Supporting Information

Samarium-Promoted Coupling of 1,10-Phenanthroline with Carbonyl Compounds for Synthesis of New Ligands

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General Procedures: All NMR spectra (300 MHz for ^1H NMR and 75 MHz, for ^{13}C NMR) were recorded in CDCl_3 and chemical shifts were given relative to TMS (0.00 for ^1H) and CDCl_3 (77.23 for ^{13}C) unless otherwise stated. THF was distilled from sodium-benzophenone ketyl or purified by a solvent purification system; CH_2Cl_2 was distilled from CaH . Column chromatography was performed with 60 Å silica gel (230-400 mesh). Samarium (II) iodide was synthesized using literature protocol¹ from samarium metal and 1,2-diiodomethane giving a 0.1M solution in THF. All reagents were purchased except for methyl 7-oxoheptanoate and methyl 8-oxooctanoate which were prepared using literature protocol.²

2-(1-ethyl-1-hydroxypropyl)-1,10-phenanthroline (1b).

Through use of the above General Procedure A, 3-pentanone (0.105 g, 1.22 mmol) was converted into 0.132 g (89%) of **1b** as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 9.21 (dd, $J = 4.5, 1.8$ Hz, 1H), 8.26 (one d, $J = 8.40$ Hz, 1H, one dd, $J = 8.4, 1.8$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.79 (d, $J = 8.8$ Hz, 1H), 7.64 (dd, $J = 8.1, 4.2$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 2.01 (dq, $J = 7.5, 2.1$ Hz, 4H), 0.77 (t, $J = 7.20$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.1, 150.1, 145.5, 143.7, 137.0, 136.2, 129.0, 127.3, 126.2, 122.9, 119.5, 77.3, 34.7, 8.0; IR (CHCl_3) 3417, 2967, 2929, 912 cm^{-1} ; HRMS (FAB⁺, m/z) calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}$ ($M + \text{H}^+$): 267.1497. Found: 267.1497.

2-(1-hydroxy-1-methylpropyl)-1,10-phenanthroline (1c).

Through use of the above General Procedure A, 2-butanone (0.088 g, 1.22 mmol) was converted into 0.101 g (73%) of **1c** as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 9.20 (dd, $J = 4.50, 1.8$ Hz, 1H), 8.28 (d, $J = 8.4$ Hz, 1H), 8.28 (dd, $J = 8.10, 1.80$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.79 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.40$ Hz, 1H), 7.65 (dd, $J = 8.1, 4.2$ Hz, 1H), 2.02 (two dq, $J = 13.5, 5.4$ Hz, 2H), 1.67 (s, 3H), 0.82 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.4, 150.2, 145.6, 143.7, 137.1, 136.2, 129.0, 127.3, 126.3, 126.2, 123.0, 119.3, 74.6, 35.9, 29.2, 8.2.

2-(1-hydroxy-1,2-dimethylpropyl)-1,10-phenanthroline (1d).

Through use of the above General Procedure A, 3-methyl-2-butanone (0.105 g, 1.22 mmol) was converted into 0.105 g (71%) of **1d** as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 9.18 (dd, $J = 4.4, 1.8$ Hz, 1H), 8.26 (d, $J = 8.1$ Hz, 1H), 8.26 (dd, $J = 8.10, 1.80$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 7.65 (d, $J = 8.70$ Hz, 1H), 7.64 (dd, $J = 8.10, 4.50$ Hz, 1H), 6.10 (br s, 1H), 2.19 (sep, $J = 6.60$ Hz, 1H), 1.64 (s, 3H), 1.12 (d, $J = 6.60$ Hz, 3H), 0.71 (d, $J = 6.60$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ

165.8, 150.2, 145.7, 143.6, 136.9, 136.1, 129.0, 127.3, 126.2, 126.2, 122.9, 119.5, 76.3, 38.4, 26.4, 17.5, 17.1.

2-(1-hydroxy-1,2,2-trimethylpropyl)-1,10-phenanthroline (1e).

Through use of the above general procedure A, 3,3-dimethyl-2-butanone (0.122 g, 1.22 mmol) was converted into 0.061 g (40%) of **1e** as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 9.17 (dd, $J = 4.2, 1.8$ Hz, 1H), 8.26 (dd, $J = 8.4, 1.5$ Hz, 1H), 8.23 (d, $J = 8.40$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.63 (dd, $J = 8.1, 4.5$ Hz, 1H), 1.71 (s, 3H), 1.02 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.2, 150.1, 145.8, 143.3, 136.0, 135.7, 129.0, 127.2, 126.3, 126.1, 122.9, 121.3, 78.2, 39.0, 26.1, 23.1.

2-[(1*S*,3*R*,4*S*,5*R*)-(3-hydroxy-1-isopropyl-4-methylbicyclo-

[3.1.0]hex-3-yl)]-1,10-phenanthroline (1f).

Through use of the above General Procedure A, (-)-thujone (0.186 g, 1.22 mmol) was converted into 0.083 g (45%) of **1f** as a colorless oil: $[\alpha]_D^{20} = -4.0^\circ$ ($c = 0.5$, ethanol); ^1H NMR (300 MHz, CDCl_3) δ 9.16 (dd, $J = 4.5, 1.8$ Hz, 1H), 8.27 (d, $J = 8.4$ Hz, 1H), 8.24 (dd, $J = 8.10, 1.80$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.72 (d, $J = 8.40$ Hz, 1H), 7.62 (dd, $J = 8.10, 4.50$ Hz, 1H), 6.38 (br s, 1H), 2.75 (dq, $J = 6.6, 4.5$ Hz, 1H), 2.50 (dd, $J = 13.5, 1.2$ Hz, 1H), 2.21 (d, $J = 13.5$ Hz, 1H), 1.53 (sep, 6.9 Hz, 1H), 1.37 (t, $J = 3.9$ Hz, 1H), 1.31 (dd, $J = 4.2, 8.4$ Hz, 1H), 1.07 (d, $J = 6.9$ Hz, 3H), 0.95 (d, $J = 6.9$ Hz, 3H), 0.89 (d, $J = 6.9$ Hz, 3H), 0.37 (dd, $J = 4.5, 9.0$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.1, 150.2, 145.6, 142.9, 137.1, 136.1, 129.0, 127.2, 126.3, 126.1, 122.9, 119.7, 81.9, 48.7, 46.7, 33.0, 32.7, 29.5, 20.1, 19.9, 13.1, 11.6; IR (CHCl_3) 3381, 2957, 2928, 850 cm^{-1} ; HRMS (FAB $^+$, m/z) calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$): 333.1967. Found: 333.1943.

2-[(2R*,5S*)-(1-hydroxy-2-isopropyl-5-methylcyclohexyl)]-1,10-phenanthroline (1g).

Through use of the above General Procedure A, *dl*-menthone (0.186 g, 1.22 mmol) was converted into 0.100 g (54%) of **1g** as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 9.17 (dd, $J = 4.2, 1.8$ Hz, 1H), 8.26 (d, $J = 8.4$ Hz, 1H), 8.24 (dd, $J = 8.1, 1.8$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.62 (dd, $J = 8.1, 4.5$ Hz, 1H), 2.12 (m, 1H), 1.94 (m, 2H), 1.84 (m, 2H), 1.71 (m, 2H), 1.42 (m, 1H), 0.89 (m, 6H), 0.69 (d, $J = 6.60$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.0, 150.2, 145.6, 143.7, 137.0, 136.0, 129.0, 127.3, 126.2, 126.1, 122.9, 119.2, 78.0, 51.0, 49.6, 35.4, 28.5, 27.8, 23.8, 22.4, 22.2, 18.8

2-(1-hydroxyethyl)-1,10-phenanthroline (1h)

Through the use of General Procedure B, 36 mg (0.2 mmol) of 1,10-phenanthroline was converted into 41 mg (91%) of **1h** as an orange oil: ^1H NMR (300 MHz, CDCl_3) δ 9.12 (dd, $J = 4.5, 1.7$ Hz, 1H), 8.21 (m, 2H), 7.75 (m, 3H), 7.58 (dd, $J = 8.0, 4.3$ Hz, 1H), 5.37 (q, $J = 6.6$ Hz, 1H), 1.70 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.0, 150.2,

145.9, 144.7, 137.1, 136.5, 129.1, 127.9, 126.7, 126.2, 123.1, 120.2, 77.7, 77.2, 76.8, 70.8, 24.7; IR (film) 3368, 1557, 1490, 856 cm^{-1} ; HRMS (FAB⁺, m/z) calcd for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$) 225.1028; found 225.1034.

2-(1-hydroxypropyl)-1,10-phenanthroline (1i)

Through the use of General Procedure B, 72 mg (0.4 mmol) of 1,10-phenanthroline was converted into 90 mg (94%) of **1i** as an orange oil: ¹H NMR (300 MHz, CDCl_3) δ 9.13 (dd, $J = 4.4, 1.9$ Hz, 1H), 8.23 (dd, $J = 8.0, 1.7$ Hz, 1H), 8.22 (d, $J = 8.3$ Hz, 1H), 7.78 (d, $J = 9$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.71 (d, $J = 8.3$ Hz, 1H), 7.59 (dd, $J = 7.9, 4.4$ Hz, 1H), 5.14 (dd, $J = 7.6, 4.6$ Hz, 1H), 2.07 (m, 1H), 1.96 (m, 1H), 1.07 (t, $J = 7.3$ Hz, 3H); ¹³C NMR (75 MHz, CDCl_3) δ 163.9, 150.2, 136.9, 136.6, 129.2, 128.0, 126.7, 126.3, 123.2, 120.8, 77.7, 77.2, 76.8, 75.6, 31.7, 10.1; IR ν 3351, 1620, 1606, 1591, 852 cm^{-1} ; MS (FAB⁺, m/z) calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$) 239.1184; found 239.1185.

2-(1-hydroxyhexyl)-1,10-phenanthroline (1j)

Through the use of General Procedure B, 36 mg (0.2 mmol) of 1,10-phenanthroline was converted into 40 mg (72%) of **1j** as an orange oil: ^1H NMR (300 MHz, CDCl_3) δ 9.21 (dd, $J = 4.4, 1.7$ Hz, 1H), 8.30 (dd, $J = 7.9, 1.7$ Hz, 1H), 8.26 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.79 (d, $J = 8.8$ Hz, 1H), 7.71 (d, $J = 8.3$ Hz, 1H), 7.66 (dd, $J = 8.1, 4.5$ Hz, 1H), 5.17 (dd, $J = 8.1, 4.3$ Hz, 1H), 1.94 (m, 2H), 1.56 (m, 2H), 1.34 (m, 4H), 0.87 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.2, 150.2, 145.9, 144.9, 136.8, 129.1, 127.9, 126.7, 126.2, 123.1, 120.7, 77.7, 77.2, 76.8, 74.7, 39.0, 32.1, 25.6, 22.8, 14.2; IR (film) 3350, 1619, 1591, 852 cm^{-1} ; HRMS (FAB $^+$, m/z) calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$) 281.1654; found 281.1662.

2-(1-hydroxy-3,3-dimethylbutyl)-1,10-phenanthroline (1l)

Through the use of General Procedure B, 36 mg (0.2mmol) of 1,10-phenanthroline was converted into 49 mg (87%) of **1l** as an orange oil: ^1H NMR (300 MHz, CDCl_3) δ 9.16 (dd, $J = 4.4, 1.9$ Hz, 1H), 8.19 (dd, $J = 8.1, 1.9$ Hz, 1H), 8.16 (d, $J = 8.3$ Hz, 1H), 7.74 (d, $J = 9$ Hz, 1H), 7.70 (d, $J = 8.8$ Hz, 1H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.57 (dd, $J = 8.0, 4.5$

Hz, 1H), 5.28 (dd, $J = 9.1, 3.2$ Hz, 1H), 1.84 (m, 2H), 1.12 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.1, 150.3, 145.9, 144.7, 136.9, 136.3, 129.1, 127.9, 126.6, 126.2, 123.0, 120.8, 77.7, 77.2, 76.8, 72.9, 52.4, 31.2, 30.6; IR (film) 3339, 2951, 1589, 855 cm^{-1} ; HRMS (FAB^+ , m/z) calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$) 281.1654, found 281.1656.

2-(1-hydroxy-1-cyclohexylmethyl)-1,10-phenanthroline (1m)

Through the use of General Procedure B, 36 mg (0.2 mmol) of 1,10-phenanthroline was converted into 39 mg (68%) of **1m** as an orange oil: ^1H NMR (300MHz, CDCl_3) δ 9.16 (dd, $J = 4.5, 1.7$ Hz, 1H), 8.22 (dd, $J = 8.0, 1.7$ Hz, 1H), 8.18 (d, 8.3 Hz, 1H), 7.77 (d, $J = 8.8$ Hz, 1H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.69 (d, $J = 8.1$ Hz, 1H), 7.58 (dd, $J = 8.1, 4.5$ Hz, 1H), 4.97 (d, $J = 5.4$ Hz, 1H), 2.1-1.1 (m, 11H); ^{13}C NMR (75 MHz, CDCl_3) δ 163.6, 150.3, 145.9, 144.9, 136.5, 136.3, 129.1, 127.9, 126.7, 126.1, 123.0, 121.6, 79.0, 77.7, 77.2, 76.8, 45.2, 30.2, 27.5, 26.6, 26.5, 26.3; IR (film) 3351, 2927, 2852, 1620, 1590, 857 cm^{-1} ; HRMS (FAB^+ , m/z) calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$) 293.1654, found 293.1628.

2-(1-hydroxy-1-cyclopropylmethyl)-1,10-phenanthroline (1n)

Through the use of General Procedure B, 36 mg (0.2 mmol) of 1,10-phenanthroline was converted into 40 mg (80%) of **1n** as an orange oil: ^1H NMR (300 MHz, CDCl_3) δ 9.15 (dd, $J = 4.3, 1.7$ Hz, 1H), 8.21 (m, 2H), 7.81 (d, $J = 8.3$ Hz, 1H), 7.77 (d, $J = 8.8$ Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 1H), 7.58 (dd, $J = 8.1, 4.3$ Hz, 1H), 4.61 (d, $J = 7.5$ Hz, 1H), 1.33 (m, 2H), 0.74-0.58 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 163.4, 150.2, 145.9, 144.7, 136.9, 129.1, 128.1, 126.7, 126.3, 123.1, 120.9, 77.7, 77.2, 76.8, 18.3, 3.0, 2.8; IR (film) 3338, 1619, 1591, 850 cm^{-1} ; HRMS (FAB^+ , m/z) calcd for $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}$ ($M + \text{H}^+$) 251.1184, found 251.1207.

2-(1-hydroxy-2-phenylethyl)-1,10-phenanthroline (1o).

Through the use of General Procedure B, 36 mg (0.2 mmol) of 1,10-phenanthroline was converted into 86 mg (72%) of **1o** as an orange oil: ^1H NMR (300 MHz, CDCl_3) δ 9.24 (dd, $J = 4.5, 1.7$ Hz, 1H), 8.34 (dd, $J = 8.1, 1.3$ Hz, 1H), 8.20 (d, $J = 8.3$ Hz, 1H), 7.83 (d, $J = 1.7$ Hz, 2H), 7.70 (dd, $J = 8.1, 4.5$ Hz, 1H), 7.26 (m, 5H), 5.39 (dd, $J = 7.7, 5.6$ Hz, 1H), 3.28 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 163.3, 150.3, 146.1, 145.1, 138.4,

136.6, 136.4, 130.0, 129.2, 128.5, 128.1, 126.7, 126.5, 126.3, 123.1, 121.1, 77.6, 77.2, 76.8, 75.7, 45.5; IR (KBr) 3222, 2911, 1628, 1601, 1555, 1530, 1493, 1394, 860 cm^{-1} ; HRMS (FAB⁺, m/z) calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$) 301.1341, found 301.1371.

2-(1-hydroxy-2,2-diphenylethyl)-1,10-phenanthroline (1p).

Through the use of General Procedure B, 72 mg (0.4 mmol) of 1,10-phenanthroline was converted into 75 mg (50%) of **1p** as a white solid: Mp = 200 °C dec; ¹H NMR (300 MHz, CDCl_3) δ 9.24 (dd, J = 4.4, 1.5 Hz, 1H), 8.32 (d, J = 7.9 Hz, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 9 Hz, 1H), 7.68 (dd, J = 8.1, 4.5 Hz, 1H), 7.42 (d, J = 7.7 Hz, 2H), 7.3-7.1 (m, 10H), 5.88 (d, J = 7.7 Hz, 1H), 4.67 (d, J = 7.9 Hz, 1H). ¹³C NMR (75 MHz, d -DMSO) δ 163.4, 149.7, 143.0, 142.2, 136.3, 129.3, 128.7, 128.6, 128.0, 127.8, 127.3, 126.6, 126.1, 125.9, 123.2, 121.6, 76.5, 56.9, 40.3, 40.1, 39.8, 39.5, 39.2, 39.0, 38.7; IR (KBr) 3400, 1592, 1554, 1488, 1450, 1384, 853 cm^{-1} ; HRMS (FAB⁺, m/z) calcd for $\text{C}_{26}\text{H}_{21}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$) 377.1654, found 377.1660.

1q

2-[(6-hydroxy)methylhexanoyl]-1,10-phenanthroline (1q).

Through the use of General Procedure B, 36 mg (0.2 mmol) of 1,10-phenanthroline was converted into 42 mg (64%) of **1q** as an orange oil: ^1H NMR (500 MHz, CDCl_3) δ 9.15 (dd, $J = 4.2, 2.0$ Hz, 1H), 8.25 (m, 2H), 7.80 (dd, $J = 14.3, 8.9$ Hz, 2H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.63 (q, $J = 4.5$ Hz, 1H), 5.14 (q, $J = 4.0$ Hz, 1H), 3.64 (s, 3H), 2.32 (t, $J = 7.4$ Hz, 2H), 2.00 (m, 1H), 1.90 (m, 1H), 1.69 (m, 2H), 1.61 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 174.4, 163.7, 150.3, 145.9, 144.9, 137.0, 136.5, 129.2, 128.0, 126.7, 126.4, 123.2, 120.6, 77.5, 77.2, 77.0, 74.3, 51.7, 38.5, 34.2, 25.5, 25.1; IR (film) 3368, 1732, 1620, 1591, 854 cm^{-1} ; HRMS (FAB $^+$, m/z) calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_3$ ($\text{M} + \text{H}^+$) 325.1552, found 325.1543.

1r

2-[(7-hydroxy)methylheptanoyl]-1,10-phenanthroline (1r).

Through the use of General Procedure B, 108 mg (0.6 mmol) of 1,10-phenanthroline was converted into 190 mg (94%) of **1r** as an orange oil: ^1H NMR (300 MHz, CDCl_3) δ 9.11 (dd, $J = 4.4, 1.7$ Hz, 1H), 8.19 (dd, $J = 8.0, 1.7$ Hz, 1H), 8.17 (d, $J = 8.3$ Hz, 1H), 7.72

(m, 3H), 7.55 (dd, $J = 8.1, 4.5$ Hz, 1H), 5.19 (dd, $J = 7.9, 4.5$ Hz, 1H), 3.61 (s, 3H), 2.2 (t, $J = 7.3$ Hz, 2H), 1.94 (m, 2H), 1.60 (m, 4H), 1.36 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.2, 150.3, 145.0, 136.8, 136.2, 129.1, 128.0, 126.6, 126.2, 123.0, 120.5, 77.6, 77.2, 76.8, 74.5, 51.4, 38.6, 34.2, 29.3, 25.4, 25.0; IR (film) 3368, 2938, 2859, 1733, 1591, 1556 cm^{-1} ; HRMS (FAB^+ , m/z) calcd for $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_3$ ($\text{M} + \text{H}^+$) 339.1709, found 339.1687.

2-(1-ethyl-1-methoxypropyl)-1,10-phenanthroline (3b).

Through use of the above general procedure, NaH (0.035g, 1.5 mmol), MeI (0.092 mL, 1.5 mmol), and **1b** (0.098 g, 0.368 mmol) were employed, yielding 0.066 g (65%) of **3b** as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 9.24 (dd, $J = 4.5, 1.8$ Hz, 1H), 8.23 (dd, $J = 8.4, 1.8$ Hz, 1H), 8.20 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.60 (dd, $J = 7.8, 4.5$ Hz, 1H), 3.24 (s, 3H), 2.34 (dq, $J = 7.5$ Hz, 2H), 2.24 (dq, $J = 7.5$ Hz, 2H), 0.73 (t, $J = 7.50$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.9, 150.3, 146.5, 145.3, 136.1, 135.5, 128.9, 127.2, 126.6, 125.9, 122.5, 121.5, 84.3, 49.8, 28.2, 7.5; IR (CHCl_3) 2969, 2935, 910 cm^{-1} ; HRMS (FAB^+ , m/z) calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$): 281.1654. Found: 281.1646.

2-(1-methoxy-1-methylpropyl)-1,10-phenanthroline (3c).

Through use of the above general procedure, NaH (0.034g, 1.5 mmol), MeI (0.091 mL, 1.5 mmol), and **1c** (0.092 g, 0.365 mmol) were employed, yielding 0.070 g (72%) of **3c** as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 9.24 (dd, J = 4.6, 1.8 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 8.24 (dd, J = 8.1, 1.8 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.7, Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.62 (dd, J = 8.1, 4.2 Hz, 1H), 3.22 (s, 3H), 2.19 (q, J = 7.5 Hz, 2H), 1.83 (s, 3H), 0.90(t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.9, 150.5, 146.5, 145.3, 136.1, 136.1, 128.9, 127.4, 126.5, 126.1, 122.5, 120.7, 82.1, 50.9, 32.7, 22.6, 8.0; IR (CHCl_3) 2970, 2932, 910 cm^{-1} ; HRMS (FAB $^+$, m/z) calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$): 267.1497. Found: 267.1504.

2-(1-methoxy-1,2-dimethylpropyl)-1,10-phenanthroline (3d).

Through use of the above general procedure, NaH (0.020g, 0.74 mmol), MeI (0.046 mL, 0.74 mmol), and **1d** (0.052 g, 0.185 mmol) were employed, yielding 0.052 g (70%) of **3d** as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 9.24 (dd, J = 4.4, 1.8 Hz, 1H), 8.24 (dd,

$J = 8.1, 1.8$ Hz, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.40$ Hz, 1H), 7.81 (d, $J = 8.8$ Hz, 1H), 7.74 (d, $J = 8.8$ Hz, 1H), 7.60 (dd, $J = 8.1, 4.5$ Hz, 1H), 3.17 (s, 3H), 2.25 (sep, $J = 6.8$ Hz, 1H), 1.88 (s, 3H), 1.00 (d, $J = 6.6$ Hz, 3H), 0.71 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.2, 150.5, 146.5, 145.1, 136.1, 135.8, 128.9, 127.4, 126.5, 126.1, 122.5, 121.1, 84.4, 51.3, 39.1, 17.7, 17.4, 16.6; IR (CHCl_3) 2961, 2928, 866.4 cm^{-1} ; HRMS (FAB^+ , m/z) calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$): 281.1654. Found: 281.1651.

2-(1-methoxy-1,2,2-trimethylpropyl)-1,10-phenanthroline (3e).

Through use of the above general procedure, NaH (0.008g, 0.3 mmol), MeI (0.020 mL, 0.3 mmol), and **1e** (0.023 g, 0.08 mmol) were employed, yielding 0.013 g (55%) of **3e** as a colorless oil: ^1H NMR (300 MHz, CDCl_3) δ 9.23 (dd, $J = 4.5, 1.8$ Hz, 1H), 8.23 (dd, $J = 7.8, 1.8$ Hz, 1H), 8.17 (d, $J = 8.7$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.7$ Hz, 1H), 7.74 (d, $J = 8.7$ Hz, 1H), 7.60 (dd, $J = 8.0, 4.4$ Hz, 1H), 3.21 (s, 3H), 1.94 (s, 3H), 0.98 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 163.8, 150.4, 145.1, 143.9, 136.0, 134.3, 128.8, 127.2, 126.5, 126.0, 122.5, 121.4, 86.2, 51.4, 38.8, 26.1, 17.8; IR (CHCl_3) 2957, 2928, 857 cm^{-1} ; HRMS (FAB^+ , m/z) calcd for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}$ ($\text{M} + \text{H}^+$): 295.1810. Found: 295.1818.

2-[(1*S*,3*R*,4*S*,5*R*)-(3-methoxy-1-isopropyl-4-methylbicyclo[3.1.0]-hex-3-yl)]-1,10-phenanthroline (3f).

Through use of the above general procedure, NaH (0.120g, 5.0 mmol), MeI (0.70 mL, 5.0 mmol), and **1f** (0.430 g, 1.24 mmol) were employed, yielding 0.334 g (75%) of **3f** as a colorless oil: $[\alpha]_D^{20} = +27.4^\circ$ ($c = 0.85$, ethanol); ^1H NMR (300 MHz, benzene- d_6) δ 9.05 (dd, $J = 4.2, 1.8$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.55 (dd, $J = 8.1, 1.8$ Hz, 1H), 7.33 (d, $J = 8.8$ Hz, 1H), 7.23 (d, $J = 8.8$ Hz, 1H), 6.92 (dd, $J = 8.1, 4.2$ Hz, 1H), 4.15 (dd, $J = 14.4, 1.8$ Hz, 1H), 2.95 (s, 3H), 2.75 (dq, $J = 6.9, 4.5$ Hz, 1H), 2.53 (d, $J = 14.4$ Hz, 1H), 1.73 (sep, $J = 6.9$ Hz, 1H), 1.34 (t, $J = 3.9$ Hz, 1H), 1.28 (two d, $J = 6.90$ Hz, 6H), 1.20 (ddd, $J = 4.2, 4.2, 3.9$ Hz, 1H), 0.96 (d, $J = 6.9$ Hz, 3H), 0.40 (dd, $J = 7.8, 3.6$ Hz, 1H); ^{13}C NMR (75 MHz, benzene- d_6) δ 164.3, 150.2, 147.2, 146.5, 135.9, 135.3, 128.9, 127.5, 126.4, 126.1, 122.6, 120.3, 90.5, 50.8, 48.6, 33.9, 32.9, 30.2, 28.5, 20.8, 19.9, 11.4; NOESY: to determine the stereochemistry at C3, a NOESY was run giving crosspeaks for protons which are close in space. Some of the crucial crosspeaks are shown below and this was used to conclude that the stereochemistry is *R* at C3.

NOE crosspeaks
seen:

IR (CHCl₃) 2958, 2868, 856 cm⁻¹; HRMS (FAB⁺, *m/z*) calcd for C₂₃H₂₇N₂O (M + H⁺):

347.2123. Found: 347.2137.

2-[(2*R,5*S**)-(1-methoxy-2-isopropyl-5-methylcyclohexyl)]-1,10-phenanthroline (3g).**

Through use of the above general procedure, NaH (0.030g, 1.2 mmol), MeI (0.075 mL, 1.2 mmol), and **1g** (0.100 g, 0.298 mmol) were employed, yielding 0.092 g (88%) of **3g** as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 9.23 (dd, *J* = 4.4, 1.8 Hz, 1H), 8.24 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.20 (d, *J* = 8.40 Hz, 1H), 7.90 (d, *J* = 8.40 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.61 (dd, *J* = 8.1, 4.2 Hz, 1H), 3.22 (s, 3H), 2.64 (dd, *J* = 14.7, 12.6 Hz, 1H), 2.23 (br dm, *J* = 14.7 Hz, 1H), 1.80 (m, 4H), 1.60 (m, 1H), 1.46 (sep, *J* = 6.9 Hz, 1H), 1.29 (m, 1H), 1.05 (d, *J* = 6.6 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.56 (d, *J* = 6.90 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 165.5, 150.4, 146.3, 146.1, 136.2, 134.9, 128.9, 127.2, 126.6, 125.9, 122.5, 121.9, 85.9, 51.6, 50.4, 39.3, 34.7, 28.1, 26.8, 23.4, 22.4, 21.2, 18.2; IR (CHCl₃) 2958, 2868, 855.5 cm⁻¹; HRMS (FAB⁺, *m/z*) calcd for C₂₃H₂₉N₂O (M + H⁺): 349.2275. Found: 349.2270.

2-(2-butyl)-1,10-phenanthroline (5c).

Through use of the above general procedure, 0.1 M SmI₂ (4.2 mL, 0.42 mmol) was added to **3c** (0.045 g, 0.68 mmol) yielding 0.011 g (66%) of **5c** as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 9.25 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.24 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.61 (dd, *J* = 8.1, 4.20 Hz, 1H), 7.56 (d, *J* = 8.40 Hz, 1H), 3.43 (sext, *J* = 7.20 Hz, 1H), 1.90 (m, 1H), 1.77 (m, 1H), 1.42 (d, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.50 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 168.0, 150.2, 145.6, 144.8, 136.4, 136.1, 128.8, 127.1, 126.5, 125.4, 122.5, 120.5, 44.6, 30.2, 20.6, 12.1; IR (CHCl₃) 2966, 2931, 851 cm⁻¹; HRMS (FAB⁺, *m/z*) calcd for C₁₆H₁₇N₂ (M + H⁺): 237.1392. Found: 237.1402.

2-(1,2-dimethylpropyl)-1,10-phenanthroline (5d).

Through use of the above general procedure, 0.1 M SmI₂ (4.6 mL, 0.46 mmol) was added to **3d** (0.052 g, 0.18 mmol) yielding 0.27 g (58%) of **5d** as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 9.24 (dd, *J* = 4.4, 1.8 Hz, 1H), 8.23 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.18 (d, *J* =

8.4 Hz, 1H), 7.79 (d, $J = 8.8$ Hz, 1H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.60 (dd, $J = 8.1, 4.5$ Hz, 1H), 7.53 (d, $J = 8.40$ Hz, 1H), 3.24 (dq, $J = 6.9, 1.5$ Hz, 1H), 2.11 (dsep, $J = 6.9, 2.1$ Hz, 1H), 1.41 (d, $J = 7.2$ Hz, 3H), 1.06 (d, $J = 6.3$ Hz, 3H), 0.83 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 162.1, 150.0, 147.4, 146.1, 136.2, 135.8, 128.9, 127.4, 126.7, 125.4, 122.6, 121.3, 49.8, 33.8, 21.7, 20.0, 18.3; IR (CHCl_3) 2958, 2924, 852 cm^{-1} ; HRMS (FAB $^+$, m/z) calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2$ ($\text{M} + \text{H}^+$): 251.1548. Found: 251.1531.

2-[(1*S*,3*S*,4*S*,5*R*)-(1-isopropyl-4-methylbicyclo[3.1.0]hex-3-yl)]-1,10-phenanthroline (5f).

Through use of the above general procedure, 0.1 M SmI_2 (9.31 mL, 0.931 mmol) was added to **3f** (0.129 g, 0.372 mmol) yielding 0.080 g (68%) of **5f** as a colorless oil: $[\alpha]_{\text{D}}^{20} = +38.5^\circ$ ($c = 0.27$, ethanol); ^1H NMR (300 MHz, CDCl_3) δ 9.24 (dd, $J = 4.2, 1.8$ Hz, 1H), 8.21 (dd, $J = 8.1, 1.8$ Hz, 1H), 8.17 (d, $J = 8.40$ Hz, 1H), 7.77 (d, $J = 8.8$ Hz, 1H), 7.70 (d, $J = 8.8$ Hz, 1H), 7.61 (d, $J = 8.1$ Hz, 1H), 7.60 (dd, $J = 8.1, 4.2$ Hz, 1H), 3.05 (ddd, $J = 10.80, 7.50$ Hz, 1H), 2.64 (dq, $J = 6.6, 4.2$ Hz, 1H), 2.31 (dd, $J = 12.3, 7.2$ Hz, 1H), 1.98 (br t, $J = 12.0$ Hz, 1H), 1.54 (sep, $J = 6.9$ Hz, 1H), 1.01 (two d, $J = 6.6$ Hz, 6H), 0.90 (d, $J = 6.9$ Hz, 3H), 0.69 (br t, $J = 4.5$ Hz, 1H), 0.57 (d, $J = 7.2$ Hz, 1H), 0.25 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.2, 150.3, 146.2, 145.3, 136.2, 135.9, 128.8, 127.1, 126.4, 125.5, 122.5, 121.1, 51.4, 42.3, 38.0, 32.7, 32.5, 28.6, 20.0, 19.8, 16.7, 9.3; IR

(CHCl₃) 3049, 2927, 850 cm⁻¹; HRMS (FAB⁺, *m/z*) calcd for C₂₂H₂₅N₂ (M + H⁺):

317.2018. Found: 317.2029.

^1H of 2-(1-Hydroxycyclohexyl)-1,10-phenanthroline (**1a**).

phenan/cyclohexanone addn
 Solvent: CDCl3
 Ambient temperature
 File: DAVE
 UNITplus-300 "nmr2"
 PULSE SEQUENCE
 Relax: delay 3.000 sec
 Pulse: 81.3 degrees
 Acq. time 0.970 sec
 Width 19002.4 Hz
 10112 repetitions
 OBSERVE C13, 75.4216951 MHz
 DECOUPLE H1, 299.9079281 MHz
 Power 42 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 11.2 hours

1a

2-(1-Hydroxycyclohexyl)-1,10-phenanthroline

^1H of 2-(1-Ethyl-1-hydroxypropyl)-1,10-phenanthroline (**1b**).

phenan/pentanone addn
 Solvent: CDCl3
 Ambient temperature
 Unit: plus-300 "nmr2"
 PULSE SEQUENCE
 Relax: delay 4.000 sec
 Pulse: 61.3 degrees
 Acq. time 0.971 sec
 Width 18001.8 Hz
 4848 repetitions
 OBSERVE: C13, 75.4217003 MHz
 DECOUPLE: H1, 299.9479281 MHz
 Power 42 dB
 continuously ON
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 6.7 hours

2-(1-Ethyl-1-hydroxypropyl)-1,10-phenanthroline

^1H of 2-(1-Hydroxy-1-methylpropyl)-1,10-phenanthroline (1c).

phenan/2-butanone
 Solvent: CDCl₃
 Ambient temperature
 UNITYplus-300 "nmr1"
 PULSE SEQUENCE
 Relax: delay 4.000 sec
 Pulse 40.5 degrees
 Acq. time 1.815 sec
 Width 18001.8 Hz
 4752 repetitions
 OBSERVE C13, 75.3594510 MHz
 DECOUPLE H1, 299.7003818 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 Single precision data
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 7.7 hours

1c

2-(1-Hydroxy-1-methylpropyl)-1,10-phenanthroline

^1H of 2-(1-Hydroxy-1,2-dimethylpropyl)-1,10-phenanthroline (**1d**).

^1H of 2-(1-Hydroxy-1,2,2-trimethylpropyl)-1,10-phenanthroline (**1e**).

phenan/3,3-dimethyl-2-butanone
 Solvent: CDCl₃
 Ambient temperature
 UNITYplus-300 "nmr2"
 PULSE SEQUENCE
 Relax. delay 4.000 sec
 Pulse 81.3 degrees
 Acq. time 0.971 sec
 Width 18001.8 Hz
 8752 repetitions
 OBSERVE C13, 75.4216976 MHz
 DECOUPLE H1, 299.9479281 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FI size 65536
 Total time 12.1 hours

2-(1-Hydroxy-1,2,2-trimethylpropyl)-1,10-phenanthroline

¹H of 2-[(1*S*,3*R*,4*S*,5*R*)-(3-Hydroxy-1-isopropyl-4-methylbicyclo[3.1.0]hex-3-yl)]-1,10-phenanthroline (**1f**).

1f

2-[(1S,3R,4S,5R)-(3-Hydroxy-1-isopropyl-4-methylbicyclo[3.1.0]hex-3-yl)]-1,10-phenanthroline

^1H of 2-[(2R*,5S*)-(1-Hydroxy-2-isopropyl-5-methylcyclohexyl)]-1,10-phenanthroline (**1g**).

phenanthroline
 Solvent: CDCl₃
 Ambient temperature
 UNITYplus-300 "marl"
 PULSE SEQUENCE
 Relax delay 4.000 sec
 Pulse 40.5 degrees
 Acq. time 1.815 sec
 Width 18001.8 Hz
 6184 repetitions
 OBSERVE C13, 75.3594521 MHz
 DECOUPLE H1, 299.7003818 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 Single precision data
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 10.0 hours

1g

2-((2R*,5S*)-1-(Hydroxy-2-isopropyl-5-methylcyclohexyl)-1,10-phenanthroline

STANDARD PROTON PARAMETERS

Pulse Sequence: szpul
 Solvent: CDCl₃
 Ambient temperature
 INOVA-500 "inovas5"
 Relax. delay 1.000 sec
 Pulse 90.0 degrees
 Acq. time 2.022 sec
 Width 8104.5 Hz
 16 Repetitions
 OBSERVE H1, 499.8611708 MHz
 DATA PROCESSING
 FT size 32768
 Total time 0 min, 48 sec

2-(1-hydroxyethyl)-1,10-phenanthroline

S35

new experiment

Pulse Sequence: szpu1

Solvent: CDCl₃

Ambient temperature

UNITYplus-500 "nmr2a.chem.nd.edu"

Relax. delay 2.000 sec

Acq. time 0.357 sec

Width 17116.0 Hz

436 repetitions

OBSERVE C13, 75.4216834 MHz

DECOUPLE H1, 299.9483516 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 38 min, 56 sec

2-(1-hydroxyethyl)-1,10-phenanthroline

STANDARD III OBSERVE

Pulse Sequence: szpul

Solvent: CDCl3

Ambient temperature

File: jaw-1-200a

INDVA-500 "hloch.chem.nd.edu"

Relax. delay 1.000 sec

Pulse 90.0 degrees

Acq. time 2.337 sec

Width 3506.0 Hz

16 repetitions

OBSERVE H1, 299.693028 MHz

DATA PROCESSING

File size 32768

Total time 0 min, 53 sec

2-(1-hydroxypropyl)-1,10-phenanthroline

new experiment

Pulse Sequence: szpul

Solvent: CDCl₃

Ambient temperature

UNITYplus-300 "nmr2a.chem.ind.edu"

Relax. delay 2.000 sec

Pulse 96.4 degrees

Acq. time 0.957 sec

Width 17116.0 Hz

704 repetitions

OBSERVE C13, 75.4216819 MHz

DECOUPLE H1, 299.9483516 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 38 min, 56 sec

INDEX	FREQUENCY	PPM	HEIGHT
1	12365.206	163.948	29.2
2	11327.812	150.193	46.0
3	10326.460	136.916	69.4
4	10306.088	136.646	51.9
5	9741.424	129.159	25.7
6	9654.191	128.003	28.0
7	9559.645	126.749	68.3
8	9522.035	126.251	71.0
9	9289.066	123.162	58.3
10	9107.287	120.752	63.1
11	5856.680	77.652	128.4
12	5824.816	77.230	137.5
13	5792.953	76.808	134.4
14	5704.675	75.637	45.5
15	2389.297	31.679	56.1
16	761.643	10.098	52.6

2-(1-hydroxypropyl)-1,10-phenanthroline

STANDARD 1H OBSERVE

Pulse Sequence: szpu1
Solvent: CDCl3
Ambient temperature
File: jaw267
INOVA-500 "hloch.chem.ind.edu"

Relax. delay 0.100 sec
Pulse 162.6 degrees
Acq. time 4.096 sec
Width 4000.0 Hz
16 repetitions
OBSERVE H1 299.9468584 MHz
DATA PROCESSING
F1 size 65536
Total time 1 min, 7 sec

2-(1-hydroxyhexyl)-1,10-phenanthroline

new experiment

Pulse Sequence: szpul

Solvent: CDCl₃

Ambient temperature

UNITYPUS-300 "nmr2a.chem.nd.edu"

Relax. delay 2.000 sec

Pulse 96.4 degrees

Acq. time 0.957 sec

Width 17116.0 Hz

432 Repetitions

OBSERVE C13, 75.4216840 MHz

DECOUPLE H1, 299.9483516 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FI size 65536

Total time 8 hr, 14 min, 40 sec

2-(1-hydroxyhexyl)-1,10-phenanthroline

INDEX	FREQUENCY	PPM	HEIGHT
1	12386.100	164.225	32.2
2	11326.767	150.179	90.2
3	11004.475	145.906	14.8
4	10927.689	144.888	15.9
5	10317.580	136.799	90.2
6	10290.940	136.445	93.2
7	9736.200	129.090	22.8
8	9645.311	127.885	30.3
9	9552.332	126.652	90.6
10	9515.767	126.168	88.9
11	9285.409	123.113	90.1
12	9103.108	120.696	84.5
13	5856.680	77.652	56.2
14	5824.817	77.230	57.0
15	5792.431	76.801	56.0
16	5632.068	74.674	81.1
17	2940.902	38.993	91.7
18	2421.161	32.102	104.0
19	1930.148	25.581	99.9
20	1719.117	22.793	88.9
21	1074.533	14.247	70.9