

Supporting Information

for

Synthesis and stereochemical assignments of diastereomeric Ni(II) complexes of glycine Schiff base with (*R*)-2-(*N*-{2-[*N*-alkyl-*N*-(1-phenylethyl)amino]acetyl}amino)benzophenone; a case of configurationally stable stereogenic nitrogen

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Experimental data for compounds 4c–f, 5c–e and 6c–e.

(S)-N-(2-benzoylphenyl)-2-(ethyl-(1-phenylethyl)amino)acetamide (4c):

From **4a** (2.58 g, 7.20 mmol) and EtI (2.31 mL, 28.8 mmol), 1.0 g (35.9%) of **4c**. Colorless oil; $[\alpha]_D^{25} = +36.0$ ($c = 1.25$, CHCl_3). $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.16 (t, $J = 7.1$ Hz, 3H), 1.44 (d, $J = 6.8$ Hz, 3H), 2.56–2.69 (m, 1H), 2.72–2.85 (m, 1H), 3.16 (d, $J = 17.4$ Hz, 1H), 3.26 (d, $J = 17.3$ Hz, 1H), 4.02 (q, $J = 6.7$ Hz, 1H), 7.12 (td, $J = 7.6, 1.0$ Hz, 1H), 7.16–7.20 (m, 3H), 7.44–7.49 (m, 2H), 7.50–7.60 (m, 4H), 7.66 (tt, $J = 7.4, 1.3$ Hz, 1H), 7.86 (d, $J = 7.5$ Hz, 2H), 8.65 (d, $J = 8.4$ Hz, 1H), 11.54 (br, 1H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 11.9, 17.1, 46.8, 55.1, 59.9, 121.2, 121.8, 125.0, 126.8, 127.6, 127.9, 128.1, 129.9, 131.9, 132.4, 132.9, 138.2, 138.7, 142.5, 171.9, 197.5. HRMS: calcd for $\text{C}_{25}\text{H}_{27}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 387.2073, found 387.2087.

(S)-N-(2-benzoylphenyl)-2-((1-phenylethyl)(propyl)amino)acetamide (4d):

From **4a** (3.68 g, 10.25 mmol) and *n*-PrBr (1.4 mL, 15.38 mmol), 1.01 g (15.1%) of **4d**. Colorless oil. $[\alpha]_D^{25} = +28.8$ ($c = 1.02$, CHCl_3). $^1\text{H-NMR}$ (300 MHz, CDCl_3): 0.81 (t, $J = 7.5$ Hz, 3H), 1.42 (d, $J = 6.6$ Hz, 3H), 1.61 (sext, $J = 8.1$ Hz, 2H), 2.40–2.55 (m, 1H), 2.58–2.70 (m, 1H), 3.14 (d, $J = 17.4$ Hz, 1H), 3.25 (d, $J = 17.4$ Hz, 1H), 3.98 (q, $J = 6.6$ Hz, 1H), 7.07–7.17 (m, 4H), 7.42–7.54 (m, 6H), 7.60–7.63 (m, 1H), 7.82–7.86 (m, 2H), 8.64 (dd, $J = 8.7, 0.9$ Hz, 1H), 11.45 (br, 1H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 11.6, 17.1, 20.3, 55.3, 55.8, 60.5, 121.4, 121.9, 125.3, 126.9, 127.8, 128.0, 128.1, 130.0, 131.9, 132.5, 133.0, 138.2, 138.7, 142.4, 172.0, 197.6. HRMS: calcd for $\text{C}_{26}\text{H}_{29}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 401.2229, found 401.2233.

(S)-N-(2-benzoylphenyl)-2-(benzyl-(1-phenylethyl)amino)acetamide (4e):

From **4a** (2.61 g, 7.28 mmol) and BnBr (1.32 mL, 10.92 mmol), 3.0 g (91.7%) of **4e**. Colorless oil; $[\alpha]_D^{25} = +28.1$ ($c = 3.81$, CHCl_3). $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.43 (d, $J = 6.9$ Hz, 3H), 1.47 (s, 1H), 3.02 (d, $J = 16.8$ Hz, 1H), 3.22 (d, $J =$

16.8 Hz, 1H), 3.36 (d, J = 12.9 Hz, 1H), 3.72 (d, J = 13.2 Hz, 1H), 3.84 (q, J = 7.2 Hz, 1H), 6.96–7.01 (m, 4H), 7.13–7.20 (m, 3H), 7.37–7.48 (m, 8H), 7.55–7.57 (m, 1H), 7.78–7.81 (m, 2H), 8.44 (dd, J = 7.5, 1.2 Hz, 1H), 11.22 (br, 1H). ^{13}C -NMR (75 MHz, CDCl_3): 17.1, 55.4, 56.9, 60.8, 121.3, 121.8, 125.1, 127.0, 127.9, 128.1, 128.1, 129.3, 130.1, 131.8, 132.6, 132.9, 137.8, 138.1, 138.7, 141.4, 171.4, 197.6. HRMS: calcd for $\text{C}_{30}\text{H}_{29}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 449.2229, found 449.2250.

(S)-N-(2-benzoylphenyl)-2-(phenethyl-(1-phenylethyl)amino)acetamide (4f):

From **4a** (3.07 g, 7.36 mmol) and $\text{Ph}(\text{CH}_2)_2\text{Br}$ (1.76 mL, 12.85 mmol), 505 mg (14.8%) of **4f**. Colorless oil; $[\alpha]_{\text{D}}^{25} = +6.1$ (c = 0.59, CHCl_3). ^1H -NMR (300 MHz, CDCl_3): 1.46 (d, J = 6.3 Hz, 3H), 2.72–2.93 (m, 3H), 3.22 (d, J = 17.1 Hz, 1H), 3.32 (d, J = 17.1 Hz, 1H), 4.09 (q, J = 6.9 Hz, 1H), 6.99–7.09 (m, 2H), 7.10–7.37 (m, 9H), 7.38–7.46 (m, 3H), 7.47–7.62 (m, 8H), 8.60 (dd, J = 9.6, 2.1 Hz, 1H), 11.55 (br, 1H). ^{13}C -NMR (75 MHz, CDCl_3): 17.3, 33.7, 55.2, 55.8, 60.4, 121.5, 122.1, 125.3, 125.9, 127.2, 127.9, 128.2, 128.3, 128.5, 130.1, 132.2, 132.6, 133.2, 138.4, 138.8, 139.7, 142.3, 171.8, 197.8. HRMS: calcd for $\text{C}_{31}\text{H}_{31}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 463.2386, found 463.2398.

5c and 6c: From **4c** (240 mg, 0.62 mmol), 210 mg (67.7 %) of a 61:39 mixture of **5c** and **6c**. Data of **5c**: Red solid. M.p. 207–210 °C. $[\alpha]_{\text{D}}^{25} = -150.8$ (c = 1.0, CH_2Cl_2). ^1H -NMR (300 MHz, CDCl_3): 2.05–2.20 (m, 1H), 2.41 (t, J = 6.9 Hz, 3H), 2.59 (d, J = 17.1 Hz, 1H), 2.79 (d, J = 6.6 Hz, 3H), 2.85–2.95 (m, 1H), 3.76 (d, J = 6.0 Hz, 2H), 3.95 (d, J = 17.1 Hz, 1H), 4.14 (q, J = 6.9 Hz, 1H), 6.77–6.90 (m, 2H), 7.06–7.09 (m, 2H), 7.31–7.34 (m, 6H), 7.35–7.54 (m, 3H), 8.63 (dd, J = 8.7, 1.2 Hz, 1H). ^{13}C -NMR (75 MHz, CDCl_3): 14.0, 20.8, 55.0, 56.5, 61.3, 64.2, 121.0, 124.2, 125.1, 125.9, 126.0, 128.5, 128.9, 129.5, 129.6, 129.8, 132.6, 133.5, 134.7, 134.9, 142.7, 171.8, 177.2, 180.0. HRMS: calcd for $\text{C}_{27}\text{H}_{28}\text{N}_3\text{O}_3\text{Ni}$

[M + H]⁺ 500.1484, found 500.1485. Data of **6c**: Red solid. M.p. 210-213 °C. $[\alpha]_D^{25} = +1226.4$ (*c* = 1.0, CH₂Cl₂). ¹H-NMR (300 MHz, CDCl₃): 1.78 (d, *J* = 6.9 Hz, 3H), 2.05–2.20 (m, 1H), 2.36 (t, *J* = 6.9 Hz, 3H), 2.85–2.95 (m, 1H), 3.35 (d, *J* = 17.4 Hz, 1H), 3.48 (d, *J* = 17.1 Hz, 1H), 3.64 (d, *J* = 19.8 Hz, 1H), 3.75 (d, *J* = 20.1 Hz, 1H), 4.50 (q, *J* = 7.2 Hz, 1H), 6.68–6.75 (m, 2H), 6.94–7.06 (m, 2H), 7.19–7.51 (m, 6H), 8.06 (d, *J* = 7.2 Hz, 2H), 8.35 (d, *J* = 7.8 Hz, 1H). ¹³C-NMR (75 MHz, CDCl₃): 13.6, 14.1, 50.6, 55.2, 61.0, 66.7, 120.8, 124.2, 125.1, 125.8, 126.1, 128.9, 129.2, 129.4, 129.6, 129.7, 130.0, 132.2, 133.1, 134.7, 138.7, 142.4, 171.5, 177.2, 179.1. HRMS: calcd for C₂₇H₂₈N₃O₃Ni [M + H]⁺ 500.1484, found 500.1493.

5d and 6d: From **4d** (1.0 g, 2.50 mmol), 901 mg (70.1 %) of a 74:26 mixture of **5d** and **6d**. Data of **5d**: Red solid. M.p. 155-157 °C. $[\alpha]_D^{25} = -55.0$ (*c* = 1.0, CH₂Cl₂). ¹H-NMR (300 MHz, CDCl₃): 1.10 (t, *J* = 7.5 Hz, 3H), 1.98 (td, *J* = 4.2, 1.5 Hz, 1H), 2.45–2.60 (m, 1H), 2.56 (d, *J* = 17.1 Hz, 1H), 2.73 (td, *J* = 4.2, 1.5 Hz, 1H), 2.80 (d, *J* = 6.9 Hz, 3H), 3.76 (d, *J* = 7.8 Hz, 2H), 3.98 (d, *J* = 17.1 Hz, 1H), 4.05–4.15 (m, 1H), 4.13 (q, *J* = 6.9 Hz, 1H), 6.74–6.80 (m, 1H), 6.82–6.91 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.05–7.10 (m, 2H), 7.29–7.37 (m, 5H), 7.50–7.55 (m, 3H), 8.65 (dd, *J* = 8.7, 0.9 Hz, 1H). ¹³C-NMR (75 MHz, CDCl₃): 11.8, 20.7, 22.2, 56.9, 61.2, 62.5, 64.1, 120.9, 124.1, 125.0, 125.8, 125.9, 128.4, 128.9, 129.4, 129.5, 129.8, 132.5, 133.4, 134.6, 134.8, 142.6, 171.7, 177.2, 179.9. HRMS: calcd for C₂₈H₃₀N₃O₃Ni [M + H]⁺ 514.1641, found 514.1642. Data of **6d**: Red solid. M.p. 156-158 °C. $[\alpha]_D^{25} = +1033.3$ (*c* = 1.0, CH₂Cl₂). ¹H-NMR (300 MHz, CDCl₃): 1.15 (t, *J* = 7.5 Hz, 3H), 1.72 (d, *J* = 6.9 Hz, 3H), 1.99 (td, *J* = 4.2, 1.5 Hz, 1H), 2.30–2.45 (m, 1H), 2.79 (td, *J* = 4.2, 1.5 Hz, 1H), 3.30 (d, *J* = 17.1 Hz, 1H), 3.55 (d, *J* = 17.1 Hz, 1H), 3.68 (d, *J* = 20.1 Hz, 2H), 4.05–4.20 (m, 1H), 6.64–6.92 (m, 1H), 4.65 (q, *J* = 6.9 Hz, 1H), 6.60–6.80 (m, 2H), 6.96–7.00 (m,

1H), 7.16–7.22 (m, 1H), 7.30–7.35 (m, 1H), 7.45–7.51 (m, 4H), 8.06 (d, $J = 6.9$ Hz, 1H), 8.35 (dd, $J = 8.7, 0.9$ Hz, 1H). ^{13}C -NMR (75 MHz, CDCl_3): 12.0, 13.7, 22.1, 55.9, 58.6, 61.1, 66.4, 120.7, 124.1, 125.0, 125.8, 126.0, 128.9, 129.2, 129.4, 129.6, 129.6, 130.0, 132.2, 133.1, 134.6, 138.9, 142.4, 171.4, 177.1, 179.3. HRMS: calcd for $\text{C}_{28}\text{H}_{30}\text{N}_3\text{O}_3\text{Ni}$ $[\text{M} + \text{H}]^+$ 514.1641, found 514.1649.

5e and 6e: From **4e** (1.0 g, 2.23 mmol), 287 mg (31.5 %) of a 76:24 mixture of **5e** and **6e**. Data of **5e**: Red solid. M.p. 136–138 °C. $[\alpha]_{\text{D}}^{25} = +303.6$ ($c = 1.0$, CH_2Cl_2). ^1H -NMR (300 MHz, CDCl_3): 2.81 (d, $J = 17.4$ Hz, 1H), 2.89 (d, $J = 6.9$ Hz, 3H), 2.95 (d, $J = 12.0$ Hz, 1H), 3.72 (d, $J = 20.1$ Hz, 1H), 3.85 (d, $J = 19.8$ Hz, 1H), 4.01 (d, $J = 17.1$ Hz, 1H), 4.27 (t, $J = 7.2$ Hz, 1H), 4.29 (d, $J = 10.5$ Hz, 1H), 6.63–6.75 (m, 2H), 7.02–7.27 (m, 4H), 7.38–7.53 (m, 10H), 8.11 (d, $J = 8.1$ Hz, 1H), 8.32 (d, $J = 8.4$ Hz, 2H). ^{13}C -NMR (75 MHz, CDCl_3): 20.7, 56.4, 61.2, 65.1, 65.6, 120.6, 124.1, 124.8, 125.8, 126.1, 128.6, 128.9, 129.1, 129.2, 129.4, 129.6, 130.1, 132.1, 132.3, 132.9, 134.6, 134.8, 142.2, 171.5, 177.2, 179.3. HRMS: calcd for $\text{C}_{32}\text{H}_{30}\text{N}_3\text{O}_3\text{Ni}$ $[\text{M} + \text{H}]^+$ 562.1641, found 562.1639. Data of **6e**: Red solid. M.p. 142–145 °C. $[\alpha]_{\text{D}}^{25} = +361.5$ ($c = 1.0$, CH_2Cl_2). ^1H -NMR (300 MHz, CDCl_3): 2.82 (d, $J = 17.1$ Hz, 1H), 2.89 (d, $J = 6.9$ Hz, 3H), 2.95 (d, $J = 12.0$ Hz, 1H), 3.72 (d, $J = 20.1$ Hz, 1H), 3.85 (d, $J = 20.1$ Hz, 1H), 4.01 (d, $J = 17.4$ Hz, 1H), 4.27 (t, $J = 7.2$ Hz, 1H), 4.30 (d, $J = 11.1$ Hz, 1H), 6.64–7.11 (m, 6H), 7.38–7.53 (m, 12H), 8.11 (d, $J = 8.7$ Hz, 1H), 8.32 (d, $J = 6.9$ Hz, 2H). ^{13}C -NMR (75 MHz, CDCl_3): 20.7, 56.4, 61.2, 65.2, 65.7, 120.6, 124.2, 124.9, 125.8, 126.1, 128.7, 129.0, 129.2, 129.2, 129.4, 129.6, 130.1, 132.1, 132.9, 134.6, 134.8, 142.3, 171.5, 177.3, 179.3. HRMS: calcd for $\text{C}_{32}\text{H}_{30}\text{N}_3\text{O}_3\text{Ni}$ $[\text{M} + \text{H}]^+$ 562.1641, found 562.1638.