	C12-C13	1.397(10)
C13-C41	1.421(11)	C13-C14	1.440(9)	C14-C15	1.407(10)
C14-C44	1.418(10)	C15-C16	1.401(10)	C15-C27	1.496(9)
C17-C18	1.359(10)	C17-C26	1.458(8)	C18-C19	1.401(10)
C19-C20	1.381(11)	C20-C21	1.376(11)	C21-C26	1.409(9)
C21-C22	1.420(10)	C22-C23	1.305(12)	C23-C24	1.424(12)
C24-C25	1.389(9)	C25-C26	1.410(10)	C27-C28	1.379(10)
C27-C36	1.420(10)	C28-C29	1.415(10)	C29-C30	1.386(12)
C30-C31	1.411(12)	C31-C36	1.420(9)	C31-C32	1.430(12)
C32-C33	1.348(13)	C33-C34	1.373(12)	C34-C35	1.363(11)
C35-C36	1.442(11)	C37-C38	1.378(13)	C38-C39	1.368(14)
C39-C40	1.361(12)	C41-C42	1.338(13)	C42-C43	1.409(12)
C43-C44	1.348(11)	Ni'-N1'	1.821(7)	Ni'-O2'	1.835(5)
Ni'-N2'	1.847(6)	Ni'-O1'	1.849(4)	O1'-C1'	1.332(9)
O2'-C16'	1.333(9)	O3'-C18'	1.374(8)	O4'-C28'	1.356(7)
N1'-C7'	1.288(10)	N1'-C8'	1.486(9)	N2'-C10'	1.305(9)
N2'-C9'	1.507(8)	C1'-C2'	1.387(9)	C1'-C6'	1.424(10)
C2'-C3'	1.436(9)	C2'-C17'	1.489(9)	C3'-C4'	1.412(9)
C3'-C40'	1.426(9)	C4'-C37'	1.411(9)	C4'-C5'	1.425(9)
C5'-C6'	1.368(10)	C6'-C7'	1.470(10)	C8'-C9'	1.496(10)
C10'-C11'	1.430(10)	C11'-C12'	1.396(11)	C11'-C16'	1.434(9)

C12'-C13'	1.421(10)	C13'-C14'	1.397(9)	C13'-C41'	1.420(10)
C14'-C15'	1.418(9)	C14'-C44'	1.439(9)	C15'-C16'	1.389(10)
C15'-C27'	1.462(9)	C17'-C18'	1.397(9)	C17'-C26'	1.454(8)
C18'-C19'	1.401(10)	C19'-C20'	1.378(10)	C20'-C21'	1.414(10)
C21'-C22'	1.405(9)	C21'-C26'	1.446(8)	C22'-C23'	1.327(10)
C23'-C24'	1.407(10)	C24'-C25'	1.362(9)	C25'-C26'	1.405(8)
C27'-C28'	1.387(9)	C27'-C36'	1.416(9)	C28'-C29'	1.422(9)
C29'-C30'	1.374(10)	C30'-C31'	1.389(10)	C31'-C32'	1.403(10)
C31'-C36'	1.462(9)	C32'-C33'	1.351(11)	C33'-C34'	1.442(10)
C34'-C35'	1.372(10)	C35'-C36'	1.441(9)	C37'-C38'	1.376(10)
C38'-C39'	1.425(11)	C39'-C40'	1.376(10)	C41'-C42'	1.385(11)
C42'-C43'	1.402(11)	C43'-C44'	1.325(10)		

Table S5. Bond Angles (deg) in Compound **19**

N2-Ni-N1	86.1(3)	N2-Ni-O2	94.9(2)	N1-Ni-O2	176.8(3)
N2-Ni-O1	178.0(3)	N1-Ni-O1	94.9(3)	O2-Ni-O1	84.2(2)
C1-O1-Ni	125.4(4)	C16-O2-Ni	127.6(4)	C7-N1-C8	120.3(7)
C7-N1-Ni	126.9(5)	C8-N1-Ni	112.8(5)	C10-N2-C9	118.8(6)
C10-N2-Ni	127.8(5)	C9-N2-Ni	113.4(5)	O1-C1-C6	124.4(7)
O1-C1-C2	118.1(7)	C6-C1-C2	117.5(8)	C3-C2-C1	119.0(6)
C3-C2-C17	120.7(6)	C1-C2-C17	120.0(6)	C2-C3-C4	119.7(6)
C2-C3-C40	121.9(6)	C4-C3-C40	118.2(7)	C5-C4-C37	121.5(8)
C5-C4-C3	119.5(8)	C37-C4-C3	119.0(7)	C6-C5-C4	120.0(7)
C5-C6-C1	123.4(7)	C5-C6-C7	116.8(7)	C1-C6-C7	119.8(8)
N1-C7-C6	125.6(8)	C9-C8-N1	107.2(5)	C8-C9-N2	106.2(6)
N2-C10-C11	125.4(7)	C12-C11-C16	119.5(7)	C12-C11-C10	119.2(7)
C16-C11-C10	121.3(7)	C11-C12-C13	122.7(7)	C12-C13-C41	122.1(7)
C12-C13-C14	117.6(7)	C41-C13-C14	119.8(7)	C15-C14-C44	122.9(7)
C15-C14-C13	120.7(7)	C44-C14-C13	116.4(7)	C16-C15-C14	119.3(6)
C16-C15-C27	120.6(6)	C14-C15-C27	120.0(6)	O2-C16-C15	119.2(6)
O2-C16-C11	121.0(7)	C15-C16-C11	119.7(7)	C18-C17-C26	117.9(6)
C18-C17-C2	122.4(6)	C26-C17-C2	119.6(6)	C17-C18-O3	121.7(7)
C17-C18-C19	122.5(7)	O3-C18-C19	115.7(7)	C20-C19-C18	118.8(8)
C21-C20-C19	121.5(7)	C20-C21-C26	119.9(6)	C20-C21-C22	121.6(7)
C26-C21-C22	118.5(7)	C23-C22-C21	122.3(8)	C22-C23-C24	121.1(8)
C25-C24-C23	118.4(8)	C24-C25-C26	121.1(7)	C21-C26-C25	118.5(6)
C21-C26-C17	118.8(6)	C25-C26-C17	122.6(6)	C28-C27-C36	117.6(7)
C28-C27-C15	121.8(7)	C36-C27-C15	120.5(7)	C27-C28-O4	121.7(7)
C27-C28-C29	122.6(7)	O4-C28-C29	115.6(7)	C30-C29-C28	118.2(8)
C29-C30-C31	121.4(7)	C30-C31-C36	118.3(7)	C30-C31-C32	123.0(8)
C36-C31-C32	118.6(8)	C33-C32-C31	120.9(8)	C32-C33-C34	121.2(8)
C35-C34-C33	121.2(9)	C34-C35-C36	120.4(8)	C27-C36-C31	120.8(8)
C27-C36-C35	121.4(7)	C31-C36-C35	117.7(6)	C38-C37-C4	121.4(9)
C39-C38-C37	117.6(9)	C40-C39-C38	125.4(9)	C39-C40-C3	118.2(8)
C42-C41-C13	120.9(8)	C41-C42-C43	119.8(9)	C44-C43-C42	121.4(8)

C43-C44-C14	121.7(7)	N1'-Ni'-O2'	175.4(3)	N1'-Ni'-N2'	86.0(3)
O2'-Ni'-N2'	94.4(2)	N1'-Ni'-O1'	94.0(2)	O2'-Ni'-O1'	85.9(2)
N2'-Ni'-O1'	176.0(3)	C1'-O1'-Ni'	127.8(4)	C16'-O2'-Ni'	127.9(4)
C7'-N1'-C8'	118.8(7)	C7'-N1'-Ni'	126.2(5)	C8'-N1'-Ni'	114.8(5)
C10'-N2'-C9'	119.6(6)	C10'-N2'-Ni'	127.0(5)	C9'-N2'-Ni'	113.3(5)
O1'-C1'-C2'	119.5(6)	O1'-C1'-C6'	121.2(6)	C2'-C1'-C6'	119.2(7)
C1'-C2'-C3'	118.8(6)	C1'-C2'-C17'	122.2(6)	C3'-C2'-C17'	119.0(6)
C4'-C3'-C40'	116.7(6)	C4'-C3'-C2'	120.7(6)	C40'-C3'-C2'	122.5(6)
C37'-C4'-C3'	120.7(6)	C37'-C4'-C5'	121.8(6)	C3'-C4'-C5'	117.5(6)
C6'-C5'-C4'	121.3(7)	C5'-C6'-C1'	120.8(7)	C5'-C6'-C7'	118.2(7)
C1'-C6'-C7'	120.9(7)	N1'-C7'-C6'	124.8(7)	N1'-C8'-C9'	105.7(6)
C8'-C9'-N2'	105.7(5)	N2'-C10'-C11'	123.1(7)	C12'-C11'-C10'	115.3(7)
C12'-C11'-C16'	121.6(7)	C10'-C11'-C16'	122.4(8)	C11'-C12'-C13'	119.0(6)
C14'-C13'-C41'	122.1(7)	C14'-C13'-C12'	118.7(7)	C41'-C13'-C12'	119.1(7)
C13'-C14'-C15'	122.4(6)	C13'-C14'-C44'	115.5(7)	C15'-C14'-C44'	122.2(6)
C16'-C15'-C14'	118.9(6)	C16'-C15'-C27'	121.1(6)	C14'-C15'-C27'	119.6(6)
O2'-C16'-C15'	119.2(6)	O2'-C16'-C11'	121.7(7)	C15'-C16'-C11'	119.1(7)
C18'-C17'-C26'	117.6(6)	C18'-C17'-C2'	122.5(6)	C26'-C17'-C2'	119.9(6)
O3'-C18'-C17'	122.6(6)	O3'-C18'-C19'	115.3(6)	C17'-C18'-C19'	122.0(6)
C20'-C19'-C18'	120.2(7)	C19'-C20'-C21'	122.1(6)	C22'-C21'-C20'	124.0(6)
C22'-C21'-C26'	118.6(6)	C20'-C21'-C26'	117.3(6)	C23'-C22'-C21'	123.4(6)
C22'-C23'-C24'	118.6(6)	C25'-C24'-C23'	120.9(7)	C24'-C25'-C26'	122.2(6)
C25'-C26'-C21'	116.1(5)	C25'-C26'-C17'	123.1(6)	C21'-C26'-C17'	120.6(6)
C28'-C27'-C36'	117.3(6)	C28'-C27'-C15'	121.3(6)	C36'-C27'-C15'	121.4(6)
O4'-C28'-C27'	119.3(6)	O4'-C28'-C29'	118.9(5)	C27'-C28'-C29'	121.6(6)
C30'-C29'-C28'	120.2(6)	C29'-C30'-C31'	121.7(6)	C30'-C31'-C32'	123.0(6)
C30'-C31'-C36'	117.3(7)	C32'-C31'-C36'	119.8(6)	C33'-C32'-C31'	122.1(7)
C32'-C33'-C34'	119.5(7)	C35'-C34'-C33'	120.7(7)	C34'-C35'-C36'	121.0(7)
C27'-C36'-C35'	121.5(6)	C27'-C36'-C31'	121.7(6)	C35'-C36'-C31'	116.8(6)
C38'-C37'-C4'	121.3(7)	C37'-C38'-C39'	118.9(8)	C40'-C39'-C38'	120.0(7)
C39'-C40'-C3'	122.3(7)	C42'-C41'-C13'	119.9(7)	C41'-C42'-C43'	117.5(8)
C44'-C43'-C42'	123.3(8)	C43'-C44'-C14'	121.7(7)		

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