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SUPPORTING INFORMATION

Title: Resolution of Racemic *N*-Benzyl α-Amino Acids by Liquid-Liquid Extraction: A Practical Method Using a Lipophilic Chiral Cobalt(III) Salen Complex and Mechanistic Studies
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Contents:

General: Proton NMR spectra were recorded on a spectrometer operating at 400.13 MHz. Proton chemical shifts are reported in ppm (δ) with the solvent reference relative to tetramethylsilane (TMS) employed as the internal standard (D_2O δ 4.70 ppm, $CDCl_3$ δ 7.26 ppm). The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, dd = doublet of doublet. Carbon NMR spectra were recorded on a 400 spectrometer operating at 100.56 MHz, with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.0). Infrared spectra were recorded on a standard FT/IR; peaks are reported in cm^{-1}. Optical rotation values were measured on an automatic polarimeter with a 1 dm cell at the sodium D line. HPLC determination of the enantiomeric excesses was carried out on a Waters 515 HPLC machine equipped with a Waters 996 PAD diode array detector (detection wavelength 254 or 215 nm) using a chiral stationary phase (ASTEC Chirobiotic R chiral column, 50 x 4.6 mm or ASTEC Chirobiotic T chiral column 250 x 4.6 mm). High resolution mass spectra (HRMS) were performed on a hybrid quadrupole time of flight mass spectrometer equipped with an ESI ion source. A Reserpine solution 100 pg/μl (about 100 count/s), 0.1% $HCOOH/CH_3CN$ 1:1, was used as reference compound (Lock Mass).

Materials: All commercially available reagents were used as received. (*R*,*R*)-*N*,*N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclo-hexanediaminocobalt(II) ([Co^{II}(**3**)]) was purchased from Sigma-Aldrich. (*R*),(*R*)-*trans*-cyclohexane-1,2-diamine tartrate salt[1] and (*R*,*R*)-*N*,*N'*-bis-salicylidene-1,2-cyclohexanediamine[2] (**1**) were prepared as reported. Extractions were performed using HPLC grade water and dichloromethane.

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[1] H-J. Schanz, M. A. Linseis, D. G. Gilheany, *Tetrahedron: Asymmetry* **2003**, *14*, 2763-2769.

[2] X. Yao, M. Qiu, W. Lü. H. Chen, Z. Zheng, *Tetrahedron: Asymmetry* **2001**, *12*, 197-204.

Synthesis of Ligands, Cobalt Complexes and *N*-Substituted Amino Acids

Synthesis of (*R*,*R*)-*N*,*N′*-Bis(3-Methyl-Salicylidene)-1,2-Cyclohexanediamine (2): Prepared according to the method reported by Jacobsen *et al.*[3] A 250 mL flask fitted with a reflux condenser was charged with (*R*),(*R*)-*trans*-cyclohexane-1,2-diamine tartrate salt (1.950 g, 7.35 mmol), K_2CO_3 (2.030 g, 14.68 mmol) and H_2O (15 mL). The mixture was stirred to dissolve the solids, then EtOH (70 mL) was added and the yellow suspension was heated to 70 °C for 20 min. A solution of 2-hydroxy-3-methyl-benzaldehyde (2.000 g, 14.68 mmol) in EtOH (20 mL) was added dropwise over 15 min. The mixture was stirred at 70 °C for 2 h, cooled in ice then H_2O (60 mL) was added. The resulting yellow precipitate was collected by filtration and washed with cold EtOH (2 x 10 mL). The solid was dissolved in dichloromethane (40 mL) and washed with H_2O (2 x 25 mL), aqueous NaCl (2 x 25 mL) then the organic phase was dried (Na_2SO_4) and volatiles removed under reduced pressure to give the product as a yellow oil, which solidified and was then recrystallised from acetone. Yield: 1.52 g (60%). $[\alpha]_D = -468$ ($c = 0.103$, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 13.61$ (bs, 2H), 8.29 (s, 2H), 7.14 (d, $J = 7.6$ Hz, 2H), 7.03 (d, $J = 7.6$ Hz, 2H), 6.76-6.72 (m, 2H), 3.36-3.30 (m, 2H), 2.26 (s, 6H), 1.98-1.88 (m, 4H), 1.79-1.68 (m, 2H), 1.52-1.46 ppm (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 164.9$, 159.3, 133.2, 129.1, 125.7, 118.1, 117.9, 72.6, 33.2, 24.2, 15.4 ppm; HRMS (ESI) calcd. for $C_{22}H_{26}N_2O_2$ 373.1887 $[M]^+$; found: 373.1884.

(*R*,*R*)-*N*,*N′*-Bis-Salicylidene-1,2-Cyclohexanediaminocobalt(II) - [Co^{II}(1)]: Prepared from (*R*,*R*)-*N*,*N′*-Bis-salicylidene-1,2-cyclohexanediamine (**1**) and cobalt(II) acetate as previously reported.[4] Yield: 83%. $[\alpha]_D = -1398$ ($c = 0.049$, $CHCl_3$). Lit. value[4] $[\alpha]_D = 1420$ ($c = 0.050$, $CHCl_3$); HRMS (ESI) calcd. for $C_{20}H_{20}N_2O_2Co$ 379.0857 $[M]^+$; found: 379.0855.

(*R*,*R*)-*N*,*N′*-Bis(3-Methyl-Salicylidene)-1,2-Cyclohexanediaminocobalt(II) - [Co^{II}(2)]: Prepared from (*R*,*R*)-*N*,*N′*-Bis(3-methyl-salicylidene)-1,2-cyclohexanediamine (**2**) and cobalt(II) acetate according to the method reported by Belokon *et al.*[4] Yield: 81%. $[\alpha]_D = -745$ ($c = 0.050$, $CHCl_3$); FT-IR (Nujol): $\upsilon =$ 2959, 2725, 2672, 1608, 1525, 1507, 1354, 1201, 1175 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{24}N_2O_2Co$ 407.1164 $[M]^+$; found: 407.1155.

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[3] J. F. Larrow, E. N. Jacobsen, *J. Org. Chem.* **1994**, *59*, 1939-1942.

[4] Y. N. Belokon, J. Fuentes, M. North, J. W. Steed, *Tetrahedron* **2004**, *60*, 3191-3204.

General Procedure for the Preparation of Cobalt(III) Acetate Complexes [Co^{III}(1-3)(OAc)]: Complexes [Co^{III}(**1-3**)(OAc)] were prepared following a slightly modified literature procedure.[5] Glacial acetic acid (0.35 mL, 6.0 mmol) was added to a stirred solution of the (salen)cobalt(II) complex (0.300 mmol) in toluene (20 mL) under air. An immediate colour change from bright red to brown was observed. The solution was stirred for a further 30 min before volatiles were removed under reduced pressure to leave the (salen)cobalt (III) acetates [Co^{III}(**1-3**)(OAc)] as brown powders, which were used directly in subsequent extractions without further purification.

(*R*,*R*)-*N*,*N'*-Bis-Salicylidene)-1,2-Cyclohexanediaminocobalt(III) acetate - [Co^{III}(1)(OAc)]: ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 8.42 (s, 2H), 7.43-7.25 (m, 4H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.97 (m, 2H), 3.52-3.45 (m, 2H), 2.09-1.75 (m, 5H), 1.65-1.51 ppm (m, 3H).

(*R*,*R*)-*N*,*N'*-Bis(3-methyl-Salicylidene)-1,2-Cyclohexanediaminocobalt(III) acetate - [Co^{III}(2)(OAc)]: ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.54 (bs, 2H), 7.39-7.15 (m, 4H), 6.57 (bs 2H), 6.97 (m, 2H), 4.03 (bs, 2H), 2.12-1.90 (m, 3H), 1.87 (s, 6H), 1.66-1.50 ppm (m, 3H).

(*R*,*R*)-*N*,*N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclo-hexanediaminocobalt(III) acetate - [Co^{III}(3)(OAc)]: Spectroscopic data was consistent with that previously reported.[6]

(*R*,*R*)-*N*,*N'*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) Trifluoromethanesulfonate - [Co^{III}(3)(OTf)]: Prepared according to a reported method:[7] To a stirred solution of complex [Co^{II}(**3**)] (0.181 g, 0.300 mmol) in toluene (20 mL), in a 50 mL flask wrapped in foil, was added silver trifluoromethanesulfonate (0.076 g, 0.300 mmol) and the mixture was stirred for 1 h. After removal of silver by filtration, the filtrate was concentrated to a green powder which was used immediately in an extraction without further purification. Yield: 0.206 g (99%).

(*R*,*R*)-*N*,*N'*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) Hexafluorophosphate - [Co^{III}(3)(PF$_6$)]: Prepared according to a reported method:[7] To a stirred solution of complex [Co^{II}(**3**)] (0.181 g, 0.300 mmol) in MeCN (20 mL), was added ferrocenium hexafluorophosphate (0.099 g, 0.300 mmol) with an immediate colour change from red to dark green observed. The mixture was stirred for 30 min before volatiles were removed under reduced pressure and the brown residue washed with hexane (3 x 10 mL) to remove ferrocene. The resulting

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[5] S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunage, K. B. Hansen, A. E. Gould, M. E. Furrow, E. N. Jacobsen, *J. Am. Chem. Soc.* **2002**, *124*, 1307-1315.

[6] L. P. C. Nielsen, C. P. Stevenson, D. G. Blackmond, E. N. Jacobsen, *J. Am. Chem. Soc.* **2004**, *126*, 1360-1362.

[7] G-J. Kim, H. Lee, S-J. Kim, *Tetrahedron Lett.* **2003**, *44*, 5005-5008.

green powder was used immediately in an extraction without further purification. Yield: 0.222 g (99%).

Typical Procedure for the Synthesis of *N*-Benzyl Amino Acids: These were prepared according to the method reported by Quitt *et al.* as follows:[8] Benzaldehyde (5.09 mL, 50.0 mmol) was added to a vigorously stirred solution of the amino acid (50.0 mmol) in aqueous NaOH (2 M, 25 mL). The emulsion was stirred for 30 min before the mixture was cooled in an ice bath and sodium borohydride (0.570 g, 15.0 mmol) was added in small portions over 15 min. The mixture was allowed to warm to room temperature then stirred for a further hour before a second equivalent of benzaldehyde (5.09 mL, 50.0 mmol) was added. The mixture was stirred vigorously for 30 min, cooled in an ice bath and sodium borohydride (0.570 g, 15.0 mmol) was added in small portions over 15 min. The mixture was stirred for a further 2 h then diluted with H_2O (30 mL) and washed with dichloromethane (2 x 30 mL). Hydrochloric acid (1 M) was added until neutral pH was obtained and the resulting white precipitate was collected by filtration, washed with water (2 x 10 mL) and then acetone (2 x 10 mL) to give the *N*-benzyl amino acid as a white powder.

(*rac*)-*N*-Benzylalanine [2-*N*-Benzylamino Propionic Acid]: Yield = 71%. Analytical and spectroscopic data was consistent with that previously reported.[9] ^{1}H-NMR (200 MHz, D_2O): δ = 7.29-7.25 (m, 5H), 4.00 (m, 2H), 3.47 (q, J = 7.0 Hz, 1H), 1.27 ppm (d, J = 7.0 Hz, 3H); HPLC conditions: Chirobiotic R (50 x 4.6 mm) column (9:1 H_2O:CH_3CN), 1.0 mL/min, (*S*) enantiomer t_R = 1.141 min, (*R*) enantiomer t_R = 2.754 min.

(*rac*)-*N*-Benzylthreonine [2-*N*-Benzylamino-3-Hydroxy Butyric Acid]: Yield = 56%. Analytical and spectroscopic data was consistent with that previously reported.[10] ^{1}H-NMR (400 MHz, D_2O-NaOH): δ = 7.35-7.23 (m, 5H), 3.74-3.71 (overlapping m, 1H), 3.73 (overlapping AB, J = 12.8 Hz, 1H), 3.52 (AB, J = 12.8 Hz, 1H), 2.88 (d, J = 6.8 Hz, 1H), 1.06 ppm (d, J = 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, D_2O-NaOH): δ = 180.0, 139.1, 128.7, 127.3, 69.5, 68.6, 51.4, 19.0 ppm; HPLC conditions: Chirobiotic R (50 x 4.6 mm) column (H_2O), 0.5 mL/min, (*S*) enantiomer t_R = 3.331 min, (*R*) enantiomer t_R = 4.008 min.

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[8] P. Quitt, J. Hellerbach, K. Vogler, *Helv. Chim. Acta* **1963**, *46*, 327-333.

[9] R. Kadyrov, T. H. Riermeier, U. Dingerdissen, V. Tararov, A. Boerner, *J. Org. Chem.* **2003**, *68*, 4067-4070.

[10] V. I. Tararov, R. Kadyrov, C. Fischer, A. Broener, *Synlett.* **2004**, *11*, 1961-1962.

***(rac)*-*N*-Benzylserine [2-*N*-Benzylamino-3-Hydroxy Propionic Acid]:** Yield: = 40%. Analytical and spectroscopic data was consistent with that previously reported.[10] ^{1}H-NMR (400 MHz, D_2O-NaOH): δ = 7.39-7.22 (m, 5H), 3.69 (d, *J* = 12.4 Hz, 1H), 3.59 (d, *J* = 5.2 Hz, 1H), 3.52 (d, *J* = 12.4 Hz, 1H), 3.07 (t, *J* = 5.2 Hz, 1H) ppm; ^{13}C-NMR (100 MHz, D_2O-NaOH): δ = 179.8, 138.9, 131.2, 128.7, 128.6, 128.2, 127.3, 64.2, 63.0, 51.1 ppm; HPLC conditions: Chirobiotic R (50 x 4.6 mm), (9:1 H_2O:CH_3OH), 1 ml/min, (*S*) enantiomer t_R = 1.258 min, (*R*) enantiomer t_R = 2.176 min.

(*rac*)-*N*-Benzylvaline [2-*N*-Benzylamino-3-Methyl Butyric Acid]: Yield = 60%. Analytical and spectroscopic data was consistent with that previously reported.[11] ^{1}H-NMR (400 MHz, D_2O-NaOH): δ = 7.33-7.22 (m, 5H), 3.67 (AB, *J* = 12.8 Hz, 1H), 3.45 (AB, *J* = 12.8 Hz, 1H), 2.76 (d, *J* = 6.0 Hz, 1H), 1.75-1.68 (m, 1H), 0.82 (d, *J* = 6.8 Hz, 3H), 0.78 ppm (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, D_2O-NaOH): δ = 181.7, 139.0, 128.7, 128.6, 127.3, 69.0, 51.6, 30.7, 18.8, 18.4 ppm; HPLC conditions: Chirobiotic R (50 x 4.6 mm) column (9:1 H_2O:CH_3CN), 1.0 mL/min, (*S*) enantiomer t_R = 1.175 min, (*R*) enantiomer t_R = 2.199 min.

(*rac*)-*N*-Benzylphenylalanine [2-*N*-Benzylamino-3-Phenyl Propionic Acid]: Yield = 91%. Analytical and spectroscopic data was consistent with that previously reported.[12] ^{1}H-NMR (400 MHz, D_2O-NaOH): δ = 7.30-7.12 (m, 10H), 3.65 (AB, *J* = 12.4 Hz, 1H), 3.46 (AB, *J* = 12.4 Hz, 2H), 3.28-3.23 (m, 1H), 2.86-2.74 ppm (m, 2H); ^{13}C-NMR (100 MHz, D_2O-NaOH): δ = 181.1, 138.8, 138.0, 129.3, 128.6, 128.5, 127.3, 126.6, 64.5, 51.0, 39.0 ppm; HPLC conditions: Chirobiotic R (50 x 4.6 mm) column (9:1 H_2O:CH_3CN), 1.0 mL/min, (*S*) enantiomer t_R = 1.824 min, (*R*) enantiomer t_R = 2.489 min.

(*rac*)-*N*-Benzylleucine [2-*N*-Benzylamino-4-Methyl Pentanoic Acid]: Yield = 65%. Analytical and spectroscopic data was consistent with that previously reported.[11] ^{1}H-NMR (400 MHz, D_2O-NaOH): δ = 7.34-7.23 (m, 5H), 3.66 (AB, *J* = 12.4 Hz, 1H), 3.47 (AB, *J* = 12.4 Hz, 1H), 3.04-3.00 (m, 1H), 1.52-1.44 (m, 1H), 1.38-1.24 (m, 2H), 0.80 (d, *J* = 6.4 Hz, 3H), 0.77 ppm (d, *J* = 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, D_2O-NaOH): δ = 183.0, 138.9, 128.8, 128.6, 127.3, 91.9, 51.1, 42.6, 24.8, 22.5, 21.7 ppm; HPLC conditions: Chirobiotic R (50 x 4.6 mm) column (9:1 H_2O:CH_3CN), 1.0 mL/min, (*S*) enantiomer t_R= 1.304 min, (*R*) enantiomer t_R= 1.909 min.

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[11] N. A. Hassan, E. Bayer, J. C. Jochims, *J. Chem. Soc. Perkin Trans. 1* **1998**, 22, 3747-3758.

[12] G. Verardo, P. Geatti, E. Pol, A. G. Giumanini, *Can. J. Chem.* **2002**, *80*, 779-788.

Synthesis of *(rac)-N*-Benzyl-*N*-Methylphenylalanine [2-(*N*-Benzyl-*N*-Methylamino)-3-Phenyl Propionic Acid].[8] Finely powdered *N*-benzylphenylalanine (1.27 g, 5 mmol) was treated with a mixture of formic acid (2.07 g, 1.7 mL, 45 mmol) and an aqueous solution of formaldehyde (0.54 g, 37% w/w, 1.5 mL, 18 mmol) at 100°C, in a round bottom flask equipped with a reflux condenser. After 4 h the reaction was cooled to room temperature and the solvents were evaporated under vacuum. A colourless oily residue was obtained which was crystallized from hot water to give the desired compound as a colourless solid. Yield: 80 %. ^{1}H-NMR (400 MHz, D_2O-NaOH): δ = 7.40-7.20 (m, 10H), 3.67 (AB system, J_{AB} = 12.8 Hz, v_1 = 1533.1 Hz, v_2 = 1403.7 Hz, 2H), 3.37-3.31 (m, 1H), 3.01 (dd, J_1 = 13.1 Hz, J_2 = 10.0 Hz, 1H), 2.92 (dd, J_1 = 13.1 Hz, J_2 = 5.4 Hz, 1H), 2.20 (s, 3H) ppm; ^{13}C-NMR (100 MHz, D_2O-NaOH): δ = 179.3, 139.8, 138.9, 130.7, 129.9, 129.3, 129.2, 128.2, 127.1, 72.2, 58.4, 39.0, 37.0 ppm; HRMS (ESI): calcd. for $C_{17}H_{19}NO_2$ 292.1308 $[M+Na]^+$; found: 292.1306.

Synthesis of *(rac)-N*-Methylphenylalanine [2-(*N*-Methylamino)-3-Phenyl Propionic Acid].[8] *N*-benzyl-*N*-methylphenylalanine (0.20 g, 0.74 mmol) was dissolved in glacial acetic acid (2.90 mL) and concentrated aqueous (36.6% w/w) hydrochloric acid (100 μL). The resulting solution was hydrogenated using palladium on charcoal (10 % Pd, 0.01 g). After hydrogenation the catalyst was filtered off and the filtrate was evaporated under vacuum to obtain an oily product. The oily residue was dissolved in water and neutralized with saturated $NaHCO_3$ to *ca* pH 7. During neutralization white crystals precipitated which were collected and recrystallized from water. Analytical and spectroscopic data was consistent with that previously reported.[13] Yield: 45%. ^{1}H-NMR (400 MHz, D_2O-NaOH): δ = 7.27-7.13 (m, 5H), 3.11 (t, J = 6.8 Hz, 1H), 2.84-2.71 (m, 2H), 2.12 (s, 3H) ppm; ^{13}C-NMR (100 MHz, D_2O-NaOH): δ = 181.4, 138.0, 129.2, 128.4, 126.5, 66.8, 38.9, 33.0 ppm; HRMS (ESI): calcd. for $C_{10}H_{13}NO_2$ 180.1019 $[M+H]^+$; found: 180.1016. HPLC conditions: Chirobiotic T (250 x 4.6 mm) column (1:1 H_2O:CH_3OH), 1.0 mL/min, (*S*) enantiomer t_R = 9.817 min, (*R*) enantiomer t_R = 13.126 min.

Synthesis of *(rac)-N,N*-Dimethylphenylalanine [2-(*N,N*-Dimethylamino)-3-Phenyl Propionic Acid].[14] Phenylalanine (1.00 g, 6 mmol) was suspended in water (70 mL) and aqueous formaldehyde (4 mL, 37% w/w, 50 mmol) and palladium on charcoal (10 % Pd, 1.00 g) were added. Hydrogenation was carried out for 48 h at atmospheric pressure. The resulting aqueous

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[13] G. G. Harrigan, W. Y. Yoshida, R. E. Moore, D. G. Nagle, P. U. Park, J. Biggs, V. J. Paul, S. L. Moorberry, T. H. Corbett, *J. Nat. Prod.* **1998**, *61*, 1221-1225.

[14] D. Arbain, J. Langley, K. Picker, W. C: Taylor, *Aust. J. Chem.* **1991**, *44*, 887-890.

slurry was heated to reflux, then filtered hot, and the water removed from the filtrate under vacuum. The crude solid was dissolved in a minimum of hot methanol and the solution cooled to yield crystals of *N*,*N*-dimethylphenylalanine. Analytical and spectroscopic data was consistent with that previously reported.[14] Yield: 25%. ^{1}H-NMR (400 MHz, D_2O-NaOH): δ = 7.38-7.20 (m, 5H), 3.81-3.75 (m, 1H), 3.06 (dd, J_1 = 13.7 Hz, J_2 = 9.0 Hz, 1H), 3.28 (dd, J_1 =13.7 Hz, J_2 = 5.8 Hz, 1H), 2.87 (s, 6H) ppm; ^{13}C-NMR (100 MHz, D_2O-NaOH): δ = 172.6, 135.6, 129.5, 129.3, 127.8, 72.5, 54.2, 34.4 ppm; HRMS (ESI): calcd. for $C_{11}H_{15}NO_2$ 194.1176 $[M+H]^+$; found: 194.1173. HPLC conditions: Chirobiotic T (250 x 4.6 mm) column (1:1 H_2O:CH_3OH), 1.0 mL/min, (*S*) enantiomer t_R = 14.764 min, (*R*) enantiomer t_R = 20.595 min.

Synthesis of *(rac)-N*-Benzyl-*N*-Methylalanine [2-(*N*-Benzyl-*N*-Methylamino) Propionic Acid].[8] Finely powdered *N*-benzylalanine (0.89 g, 5 mmol) was treated with a mixture of formic acid (0.57 mL, 0.69 g, 6 mmol) and an aqueous solution of formaldehyde (37%, 0.5 mL, 0.18 g, 6 mmol) at 100°C, in a round bottom flask equipped with a reflux condenser. After 1.5 h the reaction mixture was cooled to room temperature and solvents were evaporated under vacuum. A colourless oily residue was obtained which was crystallized from methanol/diethyl ether to give the desired compound as a colourless solid. Yield: 72 %. ^{1}H-NMR (400 MHz, D_2O-NaOH): (major) δ = 7.40 (s, 5H), 4.18 (AB system, J_{AB} = 12.8 Hz, v_1 = 1719.6 Hz, v_2 = 1625.2 Hz, 2H), 3.54-3.51 (m, 1H), 2.64 (s, 3H), 1.48 (d, *J* = 6.9 Hz, 1H) ppm, (minor) δ = 7.40 (s, 5H), 4.12 (AB system, J_{AB} = 12.8 Hz, v_1 = 1749.4 Hz, v_2 = 1547.4 Hz, 2H), 3.84-3.75 (m, 1H), 2.64 (s, 3H), 1.39 (d, *J* = 7.0 Hz, 1H) ppm; ^{13}C-NMR (100 MHz, D_2O-NaOH): (major) δ = 174.2, 131.6, 130.8, 130.1, 129.2, 64.3, 59.5, 36.0, 12.8 ppm, (minor) δ = 173.4, 131.6 130.8, 130.1, 129.2, 64.9, 55.9, 37.8, 10.3 ppm; HRMS (ESI): calcd. for $C_{11}H_{15}NO_2$ 194.1176 $[M+H]^+$; found: 194.1172.

Synthesis of *(rac)-N*-Methylalanine [2-(*N*-Methylamino) Propionic Acid].[8] *N*-benzyl-*N*-methylalanine (0.20 g, 1.03 mmol) was dissolved in glacial acetic acid (2.90 mL). The resulting solution was hydrogenated using palladium on charcoal (10 % Pd, 0.01 g). After hydrogenation the catalyst was filtered off and the filtrate was evaporated under vacuum to obtain an oily product. *N*-methylalanine was crystallised from methanol/ether. Yield: 70%. Analytical and spectroscopic data was consistent with that previously reported.[14] ^{1}H-NMR (400 MHz, D_2O): δ = 3.64 (q, *J* = 7.2 Hz, 1H), 2.85 (s, 6H), 1.50 (d, *J* = 7.2 Hz, 3H) ppm; ^{13}C-NMR (100 MHz, D_2O): δ = 175.4, 59.5, 31.6, 15.2 ppm; HRMS (ESI): calcd. for $C_5H_{11}NO_2Na$ 140.0682 $[M+Na]^+$; found: 140.0680. HPLC conditions: Chirobiotic T (250 x 4.6 mm), (6:4 CH_3OH:H_2O), 1 ml/min, (*S*) enantiomer t_R = 4.572 min, (*R*) enantiomer t_R = 5.229 min.

Synthesis of *(rac)-N,N*-Dimethylalanine [2-(*N,N*-Dimethylamino) Propionic Acid].[15] Alanine (1.00 g, 11.2 mmol) was suspended in water (25 mL) and aqueous formaldehyde (37% w/w, 3.64 mL, 44.8 mmol) and palladium on charcoal (10 % Pd, 1.00 g) were added. Hydrogenation was carried out for 24 h at atmospheric pressure. The resulting aqueous slurry was heated to reflux, then filtered hot, and the water removed from the filtrate under vacuum. The crude solid was dissolved in a minimum of hot methanol and the solution cooled to yield crystals of *N,N*-dimethylalanine. Yield: 34%. Analytical and spectroscopic data was consistent with that previously reported.[16] ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 3.50$ (q, $J = 7.2$ Hz, 1H), 2.59 (s, 3H), 1.36 (d, $J = 7.2$ Hz, 3H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 171.7$, 65.3, 40.5, 13.1 ppm.

Synthesis of *(rac)-N,N*-Dibenzylalanine [2-(*N,N*-Dibenzylamino) Propionic Acid].[17] Benzyl chloride (10 mL, 86 mmol) was added dropwise to a solution of alanine (1.80 g, 20 mmol) in ethanol (20 mL), water (10 mL) and 7M aqueous KOH (6 mL). After heating to reflux during 1 h, ethanol was distilled off and the solution was acidified with glacial acetic acid and extracted with chloroform to obtain an oily product. The product was heated to 120°C in order to remove benzyl alcohol formed by hydrolysis of benzyl chloride. The oily residue was heated to reflux for 5 min in a 20% w/w solution of KOH in propylene-glycol (5 mL). The resulting solution was diluted with water (30 mL), acidified with acetic acid, and the mixture was extracted with chloroform and evaporated to dryness. The crude material was recrystallized from hexane. Yield: 40%. Analytical and spectroscopic data was consistent with that previously reported.[18] ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 7.46$-7.25 (m, 10H), 3.77 (AB system, $J_{AB} = 13.2$ Hz, $v_1 = 1559.8.1$ Hz, $v_2 = 1453.0$ Hz, 4H), 3.63 (d, $J = 13.4$ Hz, 2H), 3.60 (q, $J = 7.1$ Hz, 1H), 1.43 (d, $J = 7.1$ Hz, 3H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): $\delta = 175.7$, 137.5, 129.7, 129.5, 128.7, 58.2, 55.2, 10.8 ppm; HRMS (ESI): calcd. for $C_{17}H_{19}NO_2$ 270.1489 $[M+H]^+$; found: 270.1488.

Synthesis of (*R*)-*N*-Bn-Ala and (*S*)-*N*-Bn-Ala. The synthesis was carried out according to the method used for preparation of racemic *N*-Bn-Ala starting from the corresponding pure enantiomers. Spectroscopic data for both (*R*)-*N*-Bn-Ala[19] and (*S*)-*N*-Bn-Ala[20] were in accordance with literature data.

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[15] R. E. Bowman, H. H. Stroud, *J. Chem. Soc.* **1950**, 1342-1345.

[16] S. G. Ang, S. H. Low, *Aust. J. Chem.* **1991**, *44*, 1591-1601.

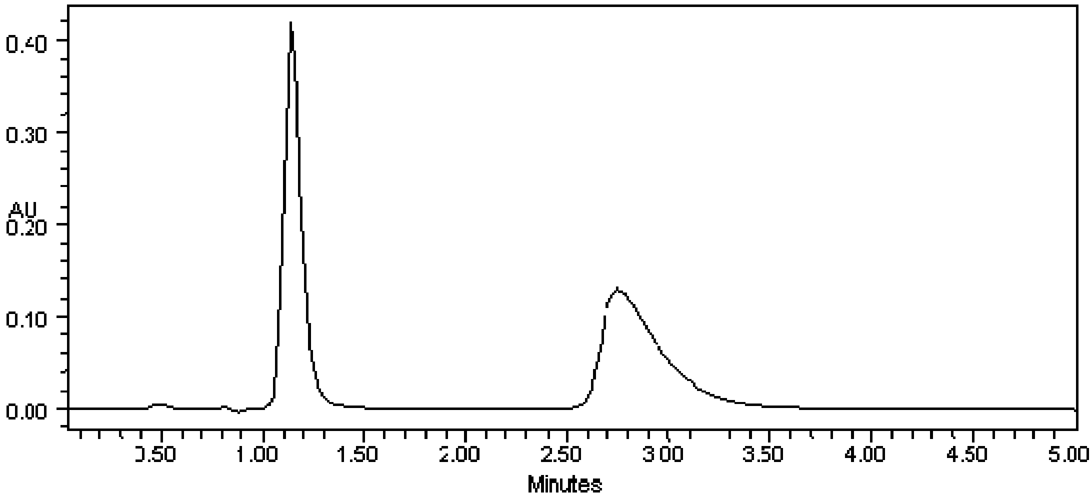
[17] L. Velluz, G. Amiard, R. Heymès, *Bull. Soc. Chim. Fr.* **1954**, 1012-1015.

[18] R. V. Hoffman, J. Tao, *J. Org. Chem.* **1997**, *62*, 2292-2297.

[19] H. Kubota, A. Kubo, M. Takahashi, R. Shimizu, T. Da-te, K. Okamura, K. Nunami, *J. Org. Chem.* **1995**, *60*, 6776-6784.

Determination of Enantiomeric Excesses by HPLC: *N*-Bn-Ala

HPLC conditions: Chirobiotic R (50 x 4.6 mm) column (9:1 H_2O:CH_3CN), 1.0 mL/min, (*S*) enantiomer t_R = 1.141 min, (*R*) enantiomer t_R = 2.754 min.



Racemic *N*-Bn-Ala

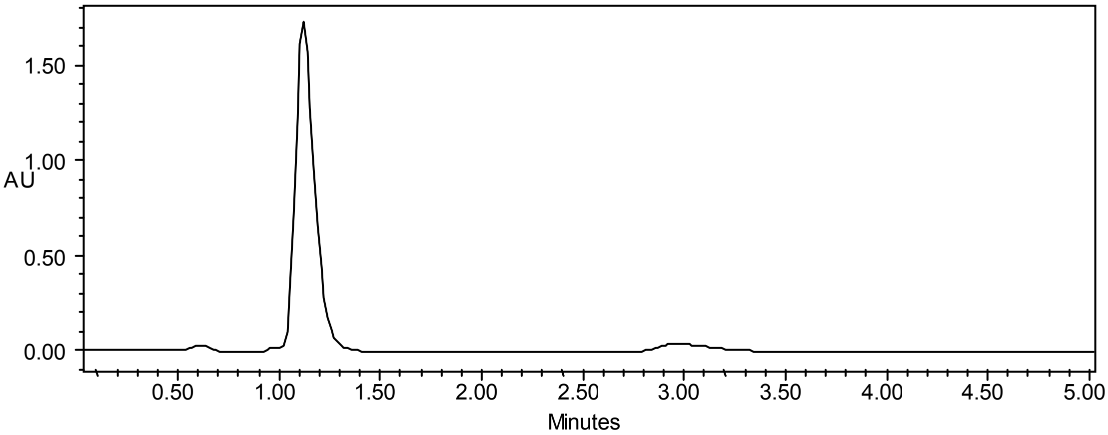


Figure 1. HPLC trace of the aqueous phase following extraction of *N*-Bn-Ala with [Co^{III}(**3**)(OAc)] (93% ee).

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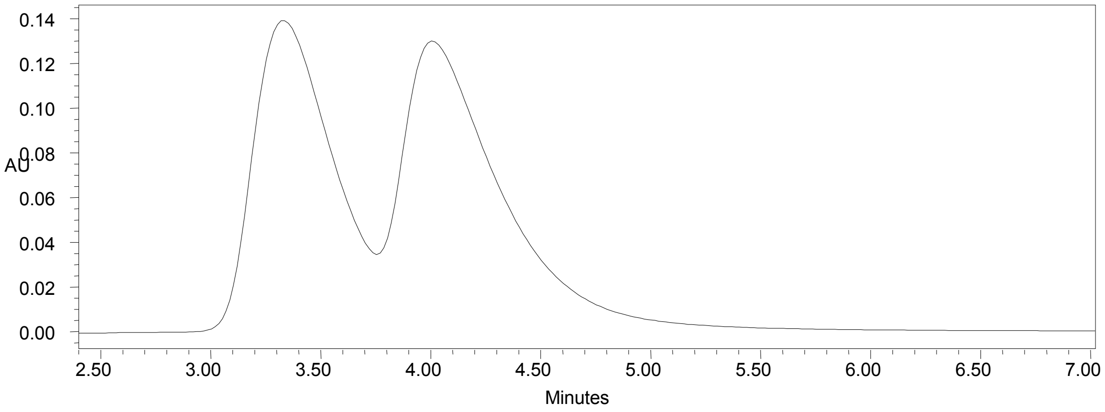
[20] G. Lelais, D. Seebach, *Helv. Chim. Acta* **2003**, *86*, 4152-4168.

Determination of Enantiomeric Excesses by HPLC: *N*-Bn-Thr

HPLC conditions: Chirobiotic R (50 x 4.6 mm) column (H_2O), 0.5 mL/min, (*S*) enantiomer t_R = 3.331 min, (*R*) enantiomer t_R = 4.008 min.



Racemic *N*-Bn-Thr

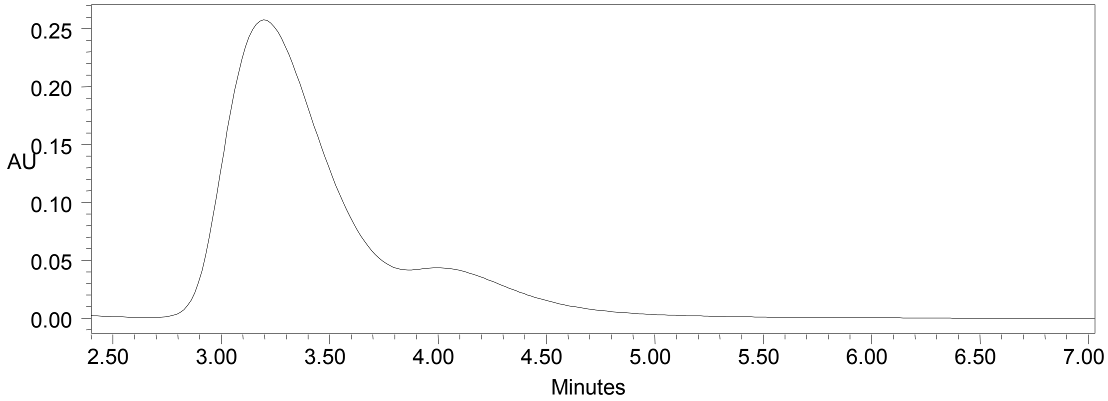


Figure 2a. HPLC trace of the aqueous phase following extraction of *N*-Bn-Thr with [Co^{III}(**3**)(OAc)]: 0.94 equiv extracted into the organic phase; >90% ee *N*-Bn-Thr remained in the aqueous phase.

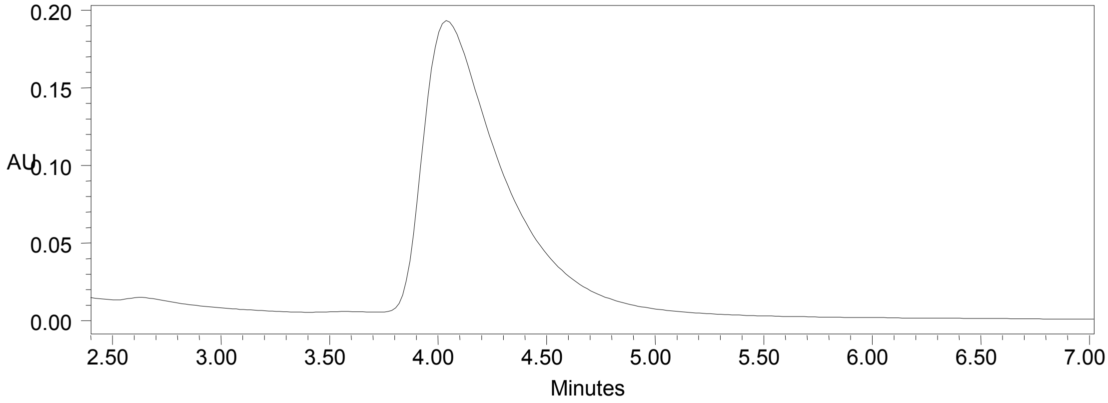
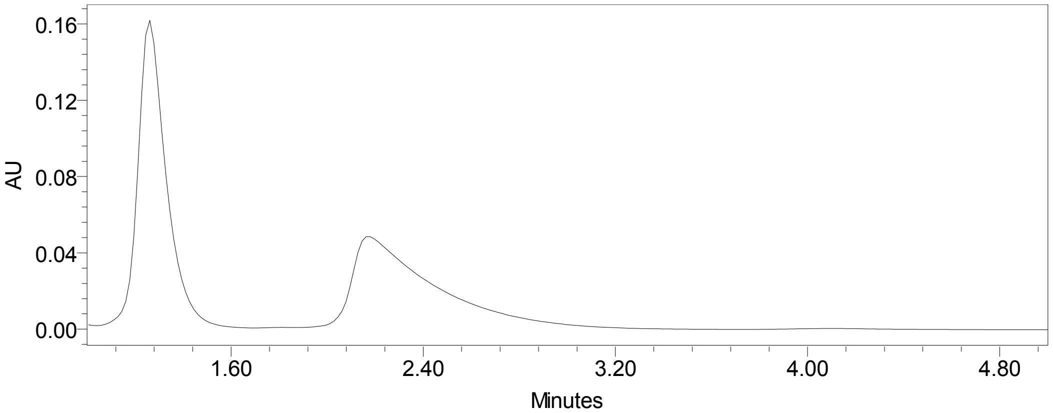


Figure 2b. HPLC trace of the aqueous phase following counter-extraction of [Co^{III}(**3**)(*N*-Bn-Thr)] with sodium dithionite (96% ee).

Determination of Enantiomeric Excesses by HPLC: *N*-Bn-Ser

HPLC conditions: Chirobiotic R (50 x 4.6 mm), (9:1 H_2O:CH_3OH), 1 ml/min, (*S*) enantiomer t_R = 1.258 min, (*R*) enantiomer t_R = 2.176 min.



Racemic *N*-Bn-Ser

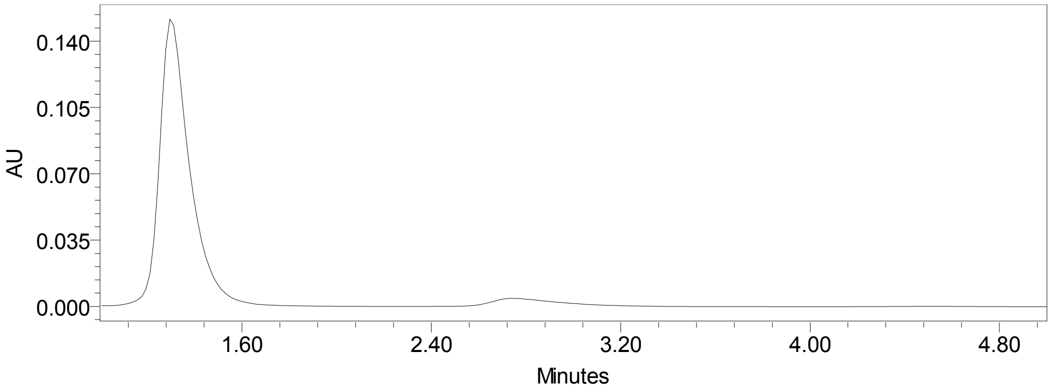
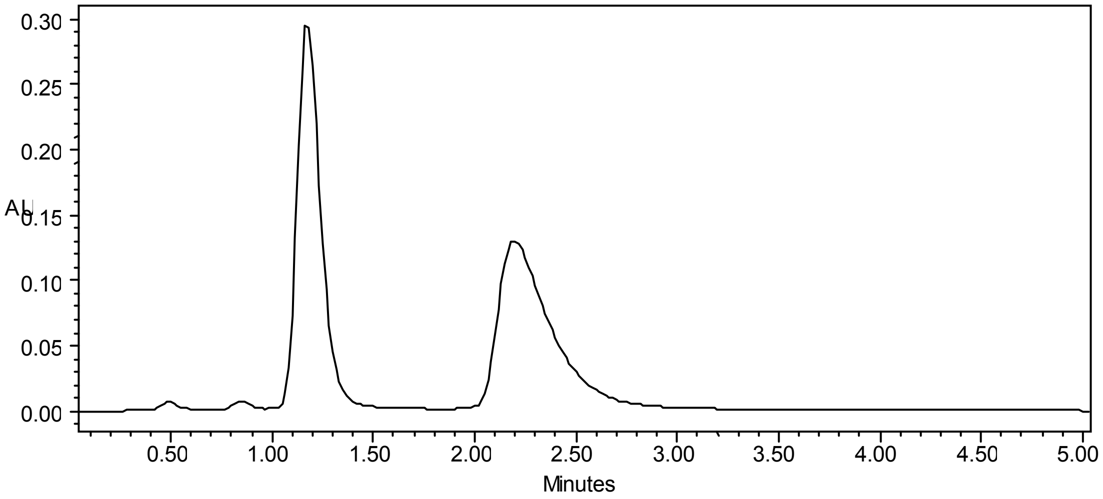


Figure 3. HPLC trace of the aqueous phase following extraction of *N*-Bn-Ser with [Co^{III}(**3**)(OAc)] (90% ee).

Determination of Enantiomeric Excesses by HPLC: *N*-Bn-Val

HPLC conditions: Chirobiotic R (50 x 4.6 mm) column (9:1 H_2O:CH_3CN), 1.0 mL/min, (*S*) enantiomer t_R = 1.175 min, (*R*) enantiomer t_R = 2.199 min.



Racemic *N*-Bn-Val

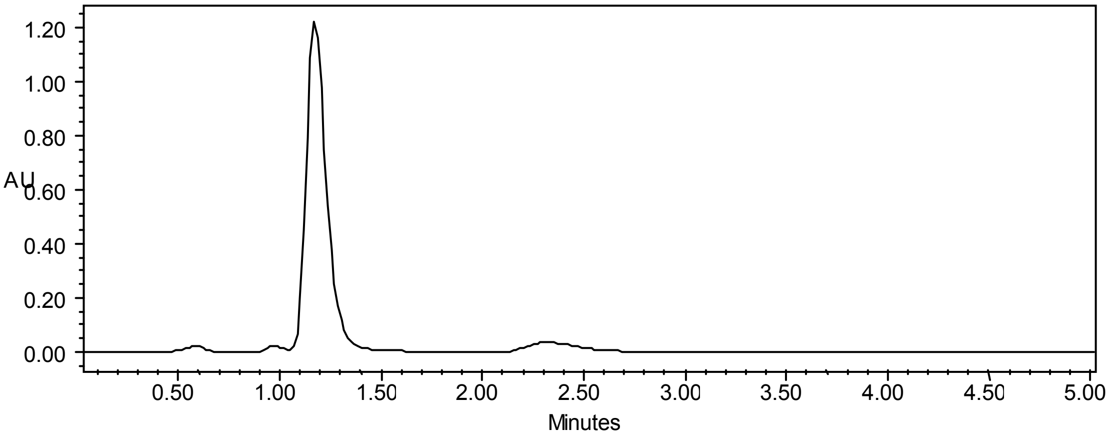
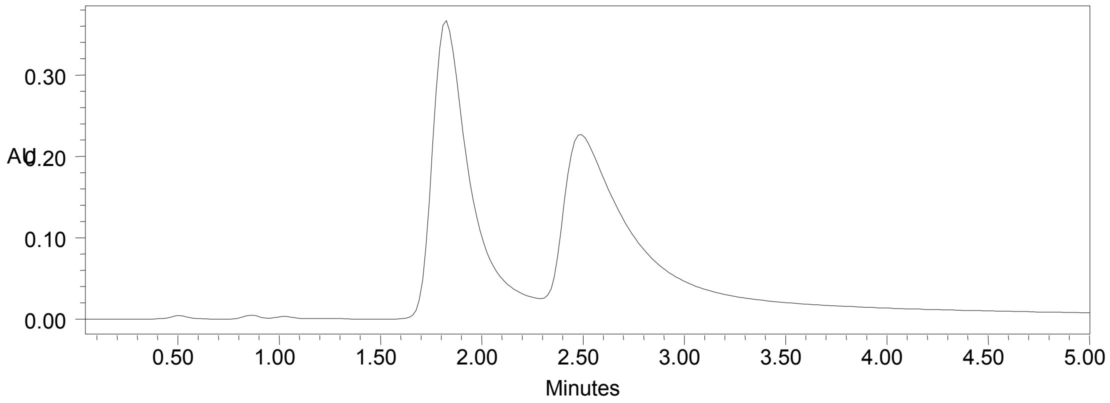


Figure 4. HPLC trace of the aqueous phase following extraction of *N*-Bn-Val with [Co^{III}(**3**)(OAc)] (90% ee).

Determination of Enantiomeric Excesses by HPLC: *N*-Bn-Phe

HPLC conditions: Chirobiotic R (50 x 4.6 mm) column (9:1 H_2O:CH_3CN), 1.0 mL/min, (*S*) enantiomer t_R = 1.824 min, (*R*) enantiomer t_R = 2.489 min.



Racemic *N*-Bn-Phe

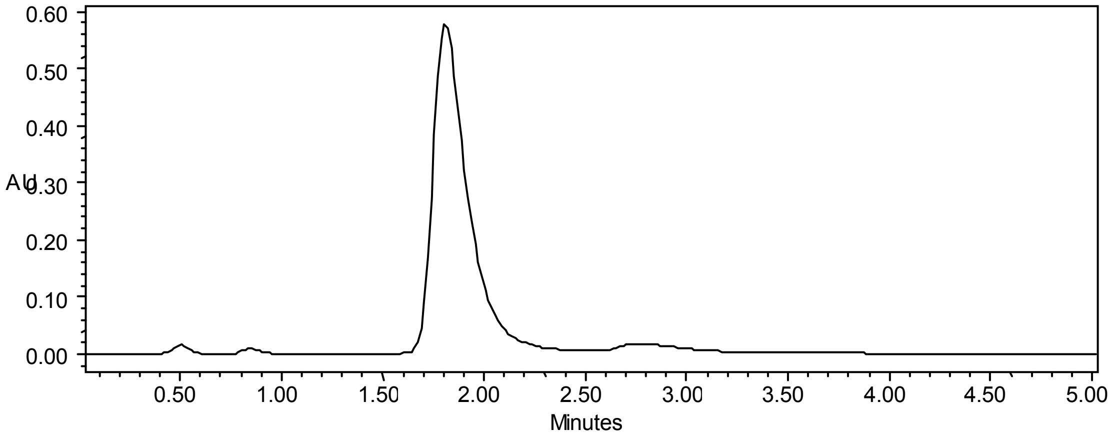
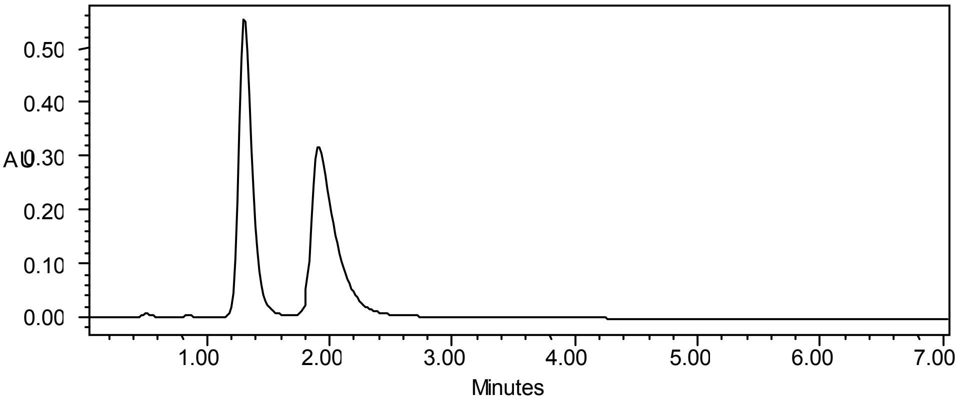


Figure 5. HPLC trace of the aqueous phase following extraction of *N*-Bn-Phe with [Co^{III}(**3**)(OAc)] (93% ee).

Determination of Enantiomeric Excesses by HPLC: *N*-Bn-Leu

HPLC conditions: Chirobiotic R (50 x 4.6 mm) column (9:1 H_2O:CH_3CN), 1.0 mL/min, (*S*) enantiomer t_R = 1.304 min, (*R*) enantiomer t_R = 1.909 min.



Racemic *N*-Bn-Leu

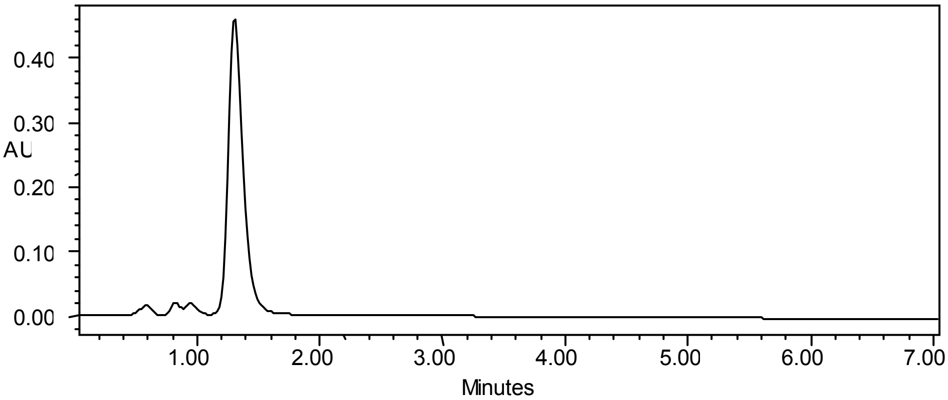
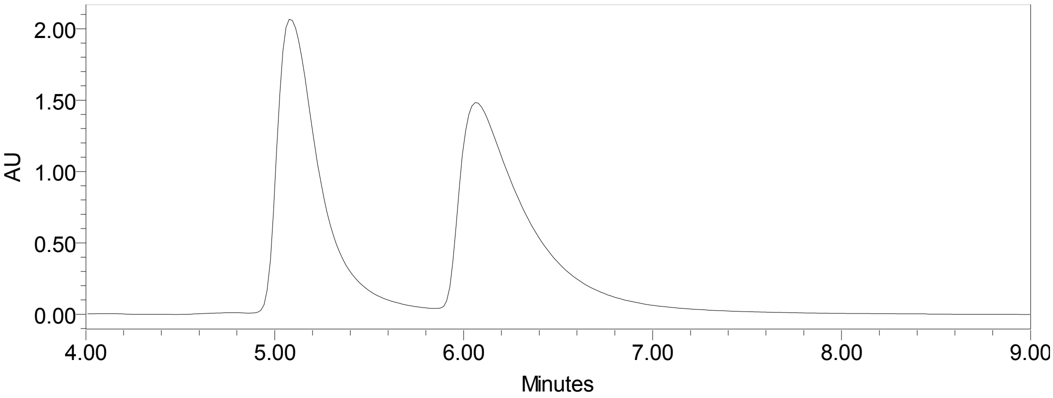


Figure 6. HPLC trace of the aqueous phase following extraction of *N*-Bn-Leu with [Co^{III}(**3**)(OAc)] (99% ee).

Determination of Enantiomeric Excesses by HPLC: Phe

HPLC conditions: Chirobiotic T (250 x 4.6 mm) column (1:1 H_2O:CH_3OH), 1.0 mL/min, (*S*) enantiomer t_R = 5.070 min, (*R*) enantiomer t_R = 6.060 min.



Racemic Phe

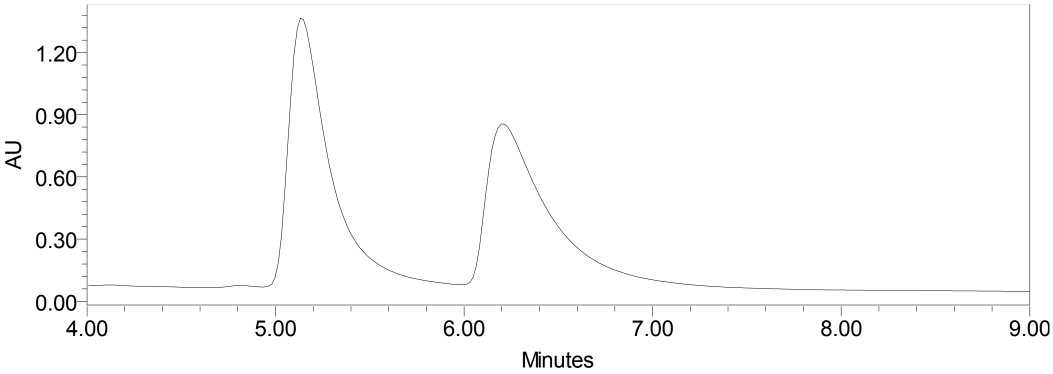


Figure 7a. HPLC trace of the aqueous phase following extraction of Phe with [Co^{III}(**3**)(OAc)]: 0.98 equiv extracted into the organic phase; 10% ee Phe remained in the aqueous phase.

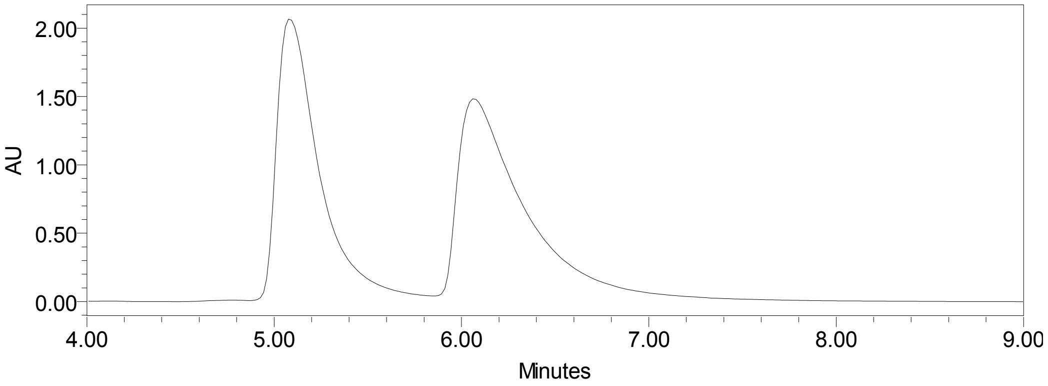
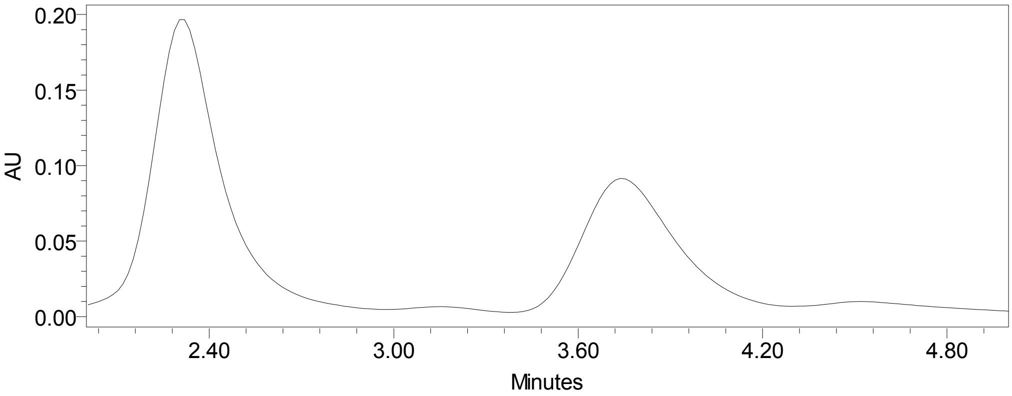


Figure 7b. HPLC trace of the aqueous phase following counter-extraction of [Co^{III}(**3**)(Phe)] with sodium dithionite (10% ee).

Determination of Enantiomeric Excesses by HPLC: Pro

HPLC conditions: Chirobiotic T (250 x 4.6 mm) column (1:1 H_2O:CH_3OH), 0.5 mL/min, (*S*) enantiomer t_R = 2.444 min, (*R*) enantiomer t_R = 4.371 min.



Racemic Pro

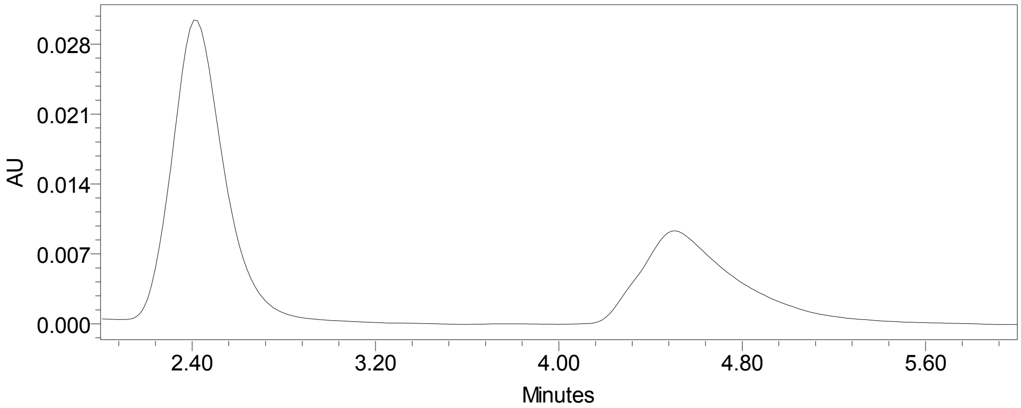


Figure 8a. HPLC trace of the aqueous phase following extraction of Pro with [Co^{III}(**3**)(OAc)]: 0.80 equiv extracted into the organic phase; 10% ee Pro remained in the aqueous phase.

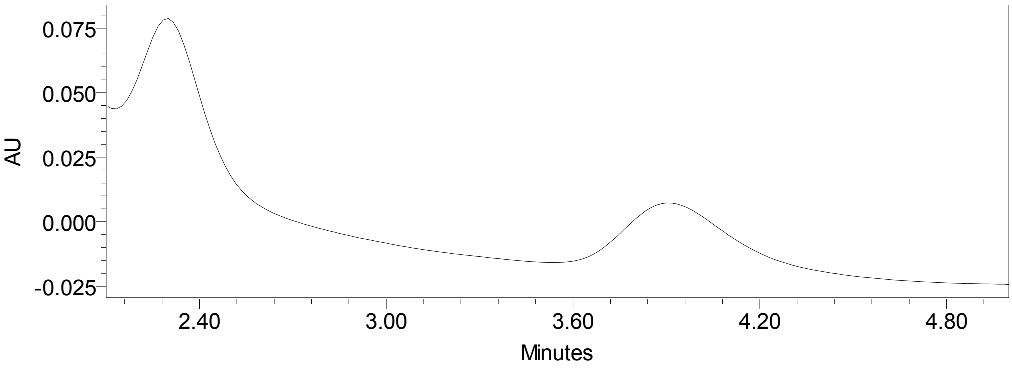
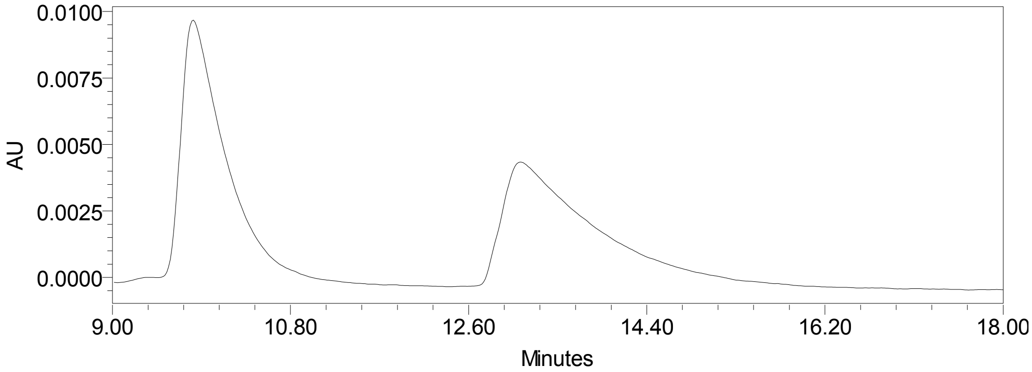


Figure 8b. HPLC trace of the aqueous phase following counter-extraction of [Co^{III}(**3**)(Pro)] with sodium dithionite (12% ee).

Determination of Enantiomeric Excesses by HPLC: *N*-Me-Phe

HPLC conditions: Chirobiotic T (250 x 4.6 mm) column (1:1 H_2O:CH_3OH), 1.0 mL/min, (*S*) enantiomer t_R = 9.817 min, (*R*) enantiomer t_R = 13.126 min.



Racemic *N*-Me-Phe

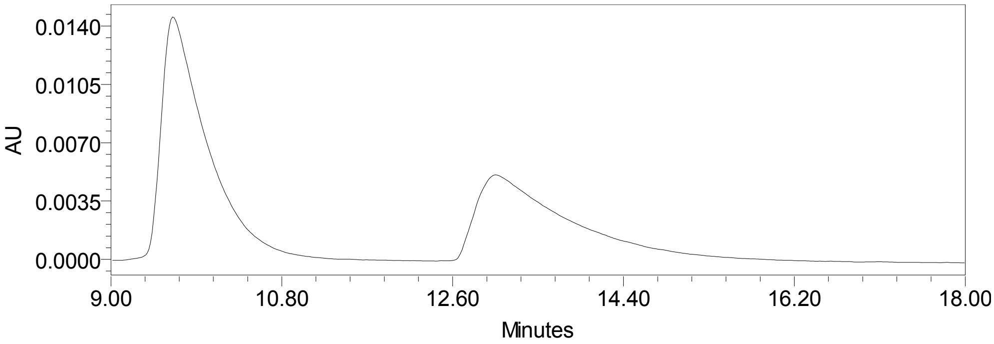


Figure 9a. HPLC trace of the aqueous phase following extraction of *N*-Me-Phe with [Co^{III}(**3**)(OAc)]: 0.97 equiv extracted into the organic phase; 20% ee *N*-Me-Phe remained in the aqueous phase.

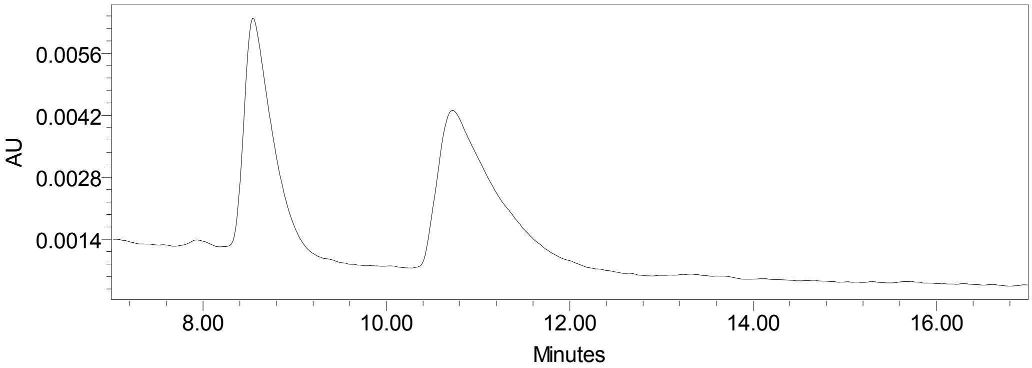
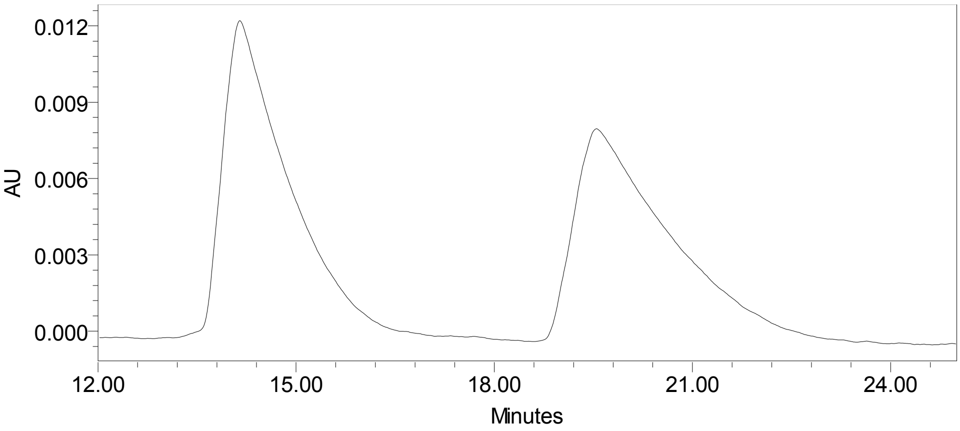


Figure 9a. HPLC trace of the aqueous phase following counter-extraction of [Co^{III}(**3**)(*N*-Me-Phe)] with sodium dithionite (20% ee).

Determination of Enantiomeric Excesses by HPLC: *N,N*-Me$_2$-Phe

HPLC conditions: Chirobiotic T (250 x 4.6 mm) column (1:1 H_2O:CH_3OH), 1.0 mL/min, (*S*) enantiomer t_R = 14.764 min, (*R*) enantiomer t_R = 20.595 min.



Racemic *N,N*-Me$_2$-Phe

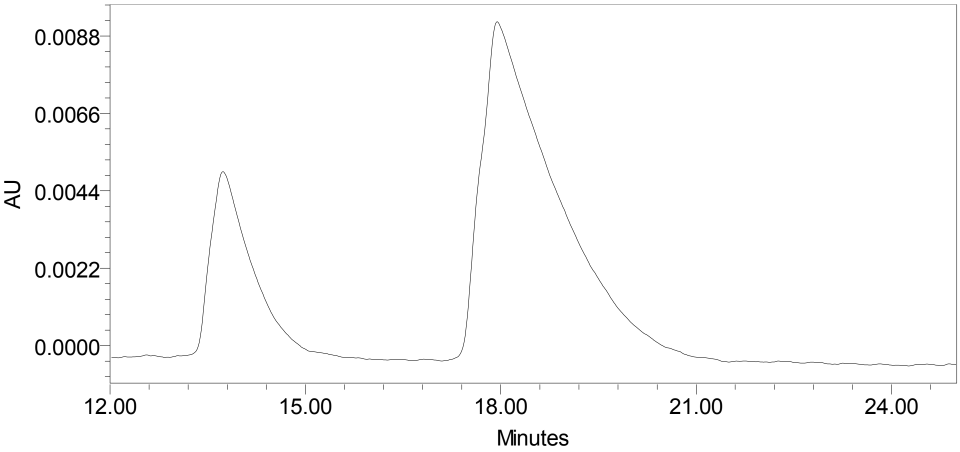


Figure 10a. HPLC trace of the aqueous phase following extraction of *N,N*-Me$_2$-Phe with [Co^{III}(**3**)(OAc)]: 0.70 equiv extracted into the organic phase; 50% ee *N,N*-Me$_2$-Phe remained in the aqueous phase.

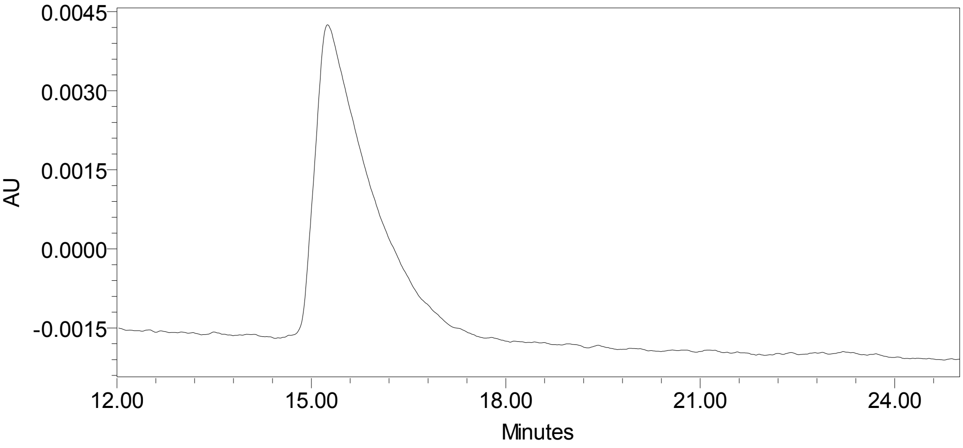
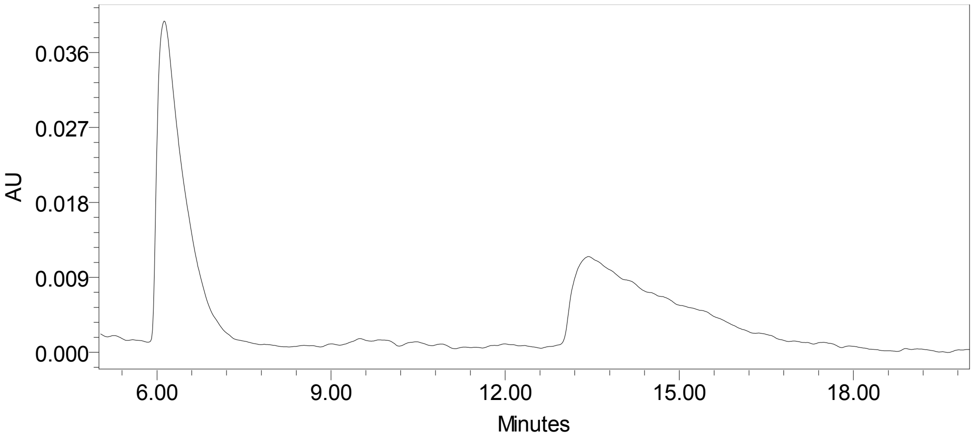


Figure 10b. HPLC trace of the aqueous phase following counter-extraction of [Co^{III}(**3**)(*N,N*-Me$_2$Phe)] with sodium dithionite (100% ee).

Determination of Enantiomeric Excesses by HPLC: *N*-Me-Ala

HPLC conditions: Chirobiotic T (250 x 4.6 mm) column (6:4 CH_3OH:H_2O), 1.0 mL/min, (*S*) enantiomer t_R = 6.203 min, (*R*) enantiomer t_R = 13.190 min.



Racemic *N*-Me-Ala

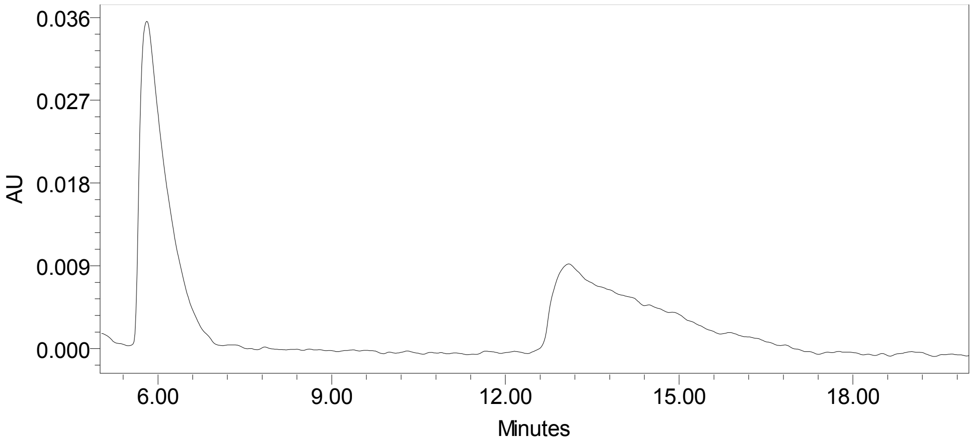


Figure 11a. HPLC trace of the aqueous phase following extraction of *N*-Me-Ala with [Co^{III}(**3**)(OAc)]: 0.20 equiv extracted into the organic phase; 0% ee *N,N*-Me_2-Phe remained in the aqueous phase.

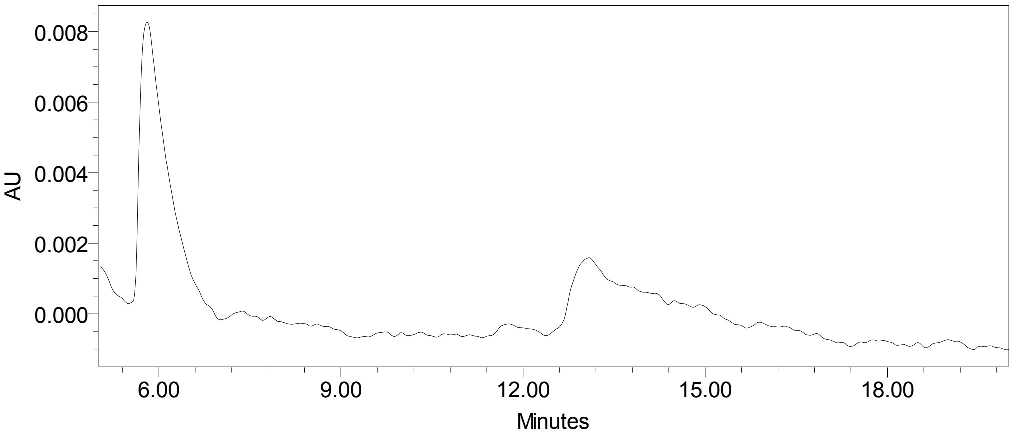
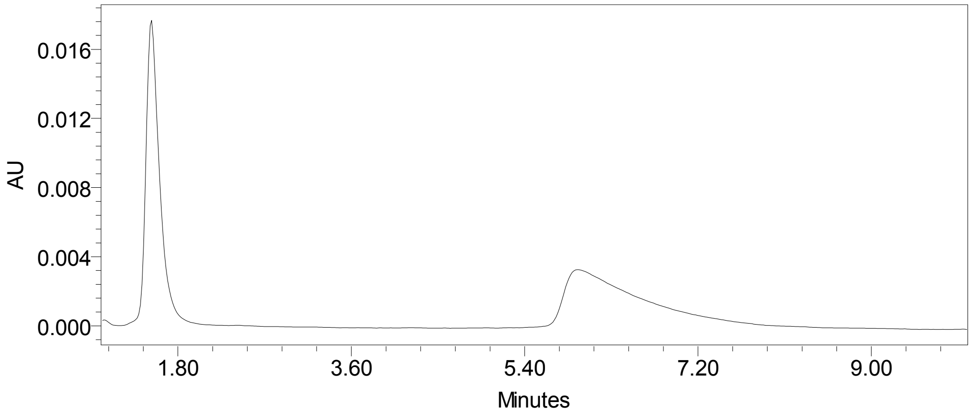


Figure 11b. HPLC trace of the aqueous phase following counter-extraction of [Co^{III}(**3**)(*N*-Me-Ala)] with ascorbic acid (0% ee).

Transformation of [Co^{III}(3)(*S*-*N*-Bn-Ala)] into [Co^{III}(3)(*R*-*N*-Bn-Ala)]

To a solution of the [Co^{III}(**3**)(*S*-*N*-Bn-Ala)] complex (prepared as described below on page 44, 0.029 g, 0.0375 mmol) in dichloromethane (5 mL) at 10°C in a 25 mL round-bottom flask, was added a precooled (10 °C) solution of *R*-*N*-Bn-Ala (0.014 g, 2 eq, 0.075 mmol) in H_2O (3.75 mL). The biphasic mixture was stirred vigorously at 10°C; 100 µL aliquots of water phase were collected at t = 0.5, 1, 16 h and analyzed by HPLC in order to assess the enantiomeric composition of the aqueous phase.

HPLC conditions: Chirobiotic R (50 x 4.6 mm) column (1:1 H_2O:CH_3OH), 1.0 mL/min, (*S*) enantiomer t_R = 1.540 min, (*R*) enantiomer t_R = 5.957 min.



Racemic *N*-Bn-Ala

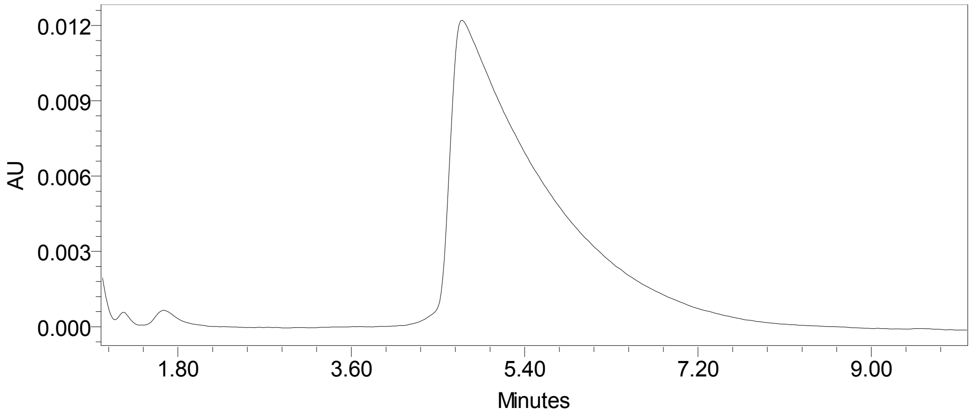


Figure 12a. HPLC trace of the aqueous phase after **0.5 h** (98% ee, *R*-enantiomer) following extraction of *R*-*N*-Bn-Ala (2 equiv) with [Co^{III}(**3**)(*S*-*N*-Bn-Ala)].

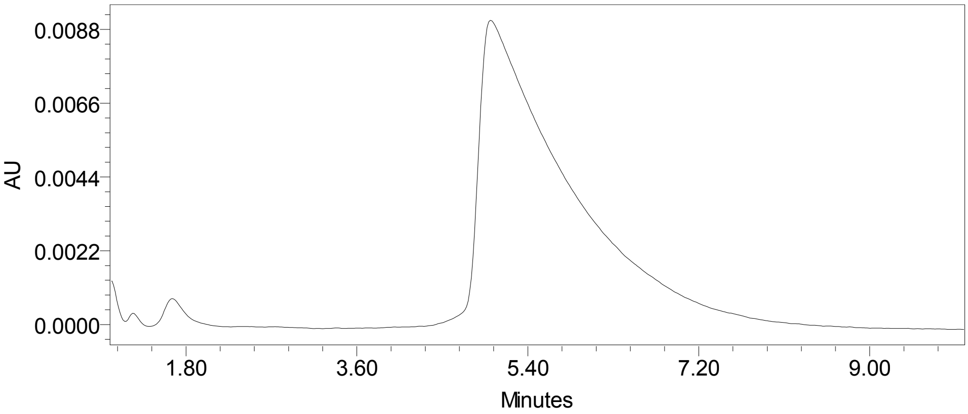


Figure 12b. HPLC trace of the aqueous phase after **1 h** (96% ee, *R*-enantiomer) following extraction of *R*-*N*-Bn-Ala (2 equiv) with [Co^{III}(**3**)(*S*-*N*-Bn-Ala)].

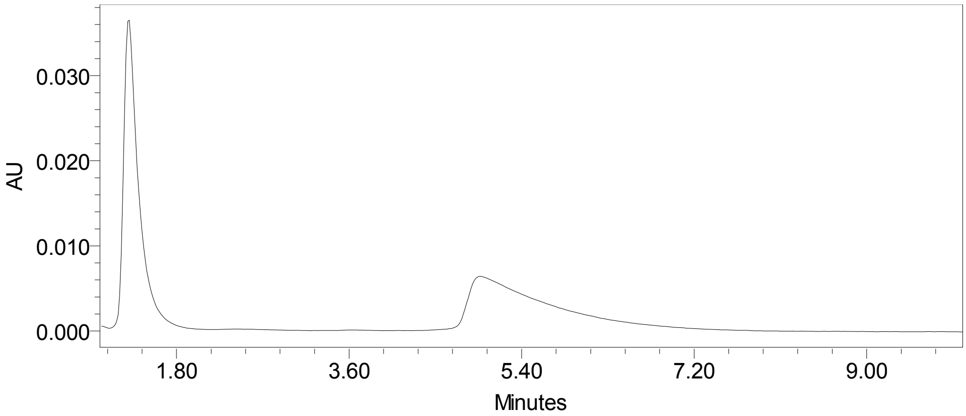
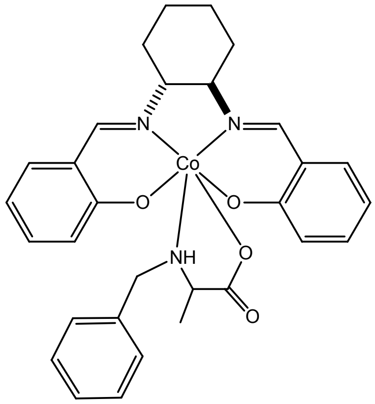


Figure 12c. HPLC trace of the aqueous phase after **16 h** (5% ee, *S*-enantiomer) following extraction of *R*-*N*-Bn-Ala (2 equiv) with [Co^{III}(**3**)(*S*-*N*-Bn-Ala)].

Extraction of *N*-Benzyl Alanine Using Complex [Co^{II}(1-2)] and [Co^{III}(1-2)(OAc)]

To a solution of the cobalt complex (0.3 mmol) in dichloromethane (40 mL) at 10 °C in a 100 mL round-bottom flask, was added a precooled (10 °C) solution of racemic *N*-benzylalanine (0.108 g, 2 eq, 0.600 mmol) in H_2O (30 mL). The biphasic mixture was stirred vigorously for 24 h at 10 °C, then transferred to a separating funnel, the organic phase removed and the aqueous phase washed once with dichloromethane (10 mL). The combined dichloromethane extracts were washed once with H_2O (10 mL) before volatiles were removed under reduced pressure to leave the complexes [Co^{III}(**1-2**)(*N*-Bn-Ala)] as green powders. The aqueous phases were combined and an aliquot removed which was filtered on micropore filters before the ee was determined by chiral HPLC as described above. The aqueous phase was evaporated to leave *N*-benzylalanine as a white powder.

(*R*,*R*)-*N*,*N'*-Bis-Salicylidene-1,2-Cyclohexanediaminocobalt(III) (*R*)-*N*-Benzyl Alaninate - [Co^{III}(1)(*N*-Bn-Ala)]



Spectroscopic data was consistent with that previously reported.[21] Yield: 0.162 g (92%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1H), 7.68 (s, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.32-7.22 (m, 7H), 7.12 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 6.60 (d, J = 8.0 Hz, 1H), 6.60-6.54 (m, 2H), 4.36 (dd, J_1 = 14.0 Hz, J_2 = 12.0 Hz, 1H), 4.32-4.21 (m, 1H), 4.20-4.12 (m, 2H), 3.39-3.32 (m, 1H), 3.29-3.18 (m, 1H), 2.84 (d, J = 9.5 Hz, 1H), 2.43-2.38 (m, 1H), 2.04-1.81 (m, 4H), 1.62-1.39 (m, 3H), 0.78 ppm (d, J = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 183.2, 166.1, 165.9, 164.0, 160.6, 136.3, 135.1, 134.7, 132.7, 129.1, 129.0, 128.3, 125.3, 123.3, 123.2, 118.1, 116.7, 114.3, 75.3, 71.1, 60.3, 54.5, 30.7, 29.3, 24.6, 23.9, 20.7 ppm; FT-IR (Nujol): υ = 2921, 2726, 2360, 2333, 1623, 1598, 1532, 1313, 1197, 1148, 1123, 1092, 1026, 964, 904 cm^{-1}; HRMS (ESI): calcd. for $C_{30}H_{32}N_3O_4CoNa$ 580.1623 [M+Na]$^+$; found: 580.1625.

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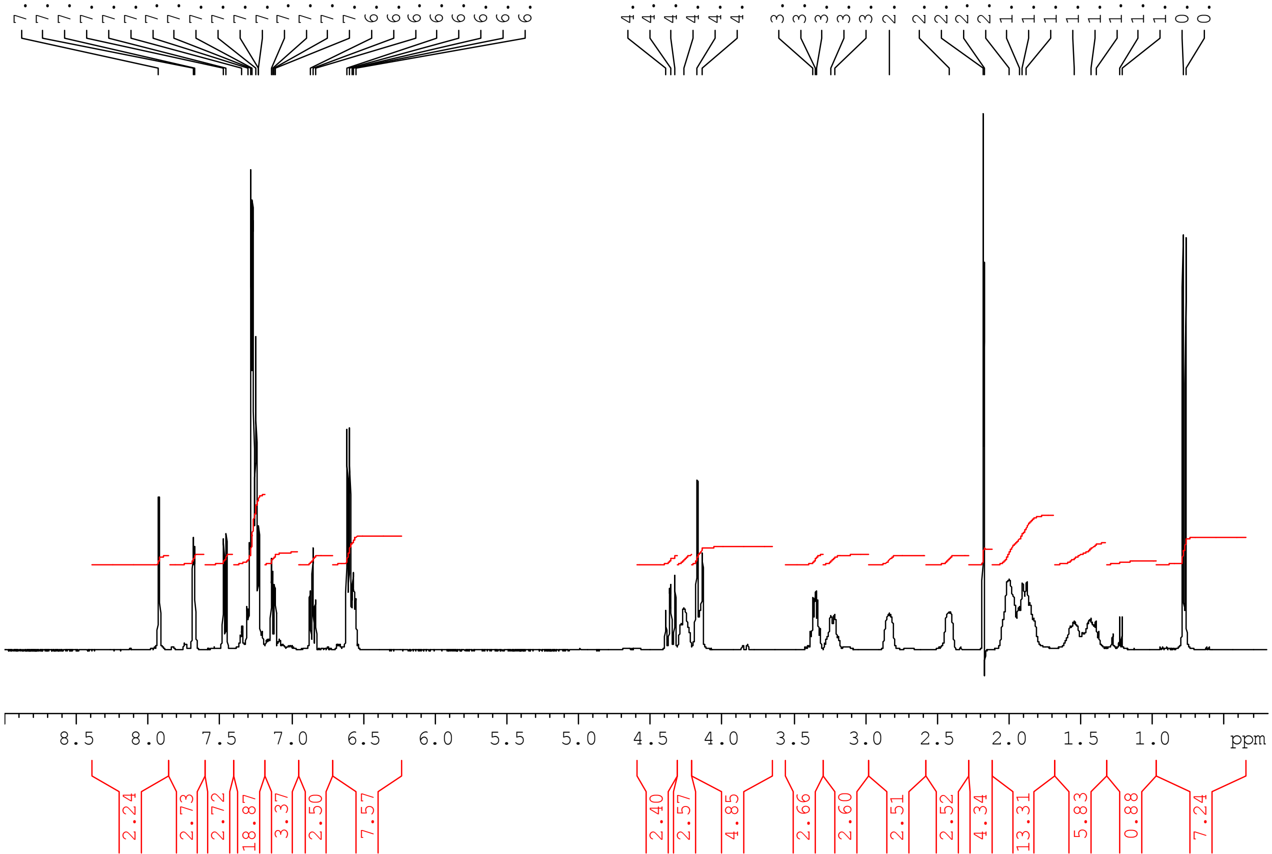
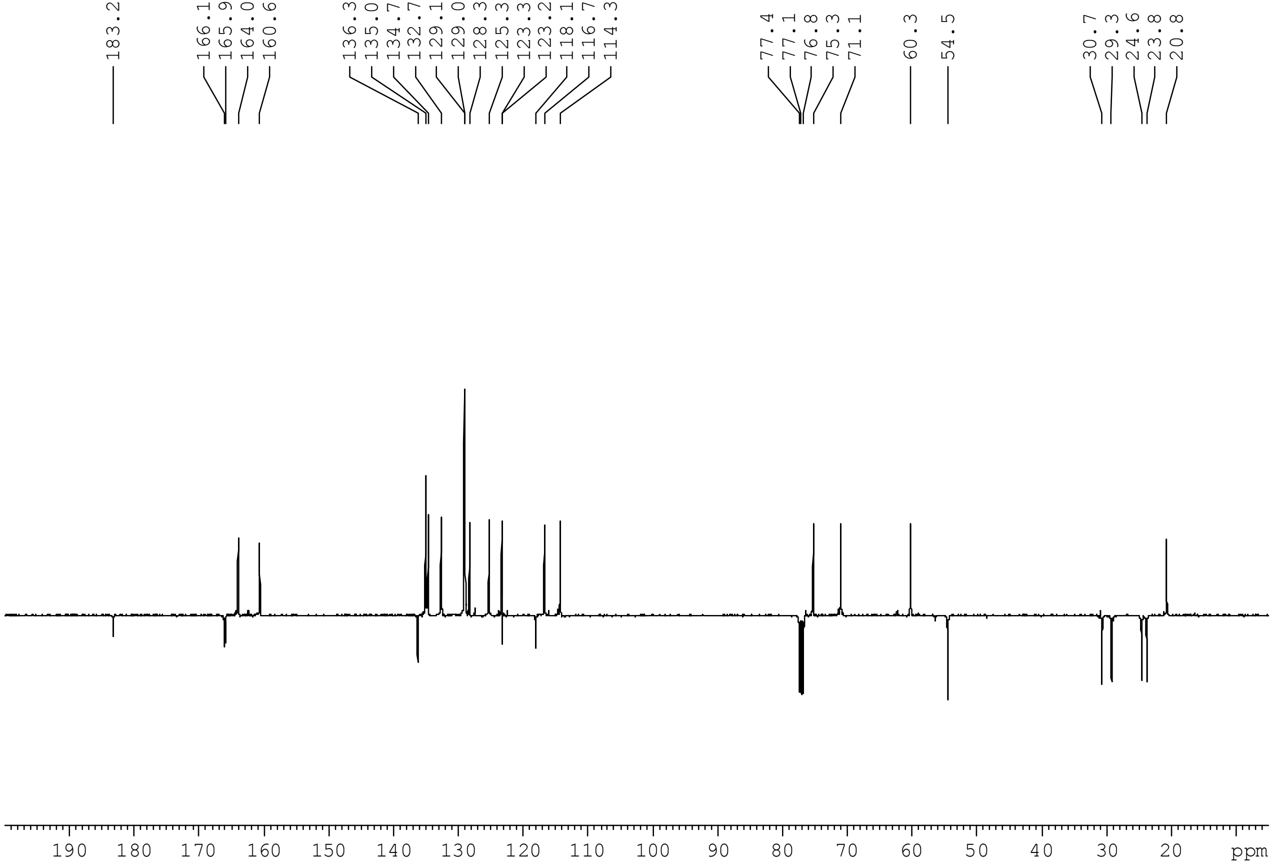
[21] Y. Fujii, M. Matsufuru, A. Saito, S. Tsuchiya, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2029-2038.

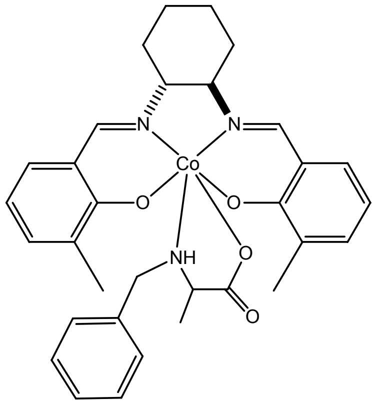
^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**1**)(*N*-Bn-Ala)]



^{13}C-NMR (100 MHz, CDCl$_3$) [Co^{III}(**1**)(*N*-Bn-Ala)]

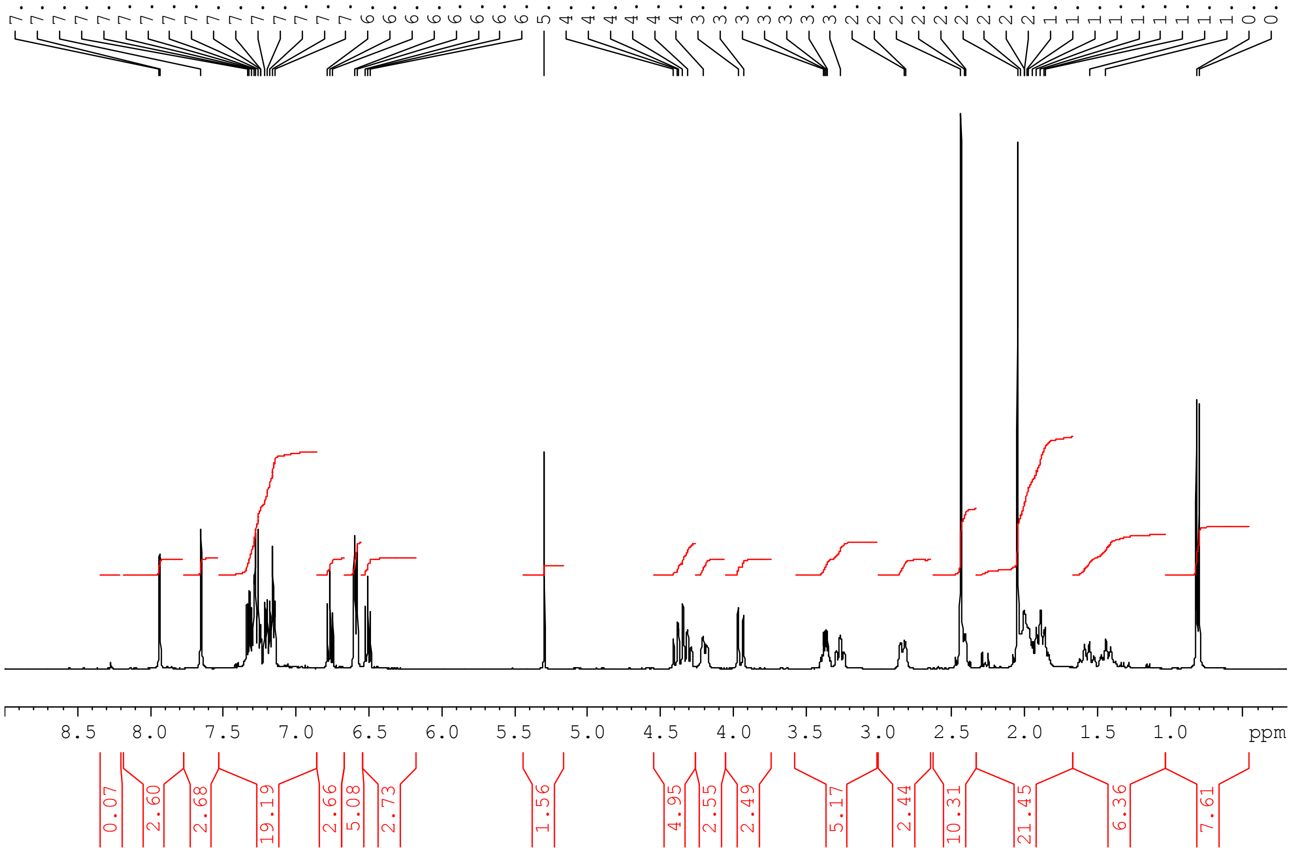


(*R*,*R*)-*N*,*N'*-Bis(3-Methyl-Salicylidene)-1,2-Cyclohexanediaminocobalt(III) (*R*)-*N*-Benzyl Alaninate - [Co^{III}(2)(*N*-Bn-Ala)]

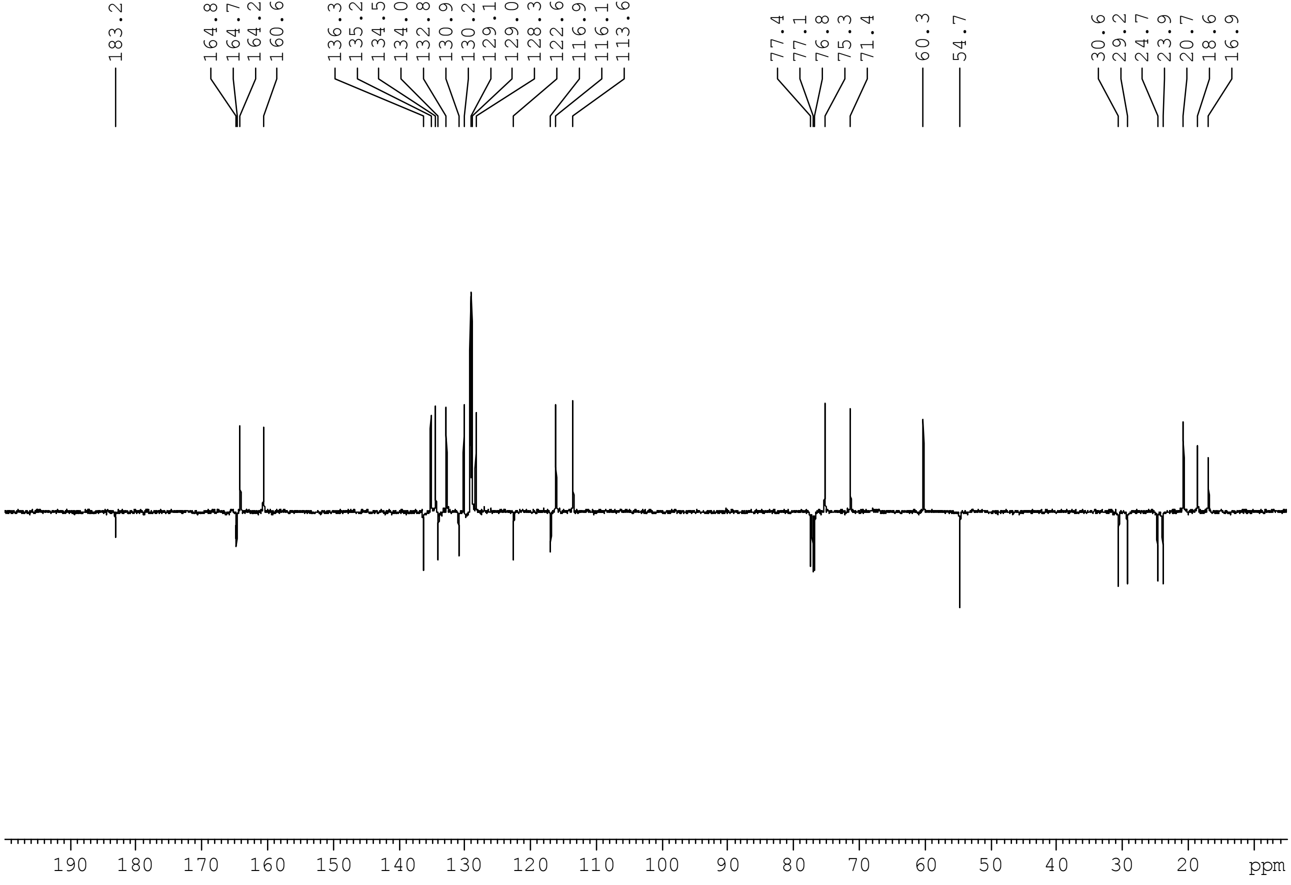


Yield: 0.175 g (99%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.94 (s, 1H), 7.66 (s, 1H), 7.36-7.15 (m, 7H), 6.78-6.75 (m, 1H), 6.61-6.59 (m, 2H), 6.53-6.49 (m, 1H), 4.41-4.38 (m, 1H), 4.39 (dd, J_1 = 8.5 Hz, J_2 = 14.1 Hz, 1H), 4.21-4.19 (m, 1H), 3.95 (d, J = 14.1 Hz, 1H), 3.42-3.35 (m, 1H), 3.29-3.23 (m, 1H), 2.92 (d, J = 9.5 Hz, 1H), 2.43 (s, 3H), 2.43-2.40 (m, 1H), 2.05 (s, 3H), 2.04-1.84 (m, 3H), 1.61-1.40 (m, 3H), 0.81 ppm (d, J = 7.3 Hz, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 183.2, 164.8, 164.7, 164.2, 160.6, 136.3, 135.2, 134.5, 134.0, 132.8, 131.0, 130.2, 129.2, 129.0, 128.3, 122.6, 116.9, 116.1, 113.6, 75.3, 71.4, 60.3, 54.7, 30.6, 29.2, 24.7, 23.9, 20.7, 18.6, 16.9 ppm; FT-IR (Nujol): υ = 2902, 2725, 1632, 1596, 1546, 1225, 1156, 1089, 1040, 966, 897 cm^{-1}; HRMS (ESI): calcd. for $C_{32}H_{36}N_3O_4CoNa$ 608.1936 [*M*+Na]$^+$; found: 608.1933. Elemental analysis calcd (%) for $C_{32}H_{36}N_3O_4Co$ (M_W = 585.59): C 65.64, H 6.20, N 7.18; found: C 65.37, H 6.29, N 7.03.

^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**2**)(*N*-Bn-Ala)]



^{13}C-NMR (100 MHz, CDCl$_3$) [Co^{III}(**2**)(*N*-Bn-Ala)]



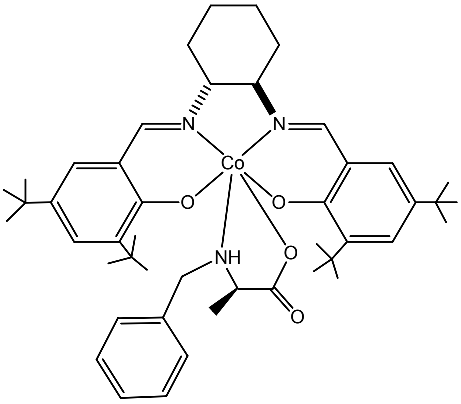
Experimental Procedures Using Complex [Co^{III}(3)(OAc)], Structural Characterization and NMR Spectra

General Procedure for the Extraction of Hydrophilic *N*-Benzyl Amino Acids Using Complex [Co^{III}(3)(OAc)] (Method A): The following procedure for the extraction of *N*-Bn-Ala is typical for hydrophilic *N*-benzyl amino acids. To a solution of the cobalt complex [Co^{III}(**3**)(OAc)] (0.198 g, 0.300 mmol) in dichloromethane (40 mL) at 10°C in a 100 mL round-bottom flask, was added a precooled (10°C) solution of racemic *N*-benzylalanine (0.108 g, 2 eq, 0.600 mmol) in H_2O (30 mL). The biphasic mixture was stirred vigorously for 24 h at 10°C, then transferred to a separating funnel, the organic phase removed and the aqueous phase washed once with dichloromethane (10 mL). The combined dichloromethane extracts were washed once with H_2O (10 mL) before volatiles were removed under reduced pressure to leave complex [Co^{III}(**3**)(*N*-Bn-Ala)] as a green powder (0.233 g, yield = 99%). The aqueous phases were combined and an aliquot removed which was filtered on micropore filters before the *ee* (93%) was determined by chiral HPLC: Chirobiotic R (50 x 4.6 mm) column (9:1 H_2O:CH_3CN); 1.0 mL/min; (*S*) enantiomer, 96.5%, t_R = 1.141 min; (*R*) enantiomer, 3.5%, t_R = 2.754 min. The aqueous phase was evaporated to leave *N*-benzylalanine as a white powder (0.053 g , yield = 99%).

General Procedure for the Extraction of Hydrophobic *N*-Benzyl Amino Acids Using Complex [Co^{III}(3)(OAc)] (Method B): The following procedure for the extraction of *N*-Bn-Phe is typical for hydrophobic *N*-benzyl amino acids. To a solution of [Co^{III}(**3**)(OAc)] complex (0.090 g, 0.150 mmol) in dichloromethane (20 mL) at 10°C in a 50 mL round-bottom flask, was added H_2O (15 mL) and racemic *N*-benzylphenylalanine (0.076 g, 2 eq, 0.300 mmol). The mixture was stirred vigorously for 24 h at 10°C, then transferred to a separating funnel, the organic phase removed and the aqueous phase washed once with dichloromethane (10 mL). The combined dichloromethane extracts were washed once with H_2O (10 mL) before volatiles were removed under reduced pressure to leave the complex [Co^{III}(**3**)(*N*-Bn-Phe)] as a dark green powder (0.127 g , 99% yield). The aqueous phase was filtered to recover *N*-benzylphenylalanine as a white powder which was washed with dichloromethane (5 mL), water (5 mL) and acetone (5 mL), then dried *in vacuo* (0.037 g, 99% yield). The *ee* (93%) of recovered *N*-Bn-Phe was determined by chiral HPLC: Chirobiotic R (50 x 4.6 mm) column (9:1 H_2O:CH_3CN); 1.0 mL/min; (*S*) enantiomer, 96.5%, t_R = 1.824 min; (*R*) enantiomer, 3.5%, t_R = 2.776 min.

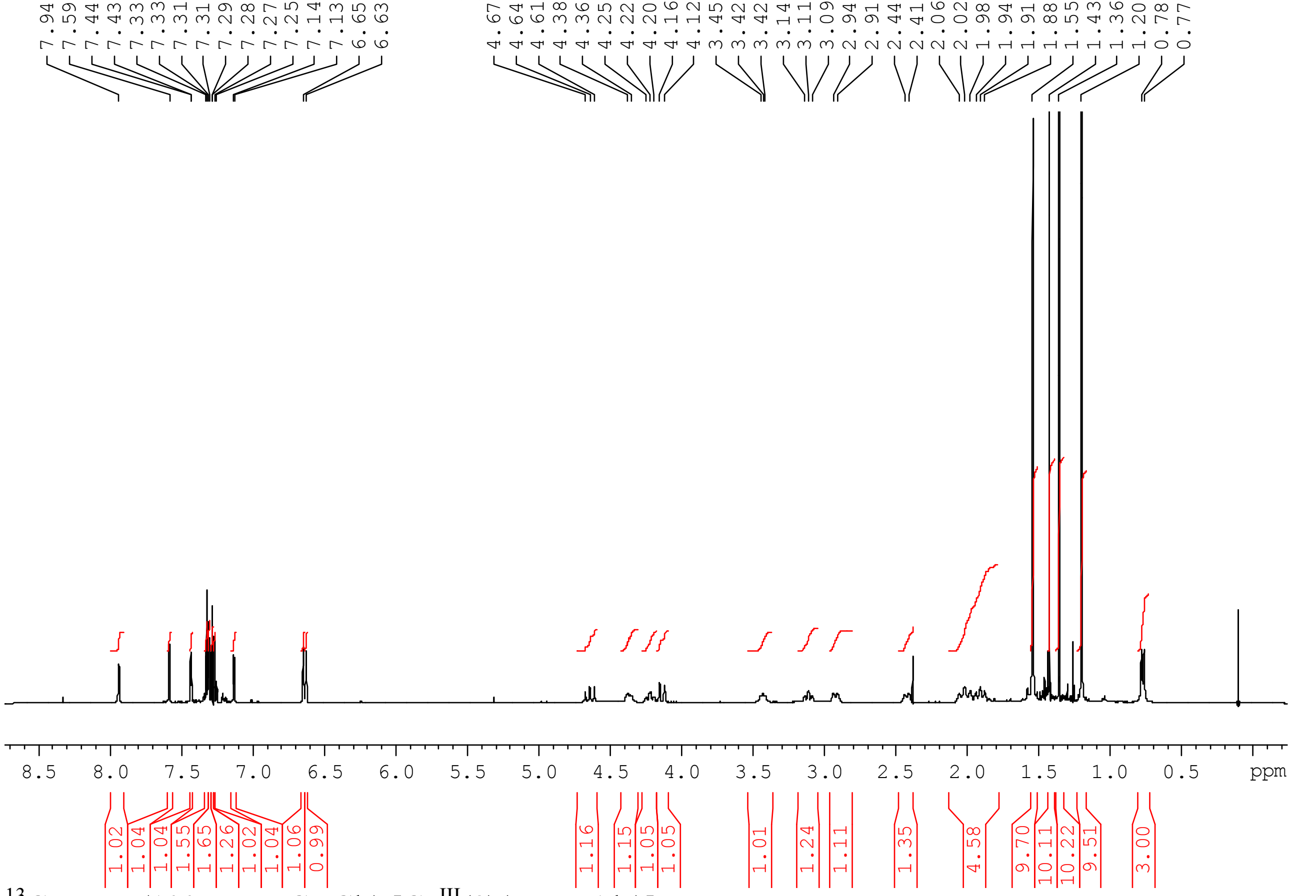
General Procedure for the Extraction of Hydrophobic *N*-Benzyl Amino Acids Using Complex [Co^{III}(3)(OAc)] without Water (Method C): The following procedure for the extraction of *N*-Bn-Val is typical for hydrophobic *N*-benzyl amino acids. To a stirred, cooled (10°C) solution of [Co^{III}(**3**)(OAc)] complex (0.045 g, 0.075 mmol) in dichloromethane (10 mL) was added powdered racemic *N*-benzylvaline (0.031 g, 2 eq, 0.150 mmol). The mixture was stirred at 10°C for 24 h, then filtered to recover uncomplexed *N*-Bn-Val as a white powder, which was washed with dichloromethane (5 mL) and dried (0.015 g, 99% yield). The *ee* (94%) of recovered *N*-Bn-Val was determined by chiral HPLC: Chirobiotic R (50 x 4.6 mm) column (9:1 H_2O:CH_3CN); 1.0 mL/min; (*S*) enantiomer, 97%, t_R = 1.175 min; (*R*) enantiomer, 3%, t_R = 2.199 min. The dichloromethane phase was concentrated under reduced pressure to leave the complex [Co^{III}(**3**)(*N*-Bn-Val)] as a dark green powder (0.060 g, 99% yield).

(*R*,*R*)-*N*,*N′*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) (*R*)-*N*-Benzyl Alaninate - [Co^{III}(3)(*N*-Bn-Ala)]

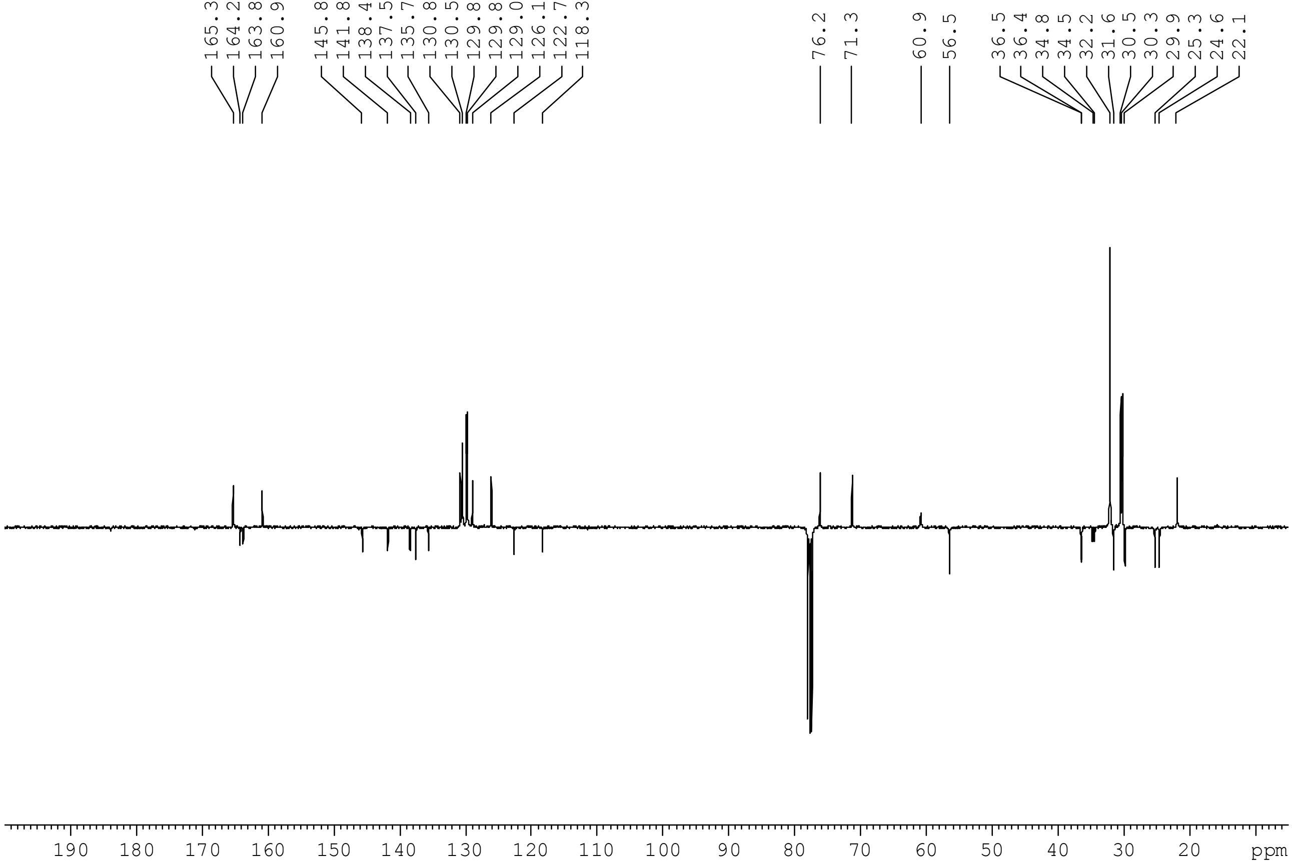


According to method A. Yield: 0.233 g (99%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.94 (s, 1H), 7.59 (s, 1H), 7.43 (d, *J* = 2.6 Hz, 1H), 7.35-7.25 (m, 5H), 7.14 (d, *J* = 2.6 Hz, 1H), 6.64 (s, 1H), 6.62 (s, 1H), 4.65 (dd, J_1 = 13.4 Hz, J_2 = 11.8 Hz, 1H), 4.38-4.35 (m, 1H), 4.25-4.20 (m, 1H), 4.15 (d, *J* = 13.4 Hz, 1H), 3.46-3-39 (m, 1H), 2.92 (d, *J* = 9.7 Hz, 1H), 2.42 (d, *J* = 9.7 Hz, 1H), 2.06-1.88 (m, 3H), 1.59-1.52 (m, 4H), 1.55 (s, 9H), 1.43 (s, 9H), 1.37 (s, 9H), 1.21 (s, 9H), 0.78 ppm (d, *J* = 7.3 Hz, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 183.9, 165.3, 164.2, 163.8, 160.9, 145.7, 141.8, 138.4, 137.5, 135.7, 130.8, 130.5, 129.8, 129.8, 129.0, 126.1, 122.6, 118.3, 76.2, 71.3, 60.9, 56.5, 36.5, 36.4, 34.8, 34.5, 32.2, 31.6, 30.5, 30.3, 29.9, 25.3, 24.6, 21.9 ppm; FT-IR (Nujol): υ = 3252, 2928, 2724, 1640, 1614, 1543, 1523, 1406, 1319, 1270, 1255, 1235, 1201, 1167, 1095, 1007, 961, 931, 913 cm^{-1}; HRMS (ESI): calcd. for $C_{46}H_{64}N_3O_4CoNa$ 804.4127 [*M*+Na]$^+$; found: 804.4147. Elemental analysis calcd (%) for $C_{46}H_{64}N_3O_4Co$ (M_W = 781.97): C 70.66, H 8.25, N 5.37; found: C 70.28, H 8.27, N 5.12.

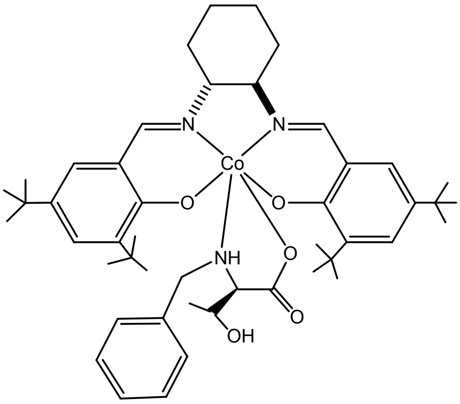
^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**3**)(*N*-Bn-Ala)]



^{13}C-NMR (100 MHz, CDCl$_3$) [Co^{III}(**3**)(*N*-Bn-Ala)]

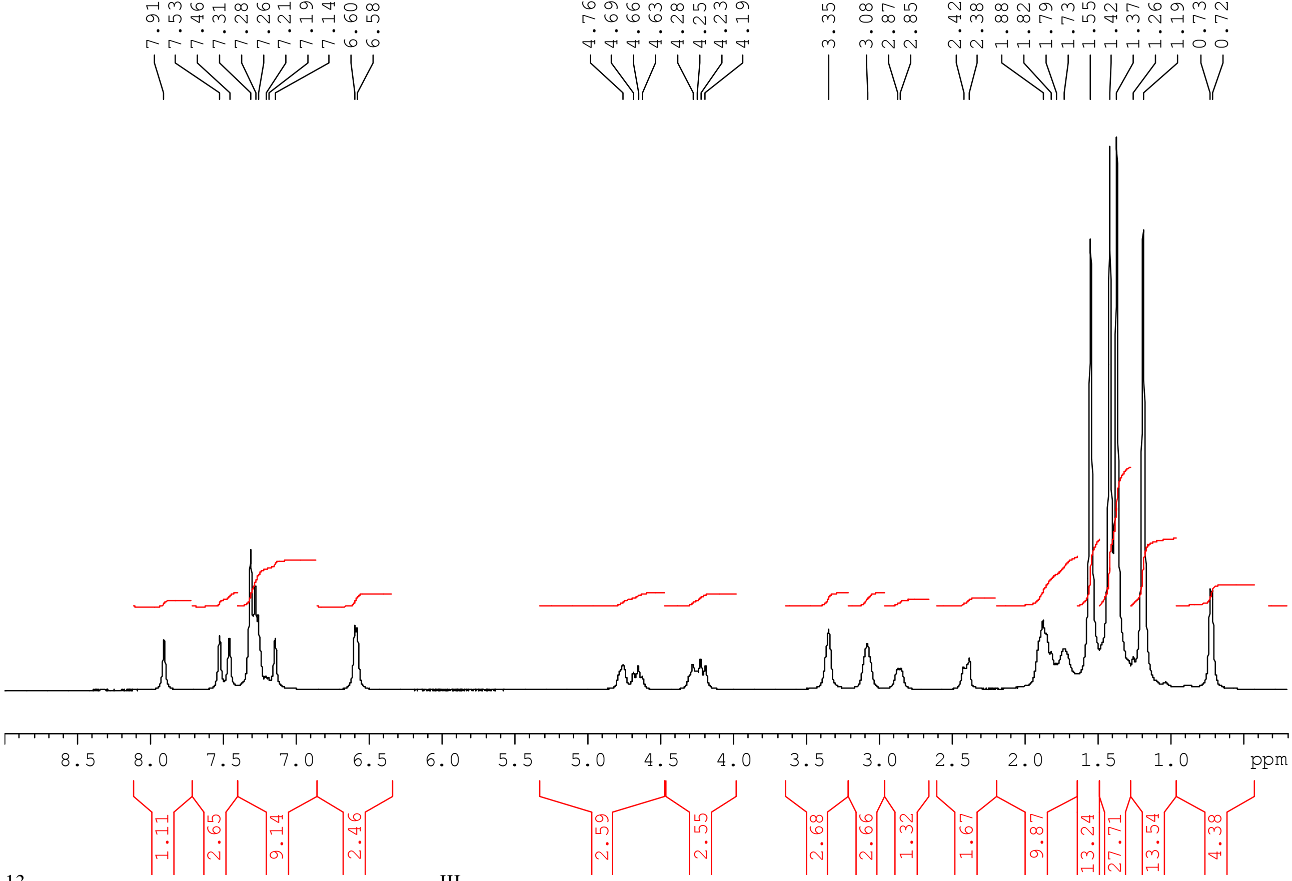


(*R*,*R*)-*N*,*N'*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) (*R*)-*N*-Benzyl Threoninate - [Co^{III}(3)(*N*-Bn-Thr)]

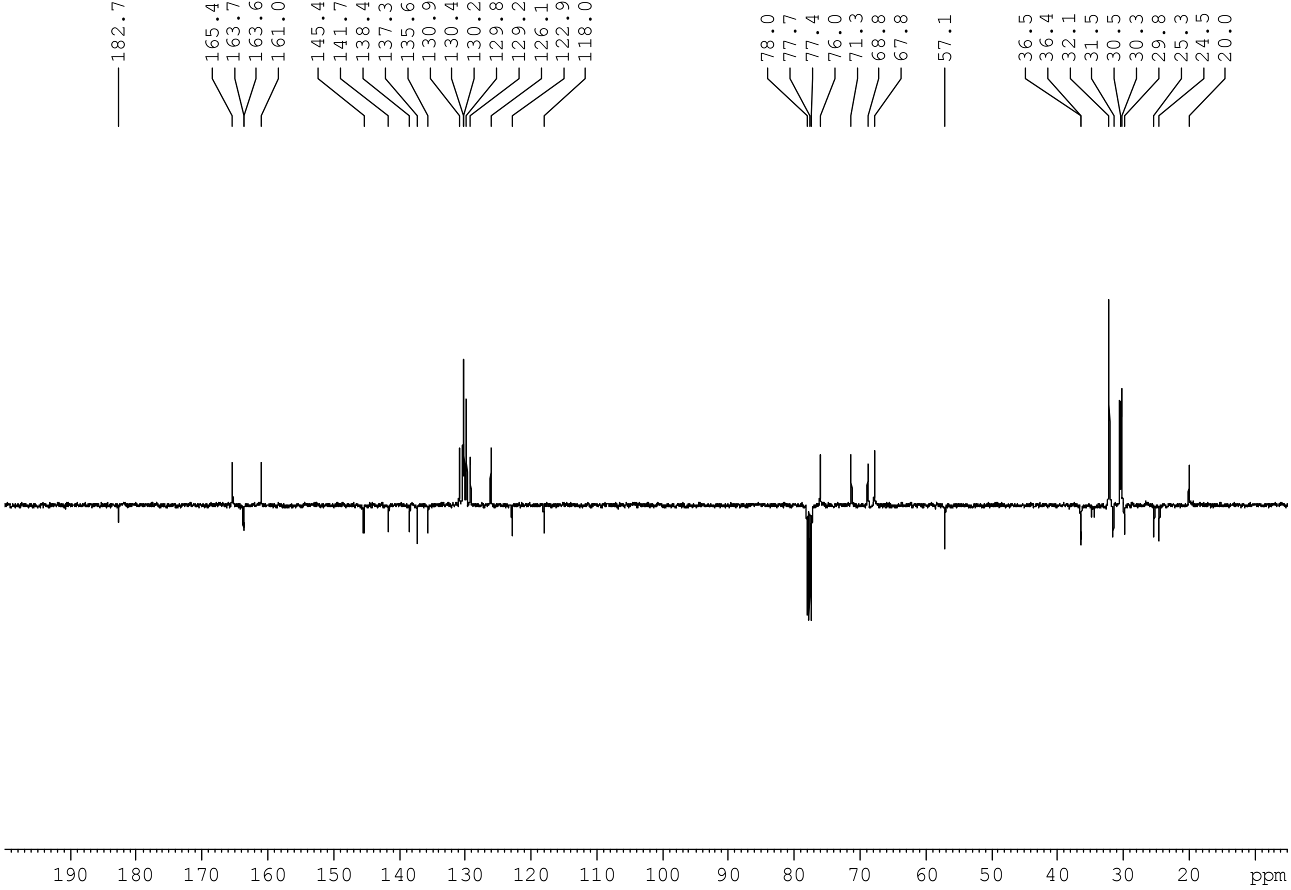


According to method A. Yield: 0.121 g (94%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.91 (s, 1H), 7.53 (s, 1H), 7.46 (s, 1H), 7.32-7.16 (m, 5H), 7.14 (s, 1H), 6.60 (s, 1H), 6.58 (s, 1H), 4.81-4.60 (m, 2H), 4.33-4.18 (m, 2H), 3.40-3.34 (m, 2H), 3.15-3.03 (m, 2H), 2.86 (d, *J* = 8.4 Hz, 1H), 2.45-2.35 (m, 1H), 2.00-1.81 (m, 3H), 1.60-1.52 (m, 3H), 1.55 (s, 9H), 1.42 (s, 9H), 1.37 (s, 9H), 1.19 (s, 9H), 0.72 ppm (d, *J* = 4.4 Hz, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 182.7, 165.4, 163.7, 163.6, 161.0, 145.4, 141.7, 138.5, 137.3, 135.6, 130.9, 130.4, 130.2, 129.8, 129.2, 126.1, 122.9, 118.0, 76.0, 71.3, 68.8, 67.8, 57.1, 36.5, 36.4, 32.1, 31.5, 30.5, 30.3, 29.8, 25.3, 24.5, 20.0 ppm; FT-IR (Nujol): υ = 3367, 2918, 2723, 1655, 1631, 1574, 1544, 1526, 1406, 1270, 1256, 1208, 1168, 1128, 1098, 1056, 1024, 987, 932, 915 cm^{-1}; HRMS (ESI): calcd. for $C_{47}H_{66}N_3O_5CoNa$ 834.4227 [*M*+Na]$^+$; found: 834.4259. Elemental analysis calcd (%) for $C_{47}H_{66}N_3O_5Co$ (M_W = 811.99): C 69.52, H 8.19, N 5.17; found: C 69.21, H 8.21, N 4.87.

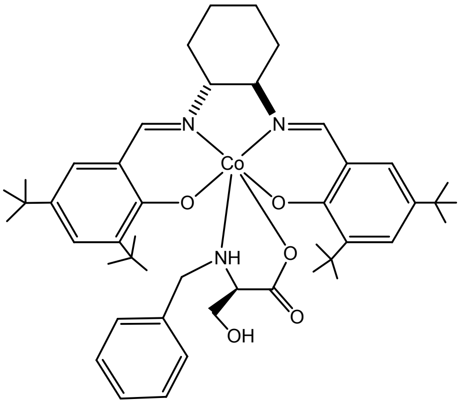
^{1}H-NMR (400 MHz, CDCl$_3$) [Co$^{\mathrm{III}}$(**3**)(*N*-Bn-Thr)]



^{13}C-NMR (100 MHz, CDCl$_3$) [Co$^{\mathrm{III}}$(**3**)(*N*-Bn-Thr)]

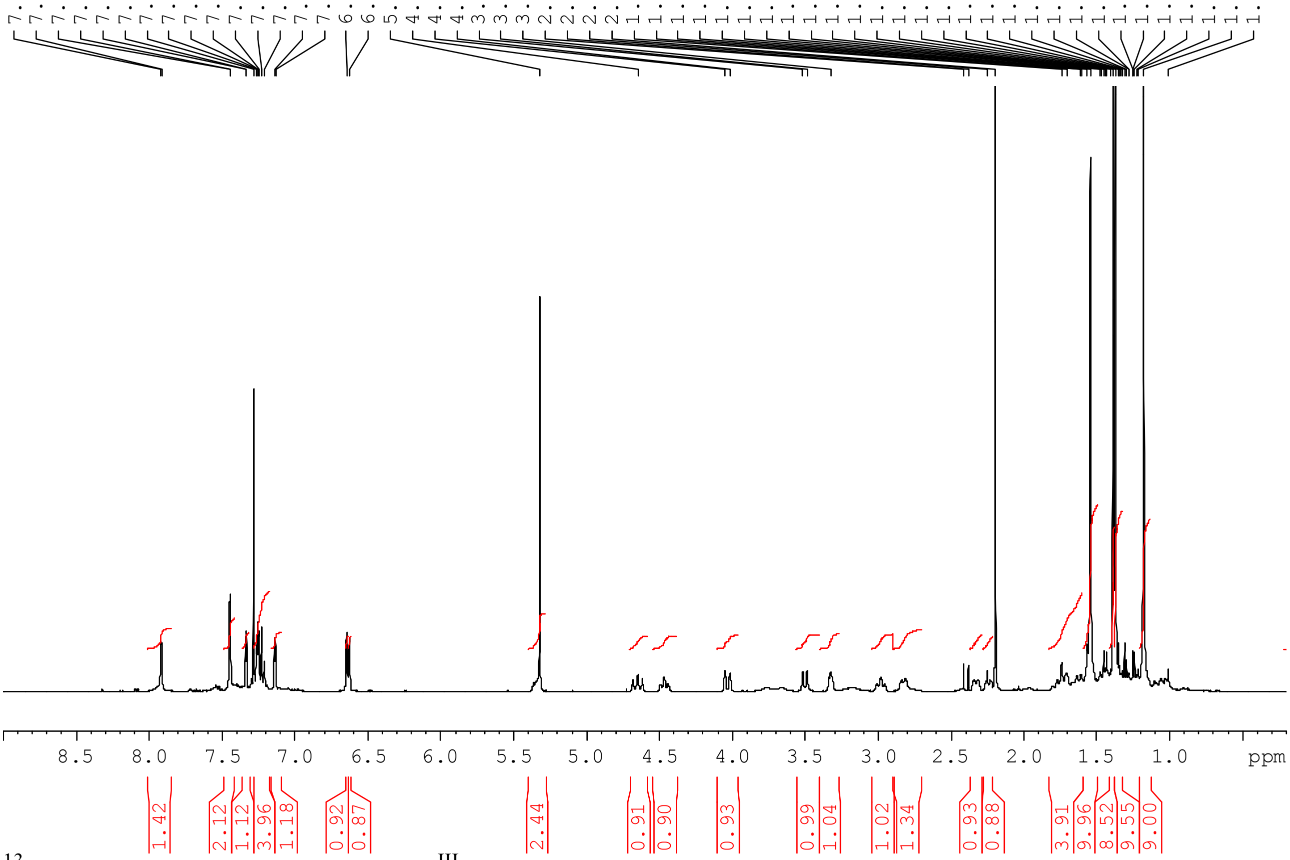


(*R*,*R*)-*N*,*N′*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) (*R*)-*N*-Benzyl Serinate - [Co^{III}(3)(*N*-Bn-Ser)]

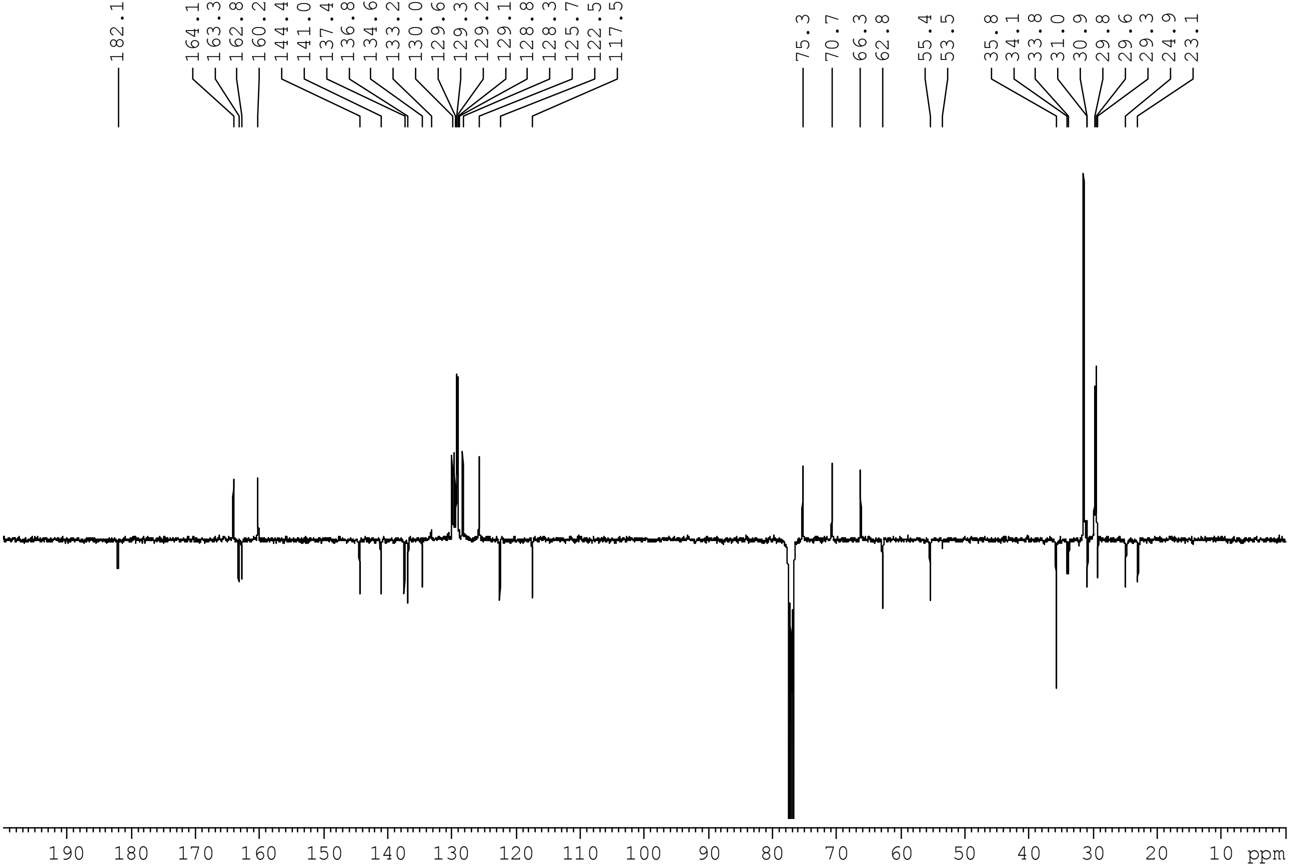


According to method A. Yield: 0.107 g (90%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.91 (s, 1H), 7.44 (s, 2H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.27-7.20 (m, 4H), 7.13 (d, J = 2.5 Hz, 1H), 6.64 (s, 1H), 6.62 (s, 1H), 5.37-5.30 (m, 3H), 4.65 (t, *J* = 13.6 Hz, 1H), 4.52-4.40 (m, 1H), 4.03 (d, *J* = 13.6 Hz, 1H), 3.50 (d, *J* = 11.2 Hz, 1H), 3.36-3.29 (m, 1H), 2.88-2.72 (m, 2H), 2.37-2.29 (m, 1H), 2.27-2.21 (m, 1H), 1.82-1.59 (m, 4H), 1.54 (s, 9H), 1.38 (s, 9H), 1.37 (s, 9H), 1.18 (s, 9H) ppm; ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 182.1, 164.1, 163.3, 162.8, 160.2, 144.4, 141.0, 137.4, 136.8, 134.6, 133.2, 129.6, 129.3, 129.2, 129.1, 128.8, 128.3, 125.7, 122.5 117.5, 75.3, 70.7, 66.3, 62.8, 55.4, 53.5, 35.8, 34.1, 33.8, 31.0, 30.9, 29.8, 29.6, 29.3, 24.9, 23.1 ppm; FT-IR (Nujol): υ = 2923, 2360, 1459, 1167, 2854, 1633, 1376, 721 cm^{-1}; HRMS (ESI): calcd. for $C_{46}H_{64}N_3O_5CoNa$ 820.4070 [*M*+Na]$^+$; found: 820.4068.

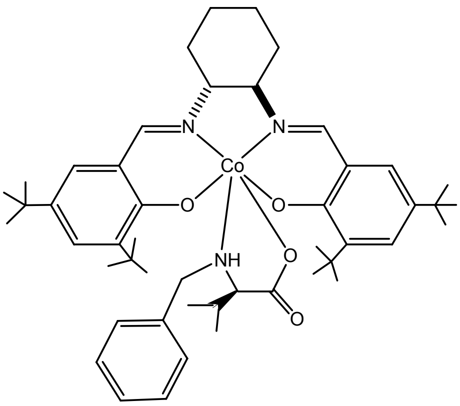
^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**3**)(*N*-Bn-Ser)]



^{13}C-NMR (100 MHz, CDCl$_3$) [Co^{III}(**3**)(*N*-Bn-Ser)]

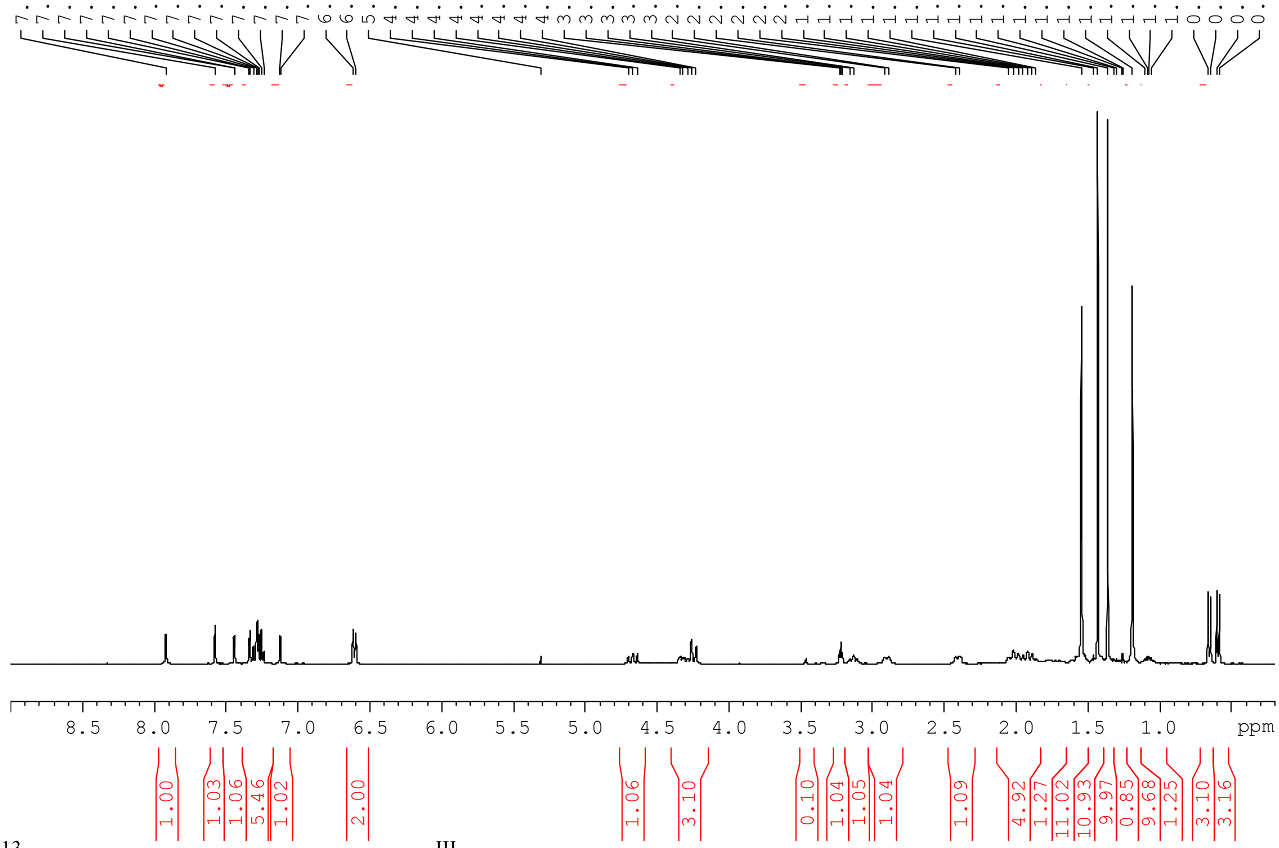


(***R***,***R***)-***N***,***N′***-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) (***R***)-***N***-Benzyl Valinate - [Co^{III}(3)(***N***-Bn-Val)]

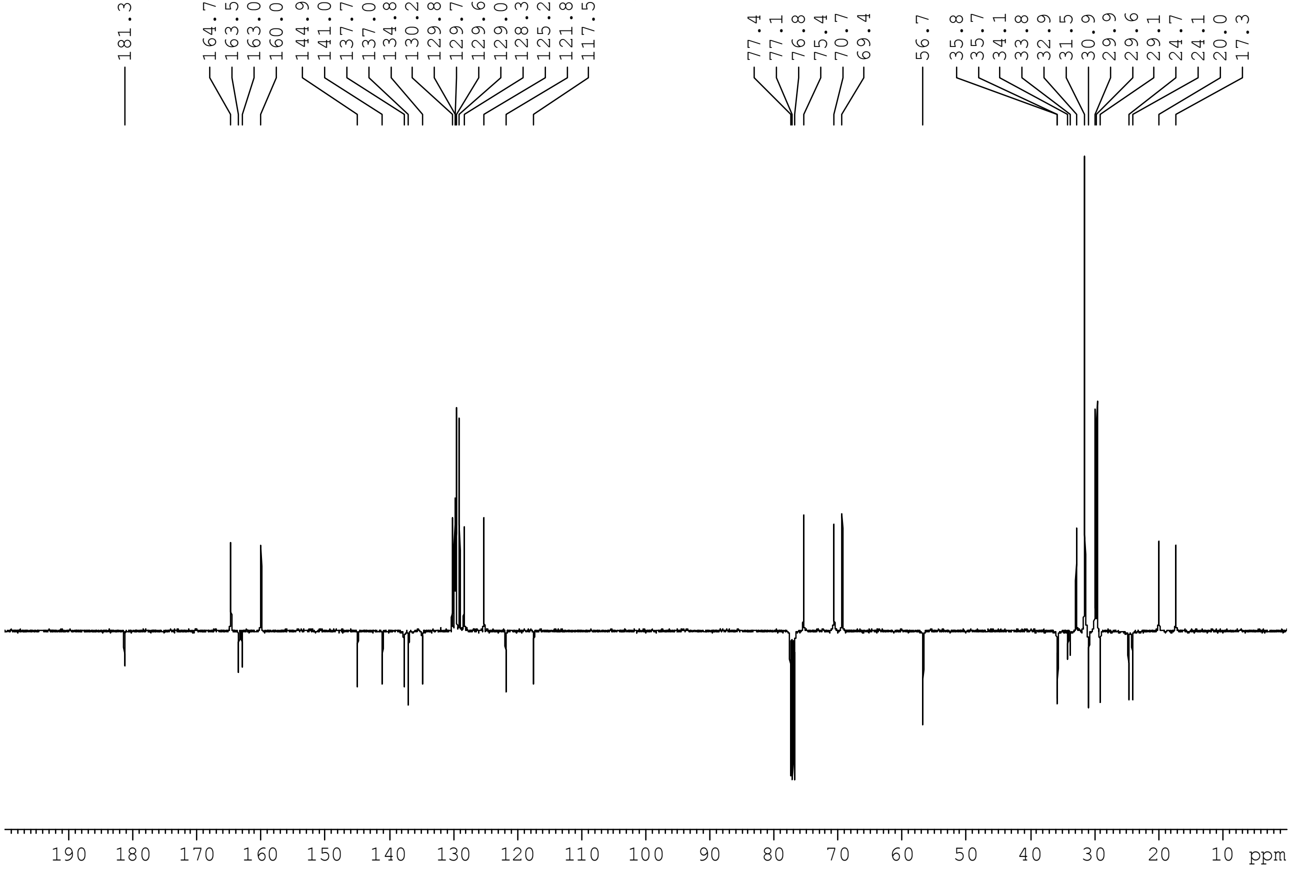


According to method A. Yield: 0.120 g (98%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.92 (s, 1H), 7.58 (s, 1H), 7.44 (d, *J* = 2.5 Hz, 1H), 7.35-7.25 (m, 5H), 7.12 (d, *J* = 2.5 Hz, 1H), 6.62 (s, 1H), 6.60 (s, 1H), 4.67 (dd, J_1 = 11.7 Hz, J_2 = 13.6 Hz, 1H), 4.34-4.25 (m, 2H), 4.25 (d, *J* = 13.6 Hz, 1H), 3.23-3.20 (m, 1H), 3.16-3.11 (m, 1H), 2.90 (d, *J* = 9.5 Hz, 1H), 2.43-2.38 (m, 1H), 2.06-1.88 (m, 3H), 1.61-1.52 (m, 3H), 1.54 (s, 9H), 1.43 (s, 9H), 1.36 (s, 9H), 1.19 (s, 9H), 1.13-1.04 (m, 1H), 0.66 (d, *J* = 6.9 Hz, 3H), 0.59 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 181.3, 164.7, 163.5, 163.0, 160.0, 144.9, 141.0, 137.7, 137.0, 134.8, 130.2, 129.8, 129.7, 129.6, 129.0, 128.3, 125.2, 121.8, 117.5, 75.4, 70.7, 69.4, 56.7, 35.9, 35.7, 34.1, 33.8, 31.5, 30.9, 29.9, 29.6, 29.1, 24.7, 24.1, 20.0, 17.3 ppm; FT-IR (Nujol): υ = 2923, 2853, 1655, 1635, 1617, 1545, 1525, 1407, 1319, 1257, 1201, 1169, 1096, 1025, 988, 933, 913 cm^{-}1; HRMS (ESI): calcd. for $C_{48}H_{68}N_3O_4CoNa$ 832.4434 [*M*+Na]$^+$; found: 832.4419. Elemental analysis calcd (%) for $C_{48}H_{68}N_3O_4Co$ (M_W = 810.02): C 71.17, H 8.46, N 5.18; found: C 70.85, H 8.53, N 4.97.

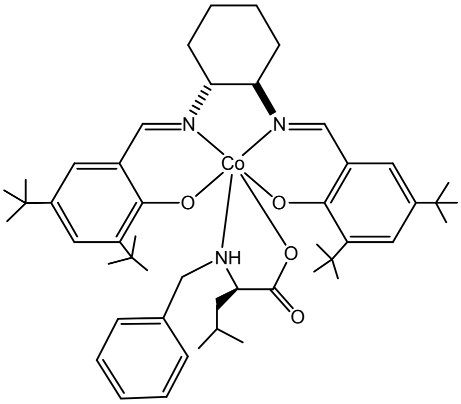
^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**3**)(*N*-Bn-Val)]



^{13}C-NMR (100 MHz, CDCl$_3$) [Co^{III}(**3**)(*N*-Bn-Val)]

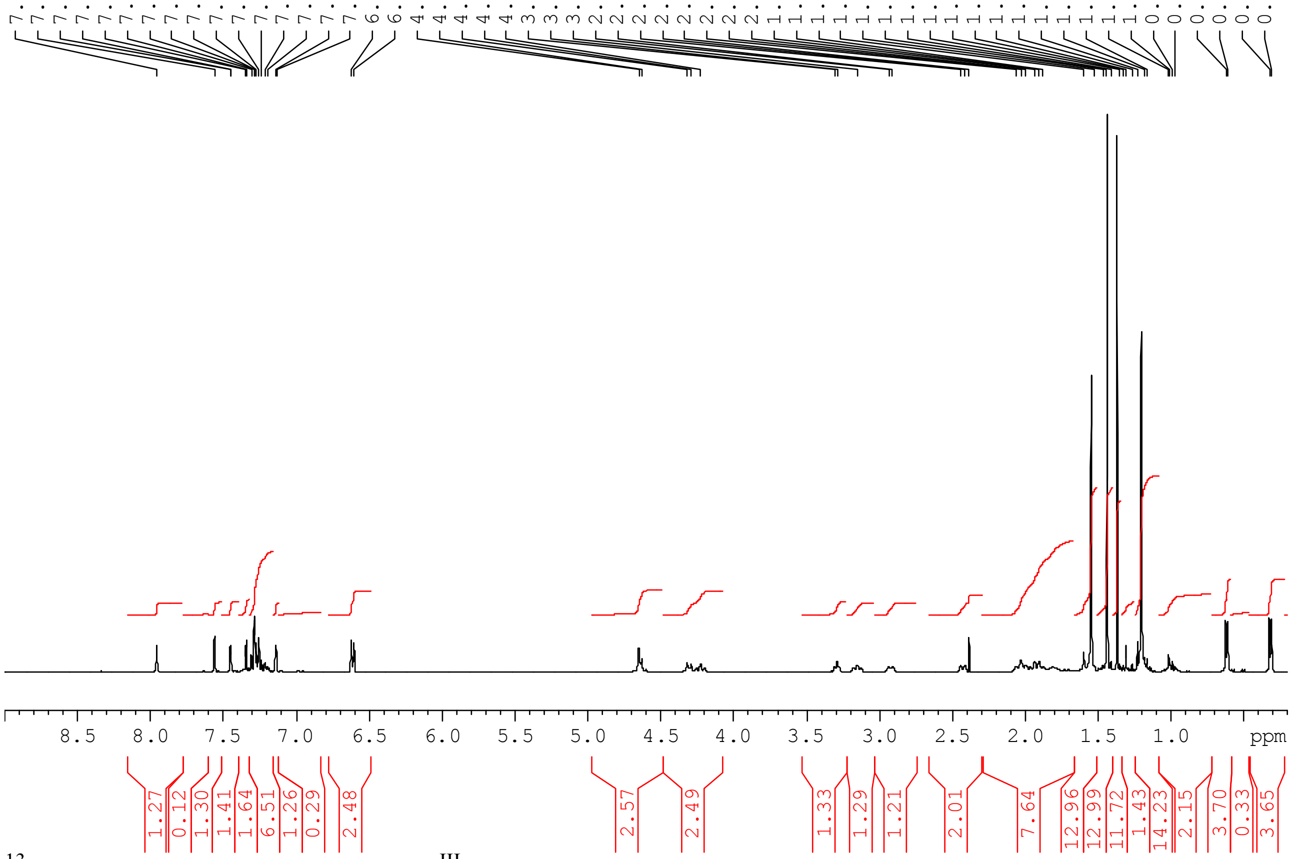


(*R*,*R*)-*N*,*N'*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) (*R*)-*N*-Benzyl Leucinate - [Co^{III}(3)(*N*-Bn-Leu)]

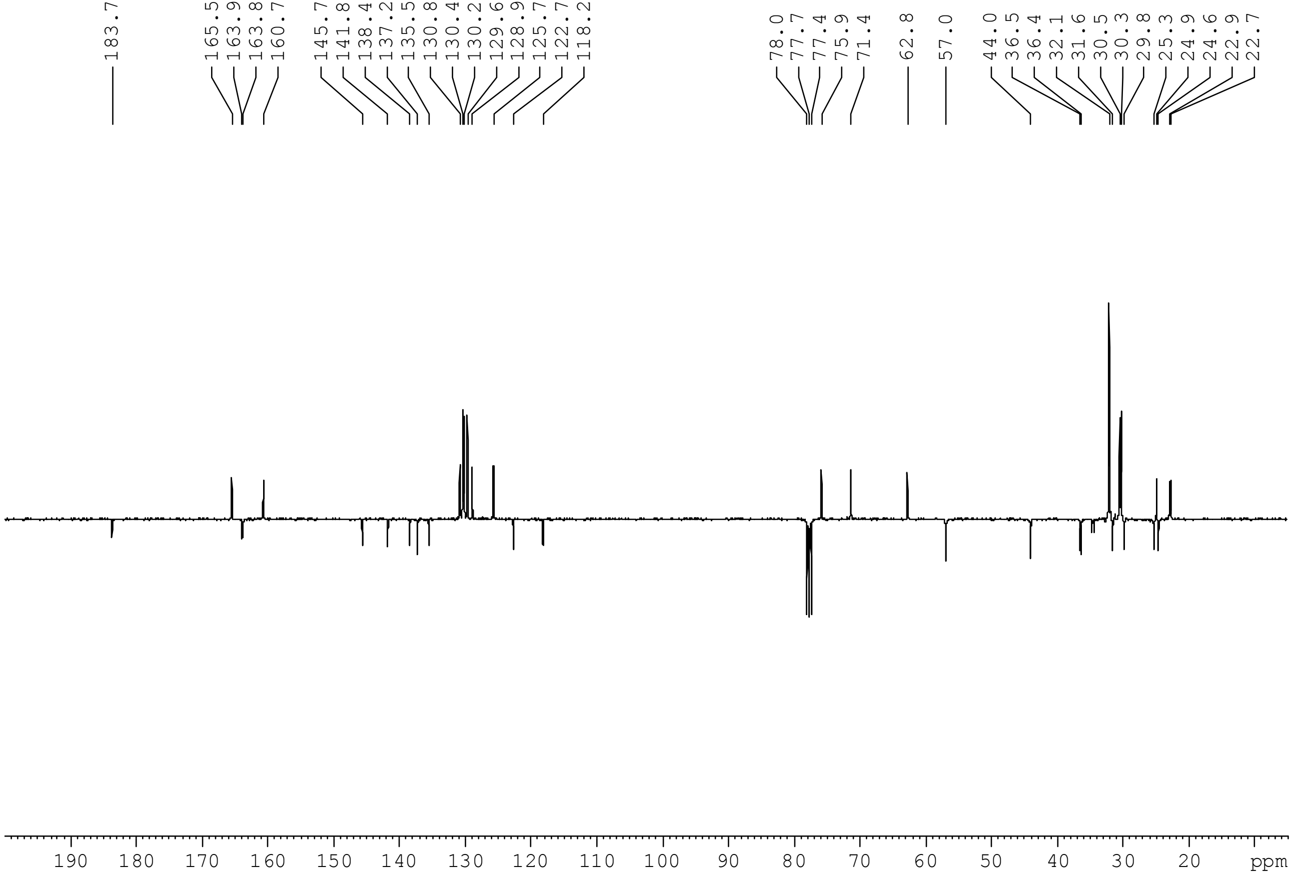


According to method A. Yield: 0.122 g (99%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.96 (s, 1H), 7.56 (s, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 2.8 Hz, 1H), 7.33-7.19 (m, 4H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.62 (s, 1H), 6.60 (s, 1H), 4.67-4.61 (m, 2H), 4.34-4.29 (m, 1H), 4.29-4.19 (m, 1H), 3.31-3.27 (m, 1H), 3.18-3.12 (m, 1H), 2.92 (d, *J* = 10.4 Hz, 1H), 2.44-2.39 (m, 1H), 2.06-1.70 (m, 5H), 1.65-1.52 (m, 3H), 1.54 (s, 9H), 1.43 (s, 9H), 1.35 (s, 9H), 1.19 (s, 9H), 1.03-0.97 (m, 1H), 0.63 (d, *J* = 6.4 Hz, 3H), 0.31 ppm (d, *J* = 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 183.7, 165.5, 163.9, 163.8, 160.7, 145.7, 141.8, 138.4, 137.2, 135.5, 130.8, 130.4, 130.2, 129.7, 128.9, 125.7, 122.7, 118.2, 75.9, 71.4, 62.8, 57.0, 44.0, 36.5, 36.4, 32.1, 31.6, 30.5, 30.3, 29.8, 25.3, 24.9, 24.6, 22.9, 22.7 ppm; FT-IR (Nujol): υ = 3253, 2924, 2726, 1660, 1640, 1544, 1523, 1406, 1269, 1256, 1203, 1168, 1095, 1028, 983, 953, 931 cm^{-1}; HRMS (ESI): calcd. for $C_{49}H_{70}N_3O_4CoNa$ 846.4591 [*M*+Na]$^+$; found: 846.4592. Elemental analysis calcd (%) for $C_{49}H_{70}N_3O_4Co$ (M_W = 824.06): C 71.42, H 8.56, N 5.10; found: C 71.10, H 8.43, N 4.91.

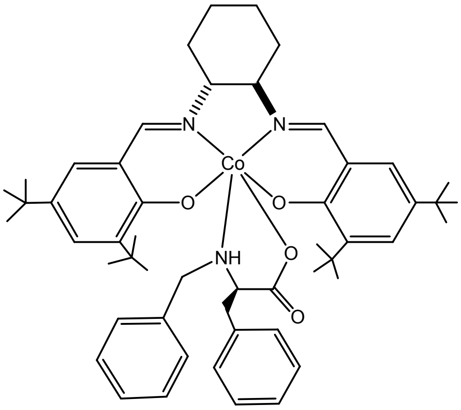
^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**3**)(*N*-Bn-Leu)]



^{13}C-NMR (100 MHz, CDCl$_3$) [Co^{III}(**3**)(*N*-Bn-Leu)]

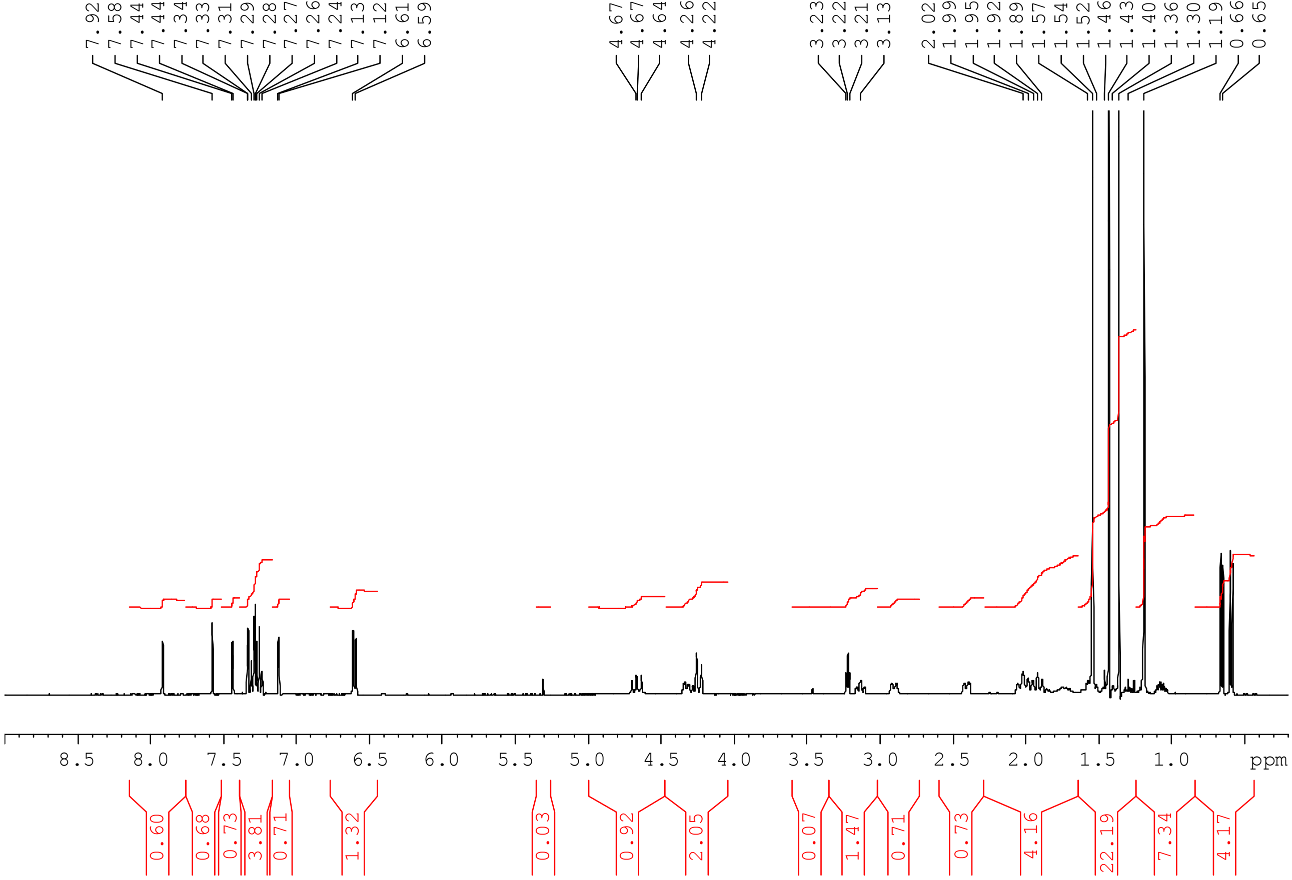


(*R*,*R*)-*N*,*N'*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) (*R*)-*N*-Benzyl Phenylalaniate - [Co^{III}(3)(*N*-Bn-Phe)]

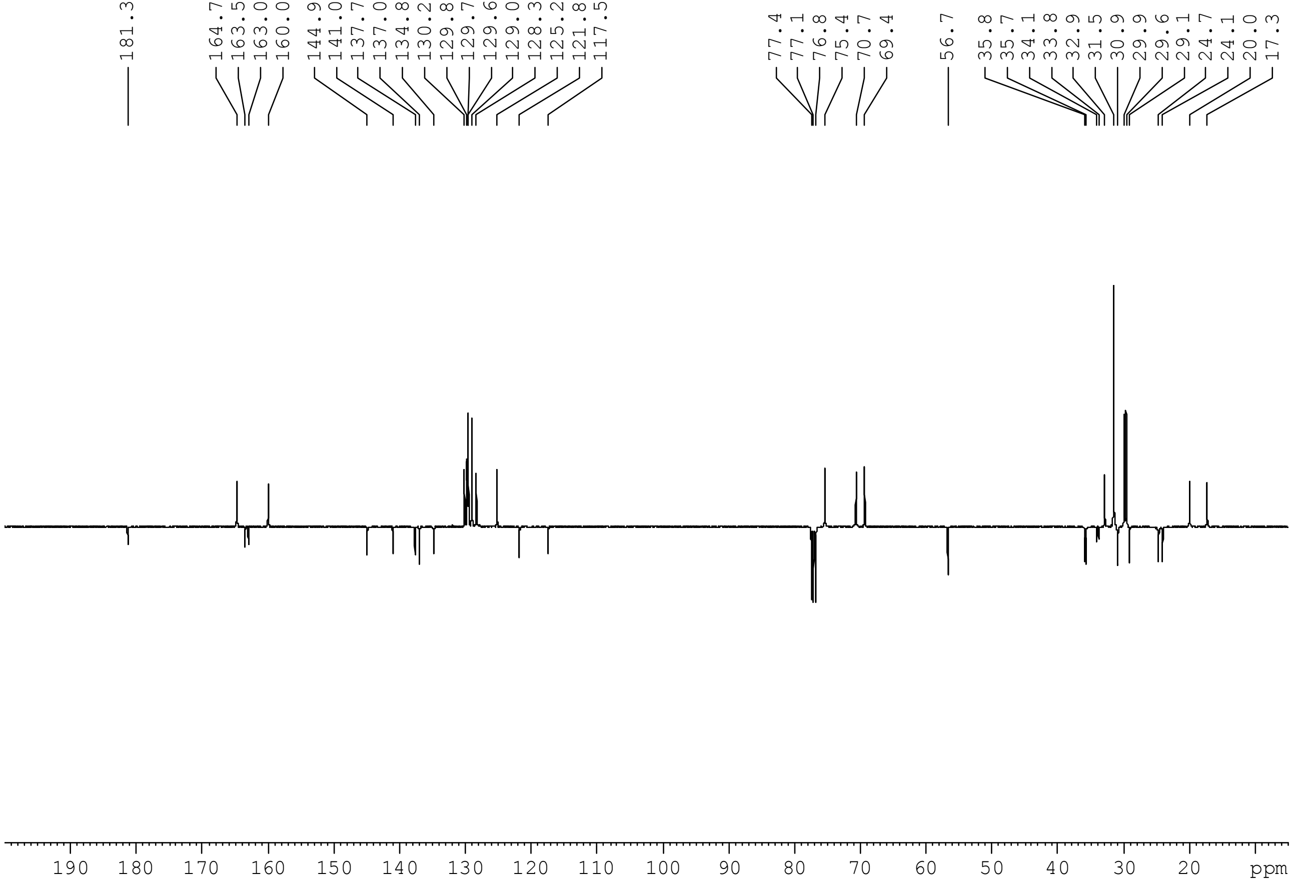


According to method B. Yield: 0.127 g (99%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.82 (s, 1H), 7.44-7.25 (m, 8H), 7.10 (s, 1H), 7.06 (s, 1H), 6.84 (d, J = 7.2 Hz, 2H), 6.73 (d, J = 6.0 Hz, 2H), 6.34 (s, 1H), 4.83-4.75 (m, 1H), 4.40-4.37 (m, 1H), 4.04 (d, J = 14.0 Hz, 1H), 3.80 (s, 2H), 3.21 (d, J = 13.6 Hz, 1H), 2.87-2.79 (m, 2H), 2.06-1.88 (m, 6H), 1.63-1.52 (m, 3H), 1.53 (s, 9H), 1.47 (s, 9H), 1.36 (s, 9H), 1.15 ppm (s, 9H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 182.7, 165.0, 163.8, 163.6, 159.5, 145.3, 141.6, 137.9, 137.1, 135.5, 132.6, 131.6, 130.7, 130.7, 130.5, 129.9, 129.7, 129.4, 128.9, 127.8, 126.6, 124.4, 122.3, 118.3, 76.0, 70.7, 56.9, 38.1, 36.4, 34.7, 34.4, 32.3, 32.2, 31.4, 30.6, 30.3, 29.8, 25.4, 24.7 ppm; FT-IR (Nujol): υ = 2923, 2853, 1658, 1644, 1621, 1574, 1567, 1546, 1523, 1406, 1256, 1200, 1168, 1124, 1096, 1017, 978, 913 cm^{-1}; HRMS (ESI): calcd. for $C_{52}H_{68}N_3O_4CoNa$ 880.4434 [*M*+Na]$^+$; found: 880.4411. Elemental analysis calcd (%) for $C_{52}H_{68}N_3O_4Co$ (M_W = 858.06): C 72.79, H 7.99, N 4.90; found: C 72.40, H 7.80, N 4.61.

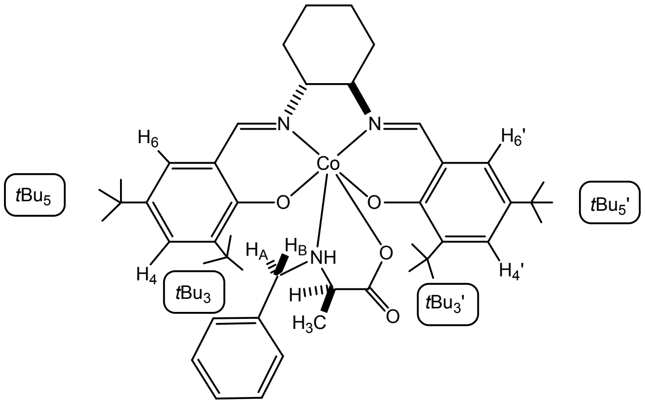
^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**3**)(*N*-Bn-Phe)]



^{13}C-NMR (100 MHz, CDCl$_3$) [Co^{III}(**3**)(*N*-Bn-Phe)]

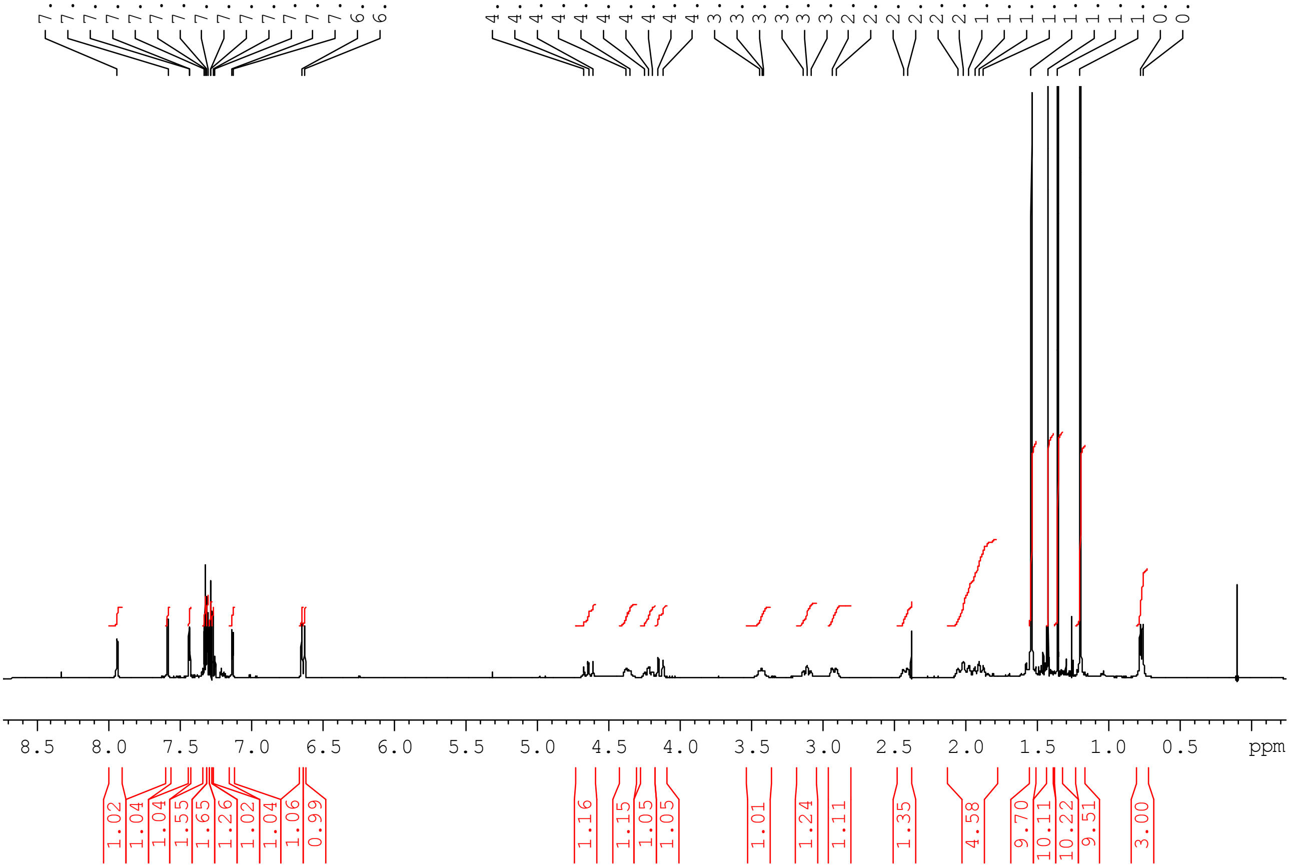


(R,R)-N,N'-Bis(3,5-Di-tert-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) (R)-*N*-Benzyl Alaninate - [Co^{III}(3)(*R*-*N*-Bn-Ala)]

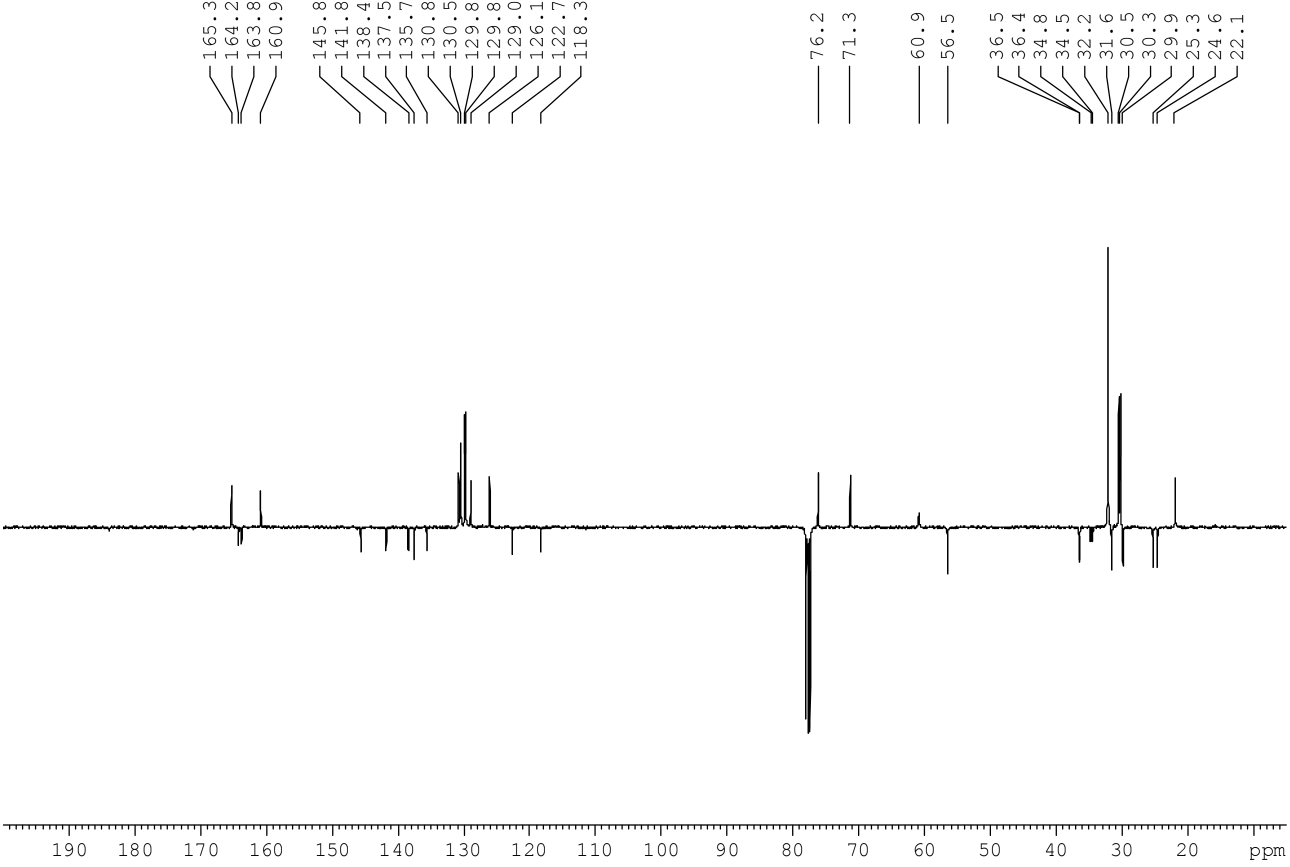


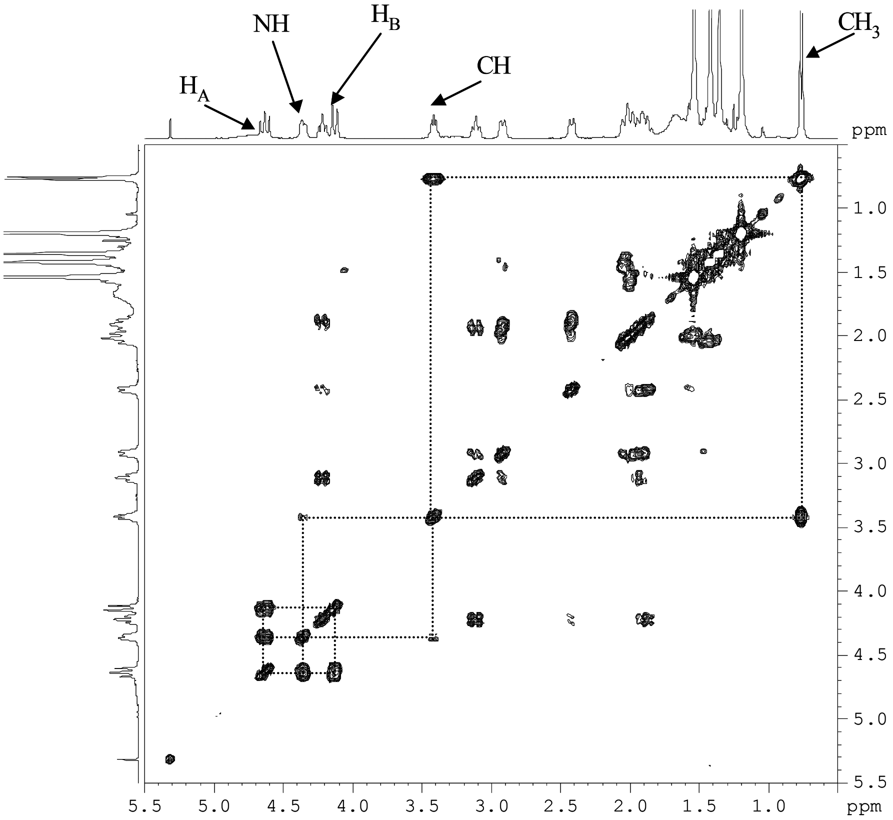
To a solution of the [Co^{III}(**3**)(OAc)] complex (0.025 g, 0.0375 mmol) in dichloromethane (5 mL) at 10°C in a 25 mL round-bottom flask, was added a precooled (10°C) solution of (*R*)-*N*-Bn-Ala (0.013 g, 2 eq, 0.075 mmol) in H_2O (3.75 mL). The biphasic mixture was stirred vigorously for 24 h at 10°C, then transferred to a separating funnel, the organic phase removed and the aqueous phase washed once with dichloromethane (10 mL). The combined dichloromethane extracts were washed once with H_2O (10 mL) before volatiles were removed under reduced pressure to obtain [Co^{III}(**3**)(*R*-*N*-Bn-Ala)] as a green powder. Yield: 0.029 g (99%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.94 (s, 2H), 7.58 (br s, 1H), 7.43 (d, *J* = 2.6 Hz, 1H), 7.34-7.25 (m, 4H), 7.13 (d, *J* = 2.6 Hz, 1H), 6.64 (s, 1H), 6.62 (s, 1H), 4.64 (dd, J_1 = 13.6 Hz, J_2 = 12.0 Hz, 1H), 4.38-4.35 (m, 1H), 4.24-4.19 (m, 1H), 4.15 (d, *J* = 13.6 Hz, 1H), 3.44-3.41 (m, 1H), 3.13-3.09 (m, 1H), 2.93-2.90 (m, 1H), 2.43-2.40 (m, 2H), 2.05-1.88 (m, 5H), 1.54 (s, 9H), 1.42 (s, 9H), 1.36 (s, 9H), 1.20 (s, 9H), 0.77 (d, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 183.9, 165.3, 164.2, 163.8, 160.9, 145.7, 141.8, 138.4, 137.5, 135.7, 130.8, 130.5, 129.8, 129.8, 129.0, 126.1, 122.6, 118.3, 76.2, 71.3, 60.9, 56.5, 36.5, 36.4, 34.8, 34.5, 32.2, 31.6, 30.5, 30.3, 29.9, 25.3, 24.6, 21.9 ppm. FT-IR (Nujol): υ = 3252, 2922, 2724, 1628, 1524, 1458, 1406, 1319, 1270, 1255, 1235, 1201, 1167, 1097, 1007, 961, 931, 911 cm^{-1}; HRMS (ESI): calcd. for $C_{46}H_{64}N_3O_4CoNa$ 804.4120 [*M*+Na]$^+$; found: 804.4131.

^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**3**)(*R*-*N*-Bn-Ala)]

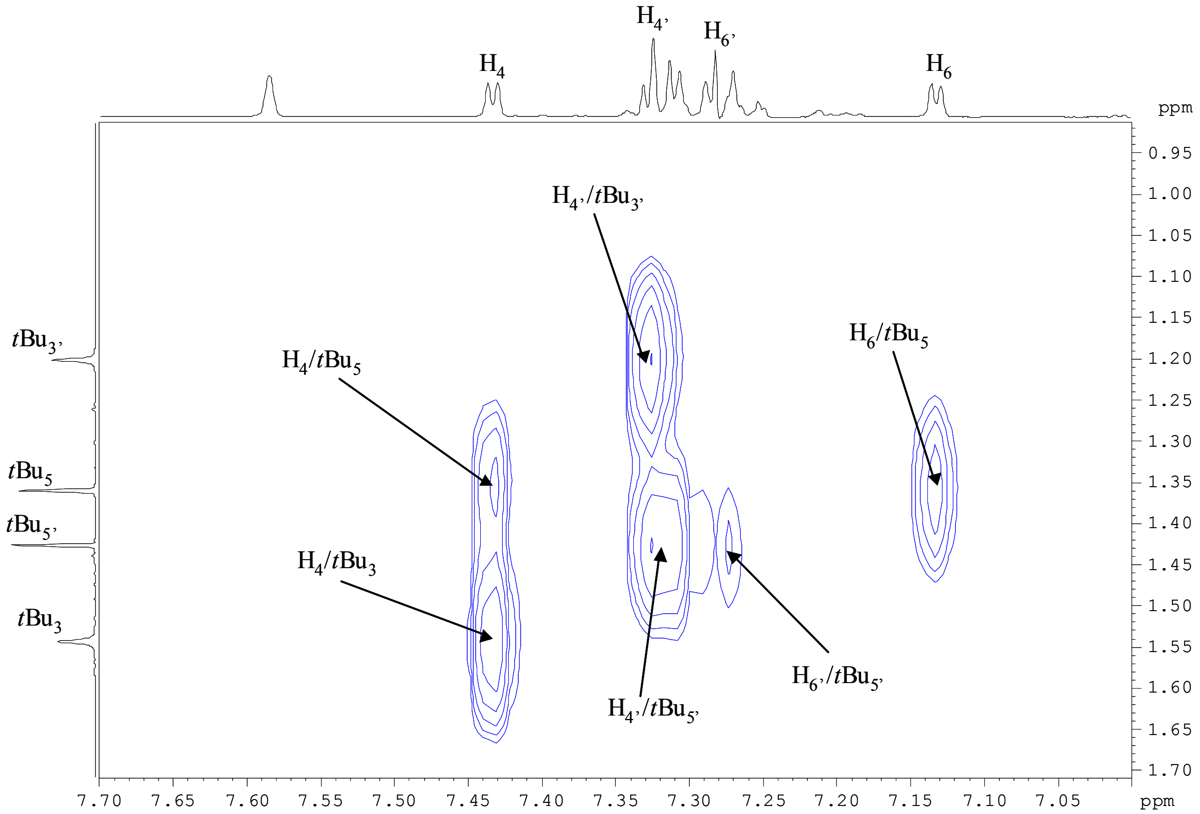


^{13}C-NMR (100 MHz, CDCl$_3$) [Co^{III}(**3**)(*R*-*N*-Bn-Ala)]

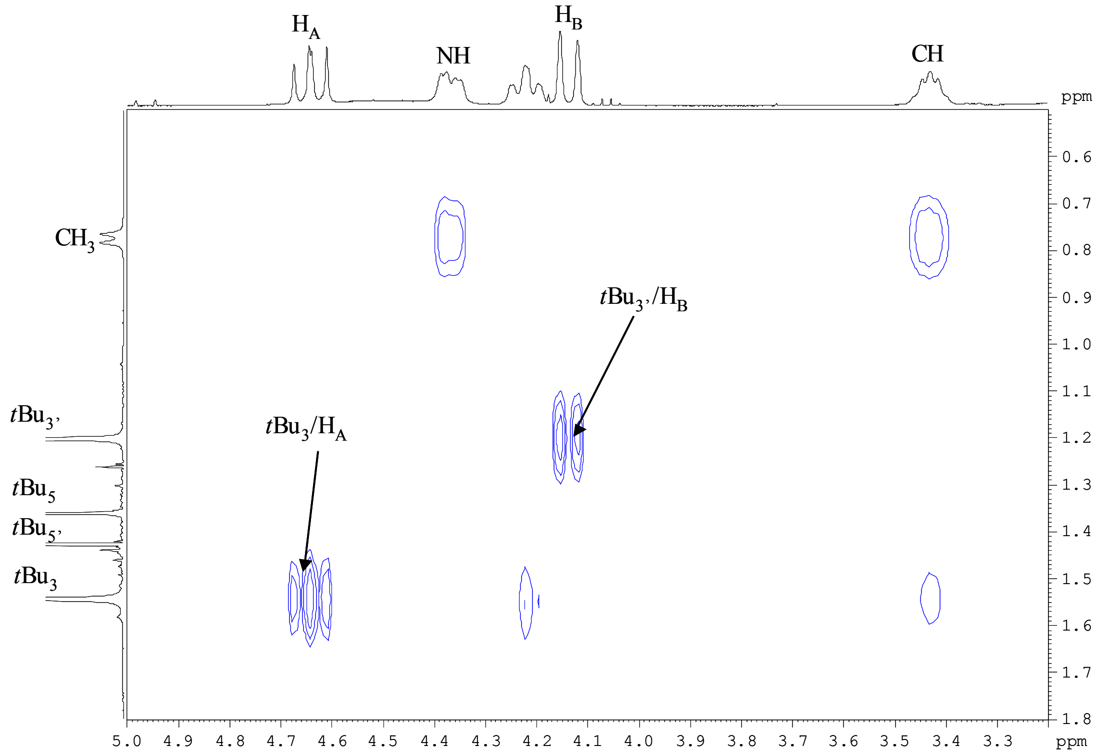




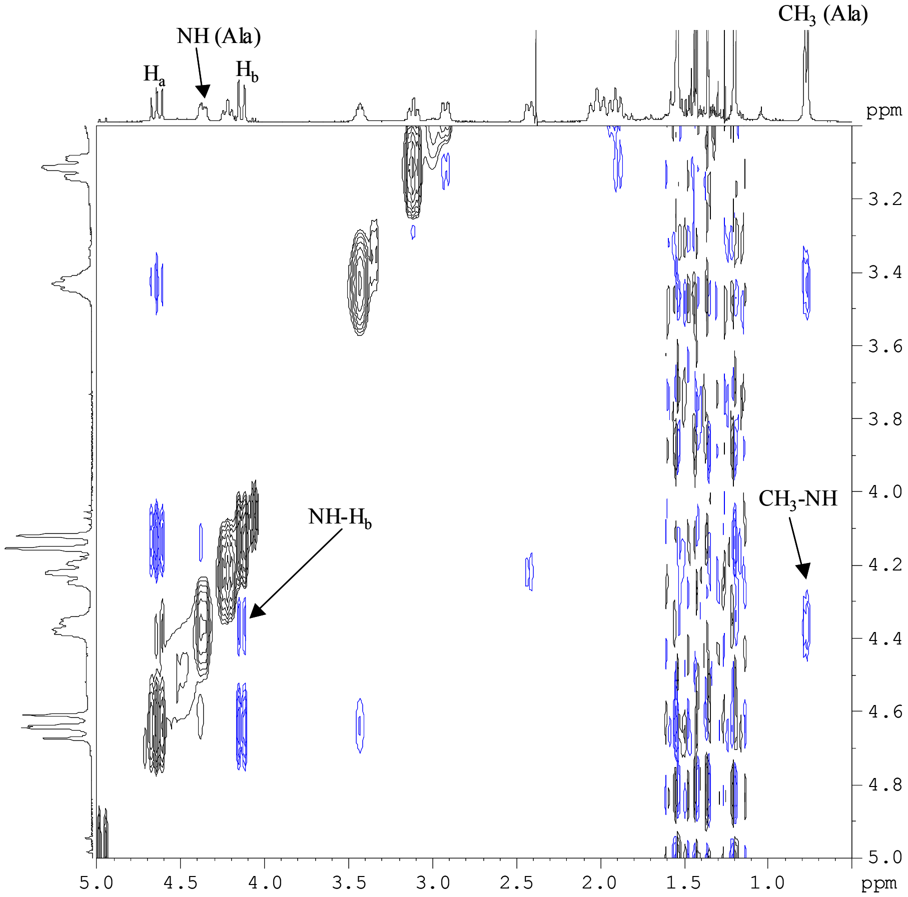
Section of ^{1}H-COSY spectrum of [Co^{III}(**3**)(*R*-*N*-Bn-Ala)] with cross-peaks corresponding to the interactions of the hydrogen atoms of the *R*-*N*-Bn-Ala portion.



Section of ^{1}H-NOESY spectrum of [Co^{III}(**3**)(*R*-*N*-Bn-Ala)] showing spatial interactions between *t*-butyl groups and the aromatic protons of the salen ligand.

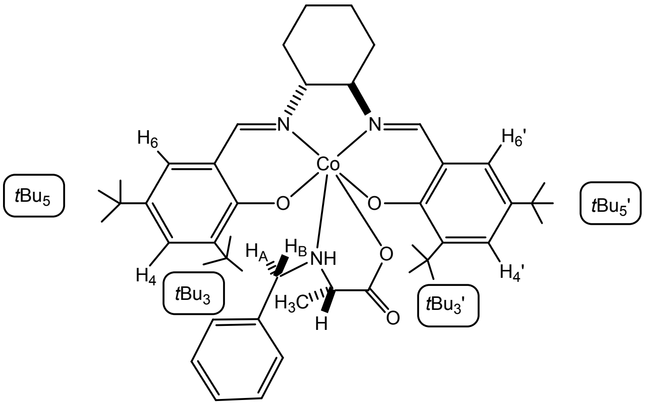


Section of ^{1}H-NOESY spectrum of [Co^{III}(**3**)(*R*-*N*-Bn-Ala)] showing spatial interactions between protons H$_A$ and H$_B$ of the benzyl group of (*R*)-*N*-Bn-Ala and *t*-butyl groups of the chiral salen ligand.



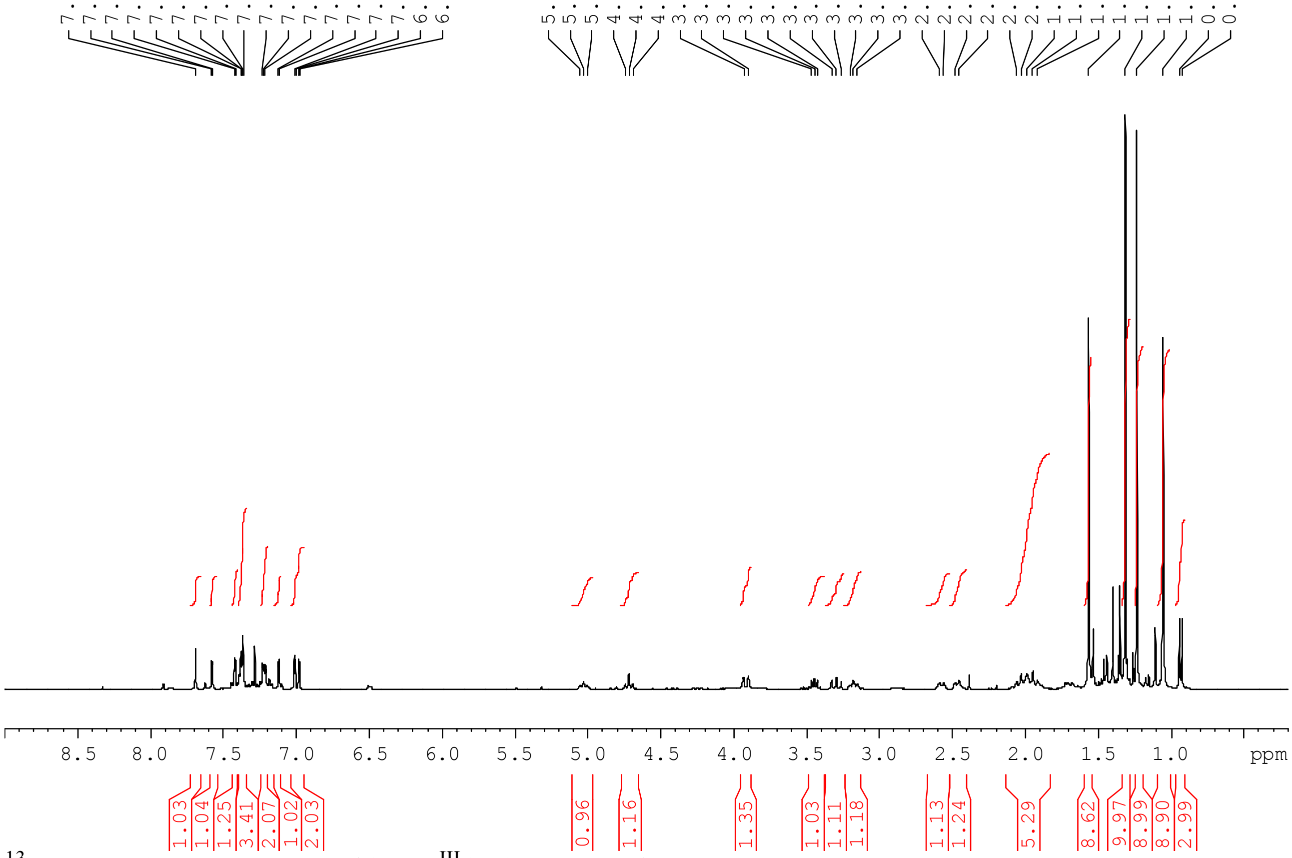
Section of ^{1}H-NOESY spectrum of [Co^{III}(**3**)(*R*-*N*-Bn-Ala)] showing spatial interactions between proton N-H and CH$_3$ and proton H$_B$ of the benzyl group of (*R*)-*N*-Bn-Ala.

(*R*,*R*)-*N*,*N′*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) (*S*)-*N*-Benzyl Alaninate [Co^{III}(3)(*S*-*N*-Bn-Ala)]

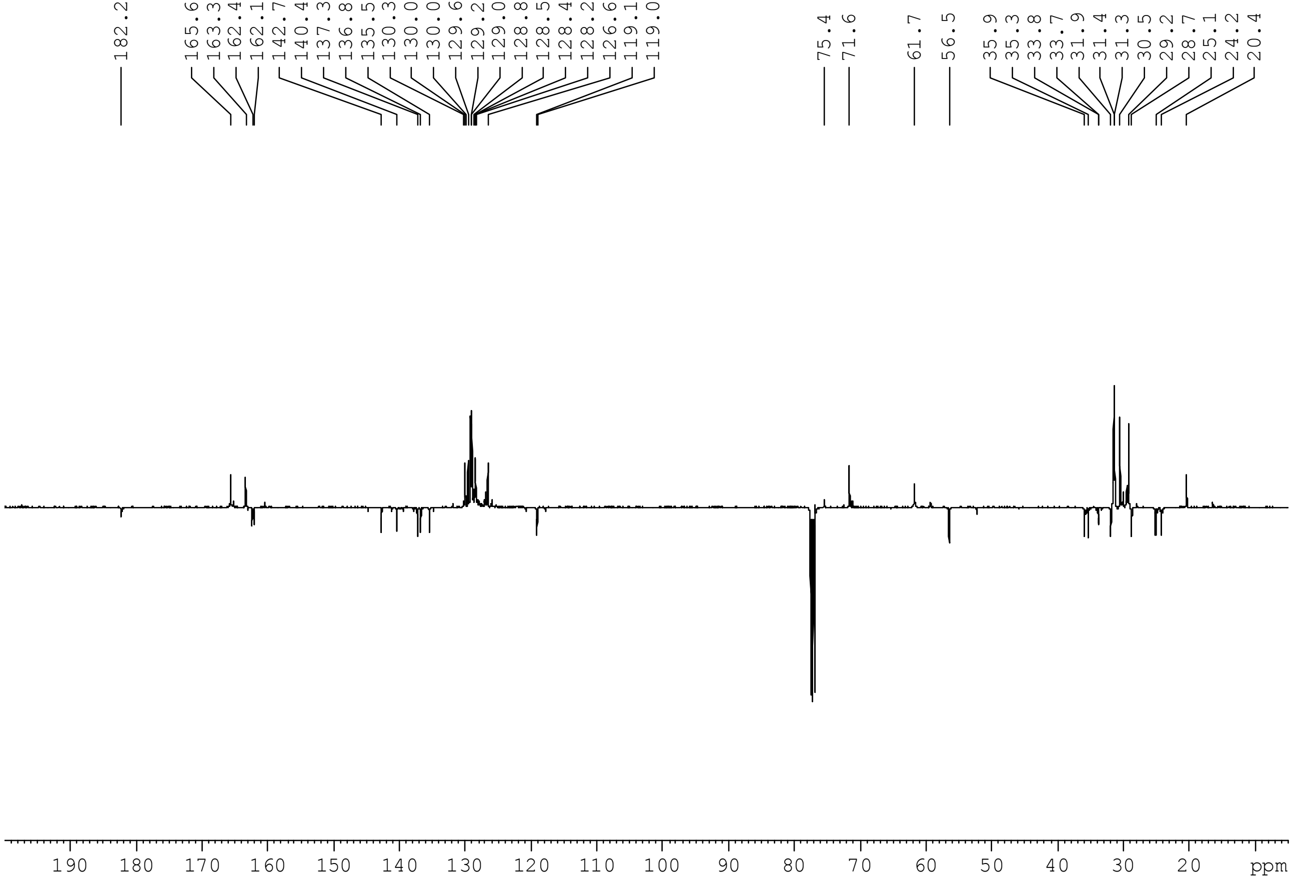


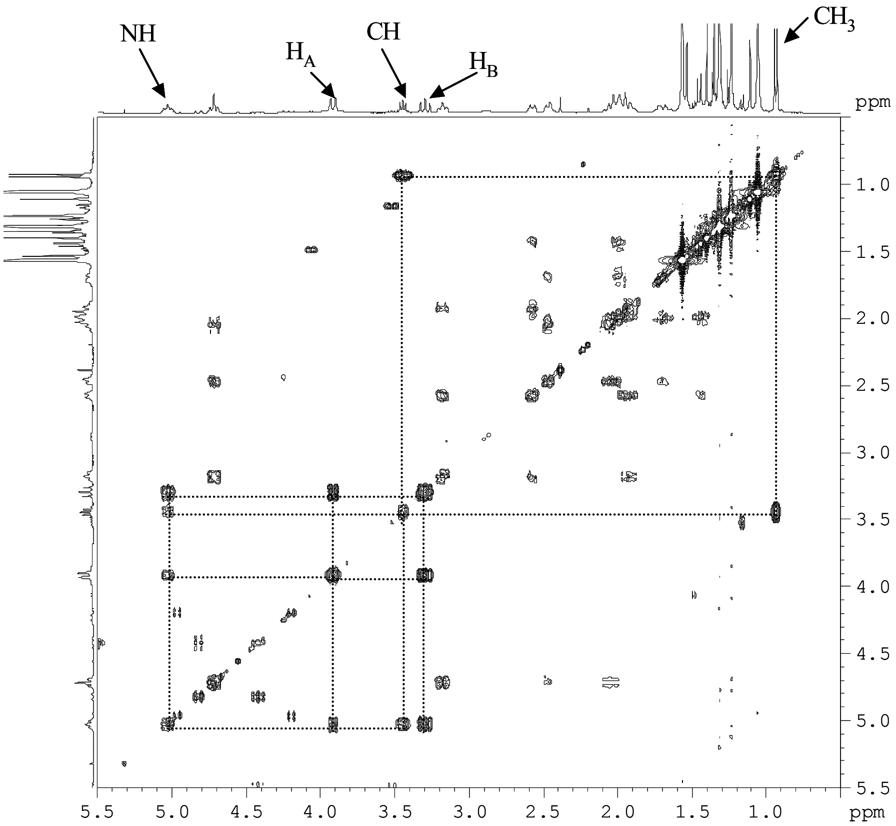
To a solution of the [Co^{III}(**3**)(OAc)] complex (0.025 g, 0.0375 mmol) in dichloromethane (5 mL) at 10°C in a 25 mL round-bottom flask, was added a precooled (10°C) solution of (*S*)-*N*-Bn-Ala (0.067 g, 10 eq, 0.075 mmol) in H_2O (3.75 mL). The biphasic mixture was stirred vigorously for 144 h at 10°C, then transferred to a separating funnel, the organic phase removed and the aqueous phase washed once with dichloromethane (10 mL). The combined dichloromethane extracts were washed once with H_2O (10 mL) before volatiles were removed under reduced pressure to obtain [Co^{III}(**3**)(*S*-*N*-Bn-Ala)] as a green powder. Yield: 0.028 mg (97%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.69 (s, 2H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 2.6 Hz, 1H), 7.38-7.36 (m, 2H), 7.23-7.21 (m, 2H), 7.11 (d, *J* = 2.6 Hz, 1H), 7.00 (d, *J* = 2.2 Hz, 1H), 6.97 (d, *J* = 2.2 Hz, 1H), 5.05-5.00 (m, 1H), 4.74-4.69 (m, 1H), 3.92 (d, *J* = 12.6 Hz, 1H), 3.46-3.42 (m, 1H), 3.29 (dd, J_1 = 12.6 Hz, J_2 = 14.1 Hz, 1H), 3.20-3.15 (m, 1H), 2.62-2.53 (m, 1H), 2.50-2.42 (m, 1H), 2.38 (s, 1H), 2.11-1.82 (m, 5H), 1.56 (s, 9H), 1.31 (s, 9H), 1.23 (s, 9H), 1.05 (s, 9H), 0.93 ppm (d, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 182.2, 165.6, 163.3, 162.4, 162.1, 142.7, 140.4, 137.3, 136.8, 135.5, 130.3, 130.0, 129.6, 129.2, 129.0, 128.8, 128.5, 128.4, 128.2, 126.1, 119.1, 119.0, 75.4, 71.6, 61.7, 56.5, 35.9, 35.3, 33.8, 33.7, 31.9, 31.4, 31.3, 30.5, 29.2, 28.7, 25.1, 24.2, 20.4 ppm. FT-IR (Nujol): υ = 3252, 2921, 1635, 1526, 1458, 1377, 1361, 1321, 1255, 1201, 1168, 1100, 1025, 931, 915 cm^{-1}. HRMS (ESI): calcd. for $C_{46}H_{64}N_3O_4CoNa$ 804.4120 [*M*+Na]$^+$; found: 804.4131.

^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**3**)(*S*-*N*-Bn-Ala)]

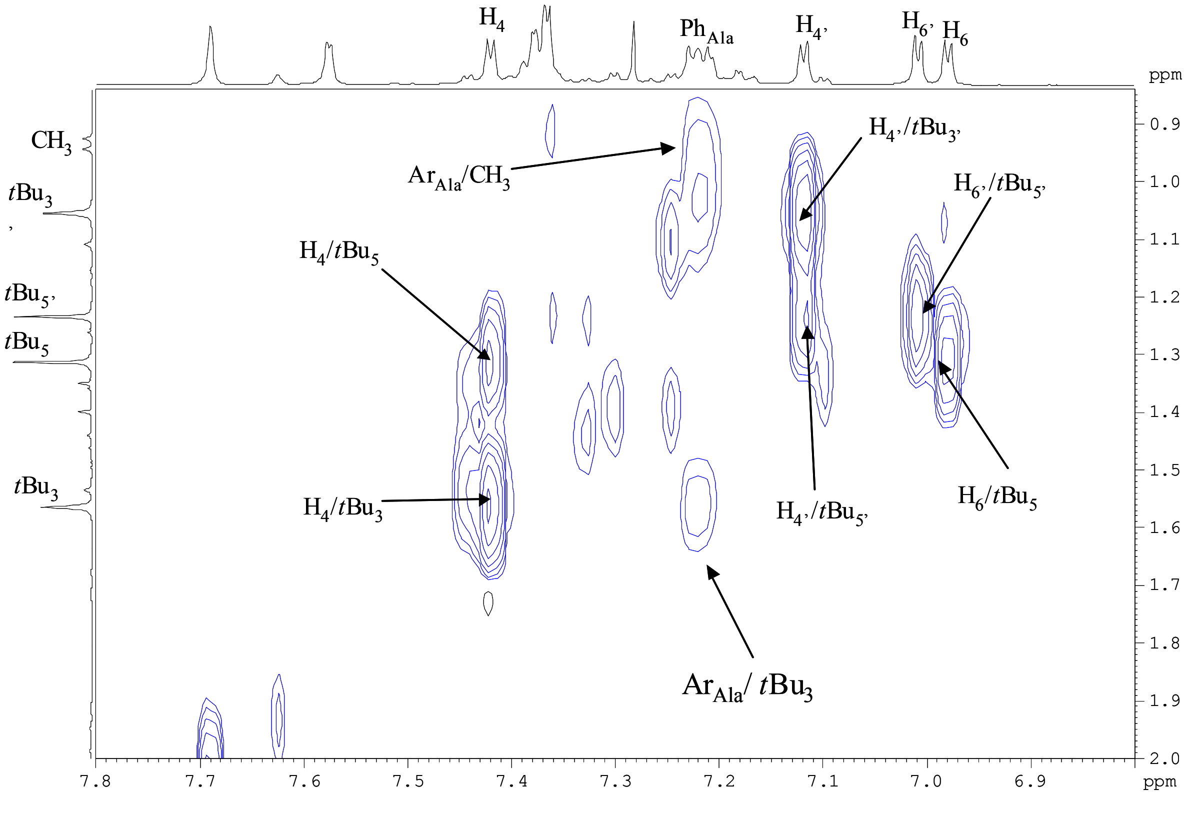


^{13}C-NMR (100 MHz, CDCl$_3$) [Co^{III}(**3**)(*S*-*N*-Bn-Ala)]



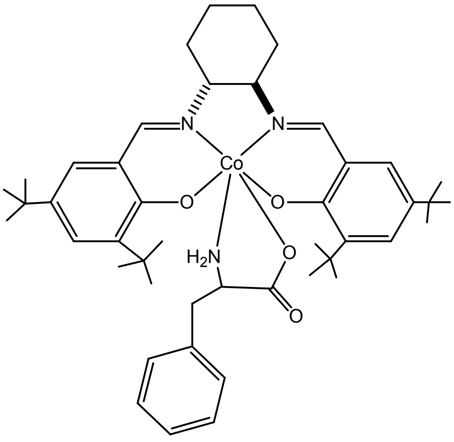


Section of ^{1}H-COSY spectrum of [Co^{III}(**3**)(*S*-*N*-Bn-Ala)] with cross-peaks corresponding to the interactions of the hydrogen atoms of the *S*-*N*-Bn-Ala portion.



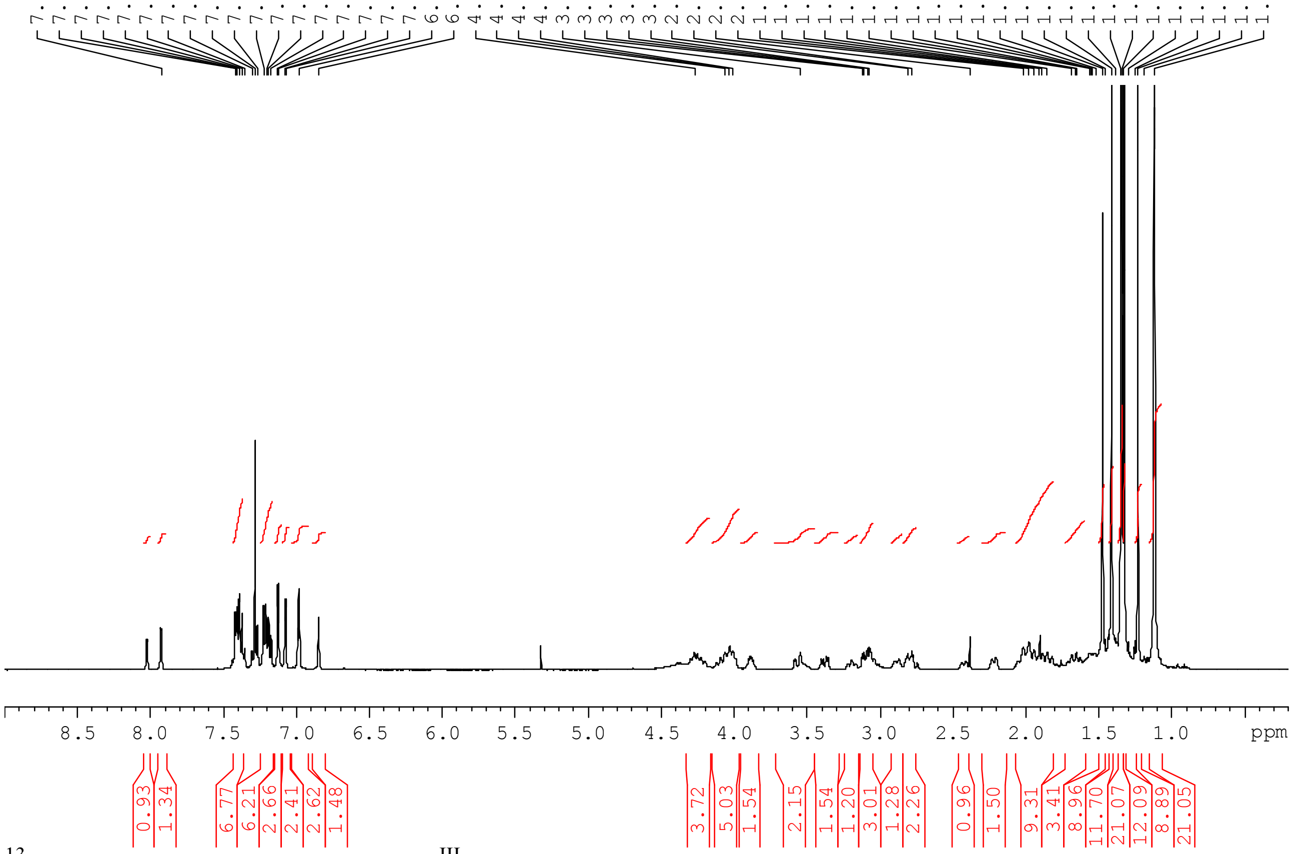
Section of ^{1}H-NOESY spectrum of [Co^{III}(**3**)(*S*-*N*-Bn-Ala)] showing spatial interactions between *t*-butyl groups and the aromatic protons of the salen ligand as well as other NOESY interactions in the complex.

(*R*,*R*)-*N*,*N'*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) Phenylalaninate - [Co^{III}(3)(Phe)]

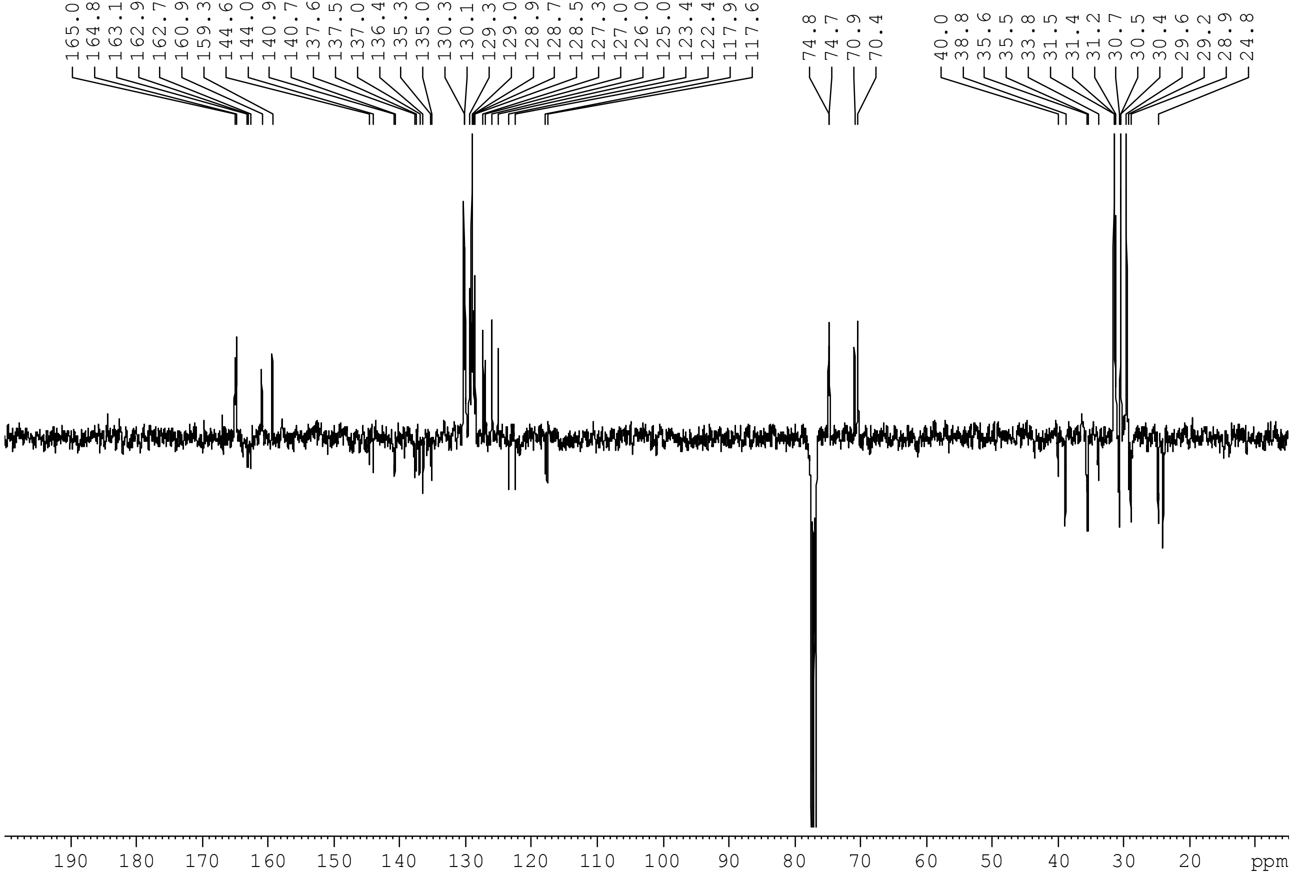


According to method A. Yield: 55.5 mg (97%). ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 8.02 (s, 1H), 7.92 (s, 1H), 7.44-7.33 (m, 6H), 7.23-7.15 (m, 6H), 7.12 (d, *J* = 2.8 Hz, 2H), 7.07 (d, *J* = 2.0 Hz, 2H), 7.00-6.96 (m, 3H), 6.84 (s, 1H), 4.32-4.16 (m, 2H), 4.13-3.96 (m, 4H), 3.93-3.83 (m, 1H), 3.61-3.47 (m, 2H), 3.38 (dd, J_1 = 13.6 Hz, J_2 = 5.6 Hz, 1H), 3.24-3.14 (m, 1H), 3.13-3.04 (m, 1H), 2.92-2.84 (m, 1H), 2.83-2.76 (m, 2H), 2.46-2.40 (m, 1H), 2.26-2.16 (m, 1H), 2.08-1.77 (m, 9H), 1.79.-1.60 (m, 3H), 1.47 (s, 9H), 1.41 (s, 9H), 1.36-1.33 (m, 3H), 1.47 (s, 9H), 1.41 (s, 9H), 1.36-1.32 (m, 18H), 1.32 (s, 9H), 1.23 (s, 9H), 1.13-1.01 (m, 18H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 165.0, 164.8, 163.1, 162.9, 162.7, 160.9, 159.3, 144.6, 144.0, 140.9, 140.7, 137.6, 137.5, 137.0, 136.4, 135.3, 135.0, 130.3, 130.1, 129.3, 129.0, 128.9, 128.7, 128.5, 127.3, 127.0, 126.0, 125.0, 123.4, 122.4, 117.9, 117.6, 74.8, 74.7, 70.9, 70.4, 40.0, 38.8, 35.6, 35.5, 33.8, 31.5, 31.4, 31.2, 30.7, 30.5, 30.4, 29.6, 29.2, 28.9, 24.8 ppm; FT-IR (Nujol): υ = 3324, 2922, 1632, 1526, 1460, 1376, 1255, 1202, 1167, 1096, 834 cm^{-1}. HRMS (ESI): calcd. for $C_{45}H_{62}N_3O_4Na$ 790.3964 [*M*+Na]$^+$; found: 790.3952.

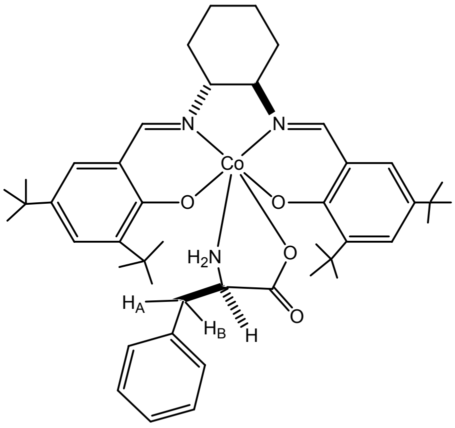
^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**3**)(Phe)] after extraction



^{13}C-NMR (100 MHz, CDCl$_3$) [Co^{III}(**3**)(Phe)] after extraction

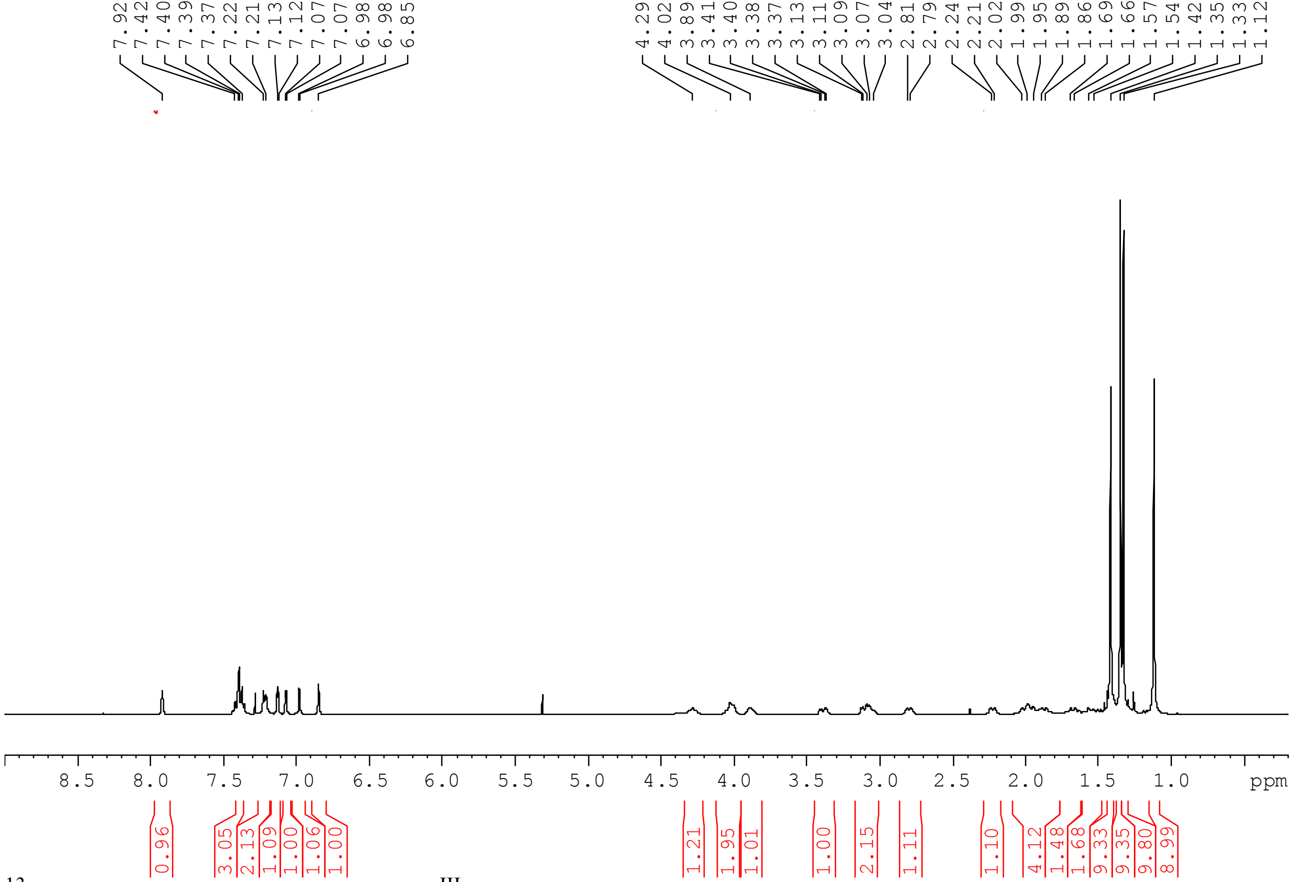


(*R*,*R*)-*N*,*N'*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) (*R*)-Phenylalaninate - [Co^{III}(3)(*R*-Phe)]

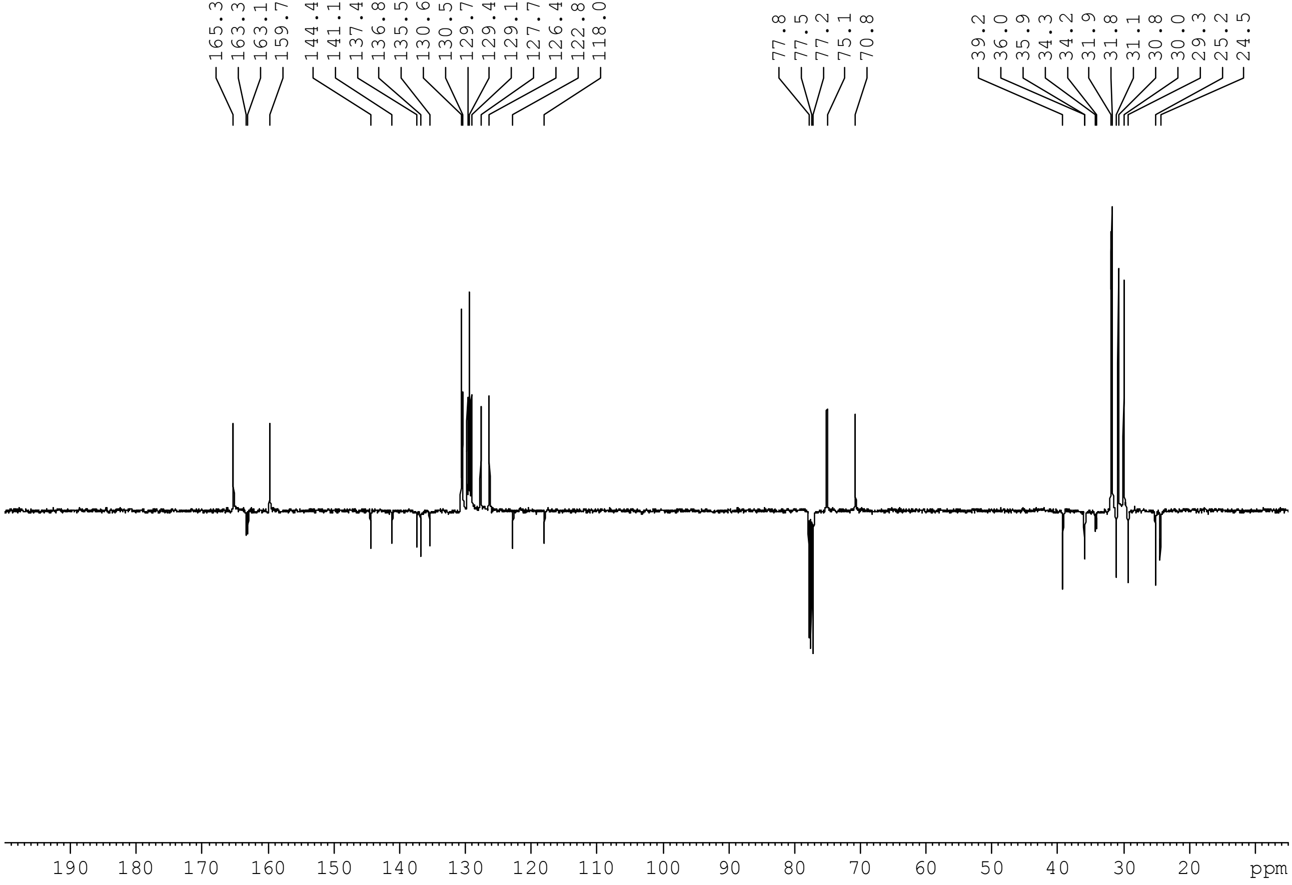


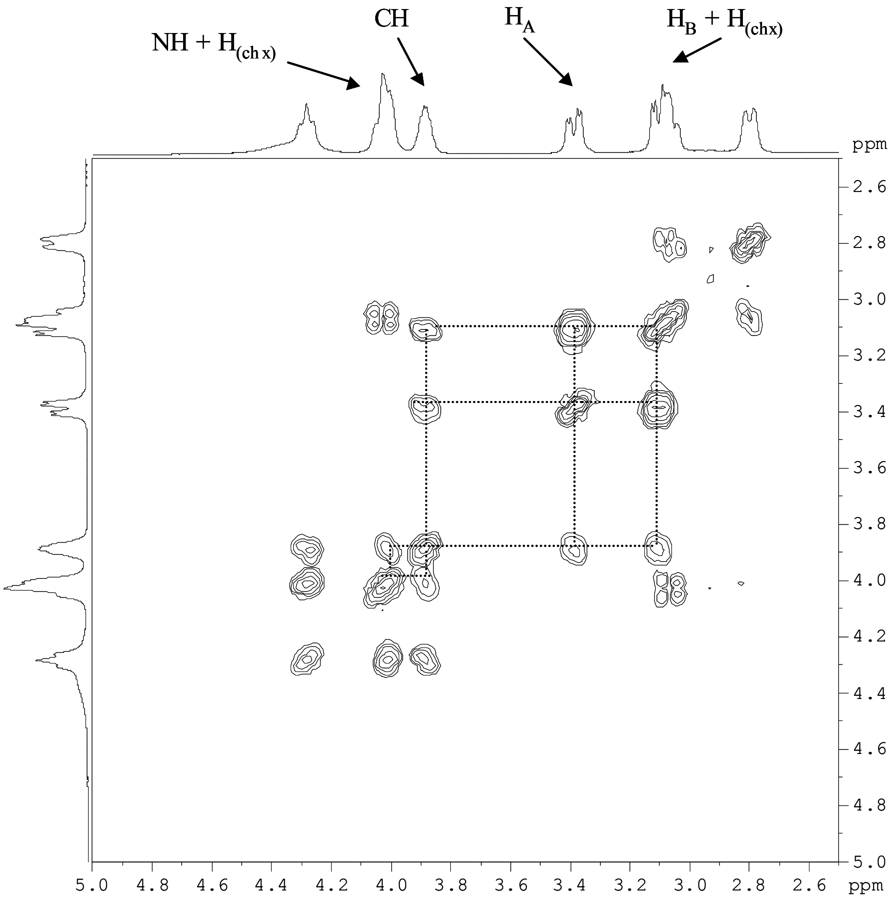
To a solution of the [Co^{III}(**3**)(OAc)] complex (0.025 g, 0.0375 mmol) in dichloromethane (5 mL) at 10°C in a 25 mL round-bottom flask, was added a precooled (10°C) solution of *R*-Phe (0.012 g, 2 eq, 0.075 mmol) in H_2O (3.75 mL). The biphasic mixture was stirred vigorously for 24 h at 10°C, then transferred to a separating funnel, the organic phase removed and the aqueous phase washed once with dichloromethane (10 mL). The combined dichloromethane extracts were washed once with H_2O (10 mL) before volatiles were removed under reduced pressure to obtain [Co^{III}(**3**)(*R*-Phe)] as a green powder. Yield: 0.027 g (95%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 7.42-7.37 (m, 4H), 7.21 (d, J = 6.2 Hz, 2H), 7.12 (d, J = 2.5 Hz, 1H), 7.07 (d, J = 2.5 Hz, 1H), 6.97 (d, J = 2.5 Hz, 1H), 6.84 (s, 1H), 4.32-4.20 (m, 1H), 4.08-3.99 (m, 2H), 3.92-3.83 (m, 1H), 3.38 (dd, J_1 = 13.6 Hz, J_2 = 4.2 Hz, 1H), 3.12-3.04 (m, 2H), 2.79 (d, J = 9.6 Hz, 1H), 2.22 (d, J = 9.6 Hz, 1H), 2.02-1.88 (m, 4H), 1.69-1.64 (m, 1H), 1.57-1.53 (m, 1H), 1.41 (s, 9H), 1.35 (s, 9H), 1.33 (s, 9H), 1.12 ppm (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.3, 163.3, 163.1, 159.7, 144.4, 141.1, 137.4, 136.8, 135.5, 130.6, 130.5, 129.7, 129.4, 129.1, 127.7, 126.4, 122.8, 118.0, 77.8, 77.5, 75.1, 70.8, 39.2, 36.0, 35.9, 34.3, 34.2, 31.9, 31.1, 30.8, 30.0, 29.3, 25.2, 24.5 ppm. FT-IR (Nujol): υ = 3324, 2929, 1628, 1524, 1458, 1375, 1321, 1254, 1202, 1166, 1097, 926 cm^{-1}. HRMS (ESI): calcd. for $C_{45}H_{62}N_3O_4CoNa$ 790.3964 [M+Na]$^+$; found: 790.3941.

^{1}H-NMR (400 MHz, $CDCl_3$) [Co^{III}(**3**)(*R*-Phe)]

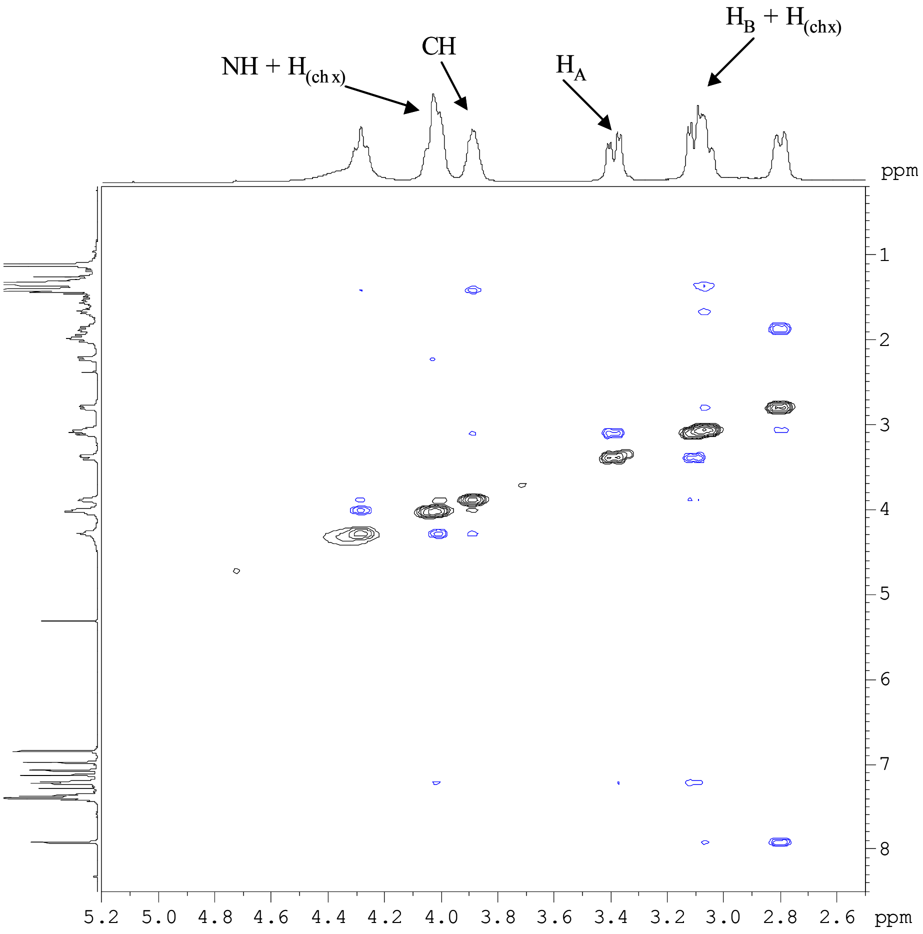


^{13}C-NMR (100 MHz, $CDCl_3$) [Co^{III}(**3**)(*R*-Phe)]



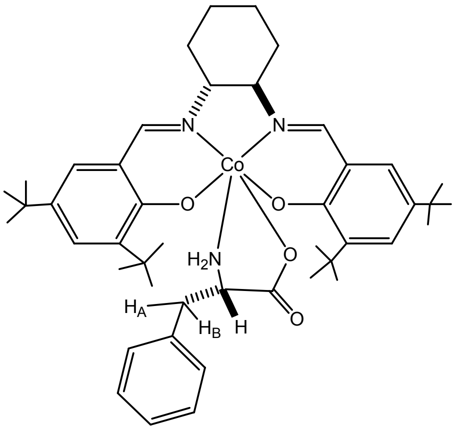


Section of COSY spectra of [Co^{III}(**3**)(*R*-Phe)] with cross signals corresponding to interactions of hydrogen atoms of *R*-Phe.



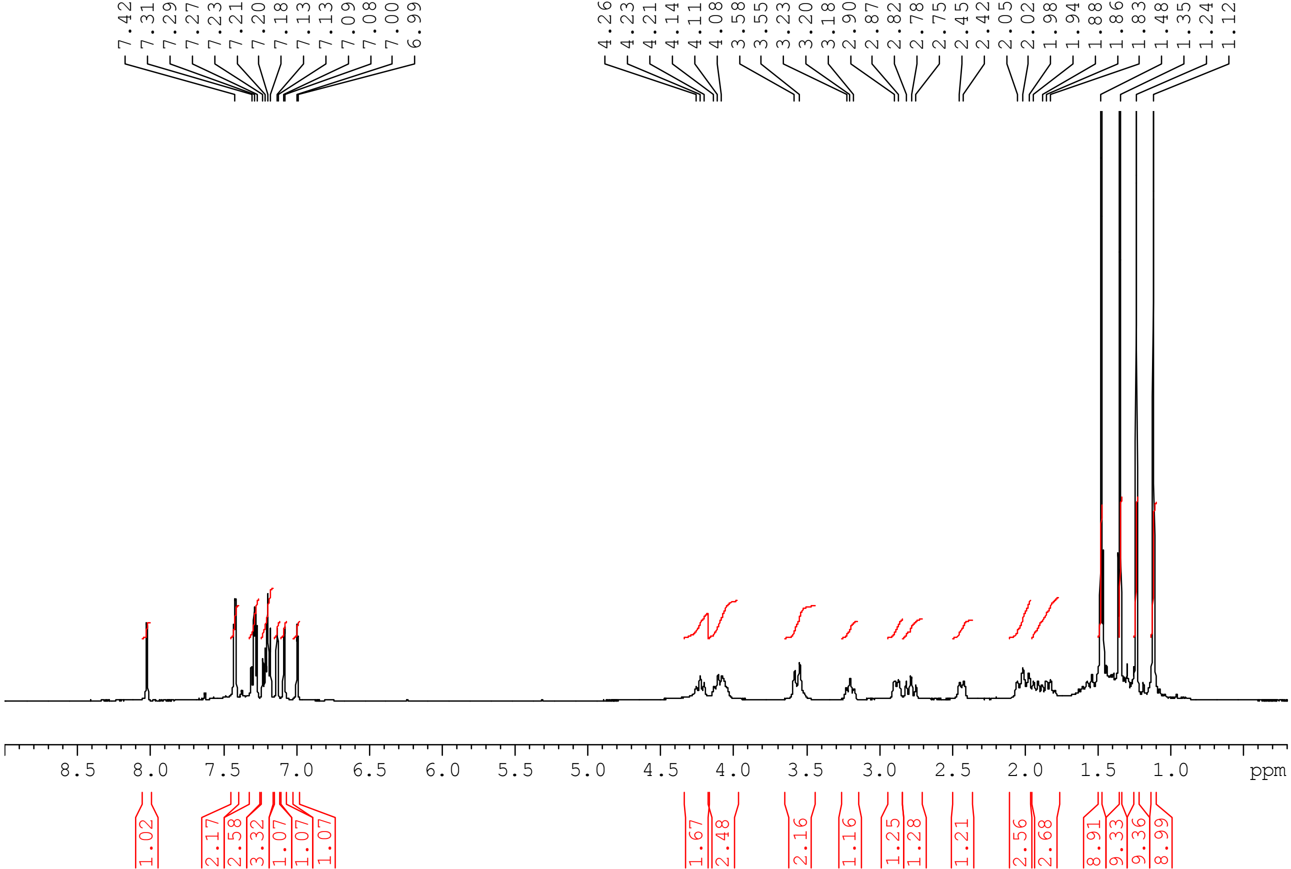
Section of ^{1}H-NOESY spectrum of [Co^{III}(**3**)(*R*-Phe)]. No significant NOESY interactions between *R*-Phe protons and the chiral selector can be observed.

(*R*,*R*)-*N*,*N′*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) (*S*)-Phenylalaninate - [Co^{III}(3)(*S*-Phe)]

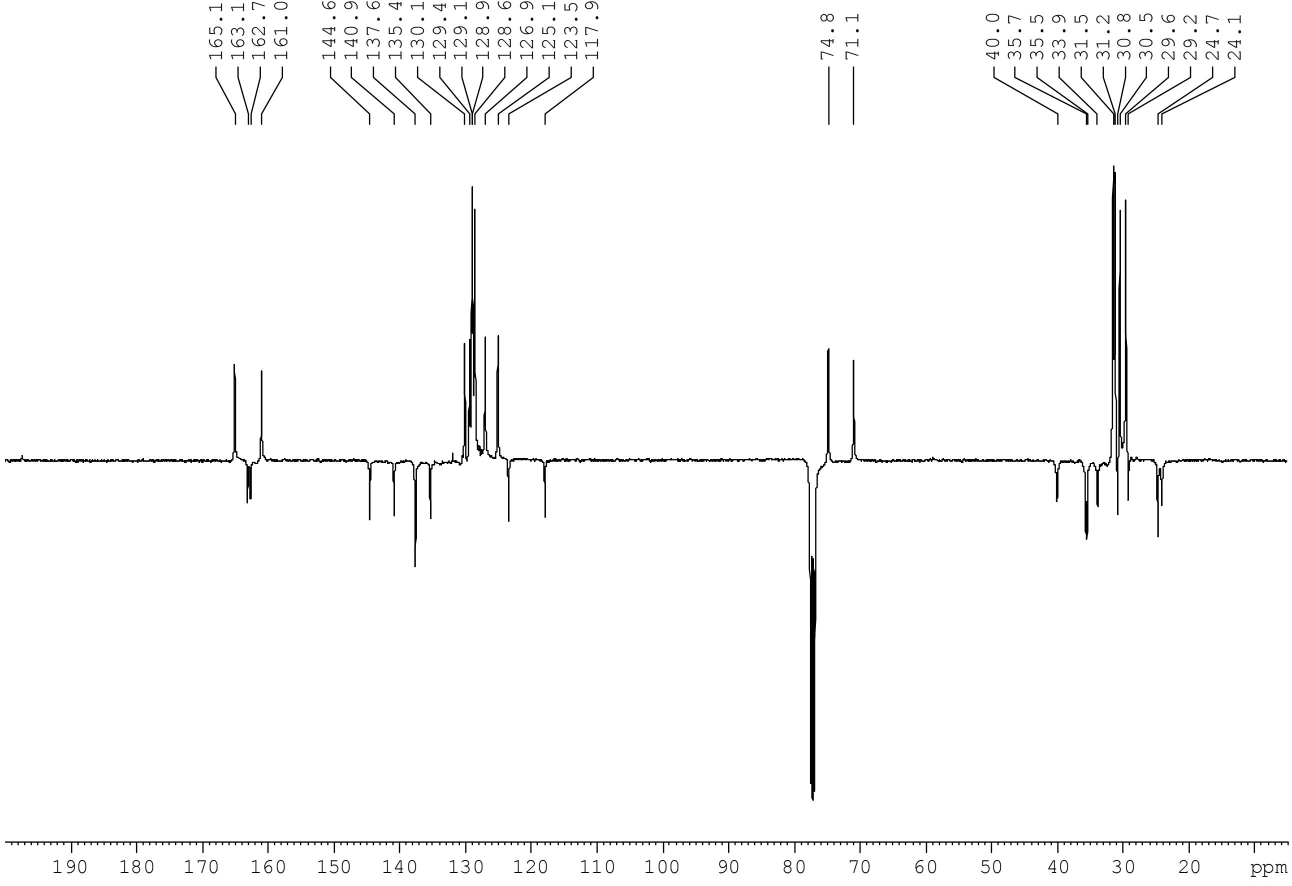


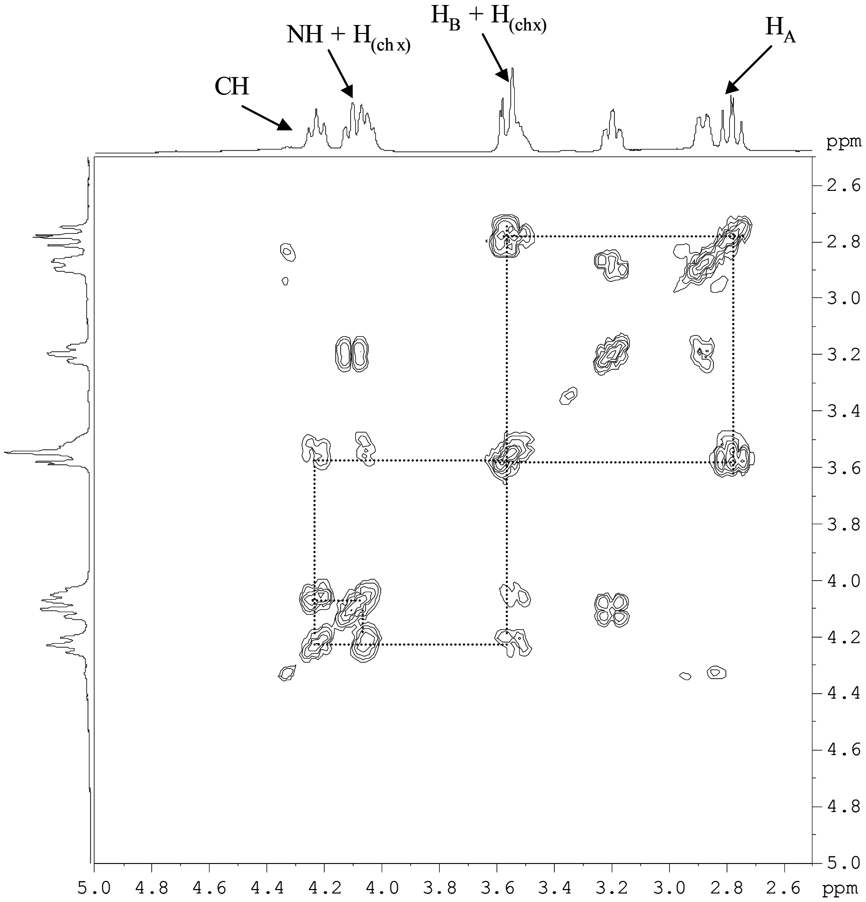
To a solution of the [Co^{III}(**3**)(OAc)] complex (0.025 g, 0.0375 mmol) in dichloromethane (5 mL) at 10°C in a 25 mL round-bottom flask, was added a precooled (10°C) solution of *S*-Phe (0.012 g, 2 eq, 0.075 mmol) in H_2O (3.75 mL). The biphasic mixture was stirred vigorously for 24 h at 10°C, then transferred to a separating funnel, the organic phase removed and the aqueous phase washed once with dichloromethane (10 mL). The combined dichloromethane extracts were washed once with H_2O (10 mL) before volatiles were removed under reduced pressure to obtain [Co^{III}(**3**)(*S*-Phe)] as a green powder. Yield: 0.027 g (94%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.00 (s, 1H), 7.42 (d, *J* = 2.5 Hz, 1H), 7.41 (s, 1H), 7.31-7.15 (m, 5H), 7.12 (d, *J* = 2.5 Hz, 1H), 7.08 (d, *J* = 2.5 Hz, 1H), 6.98 (d, *J* = 2.5 Hz, 1H), 4.25-4.20 (m, 1H), 4.13-4.03 (m, 2H), 3.57-3.53 (m, 2H), 3.22-3.17 (m, 1H), 2.87 (d, *J* = 9.7 Hz, 1H), 2.78 (dd, J_1 = 14.7 Hz, J_2 = 11.5 Hz, 1H), 2.42 (d, *J* = 9.7 Hz, 1H), 2.05-1.79 (m, 6H), 1.48 (s, 9H), 1.39 (s, 9H), 1.23 (s, 9H), 1.12 ppm (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.1, 163.1, 162.7, 161.0, 144.6, 140.9, 137.6, 135.4, 130.1, 129.4, 129.1, 128.8, 128.6, 125.1, 123.5, 117.9, 74.8, 71.1, 40.0, 35.7, 35.5, 33.9, 31.5, 31.2, 30.8, 30.5, 29.6, 29.2, 24.7, 24.1 ppm. FT-IR (Nujol): υ = 3324, 2922, 1636, 1528, 1458, 1376, 1321, 1255, 1204, 1168, 1099, 930 cm^{-1}. HRMS (ESI): calcd. for $C_{45}H_{62}N_3O_4CoNa$ 790.3964 [*M*+Na]$^+$; found: 790.3942.

^{1}H-NMR (400 MHz, $CDCl_3$) [Co^{III}(**3**)(*S*-Phe)]

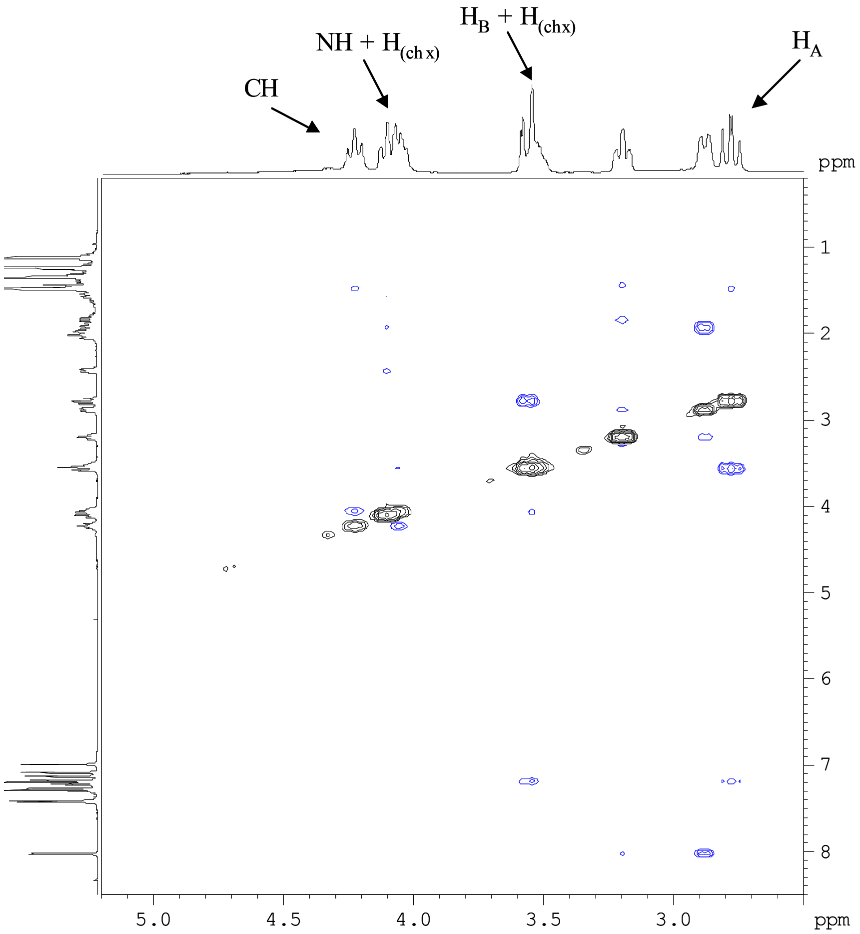


^{13}C-NMR (100 MHz, $CDCl_3$) [Co^{III}(**3**)(*S*-Phe)]



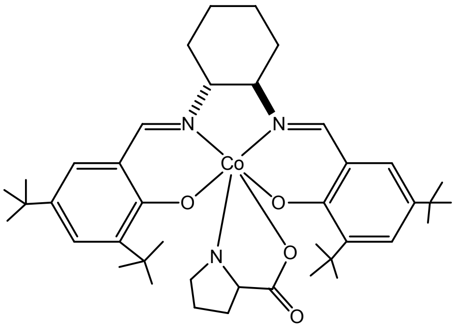


Section of COSY spectra of [Co^{III}(**3**)(*S*-Phe)] with cross signals corresponding to interactions of hydrogen atoms of *S*-Phe.

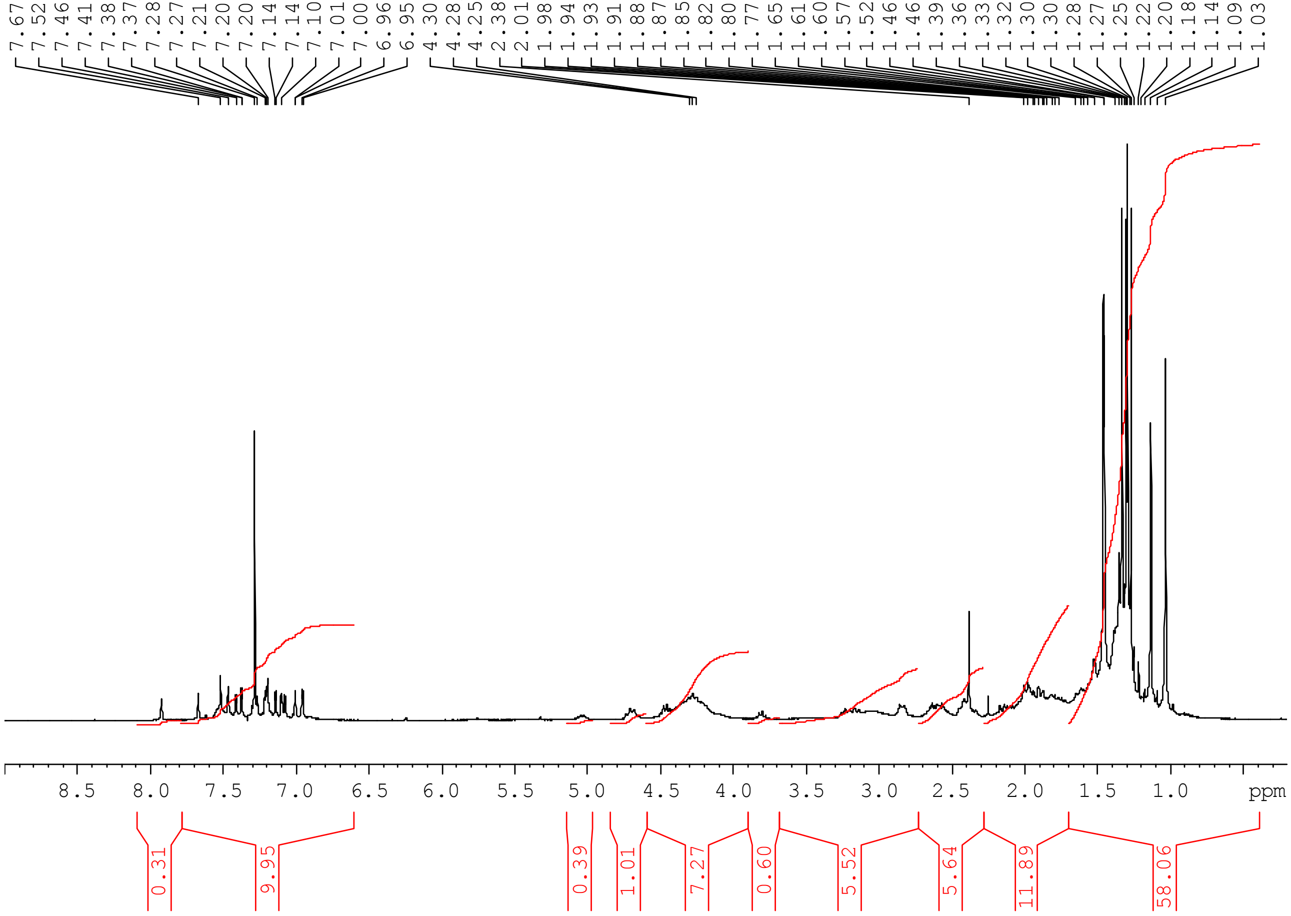


Section of ^{1}H-NOESY spectrum of [Co^{III}(**3**)(*S*-Phe)]. No significant NOESY interactions between *S*-Phe protons and the chiral selector can be observed.

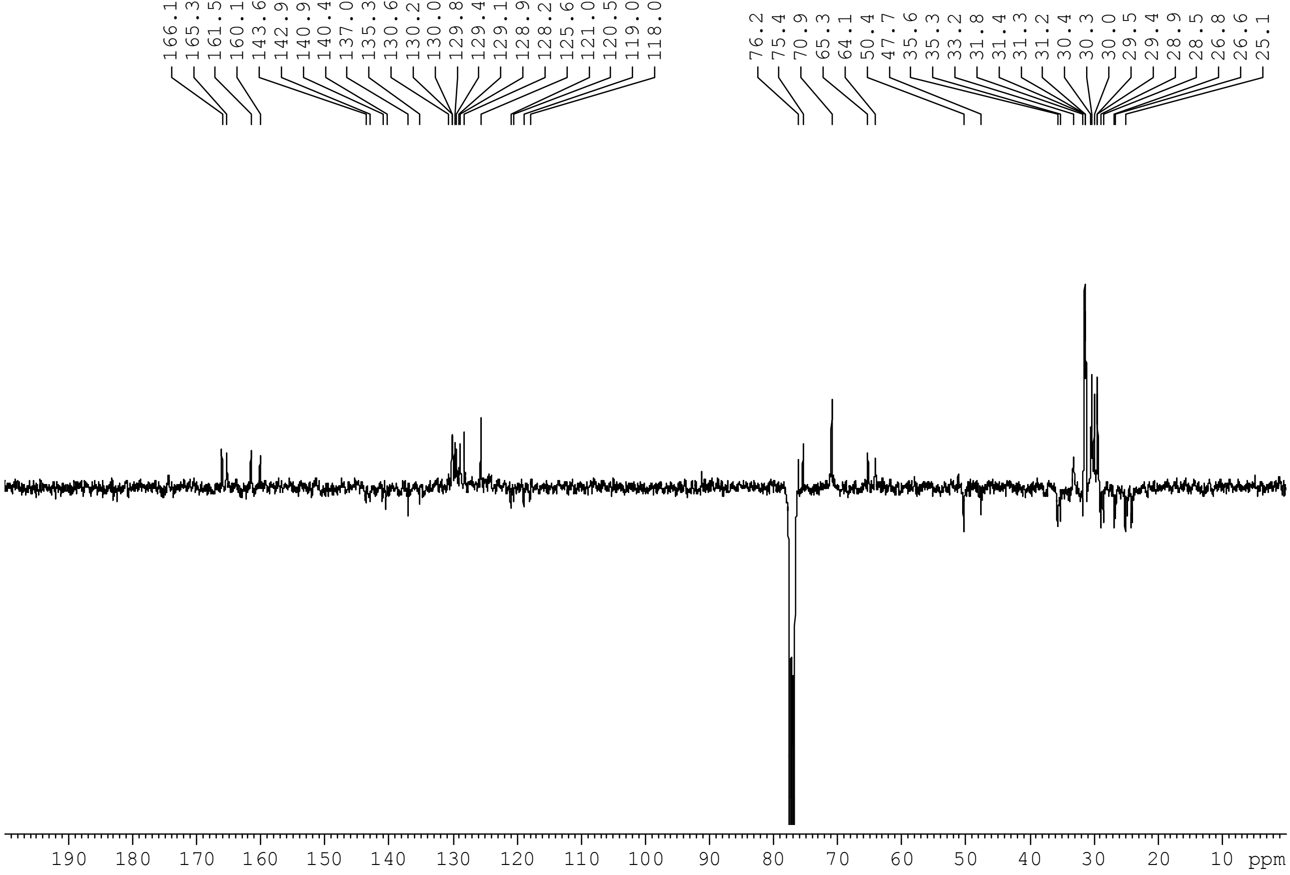
(*R*,*R*)-*N*,*N′*-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) Prolinate - [Co^{III}(3)(Pro)]



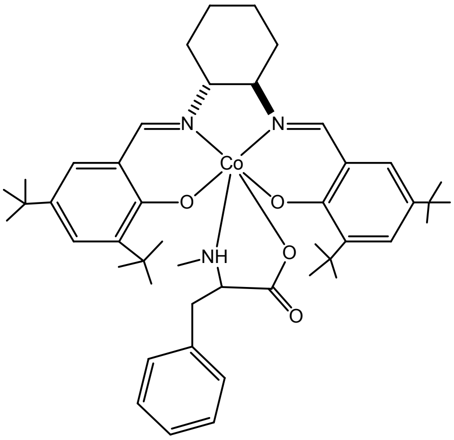
^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**3**)(Pro)] after extraction



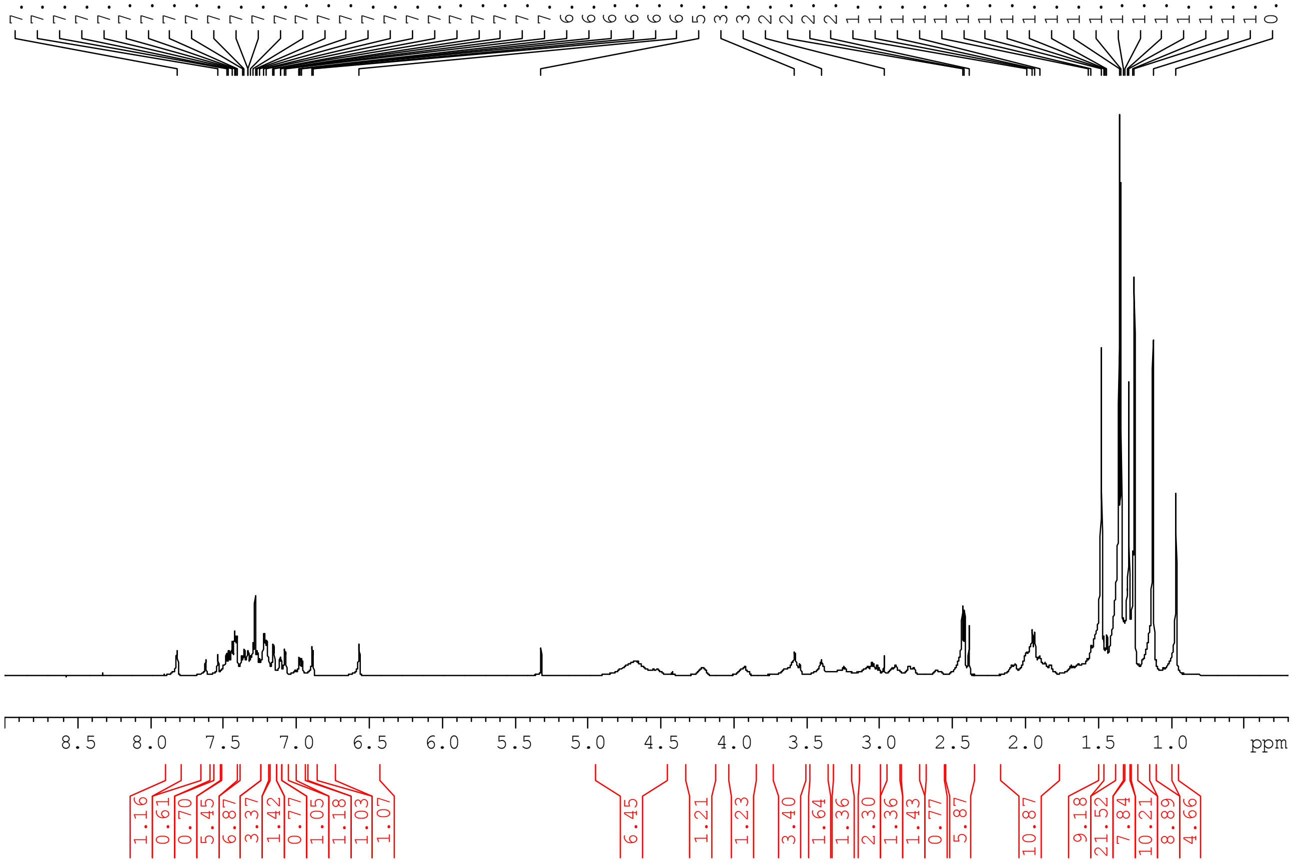
^{13}C-NMR (100 MHz, $CDCl_3$) [Co^{III}(**3**)(Pro)] after extraction



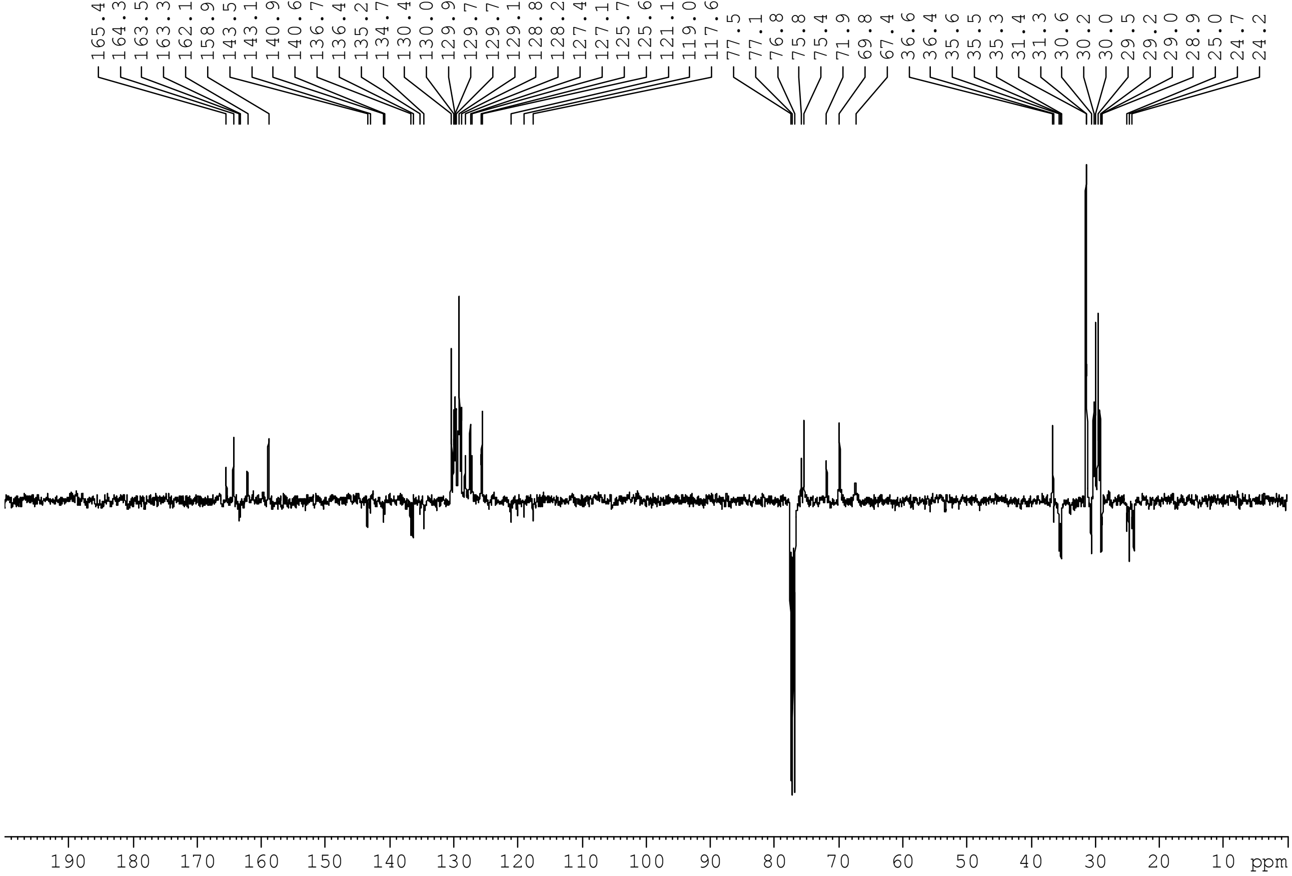
(***R***,***R***)-***N***,***N′***-Bis(3,5-Di-*tert*-Butylsalicylidene)-1,2-Cyclohexanediaminocobalt(III) N-Methylphenylalaninate - [Co^{III}(3)(*N*-MePhe)]



^{1}H-NMR (400 MHz, CDCl$_3$) [Co^{III}(**3**)(*N*-MePhe)] after extraction



^{13}C-NMR (100 MHz, $CDCl_3$) [Co^{III}(**3**)(*N*-MePhe)] after extraction



High resolution mass spectometry HRMS (ESI) data for [Co^{III}(3)(AA)] complexes.

Entry	Substrate (AA)	Product	Expected molecular ion	Found
1	Phe	[Co^{III}(**3**)(Phe)]	790.3964 [M+Na]$^+$	790.3952
2	Pro	[Co^{III}(**3**)(Pro)]	740.3808 [M+Na]$^+$	740.3787
3	*N*-Me-Phe	[Co^{III}(**3**)(*N*-Me-Phe)]	804.4121 [M+Na]$^+$	804.4121
4	*N,N*-Me$_2$-Phe	[Co^{III}(**3**)(*N*-Me$_2$-Phe)]	796.4458 [M+H]$^+$	796.4487
5	*N*-Bn-Phe	[Co^{III}(**3**)(*N*-Bn-Phe)]	880.4434 [M+Na]$^+$	880.4411
6	*N*-Me-Ala	[Co^{III}(**3**)(*N*-Me-Ala)]	728.3808 [M+Na]$^+$	728.3804
7	*N*-Bn-Ala	[Co^{III}(**3**)(*N*-Bn-Ala)]	804.4127 [M+Na]$^+$	804.4147

In the case of the extraction of *N*-benzyl-*N*-methylpenylalanine, *N*,*N*-dimethylalanine, *N*-benzyl-*N*-methylalanine, *N*,*N*-dibenzylalanine the Co^{III} complexes were not formed, as it was confirmed by NMR and HR-MS analysis.

Computational Methods

Creating the model of [Co^{III}(*R,R*-3)(*N*-Bn-Ala)]. The structure was optimized, starting from the X-ray structure of (α-Me-salen)(*S*-*N*-Bn-Ala),[22] using molecular mechanics MM+ in HyperChem.[23] Automatically assigned atomic types were used. The resulting geometry was then systematically modified to obtain eight possible diastereomers, as described below and in the Modelling Studies section of article. The absolute configuration of ligand **3** (*R,R*) and it's coordination mode to cobalt were retained. Modifications consisted of varying (*i*) the *R/S* configuration of the amino acid carbon, (*ii*) the *R/S* configuration of the amino acid nitrogen (nitrogen bound to cobalt cannot change stereochemistry through pyramidal inversion), (*iii*) the coordination mode to cobalt of the amino acid (with the nitrogen and oxygen atoms either facial or meridional), giving a total of 8 diastereomers.

Conformational search. Each diastereomer was subjected to the conformational search using MM+ molecular mechanics in HyperChem.[23] The following three dihedral angles were varied using a conformational search procedure implemented in the program: C(α-aminoacid) – N(aminoacid) – C(benzyl methylene) – C(ipso phenyl), N(aminoacid) – C(benzyl methylene) – C(ipso phenyl) – C(ortho phenyl), and one angle in the cyclohexane ring (with ring constraint). The following settings were used: (*i*) "usage-directed" variation of conformations with the maximum energy criterion of 14 kcal/mol above the lowest; (*ii*) "skip structure", if atoms are closer than 0.5 Å or torsion angles are within 15° of the previous structure; (*iii*) "discard structure", if a chiral center changes; (*iv*) consider structures as a duplicate, if energy varied within 0.07 kcal/mol, torsion angles varied within 7°, RMS error is within 0.3 Å (ignoring hydrogens); (*v*) optimize until gradient falls below 0.01 kcal/(Å mol).

The obtained conformations within 10 kcal/mol range from the lowest energy structure were evaluated and on average seven non-similar conformers were selected by careful visual comparison for further computation.

Ab-initio optimization. Final optimization was performed with the Jaguar software,[24] using the DFT method at the B3LYP[25]/LAV3P* level of theory. This basis set is of double-ζ quality with

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[22] Y. Kushi, T. Tada, Y. Fujii, H. Yoneda, *Bull.Chem.Soc.Jpn.* **1982**, *55*, 1834-1839.

[23] HyperChem(TM) Professional 7.51, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA.

[24] Jaguar, version 6.0, Schrödinger, LLC, New York, NY, 2005.

[25] Becke's three parameter hybrid method using the LYP (C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789) correlation functional: A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

polarization functions on heavy atoms and consists of the 6-31G*[26] basis set for 1st row elements and Hay-Wadt ECP basis set[27] with reduced core on transition metal. A default procedure had serious problem achieving SCF convergence, therefore non-standard options had to be used, namely (*i*) define formal atomic charges on metal center and oxygen atoms in atomic section; (*ii*) construct a high quality initial guess using ligand field theory including d-d repulsion; (*iii*) use fractional occupation number method for thermal smearing during SCF. During this optimization several conformers converged towards the common minimum and these duplicates were removed.

Boltzmann population analysis. Ab-initio electronic energies for all calculated structures were used as the input for population analysis using Boltzmann distribution. Temperature of 283 K was used.

Structure of [$\mathbf{Co^{III}}$(*R,R*-3)(*N*-Bn-Ala)], in meridional N_3O_3, Δ (cobalt), *R* (carbon stereocenter), *S* (nitrogen stereocenter) configuration, depicted in Figure 3, molecule a, in the article. Showed as XYZ file.

```
118
RS3a
O         -0.06820         0.02320         0.38530
O          2.59990        -0.50480         0.00510
N          1.77330         2.18760         0.39460
N          2.73540         1.45070        -1.84430
C          2.80730         3.08800        -0.14810
C          2.77150         2.90670        -1.68980
C         -0.51900         0.56200         1.48610
C         -1.69110         0.02180         2.14460
C         -2.09090         0.58710         3.34640
C         -1.46040         1.68020         3.98950
C         -0.37470         2.21600         3.33700
C          0.09990         1.69490         2.10730
C          1.18030         2.42150         1.51680
C          3.50290        -1.12370        -0.70010
C          4.11770        -2.33780        -0.20800
C          5.00160        -3.00410        -1.04420
C          5.41680        -2.55970        -2.32940
C          4.92400        -1.34010        -2.73890
C          3.98510        -0.61860        -1.95970
C          3.72960         0.75490        -2.29470
H         -2.96430         0.16820         3.83220
H          0.14950         3.07420         3.74800
H          5.42900        -3.93260        -0.68460
```

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[26] a) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **1972,** *56*, 2257-2261; b) P. C. Hariharan and J. A. Pople, *Theo. Chim. Acta* **1973,** *28*, 213-222.

[27] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270-283.

H	5.24830	-0.89150	-3.67380
H	1.50730	3.29280	2.08850
H	4.48170	1.25700	-2.90950
Co	1.30120	0.72370	-0.76520
C	2.68890	4.57530	0.21830
H	2.77910	4.72050	1.30120
H	1.69450	4.93790	-0.07610
C	3.91020	3.67370	-2.36430
H	3.87100	3.53430	-3.45230
H	4.88440	3.29520	-2.02140
H	1.80880	3.28870	-2.04310
H	3.78560	2.71110	0.19210
C	3.78890	5.38900	-0.49000
H	3.65740	6.45410	-0.26400
H	4.76900	5.10280	-0.08070
C	3.79200	5.16770	-2.01100
H	4.61790	5.72380	-2.47100
H	2.86430	5.56890	-2.44250
C	3.82920	-2.84160	1.22280
C	4.26060	-1.75040	2.23580
C	2.32640	-3.15430	1.41580
C	4.61590	-4.12570	1.55700
H	5.33550	-1.54590	2.15330
H	3.71400	-0.81980	2.06790
H	4.05960	-2.08860	3.26030
H	1.99100	-3.91920	0.70350
H	2.15280	-3.54540	2.42650
H	1.71690	-2.25910	1.28720
H	4.39320	-4.42530	2.58750
H	4.33680	-4.96380	0.90640
H	5.70050	-3.98010	1.48550
C	6.40950	-3.40110	-3.14940
C	6.73870	-2.74720	-4.50530
C	7.73190	-3.56470	-2.36080
C	5.80330	-4.79810	-3.42440
H	5.84090	-2.61230	-5.11990
H	7.21880	-1.76920	-4.38110
H	7.43220	-3.38380	-5.06670
H	7.57610	-4.06330	-1.39810
H	8.44970	-4.16590	-2.93320
H	8.19010	-2.58890	-2.16050
H	6.50890	-5.41920	-3.99040
H	5.56200	-5.33000	-2.49750
H	4.88090	-4.71430	-4.01170
C	-2.49310	-1.14430	1.52810
C	-3.73980	-1.51760	2.35820
C	-3.00130	-0.73480	0.12350
C	-1.60540	-2.40950	1.45590
H	-3.48090	-1.87310	3.36280
H	-4.43800	-0.67820	2.45760
H	-4.27510	-2.33080	1.85330
H	-2.18930	-0.37040	-0.50620

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H           -3.74340         0.06850         0.20490
H           -2.13760        -3.22480         0.94770
H           -0.67420        -2.21540         0.92550
H           -1.35200        -2.75450         2.46580
C           -2.01370         2.21880         5.31970
C           -1.98440         1.10020         6.38850
C           -1.18860         3.40710         5.84970
C           -3.47170         2.69870         5.12090
H           -2.58220         0.23290         6.08770
H           -0.95920         0.75350         6.56370
H           -2.38730         1.46680         7.34150
H           -1.19970         4.25380         5.15300
H           -1.60830         3.75760         6.80010
H           -0.14420         3.12740         6.03220
H           -3.88600         3.07790         6.06410
H           -3.51930         3.50520         4.37980
H           -4.12390         1.88980         4.77400
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C           -0.47320         1.50330        -2.70980
O           -1.19760         2.19850        -3.40740
C           -0.14030         0.06600        -3.16990
N            0.78530        -0.60590        -2.20190
C            0.40300         0.06350        -4.60130
H           -0.29350         0.61270        -5.23990
H            1.37620         0.56810        -4.65180
H            0.51500        -0.95690        -4.98170
H           -1.08900        -0.47990        -3.15680
C            0.28720        -1.92300        -1.69940
H            0.94430        -2.20790        -0.87830
H           -0.69880        -1.74780        -1.27600
C            0.24650        -3.00870        -2.75250
C            1.42760        -3.65850        -3.14100
C           -0.96170        -3.39650        -3.34540
C            1.40080        -4.66120        -4.10920
H            2.37070        -3.38810        -2.67000
C           -0.99060        -4.40060        -4.31490
H           -1.88870        -2.91730        -3.03700
C            0.19140        -5.03300        -4.70090
H            2.32310        -5.16160        -4.39440
H           -1.93700        -4.69140        -4.76400
H            0.17010        -5.81790        -5.45280
H            1.67060        -0.78610        -2.67750
```

Structure of [Co^{III}(*R,R*-3)(*N*-Bn-Ala)], in meridional N_3O_3, Δ (cobalt), *S* (carbon stereocenter), *R* (nitrogen stereocenter) configuration, depicted in Figure 3, molecule b, in the article. Showed as XYZ file.

```
118
SR2
O            0.37130        -0.08510         0.36670
```

O	3.07130	0.01170	0.34710
N	1.67390	2.41910	0.18950
N	3.03050	1.66130	-1.81240
C	2.42020	3.50890	-0.46810
C	2.64640	3.07340	-1.93990
C	-0.10090	0.37090	1.49540
C	-1.08430	-0.39080	2.23050
C	-1.48820	0.08530	3.46960
C	-1.04530	1.29130	4.06800
C	-0.17100	2.04940	3.32100
C	0.29980	1.62790	2.05240
C	1.11160	2.57080	1.34120
C	4.26260	-0.33870	-0.05030
C	5.05860	-1.24240	0.74810
C	6.26880	-1.67360	0.22670
C	6.83000	-1.25130	-1.00780
C	6.11990	-0.29990	-1.70660
C	4.85640	0.15870	-1.25880
C	4.26440	1.27730	-1.92540
H	-2.20810	-0.50410	4.02460
H	0.18250	3.00870	3.68870
H	6.84100	-2.38700	0.80790
H	6.50750	0.12120	-2.63030
H	1.23010	3.53920	1.83580
H	4.94190	1.90160	-2.51490
Co	1.67670	0.75090	-0.76380
C	1.77150	4.90060	-0.43060
H	1.63080	5.24250	0.60170
H	0.77650	4.84030	-0.89100
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C	4.34930	-0.47970	3.04710
C	3.23920	-2.49780	1.99900
C	5.58300	-2.63680	2.83160
H	5.28930	0.06920	3.18620
H	3.60690	0.20020	2.62460
H	3.99870	-0.80210	4.03590
H	3.37420	-3.38440	1.36530
H	2.90520	-2.84310	2.98590
H	2.45380	-1.87400	1.57110
H	5.19620	-2.91790	3.81790
H	5.75060	-3.56460	2.27150

H	6.55210	-2.14740	2.98540
C	8.16660	-1.84670	-1.48380
C	8.62220	-1.24130	-2.82520
C	9.27220	-1.57520	-0.43560
C	8.00670	-3.37450	-1.67580
H	7.89140	-1.42210	-3.62240
H	8.78530	-0.15960	-2.74910
H	9.56970	-1.69630	-3.13660
H	9.03280	-2.01650	0.53790
H	10.22770	-2.00210	-0.76610
H	9.41470	-0.49820	-0.28750
H	8.95220	-3.82330	-2.00590
H	7.70900	-3.87300	-0.74690
H	7.24380	-3.59570	-2.43150
C	-1.68630	-1.68790	1.64510
C	-2.76510	-2.30360	2.56080
C	-2.36820	-1.37680	0.28900
C	-0.58640	-2.75950	1.46130
H	-2.36040	-2.60770	3.53360
H	-3.60100	-1.61590	2.73460
H	-3.17350	-3.20150	2.08200
H	-1.67880	-0.89910	-0.40940
H	-2.74780	-2.30120	-0.16590
H	-3.21940	-0.70050	0.43280
H	-1.01300	-3.66820	1.01560
H	0.21790	-2.39690	0.81970
H	-0.14640	-3.03390	2.42740
C	-1.56470	1.69960	5.45700
C	-1.19550	0.60860	6.49030
C	-0.95630	3.03250	5.93310
C	-3.10280	1.86190	5.41250
H	-1.62800	-0.36350	6.22940
H	-0.10820	0.48300	6.55460
H	-1.56640	0.88020	7.48700
H	-1.21710	3.86050	5.26360
H	-1.33940	3.28220	6.92950
H	0.13630	2.97720	6.00230
H	-3.48980	2.14330	6.40030
H	-3.39230	2.64210	4.69870
H	-3.60230	0.93440	5.11210
O	0.30270	1.47130	-1.84750
C	0.10300	0.90880	-3.00930
O	-0.54420	1.41000	-3.91790
C	0.74550	-0.48610	-3.20310
N	1.35930	-0.92480	-1.91570
C	-0.30140	-1.44110	-3.79150
H	1.57060	-0.36010	-3.91510
C	2.43760	-1.94960	-2.02010
H	0.61900	-1.29090	-1.31220
H	-0.77140	-0.93400	-4.63820
H	-1.08450	-1.65720	-3.05410
H	0.13100	-2.38390	-4.12720

C	2.06800	-3.29160	-2.62090
H	3.25370	-1.50080	-2.58940
H	2.79700	-2.10440	-1.00210
C	1.25600	-4.19160	-1.91730
C	2.57590	-3.67780	-3.86670
C	0.93980	-5.43680	-2.45840
H	0.87010	-3.91800	-0.93740
C	2.26600	-4.92590	-4.40950
H	3.21980	-2.99470	-4.41750
C	1.44250	-5.80670	-3.70790
H	0.30640	-6.12280	-1.90160
H	2.66770	-5.20930	-5.37920
H	1.19820	-6.77880	-4.12860

Results of population analysis. Results for meridional N_3O_3, Δ (cobalt) structures and their respective diastereomers. The conformers described in the article are highlighted in green.

carbon stereocenter, nitrogen stereocenter		SCF Energy (Hartree)	Relative energy (J/mol)	Population (%)
R,R	1	-2401.776175	26 542	0.00
	2	-2401.782382	10 246	1.22
	3	-2401.778174	21 295	0.01
	4	-2401.778269	21 045	0.01
	5	-2401.772013	37 469	0.00
	6	-2401.771768	38 113	0.00
	7	-2401.773472	33 638	0.00
R,S	1	*duplicate*	-	0.00
	2	*duplicate*	-	0.00
	3	-2401.786284	0	94.71
	4	-2401.77569	27 816	0.00
	5	-2401.769111	45 090	0.00
	6	-2401.764555	57 051	0.00
	7	-2401.754441	83 605	0.00
S,R	1	-2401.778481	20 489	0.02
	2	-2401.783446	7 451	3.99
	3	-2401.77262	35 875	0.00
	4	-2401.776334	26 125	0.00
	5	-2401.768042	47 896	0.00
	6	-2401.773136	34 522	0.00
	7	-2401.77637	26 030	0.00
S,S	1	-2401.77762	22 748	0.01
	2	-2401.774191	31 752	0.00
	3	-2401.767213	50 072	0.00
	4	-2401.764924	56 082	0.00
	5	-2401.779147	18 738	0.03