Supporting Information for:

Facile Synthesis of Substituted Phenanthroline Ligands by Samarium-Promoted Coupling of Phenanthroline with Ketones

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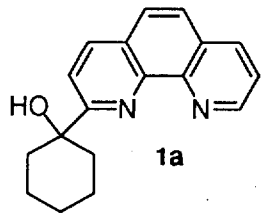
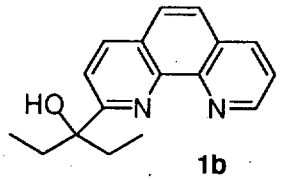
General Procedure for SmI_2 Mediated Addition of Carbonyl Compounds to Phenanthroline. To a stirred solution of 1,10-phenanthroline (0.1 g, 0.55 mmol) in THF (5 mL) was added a 0.1 *M* solution of SmI_2 in THF (12.2 mL, 1.22 mmol) at 25°C. After being stirred for 5 min, the carbonyl compound (1.22 mmol) was added, and the resulting mixture was stirred for 12 h at 25 °C and monitored by TLC. Upon completion of the reaction, satd aq NH_4Cl was added to quench the reaction, and the resulting mixture was extracted with CH_2Cl_2. The organic extracts were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated. The product was purified by flash chromatography (alumina, ethyl acetate/hexane gradient).



1a

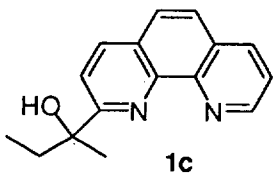
2-[(1-Hydroxycyclohexyl)]-1,10-phenanthroline (1a). Through use of the above general procedure, cyclohexanone (0.120 g, 1.22 mmol) was converted into 0.134 g (88%) of **1a** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 9.18 (dd, J = 4.20, 1.80

Hz, H_{P9}), 8.28 (d, J = 8.40 Hz, H_{P4}), 8.27 (dd, J = 8.40, 1.80 Hz, H_{P7}), 7.82 and 7.79 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 7.76 (d, J = 8.40 Hz, H_{P3}), 7.65 (dd, J = 8.10, 4.50 Hz, H_{P8}), 2.08-1.71 (m, 10H, cyclohexyl); ^{13}C NMR (75 MHz) δ 166.52, 150.31, 145.81, 143.96, 137.15, 136.06, 129.00, 127.46, 126.28, 126.20, 122.93, 119.21, 73.50, 38.63, 23.70, 22.15; IR ($CHCl_3$) 3352 (OH), 3048 (C-H Ar), 2928 (CH), 909 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{18}H_{19}N_2O$ (MH^+): 279.1497. Found: 279.1490.



1b

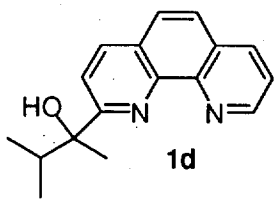
2-[(1-Ethyl-1-hydroxypropyl)]-1,10-phenanthroline (1b). Through use of the above general procedure, 3-pentanone (0.105 g, 1.22 mmol) was converted into 0.132 g (89%) of **1b** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) d 9.21 (dd, J = 4.50, 1.80 Hz, H_{P9}), 8.26 (one d, J = 8.40 Hz, H_{P4}, one dd, J = 8.40, 1.80 Hz, H_{P7}), 7.82 and 7.79 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 7.64 (dd, J = 8.10, 4.20 Hz, H_{P8}), 7.61 (d, J = 8.40 Hz, H_{P3}), 2.01 (dq, J = 7.50, 2.10 Hz, $CH(C\underline{H}_2CH_3)_2$), 0.77 (t, J = 7.20 Hz, $CH(CH_2C\underline{H}_3)_2$); ^{13}C NMR (75 MHz) δ 164.10, 150.14, 145.52, 143.67, 136.96, 136.24, 128.99, 127.25, 126.22, 122.92, 119.49, 77.27, 34.69, 7.98; IR ($CHCl_3$) 3417 (OH), 2967 (C-H Ar), 2929 (CH), 912 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{17}H_{19}N_2O$ (MH^+): 267.1497. Found: 267.1497.



1c

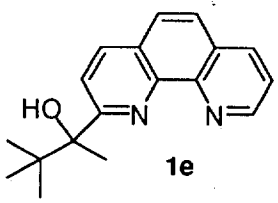
2-[(1-Hydroxy-1-methylpropyl)]-1,10-phenanthroline (1c). Through use of the above general procedure, 2-butanone (0.088 g, 1.22 mmol) was converted into 0.101 g (73%) of **1c** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.20 (dd, J = 4.50, 1.80 Hz,

H_{P9}), 8.28 (d, J = 8.40 Hz, H_{P4}), 8.28 (dd, J = 8.10, 1.80 Hz, H_{P7}), 7.82 and 7.79 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 7.67 (d, J = 8.40 Hz, H_{P3}), 7.65 (dd, J = 8.10, 4.20 Hz, H_{P8}), 2.02 (two dq, J = 13.5, 5.4 Hz, $C\underline{H}_2CH_3$), 1.67 (s, $C(OH)C\underline{H}_3$), 0.82 (t, J = 7.35 Hz, $CH_2C\underline{H}_3$); ^{13}C NMR (75 MHz) δ 165.41, 150.23, 145.63, 143.74, 137.14, 136.18, 129.02, 127.34, 126.29, 126.20, 122.95, 119.29, 74.64, 35.94, 29.17, 8.23.



1d

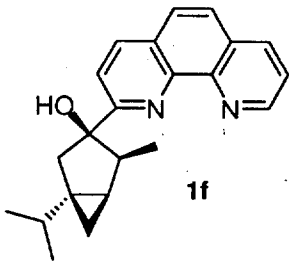
2-[(1-Hydroxy-1,2-dimethylpropyl)]-1,10-phenanthroline (1d). Through use of the above general procedure, 3-methyl-2-butanone (0.105 g, 1.22 mmol) was converted into 0.105 g (71%) of **1d** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 9.18 (dd, J = 4.40, 1.80 Hz, H_{P9}), 8.26 (one d, J = 8.10 Hz, H_{P4}, one dd, J = 8.10, 1.80 Hz, H_{P7}), 7.82 and 7.78 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 7.65 (d, J = 8.70 Hz, H_{P3}), 7.64 (dd, J = 8.10, 4.50 Hz, H_{P8}), 6.10 (br s, OH), 2.19 (sep, J = 6.60 Hz, $C\underline{H}(CH_3)_2$), 1.64 (s, $C(OH)C\underline{H}_3$), 1.12 (d, J = 6.60 Hz, $CH(C\underline{H}_3)CH_3$), 0.71 (d, J = 6.60 Hz, $CH(CH_3)C\underline{H}_3$); ^{13}C NMR (75 MHz) δ 165.84, 150.19, 145.70, 143.63, 136.87, 136.08, 129.00, 127.31, 126.24, 126.16, 122.89, 119.54, 76.29, 38.43, 26.43, 17.46, 17.09.



1e

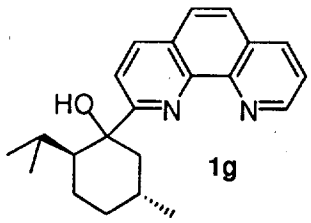
2-[1-Hydroxy-1,2,2-trimethylpropyl)]-1,10-phenanthroline (1e). Through use of the above general procedure, 3,3-dimethyl-2-butanone (0.122 g, 1.22 mmol) was converted into 0.061 g (40%) of **1e** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 9.17 (dd, J = 4.20, 1.80 Hz, H_{P9}), 8.26 (dd, J = 8.40, 1.50 Hz, H_{P7}), 8.23 (d, J = 8.40 Hz,

H_{P4}), 7.82 and 7.78 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 7.70 (d, J = 8.40 Hz, H_{P3}), 7.63 (dd, J = 8.10, 4.50 Hz, H_{P8}), 1.71 (s, $C\underline{H}_3$), 1.02 (s, $(C\underline{H}_3)_3$); ^{13}C NMR (75 MHz) δ 164.19, 150.13, 145.81, 143.32, 136.04, 135.73, 128.97, 127.23, 126.32, 126.09, 122.91, 121.31, 78.19, 38.99, 26.08, 23.06.



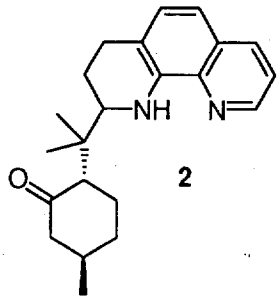
1f

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, (-)-thujone (0.186 g, 1.22 mmol) was converted into 0.083 g (45%) of **1f** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 9.16 (dd, J = 4.50, 1.80 Hz, H_{P9}), 8.27 (d, J = 8.40 Hz, H_{P4}), 8.24 (dd, J = 8.10, 1.80 Hz, H_{P7}), 7.82 and 7.76 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 7.72 (d, J = 8.40 Hz, H_{P3}), 7.62 (dd, J = 8.10, 4.50 Hz, H_{P8}), 6.38 (br s, OH), 2.75 (dq, J = 6.6, 4.5 Hz, $C\underline{H}CH_3$), 2.50 (dd, J = 13.5, 1.2 Hz, C(OH)C$\underline{H}$H), 2.21 (d, J = 13.5 Hz, C(OH)CH$\underline{H}$), 1.53 (sep, 6.9 Hz, $C\underline{H}(CH_3)_2$), 1.37 (t, J = 3.9 Hz, cyclopropyl-H), 1.31 (dd, J = 4.2, 8.4 Hz, cyclopropyl-H), 1.07 (d, J = 6.9 Hz, $C\underline{H}_3$), 0.95 (d, J = 6.9 Hz, $C\underline{H}_3$), 0.89 (d, J = 6.9 Hz, $C\underline{H}_3$), 0.37 (dd, J = 4.5, 9.0 Hz, cyclopropyl-H); ^{13}C NMR (75 MHz) δ 165.09, 150.16, 145.56, 142.86, 137.10, 136.05, 128.98, 127.17, 126.29, 126.05, 122.87, 119.72, 81.85, 48.66, 46.71, 33.01, 32.70, 29.53, 20.10, 19.94, 13.12, 11.60; IR ($CHCl_3$) 3381 (OH), 2957 (C-H Ar), 2928 (CH), 850 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{22}H_{25}N_2O$ (MH^+): 333.1967. Found: 333.1943.



1g

2-[(2*R,5*S**)-(1-Hydroxy-2-isopropyl-5-methylcyclohexyl)]-1,10-phenanthroline (1g).** Through use of the above general procedure, dl-menthone (0.186 g, 1.22 mmol) was converted into 0.100 g (54%) of **1g** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.17 (dd, J = 4.20, 1.80 Hz, H_{P9}), 8.26 (d, J = 8.40 Hz, H_{P4}), 8.24 (dd, J = 8.10, 1.80 Hz, H_{P7}), 7.82 and 7.78 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 7.68 (d, J = 8.40 Hz, H_{P3}), 7.62 (dd, J = 8.10, 4.50 Hz, H_{P8}), 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) δ 165.96, 150.22, 145.64, 143.73, 136.98, 135.98, 128.95, 127.26, 126.18, 126.12, 122.87, 119.18, 77.98, 50.96, 49.63, 35.35, 28.47, 27.82, 23.76, 22.39, 22.18, 18.84.

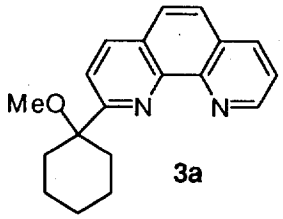


2

2-{1-methyl-1-[(4*R*)-4-methyl-2-oxocyclohexyl]ethyl}1,2,3,4-tetrahydrophenanthroline (2). Through use of the above general procedure, (*R*)-(+)-pulegone (0.186 g, 1.22 mmol) was converted into 0.092 g (50%) of **2** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (dd, J = 3.90, 1.50 Hz, H_{P9}), 7.97 (dd, J = 8.40, 1.80 Hz, H_{P7}), 7.28 (dd, J = 8.40, 4.50 Hz, H_{P8}), 7.02 and 6.92 (two d, J = 8.10 Hz, H_{P5} and H_{P6}), 5.93 (br s, NH), 4.57 (br s, 1H), 2.71 (dt, J = 11.6, 4.3 Hz, 1H), 2.46 (m, 2H), 2.25 (m, 1H), 2.10 (m, 2H), 1.93 (m, 3H), 1.24 (m, 3H), 1.1 (s, 3H), 1.09 (s, 3H), 0.92 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz) δ 213.43, 147.20, 138.41, 136.58, 135.91, 128.85, 127.95, 122.86,

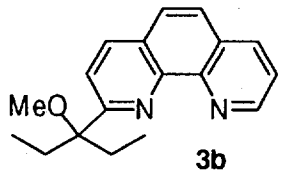
120.61, 112.90, 65.10, 60.32, 59.10, 59.01, 55.15, 29.44, 29.31, 29.04, 28.56, 27.47, 23.88, 19.80; IR ($CHCl_3$) 3436 (NH), 2956 (CH), 1688 (C=O), 909 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{22}H_{29}N_2O$ (MH^+): 335.2123. Found: 335.2134.

General Procedure for Synthesis of 2-(Methoxyalkyl)-phenanthrolines. To a stirred solution of the alcohol (1 equiv.) in THF was added NaH (4 equiv.) in one portion followed by MeI (4 equiv.). The mixture was stirred at 25 °C and monitored by TLC. Upon completion of the reaction, satd aq NH_4Cl was added to quench the reaction, and the resulting mixture was extracted with CH_2Cl_2. The organic extracts were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated. The product was purified by flash chromatography (alumina gel, ethyl acetate/hexane gradient).



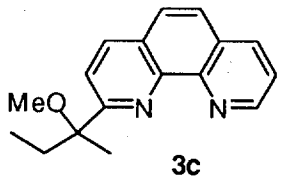
3a

2-[(1-Methoxycyclohexyl)]-1,10-phenanthroline (3a). Through use of the above general procedure, NaH (0.110g, 4.6 mmol), MeI (0.65 mL, 4.6 mmol), and **1a** (0.320 g, 1.15 mmol) were employed, yielding 0.301 g (90%) of **3a** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 9.24 (dd, *J* = 4.50, 1.80 Hz, H_{P9}), 8.25 (d, *J* = 8.40 Hz, H_{P4}, dd, *J* = 8.10, 2.40 Hz, H_{P7}), 7.96 (d, *J* = 8.40 Hz, H_{P3}), 7.82 and 7.75 (two d, *J* = 8.80 Hz, H_{P5} and H_{P6}), 7.61 (dd, *J* = 8.10, 4.50 Hz, H_{P8}), 3.11 (s, 3H, OCH_3), 2.23 (m, 4H, cyclohexyl), 1.74 (m, 6H, cyclohexyl); ^{13}C NMR (75 MHz) δ 166.33, 150.49, 146.33, 145.11, 136.40, 136.04, 128.77, 127.41, 126.38, 126.03, 122.40, 120.45, 80.46, 50.45, 33.83, 25.08, 21.69; IR ($CHCl_3$) 3048 (C-H Ar), 2933 (CH), 908 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{19}H_{21}N_2O$ (MH^+): 293.1654. Found: 293.1665.



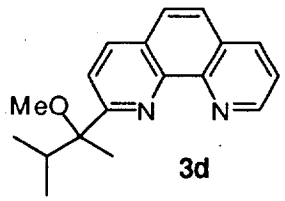
3b

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: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.24 (dd, J = 4.50, 1.80 Hz, H_{P9}), 8.23 (dd, J = 8.40, 1.80 Hz, H_{P7}), 8.20 (d, J = 8.40 Hz, H_{P4}), 7.97 (d, J = 8.40 Hz, H_{P3}), 7.78 and 7.72 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 7.60 (dd, J = 7.80, 4.50 Hz, H_{P8}), 3.24 (s, $OC\underline{H}_3$), 2.34 and 2.24 (two dq, J = 7.5 Hz, $(C\underline{H}_2CH_3)_2$), 0.73 (t, J = 7.50 Hz, $(CH_2C\underline{H}_3)_2$); ^{13}C NMR (75 MHz) δ 164.85, 150.31, 146.45, 145.28, 136.10, 135.54, 128.89, 127.24, 126.55, 125.88, 122.48, 121.52, 84.26, 49.80, 28.17, 7.54; IR ($CHCl_3$) 2969 (C-H Ar), 2935 (CH), 910 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{18}H_{21}N_2O$ (MH^+): 281.1654. Found: 281.1646.



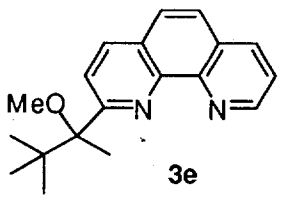
3c

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: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.24 (dd, J = 4.65, 1.80 Hz, H_{P9}), 8.24 (one d, J = 8.40 Hz, H_{P4}, one dd, J = 8.10, 1.80 Hz, H_{P7}), 7.96 (d, J = 8.40 Hz, H_{P3}), 7.82 and 7.75 (two d, J = 8.70 Hz, H_{P5} and H_{P6}), 7.62 (dd, J = 8.10, 4.20 Hz, H_{P8}), 3.22 (s, $OC\underline{H}_3$), 2.19 (q, J = 7.50 Hz, $C\underline{H}_2CH_3$), 1.83 (s, CH_3), 0.90(t, J = 7.50 Hz, $CH_2C\underline{H}_3$); ^{13}C NMR (75 MHz) δ 165.87, 150.48, 146.48, 145.31, 136.11, 136.07, 128.90, 127.43, 126.48, 126.07, 122.52, 120.66, 82.06, 50.85, 32.66, 22.62, 7.96; IR ($CHCl_3$) 2970 (C-H Ar), 2932 (CH), 910 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{17}H_{19}N_2O$ (MH^+): 267.1497. Found: 267.1504.



3d

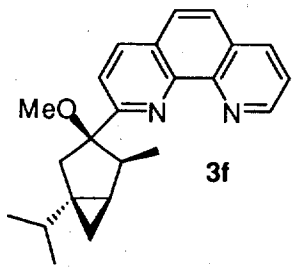
2-[(1-Methoxy-1,2-dimethylpropyl)]-1,10-phenanthroline (3d). Through use of the above general procedure, NaH (0.020g, 0.74 mmol), MeI (0.046 mL, 0.74 mmol), and **1d** (0.052 g, 0.185 mmol) were employed, yielding 0.052 g (70%) of **3d** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.24 (dd, J = 4.40, 1.80 Hz, H_{P9}), 8.24 (dd, J = 8.10, 1.80 Hz, H_{P7}), 8.11 (d, J = 8.40 Hz, H_{P4}), 7.88 (d, J = 8.40 Hz, H_{P3}), 7.81 and 7.74 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 7.60 (dd, J = 8.10, 4.50 Hz, H_{P8}), 3.17 (s, $OC\underline{H}_3$), 2.25 (sep, J = 6.80 Hz, $C\underline{H}(CH_3)_2$), 1.88 (s, $C\underline{H}_3$), 1.00 (d, J = 6.60 Hz, $CH(C\underline{H}_3)CH_3$), 0.71 (d, J = 6.90 Hz, $CH(CH_3)C\underline{H}_3$); ^{13}C NMR (75 MHz) δ 165.28, 150.46, 146.51, 145.13, 136.07, 135.76, 128.87, 127.39, 126.46, 126.07, 122.49, 121.06, 84.40, 51.25, 39.10, 17.72, 17.43, 16.64; IR ($CHCl_3$) 2961 (C-H Ar), 2928 (CH), 866.4 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{18}H_{21}N_2O$ (MH^+): 281.1654. Found: 281.1651.



3e

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: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.23 (dd, J = 4.50, 1.80 Hz, H_{P9}), 8.23 (dd, J = 7.80, 1.80 Hz, H_{P7}), 8.17 (d, J = 8.70 Hz, H_{P4}), 7.88 (d, J = 8.40 Hz, H_{P3}), 7.81 and 7.74 (two d, J = 8.70 Hz, H_{P5} and H_{P6}), 7.60 (dd, J = 8.00, 4.40 Hz, H_{P8}), 3.21 (s, $OC\underline{H}_3$), 1.94 (s, $C\underline{H}_3$), 0.98 (s, $(C\underline{H}_3)_3$); ^{13}C NMR (75 MHz) δ 163.79, 150.37, 145.12, 143.90, 135.97,

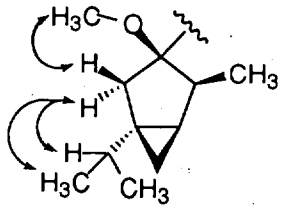
134.34, 128.82, 127.18, 126.47, 125.99, 122.53, 121.43, 86.16, 51.36, 38.83, 26.10, 17.78; IR ($CHCl_3$) 2957 (C-H Ar), 2928 (CH), 857 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{19}H_{23}N_2O$ (MH^+): 295.1810. Found: 295.1818.



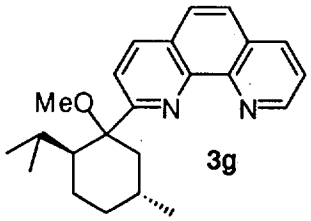
3f

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: ^1H NMR (300 MHz, benzene-d_6) δ 9.05 (dd, J = 4.20, 1.8 Hz, H_{P9}), 7.68 and 7.65 (two d, J = 8.40 Hz, H_{P3} and H_{P4}), 7.55 (dd, J = 8.10, 1.80 Hz, H_{P7}), 7.33 and 7.23 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 6.92 (dd, J = 8.10, 4.20 Hz, H_{P8}), 4.15 (dd, J = 14.4, 1.80 Hz, $C(OCH_3)C\underline{H}H$), 2.95 (s, $OC\underline{H}_3$), 2.75 (dq, J = 6.90, 4.50 Hz, $C\underline{H}CH_3$), 2.53 (d, J = 14.4 Hz, $C(OCH_3)CH\underline{H}$), 1.73 (sep, J = 6.90 Hz, $C\underline{H}(CH_3)_2$), 1.34 (t, J = 3.90 Hz, cyclopropyl-H), 1.28 (two d, J = 6.90 Hz, $CH(C\underline{H}_3)_2$), 1.20 (ddd, J = 4.20, 4.20, 3.90 Hz, cyclopropyl-H), 0.96 (d, J = 6.90 Hz, $CH(C\underline{H}_3)$, 0.40 (dd, J = 7.8, 3.60 Hz, cyclopropyl-H); ^{13}C NMR (75 MHz, benzene-d_6) δ 164.31, 150.24, 147.17, 146.49, 135.87, 135.32, 128.86, 127.48, 126.38, 126.08, 122.61, 120.33, 90.45, 50.77, 48.61, 33.88, 32.90, 30.17, 28.46, 20.82, 19.86, 11.43; 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. This spectrum can be seen on page 133 and was used to conclude that the stereochemistry is *R*.

NOE crosspeaks seen:



IR ($CHCl_3$) 2958 (C-H Ar), 2868 (CH), 856 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{23}H_{27}N_2O$ (MH^+): 347.2123. Found: 347.2137.

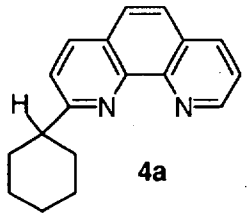


3g

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, $CDCl_3$) δ 9.23 (dd, *J* = 4.40, 1.80 Hz, H_{P9}), 8.24 (dd, *J* = 8.05, 1.80 Hz, H_{P7}), 8.20 (d, *J* = 8.40 Hz, H_{P4}), 7.90 (d, *J* = 8.40 Hz, H_{P3}), 7.82 and 7.74 (two d, *J* = 8.80 Hz, H_{P5} and H_{P6}), 7.61 (dd, *J* = 8.10, 4.20 Hz, H_{P8}), 3.22 (s, $OC\underline{H}_3$), 2.64 (dd, *J* = 14.7, 12.6 Hz, $C(OCH_3)C\underline{H}H$), 2.23 (br dm, *J* = 14.7 Hz, $C(OCH_3)CH\underline{H}$), 1.80 (m, 4H), 1.60 (m, 1H), 1.46 (sep, *J* = 6.90 Hz, $C\underline{H}(CH_3)_2$), 1.29 (m, 1H), 1.05 (d, *J* = 6.6 Hz, $CHC\underline{H}_3$), 1.00 (d, *J* = 6.90 Hz, $CH(C\underline{H}_3)CH_3$), 0.56 (d, *J* = 6.90 Hz, $CH(CH_3)C\underline{H}_3$); ^{13}C NMR (75 MHz) δ 165.46, 150.42, 146.32, 146.13, 136.19, 134.86, 128.85, 127.21, 126.58, 125.93, 122.50, 121.90, 85.86, 51.56, 50.39, 39.30, 34.74, 28.10, 26.82, 23.35, 22.44, 21.16, 18.23; IR ($CHCl_3$) 2958 (C-H Ar), 2868 (CH), 855.5 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{23}H_{29}N_2O$ (MH^+): 349.2275. Found: 349.2270.

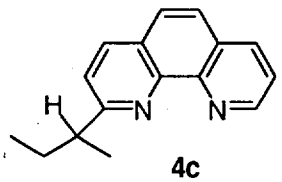
General Procedure for SmI_2 Mediated Demethoxylation of 2-(Methoxyalkyl)phenanthrolines. To a stirred solution of the 2-(methoxyalkyl)phenanthroline in

THF (5 mL) was added a 0.1 *M* solution of SmI_2 in THF (2.5 equiv.) at 25°C. The mixture was stirred at 25 °C and monitored by TLC. Upon completion of the reaction, satd aq NH_4Cl was added to quench the reaction, and the resulting mixture was extracted with CH_2Cl_2. The organic extracts were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated. The product was purified by flash chromatography (alumina, ethyl acetate/hexane gradient).



4a

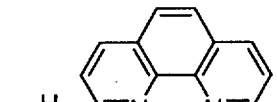
2-[(Cyclohexyl)]-1,10-phenanthroline (4a). Through use of the above general procedure, 0.1 *M* SmI_2 (17.1 mL, 1.71 mmol) was added to **3a** (0.200 g, 0.684 mmol) yielding 0.119 g (66%) of **4a** as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 9.19 (dd, *J* = 4.50, 1.80 Hz, H_{P9}), 8.16(dd, *J* = 8.10, 1.80 Hz, H_{P7}), 8.12 (d, *J* = 8.40 Hz, H_{P4}), 7.71 and 7.64 (two d, *J* = 8.80 Hz, H_{P5} and H_{P6}), 7.54 (dd, *J* = 8.10, 4.20 Hz, H_{P8}), 7.53 (d, *J* = 8.40 Hz, H_{P3}), 3.33 (tt, *J* = 3.00-3.30 Hz, ArCH), 2.12-1.28 (m, 10H, $(CH_2)_5$); ^{13}C NMR (75 MHz) δ 167.47, 150.21, 146.14, 145.34, 136.31, 135.86, 128.67, 127.05, 126.33, 125.35, 122.46, 120.48, 47.74, 33.28, 26.34, 26.04; IR ($CHCl_3$) 3049 (C-H Ar), 2929 (CH), 908 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{18}H_{19}N_2$ (MH^+): 263.1548. Found: 263.1534.



4c

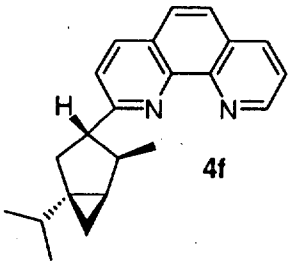
2-[(2-Butyl)]-1,10-phenanthroline (4c). Through use of the above general procedure, 0.1 *M* SmI_2 (4.2 mL, 0.42 mmol) was added to **3c** (0.045 g, 0.68 mmol) yielding

0.011 g (66%) of **4c** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.25 (dd, J = 4.20, 1.50 Hz, H_{P9}), 8.24 (dd, J = 7.80, 1.50 Hz, H_{P7}), 8.19 (d, J = 8.40 Hz, H_{P4}), 7.79 and 7.71 (two d, J = 8.70 Hz, H_{P5} and H_{P6}), 7.61 (dd, J = 8.10, 4.20 Hz, H_{P8}), 7.56 (d, J = 8.40 Hz, H_{P3}), 3.43 (sext, J = 7.20 Hz, C<u>H</u>CH_3), 1.90 and 1.77 (two ddq, J = 7.50 Hz, C<u>H</u>$_2$$CH_3$), 1.42 (d, J = 7.20 Hz, CHC<u>H</u>$_3$), 0.96 (t, J = 7.50 Hz, CH_2C<u>H</u>$_3$); ^{13}C NMR (75 MHz) δ 168.01, 150.21, 145.45, 144.83, 136.39, 136.09, 128.79, 127.14, 126.48, 125.43, 122.54, 120.46, 44.60, 30.23, 20.63, 12.13; IR ($CHCl_3$) 2966 (C-H Ar), 2931 (CH), 851 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{16}H_{17}N_2$ (MH^+): 237.1392. Found: 237.1402.



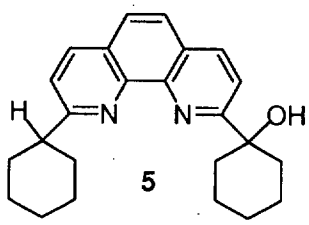
4d

2-(1,2-Dimethylpropyl)-1,10-phenanthroline (4d). Through use of the above general procedure, 0.1 *M* SmI_2 (4.6 mL, 0.46 mmol) was added to **3d** (0.052 g, 0.18 mmol) yielding 0.27 g (58%) of **4d** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.24 (dd, J = 4.40, 1.80 Hz, H_{P9}), 8.23 (dd, J = 8.10, 1.80 Hz, H_{P7}), 8.18 (d, J = 8.40 Hz, H_{P4}), 7.79 and 7.72 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 7.60 (dd, J = 8.10, 4.50 Hz, H_{P8}), 7.53 (d, J = 8.40 Hz, H_{P3}), 3.24 (dq, J = 6.90, 1.50 Hz, C<u>H</u>CH_3), 2.11 (dsep, J = 6.90, 2.10 Hz, C<u>H</u>$(CH_3)_2$), 1.41 (d, J = 7.20 Hz, CHC<u>H</u>$_3$), 1.06 (d, J = 6.30 Hz, $CH(C$<u>H</u>$_3)CH_3$), 0.83 (d, J = 6.60 Hz, $CH(CH_3)C$<u>H</u>$_3$); ^{13}C NMR (75 MHz) δ 162.06, 150.02, 147.35, 146.13, 136.16, 135.76, 128.87, 127.39, 126.67, 125.37, 122.61, 121.32, 49.78, 33.81, 21.69, 19.96, 18.30; IR ($CHCl_3$) 2958 (C-H Ar), 2924 (CH), 852 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{17}H_{19}N_2$ (MH^+): 251.1548. Found: 251.1531.



4f

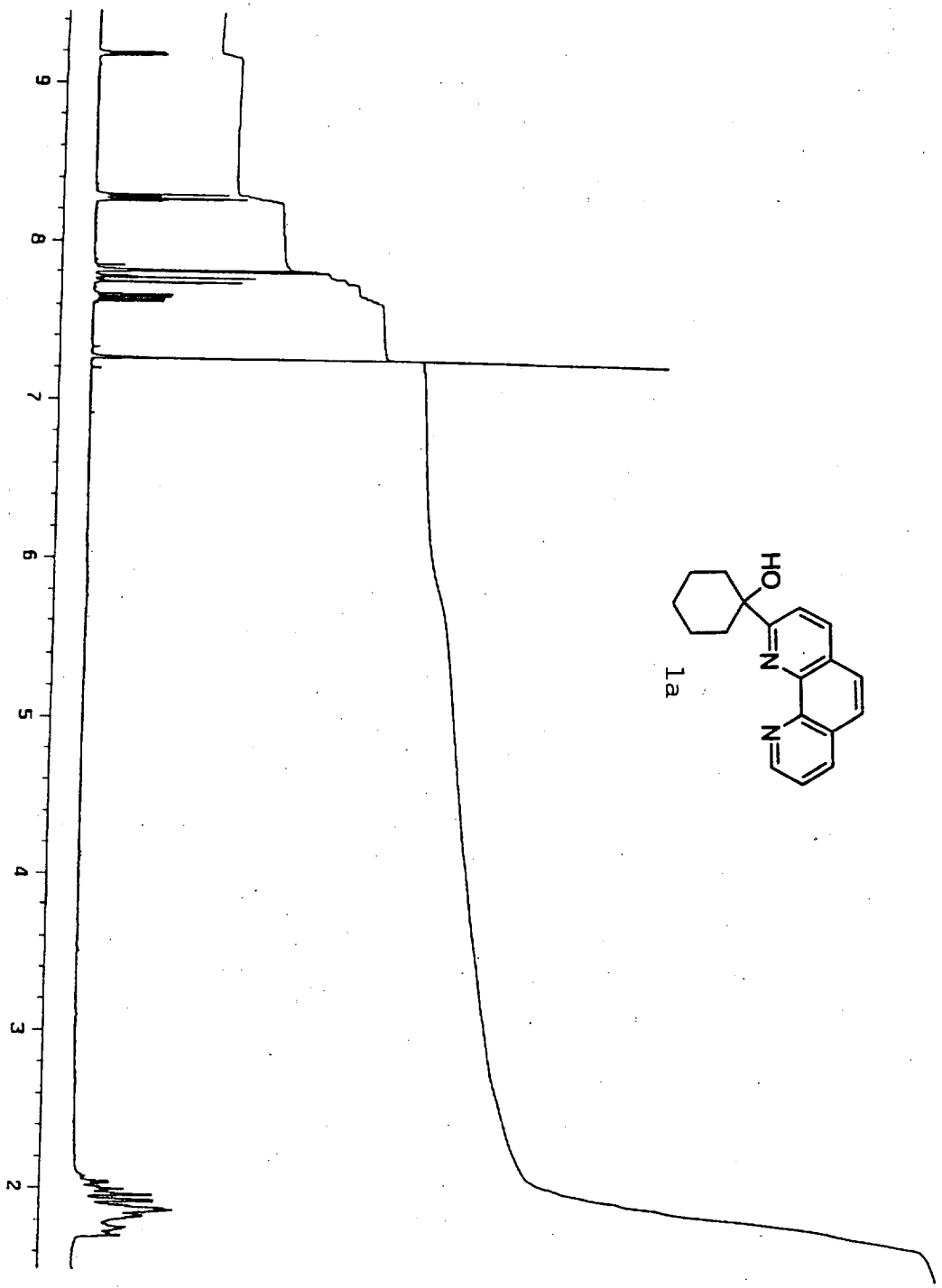
2-[(1*S*,3*S*,4*S*,5*R*)-(1-isopropyl-4-methylbicyclo[3.1.0]hex-3-yl)]-1,10-phenanthroline (4f). Through use of the above general procedure, 0.1 *M* SmI_2 (9.31 mL, 0.931 mmol) was added to **3f** (0.129 g, 0.372 mmol) yielding 0.080 g (68%) of **4f** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.24 (dd, *J* = 4.20, 1.80 Hz, H_{P9}), 8.21 (dd, *J* = 8.10, 1.80 Hz, H_{P7}), 8.17 (d, *J* = 8.40 Hz, H_{P4}), 7.77 and 7.70 (two d, *J* = 8.80 Hz, H_{P5} and H_{P6}), 7.61 (d, *J* = 8.10 Hz, H_{P3}), 7.60 (dd, *J* = 8.10, 4.20 Hz, H_{P8}), 3.05 (ddd, *J* = 10.80, 7.50 Hz, ArCH), 2.64 (dq, *J* = 6.60, 4.20 Hz, C<u>H</u>CH_3), 2.31 (dd, *J* = 12.30, 7.20 Hz, Ar(CH)C<u>H</u>H), 1.98 (br t, *J* = 12.00 Hz, Ar(CH)CH<u>H</u>), 1.54 (sep, *J* = 6.90 Hz, C<u>H</u>$(CH_3)_2$), 1.01 (two d, *J* = 6.60 Hz, two C<u>H</u>$_3$), 0.90 (d, *J* = 6.90 Hz, C<u>H</u>$_3$), 0.69 (br t, *J* = 4.50 Hz, cyclopropyl-H), 0.57 (d, *J* = 7.20 Hz, cyclopropyl-H), 0.25 (m, cyclopropyl-H); ^{13}C NMR (75 MHz) δ 165.17, 150.29, 146.24, 145.34, 136.24, 135.88, 128.78, 127.11, 126.35, 125.51, 122.48, 121.06, 51.40, 42.30, 38.04, 32.73, 32.48, 28.60, 19.99, 19.83, 16.73, 9.33; IR ($CHCl_3$) 3049 (C-H Ar), 2927 (CH), 850 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{22}H_{25}N_2$ (MH^+): 317.2018. Found: 317.2029.



5

9-[(1-Cyclohexyl)]-2-[(1-Hydroxycyclohexyl)]-1,10-phenanthroline (5). Through use of the above general procedure for addition of ketones to phenanthrolines, cyclohexanone (0.094 g, 0.953 mmol) was added to **4a** (0.100 g, 0.381 mmol) and 0.1 *M* SmI_2 (8.38 mL, 0.838 mmol) and converted into 0.083 g (60%) of **5** as a colorless oil: ^{1}H

NMR (300 MHz, $CDCl_3$) δ 8.24 and 8.14 (two d, J = 8.40 Hz, H_{P2} and H_{P9}), 7.76 and 7.70 (two d, J = 8.80 Hz, H_{P5} and H_{P6}), 7.66 and 7.52 (two d, J = 8.40 Hz, H_{P4} and H_{P7}), 3.06 (tt, J = 11.85, 3.30 Hz, $(CH_2)_5C\underline{H}$(phenan)), 2.18-1.74 (m, 10H), 1.52-1.33 (m, 10H); ^{13}C NMR (75 MHz) δ 166.98, 165.25, 144.88, 143.44, 137.16, 136.01, 127.49, 127.28, 126.21, 124.85, 121.47, 118.65, 73.16, 47.24, 36.75, 32.81, 26.64, 26.12, 25.75, 22.71; IR ($CHCl_3$) 3338 (OH), 3042 (C-H Ar), 2927 (CH), 852 (C-H Ar) cm^{-1}; HRMS *m/e* Calcd for $C_{24}H_{29}N_2O$ (MH^+): 361.2280. Found: 361.2272.



^{1}H of 2-[(1-Hydroxycyclohexyl)]-1,10-phenanthroline (1a).

^{1}H of 2-[(1-Ethyl-1-hydroxypropyl)]-1,10-phenanthroline (1b).

1b

^{1}H of 2-[(1-Hydroxy-1-methylpropyl)]-1,10-phenanthroline (1c).

1c

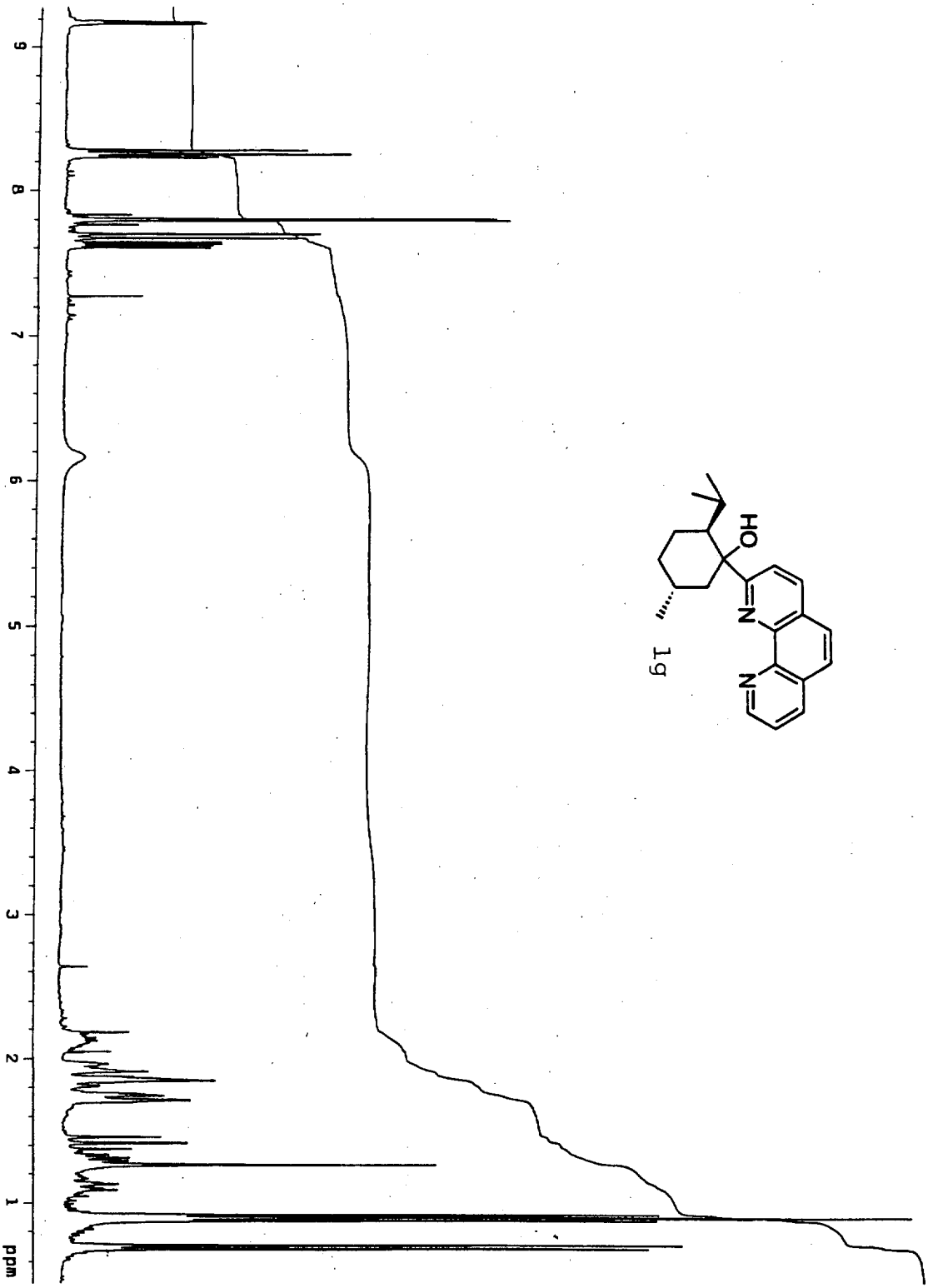
^{1}H of 2-[(1-Hydroxy-1,2-dimethy]propy])]-1,10-phenanthroline (1d).

1d

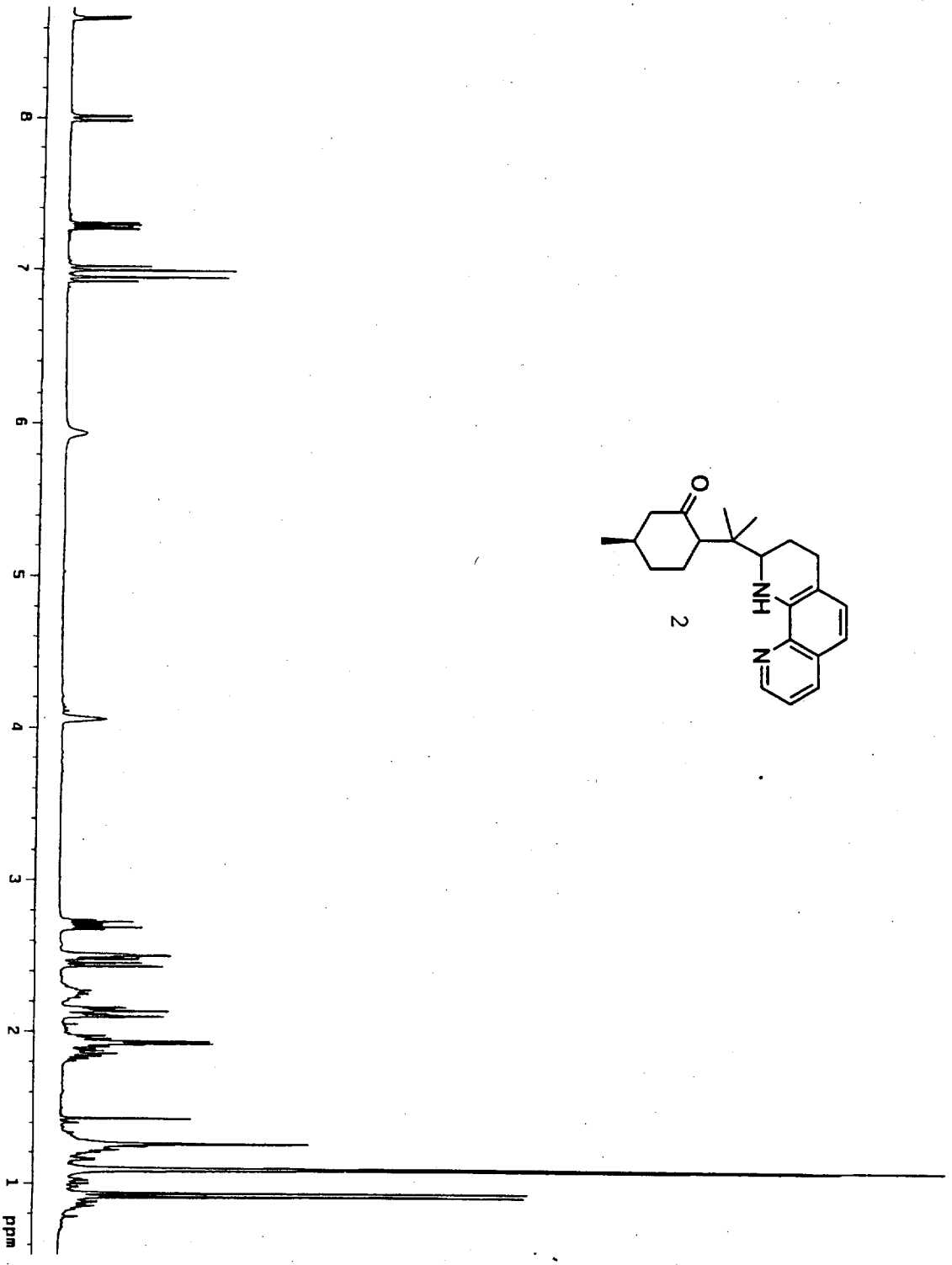
^{1}H of 2-[(1-Hydroxy-1,2,2-trimethylpropyl)]-1,10-phenanthroline (1e).

1e

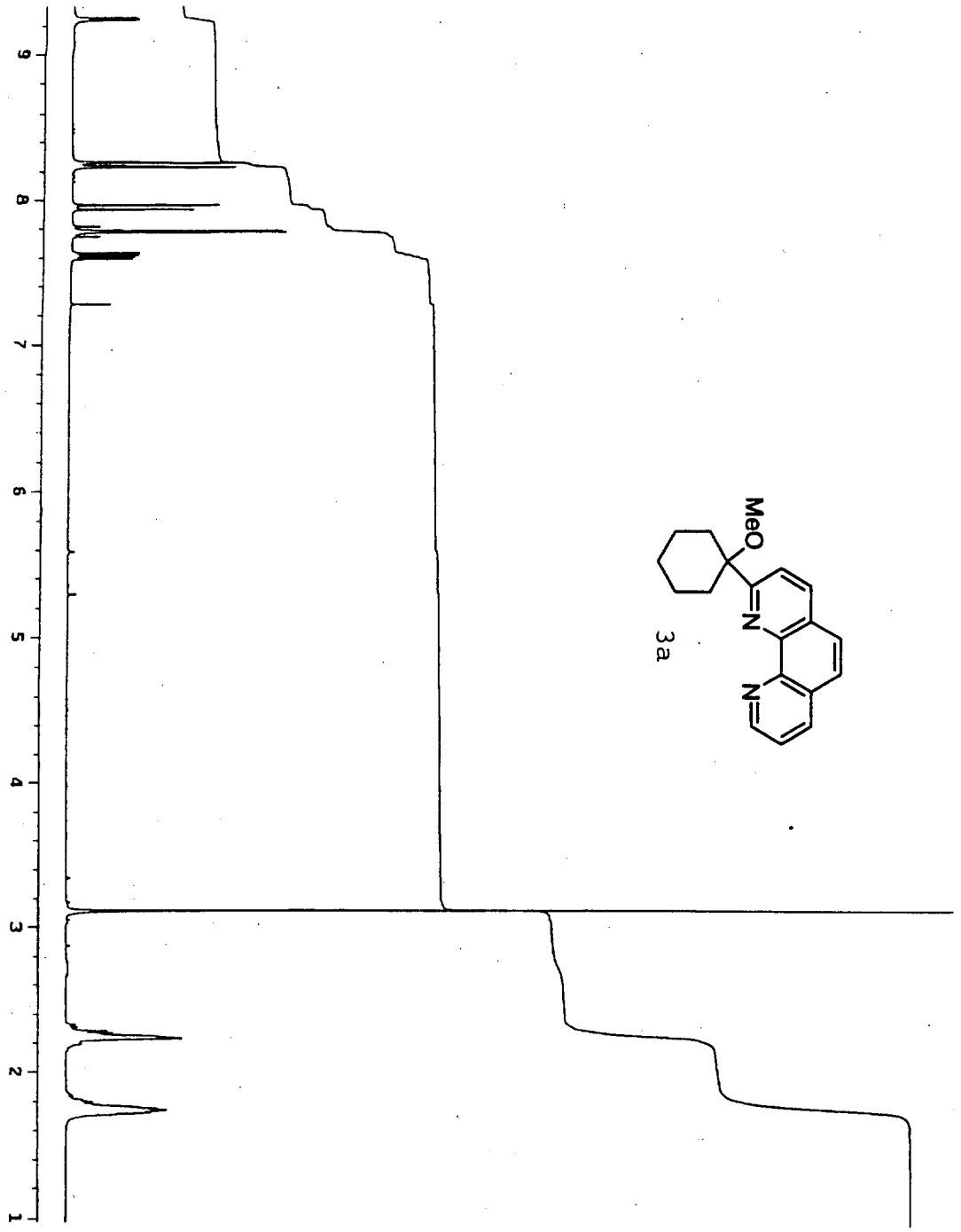
^1H of 2-[(1*S*,3*R*,4*S*,5*R*)-(3-Hydroxy-1-isopropyl-4-methylbicyclo[3.1.0]hex-3-yl)]-1,10-phenanthroline (**1f**).



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



^{1}H of 2-{1-methyl-1-[(4*R*)-4-methyl-2-oxocyclohexyl]ethyl}1,2,3,4-tetrahydro phenanthroline (2).



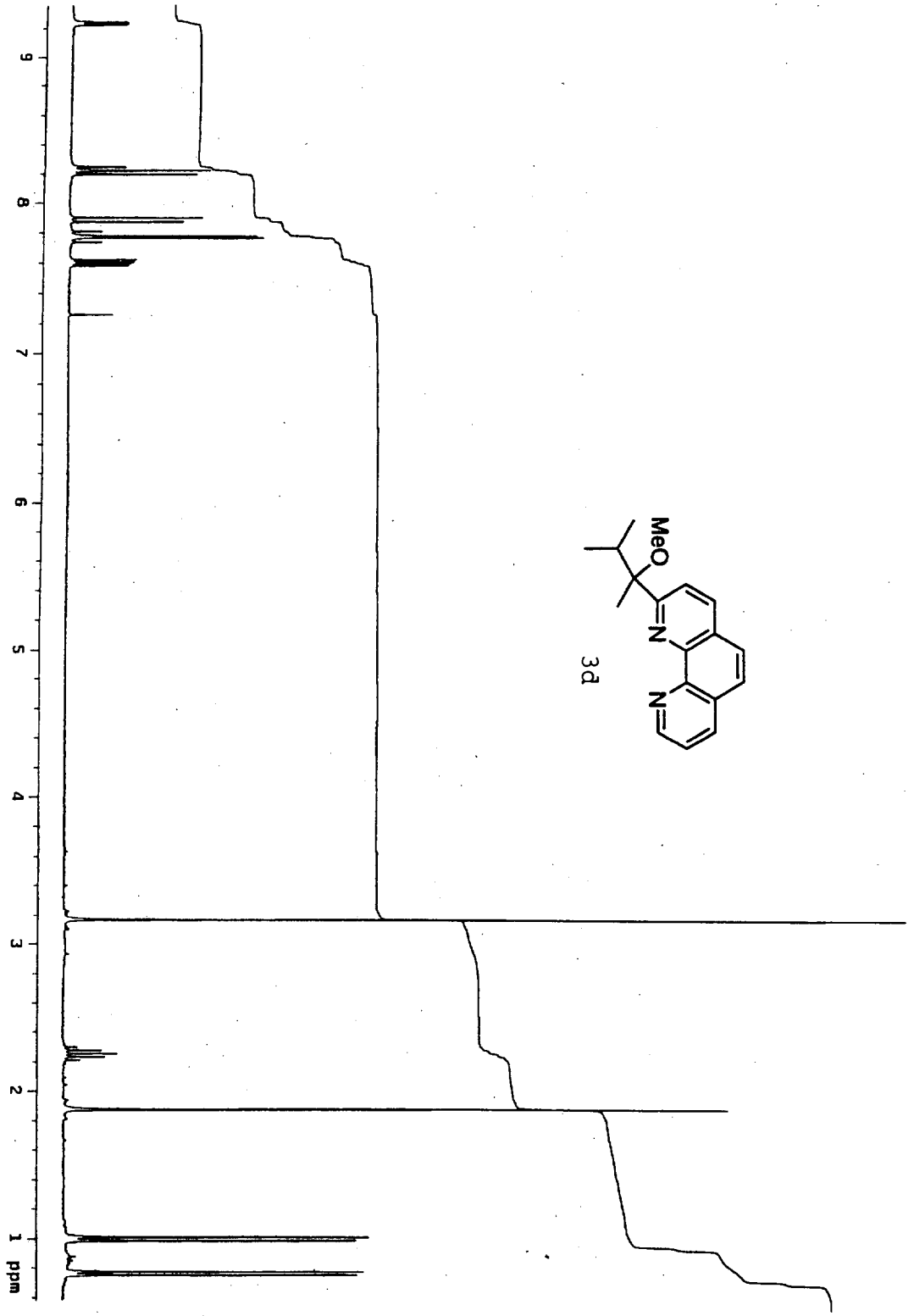
^{1}H of 2-[(1-Methoxycyclohexyl)]-1,10-phenanthroline (3a).

^{1}H of 2-[(1-Ethyl-1-methoxypropyl)]-1,10-phenanthroline (3b).

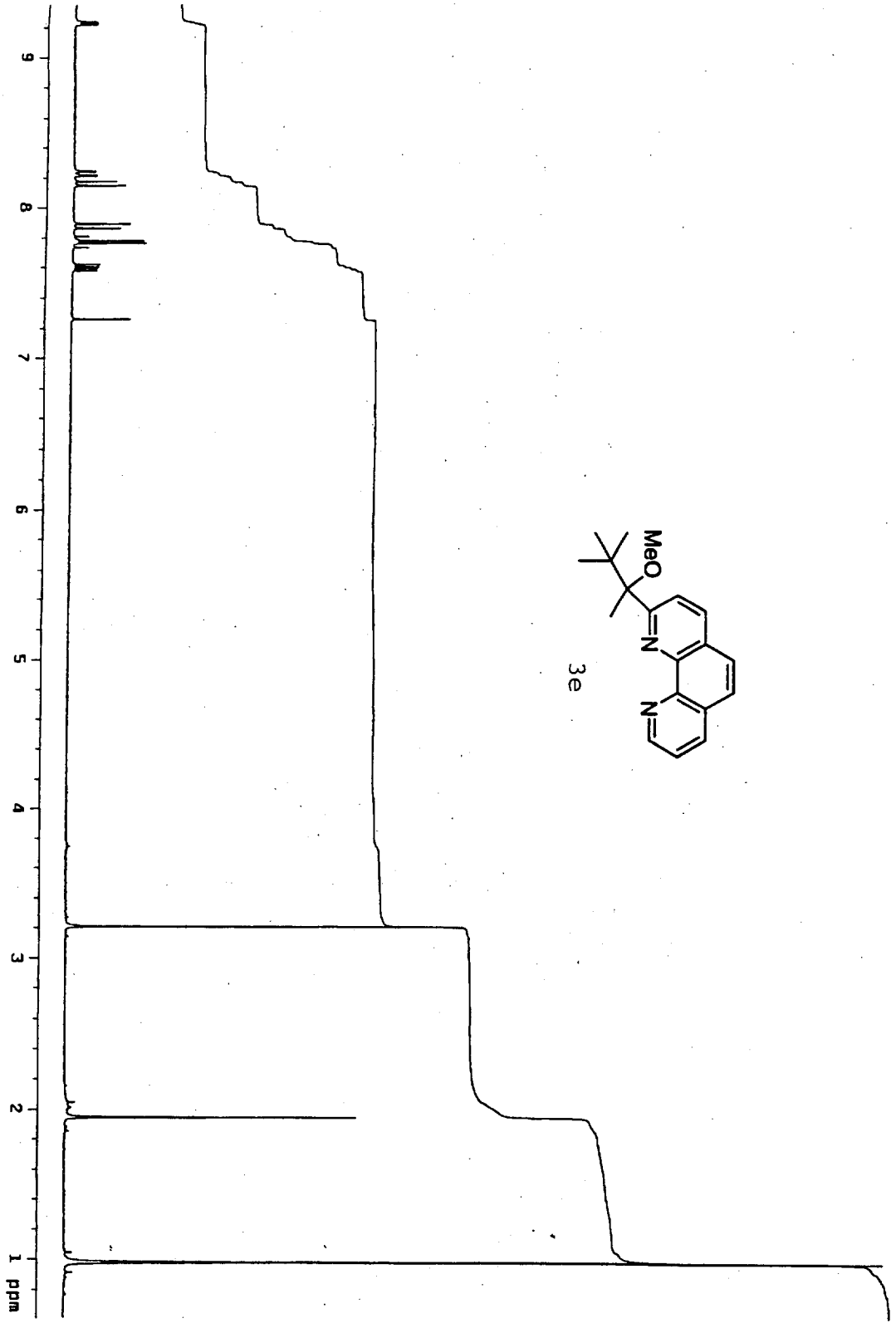
3b

^{1}H of 2-[(1-Methoxy-1-methylpropyl)]-1,10-phenanthroline (3c).

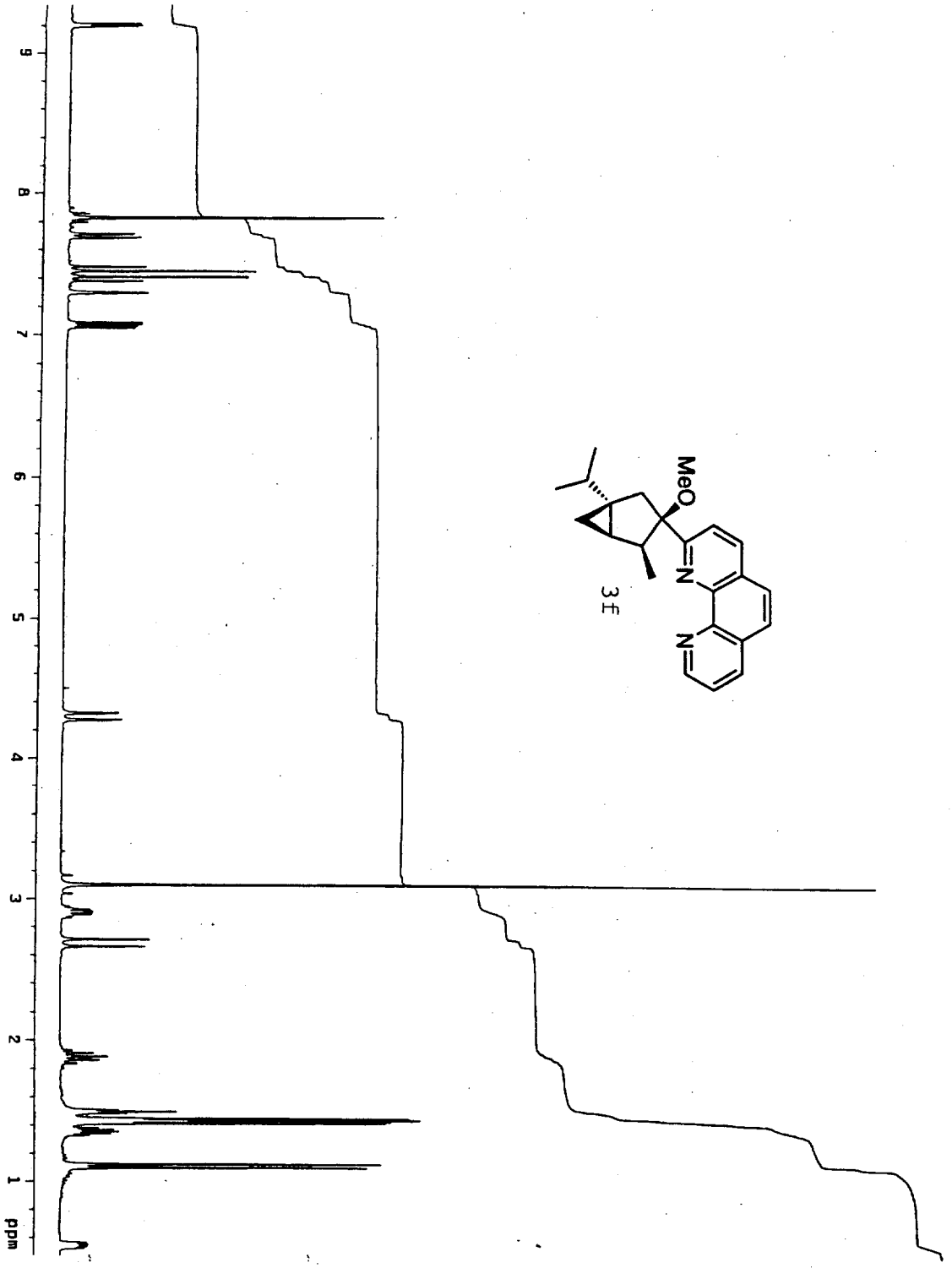
3c



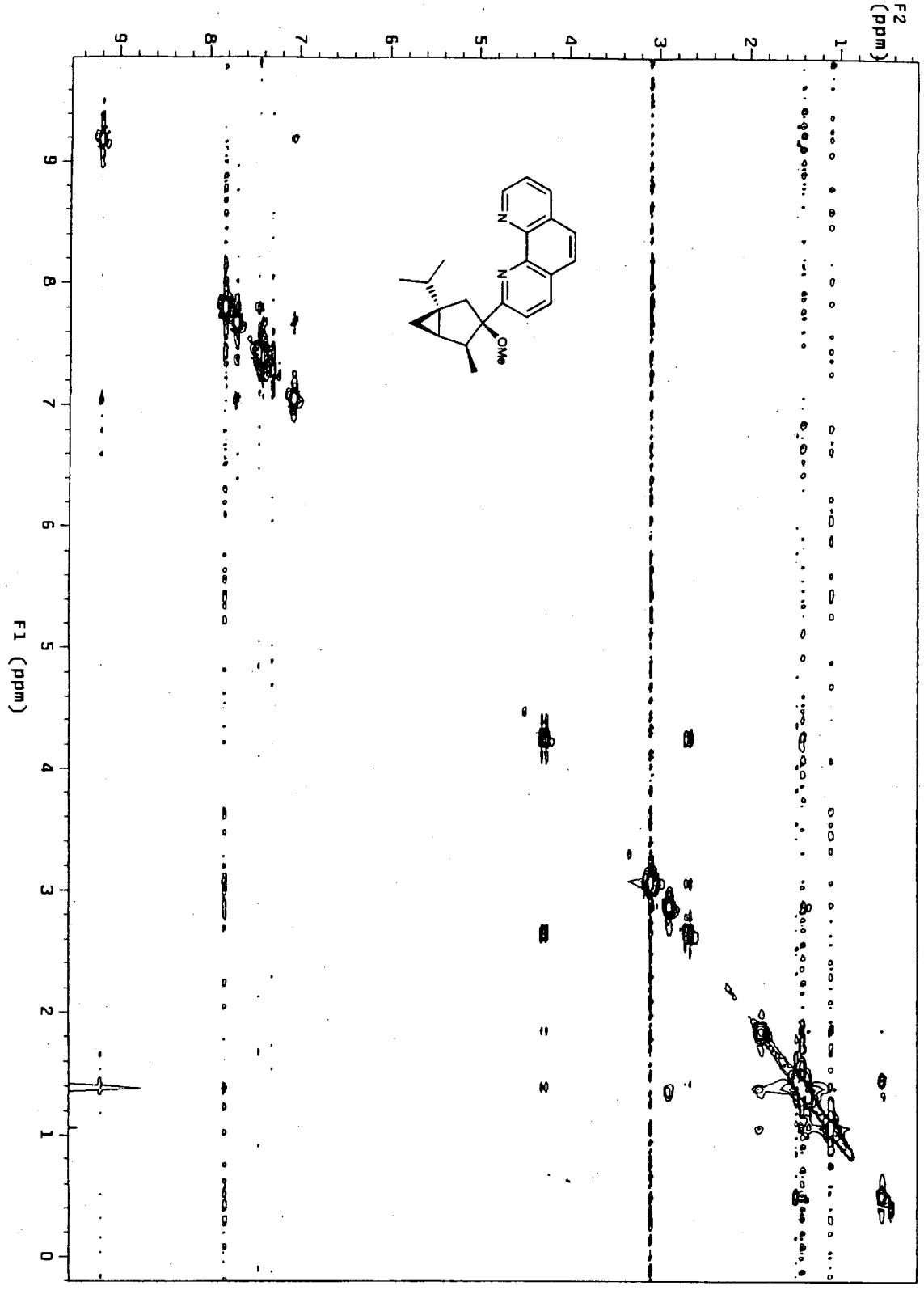
^{1}H of 2-[(1-Methoxy-1,2-dimethylpropyl)]-1,10-phenanthroline (3d).



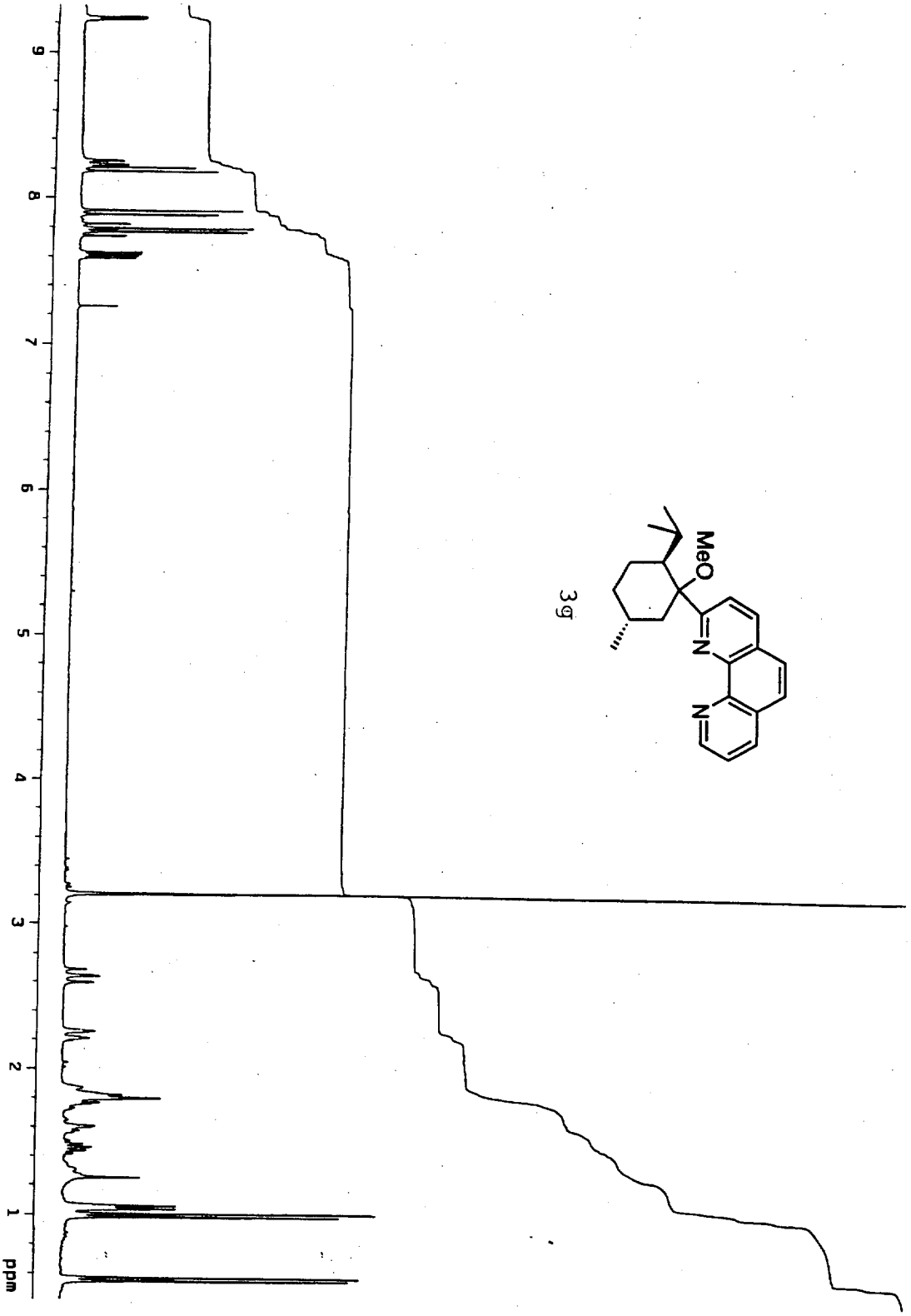
^{1}H of 2-[(1-Methoxy-1,2,2-trimethylpropyl)]-1,10-phenanthroline (3e).



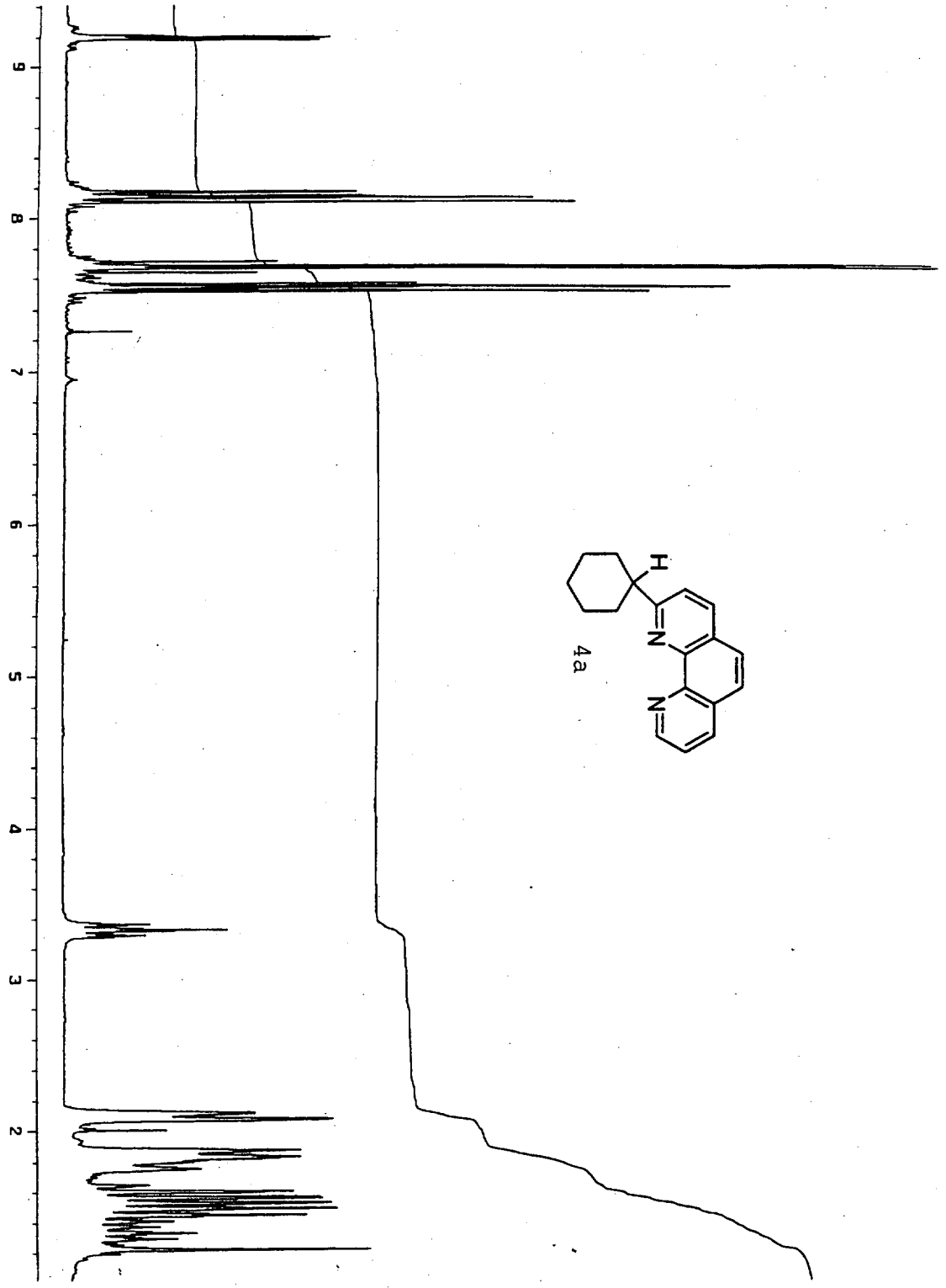
^{1}H of 2-[(1*S*,3*R*,4*S*,5*R*)-(3-Methoxy-1-isopropyl-4-methylbicyclo[3.1.0]hex-3-yl)]-1,10-phenanthroline (3f).



NOESY of 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).



^{1}H of 2-[(2*R**,5*S**)-(1-Methoxy-2-isopropyl-5-methylcyclohexyl)]-1,10-phenanthroline (3g).



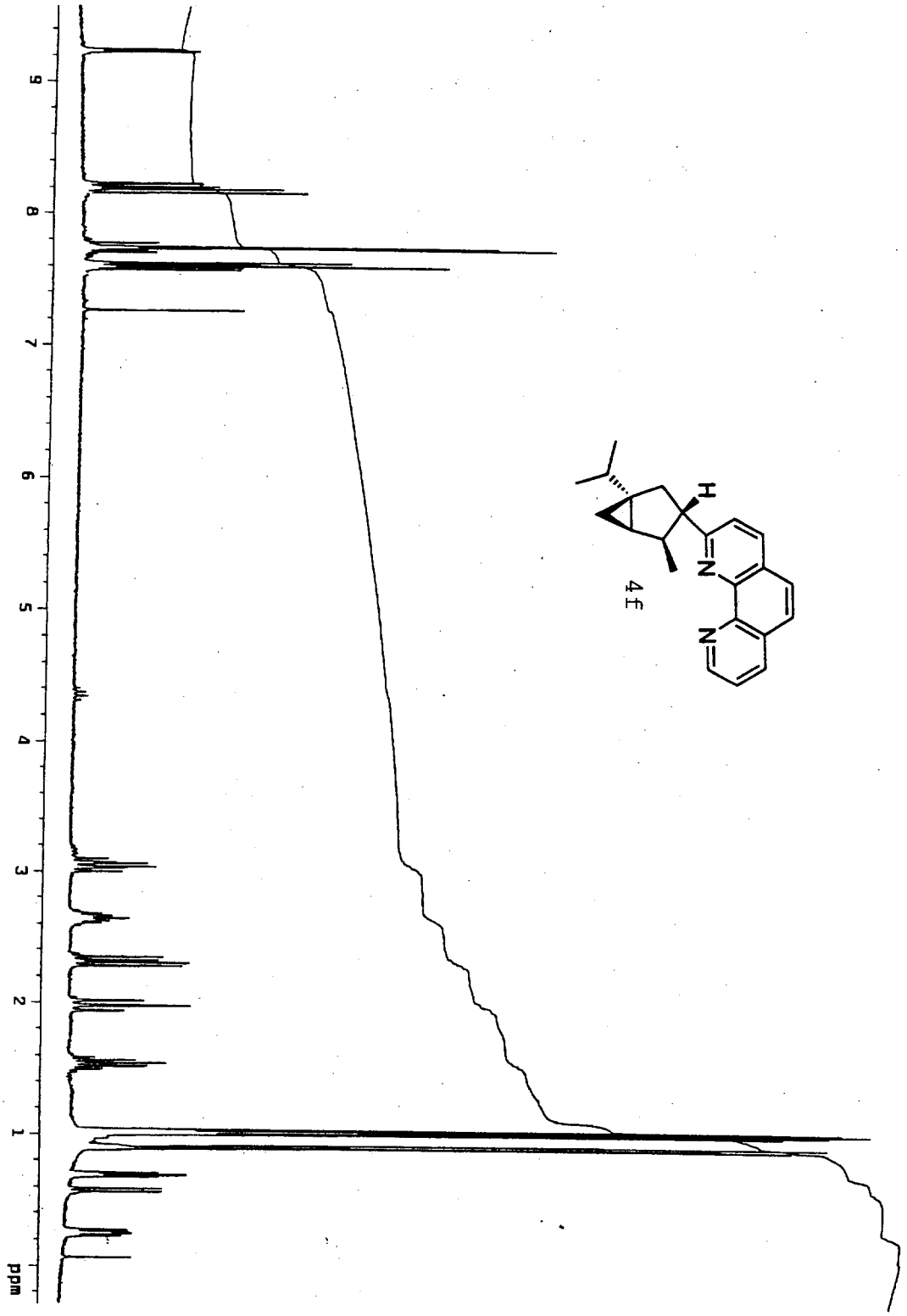
^{1}H of 2-[(Cyclohexyl)]-1,10-phenanthroline (**4a**).

^{1}H of 2-[(2-butyl)]-1,10-phenanthroline (4c).

4c

^{1}H of 2-[(1,2-Dimethylpropyl)]-1,10-phenanthroline (4d).

4d



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

^1H of 9-[(1-Cyclohexyl)]-2-[(1-Hydroxycyclohexyl)]-1,10-phenanthroline (5).