Asymmetric C(sp^3)-H/C(Ar) Coupling Reactions. Highly Enantioenriched Indolines via Regiodivergent Reaction of a Racemic Mixture

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Electronic Supplementary Information

Index

1.1 General Techniques and Chemicals:

Chemicals were purchased from Aldrich, Fluka, Acros, Alfa or Aesar and used without further purification.

N-alkyl-2-bromoaniline [1-2] and methyl *N*-alkyl-2-bromophenyl carbamate[3] were prepared by literature procedures. Solvents were purified by filtration on drying columns using a Solvtec© system. Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under nitrogen and glassware was further dried by heating under vacuum as necessary. F.c. (FC): silica gel 60 (40μm). Molecular sieve 4Å was used without activation. Analysis with HPLC was performed using an Agilent 1100 series chromatograph with a JASCO PU–980 pump and Agilent 1100 Series detection system.

^{1}H, ^{13}C-NMR spectra were recorded on Bruker AMX-500, AMX-400 or AMX-300 MHz; δ-in ppm, pattern abbreviation: broad (*brd*), quartet (*q*), quintet (*quint*), multiplet (*m*). Fourier transform (FT) spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per million (ppm) downfield of tetramethylsilane. Infrared spectra were recorded on a Perkin–Elmer Spectrum One photometer. HRMS analyses were measured on a VG analytical 7070E instrument. Optical rotations were measured at 20 ºC on a Perkin Elmer 241 polarimeter using a quartz cell (l = 10 cm) with a Na high-pressure lamp (λ = 589 nm). Melting points were determined on a Büchi M-560 apparatus and are uncorrected.

Starting Materials:

Mesitylene was distilled over CaH_2 under nitrogen. Dry xylenes, benzene, cesium carbonate, cesium pivalate, pivalic acid, molecular sieves 4Å, methyl-, ethyl-, benzyl-chloroformate, alkanone, (L)-(-)- and (D)-(+)- norephedrine and 2-bromoaniline were purchased from Sigma-Aldrich, Fluka, Alfa Aesar or Acros. The substrates **1** and *N*-alkylanilines were prepared by general procedure or previously reported procedure. [1-2]

1.2 Representative procedure 1 (RP1) for *N*-alkyl-2-bromoaniline by reductive amination: [1]

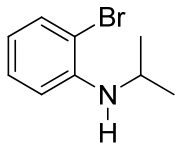
2-Bromoaniline (1.7 g, 10 mmol), molecular sieves 4Å (2.5 g) and alkanone (20-50 mmol, 2-5 equivs.) was dissolved in benzene (50 mL). The reaction mixture was stirred under reflux in a Dean-Stark apparatus for 4 days and then filtered through celite and washed with diethyl ether.

The filtrate was evaporated by rotary evaporator and dried under vacuum. The crude imine product was dissolved in absolute methanol (50 mL) and $NaBH_4$ (1.14 g, 30 mmol, 3 equivs.) was added slowly under nitrogen. The reaction mixture was stirred for 2 hours at room temperature (r.t.). 1N-KOH aq. (50 mL) was added and the mixture was extracted with dichloromethane (3×30 mL). The organic phase was dried over Na_2SO_4. After filtration and evaporation, the residue was purified by f.c.(f.c.) (silica gel; diethyl ether/pentane as eluent) affording *N*-alkyl-o-bromoaniline.

Representative procedure 2 (RP2) for palladium-catalyzed *N*-arylation:[2]

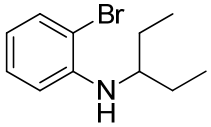
$Pd_2(dba)_3$ **(**2 mol%), *rac*-BINAP (6 mol%), and sodium *tert*-butoxide (1.4 equivs.) were sequentially filled into a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry toluene, amine (1.1 equivs.) and 1,2-dibromobenzene (1 equiv.) was added under nitrogen. The resulting reaction mixture was stirred at 110 °C in a Schlenk tube behind a protection shield for 24 hours. The reaction mixture was cooled to r.t. (r.t) and diluted with ethylacetate followed by filtration through the pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; diethyl ether/pentane as eluent) to afford 2-bromo-*N*-alkylaniline.

2-Bromo-*N*-isopropylaniline: [3]



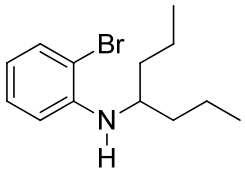
Synthesized by RP1, colorless oil, 26% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.24 (d, J = 6.4, 6H), 3.64 (oct, J = 6.4, 1H), 4.13 (d, J = 6.8 Hz, 1H), 6.51 (td, J = 7.6, 1.6 Hz, 1H), 6.63 (dd, J = 7.6, 1.6Hz, 1H), 7.15 (dd, J = 7.6, 1.6 Hz, 1H), 7.39 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 23.1, 44.5, 110.0, 112.0, 117.4, 128.6, 132.7, 144.4. IR (neat): υ = 736, 1017, 1112, 1153, 1175, 1285, 1318, 1366, 1384, 1425, 1462, 1506, 1595, 2929, 2966, 3405 cm^{-1}; HRMS calcd. for $C_9H_{12}NBr$ 213.0153, found 213.0150.

2-Bromo-*N*-(pentan-3-yl)aniline: [1]



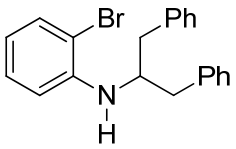
Synthesized by RP1, colorless oil, 32% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.92 (t, J = 7.6 Hz, 3H), 1.44-1.68 (m, 4H), 3.20-3.32 (m, 1H), 4.12 (d, J = 8 Hz, 1H), 6.49 (td, J = 7.6, 1.2 Hz, 1H), 6.60 (dd, J = 8.4, 1.2 Hz, 1H), 7.12 (td, J = 7.4, 1.2 Hz, 1H), 7.39 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 10.3, 26.9, 55.8, 110.0, 111.8, 117.1, 128.6, 132.7, 145.1. IR (neat): υ = 736, 1016, 1163, 1237, 1286, 1321, 1381, 1427, 1459, 1507, 1594, 2875, 2931, 2963, 3410 cm^{-1}; HRMS calcd. for $C_{11}H_{16}NBr$ 241.0466, found 241.0470.

2-Bromo-*N*-(heptan-4-yl)aniline:



Synthesized by RP1, colorless oil, 11% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.91 (t, J = 7.6 Hz, 3H), 1.25-1.50 (m, 8H), 3.32-3.44 (m, 1H), 4.09 (d, J = 8.4 Hz, 1H), 6.48 (td, J = 7.6, 1.6 Hz, 1H), 6.60 (dd, J = 8.4, 1.6 Hz, 1H), 7.12 (td, J = 7.6, 1.6 Hz, 1H), 7.38 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 14.4, 19.3, 37.3, 52.8, 109.9, 111.6, 116.9, 128.6, 132.7, 145.0. MS (ESI, 70 eV): *m/z* (%) = 270 $(M+H)^+$; IR (neat): υ = 1016, 1184, 1114, 1162, 1287, 1030, 1378, 1427, 1458, 1508, 1594, 2870, 2930, 2957, 3406 cm^{-1}; HRMS calcd. for $C_{13}H_{20}BrN$ 270.0851, found 270.0863.

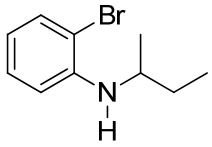
2-Bromo-*N*-(1,3-diphenylpropan-2-yl)aniline:



Synthesized by RP1, colorless oil, 5% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 2.84 (qd, J = 14, 6 Hz, 4H), 3.95 (quint, J = 6 Hz, 1H), 4.25-4.65 (brd, 1H), 6.51 (td, J = 7.6, 1.6 Hz, 1H), 6.67 (dd, J = 8, 1.2 Hz, 1H), 7.13 (dd, J = 7.2, 1.2 Hz, 1H), 7.16-7.24 (m, 6H), 7.25-7.33 (m, 4H), 7.38 (dd, J = 7.6, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 39.9, 55.3, 110.4, 111.8, 117.7, 126.7, 128.6, 128.7, 129.7, 132.8, 138.4, 144.0. MS (ESI, 70 eV): *m/z* (%) = 366 $(M+H)^+$; IR

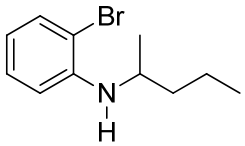
(neat): υ = 737, 1017, 1088, 1126, 1286, 1320, 1429, 1454, 1495, 1594, 2922, 3026, 3062, 3400 cm^{-1}; HRMS calcd. for $C_{12}H_{16}NBr$ 366.0851, found 366.0849

2-Bromo-*N*-(sec-butyl)aniline: [3]



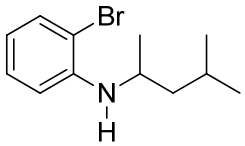
Synthesized by RP1, colorless oil, 66% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.95 (t, *J* = 7.6 Hz, 1H), 1.20 (t, *J* = 6.4 Hz, 1H), 1.45-1.67 (m, 2H), 3.32-3.47 (m, 1H), 4.13 (d, *J* = 6.8 Hz, 1H), 6.50 (td, *J* = 8, 1.6 Hz, 1H), 6.61 (dd, *J* = 8, 0.8 Hz, 1H), 7.14 (td, *J* = 7.6, 0.8 Hz, 1H), 7.39 (dd, *J* = 8, 1.6 Hz, 1H).

2-Bromo-*N*-(pentan-2-yl)aniline:



Synthesized by RP1, colorless oil, 45% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.91 (t, *J* =7.2 Hz, 1H), 1.19 (d, *J* = 6.4 Hz, 1H), 1.31-1.65 (m, 4H), 3.40-3.56 (m, 1H), 3.95-4.35 (brd, 1H), 6.50 (td, *J* = 7.6, 1.6 Hz, 1H), 6.61 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.13 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.39 (dd, *J* = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 14.3, 19.5, 20.9, 39.4, 48.6, 110.0, 111.8, 117.3, 128.6, 132.7, 144.6. MS (ESI, 70 eV): *m/z* (%) = 242 $(M+H)^+$; IR (neat): υ = 739, 1018, 1048, 1112, 1166, 1286, 1321, 1378, 1426, 1459, 1508, 1595, 2871, 2930, 2960, 3408 cm^{-1}; ESI-HRMS calcd. for $C_{11}H_{17}BrN$ 242.0538, found 242.0534.

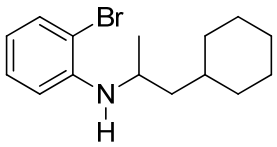
2-Bromo-*N*-(4-methylpentan-2-yl)aniline:



Synthesized by RP2, Colorless oil, 59% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.92 (t, *J* = 7.2 Hz, 1H), 1.19 (d, *J* = 6, Hz, 3H), 1.31-1.65 (m, 4H), 3.40-3.55 (m, 1H), 3.90-4.40 (brd, 1H),

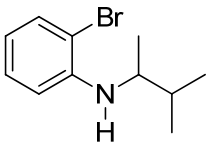
6.50 (td, J = 7.6, 1.6 Hz, 1H), 6.61 (dd, J = 8.4, 1.6 Hz, 1H), 7.13 (dd, J = 7.6, 1.6 Hz, 1H), 7.39 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 21.2, 22.8, 23.1, 25.3, 46.9, 46.9, 110.0, 111.7, 117.2, 128.6, 132.7, 144.6. MS (EI, 70 eV): m/z (%) = 255 $(M)^+$; IR (neat): υ = 737, 1017, 1114, 1166, 1287, 1320, 1367, 1425, 1459, 1507, 1594, 2869, 2926, 2957, 3407 cm^{-1}; EI-HRMS calcd. for $C_{12}H_{18}BrN$ 255.0623, found 255.0621.

2-bromo-*N*-(1-cyclohexylpropan-2-yl)aniline:



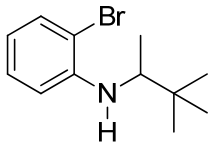
Synthesized by RP1, colorless oil, 17% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.82-1.03 (m, 2H), 1.06-1.56 (m, 6H), 1.18 (d, J = 6.4, Hz, 3H), 1.57-1.81 (m, 5H), 3.50-3.64 (m, 1H), 3.92-4.30 (brd, 1H), 6.50 (td, J = 7.6, 1.2 Hz, 1H), 6.62 (dd, J = 8, 1.2 Hz, 1H), 7.14 (d, J = 7.8, 1.2 Hz, 1H), 7.39 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 26.5, 26.8, 33.6, 33.8, 34.8, 45.4, 46.2, 110.1, 111.8, 117.2, 128.6, 132.7, 144.6. IR (neat): υ = 736, 1017, 1162, 1212, 1242, 1286, 1320, 1377, 1425, 1448, 1507, 1595, 2848, 2920, 3409 cm^{-1}; ESI-HRMS calcd. for $C_{15}H_{23}BrN$ 296.1008, found 296.1014.

2-Bromo-*N*-(3-methylbutan-2-yl)aniline:



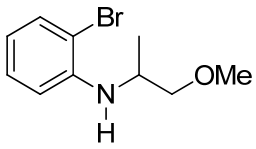
Synthesized by RP2, colorless oil, 62% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.93 (d, J = 6.8 Hz,, 3H), 0.99 (d, J = 7.2 Hz, 3H), 1.13 (d, J = 6.4 Hz, 3H), 3.31-3.42 (m, 1H), 4.00-4.45 (brd, 1H), 6.49 (td, J = 7.2, 1.2 Hz, 1H), 6.61 (dd, J = 8, 1.6 Hz, 1H), 7.13 (td, J = 8, 1.6 Hz, 1H), 7.39 (dd, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 16.8, 17.9, 19.2, 32.4, 53.8, 110.1, 111.9, 117.1, 128.6, 132.7, 144.7. IR (neat): υ = 736, 1016, 1107, 1163, 1242, 1284, 1322, 1388, 1373, 1427, 1458, 1506, 1594, 2873, 2961, 3412 cm^{-1}; EI-HRMS calcd. for $C_{11}H_{16}BrN$ 241.0466, found 241.0467.

2-Bromo-*N*-(3,3-dimethylbutan-2-yl)aniline:



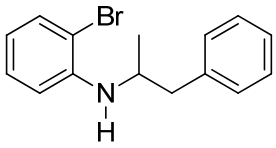
Synthesized by RP2, colorless oil, 55% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.98 (s, 9H), 1.11 (d, J = 6.4 Hz, 3H), 3.19-3.32 (m, 1H), 4.26 (d, J = 7.2 Hz, 1H), 6.48 (td, J = 8, 1.6 Hz, 1H), 6.63 (dd, J = 8, 0.8 Hz, 1H), 7.13 (td, J = 8, 1.6 Hz, 1H), 7.38 (dd, J = 7.6, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 16.0, 27.0, 35.1, 57.5, 110.2, 111.7, 117.2, 128.7, 132.7, 145.2. IR (neat): υ = 735, 1016, 1106, 1140, 1285, 1321, 1373, 1396, 1427, 1459, 1509, 1592, 2870, 2963, 3412 cm^{-1}; EI-HRMS calcd. for $C_{12}H_{18}BrN$ 255.0623, found 255.0624.

2-Bromo-*N*-(1-methoxypropan-2-yl)aniline:



Synthesized by RP2, colorless oil, 58% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.25 (d, J = 6.4 Hz, 3H), 3.38 (s, 3H), 3.42 (qd, J = 9.6, 4.8 Hz, 2H), 3.61-3.73 (m, 1H), 4.15-4.85 (brd, 1H), 6.53 (td, J = 8, 1.6 Hz, 1H), 6.67 (dd, J = 8, 1.2 Hz, 1H), 7.14 (td, J = 7.6, 1.6 Hz, 1H), 7.40 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 M5Hz): δ = 18.2, 48.7, 59.4, 110.4, 112.1, 117.9, 128.6, 132.8, 144.4. IR (neat): υ = 738, 922, 986, 1018, 1100, 1166, 1198, 1239, 1284, 1319, 1369, 1388, 1428, 1457, 1504, 1595, 2829, 2879, 2926, 2977, 3403 cm^{-1}; ESI-HRMS calcd. for $C_{10}H_{15}BrNO$ 244.0331, found 244.0327.

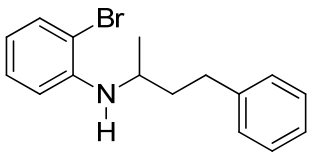
2-Bromo-*N*-(1-phenylpropan-2-yl)aniline:



Synthesized by RP1, colorless oil, 47% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.20 (d, J = 6.4 Hz, 3H), 2.71 (qd, J = 13.2, 4.8 Hz, 2H), 3.72-3.86 (m, 1H), 4.10-4.42 (brd, 1H), 6.54 (td, J = 7.6, 1.2 Hz, 1H), 6.70 (dd, J = 8.4, 1.6 Hz, 1H), 7.13-7.26 (m, 4H), 7.26-7.34 (m, 2H), 7.42 (dd, J = 7.6, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 20.3, 42.5, 49.8, 110.2, 112.0, 117.7, 126.6, 128.6, 128.7, 129.7, 132.8, 138.4, 144.1. IR (neat): υ = 737, 1016, 1046, 1112, 1151,

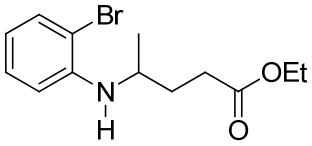
1201, 1245, 1283, 1319, 1377, 1427, 1453, 1498, 1594, 2926, 2967, 3026, 3063, 3401 cm^{-1}; EI-HRMS calcd. for $C_{15}H_{16}BrN$ 289.0466, found 289.0462.

2-Bromo-*N*-(4-phenylbutan-2-yl)aniline: [4]



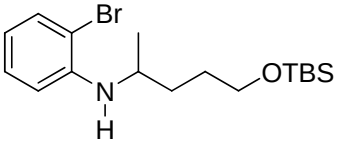
Synthesized by RP1, colorless oil, 43% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.26 (d, J = 6.4 Hz, 3H), 1.76-2.00 (m, 2H), 2.73 (t, J = 8 Hz, 2H), 3.44-3.58 (m, 1H), 4.02-4.30 (brd, 1H), 6.48-6.56 (m, 2H), 7.12 (td, J = 7.6, 1.6 Hz, 1H), 7.15-7.22 (m, 3H), 7.25-7.32 (m, 2H), 7.41 (dd, J = 8.4, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 21.0, 32.6, 38.9, 48.2, 110.1, 112.0, 117.5, 126.1, 128.6, 132.7, 141.9, 144.3. IR (neat): υ = 740, 1017, 1061, 1094, 1161, 1190, 1286, 1320, 1378, 1426, 1457, 1506, 1595, 2926, 2965, 3026, 3062, 3403 cm^{-1}; EI-HRMS calcd. for $C_{16}H_{18}BrN$ 303.0623, found 303.0620.

Ethyl 4-((2-bromophenyl)amino)pentanoate:



Synthesized by RP1, colorless oil, 8% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 1.22 (t, J = 7.2 Hz, 3H), 1.22 d, J = 6.4 Hz, 3H), 1.78-2.00 (m, 2H), 2.41 (t, J = 7.6 Hz, 2H), 4.11 (q, J = 7.2 Hz, 1H), 4.11 (brd, 1H), 6.52 (td, J = 8, 1.2 Hz, 1H), 6.64 (dd, J = 8.4, 1.2 Hz, 1H), 7.14 (d, J = 7.8, 1.2 Hz, 1H), 7.39 (dd, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 14.4, 20.9, 31.2, 31.9, 48.4, 60.7, 110.2, 112.0, 117.7, 128.7, 132.8, 144.3, 173.7. IR (neat): υ = 739, 1017, 1095, 1119, 1178, 1215, 1258, 1320, 1375, 1428, 1460, 1506, 1595, 1729, 2972, 3383 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{19}BrNO_2$ 300.0593, found 300.0597.

2-Bromo-*N*-(5-((tert-butyldimethylsilyl)oxy)pentan-2-yl)aniline:

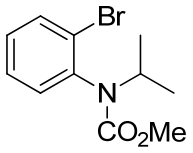


Synthesized by RP1, colorless oil, 50% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.03 (s, 3H), 0.03 (s, 3H), 0.87 (s, 9H), 1.21 (d, J = 6.4 Hz, 3H), 3.44-3.56 (m, 1H), 3.62 (t, J = 6 Hz, 2H), 3.98-4.32 (brd, 1H), 6.50 (td, J = 8, 1.6 Hz, 1H), 6.61 (dd, J = 8, 1.2 Hz, 1H), 7.13 (td, J = 7.6, 1.6 Hz, 1H), 7.38 (dd, J = 7.6, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = -5.1, 18.6, 21.0, 26.2, 29.5, 33.4, 48.7, 63.2, 110.0, 111.9, 117.3, 128.6, 132.7, 144.5. IR (neat): υ = 737, 833, 939, 1017, 1092, 1206, 1252, 1285, 1321, 1381, 1427, 1460, 1508, 1596, 2857, 2929, 3409 cm^{-1}; ESI-HRMS calcd. for $C_{17}H_{31}BrNOSi$ 372.1335, found 372.1336.

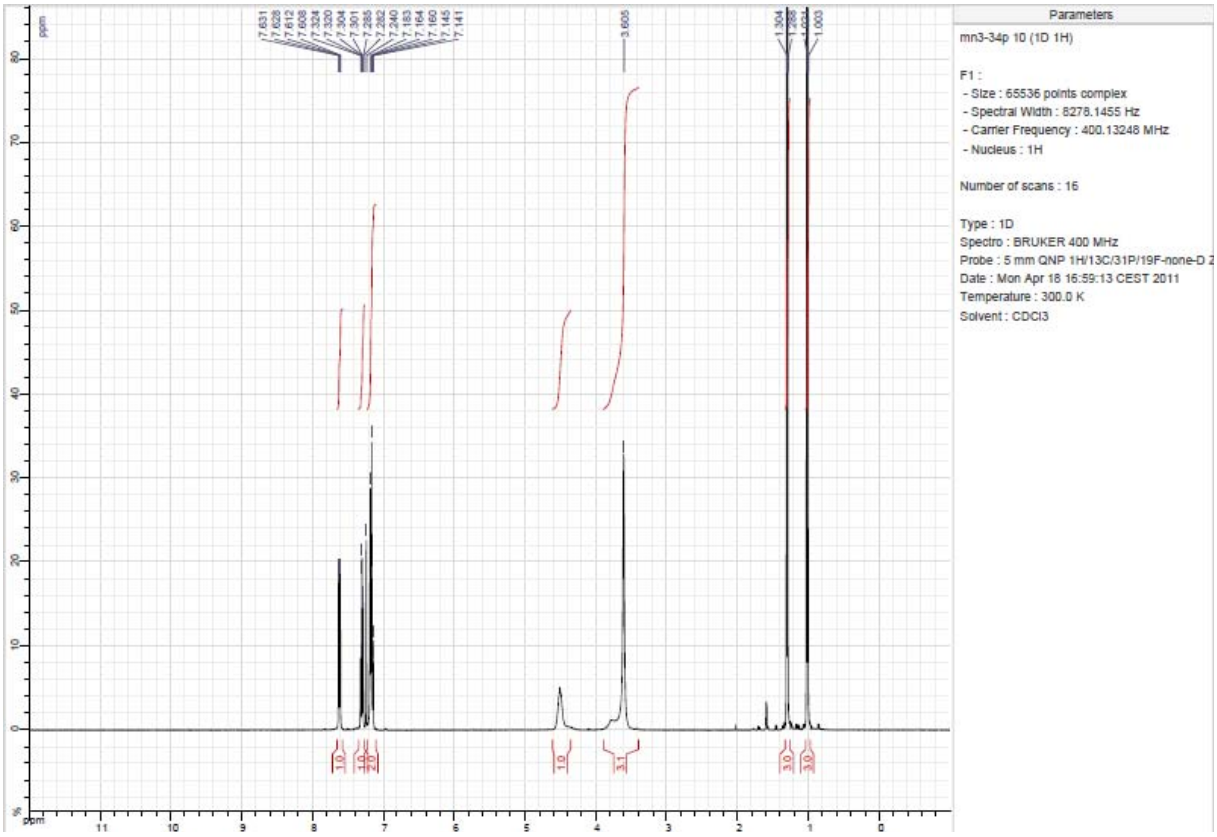
1.3 Representative synthesis of methyl *N*-cycloalkyl-2-bromophenylcarbamate 1 and 6:

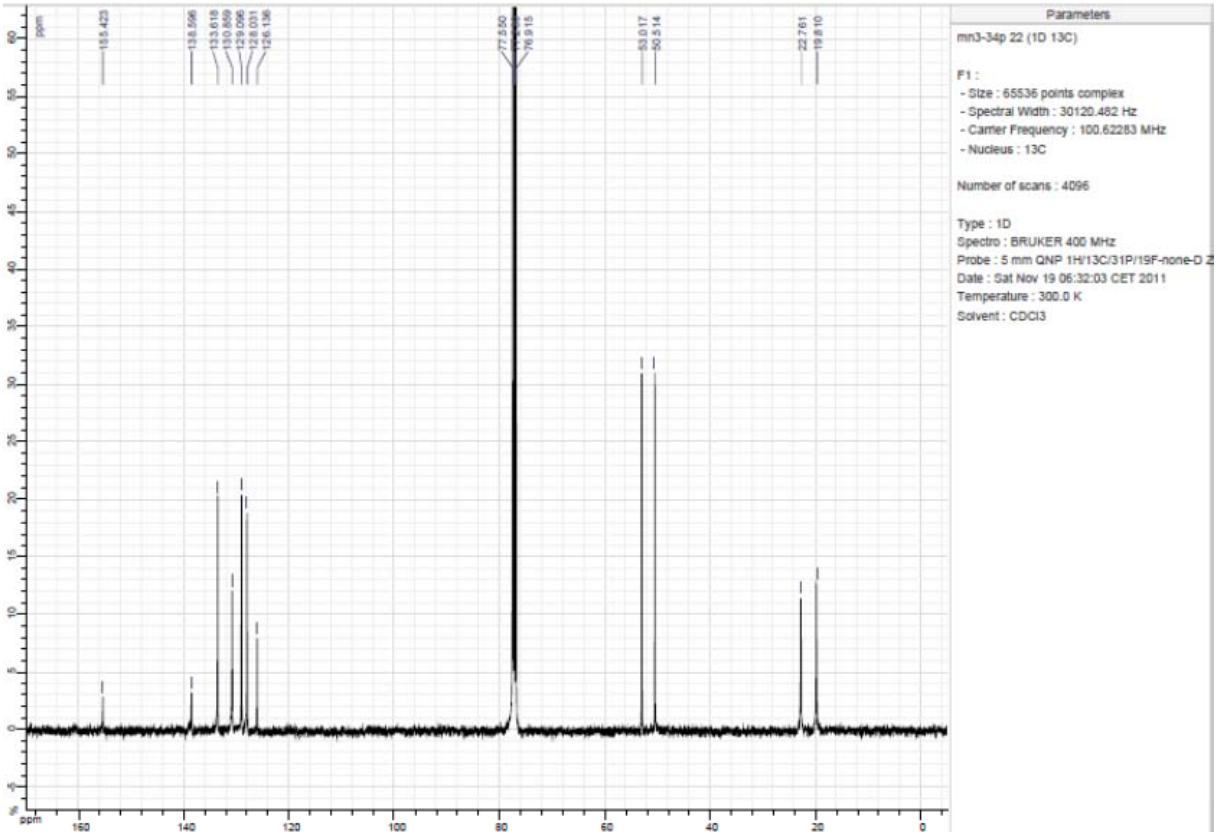
N-alkyl-*o*-bromoaniline was dissolved in methyl chloroformate (15 equivs.). The reaction mixture was refluxed for 4-24 hours and then poured into water and extracted with dichloromethane. The organic phase was dried over $MgSO_4$ and evaporated after filtration. The filtrate was evaporated by rotary evaporator and purified by f.c.. (silica gel; ethyl acetate/pentane as eluent) affording carbamate **1** or **6**.

Methyl (2-bromophenyl)(isopropyl)carbamate **1a**: [3]

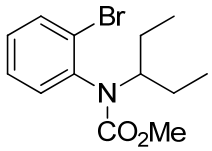


White solid, 77% yield, M.p. 47 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.01 (d, J = 7.2 Hz, 3H), 1.30 (d, J = 6.4 Hz, 3H), 3.61 (s, 3H), 4.36-4.42 (m, 1H), 7.15 (dd, J = 7.6, 1.6 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.30 (td, J = 7.6, 1.6 Hz, 1H), 7.62 (d, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 19.8, 22.8, 50.5, 53.0, 126.1, 128.0, 129.1, 130.8, 133.6, 138.6, 155.4. MS (ESI, 70 eV): *m/z* (%) = 253 $(M)^{+}$; IR (neat): υ = 726, 755, 785, 861, 955, 980, 1051, 1095, 1134, 1194, 1249, 1265, 1276, 1319, 1368, 1390, 1441, 1477, 1586, 1706, 2977 cm^{-1}; ESI-HRMS calcd. for $C_{11}H_{14}NNaO_2Br$ 294.0100, found 253.0099.

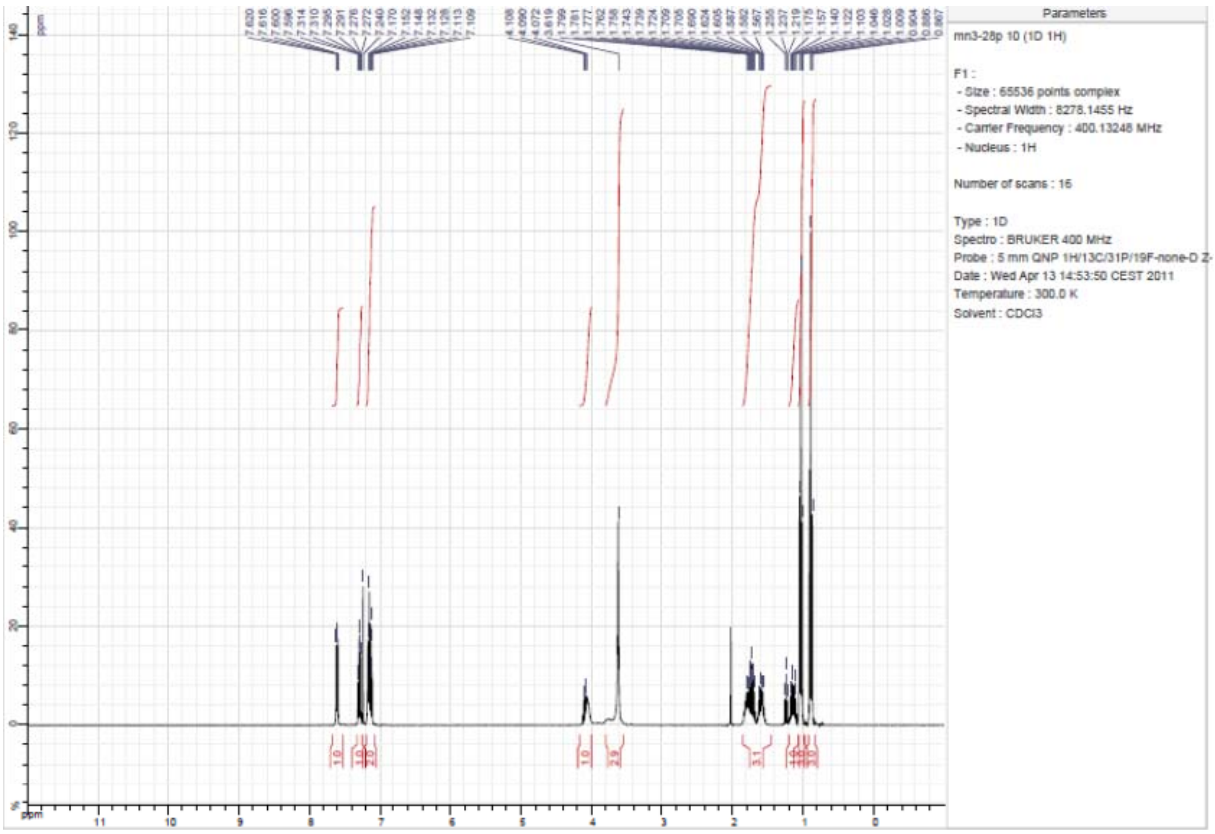


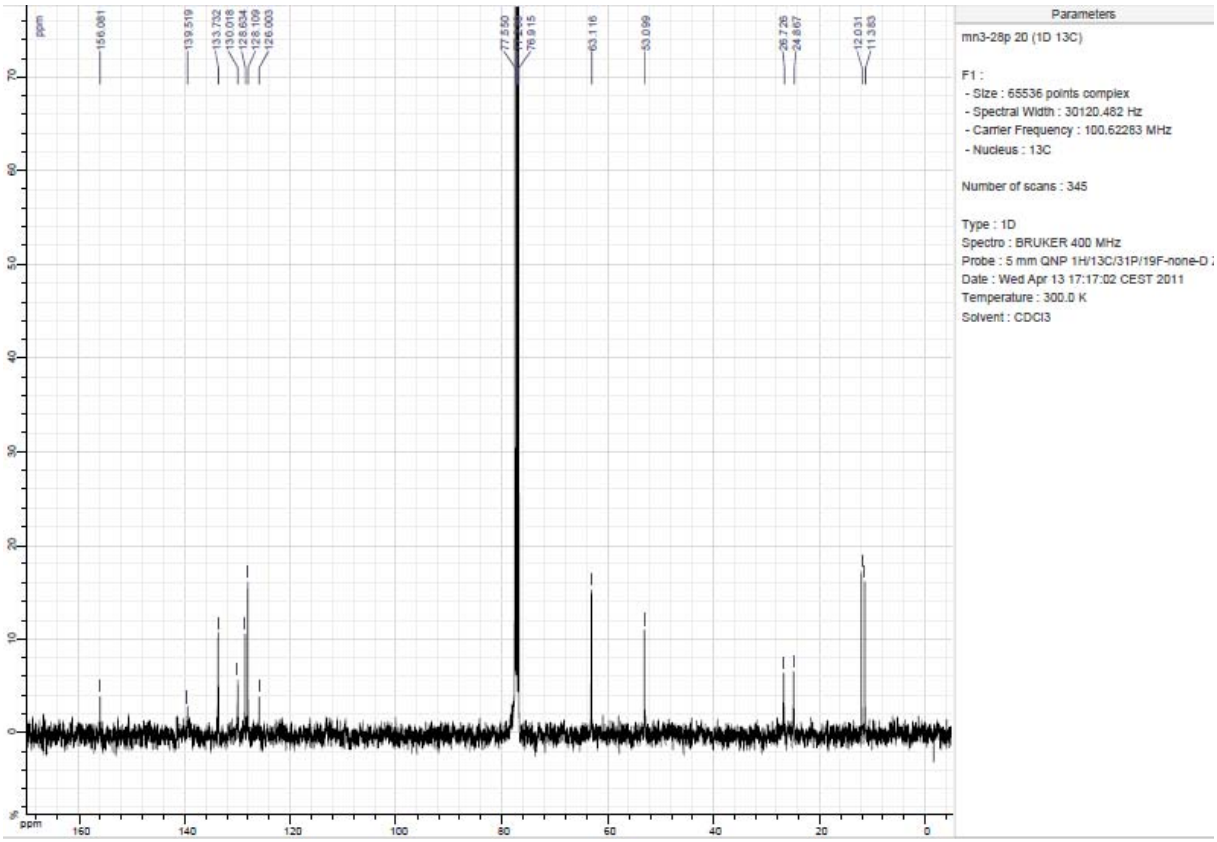


Methyl (2-bromophenyl)(pentan-3-yl)carbamate **1b**:

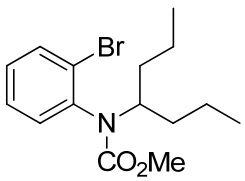


White solid, 93% yield, M.p. 36 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.16-1.46 (m, 5H), 1.58-1.69 (m, 1H), 1.70-1.82 (m, 2H), 1.96-2.10 (m, 2H), 3.22-3.36 (m, 1H), 4.22 (d, J = 7.6 Hz, 1H), 6.50 (td, J = 8, 1.2 Hz, 1H), 6.63 (dd, J = 8 Hz, 1H), 7.13 (d, J = 8, 1.2 Hz, 1H), 7.39 (dd, J = 8, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 25.6, 26.1, 30.4, 33.1, 53.0, 58.4, 126.2, 127.9, 129.0, 131.1, 133.5, 138.8, 155.5. MS (ESI, 70 eV): *m/z* (%) = 253 $(M)^+$; IR (neat): υ = 736, 853, 888, 923, 1016, 1096, 1126, 1148, 1231, 1253, 1285, 1319, 1366, 1429, 1451, 1505, 1592, 2852, 2927, 3404 cm^{-1}; HRMS calcd. for $C_{12}H_{16}NBr$ 253.0466, found 253.0466.

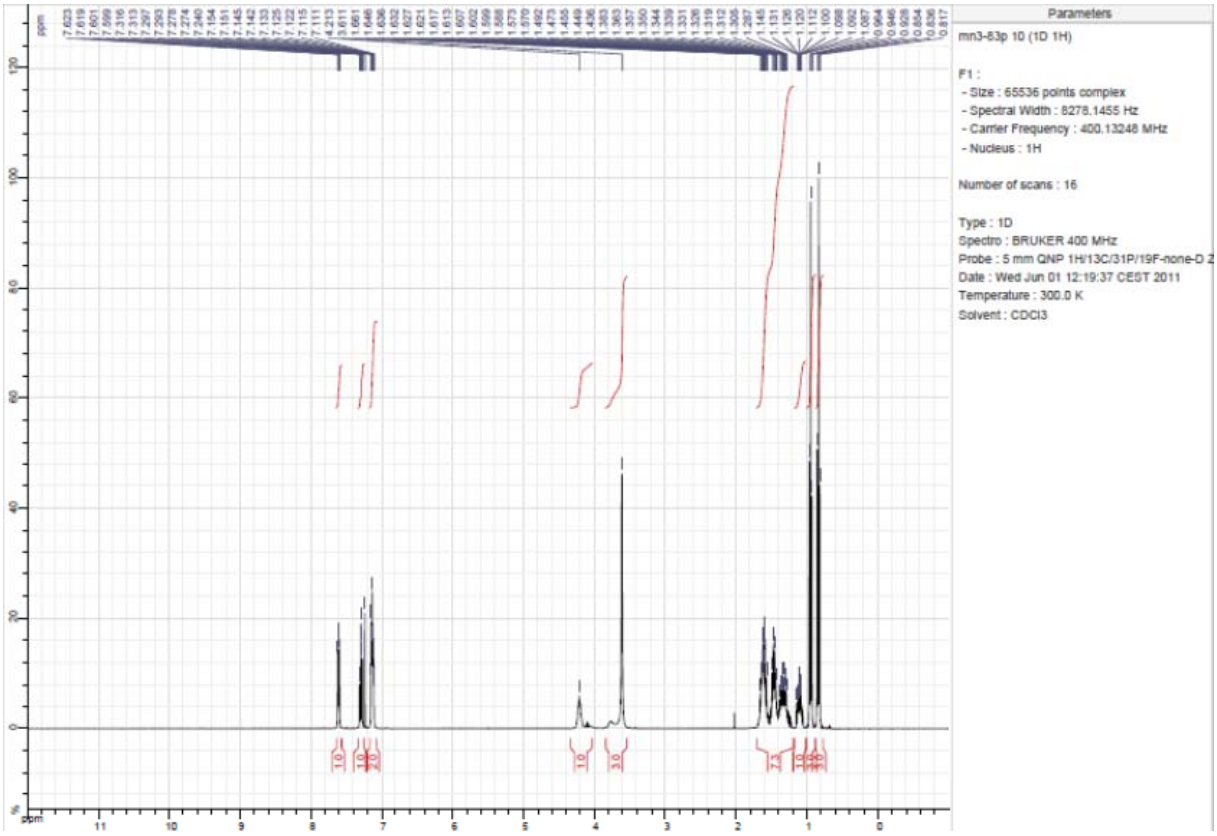


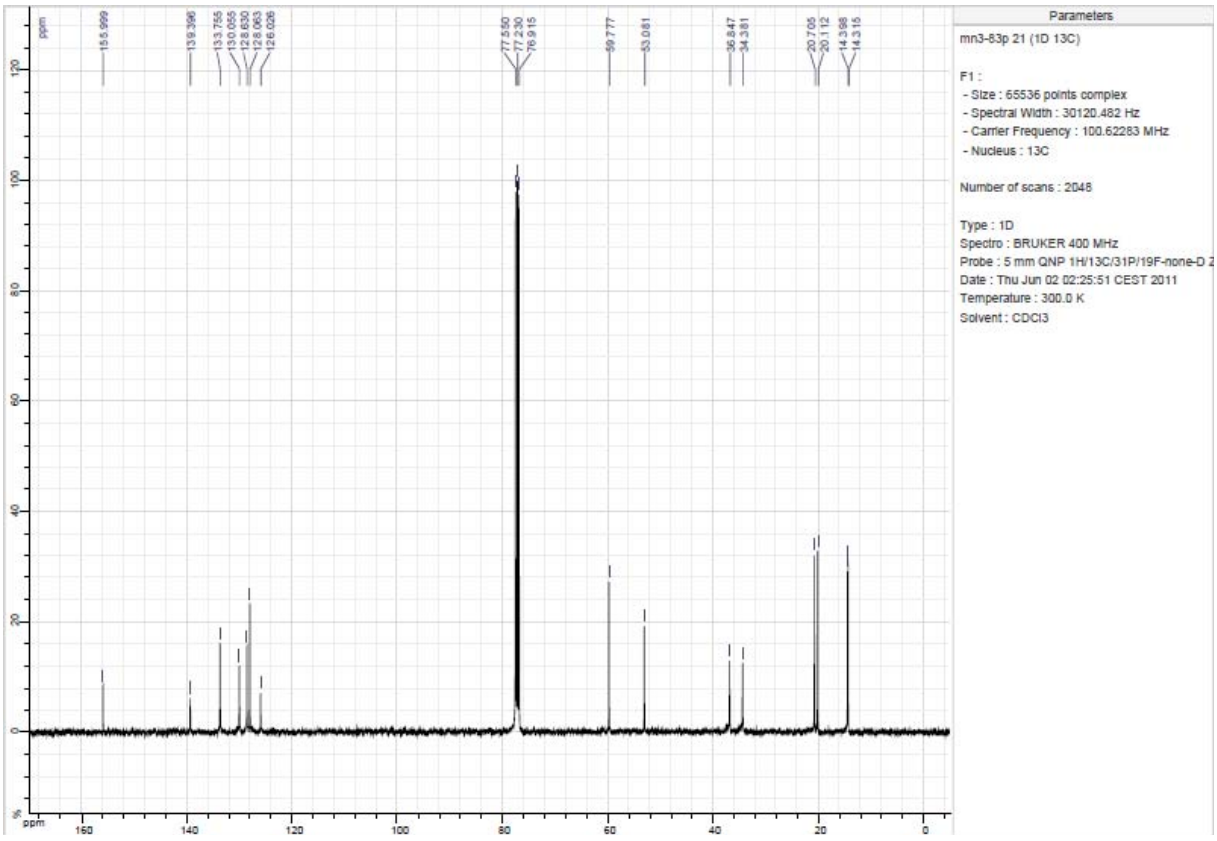


Methyl (2-bromophenyl)(heptan-4-yl)carbamate **1c**:

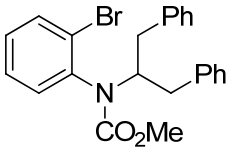


White solid, 97% yield, M.p. 41 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.84 (t, J = 7.2 Hz, 1H), 0.95 (t, J = 7.2 Hz, 1H), 1.03-1.18 (m, 1H), 1.20-1.72 (m, 7H), 3.61 (s, 3H), 4.04-4.34 (m, 1H), 7.08-7.18 (m, 2H), 7.30 (td, J = 7.6, 1.2 Hz, 1H), 7.61 (dd, J = 8.8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 14.3, 14.4, 20.1, 20.7, 34.4, 36.8, 53.1, 59.8, 53.1, 59.8, 126.0, 128.1, 128.6, 130.1, 139.4, 156.0. MS (ESI, 70 eV): m/z (%) = 328 $(M+H)^+$; IR (neat): υ = 744, 763, 905, 930, 1001, 1031, 1058, 1108, 1191, 1264, 1289, 1318, 1389, 1440, 1473, 1585, 1707, 2871, 2957 cm^{-1}; HRMS calcd. for $C_{15}H_{23}BrNO_2$ 328.0906, found 328.0904.

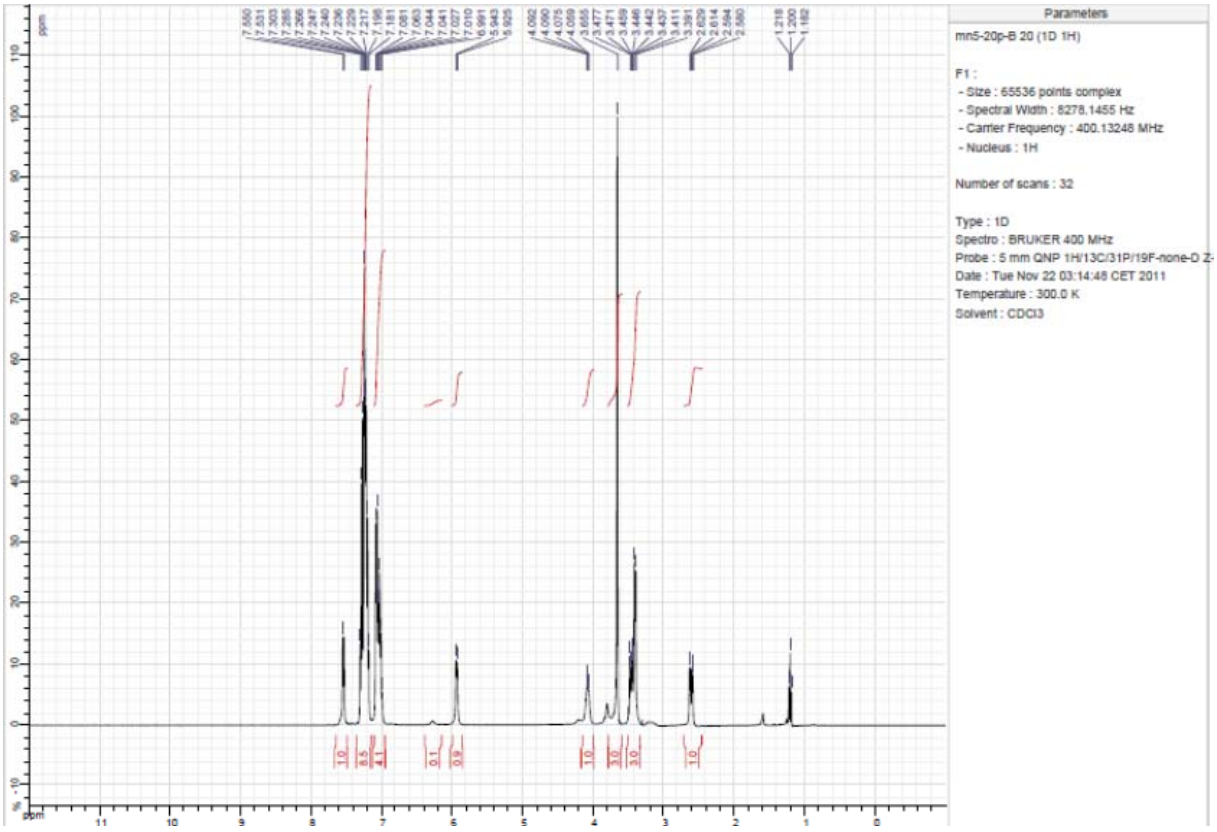


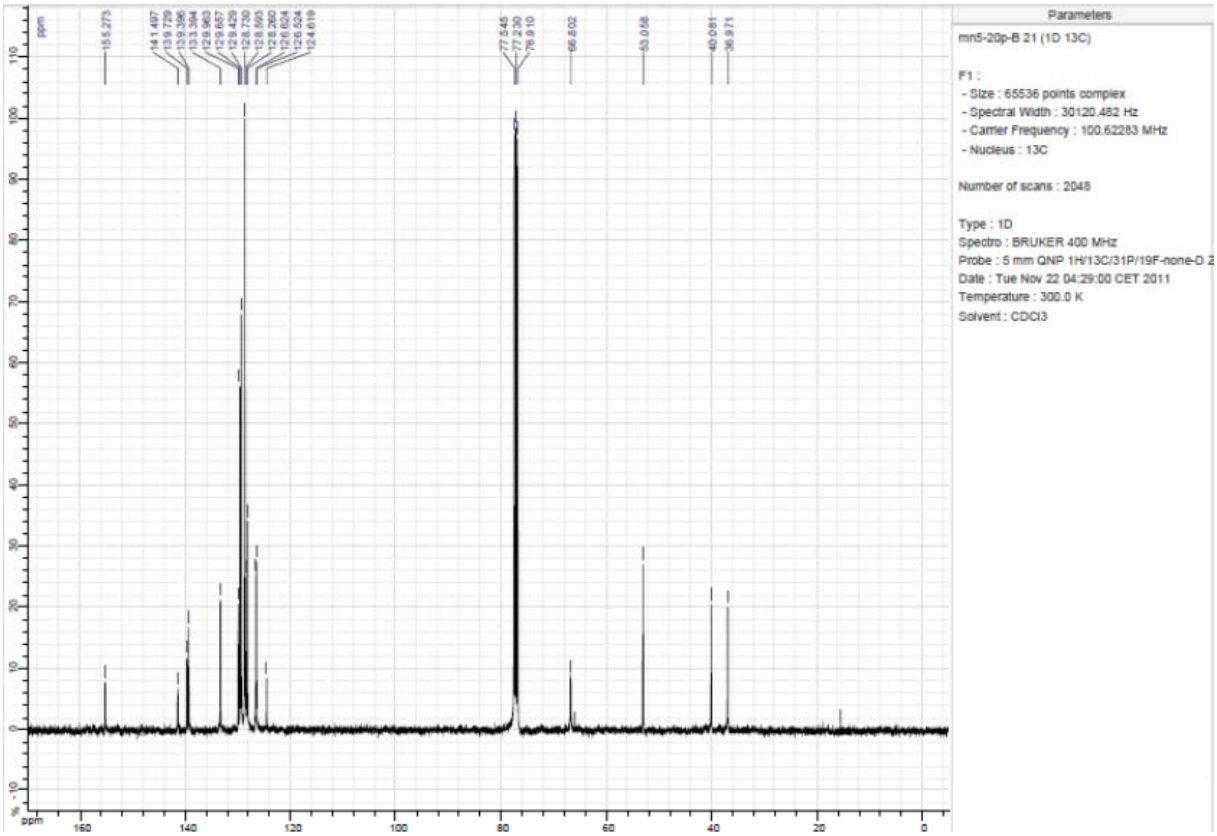


Methyl (2-bromophenyl)(1,3-diphenylpropan-2-yl)carbamate **1d**:

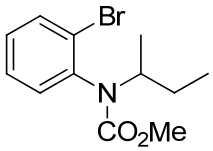


White solid, M.p. 77 ºC, 88% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 2.60 (dd, J = 14, 6 Hz, 1H), 3.40 (d, J = 8 Hz, 2H), 3.42-3.51 (m, 1H), 3.66 (s, 3H), 4.00-4.15 (m, 1H), 5.93 (d, J = 7.2 Hz, 1H), 6.15-6.39 (brd, 0.1H), 6.96-7.11 (m, 4H), 7.15-7.36 (m, 8H), 7.54 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 37.0, 40.1, 53.1, 66.8, 124.6, 126.5, 126.6, 128.3, 128.6, 128.7, 129.4, 129.7, 130.0, 133.4, 139.4, 139.7, 141.5, 155.3. MS (ESI, 70 eV): *m/z* (%) = 424 $(M+H)^+$; IR (neat): υ = 699, 720, 750, 789, 917, 943, 994, 1029, 1061, 1129, 1155, 1191, 1217, 1265, 1293, 1401, 1441, 1474, 1495, 1584, 1602, 1707, 2951, 3027 cm^{-1}; ESI-HRMS calcd. for $C_{23}H_{23}NOBr$ 424.0906, found 424.0897.

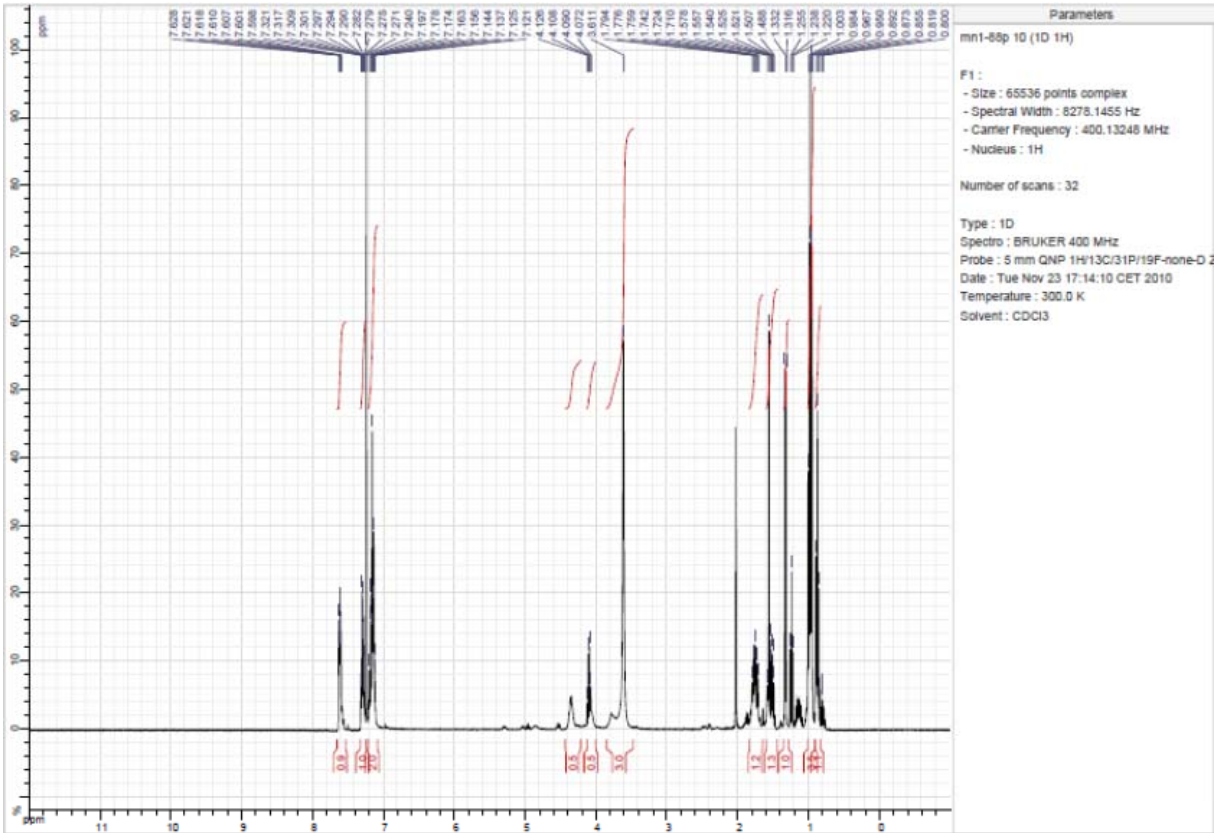


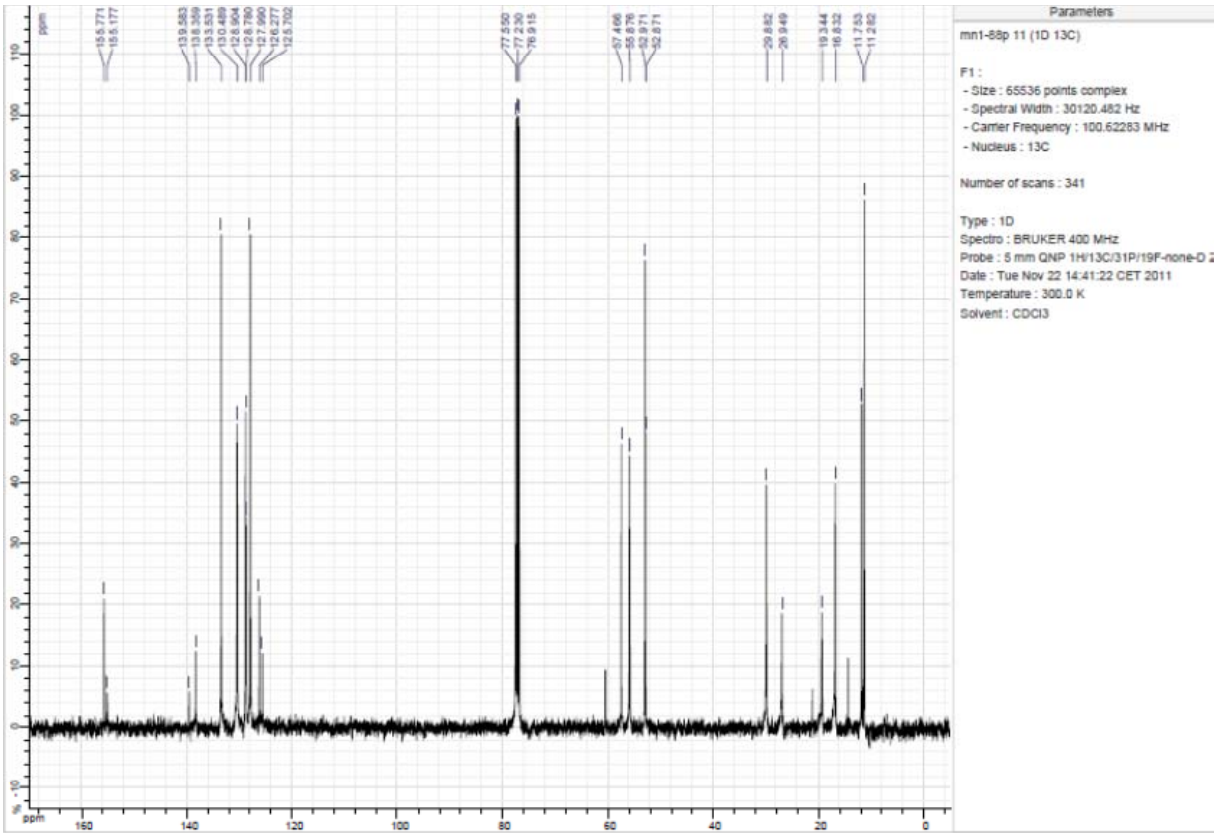


Methyl (2-bromophenyl)(*sec*-butyl)carbamate **6a**: [3]

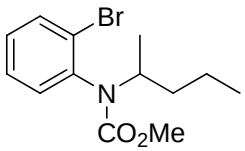


Colorless oil, 98% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.87 (t, J = 7.6 Hz, 1H), 0.96 (d, J = 6.8 Hz, 2H), 0.98 (t, J = 7.6 Hz, 2H), 1.32 (d, J = 6.4 Hz, 1H), 1.45-1.60 (m, 0.8H), 1.66-1.84 (m, 1.2H), 3.61 (s, 3H), 4.01-4.13 (m, 0.5H), 4.22-4.44 (m, 0.5H), 7.09-7.22 (m, 2H), 7.25-7.33 (m, 1H), 7.54-7.66 (m, 1H). ^{13}C NMR (100 MHz): δ = 11.3, 11.8, 16.8, 19.3, 26.9, 29.9, 52.9, 53.0, 55.9, 57.5, 125.7, 126.3, 128.0, 128.8, 128.9, 130.5, 133.5, 138.4, 139.6, 155.2, 155.8. MS (ESI, 70 eV): *m/z* (%) = 286 $(M+H)^+$; IR (neat): υ = 730, 753, 840, 935, 953, 998, 1028, 1052, 1093, 1120, 1191, 1244, 1266, 1295, 1310, 1325, 1389, 1439, 1475, 1585, 1706, 2877, 2968 cm^{-1}; ESI-HRMS calcd. for $C_{12}H_{17}BrN$ 286.0437, found 286.0432.

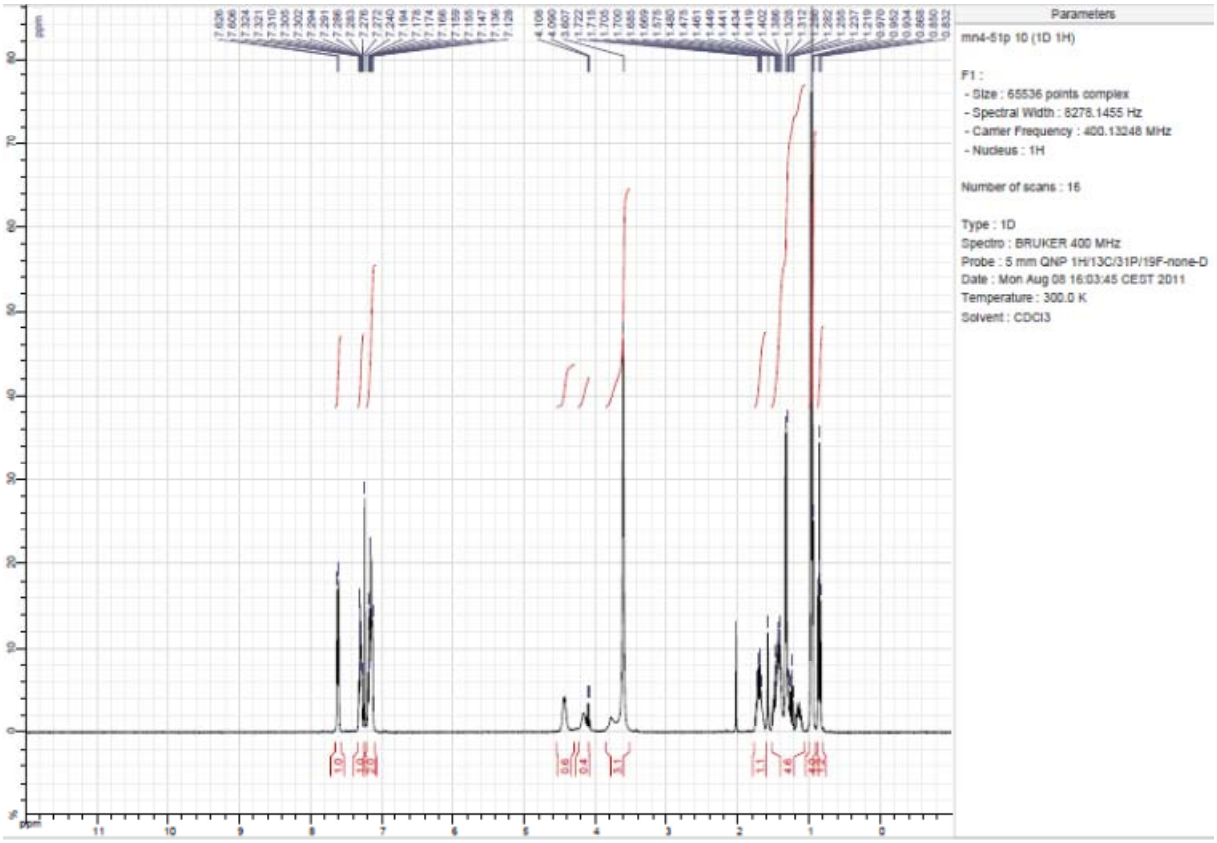


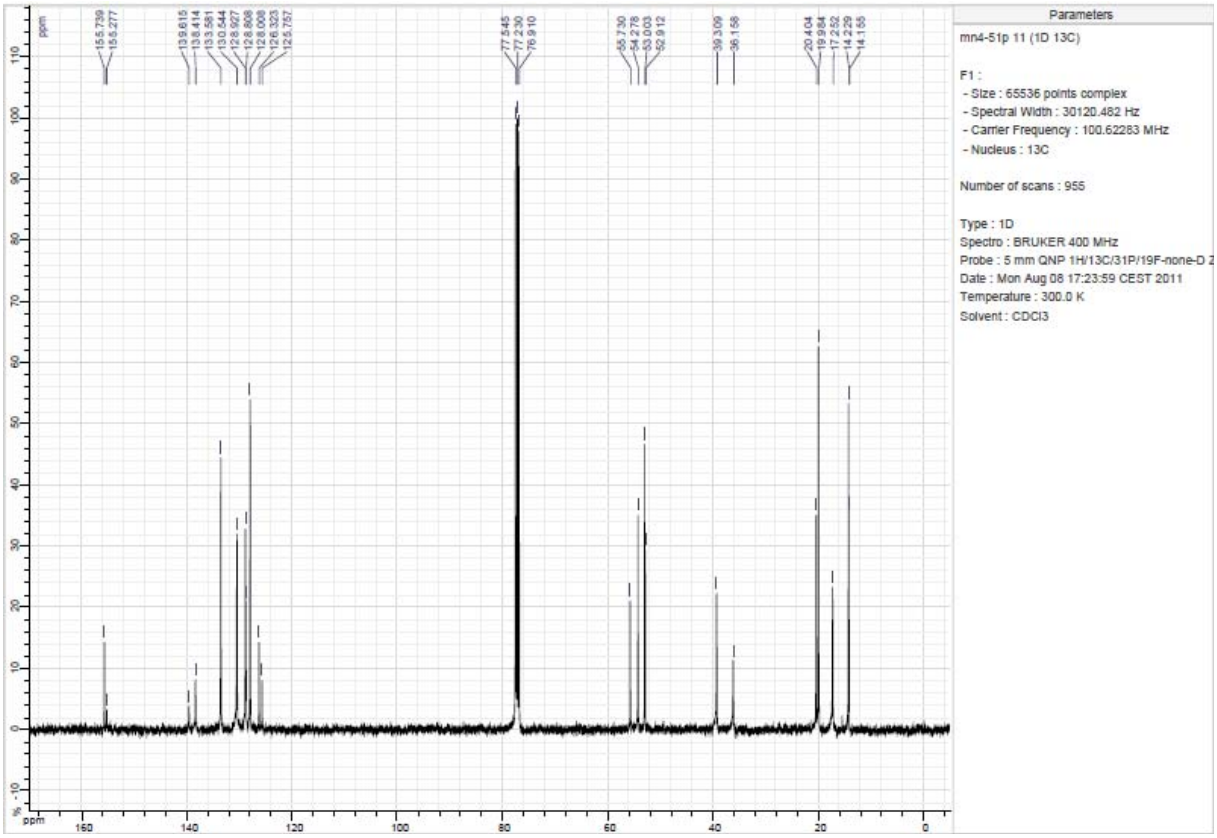


Methyl (2-bromophenyl)(pentan-2-yl)carbamate **6b**:

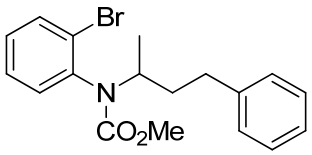


Colorless oil, 99% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.85 (t, J = 7.2 Hz, 1.2H), 0.91-1.00 (m, 4H), 1.07-1.53 (m, 3.8H), 1.61-1.77 (m, 1H), 3.61 (s, 3H), 4.10-4.24 (m, 0.4H), 4.30-4.55 (m, 0.6H), 7.10-7.22 (m, 2H), 7.26-7.34 (m, 1H), 7.38 (d, J = 8, 1H). ^{13}C NMR (100 MHz): δ = 14.2, 14.2, 17.3, 20.0, 20.4, 52.9, 53.0, 54.3, 55.7, 125.8, 126.3, 128.0, 128.8, 128.9, 130.5, 138.4, 139.6, 155.3, 155.7. MS (ESI, 70 eV): m/z (%) = 300 $(M+H)^+$; IR (neat): υ = 728, 746, 761, 785, 869, 911, 951, 1028, 1056, 1301, 1191, 1264, 1319, 1390, 1440, 1475, 1585, 1605, 2872, 2957 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{19}BrNO_2$ 300.0593, found 300.0604.

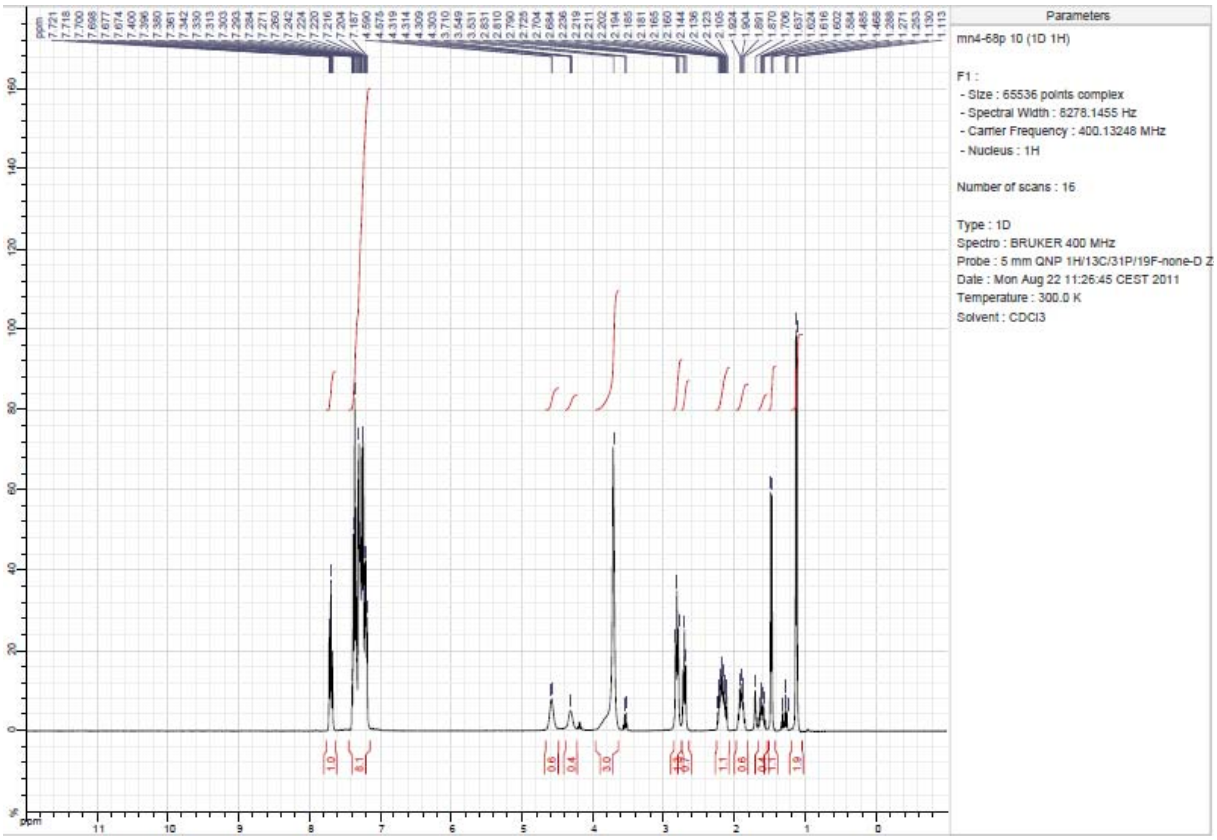


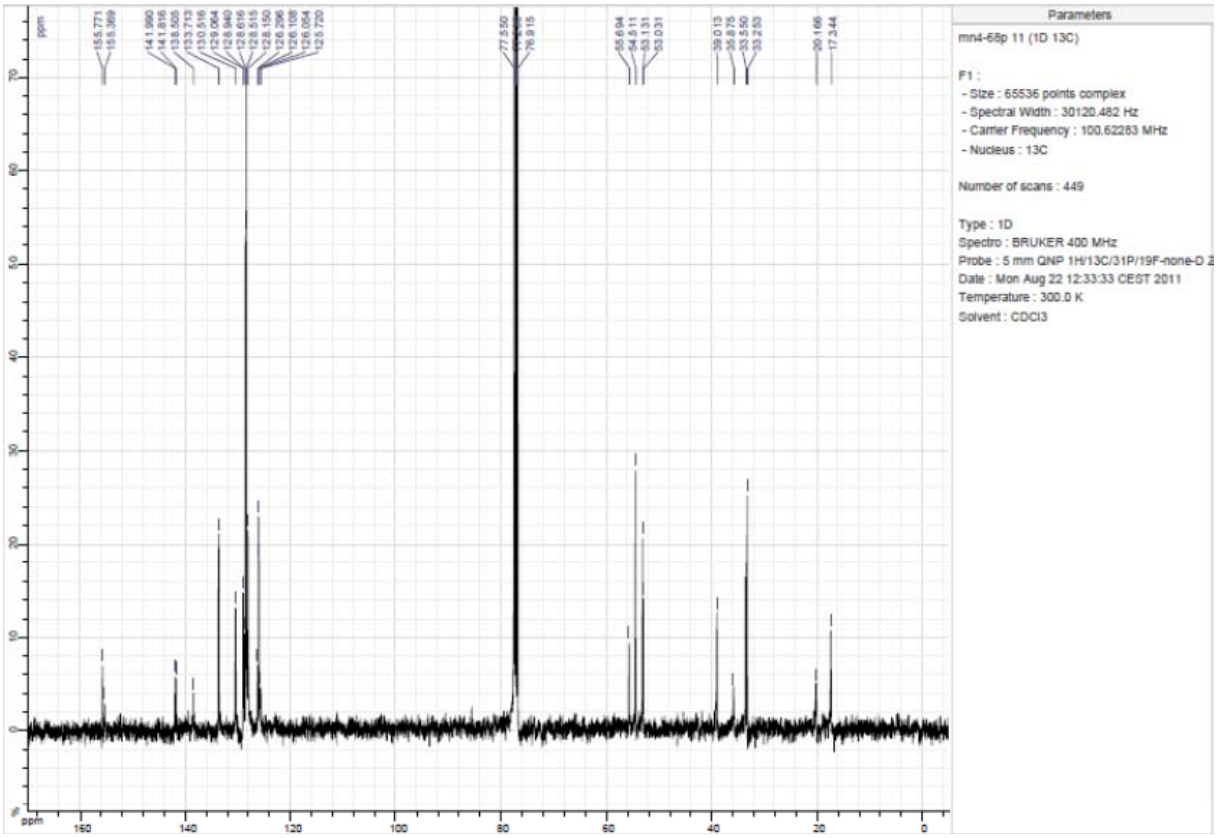


Methyl (2-bromophenyl)(4-phenylbutan-2-yl)carbamate **6c**:

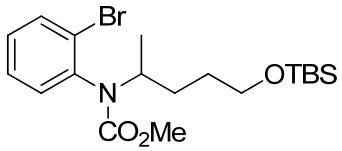


White solid, 88% yield, M.p. 61 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 1.12 (d, J = 6.8 Hz, 1.9H),): 1.48 (d, J = 6.8 Hz, 1.1H), 1.55-1.67 (m, 0.4H), 1.82-1.99 (m, 0.6H), 2.08-2.26 (m, 1H), 2.70 (d, J = 8.4 Hz, 0.7H), 2.81 (t, J = 8.4 Hz, 1.3H), 3.71 (s, 3H), 4.23-4.39 (m, 0.4H), 4.49-4.67 (m, 0.6H), 7.15-7.45 (m, 8H), 7.70 (td, J = 8.4, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = 17.3, 20.2, 33.3, 33.6, 35.9, 39.0, 53.0, 53.1, 54.5, 55.7, 125.7, 126.1, 126.1, 126.3, 128.2, 128.5, 128.6, 128.9, 129.1, 133.7, 138.5, 141.8, 142.0, 155.4, 155.8. MS (ESI, 70 eV): *m/z* (%) = 278 $(M+H)^+$; IR (neat): υ = 724, 750, 783, 952, 1029, 1043, 1060, 1117, 1190, 1317, 1389, 1440, 1475, 1585, 1705, 2950, 3026 cm^{-1}; ESI-HRMS calcd. for $C_{15}H_{20}NO_4$ 278.1386, found 278.1390.

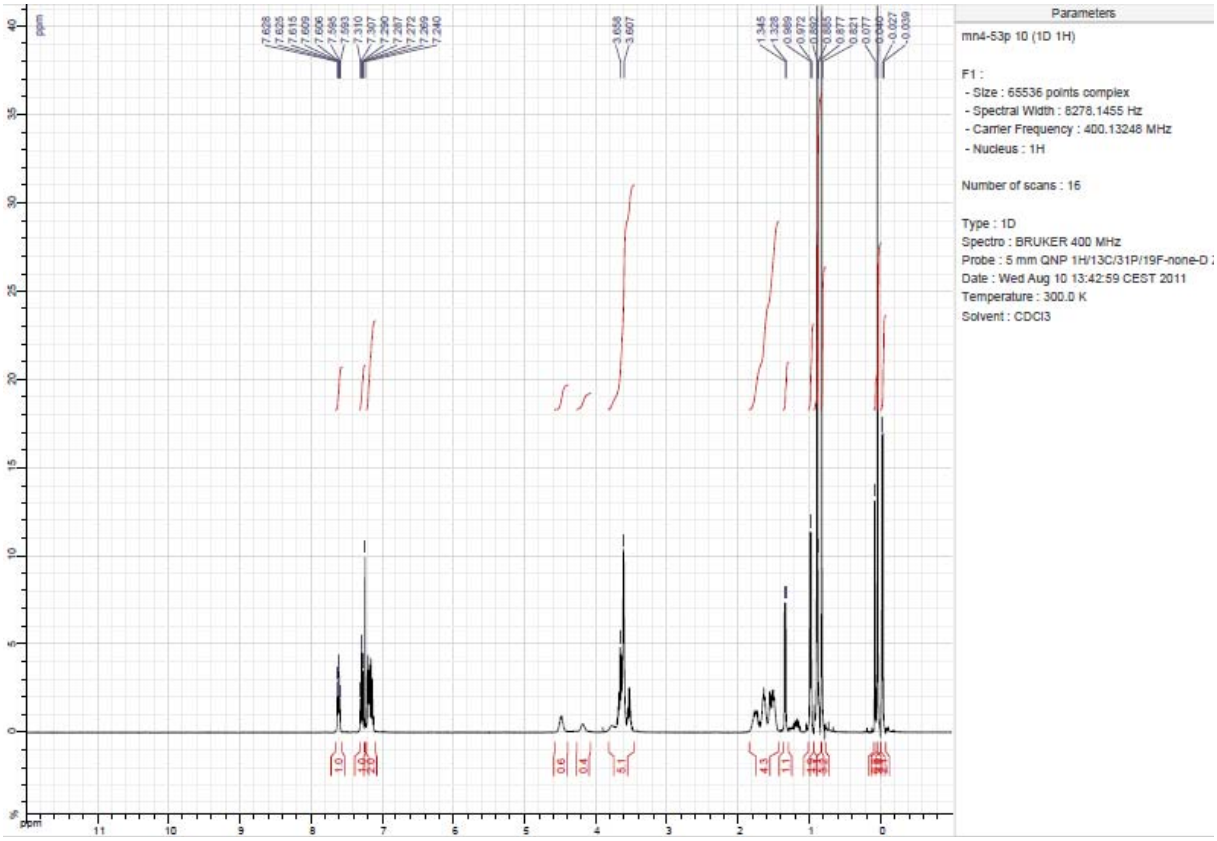


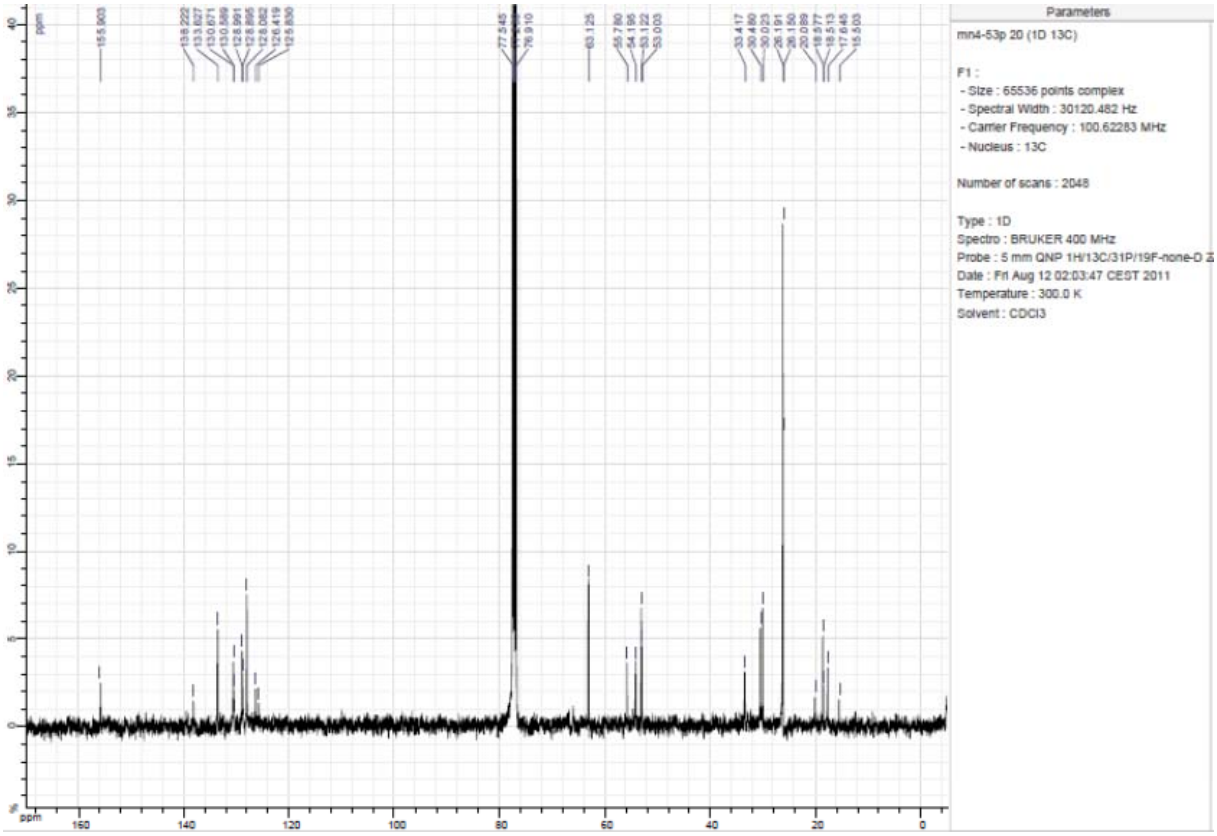


Methyl (2-bromophenyl)(5-((*tert*-butyldimethylsilyl)oxy)pentan-2-yl)carbamate **6d**:

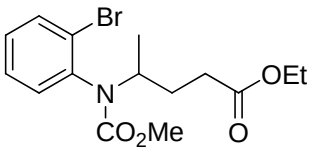


Colorless oil, 29% yield, ^{1}H NMR (400 MHz, $CDCl_3$): -0.04 (s, 1H), -0.03 (s, 1H), 0.04 (s, 3.8H), 0.08 (s, 0.8H), 0.82 (s, 3.2H),), 0.88 (d J = 6.8 Hz, 1.1H), 0.89 (s, 5H), 0.98 (d J = 6.8 Hz, 1.9H),), 1.34 (d J = 6.8 Hz, 1.1H), 1.44-1.85 (m, 4H), 3.47-3.74 (m, 2H), 3.61 (s, 3H), 4.08-4.28 (m, 0.4H), 4.40-4.58 (m, 0.6H) 7.10-7.23 (m, 2H), 7.29 (td, J = 8, 1.2 Hz, 1H), 7.14 (d, J = 8, 1.2 Hz, 1H), 7.38 (dd, J = 8, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ = -5.2, -5.1, 15.5, 17.6, 18.5, 18.6, 20.1, 26.2, 26.2, 30.0, 30.5, 33.4, 53.0, 53.1, 54.2, 55.8, 63.1, 125.8, 126.4, 128.1, 128.9, 129.0, 130.6, 130.7, 138.2, 155.9 . MS (ESI, 70 eV): m/z (%) = 430 $(M+H)^+$; IR (neat): υ = 729, 774, 833, 939, 1006, 1030, 1090, 1192, 1252, 1321, 1390, 1441, 1475, 1586, 1711, 2857, 2952 cm^{-1}; ESI-HRMS calcd. for $C_{19}H_{33}BrNO_3Si$ 430.1407, found 430.1406.

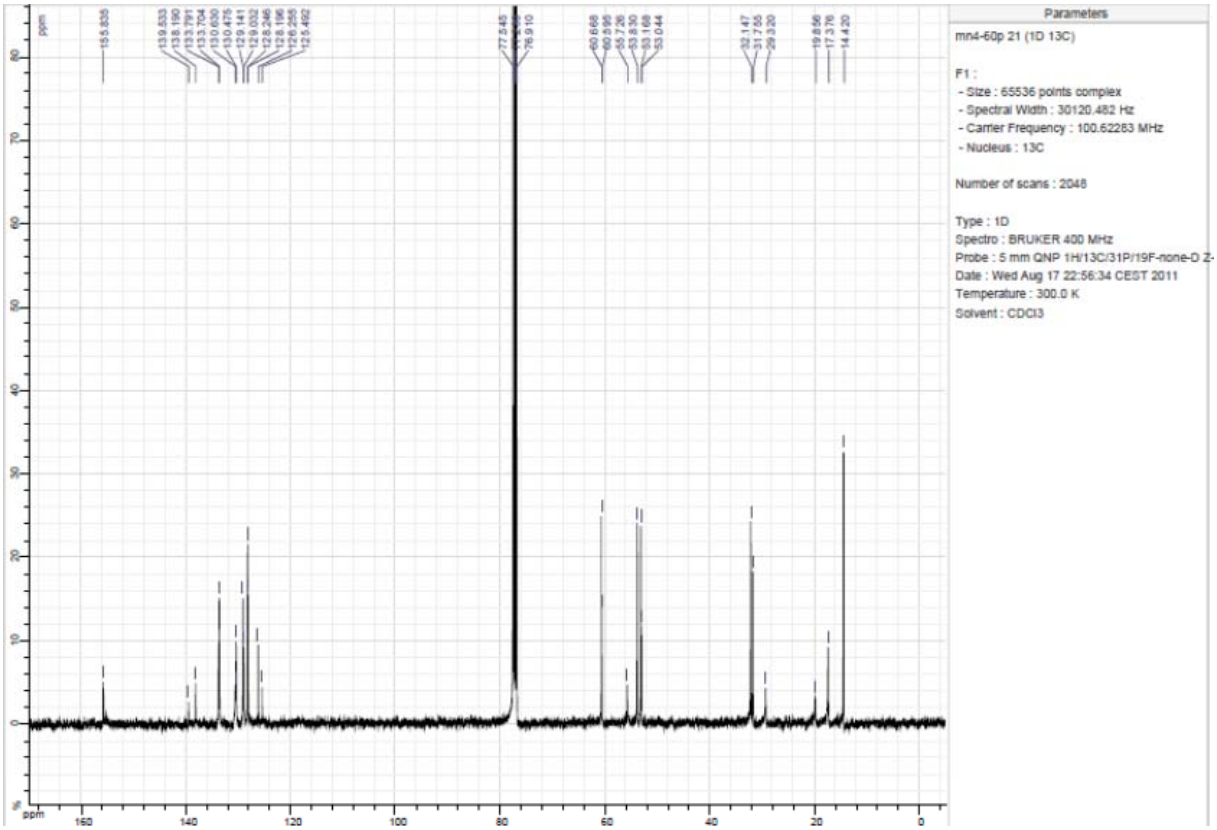


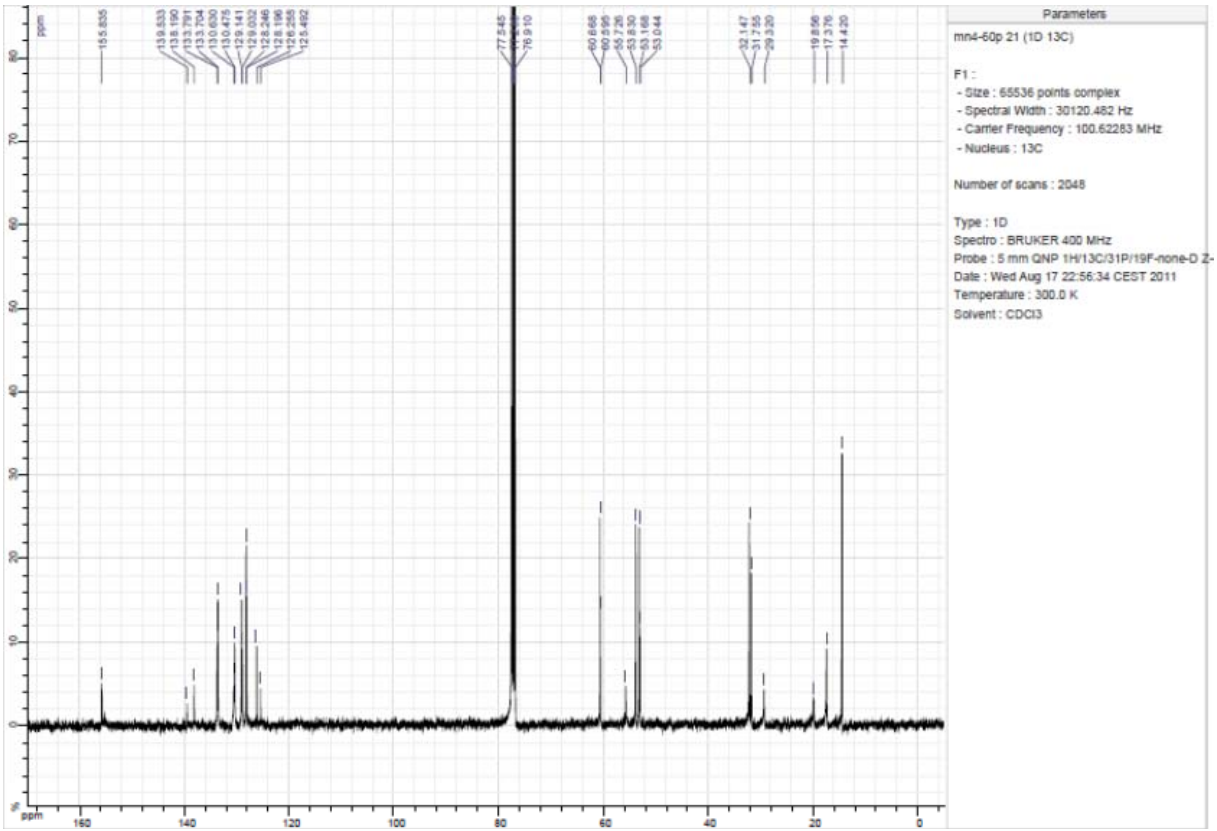


Ethyl 4-((2-bromophenyl)(methoxycarbonyl)amino)pentanoate **6e**:

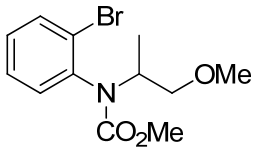


Colorless oil, >99% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.99 (d, J = 6.8 Hz, 2H), 1.45-1.28 (m, 3.2H), 1.34 (d, J = 6.8 Hz, 1H), 1.54-1.68 (m, 0.8H), 1.68-1.81 (m, 2H), 1.77-1.91 (m, 0.7H), 1.97-2.14 (m, 1H), 2.36 (t, J = 7.6 Hz, 0.7H), 2.45 (t, J = 7.6 Hz, 1.3H), 3.61 (s, 3H), 4.02-4.20 (m, 2.3H), 4.30-4.56 (m, 0.7H), 7.11-7.23 (m, 2H), 7.26-7.35 (m, 1H), 7.62 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 14.4, 17.4, 19.9, 29.3, 31.8, 32.1, 53.0, 53.2, 53.8, 55.7, 60.6, 60.7, 125.5, 126.3, 128.2, 128.2, 129.0, 129.1, 130.5, 130.6, 133.7, 133.8, 138.2, 139.5, 155.8. MS (ESI, 70 eV): m/z (%) = 358 $(M+H)^+$; IR (neat): υ = 758, 785, 856, 946, 1029, 1076, 1119, 1129, 1319, 1390, 1441, 1475, 1586, 1706, 2980 cm^{-1}; ESI-HRMS calcd. for $C_{15}H_{21}BrNO_4$ 358.0648, found 358.0640.

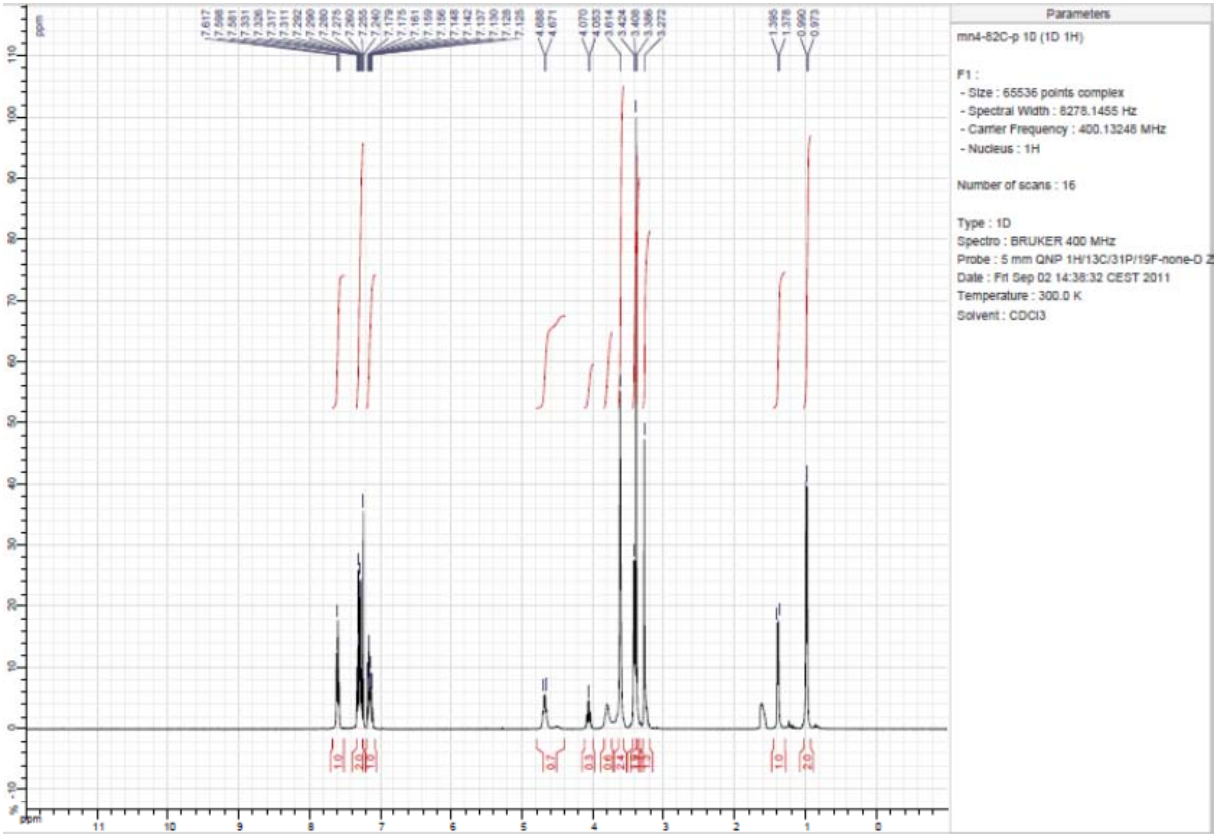


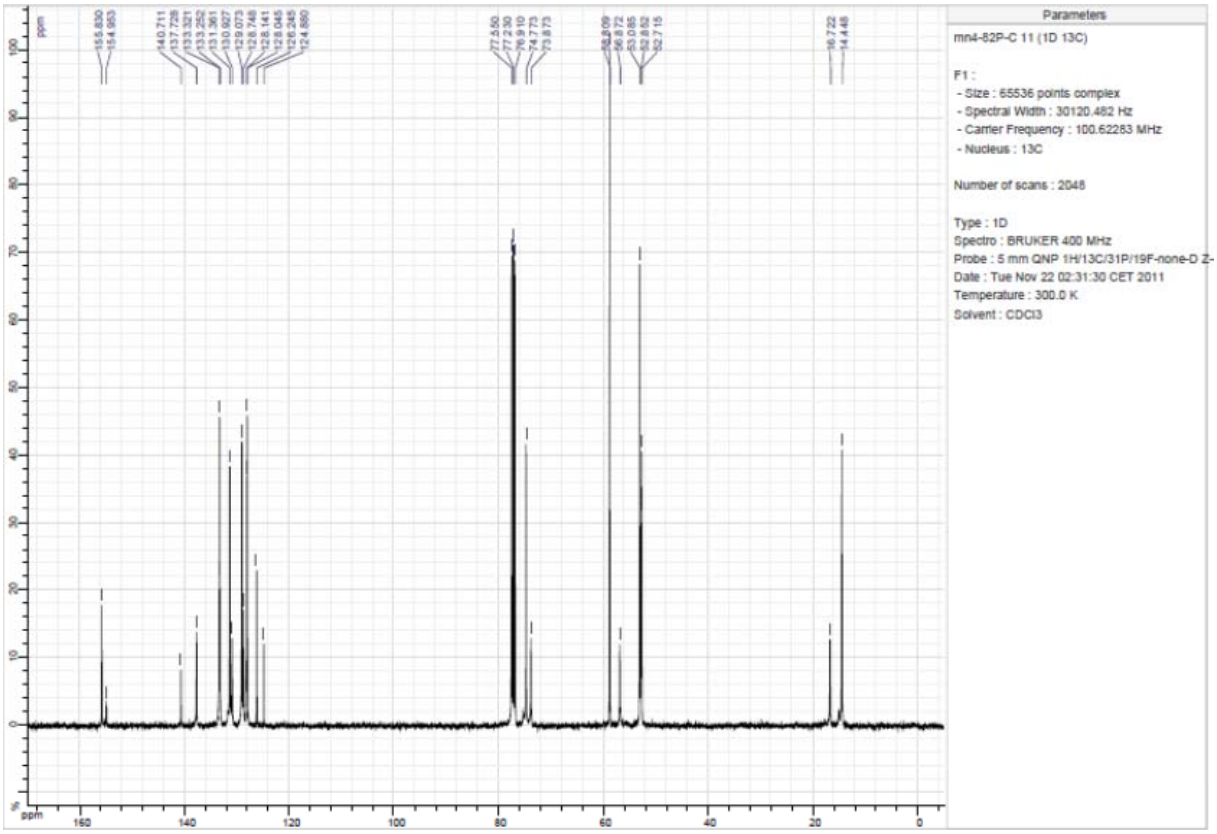


Methyl (2-bromophenyl)(1-methoxypropan-2-yl)carbamate **6f**:

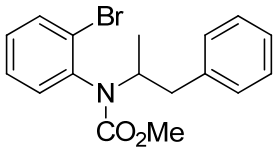


White solid, 87% yield, M.p. 39 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.98 (d, J = 6.8 Hz, 2H), 1.39 (d, J = 6.8 Hz, 1H), 3.27 (s, 1.3H), 3.39 (s, 1.7H), 3.42 (d, J = 6.4 Hz, 2H), 3.61 (s, 2.4H), 3.74-3.85 (m, 0.6H), 4.00-4.12 (m, 0.3H), 4.40-4.80 (m, 0.7H), 7.25-7.34 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = 14.4, 16.7, 52.7, 52.9, 53.1, 73.9, 74.8, 124.9, 126.2, 128.0, 128.1, 128.7, 129.1, 130.9, 131.4, 133.3, 133.3, 155.0, 155.8. MS (ESI, 70 eV): *m/z* (%) = 302 $(M+H)^+$; IR (neat): υ = 728, 759, 786, 928, 958, 982, 1045, 1029, 1073, 1103, 1154, 1194, 1268, 1298, 1318, 1375, 1441, 1475, 1586, 1706, 2582, 2951 cm^{-1}; HRMS calcd. for $C_{12}H_{17}BrNO_3$ 302.0386, found 302.0390.

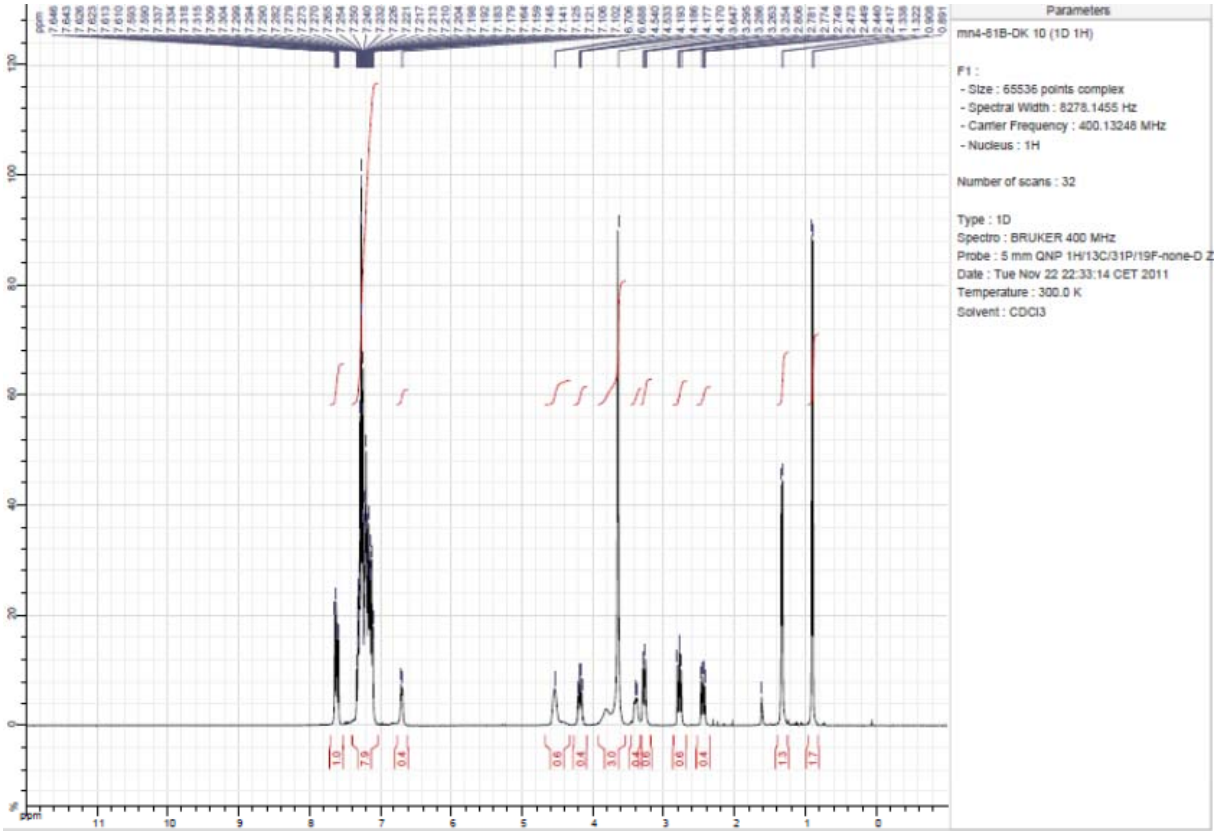


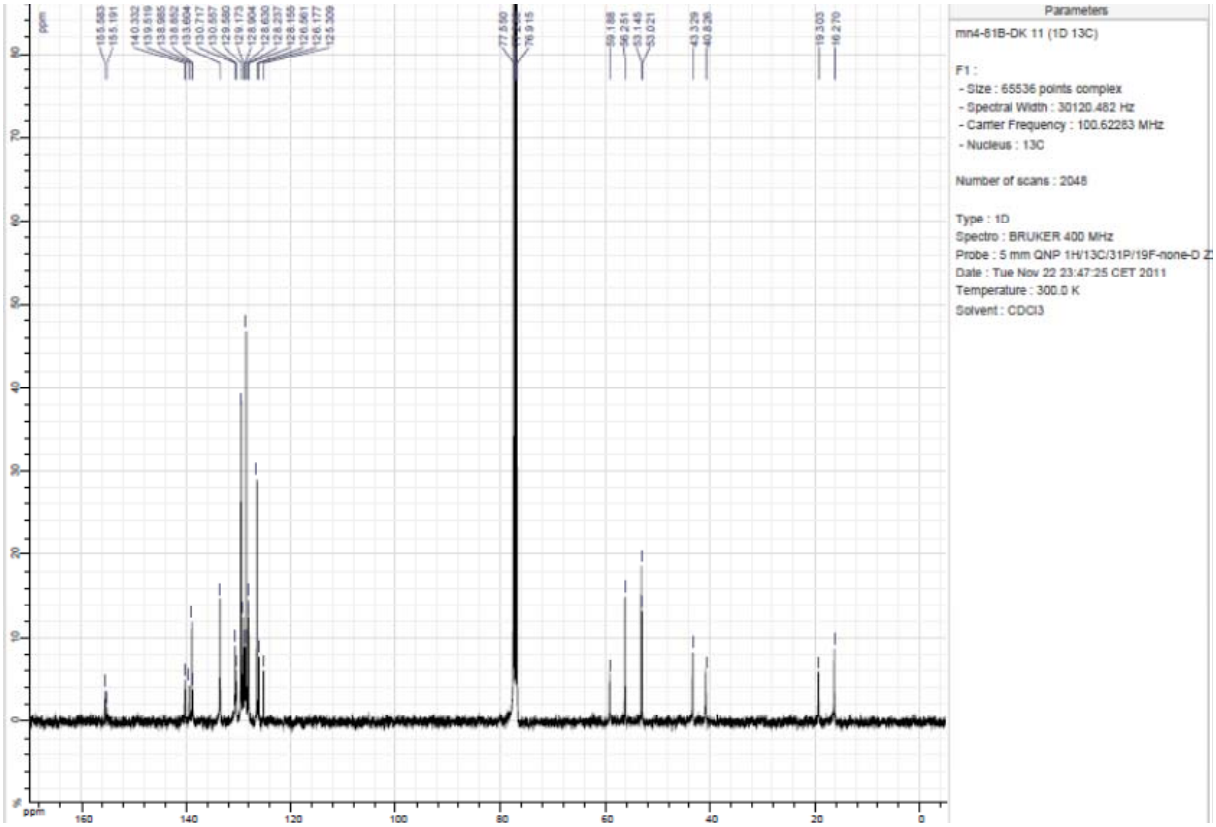


Methyl (2-bromophenyl)(1-phenylpropan-2-yl)carbamate **6g**:

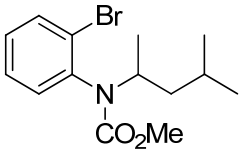


White solid, 97% yield, M.p. 102 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.90 (d, J = 6.8 Hz, 1.7H), 0.83 (d, J = 6.8 Hz, 1.3H), 2.44 (dd, J = 12.8, 9.2 Hz, 0.4H), 2.78 (dd, J = 12.8, 10 Hz, 0.6H), 3.27 (dd, J = 12.8, 8.4 Hz, 0.6H), 3.33-3.43 (m, 0.4H), 3.65 (s, 3H), 4.10-4.26 (m, 0.4H), 4.34-4.64 (m, 0.6H), 6.70 (d, J = 7.2 Hz, 0.4H), 7.05-7.37 (m, 7.6H), 7.56-7.66 (m, 1H). ^{13}C NMR (100 MHz): δ = 16.3, 19.3, 40.8, 43.3, 53.0, 53.1, 56.3, 59.2, 125.3, 126.2, 126.6, 128.2, 128.2, 128.6, 128.9, 129.2, 129.6, 130.6, 130.7, 133.6, 138.9, 139.5, 140.3, 155.2, 155.6. MS (ESI, 70 eV): m/z (%) = 348 $(M+H)^+$; IR (neat): υ = 700, 729, 744, 761, 830, 860, 915, 951, 983, 1029, 1069, 1167, 1191, 1293, 1325, 1388, 1440, 1475, 1585, 1704, 2951, 2978, 3027, 3062 cm^{-1}; HRMS calcd. for $C_{17}H_{19}BrNO_2$ 348.0593, found 348.0589.

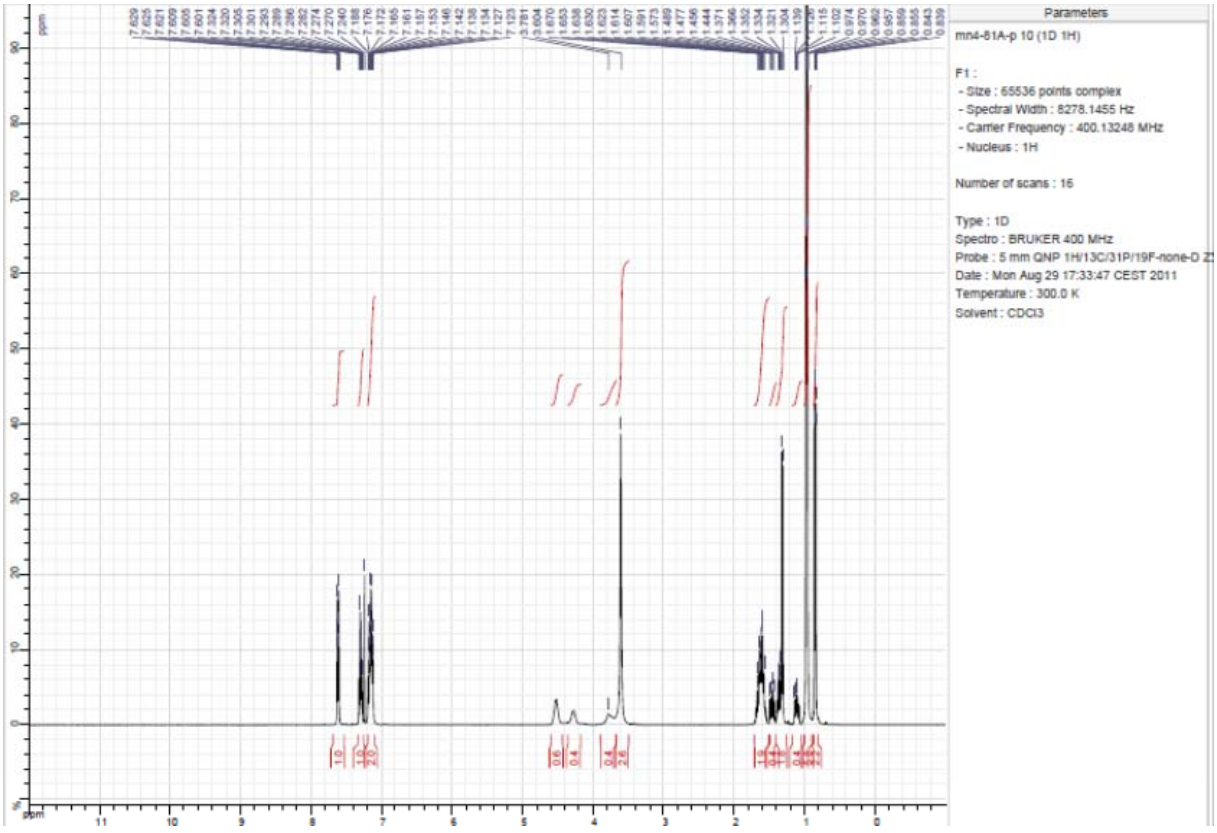


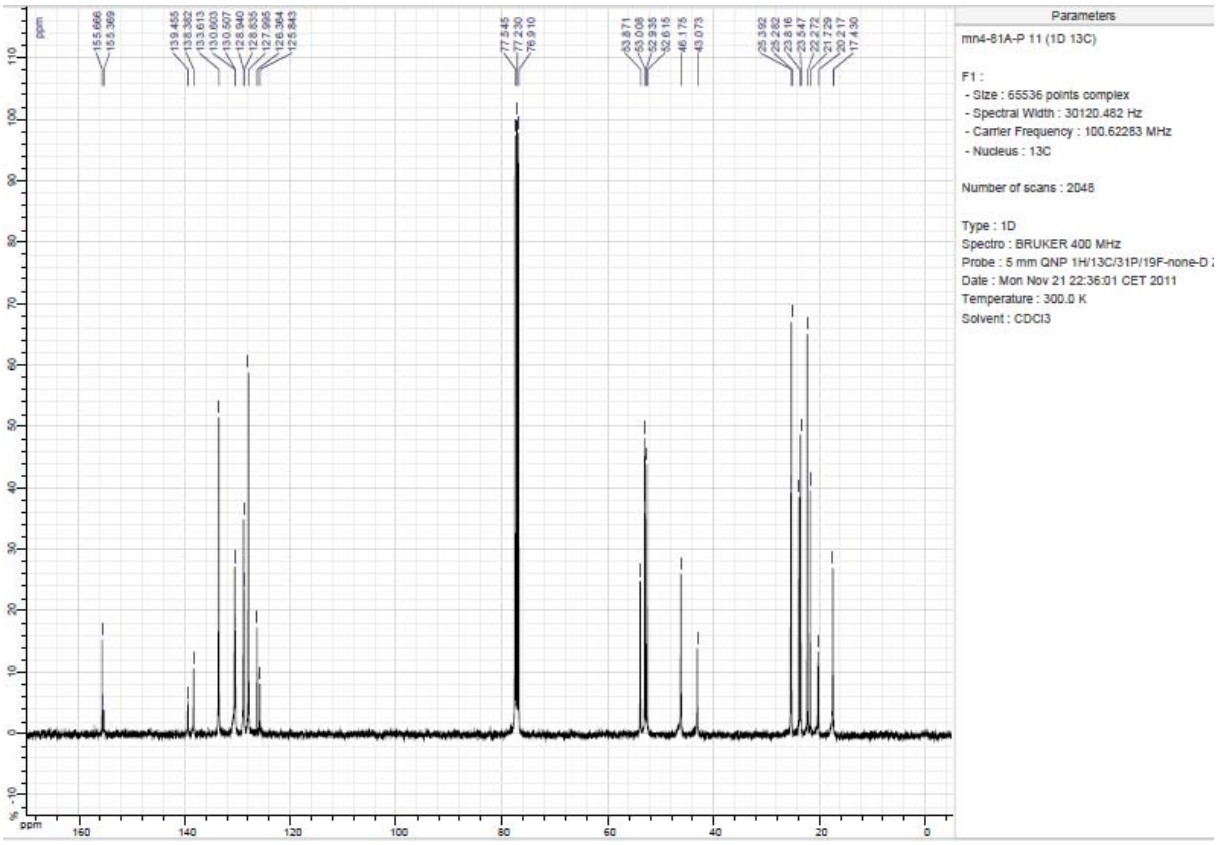


Methyl (2-bromophenyl)(4-methylpentan-2-yl)carbamate **6h**:

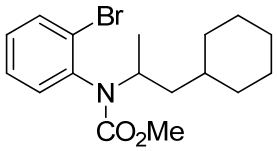


White solid, 91% yield, M.p. 51 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.82-0.88 (m, 2.2H), 0.91-1.01 (m, 5.8H), 1.05-1.18 (m, 0.4H), 1.26-1.41 (m, 0.4H), 1.41-1.50 (m, 0.4H), 1.51-1.72 (m, 1.4H), 3.60 (s, 2.6H), 3.78 (s, 0.4H), 4.18-4.36 (brd, 0.4H), 4.44-4.60 (m, 0.6H), 7.10-7.20 (m, 2H), 7.26-7.34 (m, 1H), 7.62 (dt, J = 8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz): δ = ^{13}C NMR (100 MHz): δ = 17.4, 20.2, 21.7, 22.3, 23.5, 23.8, 25.3, 25.4, 43.1, 46.2, 52.6, 52.9, 53.0, 53.9, 125.8, 126.4, 128.0, 128.8, 128.9, 130.5, 130.6, 133.6, 138.4, 139.5, 155.4, 155.7. MS (ESI, 70 eV): *m/z* (%) = 314 $(M+H)^+$; IR (neat): υ = 728, 757, 784, 950, 1030, 1061, 1108, 1168, 1191, 1264, 1290, 1317, 1366, 1389, 1400, 1474, 1585, 1705, 2954 cm^{-1}; ESI-HRMS calcd. for $C_{14}H_{21}BrNO$ 314.0750, found 314.0748.

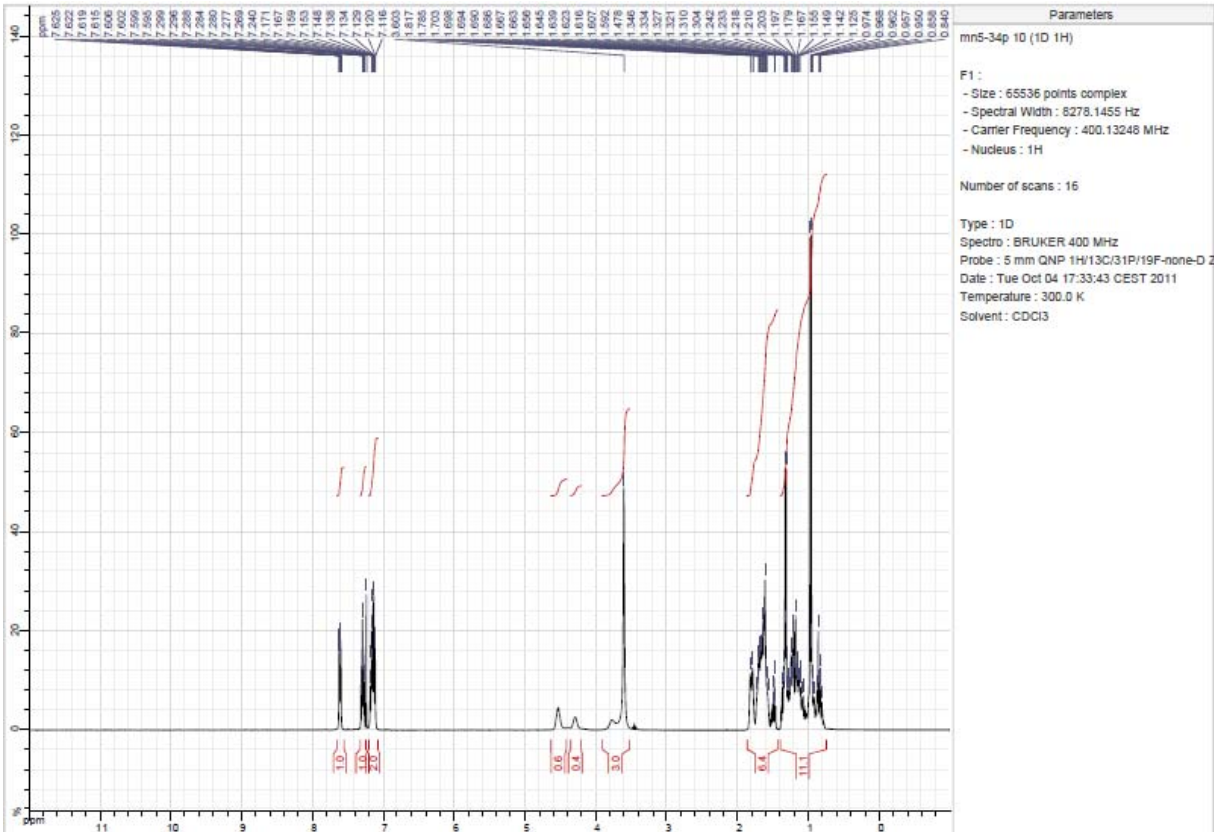


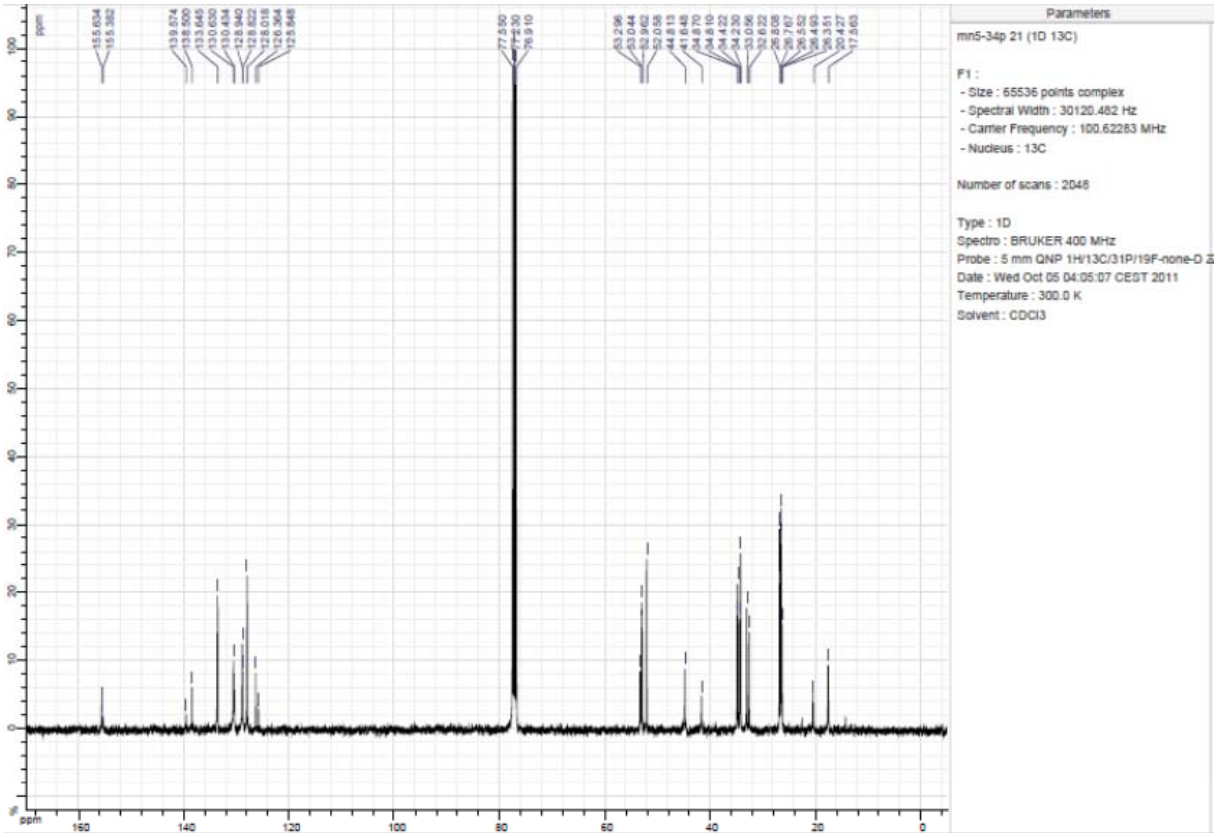


Methyl (2-bromophenyl)(1-cyclohexylpropan-2-yl)carbamate **6i**:

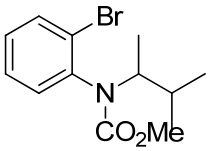


White solid, 94% yield, M.p. 59 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.75-1.40 (m, 11.1H), 1.44-1.87 (m, 5.9H), 3.60 (s, 3H), 4.21-4.36 (m, 0.4H), 4.42-4.64 (m, 0.6H), 7.08-7.21 (m, 2H),7.25-7.33 (m, 1H), 7.56-7.66 (m, 1H). ^{13}C NMR (100 MHz): δ = 17.6, 20.4, 26.4, 26.5, 26.6, 26.8, 26.8, 41.6, 44.8, 52.1, 53.0, 53.0, 53.3, 125.8, 126.4, 128.0, 128.8, 128.9, 130.4, 130.6, 133.6, 138.5, 139.6, 155.4, 155.6. MS (ESI, 70 eV): *m/z* (%) = 354 $(M+H)^+$; IR (neat): υ = 728, 755, 843, 877, 950, 1030, 1068, 1115, 1190, 1264, 1286, 1314, 1370, 1391, 1440, 1475, 1586, 1606, 2850, 2921 cm^{-1}; ESI-HRMS calcd. for $C_{17}H_{25}BrNO_2$ 354.1063, found 354.1054.

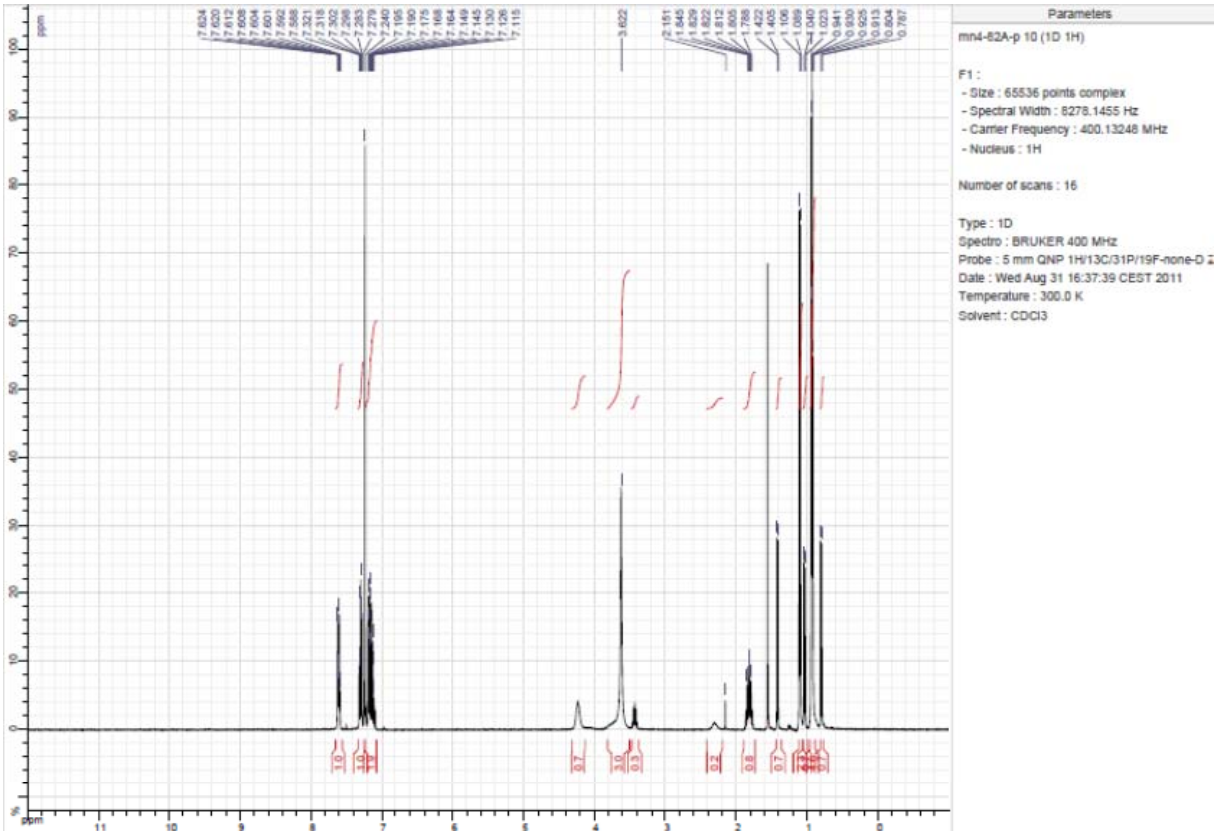


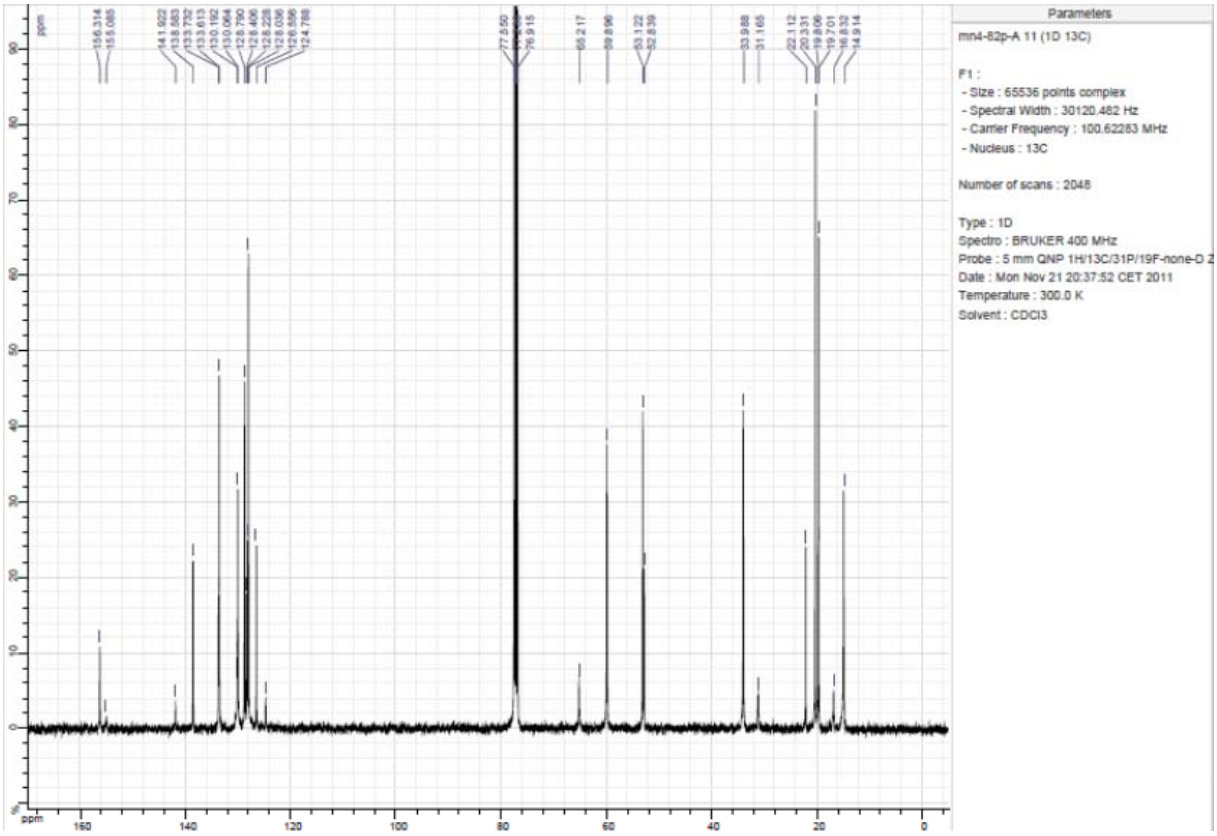


Methyl (2-bromophenyl)(3-methylbutan-2-yl)carbamate **6j**:

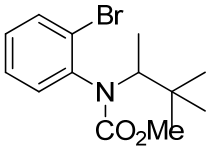


Colorless oil, 88% yield, ^{1}H NMR (400 MHz, $CDCl_3$): 0.80 (d, J = 6.8 Hz, 0.7H), 0.92 (d, J = 6.8 Hz, 2.3H), 0.93 (d, J = 6.4 Hz, 2.3H), 1.03 (d, J = 7.6 Hz, 0.7H), 1.10 (d, J = 6.8 Hz, 1H), 1.74-1.90 (m, 0.8H), 2.20-2.42 (m, 0.2H), 3.38-3.48 (m, 0.3 H), 3.62 (s, 3H), 4.14-4.32 (m, 0.7H), 7.08-7.23 (m, 2H), 7.30 (td, J = 7.6, 1.2 Hz, 1H), 7.56-7.66 (m, 1H). ^{13}C NMR (100 MHz): δ 14.9, 16.8, 19.7, 19.8, 20.3, 22.1, 31.2, 34.0, 52.8, 53.1, 59.9, 65.2, 124.8, 126.6, 128.0, 128.2, 128.4, 128.8, 130.1, 130.2, 133.6, 133.7, 138.6, 141.9, 155.1, 156.3. MS (ESI, 70 eV): m/z (%) = 300 $(M+H)^+$; IR (neat): υ = 731, 755, 900, 949, 986, 1031, 1054, 1092, 1109, 1160, 1191, 1262, 1306, 1383, 1440, 1474, 1585, 1706, 2875, 2964 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{19}BrNO_2$ 300.0593, found 300.0583.

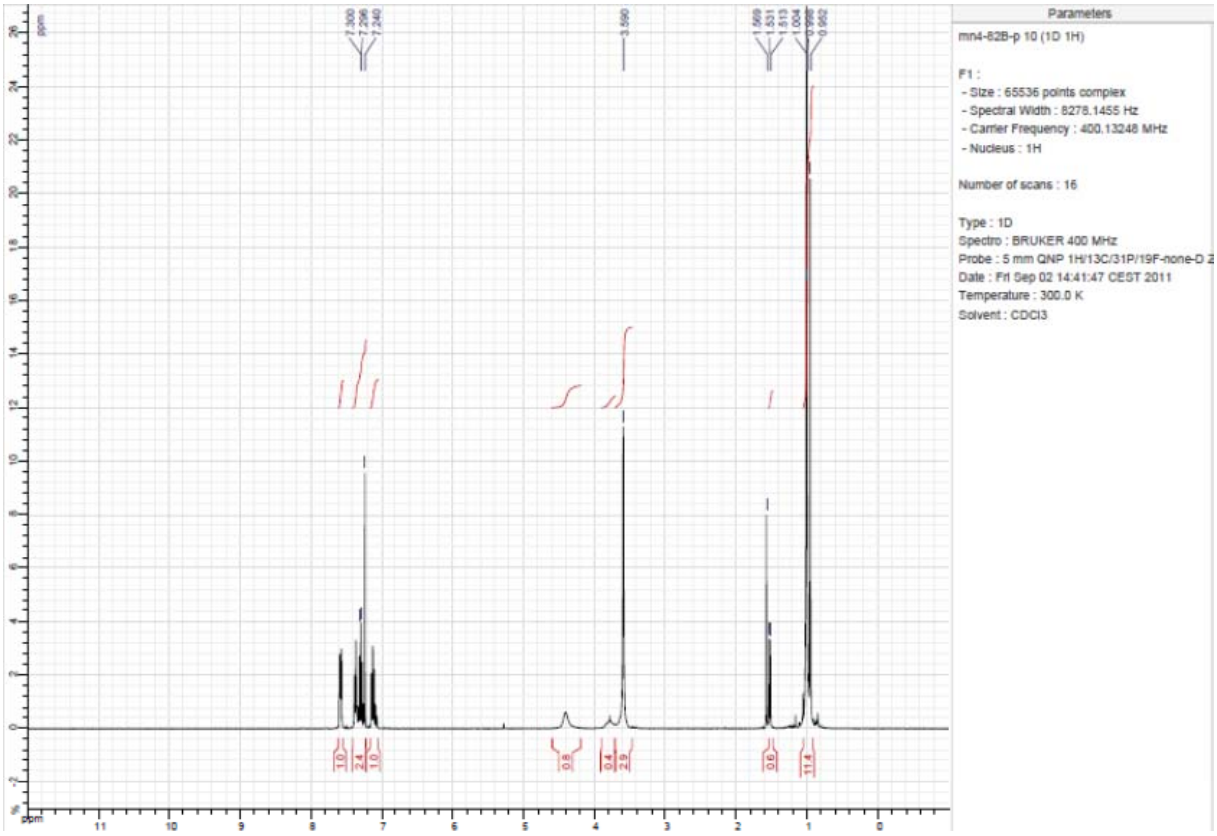




Methyl (2-bromophenyl)(3,3-dimethylbutan-2-yl)carbamate **6k**:



White solid, 48% yield, M.p. 67 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): 0.92-1.06 (m, 11.6H), 1.52 (d, J = 7.2 Hz, 0.6H), 3.59 (s, 3H), 3.71-3.91 (m, 0.2H), 4.20-4.60 (m, 0.8H), 7.06-7.17 (m, 1H), 7.23-7.41 (m, 2H), 7.55-7.62 (m, 1H). ^{13}C NMR (100 MHz): δ = 12.6, 16.4, 27.8, 28.5, 36.6, 36.9, 53.0, 53.2, 57.0, 58.9, 62.1, 66.4, 126.7, 127.6, 127.8, 128.3, 128.7, 131.3, 133.5, 134.1, 140.2, 142.6, 156.0. MS (ESI, 70 eV): m/z (%) = 314 $(M+H)^+$; IR (neat): υ = 731, 755, 900, 949, 986, 1031, 1054, 1092, 1109, 1160, 1191, 1261, 1306, 1283, 1440, 1474, 1585, 1706, 2875, 2964 cm^{-1}; ESI-HRMS calcd. for $C_{14}H_{21}BrNO_2$ 314.0750, found 314.0752.



1.4 Representative racemic synthesis of indolines 2 and 7:

Carbamate (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), pivalic acid (6.1 mg, 0.06 mmol), cecium carbonate (97.5 mg, 0.3 mmol), and $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol) were sequentially filled into a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylenes were added under nitrogen and the resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield overnight (17-24 h). The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the racemic indoline.

1.5 Racemic synthesis of indoline 7a using $PCy_3 \cdot HBF_4$ as a ligand:

Substrate **6a** (57.2 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), pivalic acid (6.1 mg, 0.06 mmol), cecium carbonate (97.5 mg, 0.3 mmol), and $PCy_3 \cdot HBF_4$ (14.7 mg, 0.04 mmol) were placed into a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylenes 2 mL were added under nitrogen and the resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 17 hours. The reaction mixture was

cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c. (silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the racemic indoline **7a** in 91% yield (37.3 mg).

Racemic synthesis of indoline 7a using IPr·HCl as a ligand:

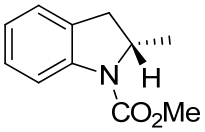
Substrate **6a** (57.2 mg, 0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), [Pd(π-cinnamyl)Cl]$_2$ (5.2 mg, 0.01 mmol), cesium pivalate (46.8 mg, 0.2 mmol) and IPr·HCl (8.5 mg, 0.02 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylene (2 mL) was added under nitrogen. The resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 17 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through the pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c.(silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the indoline **7a** in 91% yield (37.5 mg).

1.6 Representative procedure for the asymmetric NHC-palladium catalyzed C-H activation:

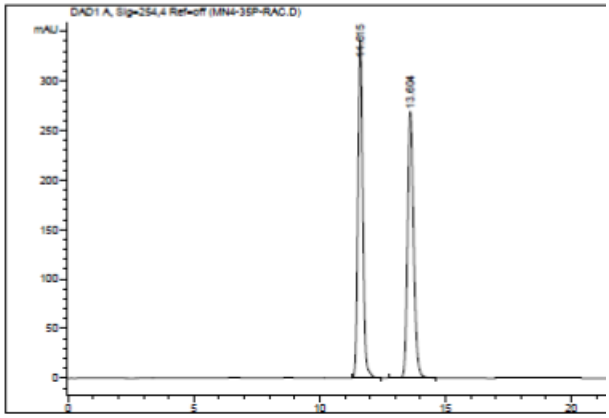
Carbamate **1a** (62.4 mg, 0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), [Pd(π-cinnamyl)Cl]$_2$ (2.6 mg, 0.005 mmol), cesium pivalate (46.8 mg, 0.2 mmol) and NHC·HI (0.01 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry mesitylene (2 mL) was added under nitrogen. The resulting reaction mixture was stirred at 160 °C in the Schlenk tube behind a protective shield for 3 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c.(silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the indoline methyl carbamate **2a**.

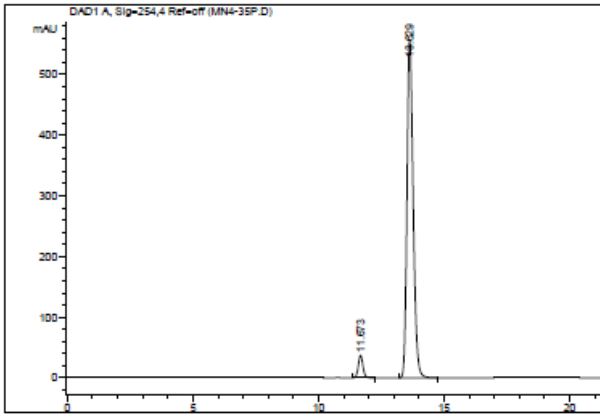
1.7 Synthesis, spectra, analysis of substrates 2a-d and 7a-h, and 8a-h

(*S*)-methyl 2-methylindoline-1-carboxylate **2a**: [3]



Colorless oil, 84% yield (32.1 mg), 90% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$): 1.27 (d, J = 7.2 Hz, 1H), 2.62 (dd, J = 16, 2 Hz, 1H), 3.35 (dd, J = 16, 9.6 Hz, 1H), 3.83 (s, 3H), 4.40-4.65 (m, 1H), 6.57 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.44-8.10 (brd, 1H).





Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.615	BB	0.2055	4543.38916	340.79941	50.1157
2	13.604	BB	0.2601	4522.40381	268.98697	49.8843
Totals :				9065.79297	609.78638	

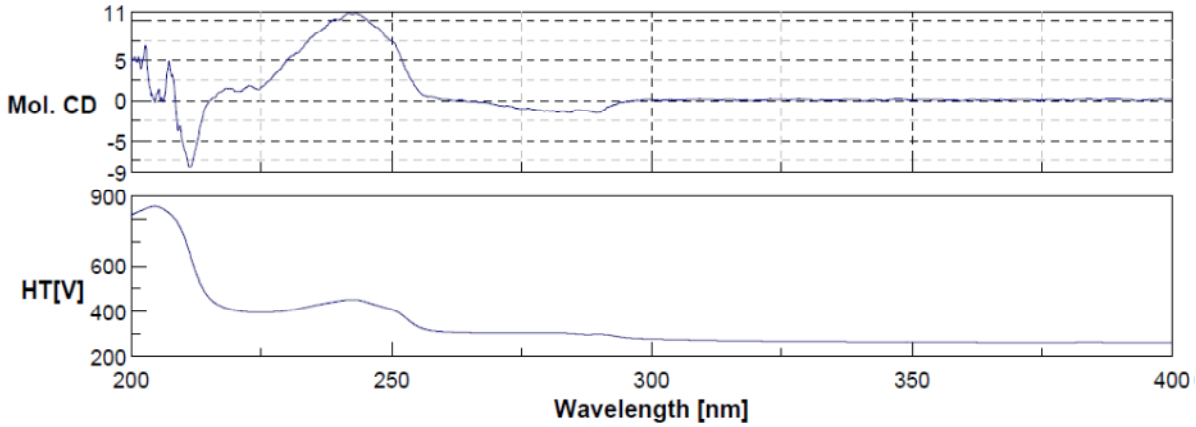
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

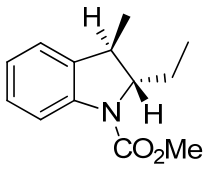
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.673	BB	0.1985	483.13275	37.44048	4.8096
2	13.629	BB	0.2643	9562.10547	557.08234	95.1904
Totals :				1.00452e4	594.52282	

The enantiomer ration was determined by HPLC: (chiral column: AS-H, *n*-hexane/ *i*-propanol = 99 : 1, 0.5 mL/min, 254 nm); t_R = 11.7 min [minor] and 13.6 min [major]. $[\alpha]_D^{20}$ = +52.0 (*c* = 0.5 in CH_2Cl_2).

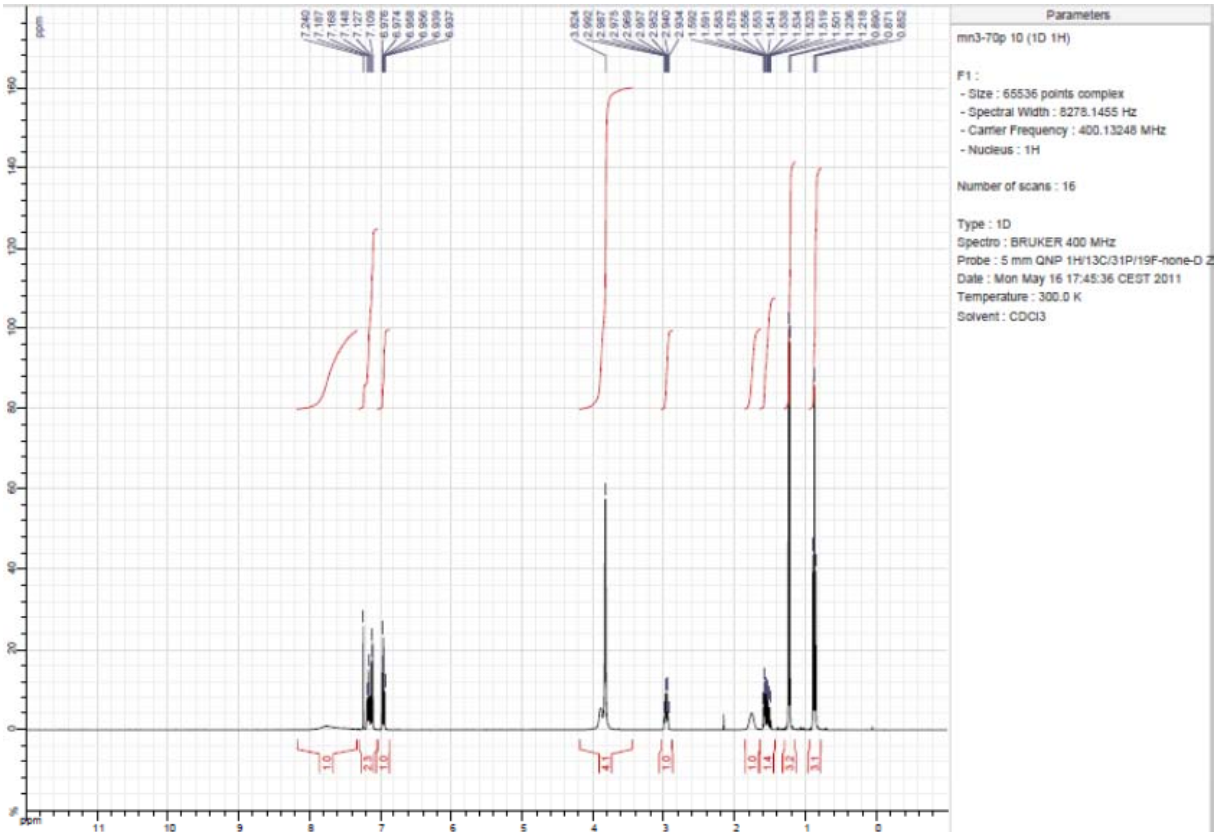


CD spectrum: 0.000052 M in *n*-hexane at 20 °C

(2*S*,3*R*)-methyl 2-ethyl-3-methylindoline-1-carboxylate **2b**:



Colorless oil, 92% yield (40.3 mg), 97% *ee,* ^{1}H NMR (400 MHz, $CDCl_3$): 0.87 (t, J = 7.6 Hz, 3H), 1.23 (d, J = 6.8 Hz, 3H), 1.46-1.61 (m, 1H), 1.70-1.82 (m, 1H), 2.96 (qd, J = 6.8, 1.6 Hz, 1H), 3.82 (s, 3H), 3.78-3.98 (m, 1H), 7.03 (s, 1H), 6.96 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.34-8.12 (brd, 1H). ^{13}C NMR (100 MHz): δ = 9.2, 22.8, 27.1, 40.2, 52.7, 66.9, 115.4, 123.0, 124.4, 127.8, 136.2, 136.4, 154.2. MS (ESI, 70 eV): *m/z* (%) = 220 $(M+H)^+$; IR (neat): υ = 753, 820, 1019, 1065, 1137, 1192, 1216, 1284, 1312, 1335, 1391, 1441, 1485, 1602, 1706, 2963 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{18}NO_2$ 220.1332, found 220.1332.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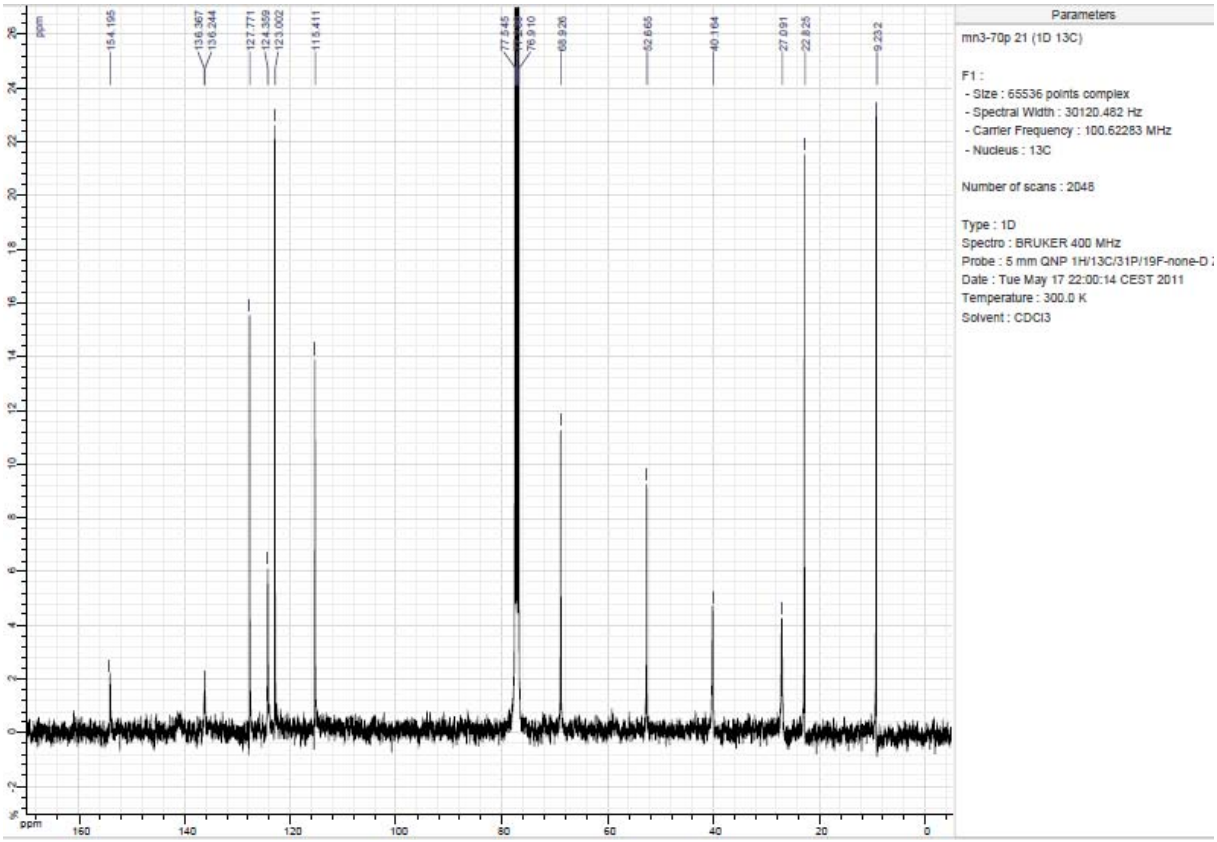
F1 :
- Size : 65536 points complex
- Spectral Width : 8278.1455 Hz
- Carrier Frequency : 400.13248 MHz
- Nucleus : 1H
Number of scans : 16
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F-none-D Z
Date : Mon May 16 17:45:36 CEST 2011
Temperature : 300.0 K
Solvent : CDCl3


Parameters
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F1 :
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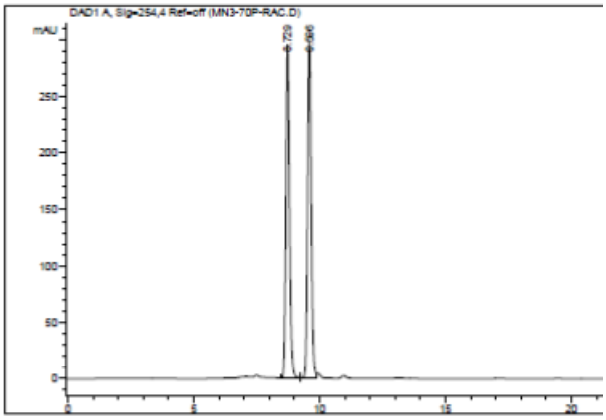
- Spectral Width : 30120.482 Hz
- Carrier Frequency : 100.62283 MHz
- Nucleus : 13C
Number of scans : 2048
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F-none-D
Date : Tue May 17 22:00:14 CEST 2011
Temperature : 300.0 K
Solvent : CDCl3



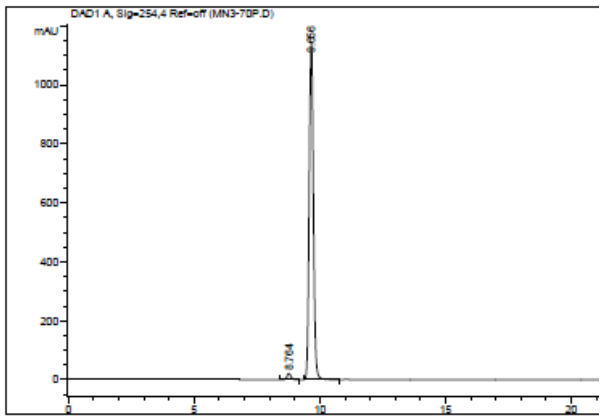
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.729	VV	0.1534	2972.20752	295.36627	49.9283
2	9.596	VV	0.1545	2980.74219	298.47058	50.0717

Totals : 5952.94971 593.83685



Area Percent Report

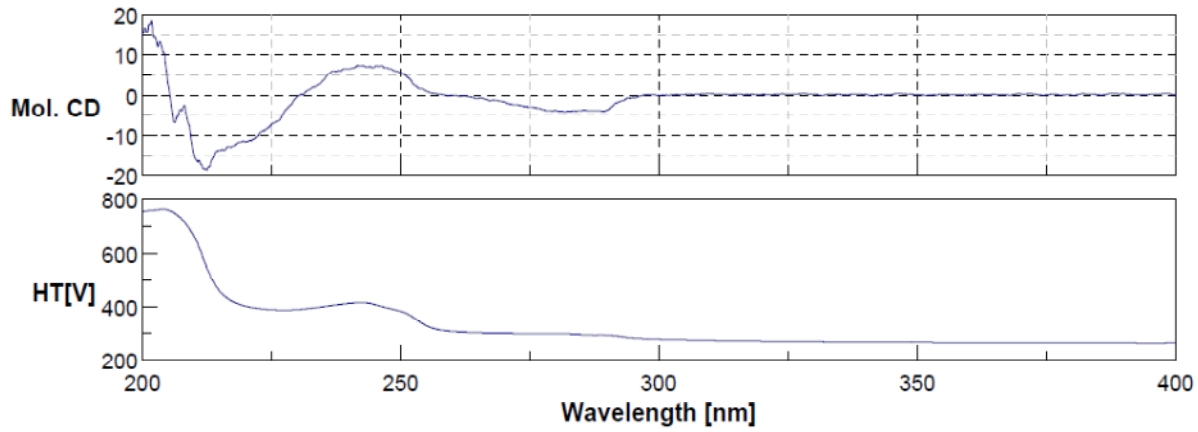
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.764	VB	0.1688	231.71776	21.32372	1.7403
2	9.656	BB	0.1793	1.30829e4	1145.18262	98.2597

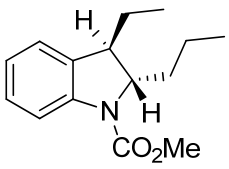
Totals : 1.33146e4 1166.50634

The ratio of enantiomers was determined by HPLC: (chiral column: AS-H, *n*-hexane/ *i*-propanol = 99 : 1, 0.5 mL/min, 254 nm); t_R = 8.7 min [minor] and 9.6 min [major]. $[\alpha]_D^{20}$ = +6.3 (*c* = 1.0 in CH_2Cl_2).

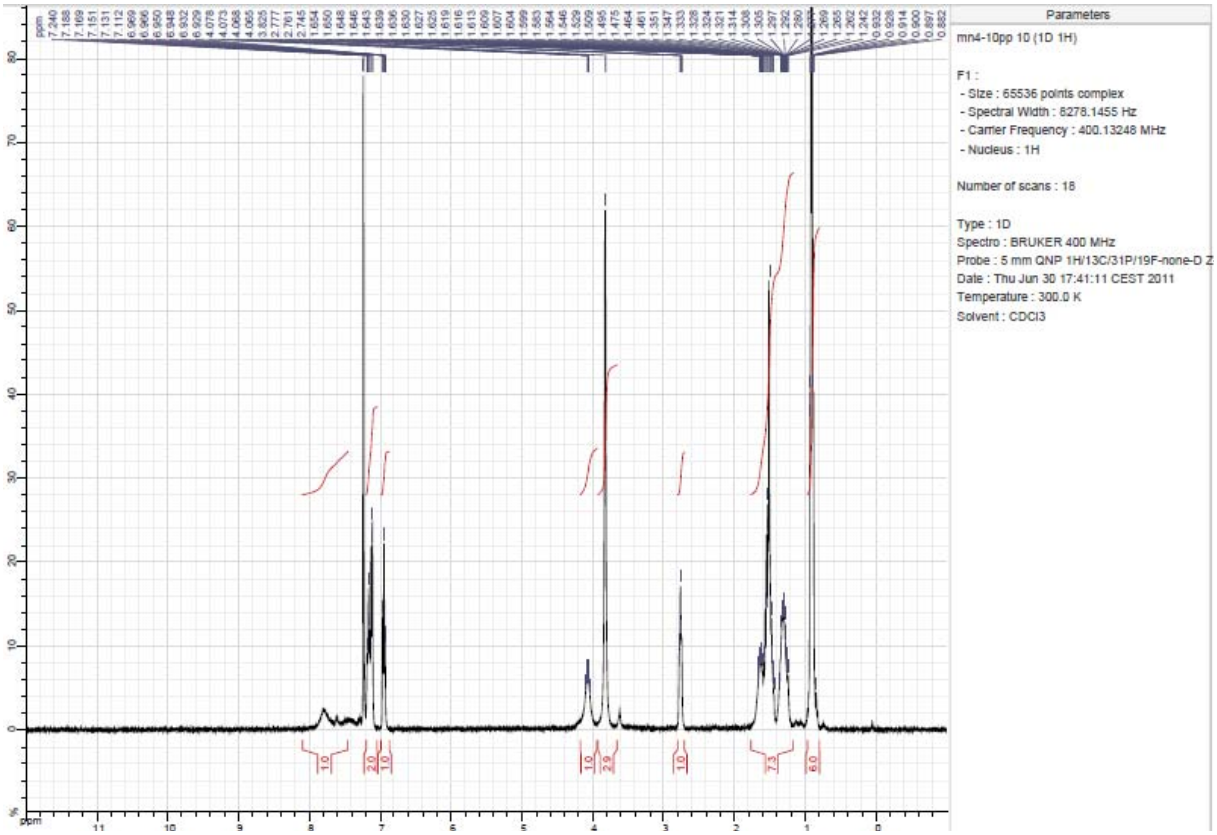


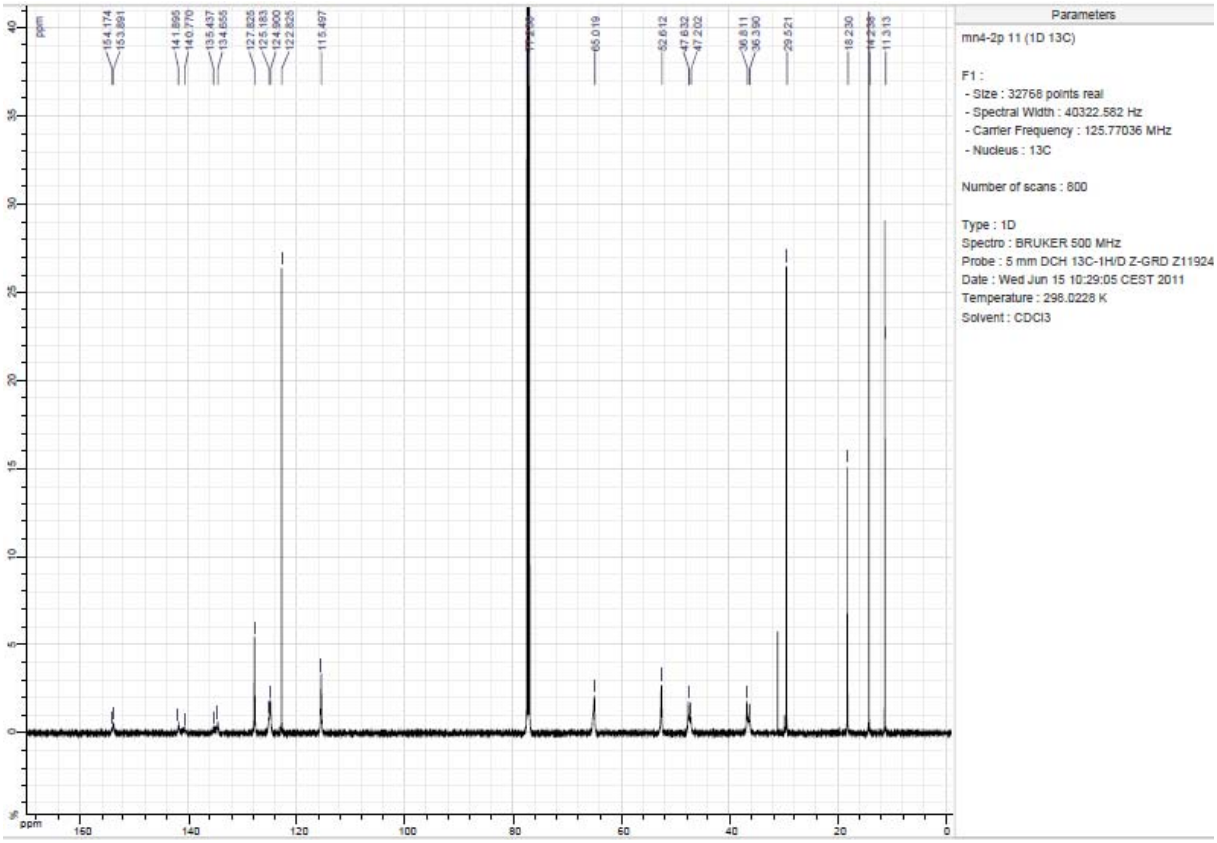
CD spectrum: 0.000023 M in *n*-hexane at 20 °C

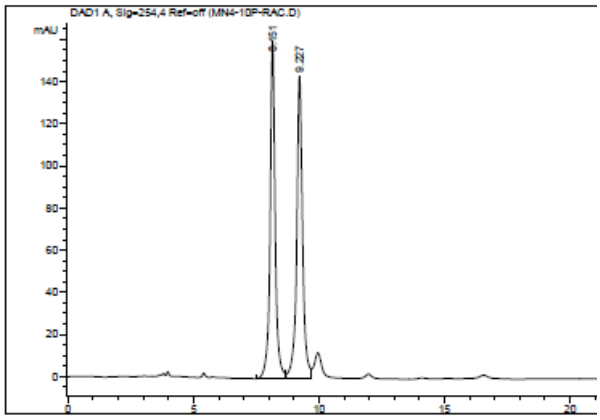
(2*S*,3*R*)-methyl 3-ethyl-2-propylindoline-1-carboxylate **2c**:

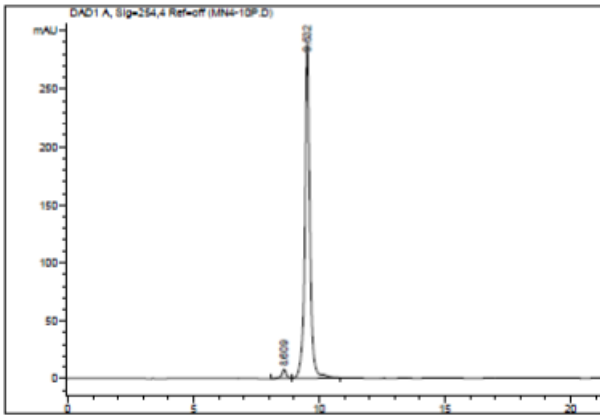


Colorless oil, 92% yield (45.4 mg), 97% *ee,* ^{1}H NMR (400 MHz, $CDCl_3$): 0.81-0.98 (m, 6H), 1.18-1.78 (m, 6H), 2.76 (t, J = 6.4 Hz, 1H), 3.83 (s, 3H), 3.95-4.18 (m, 1H), 6.95 (td, J = 7.6, 0.8 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.46-8.10 (m, 1H). ^{13}C NMR (100 MHz): δ = 11.3, 14.2, 18.2, 29.5, 31.1, 36.4, 36.8, 47.2, 47.6, 52.6, 65.0, 115.5, 122.8, 124.9, 125.2, 127.8, 134.7, 135.4, 140.8, 141.9, 153.9, 154.2. MS (ESI, 70 eV): *m/z* (%) = 248 $(M+H)^+$; IR (neat): υ = 748, 794, 869, 931, 1022, 1064, 1116, 1135, 1190, 1209, 1269, 1284, 1306, 1332, 1389, 1441, 1461, 1483, 1602, 1703, 2873, 2931, 2958 cm^{-1}; ESI-HRMS calcd. for $C_{15}H_{22}NO_2$ 248.1645, found 248.1642.









Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.151	BV	0.2100	2278.67578	160.18820	49.6975
2	9.227	VV	0.2374	2306.41821	143.60440	50.3025
Totals :				4585.09399	303.79260	

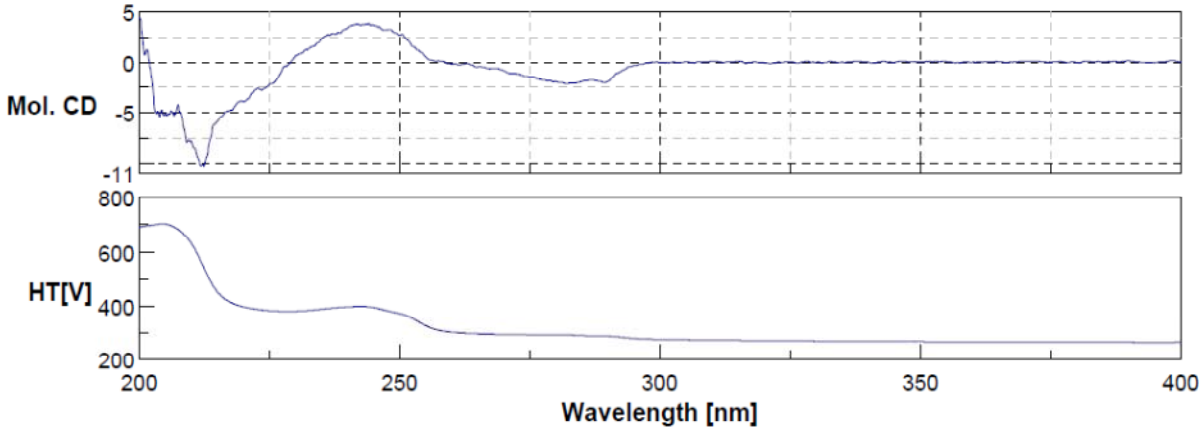
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

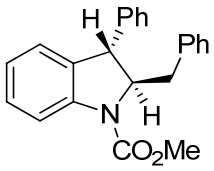
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.609	BV	0.1815	96.41615	7.73317	2.3341
2	9.532	VB	0.2040	4034.26855	290.59344	97.6659
Totals :				4130.68470	298.32661	

The enantiomer ratio was determined by HPLC: (chiral column: (*R*,*R*)-Whelk-O1, *n*-hexane/*i*-propanol = 99.05 : 0.5, 1.0 mL/min, 254 nm); t_R = 8.2 min [minor] and 9.3 min [major]. $[\alpha]_D^{20}$ = +9.0 (*c* = 2.0 in CH_2Cl_2).

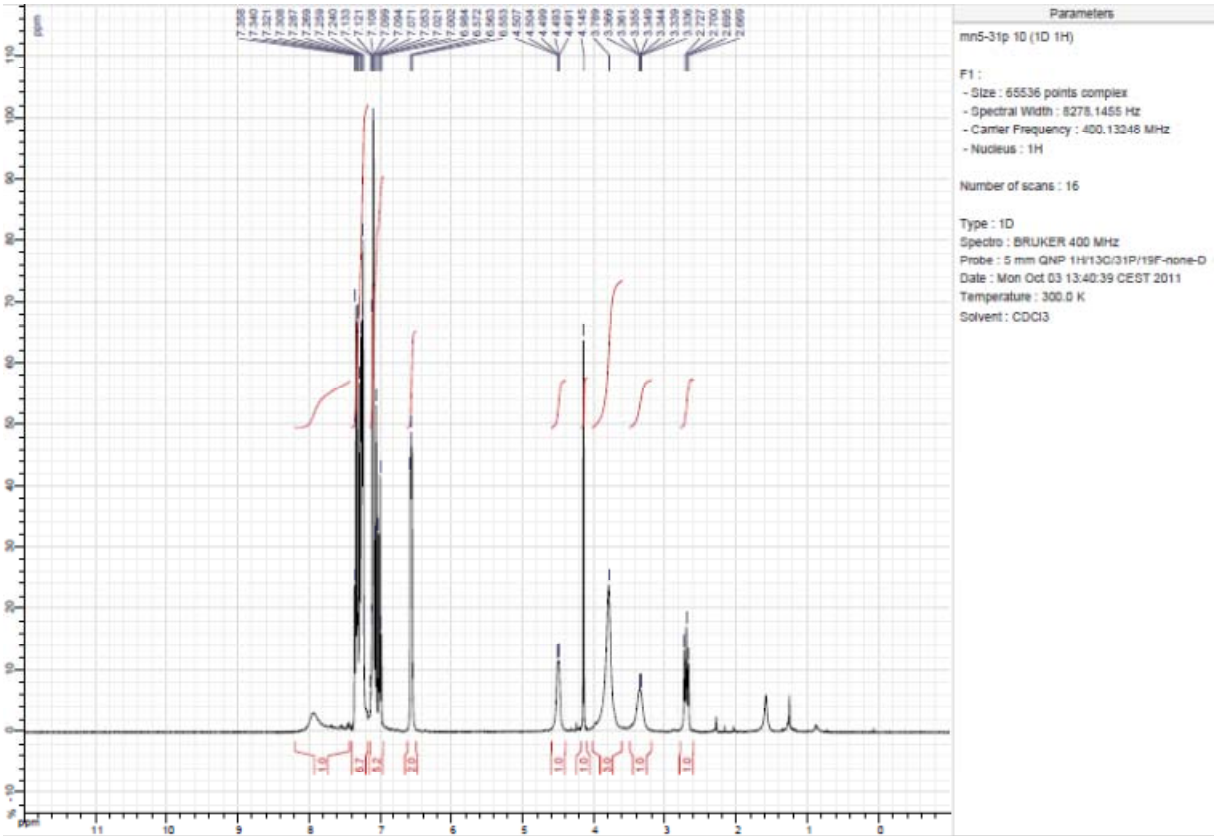


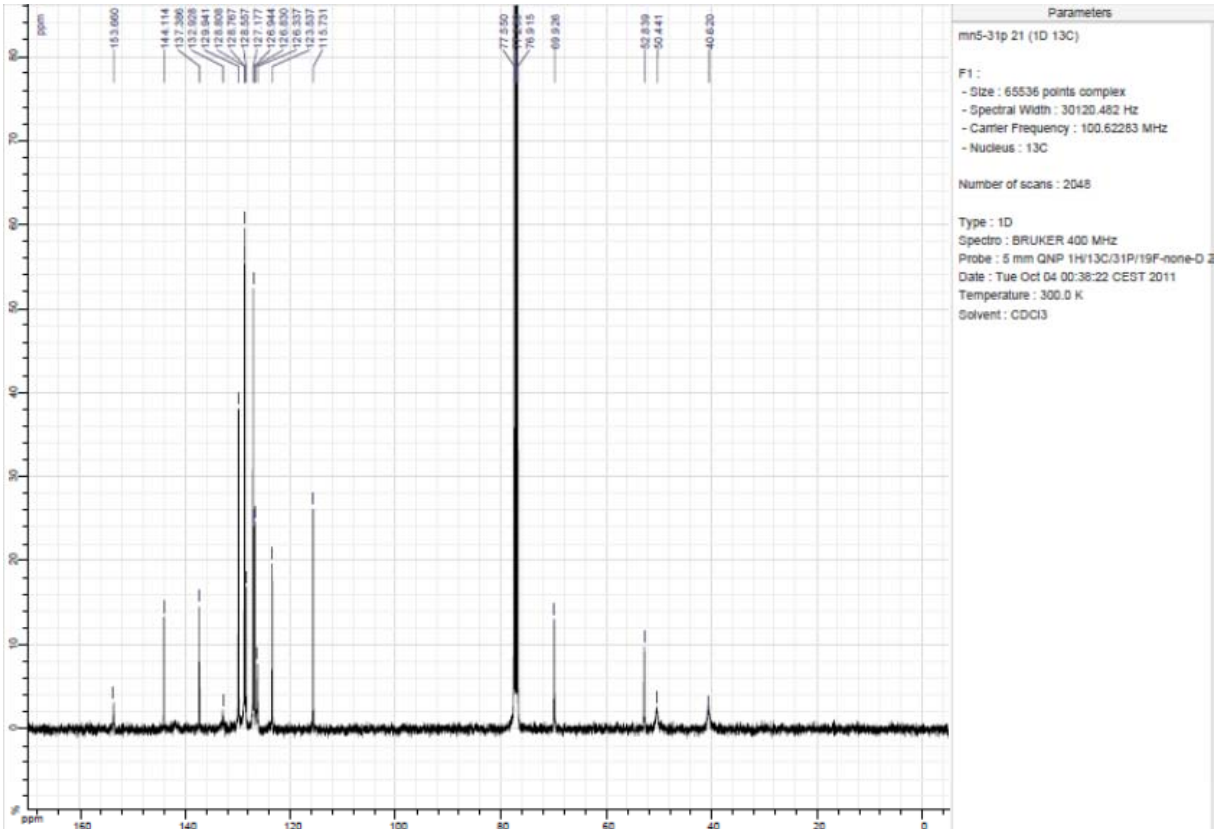
CD spectrum: 0.000049 M in *n*-hexane at 20 °C

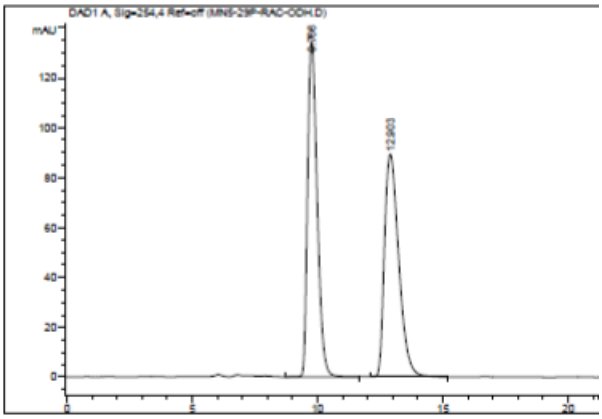
(2*R*,3*S*)-methyl 2-benzyl-3-phenylindoline-1-carboxylate **2d**:

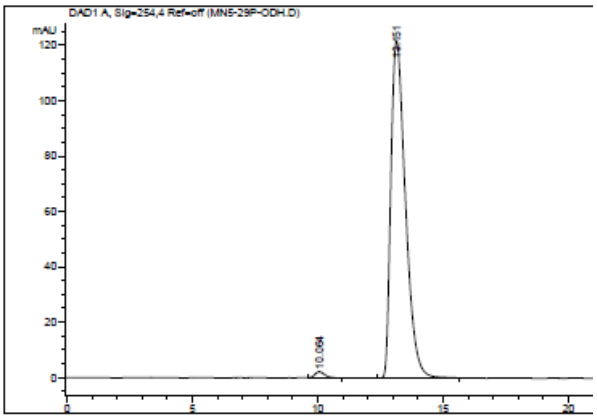


White solid, 82% yield (56.3 mg), M.p. 75 ºC, 98% *ee,* ^{1}H NMR (400 MHz, $CDCl_3$): 2.70 (dd, *J* = 12.8, 10.8 Hz, 1H), 3.20-3.50 (brd, 1H), 3.79 (s, 3H), 4.15 (s, 1H), 4.40-4.60 (m, 1H), 6.50-6.62 (m, 2H), 6.96-7.14 (m, 5H), 7.18-7.41 (m, 6H),.44-8.20 (brd, 1H). ^{13}C NMR (100 MHz): δ = 40.6, 50.4, 52.8, 69.9, 115.7, 123.5, 126.3, 126.8, 126.9, 127.2, 128.6, 128.8, 128.8, 129.9, 132.9, 137.4, 144.1, 153.7. MS (ESI, 70 eV): *m/z* (%) = 344 $(M+H)^+$; IR (neat): υ = 698, 733, 757, 792, 849, 878, 919, 1057,1079, 1136, 1157, 1193, 1246, 1278, 1304, 1342, 1390, 1441, 1484, 1598, 1711, 2952, 3027 cm^{-1}; ESI-HRMS calcd. for $C_{23}H_{22}NO_2$ 344.1645, found 344.1648.


Parameters
mn5-31p 10 (1D 1H)
F1 :
- Size : 65536 points complex
- Spectral Width : 8278.1455 Hz
- Carrier Frequency : 400.13248 MHz
- Nucleus : 1H
Number of scans : 16
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F-none-D
Date : Mon Oct 03 13:40:39 CEST 2011
Temperature : 300.0 K
Solvent : CDCl3


Parameters
mn5-31p 21 (1D 13C)
F1 :
- Size : 65536 points complex
- Spectral Width : 30120.482 Hz
- Carrier Frequency : 100.62283 MHz
- Nucleus : 13C
Number of scans : 2048
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F-none-D
Date : Tue Oct 04 00:38:22 CEST 2011
Temperature : 300.0 K
Solvent : CDCl3





Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.766	VB	0.4148	3584.62671	134.57677	50.1972
2	12.903	BB	0.6243	3556.45947	89.36578	49.8028

Area Percent Report

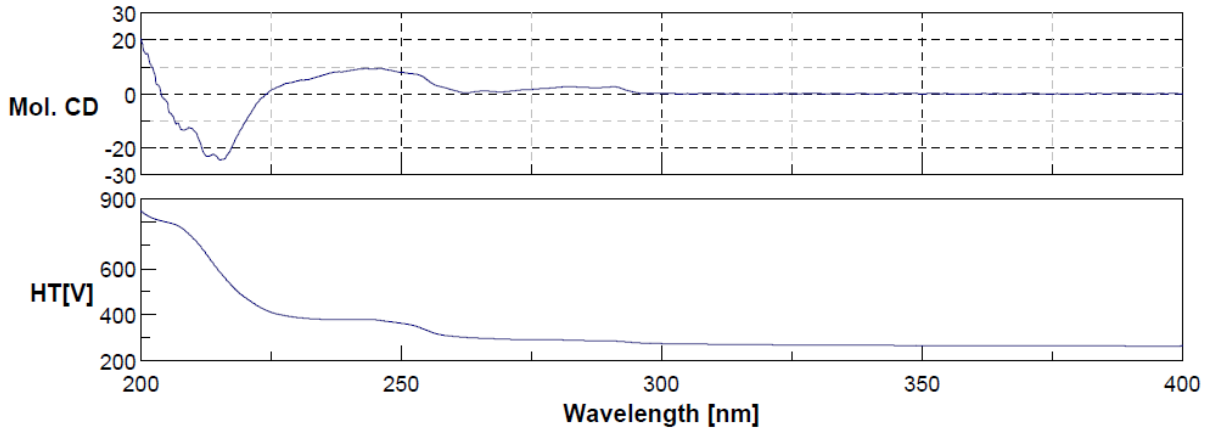
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.064	VB	0.4191	59.28425	2.19530	1.1900
2	13.151	BB	0.6320	4922.44824	121.66162	98.8100

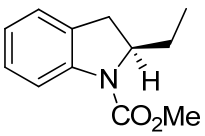
Totals : 4981.73249 123.85693

The ratio of enantiomers was determined by HPLC: (chiral column: OD-H, *n*-hexane/ *i*-propanol = 99 : 1, 1.0 mL/min, 254 nm); t_R = 10.1 min [minor] and 13.2 min [major]. $[\alpha]_D^{20}$ = +107.8 (*c* = 1.0 in CH_2Cl_2).

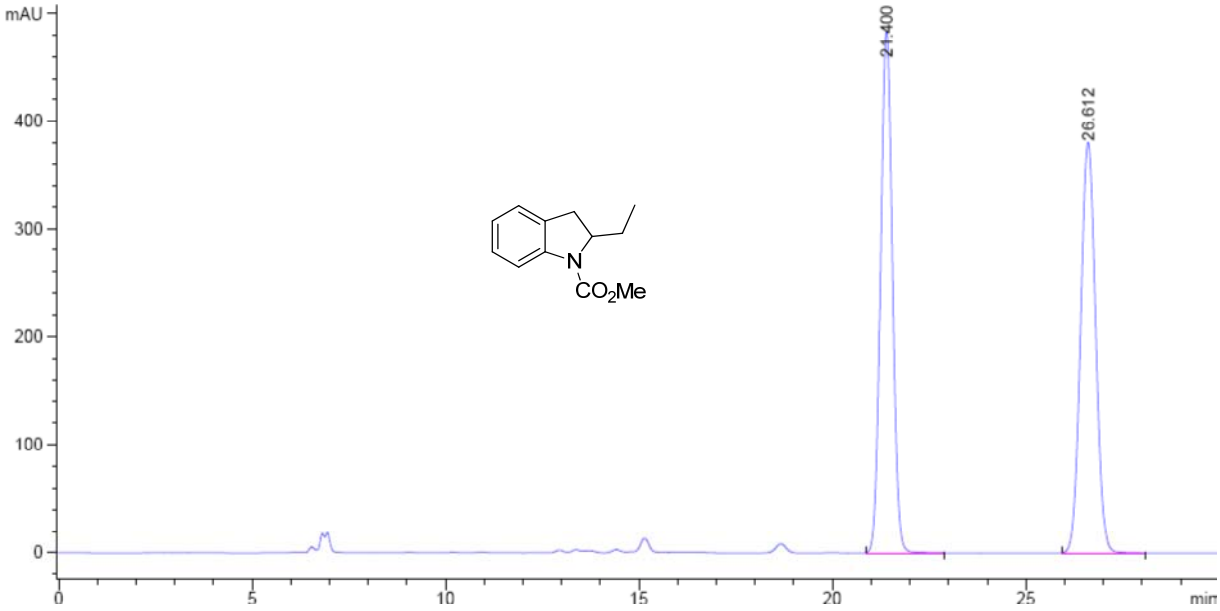


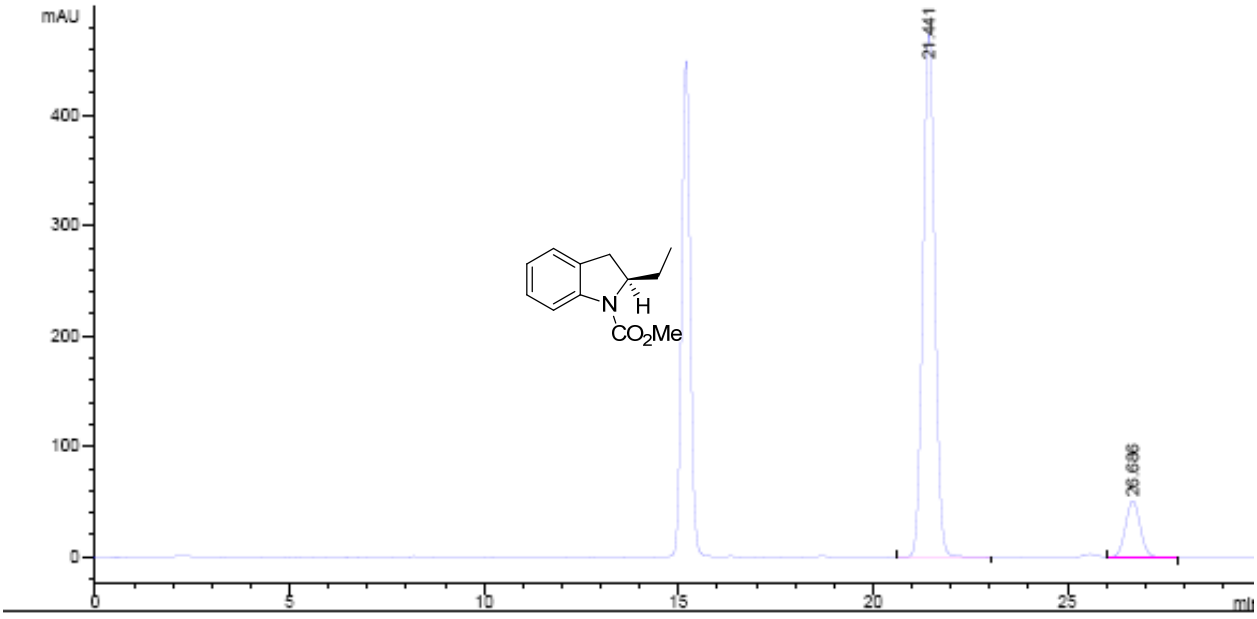
CD spectrum: 0.000052 M in *n*-hexane at 20 °C

(*R*)-methyl 2-ethylindoline-1-carboxylate **7a**; (*S*,*S*)-NHC·HI (**3**) was used.



Colorless oil, 57% yield calcd. by NMR (23.2 mg), 77% *ee,* ^{1}H NMR (400 MHz, $CDCl_3$): 0.86 (t, J = 7.6 Hz, 3H), 1.49-1.63 (m, 1H), 1.67-1.87 (m, 1H), 2.74 (dd, J = 16, 2.4 Hz, 1H), 3.27 (dd, J = 16, 9.6 Hz, 1H), 3.82 (s, 3H), 4.28-4.46 (m, 1H), 6.94 (td, J = 7.2, 0.8 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.34-8.10 (m, 1H).



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---------------------------------------------------------------------
                        Area Percent Report
---------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

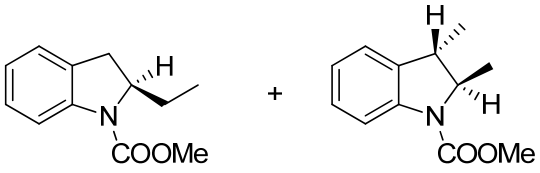
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  21.441 BB    0.3470 1.01076e4   469.88608  88.2174
   2  26.686 VB    0.4205 1350.00818   51.04708  11.7826

Totals :                  1.14576e4   520.93316

---------------------------------------------------------------------
                        *** End of Report ***
```

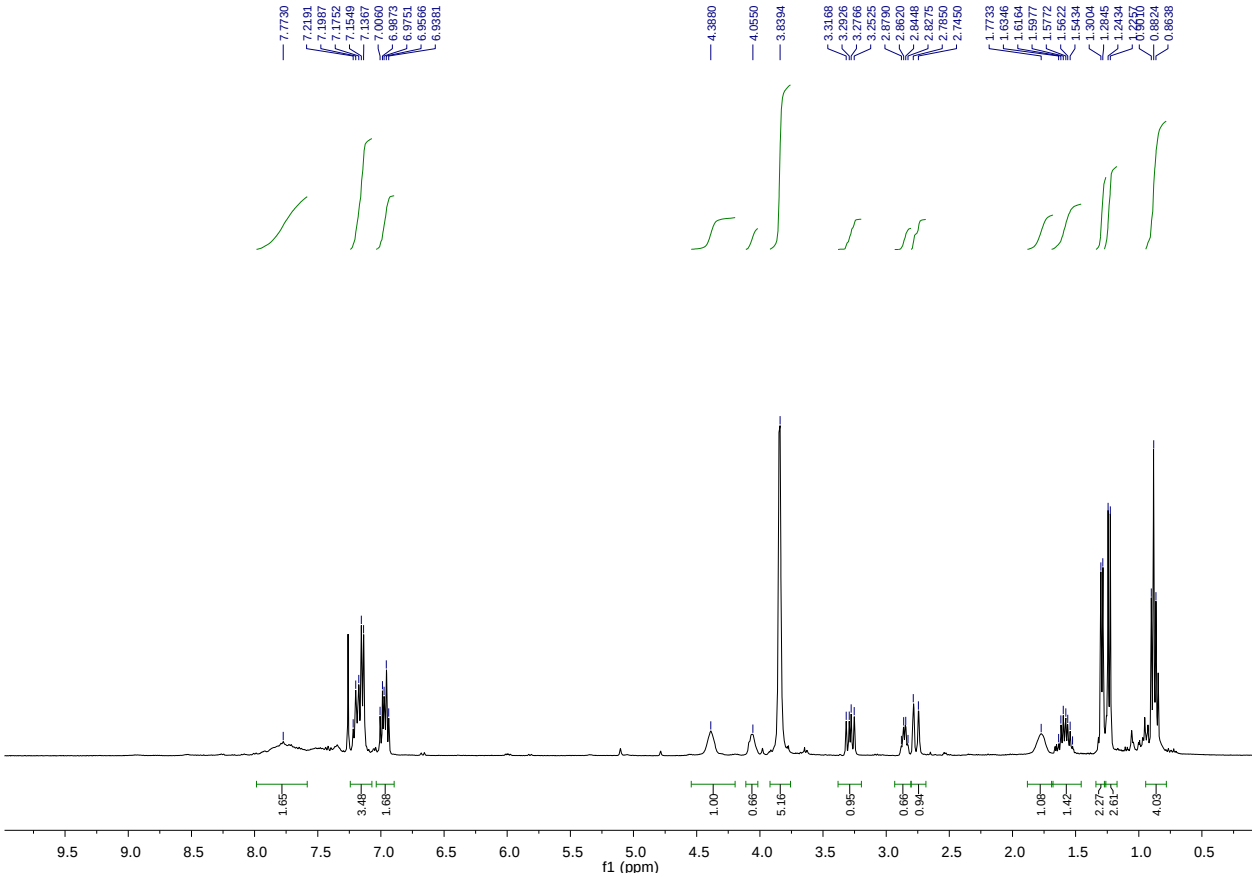
76% *ee* [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 21.44 min. (major) and 26.68 (minor)].

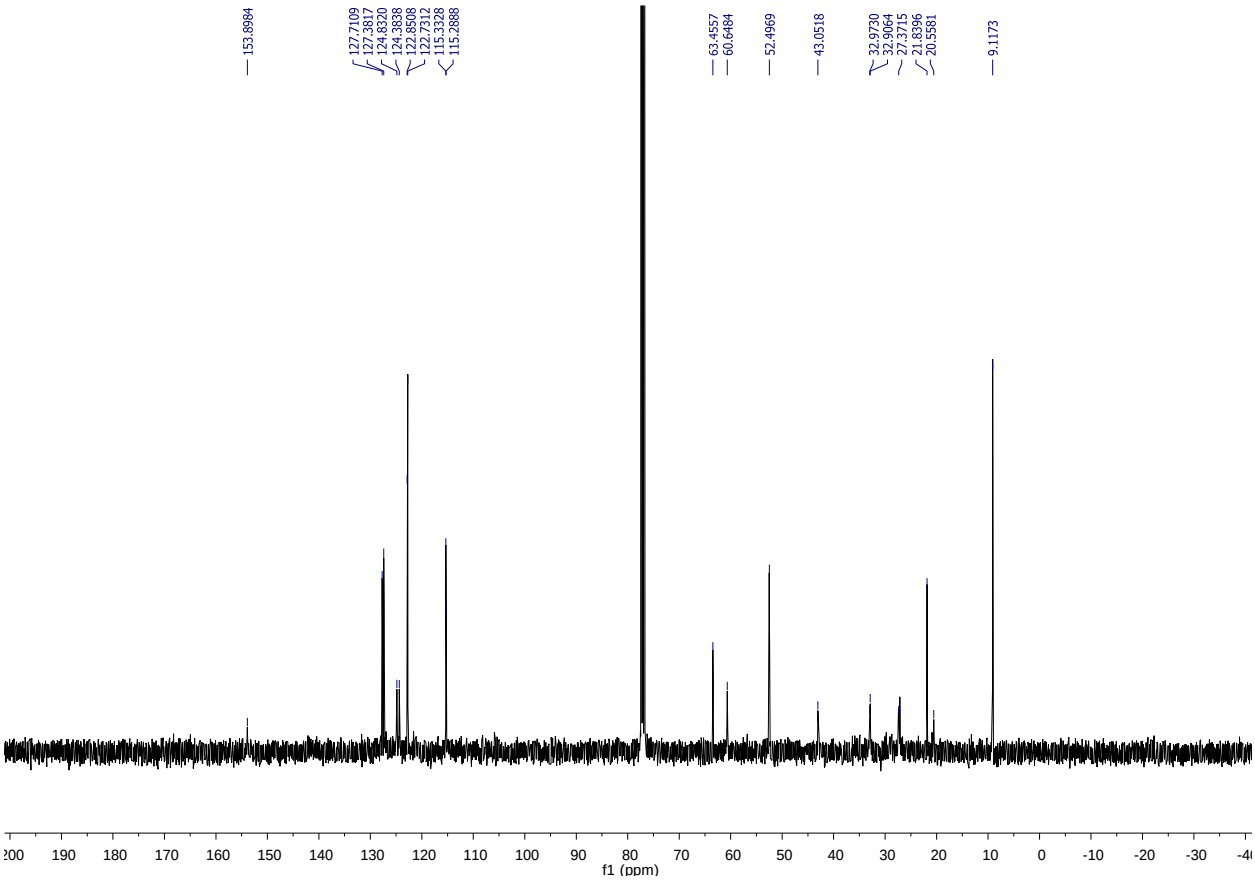
(*R*)-methyl 2-ethylindoline-1-carboxylate **7a** and (2*R*,3*S*)-methyl 2,3-dimethylindoline-1-carboxylate **8a**; (*S*,*S*)-NHC·HI (**3**) was used.



Colorless oil, **8a**: 38% yield calcd. by NMR (15.5 mg), **7a** + **8a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.4 Hz, 4H), 1.23 (d, *J* = 7.0 Hz, 2.6H), 1.29 (d, *J* = 6.3 Hz, 2.2H), 1.52-1.63 (m,

1.4H), 1.77 (brd, 1H), 2.76 (d, J = 16.0 Hz, 1H), 2.85 (q, J = 6.8 Hz, 0.65H), 3.28 (dd, J = 16.0, 9.6 Hz, 1H), 3.83 (s, 5H), 4.05 (brd, 0.65H), 4.38 (brd, 1H), 6.93-7.00 (m, 1.65H), 7.13-7.21 (m, 3.5H), 7.77 (brd, 1.65H). **7a** + **8a**: ^{13}C NMR (100 MHz, $CDCl_3$): 9.1, 20.5, 21.8, 27.3, 32.90, 32.97, 43.0, 52.4, 60.6, 63.4, 115.2, 115.3, 122.7, 122.8, 124.3, 124.8, 127.3, 127.7, 153.8.

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127.3817
124.8320
124.3838
122.8508
122.7312
115.3328
115.2888
63.4557
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52.4969
43.0518
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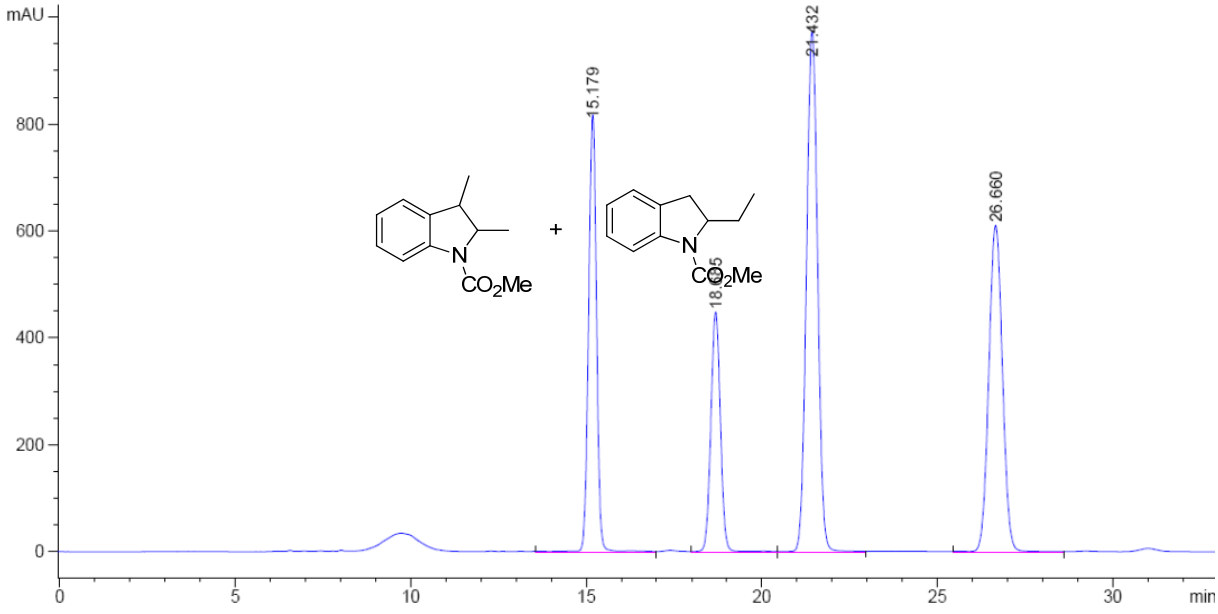
32.9064
27.3715
21.8396
20.5581
9.1173
f1 (ppm)


mAU
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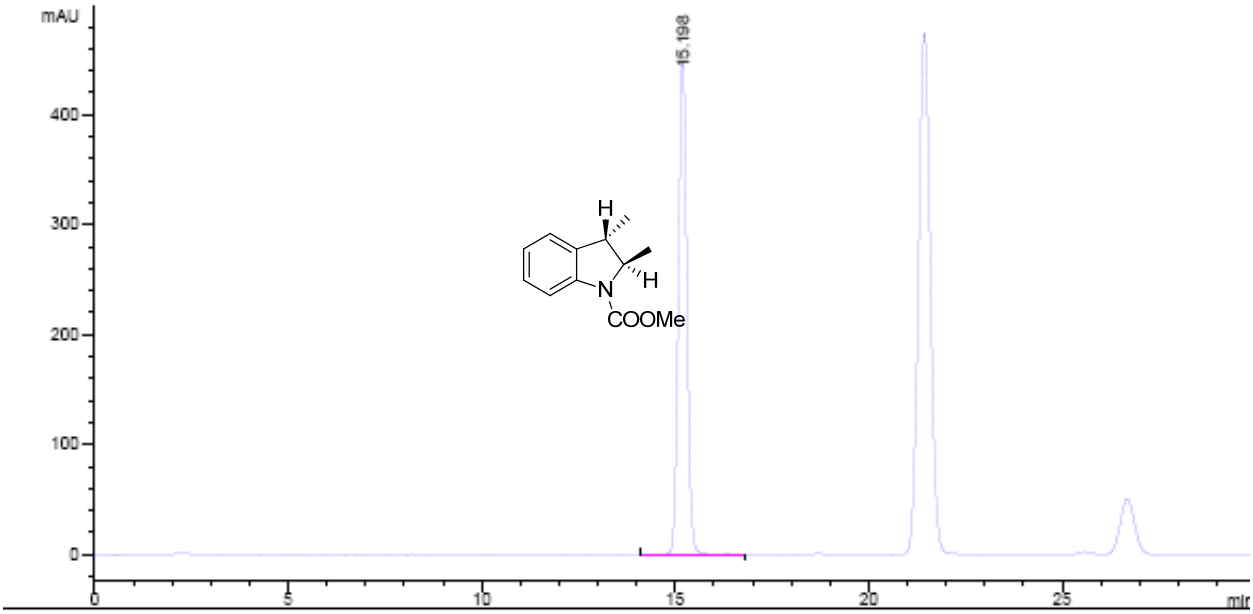
21.432
26.660
CO2Me
CO2Me
min



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

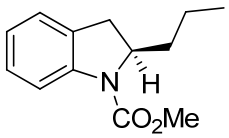
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.198	VB	0.2786	6871.64307	438.97583	100.0000

Totals : 6871.64307 438.97583

*** End of Report ***

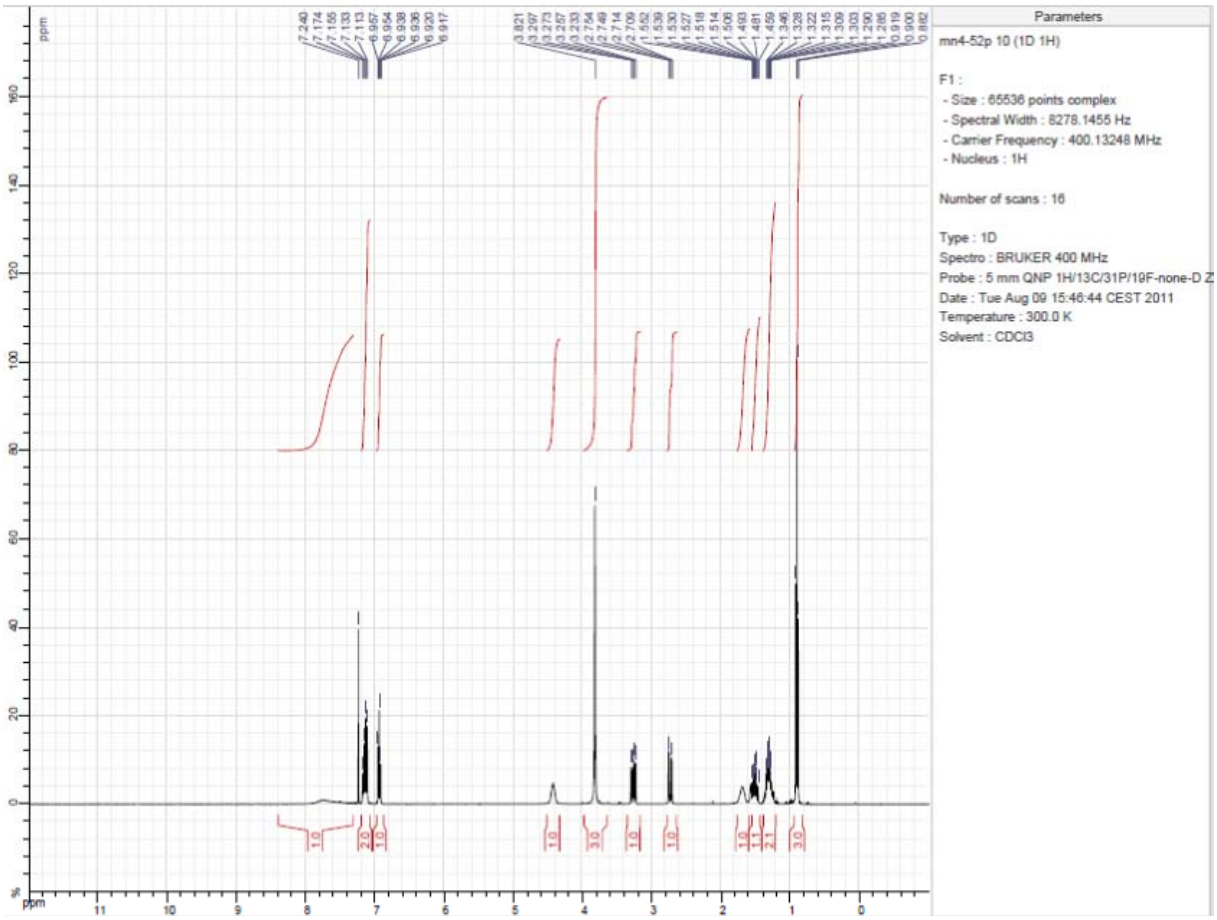
8a: >99% *ee* [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 15.19 min. (major)]

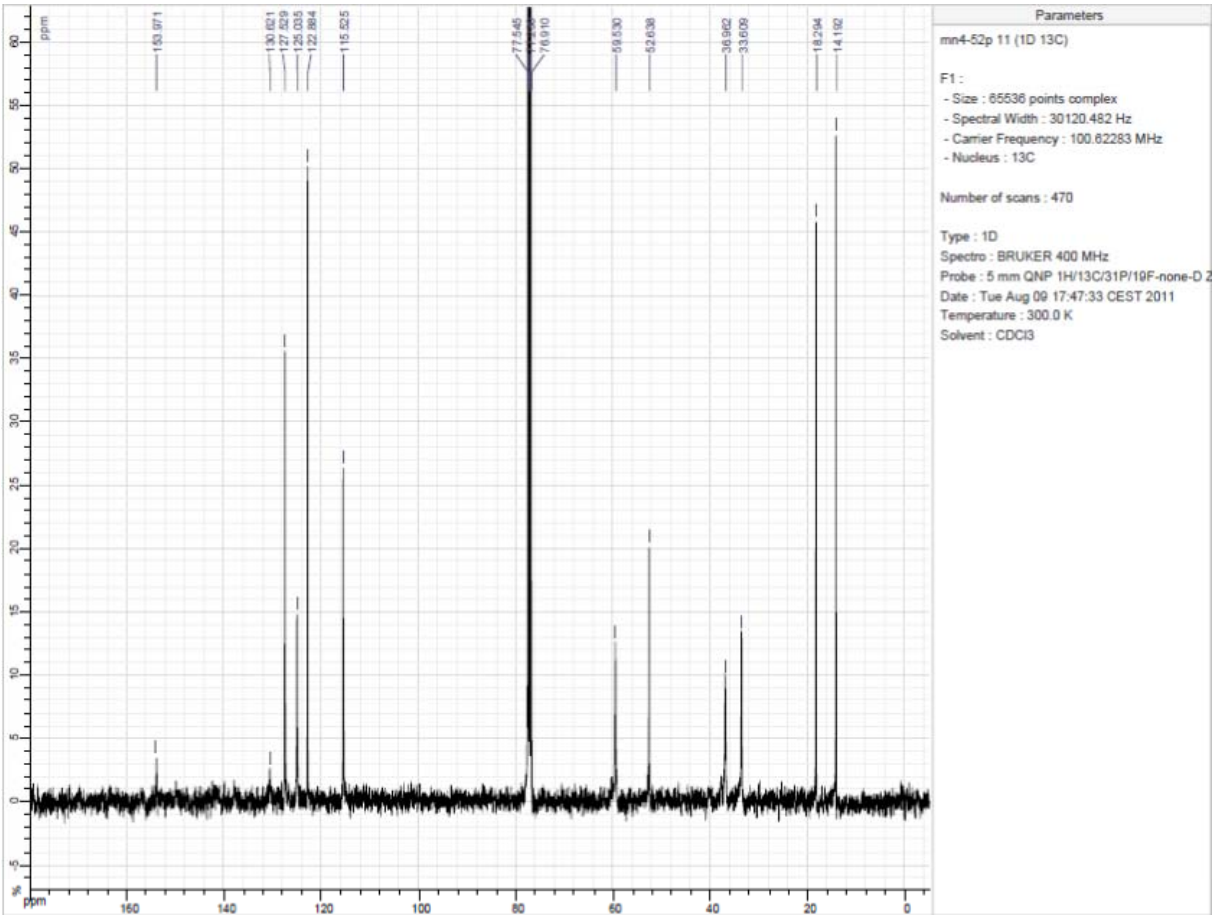
(*R*)-methyl 2-propylindoline-1-carboxylate **7b**; (*S*,*S*)-NHC·HI (**3**) was used.



68% yield calcd. by NMR (29.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): 0.90 (t, J = 7.6 Hz, 3H), 1.22-1.39 (m, 2H), 1.22-1.39 (m, 2H), 1.45-1.56 (m, 1H), 2.73 (dd, J = 16, 2 Hz, 1H), 3.27 (dd, J = 16, 9.6 Hz, 1H), 3.82 (s, 3H), 4.34-4.56 (brd, 1H), 6.94 (td, J = 7.6, 1.2 Hz, 1H), 7.12(d, J = 8 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.26-8.40 (brd, 1H). ^{13}C NMR (100 MHz): δ =

14.2, 18.3, 33.6, 37.0, 52.6, 59.5, 115.5, 122.9, 125.0, 127.5, 130.6, 154.0. MS (ESI, 70 eV): *m/z* (%) = 220 $(M+H)^+$; IR (neat): υ = 751, 1022, 1059, 1135, 1193, 1221, 1239, 1270, 1290, 1330, 1390, 1441, 1485, 1603, 1702, 2871, 2957 cm^{-1}; ESI-HRMS calcd. for $C_{13}H_{18}NO_2$ 220.1332, found 220.1320.

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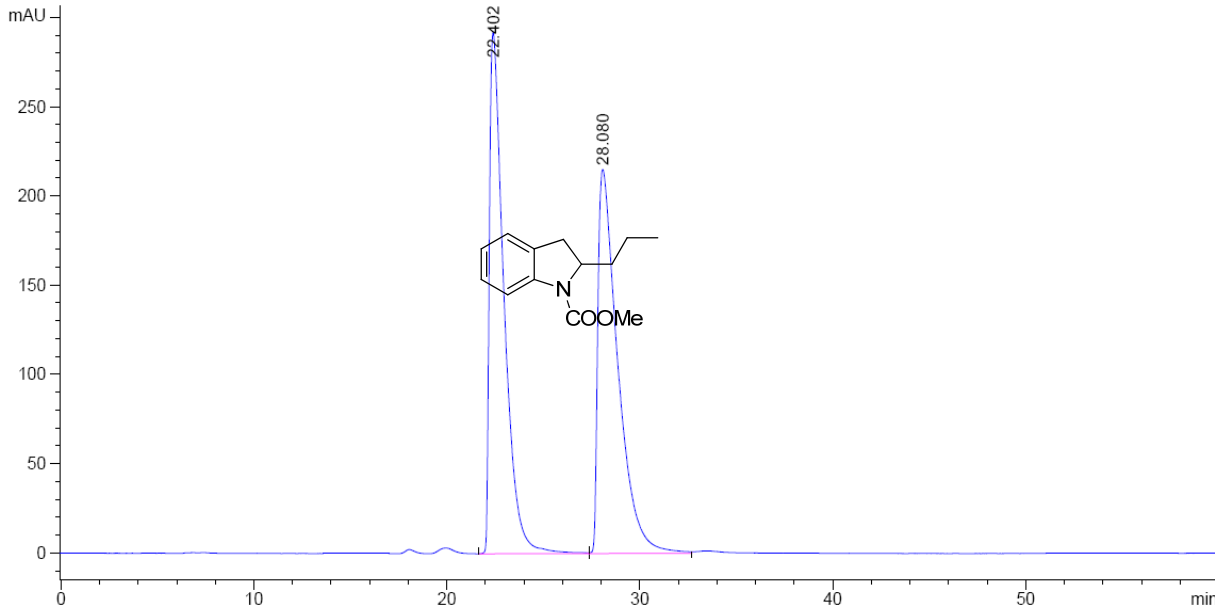
- Spectral Width : 30120.482 Hz
- Carrier Frequency : 100.62283 MHz
- Nucleus : 13C
Number of scans : 470
Type : 1D
Spectro : BRUKER 400 MHz
Date : Tue Aug 09 17:47:33 CEST 2011
Temperature : 300.0 K
Solvent : CDCl3
ppm


mAU
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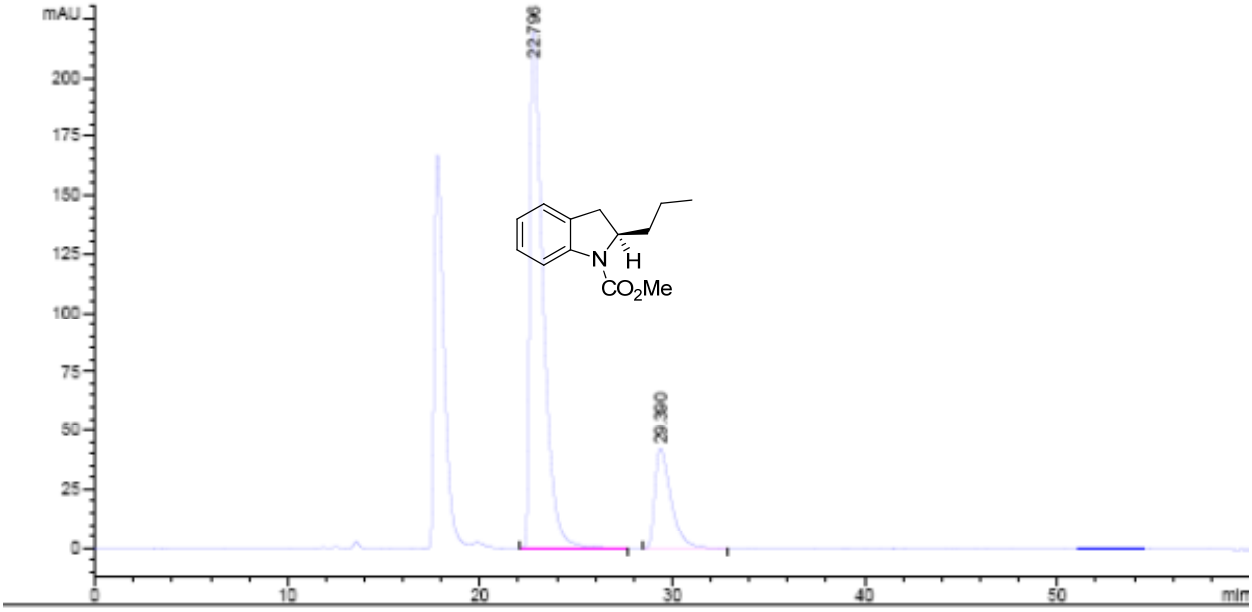
28.080
N
COOMe
min

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------------------------------------------------------------------------
                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  22.796 BB    0.7140 1.05878e4   219.79529  80.6193
   2  29.390 BB    0.8937 2545.28711   42.56399  19.3807

Totals :                  1.31331e4   262.35928

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                        *** End of Report ***
```
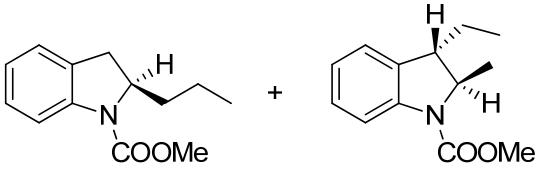
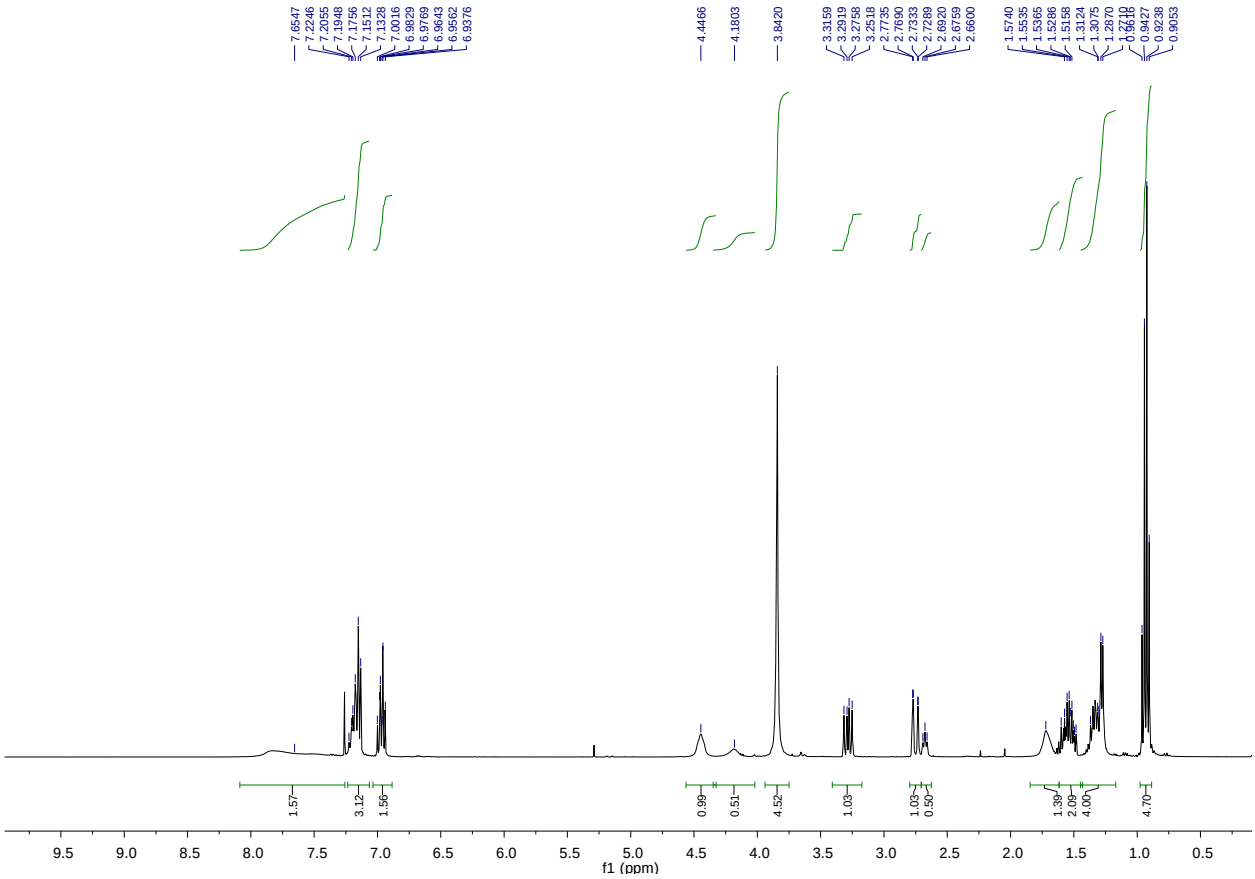

61% *ee* [chiral column: AS-H, *n*-hexane/*i*-PrOH = 100 : 0, 0.5 mL/min, 254 nm; t_R = 22.79 min. (major) and 29.39 (minor)].

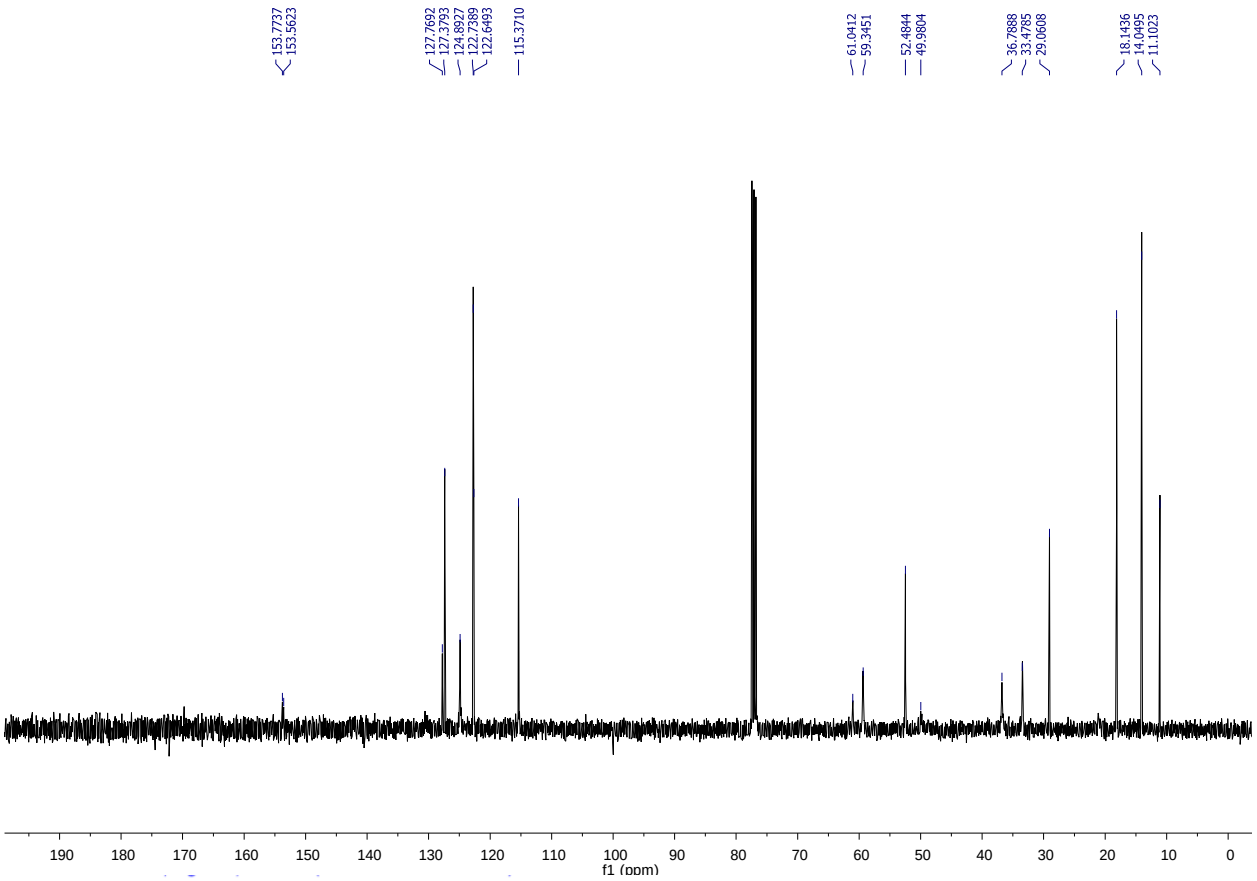
(*R*)-methyl 2-propylindoline-1-carboxylate **7b** and (2*R*,3*S*)-methyl 3-ethyl-2-methylindoline-1-carboxylate **8b**; (*S*,*S*)-NHC·HI (**3**) was used.

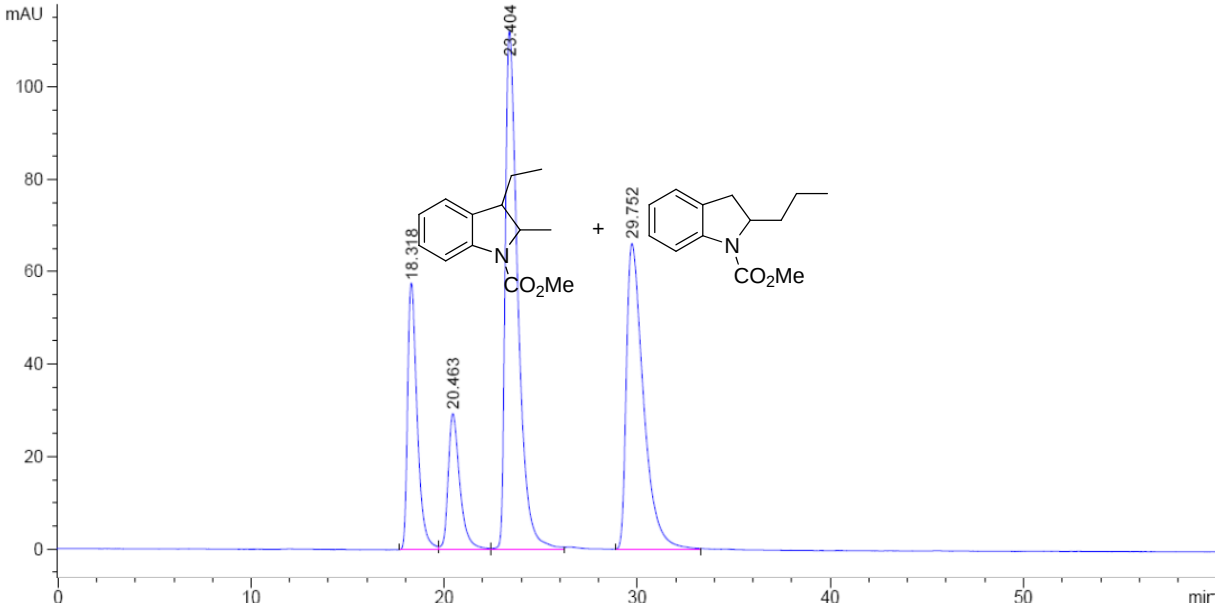


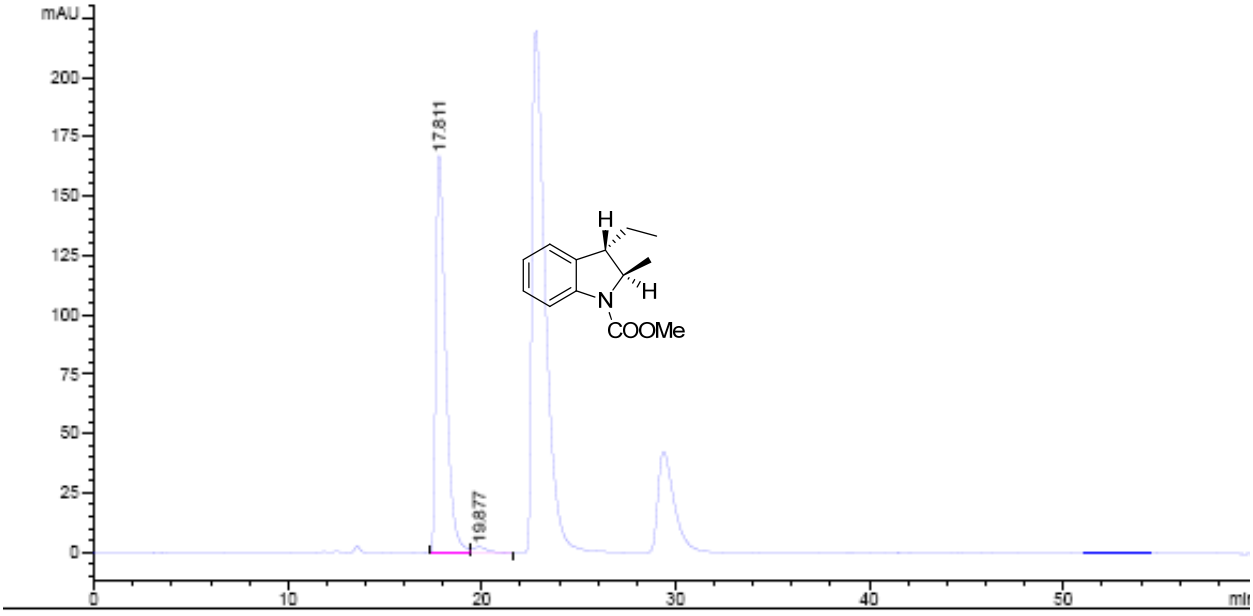
Colorless oil **8b**: 22% yield calcd. by NMR (9.6 mg), **7b** + **8b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90-0.95 (m, 4.7H), 1.27-1.36 (m, 4H), 1.48-1.59 (m, 2H), 1.72 (brd, 1.4H), 2.67 (t, *J* = 6.4

Hz, 0.5H), 2.74 (dd, *J* = 16.0, 1.8 Hz, 1H), 3.28 (dd, *J* = 16.0, 9.6 Hz, 1H), 3.84 (s, 4.5H), 4.18 (brd, 0.5H), 4.44 (brd, 1H), 6.93-7.00 (m, 1.5H), 7.13-7.22 (m, 3H), 7.65 (brd, 1.5H). **7b** + **8b**: ^{13}C NMR (100 MHz, $CDCl_3$): 11.1, 14.0, 18.1, 29.0, 33.4, 36.7, 49.9, 52.4, 59.3, 61.0, 115.3, 122.6, 122.7, 124.8, 127.3, 127.7, 153.5, 153.7.




153.7737
153.5623
127.7692
127.3793
124.8327
122.7389
122.6493
115.3710
61.0412
59.3451
52.4844
49.9804
36.7888
33.4785
29.0608
18.1436
14.0495
11.1023
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


mAU
100
80
60
40
20
0
18.318
20.463
23.404
29.752
N
CO2Me
+
N
CO2Me
0 10 20 30 40 50
mir



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

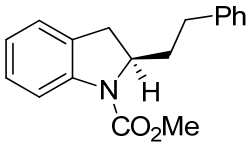
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.811	BV	0.5397	5897.93506	167.12987	97.7527
2	19.877	VB	0.7546	135.59413	2.49281	2.2473

Totals : 6033.52919 169.62268

*** End of Report ***

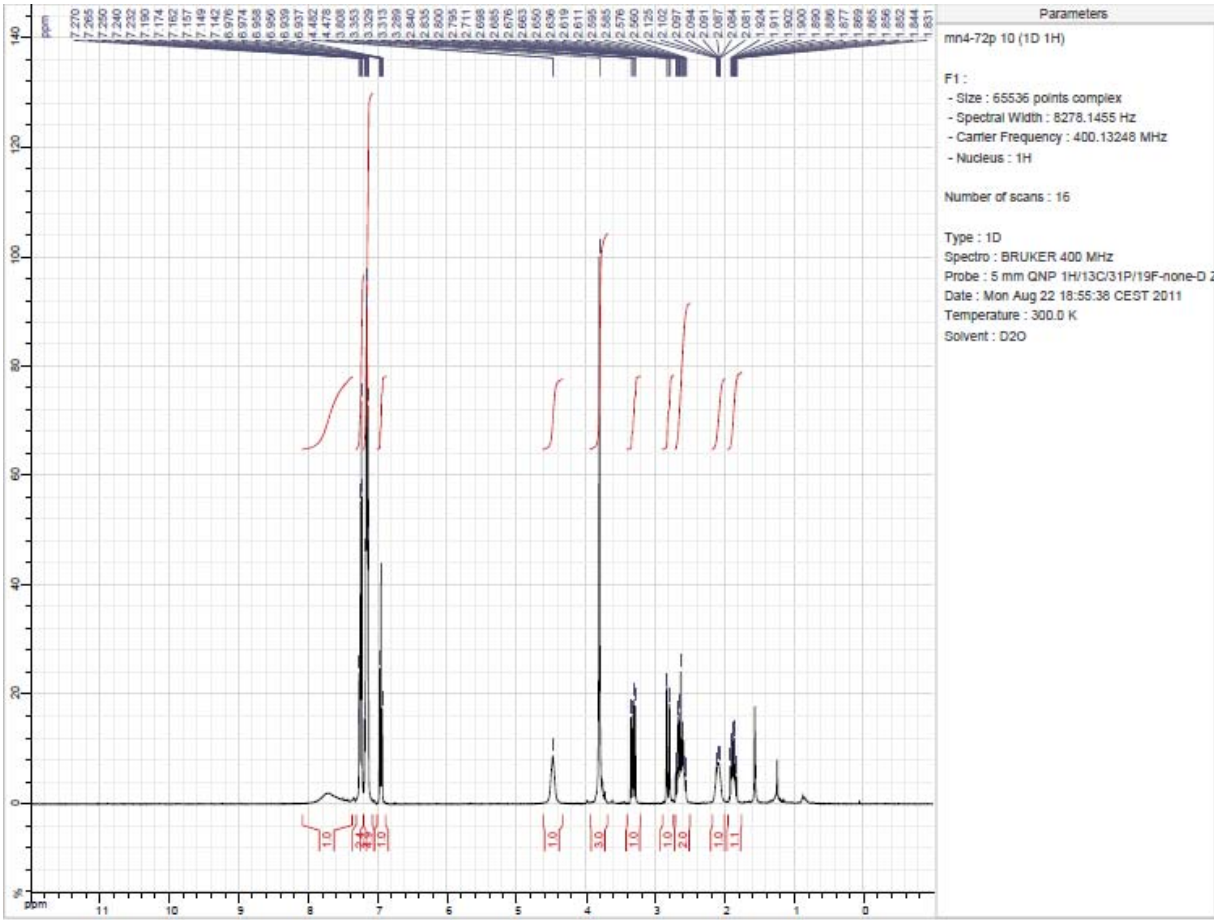
8b: 96% *ee* [chiral column: AS-H, *n*-hexane/*i*-PrOH = 100 : 0, 0.5 mL/min, 254 nm; t_R = 17.81 min. (major) and 19.87 (minor)].

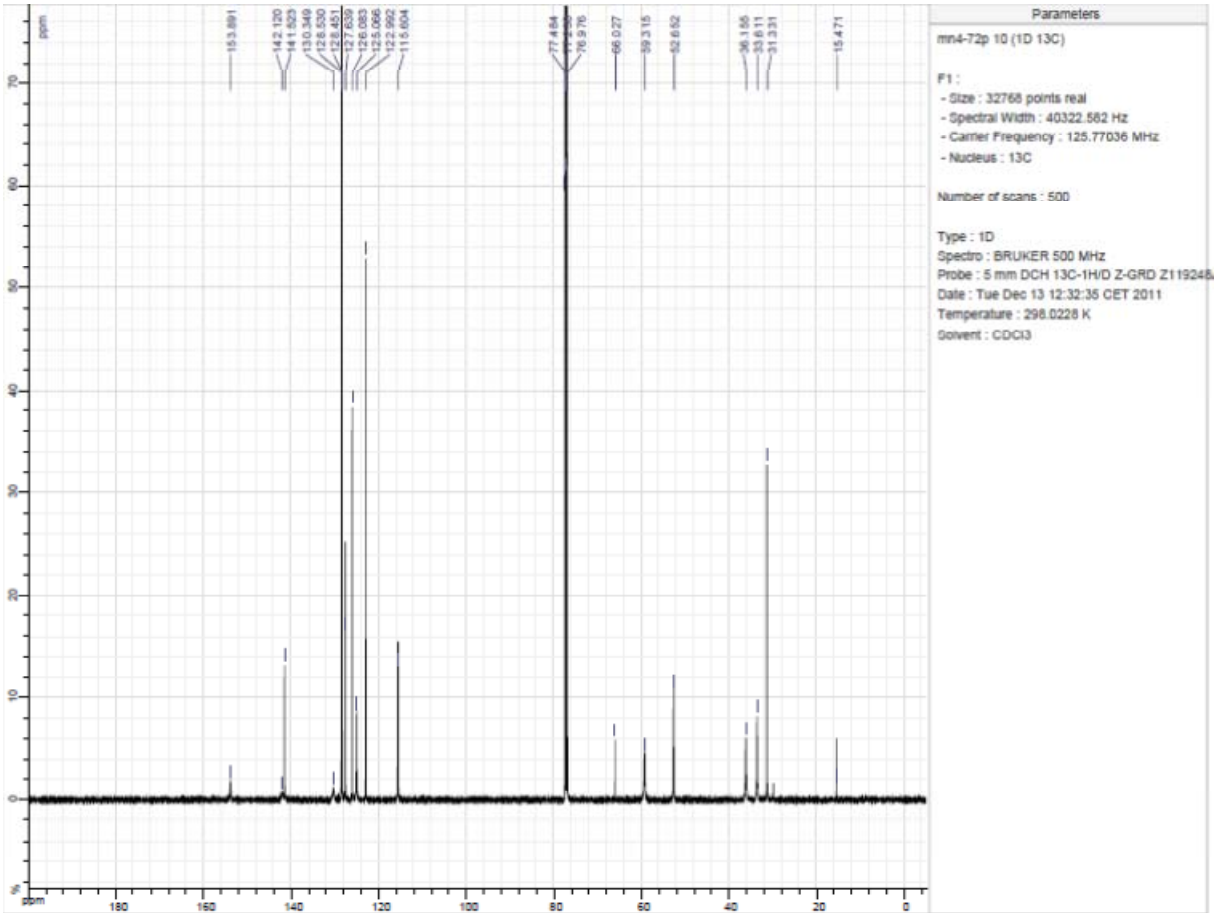
(*R*)-methyl 2-phenethylindoline-1-carboxylate **7c**; (*S*,*S*)-NHC·HI (**4**) was used.

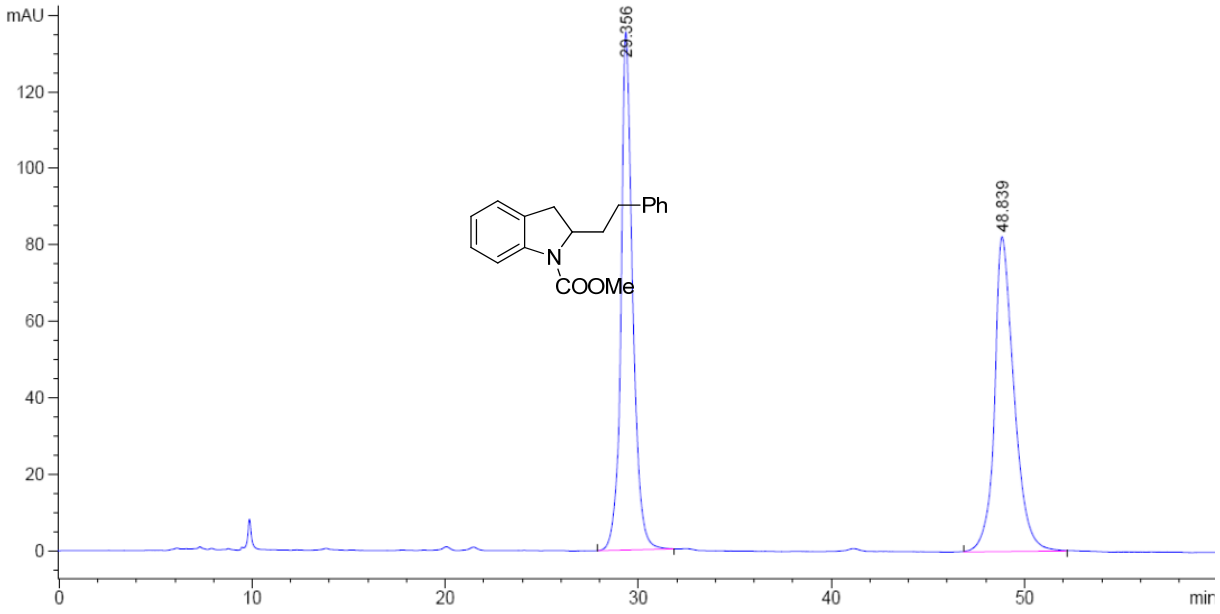


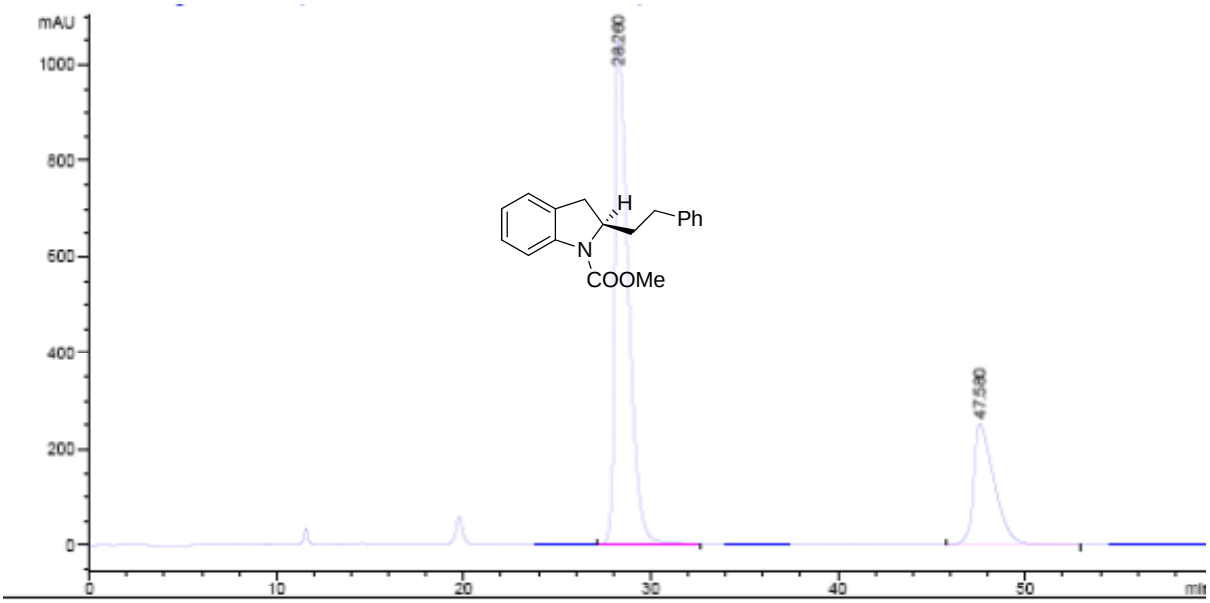
Colorless oil, 62% yield (34.8 mg), ^{1}H NMR (400 MHz, $CDCl_3$): 1.80-1.96 (m, 1H), 2.00-2.18 (m, 1H), 2.52-2.72 (m, 2H), 2.82 (dd, *J* = 16, 2 Hz, 1H), 3.32 (dd, *J* = 16, 9.6 Hz, 1H), 3.81 (s, 3H), 4.34-4.60 (brd, 1H), 6.96 (t, *J* = 7.2, 0.8 Hz, 1H), 7.10-7.22 (m, 5H), 7.26-7.30

(m, 2H), 7.40-8.10 (brd, 1H). ^{13}C NMR (125 MHz): δ = 15.5, 31.3, 33.6, 36.2, 52.7, 59.3, 66.0, 115.6, 123.0, 125.1, 126.1, 127.6, 128.5, 130.3, 141.5, 142.1, 153.9. MS (ESI, 70 eV): *m/z* (%) = 282 $(M+H)^+$; IR (neat): υ = 749, 840, 942, 1056, 1130, 1191, 1225, 1289, 1330, 1389, 1440, 1484, 1602, 1701, 2858, 2952, 3027 cm^{-1}; ESI-HRMS calcd. for $C_{18}H_{20}NO_2$ 282.1488, found 282.1480.




153.891
142.120
141.523
130.349
128.530
128.451
127.639
126.683
125.066
122.992
115.604
77.484
76.976
66.027
59.315
52.652
36.155
33.611
31.331
15.471
Parameters
mn4-72p 10 (1D 13C)
F1 :
- Size : 32768 points real
- Spectral Width : 40322.582 Hz
- Carrier Frequency : 125.77036 MHz
- Nucleus : 13C
Number of scans : 500
Type : 1D
Spectro : BRUKER 500 MHz
Probe : 5 mm DCH 13C-1H/D Z-GRD Z119248
Date : Tue Dec 13 12:32:35 CET 2011
Temperature : 298.0228 K
Solvent : CDCl3
ppm


mAU
29.356
48.839
Ph
N
COOMe
min

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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  28.260 BV    0.7789 5.39535e4  1050.97388  73.5913
   2  47.580 BB    1.1546 1.93616e4   252.49791  26.4087

Totals :                  7.33152e4  1303.47179

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                        *** End of Report ***
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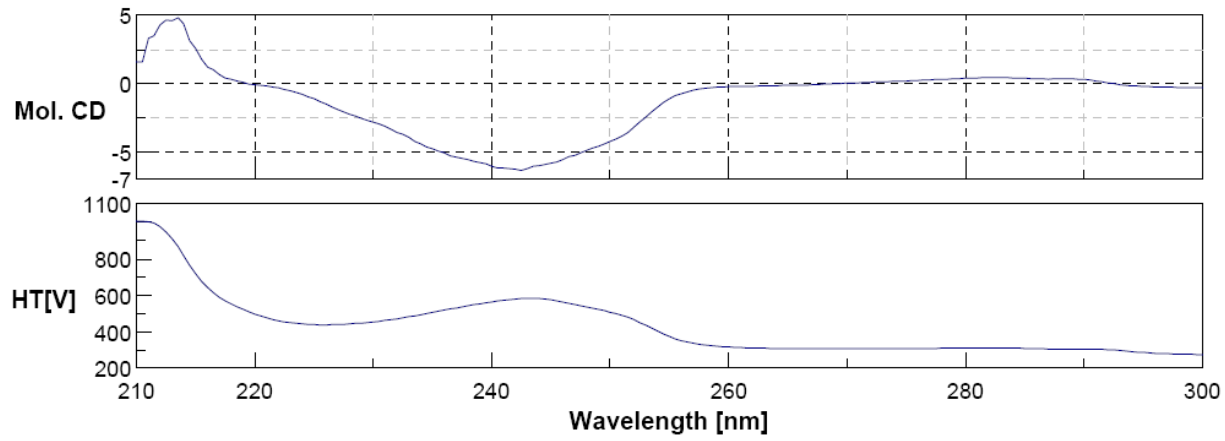
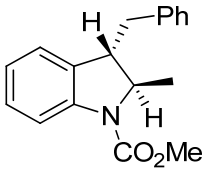
$[\alpha]_D^{20}$ = -19.4 (*c* = 1.0 in CH_2Cl_2), 47% *ee*, [chiral column: (*R*,*R*)-Whelk-O1, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 28.26 min. (major) and 47.58 min. (minor)].

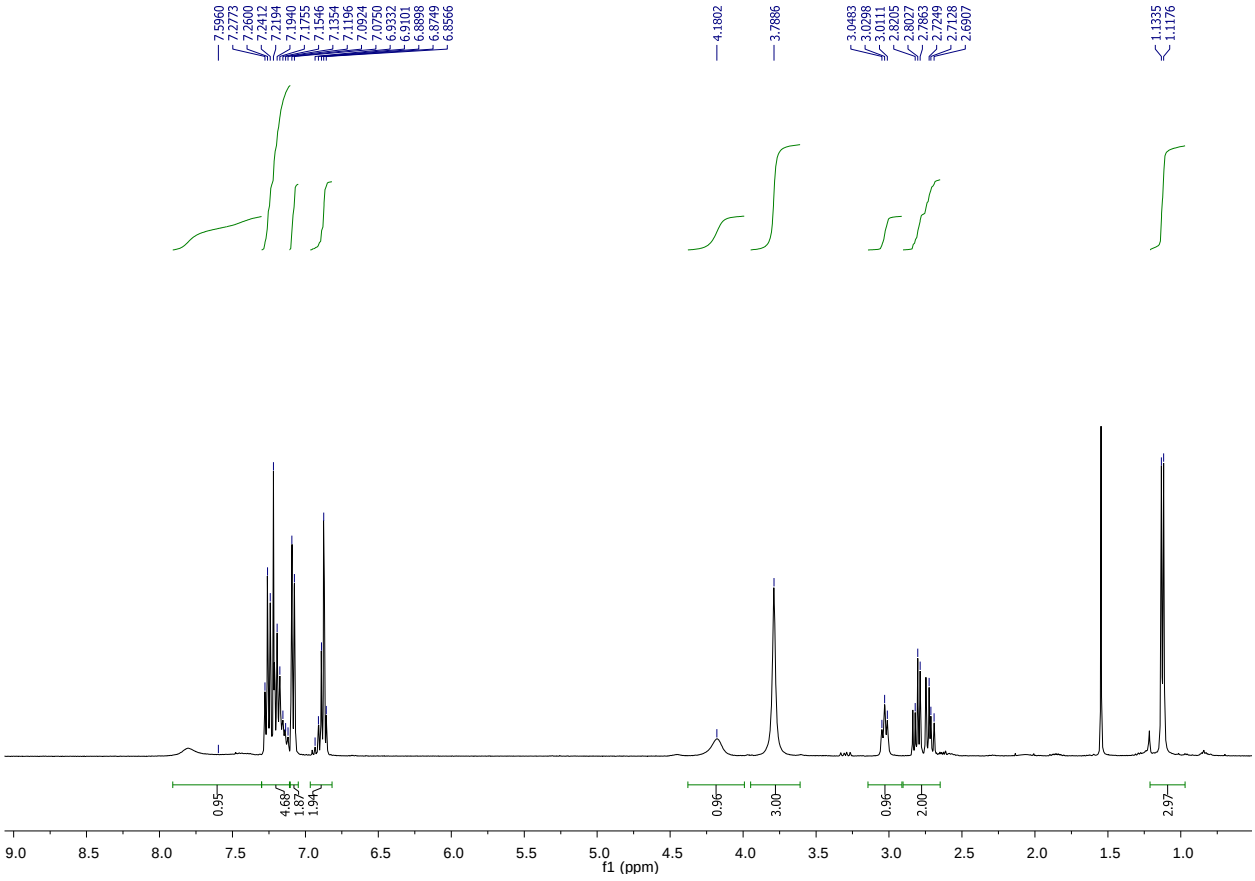


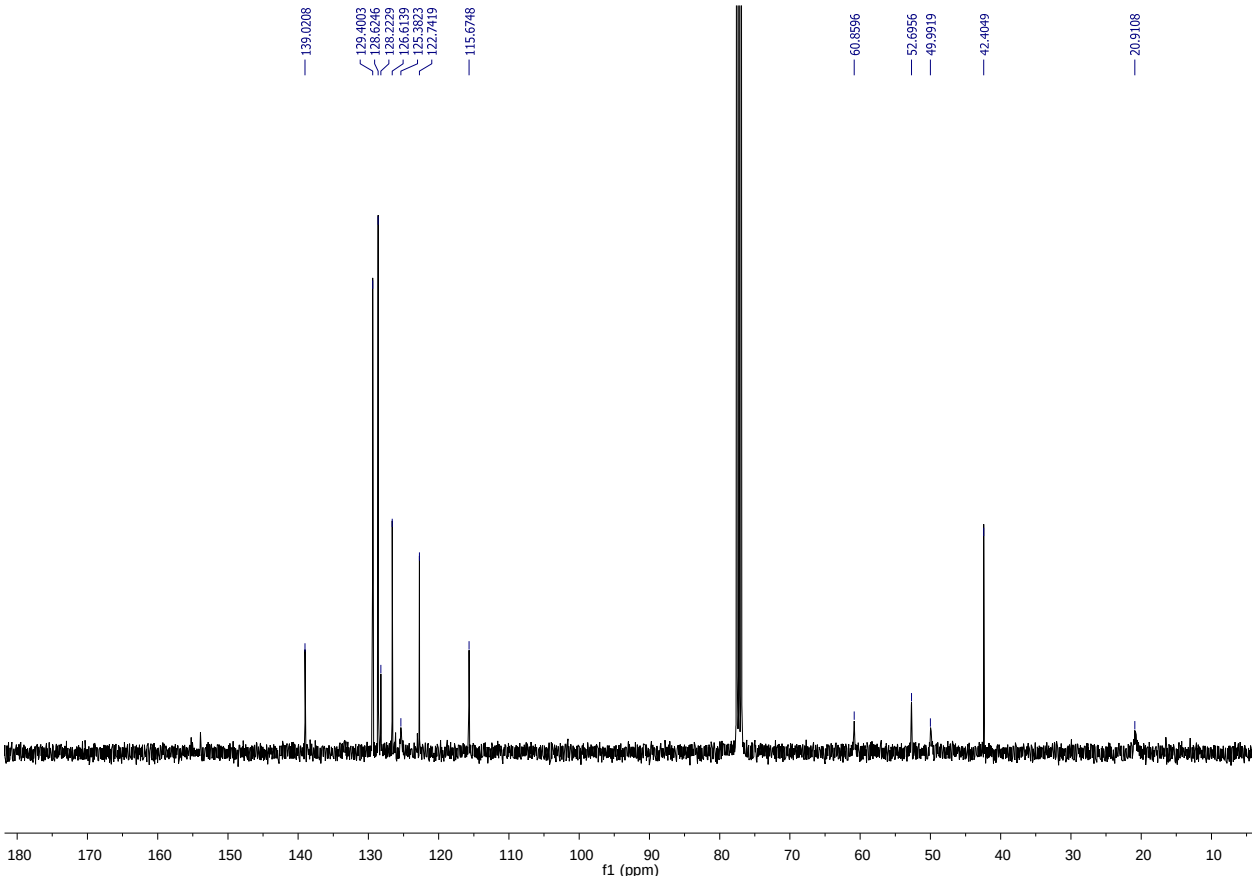
CD spectrum: 0.0001 M in *n*-hexane at 20 °C.

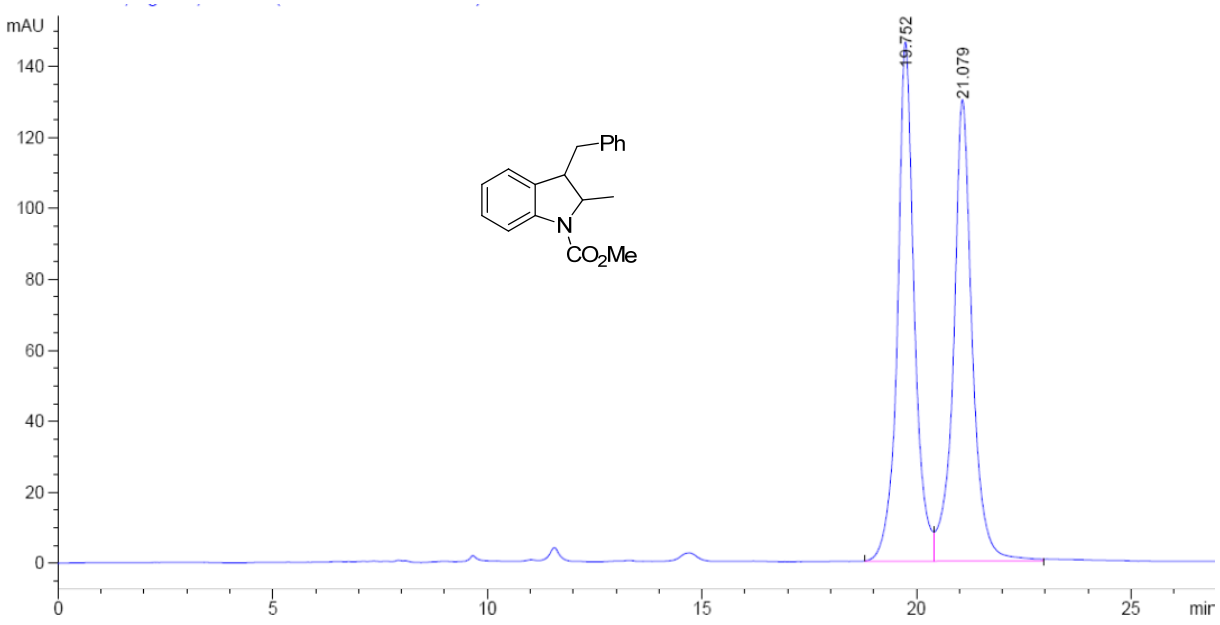
(2*R*,3*S*)-methyl 3-benzyl-2-methylindoline-1-carboxylate **8c**; (*S*,*S*)-NHC·HI (**4**) was used.



Colorless oil, 32% yield (17.9 mg), ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (d, J = 6.4 Hz, 3H), 2.69-2.82 (m, 2H), 3.02 (t, J = 14.9 Hz, 1H), 3.78 (s, 3H), 4.18 (brd, 1H), 6.85-6.93 (m, 2H), 7.08 (d, J = 6.9 Hz, 2H), 7.13-7.27 (m, 4H), 7.59 (brd, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 20.9, 42.4, 49.9, 52.6, 60.8, 115.6, 122.7, 125.3, 126.6, 128.2, 128.6, 129.4, 139.0. IR (neat, cm^{-1}): 2947, 1701, 1601, 1482, 1439, 1387, 1280, 1190, 1059, 748, 698. EI-HRMS: calcd. for $C_{18}H_{20}NO_2$: 282.1488, found: 282.1479.




139.0208
129.4003
128.6246
128.2229
126.6139
125.3823
122.7419
115.6748
60.8596
52.6956
49.9919
42.4049
20.9108
f1 (ppm)


mAU
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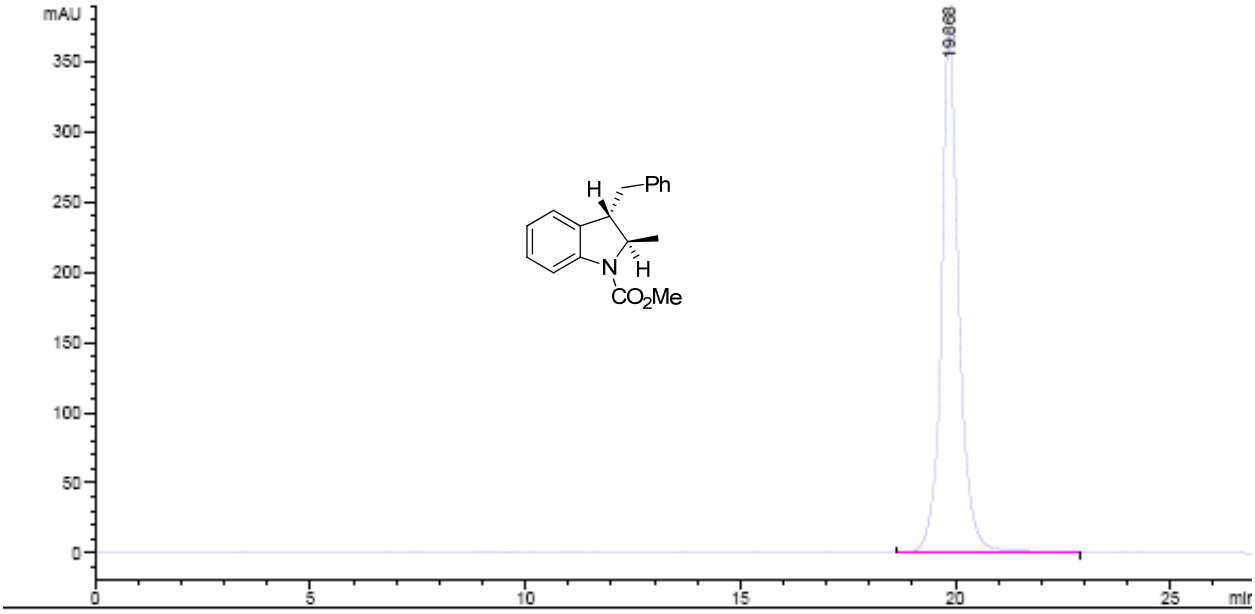
21.079
Ph
N
CO2Me
min

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---------------------------------------------------------------------
                      Area Percent Report
---------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.868 BB    0.4490 1.06690e4   369.40372 100.0000

Totals :                  1.06690e4   369.40372

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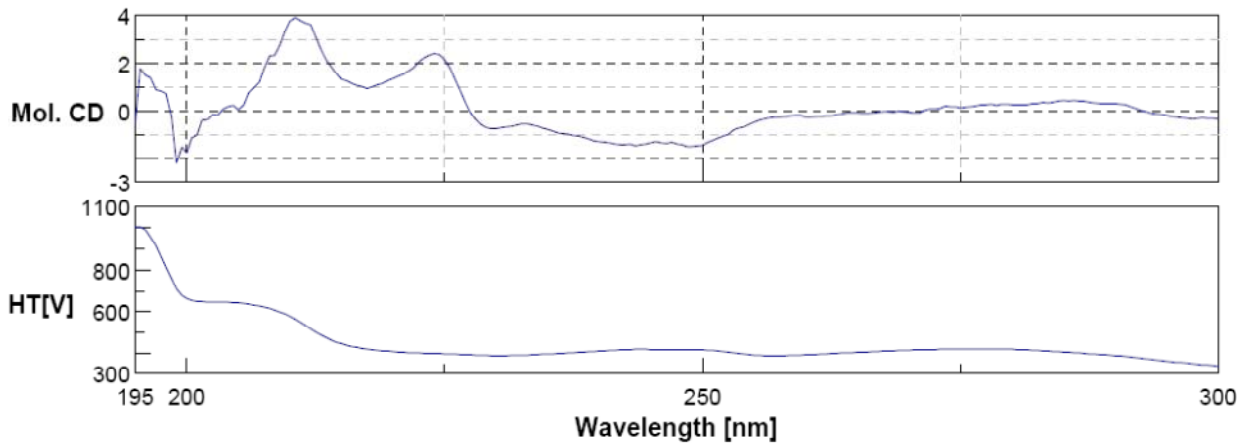
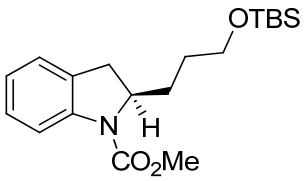
                      *** End of Report ***
```

$[\alpha]_D^{25}$ = +15.4 (c = 0.5 in CH_2Cl_2), >99% *ee*, [chiral column: (*R*,*R*)-Whelk-O1, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 19.86 min. (major)].

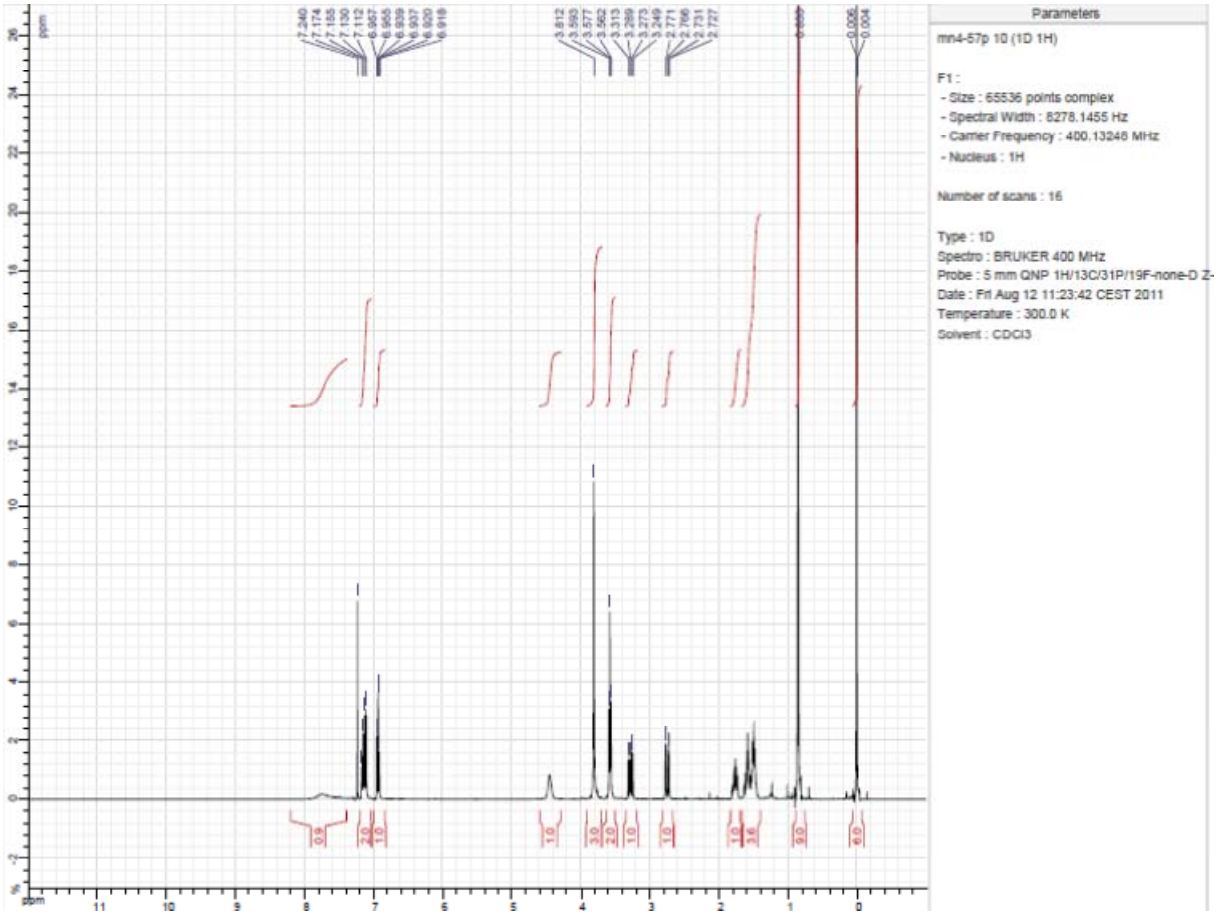


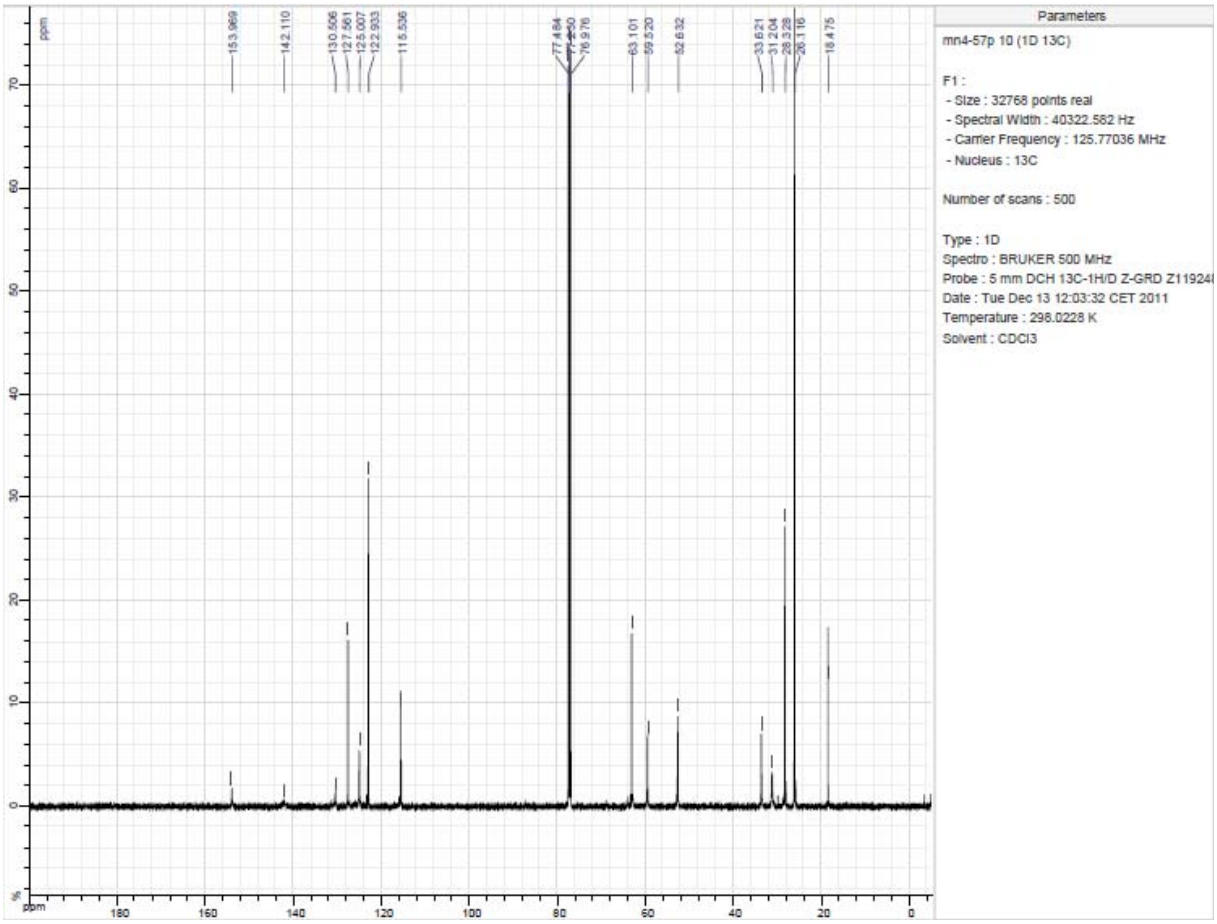
CD spectrum: 0.0001 M in *n*-hexane at 20 °C.

(*R*)-methyl 2-(3-((tert-butyldimethylsilyl)oxy)propyl)indoline-1-carboxylate **7d**; (*S*,*S*)-NHC·HI (**3**) was used.



Colorless oil, 68% yield (47.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$): 0.00 (s, 3H), 0.01 (s, 3H), 0.86 (s, 9H), 1.41-1.67 (m, 3H), 1.70-1.84 (m, 1H), 2.75 (dd, J = 16, 2 Hz, 1H), 3.28 (dd, J = 16, 9.6 Hz, 1H), 3.58 (t, J = 6.4 Hz, 2H), 3.81 (s, 3H), 4.30-4.60 (brd, 1H), 6.94 (td, J = 7.2, 0.8 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.40-8.20 (brd, 1H). ^{13}C NMR (125 MHz): δ = 18.5, 26.1, 28.3, 31.2, 33.6, 52.6, 59.5, 63.1, 115.5, 122.9, 125.0, 127.6, 130.5, 154.0. MS (ESI, 70 eV): *m/z* (%) = 350 $(M+H)^+$; IR (neat): υ = 751, 833, 938, 1022, 1059, 1093, 1132, 1191, 1227, 1251, 1284, 1307, 1330, 1390, 1441, 1463, 1486, 1603, 1705, 2857, 2930, 2952 cm^{-1}; EI-HRMS calcd. for $C_{19}H_{32}NO_3Si$ 350.2145, found 350.2150.

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130.506
127.561
125.007
122.933
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77.484
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76.976
63.101
59.520
52.632
33.621
31.204
28.328
26.116
18.475
Parameters
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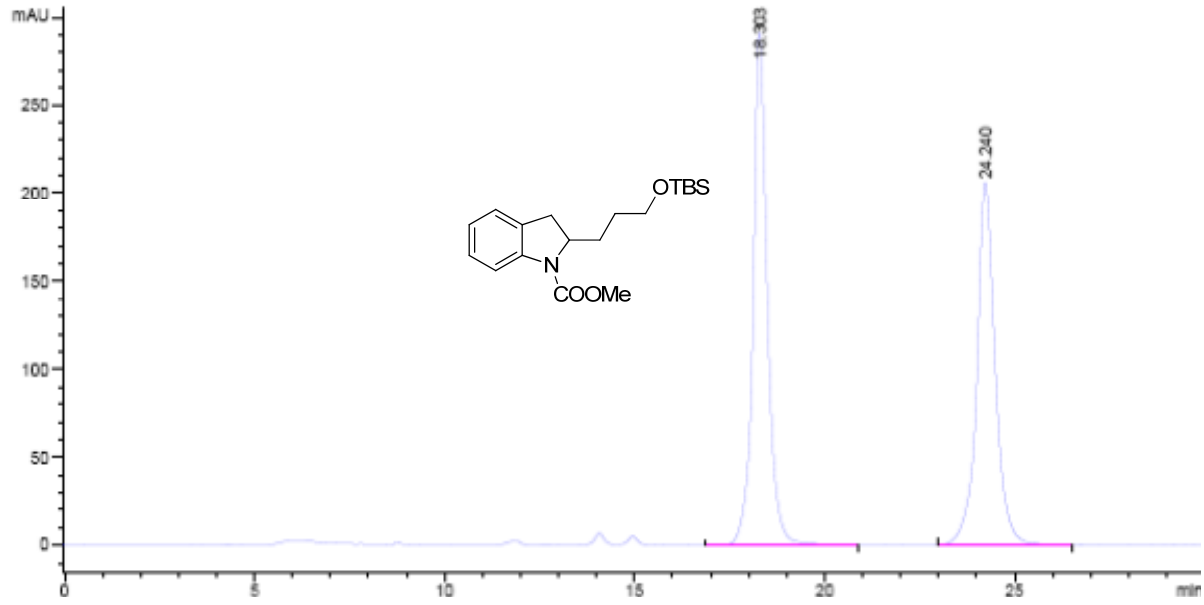
F1 :
- Size : 32768 points real
- Spectral Width : 40322.582 Hz
- Carrier Frequency : 125.77036 MHz
- Nucleus : 13C
Number of scans : 500
Type : 1D
Spectro : BRUKER 500 MHz
Date : Tue Dec 13 12:03:32 CET 2011
Temperature : 296.0228 K
Solvent : CDCl3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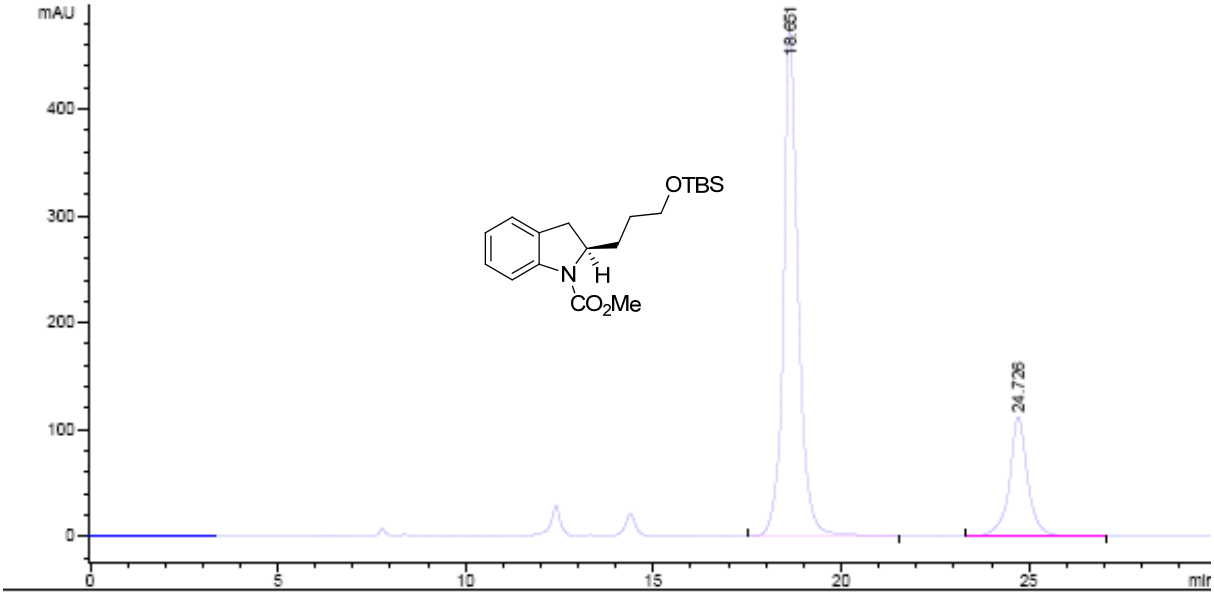
OTBS
N
COOMe
min



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

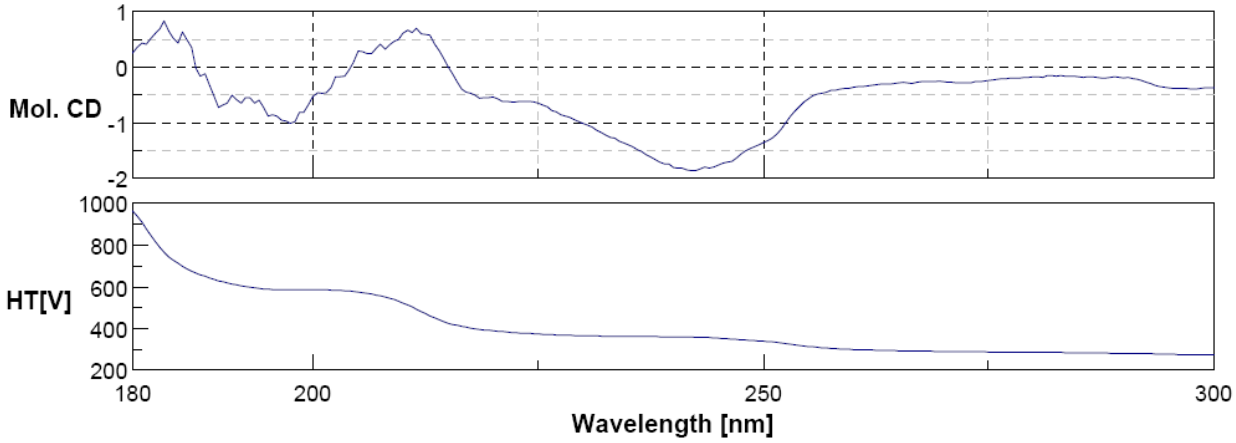
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.651	BB	0.4199	1.31376e4	473.17184	77.3458
2	24.726	BB	0.5140	3847.94482	111.66259	22.6542

Totals : 1.69856e4 584.83443

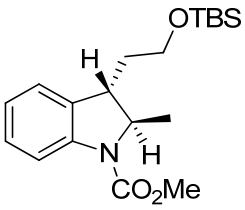
*** End of Report ***

$[\alpha]_D^{25}$ = -18.8 (*c* = 1.0 in CH_2Cl_2), 55% *ee*, [chiral column: (*R*,*R*)-Whelk-O1, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 18.65 min. (major) and 24.72 min. (minor)].

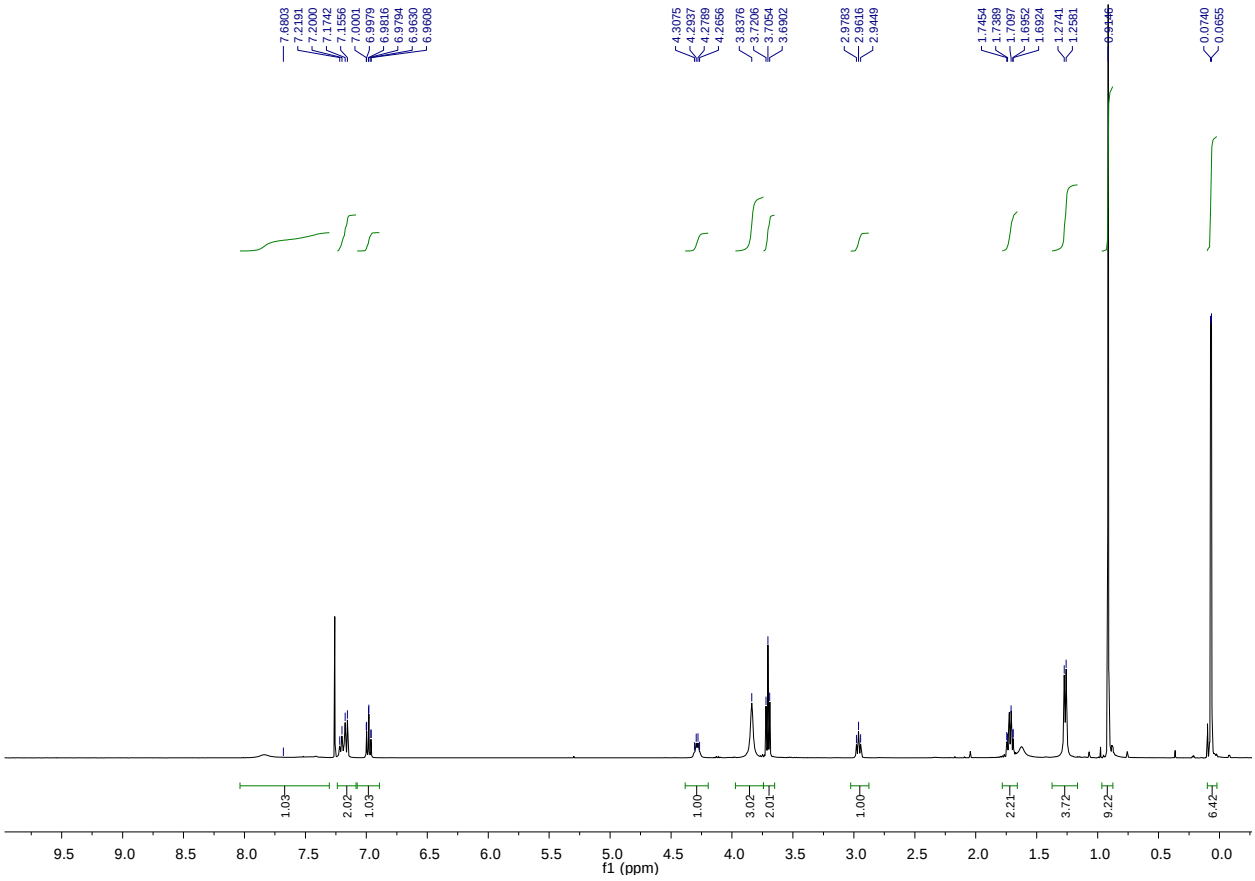


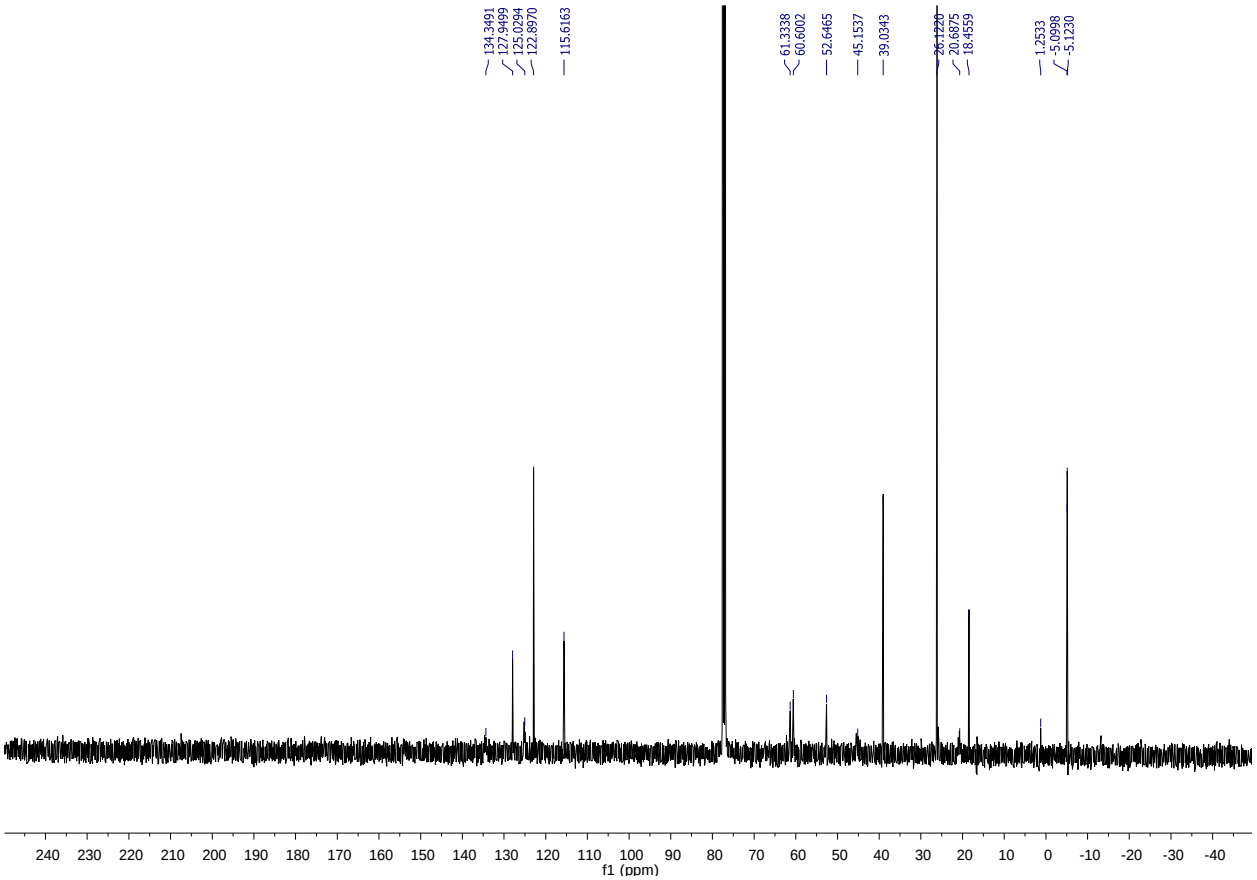
CD spectrum: 0.0001 M in *n*-hexane at 20 °C

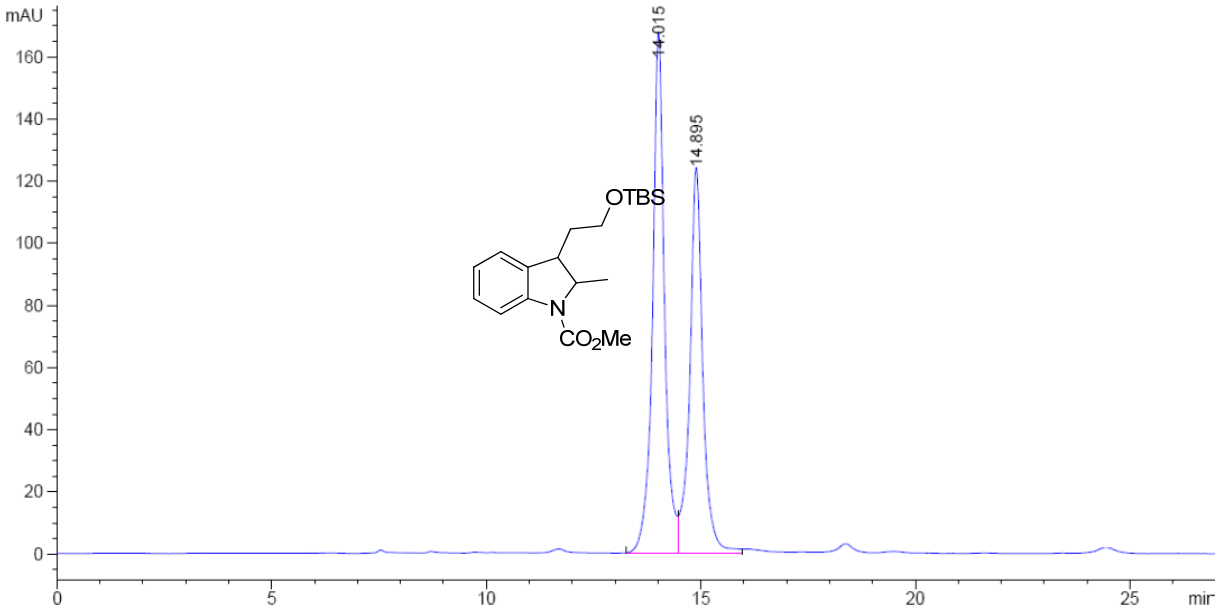
(2*R*,3*S*)-methyl 3-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-2-methylindoline-1-carboxylate **8d**; (*S*,*S*)-NHC·HI (**3**) was used.

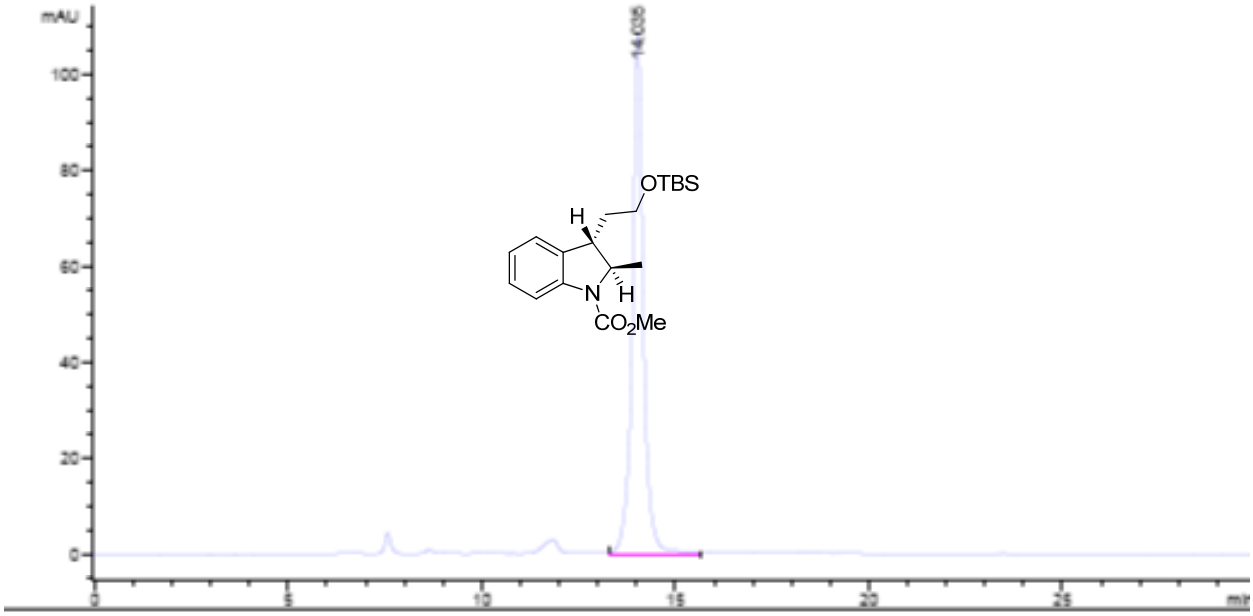


Colorless oil, 21% yield (14.6 mg), ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.06 (d, *J* = 3.4 Hz, 6H), 0.91 (s, 9H), 1.26 (d, *J* = 6.4 Hz, 3H), 1.69-1.74 (m, 2H), 2.96 (t, *J* = 6.7 Hz, 1H), 3.71 (d, *J* = 6.0 Hz, 2H), 3.83 (s, 3H), 4.26-4.30 (m, 1H), 6.97 (td, *J* = 7.4, 0.9 Hz, 1H), 7.15-7.21 (m, 2H), 7.61 (brd, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 5.0, 1.2, 18.4, 20.6, 26.1, 39.0, 45.1, 52.6, 60.6, 61.3, 115.6, 122.8, 125.0, 127.9, 134.4. IR (neat, cm^{-1}): 2926, 2854, 1705, 1602, 1485, 1440, 1389, 1250, 1094, 1054, 938, 832, 749. EI-HRMS: calcd. for $C_{19}H_{32}NO_3Si$ $[M+H]^+$: 350.2145, found: 350.2137.




134.3491
127.9499
125.0294
122.8970
115.6163
61.3338
60.6002
52.6465
45.1537
39.0343
26.1220
20.6875
18.4559
1.2533
-5.0998
-5.1230
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


mAU
160
140
120
100
80
60
40
20
0
14.015
14.895
OTBS
N
CO2Me
0
5
10
15
20
25
min



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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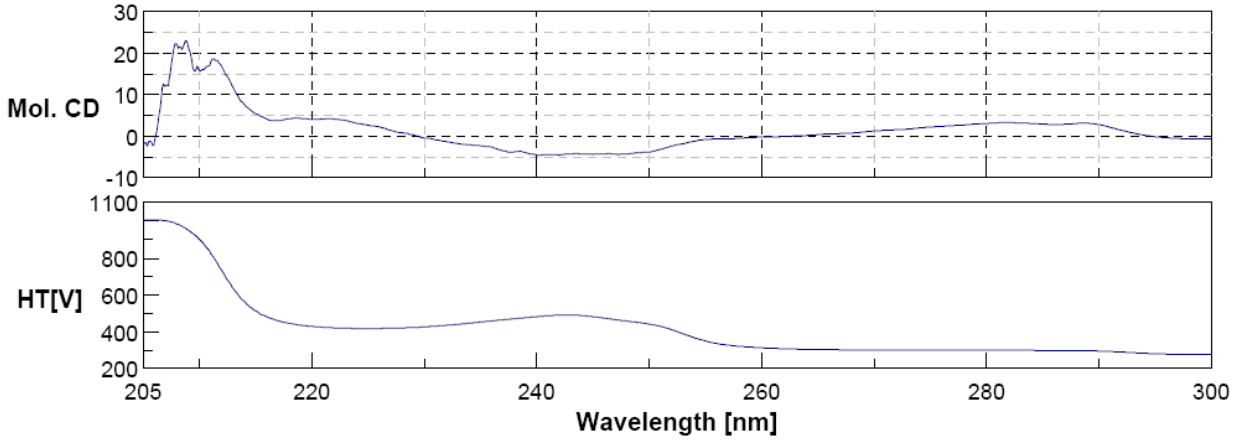
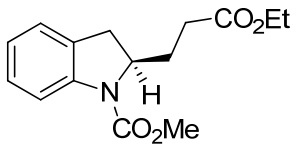
Totals :				2147.29150	106.52612	

$[\alpha]_D^{25}$ = +6.6 (*c* = 0.5 in CH_2Cl_2), >99% ee, [chiral column: (*R*,*R*)-Whelk-O1, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 14.03 min. (major)].

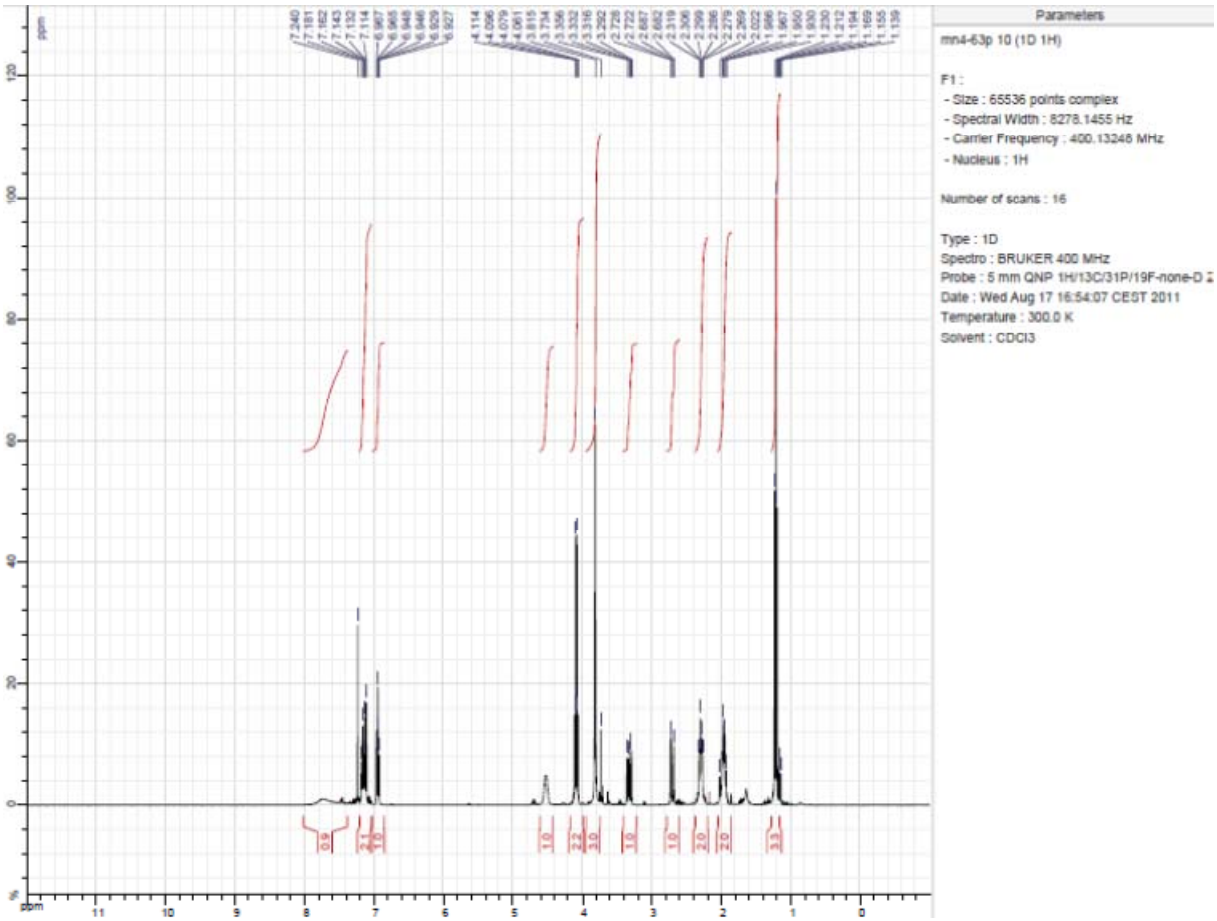


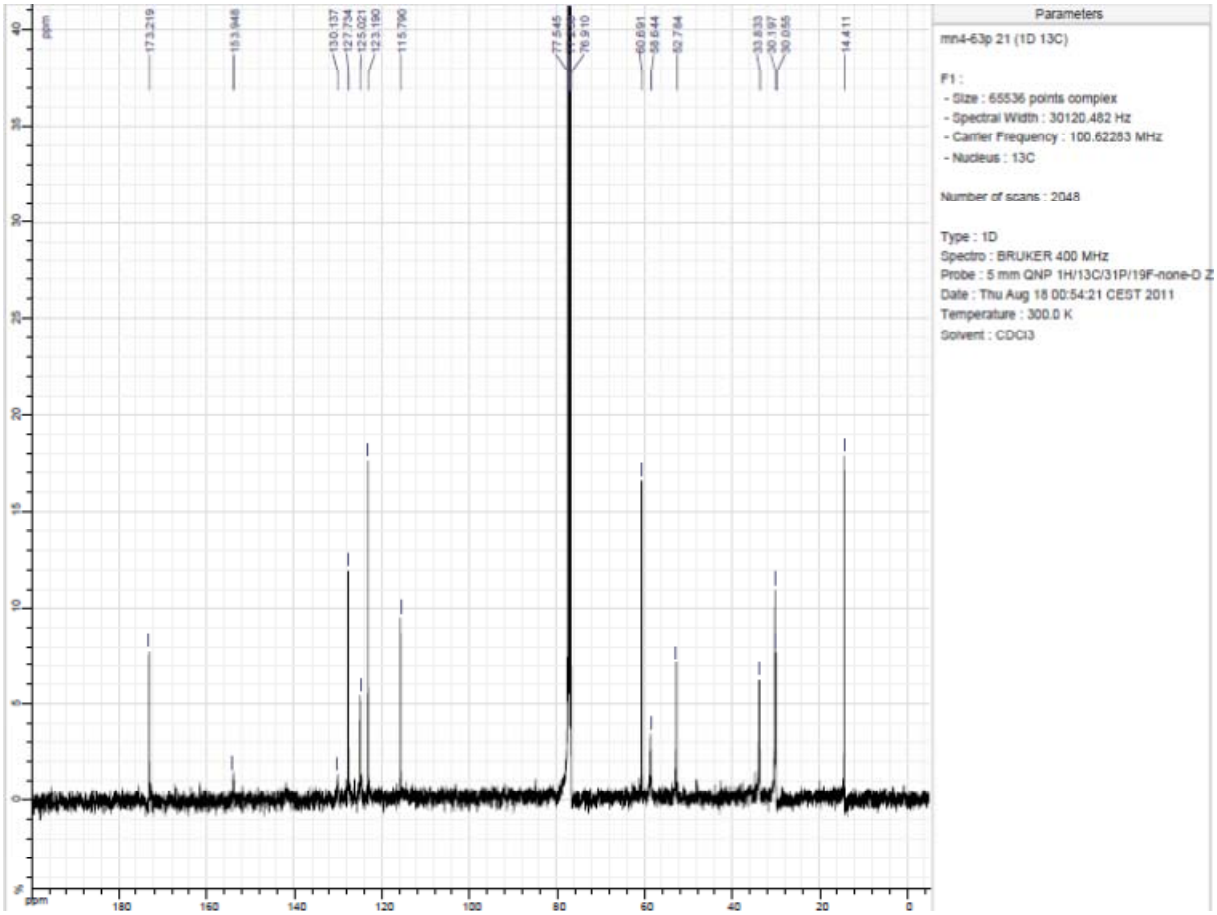
CD spectrum: 0.0001 M in *n*-hexane at 20 °C

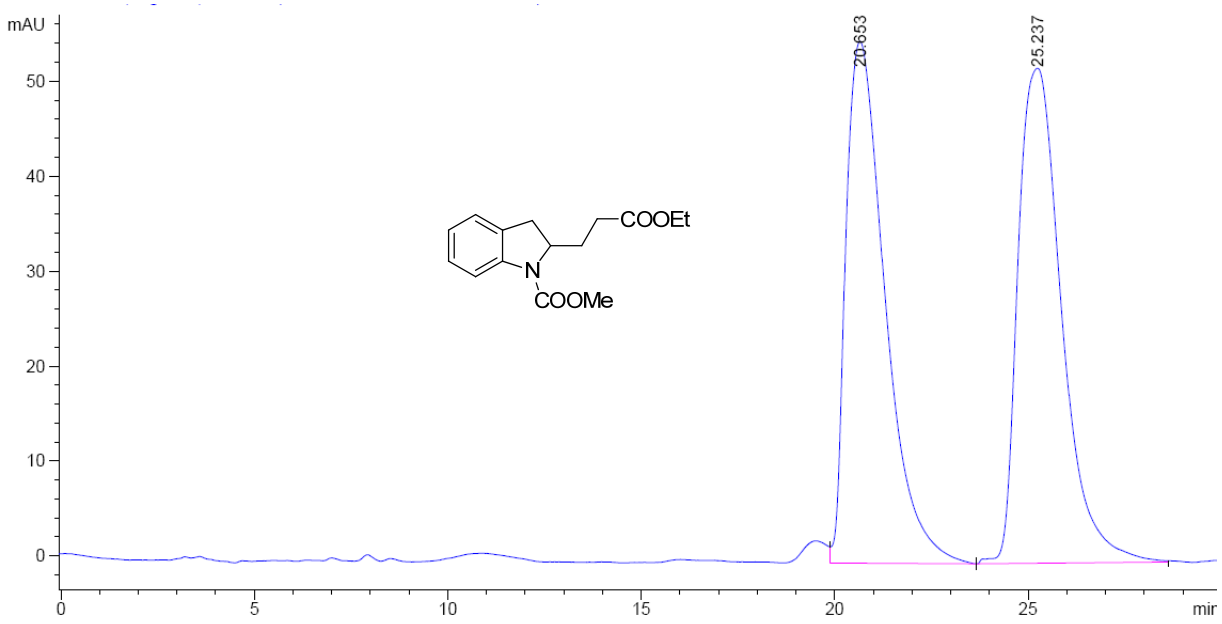
(*R*)-methyl 2-(3-ethoxy-3-oxopropyl)indoline-1-carboxylate **7e**; (*S*,*S*)-NHC·HI (**3**) was used.

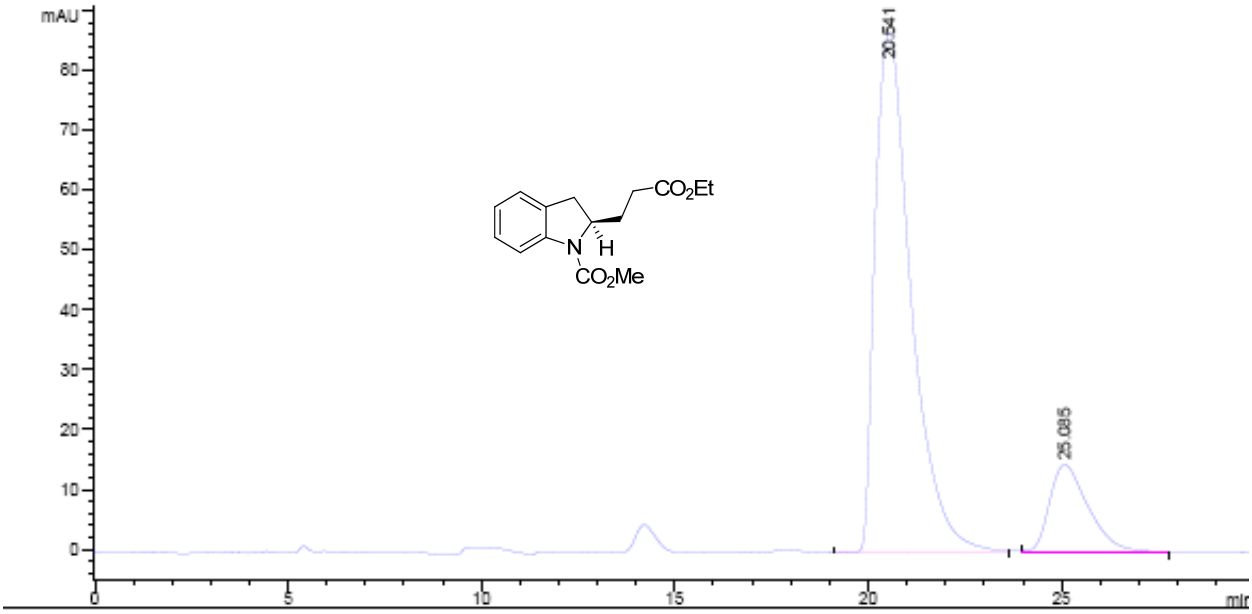


Colorless oil, 63% yield (55.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$): 1.21 (t, J = 7.2 Hz, 3H), 1.88-2.79 (m, 1H), 2.21-2.38 (m, 2H), 2.71 (dd, J = 16.4, 2.4 Hz, 1H), 3.32 (dd, J = 16, 9.6 Hz, 1H), 3.82 (s, 3H), 4.09 (q, J = 7.2 Hz, 2H), 4.44-4.63 (brd, 1H), 6.95 (td, J = 7.6, 0.8 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.48-7.80 (brd, 1H). ^{13}C NMR (100 MHz): δ = 14.4, 30.1, 30.2, 52.8, 58.6, 60.7, 115.8, 123.2, 125.0, 127.7, 130.1, 153.9, 173.2. MS (ESI, 70 eV): *m/z* (%) = 300 $(M+Na)^+$; IR (neat): υ = 753, 859, 941, 1023, 1057, 1089, 1130, 1186, 1225, 1285, 1330, 1389, 1441, 1435, 1503, 2956 cm^{-1}; EI-HRMS calcd. for $C_{15}H_{19}NO_4Na$ 300.1206, found 300.1206.




Parameters
mn4-63p 21 (1D 13C)
F1 :
- Size : 65536 points complex
- Spectral Width : 30120.482 Hz
- Carrier Frequency : 100.62283 MHz
- Nucleus : 13C
Number of scans : 2048
Type : 1D
Spectro : BRUKER 400 MHz
Probe : 5 mm QNP 1H/13C/31P/19F-none-D Z
Date : Thu Aug 18 00:54:21 CEST 2011
Temperature : 300.0 K
Solvent : CDCl3
173.219
153.948
130.137
127.734
125.021
123.190
115.790
77.645
76.910
60.691
58.644
52.784
33.833
30.197
30.055
14.411
ppm


mAU
20.653
25.237
COOEt
N
COOMe
min



Area Percent Report

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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  20.541 VB    1.0079 5656.80176   86.85279  84.5214
   2  25.085 BB    1.0424 1035.94446   14.69674  15.4786

Totals :                  6692.74622  101.54953

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                          *** End of Report ***
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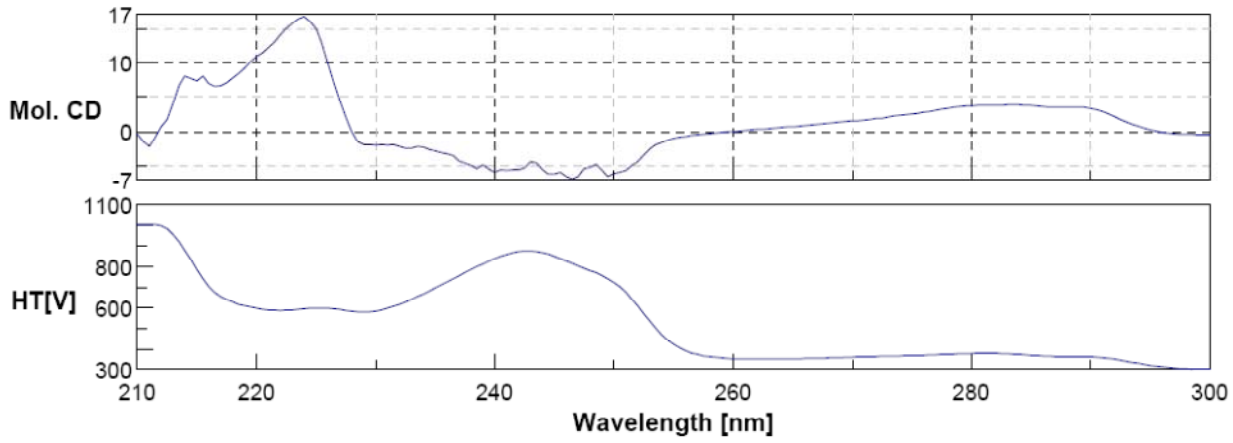
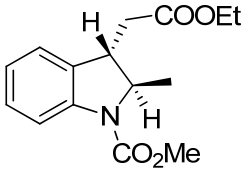
$[\alpha]_D^{20}$ = -31.78 (*c* = 1.0 in CH_2Cl_2), 69% *ee*, [chiral column: OD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 20.54 min. (major) and 25.08 (minor)].

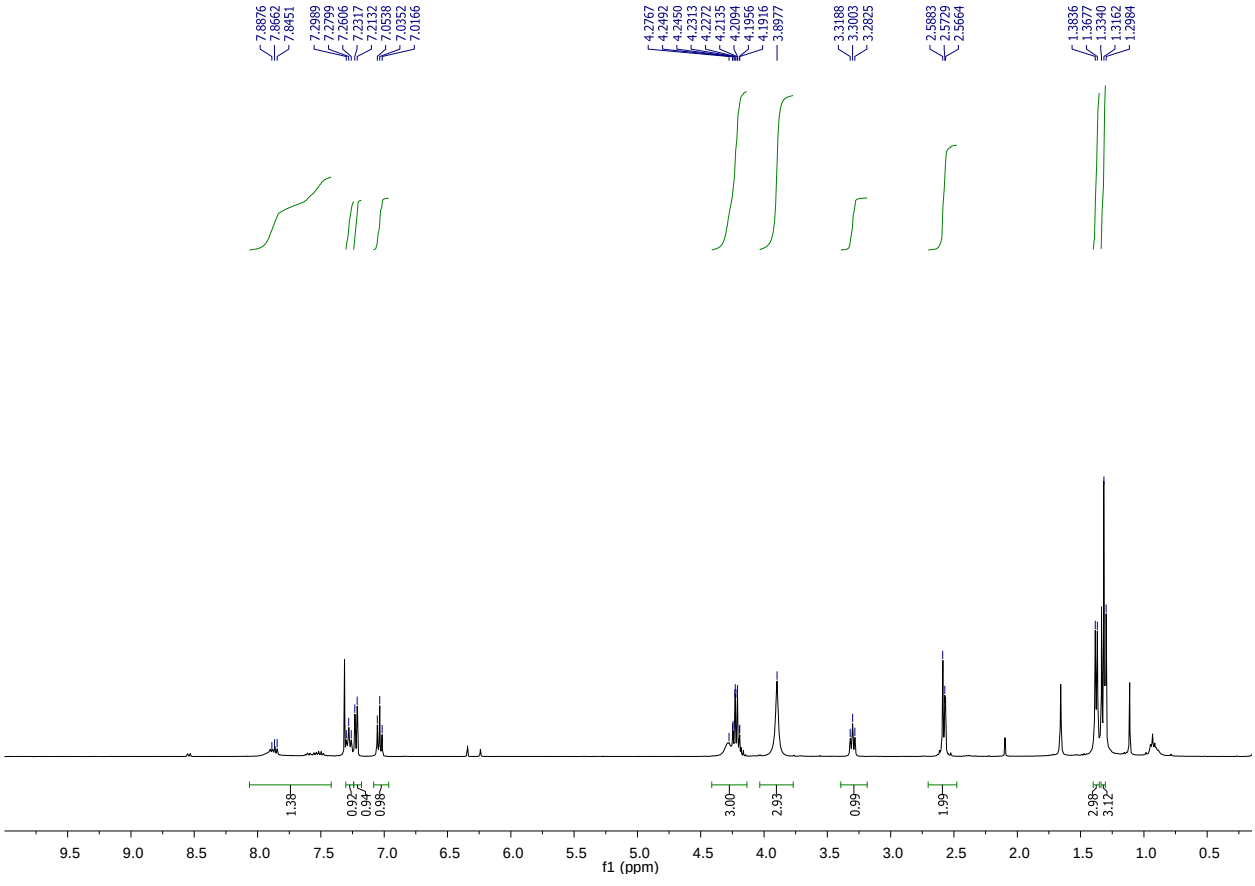


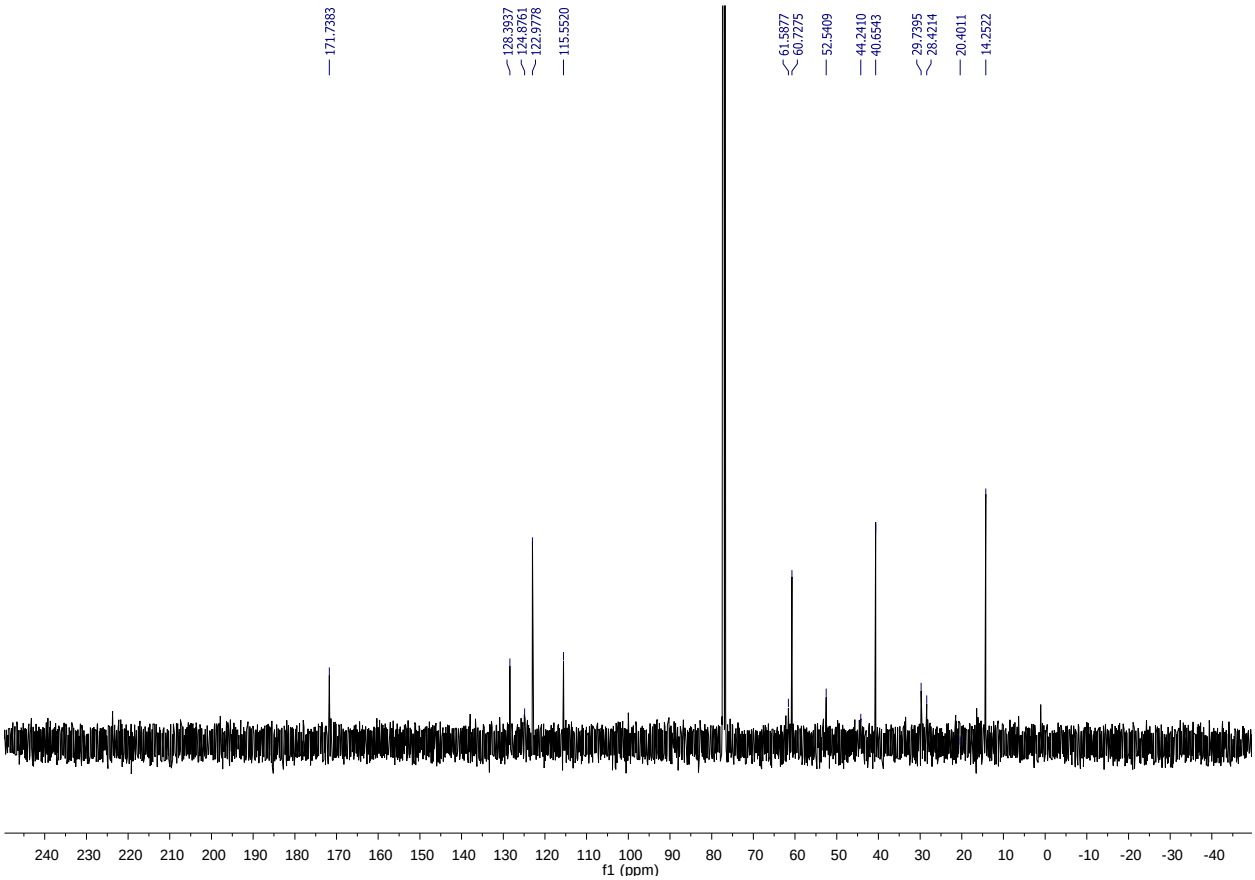
CD spectrum: 0.0001 M in *n*-hexane at 20 °C.

(2*R*,3*S*)-methyl 3-(2-ethoxy-2-oxoethyl)-2-methylindoline-1-carboxylate **8e**; (*S*,*S*)-NHC·HI (**3**) was used.



Colorless oil, 36% yield (19.9 mg), ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (t, *J* = 7.1 Hz, 3H), 1.37 (d, *J* = 6.4 Hz, 3H), 2.56-2.58 (m, 2H), 3.30 (t, *J* = 7.4 Hz, 1H), 3.89 (s, 3H), 4.22 (qd, *J* = 7.2, 1.7 Hz, 2H), 4.27 (brd, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.47-7.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.2, 20.4, 28.4, 29.7, 40.6, 44.2, 52.5, 60.7, 61.5, 115.5, 122.9, 124.8, 128.3, 171.7. IR (neat, cm^{-1}): 2958, 1704, 1602, 1484, 1440, 1336, 1281, 1170, 1059, 1023, 752. EI-HRMS: calcd. for $C_{15}H_{20}NO_4$: 278.1386, found: 278.1380.




171.7383
128.3937
124.8761
122.9778
115.5520
61.5877
60.7275
52.5409
44.2410
40.6543
29.7395
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14.2522
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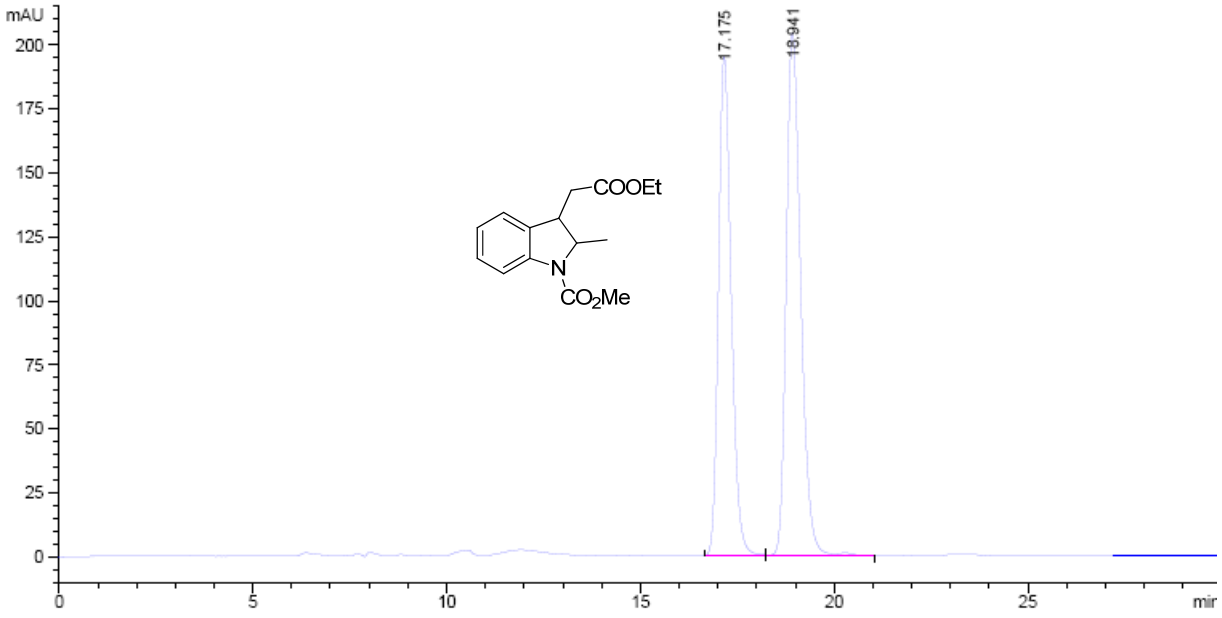
f1 (ppm)


mAU
200
175
150
125
100
75
50
25
0
17.175
18.941
COOEt
N
CO2Me
0
5
10
15
20
25
min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---------------------------------------------------------------------
                      Area Percent Report
---------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  17.040 BV    0.3541 8920.82617  391.05496  99.1643
   2  19.019 VB    0.4779   75.17872    2.32065   0.8357

Totals :                  8996.00489  393.37562

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                      *** End of Report ***
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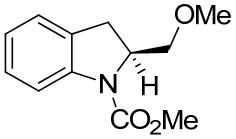
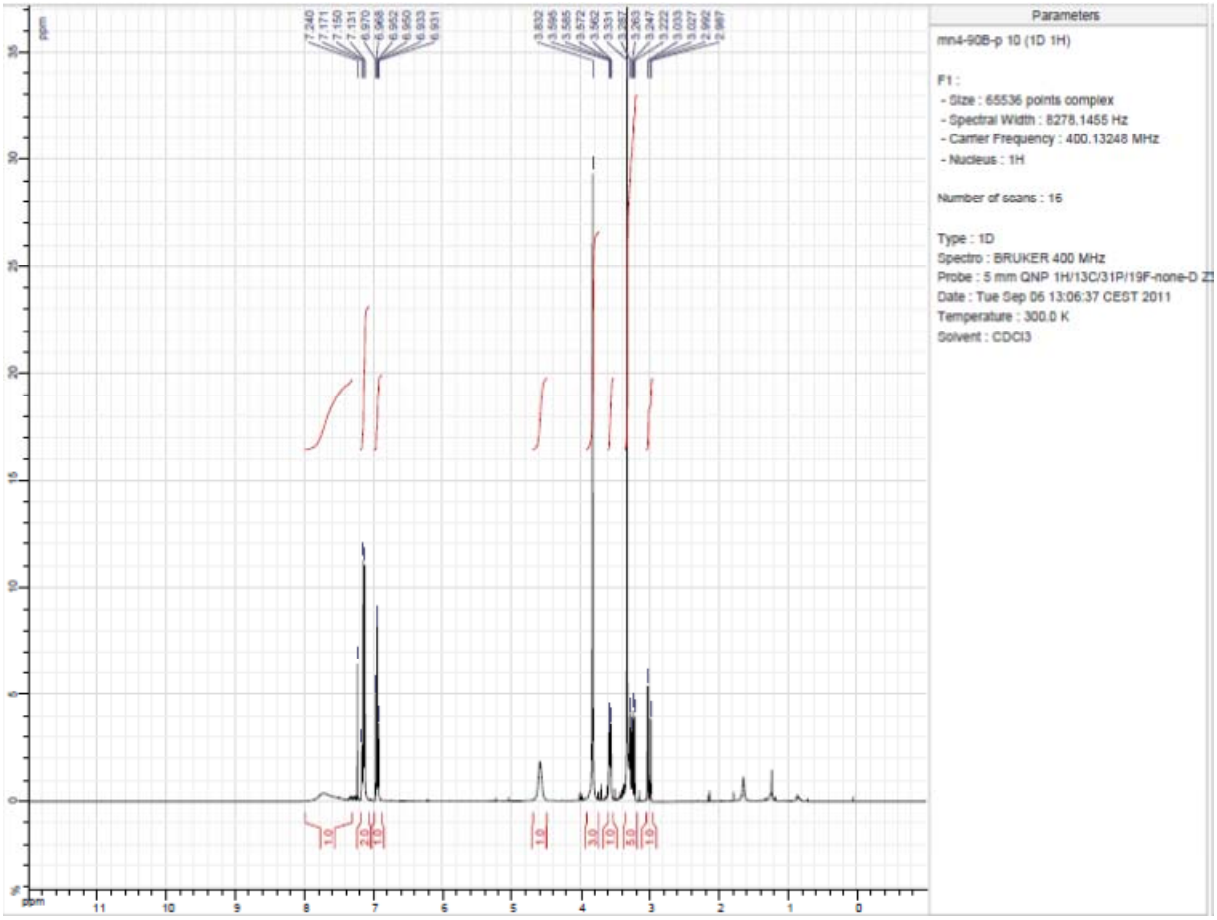
$[\alpha]_D^{20}$ = -8.43 (*c* = 0.5 in CH_2Cl_2). 98% *ee*, [chiral column: AS-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 17.04 min. (major) and 19.01 (minor)].

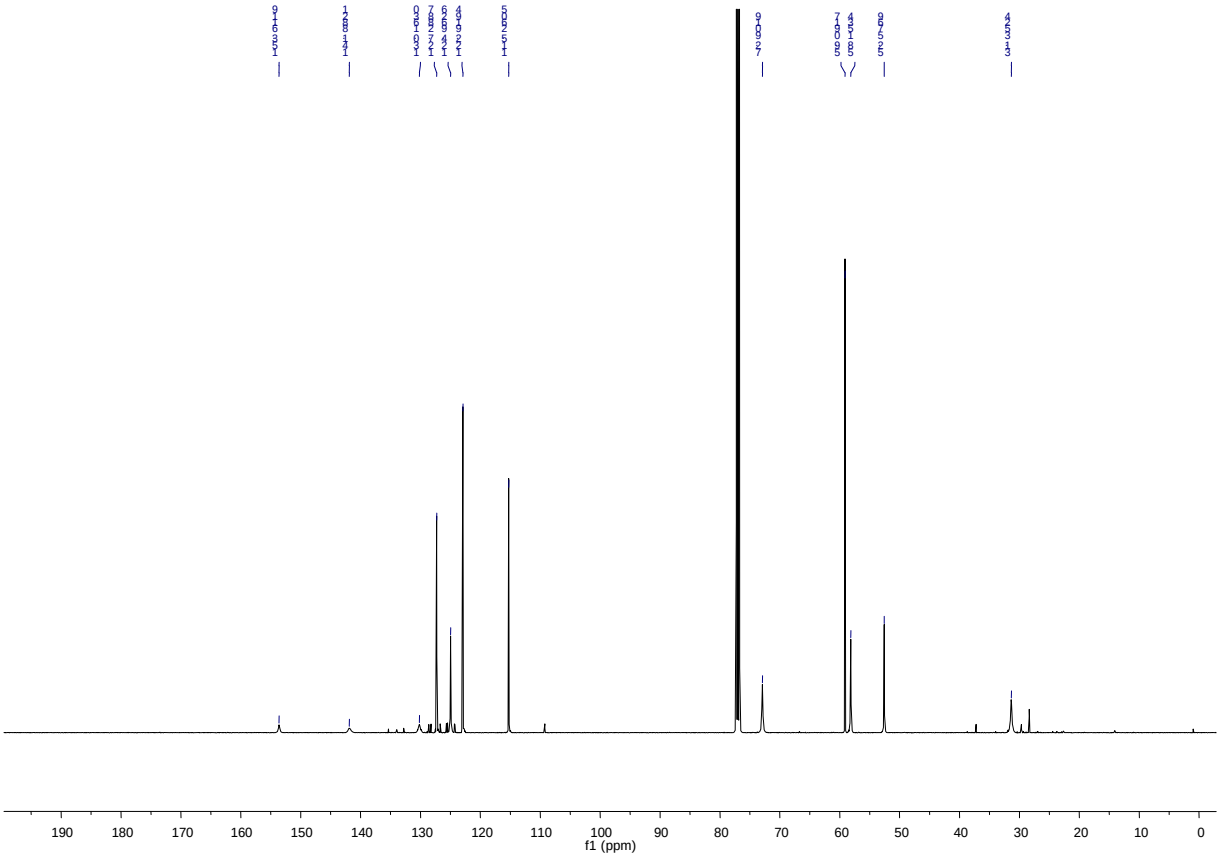
(*S*)-methyl 2-(methoxymethyl)indoline-1-carboxylate **7f**; (*S*,*S*)-NHC·HI (**3**) was used.

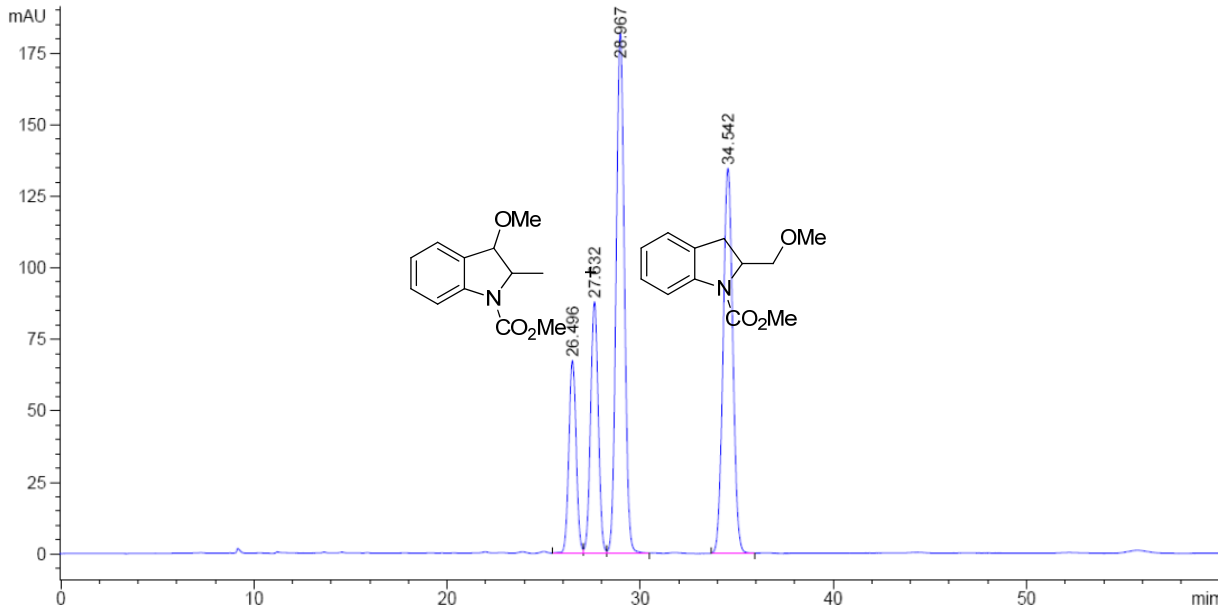


Colorless oil, 62% yield, calcd. by NMR (27.4 mg), ^{1}H NMR (400 MHz, $CDCl_3$): 3.01 (dd, *J* = 16.4, 2.4 Hz, 1H), 3.25 (dd, *J* = 16, 9.6 Hz, 1H), 3.58 (dd, *J* = 9.2, 4 Hz, 1H), 3.83 (s, 3H), 4.50-4.70 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 8.4 Hz, 1H), 7.32-8.00 (brd, 1H). ^{13}C NMR (125 MHz): δ = 31.3, 52.5, 58.1, 59.0, 72.9, 115.2, 122.9, 124.9, 127.2, 130.1, 141.8,

153.6. MS (ESI, 70 eV): *m/z* (%) = 244 $(M+H)^+$; IR (neat): υ = 712, 752, 833, 860, 939, 972, 1021, 1055, 1116, 1137, 1192, 1225, 1282, 11308, 1332, 1379, 1440, 1462, 1484, 1602, 1702, 2926 cm^{-1}; ESI-HRMS calcd. for $C_{12}H_{15}NO_3Na$ 244.0944, found 244.0944.




190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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75
50
25
0
0
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20
30
40
50
min
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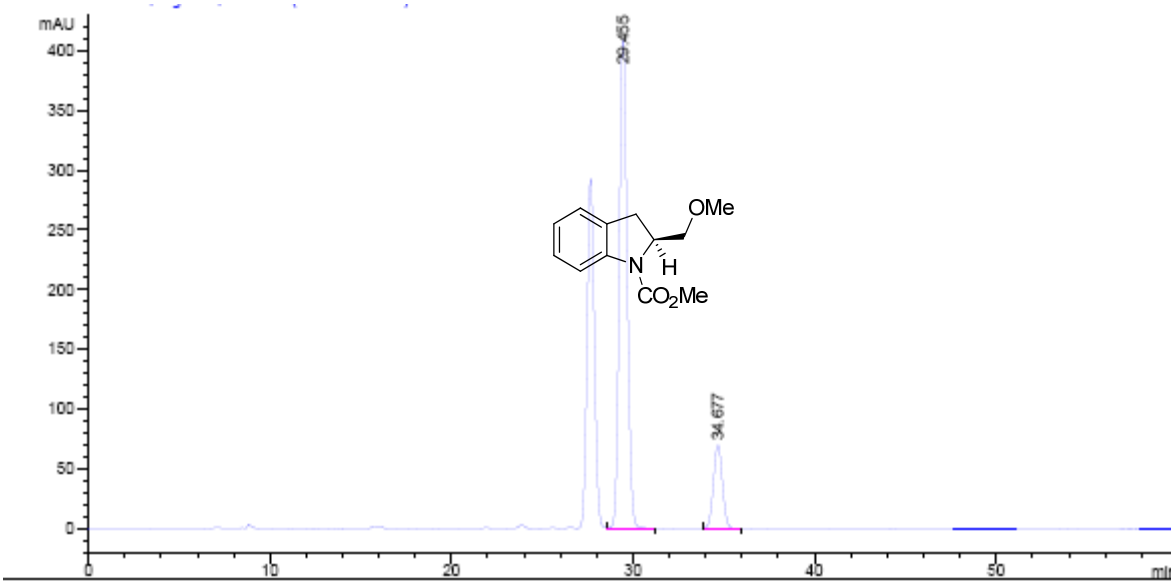
28.967
34.542
OMe
N
CO2Me
OMe
N
CO2Me

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                      Area Percent Report
---------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
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   2  34.677 BB     0.5486 2418.88599   69.75639  16.3091

Totals :                  1.48315e4   477.05186

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                      *** End of Report ***
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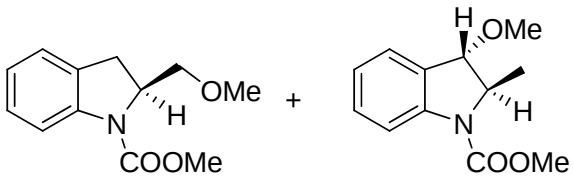
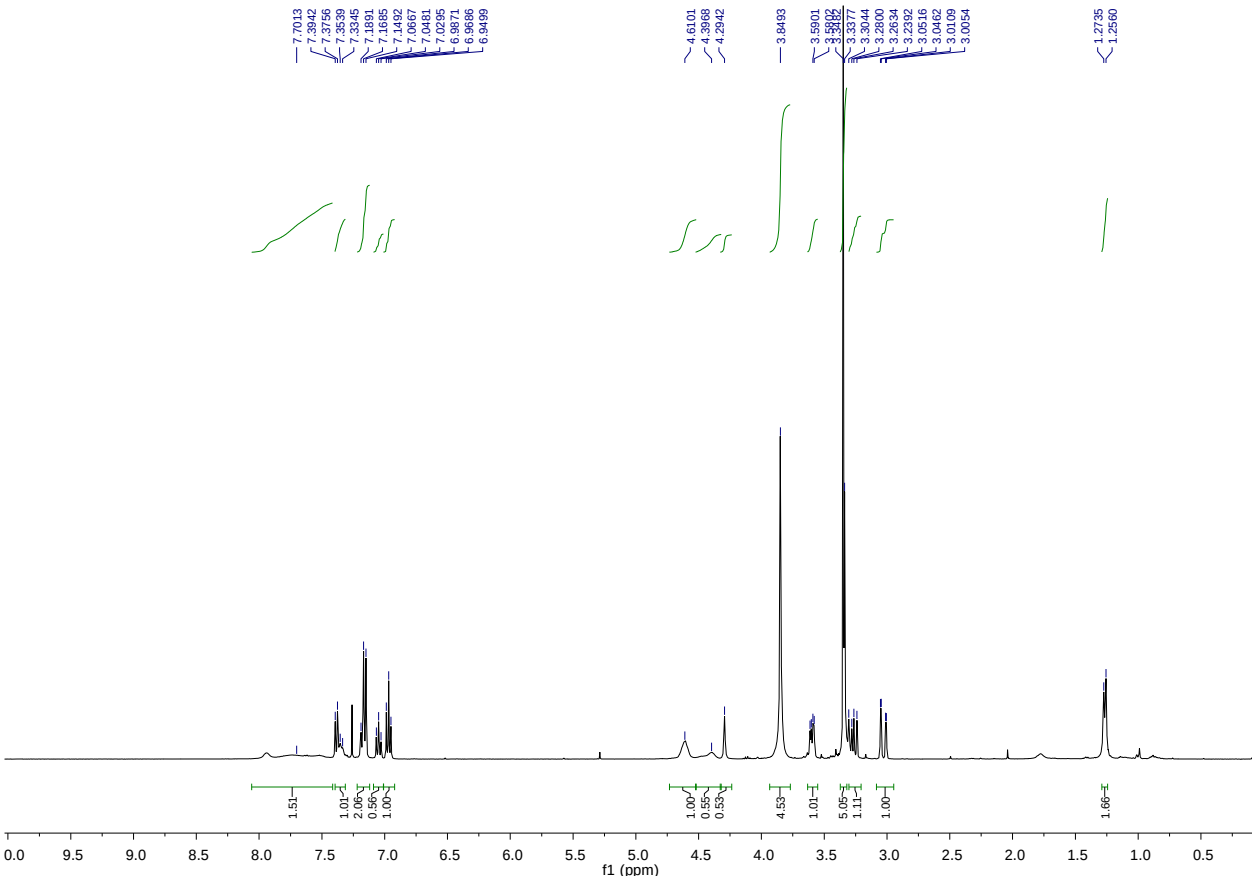
7f: 67% *ee* [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 29.45 min. (major) and 34.67 (minor)].

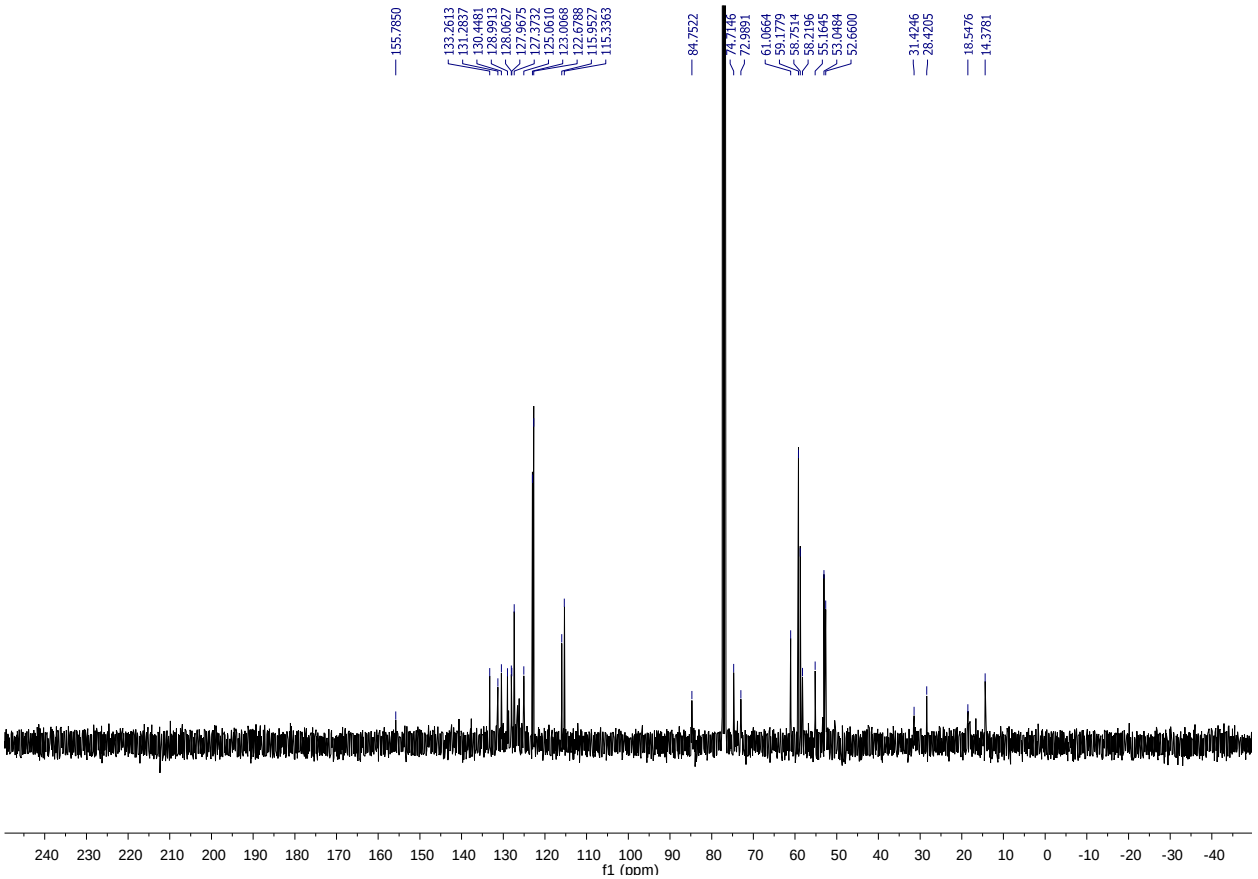
(*S*)-methyl 2-(methoxymethyl)indoline-1-carboxylate **7f** and (2*R*,3*S*)-methyl 3-methoxy-2-methylindoline-1-carboxylate **8f**; (*S*,*S*)-NHC·HI (**3**) was used.



Colorless oil, 24% yield calcd. by NMR (10.6 mg), **7f** + **8f**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (d, *J* = 7.0 Hz, 1.5H), 3.03 (dd, *J* = 16.2, 2.1 Hz,. 1H), 3.27 (dd, *J* = 16.4, 9.7 Hz, 1H), 3.33 (s, 1.5H), 3.34 (s, 3H), 3.60 (dd, *J* = 9.0, 3.9 Hz, 1H), 3.84 (s, 4.5H), 4.29 (brd, 0.5H),

4.39 (brd, 0.5H), 4.61 (brd, 1H), 6.96 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 7.4 Hz, 0.5H), 7.14-7.18 (m, 2H), 7.33-7.39 (m, 1H), 7.70 (brd, 1.5H). **7f** + **8f**: ^{13}C NMR (100 MHz, $CDCl_3$): 14.3, 18.5, 28.4, 31.4, 52.6, 53.0, 55.1, 58.2, 58.7, 59.1, 61.0, 72.9, 74.7, 84.7, 115.3, 115.9, 122.6, 123.0, 125.0, 127.3, 127.9, 128.0, 128.9, 130.4, 131.2, 133.2, 155.7.

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131.2837
130.4481
128.9913
128.0627
127.9675
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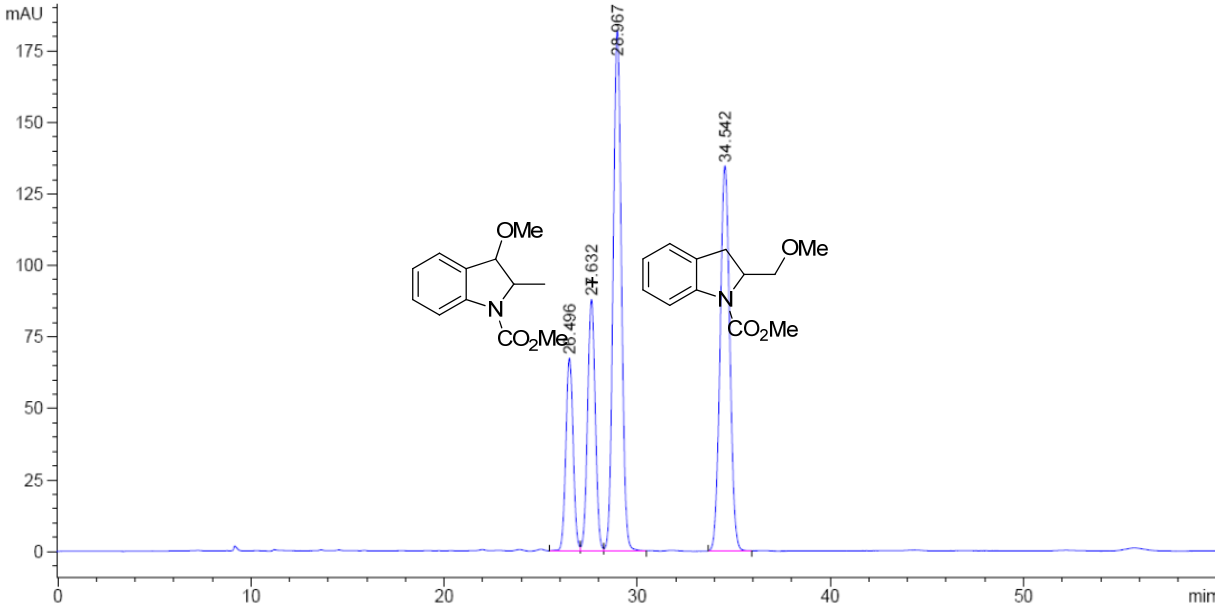
125.0610
123.0068
122.6788
115.9527
115.3363
84.7522
74.7146
72.9891
61.0664
59.1779
58.7514
58.2196
55.1645
53.0484
52.6600
31.4246
28.4205
18.5476
14.3781
f1 (ppm)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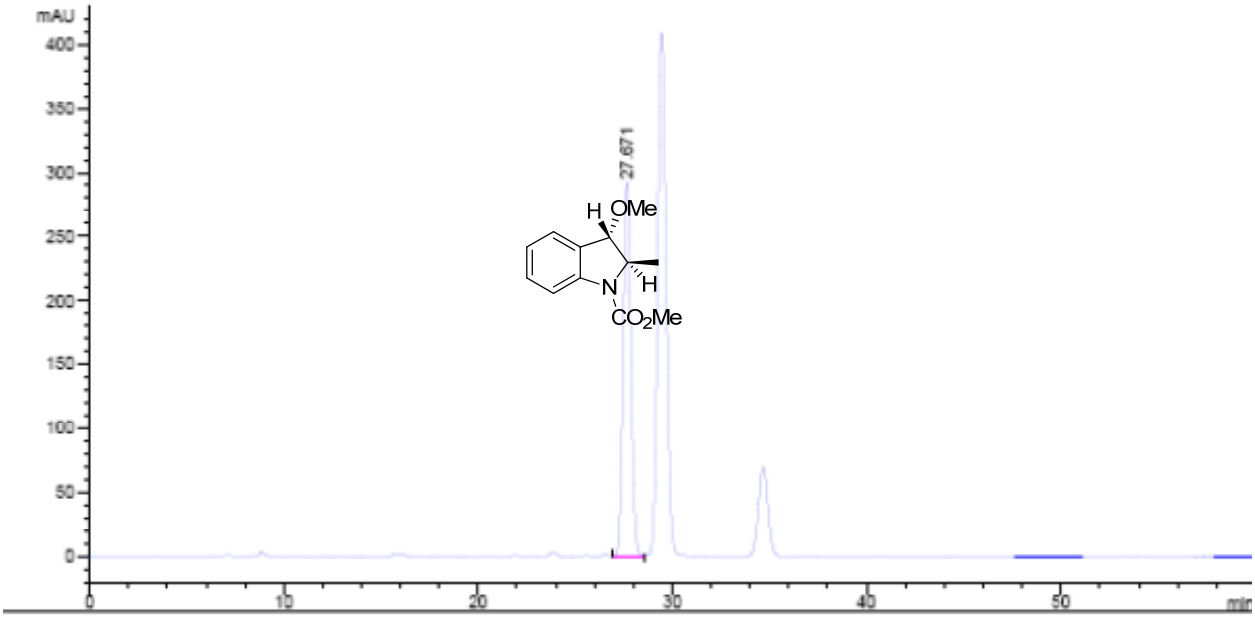
OMe
N
CO2Me
25.632
25.496
OMe
N
CO2Me
min



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

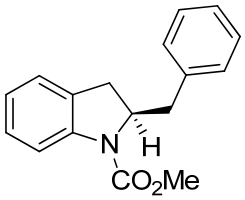
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.671	VV	0.4539	8144.41992	291.55579	100.0000

Totals : 8144.41992 291.55579

*** End of Report ***

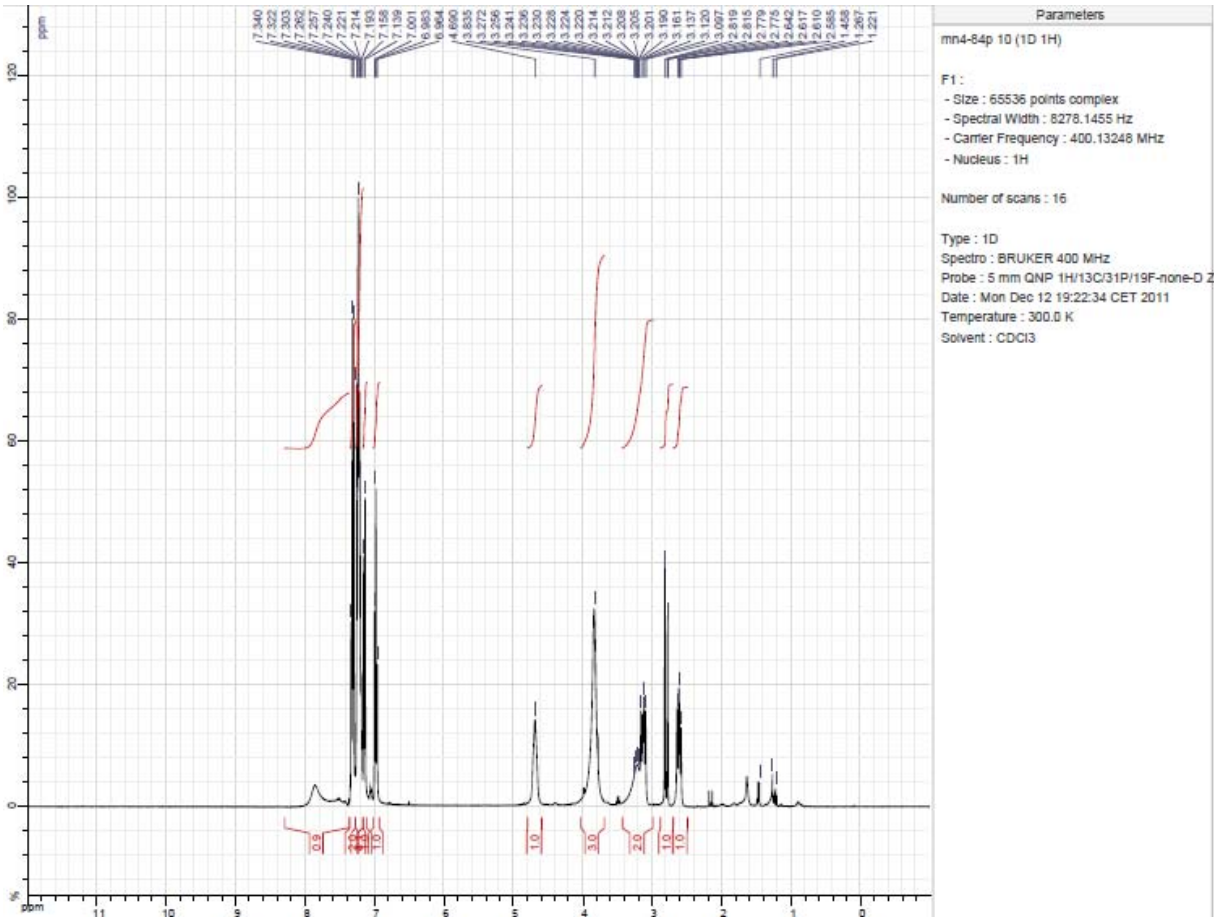
8f: >99% *ee* [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 27.67 min. (major)].

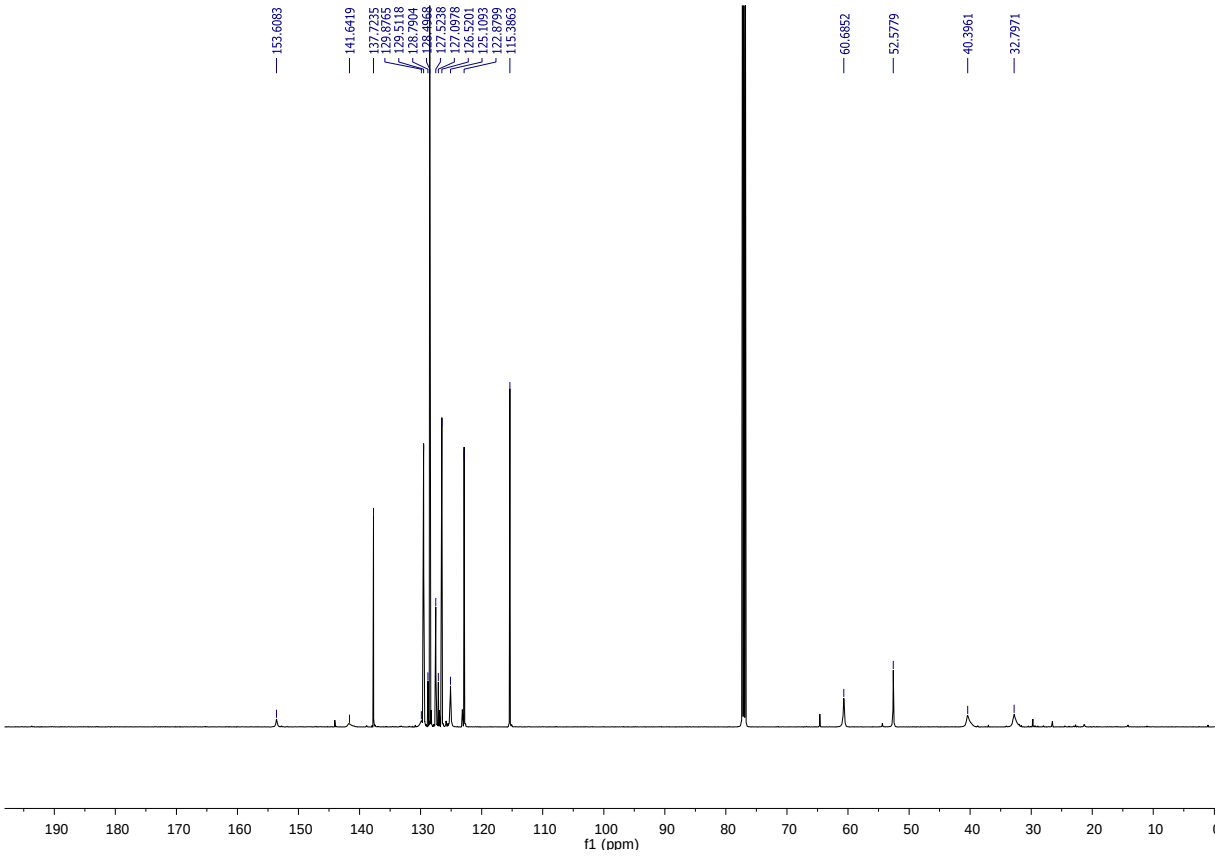
(*R*)-methyl 2-benzylindoline-1-carboxylate **7g**; (*S*,*S*)-NHC·HI (**4**) was used.

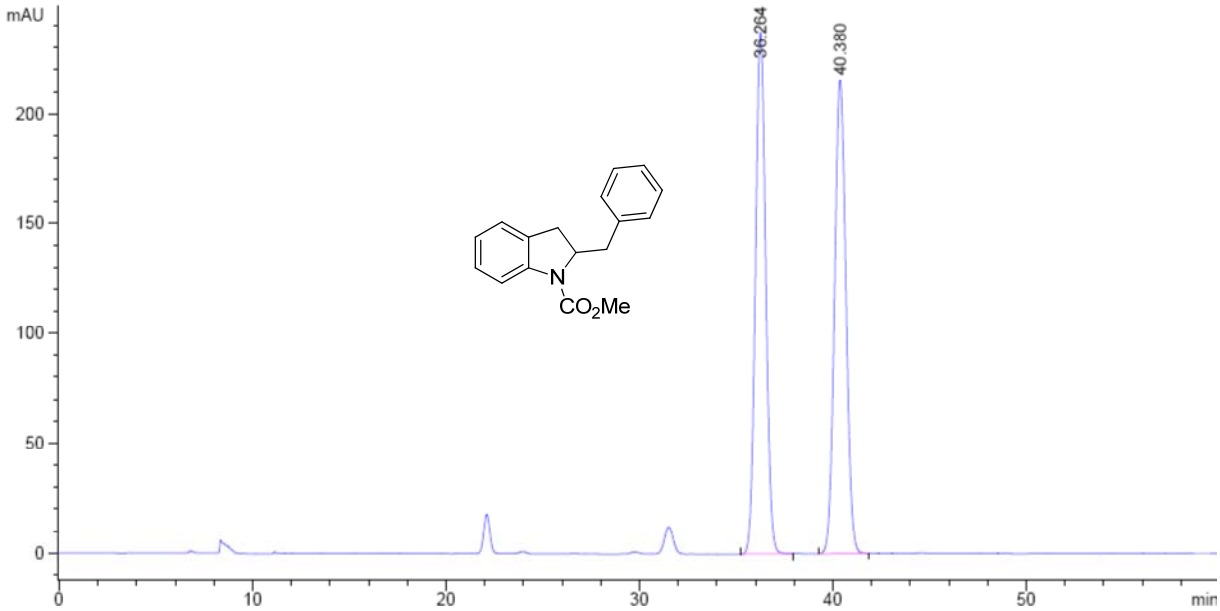


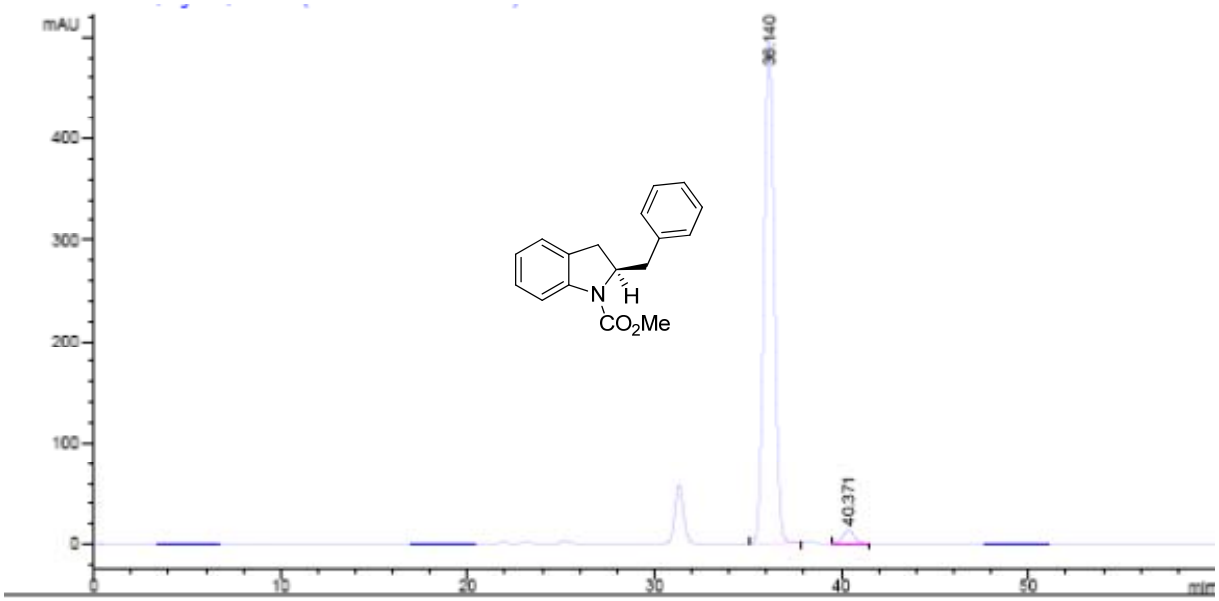
Colorless oil, 49% yield (26.2 mg), 95% *ee*, ^{1}H NMR (400 MHz, $CDCl_3$): 2.61 (dd, *J* = 12.8, 10 Hz, 1H), 2.80 (dd, *J* = 16, 1.6 Hz, 1H), 3.13 (dd, *J* = 16.4, 9.6 Hz, 1H), 3.00-3.42 (m, 1H), 3.84 (s, 3H), 4.60-4.80 (m, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.17-7.28

(m, 4H), 7.28-7.36 (m, 2H), 7.38-8.30 (brd, 1H). ^{13}C NMR (125 MHz): δ = 32.7, 40.3, 52.5, 60.6, 115.3, 122.8, 125.1, 126.5, 127.0, 127.5, 128.4, 128.7, 129.5, 137.7, 141.6, 153.6. MS (ESI, 70 eV): *m/z* (%) = 268 $(M+H)^+$; IR (neat): υ = 698, 725, 759, 845, 870, 894, 918, 936, 1020, 1058, 1087, 1128, 1145, 1191, 1232,1275, 1309, 1359, 1391, 1441, 1484, 1602, 1703, 2855, 2913, 2948, 3029, 3064 cm^{-1}; ESI-HRMS calcd. for $C_{17}H_{18}NO_2$ 268.1332, found 268.1338.




153.6083
141.6419
137.7235
129.8765
129.5118
128.7904
127.5238
127.0978
126.5201
125.1093
122.8799
115.3863
60.6852
52.5779
40.3961
32.7971
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


mAU
200
150
100
50
0
36.264
40.380
N
CO2Me
0 10 20 30 40 50
min

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---------------------------------------------------------------------
                        Area Percent Report
---------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  36.140 BB    0.5950 1.88282e4   495.83286  97.3249
   2  40.371 BB    0.6395  517.52594   12.59264   2.6751

Totals :                  1.93457e4   508.42550

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                        *** End of Report ***
```
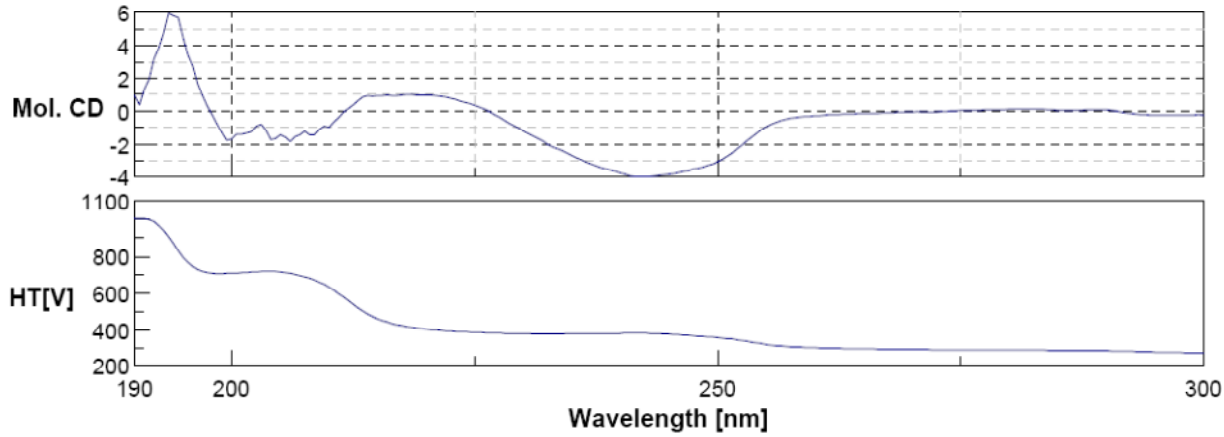
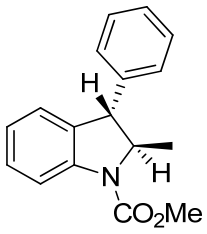

$[\alpha]_D^{25}$ = -21.25 (*c* = 1.0 in CH_2Cl_2), 95% *ee*, [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 36.14 min. (major) and 40.37 (minor)].

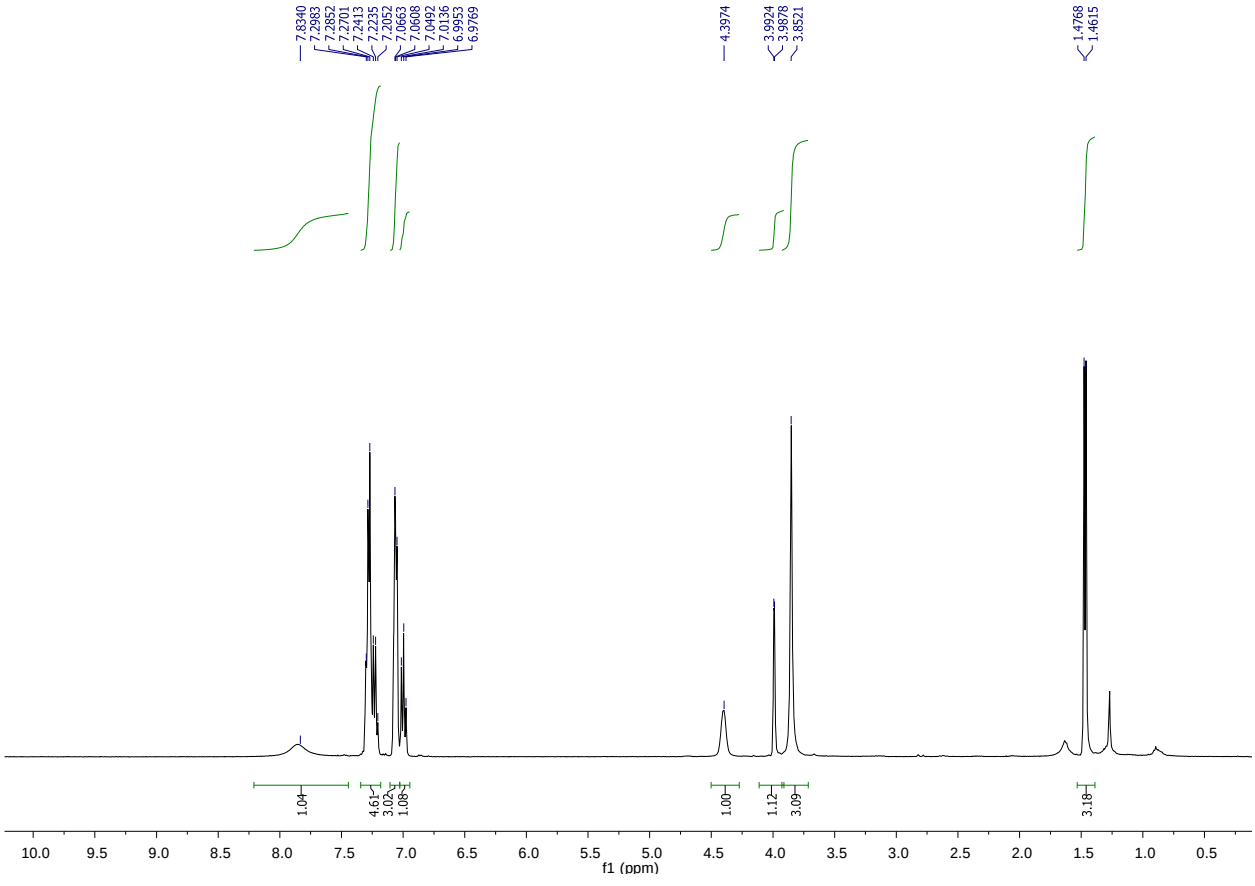


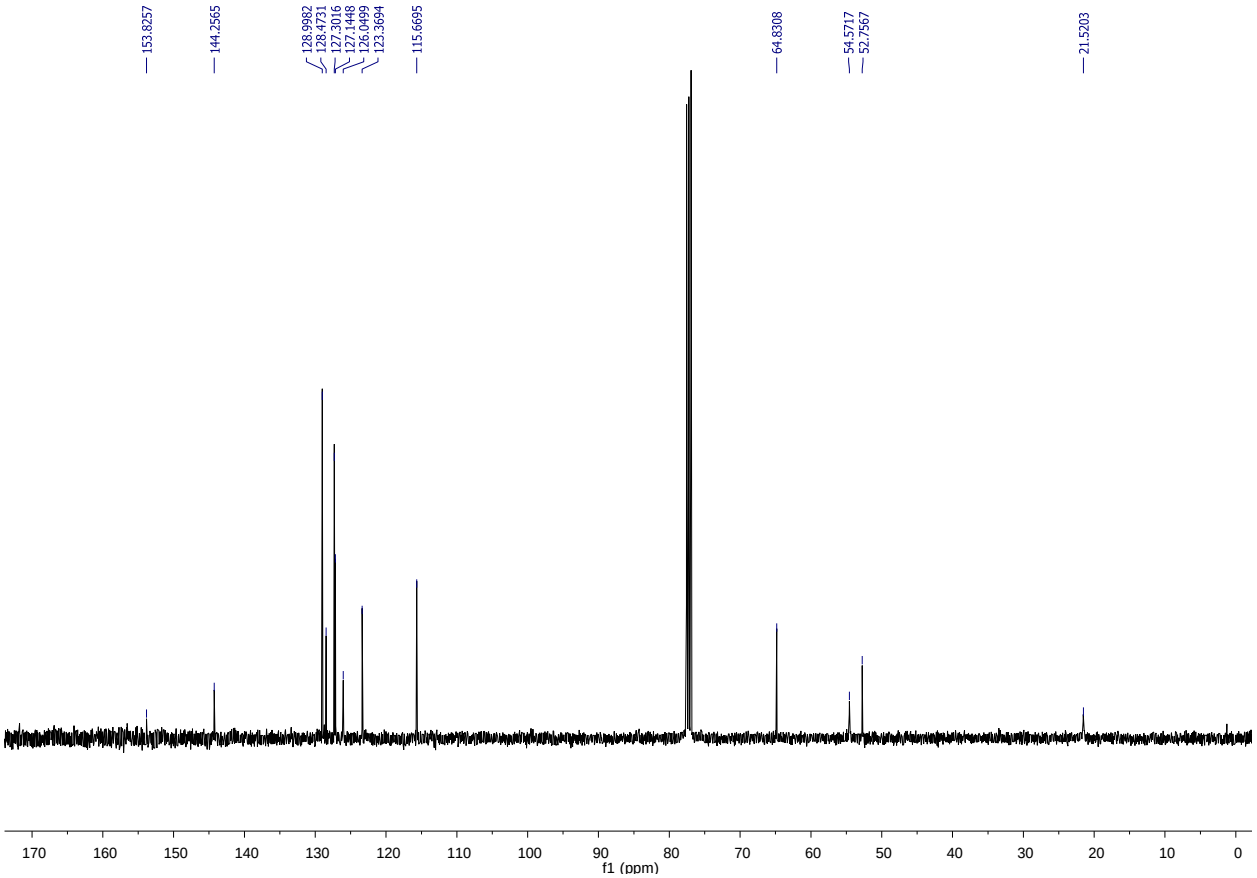
CD spectrum: 0.0001 M in *n*-hexane at 20 °C.

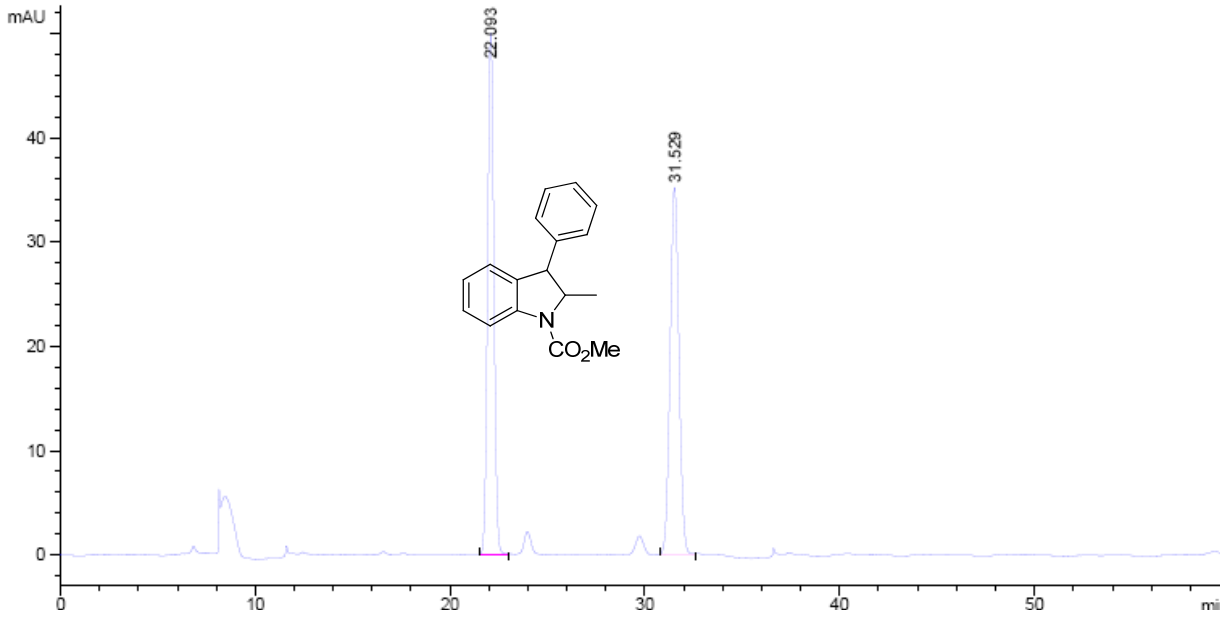
(2*R*,3*S*)-methyl 2-methyl-3-phenylindoline-1-carboxylate **8g**; (*S*,*S*)-NHC·HI (**4**) was used.

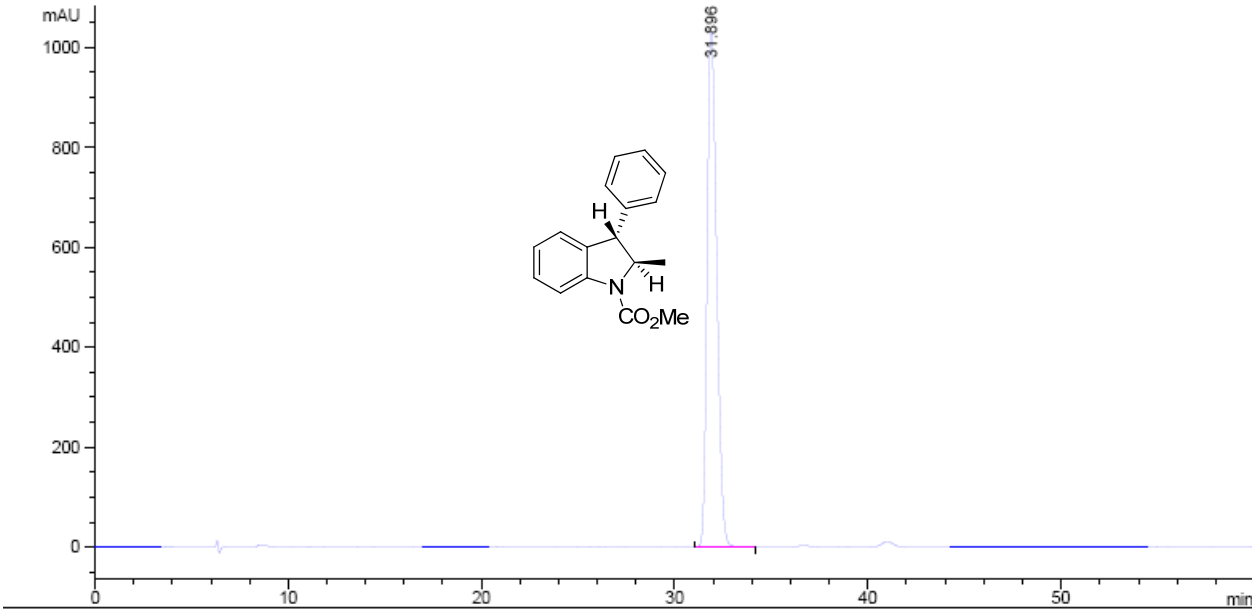


Colorless oil, 44% yield (23.5 mg), ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 (d, *J* = 6.1 Hz, 3H), 3.85 (s, 3H), 3.98 (d, *J* = 1.8 Hz, 1H), 4.39 (brd, 1H), 6.99 (t, *J* = 7.3 Hz, 1H), 7.03-7.06 (m, 3H), 7.20-7.29 (m, 4H), 7.81 (brd, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 21.5, 52.7, 54.5, 64.8, 115.6, 123.3, 126.0, 127.1, 127.3, 128.4, 128.9, 144.2, 153.8. IR (neat, cm^{-1}): EI-HRMS: calcd. for $C_{17}H_{18}NO_2$: 268.1332, found: 268.1332.




153.8257
144.2565
128.9982
128.4731
127.3016
127.1448
126.0499
123.3694
115.6695
64.8308
54.5717
52.7567
21.5203
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


mAU
40
30
20
10
0
22.093
31.529
N
CO2Me
0
10
20
30
40
50
mi

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================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  31.896 BB    0.5378 3.55467e4  1032.11169 100.0000

Totals :                  3.55467e4  1032.11169

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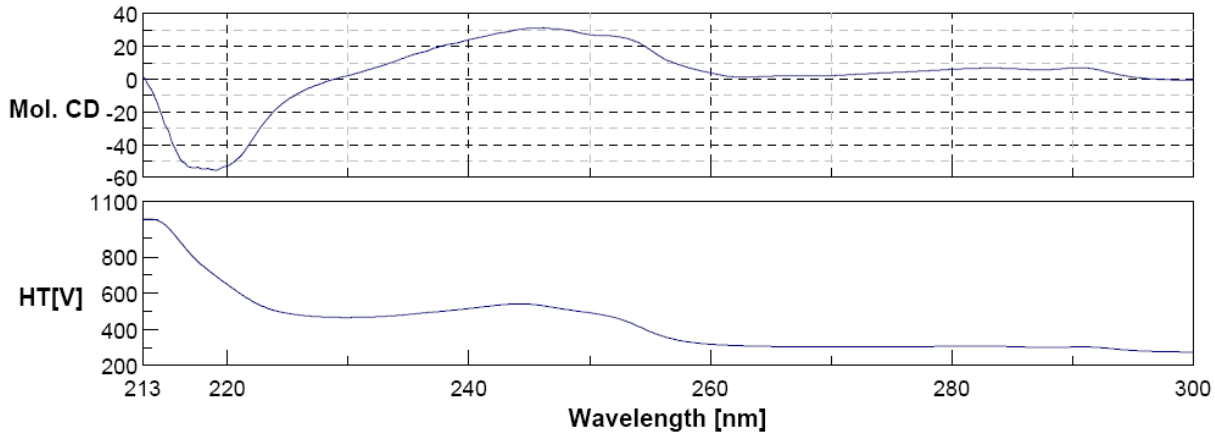
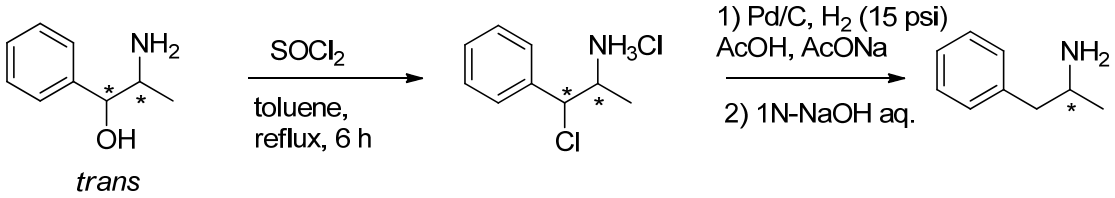
                          *** End of Report ***
```

$[\alpha]_D^{20} = +110.15$ (c = 1.0 in CH_2Cl_2), >99% *ee* [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 31.89 min. (major)].



CD spectrum: 0.0001 M in *n*-hexane at 20 °C.

1.8. Preparation of (*S*)- and (*R*)-1-phenylpropan-2-amine: [5]

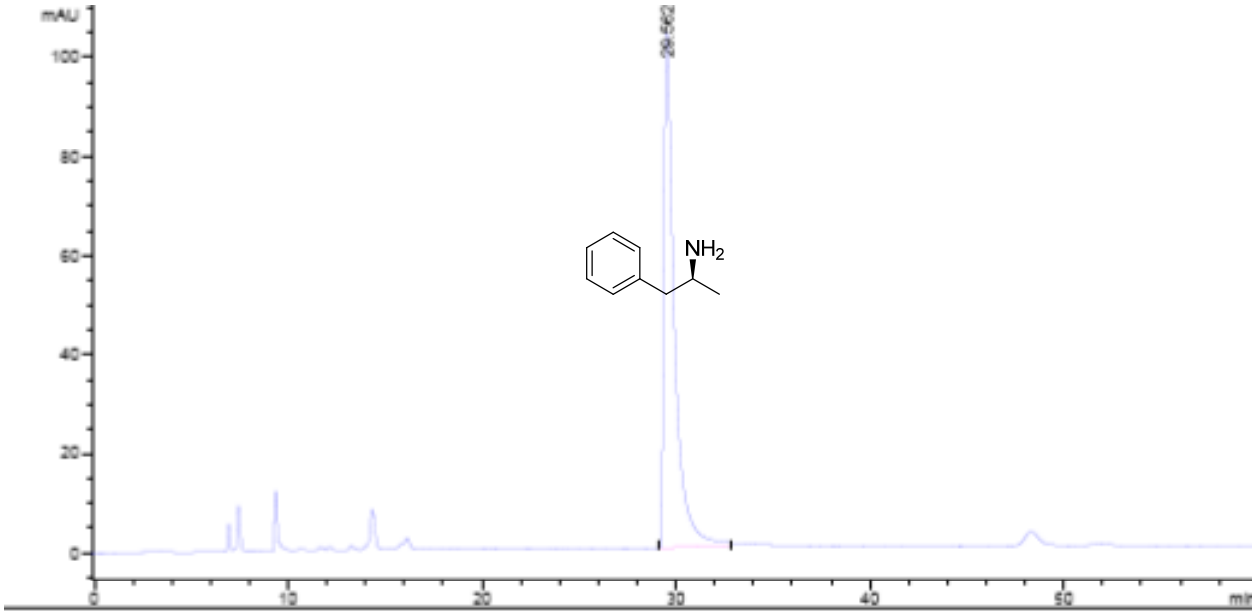


To a solution of (L)-(-)-norephedrine (4.0 g, 26.5 mmol, 1 eq.) in toluene (40 mL), thionyl chloride (4.0 g, 33.6 mmol, 1.26 eq.) was slowly added and the reaction mixture stirred at 60 °C for 6 hours. After cooling the reaction mixture to 10 °C, the product started to precipitate. The solid was collected by filtration, washed with toluene (20 mL) and dried in vacuo to afford the crude (L)-(-)-chloroamphetamine hydrochloride (5.1g, 95%).

A two neck round bottom flask (100 mL) with a magnetic stirring bar was charged with (L)-(-)-chloroamphetamine hydrochloride (5.0 g, 24.2 mmol), water (12 mL) and activated charcoal (5 g). Then 0.31 g of Pd/C (50 wt% water wet) was added along with sodium acetate (4.5 g, 54 mmol), and acetic acid (11.0 g, 183 mmol). The flask was put under a H_2 atmosphere (H_2 filled balloon) and stirred at 20 °C for 24 hours. The reaction mixture was filtered through a pad of celite and washed with water. The pH of the filtrate was adjusted to pH 12 with sodium hydroxide. The crude product was extracted with ethyl acetate, washed with brine and dried over $MgSO_4$. After filtration, volatiles were removed by rotary evaporator affording (*S*)-1-phenylpropan-2-amine in (3.2 g, 98%).

(*S*)-1-Phenylpropan-2-amine:

Colorless oil, $[\alpha]_D^{25} = +23.1$ (*c* = 1.0 in CH_2Cl_2), >99% *ee*, [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 29.56 min. (major)].

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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  29.562 BB    0.5622 3946.68872  102.27239 100.0000

Totals :                  3946.68872  102.27239

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                        *** End of Report ***
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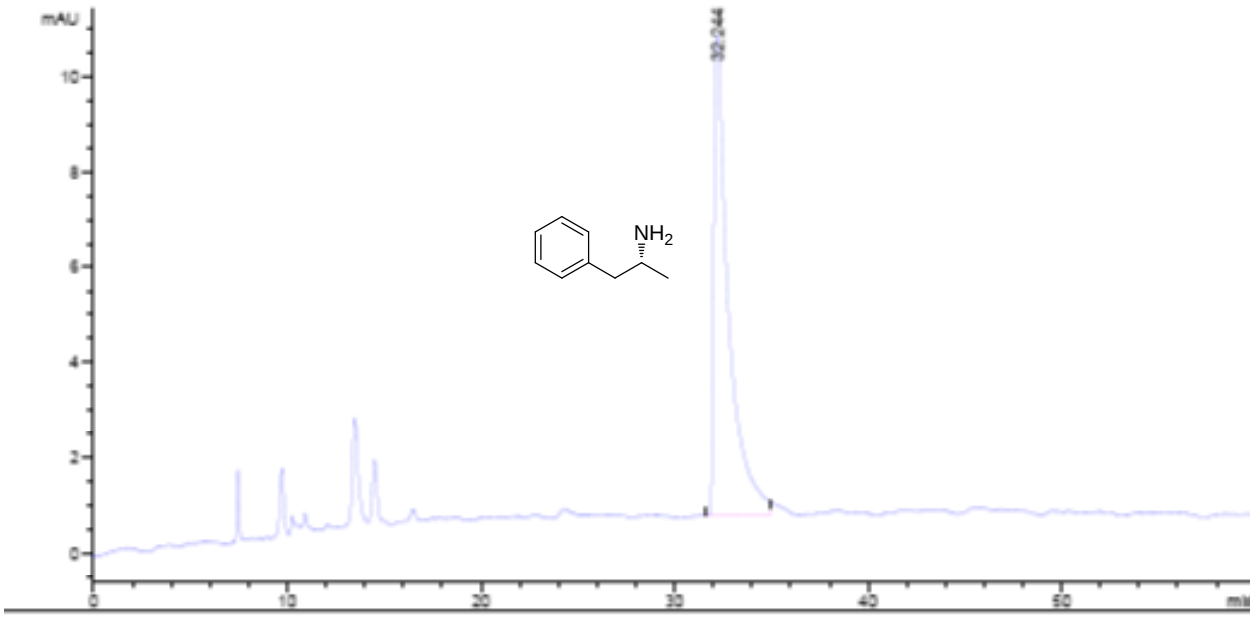
(*R*)-1-phenylpropan-2-amine: Colorless oil, $[\alpha]_D^{25}$ = -24.15 (*c* = 1.0 in CH_2Cl_2), >99% *ee* [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 32.24 min. (major)].

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                      Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  32.244 BB    0.7621  529.71918    9.99876 100.0000

Totals :                   529.71918    9.99876

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                      *** End of Report ***
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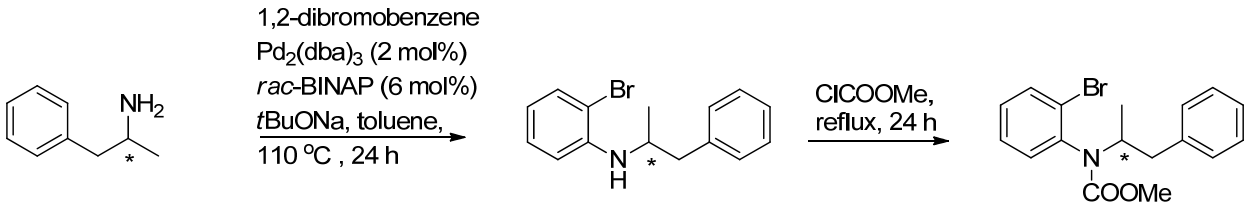
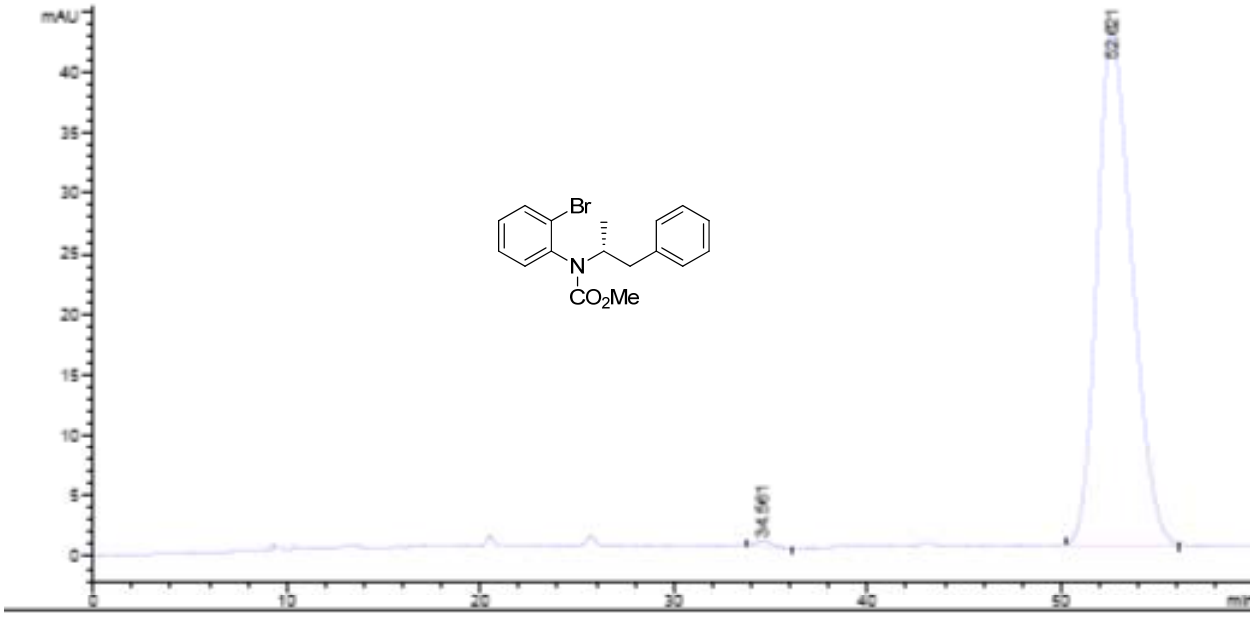
1.9 Preparation of enantio-pure (*R*)- and (*S*)-methyl (2-bromophenyl)(1-phenylpropan-2-yl)carbamate 6g:



6g

(*R*)-methyl (2-bromophenyl)(1-phenylpropan-2-yl)carbamate **6g**:

$[\alpha]_D^{25}$ = -29.15 (*c* = 1.0 in CH_2Cl_2), 99% *ee*, [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 34.56 min. (minor) and 52.62 min. (major)].



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

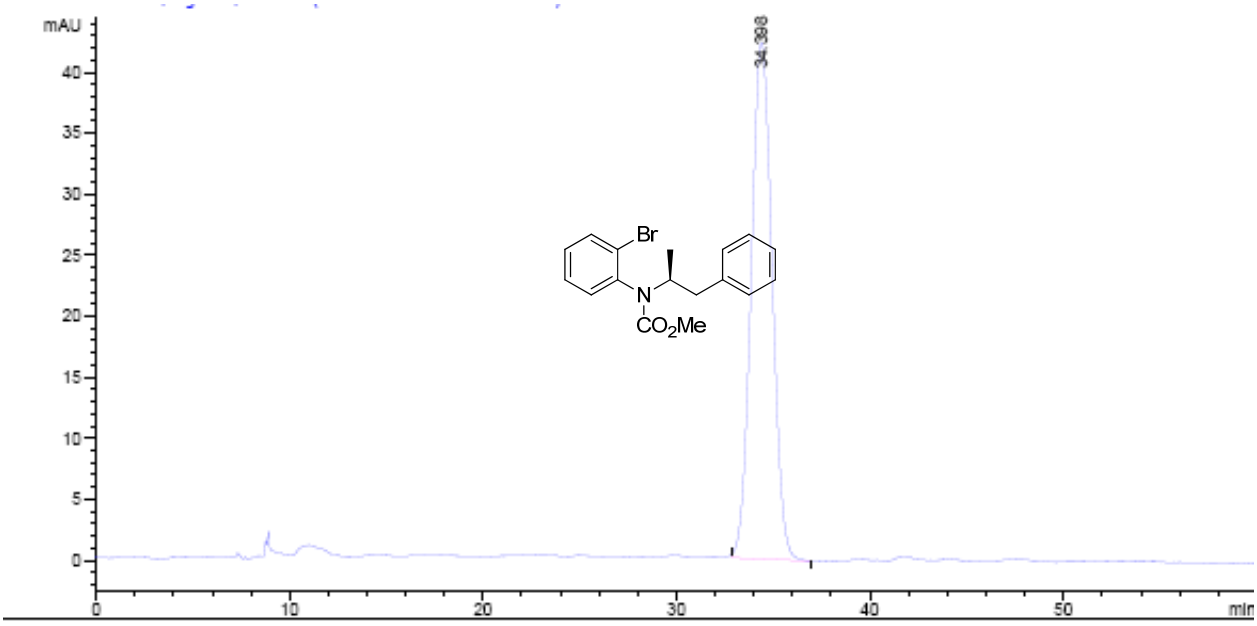
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.561	BB	0.7814	31.66782	4.82730e-1	0.5916
2	52.621	BB	1.8124	5321.57129	42.27932	99.4084
Totals :				5353.23911	42.76205	

*** End of Report ***

(*S*)-methyl (2-bromophenyl)(1-phenylpropan-2-yl)carbamate **6g**:

$[\alpha]_D^{25}$ = +30.8 (*c* = 1.0 in CH_2Cl_2), >99% *ee*, [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 34.39 min. (major)].

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------------------------------------------------------------------------
                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  34.398 BB    1.1820 3182.51099   42.28788 100.0000

Totals :                  3182.51099   42.28788

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                        *** End of Report ***
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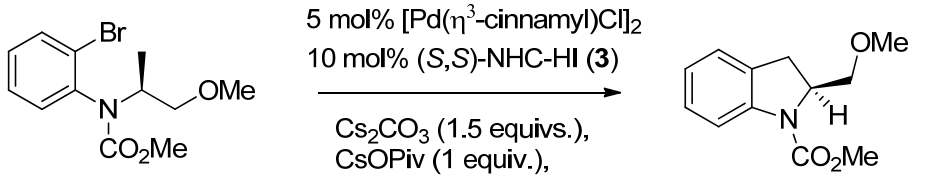
1.10 Synthesis of (*S*)-methyl 2-(methoxymethyl)indoline-1-carboxylate 7f:

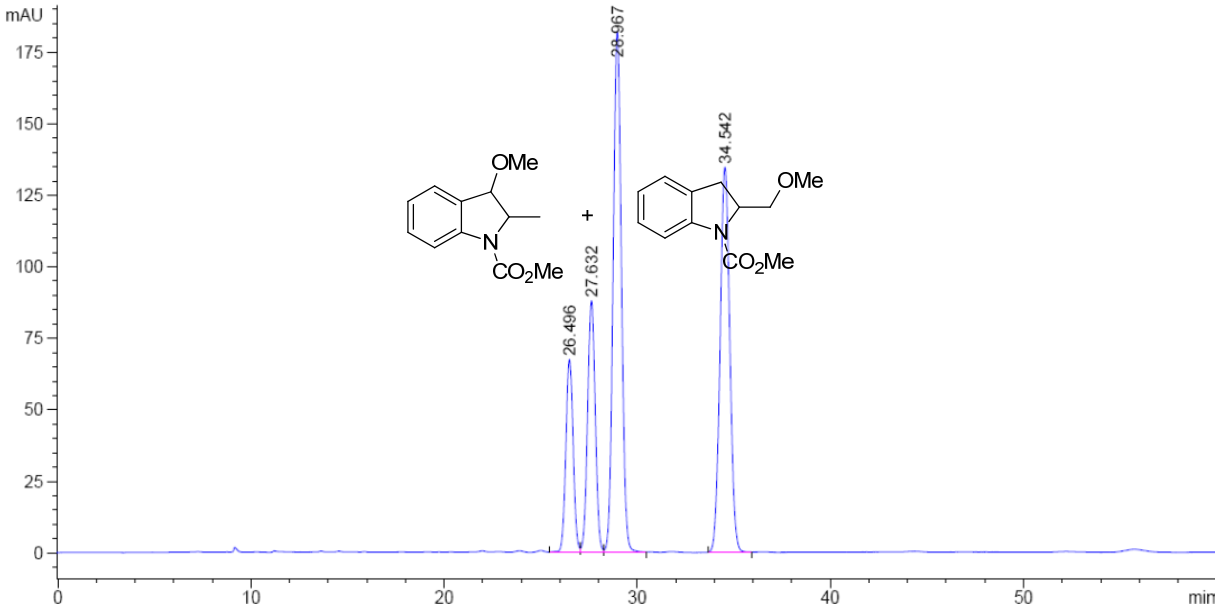


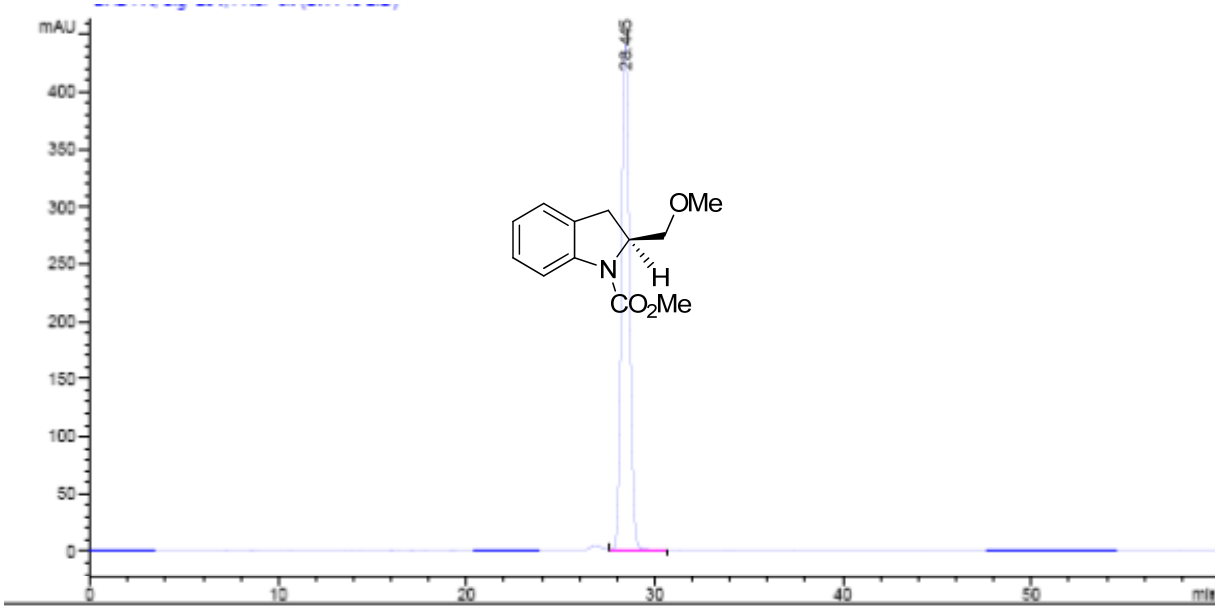
(*S*)-**6f** (>99% ee)

(*S*)-**7f** 97%, >99% ee

Carbamate (*S*)-**6f** [6] (60.4 mg, 0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), [Pd(π-cinnamyl)Cl]$_2$ (5.2 mg, 0.01 mmol), cesium pivalate (46.8 mg, 0.2 mmol) and (*S*,*S*)-NHC·HI (**3**) (11.8 mg, 0.02 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylenes (2 mL) was added under nitrogen. The resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 24 hours. The

reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c.(silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the indoline methyl carbamate (*R*)-**7f** in 97% yield (42.8 mg) and >99% ee [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 28.44 min. (major)].



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*********************************************************************
                        Area Percent Report
*********************************************************************

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]    [mAU*s]     [mAU]       %
---|-------|----|-------|----------|----------|--------|
   1  28.445 VB    0.4907 1.30570e4   439.32993 100.0000

Totals :                  1.30570e4   439.32993

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                        *** End of Report ***
```
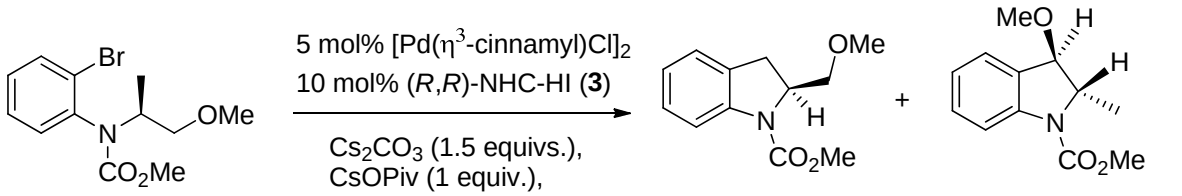

1.11 Synthesis of (2*S*,3*R*)-methyl 3-methoxy-2-methylindoline-1-carboxylate 8f:



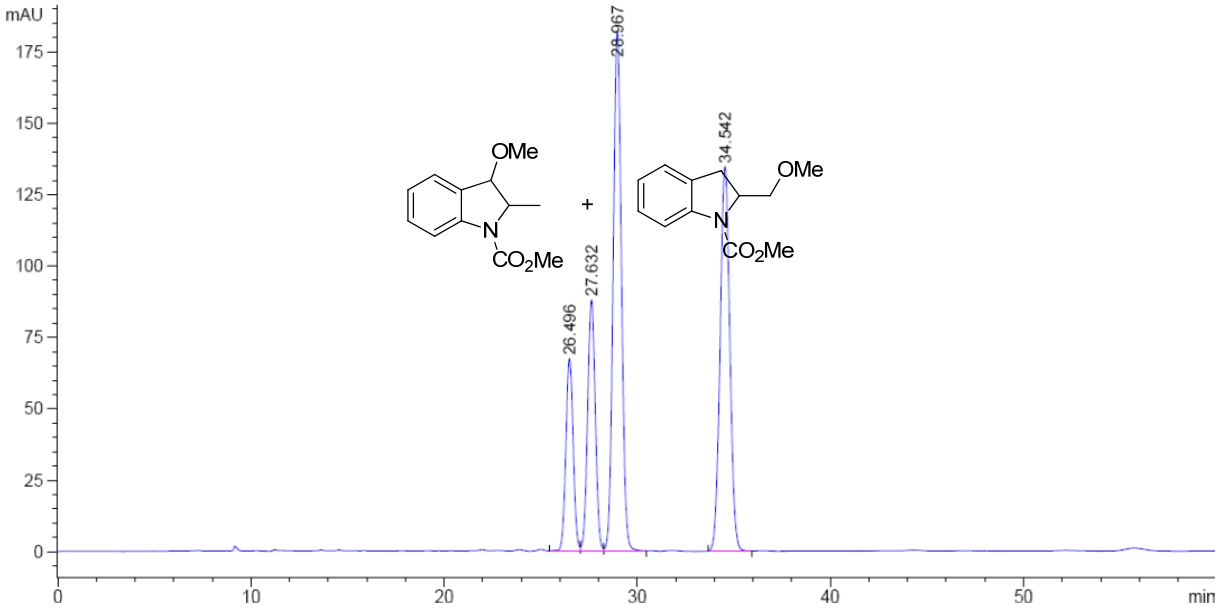
(*S*)-**6f** (>99% ee)

(*S*)-**7f** >99% ee : (2*S*,3*R*)-**8f** >99% ee

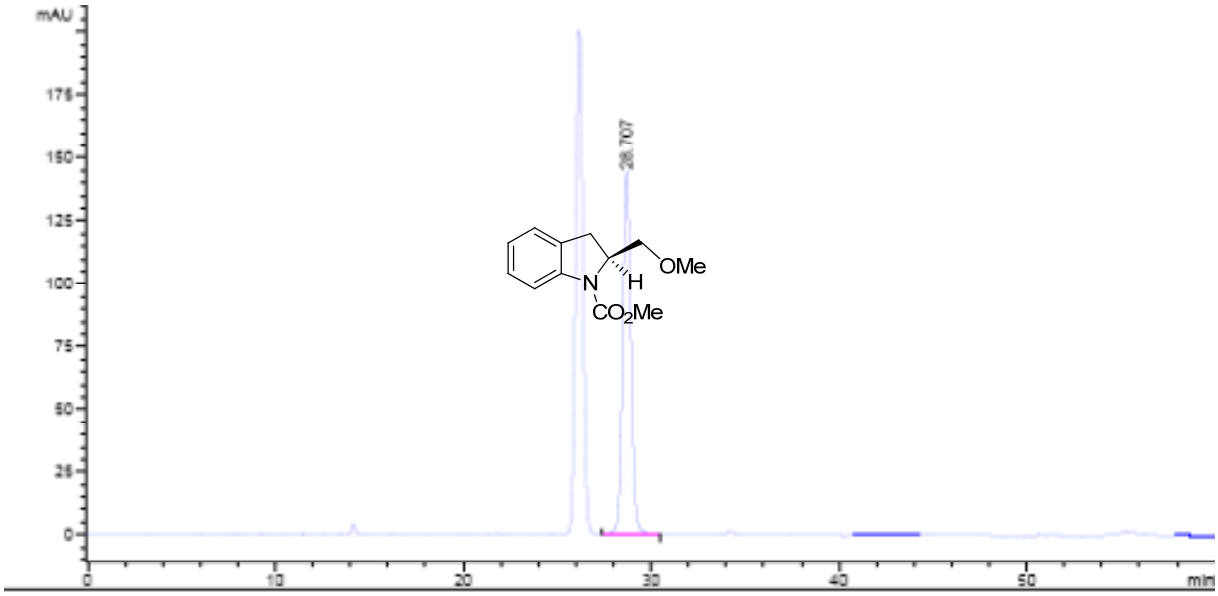
57 : 43

Carbamate (*S*)-**6f** (60.4 mg, 0.2 mmol), cesium carbonate (97.5 mg, 0.3 mmol), [Pd(*π*-cinnamyl)Cl]$_2$ (5.2 mg, 0.01 mmol), cesium pivalate (46.8 mg, 0.2 mmol) and (*R*,*R*)-NHC·HI (**3**) (11.8 mg, 0.02 mmol) were placed in a Schlenk flask. After the flask was evacuated and backfilled with nitrogen, dry xylenes (2 mL) was added under nitrogen. The resulting reaction mixture was stirred at 140 °C in the Schlenk tube behind a protective shield for 24 hours. The reaction mixture was cooled to r.t. and diluted with dichloromethane (2 mL) followed by

filtration through a pad of celite. The filtrate was evaporated by rotary evaporator and the volatiles were removed under vacuum. The residue was purified by f.c.(silica gel; diethyl acetate : pentane = 1 : 30 as eluent) to afford the mixture of indolines (*R*)-**7f** (>99% ee) in 54.1 % yield (25.2 mg; yield calcd. by NMR) and (2*S*,3*R*)-**8f** (>99% ee) in 40.8 % yield (18.1 mg; yield calcd. by NMR).



7f: >99% *ee* [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 28.70 min. (major)].



Area Percent Report

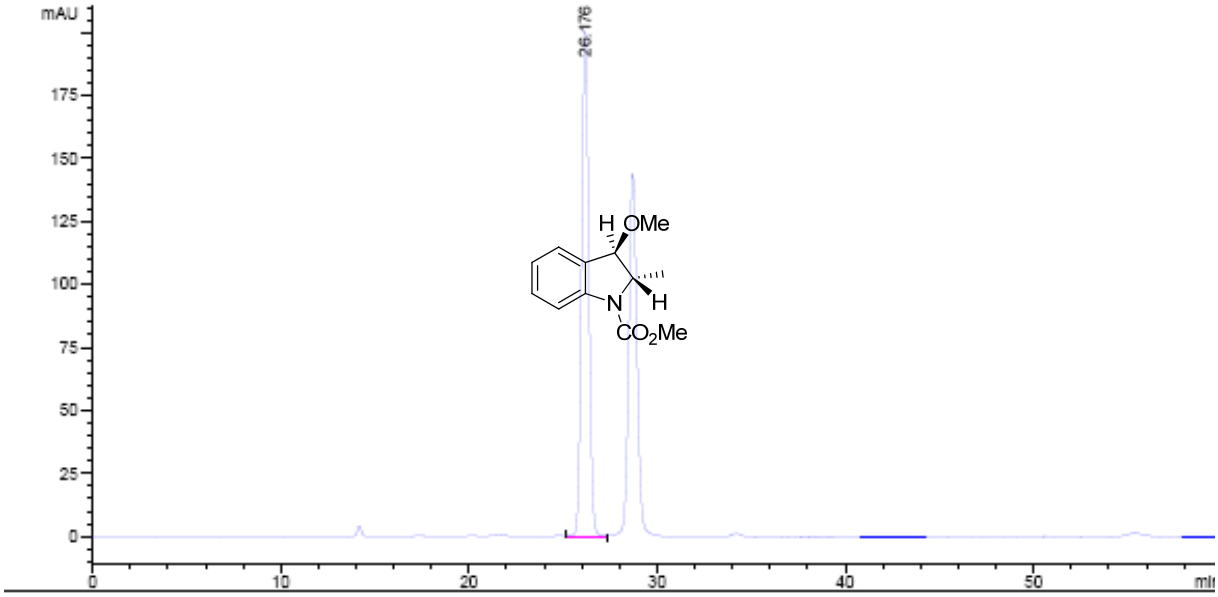
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.707	VB	0.4836	4372.61426	143.44002	100.0000
Totals :				4372.61426	143.44002	

*** End of Report ***

8f: >99% *ee* [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 26.17 min. (major)].

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---------------------------------------------------------------------
                        Area Percent Report
---------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

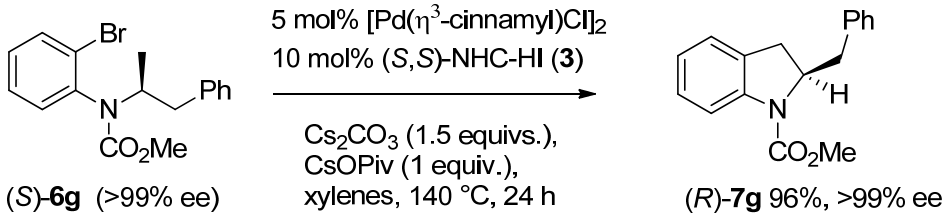

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.176 VV    0.4387 5325.93115  199.97041 100.0000

Totals :                  5325.93115  199.97041

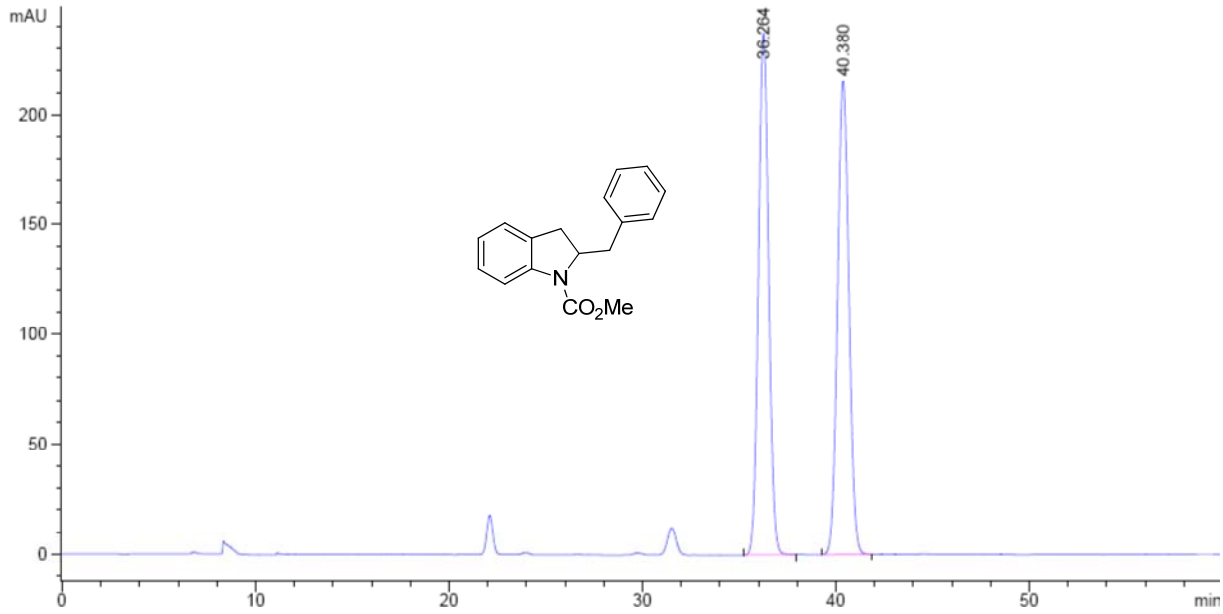
---------------------------------------------------------------------
                        *** End of Report ***
```

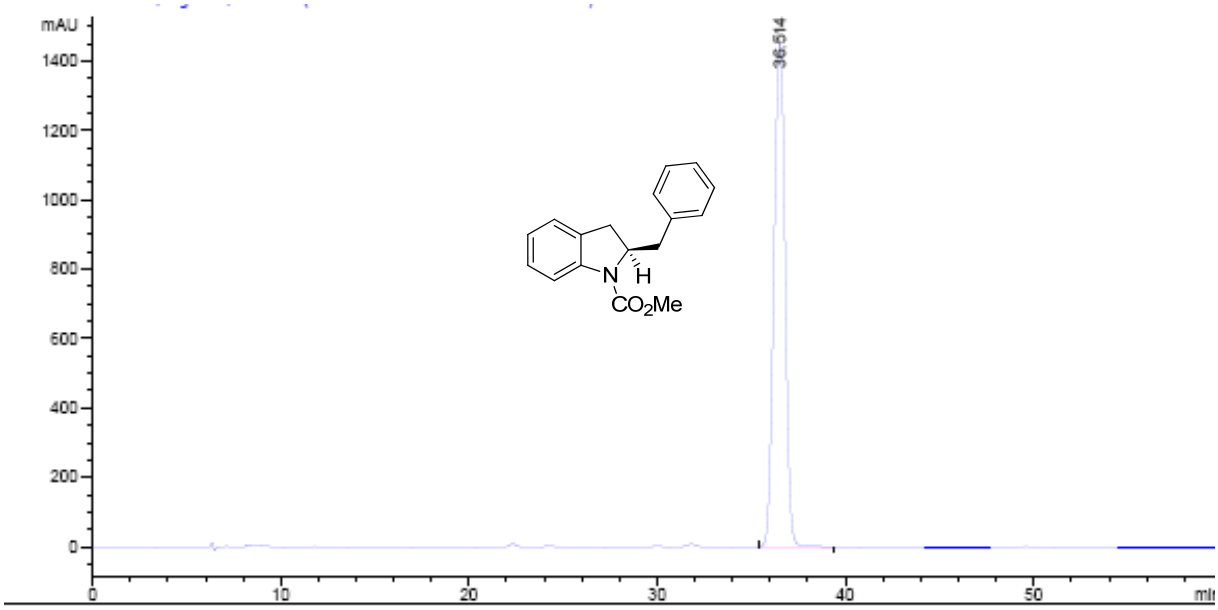
1.12 Synthesis of (*R*)-methyl 2-benzylindoline-1-carboxylate 7g:



(*S*)-**6g** (>99% ee) (*R*)-**7g** 96%, >99% ee

The same procedure as for (*S*)-**7f** applied to the synthesis of (*R*)-**7g**. Carbamate (*S*)-**6g** was used. (*R*)-**7g** formed in 96% yield (51.2 mg), >99% ee [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 36.51 min. (major)].





Area Percent Report

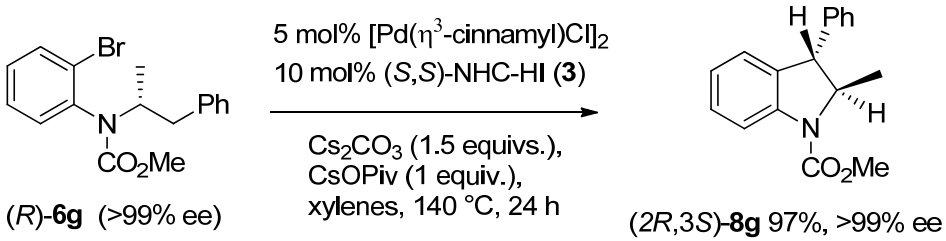
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.514	BB	0.6576	5.98873e4	1450.77393	100.0000
Totals :				5.98873e4	1450.77393	

*** End of Report ***

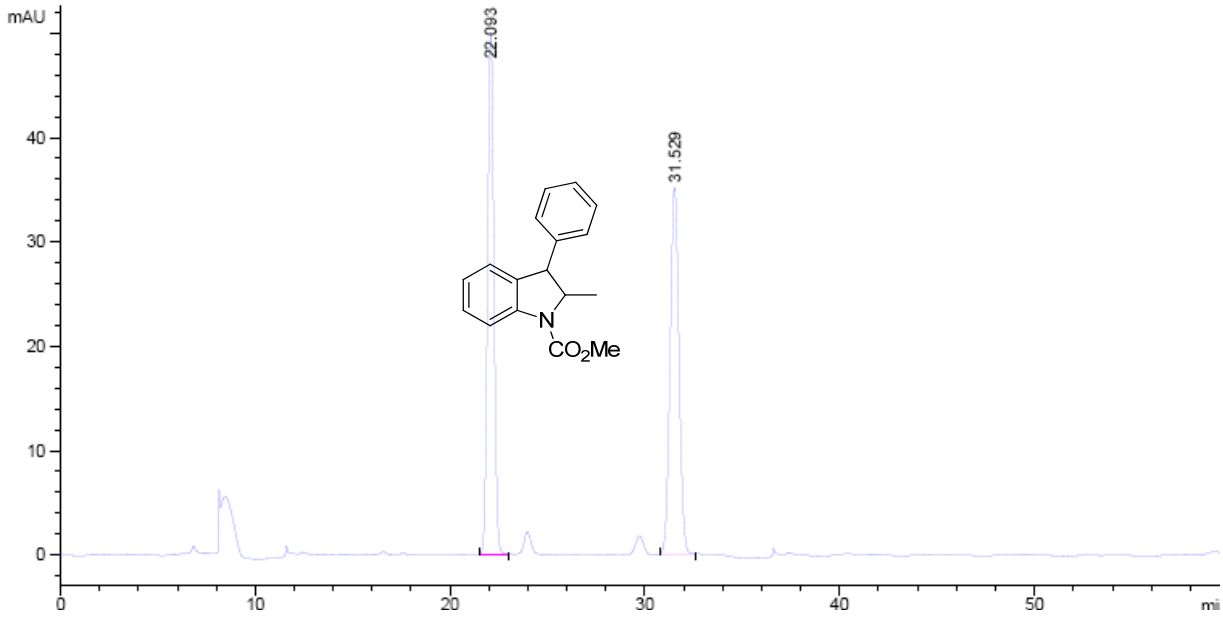
1.13 Synthesis of (2*R*,3*S*)-methyl 2-methyl-3-phenylindoline-1-carboxylate 8g:

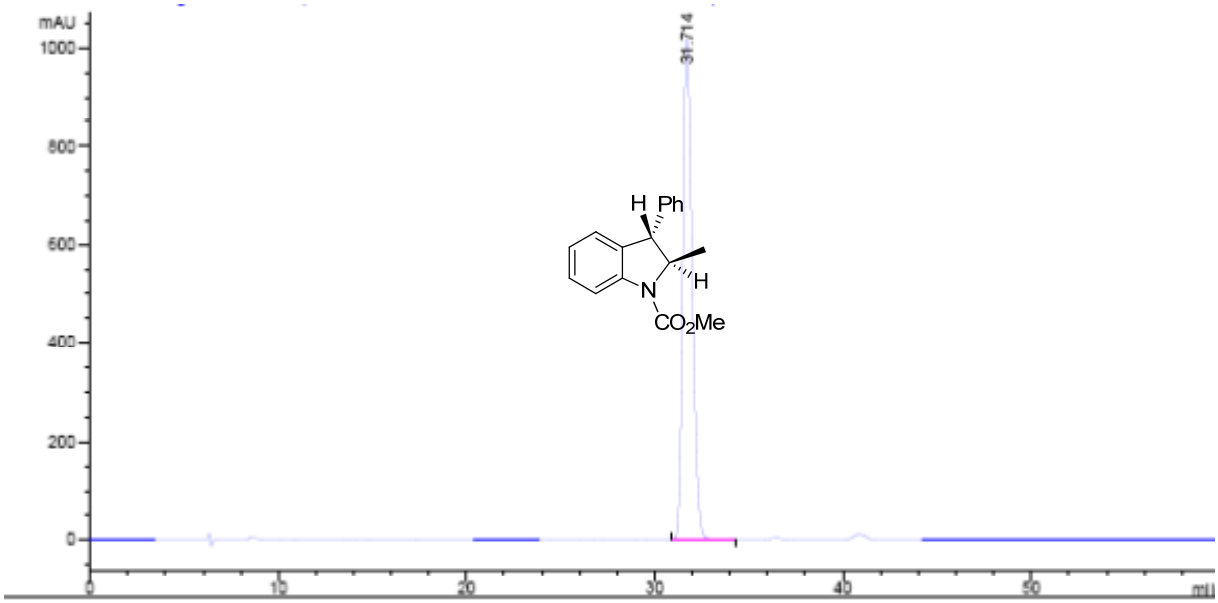


(*R*)-**6g** (>99% ee)

(2*R*,3*S*)-**8g** 97%, >99% ee

The same procedure as for (2*S*,3*R*)-**8f** applied to the synthesis of (2*R*,3*S*)-**8g**. Carbamate (*R*)-**6g** was used. (2*R*,3*S*)-**8g** formed in 97% yield (51.8 mg), >99% ee [chiral column: AD-H, *n*-hexane/*i*-PrOH = 99 : 1, 0.5 mL/min, 254 nm; t_R = 31.71 min. (major)].





Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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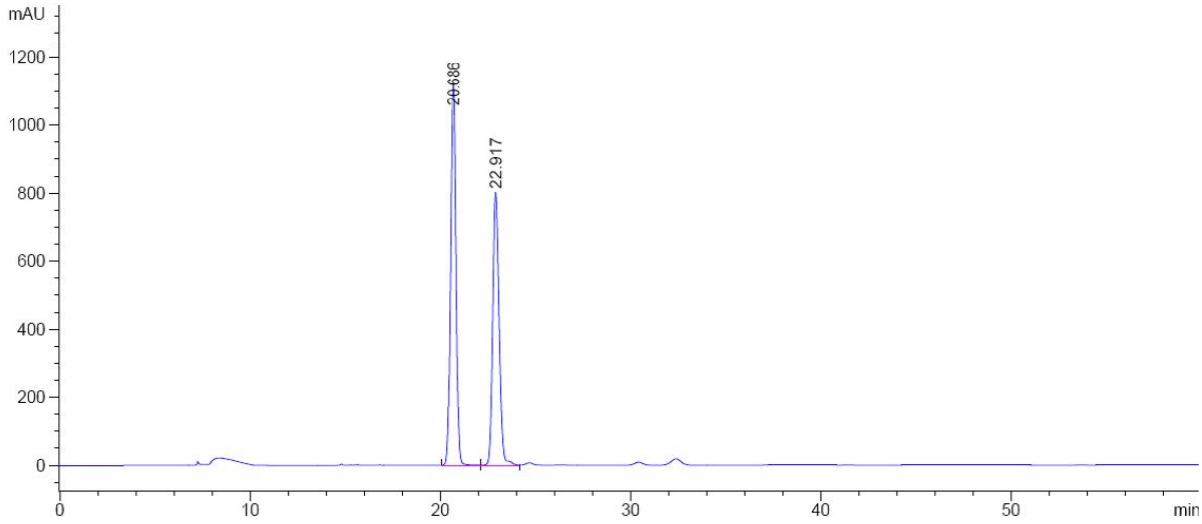
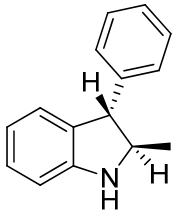
Totals :				3.54306e4	1017.71436	

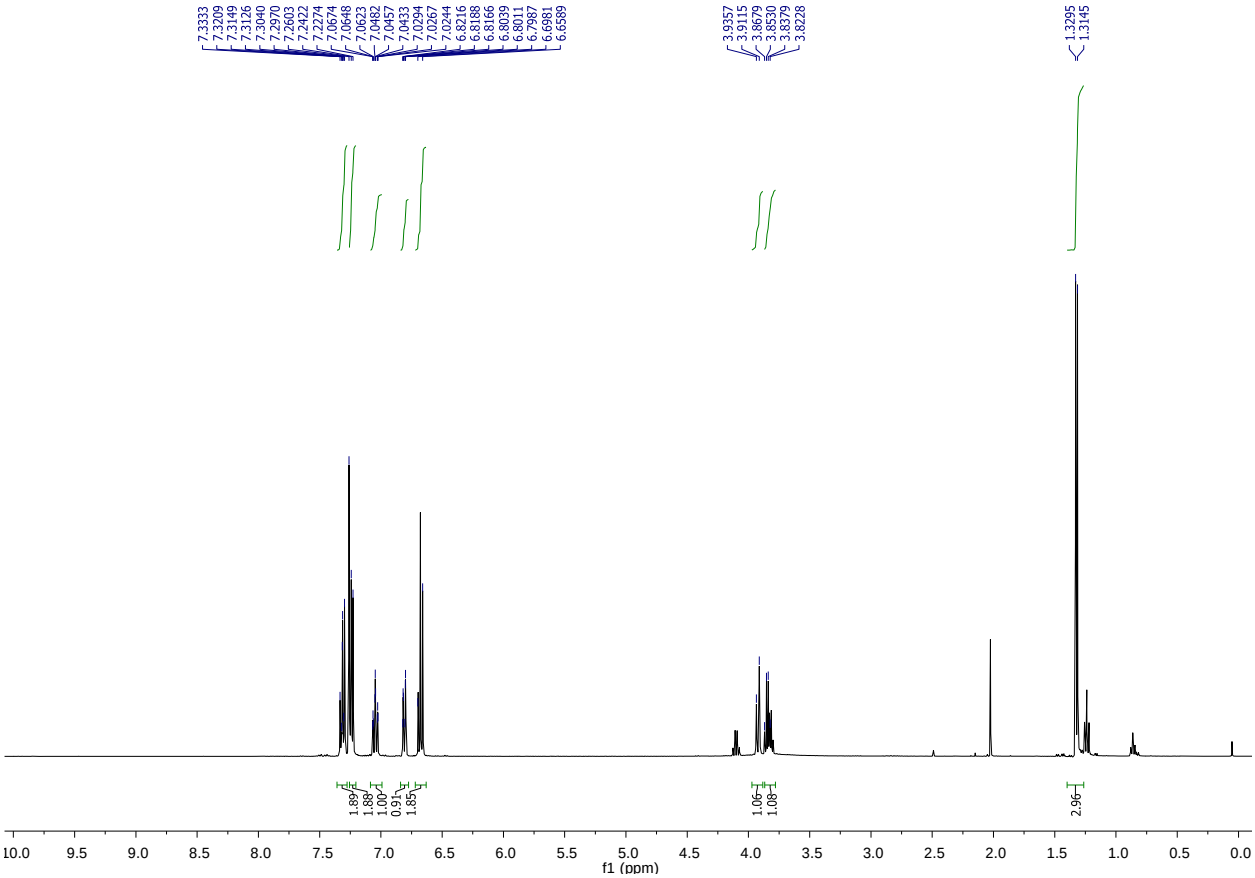
*** End of Report ***

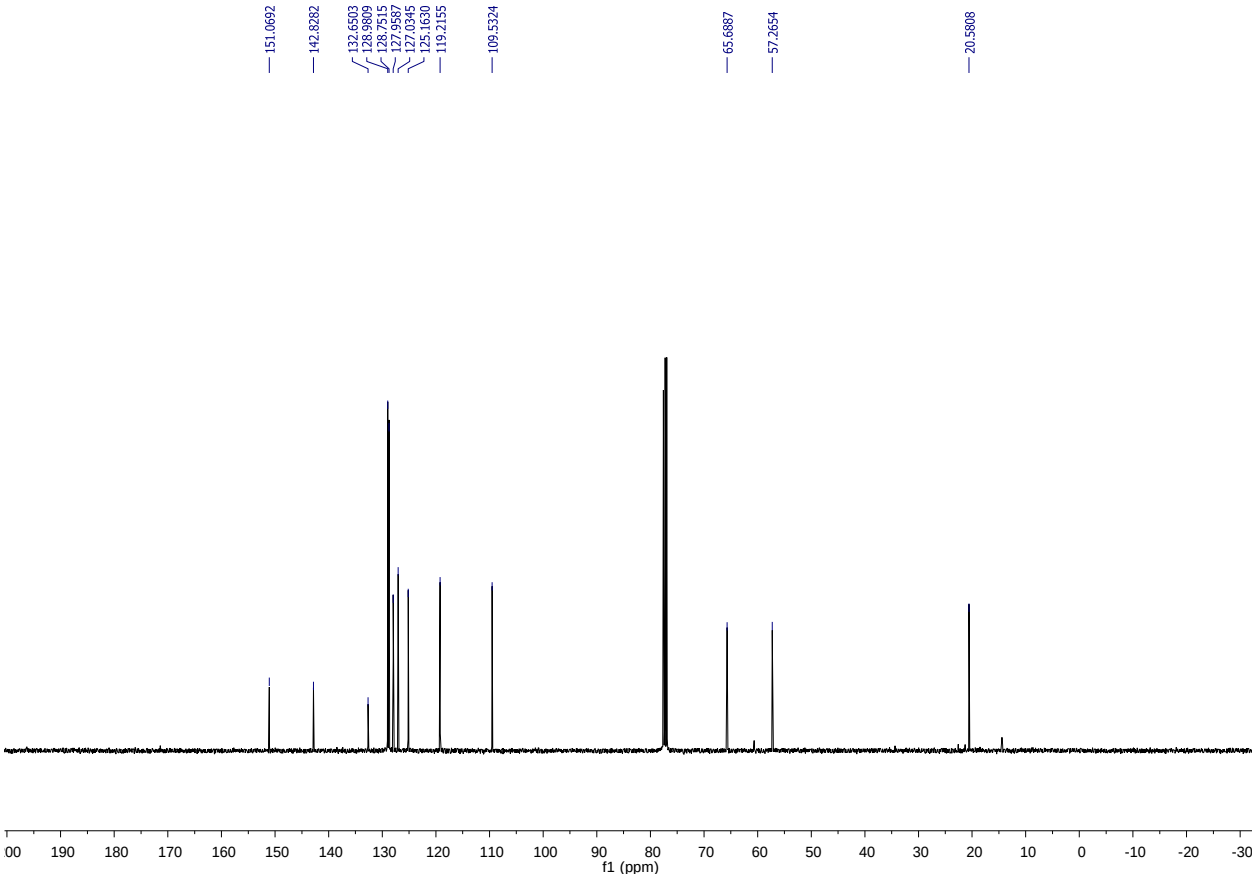


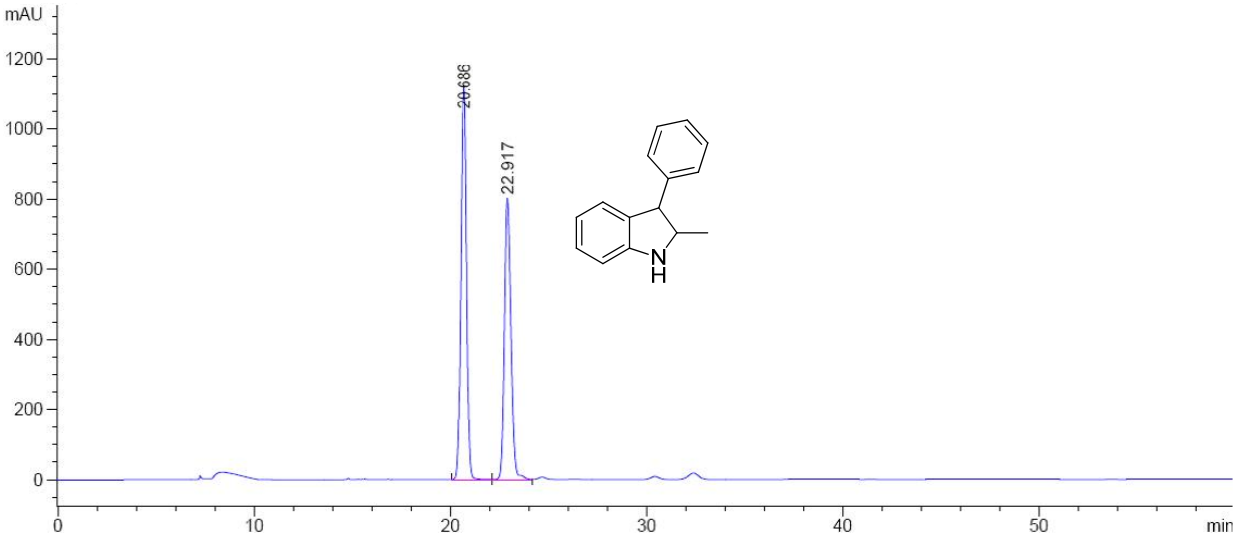
(2*R*,3*S*)-2-methyl-3-phenylindoline (9):

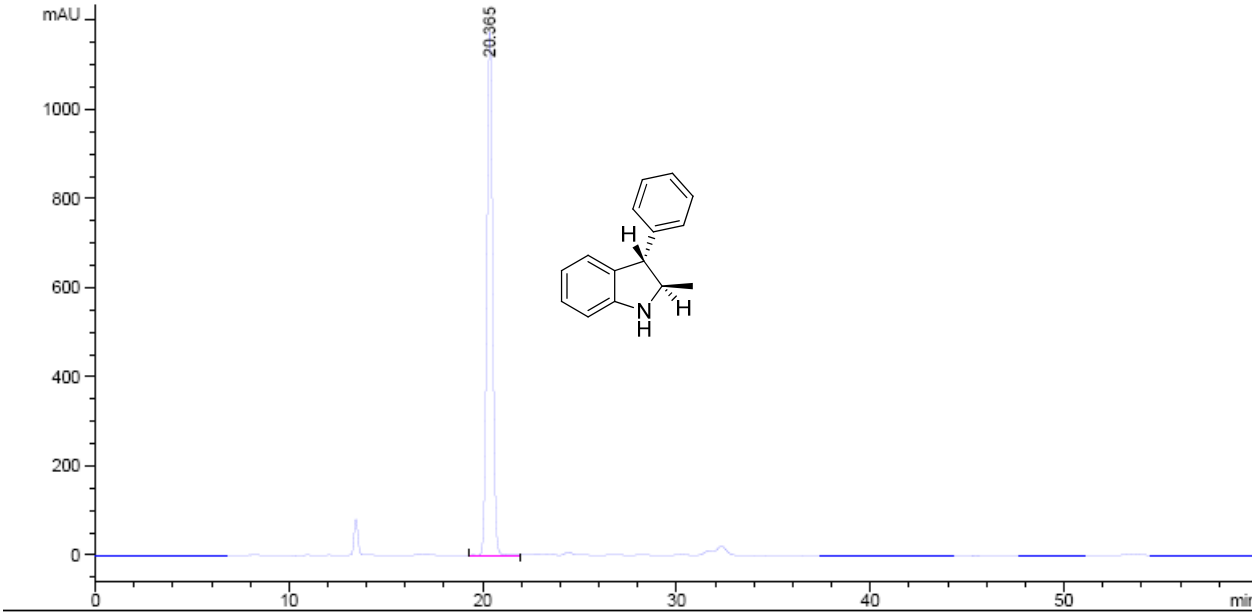


To a solution of (2*R*,3*S*)-**8g** (53.4 mg, 0.2 mmol, 1 equiv.) in THF/MeOH (2.5 mL/ 5 mL) was added 5N-NaOH aq. (2 mL, 10 mmol, 50 equivs). This mixture was refluxed for 24 hours. After cooling to r.t. it was extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4. After filtration and evaporation the crude residue was purified by flash column chromatography (silica gel; eluent: ethyl acetate:pentane = 1:20) affording indoline **9** as a colorless oil in 92% yield (38.4 mg,)
$[\alpha]_D^{20}$ = +35.0 (*c* = 0.5 in CH_2Cl_2). >99% *ee*, [chiral column, AD-H, *n*-hexane/*i*-PrOH = 99:1, 0.5 mL/min, 254 nm, t_R = 20.36 min. (major)]. ^{1}H NMR (400 MHz, $CDCl_3$): 1.31 (d, *J* = 6.0 Hz, 3H), 3.84 (q, *J* = 5.9 Hz, 1H), 3.92 (d, *J* = 9.6 Hz, 1H), 6.65-6.69 (m, 2H), 6.79-6.82 (m, 2H), 7.70 (tt, *J* = 7.6, 1.0 Hz, 1H), 7.22-7.26 (m, 2H), 7.29-7.33 (m, 2H). ^{13}C NMR (100 MHz) δ 20.5, 57.2, 65.6, 109.5, 119.2, 125.1, 127.0, 127.9, 128.7, 128.9, 132.6, 142.8, 151.0. IR (neat, cm^{-1}): 3364, 3028, 2963, 2854, 1732, 1605, 1482, 1464, 1375, 1245, 1214, 1017, 746, 698. HRMS (EI): calcd. for $C_{18}H_{19}N_2O$ ($[M+H]^+$): 210.1277, found: 210.1280.


7.3333
7.3209
7.3149
7.3126
7.3040
7.2970
7.2603
7.2422
7.2274
7.0674
7.0648
7.0623
7.0482
7.0457
7.0433
7.0294
7.0267
7.0244
6.8216
6.8188
6.8166
6.8039
6.8011
6.7987
6.6981
6.6589
3.9357
3.9115
3.8679
3.8530
3.8379
3.8228
1.3295
1.3145
1.89
1.88
1.00
0.91
1.85
1.06
1.08
2.96
f1 (ppm)


151.0692
142.8282
132.6503
128.9809
128.7515
127.9587
127.0345
125.1630
119.2155
109.5324
65.6887
57.2654
20.5808
f1 (ppm)



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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  20.365 BB    0.3408 2.43212e4  1159.14490 100.0000

Totals :                  2.43212e4  1159.14490

=====================================================================
                        *** End of Report ***
```

1.15 IR and vibrational circular dichroism (VCD) spectra:

IR and vibrational circular dichroism (VCD) spectra were recorded on a Bruker PMA 50 accessory coupled to a Tensor 27 Fourier transform infrared spectrometer. A photoelastic modulator (Hinds PEM 90) set at l/4 retardation was used to modulate the handedness of the circular polarized light. Demodulation was performed by a lock-in amplifier (SR830 DSP). An optical low-pass filter (< 1800 cm^{-1}) in front of the photoelastic modulator was used to enhance the signal/noise ratio. Solutions of ca. 10 mg in 500 µl CD_2Cl_2were prepared and measured in a cell equipped with CaF_2 windows and a 130 µm spacer. The neat solvent served as the reference. For both the sample and reference 8400 scans at 4 cm^{-1} resolution were averaged.

Computational methods. Density functional theory (DFT) as implemented in Gaussian03 was used to study the structure of **2a** and **8g** and to calculate the corresponding IR and VCD spectra.(ref Gausian) The calculations were performed using the b3lyp functional (ref A.D. Becke, J.Chem.Phys. 98 (1993) 5648-5652, C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785-789.) and a 6-31G(d) basis set.(ref: R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. 54 (1971) 724). Prior to the calculation of the spectra all degrees of freedom were completely relaxed. IR and VCD spectra were constructed from calculated dipole and rotational strengths using the GaussView program.[7]

Discussion of results:

VCD spectroscopy was used to determine the stereochemistry of the indolines **2a** and **8g**. For both compounds four isomers are possible, corresponding to the *cis* and *trans* arrangement of the two substituents and the corresponding enantiomers. In addition one has to consider conformational freedom. For the phenyl-methyl compound two conformers are possible corresponding to the arrangement of the ester group. For the methyl-ethyl compound

additionally three positions are feasible for the ethyl group leading to a total of six conformers for each stereoisomer. All the conformers were calculated. The discussion presented here is however based only on the most stable conformer of the corresponding compound. A more detailed discussion will be given elsewhere.

Indoline **2a**:

The IR and VCD spectra of the *cis* and *trans* compound are quite similar, particularly for the carbonyl vibration, the weak band measure around 1600 cm^{-1} and the group of bands slightly below 1500 cm^{-1} (calculated slightly above 1500 cm^{-1}). A clear distinction is possible based on the strong band measure at around 1400 cm^{-1} (calculated at 1460 cm^{-1}). For the *cis* compound this band is calculated positive in the VCD and has opposite phase as the carbonyl band. For the *trans* this band is calculated strongly negative and has the same phase as the carbonyl band, as is observed in the experiment. In the experiment there is a positive band at 1460, which is due to another conformer.

Conclusion: Analysis of the VCD spectra strongly indicates that the measured compound corresponds to the *trans* compound and the enantiomer corresponds to the one considered in the calculation.

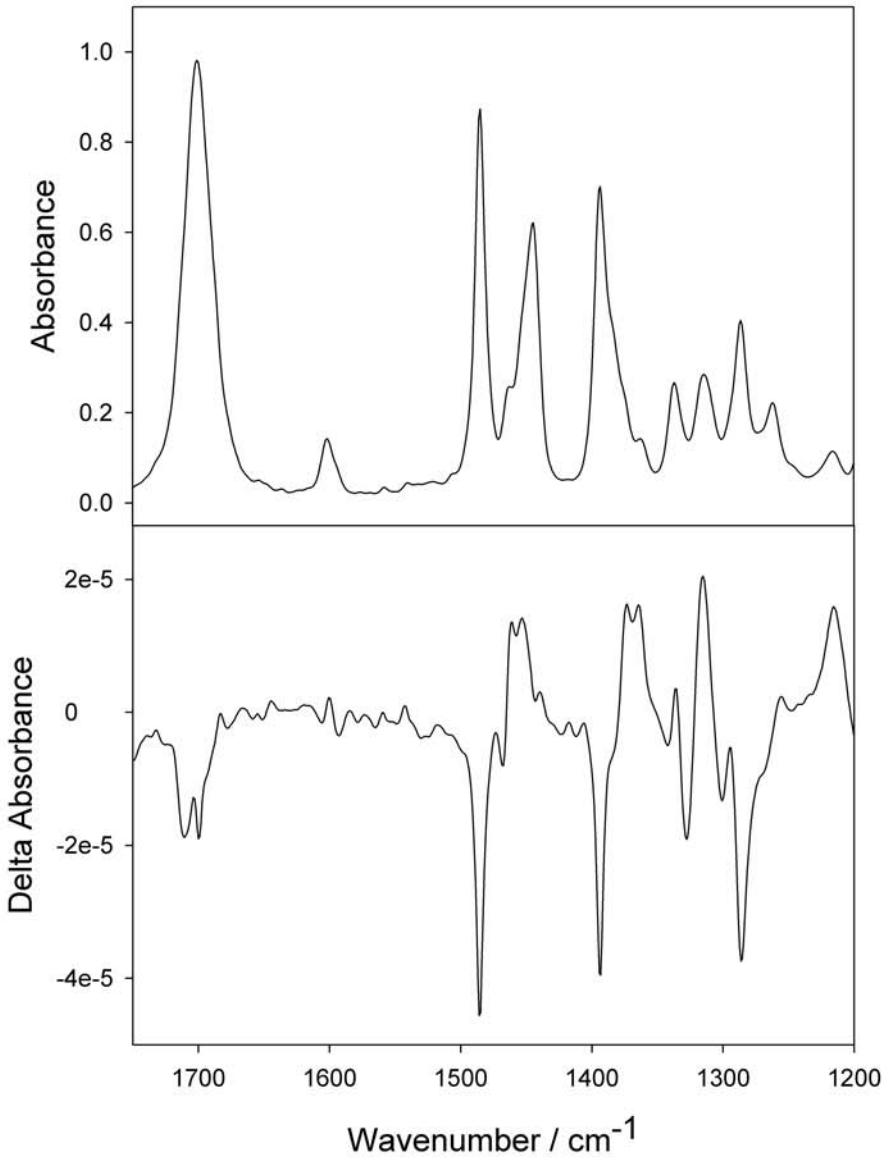
Indoline **8g**:

The IR and VCD spectra of the *cis* and *trans* compound are again quite similar. Also in this case the region around the strong band measure slightly below 1400 cm^{-1} (calculated slightly above 1400 cm^{-1}) is most conclusive. For the *cis* there are positive and negative bands, whereas for the *trans* only strong negative bands are calculated. The experiment reveals two strong positive bands, where the stronger one corresponds to a relatively weak band in the IR. This is a strong indication for the *trans* configuration. Furthermore, for the *cis* a relatively strong carbonyl band in the VCD is predicted, in contrast to the experiment. The

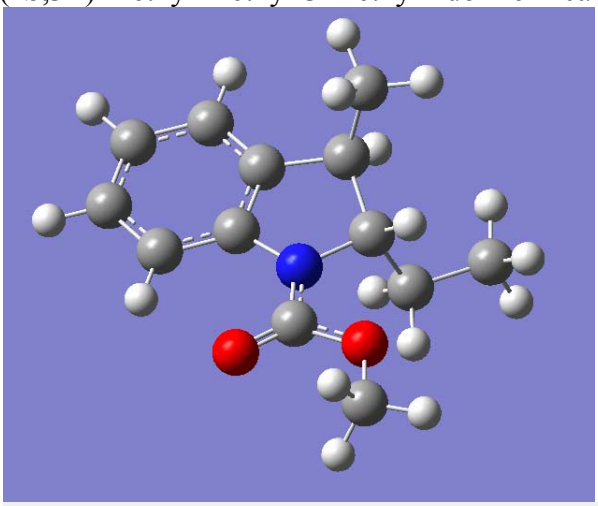
bands calculated for the trans have opposite sign compared to the measured spectrum, which shows that the enantiomer considered in the calculation has opposite absolute configuration with respect to the measured compound.

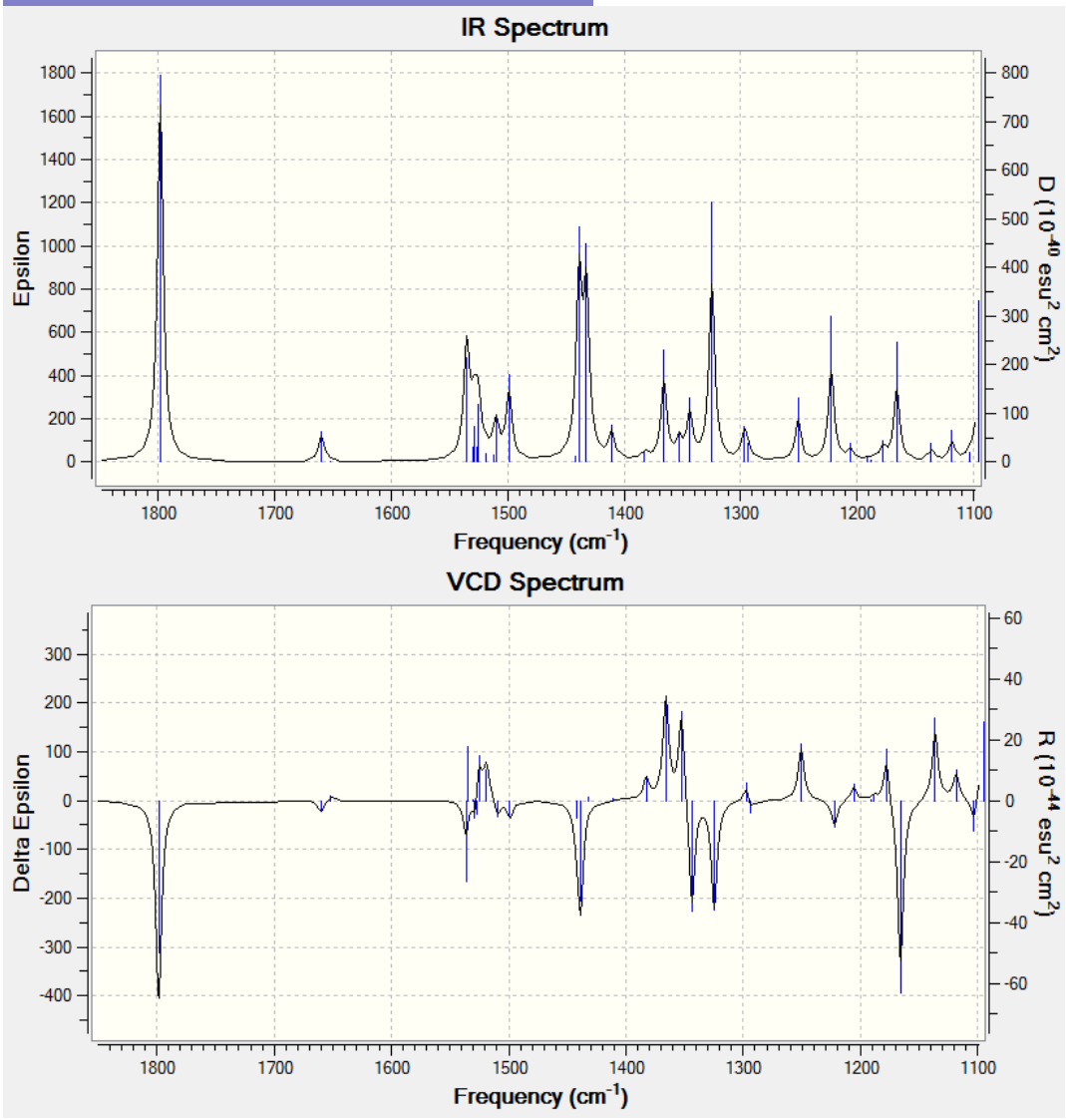
Conclusion: Analysis of the VCD spectra strongly indicates that the measured compound corresponds to the *trans* compound and the enantiomer measured has opposite absolute configuration with respect to the one calculated.

Indoline **2a**:
Experimental spectra

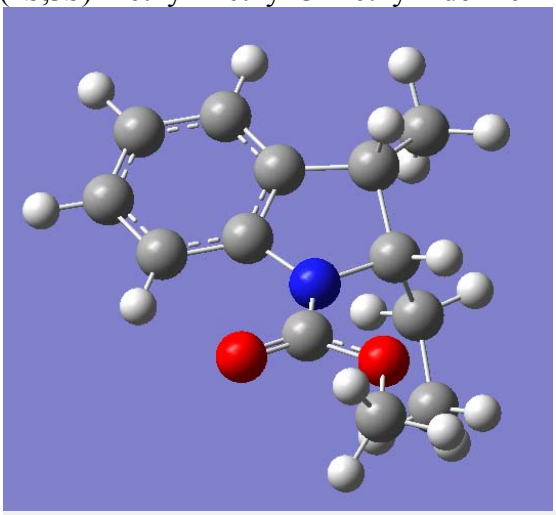


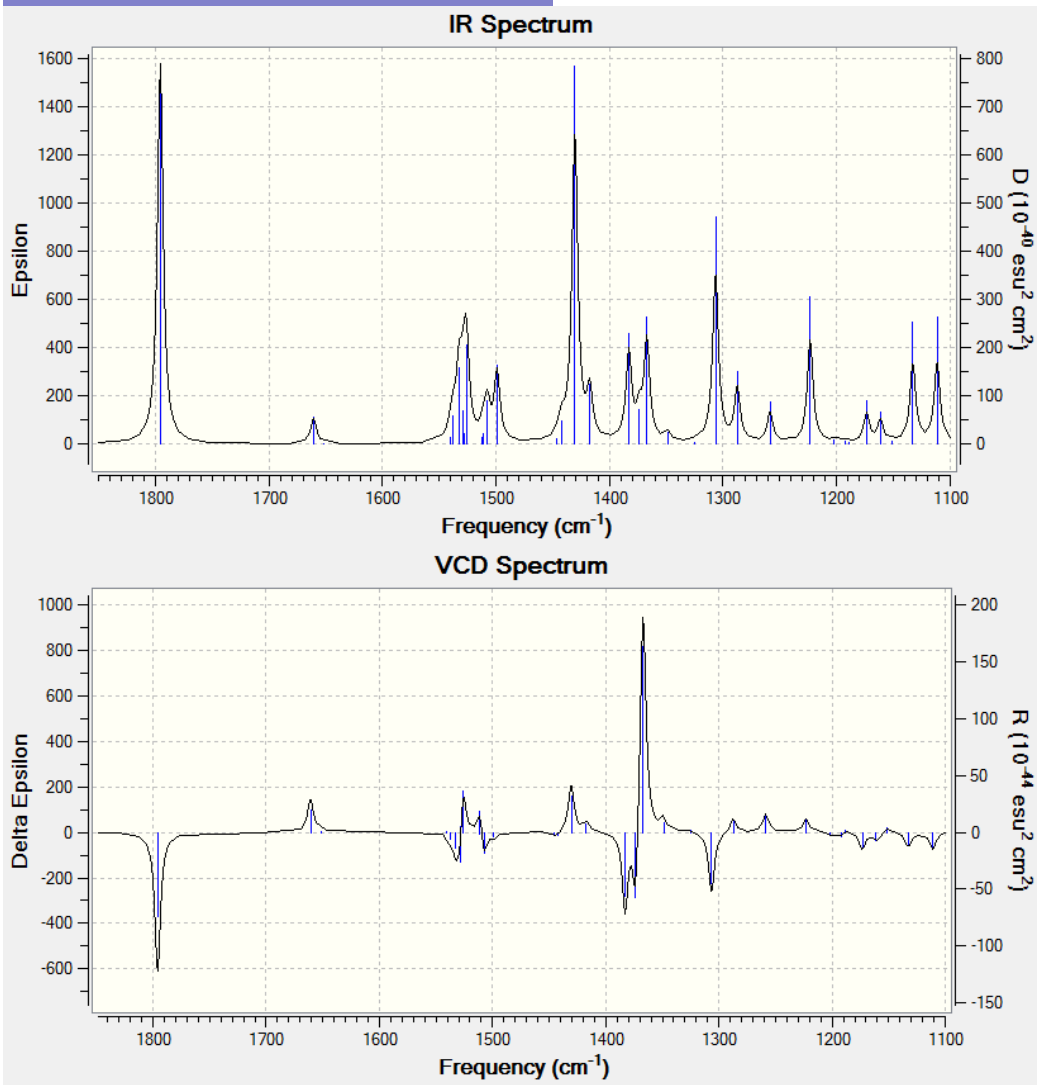
(2*S*,3*R*)-methyl 2-ethyl-3-methylindoline-1-carboxylate **2a**:



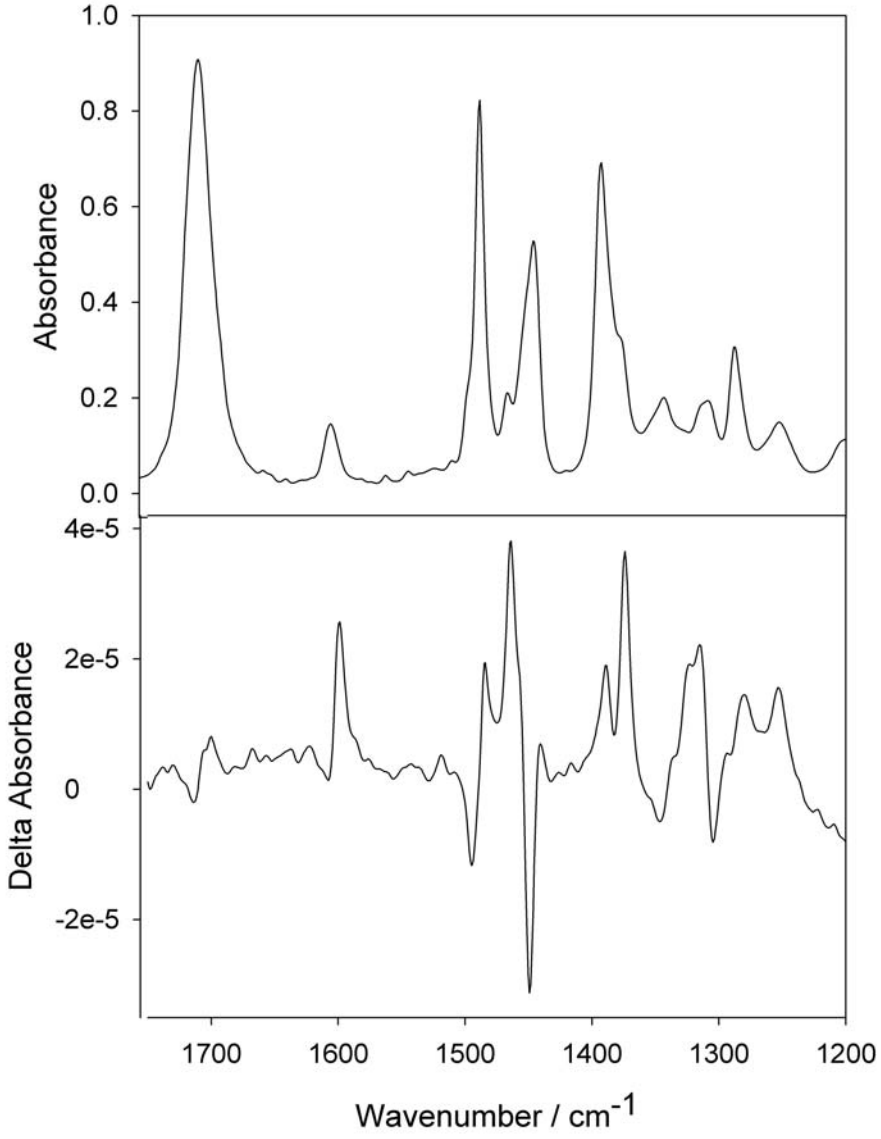


(2*S*,3*S*)-methyl 2-ethyl-3-methylindoline-1-carboxylate **2a**:

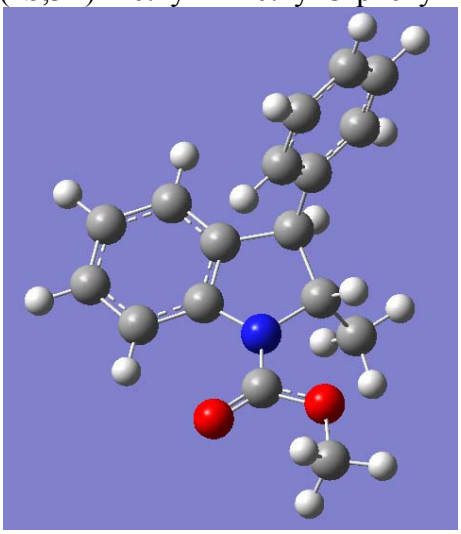


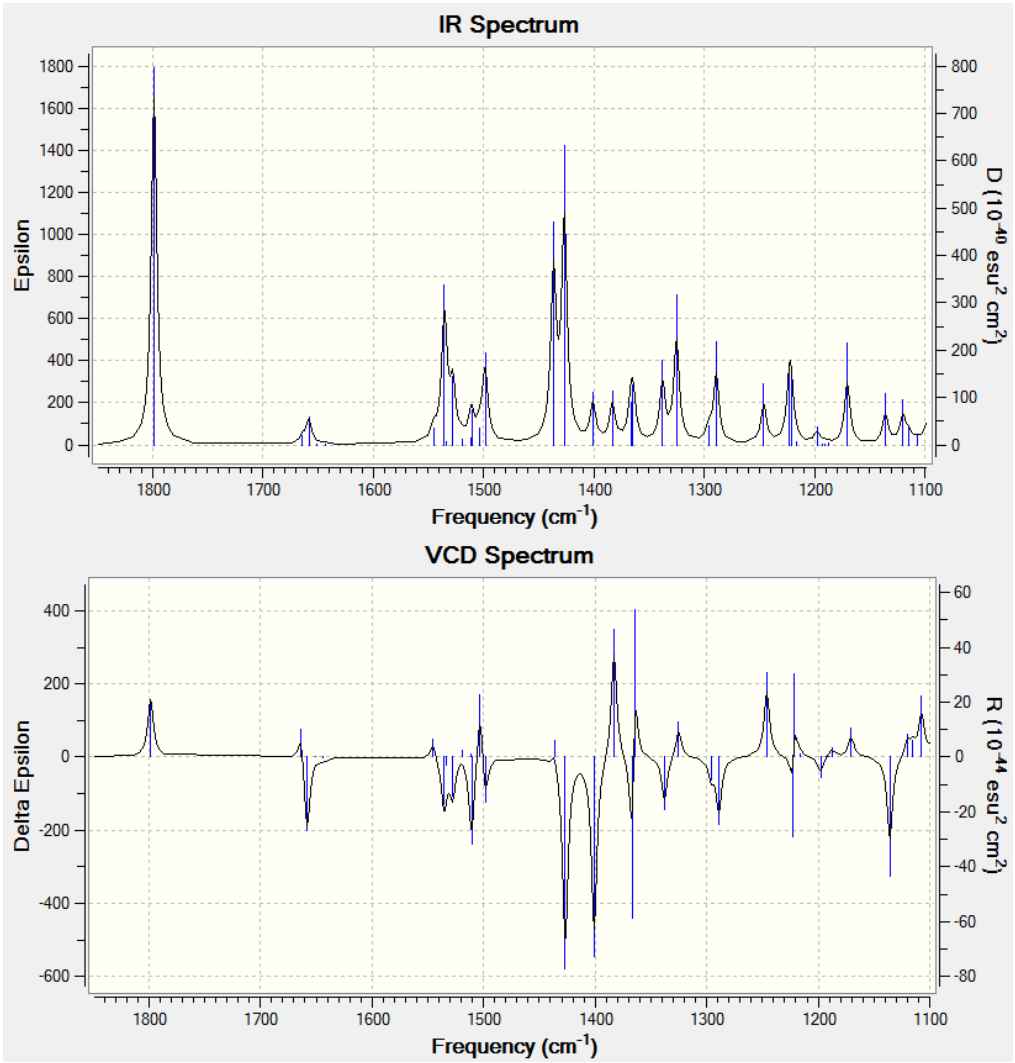


Indoline **8g**:
Experimental spectra

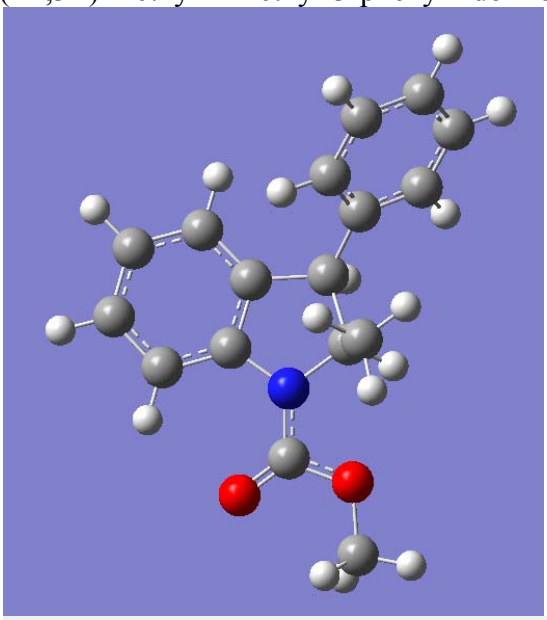


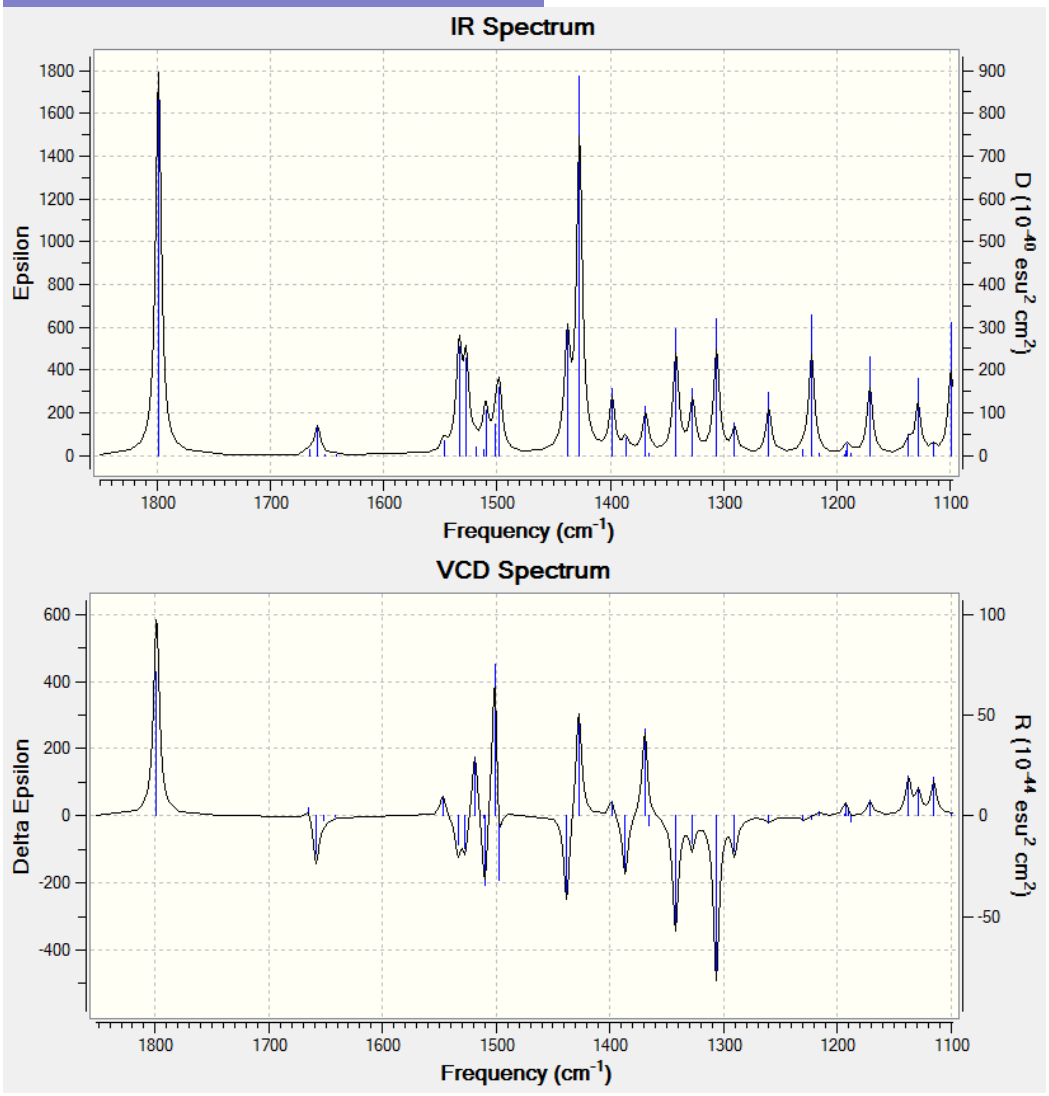
(2*S*,3*R*)-methyl 2-methyl-3-phenylindoline-1-carboxylate **8g**:





(2*R*,3*R*)-methyl 2-methyl-3-phenylindoline-1-carboxylate **8g:**





1.16 References:

[1] D. J. Cho, C. J. Wu, Sujith S, W. –S. Han, S. O. Kang, and B. Y. Lee, *Organometallics* **2006**, *25*, 2133-2134.

[2] F. M. Rivas, U. Riaz, A. Giessert, J. A. Smulik, S. T. Diver, *Org. Lett.* **2001**, *3*, 2673-2676.

[3] T. Watanabe, S. Oishi, N. Fujii, H. Ohno, *Org. Lett.* **2008**, *10*, 1759-1762.

[4] H. V. Bailey, W. Heaton, N. Vicker, B. V. L. Potter, *Synlett*, **2006**, 2444-2448.

[5] G. Buenger, J. Douglas, P. Jass, E. Michalson, M. Schiesher US 2009/0292143A1 and references therein.

[6] Carbamate (*S*)-**6f** synthesized by similar procedure as for *rac*-**6f** starting from enantiopure commercially available (*S*)-1-methoxypropan-2-amine.

[7] Gaussian 03, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

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